

***N*-Heterocyclic Carbene-Catalyzed Enantioselective [3 + 2] Annulation of Enals with Propargylic Imines: Access to γ,γ -Disubstituted Pyrrolidin-2-ones Bearing Quaternary Stereogenic Center**

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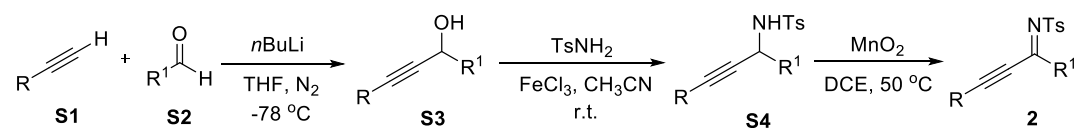
I. Materials and methods

All reagents and solvents were commercially available and were used without further purification. Flash column chromatography was performed over silica gel 200-300 mesh. Melting points were measured with a Fisher Johns apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker spectrometers at 300 MHz or 400 MHz and are reported relative to residual solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ , ppm), multiplicity, coupling constant (J , Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift at 75 MHz or 101 MHz and reported in terms of chemical shift (δ ppm). The solvent signals were used as references (residual CHCl_3 in CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.0$ ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High-resolution mass spectra were obtained on Agilent 6520 Accurate-Mass Q-TOF LC/MS mass spectrometer with ESI source. The d.r. values and er values for asymmetric study were determined via chiral HPLC analysis on SHIMADZU LC20A. XRD was analyzed on Bruker smart Apex 2, Bruker D8 Venture.

II. Experimental Procedures

A. General procedure for the synthesis of substrates.

All the enals **1** were synthesized according to the reported methods.¹ Most of the propargylic imines **2** were synthesized as the following method.²



Synthesis of **2**:

To a solution of **S1** (20 mmol, 1.0 equiv) in anhydrous THF (50 mL) was added *n*-BuLi (2.5 M in hexane, 24 mmol, 1.2 equiv) at $-78\text{ }^{\circ}\text{C}$ under N_2 atmosphere. The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 mins, and then was stirred at room temperature for 1 h. After cooling to $-78\text{ }^{\circ}\text{C}$ again, **S2** (20 mmol, 1.0 equiv) was added to the mixture, which was warmed up to room temperature gradually, and was stirred for an additional hour before quenched with aqueous NH_4Cl . After extracting with ethyl acetate ($3 \times 20\text{ mL}$), combined organic phases was washed with water and brine, dried over anhydrous MgSO_4 . After filtration of MgSO_4 , the filtrate was concentrated under reduced pressure. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate) to give the desired propargyl alcohol **S3** as an oil in quantitative yield³.

To a 25 mL round flask were successively added **S3** (10 mmol, 1.0 equiv), TsNH_2 (11 mmol, 1.1 equiv), CH_3CN (5 mL), and anhydrous FeCl_3 (1 mmol, 10 mol%). Then the mixture was magnetically stirred at room temperature for 2 h. After that, the solvent was concentrated under

reduced pressure and then the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford **S4**.

To a stirred solution of **S4** (10 mmol, 1.0 equiv) in DCE (20 mL) was added the activated manganese dioxide (100 mmol, 10.0 equiv) at room temperature. After stirring vigorously for 11 h at 50 °C, the insoluble materials were filtered. Then the filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give substrates **2**.

B. General procedure for the annulation of enals with propargylic imines for the synthesis of products **3.**

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **1a** (0.24 mmol, 1.2 equiv), **2a** (0.2 mmol, 1.0 equiv), Cs₂CO₃ (0.06 mmol, 30 mol%), and NHC catalyst A (0.02 mmol, 10 mol%). Then the tube was sealed with a rubber stopper, and was evacuated and refilled with nitrogen for three times. After that, Mesitylene (4 mL) and *t*BuOH (0.4 mL) was added, and the reaction mixture was allowed to be stirred for 3 h at room temperature. After completion of the reaction, the reaction mixture was filtered and concentrated under reduced pressure, then the residue was subjected to column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to afford the desired product **3**. The d.r. and the er values were determined by HPLC analysis.

C. General procedure for the scale-up synthesis of product **3a.**

To a 50 mL Schlenk tube equipped with a magnetic stir bar, was added **1a** (1.2 mmol, 1.2 equiv), **2a** (1 mmol, 1.0 equiv), Cs₂CO₃ (0.3 mmol, 30 mol%), and NHC catalyst A (0.1 mmol, 10 mol%). The tube was sealed with a rubber stopper, and was evacuated and refilled with nitrogen for three times. Mesitylene (10 mL) and *t*BuOH (1 mL) was added and the reaction mixture was allowed to be stirred for 12 h at room temperature. After completion of the reaction, the reaction mixture was filtered and concentrated under reduced pressure, then the residue was subjected to column chromatography using petroleum ether/ethyl acetate = 10/1 as eluent to afford the desired product **3a**. The d.r. and the er values were determined by HPLC analysis.

D. General procedure for the synthesis of product **4^{4,5}.**

To a solution of **3a** (0.2 mmol, 1.0 equiv) in THF (5 mL) was added SmI₂ (0.1 M, 1 mmol, 5.0 equiv) dropwise at 0 °C. After stirring for 10 mins at 0 °C, the resulting mixture was warmed to room temperature during 20 mins. Then 1 M HCl (5 mL) was added and the mixture was stirred for 5 mins. After extracting with CH₂Cl₂ (3 x 10 mL) and washing with brine (10 mL), the organic phase

was dried over anhydrous Na₂SO₄. After filtrating, the solvent was removed under reduced pressure. Pure compound **4** (47.6 mg, 62%) was obtained as a white solid after eluting the crude on a small plug of silica (petroleum ether/ethyl acetate = 10/1) under pressure. The d.r. and the er values were determined by HPLC analysis.

E. General procedure for the removal of tosyl group of products **3g-3j, **3l**, **3m**, **3o**, **3p**, **3t**, **3u**^{4,5}.**

The procedure for removing the tosyl group of products **3g-3j**, **3l**, **3m**, **3o**, **3p**, **3t**, **3u** was conducted in 0.05 mmol scale following the general procedure for the synthesis of product **4**. Then the d.r. and the er values were determined by HPLC analysis.

F. General procedure for the synthesis of product **5⁵.**

To a solution of **3a** (0.2 mmol, 1.0 equiv) in MeOH (5 mL) was added 5% Pd/C (0.02 mmol, 10 mol%) at room temperature. Then the reaction system was evacuated twice under reduced pressure, and a H₂ balloon was placed on the stopper. After stirring for 12 h at room temperature, the resulting mixture was filtered through celite and the filtrate was concentrated. And the residue was purified by column chromatography on a silica gel column (petroleum ether/ethyl acetate = 20/1) to afford the desired product **5** (58 mg, 56%). The d.r. and the er values were determined by HPLC analysis.

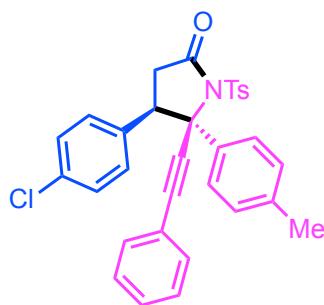
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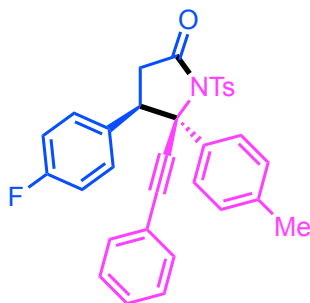
IV. Characterization data

Note: All of the yields given below were the overall yields for the mixture of the two diastereoisomers of products **3a-3z**. For products **3a-3e**, **3g**, **3i-3n**, **3p**, **3s**, and **3x-3z**, only the major diastereoisomer could be isolated through recrystallization from the mixture, thus the structures and names of **3a-3e**, **3g**, **3i-3n**, **3p**, **3s**, and **3x-3z** were given according to the major enantiomers of their major diastereoisomers. And the melting points, the specific rotations, the NMR and the HRMS were determined using the purely isolated major diastereoisomer of **3a-3e**, **3g**, **3i-3n**, **3p**, **3s**, and

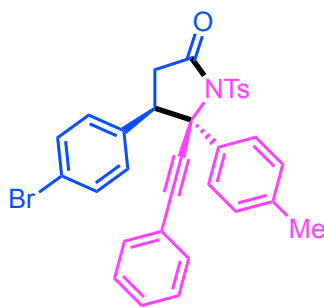
3x-3z as the samples. For products **3f**, **3h**, **3o**, **3q**, **3r**, and **3t-3w**, it was difficult to realize the isolation of the two diastereoisomers. Thus, the structures and names of **3f**, **3h**, **3o**, **3q**, **3r**, and **3t-3w** were given without the consideration of the stereochemistry. And the melting points, the specific rotations, the NMR and the HRMS were determined using the mixture of the diastereoisomers of **3f**, **3h**, **3o**, **3q**, **3r**, and **3t-3w** as the samples. The absolute configuration of the major diastereomer of **3c** was assigned to be (4*R*, 5*S*) by an X-ray crystallographic analysis of the related enantiopure sample. And the absolute configuration of other products was assigned by analogy.



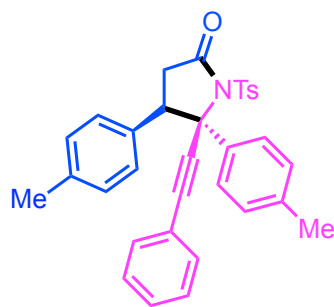
(4*R*,5*S*)-4-(4-chlorophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3a). White solid. 91.8 mg, 85% yield. mp: 181-182 °C. $[\alpha]_D^{25} = -108.621$ ($c = 0.058$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, t_R (major) = 27.954 min, t_R (minor) = 35.411 min; er (minor diastereoisomer) = 88:12, t_R (major) = 30.800 min, t_R (minor) = 25.577 min. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.40-7.30 (m, 5H), 7.23 (dd, $J = 8.1, 4.6$ Hz, 4H), 7.17 (dt, $J = 8.5, 2.8$ Hz, 2H), 6.76 (dt, $J = 8.6, 2.8$ Hz, 2H), 3.78 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.06 (dd, $J = 16.7, 13.0$ Hz, 1H), 2.73 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.43, 145.06, 138.27, 137.09, 135.39, 134.13, 132.29, 131.60, 130.22, 129.62, 129.25, 129.16, 128.96, 128.46, 128.00, 126.13, 121.46, 91.40, 84.60, 72.62, 54.81, 35.58, 21.68, 21.21. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 540.1395, found: 540.1388.



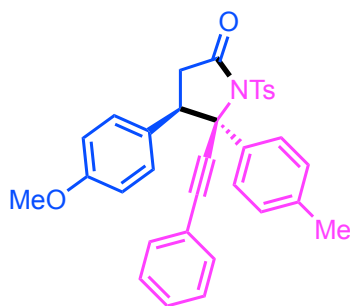
(4*R*,5*S*)-4-(4-fluorophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3b). White solid. 83.6 mg, 80% yield. mp: 225-226 °C. $[\alpha]_D^{25} = -236.145$ ($c = 0.166$ in CHCl_3). HPLC DAICEL CHIRALCEL IF, *n*-hexane/ethanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, $t_R(\text{major}) = 74.594$ min, $t_R(\text{minor}) = 142.223$ min; er (minor diastereoisomer) = 90:10, $t_R(\text{major}) = 116.933$ min, $t_R(\text{minor}) = 71.303$ min. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.3$ Hz, 2H), 7.48-7.45 (m, 2H), 7.39-7.30 (m, 5H), 7.23 (dd, $J = 8.3, 2.6$ Hz, 4H), 6.90 (t, $J = 8.6$ Hz, 2H), 6.83-6.78 (m, 2H), 3.80 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.07 (dd, $J = 16.7, 13.1$ Hz, 1H), 2.73 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.53, 162.56 (d, $^1J_{\text{C-F}} = 247.5$ Hz), 145.03, 138.20, 137.17, 135.41, 131.57, 130.49 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 129.61, 129.49 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 129.21, 129.12, 128.95, 128.43, 126.13, 121.51, 114.75 (d, $^2J_{\text{C-F}} = 21.5$ Hz), 91.32, 84.66, 72.9, 54.68, 35.74, 21.67, 21.20. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{FNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 524.1690, found: 524.1682.



(4*R*,5*S*)-4-(4-bromophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3c). White solid. 98.2 mg, 84% yield. mp: 179-181 °C. $[\alpha]_D^{25} = -189.744$ ($c = 0.390$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, $t_R(\text{major}) = 30.275$ min, $t_R(\text{minor}) = 36.747$ min; er (minor diastereoisomer) = 87:13, $t_R(\text{major}) = 32.226$ min, $t_R(\text{minor}) = 26.713$ min. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.43-7.31 (m, 7H), 7.24-7.21 (m, 4H), 6.70 (d, $J = 8.4$ Hz, 2H), 3.77 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.06 (dd, $J = 16.7, 13.0$ Hz, 1H), 2.73 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.39, 145.05, 138.26, 137.06, 135.36, 132.83, 131.60, 130.93, 130.54, 129.59, 129.24, 129.16, 128.95, 128.45, 126.11, 122.32, 121.43, 91.41, 84.56, 72.52, 54.85, 35.50, 21.66, 21.19. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 584.0890, found: 584.0886.

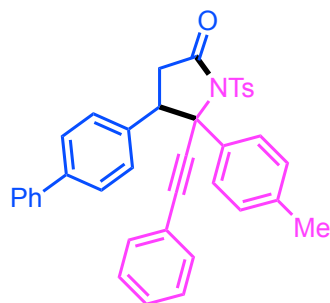


(4*R*,5*S*)-5-(phenylethynyl)-4,5-di-*p*-tolyl-1-tosylpyrrolidin-2-one (3d). White solid. 86.8 mg, 83% yield. mp: 175-176 °C. $[\alpha]_D^{25} = -235.5$ ($c = 0.2$ in CHCl_3). HPLC DAICEL CHIRALCEL IF, *n*-hexane/ethanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 95:5, $t_R(\text{major}) = 68.892$ min, $t_R(\text{minor}) = 126.620$ min; er (minor diastereoisomer) = 84:16, $t_R(\text{major}) = 101.639$ min, $t_R(\text{minor}) = 63.789$ min. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H), 7.38-7.33 (m, 5H), 7.22 (dd, $J = 8.2, 4.5$ Hz, 4H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 7.8$ Hz, 2H), 3.78 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.11 (dd, $J = 16.8, 13.1$ Hz, 1H), 2.71 (dd, $J = 16.8, 7.2$ Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.92, 144.90, 137.97, 137.89, 137.48, 135.51, 131.64, 130.64, 129.60, 129.09, 128.94, 128.90, 128.83, 128.49, 128.33, 126.16, 121.79, 91.01, 85.05, 72.90, 55.09, 35.75, 21.64, 21.19, 21.08. HRMS (ESI) m/z : Calcd. for $\text{C}_{33}\text{H}_{30}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 520.1941, found: 520.1930.

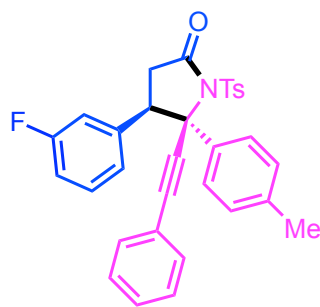


(4*R*,5*S*)-4-(4-methoxyphenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3e). White solid. 84.1 mg, 79% yield. mp: 201-203 °C. $[\alpha]_D^{25} = -235.537$ ($c = 0.242$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 95:5, $t_R(\text{major}) = 38.633$ min, $t_R(\text{minor}) = 50.427$ min; er (minor diastereoisomer) = 88:12, $t_R(\text{major}) = 42.139$ min, $t_R(\text{minor}) = 35.971$ min. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 2H), 7.38-7.34 (m, 5H), 7.22 (dd, $J = 8.2, 2.2$ Hz, 4H), 6.78- 6.72 (m, 4H), 3.79-3.73 (m, 4H), 3.08 (dd, $J = 16.7, 13.2$ Hz, 1H), 2.71 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.90, 159.38, 144.92,

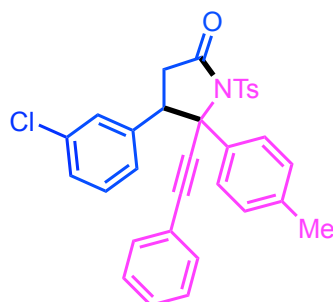
137.96, 137.44, 135.48, 131.63, 130.01, 129.61, 129.10, 128.96, 128.90, 128.35, 126.15, 125.55, 121.75, 113.16, 91.02, 85.01, 72.96, 55.18, 54.82, 35.83, 21.65, 21.20. HRMS (ESI) m/z : Calcd. for $C_{33}H_{30}NO_4S$ ($M+H$)⁺: 536.1890, found: 536.1887.



4-([1,1'-biphenyl]-4-yl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3f, mixture of the diastereoisomers). White solid. 86.5 mg, 74% yield. mp: 184-185 °C. $[\alpha]_D^{25} = +22.951$ ($c = 0.244$ in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/ethanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, t_R major = 108.971 min, t_R minor = 189.552 min; er (minor diastereoisomer) = 85:15, t_R major = 160.871 min, t_R minor = 97.885 min; 1H NMR (400 MHz, $CDCl_3$) mixture of the diastereoisomers: δ 8.15 (d, $J = 8.3$ Hz, 0.67H, minor dr), 8.04 (d, $J = 8.3$ Hz, 1.27 H, major dr), 7.64-7.59 (m, 1H), 7.55-7.51 (m, 3H), 7.45-7.38 (m, 4H), 7.36-7.30 (m, 5H), 7.28-7.21 (m, 3H), 7.13 (d, $J = 8.2$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.3$ Hz, 1.24H, major dr), 6.86 (d, $J = 8.2$ Hz, 0.71H, minor dr), 4.19 (dd, $J = 13.6, 7.6$ Hz, 0.35H, minor dr), 3.86 (dd, $J = 12.8, 7.2$ Hz, 0.65H, major dr), 3.15 (dd, $J = 16.8, 12.8$ Hz, 0.63H, major dr), 3.04 (dd, $J = 16.7, 13.7$ Hz, 0.37H, minor dr), 2.77 (dd, $J = 16.7, 7.2$ Hz, 0.65H, major dr), 2.63 (dd, $J = 16.7, 7.2$ Hz, 0.35H, minor dr), 2.43 (s, 1.01H, minor dr), 2.42 (s, 1.79H, major dr), 2.40 (s, 1.96H, major dr), 2.28 (s, 0.97H, minor dr). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.73, 172.20, 144.93, 140.85, 140.61, 140.31, 140.23, 138.04, 138.00, 137.42, 136.25, 135.43, 133.62, 132.93, 132.84, 131.75, 131.57, 129.54, 129.29, 129.20, 129.14, 129.05, 129.01, 128.95, 128.89, 128.77, 128.71, 128.52, 128.33, 127.38, 126.91, 126.85, 126.41, 126.38, 126.15, 122.07, 121.61, 91.16, 89.07, 87.28, 84.96, 72.75, 71.11, 55.03, 53.67, 35.61, 34.53, 21.64, 21.61, 21.17, 20.96. HRMS (ESI) m/z : Calcd. for $C_{38}H_{31}NO_3S$ ($M+H$)⁺: 582.2097, found: 582.2088.

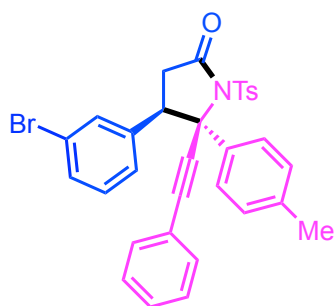


(4*R*,5*S*)-4-(3-fluorophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3g). White solid. 75.1 mg, 72% yield. mp: 191-192 °C. $[\alpha]_D^{25} = -175.352$ ($c = 0.284$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 97:3, $t_R(\text{major}) = 26.617$ min, $t_R(\text{minor}) = 18.629$ min; er (minor diastereoisomer) = 90:10, $t_R(\text{major}) = 28.931$ min, $t_R(\text{minor}) = 22.764$ min, er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.41-7.32 (m, 5H), 7.23 (t, $J = 7.0$ Hz, 4H), 7.19-7.13 (m, 1H), 6.97 (td, $J = 8.6, 2.3$ Hz, 1H), 6.59 (dd, $J = 19.8, 9.6$ Hz, 2H), 3.82 (dd, $J = 12.7, 7.2$ Hz, 1H), 3.17-2.98 (m, 1H), 2.78-2.71 (m, 1H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.34, 162.22 (d, $^1J_{\text{C-F}} = 246.7$ Hz), 145.07, 138.31, 137.17, 136.53 (d, $^3J_{\text{C-F}} = 7.7$ Hz), 135.36, 131.61, 129.57, 129.27, 129.20, 129.13, 128.96, 128.43, 126.11, 124.75 (d, $^4J_{\text{C-F}} = 2.9$ Hz), 121.46, 115.78 (d, $^2J_{\text{C-F}} = 22.1$ Hz), 115.11 (d, $^2J_{\text{C-F}} = 21.0$ Hz), 91.40, 84.54, 72.53, 54.89, 35.56, 21.67, 21.21. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{FNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 524.1690, found: 524.1687.



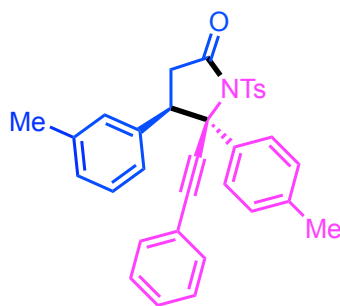
4-(3-chlorophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3h, mixture of the diastereoisomers). White solid. 48.5 mg, 45% yield. mp: 180-183 °C. $[\alpha]_D^{25} = +25.788$ ($c = 0.296$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, $t_R(\text{major}) = 31.904$ min, $t_R(\text{minor}) = 18.654$ min; er (minor diastereoisomer) = 83:17, $t_R(\text{major}) = 28.012$ min, $t_R(\text{minor}) = 25.292$ min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ

8.12 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.60-7.58 (m, 1H), 7.49-7.33 (m, 5H), 7.30-7.22 (m, 4H), 7.17-7.00 (m, 3H), 6.97 (s, 0.49H, major dr), 6.74 (s, 0.44H, minor dr), 6.67 (d, $J = 7.8$ Hz, 0.44H, minor dr), 6.60 (d, $J = 7.7$ Hz, 0.50H, major dr), 4.09 (dd, $J = 12.3, 7.6$ Hz, 0.47H, minor dr), 3.78 (dd, $J = 12.7, 7.2$ Hz, 0.53H, major dr), 3.06 (dd, $J = 16.7, 12.7$ Hz, 0.52H, major dr), 2.96 (dd, $J = 16.8, 13.6$ Hz, 0.47H, minor dr), 2.75 (dd, $J = 16.7, 7.2$ Hz, 0.52H, major dr), 2.61 (dd, $J = 16.7, 7.6$ Hz, 0.48H, minor dr), 2.44 (s, 1.33H, minor dr), 2.42 (s, 1.43H, major dr), 2.40 (s, 1.61H, major dr), 2.30 (s, 1.37H, minor dr). ^{13}C NMR (101 MHz, CDCl_3): δ 172.29, 171.80, 145.07, 138.43, 138.30, 137.16, 136.17, 136.08, 135.98, 135.35, 133.77, 133.73, 133.36, 131.77, 131.71, 129.56, 129.26, 129.15, 129.13, 129.06, 129.03, 129.02, 128.97, 128.90, 128.89, 128.75, 128.57, 128.41, 128.35, 128.07, 127.51, 126.71, 126.05, 121.93, 121.39, 91.55, 88.66, 87.66, 84.54, 72.51, 70.92, 54.94, 53.59, 35.49, 34.32, 21.70, 21.66, 21.19, 21.94. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 540.1395, found: 540.1392.

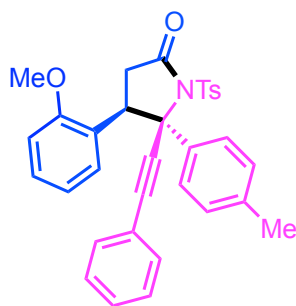


(4*R*,5*S*)-4-(3-bromophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3i). White solid. 81 mg, 69% yield. mp: 201-203 °C. $[\alpha]_{\text{D}}^{25} = -149.874$ ($c = 0.264$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, n -hexane/ i -propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 97:3, $t_{\text{R}}(\text{major}) = 69.370$ min, $t_{\text{R}}(\text{minor}) = 38.973$ min; er (minor diastereoisomer) = 88:12, $t_{\text{R}}(\text{major}) = 60.329$ min, $t_{\text{R}}(\text{minor}) = 55.888$ min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.41-7.34k (m, 6H), 7.25-7.22 (m, 4H), 7.14 (t, $J = 1.8$ Hz, 1H), 7.04 (t, $J = 7.8$ Hz, 1H), 6.63 (d, $J = 8.4$ Hz, 1H), 3.77 (dd, $J = 12.6, 7.2$ Hz, 1H), 3.05 (dd, $J = 16.7, 12.7$ Hz, 1H), 2.74 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.26, 145.07, 138.29, 137.14, 136.32, 135.33, 131.76, 131.60, 131.28, 129.56, 129.32, 129.25, 129.16, 128.97, 128.40, 128.02, 126.04, 121.90, 121.35, 91.58, 84.51, 72.53, 54.95, 35.46, 21.67, 21.19. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{27}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 584.0890, found:

584.0887.

