**Supplementary information for**

# Au(I)-Catalyzed Domino Cyclization of 1,6-Diynes Incorporated with Indole

Guzhou Chen,[1,⊥] Peng-Yu Liu,[2,⊥] Huanhuan Zou,[1,⊥] Jiadong Hu, [3] Xiaowu Fang,[1] Dongyang Xu,[1] Yu-Peng He,*[,2] Hongbo Wei,*[,1] and Weiqing Xie*,[1,4]

[1]Shaanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry & Pharmacy, Northwest A&F University, 22 Xinong Road, Yangling 712100, Shaanxi, China
[2]Key Laboratory of Petrochemical Catalytic Science and Technology, Liaoning Shihua University, Dandong Road West 1, Fushun 113001, China
[3]Yangling Vocational & Technical College
[4]Key Laboratory of Botanical Pesticide R&D in Shaanxi Province, Yangling, Shaanxi 712100, China

[⊥]G.C, P.Y.L and H.Z. contributed equally

*Corresponding authors
*E-mail: yupeng.he@lnpu.edu.cn; weihb@nwafu.edu.cn ; xiewq@nwafu.edu.cn

# Contents

# 1. General Information

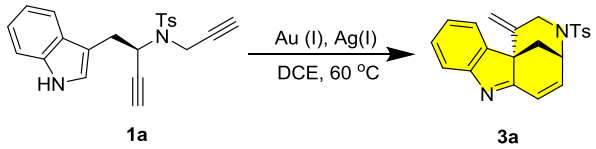
Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction was conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvents were treated as follow: tetrahydrofuran and diethyl ether were distilled from sodium under argon atmosphere, dichloromethane and toluene was distilled from calcium hydride under argon atmosphere. Anhydrous 1,2-dichloroethane, methanol and N,N-dimethylacetamide were commercial available (Adamas, SafeDry, with molecular sieves). Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm, 200-400 mesh, Silicycle P60). NMR data including $^{1}H$ NMR or $^{13}C$ NMR spectra were recorded on Bruker AVANCE III 500MHz. All of the $^{13}C$ NMR spectra were broad band proton-decoupled. $^{1}H$ NMR Chemical shifts were reported in ppm relative to residual signals of the solvents ($CDCl_3$: 7.26 ppm; $(CD_3)_2CO$: 2.05 ppm). $^{13}C$ NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$:77.16 ppm; $(CD_3)_2CO$: 206.26 ppm). Optical rotations were measured on Anton Paar MCP 300 polarimeter. High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI).

# 2. Reaction Conditions Optimization of Au(I) Catalyzed Cyclization of Indole Tethered 1,6-diynes

## 2.1 General Procedure

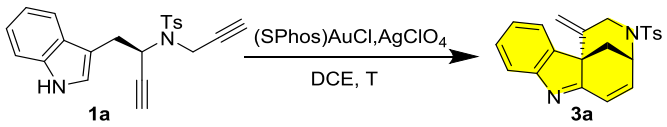
A flame-dried Schlenk flask equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv), (SPhos)AuCl (5% mmol) and $AgClO_4$ (5% mmol). The flask was capped with a rubber septum, then placed under an argon atmosphere, anhydrous DCE (2 mL) was added, the reaction mixture was stirred at 60 $^oC$ in oil bath until the starting material completely consumed monitored by TLC. The solution was directly concentrated under reduced pressure and purified by flash column chromatography to afford **3a**.

**Table S1. The Screening of metal catalysts for the Model Reaction**




| entry | Au(I) | Ag(I) | solvent | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | $(PPh_3)AuCl$ | --- | DCE | 64 | trace |
| 2 | $(PPh_3)AuCl$ | $AgSbF_6$ | DCE | 40 | 55 |
| 3 | $(PPh_3)AuCl$ | AgOTf | DCE | 22 | 50 |
| 4 | $(PPh_3)AuCl$ | $Ag(NTf_2)$ | DCE | 44 | 56 |
| 5 | $(PPh_3)AuCl$ | $AgClO_4$ | DCE | 24 | 69 |
| 6 | (SMe)AuCl | $AgClO_4$ | DCE | 24 | 20 |
| 7 | (IMes)AuCl | $AgClO_4$ | DCE | 24 | 57 |
| 8 | (XPhos)AuCl | $AgClO_4$ | DCE | 8 | 74 |
| 9 | (SPhos)AuCl | $AgClO_4$ | DCE | 4 | 85 |
| 10 | JohnPhosAuCl | $AgClO_4$ | DCE | 24 | 68 |

**Table S2. The Screening of temperature for the Model Reaction**

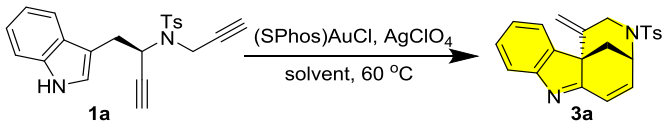



| entry | Au(I) | Ag(I) | Temperature ($^oC$) | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | (SPhos)AuCl | $AgClO_4$ | 60 | 4 | 85 |
| 2 | (SPhos)AuCl | $AgClO_4$ | rt | 24 | 69 |
| 3 | (SPhos)AuCl | $AgClO_4$ | 40 | 24 | 74 |
| 4 | (SPhos)AuCl | $AgClO_4$ | 50 | 20 | 84 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | (SPhos)AuCl | $AgClO_4$ | 70 | 7 | 77 |

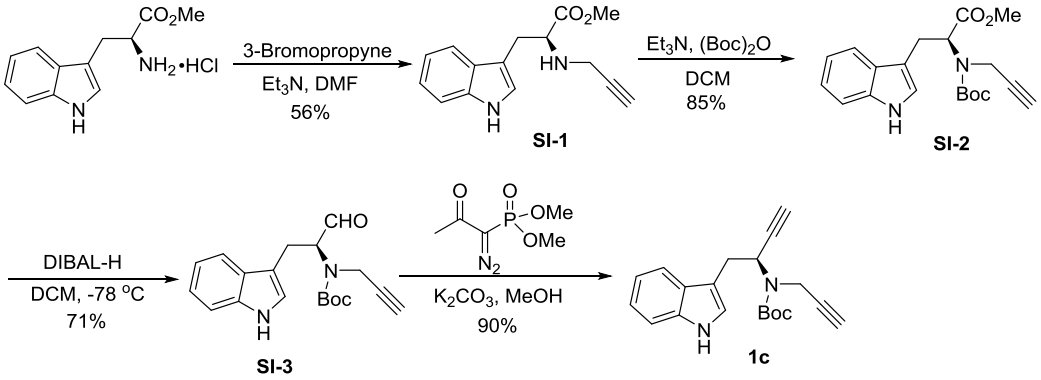
**Table S3. The Screening of solvents for the Model Reaction**

| entry | Au(I) | Ag(I) | solvent | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | (SPhos)AuCl | $AgClO_4$ | DCE | 4 | 85 |
| 2 | (SPhos)AuCl | $AgClO_4$ | Toluene | 7 | 52 |
| 3 | (SPhos)AuCl | $AgClO_4$ | THF | 5 | 66 |
| 4 | (SPhos)AuCl | $AgClO_4$ | $CH_3CN$ | 24 | 66 |
| 5 | (SPhos)AuCl | $AgClO_4$ | $CHCl_3$ | 6 | 78 |
| 6 | (SPhos)AuCl | $AgClO_4$ | 2-Methyltetrahydrofuran | 4 | 71 |
| 7 | (SPhos)AuCl | $AgClO_4$ | MTBE | 10 | 38 |
| 8 | (SPhos)AuCl | $AgClO_4$ | DME | 7 | 44 |
| 9 | (SPhos)AuCl | $AgClO_4$ | 1,4-Dioxane | 4.5 | 68 |



# 3. Experimental Details and Characterization Data

Preparation of Indole Tethered 1,6-diyne **1c**.




L-Tryptophan methyl ester hydrochloride (39.2 mmol, 10.0 g), $Et_3N$ (39.2 mmol, 5 mL) and $K_2CO_3$ (39.2 mmol, 5.5 g) were stirred in DMF (60 mL) at rt for 15 min. Subsequently, 3-bromopropyne (47.0 mmol, 4 mL) was added and the reaction mixture was stirred overnight at rt. The suspension was filtered through a short pad of celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether= 1/1 to afford **SI-1** (5.6 g, 56% yield) as a pale-yellow oil. $R_f$ = 0.1 (ethyl acetate/petroleum ether = 1/1, v/v).

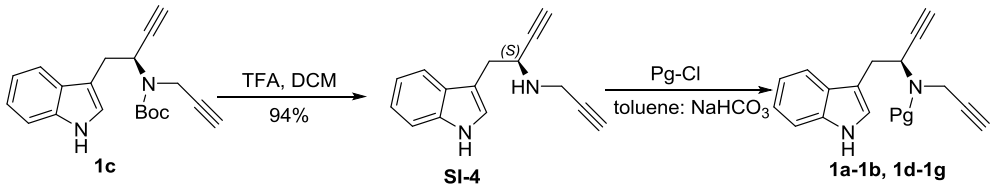
$Et_3N$ (32.7 mmol, 4.5mL) and $(Boc)_2O$ (24.0 mmol, 5.4 g) were added to **SI-1** in anhydrous dichloromethane (70 mL) at 0 $^oC$, The reaction was warmed to rt and stirred for another 4h. The solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether= 10/1 to afford **SI-2** (6.6 g, 85% yield) as a pale-yellow oil. $R_f$ = 0.4 (ethyl acetate/petroleum ether = 3/1, v/v).

DIBAL-H (1.5 M in toluene, 14.2 mmol, 9.4 mL) was added drop-wise to a suspension of **SI-2** (3.4 g, 9.5 mmol) in anhydrous dichloromethane (33 mL) at -78 $^oC$. The reaction was allowed to stirred for 15 min before being quenched with aqueous potassium sodium tartrate (20 mL). The crude mixture was filtered through celite. The aqueous phase was extracted with dichloromethane (10 mL×3) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether=12/1 to afford **SI-3** (2.2 g, 71% yield) as a pale-yellow oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether =2/1, v/v).

**NOTE:** The by-product alcohol can be further oxidized by IBX to afford **SI-3**.

**SI-3** (9.8 mmol, 3.2 g) was dissolved in anhydrous MeOH (20 mL), $K_2CO_3$ (39.2 mmol, 5.5 g) was added and then dimethyl (1-diazo-2-oxopropyl) phosphonate (14.7 mmol, 2.8 g) in MeOH (20 mL) was added slowly. The reaction mixture was stirred at rt for 30 min. The crude mixture was filtered through celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether= 15/1 to afford **1c** (2.9 g, 90% yield) as a colorless oil. $R_f$ = 0.8 (ethyl acetate/petroleum ether = 2/1, v/v).

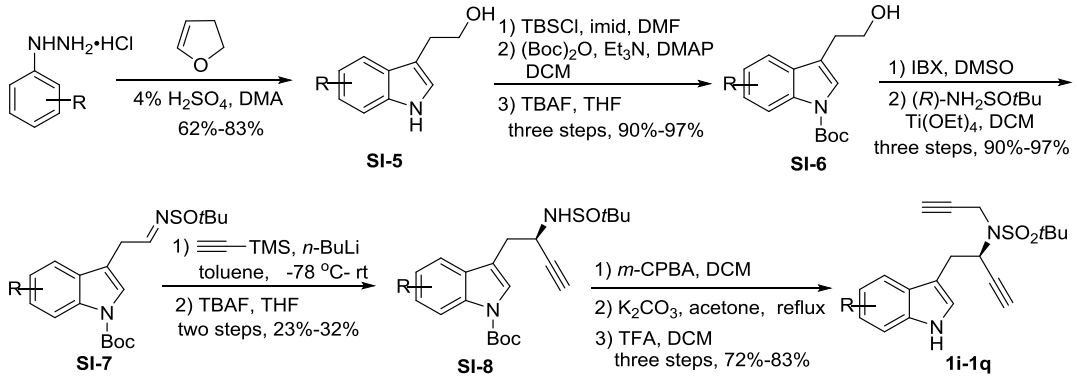
***General procedure A*. Preparation of Indole Tethered 1,6-diynes 1a-1b, 1d-1g.**




**1c** (0.6 mmol, 200 mg) was dissolved in DCM (3 mL), TFA (1mL) was added and the solution was stirred for 30 min. The reaction was quenched with saturated aqueous sodium hydrogen carbonate solution. The organic phase was isolated and the aqueous phase extracted thoroughly with further dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo to afford **SI-4** (129.0 mg, 94% yield) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/2, v/v).

**SI-4** (200.0 mg, 0.9 mmol) was stirred in toluene: $NaHCO_3$ (aq) (8 mL:12 mL) at rt, then acyl chloride was added drop-wise to a suspension of solution, TLC monitoring showed full consumption of starting material, the reaction mixture was quenched with $H_2O$ (10 mL), and extracted with ethyl acetate (10 mL×3), the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography to afford product.

***General procedure B.*** **Preparation of Indole Tethered 1,6-diynes 1i-1q.**




To a solution of phenyhydrazine-HCl (10.0 g, 55.8 mmol) in 4% $H_2SO_{4(aq)}$ (10 mL) and *N*,*N*-dimethyl acetamide (DMA, 30 mL) at 100 ℃ in oil bath was added dihydrofuran (4.4 mL, 55.8 mmol) dropwise. The reaction was aged for 2 hours, then cooled to room temperature, extracted with ethyl acetate (20 mL) and washed with water (30 mL) 3 times, dried over $MgSO_4$, filtered and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography to afford **SI-5** (62%-83%).

TBSCl (47.6 mmol, 7.2 g) was added to a solution of **SI-5** (43.3 mmol, 8.5 g) and imid (86.6 mmol, 5.8 g) in DMF (40 mL) at 0 °C, and the reaction mixture was stirred at rt for 3h. The reaction mixture was quenched with water (200 mL) and extracted with ethyl acetate (40 mL×3) and dried over $MgSO_4$, The solution was filtered and concentrated under reduced pressure to give the crude product that was used

in the next step without further purification. To a solution of the above crude product in dry DCM (40 mL) was added $(Boc)_2O$ (51.9 mmol, 11.1 g), $Et_3N$ (129.9 mmol, 17.7 mL) and DMAP (2.2 mmol, 258 mg) at 0 °C, after stiring at 0 °C for 15 min and then at rt for 1h. The reaction mixture was diluted with DCM (20 mL) and washed with brine, dried over $MgSO_4$, then the solution was filtered and concentrated under reduced pressure to give the crude product that was used in the next step without further purification. The crude product was dissolved in THF (40 mL), TBAF (1 M in THF, 51.9 mmol, 48 mL) was added slowly. The reaction mixture was stirred at rt for 30 min, the reaction mixture was quenched with water (10 mL), and extracted with ethyl acetate (15 mL×3), the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography to afford **SI-6** (three steps, 90%-97%).

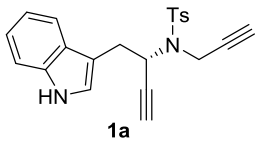
IBX (27.0 mmol, 7.6 g) was added to a solution of **SI-6** (13.5 mmol, 4.0 g) in DMSO (20 mL) at rt, after stirring for 1h and then the suspension was filtered through a short pad of celite, and the solvent was diluted with ethyl acetate (20 mL), extracted with $H_2O$ (15 mL×3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo to give the crude aldehyde that was used in the next step without further purification. The above crude aldehyde, (*R*)-$NH_2SO$*t*Bu (13.5 mmol, 1.6 g) and $Ti(OEt)_4$ (40.5 mmol, 8.5 mL)were dissolved in dry DCM (20 mL), the solution was stirred at 50 °C in oil bath for 2h[1]. The reaction was cooled to rt and quenched with $H_2O$ (20 mL), then the suspension was filtered through a short pad of celite, and the solvent was extracted with DCM (15 mL×3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography to afford **SI-7** (two steps, 26%-47%).

Weight out trimethylsilylacetylene (14.0 mmol, 2.0 mL) in dry toluene (5 mL) at -78 °C under argon, the solution was stirred at this temperature for 5 min, then added *n*-BuLi (10.5 mmol, 4.2 mL) dropwise with stirring over 5 min. After complete addition, stirring the reaction mixture for an additional 30 min at -78 °C. **SI-7** (3.5 mmol, 1.4 g) in dry toluene (5 mL) was added to the above solution slowly at -78 °C, after stirring at this temperature for 15 min[2]. The reaction mixture was quenched with aqueous potassium sodium tartrate (20 mL), extracted with ethyl acetate (10 mL×3), dried ($MgSO_4$) and concentrated in vacuo to give the pure alkyne (The compound has a single structure without any isomer identified by NMR) that was used in the next step without further purification. TBAF (1M in THF, 4.2 mmol, 4.2 mL) was added to the solution of the above crude alkyne in THF (10 mL) at 0 °C, after stirring for 30 min, the solution was extracted with ethyl acetate, the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography to afford **SI-8** (two steps, 23%-32%).

To a solution of the corresponding **SI-8** (0.7 mmol, 300 mg) in dry $CH_2Cl_2$ (10.0 mL), *m*-CPBA (1.0 mmol, 177 mg) was added at rt in one portion. When the reaction was completed (about 20 minutes), the reaction was quenched with saturated solution of $NaHCO_3$ (10 mL), extracted with $CH_2Cl_2$ (3x10 mL). Finally, the organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated, obtaining the corresponding pure sulfonylimines without further purification. 3-bromopropyne (2.1 mmol, 181 $\mu$L) was added to a solution of the above sulfonylimine and $K_2CO_3$ (2.1 mmol, 274.0 mg) in acetone (10 mL) at rt, then the solution was reflux overnight. When the reaction was finished, the suspension was filtered through a short pad of celite, and the solvent was concentrated under reduced pressure to obtain the corresponding pure diyne without further purification. The above diyne was dissolved in DCM (4 mL), TFA (1mL) was added and the solution was stirred for 30 min. The reaction was quenched with saturated aqueous sodium hydrogen carbonate solution. The organic phase was isolated and the aqueous phase extracted thoroughly with further dichloromethane. The combined organic

layers were washed with brine, dried over ($MgSO_4$) and concentrated in vacuo to afford products. (three steps, 72%-83%).

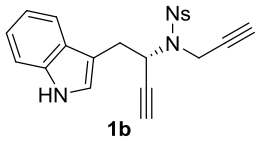
**(*S*)-*N*-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1a)**



1a

Product **1a** was prepared according to the ***General procedure A*** starting from **SI-4** (200.0 mg, 0.9 mmol) and Tosyl chloride (1.3 mmol, 247.8 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1a** (366.6 mg, 75% yield) as a pale-yellow solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 6.74 (*c* 0.1375, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.15 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25-7.18 (m, 4H), 7.17-7.11 (m, 2H), 5.03 (m, 1H), 4.31 (dd, *J* = 18.4, 2.5 Hz, 1H), 4.14 (dd, *J* = 18.4, 2.5 Hz, 1H), 3.46-3.30 (m, 2H), 2.40 (s, 3H), 2.31 (t, *J* = 2.5 Hz, 1H), 2.23 (d, *J* = 2.3 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 136.1, 136.1, 129.5, 127.6, 127.2, 123.6, 122.0, 119.5, 118.6, 111.4, 110.5, 80.1, 79.9, 75.1, 72.9, 51.7, 34.0, 32.1, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_2S$ 377.1318; found 377.1314.

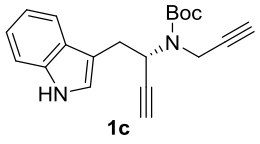
**(S)-*N*-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1b)**



1b

Product **5b** was prepared according to the ***General procedure A*** starting from **SI-4** (200.0 mg, 0.9 mmol) and 4-nitrobenzenesulfonyl chloride (1.3 mmol, 288.1 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1b** (370.0 mg, 70% yield) as a yellow solid. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -4.14 (*c* 0.1500, CHCl3). **1H NMR (500 MHz, CDCl3)** δ 8.07 (d, *J* = 8.9 Hz, 2H), 8.00 (s, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.21-7.15 (m, 1H), 7.14-7.10 (m, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 5.01 (td, *J* = 7.4, 2.3 Hz, 1H), 4.39 (dd, *J* = 18.6, 2.5 Hz, 1H), 4.21 (dd, *J* = 18.5, 2.5 Hz, 1H), 3.32 (qd, *J* = 14.6, 7.5 Hz, 2H), 2.35 (d, *J* = 2.3 Hz, 1H), 2.31 (t, *J* = 2.5 Hz, 1H). **13C NMR (126 MHz, CDCl3)** δ 149.7, 144.9, 136.0, 128.5, 126.8, 123.7, 123.6, 122.4, 119.8, 118.4, 111.3, 110.1, 79.8, 79.2, 75.2, 73.5, 51.7, 33.9, 31.8. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{21}H_{18}N_3O_4S$ 408.1013; found 408.1003.

**(*S*)-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)(prop-2-yn-1-yl)*tert*-butylcarbamate (1c)**

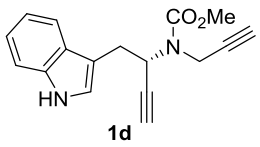


1c

$[\alpha]_D^{20}$ = -2.77 (*c* 0.1250, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 10.09 (s, 1H), 7.71 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.12-5.31 (m, 1H), 4.39-4.01 (m, 2H), 3.22 -3.29 (m, 2H), 2.69-2.70 (m, 1H), 2.72 (t, *J* = 2.5 Hz, 1H), 1.16-1.49 (m, 9H). **$^{13}$C NMR (126 MHz, Acetone-$d_6$)** δ 153.5, 136.7, 127.6, 124.1, 123.7, 121.3, 118.7, 118.3, 111.4, 110.3, 81.6, 81.4, 79.9, 74.5, 71.3, 49.7, 49.1, 32.9, 32.7, 30.9, 27.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_2$ 323.1754; found 323.1746.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(*S*)-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)(prop-2-yn-1-yl)methylcarbamate (1d)**

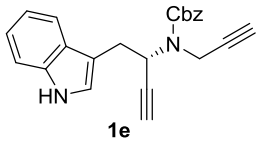


1d

Product **1d** was prepared according to the ***General procedure A*** starting from **SI-4** (100.0 mg, 0.45 mmol) and **methyl chloroformate** (0.63 mmol, 52.0 $\mu$L). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1b** (135.0 mg, 71% yield) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = -5.41 (*c* 0.1250, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-*d*$_6$)** δ 10.05 (s, 1H), 7.76 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.30 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.51-5.05 (m, 1H), 4.38-4.11 (m, 2H), 3.75-3.54 (m, 3H), 3.50 -3.20 (m, 2H), 2.92 (s, 1H), 2.75 (t, *J* = 2.3 Hz, 1H). **$^{13}$C NMR (126 MHz, Acetone-*d*$_6$)** δ 155.4, 155.3, 136.7, 136.6, 127.6, 127.5, 123.9, 121.4, 118.9, 118.4, 111.5, 111.4, 110.2, 110.1, 81.3, 80.9, 74.9, 71.9, 52.4, 49.9, 33.1, 31.1, 30.9. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{17}H_{17}N_2O_2$ 281.1285; found 281.1277.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(*S*)-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)(prop-2-yn-1-yl)benzylcarbamate (1e)**

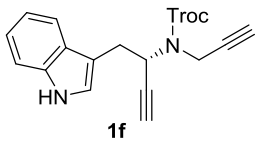


1e

Product **5e** was prepared according to the ***General procedure A*** starting from **SI-4** (200.0 mg, 0.9 mmol) and benzyl chloroformate (1.3 mmol, 182.0 $\mu$L). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1e** (233.9 mg, 73% yield) as a pale-yellow solid. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 3.13 (*c* 0.1300, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-*d*$_6$)** δ 10.09 (s, 1H), 7.76 (s, 0.5H), 7.61-7.19 (m, 7H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05-6.97 (m, 1H), 5.39-4.96 (m, 3H), 4.39-4.21 (m, 2H), 3.84-3.28 (m, 2H), 2.97-2.94 (m, 1H), 2.78 (t, *J* = 2.5 Hz, 1H). **$^{13}$C NMR (126 MHz, Acetone-*d*$_6$)** δ 154.4, 153.9, 136.2, 127.9, 127.6, 127.4, 127.1, 123.6, 123.3, 120.9, 118.4, 117.9, 110.9, 110.8, 109.6, 80.7, 80.5, 74.6, 71.5, 66.8, 66.7, 49.5, 32.8, 32.6, 30.8, 30.4. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_2$ 357.1598; found 357.1586.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(*S*)-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)(prop-2-yn-1-yl)-2,2,2-trichloroethylcarbamate (1f)**

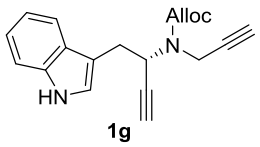


1f

Product **5f** was prepared according to the ***General procedure A*** starting from **SI-4** (100.0 mg, 0.45 mmol) and 2,2,2-trichloroethyl chloroformate (0.63 mmol, 90.8 $\mu$L). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1f** (146.1 mg, 82% yield) as a pale-yellow oil. $R_f$ = 0.7 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = -5.68 (*c* 0.0950, $CDCl_3$). **$^1$H NMR (500 MHz, Acetone-*d*$_6$)** δ 10.07 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.14-7.10 (m, 1H), 7.07-7.03 (m, 1H), 5.32-5.28 (m, 1H), 4.94-4.57 (m, 2H), 4.36-4.22 (m, 2H), 3.45-3.28 (m, 2H), 2.96 (d, *J* = 7.5 Hz, 1H), 2.77 (s, 1H). **$^{13}$C NMR (126 MHz, Acetone-*d*$_6$)** δ 153.3, 136.7, 127.5, 124.2, 121.4, 118.9, 118.4, 111.4, 109.8, 95.5, 80.7, 80.2, 75.4, 74.9, 72.5, 50.3, 33.9, 31.2,.**HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{18}H_{16}Cl_3N_2O_2$ 397.0272; found 397.0259.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(*S*)-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)(prop-2-yn-1-yl)allylcarbamate (1g)**

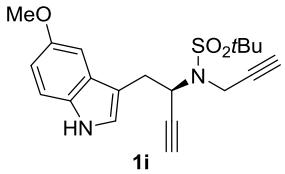


**1g**

Product **1g** was prepared according to the ***General procedure A*** starting from **SI-4** (116.0 mg, 0.52 mmol) and allyl chloroformate (0.8 mmol, 84.0 $\mu$L). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1g** (123.0 mg, 78% yield) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = -1.61 (*c* 0.1450, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 10.09 (s, 1H), 7.73 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.16-7.11 (m, 1H), 7.10-7.04 (m, 1H), 5.99-5.76 (m, 1H), 5.42-5.21 (m, 3H), 4.68-4.30 (m, 3H), 4.23-4.19 (m, 1H), 3.37-3.30 (m, 2H), 2.96-2.92 (m, 1H), 2.76 (t, *J* = 2.5 Hz, 1H). **$^{13}$C NMR (126 MHz, Acetone-$d_6$)** δ 154.3, 136.7, 133.0, 127.5, 123.8, 121.3, 118.8, 118.3, 117.2, 116.4, 111.4, 110.1, 81.2, 80.9, 74.9, 71.9, 66.0, 49.9, 33.1, 31.3, 30.9. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$ 307.1441; found 307.1433.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

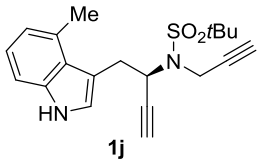
**(*R*)-*N*-(1-(5-methoxy-1*H*-indol-3-yl)but-3-yn-2-yl)-2-methyl-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1i)**



**1i**

Product **1i** was prepared according to the ***General procedure B*** starting from 4-methoxyphenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether= 1/10 to afford **1i** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -49.02 (*c* 0.0850 $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.27 (s, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.93-4.8 (m, 1H), 4.34 (s, 2H), 3.89 (s, 3H), 3.52-3.42 (m, 2H), 2.41 (d, *J* = 2.3 Hz, 1H), 2.37 (t, *J* = 2.4 Hz, 1H), 1.42 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 154.2, 131.2, 127.7, 123.9, 112.6, 112.0, 110.9, 100.4, 81.3, 81.2, 74.8, 72.6, 62.4, 55.9, 53.4, 35.2, 33.2, 24.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_3S$ 373.1580; found 373.1576.

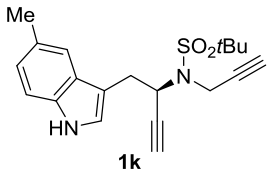
**(*R*)-2-methyl-*N*-(1-(4-methyl-1*H*-indol-3-yl)but-3-yn-2-yl)-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1j)**



**1j**

Product **1j** was prepared according to the ***General procedure B*** starting from 3-methylphenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1j** as a yellow oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -6.03 (*c* 0.0950, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.17 (s, 1H), 7.21-7.18 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.1 Hz, 1H), 4.95-4.91 (m, 1H), 4.48-4.25 (m, 2H), 3.76-3.58 (m, 2H), 2.79 (s, 3H), 2.45 (d, *J* = 2.3 Hz, 1H), 2.40 (t, *J* = 2.5 Hz, 1H), 1.43 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 136.5, 130.7, 125.5, 123.8, 122.0, 121.4, 111.4, 109.3, 81.3, 81.3, 75.3, 72.6, 62.5, 54.3, 35.3, 33.5, 24.6, 20.5. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1628; found 357.1631.

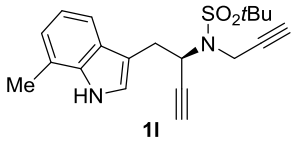
**(*R*)-2-methyl-*N*-(1-(5-methyl-1H-indol-3-yl)but-3-yn-2-yl)-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1k)**



1k

Product **1k** was prepared according to the ***General procedure B*** starting from 4-methylphenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1k** as a pale-yellow solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -34.14 (*c* 0.1075, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.12 (s, 1H), 7.58 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 2.3 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.5 Hz, 1H), 5.10-4.80 (m, 1H), 4.61-4.29 (m, 2H), 3.57-3.48 (m 7.7 Hz, 2H), 2.54 (s, 3H), 2.46 (d, *J* = 2.3 Hz, 1H), 2.44 (t, *J* = 2.5 Hz, 1H), 1.48 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 134.5, 128.8, 127.6, 123.7, 123.6, 118.4, 110.9, 110.4, 81.6, 81.3, 74.8, 72.7, 62.4, 53.6, 35.1, 32.6, 24.6, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 57.1631; found 357.1629.

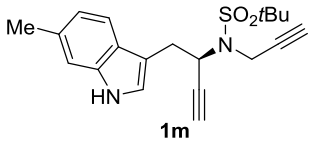
**(*R*)-2-methyl-*N*-(1-(7-methyl-1H-indol-3-yl)but-3-yn-2-yl)-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1l)**



1l

Product **1l** was prepared according to the ***General procedure B*** starting from 2-methylphenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1l** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -34.45 (*c* 0.1075, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.04 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.1 Hz, 1H), 5.09-4.81 (m, 1H), 4.40-4.32 (m, 2H), 3.60-3.30 (m, 2H), 2.48 (s, 3H), 2.40 (d, *J* = 2.3 Hz, 1H), 2.38 (t, *J* = 2.5 Hz, 1H), 1.43 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 135.7, 126.9, 123.1, 122.7, 120.4, 119.9, 116.6, 111.5, 81.3, 81.3, 74.9, 72.6, 62.4, 53.5, 35.1, 32.9, 24.5, 16.6.
**HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found 357.1627.

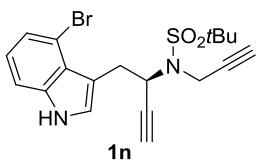
**(*R*)-2-methyl-*N*-(1-(6-methyl-1*H*-indol-3-yl)but-3-yn-2-yl)-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1m)**



1m

Product **1m** was prepared according to the ***General procedure B*** starting from 3-methylphenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1m** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -7.30 (*c* 0.1000, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.5 Hz, 1H), 4.91-4.88 (m, 1H), 4.37-4.30 (m, 2H), 3.61-3.36 (m, 2H), 2.46 (s, 3H), 2.38 (d, *J* = 2.3 Hz, 1H), 2.36 (t, *J* = 2.4 Hz, 1H), 1.41 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 136.6, 131.9, 125.2, 122.6, 121.5, 118.6, 111.1, 111.0, 81.3, 74.7, 72.5, 62.3, 53.5, 35.1, 32.7, 29.7, 24.5, 21.7. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found 357.1624.

**(*R*)-*N*-(1-(4-bromo-1*H*-indol-3-yl)but-3-yn-2-yl)-2-methyl-N-(prop-2-yn-1-yl)propane-2-sulfonamide (1n)**

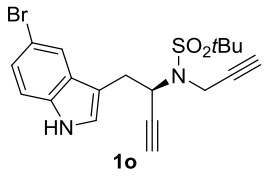


1n

Product **1n** was prepared according to the ***General procedure B*** starting from 3-bromophenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1n** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 37.50 (*c* 0.1625, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ

8.39 (s, 1H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 5.22-5.08 (m, 1H), 4.54-4.27 (m, 2H), 3.85 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.66 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.53-2.52 (m, 2H), 1.42 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 137.4, 126.1, 125.5, 123.9, 122.6, 113.7, 111.1, 110.9, 81.5, 81.4, 74.9, 72.9, 62.5, 54.3, 35.4, 31.6, 24.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0572.

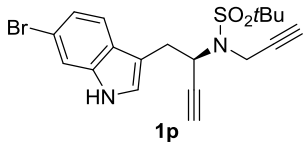
**(*R*)-*N*-(1-(5-bromo-1*H*-indol-3-yl)but-3-yn-2-yl)-2-methyl-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide** (1o)



1o

Product **1o** was prepared according to the ***General procedure B*** starting from 4-bromophenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1o** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -21.29 (*c* 0.0825, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 10.38 (s, 1H), 7.89 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.24 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.90-4.85 (m, 1H), 4.29-4.32 (m, 2H), 3.59 (dd, *J* = 13.8, 10.8 Hz, 1H), 3.39 (dd, *J* = 13.9, 4.5 Hz, 1H), 3.07 (s, 1H), 2.94 (t, *J* = 2.5 Hz, 1H), 1.42 (s, 9H). **$^{13}$C NMR (126 MHz, Acetone-$d_6$)** δ 135.36, 129.3, 125.6, 124.0, 120.9, 113.3, 111.8, 110.0, 81.5, 80.8, 76.0, 73.2, 61.8, 53.5, 34.7, 32.7, 23.8. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0573.

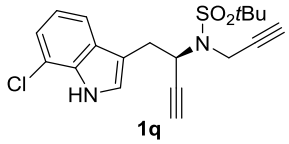
**(*R*)-*N*-(1-(6-bromo-1H-indol-3-yl)but-3-yn-2-yl)-2-methyl-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1p)**



1p

Product **1p** was prepared according to the ***General procedure B*** starting from 3-bromophenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1p** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -22.67 (*c* 0.1175, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 10.42 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.02-4.98 (m, 1H), 4.53-4.43 (m, 2H), 3.69 (dd, *J* = 13.8, 10.8 Hz, 1H), 3.49 (dd, *J* = 13.8, 4.4 Hz, 1H), 3.15 (d, *J* = 2.3 Hz, 1H), 3.03 (t, *J* = 2.4 Hz, 1H), 1.50 (s, 9H). **$^{13}$C NMR (126 MHz, Acetone)** δ 137.5, 126.4, 125.1, 121.9, 119.9, 114.5, 114.3, 110.6, 81.5, 80.7, 76.0, 73.1, 61.8, 53.6, 34.7, 32.8, 23.8. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0571.

**(*R*)-*N*-(1-(7-chloro-1*H*-indol-3-yl)but-3-yn-2-yl)-2-methyl-*N*-(prop-2-yn-1-yl)propane-2-sulfonamide (1q)**

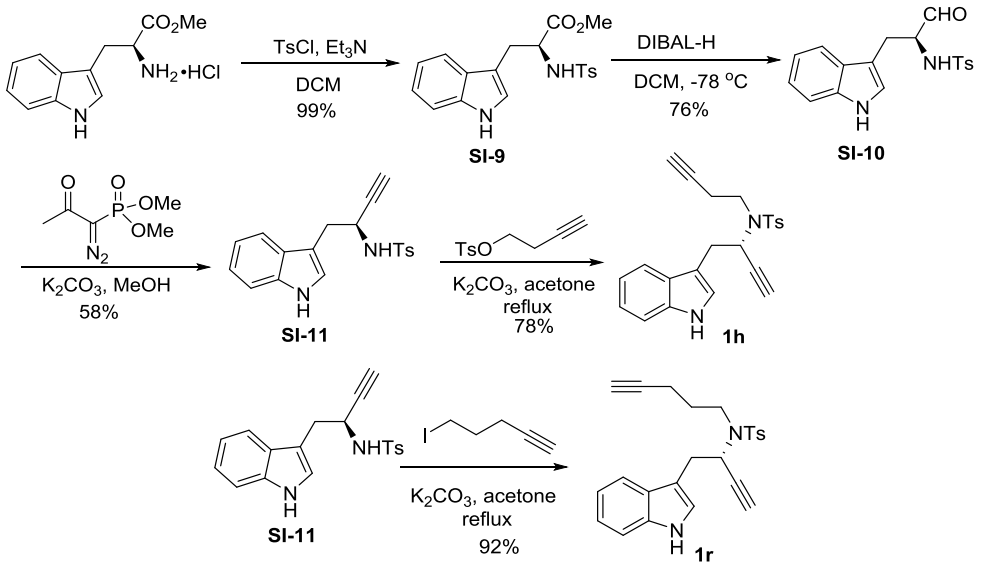


1q

Product **1q** was prepared according to the ***General procedure B*** starting from 2-chlorophenylhydrazine hydrochloride. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **1q** as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -22.04 (*c* 0.1600, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 4.91-4.88 (m, 1H), 4.38-4.31 (m, 2H), 3.57-3.41 (m, 2H), 2.43 (d, *J* = 2.3 Hz, 1H), 2.39 (t, *J* = 2.5 Hz, 1H), 1.42 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 133.4, 128.8, 124.1, 121.5, 120.5, 117.6, 116.7,

112.2, 81.2, 81.0, 75.2, 72.7, 62.5, 53.5, 35.2, 32.9, 24.5. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}ClN_2O_2S$ 377.1085; found 377.1077.

**Preparation of Indole Tethered 1,6-diynes 1h, 1r**

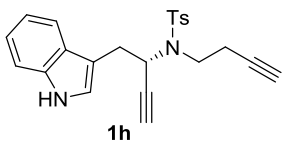



L-Tryptophan methyl ester hydrochloride (39.2 mmol, 10.0 g) and TsCl (41.1 mmol, 7.8 g) were dissolved in DCM (40 mL), $Et_3N$ (117.6 mmol, 16.4 mL) was added dropwise at 0 °C, then the solution was stirred at rt for 6h. The reaction solution was washed with saturated ammonium chloride solution (20 mL×3), The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude product was triturated in ethyl acetate (20 mL) for 1h, The suspension was filtered through a short pad of celite to afford **SI-9** (14.4 g, 99%) as a colorless solid, $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/1, v/v).

DIBAL-H (1.5 M in toluene, 8.0 mmol, 5.4 mL) was added dropwise to a suspension of **SI-9** (5.3 mmol, 2.0 g) in anhydrous dichloromethane (30 mL) at -78 °C. The reaction was allowed to stirred for 15 min before being quenched with aqueous potassium sodium tartrate (10 mL). The crude mixture was filtered through celite and the phases separated. The aqueous phase was extracted with dichloromethane (10 mL×3) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/6 to afford **SI-10** (2.9 g, 76% yield) as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/1, v/v). **NOTE:** The by-product alcohol can be further oxidized by IBX to afford **SI-10**.

**SI-10** (2.4 mmol, 819.0 mg) was dissolved in anhydrous MeOH (10 mL), $K_2CO_3$ (7.1 mmol, 928.0 mg) was added and then dimethyl (1-diazo-2-oxopropyl)phosphonate (3.57 mmol, 685.4 mg) in MeOH (10 mL) was added slowly. The reaction mixture was stirred at rt for 30 min. The crude mixture was filtered through celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with methanol/dichloromethane = 1/250 to afford **SI-11** (467.0 mg, 58% yield) as a yellow solid. $R_f$ = 0.6 (methanol/dichloromethane = 1/50, v/v).

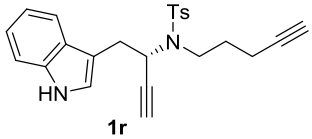
**(*S*)-*N*-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)-*N*-(but-3-yn-1-yl)-4-methylbenzenesulfonamide (1h)**



**1h**

3-Butynyl *p*-toluenesulfonate (1.2 mmol, 265.4 mg) was added to a solution of **SI-11** (0.59 mmol, 200.0 mg) and $K_2CO_3$ (1.2 mmol, 165.6 mg) in acetone (10 mL) at rt, then the solution was reflux in oil bath overnight. When the reaction was finished, the suspension was filtered through a short pad of celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to obtain **1h** (179.5 mg, 78%) as a brown solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -2.00 (*c* 0.1200, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.17-7.12 (m, 1H), 5.04-5.00 (m, 1H), 3.47-3.41 (m, 2H), 3.28 (dd, *J* = 14.3, 6.1 Hz, 1H), 3.17 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.83-2.76 (m, 1H), 2.59-2.52 (m, 1H), 2.40 (s, 3H), 2.10 (d, *J* = 2.3 Hz, 1H), 2.05 (t, *J* = 2.6 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 143.7, 136.1, 135.7, 129.2, 127.7, 127.2, 123.1, 122.2, 119.7, 118.6, 111.3, 110.5, 81.2, 80.5, 74.4, 70.4, 51.4, 44.3, 32.6, 21.6, 21.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2S$ 391.1475; found 391.1468.

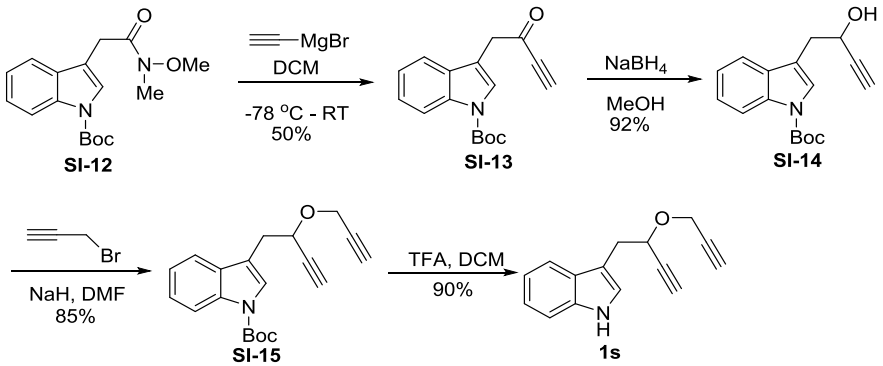
**(*S*)-*N*-(1-(1*H*-indol-3-yl)but-3-yn-2-yl)-4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (1r)**



**1r**

5-Iodo-1-pentyne (1.2 mmol, 228.9 mg) was added to a solution of **SI-11** (0.59 mmol, 200.0 mg) and $K_2CO_3$ (1.2 mmol, 165.6 mg) in acetone (10 mL) at rt, then the solution was reflux in oil bath overnight. When the reaction was finished, the suspension was filtered through a short pad of celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to obtain **1r** (220 mg, 92%) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether =1/3, v/v). $[\alpha]_D^{20}$ = 9.13 (*c* 0.1475, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.15 (s, 1H), 7.75-7.69 (m, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.23-7.19 (m, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.18-7.11 (m, 1H), 5.08-5.04 (m, 1H), 3.40 (td, *J* = 8.9, 6.0 Hz, 2H), 3.31 (dd, *J* = 14.2, 6.1 Hz, 1H), 3.20 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.40 (s, 3H), 2.30-2.26 (m, 2H), 2.15-2.05 (m, 2H), 2.04 (t, *J* = 2.6 Hz, 1H), 1.99-1.90 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 143.5, 136.1, 135.9, 129.5, 127.7, 127.3, 123.2, 122.1, 119.6, 118.7, 111.3, 110.6, 83.5, 80.6, 74.4, 69.3, 51.6, 44.7, 32.7, 29.7, 21.6, 16.1. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_2S$ 405.1631; found 405.1627.

**Preparation of Indole Tethered 1,6-diyne 1s**

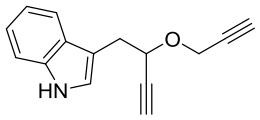


To a solution of **S1-12**[3] (4.7 mmol, 1.5 g) in DCM (15 mL) at -78 °C was added ethynyl magnesium bromide (0.5 M in THF, 14.1 mmol, 28.2 mL) slowly, then the solution was warmed to rt and stirred for 2h. The reaction mixture was quenchend with aqueous potassium sodium tartrate (10 mL), extracted with dichloromethane (10 mL×3) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/25 to afford **SI-13** (665.3 mg, 50% yield) as a colorless oil. $R_f$ = 0.8 (ethyl acetate/petroleum ether = 1/5, v/v).

$NaBH_4$ (7.1 mmol, 267.0 mg) was added to a solution of **SI-13** (1.8 mmol, 500 mg) in MeOH (10 mL), the mixture solution was stirred for 30 min at rt, and quenched by saturated ammonium chloride (5 mL), extracted with ethyl acetate (10 mL×3) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/20 to afford **SI-14** (501.6 mg, 92% yield) as a colorless oil. $R_f$ = 0.2 (ethyl acetate/petroleum ether = 1/10, v/v).

A solution of NaH (0.8 mmol, 20.2 mg) in DMF (2 mL) was cooled to 0 °C, **SI-14** (0.7 mmol, 195.0 mg) in DMF (2 mL) was added dropwise, the mixture was warmed up to rt and stirred for 20 min and 3-bromopropyne (0.8 mmol, 73.0 $\mu$L) was added. The reaction mixture was stirred until the starting material completely consumed monitored by TLC, then quenchend with $H_2O$ (10 mL), extracted with ethyl acetate (10 mL×3) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/30 to afford **SI-15** (188.2 mg, 85% yield) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/10, v/v).

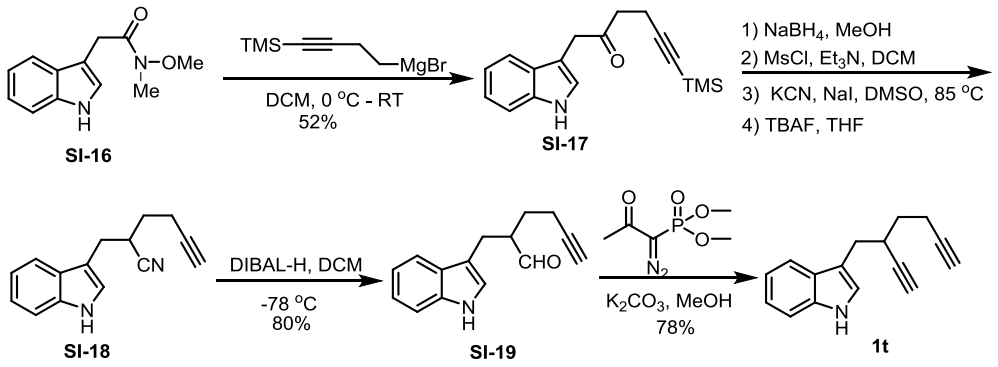
**3-(2-(prop-2-yn-1-yloxy)but-3-yn-1-yl)-1*H*-indole (1s)**



**1s**

**SI-15** (0.5 mmol, 162.0 mg) was dissolved in DCM (5 mL), TFA (0.7 mL) was added and the solution was stirred for 30 min. The reaction was quenched with saturated aqueous sodium hydrogen carbonate solution. The organic phase was isolated and the aqueous phase extracted thoroughly with further dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/15 to afford **1s** (101.0 mg, 90% yield) as a colorless oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/5, v/v). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.32-7.27 (m, 1H), 7.22-7.16 (m, 2H), 4.84 (d, *J* = 2.6 Hz, 2H), 4.66 (t, *J* = 6.3 Hz, 1H), 3.31-3.13 (m, 2H), 2.49 (d, *J* = 2.1 Hz, 1H), 2.42 (t, *J* = 2.5 Hz, 1H), 2.26 (s, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 136.2, 128.6, 126.6, 122.3, 119.8, 119.4, 110.0, 109.5, 84.8, 77.7, 73.6, 73.2, 62.3, 35.8, 33.8. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070; found 224.1066.

**Preparation of Indole Tethered 1,6-diyne 1t**



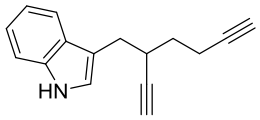

To a solution of **S1-16**[3] (3.5 mmol, 756.0 mg) in DCM (10 mL) at 0 °C was added 4-trimethylsilyl-3-butynyl-1-magnesium bromide (0.5 M in THF, 10.4 mmol, 20.0 mL) slowly, then the solution was warmed to rt and stirred for 3h. The reaction mixture was quenchend with saturated ammonium chloride (10 mL), extracted with dichloromethane (10 mL×3) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/20 to afford **SI-17** (515.0 mg, 52% yield) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/5, v/v).

$NaBH_4$ (7.2 mmol, 272.0 mg) was added to a solution of **SI-17** (1.8 mmol, 508.0 mg) in MeOH (10 mL), the mixture solution was stirred for 30 min at rt, and quenched by saturated ammonium chloride (5 mL), extracted with ethyl acetate (10 mL×3) and concentrated in vacuo to give the crude product that was used in the next step without further purification. The above crude product and $Et_3N$ (5.3 mmol, 732.0 $\mu$L) was dissolved in DCM (8 mL), MsCl (2.6 mmol, 205.0 $\mu$L) was added in the solution slowly at rt. The reaction mixture was stirred for 30 min, then washed by saturated ammonium chloride (10 mL×3) and concentrated in vacuo to give the crude product that was used in the next step without further purification.

A stirred solution of the above crude product, KCN (3.5 mmol, 229.2 mg) and NaI (0.02 mmol, 2.6 mg) in DMSO (12 mL) was heated at 85 °C in oil bath for 2h. The reaction was cooled to room temperature and quenched with water and extracted with ethyl acetate (10 mL × 3). The organic fractions were collected, and washed with brine (3 × 10 mL), dried over $Na_2SO_4$, and filtered, concentrated. The residue was dissolved in THF (5 mL), TBAF (1M in THF, 2.6 mmol, 2.6 mL) was added, after stirring for 30 min, the reaction solution was quenched with water and extracted with ethyl acetate (5 mL × 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **SI-18** (175.0 mg, 44% yield) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/5, v/v).

To a solution of nitrile **SI-18** (0.7 mmol, 150 mg) in dry DCM (5 mL) cooled at -78 °C, and stirred under argon was added DIBAL-H (1.5 M in toluene, 1.3 mmol, 0.9 mL) dropwise. After being stirred at this temperature for 20 min, then the solution was warmed to rt. Rochelle salt was added and mixture was stirred for 30 min until the layers appeared clear. The reaction mixture was extracted with ethyl acetate (5 mL × 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **SI-19** (120.0 mg, 80% yield) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/5, v/v).

**3-(2-ethynylhex-5-yn-1-yl)-1*H*-indole (1t)**



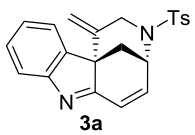

**1t**

**SI-19** (444.4 $\mu$mol, 100 mg) was dissolved in anhydrous MeOH (5 mL), $K_2CO_3$ (1.3 mmol, 176 mg) was added and then dimethyl (1-diazo-2-oxopropyl)phosphonate (0.7 mmol, 130 mg) in MeOH (2 mL) was added slowly. The reaction mixture was stirred at rt for 30 min. The crude mixture was filtered through celite, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/20 to afford **1t** (76.7 mg, 87% yield) as a colorless oil. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/5, v/v). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.01 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.21 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.16-7.08 (m, 2H), 3.34 (ddd, *J* = 11.1, 8.8, 5.6 Hz, 1H), 2.71-2.60 (m, 2H), 2.29-2.17 (m, 2H), 2.17-2.03 (m, 2H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.99 (t, *J* = 2.5 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 136.5, 126.8, 122.2, 121.4, 119.5, 119.2, 117.9, 111.5, 84.5, 83.2, 70.0, 68.7, 34.8, 33.2, 25.4, 16.8. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{16}H_{16}N$ 222.1277; found 222.1276.

***General procedure C.*** **Preparation of Polycyclic Spiroindolenine 3a-3q.**

A flame-dried Schlenk flask equipped with a magnetic stir bar was charged with **1** (0.2 mmol, 1.0 equiv), (SPhos)AuCl (5% mmol) and $AgClO_4$ (5% mmol). The flask was capped with a rubber septum, then placed under an argon atmosphere, anhydrous DCE (4 mL) was added, the reaction mixture was stirred at 60 $^o$C in oil bath until the starting material completely consumed monitored by TLC. The solution was directly concentrated under reduced pressure and purified by flash column chromatography to afford **3**.

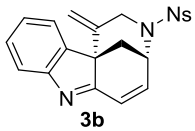
**(4*R*,11b*S*)-1-methylene-3-tosyl-1,2,3,4-tetrahydro-4,11b-methanoazocino[5,4-*b*]indole (3a)**




**3a**

Product **3a** was prepared according to the ***General procedure C*** starting from **1a** (0.2 mmol, 75.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3a** (32.0 mg, 85%) as a colorless solid. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -105.02 (*c* 0.1075, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.78-7.76 (m, 2H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.40-7.37 (m, 1H), 7.36-7.34 (d, *J* = 8.1 Hz, 2H), 7.28-7.24 (m, 1H), 7.21 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.81 (d, *J* = 9.9 Hz, 1H), 5.99-5.95 (m, 1H), 4.93 (dt, *J* = 6.0, 3.0 Hz, 1H), 4.83 (d, *J* = 1.8 Hz, 1H), 4.51 (d, *J* = 1.7 Hz, 1H), 4.35 (d, *J* = 14.2 Hz, 1H), 3.99 (dt, *J* = 14.3, 2.0 Hz, 1H), 2.47 (s, 3H), 2.45-2.42(m, 1H), 1.75 (dd, *J* = 12.4, 3.3 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 177.5, 156.2, 144.0, 138.7, 137.9, 136.55, 133.9, 130.0, 128.9, 128.7, 127.4, 125.9, 124.1, 121.9, 113.2, 58.5, 49.8, 46.5, 39.0, 21.7. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_2S$ 377.1318; found 377.1315.

**(4*R*,11b*S*)-1-methylene-3-((4-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydro-4,11b-methanoazocino[5,4-*b*]indole (3b)**

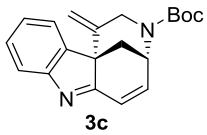



**3b**

Product **3b** was prepared according to the ***General procedure C*** starting from **1b** (0.2 mmol, 81.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3b** (57.0 mg, 70%) as a colorless solid. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -1.31 (*c* 0.1500, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.56-8.33 (m, 2H), 8.21-7.99 (m, 2H), 7.65 (dt, *J* = 7.7, 0.8 Hz, 1H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (td, J = 7.5, 1.1 Hz, 1H), 7.22 (dt, J = 7.4, 1.0 Hz, 1H),

6.90 (d, *J* = 9.9 Hz, 1H), 6.05-6.03 (m, 1H), 5.00-4.98 (m, 1H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.56 (d, *J* = 1.7 Hz, 1H), 4.39 (d, *J* = 14.4 Hz, 1H), 4.10 (dt, *J* = 14.5, 1.9 Hz, 1H), 2.43 (ddd, *J* = 12.5, 2.8, 1.4 Hz, 1H), 1.82 (dd, *J* = 12.5, 3.2 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 176.8, 156.2, 150.3, 145.7, 138.3, 137.4, 132.9, 129.4, 129.2, 128.5, 126.2, 124.6, 124.1, 122.2, 113.8, 58.4, 50.3, 46.6, 39.0. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{21}H_{18}N_3O_4S$ 408.1013; found 408.1003.

**(4*R*,11b*S*)-1-methylene-1,2-dihydro-4,11b-methanoazocino[5,4-*b*]indole-3(4*H*)-tert-butylcarboxylate (3c)**

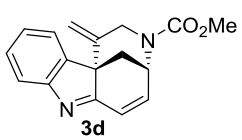


3c

Product **3c** was prepared according to the General procedure C starting from **1c** (0.2 mmol, 64.6 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3c** (56.2 mg, 87%) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -8.76 (*c* 0.1250, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 7.59 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.42-7.38 (m, 2H), 7.30 (td, *J* = 7.4, 1.1 Hz, 1H), 6.88 (d, *J* = 9.9 Hz, 1H), 6.46 (s, 1H), 5.16 (s, 1H), 4.83 (s, 1H), 4.55 (d, *J* = 15.4 Hz, 1H), 4.42-4.39 (m, 1H), 4.13-3.93 (m, 1H), 2.47 (s, 1H), 1.81 (dd, *J* = 12.5, 3.2 Hz, 1H), 1.50 (s, 9H). **$^{13}$C NMR (126 MHz, Acetone)** δ 178.3, 156.8, 140.9, 139.8, 135.8, 128.5, 127.0, 126.4, 125.5, 124.1, 121.4, 110.8, 79.7, 58.9, 48.1, 44.5, 38.1, 27.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_2$ 323.1754; found 323.1752.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(4*R*,11b*S*)-1-methylene-1,2-dihydro-4,11b-methanoazocino[5,4-*b*]indole-3(4*H*)-methylcarboxylate (3d)**

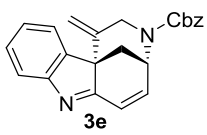


3d

Product **3d** was prepared according to the ***General procedure C*** starting from **1d** (0.2 mmol, 56.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3d** (39.4 mg, 70%) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -8.15 (*c* 0.090, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 7.60 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.45-7.35 (m, 2H), 7.29 (td, *J* = 7.4, 1.1 Hz, 1H), 6.89 (d, *J* = 9.8 Hz, 1H), 6.54-6.33 (m, 1H), 5.19-5.14 (m, 1H), 4.84-4.93(m, 1H), 4.57-4.54 (m, 1H), 4.45-4.36 (m, 1H), 4.20-4.01 (m, 1H), 3.72 (s, 3H), 2.48 (d, *J* = 12.4 Hz, 1H), 1.85-1.73 (m, 1H). **$^{13}$C NMR (126 MHz, Acetone)** δ 178.1, 156.8, 155.1, 140.5, 139.6, 135.6, 128.6, 127.3, 125.6, 124.2, 121.5, 111.1, 58.8, 52.3, 47.5, 44.9, 38.1. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{17}H_{17}N_2O_2$ 281.1285; found 281.1284.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(4*R*,11b*S*)-1-methylene-1,2-dihydro-4,11b-methanoazocino[5,4-*b*]indole-3(4*H*)-benzylcarboxylate (3e)**



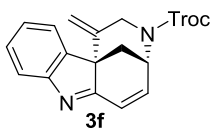
3e

Product **3e** was prepared according to the ***General procedure C*** starting from **1e**

(0.2 mmol, 71.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3e** (58.5 mg, 82%) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -12.34 (*c* 0.1725, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.44-7.37 (m, 6H), 7.34-7.27 (m, 2H), 6.98 (d, *J* = 9.7 Hz, 1H), 6.57-6.34 (m, 1H), 5.34-5.22 (m, 3H), 4.86 (d, *J* = 25.4 Hz, 1H), 4.73-4.62 (m, 1H), 4.54 (s, 1H), 4.29-4.13 (m, 1H), 2.53 (dd, *J* = 12.6, 2.7 Hz, 1H), 1.92-1.86 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 178.3, 156.3, 154.8, 139.2, 136.4, 135.6, 128.8, 128.6, 128.3, 128.1, 127.6, 125.8, 124.1, 122.0, 121.8, 112.4, 67.6, 58.8, 47.6, 45.3, 38.4. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_2$ 357.1598; found 357.1593.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(4*R*,11b*S*)-1-methylene-1,2-dihydro-4,11b-methanoazocino[5,4-*b*]indole-3(4*H*)-2,2,2-trichloroethyl carboxylate (3f)**

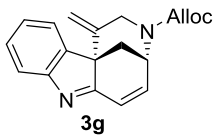


**3f**

Product **3f** was prepared according to the ***General procedure C*** starting from **1f** (0.2 mmol, 79.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3f** (69.9 mg, 88%) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20.0}$ = -12.91 (*c* 0.0950, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 7.63-7.58 (m, 1H), 7.42-7.40 (m, 2H), 7.32-7.29 (m, 1H), 6.94 (dd, *J* = 13.9, 9.6 Hz, 1H), 6.54 (t, *J* = 8.2 Hz, 1H), 5.37-5.16 (m, 1H), 4.98 (d, *J* = 12.2 Hz, 1H), 4.94-4.85 (m, 2H), 4.73-4.61 (m, 1H), 4.45 (s, 1H), 4.35-4.12 (m, 1H), 2.59 (dd, *J* = 38.2, 12.7 Hz, 1H), 1.93-1.82 (m, 1H). **$^{13}$C NMR (126 MHz, Acetone)** δ 177.9, 156.8, 139.9, 135.3, 128.7, 127.9, 127.5, 125.7, 124.2, 121.5, 111.7, 99.9, 95.9, 74.8, 58.8, 48.2, 45.3, 37.9. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{18}H_{16}C_{l3}N_2$ 97.0272; found 397.0265.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

**(4*R*,11b*S*)-1-methylene-1,2-dihydro-4,11b-methanoazocino[5,4-*b*]indole-3(4*H*)-allylcarboxylate (3g)**

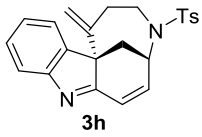


**3g**

Product **3g** was prepared according to the ***General procedure C*** starting from **3g** (0.2 mmol, 61.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3g** (52.2 mg, 85%) as a colorless oil. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20.0}$ = -6.06 (*c* 0.1150, $CHCl_3$). **$^1$H NMR (500 MHz, Acetone-$d_6$)** δ 7.66-7.57 (m, 1H), 7.44-7.41 (m, 2H), 7.32 (td, *J* = 7.3, 1.1 Hz, 1H), 6.93 (d, *J* = 9.8 Hz, 1H), 6.51-6.50 (m, 1H), 6.05-5.99 (m, 1H), 5.44-5.33 (m, 1H), 5.28-5.19 (m, 2H), 4.88 (s, 1H), 4.72-4.62 (m, 3H), 4.44 (s, 1H), 4.28-4.07 (m, 1H), 2.53 (s, 1H), 1.86 (dd, *J* = 12.5, 3.1 Hz, 1H). **$^{13}$C NMR (126 MHz, Acetone)** δ 178.1, 156.9, 140.5, 139.6, 135.5, 133.4, 128.6, 126.2, 125.6, 124.2, 121.4, 116.6, 112.2, 111.1, 65.8, 58.9, 47.8, 45.0, 38.1. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$ 307.1441; found 307.1437.

