# Diastereodivergent *cis*- and *trans*-fused [4+2] annulations of cyclic 1,3-dienes and 1-azadienes via ligand-controlled palladium catalysis

Yuan Hu,[a] Jin-Yu Huang,[a] Ru-Jie Yan,[a] Zhi-Chao Chen,*[a] Qin Ouyang,[b] Wei Du,[a] and Ying-Chun Chen*[ab]

[a] Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry and Sichuan Province, and Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu 610041, China.

[b] College of Pharmacy, Third Military Medical University, Shapingba, Chongqing 400038, China.

*Corresponding Authors: chenzhichao@scu.edu.cn; ycchen@scu.edu.cn

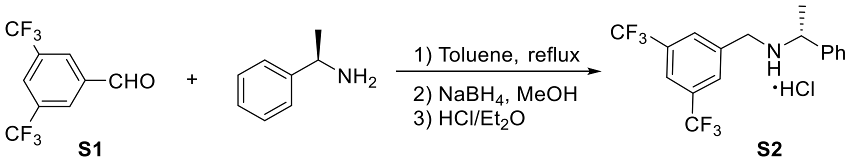
## Supplementary Information

## 1. General methods and materials

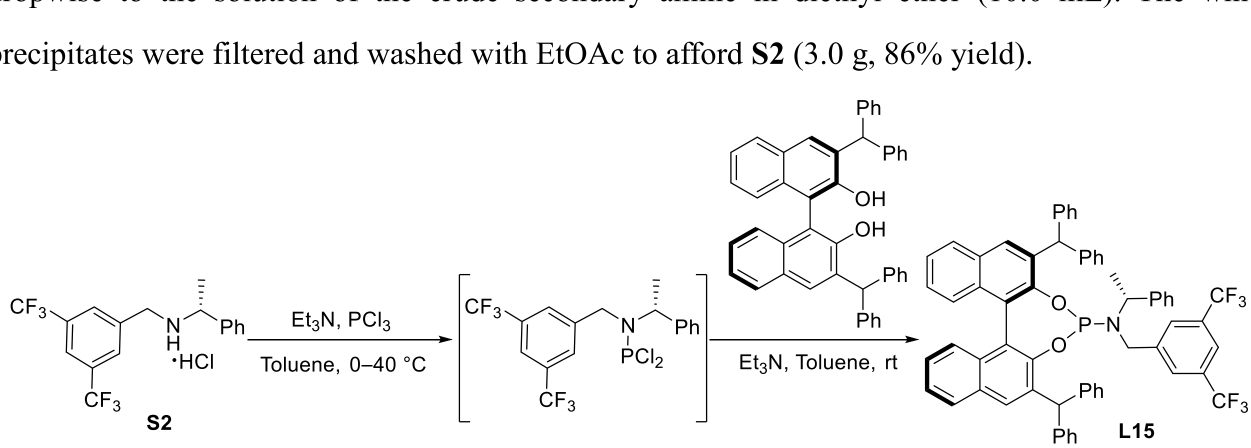
Unless otherwise noted, the reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath. $^{1}H$ NMR (400 or 600 MHz), $^{13}C$ NMR (100 or 150 MHz), $^{31}P$ NMR (162 MHz) and $^{19}F$ NMR (375 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend$^{TM}$ 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, ddd = doublet of doublet of doublets, dt = doublet of triplets, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Xcalibur or Bruker APEX-II CCD diffractometer, and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2050823, 2050825–2050826 and 2219802–2219806). In each case, enantiomeric excess was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak ID Column (250 × 4.6 mm), Chiralpak IE Column (250 × 4.6 mm), Chiralpak IF Column (250 × 4.6 mm), Chiralpak IG Column (250 × 4.6 mm), Chiralpak IH Column (250 × 4.6 mm). UV detection was monitored at 254 nm. The specific optical rotation was obtained from Rudolph Research Analytical Autopol I automatic polarimeter in $CHCl_3$ solution at 25 °C. The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (300–400 mesh) eluting with ethyl acetate (EtOAc)/petroleum ether or dichloromethane (DCM)/petroleum ether. TLC was performed on glass-backed silica plates. UV light, $I_2$, and solution of potassium permanganate were used to visualize products or starting materials. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Toluene was freshly distilled from $CaH_2$ under an atmosphere of dry argon. Dried solvents and liquid reagents were transferred via oven-dried syringe. Petroleum ether and EtOAc were distilled. 1,3-Cyclohexadiene **1a**, cycloheptadiene **6** and cycloheptatriene **10** were used without purification as commercially available. Dicyclopentadiene was cracked at 170 °C and redistilled to give 1,3-cyclopentadiene **13**. The ligand **L7**,[1] **L12**,[1] **1b**,[2] 1-azadiene **2**,[3] 1,3-diene **15**,[4] internal diene **18**,[5] 2-*N*-tosyliminoacrylate **22**[6] and 1-oxadiene **24**[7] were prepared according to the literature procedures.

(1) X. Song, J. Zhang, Y. X. Wu, Q. Ouyang, W. Du and Y.-C. Chen, *J. Am. Chem. Soc*., 2022, **144**, 9564−9569.
(2) H. E. Burks, L. T. Kliman and J. P. Morken, *J. Am. Chem. Soc*., 2009, **131**, 9134–9135.
(3) Z.-Q. Rong, M. Wang, C. H. E. Chow and Y. Zhao, *Chem. Eur. J*., 2016, **22**, 9483−9487.
(4) A. Lishchynskyi and K. Muñiz, *Chem. Eur. J*., 2022, **18**, 2212–2216.
(5) F. Carlet, G. Bertarini, G. Broggini and G. Poli, *Eur. J. Org. Chem*., 2021, 2162–2168.
(6) H. Liu, Q. Zhang, L. Wang and X. Tong, *Chem. Eur. J*., 2010, **16**, 1968–1972.
(7) A. P. Dieskau, M. S. Holzwarth and B. Plietker, *J. Am. Chem. Soc*., 2012, **134**, 5048–5051.

## 2. Preparation and characterization of ligand L15



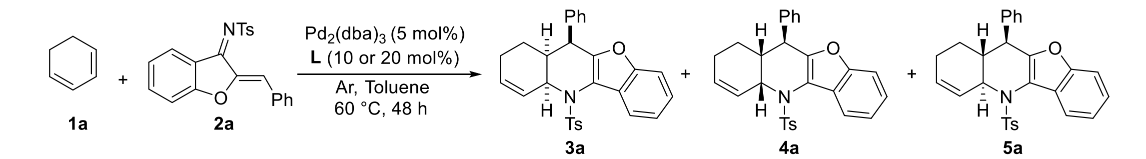

The mixture of **S1** (2.42 g, 10.0 mmol) and (*R*)-1-phenylethylamine (1.21 g, 10.0 mmol) in toluene (12 mL) was stirred at 110 °C for 2 h. After cooled to room temperature, anhydrous $MgSO_4$ (30.0 g) was added to the mixture and stirred for 30 min, followed by filtration and concentration. The residue was dissolved in methanol (20.0 mL), and $NaBH_4$ (378.0 mg, 10.00 mmol) was added in three portions at 0 °C. After 30 min, the mixture was quenched with water (20.0 mL), and extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. Then concentrated HCl (aq) (2.0 mL) was added dropwise to the solution of the crude secondary amine in diethyl ether (10.0 mL). The white precipitates were filtered and washed with EtOAc to afford **S2** (3.0 g, 86% yield).

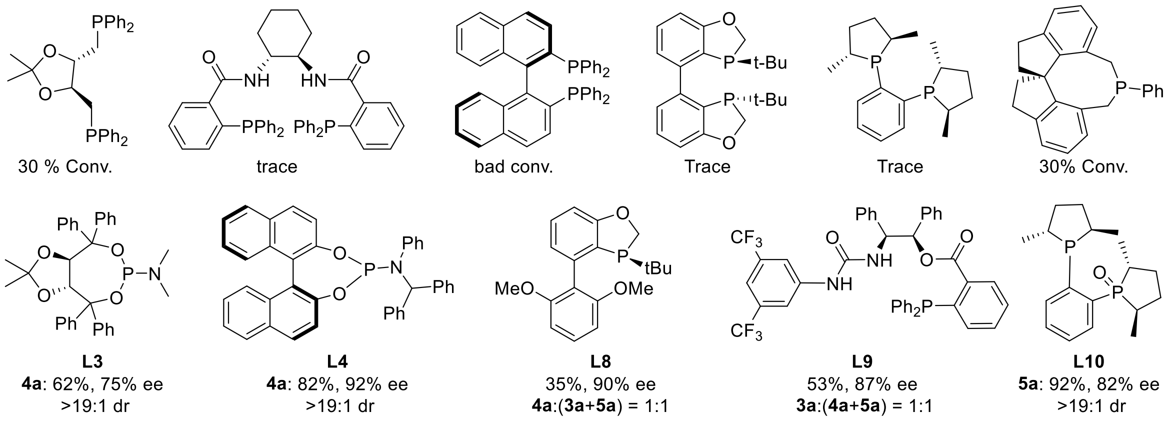



Triethylamine (0.1 mL, 1.2 mmol, 6.0 equiv) was added dropwise to a stirred ice-cooled solution of $PCl_3$ (0.11 mL, 1.2 mmol, 6.0 equiv) in dry toluene (1.0 mL) under argon atmosphere. The resultant mixture was gradually warmed to 40 °C before **S2** (154.0 mg, 0.4000 mmol, 2.0 equiv) was added. After stirred for additional 4 h, the mixture was concentrated in vacuo. The residue was dissolved in dry toluene, and (*R*)-3,3'-dibenzhydryl-[1,1'-binaphthalene]-2,2'-diol (124.0 mg, 0.2000 mmol) and triethylamine (0.10 mL, 1.2 mmol, 6.0 equiv) were added sequentially under argon atmosphere. Then the mixture was stirred at room temperature for 12 h. The mixture was concentrated, and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/100) to give ligand **L15**: 94 mg (0.095 mmol), as a white solid, 47% yield; mp = 141–143 °C; $[\alpha]_D^{25}$ = –139.0 (*c* = 0.41 in $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.54 (s, 2H), 7.45 (d, *J* = 5.4 Hz, 2H), 7.41–6.96 (m, 29H), 6.90–6.77 (m, 2H), 6.29 (s, 1H), 5.80 (s, 1H), 4.18 (d, *J* = 15.7 Hz, 1H), 4.09–3.88 (m, 1H), 3.47 (d, *J* = 15.6 Hz, 1H), 1.35 (dd, *J* = 7.3, 2.5 Hz, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 148.71, 148.67, 147.7, 143.9, 143.7, 142.9, 142.6, 142.1, 142.0, 141.6, 135.8, 135.1, 132.4, 132.0, 131.8, 131.4, 131.2, 130.9 (d, $^2J_{FC}$ = 33.0 Hz), 130.8, 130.5, 130.1, 129.89, 129.86, 128.8, 128.7, 128.6, 128.4, 128.31, 128.28, 128.12, 128.07, 128.0, 127.5, 127.4, 127.0, 126.9, 126.7, 126.49, 126.45, 126.3, 125.8, 125.7, 124.9, 124.6, 124.3, 123.4 (d, $^1J_{FC}$ = 272.2 Hz), 122.13, 122.10, 120.6 (m), 57.5 (d, *J* = 34.7 Hz), 51.0, 50.3, 47.3 (d, *J* = 4.6 Hz), 21.7 (d, *J* = 24.3 Hz); $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –62.6; $^{31}P$ NMR (162 MHz, $CDCl_3$): δ (ppm) 139.4 (d, *J* = 12.0 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{63}H_{47}F_6NO_2P^+$ 994.3243; Found 994.3246.

# 3. Detailed screening conditions

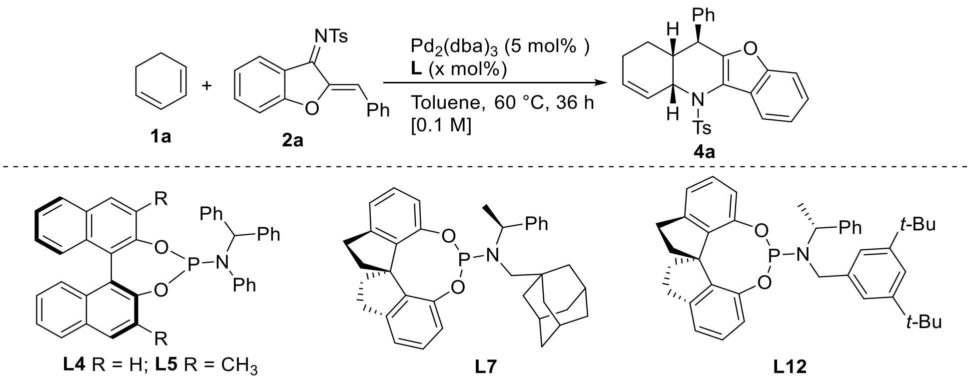
## 3.1 Preliminary ligand screenings for diastereodivergent [4+2] annulation



A series of chiral ligands derived from different backbones were investigated. As outlined above, phosphoramidite ligands **L3** and **L4** led to the exclusive formation of **4a**, while 1,2-aminoalcohol-drived **L9** and (*R,R*)-Me-DuPhos monoxide **L10** were favourable to produce **3a** and **5a**, respectively. More relevant ligands and other parameters were screened subsequently in order to realise the diastereodivergent synthesis.

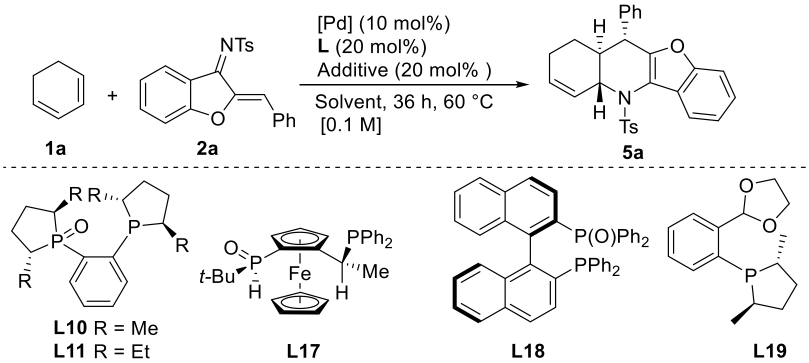
### 3.2 Detailed screening conditions for asymmetric synthesis of 4a

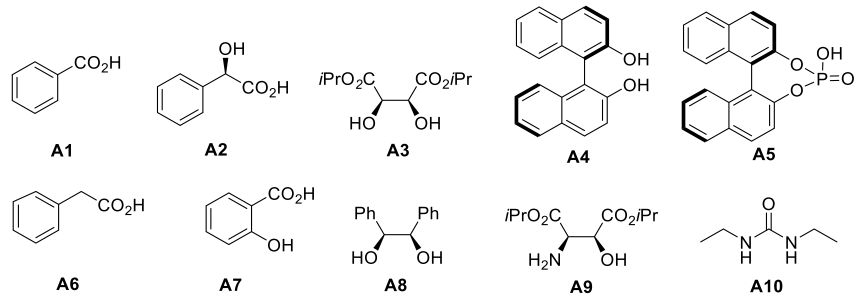



| Entry | L | x | Yield (%)[b] | **4a**:(**3a**+**5a**)[c] | ee (%)[d] |
|---|---|---|---|---|---|
| 1 | **L4** | 20 | 82 | >19:1 | 93 |
| 2 | **L5** | 20 | 30 | 4:1 | 71 |
| 3 | **L7** | 20 | 95 | >19:1 | 98 |
| 4 | **L7** | 10 | 95 | >19:1 | 98 |
| 5[e] | **L7** | 10 | 50 | >19:1 | 98 |
| 6 | **L12** | 10 | 60 | >19:1 | 91 |

[a] Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (x mol%) in dry toluene (0.5 mL) at 60 °C for 36 h under Ar. [b] Yield of isolated product. [c] Determined by $^1$H NMR analysis. [d] The data referred to ee of **4a**, determined by HPLC analysis on a chiral stationary phase. [e] $Pd_2(dba)_3$ (2.5 mol%).

### 3.3 Detailed screening conditions for asymmetric synthesis of 5a

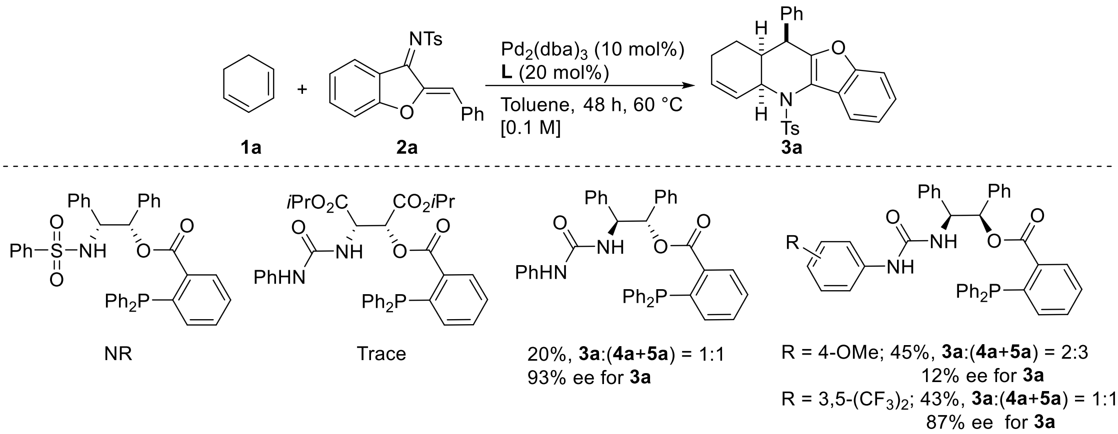





| Entry | [Pd] | **L** | Solvent | Additive | Yield (%)[b] | **5a**:(**3a**+**4a**)[c] | ee (%)[d] |
|---|---|---|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$ | **L10** | Toluene | / | 92 | >19:1 | 82 |
| 2 | $Pd_2(dba)_3$ | **L11** | Toluene | / | Trace | / | / |
| 3 | $Pd_2(dba)_3$ | **L17** | Toluene | / | Trace | / | / |
| 4 | $Pd_2(dba)_3$ | **L18** | Toluene | / | Trace | / | / |
| 5 | $Pd_2(dba)_3$ | **L19** | Toluene | / | Trace | / | / |
| 6 | $Pd_2(dba)_3$ | **L10** | THF | / | 51 | 10:1 | 80 |
| 7 | $Pd_2(dba)_3$ | **L10** | 2-Me-THF | / | 61 | >19:1 | 80 |
| 8 | $Pd_2(dba)_3$ | **L10** | $PhCF_3$ | / | 10 | 7:1 | 77 |
| 9 | $Pd_2(dba)_3$ | **L10** | Dioxane | / | 35 | 11:1 | 82 |
| 10 | $Pd_2(dba)_3$ | **L10** | $CH_2Cl_2$ | / | 26 | 7:3 | 83 |
| 11 | $Pd_2(dba)_3$ | **L10** | $CHCl_3$ | / | 20 | 1:2 | 89 |
| 12 | $Pd_2(dba)_3$ | **L10** | Xylene | / | Trace | / | / |
| 13 | $Pd_2(dba)_3$ | **L10** | EtOAc | / | Trace | / | / |
| 14 | $Pd_2(dba)_3$ | **L10** | Anisole | / | Trace | / | / |
| 15 | $Pd_2(dba)_3$ | **L10** | Toluene | **A1** | 33 | >19:1 | 83 |
| 16 | $Pd_2(dba)_3$ | **L10** | Toluene | **A2** | 76 | >19:1 | 80 |
| 17 | $Pd_2(dba)_3$ | **L10** | Toluene | **A3** | 75 | >19:1 | 80 |
| 18 | $Pd_2(dba)_3$ | **L10** | Toluene | **A4** | 58 | >19:1 | 80 |
| 19 | $Pd_2(dba)_3$ | **L10** | Toluene | **A5** | Trace | / | / |
| 20 | $Pd_2(dba)_3$ | **L10** | Toluene | **A6** | Trace | / | / |
| 21 | $Pd_2(dba)_3$ | **L10** | Toluene | **A7** | Trace | / | / |
| 22 | $Pd_2(dba)_3$ | **L10** | Toluene | **A8** | 73 | >19:1 | 80 |
| 23 | $Pd_2(dba)_3$ | **L10** | Toluene | **A9** | 70 | >19:1 | 80 |
| 24 | $Pd_2(dba)_3$ | **L10** | Toluene | **A10** | 76 | >19:1 | 80 |
| 25 | $[Pd(allyl)Cl]_2$ | **L10** | Toluene | / | 90 | >19:1 | 80 |
| 26 | $Pd(OAc)_2$ | **L10** | Toluene | / | 39 | >19:1 | 80 |
| 27 | $Pd(CH_3CN)_2Cl_2$ | **L10** | Toluene | / | NR | / | / |
| 28[e] | $Pd_2(dba)_3$ | **L10** | Toluene | / | 56 | >19:1 | 82 |
| 29[f] | $Pd_2(dba)_3$ | **L10** | Toluene | / | 25 | >19:1 | 82 |

[a] Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.05 mmol), [Pd] source (10 mol%), **L** (20 mol%), acid additive (20 mol%) in dry toluene (0.5 mL) at 60 °C for 36 h under Ar. [b] Yield of isolated product. [c] Determined by HPLC analysis. [d] The data referred to ee of **5a**, determined by HPLC analysis on a chiral stationary phase. [e] At 50 ℃. [f] With **L10** (10 mol%).

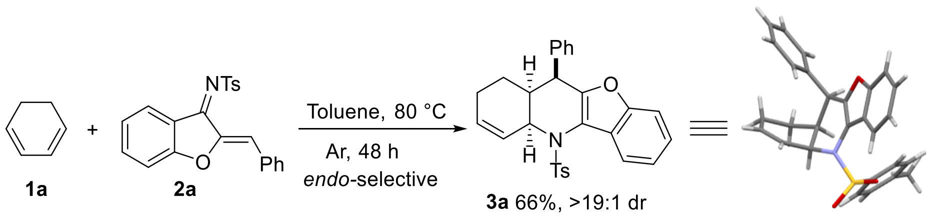
### 3.4 Detailed screening conditions for asymmetric synthesis of 3a




As the reaction of **1a** with **2a** could not proceeded without palladium at 60 ℃, the potential asymmetric synthesis of **3a** also might be achieved. Although a series of 1,2-aminoalcohol-drived bifunctional ligands were screened, bad diastereoselectivity was generally observed. As a result, currently successful construction of chiral *endo*-**3a** has not been realised yet.

## 4.General procedure for ligand-controlled diastereodivergent synthesis

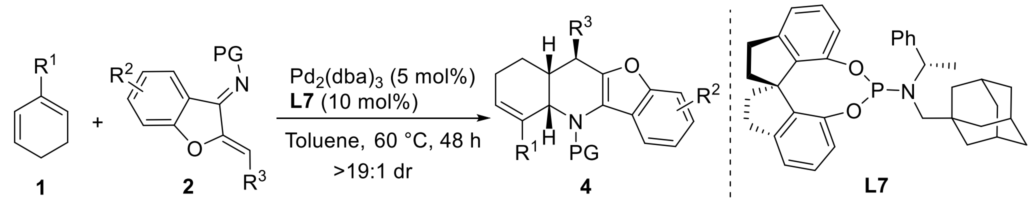
### 4.1 Procedure for synthesis of 3a




To an oven dried 10 mL Schlenk tube equipped with a stirring bar was added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (0.5 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 80 °C for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel

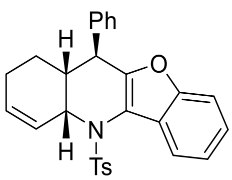
(EtOAc/petroleum ether = 1/50) to give product **3a**: 30.0 mg (0.0658 mmol), as a white solid, 66% yield; >19:1 dr; mp: 192–194 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39–7.28 (m, 3H), 7.28–7.11 (m,5H), 7.05–6.97 (m, 2H), 5.72 (dd, *J* = 10.2, 2.6 Hz, 1H), 5.39–5.33 (m, 1H), 4.72–4.64 (m, 1H), 3.70 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H), 2.08–1.98 (m, 1H), 1.74–1.62 (m, 1H), 1.61–1.43 (m, 2H), 0.62–0.42 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.9, 148.6, 144.0, 138.0, 134.3, 132.0, 130.3, 129.7, 127.6, 127.5, 127.1, 126.9, 124.7, 124.3, 123.0, 122.4, 117.9, 111.2, 55.9, 41.9, 34.8, 22.0, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_3SNa^+$ 478.1447; Found 478.1456. *Its relative configuration has been determined by X-ray diffraction analysis.*

### 4.2 General procedure for asymmetric synthesis of *exo*-4




**General procdure**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 1-azadiene **2** (0.1 mmol, 1.0 equiv), $Pd_2(dba)_3$ (5 mol%) and **L7** (10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1** (0.20 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc) to afford product **4**.

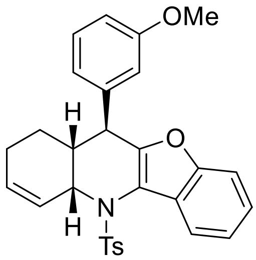
*Note: Racemic **4** was obtained by using $Pd_2(dba)_3$ in combination with racemic **L7**. The drs indicated the diastereomeric purity of the isolated products.*



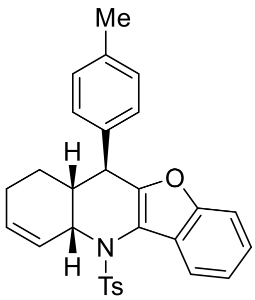

**Synthesis of 4a**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methyl benzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4a**: 43.1 mg (0.0948 mmol), as a white solid, 95% yield; mp 186–188 ℃; $[\alpha]_D^{25}$ = +248.2 (*c* = 0.34 in $CHCl_3$); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 15.12 min (major), $t_R$ = 19.19 min (minor); $^1$H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.35–7.22 (m, 5H), 7.21–7.19 (m, 1H), 7.17–7.04 (m, 2H), 6.50 (d, *J* = 7.2 Hz, 2H), 5.79–5.67 (m, 1H), 5.57 (d, *J* = 10.2 Hz, 1H), 5.10–4.96 (m, 1H), 3.82 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H), 2.27–2.18 (m, 1H), 2.13–2.04 (m, 1H), 1.81–1.74 (m, 1H), 1.71–1.59 (m, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ (ppm) 154.2, 150.0, 144.0, 139.7, 134.7, 129.94, 129.87, 128.33, 128.31, 128.1, 128.0, 127.2, 124.7, 124.4, 123.0, 122.4, 116.9, 111.1, 58.3, 39.3, 36.6, 22.1, 21.6, 20.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_3S^+$ 456.1628; Found 456.1629.

**Asymmetric synthesis of 4a on a 1.0 mmol scale:** To an oven-dried 100 mL Schlenk tube equipped with a magnetic stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (375 mg, 1.00 mmol, 1.0 equiv), $Pd_2(dba)_3$ (46.0 mg, 0.0500 mmol, 5 mol%) and ligand **L7** (55.0 mg, 0.100 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (10 mL) and 1,3-cyclohexadiene **1a** (191 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2a**, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4a**: 421.2 mg (0.9245 mmol), as a white solid, 92% yield; >19:1 dr; 98% ee.

**Synthesis of *ent*-4a**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and *ent*-**L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product *ent*-**4a**: 41.8 mg (0.0917 mmol), as a white solid, 92% yield; $[\alpha]_D^{25}$ = –260.0 (*c* = 0.33 in $CHCl_3$); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.92 min (minor), $t_R$ = 18.63 min (major).

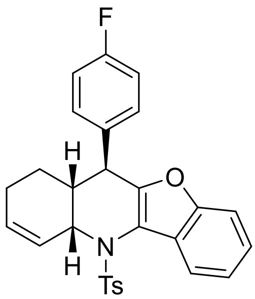



**Synthesis of 4b**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-3-methoxybenzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2b** (40.5 mg, 0.100 mmol, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2b**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4b**: 44.3 mg (0.0912 mmol), as a white solid, 91% yield; mp 199–201 °C; $[\alpha]_D^{25}$ = +272.6 (*c* = 0.27 in $CHCl_3$); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 19.89 min (major), $t_R$ = 22.13 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.35–7.25 (m, 5H), 7.11–7.02 (m, 1H), 6.74 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.16 (s, 1H), 6.11 (d, *J* = 7.5 Hz, 1H), 5.77–5.67 (m, 1H), 5.57 (d, *J* = 10.3 Hz, 1H), 5.09–4.96 (m, 1H), 3.80 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 3H), 2.41 (s, 3H), 2.29–2.15 (m, 1H), 2.14–2.00 (m, 1H), 1.84–1.71 (m, 1H), 1.71–1.60 (m, 2H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ (ppm) 159.7, 154.2, 149.8, 144.3, 141.2, 134.6, 130.0, 129.9, 129.3, 128.3, 127.9, 124.7, 124.4, 122.9, 122.5, 120.6, 117.0, 115.2, 111.2, 111.1, 58.3, 55.1, 39.2, 36.3, 22.2, 21.5, 20.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}NO_4S^+$ 486.1734; Found 486.1741.

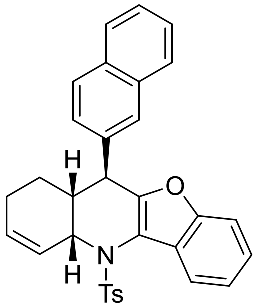



**Synthesis of 4c**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((*E*)-2-((*Z*)-4-methylbenzylidene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide **2c** (38.9 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2c**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4c**: 42.3 mg (0.0901 mmol), as a white solid, 90% yield; mp 174–176 °C; $[\alpha]_D^{25}$ = +231.1 (*c* = 0.33 in

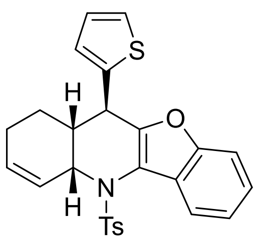
$CHCl_3$); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.98 min (major), $t_R$ = 19.85 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 7.7, 1H), 7.71–7.49 (m, 2H), 7.34–7.21 (m, 5H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.49–6.29 (m, 2H), 5.81–5.65 (m, 1H), 5.59–5.55 (m, 1H), 5.04–5.02 (m, 1H), 3.79 (d, *J* = 9.9 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 2.22–2.19 (m, 1H), 2.12–2.04 (m, 1H), 1.78–1.73 (m, 1H), 1.71–1.58 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 150.3, 144.1, 137.0, 136.6, 134.8, 129.92, 129.85, 129.1, 128.4, 128.1, 124.8, 124.4, 123.0, 122.4, 116.9, 111.2, 58.3, 38.9, 36.6, 22.2, 21.6, 21.1, 20.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{28}NO_3S^+$ 470.1784; Found 470.1793.



**Synthesis of 4d**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-4-fluorobenzylidene)benzofuran-3(2*H*) - ylidene)-4-methylbenzenesulfonamide **2d** (39.3 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2d**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4d**: 47.0 mg (0.0992 mmol), as a white solid, 99% yield; mp 187–189 °C; $[\alpha]_D^{25}$ = +213.8 (*c* = 0.58 in $CHCl_3$); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.60 min (major), $t_R$ = 19.85 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 7.6 Hz, 1H), 7.70–7.46 (m, 2H), 7.50–7.14 (m, 5H), 6.94–6.68 (m, 2H), 6.64–6.29 (m, 2H), 5.74–5.70 (m, 1H), 5.57 (dt, *J* = 10.2, 2.0 Hz, 1H), 5.07–5.00 (m, 1H), 3.81 (d, *J* = 9.9 Hz, 1H), 2.45 (s, 3H), 2.33–1.93 (m, 2H), 1.73–1.64 (m, 2H), 1.61–1.59 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.9 (d, $^1J_{FC}$ = 246.2 Hz), 154.2, 149.7, 144.1, 135.39, 135.36, 134.8, 129.91, 129.87, 129.6 (d, $^3J_{FC}$ = 7.9 Hz), 128.3, 128.1, 124.64, 124.56, 123.1, 122.5, 117.0, 115.3 (d, $^2J_{FC}$ = 21.3 Hz), 111.1, 58.3, 38.5, 36.7, 22.0, 21.6, 20.5; $^{19}$F NMR (375 MHz, $CDCl_3$) δ (ppm) –115.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}FNO_3SNa^+$ 496.1353; Found 496.1359.

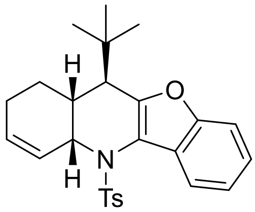


**Synthesis of 4e**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((2*Z*,3*E*)-2-(naphthalen-2-ylmethylene)-benzofuran-3(2*H*)-ylidene)benzenesulfonamide **2e** (42.6 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2e**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4e**: 44.6 mg (0.0882 mmol), as a white solid, 88% yield; mp 240–242 °C; $[\alpha]_D^{25}$ = +343.4 (*c* = 0.39 in $CHCl_3$); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 19.67 min (major), $t_R$ = 25.58 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, *J* = 7.9 Hz, 1H), 7.81–7.73 (m, 1H), 7.71–7.58 (m, 3H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.50–7.38 (m, 2H), 7.37–7.18 (m, 7H), 6.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.81–5.71 (m, 1H), 5.66–5.56 (m, 1H), 5.14–5.02 (m, 1H), 4.01 (d, *J* = 9.9 Hz, 1H), 2.45 (s, 3H), 2.37–2.24 (m, 1H), 2.22–2.01 (m, 1H), 1.89–1.84 (m, 1H), 1.70–1.63 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 149.9, 144.2, 137.0, 134.8, 133.2, 132.6, 130.01, 129.99, 128.3, 128.1, 127.6, 127.5, 127.4, 126.2, 125.9, 125.6, 124.7, 124.5, 123.0, 122.5, 117.2, 111.1, 58.3, 39.4, 36.4, 22.1, 21.7, 20.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}NO_3SNa^+$ 528.1604; Found 528.1609.

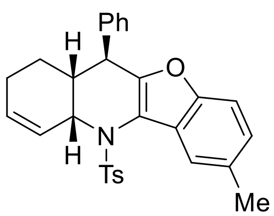


**Synthesis of 4f**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((2*Z*,3*E*)-2-(thiophen-2-ylmethylene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide **2f** (38.1 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2f**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4f**: 44.4 mg (0.0962 mmol), as a white solid, 96% yield; mp 169–171 °C; $[\alpha]_D^{25}$ = +216.6 (*c* = 0.27 in $CHCl_3$); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate

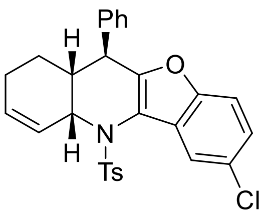
=1.0 mL/min, λ = 254 nm) $t_R$ = 16.48 min (major), $t_R$ = 20.26 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24–8.13 (m, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.36–7.30 (m, 2H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.28–7.24 (m, 2H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.87 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.72–5.68 (m, 1H), 5.56 (dt, *J* = 10.2, 2.0 Hz, 1H) , 5.03–4.90 (m, 1H), 4.17 (d, *J* = 9.9 Hz, 1H), 2.41 (s, 3H), 2.25–1.98 (m, 2H), 1.83–1.63 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 148.7, 144.1, 142.0, 134.5, 130.03, 129.97, 128.2, 127.8, 126.6, 126.0, 124.7, 124.6, 124.4, 123.0, 122.7, 116.5, 111.2, 58.1, 36.6, 34.4, 22.6, 21.6, 20.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{23}NO_3S_2Na^+$ 484.1012; Found 484.1021.




**Synthesis of 4g**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((2*Z*,3*E*)-2-(2,2-dimethylpropylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2g** (35.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2g**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4g**: 40.0 mg (0.0918 mmol), as a white solid, 92% yield; mp 173–175 ℃; $[\alpha]_D^{25}$ = +60 (*c* = 0.37 in $CHCl_3$); >19:1 dr; 98% ee, determined by HPLC analysis (Daicel Chiralpak IC, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 8.38 min (major), $t_R$ = 17.07 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10–7.96 (m, 1H), 7.79–7.67 (m, 2H), 7.45–7.33 (m, 1H), 7.29–7.21 (m, 4H), 5.66–5.61 (m, 1H), 5.30–5.29 (m, 1H), 4.90–4.70 (m, 1H), 2.62 (d, *J* = 7.8 Hz, 1H), 2.39 (s, 3H), 2.37–2.28 (m, 1H), 2.19–2.08 (m, 1H), 2.02–1.79 (m, 3H), 0.74 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.72, 153.66, 143.8, 136.6, 130.8, 129.8, 128.9, 128.0, 124.9, 123.9, 122.8, 121.4, 115.7, 110.9, 58.6, 42.3, 35.0, 33.5, 28.5, 26.4, 21.5, 20.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{29}NO_3SNa^+$ 458.1760; Found 458.1767.

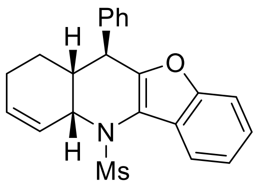



**Synthesis of 4h**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)-5-methylbenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2h** (38.9 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2h**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4h**: 46.9 mg (0.0999 mmol), as a white solid, 99% yield; mp 193–195 °C; $[\alpha]_D^{25}$ = +259.4 (*c* = 0.34 in $CHCl_3$); >19:1 dr; 94% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 12.04 min (major), $t_R$ = 14.18 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22–7.04 (m, 5H), 6.60–6.43 (m, 2H), 5.78–5.66 (m, 1H), 5.62–5.50 (m, 1H), 5.08–4.98 (m, 1H), 3.80 (d, *J* = 9.9 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.30–2.16 (m, 1H), 2.15–1.98 (m, 1H), 1.80–1.74 (m, 1H), 1.71–1.58 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.7, 150.2, 144.0, 139.8, 134.8, 132.4, 129.89, 129.86, 128.34, 128.32, 128.2, 128.1, 127.2, 125.6, 124.7, 122.1, 116.7, 110.6, 58.3, 39.3, 36.6, 22.1, 21.6, 21.5, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1604.

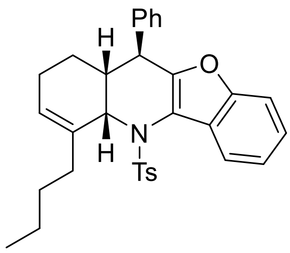



**Synthesis of 4i**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)-5-chlorobenzofuran-3(2*H*)-ylidene) -4-methylbenzenesulfonamide **2i** (41.0 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2i**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4i**: 48.2 mg (0.0984 mmol), as a white solid, 98% yield; mp 188–190 ℃; $[\alpha]_D^{25}$ = +258.0 (*c* = 0.35 in $CHCl_3$); >19:1 dr; 93% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.15 min (minor), $t_R$ = 17.53 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25–7.18 (m, 3H), 7.17–7.10 (m, 2H), 6.55–6.45 (m, 2H), 5.80–5.70 (m, 1H), 5.60–5.48 (m, 1H), 5.08–4.97 (m, 1H), 3.80 (d, *J* = 9.9 Hz, 1H), 2.45 (s, 3H), 2.30–2.17 (m, 1H), 2.15–2.04 (m, 1H), 1.82–1.74 (m, 1H), 1.73–1.59 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.6, 151.6, 144.3, 139.3, 134.6, 130.2, 130.0, 128.8, 128.4, 128.12, 128.07, 127.4, 126.0, 124.7, 122.1, 116.6, 112.1, 58.3, 39.3, 36.5, 22.0, 21.6, 20.5; HRMS (ESI-TOF) m/z: [M +

Na]+ Calcd for $C_{28}H_{24}{}^{35}ClNO_3SNa^+$ 512.1058; Found 512.1060; Calcd for $C_{28}H_{24}{}^{37}ClNO_3SNa^+$ 514.1029; Found 514.1038.

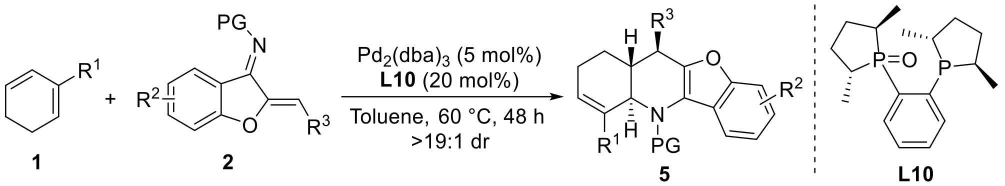



**Synthesis of 4j**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2j** (30.0 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2j**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **4j**: 33.6 mg (0.0885 mmol), as a white solid, 89% yield; mp 89–91 ℃; $[\alpha]_D^{25}$ = +10.9 (*c* = 0.55 in $CHCl_3$); >19:1 dr; 97% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 18.26 min (major), $t_R$ = 42.92 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08–7.88 (m, 1H), 7.41–7.28 (m, 4H), 7.26–7.19 (m, 4H), 5.87–5.74 (m, 1H), 5.61–5.51 (m, 1H), 5.05–4.94 (m, 1H), 4.09 (d, *J* = 9.8 Hz, 1H), 3.10 (s, 3H), 2.58–2.49 (m, 1H), 2.43–2.29 (m, 1H), 2.25–2.13 (m, 1H), 1.97–1.80 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 149.1, 139.8, 130.3, 129.0, 128.2, 128.1, 127.6, 124.6, 124.2, 123.0, 122.0, 117.1, 111.2, 58.0, 39.6, 38.6, 38.4, 22.3, 20.6; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{22}H_{21}NO_3SNa^+$ 402.1134; Found 402.1142.



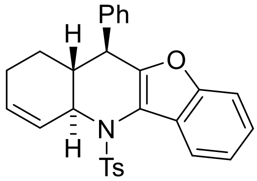

**Synthesis of 4k**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), 2-butylcyclohexa-1,3-diene **1b** (27.2 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). Then distilled toluene (1.0 mL) was added via syringe. The tube was evacuated followed by back-filled with argon for five times. The mixture was stirred at 80 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/100) to afford product **4k**: 25.6 mg (0.0500 mmol), as a white solid, 50% yield; mp 237–239 ℃; $[\alpha]_D^{25}$ = +149.2 (*c* = 0.25 in $CHCl_3$); >19:1 dr; 90% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 7.78 min (major), $t_R$ = 9.24 min (minor); $^1$H NMR δ (ppm) 8.20 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.33–7.26 (m, 5H), 7.21–7.16 (m, 1H), 7.14–7.08 (m, 2H), 6.51–6.43 (m, 2H), 5.44 (s, 1H), 5.08 (s, 1H), 3.85 (d, *J* = 10.1 Hz, 1H), 2.44 (s, 3H), 2.32–2.19 (m, 1H), 2.16–2.02 (m, 2H), 1.88–1.74 (m, 2H), 1.69–1.51 (m, 3H), 1.36–1.22 (m, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 149.1, 139.8, 130.3, 129.0, 128.2, 128.1, 127.6, 124.6, 124.2, 123.0, 122.0, 117.0, 111.2, 58.0, 39.6, 38.6, 38.4, 22.3, 20.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NO_3SNa^+$ 534.2073; Found 534.2075.

### 4.3 General procedure for asymmetric synthesis of diastereomers 5



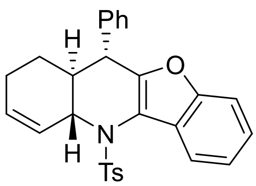

**General procdure**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 1-azadiene **2** (0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (5 mol%) and **L10** (20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1** (0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5**.

*Note: Racemic* ***5*** *was obtained by using $Pd_2(dba)_3$ in combination with racemic* ***L10****. The dr indicated the diastereomeric purity of the isolated products.*

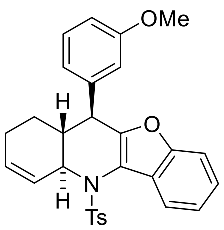



**Synthesis of 5a**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((Z)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether

= /50) to afford product **5a**: 39.2 mg (0.0860 mmol), as a white solid, 86% yield; mp 174–176 ℃; $[\alpha]_D^{25}$ = +207.3 (*c* = 0.28 in $CHCl_3$); >19:1 dr; 82% ee, determined by HPLC analysis (Daicel Chiralpak AD, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 11.75 min (major), $t_R$ = 19.31 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 7.5, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.31–7.18 (m, 8H), 6.78–6.67 (m, 2H), 6.42 (dt, *J* = 10.6, 2.8 Hz, 1H), 5.99–5.95 (m, 1H), 4.28–4.11 (m, 1H), 3.53 (d, *J* = 10.2 Hz, 1H), 2.42 (s, 3H), 2.03–1.94 (m, 1H), 1.90–1.72 (m, 1H), 1.68–1.53 (m, 2H), 1.30–1.21 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.9, 149.9, 144.0, 138.8, 135.8, 129.6, 129.1, 129.0, 128.5, 128.3, 127.4, 126.0, 125.2, 124.4, 123.0, 122.5, 122.0, 111.1, 64.5, 48.3, 38.9, 26.3, 24.3, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_3SNa^+$ 478.1447; Found 478.1447.

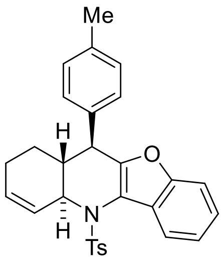



**Synthesis of *ent*-5a**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and *ent*-**L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 °C for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether =1/50) to afford product *ent*-**5a**: 41.0 mg (0.0878 mmol), as a white solid, 88% yield; $[\alpha]_D^{25}$ = –219.7 (*c* = 0.31 in $CHCl_3$); >19:1 dr; 83% ee, determined by HPLC analysis (Daicel Chiralpak AD, n-Hexane/i-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 11.78 min (minor), $t_R$ = 19.16 min (major).

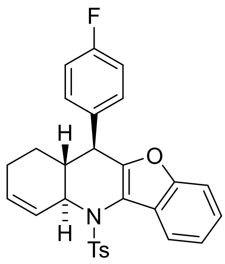



**Synthesis of 5b**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were add *N*-((*E*)-2-((*Z*)-3-methoxybenzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2b** (40.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2b**, the mixture was directly purified by flash chromatography on silica gel

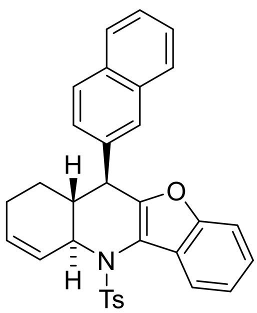
(EtOAc/petroleum ether = 1/50) to afford product **5b**: 35.8 mg (0.0737 mmol), as a white solid, 74% yield; mp 198–200 ℃; $[\alpha]_D^{25}$ = +173.3 (*c* = 0.27 in $CHCl_3$); >19:1 dr; 77% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 19.62 min (minor), $t_R$ = 21.05 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.34–7.26 (m, 4H), 7.18–7.07 (m, 1H), 6.80–6.74 (m, 1H), 6.46–6.38 (m, 1H), 6.36–6.28 (m, 2H), 6.02–5.93 (m, 1H), 4.24–4.12 (m 1H), 3.78 (s, 3H), 3.50 (d, *J* = 10.3 Hz, 1H), 2.40 (s, 3H), 2.05–1.92 (m, 1H), 1.85–1.74 (m, 1H), 1.69–1.62 (m, 1H), 1.60–1.51 (m, 2H), 1.26–1.23 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 159.6, 153.9, 149.8, 144.1, 140.3, 135.6, 129.8, 129.2, 129.0, 128.9, 126.0, 125.2, 124.4, 122.9, 122.6, 122.0, 120.9, 115.3, 111.5, 111.1, 64.4, 55.1, 48.3, 38.7, 26.4, 24.2, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_4SNa^+$ 508.1553; Found 508.1555.




**Synthesis of 5c**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((*E*)-2-((*Z*)-4-methylbenzylidene)benzofuran-3(2*H*)-ylidene)benzenesulfonamide **2c** (38.9 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2c**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5c**: 41.1 mg (0.0875 mmol), as a white solid, 88% yield; mp 187–189 ℃; $[\alpha]_D^{25}$ = +193.1 (*c* = 0.44 in $CHCl_3$); >19:1 dr; 82% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 13.20 min (major), $t_R$ = 21.41 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16–8.02 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.33–7.27 (m, 3H), 7.26–7.21 (m, 2H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.61 (d, *J* = 7.9 Hz, 2H), 6.47–6.34 (m, 1H), 6.03–5.90 (m, 1H), 4.27–4.12 (m, 1H), 3.50 (d, *J* = 10.3 Hz, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 2.08–1.90 (m, 1H), 1.85–1.70 (m, 1H), 1.68–1.60 (m, 2H), 1.28–1.15 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.9, 150.1, 144.0, 137.1, 135.8, 135.7, 129.6, 129.11, 129.06, 129.0, 128.3, 126.1, 125.2, 124.3, 122.9, 122.5, 121.9, 111.2, 64.5, 48.0, 38.9, 26.3, 24.3, 21.6, 21.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1606.

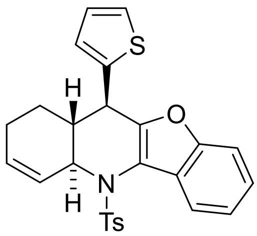


**Synthesis of 5d**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-4-fluorobenzylidene)benzofuran-3(2*H*) -ylidene)-4-methylbenzenesulfonamide **2d** (39.3 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2d**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/DCM/petroleum ether = 1/1/50) to afford product **5d**: 39.3 mg (0.0830 mmol), as a white solid, 83% yield; mp 121–123 ℃; $[\alpha]_D^{25}$ = +165.2 (*c* = 0.62 in $CHCl_3$); >19:1 dr; 79% ee, determined by HPLC analysis (Daicel Chiralpak AD, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 13.47 min (major), $t_R$ = 19.21 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.35–7.27 (m, 4H), 6.96–6.78 (m, 2H), 6.75–6.54 (m, 2H), 6.40 (d, *J* = 10.5 Hz, 1H), 6.06–5.88 (m, 1H), 4.24–4.13 (m, 1H), 3.53 (d, *J* = 10.3 Hz, 1H), 2.43 (s, 3H), 2.07–1.92 (m, 1H), 1.87–1.72 (m, 1H), 1.67–1.59 (m, 2H), 1.27–1.20 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 162.1 (d, $^1J_{FC}$ = 247.0 Hz), 153.9, 149.6, 144.1, 135.8, 134.5, 129.9, 129.8, 129.9 (d, $^3J_{FC}$ = 8.0 Hz), 129.1, 129.0, 126.0, 125.1, 124.6, 123.1, 122.6, 122.1, 115.3 (d, $^2J_{FC}$ = 21.3 Hz), 111.1, 64.5, 47.5, 39.1, 26.3, 24.3, 21.6; $^{19}F$ NMR (375 MHz, $CDCl_3$) δ (ppm) –115.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}FNO_3SNa^+$ 496.1353; Found 496.1354. Recrystallisation of the above product from petroleum ether (7.0 mL) and EtOAc (1.0 mL) gave a white solid, 20.0 mg (0.0422 mmol), 42% yield, 91% ee.

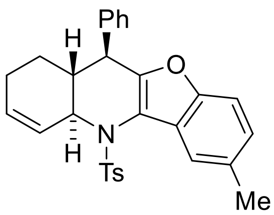


**Synthesis of 5e**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((2*Z*,3*E*)-2-(naphthalen-2-ylmethylene)-benzo furan-3(2*H*)-ylidene)benzenesulfonamide **2e** (42.6 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2e**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/DCM/petroleum ether = 1/25/50) to afford product **5e**:

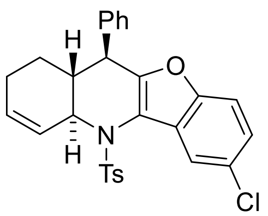
42.9 mg (0.0848 mmol), as a white solid, 85% yield; mp 198–200 ℃; $[\alpha]_D^{25}$ = +371.1 (*c* = 0.24 in $CHCl_3$); >19:1 dr; 88% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 18.82 min (major), $t_R$ = 20.63 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (d, *J* = 7.8 Hz, 1H), 7.82–7.77 (m, 1H), 7.75–7.67 (m, 3H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.50–7.43 (m, 2H), 7.38 (s, 1H), 7.33–7.25 (m, 5H), 6.70 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.45 (dt, *J* = 10.4, 2.7 Hz,1H), 6.05–5.91 (m, 1H), 4.31–4.20 (m, 1H), 3.70 (d, *J* = 10.2 Hz, 1H), 2.43 (s, 3H), 2.03–1.92 (m, 1H), 1.80–1.63 (m, 3H), 1.37–1.23 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 154.0, 149.8, 144.1, 136.2, 135.8, 133.2, 132.7, 129.7, 129.1, 128.0, 127.7, 127.6, 127.5, 126.2, 126.0, 125.9, 125.2, 124.5, 123.0, 122.6, 122.2, 111.1, 64.4, 48.5, 38.8, 26.3, 24.2, 21.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}NO_3SNa^+$ 528.1604; Found 528.1605.



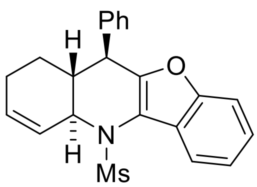

**Synthesis of 5f**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((*2Z,3E*)-2-(thiophen-2-ylmethylene)benzofuran-3(*2H*)-ylidene)benzenesulfonamide **2f** (38.1 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.6 mg, 0.01 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2f**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5f**: 39.8 mg (0.0862 mmol), as a white solid, 86% yield; mp 106–108 ℃; $[\alpha]_D^{25}$ = +161.3 (*c* = 0.48 in $CHCl_3$); >19:1 dr; 83% ee, determined by HPLC analysis (Daicel Chiralpak AD, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 8.56 min (major), $t_R$ = 10.07 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.39–7.13 (m, 6H), 6.96–6.83 (m, 1H), 6.71–6.58 (m, 1H), 6.43 (d, *J* = 10.6 Hz, 1H), 6.09–5.85 (m, 1H), 4.23–4.03 (m, 1H), 3.88 (d, *J* = 10.5 Hz, 1H), 2.40 (s, 3H), 2.07–1.93 (m, 1H), 1.84–1.68 (m, 2H), 1.55–1.42 (m, 1H), 1.30–1.15 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.9, 148.7, 144.0, 141.3, 135.6, 129.8, 129.3, 128.9, 126.6, 126.4, 125.7, 125.2, 124.6, 124.5, 123.0, 122.7, 121.6, 111.2, 64.2, 43.1, 39.1, 26.7, 24.3, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{23}NO_3S_2Na^+$ 484.1012; Found 484.1012.



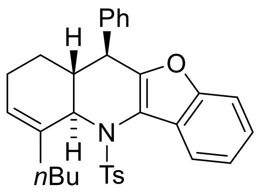
**Synthesis of 5g**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)-5-methylbenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2h** (38.9 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2h**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5g**: 40.9 mg (0.0871 mmol), as a white solid, 87% yield; mp 112–114 ℃; $[\alpha]_D^{25}$ = +242.6 (*c* = 0.39 in $CHCl_3$); >19:1 dr; 85% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 12.51 min (minor), $t_R$ = 17.10 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (s, 1H), 7.69–7.63 (m, 2H), 7.29–7.26 (m, 1H), 7.25–7.24 (m, 1H), 7.24–7.13 (m, 4H), 7.06 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.75–6.68 (m, 2H), 6.42 (dt, *J* = 10.6, 2.6 Hz, 1H), 6.01–5.92 (m, 1H), 4.22–4.13 (m, 1H), 3.51 (d, *J* = 10.2 Hz, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.04–1.92 (m, 1H), 1.85–1.72 (m, 1H), 1.67–1.56 (m, 2H), 1.27–1.22 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 152.4, 150.1, 144.0, 138.9, 135.8, 132.5, 129.6, 129.1, 128.9, 128.5, 128.3, 127.4, 126.1, 125.7, 125.2, 122.2, 121.8, 110.7, 64.5, 48.4, 38.9, 26.3, 24.3, 21.6, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1601. Recrystallisation of the above product from petroleum ether (7.0 mL) and EtOAc (1.0 mL) gave a white solid, 20.2 mg (0.0422 mmol), 42% yield, 97% ee.



**Synthesis of 5h**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-(*E*)-2-((*Z*)-benzylidene)-5-chlorobenzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2i** (41.0 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2i**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5h**: 41.7 mg (0.0851 mmol), as a white solid, 85% yield; mp 108–110 ℃; $[\alpha]_D^{25}$ = +226.9 ($c$ = 0.48 in $CHCl_3$); >19:1 dr; 87% ee, determined by HPLC analysis (Daicel Chiralpak IA, *n*-Hexane/*i*-PrOH = 60/40, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 5.49 min (minor), $t_R$ = 7.18 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12–8.07 (m, 1H), 7.68 – 7.62 (m, 2H), 7.31–7.26 (m, 2H), 7.25–7.16 (m, 5H), 6.75–6.67 (m, 2H), 6.40 (dt, *J* = 10.7, 2.7 Hz, 1H), 6.02–5.90 (m, 1H), 4.23–4.14 (m, 1H), 3.52 (d, *J* = 9.9 Hz, 1H), 2.45 (s, 3H), 2.09–1.93 (m, 1H), 1.89–1.74 (m, 1H), 1.70–1.57 (m, 2H), 1.28–1.22 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.3, 151.4, 144.2, 138.4, 135.6, 129.7, 129.2, 129.1, 128.8, 128.42, 128.39, 127.5, 126.5, 125.8, 124.7, 122.3, 121.6, 112.1, 64.5, 48.3, 38.9, 26.3, 24.2, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{24}{}^{35}ClNO_3SNa^+$ 512.1058; Found 512.1061; Calcd for $C_{28}H_{24}{}^{37}ClNO_3SNa^+$ 514.1028; Found 514.1041. Recrystallisation of the above product from petroleum ether (7.0 mL) and EtOAc (1.0 mL) gave a white solid, 27.2 mg (0.0555 mmol), 56% yield, 98% ee.



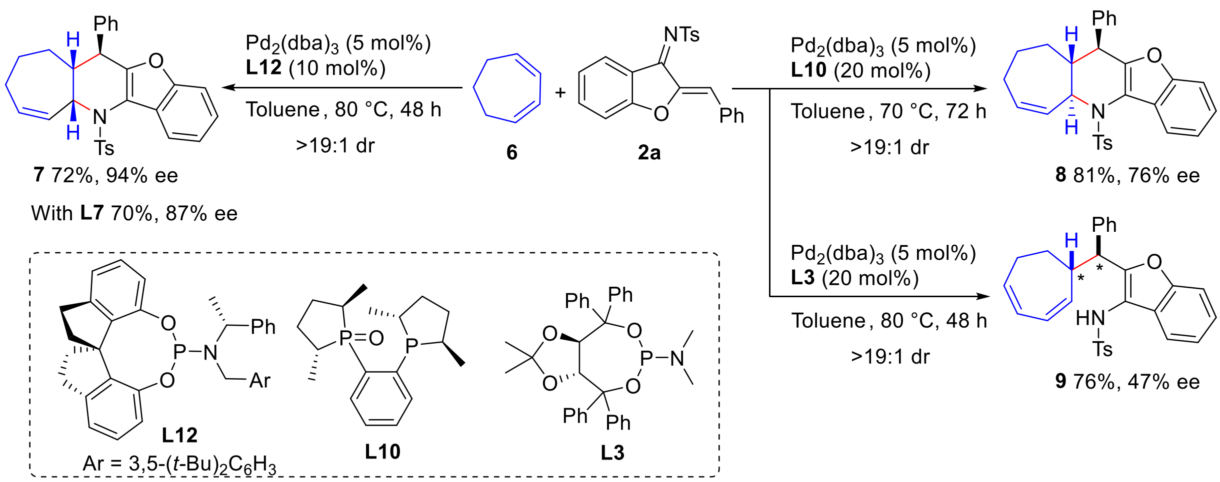

**Synthesis of 5i**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were add *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methyl benzenesulfonamide **2j** (30.0 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cyclohexadiene **1a** (19.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2j**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **5i**: 30.6 mg (0.0806 mmol), as a white solid, 81% yield; mp 166–168 ℃; $[\alpha]_D^{25}$ = +24.5 ($c$ = 0.22 in $CHCl_3$); >19:1 dr; 70% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 20.91 min (major), $t_R$ = 42.24 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.34–7.25 (m, 3H), 7.21–7.13 (m, 5H), 6.21 (dd, *J* = 10.0, 2.2 Hz, 1H), 5.95 (dt, *J* = 11.0, 3.0 Hz, 1H), 4.23–4.13 (m, 1H), 3.71 (d, *J* = 10.1 Hz, 1H), 3.09 (s, 3H), 2.44–2.31 (m, 1H), 2.10–1.97 (m, 2H), 1.96–1.89 (m, 1H), 1.46–1.35 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.8, 149.1, 139.2, 130.6, 128.9, 128.5, 127.7, 124.9, 124.8, 124.5, 122.9, 122.1, 121.5, 111.3, 63.7, 48.2, 42.4, 41.6, 26.3, 24.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{21}NO_3SNa^+$ 402.1134; Found 402.1136.

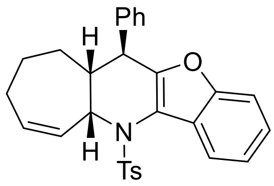



**Synthesis of 5j**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). Then degassed dry toluene (1.0 mL) and 2-butylcyclohexa-1,3-diene **1b** (27.2 mg, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 80 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/100) to afford product **5j**: 10.3 mg (0.0201 mmol), as a white solid, 20% yield, as a white solid; mp 181–183 ℃; $[\alpha]_D^{25}$ = +62.9 (*c* = 0.39 in $CHCl_3$); >19:1 dr; 53% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 256 nm) $t_R$ = 9.90 min (major), $t_R$ = 11.98 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.37–7.27 (m, 3H), 7.25–7.17 (m, 3H), 7.15–7.07 (m, 2H), 6.42 (dd, *J* = 7.1, 1.7 Hz, 2H), 5.86–5.78 (m, 1H), 4.20–4.09 (m, 1H), 3.60 (d, *J* = 10.6 Hz, 1H), 2.71–2.59 (m, 1H), 2.51–2.44 (m, 1H), 2.44 (s, 3H), 2.12–1.91 (m, 3H), 1.57–1.46 (m, 2H), 1.43–1.33 (m, 3H), 1.20–1.08 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.9, 150.8, 143.9, 139.0, 137.7, 136.2, 129.6, 129.3, 128.3, 128.2, 127.3, 125.6, 124.8, 124.4, 123.1, 123.0, 122.1, 111.3, 68.8, 49.6, 39.8, 34.1, 31.3, 26.9, 24.7, 22.6, 21.6, 14.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NO_3SNa^+$ 534.2073; Found 534.2074.

## 5. More substrate exploration

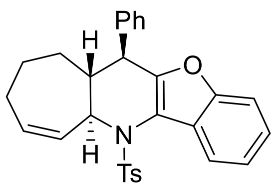
### 5.1 Exploration of more cyclic dienes and polyenes





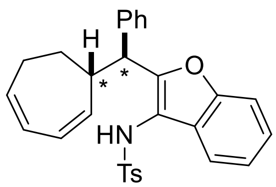

**Synthesis of 7**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L12** (6.0 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cycloheptadiene **6** (22.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **7**: 34.0 mg (0.0724 mmol), as a white solid, 72% yield; mp 181–183 ℃; $[\alpha]_D^{25}$ = +20.0 (*c* = 0.41 in $CHCl_3$); >19:1 dr; 94% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 7.38 min (major), $t_R$ = 10.04 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25–8.19 (m, 1H), 7.68–7.56 (m, 2H), 7.30–7.26 (m, 4H), 7.20–7.16 (m, 1H), 7.15–7.09 (m, 2H), 6.56–6.50 (m, 2H), 5.90–5.77(m, 1H), 5.42–5.38 (m, 1H), 5.18–5.16 (m, 1H), 3.95 (d, *J* = 11.4 Hz, 1H), 2.43 (s, 3H), 2.31–2.18 (m, 1H), 2.09 (d, *J* = 18.6 Hz, 1H), 1.80–1.64 (m, 1H), 1.53–1.42 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 150.0, 144.1, 143.3, 138.9, 135.1, 132.6, 132.3, 130.5, 129.8, 129.6, 129.0, 128.4, 128.3, 128.3, 128.2, 127.9, 127.2, 125.4, 124.6, 124.5, 123.0, 122.4, 117. 9, 111.2, 62.7, 40.6, 39.7, 29.4, 28.8, 21.5, 21.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1613.

*Note: 7 was obtained in 70 yield and 87% ee by using $Pd_2(dba)_3$ in combination with **L**7, and the configuration of 7 was assigned by analogy with products **4**.*

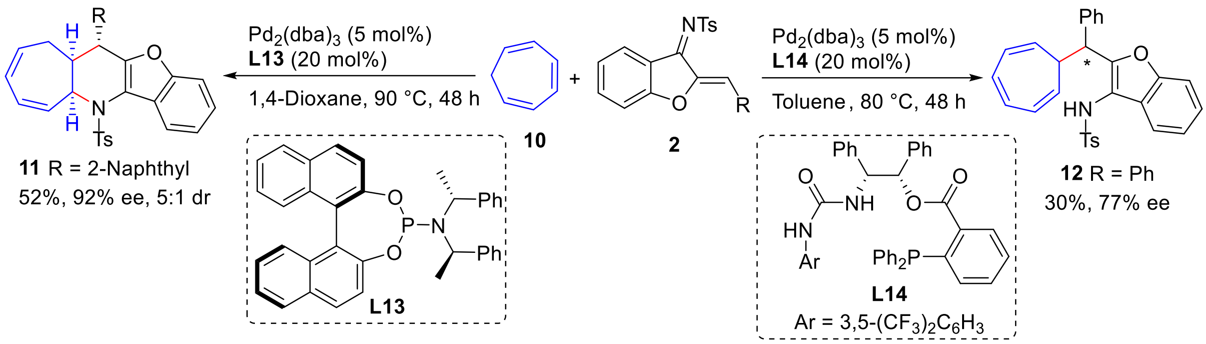


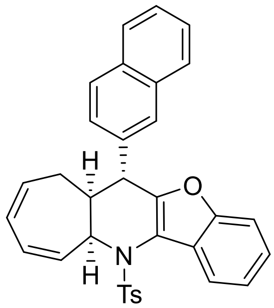

**Synthesis of 8**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cycloheptadiene **6** (22.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 70 ℃ for 72 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **8**: 37.8 mg (0.0805 mmol), as a white solid, 81%

yield; mp 199–201 ℃; $[\alpha]_D^{25}$ = –16.5 ($c$ = 0.55 in $CHCl_3$); >19:1 dr; 76% ee, determined by HPLC analysis (Daicel Chiralpak IG, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 11.72 min (major), $t_R$ = 14.73 min (minor); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03–7.95 (m, 1H), 7.54–7.48 (m, 2H), 7.37–7.27 (m, 7H), 7.26–7.21 (m, 1H), 6.94–6.83 (m, 2H), 6.09 (ddd, $J$ = 11.3, 4.0, 1.5 Hz, 1H), 5.86–5.76 (m, 1H), 4.58–4.47 (m, 1H), 2.48 (s, 3H), 2.39 (d, $J$ = 11.0 Hz, 1H), 2.23–2.10 (m, 2H), 2.09–1.99 (m, 1H), 1.71–1.59 (m, 1H), 1.54–1.46 (m, 1H), 1.27–1.20 (m, 1H), 1.16–1.07 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.8, 152.1, 144.1, 136.4, 133.7, 130.1, 129.5, 129.1, 128.6, 127.9, 127.6, 125.4, 123.9, 123.2, 121.2, 117.6, 111.4, 63.1, 50.7, 45.9, 33.3, 27.4, 25.0, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1604. *The configuration of **8** was assigned by analogy with products **5**.*

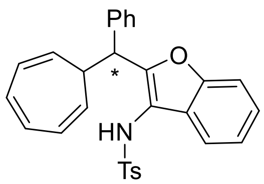



**Synthesis of 9**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L3** (10.8 mg, 0.0200 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and 1,3-cycloheptadiene **6** (22.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 80 ℃ for 36 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **9**: 34.0 mg (0.0725 mmol), as a colorless oil, 73% yield; $[\alpha]_D^{25}$ = –74.0 ($c$ = 0.34 in $CHCl_3$); >19:1 dr; 47% ee, determined by HPLC analysis (Daicel Chiralpak IE, *n*-Hexane/*i*-PrOH = 95/5, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 8.87 min (minor), $t_R$ = 10.0 min (major); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 (d, $J$ = 8.1 Hz, 2H), 7.38 (d, $J$ = 8.3 Hz, 1H), 7.25–7.17 (m, 7H), 7.16–7.08 (m, 3H), 6.11–6.01 (m, 1H), 5.93–5.82 (m, 2H), 5.69 (dd, $J$ = 11.6, 6.5 Hz, 1H), 5.45 (dd, $J$ = 11.6, 5.3 Hz, 1H), 3.88 (d, $J$ = 11.4 Hz, 1H), 3.33–3.27 (m, 1H), 2.41 (s, 3H), 2.23–2.14 (m, 2H), 1.68–1.62 (m, 1H), 1.55–1.45 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 156.0, 153.3, 143.9, 138.7, 136.8, 135.1, 134.9, 129.7, 128.6, 128.5, 127.6, 127.0, 126.0, 125.1, 124.5, 124.2, 123.0, 119.4, 113.1, 111.4, 45.9, 43.7, 29.0, 28.2, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604; Found 492.1612.



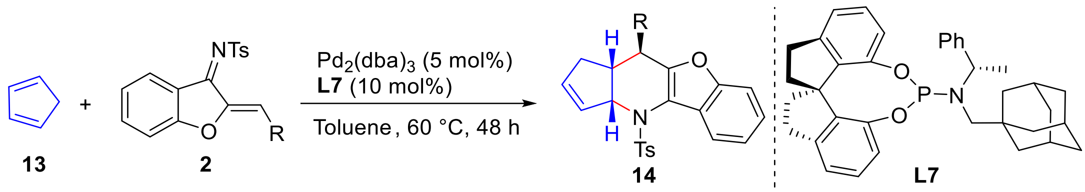



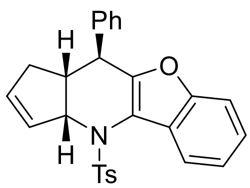
**Synthesis of 11**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((2*Z*,3*E*)-2-(naphthalen-2-ylmethylene)-benzofuran-3(2*H*)-ylidene)benzenesulfonamide **2e** (85.0 mg, 0.200 mmol, 1.0 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.010 mmol, 5 mol%) and **L13** (21.6 mg, 0.0400 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and cycloheptatriene **10** (32.0 µL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 90 ℃ for 48 h. After complete consumption of **2e**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford product **11**: 52.2 mg (0.0504 mmol), as a white solid, 50% yield; mp 241–242 ℃; $[\alpha]_D^{25}$ = –179.1 (*c* = 0.33 in $CHCl_3$); 5:1 dr; 92% ee, determined by HPLC analysis (Daicel Chiralpak IC, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 10.77 min (minor), $t_R$ = 19.23 min (major); Pure **11** for NMR analysis was obtained after recrystallisation. $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27–8.21 (m, 1H), 7.80–7.75 (m, 1H), 7.69–7.61 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48–7.42 (m, 2H), 7.35–7.30 (m, 3H), 7.28–7.26 (m, 1H), 7.23–7.21 (m, 1H), 6.47 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.96–5.86 (m, 1H), 5.79 (ddd, *J* = 12.1, 7.1, 2.9 Hz, 1H), 5.71–5.64 (m, 1H), 5.58 (d, *J* = 12.3 Hz, 1H), 5.34–5.26 (m, 1H), 4.20 (d, *J* = 11.4 Hz, 1H), 2.45 (s, 3H), 2.34–2.25 (m, 1H), 2.13–2.05 (m, 1H), 1.99–1.86 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm) 154.4, 150.4, 144.3, 136.3, 134.9, 133.3, 132.8, 132.7, 130.7, 130.0, 128.1, 128.0, 127.6, 127.51, 127.48, 126.2, 125.9, 125.7, 125.6, 124.6, 124.5, 123.1, 122.4, 117.4, 111.3, 62.7, 41.2, 38.5, 29.0, 21.7; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{33}H_{27}NO_3SNa^+$ 540.1604; Found 540.1602.



**Synthesis of 12**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$

(4.6 mg, 0.0050 mmol, 5 mol%) and **L14** (15.2 mg, 0.0200 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and cycloheptatriene **10** (16.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 80 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford **12**: 14.0 mg (0.0299 mmol), as a yellow oil, 30% yield; $[\alpha]_D^{25}$ = –32.2 (*c* = 0.34 in $CHCl_3$); 77% ee, determined by HPLC analysis (Daicel Chiralpak IH, *n*-Hexane/*i*-PrOH = 90/10, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 8.39 min (minor), $t_R$ = 9.77 min (major); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68–7.62 (m, 2H), 7.37–7.33 (m, 1H), 7.25–7.21 (m, 4H), 7.19–7.15 (m, 3H), 7.05–7.00 (m, 1H), 6.97–6.91 (m, 1H), 6.77–6.63 (m, 2H), 6.16–6.08 (m, 2H), 5.95 (s, 1H), 5.21 (dd, *J* = 9.8, 6.0 Hz, 1H), 5.07 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.39 (d, *J* = 11.8 Hz, 1H), 2.79–2.68 (m, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 156.3, 153.2, 144.1, 139.2, 136.6, 131.1, 130.6, 129.8, 128.7, 128.5, 127.6, 127.1, 125.7, 125.2, 125.1, 124.5, 124.2, 122.9, 118.8, 113.5, 111.5, 43.6, 42.3, 21.6; HRMS (ESI-ToF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{25}NO_3SNa^+$ 490.1447; Found 490.1443.

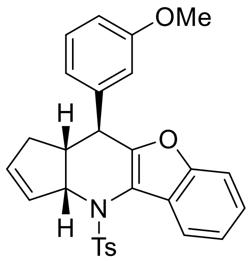


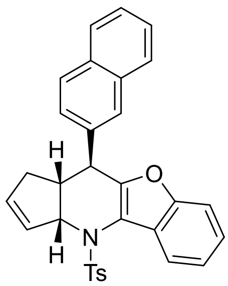

**Synthesis of 14a**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and cyclopentadiene **13** (16.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/dichloromethane = 3/1) to afford product **14a**: 29.8 mg (0.0675 mmol), as a white solid, 68% yield; mp 160–162 ℃; $[\alpha]_D^{25}$ = +278.3 (*c* = 0.46 in $CHCl_3$); 3:1 dr; 91% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.88 min (major), $t_R$ = 18.36 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.36–7.22 (m, 7H), 7.21–7.16 (m, 1H), 7.13–7.06 (m, 2H), 6.50–6.38

(m, 2H), 5.93–5.80 (m, 2H), 5.35–5.24 (m, 1H), 3.55 (d, *J* = 7.1 Hz, 1H), 2.45 (s, 3H), 2.43–2.37 (m, 1H), 2.30 (dd, *J* = 15.7, 2.8 Hz, 1H), 2.22–2.12 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 150.4, 144.1, 140.6, 134.0, 133.7, 130.3, 129.9, 128.4, 128.3, 128.2, 127.9, 127.1, 124.7, 124.5, 123.0, 122.6, 111.1, 66.2, 43.6, 43.5, 38.4, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}NO_3SNa^+$ 464.1291; Found 464.1297.

*Note: Racemic **14a–14c** were obtained by using $Pd_2(dba)_3$ in combination with racemic **L7**.*



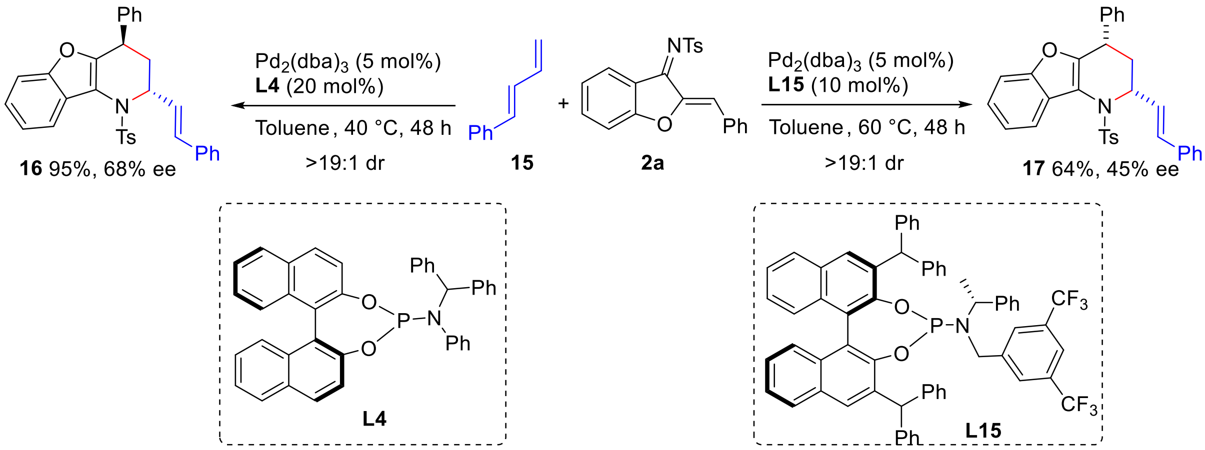

**Synthesis of 14b**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-3-methoxybenzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2b** (40.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and cyclopentadiene **13** (16.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2b**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/ dichloromethane = 3/1) to afford product **14b**: 31.9 mg, as a white solid (0.0676 mmol), 68% yield; mp 151−153 ℃; $[\alpha]_D^{25}$ = +257.0 (*c* = 0.46 in $CHCl_3$); 5:1 dr; 90% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 13.72 min (major), $t_R$ = 15.62 min (minor); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.31–8.16 (m, 1H), 7.60–7.48 (m, 2H), 7.34–7.21 (m, 6H), 7.05–6.99 (m, 1H), 6.72 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.21–6.12 (m, 1H), 6.01 (dt, *J* = 7.8, 1.2 Hz, 1H), 5.91–5.79 (m, 2H), 5.37–5.13 (m, 1H), 3.75 (s, 3H), 3.52 (d, *J* = 7.3 Hz, 1H), 2.42 (s, 3H), 2.46–2.36 (m, 1H), 2.29 (dd, *J* = 15.6, 3.0 Hz, 1H), 2.18–2.10 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 150.2, 144.3, 142.0, 134.0, 133.5, 130.3, 129.9, 129.4, 128.1, 124.7, 124.5, 122.9, 122.6, 120.3, 117.5, 115.0, 111.2, 111.1, 66.0, 55.1, 43.4, 43.2, 38.3, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_4SNa^+$ 494.1397; Found 494.1395.

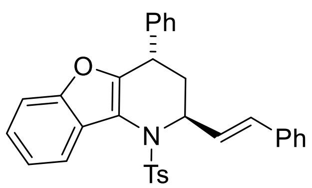



**Synthesis of 14c**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added 4-methyl-*N*-((2*Z*,3*E*)-2-(naphthalen-2-ylmethylene)-benzo furan-3(2*H*)-ylidene)benzenesulfonamide **2e** (42.6 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L7** (5.5 mg, 0.010 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times.

Then degassed dry toluene (1.0 mL) and cyclopentadiene **13** (16.0 μL, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2e**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/dichloromethane = 3/1) to afford product **14c**: 25.4 mg (0.0517 mmol), as a white solid, 52% yield; mp 175–177 ℃; $[\alpha]_D^{25}$ = +345.7 (*c* = 0.21 in $CHCl_3$); 6:1 dr; 87% ee, determined by HPLC analysis (Daicel Chiralpak ID, *n*-Hexane/*i*-PrOH = 80/20, flow rate =1.0 mL/min, λ = 254 nm) $t_R$ = 14.88 min (major), $t_R$ = 18.83 min (minor); $^1$H NMR (400 MHz, CDCl3) δ (ppm) 8.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.79–7.73 (m, 1H), 7.70–7.66 (m, 1H), 7.62–7.57 (m, 2H), 7.53–7.49 (m, 1H), 7.48–7.43 (m, 2H), 7.35–7.29 (m, 2H), 7.27–7.19 (m, 4H), 6.27 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.94–5.84 (m, 2H), 5.38–5.29 (m, 1H), 3.74 (d, *J* = 7.1 Hz, 1H), 2.50–2.41 (m, 1H), 2.39 (s, 4H), 2.29–2.24 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.7, 150.3, 144.2, 137.8, 134.0, 133.7, 133.2, 132.5, 130.4, 129.9, 128.21, 128.17, 127.58, 127.55, 127.0, 126.3, 125.9, 125.3, 124.7, 124.6, 123.0, 122.7, 117.7, 111.1, 66.1, 43.6, 43.2, 38.4, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{25}NO_3SNa^+$ 514.1447; Found 514.1443.

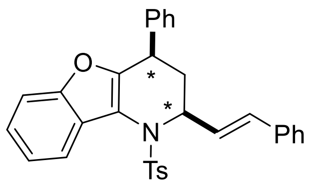
### 5.2 Exploration of linear 1,3-dienes



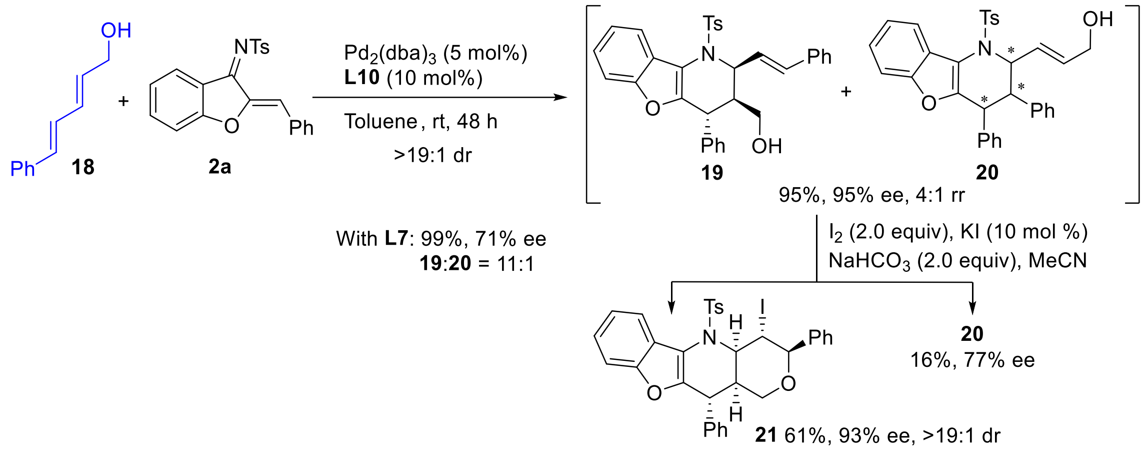

**Synthesis of 16:** To an oven-dried 10 mL tube equipped with a septum and a stirring bar were charged with $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L4** (11.4 mg, 0.0200 mmol, 10 mol%), the tube was evacuated and backfilled with argon for three times, then degassed dry toluene (1.0 mL) was added via syringe. The mixture was stirred for 30 min at room temperature before transferred to another Schlenk tube containing (*E*)-buta-1,3-dien-1-ylbenzene **15** (26.0 mg, 0.200 mmol, 2.0 equiv) and *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5

mg, 0.100 mmol, 1.0 equiv) under argon atmosphere. The resultant mixture was stirred at 40 ℃ for 48 h. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/DCM = 3/1) gave the product **16**: 48.2 mg (0.0953 mmol), as a white solid, 95% yield; mp = 255–257 ℃; >19:1 dr; $[\alpha]_D^{25}$ = –95.1 (*c* = 0.23 in $CHCl_3$); 68% ee, determined by HPLC analysis [Chiralpak column IF *n*-Hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 9.81 min, $t_R$ (minor) = 13.84 min]; $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (d, *J* = 7.8 Hz, 1H), 7.66–7.57 (m, 2H), 7.38–7.26 (m, 7H), 7.25–7.14 (m, 6H), 6.74–6.57 (m, 3H), 6.10 (dd, *J* = 15.9, 4.8 Hz, 1H), 5.20–5.11 (m, 1H), 3.96 (dd, *J* = 11.6, 7.1 Hz, 1H), 2.41 (s, 3H), 2.04 (ddd, *J* = 14.1, 7.1, 2.5 Hz, 1H), 1.54–1.47 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.0, 148.5, 144.2, 140.1, 136.1, 134.4, 132.1, 129.9, 128.51, 128.49, 128.0, 127.8, 127.6, 127.3, 126.5, 125.9, 124.7, 124.5, 123.1, 122.6, 118.1, 111.2, 58.4, 37.2, 34.5, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}NO_3SNa^+$ 528.1609; Found 528.1607.




**Synthesis of 17*:*** To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L15** (18.8 mg, 0.0200 mmol, 10 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) and (*E*)-buta-1,3-dien-1-ylbenzene **15** (26.0 mg, 0.200 mmol, 2.0 equiv) were added via syringe sequentially under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (DCM/petroleum ether = 1/3) to afford product **17**: 25.6 mg (0.0506 mmol), as a white solid, 51% yield; mp = 166–169 ℃; $[\alpha]_D^{25}$ = –30.0 (*c* = 0.40 in $CHCl_3$); >19:1 dr; 45% ee, determined by HPLC analysis [Chiralpak column IF *n*-Hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 10.68 min, $t_R$ (minor) = 20.86 min]; $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) (ppm) 8.33 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.60–7.55 (m, 2H), 7.47–7.38 (m, 2H), 7.37–7.27 (m, 4H), 7.16–7.08 (m, 6H), 6.93–6.86 (m, 2H), 6.83–6.78 (m, 2H), 6.60 (dd, *J* = 15.9, 2.2 Hz, 1H), 5.51 (dd, *J* = 15.8, 3.9 Hz, 1H), 5.09–5.00 (m, 1H), 3.99 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 2.06–1.97 (m, 1H), 1.91–1.78 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.8, 147.1, 144.2, 141.4, 136.3, 134.8, 130.1, 129.8, 128.41, 128.39, 128.2, 127.7, 127.6, 127.3, 126.53, 126.48, 124.7, 124.5, 123.1, 122.8, 118.8, 111.2, 56.7, 36.1, 33.2, 21.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for

$C_{32}H_{27}NO_3SNa^+$ 528.1609; Found 528.1609. *Its relative configuration has been determined by X-ray diffraction analysis.*



**Synthesis of 19**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added *N*-((*E*)-2-((*Z*)-benzylidene)benzofuran-3(2*H*)-ylidene)-4-methylbenzenesulfonamide **2a** (37.5 mg, 0.100 mmol, 1.0 equiv), (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-ol **18** (32.0 mg, 0.20 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L10** (6.4 mg, 0.020 mmol, 20 mol%). The tube was capped, evacuated and back-filled with argon for five times. Then dry distilled toluene (1.0 mL) was added via syringe under argon atmosphere. The mixture was stirred at room temperature for 48 h. After complete consumption of **2a**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/EA = 50/1) to afford product **19** and **20** as inseparable regioisomers: 50.9 mg (0.0950 mmol), 95% yield, as a white solid, mp = 200–202 ℃; $[\alpha]_D^{25}$ = –206.3 (*c* = 0.42 in $CHCl_3$); 4:1 rr; 95% ee, determined by HPLC analysis [Chiralpak column ID *n*-Hexane/*i*-PrOH = 60/40, flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 5.59 min, $t_R$ (minor) = 7.61 min].

**19**: $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.74–7.62 (m, 2H), 7.37–7.27 (m, 8H), 7.25–7.18 (m, 3H), 7.18–7.11 (m, 2H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.62–6.51 (m, 2H), 6.06 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.41–5.33 (m, 1H), 3.61 (d, *J* = 11.4 Hz, 1H), 3.52–3.34 (m, 2H), 2.45 (s, 3H), 1.94–1.76 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 148.3, 144.2, 138.6, 136.1, 135.0, 134.9, 129.9, 128.6, 128.5, 128.18, 128.16, 128.1, 127.6, 126.8, 124.8, 124.3, 123.1, 122.8, 121.5, 117.8, 111.2, 60.9, 60.8, 44.7, 39.9, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{29}NO_3SNa^+$ 558.1710; Found 558.1720.

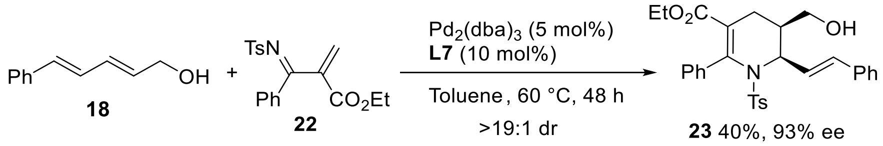
**Synthesis of 21 and recovery of 20:** The above inseparable regioisomers **19** and **20** (4:1, 53.6 mg, 0.100 mmol, 1.0 equiv), $I_2$ (50.6 mg, 0.200 mmol, 2.0 equiv), KI (1.7 mg, 0.010 mmol, 10 mol%) and

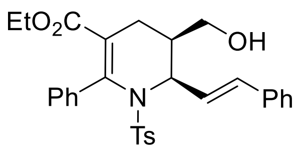
$NaHCO_3$ (16.8 mg, 0. 200 mmol, 2.0 equiv) were added into $CH_3CN$ (0.5 mL). The mixture was stirred at 40 ℃ for 2 h under argon atmosphere. After complete consumption of **19**, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford products **21** and **20**.

**21**: 40.3 mg (0.0609 mmol), as a white solid, 61% yield; mp = 169–171 ℃; $[\alpha]_D^{25}$ = –360.0 (*c* = 0.40 in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column AD *n*-Hexane/*i*-PrOH = 80/20,, flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 9.69 min, $t_R$ (minor) = 12.46 min]; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22–8.18 (m, 1H), 7.65–7.58 (m, 2H), 7.37–7.28 (m, 10H), 7.24–7.19 (m, 1H), 7.19–7.09 (m, 2H), 6.54–6.48 (m, 2H), 4.85 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.69 (d, *J* = 10.6 Hz, 1H), 4.31 (d, *J* = 10.5 Hz, 1H), 4.07 (t, *J* = 10.9 Hz, 1H), 3.85–3.81 (dd, *J* = 12.3, 1.6 Hz, 1H), 3.72 (dd, *J* = 12.3, 2.1 Hz, 1H), 2.46 (s, 3H), 1.96–1.84 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.5, 148.0, 144.5, 139.2, 138.3, 134.7, 130.1, 129.0, 128.6, 128.5, 128.4, 128.1, 127.7, 127.6, 125.0, 124.3, 123.4, 122.4, 116.7, 111.3, 86.8, 77.3, 77.0, 76.7, 67.6, 64.7, 42.4, 39.1, 32.4, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{28}INO_3SNa^+$ 684.0676; Found 684.0672.

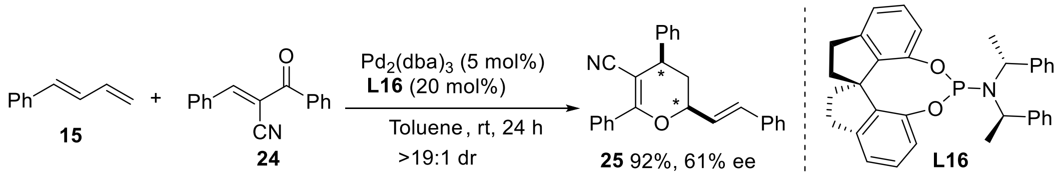
**20**: 8.7 mg, as a white solid, 16% yield (0.0162 mmol); mp = 130–132 ℃; $[\alpha]_D^{25}$ = +170.7 (*c* = 0.23 in $CHCl_3$); 77% ee, determined by HPLC analysis [Chiralpak column ID *n*-Hexane/*i*-PrOH = 60/40, flow rate: 1.0 mL/min, 254 nm, $t_R$ (major) = 6.31 min, $t_R$ (minor) = 6.83 min]; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30–8.25 (m, 1H), 7.79–7.73 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.37–7.34 (m, 1H), 7.33–7.31 (m, 2H), 7.24–7.22 (m, 1H), 7.22–7.19 (m, 1H), 7.19–7.13 (m, 1H), 7.09–7.04 (m, 1H), 7.03–6.98 (m, 4H), 6.54–6.48 (m, 2H), 5.65–5.59 (m, 2H), 5.03–4.93 (m, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.06–3.97 (m, 2H), 2.93 (dd, *J* = 11.9, 3.8 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.4, 149.0, 144.5, 138.1, 136.8, 134. 9, 134.2, 130.0, 129.0, 128.3, 128.2, 127.3, 127.1, 124.8, 124.3, 123.2, 122.6, 122.0, 111.4, 64.2, 62.6, 48.5, 41.2, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{29}NO_3SNa^+$ 558.1710; Found 558.1716.

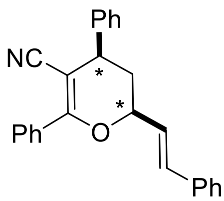
### 5.3 Exploration of linear electron-deficient heterodienes





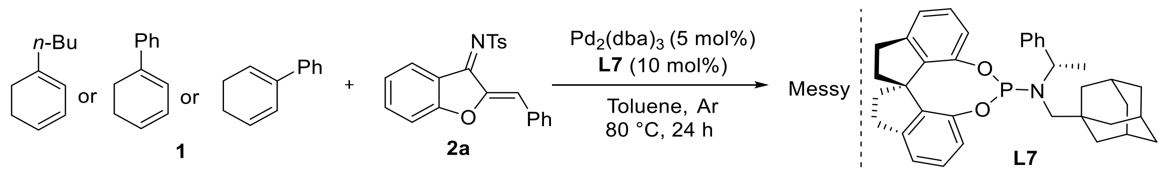
**Synthesis of 23**: To an oven dried 10 mL Schlenk tube equipped with a stirring bar were added ethyl (*Z*)-2-(phenyl(tosylimino)methyl) acrylate **22** (71.4 mg, 0.200 mmol, 1.0 equiv), 1,3-diene **18** (48.0 mg, 0.300 mmol, 1.5 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.010 mmol, 5 mol%) and **L7** (5.5 mg, 0.020 mmol, 10 mol%). The tube was evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe under argon atmosphere. The mixture was stirred at 60 ℃ for 48 h. After complete consumption of **22**, the mixture was purified by flash chromatography on silica gel twice (petroleum ether/EtOAc = 10/1, dichloromethane/EtOAc = 50:1) to afford product **23**: 41.0 mg (0.0396 mmol), as a colorless oil, 40% yield; $[\alpha]_D^{25}$ = –5.3 (*c* = 0.57 in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column ID *n*-Hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 20.05 min, $t_R$ (major) = 22.35 min]; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.38 (m, 2H), 7.37–7.32 (m, 2H), 7.32–7.16 (m, 5H), 7.13–7.08 (m, 4H), , 6.86 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 8.6 Hz, 1H), 5.44 (dd, *J* = 8.6, 4.0 Hz, 1H), 3.84 (q, *J* = 7.2 Hz, 2H), 3.70 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.49 (dd, *J* = 11.0, 8.9 Hz, 1H), 2.72 (dd, *J* = 18.5, 6.4 Hz, 1H), 2.36 (s, 3H), 2.31–2.15 (m, 1H), 2.01–1.83 (m, 1H) , 0.83 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.4, 143.4, 142.9, 137.8, 136.3, 136.2, 135.3, 129.7, 129.3, 128.7, 128.23, 128.21, 127.1, 127.0, 126.7, 121.6, 117.9, 63.9, 60.4, 57.8, 39.3, 24.9, 21.5, 13.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{31}NO_5SNa^+$ 540.1815; Found 540.1811.



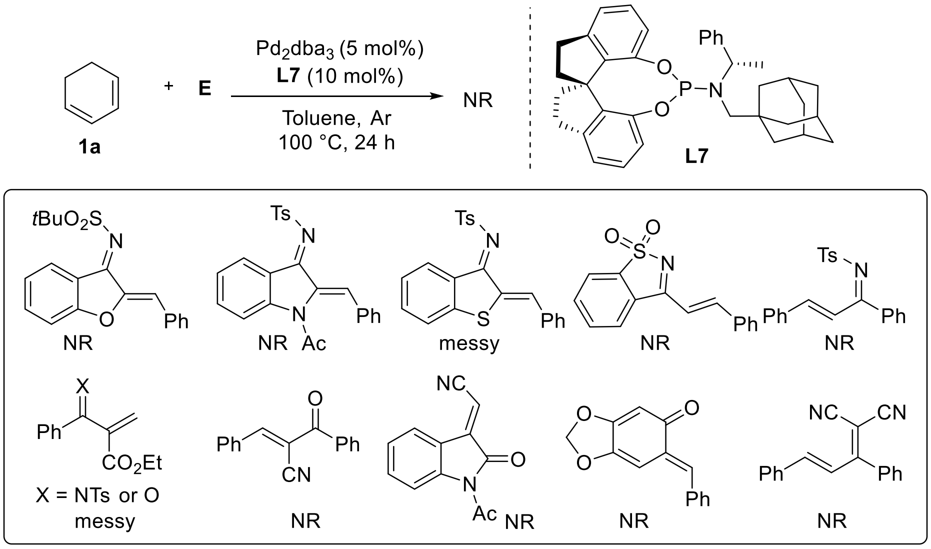



**Synthesis of 25**: To an oven dried 10 mL Schlenk tube equipped with with a stirring bar were added (*E*)-2-benzoyl-3-phenylacrylonitrile **24** (23.3 mg, 0.100 mmol, 1.0 equiv), (*E*)-buta-1,3-dien-1-ylbenzene **15** (26.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and **L16** (10.2 mg, 0.0200 mmol, 20 mol%). The tube was evacuated and back-filled with argon for five times. Then degassed dry toluene (1.0 mL) was added via syringe under argon atmosphere. The mixture was stirred at rt for 24 h. After complete consumption of **24**, the mixture was directly purified by flash chromatography on silica gel (DCM/petroleum ether = 1/3) to afford product **25**: 33.4 mg (0.092 mmol), as a white semi-solid, 92% yield; mp = 82–84 ℃; >19:1 dr; $[\alpha]_D^{25}$ = +15.2 ($c$ = 0.32 in $CHCl_3$); 61% ee, determined by HPLC analysis [Chiralpak column IB $n$-Hexane/$i$-PrOH = 80/20, flow rate: 1.0 mL/min, 254 nm, $t_R$ (minor) = 16.68 min, $t_R$ (major) = 17.68 min]; $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (dd, $J$ = 7.7, 1.9 Hz, 2H), 7.47–7.19 (m, 13H), 6.69 (d, $J$ = 16.0 Hz, 1H), 6.23 (dd, $J$ = 16.0, 6.5 Hz, 1H), 4.83 (dd, $J$ = 11.3, 6.6 Hz, 1H), 3.84 (dd, $J$ = 11.5, 6.5 Hz, 1H), 2.37 (ddd, $J$ = 14.1, 6.5, 1.9 Hz, 1H), 2.01–1.87 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.2, 141.2, 135.8, 133.1, 133.0, 130.9, 129.0, 128.7, 128.38, 128.36, 128.3, 127.63, 127.59, 126.6, 126.3, 119.6, 88.4, 78.5, 41.5, 37.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}NO_3SNa^+$ 386.1515; Found 386.1515. *Its relative configuration has been determined by X-ray diffraction analysis.*

### 5.4 Unsuccessful substrates attempts




To further expand the substrate scope, some differently substituted 1,3-cyclohexadiene were tested under the optimal conditions. Unfortunately, complex reaction profiles were generally observed as outlined above.




Meanwhile, the above outlined electron-deficient dienes were inert to the reaction under the optimized conditions.

# 6. Mechanism investigation

## 6.1 Control experiments

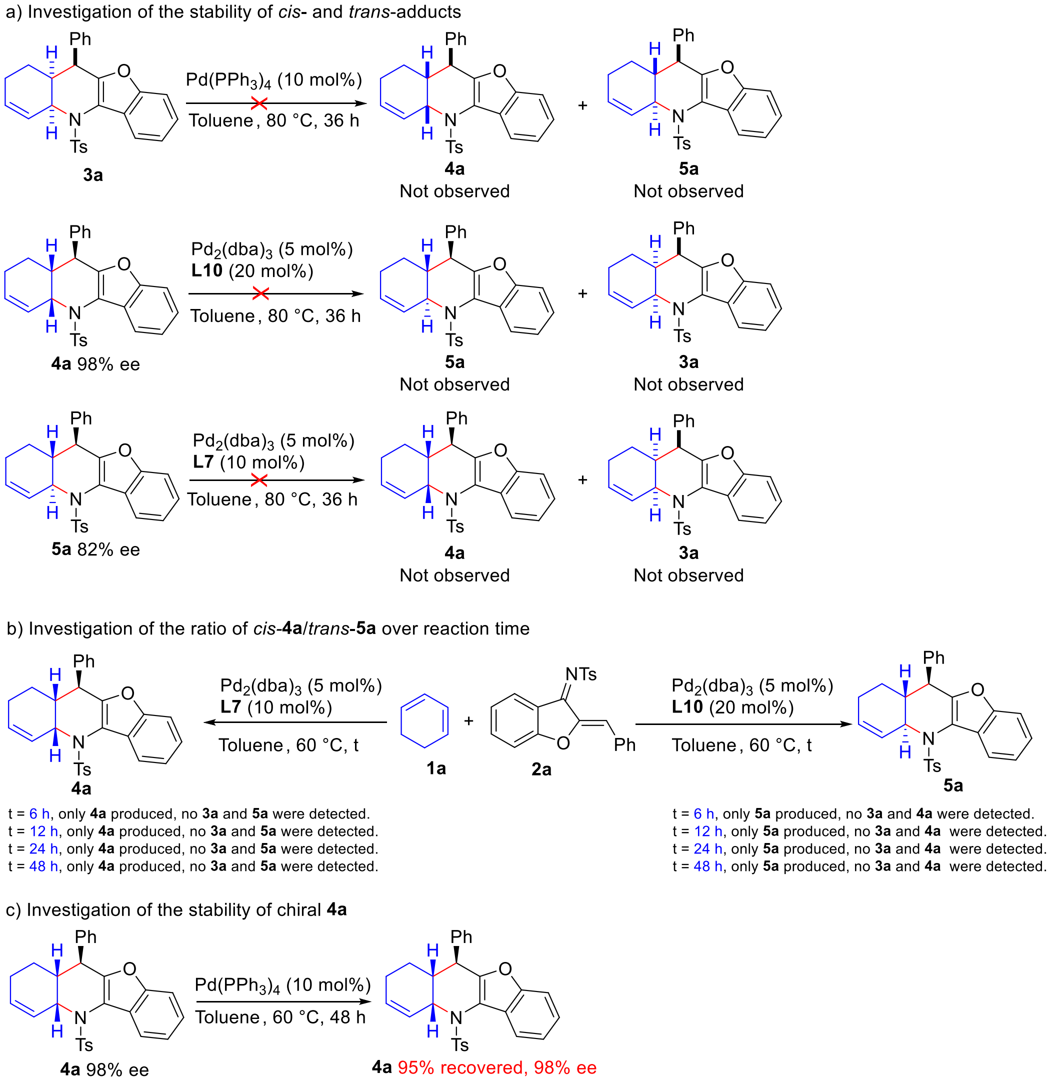
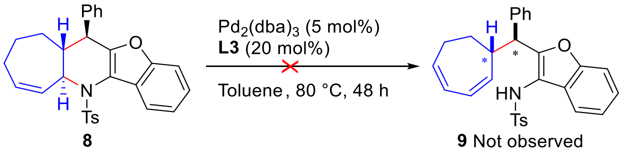
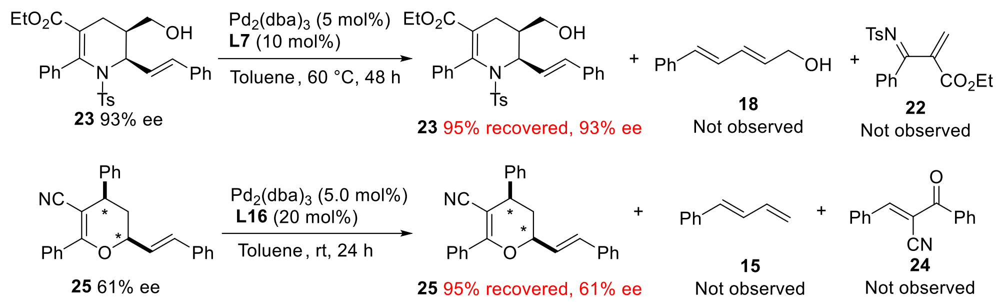



**Figure S1** Control experiments to elucidate the stability of products

As demonstrated above, products *endo-cis*-**3a**, *exo-cis*-**4a** and *trans*-**5a** were not interconvertible under diverse catalytic conditions, even at high temperature. The ratio of *cis*-**4a**/*trans*-**5a** was not changed along the reaction process, according to the $^1$H NMR analysis of the reaction solution in 6 h, 12 h, 24 h, and 48 h, respectively. In addition, the enantioselectivity of chiral **4a** kept unchanged when exposed to $Pd(PPh_3)_4$. *These results well demonstrated that the annulations of cyclic 1,3-dienes and 1-azadienes was irreversible, and the diastereoselectivity was controlled by ligand rather than thermodynamics.*



Treatment of **8** with $Pd_2(dba)_3$/**L3** in toluene at 80 ℃ for 48 h did not lead to the formation of **9**, which indicated that **8**, although bearing an allylic amine moiety, was stable and would not undergo ring opening under the catalysis of palladium.




No obvious transformations were observed by treatment of enantioenriched **23** or **25** with $Pd_2(dba)_3$/**L7**. Chiral **23** and **25** with unchanged enantioselectivity were recovered quantitatively. *The results further indicated that the reaction involving linear 1,3-diene was also irreversible*.

**6.2 Proposed origin of the divergent diasteroselectivity**

The above control experiments confirmed that the formation of both *cis*-**4a** and *trans*-**5a** was a stepwise cascade vinylogous Michael addition/allylic amination process. According to our previous works (*JACS*, **2021**, *143*, 4809; *ACIE*, **2021**, *60*, 26762), vinylogous Michael addition of HOMO-raised $\eta^2$-complex **I-A** of $Pd^0$ with 1,3-cyclohexadiene **1a** to 1-azadiene **2a** from *Si*-face in an outer sphere pattern led to the generation of intermediate **II-A**, as illustrated in Figure S2. Because of the large steric hinderance of **L7**, subsequent intramolecular nucleophilic substitution of allylic $Pd^{II}$ complex with N-Ts moiety would proceed through an outer-sphere manner to furnish *cis*-**4a**. This proposal was further confirmed by utilizing small dimethylamine-substituted ligand **L20**, which delivered *trans*-**5a** predominantly.

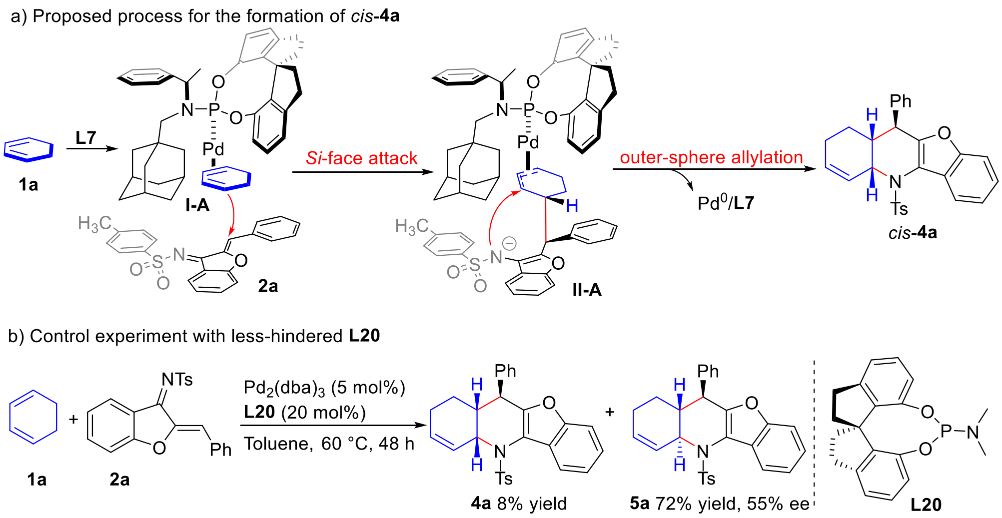



**Figure S2** Proposed mechanism for the formation of *cis*-**4a** and control experiment

On the other hand, as illustrated in Figure S3, 1,3-cyclohexadiene **1a** and $Pd_2(dba)_3$ complexed with two moleculear of **L10** to form highly reactive complex **I-B**, which attacked 1-azadiene **2a** from *Si*-face to form species **II-B**. In this case, the carbon-carbon bond rotation and ligand exchange of **II-B** were liable to form more stable electron-neutral **IV-B**, since the less bulky of **L10**. Subsequent reductive elimination deliverd *trans*-**5a**. In conclusion, the inner sphere allylic amination step caused by small steric hinderance of **L10** might be responsible for the observed *trans*-diastereoselectivity. The necessity of two equivalent of **L10** (with regard to palladium) and the effect of less steric hindered ligand were validated by control experiments S3b and S2b, respectively.

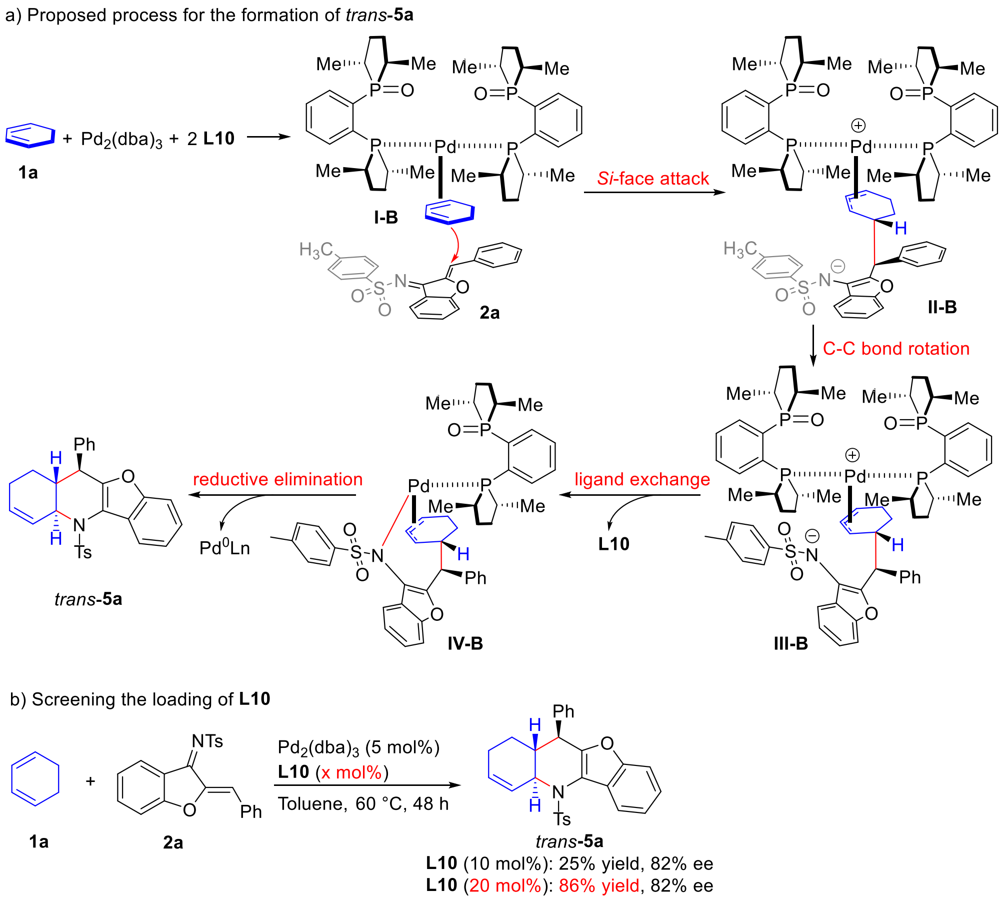



**Figure S3** Proposed mechanism for the formation of *trans*-**5a** and control experiment

## 6.3 DFT calculations for the reaction of 1-azadiene 2a and 1,3-butadiene 15

The mechanism for the reaction of **2a** and **15** with/without $Pd(PPh_3)_4$ was calculated for further elucidating the catalytic process. The assembly of **2a** and **15** without palladium is a concerted Diels–Alder process. We calculated the **diene-*endo*-TS** and **diene-*exo*-TS** for the formation of *endo*-product **17** and *exo*-product **16**, and found the energy of **diene-*endo*-TS** with a value of 27.1 kcal/mol related to the energy summary of **15** and **2a**, was 4.6 kcal/mol lower than **diene-*exo*-TS**. These results were consistent with the results that **17** was produced with excellent *endo*-diastereoselectivity upon heating. On the other hand, the reaction mechanism of **2a** and **15** in the presence of $Pd(PPh_3)_4$ is a stepwise process. Different configurations for the first addition step of the C-C bond formation have been calculated and the energy barriers were similar from **2a-TS1** and **2a-TS1′**, and the lower one with a value of 25.8 kcal/mol (**2a-TS1′**). Because **2a-INT1** and **2a-INT1′** could isomerize to each other via C-C bond rotation, the diastereoselectivity was determined by the second step. The energy of **diene-Pd-*exo*-TS** was 3.8 kcal/mol lower than that of **diene-Pd-*endo*-TS**, suggesting the *exo*-product **16** could be produced preferably, which is consistent with the experimental results.

