# *SUPPLEMENTARY INFORMATION*

# Asymmetric Synthesis of 4,5-Dihydropyrrole Derivatives via DKR: DROC of Activated Aziridines with Enaminones

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## 1. General Information

All the chemicals involved in the synthesis were purchased from Merck, TCI and were used without further purification. Thin layer chromatography (TLC) was carried out for monitoring the progress of the reactions using silica gel 60 F254 precoated plates. TLC spots were visualized using an ultraviolet (UV) lamp or $I_2$ stain. Silica gel (230–400 mesh size) was used for flash column chromatographic purification using a combination of ethyl acetate and petroleum ether as the eluent. Unless otherwise mentioned, all of the reactions were carried out in oven-dried glassware under an inert atmosphere of nitrogen or argon using dry solvents. The purity of the synthesized products was confirmed by melting point, infrared Fourier transform infrared spectroscopy (FT-IR), Proton nuclear magnetic resonance ($^1$H NMR) and ($^{13}$C{$^1$H} NMR) spectroscopy. The melting points were determined in open capillaries in an Optics Technology melting point apparatus and are uncorrected. $^1$H NMR spectra were obtained at frequencies of 400 and 500 MHz. The chemical shifts are reported in parts per million (ppm, δ) with tetramethylsilane serving as the internal standard at δ 0.00. The splitting patterns observed in the $^1$H NMR spectra are noted as singlet *(*s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), *etc.* Proton-decoupled carbon nuclear magnetic resonance ($^{13}$C{$^1$H} NMR) spectra were recorded using frequencies of 100 and 125 MHz. High-resolution mass spectrometry (HRMS) was performed using an electrospray ionization (ESI) time-of-flight (TOF) mass spectrometer. KBr pellets were used for IR spectra of solid compounds. The enantiomeric excess (*ee*) of samples was measured using chiral high-performance liquid chromatography (HPLC) equipped with OJ-H, AS-H, and OD-H columns and an ultraviolet–visible (UV/vis) detector, with a mobile phase of hexane and isopropanol, and detection at 254 nm. Melting points were determined using a hot-stage apparatus and are uncorrected. Optical rotations were measured using a 6 mL cell with a 50 mm path length and are reported as $[\alpha]_D^{25}$ (*c* in g per 100 mL solvent) at 25 °C. The monosubstituted *N*-tosylaziridines and *N*-arylsulfonylaziridines were prepared by following the literature reports.[7] All the reactions were performed in accordance with the established chemical safety protocols. Appropriate personal protective measures were taken. Experimental procedures, including the preparation of aziridines and transition-metal catalysts, were conducted in a well-ventilated fume hood. All the hazardous chemicals were handled with proper care and safety guidelines. No unusual or unexpected hazards were encountered during the experimental work.

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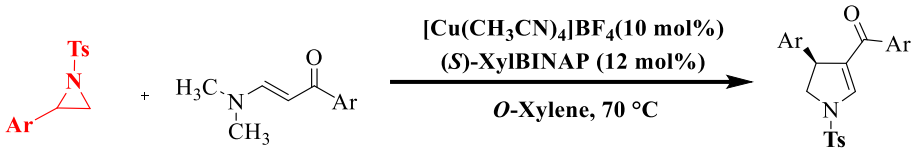
## 2. Experimental Procedures

### General procedure for the synthesis of (*E*)-3-(dimethylamino)-1-Arylprop-2-en-1-one[6]

Under an inert atmosphere, 1,1-dimethoxy-*N,N*-dimethylmethanamine (1.4 equiv.) was added to a solution of acetophenone (1.0 equiv.) in toluene, and the reaction mixture was stirred at 110 °C. Reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was extracted with ethyl acetate, and the combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as the eluent.

### General procedure for the Dynamic Kinetic Resolution of Aziridines




In a double-neck round-bottom flask, $[(CH_3CN)_4Cu]BF_4$ (10 mol%) and (*S*)-XylBINAP (12 mol%) were added under an argon atmosphere. The system was evacuated and refilled with argon five times. Subsequently, 1.0 mL of toluene was introduced, and the mixture was stirred at room temperature for 30 minutes, resulting in a clear solution. This was followed by the sequential addition of the given aziridine (1 equiv), dissolved in 1 mL toluene, and Enaminone (1 equiv), also dissolved in 1 mL toluene. The reaction mixture was stirred at room temperature and gradually heated to 70 °C using an oil bath and the disappearance of aziridine was monitored by TLC, visualized using iodine and UV light. After completion of the reaction, 10 mL of saturated aqueous $NaHCO_3$ solution and 10 mL of EtOAc were added, and the layers were separated. The aqueous layer was further extracted with EtOAc (3 x 10 mL). The organic extracts were dried over anhydrous $Na_2SO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified using flash column chromatography on silica gel (230–400 mesh), eluting with 7% ethyl acetate in petroleum ether. For the preparation of corresponding racemic products for HPLC assay, a similar method was employed using $[(CH_3CN)_4Cu]BF_4$ (15 mol%), 1 equiv of aziridine, and 1 equiv of the respective nucleophiles, all in toluene.

## 3. X-ray Crystallographic Studies

The pure compound **3a** was dissolved in minimum amount of EtOAc to ensure complete dissolution. Then hexane was added dropwise along the sides of the vial and the solvent system was set still and allowed to evaporate slowly leading to the formation of the corresponding crystals. Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite monochromatic Mo $K_\alpha$ radiation ($\lambda_\alpha$ = 0.71073 A). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages[1] and the data were corrected for absorption using the SADABS program.[2] The structures were solved and refined with the SHELX[3] and OLEX2[4] suites of programs, while additional crystallographic calculations were performed by the program PLATON. All hydrogen atoms were included in the final stages of the refinement and were refined with a typical "riding model". Disordered solvent molecules in the unit cell have been masked using Olex-2 mask program. The crystallographic figures have been generated using Diamond 3.1e[5] software. Supplementary crystallographic data including their CCDC numbers (2392388 and 2392389) of the studied compounds can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## X-Ray Crystallographic Structure of 3a.

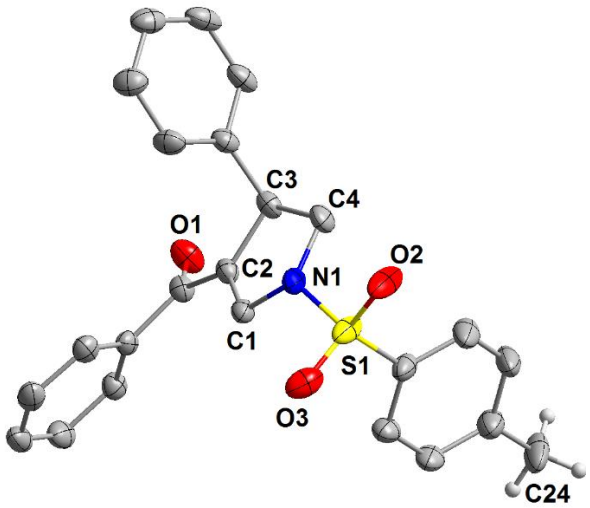



**Figure S1.** X-ray crystallographic structure of **3a** (CCDC 2447031) with important atoms labelled. All the hydrogen atoms are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

| Table 1 Crystal data and structure refinement for 3a. | |
|---|---|
| **Parameters** | **3a** |
| Empirical formula | $C_{24}H_{21}NO_3S$ |
| Formula weight | 403.48 |
| Crystal system | monoclinic |
| Space group | C2 |
| a/Å | 40.9515(11) |
| b/Å | 5.8174(2) |
| c/Å | 19.1046(5) |
| α/° | 90 |
| β/° | 115.7480(10) |
| γ/° | 90 |
| V/Å$^3$ | 4099.4(2) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.307 |
| μ/mm$^{-1}$ | 0.183 |
| F(000) | 1696.0 |
| 2Θ range for data collection/° | 3.876 to 56.608 |
| Index ranges | $-49 \leq h \leq 54$, $-7 \leq k \leq 7$, $-25 \leq l \leq 25$ |
| Reflections collected | 35300 |
| Independent reflections | 10214 [$R_{int}$ = 0.0313, $R_{sigma}$ = 0.0320] |
| Data/restraints/parameters | 10214/1/525 |
| Goodness-of-fit on $F^2$ | 1.041 |
| Final R indexes [I>=2σ (I)][a] | $R_1$ = 0.0442, $wR_2$ = 0.1178 |
| Final R indexes [all data][a] | $R_1$ = 0.0479, $wR_2$ = 0.1211 |
| CCDC No. | 2447031 |
| [a]$R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(\lvert F_o^2\rvert - \lvert F_c^2\rvert)^2 / \Sigma \lvert F_o^2\rvert^2]^{1/2}$ | |

## Supplementary References


1. SAINT+ Software for CCD Diffractometers; Bruker AXS: Madison, WI, 2000.
2. G. M. Sheldrick, SADABS 2.0; University of Göttingen: Göttingen, Germany, 2000.
3. G. M. Sheldrick, SHELXL-2014: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 2014.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339−341.
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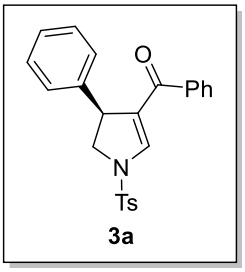
6. (a) R. Li, X. Wang, Z. Wei, C. Wu, F. Shi, *Org. Lett.* 2013, **15**, 4366; (b) Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C, -M. Park, *Chem. Commun.* 2012, **48**, 3133.

7. (a) J. U. Jeong, B. Tao, I. Sagasser, H. Henniges and K. B. Sharpless, *J. Am. Chem. Soc.*, 1998, **120**, 6844–6845. (b) M. Cernerud, H. Adolfsson and C. Moberg, *Tetrahedron: Asymmetry*, 1997, **8**, 2655–2662.

## 4. Analytical and Spectral Data of the Synthesized Compounds

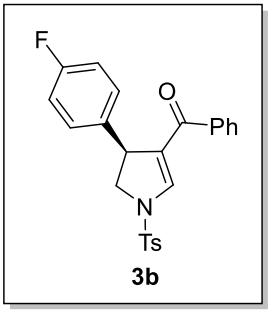
**(*S*)-Phenyl(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3a**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (32 mg, 0.183 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv.) in toluene to afford **3a** (66.25 mg, 0.164 mmol) as a white powder in 90% yield. $R_f$ 0.40 (20% ethyl acetate in petroleum ether) Mp = 148-150 °C; $[\alpha]_D^{25} = -15.189$ (*c* = 0.158 in $CH_2Cl_2$) for 95% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 97:3; flow rate = 1.0 mL/min; $t_R$ 1: 43.30 min (minor), $t_R$ 2: 54.23 min (major): $R_f$ 0.3 (10% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2924.4, 2853.6, 1625.1, 1597.0, 1493.7, 1453.9, 1366.1, 1355.7, 1238.4, 1195.2, 1160.7, 1083.0, 1032.8, 1011.9, 968.2, 885.5, 863.5, 842.4, 813.8, 795.1, 776.3, 759.2, 722.4, 667.8, 625.0, 584.1, 541.1, 494.3; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 1.1 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.08 (dd, *J* = 6.8, 1.5 Hz, 2H), 4.52 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.04 (t, *J* = 11.0 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.1 Hz, 1H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.4, 145.2, 142.8, 142.3, 139.1, 133.2, 132.1, 130.4, 128.9, 128.6, 128.4, 127.6, 127.3, 127.1, 126.8, 56.8, 47.1, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}NO_3S$ 404.1315; Found 404.1313.

**(*S*)-(4-(4-Fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**

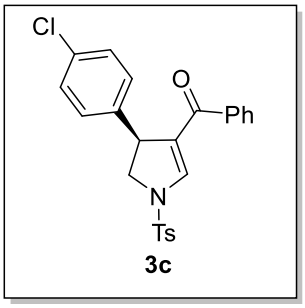


**3b**

Following the general method described above, **1b** (50 mg, 0.172 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (30 mg, 0.172 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.38 mg, 0.017 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (15.13 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3b** (57.87 mg, 0.137 mmol) as a white powder in 80% yield. $R_f$ 0.39 (20% ethyl acetate in petroleum ether) Mp = 156-158 °C; $[\alpha]_D^{25} = -32.192$ (*c* = 0.125 in $CH_2Cl_2$) for 80.06% *ee* sample. Optical

purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10 ; flow rate = 1.0 mL/min; $t_R$ 1: 29.21 min(major), $t_R$ 2: 64.89 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1624.1, 1589.3, 1575.8, 1508.3, 1462.0, 1444.7, 1367.5, 1357.9, 1238.3, 1220.9, 1184.3, 1157.3, 1085.9, 1033.8, 1012.6, 904.6, 869.9, 837.1, 815.9, 748.4, 711.4, 704.5, 663.5, 621.1, 611.4, 586.4, 540.1, 449.4, 426.4, 407.0; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.57 – 7.50 (m, 1H, 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 1.1 Hz, 1H), 7.03 (dd, *J* = 8.7, 5.3 Hz, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 4.49 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.01 (t, *J* = 11.0 Hz, 1H), 3.72 (dd, *J* = 10.8, 4.9 Hz, 1H), 2.47 (s, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 190.4, 161.94 (d, *J* = 245.8 Hz), 145.5, 143.0, 139.1, 138.2, 133.3, 132.3, 130.5, 128.8, 128.6 (d, *J* = 8.0 Hz) 128.5, 127.7, 126.7, 115.65 (d, *J* = 21.5 Hz), 56.9, 46.5, 21.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FNO_3S$ 422.1221; Found 422.1231.

**(*S*)-(4-(4-Chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**

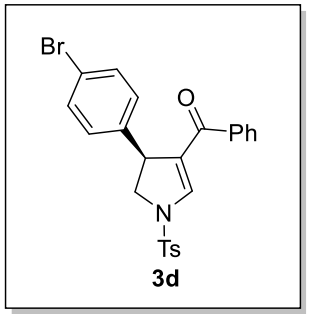


**3c**

Following the general method described above, **1c** (50 mg, 0.163 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (29 mg, 0.163 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.1 mg, 0.016 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (14.37 mg, 0.020 mmol, 0.12 equiv.) in toluene to afford **3c** (55.52 mg, 0.127 mmol) as a white powder in 78% yield. $R_f$ 0.41 (20% ethyl acetate in petroleum ether); Mp = 150-152 °C; $[\alpha]_D^{25}$= −12.855 (*c* = 0.198 in $CH_2Cl_2$) for 95.42% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 29.96 min(major), $t_R$ 2: 48.64 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1622.1, 1591.3, 1573.9, 1492.9, 1464.0, 1444.7, 1411.9, 1367.5, 1238.3, 1205.5, 1184.3, 1157.3, 1085.9, 1033.8, 1014.6, 962.5, 904.6, 869.9, 839.0, 817.8, 794.7, 779.2, 738.7, 727.2, 717.5, 704.0, 669.3, 657.7, 634.6, 619.1, 611.4, 584.4, 538.1, 516.9; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 1.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.47 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.02 (t, *J* = 11.0 Hz, 1H), 3.71 (dd, *J* = 10.8, 4.9 Hz, 1H), 2.47 (s, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 190.3, 145.4, 143.1, 140.8, 138.9, 133.2, 133.1, 132.2, 130.4, 129.0,

128.7, 128.4, 128.4, 127.6, 126.3, 56.6, 46.6, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClNO_3S$ 438.0925; Found 438.0939.

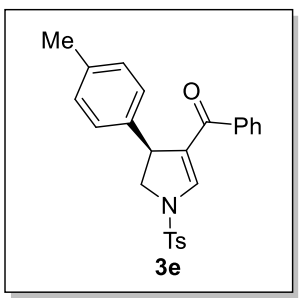
**(*S*)-(4-(4-Bromophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**



**3d**

Following the general method described above, **1d** (50 mg, 0.142 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (25 mg, 0.142 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (4.46 mg, 0.014 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (12.5 mg, 0.017 mmol, 0.12 equiv.) in toluene to afford **3d** (56.19 mg, 0.117 mmol) as a white powder in 82% yield. $R_f$ 0.42 (20% ethyl acetate in petroleum ether); Mp = 156-158 °C; $[\alpha]_D^{25}$= −20.285 (*c* = 0.154 in $CH_2Cl_2$) for 87.64% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 27.30 min(major), $t_R$ 2: 56.22 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7 1622.1, 1591.3, 1573.9, 1489.0, 1462.0, 1444.7, 1408.0, 1367.5, 1238.3, 1205.5, 1184.3, 1157.3, 1085.9, 1035.8, 1012.6, 962.5, 902.7, 868.0, 840.0, 815.9, 773.5, 725.2, 715.6, 704.0, 671.2, 611.4, 584.4, 536.2; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (s, 1H), 7.31 (d, *J* = 1.3 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.46 (dd, *J* = 11.1, 4.7 Hz, 1H), 4.02 (t, *J* = 11.0 Hz, 1H), 3.71 (dd, *J* = 10.8, 4.9 Hz, 1H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 190.3, 145.4, 143.1, 141.4, 138.9, 133.2, 132.2, 132.0, 130.4, 128.8, 128.7, 128.4, 127.6, 126.3, 121.2, 56.5, 46.6, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrNO_3S$ 482.0420; Found 482.0437.

**(*S*)-Phenyl(4-(*p*-tolyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**

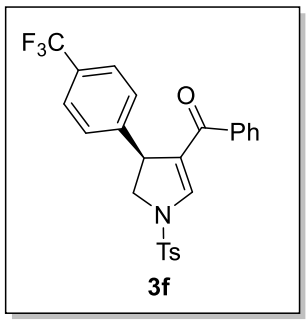


**3e**

Following the general method described above, **1e** (50 mg, 0.174 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (31 mg, 0.174 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.5 mg, 0.017 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (15.34 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3e** (68.28 mg, 0.164 mmol) as a white powder in 94% yield. $R_f$

0.42 (20% ethyl acetate in petroleum ether) Mp = 155-157 °C; $[\alpha]_D^{25}$= −15.504 (*c* = 0.121 in $CH_2Cl_2$) for 75.82% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 25.69 min(major), $t_R$ 2: 42.76 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2960.7, 2862.4, 1629.8, 1600.9, 1575.8, 1491.0, 1446.6, 1398.4, 1356.0, 1340.5, 1305.1, 1244.1, 1186.2, 1155.4, 1087.8, 1035.8, 1022.3, 1014.6, 9645.4, 887.3, 867.3, 842.9, 814.0, 790.8, 763.8, 754.2, 732.9, 711.7, 692.4, 665.4, 607.6, 586.4, 561.3, 542.0, 516.9; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 1.1 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.48 (dd, *J* = 11.4, 5.4 Hz, 1H), 4.01 (t, *J* = 10.9 Hz, 1H), 3.73 (dd, *J* = 10.7, 5.2 Hz, 1H), 2.47 (s, 3H), 2.25 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 190.4, 145.1, 142.6, 139.3, 139.1, 136.8, 133.2, 132.0, 130.3, 129.5, 128.6, 128.4, 127.6, 126.9, 56.8, 46.8, 21.7, 21.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}NO_3S$ 418.1471; Found 418.1483.

**(*S*)-Phenyl(1-tosyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrol-3-yl)methanone**

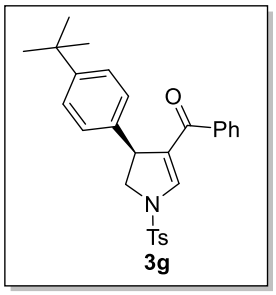


**3f**

Following the general method described above, **1f** (50 mg, 0.142 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (25 mg, 0.142 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (4.5 mg, 0.014 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (12.5 mg, 0.017 mmol, 0.12 equiv.) in toluene to afford **3f** (63.53 mg, 0.135 mmol) as a white powder in 92% yield. $R_f$ 0.40 (20% ethyl acetate in petroleum ether); Mp = 148-150 °C; $[\alpha]_D^{25}$= −29.634 (*c* = 0.115 in $CH_2Cl_2$) for 90.48% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 18.52 min(major), $t_R$ 2: 39.83 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1624.1, 1597.1, 1575.8, 1419.6, 1357.9, 1325.1, 1238.3, 1159.2, 1111.0, 1087.8, 1068.6, 1033.8, 1014.6, 900.8, 837.1, 814.0, 746.4, 719.4, 704.0, 671.2, 611.43, 582.5, 543.9, 503.4; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 0.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz ,2H), 4.57 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.07 (t, *J* = 11.0 Hz, 1H), 3.75 (dd, *J* = 10.9, 4.9 Hz, 1H), 2.49 (s, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 190.2, 146.3, 144.4 (q, *J* = 265.3 Hz), 138.9, 133.2, 132.3, 130.5, 129.4 (q, *J* = 45.8 Hz), 128.8, 128.4, 127.6, 127.5, 125.6 (q, *J* = 28.8 Hz),

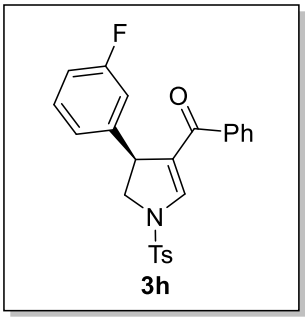
56.5, 47.0, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}F_3NO_3S$ 472.1189; Found 472.1190.

**(*S*)-(4-(4-(Tert-butyl)phenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**




Following the general method described above, **1g** (50 mg, 0.152 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (27 mg, 0.152 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (4.76 mg, 0.015 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (13.39 mg, 0.018 mmol, 0.12 equiv.) in toluene to afford **3g** (64.87 mg, 0.141 mmol) as a white powder in 93% yield. $R_f$ 0.43 (20% ethyl acetate in petroleum ether) Mp = 132-134°C; $[\alpha]_D^{25} = -16.08$ (*c* = 0.173 in $CH_2Cl_2$) for 75.28% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1:19.65 min(major), $t_R$ 2: 39.66 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2960.7, 2862.4, 1629.8, 1600.9, 1577.8, 1508.3, 1458.2, 1446.6, 1361.7, 1236.4, 1159.2, 1012.6, 966.3, 829.4, 794.7, 721.4, 696.3, 682.8, 667.4, 588.3, 576.7, 555.5, 543.9, 486.1; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 6.9 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 4.50 (dd, *J* = 11.1, 4.9 Hz, 1H), 4.01 (t, *J* = 10.9 Hz, 1H), 3.77 (dd, *J* = 10.7, 5.1 Hz, 1H), 2.48 (s, 3H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 190.5, 150.1, 145.2, 142.7, 139.1, 133.3, 132.1, 130.4, 128.6, 128.5, 127.6, 126.7, 125.7, 56.9, 46.6, 31.4, 21.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{29}NO_3S$ 460.1941; Found 460.1931

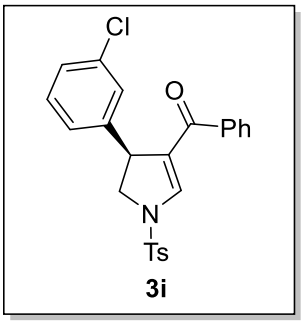
**(*S*)-(4-(3-Fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**



**3h**

Following the general method described above, **1h** (50 mg, 0.172 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (30 mg, 0.172 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.38 mg, 0.017 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (15.13 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3h** (57.14 mg, 0.135 mmol) as a white powder in 79% yield. $R_f$ 0.38 (20% ethyl acetate in petroleum ether); Mp = 100-102 °C; $[\alpha]_D^{25} = -11.729$ (*c* = 0.185 in $CH_2Cl_2$) for 87.14% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 24.24 min(major), $t_R$ 2: 73.16 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2924.1, 2854.6, 1626.0, 1597.1, 1573.9, 1446.6, 1354.0, 1236.4, 1159.2, 1085.9, 1033.8, 1014.6, 950.9, 864.1, 844.8, 812.0, 788.9, 725.2, 693.3, 663.5, 597.9, 570.9, 542.0; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 1.0 Hz, 1H), 7.13 (dd, *J* = 3.9, 1.3 Hz, 2H), 7.02 – 6.97 (m, 1H), 6.92 (dd, *J* = 2.4, 1.6 Hz 1H), 4.47 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.06 (t, *J* = 11.1 Hz, 1H), 3.69 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 190.2, 144.9 (d, *J* = 241.8 Hz), 143.3, 138.9, 134.7, 133.1, 132.2, 130.5, 130.1, 128.5 (d, *J* = 44.9 Hz), 127.5 (d, *J* = 4.3 Hz), 127.0, 126.0, 125.6, 56.6, 46.8, 21.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FNO_3S$ 422.1221; Found 422.1231.

**(*S*)-(4-(3-Chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**

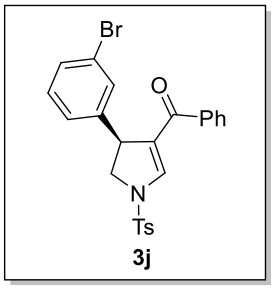


**3i**

Following the general method described above, **1i** (50 mg, 0.163 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (29 mg, 0.163 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (5.1 mg, 0.016 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (14.37 mg, 0.020 mmol, 0.12 equiv.) in toluene to afford **3i** (58.36 mg, 0.134 mmol) as a white powder in 82% yield. $R_f$ 0.40 (20% ethyl acetate in petroleum ether); Mp = 160-162 °C; $[\alpha]_D^{25} = -24.481$ (*c* = 0.137 in $CH_2Cl_2$) for 79.74% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 28.512 min(major), $t_R$ 2: 76.20 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2922.2, 2852.7, 1653.0, 1597.1, 1485.2, 1446.6, 1354.0, 1236.4, 1180.4, 1161.1, 1085.9 1012.6, 987.5, 952.8, 902.7,

883.4, 858.3, 841.0, 814.0, 783.1, 740.7, 715.6, 707.9, 694.4, 665.4, 619.1, 576.7, 542.0, 520.8; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.62 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 1.0 Hz, 1H), 7.18 (td, *J* = 8.0, 6.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.86 (td, *J* = 8.8, 2.9 Hz, 1H), 6.64 – 6.57 (m, 1H), 4.51 (dd, *J* = 11.1, 4.9 Hz, 1H), 4.07 (t, *J* = 11.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.48 (s, 3H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 190.3, 164.1, 162.1, 145.6, 144.9, 143.2, 138.97, 133.1, 132.2, 130.5, 130.4, 130.3, 128.7, 128.4, 127.6, 126.1, 123.0, 114.4, 114.2, 113.9, 113.7, 56.6, 46.8, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClNO_3S$ 438.0925; Found 438.0925.

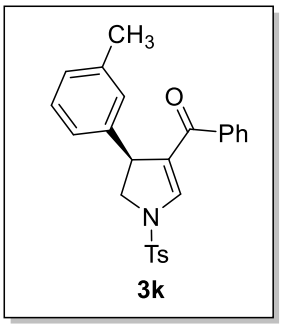
**(*S*)-(4-(3-Bromophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**



**3j**

Following the general method described above, **1j** (50 mg, 0.142 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (25 mg, 0.142 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (4.46 mg, 0.014 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (12.5 mg, 0.017 mmol, 0.12 equiv.) in toluene to afford **3j** (58.24 mg, 0.121 mmol) as a white powder in 85% yield. $R_f$ 0.42 (20% ethyl acetate in petroleum ether); Mp = 180-182 °C; $[\alpha]_D^{25} = -15.278$ (*c* = 0.147 in $CH_2Cl_2$) for 89.60% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 36.50 min(major), $t_R$ 2: 84.60 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1685.8, 1627.9, 1597.1, 1577.8, 1431.2, 1363.7, 1356.0, 1236.4, 1159.2, 1120.6, 1085.9, 1033.8, 1014.6, 972.1, 949.0, 866.0, 846.7, 792.7, 725.2, 705.9, 696.3, 680.9, 669.3, 656.7, 628.8, 609.5, 594.1, 569.0, 543.9, 511.2; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.62 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 1.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.12 (t, *J* = 1.7 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.05 (dt, *J* = 7.7, 1.4 Hz, 1H), 4.48 (dd, *J* = 11.2, 5.0 Hz, 1H), 4.06 (t, *J* = 11.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.48 (s, 3H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ 190.2, 145.5, 144.7, 143.3, 138.95, 133.1, 132.2, 130.5, 130.4, 130.0, 128.7, 128.4, 127.5, 126.0, 126.0, 123.0, 56.6, 46.8, 21.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrNO_3S$ 482.0420; Found 482.0420.

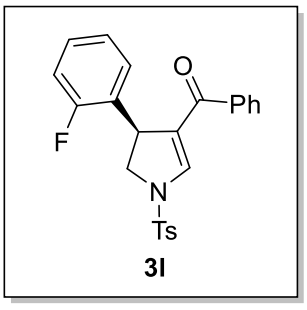
**(*S*)-Phenyl(4-(*m*-tolyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3k**

Following the general method described above, **1k** (50 mg, 0.174 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (31 mg, 0.174 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.5 mg, 0.017 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (15.34 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3k** (58.11 mg, 0.139 mmol) as a white powder in 80% yield. $R_f$ 0.42 (20% ethyl acetate in petroleum ether); Mp = 102-104 °C; $[\alpha]_D^{25}$= −21.879 (*c* = 0.133 in $CH_2Cl_2$) for 68.92% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1:14.20 min(major), $t_R$ 2:20.18 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2918.1, 2891.3, 1629.8, 1599.0, 1575.8, 1491.0, 1446.6, 1398.4, 1356.0, 1340.5, 1236.4, 1193.9, 1186.2, 1166.9, 1153.4, 1087.8, 1037.7, 1024.2, 1012.6, 968.3, 954.8, 923.9, 887.3, 869.9, 860.2, 841.0, 808.2, 796.6, 742.6, 717.5, 700.2, 669.3, 609.5, 596.0, 569.0, 542.0, 526.6; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.54 (t, *J* = 7.4, Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 1.0 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.48 (dd, *J* = 11.2, 5.1 Hz, 1H), 4.04 (t, *J* = 11.0 Hz, 1H), 3.75 (dd, *J* = 10.8, 5.2 Hz, 1H), 2.48 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 190.4, 145.2, 142.8, 142.38, 139.18, 138.48, 133.38, 132.1, 130.4, 128.7, 128.6, 128.4, 128.1, 127.8, 127.6, 126.8, 124.1, 56.9, 47.1, 21.8, 21.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}NO_3S$ 418.1471; Found 418.1476

**(*S*)-(4-(2-Fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**

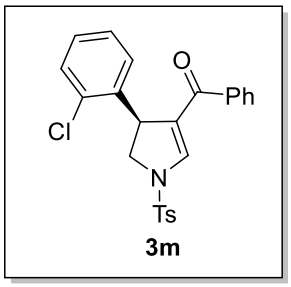


**3l**

Following the general method described above, **1l** (50 mg, 0.172 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (30 mg, 0.172 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (5.38 mg, 0.017 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (15.13 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3l** (64.38 mg, 0.153 mmol) as a white powder in 89% yield. $R_f$ 0.38 (20% ethyl acetate in petroleum ether); Mp = 142-144 °C; $[\alpha]_D^{25}$= −33.327 (*c* = 0.110 in $CH_2Cl_2$) for 91.92% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1:29.24 min(major), $t_R$ 2:53.70 min (minor). IR $\nu_{max}$ (KBr, $cm^{-1}$) 2920.2, 2891.3, 1633.7, 1602.8, 1494.8, 1365.6,

1247.9, 1228.7, 1199.7, 1186.2, 1155.4, 1087.8, 1035.8, 1022.3, 966.3, 894.97, 841.0, 814.0, 790.8, 761.9, 711.7, 692.4, 661.6, 615.3, 603.7, 586.4, 561.3, 542.0, 515.0, 499.6; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.21 – 7.12 (m, 1H), 7.02 – 6.95 (m, 3H), 4.81 (dd, *J* = 11.4, 5.8 Hz, 1H), 4.08 (t, *J* = 11.1 Hz, 1H), 3.71 (dd, *J* = 10.5, 5.8 Hz, 1H), 2.47 (s, 3H). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 190.3, δ 160.59 (d, *J* = 246.8 Hz), 145.2, 143.93, 139.1, 133.4, 132.2, 130.4, 129.0, 128.9, 128.8, 128.7, 128.51 (d, *J* = 3.8 Hz), 128.4, 127.5, 124.5, 124.5, 124.4, 115.80 (d, *J* = 21.8 Hz), 55.7, 40.9, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FNO_3S$ 422.1221; Found 422.1228.

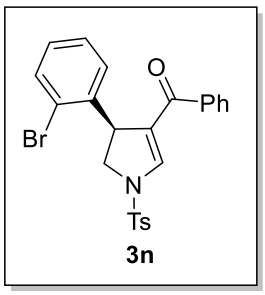
**(*S*)-(4-(2-Chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**



**3m**

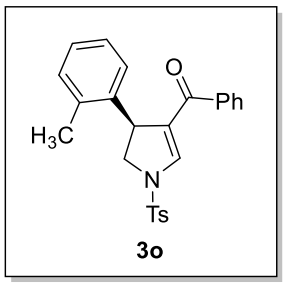
Following the general method described above, **1m** (50 mg, 0.163 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (29 mg, 0.163 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.1 mg, 0.016 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (14.37 mg, 0.020 mmol, 0.12 equiv.) in toluene to afford **3m** (68.32 mg, 0.156 mmol) as a white powder in 96% yield. $R_f$ 0.40 (20% ethyl acetate in petroleum ether); Mp = 172-174 °C; $[\alpha]_D^{25}$= −11.841 (*c* = 0.151 in $CH_2Cl_2$) for 91.14% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 24.84 min(major), $t_R$ 2: 58.10 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$) 2918.1, 2891.3, 1629.8, 1600.9, 1438.9, 1365.6, 1354.0, 1242.2, 1155.4, 1085.9, 1033.8, 1020.3, 842.9, 815.9, 754.2, 725.2, 702.1, 588.3, 553.6, 540.1, 489.9; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 (s, 1H), 7.39 – 7.31 (m, 3H), 7.15-7.09 (m, 2H), 6.94 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.97 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.12 (t, *J* = 11.1 Hz, 1H), 3.66 (dd, *J* = 10.7, 5.7 Hz, 1H), 2.46 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ 190.2, 145.3, 144.6, 139.2, 139.0, 133.5, 133.4, 132.2, 130.4, 130.0, 128.8, 128.5, 128.4, 127.9, 127.5, 127.3, 124.4, 55.7, 44.4, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClNO_3S$ 438.0925; Found 438.0910.

**(*S*)-(4-(2-Bromophenyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(phenyl)methanone**




Following the general method described above, **1n** (50 mg, 0.142 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (25 mg, 0.142 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (4.46 mg, 0.014 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (12.5 mg, 0.017 mmol, 0.12 equiv.) in toluene to afford **3n** (51.39 mg, 0.107 mmol) as a white powder in 75% yield. $R_f$ 0.42 (20% ethyl acetate in petroleum ether); Mp = 162-164 °C; $[\alpha]_D^{25} = -31.438$ (*c* = 0.114 in $CH_2Cl_2$) for 96.84% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10 ; flow rate = 1.0 mL/min; $t_R$ 1: 26.05 min(major), $t_R$ 2: 60.64 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1627.9, 1599.0, 1469.8, 1365.6, 1352.1, 1240.2, 1157.3, 1118.7, 1085.9, 1031.9, 1020.3, 1010.7, 896.9, 864.1, 842.9, 810.1, 754.2, 702.1, 659.7, 603.7, 586.36, 553.6, 540.1, 488.0; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H ), 7.62 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 1.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.12 (t, *J* = 1.7 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.05 (dt, *J* = 7.7, 1.4 Hz, 1H), 4.48 (dd, *J* = 11.2, 5.0 Hz, 1H), 4.06 (t, *J* = 11.1 Hz, 1H), 3.71 (dd, *J* = 10.9, 5.0 Hz, 1H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 190.1, 145.3, 144.7, 141.0, 139.0, 133.4, 133.3, 132.2, 130.4, 128.8, 128.8, 128.4, 127.9, 127.5, 124.6, 124.1, 55.9, 46.7, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrNO_3S$ 482.0420; Found 482.0411.

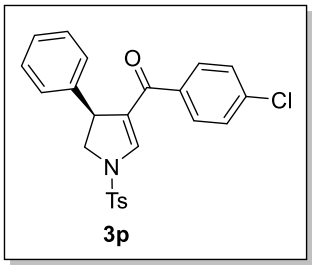
**(*S*)-Phenyl(4-(o-tolyl)-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**




Following the general method described above, **1o** (50 mg, 0.174 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **2a** (31 mg, 0.174 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (5.5 mg, 0.017 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (15.34 mg, 0.021 mmol, 0.12 equiv.) in toluene to afford **3o** (58 mg, 0.139 mmol) as a white powder in 95% yield. $R_f$ 0.41 (20% ethyl acetate in petroleum ether); Mp = 140-142 °C; $[\alpha]_D^{25} = -20.186$ (*c* = 0.129 in $CH_2Cl_2$) for 80.04% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 17.86 min(major), $t_R$ 2: 48.56 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1631.8, 1604.8, 1492.9, 1464.0, 1444.7, 1359.8, 1348.2, 1244.1, 1186.2, 1155.4, 1087.8, 1035.8, 1022.3, 1014.6, 9645.4, 887.3, 867.3, 842.9, 814.0, 790.8, 763.8, 754.2, 732.9, 711.73, 692.4, 665.4, 607.6, 586.4, 561.3, 542.0, 516.9, 476.4; $^1$H

NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 1.1 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 4.77 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.08 (t, *J* = 10.9 Hz, 1H), 3.63 (dd, *J* = 10.6, 5.6 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.4, 145.2, 143.2, 140.7, 139.1, 135.6, 133.3, 132.1, 130.6, 130.4, 128.7, 128.4, 127.6, 127.1, 126.8, 126.7, 125.8, 56.5, 43.0, 21.8, 19.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}NO_3S$ 418.1471; Found 418.1460.

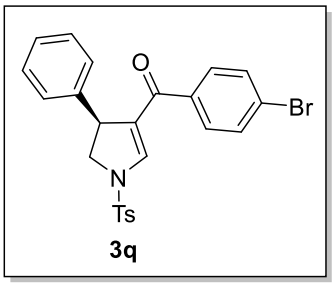
**(*S*)-(4-Chlorophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3p**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-1-(3-chlorophenyl)-3-(dimethylamino)prop-2-en-1-one **2b** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3p** (60.78 mg, 0.139 mmol) as a white powder in 76% yield. $R_f$ 0.40 (20% ethyl acetate in petroleum ether) Mp = 125-127 °C; $[\alpha]_D^{25} = -24.793$ (*c* = 0.121 in $CH_2Cl_2$) for 76.98% *ee* sample. Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10 flow rate = 1.0 mL/min; $t_R$ 1: 28.387 (major), $t_R$ 2: 56.511 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2957.1, 2918.5, 2851.2, 1624.6, 1595.1, 1493.0, 1454.7, 1360.5, 1240.2, 1161.4, 1090.5, 1032.1, 1011.3, 839.7, 814.9, 752.4, 702.7, 665.8, 584.8, 544.0, 523.3; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 14.5, 8.3 Hz, 4H), 7.28 (d, *J* = 0.7 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.07 (d, *J* = 6.6 Hz, 2H), 4.50 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.04 (t, *J* = 11.0 Hz, 1H), 3.78 (dd, *J* = 10.8, 5.1 Hz, 1H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.1, 145.4, 142.9, 142.1, 138.4, 137.3, 133.2, 130.4, 129.8, 129.0, 128.9, 127.6, 127.4, 127.3, 127.2, 127.0, 126.5, 56.8, 47.1, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClNO_3S$ 438.0925; Found 438.0923.

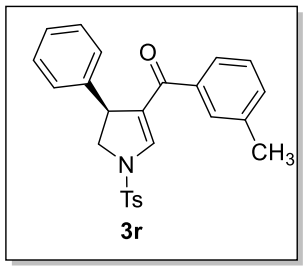
**(*S*)-(4-Bromophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3q**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv.) was reacted with (*E*)-1-(3-bromophenyl)-3-(dimethylamino)prop-2-en-1-one **2c** (33.5 mg, 0.183 mmol, 1.0 equiv.) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3q** (80.98 mg, 0.168 mmol) as a white powder in 92% yield. $R_f$ 0.41 (20% ethyl acetate in petroleum ether) Mp = 120-122 °C; $[\alpha]_D^{25} = -19.117$ (*c* = 0.136 in $CH_2Cl_2$) for 82.90% *ee* sample Optical purity was determined by chiral HPLC analysis (AS-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 31.717 (major), $t_R$ 2: 66.066 min (minor). IR $\nu_{max}$ (KBr, $cm^{-1}$): 3090.2, 2922.5, 2853.3, 1618.5, 1593.4, 1492.6, 1454.5, 1396.8, 1359.6, 1240.8, 1178.9, 1161.7, 1086.4, 1070.5, 1030.3, 1022.2, 1009.9, 968.0, 845.7, 835.4, 812.5, 752.9, 700.3, 665.7, 584.1, 542.0, 520.7, 491.9; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 0.5 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.07 (d, *J* = 6.6 Hz, 2H), 4.50 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.04 (t, *J* = 11.0 Hz, 1H), 3.78 (dd, *J* = 10.8, 5.1 Hz, 1H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 189.2, 145.4, 143.0, 142.1, 137.8, 133.2, 131.9, 130.4, 129.9, 128.9, 127.6, 127.4, 127.0, 126.9, 126.4, 56.8, 47.1, 21.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrNO_3S$ 482.0420; Found 482.0415.

**(*S*)-(4-Phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(*m*-tolyl)methanone**

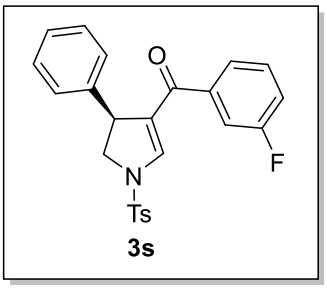


**3r**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-3-(dimethylamino)-1-(*m*-tolyl)prop-2-en-1-one **2d** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3r** (53.43 mg, 0.128 mmol) as a white powder in 70% yield. $R_f$ 0.42 (20% ethyl acetate in petroleum ether) Mp = 100-102 °C; $[\alpha]_D^{25} = -11.819$ (*c* = 0.166 in $CH_2Cl_2$) for 88.22% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 95:5; flow rate = 1.0 mL/min; $t_R$ 1: 20.218 (major), $t_R$ 2: 23.225 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2852.7, 1629.8, 1595.1, 1492.9, 1454.3, 1359.82, 1246.0, 1161.1, 1087.8, 1031.9, 889.2, 864.1, 812.0, 773.5, 738.7, 700.2, 665.4, 584.4, 543.9, 445.6; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.34 (d, *J* = 1.9 Hz, 2H), 7.29

(d, *J* = 1.1 Hz, 1H), 7.23 – 7.14 (m, 3H), 7.07 (dd, *J* = 8.0, 1.3 Hz, 2H), 4.51 (dd, *J* = 10.6, 5.1 Hz, 1H), 4.03 (t, *J* = 11.0 Hz, 1H), 3.76 (dd, *J* = 10.7, 5.1 Hz, 1H), 2.48 (s, 3H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 190.6, 145.2, 142.8, 142.3, 139.1, 138.5, 133.3, 132.9, 130.4, 129.0, 128.9, 128.5, 127.6, 127.3, 127.1, 126.9, 125.6, 56.9, 47.1, 21.8, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}NO_3S$ 418.1471; Found 418.1487.

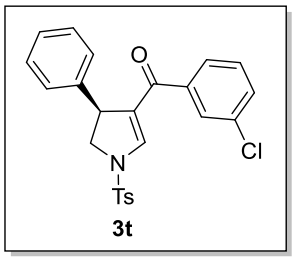
**(*S*)-(3-Fluorophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3s**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-3-(dimethylamino)-1-(3-fluorophenyl)prop-2-en-1-one **2e** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3s** (65.5 mg, 0.155 mmol) as a white powder in 85% yield. $R_f$ 0.37 (20% ethyl acetate in petroleum ether) Mp = 138-140 °C; $[\alpha]_D^{25} = -16.375$ (*c* = 0.197 in $CH_2Cl_2$) for 83.12% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 95:5; flow rate = 1.0 mL/min; $t_R$ 1: 30.639 (major), $t_R$ 2: 35.640 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2920.2, 2850.7, 1626.0, 1597.1, 1581.6, 1494.8, 1442.7, 1356.0, 1247.9, 1178.5, 1159.2, 1124.5, 1084.0, 1031.9, 962.5, 887.3, 808.2, 759.9, 746.4, 702.1, 665.4, 621.1, 588.3, 538.1, 447.5; $^1H$ NMR; (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 5.1 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.31 (d, *J* = 1.0 Hz, 1H), 7.28 (d, *J* = 9.4 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.05 (dd, *J* = 7.9, 1.5 Hz, 2H), 4.50 (dd, *J* = 11.0, 4.9 Hz, 1H), 4.06 (t, *J* = 11.0 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.2 Hz, 1H), 2.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 188.9, 163.79, 161.79, 145.49, 143.3, 142.19, 141.2, 133.29, 130.5 128.9, 127.6, 127.4, 127.0, 126.4, 124.1, 124.1, 119.1, 119.0, 115.4, 115.3, 56.9, 47.1, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FNO_3S$ 422.1221; Found 422.1241.