**Note**: The **$^1$H** and **$^{13}$C** spectrum were taken at room temperature. Its interpretation is confounded by the presence of rotamers, which cause both apparent splitting of certain peaks and extreme broadening of others.

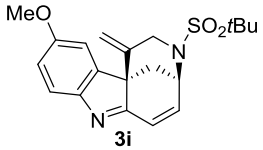
**1-methylene-4-tosyl-2,3,4,5-tetrahydro-1*H*-5,12b-methanoazonino[5,6-*b*]indole (3h)**



3h

Product **3h** was prepared according to the ***General procedure C*** starting from **1h** (0.2 mmol, 78.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3h** (59.4 mg, 76%) as a pale-yellow solid. $R_f$ = 0.3 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20.}$ = -38.65 (*c* 0.0975, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (td, *J* = 7.6, 1.3 Hz, 1H), 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 7.11 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.71 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.83-5.80 (m, 1H), 5.07-4.98 (m, 1H), 4.73 (s, 1H), 4.15 (s, 1H), 4.15-4.11 (m, 1H), 3.06 (dd, *J* = 13.8, 11.1 Hz, 1H), 2.81-2.80 (m, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.58 (dd, *J* = 14.5, 6.3 Hz, 1H), 2.46 (s, 3H), 1.89 (dd, *J* = 14.9, 7.0 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 180.8, 155.6, 145.9, 145.3, 143.7, 137.7, 136.6, 130.0, 128.3, 128.2, 127.0, 126.6, 121.7, 121.1, 115.8, 58.1, 52.0, 46.7, 38.4, 34.5, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_2S$ 391.1475; found 391.1469.

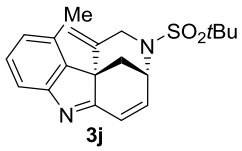
**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-10-methoxy-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[5,4-*b*]indole (3i)**



3i

Product **3i** was prepared according to the ***General procedure C*** starting from **3i** (0.2 mmol, 74.6 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3i** (62.0 mg, 83%) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 339.25 (*c* 0.1375, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 9.8 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.43-6.39 (m, 1H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.75 (dt, *J* = 6.1, 3.0 Hz, 1H), 4.59 (d, *J* = 1.3 Hz, 1H), 4.26 (dt, *J* = 15.0, 1.8 Hz, 1H), 4.21-4.09 (m, 1H), 3.85 (s, 3H), 2.52 (d, *J* = 12.4 Hz, 1H), 1.88 (dd, *J* = 12.4, 3.1 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 175.9, 158.4, 149.9, 140.3, 139.2, 134.0, 128.7, 122.4, 113.9, 112.6, 110.7, 61.4, 58.8, 55.8, 51.6, 48.3, 39.7, 24.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_3S$ 373.158040; found 373.158023.

**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-11-methyl-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[5,4-*b*]indole (3j)**

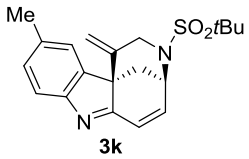


3j

Product **3j** was prepared according to the ***General procedure C*** starting from **1j** (0.2 mmol, 71.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3j** (50.0 mg, 70%) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 270.51 (*c* 0.0975, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 9.9 Hz, 1H), 6.47 (dd, *J* = 9.8, 6.0 Hz, 1H), 4.78-4.76 (m, 2H), 4.45 (s, 1H), 4.28 (d, *J* = 15.1 Hz, 1H), 4.23-4.11 (m, 1H), 2.81 (d, *J* = 12.5 Hz, 1H), 2.35 (s, 3H), 1.92 (dd, *J* = 12.7, 3.0 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 177.2, 156.2, 136.9, 136.5, 134.9, 134.9, 129.0, 128.4, 128.3, 119.5, 111.9, 61.4, 59.2, 51.4, 48.0, 37.6, 24.4,

18.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found 357.1630.

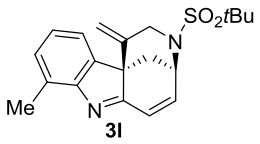
**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-10-methyl-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino [5,4-*b*]indole (3k)**



3k

Product **3k** was prepared according to the ***General procedure C*** starting from **1k** (0.2 mmol, 71.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3k** (55.7 mg, 78%) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 225.85 (*c* 0.1375, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.21-7.17 (m, 1H), 7.16 (d, *J* = 1.6 Hz, 1H), 6.99 (d, *J* = 9.9 Hz, 1H), 6.46-6.42 (m, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.77-4.71 (m, 1H), 4.59 (d, *J* = 1.3 Hz, 1H), 4.26 (dt, *J* = 15.0, 1.8 Hz, 1H), 4.14-4.12 (m, 1H), 2.55 (d, *J* = 12.3 Hz, 1H), 2.43 (s, 3H), 1.87 (dd, *J* = 12.4, 3.2 Hz, 1H), 1.45 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 176.9, 154.0, 146.1, 139.2, 138.7, 135.9, 134.7, 129.5, 125.0, 121.5, 112.6, 61.4, 58.5, 51.6, 48.3, 39.7, 24.3, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found 357.1632.

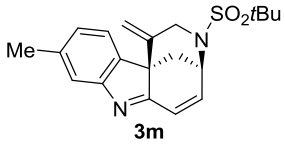
**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-8-methyl-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[ 5,4-*b*]indole (3l)**



3l

Product **3l** was prepared according to the ***General procedure C*** starting from **1l** (0.2 mmol, 71.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3l** (54.3 mg, 76%) as a colorless solid. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 452.32 (*c* 0.0950, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.23-7.12 (m, 3H), 7.04 (d, *J* = 9.8 Hz, 1H), 6.46 (dd, *J* = 9.8, 5.8 Hz, 1H), 4.81 (s, 1H), 4.75 (dt, *J* = 6.0, 2.9 Hz, 1H), 4.56 (s, 1H), 4.26 (dd, *J* = 14.5, 2.0 Hz, 1H), 4.13 (d, *J* = 15.4 Hz, 1H), 2.58 (s, 3H), 2.54 (d, *J* = 12.7 Hz, 1H), 1.86 (dd, *J* = 12.5, 3.2 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 176.8, 154.7, 139.3, 138.5, 134.8, 131.8, 130.2, 128.4, 125.8, 121.6, 112.5, 61.4, 58.8, 51.6, 48.4, 39.8, 24.3, 17.0. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found 357.1633.

**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-9-methyl-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[ 5,4-*b*]indole (3m)**

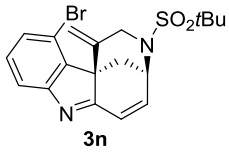


3m

Product **3m** was prepared according to the ***General procedure C*** starting from **1m** (0.2 mmol, 71.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3m** (46.4 mg, 65%) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 274.94 (*c* 0.080, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.52 (s, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 9.9 Hz, 1H), 6.55-6.48 (m, 1H), 4.86 (s, 1H), 4.80 (d, *J* = 6.1 Hz, 1H), 4.64 (s, 1H), 4.31 (d, *J* = 14.8 Hz, 1H), 4.18 (d, *J* = 11.2 Hz, 1H), 2.60 (d, *J* = 12.3 Hz, 1H), 2.48 (s, 3H), 1.91 (dd, *J* = 12.3, 3.2 Hz, 1H), 1.50 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 177.9, 156.5, 139.3, 138.9, 135.6, 135.0, 126.6, 123.8, 122.7, 122.6, 112.6, 61.4, 58.4, 51.6, 48.3, 39.8, 24.3, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_2S$ 357.1631; found

357.1630.

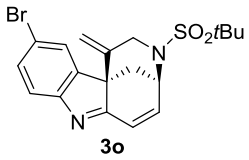
**(4*S*,11b*R*)-11-bromo-3-(tert-butylsulfonyl)-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino [5,4-*b*]indole (3n)**



**3n**

Product **3n** was prepared according to the ***General procedure C*** starting from **1n** (0.2 mmol, 84.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3n** (54.7 mg, 65%) as a yellow solid. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 381.5 (*c* 0.1025, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.36 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.24 (t, *J* = 4.0 Hz, 1H), 6.93 (d, *J* = 9.9 Hz, 1H), 6.51-6.47 (m, 1H), 4.86-4.80 (m, 1H), 4.76 (dt, *J* = 6.0, 3.1 Hz, 1H), 4.50 (d, *J* = 1.7 Hz, 1H), 4.24 (dt, *J* = 15.1, 2.0 Hz, 1H), 4.20 -4.00 (m, 1H), 3.15-3.12 (m, 1H), 1.88 (dd, *J* = 12.6, 3.3 Hz, 1H), 1.43 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 178.4, 158.0, 137.9, 136.5, 134.2, 130.6, 130.1, 127.6, 120.9, 119.5, 112.9, 61.5, 60.9, 50.9, 47.9, 36.2, 24.4. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0576.

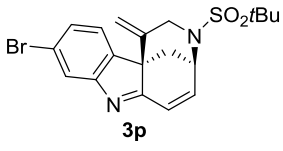
**(4*S*,11b*R*)-10-bromo-3-(tert-butylsulfonyl)-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino [5,4-*b*]indole (3o)**



**3o**

Product **6o** was prepared according to the ***General procedure C*** starting from **1o** (0.2 mmol, 84.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3o** (54.7 mg, 65%) as a pale-yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 154.57 (*c* 0.2000, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.53-7.49 (m, 2H), 7.26 (s, 1H), 6.98 (d, *J* = 9.9 Hz, 1H), 6.52-6.49 m, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 4.77 (dt, *J* = 6.0, 2.8 Hz, 1H), 4.60 (d, *J* = 1.3 Hz, 1H), 4.25 (dt, *J* = 15.1, 1.7 Hz, 1H), 4.15-4.13 (m, 1H), 2.57-2.54 (m, 1H), 1.90 (dd, *J* = 12.2, 3.2 Hz, 1H), 1.45 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 178.0, 155.3, 140.7, 138.6, 135.7, 132.1, 128.1, 127.5, 123.2, 119.7, 112.9, 61.5, 59.1, 51.4, 48.3, 39.5, 24.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0572.

**(4*S*,11b*R*)-9-bromo-3-(tert-butylsulfonyl)-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[ 5,4-*b*]indole (3p)**

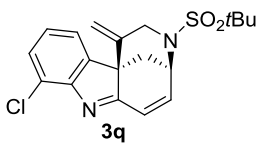


**3p**

Product **3p** was prepared according to the ***General procedure C*** starting from **1p** (0.2 mmol, 84.2 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3p** (50.0 mg, 57%) as a yellow oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 305.04 (*c* 0.2550, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 1.7 Hz, 1H), 7.42 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 9.9 Hz, 1H), 6.52-6.49 (m, 1H), 4.84 (s, 1H), 4.76 (dt, *J* = 6.1, 3.0 Hz, 1H), 4.56 (d, *J* = 1.2 Hz, 1H), 4.25 (dt, *J* = 15.0, 1.8 Hz, 1H), 4.15-4.12 (m, 1H), 2.61-2.50 (m, 1H), 1.87 (dd, *J* = 12.4, 3.2 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 179.2, 157.6, 138.6, 137.5, 136.0, 128.7, 128.1, 125.3, 125.2, 122.3, 112.8, 61.5,

58.6, 51.4, 48.2, 39.5, 24.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}BrN_2O_2S$ 421.0580; found 421.0579.

**(4*S*,11b*R*)-3-(tert-butylsulfonyl)-8-chloro-1-methylene-1,2,3,4-tetrahydro-4,11b-methanoazocino[5,4-*b*]indole (3q)**



**3q**

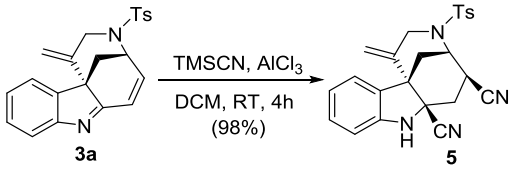
Product **3q** was prepared according to the ***General procedure C*** starting from **1q** (0.2 mmol, 74.4 mg). The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3q** (64.1 mg, 85%) as a colorless solid. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = 133.72 (*c* 0.1175, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.41-7.37 (m, 1H), 7.25-7.22 (m, 2H), 7.08 (d, *J* = 9.9 Hz, 1H), 6.54-6.50 (m, 1H), 4.84 (s, 1H), 4.77 (dt, *J* = 6.0, 3.0 Hz, 1H), 4.55 (d, *J* = 1.2 Hz, 1H), 4.25 (dt, *J* = 15.0, 1.8 Hz, 1H), 4.15 (d, *J* = 15.6 Hz, 1H), 2.62-2.50 (m, 1H), 1.91 (dd, *J* = 12.4, 3.2 Hz, 1H), 1.44 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 178.8, 152.9, 140.6, 138.6, 136.0, 129.4, 128.3, 127.2, 126.9, 122.5, 112.9, 61.5, 59.9, 51.4, 48.2, 39.7, 24.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{22}ClN_2O_2S$ 377.1085; found 377.1083.

# 4. Synthetic Transformations of Polycyclic Spiroindolenine 3a

**Scale-up synthesis o 3a**

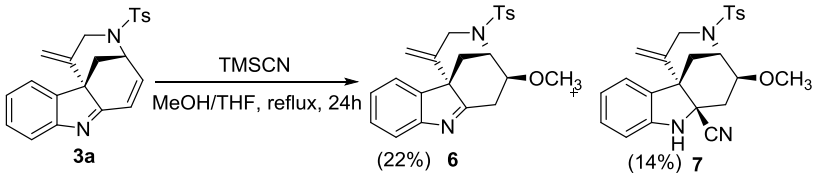
A flame-dried Schlenk flask equipped with a magnetic stir bar was charged with **1a** (3.2 mmol, 1.2 g), (SPhos)AuCl (0.16 mmol, 118 mg) and $AgClO_4$ (0.16 mmol, 33 mg). The flask was capped with a rubber septum, then placed under an argon atmosphere, anhydrous DCE (50 mL) was added, the reaction mixture was stirred at 60 $^oC$ in oil bath until the starting material completely consumed monitored by TLC. The solution was directly concentrated under reduced pressure and purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **3a** (864 mg, 72%) as a colorless solid.

**(4*R*,5*S*,6a*S*,11b*S*)-1-methylene-3-tosyl-1,2,3,4,5,6-hexahydro-4,11b-methanoazocino[5,4-*b*]indole-5,6a(7*H*)-dicarbonitrile (5)**




To a solution of **3a** (0.1 mmol, 37.6 mg) and $AlCl_3$ (5% mmol, 6.7 mg) in dry DCM (2 mL) under argon was added TMSCN (0.5 mmol, 63.0 $\mu$L). The mixture was then stirred at room temperature for 4h. Upon completion, the mixture was quenched with $H_2O$ at 0 $^oC$. The reaction mixture was extracted with DCM (5 mL× 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo[5]. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **5** (42.0 mg, 98% yield) as a yellow oil. $R_f$ = 0.7 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -118.15 (*c* 0.3750, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 6.6 Hz, 2H), 7.40 (d, *J* = 6.5 Hz, 2H), 7.15 (t, *J* = 6.0 Hz, 1H), 6.94-6.78 (m, 3H), 5.55 (d, *J* = 24.9 Hz, 2H), 4.59 (s, 1H), 4.39 (d, *J* = 14.2 Hz, 1H), 3.91 (s, 1H), 3.70 (s, 1H), 3.64 (d, *J* = 14.2 Hz, 1H), 2.83-2.71 (m, 1H), 2.58 (d, *J* = 15.5 Hz, 1H), 2.46 (s, 3H), 2.14 (d, *J* = 14.7 Hz, 1H), 1.65 (d, *J* = 14.1 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.3, 144.9, 138.3, 132.3, 132.0, 130.3, 129.1, 127.8, 123.2, 121.5, 121.1, 119.6, 119.2, 112.2, 69.4, 50.9, 50.1, 48.2, 29.4, 29.3, 27.6, 21.7. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{24}H_{23}N_4O_2S$ 431.1536; found 431.1537.

**(((4*S*,5*S*,11b*S*)-1-methylene-3-tosyl-1,2,3,4,5,6-hexahydro-4,11b-methanoazocino[5,4-*b*]indol-5-yl) oxy)methylium (6)**

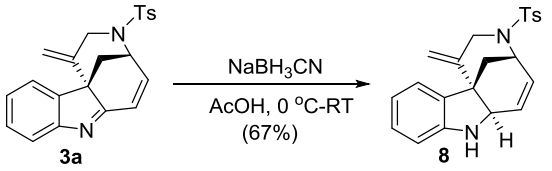



To a solution of **3a** (0.1 mmol, 37.6 mg) in THF: MeOH (1 mL: 3 mL) was added TMSCN (0.5 mmol, 63.0 $\mu$L). The mixture was then stirred at 80 $^oC$ in oil bath for 12h. The mixture was evaporated under reduced pressure[5]. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **6** (8.8 mg, 22% yield) as a pale oil. $R_f$ = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -146.39 (*c* 0.0250, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ

7.80 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.32 (td, *J* = 7.5, 1.6 Hz, 1H), 7.17-7.08 (m, 2H), 5.00-4.95 (m, 1H), 4.33 (d, J = 13.7 Hz, 1H), 4.30 (d, J = 1.9 Hz, 1H), 4.15 (dd, J = 3.8, 2.1 Hz, 1H), 4.00 (q, J = 3.4 Hz, 1H), 3.87 (dt, J = 13.6, 2.1 Hz, 1H), 3.40 (s, 3H), 3.16-3.01 (m, 2H), 2.48 (s, 3H), 2.12 (dd, J = 13.7, 2.8 Hz, 1H), 1.72 (dd, J = 13.7, 2.5 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 172.5, 157.2, 144.2, 139.4, 138.6, 133.7, 130.1, 128.4, 127.6, 125.5, 122.5, 120.5, 114.4, 80.8, 57.0, 52.0, 47.7, 30.8, 30.1, 29.7, 21.7. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3S$ 409.1580; found 409.1576.

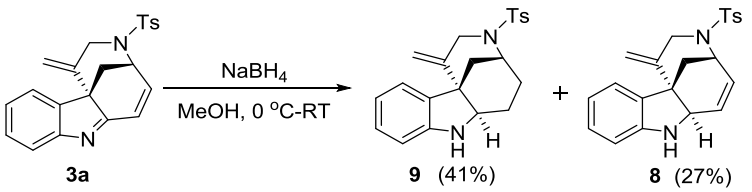
**7** (6.1 mg, 14% yield) as a pale oil. $R_f$ = 0.7 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -37.04 (*c* 0.1575, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.11 (td, *J* = 7.6, 1.3 Hz, 1H), 6.94-6.88 (m, 1H), 6.85-6.78 (m, 2H), 5.54-5.44 (m, 2H), 4.38 (s, 1H), 4.27 (d, *J* = 14.5 Hz, 1H), 3.93 (d, *J* = 3.5 Hz, 1H), 3.87-3.82 (m, 1H), 3.78 (dt, *J* = 14.4, 2.1 Hz, 1H), 3.45 (s, 3H), 2.52 (dd, *J* = 5.0, 3.4 Hz, 2H), 2.46 (s, 3H), 2.19-2.14 (m, 1H), 1.41 (dd, *J* = 14.3, 4.9 Hz, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 147.7, 144.2, 139.1, 133.2, 130.0, 128.6, 127.7, 127.4, 123.5, 122.1, 121.3, 117.9, 112.3, 76.2, 69.0, 57.5, 50.2, 48.1, 30.8, 29.7, 27.1, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{24}H_{26}N_3O_3S$ 436.1689; found 436.1682.

**(4*R*,6a*R*,11b*S*)-1-methylene-3-tosyl-1,2,3,4,6a,7-hexahydro-4,11b-methanoazocino[5,4-*b*]indole (8)**



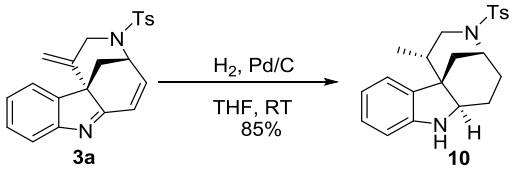

To a solution of **3a** (0.1 mmol, 37.6 mg) in AcOH (2 mL) was added $NaBH_3CN$ (0.15 mmol, 9.5 mg) at 0 °C. The mixture was then stirred at room temperature for 2h. Upon completion, the mixture was quenched with 2M NaOH $_{(aq)}$, and extracted with DCM (5 mL × 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **8** (25.0 mg, 67% yield) as a colorless solid. $R_f$ = 0.6 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = -143.44 (*c* 0.1100, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.07 (td, *J* = 7.7, 1.3 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.10 (dd, *J* = 9.9, 3.7 Hz, 1H), 5.66 (dd, *J* = 9.9, 6.2 Hz, 1H), 5.11 (s, 1H), 5.04 (s, 1H), 4.53 (dt, *J* = 6.3, 3.1 Hz, 1H), 4.27 (d, *J* = 14.3 Hz, 1H), 3.80 (dd, *J* = 3.8, 1.3 Hz, 1H), 3.66 (dt, *J* = 14.2, 1.9 Hz, 1H), 2.45 (s, 3H), 1.75-1.67 (m, 2H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 150.1, 143.5, 143.3, 136.7, 131.6, 131.6, 129.7, 128.1, 127.5, 125.1, 124.7, 119.4, 111.4, 110.6, 62.6, 48.5, 47.7, 46.0, 34.6, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O_2S$ 379.1475; found 379.1474.

**(4*S*,6a*R*,11b*S*)-1-methylene-3-tosyl-1,2,3,4,5,6,6a,7-octahydro-4,11b-methanoazocino[5,4-*b*]indole (9)**




To a solution of **3a** (0.1 mmol, 37.6 mg) in MeOH (2 mL) was added $NaBH_4$ (0.4 mmol, 15.2 mg) at 0 $^oC$. The mixture was then stirred at rt until the starting material completely consumed monitored by TLC, and quenched with ammonium chloride solution. The reaction mixture was extracted with DCM (5 mL × 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo[4]. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/15, v/v) to afford the **9** (15.6 mg, 41% yield) as a yellow oil. $R_f$ = 0.8 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = -90.19 (*c* 0.1000, $CHCl_3$). **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.74 (dd, *J* = 8.3, 3.1 Hz, 2H), 7.41-7.30 (m, 2H), 7.03 (dt, *J* = 7.8, 3.9 Hz, 1H), 6.86 (dd, *J* = 7.5, 2.9 Hz, 1H), 6.72 (td, *J* = 8.2, 2.9 Hz, 2H), 5.18 (s, 1H), 5.04 (s, 1H), 4.24 (dd, *J* = 14.2, 3.0 Hz, 1H), 3.92 (s, 1H), 3.81 (d, *J* = 14.1 Hz, 1H), 3.54 (s, 1H), 2.44 (s, 3H), 2.21-1.99 (m, 2H), 1.82-1.73 (m, 2H), 1.65-1.49 (m, 2H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 150.4, 146.3, 143.4, 135.4, 134.7, 129.8, 127.7, 127.5, 123.3, 119.3, 113.0, 110.5, 68.7, 49.6, 48.8, 48.0, 32.3, 27.2, 21.6, 21.5. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_2S$ 381.1631; found 381.1630.

**(1*S*,4*R*,6a*R*,11b*S*)-1-methyl-3-tosyl-1,2,3,4,5,6,6a,7-octahydro-4,11b-methanoazocino[5,4-*b*]indole (10)**




To a solution of **3a** (95.7 $\mu$mol, 36.0 mg) in THF (2mL) under argon was added 10% Pd/C (20% w/w, 7.2 mg). A balloon filled with $H_2$ gas was attached to the flask. The reaction mixture was left to stir for 4h at room temperature. The suspension was filtered through a short pad of celite, and the solvent was concentrated under reduced pressure[6]. The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/15 to afford **10** (31 mg, 85% yield) as acolorless oil. $R_f$ = 0.4 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -20.49 (*c* 0.0750, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.03-7.00 (m, 2H), 6.66 (td, *J* = 7.5, 1.1 Hz, 1H), 6.56 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.35-4.26 (m, 1H), 3.60 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.36 (d, *J* = 3.5 Hz, 2H), 2.44 (s, 3H), 2.05 (ddd, *J* = 13.6, 3.6, 1.2 Hz, 1H), 1.89 (dt, *J* = 7.1, 3.5 Hz, 1H), 1.82-1.70 (m, 2H), 1.55 (ddd, *J* = 13.6, 3.0, 1.2 Hz, 1H), 1.46-1.35 (m, 1H), 1.29 (d, *J* = 7.1 Hz, 3H), 1.23-1.15 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 149.9, 143.2, 137.0, 133.8, 129.7, 128.1, 127.3, 125.7, 118.1, 109.6, 63.4, 48.4, 45.5, 45.1, 38.7, 28.7, 25.6, 23.3, 21.6, 14.5. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{27}N_2O_2S$ 383.1788; found 383.1780.

# 5. X-Ray Single Crystal Diffraction Data of Compound 3b, 3q

**Preparation of single crystals**: The product **3b** was dissolved in ethyl acetate and petroleum ether was added slowly until the system was turbid, and then the solution was filtered through a glass tube filled with cotton, the filtrate was placed at 2-6 ℃ and evaporated slowly to form acicular crystals.
The product **3q** was dissolved in chloroform, the solution was placed in a quiet place and evaporated slowly at room temperature to form crystals.

### 5.1 X-Ray Data of 3b

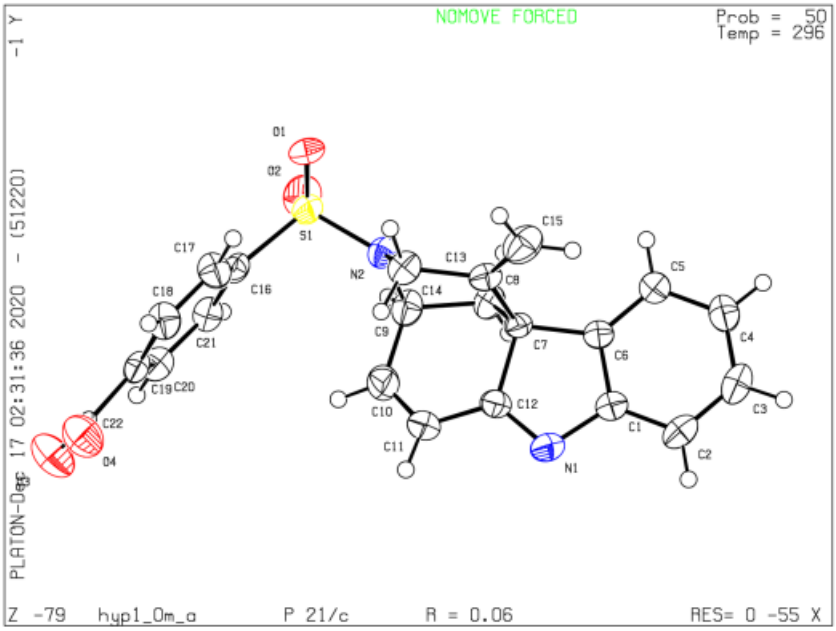



**Figure S1.** Crystal structure of compound **3b**. Displacement ellipsoids are drawn at the 50% probability level.

A specimen of $C_{22}H_{17}N_2O_4S$, approximate dimensions 0.210 mm x 0.220 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). A total of 554 frames were collected. The total exposure time was 1.29 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 17454 reflections to a maximum θ angle of 24.21° (0.87 Å resolution), of which 2998 were independent (average redundancy 5.822, completeness = 99.6%, Rint = 10.45%, Rsig = 8.39%) and 1911 (63.74%) were greater than 2σ(F2). The final cell constants of a = 6.5690(5) Å, b = 11.6246(10) Å, c = 24.507(2) Å, β = 95.391(3)°, volume = 1863.1(3) Å3, are based upon the refinement of the XYZ-centroids of 4132 reflections above 20 σ(I) with 4.840° < 2θ < 47.76°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.822. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9560 and 0.9580.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space

group P 1 21/c 1, with Z = 4 for the formula unit, $C_{22}H_{17}N_2O_4S$. The final anisotropic full-matrix least-squares refinement on F2 with 262 variables converged at R1 = 5.62%, for the observed data and wR2 = 12.74% for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was 0.378 $e^-/Å^3$ and the largest hole was -0.312 $e^-/Å^3$ with an RMS deviation of 0.057 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.445 $g/cm^3$ and F(000), 844 $e^-$.

**Table S4**. Sample and crystal data for **3b**.

| | | |
|---|---|---|
| Identification code | **3b** | |
| Chemical formula | $C_{22}H_{17}N_2O_4S$ | |
| Formula weight | 405.43 g/mol | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.210 x 0.220 x 0.220 mm | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 6.5690(5) Å | α = 90° |
| | b = 11.6246(10) Å | β = 95.391(3)° |
| | c = 24.507(2) Å | γ = 90° |
| Volume | 1863.1(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.445 $g/cm^3$ | |
| Absorption coefficient | 0.207 $mm^{-1}$ | |
| F(000) | 844 | |

**Table S5**. Data collection and structure refinement for **3b**.

| | |
|---|---|
| Theta range for data collection | 2.42 to 24.21 ° |
| Index ranges | -7<=h<=6, -13<=k<=13, -26<=l<=28 |
| Reflections collected | 17454 |
| Independent reflections | 2998 [R(int) = 0.1045] |
| Coverage of independent reflections | 99.6% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9580 and 0.9560 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |

| | |
|---|---|
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 2998 / 3 / 262 |
| Goodness-of-fit on $F^2$ | 1.063 |
| Final R indices | 1911 data; $I>2\sigma(I)$ R1 = 0.0562, wR2 = 0.1102 |
| | all data R1 = 0.1118, wR2 = 0.1274 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0430P)^2+1.2850P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.378 and -0.312 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.057 eÅ$^{-3}$ |

**Table S6**. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **3b**.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | **x/a** | **y/b** | **z/c** | **U(eq)** |
|---|---|---|---|---|
| S1 | 0.73191(14) | 0.39222(9) | 0.34270(4) | 0.0371(3) |
| O1 | 0.8947(3) | 0.4711(2) | 0.35780(11) | 0.0494(7) |
| O2 | 0.7584(4) | 0.3007(2) | 0.30537(10) | 0.0537(8) |
| O3 | 0.8691(4) | 0.6253(3) | 0.23219(13) | 0.0651(9) |
| O4 | 0.9540(4) | 0.7441(2) | 0.29541(12) | 0.0576(8) |
| N1 | 0.2683(4) | 0.2088(3) | 0.54267(13) | 0.0424(8) |
| N2 | 0.6712(4) | 0.3345(2) | 0.39918(11) | 0.0309(7) |
| C1 | 0.4300(5) | 0.1570(3) | 0.57658(14) | 0.0331(9) |
| C2 | 0.4123(6) | 0.1041(3) | 0.62601(15) | 0.0424(10) |
| C3 | 0.5851(6) | 0.0496(3) | 0.65088(15) | 0.0422(10) |
| C4 | 0.7667(6) | 0.0494(3) | 0.62665(16) | 0.0423(10) |
| C5 | 0.7838(6) | 0.1056(3) | 0.57760(15) | 0.0392(10) |
| C6 | 0.6137(5) | 0.1590(3) | 0.55261(14) | 0.0288(8) |
| C7 | 0.5778(5) | 0.2244(3) | 0.49962(13) | 0.0276(8) |
| C8 | 0.6128(6) | 0.1586(3) | 0.44725(14) | 0.0350(9) |
| C9 | 0.5349(6) | 0.2323(3) | 0.39801(15) | 0.0384(10) |
| C10 | 0.3138(6) | 0.2676(3) | 0.40110(17) | 0.0510(12) |
| C11 | 0.2310(6) | 0.2757(4) | 0.44843(17) | 0.0503(11) |
| C12 | 0.3466(5) | 0.2423(3) | 0.49891(15) | 0.0345(9) |
| C13 | 0.6891(5) | 0.3391(3) | 0.49912(14) | 0.0306(9) |
| C14 | 0.6529(6) | 0.4088(3) | 0.44698(14) | 0.0356(9) |
| C15 | 0.8108(6) | 0.3785(3) | 0.54031(17) | 0.0518(11) |

| | | | | |
|---|---|---|---|---|
| C16 | 0.5195(5) | 0.4747(3) | 0.31581(13) | 0.0304(9) |
| C17 | 0.5020(6) | 0.5870(3) | 0.33333(16) | 0.0396(10) |
| C18 | 0.3278(6) | 0.6480(3) | 0.31681(15) | 0.0395(10) |
| C19 | 0.1763(5) | 0.5968(3) | 0.28338(14) | 0.0313(9) |
| C20 | 0.1940(6) | 0.4858(3) | 0.26444(14) | 0.0356(9) |
| C21 | 0.3671(5) | 0.4245(3) | 0.28136(14) | 0.0339(9) |
| C22 | 0.9870(5) | 0.6600(3) | 0.26903(14) | 0.0225(7) |

**Table S7.** Bond lengths (Å) for **3b**.

| | | | |
|---|---|---|---|
| S1-O2 | 1.424(3) | S1-O1 | 1.431(3) |
| S1-N2 | 1.621(3) | S1-C16 | 1.769(4) |
| O3-C22 | 1.203(4) | O4-C22 | 1.203(4) |
| N1-C12 | 1.292(4) | N1-C1 | 1.420(4) |
| N2-C14 | 1.469(4) | N2-C9 | 1.487(4) |
| C1-C2 | 1.373(5) | C1-C6 | 1.391(4) |
| C2-C3 | 1.389(5) | C2-H2 | 0.93 |
| C3-C4 | 1.382(5) | C3-H3 | 0.93 |
| C4-C5 | 1.382(5) | C4-H4 | 0.93 |
| C5-C6 | 1.371(5) | C5-H5 | 0.93 |
| C6-C7 | 1.504(5) | C7-C13 | 1.521(5) |
| C7-C8 | 1.530(5) | C7-C12 | 1.531(4) |
| C8-C9 | 1.529(5) | C8-H8A | 0.97 |
| C8-H8B | 0.97 | C9-C10 | 1.518(5) |
| C9-H9 | 0.98 | C10-C11 | 1.330(5) |
| C10-H10 | 0.93 | C11-C12 | 1.443(5) |
| C11-H11 | 0.93 | C13-C15 | 1.310(5) |
| C13-C14 | 1.513(5) | C14-H14A | 0.97 |
| C14-H14B | 0.97 | C15-H15A | 0.93 |
| C15-H15B | 0.93 | C16-C21 | 1.377(5) |
| C16-C17 | 1.382(5) | C17-C18 | 1.375(5) |
| C17-H17 | 0.93 | C18-C19 | 1.365(5) |
| C18-H18 | 0.93 | C19-C20 | 1.380(5) |
| C19-C22 | 1.458(5) | C20-C21 | 1.373(5) |
| C20-H20 | 0.93 | C21-H21 | 0.93 |

**Table S8**. Bond angles (°) for **3b**.

| | | | |
|---|---|---|---|
| O2-S1-O1 | 120.76(17) | O2-S1-N2 | 107.11(16) |
| O1-S1-N2 | 106.39(15) | O2-S1-C16 | 107.75(17) |
| O1-S1-C16 | 107.07(17) | N2-S1-C16 | 107.07(15) |
| C12-N1-C1 | 106.2(3) | C14-N2-C9 | 113.0(3) |
| C14-N2-S1 | 118.9(2) | C9-N2-S1 | 120.7(2) |
| C2-C1-C6 | 121.9(3) | C2-C1-N1 | 125.9(3) |
| C6-C1-N1 | 112.1(3) | C1-C2-C3 | 117.3(4) |
| C1-C2-H2 | 121.4 | C3-C2-H2 | 121.4 |
| C4-C3-C2 | 121.0(4) | C4-C3-H3 | 119.5 |
| C2-C3-H3 | 119.5 | C3-C4-C5 | 121.1(4) |
| C3-C4-H4 | 119.5 | C5-C4-H4 | 119.5 |
| C6-C5-C4 | 118.3(3) | C6-C5-H5 | 120.9 |
| C4-C5-H5 | 120.9 | C5-C6-C1 | 120.4(3) |
| C5-C6-C7 | 132.0(3) | C1-C6-C7 | 107.5(3) |
| C6-C7-C13 | 114.4(3) | C6-C7-C8 | 116.6(3) |
| C13-C7-C8 | 108.7(3) | C6-C7-C12 | 98.8(3) |
| C13-C7-C12 | 111.0(3) | C8-C7-C12 | 106.6(3) |
| C9-C8-C7 | 108.4(3) | C9-C8-H8A | 110.0 |
| C7-C8-H8A | 110.0 | C9-C8-H8B | 110.0 |
| C7-C8-H8B | 110.0 | H8A-C8-H8B | 108.4 |
| N2-C9-C10 | 111.1(3) | N2-C9-C8 | 106.0(3) |
| C10-C9-C8 | 111.3(3) | N2-C9-H9 | 109.4 |
| C10-C9-H9 | 109.4 | C8-C9-H9 | 109.4 |
| C11-C10-C9 | 122.3(4) | C11-C10-H10 | 118.9 |
| C9-C10-H10 | 118.9 | C10-C11-C12 | 120.2(4) |
| C10-C11-H11 | 119.9 | C12-C11-H11 | 119.9 |
| N1-C12-C11 | 125.0(3) | N1-C12-C7 | 114.9(3) |
| C11-C12-C7 | 119.2(3) | C15-C13-C14 | 120.0(3) |
| C15-C13-C7 | 124.0(3) | C14-C13-C7 | 116.0(3) |
| N2-C14-C13 | 109.9(3) | N2-C14-H14A | 109.7 |
| C13-C14-H14A | 109.7 | N2-C14-H14B | 109.7 |
| C13-C14-H14B | 109.7 | H14A-C14-H14B | 108.2 |
| C13-C15-H15A | 120.0 | C13-C15-H15B | 120.0 |
| H15A-C15-H15B | 120.0 | C21-C16-C17 | 120.9(3) |
| C21-C16-S1 | 120.1(3) | C17-C16-S1 | 118.8(3) |
| C18-C17-C16 | 119.2(3) | C18-C17-H17 | 120.4 |

| | | | |
|---|---|---|---|
| C16-C17-H17 | 120.4 | C19-C18-C17 | 119.4(3) |
| C19-C18-H18 | 120.3 | C17-C18-H18 | 120.3 |
| C18-C19-C20 | 122.0(3) | C18-C19-C22 | 118.8(3) |
| C20-C19-C22 | 119.1(3) | C21-C20-C19 | 118.5(3) |
| C21-C20-H20 | 120.7 | C19-C20-H20 | 120.7 |
| C20-C21-C16 | 120.0(3) | C20-C21-H21 | 120.0 |
| C16-C21-H21 | 120.0 | O4-C22-O3 | 122.7(3) |
| O4-C22-C19 | 118.2(3) | O3-C22-C19 | 119.1(3) |

**Table S9**. Hydrogen atomic coordinates and isotropic atomic displacementparameters ($Å^2$) for **3b**.

| | **x/a** | **y/b** | **z/c** | **U(eq)** |
|---|---|---|---|---|
| H2 | 0.2898 | 0.1047 | 0.6422 | 0.051 |
| H3 | 0.5783 | 0.0128 | 0.6844 | 0.051 |
| H4 | 0.8794 | 0.0107 | 0.6436 | 0.051 |
| H5 | 0.9074 | 0.1073 | 0.5620 | 0.047 |
| H8A | 0.7574 | 0.1427 | 0.4462 | 0.042 |
| H8B | 0.5400 | 0.0859 | 0.4463 | 0.042 |
| H9 | 0.5466 | 0.1889 | 0.3642 | 0.046 |
| H10 | 0.2334 | 0.2841 | 0.3688 | 0.061 |
| H11 | 0.0982 | 0.3030 | 0.4490 | 0.06 |
| H14A | 0.5174 | 0.4427 | 0.4447 | 0.043 |
| H14B | 0.7522 | 0.4706 | 0.4473 | 0.043 |
| H15A | 0.8750 | 0.4492 | 0.5375 | 0.062 |
| H15B | 0.8330 | 0.3356 | 0.5724 | 0.062 |
| H17 | 0.6067 | 0.6208 | 0.3560 | 0.048 |
| H18 | 0.3134 | 0.7236 | 0.3283 | 0.047 |
| H20 | 0.0910 | 0.4532 | 0.2407 | 0.043 |
| H21 | 0.3815 | 0.3492 | 0.2696 | 0.041 |

**5.2 X-Ray Data of 3q**

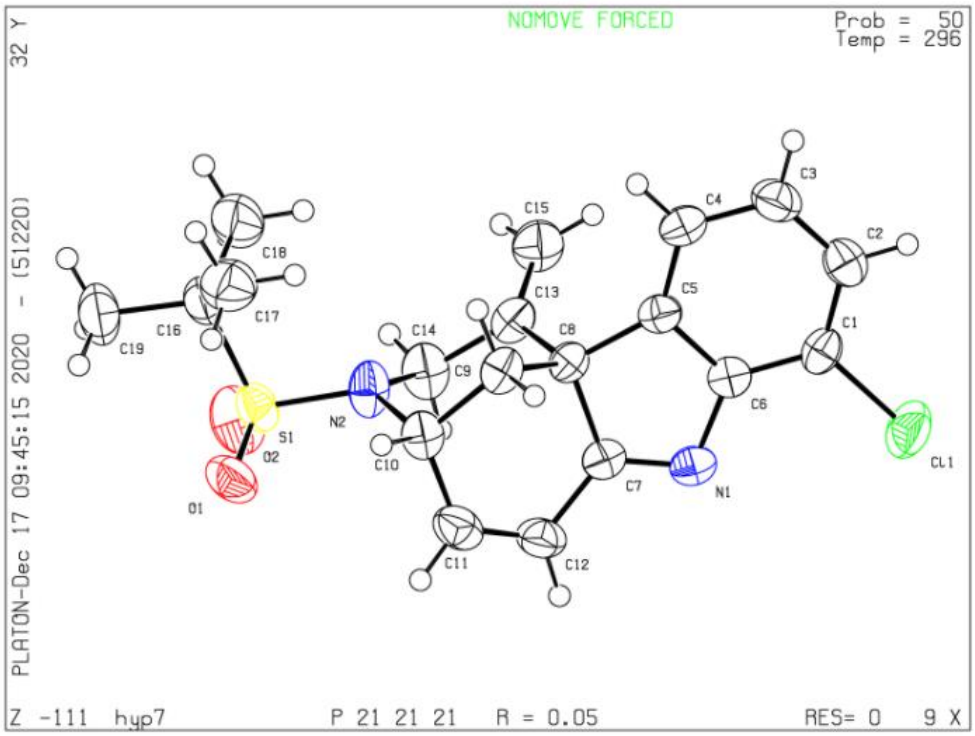



**Figure S2**. Crystal structure of compound **3q**. Displacement ellipsoids are drawn at the 50% probability level.

A colorless Block-like specimen of $C_{19}H_{21}ClN_2O_2S$, approximate dimensions 0.130 mm x 0.140 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

A total of 289 frames were collected. The total exposure time was 1.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 8444 reflections to a maximum θ angle of 25.02 °(0.84 Å resolution), of which 3265 were independent (average redundancy 2.586, completeness = 99.8%, Rint = 4.73%, Rsig = 6.36%) and 2507 (76.78%) were greater than 2σ(F2). The final cell constants of a = 7.2488(4) Å, b = 13.2678(8) Å, c = 19.4602(12) Å, volume = 1871.60(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 5518 reflections above 20 σ(I) with 5.191° < 2θ < 49.87 °. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.930. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9550 and 0.9580.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, C19H21ClN2O2S. The final anisotropic full-matrix least-squares refinement on F2 with 229 variables converged at R1 = 4.64%, for the observed data and wR2 = 9.64% for all data. The goodness-of-fit was 1.085. The largest peak in the final difference electron density synthesis was 0.177 $e^-$/Å3 and the largest hole was -0.285 $e^-/Å^3$ with an RMS deviation of 0.055 e-/$Å^3$. On the basis of the final model, the calculated density was 1.338 g/$cm^3$ and F(000), 792 $e^-$.

**Table S10**. Sample and crystal data for **3q.**

| | | |
|---|---|---|
| Identification code | **3q** | |
| Chemical formula | $C_{19}H_{21}ClN_2O_2S$ | |
| Formula weight | 376.89 g/mol | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.130 x 0.140 x 0.140 mm | |
| Crystal habit | colorless Block | |
| Crystal system | orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 7.2488(4) Å | α = 90° |
| | b = 13.2678(8) Å | β = 90° |
| | c = 19.4602(12) Å | γ = 90° |
| Volume | 1871.60(19) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.338 $g/cm^3$ | |
| Absorption coefficient | 0.330 $mm^{-1}$ | |
| F(000) | 792 | |

**Table S11**. Data collection and structure refinement for **3q**.

| | |
|---|---|
| Theta range for data collection | 1.86 to 25.02° |
| Index ranges | -8<=h<=7, -15<=k<=14, -23<=l<=20 |
| Reflections collected | 8444 |
| Independent reflections | 3265 [R(int) = 0.0473] |
| Coverage of independent reflections | 99.8% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9580 and 0.9550 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2017/1 (Sheldrick, 2017) |
| Function minimized | $\Sigma\ w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3265 / 0 / 229 |
| Goodness-of-fit on $F^2$ | 1.085 |
| Final R indices | 2507 data; I>2 σ (I) R1 = 0.0464, wR2 = 0.0855 |

| | |
|---|---|
| | all data R1 = 0.0736, wR2 = 0.0964 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0379P)^2+0.0857P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | -0.04(5) |
| Largest diff. peak and hole | 0.177 and -0.285 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.055 eÅ$^{-3}$ |

**Table S12.** Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **3q.** U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | **x/a** | **y/b** | **z/c** | **U(eq)** |
|---|---|---|---|---|
| S1 | 0.54614(16) | 0.64388(7) | 0.62533(6) | 0.0454(3) |
| Cl1 | 0.11502(16) | 0.98075(8) | 0.65383(7) | 0.0624(4) |
| O1 | 0.5168(5) | 0.6836(2) | 0.69301(15) | 0.0609(9) |
| O2 | 0.4373(5) | 0.6816(2) | 0.57000(17) | 0.0717(10) |
| N1 | 0.1918(4) | 0.2132(2) | 0.66315(16) | 0.0392(8) |
| N2 | 0.5189(5) | 0.5219(2) | 0.62851(15) | 0.0457(9) |
| C1 | 0.3211(5) | 0.0425(3) | 0.63762(19) | 0.0369(10) |
| C2 | 0.4747(6) | 0.9878(3) | 0.6202(2) | 0.0444(10) |
| C3 | 0.6411(6) | 0.0362(3) | 0.6094(2) | 0.0508(11) |
| C4 | 0.6557(5) | 0.1402(3) | 0.6153(2) | 0.0461(10) |
| C5 | 0.5003(5) | 0.1946(3) | 0.6310(2) | 0.0365(10) |
| C6 | 0.3316(5) | 0.1459(3) | 0.64250(18) | 0.0337(9) |
| C7 | 0.2668(5) | 0.3013(3) | 0.6642(2) | 0.0361(10) |
| C8 | 0.4634(5) | 0.3053(3) | 0.63806(18) | 0.0335(9) |
| C9 | 0.5772(5) | 0.3655(3) | 0.69027(19) | 0.0386(10) |
| C10 | 0.4935(6) | 0.4705(3) | 0.69558(19) | 0.0404(10) |
| C11 | 0.2927(6) | 0.4664(3) | 0.7136(2) | 0.0493(12) |
| C12 | 0.1864(6) | 0.3891(3) | 0.6967(2) | 0.0468(11) |
| C13 | 0.4774(5) | 0.3609(3) | 0.5688(2) | 0.0394(10) |
| C14 | 0.4244(7) | 0.4701(3) | 0.5707(2) | 0.0506(12) |
| C15 | 0.5310(6) | 0.3192(3) | 0.5114(2) | 0.0540(12) |
| C16 | 0.7863(6) | 0.6608(3) | 0.6048(2) | 0.0483(11) |
| C17 | 0.9018(6) | 0.6173(3) | 0.6625(3) | 0.0665(14) |
| C18 | 0.8281(8) | 0.6108(3) | 0.5367(2) | 0.0743(17) |
| C19 | 0.8155(8) | 0.7751(3) | 0.5992(3) | 0.0706(16) |

**Table S13**. Bond lengths (Å) for **3q.**

| | | | |
|---|---|---|---|
| S1-O2 | 1.426(3) | S1-O1 | 1.434(3) |
| S1-N2 | 1.632(3) | S1-C16 | 1.801(5) |
| Cl1-C1 | 1.733(4) | N1-C7 | 1.290(5) |
| N1-C6 | 1.409(5) | N2-C10 | 1.484(5) |
| N2-C14 | 1.485(5) | C1-C2 | 1.372(5) |
| C1-C6 | 1.377(5) | C2-C3 | 1.382(6) |
| C2-H2 | 0.93 | C3-C4 | 1.390(5) |
| C3-H3 | 0.93 | C4-C5 | 1.372(5) |
| C4-H4 | 0.93 | C5-C6 | 1.402(5) |
| C5-C8 | 1.499(5) | C7-C12 | 1.448(5) |
| C7-C8 | 1.514(5) | C8-C9 | 1.534(5) |
| C8-C13 | 1.539(5) | C9-C10 | 1.522(5) |
| C9-H9A | 0.97 | C9-H9B | 0.97 |
| C10-C11 | 1.498(6) | C10-H10 | 0.98 |
| C11-C12 | 1.325(6) | C11-H11 | 0.93 |
| C12-H12 | 0.93 | C13-C15 | 1.306(6) |
| C13-C14 | 1.500(5) | C14-H14A | 0.97 |
| C14-H14B | 0.97 | C15-H15A | 0.93 |
| C15-H15B | 0.93 | C16-C18 | 1.513(6) |
| C16-C17 | 1.515(6) | C16-C19 | 1.536(5) |
| C17-H17A | 0.96 | C17-H17B | 0.96 |
| C17-H17C | 0.96 | C18-H18A | 0.96 |
| C18-H18B | 0.96 | C18-H18C | 0.96 |
| C19-H19A | 0.96 | C19-H19B | 0.96 |
| C19-H19C | 0.96 | | |

**Table S14**. Bond angles (°) for **3q**.

| | | | |
|---|---|---|---|
| O2-S1-O1 | 118.8(2) | O2-S1-N2 | 108.07(19) |
| O1-S1-N2 | 108.17(17) | O2-S1-C16 | 108.9(2) |
| O1-S1-C16 | 107.6(2) | N2-S1-C16 | 104.42(19) |
| C7-N1-C6 | 106.0(3) | C10-N2-C14 | 113.3(3) |
| C10-N2-S1 | 120.3(3) | C14-N2-S1 | 119.1(2) |
| C2-C1-C6 | 120.0(4) | C2-C1-Cl1 | 119.6(3) |
| C6-C1-Cl1 | 120.4(3) | C1-C2-C3 | 120.0(4) |

| | | | |
|---|---|---|---|
| C1-C2-H2 | 120.0 | C3-C2-H2 | 120.0 |
| C2-C3-C4 | 121.0(4) | C2-C3-H3 | 119.5 |
| C4-C3-H3 | 119.5 | C5-C4-C3 | 118.6(4) |
| C5-C4-H4 | 120.7 | C3-C4-H4 | 120.7 |
| C4-C5-C6 | 120.6(3) | C4-C5-C8 | 133.0(4) |
| C6-C5-C8 | 106.3(3) | C1-C6-C5 | 119.8(3) |
| C1-C6-N1 | 127.7(3) | C5-C6-N1 | 112.4(3) |
| N1-C7-C12 | 124.5(4) | N1-C7-C8 | 115.0(3) |
| C12-C7-C8 | 119.9(3) | C5-C8-C7 | 99.5(3) |
| C5-C8-C9 | 118.4(3) | C7-C8-C9 | 107.6(3) |
| C5-C8-C13 | 112.2(3) | C7-C8-C13 | 111.9(3) |
| C9-C8-C13 | 107.1(3) | C10-C9-C8 | 107.9(3) |
| C10-C9-H9A | 110.1 | C8-C9-H9A | 110.1 |
| C10-C9-H9B | 110.1 | C8-C9-H9B | 110.1 |
| H9A-C9-H9B | 108.4 | N2-C10-C11 | 110.0(3) |
| N2-C10-C9 | 108.1(3) | C11-C10-C9 | 111.7(4) |
| N2-C10-H10 | 109.0 | C11-C10-H10 | 109.0 |
| C9-C10-H10 | 109.0 | C12-C11-C10 | 122.4(4) |
| C12-C11-H11 | 118.8 | C10-C11-H11 | 118.8 |
| C11-C12-C7 | 119.8(4) | C11-C12-H12 | 120.1 |
| C7-C12-H12 | 120.1 | C15-C13-C14 | 120.4(4) |
| C15-C13-C8 | 124.5(4) | C14-C13-C8 | 115.1(3) |
| N2-C14-C13 | 110.3(3) | N2-C14-H14A | 109.6 |
| C13-C14-H14A | 109.6 | N2-C14-H14B | 109.6 |
| C13-C14-H14B | 109.6 | H14A-C14-H14B | 108.1 |
| C13-C15-H15A | 120.0 | C13-C15-H15B | 120.0 |
| H15A-C15-H15B | 120.0 | C18-C16-C17 | 111.8(4) |
| C18-C16-C19 | 110.2(4) | C17-C16-C19 | 110.6(4) |
| C18-C16-S1 | 109.5(4) | C17-C16-S1 | 108.8(3) |
| C19-C16-S1 | 105.8(3) | C16-C17-H17A | 109.5 |
| C16-C17-H17B | 109.5 | H17A-C17-H17B | 109.5 |
| C16-C17-H17C | 109.5 | H17A-C17-H17C | 109.5 |
| H17B-C17-H17C | 109.5 | C16-C18-H18A | 109.5 |
| C16-C18-H18B | 109.5 | H18A-C18-H18B | 109.5 |
| C16-C18-H18C | 109.5 | H18A-C18-H18C | 109.5 |
| H18B-C18-H18C | 109.5 | C16-C19-H19A | 109.5 |

| | | | |
|---|---|---|---|
| C16-C19-H19B | 109.5 | H19A-C19-H19B | 109.5 |
| C16-C19-H19C | 109.5 | H19A-C19-H19C | 109.5 |
| H19B-C19-H19C | 109.5 | | |

**Table S15**. Anisotropic atomic displacement parameters ($Å^2$) for **3q**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0602(7) | 0.0328(5) | 0.0432(6) | 0.0037(5) | -0.0008(6) | 0.0069(5) |
| Cl1 | 0.0504(7) | 0.0571(7) | 0.0797(9) | 0.0004(6) | -0.0022(6) | -0.0216(6) |
| O1 | 0.082(2) | 0.0482(18) | 0.0530(19) | -0.0118(14) | 0.0176(17) | 0.0088(17) |
| O2 | 0.090(2) | 0.0541(19) | 0.072(2) | 0.0208(16) | -0.024(2) | 0.0170(19) |
| N1 | 0.0317(18) | 0.048(2) | 0.0377(19) | 0.0014(17) | 0.0010(15) | 0.0014(17) |
| N2 | 0.071(2) | 0.0383(18) | 0.0277(17) | 0.0075(15) | -0.0086(18) | -0.0098(18) |
| C1 | 0.036(2) | 0.042(2) | 0.033(2) | 0.0027(19) | -0.0060(19) | -0.0097(19) |
| C2 | 0.052(3) | 0.040(2) | 0.042(2) | -0.004(2) | -0.005(2) | 0.002(2) |
| C3 | 0.044(3) | 0.049(3) | 0.060(3) | -0.008(2) | 0.004(2) | 0.009(2) |
| C4 | 0.031(2) | 0.051(2) | 0.057(3) | -0.001(2) | 0.006(2) | -0.002(2) |
| C5 | 0.032(2) | 0.042(2) | 0.035(2) | -0.0024(18) | 0.0013(18) | -0.0006(18) |
| C6 | 0.032(2) | 0.041(2) | 0.027(2) | 0.0010(18) | -0.0056(17) | 0.001(2) |
| C7 | 0.033(2) | 0.042(2) | 0.033(2) | 0.004(2) | -0.0006(18) | 0.001(2) |
| C8 | 0.034(2) | 0.036(2) | 0.030(2) | 0.0037(17) | -0.0008(18) | -0.0018(18) |
| C9 | 0.041(2) | 0.043(2) | 0.032(2) | 0.0061(18) | -0.0057(18) | -0.005(2) |
| C10 | 0.054(3) | 0.039(2) | 0.028(2) | 0.0023(18) | -0.0051(19) | -0.002(2) |
| C11 | 0.063(3) | 0.046(3) | 0.039(3) | 0.000(2) | 0.008(2) | 0.012(3) |
| C12 | 0.040(2) | 0.048(3) | 0.052(3) | -0.001(2) | 0.006(2) | 0.011(2) |
| C13 | 0.040(2) | 0.048(2) | 0.030(2) | 0.0000(19) | -0.0034(18) | -0.010(2) |
| C14 | 0.071(3) | 0.048(2) | 0.033(2) | 0.0048(19) | -0.010(2) | -0.003(3) |
| C15 | 0.068(3) | 0.058(3) | 0.036(2) | 0.002(2) | 0.004(2) | -0.004(3) |
| C16 | 0.064(3) | 0.035(2) | 0.046(3) | 0.000(2) | 0.007(2) | 0.000(2) |
| C17 | 0.056(3) | 0.067(3) | 0.077(3) | 0.004(3) | 0.003(3) | 0.007(3) |
| C18 | 0.104(5) | 0.060(3) | 0.059(3) | -0.015(2) | 0.028(3) | -0.009(3) |
| C19 | 0.101(4) | 0.037(3) | 0.073(4) | -0.003(2) | 0.011(3) | -0.011(3) |

**Table S16**. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **3q**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H2 | 0.4669 | -0.0819 | 0.6156 | 0.053 |
| H3 | 0.7448 | -0.0015 | 0.5980 | 0.061 |
| H4 | 0.7684 | 0.1723 | 0.6088 | 0.055 |
| H9A | 0.5744 | 0.3325 | 0.7347 | 0.046 |
| H9B | 0.7046 | 0.3700 | 0.6752 | 0.046 |
| H10 | 0.5591 | 0.5085 | 0.7312 | 0.049 |
| H11 | 0.2408 | 0.5201 | 0.7374 | 0.059 |
| H12 | 0.0605 | 0.3911 | 0.7058 | 0.056 |
| H14A | 0.4584 | 0.5020 | 0.5277 | 0.061 |
| H14B | 0.2919 | 0.4761 | 0.5762 | 0.061 |
| H15A | 0.5365 | 0.3574 | 0.4713 | 0.065 |
| H15B | 0.5637 | 0.2515 | 0.5105 | 0.065 |
| H17A | 0.8846 | 0.5457 | 0.6644 | 0.1 |
| H17B | 0.8644 | 0.6468 | 0.7053 | 0.1 |
| H17C | 1.0296 | 0.6321 | 0.6543 | 0.1 |
| H18A | 0.9519 | 0.6269 | 0.5229 | 0.111 |
| H18B | 0.7431 | 0.6346 | 0.5025 | 0.111 |
| H18C | 0.8159 | 0.5390 | 0.5414 | 0.111 |
| H19A | 0.7888 | 0.8061 | 0.6427 | 0.106 |
| H19B | 0.7348 | 0.8021 | 0.5647 | 0.106 |
| H19C | 0.9413 | 0.7887 | 0.5868 | 0.106 |

# 6. DFT studies

## 6.1 Computational Methods

A DFT study was performed using Gaussian 16 suite of quantum chemical programs (rev. A.03)[7]. All geometry optimizations and frequency calculations were computed using the dispersion-corrected Hybrid GGA functional B3LYP[8]-D3(BJ)[9] with SDD[10] basis set for Au and 6-31G(d)[11] basis set for other atoms. All located transition states were connected to the nearest minima by the Intrinsic Reaction Coordinate (IRC) calculations[12], performed at the same level of theory with subsequent optimization of the resulting structures. Frequency analysis was carried out for the optimized geometries to verify them as either minima or saddle points by the presence of zero or one imaginary harmonic vibrational frequency, respectively. Solvent effects of dichloroethane were incorporated for all calculations using the SMD[13] continuum solvation model. Single point energy was computed at the 6-311+G(d,p) basis set for other atoms, and SDD basis set for Au. Enthalpies and Gibbs free energies were evaluated at the reaction temperature of 333.15K. PM-Mulliken LMO[14], Hirshfield atomic charge and orbital composition analysis by Hirshfeld method[15], IGM analysis based on promolecular density[16] for weak interaction was conducted by using Multiwfn[17]. The corresponding structure, orbitals, IGM pictures were generated using VMD[18].