Comparing the two reaction [with/without $Pd(PPh_3)_4$], the reaction of **2a** and **15** in the absence of $Pd(PPh_3)_4$ needed higher temperature as the energy barriers was 27.1 kcal/mol, which was 1.3 kcal/mol higher than the highest energy barrier of the reaction with $Pd(PPh_3)_4$ (25.8 kcal/mol). Thanks to the $Pd^0$-π-Lewis base activation, **INT1** showed significantly raised reactivity than parent **15**. These DFT calculations were consistent with the experimental results.

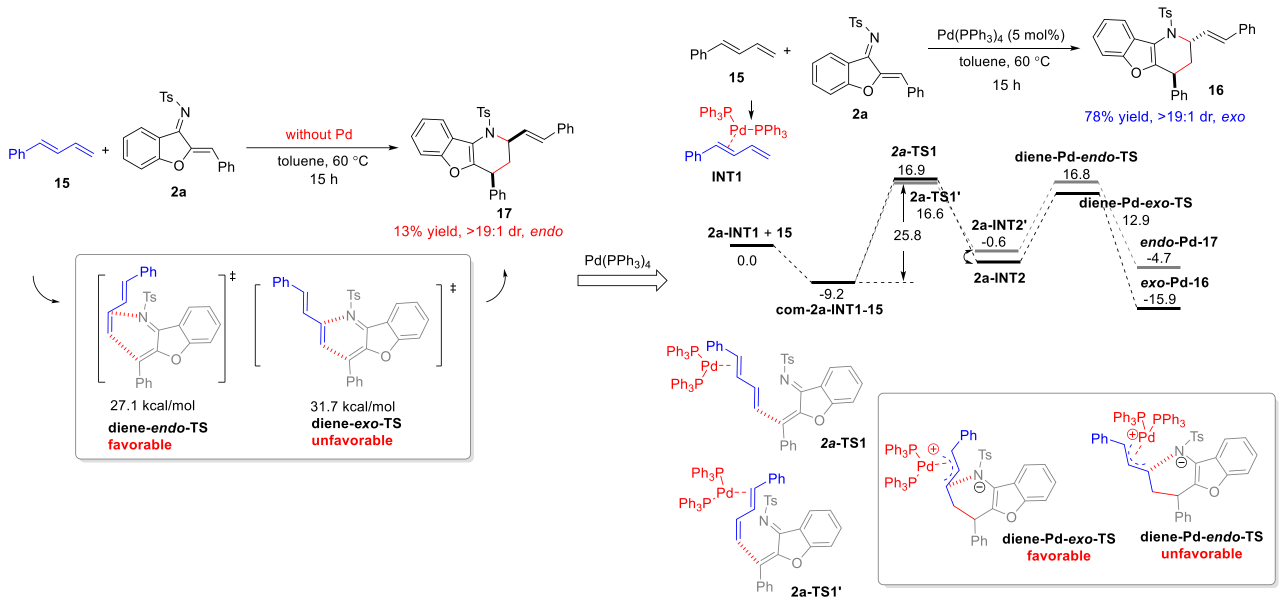
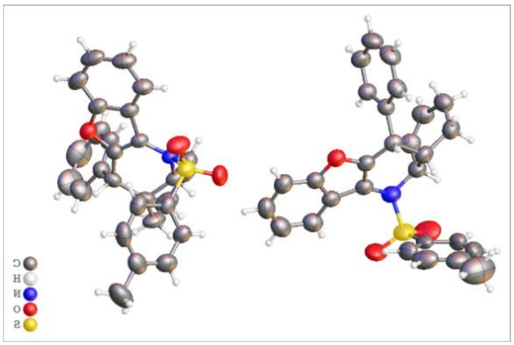
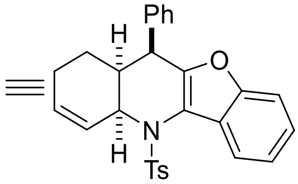



**Figure S4** Computed potential energy surface of the reaction of **2a** and **15** with/without $Pd(PPh_3)_4$ at the B3LYP-D3/6-31(d)//B3LYP-D3/6-311++G(d,p) and SDD for Pd (toluene) level and are given in kcal/mol.

## 7. Crystal data and structural refinement

**Procedure for the recrystallization of racemic 3a**: To a 10 mL tube containing **3a** (16 mg) were added *n*-hexane (2 mL) and THF (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of **3a**. The data were collected by Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 290.0 K. CCDC 2050825 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





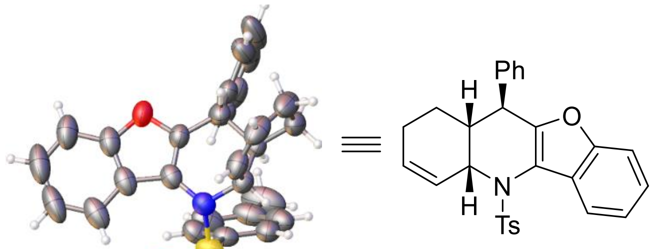

**3a**

(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **3a** |
| Empirical formula | $C_{28}H_{25}NO_3S$ |
| Formula weight | 455.55 |
| Temperature/K | 290.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.6139(7) |
| b/Å | 13.4764(10) |
| c/Å | 14.9925(10) |
| α/° | 92.051(3) |
| β/° | 93.362(3) |
| γ/° | 94.406(3) |
| Volume/Å$^3$ | 2333.7(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.297 |
| μ/mm$^{-1}$ | 0.169 |
| F(000) | 960.0 |
| Crystal size/mm$^3$ | 0.3 × 0.3 × 0.2 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.994 to 55.098 |
| Index ranges | $-15 \leq h \leq 14$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$ |
| Reflections collected | 85300 |
| Independent reflections | 10757 [$R_{int}$ = 0.1297, $R_{sigma}$ = 0.1036] |
| Data/restraints/parameters | 10757/0/597 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.038 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0603, $wR_2$ = 0.1328 |
| Final R indexes [all data] | $R_1$ = 0.1390, $wR_2$ = 0.1605 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.17/-0.33 |

**Procedure for the recrystallization of chiral 4a**: To a 10 mL tube containing **4a** (20 mg) were added *n*-hexane (2 mL) and *i*-PrOH (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **4a**. The data were collected by an Agilent Gemini equipped a Cu radiation source (Kα = 1.54184 Å) at 292.90 K. CCDC 2050826 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



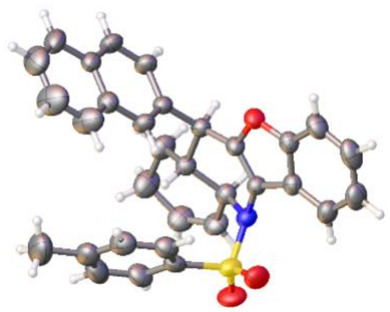

**4a**

(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **4a** |
| Empirical formula | $C_{28}H_{25}NO_3S$ |
| Formula weight | 455.55 |
| Temperature/K | 292.90(10) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 11.0546(3) |
| b/Å | 11.54205(18) |
| c/Å | 18.2492(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/$Å^3$ | 2328.47(8) |
| Z | 4 |

| | |
|---|---|
| $\rho_{calc}g/cm^3$ | 1.299 |
| $\mu/mm^{-1}$ | 1.475 |
| F(000) | 960.0 |
| Crystal size/mm$^3$ | 0.4 × 0.2 × 0.1 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.066 to 142.848 |
| Index ranges | $-13 \le h \le 13$, $-14 \le k \le 8$, $-21 \le l \le 22$ |
| Reflections collected | 12665 |
| Independent reflections | 4476 [$R_{int}$ = 0.0352, $R_{sigma}$ = 0.0307] |
| Data/restraints/parameters | 4476/0/299 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0564, $wR_2$ = 0.1522 |
| Final R indexes [all data] | $R_1$ = 0.0596, $wR_2$ = 0.1590 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.27/-0.27 |
| Flack parameter | 0.011(12) |

**Procedure for the recrystallization of chiral 5e**: To a 10 mL tube containing **5e** (15 mg) were added *n*-hexane (1.5 mL) and *i*-PrOH (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **5e**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 301.0 K. CCDC 2219802 (**5e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



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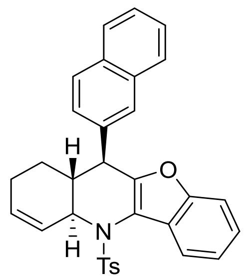



**5e**

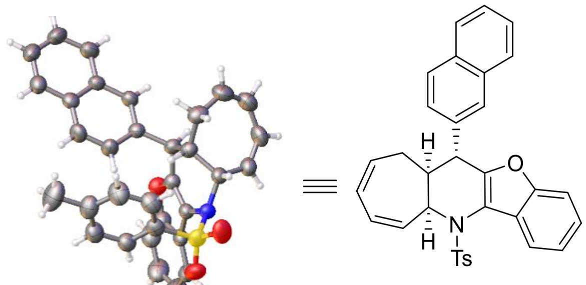
(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **5e** |
| Empirical formula | $C_{32}H_{27}NO_3S$ |

| | |
|---|---|
| Formula weight | 505.60 |
| Temperature/K | 301.0 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 8.7448(3) |
| b/Å | 12.1996(5) |
| c/Å | 23.9382(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2553.80(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.315 |
| μ/mm$^{-1}$ | 0.162 |
| F(000) | 1064.0 |
| Crystal size/mm$^3$ | 0.36 × 0.15 × 0.13 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/ ° | 4.768 to 55.018 |
| Index ranges | $-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-31 \leq l \leq 31$ |
| Reflections collected | 38309 |
| Independent reflections | 5866 [$R_{int}$ = 0.0960, $R_{sigma}$ = 0.0518] |
| Data/restraints/parameters | 5866/0/335 |
| Goodness-of-fit on F$^2$ | 1.008 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0389, $wR_2$ = 0.0801 |
| Final R indexes [all data] | $R_1$ = 0.0727, $wR_2$ = 0.0915 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.13/-0.25 |
| Flack parameter | -0.01(4) |

**Procedure for the recrystallization of chiral 11**: To a 10 mL tube containing **11** (15 mg) were added *n*-hexane (1.5 mL) and EtOAc (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **11**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2219803

(**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



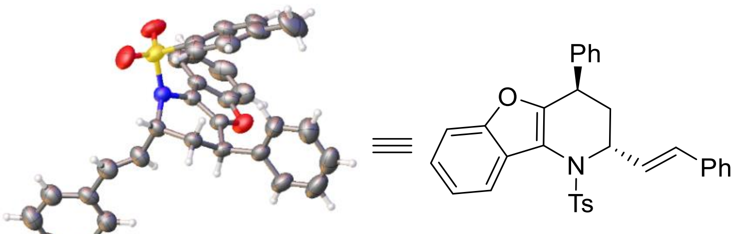

**11**

(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **11** |
| Empirical formula | $C_{33}H_{27}NO_3S$ |
| Formula weight | 517.61 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 9.7335(10) |
| b/Å | 12.7669(13) |
| c/Å | 10.7629(11) |
| α/° | 90 |
| β/° | 90.849(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1337.3(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.285 |
| μ/mm$^{-1}$ | 0.156 |
| F(000) | 544.0 |
| Crystal size/mm$^3$ | 0.31 × 0.23 × 0.11 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.186 to 55.136 |
| Index ranges | $-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-13 \leq l \leq 14$ |
| Reflections collected | 28070 |
| Independent reflections | 6155 [$R_{int}$ = 0.0588, $R_{sigma}$ = 0.0466] |

| | |
|---|---|
| Data/restraints/parameters | 6155/1/344 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0540, $wR_2$ = 0.1333 |
| Final R indexes [all data] | $R_1$ = 0.0738, $wR_2$ = 0.1450 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.56/-0.22 |
| Flack parameter | 0.08(3) |

**Procedure for the recrystallization of chiral 16**: To a 10 mL tube containing **16** (15 mg) were added *n*-hexane (1.5 mL) and THF (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **16**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 300.0 K. CCDC 2219804 (**16**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



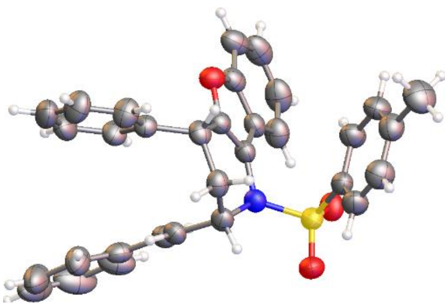

**16**

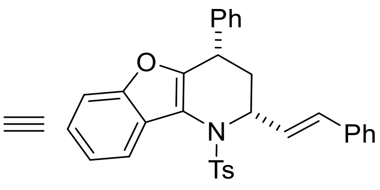
(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **16** |
| Empirical formula | $C_{32}H_{27}NO_3S$ |
| Formula weight | 505.60 |
| Temperature/K | 300.0 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 7.9263(6) |
| b/Å | 10.6732(11) |
| c/Å | 31.221(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |

| | |
|---|---|
| Volume/Å$^3$ | 2641.2(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.271 |
| μ/mm$^{-1}$ | 0.157 |
| F(000) | 1064.0 |
| Crystal size/mm$^3$ | 0.41 × 0.12 × 0.11 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.032 to 54.916 |
| Index ranges | -10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -40 ≤ l ≤ 34 |
| Reflections collected | 23184 |
| Independent reflections | 6027 [$R_{int}$ = 0.0697, $R_{sigma}$ = 0.0658] |
| Data/restraints/parameters | 6027/0/335 |
| Goodness-of-fit on F$^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0493, $wR_2$ = 0.0937 |
| Final R indexes [all data] | $R_1$ = 0.1072, $wR_2$ = 0.1168 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.32/-0.23 |
| Flack parameter | -0.05(6) |

**Procedure for the recrystallization of racemic 17**: To a 10 mL tube containing **17** (15 mg) were added *n*-hexane (1.5 mL) and *i*-PrOH (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of **17**. The data were collected by an Agilent Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 294.93 K. CCDC 2050823 (**17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.






**17**

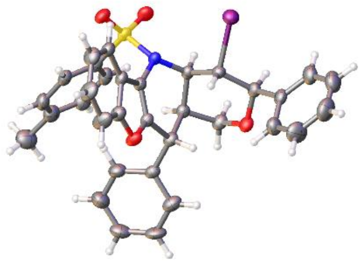
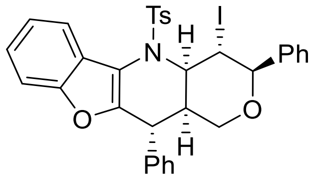
(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **17** |

| | |
|---|---|
| Empirical formula | $C_{32}H_{27}NO_3S$ |
| Formula weight | 505.60 |
| Temperature/K | 294.93(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 13.2549(3) |
| b/Å | 11.5853(4) |
| c/Å | 17.1735(4) |
| α/° | 90 |
| β/° | 97.293(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 2615.86(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.284 |
| μ/mm$^{-1}$ | 1.368 |
| F(000) | 1064.0 |
| Crystal size/mm$^3$ | 0.5 × 0.4 × 0.3 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.956 to 143.642 |
| Index ranges | -16 ≤ h ≤ 16, -12 ≤ k ≤ 14, -15 ≤ l ≤ 21 |
| Reflections collected | 14291 |
| Independent reflections | 5019 [$R_{int}$ = 0.0407, $R_{sigma}$ = 0.0332] |
| Data/restraints/parameters | 5019/0/335 |
| Goodness-of-fit on F$^2$ | 1.033 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0607, $wR_2$ = 0.1639 |
| Final R indexes [all data] | $R_1$ = 0.0687, $wR_2$ = 0.1763 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.26/-0.45 |

**Procedure for the recrystallization of chiral 21**: To a 10 mL tube containing **21** (15 mg) were added *n*-hexane (1.5 mL) and THF (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **21**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2219805

(**21**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

 ≡ 

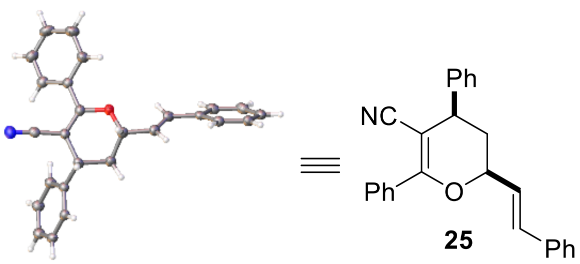

**21**

(ellipsoid contour probability 50%)

| | |
|---|---|
| Identification code | **21** |
| Empirical formula | $C_{33}H_{28}INO_4S$ |
| Formula weight | 661.52 |
| Temperature/K | 161.0 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 11.0840(12) |
| b/Å | 11.2741(10) |
| c/Å | 27.234(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 3403.2(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.291 |
| μ/mm$^{-1}$ | 1.035 |
| F(000) | 1336.0 |
| Crystal size/mm$^3$ | 0.35 × 0.22 × 0.09 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.738 to 55.044 |
| Index ranges | $-14 \le h \le 14, -13 \le k \le 14, -35 \le l \le 35$ |
| Reflections collected | 51913 |
| Independent reflections | 7778 [$R_{int}$ = 0.0814, $R_{sigma}$ = 0.0497] |
| Data/restraints/parameters | 7778/0/362 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.020 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0286, $wR_2$ = 0.0596 |
| Final R indexes [all data] | $R_1$ = 0.0420, $wR_2$ = 0.0633 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.45 |
| Flack parameter | 0.001(10) |

**Procedure for the recrystallization of racemic 25**: To a 10 mL tube containing **25** (15 mg) were added *n*-hexane (1.5 mL) and *i*-PrOH (2.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the relative configuration of **25**. The data were collected by a Bruker APEX-II CCD equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2219806 (**25**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



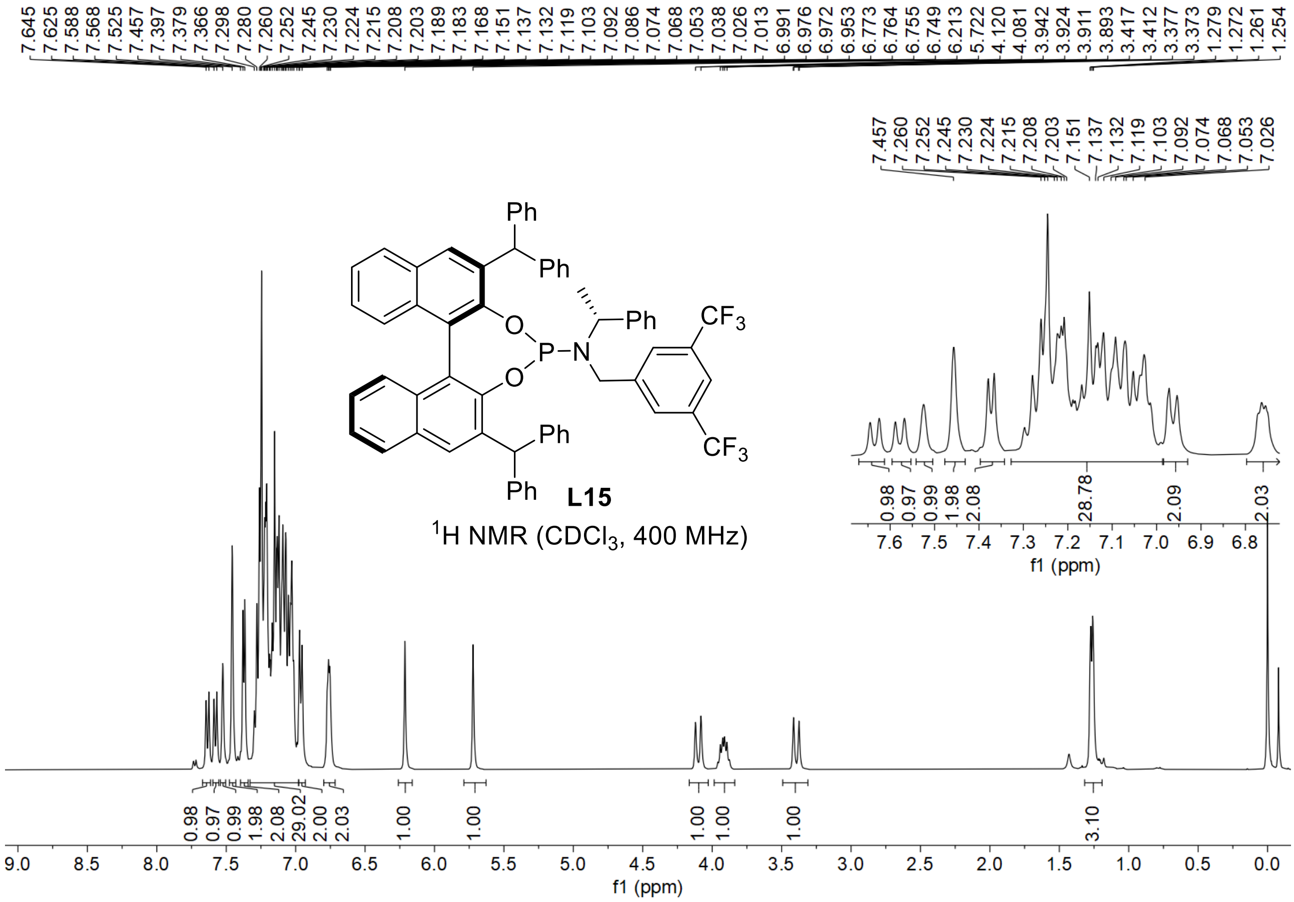

**25**

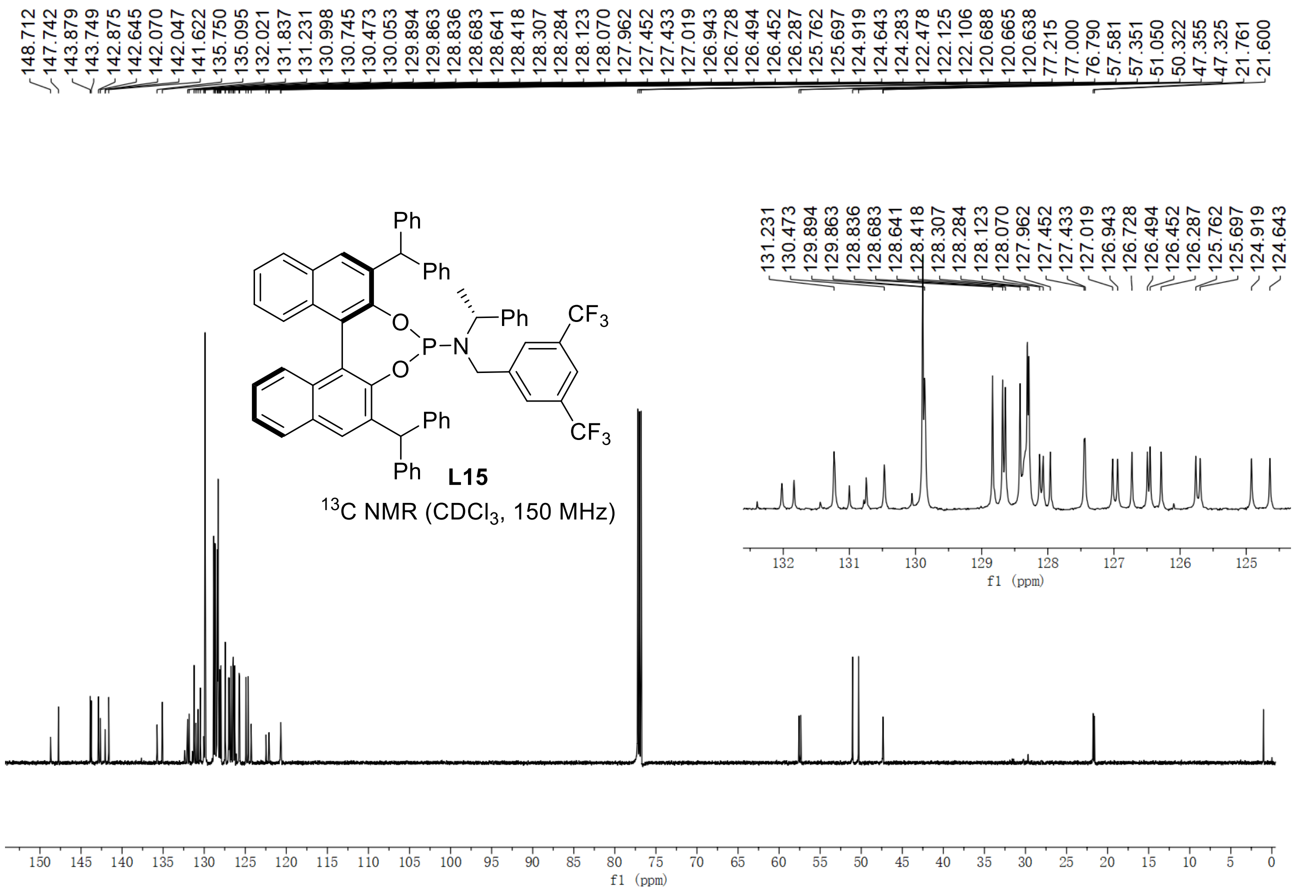
(ellipsoid contour probability 50%)

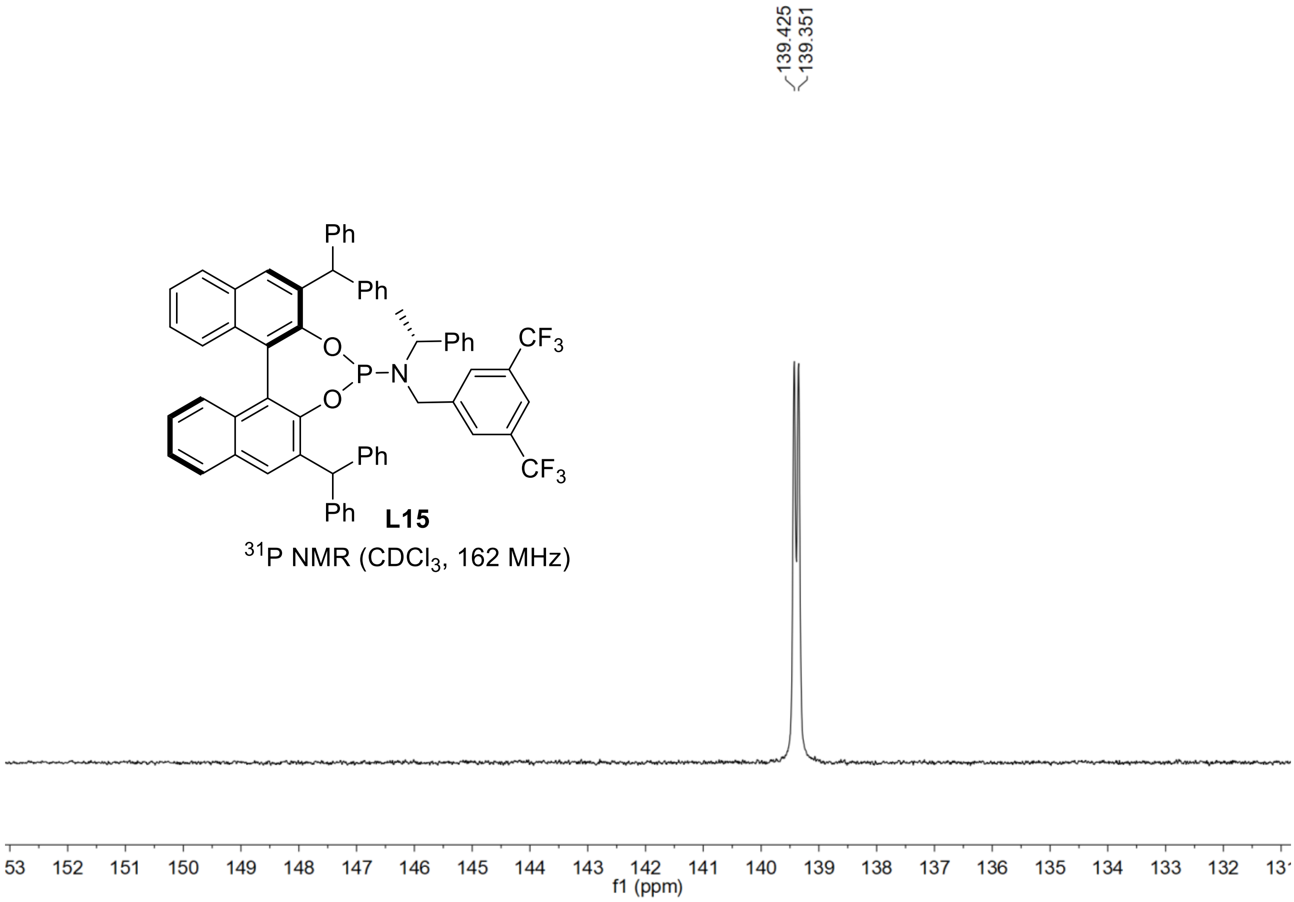
| | |
|---|---|
| Identification code | **25** |
| Empirical formula | $C_{26}H_{21}NO$ |
| Formula weight | 363.44 |
| Temperature/K | 149.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.7659(11) |
| b/Å | 13.1580(15) |
| c/Å | 27.887(3) |
| α/° | 90 |
| β/° | 100.454(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 3884.8(7) |

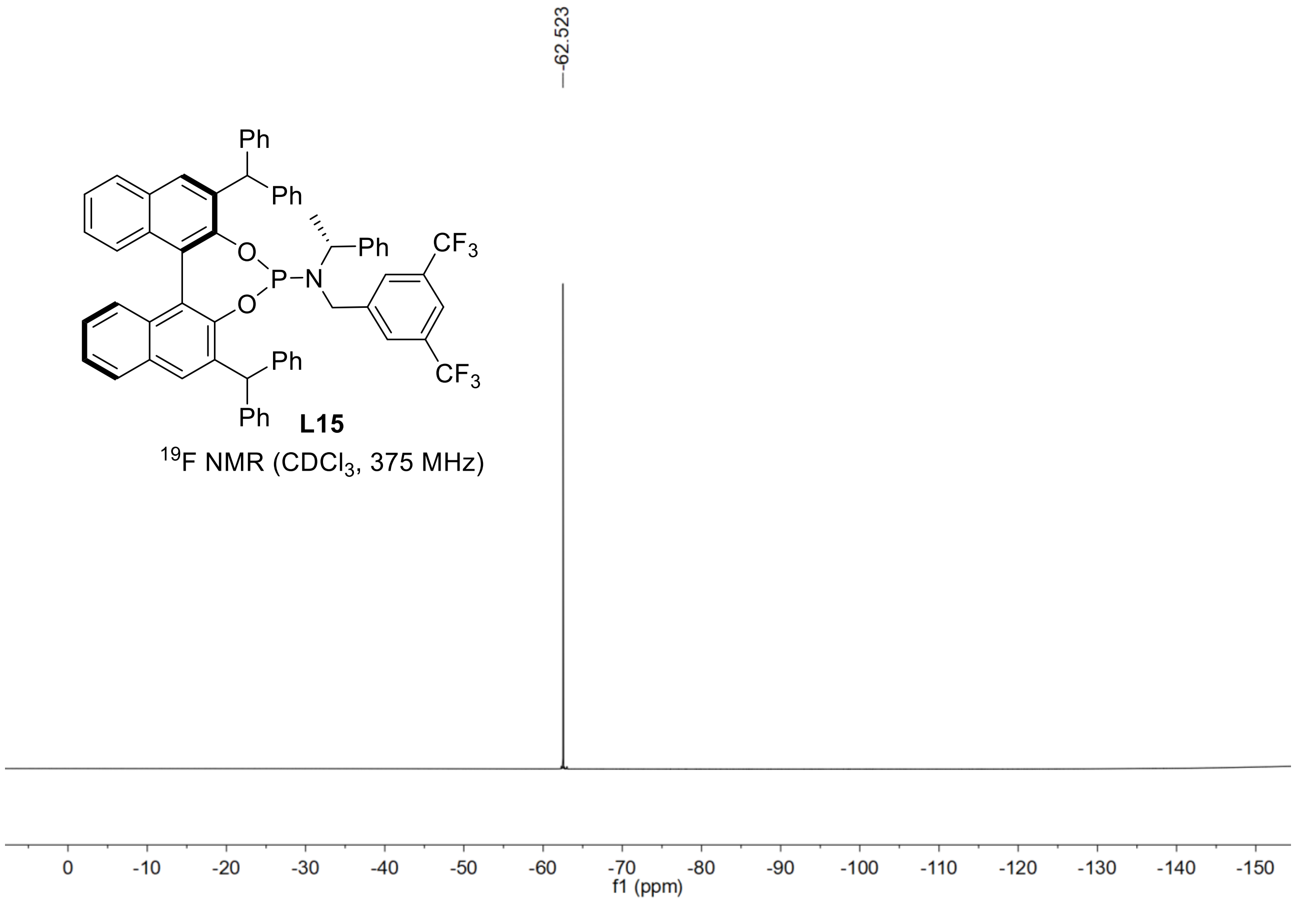
| | |
|---|---|
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.243 |
| μ/mm$^{-1}$ | 0.075 |
| F(000) | 1536.0 |
| Crystal size/mm$^3$ | 0.45 × 0.13 × 0.04 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/ ° | 4.29 to 55.022 |
| Index ranges | $-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-36 \leq l \leq 33$ |
| Reflections collected | 36992 |
| Independent reflections | 8881 [$R_{int}$ = 0.1161, $R_{sigma}$ = 0.1068] |
| Data/restraints/parameters | 8881/0/505 |
| Goodness-of-fit on $F^2$ | 1.021 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0681, $wR_2$ = 0.1649 |
| Final R indexes [all data] | $R_1$ = 0.1112, $wR_2$ = 0.1963 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.37/-0.32 |

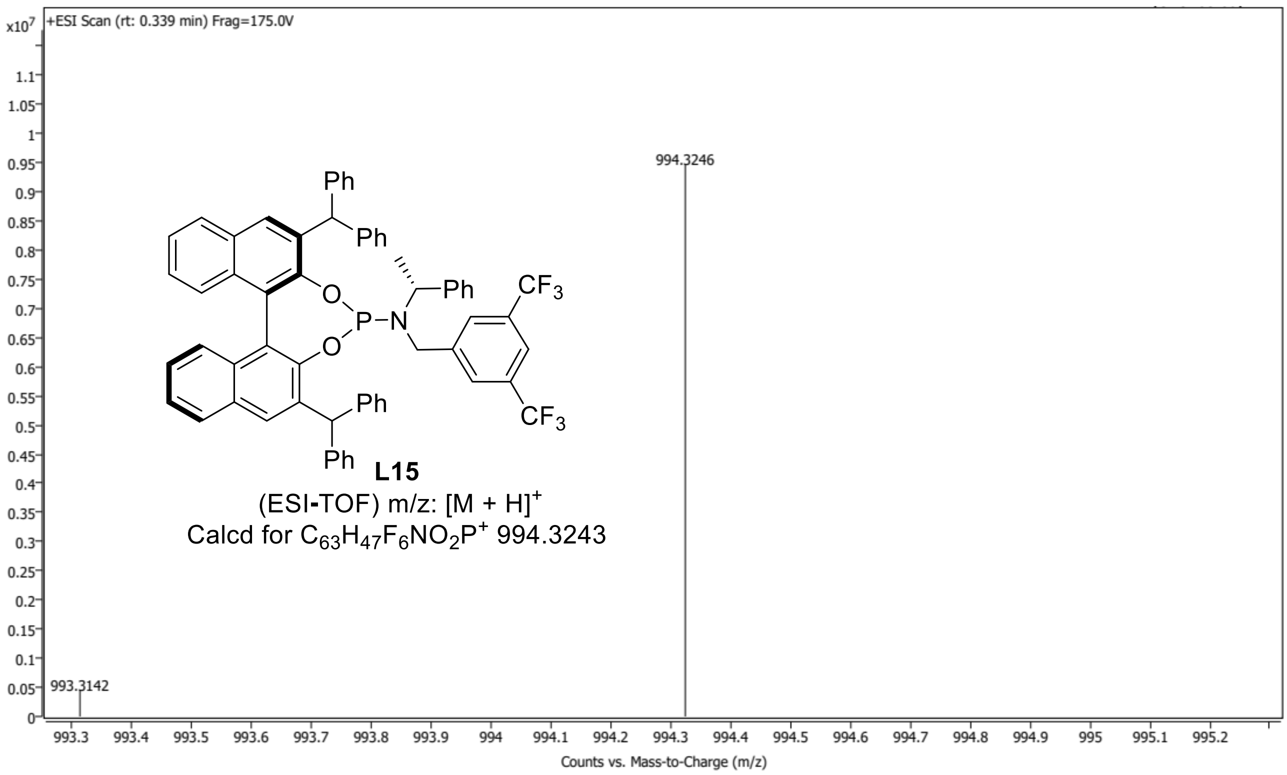
# 8. NMR, HRMS spectra and HPLC chromatograms




139.425
139.351
Ph
Ph
Ph
CF3
O
P
N
O
Ph
CF3
Ph
L15
31P NMR (CDCl3, 162 MHz)
53 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132
f1 (ppm)

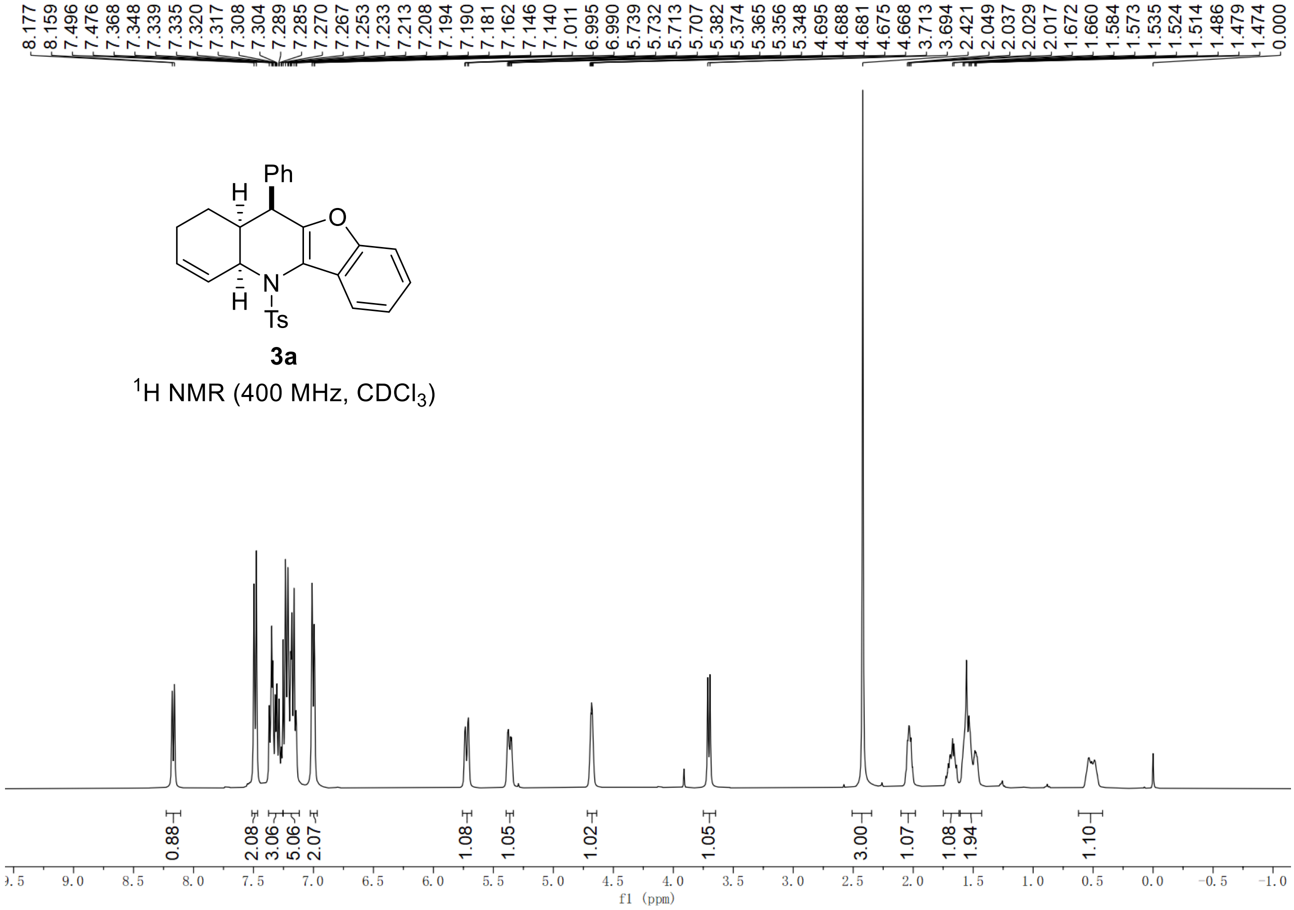

-62.523
Ph
Ph
Ph
CF3
O
P
N
O
Ph
CF3
Ph
L15
19F NMR (CDCl3, 375 MHz)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)



+ESI Scan (rt: 0.339 min) Frag=175.0V
x10^7
994.3246
993.3142
Counts vs. Mass-to-Charge (m/z)
L15
(ESI-TOF) m/z: [M + H]+
Calcd for C63H47F6NO2P+ 994.3243

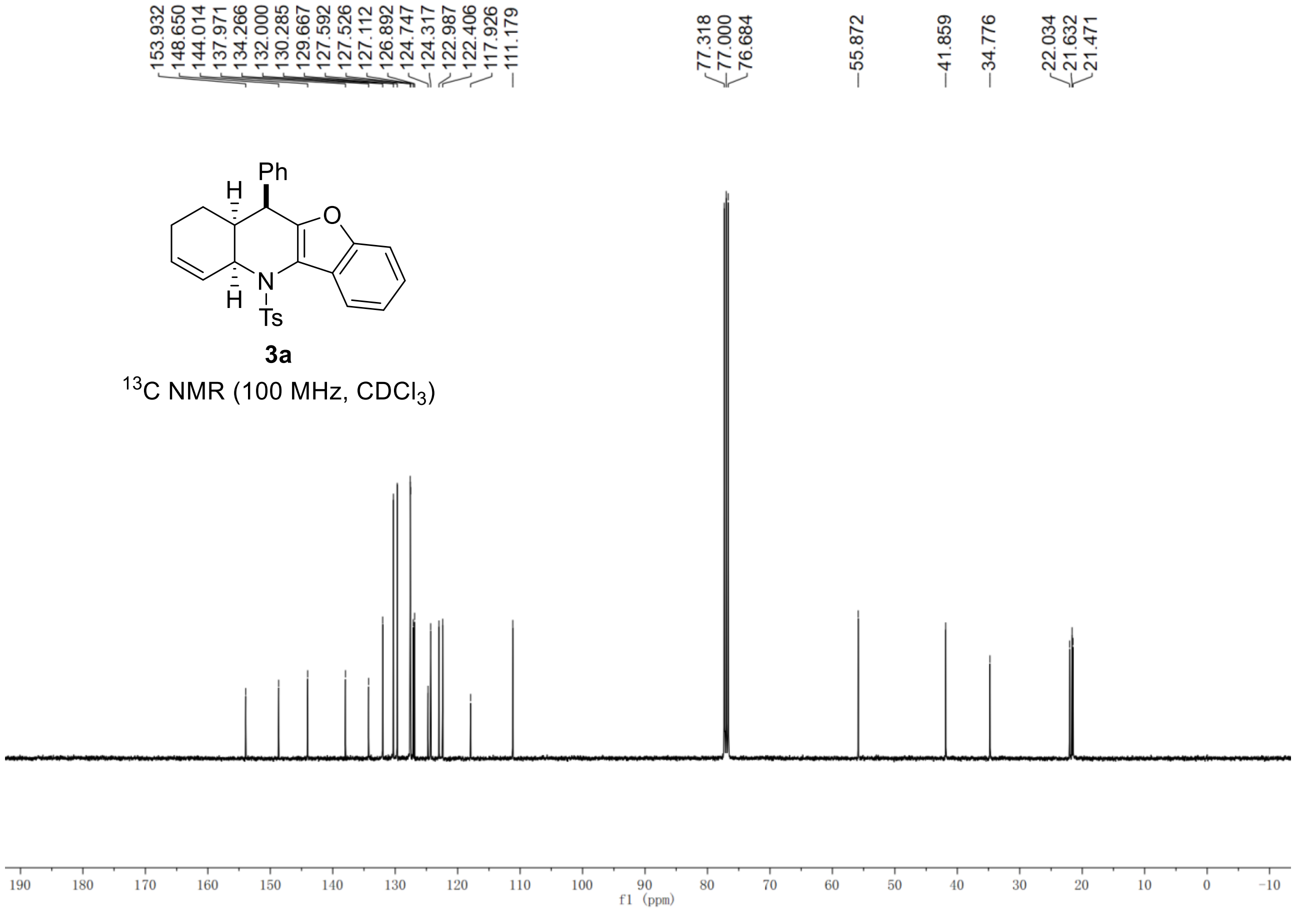
**3a**

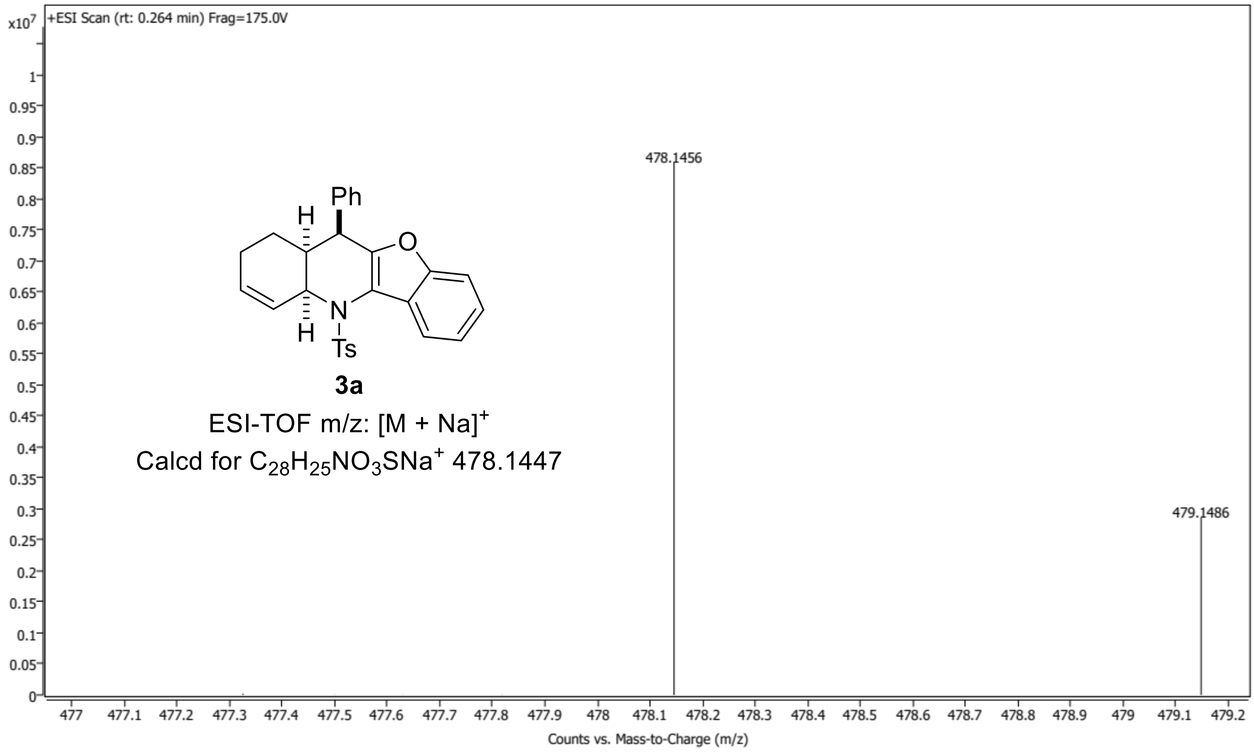
$^{1}$H NMR (400 MHz, $CDCl_3$)



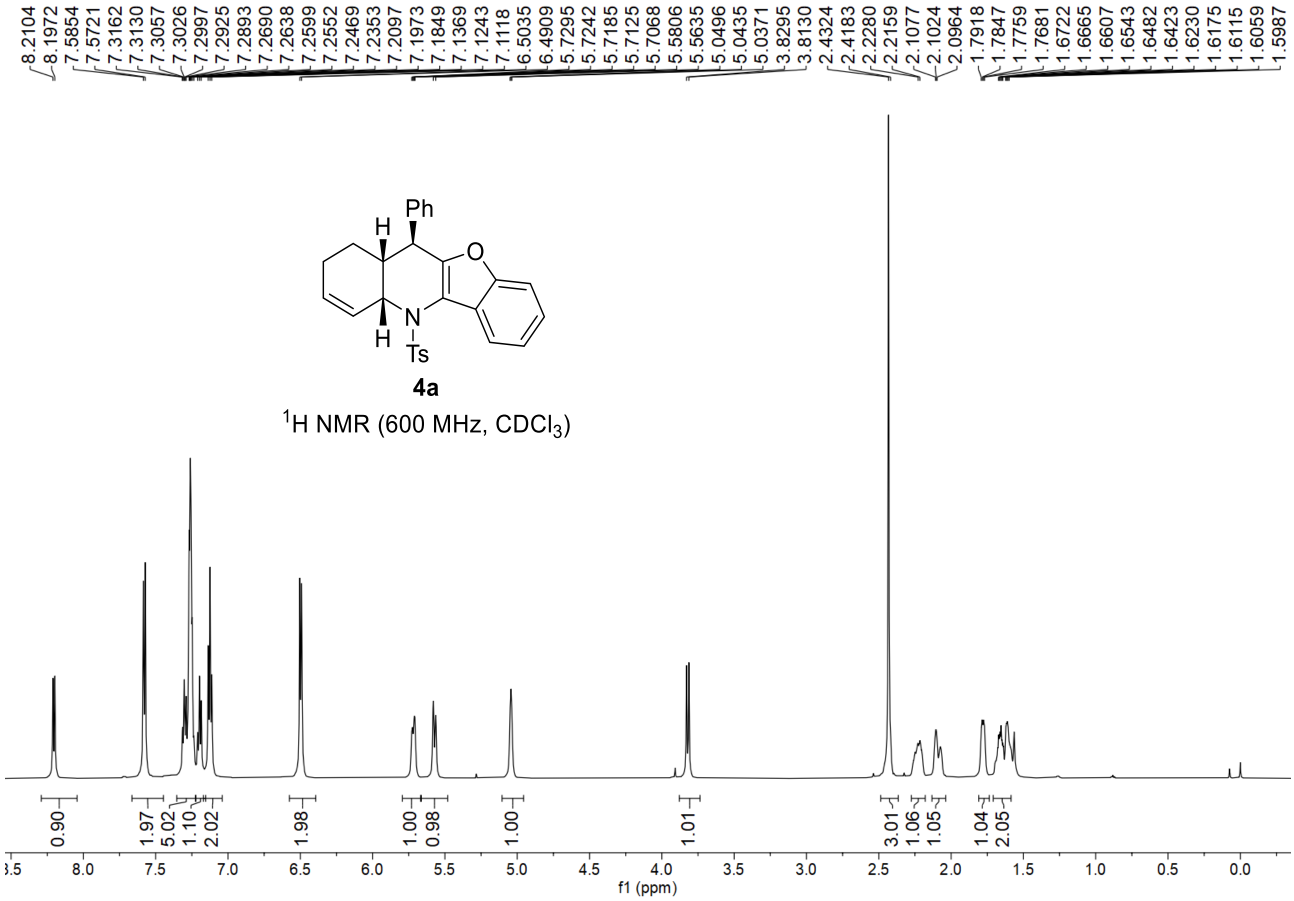

**3a**

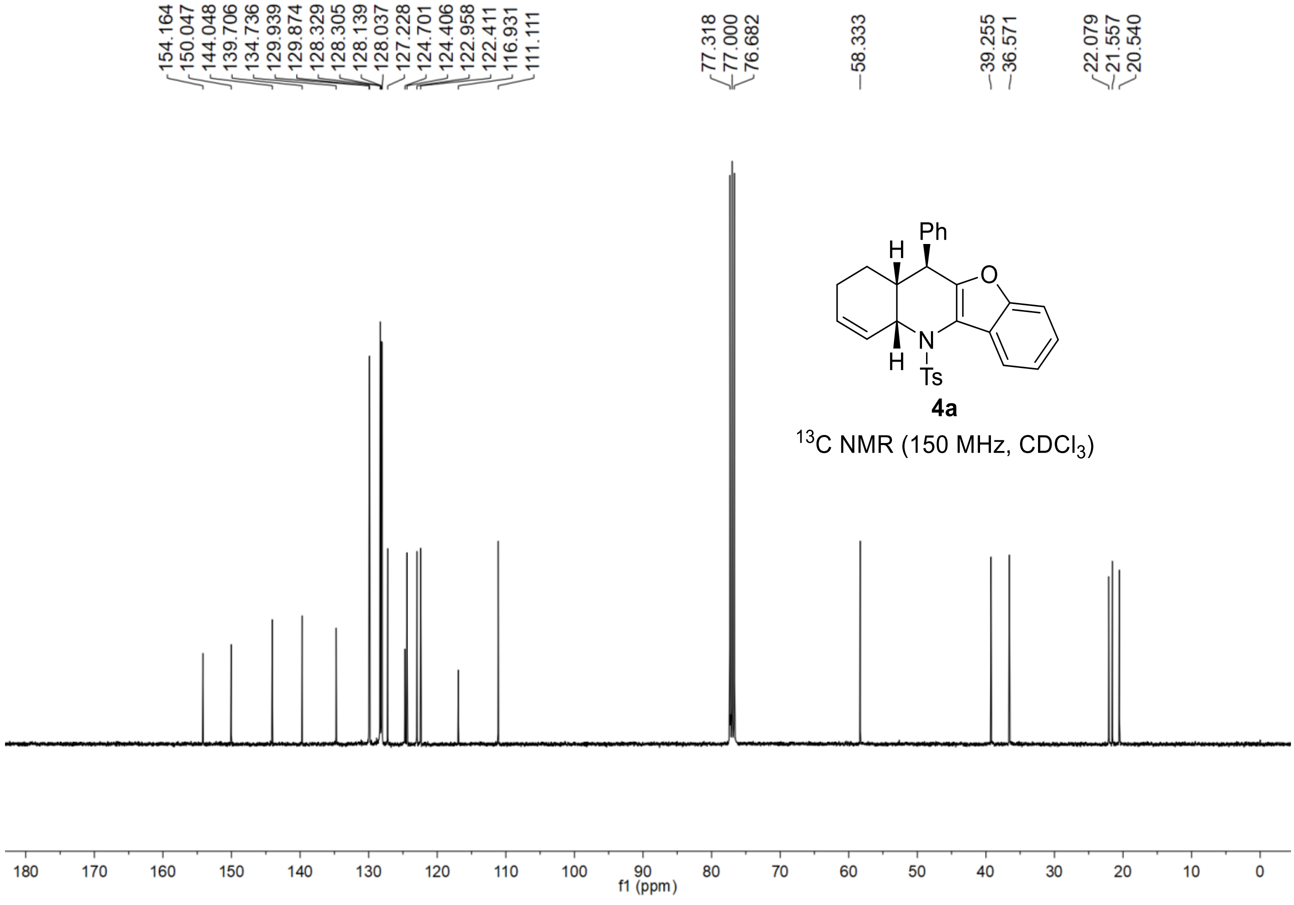
$^{13}$C NMR (100 MHz, $CDCl_3$)

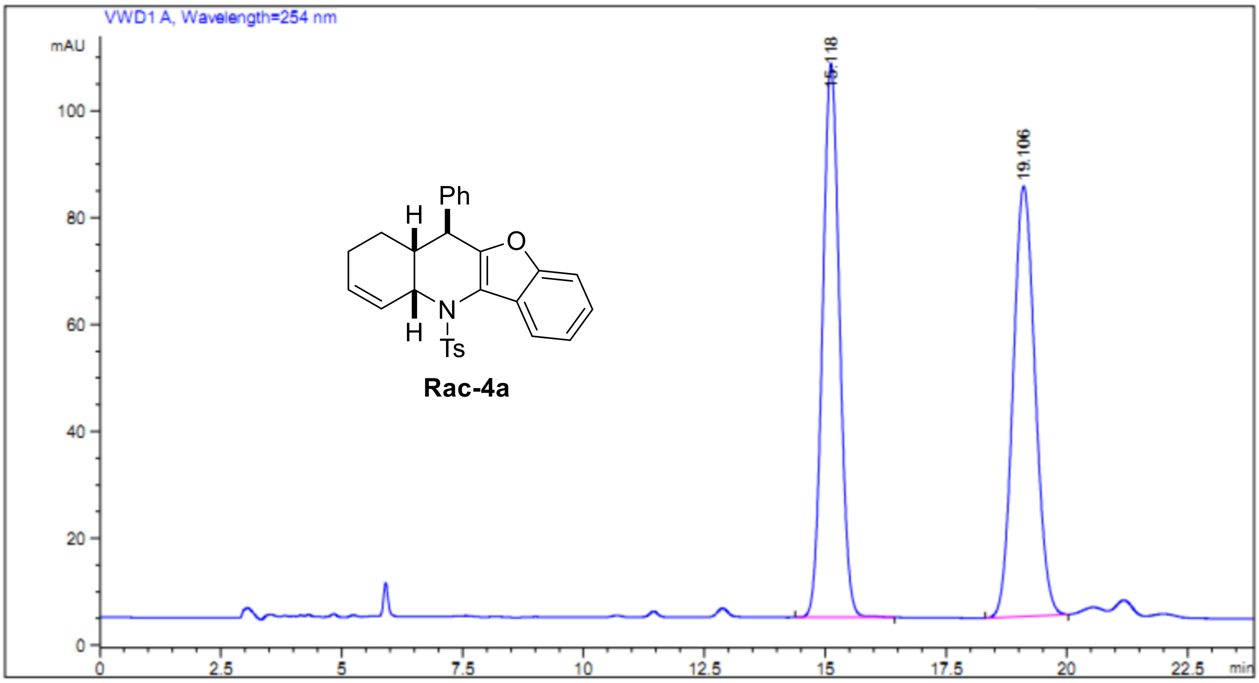




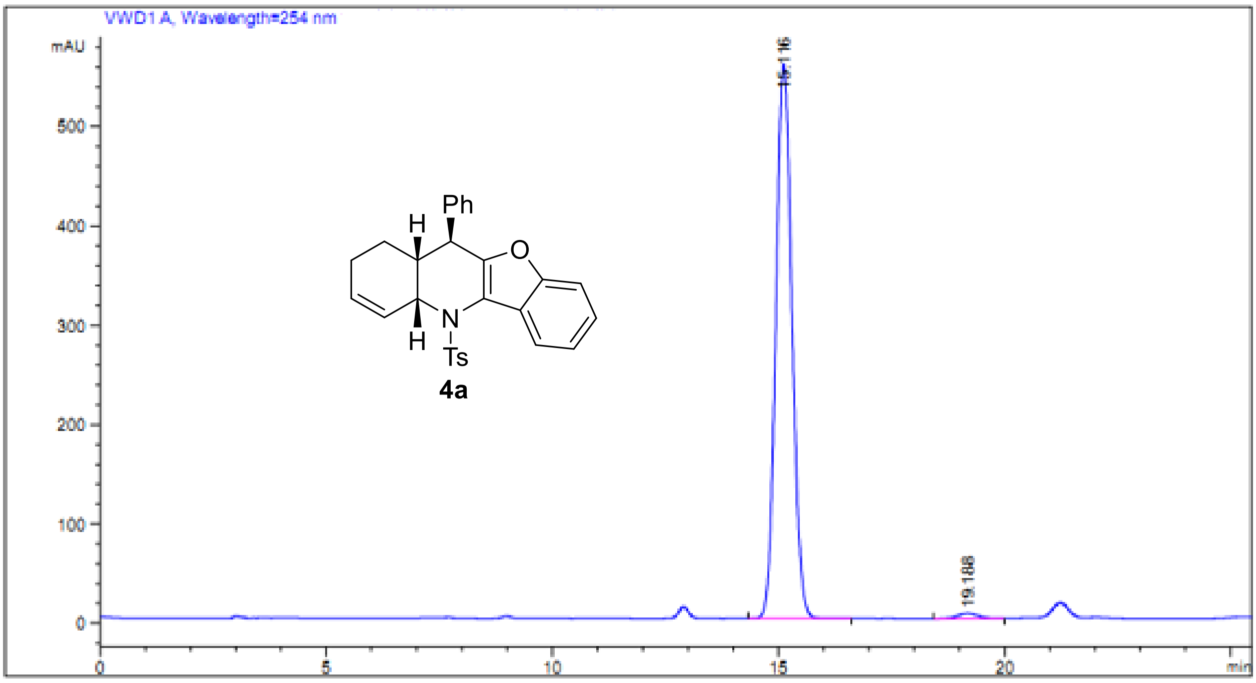
x10^7
+ESI Scan (rt: 0.264 min) Frag=175.0V
478.1456
479.1486
Ph
H
O
N
H
Ts
3a
ESI-TOF m/z: [M + Na]+
Calcd for C28H25NO3SNa+ 478.1447
Counts vs. Mass-to-Charge (m/z)


8.2104
8.1972
7.5854
7.5721
7.3162
7.3130
7.3057
7.3026
7.2997
7.2925
7.2893
7.2690
7.2638
7.2599
7.2552
7.2469
7.2353
7.2097
7.1973
7.1849
7.1369
7.1243
7.1118
6.5035
6.4909
5.7295
5.7242
5.7185
5.7125
5.7068
5.5806
5.5635
5.0496
5.0435
5.0371
3.8295
3.8130
2.4324
2.4183
2.2280
2.2159
2.1077
2.1024
2.0964
1.7918
1.7847
1.7759
1.7681
1.6722
1.6665
1.6607
1.6543
1.6482
1.6423
1.6230
1.6175
1.6115
1.6059
1.5987
Ph
H
O
N
H
Ts
4a
1H NMR (600 MHz, CDCl3)
0.90
1.97
5.02
1.10
2.02
1.98
1.00
0.98
1.00
1.01
3.01
1.06
1.05
1.04
2.05
f1 (ppm)

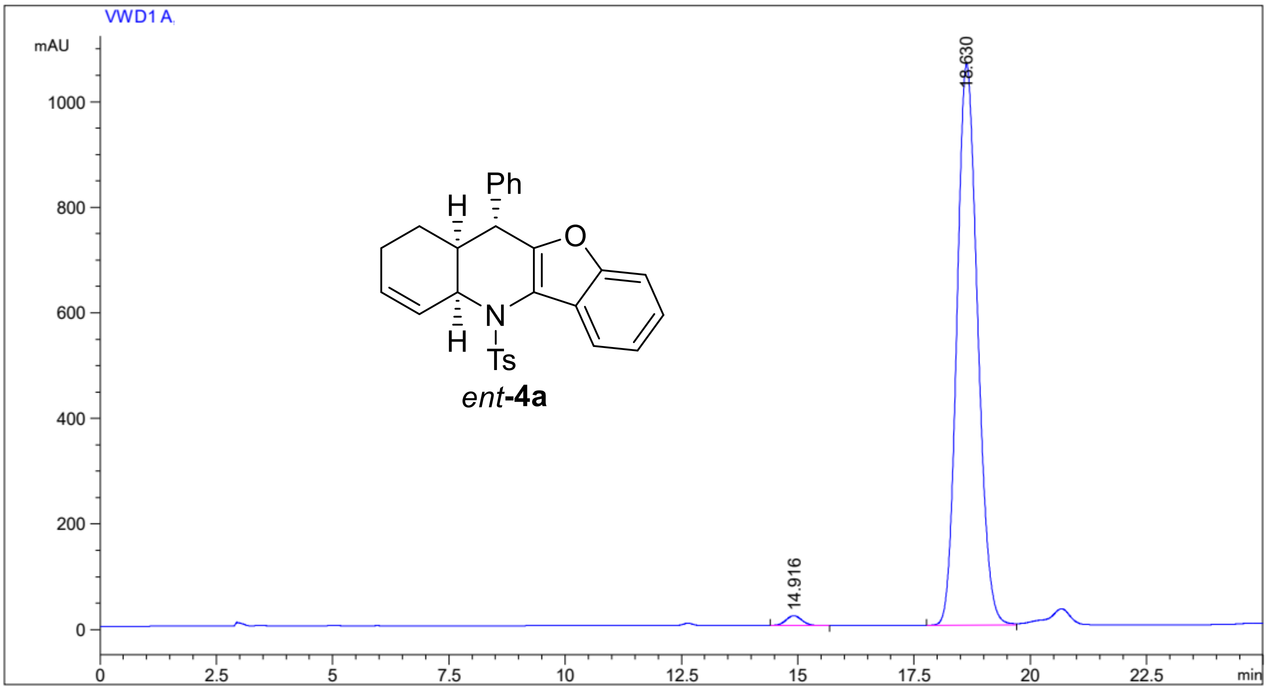

154.164
150.047
144.048
139.706
134.736
129.939
129.874
128.329
128.305
128.139
128.037
127.228
124.701
124.406
122.958
122.411
116.931
111.111
77.318
77.000
76.682
58.333
39.255
36.571
22.079
21.557
20.540
Ph
H
O
N
H
Ts
4a
13C NMR (150 MHz, CDCl3)
f1 (ppm)



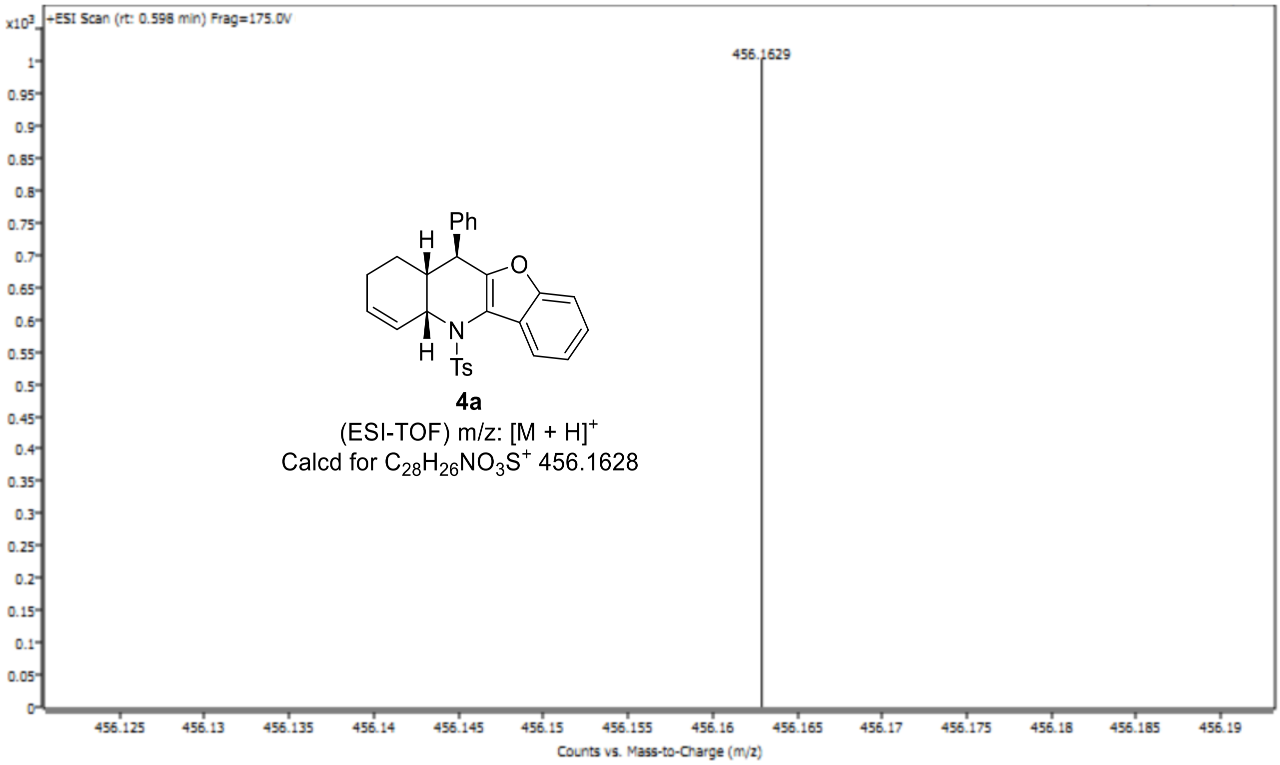

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 15.118 | BB | 0.3786 | 2521.94507 | 103.63020 | 49.7283 |
| 2 | 19.106 | BB | 0.4916 | 2549.49829 | 80.53268 | 50.2717 |

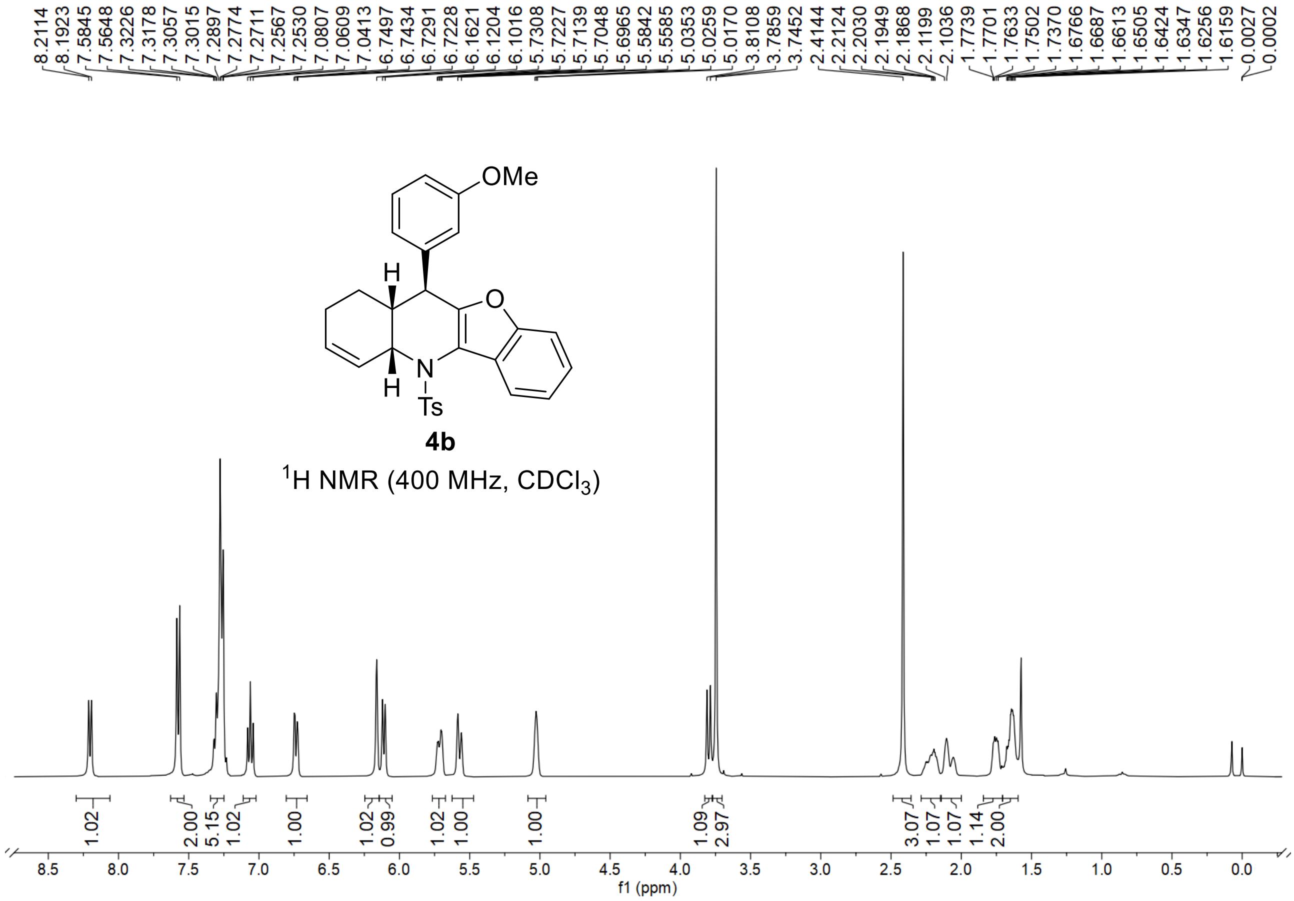


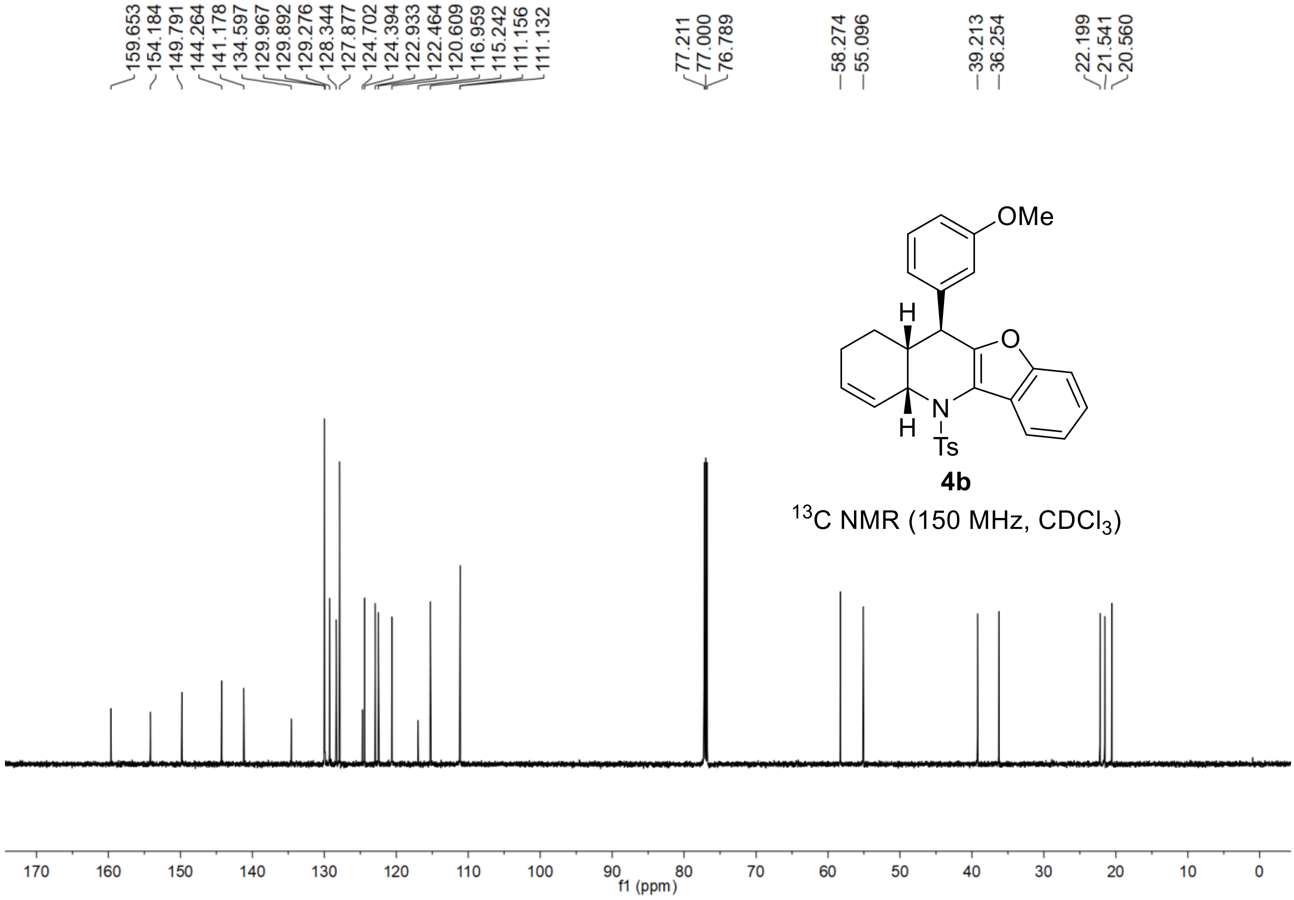

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 15.116 | BB | 0.3858 | 1.37939e4 | 558.28955 | 98.7704 |
| 2 | 19.188 | BB | 0.5049 | 171.71707 | 5.35892 | 1.2296 |

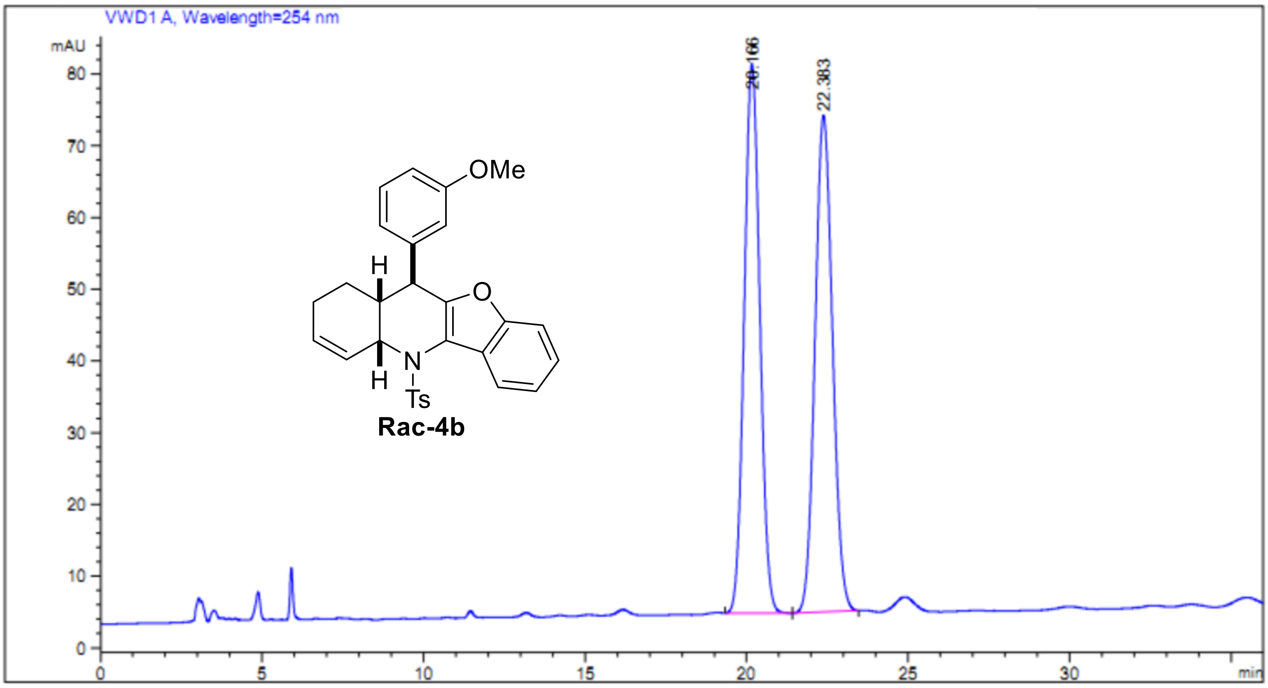



| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 14.916 | VB | 0.3736 | 448.99615 | 18.68349 | 1.3493 |
| 2 | 18.630 | BV | 0.4810 | 3.28265e4 | 1063.50916 | 98.6507 |

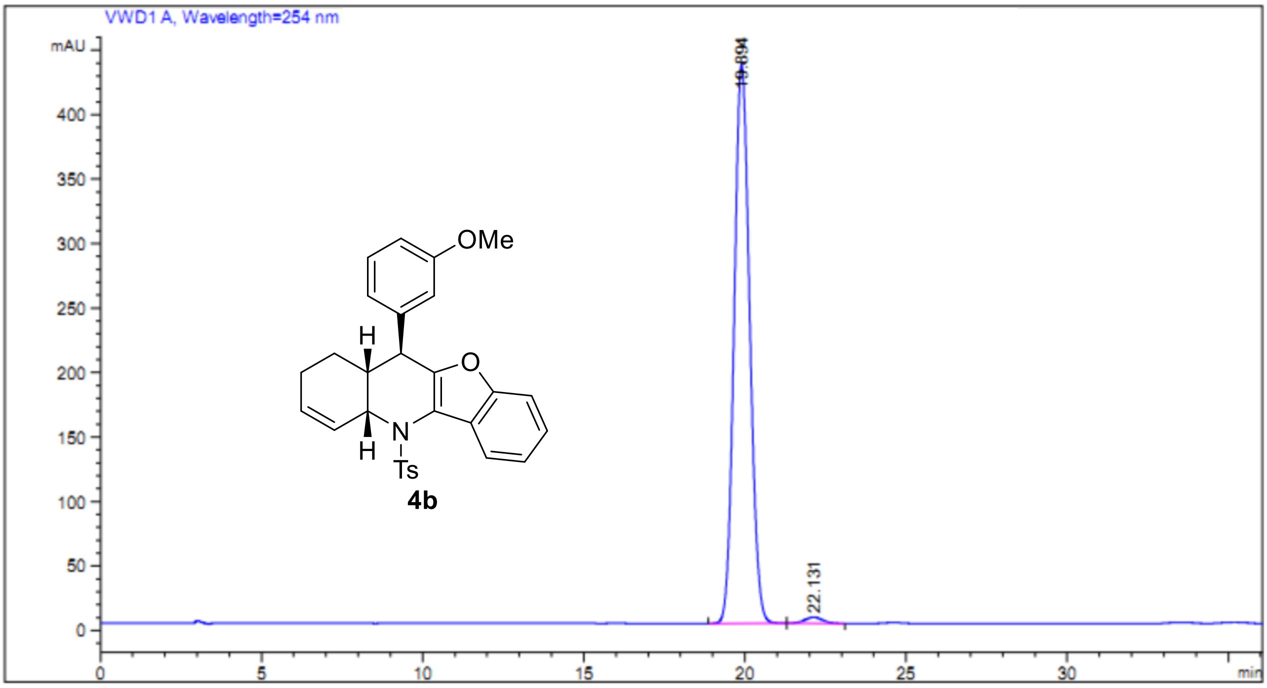



8.2114
8.1923
7.5845
7.5648
7.3226
7.3178
7.3057
7.3015
7.2897
7.2774
7.2711
7.2567
7.2530
7.0807
7.0609
7.0413
6.7497
6.7434
6.7291
6.7228
6.1621
6.1204
6.1016
5.7308
5.7227
5.7139
5.7048
5.6965
5.5842
5.5585
5.0353
5.0259
5.0170
3.8108
3.7859
3.7452
2.4144
2.2124
2.2030
2.1949
2.1868
2.1199
2.1036
1.7739
1.7701
1.7633
1.7502
1.7370
1.6766
1.6687
1.6613
1.6505
1.6424
1.6347
1.6256
1.6159
0.0027
0.0002
OMe
H
O
N
H
Ts
4b
$^{1}$H NMR (400 MHz, CDCl$_3$)
1.02
2.00
5.15
1.02
1.00
1.02
0.99
1.02
1.00
1.00
1.09
2.97
3.07
1.07
1.07
1.14
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

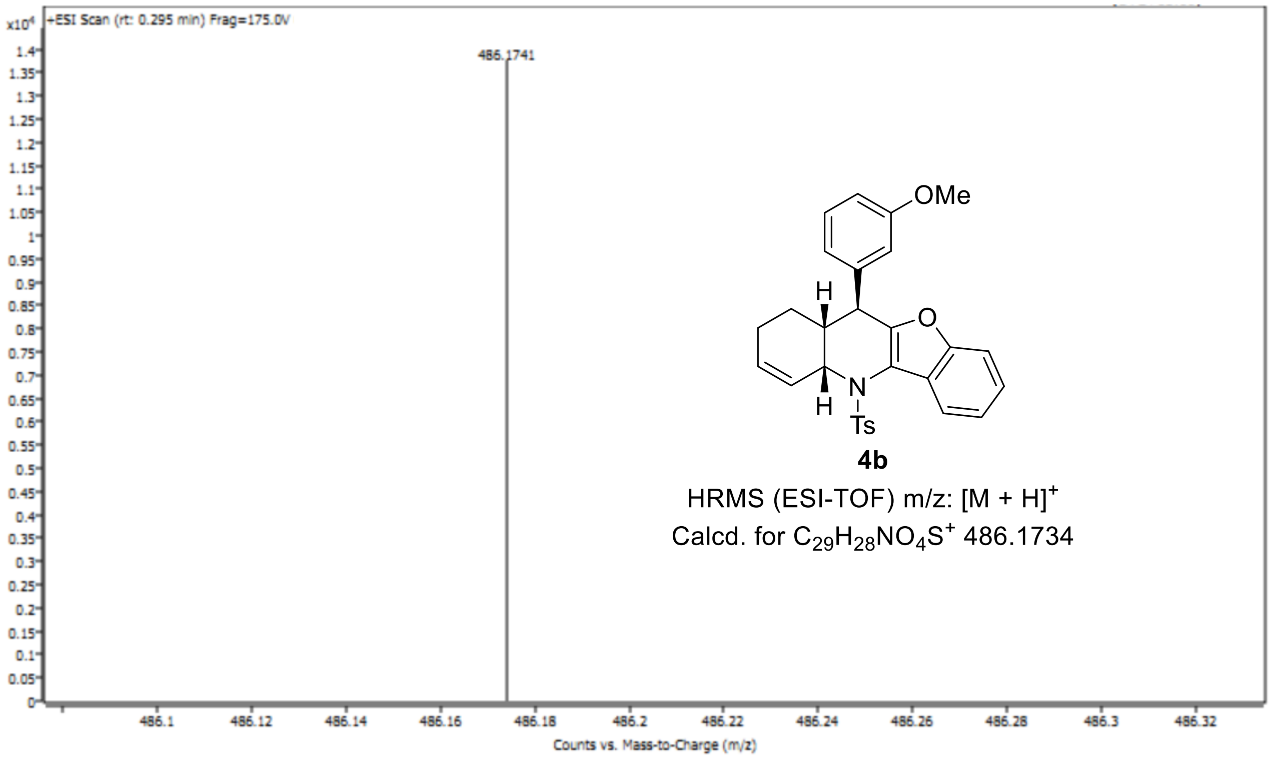

159.653
154.184
149.791
144.264
141.178
134.597
129.967
129.892
129.276
128.344
127.877
124.702
124.394
122.933
122.464
120.609
116.959
115.242
111.156
111.132
77.211
77.000
76.789
58.274
55.096
39.213
36.254
22.199
21.541
20.560
OMe
H
O
N
H
Ts
4b
$^{13}$C NMR (150 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



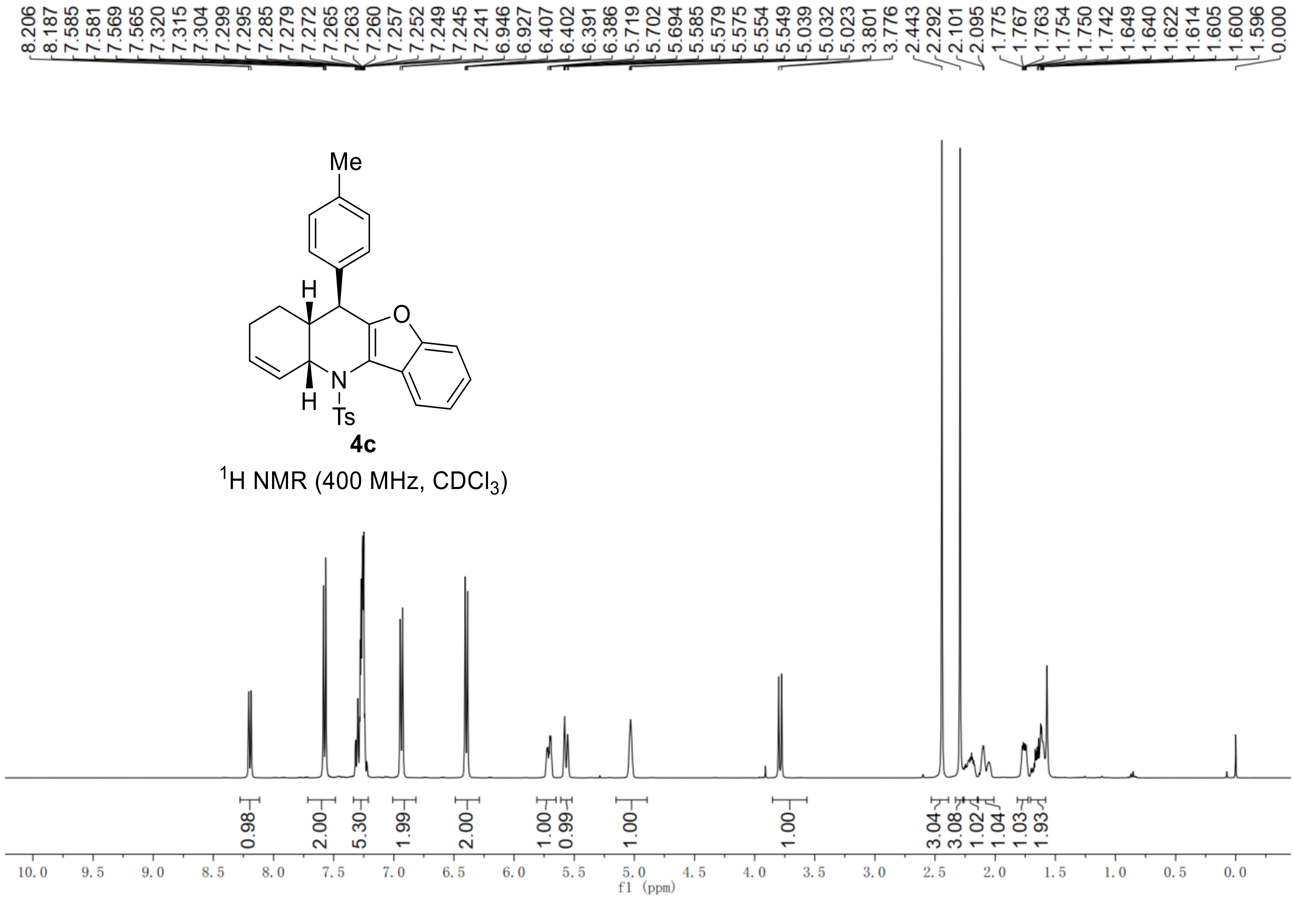

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 20.166 | BB | 0.5234 | 2574.43481 | 76.55724 | 49.6797 |
| 2 | 22.383 | BB | 0.5908 | 2607.63110 | 69.23320 | 50.3203 |



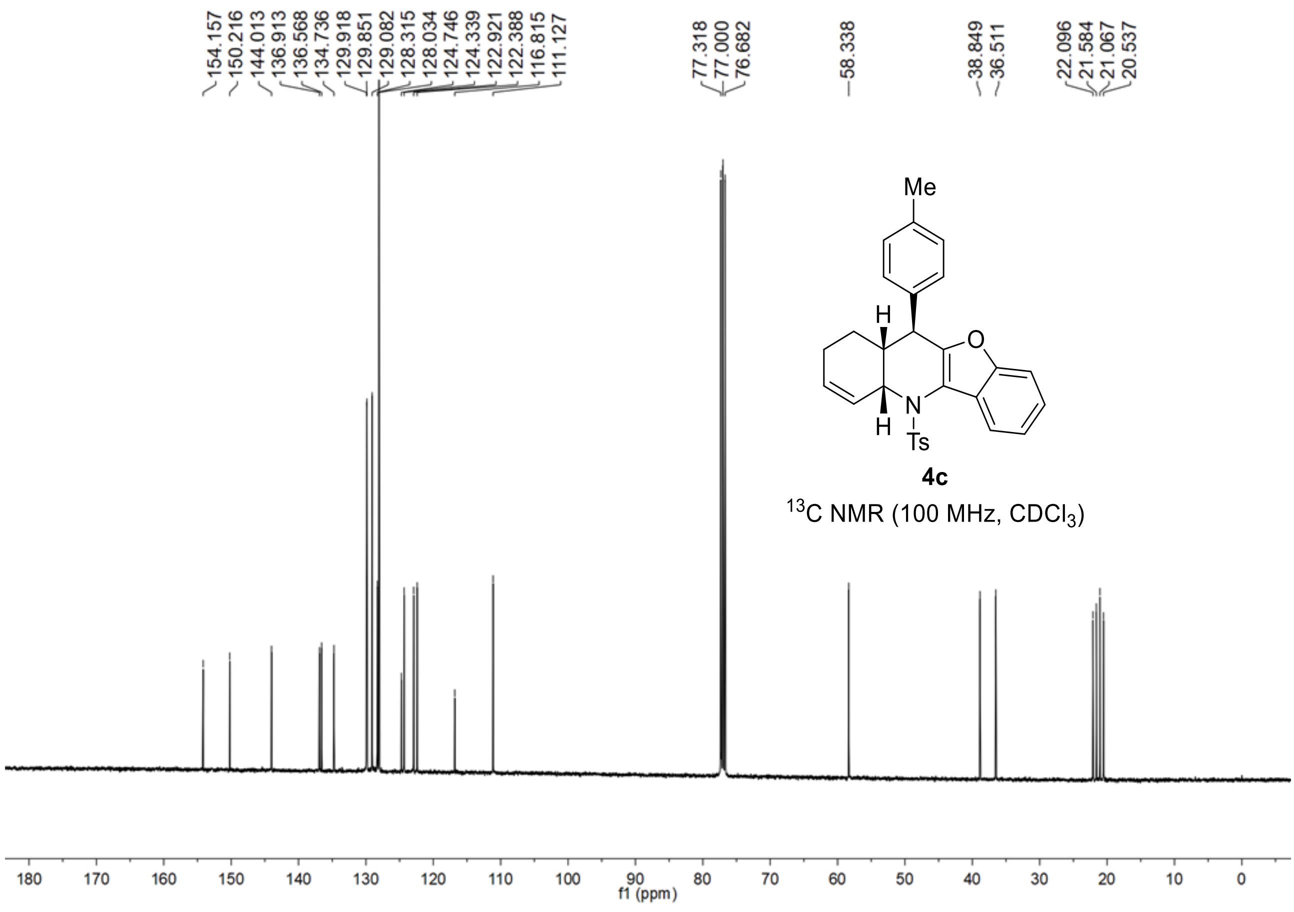

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 19.894 | BB | 0.5217 | 1.45212e4 | 433.71042 | 98.7962 |
| 2 | 22.131 | BB | 0.5673 | 176.94371 | 4.73173 | 1.2038 |



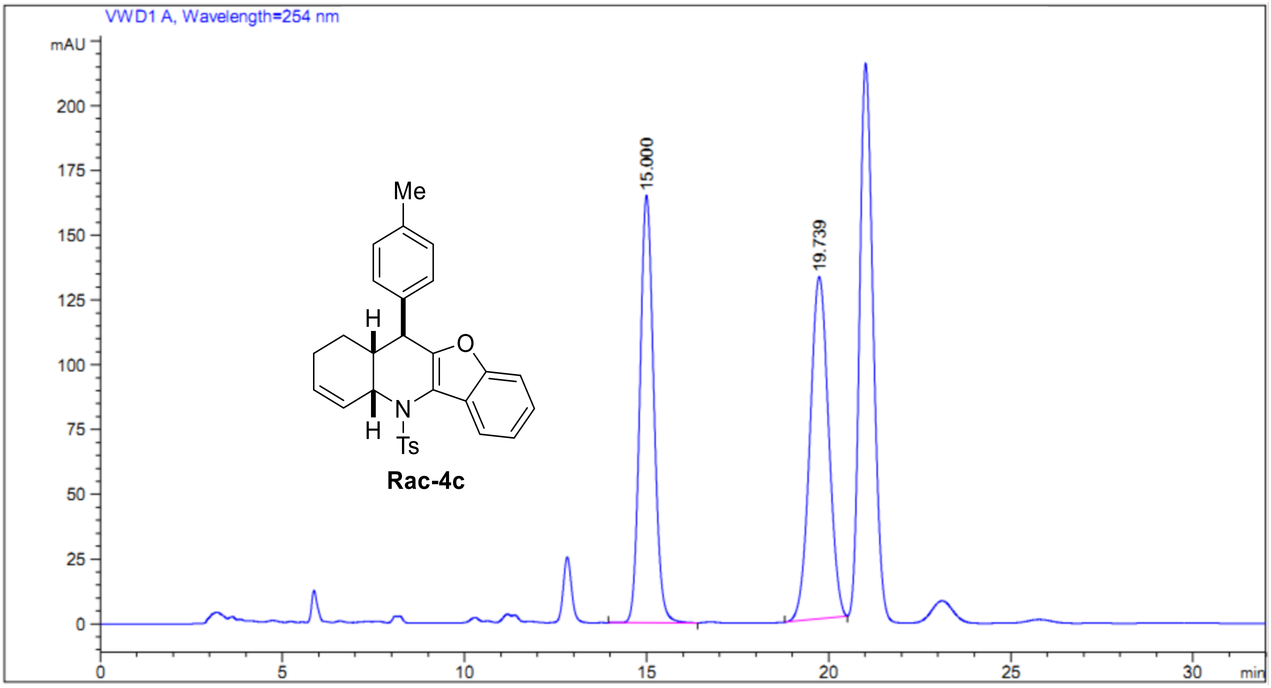
x10^6
+ESI Scan (rt: 0.295 min) Frag=175.0V
486.1741
OMe
H
O
N
H
Ts
4b
HRMS (ESI-TOF) m/z: [M + H]$^+$
Calcd. for $C_{29}H_{28}NO_4S^+$ 486.1734
486.1
486.12
486.14
486.16
486.18
486.2
486.22
486.24
486.26
486.28
486.3
486.32
Counts vs. Mass-to-Charge (m/z)



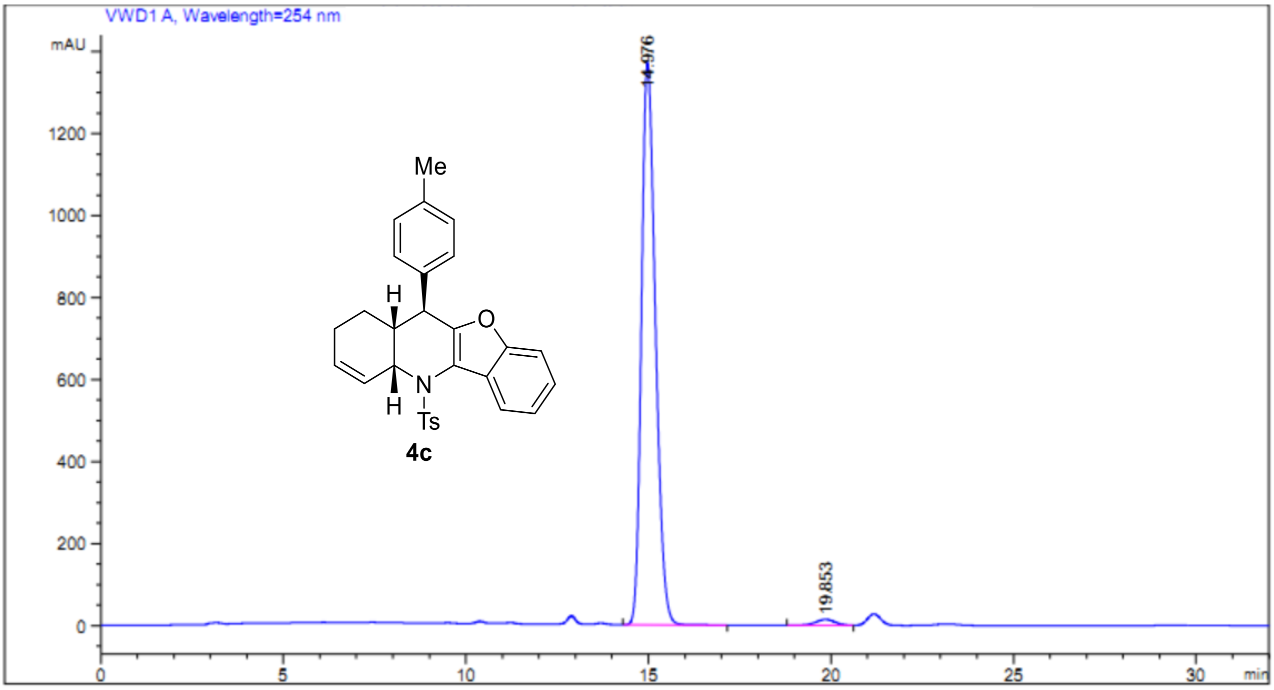
4c
1H NMR (400 MHz, CDCl3)

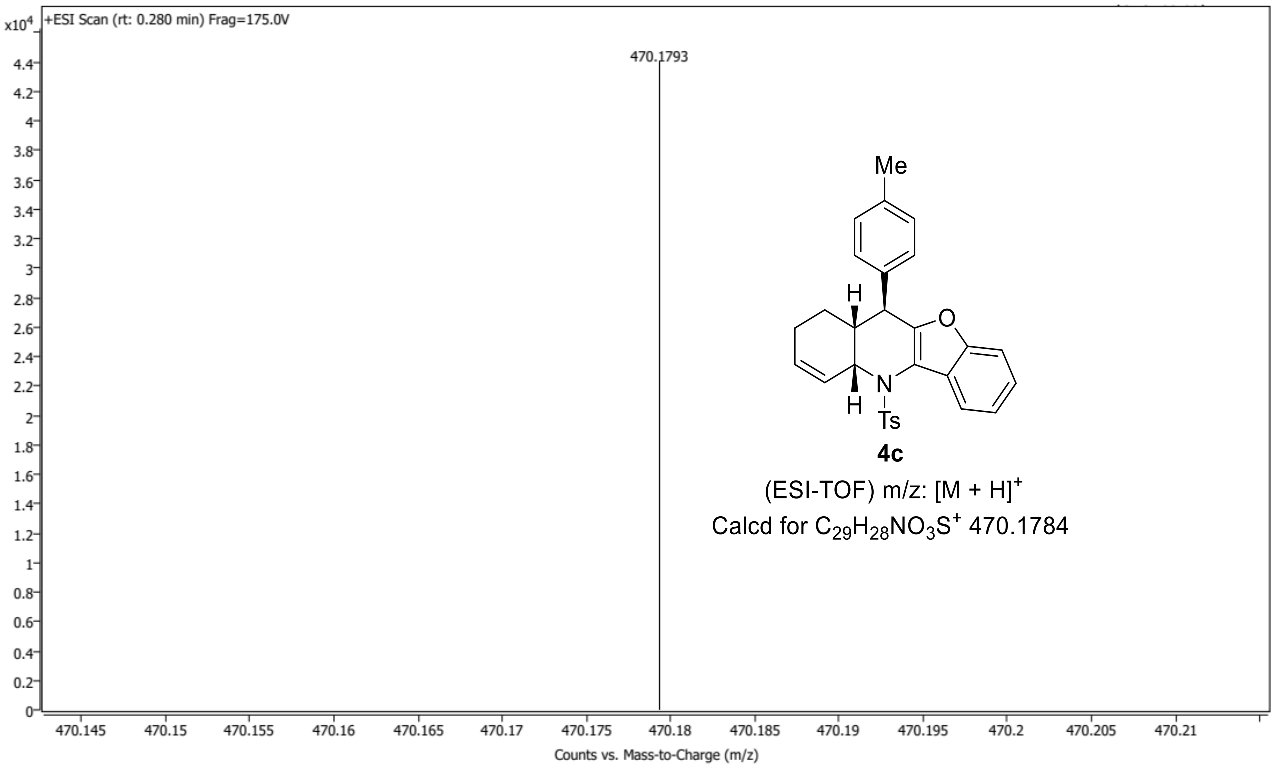
4c
13C NMR (100 MHz, CDCl3)



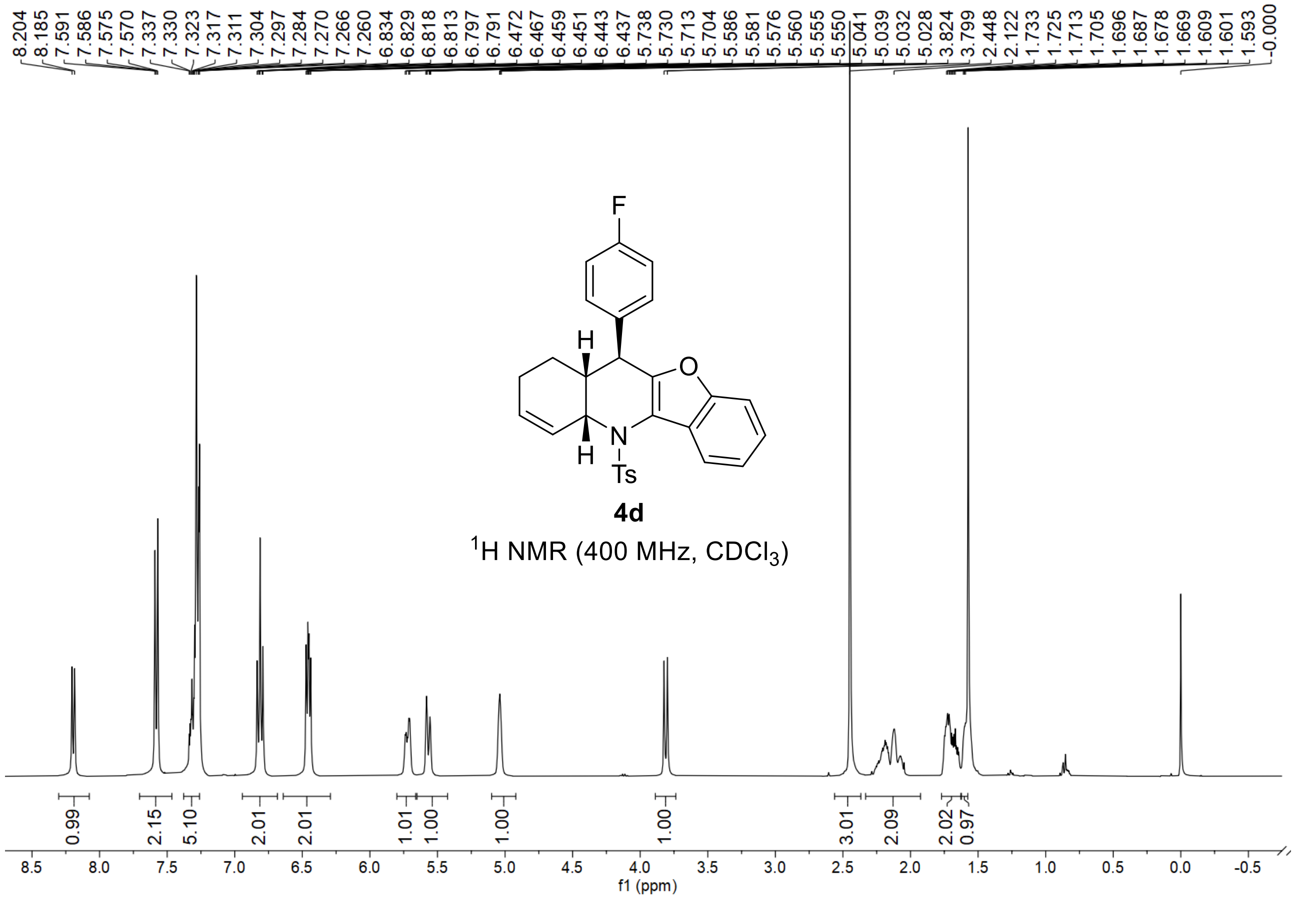

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 15.000 | BV | 0.4098 | 4355.52246 | 165.03610 | 48.0408 |
| 2 | 19.739 | BB | 0.5558 | 4710.77832 | 132.09181 | 51.9592 |




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.976 | BBA | 0.4141 | 3.63380e4 | 1370.75256 | 98.5370 |
| 2 | 19.853 | BB | 0.5811 | 539.50513 | 14.45436 | 1.4630 |

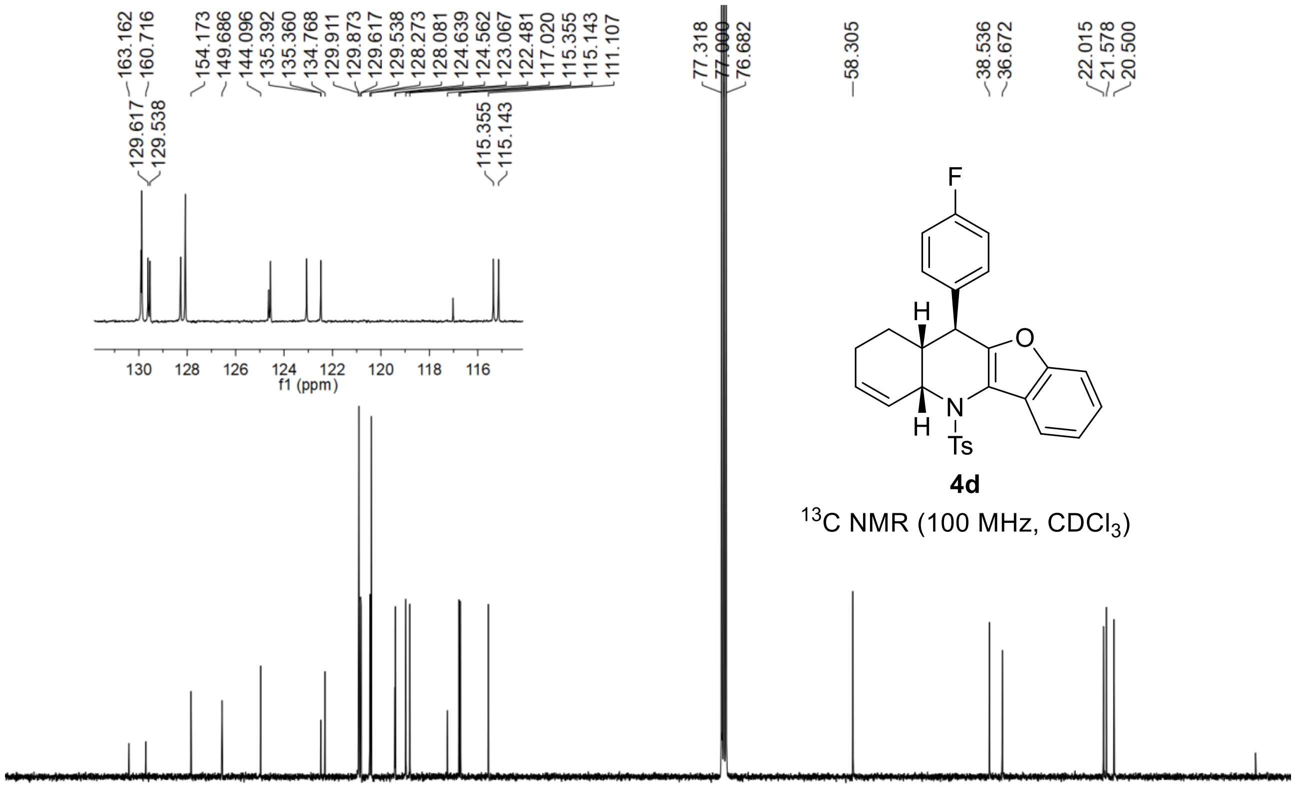


x10^4
+ESI Scan (rt: 0.280 min) Frag=175.0V
470.1793
Me
H
O
N
H
Ts
4c
(ESI-TOF) m/z: [M + H]+
Calcd for C29H28NO3S+ 470.1784
Counts vs. Mass-to-Charge (m/z)