**(*S*)-(3-Chlorophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**

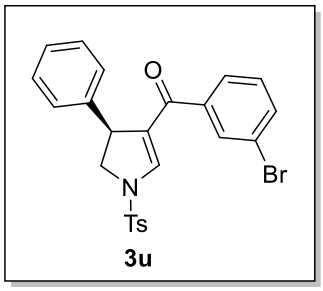


**3t**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-1-(3-chlorophenyl)-3-(dimethylamino)prop-2-en-1-one **2f** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3t** (50.38 mg, 0.115 mmol) as a white powder in 63% yield. $R_f$ 0.40 (20%

ethyl acetate in petroleum ether) Mp = 116-118 °C; $[\alpha]_D^{25}$= −13.933 (*c* = 0.151 in $CH_2Cl_2$) for 85.24% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 95:5; flow rate = 1.0 mL/min; $t_R$ 1: 29.143 (major), $t_R$ 2: 36.835 min (minor). IR $\nu_{max}$ (KBr, $cm^{-1}$) 2922.2, 2852.7, 1626.0, 1597.1, 1568.1 1492.9, 1454.3, 1417.7, 1365.6, 1305.8, 1236.4, 1159.2, 1087.8, 1014.6, 895.0, 868.0, 812.0, 779.2, 759.9, 748.4, 721.4, 700.2, 667.4, 586.4, 542.0, 445.6; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 3H), 7.29 (s, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 6.6 Hz, 2H), 4.49 (dd, *J* = 11.1, 5.1 Hz, 1H), 4.06 (t, *J* = 11.0 Hz, 1H), 3.75 (dd, *J* = 10.8, 5.2 Hz, 1H), 2.50 (s, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): δ 188.7, 145.4, 143.5, 142.1, 141.0, 134.9, 133.2, 131.4, 130.5, 130.3, 130.0, 129.9, 129.2, 129.1, 128.9, 127.8, 127.6, 127.4, 127.3, 127.2, 127.06, 126.9, 126.5, 122.8, 57.0, 47.1, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClNO_3S$ 438.0925; Found 438.0926.

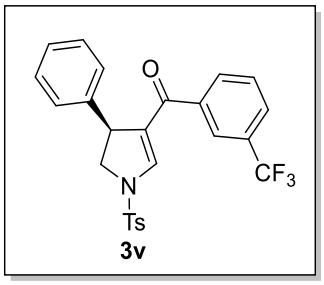
**(*S*)-(3-Bromophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3u**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-1-(3-bromophenyl)-3-(dimethylamino)prop-2-en-1-one **2g** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3u** (61.62 mg, 0.128 mmol) as a white powder in 70% yield. $R_f$ 0.37 (20% ethyl acetate in petroleum ether) Mp = 106-108 °C; $[\alpha]_D^{25}$= −13.227 (*c* = 0.132 in $CH_2Cl_2$) for 86.38% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 95:5; flow rate = 1.0 mL/min; $t_R$ 1: 23.034 (major), $t_R$ 2: 28.798 min (minor); $R_f$ 0.38 (20% ethyl acetate in petroleum ether); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2924.1, 2854.8, 1629.8, 1593.2, 1566.2, 1492.9, 1454.3, 1417.7, 1361.7, 1232.5, 1159.2, 1089.8, 1031.9, 896.9, 864.1, 812.0, 744.5, 719.4, 698.2, 665.4, 584.4, 545.8, 445.6; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.70 (t, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 1.1 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.03 (dd, *J* = 7.9, 1.6 Hz, 2H), 4.49 (dd, *J* = 10.9, 4.9 Hz, 1H), 4.06 (t, *J* = 11.0 Hz, 1H), 3.75 (dd, *J* = 10.8, 5.2 Hz, 1H), 2.50 (s, 3H). $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): δ 188.7, 145.4, 143.5, 142.1, 141.0, 134.9, 133.2, 131.4, 130.5, 130.3, 128.9, 127.6, 127.4, 127.3, 127.2, 127.1, 126.9, 126.5, 122.8, 57.0, 47.1, 21.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrNO_3S$ 482.0420; Found 482.0415.

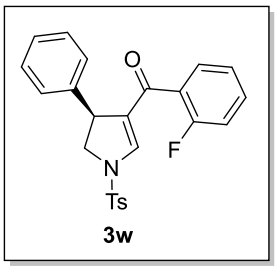
**(*S*)-(4-Phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)(3-(trifluoromethyl)phenyl)methanone**



**3v**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv.) was reacted with (*E*)-3-(dimethylamino)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one **2h** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv.) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv.) in toluene to afford **3v** (73.28 mg, 0.115 mmol) as a white powder in 85% yield. $R_f$ 0.36 (20% ethyl acetate in petroleum ether); Mp = 145-147 °C; $[\alpha]_D^{25}$= −12.917 (*c* = 0.181 in $CH_2Cl_2$) for 75.38% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 16.749 (major), $t_R$ 2: 21.391 min (minor); IR $\nu_{max}$ (KBr, $cm^{-1}$): 2922.2, 2850.8, 1635.6, 1599.0, 1494.8, 1454.3, 1365.6, 1323.2, 12593.5, 1234.4, 1159.2, 1118.7, 1085.9, 1072.4, 1024.2, 1014.6, 960.5, 900.8, , 866.0, 814.0, 771.5, 758.0, 746.4, 698.2, 669.3, 592.1, 538.1; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 3H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 1.0 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.03 (dd, *J* = 7.8, 1.6 Hz, 2H), 4.51 (dd, *J* = 10.9, 5.1 Hz, 1H), 4.09 (t, *J* = 11.0 Hz, 1H), 3.76 (dd, *J* = 10.8, 5.3 Hz, 1H), 2.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.9, 145.5, 143.7, 140.8 (q, *J* = 226.2 Hz), 133.0, 131.5, 130.5, 130.0, 129.4 (q, 65.8 Hz), 128.9, 128.6, 128.5, 127.8, 127.5 (q, 14.5 Hz), 126.4, 125.1 (q, J = 4.2 Hz), 56.97, 47.1, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}F_3NO_3S$ 472.1189; Found 472.1188.

**(*S*)-(2-Fluorophenyl)(4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)methanone**



**3w**

Following the general method described above, **1a** (50 mg, 0.183 mmol, 1.0 equiv) was reacted with (*E*)-3-(dimethylamino)-1-(2-fluorophenyl)prop-2-en-1-one **2i** (33.5 mg, 0.183 mmol, 1.0 equiv) and $[Cu(CH_3CN)_4]BF_4$ (6 mg, 0.018 mmol, 0.1 equiv) in the presence of (*S*)-XylBINAP (16.1 mg, 0.022 mmol, 0.12 equiv) in toluene to afford **3w** (51.63 mg, 0.123 mmol) as a white powder in 67% yield. $R_f$ 0.36 (20% ethyl acetate in petroleum ether) Mp = 152-154 °C; $[\alpha]_D^{25}$= −18.359 (*c* = 0.139 in $CH_2Cl_2$) for 90.68% *ee* sample. Optical purity was determined by chiral HPLC analysis (OD-H column), hexane−2-propanol, 90:10; flow rate = 1.0 mL/min; $t_R$ 1: 20.658 (major), $t_R$ 2: 25.425 min (minor); $^1$H

NMR (500 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.3 Hz, 2H), 7.46 (dd, $J$ = 15.5, 7.2 Hz, 1H), 7.39 (d, $J$ = 8.1 Hz, 2H), 7.36 (t, $J$ = 6.4 Hz, 1H), 7.28 (d, $J$ = 1.4 Hz, 1H), 7.23 – 7.10 (m, 5H), 7.02 (dd, $J$ = 7.7, 1.7 Hz, 2H), 4.48 (dd, $J$ = 11.1, 5.0 Hz, 1H), 4.08 (t, $J$ = 11.0 Hz, 1H), 3.68 (dd, $J$ = 10.8, 5.1 Hz, 1H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 186.7, 159.31 (d, $J$ = 250.2 Hz), 145.3, 144.8, 142.2, 133.14, 132.7, 132.6, 130.4, 130.1, 128.8, 127.7, 127.3, 127.1, 124.54 (d, $J$ = 3.2 Hz), 116.37 (d, $J$ = 22.1 Hz), 57.3, 46.6, 21.8. IR $\nu_{max}$ (KBr, $cm^{-1}$) 2918.3, 2848.6, 1629.8, 1595.1, 1485.2, 1450.5, 1356.0, 1236.4, 1159.2, 1084.0, 1012.6, 966.3, 895.0, 858.3, 814.0, 800.5, 781.2, 750.3, 719.4, 700.2, 667.4, 588.3, 538.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FNO_3S$ 422.1221; Found 422.1217.

## $^1H$ and ($^{13}C\{^1H\}$ NMR) NMR Spectra, and HPLC chromatograms of the synthesized compounds

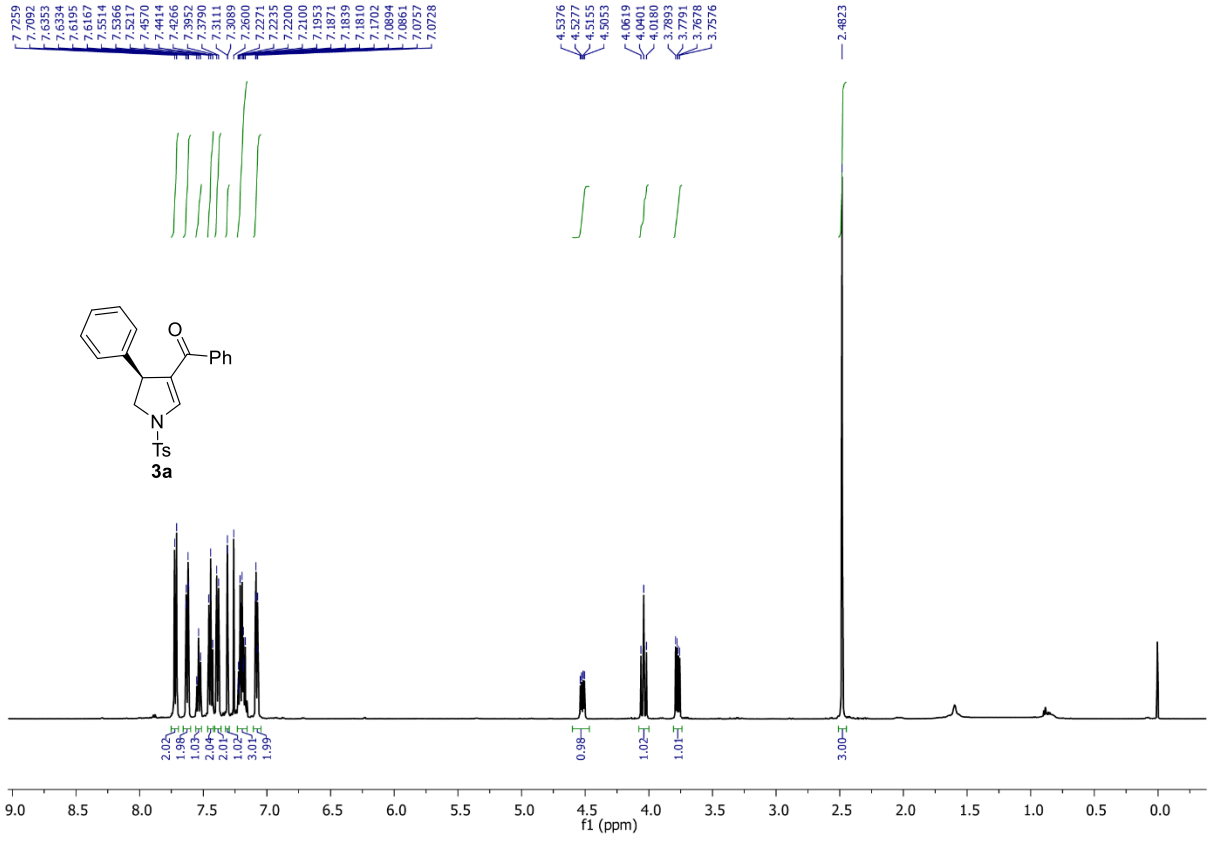



**Figure S2.** $^1H$ NMR spectrum of **3a** (500 MHz, $CDCl_3$)

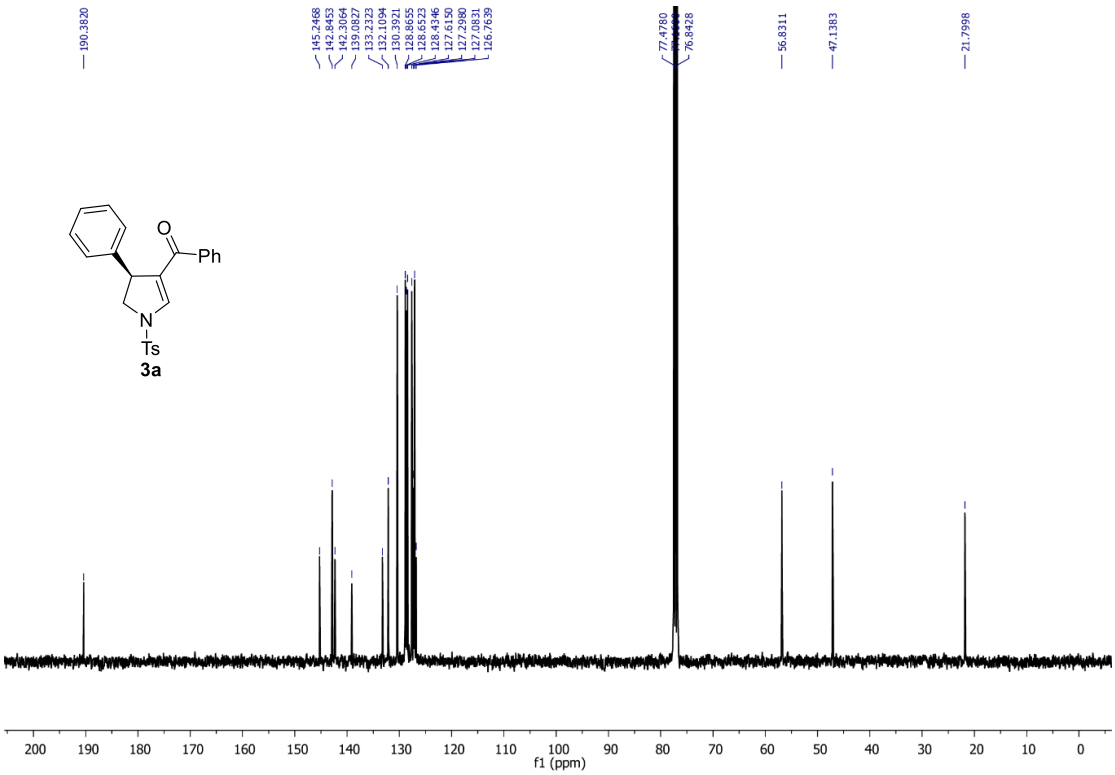
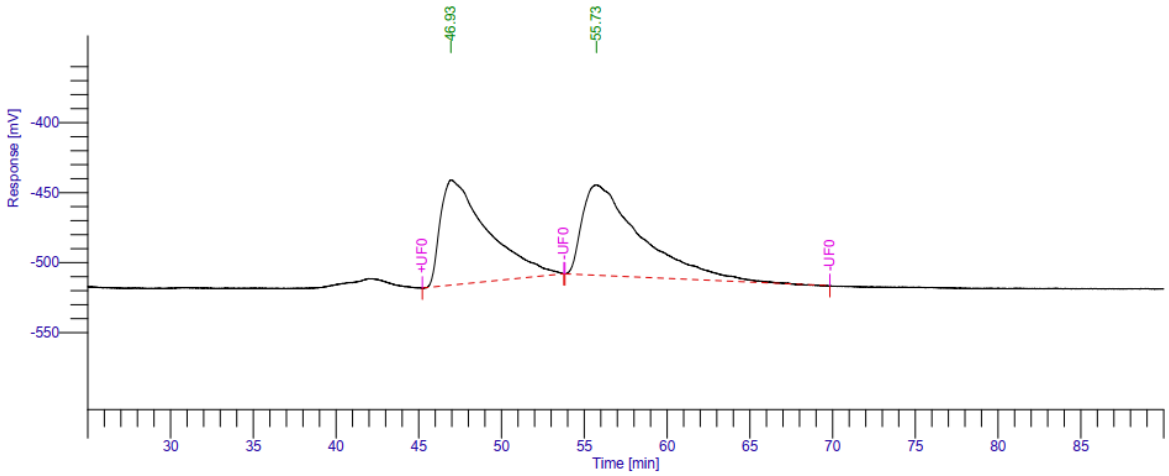



**Figure S3**. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (125 MHz, $CDCl_3$)

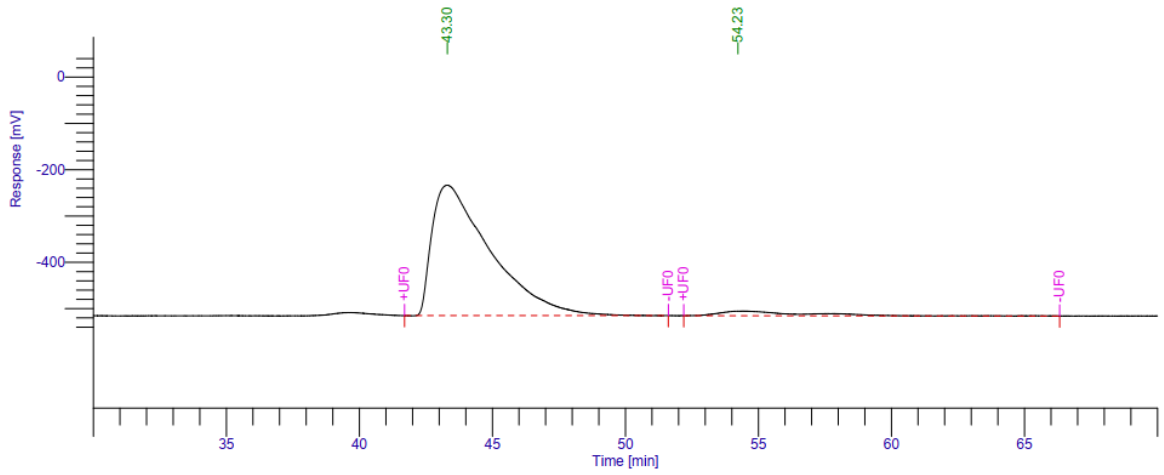



AKS-4-64RAC, OD-H

AKS-4-64RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 46.933 | 14893032.39 | 75183.71 | 48.42 | 48.42 | | | *MM | 14.8930 | 14.8930 |
| 2 | | 55.726 | 15863488.81 | 64584.09 | 51.58 | 51.58 | | | *MM | 15.8635 | 15.8635 |
| | | | 30756521.20 | 139767.80 | 100.00 | 100.00 | | | | 30.7565 | 30.7565 |

**Figure S4**. HPLC chromatogram of racemic compound **3a** (OD-H column; 97:3 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-4-177Chiral, OD-H

AKS-4-177Chiral, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 43.303 | 42860058.36 | 281625.34 | 97.69 | 97.69 | | | *MM | 42.8601 | 42.8601 |
| 2 | | 54.230 | 2110923.84 | 9995.90 | 2.31 | 2.31 | | | *MM | 2.1109 | 2.1109 |
| | | | 44970982.20 | 291621.25 | 100.00 | 100.00 | | | | 44.9710 | 44.9710 |

**Figure S5**. HPLC chromatogram of chiral compound **3a** (OD-H column; 97:3 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

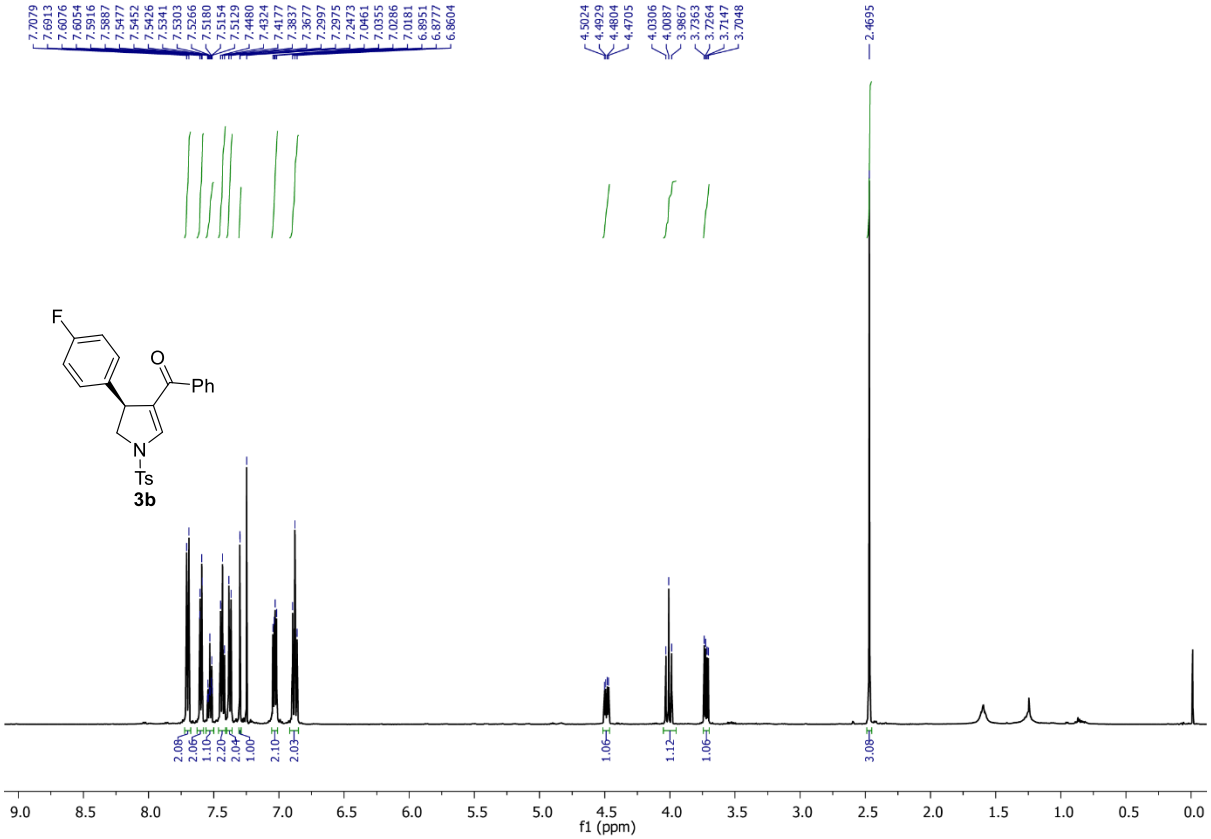



**Figure S6.** $^{1}H$ NMR spectrum of **3b** (500 MHz, $CDCl_3$)

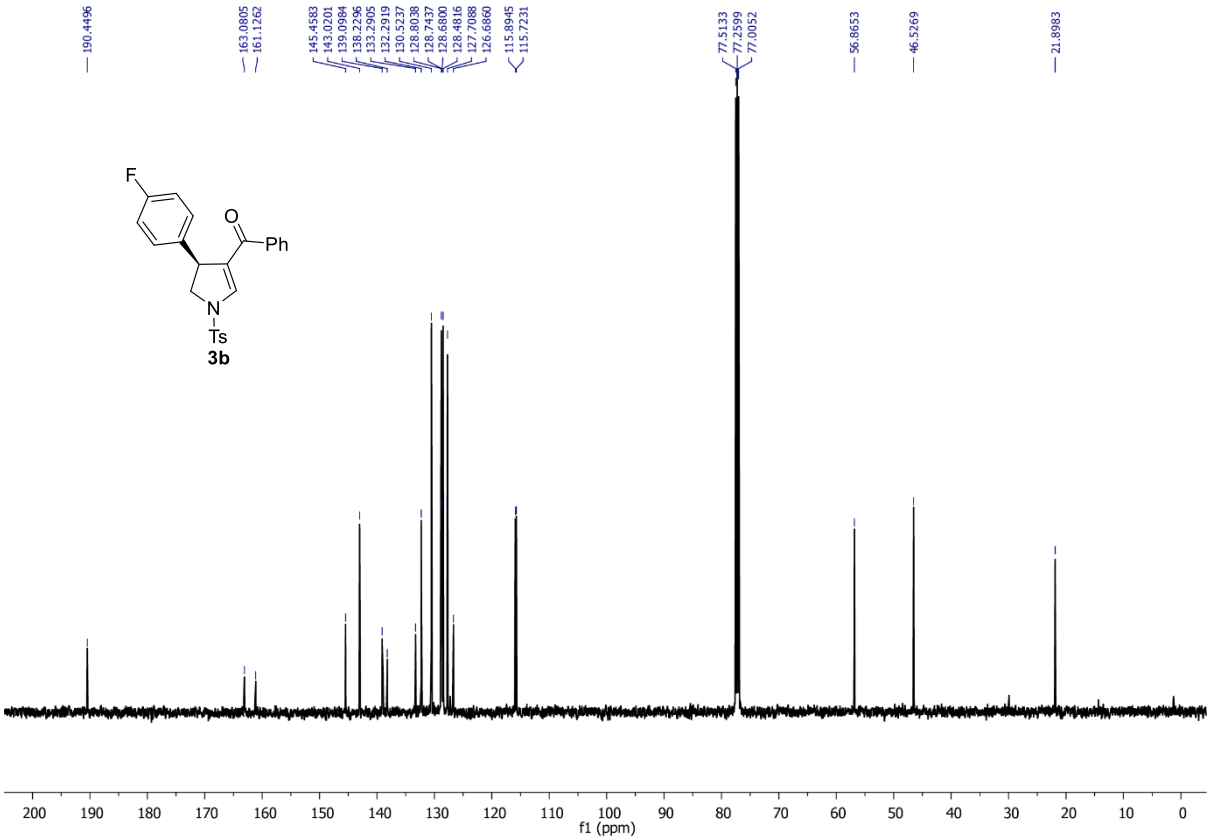



**Figure S7**. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (125 MHz, $CDCl_3$)

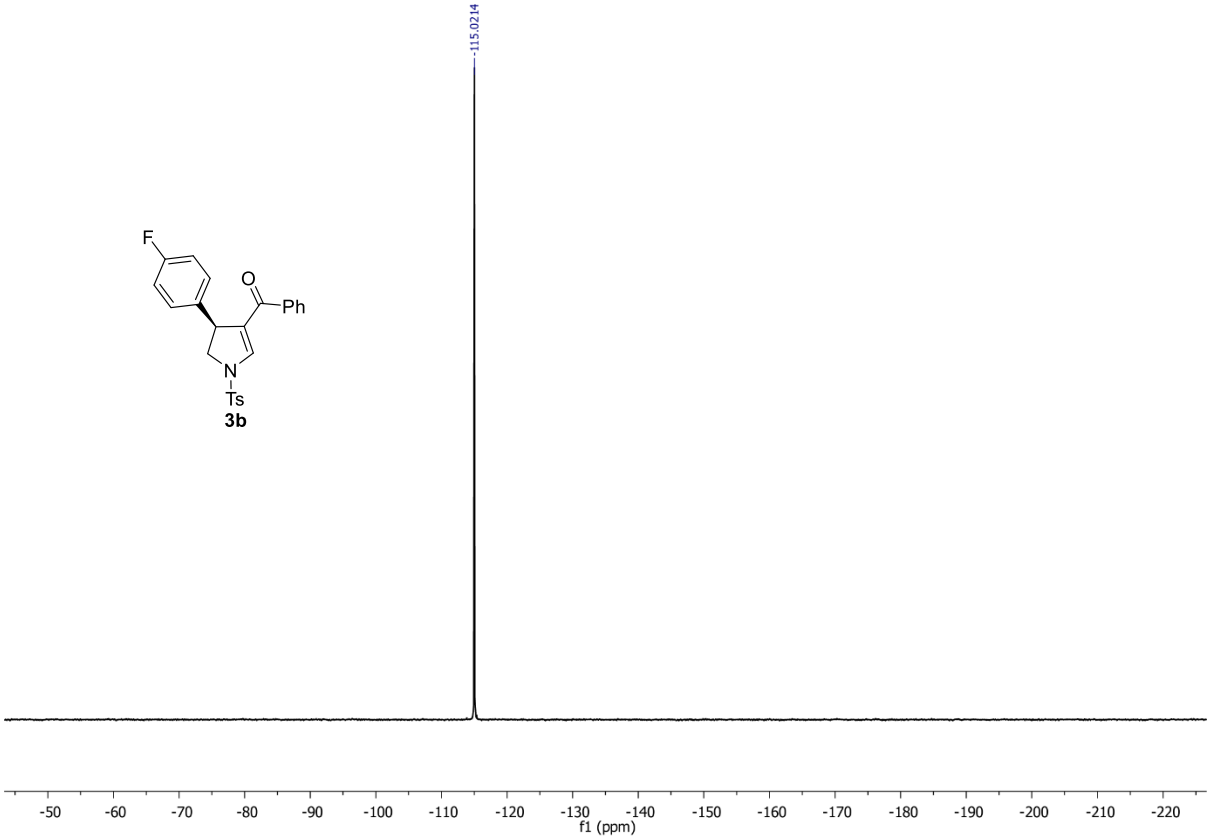
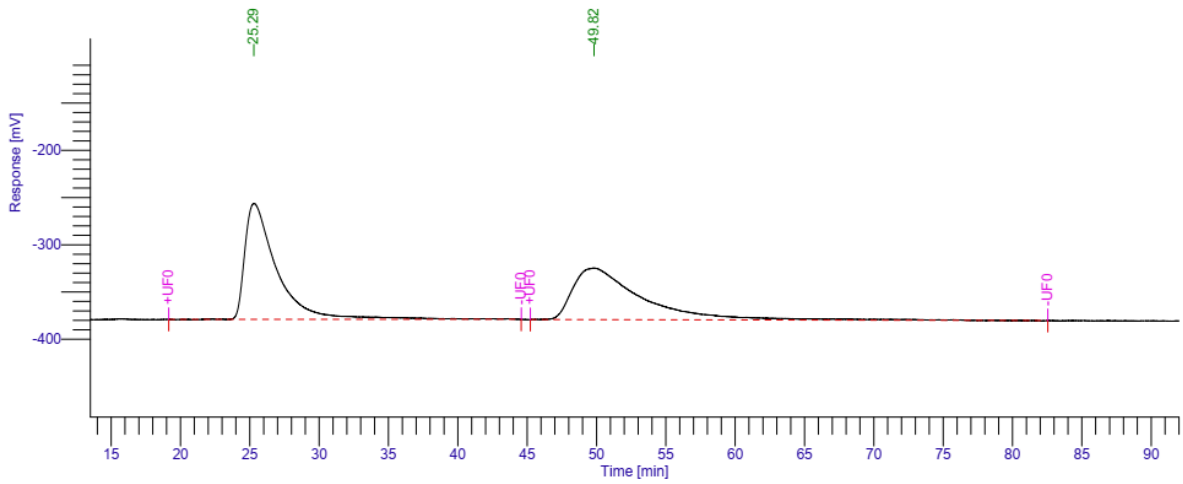



**Figure S8.** $^{19}F$ NMR spectrum of **3b** (500 MHz, $CDCl_3$)

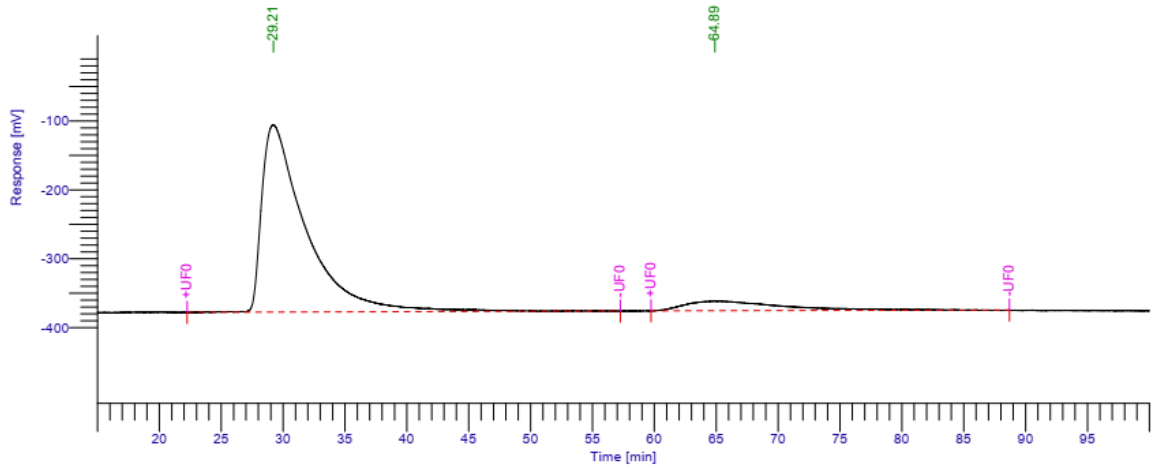



AKS-5-50RAC, AS-H

AKS-5-50RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 25.293 | 19790913.23 | 122761.93 | 51.36 | 51.36 | | | *MM | 19.7909 | 19.7909 |
| 2 | | 49.815 | 18745477.60 | 54572.71 | 48.64 | 48.64 | | | *MM | 18.7455 | 18.7455 |
| 3 | | 110.016 | 62.26 | 57.33 | 0.00 | 0.00 | | | BB | 0.0001 | 0.0001 |
| | | | 38536453.08 | 177391.97 | 100.00 | 100.00 | | | | 38.5365 | 38.5365 |

**Figure S9**. HPLC chromatogram of racemic compound **3b** (As-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-49CHIRAL, AS-H

AKS-5-49CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 29.209 | 67318576.82 | 272001.17 | 90.03 | 90.03 | | | *MM | 67.3186 | 67.3186 |
| 2 | | 64.885 | 7456464.42 | 13911.86 | 9.97 | 9.97 | | | *MM | 7.4565 | 7.4565 |
| | | | 74775041.24 | 285913.02 | 100.00 | 100.00 | | | | 74.7750 | 74.7750 |

**Figure S10**. HPLC chromatogram of chiral compound **3b** (As-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

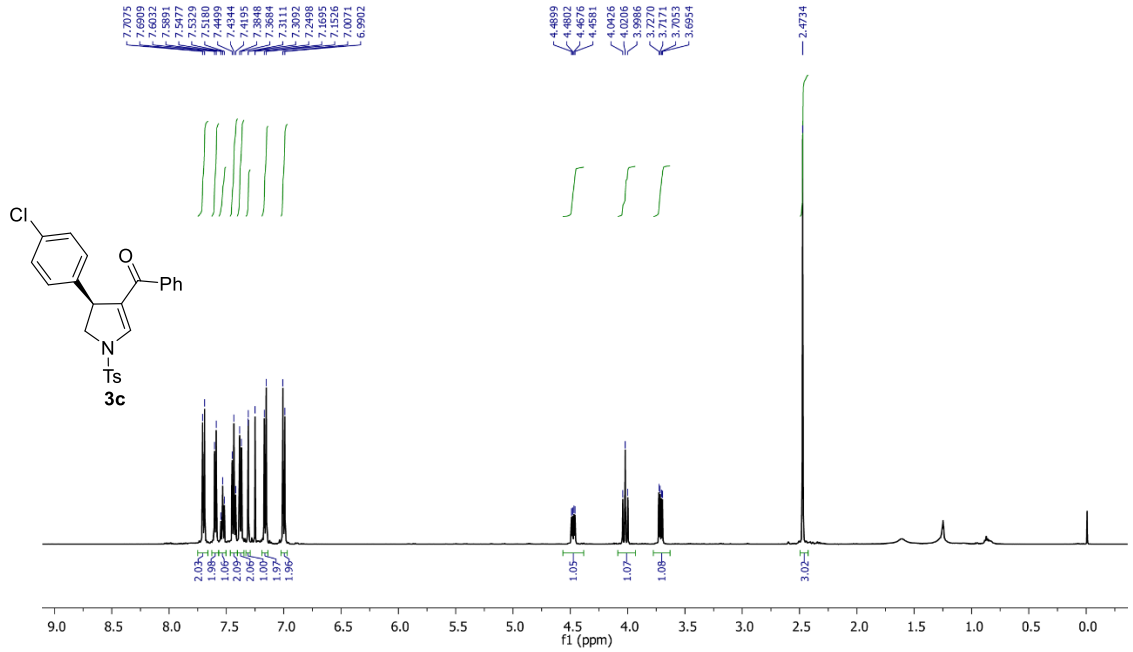



**Figure S11.** $^{1}$H NMR spectrum of **3c** (500 MHz, $CDCl_3$)

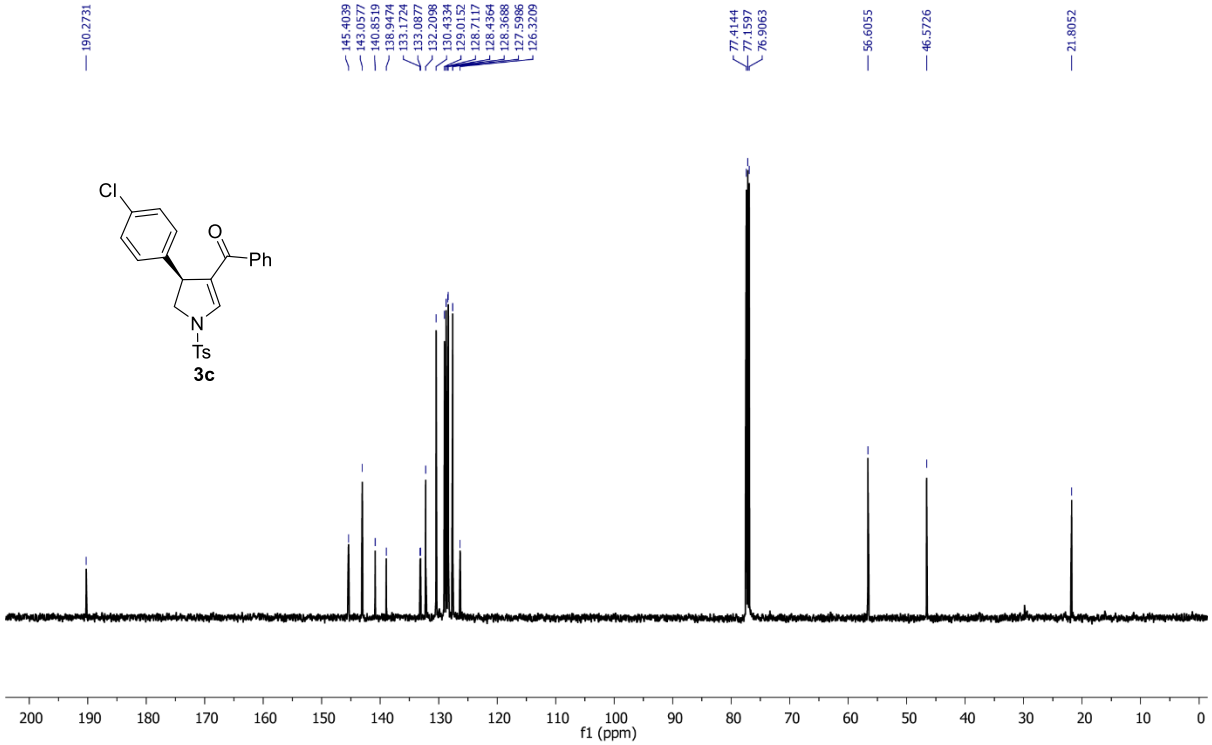
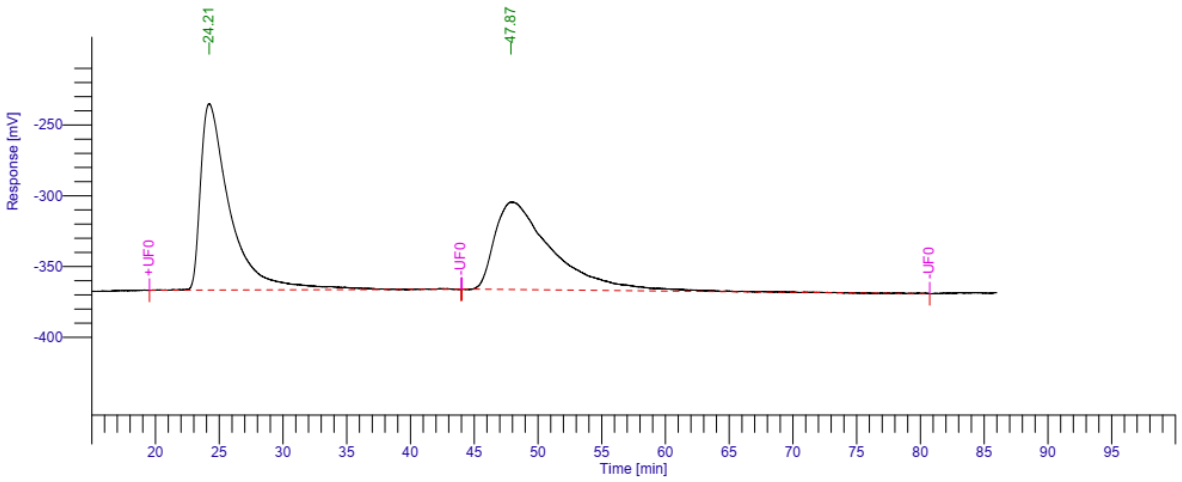



**Figure S12**. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (125 MHz, $CDCl_3$)

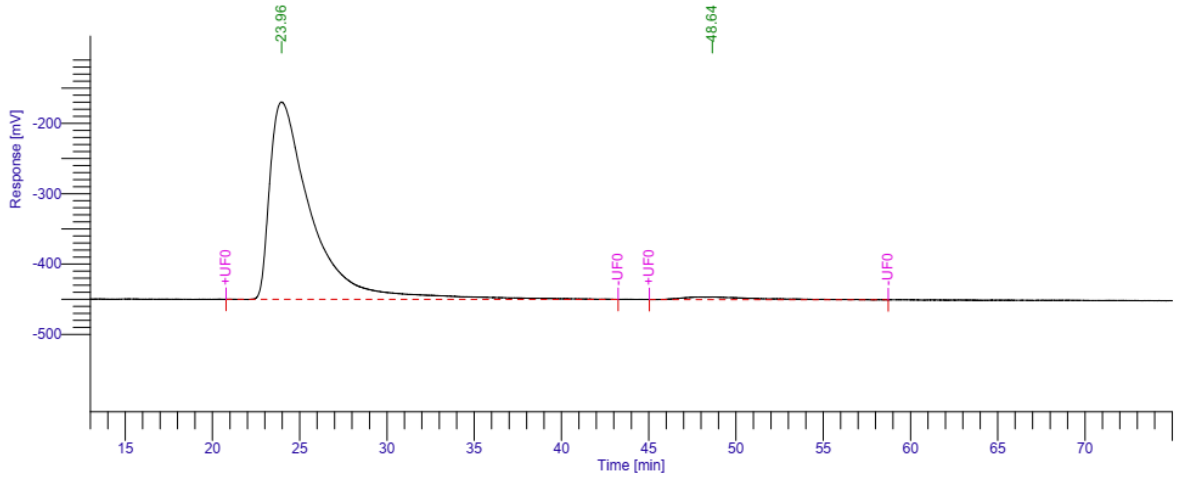



AKS-5-44RAC, AS-H

AKS-5-44RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 24.207 | 21106177.70 | 131700.61 | 52.07 | 52.07 | | | *MM | 21.1062 | 21.1062 |
| 2 | | 47.872 | 19425578.16 | 61811.21 | 47.93 | 47.93 | | | *MM | 19.4256 | 19.4256 |
| | | | 40531755.87 | 193511.82 | 100.00 | 100.00 | | | | 40.5318 | 40.5318 |

**Figure S13**. HPLC chromatogram of racemic compound **3c** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-43CHIRAL, AS-H

AKS-5-43CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 23.958 | 46310204.64 | 280318.73 | 97.71 | 97.71 | | | *MM | 46.3102 | 46.3102 |
| 2 | | 48.642 | 1086451.13 | 3760.27 | 2.29 | 2.29 | | | *MM | 1.0865 | 1.0865 |
| | | | 47396655.77 | 284079.00 | 100.00 | 100.00 | | | | 47.3967 | 47.3967 |