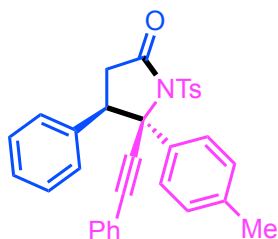


(4R,5S)-5-(phenylethynyl)-4-(*m*-tolyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3j). White solid. 81.4 mg, 78% yield. mp: 213-215 °C. $[\alpha]_D^{25} = -191.060$ ($c = 0.302$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 97:3, $t_R(\text{major}) = 25.636$ min, $t_R(\text{minor}) = 18.896$ min; er (minor diastereoisomer) = 90:10, $t_R(\text{major}) = 28.816$ min, $t_R(\text{minor}) = 22.429$ min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.40-7.29 (m, 5H), 7.23 (dd, $J = 8.2, 2.5$ Hz, 4H), 7.08 (d, $J = 4.9$ Hz, 2H), 6.68 (s, 1H), 6.60 (t, $J = 4.7$ Hz, 1H), 3.76 (dd, $J = 12.6, 7.3$ Hz, 1H), 3.10 (dd, $J = 16.8, 12.2$ Hz, 1H), 2.73 (dd, $J = 16.8, 7.3$ Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.92, 144.91, 138.01, 137.62, 137.31, 135.56, 133.98, 131.64, 129.58, 129.50, 129.09, 128.94, 128.85, 128.31, 127.66, 126.20, 126.13, 121.78, 91.08, 85.17, 72.85, 55.33, 35.69, 21.65, 21.31, 21.18. HRMS (ESI) m/z : Calcd. for $\text{C}_{33}\text{H}_{30}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 520.1941, found: 520.1928.

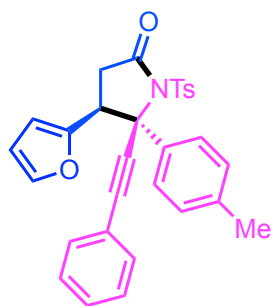


(4R,5S)-4-(2-methoxyphenyl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3k). White solid. 39.1 mg, 37% yield. mp: 210-212 °C. $[\alpha]_D^{25} = -241.589$ ($c = 0.214$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 91:9, $t_R(\text{major}) = 30.781$ min, $t_R(\text{minor}) = 50.525$ min; er (minor diastereoisomer) = 79:21, $t_R(\text{major}) = 37.600$ min, $t_R(\text{minor}) = 27.869$ min. ^1H NMR (400 MHz,

CDCl₃): δ 8.05 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H), 7.34- 7.19 (m, 10H), 7.14 (d, J = 7.2 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.13 (t, J = 8.3 Hz, 1H), 3.14 (s, 3H), 2.84 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 173.50, 157.81, 144.64, 139.60, 137.55, 135.99, 131.69, 129.56, 129.52, 129.07, 129.03, 128.87, 128.72, 128.24, 125.54, 125.26, 122.06, 119.90, 110.37, 89.90, 86.44, 72.28, 54.46, 49.11, 35.83, 21.62, 21.06. HRMS (ESI) m/z : Calcd. for C₃₃H₃₀NO₄S (M+H)⁺: 536.1890, found: 536.1876.

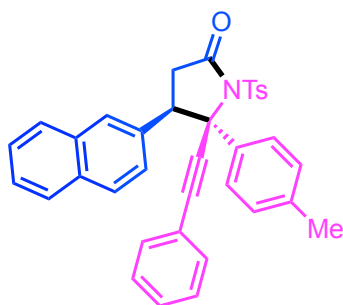


(4R,5S)-4-phenyl-5-(phenylethynyl)-5-(p-tolyl)-1-tosylpyrrolidin-2-one (3l). White solid. 77.5 mg, 77% yield. mp: 217-219 °C. $[\alpha]_D^{25}$ = -240.588 (c = 0.17 in CHCl₃). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 96:4, t_R (major) = 28.148 min, t_R (minor) = 20.525 min; er (minor diastereoisomer) = 88:12, t_R (major) = 33.453 min, t_R (minor) = 24.127 min; er was determined by chiral HPLC after removing the tosyl group. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.39-7.29 (m, 5H), 7.27-7.19 (m, 7H), 6.85 (d, J = 7.1 Hz, 2H), 3.83 (dd, J = 12.9, 7.2 Hz, 1H), 3.13 (dd, J = 16.8, 12.9 Hz, 1H), 2.74 (dd, J = 16.7, 7.2 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 172.83, 144.95, 138.06, 137.45, 135.49, 133.86, 131.61, 129.60, 129.15, 128.98, 128.93, 128.34, 128.16, 127.88, 127.80, 126.17, 121.69, 91.13, 84.92, 72.81, 55.32, 35.59, 21.66, 21.20. HRMS (ESI) m/z : Calcd. for C₃₂H₂₇NO₃S (M+H)⁺: 506.1784, found: 506.1792.

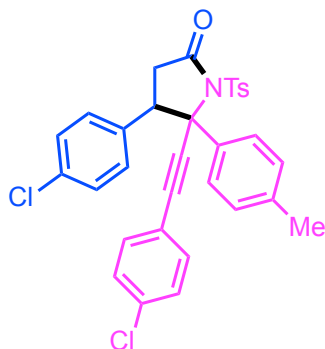


(4S,5S)-4-(furan-2-yl)-5-(phenylethynyl)-5-(p-tolyl)-1-tosylpyrrolidin-2-one (3m). White solid. 55.7 mg, 56% yield. mp: 184-185 °C. $[\alpha]_D^{25}$ = -172.868 (c = 0.172 in CHCl₃). HPLC DAICEL

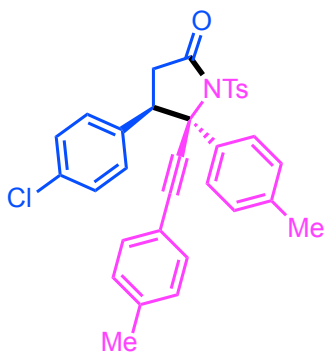
CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (minor diastereoisomer) = 94:6, t_R (major) = 26.627 min, t_R (minor) = 21.197 min; er (major diastereoisomer) = 87:13, t_R (major) = 22.966 min, t_R (minor) = 19.663 min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.43-7.35 (m 5H), 7.30 (d, J = 1.0 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.29 (dd, J = 3.1, 1.8 Hz, 1H), 5.93 (d, J = 3.2 Hz, 1H), 3.86 (dd, J = 11.8, 7.7 Hz, 1H), 3.13 (dd, J = 17.0, 11.9 Hz, 1H), 2.80 (dd, J = 17.0, 7.7 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.16, 149.09, 144.98, 142.39, 138.13, 137.79, 135.38, 131.76, 129.56, 129.28, 128.95, 128.92, 128.33, 125.87, 121.77, 110.42, 108.80, 90.04, 84.42, 71.55, 49.74, 34.30, 21.66, 21.19. HRMS (ESI) m/z : Calcd. for $\text{C}_{30}\text{H}_{25}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$) $^+$: 496.1577, found: 496.1571.



(4*R*,5*S*)-4-(naphthalen-2-yl)-5-(phenylethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3n). White solid. 95.8 mg, 82% yield. mp: 241-242 °C. $[\alpha]_D^{25} = -106.848$ ($c = 0.404$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 94:6, t_R (major) = 40.007 min, t_R (minor) = 45.466 min; er (minor diastereoisomer) = 90:10, t_R (major) = 33.270 min, t_R (minor) = 31.505 min. ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 8.7 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.47-7.42 (m, 2H), 7.35-7.19 (m, 10H), 6.92 (d, J = 8.4 Hz, 1H), 3.98 (dd, J = 12.6, 7.2 Hz, 1H), 3.25 (dd, J = 16.7, 12.8 Hz, 1H), 2.83 (dd, J = 16.7, 7.2 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.80, 144.96, 138.12, 137.56, 135.55, 133.03, 132.76, 131.61, 131.56, 129.61, 129.19, 128.96, 128.93, 128.28, 128.10, 127.82, 127.52, 127.26, 126.80, 126.19, 126.17, 126.10, 121.59, 91.29, 85.08, 72.93, 55.53, 35.83, 21.66, 21.21. HRMS (ESI) m/z : Calcd. for $\text{C}_{36}\text{H}_{30}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 556.1941, found: 556.1933.

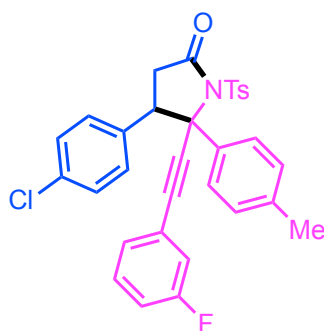


4-(4-chlorophenyl)-5-((4-chlorophenyl)ethynyl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (3o, mixture of the diastereoisomers). White solid. 93.2 mg, 81 % yield. mp: 167–171 °C. $[\alpha]_D^{25} = -51.756$ ($c = 1.158$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, t_R (major) = 44.336 min, t_R (minor) = 19.170 min; er (minor diastereoisomer) = 85:15, t_R (major) = 26.488 min, t_R (minor) = 29.107 min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, $J = 8.3$ Hz, 1H), 7.97 (d, $J = 8.3$ Hz, 1H), 7.49 (d, $J = 8.5$ Hz, 1H), 7.42 (dd, $J = 14.0, 8.3$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 3H), 7.17 (d, $J = 8.4$ Hz, 1H), 7.08–6.98 (m, 3H), 6.74 (d, $J = 8.4$ Hz, 1H), 6.69 (d, $J = 8.4$ Hz, 1H), 4.09 (dd, $J = 13.6, 7.6$ Hz, 0.52H, major dr), 3.78 (dd, $J = 12.8, 7.2$ Hz, 0.49H, minor), 3.05 (dd, $J = 16.7, 12.8$ Hz, 0.47H), 2.94 (dd, $J = 16.8, 13.6$ Hz, 0.48H), 2.74 (dd, $J = 16.7, 7.2$ Hz, 0.47H), 2.60 (dd, $J = 16.8, 7.6$ Hz, 0.48H), 2.44 (s, 1.3H), 2.42 (s, 3H), 2.31 (s, 1.5H). ^{13}C NMR (101 MHz, CDCl_3): δ 13C NMR (101 MHz, Chloroform- d) δ 172.32, 171.77, 145.14, 138.41, 138.39, 136.92, 136.18, 135.47, 135.33, 135.32, 134.21, 134.05, 133.17, 133.01, 132.82, 132.39, 132.34, 130.13, 129.90, 129.53, 129.28, 129.00, 128.85, 128.13, 128.04, 126.15, 126.10, 120.40, 119.92, 90.26, 89.82, 86.33, 85.71, 72.49, 70.87, 54.69, 53.32, 35.54, 34.51, 21.71, 21.68, 21.20, 21.01. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 574.1005, found: 574.1000.



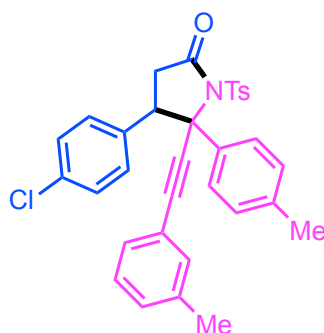
(4*R*, 5*S*)-4-(4-chlorophenyl)-5-(*p*-tolyl)-5-(*p*-tolyethynyl)-1-tosylpyrrolidin-2-one (3p). White

solid. 86.9 mg, 78 % yield. mp:163-168 °C. $[\alpha]_D^{25} = -53.963$ ($c = 0.9$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, n -hexane/ i -propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, $t_R(\text{major}) = 49.335$ min, $t_R(\text{minor}) = 21.073$ min; er (minor diastereoisomer) = 87:13, $t_R(\text{major}) = 33.430$ min, $t_R(\text{minor}) = 30.732$ min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.12 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 7.09-7.02 (m, 6H), 6.71 (d, $J = 8.5$ Hz, 2H), 4.10 (dd, $J = 13.6, 7.5$ Hz, 1H), 2.95 (dd, $J = 16.7, 13.6$ Hz, 1H), 2.59 (dd, $J = 16.7, 7.6$ Hz, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 171.89, 144.98, 139.38, 138.19, 136.22, 133.87, 133.49, 132.47, 131.66, 129.91, 129.30, 129.23, 128.99, 128.92, 128.02, 126.13, 118.83, 88.10, 87.66, 70.99, 53.34, 34.49, 21.68, 21.57, 20.99. HRMS (ESI) m/z : Calcd. for $\text{C}_{33}\text{H}_{29}\text{ClINO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 554.1551, found: 554.1547.

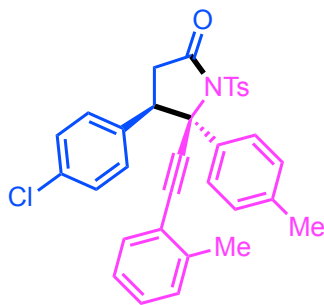


4-(4-chlorophenyl)-5-((3-fluorophenyl)ethynyl)-5-(p -tolyl)-1-tosylpyrrolidin-2-one (3q, mixture of the diastereoisomers). White solid. 88.7 mg, 79 % yield. mp:161-164 °C. $[\alpha]_D^{25} = +10.714$ ($c = 0.308$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, n -hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, $t_R(\text{major}) = 26.408$ min, $t_R(\text{minor}) = 46.672$ min; er (minor diastereoisomer) = 90:10, $t_R(\text{major}) = 40.252$ min, $t_R(\text{minor}) = 23.166$ min. ^1H NMR (400 MHz, CDCl_3): δ 8.08 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.40-7.23 (m, 5H), 7.19-6.97 (m, 6H), 6.76 (d, $J = 8.1$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 4.10 (dd, $J = 13.4, 7.6$ Hz, 0.5H), 3.78 (dd, $J = 12.7, 7.3$ Hz, 0.52H), 3.05 (dd, $J = 16.7, 12.7$ Hz, 0.5H), 2.94 (dd, $J = 16.8, 13.5$ Hz, 0.47H), 2.74 (dd, $J = 16.7, 7.3$ Hz, 0.52H), 2.60 (dd, $J = 16.7, 7.6$ Hz, 0.49H), 2.45 (s, 1.36H, minor dr), 2.42 (s, 3H), 2.31 (s, 1.45H, major dr). ^{13}C NMR (101 MHz, CDCl_3): δ 172.31, 171.76, 162.39 (d, $^1J_{\text{C-F}} = 248.4$ Hz), 162.23 ($^1J_{\text{C-F}} = 248.3$ Hz), 145.19, 138.41 (d, $^4J_{\text{C-F}} = 2.6$ Hz), 136.81, 136.13, 135.39, 134.23, 134.04, 133.07, 132.25 (d, $^4J_{\text{C-F}} = 3.2$ Hz), 130.31, 130.23, 130.15 (d, $^3J_{\text{C-F}} = 8.6$ Hz), 130.13, 129.90, 129.53, 129.29, 129.01, 128.97,

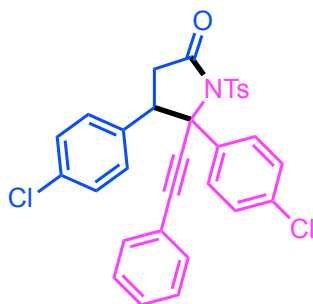
128.13, 128.05, 127.69, 127.66, 127.53, 127.50, 128.10 (d, $^3J_{C-F}$ = 7.3 Hz), 127.68 (d, $^4J_{C-F}$ = 3.1 Hz), 127.51 (d, $^4J_{C-F}$ = 3.1 Hz), 126.11, 126.07, 123.74, 123.65, 123.24, 123.15, 118.56 (d, $^2J_{C-F}$ = 23.0 Hz), 118.42 (d, $^2J_{C-F}$ = 23.1 Hz), 116.60 (d, $^2J_{C-F}$ = 21.1 Hz), 116.56 (d, $^2J_{C-F}$ = 21.2 Hz), 90.06, 90.02, 89.69, 86.18, 86.15, 85.58, 72.41, 70.77, 54.71, 53.29, 35.49, 34.47, 21.71, 21.67, 21.20, 21.02. HRMS (ESI) m/z: Calcd. for $C_{32}H_{26}ClFNO_3S$ (M+H) $^+$: 558.1300, found: 558.1297.



4-(4-chlorophenyl)-5-(*p*-tolyl)-5-(*m*-tolylethynyl)-1-tosylpyrrolidin-2-one (3r, mixture of the diastereoisomers). White solid. 68.0 mg, 61% yield. mp: 178–182 °C. $[\alpha]_D^{25}$ = - 50.100 (c = 0.042 in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 94:6, t_R (major) = 25.959 min, t_R (minor) = 34.182 min; er (minor diastereoisomer) = 80:20, t_R (major) = 29.924 min, t_R (minor) = 24.486 min. 1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 7.9 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.35–7.18 (m, 1H), 7.14–7.04 (m, 4H), 6.78 (d, J = 7.9 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.12 (dd, J = 13.8, 7.8 Hz, 0.48H), 3.80 (dd, J = 12.9, 7.2 Hz, 0.52H), 3.07 (dd, J = 16.6, 12.9 Hz, 0.51H), 2.97 (dd, J = 17.1, 14.0 Hz, 0.45H), 2.75 (dd, J = 16.6, 7.0 Hz, 0.49H), 2.61 (dd, J = 16.9, 7.6 Hz, 0.44H), 2.46 (s, 1.4H), 2.43 (s, 4H), 2.38 (s, 1.58H), 2.33 (s, 1.42H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.43, 171.88, 144.98, 138.31, 138.24, 138.22, 138.14, 137.18, 136.27, 135.44, 134.09, 133.92, 133.46, 132.49, 132.43, 132.39, 132.28, 130.21, 130.01, 129.92, 129.64, 129.25, 129.23, 129.05, 128.95, 128.82, 128.59, 128.45, 128.32, 128.06, 127.99, 126.17, 126.14, 121.77, 121.26, 91.65, 88.43, 87.72, 84.23, 72.64, 70.97, 54.78, 53.37, 35.59, 34.52, 21.69, 21.66, 21.25, 21.19, 21.00. HRMS (ESI) m/z: Calcd. for $C_{33}H_{29}ClNO_3S$ (M+H) $^+$: 554.1551, found: 554.1544.

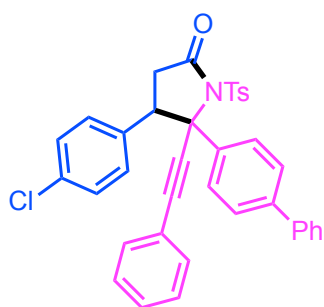


(4*R*,5*S*)-4-(4-chlorophenyl)-5-(*p*-tolyl)-5-(*o*-tolylethynyl)-1-tosylpyrrolidin-2-one (3s). White solid. 81.0 mg, 73 % yield. mp: 195-197 °C. $[\alpha]_D^{25} = -117.227$ ($c = 0.238$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er(major diastereoisomer) = 94:6, t_R (major) = 48.599 min, t_R (minor) = 63.225 min; er (minor diastereoisomer) = 73:27, t_R (major) = 51.590 min, t_R (minor) = 41.854 min. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.30-7.14 (m, 10H), 6.75 (d, $J = 8.5$ Hz, 2H), 3.80 (dd, $J = 13.0, 7.1$ Hz, 1H), 3.11 (dd, $J = 16.6, 13.0$ Hz, 1H), 2.74 (dd, $J = 16.6, 7.1$ Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.48, 144.98, 140.67, 138.31, 137.08, 135.68, 134.08, 132.44, 132.09, 130.12, 129.61, 129.46, 129.22, 129.08, 128.97, 128.05, 126.34, 125.55, 121.36, 90.67, 88.04, 72.82, 54.49, 35.62, 21.65, 21.21, 20.62. HRMS (ESI) m/z : Calcd. for $\text{C}_{33}\text{H}_{29}\text{ClINO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 554.1551, found: 554.1551.



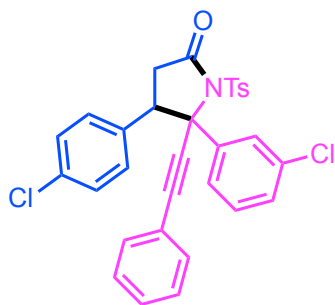
4,5-bis(4-chlorophenyl)-5-(phenylethynyl)-1-tosylpyrrolidin-2-one (3t, mixture of the diastereoisomers). White solid. 81.4 mg, 77% yield. mp: 178-182 °C. $[\alpha]_D^{25} = +23.856$ ($c = 0.306$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 86:14, t_R (major) = 29.626 min, t_R (minor) = 32.368 min; er (minor diastereoisomer) = 95:5, t_R (major) = 50.511 min, t_R (minor) = 21.123 min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.4$ Hz, 1.23H, major dr), 8.01 (d, $J = 8.4$ Hz, 0.79H, minor dr), 7.58-7.10 (m, 13H), 6.75 (dd, $J = 12.2, 8.5$ Hz, 2H), 4.13 (dd, $J = 13.4, 7.7$ Hz, 0.67H, major dr), 3.73 (dd, $J = 13.1, 7.1$ Hz,

0.41H, minor dr), 3.08 (dd, $J = 16.7, 13.2$ Hz, 0.42H, minor dr), 2.92 (dd, $J = 16.8, 13.5$ Hz, 0.61H, major dr), 2.74 (dd, $J = 16.7, 7.2$ Hz, 0.44H, minor dr), 2.63 (dd, $J = 16.8, 7.7$ Hz, 0.63H, major dr), 2.44 (s, 1.67H, major dr), 2.41 (s, 1.32H, minor dr). ^{13}C NMR (101 MHz, CDCl_3): δ 172.15, 171.55, 145.32, 145.30, 138.79, 135.89, 135.31, 135.08, 134.55, 134.41, 134.29, 132.01, 131.78, 131.64, 131.60, 130.22, 129.79, 129.62, 129.40, 129.38, 129.34, 129.04, 129.01, 128.74, 128.65, 128.53, 128.41, 128.34, 128.15, 127.65, 121.57, 121.09, 91.85, 88.11, 87.91, 83.86, 72.10, 70.43, 54.88, 53.24, 35.55, 34.28, 21.72, 21.69. HRMS (ESI) m/z : Calcd. for $\text{C}_{31}\text{H}_{24}\text{Cl}_2\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 560.0848, found: 560.0858.

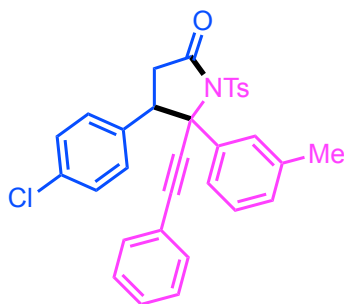


5-([1,1'-biphenyl]-4-yl)-4-(4-chlorophenyl)-5-(phenylethynyl)-1-tosylpyrrolidin-2-one (3u, mixture of the diastereoisomers). Light yellow solid. 81.0 mg, 67% yield. mp: 221-226 °C; $[\alpha]_{\text{D}}^{25} = -18.015$ ($c = 0.272$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, n -hexane/ i -propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 95:5, t_{R} (major) = 105.478 min, t_{R} (minor) = 35.053 min; er (minor diastereoisomer) = 81:19, t_{R} (major) = 44.307 min, t_{R} (minor) = 72.832 min; er was determined by chiral HPLC after removing the tosyl group. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 8.0$ Hz, 1.56H, major dr), 8.05 (d, $J = 8.0$ Hz, 0.70H, minor dr), 7.70-7.57 (m, 5H), 7.51-7.36 (m, 8H), 7.2-7.19 (m, 4H), 7.09 (d, $J = 8.1$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 0.74H, minor dr), 6.77 (d, $J = 8.1$ Hz, 1.26H, major dr), 4.17 (dd, $J = 13.4, 7.5$ Hz, 0.77H, major dr), 3.84 (dd, $J = 12.8, 7.1$ Hz, 0.36H, minor dr), 3.11 (dd, $J = 16.6, 12.8$ Hz, 0.31H, minor dr), 3.00 (dd, $J = 16.8, 13.5$ Hz, 0.71H, major dr), 2.78 (dd, $J = 16.6, 7.1$ Hz, 0.35H, minor dr), 2.66 (dd, $J = 16.8, 7.7$ Hz, 0.72H, major dr), 2.46 (s, 1.78H, major dr), 2.43 (s, 1.43H, minor dr). ^{13}C NMR (101 MHz, CDCl_3): δ 172.36, 171.80, 145.16, 141.25, 141.12, 140.16, 140.14, 139.10, 136.11, 135.46, 135.31, 134.23, 134.11, 132.29, 132.18, 131.80, 131.62, 130.26, 129.91, 129.62, 129.30, 129.23, 129.04, 129.00, 128.82, 128.79, 128.61, 128.48, 128.14, 128.06, 127.57, 127.55, 127.14, 127.08, 127.05, 126.88, 126.69, 126.66, 121.83, 121.36, 91.61, 88.53, 87.74, 84.41, 72.49, 70.85, 54.81, 53.46,

35.62, 34.47, 21.71, 21.68. HRMS (ESI) m/z : Calcd. for $C_{37}H_{29}ClNO_3S$ ($M+H$)⁺: 602.1551, found: 602.1551.