## 6.2 Absolute values and cartesian coordinates (Å) for optimised structures

**Table S17.** Zero-point energy corrections (ZPE), electronic energies (E), enthalpies (H), Gibbs free energies (G (T=333.15 K)) for all computed structures are given in Hartree. Imaginary frequencies are in $cm^{-1}$, and relative free energies (ΔG) are in kcal/mol.

| Structure | ZPE | E | H | G | Imaginary frequency | ΔG |
|---|---|---|---|---|---|---|
| $Au[(PCH_3)_3]ClO_4$ | 0.131799 | -1357.917292 | -1357.767523 | -1357.837136 | - | |
| $Au[(PCH_3)_3]+$ | 0.116075 | -596.8620435 | -596.7350625 | -596.7852395 | - | |
| **$ClO_4^-$** | 0.014801 | -761.0150083 | -760.9942063 | -761.0316603 | - | |
| **$HClO_4$** | 0.025627 | -761.4332607 | -761.4006677 | -761.4399777 | - | |
| **Int1** | 0.369637 | -1508.786617 | -1508.384813 | -1508.484046 | - | 0 |
| **Int2** | 0.487445 | -2105.695574 | -2105.164331 | -2105.290504 | - | -13.31507194 |
| **Ts1_S** | 0.48646 | -2105.6761995 | -2105.146557 | -2105.273837 | -231.07 | -2.855860761 |
| **Ts1_R** | 0.486855 | -2105.679768 | -2105.15008 | -2105.274448 | -142.72 | -3.239457624 |
| **Int5_S** | 0.490378 | -2105.703982 | -2105.171144 | -2105.29657 | - | -17.12123384 |
| **Int5_R** | 0.490754 | -2105.703226 | -2105.170187 | -2105.294398 | - | -15.75815662 |
| **Int3** | 0.487658 | -2105.691594 | -2105.160368 | -2105.286999 | - | -11.11558664 |
| **Ts4** | 0.488706 | -2105.675155 | -2105.144592 | -2105.26452 | -230.72 | 2.990147901 |
| **Int4** | 0.492403 | -2105.701862 | -2105.168032 | -2105.287648 | - | -11.52265238 |
| **Ts2_S** | 0.488766 | -2105.682759 | -2105.152119 | -2105.274902 | -251.45 | -3.524472666 |
| **Ts2_R** | 0.488903 | -2105.681717 | -2105.150761 | -2105.27528 | -278.30 | -3.761608695 |
| **Int6_S** | 0.490542 | -2105.702246 | -2105.169598 | -2105.29225 | - | -14.41051615 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Int6_R** | 0.490169 | -2105.702534 | -2105.170947 | -2105.291615 | - | -14.01211005 |
| **Ts3_S** | 0.49981 | -2866.715411 | -2866.165999 | -2866.312312 | -1235.66 | -7.132404162 |
| **Ts3_R** | 0.500291 | -2866.715102 | -2866.165549 | -2866.308034 | -1140.68 | -4.447853631 |
| **Int7** | 0.478117 | -2105.283142 | -2104.805025 | -2104.885899 | - | -15.64457731 |
| **Ts5** | 0.500299 | -2866.736412 | -2866.186921 | -2866.328761 | -940.98 | -4.755835539 |
| **Int8** | 0.373179 | -1508.845188 | -1508.441388 | -1508.538541 | - | -34.19590645 |
| **Int9** | 0.490971 | -2105.753122 | -2105.220009 | -2105.343527 | - | -46.58753467 |
| **Ts6** | 0.491591 | -2105.743816 | -2105.252225 | -2105.33006 | -279.99 | -38.136732 |
| **Int10** | 0.49581 | -2105.7743102 | -2105.238645 | -2105.355039 | - | -53.81136704 |
| **Ts7** | 0.518188 | -2867.2249468 | -2867.224947 | -2867.224947 | -1150.5 | -39.86966361 |
| **Int11** | 0.494782 | -2105.791987 | -2105.2572 | -2105.374926 | - | -66.29053291 |

$Au[(PCH_3)_3]ClO_4$

| | | | |
|---|---|---|---|
| Au | 7.17268900 | 3.08218200 | -1.40226900 |
| P | 8.85711000 | 1.93525100 | -2.39311700 |
| C | 10.36516700 | 2.93959500 | -2.62269600 |
| C | 9.37978800 | 0.47026900 | -1.43606400 |
| C | 8.42063500 | 1.31274600 | -4.05380700 |
| H | 10.13404700 | 3.80670500 | -3.24840500 |
| H | 11.14388200 | 2.33774600 | -3.10361700 |
| H | 10.72180400 | 3.28943500 | -1.64943900 |
| H | 9.71792100 | 0.78408200 | -0.44408200 |
| H | 10.19622700 | -0.04173700 | -1.95690000 |
| H | 8.53259000 | -0.21252400 | -1.32260200 |
| H | 7.55689300 | 0.64562500 | -3.97969800 |
| H | 9.26918400 | 0.76675700 | -4.48015000 |
| H | 8.16443900 | 2.15486600 | -4.70339900 |
| Cl | 5.65464200 | 4.49327500 | 0.98896800 |
| O | 5.52594700 | 4.17265600 | -0.54893800 |
| O | 6.87569900 | 5.31151500 | 1.18427700 |
| O | 4.42695400 | 5.23751900 | 1.33562200 |
| O | 5.74975300 | 3.20526000 | 1.71752200 |

$Au[(PCH_3)_3]^+$

| | | | |
|---|---|---|---|
| Au | 5.81484500 | 3.82971500 | 1.17429400 |
| P | 7.34683200 | 2.84151700 | -0.15704100 |
| C | 8.78267200 | 3.92223000 | -0.45725200 |
| C | 7.98881500 | 1.29638900 | 0.56357900 |
| C | 6.65463300 | 2.41420700 | -1.78729300 |
| H | 8.45236100 | 4.84637700 | -0.93950200 |
| H | 9.49227700 | 3.40051900 | -1.10921700 |
| H | 9.26623900 | 4.16297300 | 0.49350500 |
| H | 8.46726100 | 1.50848000 | 1.52380000 |
| H | 8.72210500 | 0.86118900 | -0.12461100 |
| H | 7.16604800 | 0.59243400 | 0.71613900 |

| | | | |
|---|---|---|---|
| H | 5.82070400 | 1.71836900 | -1.66001800 |
| H | 7.43624100 | 1.94502700 | -2.39531000 |
| H | 6.29740800 | 3.32042700 | -2.28421200 |

$ClO_4^-$

| | | | |
|---|---|---|---|
| Cl | 1.34397000 | -0.32213900 | -0.03285700 |
| O | 1.84343700 | 0.38326100 | -1.25536900 |
| O | 1.84343700 | 0.38326100 | 1.18965600 |
| O | 1.84341600 | -1.73352200 | -0.03285700 |
| O | -0.15350600 | -0.32230400 | -0.03285700 |

$HClO_4$

| | | | |
|---|---|---|---|
| Cl | 1.34536000 | -0.29244500 | -0.00259800 |
| O | 2.05716000 | 0.70363900 | -1.17023100 |
| O | 1.84089100 | 0.33013400 | 1.21928200 |
| O | 1.86588100 | -1.63770300 | -0.26090400 |
| O | -0.10083200 | -0.17638500 | -0.20925000 |
| H | 1.75335700 | 0.34963800 | -2.04235600 |

**Int1**

| | | | |
|---|---|---|---|
| C | -4.06170900 | 0.75011200 | -0.31342900 |
| C | -3.51244000 | 1.81375000 | 0.42281600 |
| C | -3.87584800 | 3.15015600 | 0.08863800 |
| C | -4.76723900 | 3.43937300 | -0.95043200 |
| C | -5.29277600 | 2.36566900 | -1.66351800 |
| C | -4.94387600 | 1.03437600 | -1.34955500 |
| H | -3.80156800 | -0.27603700 | -0.07580400 |
| H | -5.03568200 | 4.46403800 | -1.19178800 |
| H | -5.98524600 | 2.55731500 | -2.47859000 |
| H | -5.37013900 | 0.22069400 | -1.92983200 |
| N | -3.19821500 | 3.98262800 | 0.95431700 |
| H | -3.26340700 | 4.99082300 | 0.96979600 |
| C | -2.42712800 | 3.22362000 | 1.81200500 |
| C | -2.58916000 | 1.88791700 | 1.52899800 |
| H | -1.81311500 | 3.69968600 | 2.56413800 |
| C | -1.90389600 | 0.72466300 | 2.17117800 |
| H | -2.61648200 | -0.08411300 | 2.36875100 |
| H | -1.45811400 | 1.01930700 | 3.12603700 |
| C | -0.80739700 | 0.12537900 | 1.24827100 |
| H | -1.27430500 | -0.02766100 | 0.27061900 |
| N | -0.42030700 | -1.21851800 | 1.73041300 |
| C | 0.39869900 | -1.33763300 | 2.94976200 |
| H | 0.19575400 | -2.31614400 | 3.39210100 |
| H | 0.02238800 | -0.58620200 | 3.64962400 |

| | | | |
|---|---|---|---|
| C | 1.84605400 | -1.17679300 | 2.76395400 |
| C | 3.04160100 | -1.08445200 | 2.62053900 |
| H | 4.09677800 | -0.98809400 | 2.47713800 |
| C | 1.22494400 | 1.84233300 | 0.97708300 |
| C | 0.32077300 | 1.04843000 | 1.07987400 |
| H | 2.04289900 | 2.52311700 | 0.87405200 |
| S | -0.13164900 | -2.36898100 | 0.52774500 |
| O | 0.22157400 | -3.60338200 | 1.24479300 |
| O | 0.77261300 | -1.86437000 | -0.51757600 |
| C | -1.75955400 | -2.52071100 | -0.18588000 |
| C | -2.81636500 | -2.96360900 | 0.61656400 |
| C | -1.94980300 | -2.21736300 | -1.53165600 |
| C | -4.07955500 | -3.09172400 | 0.05243000 |
| H | -2.65196300 | -3.19422900 | 1.66384500 |
| C | -3.22576700 | -2.35197600 | -2.07979600 |
| H | -1.11672800 | -1.87215600 | -2.13328400 |
| C | -4.30491500 | -2.78524700 | -1.30140500 |
| H | -4.90871500 | -3.42837200 | 0.66880000 |
| H | -3.38454400 | -2.10730300 | -3.12598100 |
| C | -5.68815200 | -2.90328400 | -1.88474500 |
| H | -6.38740800 | -2.23658100 | -1.36563600 |
| H | -5.69677700 | -2.64648700 | -2.94784900 |
| H | -6.07604600 | -3.92324700 | -1.77514200 |

**Int2**

| | | | |
|---|---|---|---|
| C | -3.81948200 | 0.86438900 | -0.59216600 |
| C | -3.47813800 | 1.80350100 | 0.39626500 |
| C | -3.92329200 | 3.14954700 | 0.25982100 |
| C | -4.69389300 | 3.56942300 | -0.83042700 |
| C | -5.01314500 | 2.61843500 | -1.79559100 |
| C | -4.58112200 | 1.27911900 | -1.67874200 |
| H | -3.49984000 | -0.16755600 | -0.50418100 |
| H | -5.02902600 | 4.59893400 | -0.91850200 |
| H | -5.60874300 | 2.91319200 | -2.65503000 |
| H | -4.84867500 | 0.56286300 | -2.45080600 |
| N | -3.45224900 | 3.84574800 | 1.35414700 |
| H | -3.62452100 | 4.82311300 | 1.54578400 |
| C | -2.73398000 | 2.99350900 | 2.16680600 |
| C | -2.72295600 | 1.72878100 | 1.62332100 |
| H | -2.28453700 | 3.35526100 | 3.08150500 |
| C | -2.02763100 | 0.51619400 | 2.14926000 |
| H | -2.68119800 | -0.36239500 | 2.11055100 |
| H | -1.72367500 | 0.66294500 | 3.18981100 |
| C | -0.78167500 | 0.13963800 | 1.29577000 |

| | | | |
|---|---|---|---|
| H | -1.10934400 | 0.08197500 | 0.25451700 |
| N | -0.26978200 | -1.18449000 | 1.66103600 |
| C | 0.44311700 | -1.38392000 | 2.93267100 |
| H | 0.27619400 | -2.41449200 | 3.25416800 |
| H | -0.04162100 | -0.73669100 | 3.66904000 |
| C | 1.88413400 | -1.10636000 | 2.88971300 |
| C | 3.07386300 | -0.89591600 | 2.85578600 |
| H | 4.12521100 | -0.70467100 | 2.82953700 |
| Au | 2.18008000 | 0.97918900 | 0.19097200 |
| P | 3.78047200 | 0.02526800 | -1.17955800 |
| C | 0.87926900 | 2.24451100 | 1.57241300 |
| C | 0.22207800 | 1.22316800 | 1.38165700 |
| C | 5.23685900 | 1.08225400 | -1.50023800 |
| C | 4.43770300 | -1.53025600 | -0.48298100 |
| C | 3.11982600 | -0.41813500 | -2.82436600 |
| H | 4.91650500 | 2.00663700 | -1.99020600 |
| H | 5.94726200 | 0.55515400 | -2.14620700 |
| H | 5.72358800 | 1.33322700 | -0.55299700 |
| H | 4.95508800 | -1.32272100 | 0.45778100 |
| H | 5.13777600 | -1.98804700 | -1.19029200 |
| H | 3.60704500 | -2.21371600 | -0.28995800 |
| H | 2.28481800 | -1.11172400 | -2.69709100 |
| H | 3.90387400 | -0.89070600 | -3.42592200 |
| H | 2.76392700 | 0.48355300 | -3.33161800 |
| H | 1.29741800 | 3.18762200 | 1.86898500 |
| S | 0.04929900 | -2.26586200 | 0.40877600 |
| O | 0.46241700 | -3.50943900 | 1.07211300 |
| O | 0.94145900 | -1.68480500 | -0.61313100 |
| C | -1.56172500 | -2.42906400 | -0.32865000 |
| C | -2.63794500 | -2.83584500 | 0.46794300 |
| C | -1.72042700 | -2.16964000 | -1.68915400 |
| C | -3.89166100 | -2.96732400 | -0.11691700 |
| H | -2.49749200 | -3.03537500 | 1.52497400 |
| C | -2.98693000 | -2.30905500 | -2.25661300 |
| H | -0.87230600 | -1.85667300 | -2.28701200 |
| C | -4.08773600 | -2.69871600 | -1.48330600 |
| H | -4.73632900 | -3.27352000 | 0.49368100 |
| H | -3.12251200 | -2.10064400 | -3.31377300 |
| C | -5.46485700 | -2.78936900 | -2.08426800 |
| H | -6.08582100 | -1.95089000 | -1.74324100 |
| H | -5.42768400 | -2.75770900 | -3.17700600 |
| H | -5.97190500 | -3.71141700 | -1.77890200 |

**Ts1_S**

| | | | |
|---|---|---|---|
| C | 3.97015700 | -2.78203000 | 1.49330600 |
| C | 3.78364500 | -2.18921800 | 0.23350400 |
| C | 4.28375500 | -2.85025100 | -0.92199700 |
| C | 4.95082400 | -4.07712800 | -0.85419400 |
| C | 5.11940100 | -4.64111400 | 0.40637900 |
| C | 4.63477900 | -4.00080000 | 1.56730000 |
| H | 3.60174500 | -2.29531700 | 2.39217000 |
| H | 5.32235700 | -4.56610200 | -1.74975200 |
| H | 5.63496000 | -5.59250300 | 0.49919600 |
| H | 4.78684200 | -4.47128800 | 2.53444100 |
| N | 3.96883000 | -2.05945000 | -2.01366400 |
| H | 4.17602900 | -2.28409300 | -2.97819100 |
| C | 3.29561900 | -0.94420000 | -1.59948900 |
| C | 3.14506600 | -0.96956900 | -0.21491600 |
| H | 2.97358900 | -0.19717100 | -2.31159800 |
| C | 2.53056600 | 0.08131300 | 0.65223300 |
| H | 3.07090900 | 1.03176900 | 0.58475500 |
| H | 2.59233800 | -0.24843600 | 1.69177800 |
| C | 1.04168700 | 0.40578800 | 0.30702500 |
| H | 1.03989100 | 1.09703200 | -0.54131500 |
| N | 0.40393300 | 1.10842600 | 1.41637800 |
| C | 0.09243500 | 0.39795500 | 2.66826600 |
| H | 0.10265600 | 1.12848400 | 3.48046200 |
| H | 0.91720100 | -0.29521500 | 2.85207500 |
| C | -1.17932600 | -0.33551500 | 2.69049300 |
| C | -2.23062300 | -0.93121400 | 2.74537500 |
| H | -3.16050300 | -1.45693100 | 2.78927800 |
| Au | -1.73218300 | -1.09736300 | -0.42290200 |
| P | -4.04482500 | -1.05721100 | -0.60786300 |
| C | 0.85606400 | -1.85009900 | -0.76080200 |
| C | 0.36521300 | -0.84170600 | -0.19788500 |
| C | -4.88362900 | -2.49249900 | 0.15755200 |
| C | -4.73231900 | 0.41212400 | 0.23577100 |
| C | -4.69561700 | -0.97605200 | -2.31549600 |
| H | -4.59030000 | -3.40756200 | -0.36599500 |
| H | -5.97076500 | -2.37191800 | 0.09982800 |
| H | -4.58165700 | -2.57555000 | 1.20608400 |
| H | -4.42979700 | 0.40456000 | 1.28663400 |
| H | -5.82549600 | 0.41153400 | 0.16603900 |
| H | -4.33201000 | 1.31622000 | -0.23066500 |
| H | -4.29929300 | -0.08524700 | -2.81224700 |
| H | -5.78998300 | -0.92885200 | -2.30088200 |
| H | -4.37660000 | -1.86281200 | -2.87157200 |
| H | 1.01760900 | -2.78103600 | -1.27025900 |

| | | | |
|---|---|---|---|
| S | -0.61308000 | 2.39408000 | 1.00679500 |
| O | -1.09791200 | 2.92840100 | 2.28649700 |
| O | -1.60029400 | 2.00958600 | -0.01926200 |
| C | 0.54743400 | 3.51193600 | 0.24953400 |
| C | 1.66098400 | 3.93553100 | 0.98223000 |
| C | 0.31736100 | 3.96158100 | -1.05006700 |
| C | 2.55569100 | 4.81952900 | 0.38978100 |
| H | 1.82954900 | 3.57005500 | 1.98969700 |
| C | 1.22598900 | 4.84894800 | -1.62515700 |
| H | -0.55126600 | 3.61672600 | -1.59926600 |
| C | 2.35273900 | 5.29044500 | -0.91884100 |
| H | 3.42818200 | 5.14912400 | 0.94675000 |
| H | 1.05855100 | 5.20025500 | -2.63927300 |
| C | 3.31797900 | 6.26657600 | -1.53762300 |
| H | 4.34702700 | 6.06192900 | -1.22430100 |
| H | 3.27250300 | 6.23590400 | -2.63054700 |
| H | 3.08092500 | 7.29231200 | -1.22537400 |

**Ts1_R**

| | | | |
|---|---|---|---|
| C | -3.73033800 | 1.05586500 | -0.65198700 |
| C | -3.20728800 | 1.94939100 | 0.29571300 |
| C | -3.46375400 | 3.33912700 | 0.16637700 |
| C | -4.21673500 | 3.86102100 | -0.88809600 |
| C | -4.72098600 | 2.95472100 | -1.81782200 |
| C | -4.48395100 | 1.56899800 | -1.70198500 |
| H | -3.55045600 | -0.01160900 | -0.56542700 |
| H | -4.40221500 | 4.92695000 | -0.97690700 |
| H | -5.31276400 | 3.32445000 | -2.65001700 |
| H | -4.89688000 | 0.89401500 | -2.44593600 |
| N | -2.84198000 | 3.97699500 | 1.23303900 |
| H | -2.84093100 | 4.97553400 | 1.39728400 |
| C | -2.20099000 | 3.05879800 | 2.01122700 |
| C | -2.38806500 | 1.77793300 | 1.47807800 |
| H | -1.69188400 | 3.34909400 | 2.91937500 |
| C | -1.88399400 | 0.49511300 | 2.03009700 |
| H | -2.67495500 | -0.25957700 | 2.07524900 |
| H | -1.48950000 | 0.64675700 | 3.03841500 |
| C | -0.76136700 | -0.06384900 | 1.10216700 |
| H | -1.24390900 | -0.34348400 | 0.16153700 |
| N | -0.18293300 | -1.28277800 | 1.64496900 |
| C | 0.66604300 | -1.24237800 | 2.84378800 |
| H | 0.58876500 | -2.21175500 | 3.34237900 |
| H | 0.22479600 | -0.50236300 | 3.51639200 |
| C | 2.08018000 | -0.92326400 | 2.61105700 |

| | | | |
|---|---|---|---|
| C | 3.25416900 | -0.68827600 | 2.44118400 |
| H | 4.29147300 | -0.47899500 | 2.29087100 |
| Au | 2.02095200 | 0.78007100 | -0.20356200 |
| P | 4.03148800 | 0.26487000 | -1.24397500 |
| C | -0.18634600 | 2.30213900 | 0.75710400 |
| C | 0.15704200 | 1.07588400 | 0.73204500 |
| C | 5.48897700 | 1.13100700 | -0.55304600 |
| C | 4.41657300 | -1.51736300 | -1.09357900 |
| C | 4.08863300 | 0.60838000 | -3.04089100 |
| H | 5.37236400 | 2.20974700 | -0.69569600 |
| H | 6.40347500 | 0.79449900 | -1.05351800 |
| H | 5.56506400 | 0.92550700 | 0.51905600 |
| H | 4.48297200 | -1.78855600 | -0.03597200 |
| H | 5.36481300 | -1.74547100 | -1.59237200 |
| H | 3.61028500 | -2.09964100 | -1.54786400 |
| H | 3.28788900 | 0.05492200 | -3.54094900 |
| H | 5.05562300 | 0.30358000 | -3.45566000 |
| H | 3.93882600 | 1.67847100 | -3.21416800 |
| H | -0.09609800 | 3.33751300 | 0.48258100 |
| S | 0.08234400 | -2.54862800 | 0.55875900 |
| O | 0.46568100 | -3.69901200 | 1.38899500 |
| O | 0.96976800 | -2.15963900 | -0.55279900 |
| C | -1.56199100 | -2.73583400 | -0.10311200 |
| C | -2.61995900 | -3.00853900 | 0.77037500 |
| C | -1.77426500 | -2.56070600 | -1.46988500 |
| C | -3.90967600 | -3.08758600 | 0.25700100 |
| H | -2.43840600 | -3.14224200 | 1.83159300 |
| C | -3.07509200 | -2.64575200 | -1.96509200 |
| H | -0.93887700 | -2.34694100 | -2.12680300 |
| C | -4.15889600 | -2.89744100 | -1.11332900 |
| H | -4.73930900 | -3.29424100 | 0.92715400 |
| H | -3.25103700 | -2.50508100 | -3.02764200 |
| C | -5.56776200 | -2.92793100 | -1.64358100 |
| H | -6.06546000 | -1.96580100 | -1.46257800 |
| H | -5.58493600 | -3.11273300 | -2.72176700 |
| H | -6.16395000 | -3.70019100 | -1.14623400 |

**Int5_S**

| | | | |
|---|---|---|---|
| C | 4.17892100 | -2.82565400 | 1.44123100 |
| C | 4.06427700 | -2.26877200 | 0.17473300 |
| C | 5.07244800 | -2.50121300 | -0.76789200 |
| C | 6.20514200 | -3.26217200 | -0.52010400 |
| C | 6.30985200 | -3.81093500 | 0.76206500 |
| C | 5.31438200 | -3.59564400 | 1.72525400 |

| | | | |
|---|---|---|---|
| H | 3.40933000 | -2.67016100 | 2.19103900 |
| H | 6.96698600 | -3.41971800 | -1.27605500 |
| H | 7.17735700 | -4.41288800 | 1.01280300 |
| H | 5.42528600 | -4.03709800 | 2.71080800 |
| N | 4.69560000 | -1.82171300 | -1.96042000 |
| H | 5.24568300 | -1.83394000 | -2.81885600 |
| C | 3.56539500 | -1.19099400 | -1.82050300 |
| C | 2.97986200 | -1.43607300 | -0.46962800 |
| H | 3.12542800 | -0.61547000 | -2.62556900 |
| C | 2.52855500 | -0.14283800 | 0.26006400 |
| H | 3.07807900 | 0.74510400 | -0.06165000 |
| H | 2.71622600 | -0.27923800 | 1.32787200 |
| C | 1.00715700 | -0.03030400 | -0.01688200 |
| H | 0.84293300 | 0.65645500 | -0.85338500 |
| N | 0.30333600 | 0.56102700 | 1.13392400 |
| C | 0.10755600 | -0.21565100 | 2.36676700 |
| H | 0.22857200 | 0.45383500 | 3.22271600 |
| H | 0.92659300 | -0.93938700 | 2.40548000 |
| C | -1.17237400 | -0.92456000 | 2.49448200 |
| C | -2.22384400 | -1.49559200 | 2.66935300 |
| H | -3.15476900 | -2.00371800 | 2.80157000 |
| Au | -1.44332500 | -1.85165700 | -0.64293600 |
| P | -3.75468700 | -2.17378700 | -0.85222600 |
| C | 1.63615500 | -2.17772000 | -0.69369100 |
| C | 0.55576900 | -1.42025700 | -0.44492300 |
| C | -4.44132200 | -3.56014400 | 0.13203200 |
| C | -4.69690400 | -0.70713700 | -0.28560200 |
| C | -4.37193100 | -2.47994100 | -2.55129300 |
| H | -3.98721000 | -4.50116600 | -0.19399600 |
| H | -5.52821400 | -3.61943300 | 0.00881000 |
| H | -4.20458500 | -3.40633300 | 1.18911900 |
| H | -4.42807500 | -0.48095600 | 0.75040600 |
| H | -5.77501800 | -0.88969400 | -0.35453600 |
| H | -4.43196600 | 0.15514900 | -0.90432000 |
| H | -4.08306500 | -1.64540400 | -3.19799700 |
| H | -5.46288700 | -2.57952100 | -2.55356000 |
| H | -3.92321000 | -3.39805100 | -2.94356100 |
| H | 1.65703300 | -3.19440500 | -1.07178800 |
| S | -0.76070700 | 1.81472300 | 0.83335700 |
| O | -1.25763300 | 2.23321100 | 2.15346200 |
| O | -1.74186600 | 1.48585900 | -0.21606300 |
| C | 0.33832200 | 3.04979900 | 0.16291200 |
| C | 1.46152200 | 3.43550000 | 0.90201800 |
| C | 0.04664200 | 3.63486100 | -1.06760300 |

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|---|---|---|---|
| C | 2.30075800 | 4.41723800 | 0.38816200 |
| H | 1.68006000 | 2.96553600 | 1.85526000 |
| C | 0.90040300 | 4.61905400 | -1.56679800 |
| H | -0.82777600 | 3.31852100 | -1.62502600 |
| C | 2.03361900 | 5.02512900 | -0.85104500 |
| H | 3.17872300 | 4.71887100 | 0.95290400 |
| H | 0.68260100 | 5.07659200 | -2.52768300 |
| C | 2.94283100 | 6.10213300 | -1.38244000 |
| H | 3.99689600 | 5.83159300 | -1.25445300 |
| H | 2.75904900 | 6.29269700 | -2.44396200 |
| H | 2.78387500 | 7.04407800 | -0.84141200 |

**Int5_R**

| | | | |
|---|---|---|---|
| C | -3.17936800 | 1.91333100 | -1.31577800 |
| C | -3.02511200 | 2.42842400 | -0.03556600 |
| C | -3.84908100 | 3.47776700 | 0.38415800 |
| C | -4.83879800 | 4.04886000 | -0.40237500 |
| C | -4.99012100 | 3.51356000 | -1.68520900 |
| C | -4.17514900 | 2.46376100 | -2.13270800 |
| H | -2.54516800 | 1.10742800 | -1.67223300 |
| H | -5.45808500 | 4.86405600 | -0.04363700 |
| H | -5.74951700 | 3.92120400 | -2.34462300 |
| H | -4.31690200 | 2.07227800 | -3.13529300 |
| N | -3.46645700 | 3.80129300 | 1.71593800 |
| H | -3.90110500 | 4.54029900 | 2.26804000 |
| C | -2.49724600 | 3.04394000 | 2.14071200 |
| C | -2.06114000 | 2.08959900 | 1.08540000 |
| H | -2.08455700 | 3.14875200 | 3.13675900 |
| C | -2.05758200 | 0.60530400 | 1.54424400 |
| H | -3.01492700 | 0.11129800 | 1.36778400 |
| H | -1.83607800 | 0.55954700 | 2.61413700 |
| C | -0.89301700 | -0.02199000 | 0.74149100 |
| H | -1.28125100 | -0.38767000 | -0.21458100 |
| N | -0.34697700 | -1.20036500 | 1.43114300 |
| C | 0.47033000 | -1.04776600 | 2.64359700 |
| H | 0.22985500 | -1.86592300 | 3.32805000 |
| H | 0.14091600 | -0.12152400 | 3.12261900 |
| C | 1.92538400 | -1.00526600 | 2.44700600 |
| C | 3.13034200 | -1.01079100 | 2.34524600 |
| H | 4.19345900 | -1.00983500 | 2.23616300 |
| Au | 1.92442100 | 0.77723300 | -0.34006900 |
| P | 4.01477300 | 0.22655200 | -1.24460000 |
| C | -0.58116100 | 2.28837900 | 0.66305500 |
| C | 0.05989100 | 1.12960900 | 0.44517400 |
| C | 5.45640800 | 0.80419100 | -0.26963300 |

| | | | |
|---|---|---|---|
| C | 4.24740400 | -1.58708200 | -1.37193400 |
| C | 4.34415500 | 0.84510900 | -2.93909400 |
| H | 5.45161500 | 1.89793200 | -0.22541700 |
| H | 6.39250900 | 0.46374900 | -0.72555700 |
| H | 5.38643200 | 0.41454500 | 0.75035800 |
| H | 4.11444800 | -2.04121300 | -0.38574900 |
| H | 5.24642000 | -1.82346600 | -1.75460900 |
| H | 3.49133300 | -2.00189400 | -2.04496200 |
| H | 3.57152700 | 0.47137500 | -3.61836500 |
| H | 5.32712300 | 0.51047600 | -3.28851400 |
| H | 4.31189200 | 1.93925200 | -2.94101900 |
| H | -0.21823300 | 3.29045000 | 0.46089600 |
| S | -0.10749500 | -2.57977300 | 0.51284200 |
| O | 0.36301300 | -3.60417400 | 1.45835200 |
| O | 0.69029700 | -2.32299600 | -0.69963100 |
| C | -1.77620500 | -2.92962000 | -0.01210500 |
| C | -2.77452200 | -3.08954100 | 0.95503900 |
| C | -2.05781700 | -3.05737800 | -1.37035800 |
| C | -4.07066900 | -3.37434900 | 0.54286800 |
| H | -2.54046600 | -2.98230400 | 2.00908100 |
| C | -3.36537300 | -3.34419800 | -1.76488700 |
| H | -1.26903900 | -2.92811100 | -2.10277800 |
| C | -4.38700400 | -3.50455400 | -0.82117400 |
| H | -4.85327100 | -3.49798400 | 1.28660400 |
| H | -3.59378700 | -3.44290200 | -2.82223800 |
| C | -5.80075400 | -3.80306000 | -1.24679400 |
| H | -6.47500400 | -2.98403300 | -0.96651600 |
| H | -5.87051300 | -3.94496800 | -2.32912100 |
| H | -6.17548400 | -4.70923000 | -0.75617600 |

**Int3**

| | | | |
|---|---|---|---|
| C | 4.83794800 | -1.15852000 | -0.61249200 |
| C | 4.11520600 | -0.84556700 | 0.55407600 |
| C | 3.72479900 | -1.91102400 | 1.41944700 |
| C | 4.02142400 | -3.24980300 | 1.14491000 |
| C | 4.72910800 | -3.52500100 | -0.02091500 |
| C | 5.13526300 | -2.48882800 | -0.88858700 |
| H | 5.15515600 | -0.37039100 | -1.28665700 |
| H | 3.71132800 | -4.04234200 | 1.82016300 |
| H | 4.97713400 | -4.55427100 | -0.26419500 |
| H | 5.69355300 | -2.73721700 | -1.78698700 |
| N | 3.03852200 | -1.35061500 | 2.47665300 |
| H | 2.68168600 | -1.85448100 | 3.27666900 |
| C | 2.98808200 | 0.01589300 | 2.31159600 |

| | | | |
|---|---|---|---|
| C | 3.62256500 | 0.37982700 | 1.14425100 |
| H | 2.50212100 | 0.63893000 | 3.04960500 |
| C | 3.75926800 | 1.79515600 | 0.66902200 |
| H | 4.81179600 | 2.06247900 | 0.51318800 |
| H | 3.37928100 | 2.45408600 | 1.45652100 |
| C | 3.00217100 | 2.19531900 | -0.63255300 |
| H | 2.87140000 | 3.27843900 | -0.58315100 |
| N | 1.62998700 | 1.62933300 | -0.67765400 |
| C | 1.43551400 | 0.28999200 | -1.24404800 |
| H | 2.40952500 | -0.09507500 | -1.55796600 |
| H | 0.81205600 | 0.33216100 | -2.14180200 |
| C | 0.87101500 | -0.66832500 | -0.28312100 |
| C | 0.50981400 | -1.49913000 | 0.54602200 |
| H | 0.48459700 | -2.22582500 | 1.33497800 |
| Au | -1.49786900 | -1.02991400 | -0.35122100 |
| P | -3.74446500 | -1.17076800 | -0.87839600 |
| C | 4.33702800 | 1.68026800 | -2.89225600 |
| C | 3.73675900 | 1.90570600 | -1.86809300 |
| C | -4.79284400 | -1.37615800 | 0.60412200 |
| C | -4.43516400 | 0.26264400 | -1.77674800 |
| C | -4.10993100 | -2.61522100 | -1.93710400 |
| H | -4.50653400 | -2.29384000 | 1.12679300 |
| H | -5.84597400 | -1.43896600 | 0.30935400 |
| H | -4.65079100 | -0.52604300 | 1.27661500 |
| H | -4.43446400 | 1.14458600 | -1.13274900 |
| H | -5.46429200 | 0.03693900 | -2.07696400 |
| H | -3.83343000 | 0.46697500 | -2.66701600 |
| H | -3.57362800 | -2.51486600 | -2.88552500 |
| H | -5.18631300 | -2.67466000 | -2.13120400 |
| H | -3.77774700 | -3.52959600 | -1.43663500 |
| H | 4.86928700 | 1.48355900 | -3.79880600 |
| S | 0.32882600 | 2.68950300 | -0.83905700 |
| O | -0.39000600 | 2.41503500 | -2.09484600 |
| O | 0.85388000 | 4.04030200 | -0.59277900 |
| C | -0.74439300 | 2.21185900 | 0.49821400 |
| C | -2.12118500 | 2.21352300 | 0.27643500 |
| C | -0.21125800 | 1.89125200 | 1.74884200 |
| C | -2.97353000 | 1.86668600 | 1.32396300 |
| H | -2.51726400 | 2.46591700 | -0.70013500 |
| C | -1.07672800 | 1.53041100 | 2.77579400 |
| H | 0.86079200 | 1.89384800 | 1.90496600 |
| C | -2.46832700 | 1.50533400 | 2.57930800 |
| H | -4.04646400 | 1.86429200 | 1.15761300 |
| H | -0.66926000 | 1.26525100 | 3.74772800 |

| | | | |
|---|---|---|---|
| C | -3.39033600 | 1.07660700 | 3.69019800 |
| H | -4.43081300 | 1.32848600 | 3.46518300 |
| H | -3.33298500 | -0.00874100 | 3.84540300 |
| H | -3.11656100 | 1.55191900 | 4.63862400 |

**Ts4**

| | | | |
|---|---|---|---|
| C | 4.25727283 | 1.96552680 | 0.34463883 |
| C | 3.70942983 | 1.10652280 | -0.61614217 |
| C | 3.41684683 | 1.62005280 | -1.90540517 |
| C | 3.61822183 | 2.95263080 | -2.25646117 |
| C | 4.15364683 | 3.78975880 | -1.27862417 |
| C | 4.47468983 | 3.29901580 | 0.00063483 |
| H | 4.50411183 | 1.59732280 | 1.33404683 |
| H | 3.37304783 | 3.31808880 | -3.24892817 |
| H | 4.33156583 | 4.83526780 | -1.51121717 |
| H | 4.90232183 | 3.97521380 | 0.73514283 |
| N | 2.90949383 | 0.56378880 | -2.66550117 |
| H | 2.62136983 | 0.63182680 | -3.63508617 |
| C | 2.88367883 | -0.56448320 | -1.93261417 |
| C | 3.29366983 | -0.30117320 | -0.61475517 |
| H | 2.53304883 | -1.49701620 | -2.35068017 |
| C | 3.75607383 | -1.43588320 | 0.27296983 |
| H | 4.85014983 | -1.41280020 | 0.33916283 |
| H | 3.49233383 | -2.36929520 | -0.23070017 |
| C | 3.20658883 | -1.54613520 | 1.71618683 |
| H | 3.34240083 | -2.58494320 | 2.02629383 |
| N | 1.76508283 | -1.27342520 | 1.80824983 |
| C | 1.31049083 | 0.05589780 | 1.43352183 |
| H | 2.02931283 | 0.77603880 | 1.83889183 |
| H | 0.34957183 | 0.26391780 | 1.91465283 |
| C | 1.14031083 | 0.28211980 | -0.01842417 |
| C | 0.38183183 | 0.73978480 | -0.93855317 |
| H | 0.60793283 | 0.92248980 | -1.98440117 |
| Au | -1.60788117 | 0.99065080 | -0.28311717 |
| P | -3.80902717 | 1.23231580 | 0.41714983 |
| C | 4.50988383 | -0.00336920 | 3.47254883 |
| C | 3.91807983 | -0.69641420 | 2.67984083 |
| C | -4.78902117 | 2.42560780 | -0.56393617 |
| C | -4.77009017 | -0.32474420 | 0.35930183 |
| C | -3.95590717 | 1.80611480 | 2.14910183 |
| H | -4.32205517 | 3.41363480 | -0.50846917 |
| H | -5.81194617 | 2.48397180 | -0.17665817 |
| H | -4.81344717 | 2.10534480 | -1.61002617 |
| H | -4.83171317 | -0.67948920 | -0.67353417 |

| | | | |
|---|---|---|---|
| H | -5.78176117 | -0.15645620 | 0.74439383 |
| H | -4.27444817 | -1.08618220 | 0.96896483 |
| H | -3.46540117 | 1.08775680 | 2.81332283 |
| H | -5.01096117 | 1.89882480 | 2.42885883 |
| H | -3.46398517 | 2.77759480 | 2.25607083 |
| H | 5.03078283 | 0.60334480 | 4.18272883 |
| S | 0.63074083 | -2.49271920 | 1.95986983 |
| O | -0.41661517 | -1.99206720 | 2.86022483 |
| O | 1.38787983 | -3.70491520 | 2.29676983 |
| C | -0.12070017 | -2.68928620 | 0.35514783 |
| C | -1.45264117 | -2.32057520 | 0.17600583 |
| C | 0.64558383 | -3.16928720 | -0.71070317 |
| C | -2.01571117 | -2.41657520 | -1.09660317 |
| H | -2.03671417 | -1.96452220 | 1.01583483 |
| C | 0.07084983 | -3.24897720 | -1.97409817 |
| H | 1.67166383 | -3.48282520 | -0.55624217 |
| C | -1.26350117 | -2.86339420 | -2.18999417 |
| H | -3.05451117 | -2.13658220 | -1.24008717 |
| H | 0.65956383 | -3.62487320 | -2.80638017 |
| C | -1.86309717 | -2.91814920 | -3.57049517 |
| H | -2.95657217 | -2.91365720 | -3.53054117 |
| H | -1.54905217 | -2.04852020 | -4.16327217 |
| H | -1.53802817 | -3.81305220 | -4.11171417 |

**Int4**

| | | | |
|---|---|---|---|
| C | 4.14205700 | 1.68171800 | 0.87881000 |
| C | 3.64355200 | 1.18005300 | -0.31725500 |
| C | 4.07585400 | 1.76708800 | -1.51477600 |
| C | 4.99064300 | 2.80436100 | -1.59891400 |
| C | 5.49119200 | 3.28498200 | -0.38513700 |
| C | 5.06759800 | 2.73401100 | 0.82956900 |
| H | 3.83781800 | 1.26962900 | 1.83143000 |
| H | 5.29388500 | 3.22137800 | -2.55324700 |
| H | 6.21023500 | 4.09772700 | -0.38823600 |
| H | 5.46418200 | 3.12933200 | 1.75954500 |
| N | 3.39216400 | 1.11763200 | -2.58055400 |
| H | 3.53213600 | 1.34606000 | -3.56513100 |
| C | 2.57234600 | 0.21176200 | -2.15252100 |
| C | 2.62314500 | 0.09187200 | -0.65869000 |
| H | 1.97036400 | -0.38731400 | -2.82409800 |
| C | 3.10090500 | -1.38031500 | -0.39243700 |
| H | 4.16336200 | -1.47209900 | -0.63116300 |
| H | 2.54448700 | -2.03050800 | -1.07133000 |
| C | 2.84123800 | -1.90989700 | 1.03521300 |

| | | | |
|---|---|---|---|
| H | 2.91272800 | -2.99977000 | 0.98370300 |
| N | 1.48310200 | -1.59083600 | 1.50467400 |
| C | 1.08850000 | -0.17805700 | 1.36309500 |
| H | 1.72153700 | 0.38782400 | 2.05799400 |
| H | 0.05801700 | -0.06223200 | 1.69949700 |
| C | 1.23229600 | 0.34028300 | -0.04656700 |
| C | 0.25088200 | 0.99087400 | -0.69711200 |
| H | 0.50329900 | 1.36487900 | -1.69543900 |
| Au | -1.67141000 | 1.26186000 | -0.02141900 |
| P | -3.88371100 | 1.48336000 | 0.73862900 |
| C | 4.64368200 | -1.11100000 | 2.84405200 |
| C | 3.82323800 | -1.45101000 | 2.02617000 |
| C | -4.79155900 | 2.94463900 | 0.10508800 |
| C | -4.96135000 | 0.06271000 | 0.30890800 |
| C | -4.02581000 | 1.61554400 | 2.56180300 |
| H | -4.26384400 | 3.85650400 | 0.40197800 |
| H | -5.81143900 | 2.96926100 | 0.50406900 |
| H | -4.83051900 | 2.90419200 | -0.98808700 |
| H | -5.03652900 | -0.02231800 | -0.77942500 |
| H | -5.96351100 | 0.19943000 | 0.72989400 |
| H | -4.52660700 | -0.86000900 | 0.70521100 |
| H | -3.58487700 | 0.72732900 | 3.02565000 |
| H | -5.07549200 | 1.69929000 | 2.86386300 |
| H | -3.47737200 | 2.49767100 | 2.90700000 |
| H | 5.36614700 | -0.79728700 | 3.56721300 |
| S | 0.28656800 | -2.76155700 | 1.47370900 |
| O | -0.71037600 | -2.34772300 | 2.46933900 |
| O | 0.98547000 | -4.04811800 | 1.60059700 |
| C | -0.51791700 | -2.71495100 | -0.11833100 |
| C | -1.76215100 | -2.09447900 | -0.24028400 |
| C | 0.12607200 | -3.26059400 | -1.23092500 |
| C | -2.35205900 | -2.00087900 | -1.49823300 |
| H | -2.25827500 | -1.69299400 | 0.63473800 |
| C | -0.47399500 | -3.14858500 | -2.48334300 |
| H | 1.07249900 | -3.77946400 | -1.12143900 |
| C | -1.71472800 | -2.51157300 | -2.63833100 |
| H | -3.32003600 | -1.51824700 | -1.59562300 |
| H | 0.02133800 | -3.57276100 | -3.35222800 |
| C | -2.36522200 | -2.39297200 | -3.99198900 |
| H | -2.63385300 | -1.35224200 | -4.20917600 |
| H | -1.70407700 | -2.75070600 | -4.78679000 |
| H | -3.29173000 | -2.97932800 | -4.03254000 |

**Ts2S**

| | | | |
|---|---|---|---|
| C | 5.32953000 | -1.12200600 | 1.74650000 |
| C | 4.48442600 | -1.42987300 | 0.67022300 |
| C | 4.67100300 | -2.62682600 | -0.07461100 |
| C | 5.67565200 | -3.54248800 | 0.26183700 |
| C | 6.50421800 | -3.21254000 | 1.32803000 |
| C | 6.34238800 | -2.01665300 | 2.06255600 |
| H | 5.18981900 | -0.20557000 | 2.31128400 |
| H | 5.80716900 | -4.46346300 | -0.29650700 |
| H | 7.30181100 | -3.89562000 | 1.60482500 |
| H | 7.01602400 | -1.80345800 | 2.88625300 |
| N | 3.74103400 | -2.67067300 | -1.08874400 |
| H | 3.54970000 | -3.49035500 | -1.65117300 |
| C | 2.85293800 | -1.59055800 | -0.97251100 |
| C | 3.34339300 | -0.75771700 | 0.10538300 |
| H | 2.36346800 | -1.22509200 | -1.86889500 |
| C | 2.83525500 | 0.63736400 | 0.29915900 |
| H | 3.29621600 | 1.31980000 | -0.42293700 |
| H | 3.08930900 | 0.98736900 | 1.30213400 |
| C | 1.30074100 | 0.57964700 | 0.10277600 |
| H | 1.08504700 | 0.66168600 | -0.97208000 |
| N | 0.64465300 | 1.72017900 | 0.73967100 |
| C | 0.67171700 | 1.90011400 | 2.19972100 |
| H | 0.87499300 | 2.95239600 | 2.41799100 |
| H | 1.52745100 | 1.32620000 | 2.56419200 |
| C | -0.52828000 | 1.48880500 | 2.93765600 |
| C | -1.49472100 | 1.21391700 | 3.61027400 |
| H | -2.35534100 | 0.96467900 | 4.19230800 |
| Au | -1.03481200 | -1.18798700 | 1.24202100 |
| P | -3.25058200 | -1.60250200 | 1.89400000 |
| C | 1.79385100 | -1.75383000 | 0.27599900 |
| C | 0.84932800 | -0.81110400 | 0.53008400 |
| C | -4.08478000 | -2.94314300 | 0.96397800 |
| C | -3.45719800 | -2.07849500 | 3.65166500 |
| C | -4.33934900 | -0.14702600 | 1.66724800 |
| H | -4.08086200 | -2.70211900 | -0.10356000 |
| H | -5.11891600 | -3.06121600 | 1.30545100 |
| H | -3.54382400 | -3.88280700 | 1.11349300 |
| H | -2.91815800 | -3.01226800 | 3.84042200 |
| H | -4.51787400 | -2.21844300 | 3.88705700 |
| H | -3.04099400 | -1.29963600 | 4.29686000 |
| H | -3.93747300 | 0.70427400 | 2.22350300 |
| H | -5.35456900 | -0.36838700 | 2.01415200 |
| H | -4.36724700 | 0.11849800 | 0.60601600 |
| H | 1.82062700 | -2.76374100 | 0.66965500 |

| | | | |
|---|---|---|---|
| S | -0.54082800 | 2.51915500 | -0.13091200 |
| O | -0.98053100 | 3.62352500 | 0.73352900 |
| O | -1.54750600 | 1.58641200 | -0.66582800 |
| C | 0.39378900 | 3.14479900 | -1.51489100 |
| C | 1.52615500 | 3.92724700 | -1.27068400 |
| C | -0.03924500 | 2.88186600 | -2.81433000 |
| C | 2.23303500 | 4.44376200 | -2.35162400 |
| H | 1.85106600 | 4.12381700 | -0.25426800 |
| C | 0.68146400 | 3.40987500 | -3.88424900 |
| H | -0.92270600 | 2.27579500 | -2.98032900 |
| C | 1.82498600 | 4.19251800 | -3.67205100 |
| H | 3.11409300 | 5.05319200 | -2.17147000 |
| H | 0.35006600 | 3.21195200 | -4.89980700 |
| C | 2.61401900 | 4.73180000 | -4.83619400 |
| H | 1.96251100 | 4.96449900 | -5.68469400 |
| H | 3.16413600 | 5.63676200 | -4.55999900 |
| H | 3.34873700 | 3.99236500 | -5.18195700 |

**Ts2R**

| | | | |
|---|---|---|---|
| C | 2.43799100 | -1.89520800 | -2.34803500 |
| C | 2.08049100 | -2.19575500 | -1.02894500 |
| C | 2.18110200 | -3.52456800 | -0.54169500 |
| C | 2.60524900 | -4.57338600 | -1.36381200 |
| C | 2.95891100 | -4.25204700 | -2.67079300 |
| C | 2.88325400 | -2.93157500 | -3.16085500 |
| H | 2.36698400 | -0.87803900 | -2.72063700 |
| H | 2.66554800 | -5.59105300 | -0.99232400 |
| H | 3.30473800 | -5.04125900 | -3.33180200 |
| H | 3.17149200 | -2.72771000 | -4.18716400 |
| N | 1.80920700 | -3.53828600 | 0.79020600 |
| H | 1.63463600 | -4.38016300 | 1.32483100 |
| C | 1.35108700 | -2.27974900 | 1.16792900 |
| C | 1.55276800 | -1.38722500 | 0.05360700 |
| H | 1.36266400 | -2.00021200 | 2.21255800 |
| C | 1.50549100 | 0.09718100 | 0.22486400 |
| H | 1.74670400 | 0.59031800 | -0.71833500 |
| H | 2.23862300 | 0.41336200 | 0.96906300 |
| C | 0.04733800 | 0.48546100 | 0.66831100 |
| H | -0.35731900 | 1.14404100 | -0.10402800 |
| N | -0.12258200 | 1.21783800 | 1.92374100 |
| C | 0.12581700 | 0.55484500 | 3.20991400 |
| H | -0.41646500 | -0.39570000 | 3.18072600 |
| H | -0.34178400 | 1.15902500 | 3.98989100 |
| C | 1.53731200 | 0.31720500 | 3.54316300 |

| | | | |
|---|---|---|---|
| C | 2.69518300 | 0.11633900 | 3.82454900 |
| Au | -2.85996500 | -0.54339500 | 0.73492400 |
| P | -5.18030000 | -0.23486000 | 0.90628700 |
| C | -0.14123600 | -1.91049500 | 0.44580500 |
| C | -0.82149700 | -0.75476100 | 0.62923500 |
| C | -5.64066200 | 1.23236500 | 1.90166300 |
| C | -6.02138600 | 0.01318900 | -0.70222000 |
| C | -6.07721700 | -1.62684600 | 1.68996600 |
| H | -5.24249400 | 1.12447700 | 2.91543800 |
| H | -6.72980000 | 1.33895900 | 1.94817600 |
| H | -5.20635300 | 2.12933300 | 1.44930000 |
| H | -5.59634500 | 0.88835500 | -1.20337800 |
| H | -7.09549400 | 0.16648600 | -0.55181600 |
| H | -5.86478400 | -0.86514900 | -1.33608300 |
| H | -5.91557800 | -2.53989800 | 1.10848100 |
| H | -7.15021100 | -1.41184900 | 1.73804700 |
| H | -5.69284500 | -1.78279600 | 2.70280600 |
| H | -0.55234900 | -2.83899700 | 0.06431800 |
| S | -0.04424800 | 2.89703800 | 1.84634800 |
| O | -0.30531600 | 3.37742000 | 3.20861200 |
| O | -0.91634800 | 3.29502400 | 0.73243500 |
| C | 1.62658400 | 3.31300900 | 1.39478100 |
| C | 2.60683100 | 3.37969700 | 2.38766900 |
| C | 1.94696800 | 3.48526900 | 0.04615500 |
| C | 3.92656700 | 3.61667500 | 2.01420900 |
| H | 2.34358500 | 3.24731800 | 3.43044100 |
| C | 3.27348300 | 3.72032100 | -0.30657300 |
| H | 1.17063500 | 3.44115600 | -0.70926000 |
| C | 4.28114500 | 3.78715900 | 0.66713200 |
| H | 4.69530900 | 3.67080800 | 2.78002000 |
| H | 3.53113300 | 3.85620300 | -1.35322600 |
| C | 5.70890400 | 4.06757700 | 0.27845300 |
| H | 6.41128900 | 3.61476700 | 0.98548200 |
| H | 5.93052500 | 3.69062100 | -0.72503100 |
| H | 5.90176200 | 5.14867200 | 0.27243700 |
| H | 3.72279900 | -0.04805000 | 4.07092900 |

**Int6S**

| | | | |
|---|---|---|---|
| C | 4.41361400 | -0.18624100 | 0.89355300 |
| C | 3.88855200 | -1.06248500 | -0.10292000 |
| C | 4.18804400 | -2.48012800 | -0.06018300 |
| C | 5.03569600 | -3.00740200 | 0.94069500 |
| C | 5.52687300 | -2.12124400 | 1.87300500 |
| C | 5.21908400 | -0.72042600 | 1.86289400 |

| | | | |
|---|---|---|---|
| H | 4.17104300 | 0.87115700 | 0.86365800 |
| H | 5.27338000 | -4.06485300 | 0.97293900 |
| H | 6.17576400 | -2.49625200 | 2.65908100 |
| H | 5.64129100 | -0.08966800 | 2.63780900 |
| N | 3.52563100 | -3.10300200 | -1.04124500 |
| H | 3.60603500 | -4.08729200 | -1.26682000 |
| C | 2.74112300 | -2.15287800 | -1.82155900 |
| C | 3.02800600 | -0.85252000 | -1.16244100 |
| H | 3.08596400 | -2.16993600 | -2.86546500 |
| C | 2.16417400 | 0.28218700 | -1.47581000 |
| H | 2.10171900 | 0.44604500 | -2.55646800 |
| H | 2.46972800 | 1.20404100 | -0.98133000 |
| C | 0.70400100 | -0.12672100 | -1.00417700 |
| H | 0.03726200 | 0.59387200 | -1.48149300 |
| N | 0.53919700 | 0.05355200 | 0.44989200 |
| C | 0.73723300 | -1.03699700 | 1.41691000 |
| H | 1.24979000 | -0.64192600 | 2.29760900 |
| H | 1.41388900 | -1.75230500 | 0.94837100 |
| C | -0.48727800 | -1.73218500 | 1.83300200 |
| C | -1.47523500 | -2.31733000 | 2.21179600 |
| H | -2.35461700 | -2.82538500 | 2.54507000 |
| Au | -1.73024800 | -1.90087200 | -1.29138700 |
| P | -4.03056800 | -2.22271400 | -0.99280700 |
| C | 1.22252800 | -2.42767200 | -1.79364500 |
| C | 0.29990900 | -1.51982100 | -1.44123000 |
| C | -4.50652800 | -3.91553200 | -0.47531600 |
| C | -4.70991600 | -1.13591000 | 0.31725300 |
| C | -5.08083100 | -1.88229600 | -2.45597200 |
| H | -4.22259900 | -4.62890300 | -1.25537400 |
| H | -5.58658600 | -3.97725000 | -0.30260700 |
| H | -3.97624200 | -4.17676800 | 0.44584500 |
| H | -4.17950700 | -1.32184600 | 1.25600900 |
| H | -5.78075100 | -1.31987600 | 0.45738100 |
| H | -4.55292500 | -0.08989500 | 0.03608500 |
| H | -4.92596100 | -0.84853000 | -2.78056900 |
| H | -6.13883800 | -2.03214000 | -2.21443200 |
| H | -4.79680900 | -2.55216400 | -3.27363300 |
| H | 0.95883200 | -3.43359300 | -2.11005800 |
| S | -0.27948100 | 1.42219100 | 0.96617200 |
| O | -0.38789400 | 1.29813600 | 2.42560400 |
| O | -1.48884300 | 1.62827100 | 0.15267700 |
| C | 0.86465700 | 2.72827800 | 0.56902000 |
| C | 2.00450300 | 2.88310300 | 1.36544200 |
| C | 0.65747300 | 3.51659000 | -0.56071300 |

| | | | |
|---|---|---|---|
| C | 2.94514900 | 3.84397200 | 1.01304200 |
| H | 2.14856400 | 2.26478200 | 2.24514100 |
| C | 1.61446200 | 4.47430600 | -0.89934200 |
| H | -0.23367000 | 3.38235000 | -1.16348800 |
| C | 2.76759600 | 4.65136300 | -0.12480900 |
| H | 3.83135400 | 3.97559600 | 1.62801100 |
| H | 1.46094200 | 5.09247900 | -1.77920600 |
| C | 3.79116900 | 5.69692500 | -0.48159600 |
| H | 4.80781500 | 5.29163900 | -0.42560000 |
| H | 3.62878500 | 6.08873500 | -1.49000600 |
| H | 3.74234600 | 6.54101300 | 0.21847600 |

**Int6R**

| | | | |
|---|---|---|---|
| C | 4.49416000 | -1.22439800 | -0.23061200 |
| C | 3.45038000 | -1.95109200 | 0.41817100 |
| C | 3.29137900 | -3.37158400 | 0.17506600 |
| C | 4.18125500 | -4.06145500 | -0.68050300 |
| C | 5.17923800 | -3.32036400 | -1.27161500 |
| C | 5.34014200 | -1.91085800 | -1.05874200 |
| H | 4.60166200 | -0.15859400 | -0.05908800 |
| H | 4.07166900 | -5.12500600 | -0.86123300 |
| H | 5.87913800 | -3.82047000 | -1.93465400 |
| H | 6.14896600 | -1.39673400 | -1.56694900 |
| N | 2.22025900 | -3.81734200 | 0.83857000 |
| H | 1.90700300 | -4.78049100 | 0.86106300 |
| C | 1.57230500 | -2.73470700 | 1.57052700 |
| C | 2.43360000 | -1.56145000 | 1.26675500 |
| H | 1.54268200 | -2.98050700 | 2.64043600 |
| C | 1.93099200 | -0.22792300 | 1.59864800 |
| H | 2.64906700 | 0.56374800 | 1.38139000 |
| H | 1.63148700 | -0.17331700 | 2.64976100 |
| C | 0.63861400 | -0.02175200 | 0.71167800 |
| H | 0.99063000 | 0.11127200 | -0.31522600 |
| N | 0.00176100 | 1.23721000 | 1.09262400 |
| C | -0.69612800 | 1.38637000 | 2.37238000 |
| H | -0.30608900 | 2.25732900 | 2.90840800 |
| H | -0.44139100 | 0.50238400 | 2.96421500 |
| C | -2.15696900 | 1.49694100 | 2.27729900 |
| C | -3.35813400 | 1.63271800 | 2.25804100 |
| H | -4.41999000 | 1.74933500 | 2.22916100 |
| Au | -2.17667600 | -0.83593100 | -0.08114700 |
| P | -4.23398900 | -0.23168000 | -1.02319200 |
| C | 0.14792100 | -2.43670000 | 1.04911200 |
| C | -0.29236300 | -1.21954700 | 0.69128000 |
| C | -5.70092700 | -0.48405100 | 0.04727700 |

| | | | |
|---|---|---|---|
| C | -4.27026400 | 1.55247700 | -1.44163300 |
| C | -4.67466700 | -1.07553200 | -2.59005900 |
| H | -5.80874300 | -1.54948900 | 0.27394300 |
| H | -6.60777100 | -0.12610800 | -0.45239300 |
| H | -5.56472900 | 0.06027600 | 0.98603700 |
| H | -4.06689100 | 2.13990500 | -0.54156800 |
| H | -5.24511500 | 1.83469300 | -1.85431100 |
| H | -3.48630200 | 1.76659800 | -2.17374100 |
| H | -3.88494000 | -0.90593500 | -3.32863100 |
| H | -5.62444100 | -0.69311000 | -2.97984600 |
| H | -4.76258700 | -2.15210400 | -2.41275700 |
| H | -0.47792700 | -3.32273600 | 0.97890400 |
| S | 0.02061600 | 2.50126300 | 0.00429000 |
| O | -0.47908500 | 3.66777000 | 0.74490900 |
| O | -0.62922400 | 2.10649800 | -1.25534400 |
| C | 1.76308900 | 2.68823400 | -0.33367500 |
| C | 2.58232800 | 3.26042000 | 0.64449800 |
| C | 2.29823700 | 2.16882000 | -1.51168600 |
| C | 3.95646800 | 3.29988400 | 0.43275500 |
| H | 2.15235800 | 3.66089100 | 1.55665100 |
| C | 3.67897400 | 2.21146400 | -1.70353500 |
| H | 1.64613900 | 1.73055400 | -2.25876900 |
| C | 4.52674200 | 2.77033300 | -0.73793300 |
| H | 4.60074000 | 3.74203000 | 1.18767900 |
| H | 4.10358400 | 1.79922200 | -2.61433200 |
| C | 6.01695600 | 2.81810500 | -0.95138400 |
| H | 6.55833400 | 2.59352500 | -0.02598700 |
| H | 6.33272700 | 2.10753900 | -1.72133900 |
| H | 6.33050100 | 3.81947200 | -1.27446500 |

**Ts3S**

| | | | |
|---|---|---|---|
| C | 4.94254200 | -0.14505400 | 0.37724700 |
| C | 4.07297400 | -1.10848200 | -0.18486400 |
| C | 4.38085100 | -2.50588400 | -0.06493600 |
| C | 5.56042300 | -2.94094300 | 0.56702200 |
| C | 6.38681400 | -1.97004700 | 1.10416200 |
| C | 6.08262500 | -0.58361100 | 1.01896200 |
| H | 4.70769100 | 0.91246600 | 0.30013000 |
| H | 5.80128600 | -3.99682900 | 0.63730400 |
| H | 7.29877200 | -2.27434100 | 1.60984800 |
| H | 6.76777300 | 0.13315700 | 1.46104400 |
| N | 3.38499500 | -3.22148100 | -0.65259300 |
| H | 3.41110200 | -4.21925600 | -0.82135400 |
| C | 2.46462500 | -2.33153800 | -1.26416300 |

| | | | |
|---|---|---|---|
| C | 2.86293600 | -1.01970400 | -0.90346700 |
| C | 1.99039600 | 0.11185700 | -1.29313700 |
| H | 2.11549700 | 0.29579900 | -2.36841200 |
| H | 2.26546400 | 1.03480400 | -0.77899900 |
| C | 0.48322100 | -0.23220300 | -1.06993300 |
| H | -0.08550600 | 0.41954900 | -1.73377700 |
| N | 0.00826700 | 0.09606200 | 0.29125500 |
| C | 0.45200800 | -0.69845600 | 1.44354600 |
| H | 0.83369600 | -0.04558900 | 2.23407800 |
| H | 1.29539700 | -1.30937400 | 1.11253400 |
| C | -0.60068000 | -1.56773600 | 1.98198800 |
| C | -1.46069300 | -2.28796800 | 2.43213500 |
| H | -2.22733800 | -2.92077500 | 2.82537800 |
| Au | -1.95705900 | -2.01142800 | -1.28949600 |
| P | -4.26914100 | -2.25116800 | -1.00012200 |
| C | 1.02388200 | -2.63816800 | -1.45957200 |
| C | 0.07923500 | -1.67599200 | -1.37205000 |
| C | -4.82349200 | -3.90805100 | -0.44238600 |
| C | -4.89226100 | -1.10950000 | 0.29252900 |
| C | -5.31420400 | -1.89387200 | -2.46376900 |
| H | -4.56864900 | -4.65379500 | -1.20204400 |
| H | -5.90576600 | -3.91826400 | -0.27237200 |
| H | -4.30768200 | -4.16751700 | 0.48762700 |
| H | -4.36813400 | -1.31041200 | 1.23227500 |
| H | -5.97087900 | -1.23334300 | 0.43952600 |
| H | -4.67929100 | -0.07776900 | -0.00440000 |
| H | -5.11403900 | -0.87534000 | -2.81108100 |
| H | -6.37669700 | -1.99011200 | -2.21429800 |
| H | -5.06584300 | -2.59235200 | -3.26911200 |
| H | 0.77148900 | -3.67485900 | -1.66791200 |
| S | -0.73263900 | 1.55912300 | 0.56364800 |
| O | -1.18163000 | 1.53699600 | 1.96245600 |
| O | -1.69318400 | 1.79003000 | -0.52536700 |
| C | 0.56497000 | 2.77242400 | 0.39985700 |
| C | 1.48240500 | 2.92455800 | 1.44480100 |
| C | 0.73136200 | 3.44741100 | -0.80935400 |
| C | 2.57996900 | 3.75979900 | 1.26276900 |
| H | 1.33770800 | 2.40260300 | 2.38475800 |
| C | 1.83601800 | 4.28268900 | -0.97171600 |
| H | 0.01222800 | 3.31531700 | -1.60983100 |
| C | 2.77706400 | 4.44736900 | 0.05339800 |
| H | 3.29671800 | 3.88327700 | 2.07019100 |
| H | 1.97223700 | 4.80960000 | -1.91193600 |
| C | 3.96250300 | 5.36021800 | -0.12141900 |

| | | | |
|---|---|---|---|
| H | 4.86678700 | 4.92519300 | 0.31791100 |
| H | 4.15440600 | 5.56689000 | -1.17860200 |
| H | 3.78903100 | 6.32167200 | 0.37979900 |
| H | 2.89087300 | -2.23826300 | -2.56115900 |
| Cl | 4.57173800 | -1.60391400 | -4.06473100 |
| O | 4.42463200 | -0.16189300 | -3.76958400 |
| O | 5.54148000 | -2.25050900 | -3.15552500 |
| O | 4.87231000 | -1.85793000 | -5.48525800 |
| O | 3.16242100 | -2.28535300 | -3.80821900 |