**Figure S14**. HPLC chromatogram of chiral compound **3c** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

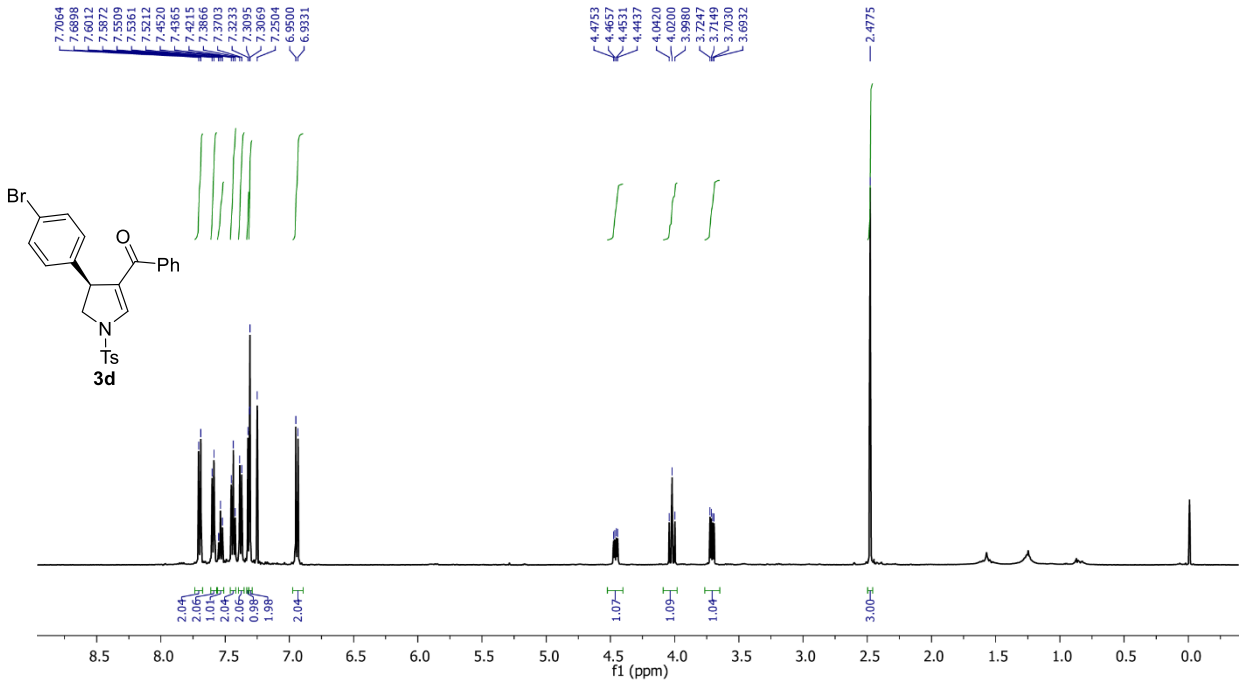



**Figure S15.** $^{1}$H NMR spectrum of **3d** (500 MHz, $CDCl_3$)

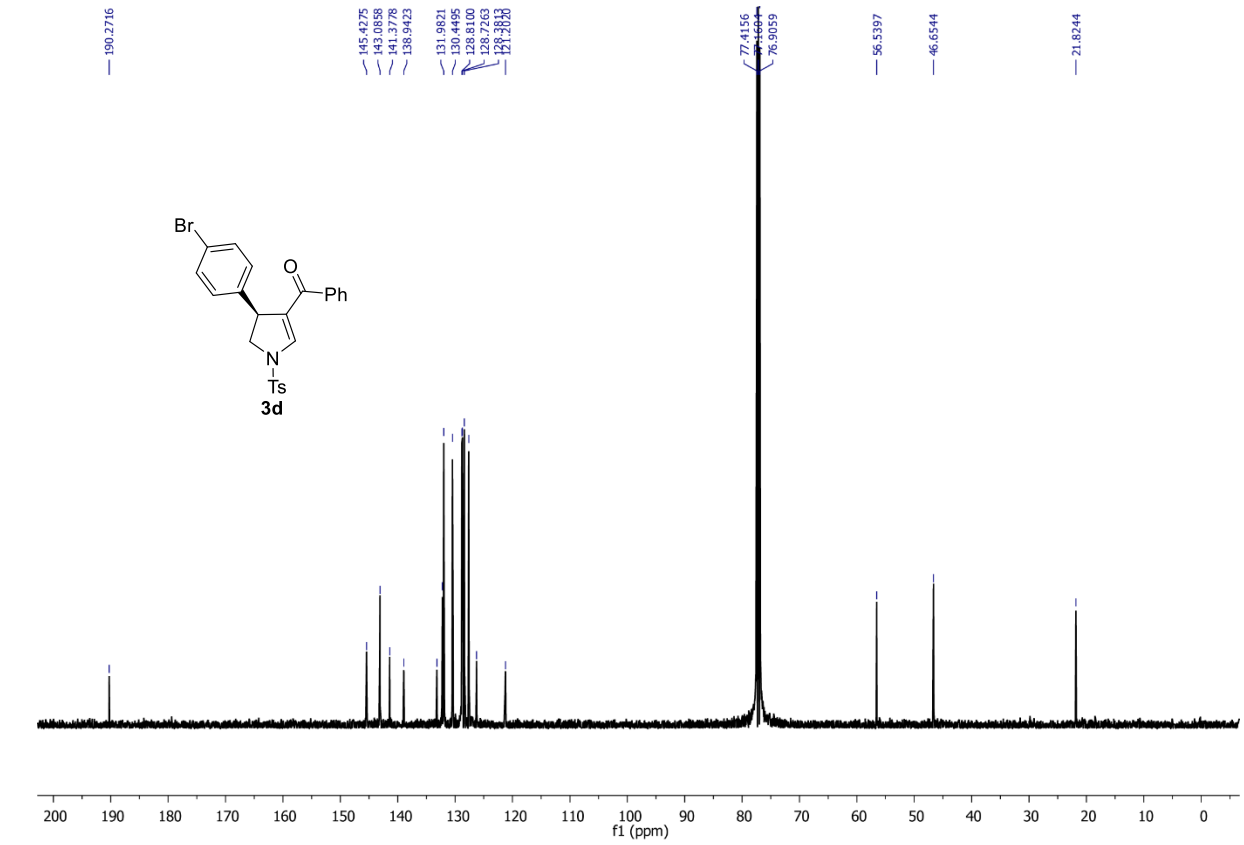
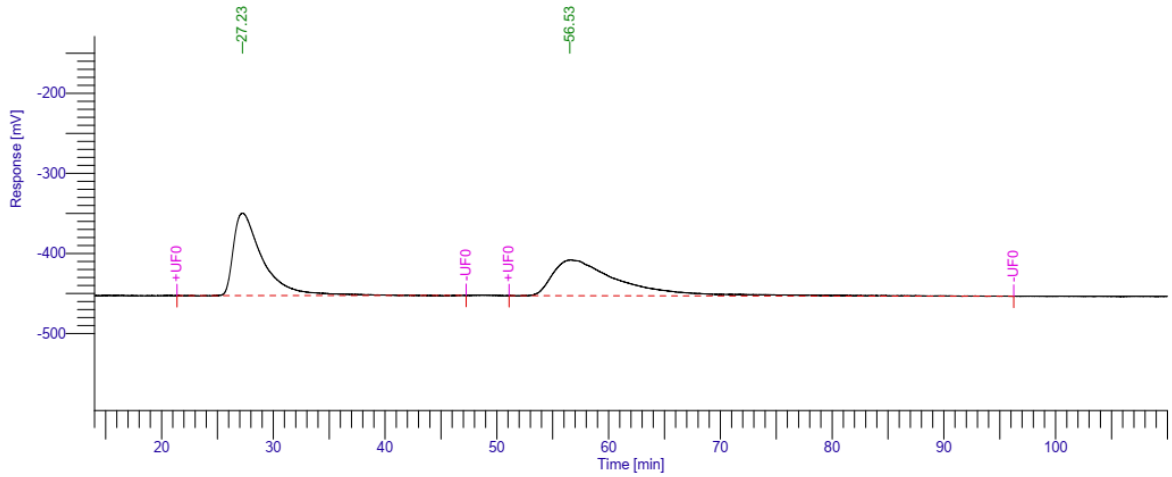



**Figure S16**. $^{13}C\{^{1}H\}$ NMR spectrum of **3d** (125 MHz, $CDCl_3$)

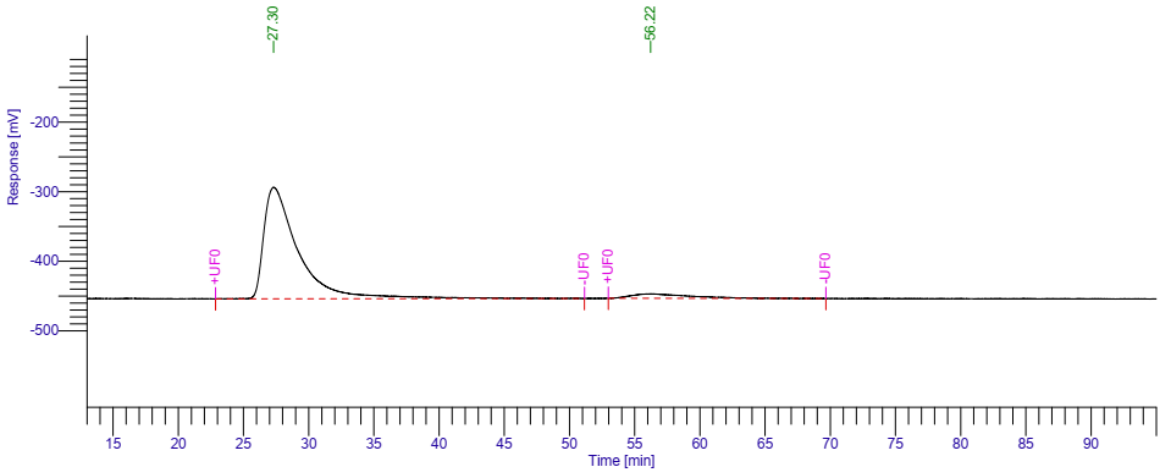



AKS-5-46RAC, AS-H

AKS-5-46RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 27.229 | 18697576.31 | 102994.36 | 50.21 | 50.21 | | | *MM | 18.6976 | 18.6976 |
| 2 | | 56.525 | 18542026.69 | 44743.28 | 49.79 | 49.79 | | | *MM | 18.5420 | 18.5420 |
| | | | 37239603.00 | 147737.65 | 100.00 | 100.00 | | | | 37.2396 | 37.2396 |

**Figure S17**. HPLC chromatogram of racemic compound **3d** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-45CHIRAL, AS-H

AKS-5-45CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 27.302 | 29482627.56 | 160219.22 | 93.82 | 93.82 | | | *MM | 29.4826 | 29.4826 |
| 2 | | 56.217 | 1940883.66 | 6370.78 | 6.18 | 6.18 | | | *MM | 1.9409 | 1.9409 |
| | | | 31423511.22 | 166590.00 | 100.00 | 100.00 | | | | 31.4235 | 31.4235 |

**Figure S18**. HPLC chromatogram of chiral compound **3d** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

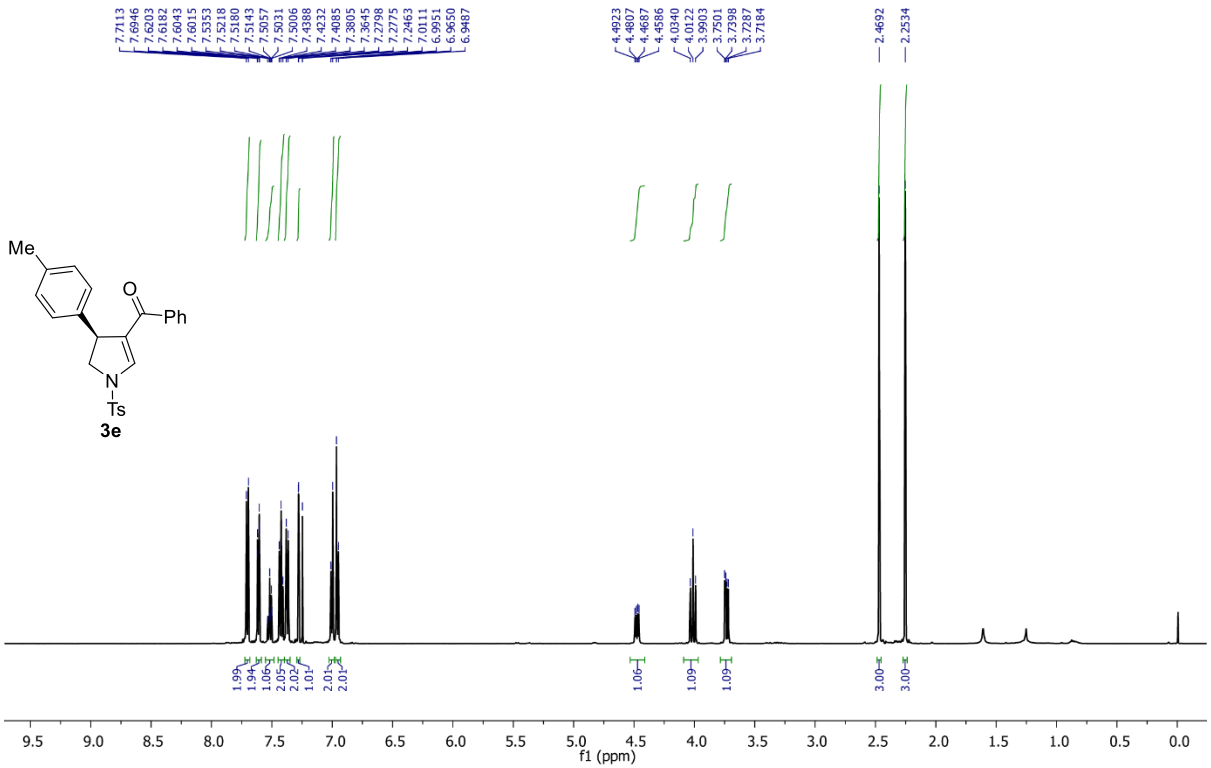



**Figure S19.** $^{1}$H NMR spectrum of **3e** (500 MHz, $CDCl_3$)

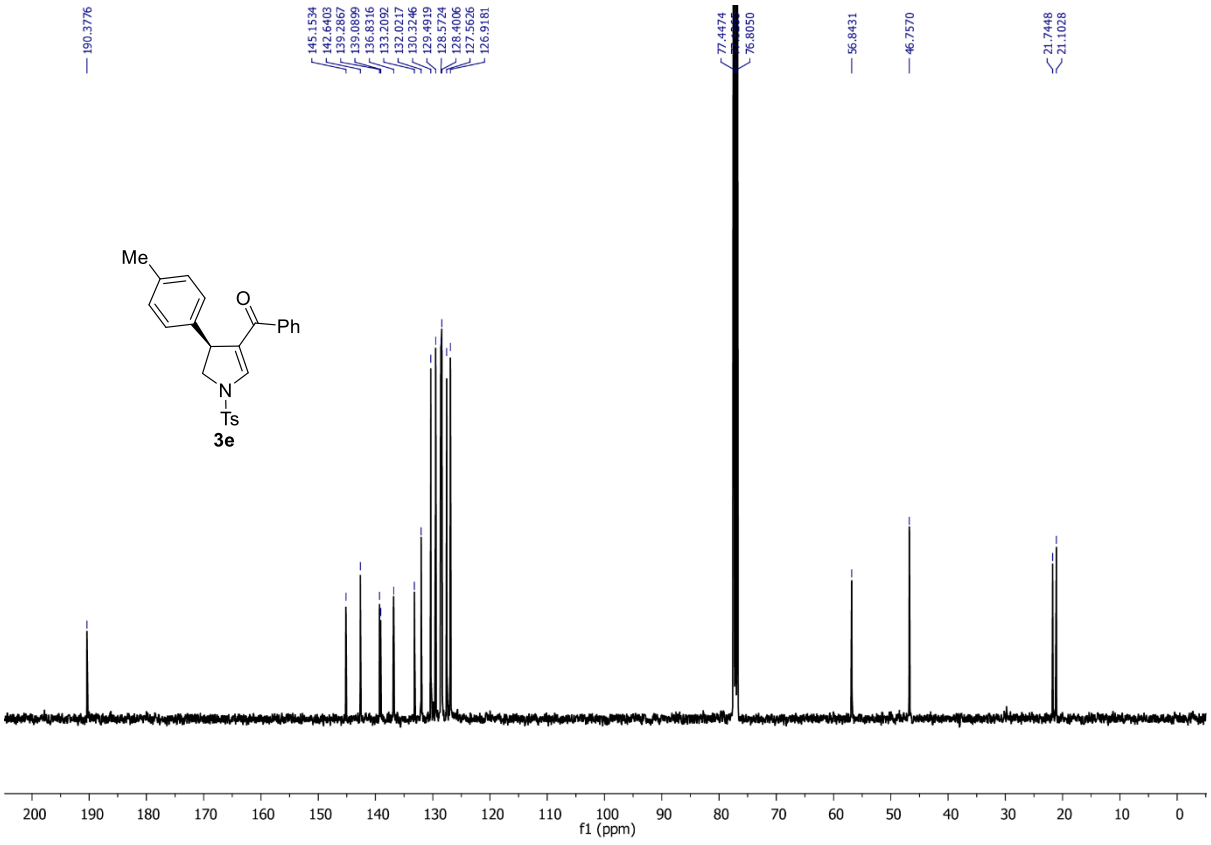
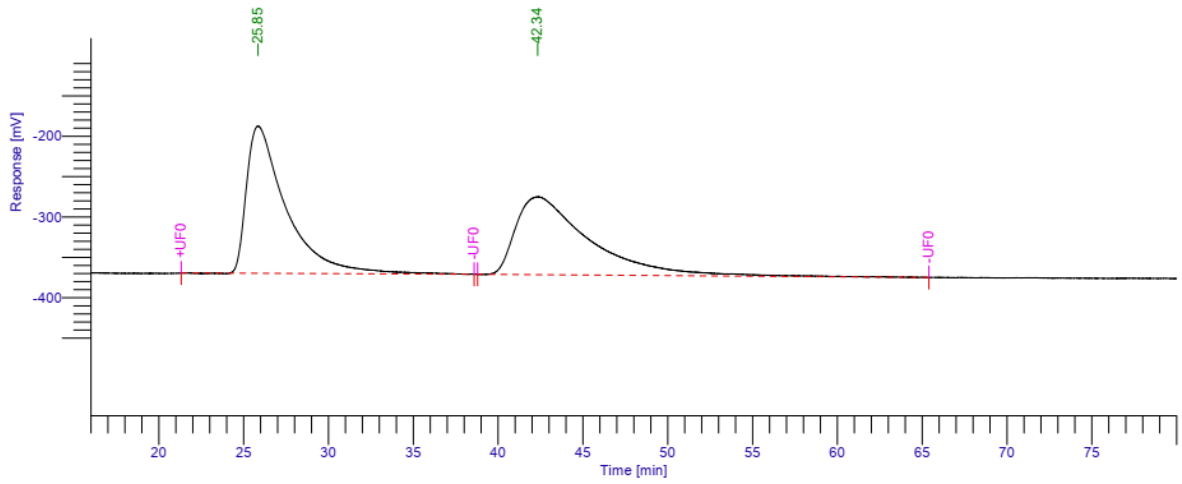



**Figure S20**. $^{13}C\{^{1}H\}$ NMR spectrum of **3e** (125 MHz, $CDCl_3$)

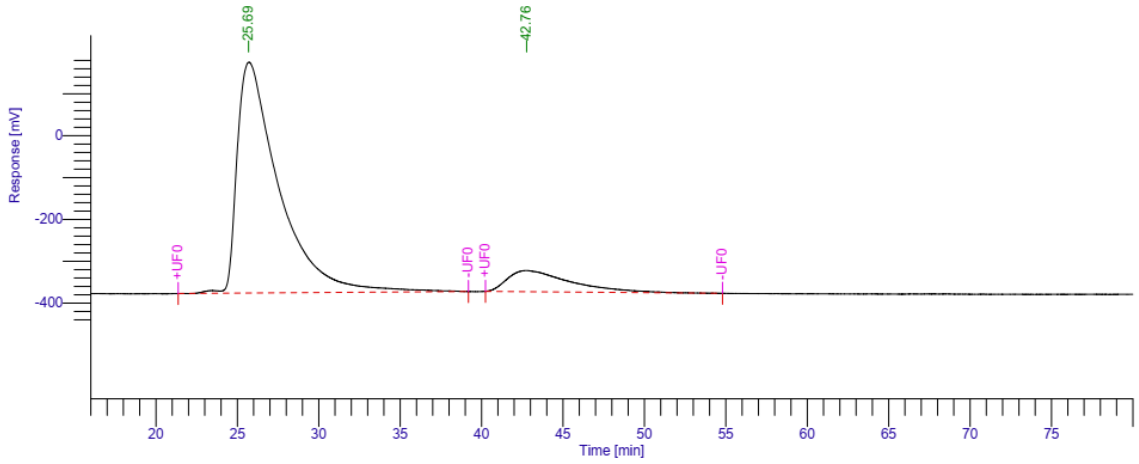



AKS-5-48RAC, AS-H

AKS-5-48RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 25.850 | 29491868.30 | 182382.48 | 50.50 | 50.50 | | | *MM | 29.4919 | 29.4919 |
| 2 | | 42.335 | 28907217.14 | 96331.93 | 49.50 | 49.50 | | | *MM | 28.9072 | 28.9072 |
| | | | 58399085.45 | 278714.41 | 100.00 | 100.00 | | | | 58.3991 | 58.3991 |

**Figure S20**. HPLC chromatogram of racemic compound **3e** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-47CHIRAL, AS-H

AKS-5-47CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 25.689 | 98328516.60 | 551531.04 | 87.91 | 87.91 | | | *MM | 98.3285 | 98.3285 |
| 2 | | 42.761 | 13523262.39 | 50572.42 | 12.09 | 12.09 | | | *MM | 13.5233 | 13.5233 |
| | | | 1.12e+08 | 602103.46 | 100.00 | 100.00 | | | | 111.8518 | 111.8518 |

**Figure S21**. HPLC chromatogram of chiral compound **3e** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

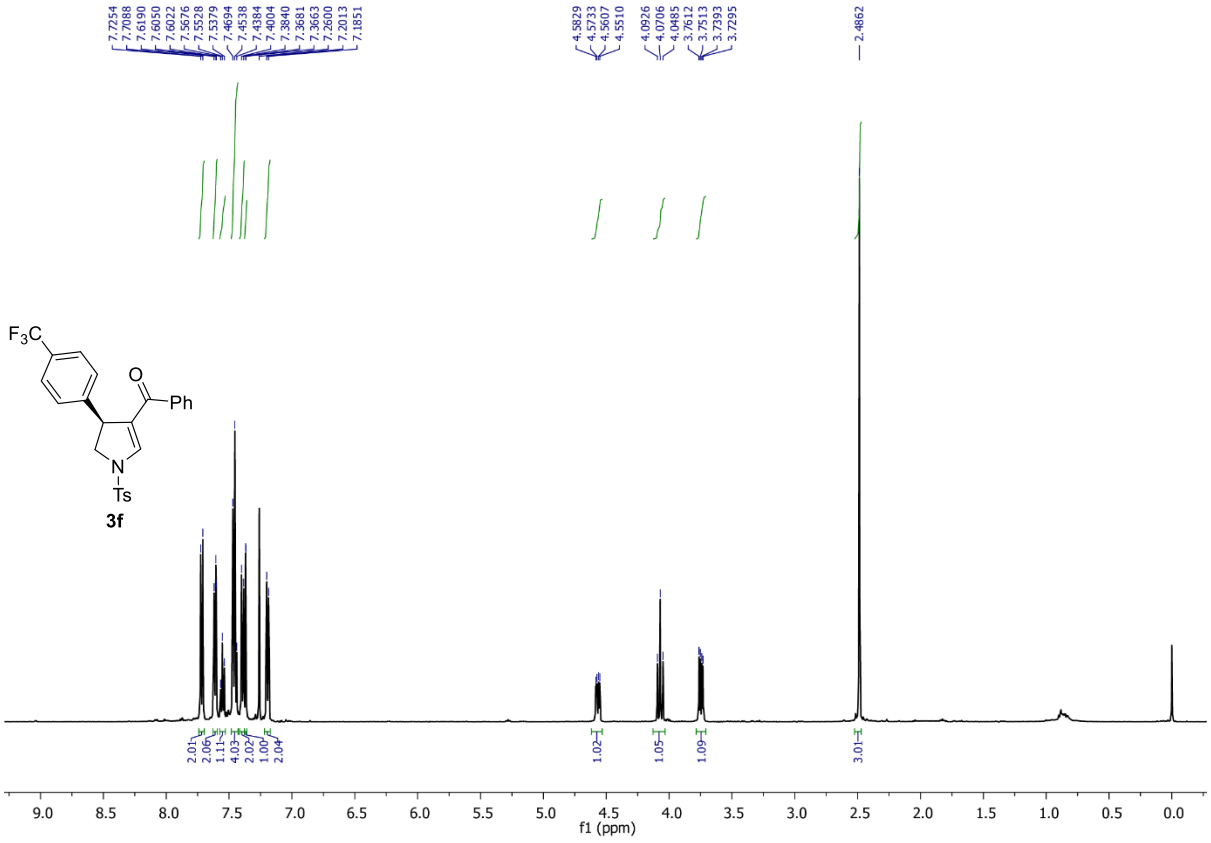



**Figure S22.** $^{1}$H NMR spectrum of **3f** (500 MHz, $CDCl_3$)

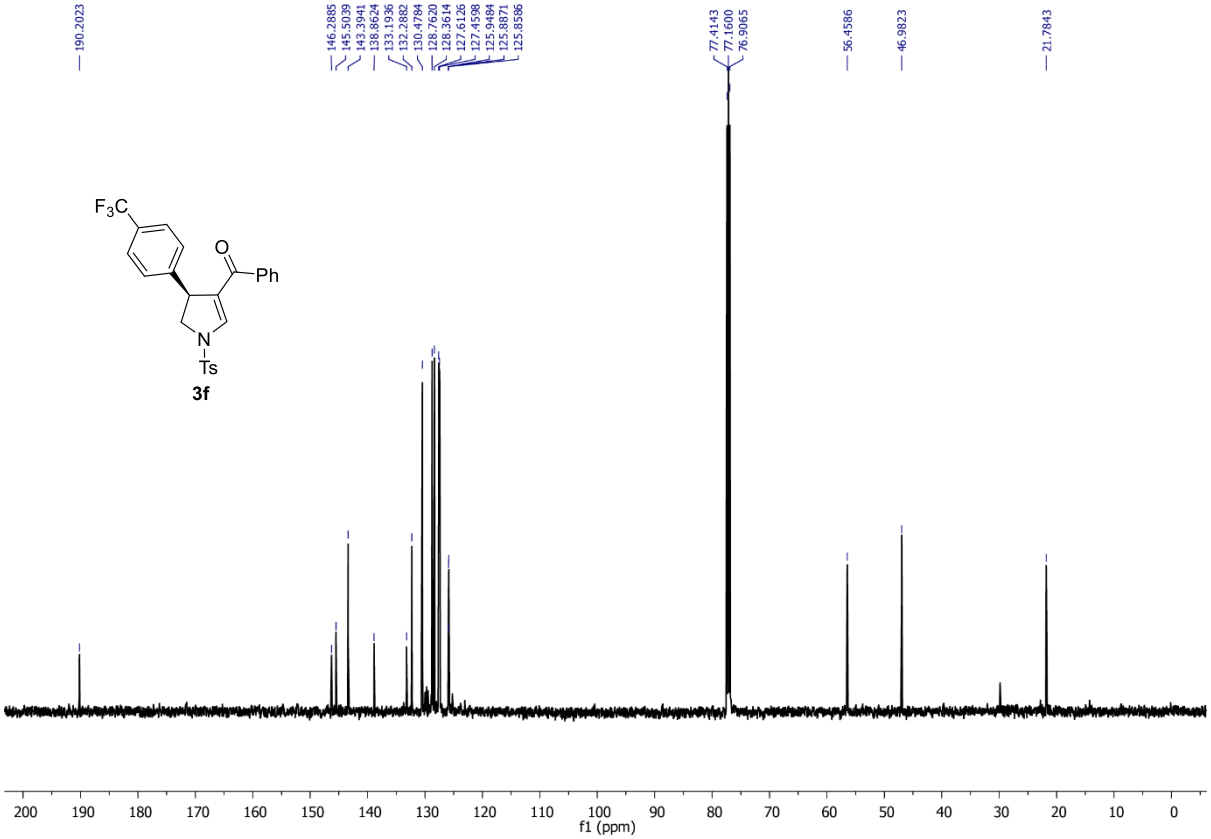



**Figure S23**. $^{13}C\{^{1}H\}$ NMR spectrum of **3f** (125 MHz, $CDCl_3$)

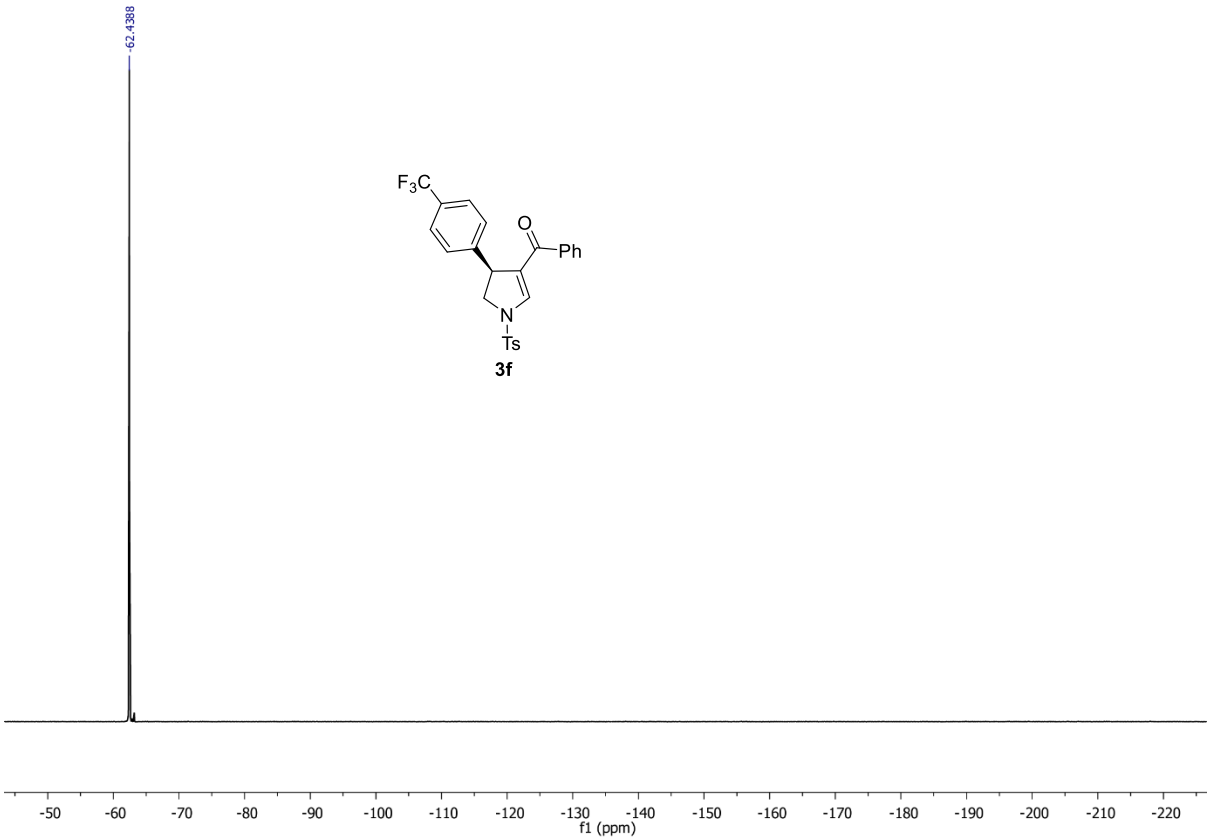
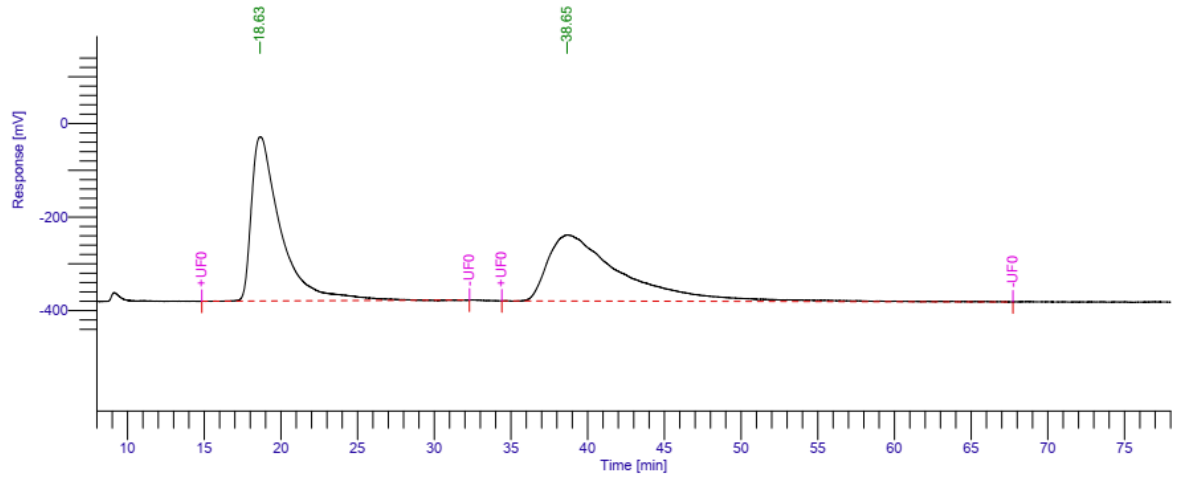



**Figure S24.** $^{19}F$ NMR spectrum of **3f** (500 MHz, $CDCl_3$)

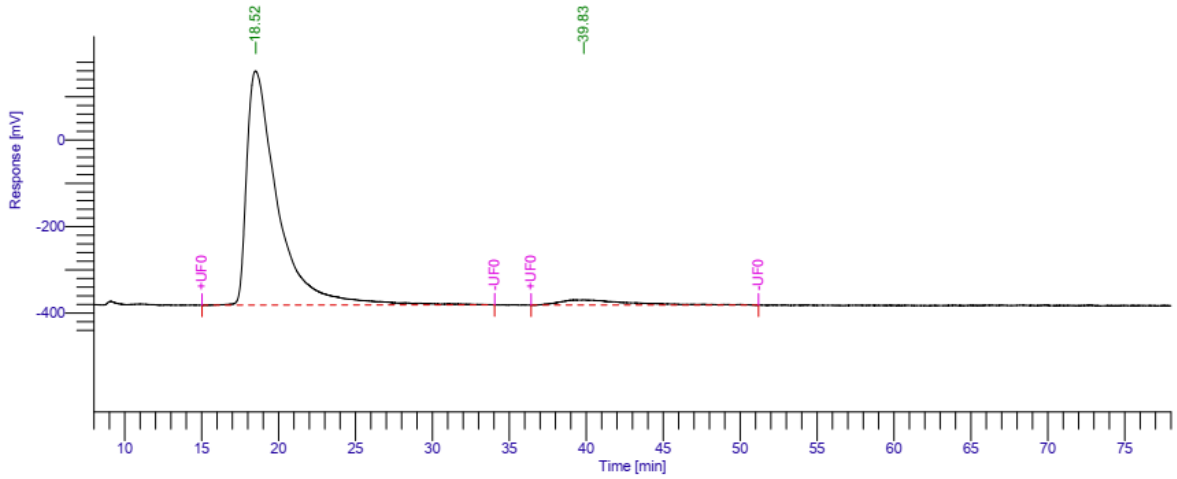



AKS-5-73RAC, AS-H

AKS-5-73RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 18.634 | 46384310.44 | 351121.39 | 49.61 | 49.61 | | | *MM | 46.3843 | 46.3843 |
| 2 | | 38.654 | 47113239.01 | 141179.45 | 50.39 | 50.39 | | | *MM | 47.1132 | 47.1132 |
| | | | 93497549.45 | 492300.85 | 100.00 | 100.00 | | | | 93.4975 | 93.4975 |

**Figure S25**. HPLC chromatogram of racemic compound **3f** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-72CHIRAL, AS-H

AKS-5-72CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 18.517 | 75413101.88 | 541282.01 | 95.24 | 95.24 | | | *MM | 75.4131 | 75.4131 |
| 2 | | 39.835 | 3771089.16 | 11833.74 | 4.76 | 4.76 | | | *MM | 3.7711 | 3.7711 |
| | | | 79184191.04 | 553115.75 | 100.00 | 100.00 | | | | 79.1842 | 79.1842 |

**Figure S26**. HPLC chromatogram of chiral compound **3f** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

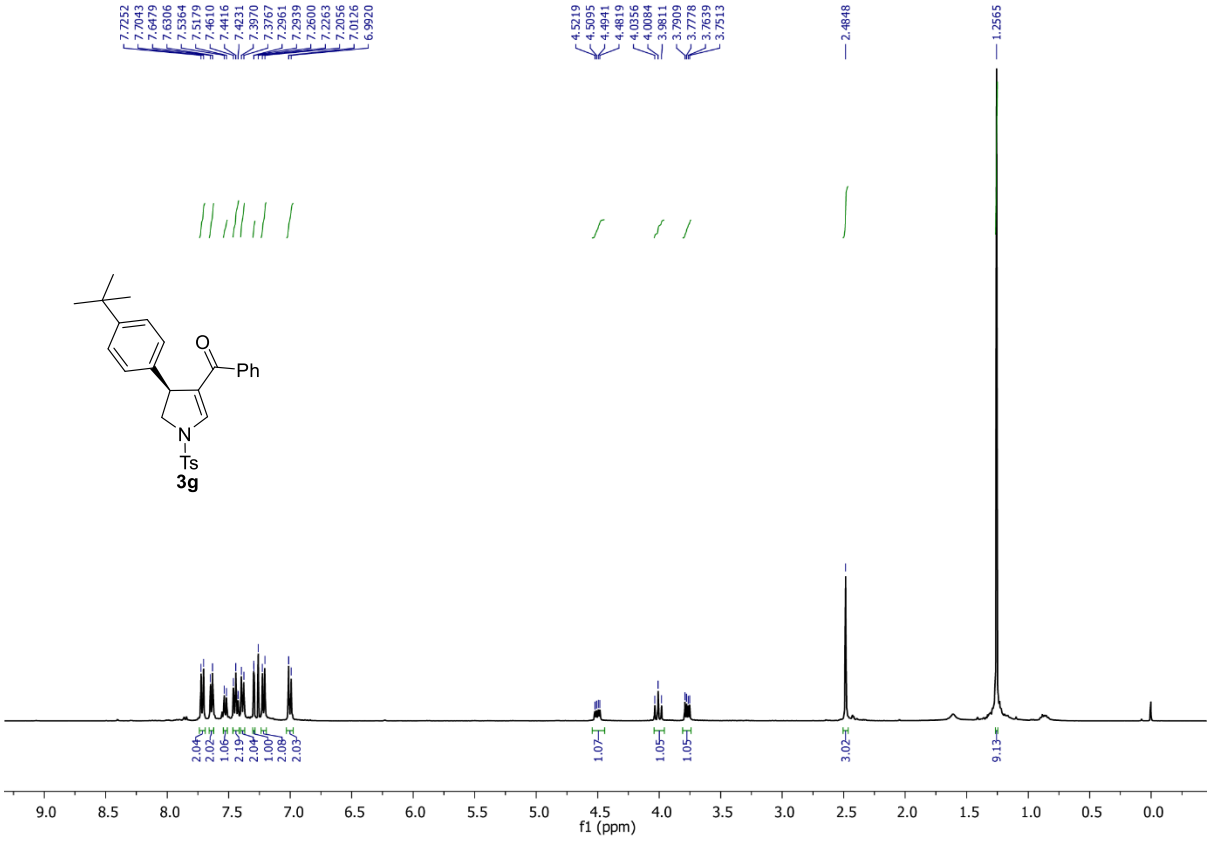



**Figure S27.** $^{1}H$ NMR spectrum of **3g** (500 MHz, $CDCl_3$)

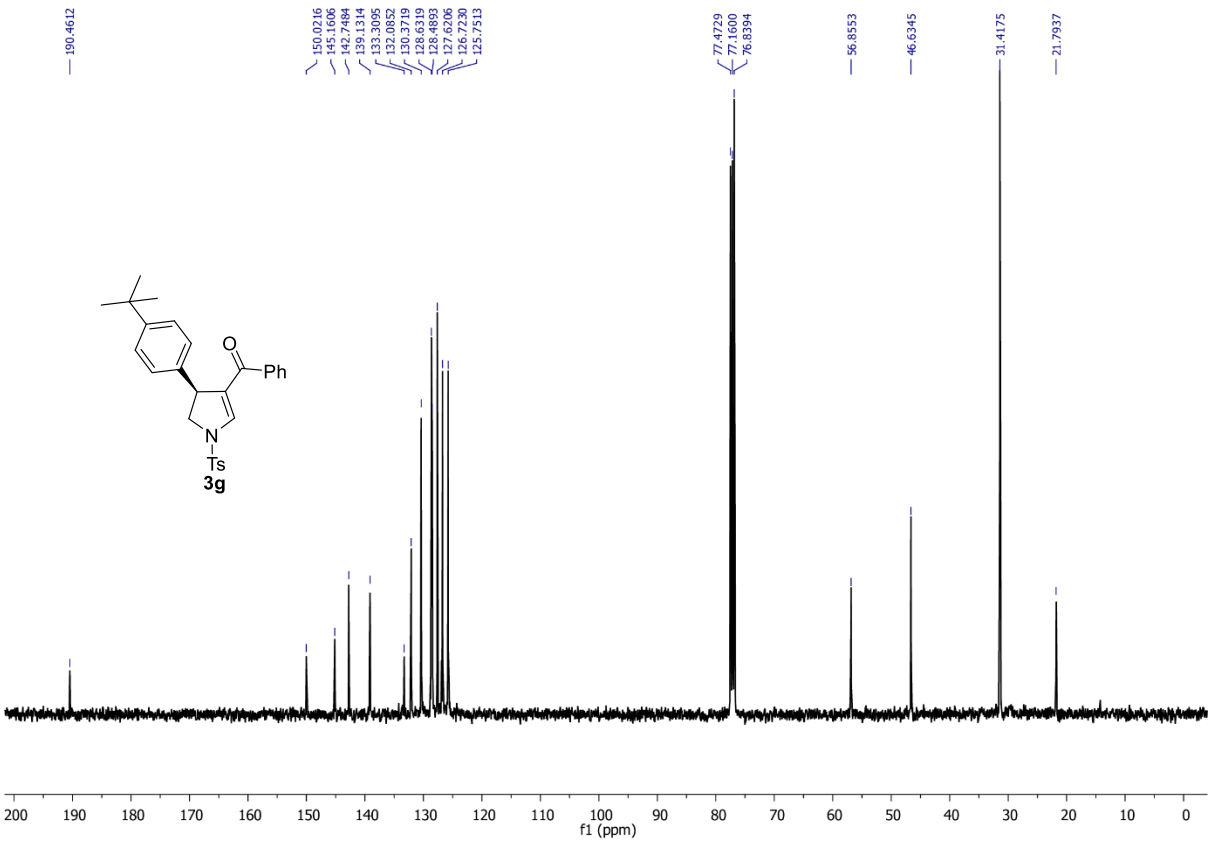
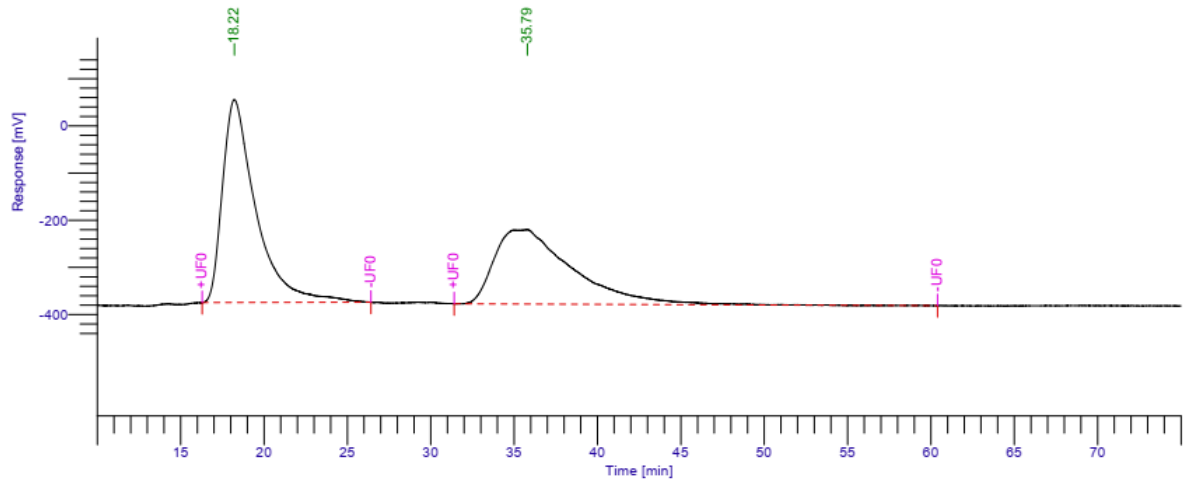