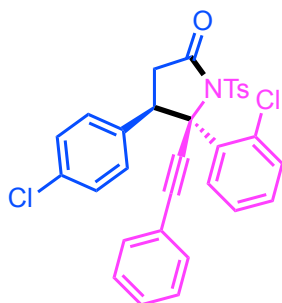


5-(3-chlorophenyl)-4-(4-chlorophenyl)-5-(phenylethynyl)-1-tosylpyrrolidin-2-one (3v, mixture of the diastereoisomers). White solid. 97.6 mg, 87% yield. mp: 115-119 °C. $[\alpha]_D^{25} = -3.333$ ($c = 0.03$ in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, n -hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm er (major diastereoisomer) = 93:7, t_R (major) = 24.473 min, t_R (minor) = 21.121 min; er (minor diastereoisomer) = 80:20, t_R (major) = 19.042 min, t_R (minor) = 30.609 min. 1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, $J = 8.3$ Hz, 1H), 7.99 (d, $J = 8.3$ Hz, 1H), 7.60-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.47-7.33 (m, 5H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.25-7.09 (m, 5H), 6.78 (d, $J = 8.4$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 4.15 (dd, $J = 13.2, 7.7$ Hz, 0.56H), 3.74 (dd, $J = 13.0, 7.1$ Hz, 0.48H), 3.10 (dd, $J = 16.7, 13.0$ Hz, 0.46H), 2.93 (dd, $J = 16.9, 13.2$ Hz, 0.56H), 2.75 (dd, $J = 16.7, 7.2$ Hz, 0.45H), 2.66 (dd, $J = 16.9, 7.7$ Hz, 0.55H), 2.44 (s, 1.57H, major dr), 2.42 (s, 1.43H, minor dr). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.11, 171.53, 145.30, 145.29, 142.19, 138.78, 135.80, 135.21, 134.47, 134.40, 134.36, 134.32, 132.01, 131.80, 131.72, 131.63, 130.17, 129.81, 129.64, 129.49, 129.45, 129.36, 129.31, 129.09, 129.05, 128.71, 128.62, 128.57, 128.47, 128.26, 128.13, 126.63, 126.37, 124.68, 124.30, 121.52, 121.08, 91.98, 88.06, 87.94, 83.68, 71.96, 70.36, 54.68, 53.33, 35.58, 34.19, 21.68, 21.65. HRMS (ESI) m/z : Calcd. for $C_{31}H_{24}Cl_2NO_3S$ ($M+H$)⁺: 560.0848, found: 560.0853.



4-(4-chlorophenyl)-5-(phenylethynyl)-5-(*m*-tolyl)-1-tosylpyrrolidin-2-one (3w, mixture of the diastereoisomers). White solid. 92.8 mg, 86% yield. mp: 139-142 °C. $[\alpha]_D^{25} = -54.206$ ($c = 0.642$

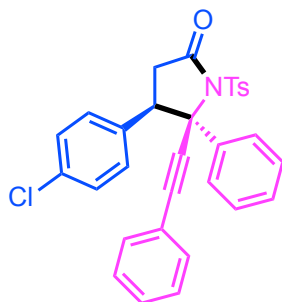
in CHCl₃). HPLC DAICEL CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 97:3, t_R (major) = 33.157 min, t_R (minor) = 23.025 min; er (minor diastereoisomer) = 91:9, t_R (major) = 20.324 min, t_R (minor) = 40.646 min. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (dt, J = 8.3, 2.0 Hz, 0.57H, minor dr), 7.99 (dt, J = 8.4, 2.2 Hz, 1.43H, major dr), 7.60-7.57 (m, 0.6H), 7.46-7.44 (m, 0.54H), 7.43-7.31 (m, 6H), 7.30-7.27 (m, 1H), 7.24-7.11 (m, 4H), 7.08-7.02 (m, 1H), 6.76 (dt, J = 8.5, 2.8 Hz, 1.51H, major dr), 6.69 (dt, J = 8.5, 2.3 Hz, 0.66H, minor dr), 4.12 (dd, J = 13.6, 7.6 Hz, 0.38H, minor dr), 3.78 (dd, J = 12.9, 7.2 Hz, 0.77H, major dr), 3.09 (dd, J = 16.7, 12.9 Hz, 0.78H, major dr), 2.94 (dd, J = 16.8, 13.5 Hz, 0.36H, minor dr), 2.74 (dd, J = 16.7, 7.2 Hz, 0.83H, major dr), 2.61 (dd, J = 16.8, 7.6 Hz, 0.40H, minor dr), 2.44 (s, 1H), 2.41 (s, 2H), 2.39 (s, 2H), 2.21 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 172.40, 171.90, 145.05, 145.02, 139.90, 138.12, 137.85, 136.16, 135.51, 134.11, 133.96, 132.45, 132.38, 131.77, 131.61, 130.20, 129.82, 129.51, 129.28, 129.22, 129.17, 129.13, 129.05, 128.95, 128.56, 128.42, 128.35, 128.12, 127.95, 126.98, 126.63, 123.59, 123.27, 121.94, 121.48, 91.43, 88.77, 87.52, 84.57, 72.62, 71.02, 54.70, 53.47, 35.60, 34.38, 21.67, 21.64, 21.43. HRMS (ESI) m/z : Calcd. for C₃₂H₂₇ClNO₃S (M+H)⁺: 540.1395, found: 540.1423.



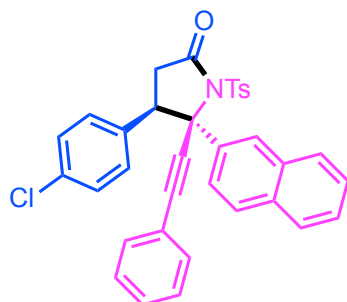
(4*R*,5*R*)-5-(2-chlorophenyl)-4-(4-chlorophenyl)-5-(phenylethynyl)-1-tosylpyrrolidin-2-one

(3x). White solid. 54.1 mg, 48% yield. mp: 99-101 °C. [α]_D²⁵ = - 45.571 (c = 0.858 in CHCl₃). HPLC DAICEL CHIRALCEL IF, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 92:8, t_R (major) = 55.206 min, t_R (minor) = 48.262 min; er (minor diastereoisomer) = 83:17, t_R (major) = 51.516 min, t_R (minor) = 42.404 min. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.41-7.29 (m, 5H), 7.23-7.15 (m, 6H), 6.79 (d, J = 8.1 Hz, 2H), 4.57 (s, 1H), 3.06 (s, 1H), 2.83 (dd, J = 17.0, 8.0 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 172.01, 145.05, 135.23, 134.02, 132.32, 131.71, 131.54, 130.14, 129.43, 129.22, 128.95, 128.40, 128.09, 126.90, 121.25, 92.62, 84.43, 72.29,

47.99, 35.24, 21.66. HRMS (ESI) m/z : Calcd. for $C_{31}H_{24}Cl_2NO_3S$ ($M+H$)⁺: 560.0848, found: 560.0855.

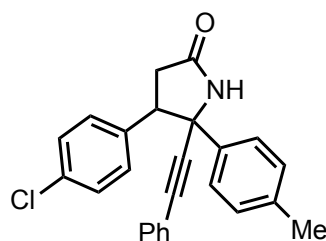


4-(4-chlorophenyl)-5-phenyl-5-(phenylethynyl)-1-tosylpyrrolidin-2-one (3y). White solid. 91.2 mg, 87% yield. mp: 173-175 °C. $[\alpha]_D^{25} = -297.600$ ($c = 0.250$ in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, n -hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 95:5, t_R (major) = 40.189 min, t_R (minor) = 28.49 min; er (minor diastereoisomer) = 88:12, t_R (major) = 23.263 min, t_R (minor) = 47.540 min. 1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.59 (dd, $J = 7.9, 1.8$ Hz, 2H), 7.46-7.32 (m, 8H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 3.79 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.09 (dd, $J = 16.7, 13.1$ Hz, 1H), 2.74 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.40, 140.01, 135.32, 134.19, 132.12, 131.60, 130.21, 129.60, 129.21, 128.98, 128.52, 128.48, 128.46, 128.01, 126.20, 121.37, 91.59, 84.36, 72.65, 54.87, 35.60, 21.67. HRMS (ESI) m/z : Calcd. for $C_{31}H_{25}ClNO_3S$ ($M+H$)⁺: 526.1238, found: 526.1233.

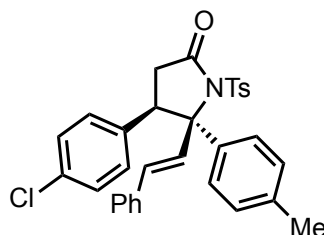


(4R,5S)-4-(4-chlorophenyl)-5-(naphthalen-2-yl)-5-(phenylethynyl)-1-tosylpyrrolidin-2-one (3z). White solid. 104.1 mg, 90% yield. mp: 233-235 °C. $[\alpha]_D^{25} = -171.635$ ($c = 0.322$ in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, n -hexane/ethanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 95:5, t_R (major) = 34.092 min, t_R (minor) = 35.847 min; er (minor diastereoisomer) = 82:18, t_R (major) = 32.010 min, t_R (minor) = 27.005 min. 1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $J = 8.1$ Hz, 2H), 7.97 (d, $J = 8.7$ Hz, 1H), 7.94-7.90 (m, 2H), 7.83-7.80 (m, 1H),

7.77 (dd, $J = 8.6, 2.1$ Hz, 1H), 7.54 (tt, $J = 6.9, 5.2$ Hz, 2H), 7.43-7.39 (m, 5H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.73 (d, $J = 8.5$ Hz, 2H), 3.91 (dd, $J = 13.0, 7.2$ Hz, 1H), 3.15 (dd, $J = 16.7, 13.0$ Hz, 1H), 2.79 (dd, $J = 16.7, 7.2$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.43, 145.14, 137.07, 135.32, 134.18, 133.08, 132.67, 132.08, 131.67, 130.22, 129.59, 129.26, 128.99, 128.76, 128.58, 128.49, 128.01, 127.67, 126.62, 126.50, 126.13, 123.22, 121.41, 91.73, 84.41, 72.84, 54.29, 35.60, 21.67. HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{27}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 576.1395, found 576.1394.



4-(4-chlorophenyl)-5-(phenylethynyl)-5-(*p*-tolyl)pyrrolidin-2-one (4, mixture of the diastereoisomers). Colorless liquid. 58 mg, 62 % yield. $[\alpha]_{\text{D}}^{25} = -20.171$ ($c = 0.704$ in CHCl_3). HPLC DAICEL CHIRALCEL IC, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm: er (major diastereoisomer) = 96:4, t_{R} (major) = 44.341 min, t_{R} (minor) = 21.535 min; er (minor diastereoisomer) = 93:7, t_{R} (major) = 35.718 min, t_{R} (minor) = 28.741 min. ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.47 (m, 0.80H), 7.37-7.22 (m, 6.60H), 7.18 (d, $J = 8.0$ Hz, 1.19H), 7.07 (d, $J = 8.5$ Hz, 0.76H), 7.00-6.95 (m, 2.60H), 6.78 (d, $J = 8.5$ Hz, 0.70H), 6.52 (d, $J = 31.1$ Hz, 1H), 4.22 (dd, $J = 10.1, 8.3$ Hz, 0.37H), 3.67 (dd, $J = 12.0, 7.5$ Hz, 0.81H), 3.06 (dd, $J = 16.5, 12.0$ Hz, 0.60H), 2.79-2.67 (m, 1.32H), 2.37 (s, 1.73H), 2.27 (s, 1.27H). ^{13}C NMR (101 MHz, CDCl_3): δ 176.10, 138.37, 137.94, 137.36, 134.90, 134.53, 134.05, 133.65, 133.30, 131.69, 131.45, 130.23, 129.72, 129.25, 128.84, 128.75, 128.73, 128.41, 128.34, 127.99, 127.95, 126.20, 125.87, 121.95, 121.86, 90.07, 89.52, 86.88, 85.30, 65.83, 64.14, 56.21, 54.55, 35.65, 34.48, 21.05, 20.91. HRMS (ESI) m/z : Calcd. for $\text{C}_{25}\text{H}_{20}\text{ClNNaO}$ ($\text{M}+\text{Na}$) $^+$: 408.1126, found: 408.1124.

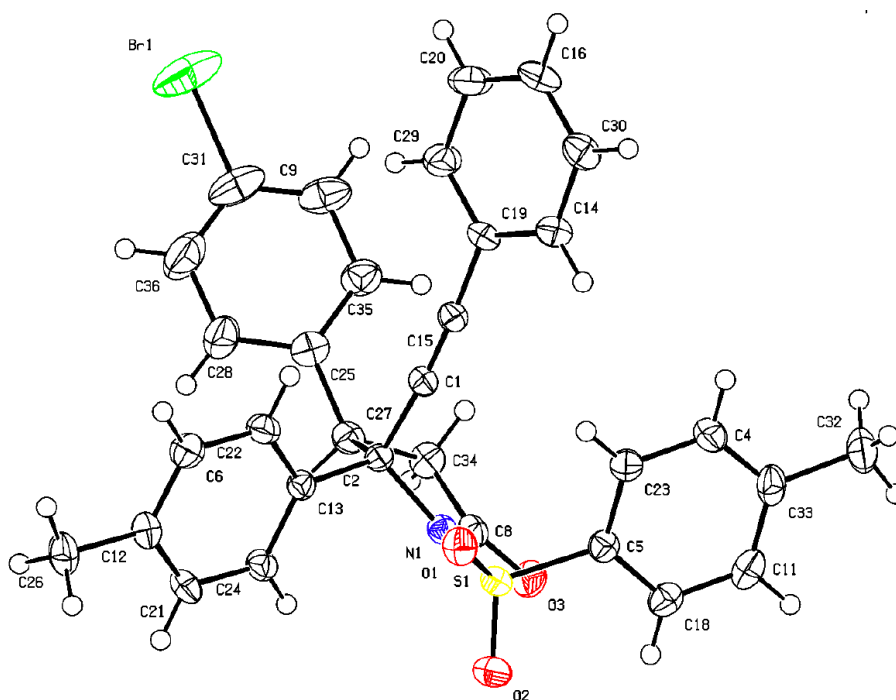


(4*R*,5*S*)-4-(4-chlorophenyl)-5-((*E*)-styryl)-5-(*p*-tolyl)-1-tosylpyrrolidin-2-one (5). White solid. 58.0 mg, 56 % yield. mp: 201-204 °C. $[\alpha]_{\text{D}}^{25} = -115.027$ ($c = 0.366$ in CHCl_3). HPLC DAICEL

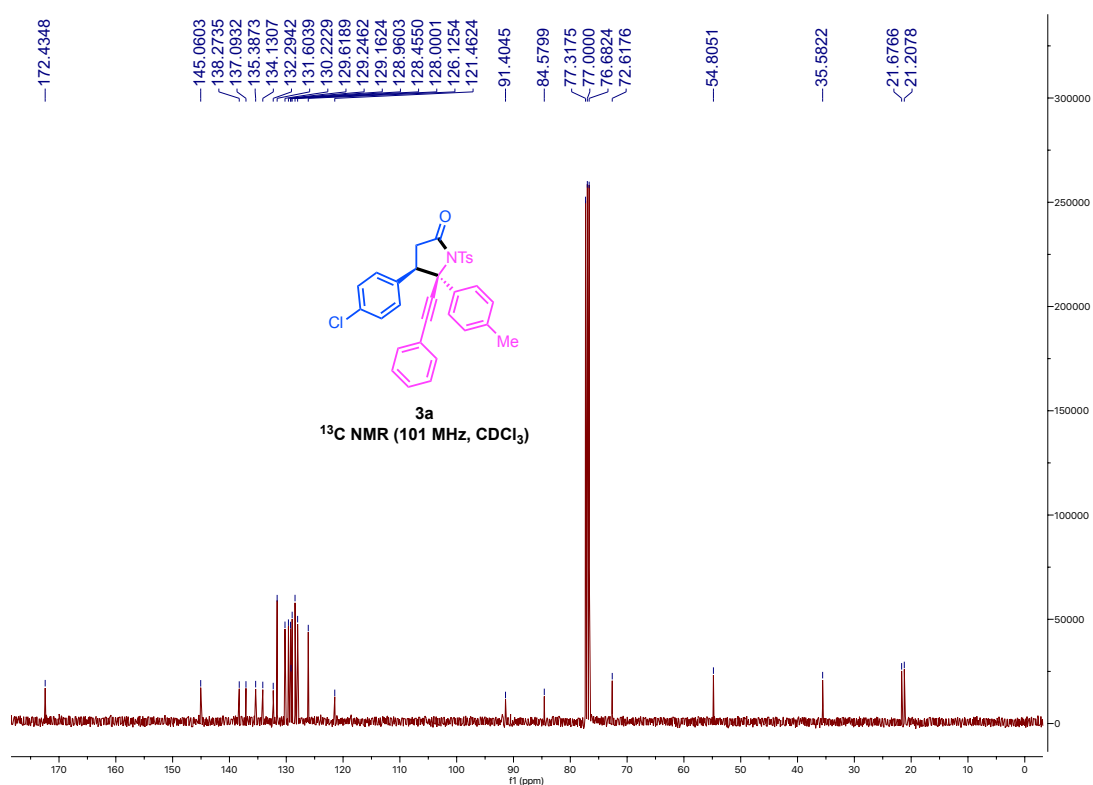
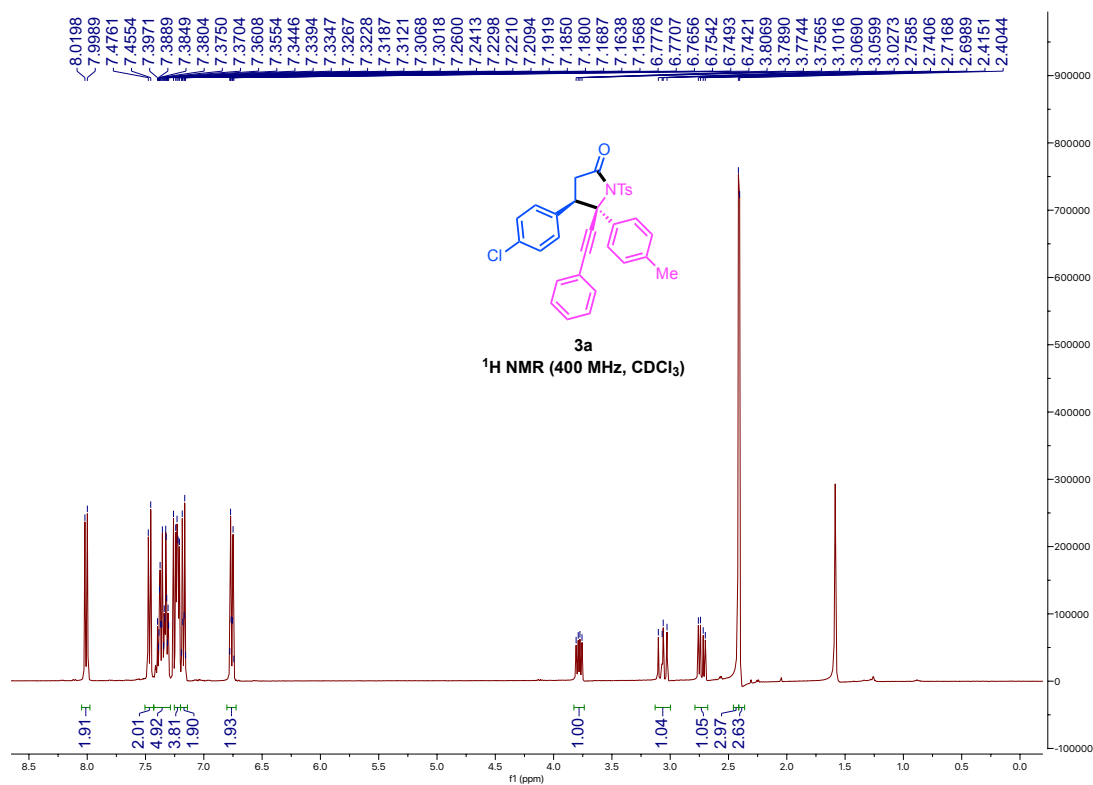
CHIRALCEL IC, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm: er (major diastereoisomer) = 92:8, t_R (major) = 25.925 min, t_R (minor) = 21.164 min; er (minor diastereoisomer) = 98:2, t_R (major) = 18.269 min, t_R (minor) = 19.578 min. ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.5 Hz, 3H), 7.23-7.16 (m, 3H), 7.06-7.00 (m, 3H), 6.97 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 6.79 (br, 2H), 6.33 (d, J = 13.1 Hz, 1H), 6.25 (d, J = 8.2 Hz, 2H), 4.33 (dd, J = 13.4, 7.9 Hz, 1H), 2.75 (dd, J = 16.9, 13.3 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.23 (dd, J = 17.0, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 172.95, 145.41, 137.50, 137.45, 136.49, 135.52, 134.60, 134.23, 134.05, 133.26, 129.79, 129.66, 129.27, 128.78, 128.71, 128.66, 127.91, 127.87, 126.33, 74.71, 43.58, 34.58, 21.76, 21.05. HRMS (ESI) m/z : Calcd. for $\text{C}_{32}\text{H}_{29}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$: 542.1551, found: 542.1549.