**Ts3R**

| | | | |
|---|---|---|---|
| C | 4.80756100 | 1.46525700 | -1.43163900 |
| C | 3.84099600 | 0.47497000 | -1.72631200 |
| C | 4.07024100 | -0.44892000 | -2.80249100 |
| C | 5.25801400 | -0.41165200 | -3.55610000 |
| C | 6.17759500 | 0.57212500 | -3.24059700 |
| C | 5.95739500 | 1.50783100 | -2.19218600 |
| H | 4.63703600 | 2.17031500 | -0.62388200 |
| H | 5.43586000 | -1.12350900 | -4.35572600 |
| H | 7.09999900 | 0.63445200 | -3.81081100 |
| H | 6.71528600 | 2.25842300 | -1.99022900 |
| N | 3.00036700 | -1.28251600 | -2.89331300 |
| H | 2.94704100 | -2.09731500 | -3.49164200 |
| C | 2.10244400 | -1.00824700 | -1.83301300 |
| C | 2.59366000 | 0.14018900 | -1.16383500 |
| C | 1.77306300 | 0.73095100 | -0.07246700 |
| H | 2.13147700 | 1.72495400 | 0.19953600 |
| H | 1.86854700 | 0.09798900 | 0.81904000 |
| C | 0.29118500 | 0.77531800 | -0.52942100 |
| H | 0.19178400 | 1.55929400 | -1.28910900 |
| N | -0.60205700 | 1.18827300 | 0.57428200 |
| C | -0.61309200 | 0.38674100 | 1.80839900 |
| H | -0.10544300 | 0.90616800 | 2.63014600 |
| H | -0.02695900 | -0.51114300 | 1.59595400 |
| C | -1.95511200 | -0.02507100 | 2.23059600 |
| C | -3.03553000 | -0.39509500 | 2.62653400 |
| H | -3.99708700 | -0.70397400 | 2.97555200 |
| Au | -2.27205000 | -0.77979500 | -1.12468200 |
| P | -4.60210600 | -0.97506400 | -0.96534800 |
| C | 0.64585500 | -1.30426400 | -1.84614100 |
| C | -0.22711600 | -0.50681800 | -1.19321100 |
| C | -5.18752800 | -2.36128300 | 0.08332500 |
| C | -5.36993000 | 0.51583400 | -0.22413200 |
| C | -5.50264900 | -1.20338300 | -2.54706200 |

| | | | |
|---|---|---|---|
| H | -4.86433900 | -3.31023000 | -0.35646300 |
| H | -6.28012400 | -2.35266100 | 0.16400500 |
| H | -4.74738200 | -2.27354100 | 1.08095300 |
| H | -4.92421600 | 0.70337300 | 0.75714200 |
| H | -6.45291700 | 0.38703400 | -0.11942300 |
| H | -5.16647700 | 1.38035100 | -0.86409400 |
| H | -5.28127800 | -0.36486100 | -3.21485900 |
| H | -6.58333100 | -1.25368700 | -2.37405600 |
| H | -5.16877200 | -2.12880200 | -3.02691100 |
| H | 0.33051000 | -2.20719800 | -2.36226000 |
| S | -1.02859000 | 2.79762500 | 0.66573900 |
| O | -1.84869000 | 2.93520200 | 1.87591700 |
| O | -1.56445000 | 3.18122900 | -0.64810400 |
| C | 0.49358200 | 3.69499900 | 0.90696400 |
| C | 1.07070500 | 3.71552800 | 2.18110200 |
| C | 1.15534800 | 4.24073500 | -0.19326300 |
| C | 2.33074900 | 4.28235800 | 2.34184300 |
| H | 0.54044500 | 3.29835300 | 3.03028000 |
| C | 2.41747300 | 4.80520000 | -0.01213300 |
| H | 0.69313300 | 4.21705500 | -1.17361200 |
| C | 3.02596400 | 4.82938500 | 1.25051900 |
| H | 2.78590500 | 4.30037300 | 3.32836600 |
| H | 2.93896700 | 5.23040400 | -0.86504100 |
| C | 4.38647900 | 5.44646900 | 1.44452400 |
| H | 5.01886100 | 4.81867200 | 2.08206700 |
| H | 4.89730400 | 5.59570700 | 0.48853700 |
| H | 4.30302700 | 6.42477700 | 1.93564900 |
| Cl | 4.12033200 | -2.54314700 | 0.73527300 |
| O | 2.71222100 | -2.76409700 | 0.04885200 |
| O | 5.12453800 | -2.43623900 | -0.34481600 |
| O | 4.33210200 | -3.72868400 | 1.58649200 |
| O | 4.03650500 | -1.29424700 | 1.52553900 |
| H | 2.50330000 | -1.83805100 | -0.83726900 |

**Int7**

| | | | |
|---|---|---|---|
| C | 4.86399200 | 1.18580100 | -0.75565400 |
| C | 3.80406600 | 0.41632200 | -1.27173300 |
| C | 4.06268600 | -0.47066600 | -2.36815000 |
| C | 5.33126000 | -0.58780300 | -2.94253000 |
| C | 6.35803200 | 0.18865400 | -2.40877700 |
| C | 6.12628100 | 1.06536000 | -1.32688500 |
| H | 4.69294600 | 1.86704600 | 0.07401800 |
| H | 5.50902100 | -1.26304900 | -3.77507400 |
| H | 7.35527100 | 0.11751600 | -2.83413400 |

| | | | |
|---|---|---|---|
| H | 6.95102000 | 1.65621600 | -0.93718100 |
| N | 2.87535800 | -1.10369100 | -2.67858200 |
| H | 2.73854800 | -1.74652300 | -3.44661100 |
| C | 1.87645400 | -0.63567100 | -1.84039600 |
| C | 2.41244400 | 0.29316700 | -0.96746500 |
| C | 1.54605500 | 0.87481900 | 0.10729800 |
| H | 1.88942700 | 1.86518100 | 0.41394600 |
| H | 1.57786900 | 0.23616900 | 1.00406400 |
| C | 0.10168900 | 0.96360000 | -0.43237600 |
| H | 0.10307600 | 1.71565200 | -1.23206900 |
| N | -0.85684700 | 1.46969700 | 0.57974500 |
| C | -0.93966300 | 0.76912300 | 1.87113200 |
| H | -0.41335300 | 1.31494800 | 2.66431800 |
| H | -0.40936600 | -0.17677700 | 1.73596000 |
| C | -2.31085900 | 0.47212700 | 2.29502800 |
| C | -3.41602100 | 0.19346200 | 2.69749200 |
| H | -4.40006100 | -0.02605400 | 3.05130500 |
| Au | -2.44558400 | -0.66531600 | -0.99760400 |
| P | -4.77012300 | -0.93865400 | -0.83842000 |
| C | 0.48519700 | -1.04291200 | -1.80926600 |
| C | -0.41671300 | -0.32235100 | -1.08848000 |
| C | -5.31161000 | -2.18966200 | 0.38985900 |
| C | -5.62131600 | 0.60241800 | -0.32472200 |
| C | -5.63626000 | -1.43258500 | -2.37847600 |
| H | -4.94980400 | -3.17672700 | 0.08440100 |
| H | -6.40435100 | -2.21236100 | 0.46658400 |
| H | -4.88152600 | -1.95014700 | 1.36666000 |
| H | -5.19641700 | 0.95368900 | 0.62007600 |
| H | -6.69734600 | 0.43367400 | -0.20569700 |
| H | -5.45638600 | 1.37411400 | -1.08343900 |
| H | -5.44805200 | -0.68615800 | -3.15660700 |
| H | -6.71545900 | -1.51380600 | -2.20772700 |
| H | -5.25014800 | -2.39798900 | -2.72075300 |
| H | 0.18622000 | -1.92124400 | -2.37787800 |
| S | -1.21203900 | 3.10010900 | 0.54422700 |
| O | -2.05462200 | 3.36582900 | 1.71807700 |
| O | -1.69989400 | 3.40996800 | -0.80744000 |
| C | 0.34173200 | 3.94997700 | 0.75934700 |
| C | 0.87040700 | 4.07839600 | 2.04577500 |
| C | 1.07532100 | 4.33947100 | -0.36445900 |
| C | 2.15687900 | 4.59175700 | 2.19923200 |
| H | 0.28584700 | 3.78454300 | 2.91083600 |
| C | 2.35919300 | 4.84777700 | -0.19127500 |
| H | 0.64893100 | 4.23398800 | -1.35558300 |

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|---|---|---|---|
| C | 2.92274200 | 4.97402900 | 1.08835300 |
| H | 2.57530600 | 4.69377900 | 3.19663800 |
| H | 2.93718100 | 5.14549700 | -1.06196800 |
| C | 4.31509300 | 5.52438500 | 1.25629100 |
| H | 4.68609700 | 5.36936000 | 2.27373800 |
| H | 5.01316800 | 5.05046700 | 0.55681000 |
| H | 4.33592800 | 6.60264200 | 1.05161200 |

**Ts5**

| | | | |
|---|---|---|---|
| C | 4.40895700 | 0.78506700 | -1.42632000 |
| C | 3.17164700 | 0.22241600 | -1.79874300 |
| C | 3.11183700 | -0.64187500 | -2.94094900 |
| C | 4.24870500 | -0.93544800 | -3.70396100 |
| C | 5.45282600 | -0.36404100 | -3.30855600 |
| C | 5.53384900 | 0.48772100 | -2.18186200 |
| H | 4.47308000 | 1.44412800 | -0.56481400 |
| H | 4.18994700 | -1.58874000 | -4.56958700 |
| H | 6.35295100 | -0.57610200 | -3.87865000 |
| H | 6.49492400 | 0.91470600 | -1.90944800 |
| N | 1.80821500 | -1.05871500 | -3.08488000 |
| H | 1.45734600 | -1.64110200 | -3.83329300 |
| C | 1.03235800 | -0.46722100 | -2.09888300 |
| C | 1.84283900 | 0.32019400 | -1.29026500 |
| C | 1.26526700 | 0.98469600 | -0.07815000 |
| H | 1.80764600 | 1.89708000 | 0.18031500 |
| H | 1.33549300 | 0.31048000 | 0.78940700 |
| C | -0.20463200 | 1.31559100 | -0.39936200 |
| H | -0.18556100 | 2.02097900 | -1.23925400 |
| N | -0.90934100 | 2.02159400 | 0.68561500 |
| C | -0.97546100 | 1.42076700 | 2.02644400 |
| H | -0.38399800 | 1.99400300 | 2.74969600 |
| H | -0.50814500 | 0.43581400 | 1.95558500 |
| C | -2.34850700 | 1.25655100 | 2.51012700 |
| C | -3.46954300 | 1.08961300 | 2.92813200 |
| H | -4.46346300 | 0.94913200 | 3.29381100 |
| C | -0.36188100 | -0.67919600 | -1.82389300 |
| C | -1.01242500 | 0.11422500 | -0.90991900 |
| H | -0.87272700 | -1.51426600 | -2.29876000 |
| S | -1.03652400 | 3.68067600 | 0.55695000 |
| O | -1.65591700 | 4.14200700 | 1.80618500 |
| O | -1.66317200 | 3.98092300 | -0.73898600 |
| C | 0.64307900 | 4.27738700 | 0.48763300 |
| C | 1.36481300 | 4.40578700 | 1.67641800 |
| C | 1.25982400 | 4.45300400 | -0.75403200 |

| | | | |
|---|---|---|---|
| C | 2.72507100 | 4.70149700 | 1.61189000 |
| H | 0.87193500 | 4.27820900 | 2.63409700 |
| C | 2.62014100 | 4.74356400 | -0.79810700 |
| H | 0.68402600 | 4.35353700 | -1.66715300 |
| C | 3.37469500 | 4.86402900 | 0.37950600 |
| H | 3.29318400 | 4.80281700 | 2.53228600 |
| H | 3.10697100 | 4.87329300 | -1.76083500 |
| C | 4.84686600 | 5.17675400 | 0.31148300 |
| H | 5.33148900 | 5.03331800 | 1.28180000 |
| H | 5.35064200 | 4.54079900 | -0.42540800 |
| H | 5.01068800 | 6.21786400 | 0.00462600 |
| Au | -3.09489100 | 0.49297700 | -0.96274200 |
| P | -5.33435900 | 1.10080100 | -1.08749500 |
| C | -6.42487300 | -0.14878400 | -1.86550700 |
| C | -6.10814300 | 1.43729600 | 0.53779800 |
| C | -5.61592300 | 2.63305300 | -2.05105800 |
| H | -6.08239200 | -0.34732300 | -2.88589300 |
| H | -7.46080600 | 0.20664900 | -1.89173400 |
| H | -6.37346200 | -1.07981800 | -1.29231600 |
| H | -6.06583500 | 0.53378400 | 1.15263700 |
| H | -7.15278600 | 1.74130500 | 0.40752600 |
| H | -5.55526700 | 2.23436500 | 1.04301100 |
| H | -5.05273200 | 3.45294500 | -1.59443500 |
| H | -6.68143300 | 2.88722900 | -2.06897000 |
| H | -5.25773900 | 2.49144900 | -3.07551300 |
| Cl | -2.68040400 | -2.77645900 | 0.75920400 |
| O | -1.45144400 | -1.75849400 | 0.95295600 |
| O | -2.31611100 | -3.94933300 | 1.57046100 |
| O | -2.75506600 | -3.07914000 | -0.68580000 |
| O | -3.90355100 | -2.11191600 | 1.24745800 |
| H | -1.43588700 | -0.93611200 | 0.10641900 |

**Int8**

| | | | |
|---|---|---|---|
| C | 4.89890000 | 1.06729800 | -1.26240200 |
| C | 3.79863000 | 0.23866700 | -1.55319200 |
| C | 3.98753600 | -0.88287500 | -2.42422700 |
| C | 5.22696800 | -1.17149800 | -3.00321600 |
| C | 6.29318700 | -0.33104400 | -2.69644400 |
| C | 6.13108300 | 0.77572500 | -1.83439100 |
| H | 4.78114400 | 1.92331600 | -0.60286300 |
| H | 5.35143600 | -2.02376000 | -3.66533000 |
| H | 7.26943400 | -0.53085000 | -3.12925200 |
| H | 6.98750800 | 1.40862000 | -1.61816900 |
| N | 2.77577200 | -1.53267000 | -2.53367900 |

| | | | |
|---|---|---|---|
| H | 2.59180100 | -2.33685100 | -3.11828500 |
| C | 1.83084900 | -0.85557300 | -1.78369200 |
| C | 2.41959600 | 0.23487600 | -1.17341200 |
| C | 1.63852400 | 1.08565600 | -0.21577100 |
| H | 1.98023300 | 2.12293200 | -0.23066900 |
| H | 1.79062100 | 0.72439600 | 0.81291600 |
| C | 0.13034200 | 1.04496100 | -0.56640800 |
| H | -0.03796200 | 1.70024100 | -1.43014500 |
| N | -0.72567000 | 1.58369800 | 0.50940100 |
| C | -0.77883000 | 0.86629500 | 1.79640300 |
| H | -0.49916600 | 1.52425200 | 2.62522700 |
| H | -0.02214400 | 0.07756700 | 1.76128000 |
| C | -2.09211000 | 0.26655900 | 2.04838600 |
| C | -3.16396800 | -0.24800600 | 2.26095900 |
| H | -4.11966600 | -0.69156900 | 2.44326900 |
| C | 0.44112900 | -1.21285200 | -1.58953100 |
| C | -0.36435700 | -0.33408000 | -0.96581000 |
| H | 0.07078200 | -2.17092500 | -1.94417100 |
| S | -1.11390300 | 3.20793300 | 0.50595600 |
| O | -2.05990900 | 3.39337500 | 1.61333100 |
| O | -1.48891700 | 3.55459500 | -0.87118100 |
| C | 0.37503500 | 4.11161900 | 0.89690100 |
| C | 0.78160800 | 4.21892200 | 2.22806800 |
| C | 1.15931700 | 4.62456700 | -0.13954800 |
| C | 1.99683200 | 4.83702000 | 2.51608300 |
| H | 0.15455800 | 3.83789500 | 3.02670000 |
| C | 2.36870300 | 5.23998400 | 0.16799300 |
| H | 0.82474500 | 4.53923700 | -1.16732300 |
| C | 2.80926600 | 5.35079800 | 1.49618500 |
| H | 2.31854000 | 4.92408600 | 3.55009300 |
| H | 2.98205400 | 5.64119700 | -0.63437600 |
| C | 4.11633000 | 6.02971800 | 1.81167600 |
| H | 4.41923900 | 5.85220900 | 2.84775000 |
| H | 4.91570700 | 5.67512900 | 1.15129300 |
| H | 4.03620500 | 7.11477800 | 1.66651900 |
| H | -1.41643300 | -0.54599600 | -0.80289700 |

**Int9**

| | | | |
|---|---|---|---|
| C | 3.80030400 | -0.91887900 | -2.83256800 |
| C | 2.88965600 | 0.15395100 | -2.86776100 |
| C | 1.95148800 | 0.23236100 | -3.94720700 |
| C | 1.91602800 | -0.72175500 | -4.96944900 |
| C | 2.82848400 | -1.77065900 | -4.90387100 |
| C | 3.75982200 | -1.86993900 | -3.84599000 |

| | | | |
|---|---|---|---|
| H | 4.52042900 | -1.00048400 | -2.02273100 |
| H | 1.19830600 | -0.64737700 | -5.78142300 |
| H | 2.82462000 | -2.52812800 | -5.68250000 |
| H | 4.45788900 | -2.70233400 | -3.83091100 |
| N | 1.16821400 | 1.34831600 | -3.73928100 |
| C | 1.56193600 | 1.96110700 | -2.56209000 |
| C | 2.61509500 | 1.26053200 | -2.00396600 |
| C | 3.25946000 | 1.74829500 | -0.74401500 |
| H | 4.11314800 | 2.39666200 | -0.99007800 |
| H | 3.66240100 | 0.92469300 | -0.14556100 |
| C | 2.28736000 | 2.58721300 | 0.12250200 |
| H | 2.88244500 | 3.23799700 | 0.76252100 |
| N | 1.46777700 | 1.78678300 | 1.08487900 |
| C | 0.44792300 | 0.86689800 | 0.58913500 |
| H | -0.08964200 | 1.38564100 | -0.21092300 |
| H | -0.28126400 | 0.67323200 | 1.38109500 |
| C | 0.93596300 | -0.41690400 | 0.04692800 |
| C | 1.35239500 | -1.42966800 | -0.51052000 |
| H | 1.77563100 | -2.11629500 | -1.21964200 |
| Au | 0.79622100 | -2.35497800 | 1.45830000 |
| P | 0.34417300 | -3.94363100 | 3.07278200 |
| C | 0.97093600 | 3.12437100 | -1.94046900 |
| C | 1.32624800 | 3.44013800 | -0.67828500 |
| C | -1.12824700 | -4.94627800 | 2.66440800 |
| C | 1.71327300 | -5.13778400 | 3.26982400 |
| C | 0.02783100 | -3.28914000 | 4.74861600 |
| H | -2.00839100 | -4.29819300 | 2.61323900 |
| H | -1.28170700 | -5.71133700 | 3.43317600 |
| H | -0.98488000 | -5.42855000 | 1.69299700 |
| H | 1.90337600 | -5.63835000 | 2.31574500 |
| H | 1.45061900 | -5.88356400 | 4.02780200 |
| H | 2.61840900 | -4.60595900 | 3.57808200 |
| H | 0.91601000 | -2.76886400 | 5.11719600 |
| H | -0.21119400 | -4.11917800 | 5.42223400 |
| H | -0.81352700 | -2.59268100 | 4.71633600 |
| H | 0.24531300 | 3.71998700 | -2.48843700 |
| S | 2.17711700 | 1.37661600 | 2.55743900 |
| O | 3.09921700 | 2.47300100 | 2.88528900 |
| O | 2.70726800 | -0.00151600 | 2.54528700 |
| C | 0.76363800 | 1.40720800 | 3.63819400 |
| C | -0.00801700 | 2.57122300 | 3.72027500 |
| C | 0.47182700 | 0.28623200 | 4.41188700 |
| C | -1.09304800 | 2.59544000 | 4.58790100 |
| H | 0.23007600 | 3.43395900 | 3.10703900 |

| | | | |
|---|---|---|---|
| C | -0.61825100 | 0.33234900 | 5.28162800 |
| H | 1.08827400 | -0.60080700 | 4.33323800 |
| C | -1.41461300 | 1.47988400 | 5.38169500 |
| H | -1.70274900 | 3.49225800 | 4.65513500 |
| H | -0.85129700 | -0.53527100 | 5.89187500 |
| C | -2.59081800 | 1.53131800 | 6.32055400 |
| H | -3.51423900 | 1.77294200 | 5.78057000 |
| H | -2.73338900 | 0.57691600 | 6.83525900 |
| H | -2.45008400 | 2.31091400 | 7.07930000 |
| H | 0.87854100 | 4.28663000 | -0.16664100 |
| H | 0.40013900 | 1.64523200 | -4.32581200 |

**Ts6**

| | | | |
|---|---|---|---|
| C | 2.46551579 | 0.22009835 | -3.83618048 |
| C | 1.10609579 | 0.50699335 | -4.01918248 |
| C | 0.33915679 | -0.30259565 | -4.90544248 |
| C | 0.89181079 | -1.37416365 | -5.60613348 |
| C | 2.24873279 | -1.63067565 | -5.41405948 |
| C | 3.02587879 | -0.84478265 | -4.54069848 |
| H | 3.06783979 | 0.81655135 | -3.15721548 |
| H | 0.28849579 | -1.98257465 | -6.27288248 |
| H | 2.71457079 | -2.45384865 | -5.94744348 |
| H | 4.08018979 | -1.07388965 | -4.41644948 |
| N | -0.96663421 | 0.17251535 | -4.88673448 |
| C | -1.05689321 | 1.21939735 | -4.01554848 |
| C | 0.19195879 | 1.43411935 | -3.40202448 |
| C | 0.41422579 | 2.72867535 | -2.67388648 |
| H | 0.69010379 | 3.50991435 | -3.39678248 |
| H | 1.22855979 | 2.66137635 | -1.94830148 |
| C | -0.88333021 | 3.17460835 | -1.96811248 |
| H | -0.78456521 | 4.21408835 | -1.65558548 |
| N | -1.16645221 | 2.40620435 | -0.72038348 |
| C | -1.39319121 | 0.96674035 | -0.88155648 |
| H | -2.25719721 | 0.85239535 | -1.54086148 |
| H | -1.68847221 | 0.53631135 | 0.08125652 |
| C | -0.25700321 | 0.17858935 | -1.38551448 |
| C | 0.60926779 | -0.73938465 | -1.27141648 |
| H | 1.34773279 | -1.13454965 | -1.95994848 |
| Au | 0.63349679 | -1.50902765 | 0.70643552 |
| P | 0.80604179 | -2.53401665 | 2.78287352 |
| C | -2.19844321 | 2.07176635 | -3.79084448 |
| C | -2.11358121 | 3.02756235 | -2.84159848 |
| C | -0.80164121 | -2.94107665 | 3.55711652 |
| C | 1.69638679 | -4.13007765 | 2.69269552 |
| C | 1.72671079 | -1.56550765 | 4.03285052 |

| | | | |
|---|---|---|---|
| H | -1.39722021 | -2.03249465 | 3.67858652 |
| H | -0.64129721 | -3.40717265 | 4.53546052 |
| H | -1.34582821 | -3.63530465 | 2.90926152 |
| H | 1.16464379 | -4.80819065 | 2.01845752 |
| H | 1.76102279 | -4.58212965 | 3.68839352 |
| H | 2.70507879 | -3.96397465 | 2.30258452 |
| H | 2.73863279 | -1.37156565 | 3.66434352 |
| H | 1.78309979 | -2.12606765 | 4.97238752 |
| H | 1.22984079 | -0.60906365 | 4.21118052 |
| H | -3.09805221 | 1.93277235 | -4.38320148 |
| S | -0.24809721 | 2.86179735 | 0.63278752 |
| O | -0.29545221 | 4.33139935 | 0.65664852 |
| O | 1.07324079 | 2.20796135 | 0.66662652 |
| C | -1.23240721 | 2.17693335 | 1.94670952 |
| C | -2.57576921 | 2.54845935 | 2.06732352 |
| C | -0.63256921 | 1.30917035 | 2.85784452 |
| C | -3.32535721 | 2.02123035 | 3.11235952 |
| H | -3.02500321 | 3.22654435 | 1.34950652 |
| C | -1.39906721 | 0.80261835 | 3.90761052 |
| H | 0.41137879 | 1.04023135 | 2.74626852 |
| C | -2.75115921 | 1.14089635 | 4.04644952 |
| H | -4.37141421 | 2.29746135 | 3.21167852 |
| H | -0.93991921 | 0.13457135 | 4.62988652 |
| C | -3.58218521 | 0.56882035 | 5.16429652 |
| H | -4.33004321 | -0.13251165 | 4.77264052 |
| H | -2.96196421 | 0.03195035 | 5.88799652 |
| H | -4.12802921 | 1.35806935 | 5.69364552 |
| H | -2.96082221 | 3.66864135 | -2.62028448 |
| H | -1.73980521 | -0.21980265 | -5.40991448 |

**Int10**

| | | | |
|---|---|---|---|
| C | 4.66654600 | -0.04402700 | -1.92902700 |
| C | 3.32262000 | 0.15309000 | -2.21059200 |
| C | 2.78525900 | -0.37209600 | -3.39310800 |
| C | 3.52303100 | -1.09605600 | -4.31850200 |
| C | 4.87777500 | -1.28259600 | -4.02362900 |
| C | 5.44124400 | -0.76099600 | -2.85203200 |
| H | 5.10658600 | 0.34512100 | -1.01656900 |
| H | 3.07464000 | -1.48791100 | -5.22532200 |
| H | 5.50065500 | -1.83729600 | -4.71806700 |
| H | 6.49719900 | -0.91620100 | -2.65392800 |
| N | 1.42088600 | 0.00859000 | -3.45671200 |
| C | 1.07204500 | 0.74334500 | -2.42268000 |
| C | 2.20961000 | 0.80323800 | -1.42530600 |

| | | | |
|---|---|---|---|
| C | 2.37557300 | 2.29347700 | -1.04676900 |
| H | 2.62146700 | 2.88045500 | -1.93718400 |
| H | 3.18155500 | 2.40748900 | -0.31953500 |
| C | 1.04089100 | 2.77752200 | -0.45262200 |
| H | 1.08395400 | 3.84230000 | -0.21915300 |
| N | 0.71022500 | 2.05905300 | 0.80468600 |
| C | 0.66525900 | 0.58893800 | 0.63527300 |
| H | -0.28871600 | 0.37260700 | 0.14248600 |
| H | 0.61632200 | 0.12090800 | 1.61806500 |
| C | 1.82215600 | -0.00159000 | -0.14071500 |
| C | 2.45200900 | -1.11184200 | 0.27805100 |
| H | 3.23206900 | -1.50837200 | -0.37138700 |
| Au | 2.12256900 | -2.07275700 | 2.06949800 |
| P | 1.79437700 | -3.21088500 | 4.10310400 |
| C | -0.12283400 | 1.52224300 | -2.29378300 |
| C | -0.12844700 | 2.51779900 | -1.37847300 |
| C | 0.08447000 | -3.12299900 | 4.76093100 |
| C | 2.13596800 | -5.01060000 | 4.00653900 |
| C | 2.85821200 | -2.63710700 | 5.48250800 |
| H | -0.20645500 | -2.07740400 | 4.89026300 |
| H | 0.01221900 | -3.64410600 | 5.72184500 |
| H | -0.59964100 | -3.58905800 | 4.04445600 |
| H | 1.47702700 | -5.46705200 | 3.26127600 |
| H | 1.96998700 | -5.48841300 | 4.97829800 |
| H | 3.17421700 | -5.16835400 | 3.69801900 |
| H | 3.90779800 | -2.79862000 | 5.21648900 |
| H | 2.62895000 | -3.18689600 | 6.40198400 |
| H | 2.70449200 | -1.56781900 | 5.65013800 |
| H | -0.95177200 | 1.35393600 | -2.97414100 |
| S | 1.56708700 | 2.60546000 | 2.16431000 |
| O | 1.39953100 | 4.06790200 | 2.16941500 |
| O | 2.93861700 | 2.06597700 | 2.23090000 |
| C | 0.61791700 | 1.85343900 | 3.46819800 |
| C | -0.75264100 | 2.11573000 | 3.56095100 |
| C | 1.26795900 | 1.03949700 | 4.39437600 |
| C | -1.47810800 | 1.53489000 | 4.59473600 |
| H | -1.24108200 | 2.75159200 | 2.83030000 |
| C | 0.52451500 | 0.47992500 | 5.43350600 |
| H | 2.33053700 | 0.84823700 | 4.30042500 |
| C | -0.85299800 | 0.70796000 | 5.54442000 |
| H | -2.54495600 | 1.72580000 | 4.67168600 |
| H | 1.02093500 | -0.14881800 | 6.16614200 |
| C | -1.65752700 | 0.06444900 | 6.64278100 |
| H | -2.32503600 | -0.70532800 | 6.23470900 |

| | | | |
|---|---|---|---|
| H | -1.01034900 | -0.41019100 | 7.38593800 |
| H | -2.28969300 | 0.80008400 | 7.15301300 |
| H | -1.00430900 | 3.14895100 | -1.26451900 |
| H | 0.81782100 | -0.17940700 | -4.25590900 |

**Ts7**

| | | | |
|---|---|---|---|
| C | 4.54953500 | -0.51270100 | -1.94567700 |
| C | 3.30297200 | -0.03419300 | -2.31973000 |
| C | 2.80568300 | -0.32911800 | -3.59557900 |
| C | 3.49386300 | -1.08605200 | -4.53229000 |
| C | 4.75266700 | -1.55745200 | -4.14446900 |
| C | 5.27374300 | -1.27225400 | -2.87593500 |
| H | 4.95276800 | -0.30706100 | -0.95928100 |
| H | 3.08061800 | -1.29528000 | -5.51304700 |
| H | 5.33417800 | -2.15137600 | -4.84211600 |
| H | 6.25613700 | -1.64734400 | -2.60712400 |
| N | 1.54327600 | 0.30414400 | -3.72845100 |
| C | 1.21712900 | 0.98142700 | -2.65109100 |
| C | 2.24772000 | 0.73513300 | -1.56241000 |
| C | 2.62872800 | 2.13343100 | -1.01469000 |
| H | 3.05086900 | 2.73890300 | -1.82161400 |
| H | 3.37436800 | 2.03627700 | -0.22390800 |
| C | 1.34546100 | 2.78882000 | -0.47515700 |
| H | 1.54806400 | 3.80191700 | -0.12545300 |
| N | 0.78790500 | 2.02624300 | 0.67125200 |
| C | 0.51173700 | 0.61376000 | 0.35198000 |
| H | -0.41180700 | 0.59933700 | -0.23717500 |
| H | 0.29649300 | 0.06998700 | 1.26992900 |
| C | 1.60727400 | -0.09227100 | -0.41507600 |
| C | 1.92157800 | -1.37583800 | -0.13432300 |
| H | 2.62449100 | -1.87617200 | -0.79759700 |
| Au | 1.97404000 | -2.13979300 | 1.86336100 |
| P | 2.17411700 | -3.19315800 | 3.92002000 |
| C | 0.16548100 | 1.94373200 | -2.52674700 |
| C | 0.23994000 | 2.82960600 | -1.50747900 |
| C | 0.55600200 | -3.59096000 | 4.67727100 |
| C | 3.00760900 | -4.81479200 | 3.74476600 |
| C | 3.13359700 | -2.33624400 | 5.22226600 |
| H | -0.01530200 | -2.67356800 | 4.83752000 |
| H | 0.70201900 | -4.10478300 | 5.63376900 |
| H | -0.00559200 | -4.23564900 | 3.99561000 |
| H | 2.45853100 | -5.42940800 | 3.02498100 |
| H | 3.04490300 | -5.33085800 | 4.71026100 |
| H | 4.02612600 | -4.66396000 | 3.37384600 |

| | | | |
|---|---|---|---|
| H | 4.13303700 | -2.10254100 | 4.84283900 |
| H | 3.22173200 | -2.98123400 | 6.10336500 |
| H | 2.63934500 | -1.40543800 | 5.50861200 |
| H | -0.61198500 | 1.99231800 | -3.28265500 |
| S | 1.60014700 | 2.29731800 | 2.14096000 |
| O | 1.64643700 | 3.75985500 | 2.29287300 |
| O | 2.87342100 | 1.55404900 | 2.22246000 |
| C | 0.45880400 | 1.55804400 | 3.28380700 |
| C | -0.89523800 | 1.90492400 | 3.24602600 |
| C | 0.95427100 | 0.65539300 | 4.22324000 |
| C | -1.76234700 | 1.31056300 | 4.15581300 |
| H | -1.26384900 | 2.60841000 | 2.50741100 |
| C | 0.07105500 | 0.08665800 | 5.13924600 |
| H | 2.00862600 | 0.40673400 | 4.23298900 |
| C | -1.29609200 | 0.39081600 | 5.11091800 |
| H | -2.81901500 | 1.56120400 | 4.12762700 |
| H | 0.44860700 | -0.60975900 | 5.88174200 |
| C | -2.25515600 | -0.27170100 | 6.06358100 |
| H | -1.72881200 | -0.73659300 | 6.90240300 |
| H | -2.98047700 | 0.44627300 | 6.46143200 |
| H | -2.82495900 | -1.05674800 | 5.54944000 |
| H | -0.52433700 | 3.59135900 | -1.38970000 |
| Cl | -1.36236000 | -3.01916000 | 0.80695800 |
| O | -0.44963000 | -2.51579400 | -0.40557200 |
| O | -2.67148600 | -3.30346500 | 0.19745000 |
| O | -1.42266800 | -1.91878800 | 1.79360000 |
| O | -0.72519500 | -4.22863700 | 1.36903700 |
| H | 0.62655700 | -2.07310000 | -0.02863900 |
| H | 1.00845600 | 0.32076400 | -4.59641400 |

**Int11**

| | | | |
|---|---|---|---|
| C | 4.21113200 | -0.21998900 | -2.24732000 |
| C | 2.87231200 | 0.12181700 | -2.36058000 |
| C | 2.13225700 | -0.24270700 | -3.50581500 |
| C | 2.70917700 | -0.97639500 | -4.53871500 |
| C | 4.05858700 | -1.33083700 | -4.41332500 |
| C | 4.80286100 | -0.95024700 | -3.29089400 |
| H | 4.79496600 | 0.07030300 | -1.37852600 |
| H | 2.13228900 | -1.24513000 | -5.41816700 |
| H | 4.53852200 | -1.89563000 | -5.20715600 |
| H | 5.85316400 | -1.21841400 | -3.22683800 |
| N | 0.81156600 | 0.27228900 | -3.47321400 |
| C | 0.67968500 | 0.91260900 | -2.34976100 |
| C | 1.91143900 | 0.81508900 | -1.42352500 |

| | | | |
|---|---|---|---|
| C | 2.24012900 | 2.25794300 | -0.96759100 |
| H | 2.44476500 | 2.87345800 | -1.84830900 |
| H | 3.12410200 | 2.27139800 | -0.32481800 |
| C | 1.01064000 | 2.80274600 | -0.21780000 |
| H | 1.18180300 | 3.83133300 | 0.10039300 |
| N | 0.74286100 | 2.00824400 | 1.01586800 |
| C | 0.52257900 | 0.57567000 | 0.74713100 |
| H | -0.46091800 | 0.48820400 | 0.27994900 |
| H | 0.48345300 | 0.02753500 | 1.68931100 |
| C | 1.59593800 | -0.00481400 | -0.15940300 |
| C | 2.34777600 | -1.06581000 | 0.28101500 |
| H | 3.24048000 | -1.39792100 | -0.23807600 |
| C | -0.40868000 | 1.81104000 | -2.02569400 |
| C | -0.25000000 | 2.72752800 | -1.05086000 |
| H | -1.30330600 | 1.77990300 | -2.64141100 |
| S | 1.77319500 | 2.33152200 | 2.32848100 |
| O | 1.91412900 | 3.79434500 | 2.36591200 |
| O | 2.99196200 | 1.50204400 | 2.28638800 |
| C | 0.76346200 | 1.76861400 | 3.67993500 |
| C | -0.46974900 | 2.38771500 | 3.91110800 |
| C | 1.22430800 | 0.73688700 | 4.49532400 |
| C | -1.24759400 | 1.95232800 | 4.97655300 |
| H | -0.81403800 | 3.18771300 | 3.26434400 |
| C | 0.42821000 | 0.31547100 | 5.56102000 |
| H | 2.18501100 | 0.27463500 | 4.29802100 |
| C | -0.81289600 | 0.91141900 | 5.81656800 |
| H | -2.20827300 | 2.42409000 | 5.16438400 |
| H | 0.77793300 | -0.48798300 | 6.20273900 |
| C | -1.67212600 | 0.45718500 | 6.96708900 |
| H | -2.66565900 | 0.15051600 | 6.61838200 |
| H | -1.21841800 | -0.38579000 | 7.49607600 |
| H | -1.82203300 | 1.27128100 | 7.68693400 |
| H | -1.04405400 | 3.42854100 | -0.81272800 |
| H | 2.19516800 | -1.44064100 | 1.29003600 |
| Au | 0.72195700 | -2.12216900 | -0.93279000 |
| P | -0.62850300 | -3.52612600 | -2.18016200 |
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| H | -1.02465900 | -5.90234500 | -2.47965200 |

| | | | |
|---|---|---|---|
| H | -0.60166200 | -5.50906400 | -0.78748800 |
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| H | -2.99595800 | -3.89794200 | -2.57558900 |
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### 6.3 Independent Gradient Model (IGM) analysis

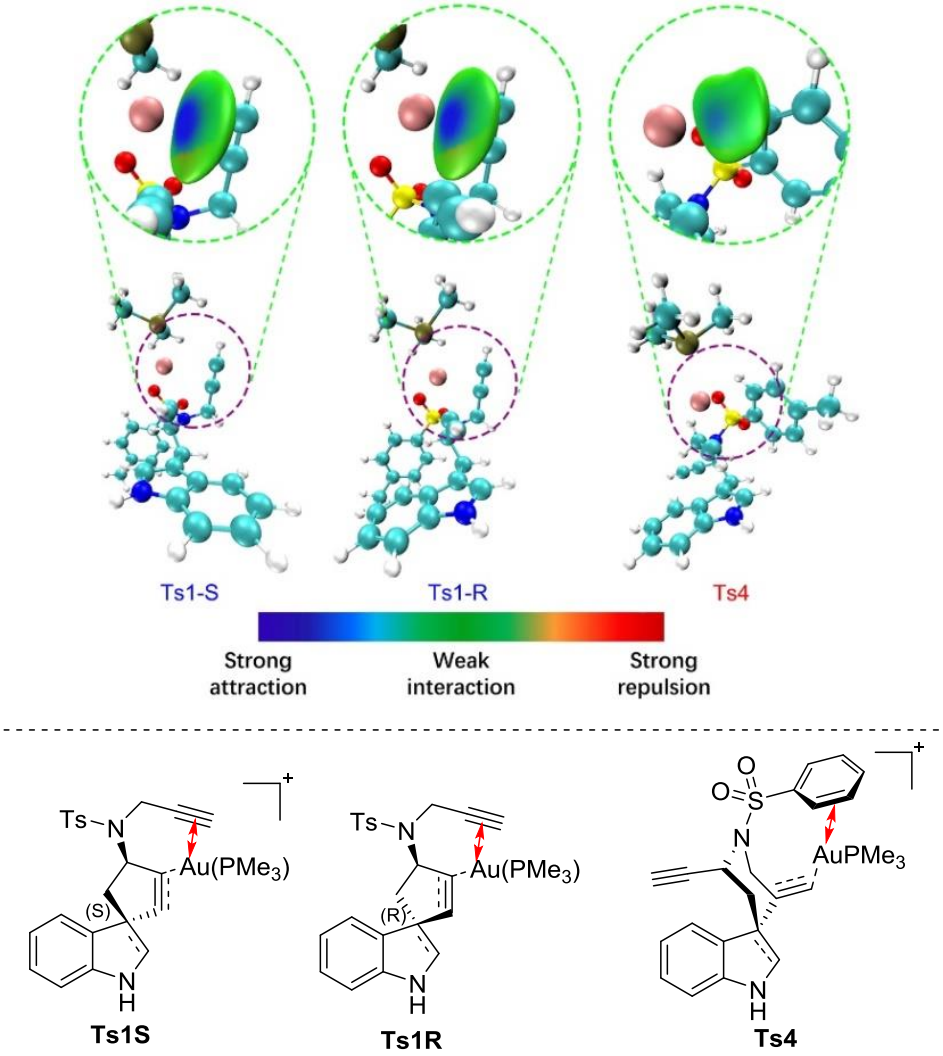


**Figure S3.** IGM Analysis of the Isosurface.

The noncovalent attractive interaction between the distal alkyne and Ts could stabilize the transition state of the spirocyclization step, thus lowering the reaction barrier. The IMG analysis showed that the interaction of distal alkyne with Au(I) in **Ts1S/R** was stronger than that of Ts group with Au(I), thus favoring the *5-endo-dig* cyclization pathway. This could be ascribed to the greater affinity of alkyne to Au(I). However, in the calculated transition state **T4**, only one C-C double of the phenyl group interacted with the Au(I)-complex, resulting in a weaker interaction. Another reason might be that alkyne moiety was more flexible than Ts group and suffered less strain stress when interacting with Au(I).

### 6.4 Wave Function Analysis

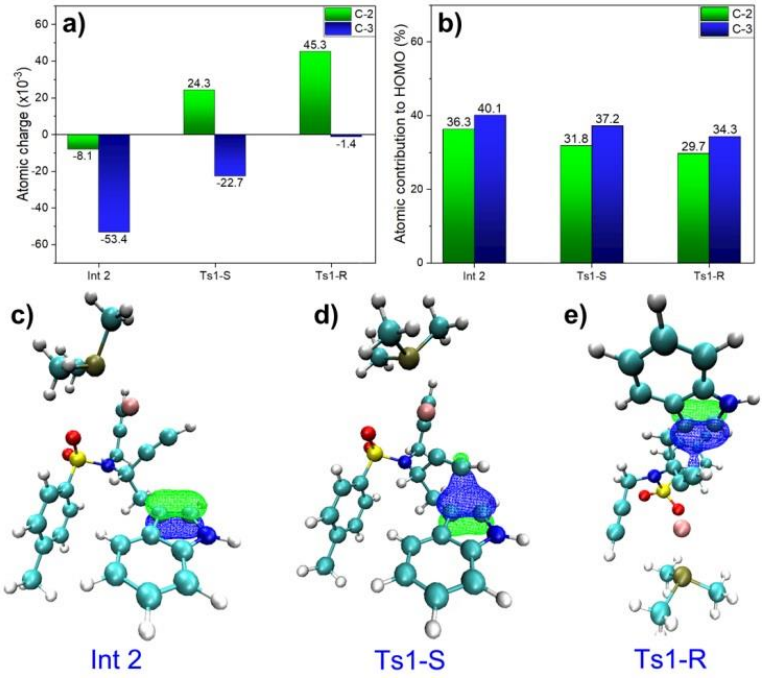


**Figure S4**. Hirshfeld Atomic Charge and Hirshfeld Method Orbital Composition Analysis of HOMOs for **Int2** and **Ts1-S/R**.

Additionally, in order to shed more light on the regioselectivity for the spirocyclization step (*5-endo-dig* spirocyclization of **Int2** to **Int5-R/S** versus direct *6-endo-dig* spirocyclization of **Int2** to **Int6-R/S**), wave function analysis consisting PM-Mulliken LMO[14], Hirshfield atomic charge[15] and Hirshfeld method orbital composition analysis[15] of **Int2** were conducted by Multiwfn[17]. Figure S1a shown that the Hirshfeld atomic charge for C-3 is -0.0534, which was obviously electron richer than that of C-2 (the atomic charge is -0.008). By comparing the atomic charge between **Int2** and **Ts1-S/R**, we found that the double bond between C-2 and C-3 became more polarized and the negative charge biased toward C-3 in **Ts1-S/R** than **Int2**. Meanwhile, the result of PM-Mulliken LMO analysis /Hirshfeld method orbital composition analysis of the HOMO of **Int2** shown that C-3 had more contribution than C-2 (C-3 40.1% vs C-2 36.3%) in Figure S1b, and this phenomenon was also observed in **Ts1-S/R**. Notably, both the sum of the contribution of C-2 and C-3 to HOMO of **Ts1-S/R** (69% and 64%) became less than that of **Int 2** (76.4%), illustrating that the electrons between C2-C3 delocated to the bond formation region. This bond-forming process was visualized in Figure S1d and S1e, in which HOMO orbital between C2-C3 in **Int2** has been attached to the carbon of the proximal alkyne in **Ts1-S/R**. All those results indicated that the C-3 of indole exhibited a higher nucleophilicity than the C-2 and preferentially attacked the alkyne/Au complex, which also rationalized the failure of locating the transition state of *6-endo-dig* cyclization.

# 7. Refernces


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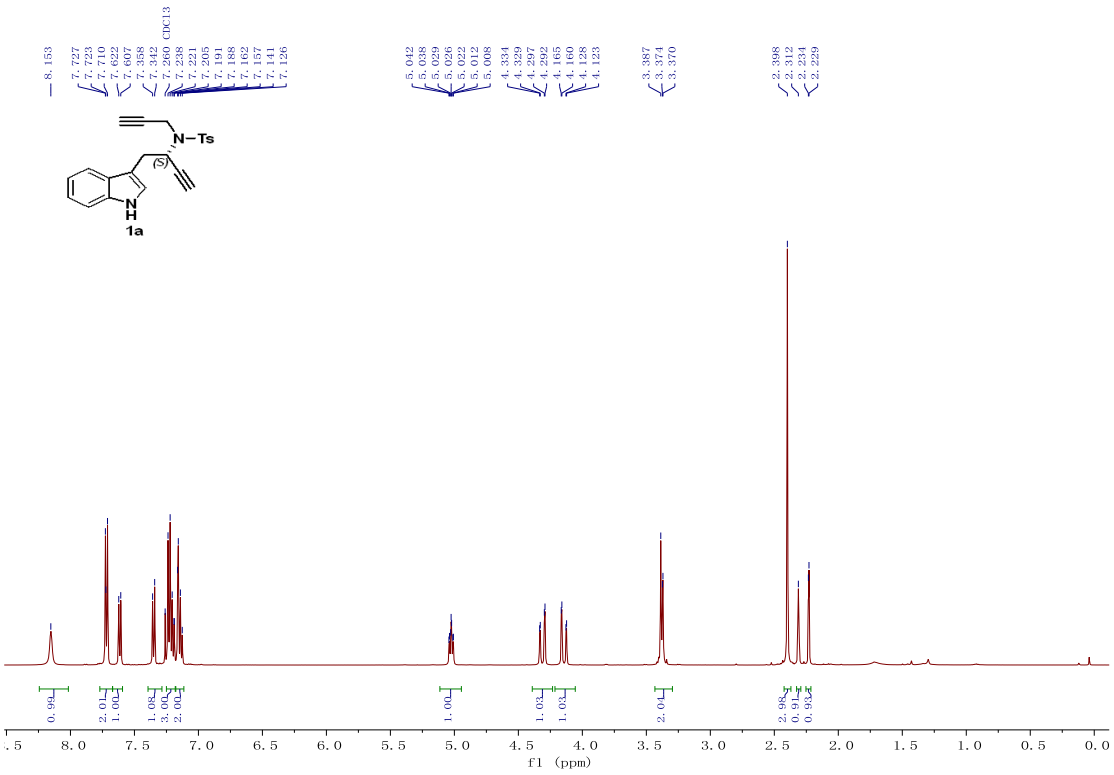
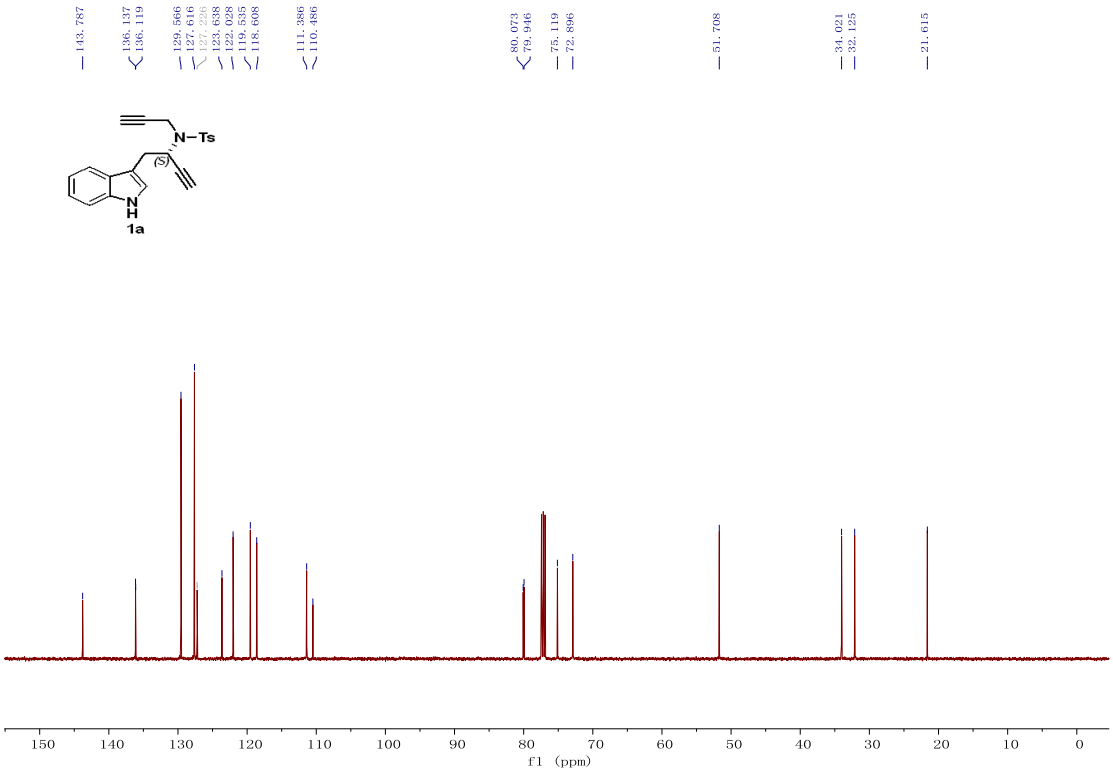
# 8. NMR Spectra

$^{1}$H NMR Spectrum of **1a** (500 MHz, $CDCl_3$)




$^{13}$C NMR Spectrum of **1a** (126 MHz, $CDCl_3$)

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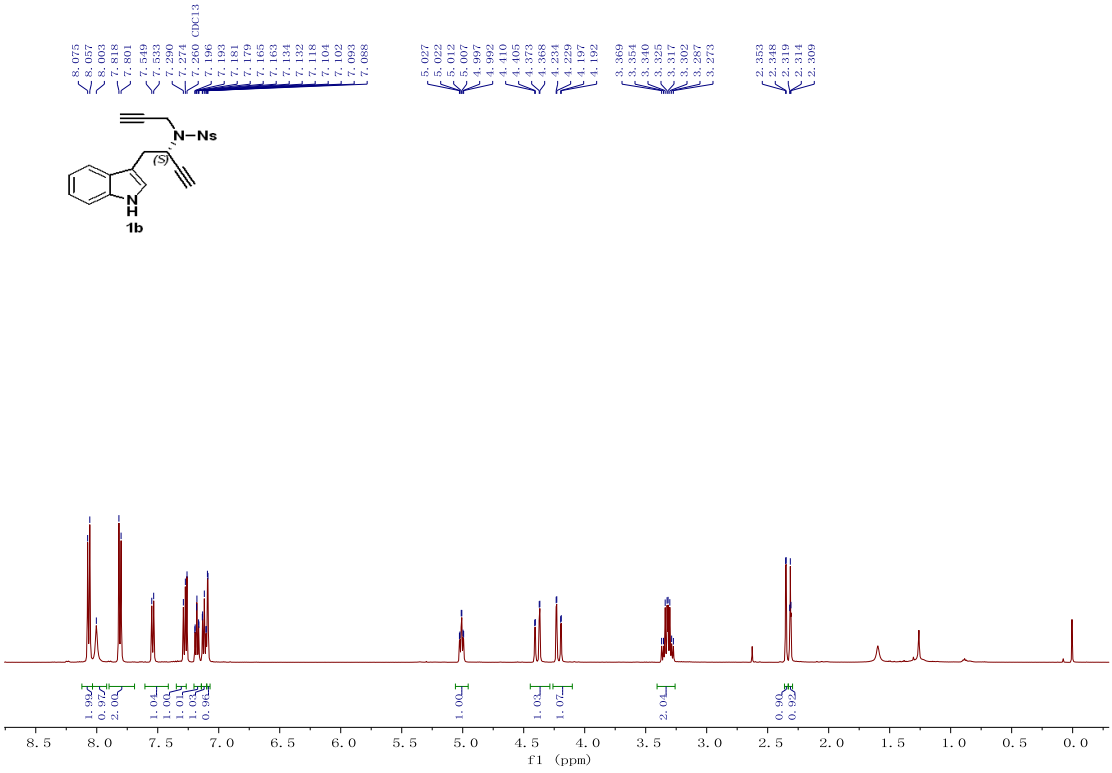


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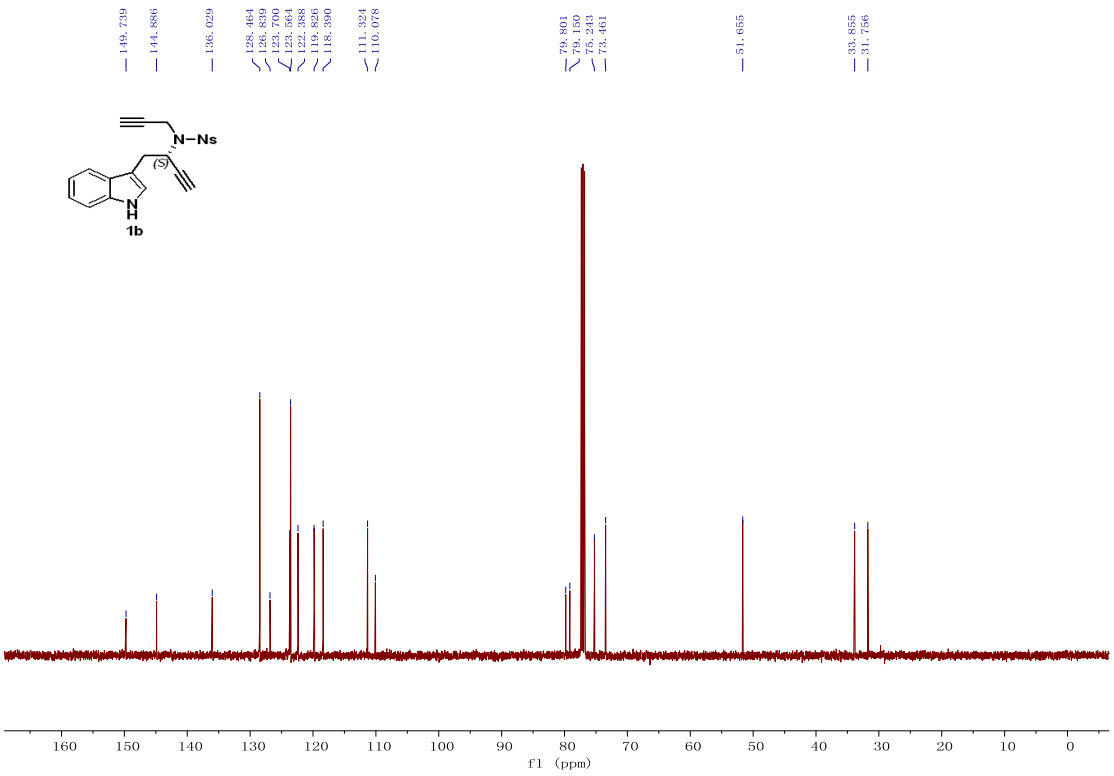
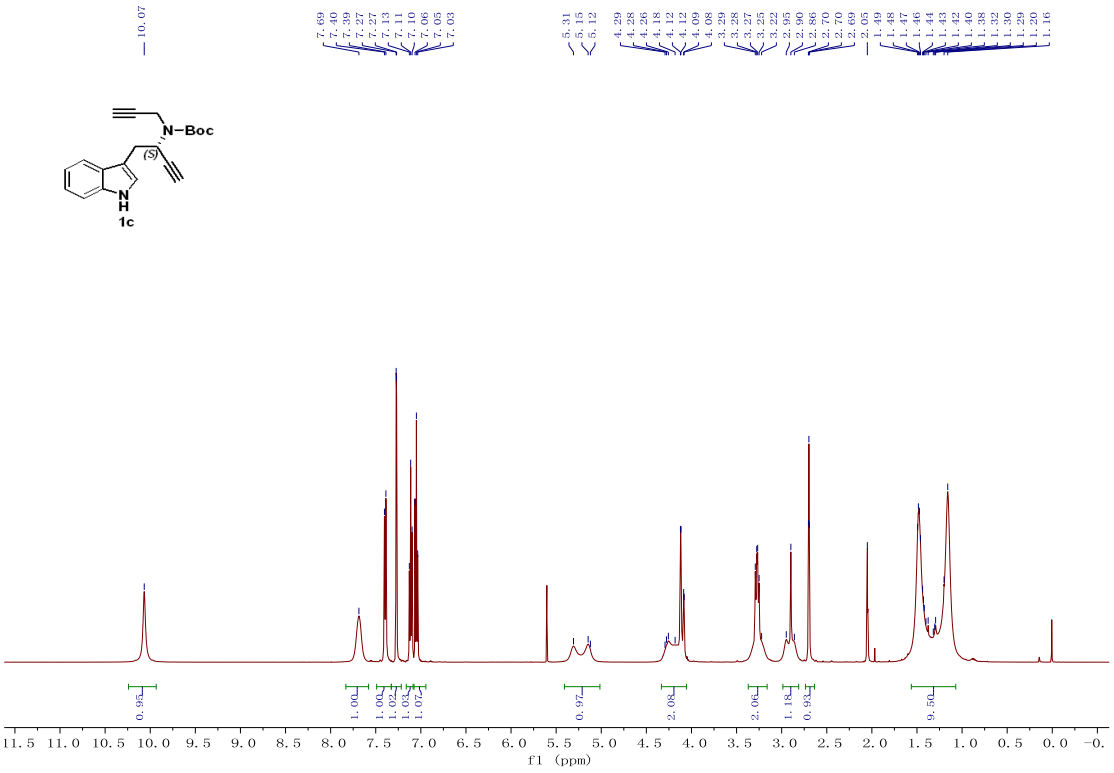
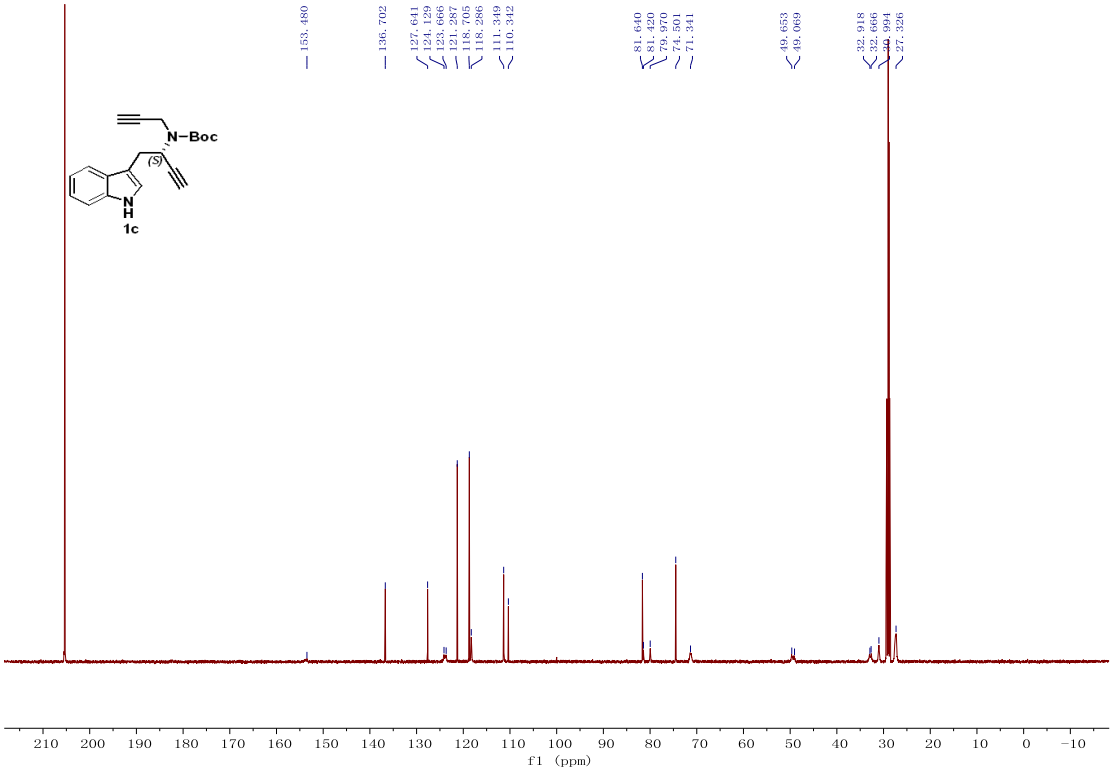



$^{1}$H NMR Spectrum of **1c** (500 MHz, Acetone-$d_6$)



$^{13}$C NMR Spectrum of **1c** (126 MHz, Acetone-$d_6$)