**Figure S28**. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** (125 MHz, $CDCl_3$)

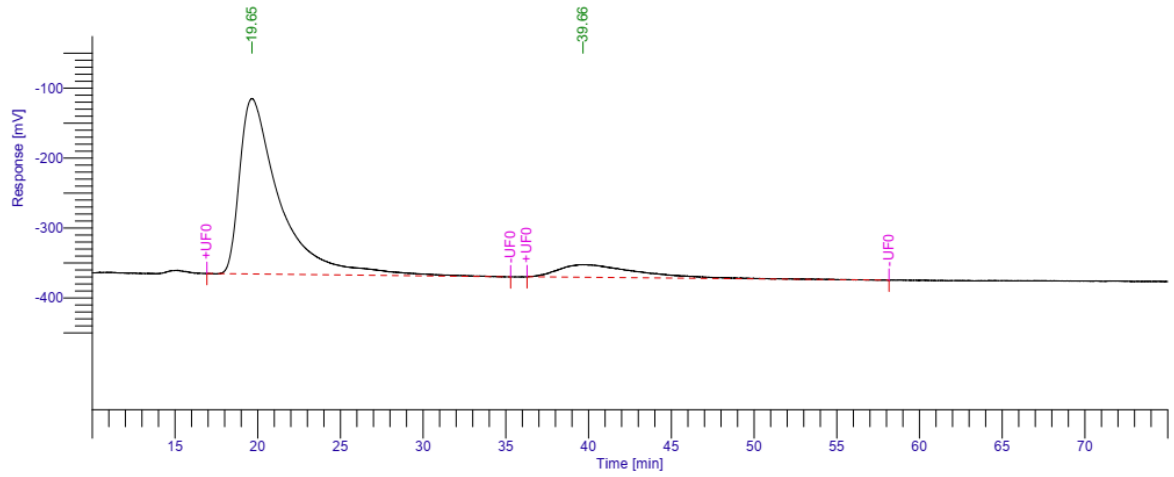



AKS-5-75RAC, AS-H

AKS-5-75RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 18.223 | 59822629.69 | 430185.29 | 53.87 | 53.87 | | | *MM | 59.8226 | 59.8226 |
| 2 | | 35.787 | 51217864.67 | 157921.19 | 46.13 | 46.13 | | | *MM | 51.2179 | 51.2179 |
| | | | 1.11e+08 | 588106.48 | 100.00 | 100.00 | | | | 111.0405 | 111.0405 |

**Figure S29**. HPLC chromatogram of racemic compound **3g** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-165CHIRAL, AS-H

AKS-5-165CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 19.653 | 42262439.93 | 251032.43 | 87.64 | 87.64 | | | *MM | 42.2624 | 42.2624 |
| 2 | | 39.659 | 5962067.21 | 18113.56 | 12.36 | 12.36 | | | *MM | 5.9621 | 5.9621 |
| | | | 48224507.15 | 269146.00 | 100.00 | 100.00 | | | | 48.2245 | 48.2245 |

**Figure S30**. HPLC chromatogram of chiral compound **3g** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

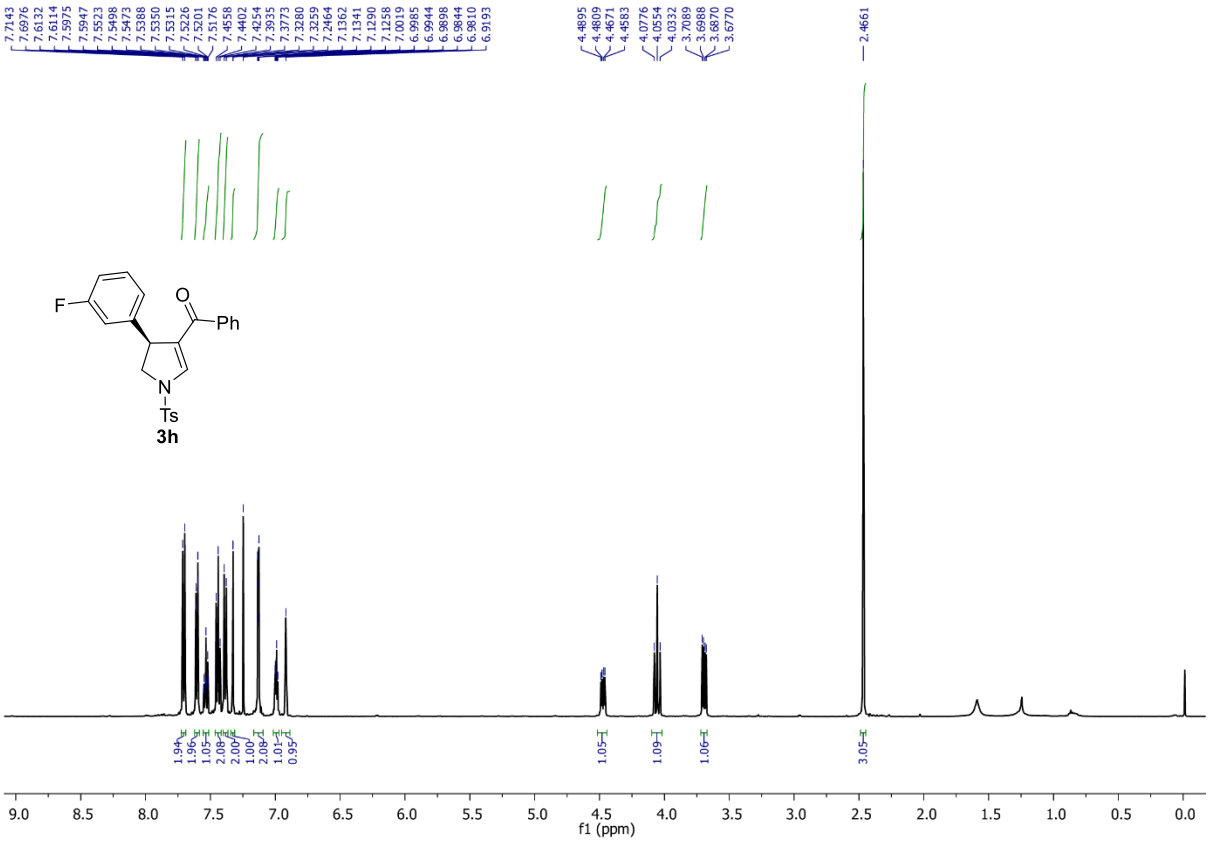



**Figure S31.** $^{1}H$ NMR spectrum of **3h** (500 MHz, $CDCl_3$)

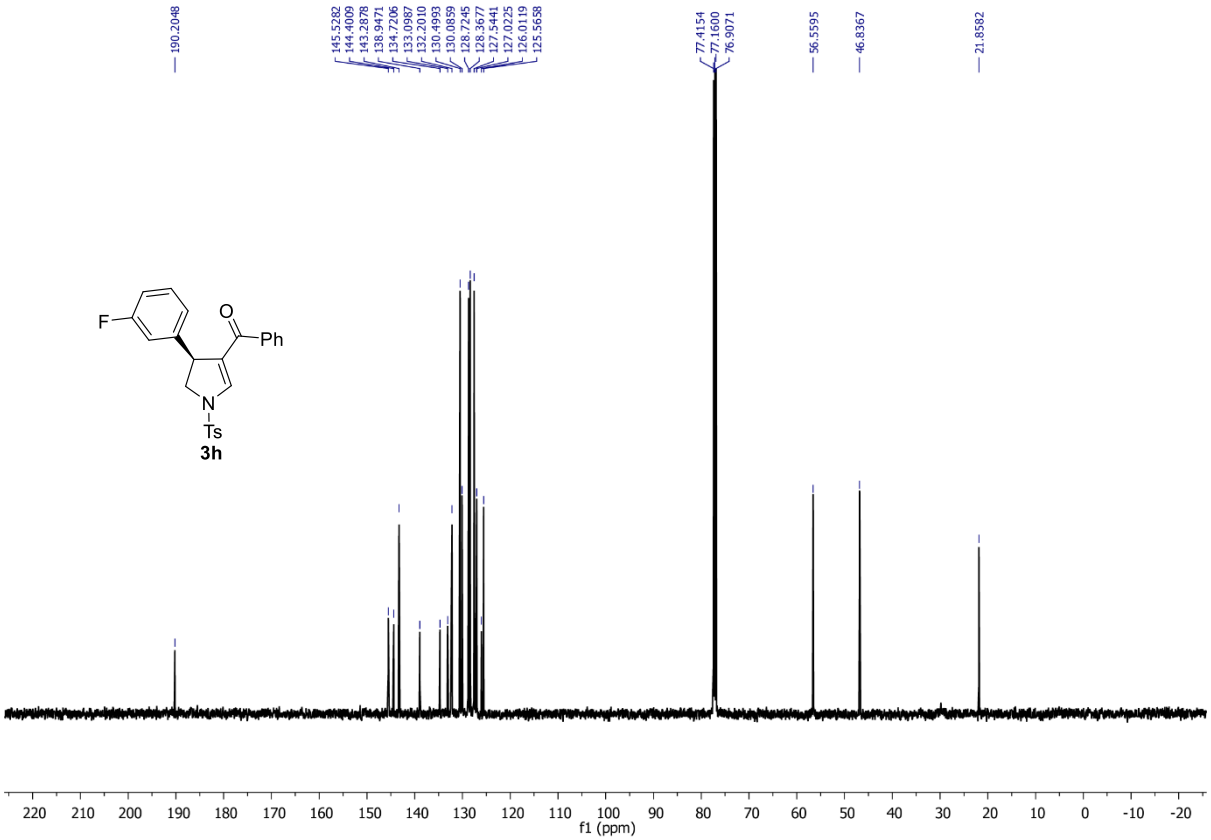



**Figure S32**. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** (125 MHz, $CDCl_3$)

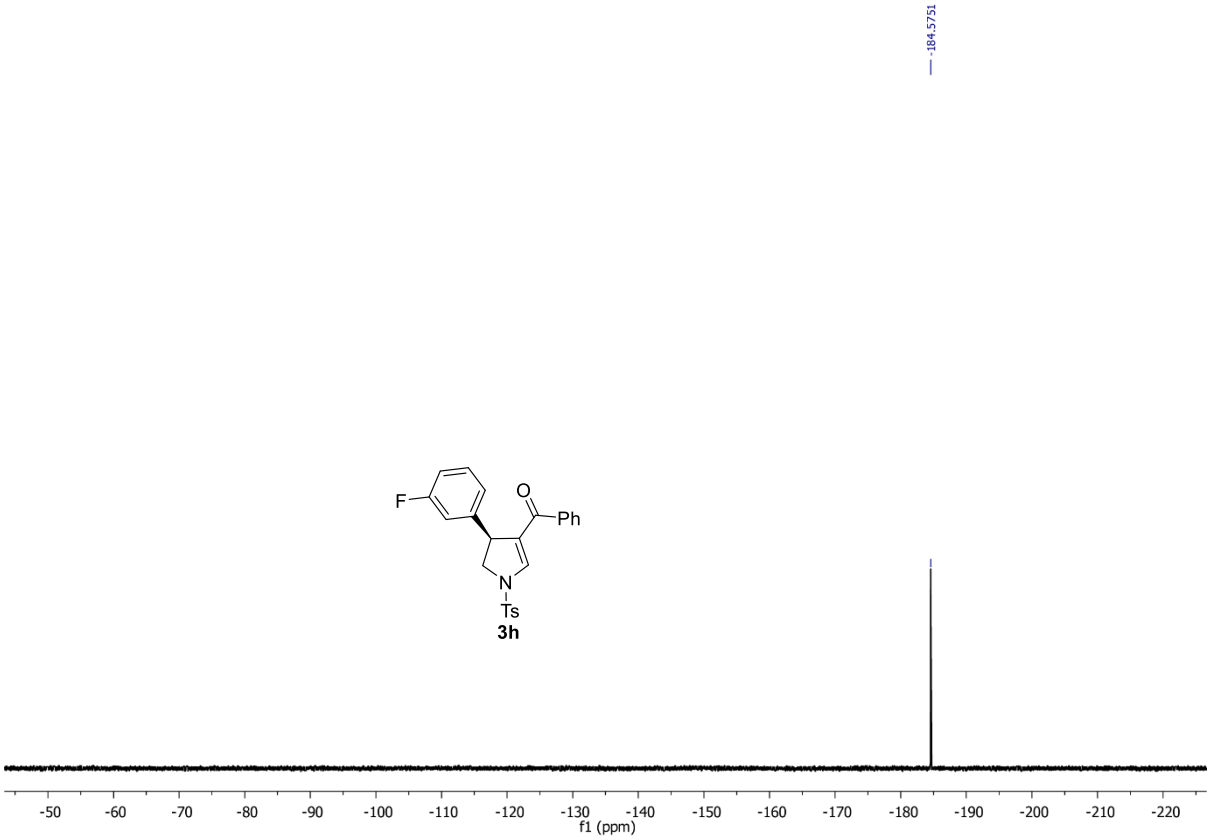
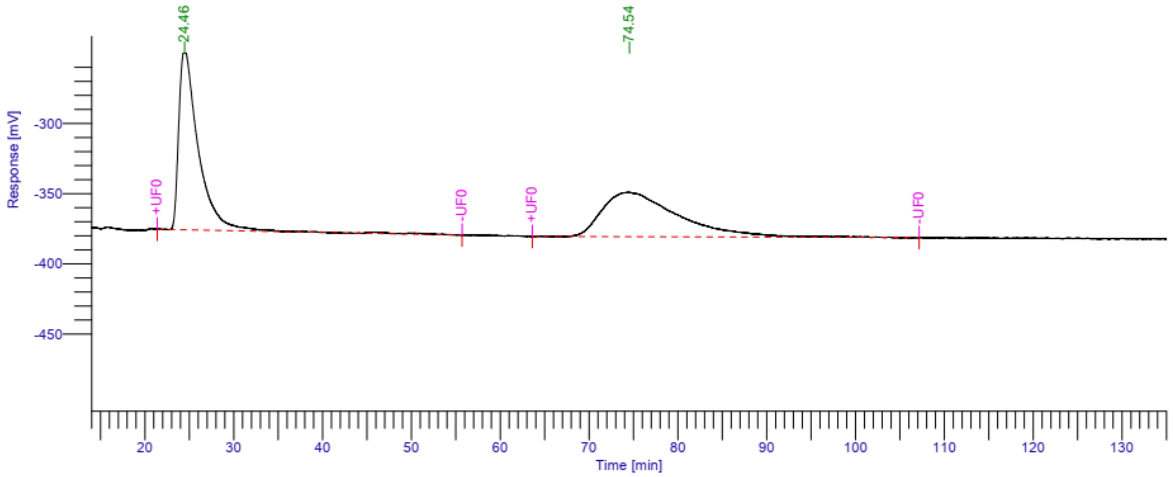



**Figure S33.** $^{19}F$ NMR spectrum of **3h** (500 MHz, $CDCl_3$)

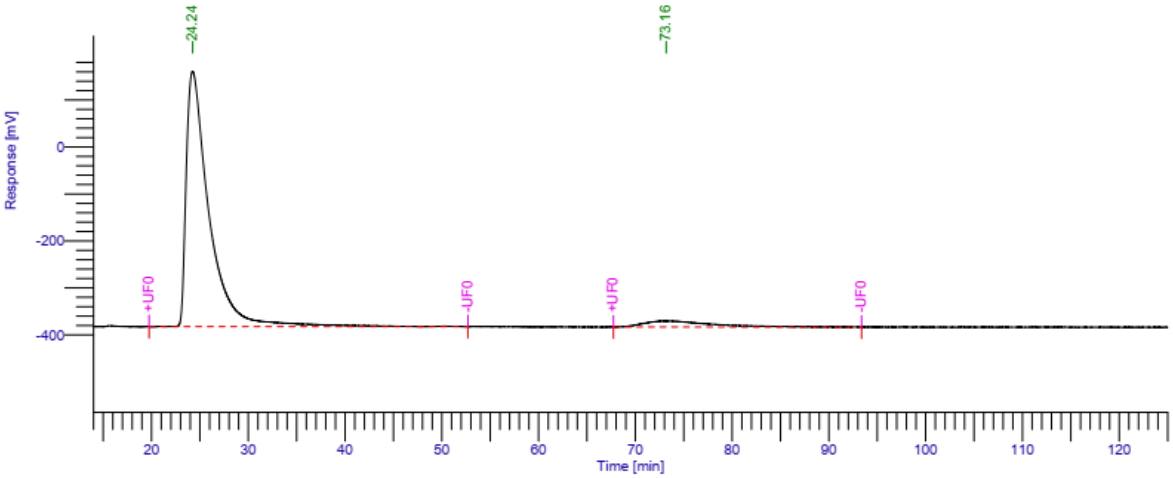



AKS-5-58RAC, AS-H

AKS-5-58RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 24.457 | 19728066.80 | 128812.53 | 51.20 | 51.20 | | | *MM | 19.7281 | 19.7281 |
| 2 | | 74.543 | 18806459.14 | 31707.57 | 48.80 | 48.80 | | | *MM | 18.8065 | 18.8065 |
| | | | 38534525.94 | 160520.10 | 100.00 | 100.00 | | | | 38.5345 | 38.5345 |

**Figure S34**. HPLC chromatogram of racemic compound **3h** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-51CHIRAL, AS-H

AKS-5-51CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 24.244 | 89303055.10 | 543321.82 | 93.57 | 93.57 | | | *MM | 89.3031 | 89.3031 |
| 2 | | 73.165 | 6132391.32 | 12841.07 | 6.43 | 6.43 | | | *MM | 6.1324 | 6.1324 |
| | | | 95435446.42 | 556162.89 | 100.00 | 100.00 | | | | 95.4354 | 95.4354 |

**Figure S35**. HPLC chromatogram of chiral compound **3h** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

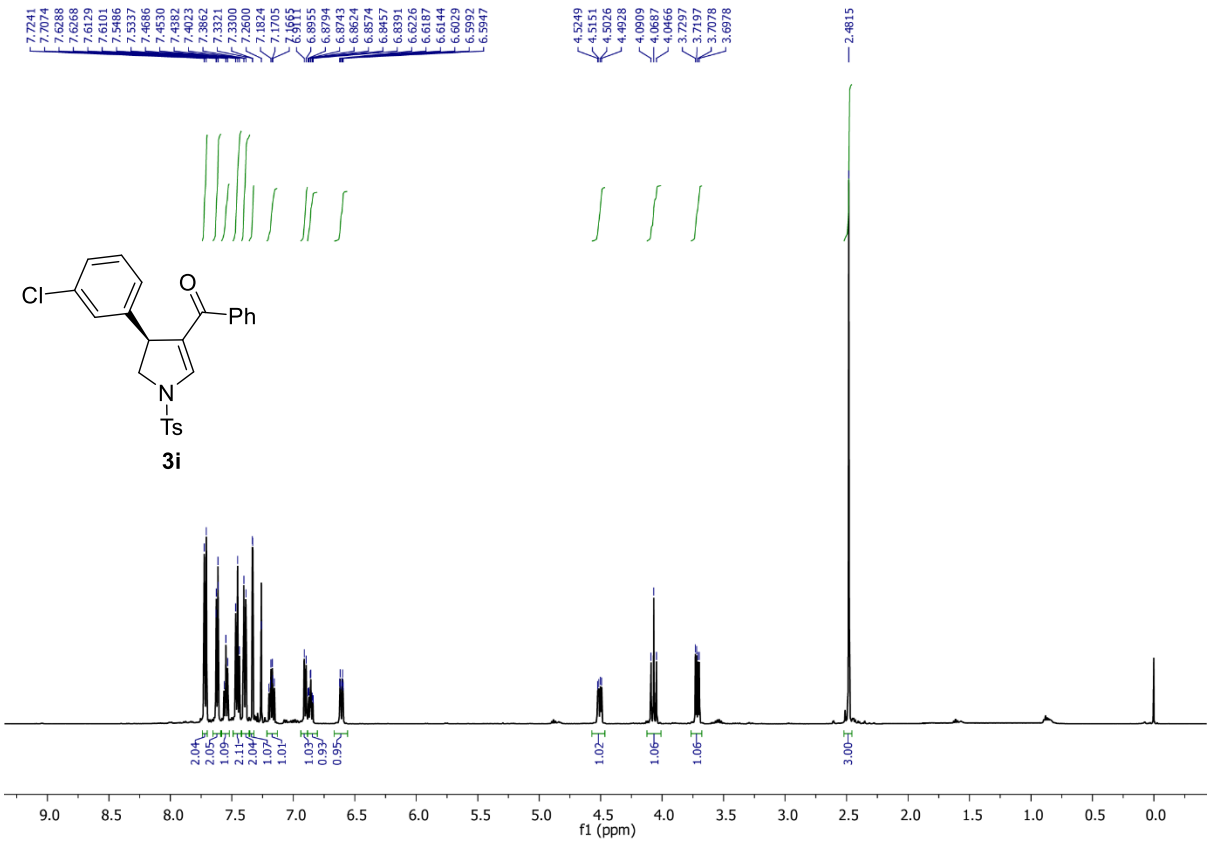



**Figure S36.** $^{1}$H NMR spectrum of **3i** (500 MHz, $CDCl_3$)

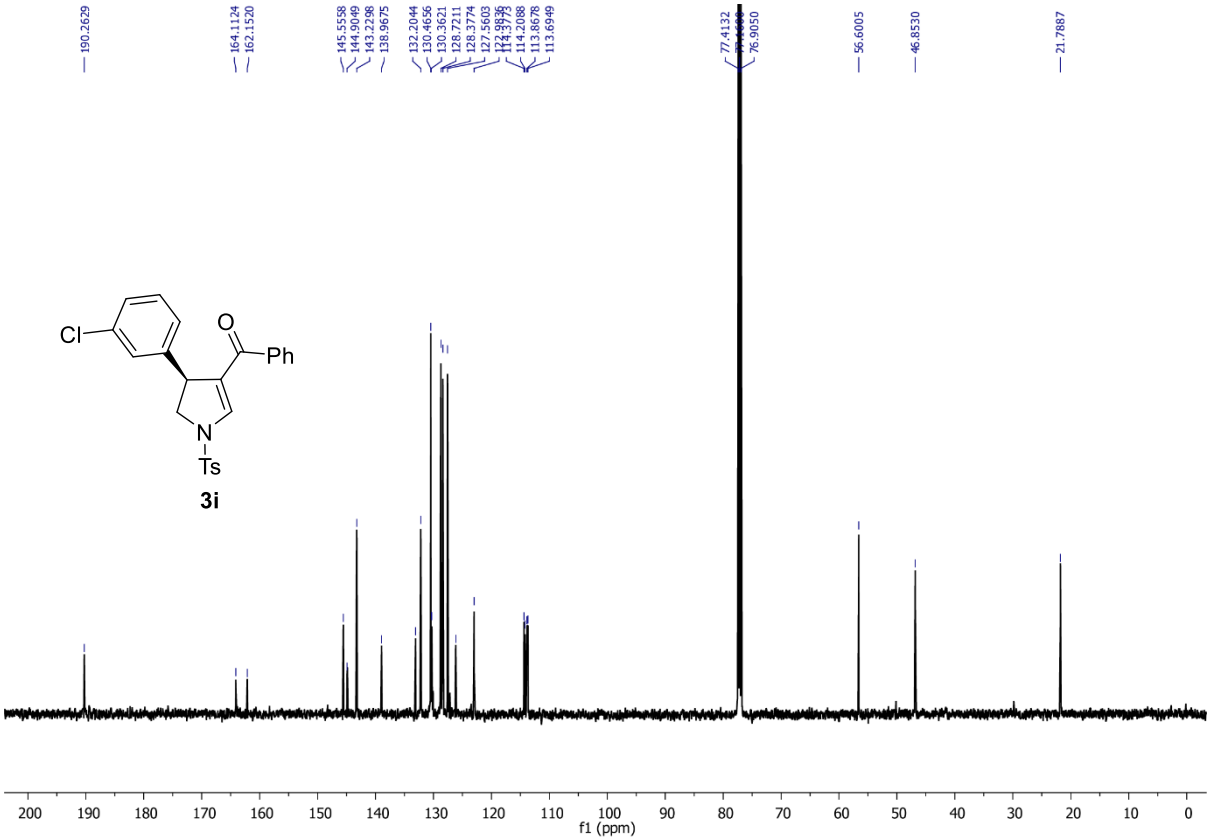
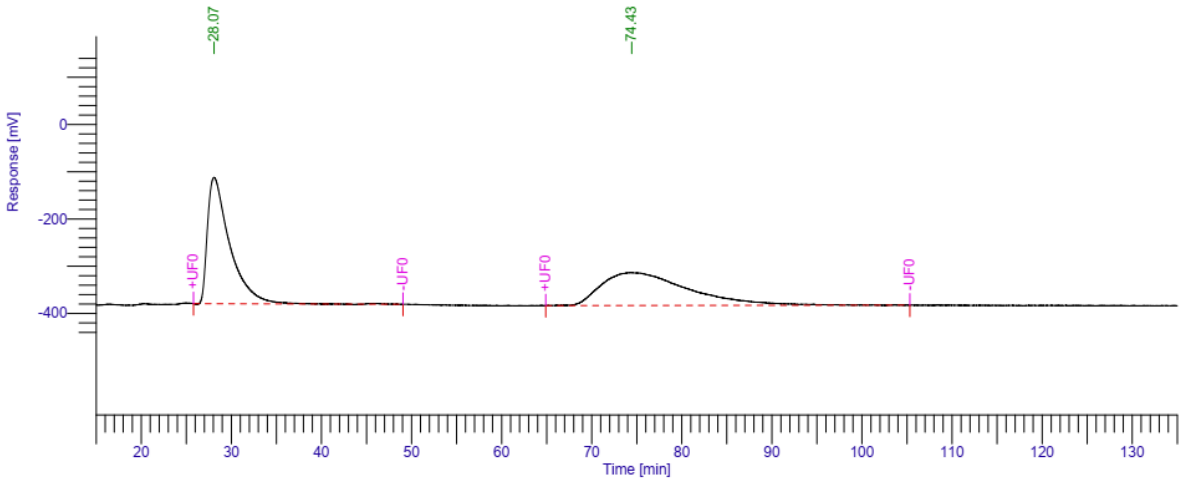



**Figure S37**. $^{13}C\{^{1}H\}$ NMR spectrum of **3i** (125 MHz, $CDCl_3$)

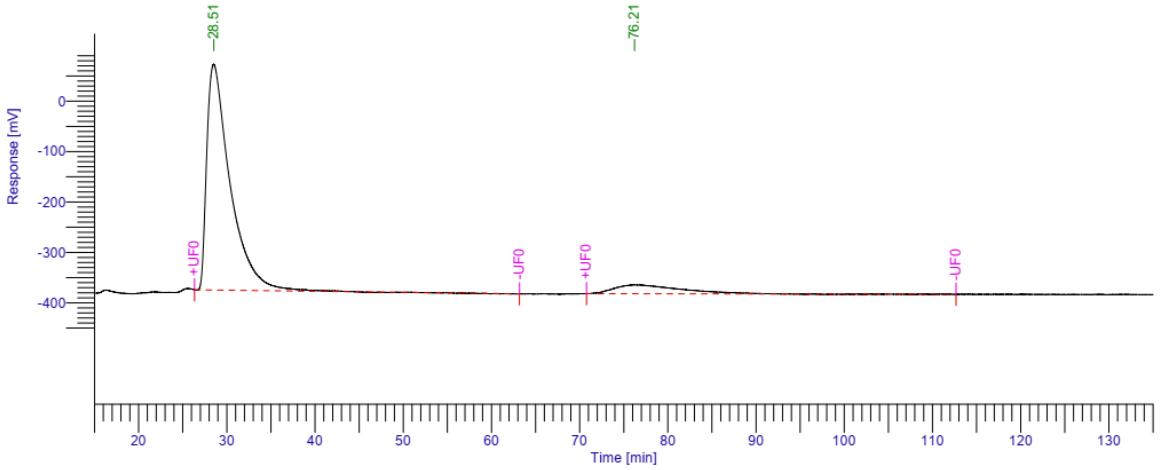



AKS-5-59RAC, AS-H

AKS-5-59RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 28.072 | 46163400.20 | 267242.72 | 49.73 | 49.73 | | | *MM | 46.1634 | 46.1634 |
| 2 | | 74.433 | 46667909.94 | 69606.62 | 50.27 | 50.27 | | | *MM | 46.6679 | 46.6679 |
| | | | 92831310.14 | 336849.34 | 100.00 | 100.00 | | | | 92.8313 | 92.8313 |

**Figure S38**. HPLC chromatogram of racemic compound **3i** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-53CHIRAL, AS-H

AKS-5-53CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 28.512 | 82580202.87 | 447932.14 | 89.87 | 89.87 | | | *MM | 82.5802 | 82.5802 |
| 2 | | 76.208 | 9312374.24 | 17708.33 | 10.13 | 10.13 | | | *MM | 9.3124 | 9.3124 |
| | | | 91892577.11 | 465640.48 | 100.00 | 100.00 | | | | 91.8926 | 91.8926 |

**Figure S39**. HPLC chromatogram of chiral compound **3i** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

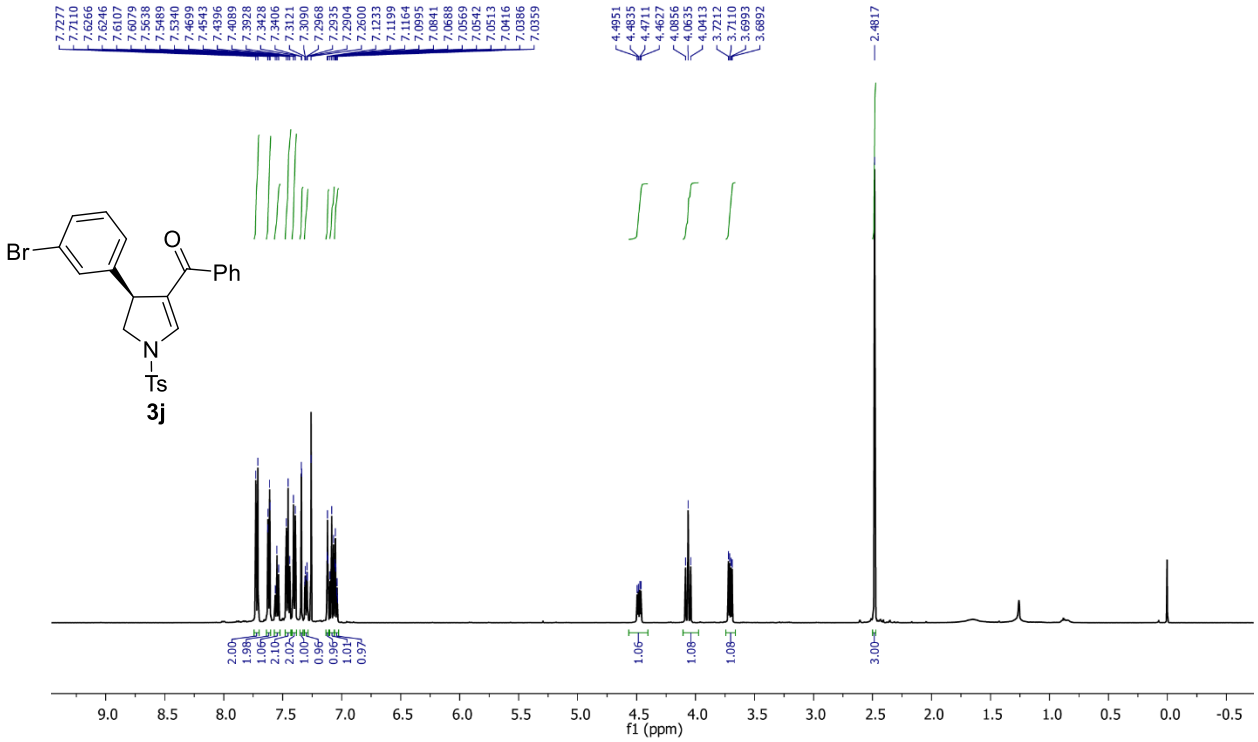



**Figure S40.** $^{1}$H NMR spectrum of **3j** (500 MHz, $CDCl_3$)

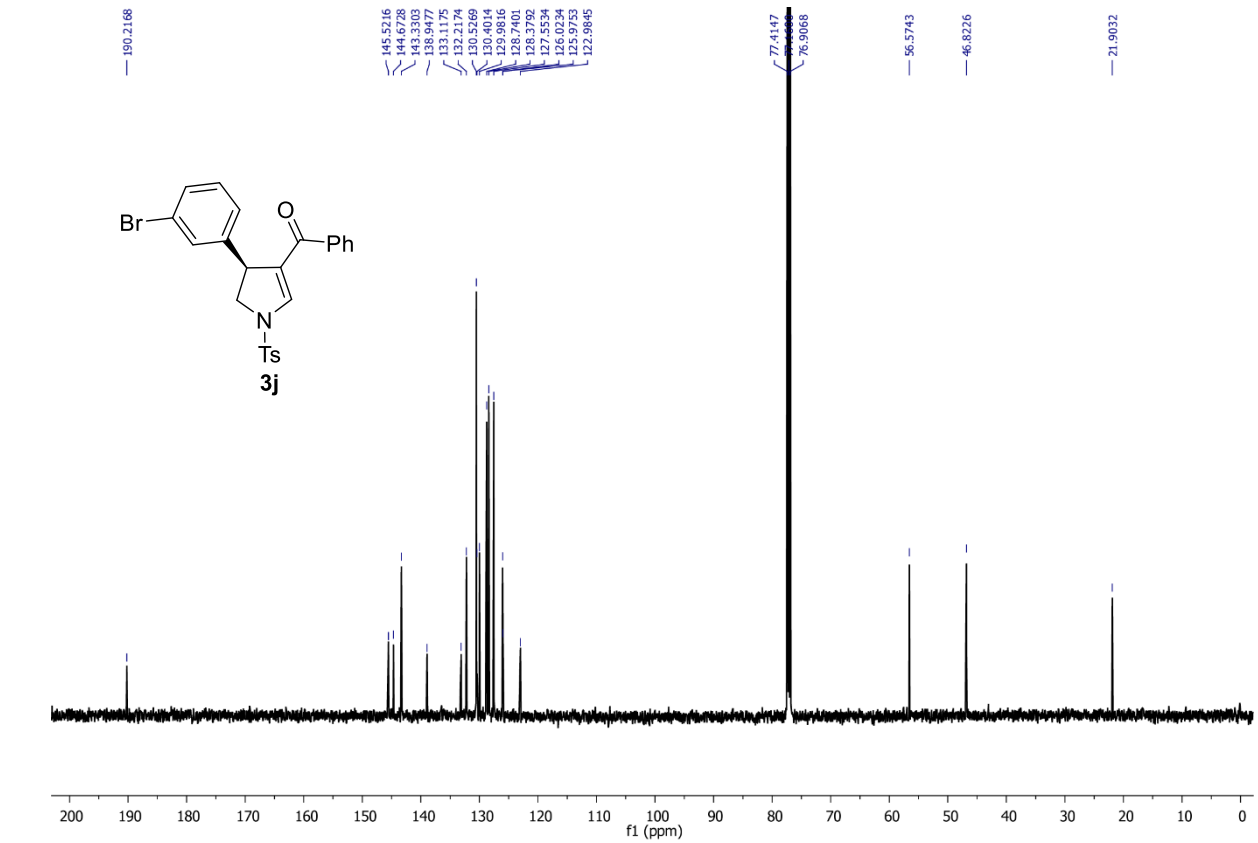
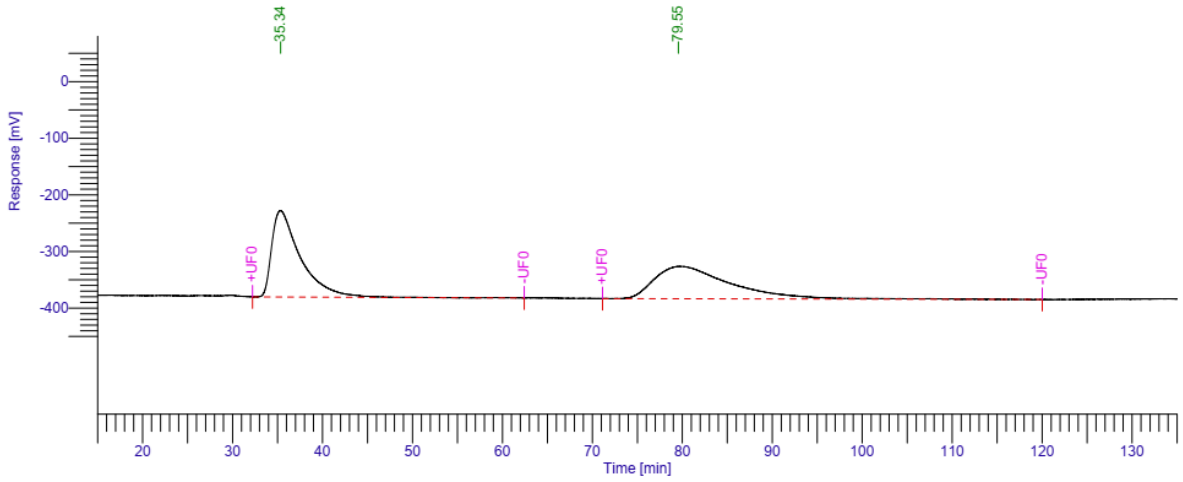



**Figure S41**. $^{13}C\{^{1}H\}$ NMR spectrum of **3j** (125 MHz, $CDCl_3$)

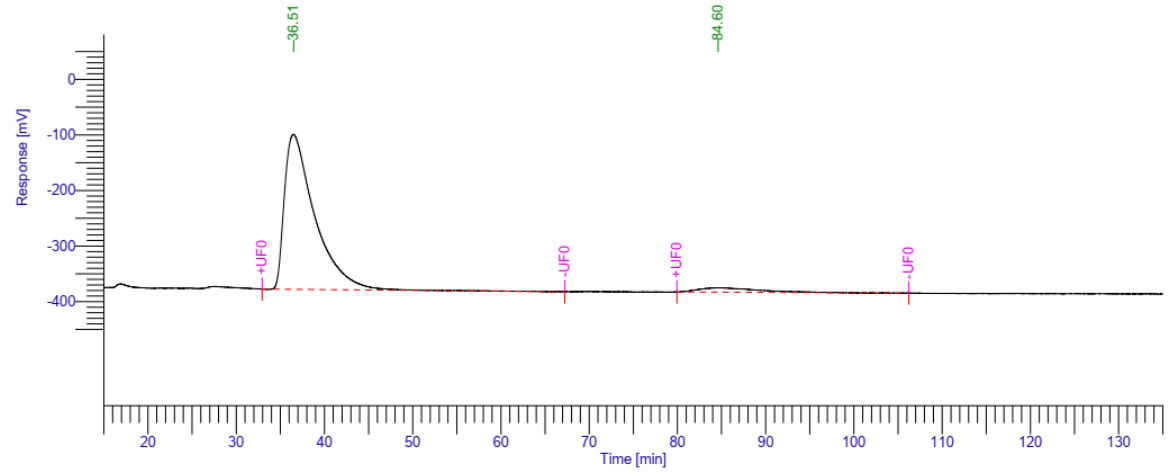



AKS-5-56RAC, AS-H

AKS-5-56RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 35.339 | 33793543.50 | 152377.68 | 50.17 | 50.17 | | | *MM | 33.7935 | 33.7935 |
| 2 | | 79.552 | 33564852.70 | 57284.64 | 49.83 | 49.83 | | | *MM | 33.5649 | 33.5649 |
| | | | 67358396.20 | 209662.33 | 100.00 | 100.00 | | | | 67.3584 | 67.3584 |

**Figure S42**. HPLC chromatogram of racemic compound **3j** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-55CHIRAL, AS-H

AKS-5-55CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 36.505 | 66767972.06 | 278915.33 | 94.80 | 94.80 | | | *MM | 66.7680 | 66.7680 |
| 2 | | 84.597 | 3659405.88 | 7727.93 | 5.20 | 5.20 | | | *MM | 3.6594 | 3.6594 |
| | | | 70427377.95 | 286643.26 | 100.00 | 100.00 | | | | 70.4274 | 70.4274 |