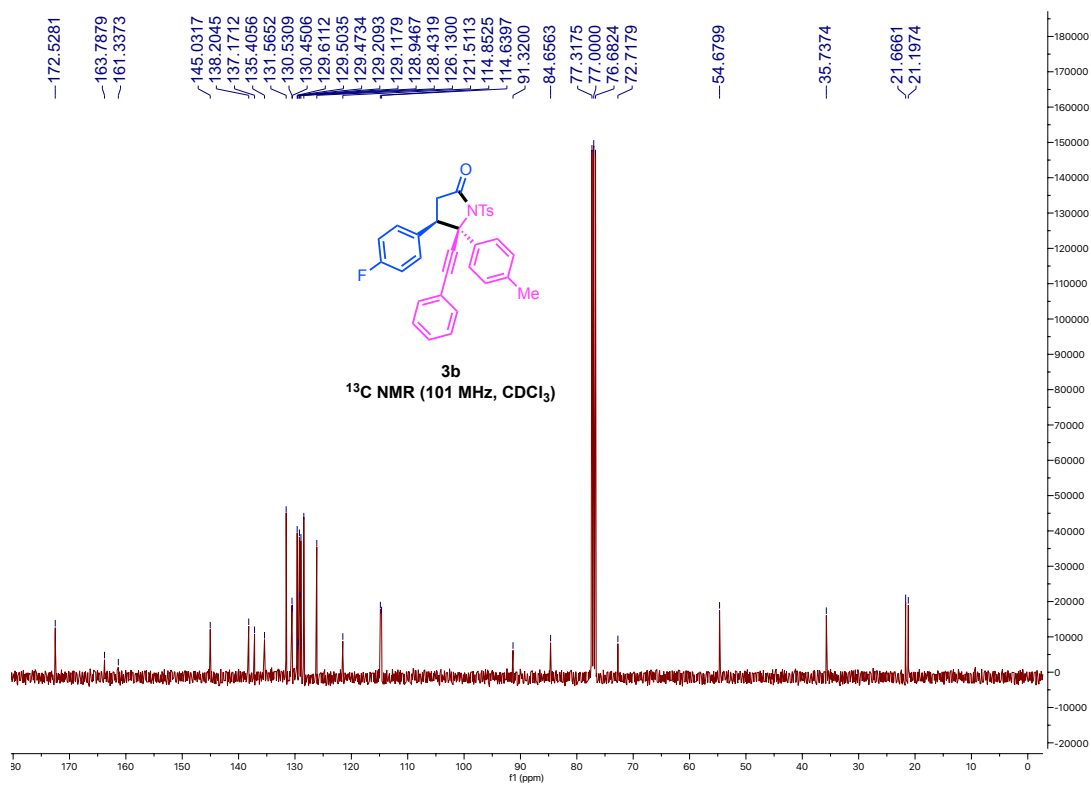
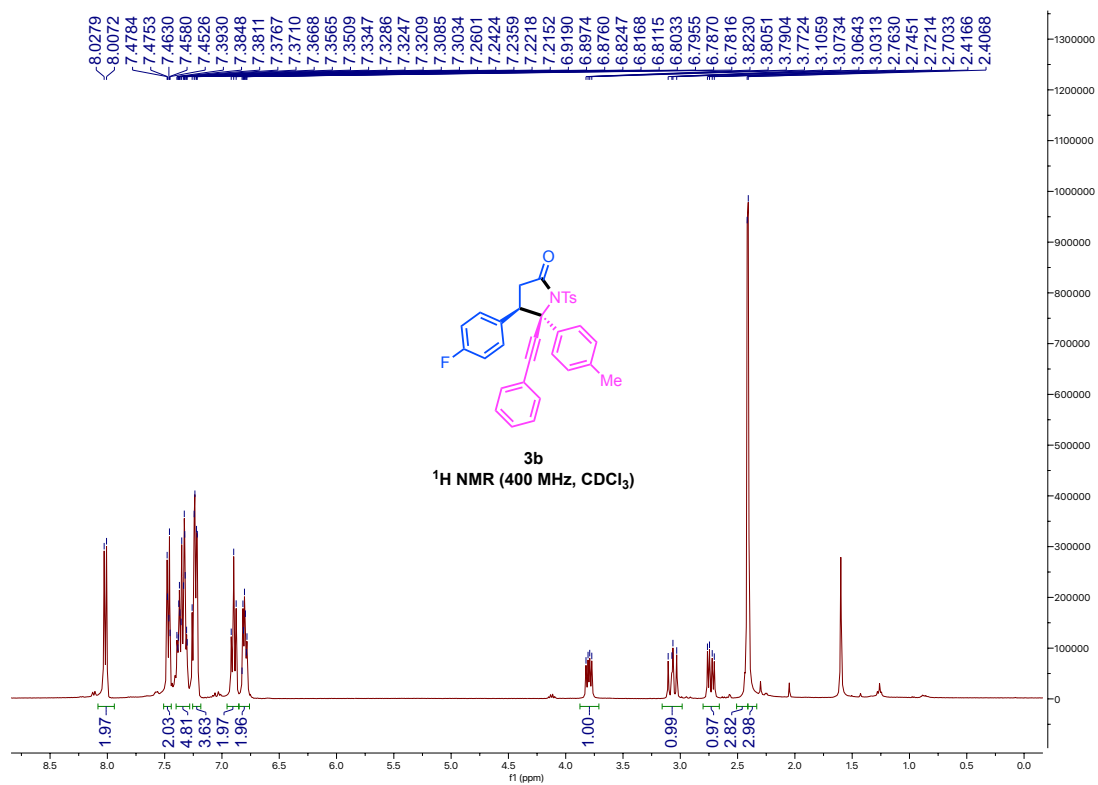
V. X-ray crystallographic data and the absolute configuration determination

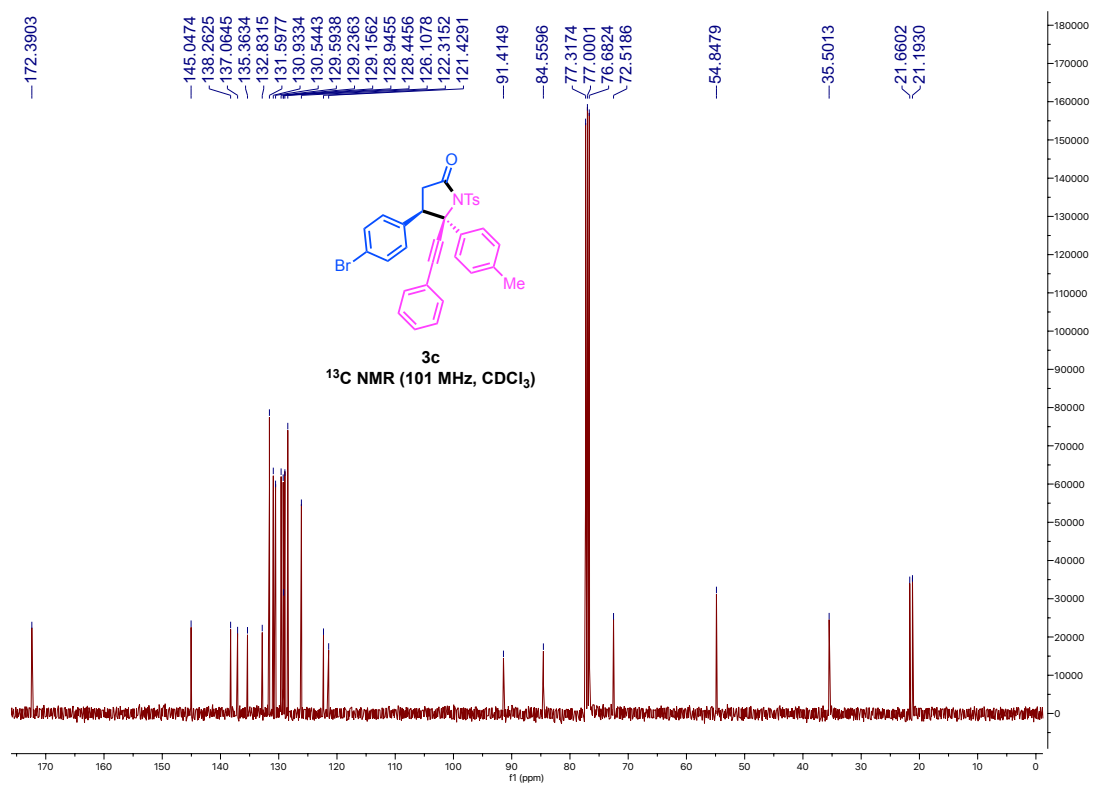
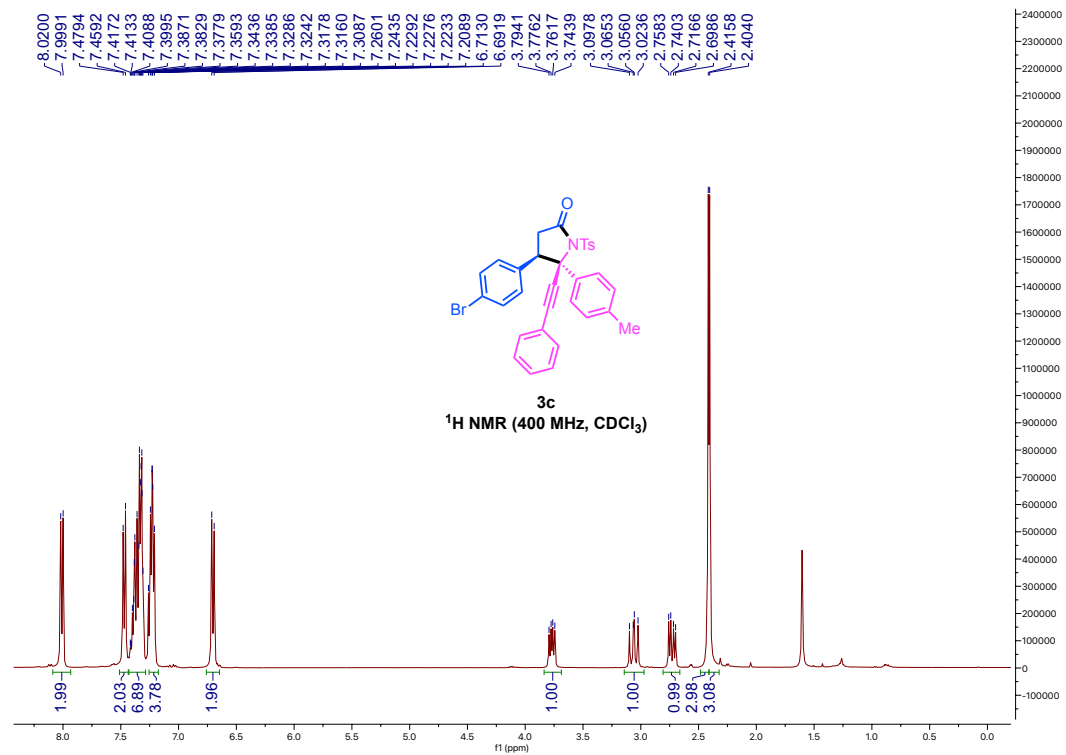
The major enantiomer of the major diastereomer of compound **3c** (> 99.5% ee after 3 times of recrystallization) was heated and dissolved by acetone in a round bottom bottle with lids, and the systems were placed in the fume hood for about 3~5 days, during which the solvent was evaporated slowly. The X-ray was detected after the crystal was formed. The X-ray data was detected on Bruker smart Apex 2, Bruker D8 Venture.

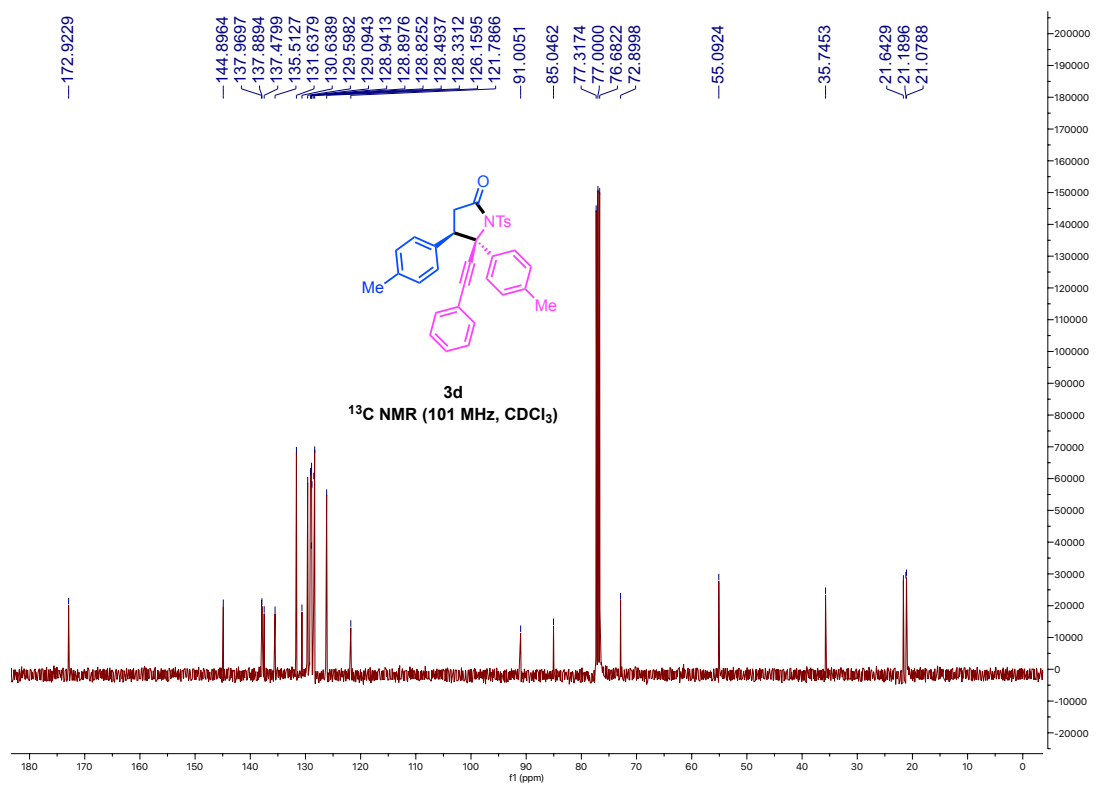
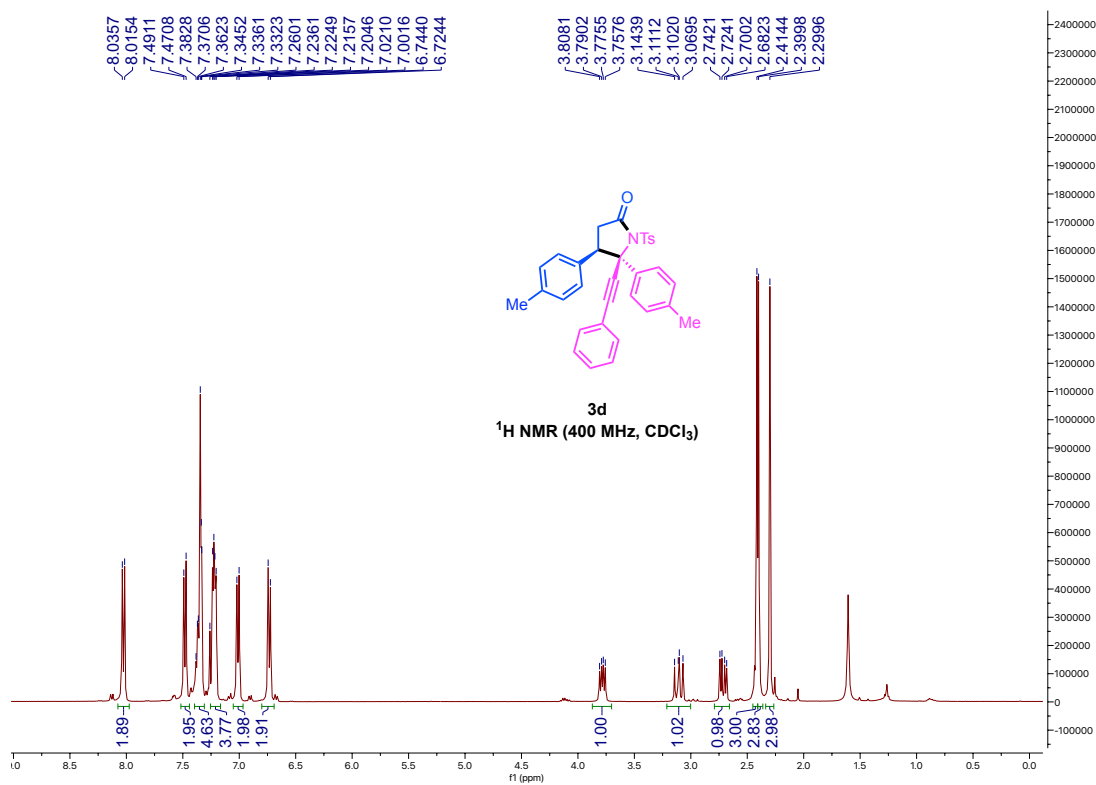


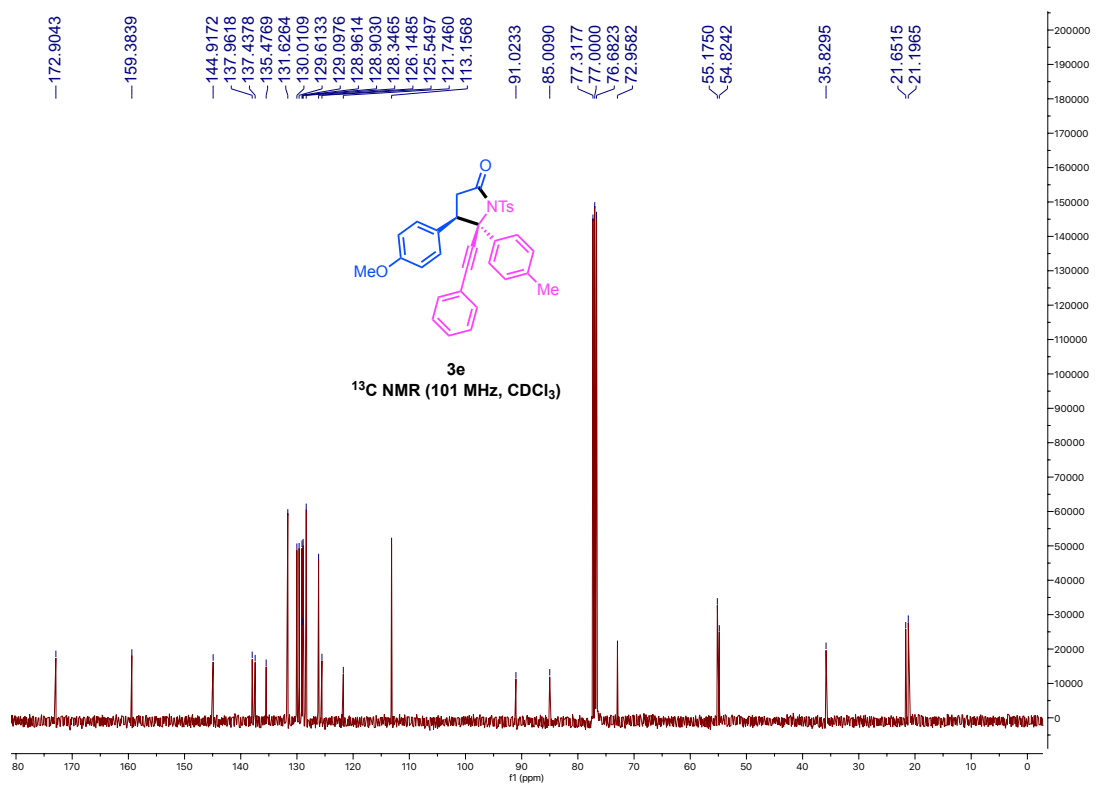
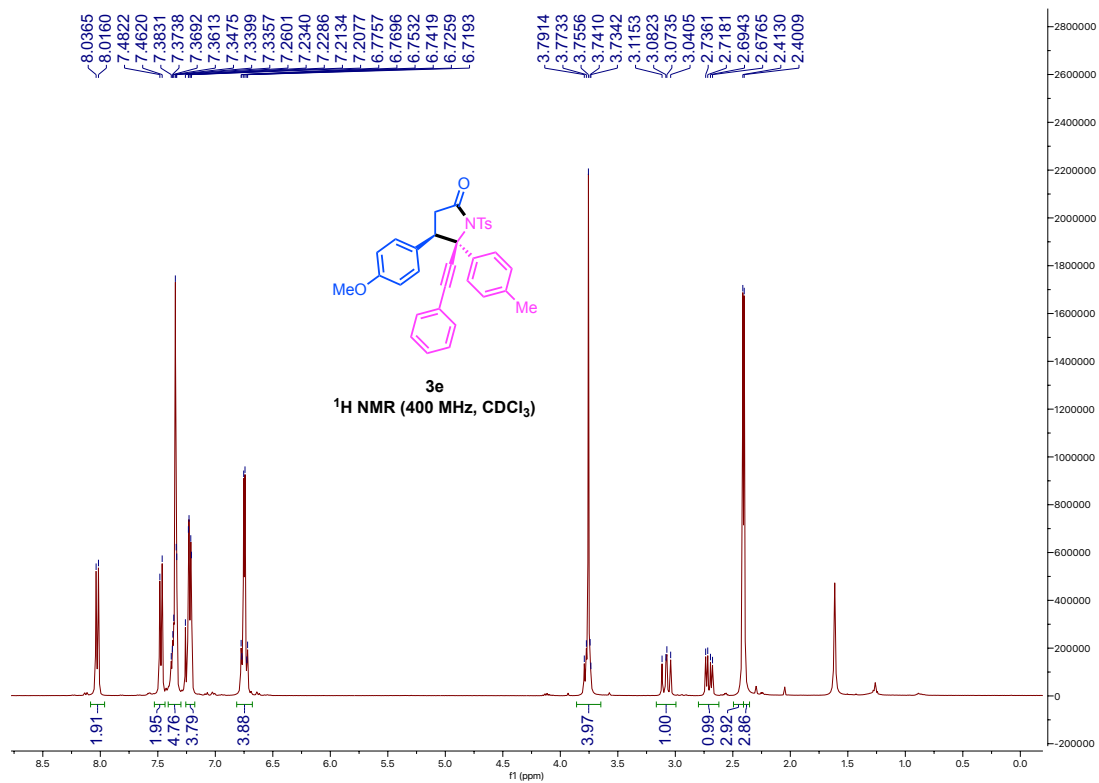
VI. ^1H NMR and ^{13}C NMR Spectra

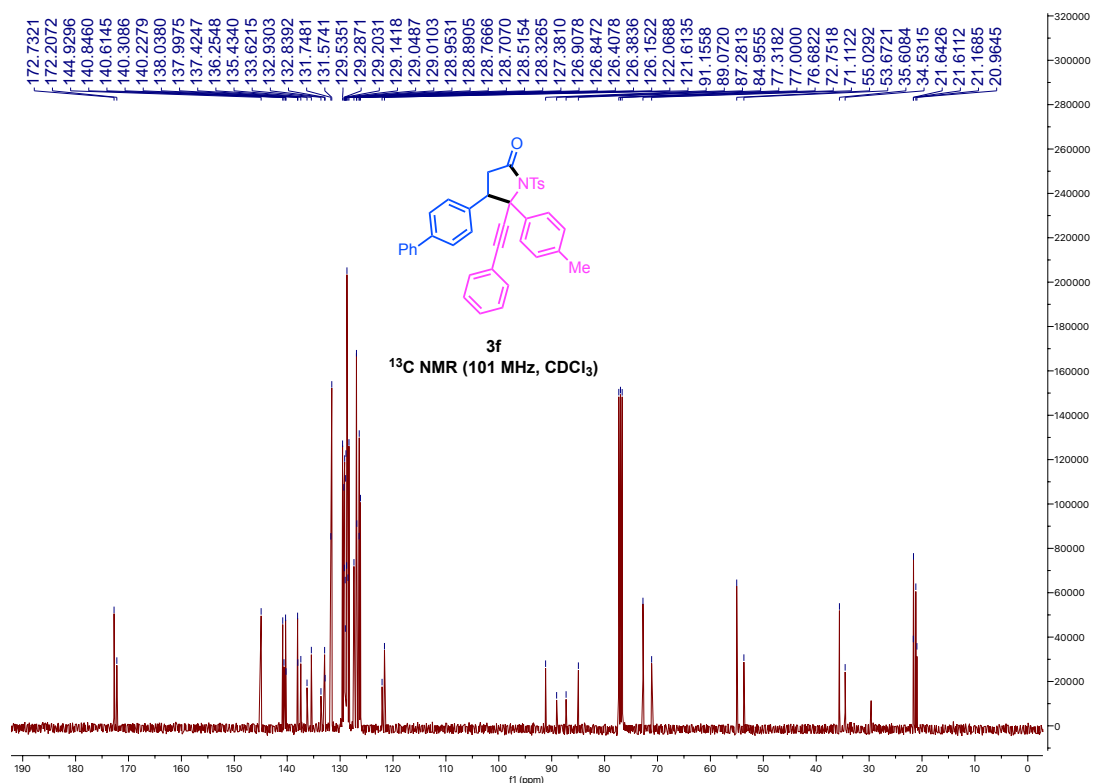
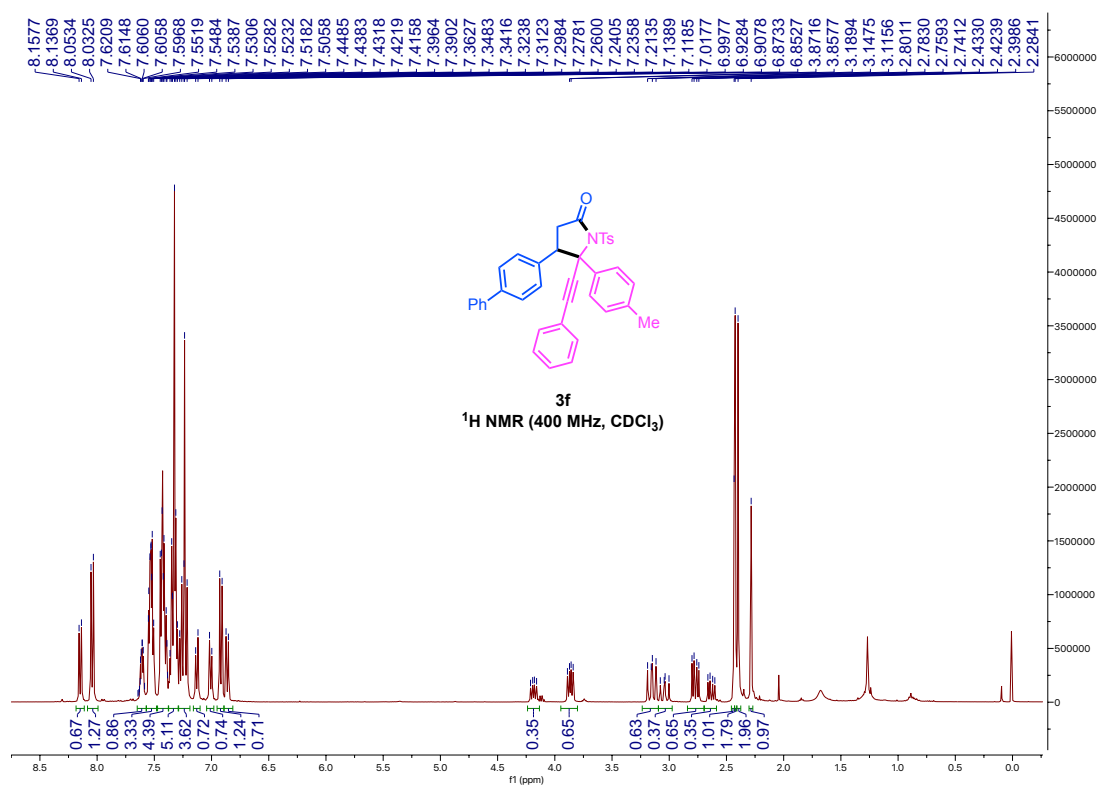