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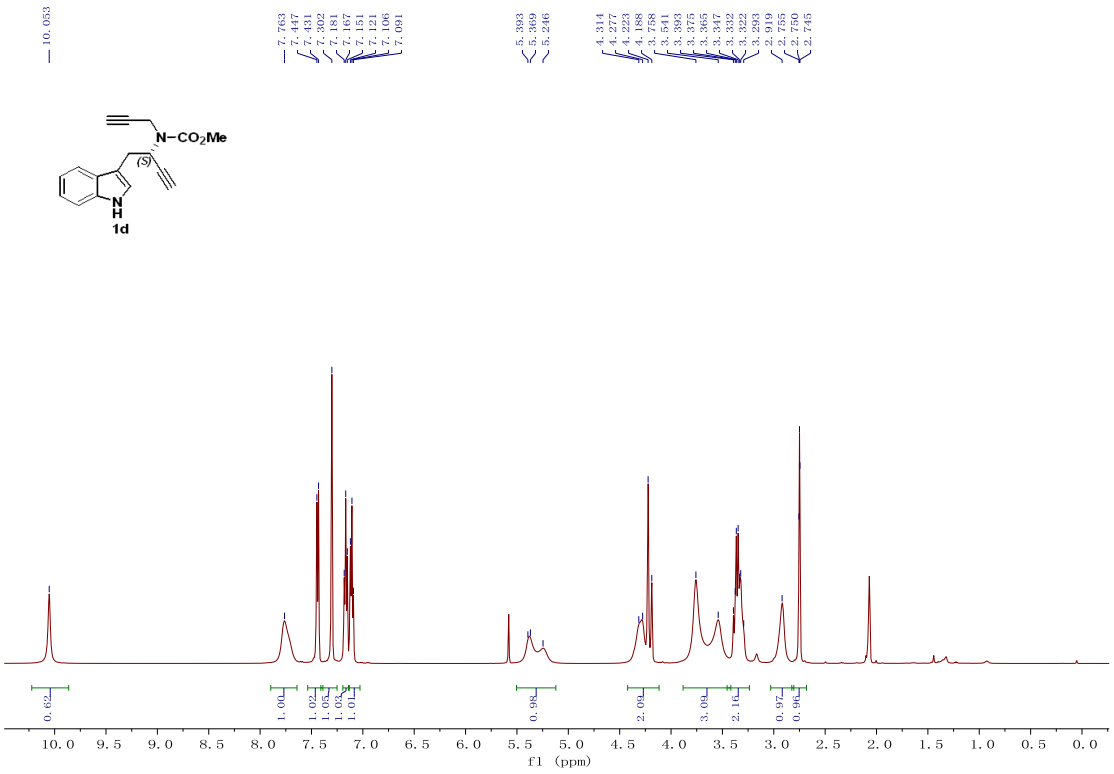


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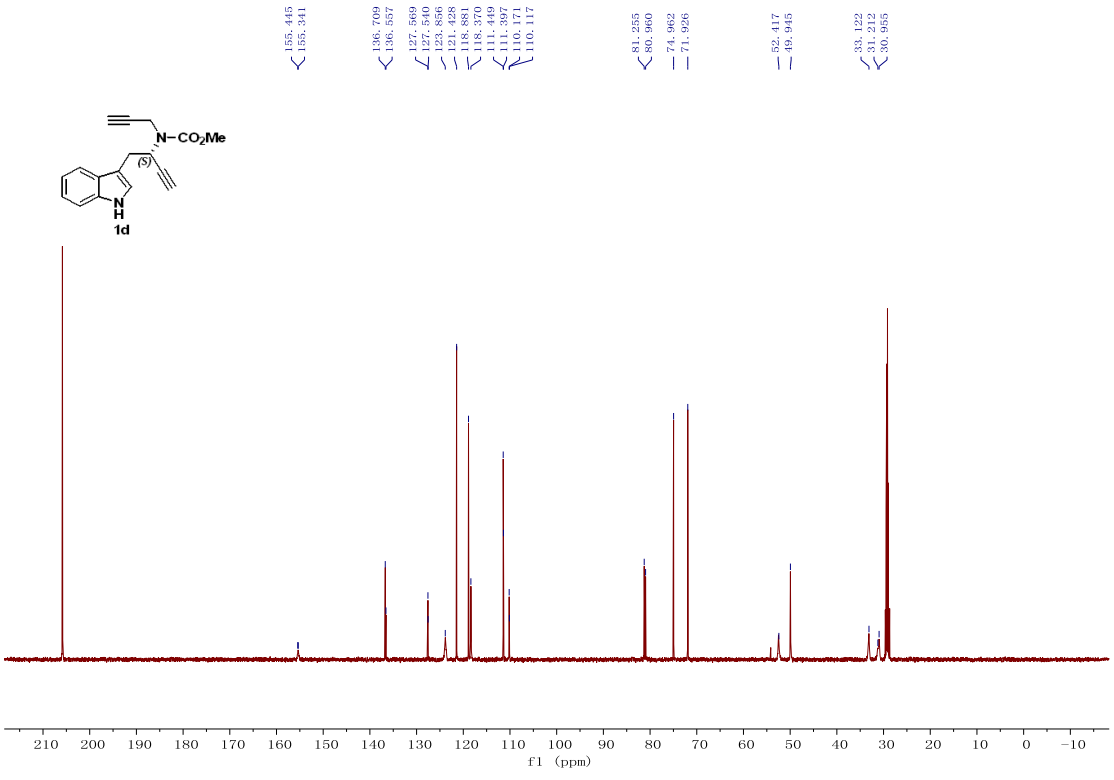

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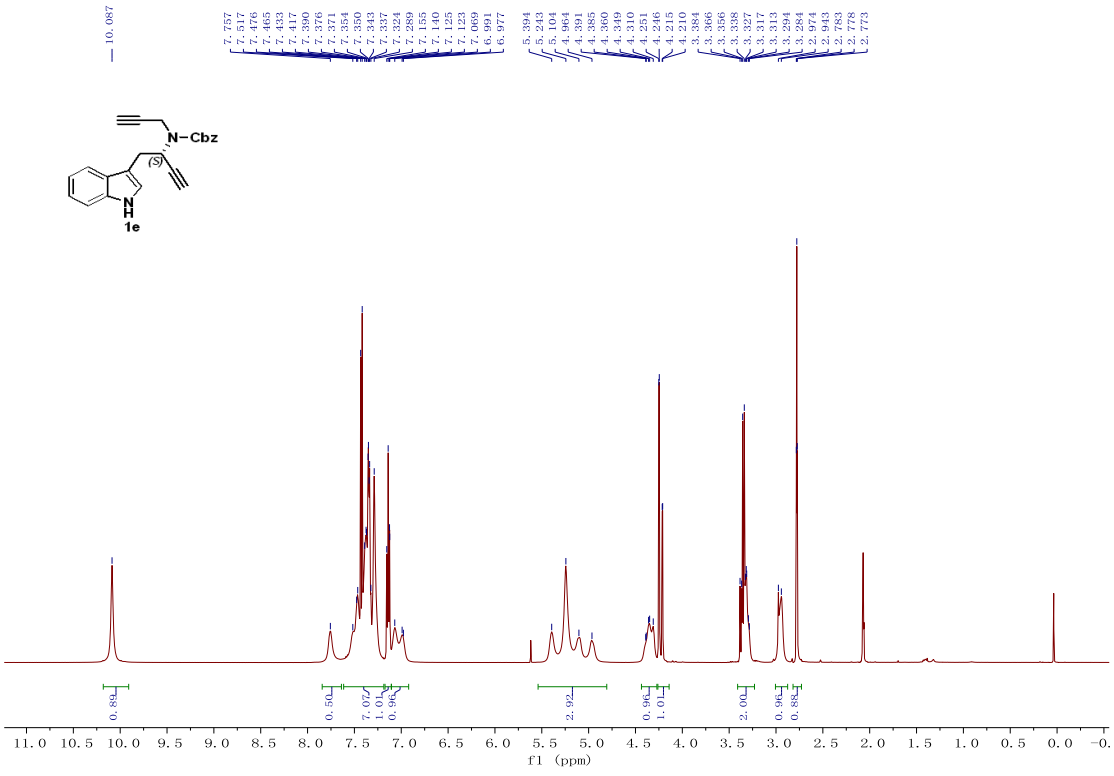


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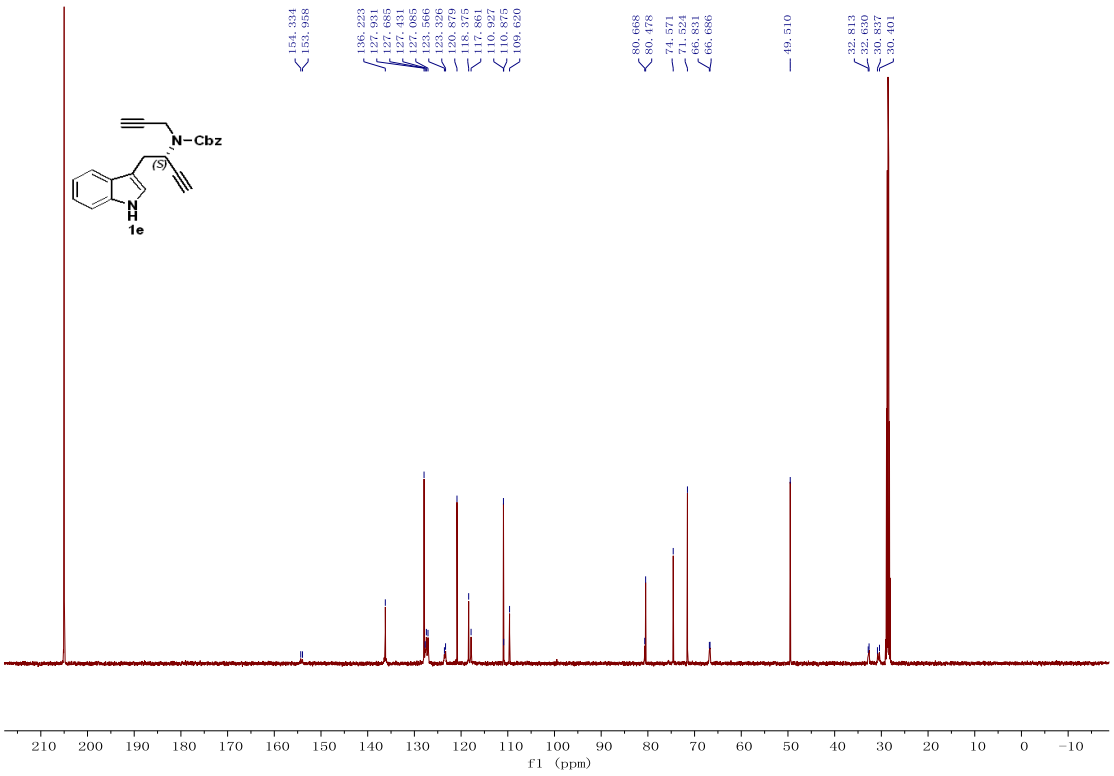
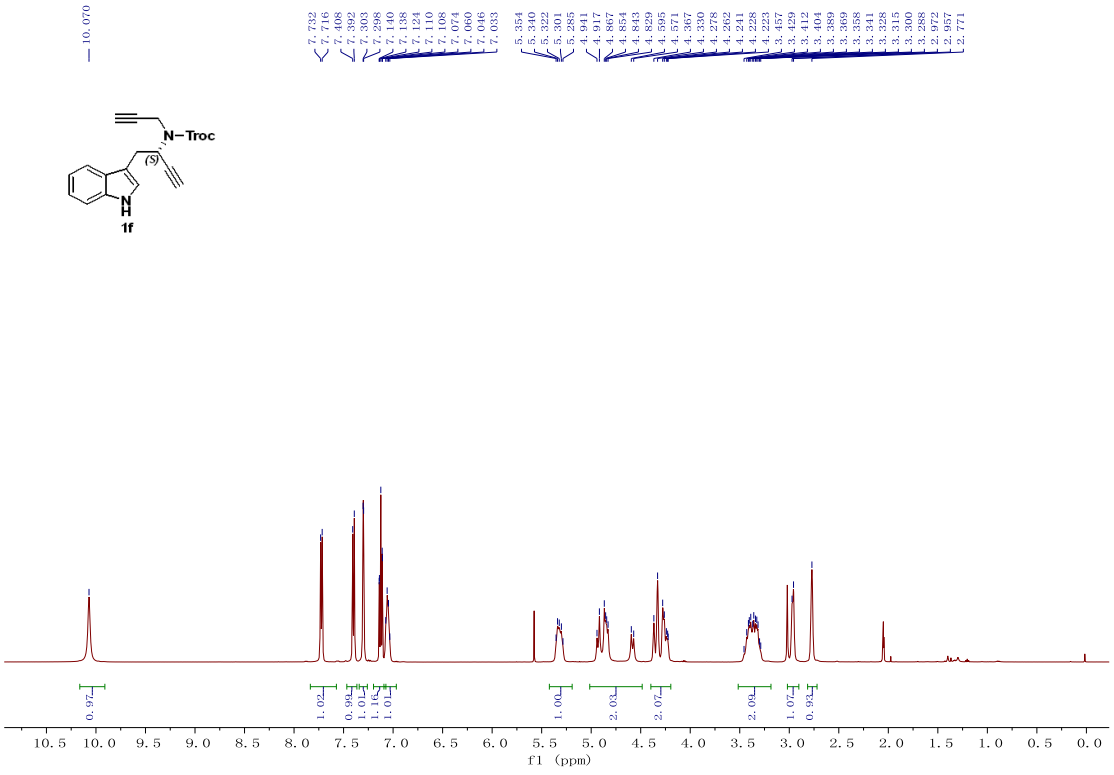



$^1$H NMR Spectrum of **1f** (500 MHz, Acetone-$d_6$)



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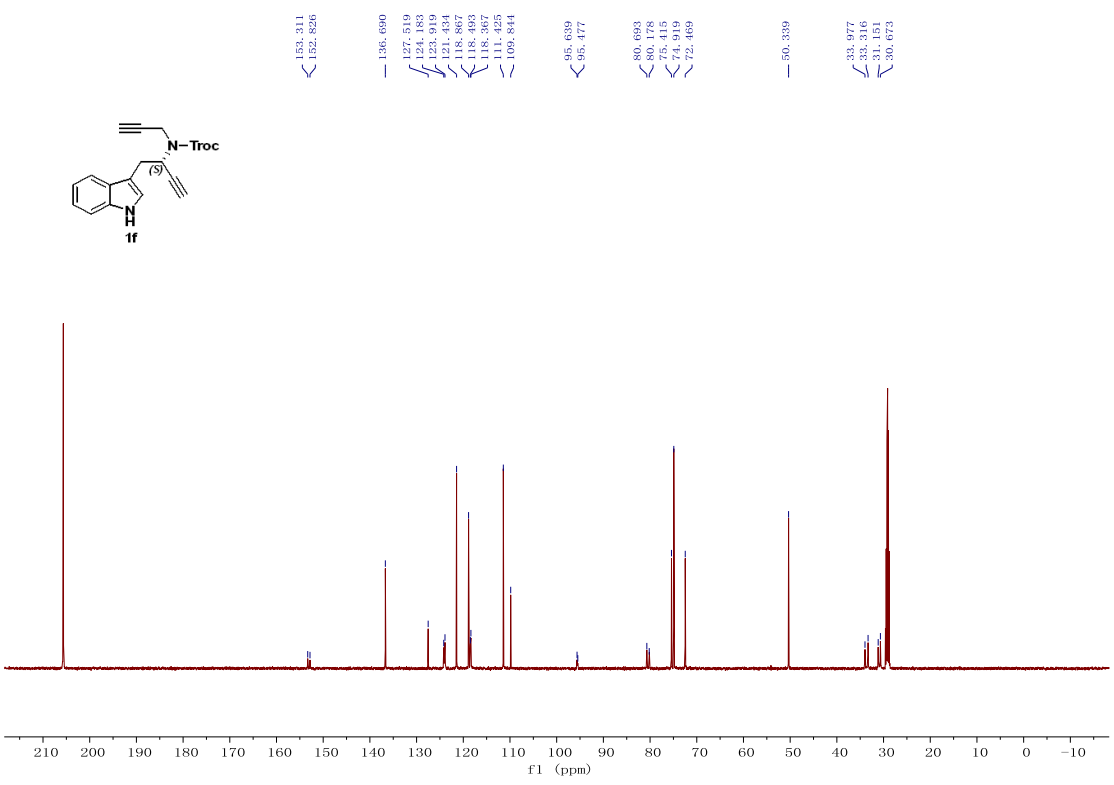


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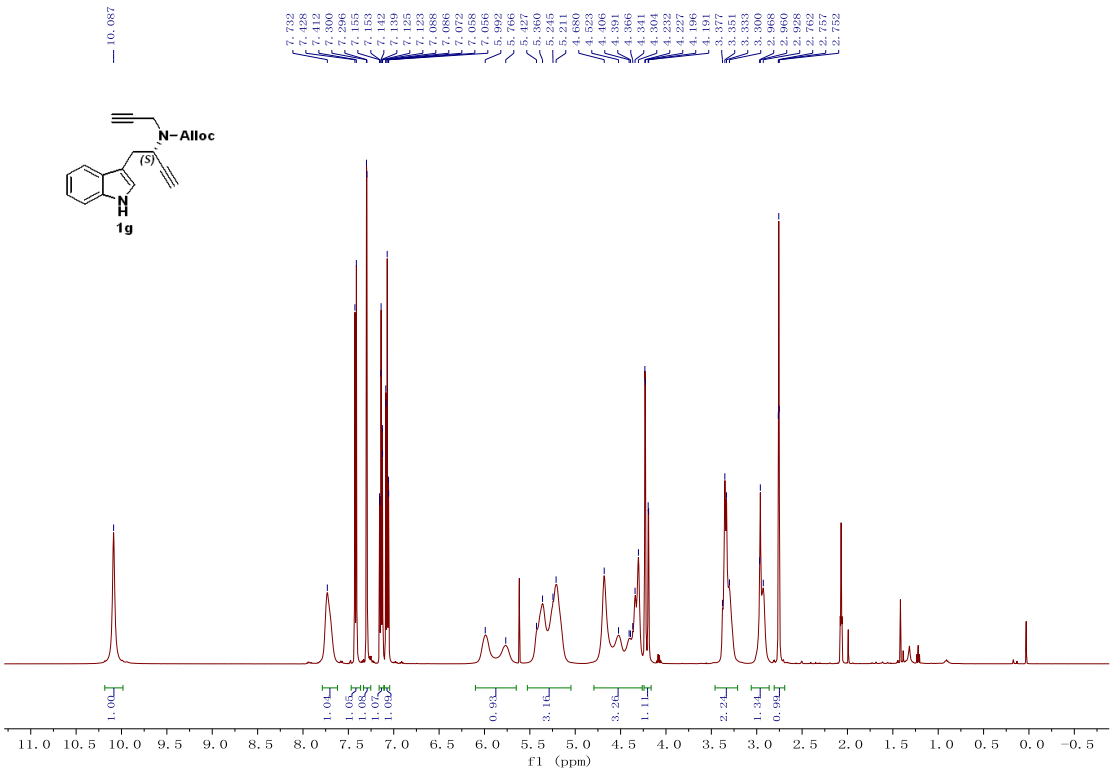
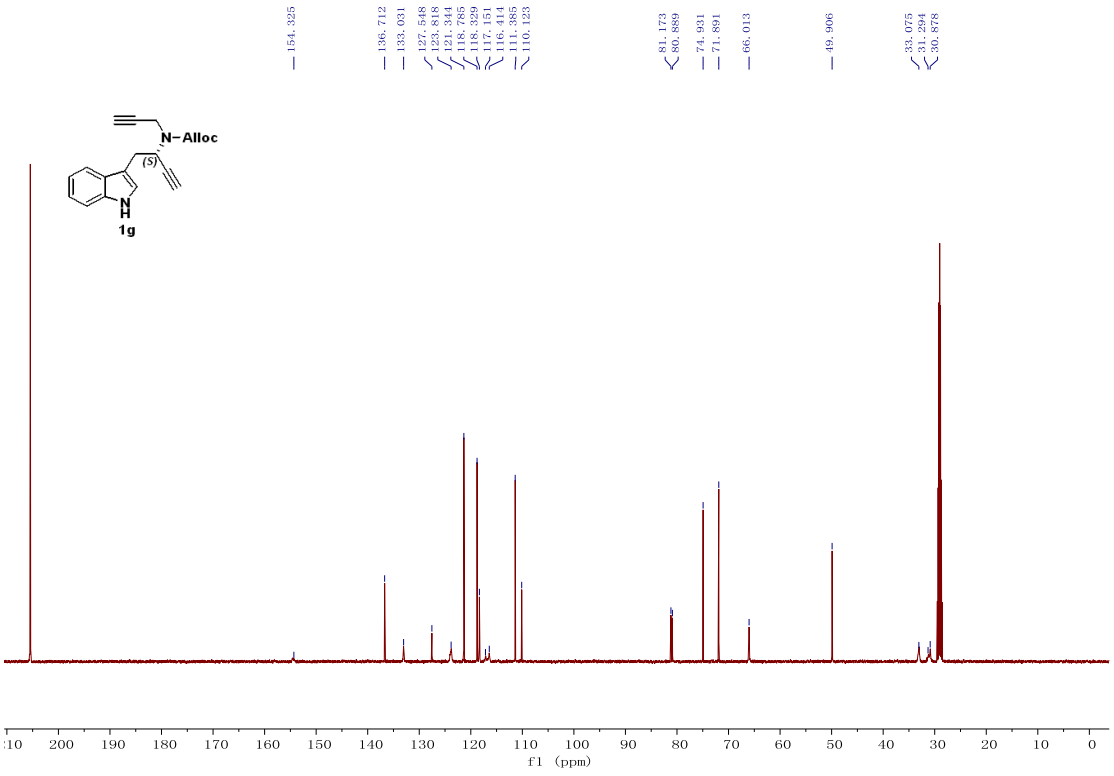
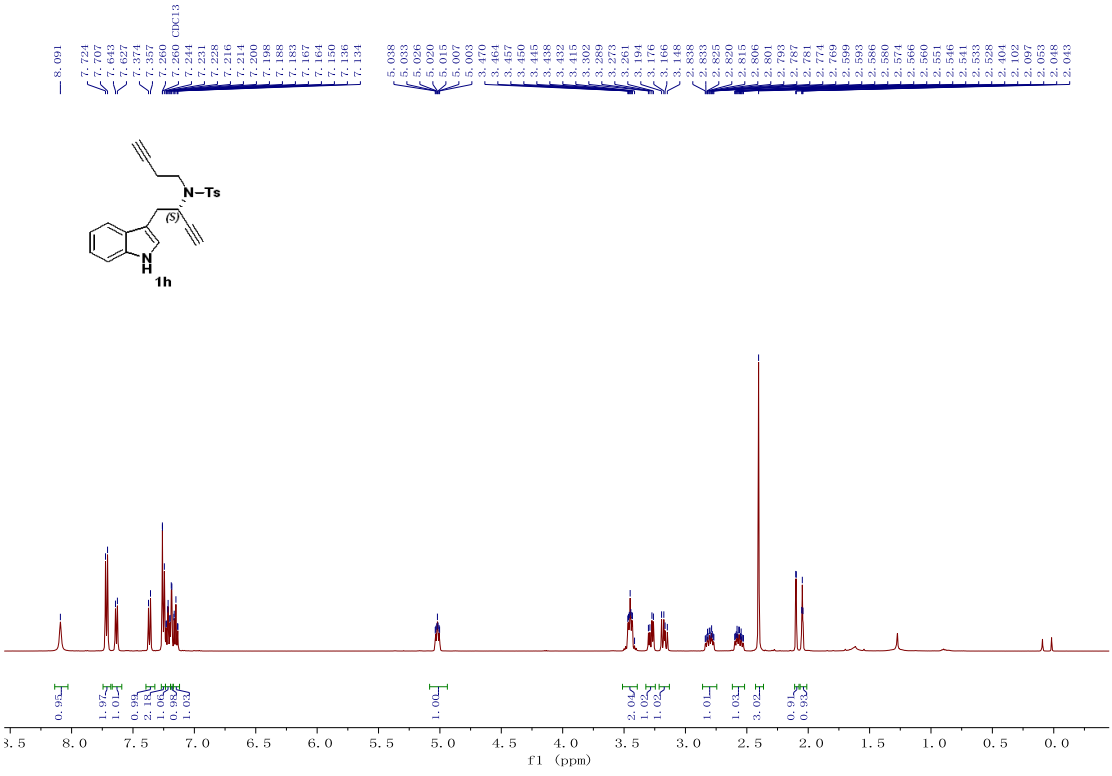



$^{13}$C NMR Spectrum of **1g** (126 MHz, Acetone-$d_6$)



$^{1}$H NMR Spectrum of **1h** (500 MHz, $CDCl_3$)

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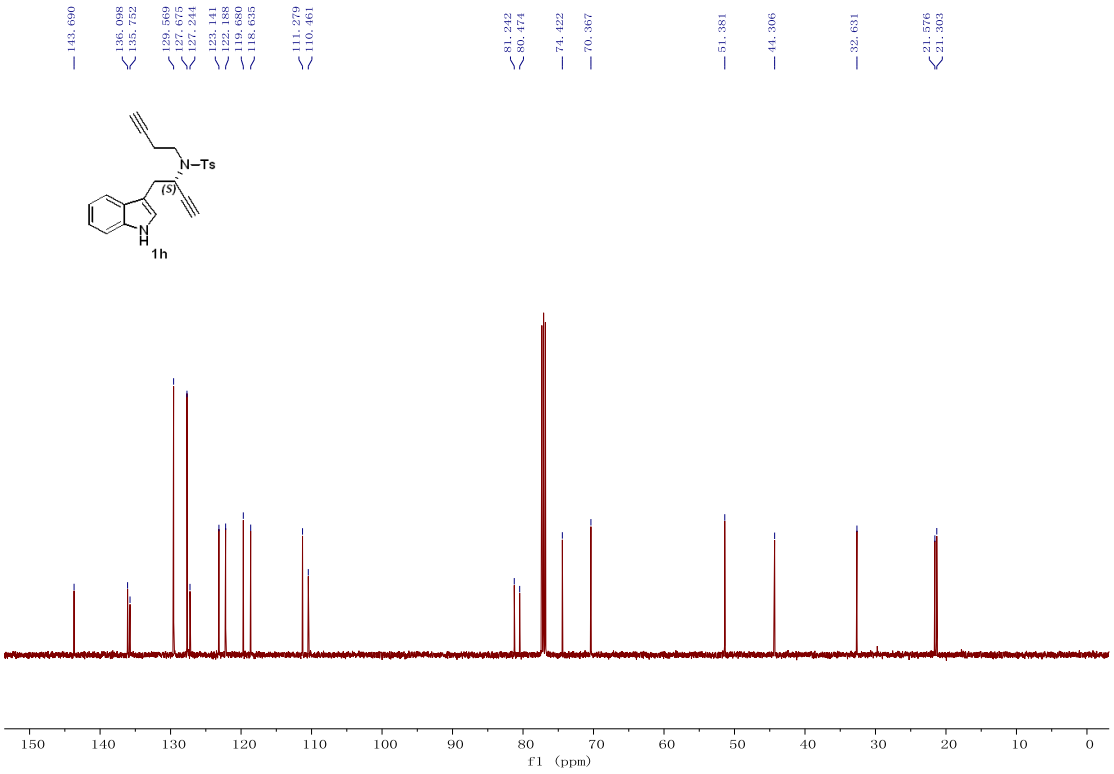


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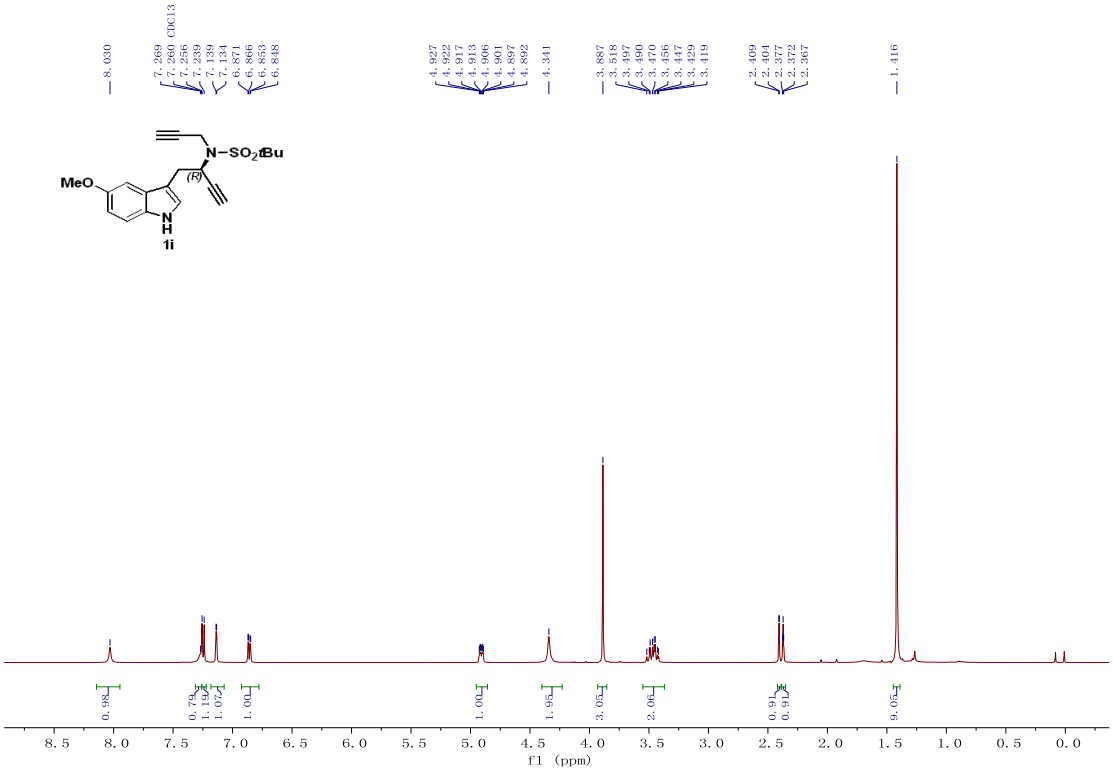
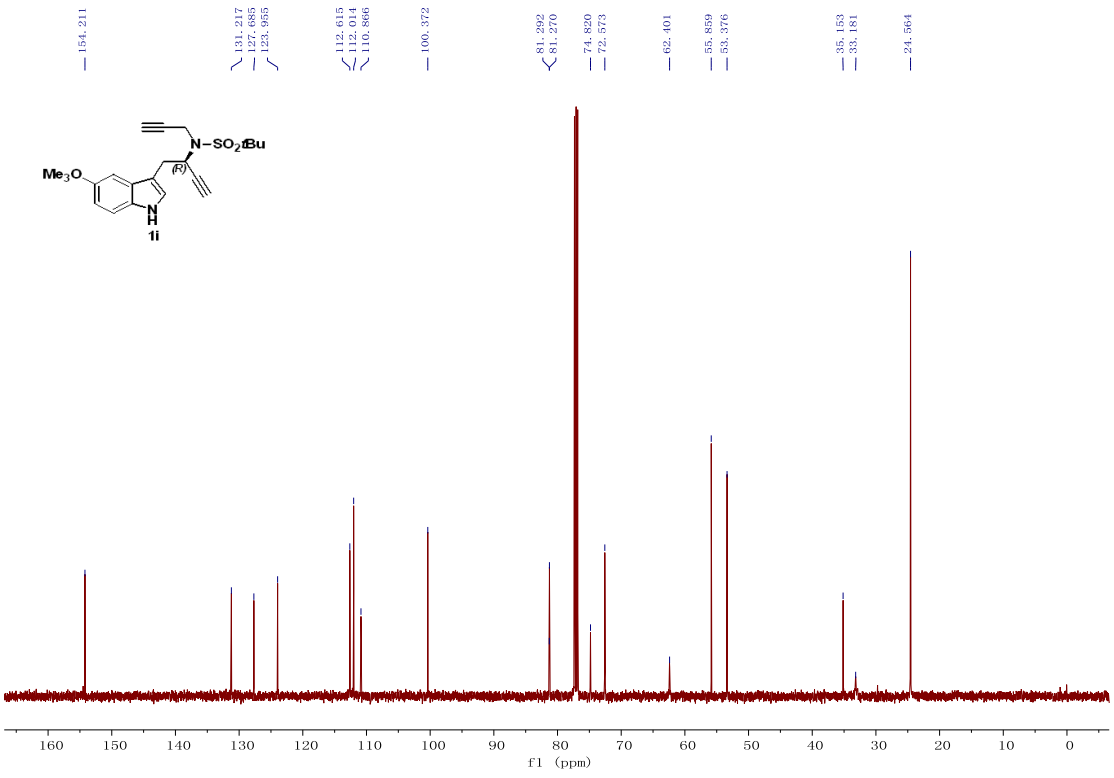
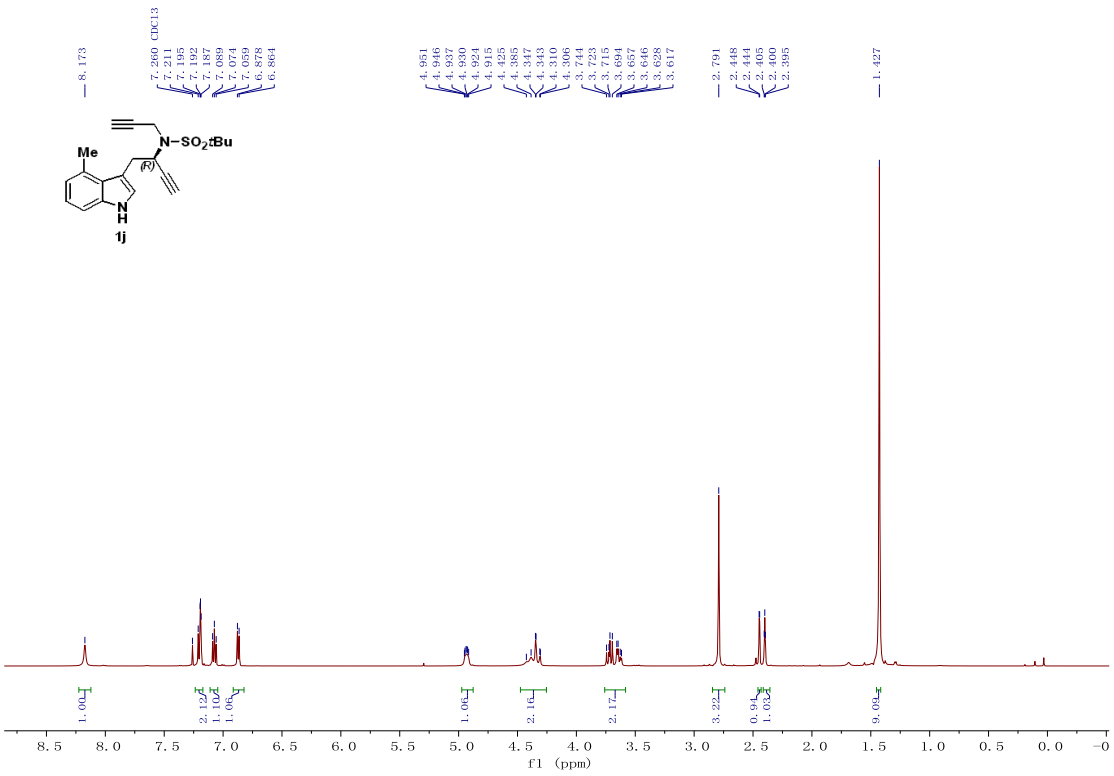


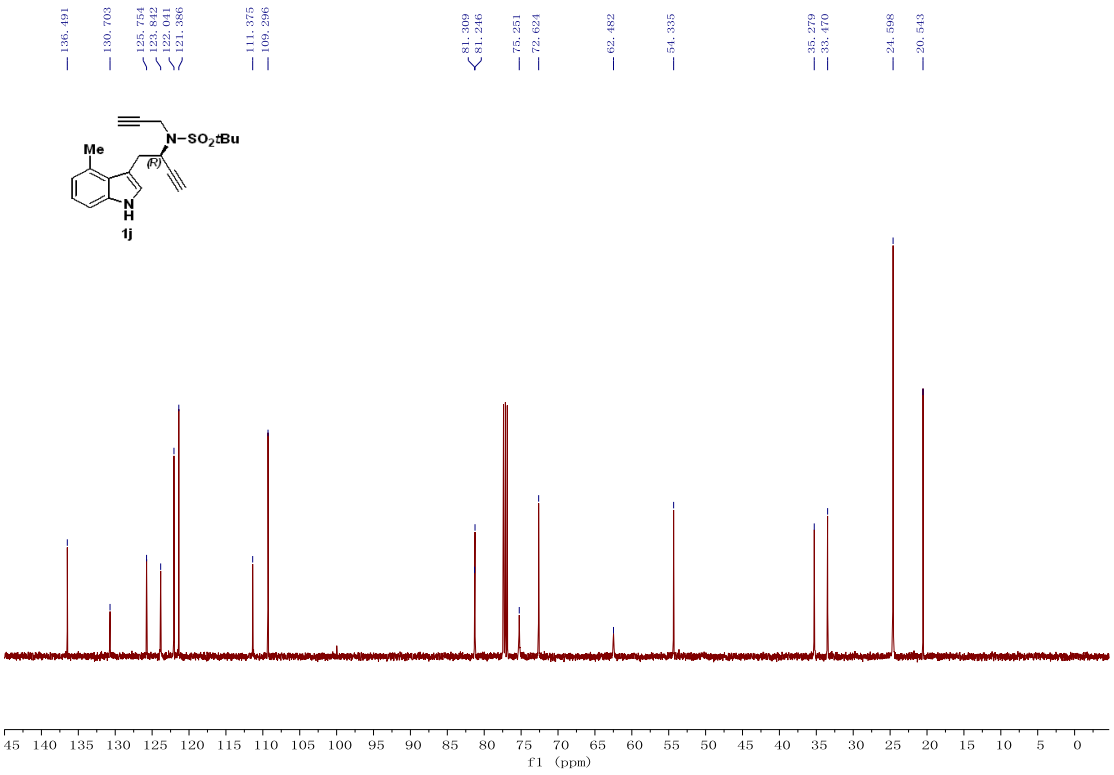
$^{13}$C NMR Spectrum of **1i** (126 MHz, $CDCl_3$)



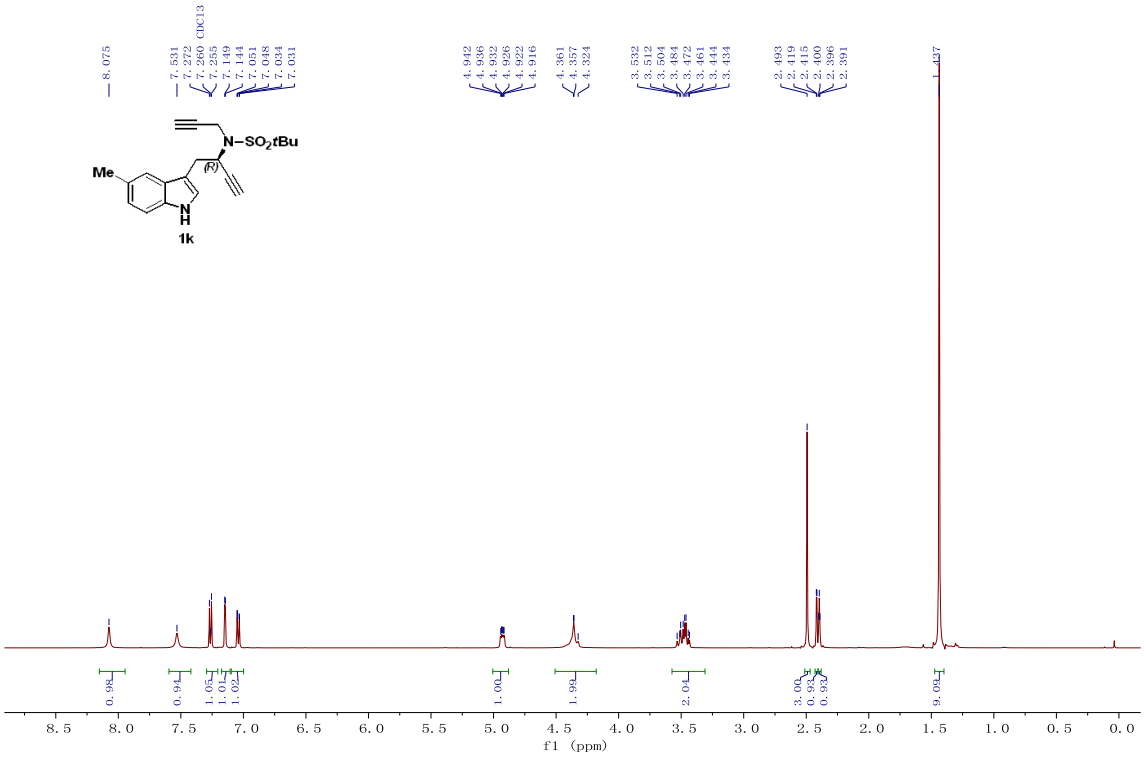

$^{1}$H NMR Spectrum of **1j** (500 MHz, $CDCl_3$)



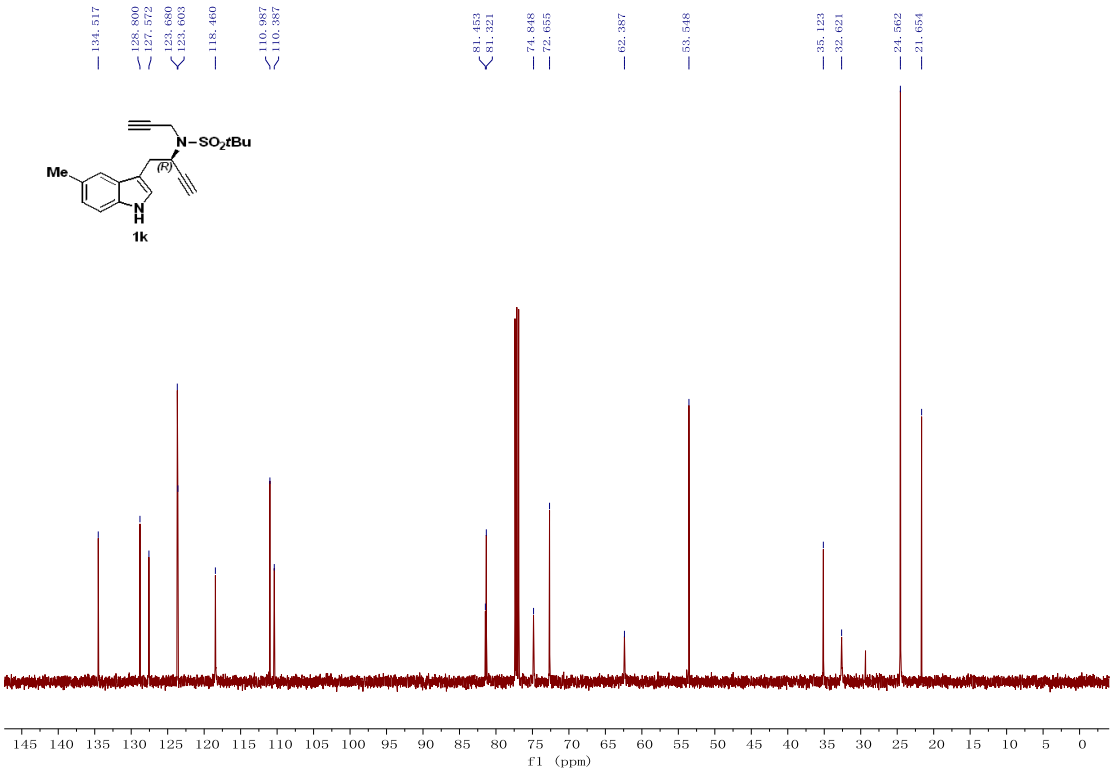

$^{13}$C NMR Spectrum of **1j** (126 MHz, $CDCl_3$)



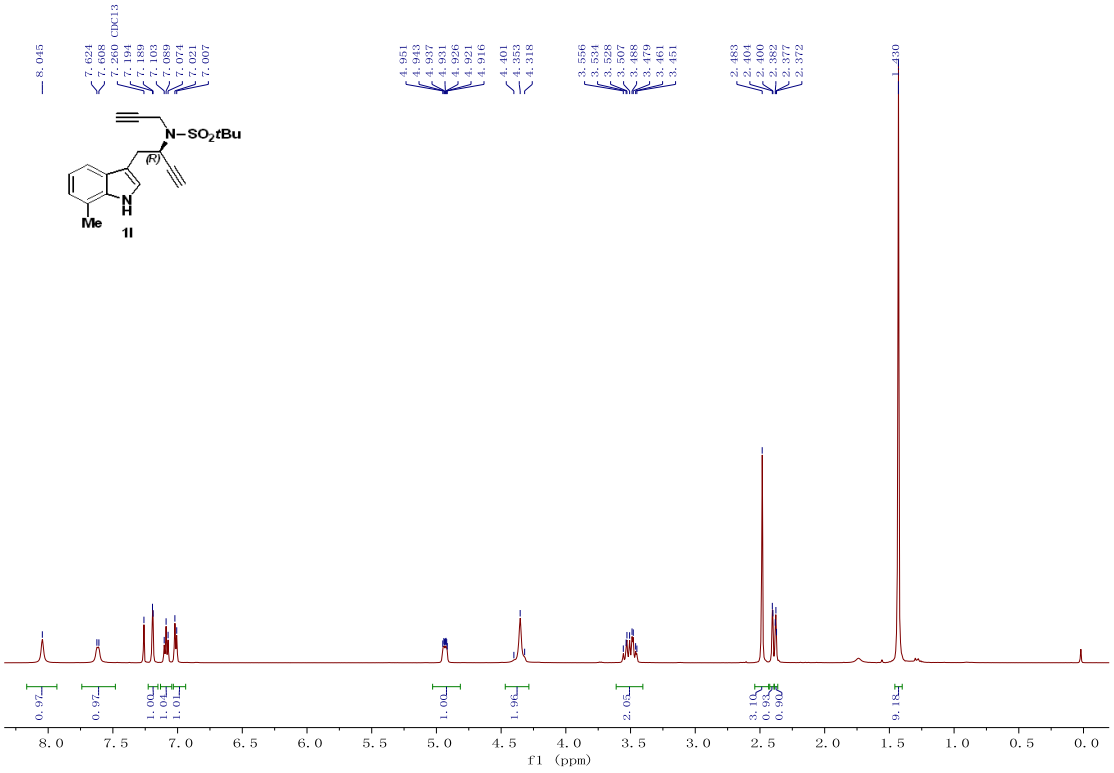
$^{1}$H NMR Spectrum of **1k** (500 MHz, $CDCl_3$)



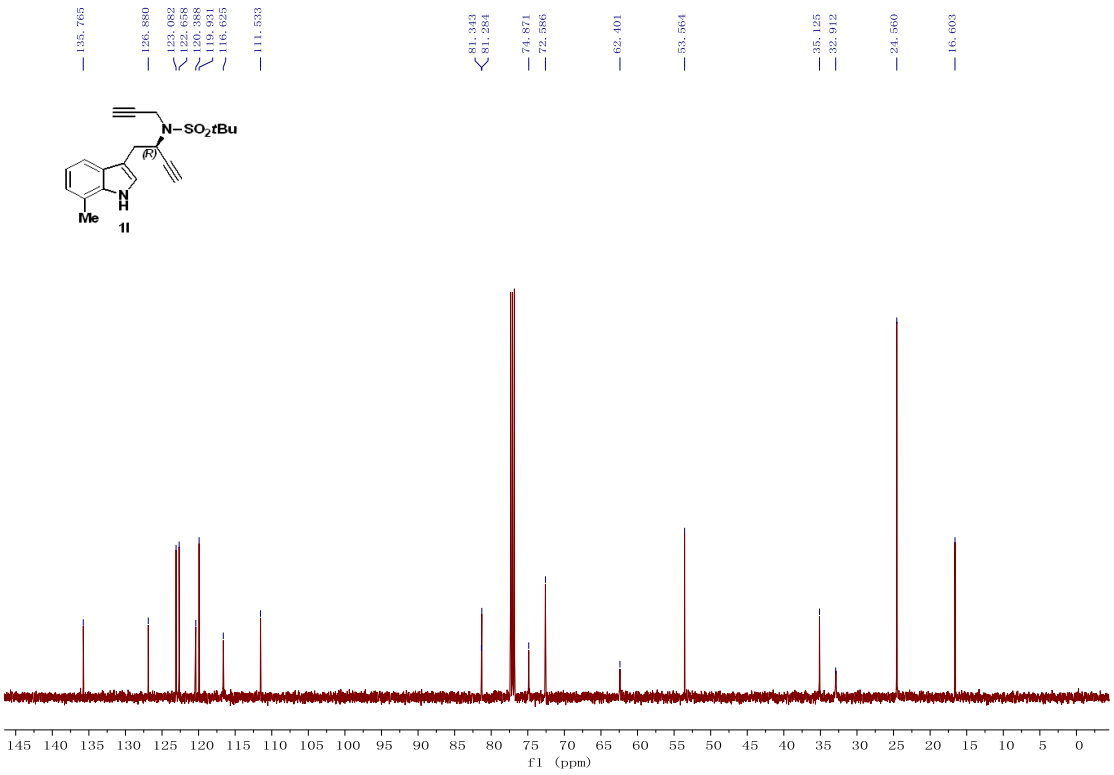

$^{13}$C NMR Spectrum of **1k** (126 MHz, $CDCl_3$)



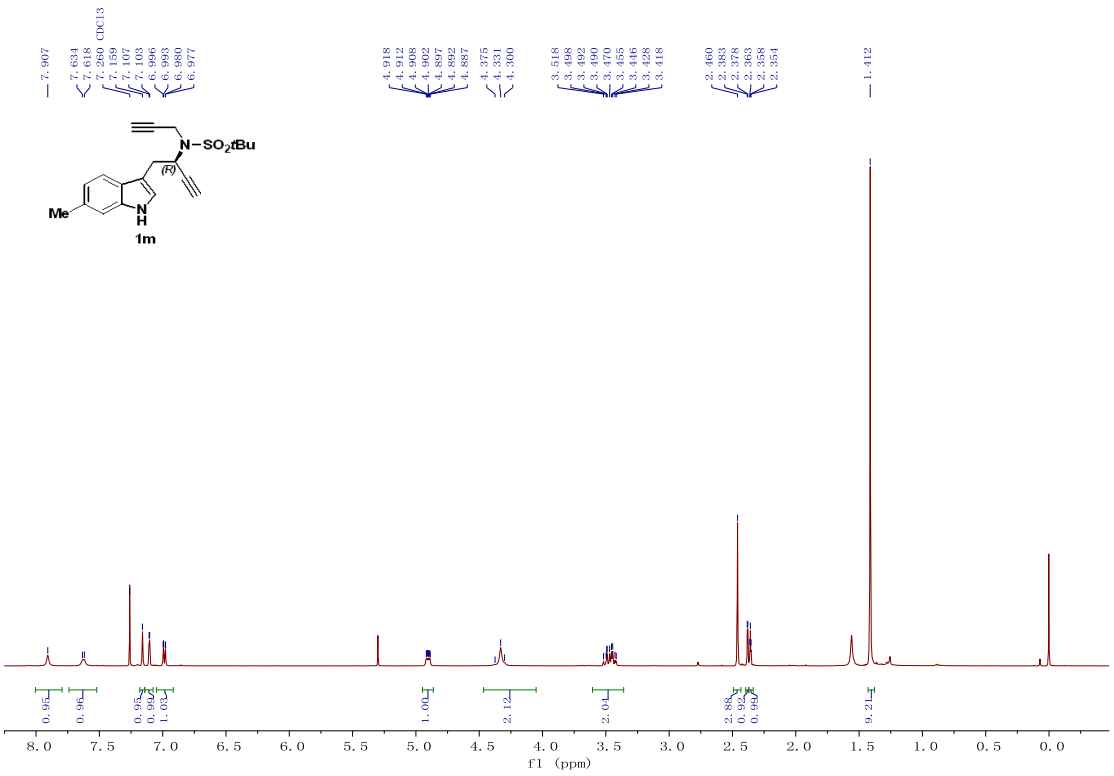

$^{1}$H NMR Spectrum of **1l** 500 MHz, $CDCl_3$)



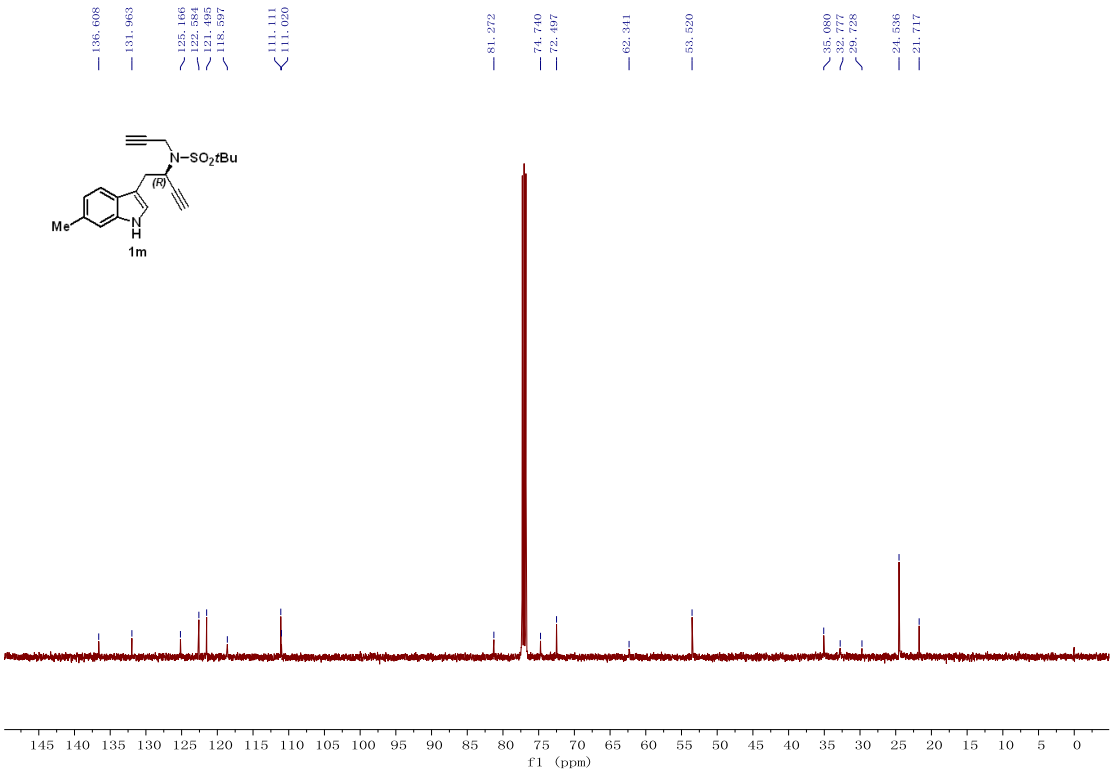
$^{13}$C NMR Spectrum of **1l** (126 MHz, $CDCl_3$)



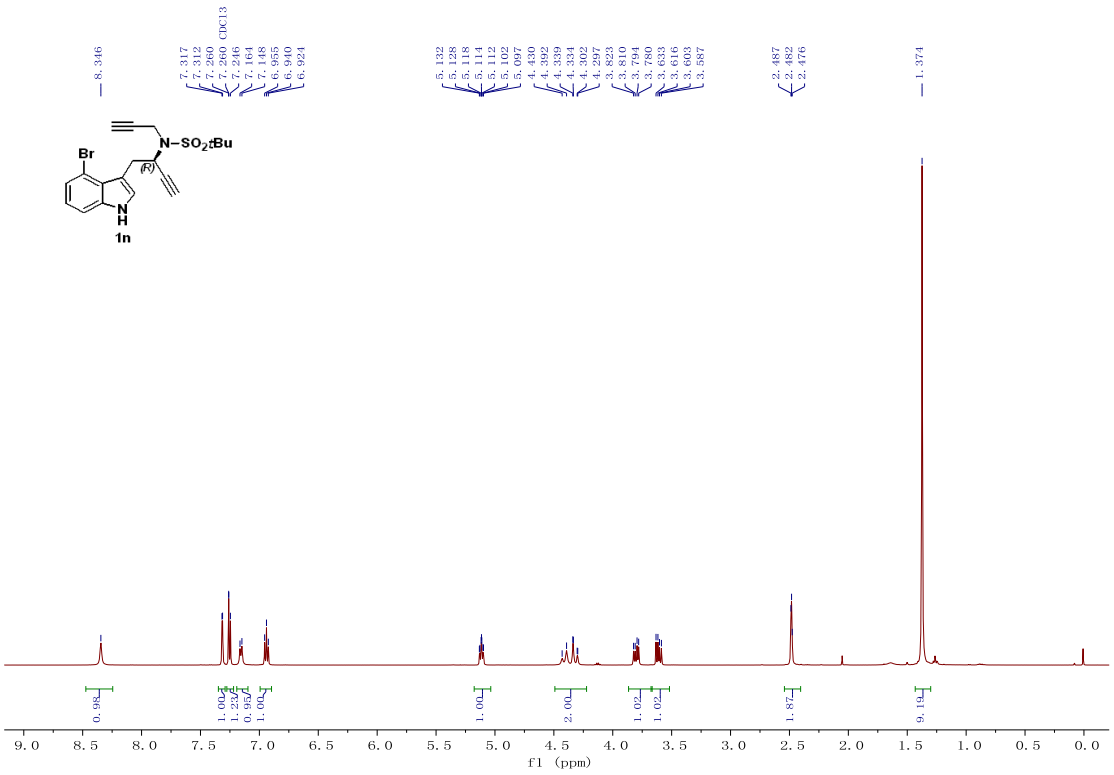

$^{1}$H NMR Spectrum of **1m** (500 MHz, $CDCl_3$)



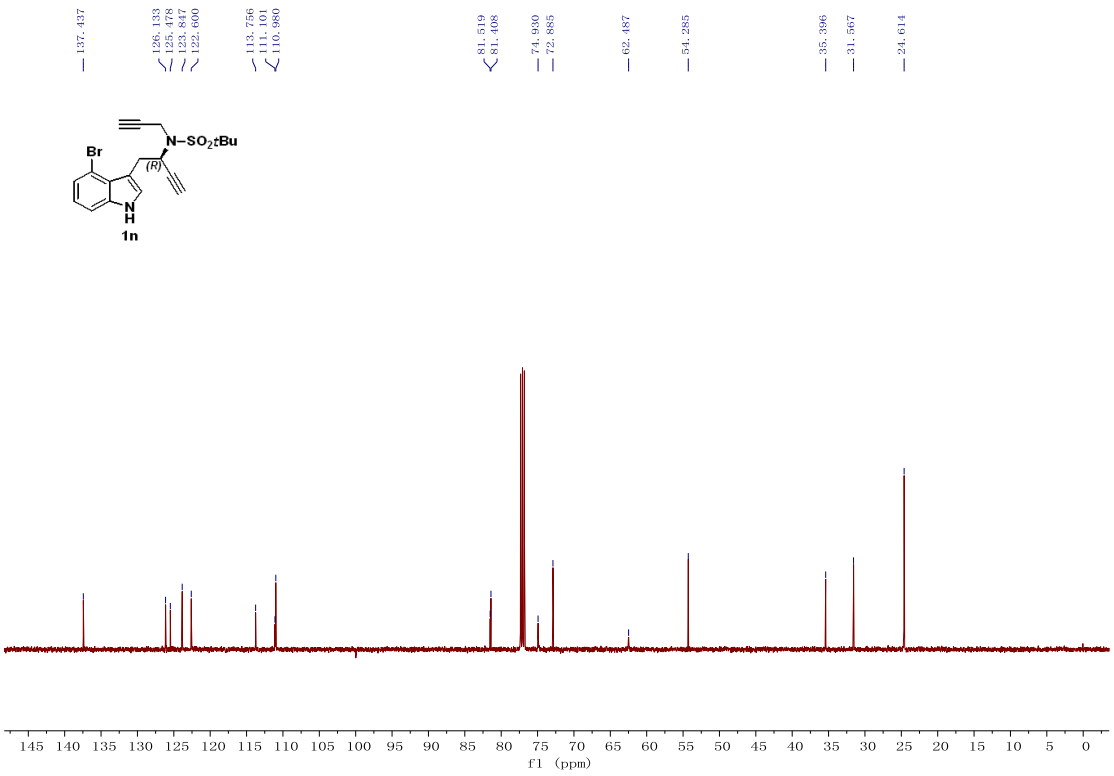

$^{13}$C NMR Spectrum of **1m** (126 MHz, $CDCl_3$)



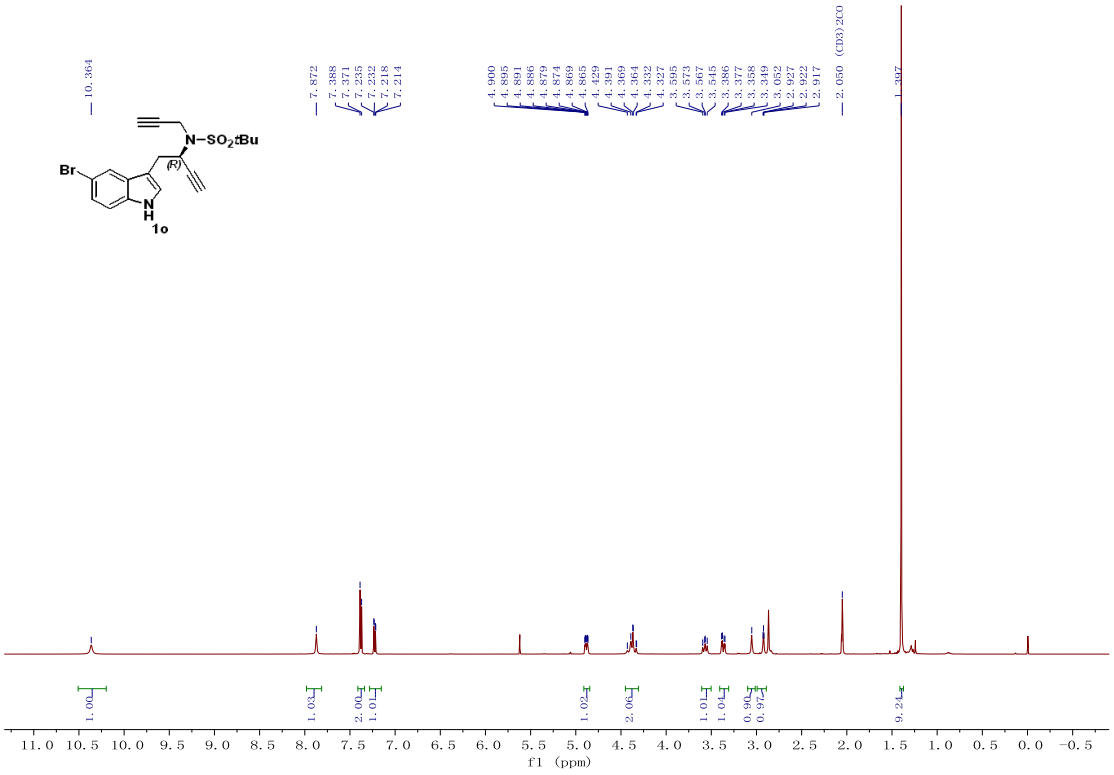
$^{1}$H NMR Spectrum of **1n** (500 MHz, $CDCl_3$)