**Figure S43**. HPLC chromatogram of chiral compound **3j** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

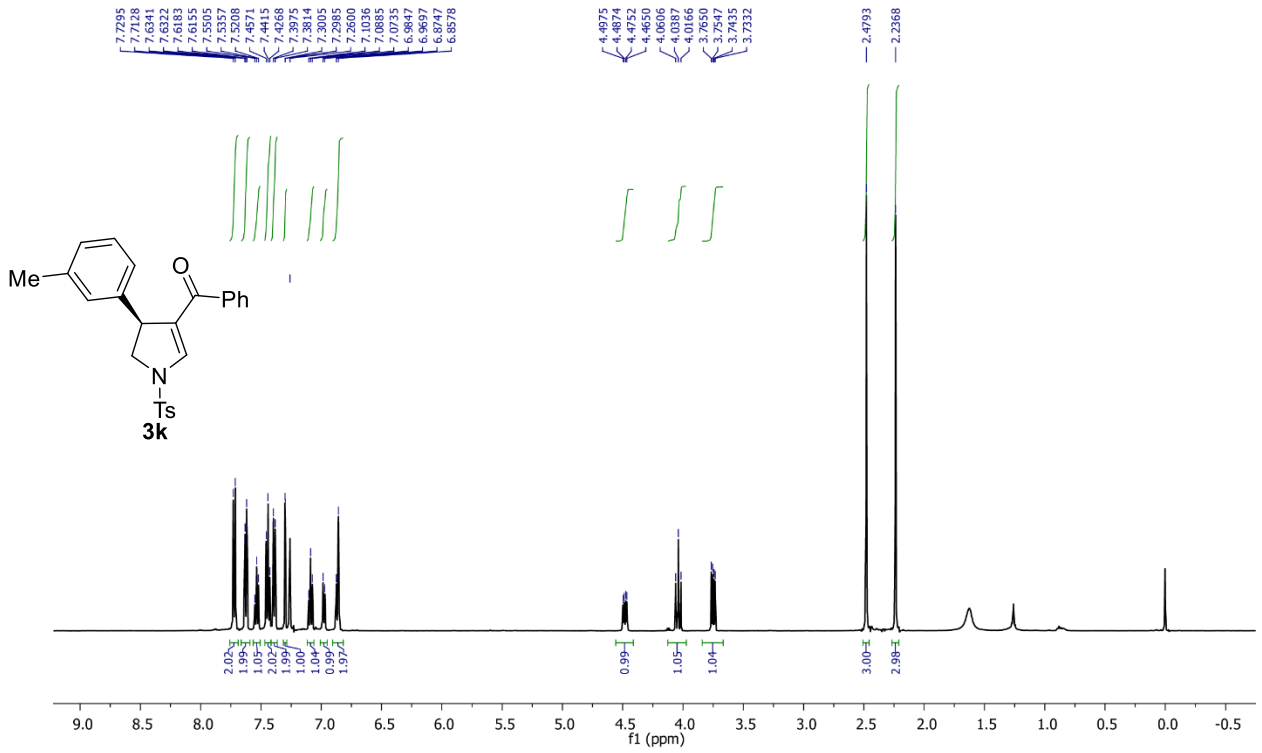



**Figure S44.** $^{1}$H NMR spectrum of **3k** (500 MHz, $CDCl_3$)

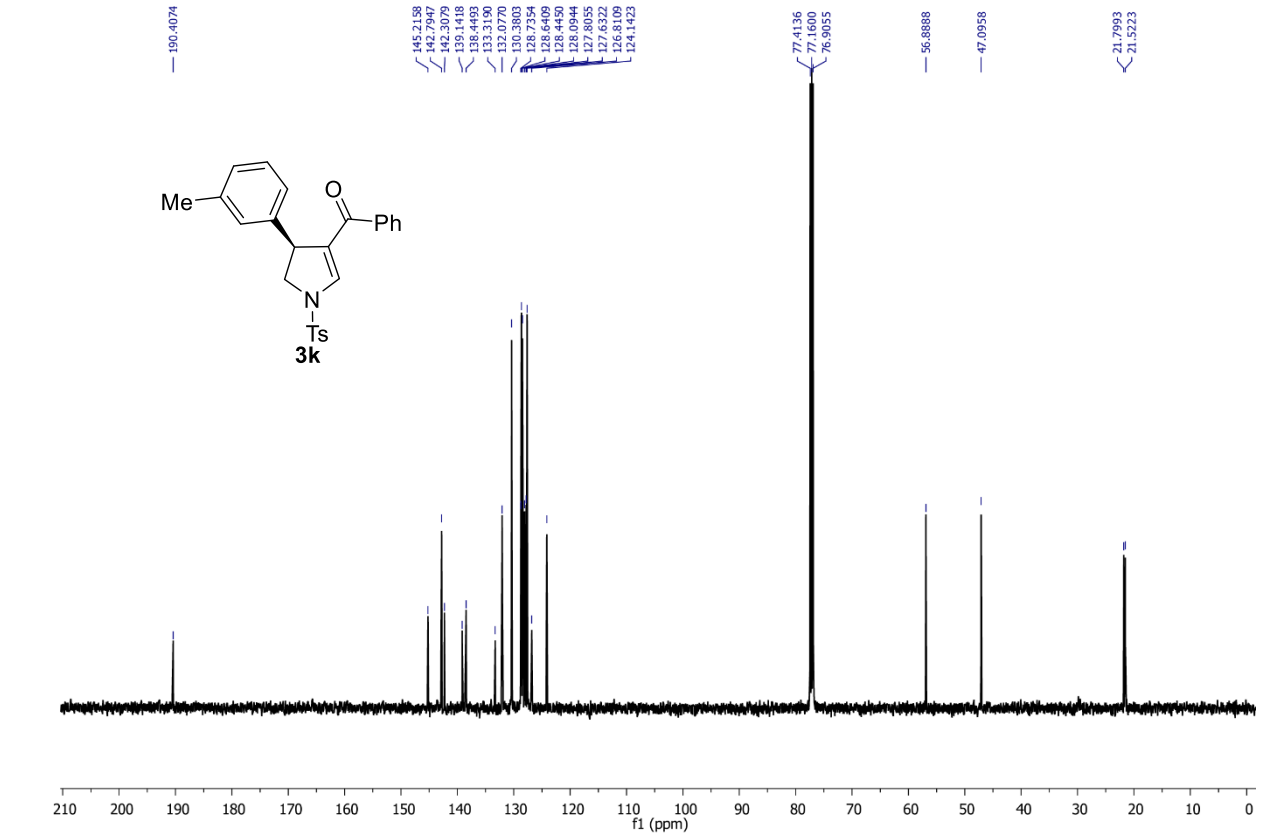
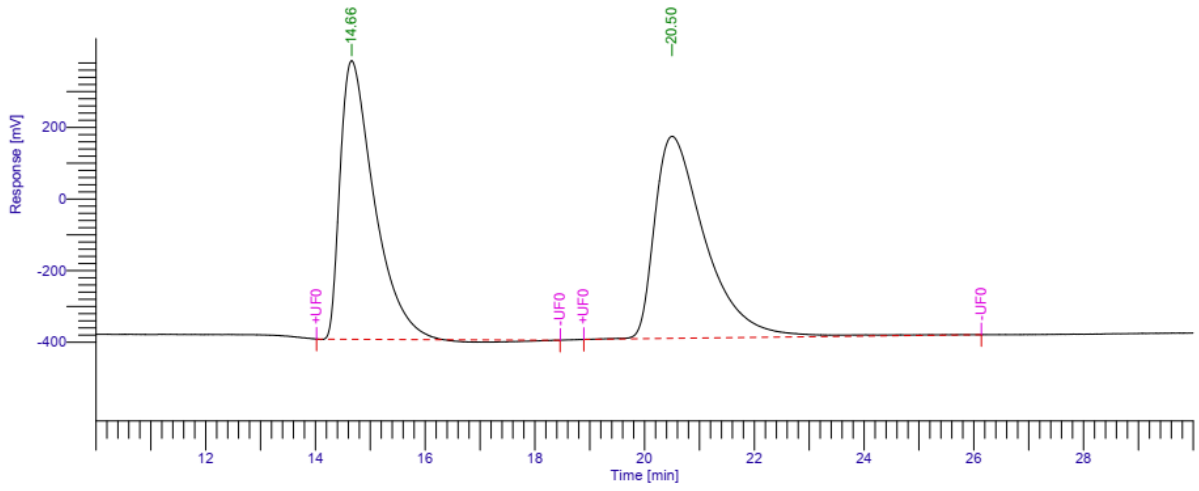



**Figure S45**. $^{13}C\{^{1}H\}$ NMR spectrum of **3k** (125 MHz, $CDCl_3$)

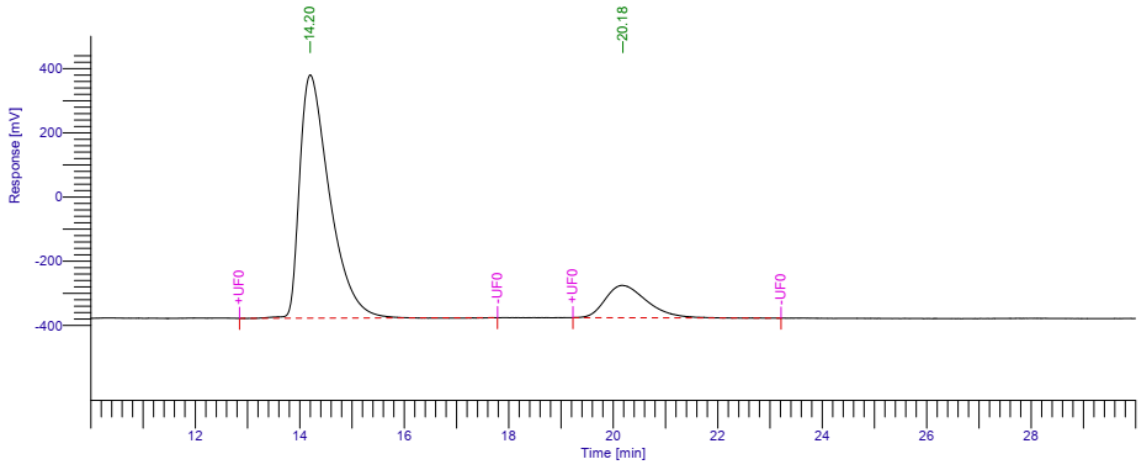



AKS-5-62RAC, OD-H

AKS-5-62RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 14.659 | 33608949.95 | 778296.07 | 48.22 | 48.22 | | | *MM | 33.6089 | 33.6089 |
| 2 | | 20.497 | 36088493.19 | 564351.14 | 51.78 | 51.78 | | | *MM | 36.0885 | 36.0885 |
| | | | 69697443.14 | 1.34e+06 | 100.00 | 100.00 | | | | 69.6974 | 69.6974 |

**Figure S46**. HPLC chromatogram of racemic compound **3k** (OD-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-61CHIRAL, OD-H

AKS-5-61CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 14.197 | 30093577.85 | 757680.02 | 84.46 | 84.46 | | | *MM | 30.0936 | 30.0936 |
| 2 | | 20.181 | 5538586.18 | 100755.35 | 15.54 | 15.54 | | | *MM | 5.5386 | 5.5386 |
| | | | 35632164.04 | 858435.36 | 100.00 | 100.00 | | | | 35.6322 | 35.6322 |

**Figure S47**. HPLC chromatogram of chiral compound **3k** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

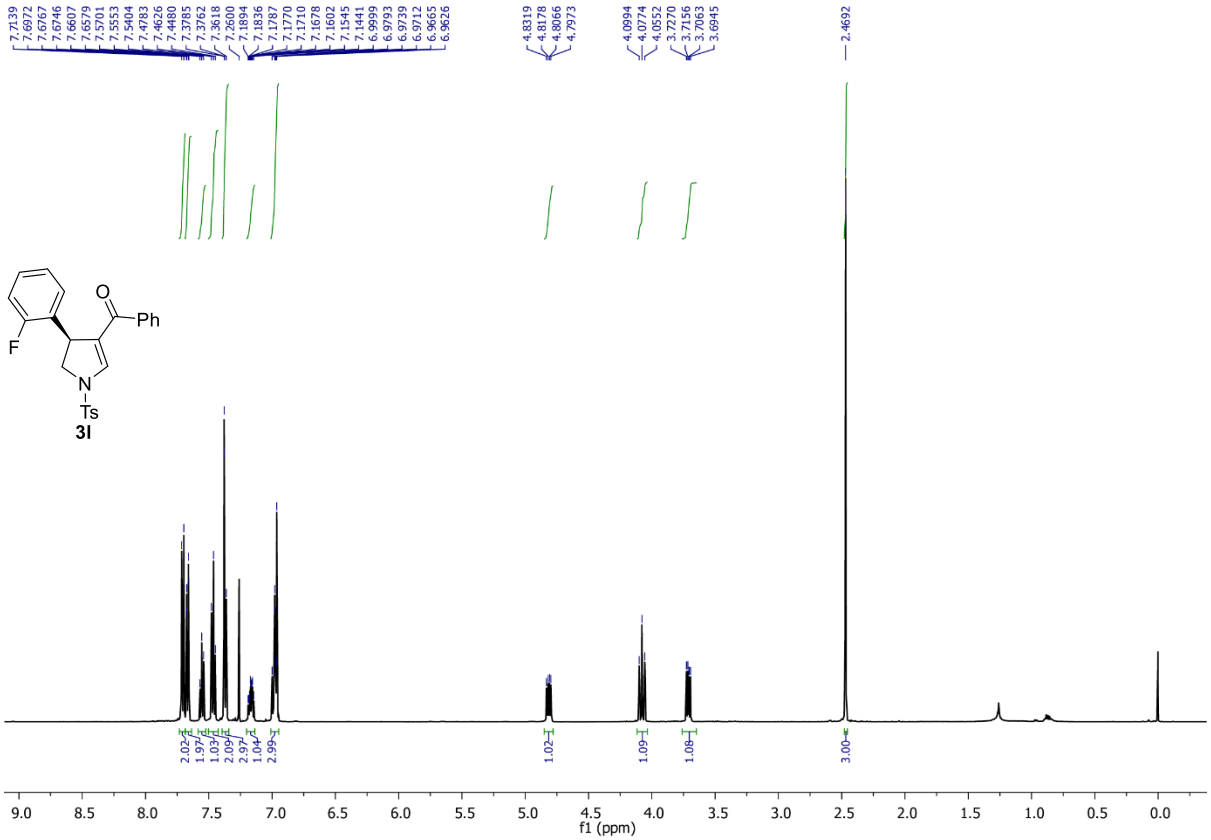



**Figure S48.** $^{1}$H NMR spectrum of **3l** (500 MHz, $CDCl_3$)

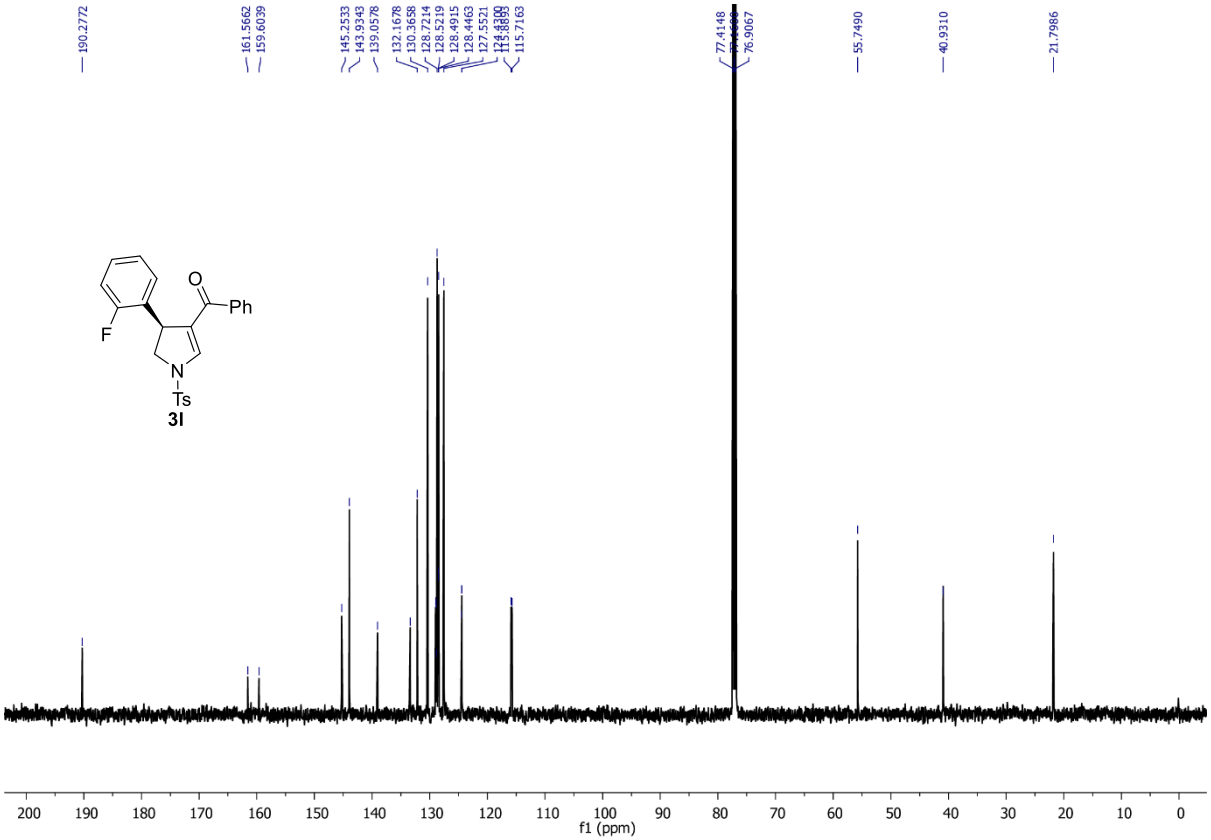



**Figure S49**. $^{13}C\{^{1}H\}$ NMR spectrum of **3l** (125 MHz, $CDCl_3$)

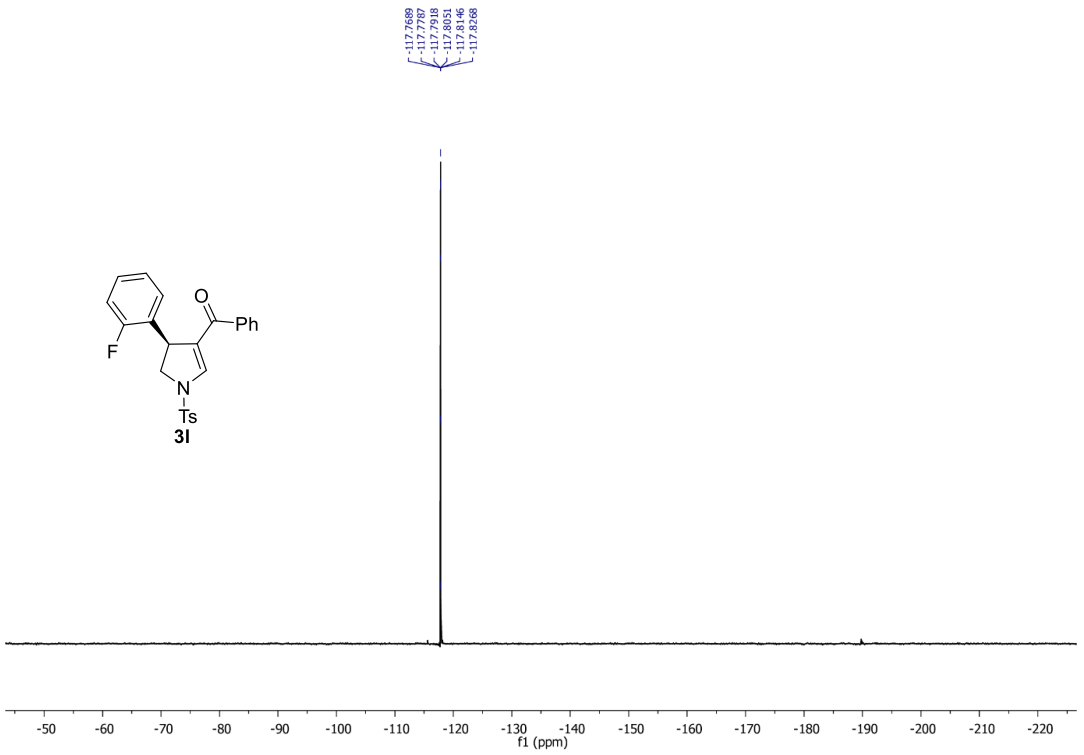
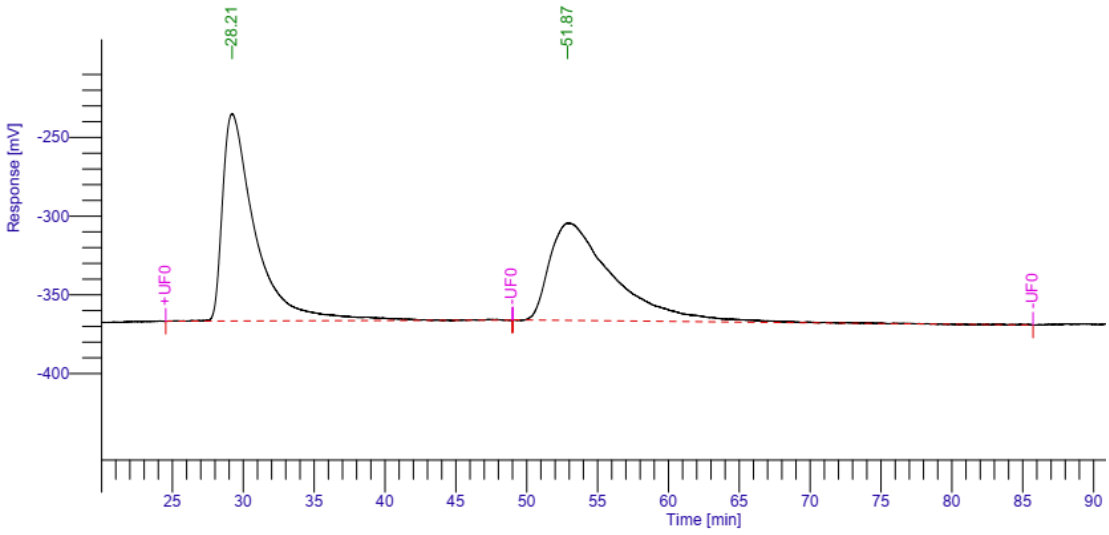



**Figure S50.** $^{19}F$ NMR spectrum of **3l** (500 MHz, $CDCl_3$)

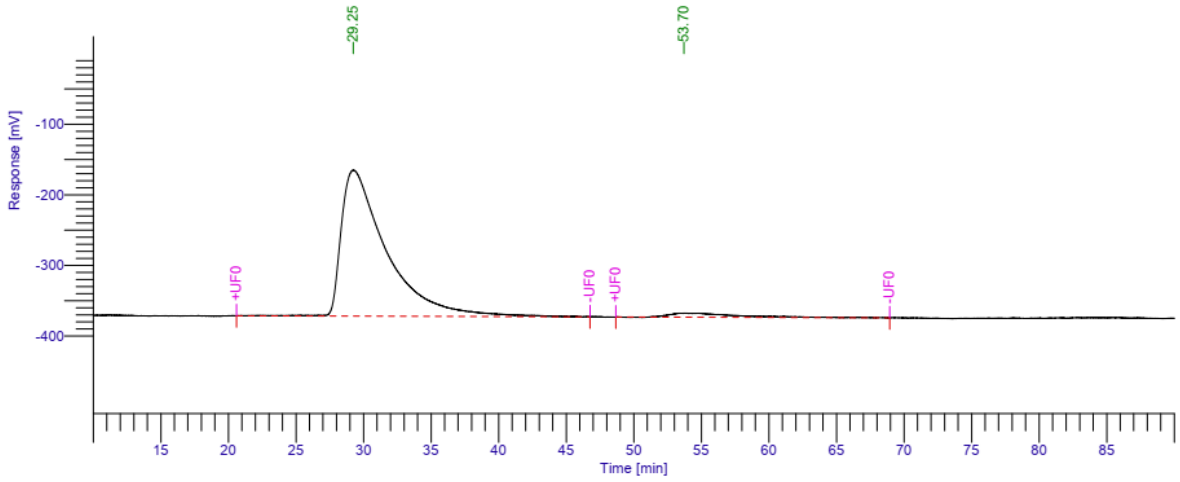



AKS-5-65RAC, AS-H

AKS-5-65RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 28.207 | 21106177.70 | 131700.61 | 52.07 | 52.07 | | | *MM | 21.1062 | 21.1062 |
| 2 | | 51.872 | 19425578.16 | 61811.21 | 47.93 | 47.93 | | | *MM | 19.4256 | 19.4256 |
| | | | 40531755.87 | 193511.82 | 100.00 | 100.00 | | | | 40.5318 | 40.5318 |

**Figure S51**. HPLC chromatogram of racemic compound **3l** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-64CHIRAL, AS-H

AKS-5-64CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 29.245 | 47758982.87 | 206976.55 | 95.96 | 95.96 | | | *MM | 47.7590 | 47.7590 |
| 2 | | 53.702 | 2010171.06 | 5840.45 | 4.04 | 4.04 | | | *MM | 2.0102 | 2.0102 |
| | | | 49769153.93 | 212817.00 | 100.00 | 100.00 | | | | 49.7692 | 49.7692 |

**Figure S52**. HPLC chromatogram of chiral compound **3l** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

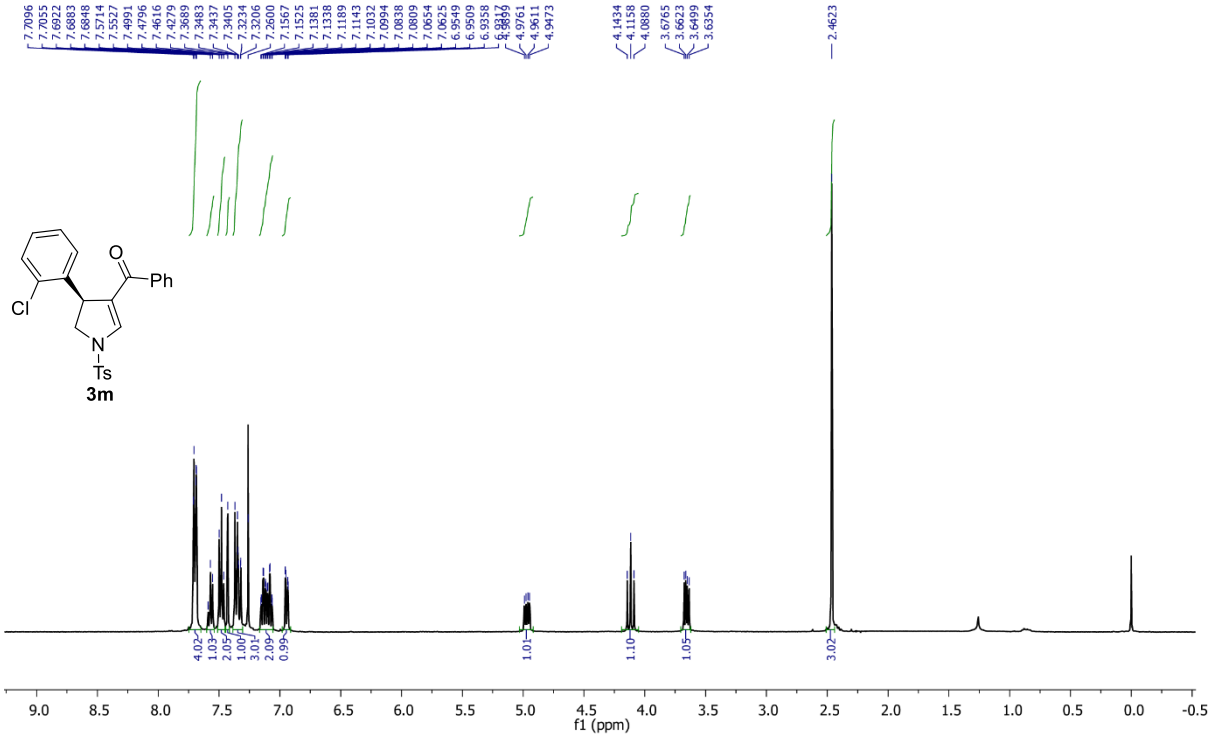



**Figure S53.** $^{1}H$ NMR spectrum of **3m** (500 MHz, $CDCl_3$)

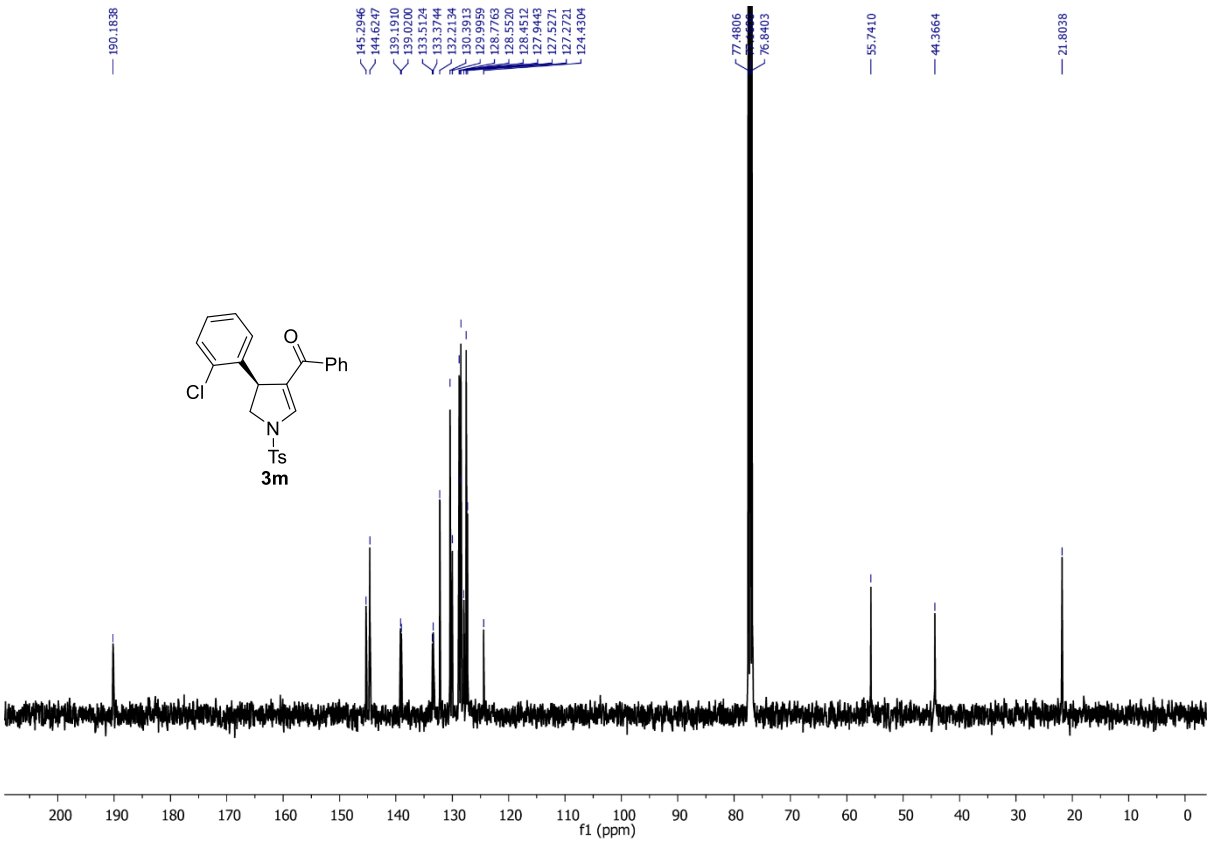
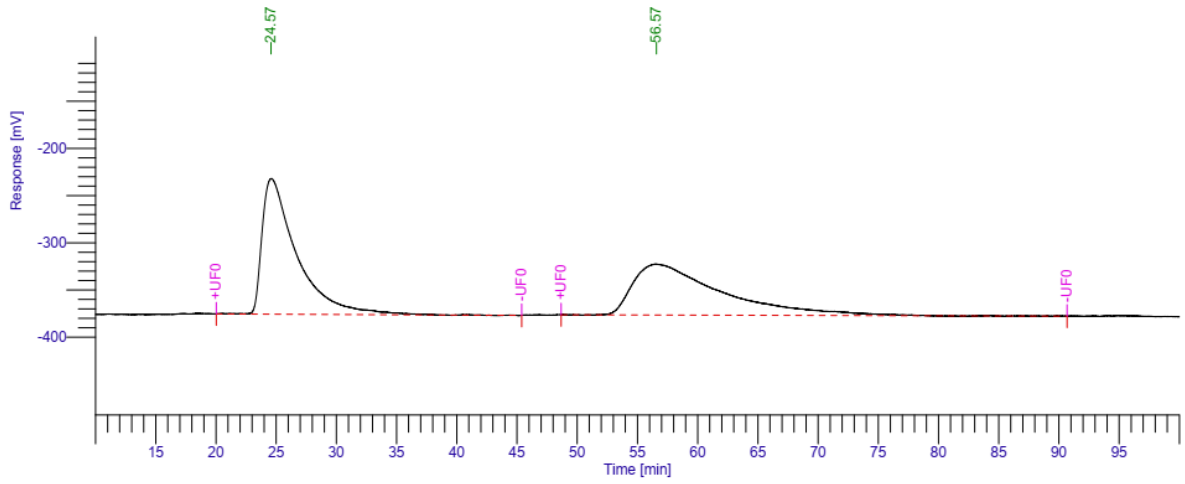



**Figure S54**. $^{13}C\{^{1}H\}$ NMR spectrum of **3m** (125 MHz, $CDCl_3$)

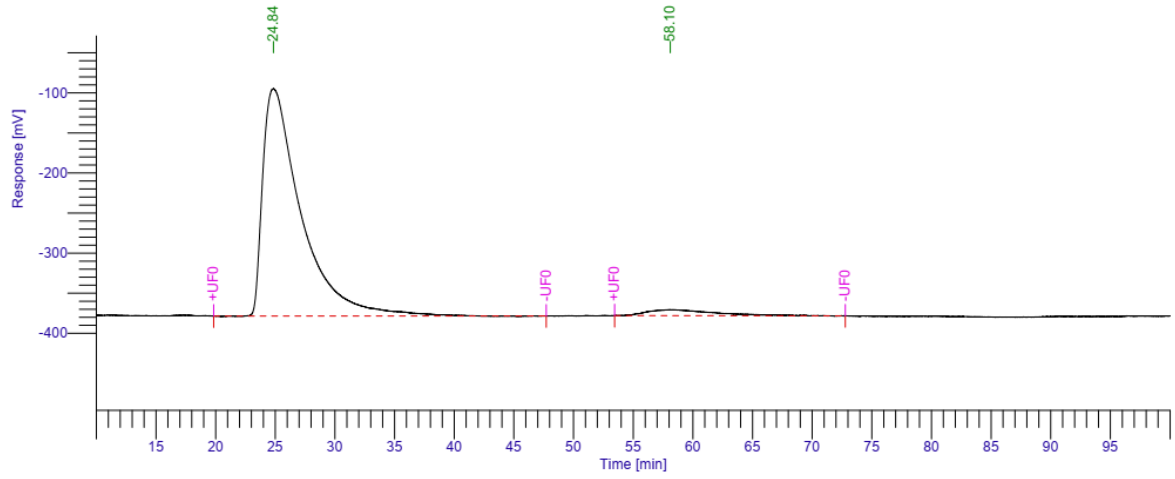



AKS-5-67RAC, AS-H

AKS-5-67RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 24.567 | 28676016.40 | 143607.50 | 51.20 | 51.20 | | | *MM | 28.6760 | 28.6760 |
| 2 | | 56.569 | 27333129.28 | 54059.89 | 48.80 | 48.80 | | | *MM | 27.3331 | 27.3331 |
| | | | 56009145.68 | 197667.39 | 100.00 | 100.00 | | | | 56.0091 | 56.0091 |

**Figure S55**. HPLC chromatogram of racemic compound **3m** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-66CHIRAL, AS-H

AKS-5-66CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 24.838 | 63235687.05 | 283735.81 | 95.57 | 95.57 | | | *MM | 63.2357 | 63.2357 |
| 2 | | 58.102 | 2934547.11 | 7485.26 | 4.43 | 4.43 | | | *MM | 2.9345 | 2.9345 |
| | | | 66170234.16 | 291221.07 | 100.00 | 100.00 | | | | 66.1702 | 66.1702 |

**Figure S56**. HPLC chromatogram of chiral compound **3m** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

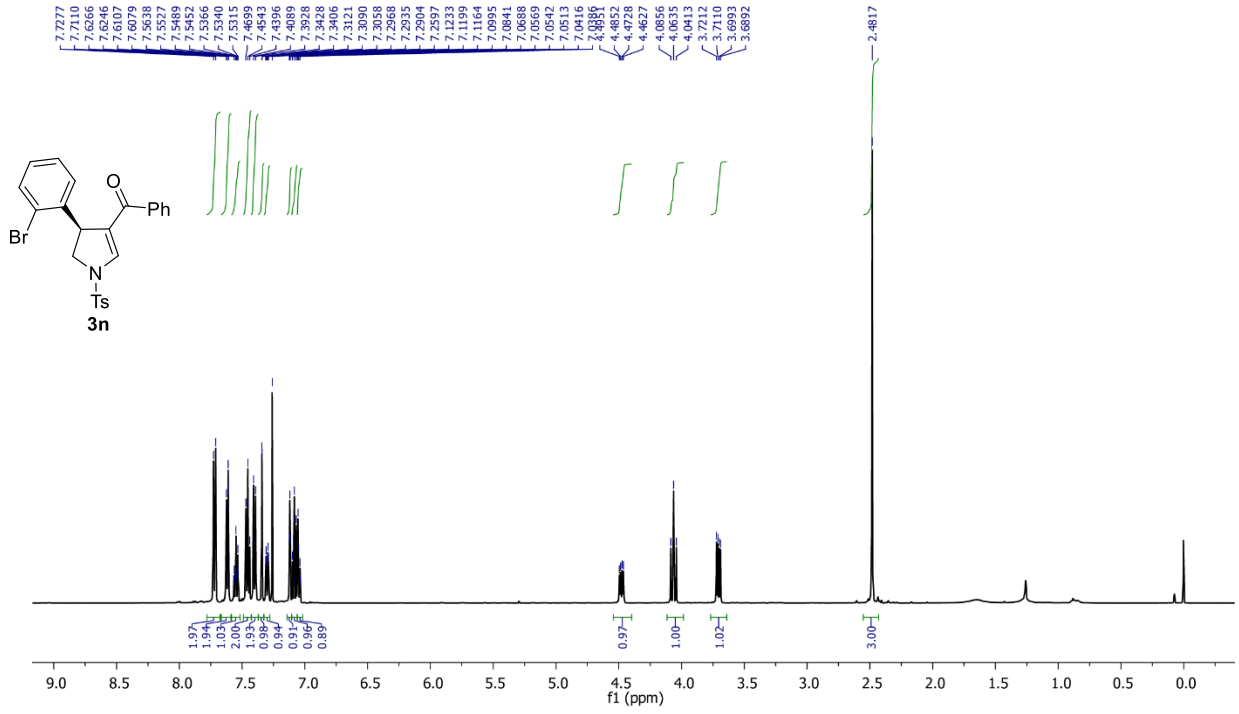



**Figure S57.** $^{1}H$ NMR spectrum of **3n** (500 MHz, $CDCl_3$)

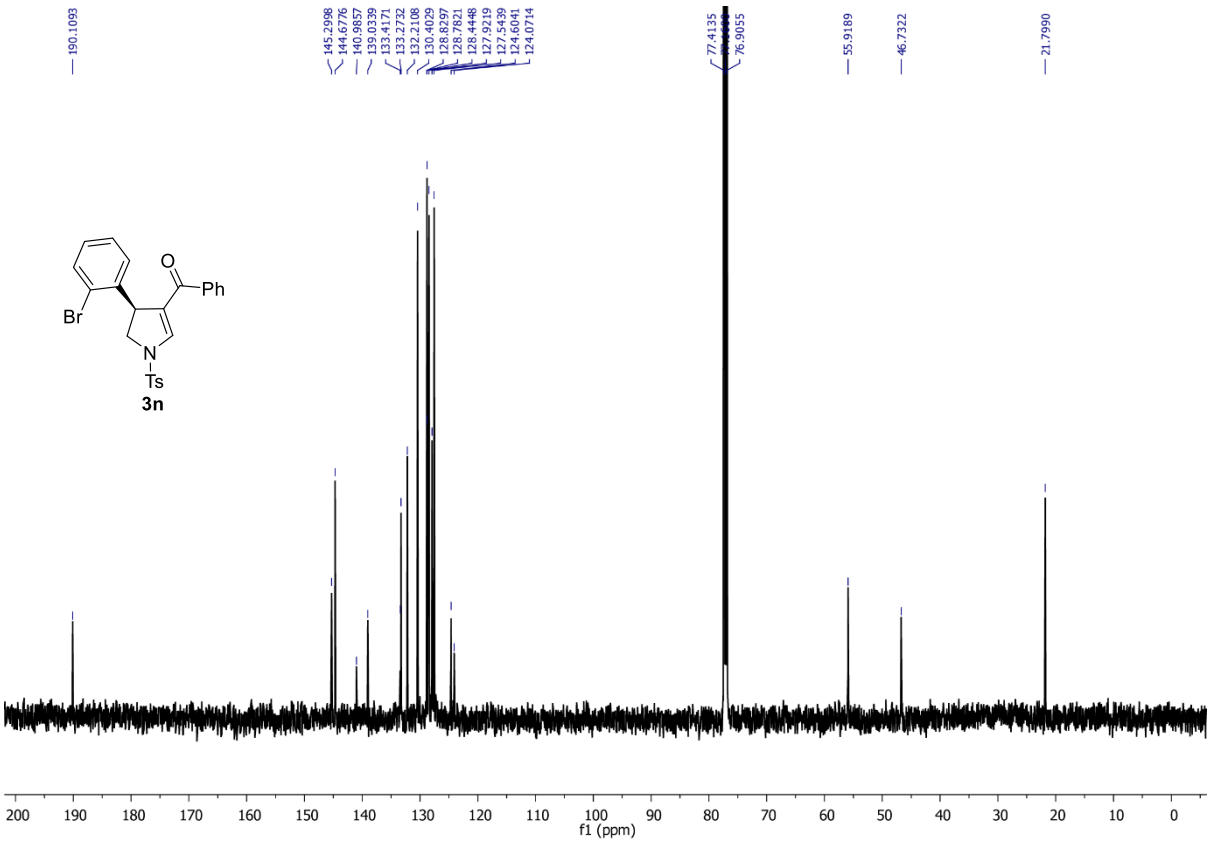
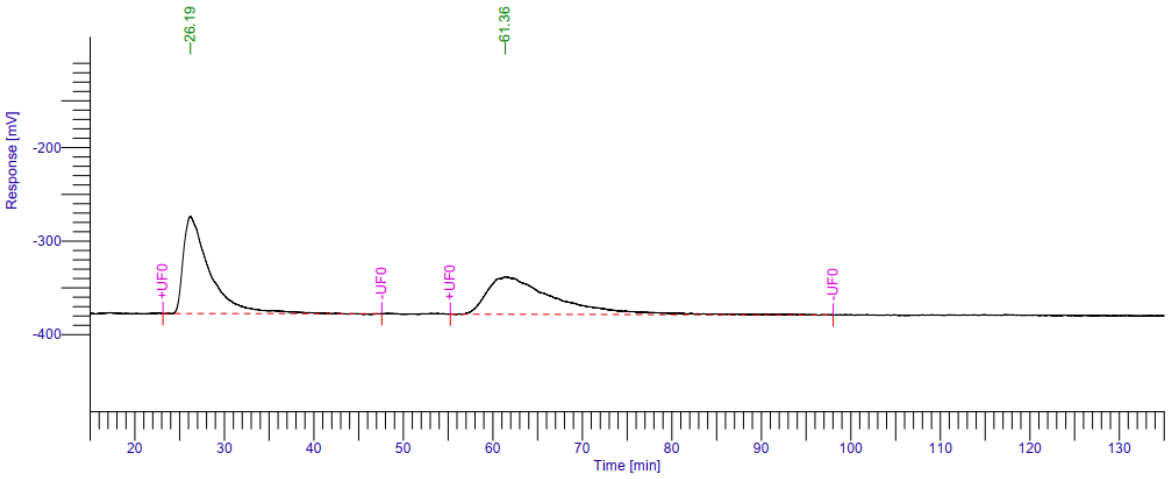



**Figure S58**. $^{13}C\{^{1}H\}$ NMR spectrum of **3n** (125 MHz, $CDCl_3$)

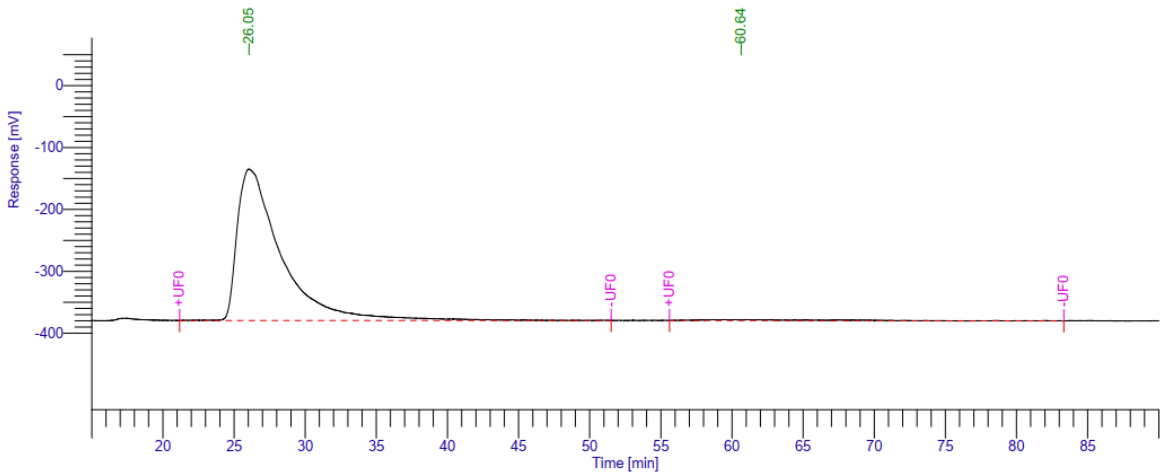



AKS-5-69RAC, AS-H

AKS-5-69RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 26.195 | 21345380.03 | 104043.98 | 50.51 | 50.51 | | | *MM | 21.3454 | 21.3454 |
| 2 | | 61.358 | 20915258.80 | 40059.35 | 49.49 | 49.49 | | | *MM | 20.9153 | 20.9153 |
| | | | 42260638.83 | 144103.32 | 100.00 | 100.00 | | | | 42.2606 | 42.2606 |

**Figure S59**. HPLC chromatogram of chiral compound **3n** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-68CHIRAL, AS-H

AKS-5-68CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 26.048 | 52513757.00 | 244679.88 | 98.42 | 98.42 | | | *MM | 52.5138 | 52.5138 |
| 2 | | 60.639 | 843846.22 | 1566.34 | 1.58 | 1.58 | | | *MM | 0.8438 | 0.8438 |
| | | | 53357603.22 | 246246.22 | 100.00 | 100.00 | | | | 53.3576 | 53.3576 |