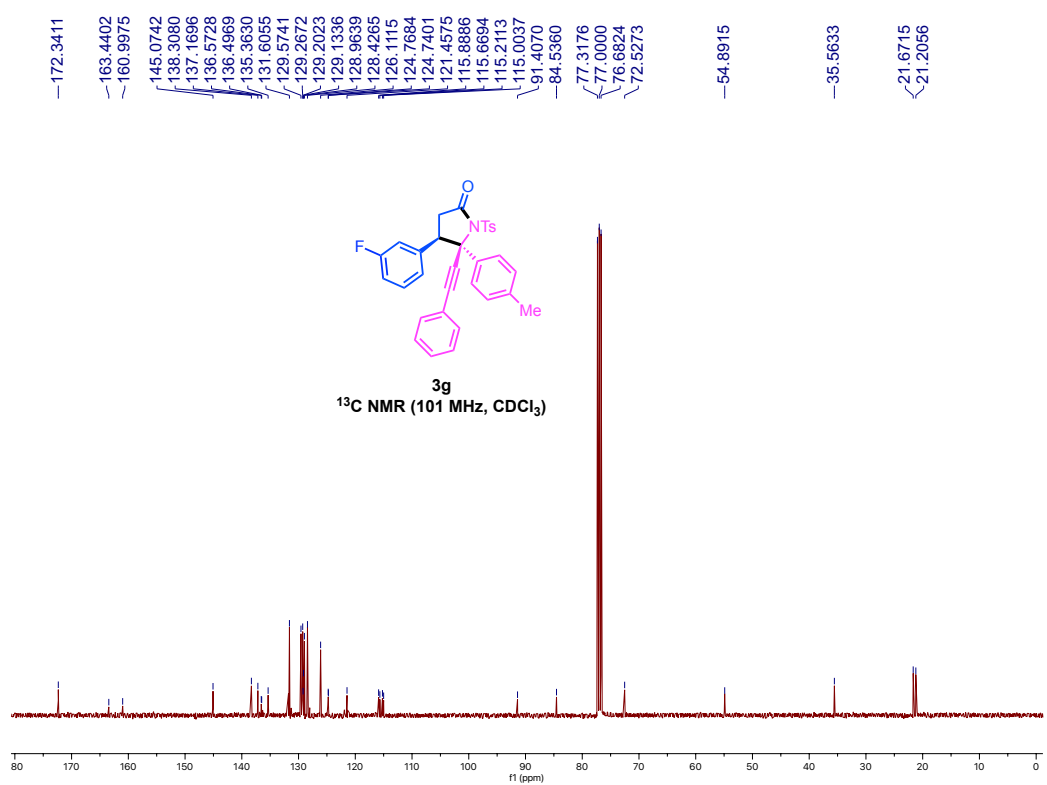
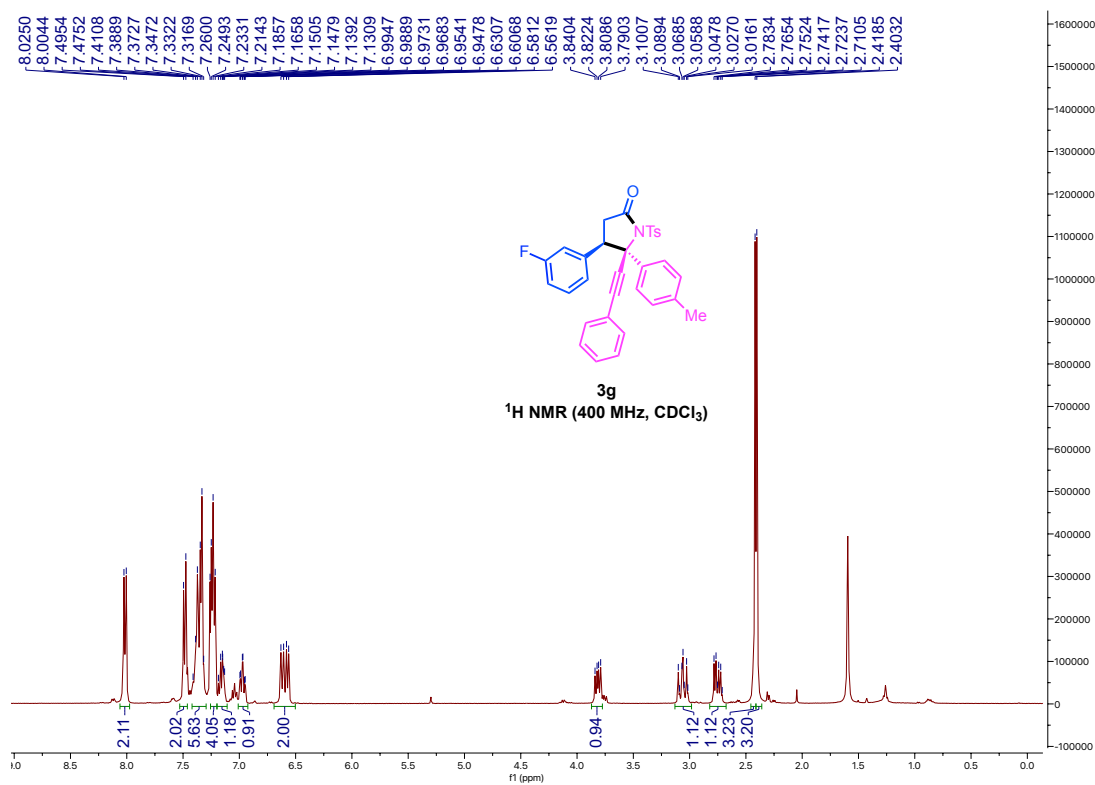


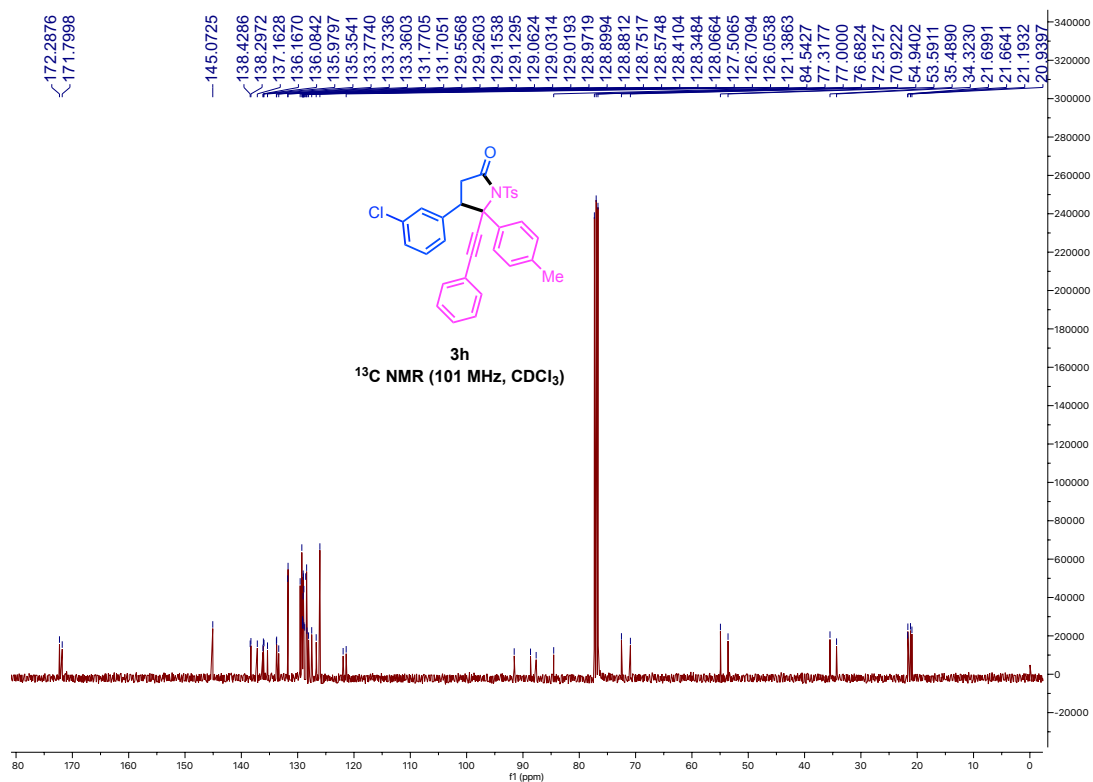
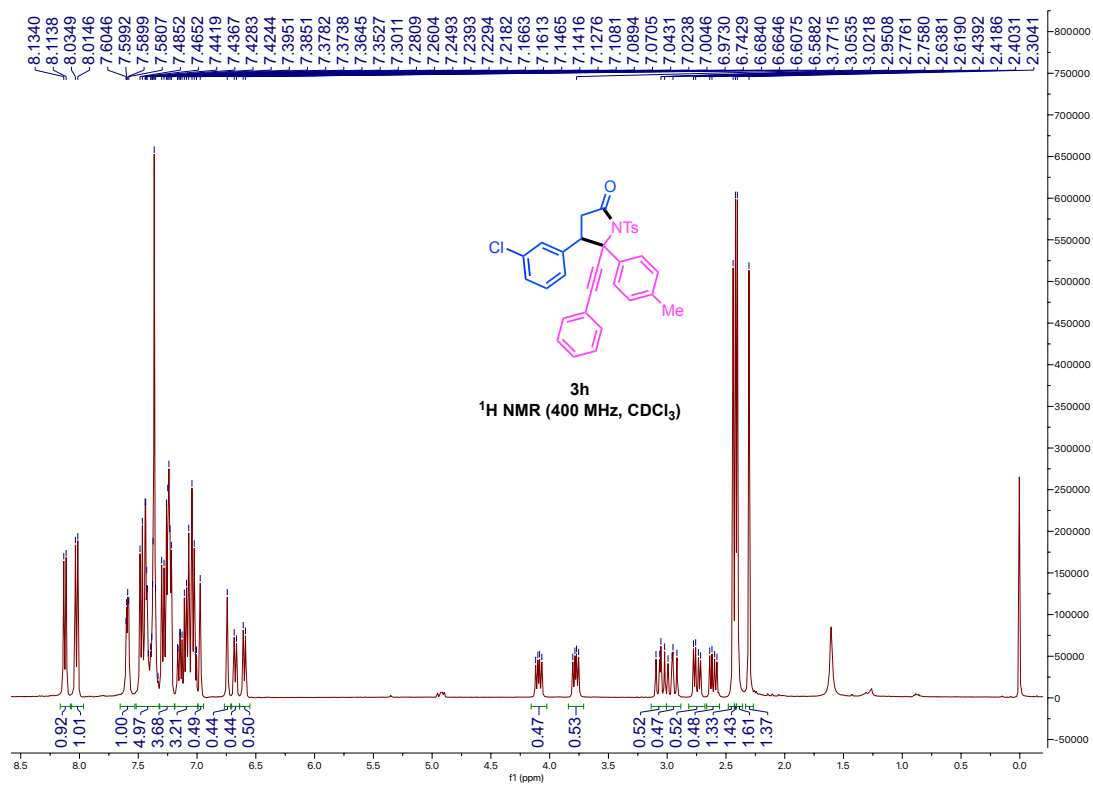


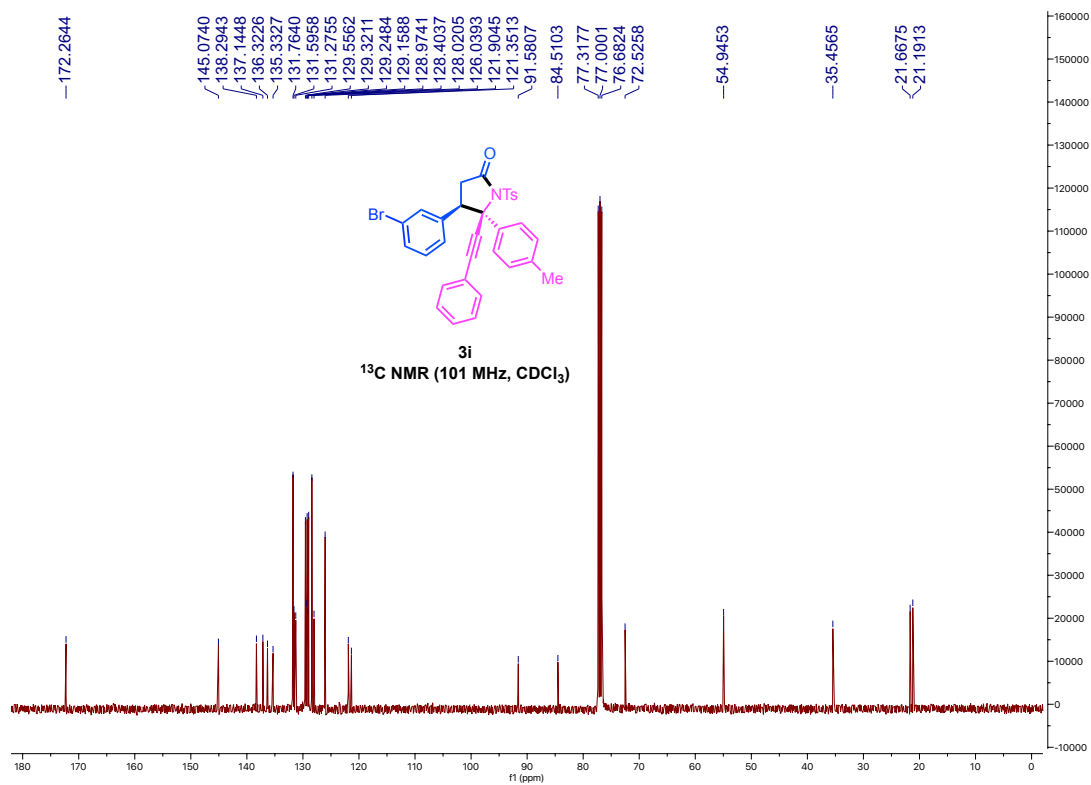
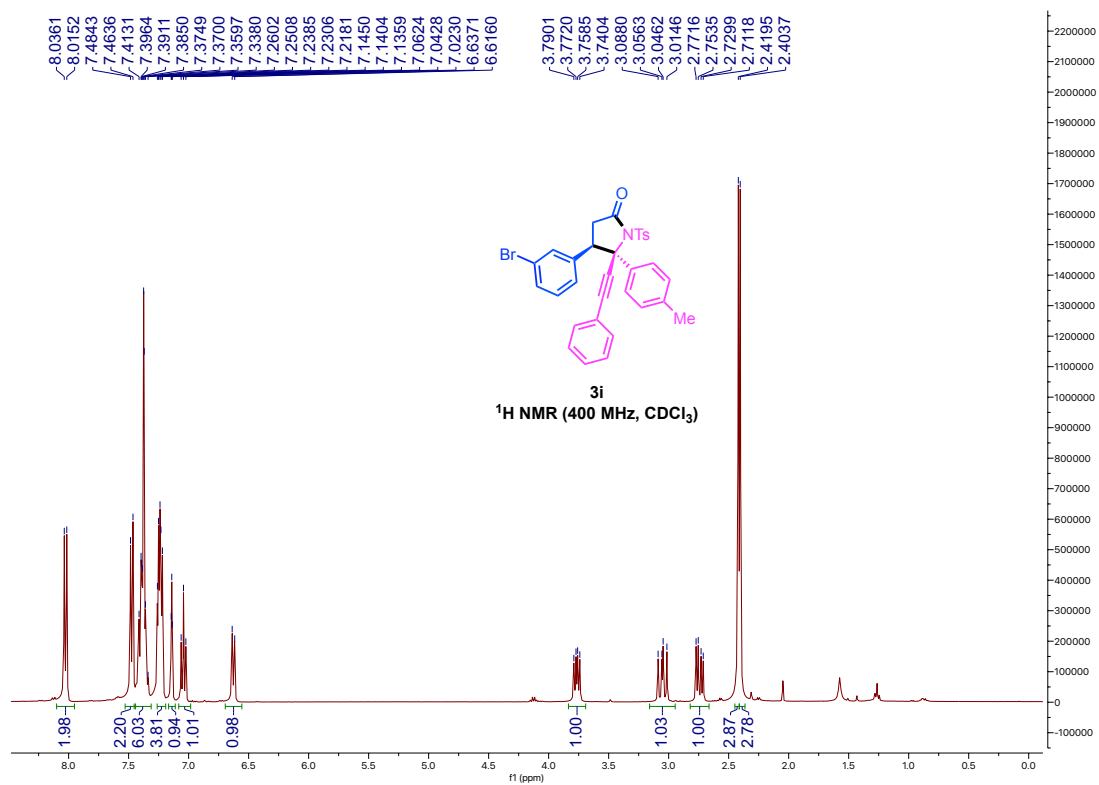


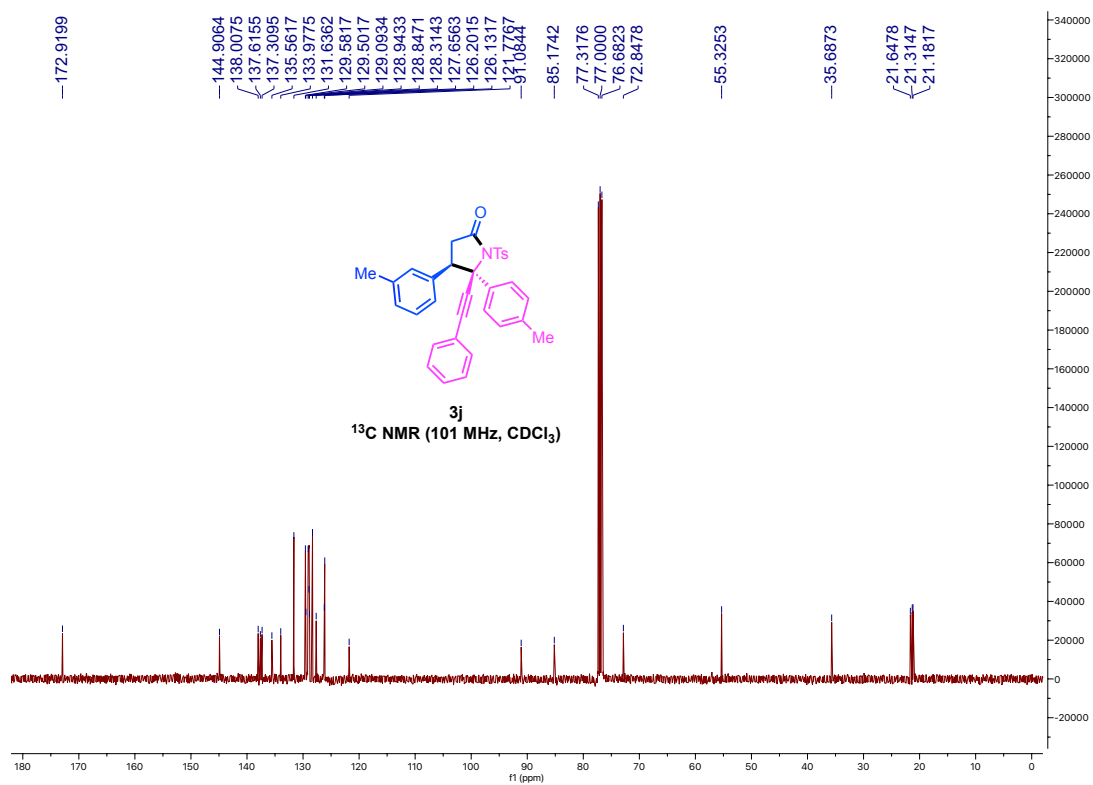
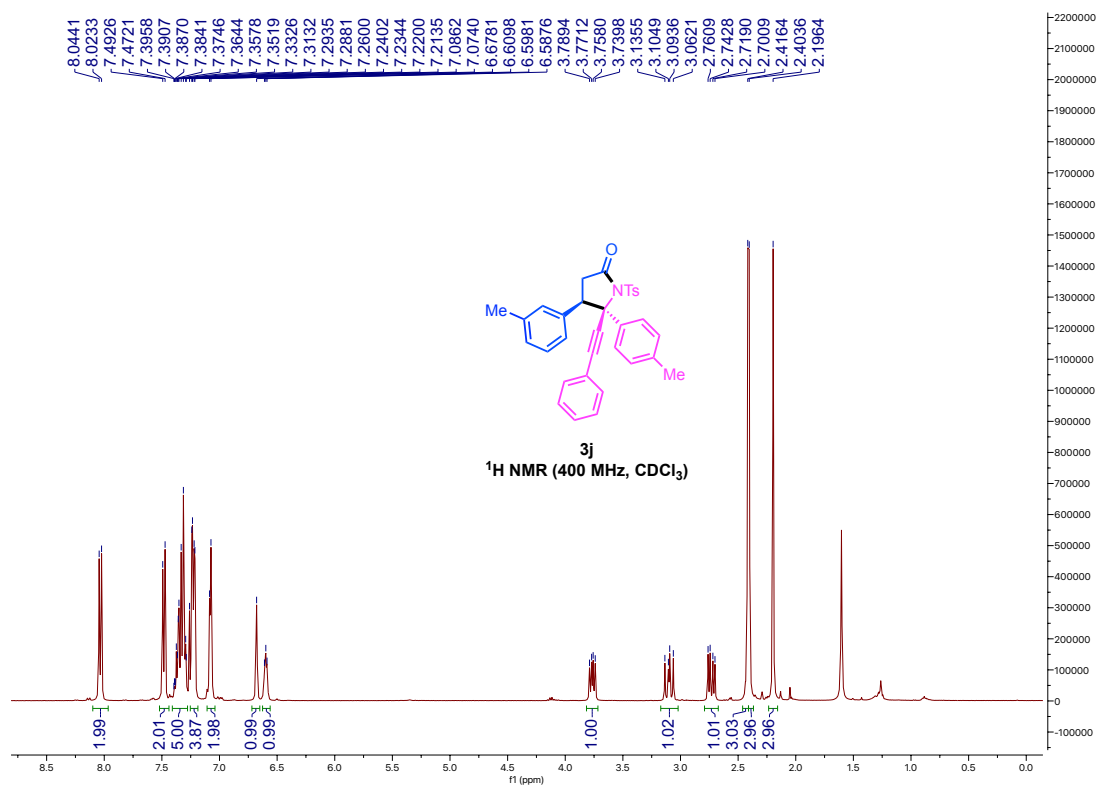


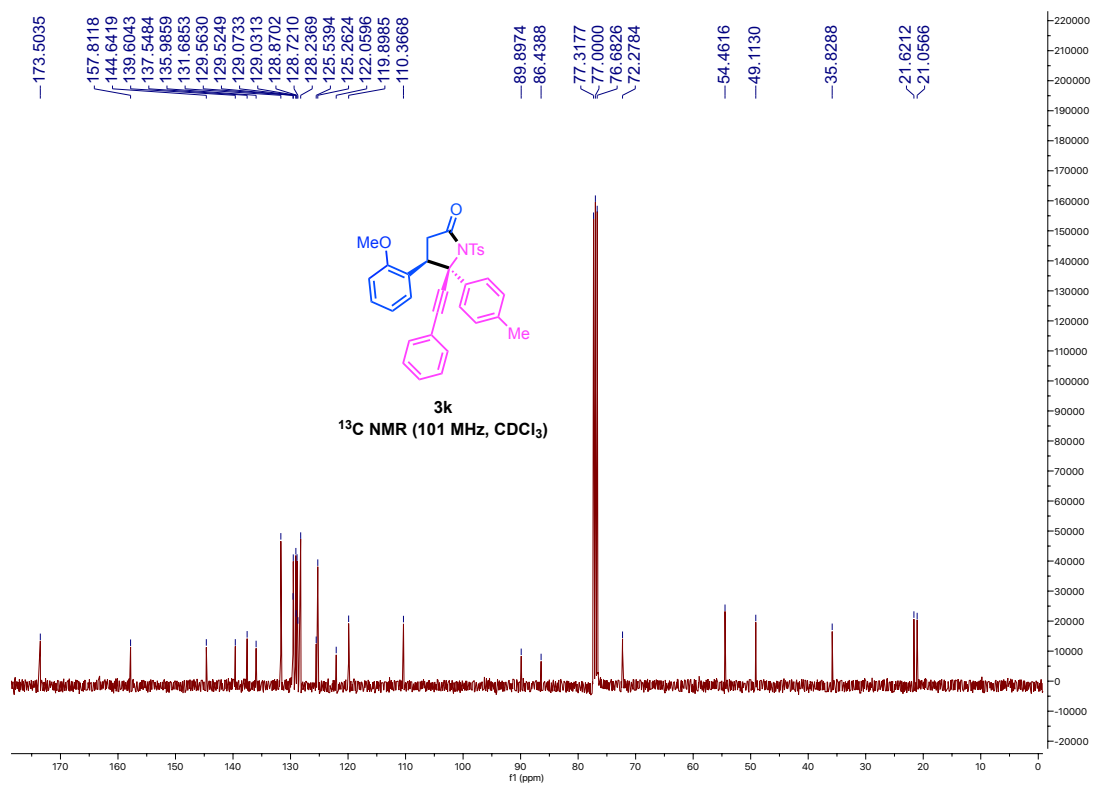
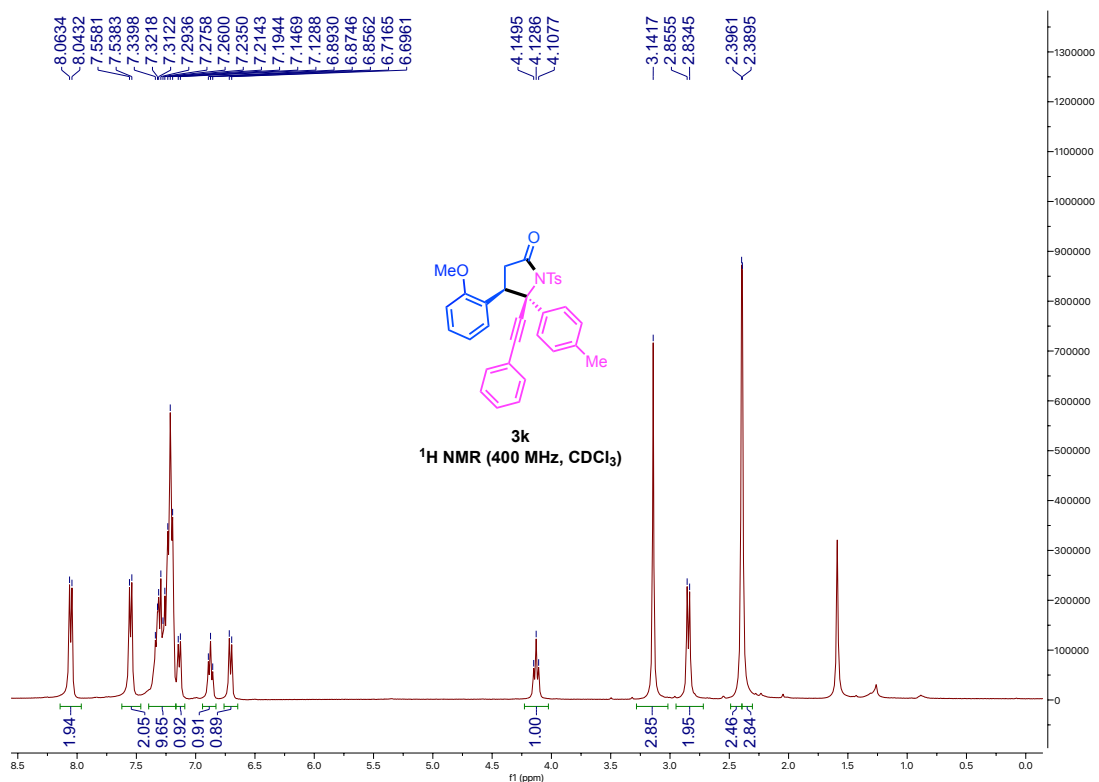