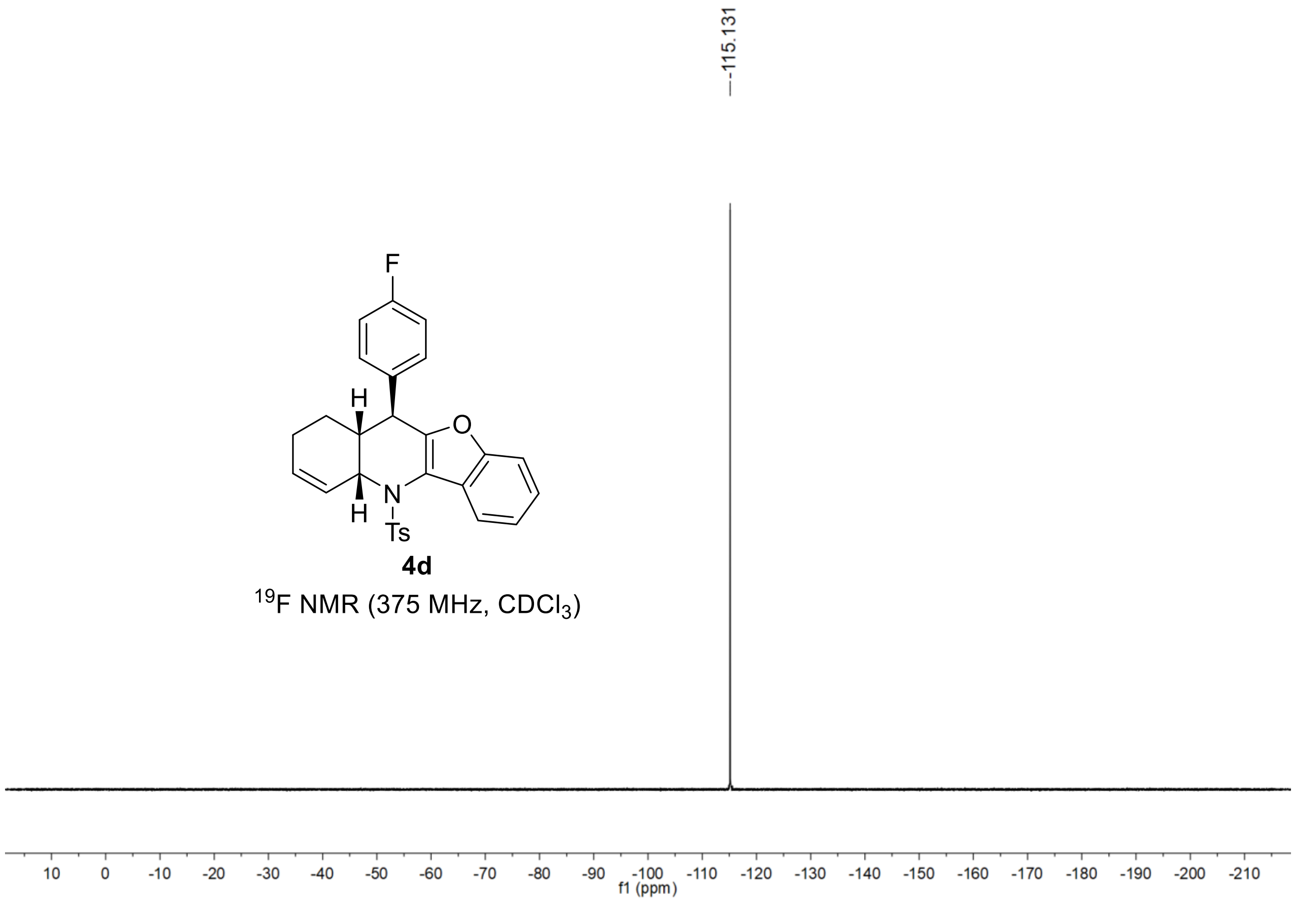
**4d**

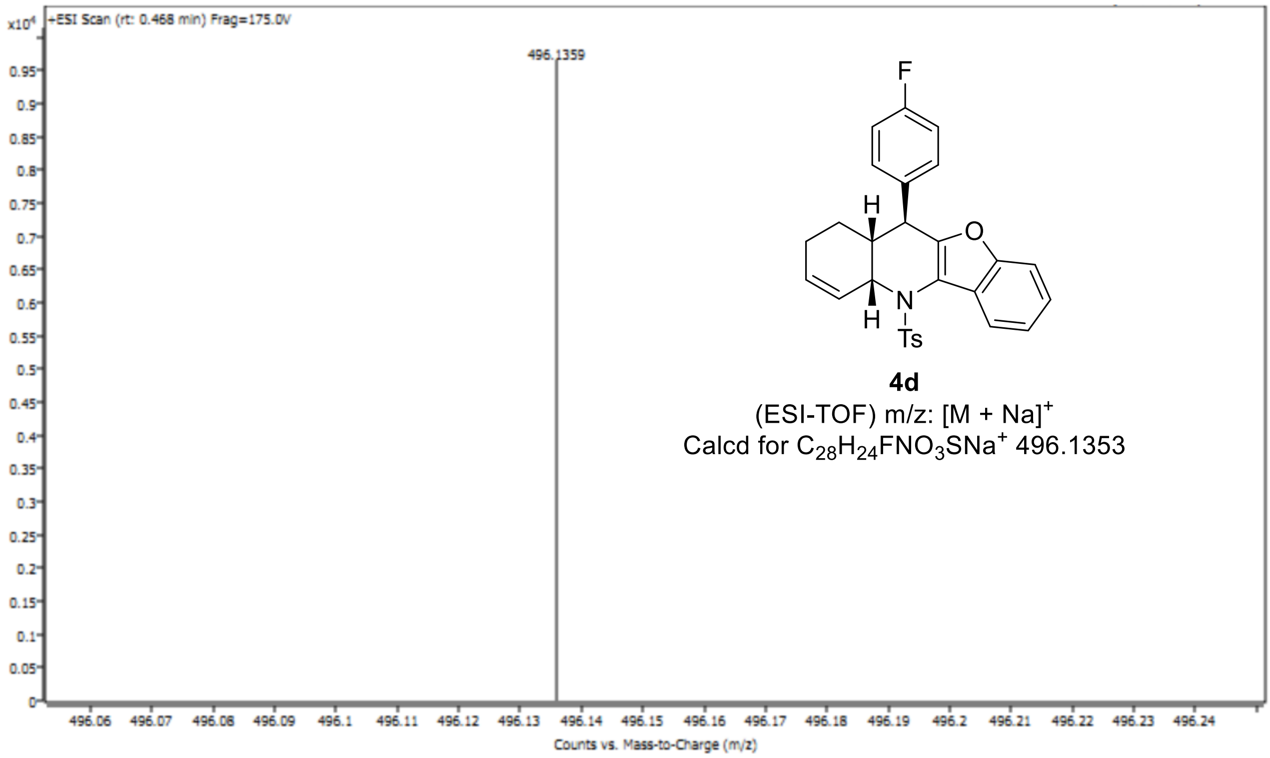
$^1H$ NMR (400 MHz, $CDCl_3$)

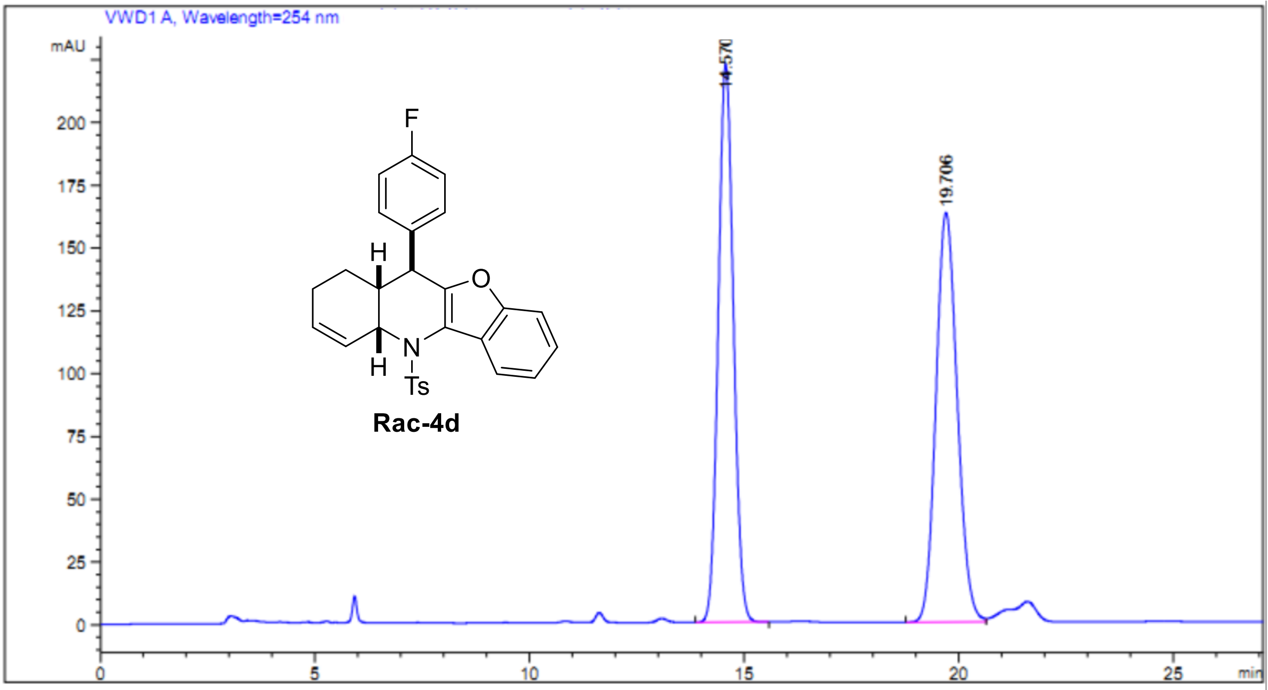


**4d**

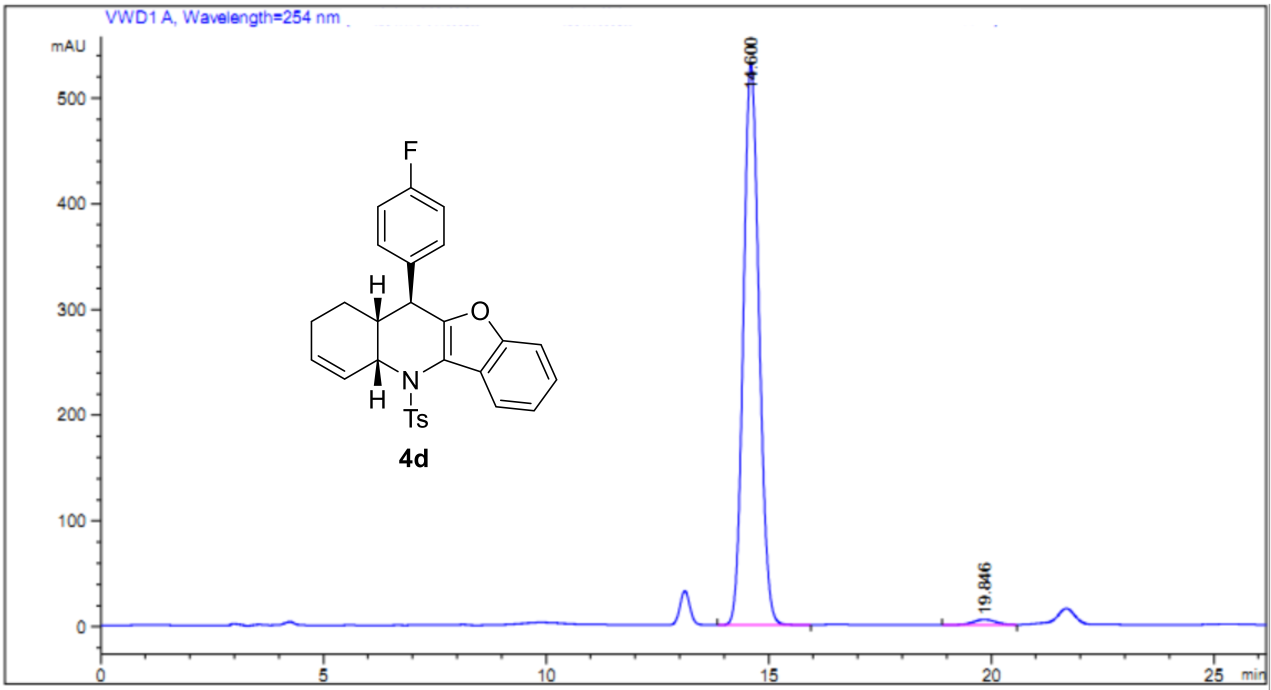
$^{13}C$ NMR (100 MHz, $CDCl_3$)


-115.131
F
H
O
N
H
Ts
4d
$^{19}$F NMR (375 MHz, $CDCl_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

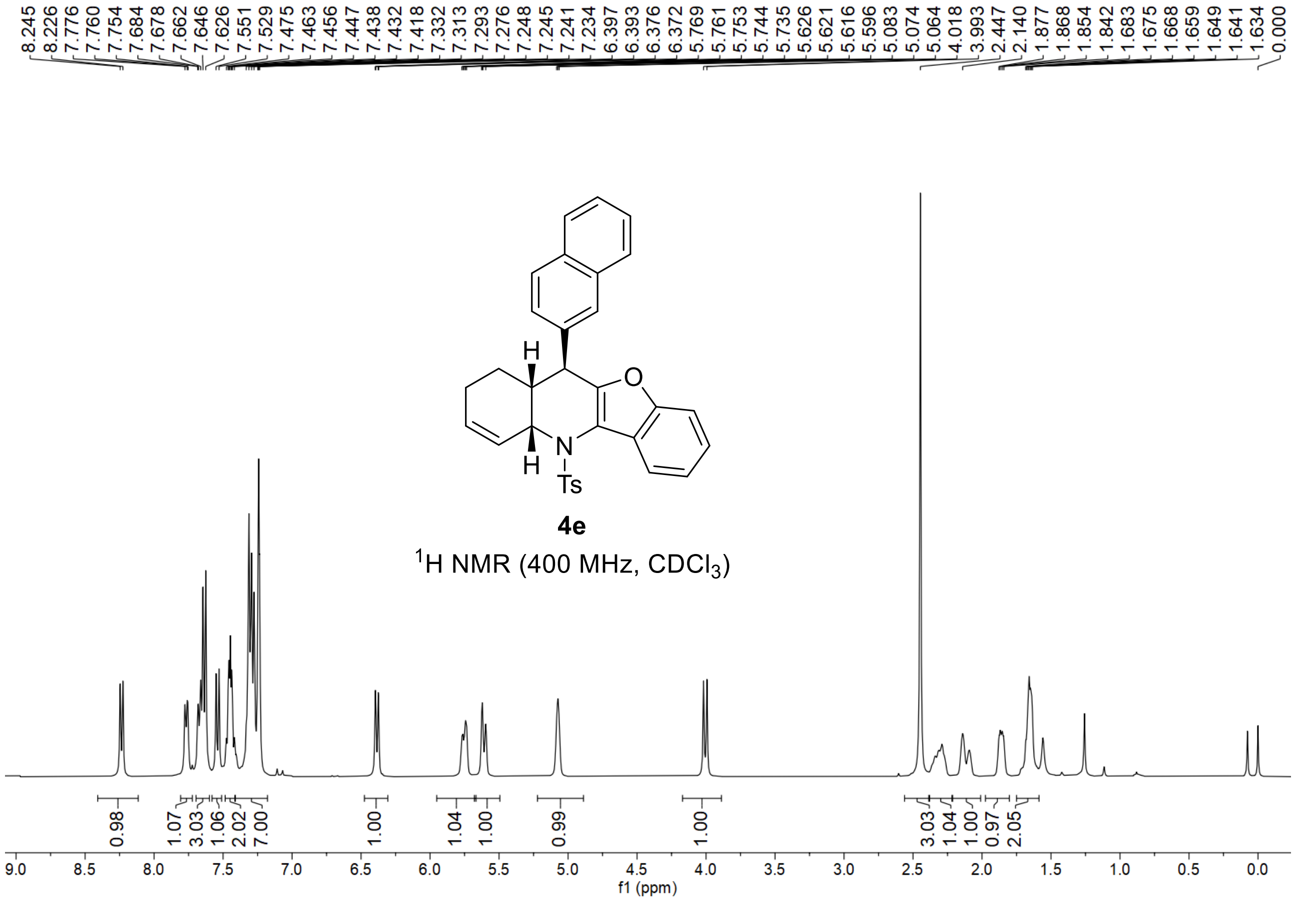

x10^4
+ESI Scan (rt: 0.468 min) Frag=175.0V
496.1359
F
H
O
N
H
Ts
4d
(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{28}H_{24}FNO_3SNa^+$ 496.1353
Counts vs. Mass-to-Charge (m/z)

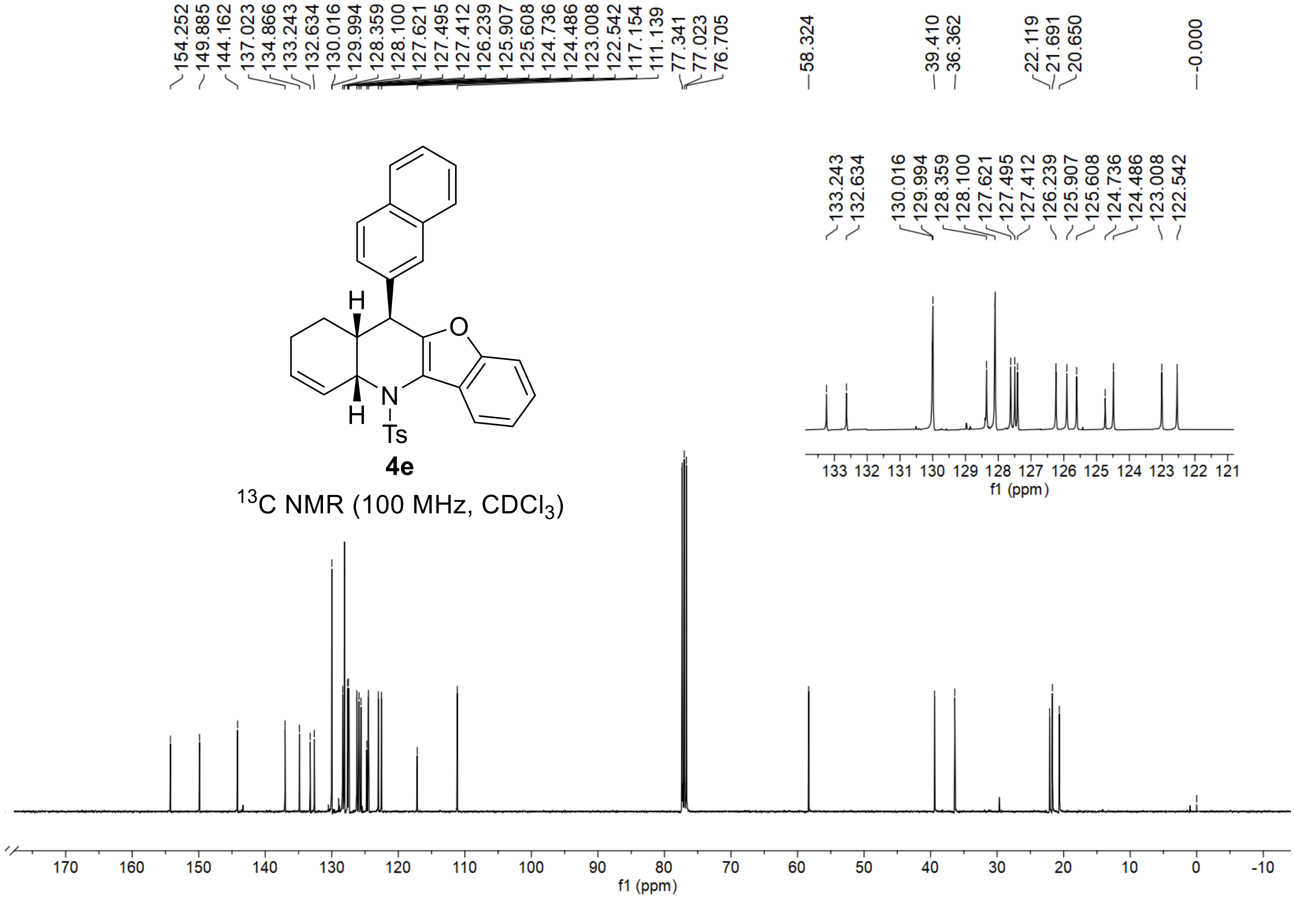


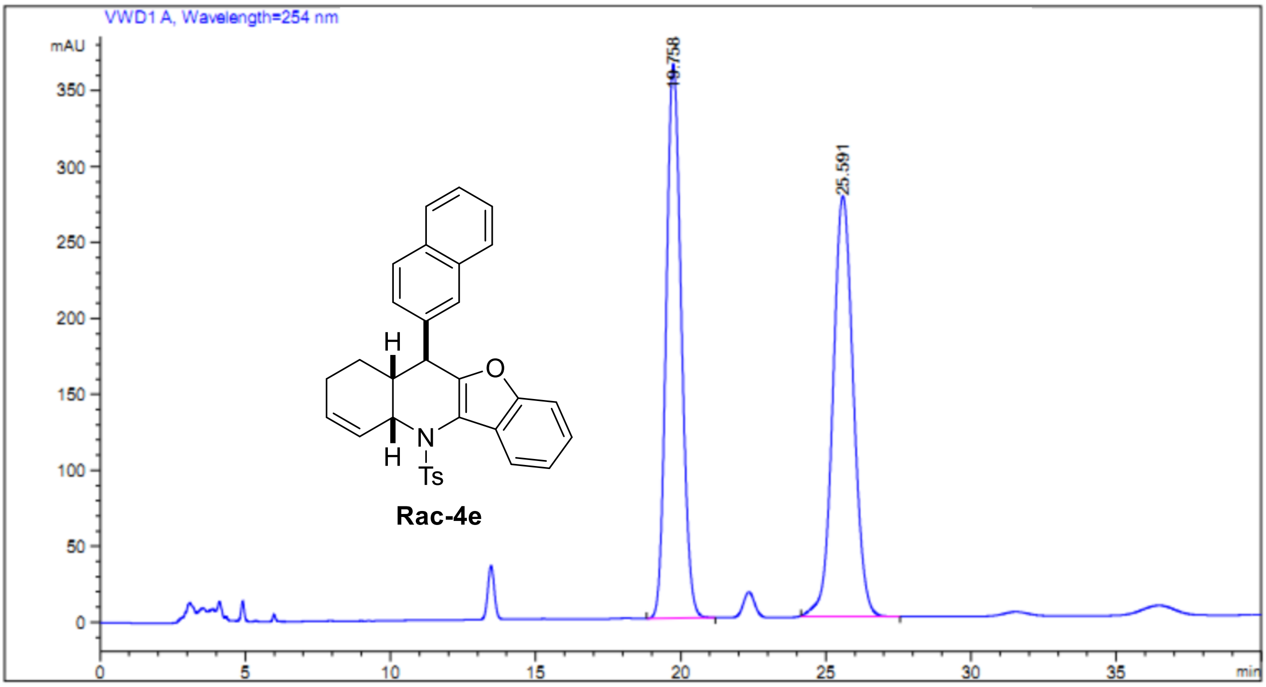

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.570 | BB | 0.3831 | 5466.55225 | 222.21568 | 49.2973 |
| 2 | 19.706 | BV | 0.5362 | 5622.40283 | 163.07292 | 50.7027 |



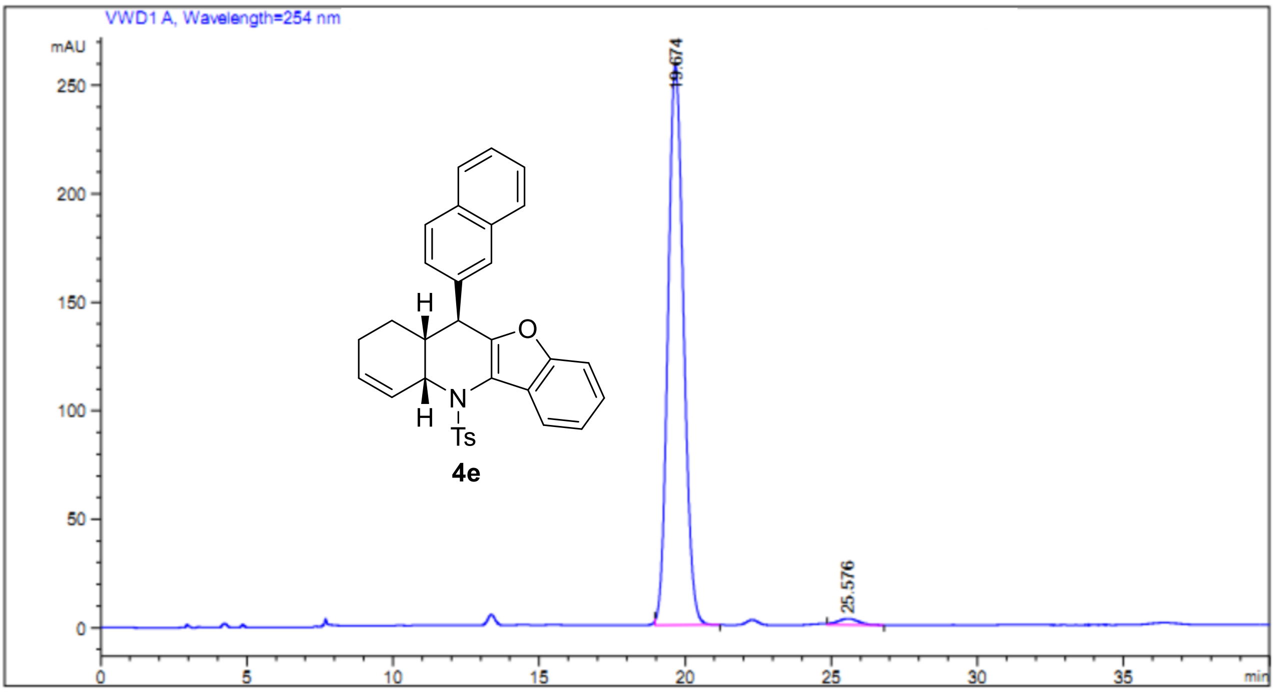

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.600 | BB | 0.3825 | 1.30177e4 | 530.24335 | 98.7264 |
| 2 | 19.846 | BB | 0.5215 | 167.93855 | 4.98060 | 1.2736 |


8.245
8.226
7.776
7.760
7.754
7.684
7.678
7.662
7.646
7.626
7.551
7.529
7.475
7.463
7.456
7.447
7.438
7.432
7.418
7.332
7.313
7.293
7.276
7.248
7.245
7.241
7.234
6.397
6.393
6.376
6.372
5.769
5.761
5.753
5.744
5.735
5.626
5.621
5.616
5.596
5.083
5.074
5.064
4.018
3.993
2.447
2.140
1.877
1.868
1.854
1.842
1.683
1.675
1.668
1.659
1.649
1.641
1.634
0.000
H
O
N
H
Ts
4e
¹H NMR (400 MHz, CDCl₃)
0.98
1.07
3.03
1.06
2.02
7.00
1.00
1.04
1.00
0.99
1.00
3.03
1.04
1.00
0.97
2.05
f1 (ppm)

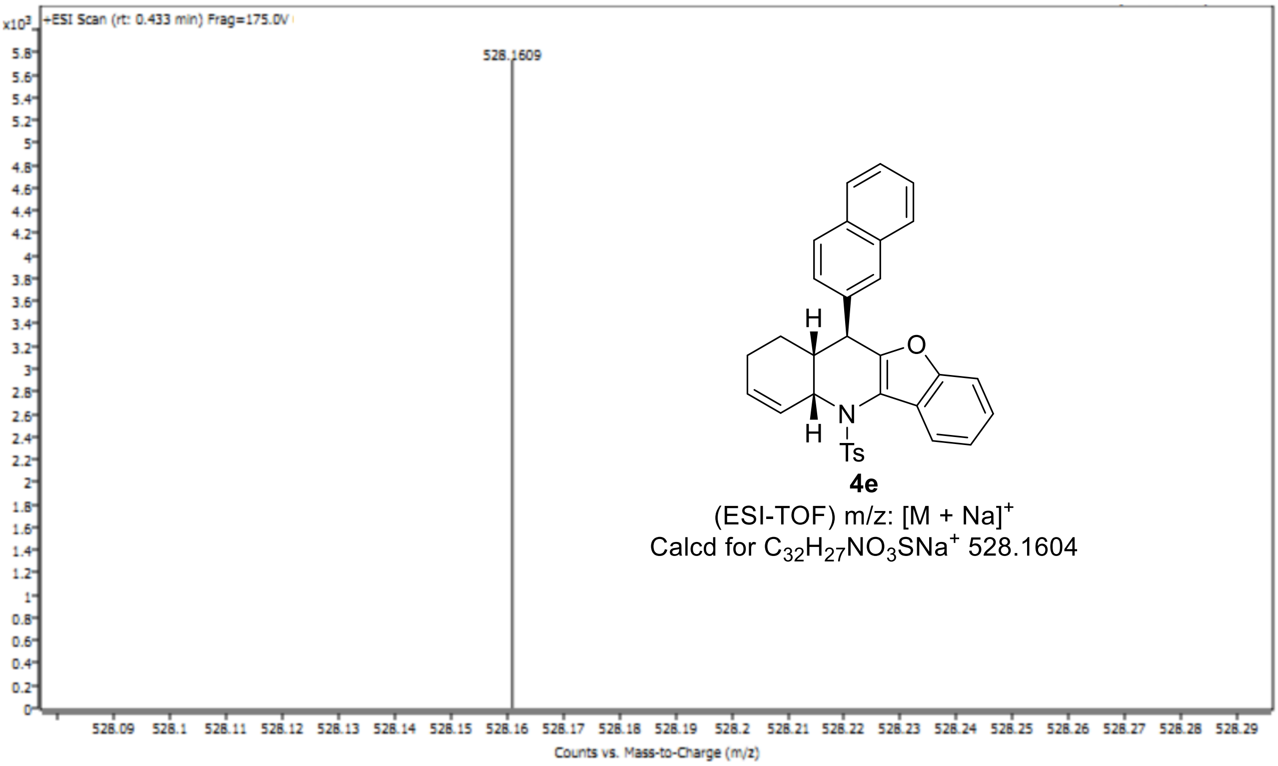

154.252
149.885
144.162
137.023
134.866
133.243
132.634
130.016
129.994
128.359
128.100
127.621
127.495
127.412
126.239
125.907
125.608
124.736
124.486
123.008
122.542
117.154
111.139
77.341
77.023
76.705
58.324
39.410
36.362
22.119
21.691
20.650
-0.000
H
O
N
H
Ts
4e
¹³C NMR (100 MHz, CDCl₃)
f1 (ppm)



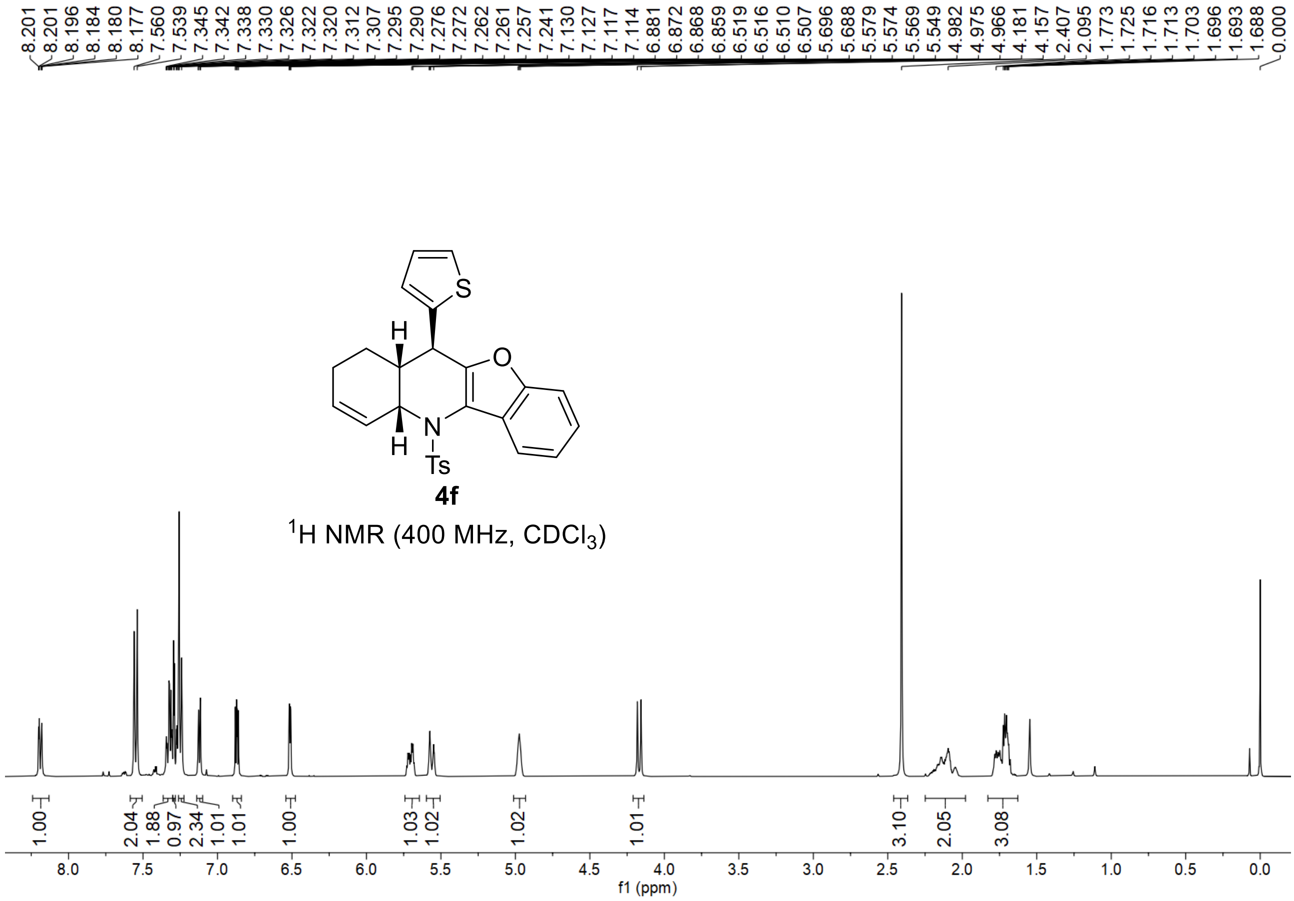

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 19.758 | BB | 0.6224 | 1.31983e4 | 353.13330 | 49.3258 |
| 2 | 25.591 | BB | 0.7636 | 1.35591e4 | 274.05035 | 50.6742 |




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 19.674 | BB | 0.6251 | 9551.05762 | 254.00978 | 98.5868 |
| 2 | 25.576 | BB | 0.7551 | 136.90572 | 2.80865 | 1.4132 |

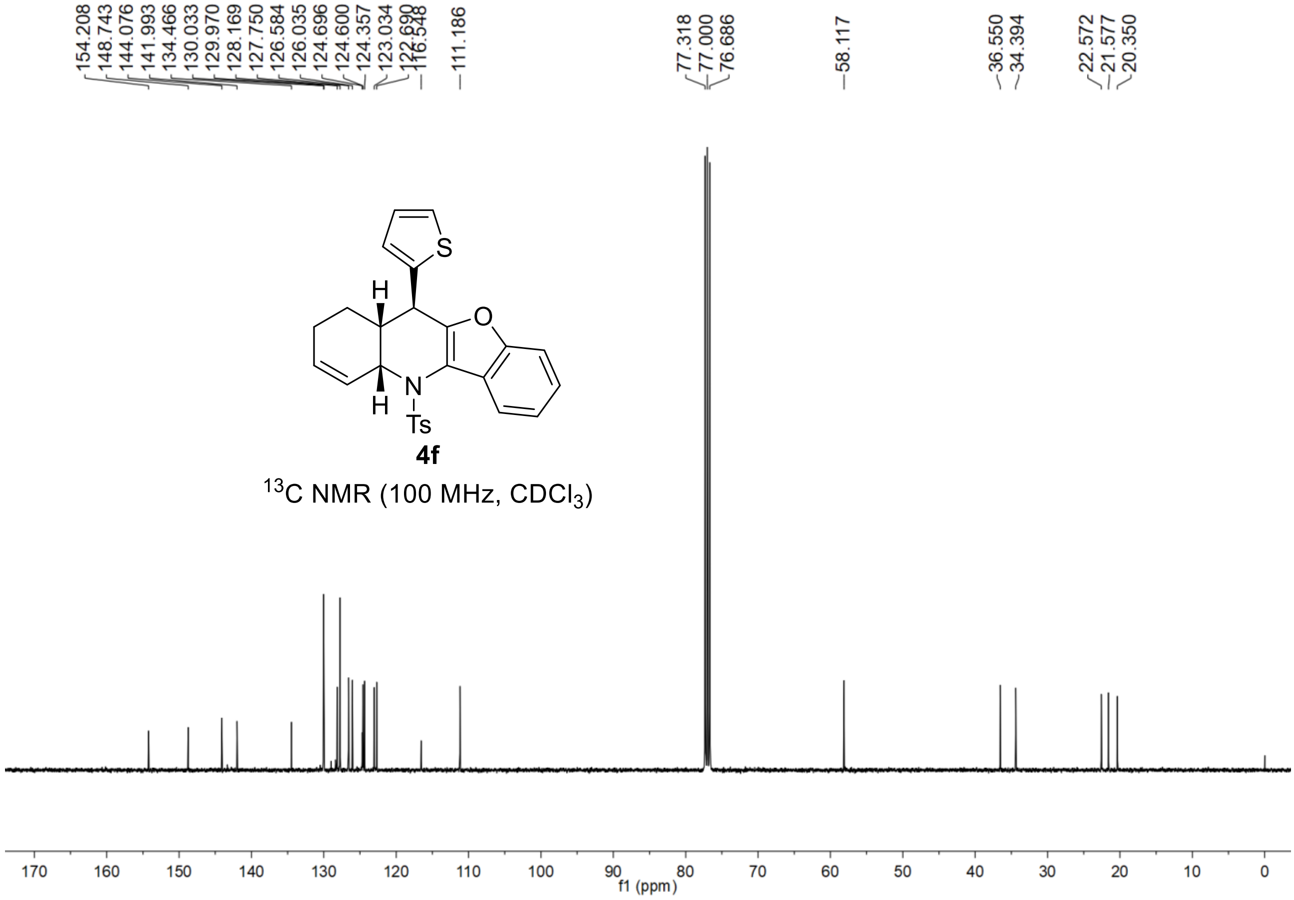


x10^3 +ESI Scan (rt: 0.433 min) Frag=175.0V
528.1609
Counts vs. Mass-to-Charge (m/z)
H
O
N
H
Ts
4e
(ESI-TOF) m/z: [M + Na]+
Calcd for $C_{32}H_{27}NO_3SNa^+$ 528.1604



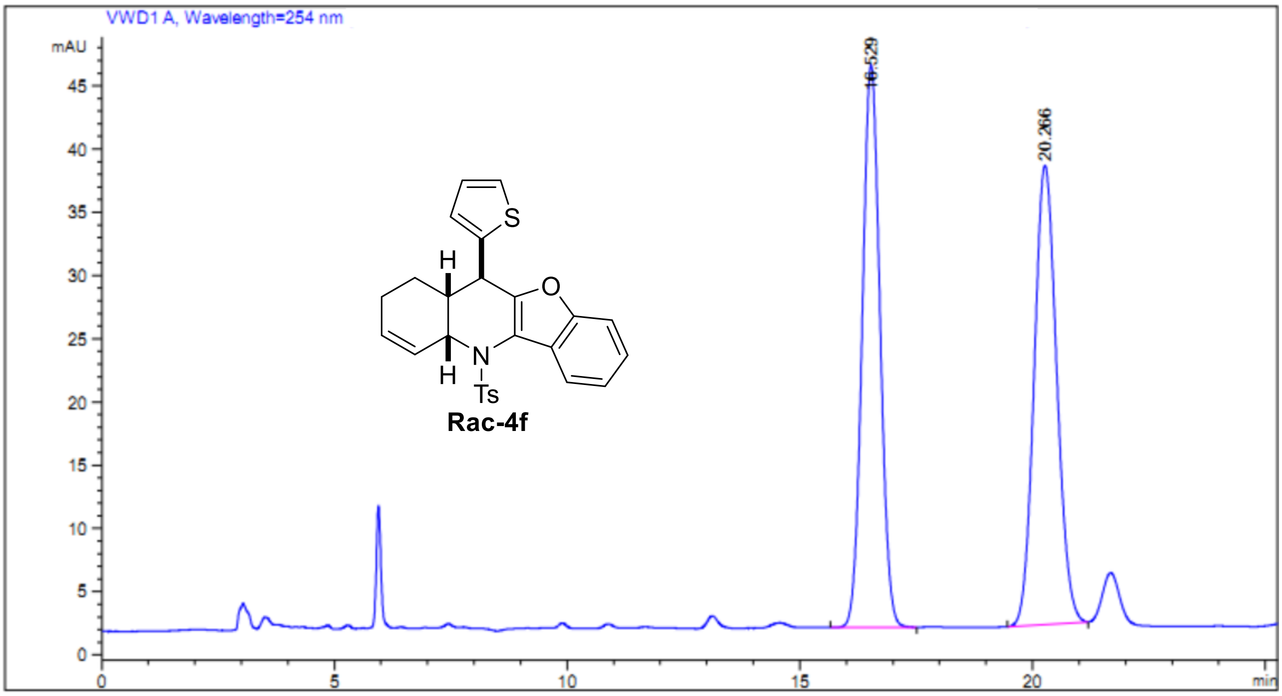

**4f**

$^1$H NMR (400 MHz, $CDCl_3$)

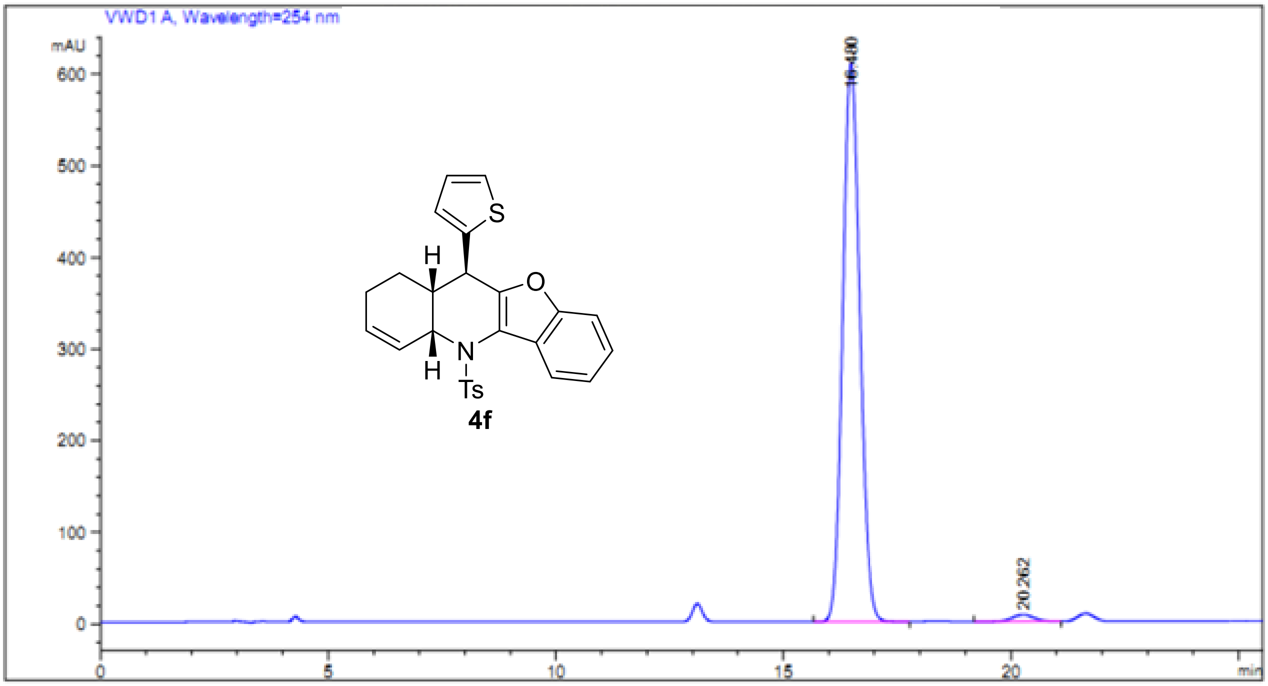



**4f**

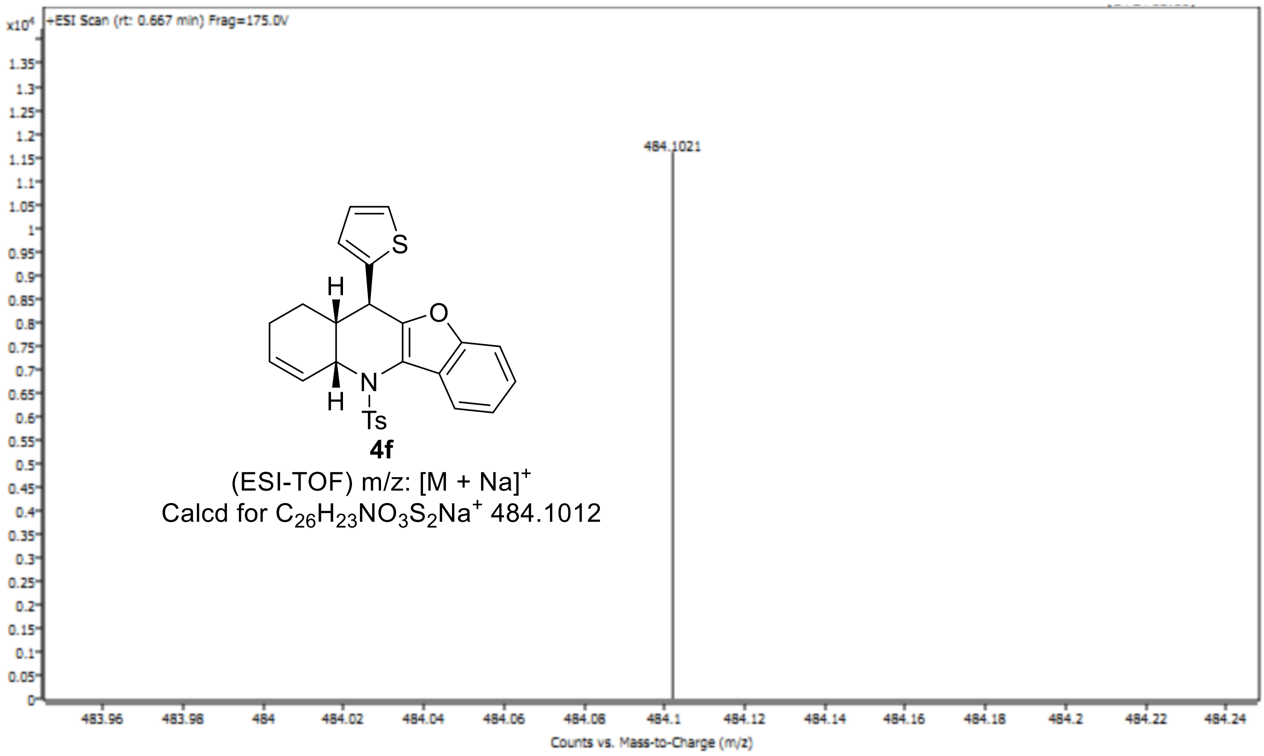
$^{13}$C NMR (100 MHz, $CDCl_3$)

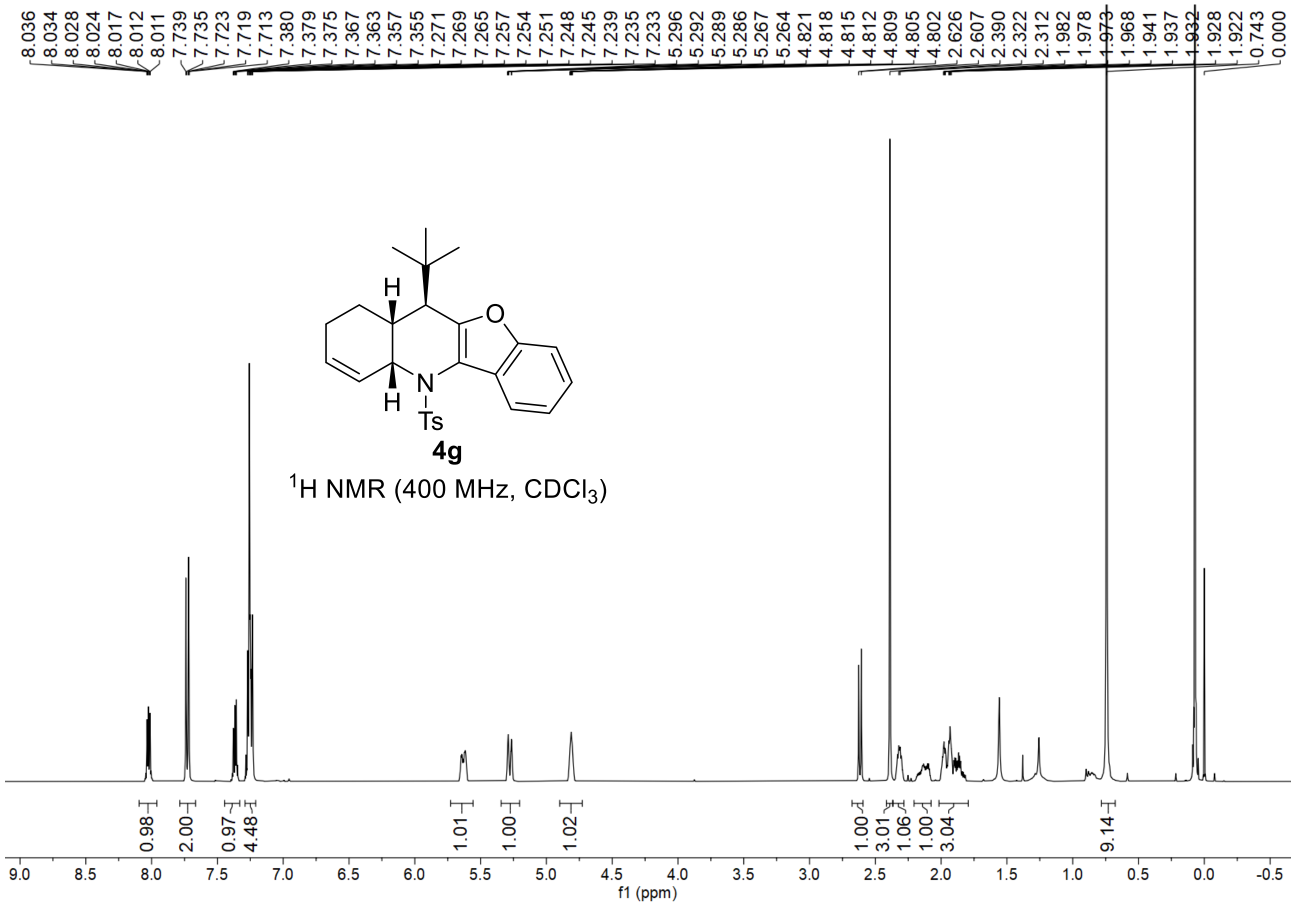


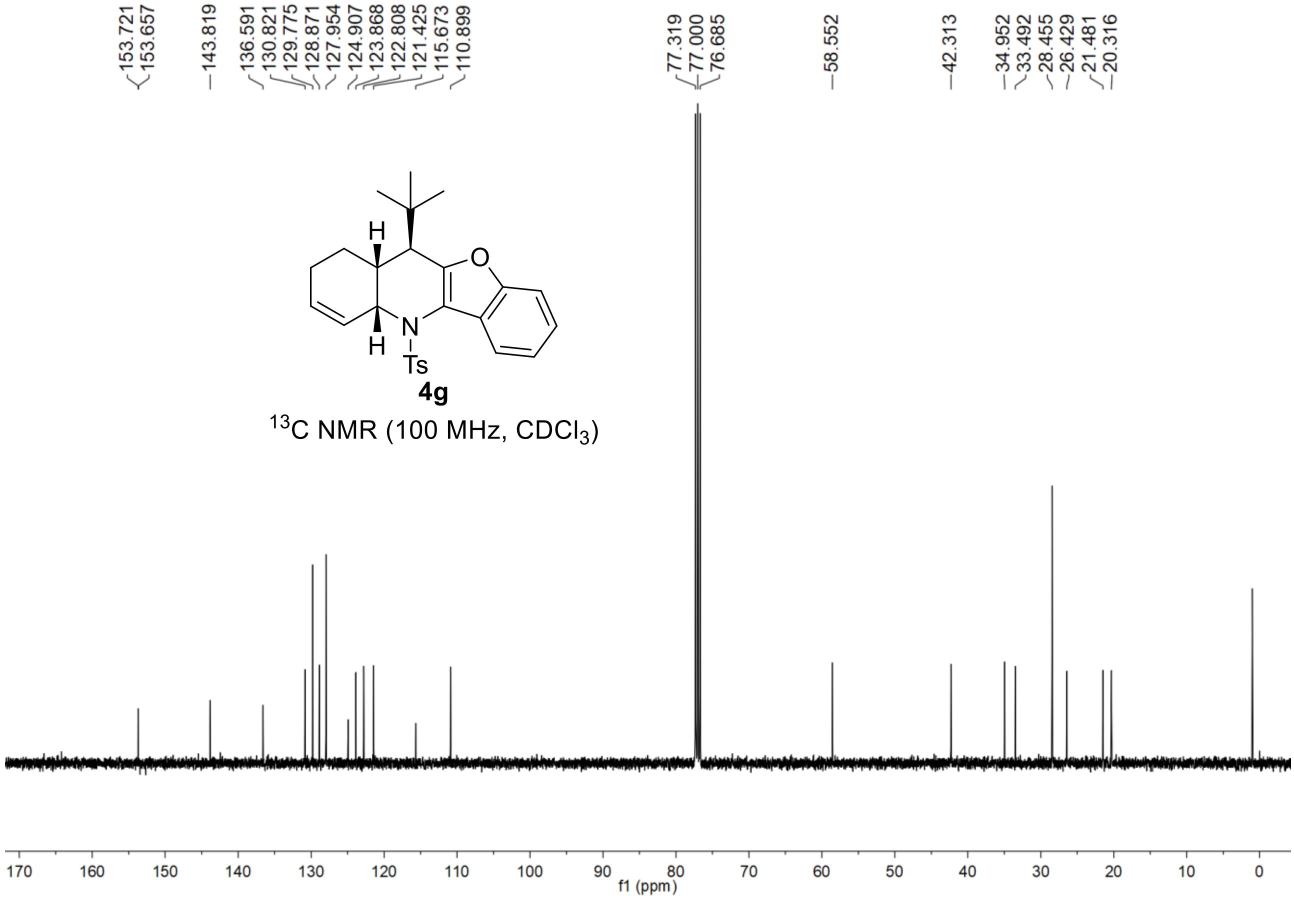

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 16.529 | BB | 0.4140 | 1178.56799 | 44.48122 | 49.1112 |
| 2 | 20.266 | BB | 0.5221 | 1221.22815 | 36.29995 | 50.8888 |

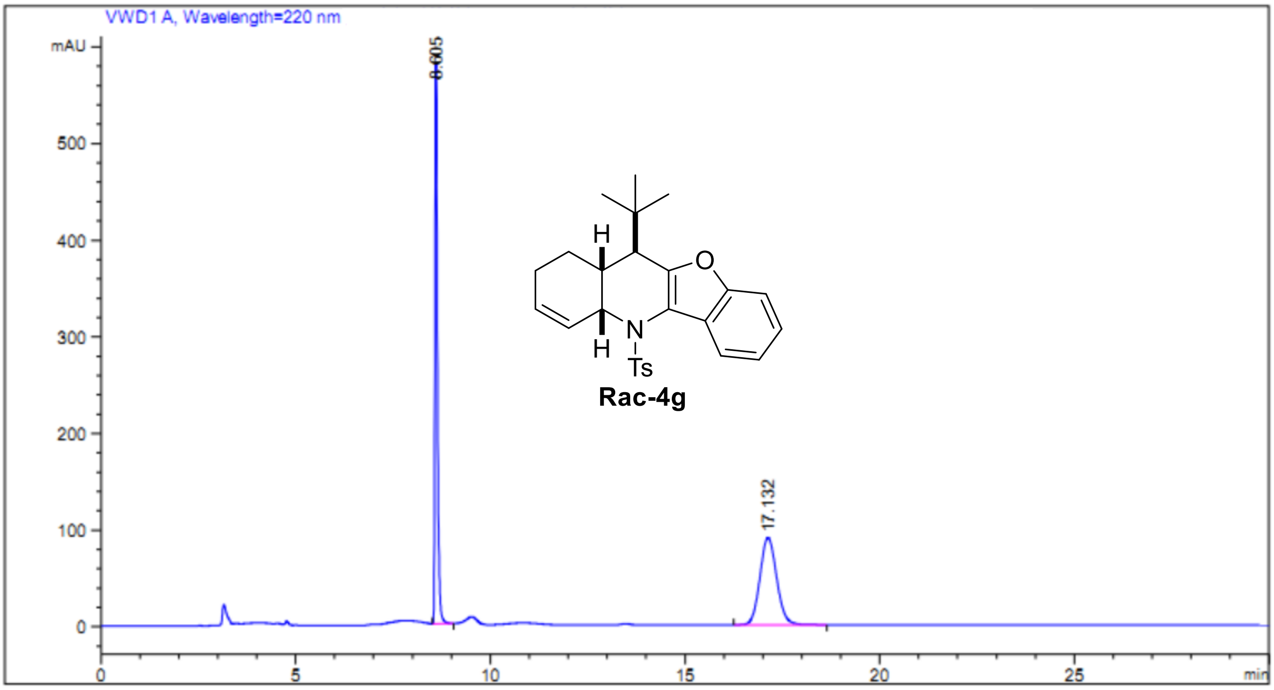



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 16.480 | BB | 0.4099 | 1.59952e4 | 608.75262 | 98.4334 |
| 2 | 20.262 | BB | 0.5349 | 254.57562 | 7.40803 | 1.5666 |

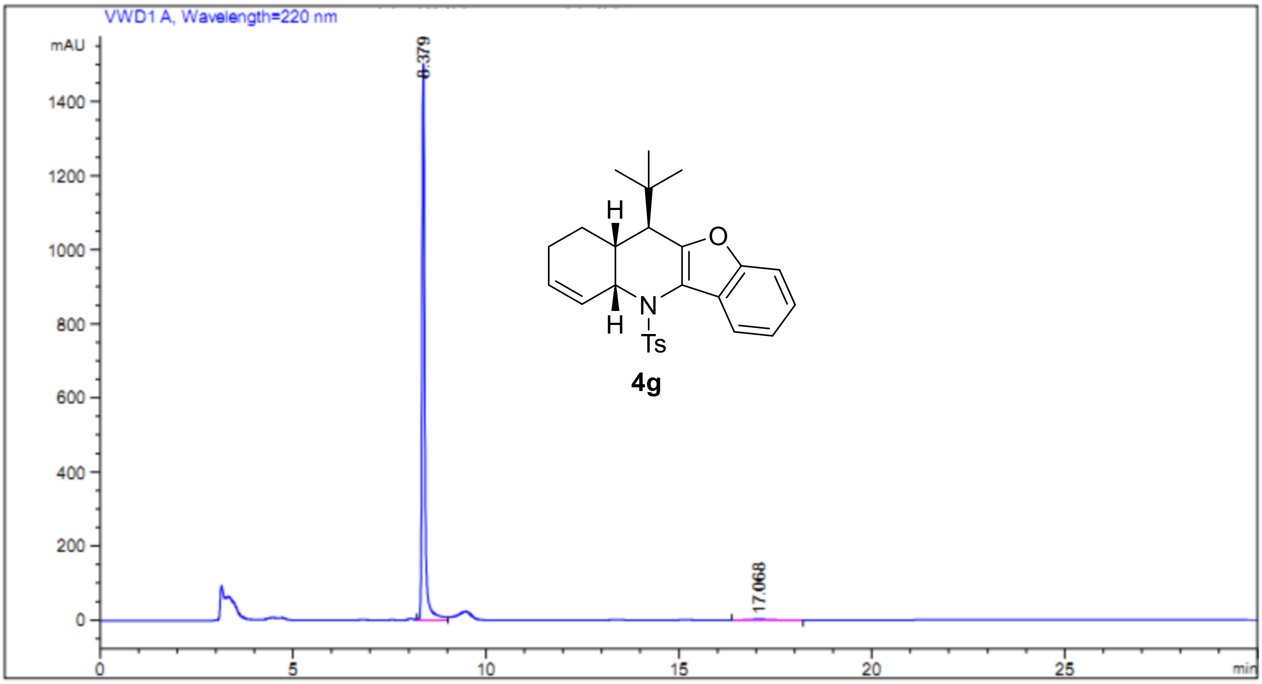

+ESI Scan (rt: 0.667 min) Frag=175.0V
x10^4
484.1021
S
H
O
N
H
Ts
4f
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H23NO3S2Na+ 484.1012
Counts vs. Mass-to-Charge (m/z)


8.036 8.034 8.028 8.024 8.017 8.012 8.011 7.739 7.735 7.723 7.719 7.713 7.380 7.379 7.375 7.367 7.363 7.357 7.355 7.271 7.269 7.265 7.257 7.254 7.251 7.248 7.245 7.239 7.235 7.233 5.296 5.292 5.289 5.286 5.267 5.264 4.821 4.818 4.815 4.812 4.809 4.805 4.802 2.626 2.607 2.390 2.322 2.312 1.982 1.978 1.973 1.968 1.941 1.937 1.932 1.928 1.922 0.743 0.000
H
O
N
H
Ts
4g
$^{1}$H NMR (400 MHz, CDCl$_3$)
0.98 2.00 0.97 4.48 1.01 1.00 1.02 1.00 3.01 1.06 1.00 3.04 9.14
f1 (ppm)

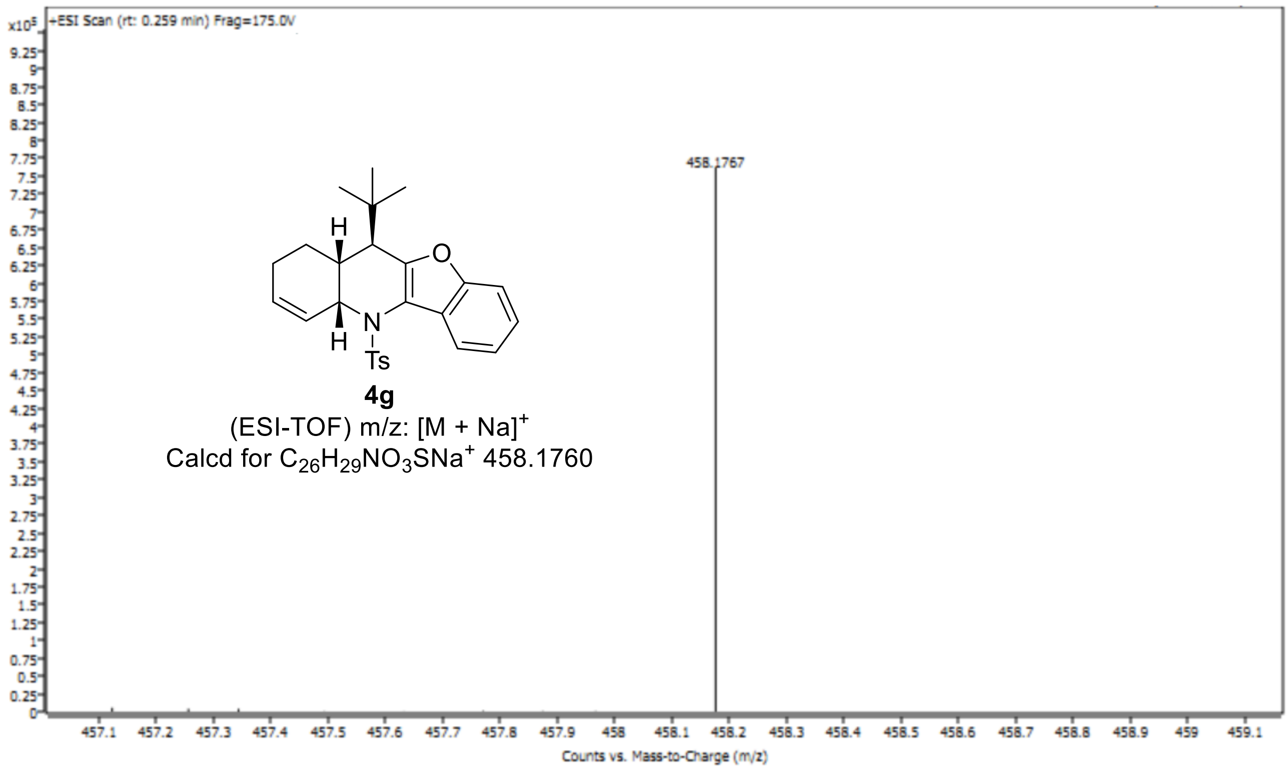

153.721 153.657 143.819 136.591 130.821 129.775 128.871 127.954 124.907 123.868 122.808 121.425 115.673 110.899 77.319 77.000 76.685 58.552 42.313 34.952 33.492 28.455 26.429 21.481 20.316
H
O
N
H
Ts
4g
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



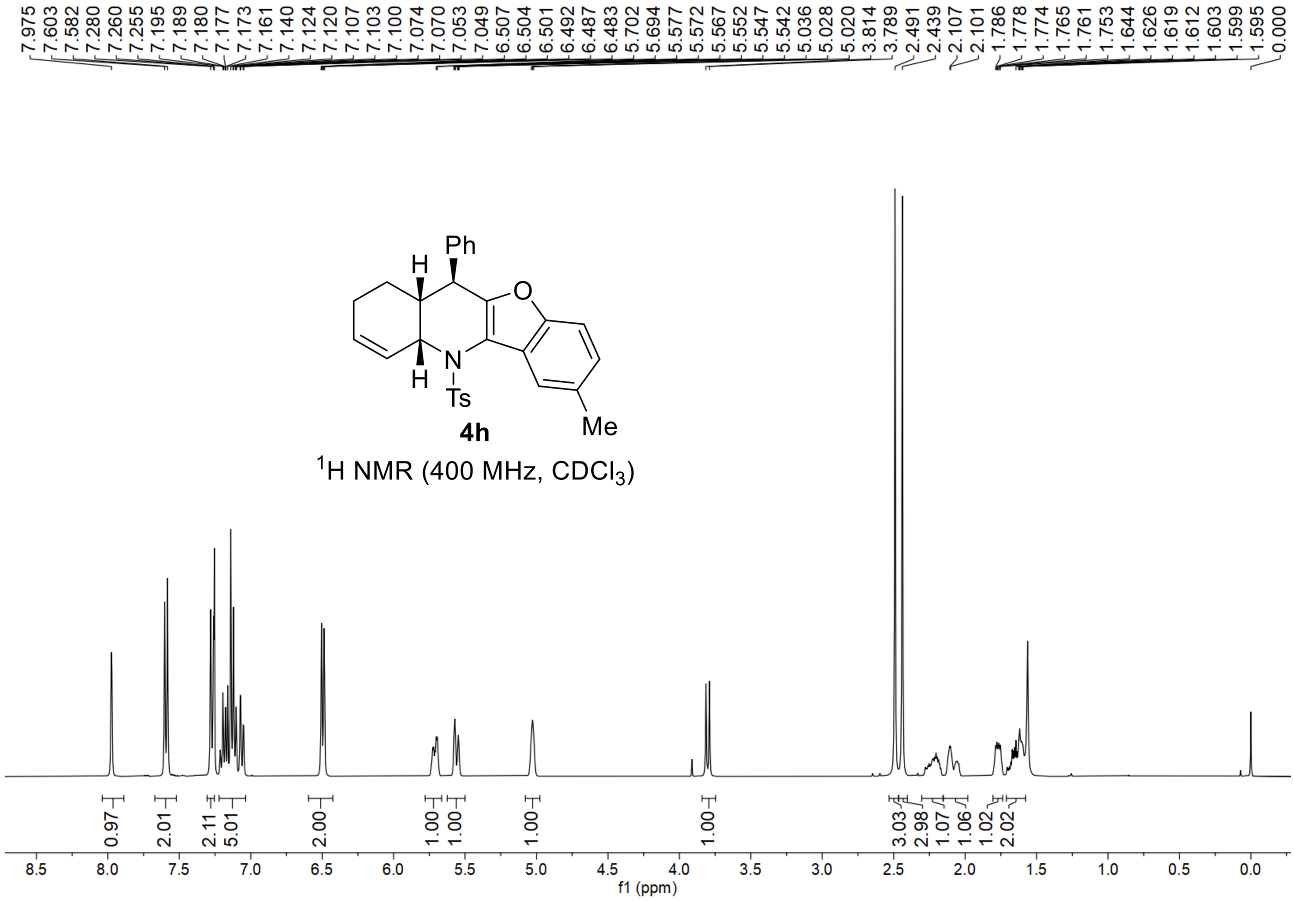

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.605 | BB | 0.0653 | 2517.97241 | 579.26654 | 48.3107 |
| 2 | 17.132 | BB | 0.4630 | 2694.06689 | 90.33281 | 51.6893 |

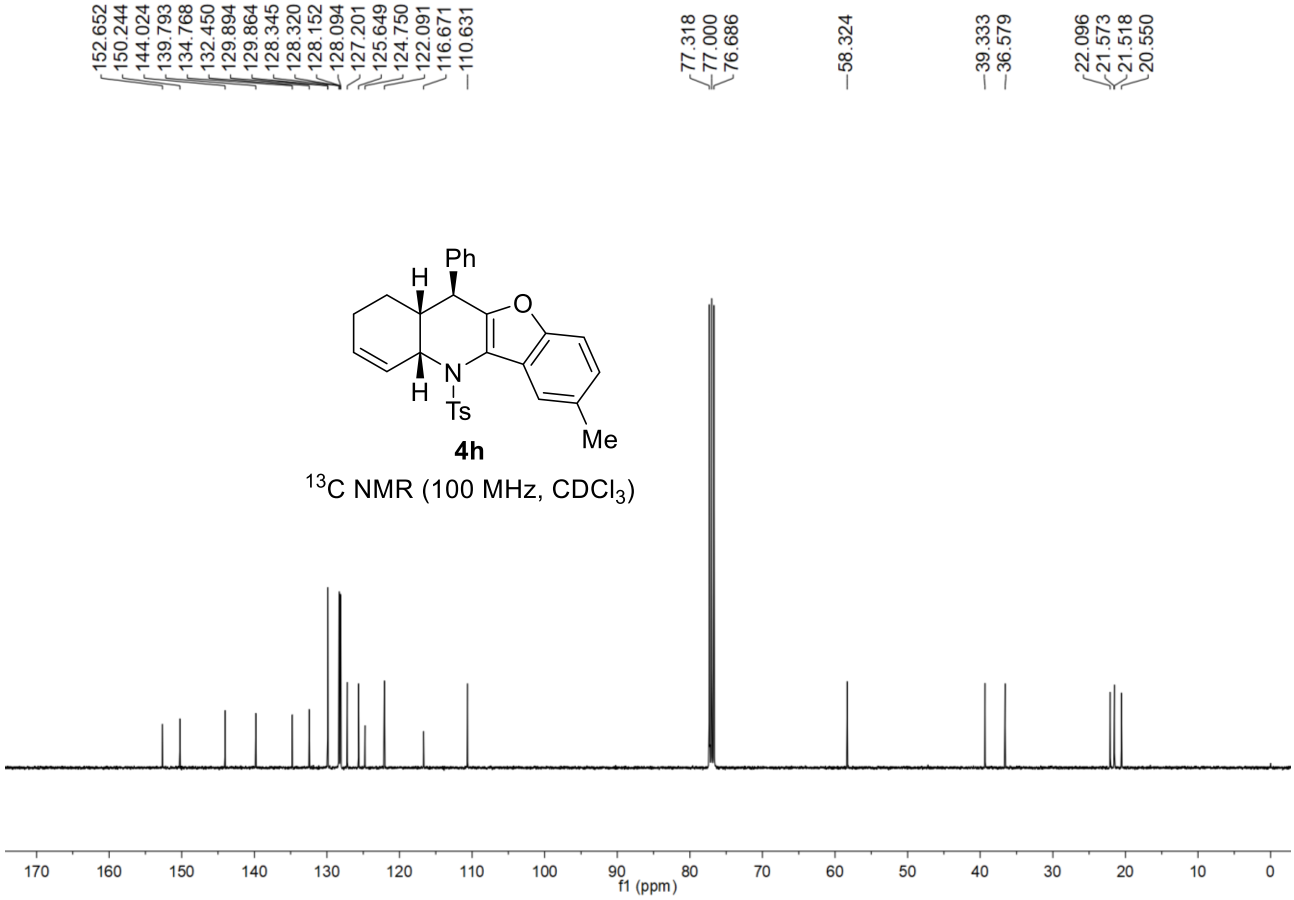


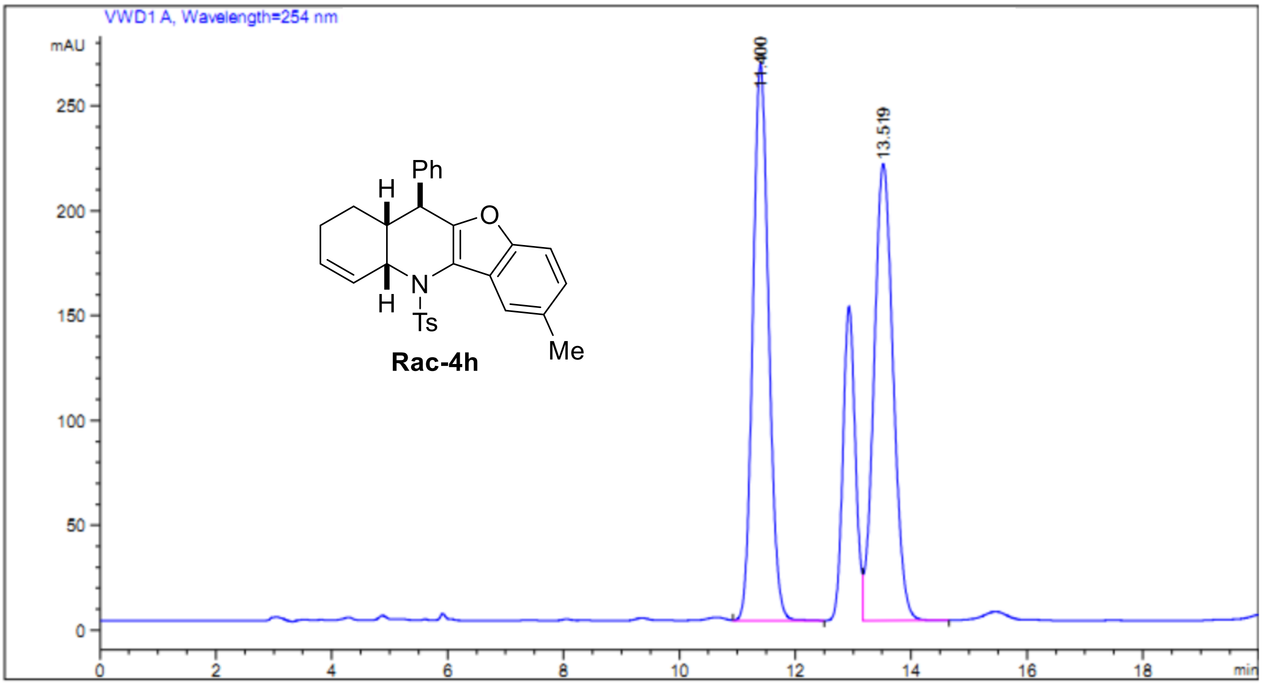

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.379 | VV | 0.0730 | 7358.41504 | 1505.52246 | 99.1065 |
| 2 | 17.068 | BB | 0.4730 | 66.34195 | 2.06153 | 0.8935 |



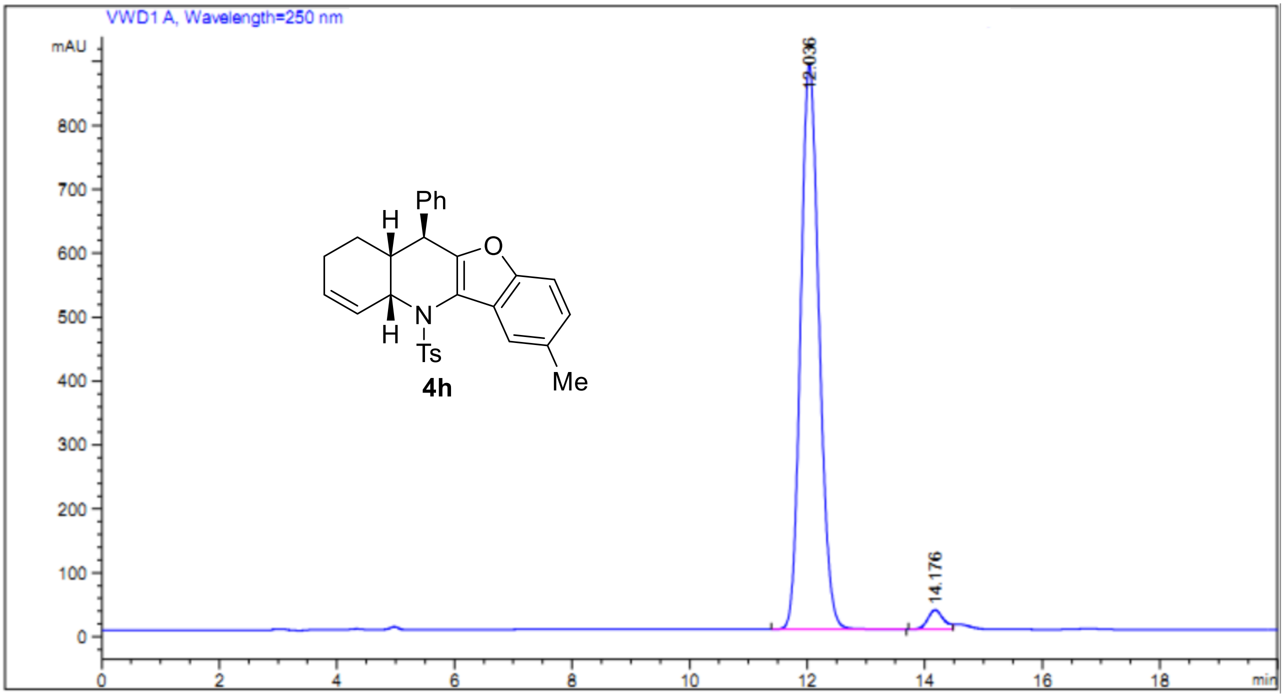
x10^5
+ESI Scan (rt: 0.259 min) Frag=175.0V
458.1767
H
H
N
Ts
O
4g
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H29NO3SNa+ 458.1760
Counts vs. Mass-to-Charge (m/z)


7.975 7.603 7.582 7.280 7.260 7.255 7.195 7.189 7.180 7.177 7.173 7.161 7.140 7.124 7.120 7.107 7.103 7.100 7.074 7.070 7.053 7.049 6.507 6.504 6.501 6.492 6.487 6.483 5.702 5.694 5.577 5.572 5.567 5.552 5.547 5.542 5.036 5.028 5.020 3.814 3.789 2.491 2.439 2.107 2.101 1.786 1.778 1.774 1.765 1.761 1.753 1.644 1.626 1.619 1.612 1.603 1.599 1.595 0.000
Ph
H
O
N
H
Ts
Me
4h
$^{1}$H NMR (400 MHz, $CDCl_3$)
0.97 2.01 2.11 5.01 2.00 1.00 1.00 1.00 1.00 3.03 2.98 1.07 1.06 1.02 2.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

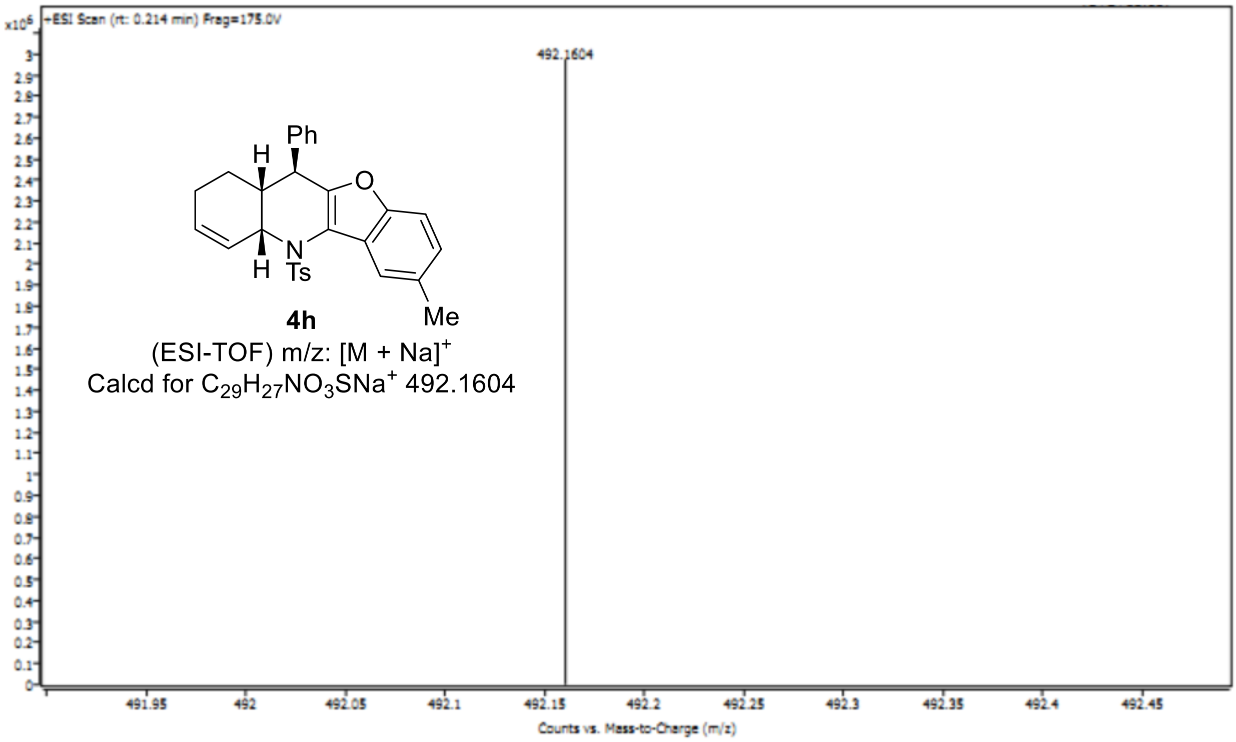

152.652 150.244 144.024 139.793 134.768 132.450 129.894 129.864 128.345 128.320 128.152 128.094 127.201 125.649 124.750 122.091 116.671 110.631
77.318 77.000 76.686
58.324
39.333 36.579
22.096 21.573 21.518 20.550
Ph
H
O
N
H
Ts
Me
4h
$^{13}$C NMR (100 MHz, $CDCl_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

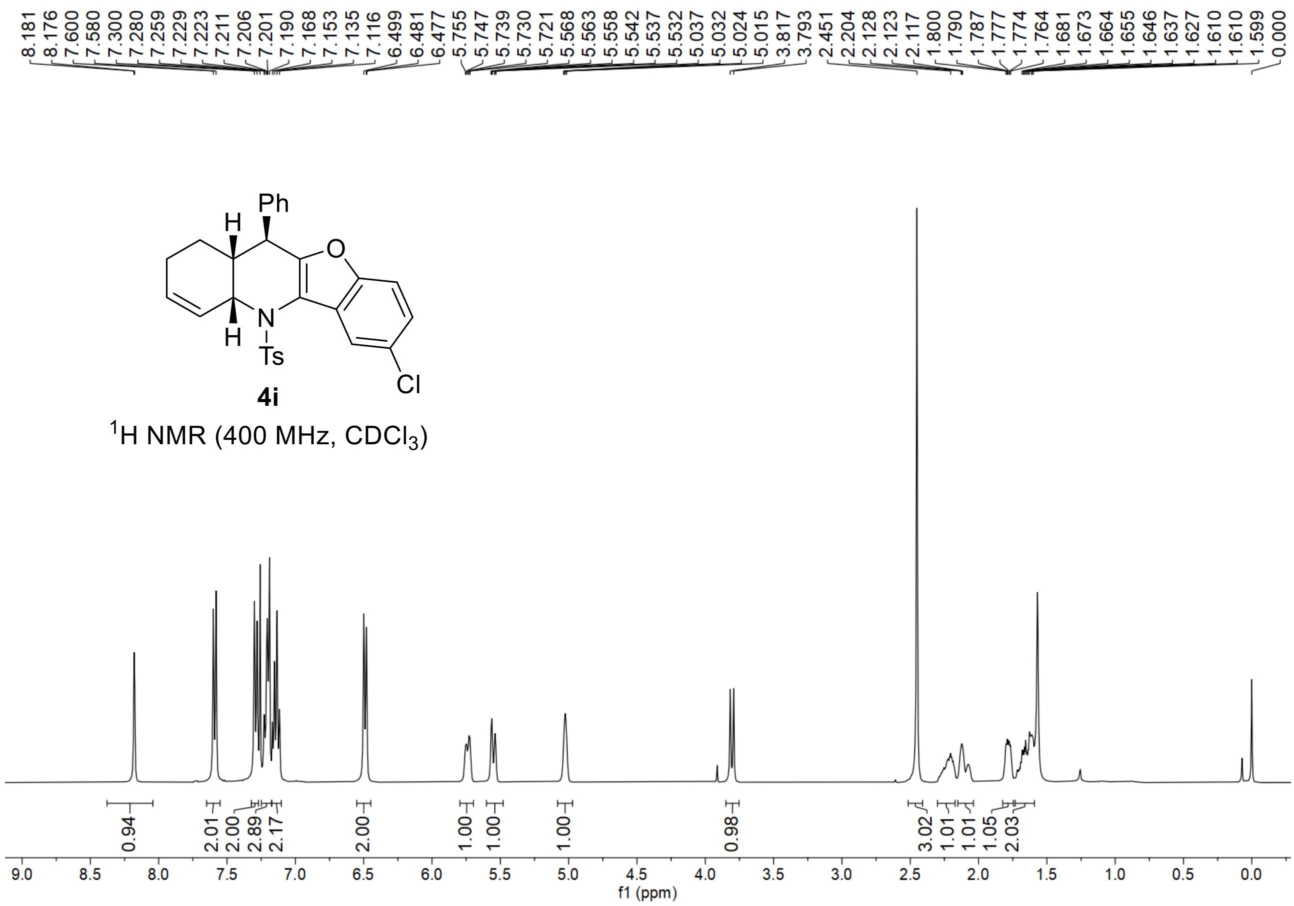


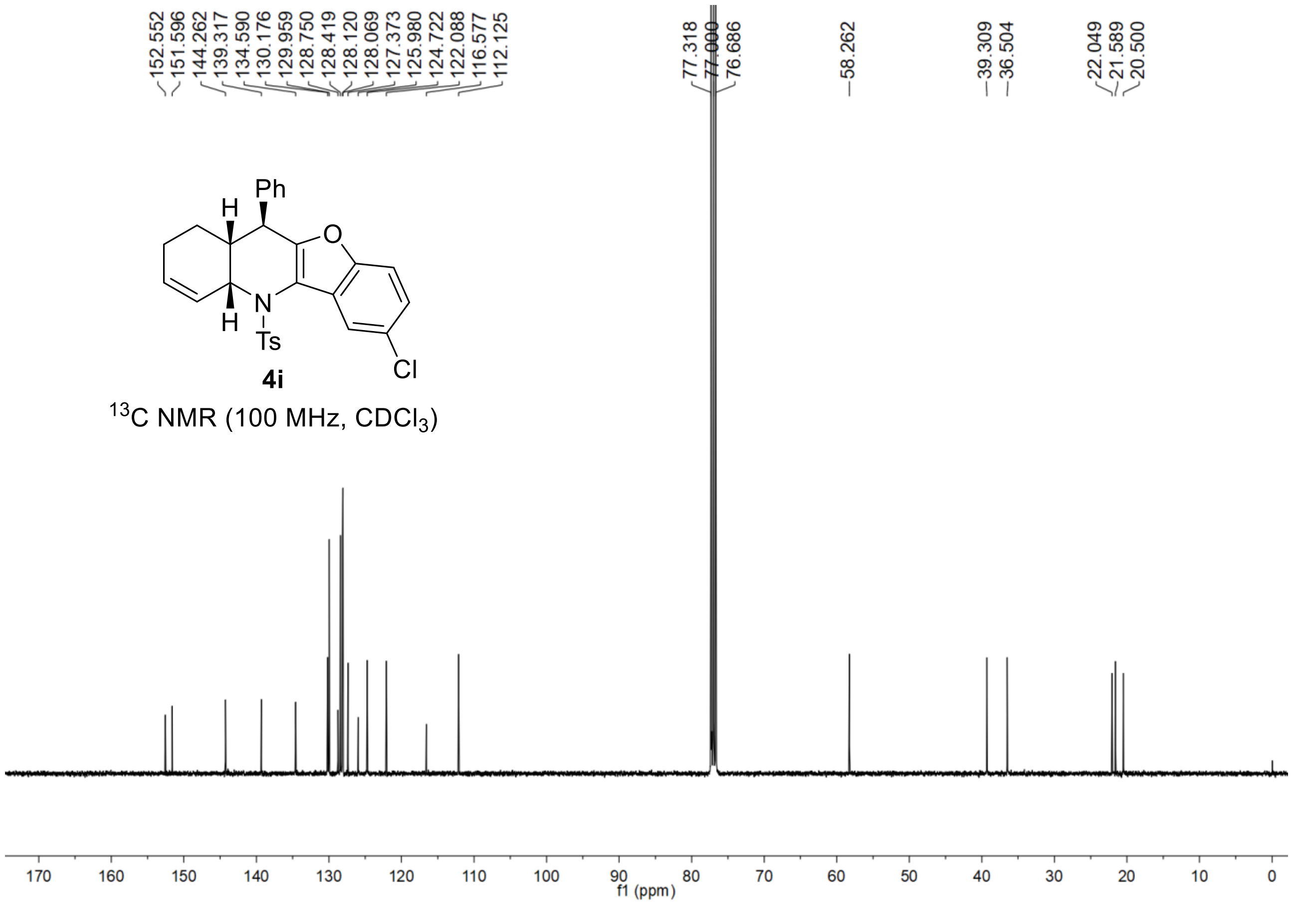

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 11.400 | VB | 0.2955 | 5037.05176 | 265.62692 | 50.1354 |
| 2 | 13.519 | VB | 0.3571 | 5009.85352 | 217.86008 | 49.8646 |

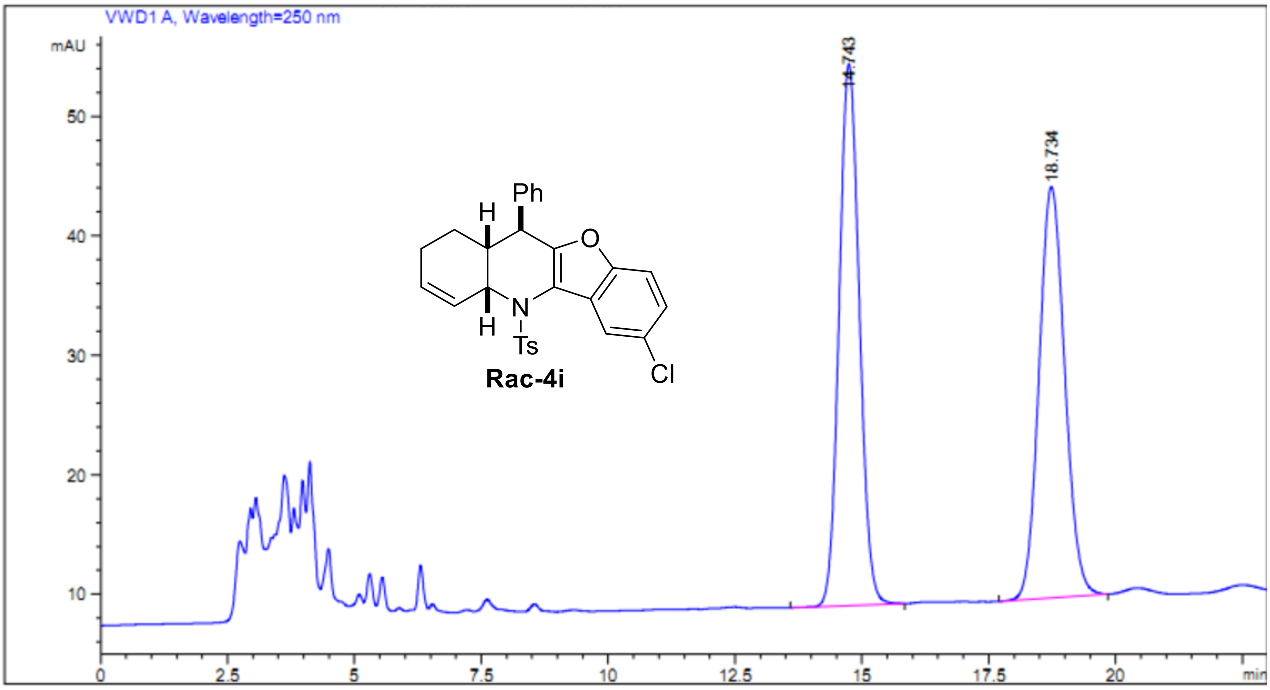



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.036 | BB | 0.3401 | 1.92412e4 | 883.25452 | 97.1641 |
| 2 | 14.176 | BV | 0.2834 | 561.59491 | 30.07371 | 2.8359 |

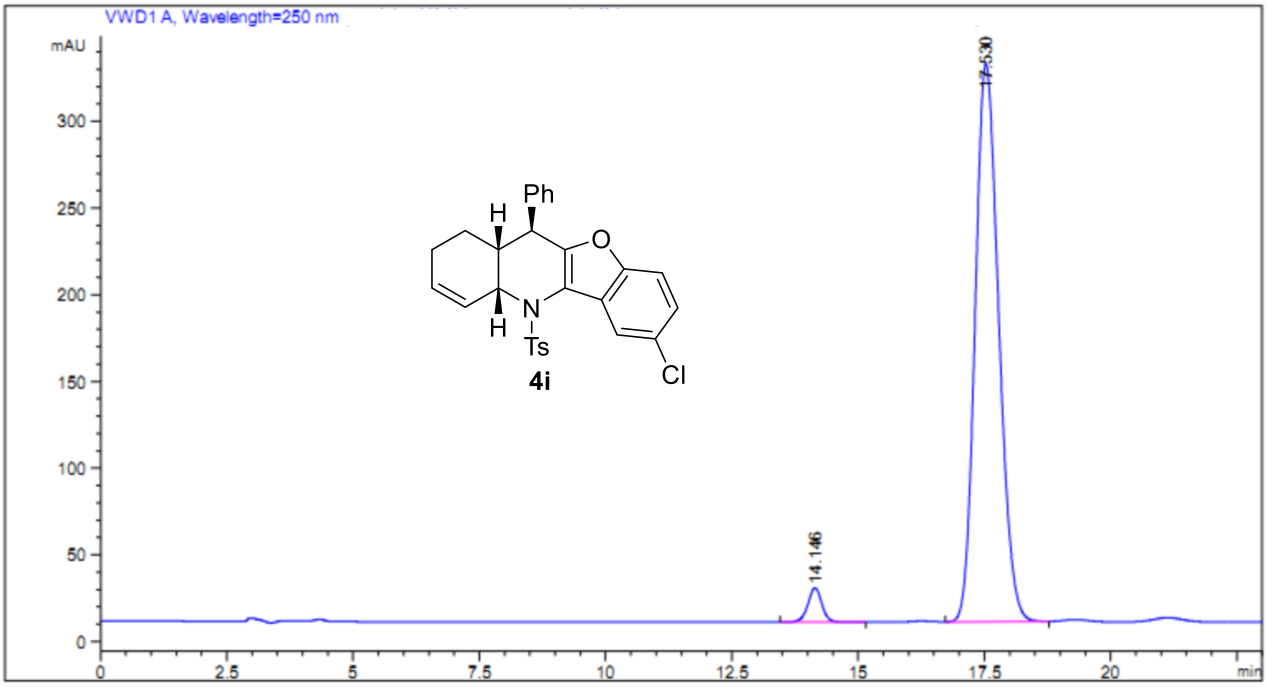

x10^6
+ESI Scan (rt: 0.214 min) Frag=175.0V
492.1604
Ph
H
O
N
H
Ts
Me
4h
(ESI-TOF) m/z: [M + Na]+
Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604
Counts vs. Mass-to-Charge (m/z)


8.181 8.176 7.600 7.580 7.300 7.280 7.259 7.229 7.223 7.211 7.206 7.201 7.190 7.168 7.153 7.135 7.116 6.499 6.481 6.477 5.755 5.747 5.739 5.730 5.721 5.568 5.563 5.558 5.542 5.537 5.532 5.037 5.032 5.024 5.015 3.817 3.793 2.451 2.204 2.128 2.123 2.117 1.800 1.790 1.787 1.777 1.774 1.764 1.681 1.673 1.664 1.655 1.646 1.637 1.627 1.610 1.610 1.599 0.000
Ph
H
O
N
H
Ts
Cl
4i
$^1$H NMR (400 MHz, CDCl$_3$)
0.94
2.01
2.00
2.89
2.17
2.00
1.00
1.00
1.00
0.98
3.02
1.01
1.01
1.05
2.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

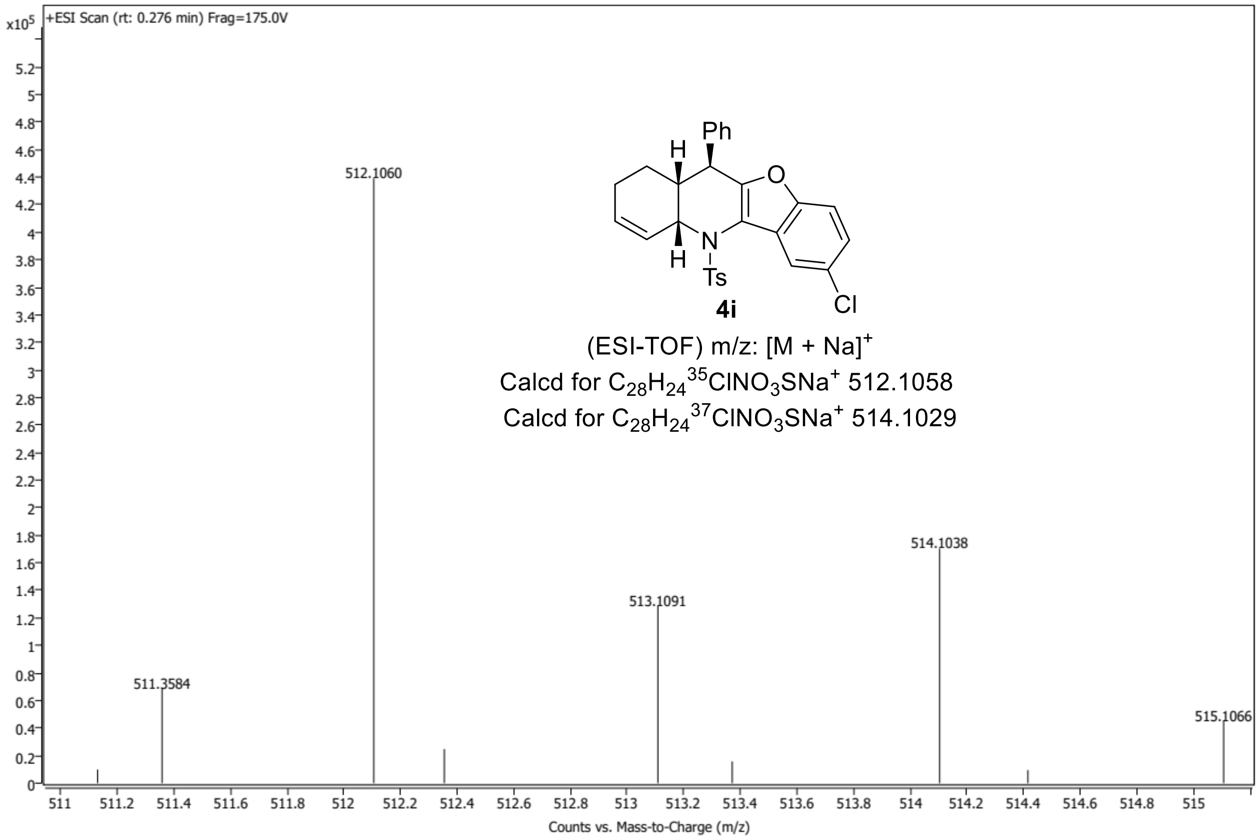

152.552 151.596 144.262 139.317 134.590 130.176 129.959 128.750 128.419 128.120 128.069 127.373 125.980 124.722 122.088 116.577 112.125
77.318 77.000 76.686
58.262
39.309 36.504
22.049 21.589 20.500
Ph
H
O
N
H
Ts
Cl
4i
$^{13}$C NMR (100 MHz, CDCl$_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

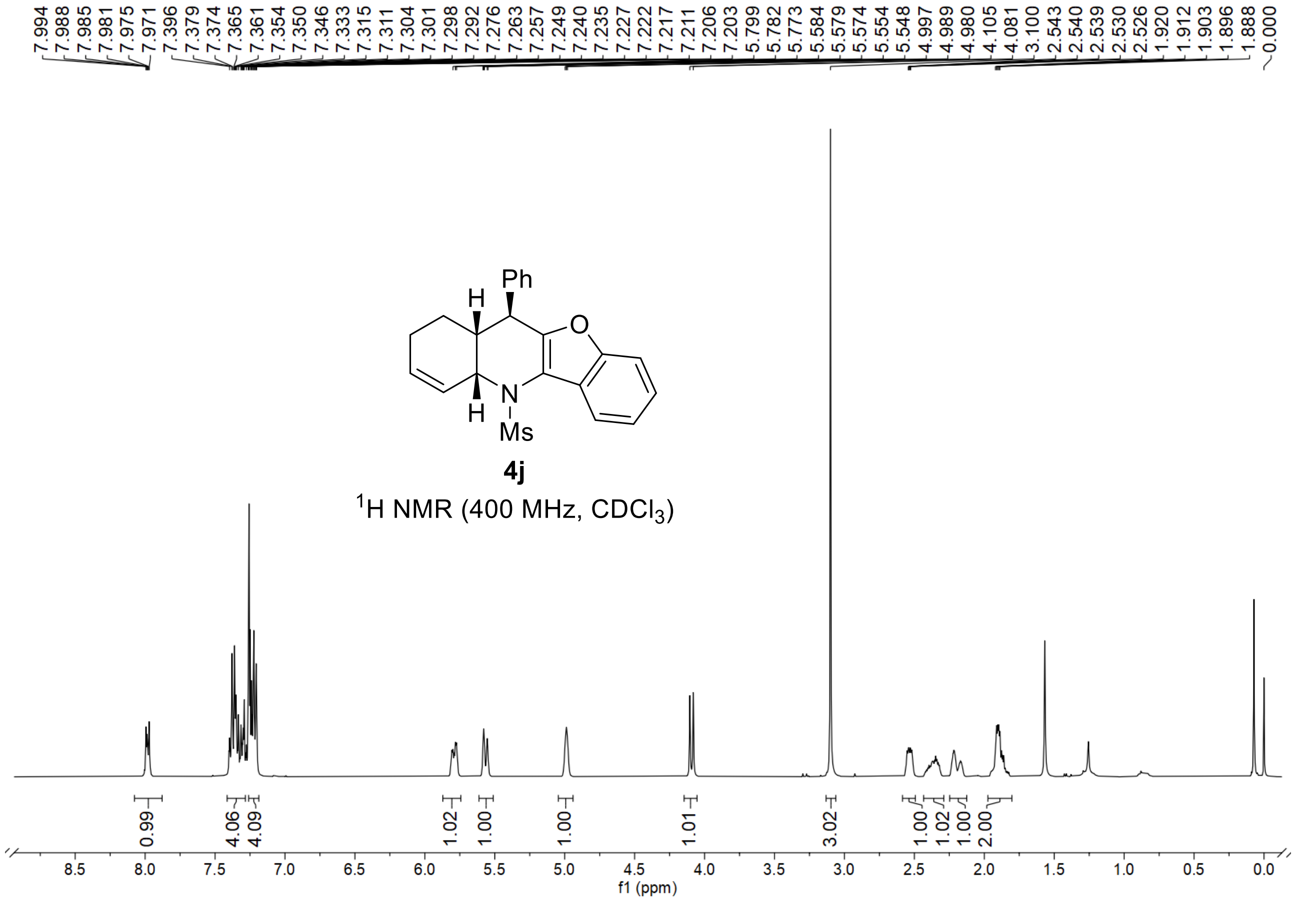


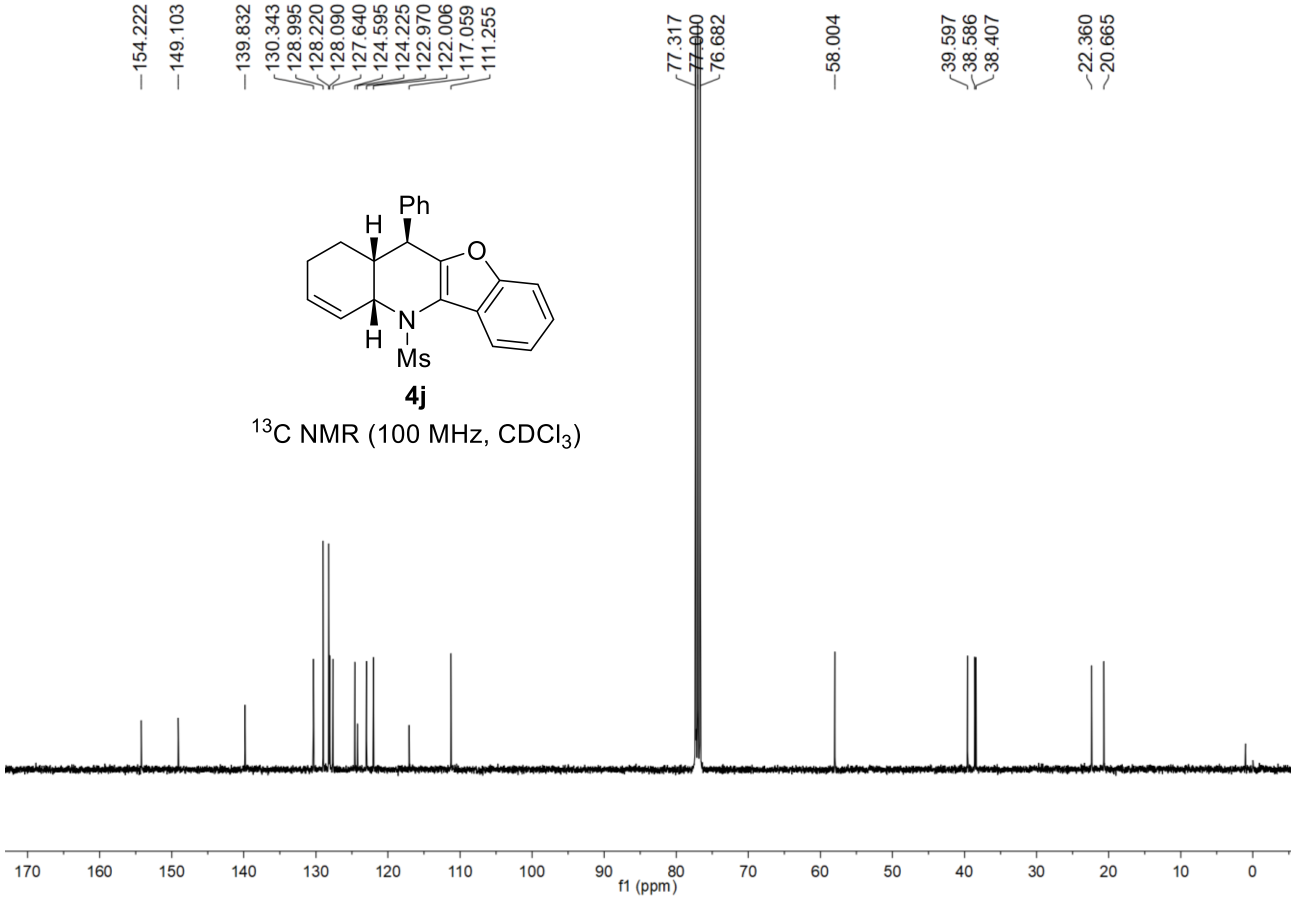

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.743 | BB | 0.4342 | 1257.26282 | 45.33516 | 50.8213 |
| 2 | 18.734 | BB | 0.5536 | 1216.62671 | 34.42382 | 49.1787 |

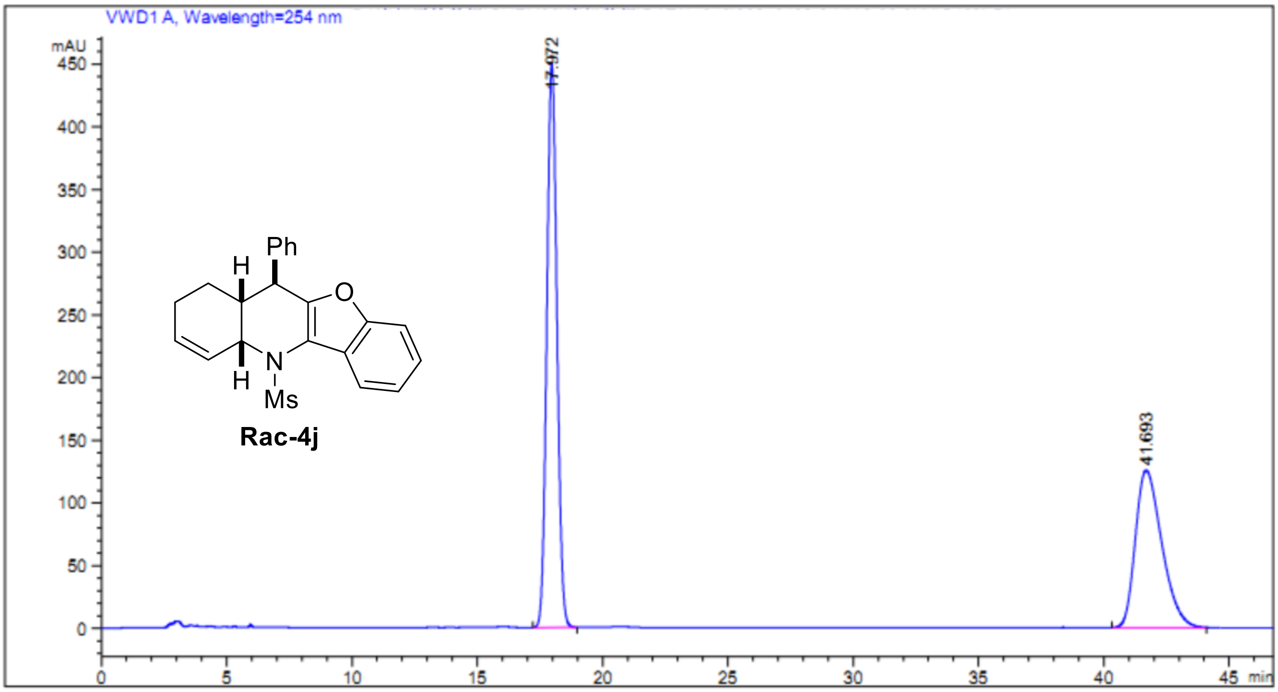



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 14.146 | BB | 0.2951 | 381.65308 | 19.77401 | 3.5419 |
| 2 | 17.530 | BB | 0.5035 | 1.03937e4 | 321.75018 | 96.4581 |