**Figure S60**. HPLC chromatogram of chiral compound **3n** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

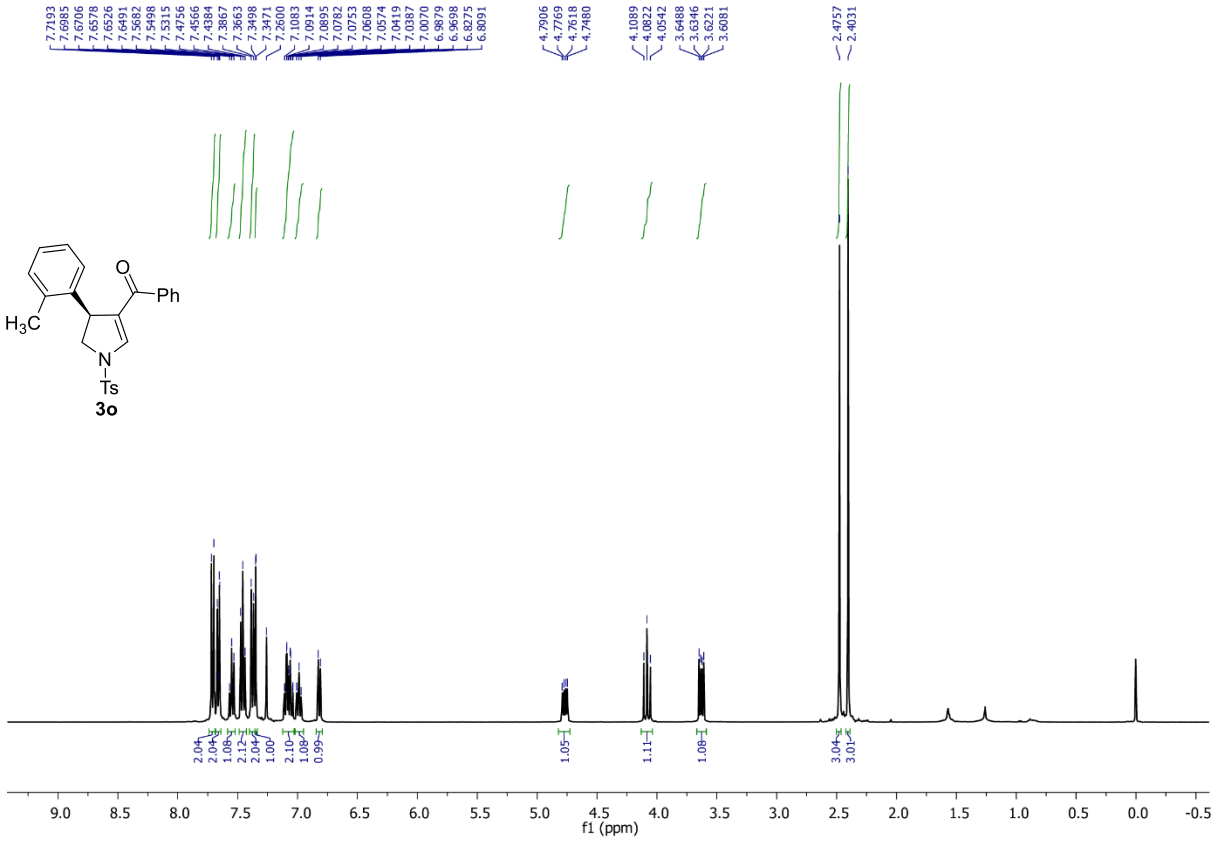



**Figure S61.** $^{1}H$ NMR spectrum of **3o** (500 MHz, $CDCl_3$)

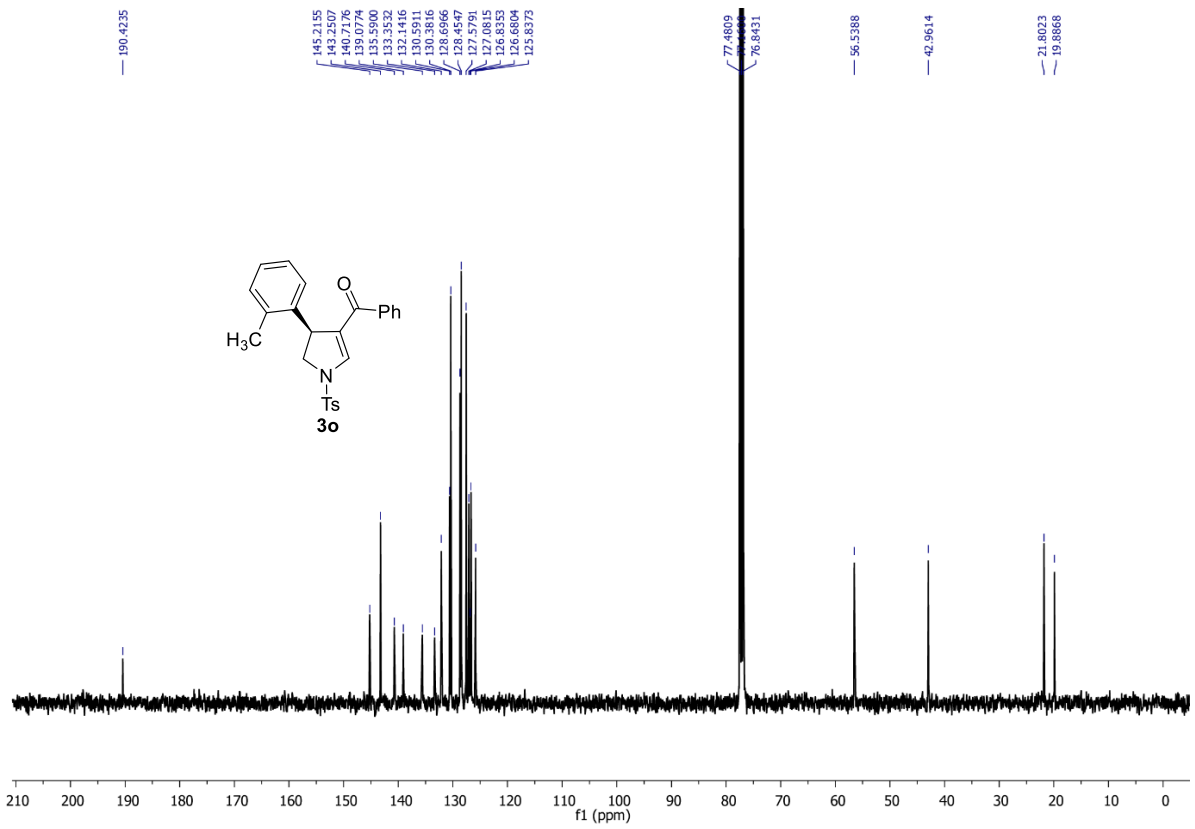
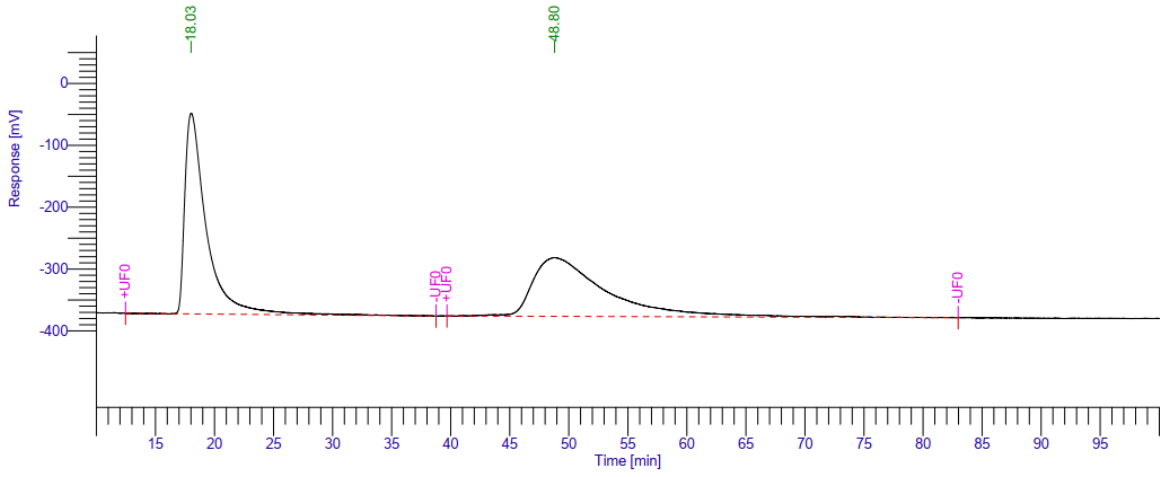



**Figure S62**. $^{13}C\{^{1}H\}$ NMR spectrum of **3o** (125 MHz, $CDCl_3$)

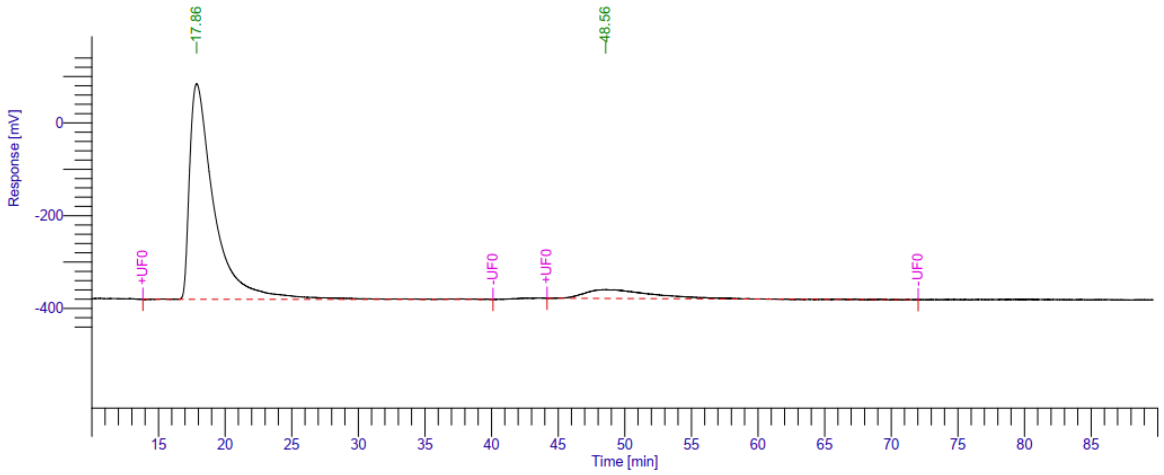



AKS-5-71RAC, AS-H

AKS-5-71RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 18.025 | 41276578.71 | 324539.71 | 50.19 | 50.19 | | | *MM | 41.2766 | 41.2766 |
| 2 | | 48.796 | 40971695.56 | 94931.23 | 49.81 | 49.81 | | | *MM | 40.9717 | 40.9717 |
| | | | 82248274.27 | 419470.94 | 100.00 | 100.00 | | | | 82.2483 | 82.2483 |

**Figure S63**. HPLC chromatogram of chiral compound **3o** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-70CHIRAL, AS-H

AKS-5-70CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 17.864 | 59588266.53 | 464696.12 | 90.02 | 90.02 | | | *MM | 59.5883 | 59.5883 |
| 2 | | 48.561 | 6606737.64 | 19029.17 | 9.98 | 9.98 | | | *MM | 6.6067 | 6.6067 |
| | | | 66195004.17 | 483725.29 | 100.00 | 100.00 | | | | 66.1950 | 66.1950 |

**Figure S64**. HPLC chromatogram of chiral compound **3o** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

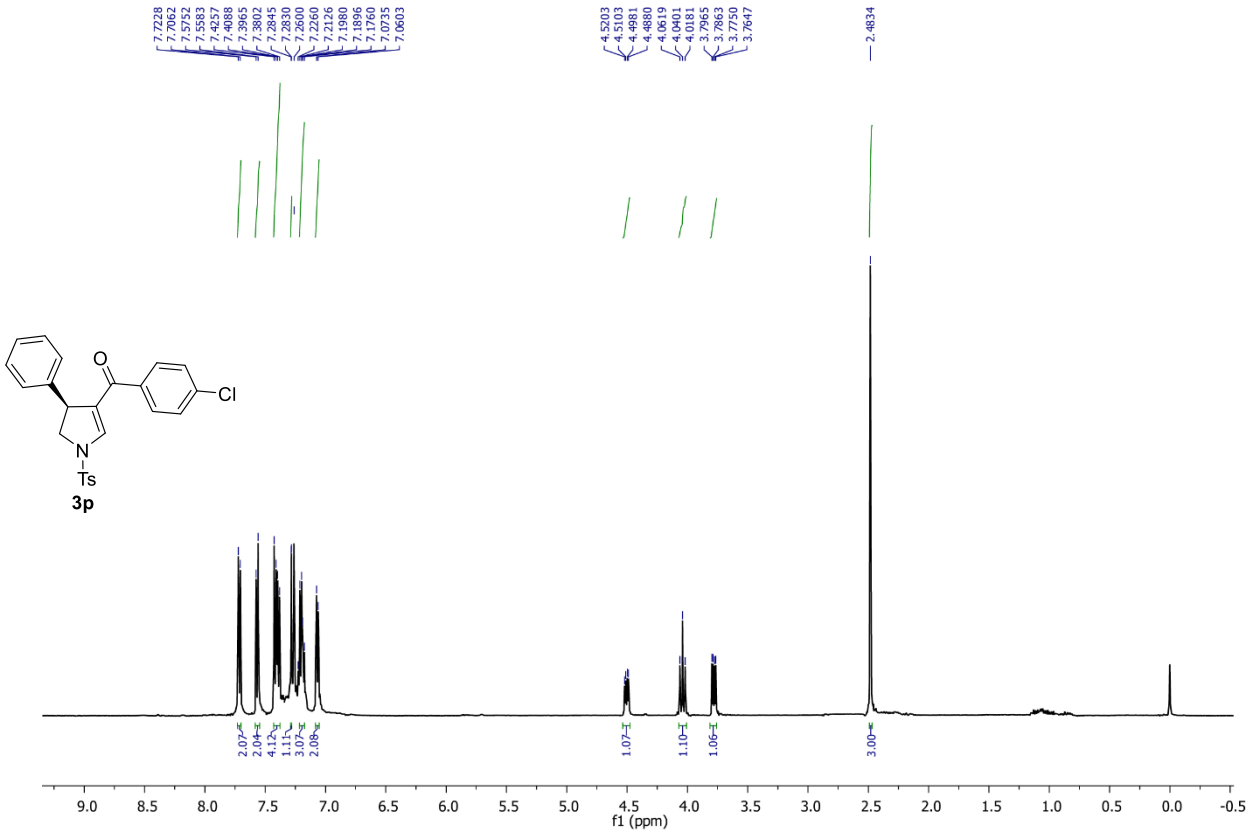



**Figure S65.** $^{1}H$ NMR spectrum of **3p** (500 MHz, $CDCl_3$)

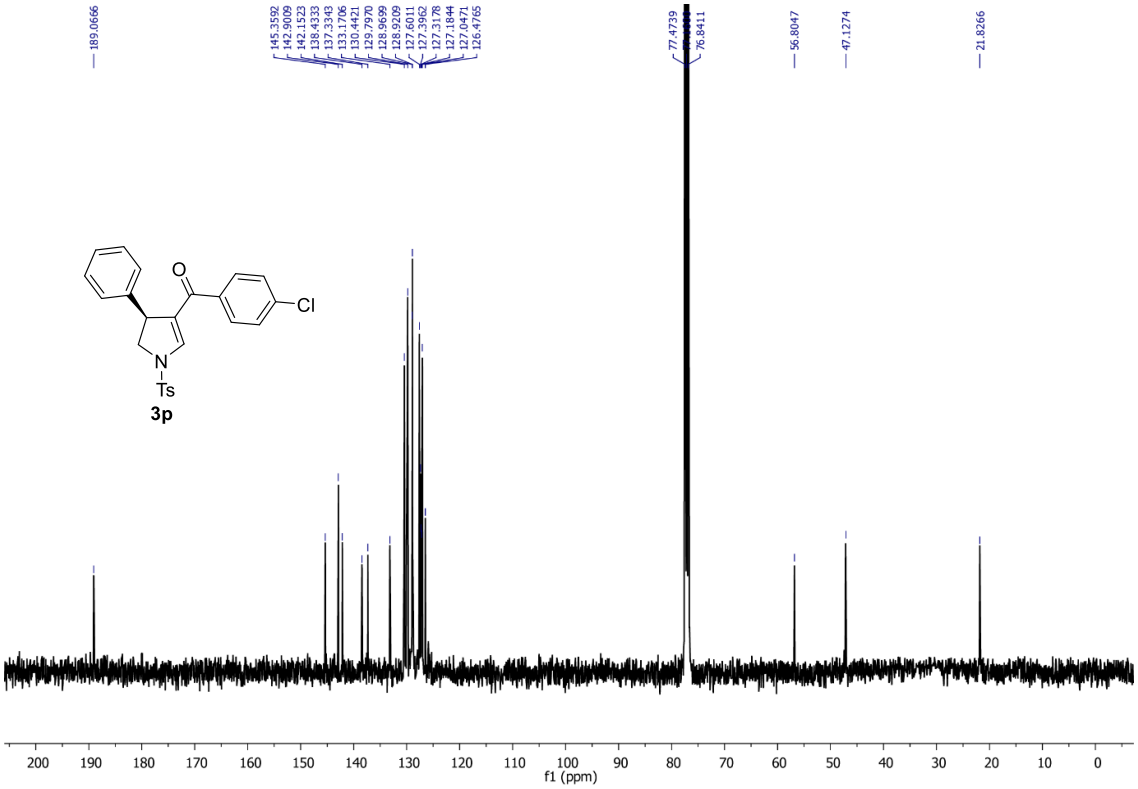
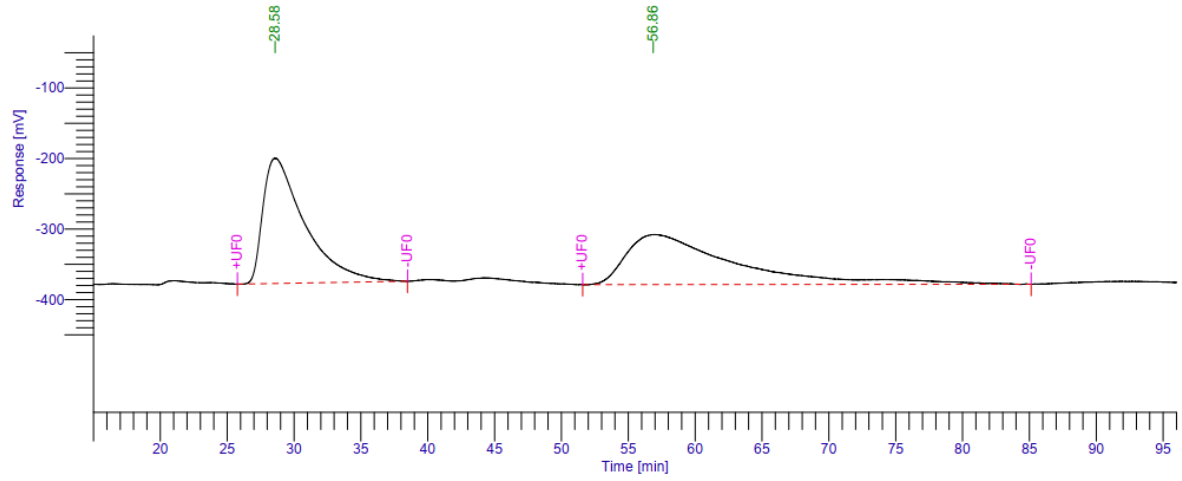



**Figure S66**. $^{13}C\{^{1}H\}$ NMR spectrum of **3p** (125 MHz, $CDCl_3$)

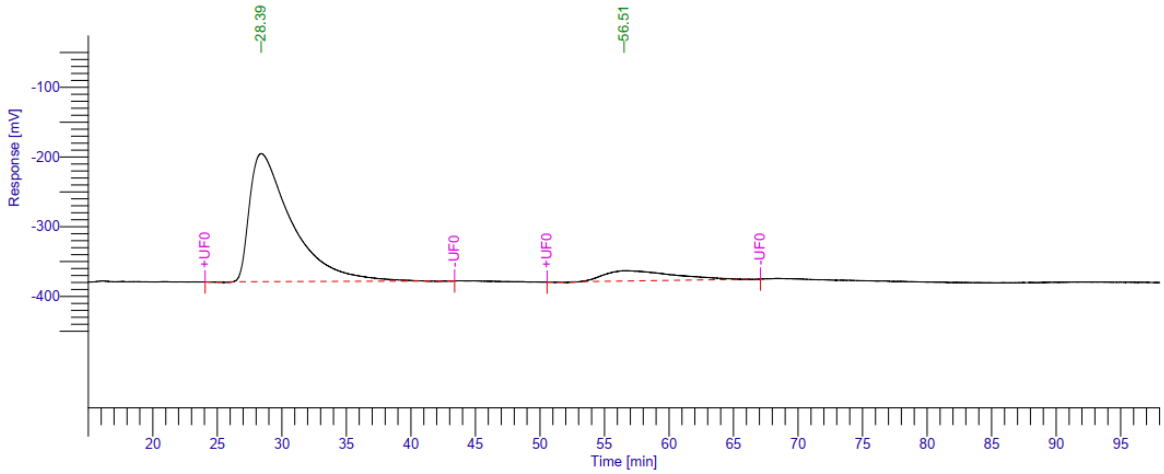



AKS-5-114RAC, AS-H

AKS-5-114RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 28.578 | 38689578.96 | 177709.23 | 49.26 | 49.26 | | | *MM | 38.6896 | 38.6896 |
| 2 | | 56.855 | 39847731.97 | 71018.65 | 50.74 | 50.74 | | | *MM | 39.8477 | 39.8477 |
| | | | 78537310.93 | 248727.89 | 100.00 | 100.00 | | | | 78.5373 | 78.5373 |

**Figure S67**. HPLC chromatogram of racemic compound **3p** (AS-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-113CHIRAL, AS-H

AKS-5-113CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 28.387 | 41788728.06 | 183806.61 | 88.49 | 88.49 | | | *MM | 41.7887 | 41.7887 |
| 2 | | 56.511 | 5437343.25 | 14909.46 | 11.51 | 11.51 | | | *MM | 5.4373 | 5.4373 |

**Figure S68**. HPLC chromatogram of chiral compound **3p** (AS-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

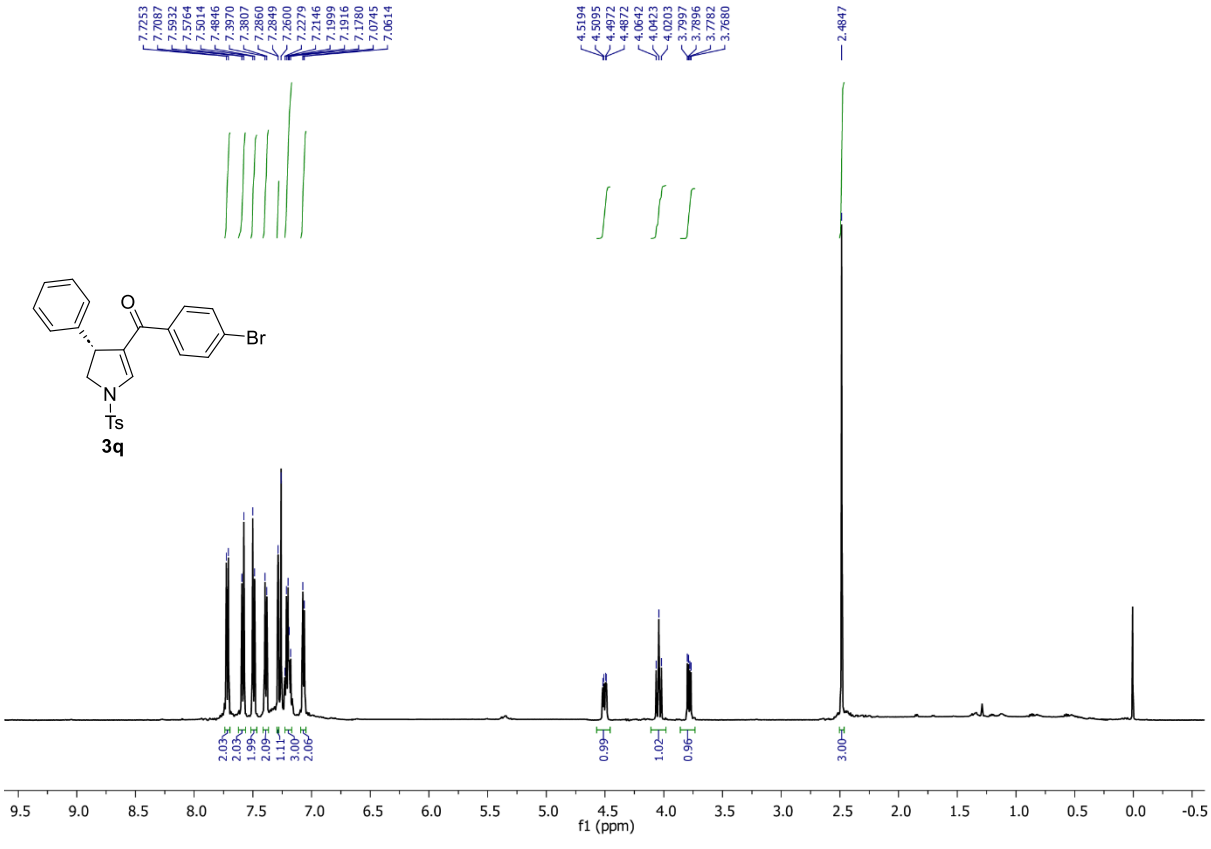



**Figure S69.** $^{1}H$ NMR spectrum of **3q** (500 MHz, $CDCl_3$)

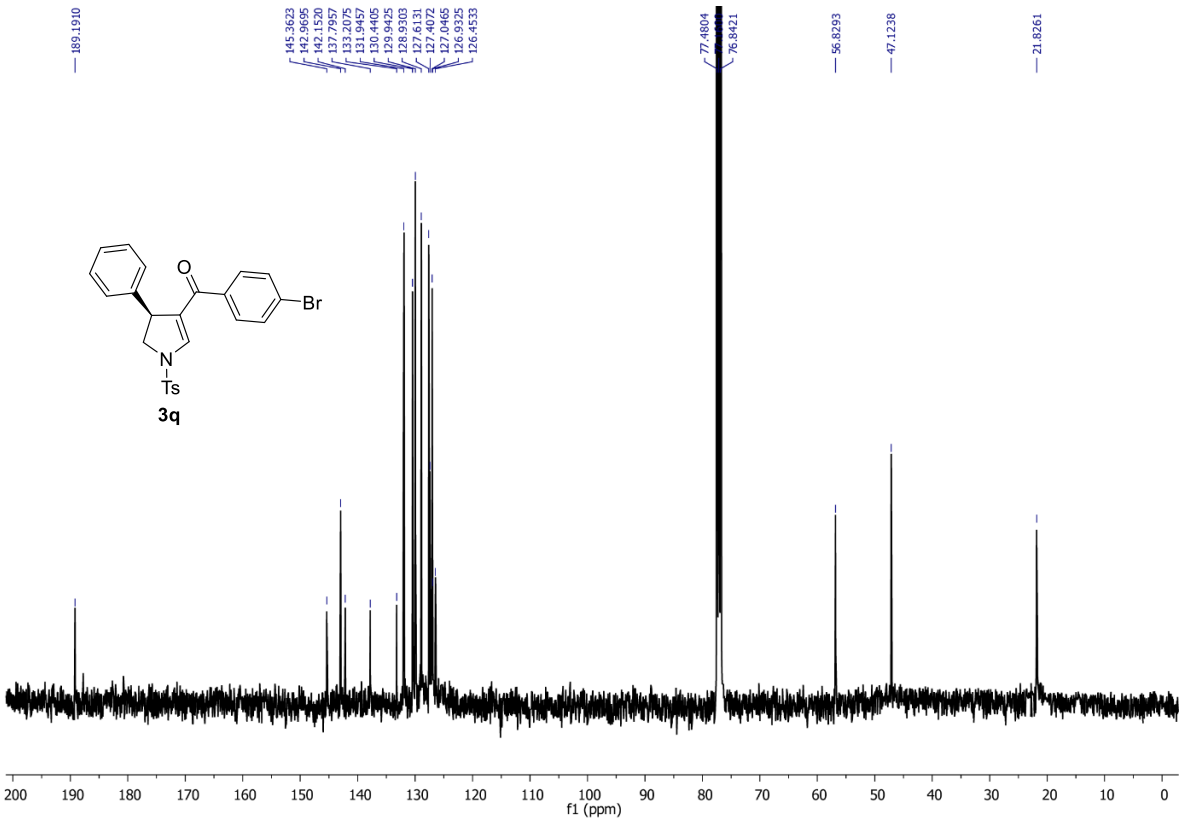
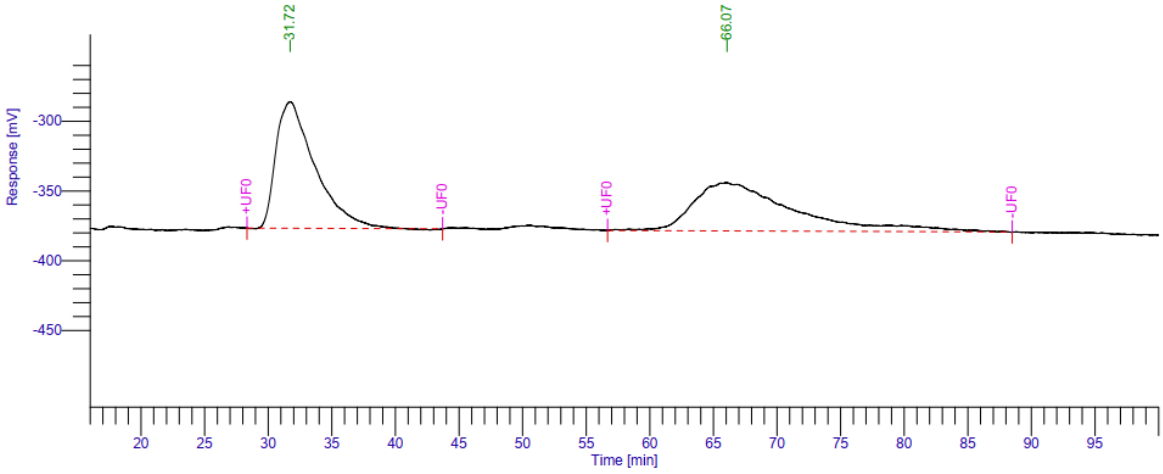



**Figure S70**. $^{13}C\{^{1}H\}$ NMR spectrum of **3q** (125 MHz, $CDCl_3$)

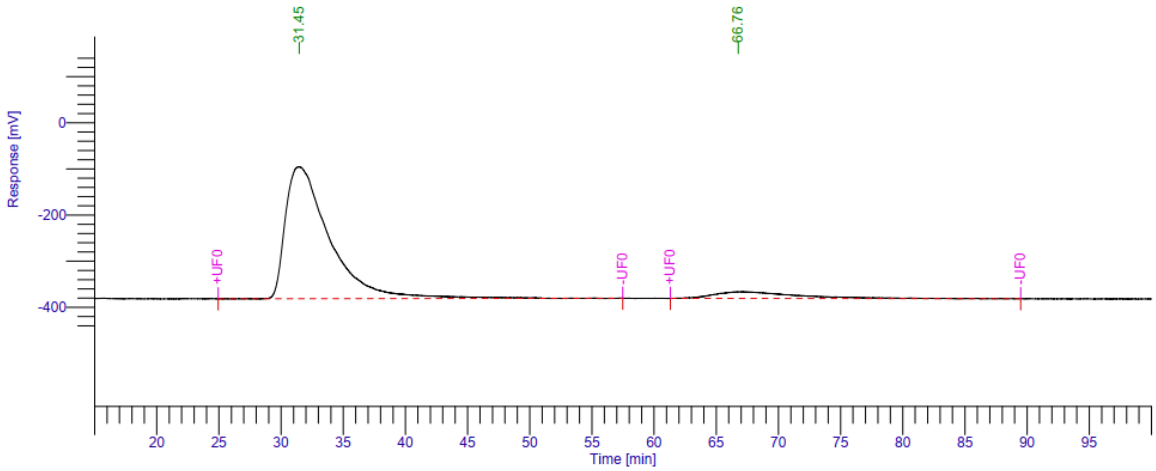



AKS-5-85RAC, AS-H

AKS-5-85RAC, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 31.717 | 19371848.67 | 90781.06 | 50.61 | 50.61 | | | *MM | 19.3718 | 19.3718 |
| 2 | | 66.066 | 18908170.19 | 34580.32 | 49.39 | 49.39 | | | *MM | 18.9082 | 18.9082 |
| | | | 38280018.86 | 125361.38 | 100.00 | 100.00 | | | | 38.2800 | 38.2800 |

**Figure S71**. HPLC chromatogram of racemic compound **3q** (As-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-84CHIRAL, AS-H

AKS-5-84CHIRAL, AS-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 31.453 | 70410055.89 | 285466.54 | 91.45 | 91.45 | | | *MM | 70.4101 | 70.4101 |
| 2 | | 66.763 | 6580549.62 | 14530.30 | 8.55 | 8.55 | | | *MM | 6.5805 | 6.5805 |
| | | | 76990605.52 | 299996.84 | 100.00 | 100.00 | | | | 76.9906 | 76.9906 |

**Figure S72**. HPLC chromatogram of chiral compound **3q** (As-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

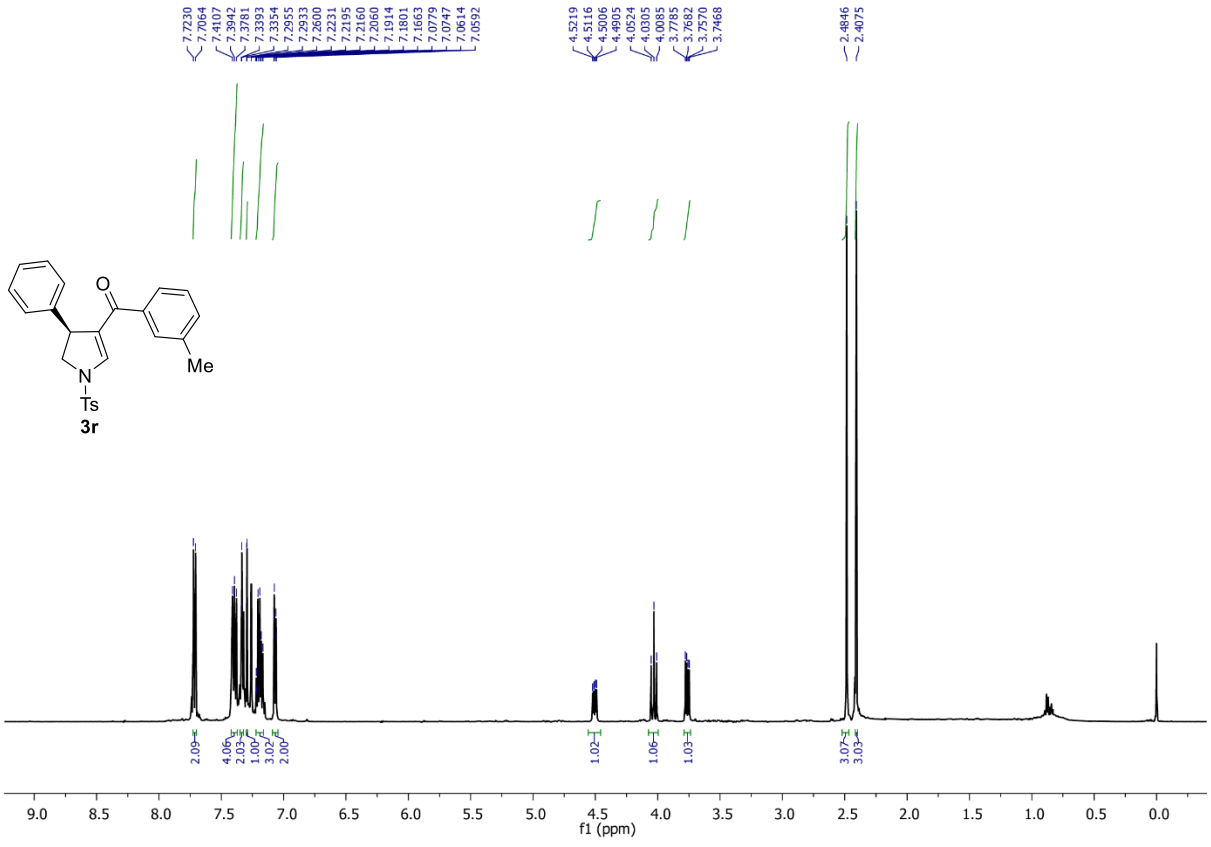



**Figure S73.** $^{1}H$ NMR spectrum of **3r** (500 MHz, $CDCl_3$)

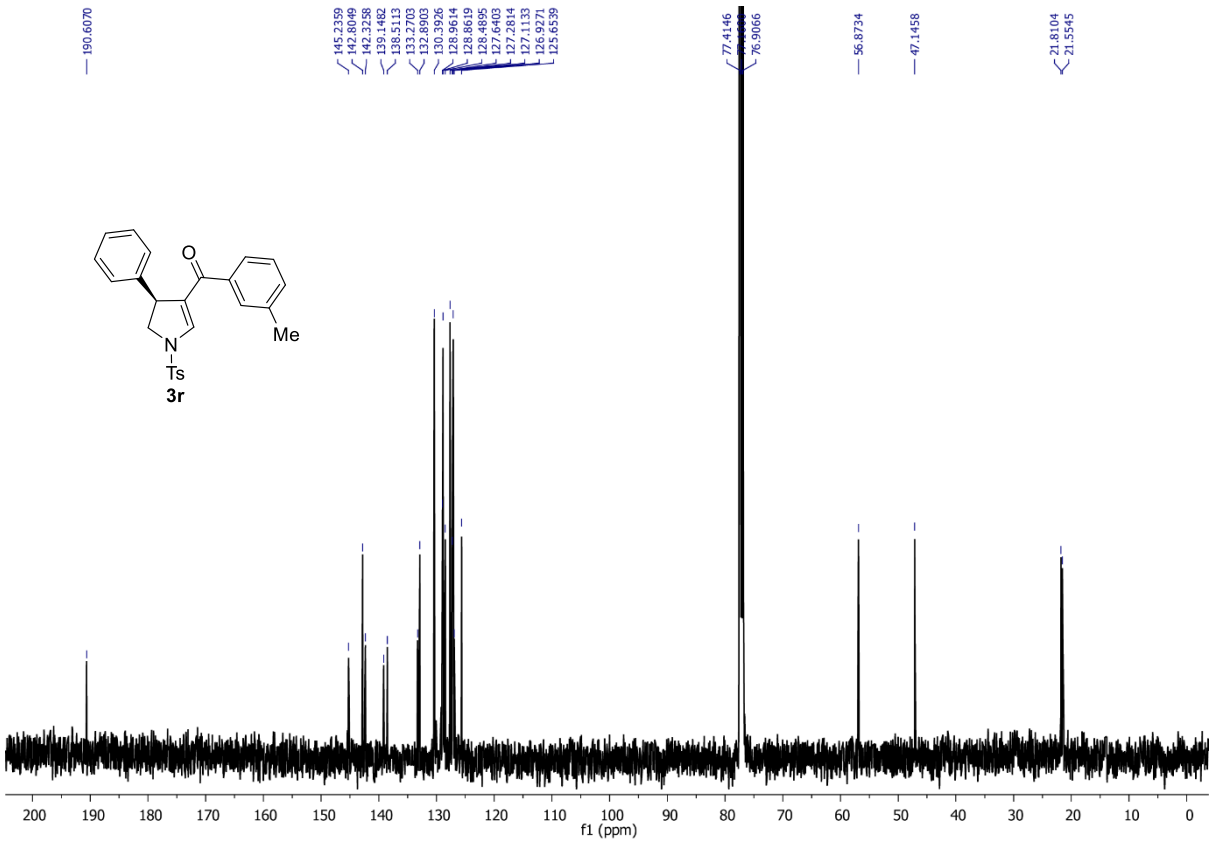
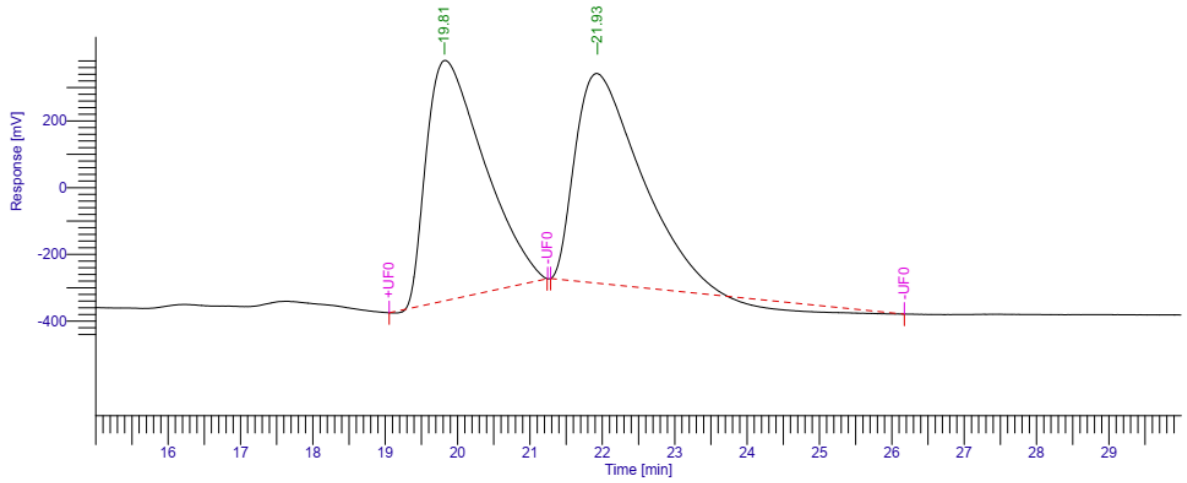



**Figure S74**. $^{13}C\{^{1}H\}$ NMR spectrum of **3r** (125 MHz, $CDCl_3$)

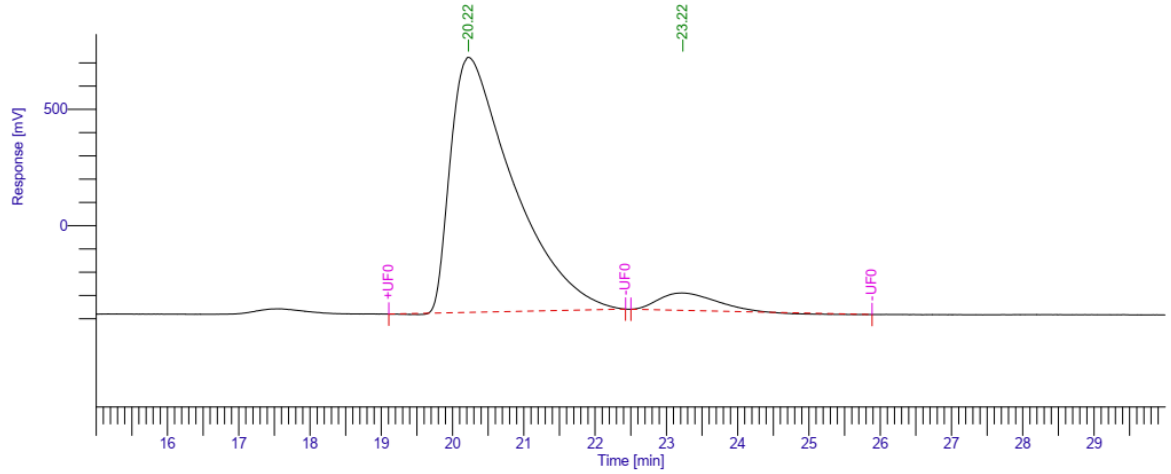



AKS-5-136RAC, OD-H

AKS-5-136RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 19.815 | 39924711.79 | 720386.31 | 49.68 | 49.68 | | | *MM | 39.9247 | 39.9247 |
| 2 | | 21.927 | 40435357.85 | 628688.85 | 50.32 | 50.32 | | | *MM | 40.4354 | 40.4354 |
| | | | 80360069.64 | 1.35e+06 | 100.00 | 100.00 | | | | 80.3601 | 80.3601 |

**Figure S75**. HPLC chromatogram of racemic compound **3r** (OD-H column; 95:5 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-135CHIRAL OD-H

AKS-5-135CHIRAL OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 20.218 | 67120969.13 | 1.10e+06 | 94.11 | 94.11 | | | *MM | 67.1210 | 67.1210 |
| 2 | | 23.225 | 4204546.87 | 74650.27 | 5.89 | 5.89 | | | *MM | 4.2045 | 4.2045 |
| | | | 71325516.00 | 1.17e+06 | 100.00 | 100.00 | | | | 71.3255 | 71.3255 |