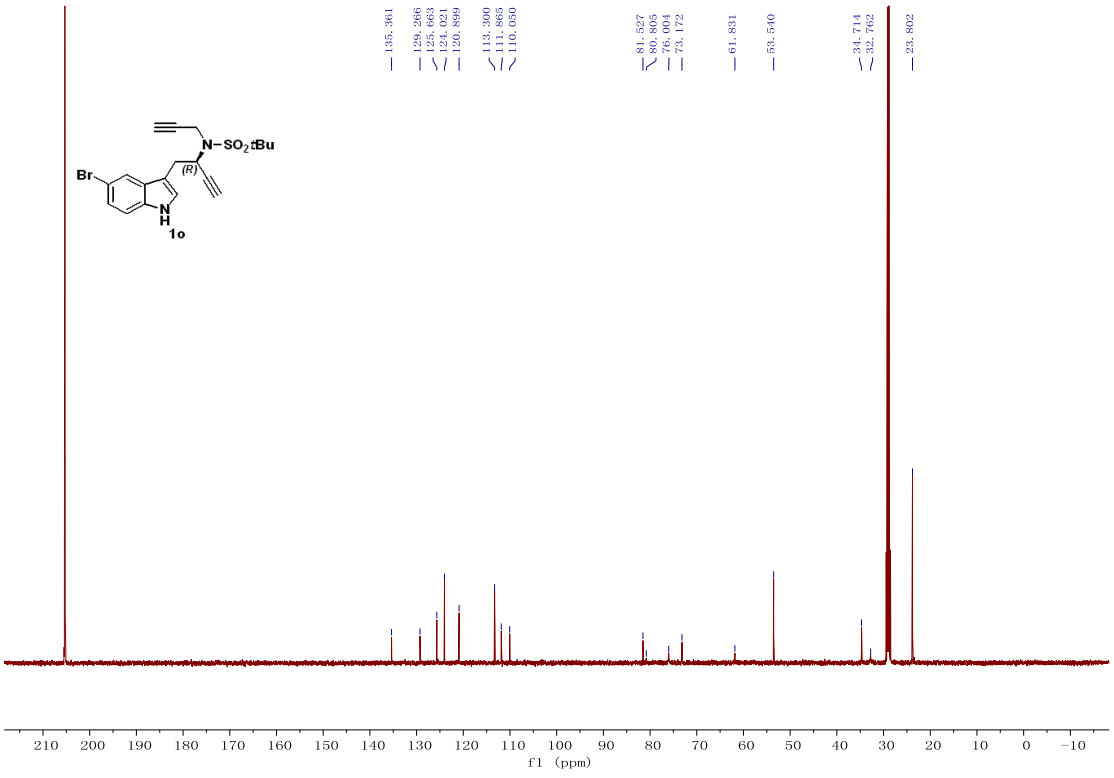

$^{13}$C NMR Spectrum of **1n** (126 MHz, $CDCl_3$)



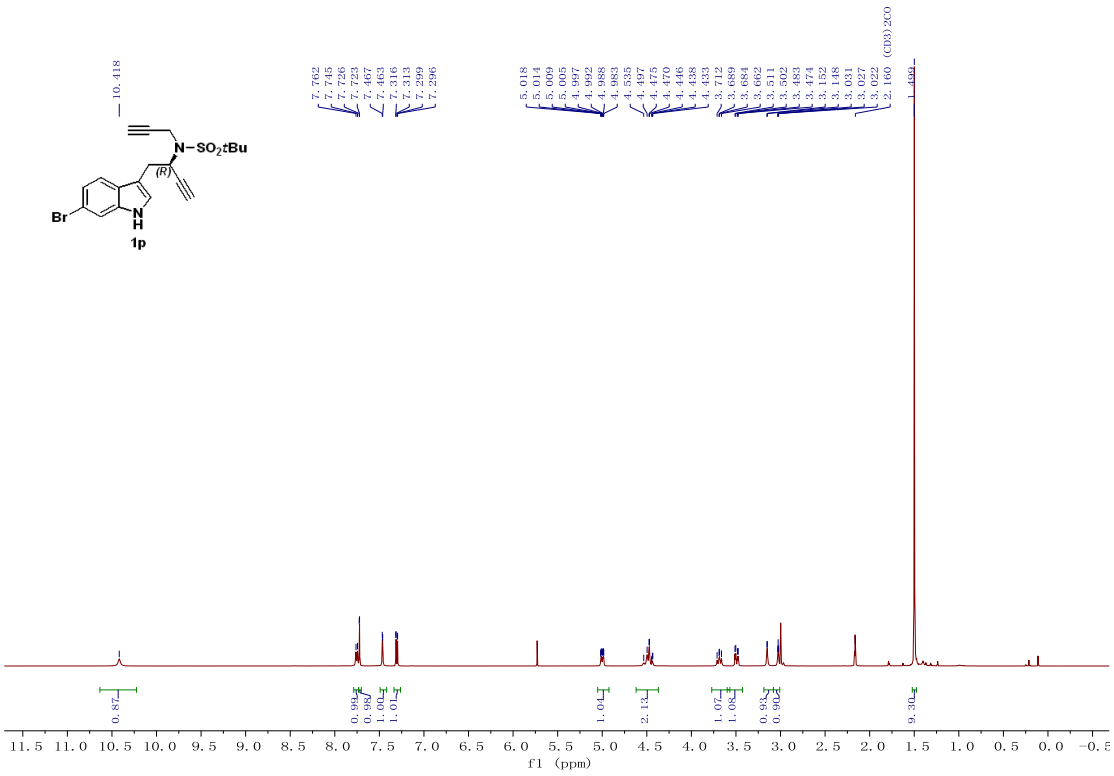

$^{1}$H NMR Spectrum of **1o** (500 MHz, $CDCl_3$)



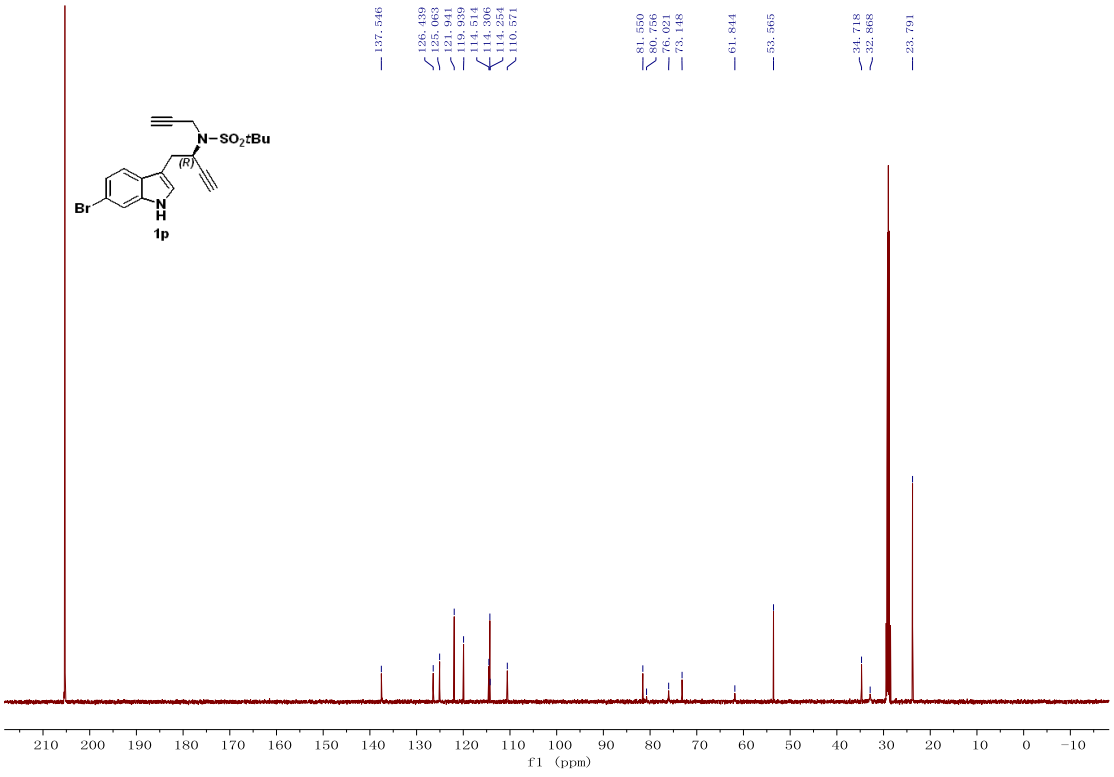
$^{13}$C NMR Spectrum of **1o** (126 MHz, $CDCl_3$)



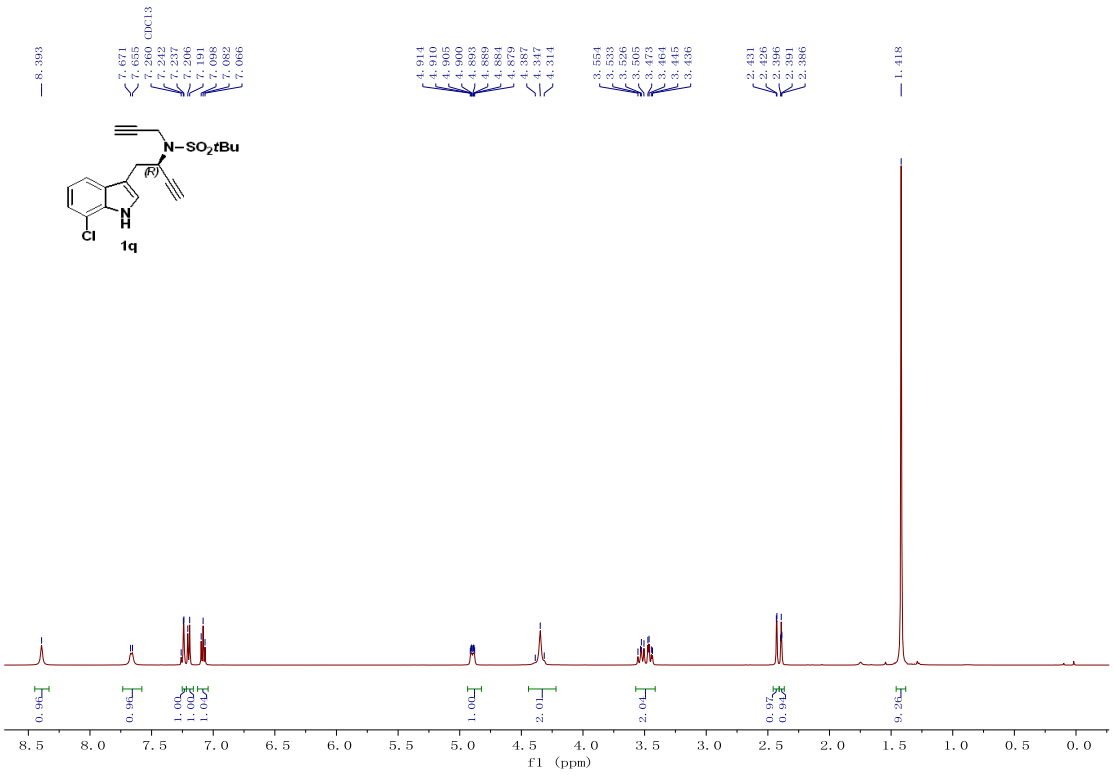

$^{1}$H NMR Spectrum of **1p** (500 MHz, $CDCl_3$)



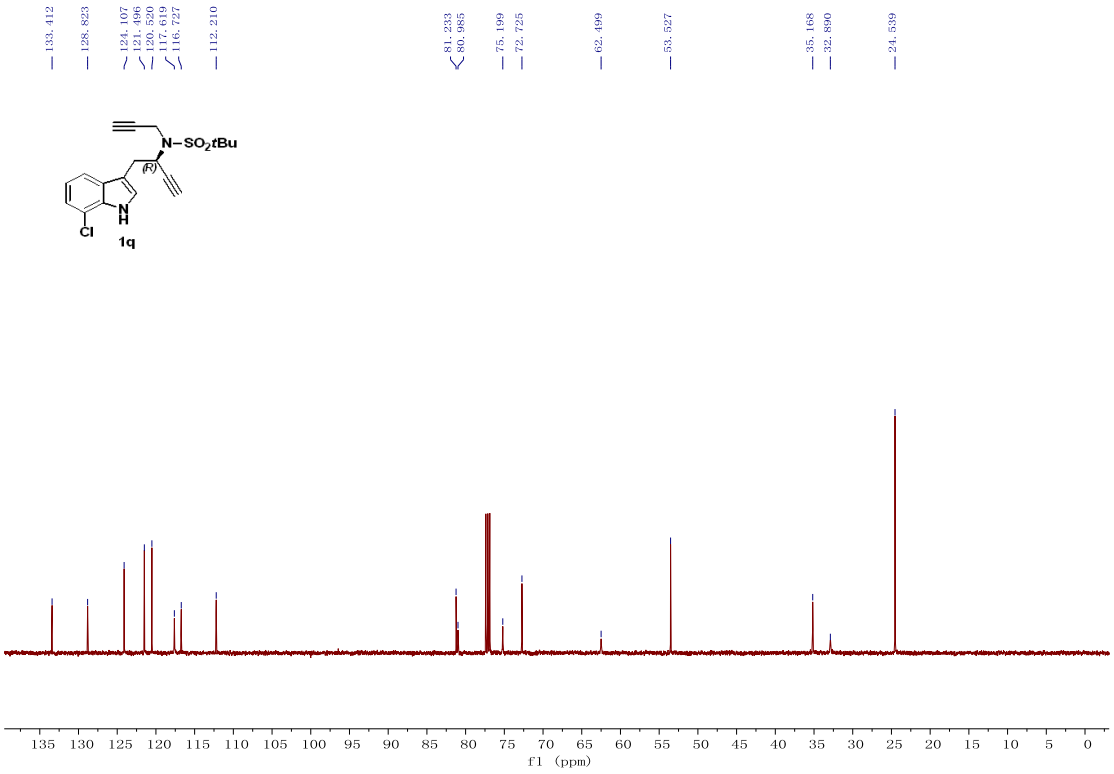

$^{13}$C NMR Spectrum of **1p** (126 MHz, $CDCl_3$)



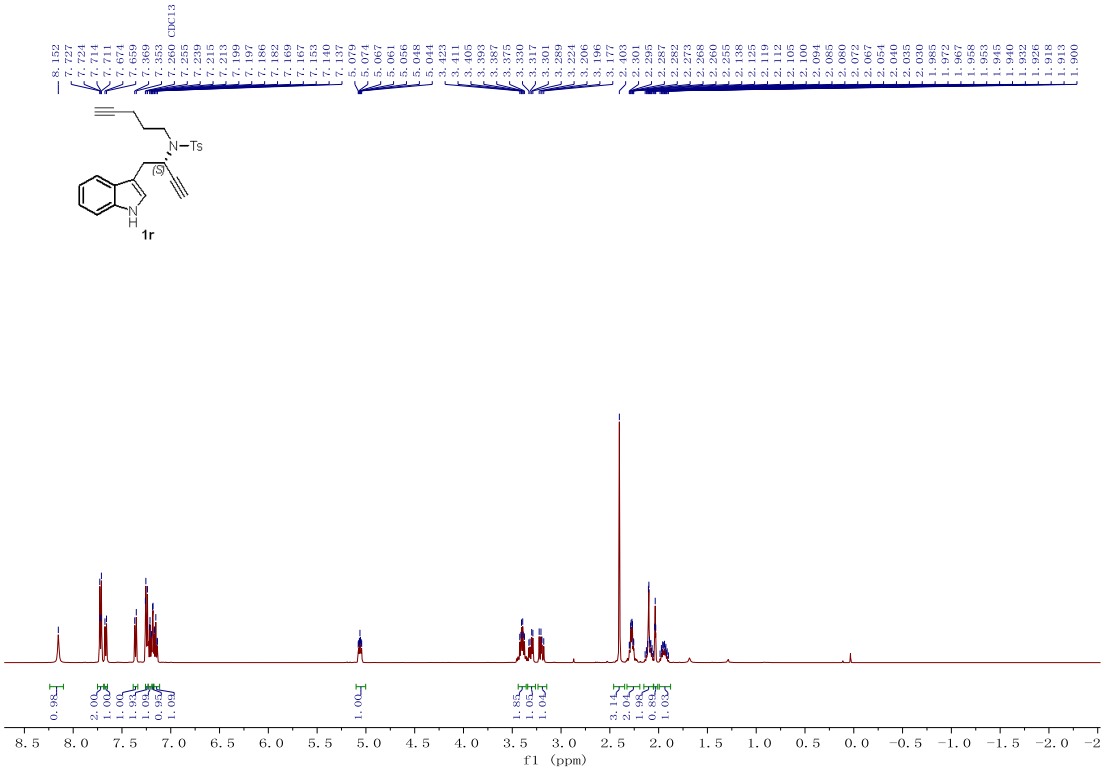
$^{1}$H NMR Spectrum of **1q** (500 MHz, $CDCl_3$)



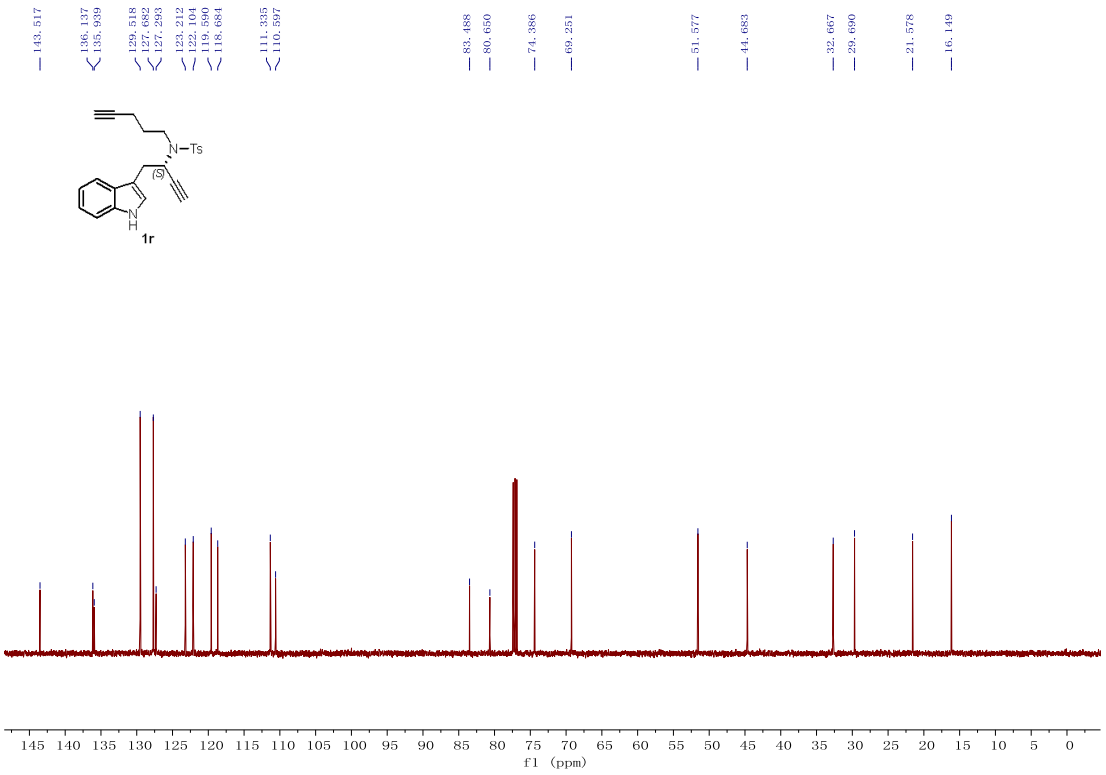

$^{13}$C NMR Spectrum of **1q** (126 MHz, $CDCl_3$)



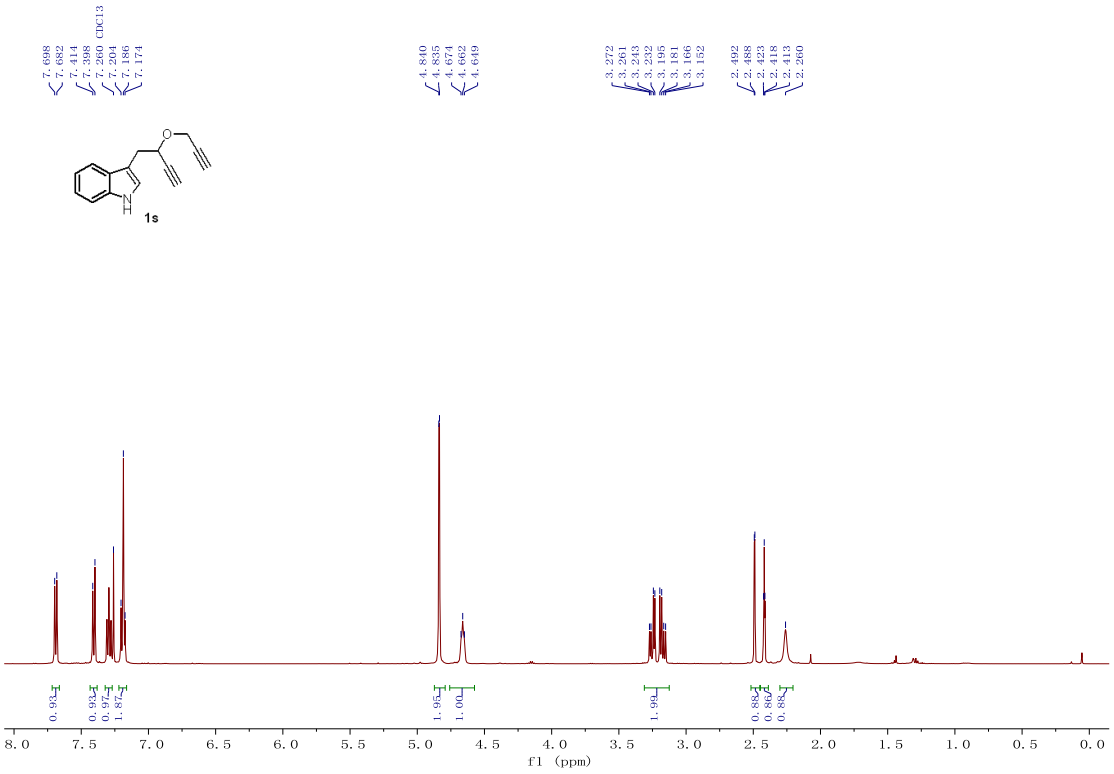

$^{1}$H NMR Spectrum of **1r** (500 MHz, $CDCl_3$)



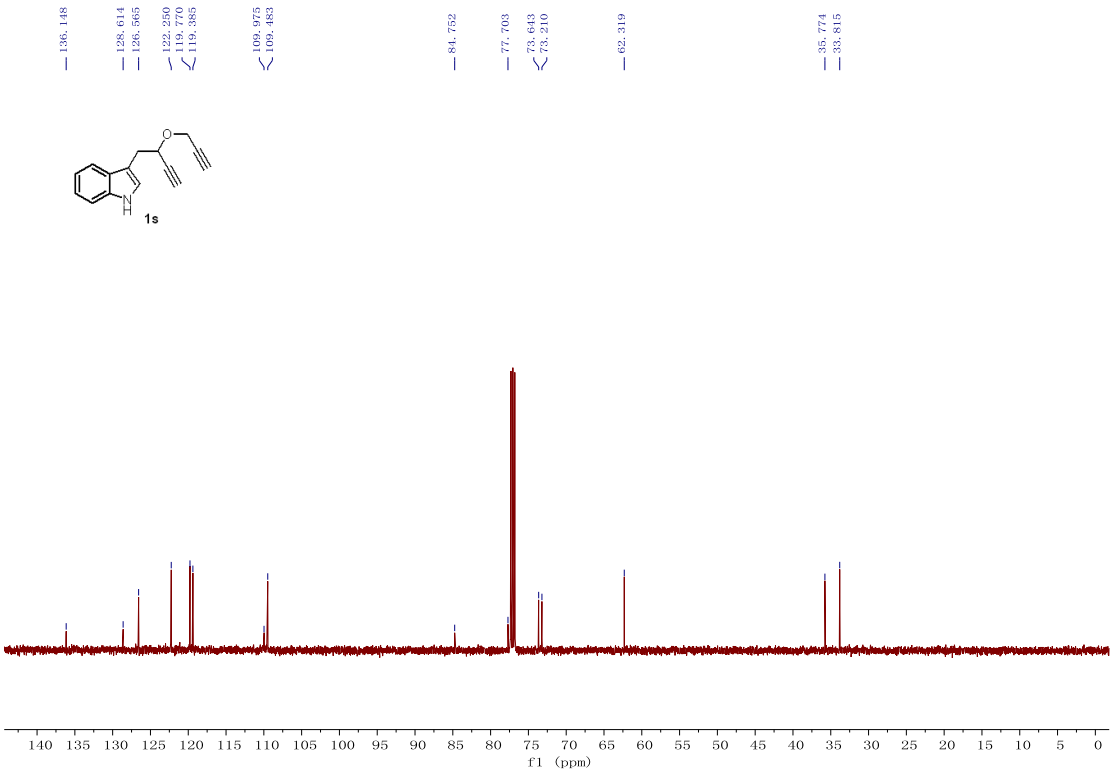
$^{13}$C NMR Spectrum of **1r** (126 MHz, $CDCl_3$)



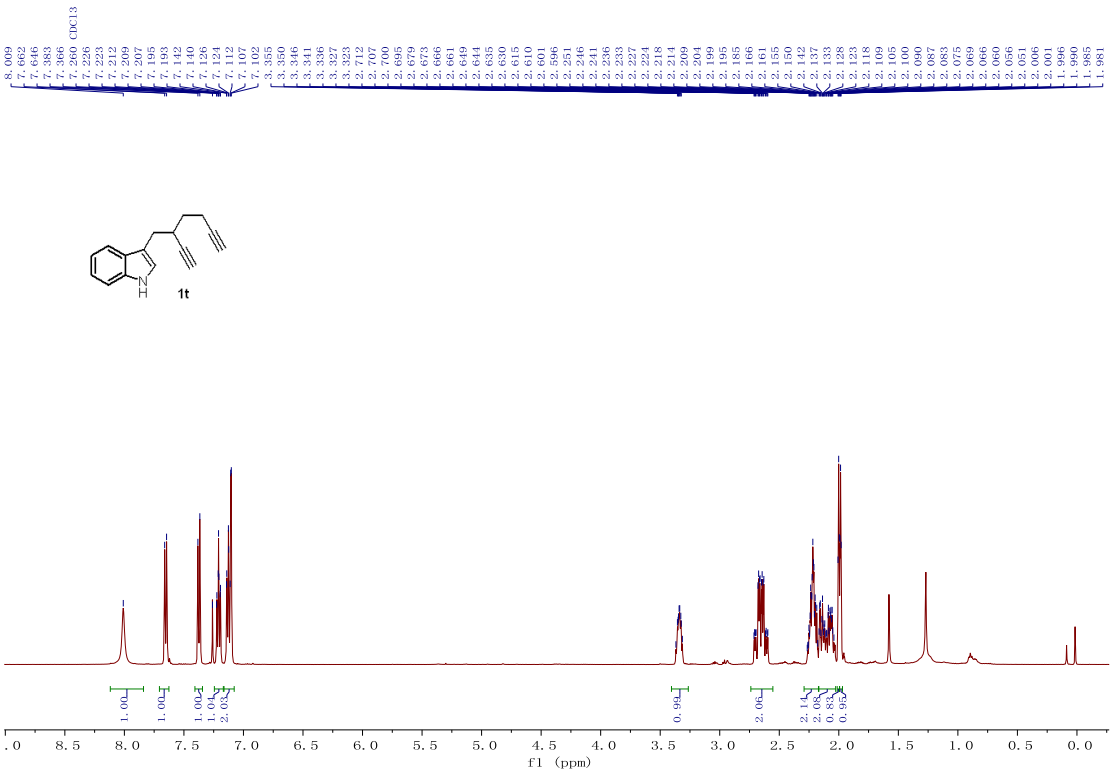

$^{1}$H NMR Spectrum of **1s** (500 MHz, $CDCl_3$)



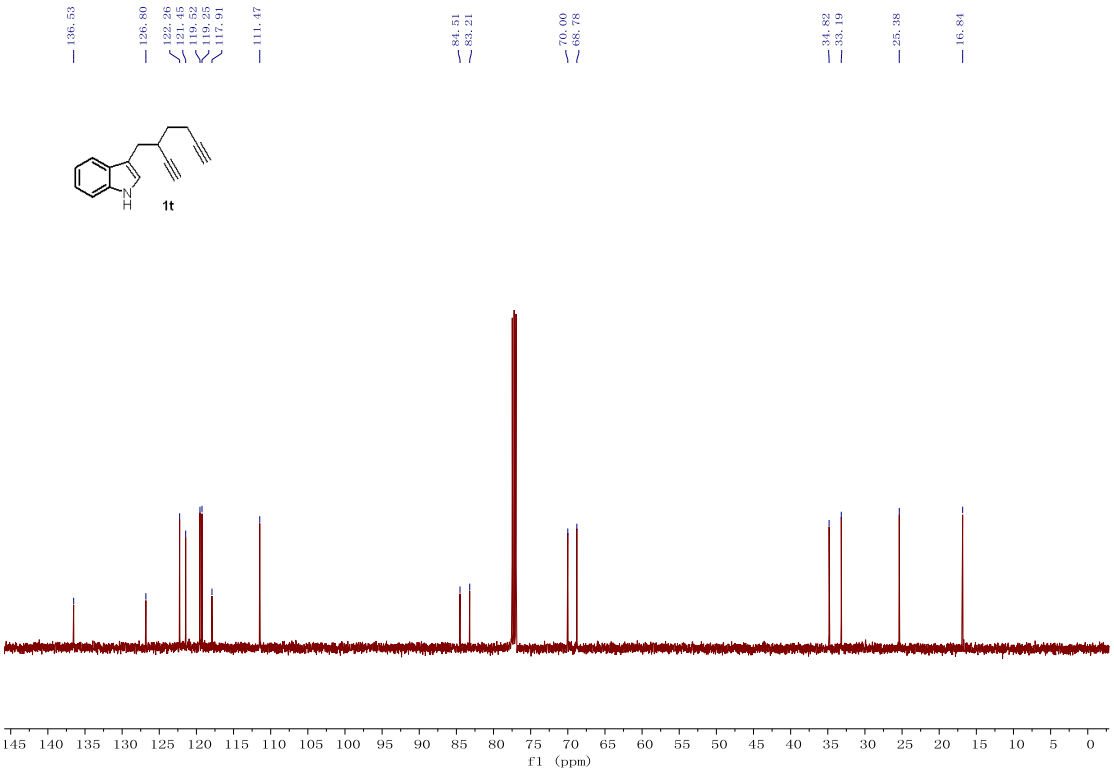

$^{13}$C NMR Spectrum of **1S** (126 MHz, $CDCl_3$)



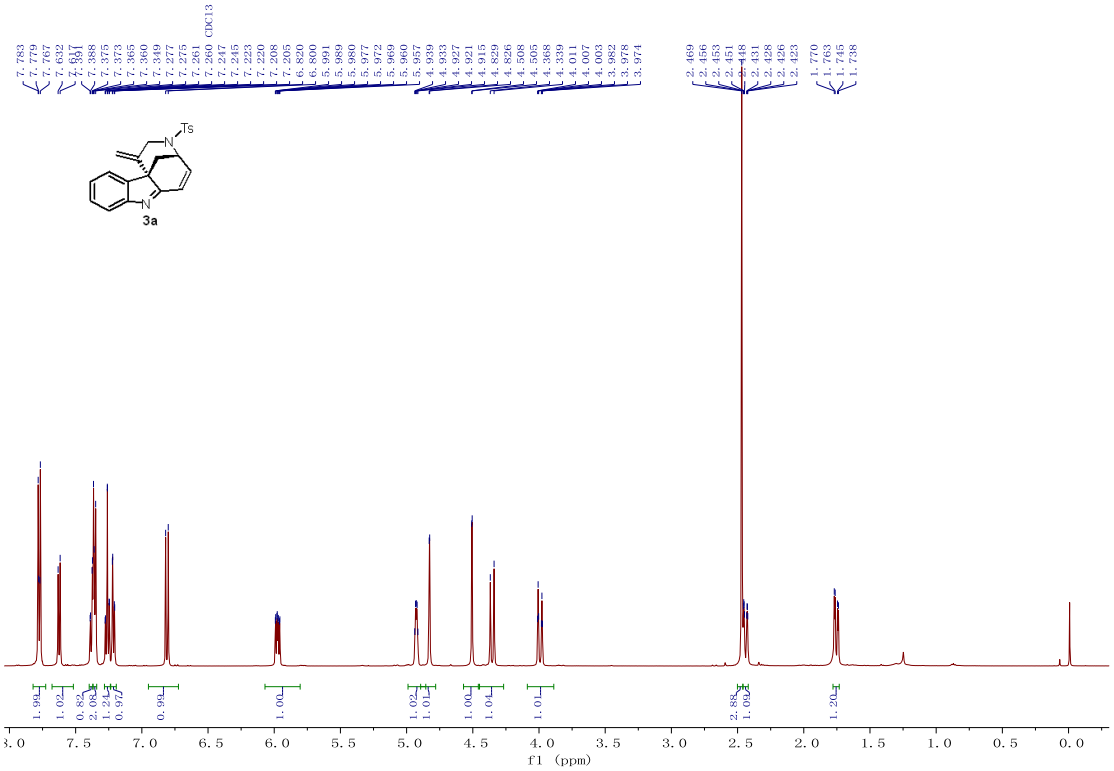
$^{1}$H NMR Spectrum of **1t** (500 MHz, $CDCl_3$)



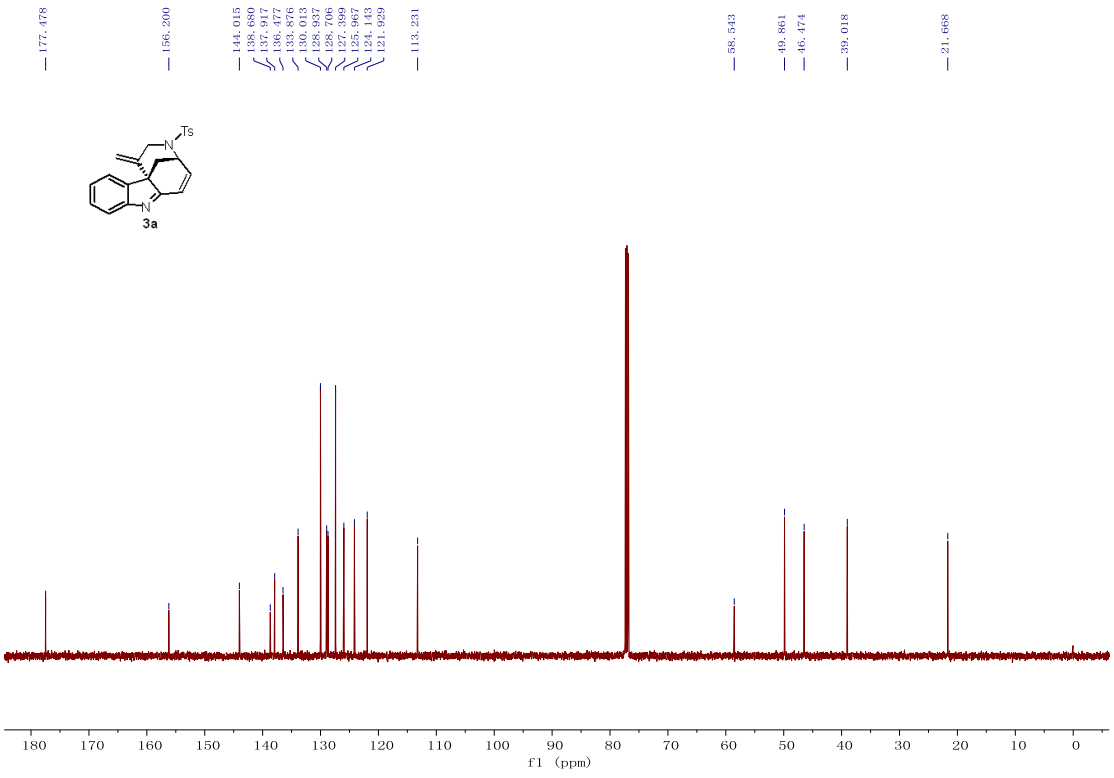

$^{13}$C NMR Spectrum of **1t** (126 MHz, $CDCl_3$)



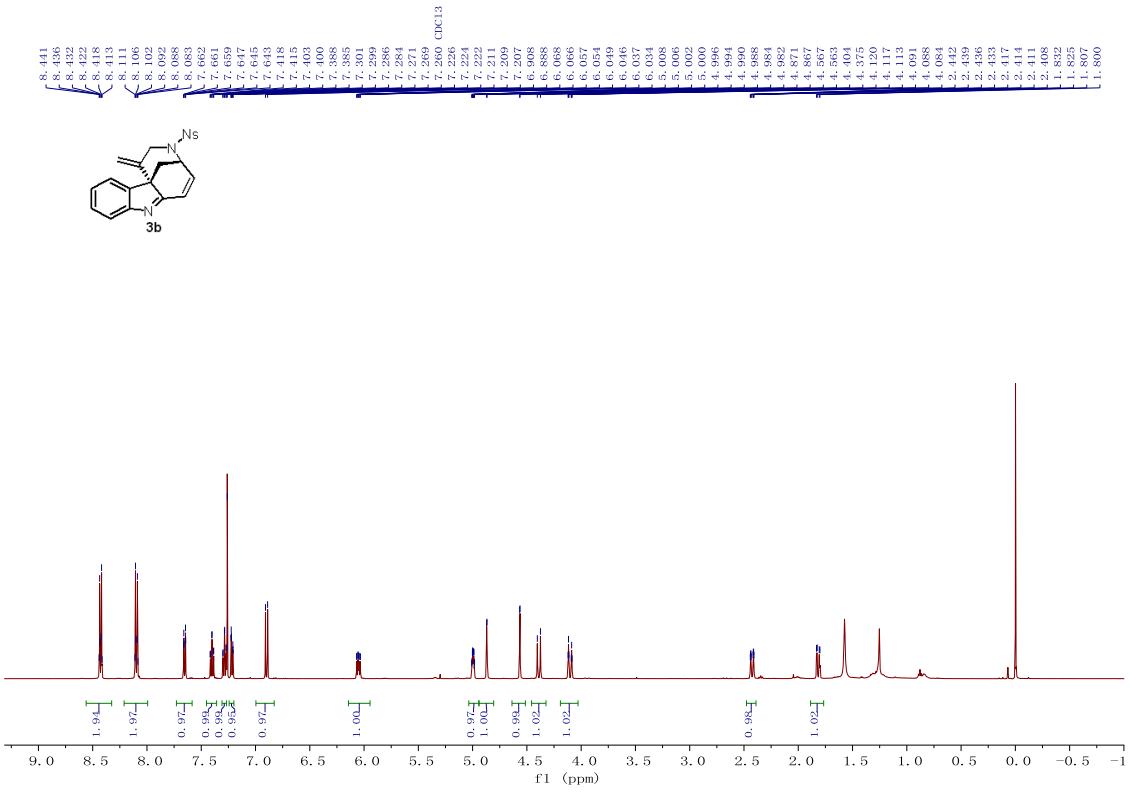

$^{1}$H NMR Spectrum of **3a** (500 MHz, $CDCl_3$)



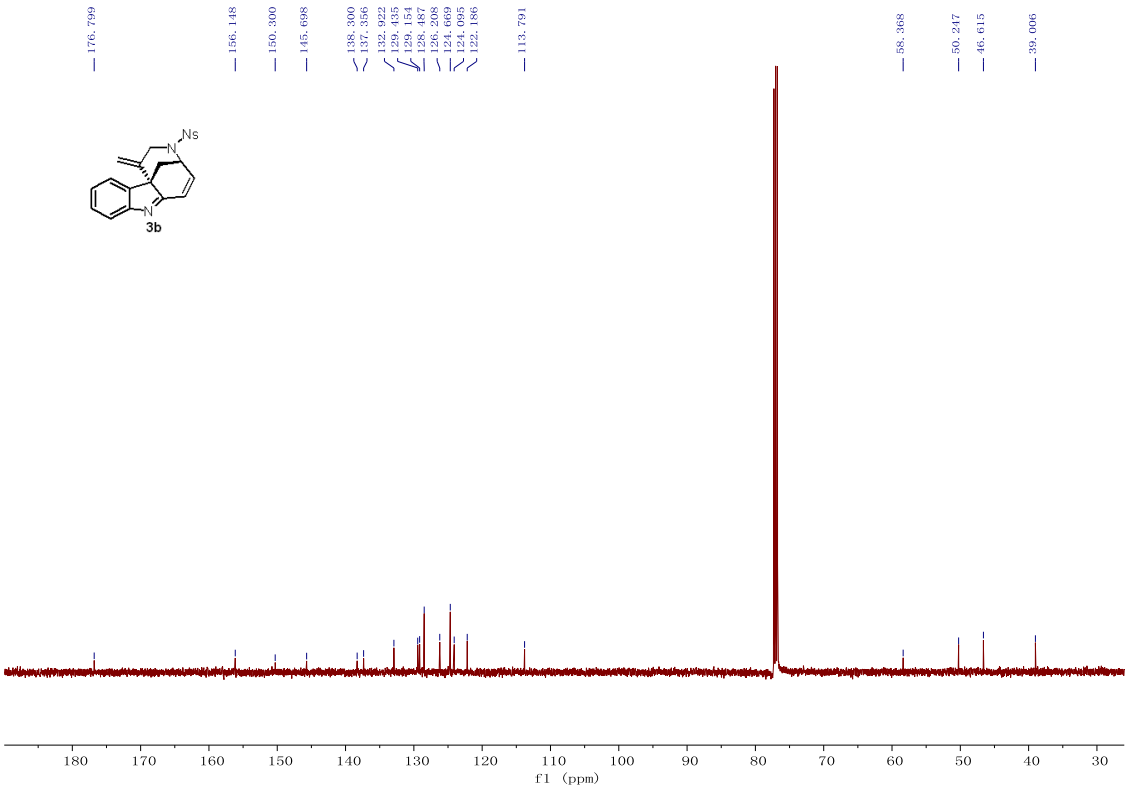
$^{13}$C NMR Spectrum of **3a** (126 MHz, $CDCl_3$)



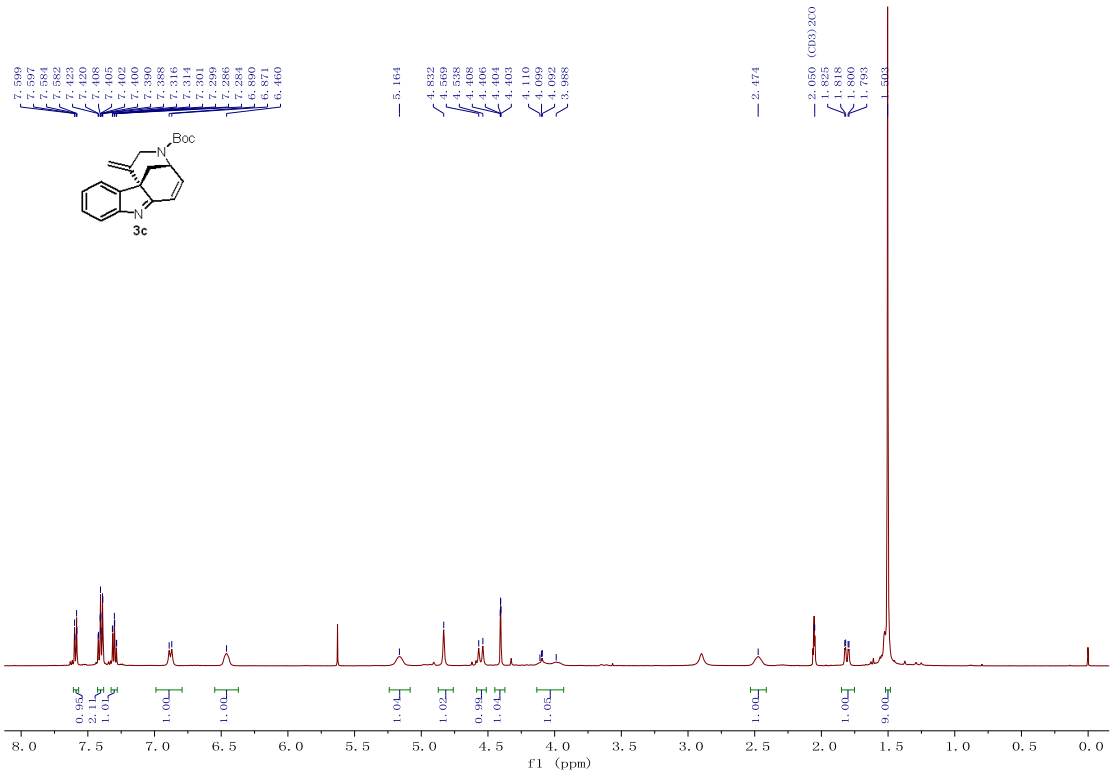

$^{1}$H NMR Spectrum of **3b** (500 MHz, $CDCl_3$)



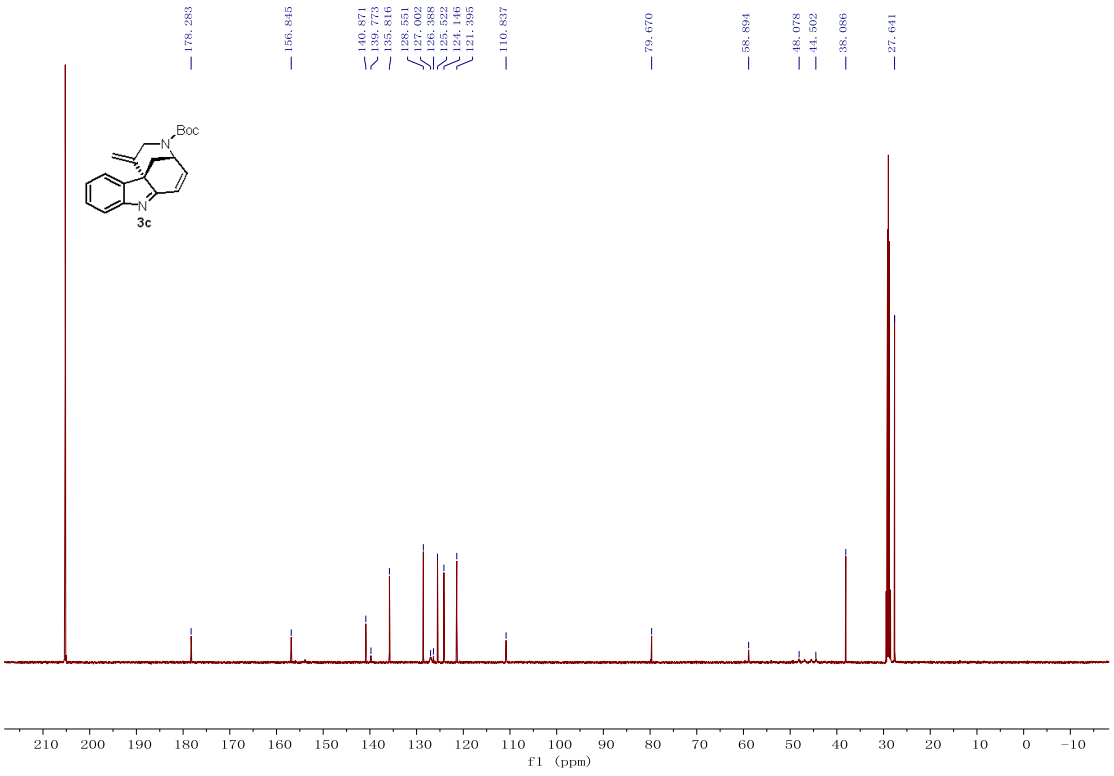

$^{13}$C NMR Spectrum of **3b** (126 MHz, $CDCl_3$)



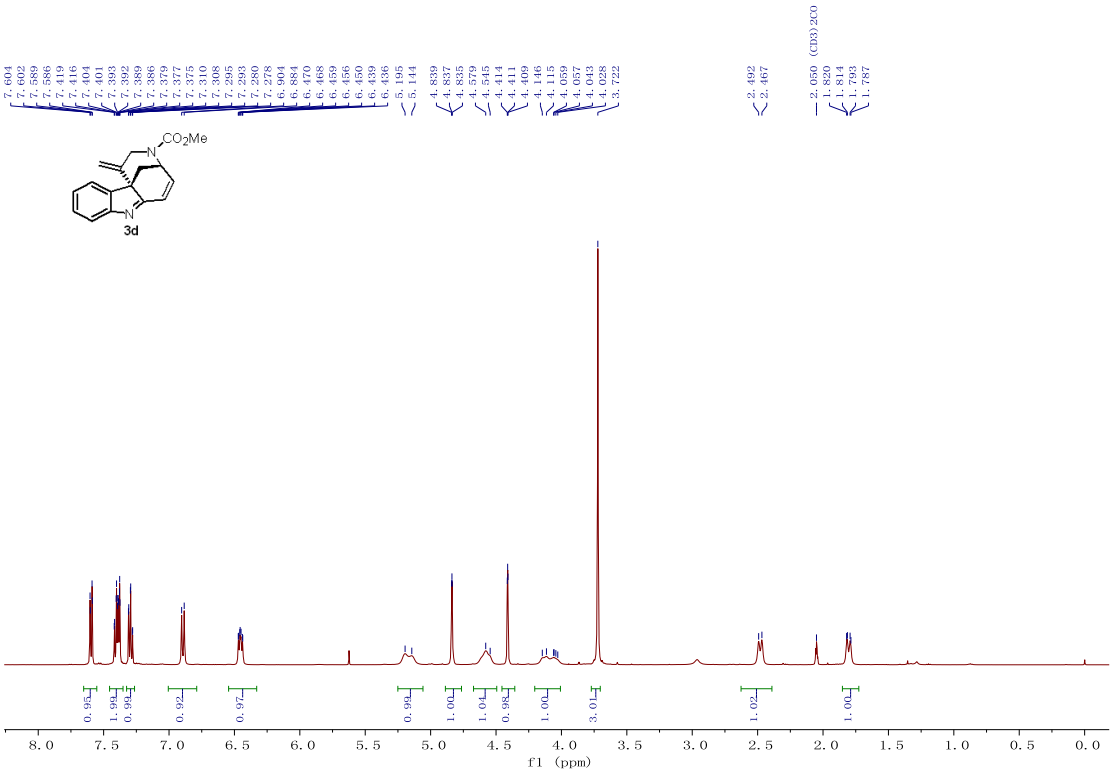

$^1$H NMR Spectrum of **3c** (500 MHz, Acetone-$d_6$)



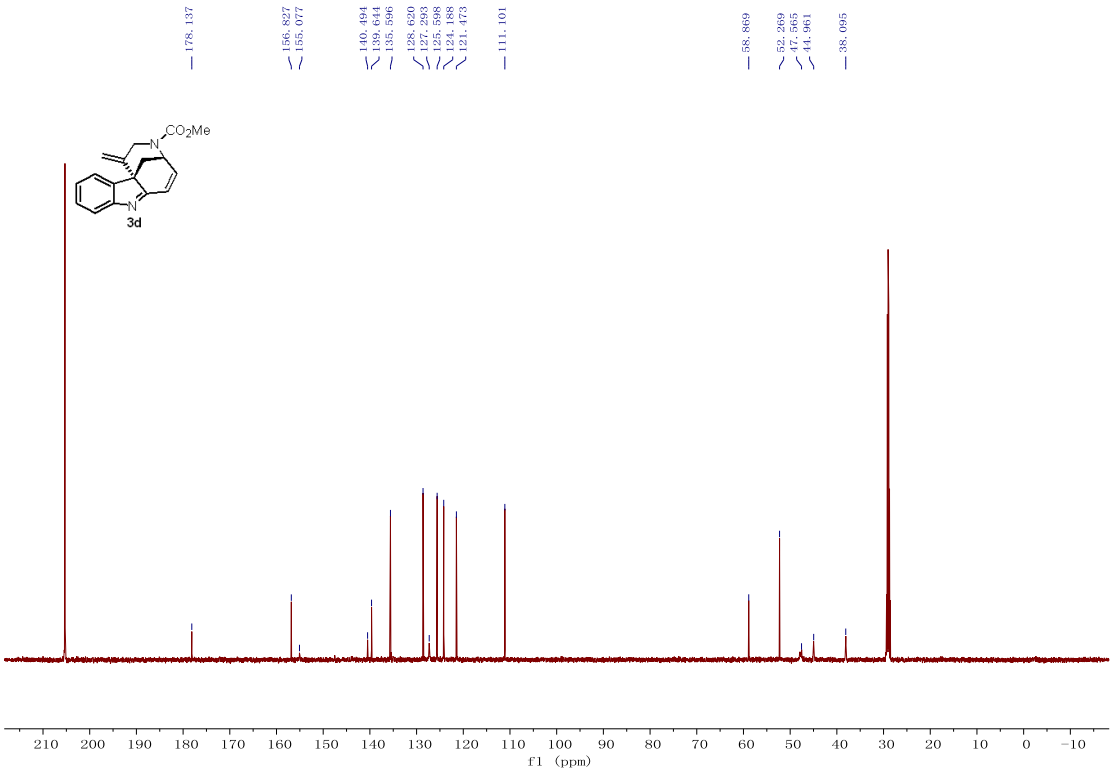

$^{13}$C NMR Spectrum of **3c** (126 MHz, Acetone-$d_6$)



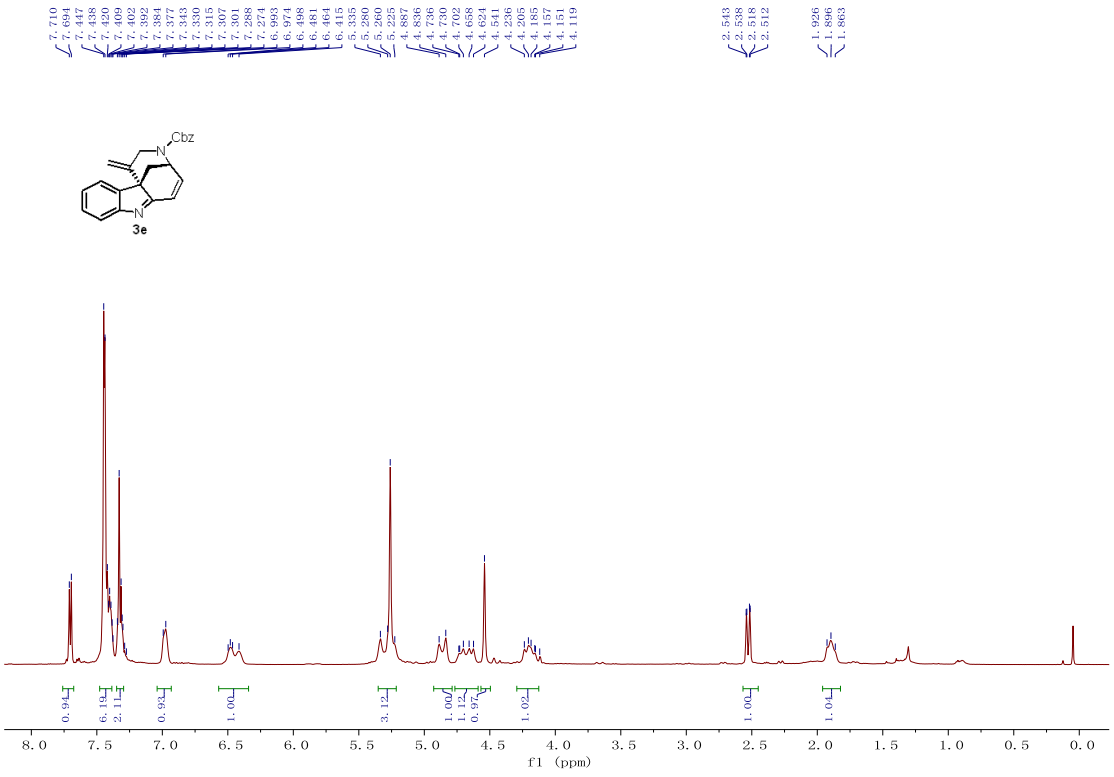
$^{1}$H NMR Spectrum of **3d** (500 MHz, Acetone-$d_6$)



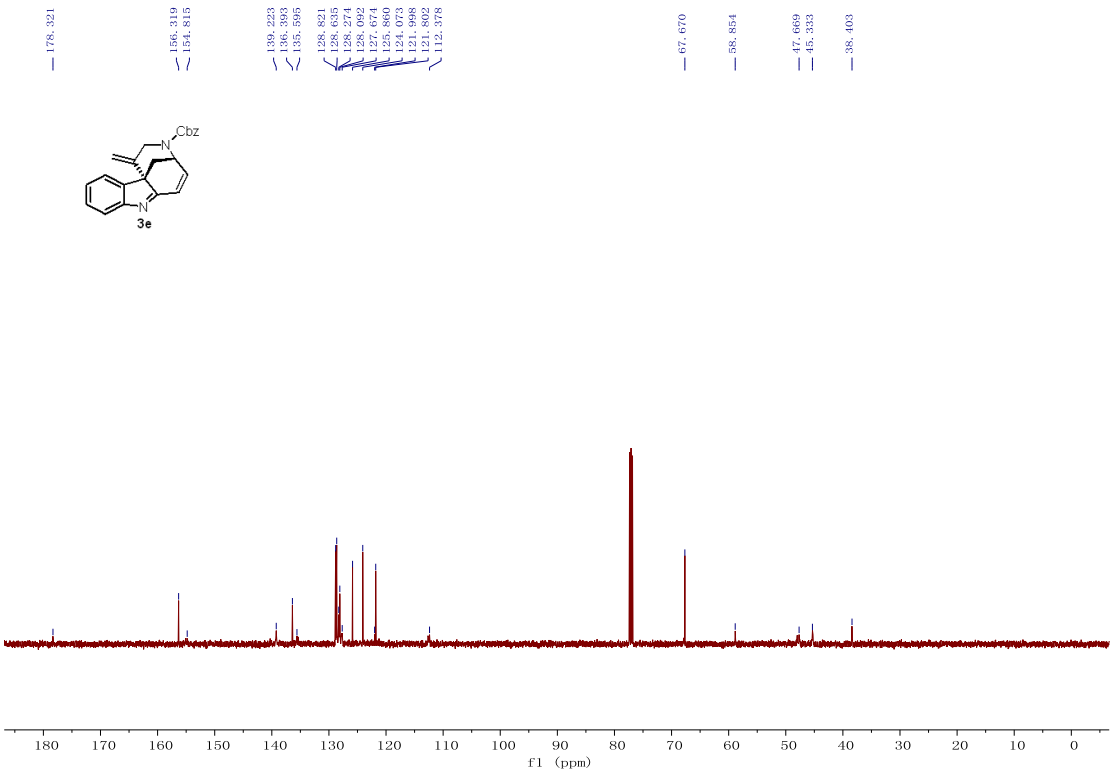

$^{13}$C NMR Spectrum of **3d** (126 MHz, Acetone-$d_6$)



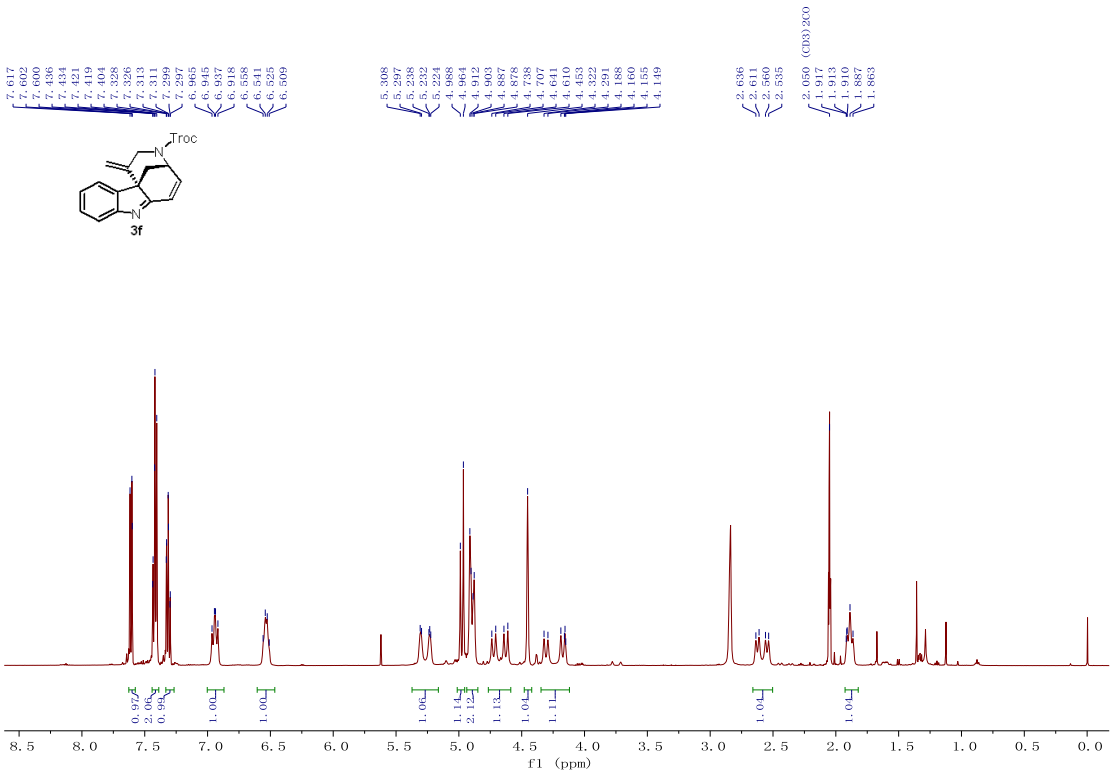

$^{1}$H NMR Spectrum of **3e** (500 MHz, $CDCl_3$)