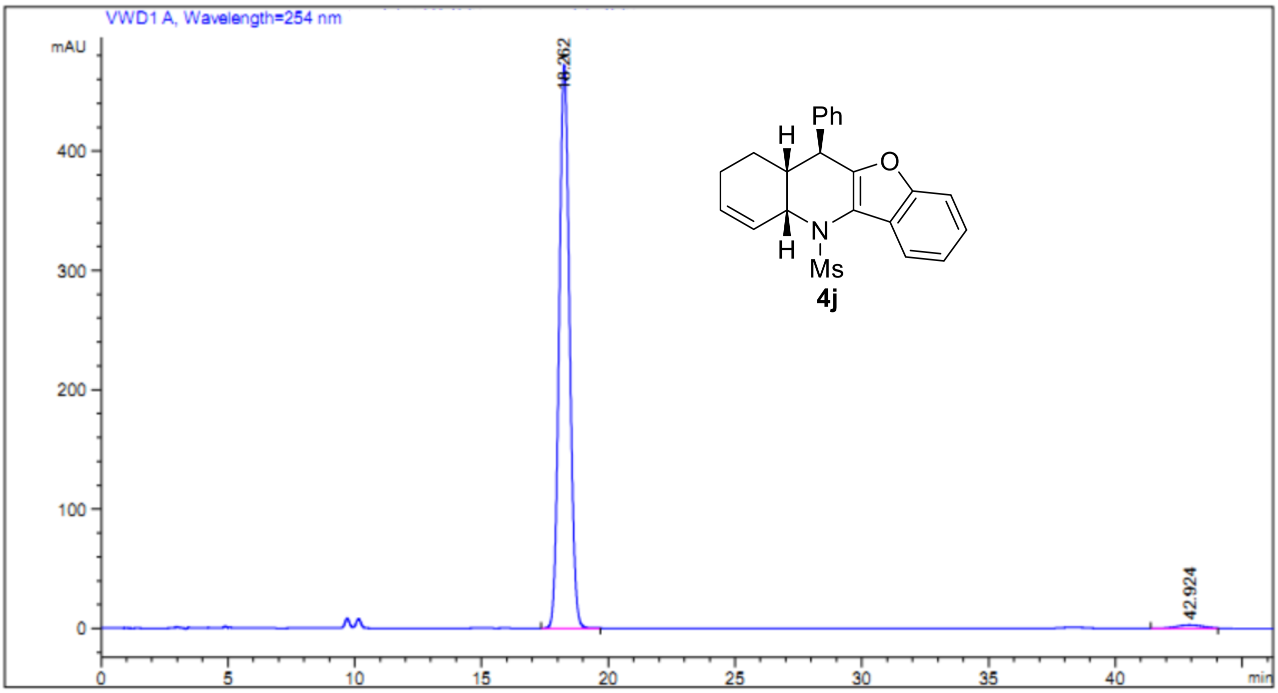

+ESI Scan (rt: 0.276 min) Frag=175.0V
x10^5
512.1060
511.3584
513.1091
514.1038
515.1066
Ph
H
O
N
H
Ts
Cl
4i
(ESI-TOF) m/z: [M + Na]+
Calcd for C28H24 35ClNO3SNa+ 512.1058
Calcd for C28H24 37ClNO3SNa+ 514.1029
Counts vs. Mass-to-Charge (m/z)


7.994 7.988 7.985 7.981 7.975 7.971 7.396 7.379 7.374 7.365 7.361 7.354 7.350 7.346 7.333 7.315 7.311 7.304 7.301 7.298 7.292 7.276 7.263 7.257 7.249 7.240 7.235 7.227 7.222 7.217 7.211 7.206 7.203 5.799 5.782 5.773 5.584 5.579 5.574 5.554 5.548 4.997 4.989 4.980 4.105 4.081 3.100 2.543 2.540 2.539 2.530 2.526 1.920 1.912 1.903 1.896 1.888 0.000
Ph
H
O
N
H
Ms
4j
$^{1}$H NMR (400 MHz, $CDCl_3$)
0.99 4.06 4.09 1.02 1.00 1.00 1.01 3.02 1.00 1.02 1.00 2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

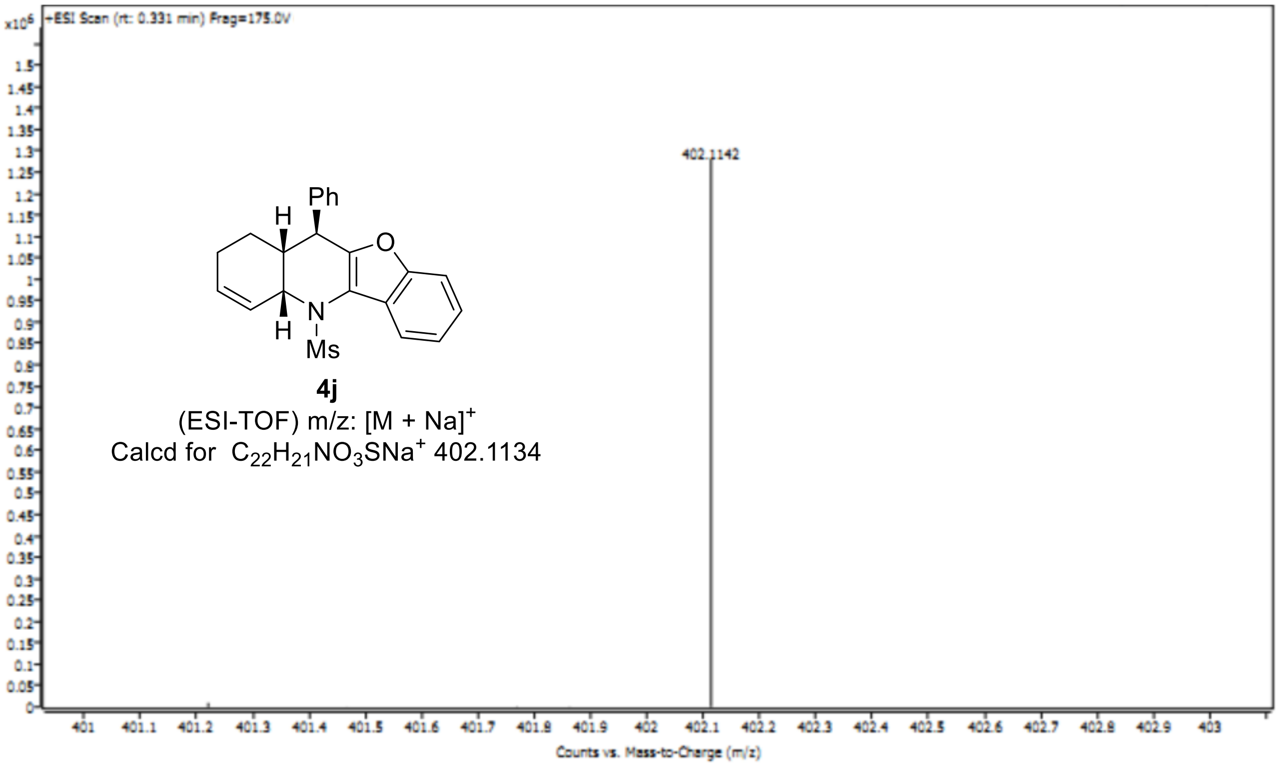

154.222 149.103 139.832 130.343 128.995 128.220 128.090 127.640 124.595 124.225 122.970 122.006 117.059 111.255 77.317 77.000 76.682 58.004 39.597 38.586 38.407 22.360 20.665
Ph
H
O
N
H
Ms
4j
$^{13}$C NMR (100 MHz, $CDCl_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



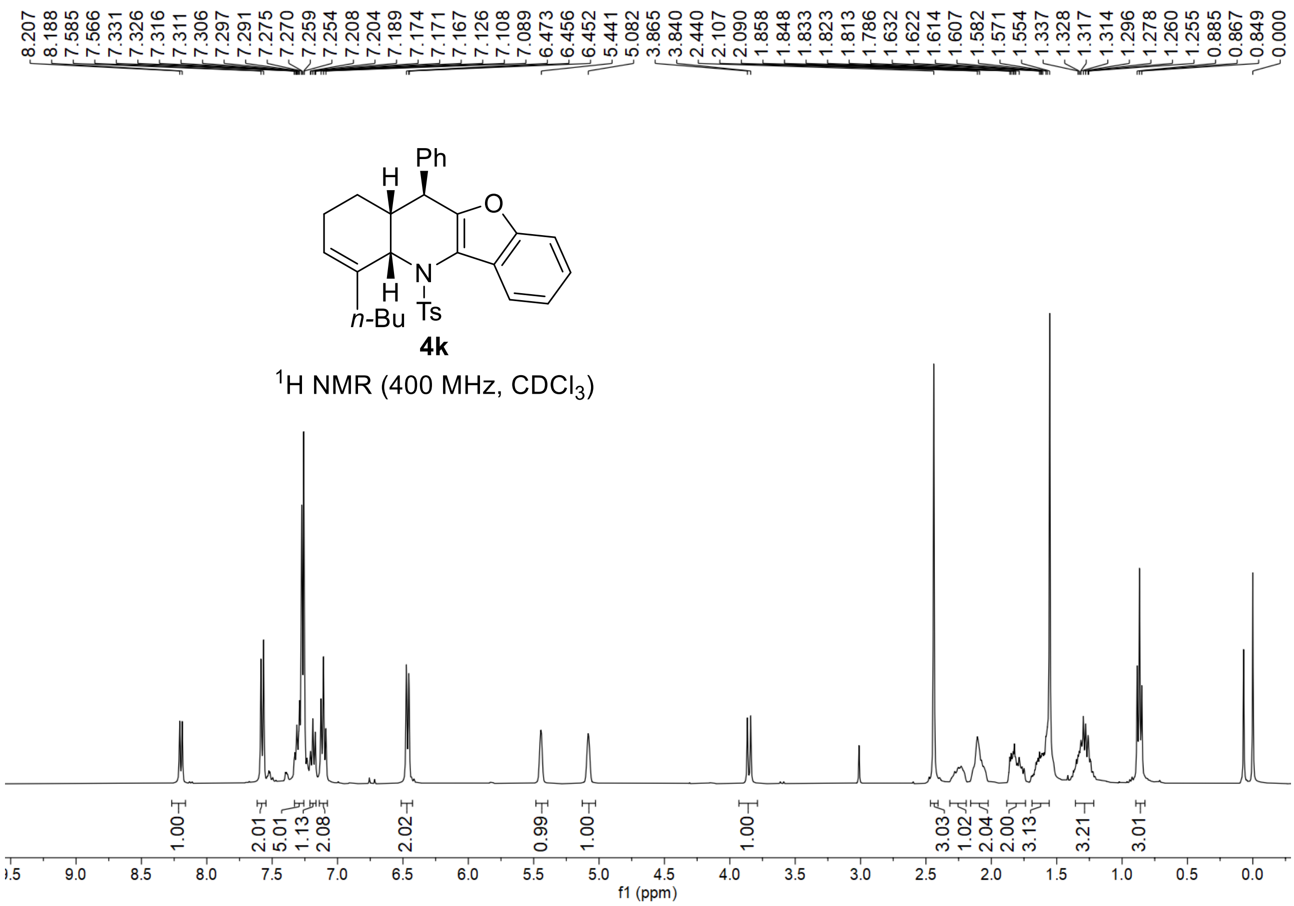

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 17.972 | BB | 0.4399 | 1.26156e4 | 448.96817 | 57.7784 |
| 2 | 41.693 | BB | 1.1233 | 9218.83301 | 125.52738 | 42.2216 |

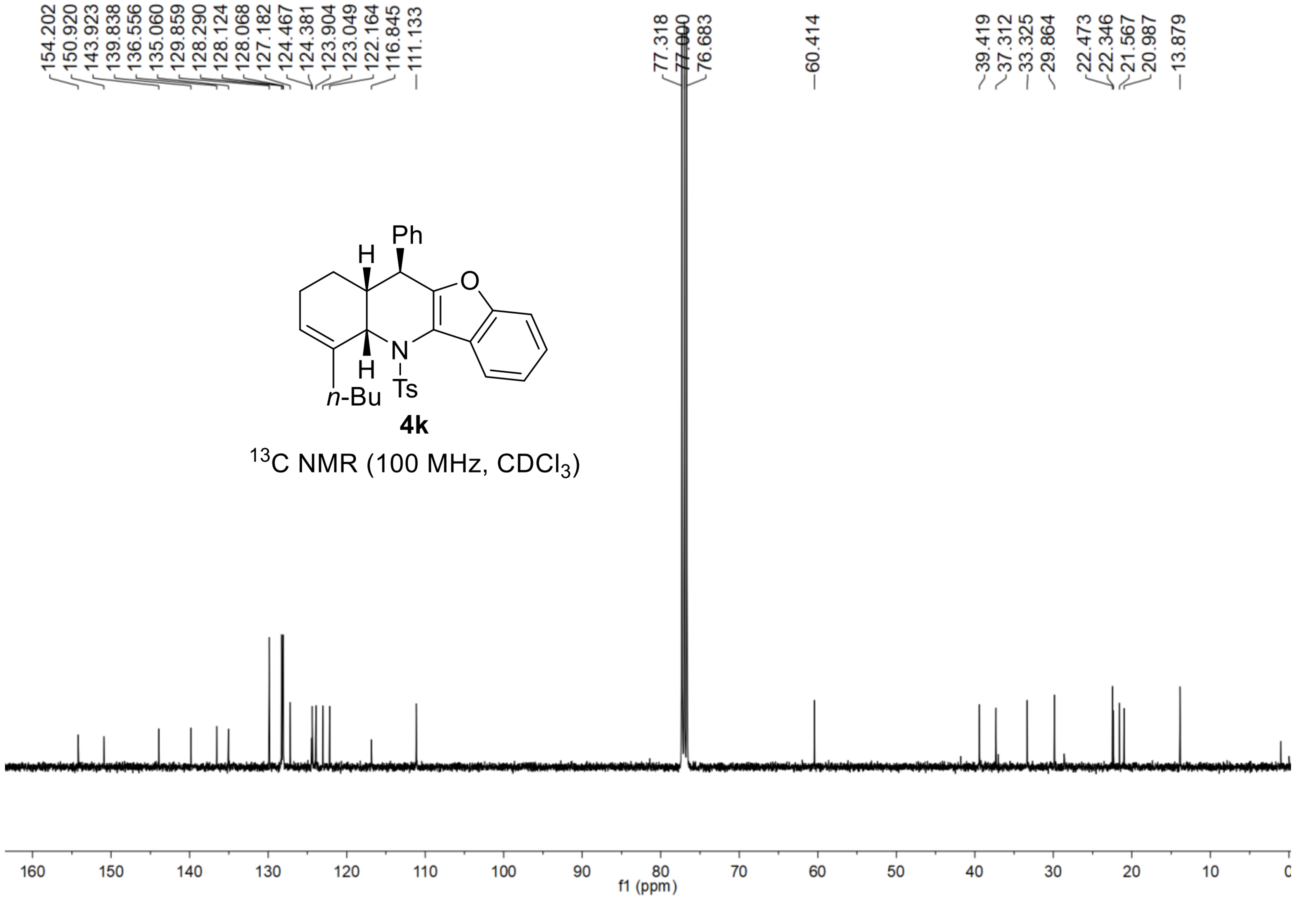


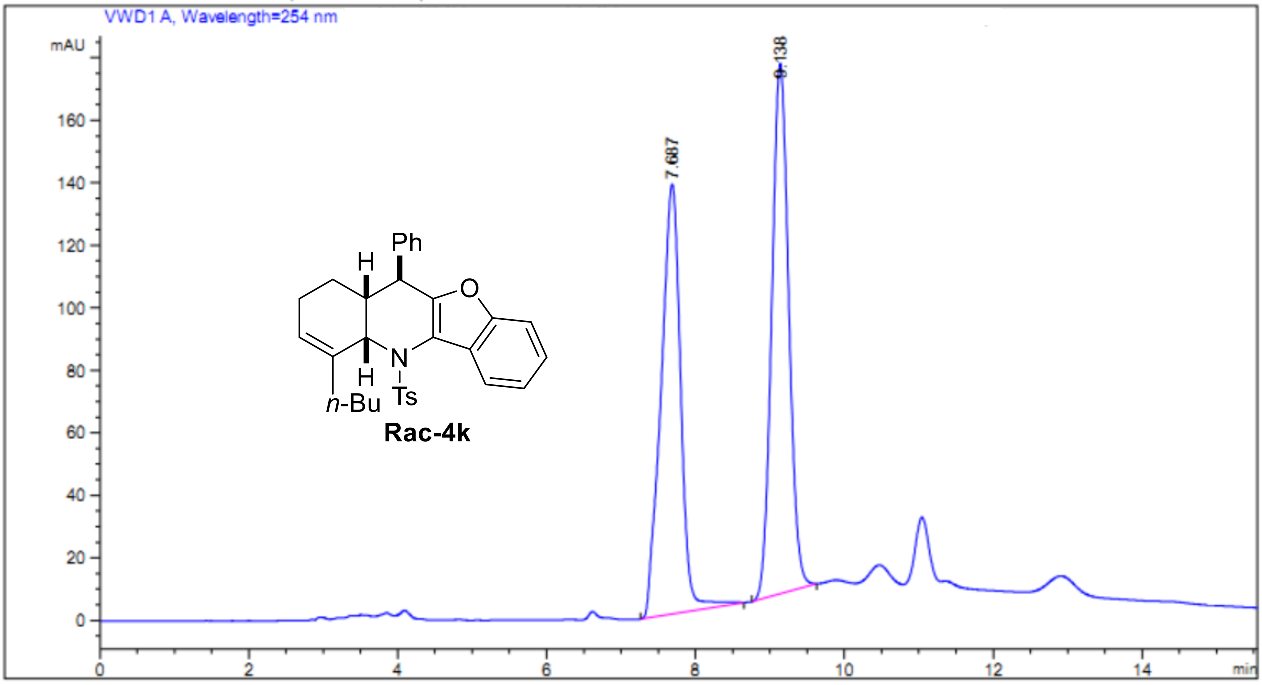

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 18.262 | BBA | 0.4451 | 1.34678e4 | 471.85791 | 98.4604 |
| 2 | 42.924 | BBA | 0.8633 | 210.59492 | 2.95057 | 1.5396 |



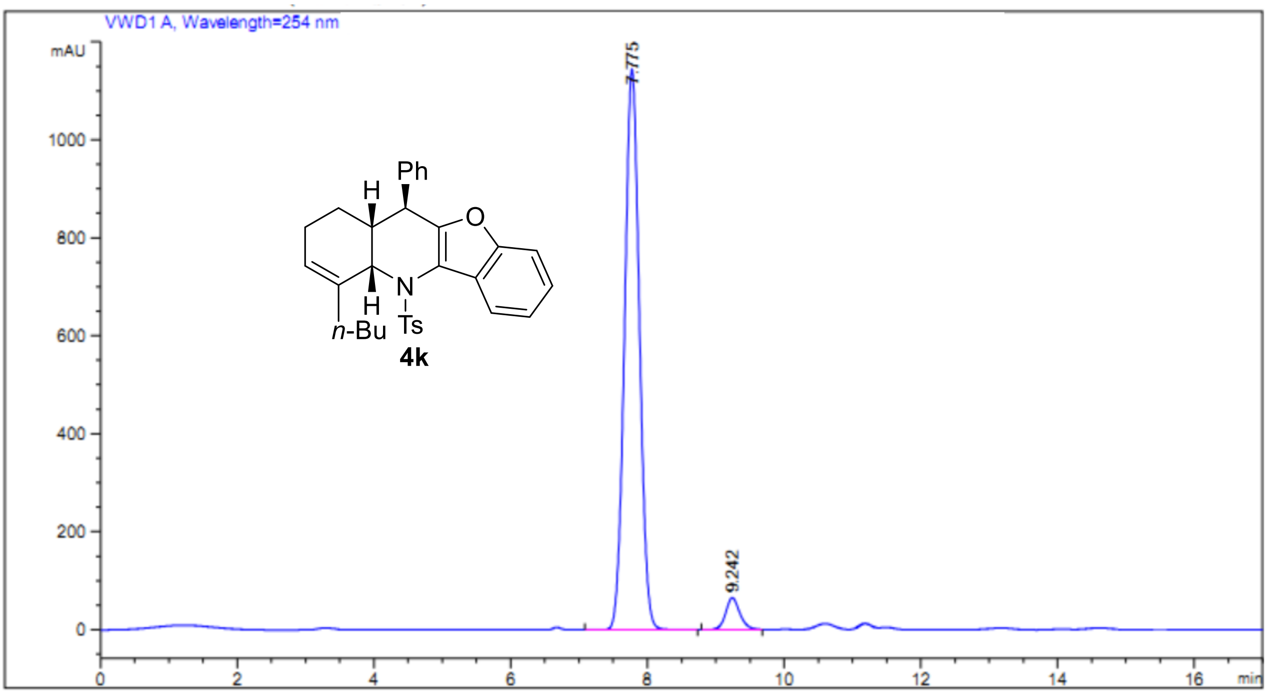
+ESI Scan (rt: 0.331 min) Frag=175.0V
x10^5
402.1142
Counts vs. Mass-to-Charge (m/z)
Ph
H
O
N
H
Ms
4j
(ESI-TOF) m/z: [M + Na]+
Calcd for C22H21NO3SNa+ 402.1134


8.207
8.188
7.585
7.566
7.331
7.326
7.316
7.311
7.306
7.297
7.291
7.275
7.270
7.259
7.254
7.208
7.204
7.189
7.174
7.171
7.167
7.126
7.108
7.089
6.473
6.456
6.452
5.441
5.082
3.865
3.840
2.440
2.107
2.090
1.858
1.848
1.833
1.823
1.813
1.786
1.632
1.622
1.614
1.607
1.582
1.571
1.554
1.337
1.328
1.317
1.314
1.296
1.278
1.260
1.255
0.885
0.867
0.849
0.000
Ph
H
O
N
H
Ts
n-Bu
4k
1H NMR (400 MHz, CDCl3)
1.00
2.01
5.01
1.13
2.08
2.02
0.99
1.00
1.00
3.03
1.02
2.04
2.00
3.13
3.21
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

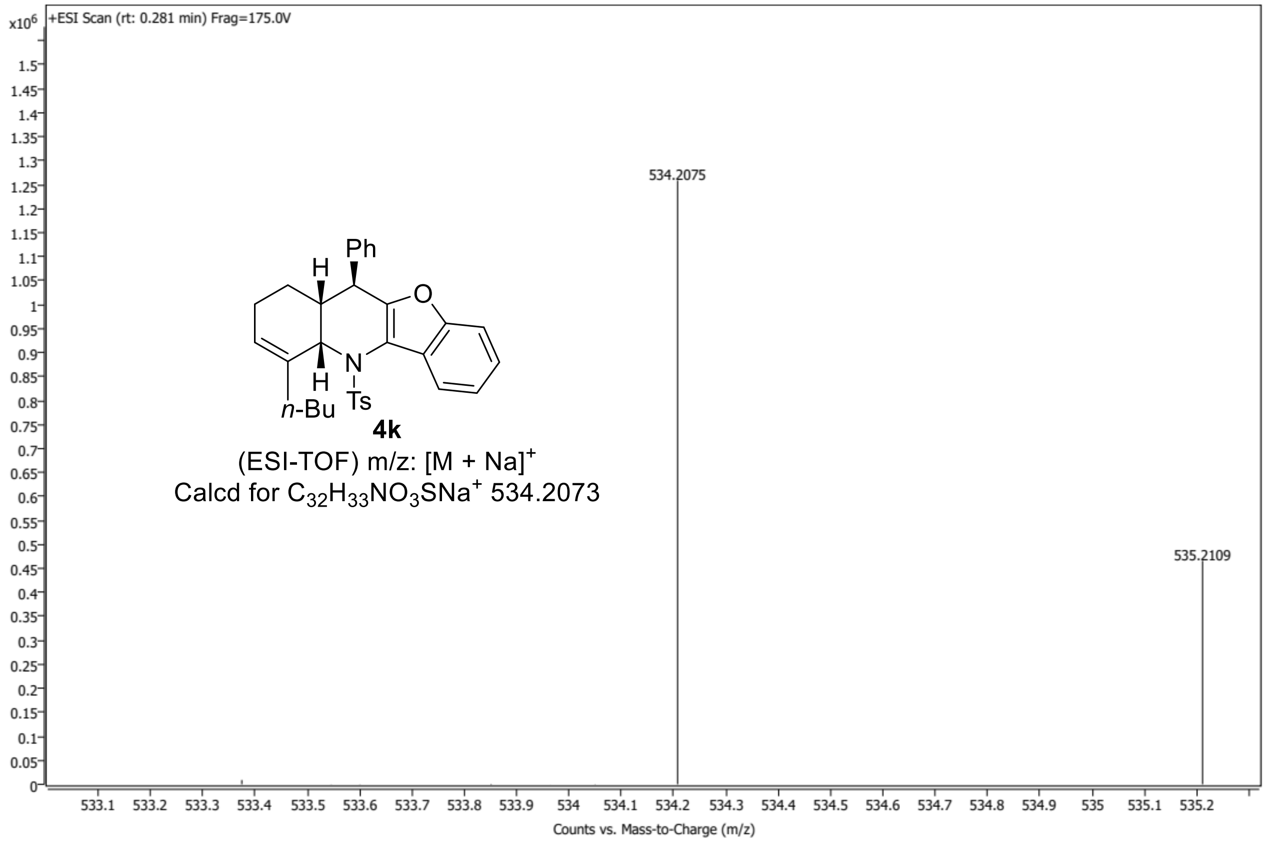

154.202
150.920
143.923
139.838
136.556
135.060
129.859
128.290
128.124
128.068
127.182
124.467
124.381
123.904
123.049
122.164
116.845
111.133
77.318
77.000
76.683
60.414
39.419
37.312
33.325
29.864
22.473
22.346
21.567
20.987
13.879
Ph
H
O
N
H
Ts
n-Bu
4k
13C NMR (100 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

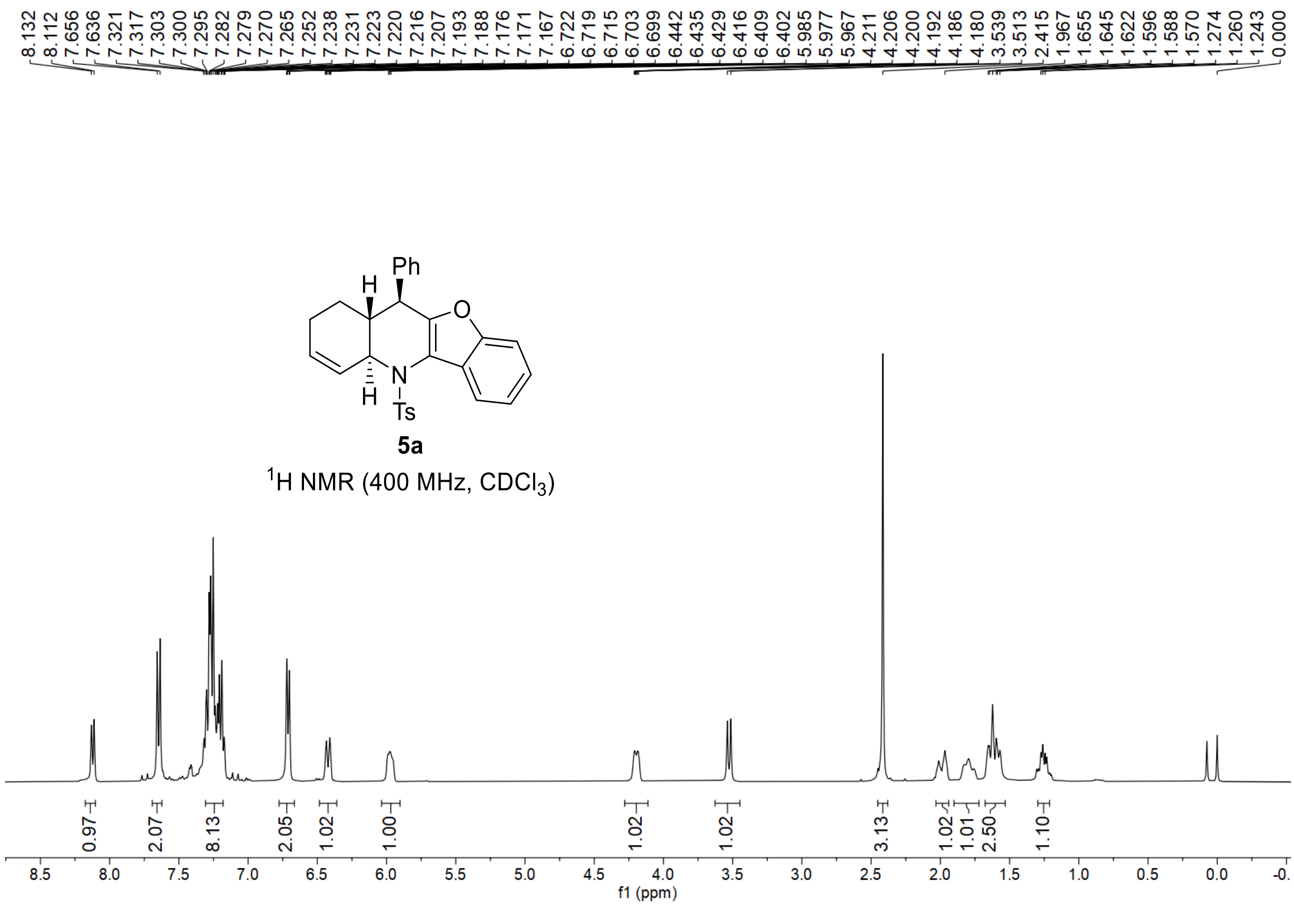


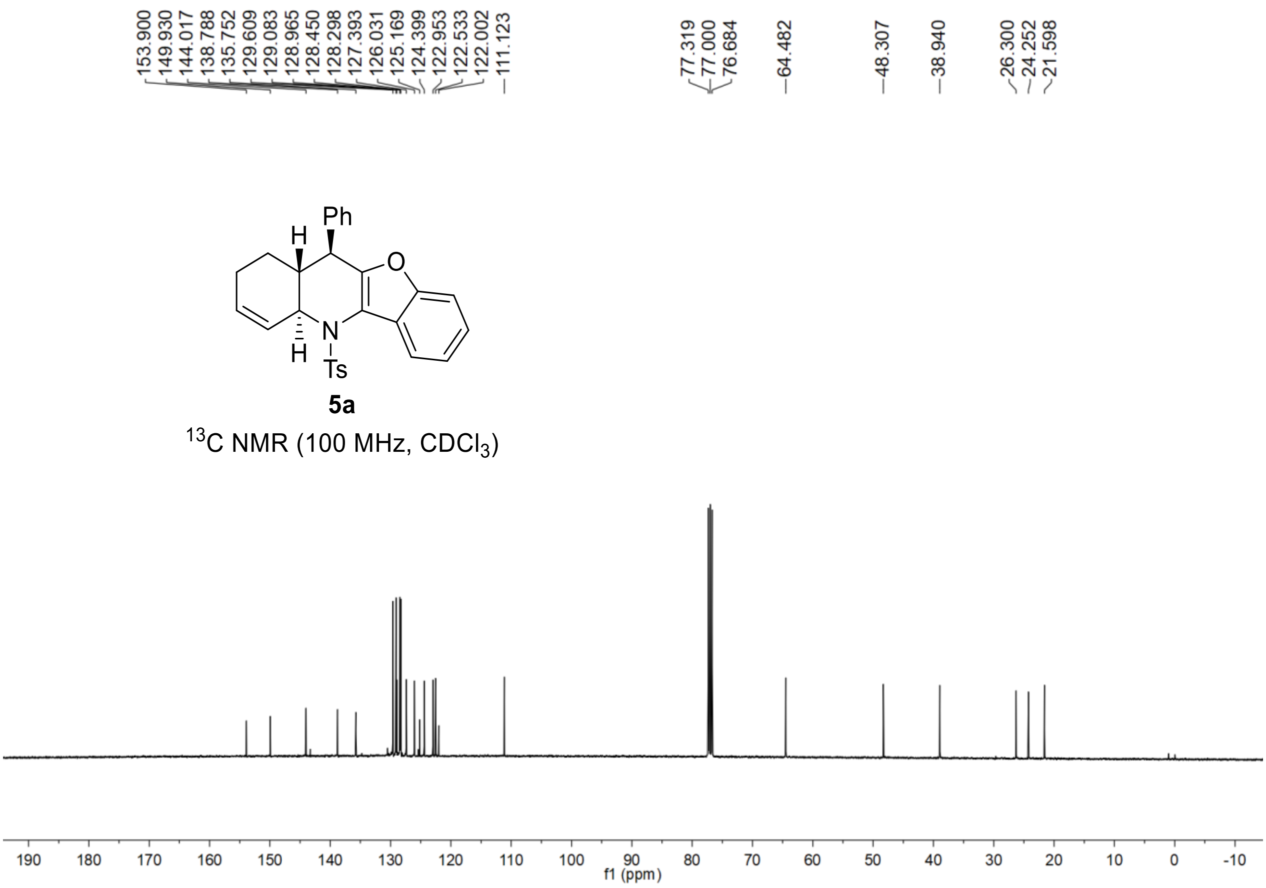

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.687 | BB | 0.2749 | 2518.17505 | 137.45985 | 48.4014 |
| 2 | 9.138 | BB | 0.2458 | 2684.51465 | 169.65187 | 51.5986 |

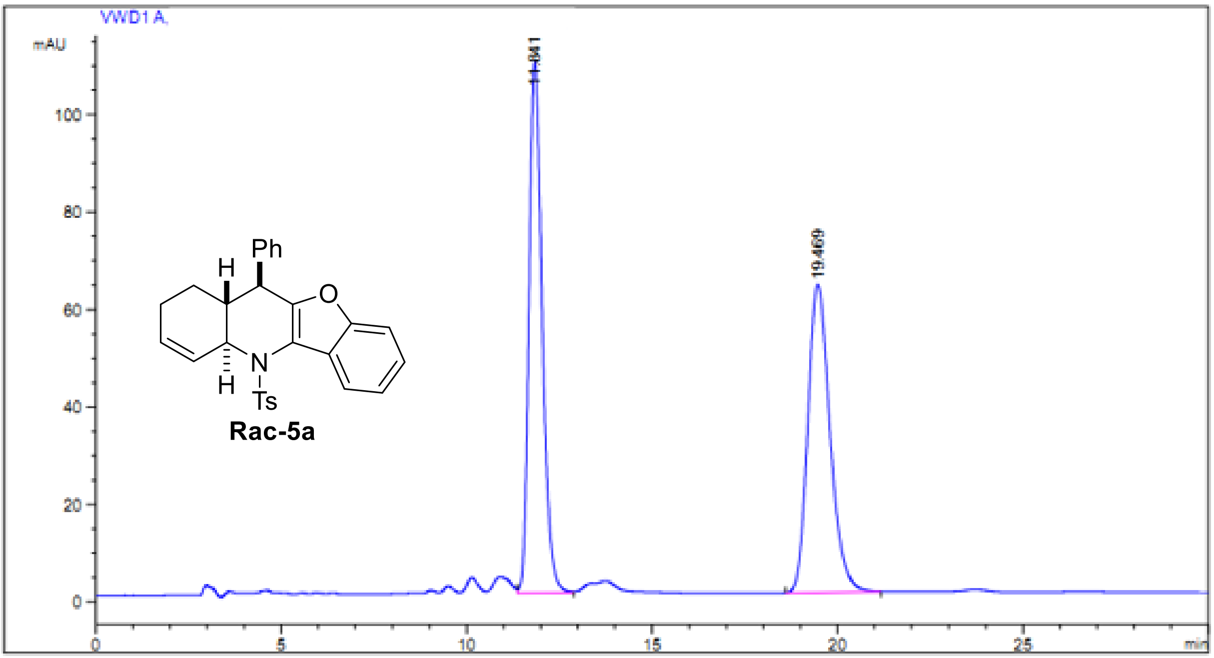



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.775 | BB | 0.2340 | 1.72324e4 | 1143.59082 | 94.8896 |
| 2 | 9.242 | BBA | 0.2157 | 928.07147 | 65.15652 | 5.1104 |

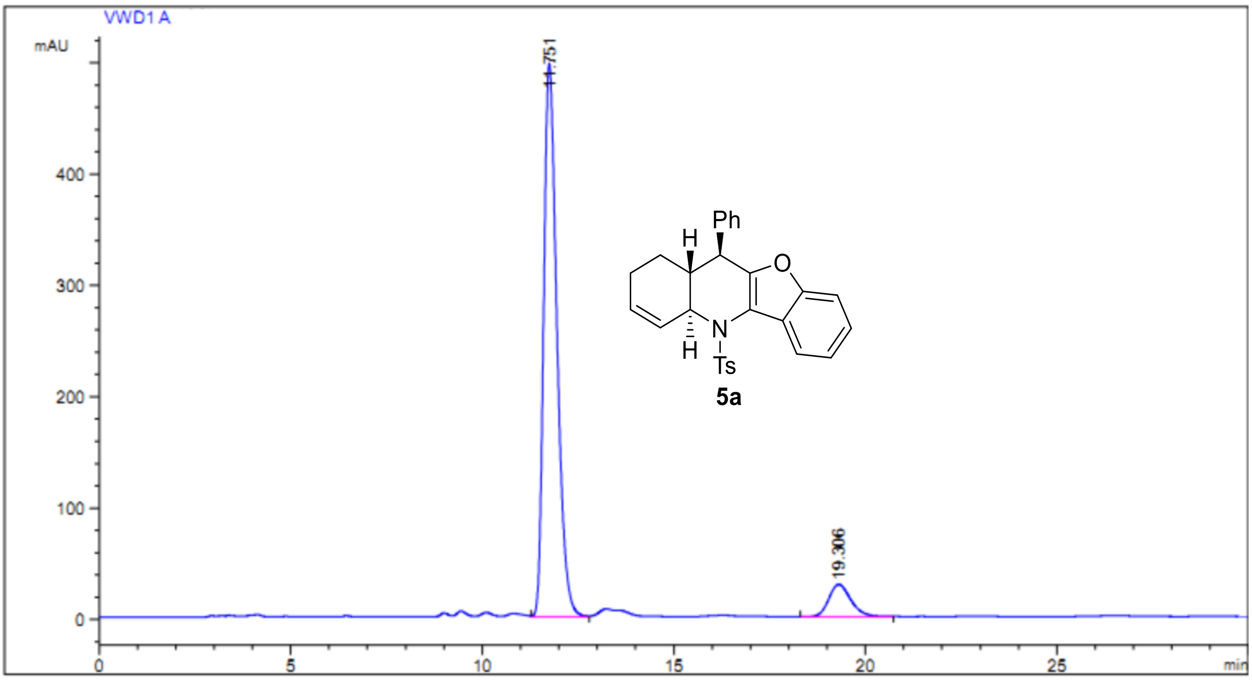

x10^6
+ESI Scan (rt: 0.281 min) Frag=175.0V
534.2075
535.2109
Ph
H
O
N
H
Ts
n-Bu
4k
(ESI-TOF) m/z: [M + Na]+
Calcd for C32H33NO3SNa+ 534.2073
Counts vs. Mass-to-Charge (m/z)


5a
$^{1}H$ NMR (400 MHz, $CDCl_3$)
8.132 8.112 7.656 7.636 7.321 7.317 7.303 7.300 7.295 7.282 7.279 7.270 7.265 7.252 7.238 7.231 7.223 7.220 7.216 7.207 7.193 7.188 7.176 7.171 7.167 6.722 6.719 6.715 6.703 6.699 6.442 6.435 6.429 6.416 6.409 6.402 5.985 5.977 5.967 4.211 4.206 4.200 4.192 4.186 4.180 3.539 3.513 2.415 1.967 1.655 1.645 1.622 1.596 1.588 1.570 1.274 1.260 1.243 0.000
0.97 2.07 8.13 2.05 1.02 1.00 1.02 1.02 3.13 1.02 1.01 2.50 1.10
f1 (ppm)

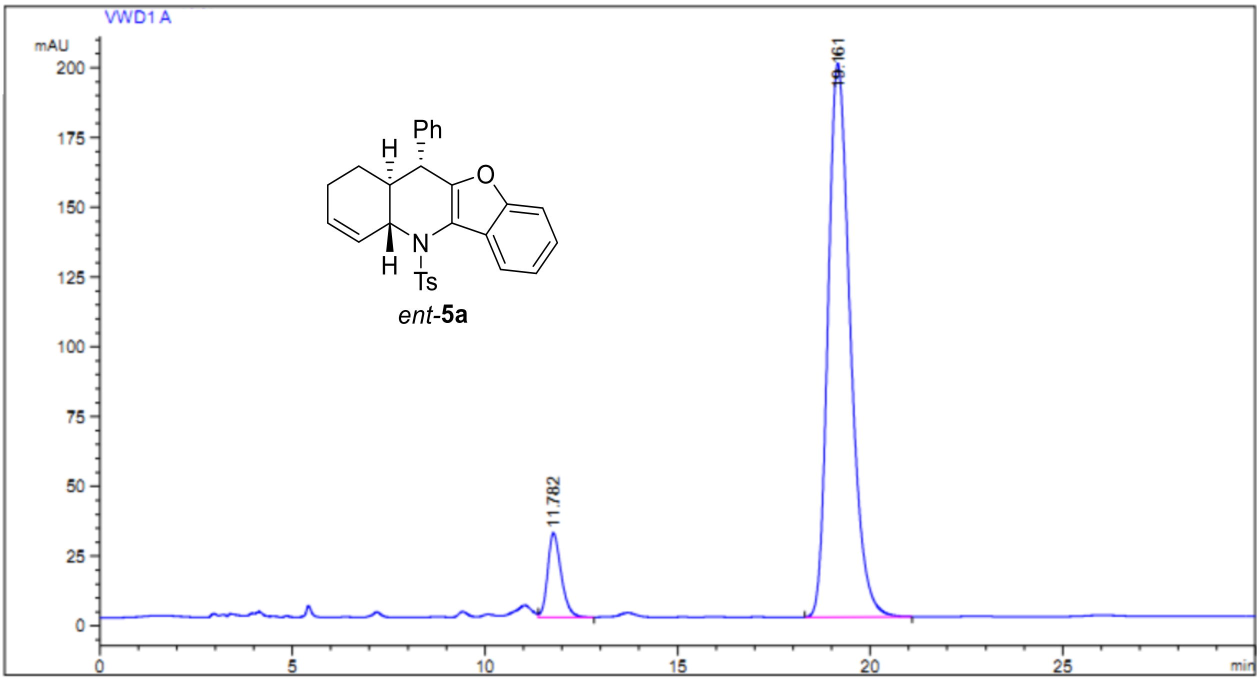

5a
$^{13}C$ NMR (100 MHz, $CDCl_3$)
153.900 149.930 144.017 138.788 135.752 129.609 129.083 128.965 128.450 128.298 127.393 126.031 125.169 124.399 122.953 122.533 122.002 111.123
77.319 77.000 76.684 64.482 48.307 38.940 26.300 24.252 21.598
f1 (ppm)



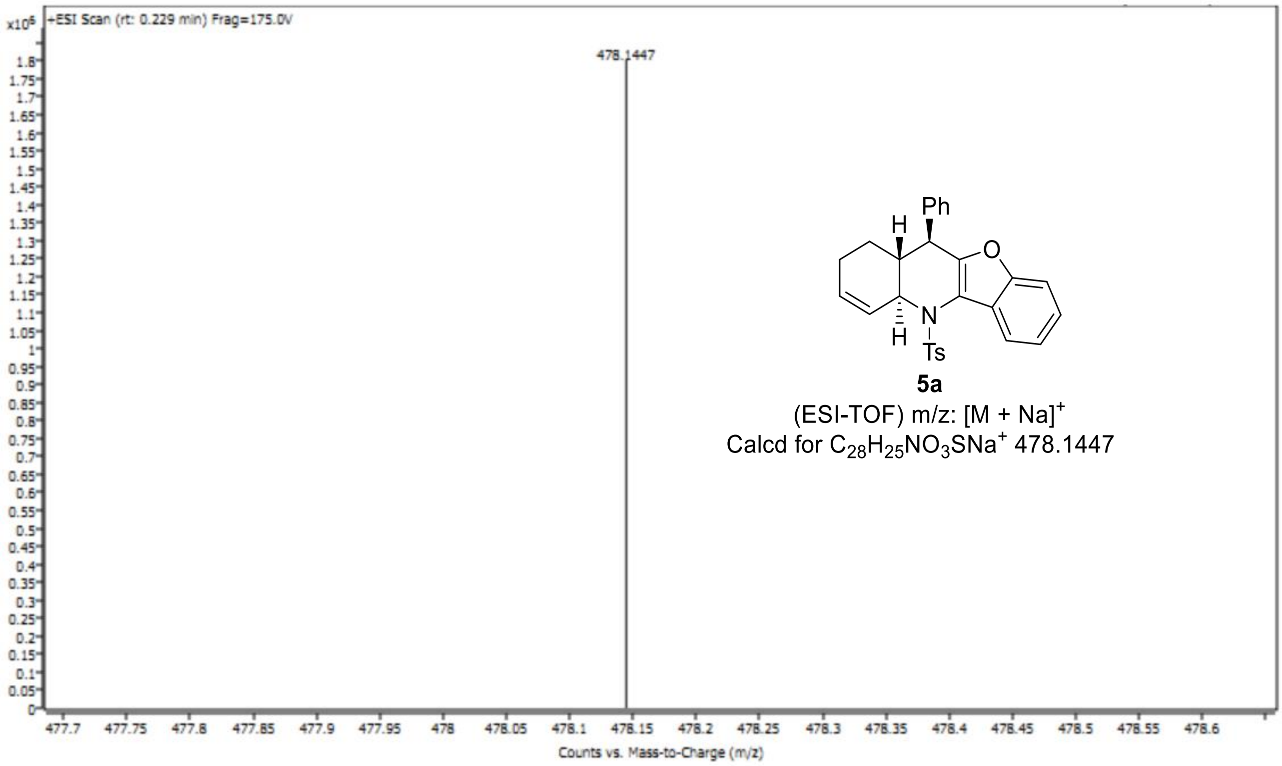

| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 11.841 | VV | 0.3804 | 2683.02319 | 108.97501 | 50.4386 |
| 2 | 19.469 | BB | 0.6404 | 2636.35767 | 63.27567 | 49.5614 |

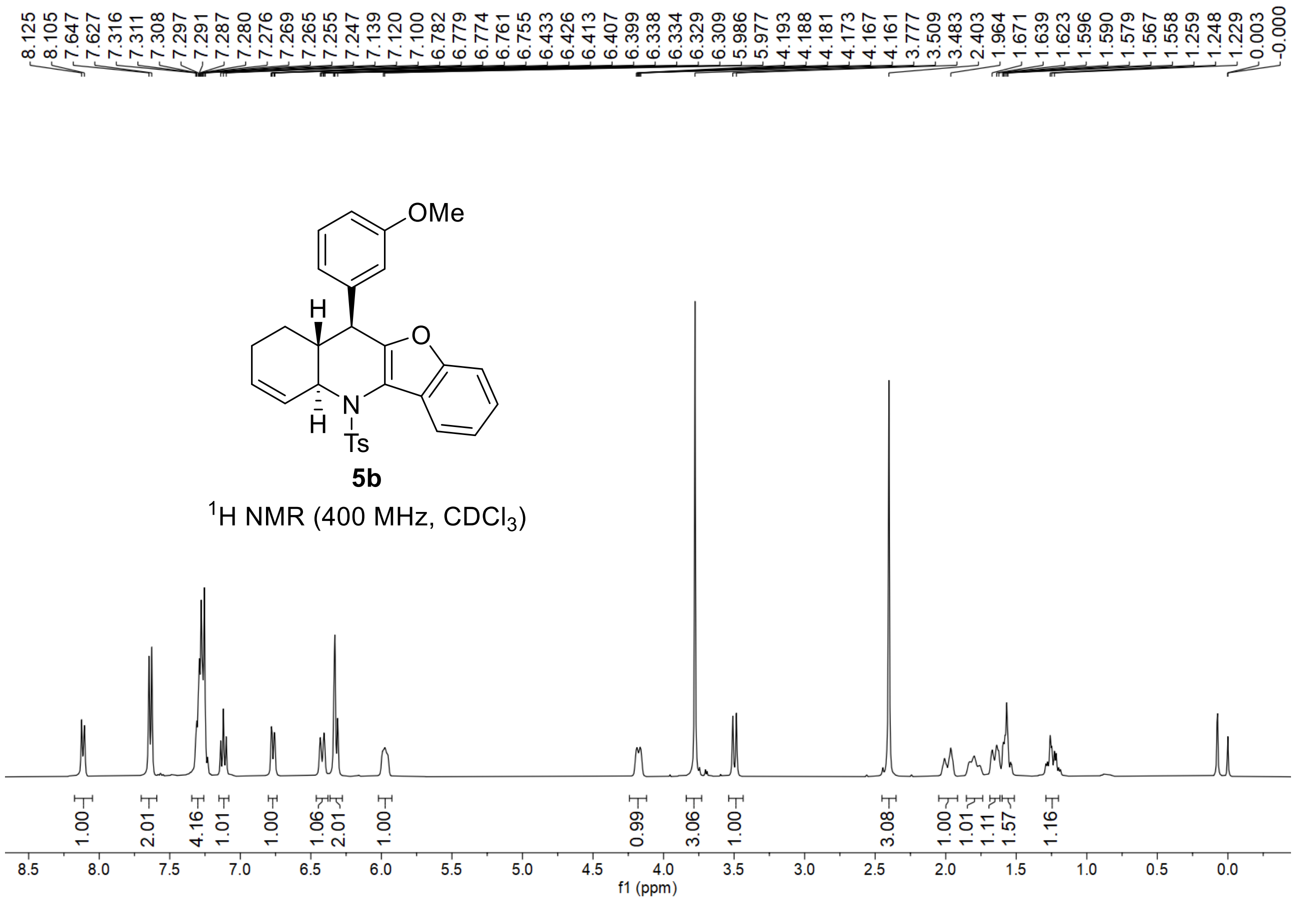


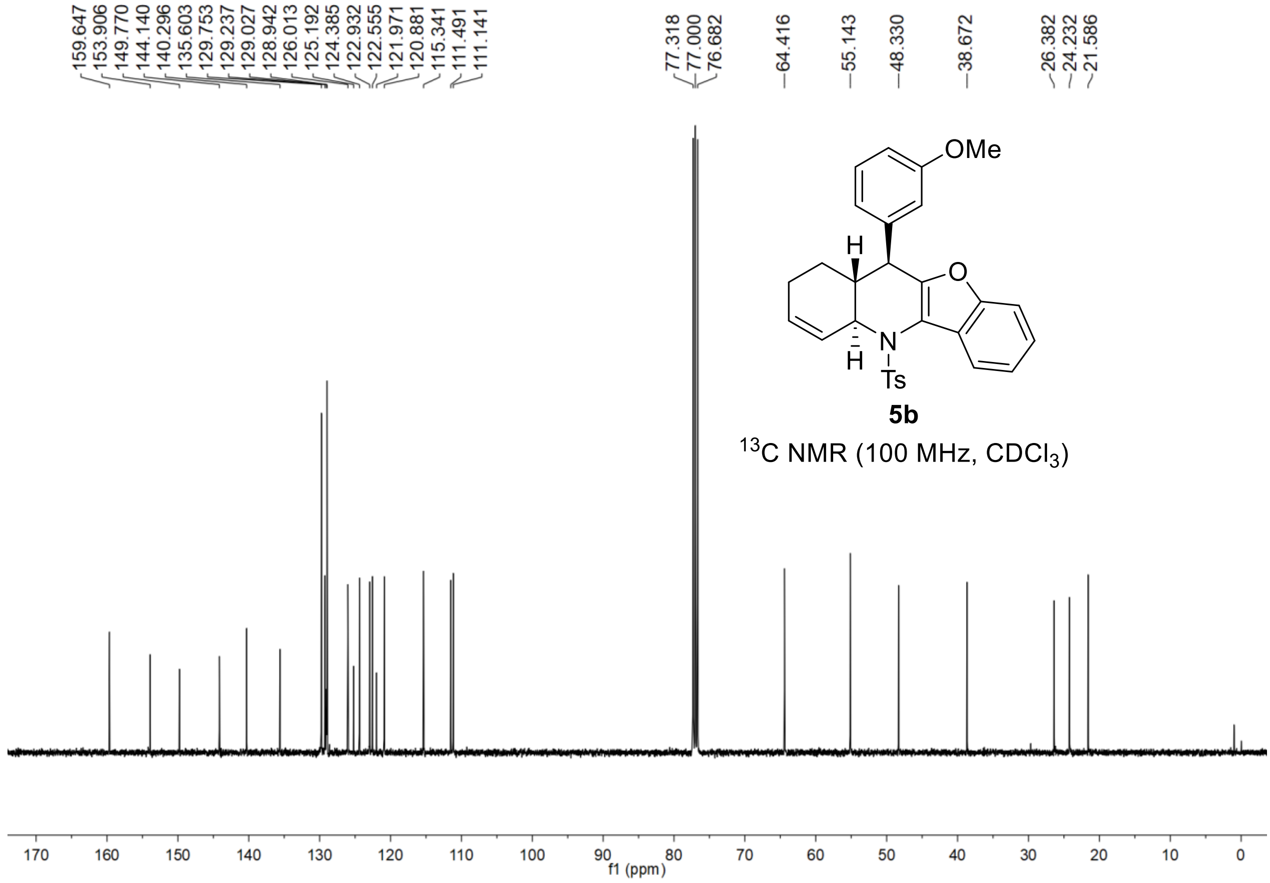

| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 11.751 | VV | 0.3670 | 1.19035e4 | 496.57968 | 91.1792 |
| 2 | 19.306 | VB | 0.6106 | 1151.56470 | 28.89340 | 8.8208 |

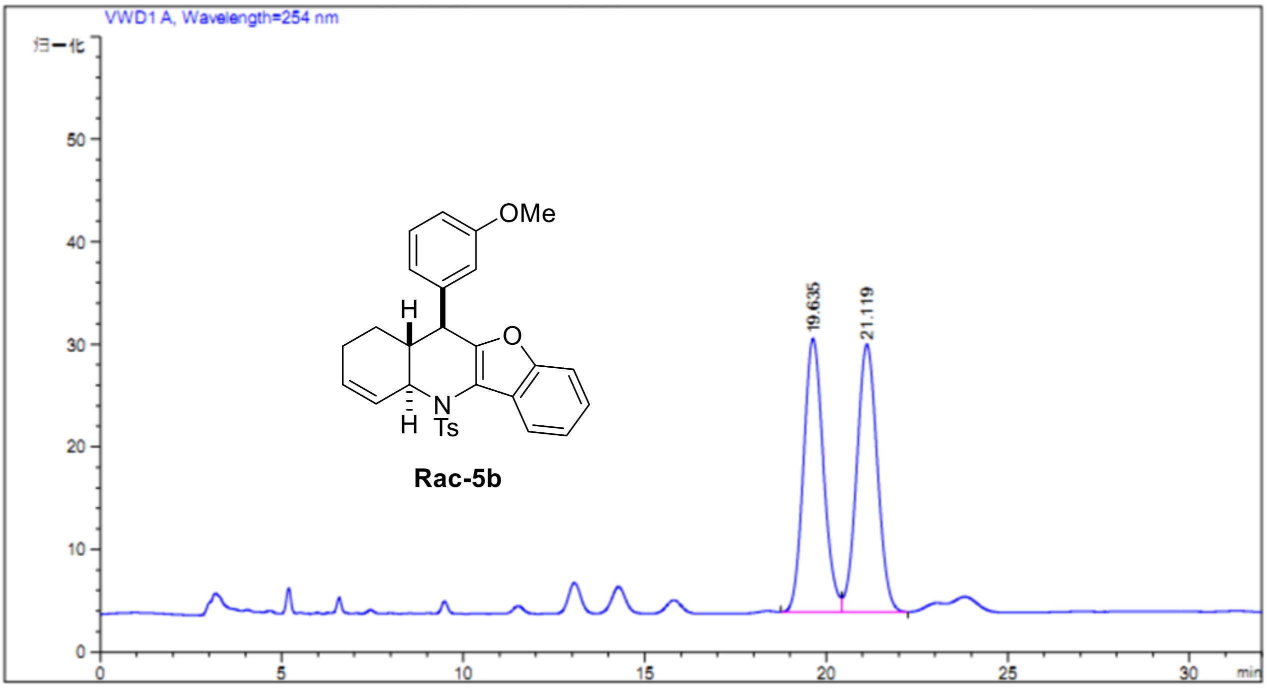



| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 11.782 | VB | 0.3732 | 740.02606 | 30.20142 | 8.5200 |
| 2 | 19.161 | BB | 0.6161 | 7945.75879 | 198.24857 | 91.4800 |

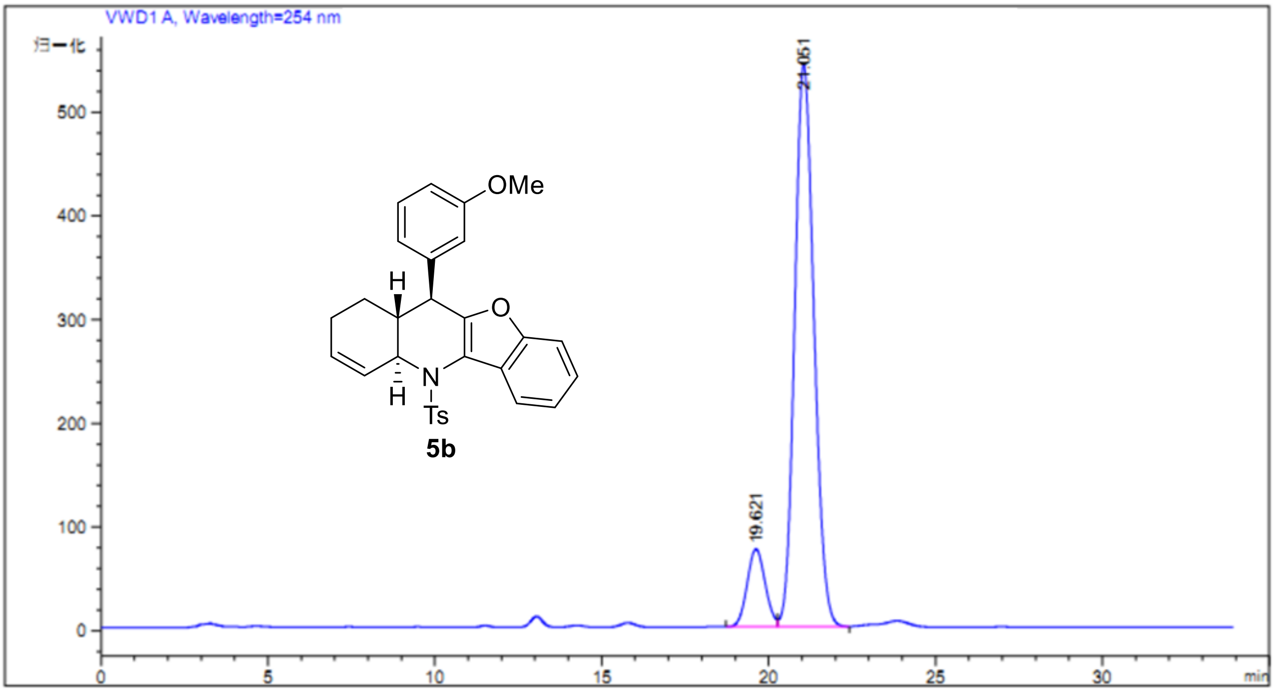



8.125
8.105
7.647
7.627
7.316
7.311
7.308
7.297
7.291
7.287
7.280
7.276
7.269
7.265
7.255
7.247
7.139
7.120
7.100
6.782
6.779
6.774
6.761
6.755
6.433
6.426
6.413
6.407
6.399
6.338
6.334
6.329
6.309
5.986
5.977
4.193
4.188
4.181
4.173
4.167
4.161
3.777
3.509
3.483
2.403
1.964
1.671
1.639
1.623
1.596
1.590
1.579
1.567
1.558
1.259
1.248
1.229
0.003
-0.000
OMe
H
O
N
H
Ts
5b
1H NMR (400 MHz, CDCl3)
1.00
2.01
4.16
1.01
1.00
1.06
2.01
1.00
0.99
3.06
1.00
3.08
1.00
1.01
1.11
1.57
1.16
f1 (ppm)

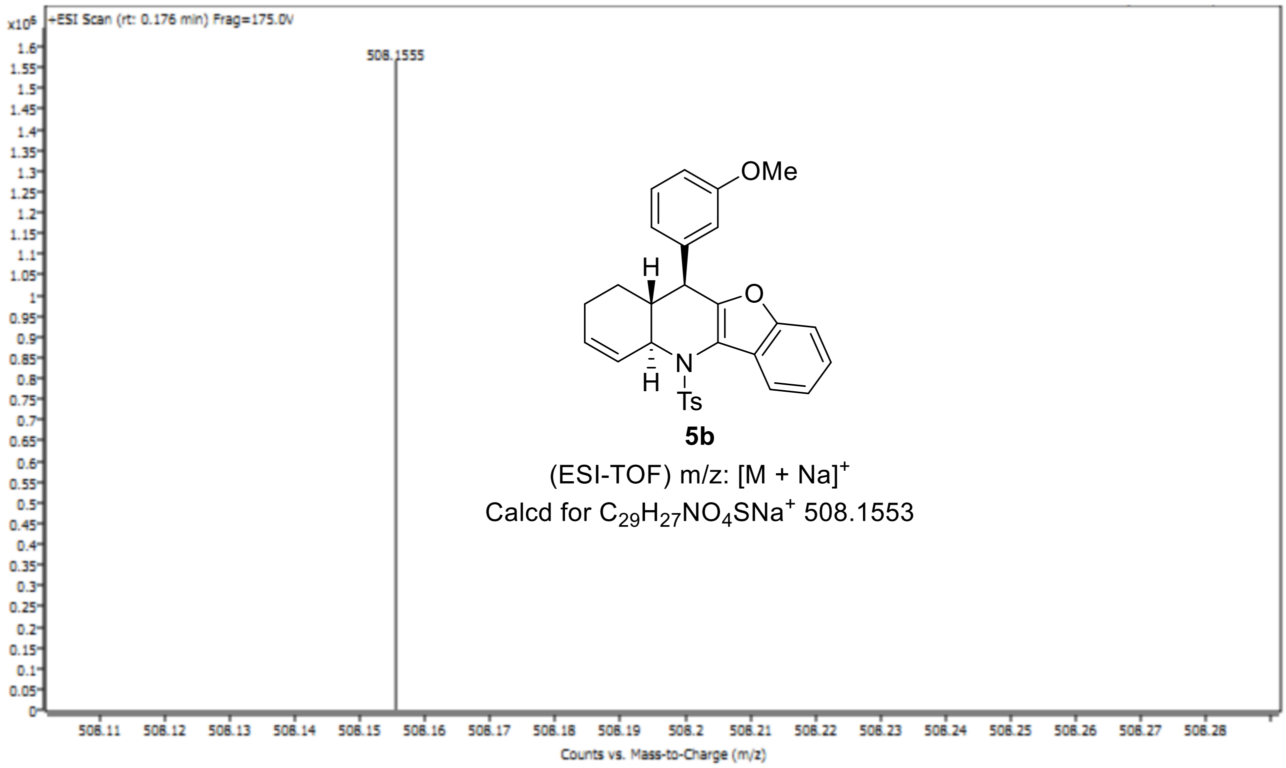

159.647
153.906
149.770
144.140
140.296
135.603
129.753
129.237
129.027
128.942
126.013
125.192
124.385
122.932
122.555
121.971
120.881
115.341
111.491
111.141
77.318
77.000
76.682
64.416
55.143
48.330
38.672
26.382
24.232
21.586
OMe
H
O
N
H
Ts
5b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



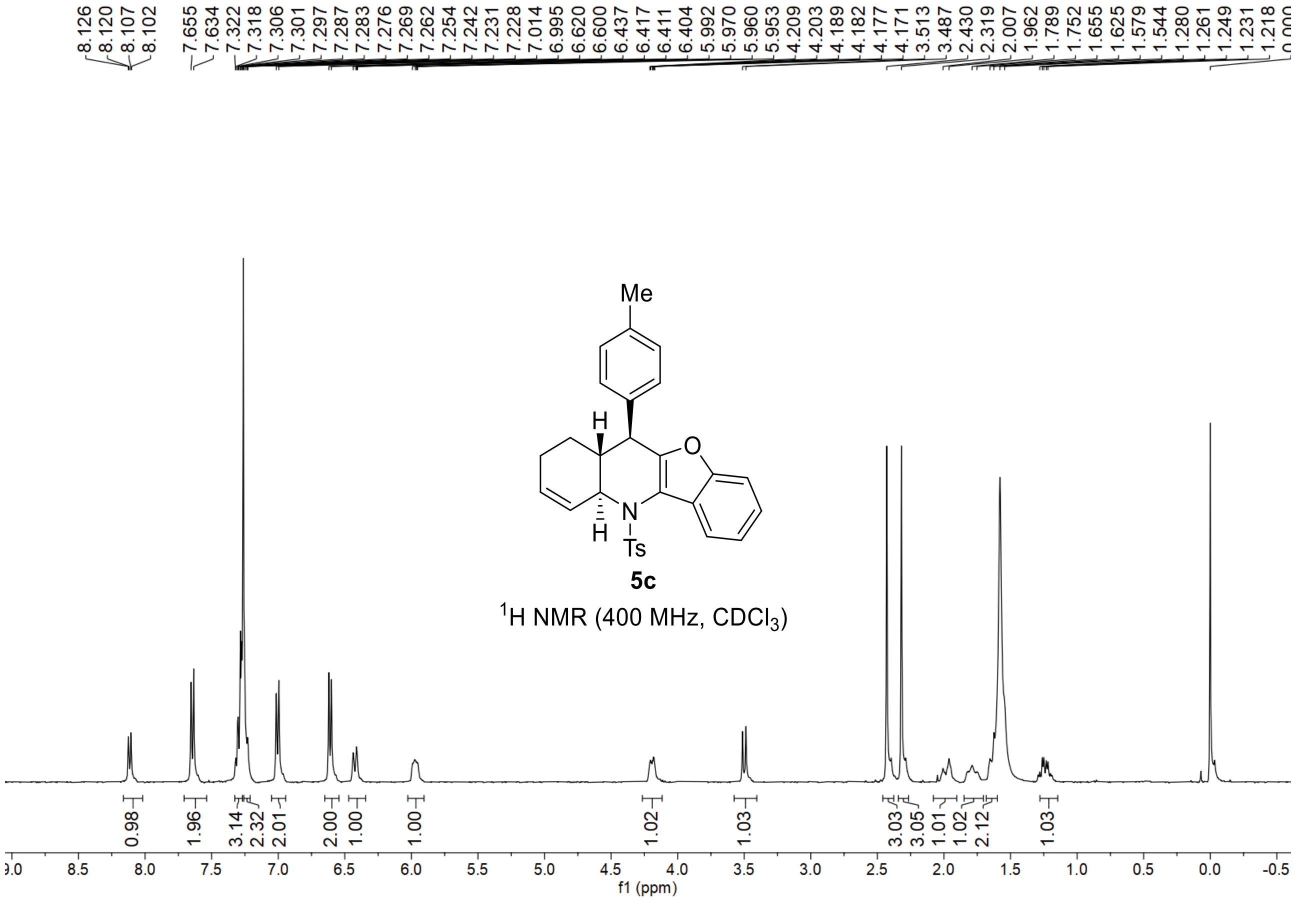

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 19.635 | BV | 0.5846 | 1015.80780 | 26.64064 | 49.7959 |
| 2 | 21.119 | VB | 0.6099 | 1024.13293 | 26.06264 | 50.2041 |

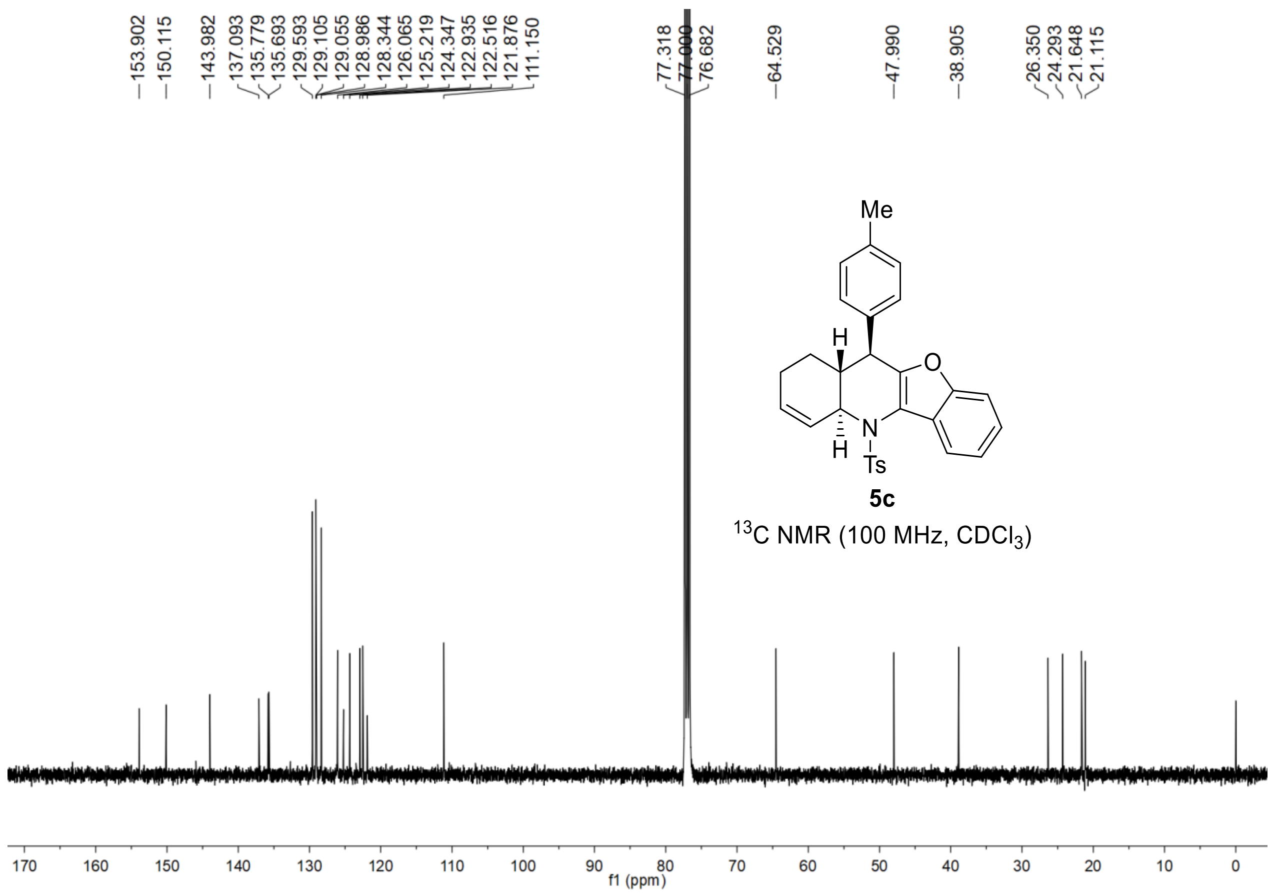


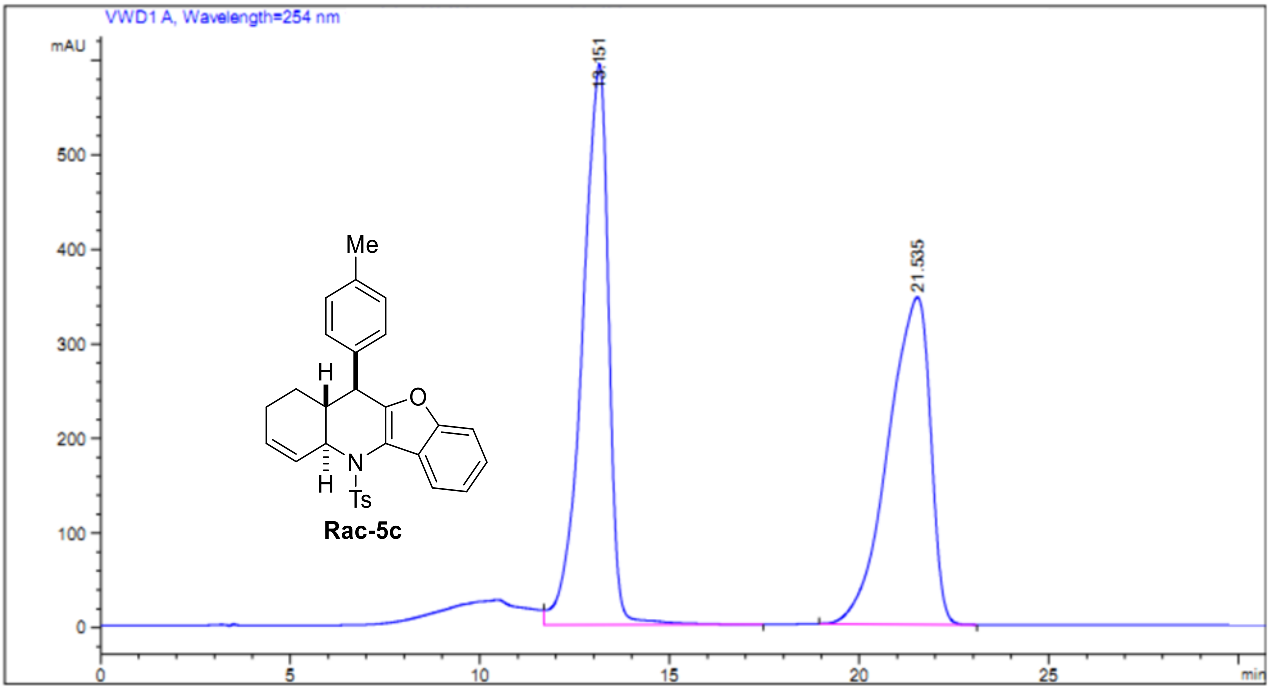

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 19.621 | BV | 0.5887 | 2819.46216 | 74.98166 | 11.4639 |
| 2 | 21.051 | VB | 0.6261 | 2.17748e4 | 541.86804 | 88.5361 |



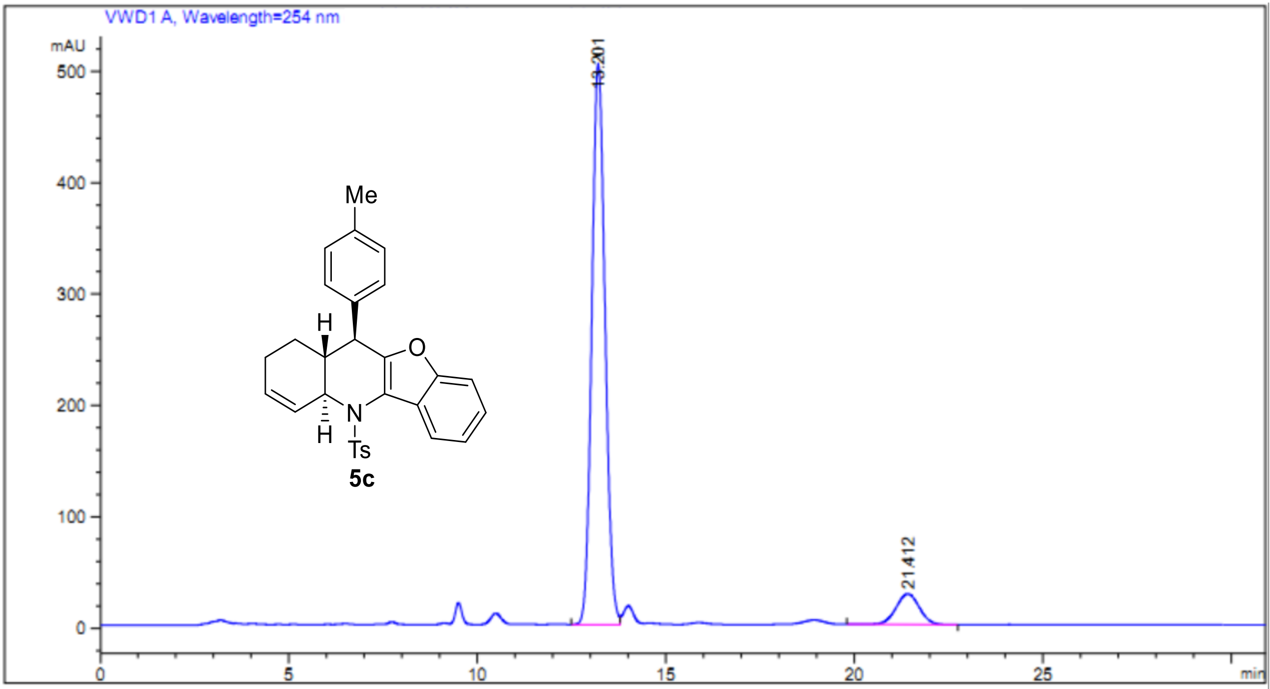
x10^6 +ESI Scan (rt: 0.176 min) Frag=175.0V
508.1555
OMe
H
O
N
H
Ts
5b
(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{29}H_{27}NO_4SNa^+$ 508.1553
Counts vs. Mass-to-Charge (m/z)


8.126 8.120 8.107 8.102 7.655 7.634 7.322 7.318 7.306 7.301 7.297 7.287 7.283 7.276 7.269 7.262 7.254 7.242 7.231 7.228 7.014 6.995 6.620 6.600 6.437 6.417 6.411 6.404 5.992 5.970 5.960 5.953 4.209 4.203 4.189 4.182 4.177 4.171 3.513 3.487 2.430 2.319 2.007 1.962 1.789 1.752 1.655 1.625 1.579 1.544 1.280 1.261 1.249 1.231 1.218
Me
H
O
N
H
Ts
5c
1H NMR (400 MHz, CDCl3)
0.98 1.96 3.14 2.32 2.01 2.00 1.00 1.00 1.02 1.03 3.03 3.05 1.01 1.02 2.12 1.03
f1 (ppm)

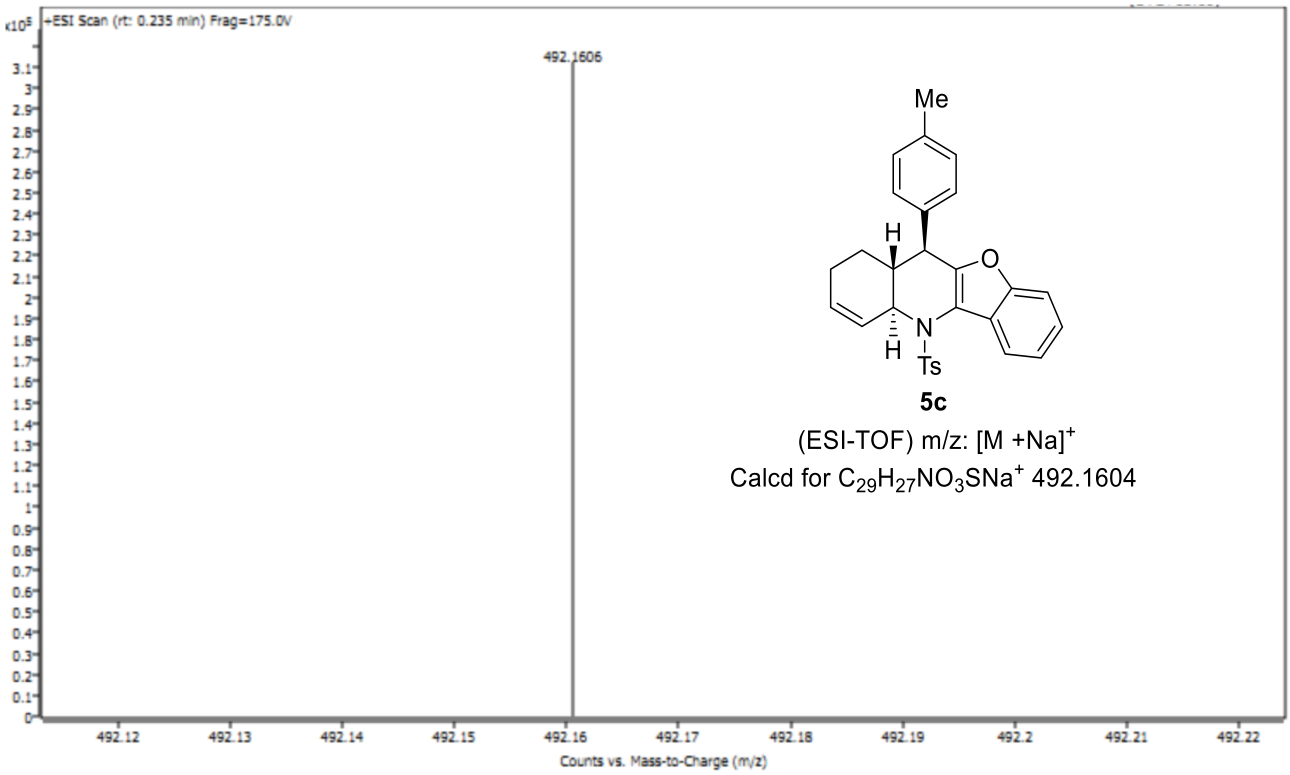

153.902 150.115 143.982 137.093 135.779 135.693 129.593 129.105 129.055 128.986 128.344 126.065 125.219 124.347 122.935 122.516 121.876 111.150 77.318 77.000 76.682 64.529 47.990 38.905 26.350 24.293 21.648 21.115
Me
H
O
N
H
Ts
5c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

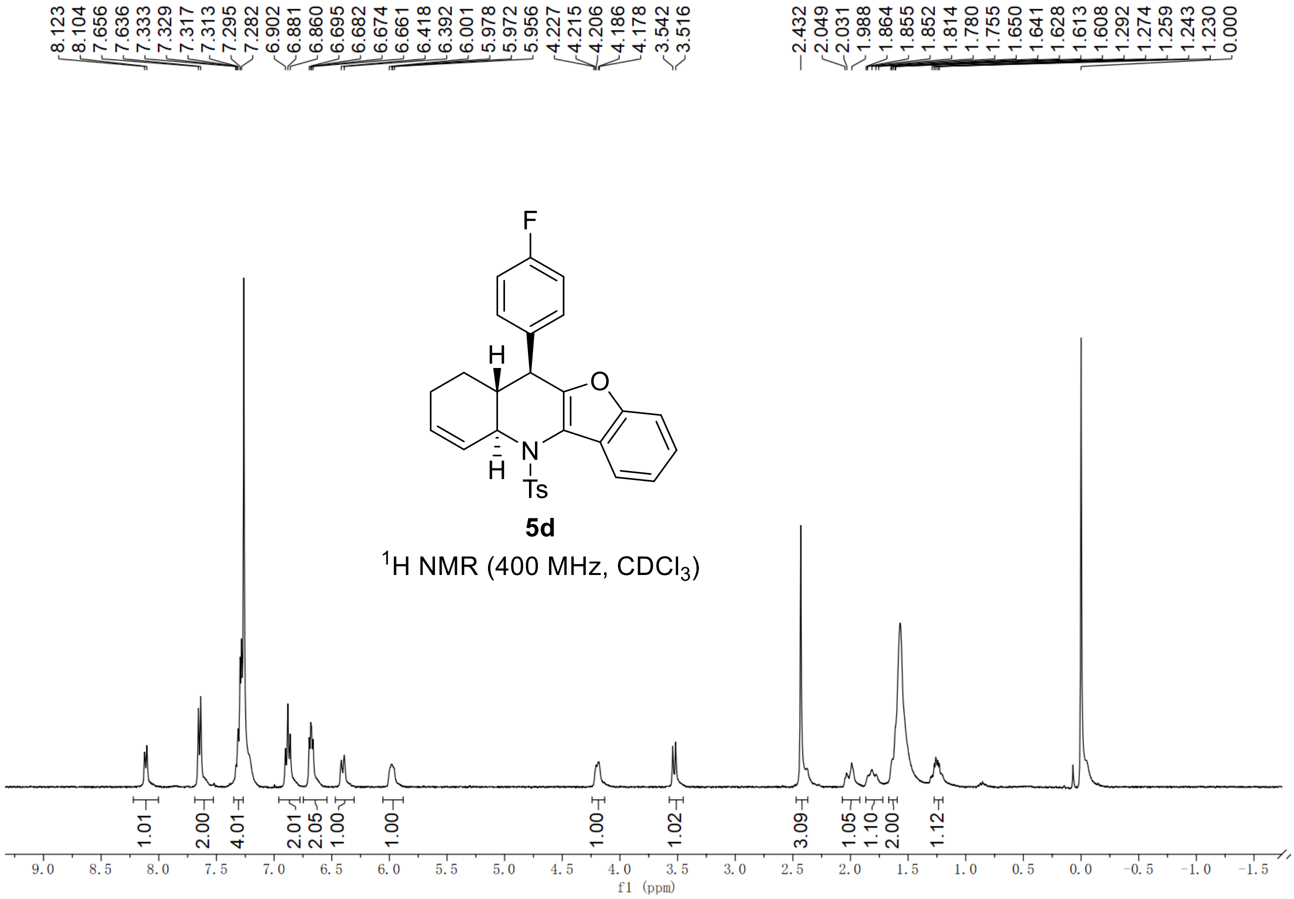
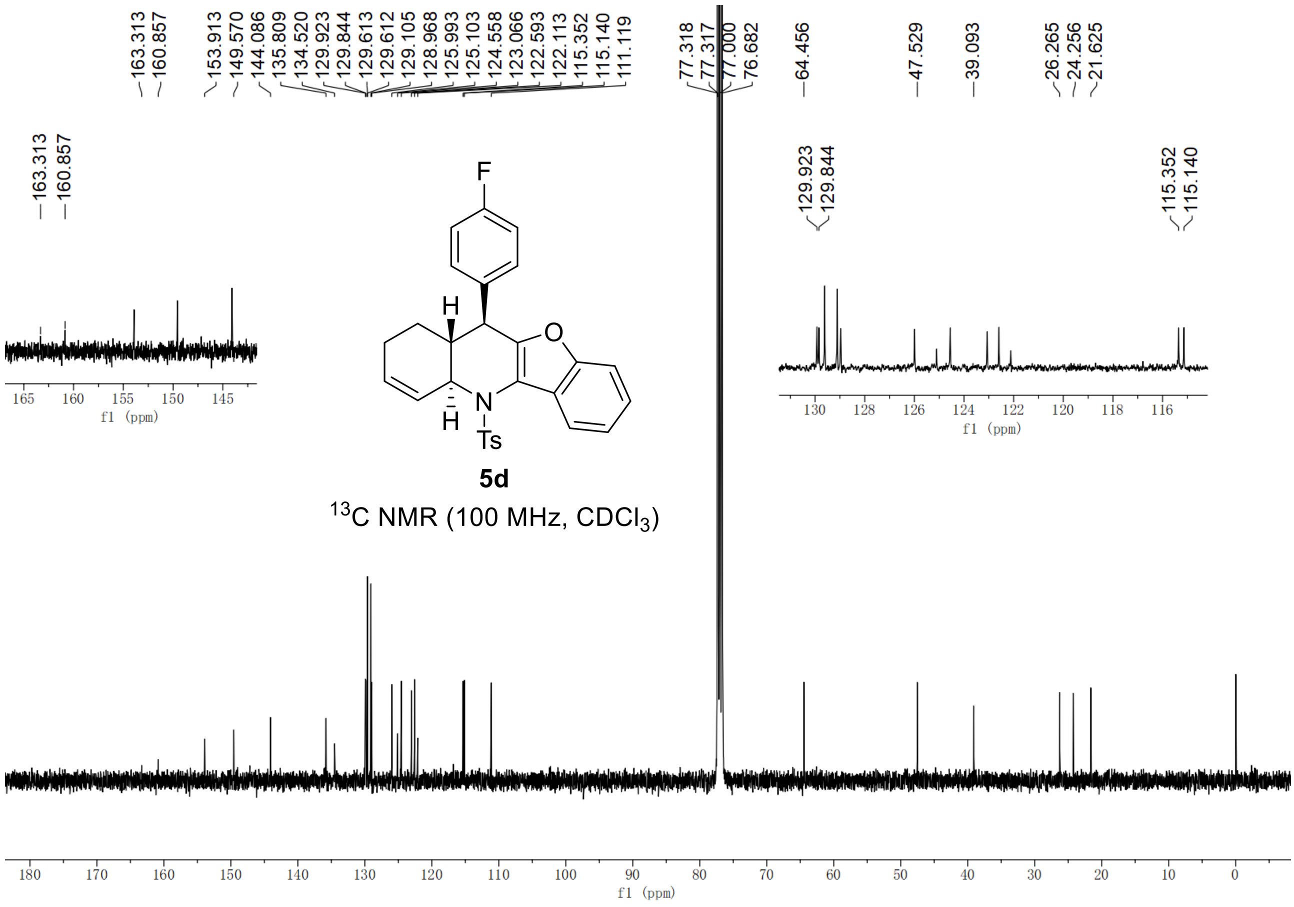


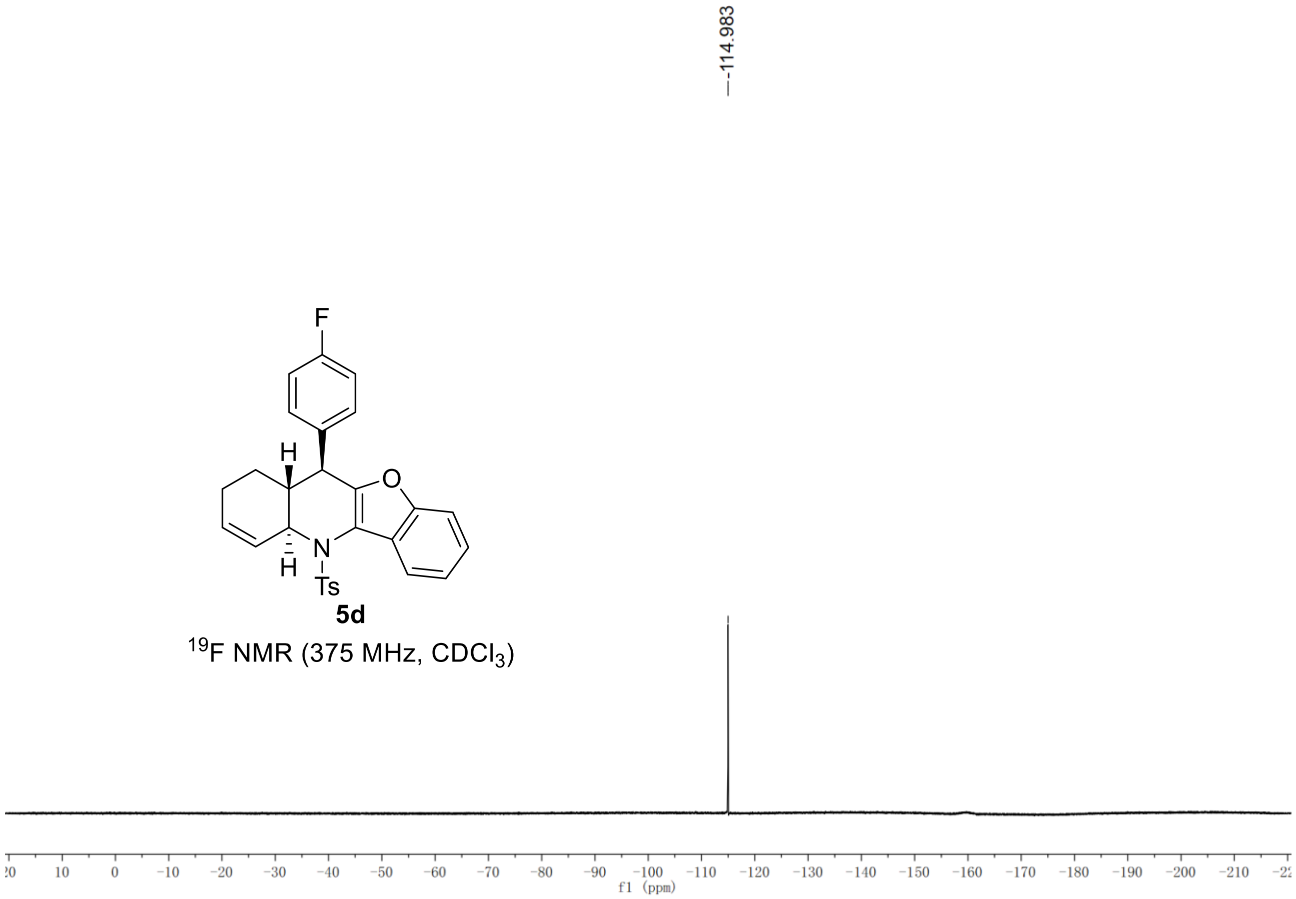

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.151 | VB | 0.7670 | 2.88403e4 | 592.89081 | 51.8688 |
| 2 | 21.535 | BB | 1.1689 | 2.67621e4 | 345.97769 | 48.1312 |




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.201 | BV | 0.3814 | 1.23008e4 | 502.99823 | 91.1729 |
| 2 | 21.412 | BB | 0.6764 | 1190.93762 | 27.53836 | 8.8271 |

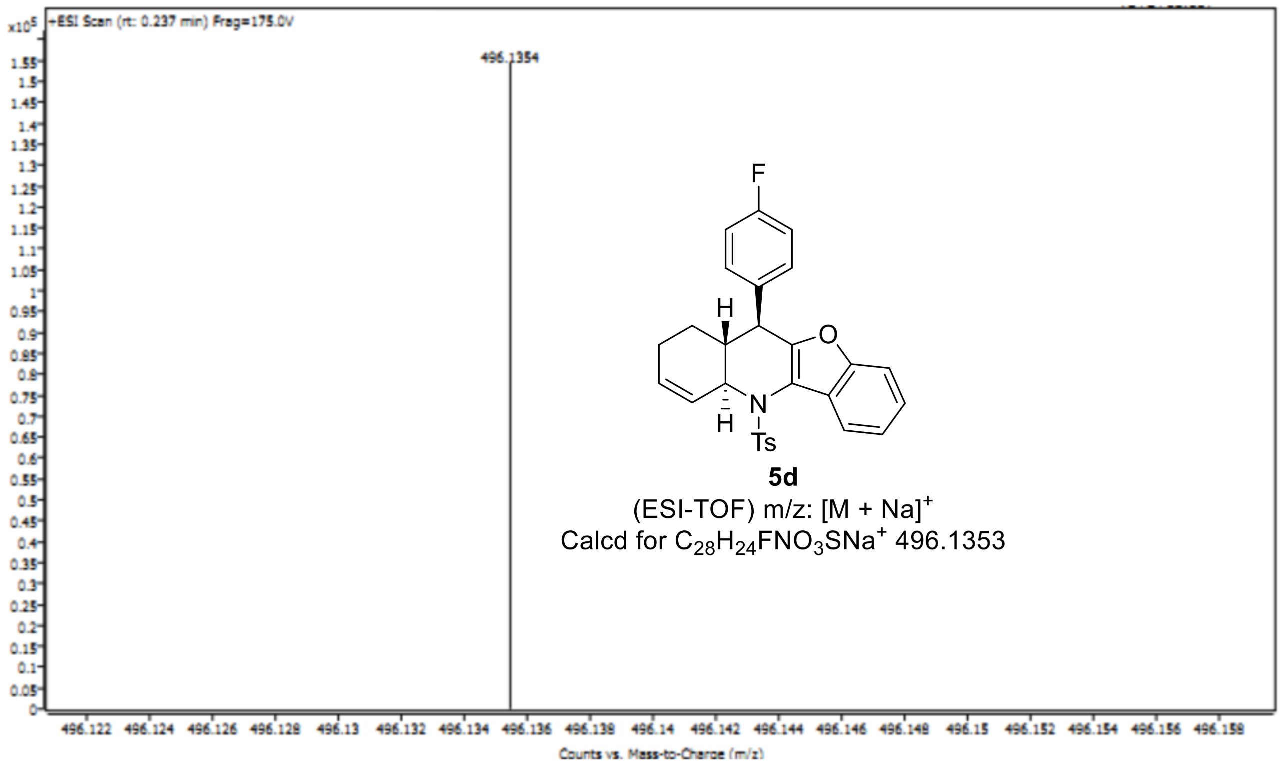

+ESI Scan (rt: 0.235 min) Frag=175.0V
x10^5
492.1606
Counts vs. Mass-to-Charge (m/z)
Me
H
O
N
H
Ts
5c
(ESI-TOF) m/z: [M +Na]+
Calcd for C29H27NO3SNa+ 492.1604


8.123
8.104
7.656
7.636
7.333
7.329
7.317
7.313
7.295
7.282
6.902
6.881
6.860
6.695
6.682
6.674
6.661
6.418
6.392
6.001
5.978
5.972
5.956
4.227
4.215
4.206
4.186
4.178
3.542
3.516
2.432
2.049
2.031
1.988
1.864
1.855
1.852
1.814
1.780
1.755
1.650
1.641
1.628
1.613
1.608
1.292
1.274
1.259
1.243
1.230
0.000
F
H
O
N
H
Ts
5d
1H NMR (400 MHz, CDCl3)
1.01
2.00
4.01
2.01
2.05
1.00
1.00
1.00
1.02
3.09
1.05
1.10
2.00
1.12
f1 (ppm)

163.313
160.857
153.913
149.570
144.086
135.809
134.520
129.923
129.844
129.613
129.612
129.105
128.968
125.993
125.103
124.558
123.066
122.593
122.113
115.352
115.140
111.119
77.318
77.317
77.000
76.682
64.456
47.529
39.093
26.265
24.256
21.625
F
H
O
N
H
Ts
5d
13C NMR (100 MHz, CDCl3)
f1 (ppm)




**5d**

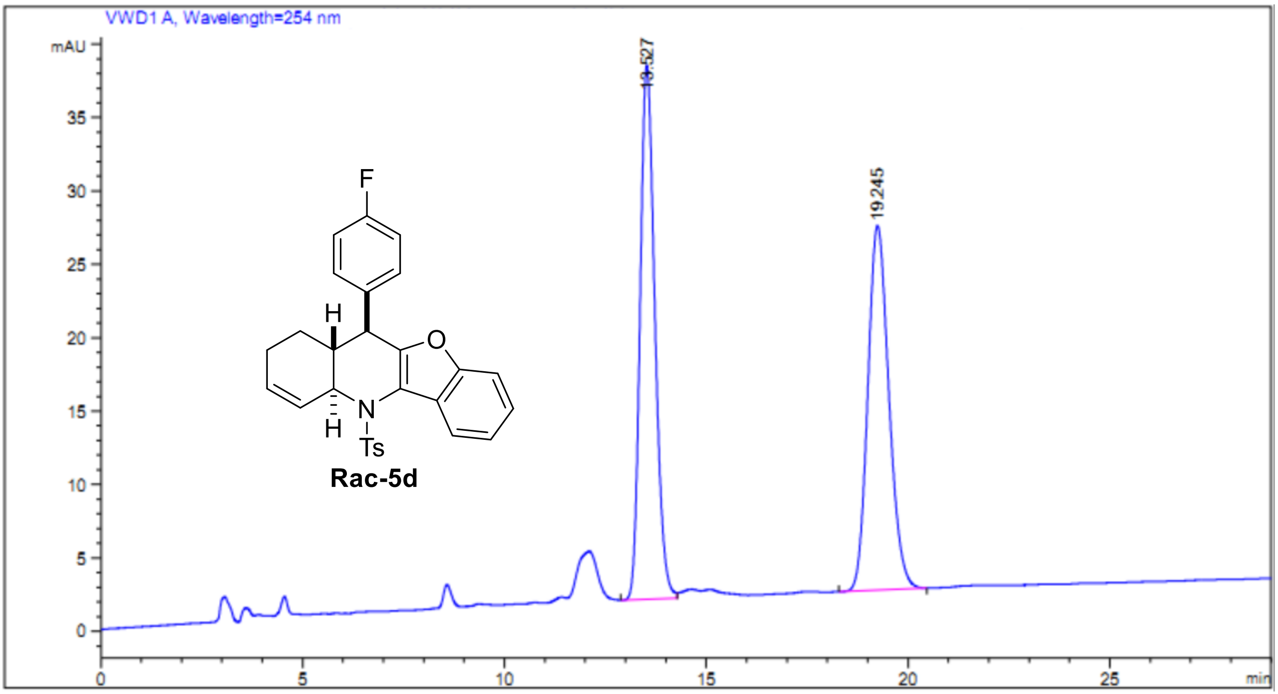
$^{19}F$ NMR (375 MHz, $CDCl_3$)



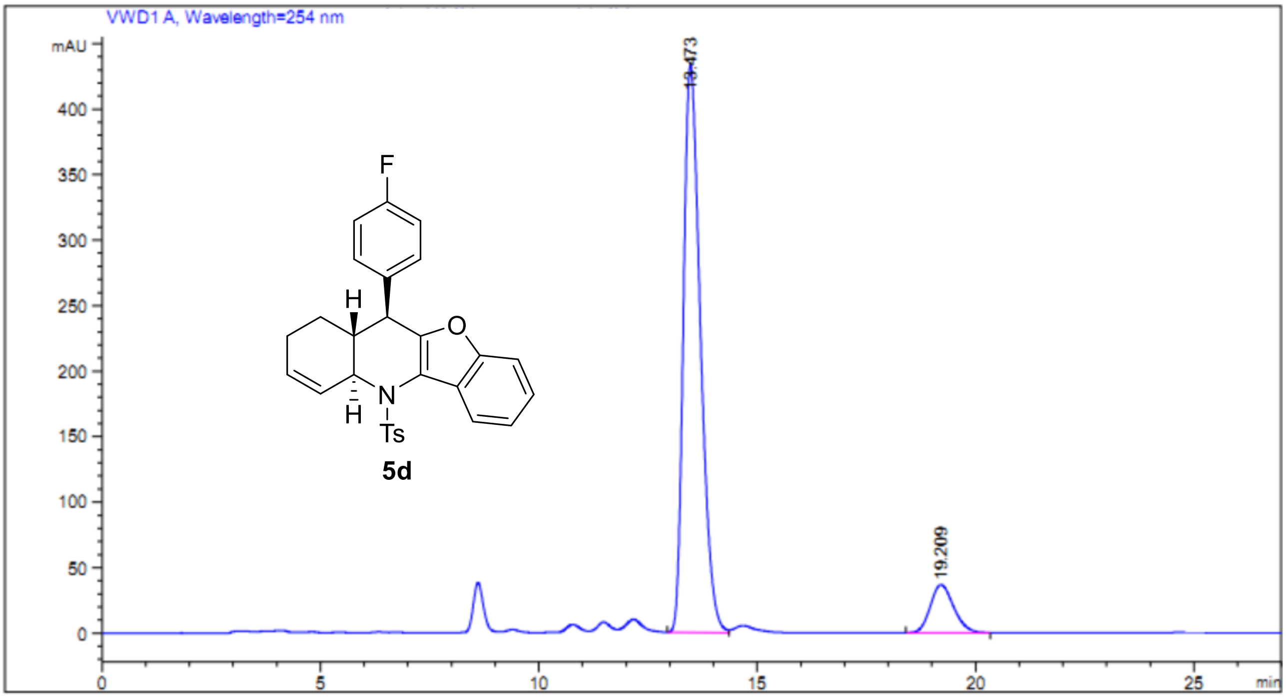

**5d**

(ESI-TOF) m/z: $[M + Na]^+$

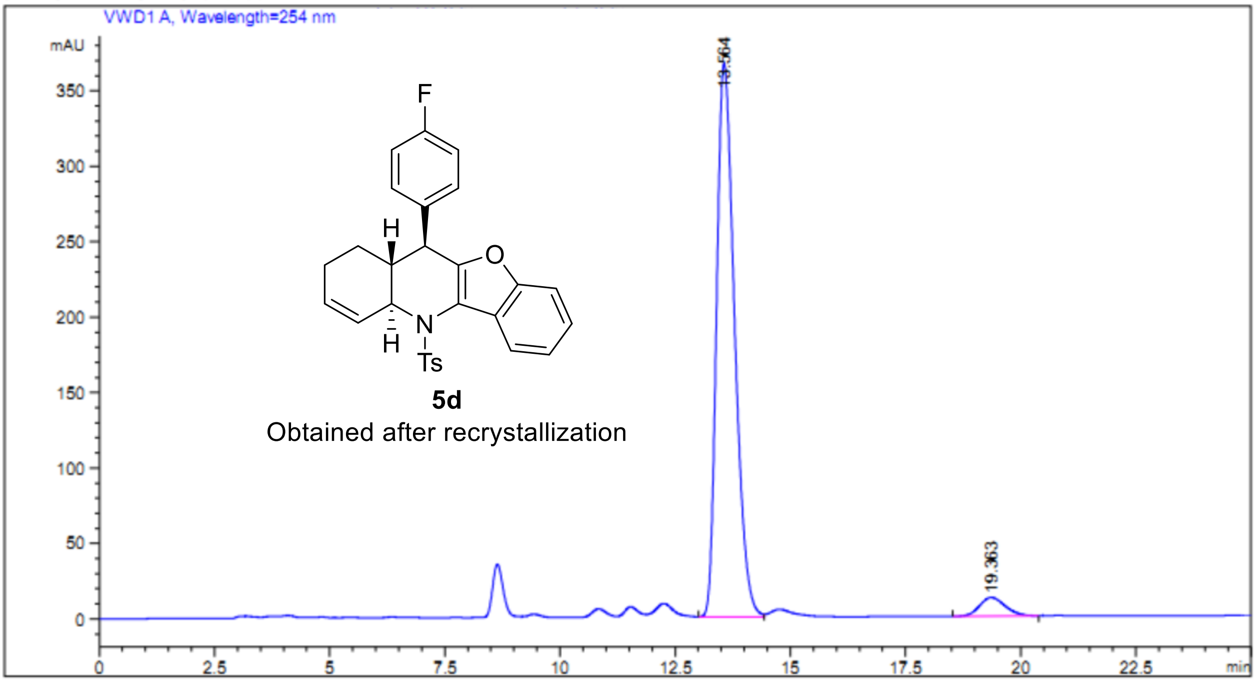
Calcd for $C_{28}H_{24}FNO_3SNa^+$ 496.1353



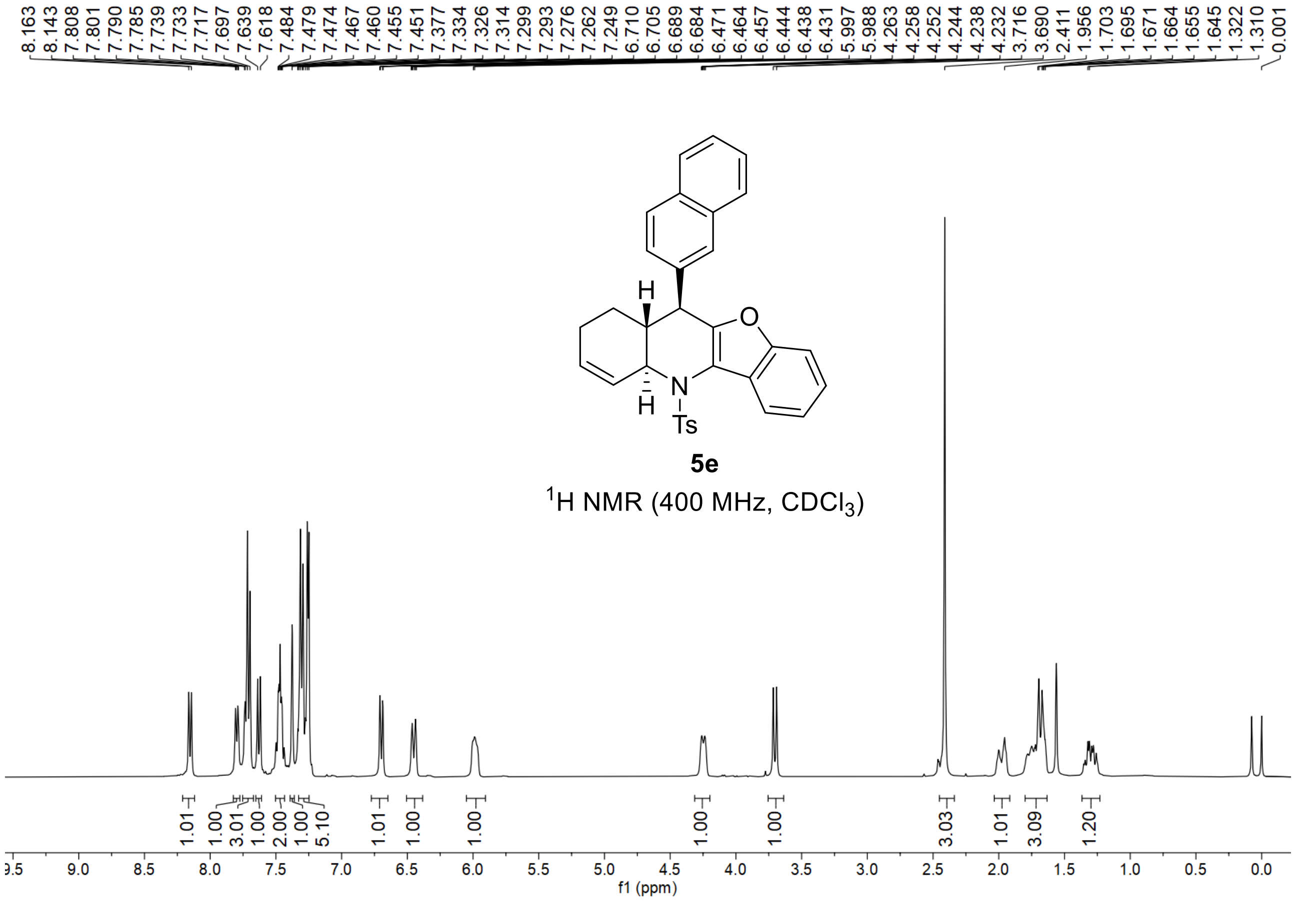

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.527 | BV | 0.3923 | 923.65717 | 36.37949 | 50.6615 |
| 2 | 19.245 | BB | 0.5595 | 899.53528 | 24.83106 | 49.3385 |