**Figure S76**. HPLC chromatogram of chiral compound **3r** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

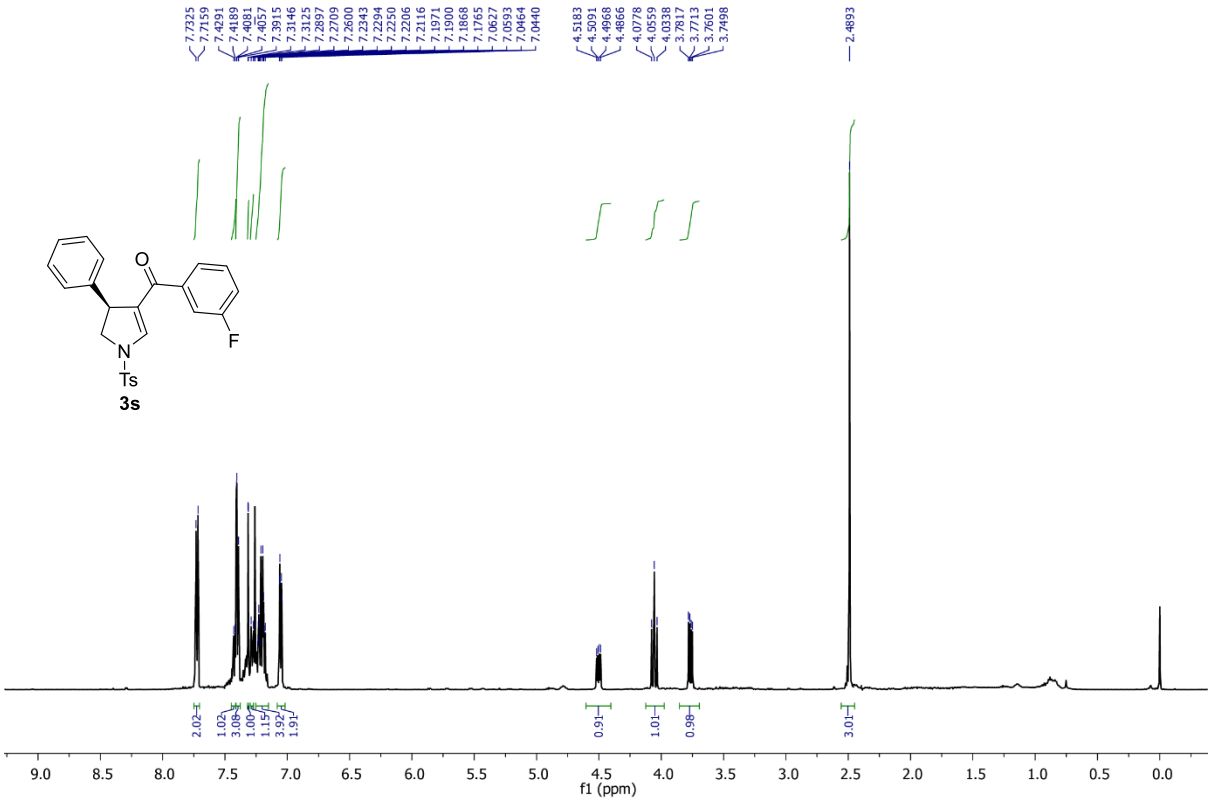



**Figure S77.** $^{1}H$ NMR spectrum of **3s** (500 MHz, $CDCl_3$)

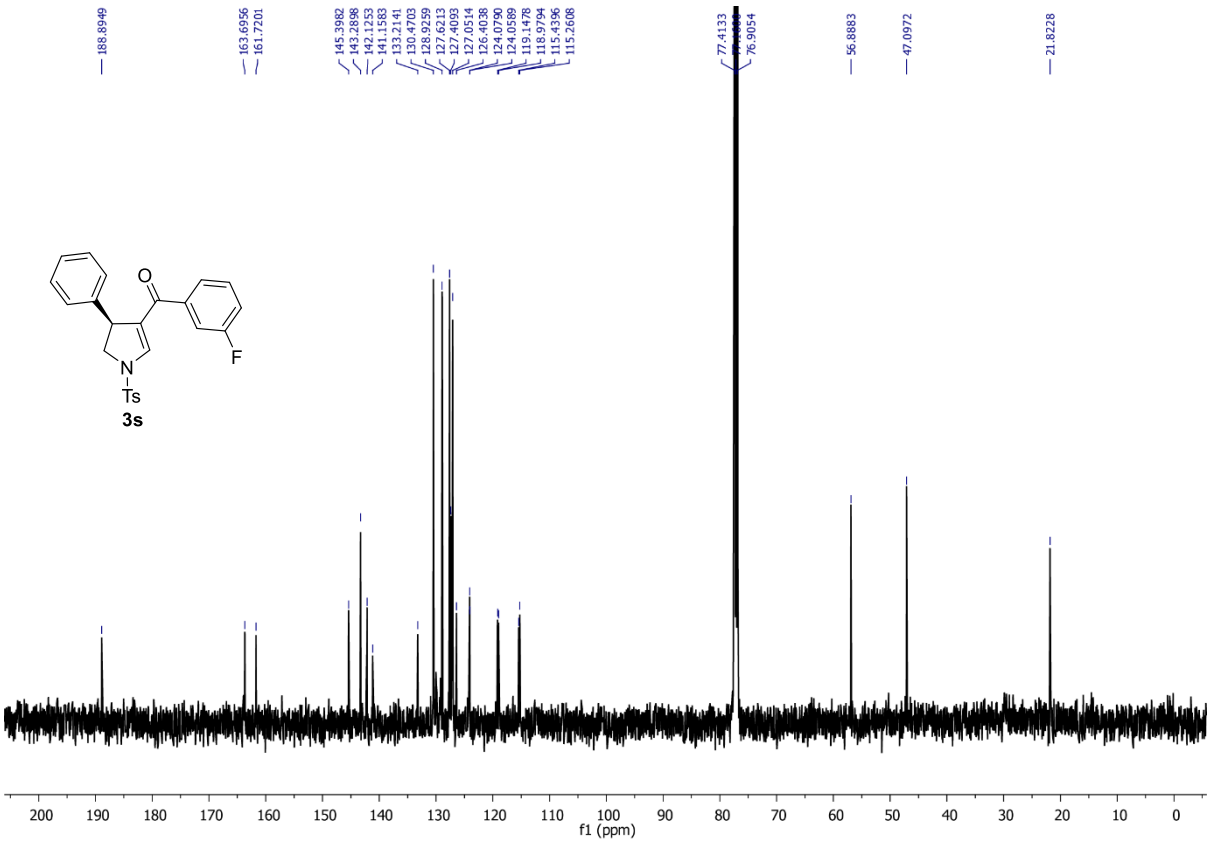



**Figure S78**. $^{13}C\{^{1}H\}$ NMR spectrum of **3s** (125 MHz, $CDCl_3$)

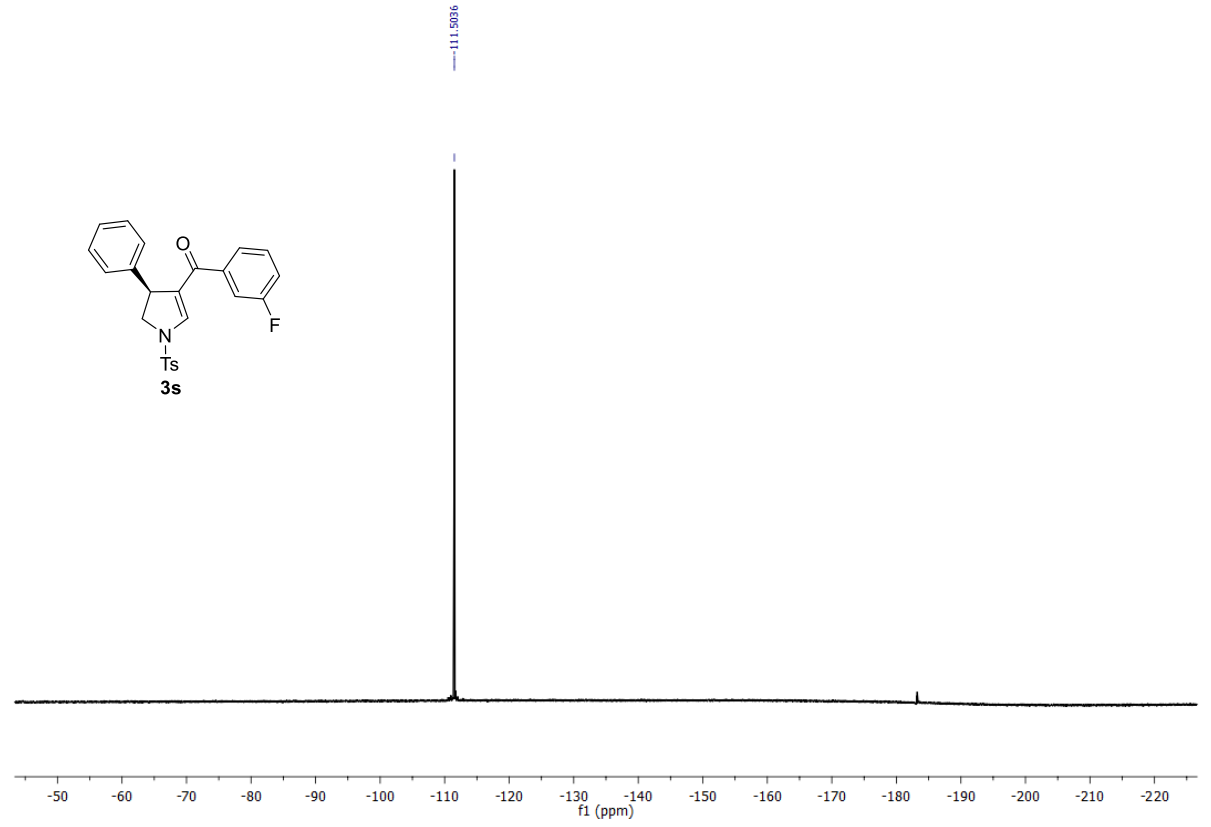
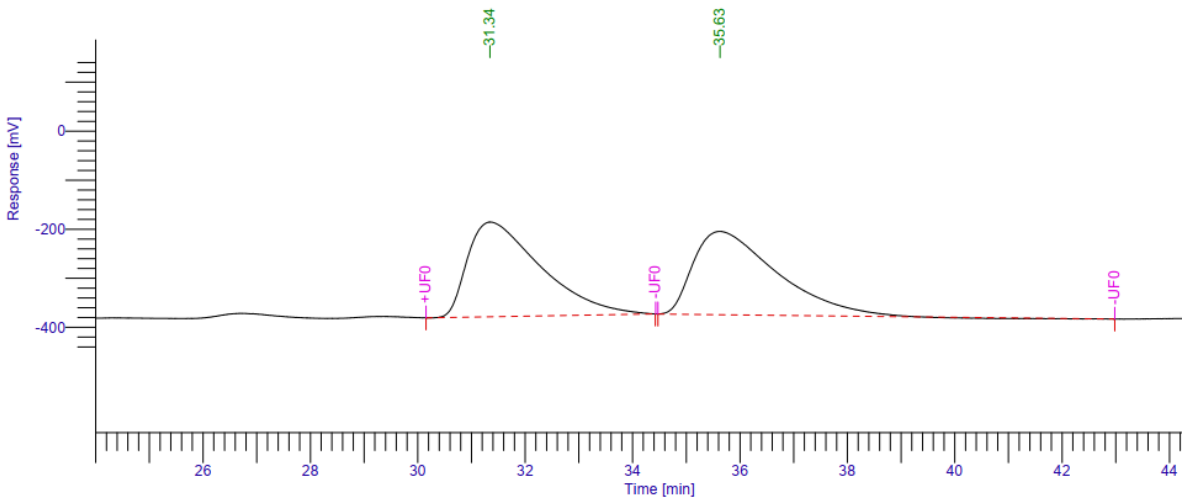



**Figure S79.** $^{19}F$ NMR spectrum of **3s** (500 MHz, $CDCl_3$)

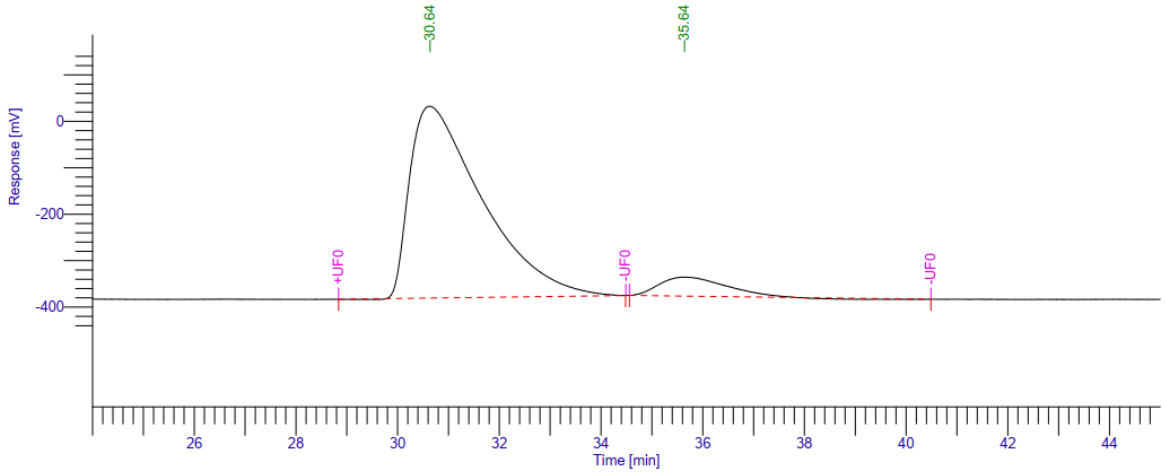



AKS-5-142RAC, OD-H

AKS-5-142RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 31.343 | 18278145.10 | 193036.95 | 49.83 | 49.83 | | | *MM | 18.2781 | 18.2781 |
| 2 | | 35.625 | 18403510.38 | 169830.69 | 50.17 | 50.17 | | | *MM | 18.4035 | 18.4035 |

**Figure S80**. HPLC chromatogram of racemic compound **3s** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-141CHIRAL, OD-H

AKS-5-141CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 30.639 | 40965757.64 | 412855.07 | 91.56 | 91.56 | | | *MM | 40.9658 | 40.9658 |
| 2 | | 35.640 | 3777024.98 | 40973.38 | 8.44 | 8.44 | | | *MM | 3.7770 | 3.7770 |
| | | | 44742782.61 | 453828.45 | 100.00 | 100.00 | | | | 44.7428 | 44.7428 |

**Figure S81**. HPLC chromatogram of chiral compound **3s** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

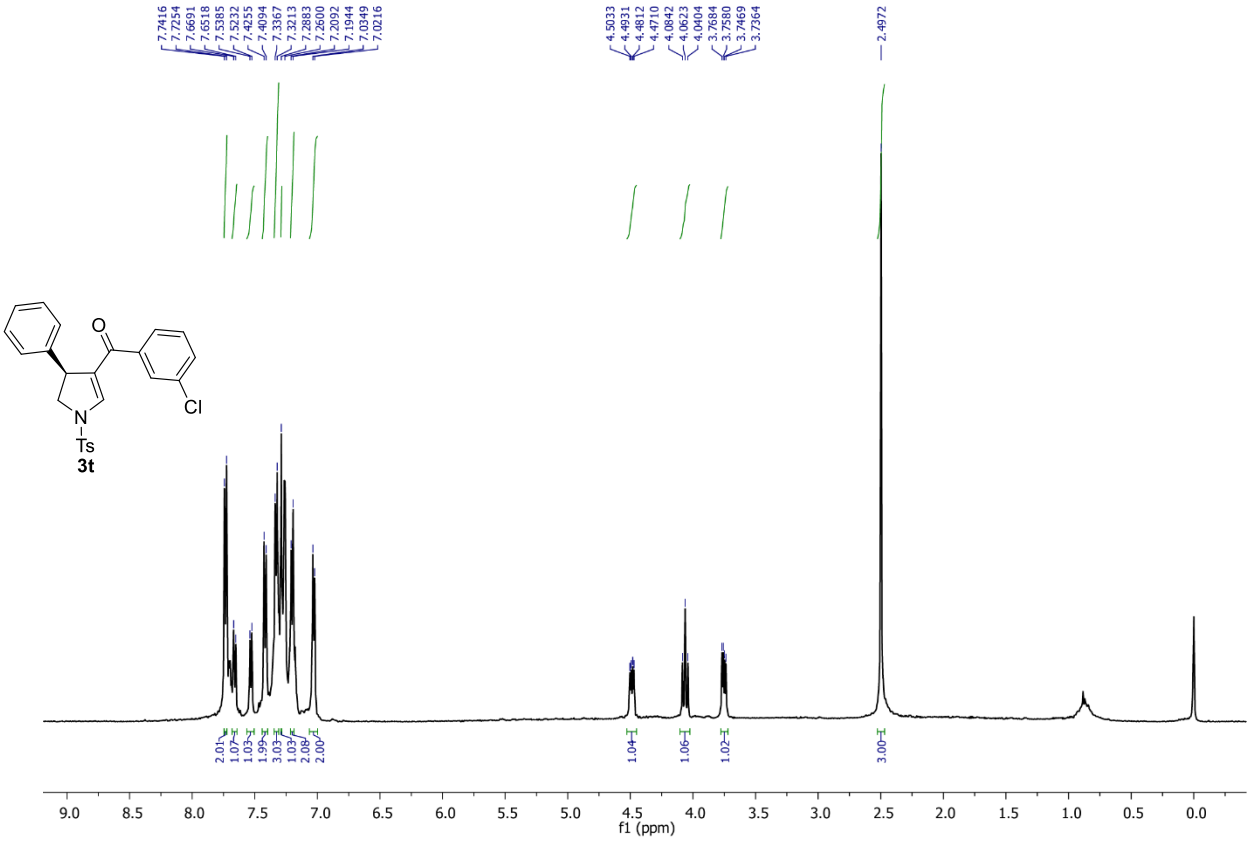



**Figure S82.** $^{1}$H NMR spectrum of **3t** (500 MHz, $CDCl_3$)

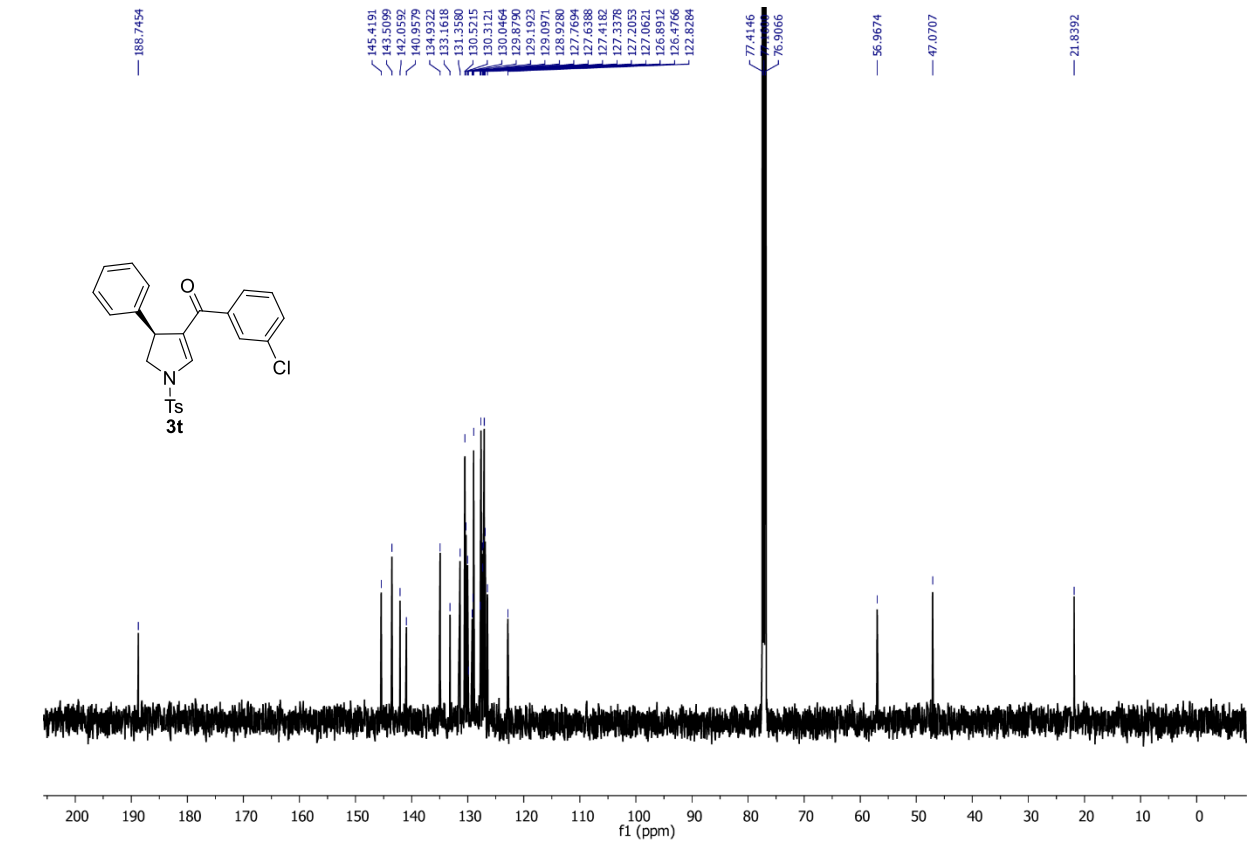
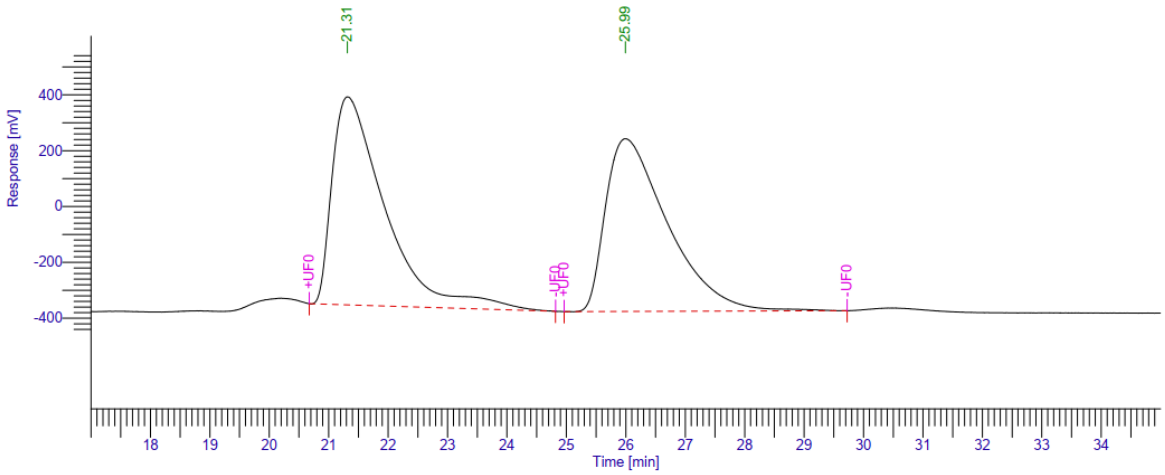



**Figure S83**. $^{13}C\{^{1}H\}$ NMR spectrum of **3t** (125 MHz, $CDCl_3$)

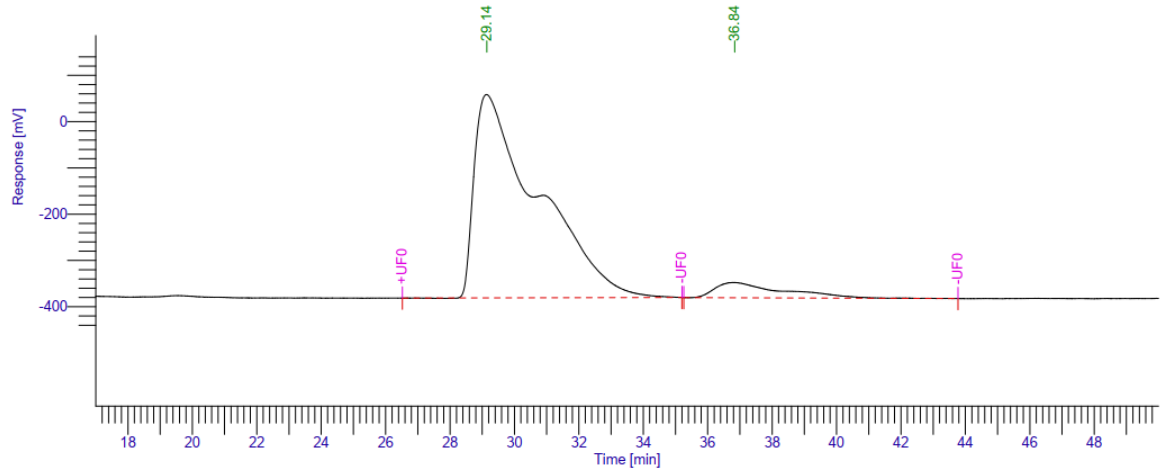



AKS-5-94RAC, OD-H

AKS-5-94RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 21.311 | 46011339.92 | 745007.10 | 50.63 | 50.63 | | | *MM | 46.0113 | 46.0113 |
| 2 | | 25.989 | 44857337.97 | 618184.71 | 49.37 | 49.37 | | | *MM | 44.8573 | 44.8573 |
| | | | 90868677.90 | 1.36e+06 | 100.00 | 100.00 | | | | 90.8687 | 90.8687 |

**Figure S84**. HPLC chromatogram of racemic compound **9a** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-168, OD-H

AKS-5-168, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 29.143 | 60074819.39 | 439212.95 | 92.62 | 92.62 | | | *MM | 60.0748 | 60.0748 |
| 2 | | 36.835 | 4788499.64 | 32971.82 | 7.38 | 7.38 | | | *MM | 4.7885 | 4.7885 |
| | | | 64863319.03 | 472184.77 | 100.00 | 100.00 | | | | 64.8633 | 64.8633 |

**Figure S85**. HPLC chromatogram of chiral compound **3t** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

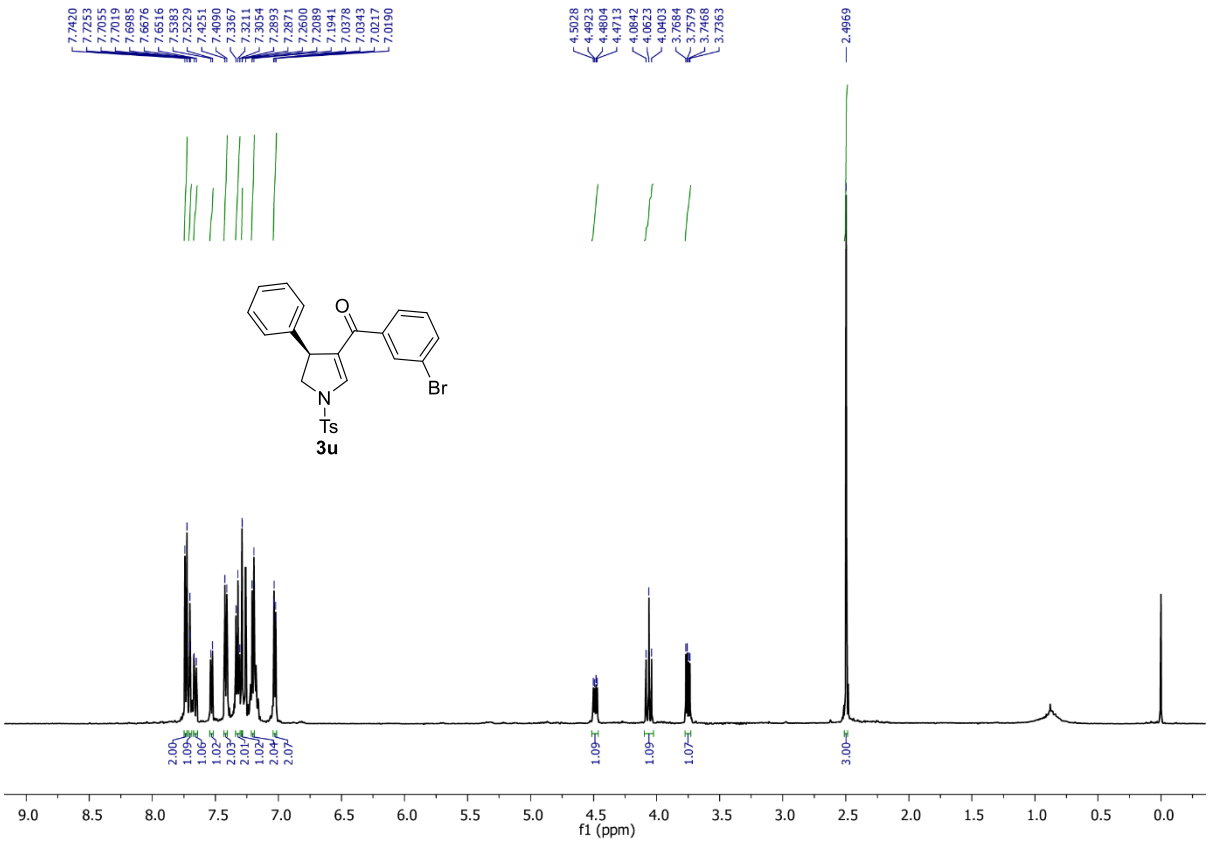



**Figure S86.** $^{1}$H NMR spectrum of **3u** (500 MHz, $CDCl_3$)

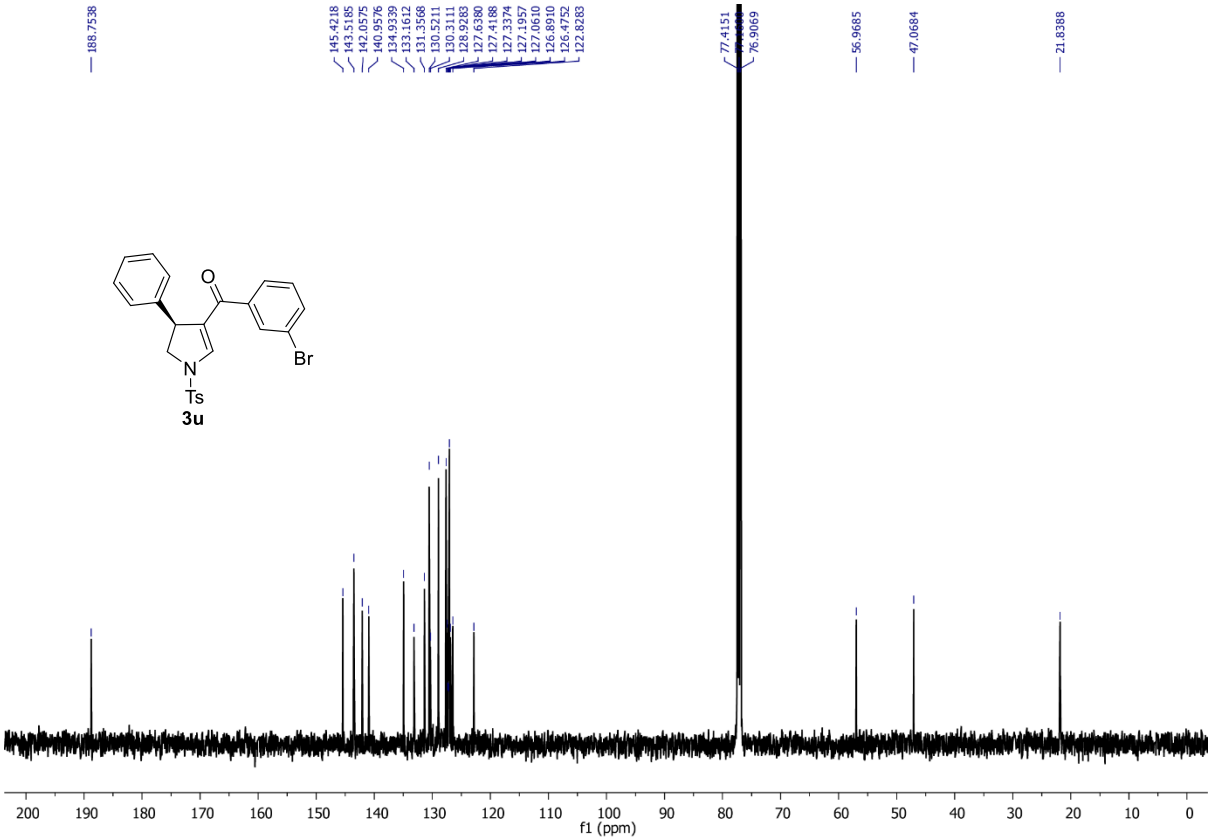
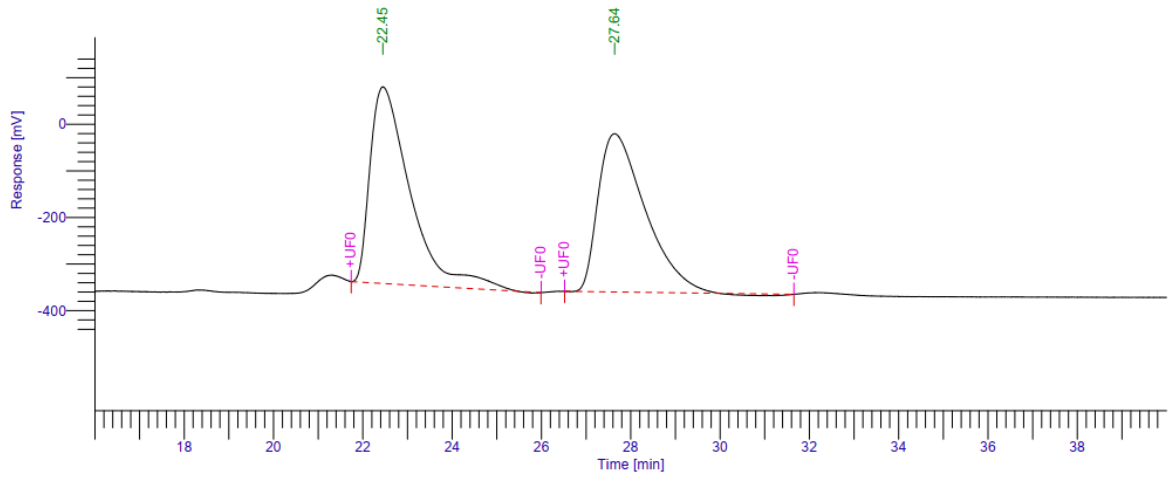



**Figure S87**. $^{13}$C{$^{1}$H} NMR spectrum of **3u** (125 MHz, $CDCl_3$)

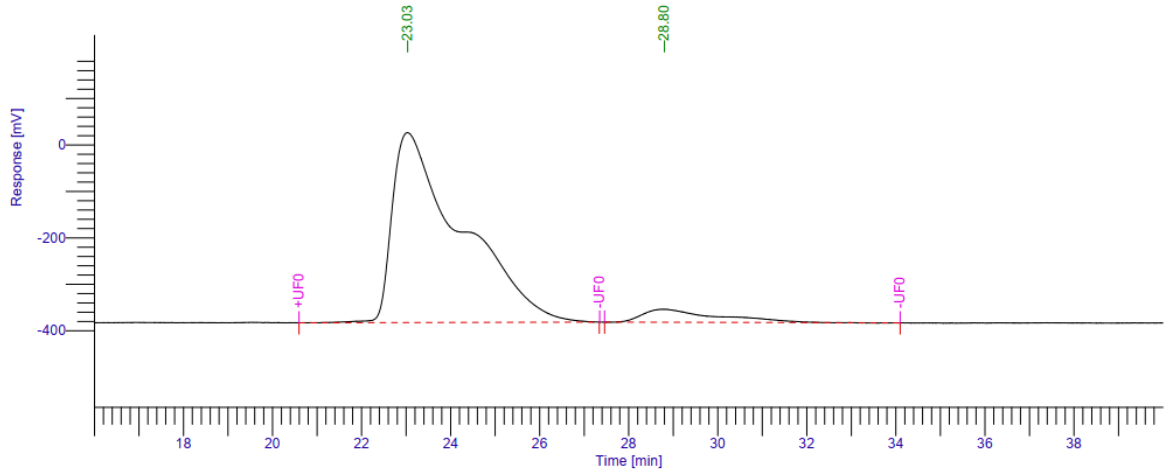



AKS-5-96RAC, OD-H

AKS-5-96RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 22.447 | 26422426.91 | 422191.46 | 51.45 | 51.45 | | | *MM | 26.4224 | 26.4224 |
| 2 | | 27.639 | 24936422.14 | 339809.20 | 48.55 | 48.55 | | | *MM | 24.9364 | 24.9364 |
| | | | 51358849.05 | 762000.66 | 100.00 | 100.00 | | | | 51.3588 | 51.3588 |

**Figure S88**. HPLC chromatogram of racemic compound **3u** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-169CHIRAL, OD-H

AKS-5-169CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 23.034 | 43805201.97 | 408850.87 | 93.19 | 93.19 | | | *MM | 43.8052 | 43.8052 |
| 2 | | 28.798 | 3201663.04 | 27906.71 | 6.81 | 6.81 | | | *MM | 3.2017 | 3.2017 |
| | | | 47006865.01 | 436757.58 | 100.00 | 100.00 | | | | 47.0069 | 47.0069 |

**Figure S89**. HPLC chromatogram of chiral compound **3u** (OD-H column; 95:5 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

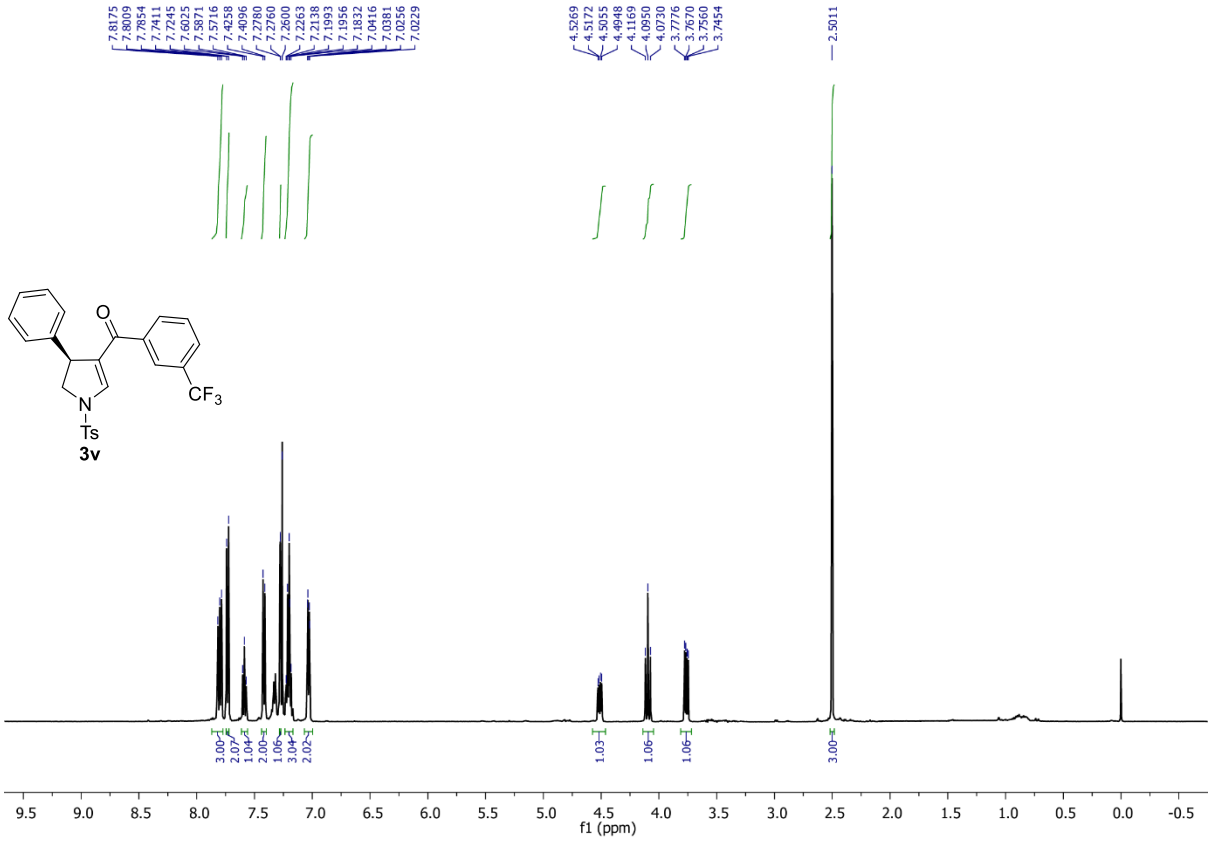



**Figure S90.** $^{1}$H NMR spectrum of **3v** (500 MHz, $CDCl_3$)

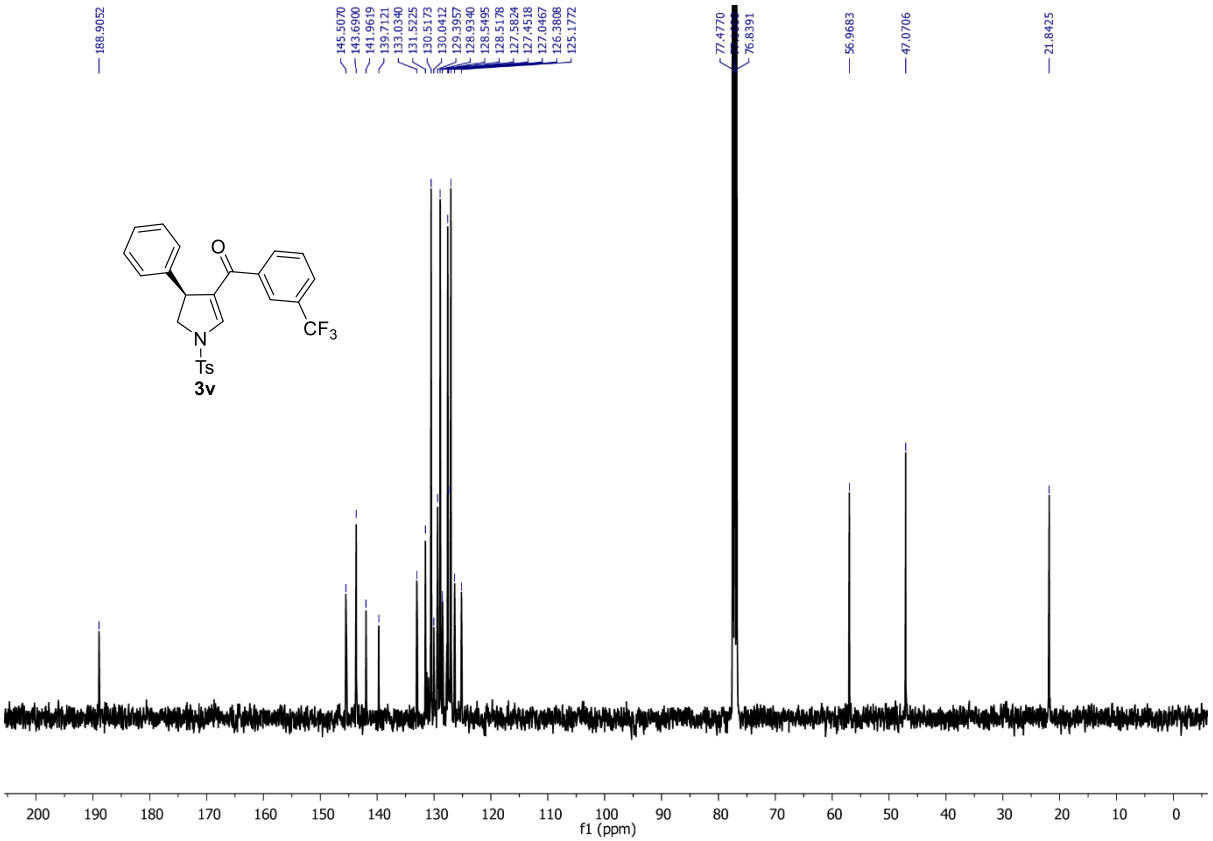



**Figure S91**. $^{13}$C{$^{1}$H} NMR spectrum of **3v** (125 MHz, $CDCl_3$)

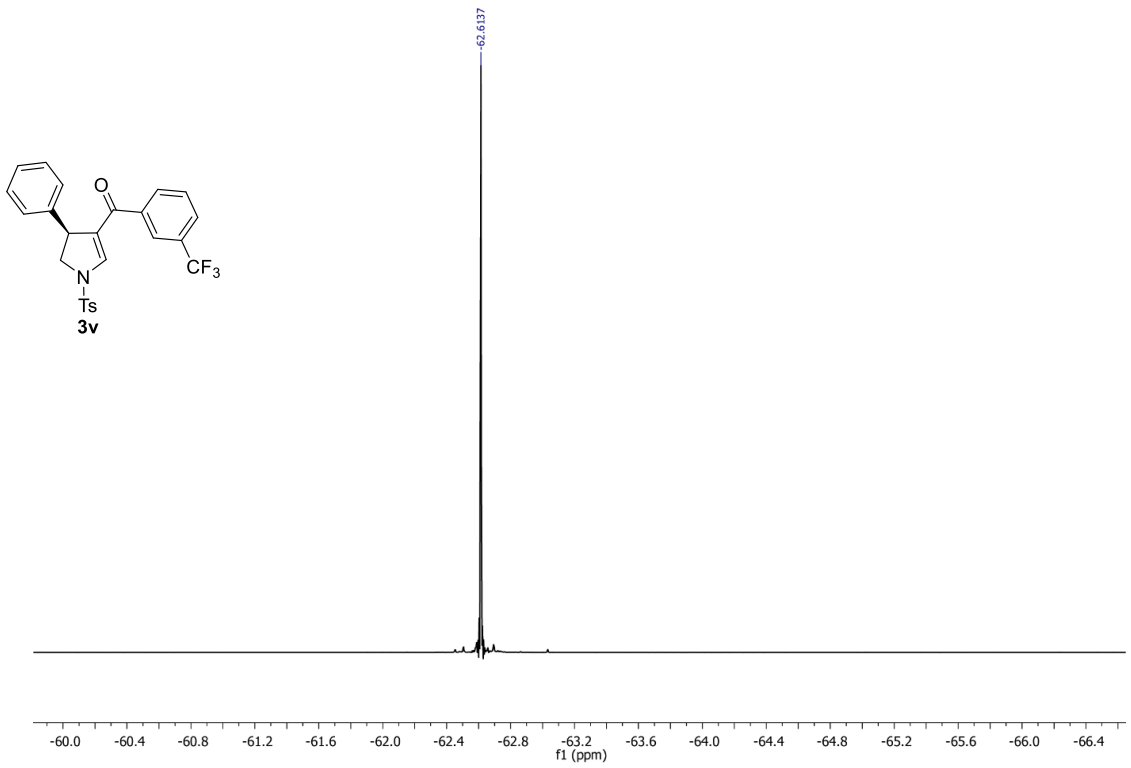
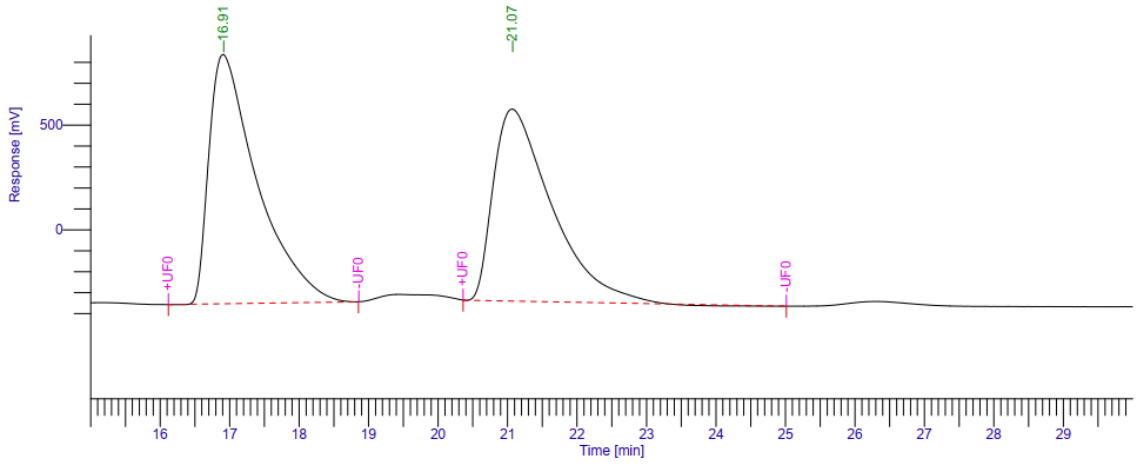