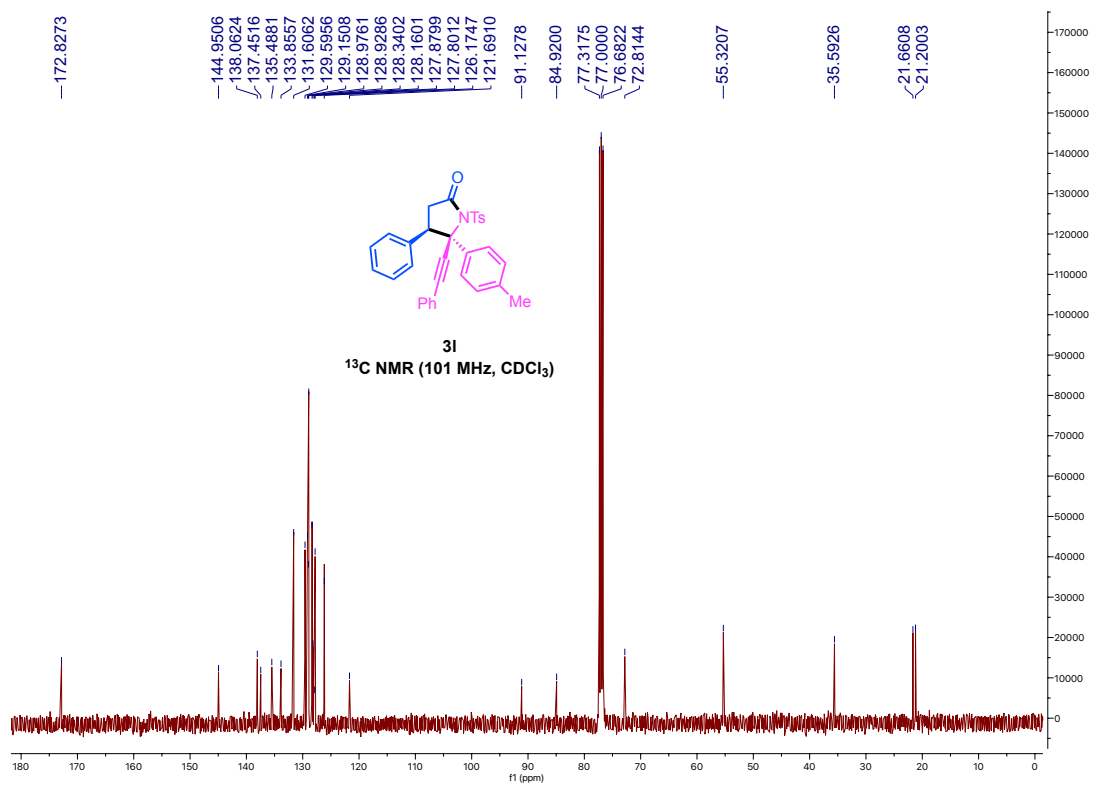
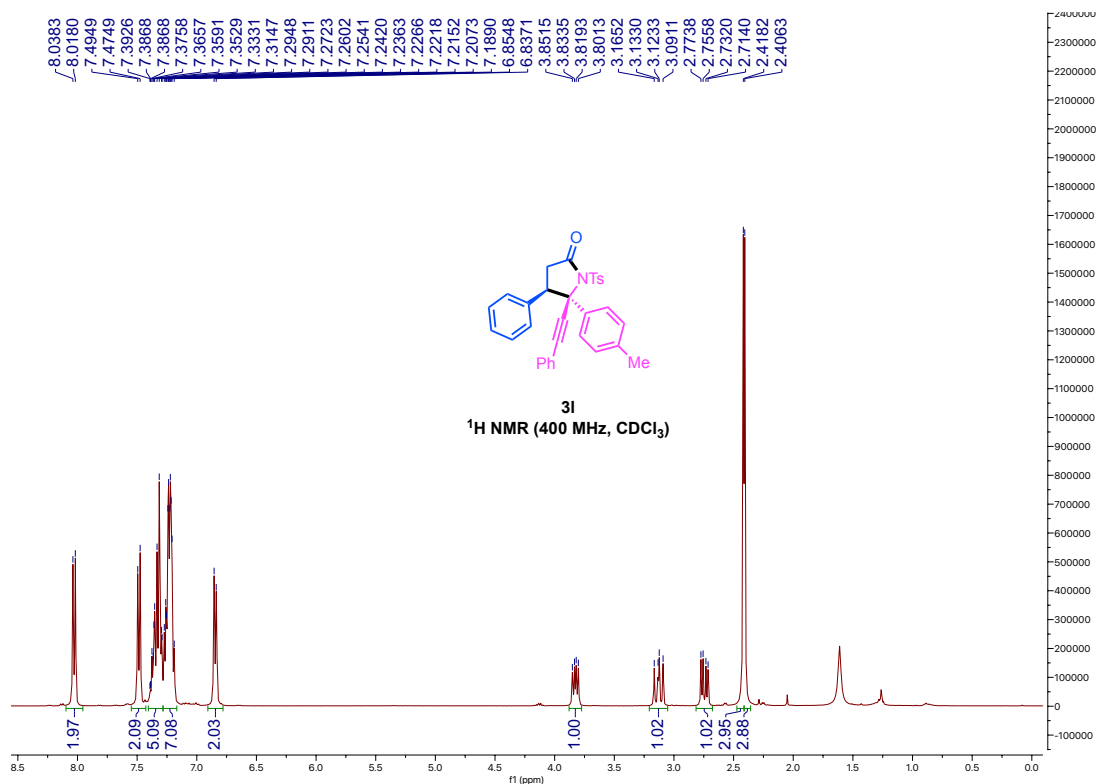


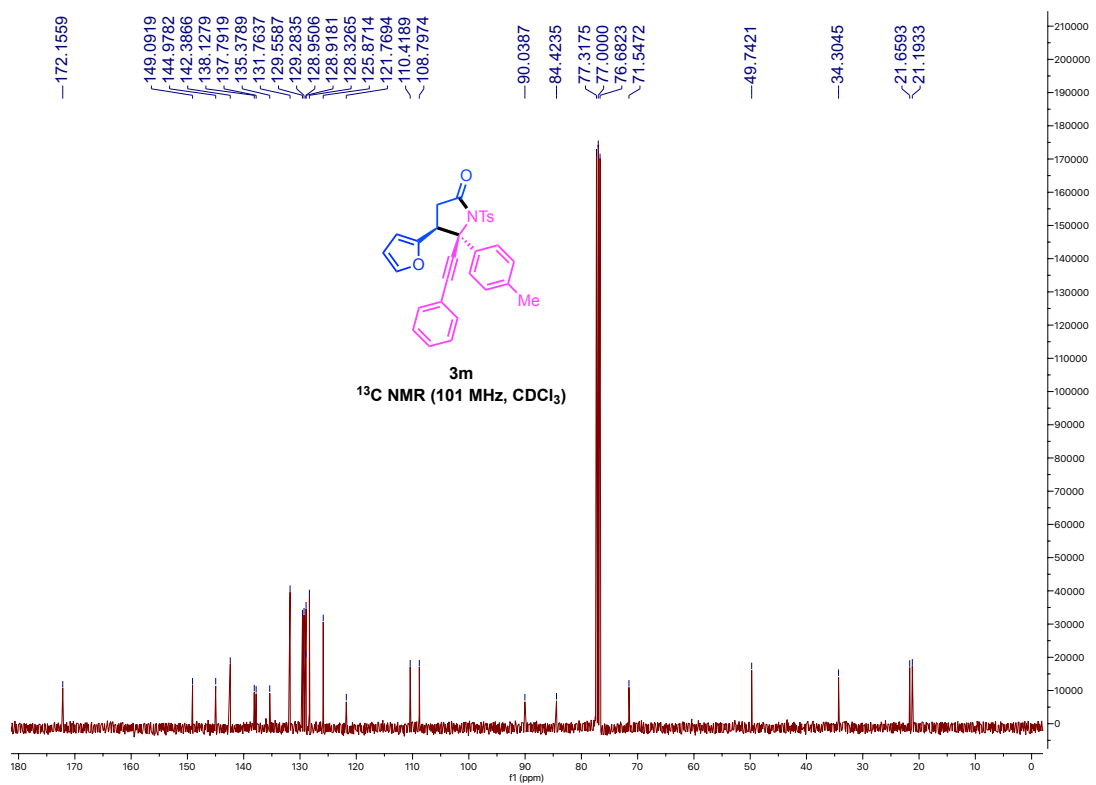
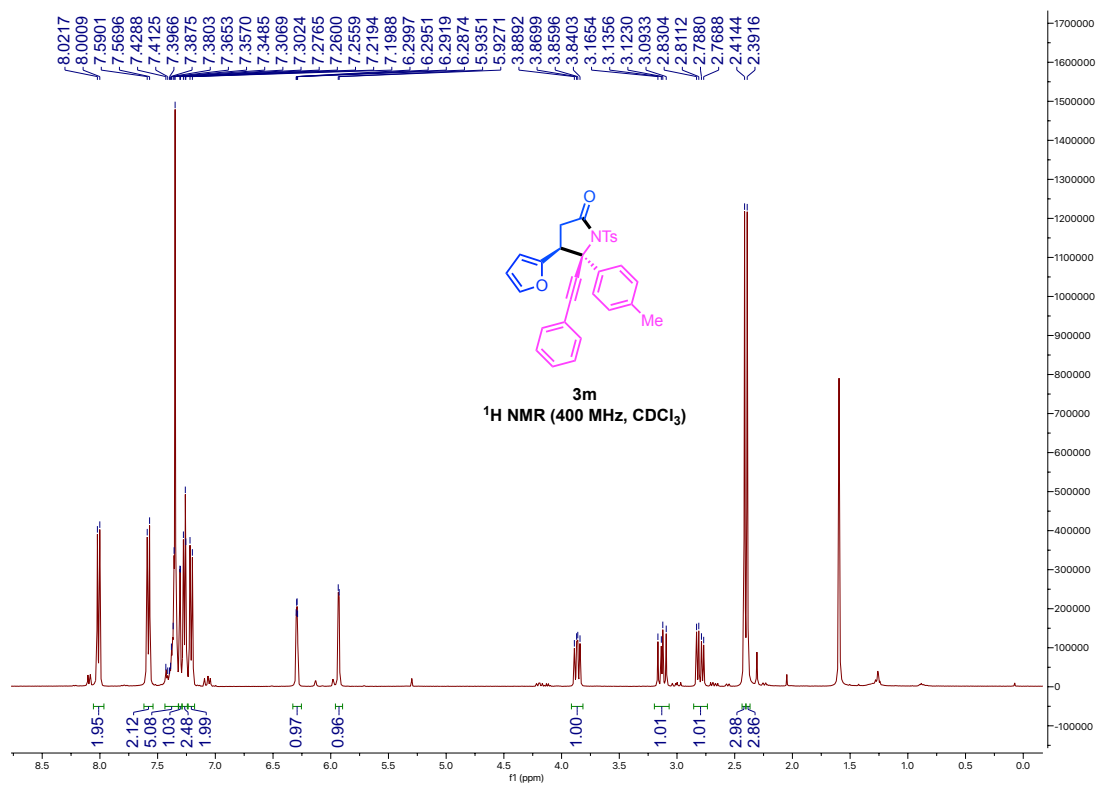


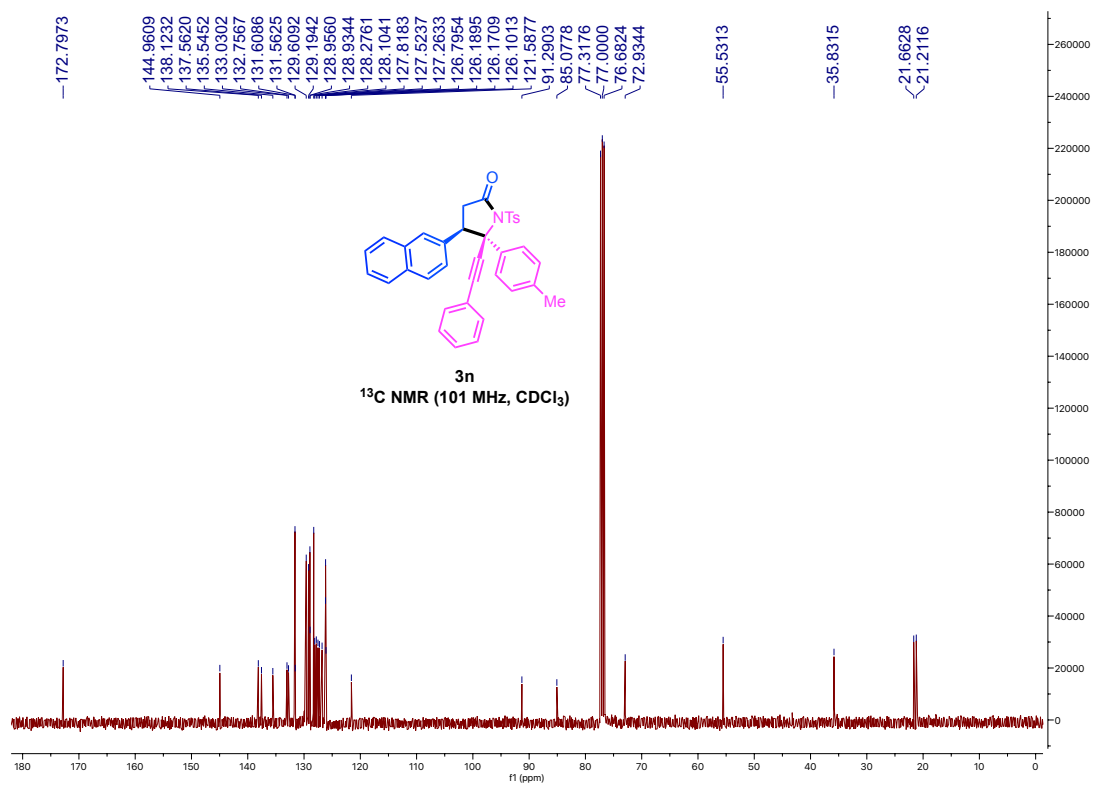
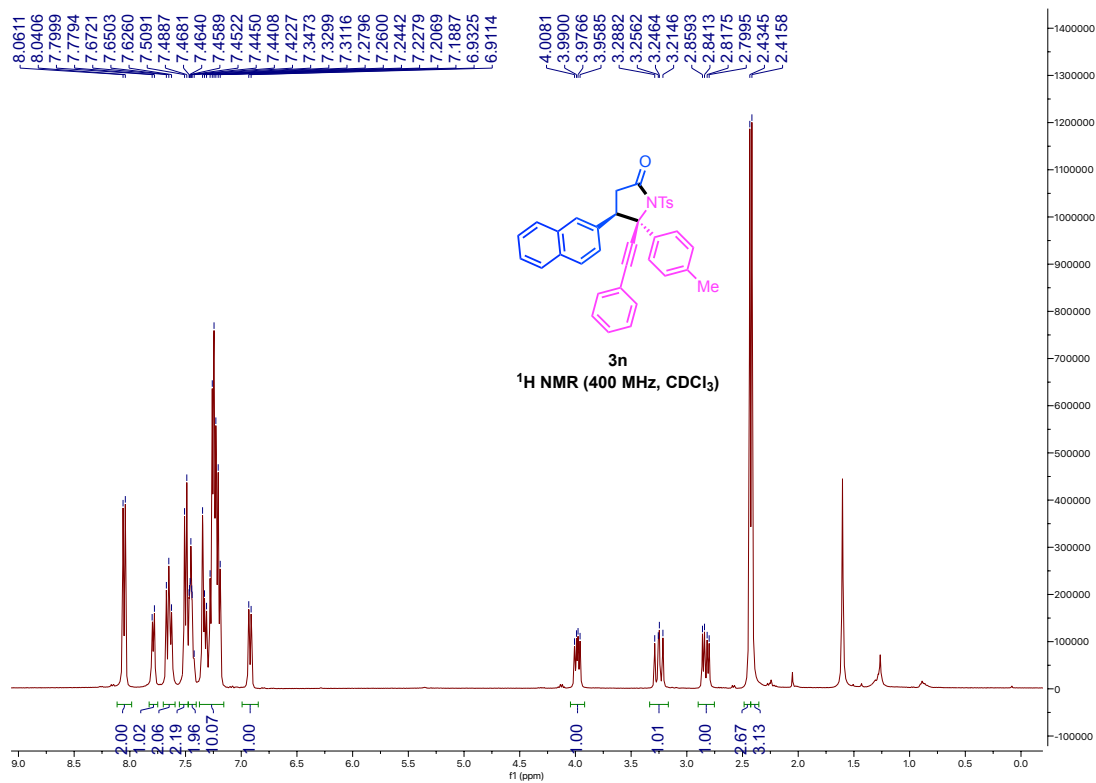


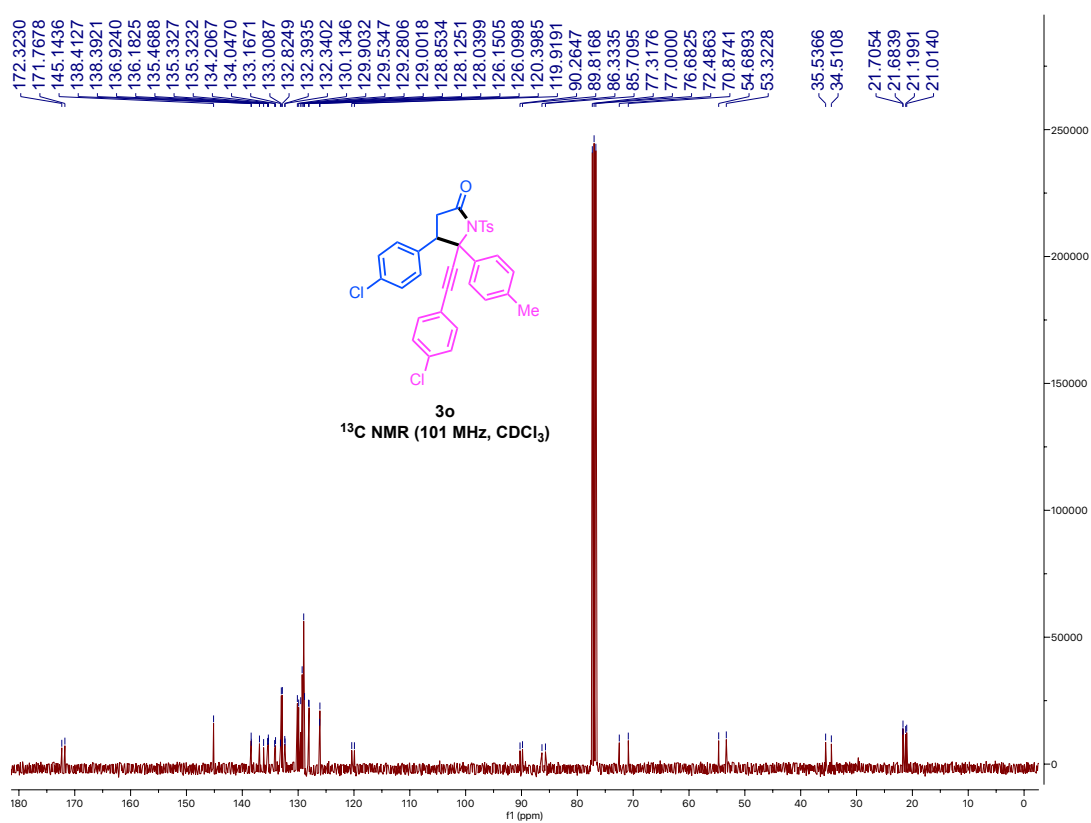
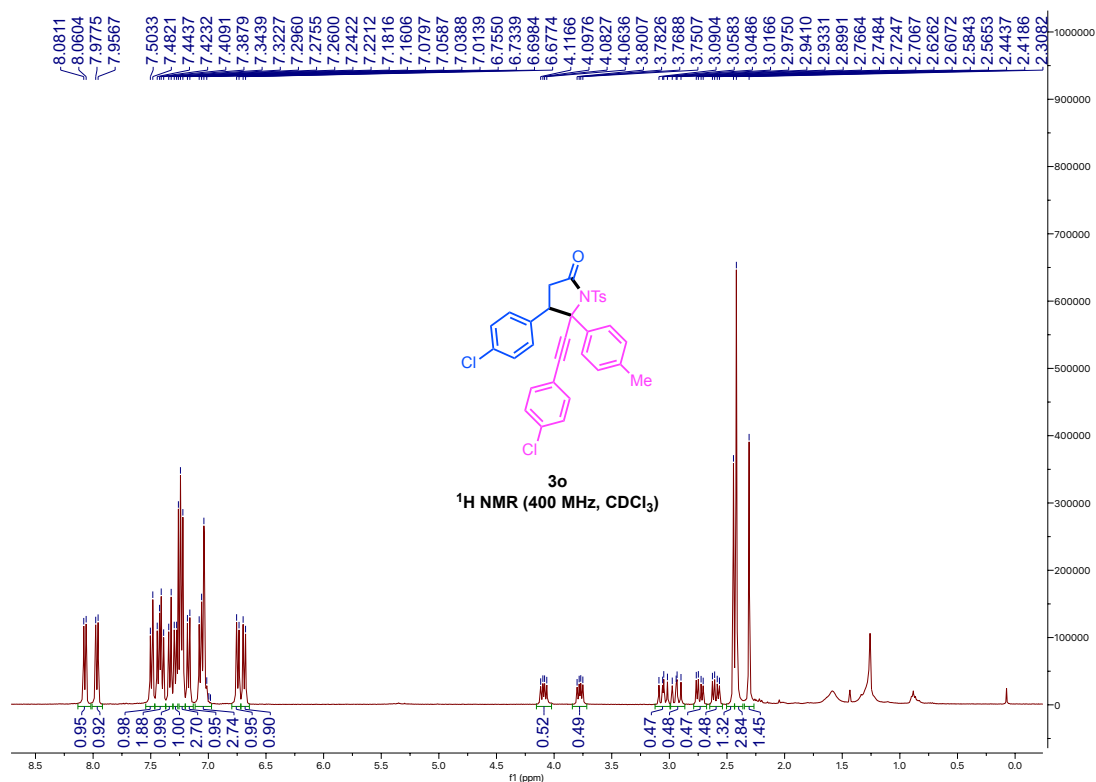