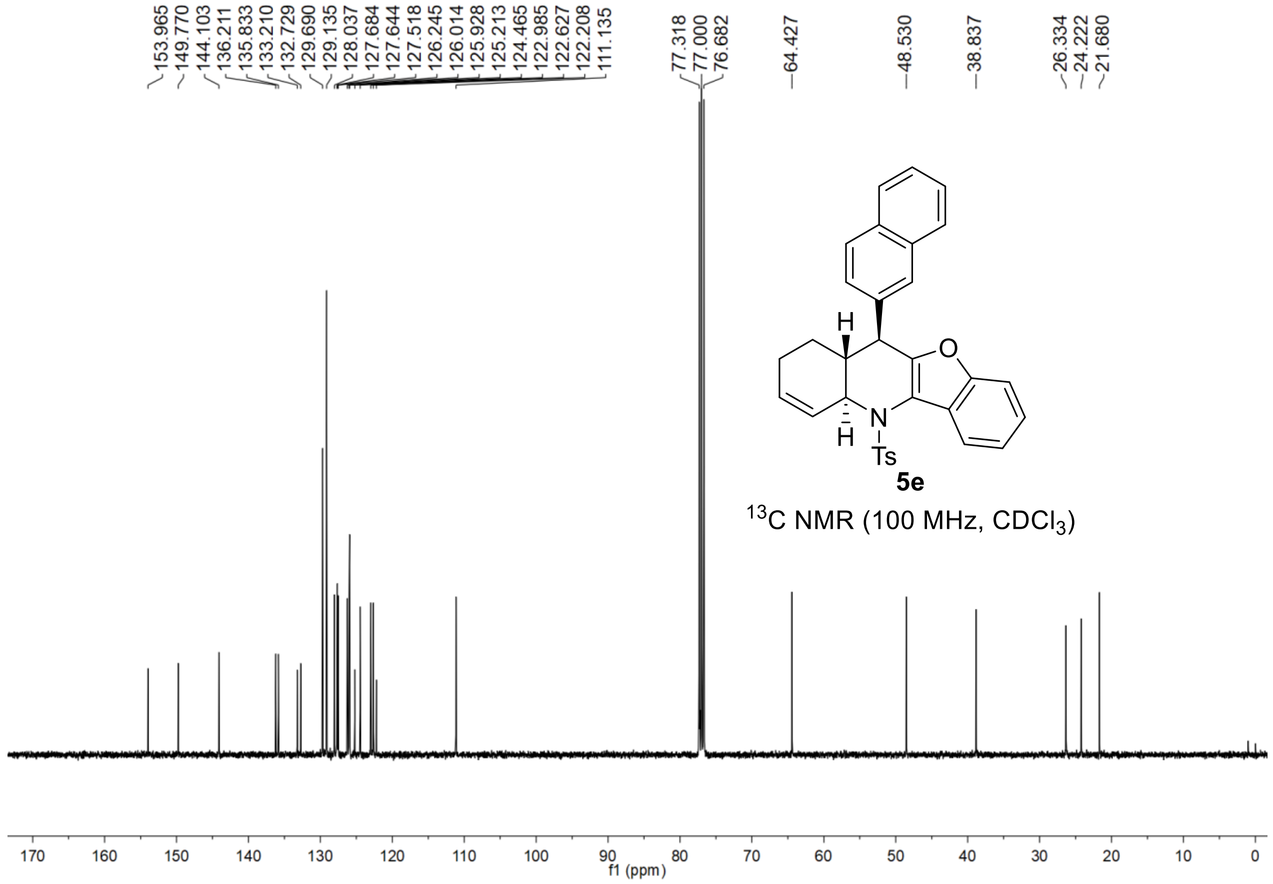


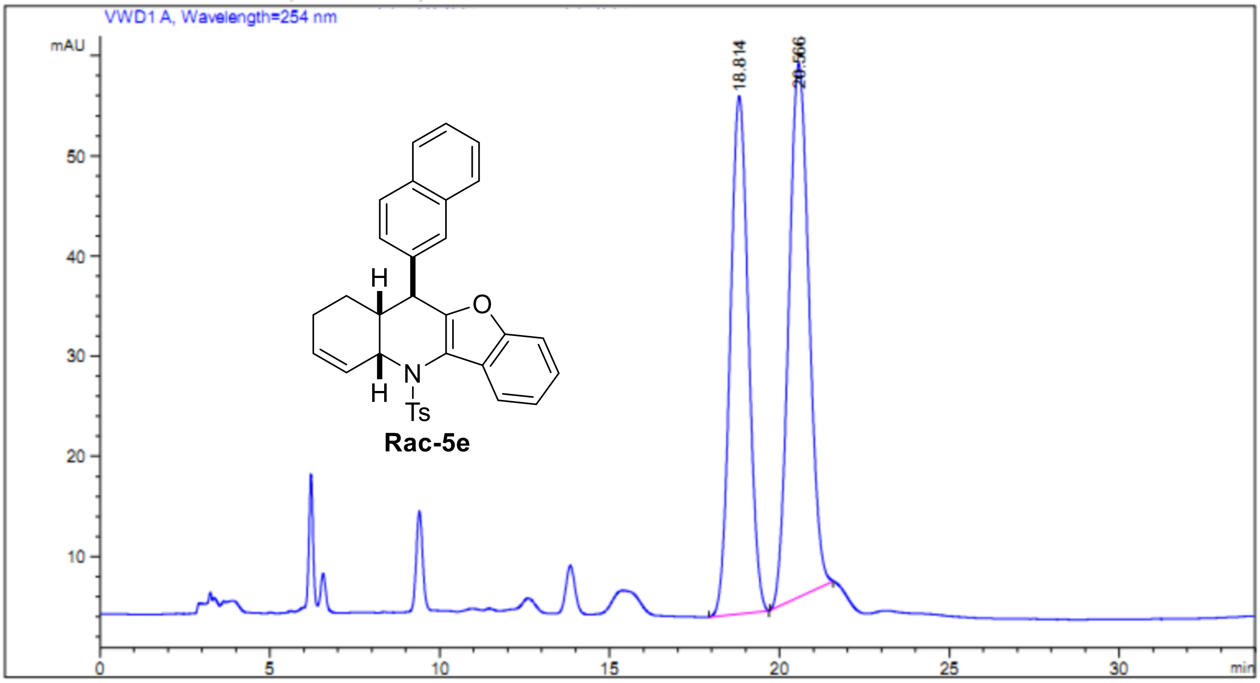

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.473 | BV | 0.4199 | 1.16948e4 | 433.10706 | 89.5814 |
| 2 | 19.209 | BB | 0.5723 | 1360.13989 | 36.68816 | 10.4186 |



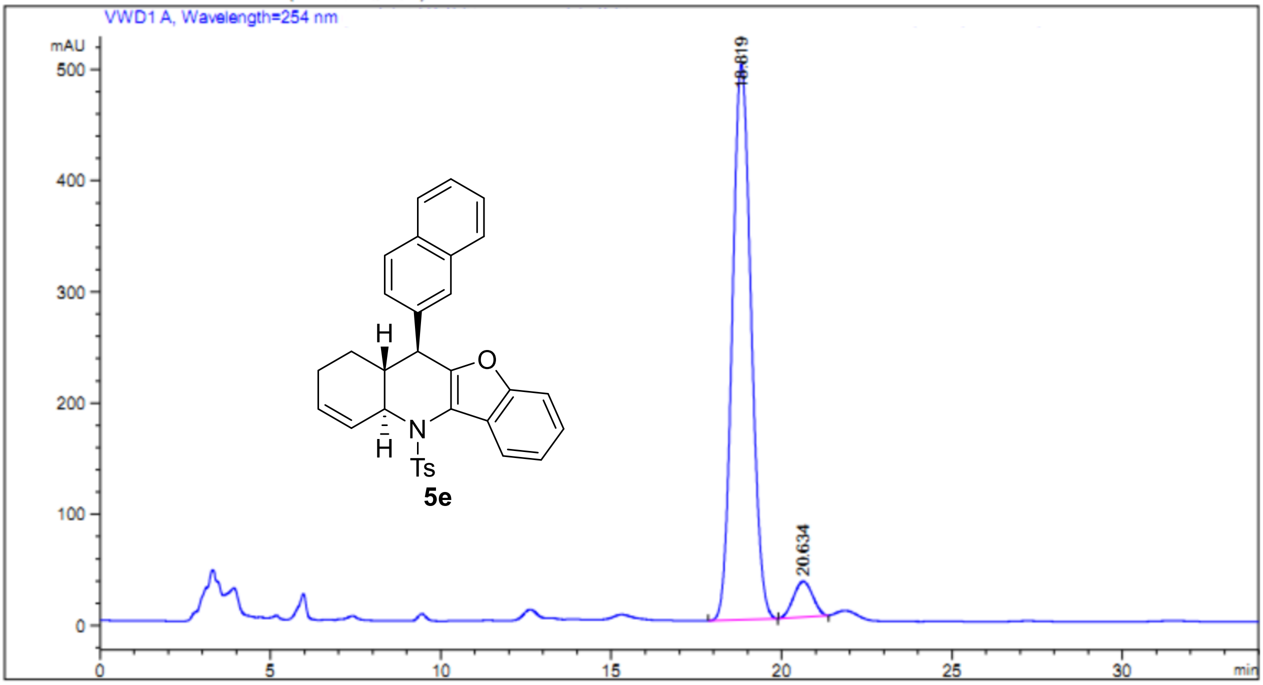

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 13.564 | BV | 0.4205 | 9921.04980 | 366.71774 | 95.3080 |
| 2 | 19.363 | VV | 0.6040 | 488.41245 | 12.43148 | 4.6920 |


8.163 8.143 7.808 7.801 7.790 7.785 7.739 7.733 7.717 7.697 7.639 7.618 7.484 7.479 7.474 7.467 7.460 7.455 7.451 7.377 7.334 7.326 7.314 7.299 7.293 7.276 7.262 7.249 6.710 6.705 6.689 6.684 6.471 6.464 6.457 6.444 6.438 6.431 5.997 5.988 4.263 4.258 4.252 4.244 4.238 4.232 3.716 3.690 2.411 1.956 1.703 1.695 1.671 1.664 1.655 1.645 1.322 1.310 0.001
H
O
N
H
Ts
5e
$^{1}$H NMR (400 MHz, CDCl$_3$)
1.01 1.00 3.01 1.00 2.00 1.00 5.10 1.01 1.00 1.00 1.00 1.00 3.03 1.01 3.09 1.20
f1 (ppm)

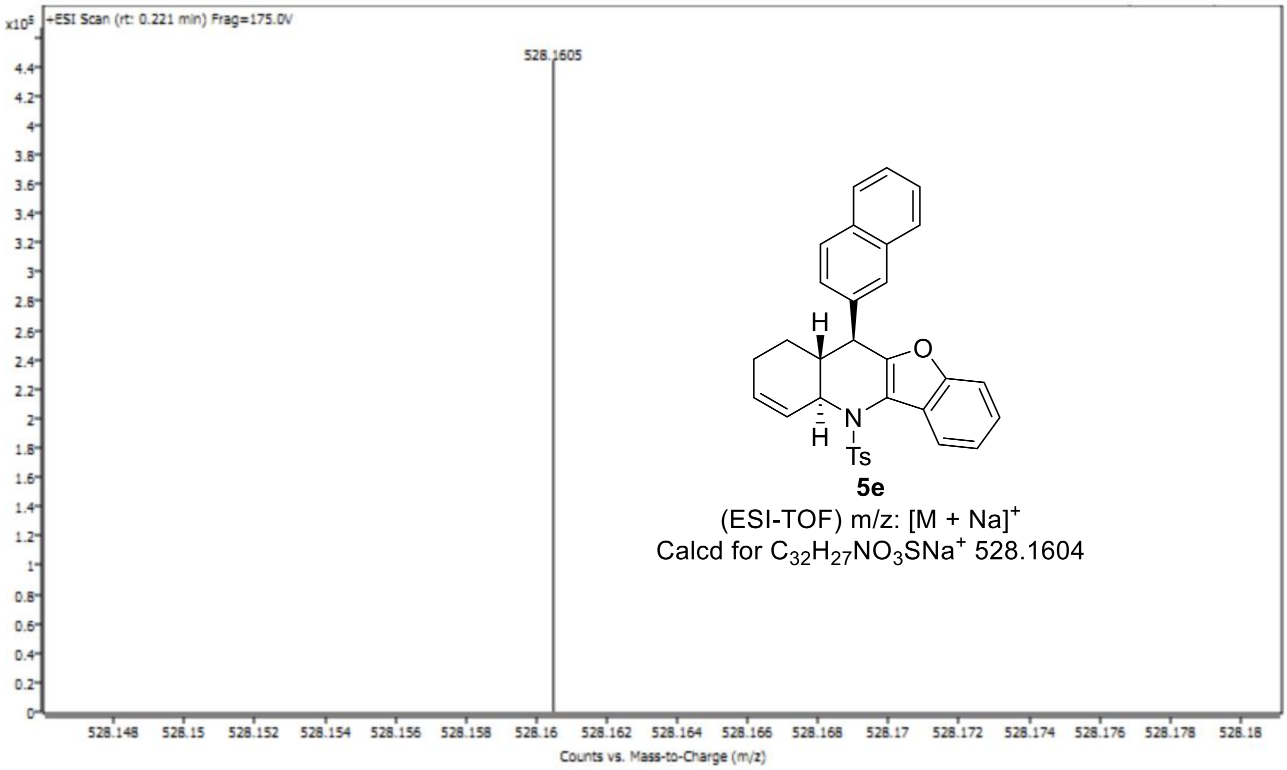

153.965 149.770 144.103 136.211 135.833 133.210 132.729 129.690 129.135 128.037 127.684 127.644 127.518 126.245 126.014 125.928 125.213 124.465 122.985 122.627 122.208 111.135
77.318 77.000 76.682
64.427
48.530
38.837
26.334 24.222 21.680
H
O
N
H
Ts
5e
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



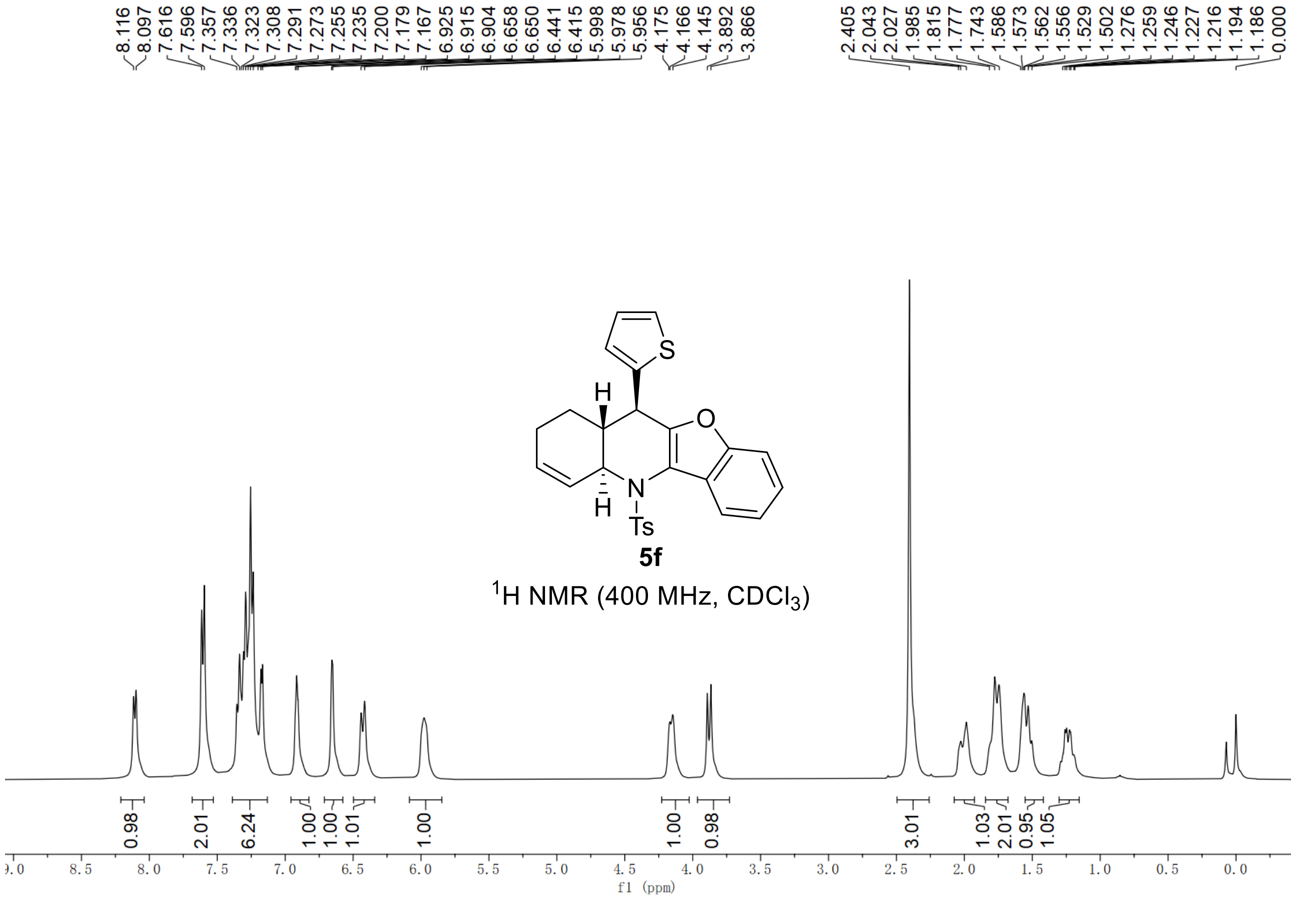

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 18.814 | BB | 0.5806 | 1914.38477 | 51.69145 | 46.5791 |
| 2 | 20.566 | BBA | 0.6454 | 2195.57861 | 53.27122 | 53.4209 |

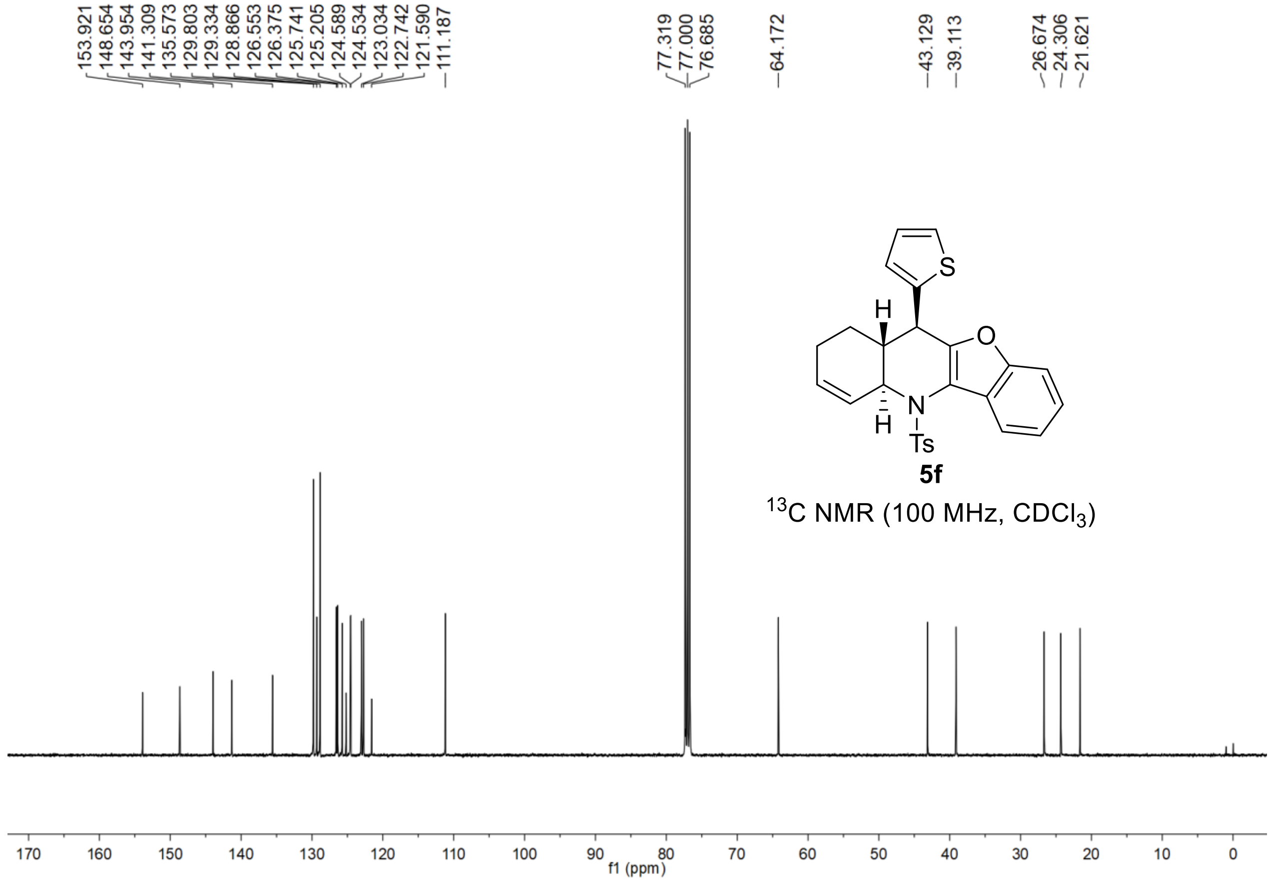


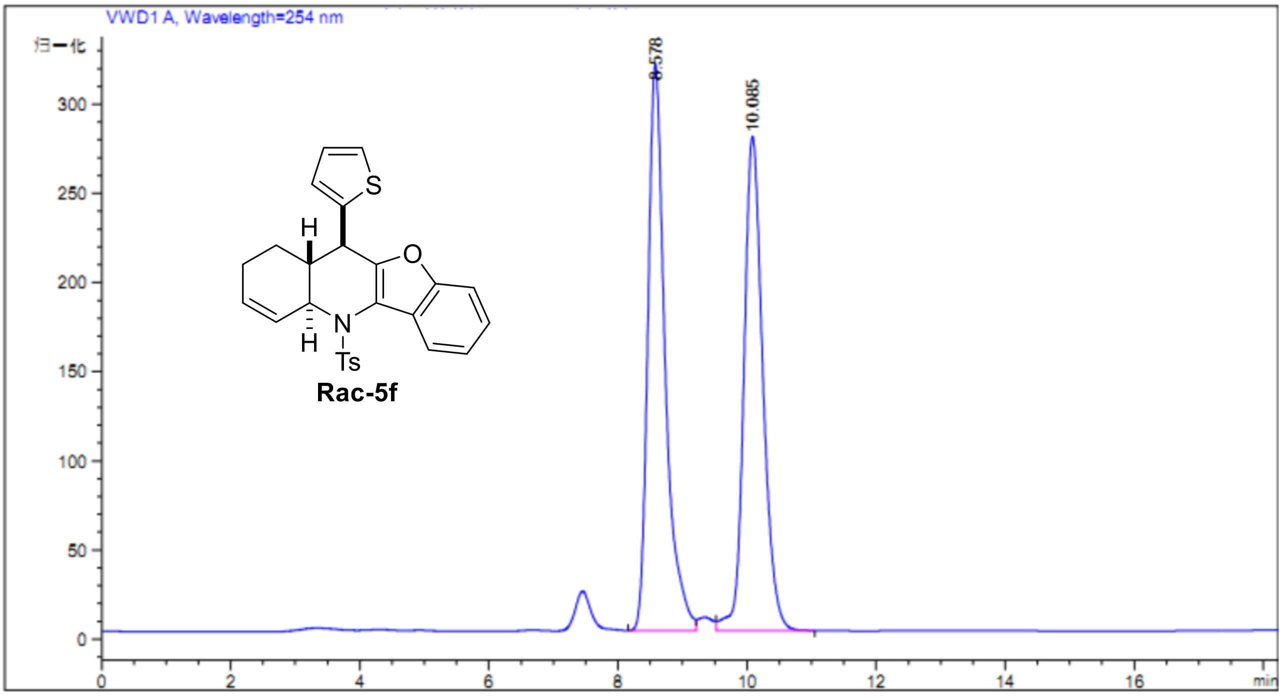

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 18.819 | BB | 0.5998 | 1.91467e4 | 499.76703 | 93.8734 |
| 2 | 20.634 | BB | 0.6256 | 1249.60059 | 32.02076 | 6.1266 |



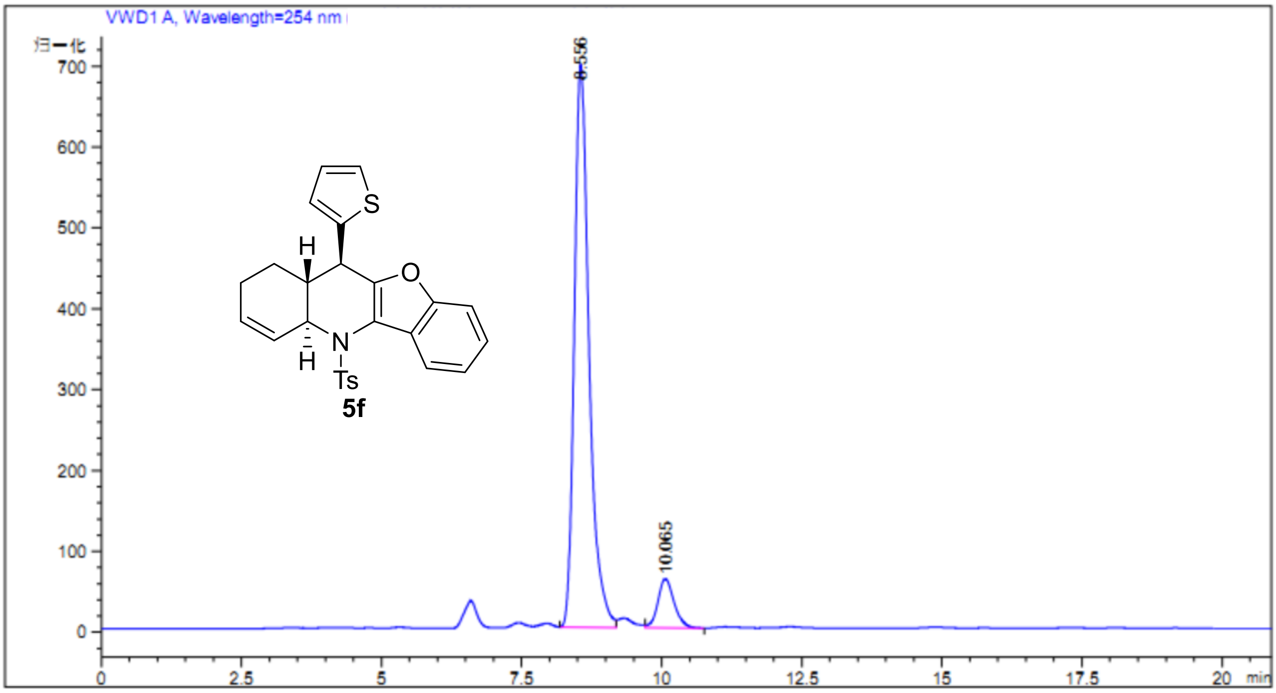
x10^5
+ESI Scan (rt: 0.221 min) Frag=175.0V
528.1605
H
O
N
H
Ts
5e
(ESI-TOF) m/z: [M + Na]+
Calcd for C32H27NO3SNa+ 528.1604
Counts vs. Mass-to-Charge (m/z)


8.116 8.097 7.616 7.596 7.357 7.336 7.323 7.308 7.291 7.273 7.255 7.235 7.200 7.179 7.167 6.925 6.915 6.904 6.658 6.650 6.441 6.415 5.998 5.978 5.956 4.175 4.166 4.145 3.892 3.866
2.405 2.043 2.027 1.985 1.815 1.777 1.743 1.586 1.573 1.562 1.556 1.529 1.502 1.276 1.259 1.246 1.227 1.216 1.194 1.186 0.000
S
H
O
N
H
Ts
5f
$^{1}$H NMR (400 MHz, $CDCl_3$)
0.98 2.01 6.24 1.00 1.00 1.01 1.00 1.00 0.98 3.01 1.03 2.01 0.95 1.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

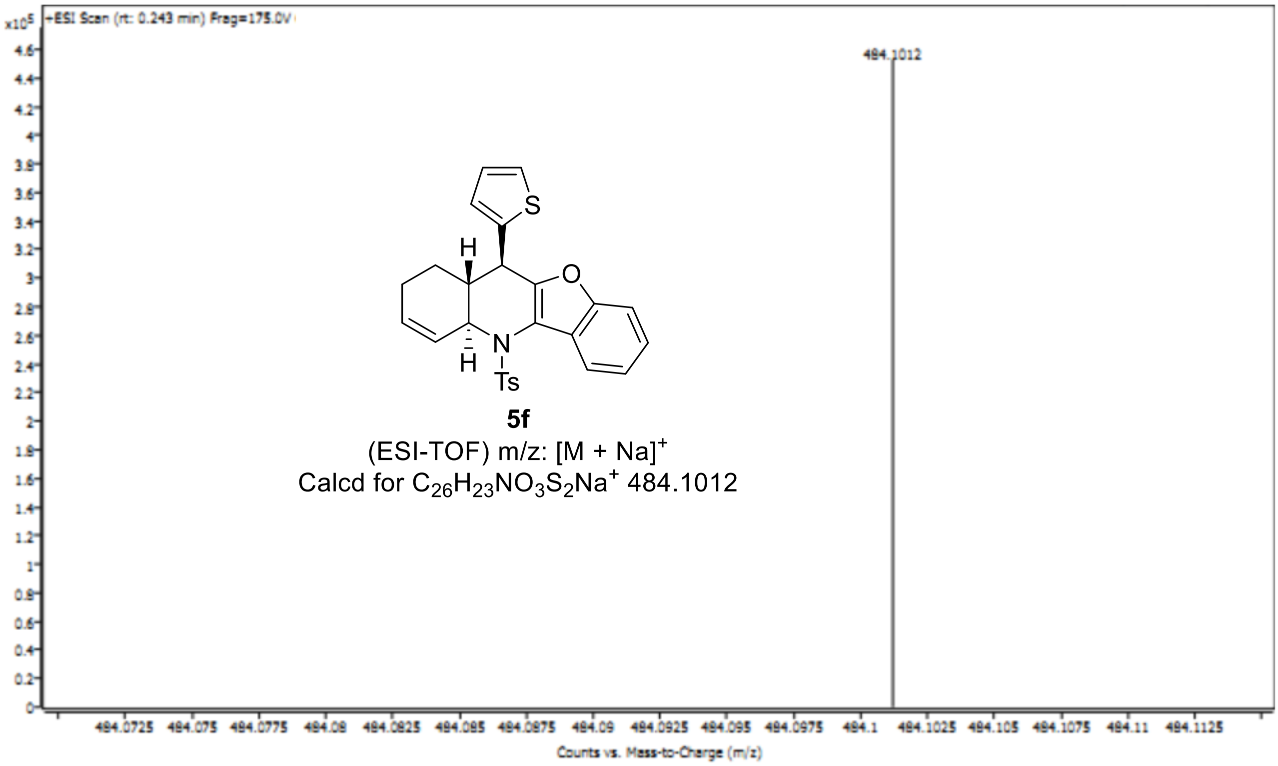

153.921 148.654 143.954 141.309 135.573 129.803 129.334 128.866 126.553 126.375 125.741 125.205 124.589 124.534 123.034 122.742 121.590 111.187
77.319 77.000 76.685
64.172
43.129 39.113
26.674 24.306 21.621
S
H
O
N
H
Ts
5f
$^{13}$C NMR (100 MHz, $CDCl_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

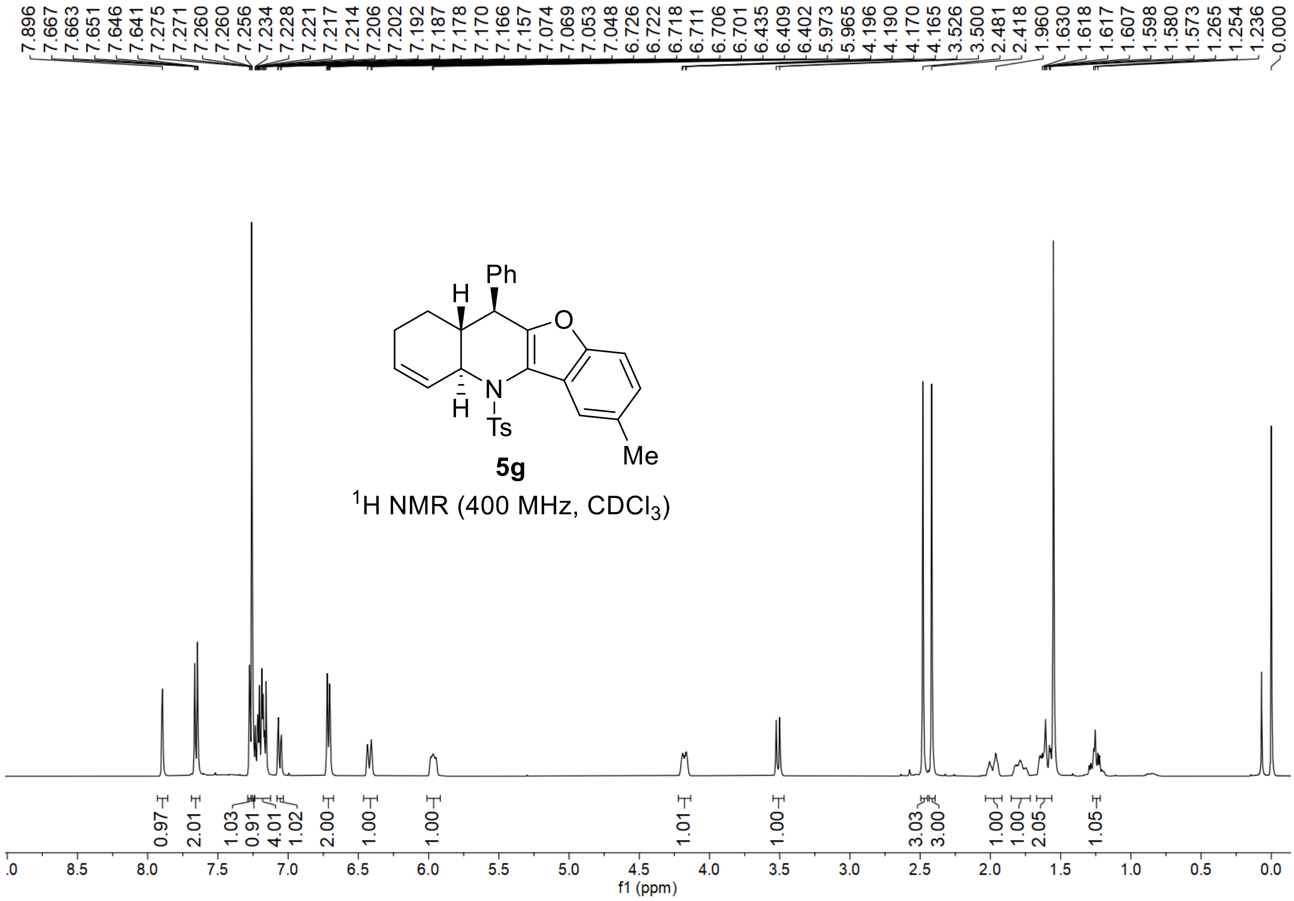



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.578 | BV | 0.2796 | 5904.43262 | 317.42151 | 51.1398 |
| 2 | 10.085 | VB | 0.3103 | 5641.23438 | 277.06821 | 48.8602 |

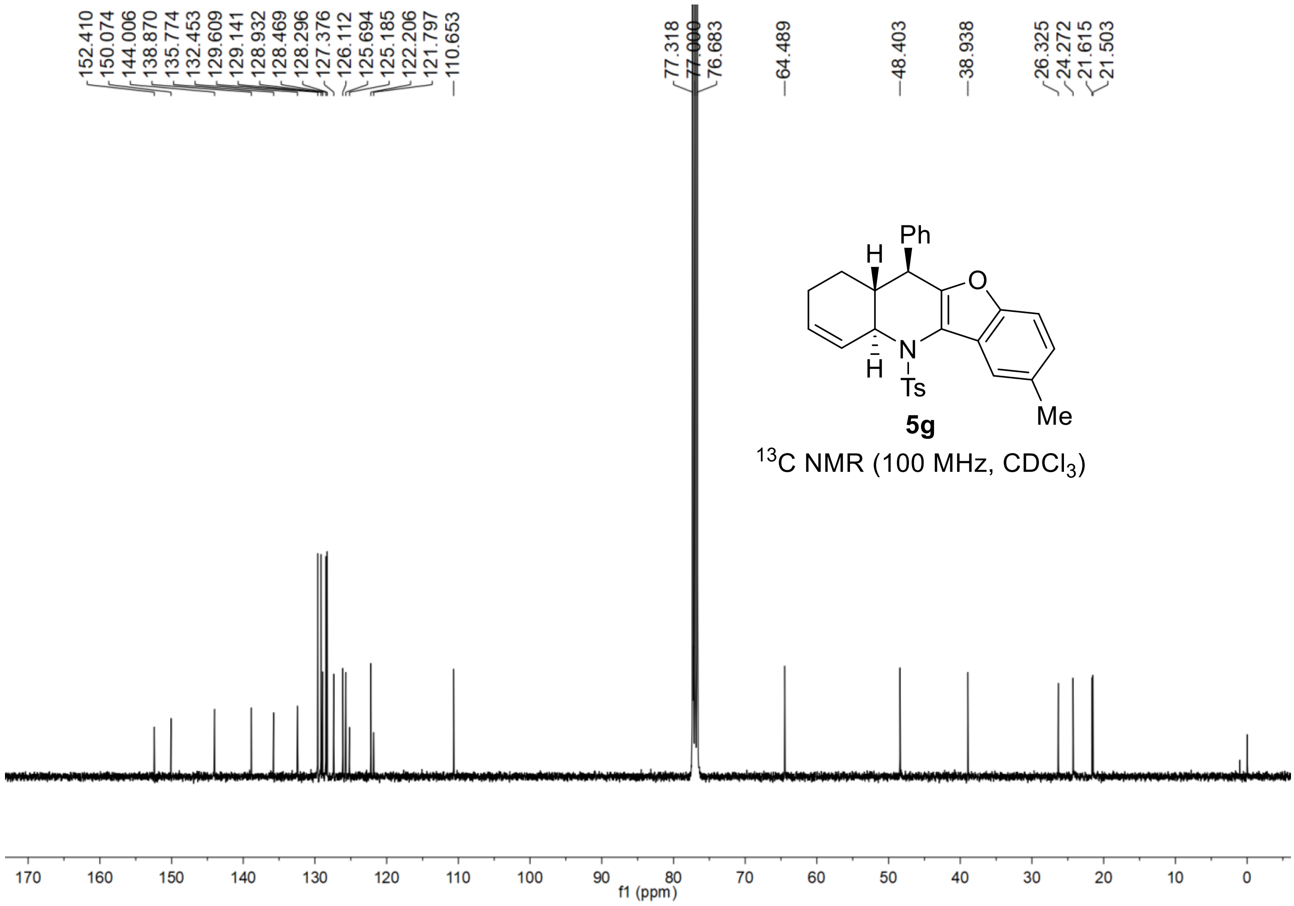



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.556 | BV | 0.2773 | 1.27241e4 | 696.05701 | 91.2607 |
| 2 | 10.065 | VB | 0.3049 | 1218.48169 | 60.47950 | 8.7393 |

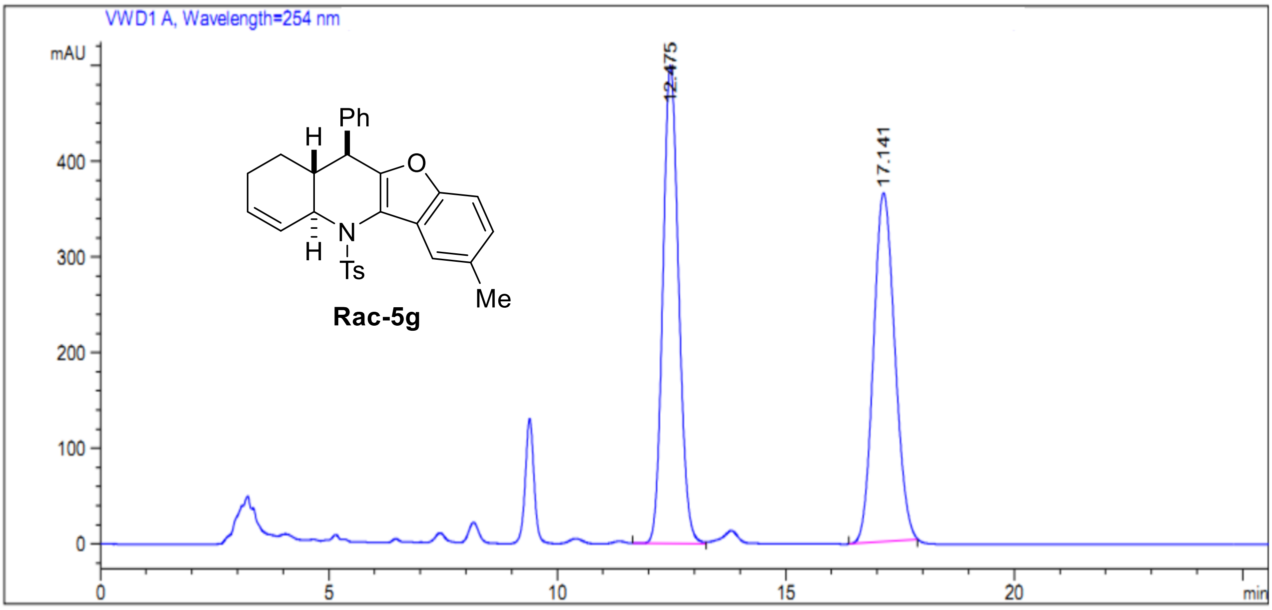

+ESI Scan (rt: 0.243 min) Frag=175.0V
x10^5
484.1012
5f
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H23NO3S2Na+ 484.1012
Counts vs. Mass-to-Charge (m/z)



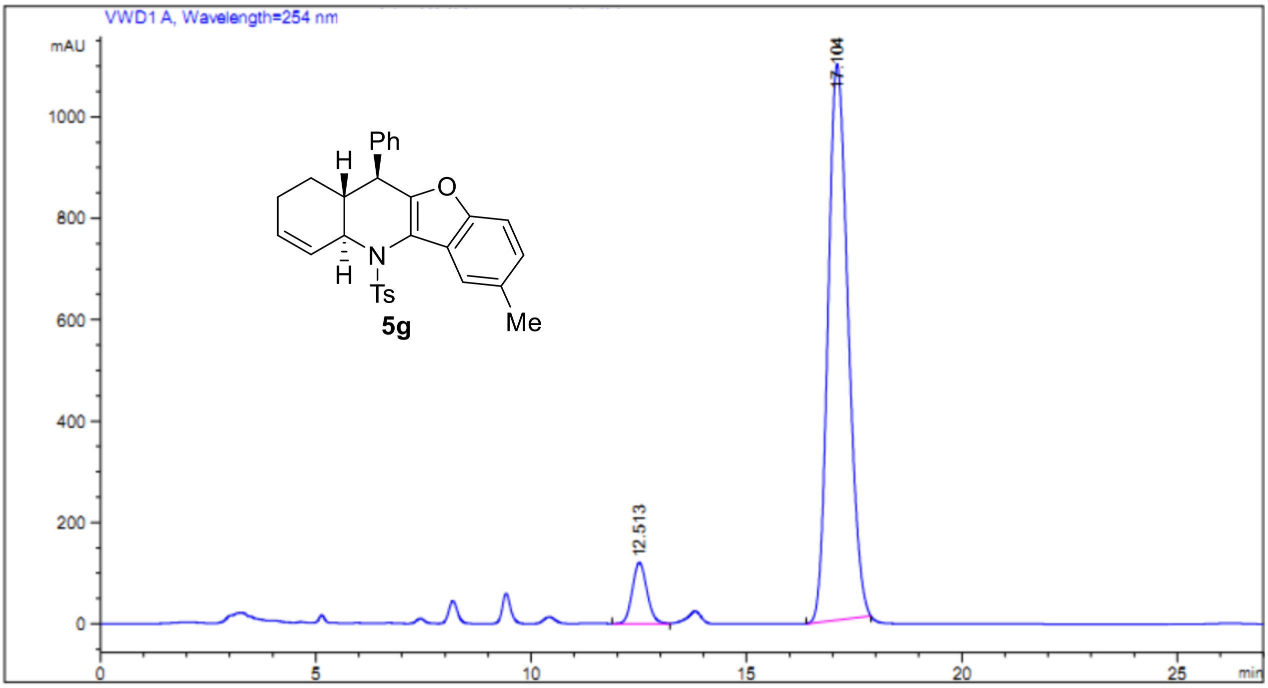
Ph
H
O
N
H
Ts
Me
5g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

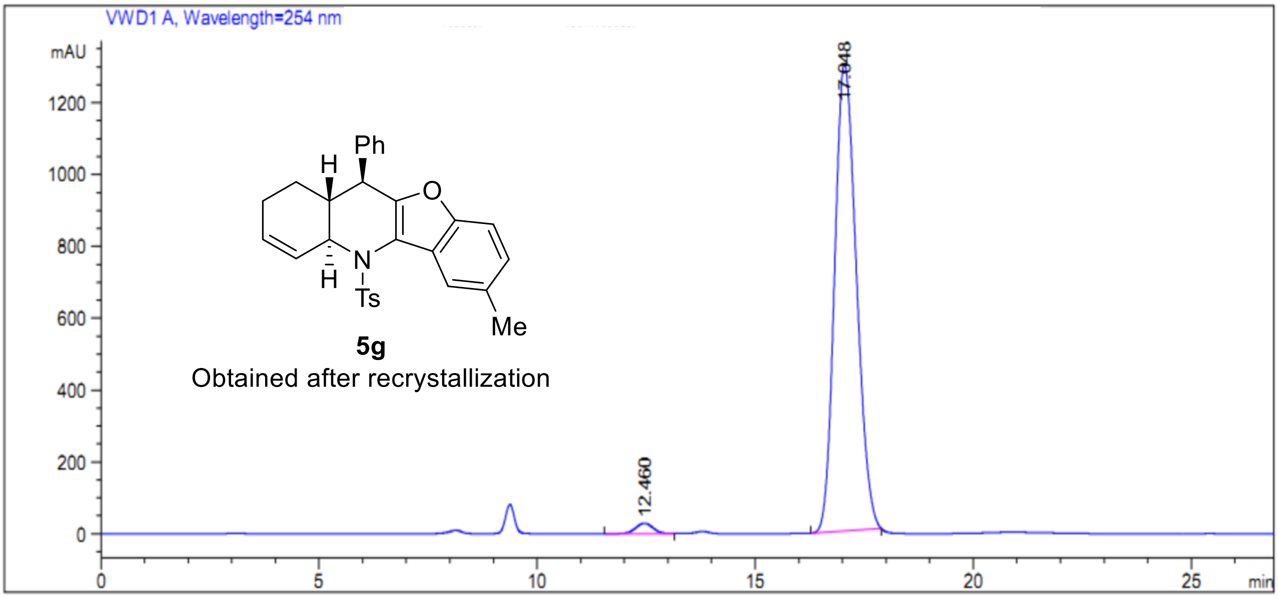
Ph
H
O
N
H
Ts
Me
5g
13C NMR (100 MHz, CDCl3)
f1 (ppm)



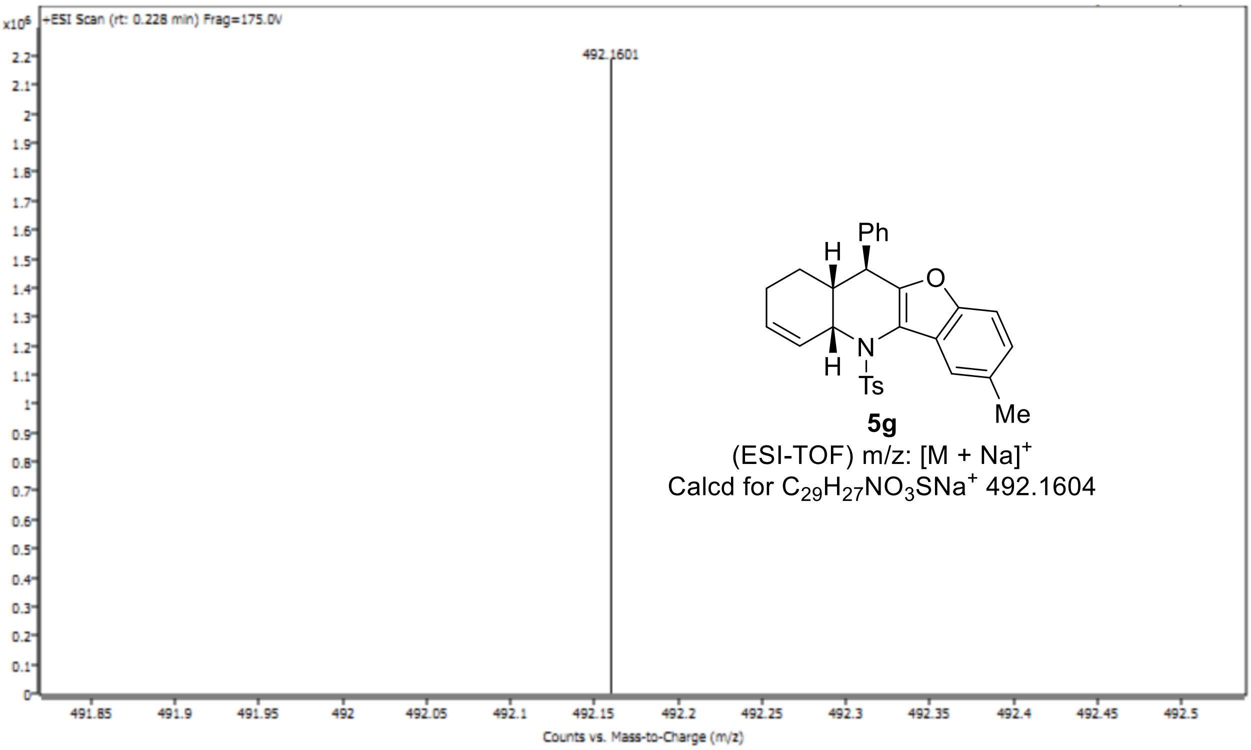

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.475 | BV | 0.3732 | 1.19901e4 | 499.58093 | 50.3257 |
| 2 | 17.141 | BBA | 0.5070 | 1.18349e4 | 364.45029 | 49.6743 |

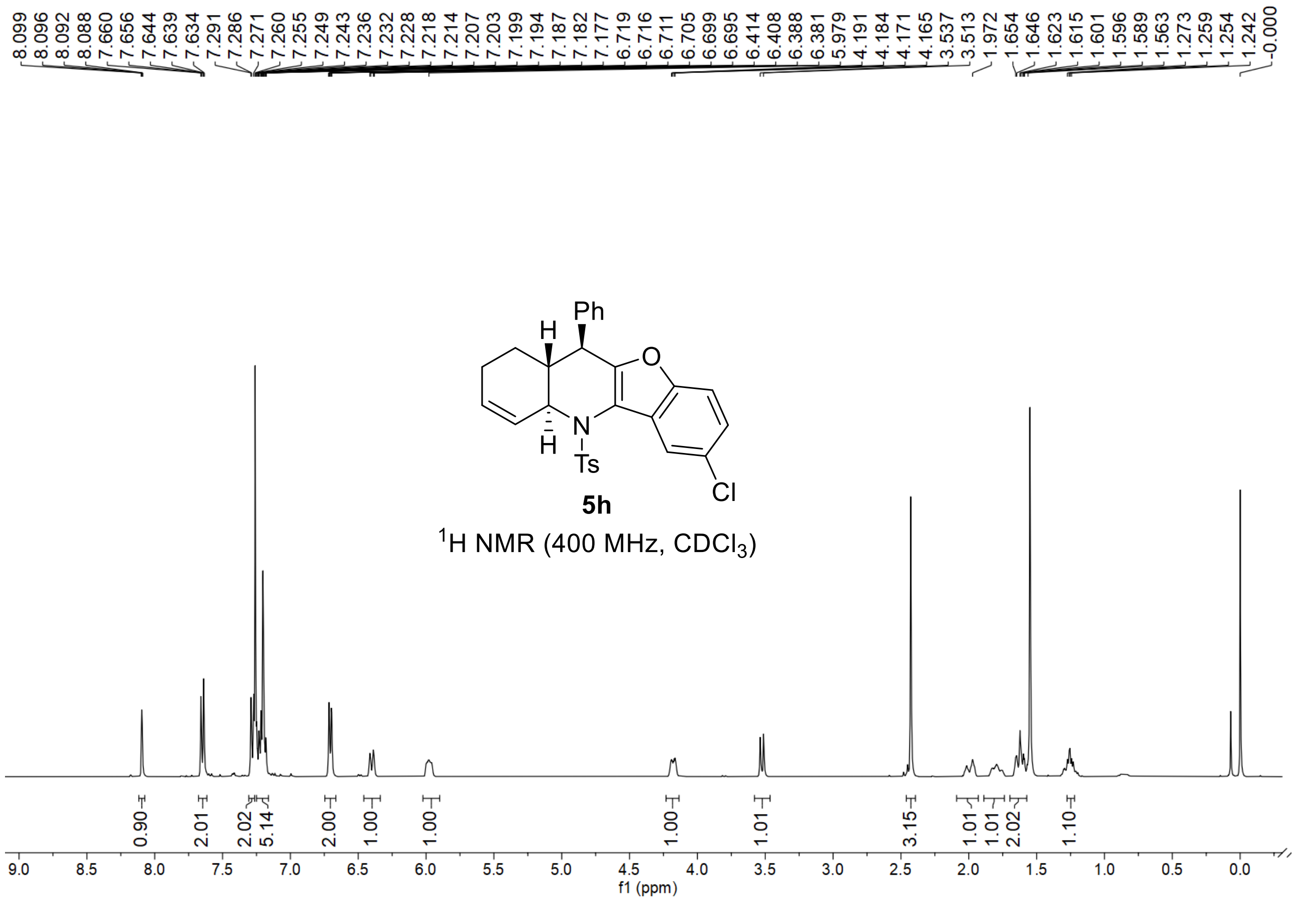


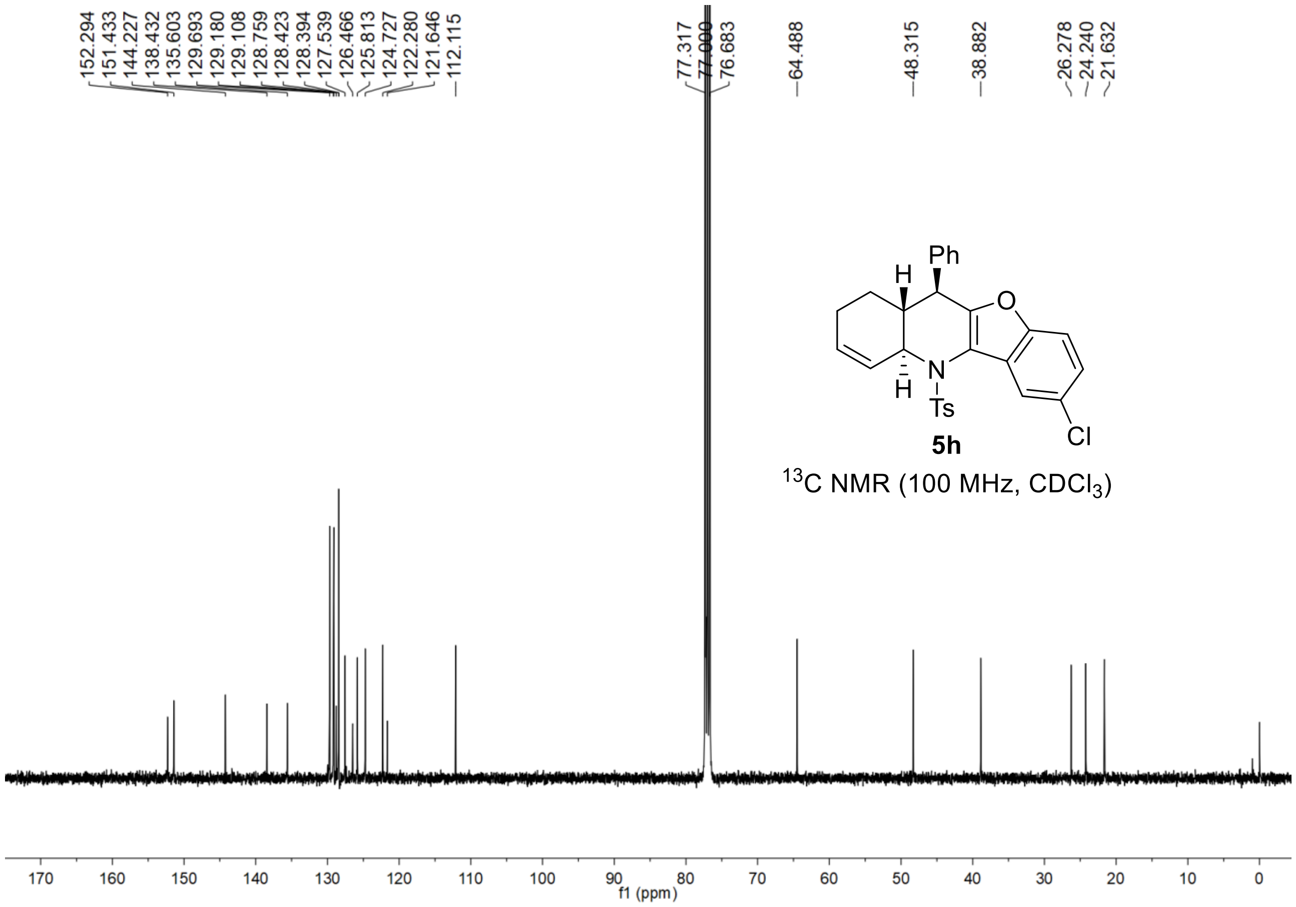

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.513 | VV | 0.3693 | 2898.59570 | 121.19361 | 7.5731 |
| 2 | 17.104 | BBA | 0.5046 | 3.53765e4 | 1096.43103 | 92.4269 |

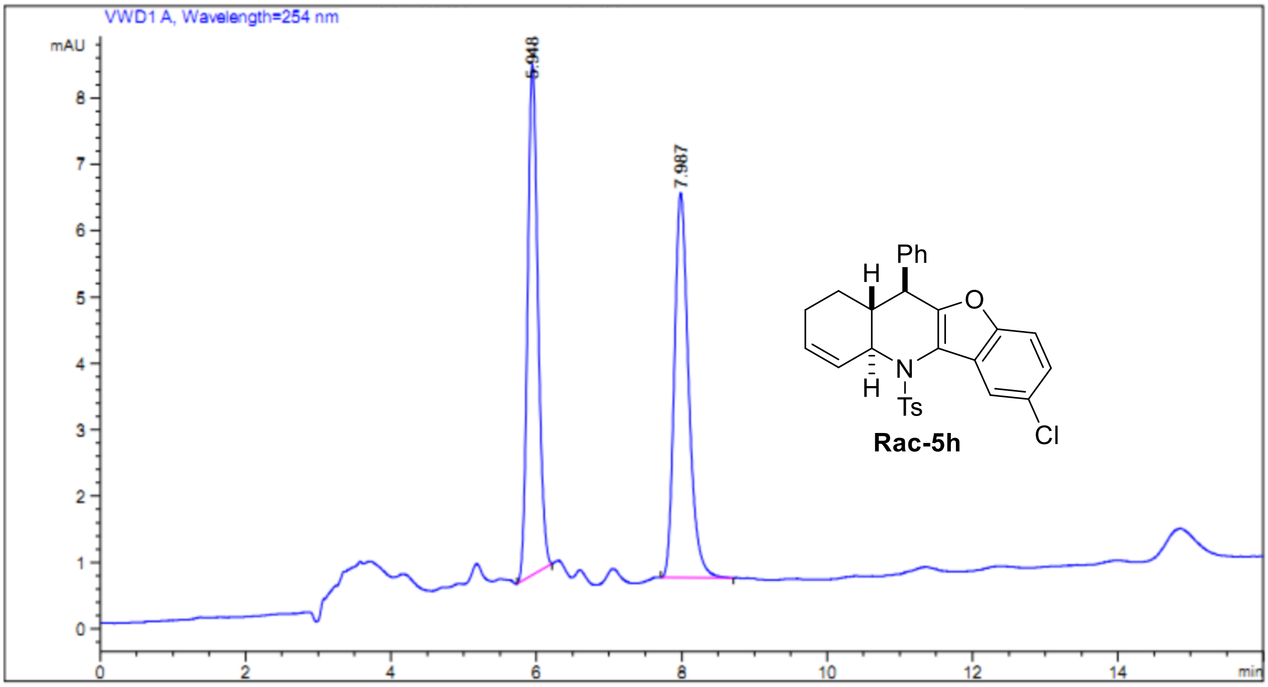



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.460 | BV | 0.4348 | 822.14380 | 29.32762 | 1.7954 |
| 2 | 17.048 | BBA | 0.5403 | 4.49707e4 | 1300.54907 | 98.2046 |

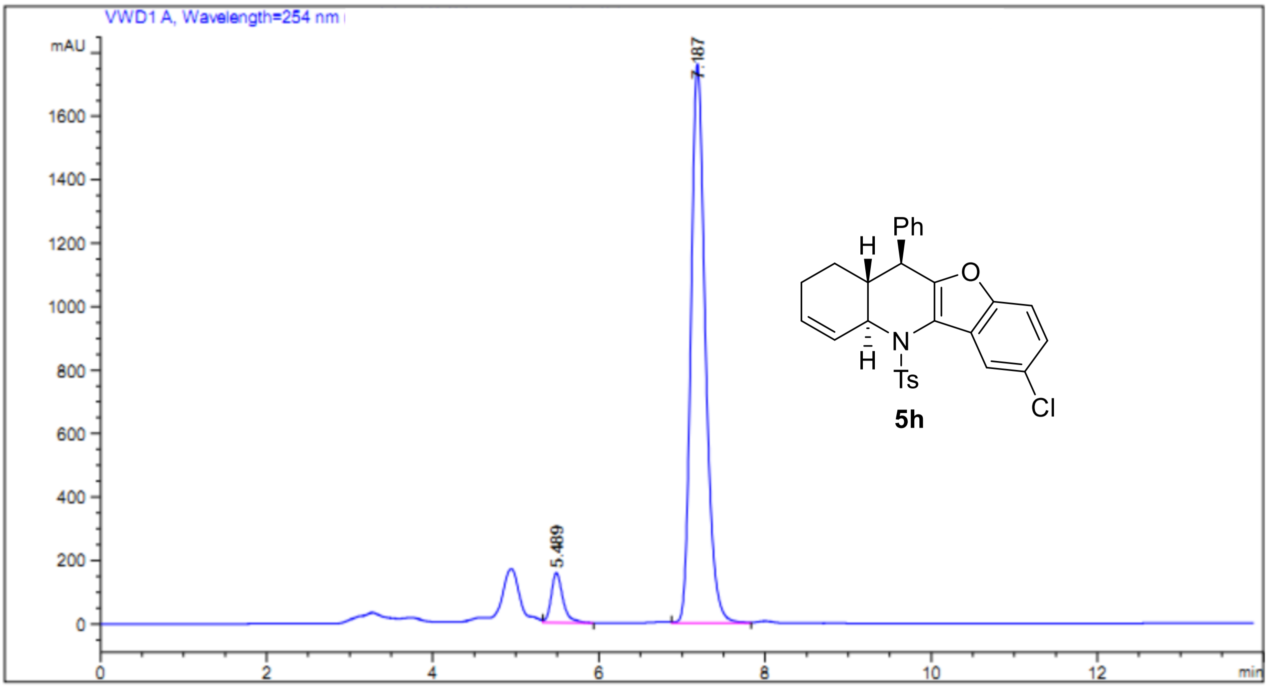



8.099 8.096 8.092 8.088 7.660 7.656 7.644 7.639 7.634 7.291 7.286 7.271 7.260 7.255 7.249 7.243 7.236 7.232 7.228 7.218 7.214 7.207 7.203 7.199 7.194 7.187 7.182 7.177 6.719 6.716 6.711 6.705 6.699 6.695 6.414 6.408 6.388 6.381 5.979 4.191 4.184 4.171 4.165 3.537 3.513 1.972 1.654 1.646 1.623 1.615 1.601 1.596 1.589 1.563 1.273 1.259 1.254 1.242 -0.000
Ph
H
O
N
H
Ts
Cl
5h
1H NMR (400 MHz, CDCl3)
0.90 2.01 2.02 5.14 2.00 1.00 1.00 1.00 1.01 3.15 1.01 1.01 2.02 1.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

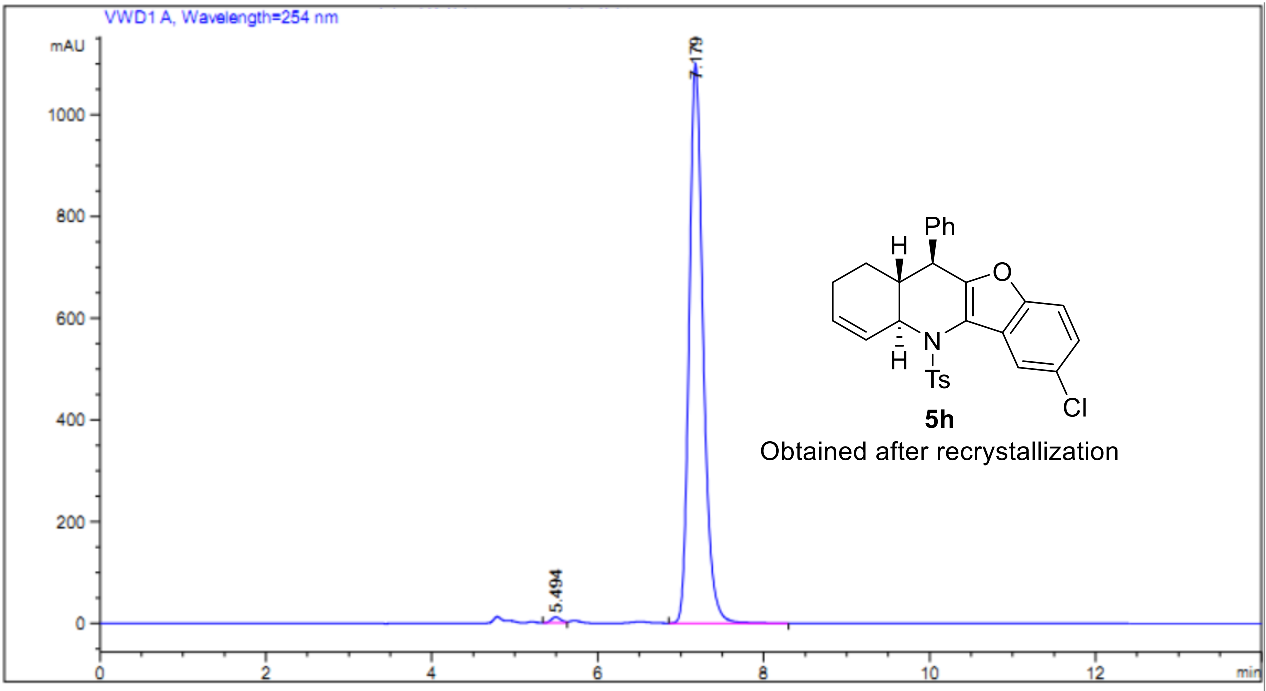

152.294 151.433 144.227 138.432 135.603 129.693 129.180 129.108 128.759 128.423 128.394 127.539 126.466 125.813 124.727 122.280 121.646 112.115
77.317 77.000 76.683
64.488
48.315
38.882
26.278 24.240 21.632
Ph
H
O
N
H
Ts
Cl
5h
13C NMR (100 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



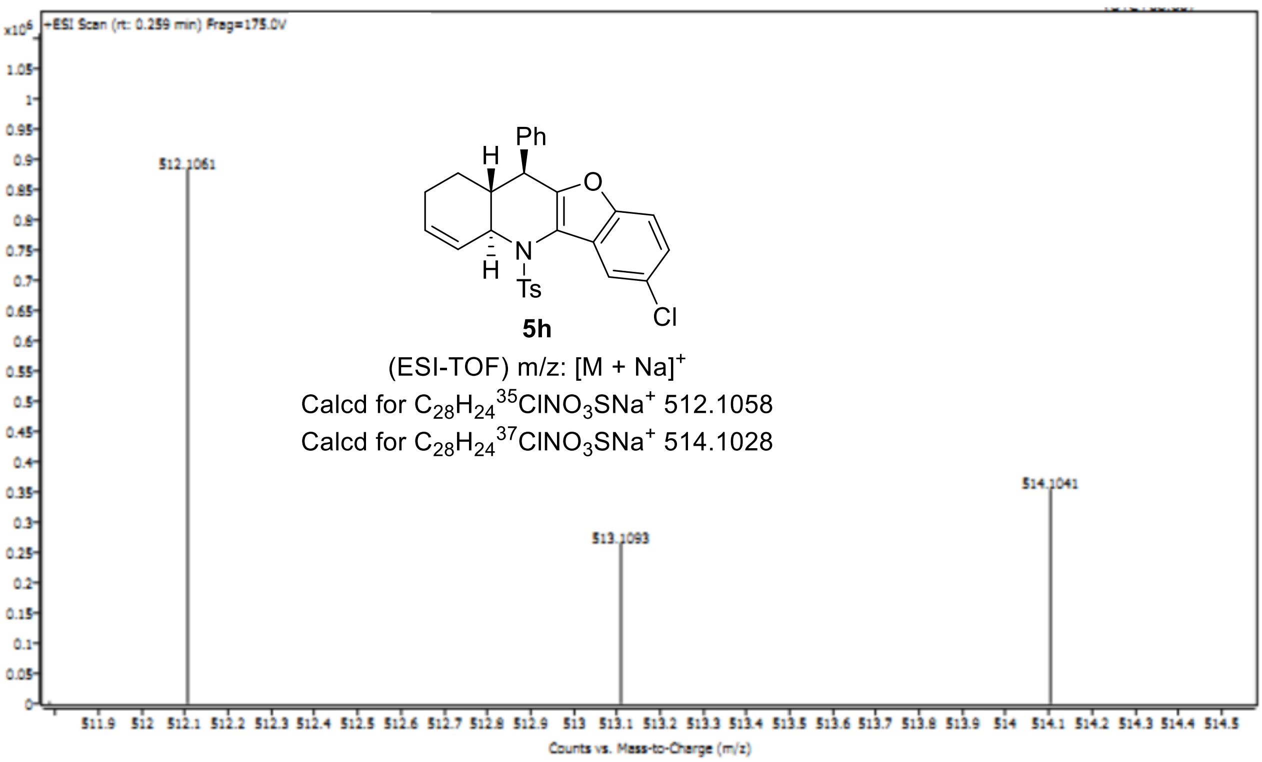

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 5.948 | BB | 0.1513 | 75.88798 | 7.70654 | 48.9486 |
| 2 | 7.987 | BB | 0.2071 | 79.14803 | 5.80458 | 51.0514 |

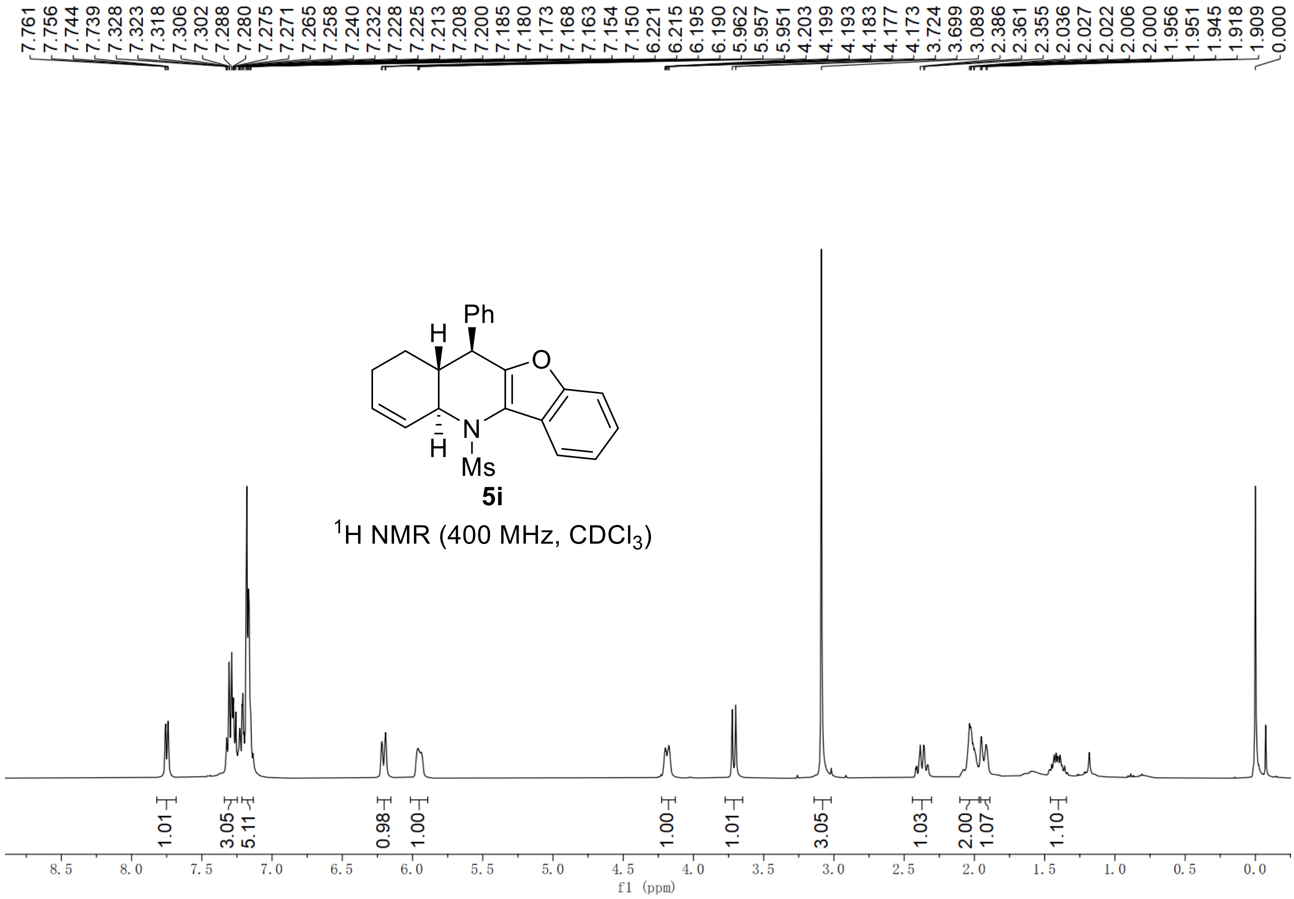


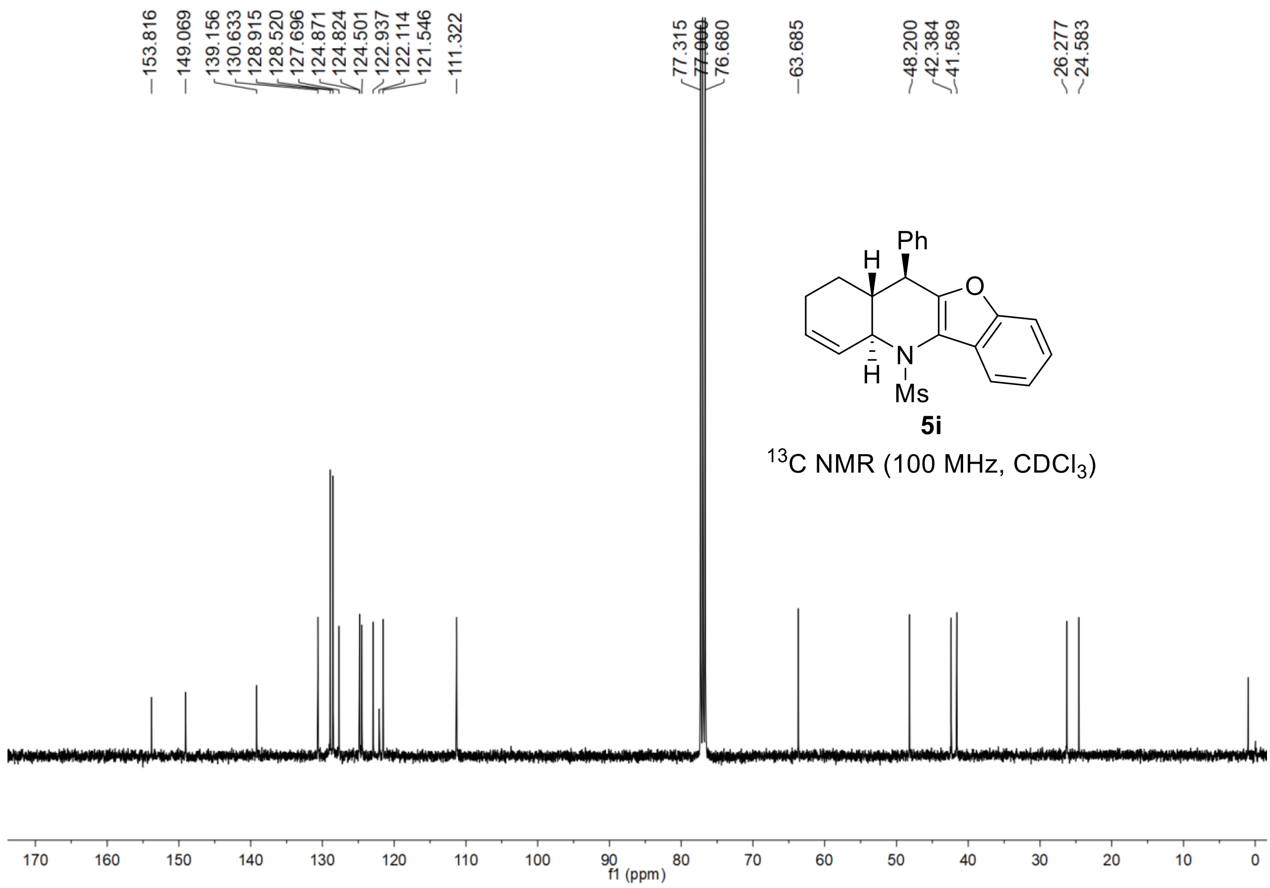

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 5.489 | VB | 0.1477 | 1536.48706 | 157.01198 | 6.7351 |
| 2 | 7.187 | VV | 0.1846 | 2.12767e4 | 1761.79443 | 93.2649 |

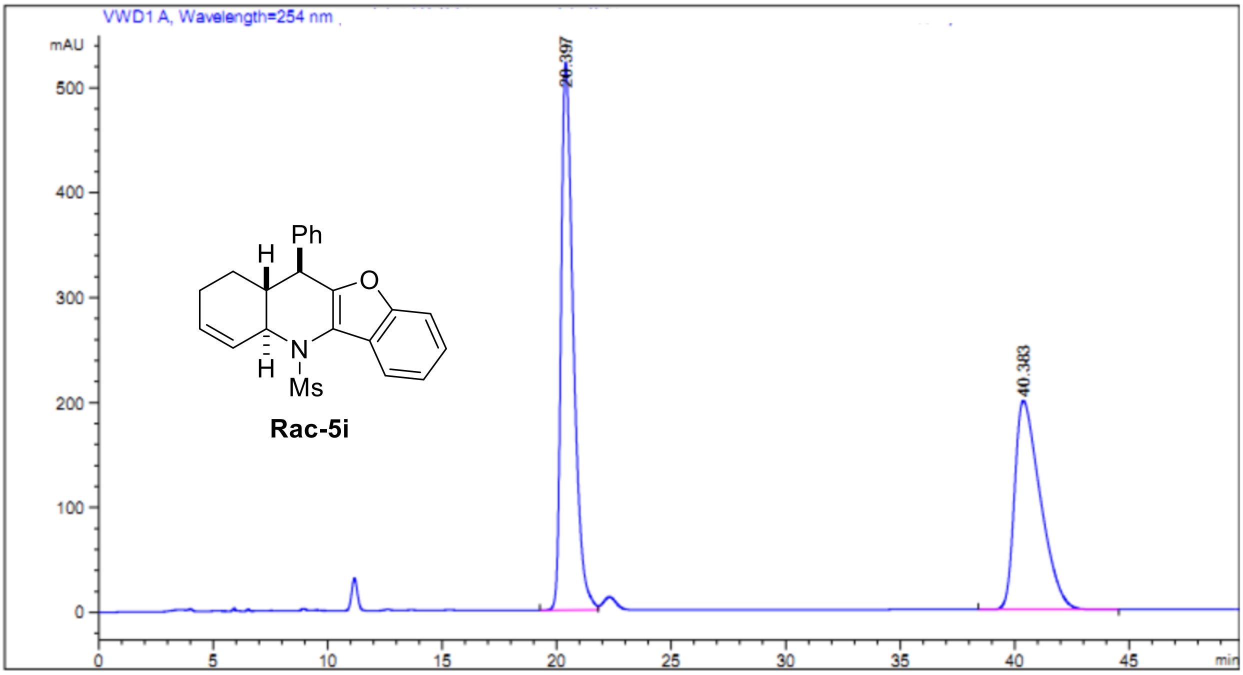



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 5.494 | BV | 0.1280 | 96.99508 | 11.61596 | 0.7467 |
| 2 | 7.179 | VB | 0.1790 | 1.28932e4 | 1100.01257 | 99.2533 |

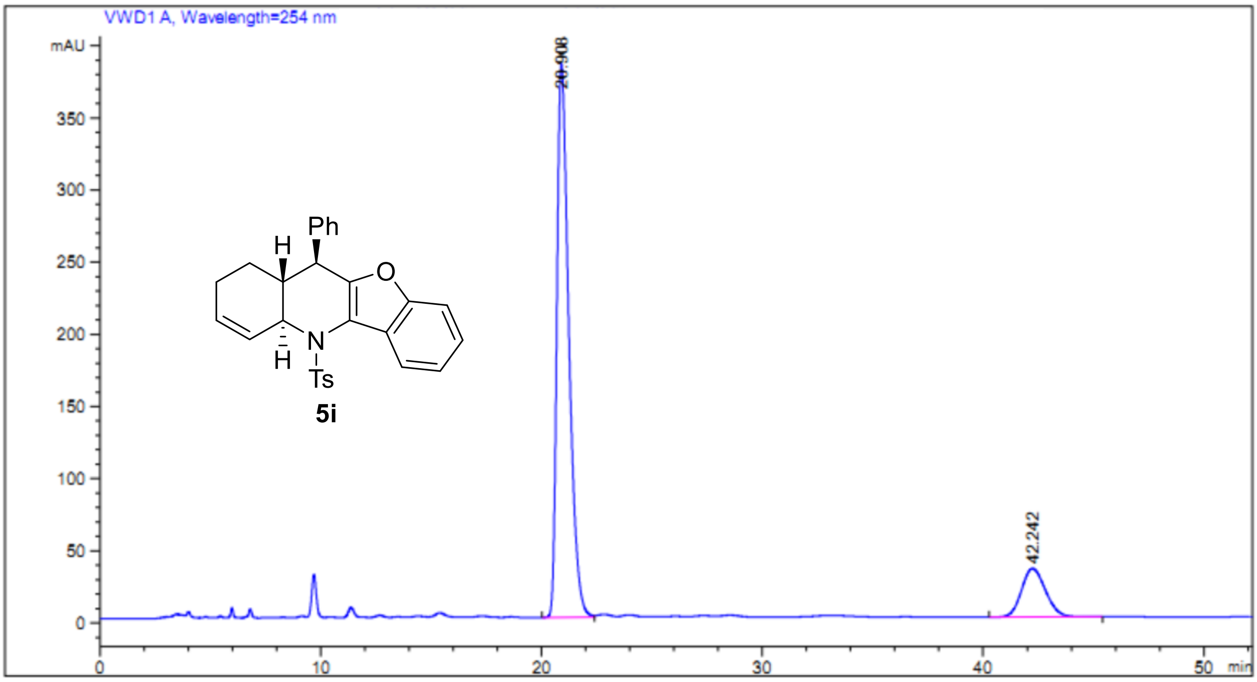



7.761 7.756 7.744 7.739 7.328 7.323 7.318 7.306 7.302 7.288 7.280 7.275 7.271 7.265 7.258 7.240 7.232 7.228 7.225 7.213 7.208 7.200 7.185 7.180 7.173 7.168 7.163 7.154 7.150 6.221 6.215 6.195 6.190 5.962 5.957 5.951 4.203 4.199 4.193 4.183 4.177 4.173 3.724 3.699 3.089 2.386 2.361 2.355 2.036 2.027 2.022 2.006 2.000 1.956 1.951 1.945 1.918 1.909 0.000
Ph
H
O
N
H
Ms
5i
$^{1}$H NMR (400 MHz, $CDCl_3$)
1.01 3.05 5.11 0.98 1.00 1.00 1.01 3.05 1.03 2.00 1.07 1.10
f1 (ppm)

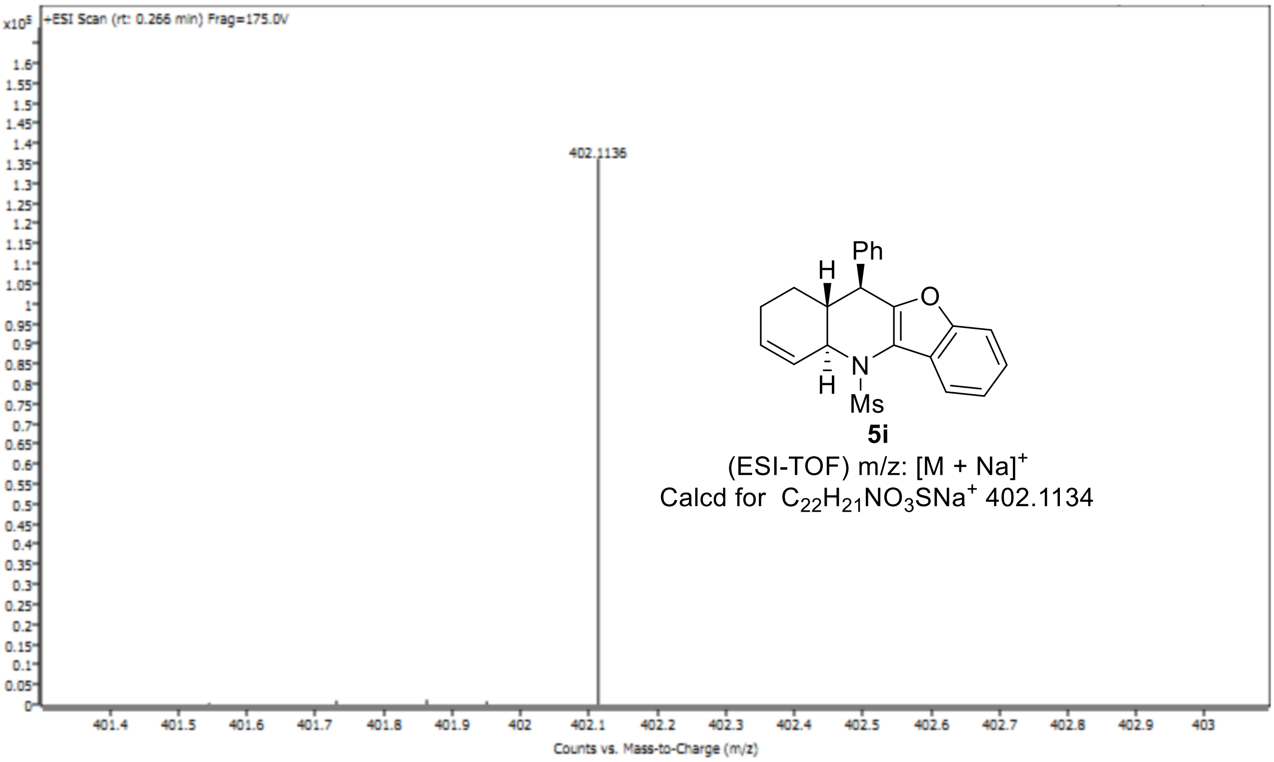

153.816 149.069 139.156 130.633 128.915 128.520 127.696 124.871 124.824 124.501 122.937 122.114 121.546 111.322 77.315 77.000 76.680 63.685 48.200 42.384 41.589 26.277 24.583
Ph
H
O
N
H
Ms
5i
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

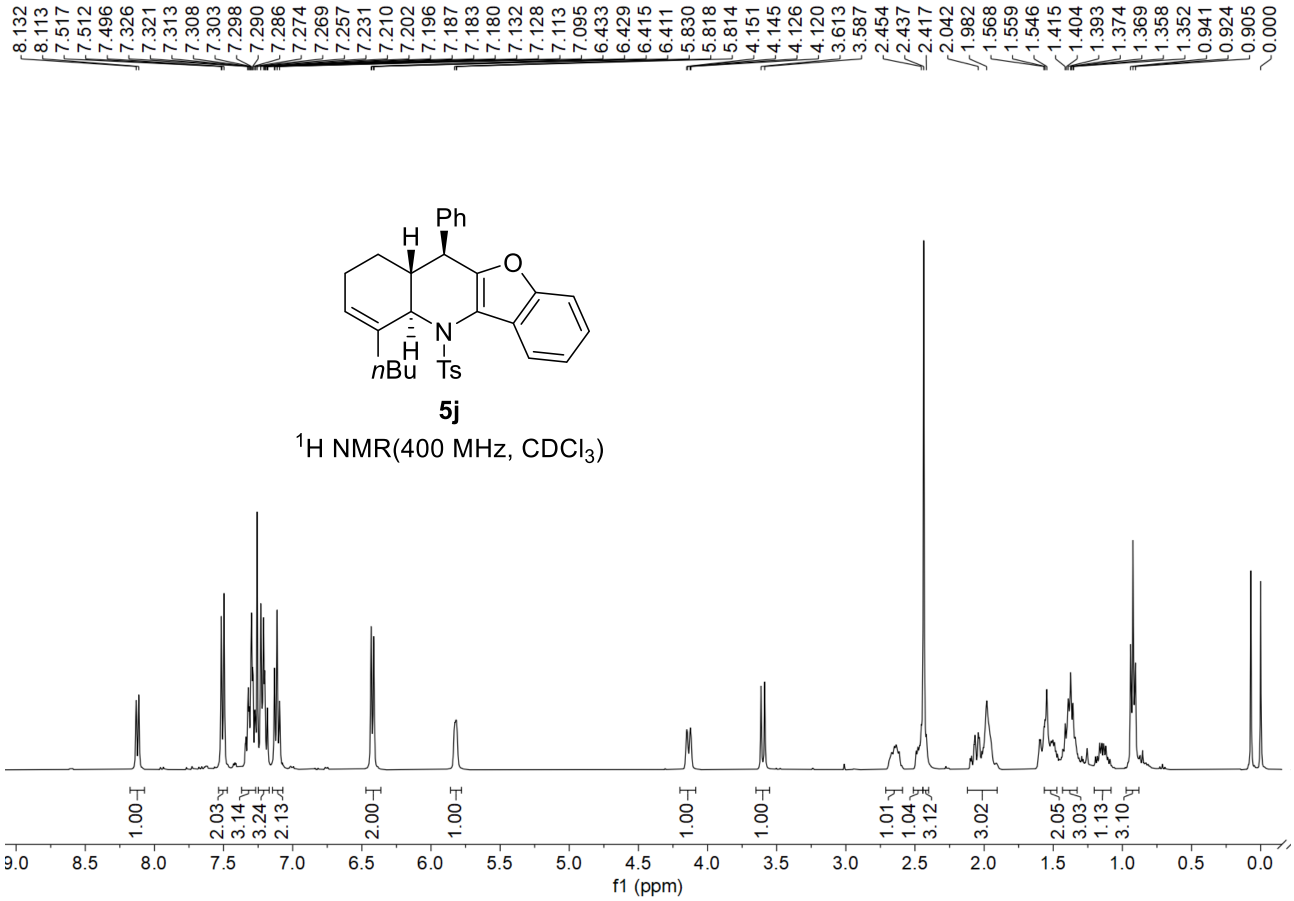



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 20.397 | BV | 0.5620 | 1.94044e4 | 521.82220 | 55.4913 |
| 2 | 40.383 | BB | 1.1802 | 1.55640e4 | 199.04520 | 44.5087 |

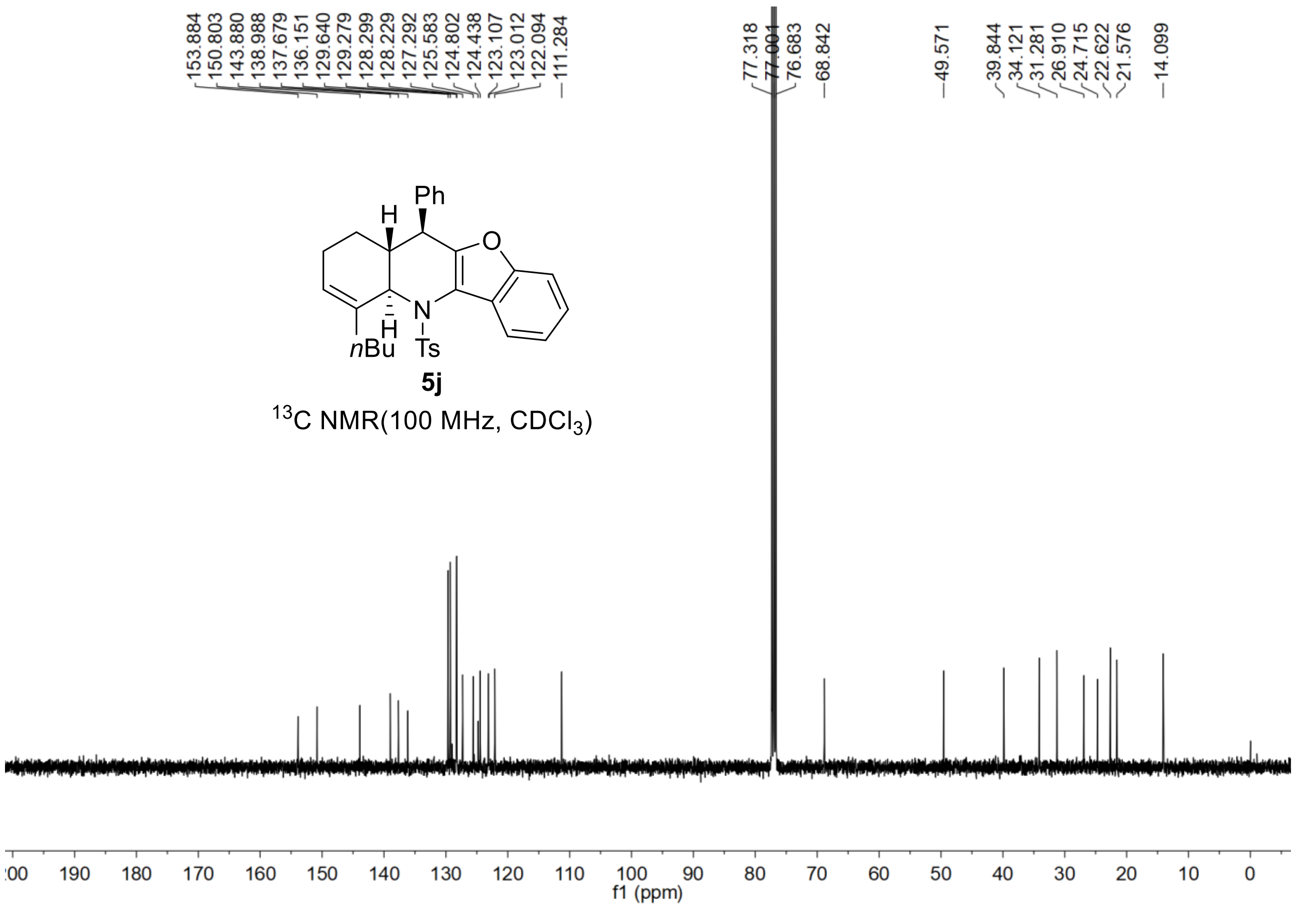



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 20.908 | BV | 0.5702 | 1.43412e4 | 383.52646 | 84.9784 |
| 2 | 42.242 | BB | 1.1768 | 2535.08228 | 33.61837 | 15.0216 |

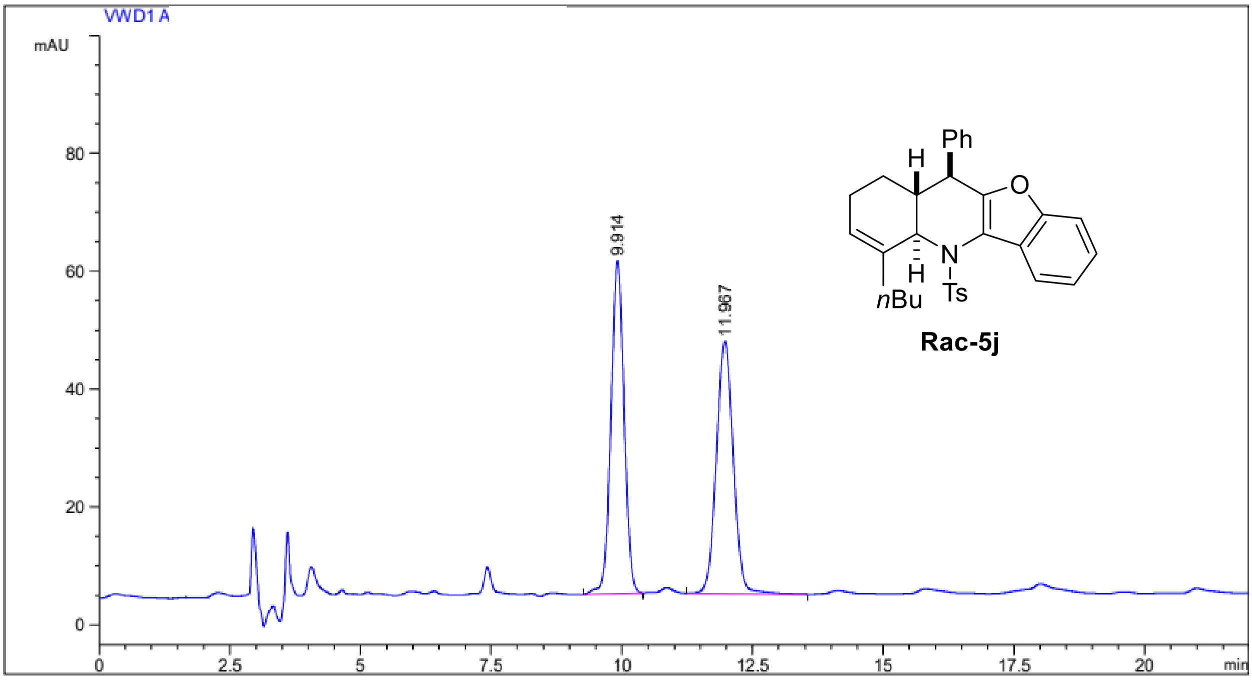

+ESI Scan (rt: 0.266 min) Frag=175.0V
x10^5
402.1136
Counts vs. Mass-to-Charge (m/z)
Ph
H
O
N
H
Ms
5i
(ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{22}H_{21}NO_3SNa^+$ 402.1134



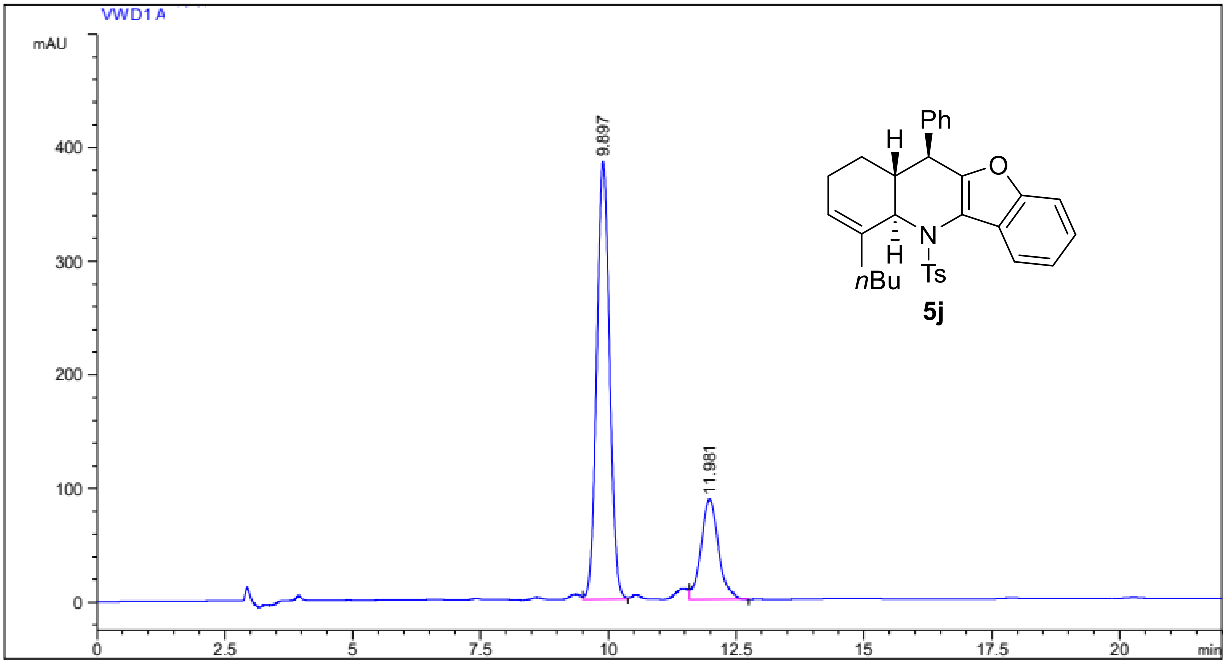
8.132 8.113 7.517 7.512 7.496 7.326 7.321 7.313 7.308 7.303 7.298 7.290 7.286 7.274 7.269 7.257 7.231 7.210 7.202 7.196 7.187 7.183 7.180 7.132 7.128 7.113 7.095 6.433 6.429 6.415 6.411 5.830 5.818 5.814 4.151 4.145 4.126 4.120 3.613 3.587 2.454 2.437 2.417 2.042 1.982 1.568 1.559 1.546 1.415 1.404 1.393 1.374 1.369 1.358 1.352 0.941 0.924 0.905 0.000
Ph
H
O
N
H
nBu
Ts
5j
1H NMR(400 MHz, CDCl3)
1.00 2.03 3.14 3.24 2.13 2.00 1.00 1.00 1.00 1.01 1.04 3.12 3.02 2.05 3.03 1.13 3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

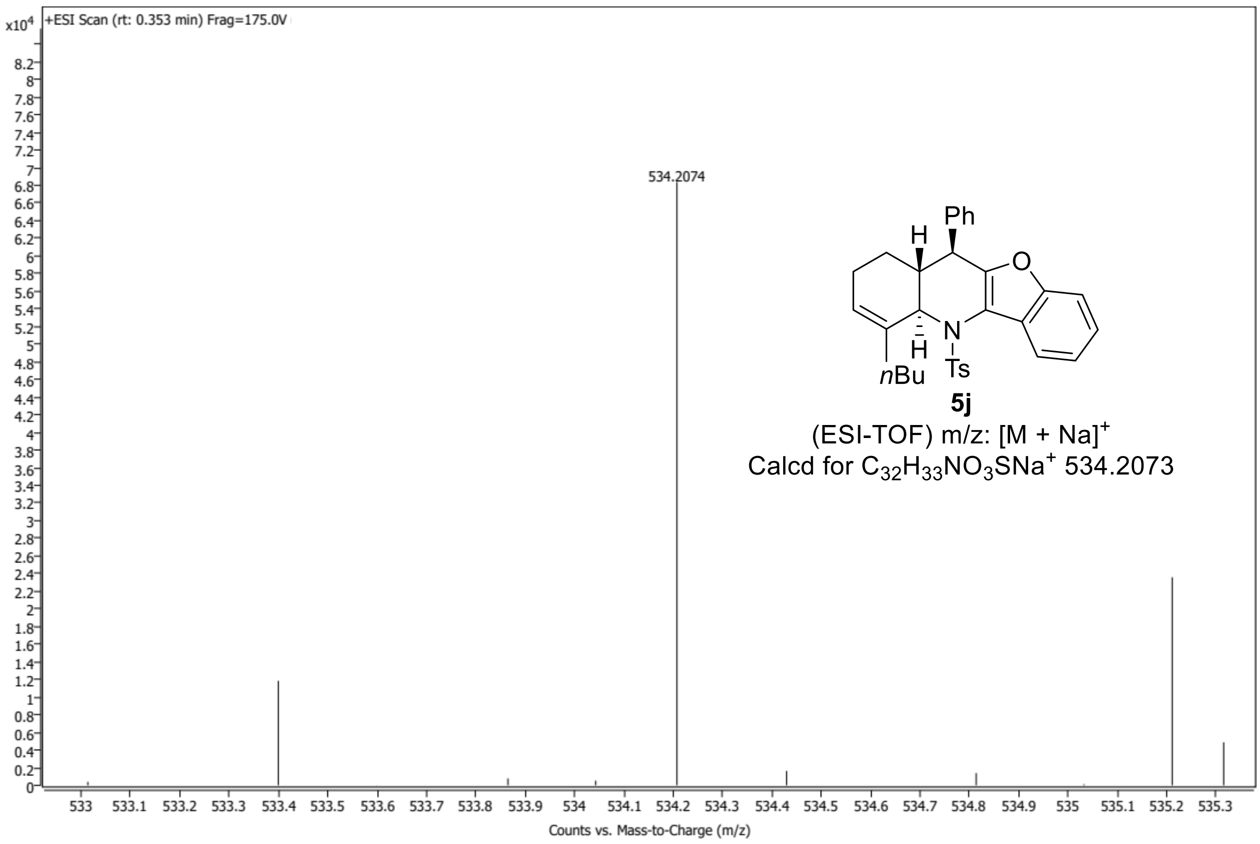
153.884 150.803 143.880 138.988 137.679 136.151 129.640 129.279 128.299 128.229 127.292 125.583 124.802 124.438 123.107 123.012 122.094 111.284
77.318 77.001 76.683 68.842
49.571
39.844 34.121 31.281 26.910 24.715 22.622 21.576
14.099
Ph
H
O
N
H
nBu
Ts
5j
13C NMR(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

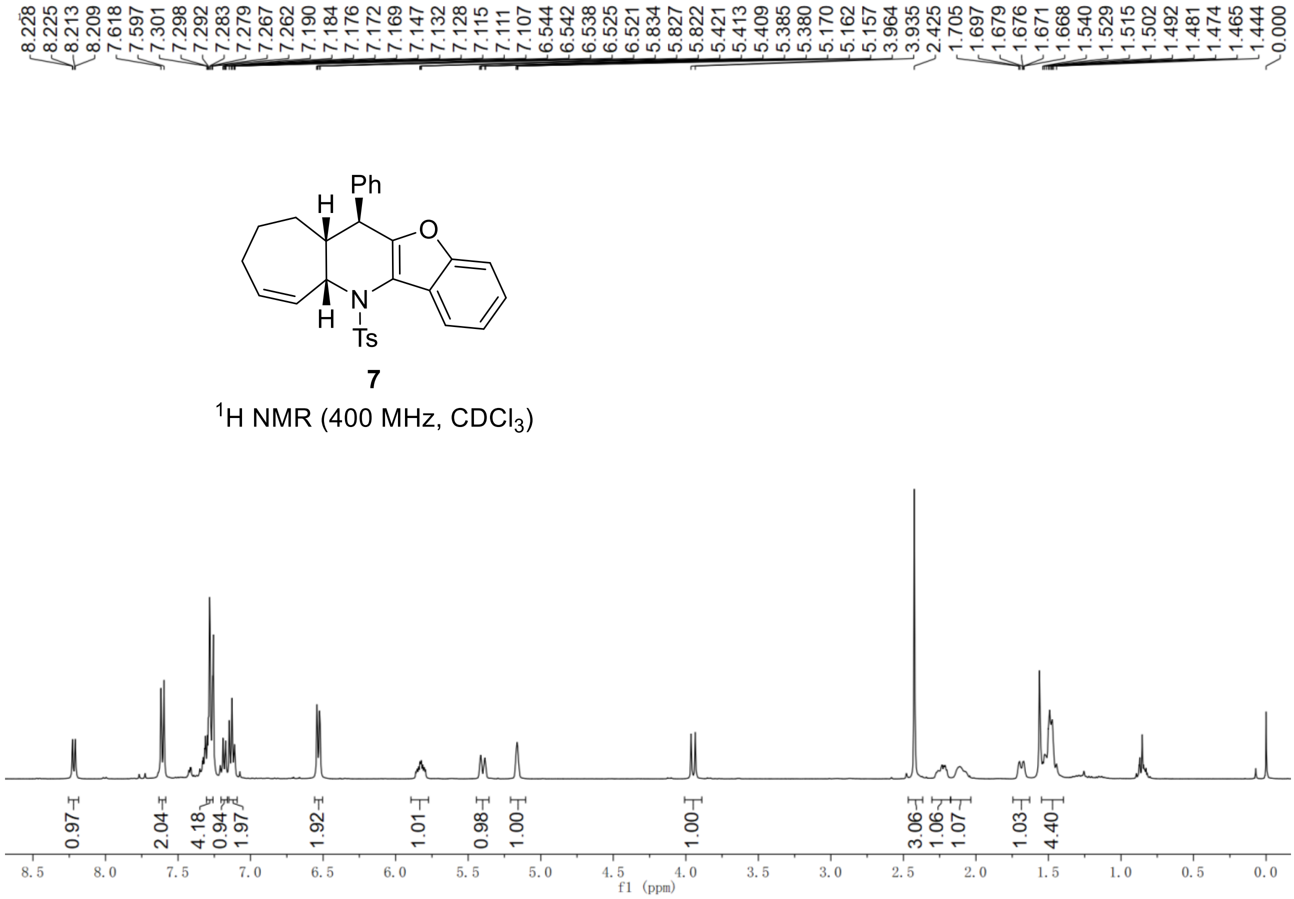


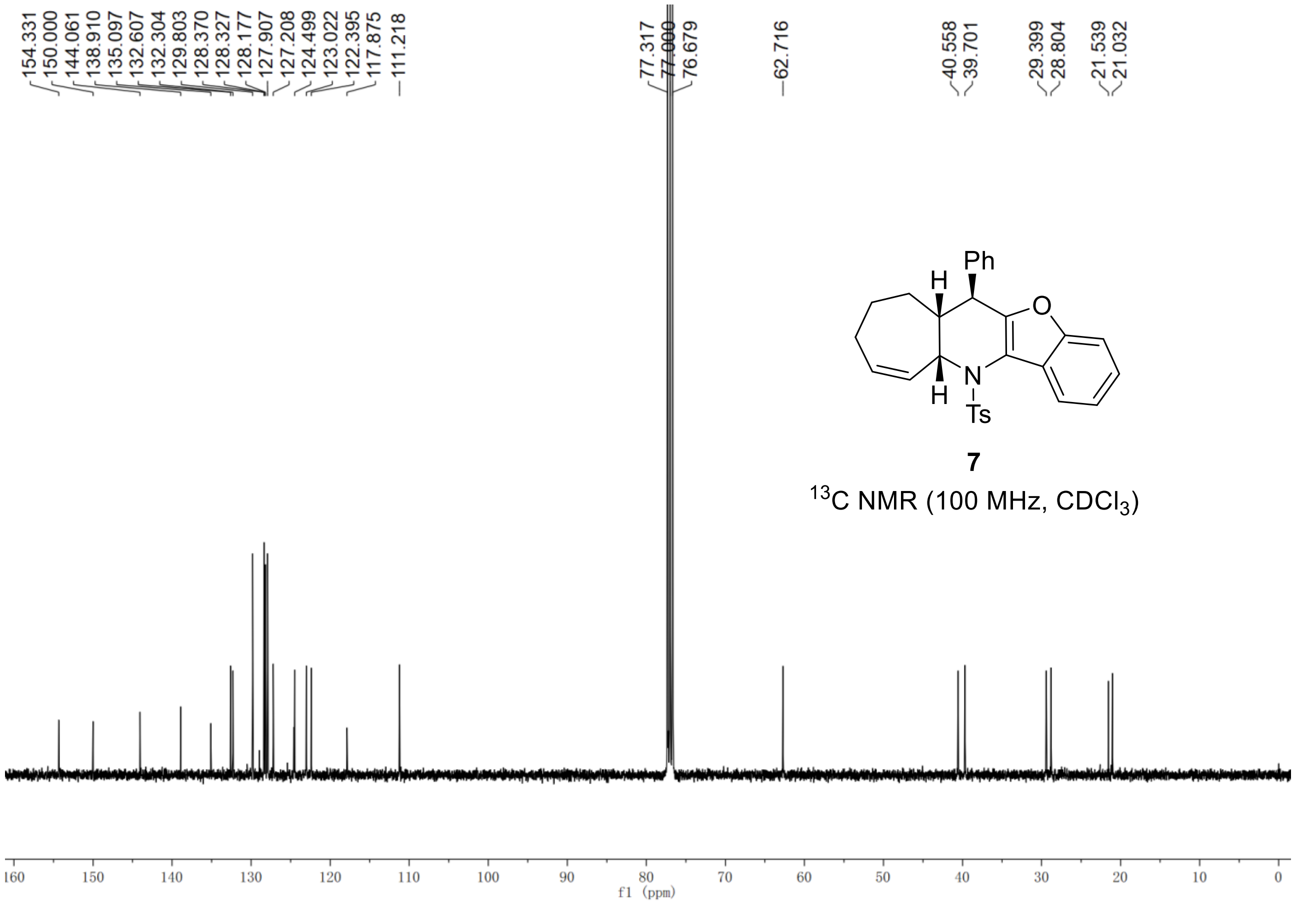

| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 9.914 | BB | 0.2718 | 991.04480 | 56.45636 | 50.5513 |
| 2 | 11.967 | BB | 0.3516 | 969.42804 | 42.80004 | 49.4487 |