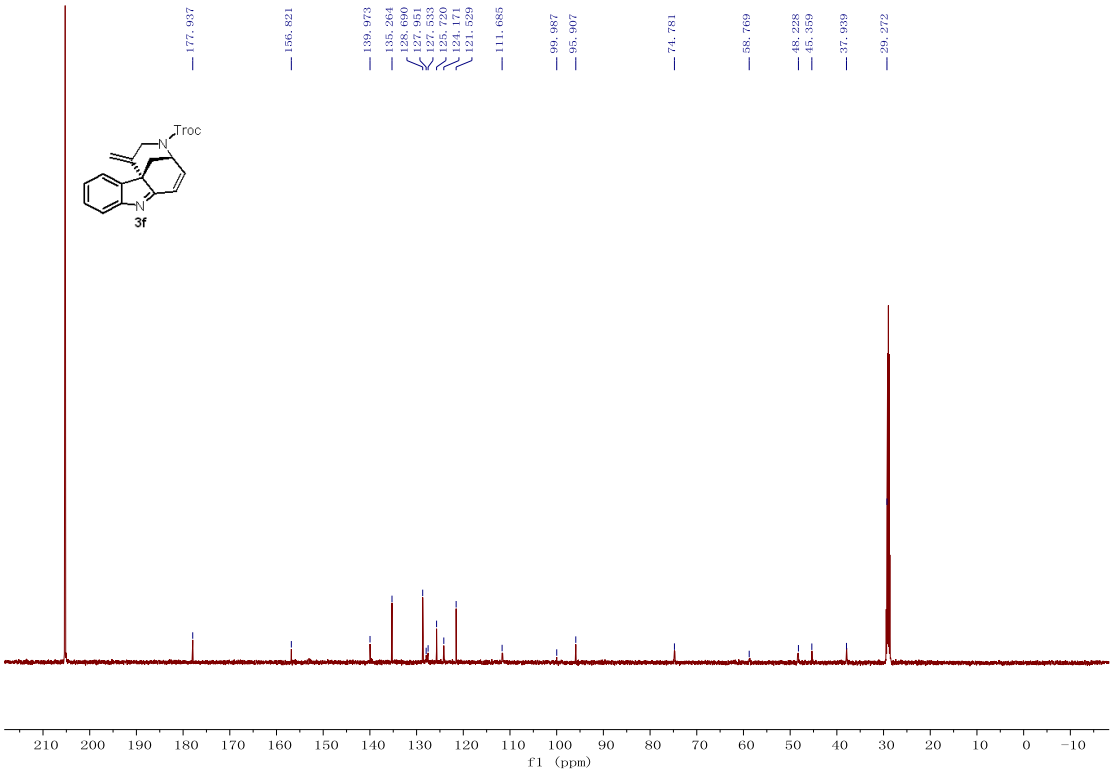
$^{13}$C NMR Spectrum of **3e** (126 MHz, $CDCl_3$)



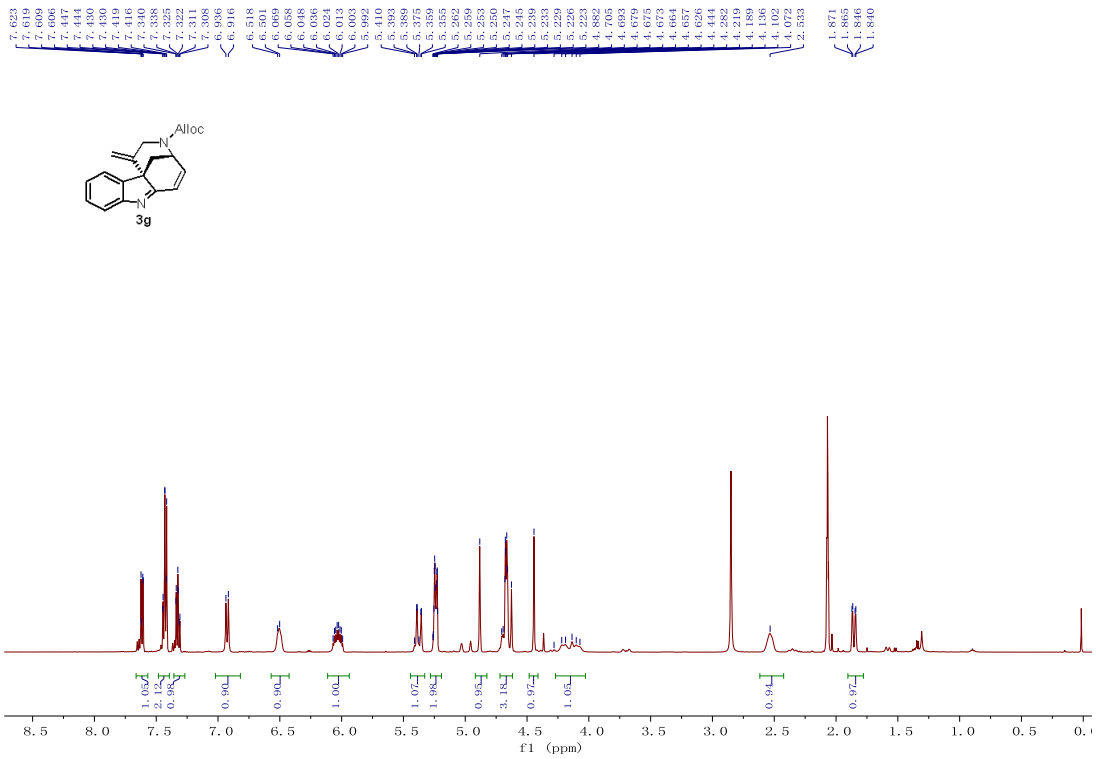

$^{1}$H NMR Spectrum of **3f** (500 MHz, Acetone-$d_6$)



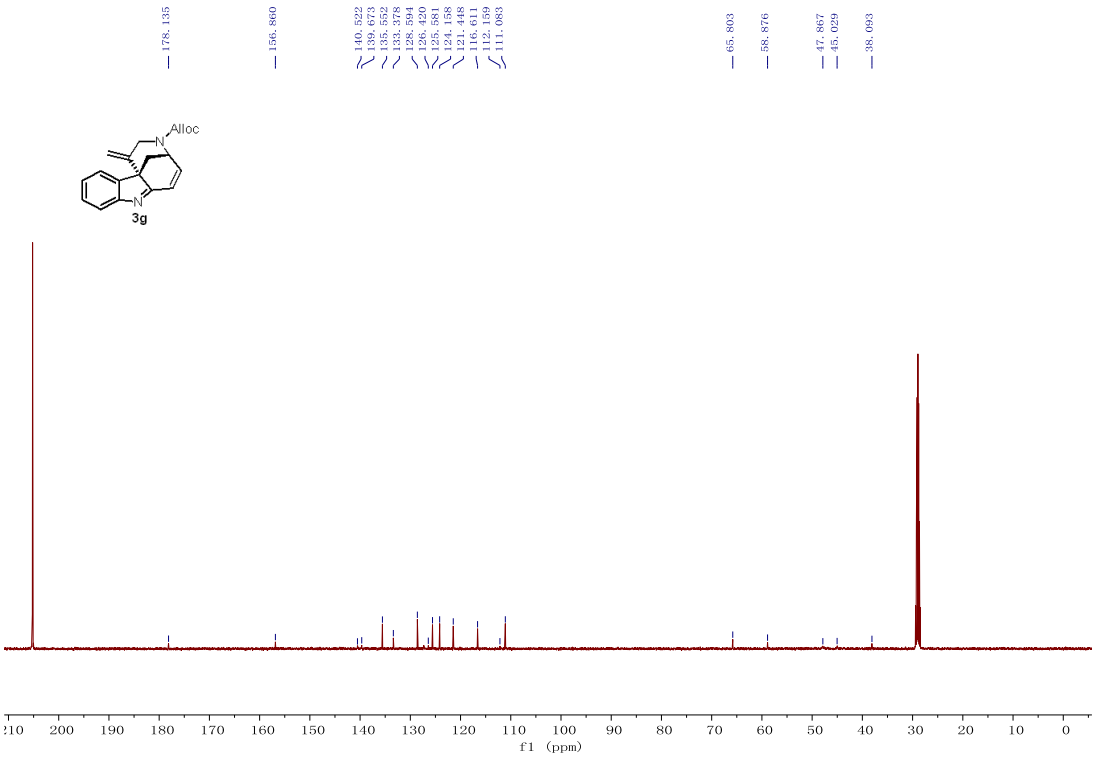

$^{13}$C NMR Spectrum of **3f** (126 MHz, Acetone-$d_6$)



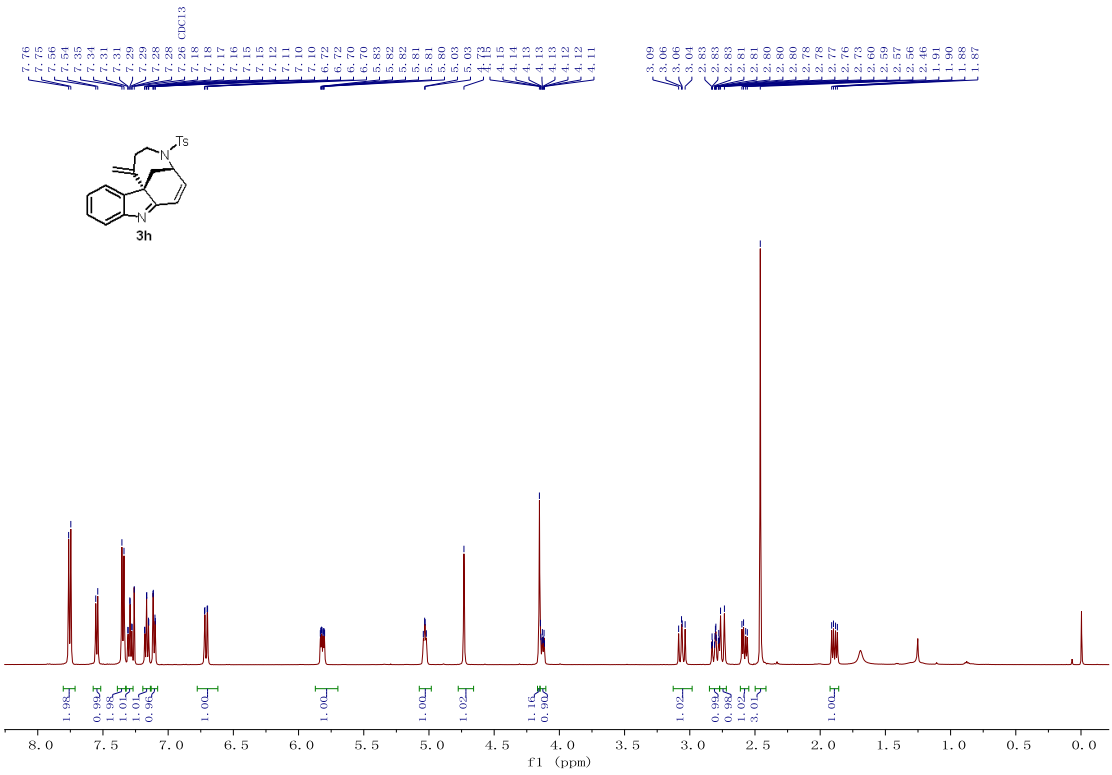
$^{1}$H NMR Spectrum of **3g** (500 MHz, Acetone-$d_6$)



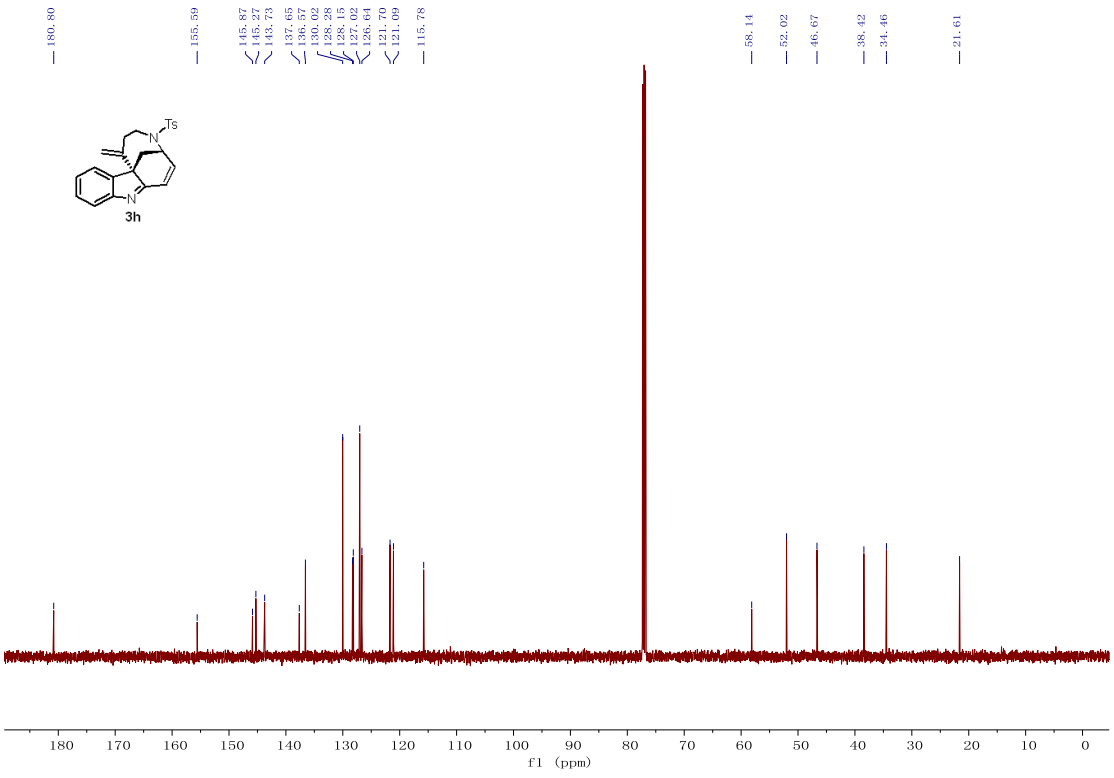

$^{13}$C NMR Spectrum of **3g** (126 MHz, Acetone-$d_6$)



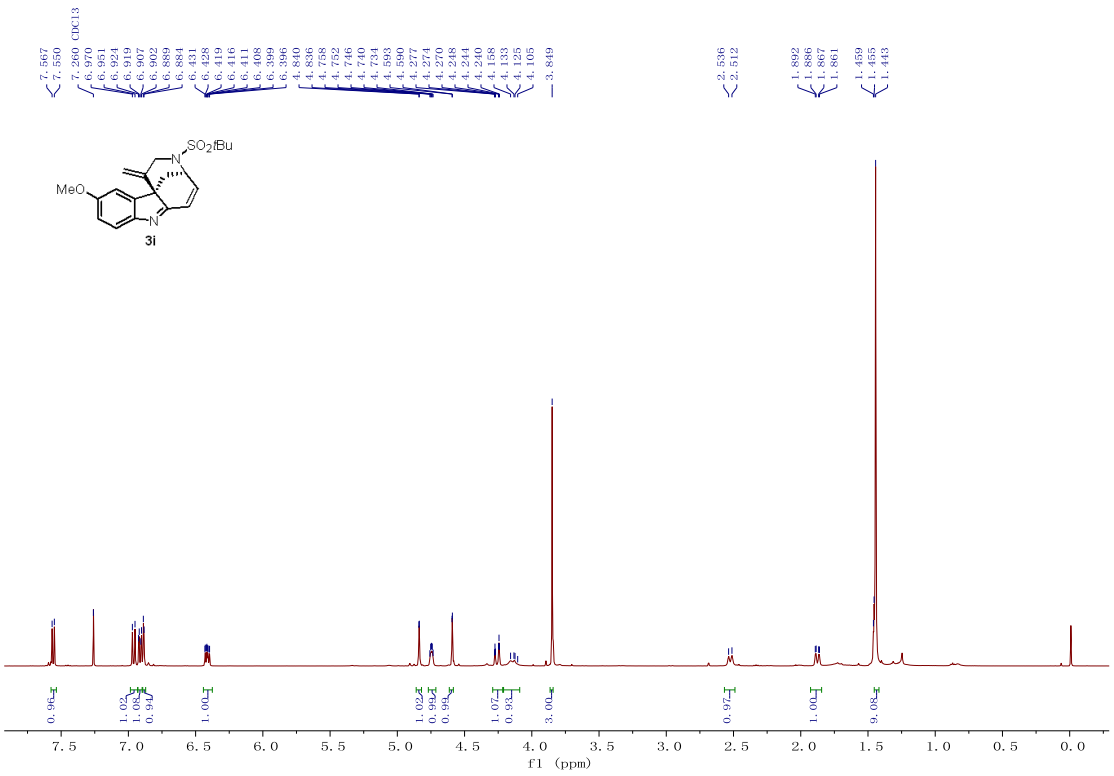

$^{1}$H NMR Spectrum of **3h** (500 MHz, $CDCl_3$)



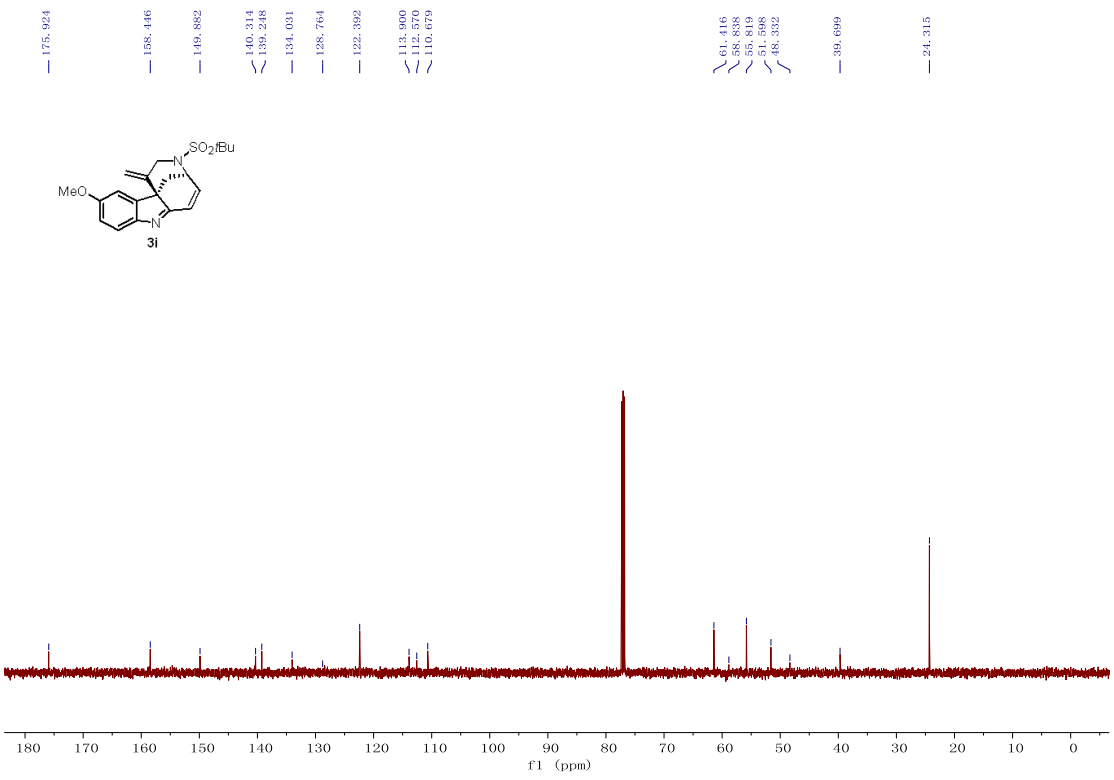
$^{13}$C NMR Spectrum of **3h** (126 MHz, $CDCl_3$)



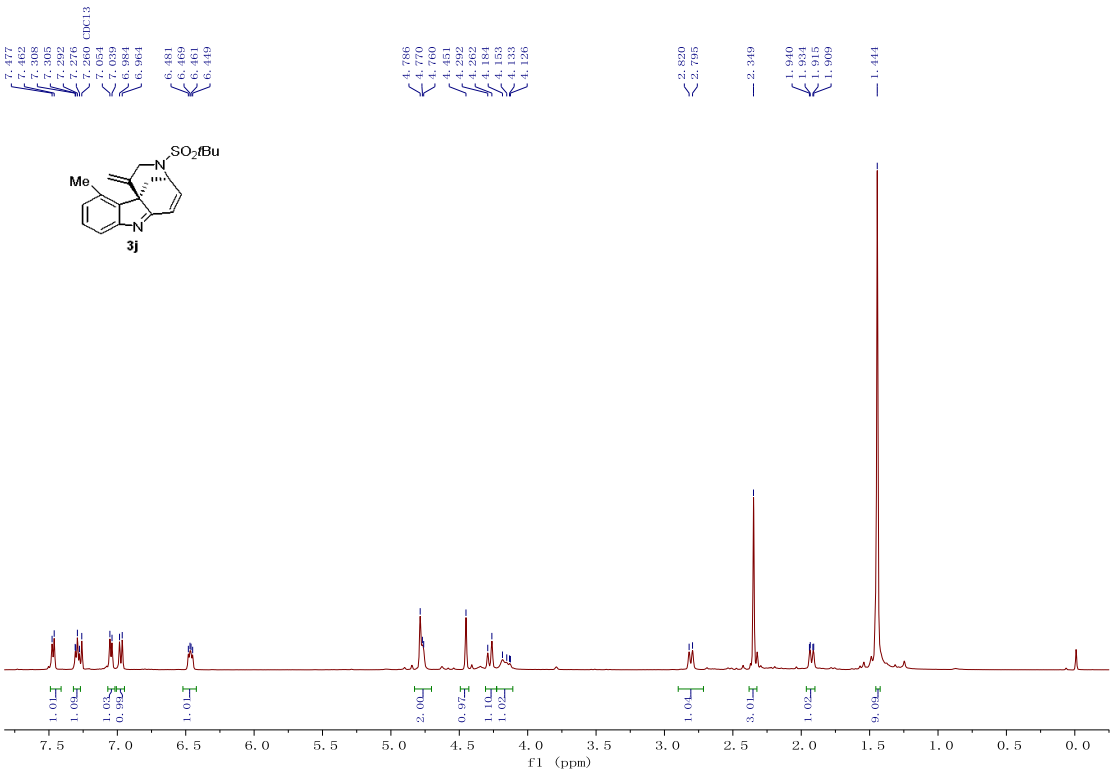

$^{1}$H NMR Spectrum of **3i** (500 MHz, $CDCl_3$)



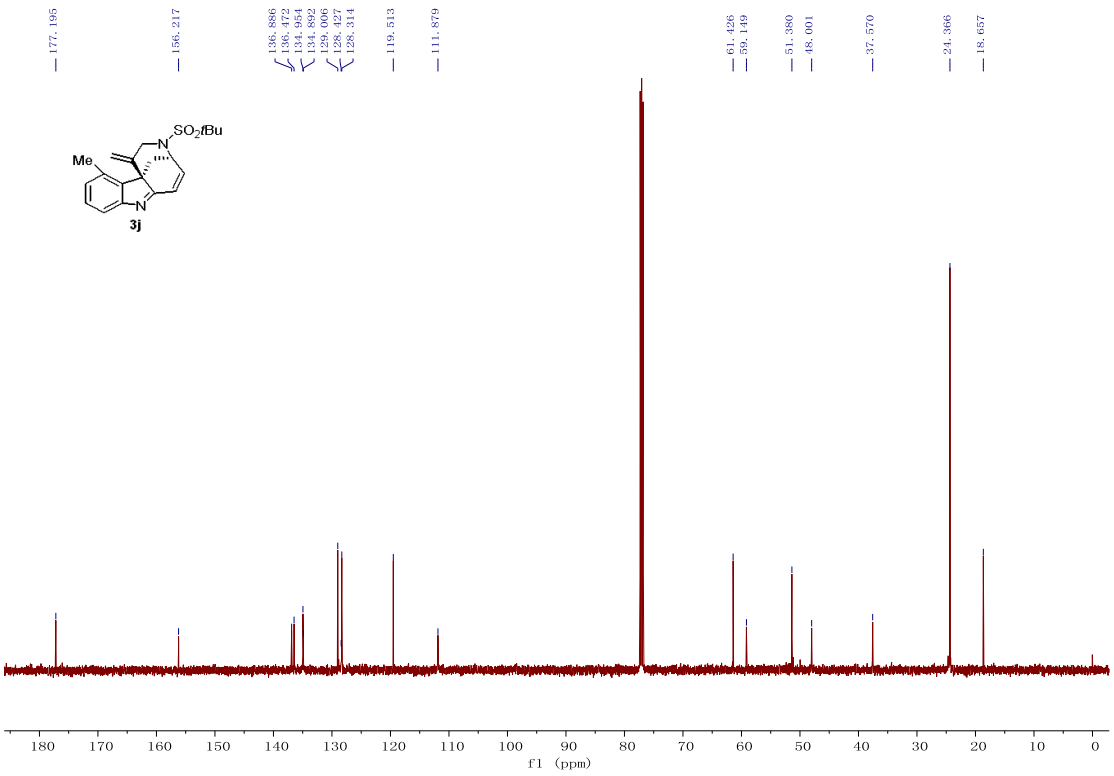

$^{13}$C NMR Spectrum of **3i** (126 MHz, $CDCl_3$)



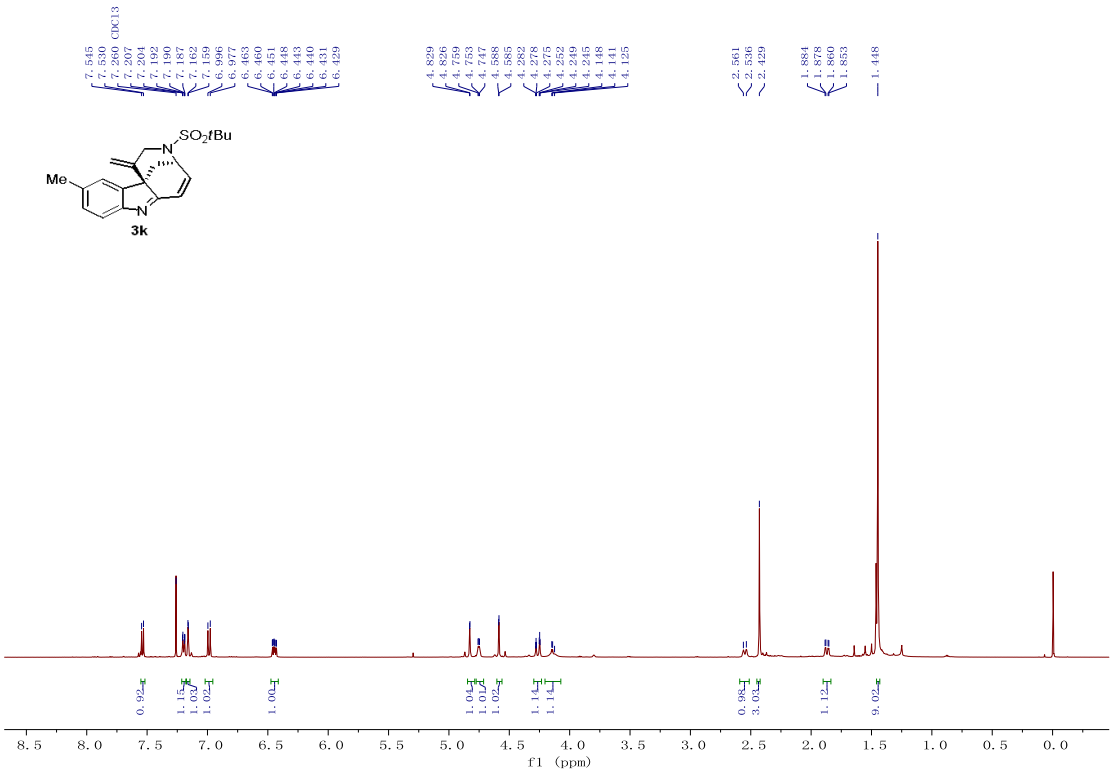
$^{1}$H NMR Spectrum of **3j** (500 MHz, $CDCl_3$)



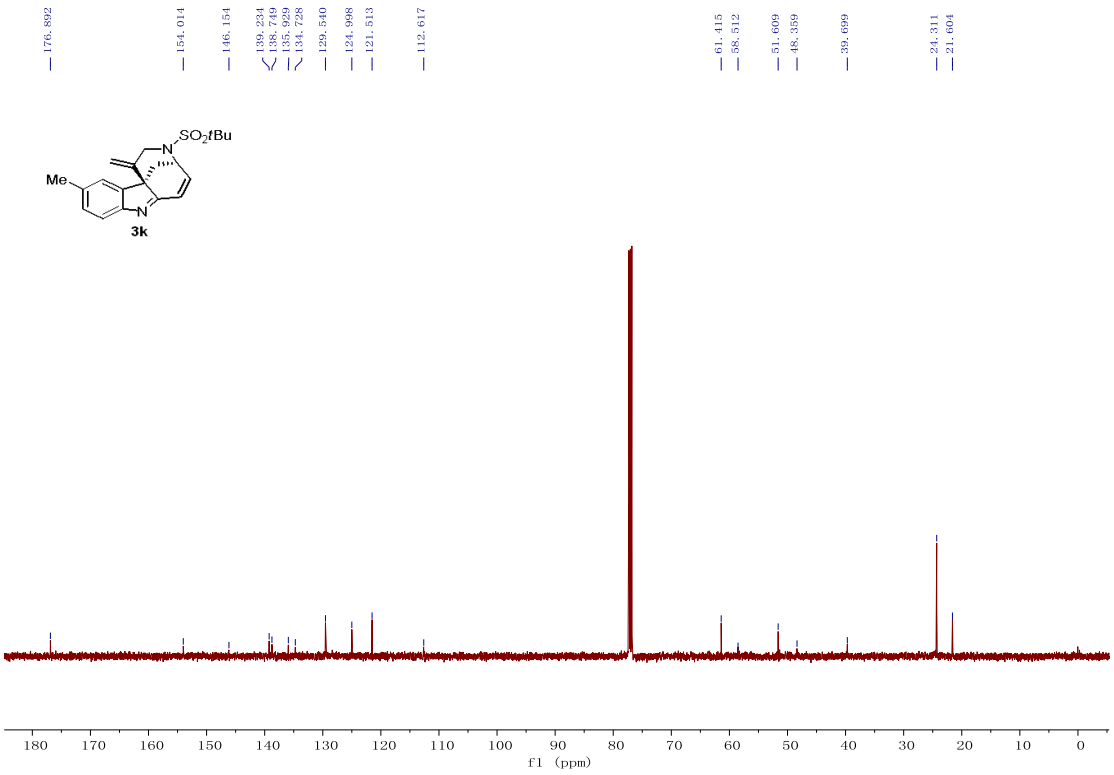

$^{13}$C NMR Spectrum of **3j** (126 MHz, $CDCl_3$)



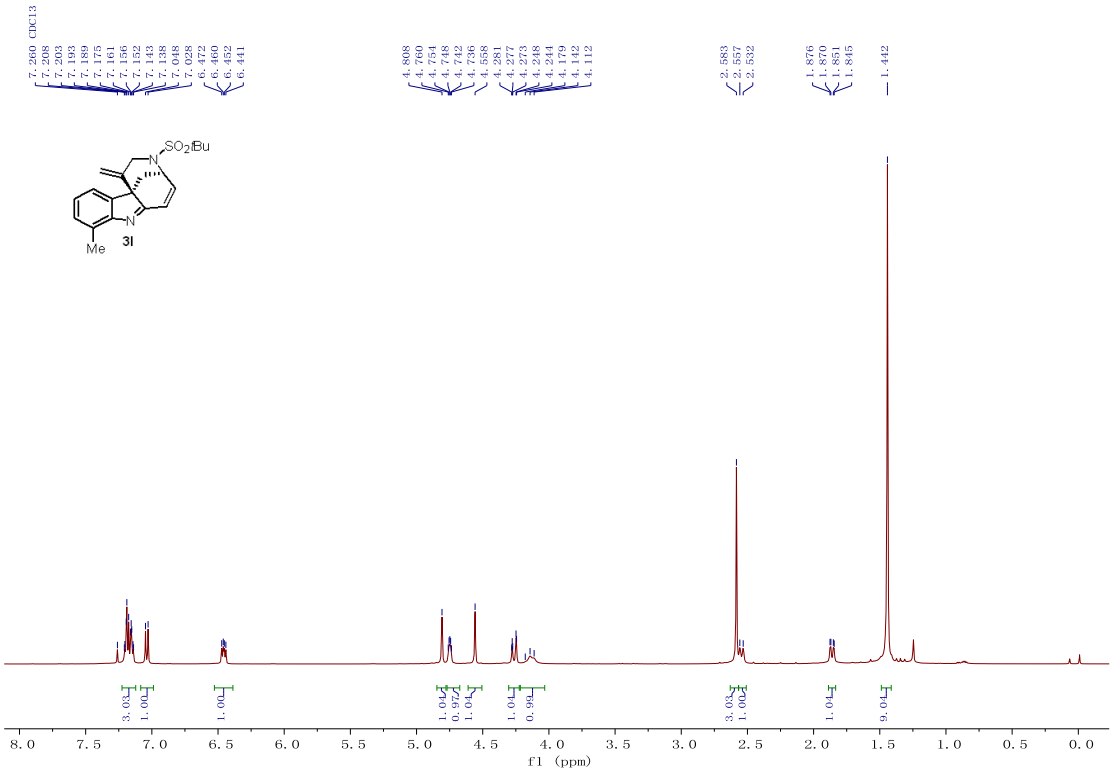

$^{1}$H NMR Spectrum of **3k** (500 MHz, $CDCl_3$)



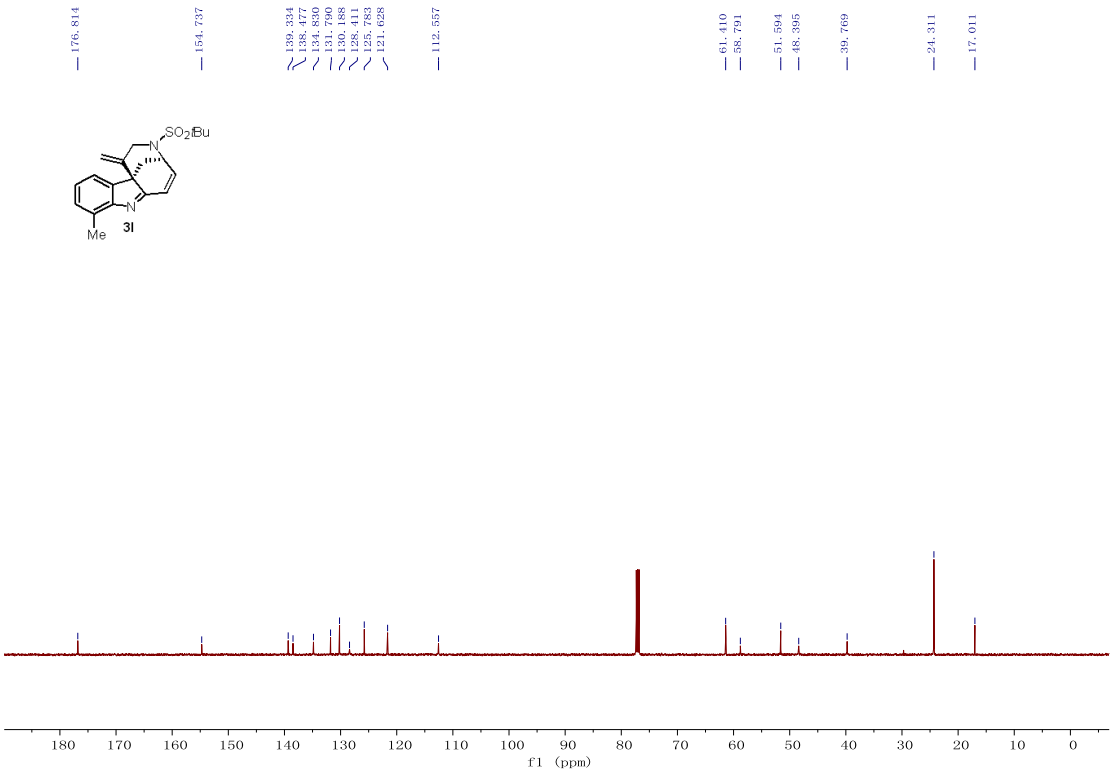
$^{13}$C NMR Spectrum of **3k** (126 MHz, $CDCl_3$)



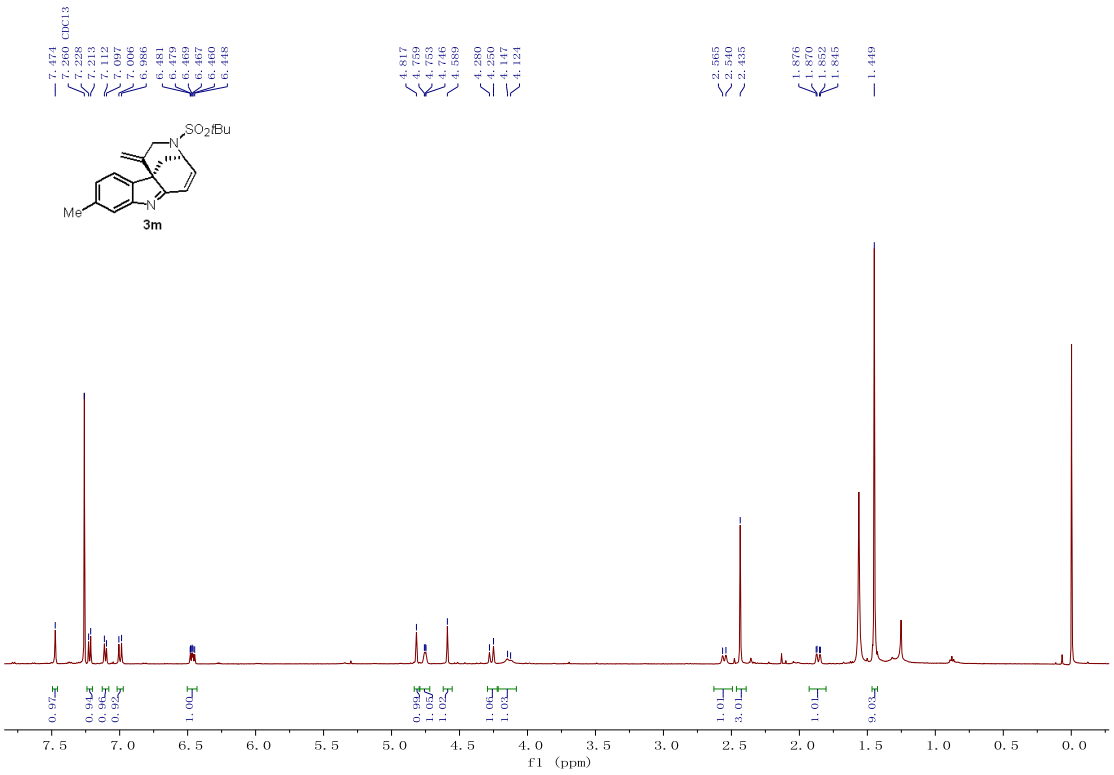

$^{1}$H NMR Spectrum of **3l** (500 MHz, $CDCl_3$)



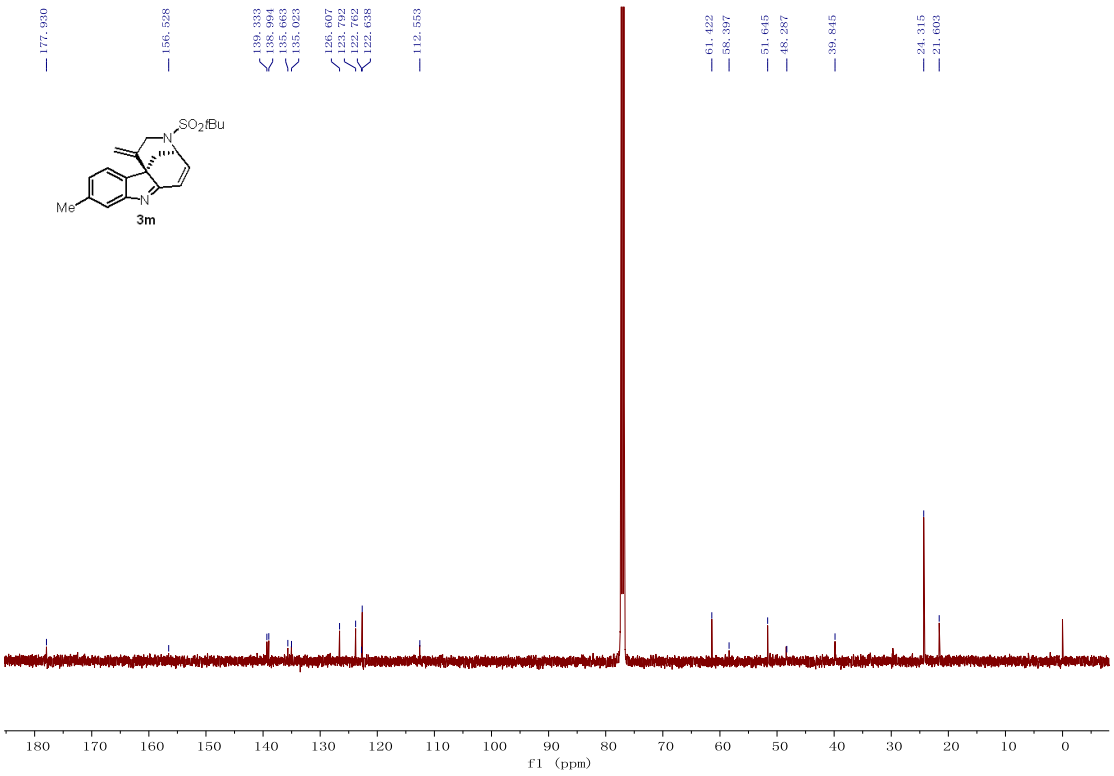

$^{13}$C NMR Spectrum of **3l** (126 MHz, $CDCl_3$)



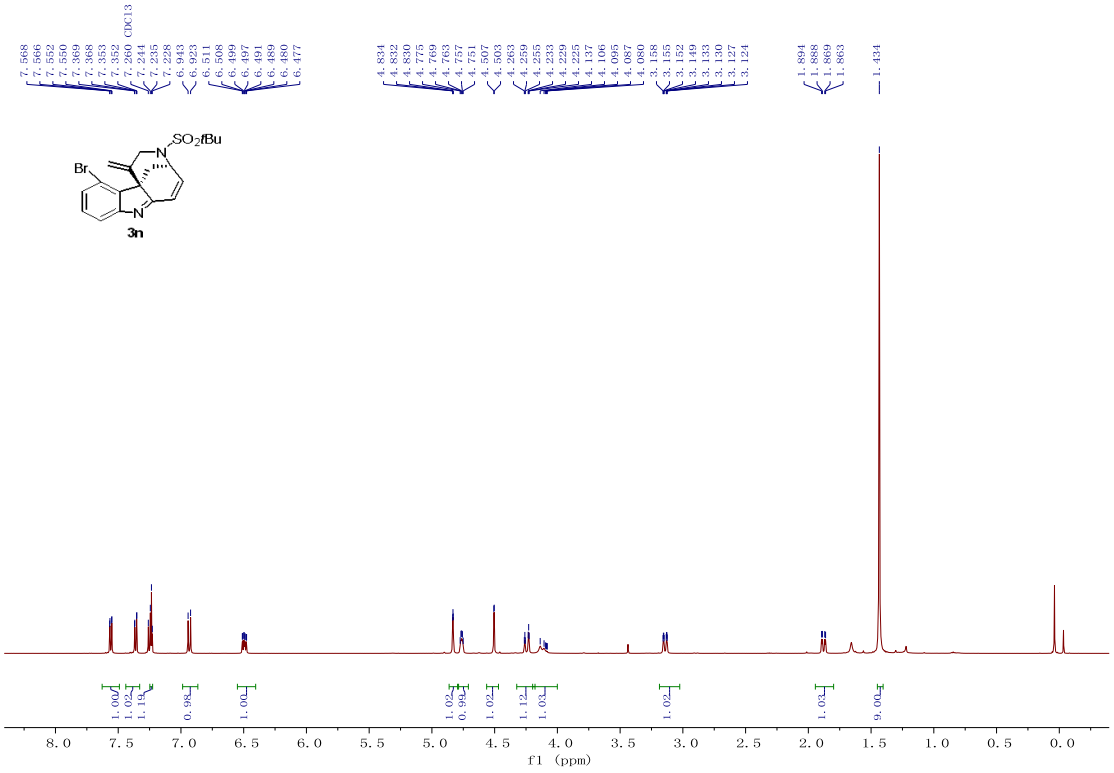
$^{1}$H NMR Spectrum of **3m** (500 MHz, $CDCl_3$)



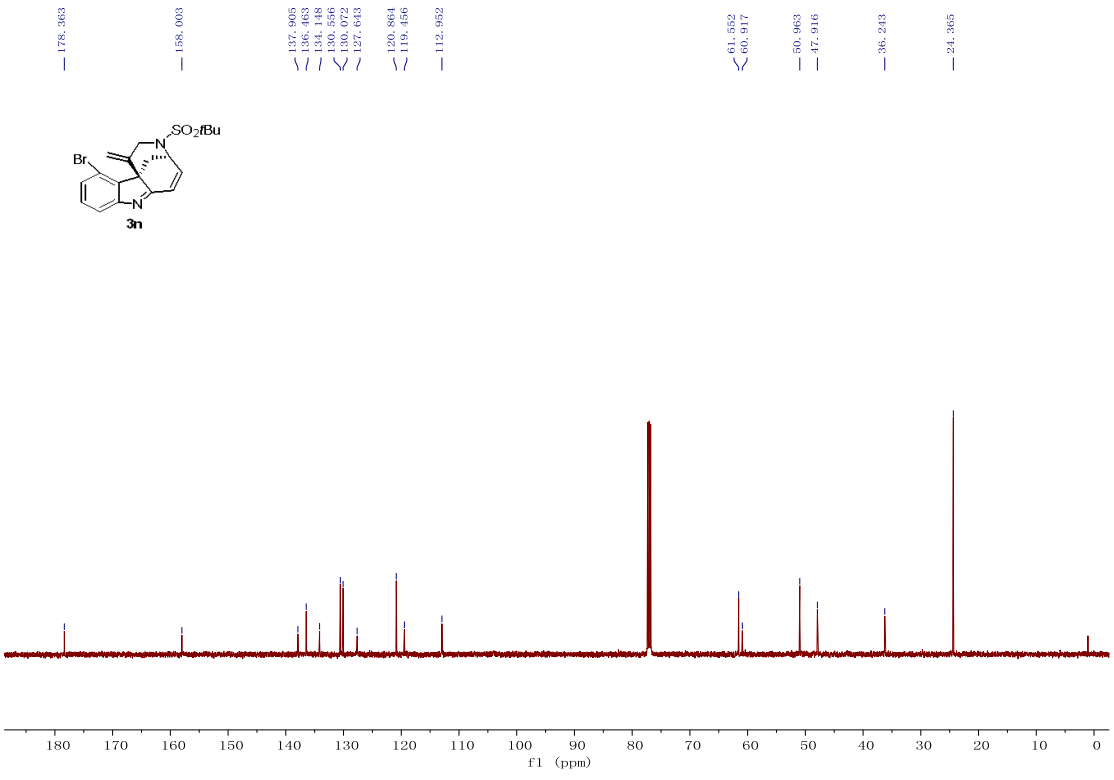

$^{13}$C NMR Spectrum of **3m** (126 MHz, $CDCl_3$)



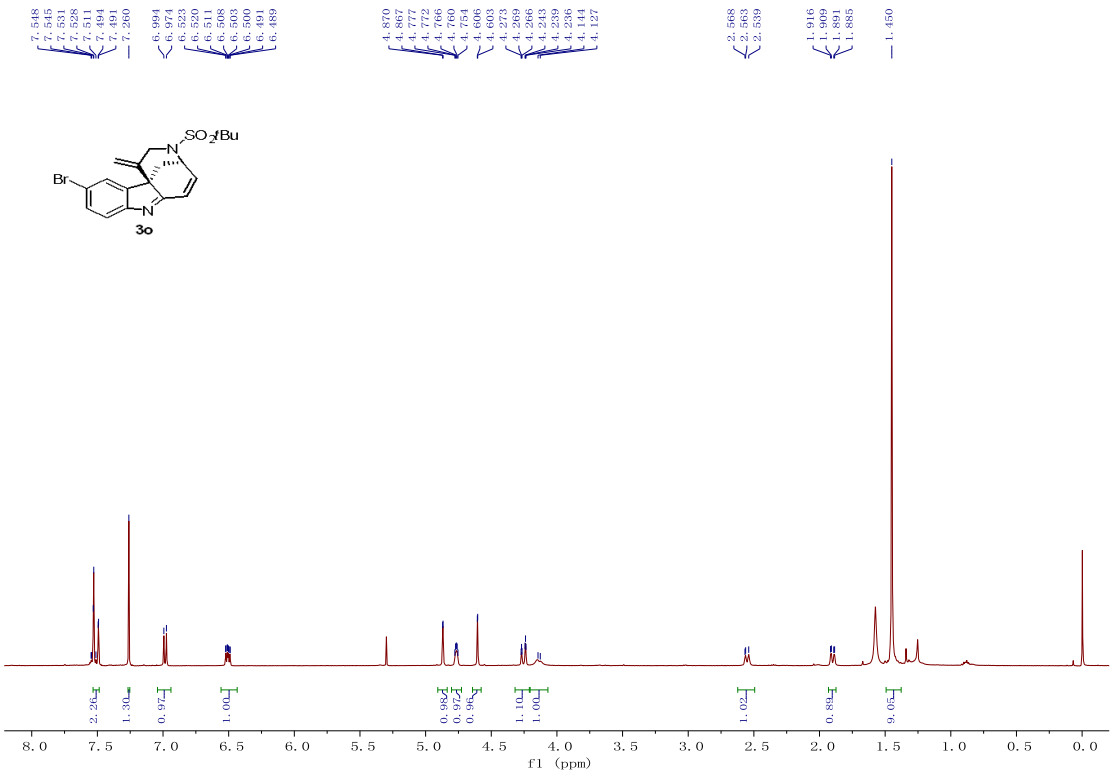

$^1$H NMR Spectrum of **3n** (500 MHz, $CDCl_3$)



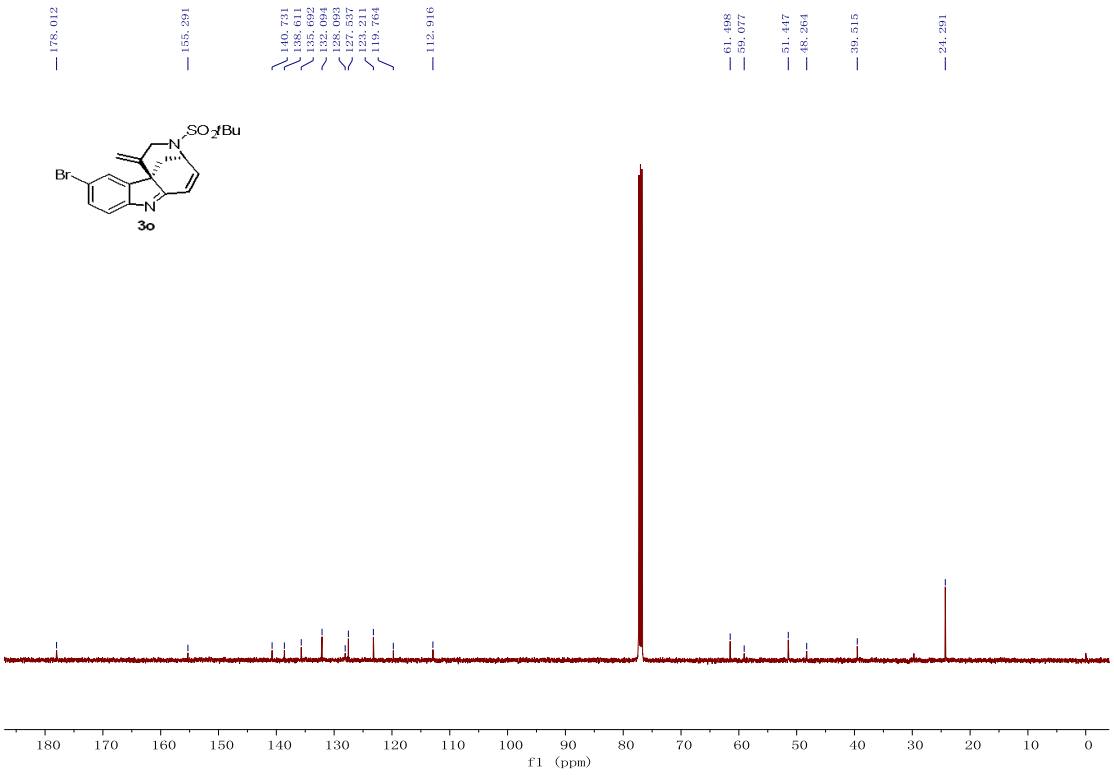
$^{13}$C NMR Spectrum of **3n** (126 MHz, $CDCl_3$)



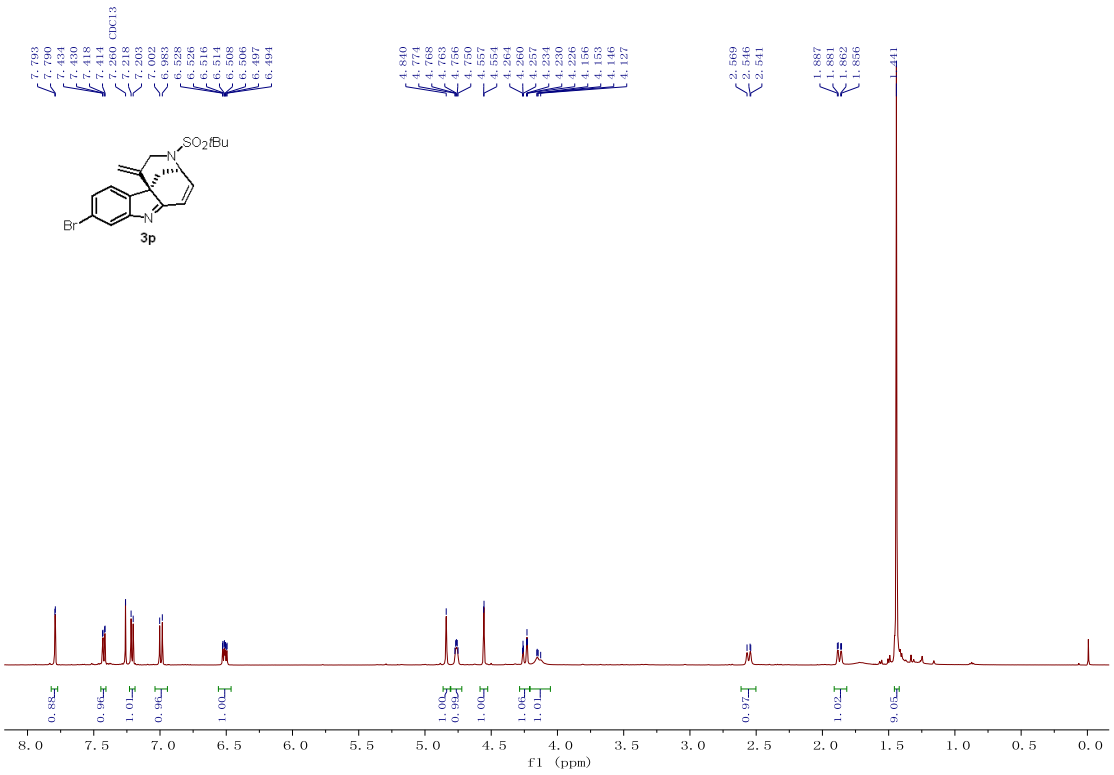

$^{1}$H NMR Spectrum of **3o** (500 MHz, $CDCl_3$)



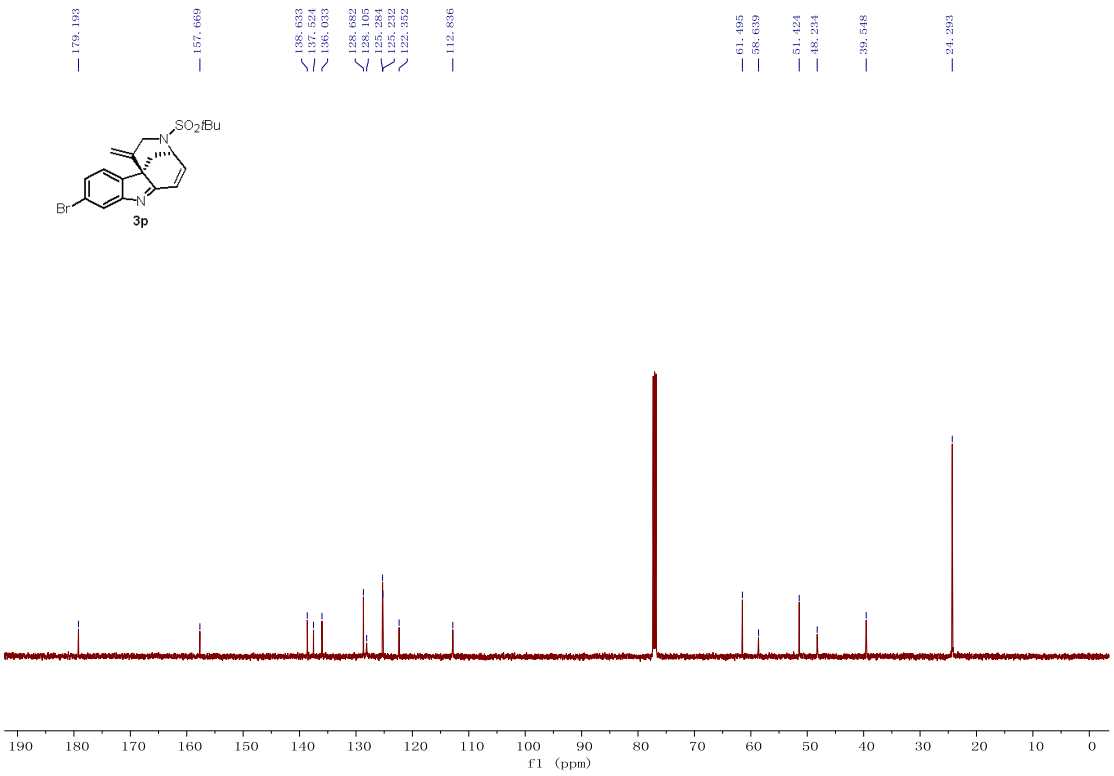

$^{13}$C NMR Spectrum of **3o** (126 MHz, $CDCl_3$)



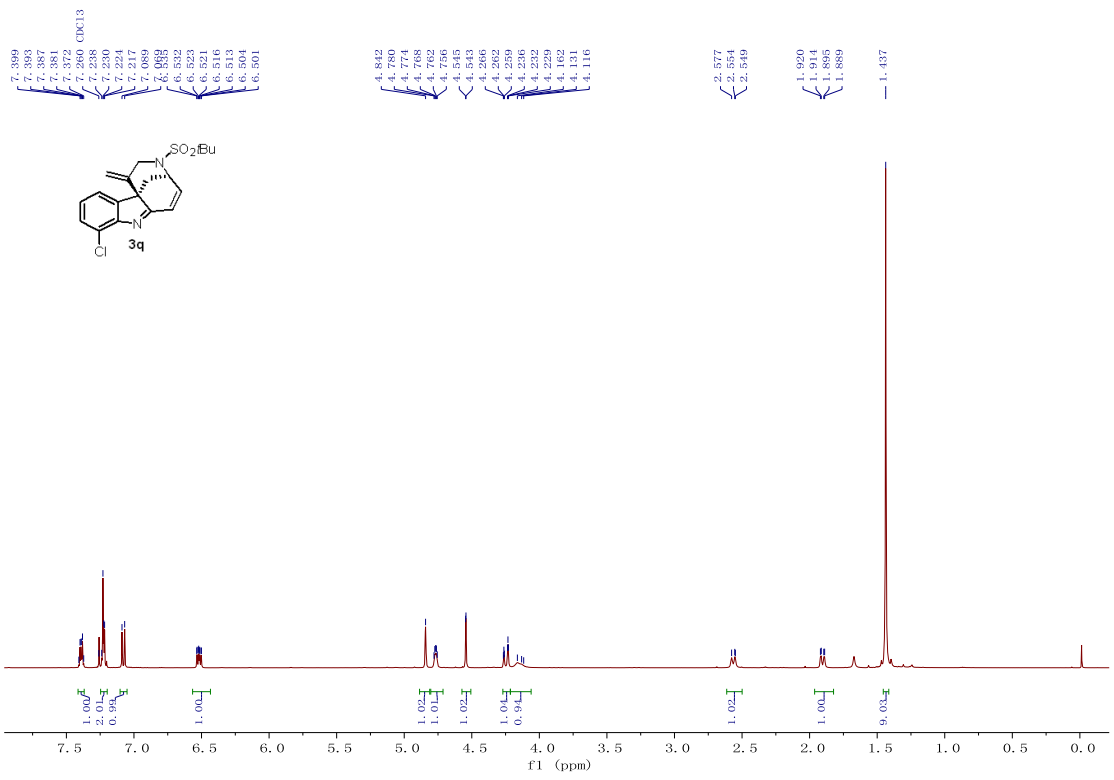
$^{1}$H NMR Spectrum of **3p** (500 MHz, $CDCl_3$)



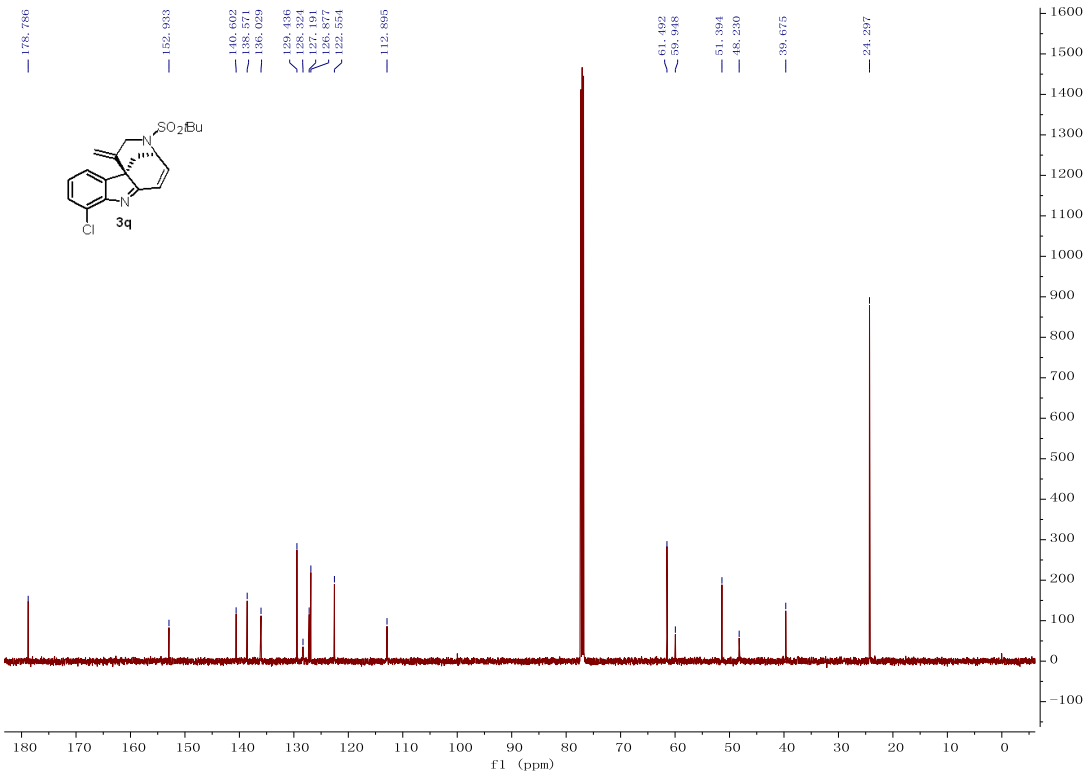

$^{13}$C NMR Spectrum of **3p** (126 MHz, $CDCl_3$)