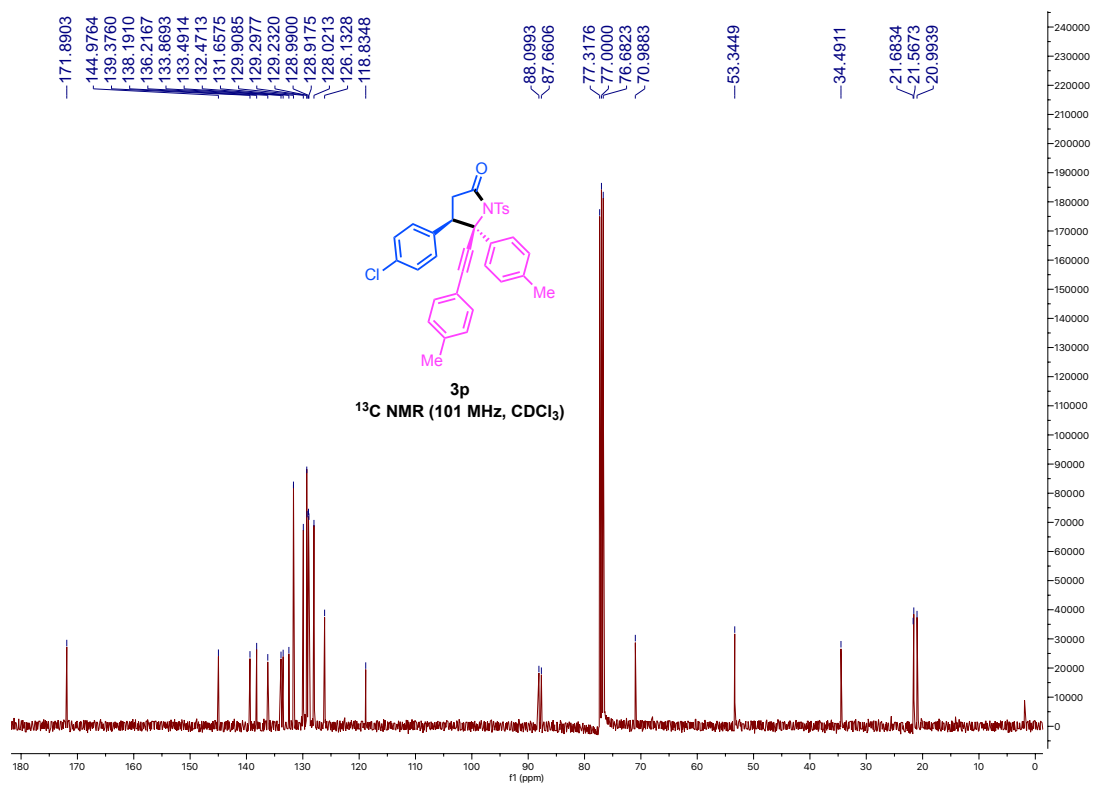
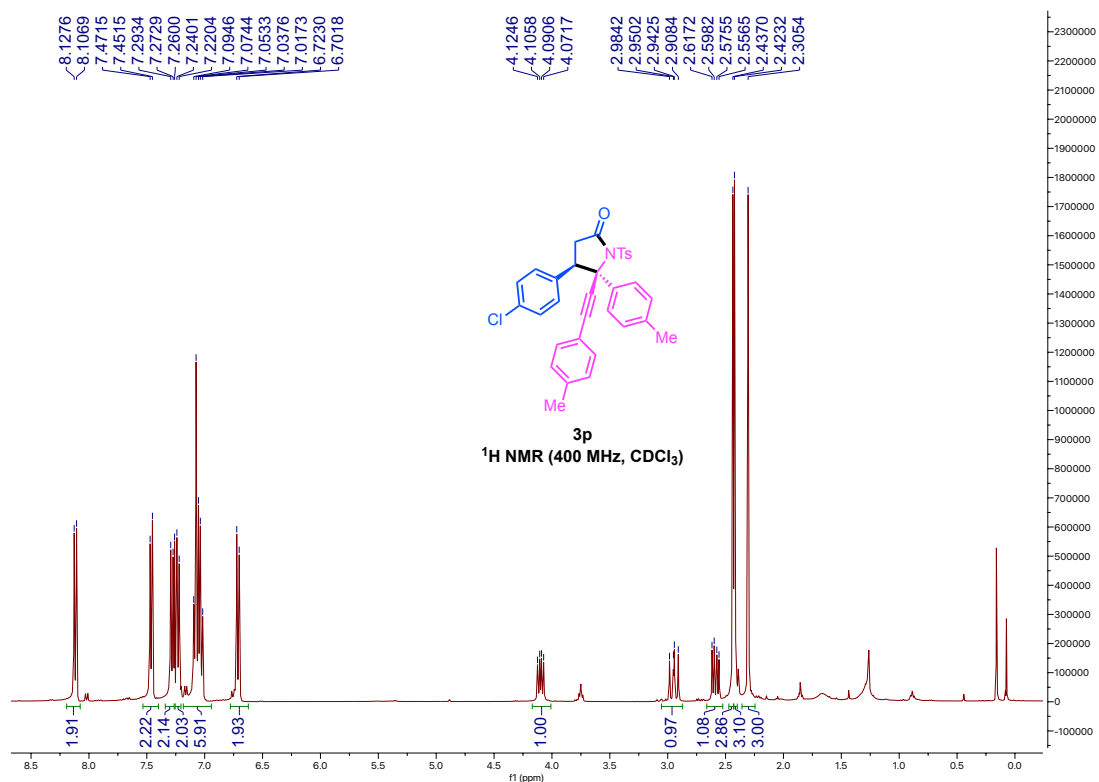


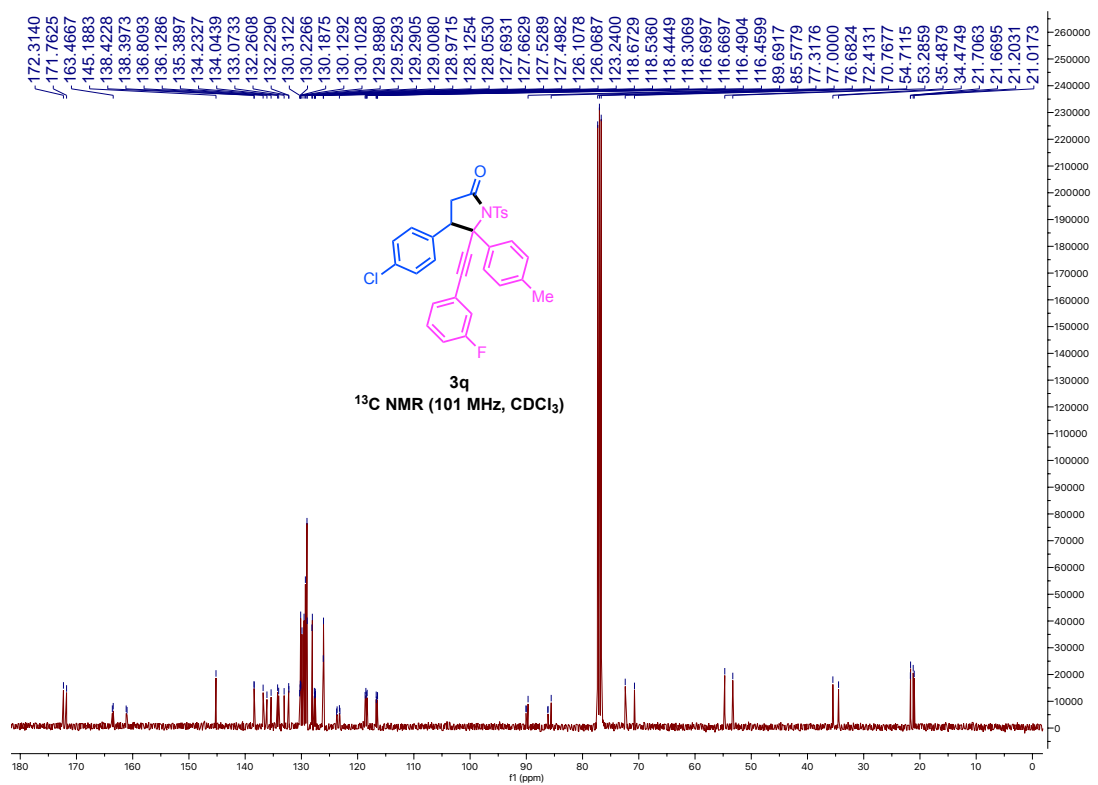
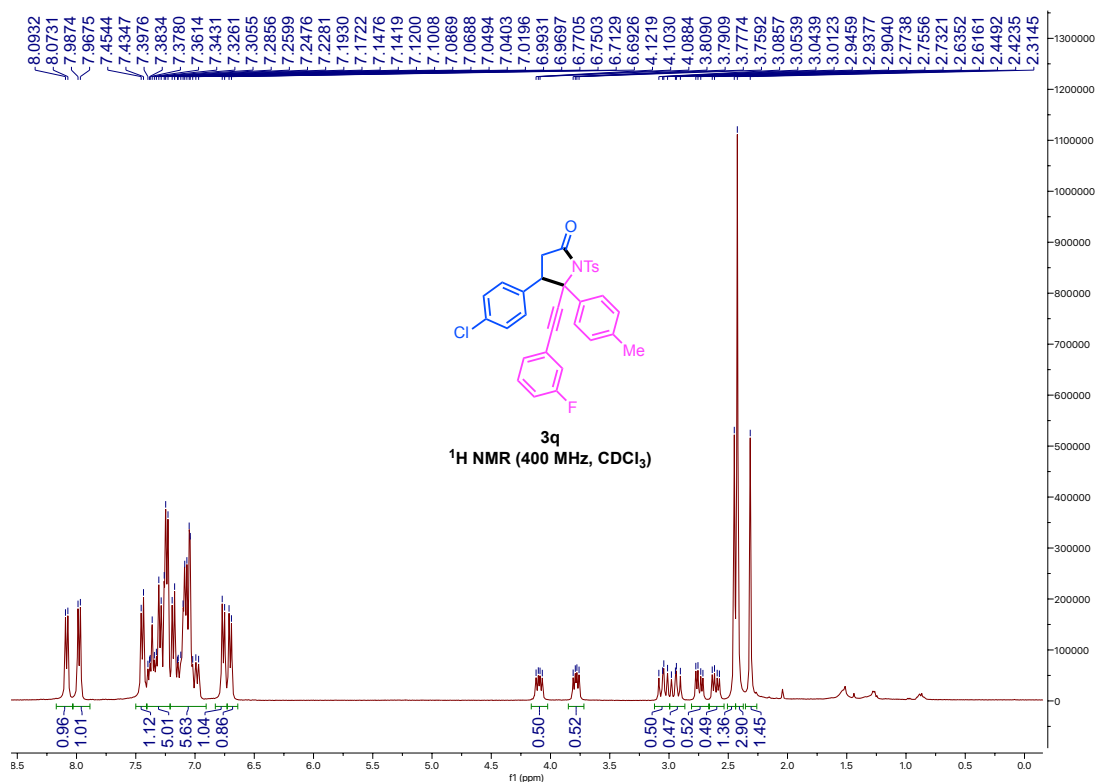


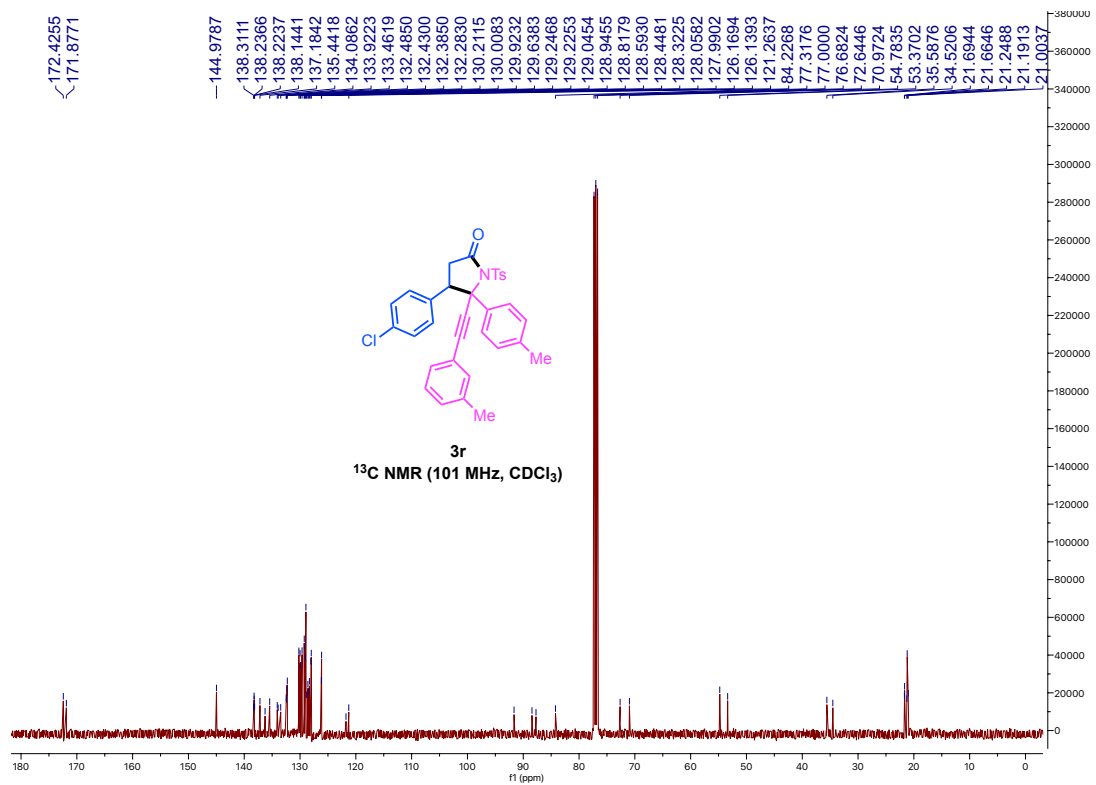
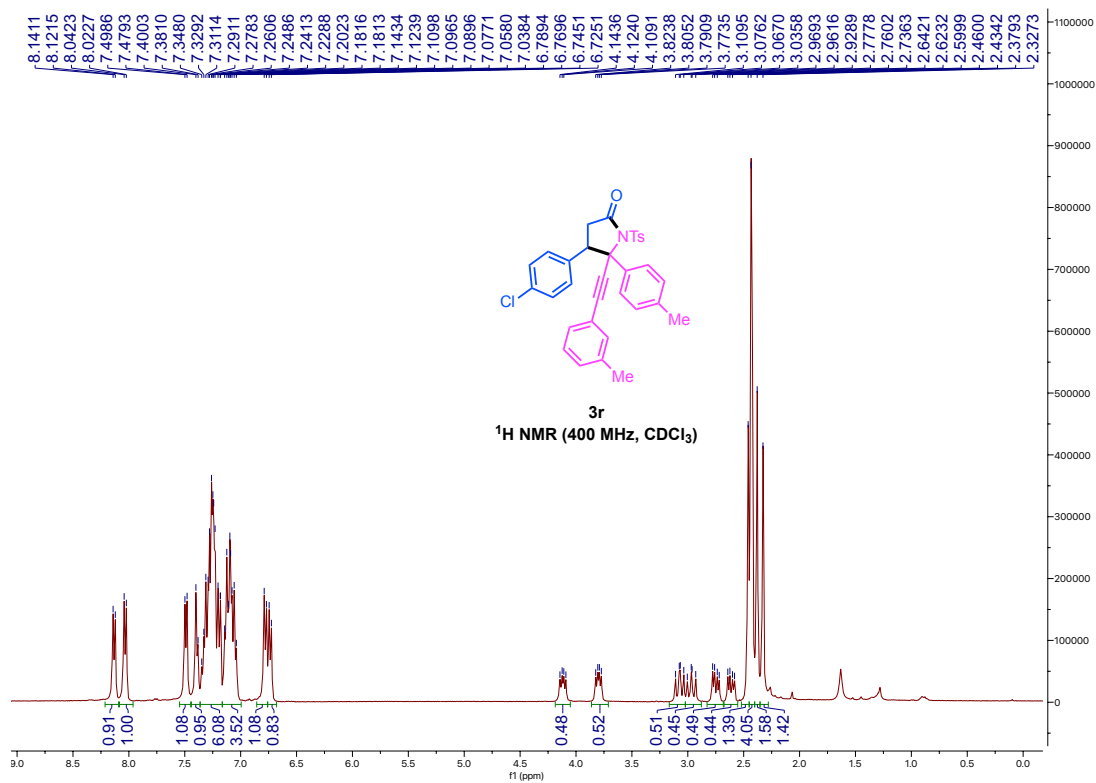


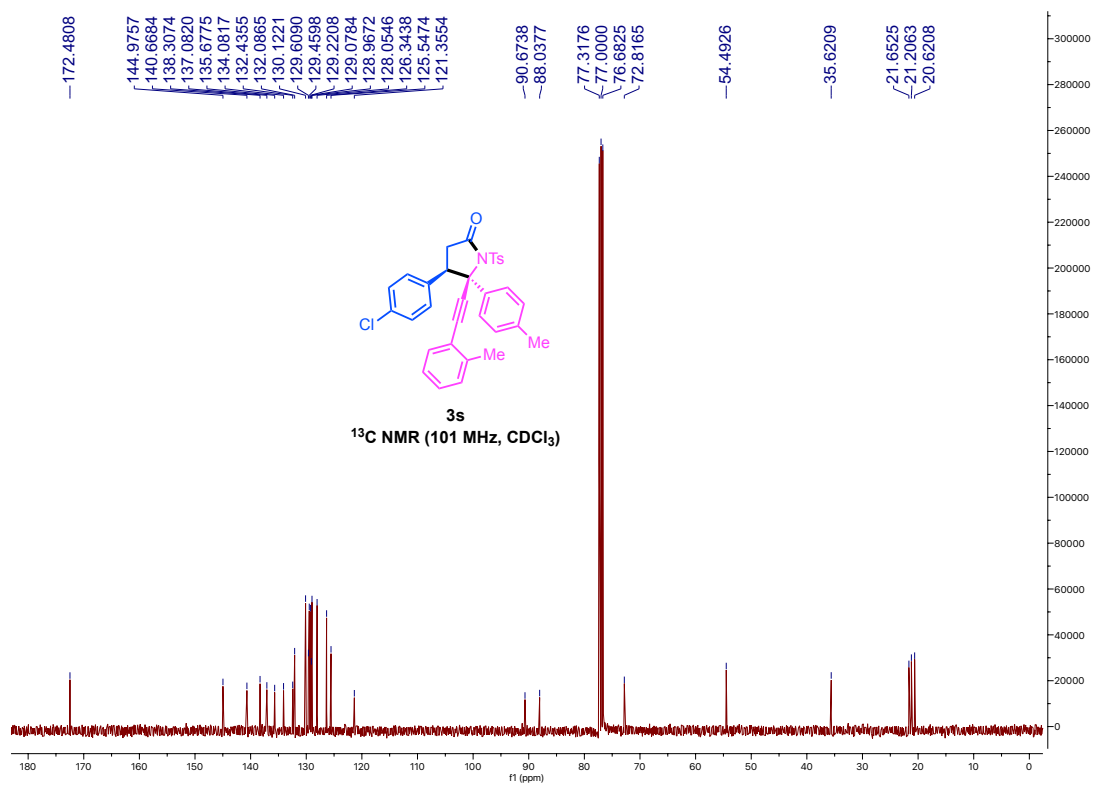
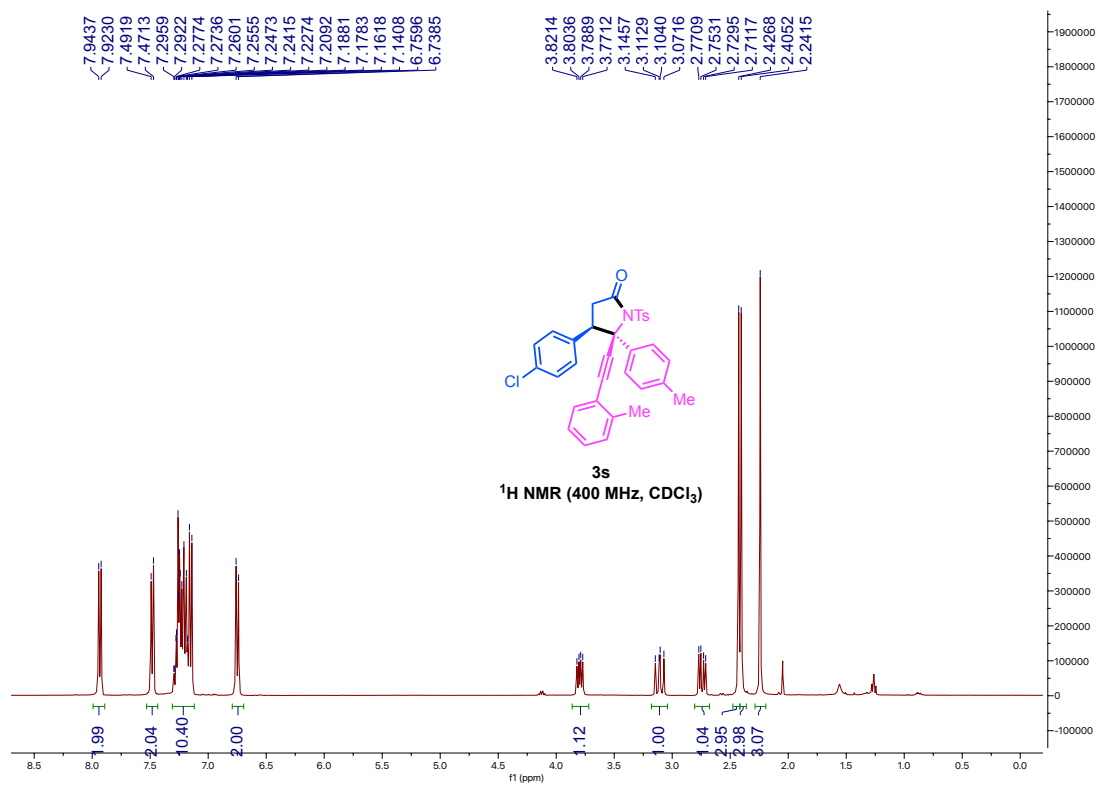


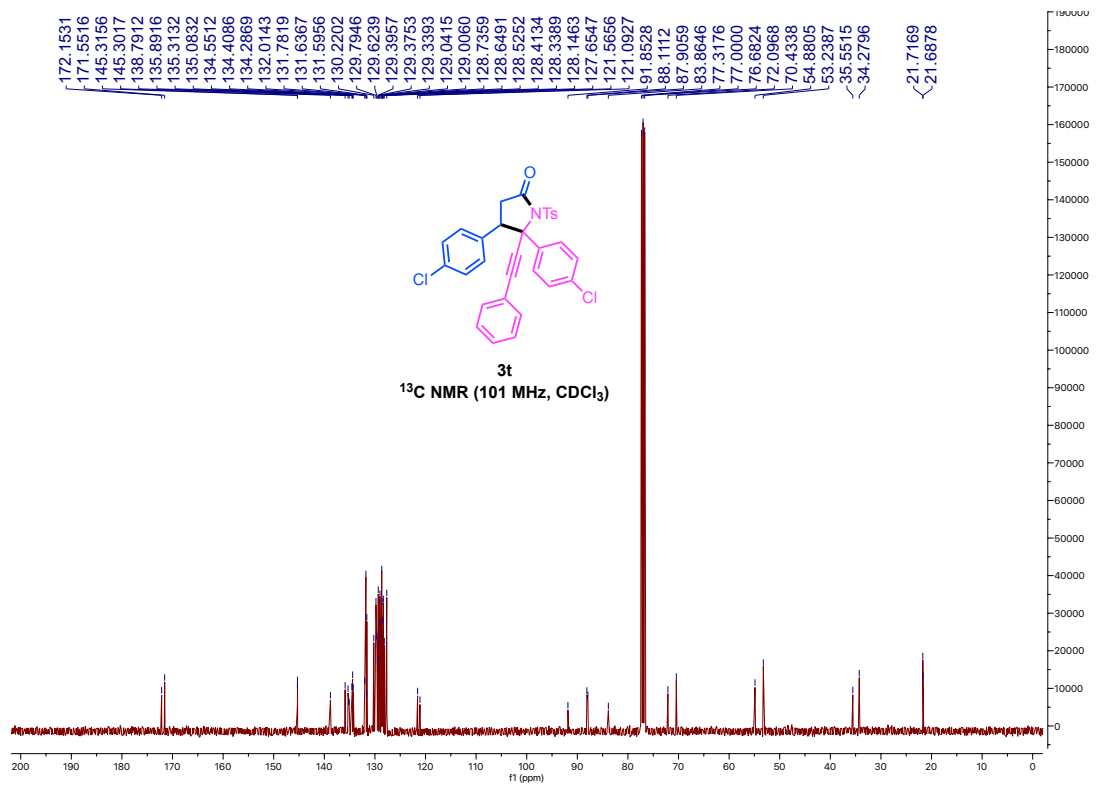
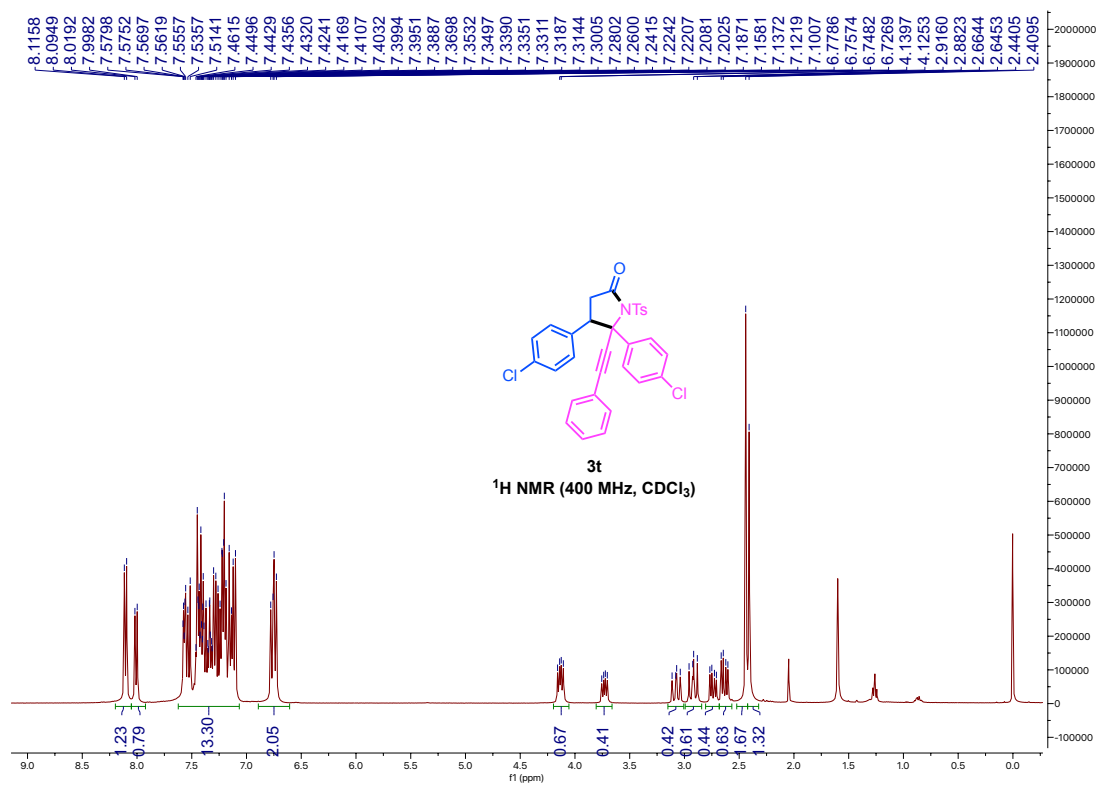