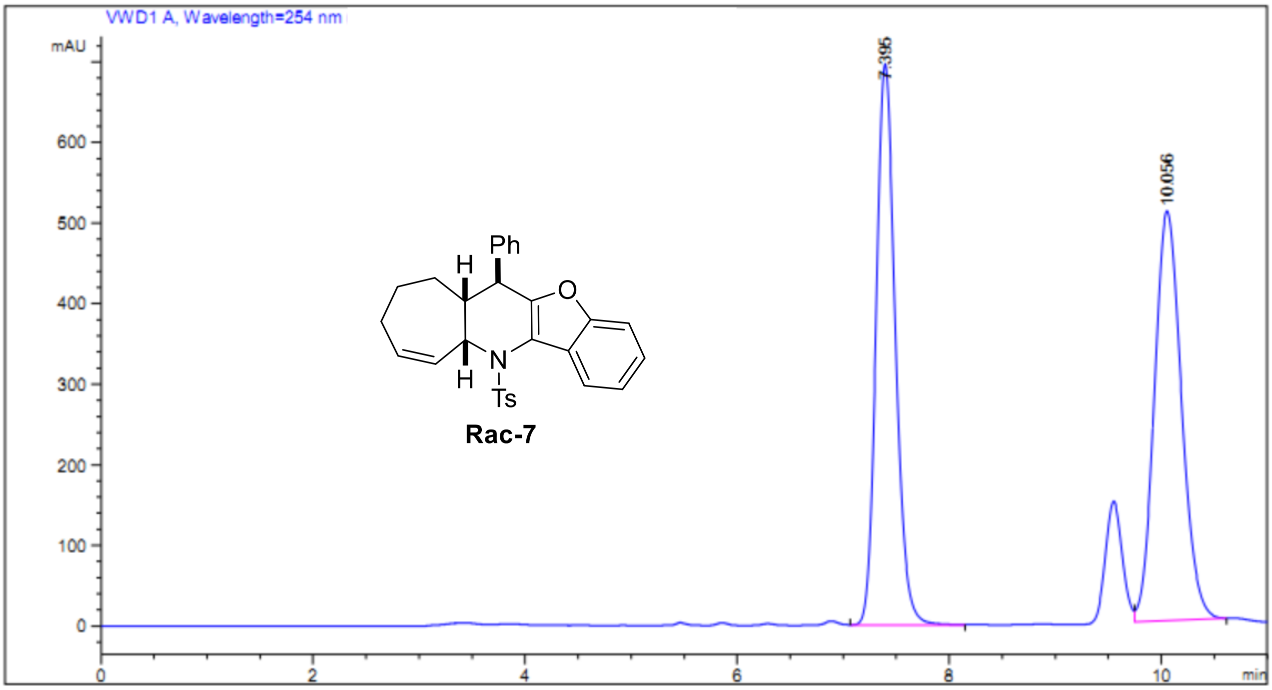



| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 9.897 | VV | 0.2713 | 6697.98730 | 385.17892 | 76.3581 |
| 2 | 11.981 | VB | 0.3631 | 2073.82251 | 87.74405 | 23.6419 |

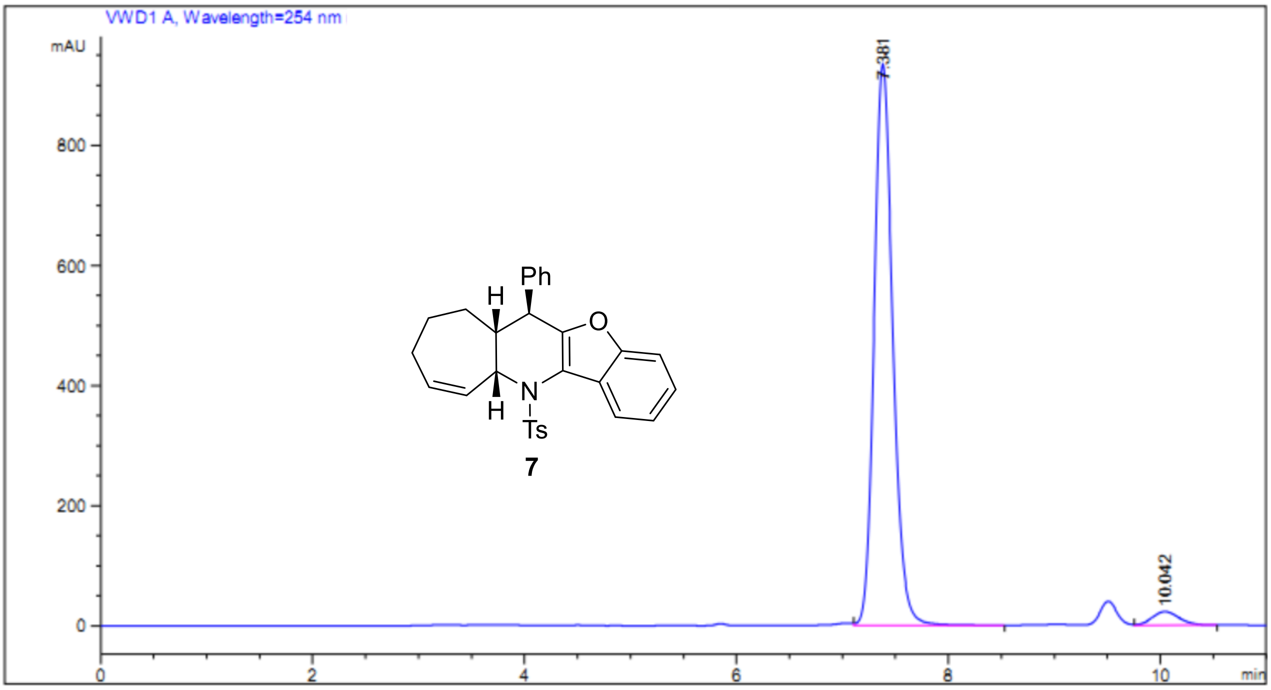

+ESI Scan (rt: 0.353 min) Frag=175.0V
x10^4
534.2074
Ph
H
O
N
H
nBu
Ts
5j
(ESI-TOF) m/z: [M + Na]+
Calcd for C32H33NO3SNa+ 534.2073
Counts vs. Mass-to-Charge (m/z)


8.228
8.225
8.213
8.209
7.618
7.597
7.301
7.298
7.292
7.283
7.279
7.267
7.262
7.190
7.184
7.176
7.172
7.169
7.147
7.132
7.128
7.115
7.111
7.107
6.544
6.542
6.538
6.525
6.521
5.834
5.827
5.822
5.421
5.413
5.409
5.385
5.380
5.170
5.162
5.157
3.964
3.935
2.425
1.705
1.697
1.679
1.676
1.671
1.668
1.540
1.529
1.515
1.502
1.492
1.481
1.474
1.465
1.444
0.000
Ph
H
O
N
H
Ts
7
$^1$H NMR (400 MHz, $CDCl_3$)
0.97
2.04
4.18
0.94
1.97
1.92
1.01
0.98
1.00
1.00
3.06
1.06
1.07
1.03
4.40
f1 (ppm)

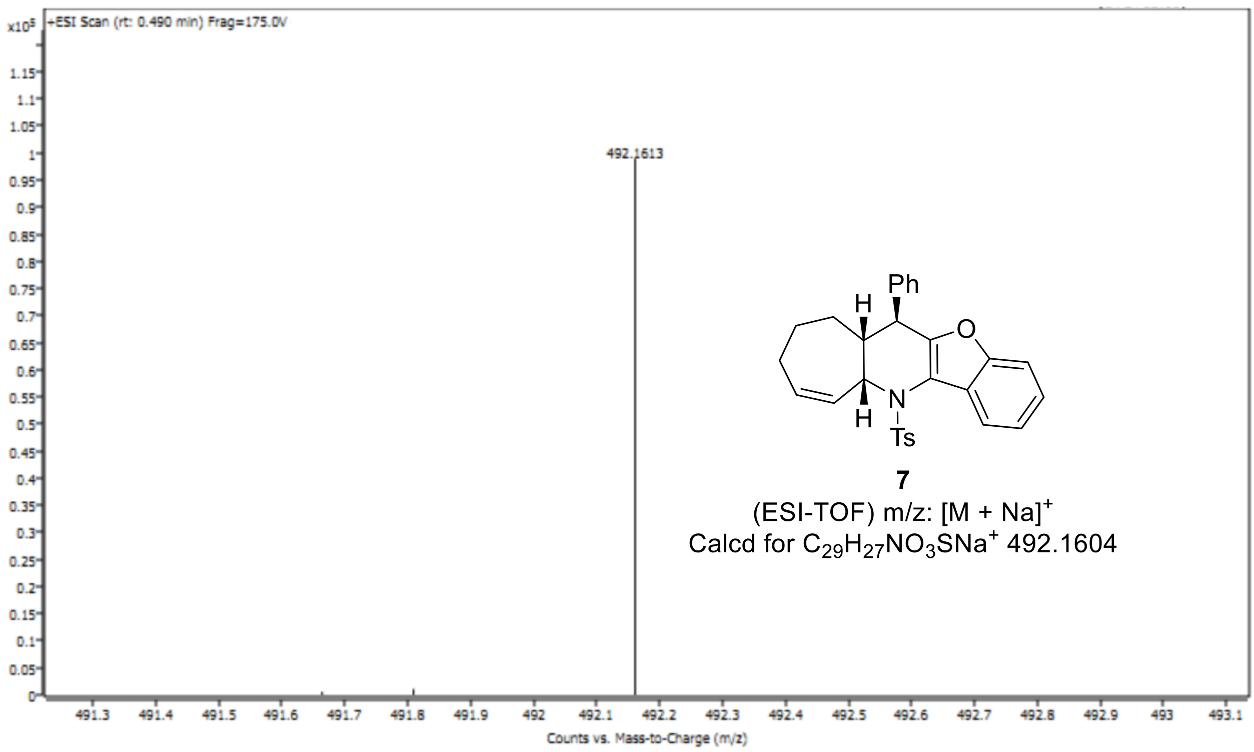

154.331
150.000
144.061
138.910
135.097
132.607
132.304
129.803
128.370
128.327
128.177
127.907
127.208
124.499
123.022
122.395
117.875
111.218
77.317
77.000
76.679
62.716
40.558
39.701
29.399
28.804
21.539
21.032
Ph
H
O
N
H
Ts
7
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

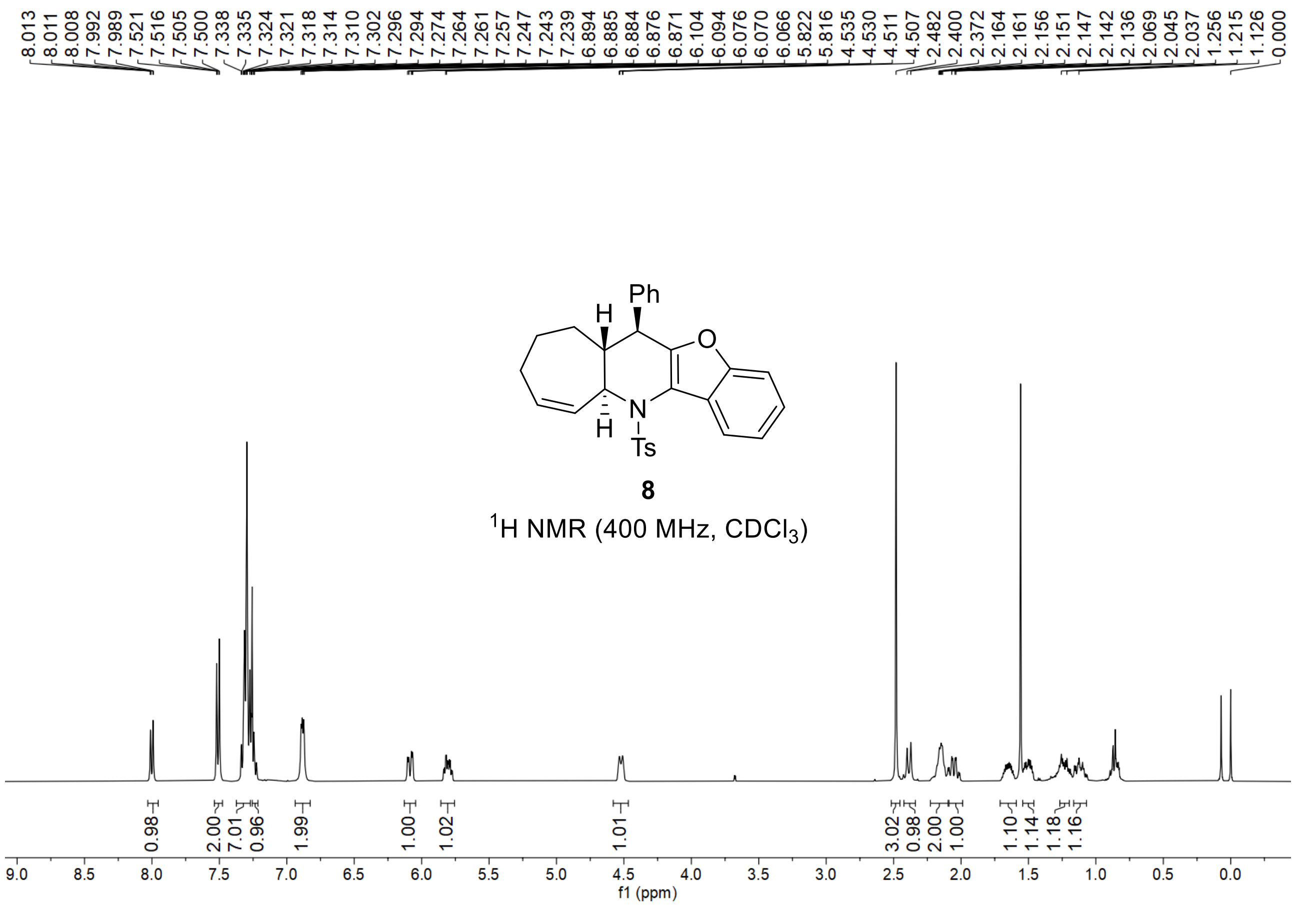


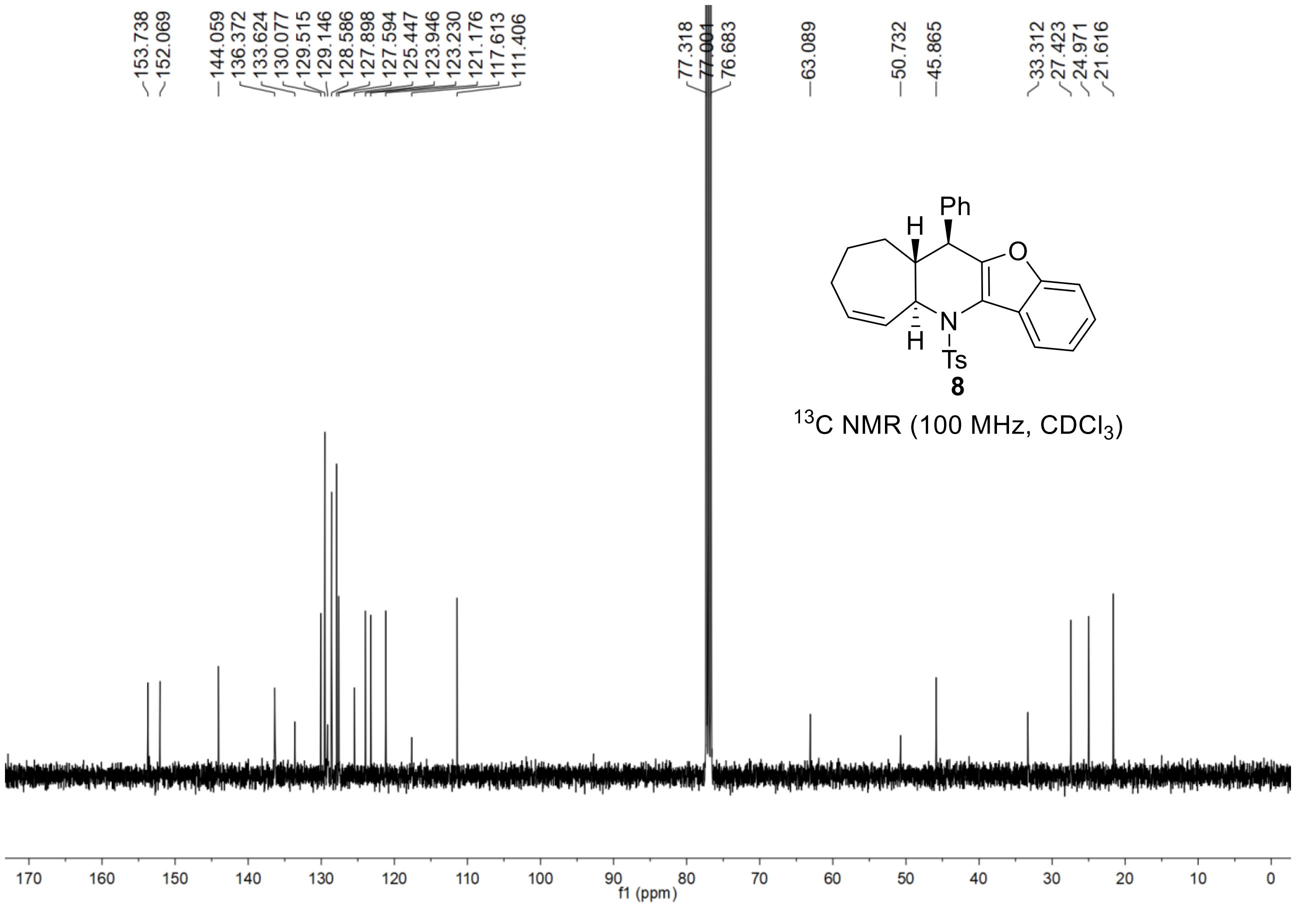

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.395 | BBA | 0.1926 | 8705.24414 | 695.48901 | 50.1577 |
| 2 | 10.056 | BB | 0.2706 | 8650.50391 | 499.21210 | 49.8423 |

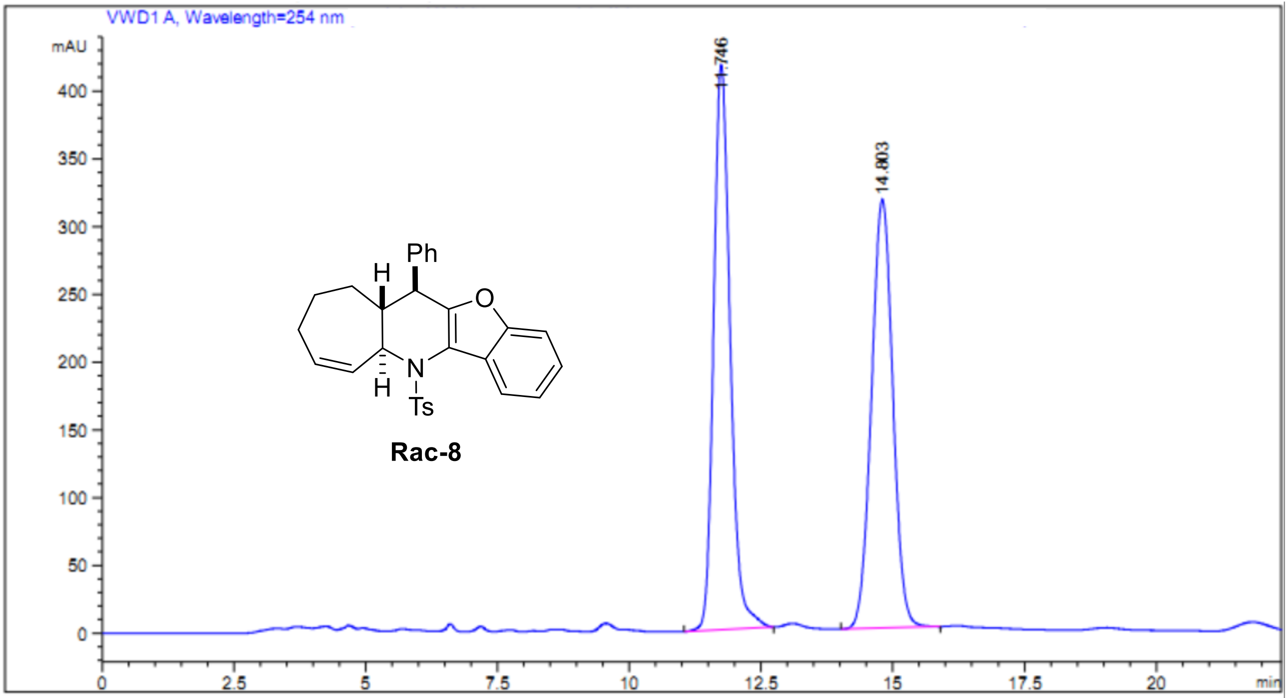



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 7.381 | BBA | 0.1884 | 1.13252e4 | 931.93732 | 96.7588 |
| 2 | 10.042 | BB | 0.2685 | 379.36380 | 22.12307 | 3.2412 |

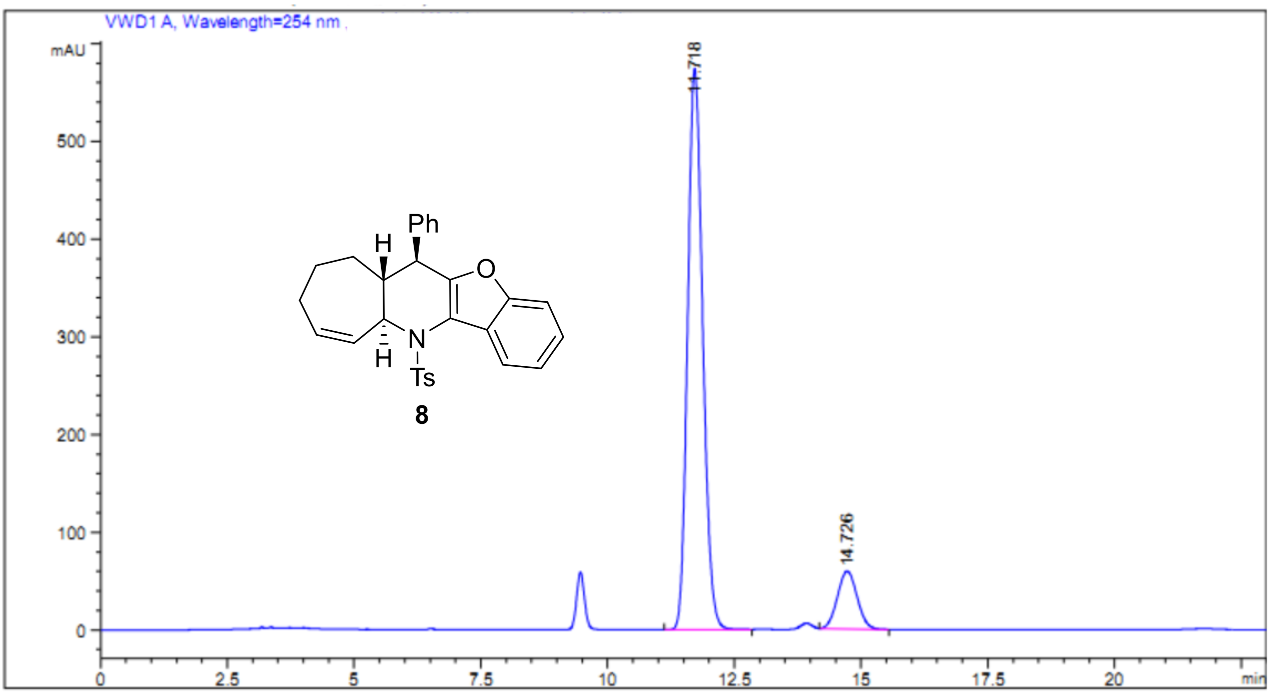

x10^5
+ESI Scan (rt: 0.490 min) Frag=175.0V
492.1613
Ph
H
O
N
H
Ts
7
(ESI-TOF) m/z: [M + Na]+
Calcd for C29H27NO3SNa+ 492.1604
Counts vs. Mass-to-Charge (m/z)


8.013
8.011
8.008
7.992
7.989
7.521
7.516
7.505
7.500
7.338
7.335
7.324
7.321
7.318
7.314
7.310
7.302
7.296
7.294
7.274
7.264
7.261
7.257
7.247
7.243
7.239
6.894
6.885
6.884
6.876
6.871
6.104
6.094
6.076
6.070
6.066
5.822
5.816
4.535
4.530
4.511
4.507
2.482
2.400
2.372
2.164
2.161
2.156
2.151
2.147
2.142
2.136
2.069
2.045
2.037
1.256
1.215
1.126
0.000
Ph
H
O
N
H
Ts
8
1H NMR (400 MHz, CDCl3)
0.98
2.00
7.01
0.96
1.99
1.00
1.02
1.01
3.02
0.98
2.00
1.00
1.10
1.14
1.18
1.16
f1 (ppm)

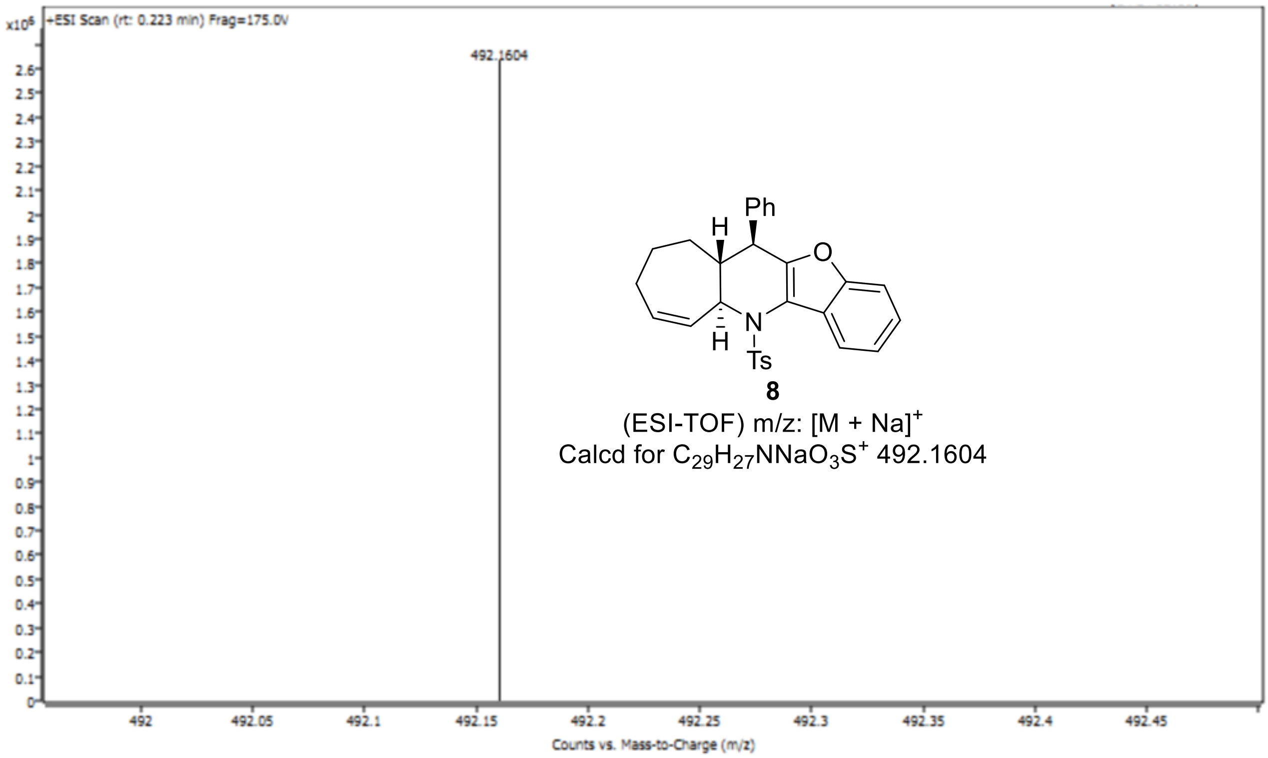

153.738
152.069
144.059
136.372
133.624
130.077
129.515
129.146
128.586
127.898
127.594
125.447
123.946
123.230
121.176
117.613
111.406
77.318
77.001
76.683
63.089
50.732
45.865
33.312
27.423
24.971
21.616
Ph
H
O
N
H
Ts
8
13C NMR (100 MHz, CDCl3)
f1 (ppm)

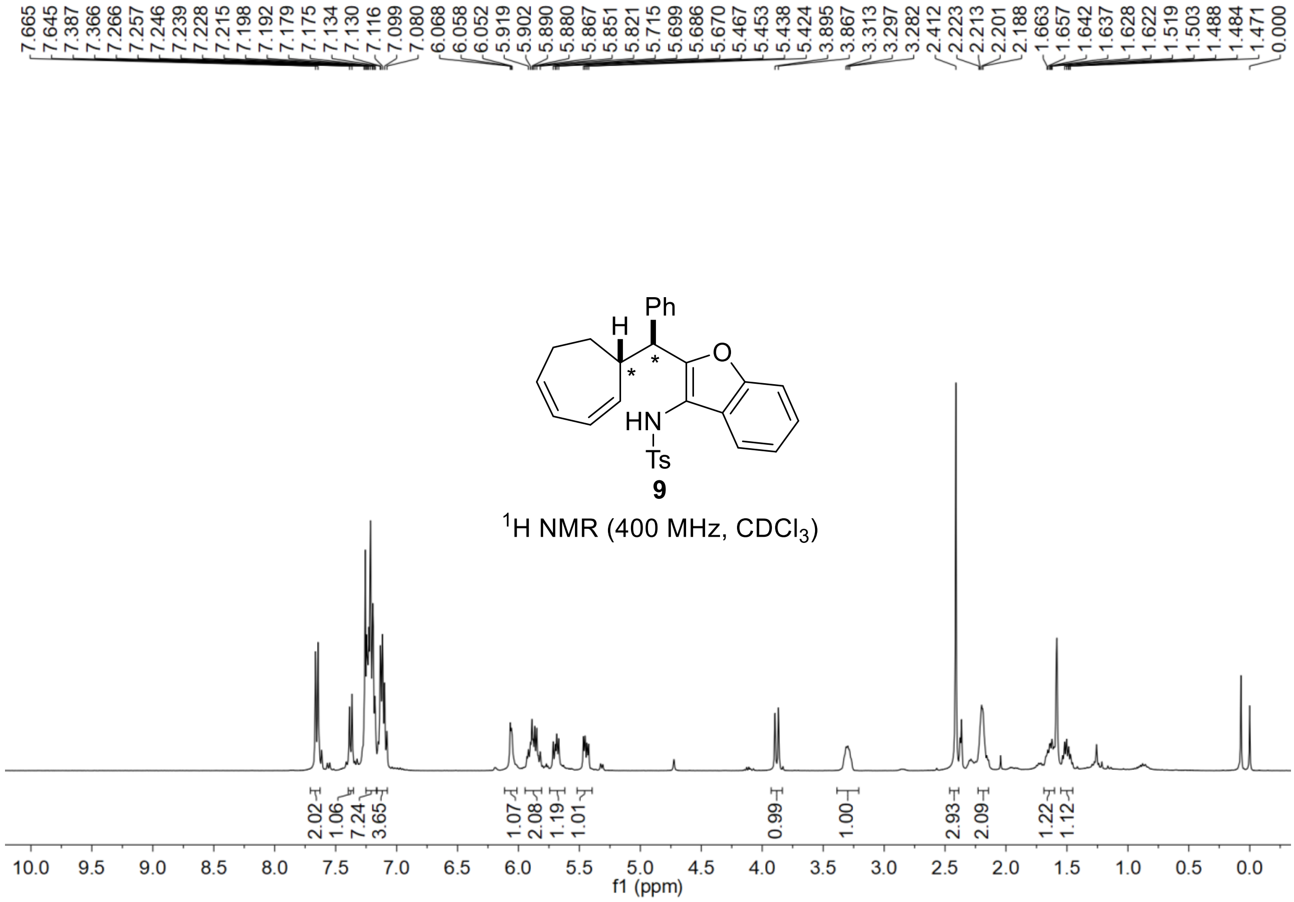


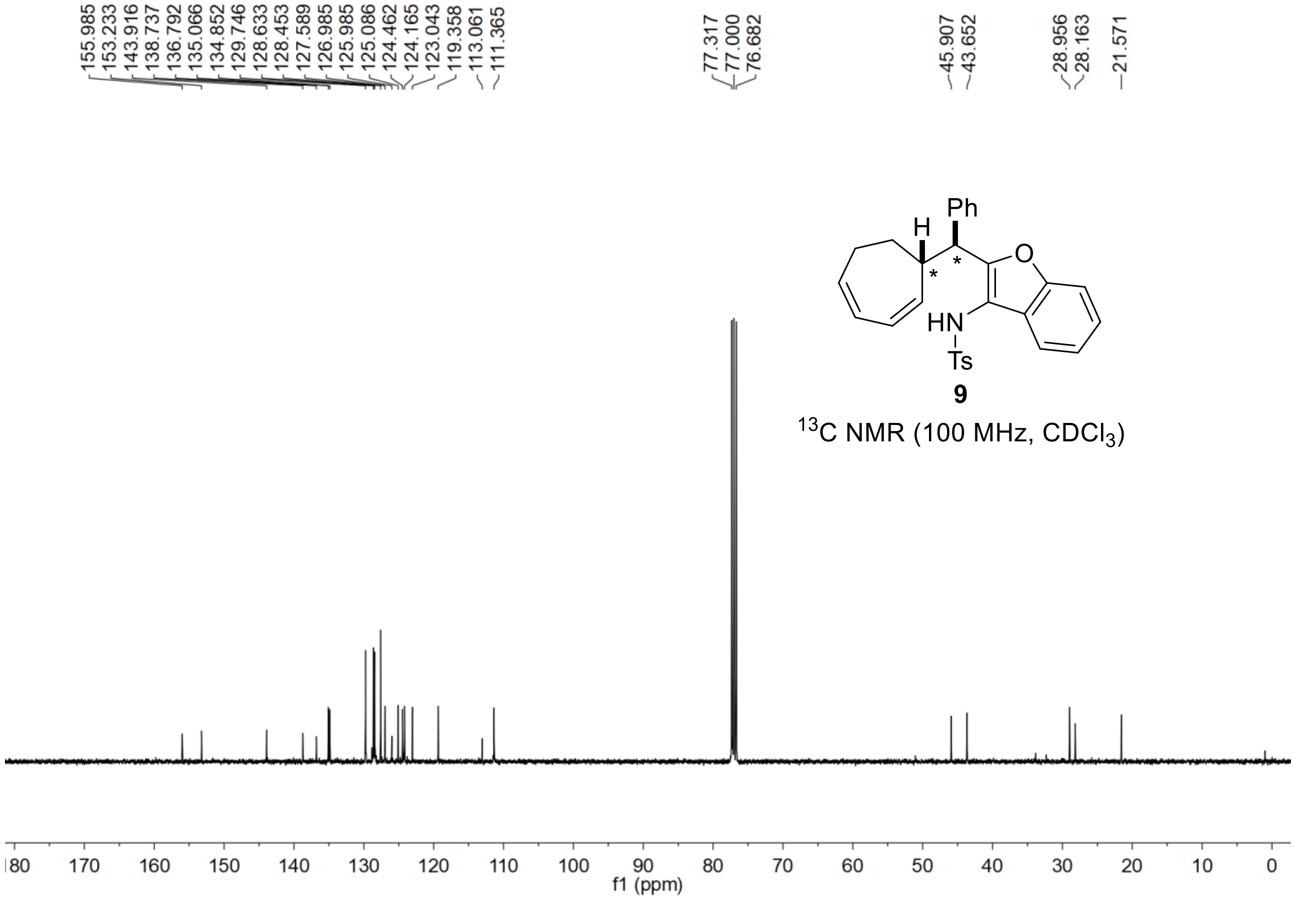

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 11.746 | BBA | 0.3386 | 9129.81934 | 416.64188 | 50.6234 |
| 2 | 14.803 | BB | 0.4393 | 8904.95898 | 316.14224 | 49.3766 |

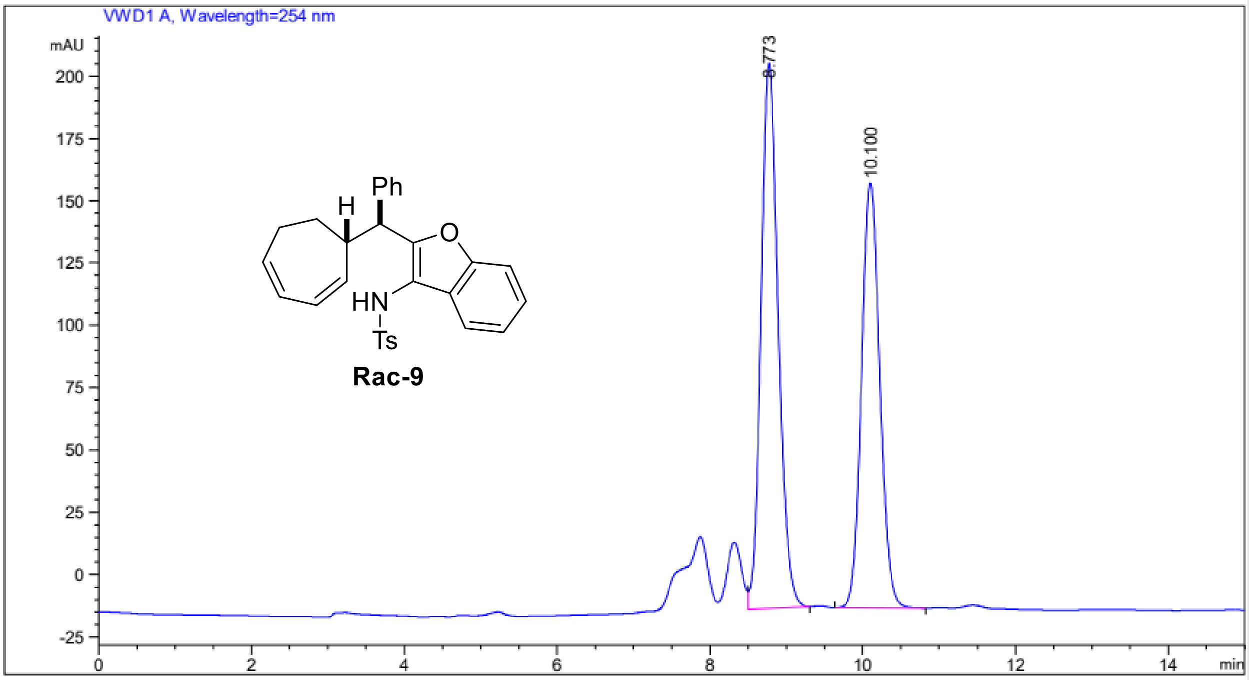



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 11.718 | BBA | 0.3223 | 1.18433e4 | 573.84747 | 88.1813 |
| 2 | 14.726 | BBA | 0.4212 | 1587.31763 | 59.08039 | 11.8187 |

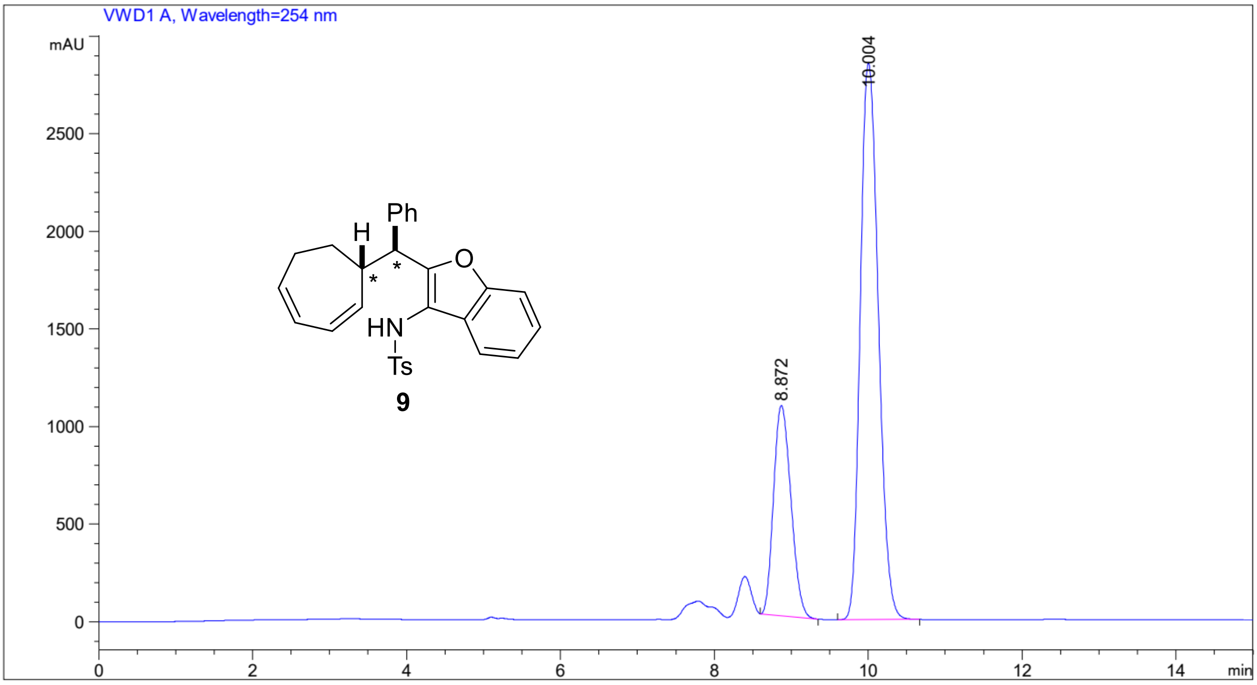

+ESI Scan (rt: 0.223 min) Frag=175.0V
x10^6
492.1604
Ph
H
O
N
H
Ts
8
(ESI-TOF) m/z: [M + Na]+
Calcd for C29H27NNaO3S+ 492.1604
Counts vs. Mass-to-Charge (m/z)


7.665 7.645 7.387 7.366 7.266 7.257 7.246 7.239 7.228 7.215 7.198 7.192 7.179 7.175 7.134 7.130 7.116 7.099 7.080 6.068 6.058 6.052 5.919 5.902 5.890 5.880 5.867 5.851 5.821 5.715 5.699 5.686 5.670 5.467 5.453 5.438 5.424 3.895 3.867 3.313 3.297 3.282 2.412 2.223 2.213 2.201 2.188 1.663 1.657 1.642 1.637 1.628 1.622 1.519 1.503 1.488 1.484 1.471 0.000
Ph
H
O
HN
Ts
9
$^1$H NMR (400 MHz, CDCl$_3$)
2.02 1.06 7.24 3.65 1.07 2.08 1.19 1.01 0.99 1.00 2.93 2.09 1.22 1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

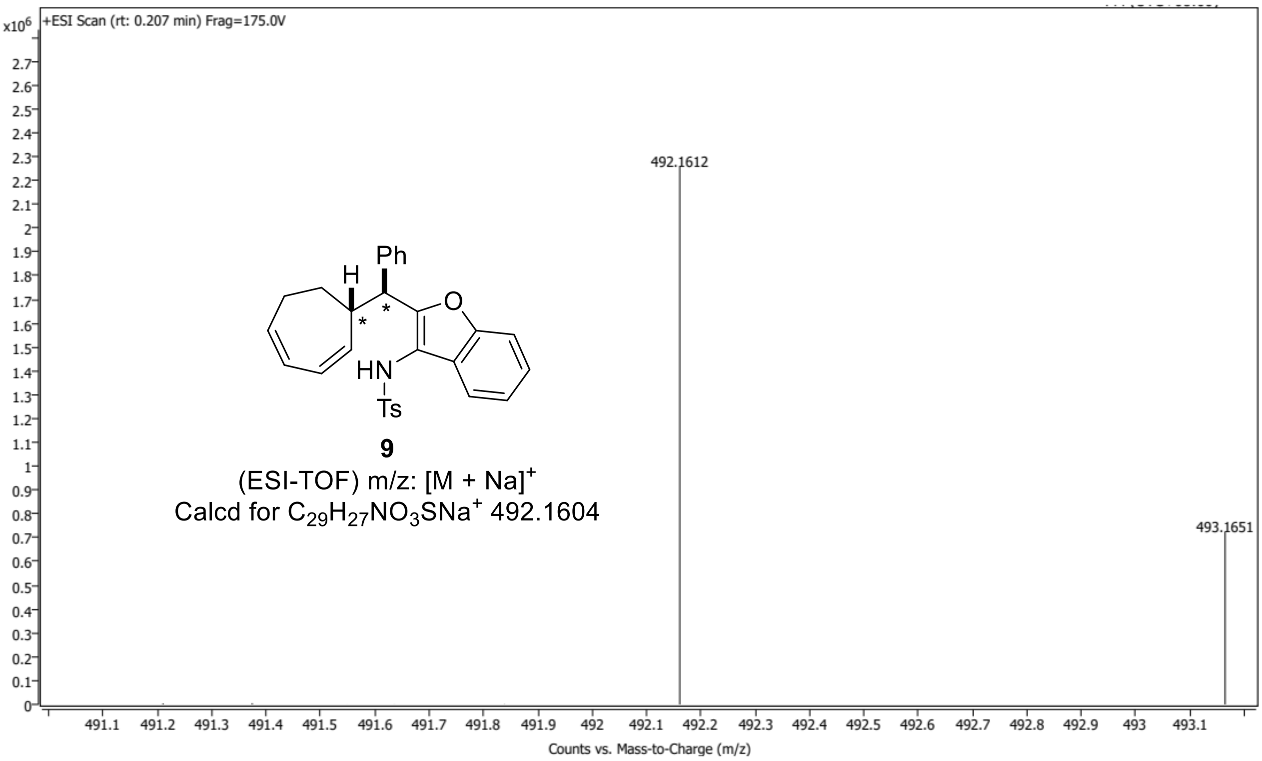

155.985 153.233 143.916 138.737 136.792 135.066 134.852 129.746 128.633 128.453 127.589 126.985 125.985 125.086 124.462 124.165 123.043 119.358 113.061 111.365
77.317 77.000 76.682
45.907 43.652
28.956 28.163
21.571
Ph
H
O
HN
Ts
9
$^{13}$C NMR (100 MHz, CDCl$_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

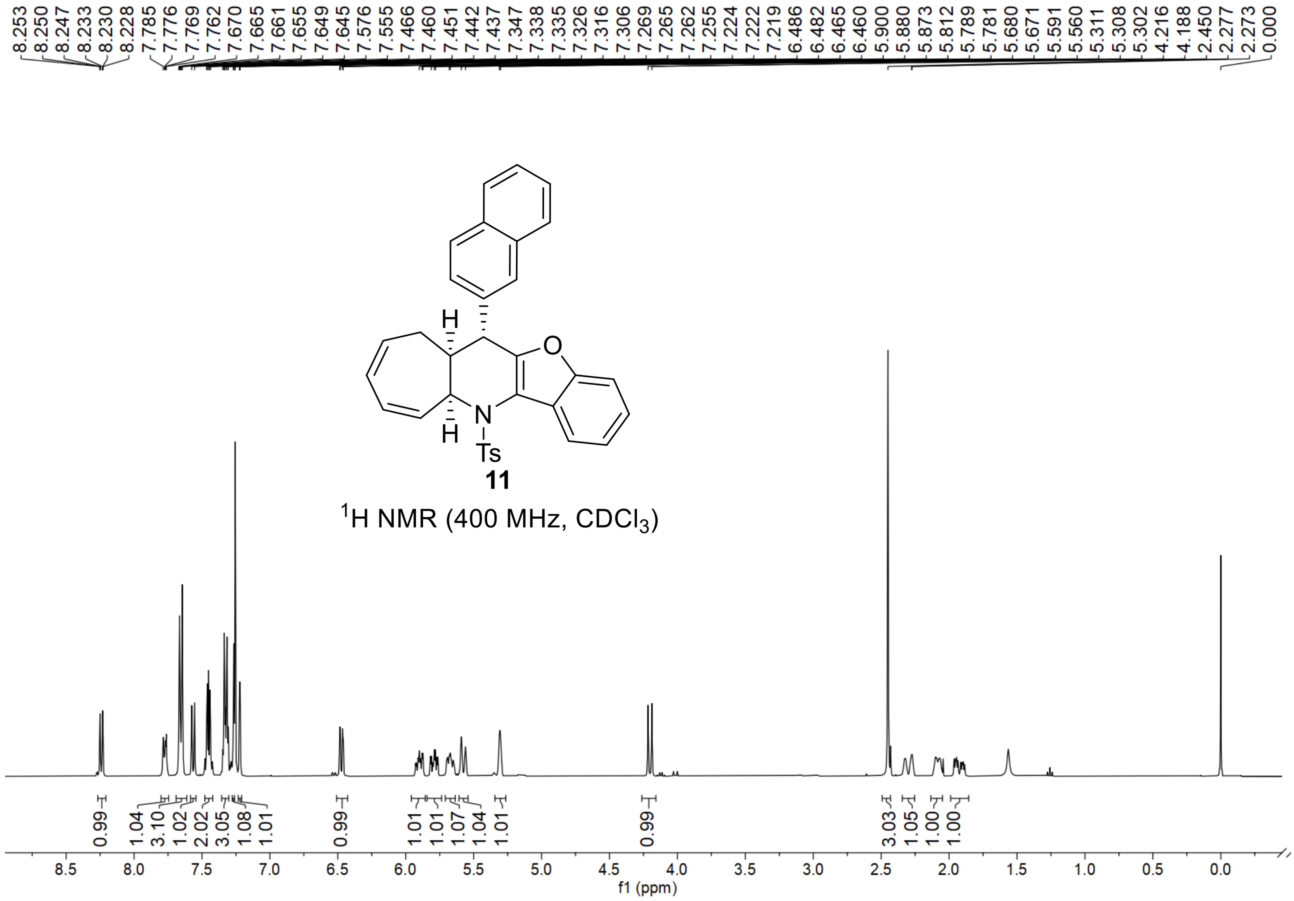


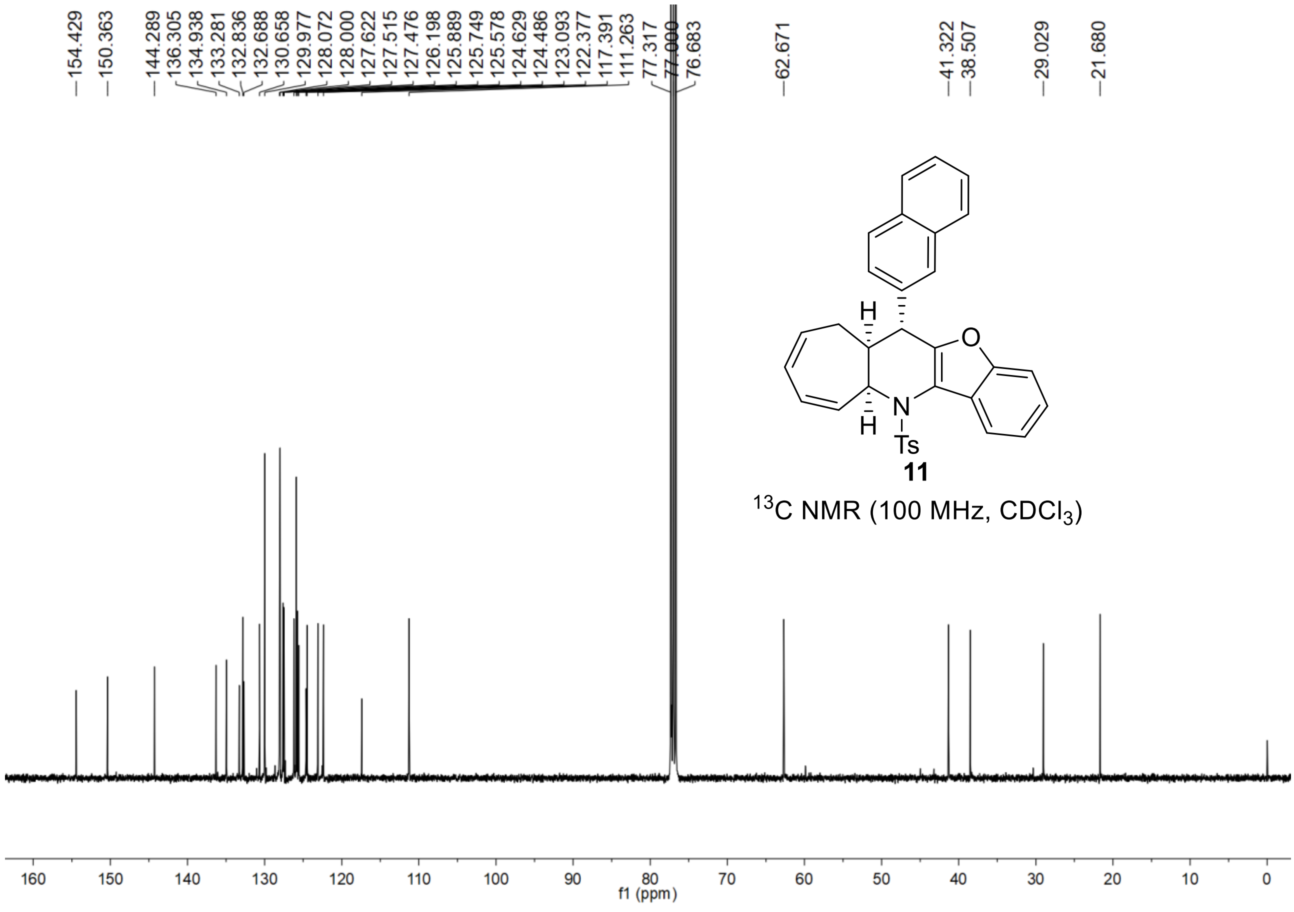

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.773 | VB | 0.2406 | 3418.23633 | 218.65475 | 54.6941 |
| 2 | 10.100 | BB | 0.2594 | 2831.50293 | 170.40413 | 45.3059 |

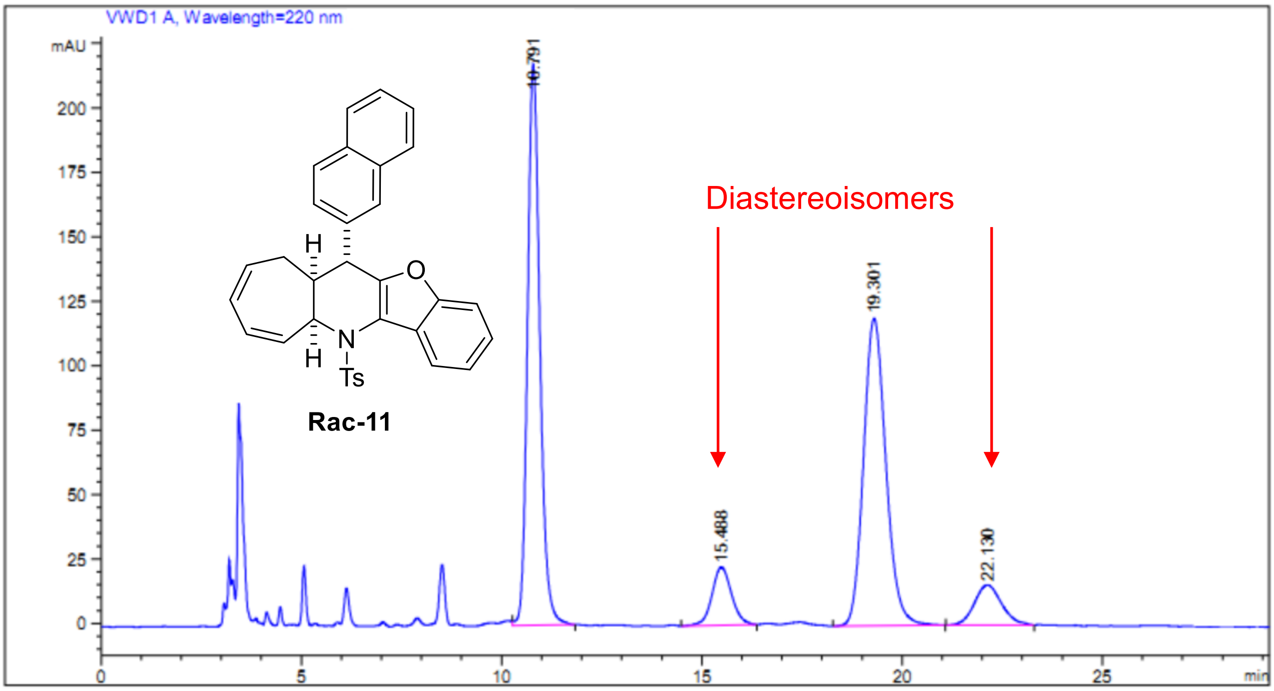



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 8.872 | BBA | 0.2502 | 1.69306e4 | 1078.31177 | 26.6872 |
| 2 | 10.004 | BBA | 0.2572 | 4.65102e4 | 2852.03198 | 73.3128 |

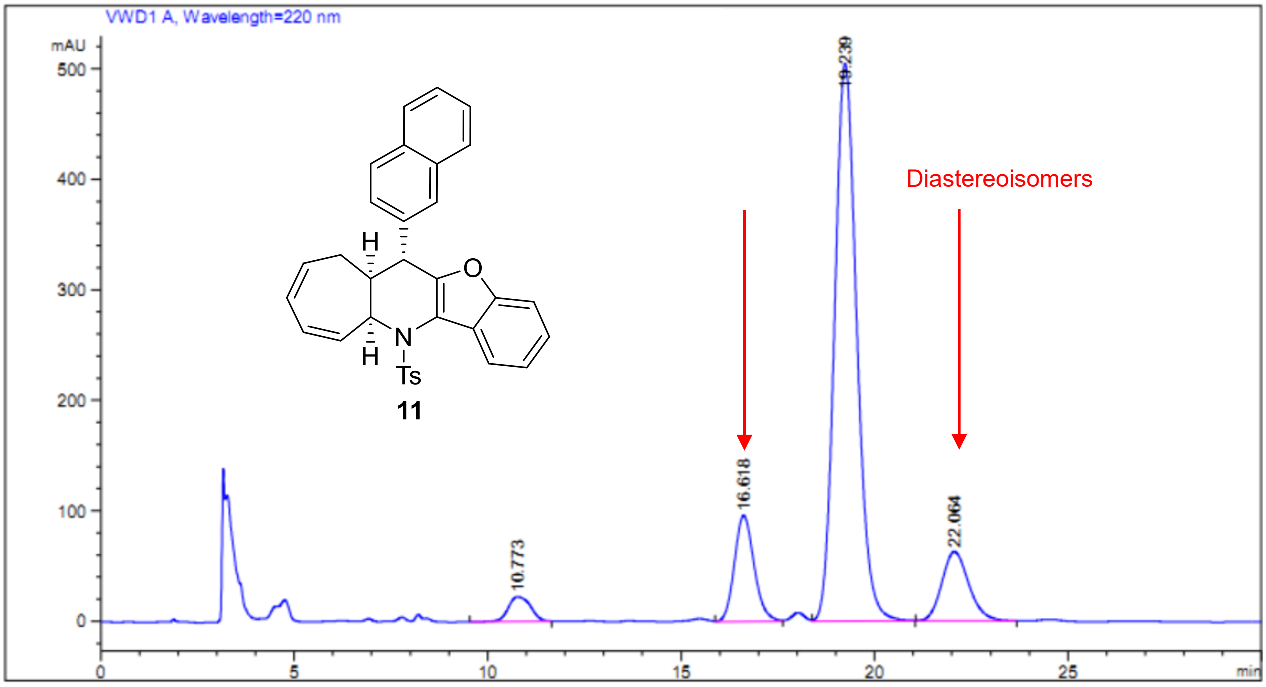

x10^6
+ESI Scan (rt: 0.207 min) Frag=175.0V
492.1612
493.1651
Ph
H
O
HN
Ts
9
(ESI-TOF) m/z: [M + Na]+
Calcd for $C_{29}H_{27}NO_3SNa^+$ 492.1604
Counts vs. Mass-to-Charge (m/z)


8.253 8.250 8.247 8.233 8.230 8.228 7.785 7.776 7.769 7.762 7.670 7.665 7.661 7.655 7.649 7.645 7.576 7.555 7.466 7.460 7.451 7.442 7.437 7.347 7.338 7.335 7.326 7.316 7.306 7.269 7.265 7.262 7.255 7.224 7.222 7.219 6.486 6.482 6.465 6.460 5.900 5.880 5.873 5.812 5.789 5.781 5.680 5.671 5.591 5.560 5.311 5.308 5.302 4.216 4.188 2.450 2.277 2.273 0.000
H
O
N
H
Ts
11
$^1$H NMR (400 MHz, CDCl$_3$)
0.99 1.04 3.10 1.02 2.02 3.05 1.08 1.01 0.99 1.01 1.01 1.07 1.04 1.01 0.99 3.03 1.05 1.00 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

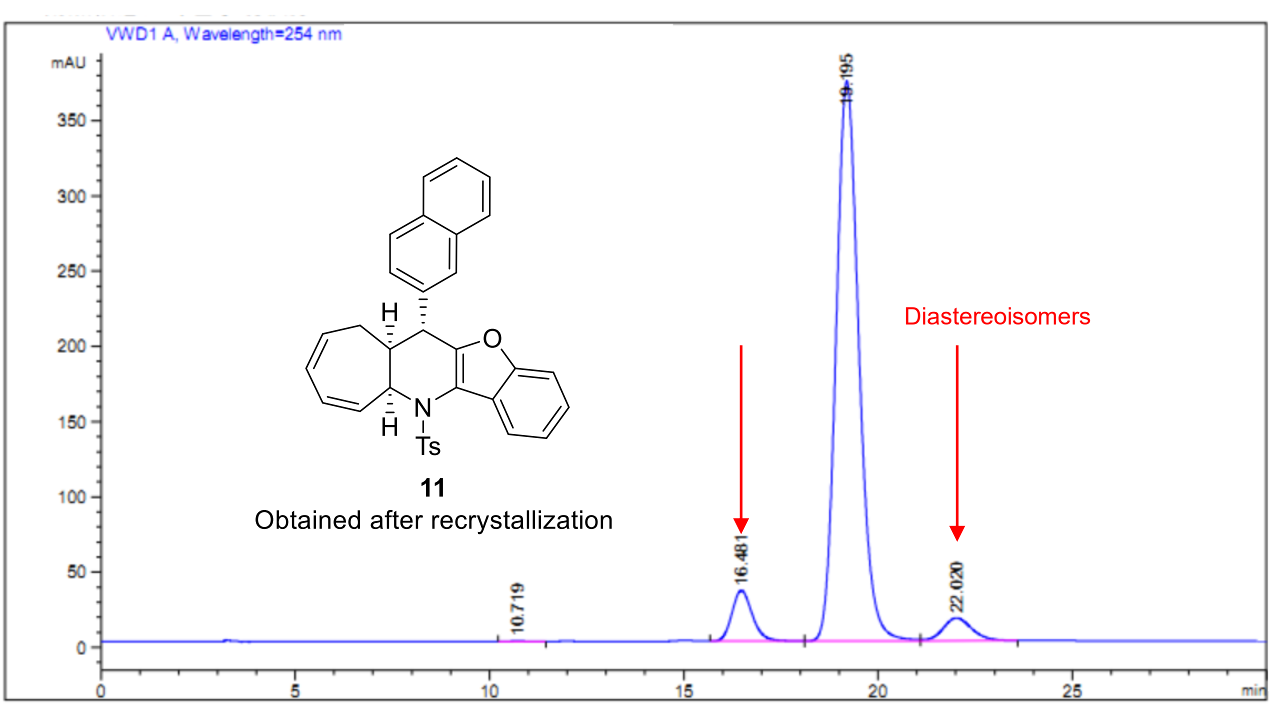

154.429 150.363 144.289 136.305 134.938 133.281 132.836 132.688 130.658 129.977 128.072 128.000 127.622 127.515 127.476 126.198 125.889 125.749 125.578 124.629 124.486 123.093 122.377 117.391 111.263 77.317 77.000 76.683 62.671 41.322 38.507 29.029 21.680
H
O
N
H
Ts
11
$^{13}$C NMR (100 MHz, CDCl$_3$)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



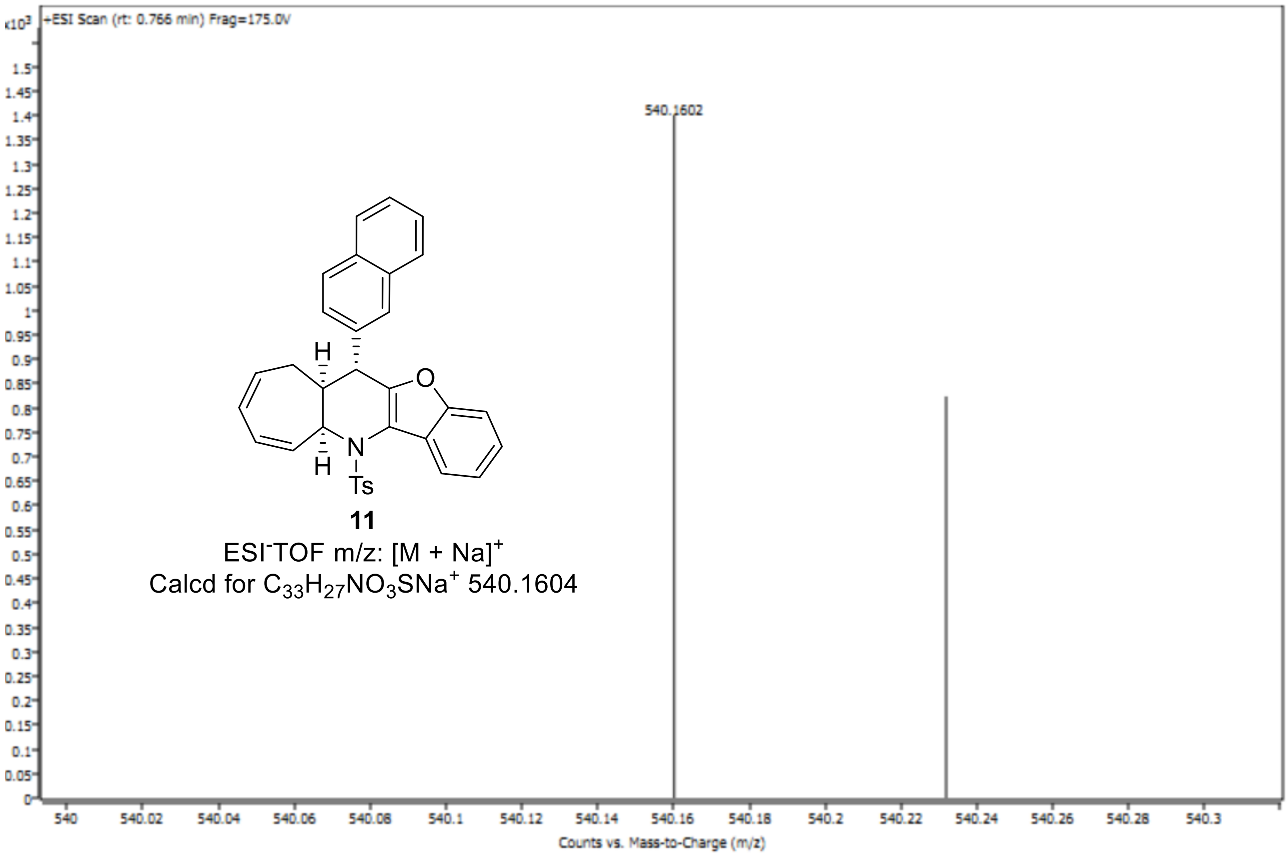

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 10.791 | VB | 0.3304 | 4667.36719 | 217.54463 | 43.1975 |
| 2 | 15.488 | BB | 0.5233 | 764.27209 | 22.48198 | 7.0735 |
| 3 | 19.301 | BB | 0.5989 | 4634.73438 | 119.27387 | 42.8955 |
| 4 | 22.130 | BB | 0.7169 | 738.33765 | 15.59334 | 6.8335 |

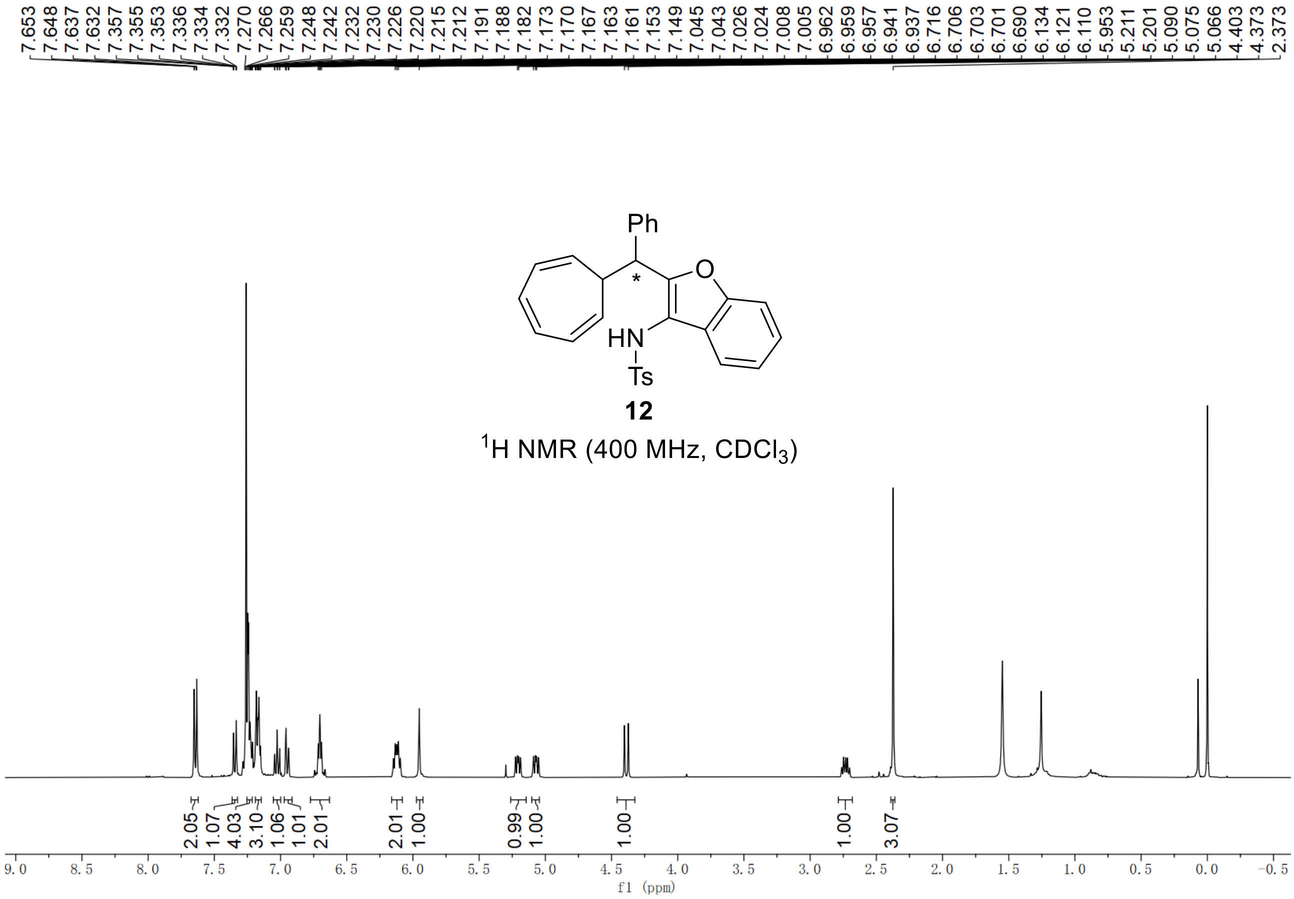


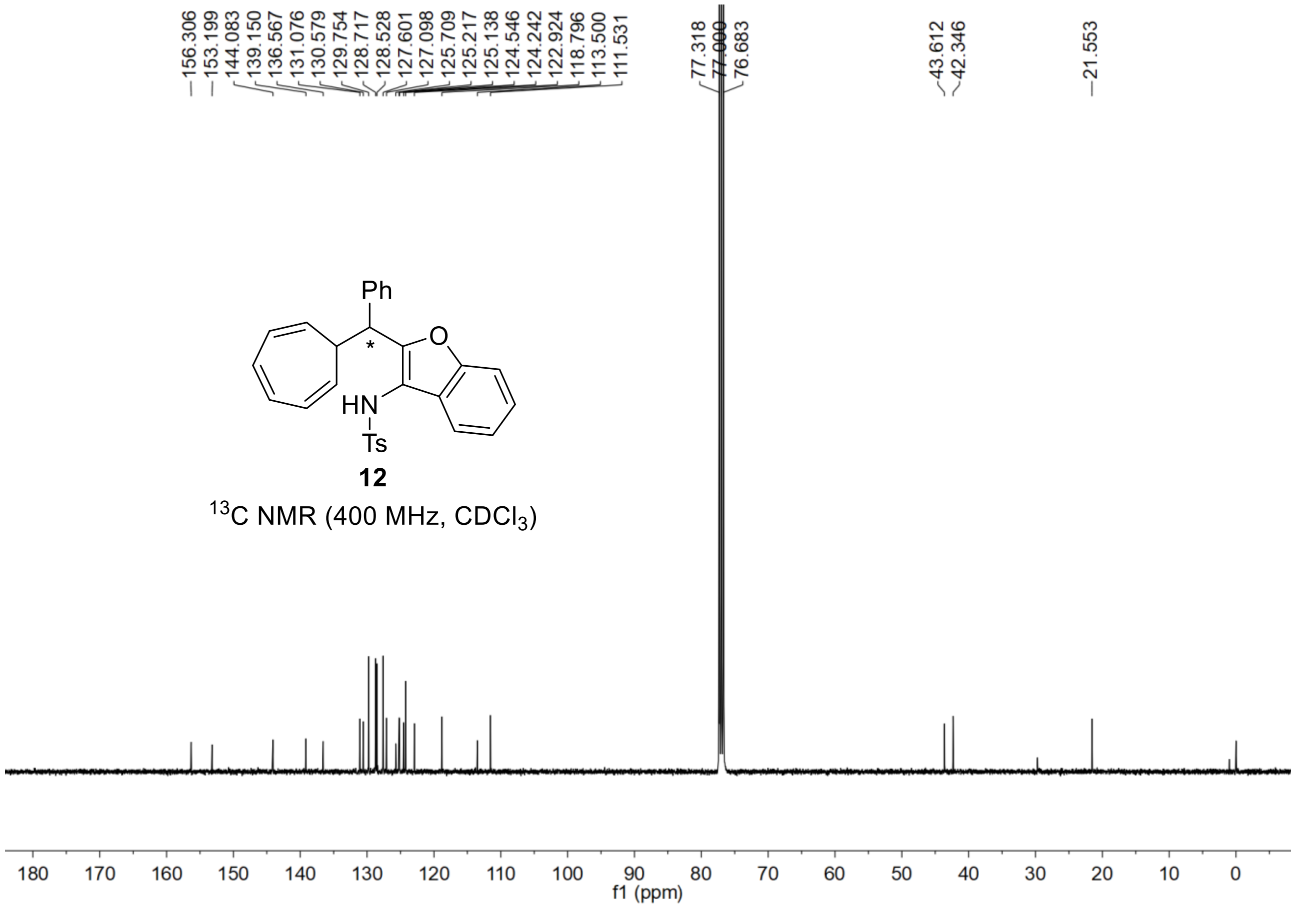

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 10.773 | BB | 0.6449 | 890.41455 | 22.37064 | 3.2569 |
| 2 | 16.618 | VV | 0.5473 | 3397.95801 | 95.90814 | 12.4288 |
| 3 | 19.239 | VB | 0.6132 | 2.00298e4 | 504.47507 | 73.2637 |
| 4 | 22.064 | BB | 0.7472 | 3021.17603 | 62.52697 | 11.0506 |

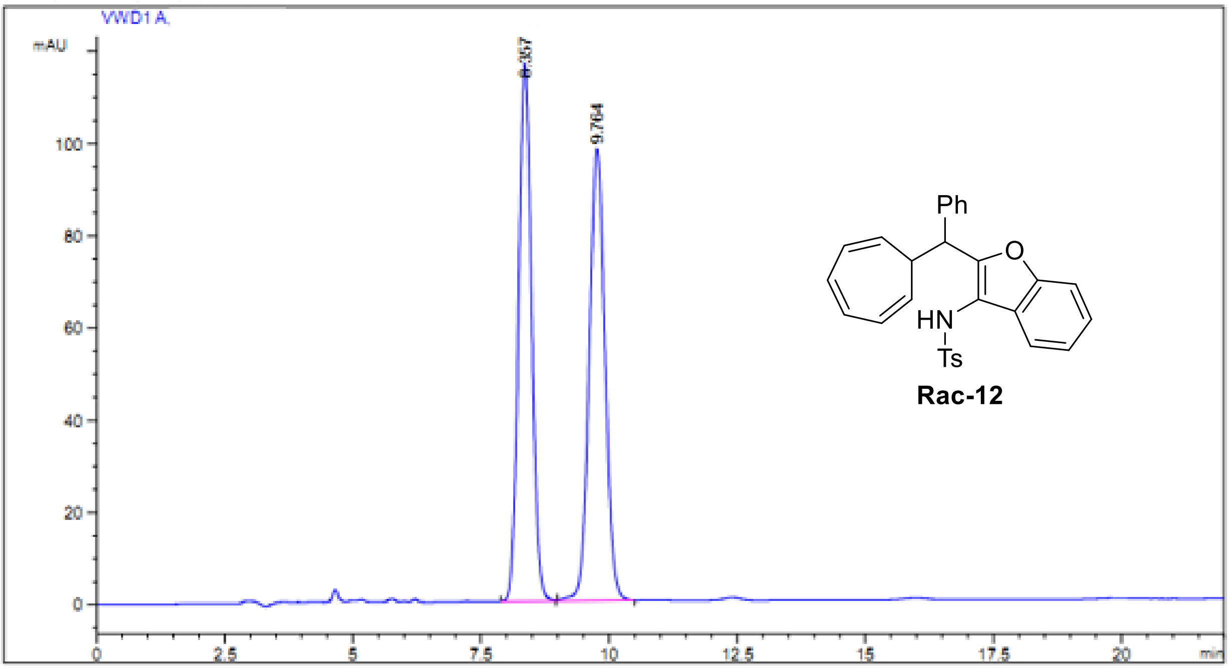



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 10.719 | VB | 0.3903 | 6.81185 | 2.07493e-1 | 0.0395 |
| 2 | 16.481 | BB | 0.5591 | 1227.66272 | 33.69169 | 7.1236 |
| 3 | 19.195 | BV | 0.6301 | 1.52169e4 | 372.03900 | 88.2974 |
| 4 | 22.020 | VBA | 0.7874 | 782.31226 | 15.14768 | 4.5394 |

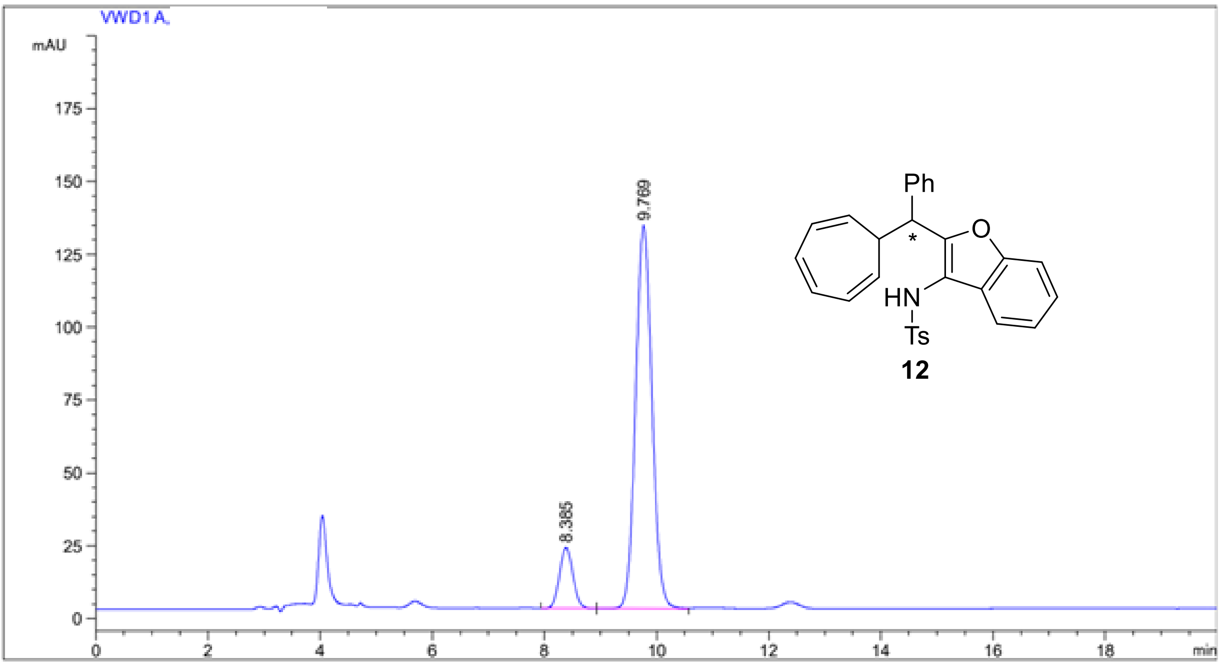



Ph
O
HN
Ts
*
12
¹H NMR (400 MHz, CDCl₃)
f1 (ppm)

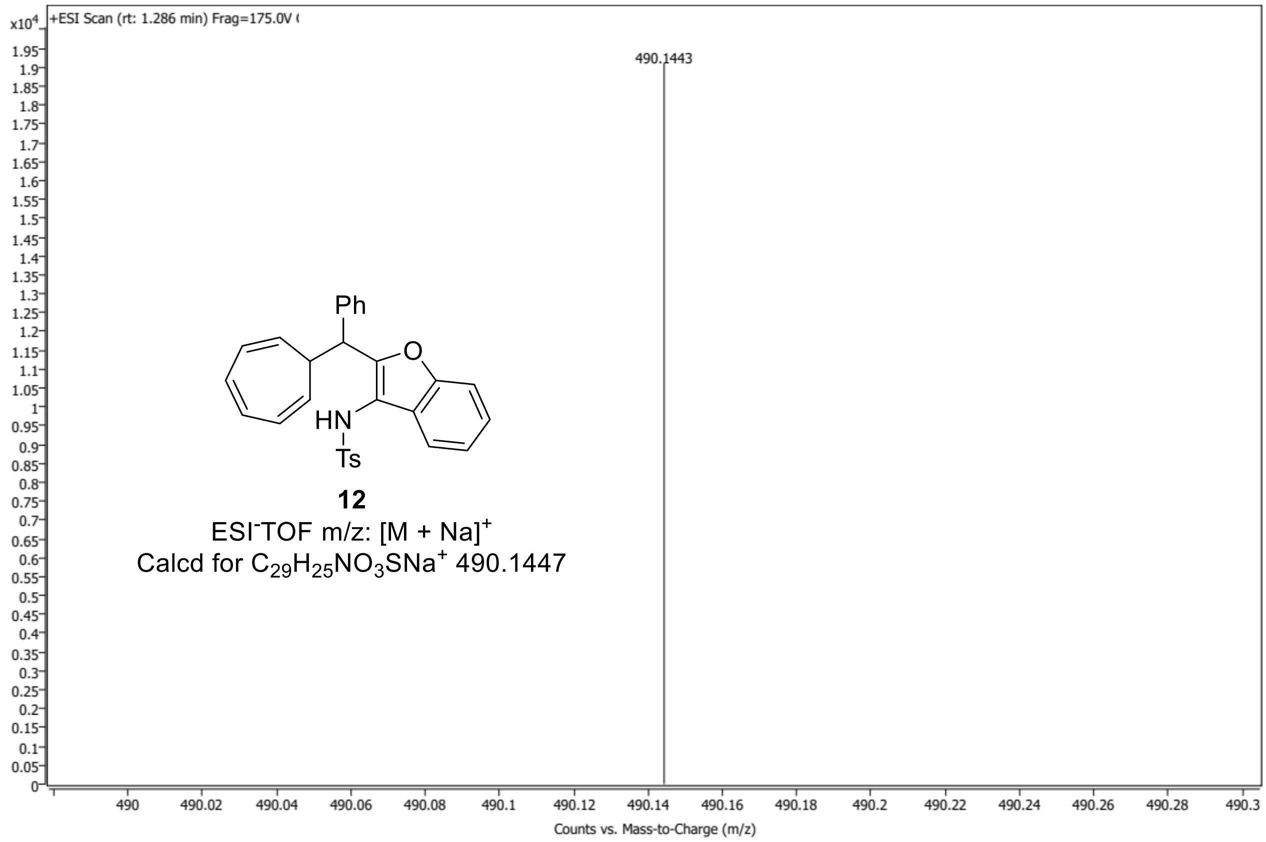

Ph
O
HN
Ts
*
12
¹³C NMR (400 MHz, CDCl₃)
f1 (ppm)



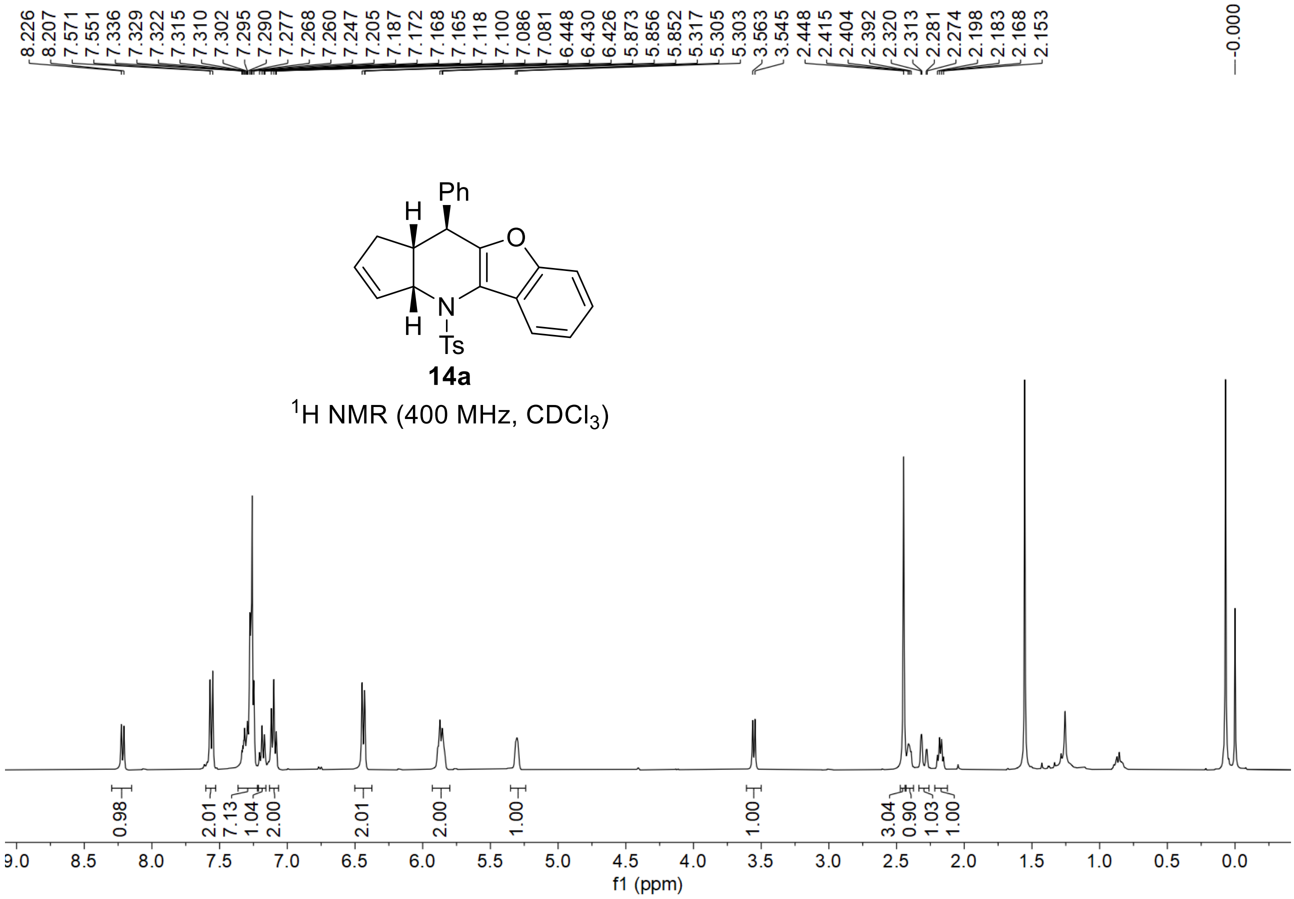

| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 8.357 | BB | 0.2756 | 2071.52319 | 116.67725 | 49.6487 |
| 2 | 9.764 | BB | 0.3333 | 2100.84229 | 97.90084 | 50.3513 |

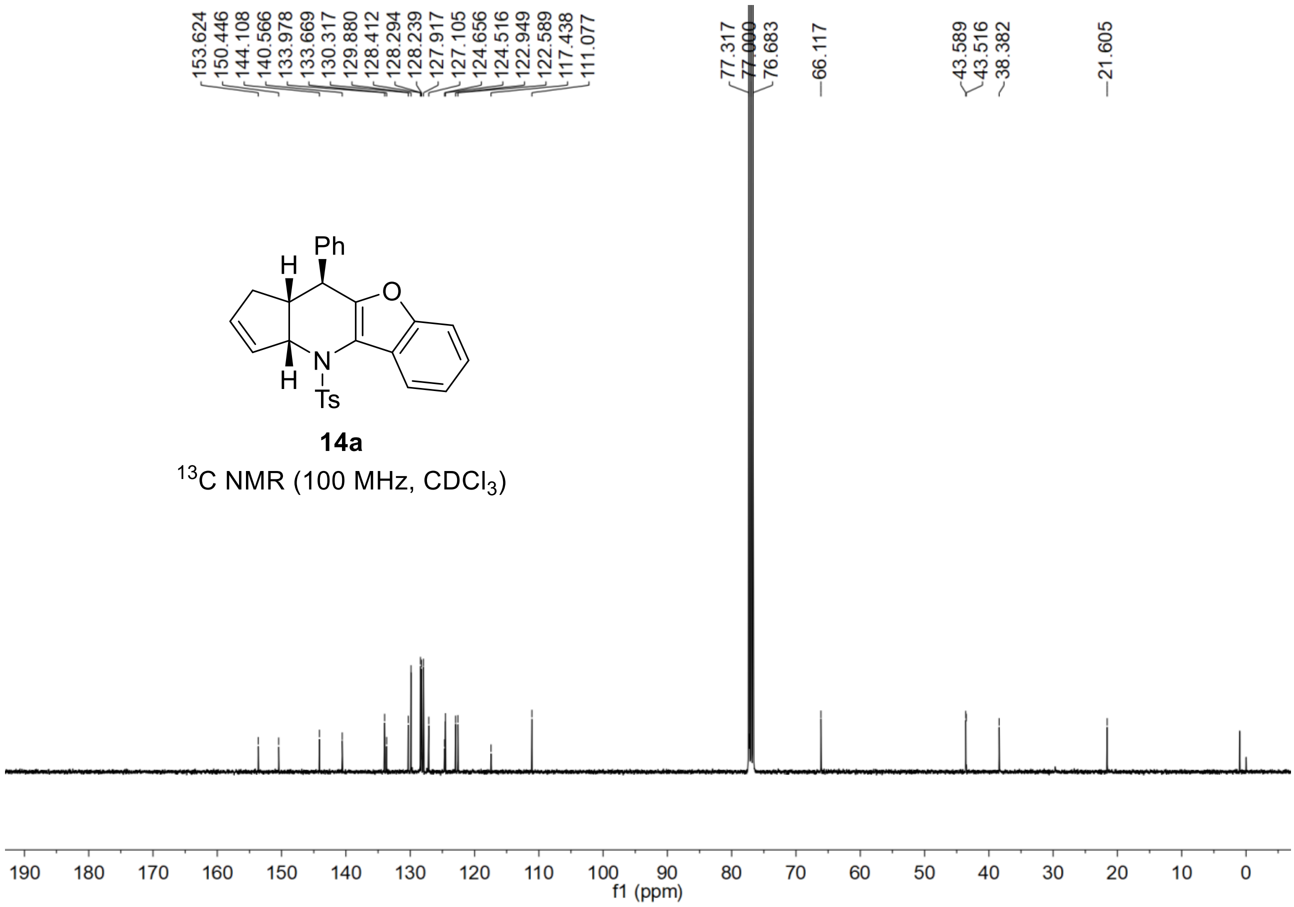


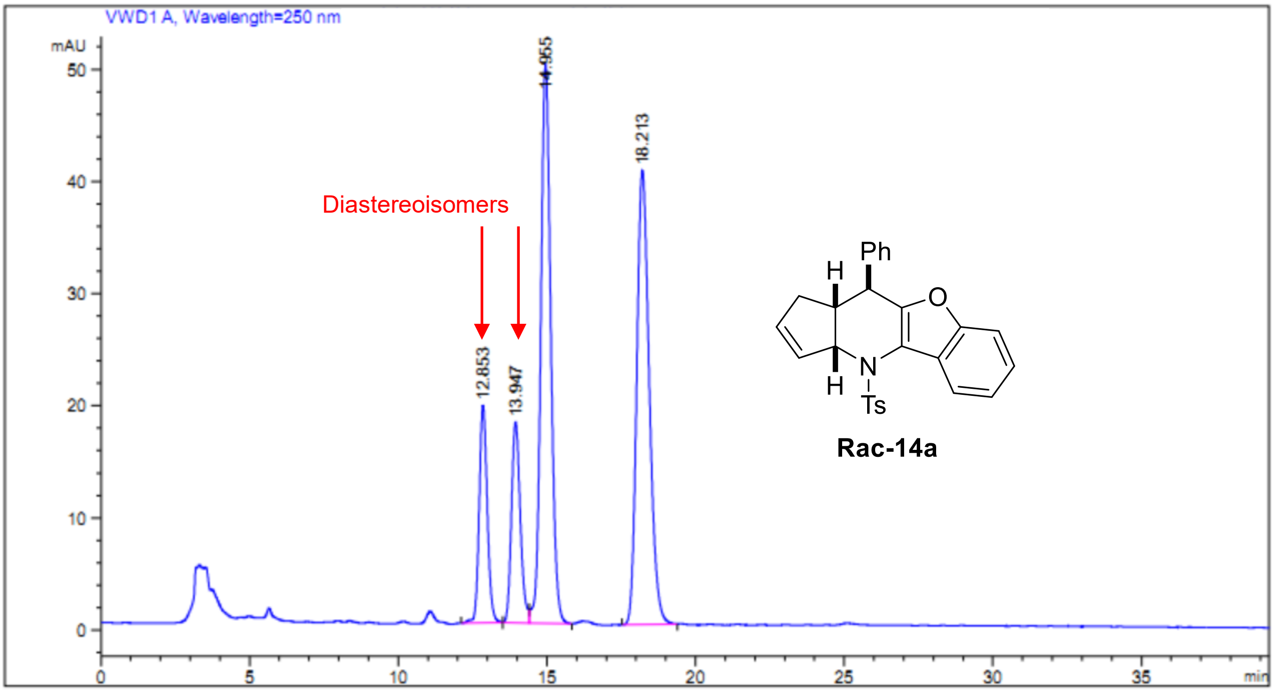

| # | [min] | | [min] | mAU *s | [mAU ] | % |
|---|---|---|---|---|---|---|
| 1 | 8.385 | BB | 0.2596 | 350.31448 | 20.90230 | 11.6298 |
| 2 | 9.769 | BV | 0.3150 | 2661.90674 | 131.40013 | 88.3702 |



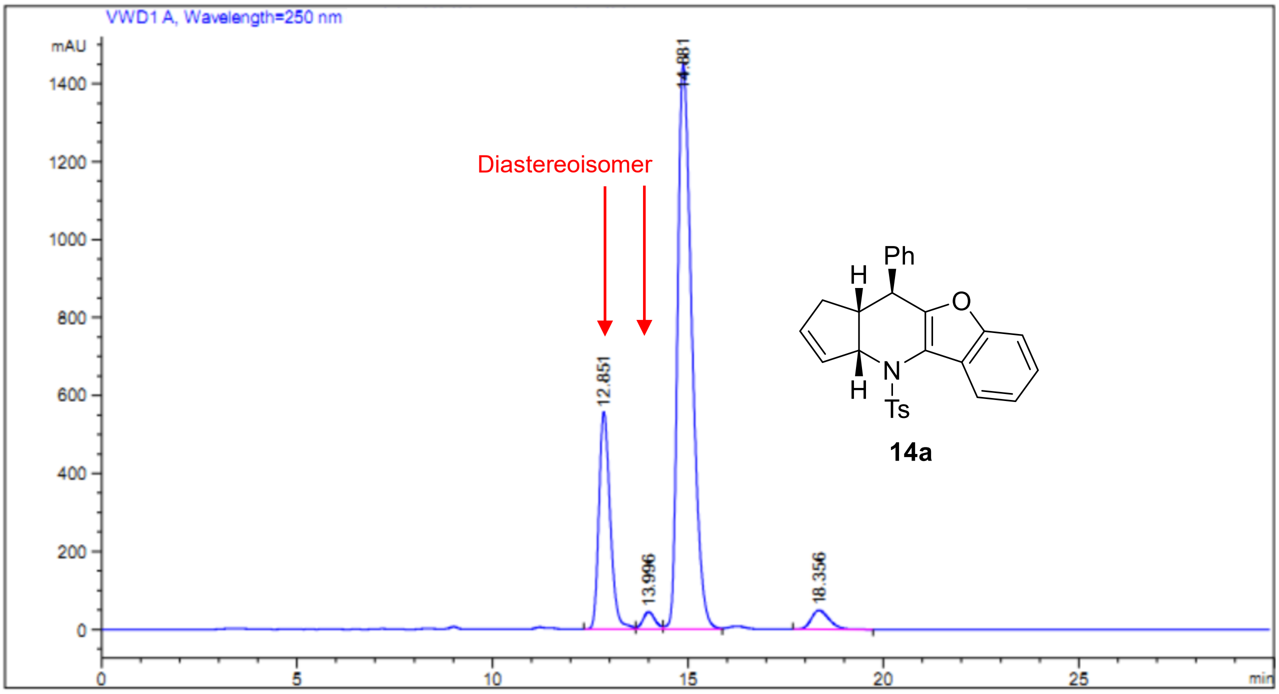
+ESI Scan (rt: 1.286 min) Frag=175.0V
x10^4
490.1443
Ph
O
HN
Ts
12
ESI-TOF m/z: [M + Na]+
Calcd for C29H25NO3SNa+ 490.1447
Counts vs. Mass-to-Charge (m/z)


8.226
8.207
7.571
7.551
7.336
7.329
7.322
7.315
7.310
7.302
7.295
7.290
7.277
7.268
7.260
7.247
7.205
7.187
7.172
7.168
7.165
7.118
7.100
7.086
7.081
6.448
6.430
6.426
5.873
5.856
5.852
5.317
5.305
5.303
3.563
3.545
2.448
2.415
2.404
2.392
2.320
2.313
2.281
2.274
2.198
2.183
2.168
2.153
0.000
Ph
H
O
H
N
Ts
14a
$^{1}$H NMR (400 MHz, CDCl$_3$)
0.98
2.01
7.13
1.04
2.00
2.01
2.00
1.00
1.00
3.04
0.90
1.03
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

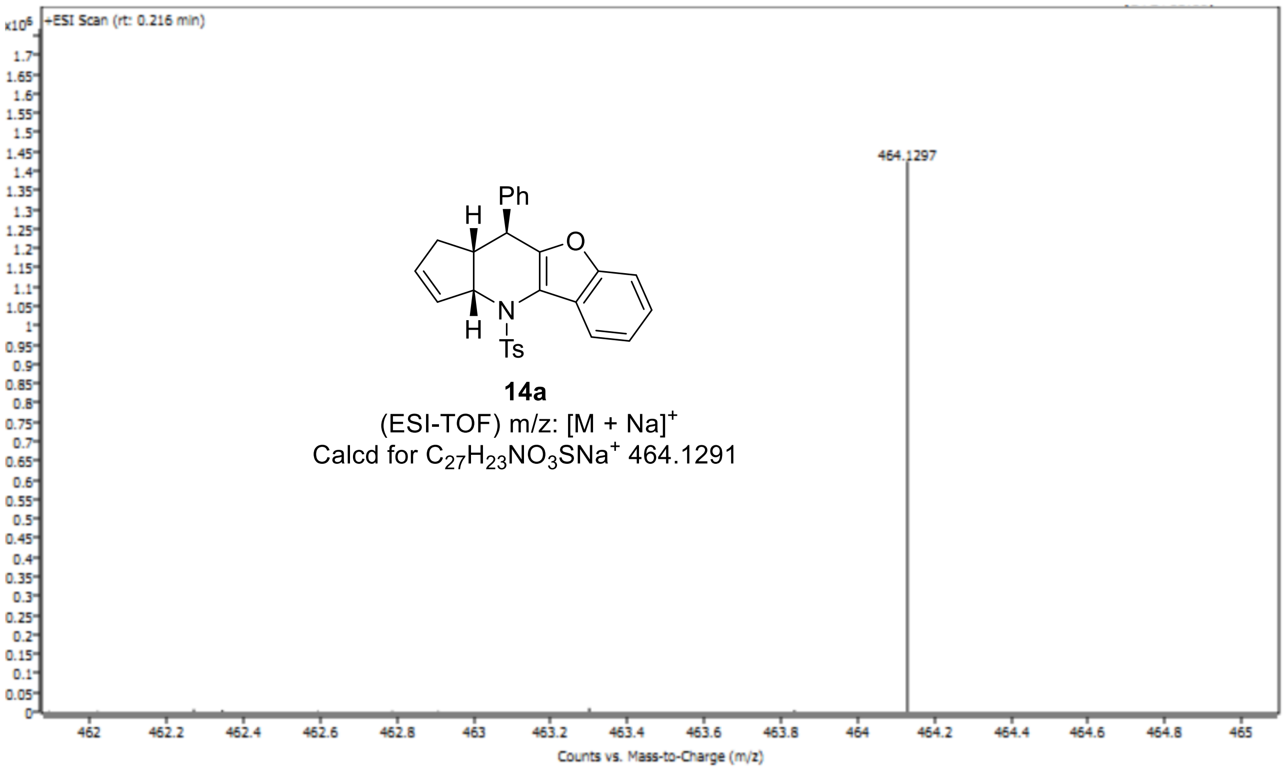

153.624
150.446
144.108
140.566
133.978
133.669
130.317
129.880
128.412
128.294
128.239
127.917
127.105
124.656
124.516
122.949
122.589
117.438
111.077
77.317
77.000
76.683
66.117
43.589
43.516
38.382
21.605
Ph
H
O
H
N
Ts
14a
$^{13}$C NMR (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



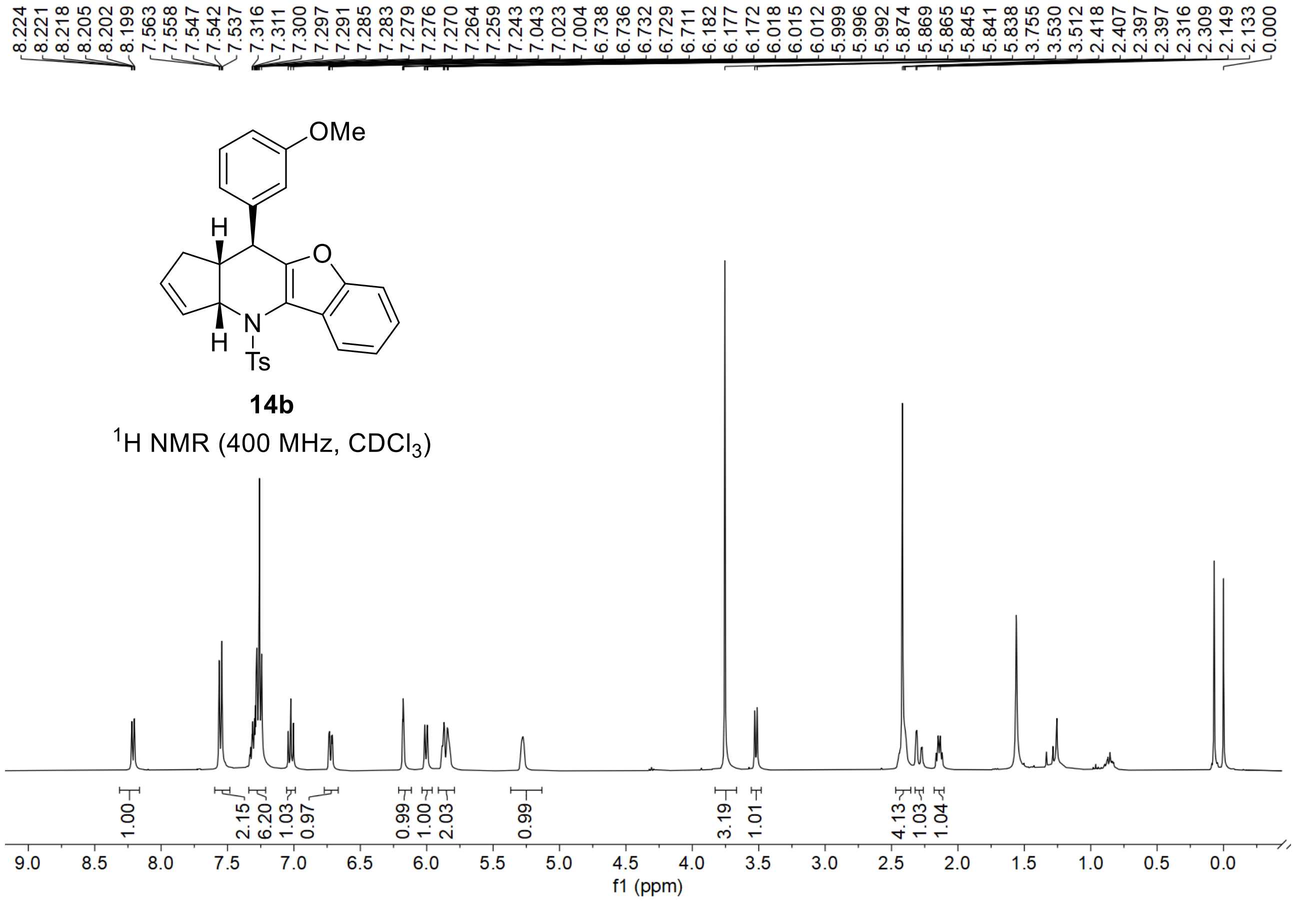

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.853 | BB | 0.2916 | 366.40060 | 19.40357 | 11.9039 |
| 2 | 13.947 | BV | 0.3182 | 369.78287 | 17.89857 | 12.0138 |
| 3 | 14.955 | VB | 0.3605 | 1160.38916 | 49.83633 | 37.6996 |
| 4 | 18.213 | BB | 0.4510 | 1181.41772 | 40.50112 | 38.3828 |



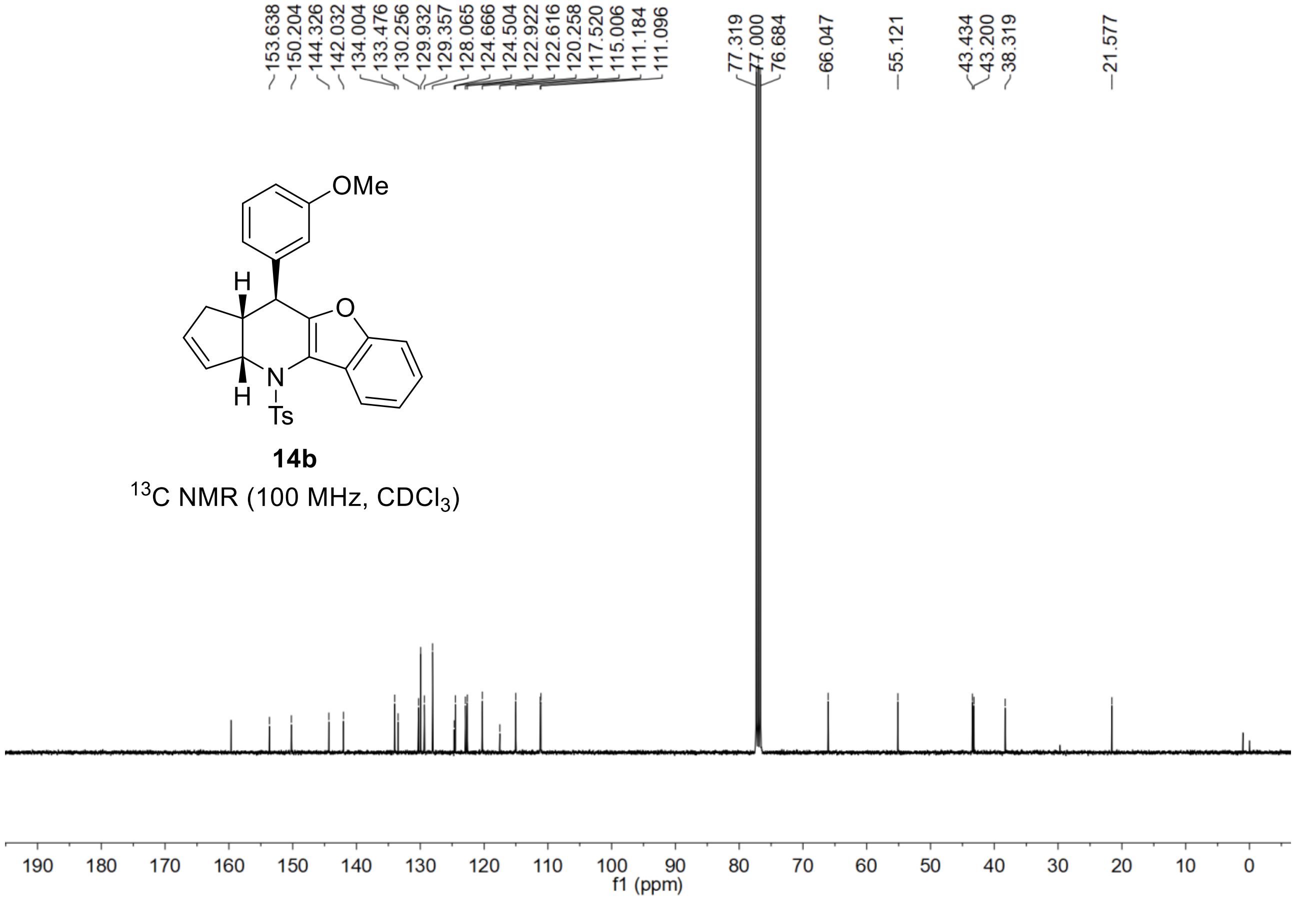

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 12.851 | BV | 0.3094 | 1.11714e4 | 557.65723 | 22.1517 |
| 2 | 13.996 | VV | 0.3319 | 960.78424 | 44.50592 | 1.9051 |
| 3 | 14.881 | VV | 0.3922 | 3.67631e4 | 1448.58972 | 72.8971 |
| 4 | 18.356 | BB | 0.4811 | 1536.18640 | 48.95470 | 3.0461 |



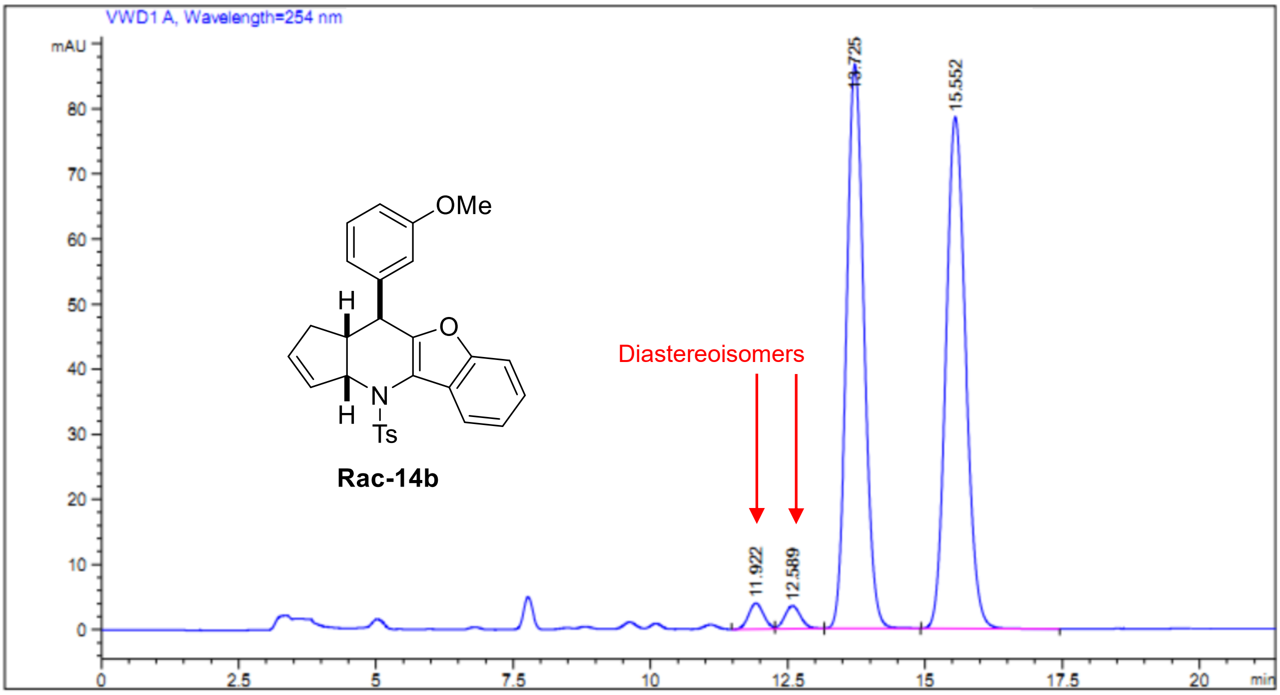
+ESI Scan (rt: 0.216 min)
x10^6
464.1297
Ph
H
O
H
N
Ts
14a
(ESI-TOF) m/z: [M + Na]+
Calcd for $C_{27}H_{23}NO_3SNa^+$ 464.1291
Counts vs. Mass-to-Charge (m/z)