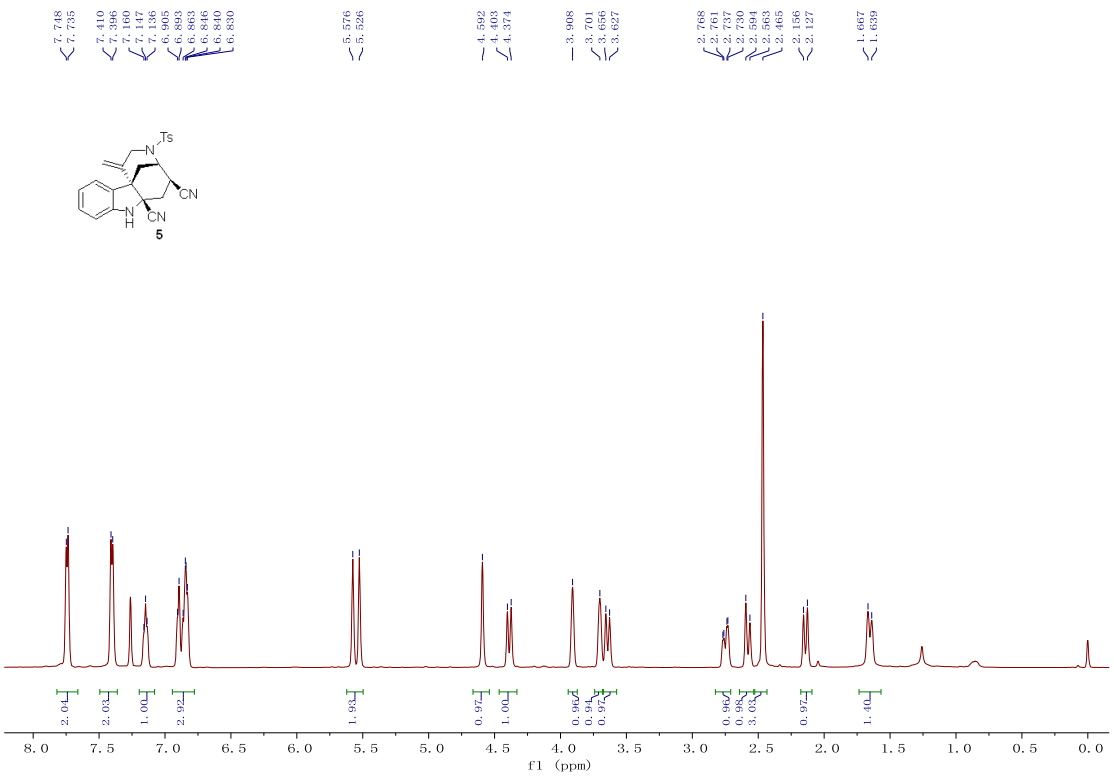

$^{1}$H NMR Spectrum of **3q** (500 MHz, $CDCl_3$)



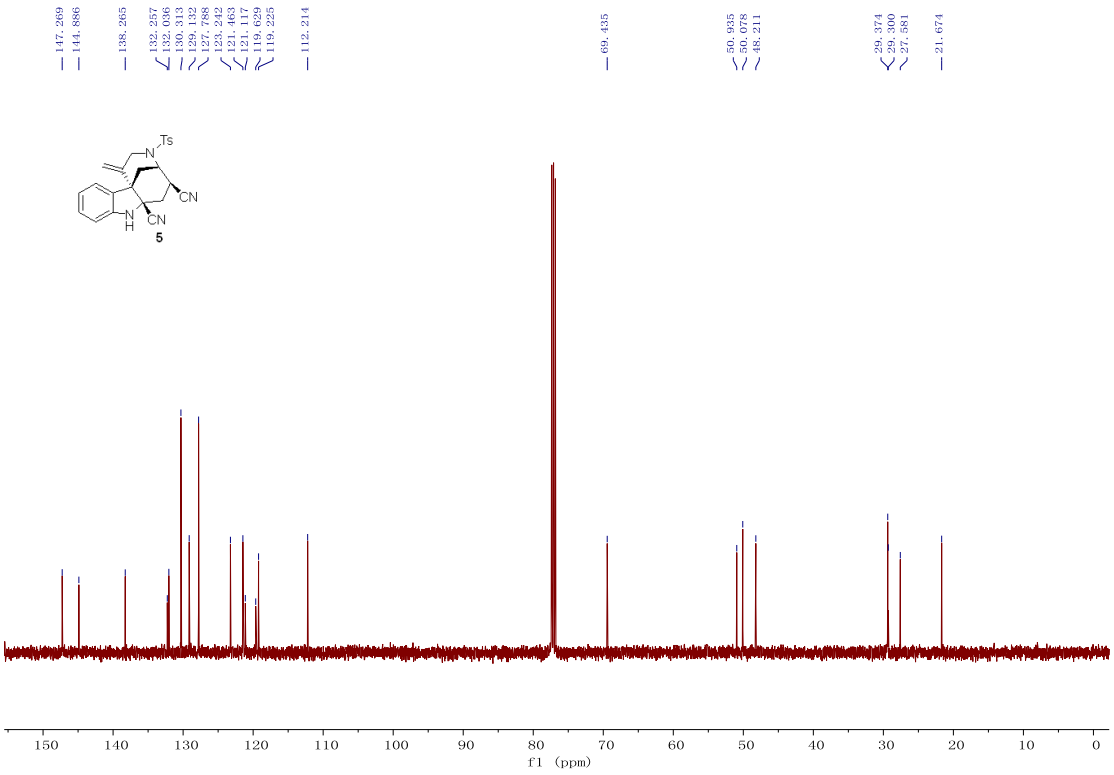
$^{13}$C NMR Spectrum of **3q** (126 MHz, $CDCl_3$)



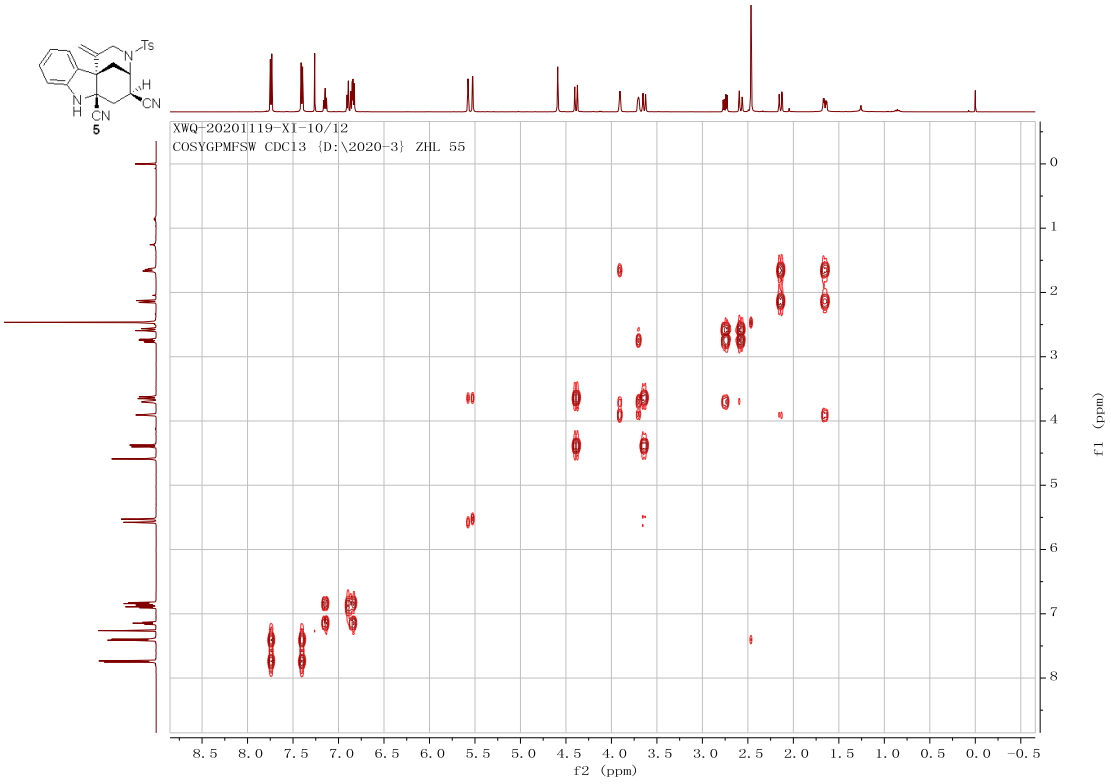

$^{1}$H NMR Spectrum of **5** (500 MHz, $CDCl_3$)



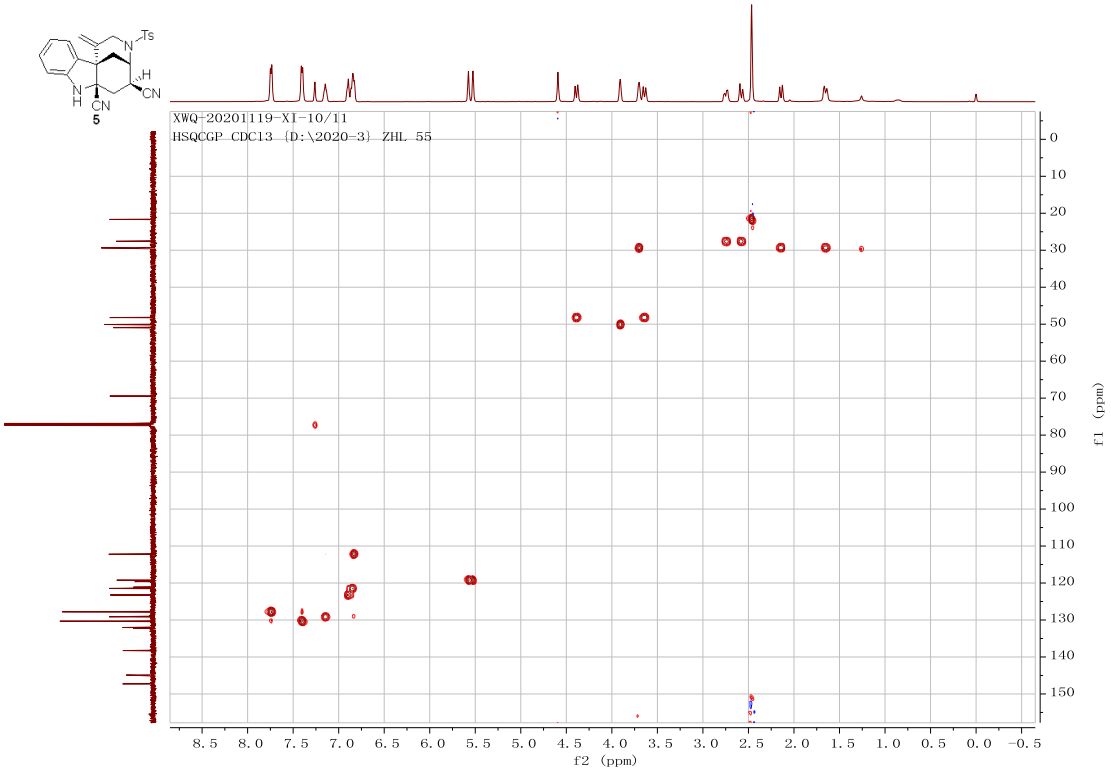

$^{13}$C NMR Spectrum of **5** (126 MHz, $CDCl_3$)



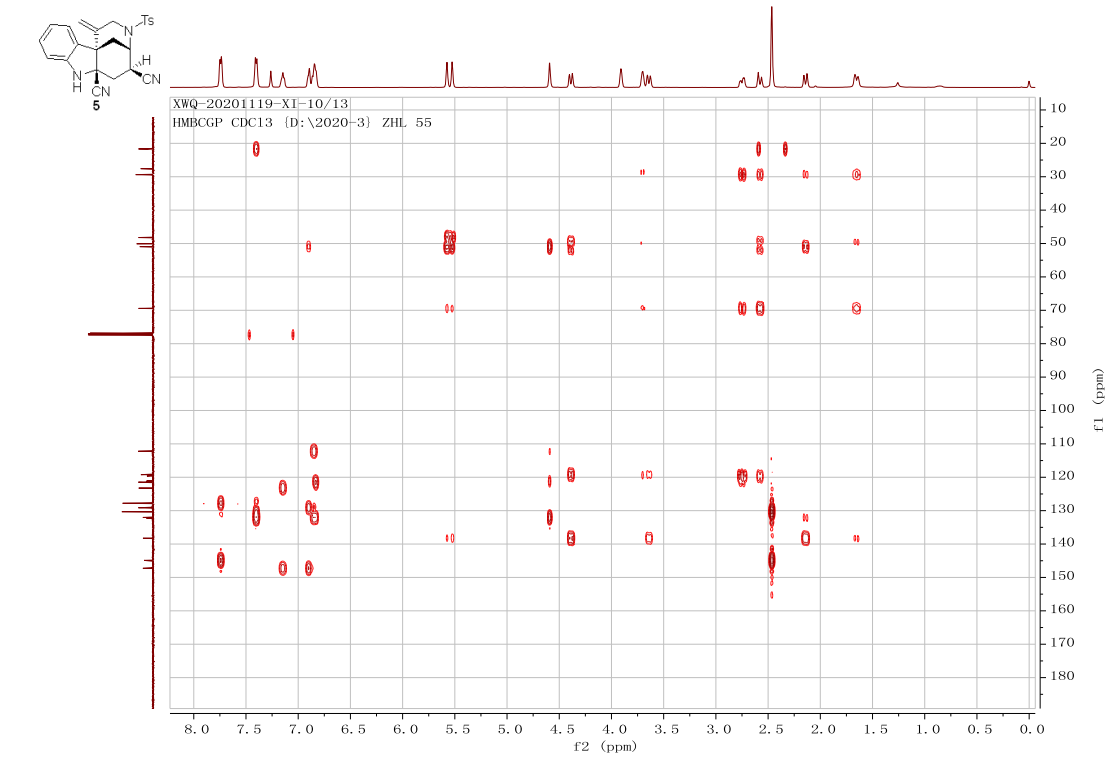
H-$^{1}$H COESY NMR Spectrum of **5** (500 MHz, $CDCl_3$)



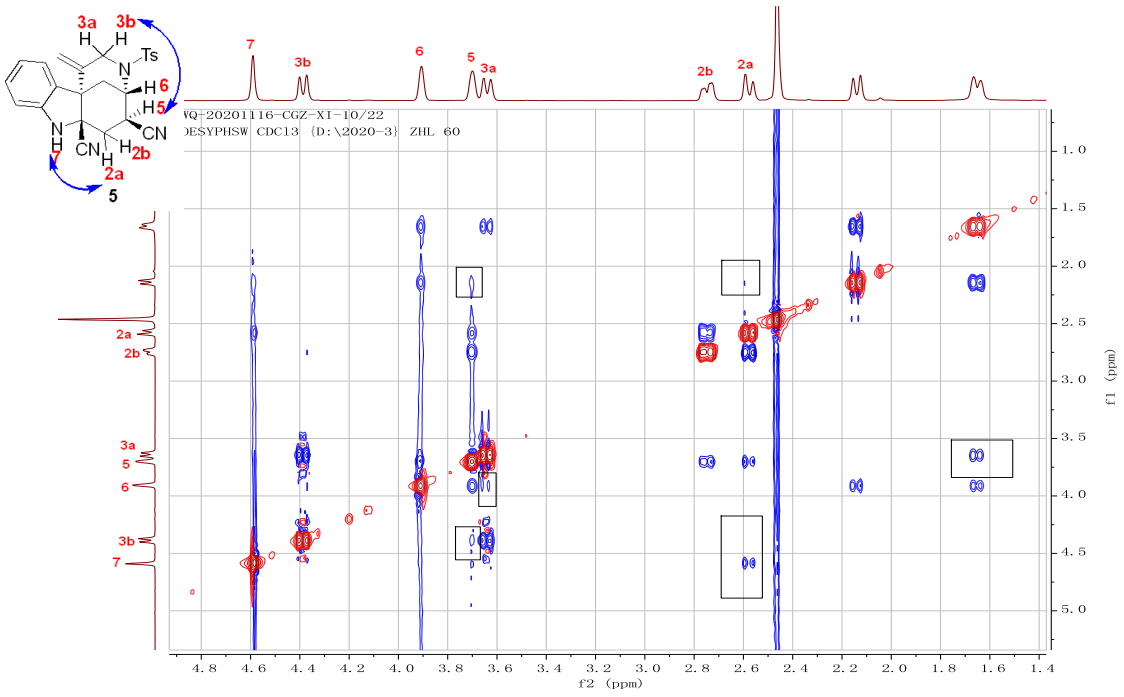

$^{1}$H-$^{13}$C HSQC Spectrum of **5** (500 MHz & 126 MHz, $CDCl_3$)



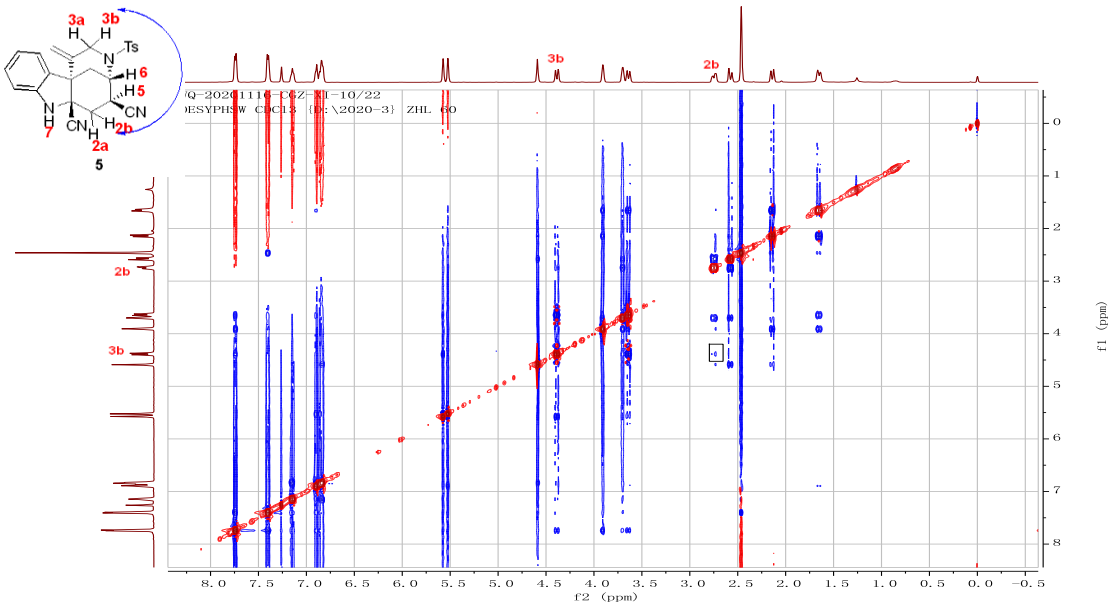

$^{1}$H-$^{13}$C HMBC Spectrum of **5** (500 MHz & 126 MHz, $CDCl_3$)



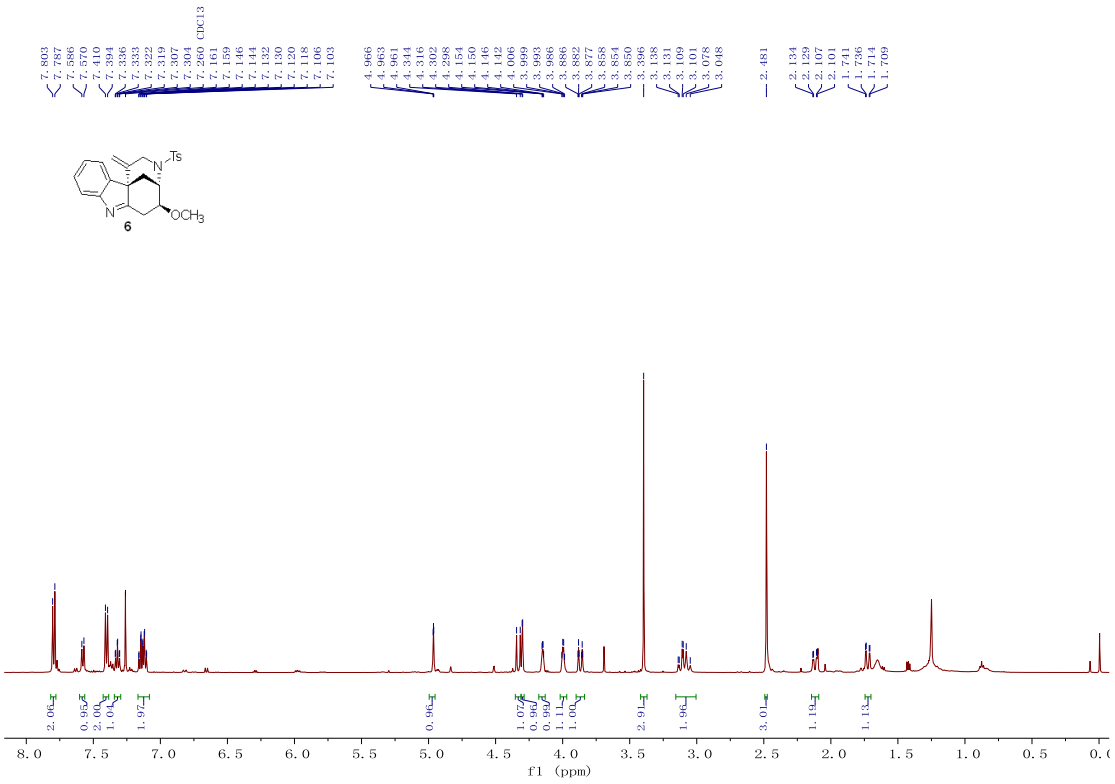
H-$^{1}$H NOESY NMR Expansion Spectrum of **5** (500 MHz, $CDCl_3$)



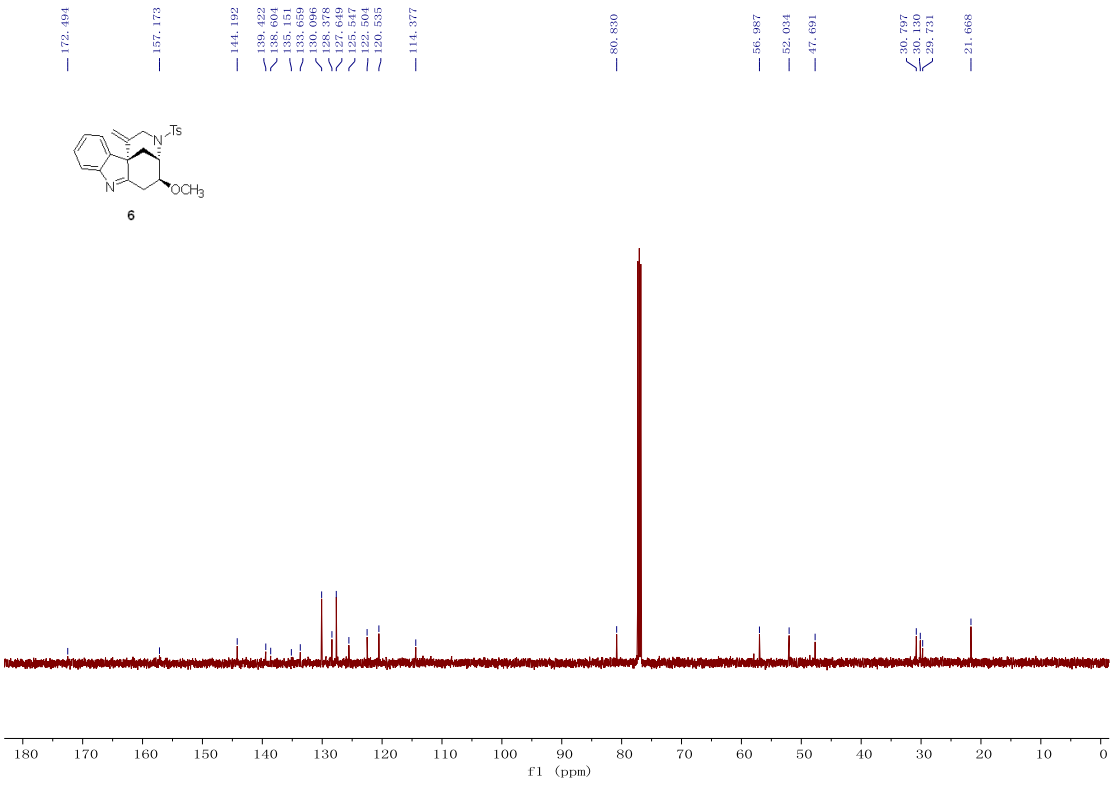

H-$^{1}$H NOESY NMR Spectrum of **5** (500 MHz, $CDCl_3$)



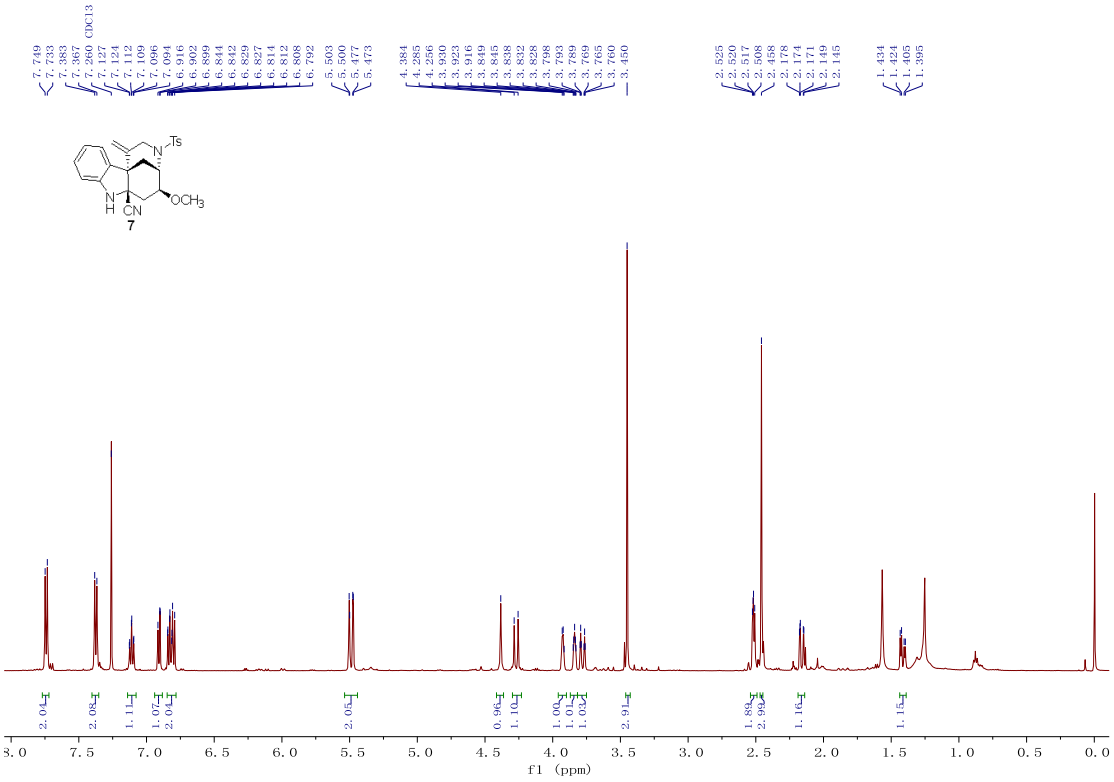

$^{1}$H NMR Spectrum of **6** (500 MHz, $CDCl_3$)



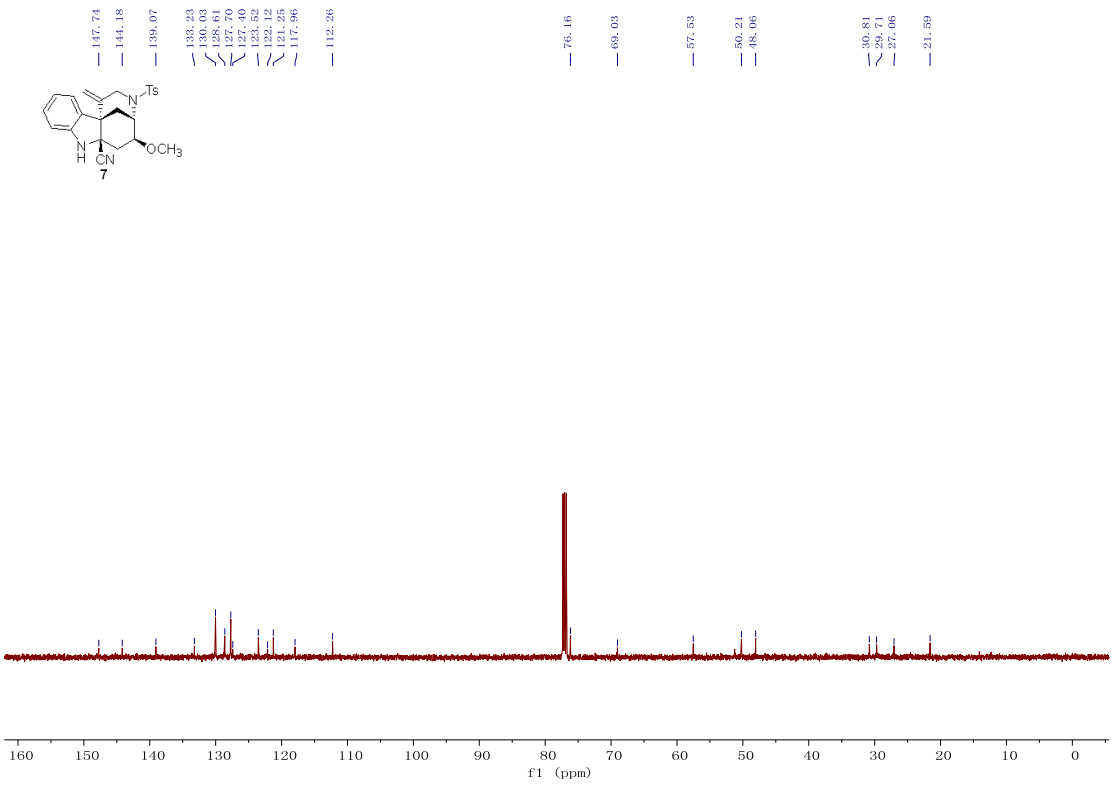
$^{13}$C NMR Spectrum of **6** (126 MHz, $CDCl_3$)



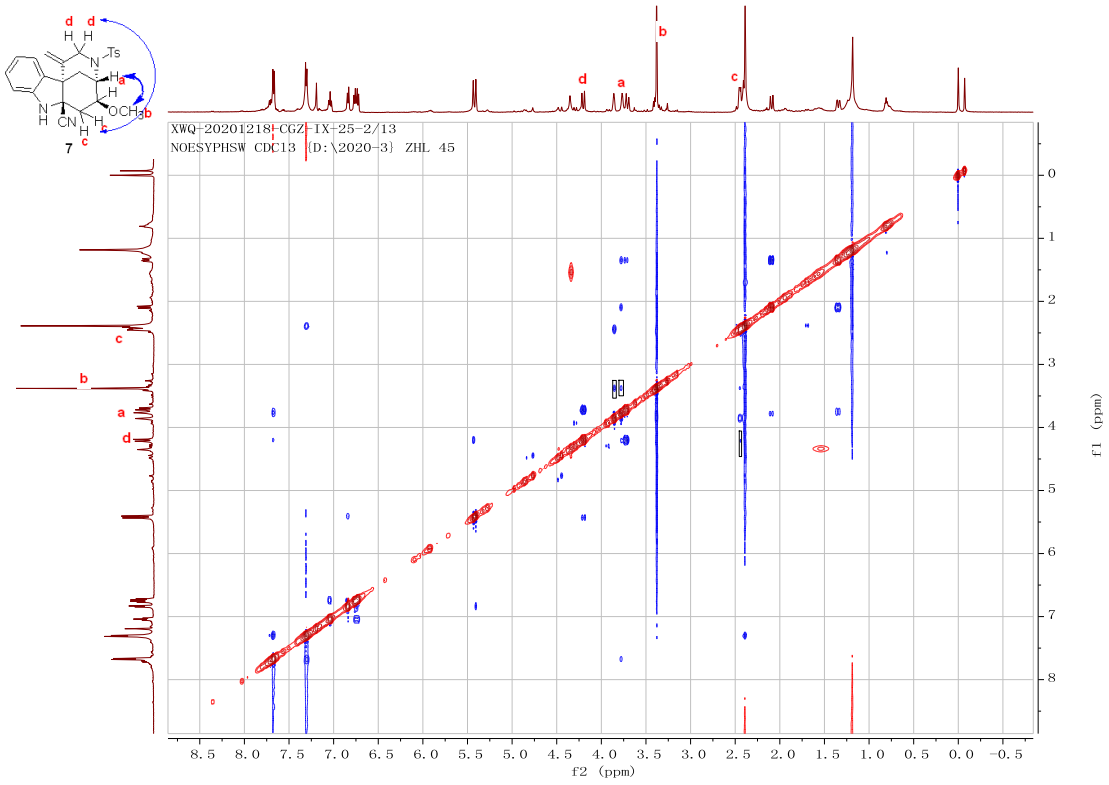

$^{1}$H NMR Spectrum of **7** (500 MHz, $CDCl_3$)



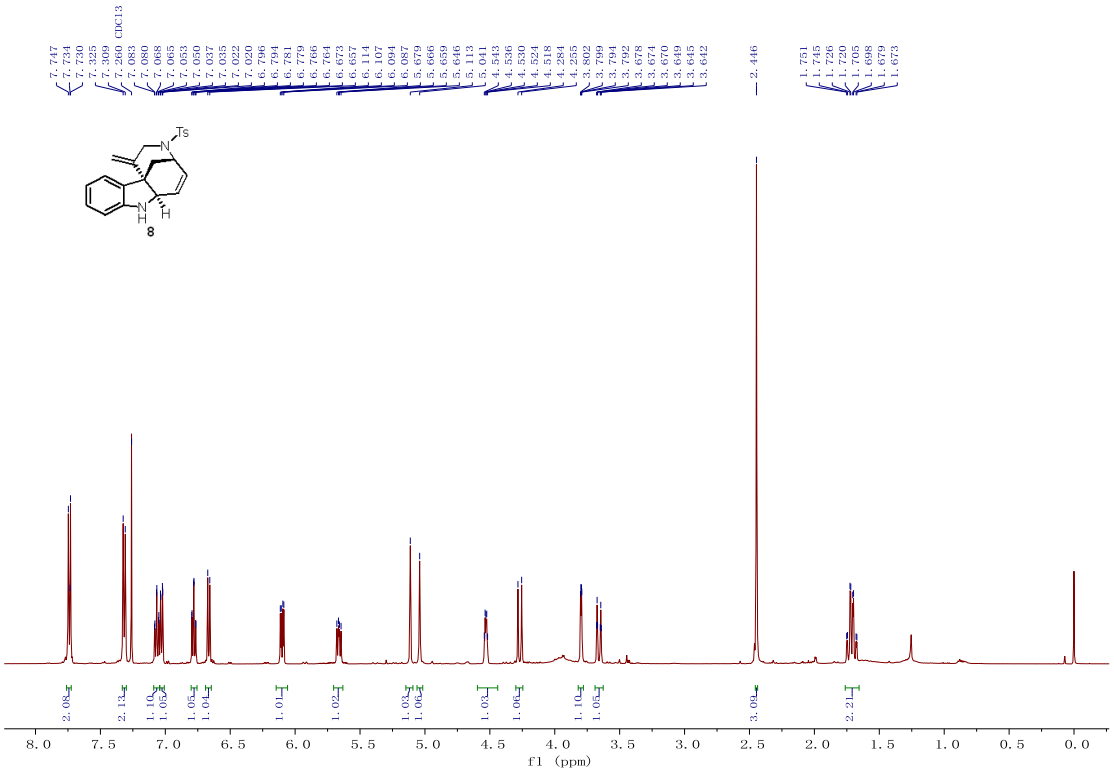

$^{13}$C NMR Spectrum of **7** (126 MHz, $CDCl_3$)



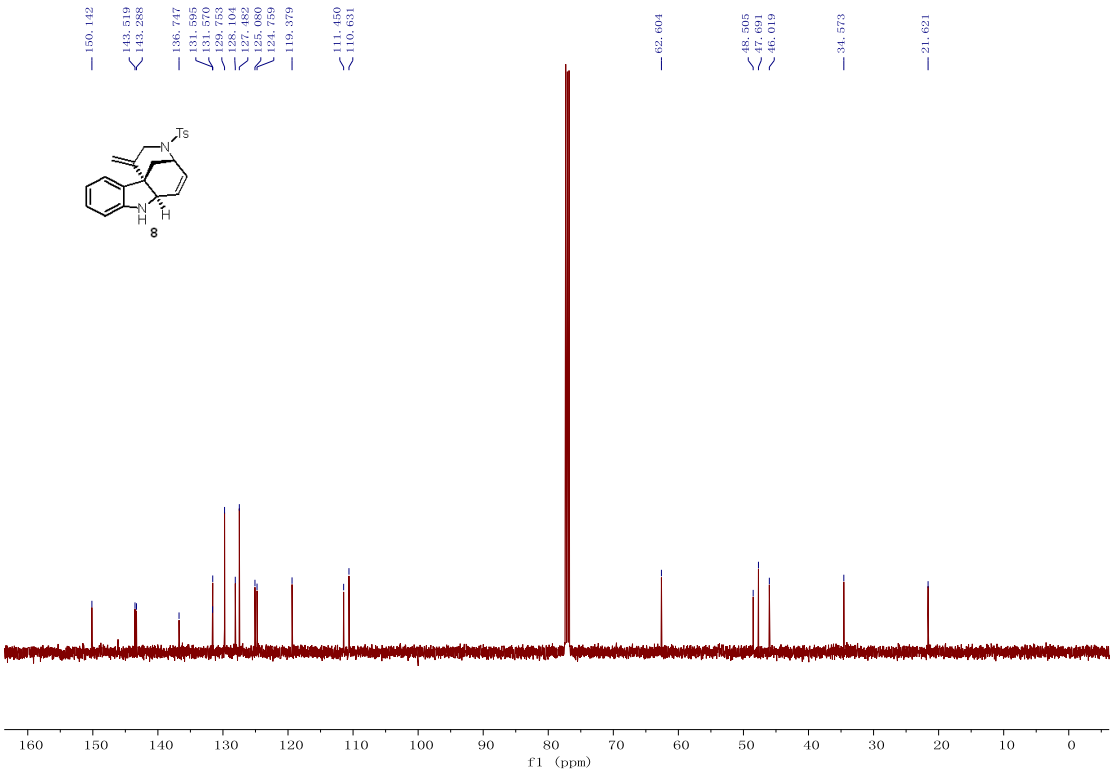
H-$^{1}$H NOESY NMR Spectrum of **7** (500 MHz, $CDCl_3$)



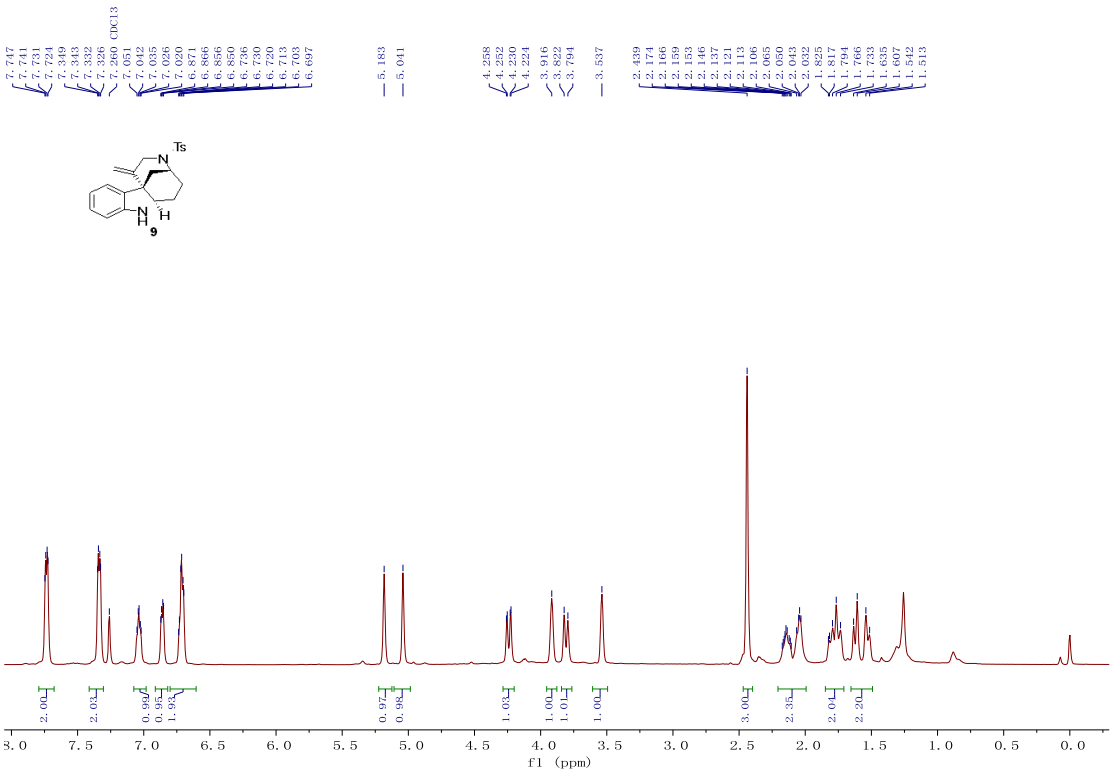

$^{1}$H NMR Spectrum of **8** (500 MHz, $CDCl_3$)



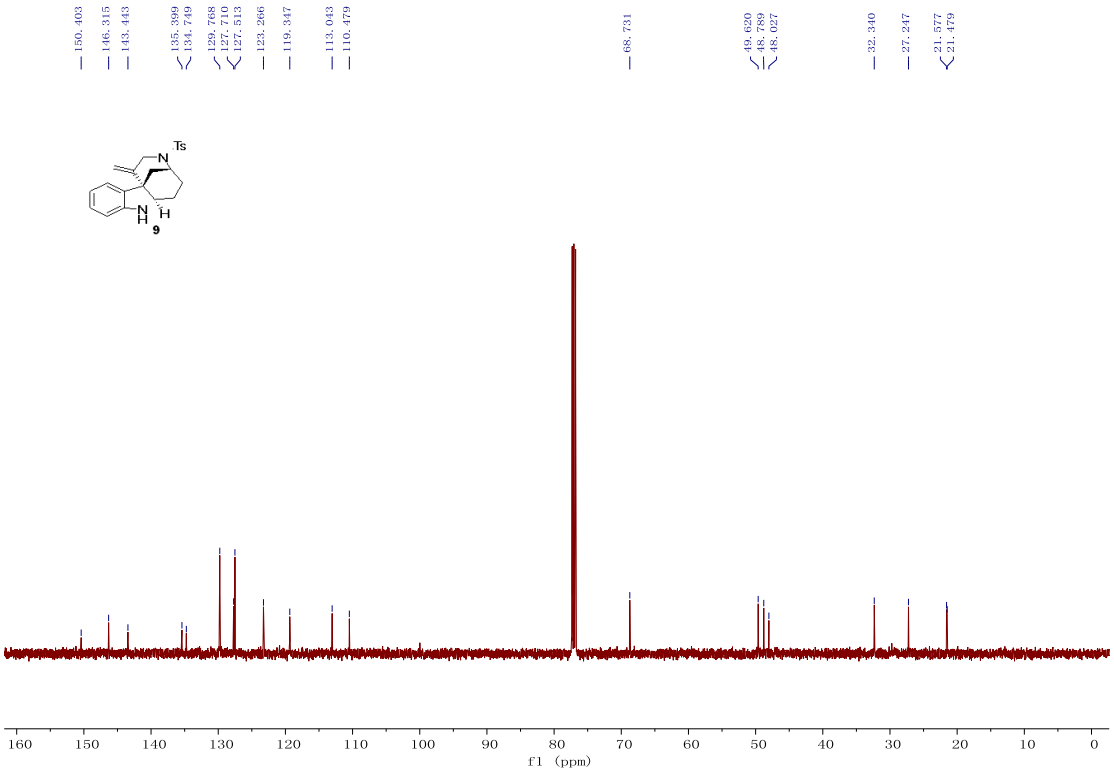

$^{13}$C NMR Spectrum of **8** (126 MHz, $CDCl_3$)



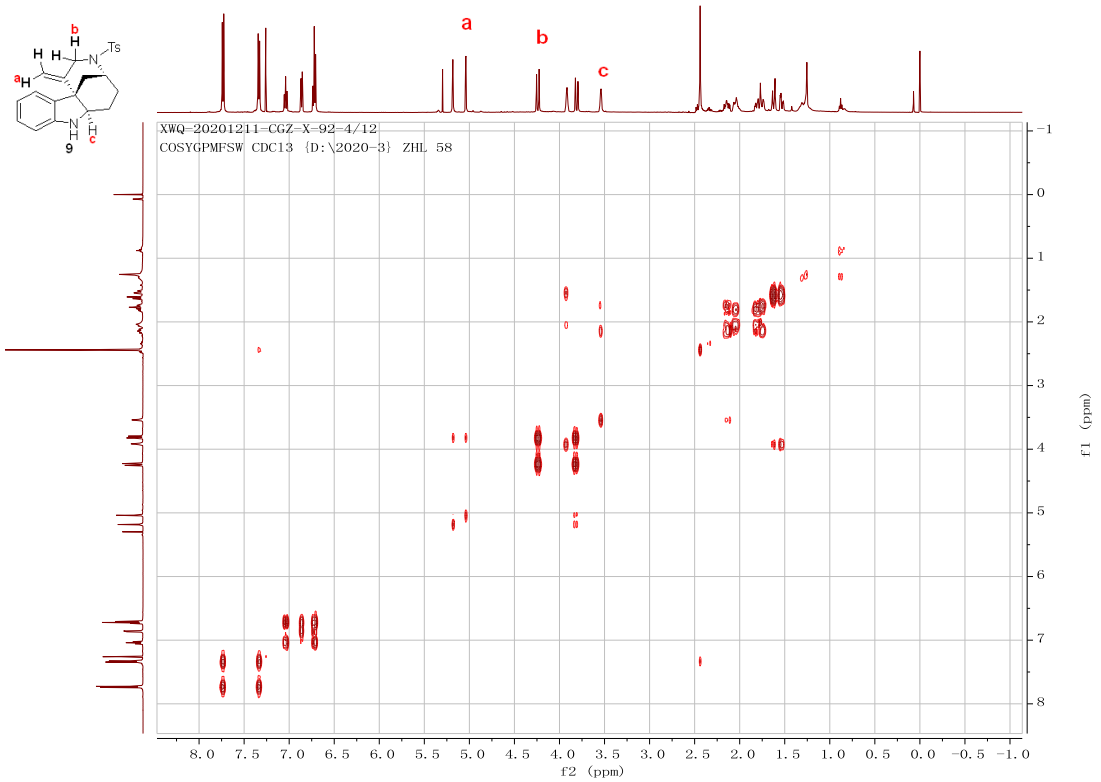
$^{1}$H NMR Spectrum of **9** (500 MHz, $CDCl_3$)



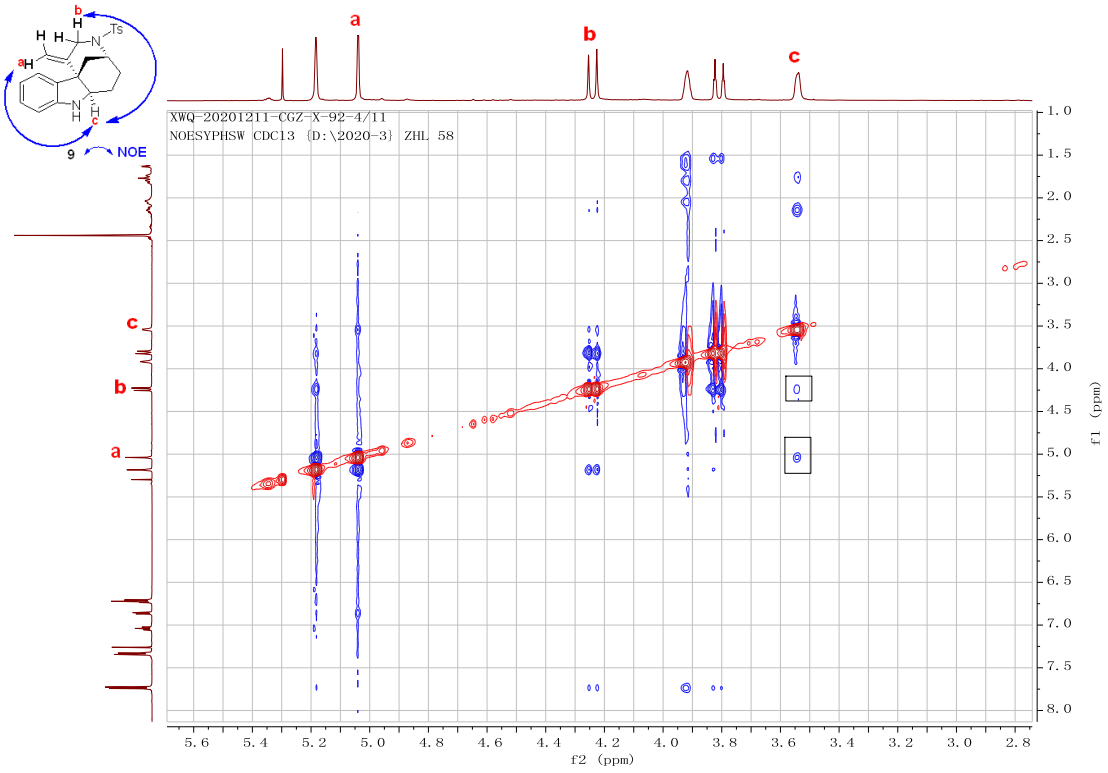

$^{13}$C NMR Spectrum of **9** (126 MHz, $CDCl_3$)



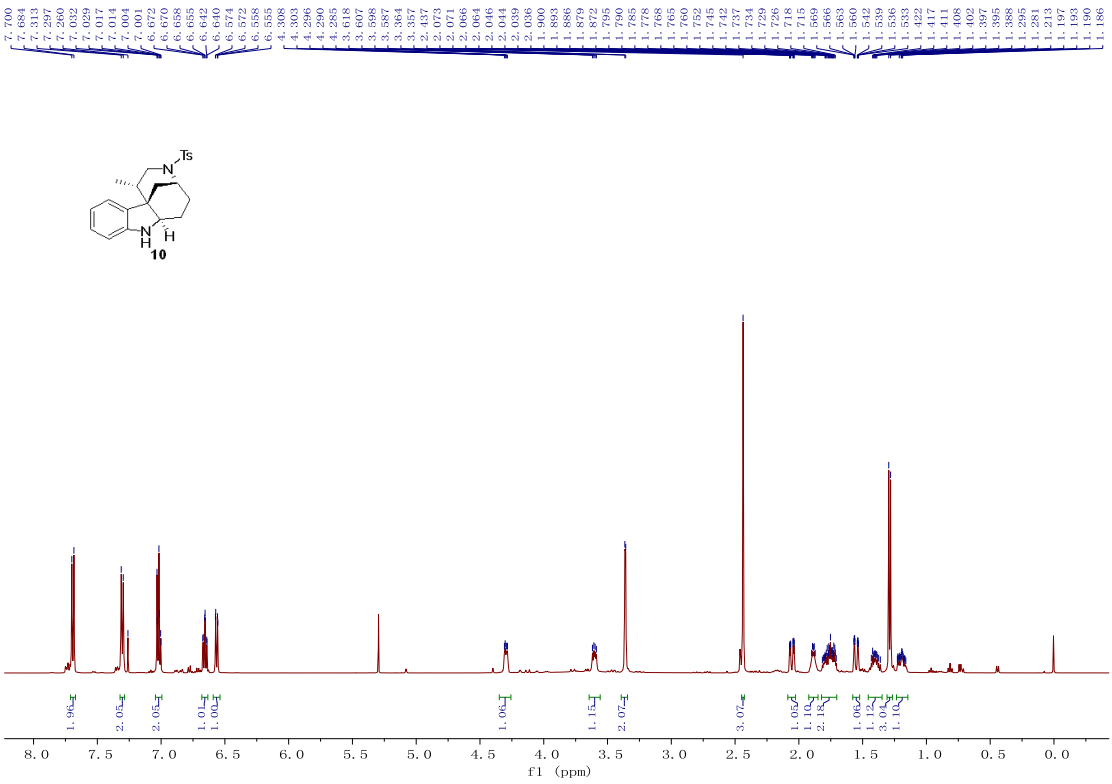

H-$^{1}$H COESY NMR Spectrum of **9** (500 MHz, $CDCl_3$)



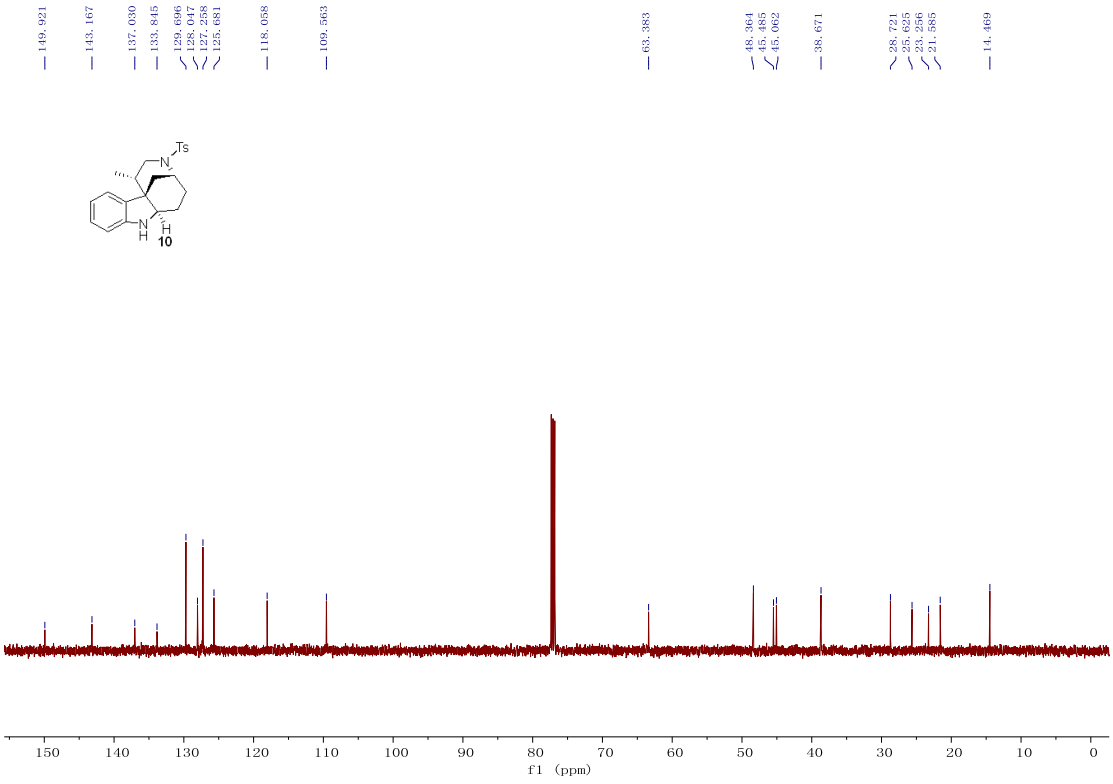
H-$^{1}$H NOESY NMR Spectrum of **9** (500 MHz, $CDCl_3$)



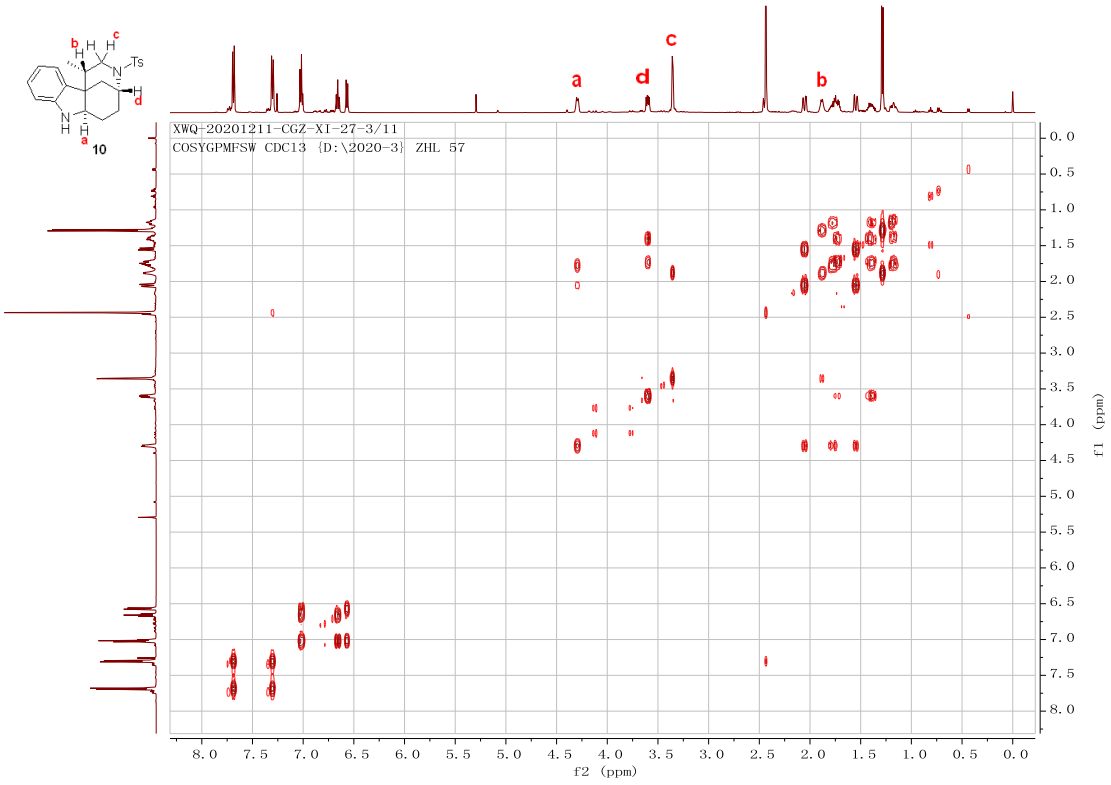

$^{1}$H NMR Spectrum of **10** (500 MHz, $CDCl_3$)



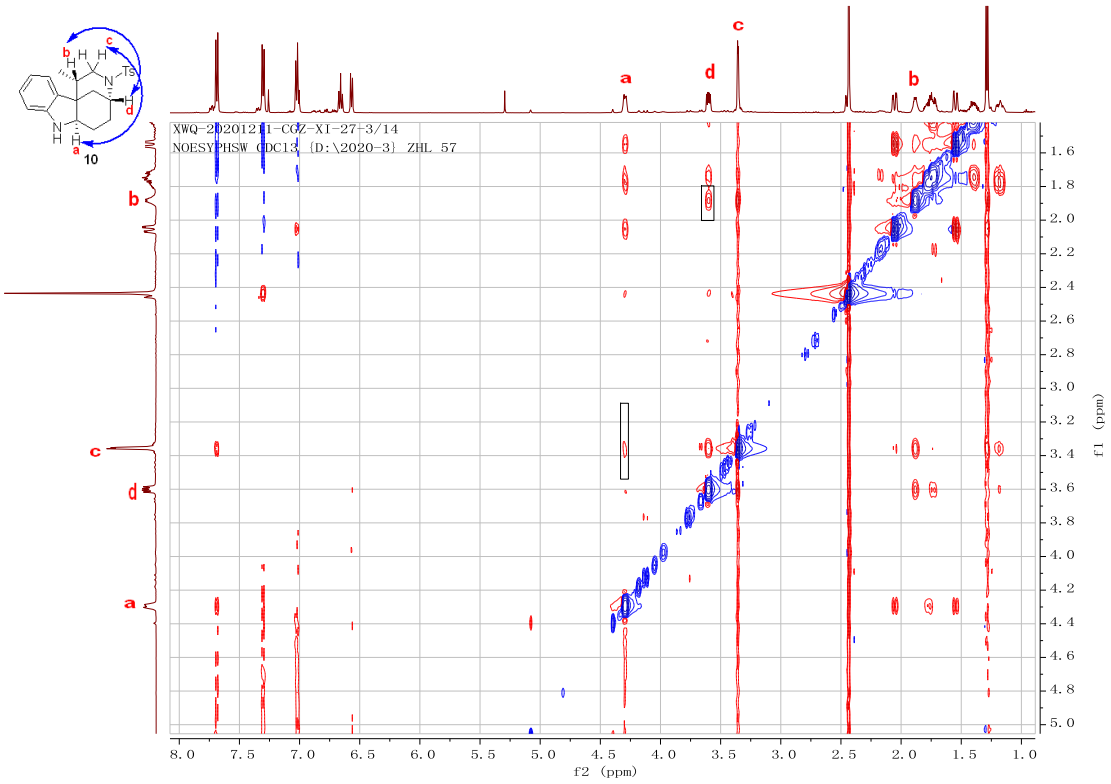

$^{13}$C NMR Spectrum of **10** (126 MHz, $CDCl_3$)



H-$^{1}$H COESY NMR Spectrum of **10** (500 MHz, $CDCl_3$)




H-$^{1}$H NOESY NMR Expansion Spectrum of **10** (500 MHz, $CDCl_3$)




H-$^{1}$H NOESY NMR Spectrum of **10** (500 MHz, $CDCl_3$)