**Figure S92.** $^{19}$F NMR spectrum of **3v** (500 MHz, $CDCl_3$)

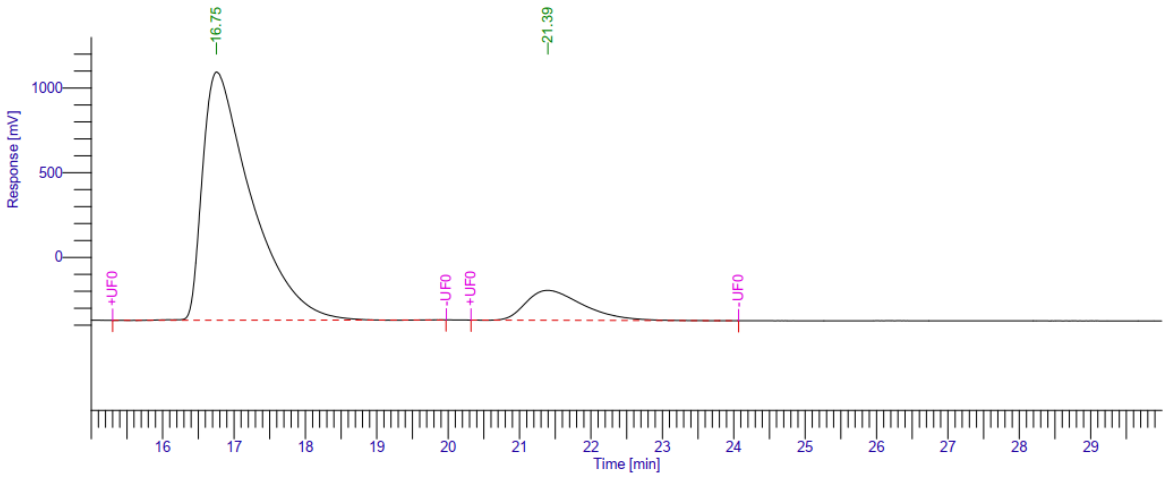



AKS-5-144RAC, OD-H

AKS-5-144RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 16.911 | 57352168.02 | 1.19e+06 | 51.67 | 51.67 | | | *MM | 57.3522 | 57.3522 |
| 2 | | 21.069 | 53655171.70 | 917058.57 | 48.33 | 48.33 | | | *MM | 53.6552 | 53.6552 |
| | | | 1.11e+08 | 2.11e+06 | 100.00 | 100.00 | | | | 111.0073 | 111.0073 |

**Figure S93**. HPLC chromatogram of racemic compound **3v** (OD-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




AKS-5-143CHIRAL, OD-H

AKS-5-143CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 16.749 | 69469714.17 | 1.47e+06 | 87.69 | 87.69 | | | *MM | 69.4697 | 69.4697 |
| 2 | | 21.391 | 9755772.36 | 176532.81 | 12.31 | 12.31 | | | *MM | 9.7558 | 9.7558 |
| | | | 79225486.53 | 1.64e+06 | 100.00 | 100.00 | | | | 79.2255 | 79.2255 |

**Figure S94**. HPLC chromatogram of chiral compound **3v** (OD-H column; 90:10 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

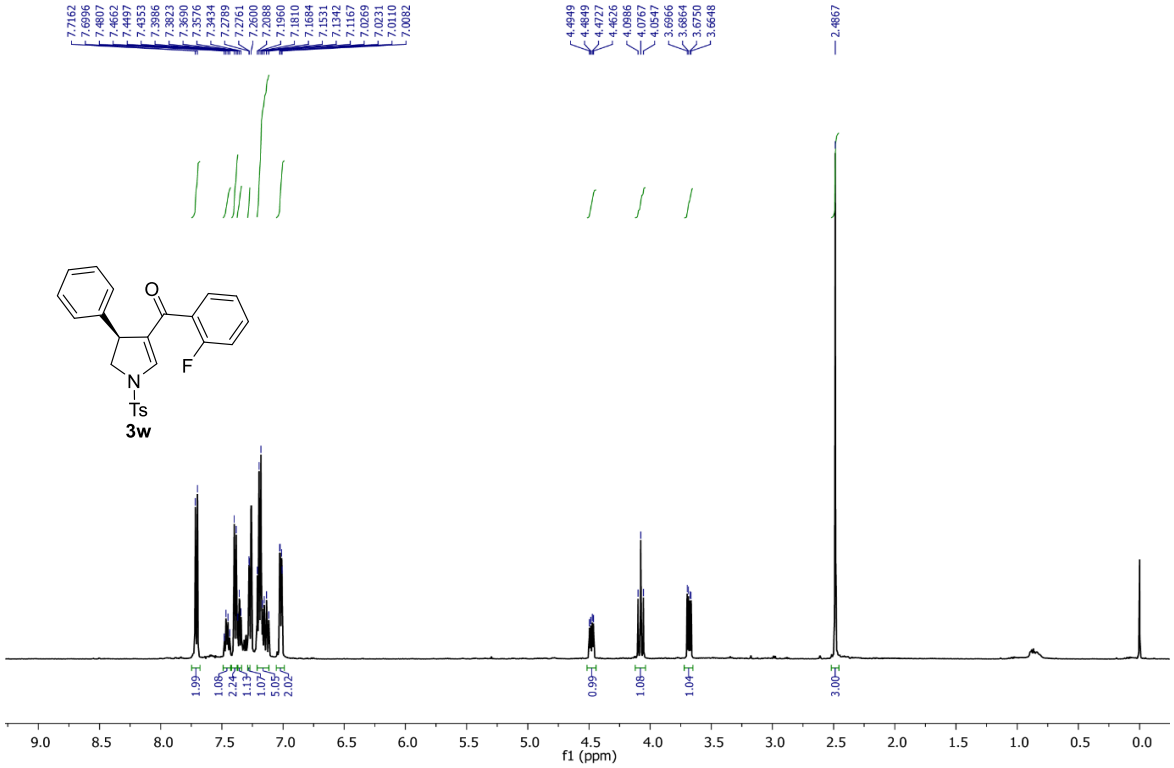



**Figure S95.** $^{1}H$ NMR spectrum of **3w** (500 MHz, $CDCl_3$)

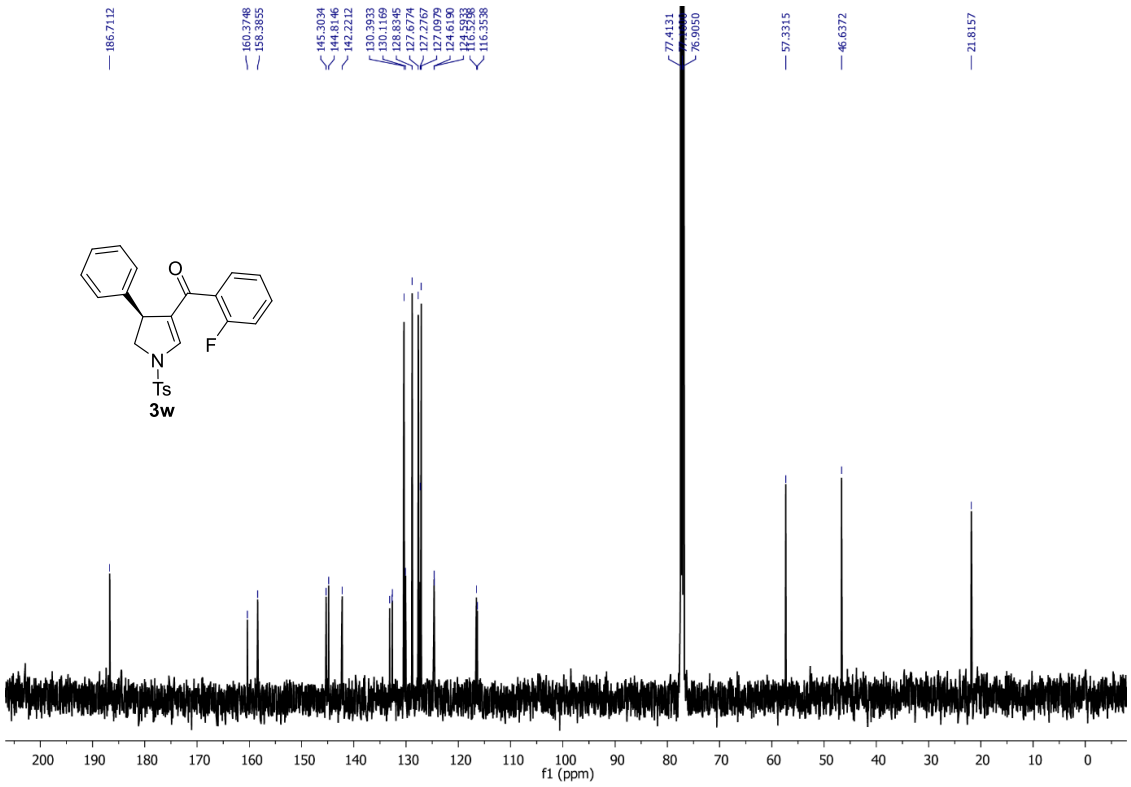



**Figure S96**. $^{13}C\{^{1}H\}$ NMR spectrum of **3w** (125 MHz, $CDCl_3$)

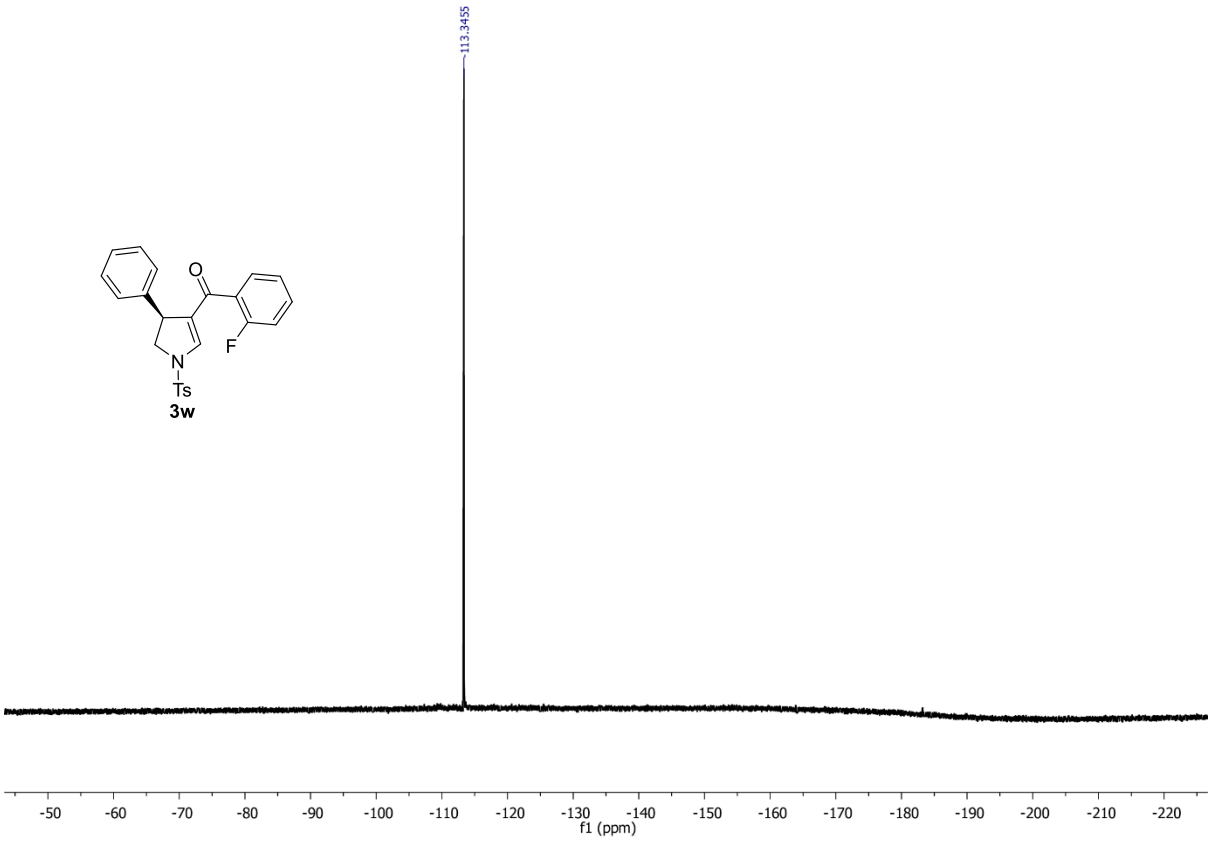
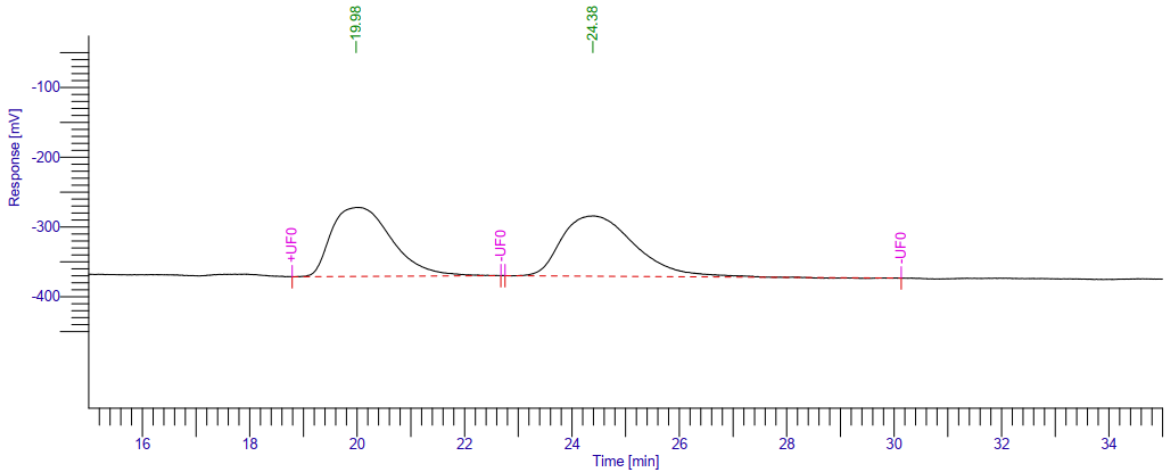



**Figure S97.** $^{19}F$ NMR spectrum of **3w** (500 MHz, $CDCl_3$)

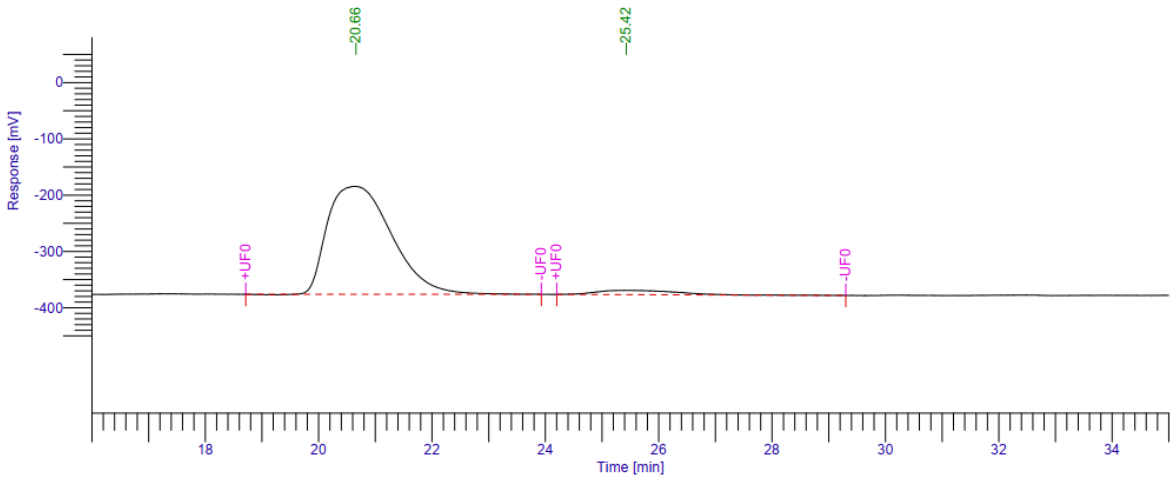



AKS-5-167RAC, OD-H

AKS-5-167RAC, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 19.976 | 7717715.83 | 98851.69 | 48.56 | 48.56 | | | *MM | 7.7177 | 7.7177 |
| 2 | | 24.383 | 8173991.75 | 86400.38 | 51.44 | 51.44 | | | *MM | 8.1740 | 8.1740 |
| | | | 15891707.58 | 185252.07 | 100.00 | 100.00 | | | | 15.8917 | 15.8917 |

**Figure S98**. HPLC chromatogram of racemic compound **3w** (OD-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)



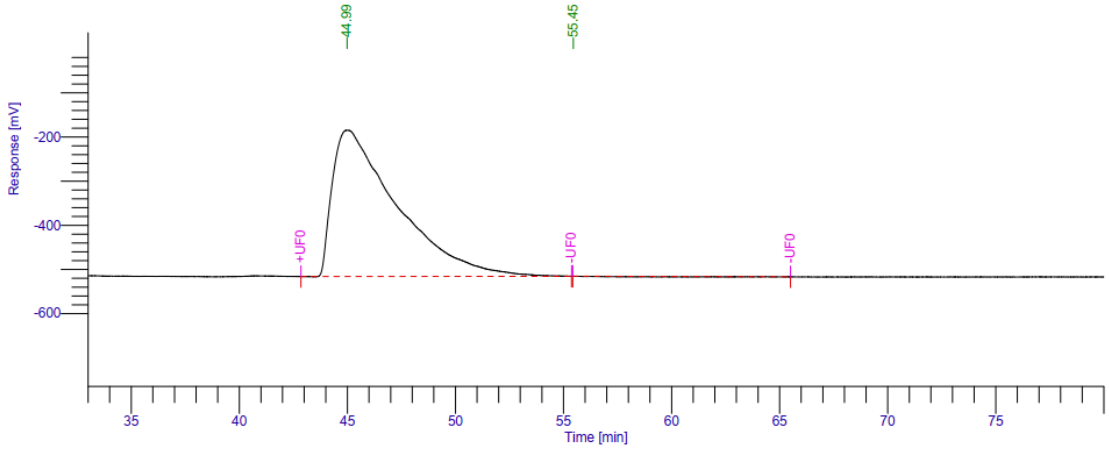

AKS-5-166CHIRAL, OD-H

AKS-5-166CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 20.658 | 15107959.16 | 191752.84 | 95.34 | 95.34 | | | *MM | 15.1080 | 15.1080 |
| 2 | | 25.425 | 738441.93 | 7598.86 | 4.66 | 4.66 | | | *MM | 0.7384 | 0.7384 |
| | | | 15846401.09 | 199351.70 | 100.00 | 100.00 | | | | 15.8464 | 15.8464 |

**Figure S99**. HPLC chromatogram of chiral compound **3w** (OD-H column; 90:10 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

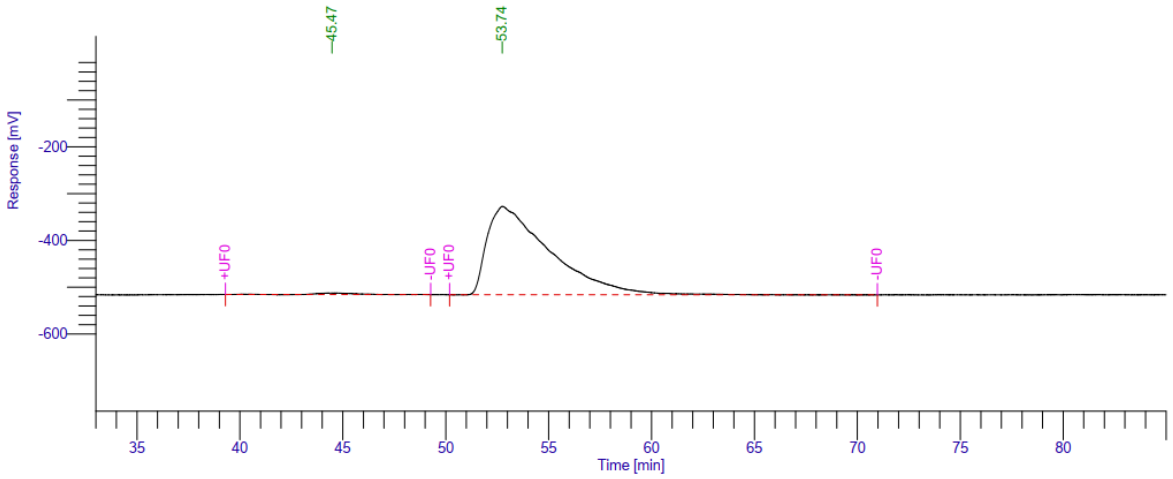
## HPLC Chromatograms of (*S*)-3a and (*R*)-3a (Obtained from non-racemic aziridines)




AKS-6-106CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 44.985 | 68771678.63 | 331249.11 | 100.00 | 100.00 | | | *MM | 68.7717 | 68.7717 |
| 2 | | 55.450 | 240.18 | 171.66 | 0.00 | 0.00 | | | *MM | 0.0002 | 0.0002 |
| | | | 68771918.81 | 331420.77 | 100.00 | 100.00 | | | | 68.7719 | 68.7719 |

**Figure S100.** HPLC chromatogram of **(*S*)-3a** (OD-H column; 97:3 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

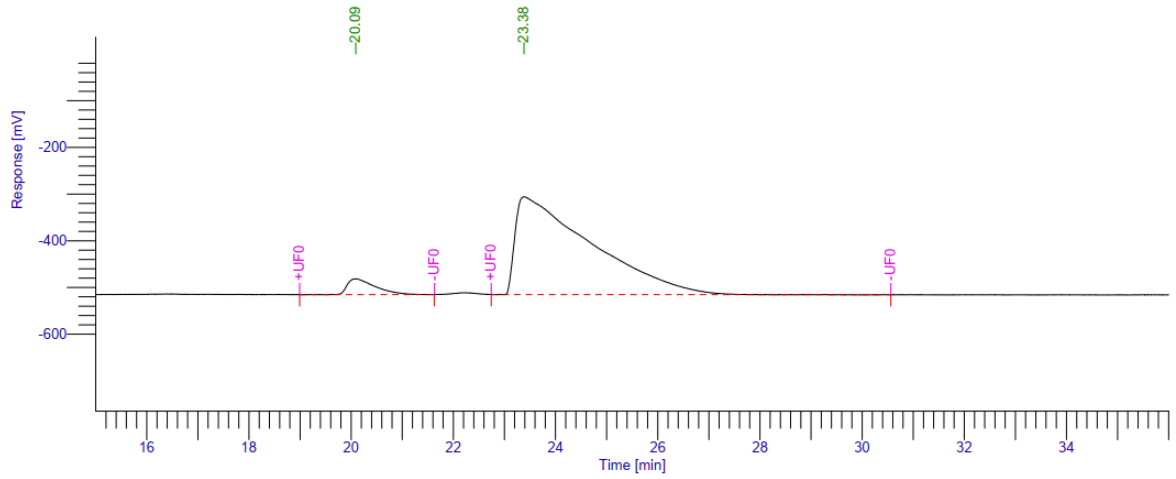



AKS-6-107CHIRAL, OD-H

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 45.466 | 403719.20 | 3231.48 | 1.00 | 1.00 | | | *MM | 0.4037 | 0.4037 |
| 2 | | 53.738 | 40009143.26 | 188716.66 | 99.00 | 99.00 | | | *MM | 40.0091 | 40.0091 |
| | | | 40412862.46 | 191948.14 | 100.00 | 100.00 | | | | 40.4129 | 40.4129 |

**Figure S101.** HPLC chromatogram of **(*R*)-3a** (OD-H column; 97:3 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

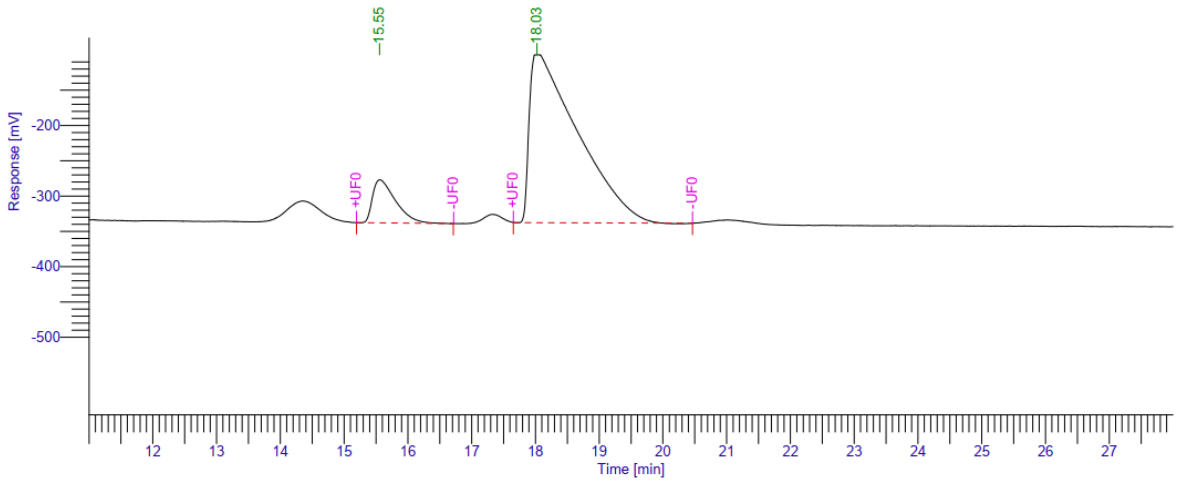
## Racemization of (*R*)-1a in the presence of Cu(I)-(*S*)-XylBINAP at 70 °C in *O*-Xylene




(*R*)-AZIRIDINE, 3 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 20.086 | 1276953.27 | 33722.33 | 5.57 | 5.57 | | | *MM | 1.2770 | 1.2770 |
| 2 | | 23.379 | 21654078.62 | 209280.63 | 94.43 | 94.43 | | | *MM | 21.6541 | 21.6541 |
| | | | 22931031.90 | 243002.96 | 100.00 | 100.00 | | | | 22.9310 | 22.9310 |

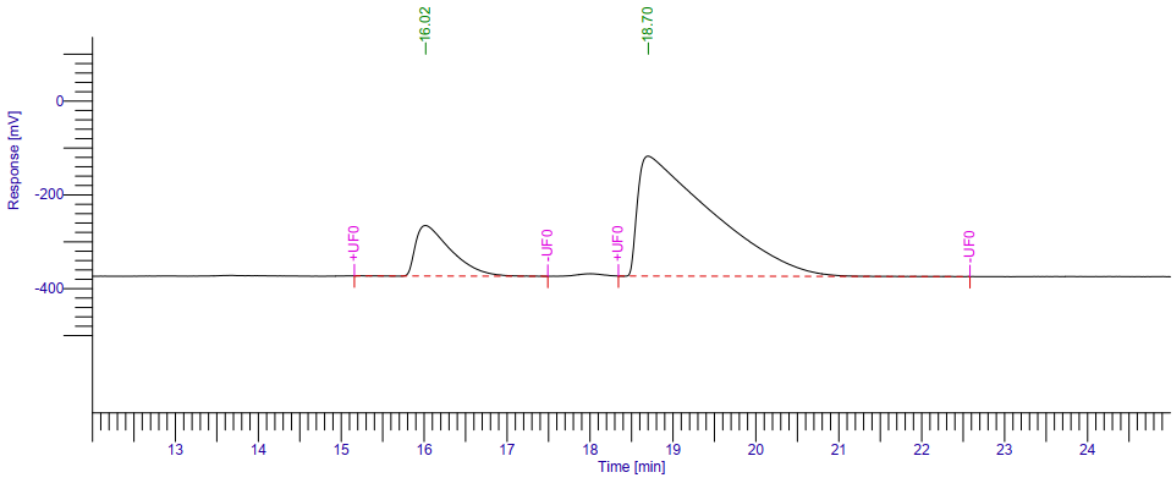
**Figure S102.** HPLC Chromatogram of racemized (*R*)-2a′ after 3 hours (*ee* 89%); (OJ-H column; 80:20 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




(*R*)-AZIRIDINE, 6 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 15.554 | 1526569.45 | 61042.49 | 10.75 | 10.75 | | | *MM | 1.5266 | 1.5266 |
| 2 | | 18.025 | 12670363.12 | 242935.64 | 89.25 | 89.25 | | | *MM | 12.6704 | 12.6704 |
| | | | 14196932.57 | 303978.13 | 100.00 | 100.00 | | | | 14.1969 | 14.1969 |

**Figure S103.** HPLC Chromatogram of racemized (*R*)-2a′ after 6 hours (*ee* 79%); (OJ-H column; 80:20 Hexane–Isopropanol; 1.0 mL $min^{-1}$

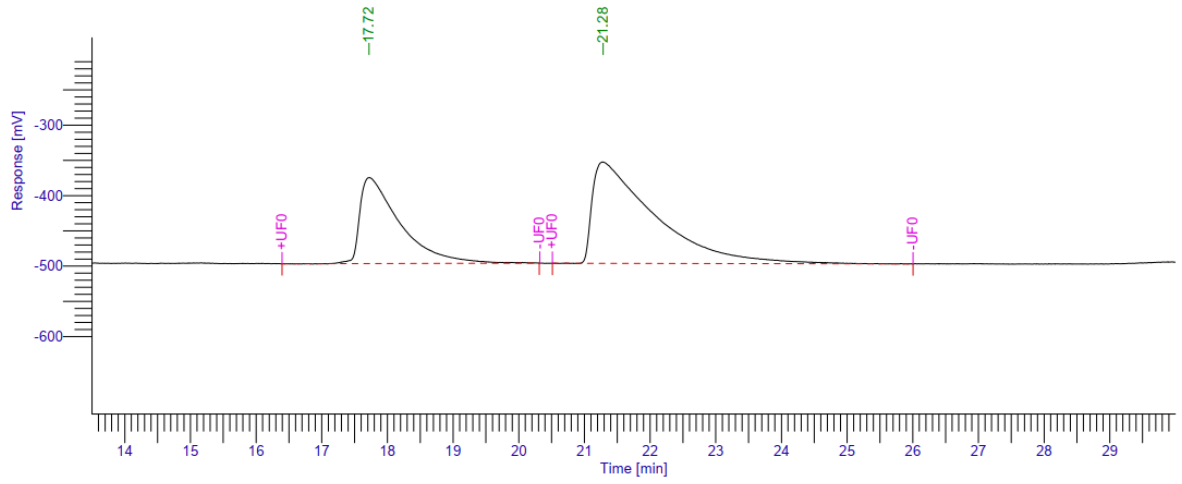



(*R*)-Aziridine, 9 h

(*R*)-Aziridine, 12 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 16.016 | 3173919.81 | 107589.15 | 16.63 | 16.63 | | | *MM | 1.5266 | 1.5266 |
| 2 | | 18.700 | 15914922.69 | 255766.27 | 83.37 | 83.37 | | | *MM | 12.6704 | 12.6704 |
| 3 | | 56.153 | 115.08 | 117.99 | 0.00 | 0.00 | | | | | |
| | | | | | | | | | | 14.1969 | 14.1969 |
| | | | 19088957.59 | 363473.41 | 100.00 | 100.00 | | | | | |

**Figure S104.** HPLC Chromatogram of racemized (*R*)-2a′ after 9 hours (*ee* 67%); (OJ-H column; 80:20 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

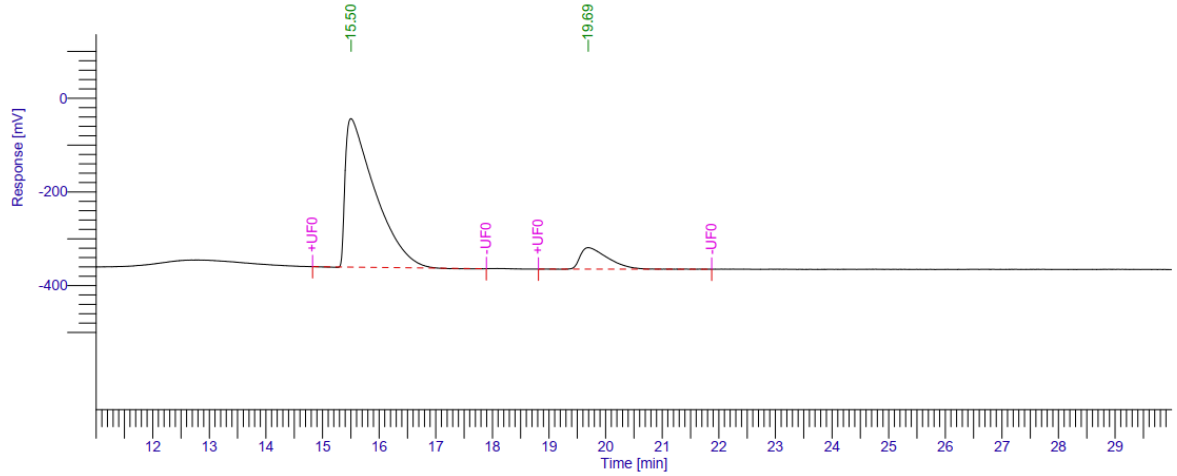



(*R*)-AZIRIDINE, 16 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 17.717 | 5166183.07 | 121906.46 | 35.27 | 35.27 | | | *MM | 5.1662 | 5.1662 |
| 2 | | 21.281 | 9480549.84 | 143885.18 | 64.73 | 64.73 | | | *MM | 9.4805 | 9.4805 |
| | | | 14646732.90 | 265791.64 | 100.00 | 100.00 | | | | 14.6467 | 14.6467 |

**Figure S105.** HPLC Chromatogram of racemized (*R*)-2a′ after 16 hours (*ee* 29%); (OJ-H column; 80:20 Hexane−Isopropanol; 1.0 mL $min^{-1}$)

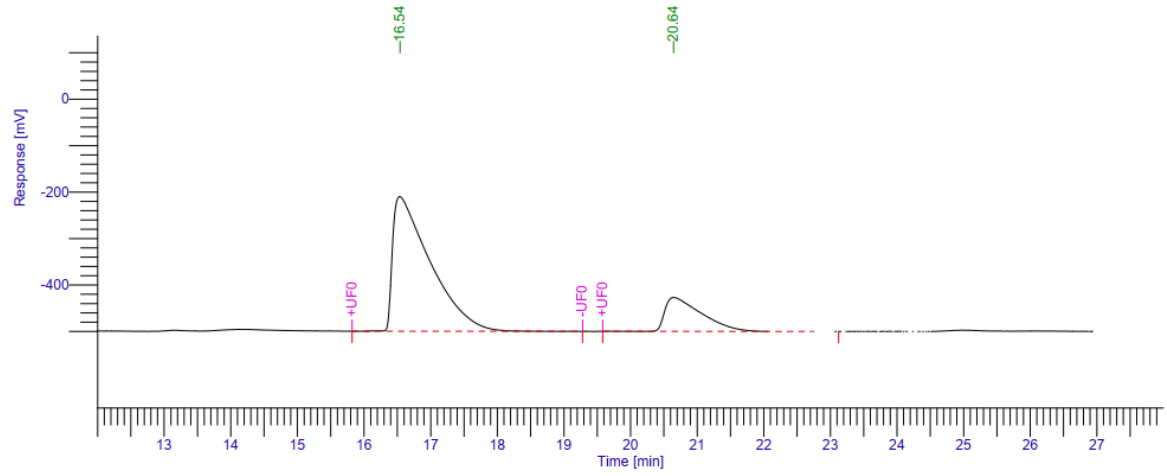
## Racemization of (*S*)-1a in the presence of Cu(I)-(*S*)-XylBINAP at 70 °C in *O*-Xylene




(S)-AZIRIDINE, 3 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 15.503 | 11587881.27 | 316887.54 | 88.33 | 88.33 | | | *MM | 11.5879 | 11.5879 |
| 2 | | 19.690 | 1531562.55 | 45820.18 | 11.67 | 11.67 | | | *MM | 1.5316 | 1.5316 |
| | | | 13119443.81 | 362707.72 | 100.00 | 100.00 | | | | 13.1194 | 13.1194 |

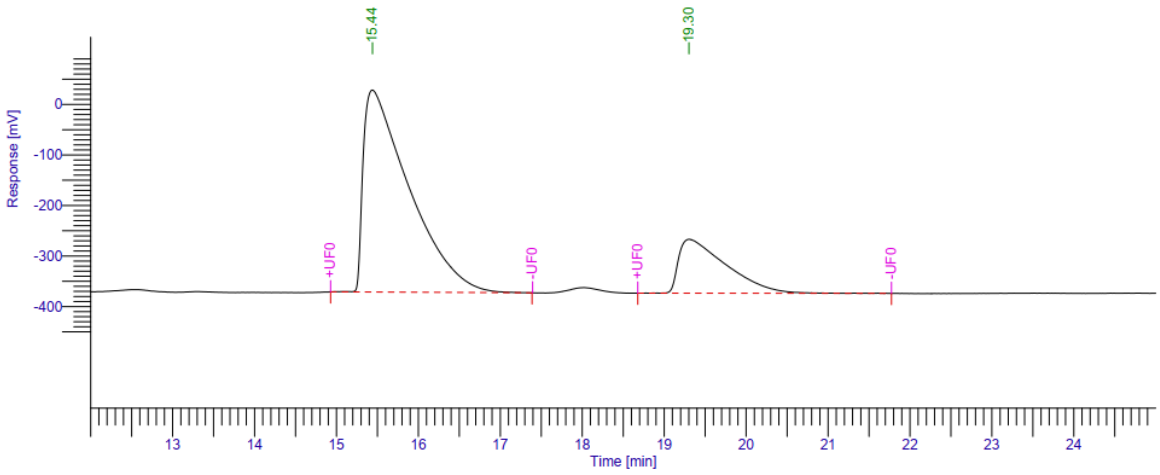
**Figure S106.** HPLC Chromatogram of racemized (*S*)-2a″ after 3 hours (*ee* 77%); (OJ-H column; 80:20 Hexane–Isopropanol; 1.0 mL $min^{-1}$)




(S)-AZIRIDINE, 6 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 16.537 | 11372666.02 | 289833.93 | 80.40 | 80.40 | | | *MM | 11.3727 | 11.3727 |
| 2 | | 20.643 | 2771973.31 | 72961.30 | 19.60 | 19.60 | | | *MM | 2.7720 | 2.7720 |
| | | | 14144639.32 | 362795.23 | 100.00 | 100.00 | | | | 14.1446 | 14.1446 |

**Figure S107.** HPLC Chromatogram of racemized (*S*)-2a″ after 6 hours (*ee* 61%); (OJ-H column; 80:20 Hexane–Isopropanol; 1.0 mL $min^{-1}$)

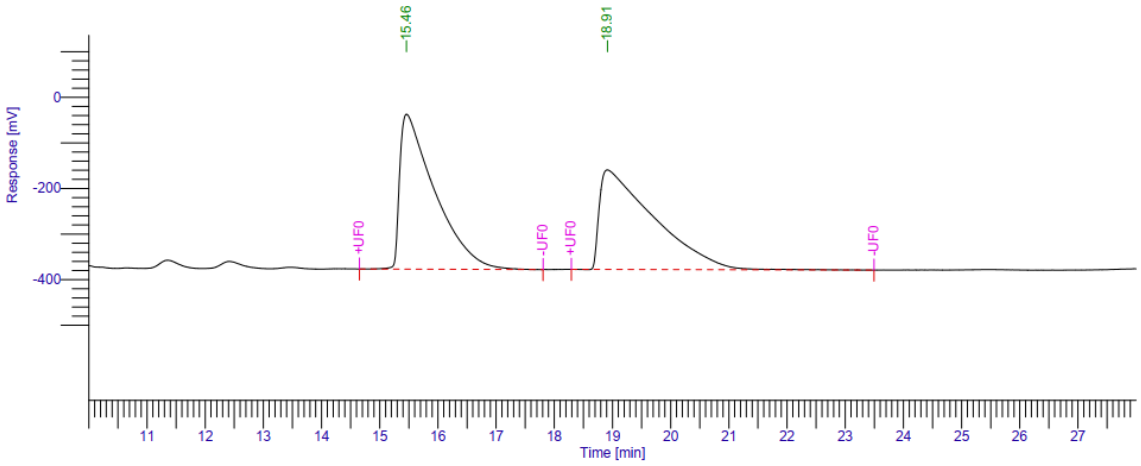



(*S*)-Aziridine, 9 h

(*S*)-Aziridine, 9 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 15.437 | 15604077.31 | 399686.39 | 78.41 | 78.41 | | | *MM | 12.6778 | 12.6778 |
| 2 | | 19.301 | 4295803.51 | 106731.95 | 21.59 | 21.59 | | | *MM | 1.3216 | 1.3216 |
| 3 | | 35.531 | 131.91 | 92.61 | 0.00 | 0.00 | | | | | |
| | | | | | | | | | | 13.9994 | 13.9994 |
| | | | 19900012.74 | 506510.95 | 100.00 | 100.00 | | | | | |

**Figure S108.** HPLC Chromatogram of racemized (*S*)-2a″ after 9 hours (*ee* 51%); (OJ-H column; 80:20 Hexane−Isopropanol; 1.0 mL $min^{-1}$)




(*S*)-Aziridine, 16 h

(*S*)-Aziridine, 16 h

| Peak # | Component Name | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] | Cal. Range | Volt Range | BL | Raw Amount | Adjusted Amount |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 15.459 | 14198744.41 | 339811.99 | 50.01 | 52.01 | | | *MM | 14.1987 | 14.1987 |
| 2 | | 18.913 | 14194230.78 | 218333.22 | 47.99 | 47.99 | | | *MM | 13.1942 | 13.1942 |
| | | | 28392975.19 | 558145.21 | 100.00 | 100.00 | | | | 27.3930 | 27.3930 |

**Figure S109.** HPLC Chromatogram of racemized (*S*)-2a″ after 16 hours (*ee* 5%); (OJ-H column; 80:20 Hexane−Isopropanol; 1.0 mL $min^{-1}$)