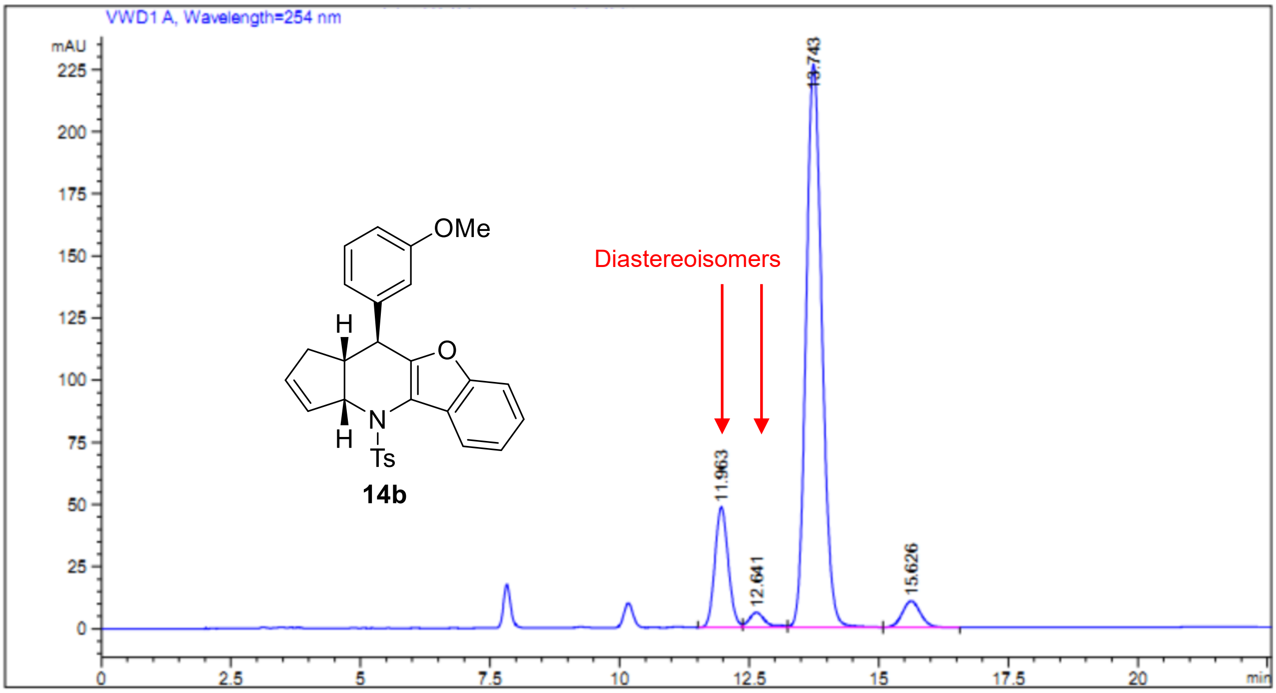
8.224 8.221 8.218 8.205 8.202 8.199 7.563 7.558 7.547 7.542 7.537 7.316 7.311 7.300 7.297 7.291 7.285 7.283 7.279 7.276 7.270 7.264 7.259 7.243 7.043 7.023 7.004 6.738 6.736 6.732 6.729 6.711 6.182 6.177 6.172 6.018 6.015 6.012 5.999 5.996 5.992 5.874 5.869 5.865 5.845 5.841 5.838 3.755 3.530 3.512 2.418 2.407 2.397 2.397 2.316 2.309 2.149 2.133 0.000
OMe
H
O
N
H
Ts
14b
$^1$H NMR (400 MHz, CDCl$_3$)
1.00 2.15 6.20 1.03 0.97 0.99 1.00 2.03 0.99 3.19 1.01 4.13 1.03 1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

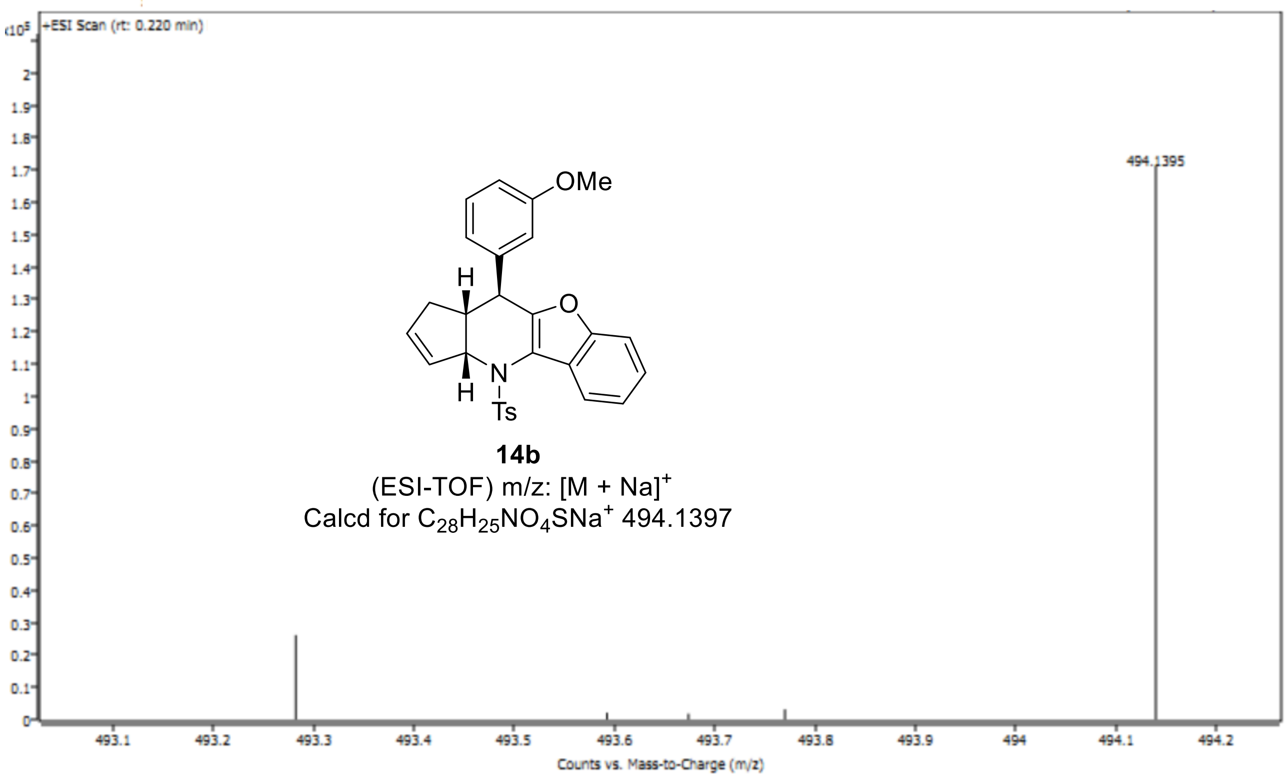
153.638 150.204 144.326 142.032 134.004 133.476 130.256 129.932 129.357 128.065 124.666 124.504 122.922 122.616 120.258 117.520 115.006 111.184 111.096
77.319 77.000 76.684
66.047
55.121
43.434 43.200 38.319
21.577
OMe
H
O
N
H
Ts
14b
$^{13}$C NMR (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

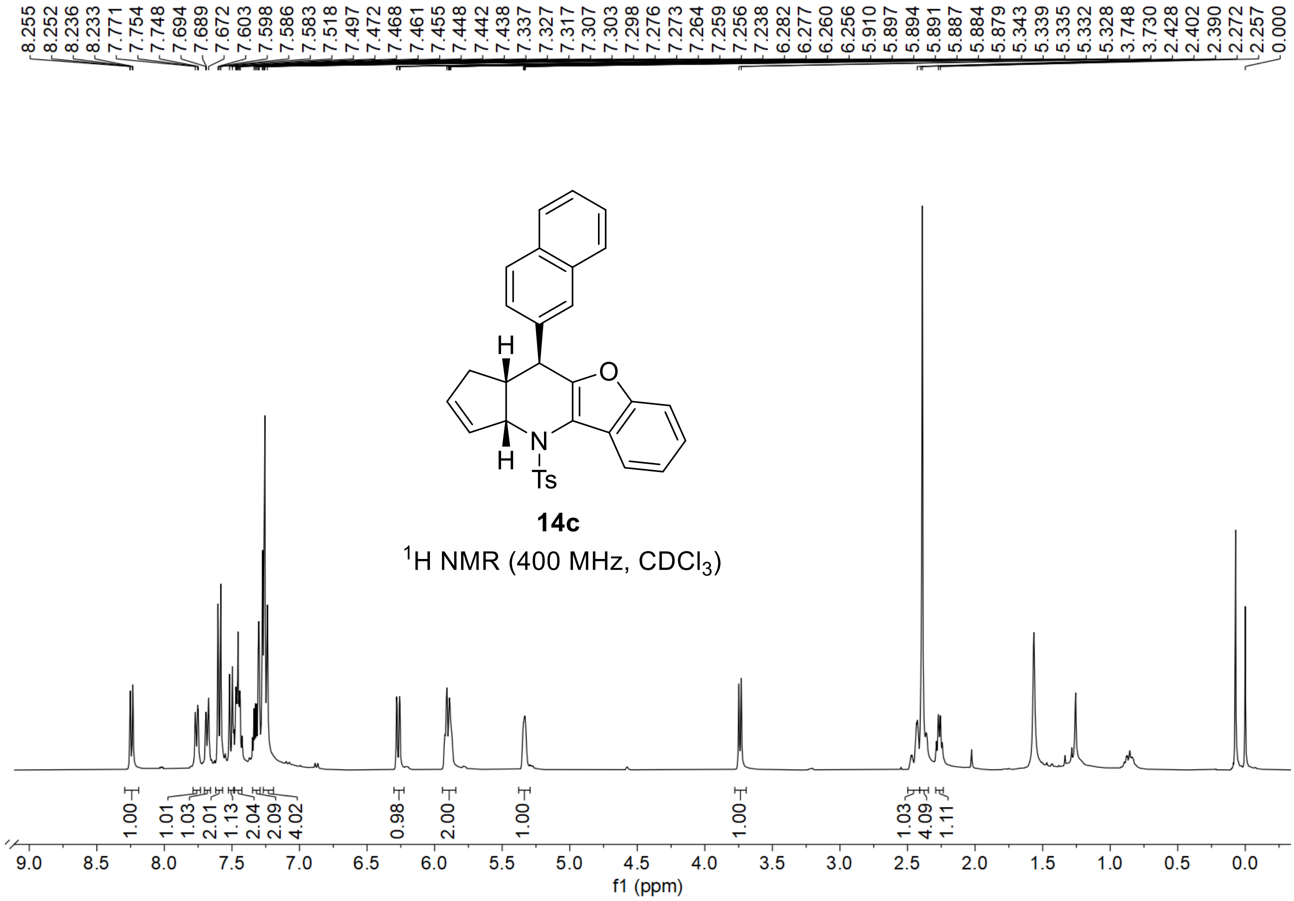
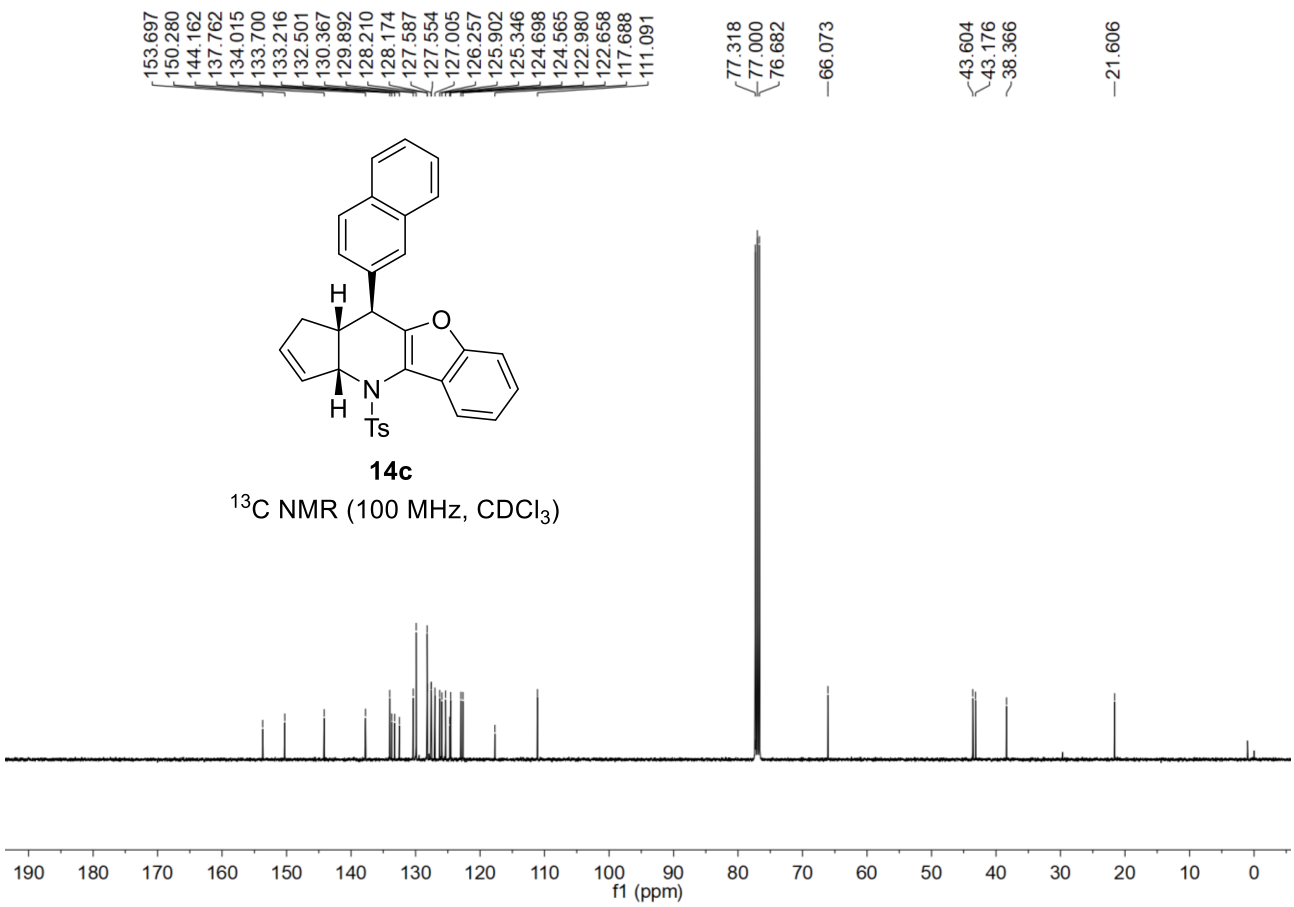


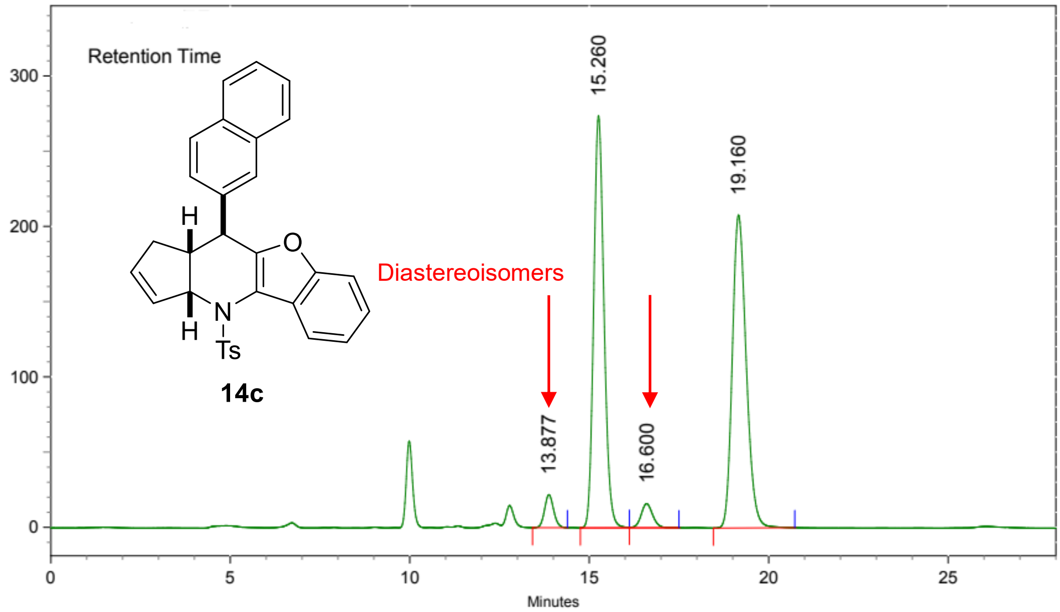

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 11.922 | BV | 0.2992 | 75.19041 | 3.97623 | 1.8714 |
| 2 | 12.589 | VB | 0.3089 | 69.20010 | 3.50649 | 1.7223 |
| 3 | 13.725 | BB | 0.3450 | 1911.88049 | 86.58559 | 47.5842 |
| 4 | 15.552 | BB | 0.3903 | 1961.61499 | 78.56947 | 48.8221 |




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 11.963 | BV | 0.2804 | 871.87396 | 48.31780 | 14.3100 |
| 2 | 12.641 | VV | 0.3276 | 131.92065 | 6.04084 | 2.1652 |
| 3 | 13.743 | VB | 0.3306 | 4833.42676 | 226.38196 | 79.3306 |
| 4 | 15.626 | BB | 0.3757 | 255.54683 | 10.55185 | 4.1943 |

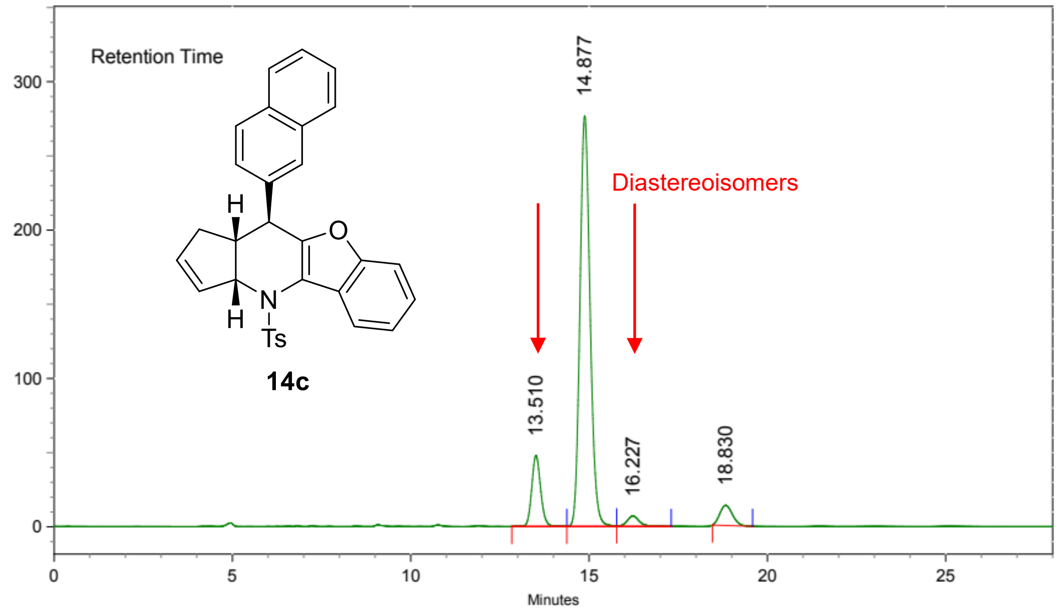

+ESI Scan (rt: 0.220 min)
x10^5
494.1395
OMe
H
O
N
H
Ts
14b
(ESI-TOF) m/z: [M + Na]+
Calcd for C28H25NO4SNa+ 494.1397
Counts vs. Mass-to-Charge (m/z)


8.255 8.252 8.236 8.233 7.771 7.754 7.748 7.694 7.689 7.672 7.603 7.598 7.586 7.583 7.518 7.497 7.472 7.468 7.461 7.455 7.448 7.442 7.438 7.337 7.327 7.317 7.307 7.303 7.298 7.276 7.273 7.264 7.259 7.256 7.238 6.282 6.277 6.260 6.256 5.910 5.897 5.894 5.891 5.887 5.884 5.879 5.343 5.339 5.335 5.332 5.328 3.748 3.730 2.428 2.402 2.390 2.272 2.257 0.000
H
O
N
H
Ts
14c
$^{1}$H NMR (400 MHz, $CDCl_3$)
1.00 1.01 1.03 2.01 1.13 2.04 2.09 4.02 0.98 2.00 1.00 1.00 1.03 4.09 1.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

153.697 150.280 144.162 137.762 134.015 133.700 133.216 132.501 130.367 129.892 128.210 128.174 127.587 127.554 127.005 126.257 125.902 125.346 124.698 124.565 122.980 122.658 117.688 111.091
77.318 77.000 76.682
66.073
43.604 43.176 38.366
21.606
H
O
N
H
Ts
14c
$^{13}$C NMR (100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



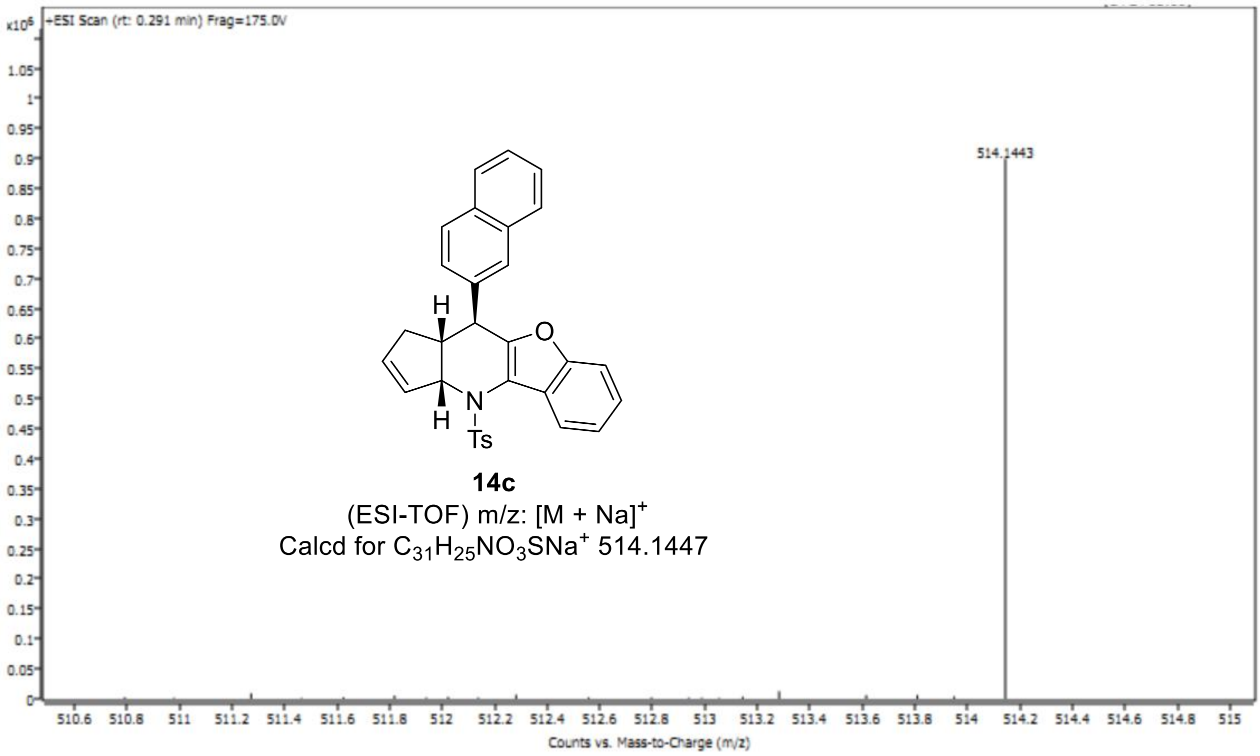

AREA PERCENT REPORT

| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 13.877 | 0.973 | 367474 | 6454178 | 3.2612 |
| 2 | 15.260 | 1.367 | 4594775 | 91634990 | 46.3023 |
| 3 | 16.600 | 1.380 | 268922 | 6026153 | 3.0450 |
| 4 | 19.160 | 2.267 | 3488554 | 93790732 | 47.3915 |

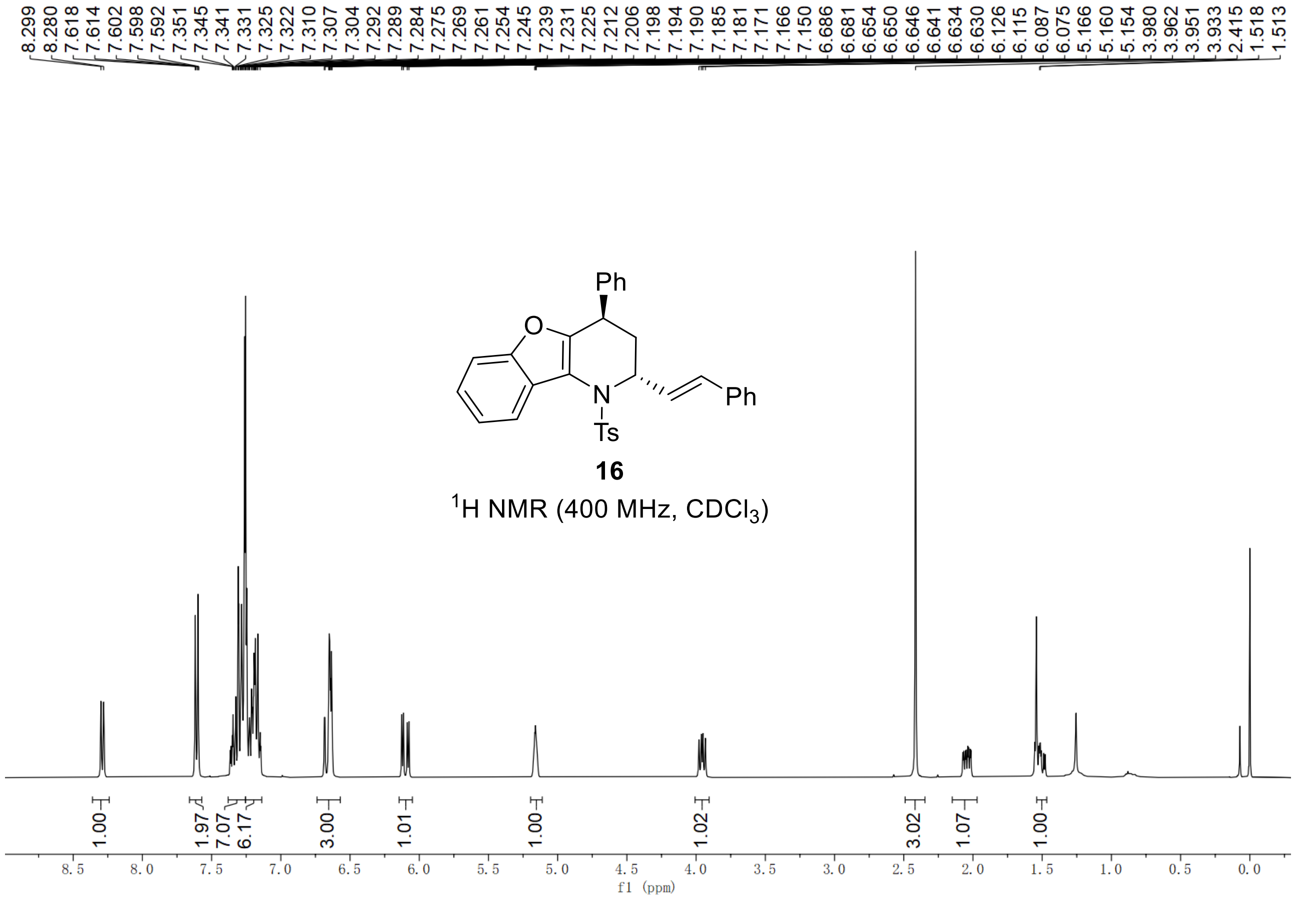


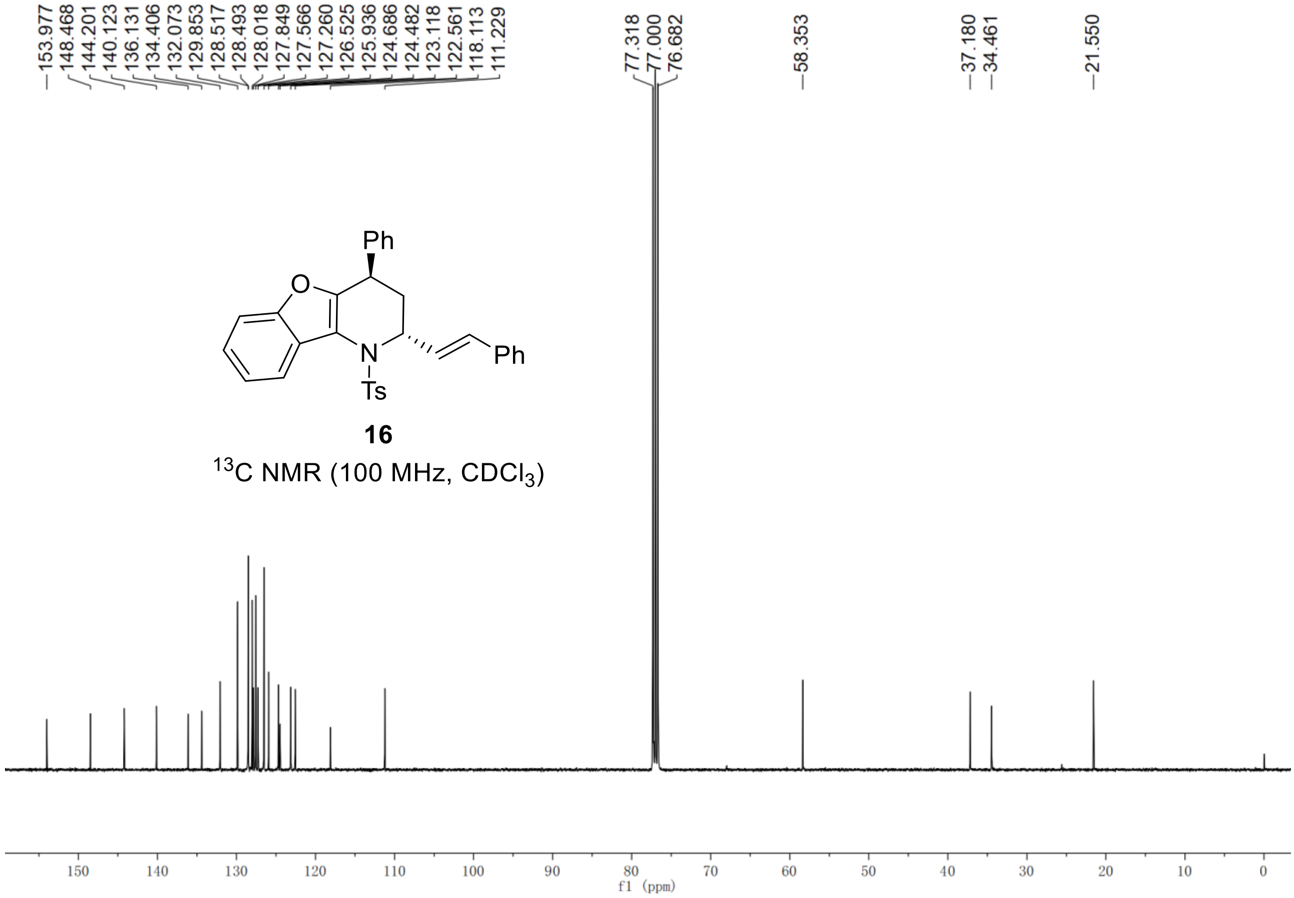

AREA PERCENT REPORT

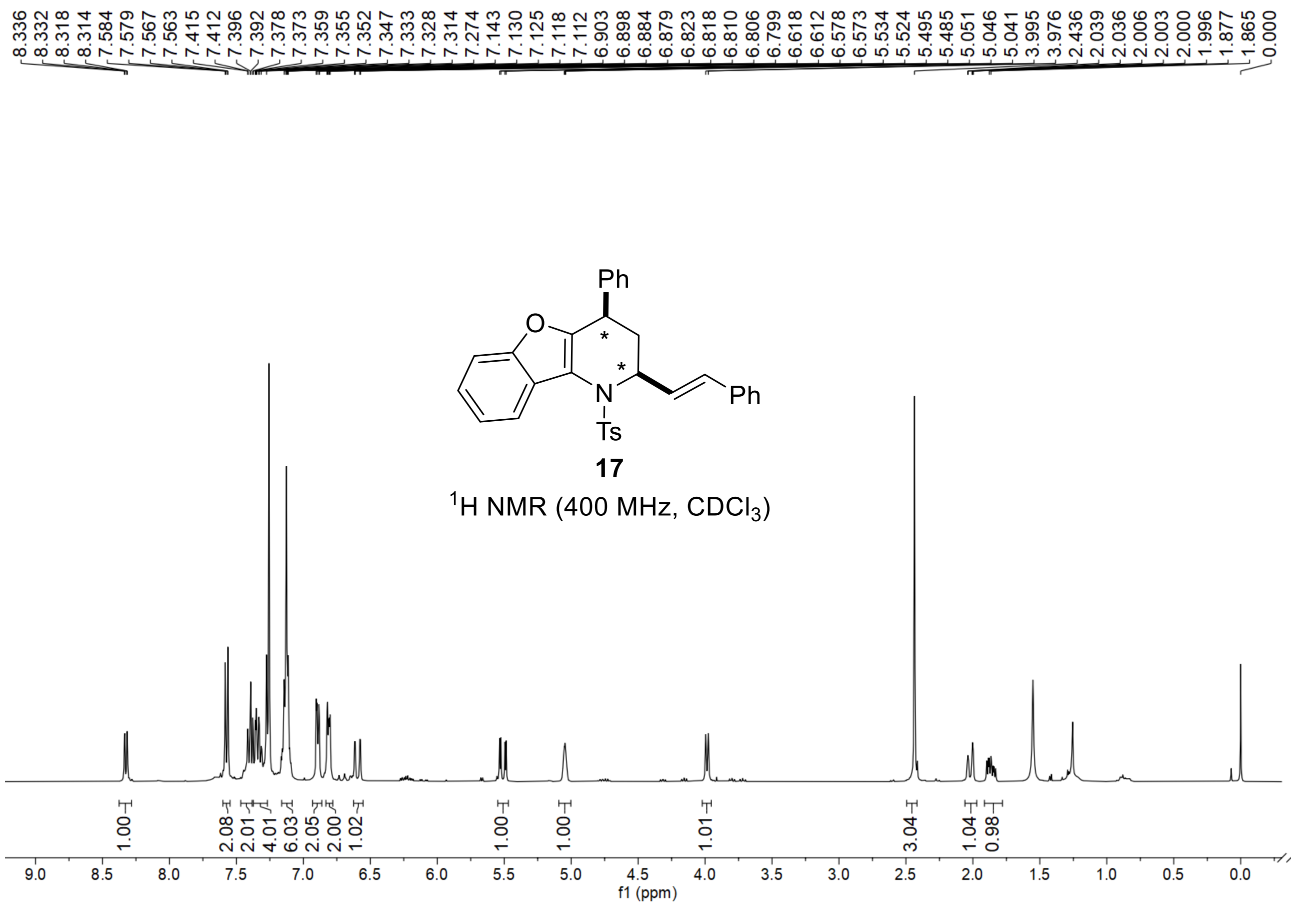
| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 13.510 | 1.543 | 804048 | 14009941 | 12.2753 |
| 2 | 14.877 | 1.397 | 4643137 | 91635596 | 80.2897 |
| 3 | 16.227 | 1.530 | 118213 | 2872015 | 2.5164 |
| 4 | 18.830 | 1.127 | 227692 | 5613675 | 4.9186 |

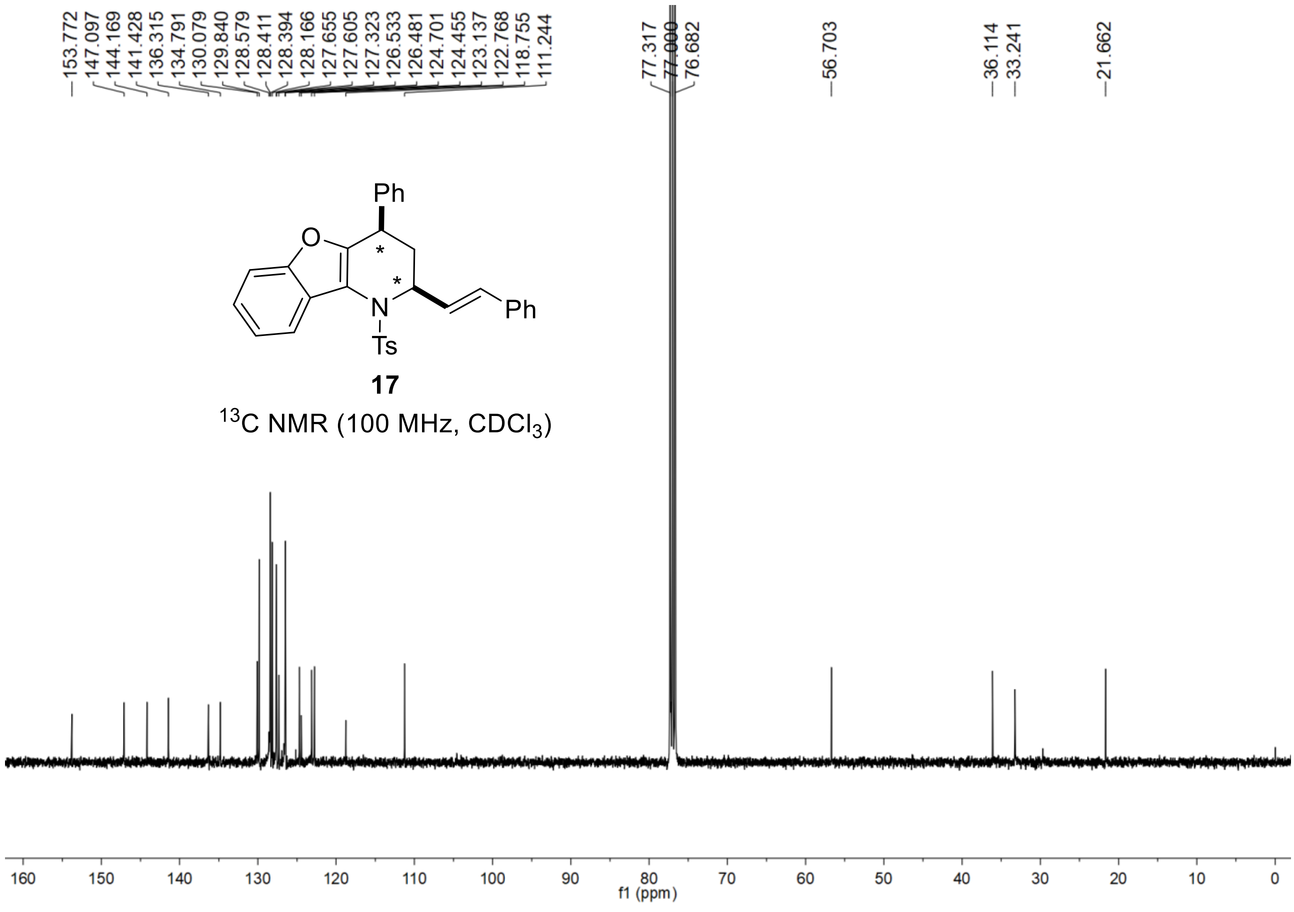


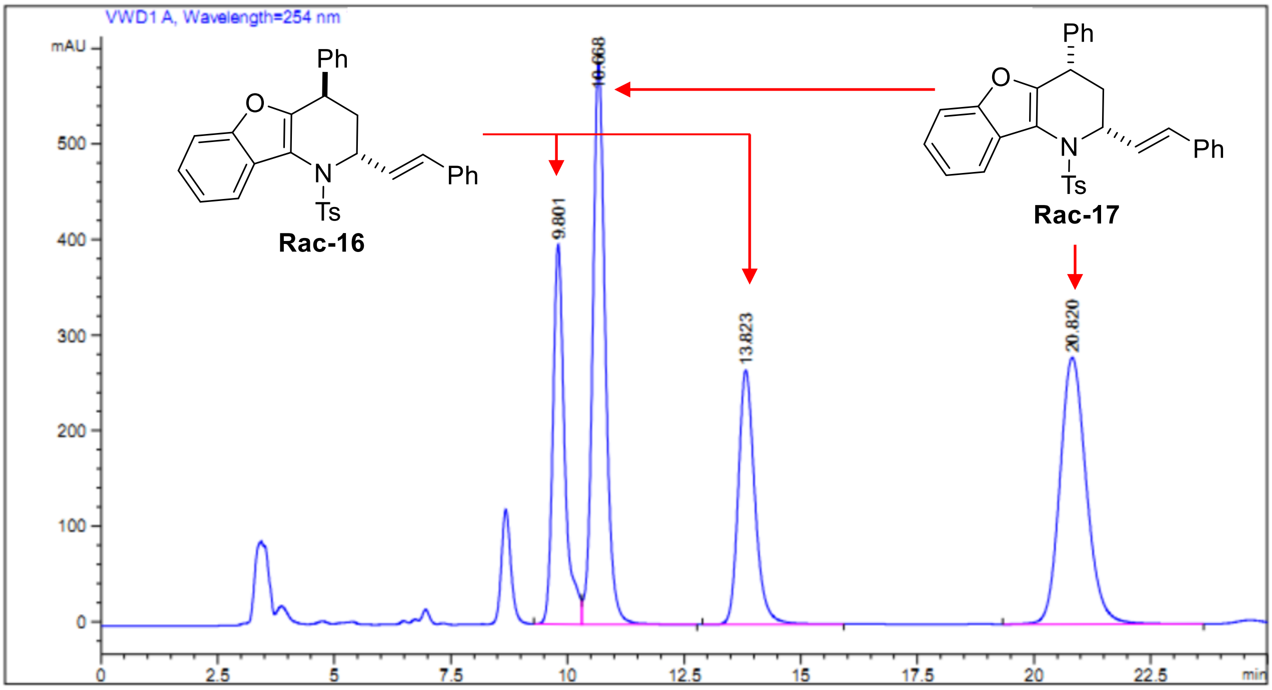
x10^6
+ESI Scan (rt: 0.291 min) Frag=175.0V
514.1443
14c
(ESI-TOF) m/z: [M + Na]+
Calcd for C31H25NO3SNa+ 514.1447
Counts vs. Mass-to-Charge (m/z)


8.299
8.280
7.618
7.614
7.602
7.598
7.592
7.351
7.345
7.341
7.331
7.325
7.322
7.310
7.307
7.304
7.292
7.289
7.284
7.275
7.269
7.261
7.254
7.245
7.239
7.231
7.225
7.212
7.206
7.198
7.194
7.190
7.185
7.181
7.171
7.166
7.150
6.686
6.681
6.654
6.650
6.646
6.641
6.634
6.630
6.126
6.115
6.087
6.075
5.166
5.160
5.154
3.980
3.962
3.951
3.933
2.415
1.518
1.513
Ph
O
N
Ts
Ph
16
$^{1}$H NMR (400 MHz, $CDCl_3$)
1.00
1.97
7.07
6.17
3.00
1.01
1.00
1.02
3.02
1.07
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

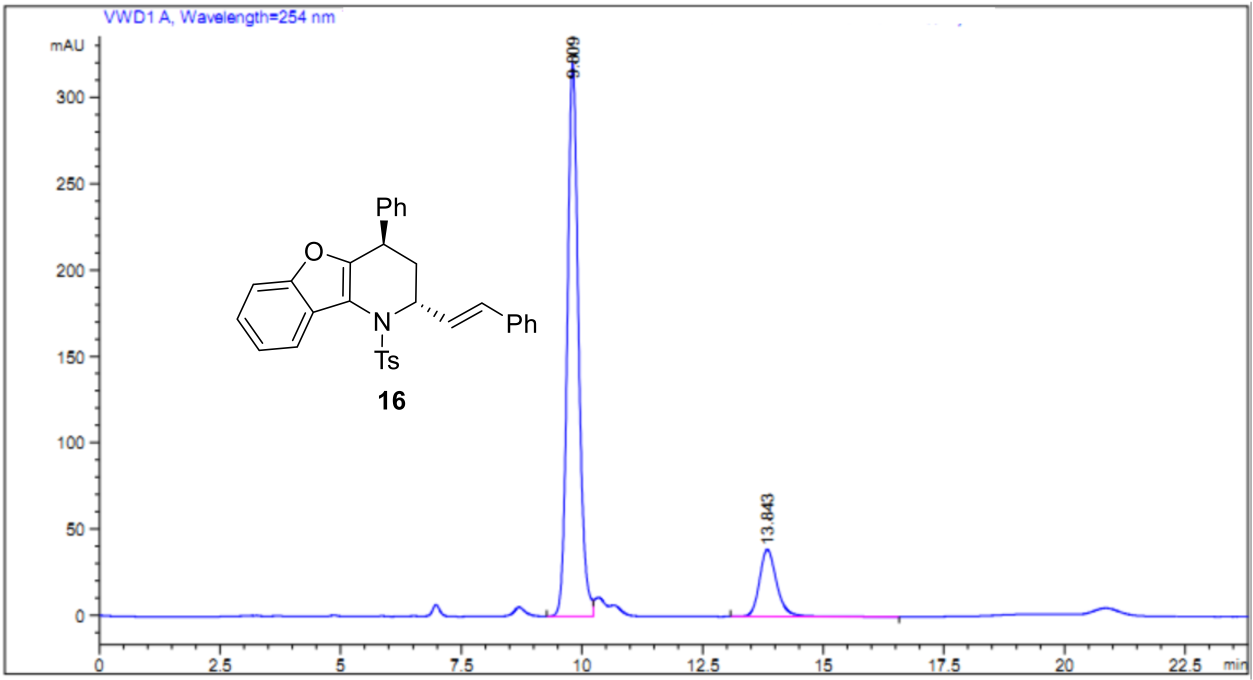

153.977
148.468
144.201
140.123
136.131
134.406
132.073
129.853
128.517
128.493
128.018
127.849
127.566
127.260
126.525
125.936
124.686
124.482
123.118
122.561
118.113
111.229
77.318
77.000
76.682
58.353
37.180
34.461
21.550
Ph
O
N
Ts
Ph
16
$^{13}$C NMR (100 MHz, $CDCl_3$)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


17
$^1$H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

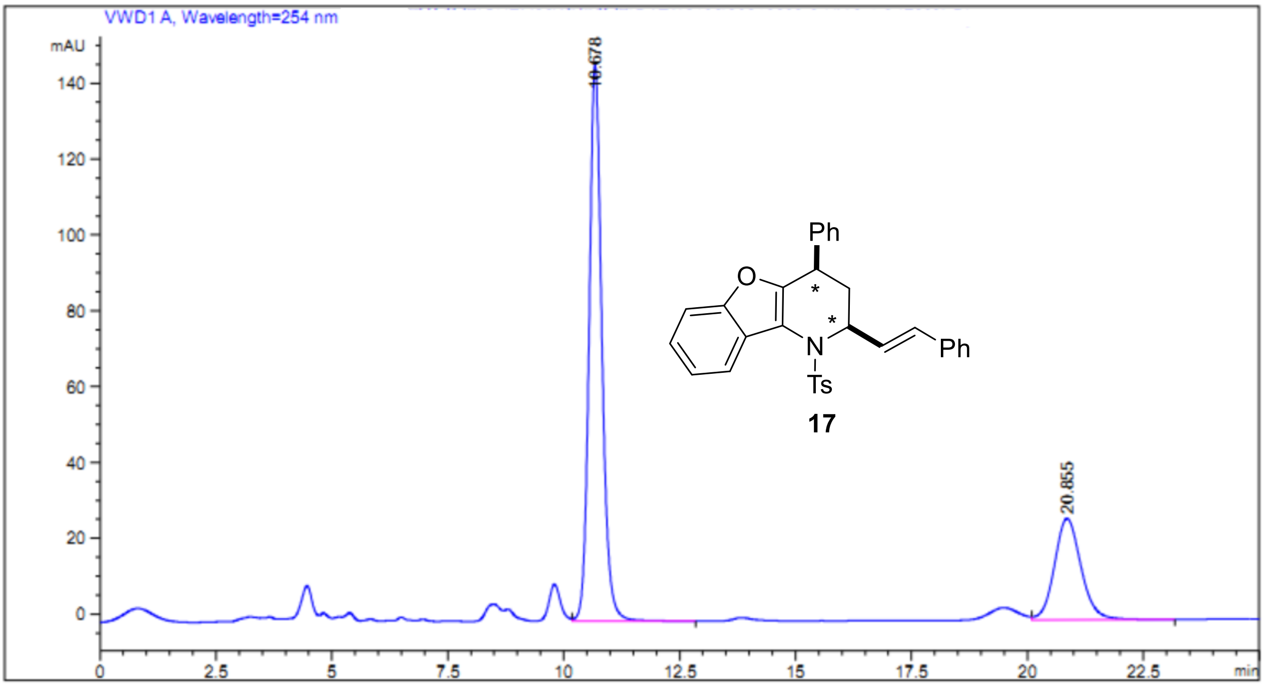

17
$^{13}$C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



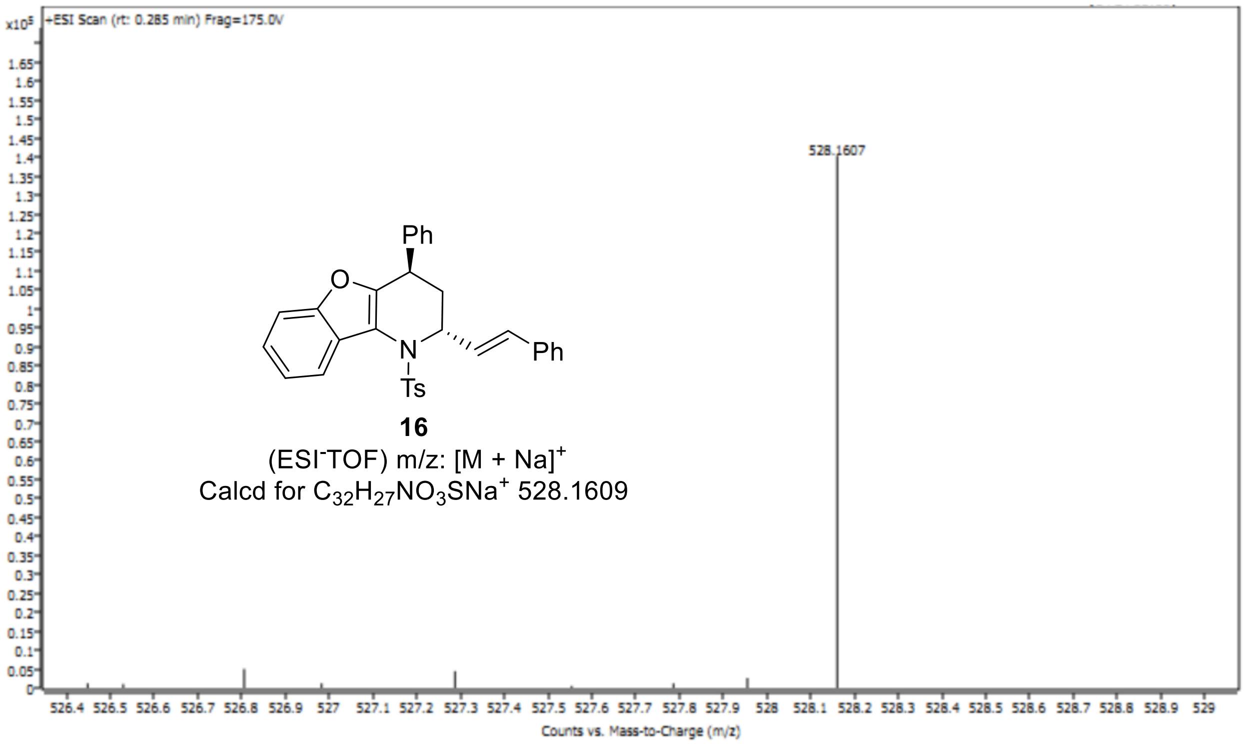

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 9.801 | BV | 0.2632 | 6980.00732 | 397.35217 | 19.5881 |
| 2 | 10.668 | VB | 0.2905 | 1.10772e4 | 585.84076 | 31.0861 |
| 3 | 13.823 | BV | 0.3827 | 6600.81689 | 266.02335 | 18.5239 |
| 4 | 20.820 | BB | 0.6042 | 1.09759e4 | 279.24176 | 30.8019 |



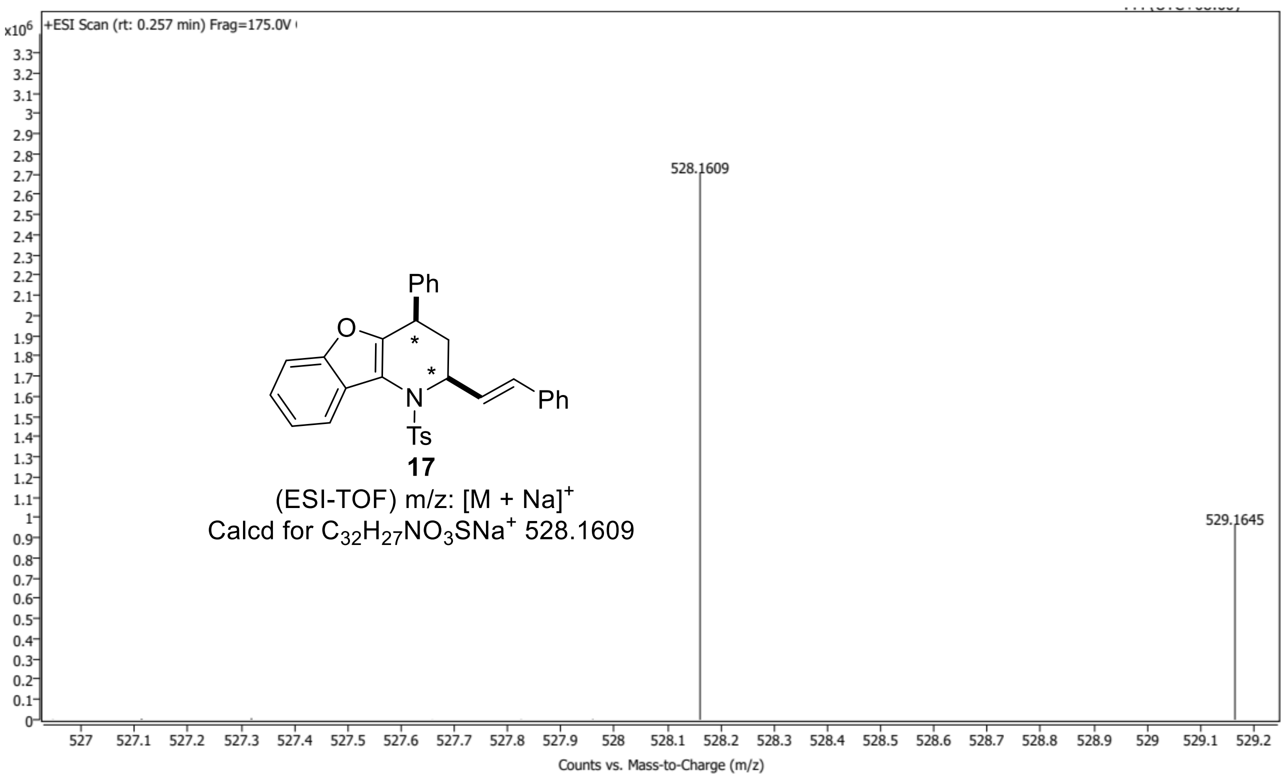

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 9.809 | BV | 0.2469 | 5171.30371 | 319.77383 | 84.2085 |
| 2 | 13.843 | BB | 0.3783 | 969.76636 | 38.89419 | 15.7915 |



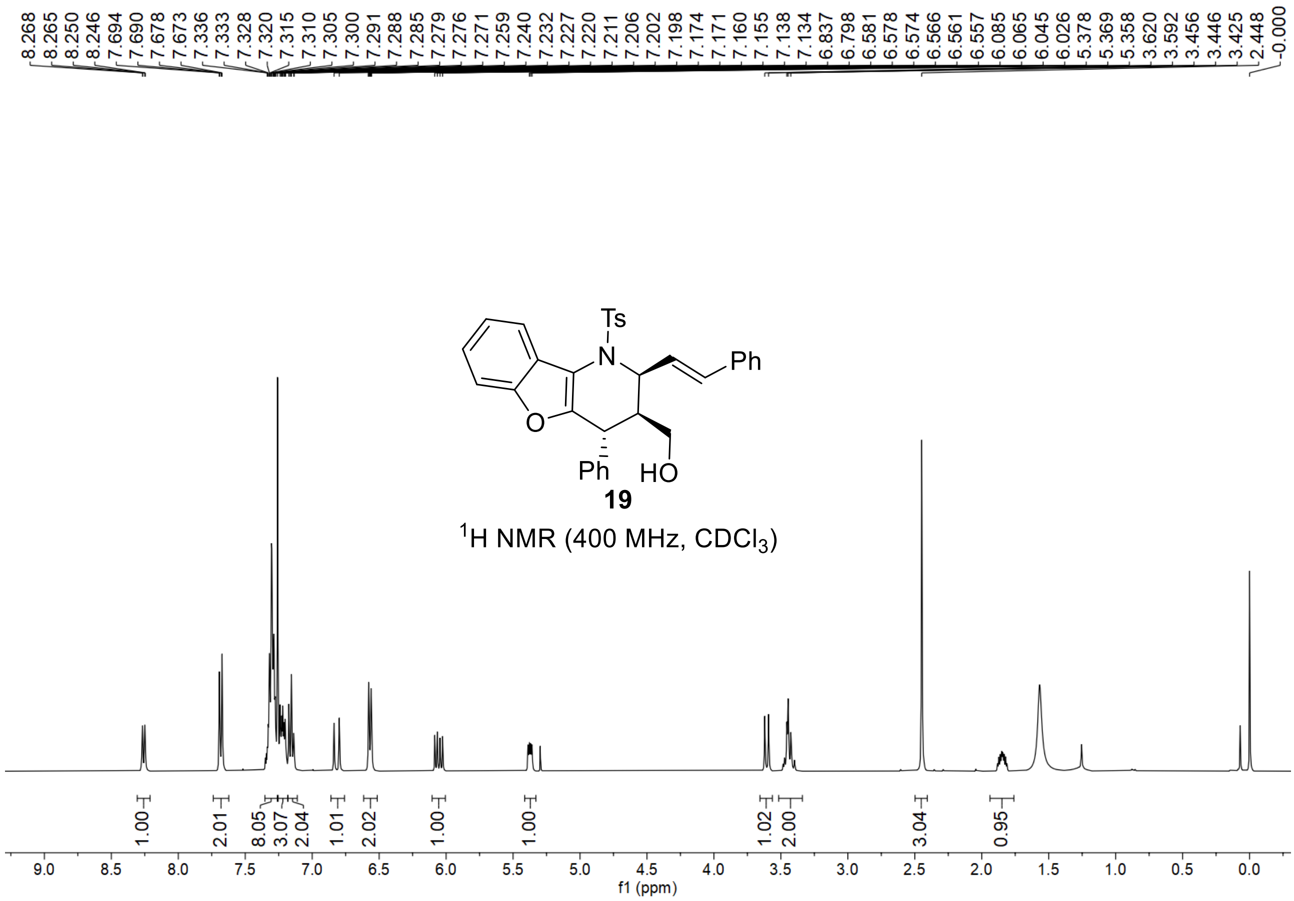

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 10.678 | VB | 0.2930 | 2803.35352 | 146.62024 | 72.3232 |
| 2 | 20.855 | VB | 0.6188 | 1072.79553 | 26.77868 | 27.6768 |



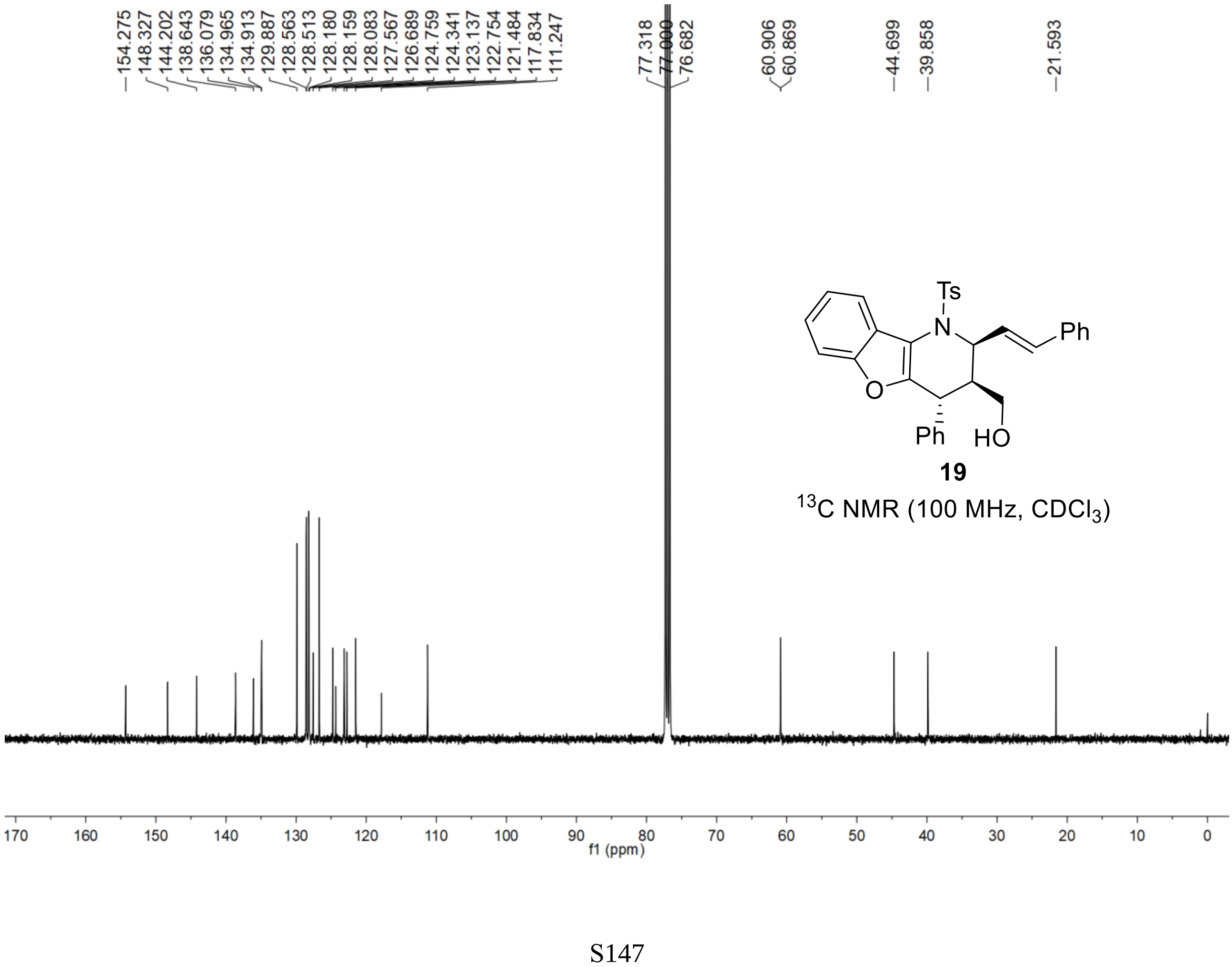

(ESI-TOF) m/z: $[M + Na]^+$
Calcd for $C_{32}H_{27}NO_3SNa^+$ 528.1609



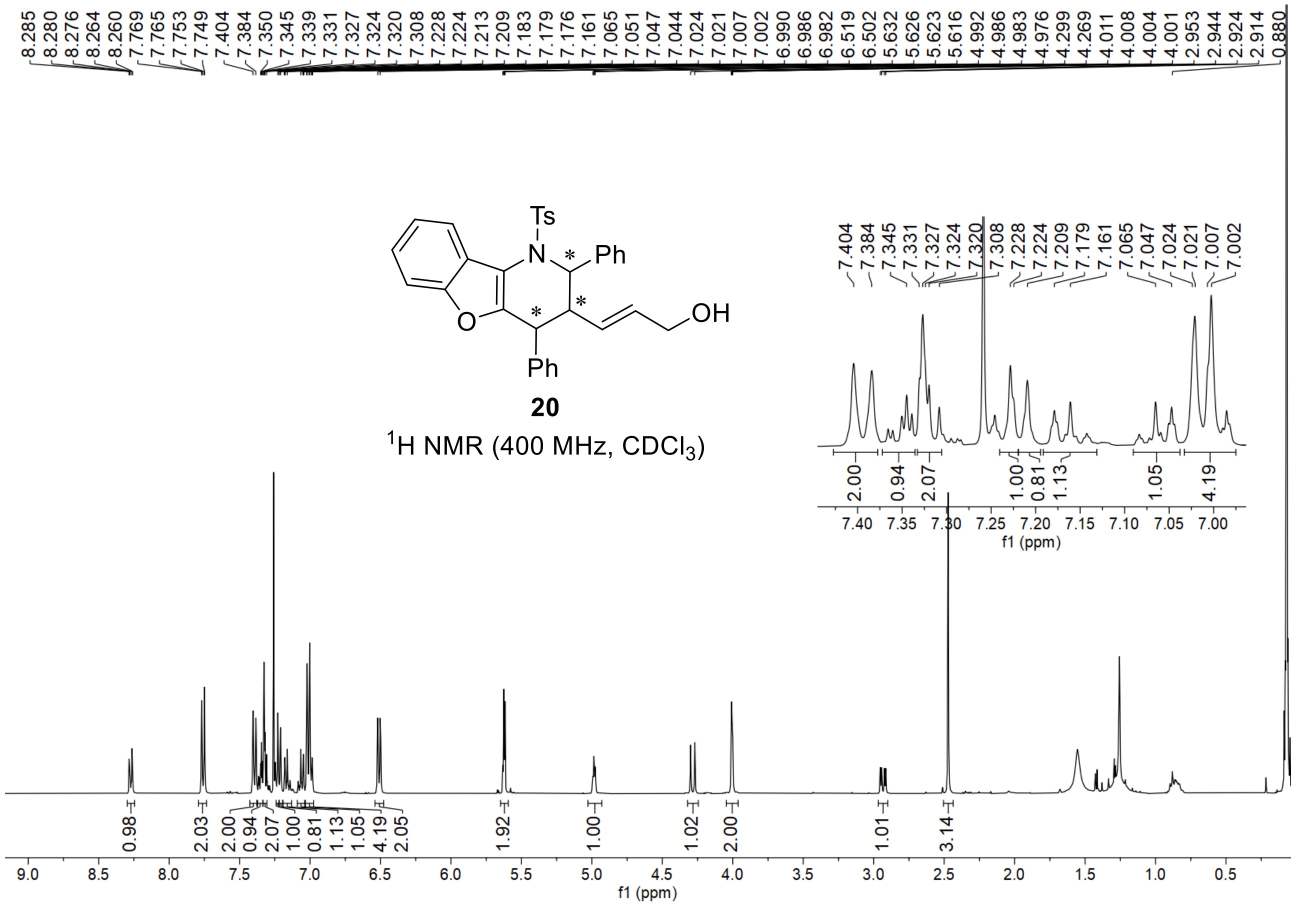
x10^6
+ESI Scan (rt: 0.257 min) Frag=175.0V
528.1609
529.1645
Ph
O
N
Ts
Ph
17
(ESI-TOF) m/z: [M + Na]+
Calcd for C32H27NO3SNa+ 528.1609
Counts vs. Mass-to-Charge (m/z)

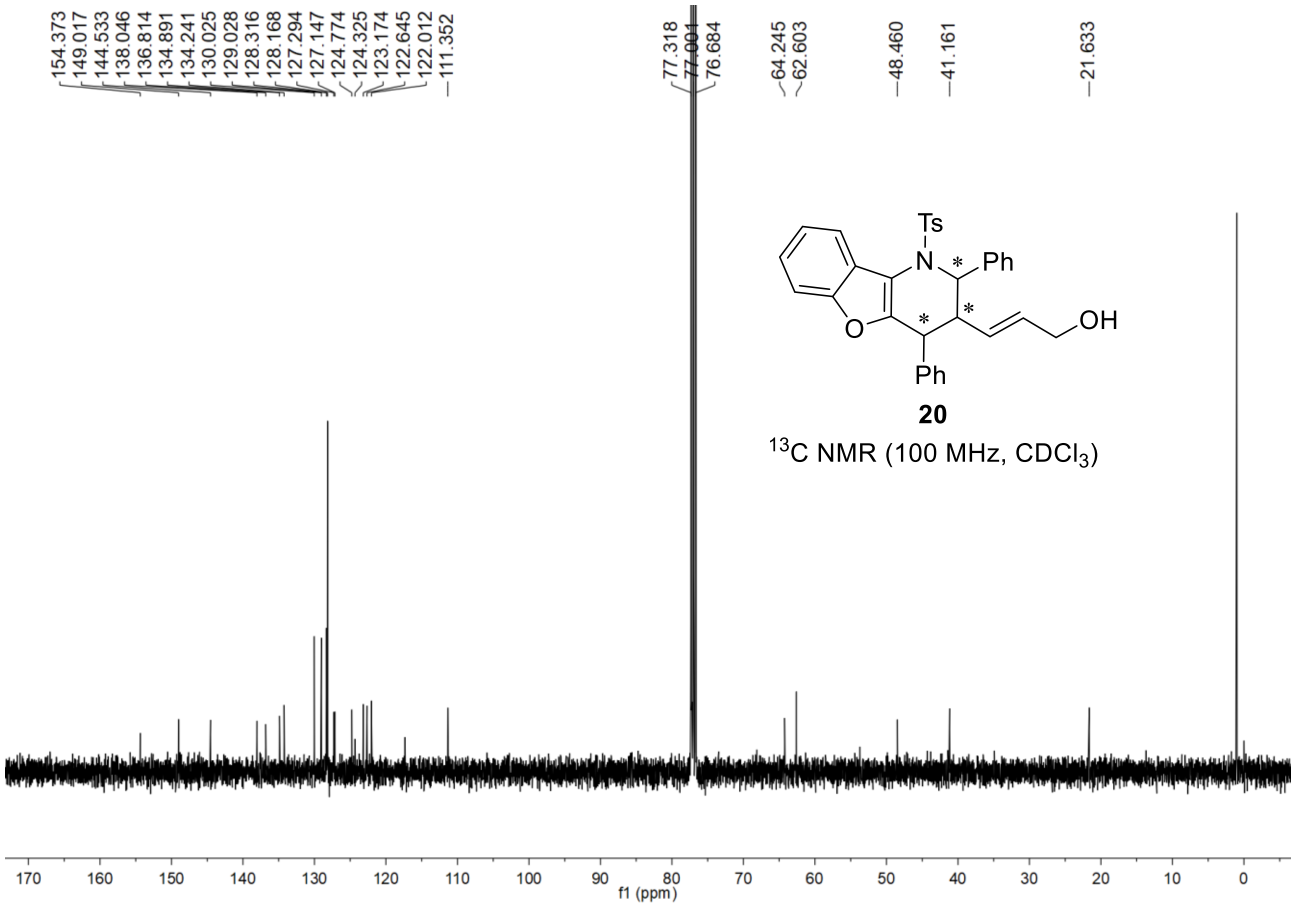


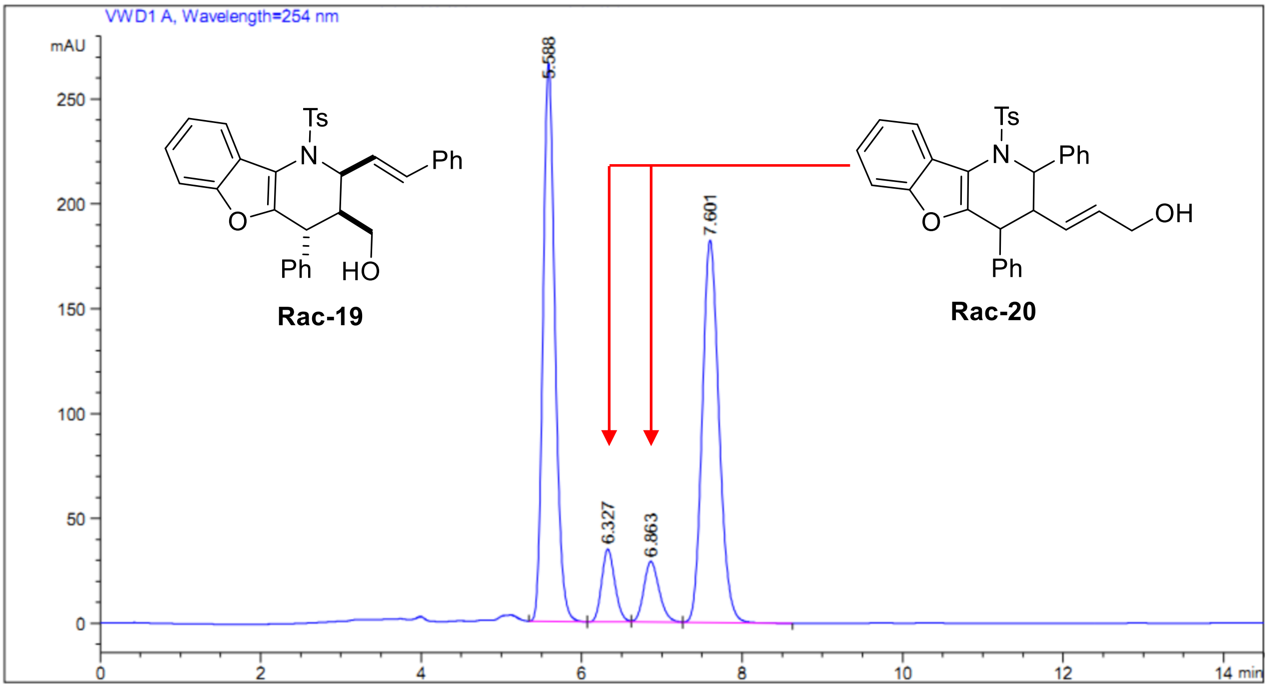
8.268
8.265
8.250
8.246
7.694
7.690
7.678
7.673
7.336
7.333
7.328
7.320
7.315
7.310
7.305
7.300
7.291
7.288
7.285
7.279
7.276
7.271
7.259
7.240
7.232
7.227
7.220
7.211
7.206
7.202
7.198
7.174
7.171
7.160
7.155
7.138
7.134
6.837
6.798
6.581
6.578
6.574
6.566
6.561
6.557
6.085
6.065
6.045
6.026
5.378
5.369
5.358
3.620
3.592
3.456
3.446
3.425
2.448
-0.000
Ts
N
Ph
O
Ph
HO
19
$^1$H NMR (400 MHz, CDCl$_3$)
1.00
2.01
8.05
3.07
2.04
1.01
2.02
1.00
1.00
1.02
2.00
3.04
0.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

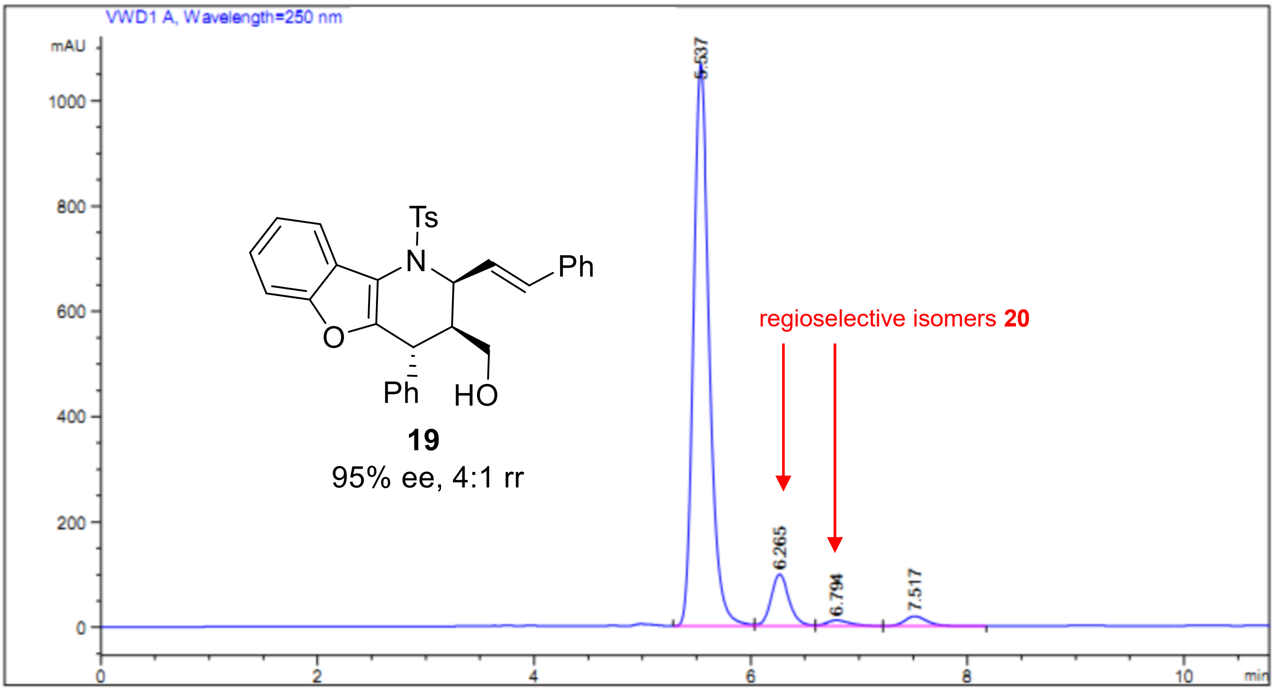
154.275
148.327
144.202
138.643
136.079
134.965
134.913
129.887
128.563
128.513
128.180
128.159
128.083
127.567
126.689
124.759
124.341
123.137
122.754
121.484
117.834
111.247
77.318
77.000
76.682
60.906
60.869
44.699
39.858
21.593
Ts
N
Ph
O
Ph
HO
19
$^{13}$C NMR (100 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.285 8.280 8.276 8.264 8.260 7.769 7.765 7.753 7.749 7.404 7.384 7.350 7.345 7.339 7.331 7.327 7.324 7.320 7.308 7.228 7.224 7.213 7.209 7.183 7.179 7.176 7.161 7.065 7.051 7.047 7.044 7.024 7.021 7.007 7.002 6.990 6.986 6.982 6.519 6.502 5.632 5.626 5.623 5.616 4.992 4.986 4.983 4.976 4.299 4.269 4.011 4.008 4.004 4.001 2.953 2.944 2.924 2.914 0.880
Ts
N
Ph
O
OH
Ph
20
$^{1}$H NMR (400 MHz, $CDCl_3$)
0.98 2.03 2.00 0.94 2.07 1.00 0.81 1.13 1.05 4.19 2.05 1.92 1.00 1.02 2.00 1.01 3.14
f1 (ppm)

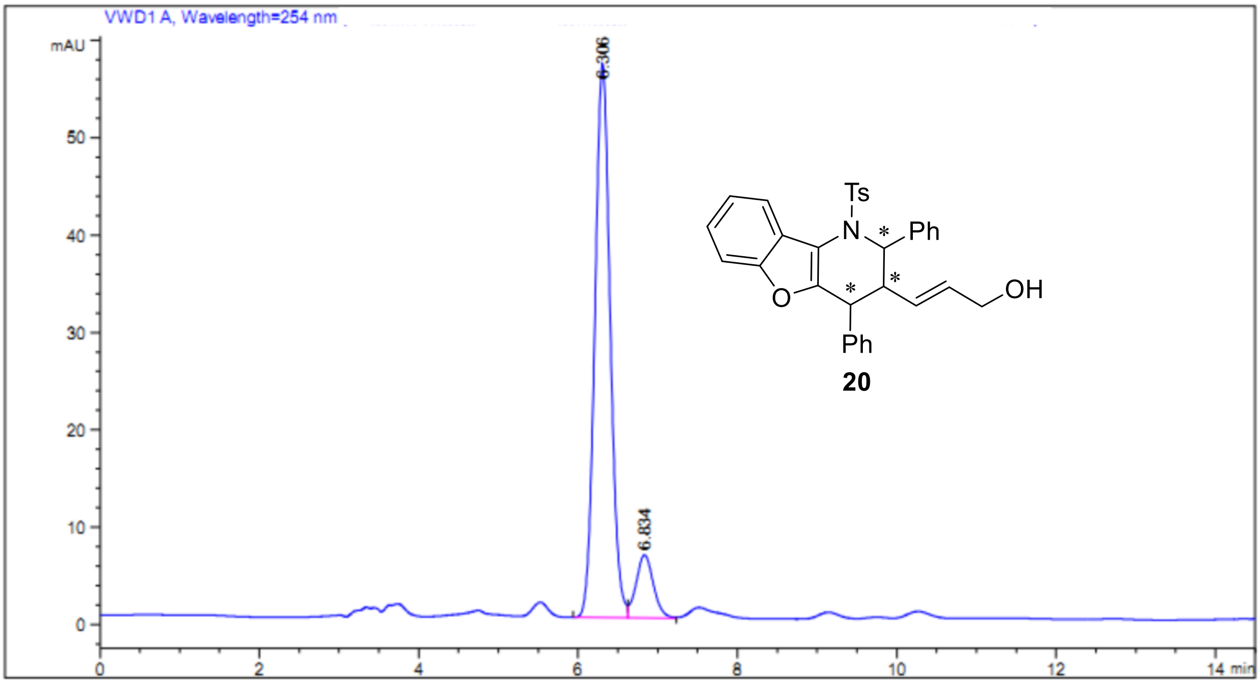

154.373 149.017 144.533 138.046 136.814 134.891 134.241 130.025 129.028 128.316 128.168 127.294 127.147 124.774 124.325 123.174 122.645 122.012 111.352
77.318 77.001 76.684 64.245 62.603 48.460 41.161 21.633
Ts
N
Ph
O
OH
Ph
20
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



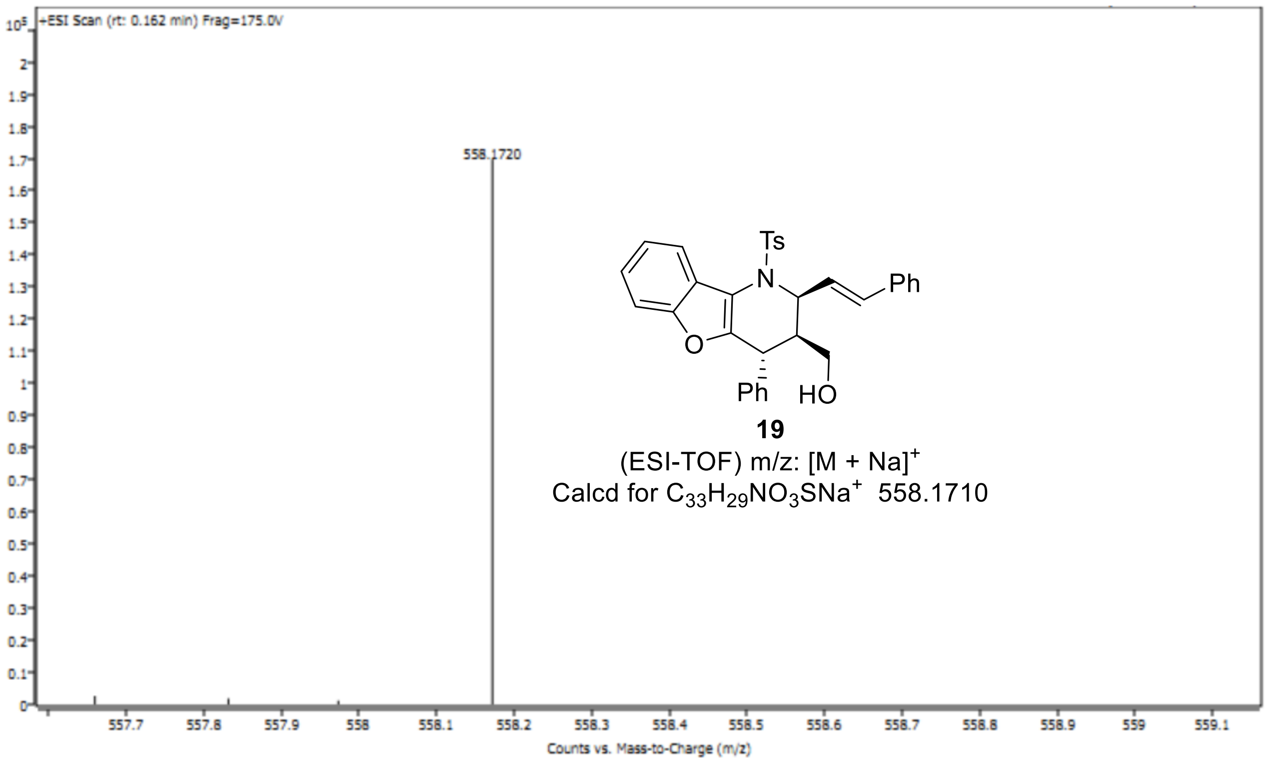

| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 5.588 | BB | 0.1605 | 2764.00415 | 266.02731 | 44.6367 |
| 2 | 6.327 | BV | 0.1775 | 398.03018 | 34.69069 | 6.4279 |
| 3 | 6.863 | VB | 0.2047 | 384.44531 | 28.90234 | 6.2085 |
| 4 | 7.601 | BB | 0.2246 | 2645.74878 | 182.30461 | 42.7269 |

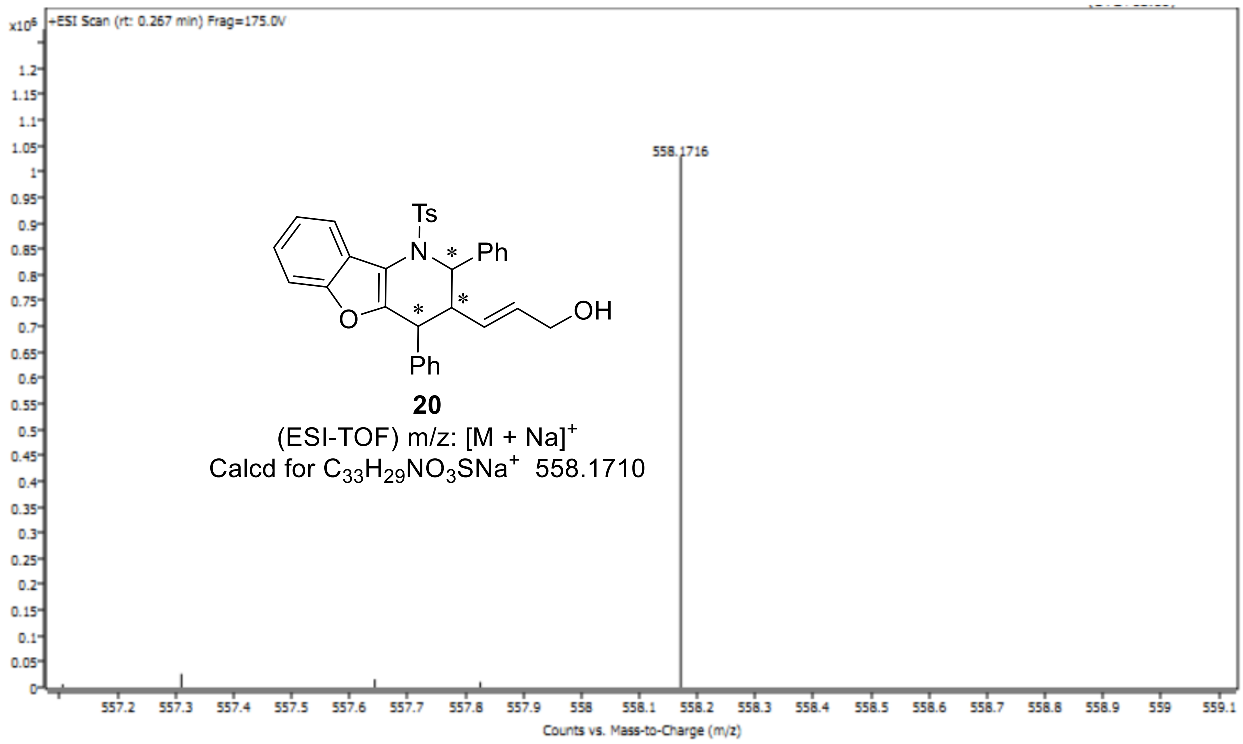



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 5.537 | BV | 0.1570 | 1.08929e4 | 1067.08411 | 87.3761 |
| 2 | 6.265 | VV | 0.1777 | 1143.10168 | 98.41490 | 9.1693 |
| 3 | 6.794 | VB | 0.2235 | 165.83662 | 11.02894 | 1.3302 |
| 4 | 7.517 | BB | 0.2234 | 264.83557 | 18.38567 | 2.1244 |

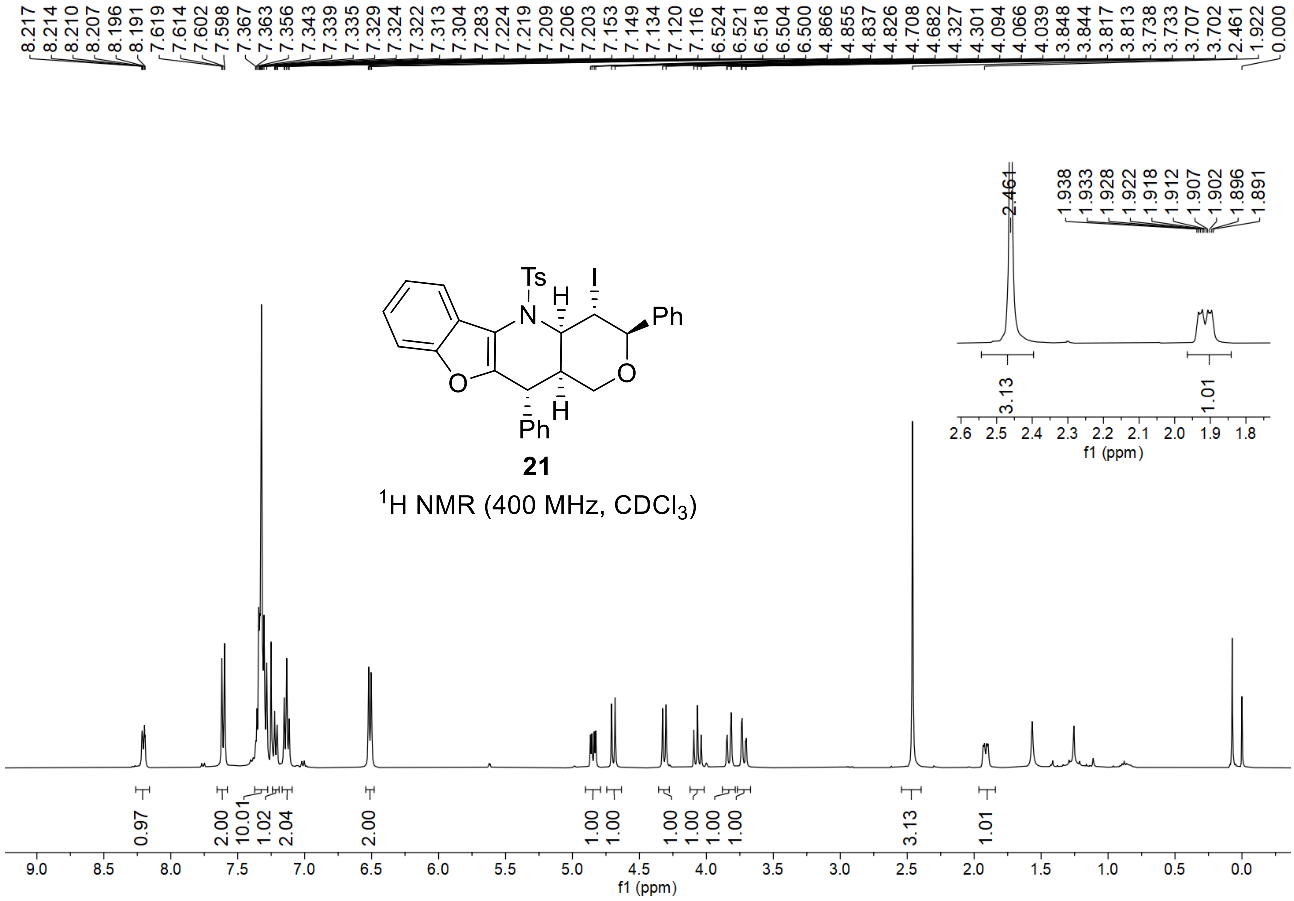



| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 6.306 | BV | 0.2059 | 762.58545 | 56.88541 | 88.6225 |
| 2 | 6.834 | VV | 0.2318 | 97.90224 | 6.47265 | 11.3775 |

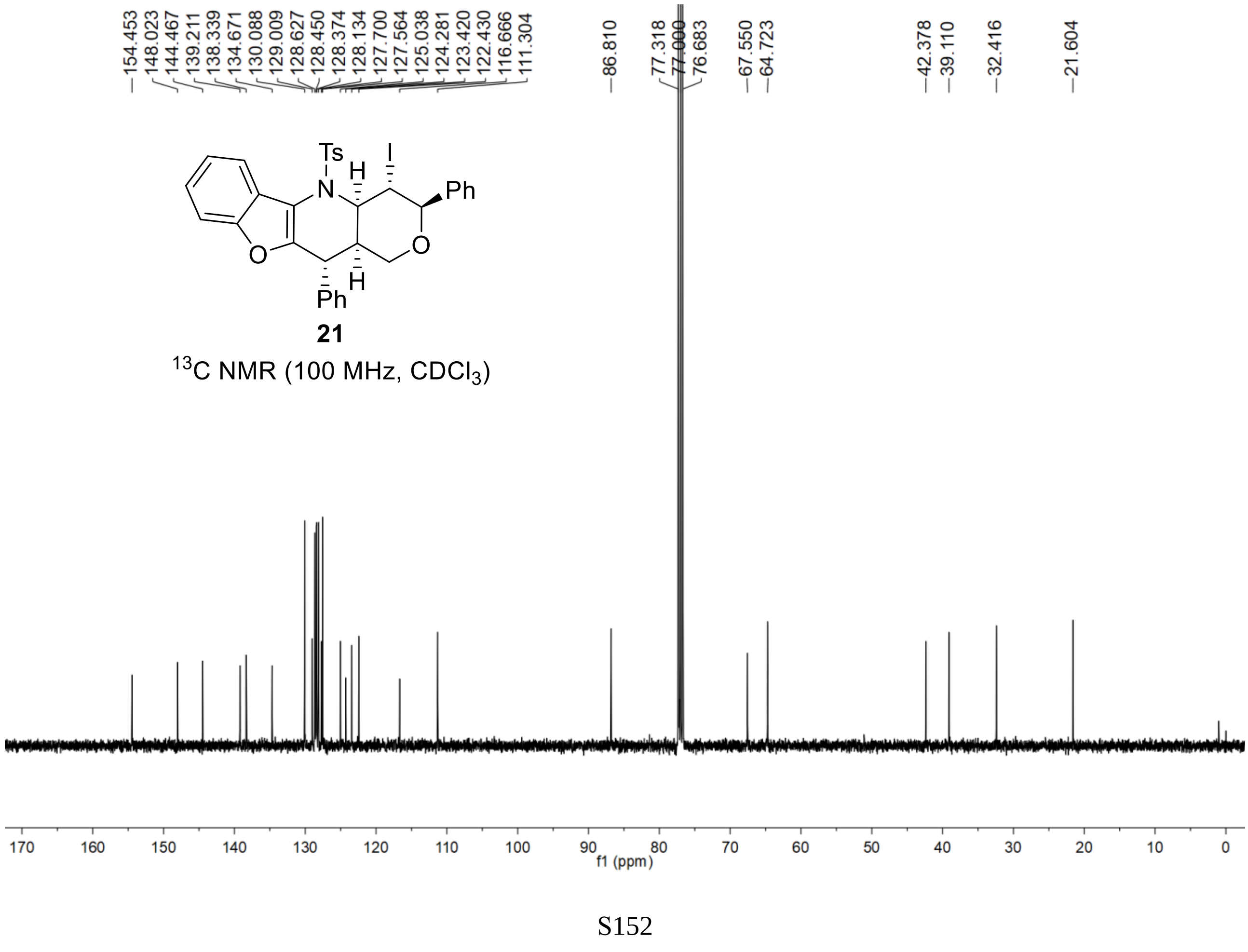




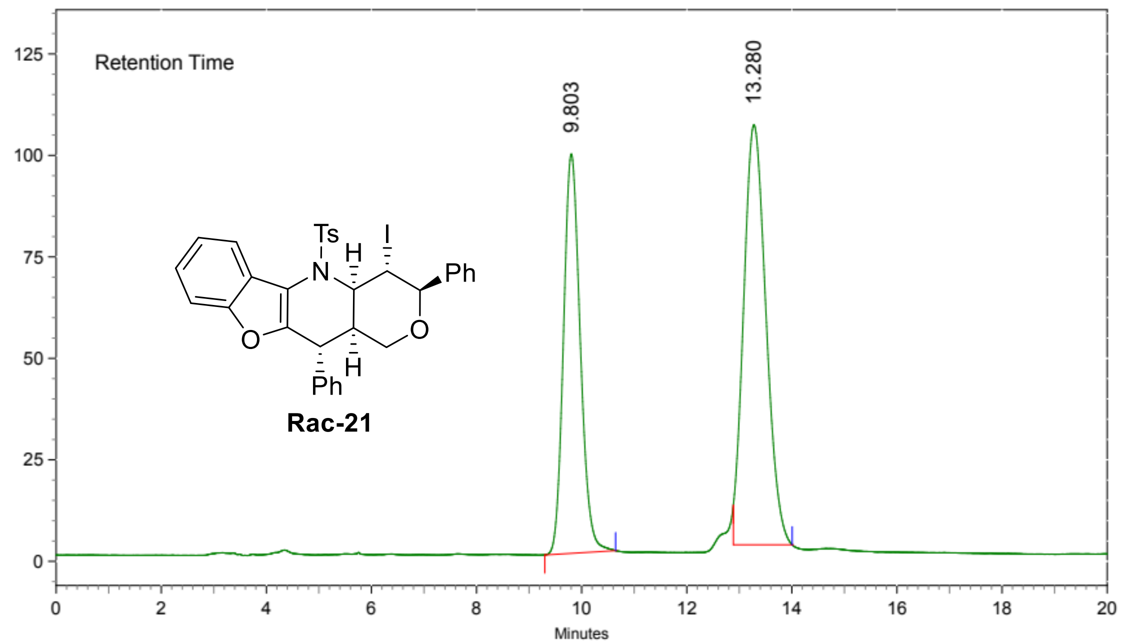
x10^5
+ESI Scan (rt: 0.267 min) Frag=175.0V
558.1716
Ts
N
Ph
OH
O
Ph
20
(ESI-TOF) m/z: [M + Na]+
Calcd for $C_{33}H_{29}NO_3SNa^+$ 558.1710
Counts vs. Mass-to-Charge (m/z)



8.217
8.214
8.210
8.207
8.196
8.191
7.619
7.614
7.602
7.598
7.367
7.363
7.356
7.343
7.339
7.335
7.329
7.324
7.322
7.313
7.304
7.283
7.224
7.219
7.209
7.206
7.203
7.153
7.149
7.134
7.120
7.116
6.524
6.521
6.518
6.504
6.500
4.866
4.855
4.837
4.826
4.708
4.682
4.327
4.301
4.094
4.066
4.039
3.848
3.844
3.817
3.813
3.738
3.733
3.707
3.702
2.461
1.922
0.000
Ts
N
H
I
Ph
O
O
Ph
H
21
$^{1}$H NMR (400 MHz, $CDCl_3$)
2.461
1.938
1.933
1.928
1.922
1.918
1.912
1.907
1.902
1.896
1.891
3.13
1.01
f1 (ppm)
0.97
2.00
10.01
1.02
2.04
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.13
1.01
f1 (ppm)

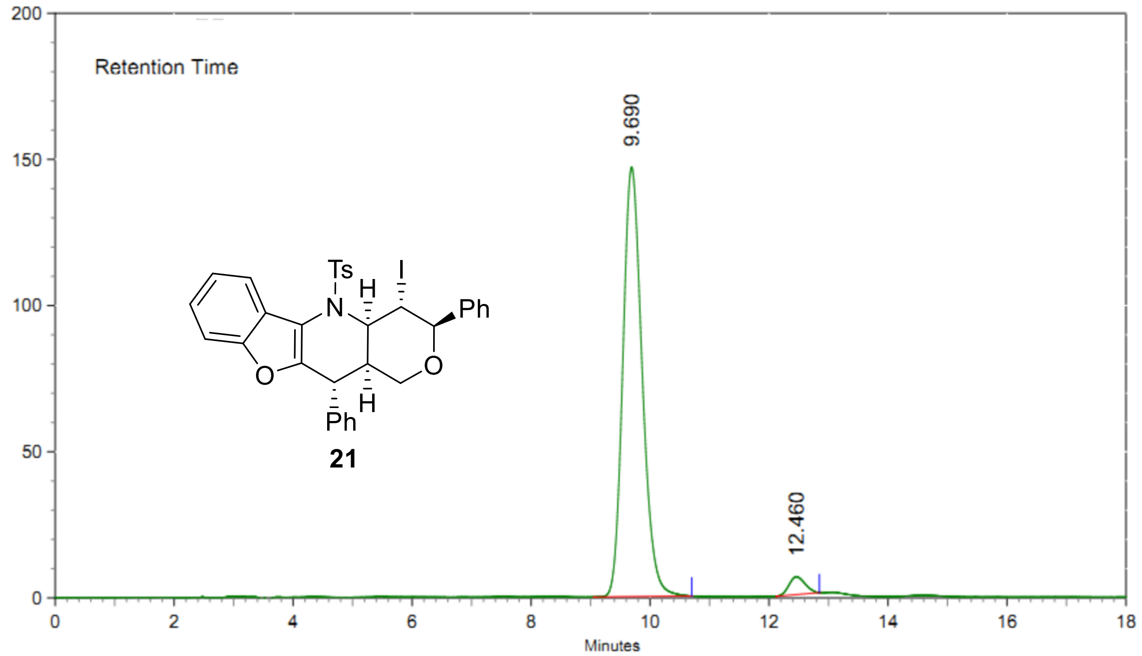



154.453
148.023
144.467
139.211
138.339
134.671
130.088
129.009
128.627
128.450
128.374
128.134
127.700
127.564
125.038
124.281
123.420
122.430
116.666
111.304
86.810
77.318
77.000
76.683
67.550
64.723
42.378
39.110
32.416
21.604
Ts
N
H
I
Ph
O
O
Ph
H
21
$^{13}$C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



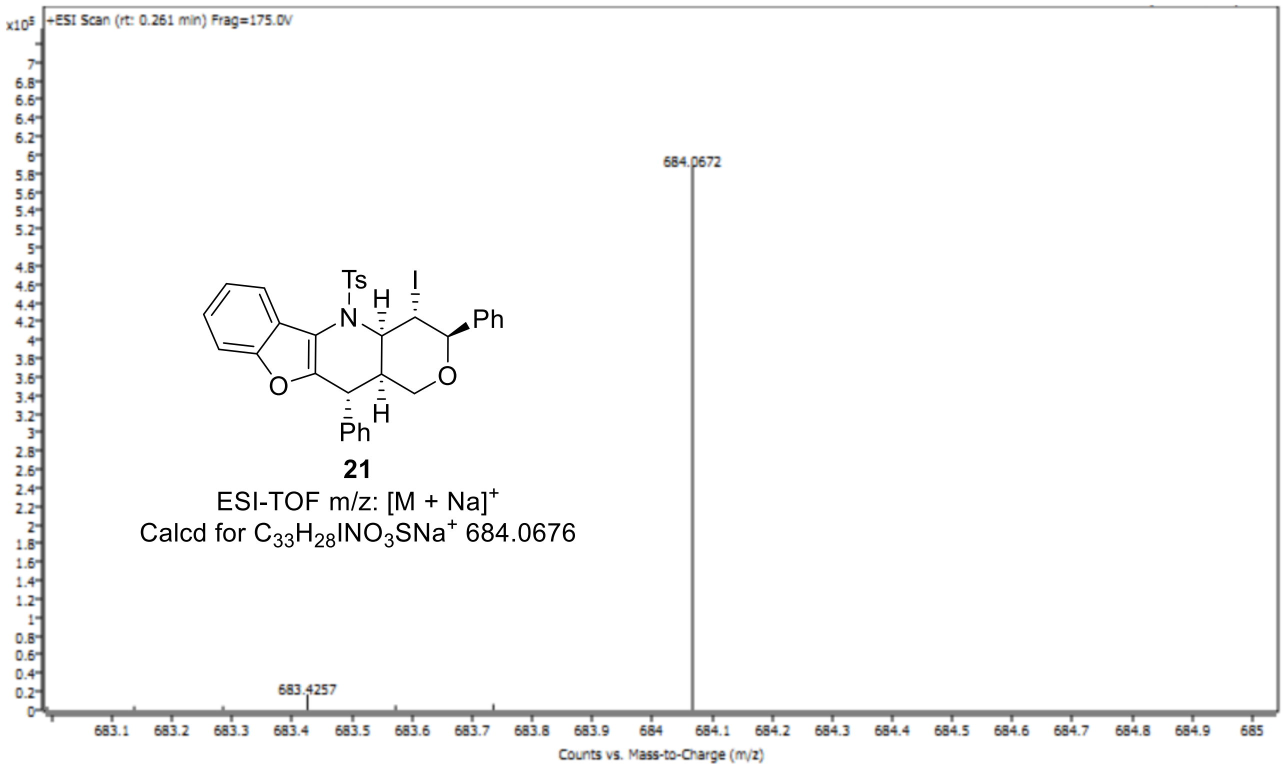

## AREA PERCENT REPORT

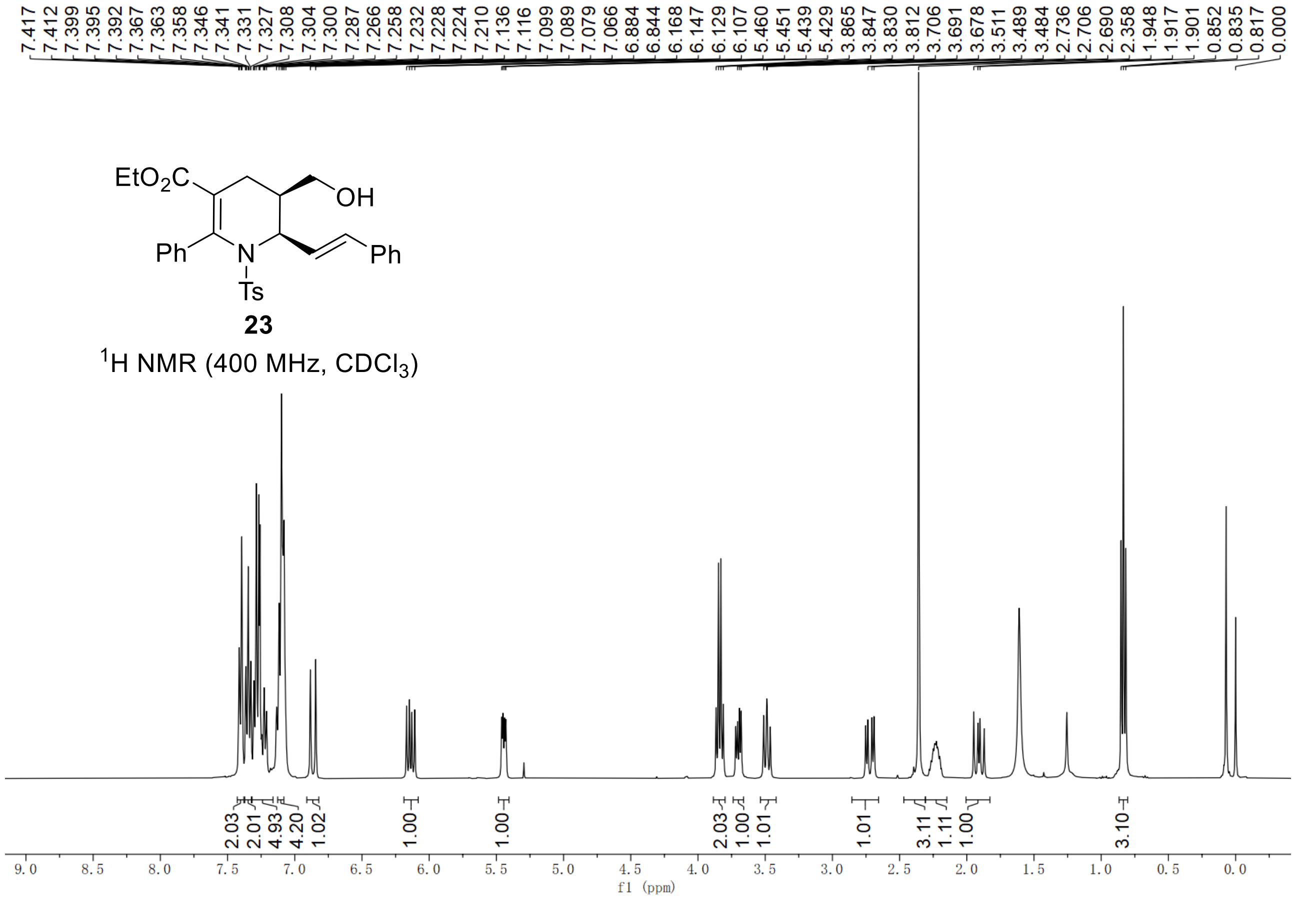
| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 9.803 | 1.347 | 1650892 | 36488077 | 41.5486 |
| 2 | 13.280 | 1.120 | 1735418 | 51332240 | 58.4514 |

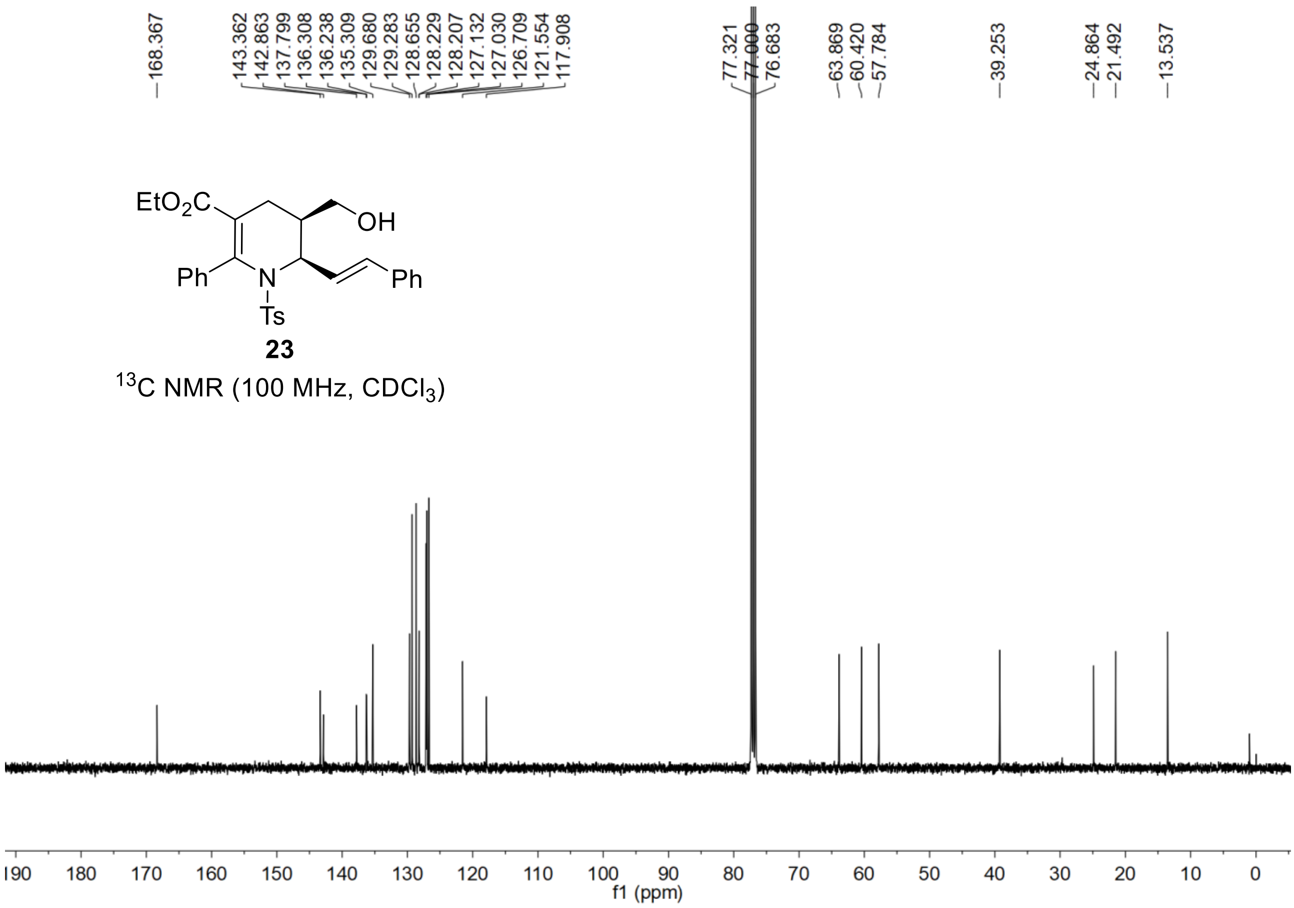


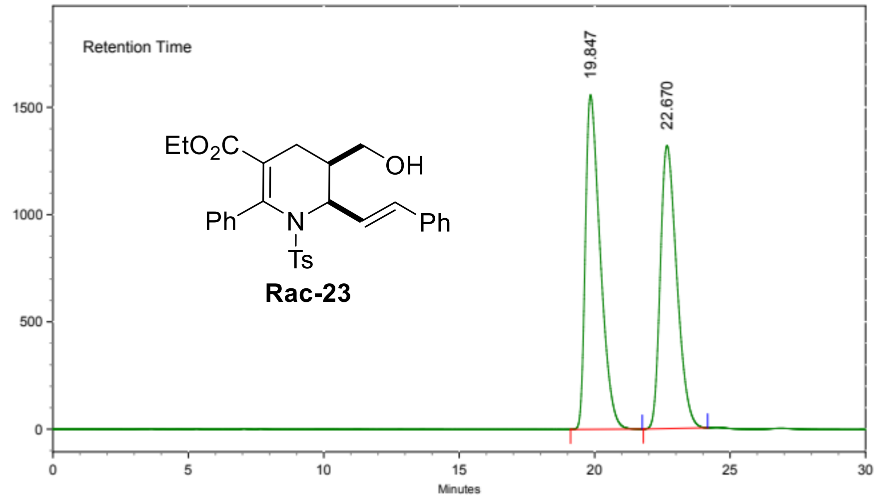

## AREA PERCENT REPORT

| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 9.690 | 1.647 | 2464746 | 55543182 | 96.6446 |
| 2 | 12.460 | 0.727 | 102311 | 1928396 | 3.3554 |


+ESI Scan (rt: 0.261 min) Frag=175.0V
x10^5
684.0672
683.4257
Ts
N
H
I
Ph
O
O
Ph
H
21
ESI-TOF m/z: [M + Na]+
Calcd for C33H28INO3SNa+ 684.0676
Counts vs. Mass-to-Charge (m/z)

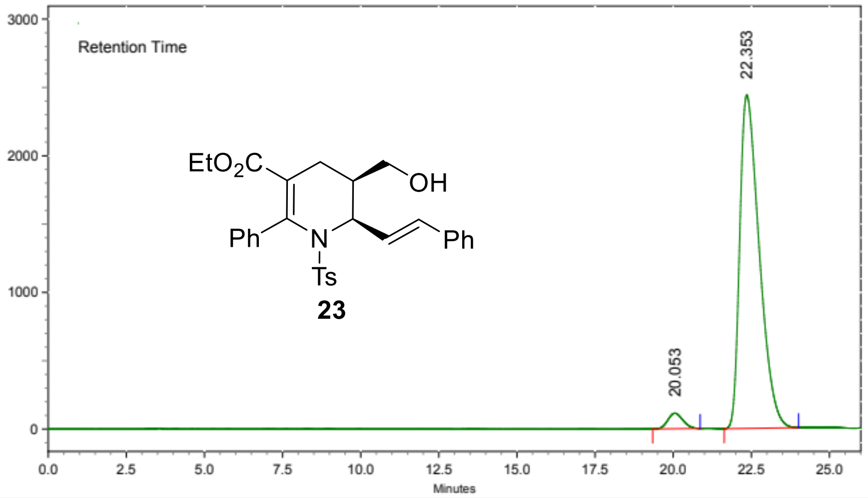

7.417 7.412 7.399 7.395 7.392 7.367 7.363 7.358 7.346 7.341 7.331 7.327 7.308 7.304 7.300 7.287 7.266 7.258 7.232 7.228 7.224 7.210 7.136 7.116 7.099 7.089 7.079 7.066 6.884 6.844 6.168 6.147 6.129 6.107 5.460 5.451 5.439 5.429 3.865 3.847 3.830 3.812 3.706 3.691 3.678 3.511 3.489 3.484 2.736 2.706 2.690 2.358 1.948 1.917 1.901 0.852 0.835 0.817 0.000
EtO2C
OH
Ph
N
Ph
Ts
23
1H NMR (400 MHz, CDCl3)
2.03 2.01 4.93 4.20 1.02 1.00 1.00 2.03 1.00 1.01 1.01 3.11 1.11 1.00 3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.367
143.362 142.863 137.799 136.308 136.238 135.309 129.680 129.283 128.655 128.229 128.207 127.132 127.030 126.709 121.554 117.908
77.321 77.000 76.683
63.869 60.420 57.784
39.253
24.864 21.492
13.537
EtO2C
OH
Ph
N
Ph
Ts
23
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



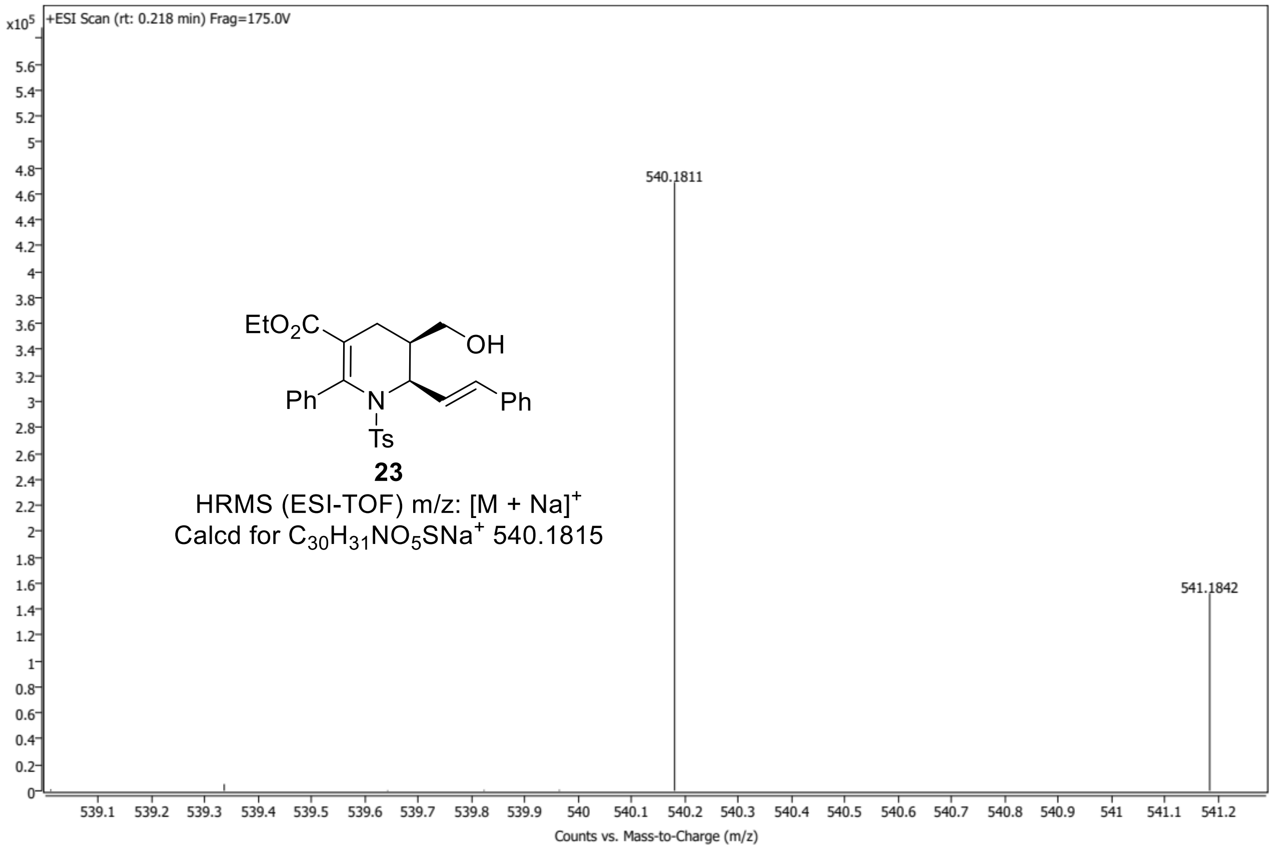

AREA PERCENT REPORT

| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 19.847 | 2.647 | 26140923 | 997199617 | 51.5302 |
| 2 | 22.670 | 2.373 | 22125655 | 937976107 | 48.4698 |

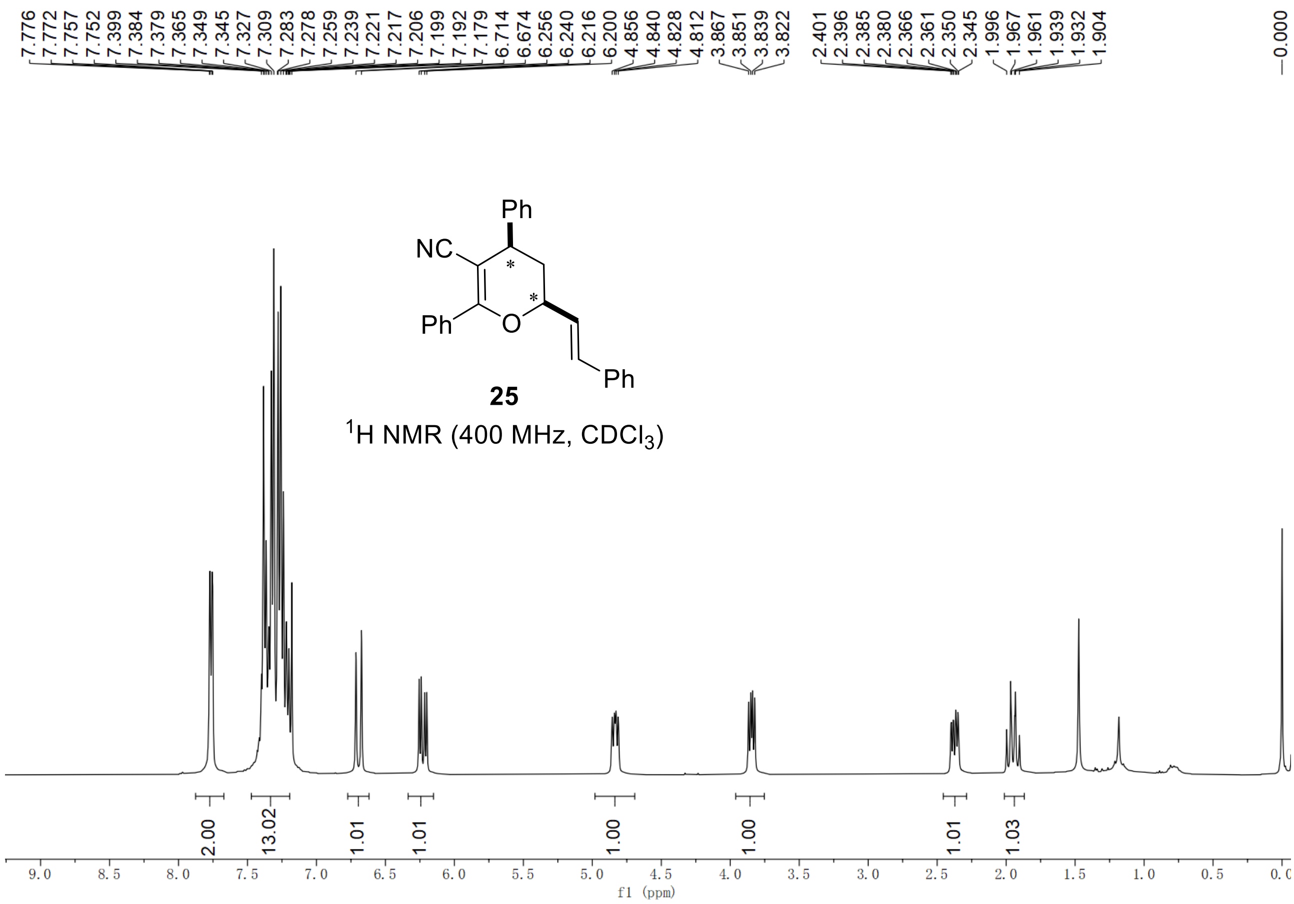


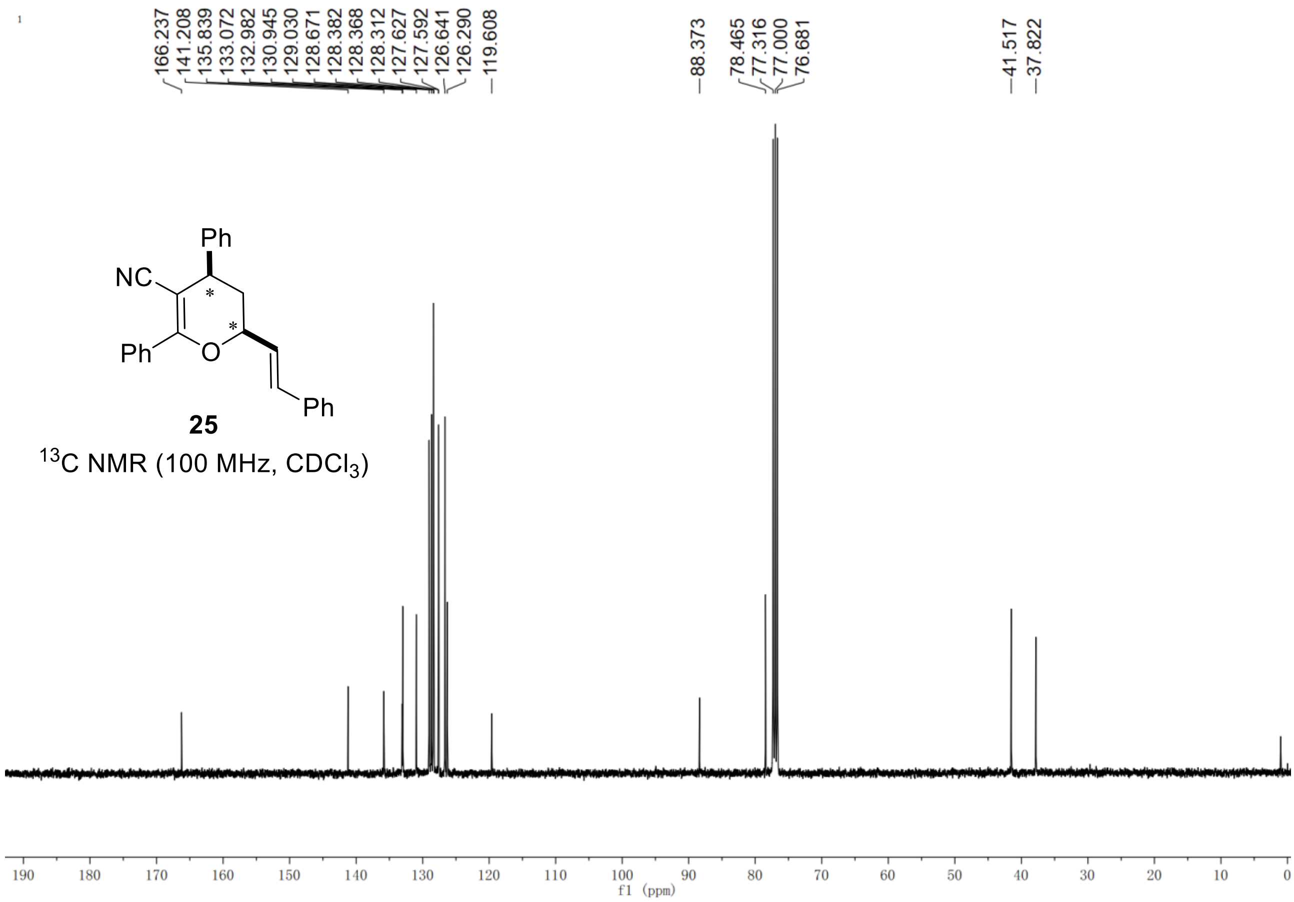

AREA PERCENT REPORT

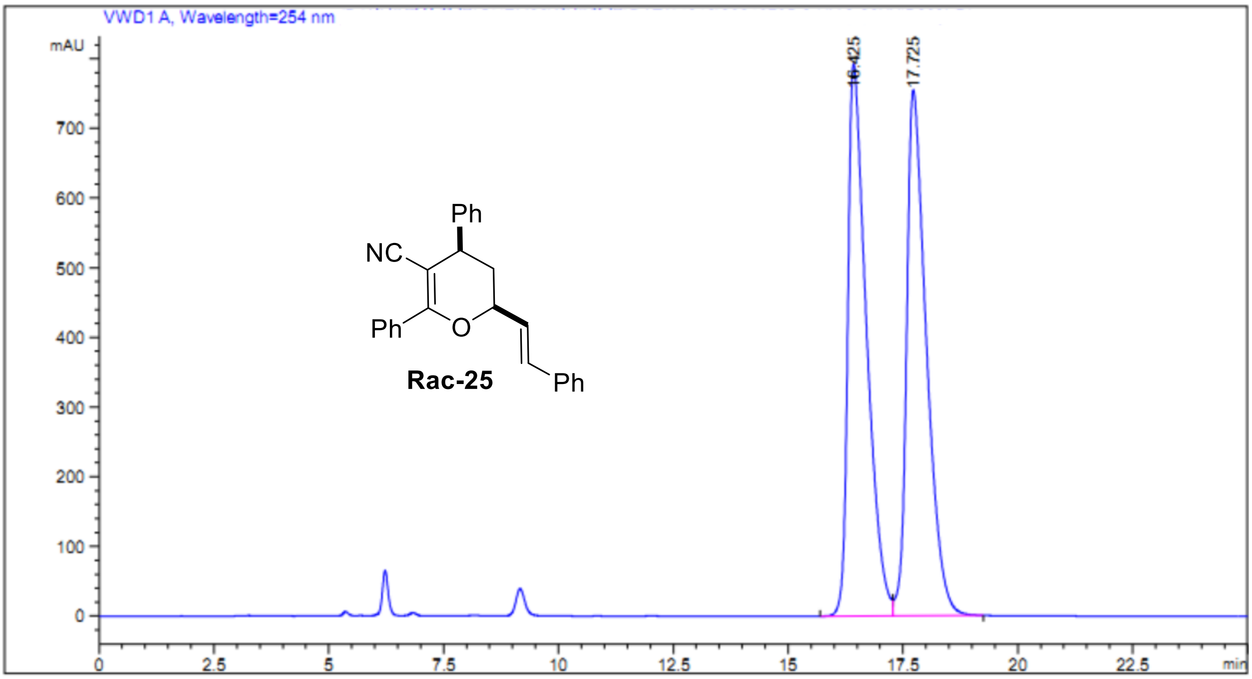
| Peak No. | Ret Time | Width | Height | Area | Area [%] |
|---|---|---|---|---|---|
| 1 | 20.053 | 1.520 | 1904713 | 63455617 | 3.4477 |
| 2 | 22.353 | 2.380 | 40920672 | 1777076269 | 96.5523 |



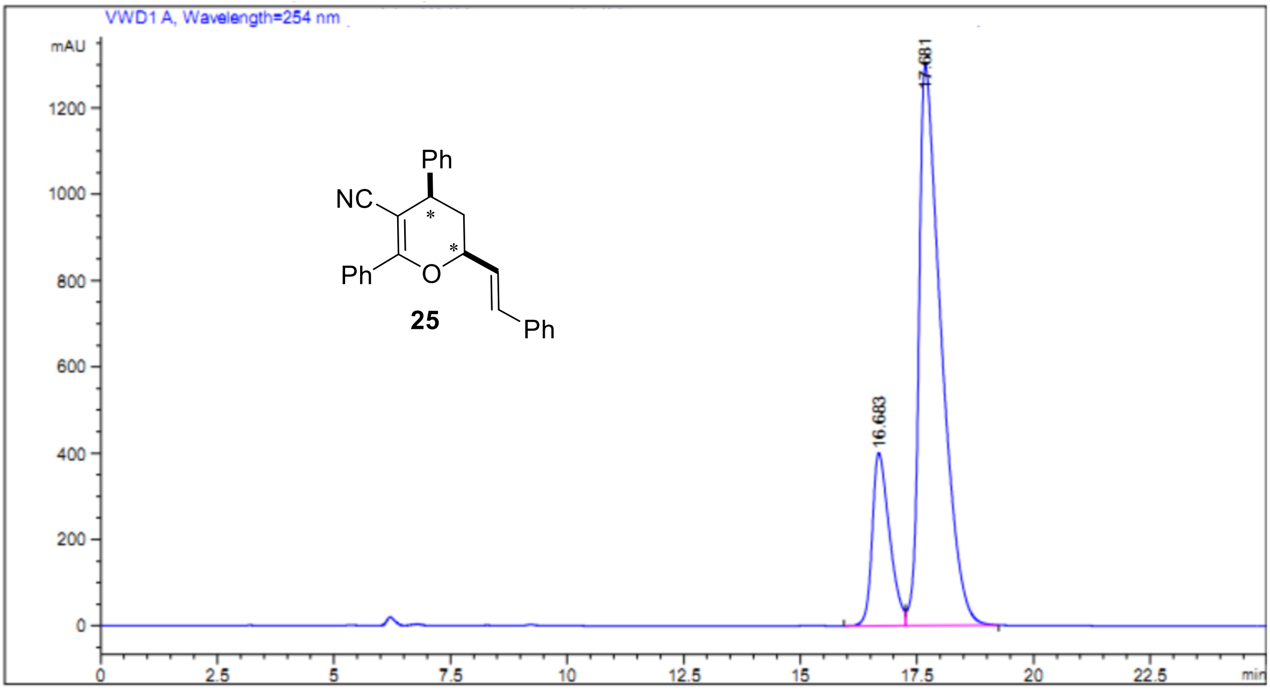
+ESI Scan (rt: 0.218 min) Frag=175.0V
x10^5
540.1811
541.1842
EtO2C
OH
Ph
N
Ph
Ts
23
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C30H31NO5SNa+ 540.1815
Counts vs. Mass-to-Charge (m/z)


7.776
7.772
7.757
7.752
7.399
7.384
7.379
7.365
7.349
7.345
7.327
7.309
7.283
7.278
7.259
7.239
7.221
7.217
7.206
7.199
7.192
7.179
6.714
6.674
6.256
6.240
6.216
6.200
4.856
4.840
4.828
4.812
3.867
3.851
3.839
3.822
2.401
2.396
2.385
2.380
2.366
2.361
2.350
2.345
1.996
1.967
1.961
1.939
1.932
1.904
0.000
Ph
NC
Ph
O
Ph
25
1H NMR (400 MHz, CDCl3)
2.00
13.02
1.01
1.01
1.00
1.00
1.01
1.03
f1 (ppm)

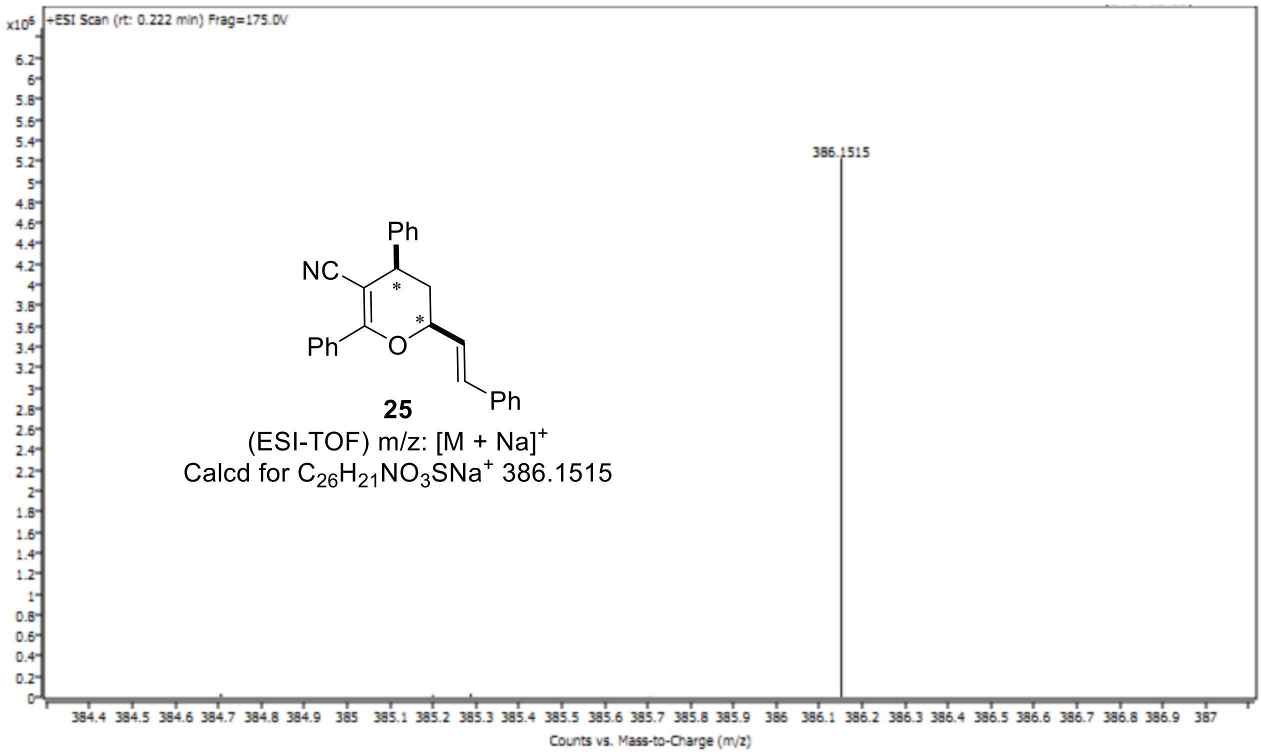

166.237
141.208
135.839
133.072
132.982
130.945
129.030
128.671
128.382
128.368
128.312
127.627
127.592
126.641
126.290
119.608
88.373
78.465
77.316
77.000
76.681
41.517
37.822
Ph
NC
Ph
O
Ph
25
13C NMR (100 MHz, CDCl3)
f1 (ppm)




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 16.425 | BV | 0.4148 | 2.23577e4 | 793.06830 | 49.7986 |
| 2 | 17.725 | VBA | 0.4460 | 2.25386e4 | 754.67340 | 50.2014 |




| # | [min] | | [min] | [mAU*s] | [mAU] | % |
|---|---|---|---|---|---|---|
| 1 | 16.683 | BV | 0.3874 | 1.03131e4 | 400.96591 | 19.3568 |
| 2 | 17.681 | VBA | 0.4803 | 4.29659e4 | 1299.76550 | 80.6432 |



+ESI Scan (rt: 0.222 min) Frag=175.0V
x10^5
386.1515
25
(ESI-TOF) m/z: [M + Na]+
Calcd for C26H21NO3SNa+ 386.1515
Counts vs. Mass-to-Charge (m/z)

## 9. Computational method

All calculations were carried out with the GAUSSIAN 09 packages[8]. The conformations of intermediates were generated by SYBYL-X 2.0 GA Conf. search module and initially optimized and screened by SYBYL-X 2.0[9]. The structures of diene and its Pd-complexes were calculated at M062X[10–14]/def2-TZVP[15] level and their molecular orbitals were calculated at M062X/def2-TZVPPD. The other geometries of all intermediates and transition states were optimized using B3LYP-D3[16,17] functional together with SDD[18] basis set for Pd atom and the standard 6-31G(d) basis set for the others[19], since these classical methods have been frequently used in the optimization of metal-complex[20–23]. All the optimized structures were calculated after considering various conformations and confirmed by frequency calculations to be either minima or transition states using the same level of theory. For transition states, intrinsic reaction coordinate analysis (IRC) was done to verify that they connect the right reactants[24]. To take solvent effects into account, solution-phase single-point calculations were performed on the gas-phase geometries. The solution-phase single point energy calculations were done using B3LYP-D3 at LANL2DZ for Pd atom and 6-31++G(d, p)[25–27] level for the others. Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using SMD model and UAKS radii[28,29]. Toluene was used as the solvent. Solution-phase single-point energies corrected by the gas-phase Gibbs free energy corrections were used to describe all the reaction energetics. The molecular orbitals were calculated at B3LYP/def2-TZVPPD. All these energies correspond to the reference state of 1 mol/L, 298 K. All energetics reported throughout the text are in kcal/mol, and the bond lengths are in angstroms (Å). Structures were generated using GaussView 6.0[30] and CYLview[31].

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**diene-*exo*-TS**

Zero-point correction=1.067183 (Hartree/Particle)

Thermal correction to Energy=1.134226

Thermal correction to Enthalpy=1.135170

Thermal correction to Gibbs Free Energy= 0.441481

E(Solv) = -1914.74329543

| | | | |
|---|---|---|---|
| C | 0.839968 | 1.454513 | -1.614024 |
| H | 1.522270 | 0.840212 | -2.195907 |
| C | 3.407484 | -3.915645 | 1.404091 |
| C | 4.638859 | -3.437017 | 0.925132 |
| C | 4.778586 | -2.119921 | 0.490024 |
| C | 3.644756 | -1.323059 | 0.545742 |
| C | 2.394102 | -1.768360 | 1.019802 |
| C | 2.282689 | -3.098111 | 1.461839 |
| O | 3.603684 | -0.010070 | 0.152505 |
| C | 2.319965 | 0.433374 | 0.407863 |
| C | 1.501224 | -0.608547 | 0.901563 |
| C | 1.856616 | 1.707441 | -0.004770 |
| N | 0.194186 | -0.338037 | 1.028605 |
| C | -1.361998 | -2.350722 | 0.006647 |
| C | -2.712954 | -2.576329 | -0.258457 |
| C | -3.083607 | -3.290110 | -1.396628 |
| C | -2.122335 | -3.784860 | -2.285203 |
| C | -0.770527 | -3.554103 | -1.994906 |
| C | -0.384554 | -2.846802 | -0.859477 |
| C | -2.526999 | -4.524573 | -3.535796 |
| S | -0.937077 | -1.437620 | 1.505515 |
| O | -2.142550 | -0.666180 | 1.845150 |
| O | -0.421829 | -2.399593 | 2.497679 |
| C | 2.799900 | 2.812761 | -0.330650 |
| C | 2.500055 | 4.104474 | 0.126371 |
| C | 3.332661 | 5.180267 | -0.174836 |
| C | 4.474768 | 4.982121 | -0.951683 |
| C | 4.775898 | 3.702554 | -1.422060 |
| C | 3.946686 | 2.625197 | -1.117408 |
| H | 3.333086 | -4.943494 | 1.746016 |
| H | 5.498384 | -4.100310 | 0.896250 |
| H | 5.719988 | -1.725792 | 0.122952 |
| H | 1.342467 | -3.460344 | 1.855427 |
| H | 1.018788 | 2.020065 | 0.613791 |
| H | -3.458523 | -2.190647 | 0.427686 |
| H | -4.137588 | -3.464099 | -1.598044 |
| H | -0.006900 | -3.936622 | -2.667653 |
| H | 0.667353 | -2.687355 | -0.656929 |
| H | -1.818374 | -5.324747 | -3.773850 |
| H | -3.521693 | -4.969141 | -3.432944 |
| H | -2.557087 | -3.849019 | -4.400739 |
| H | 1.609562 | 4.260460 | 0.730144 |
| H | 3.089238 | 6.171554 | 0.196784 |
| H | 5.125012 | 5.818839 | -1.190377 |
| H | 5.662027 | 3.541705 | -2.029655 |
| H | 4.190767 | 1.634740 | -1.482290 |
| C | -0.433174 | 0.916853 | -1.312725 |
| C | -1.512171 | 1.735963 | -0.900533 |
| C | -2.705590 | 1.227171 | -0.479837 |
| H | -2.810278 | 0.147997 | -0.456009 |
| C | -3.841641 | 1.982174 | 0.010731 |
| C | -4.027644 | 3.351561 | -0.265570 |
| C | -4.798458 | 1.319672 | 0.804937 |
| C | -5.129848 | 4.031334 | 0.238681 |

| | | | |
|---|---|---|---|
| H | -3.316932 | 3.873363 | -0.899376 |
| C | -5.895913 | 2.004999 | 1.314571 |
| H | -4.637977 | 0.274556 | 1.050678 |
| C | -6.067403 | 3.362052 | 1.031679 |
| H | -5.265102 | 5.084694 | 0.010021 |
| H | -6.616586 | 1.483166 | 1.937471 |
| H | -6.927217 | 3.896741 | 1.425037 |
| H | -1.338960 | 2.811002 | -0.866849 |
| H | -0.604458 | -0.149074 | -1.402747 |
| H | 0.841822 | 2.498558 | -1.920706 |

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**diene-*endo*-TS**

Zero-point correction=0.509294 (Hartree/Particle)

Thermal correction to Energy=0.541050

Thermal correction to Enthalpy=0.541994

Thermal correction to Gibbs Free Energy= 0.441428

E(Solv) = -1914.75064850

| | | | |
|---|---|---|---|
| C | -0.523863 | 2.014159 | -1.749314 |
| H | -1.455137 | 2.540589 | -1.951680 |
| C | 3.317416 | -1.889289 | 1.984249 |
| C | 4.290462 | -0.892190 | 1.803332 |
| C | 3.942738 | 0.389902 | 1.375831 |
| C | 2.596255 | 0.617520 | 1.136380 |
| C | 1.596072 | -0.355702 | 1.323909 |
| C | 1.968427 | -1.637427 | 1.753450 |
| O | 2.064697 | 1.806659 | 0.682937 |
| C | 0.698322 | 1.618676 | 0.609267 |
| C | 0.345441 | 0.301216 | 0.960578 |
| C | -0.206796 | 2.522164 | -0.028679 |
| N | -0.936490 | -0.063818 | 0.790256 |
| C | -3.105100 | -1.470859 | 0.522193 |
| C | -4.004773 | -0.676320 | 1.235315 |
| C | -5.317500 | -0.573576 | 0.790333 |
| C | -5.751614 | -1.260341 | -0.354792 |
| C | -4.831393 | -2.055683 | -1.044579 |
| C | -3.509291 | -2.167880 | -0.611442 |
| C | -7.185599 | -1.153779 | -0.811517 |
| S | -1.414796 | -1.605389 | 1.088548 |
| O | -1.417348 | -1.901309 | 2.532062 |
| O | -0.741730 | -2.594768 | 0.209191 |
| C | 0.091943 | 3.985527 | -0.109316 |
| C | -0.941193 | 4.900204 | 0.133106 |
| C | -0.718184 | 6.273095 | 0.039267 |
| C | 0.545014 | 6.752263 | -0.308153 |
| C | 1.579378 | 5.849107 | -0.560837 |
| C | 1.356289 | 4.476874 | -0.466912 |
| H | 3.625120 | -2.879474 | 2.304856 |
| H | 5.334507 | -1.122563 | 1.994162 |
| H | 4.679643 | 1.172171 | 1.228376 |
| H | 1.224010 | -2.409926 | 1.896434 |
| H | -1.201028 | 2.322335 | 0.369323 |
| H | -3.672151 | -0.148326 | 2.122458 |
| H | -6.022119 | 0.046556 | 1.339158 |
| H | -5.152283 | -2.597523 | -1.930596 |
| H | -2.794308 | -2.791638 | -1.136091 |
| H | -7.520135 | -0.110424 | -0.836739 |
| H | -7.319728 | -1.577354 | -1.811391 |
| H | -7.857418 | -1.691157 | -0.130217 |
| H | -1.926407 | 4.528661 | 0.404124 |

| | | | |
|---|---|---|---|
| H | -1.530400 | 6.966643 | 0.237997 |
| H | 0.722675 | 7.821311 | -0.382632 |
| H | 2.565899 | 6.214761 | -0.832008 |
| H | 2.166515 | 3.782559 | -0.657740 |
| C | -0.544614 | 0.598209 | -1.946084 |
| C | 0.678799 | -0.090774 | -1.976496 |
| C | 0.802615 | -1.455445 | -1.906633 |
| H | -0.106384 | -2.045432 | -1.915865 |
| C | 2.026154 | -2.182719 | -1.674022 |
| C | 3.303977 | -1.589161 | -1.756760 |
| C | 1.936182 | -3.533275 | -1.274505 |
| C | 4.442264 | -2.319764 | -1.451493 |
| H | 3.400944 | -0.552985 | -2.062292 |
| C | 3.080374 | -4.260989 | -0.967948 |
| H | 0.953704 | -3.979687 | -1.165729 |
| C | 4.336320 | -3.658170 | -1.056677 |
| H | 5.418251 | -1.847916 | -1.514152 |
| H | 2.993051 | -5.295895 | -0.650519 |
| H | 5.231116 | -4.225083 | -0.815798 |
| H | 1.576366 | 0.522864 | -1.921197 |
| H | -1.479689 | 0.047680 | -1.963654 |
| H | 0.325470 | 2.504116 | -2.226967 |

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**com-INT1-2a**

Zero-point correction=1.064644 (Hartree/Particle)

Thermal correction to Energy=1.133604

Thermal correction to Enthalpy=1.134548

Thermal correction to Gibbs Free Energy= 0.953350

E(Solv) = -4116.08708905

| | | | |
|---|---|---|---|
| C | 0.169423 | 2.582070 | 3.063625 |
| H | 0.188231 | 2.574899 | 4.149221 |
| C | 6.793082 | -2.000134 | -1.540711 |
| C | 6.976074 | -1.012198 | -2.523020 |
| C | 6.402294 | 0.253586 | -2.398933 |
| C | 5.641512 | 0.482012 | -1.262972 |
| C | 5.431500 | -0.488114 | -0.267130 |
| C | 6.024578 | -1.751090 | -0.406916 |
| O | 5.006544 | 1.663315 | -0.992255 |
| C | 4.348959 | 1.510295 | 0.220641 |
| C | 4.570779 | 0.145420 | 0.732644 |
| C | 3.560395 | 2.452945 | 0.774970 |
| N | 3.976005 | -0.222111 | 1.830521 |
| C | 2.371952 | -1.711613 | 3.244641 |
| C | 2.309468 | -1.049157 | 4.473529 |
| C | 1.071361 | -0.880768 | 5.084078 |
| C | -0.106124 | -1.354118 | 4.479870 |
| C | -0.006832 | -2.042750 | 3.267627 |
| C | 1.228237 | -2.231242 | 2.645784 |
| C | -1.448082 | -1.083191 | 5.112100 |
| S | 3.931125 | -1.804193 | 2.377166 |
| O | 5.015770 | -2.014060 | 3.345410 |
| O | 3.763775 | -2.759609 | 1.264002 |
| C | 3.143979 | 3.737153 | 0.243339 |
| C | 2.442959 | 4.609643 | 1.100879 |
| C | 2.005885 | 5.852484 | 0.654434 |
| C | 2.249440 | 6.245942 | -0.664526 |
| C | 2.917672 | 5.378601 | -1.533897 |
| C | 3.364031 | 4.137351 | -1.091419 |
| H | 7.256744 | -2.973053 | -1.668660 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 7.577197 | -1.236139 | -3.399638 | H | 0.388016 | 2.339627 | 0.356014 |
| H | 6.527540 | 1.024808 | -3.150279 | H | 0.861041 | 0.613376 | 2.879465 |
| H | 5.866102 | -2.519317 | 0.337378 | H | -0.186598 | 3.492165 | 2.587193 |
| H | 3.158790 | 2.172216 | 1.743454 | Pd | -1.058959 | -0.040484 | 0.217841 |
| H | 3.216143 | -0.665610 | 4.928638 | P | -2.873107 | 1.402443 | 0.087415 |
| H | 1.010664 | -0.356266 | 6.034467 | P | -1.446197 | -2.137176 | -0.706974 |
| H | -0.901081 | -2.420210 | 2.782346 | C | -2.332911 | 2.697117 | -1.109863 |
| H | 1.296885 | -2.751173 | 1.700273 | C | -2.533798 | 2.547086 | -2.489926 |
| H | -1.660103 | -0.006621 | 5.113806 | C | -1.505832 | 3.741846 | -0.662720 |
| H | -2.254446 | -1.581782 | 4.565688 | C | -1.901519 | 3.398358 | -3.397235 |
| H | -1.480726 | -1.422440 | 6.154106 | H | -3.182837 | 1.762588 | -2.861964 |
| H | 2.240348 | 4.291634 | 2.118817 | C | -0.878183 | 4.593627 | -1.569563 |
| H | 1.475893 | 6.514769 | 1.333277 | H | -1.341351 | 3.880250 | 0.400657 |
| H | 1.914210 | 7.218456 | -1.014783 | C | -1.063725 | 4.417679 | -2.942730 |
| H | 3.092552 | 5.673172 | -2.564900 | H | -2.067497 | 3.261948 | -4.462629 |
| H | 3.870331 | 3.466221 | -1.772109 | H | -0.226063 | 5.378127 | -1.201436 |
| C | 0.531241 | 1.501251 | 2.350502 | H | -0.562482 | 5.072848 | -3.649539 |
| C | 0.548673 | 1.412916 | 0.896832 | C | -4.495946 | 0.827814 | -0.565983 |
| C | 1.157176 | 0.329657 | 0.240575 | C | -5.719418 | 1.146668 | 0.037547 |
| H | 1.602163 | -0.443562 | 0.853784 | C | -4.494049 | -0.050743 | -1.662044 |
| C | 1.618756 | 0.360860 | -1.152066 | C | -6.911162 | 0.607424 | -0.450980 |
| C | 1.294432 | 1.403095 | -2.043568 | H | -5.744861 | 1.810052 | 0.894926 |
| C | 2.450636 | -0.673267 | -1.617937 | C | -5.684399 | -0.572868 | -2.160136 |
| C | 1.782283 | 1.400583 | -3.346036 | H | -3.553484 | -0.354109 | -2.108408 |
| H | 0.652776 | 2.214479 | -1.720527 | C | -6.898539 | -0.248516 | -1.551968 |
| C | 2.934375 | -0.675260 | -2.924415 | H | -7.851164 | 0.859372 | 0.032825 |
| H | 2.733863 | -1.467008 | -0.933578 | H | -5.657857 | -1.259637 | -3.000455 |
| C | 2.603502 | 0.362214 | -3.797848 | H | -7.826628 | -0.670892 | -1.926758 |
| H | 1.514803 | 2.217046 | -4.012140 | C | -3.323100 | 2.350653 | 1.587913 |
| H | 3.588523 | -1.478822 | -3.251152 | C | -3.941284 | 3.610060 | 1.551420 |
| H | 2.981665 | 0.364102 | -4.816316 | C | -3.029566 | 1.769554 | 2.828705 |

| | | | |
|---|---|---|---|
| C | -4.264583 | 4.270243 | 2.735938 |
| H | -4.164218 | 4.071649 | 0.594039 |
| C | -3.367001 | 2.424225 | 4.013930 |
| H | -2.514121 | 0.814379 | 2.853422 |
| C | -3.981896 | 3.675460 | 3.969282 |
| H | -4.740346 | 5.246385 | 2.698600 |
| H | -3.135049 | 1.964534 | 4.970666 |
| H | -4.235833 | 4.191014 | 4.891325 |
| C | -1.151111 | -2.112790 | -2.521127 |
| C | -0.969308 | -3.273202 | -3.289496 |
| C | -1.070099 | -0.862593 | -3.150746 |
| C | -0.736994 | -3.181421 | -4.661170 |
| H | -0.983715 | -4.246663 | -2.809052 |
| C | -0.835772 | -0.771228 | -4.522151 |
| H | -1.155108 | 0.038935 | -2.553315 |
| C | -0.673473 | -1.930325 | -5.280734 |
| H | -0.595632 | -4.086422 | -5.245780 |
| H | -0.755213 | 0.207339 | -4.985606 |
| H | -0.481939 | -1.862088 | -6.348107 |
| C | -3.174733 | -2.748753 | -0.508752 |
| C | -3.894646 | -2.286184 | 0.601616 |
| C | -3.802032 | -3.617904 | -1.409797 |
| C | -5.214676 | -2.682395 | 0.810225 |
| H | -3.419262 | -1.578778 | 1.276120 |
| C | -5.126283 | -4.006753 | -1.208078 |
| H | -3.265285 | -3.975220 | -2.282039 |
| C | -5.835107 | -3.539558 | -0.099300 |
| H | -5.765706 | -2.299362 | 1.664211 |
| H | -5.607212 | -4.671497 | -1.920740 |
| H | -6.870059 | -3.834662 | 0.049125 |
| C | -0.467695 | -3.595476 | -0.163925 |
| C | -0.955767 | -4.482691 | 0.805680 |
| C | 0.855276 | -3.741735 | -0.613831 |
| C | -0.132173 | -5.483283 | 1.324715 |
| H | -1.979608 | -4.391400 | 1.155127 |
| C | 1.673781 | -4.743096 | -0.096085 |
| H | 1.245213 | -3.058820 | -1.359986 |
| C | 1.184018 | -5.613758 | 0.880239 |
| H | -0.521556 | -6.159934 | 2.080571 |
| H | 2.703046 | -4.820213 | -0.430000 |
| H | 1.827752 | -6.383034 | 1.296206 |

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**2a-TS1**

Zero-point correction=1.065047 (Hartree/Particle)

Thermal correction to Energy=1.132766

Thermal correction to Enthalpy=1.133710

Thermal correction to Gibbs Free Energy= 0.955246

E(Solv) = -4116.04728734

| | | | |
|---|---|---|---|
| C | -2.473749 | 1.383475 | -0.650999 |
| H | -2.776404 | 2.001787 | 0.187922 |
| C | -6.085864 | -0.926700 | 4.305265 |
| C | -6.718288 | 0.327737 | 4.242295 |
| C | -6.647061 | 1.115450 | 3.093502 |
| C | -5.915219 | 0.602210 | 2.031533 |
| C | -5.273661 | -0.652408 | 2.061435 |
| C | -5.365510 | -1.431700 | 3.226525 |
| O | -5.728276 | 1.237863 | 0.834650 |
| C | -4.970233 | 0.377770 | 0.045031 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.641883 | -0.798690 | 0.751861 | H | -4.176117 | 1.045031 | -3.798301 |
| C | -4.361247 | 0.801953 | -1.156531 | H | -4.828661 | 2.954503 | -5.228407 |
| N | -3.822068 | -1.694698 | 0.176051 | H | -5.828504 | 4.992872 | -4.203373 |
| C | -2.455033 | -3.870330 | -0.337212 | H | -6.151860 | 5.093172 | -1.739144 |
| C | -1.836257 | -5.073359 | 0.008719 | H | -5.502351 | 3.180824 | -0.317984 |
| C | -1.274986 | -5.867512 | -0.987879 | C | -1.683354 | 0.250162 | -0.381575 |
| C | -1.322713 | -5.481722 | -2.333640 | C | -0.826671 | -0.364361 | -1.335679 |
| C | -1.964233 | -4.280230 | -2.656899 | C | -0.051420 | -1.504989 | -1.006480 |
| C | -2.524925 | -3.471234 | -1.671852 | H | -0.325343 | -2.037790 | -0.102600 |
| C | -0.667176 | -6.312440 | -3.407014 | C | 0.775661 | -2.258654 | -1.955318 |
| S | -3.090098 | -2.878102 | 1.010977 | C | 1.128562 | -1.766141 | -3.226987 |
| O | -3.985700 | -3.756278 | 1.795103 | C | 1.288222 | -3.509627 | -1.564167 |
| O | -1.918725 | -2.341692 | 1.759761 | C | 1.975405 | -2.489381 | -4.064461 |
| C | -4.804888 | 1.968368 | -1.956946 | H | 0.756220 | -0.799446 | -3.552005 |
| C | -4.613402 | 1.933033 | -3.348512 | C | 2.147077 | -4.222405 | -2.394877 |
| C | -4.976978 | 3.009670 | -4.153467 | H | 1.009545 | -3.913509 | -0.598628 |
| C | -5.536785 | 4.152959 | -3.578945 | C | 2.499149 | -3.717806 | -3.650154 |
| C | -5.719537 | 4.206643 | -2.195269 | H | 2.236493 | -2.087703 | -5.040059 |
| C | -5.354440 | 3.130157 | -1.388777 | H | 2.541868 | -5.177076 | -2.058586 |
| H | -6.167004 | -1.517275 | 5.213012 | H | 3.170085 | -4.274456 | -4.298256 |
| H | -7.274566 | 0.691487 | 5.101617 | H | -0.828059 | 0.036862 | -2.347514 |
| H | -7.130429 | 2.084068 | 3.023218 | H | -1.727263 | -0.209646 | 0.600818 |
| H | -4.895972 | -2.406557 | 3.265981 | H | -2.237462 | 1.945450 | -1.548296 |
| H | -4.043686 | -0.046790 | -1.754468 | Pd | 1.125286 | 0.258267 | -0.284435 |
| H | -1.807355 | -5.388041 | 1.046103 | P | 2.826716 | -0.799349 | 0.909939 |
| H | -0.788362 | -6.800937 | -0.716689 | P | 1.417970 | 2.576017 | -0.241040 |
| H | -2.010644 | -3.963794 | -3.695862 | C | 2.433567 | -2.507924 | 1.440959 |
| H | -3.014457 | -2.538781 | -1.917303 | C | 1.155146 | -2.750167 | 1.966246 |
| H | 0.286321 | -5.860556 | -3.707863 | C | 3.313691 | -3.582172 | 1.256297 |
| H | -0.460985 | -7.329459 | -3.058384 | C | 0.762391 | -4.043434 | 2.305721 |
| H | -1.295664 | -6.379503 | -4.302024 | H | 0.440951 | -1.941278 | 2.075942 |

| | | | |
|---|---|---|---|
| C | 2.914347 | -4.878495 | 1.585385 |
| H | 4.300018 | -3.409937 | 0.839206 |
| C | 1.640553 | -5.111958 | 2.108695 |
| H | -0.239243 | -4.198960 | 2.690743 |
| H | 3.599140 | -5.707413 | 1.427504 |
| H | 1.330706 | -6.124066 | 2.354321 |
| C | 4.389561 | -0.988073 | -0.033540 |
| C | 4.282988 | -1.296148 | -1.399382 |
| C | 5.659663 | -0.823177 | 0.534449 |
| C | 5.427214 | -1.434857 | -2.181884 |
| H | 3.304539 | -1.417307 | -1.849256 |
| C | 6.803970 | -0.949296 | -0.255612 |
| H | 5.754010 | -0.586215 | 1.588822 |
| C | 6.690919 | -1.253988 | -1.613739 |
| H | 5.325419 | -1.678389 | -3.235402 |
| H | 7.784284 | -0.811968 | 0.192395 |
| H | 7.583561 | -1.351705 | -2.225458 |
| C | 3.331530 | 0.056444 | 2.453384 |
| C | 3.046319 | -0.464434 | 3.721432 |
| C | 3.928243 | 1.325009 | 2.357345 |
| C | 3.347821 | 0.271115 | 4.869784 |
| H | 2.587644 | -1.442813 | 3.813979 |
| C | 4.242260 | 2.048194 | 3.503573 |
| H | 4.143640 | 1.751215 | 1.383082 |
| C | 3.945768 | 1.526177 | 4.764934 |
| H | 3.116474 | -0.143746 | 5.846977 |
| H | 4.693038 | 3.031250 | 3.410390 |
| H | 4.175610 | 2.098590 | 5.659073 |
| C | 1.425587 | 3.248006 | 1.466062 |
| C | 2.045593 | 4.450441 | 1.827252 |
| C | 0.781954 | 2.484553 | 2.452186 |
| C | 2.020868 | 4.881668 | 3.153944 |
| H | 2.561250 | 5.042330 | 1.078205 |
| C | 0.752553 | 2.919701 | 3.775337 |
| H | 0.329130 | 1.535741 | 2.176314 |
| C | 1.374820 | 4.118456 | 4.128386 |
| H | 2.510297 | 5.812628 | 3.427085 |
| H | 0.263887 | 2.312596 | 4.531274 |
| H | 1.364489 | 4.452568 | 5.162054 |
| C | 0.082818 | 3.517408 | -1.078180 |
| C | -0.838206 | 4.312662 | -0.387065 |
| C | -0.090421 | 3.315250 | -2.458300 |
| C | -1.919701 | 4.886312 | -1.061979 |
| H | -0.719246 | 4.472768 | 0.679477 |
| C | -1.163421 | 3.895997 | -3.128925 |
| H | 0.612819 | 2.686572 | -2.999450 |
| C | -2.087957 | 4.678603 | -2.429275 |
| H | -2.641070 | 5.483932 | -0.512028 |
| H | -1.294050 | 3.724718 | -4.193723 |
| H | -2.945876 | 5.097057 | -2.943537 |
| C | 2.925788 | 3.252932 | -1.040836 |
| C | 3.022999 | 4.588936 | -1.460322 |
| C | 4.014243 | 2.394083 | -1.245648 |
| C | 4.199879 | 5.058847 | -2.042528 |
| H | 2.172254 | 5.253743 | -1.344005 |
| C | 5.192601 | 2.864985 | -1.825870 |
| H | 3.931730 | 1.350946 | -0.967202 |
| C | 5.288410 | 4.200010 | -2.220497 |
| H | 4.266333 | 6.094869 | -2.363143 |
| H | 6.023291 | 2.181118 | -1.975216 |
| H | 6.202307 | 4.570099 | -2.676786 |

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**2a-TS1'**

Zero-point correction= 1.065449 (Hartree/Particle)

Thermal correction to Energy=1.133031

Thermal correction to Enthalpy= 1.133975

Thermal correction to Gibbs Free Energy= 0.955893

E(Solv) = -4116.04858361

| | | | |
|---|---|---|---|
| C | -2.463182 | -2.054054 | 0.072917 |
| H | -2.412139 | -2.892628 | 0.760543 |
| C | -4.974707 | 4.311576 | -0.980879 |
| C | -5.442168 | 3.747988 | -2.180585 |
| C | -5.498190 | 2.365288 | -2.351785 |
| C | -5.059660 | 1.585222 | -1.290053 |
| C | -4.557074 | 2.119574 | -0.085774 |
| C | -4.532861 | 3.513946 | 0.070803 |
| O | -5.068579 | 0.218263 | -1.273382 |
| C | -4.588357 | -0.161812 | -0.021247 |
| C | -4.204283 | 0.962869 | 0.738566 |
| C | -4.384536 | -1.511683 | 0.355927 |
| N | -3.607909 | 0.767014 | 1.929666 |
| C | -1.539679 | 1.006575 | 3.466597 |
| C | -1.738677 | -0.181814 | 4.175486 |
| C | -0.637484 | -0.902246 | 4.627402 |
| C | 0.672649 | -0.458510 | 4.382363 |
| C | 0.843715 | 0.744158 | 3.689418 |
| C | -0.251026 | 1.480819 | 3.232653 |
| C | 1.861737 | -1.268519 | 4.839935 |
| S | -2.953619 | 1.930497 | 2.849449 |
| O | -3.812015 | 2.261389 | 3.999782 |
| O | -2.377496 | 3.073409 | 2.091440 |
| C | -5.075125 | -2.664156 | -0.272054 |
| C | -5.344544 | -3.793792 | 0.518206 |
| C | -5.954703 | -4.922439 | -0.023995 |
| C | -6.302977 | -4.946598 | -1.375668 |
| C | -6.033825 | -3.832992 | -2.174165 |
| C | -5.423142 | -2.703061 | -1.633160 |
| H | -4.954368 | 5.392201 | -0.873385 |
| H | -5.772474 | 4.397361 | -2.986352 |
| H | -5.870763 | 1.908734 | -3.262707 |
| H | -4.155764 | 3.952438 | 0.985021 |
| H | -4.318181 | -1.576221 | 1.439205 |
| H | -2.748182 | -0.531549 | 4.361678 |
| H | -0.792936 | -1.817891 | 5.193421 |
| H | 1.845447 | 1.118010 | 3.507175 |
| H | -0.107850 | 2.414836 | 2.701341 |
| H | 2.050055 | -2.115207 | 4.165115 |
| H | 2.770729 | -0.659925 | 4.864636 |
| H | 1.702607 | -1.685052 | 5.840629 |
| H | -5.071799 | -3.777853 | 1.570588 |
| H | -6.160698 | -5.781400 | 0.608905 |
| H | -6.779870 | -5.824417 | -1.802648 |
| H | -6.302375 | -3.842870 | -3.227173 |
| H | -5.223199 | -1.841795 | -2.258303 |
| C | -1.707852 | -0.899865 | 0.365611 |
| C | -1.531981 | 0.117349 | -0.601215 |
| C | -0.994590 | 1.394971 | -0.324991 |
| H | -1.052026 | 1.753661 | 0.695387 |
| C | -0.956406 | 2.447483 | -1.352218 |
| C | -0.486461 | 2.202210 | -2.653923 |
| C | -1.391425 | 3.739912 | -1.020077 |
| C | -0.436799 | 3.226105 | -3.595284 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.112501 | 1.213989 | -2.905765 | C | 6.020438 | -3.202755 | 0.413916 |
| C | -1.367846 | 4.756768 | -1.973135 | H | 5.294391 | -4.642852 | 1.843662 |
| H | -1.747231 | 3.925781 | -0.013661 | H | 6.434807 | -1.692692 | -1.071984 |
| C | -0.881484 | 4.509231 | -3.257992 | H | 7.067757 | -3.397315 | 0.626504 |
| H | -0.040712 | 3.028039 | -4.587519 | C | 0.621443 | -3.450396 | 0.530262 |
| H | -1.725050 | 5.747852 | -1.707082 | C | 0.156805 | -4.669372 | 0.024303 |
| H | -0.846916 | 5.308052 | -3.993703 | C | 0.309350 | -3.090402 | 1.850288 |
| H | -1.849286 | -0.101537 | -1.620052 | C | -0.608426 | -5.517121 | 0.828255 |
| H | -1.445650 | -0.686700 | 1.395606 | H | 0.379053 | -4.951164 | -0.999596 |
| H | -2.527988 | -2.348869 | -0.972846 | C | -0.437957 | -3.945565 | 2.656202 |
| Pd | 0.761730 | -0.046534 | -0.233065 | H | 0.618636 | -2.122484 | 2.233001 |
| P | 1.570482 | -2.244183 | -0.471058 | C | -0.902513 | -5.160638 | 2.144853 |
| P | 2.527797 | 1.452898 | -0.162129 | H | -0.978319 | -6.454200 | 0.422050 |
| C | 1.364028 | -2.820611 | -2.203776 | H | -0.680266 | -3.648428 | 3.671366 |
| C | 2.178835 | -3.808401 | -2.774669 | H | -1.501230 | -5.819965 | 2.766738 |
| C | 0.347927 | -2.240853 | -2.978752 | C | 3.138370 | 1.790283 | -1.860919 |
| C | 1.977809 | -4.208297 | -4.096403 | C | 3.875544 | 2.936320 | -2.192336 |
| H | 2.972709 | -4.258014 | -2.187035 | C | 2.842202 | 0.858931 | -2.867859 |
| C | 0.145985 | -2.644070 | -4.298148 | C | 4.316355 | 3.137719 | -3.500413 |
| H | -0.275125 | -1.468486 | -2.539202 | H | 4.083850 | 3.682626 | -1.432423 |
| C | 0.962811 | -3.627735 | -4.859868 | C | 3.287814 | 1.057837 | -4.173925 |
| H | 2.615821 | -4.973060 | -4.530385 | H | 2.241952 | -0.012852 | -2.626792 |
| H | -0.643952 | -2.186748 | -4.887260 | C | 4.026424 | 2.198734 | -4.492675 |
| H | 0.811016 | -3.938902 | -5.889486 | H | 4.881798 | 4.032301 | -3.745726 |
| C | 3.316920 | -2.684648 | -0.120135 | H | 3.045808 | 0.327293 | -4.940762 |
| C | 3.678137 | -3.643309 | 0.833357 | H | 4.367380 | 2.361009 | -5.511256 |
| C | 4.325323 | -1.987947 | -0.805567 | C | 3.999937 | 0.845911 | 0.758453 |
| C | 5.025731 | -3.897625 | 1.099945 | C | 3.799807 | -0.094610 | 1.777494 |
| H | 2.909705 | -4.192234 | 1.366948 | C | 5.297447 | 1.304426 | 0.498141 |
| C | 5.666260 | -2.248956 | -0.544227 | C | 4.874636 | -0.563403 | 2.530818 |
| H | 4.059299 | -1.231040 | -1.536864 | H | 2.798069 | -0.469054 | 1.960031 |

| | | | |
|---|---|---|---|
| C | 6.374291 | 0.828055 | 1.245015 |
| H | 5.469740 | 2.024274 | -0.295063 |
| C | 6.164607 | -0.104509 | 2.263123 |
| H | 4.706557 | -1.304803 | 3.305436 |
| H | 7.378233 | 1.184239 | 1.031013 |
| H | 7.005882 | -0.479740 | 2.838846 |
| C | 2.283637 | 3.118166 | 0.560790 |
| C | 2.633018 | 3.374743 | 1.895915 |
| C | 1.623106 | 4.113850 | -0.174873 |
| C | 2.308797 | 4.593788 | 2.488903 |
| H | 3.168700 | 2.624994 | 2.468185 |
| C | 1.309295 | 5.334700 | 0.420605 |
| H | 1.352648 | 3.938145 | -1.208885 |
| C | 1.641781 | 5.576067 | 1.753846 |
| H | 2.579482 | 4.776147 | 3.524983 |
| H | 0.787640 | 6.088438 | -0.160978 |
| H | 1.383099 | 6.522957 | 2.218407 |

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**2a-INT2**

Zero-point correction= 1.069180 (Hartree/Particle)

Thermal correction to Energy= 1.136198

Thermal correction to Enthalpy=1.137142

Thermal correction to Gibbs Free Energy=0.962215

E(Solv) = -4116.08309942

| | | | |
|---|---|---|---|
| C | 2.432504 | 0.478853 | -2.023929 |
| H | 2.652920 | -0.574565 | -1.843757 |
| C | 4.388436 | 0.153024 | 4.393642 |
| C | 5.057696 | -0.952351 | 3.837015 |
| C | 5.184737 | -1.099343 | 2.453948 |
| C | 4.609552 | -0.109468 | 1.666550 |
| C | 3.916864 | 0.995027 | 2.198037 |
| C | 3.812972 | 1.135449 | 3.588299 |
| O | 4.614034 | -0.061815 | 0.300346 |
| C | 3.883136 | 1.074310 | -0.054029 |
| C | 3.446857 | 1.762764 | 1.049328 |
| C | 3.640587 | 1.318883 | -1.507588 |
| N | 2.721928 | 2.948360 | 0.997611 |
| C | 0.471286 | 4.298320 | 1.011870 |
| C | -0.517918 | 4.973441 | 1.725461 |
| C | -1.387850 | 5.833102 | 1.055169 |
| C | -1.280104 | 6.037347 | -0.325808 |
| C | -0.249716 | 5.382799 | -1.015109 |
| C | 0.619967 | 4.516426 | -0.358137 |
| C | -2.264562 | 6.908603 | -1.064809 |
| S | 1.393208 | 3.009473 | 1.856825 |
| O | 1.487112 | 3.438611 | 3.276244 |
| O | 0.560430 | 1.752675 | 1.697069 |
| C | 4.907818 | 1.124748 | -2.330073 |
| C | 5.948801 | 2.051356 | -2.179279 |
| C | 7.140360 | 1.909698 | -2.885557 |
| C | 7.314233 | 0.831722 | -3.758373 |
| C | 6.286083 | -0.096287 | -3.912588 |
| C | 5.090833 | 0.049842 | -3.203548 |
| H | 4.318706 | 0.240183 | 5.474642 |
| H | 5.490119 | -1.703179 | 4.492431 |
| H | 5.713065 | -1.938383 | 2.011753 |
| H | 3.279373 | 1.981924 | 4.008208 |
| H | 3.354748 | 2.376116 | -1.570050 |
| H | -0.584861 | 4.828111 | 2.797771 |

| | | | |
|---|---|---|---|
| H | -2.163939 | 6.352401 | 1.612468 |
| H | -0.136387 | 5.546522 | -2.084229 |
| H | 1.415585 | 4.004504 | -0.884675 |
| H | -3.016363 | 6.291201 | -1.573903 |
| H | -2.793224 | 7.584071 | -0.384393 |
| H | -1.768863 | 7.515684 | -1.830412 |
| H | 5.818622 | 2.881067 | -1.488808 |
| H | 7.934824 | 2.639573 | -2.755204 |
| H | 8.243233 | 0.718657 | -4.310501 |
| H | 6.409669 | -0.940634 | -4.586304 |
| H | 4.308753 | -0.689005 | -3.330851 |
| C | 1.184101 | 0.891222 | -1.306902 |
| C | 0.066316 | 1.437569 | -1.944968 |
| C | -1.058225 | 1.849935 | -1.186181 |
| H | -0.860050 | 2.161336 | -0.164433 |
| C | -2.291879 | 2.381463 | -1.779475 |
| C | -2.661726 | 2.149360 | -3.116595 |
| C | -3.137305 | 3.168835 | -0.980969 |
| C | -3.841942 | 2.676021 | -3.632651 |
| H | -2.027708 | 1.539948 | -3.755095 |
| C | -4.321598 | 3.691342 | -1.496249 |
| H | -2.853983 | 3.375858 | 0.044152 |
| C | -4.681667 | 3.446209 | -2.822451 |
| H | -4.110611 | 2.483985 | -4.667902 |
| H | -4.963536 | 4.287793 | -0.854516 |
| H | -5.605674 | 3.852152 | -3.224149 |
| H | 0.010164 | 1.400773 | -3.032070 |
| H | 1.296381 | 1.105757 | -0.244867 |
| H | 2.316355 | 0.608618 | -3.107431 |
| Pd | -0.694930 | -0.311849 | -0.747946 |
| P | -2.757955 | -0.706824 | 0.331701 |
| P | 0.313835 | -2.396641 | -0.353392 |
| C | -3.360345 | 0.754100 | 1.259606 |
| C | -2.434760 | 1.465351 | 2.037875 |
| C | -4.692149 | 1.184607 | 1.203978 |
| C | -2.847860 | 2.575384 | 2.773763 |
| H | -1.380953 | 1.204187 | 2.047019 |
| C | -5.094553 | 2.306004 | 1.930131 |
| H | -5.411782 | 0.663620 | 0.583433 |
| C | -4.176676 | 3.000324 | 2.720322 |
| H | -2.116236 | 3.110679 | 3.369145 |
| H | -6.127218 | 2.638777 | 1.871887 |
| H | -4.493661 | 3.873769 | 3.283339 |
| C | -4.137363 | -1.141102 | -0.790641 |
| C | -4.019231 | -0.808960 | -2.145931 |
| C | -5.314346 | -1.756008 | -0.337322 |
| C | -5.054161 | -1.088114 | -3.037622 |
| H | -3.114873 | -0.324594 | -2.495709 |
| C | -6.345790 | -2.042458 | -1.230935 |
| H | -5.418450 | -2.017486 | 0.710526 |
| C | -6.217351 | -1.710593 | -2.582084 |
| H | -4.950828 | -0.816197 | -4.084011 |
| H | -7.250885 | -2.523769 | -0.871757 |
| H | -7.023109 | -1.934450 | -3.275351 |
| C | -2.759285 | -2.043751 | 1.596283 |
| C | -2.353086 | -1.762470 | 2.909288 |
| C | -3.076458 | -3.366280 | 1.252978 |
| C | -2.280174 | -2.779565 | 3.857695 |
| H | -2.091210 | -0.751326 | 3.195662 |
| C | -3.001499 | -4.381660 | 2.206028 |
| H | -3.388555 | -3.610323 | 0.246124 |
| C | -2.605666 | -4.091468 | 3.510983 |

| | | | |
|---|---|---|---|
| H | -1.953451 | -2.544933 | 4.865659 |
| H | -3.252282 | -5.399335 | 1.920413 |
| H | -2.542860 | -4.882961 | 4.252334 |
| C | 0.608917 | -2.554624 | 1.442923 |
| C | 0.575967 | -3.756710 | 2.159684 |
| C | 0.970638 | -1.366654 | 2.101328 |
| C | 0.921509 | -3.771908 | 3.510339 |
| H | 0.256469 | -4.674829 | 1.683966 |
| C | 1.318341 | -1.389691 | 3.450850 |
| H | 0.979271 | -0.411719 | 1.585056 |
| C | 1.303969 | -2.593700 | 4.154570 |
| H | 0.885915 | -4.708454 | 4.060113 |
| H | 1.612782 | -0.464258 | 3.931176 |
| H | 1.584943 | -2.613276 | 5.203834 |
| C | 1.944708 | -2.794889 | -1.092221 |
| C | 3.131125 | -2.693073 | -0.357079 |
| C | 2.003233 | -3.142455 | -2.452774 |
| C | 4.358593 | -2.942503 | -0.973808 |
| H | 3.105474 | -2.402072 | 0.686515 |
| C | 3.229646 | -3.398653 | -3.060055 |
| H | 1.087112 | -3.220020 | -3.031428 |
| C | 4.411902 | -3.299602 | -2.319391 |
| H | 5.273662 | -2.831852 | -0.402289 |
| H | 3.264467 | -3.671686 | -4.111088 |
| H | 5.370474 | -3.482021 | -2.795853 |
| C | -0.677062 | -3.802335 | -0.990081 |
| C | -0.317273 | -5.143069 | -0.783805 |
| C | -1.790954 | -3.517675 | -1.788524 |
| C | -1.107779 | -6.169632 | -1.297315 |
| H | 0.590942 | -5.385667 | -0.243103 |
| C | -2.577157 | -4.543206 | -2.314814 |
| H | -2.047673 | -2.485185 | -1.988049 |
| C | -2.246238 | -5.872712 | -2.053110 |
| H | -0.828503 | -7.204081 | -1.118793 |
| H | -3.446669 | -4.295749 | -2.917122 |
| H | -2.858318 | -6.676895 | -2.451387 |

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**2a-INT2'**

Zero-point correction=1.068496 (Hartree/Particle)

Thermal correction to Energy=1.135904

Thermal correction to Enthalpy=1.136849

Thermal correction to Gibbs Free Energy= 0.959122

E(Solv) = -4116.07921471

| | | | |
|---|---|---|---|
| C | 2.367280 | 0.213690 | -2.115138 |
| H | 2.216706 | 1.295094 | -2.181399 |
| C | 2.259646 | -5.615619 | 0.430621 |
| C | 2.371158 | -5.831221 | -0.955931 |
| C | 2.826935 | -4.824878 | -1.808534 |
| C | 3.147170 | -3.608314 | -1.218956 |
| C | 3.049046 | -3.365743 | 0.163315 |
| C | 2.596472 | -4.391912 | 1.005940 |
| O | 3.562142 | -2.480976 | -1.877043 |
| C | 3.711526 | -1.485944 | -0.904427 |
| C | 3.420120 | -1.967278 | 0.350287 |
| C | 3.725532 | -0.066161 | -1.372328 |
| N | 3.474944 | -1.204206 | 1.513346 |
| C | 2.708087 | 0.156617 | 3.598082 |
| C | 3.970265 | 0.742612 | 3.562989 |
| C | 4.266729 | 1.779911 | 4.450272 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.320962 | 2.239685 | 5.373525 | C | 0.576965 | -1.583600 | -1.715874 |
| C | 2.059313 | 1.625240 | 5.395218 | C | -0.236088 | -2.266047 | -0.773467 |
| C | 1.750658 | 0.588901 | 4.519780 | H | 0.139326 | -2.307463 | 0.245571 |
| C | 3.651807 | 3.348898 | 6.341956 | C | -1.169047 | -3.334574 | -1.162614 |
| S | 2.211483 | -1.127319 | 2.451806 | C | -2.021479 | -3.206840 | -2.271676 |
| O | 1.844884 | -2.321918 | 3.263039 | C | -1.216712 | -4.512158 | -0.404464 |
| O | 0.981620 | -0.556129 | 1.766553 | C | -2.902140 | -4.230072 | -2.611345 |
| C | 4.898446 | 0.413750 | -2.202775 | H | -2.010233 | -2.283759 | -2.845763 |
| C | 5.185736 | 1.785590 | -2.227561 | C | -2.092949 | -5.538864 | -0.749042 |
| C | 6.227257 | 2.283227 | -3.008954 | H | -0.559700 | -4.614930 | 0.451685 |
| C | 7.001346 | 1.412179 | -3.778916 | C | -2.940206 | -5.401734 | -1.849435 |
| C | 6.722541 | 0.045131 | -3.759398 | H | -3.565673 | -4.111950 | -3.463791 |
| C | 5.676773 | -0.451962 | -2.979057 | H | -2.120060 | -6.443467 | -0.148391 |
| H | 1.901874 | -6.422682 | 1.064349 | H | -3.630568 | -6.198911 | -2.110993 |
| H | 2.091643 | -6.794545 | -1.372823 | H | 0.510823 | -1.828221 | -2.775260 |
| H | 2.914476 | -4.971366 | -2.880300 | H | 1.443745 | -0.362113 | -0.222783 |
| H | 2.492279 | -4.210154 | 2.069406 | H | 2.410289 | -0.188945 | -3.132826 |
| H | 3.695723 | 0.518855 | -0.445546 | Pd | -0.856345 | -0.140029 | -0.759819 |
| H | 4.688596 | 0.387460 | 2.833607 | P | -0.839603 | 2.158337 | -1.143172 |
| H | 5.251122 | 2.241071 | 4.421270 | P | -2.717047 | -0.461123 | 0.599849 |
| H | 1.312593 | 1.962652 | 6.110713 | C | -0.924757 | 2.532240 | -2.939019 |
| H | 0.773743 | 0.117075 | 4.544687 | C | -1.369297 | 3.772947 | -3.421343 |
| H | 2.820752 | 4.056647 | 6.439951 | C | -0.509928 | 1.554086 | -3.854034 |
| H | 3.856994 | 2.951111 | 7.344423 | C | -1.385784 | 4.030615 | -4.791779 |
| H | 4.537391 | 3.907279 | 6.022588 | H | -1.709334 | 4.532382 | -2.724805 |
| H | 4.587388 | 2.463700 | -1.623220 | C | -0.525165 | 1.814481 | -5.224351 |
| H | 6.439704 | 3.349340 | -3.011874 | H | -0.177668 | 0.589601 | -3.485617 |
| H | 7.816741 | 1.796027 | -4.386033 | C | -0.962520 | 3.053276 | -5.695389 |
| H | 7.322293 | -0.640445 | -4.352348 | H | -1.731069 | 4.994781 | -5.154067 |
| H | 5.462382 | -1.515037 | -2.968105 | H | -0.199262 | 1.048412 | -5.922085 |
| C | 1.311255 | -0.470728 | -1.297509 | H | -0.977847 | 3.255804 | -6.762426 |

| | | | |
|---|---|---|---|
| C | -2.168787 | 3.220150 | -0.464364 |
| C | -1.927731 | 4.159677 | 0.543166 |
| C | -3.471391 | 3.067147 | -0.964930 |
| C | -2.973122 | 4.944960 | 1.031488 |
| H | -0.928079 | 4.276313 | 0.946596 |
| C | -4.510675 | 3.854857 | -0.477842 |
| H | -3.671506 | 2.337990 | -1.742207 |
| C | -4.262095 | 4.800735 | 0.519771 |
| H | -2.776206 | 5.667754 | 1.817695 |
| H | -5.513286 | 3.727022 | -0.876093 |
| H | -5.071937 | 5.415995 | 0.901555 |
| C | 0.716270 | 2.940421 | -0.570293 |
| C | 1.307772 | 4.015764 | -1.248669 |
| C | 1.339747 | 2.415970 | 0.572688 |
| C | 2.506678 | 4.559477 | -0.786999 |
| H | 0.844826 | 4.417047 | -2.143947 |
| C | 2.533271 | 2.970541 | 1.036916 |
| H | 0.927942 | 1.551892 | 1.082387 |
| C | 3.118351 | 4.040540 | 0.357066 |
| H | 2.964745 | 5.384861 | -1.324789 |
| H | 3.007282 | 2.549591 | 1.917139 |
| H | 4.054830 | 4.462315 | 0.711300 |
| C | -4.311161 | -0.414164 | -0.288234 |
| C | -5.552804 | -0.553927 | 0.352411 |
| C | -4.280067 | -0.240993 | -1.679128 |
| C | -6.736016 | -0.495626 | -0.383200 |
| H | -5.593203 | -0.716362 | 1.424673 |
| C | -5.463666 | -0.185435 | -2.415290 |
| H | -3.317682 | -0.146851 | -2.174860 |
| C | -6.693423 | -0.307338 | -1.766863 |
| H | -7.691074 | -0.601577 | 0.123185 |
| H | -5.424231 | -0.048549 | -3.492196 |
| H | -7.616723 | -0.263496 | -2.337442 |
| C | -2.779292 | 0.844041 | 1.897345 |
| C | -1.585176 | 1.109280 | 2.589893 |
| C | -3.920465 | 1.598155 | 2.191947 |
| C | -1.549918 | 2.090347 | 3.579256 |
| H | -0.680120 | 0.557916 | 2.355739 |
| C | -3.878521 | 2.576791 | 3.186000 |
| H | -4.836537 | 1.450834 | 1.634277 |
| C | -2.698599 | 2.821226 | 3.887091 |
| H | -0.615283 | 2.284887 | 4.097468 |
| H | -4.770445 | 3.159540 | 3.397400 |
| H | -2.669916 | 3.588253 | 4.656207 |
| C | -2.709342 | -2.039836 | 1.540238 |
| C | -1.595271 | -2.302803 | 2.355040 |
| C | -3.706037 | -3.013847 | 1.407086 |
| C | -1.499128 | -3.505887 | 3.049860 |
| H | -0.770762 | -1.602120 | 2.415249 |
| C | -3.608348 | -4.214676 | 2.113149 |
| H | -4.545935 | -2.856635 | 0.740918 |
| C | -2.513115 | -4.460992 | 2.940648 |
| H | -0.612048 | -3.686237 | 3.649415 |
| H | -4.386230 | -4.964341 | 1.997863 |
| H | -2.438850 | -5.401376 | 3.479991 |

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**diene-Pd-*exo*-TS**

Zero-point correction=1.068229 (Hartree/Particle)

Thermal correction to Energy=1.134899

Thermal correction to Enthalpy=1.135843

Thermal correction to Gibbs Free Energy= 0.961008

E(Solv) = -4116.05953140

| | | | |
|---|---|---|---|
| C | 2.475012 | 0.399318 | -1.391204 |
| H | 2.325268 | -0.648113 | -1.121013 |
| C | 3.306996 | 2.802896 | 4.678022 |
| C | 4.127776 | 1.692778 | 4.946241 |
| C | 4.607119 | 0.888478 | 3.911664 |
| C | 4.222728 | 1.236329 | 2.623569 |
| C | 3.394078 | 2.340579 | 2.321521 |
| C | 2.936638 | 3.142769 | 3.378743 |
| O | 4.573909 | 0.555201 | 1.485492 |
| C | 3.968079 | 1.227391 | 0.441978 |
| C | 3.250282 | 2.313997 | 0.868744 |
| C | 3.951464 | 0.736753 | -0.959001 |
| N | 2.488506 | 2.983129 | -0.080538 |
| C | 0.637964 | 4.551670 | -1.068914 |
| C | -0.682020 | 4.991775 | -0.966172 |
| C | -1.414212 | 5.236253 | -2.122855 |
| C | -0.852450 | 5.030471 | -3.389249 |
| C | 0.484570 | 4.620191 | -3.466430 |
| C | 1.237563 | 4.387405 | -2.315691 |
| C | -1.693823 | 5.199275 | -4.629678 |
| S | 1.498708 | 4.171319 | 0.450719 |
| O | 2.252548 | 5.351203 | 0.917000 |
| O | 0.458756 | 3.671153 | 1.393962 |
| C | 4.849461 | -0.447294 | -1.256087 |
| C | 5.718610 | -0.414671 | -2.349921 |
| C | 6.514502 | -1.517574 | -2.667674 |
| C | 6.451008 | -2.672810 | -1.887763 |
| C | 5.583132 | -2.716281 | -0.793095 |
| C | 4.786963 | -1.615757 | -0.483201 |
| H | 2.956706 | 3.414264 | 5.504825 |
| H | 4.398942 | 1.460002 | 5.972024 |
| H | 5.251719 | 0.033889 | 4.090311 |
| H | 2.312330 | 4.005371 | 3.186082 |
| H | 4.257051 | 1.582854 | -1.587023 |
| H | -1.137945 | 5.089562 | 0.012750 |
| H | -2.453775 | 5.541654 | -2.042567 |
| H | 0.939768 | 4.467899 | -4.442131 |
| H | 2.261776 | 4.039220 | -2.373030 |
| H | -2.433889 | 4.391806 | -4.700950 |
| H | -2.246818 | 6.145469 | -4.614366 |
| H | -1.082404 | 5.177665 | -5.537222 |
| H | 5.773557 | 0.484367 | -2.958851 |
| H | 7.185943 | -1.470524 | -3.520741 |
| H | 7.074772 | -3.529825 | -2.127125 |
| H | 5.523026 | -3.608955 | -0.175991 |
| H | 4.117054 | -1.663184 | 0.367062 |
| C | 1.341629 | 1.150963 | -0.763858 |
| C | 0.144945 | 1.383472 | -1.483647 |
| C | -1.049960 | 1.788753 | -0.820070 |
| H | -0.933304 | 2.275949 | 0.140470 |
| C | -2.319514 | 2.051136 | -1.509153 |
| C | -2.588035 | 1.584272 | -2.810141 |
| C | -3.337210 | 2.747853 | -0.829840 |
| C | -3.830060 | 1.800630 | -3.404366 |
| H | -1.822998 | 1.037905 | -3.352857 |
| C | -4.578771 | 2.956229 | -1.421677 |
| H | -3.142424 | 3.121326 | 0.169067 |
| C | -4.834580 | 2.483703 | -2.712552 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.016761 | 1.429833 | -4.408817 | C | -1.805366 | -1.521086 | 2.725583 |
| H | -5.349630 | 3.490084 | -0.872830 | C | -1.337623 | -0.947142 | 3.915227 |
| H | -5.803469 | 2.647923 | -3.175362 | C | -1.603082 | -2.894769 | 2.510987 |
| H | 0.178714 | 1.308059 | -2.566600 | C | -0.667081 | -1.727013 | 4.859229 |
| H | 1.259857 | 1.100223 | 0.313714 | H | -1.487335 | 0.109688 | 4.104367 |
| H | 2.405763 | 0.440468 | -2.483190 | C | -0.947362 | -3.672439 | 3.460784 |
| Pd | -0.990246 | -0.378756 | -0.430809 | H | -1.946800 | -3.358745 | 1.593513 |
| P | -2.472370 | -0.494042 | 1.357218 | C | -0.465965 | -3.088464 | 4.634167 |
| P | -0.068935 | -2.494291 | -0.856219 | H | -0.300712 | -1.263742 | 5.770953 |
| C | -2.933432 | 1.097148 | 2.138319 | H | -0.787579 | -4.729129 | 3.269299 |
| C | -1.913609 | 2.017638 | 2.427718 | H | 0.065229 | -3.690975 | 5.365213 |
| C | -4.268485 | 1.469973 | 2.346635 | C | 1.044215 | -2.985747 | 0.522057 |
| C | -2.219718 | 3.288953 | 2.910784 | C | 1.470761 | -4.298518 | 0.760248 |
| H | -0.873867 | 1.769842 | 2.243531 | C | 1.489726 | -1.961570 | 1.373201 |
| C | -4.574031 | 2.743671 | 2.828073 | C | 2.341508 | -4.573750 | 1.815963 |
| H | -5.068483 | 0.774351 | 2.118389 | H | 1.115740 | -5.108762 | 0.132010 |
| C | -3.553482 | 3.655514 | 3.106903 | C | 2.362559 | -2.233602 | 2.424833 |
| H | -1.409754 | 3.987979 | 3.086996 | H | 1.129425 | -0.949669 | 1.219845 |
| H | -5.612826 | 3.024927 | 2.978531 | C | 2.792919 | -3.543652 | 2.644382 |
| H | -3.796879 | 4.650955 | 3.467786 | H | 2.665713 | -5.595686 | 1.992788 |
| C | -4.084138 | -1.235224 | 0.902745 | H | 2.698739 | -1.425343 | 3.067321 |
| C | -4.630490 | -0.855506 | -0.335665 | H | 3.470528 | -3.763259 | 3.464502 |
| C | -4.759734 | -2.170844 | 1.695250 | C | 1.025117 | -2.483788 | -2.334214 |
| C | -5.832806 | -1.408011 | -0.770691 | C | 2.325034 | -3.000417 | -2.345505 |
| H | -4.105666 | -0.137078 | -0.958653 | C | 0.532605 | -1.843337 | -3.483186 |
| C | -5.956799 | -2.734471 | 1.247670 | C | 3.129314 | -2.861898 | -3.479301 |
| H | -4.343849 | -2.468884 | 2.652087 | H | 2.731070 | -3.473328 | -1.459200 |
| C | -6.494264 | -2.355606 | 0.016078 | C | 1.327225 | -1.724418 | -4.620133 |
| H | -6.246038 | -1.105477 | -1.728501 | H | -0.468749 | -1.419444 | -3.468855 |
| H | -6.470242 | -3.466862 | 1.864457 | C | 2.633451 | -2.225477 | -4.615555 |
| H | -7.425333 | -2.796007 | -0.329524 | H | 4.151170 | -3.224863 | -3.454313 |

| | | | |
|---|---|---|---|
| H | 0.936878 | -1.226057 | -5.503346 |
| H | 3.263996 | -2.108570 | -5.492310 |
| C | -1.135070 | -3.950513 | -1.201358 |
| C | -0.641514 | -5.115980 | -1.808677 |
| C | -2.495774 | -3.877315 | -0.876135 |
| C | -1.487153 | -6.200004 | -2.040426 |
| H | 0.397630 | -5.165205 | -2.119937 |
| C | -3.342410 | -4.962146 | -1.108441 |
| H | -2.897265 | -2.963564 | -0.457547 |
| C | -2.836902 | -6.128241 | -1.683681 |
| H | -1.095167 | -7.098625 | -2.508678 |
| H | -4.393526 | -4.882498 | -0.846842 |
| H | -3.492730 | -6.974236 | -1.869303 |

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**diene-Pd-*endo*-TS**

Zero-point correction= 1.066491 (Hartree/Particle)

Thermal correction to Energy= 1.133862

Thermal correction to Enthalpy= 1.134806

Thermal correction to Gibbs Free Energy= 0.954264

E(Solv) = -4116.04662314

| | | | |
|---|---|---|---|
| C | -1.553581 | 2.145838 | -0.606189 |
| H | -1.484535 | 2.703343 | -1.539959 |
| C | -3.557581 | -2.000217 | 3.872430 |
| C | -3.096030 | -1.037788 | 4.789957 |
| C | -2.898438 | 0.292081 | 4.409683 |
| C | -3.171828 | 0.606408 | 3.084041 |
| C | -3.651867 | -0.332182 | 2.153645 |
| C | -3.842797 | -1.659312 | 2.552401 |
| O | -2.982157 | 1.823730 | 2.482344 |
| C | -3.339783 | 1.662079 | 1.139650 |
| C | -3.756310 | 0.368699 | 0.883282 |
| C | -2.898929 | 2.643659 | 0.125251 |
| N | -3.914863 | -0.281351 | -0.313939 |
| C | -5.945633 | -0.897638 | -1.901577 |
| C | -5.619326 | -2.103440 | -2.524105 |
| C | -6.605758 | -3.068646 | -2.704672 |
| C | -7.923001 | -2.847367 | -2.276608 |
| C | -8.225835 | -1.628208 | -1.658892 |
| C | -7.247116 | -0.653011 | -1.468989 |
| C | -8.992718 | -3.887373 | -2.507361 |
| S | -4.666901 | 0.326059 | -1.602373 |
| O | -3.763500 | 0.257494 | -2.777492 |
| O | -5.370333 | 1.612790 | -1.366828 |
| C | -2.619783 | 4.063741 | 0.573008 |
| C | -3.216106 | 5.127033 | -0.112338 |
| C | -2.878061 | 6.449835 | 0.182920 |
| C | -1.929708 | 6.727635 | 1.168298 |
| C | -1.332671 | 5.672435 | 1.864197 |
| C | -1.676637 | 4.354960 | 1.569436 |
| H | -3.681905 | -3.028062 | 4.199930 |
| H | -2.882527 | -1.334386 | 5.813139 |
| H | -2.540483 | 1.044380 | 5.105894 |
| H | -4.189001 | -2.395483 | 1.834643 |
| H | -3.671847 | 2.666806 | -0.642065 |
| H | -4.604081 | -2.267462 | -2.868811 |
| H | -6.354157 | -4.009229 | -3.190045 |
| H | -9.242815 | -1.438653 | -1.323195 |
| H | -7.478830 | 0.295542 | -0.997197 |
| H | -8.596105 | -4.902489 | -2.393732 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -9.824709 | -3.767681 | -1.805631 | C | 3.213432 | 3.945575 | 2.839540 |
| H | -9.407267 | -3.813641 | -3.521825 | H | 4.027644 | 3.697464 | 0.861602 |
| H | -3.944070 | 4.911308 | -0.889816 | C | 1.258312 | 2.622836 | 3.359787 |
| H | -3.353758 | 7.261645 | -0.360952 | H | 0.557975 | 1.339249 | 1.783677 |
| H | -1.662140 | 7.755795 | 1.397098 | C | 2.217047 | 3.563246 | 3.741494 |
| H | -0.594746 | 5.873573 | 2.636783 | H | 3.961834 | 4.675928 | 3.133654 |
| H | -1.205842 | 3.544708 | 2.113177 | H | 0.475943 | 2.318794 | 4.049246 |
| C | -1.375851 | 0.696244 | -0.842198 | H | 2.190049 | 3.995405 | 4.737623 |
| C | -1.040919 | -0.162368 | 0.206819 | C | 4.004162 | 1.882556 | -1.058888 |
| C | -0.768099 | -1.541302 | 0.024110 | C | 4.401496 | 2.659424 | -2.153149 |
| H | -1.077137 | -1.977264 | -0.924103 | C | 4.968742 | 1.137390 | -0.361893 |
| C | -0.713453 | -2.463975 | 1.164146 | C | 5.740939 | 2.684445 | -2.548333 |
| C | -0.110123 | -2.109855 | 2.383682 | H | 3.668386 | 3.246771 | -2.695113 |
| C | -1.305728 | -3.731344 | 1.054228 | C | 6.303043 | 1.169848 | -0.753950 |
| C | -0.090420 | -2.998322 | 3.452124 | H | 4.674887 | 0.526355 | 0.485637 |
| H | 0.367483 | -1.140837 | 2.481992 | C | 6.692423 | 1.940449 | -1.852665 |
| C | -1.302309 | -4.616312 | 2.130948 | H | 6.037518 | 3.290789 | -3.399677 |
| H | -1.775717 | -4.014440 | 0.117165 | H | 7.036001 | 0.579358 | -0.212994 |
| C | -0.686515 | -4.258097 | 3.330819 | H | 7.732845 | 1.956880 | -2.164281 |
| H | 0.392165 | -2.709802 | 4.381270 | C | 1.391098 | 3.031734 | -1.515706 |
| H | -1.774785 | -5.589357 | 2.028838 | C | 0.996516 | 4.260730 | -0.972655 |
| H | -0.673571 | -4.950516 | 4.167688 | C | 1.008305 | 2.706104 | -2.826800 |
| H | -1.043727 | 0.235017 | 1.217450 | C | 0.218086 | 5.144088 | -1.722534 |
| H | -1.560369 | 0.287377 | -1.830089 | H | 1.250939 | 4.514629 | 0.049538 |
| H | -0.750690 | 2.488415 | 0.045231 | C | 0.259903 | 3.603308 | -3.585916 |
| Pd | 1.109298 | -0.340016 | -0.488482 | H | 1.272230 | 1.735647 | -3.240251 |
| P | 2.251640 | 1.746369 | -0.533408 | C | -0.145310 | 4.820524 | -3.029557 |
| P | 2.703521 | -2.036905 | -0.394639 | H | -0.128859 | 6.066288 | -1.267481 |
| C | 2.290953 | 2.453361 | 1.164576 | H | -0.037070 | 3.338933 | -4.596470 |
| C | 3.252188 | 3.395457 | 1.558017 | H | -0.761787 | 5.502400 | -3.607635 |
| C | 1.299312 | 2.071428 | 2.079480 | C | 3.424738 | -2.161799 | 1.288999 |

| | | | |
|---|---|---|---|
| C | 4.112337 | -3.298154 | 1.741555 |
| C | 3.274165 | -1.071385 | 2.157588 |
| C | 4.646419 | -3.332369 | 3.029471 |
| H | 4.208191 | -4.165666 | 1.096846 |
| C | 3.811213 | -1.103600 | 3.443866 |
| H | 2.719163 | -0.200660 | 1.828510 |
| C | 4.499538 | -2.235650 | 3.882224 |
| H | 5.172677 | -4.219726 | 3.369581 |
| H | 3.679186 | -0.248165 | 4.100279 |
| H | 4.913099 | -2.268532 | 4.886131 |
| C | 4.133905 | -1.779510 | -1.518873 |
| C | 3.932454 | -1.003917 | -2.668225 |
| C | 5.397779 | -2.334664 | -1.281764 |
| C | 4.974898 | -0.786461 | -3.567815 |
| H | 2.958444 | -0.553145 | -2.838151 |
| C | 6.441677 | -2.111678 | -2.177984 |
| H | 5.573218 | -2.927511 | -0.390717 |
| C | 6.232489 | -1.337266 | -3.321116 |
| H | 4.810340 | -0.170290 | -4.446386 |
| H | 7.420906 | -2.539514 | -1.981762 |
| H | 7.050103 | -1.157029 | -4.013081 |
| C | 2.202834 | -3.755989 | -0.787414 |
| C | 2.308100 | -4.231017 | -2.104523 |
| C | 1.622608 | -4.576523 | 0.191344 |
| C | 1.850211 | -5.505535 | -2.432363 |
| H | 2.758231 | -3.607631 | -2.870637 |
| C | 1.173179 | -5.854424 | -0.141733 |
| H | 1.522220 | -4.224818 | 1.211206 |
| C | 1.283996 | -6.322617 | -1.450682 |
| H | 1.941972 | -5.862848 | -3.454128 |
| H | 0.724031 | -6.474535 | 0.628057 |
| H | 0.930462 | -7.317278 | -1.706772 |

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***exo*-Pd-16**

Zero-point correction=1.070504 (Hartree/Particle)

Thermal correction to Energy=1.137113

Thermal correction to Enthalpy=1.138057

Thermal correction to Gibbs Free Energy= 0.962391

E(Solv) = -4116.10682805

| | | | |
|---|---|---|---|
| C | 2.531249 | -0.733242 | -0.394626 |
| H | 1.694565 | -1.424962 | -0.352816 |
| C | 6.234651 | 3.387071 | 3.310184 |
| C | 6.931150 | 2.330587 | 3.926159 |
| C | 6.692266 | 1.002565 | 3.571491 |
| C | 5.735724 | 0.788553 | 2.588785 |
| C | 5.026035 | 1.826389 | 1.953846 |
| C | 5.283529 | 3.152567 | 2.320835 |
| O | 5.335166 | -0.438840 | 2.107563 |
| C | 4.372721 | -0.186721 | 1.158161 |
| C | 4.146843 | 1.151329 | 1.020693 |
| C | 3.702952 | -1.312177 | 0.449515 |
| N | 3.116607 | 1.668573 | 0.194436 |
| C | 4.156050 | 1.326932 | -2.352924 |
| C | 3.311581 | 1.036145 | -3.422855 |
| C | 3.600470 | -0.058408 | -4.235729 |
| C | 4.713809 | -0.870522 | -3.984604 |
| C | 5.569711 | -0.528851 | -2.925924 |
| C | 5.304498 | 0.567419 | -2.111022 |
| C | 4.984668 | -2.096716 | -4.819323 |

| | | | |
|---|---|---|---|
| S | 3.670482 | 2.564965 | -1.162491 |
| O | 4.877073 | 3.253971 | -0.701616 |
| O | 2.544868 | 3.311036 | -1.718932 |
| C | 3.281237 | -2.430230 | 1.392598 |
| C | 4.038887 | -3.602631 | 1.457765 |
| C | 3.649677 | -4.664429 | 2.275296 |
| C | 2.489763 | -4.561833 | 3.043993 |
| C | 1.733185 | -3.389229 | 2.996523 |
| C | 2.128467 | -2.331037 | 2.178983 |
| H | 6.450900 | 4.408567 | 3.609371 |
| H | 7.670777 | 2.551364 | 4.690207 |
| H | 7.217546 | 0.174528 | 4.035242 |
| H | 4.767986 | 3.965943 | 1.824888 |
| H | 4.425748 | -1.750803 | -0.251876 |
| H | 2.441577 | 1.658917 | -3.598507 |
| H | 2.947013 | -0.291179 | -5.072388 |
| H | 6.454942 | -1.131590 | -2.739365 |
| H | 5.967573 | 0.833935 | -1.296392 |
| H | 4.714149 | -3.006389 | -4.267923 |
| H | 4.405396 | -2.086810 | -5.747630 |
| H | 6.045396 | -2.179222 | -5.079959 |
| H | 4.935647 | -3.688028 | 0.849147 |
| H | 4.248514 | -5.570776 | 2.306788 |
| H | 2.175946 | -5.387983 | 3.675819 |
| H | 0.823134 | -3.306234 | 3.580378 |
| H | 1.520953 | -1.431549 | 2.136650 |
| C | 2.003125 | 0.642581 | 0.047309 |
| C | 0.871417 | 1.105745 | -0.834615 |
| C | 0.056890 | 2.173324 | -0.436834 |
| H | 0.223665 | 2.591025 | 0.553318 |
| C | -0.686030 | 3.054655 | -1.352747 |
| C | -0.810700 | 2.791953 | -2.729923 |
| C | -1.323126 | 4.198456 | -0.840229 |
| C | -1.561074 | 3.627862 | -3.553547 |
| H | -0.325353 | 1.919464 | -3.155486 |
| C | -2.080443 | 5.028809 | -1.662364 |
| H | -1.229667 | 4.424007 | 0.217194 |
| C | -2.208627 | 4.748077 | -3.024414 |
| H | -1.641265 | 3.403732 | -4.614265 |
| H | -2.572370 | 5.898799 | -1.235838 |
| H | -2.797225 | 5.396747 | -3.666883 |
| H | 1.001510 | 0.897659 | -1.891767 |
| H | 1.640441 | 0.572793 | 1.077961 |
| H | 2.830492 | -0.685902 | -1.441131 |
| Pd | -1.127849 | 0.290907 | -0.213552 |
| P | -3.086991 | 1.064706 | 0.844190 |
| P | -1.354637 | -1.992647 | -0.637211 |
| C | -2.794841 | 2.591759 | 1.824390 |
| C | -1.621078 | 2.661184 | 2.591262 |
| C | -3.641958 | 3.705019 | 1.777006 |
| C | -1.301653 | 3.817929 | 3.299458 |
| H | -0.945665 | 1.809431 | 2.606257 |
| C | -3.314121 | 4.869779 | 2.473753 |
| H | -4.547199 | 3.669486 | 1.180775 |
| C | -2.145565 | 4.930383 | 3.234013 |
| H | -0.387121 | 3.858943 | 3.884309 |
| H | -3.971785 | 5.732838 | 2.417132 |
| H | -1.888842 | 5.840364 | 3.768728 |
| C | -4.462771 | 1.547559 | -0.277735 |
| C | -4.126832 | 2.051586 | -1.542746 |
| C | -5.815303 | 1.427745 | 0.073321 |
| C | -5.124489 | 2.426852 | -2.441270 |

| | | | |
|---|---|---|---|
| H | -3.085533 | 2.142609 | -1.826571 |
| C | -6.812131 | 1.796041 | -0.830988 |
| H | -6.088407 | 1.039028 | 1.048576 |
| C | -6.469475 | 2.294560 | -2.090221 |
| H | -4.842350 | 2.821179 | -3.412806 |
| H | -7.857064 | 1.693797 | -0.550946 |
| H | -7.248053 | 2.579556 | -2.792600 |
| C | -3.936028 | -0.045084 | 2.041710 |
| C | -3.966267 | 0.204414 | 3.418424 |
| C | -4.514847 | -1.229037 | 1.553450 |
| C | -4.560450 | -0.712266 | 4.290012 |
| H | -3.531212 | 1.116602 | 3.812693 |
| C | -5.118507 | -2.133184 | 2.420970 |
| H | -4.489383 | -1.445078 | 0.490276 |
| C | -5.138837 | -1.879909 | 3.795125 |
| H | -4.575671 | -0.505259 | 5.356767 |
| H | -5.552233 | -3.047125 | 2.026725 |
| H | -5.598767 | -2.592449 | 4.474041 |
| C | -1.777523 | -2.942401 | 0.882808 |
| C | -2.356584 | -4.218107 | 0.867276 |
| C | -1.526746 | -2.326291 | 2.116422 |
| C | -2.671376 | -4.864599 | 2.062468 |
| H | -2.574485 | -4.703333 | -0.078354 |
| C | -1.845048 | -2.968909 | 3.311323 |
| H | -1.108093 | -1.323858 | 2.124510 |
| C | -2.416513 | -4.241241 | 3.286004 |
| H | -3.122640 | -5.852810 | 2.038354 |
| H | -1.671793 | -2.465454 | 4.257652 |
| H | -2.675951 | -4.740403 | 4.215409 |
| C | 0.060302 | -2.935164 | -1.341490 |
| C | 0.761091 | -3.916091 | -0.631094 |
| C | 0.531306 | -2.540500 | -2.606010 |
| C | 1.918933 | -4.484507 | -1.170235 |
| H | 0.427355 | -4.219057 | 0.354561 |
| C | 1.676153 | -3.116295 | -3.146508 |
| H | 0.004468 | -1.762525 | -3.153056 |
| C | 2.378843 | -4.087441 | -2.424441 |
| H | 2.463924 | -5.225295 | -0.594195 |
| H | 2.030887 | -2.799642 | -4.122865 |
| H | 3.279961 | -4.530368 | -2.840232 |
| C | -2.686972 | -2.433758 | -1.832575 |
| C | -2.732718 | -3.667038 | -2.500970 |
| C | -3.692199 | -1.490698 | -2.084420 |
| C | -3.781385 | -3.957425 | -3.373599 |
| H | -1.937963 | -4.391669 | -2.351936 |
| C | -4.742679 | -1.780297 | -2.955662 |
| H | -3.641311 | -0.520307 | -1.608154 |
| C | -4.791825 | -3.018145 | -3.597956 |
| H | -3.807061 | -4.916261 | -3.884321 |
| H | -5.508822 | -1.030871 | -3.133940 |
| H | -5.605314 | -3.248019 | -4.280516 |

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***endo*-Pd-17**

Zero-point correction=1.069223 (Hartree/Particle)

Thermal correction to Energy=1.136377

Thermal correction to Enthalpy=1.137321

Thermal correction to Gibbs Free Energy= 0.957708

E(Solv) = -4116.08424089

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.669585 | 2.391514 | -1.377746 | H | -5.623588 | 2.221104 | 3.788899 |
| H | -1.904236 | 2.636011 | -2.416387 | H | -4.949601 | -1.689516 | 0.702741 |
| C | -5.838688 | -0.973891 | 2.539889 | H | -3.330058 | 3.754982 | -1.126764 |
| C | -6.036612 | 0.117204 | 3.405871 | H | -3.857216 | -2.515837 | -2.358537 |
| C | -5.491630 | 1.372041 | 3.126838 | H | -5.506294 | -4.217302 | -1.593092 |
| C | -4.757130 | 1.480162 | 1.955017 | H | -8.425516 | -1.119811 | -1.007709 |
| C | -4.558006 | 0.407202 | 1.060395 | H | -6.770720 | 0.580066 | -1.779440 |
| C | -5.103138 | -0.845864 | 1.364783 | H | -7.594968 | -4.639460 | -0.259310 |
| O | -4.103699 | 2.611672 | 1.509941 | H | -8.837440 | -3.379638 | -0.133393 |
| C | -3.497564 | 2.263516 | 0.327928 | H | -8.612287 | -4.257009 | -1.650949 |
| C | -3.749995 | 0.967408 | 0.003379 | H | -2.681991 | 5.900326 | -0.762576 |
| C | -2.654470 | 3.211599 | -0.454155 | H | -1.378296 | 7.612775 | 0.463977 |
| N | -3.110268 | 0.348193 | -1.101206 | H | 0.156202 | 6.926730 | 2.301478 |
| C | -5.236216 | -0.881554 | -2.111607 | H | 0.351359 | 4.519650 | 2.902386 |
| C | -4.860724 | -2.225715 | -2.066633 | H | -0.964427 | 2.825812 | 1.684693 |
| C | -5.788399 | -3.168436 | -1.636219 | C | -1.694529 | 0.858681 | -1.228274 |
| C | -7.082945 | -2.785541 | -1.249217 | C | -0.958002 | 0.273404 | -0.036725 |
| C | -7.430033 | -1.431063 | -1.312124 | C | -0.879010 | -1.142744 | 0.019781 |
| C | -6.514126 | -0.472427 | -1.742979 | H | -1.199818 | -1.664812 | -0.882290 |
| C | -8.083649 | -3.818533 | -0.794409 | C | -1.076230 | -1.940116 | 1.249150 |
| S | -4.011073 | 0.336342 | -2.552372 | C | -0.404484 | -1.677886 | 2.454865 |
| O | -3.112735 | -0.218751 | -3.573155 | C | -1.968493 | -3.024387 | 1.217697 |
| O | -4.697358 | 1.616065 | -2.792835 | C | -0.598073 | -2.480438 | 3.576367 |
| C | -1.916984 | 4.245744 | 0.375580 | H | 0.316217 | -0.868450 | 2.490784 |
| C | -2.021881 | 5.600086 | 0.047381 | C | -2.173286 | -3.823634 | 2.341278 |
| C | -1.282599 | 6.564594 | 0.734892 | H | -2.497542 | -3.240491 | 0.293402 |
| C | -0.424480 | 6.180953 | 1.765550 | C | -1.482263 | -3.562063 | 3.525863 |
| C | -0.318857 | 4.830520 | 2.107884 | H | -0.040938 | -2.272582 | 4.486091 |
| C | -1.060898 | 3.873348 | 1.418598 | H | -2.868043 | -4.658168 | 2.288728 |
| H | -6.267305 | -1.938470 | 2.796592 | H | -1.628446 | -4.192269 | 4.398536 |
| H | -6.618323 | -0.018612 | 4.312861 | H | -1.108270 | 0.804249 | 0.901403 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -1.303599 | 0.415784 | -2.144863 | H | 1.777577 | 4.484729 | 0.121097 |
| H | -0.654488 | 2.734233 | -1.192431 | C | 0.981411 | 3.553129 | -3.558397 |
| Pd | 1.099658 | -0.336090 | -0.263789 | H | 1.685908 | 1.582561 | -3.056092 |
| P | 2.452542 | 1.569889 | -0.303305 | C | 0.715611 | 4.842149 | -3.086228 |
| P | 2.463326 | -2.239193 | -0.161066 | H | 0.782390 | 6.160184 | -1.380077 |
| C | 2.581764 | 2.308740 | 1.379106 | H | 0.743357 | 3.286626 | -4.584217 |
| C | 3.576795 | 3.236869 | 1.718139 | H | 0.269900 | 5.581173 | -3.745884 |
| C | 1.683655 | 1.885262 | 2.367965 | C | 3.115155 | -2.534587 | 1.534720 |
| C | 3.666150 | 3.731445 | 3.019179 | C | 3.545797 | -3.791336 | 1.984982 |
| H | 4.287405 | 3.561575 | 0.964245 | C | 3.164330 | -1.448270 | 2.419690 |
| C | 1.781829 | 2.365811 | 3.674364 | C | 4.026426 | -3.950016 | 3.284978 |
| H | 0.914701 | 1.168260 | 2.101201 | H | 3.482471 | -4.651157 | 1.325727 |
| C | 2.774513 | 3.291689 | 4.001576 | C | 3.647452 | -1.604282 | 3.718319 |
| H | 4.439468 | 4.452034 | 3.270235 | H | 2.803306 | -0.480312 | 2.091940 |
| H | 1.082265 | 2.020414 | 4.430530 | C | 4.080694 | -2.857520 | 4.153822 |
| H | 2.855565 | 3.668341 | 5.017387 | H | 4.353257 | -4.929929 | 3.621902 |
| C | 4.233675 | 1.480633 | -0.776403 | H | 3.672243 | -0.748058 | 4.386871 |
| C | 4.779913 | 2.194957 | -1.848935 | H | 4.450888 | -2.986110 | 5.167136 |
| C | 5.061374 | 0.607712 | -0.052083 | C | 3.959182 | -2.228121 | -1.232177 |
| C | 6.123684 | 2.031609 | -2.195821 | C | 3.919297 | -1.424308 | -2.379740 |
| H | 4.159659 | 2.880235 | -2.415994 | C | 5.118784 | -2.962650 | -0.954852 |
| C | 6.400795 | 0.452164 | -0.393186 | C | 5.015223 | -1.357486 | -3.238318 |
| H | 4.653092 | 0.037291 | 0.775541 | H | 3.029798 | -0.831649 | -2.575227 |
| C | 6.935907 | 1.160560 | -1.472155 | C | 6.218975 | -2.889032 | -1.808490 |
| H | 6.532680 | 2.590847 | -3.033102 | H | 5.170312 | -3.579307 | -0.063723 |
| H | 7.020994 | -0.239384 | 0.168891 | C | 6.169174 | -2.087185 | -2.950698 |
| H | 7.978468 | 1.028820 | -1.747569 | H | 4.977043 | -0.717575 | -4.114701 |
| C | 1.831983 | 2.925142 | -1.370734 | H | 7.117836 | -3.455345 | -1.579768 |
| C | 1.574069 | 4.220672 | -0.909488 | H | 7.031025 | -2.023986 | -3.609095 |
| C | 1.523254 | 2.597860 | -2.702503 | C | 1.691528 | -3.853940 | -0.579568 |
| C | 1.008454 | 5.170615 | -1.763166 | C | 1.840050 | -4.415587 | -1.855824 |

| | | | |
|---|---|---|---|
| C | 0.843357 | -4.481516 | 0.346724 |
| C | 1.155454 | -5.582040 | -2.198306 |
| H | 2.495759 | -3.943829 | -2.580855 |
| C | 0.164496 | -5.648720 | 0.001499 |
| H | 0.710806 | -4.060160 | 1.336422 |
| C | 0.316358 | -6.202643 | -1.271081 |
| H | 1.282968 | -6.007777 | -3.189906 |
| H | -0.491153 | -6.115623 | 0.730771 |
| H | -0.214781 | -7.111958 | -1.538698 |

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