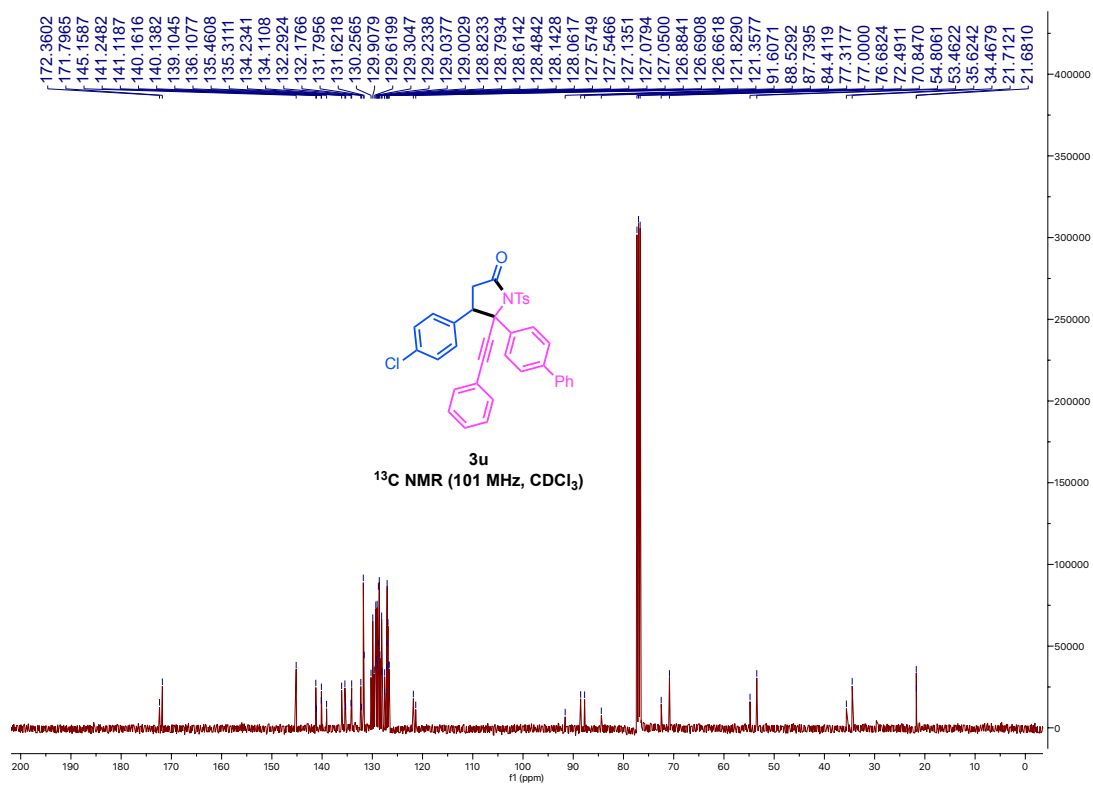
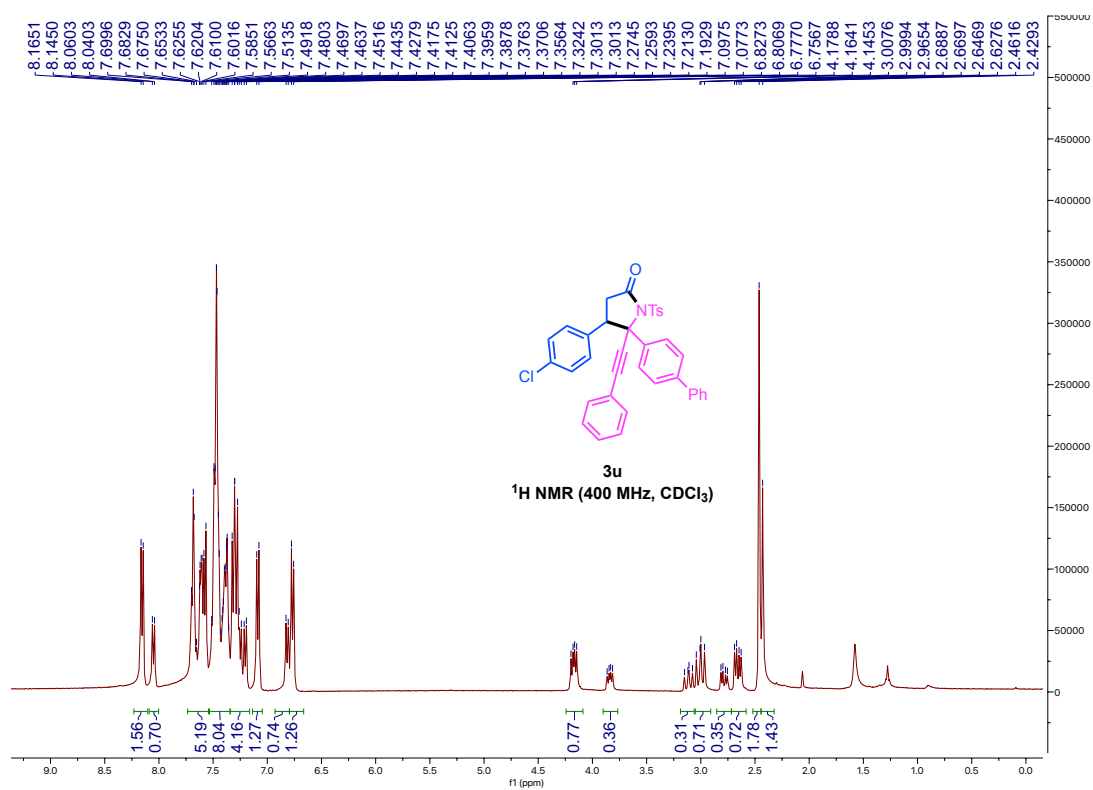


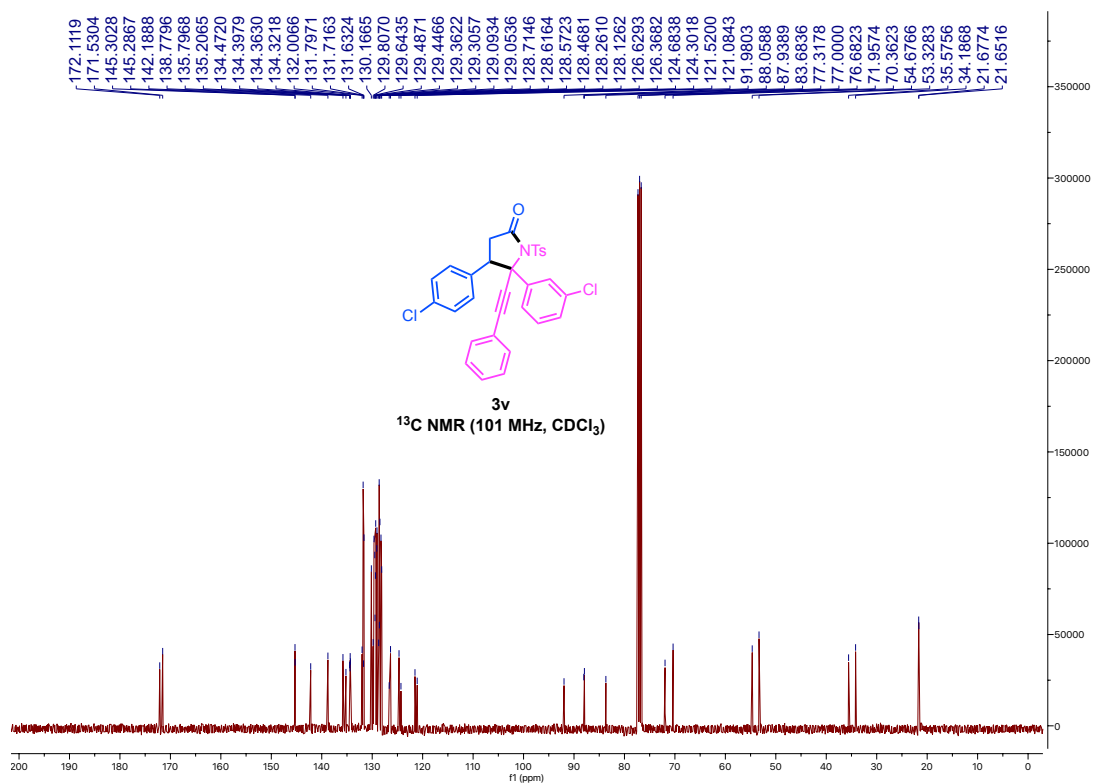
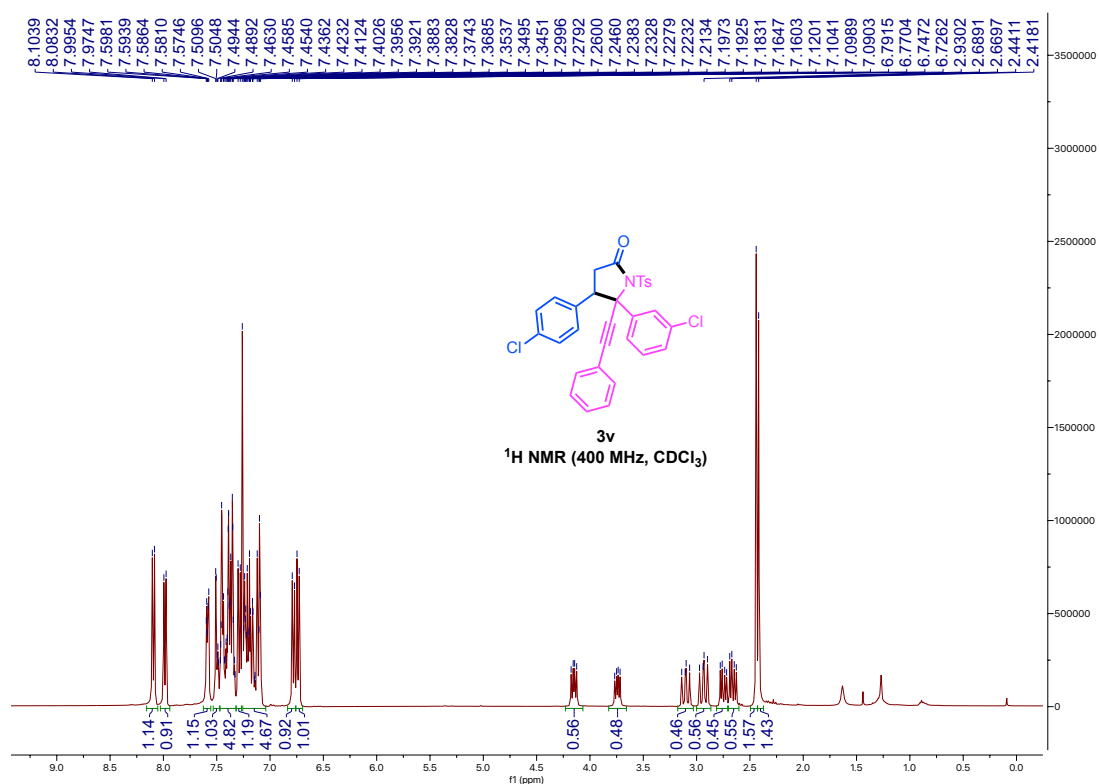


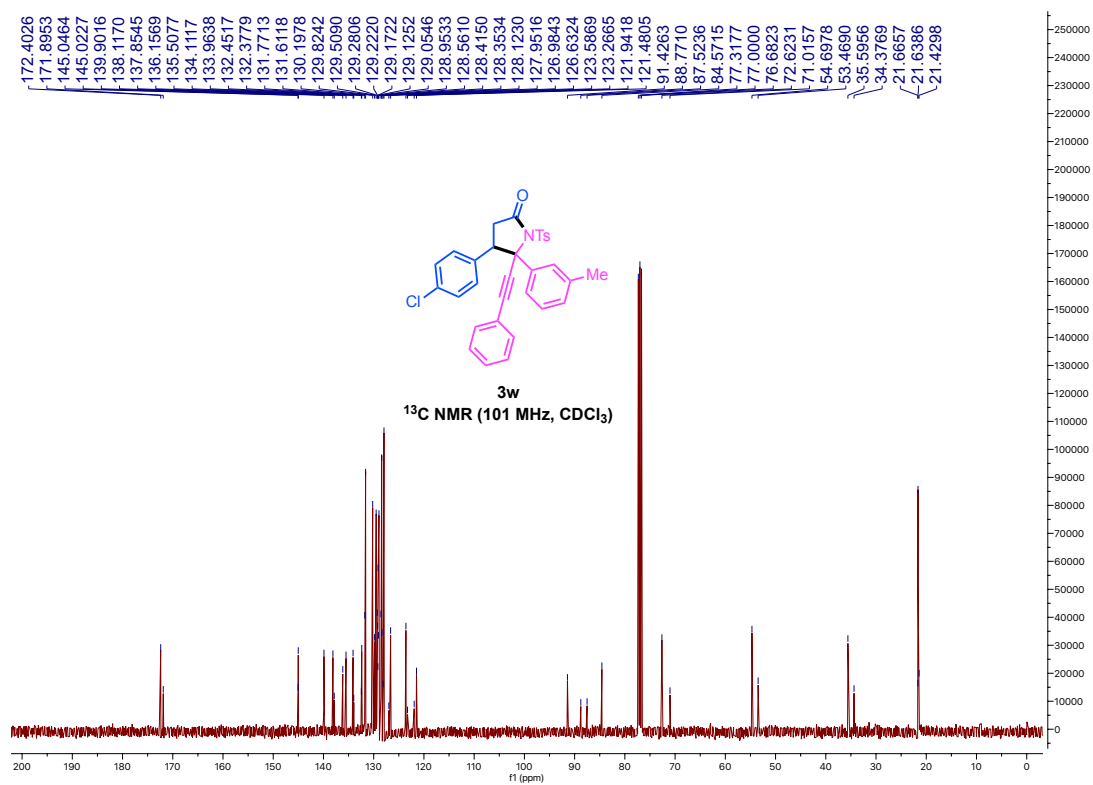
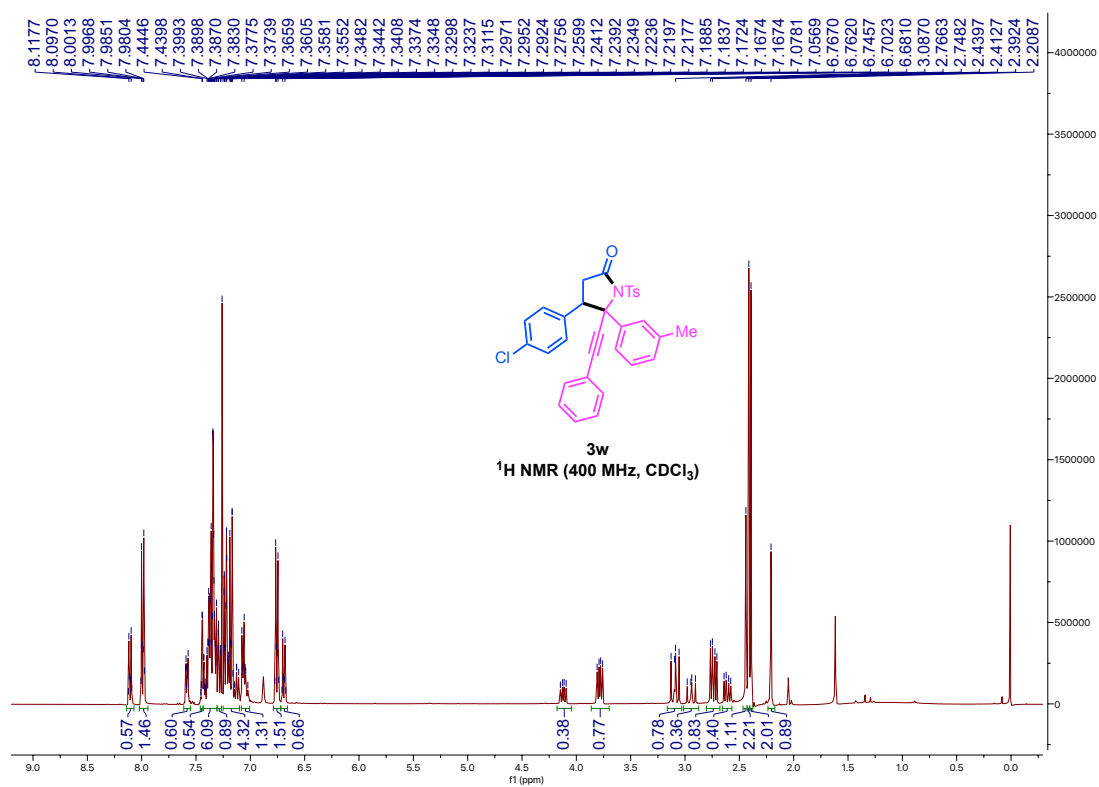


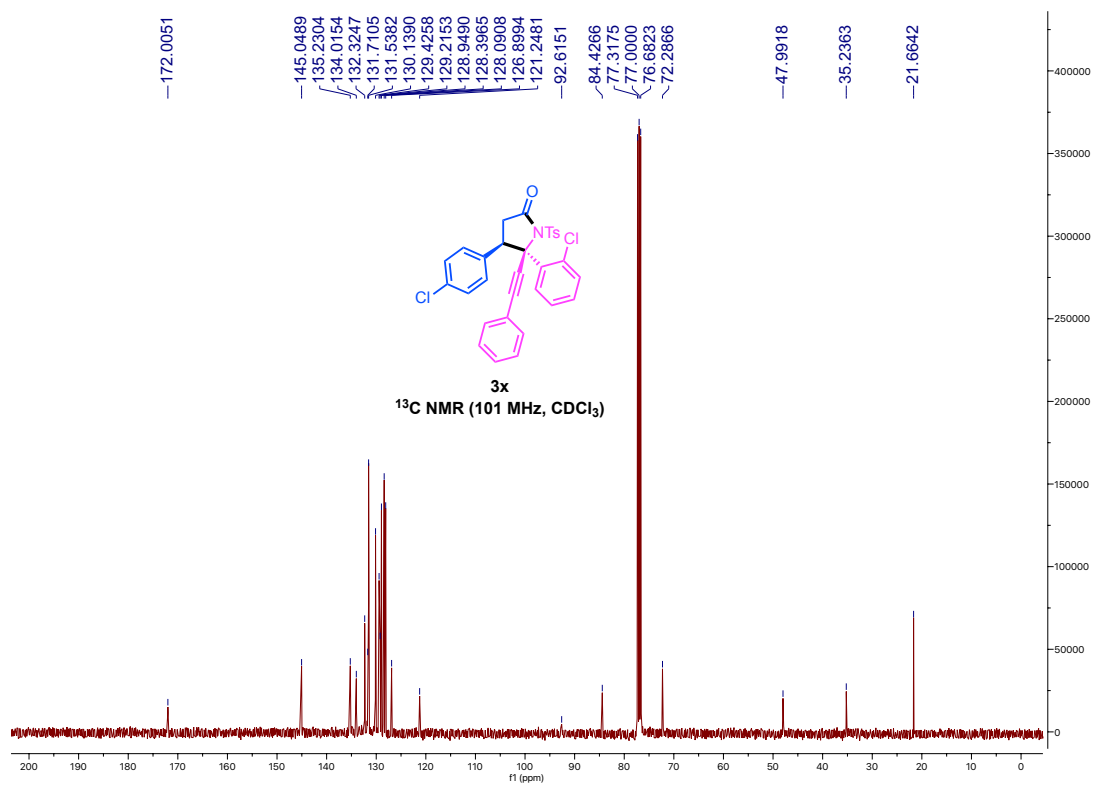
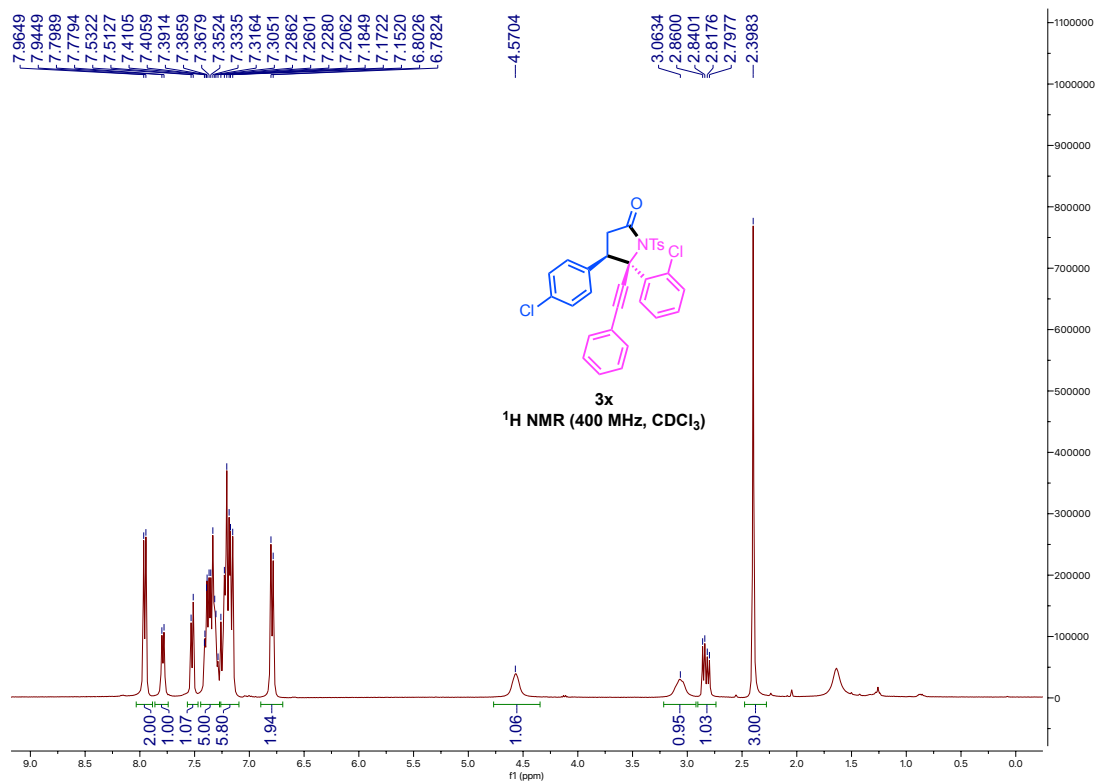


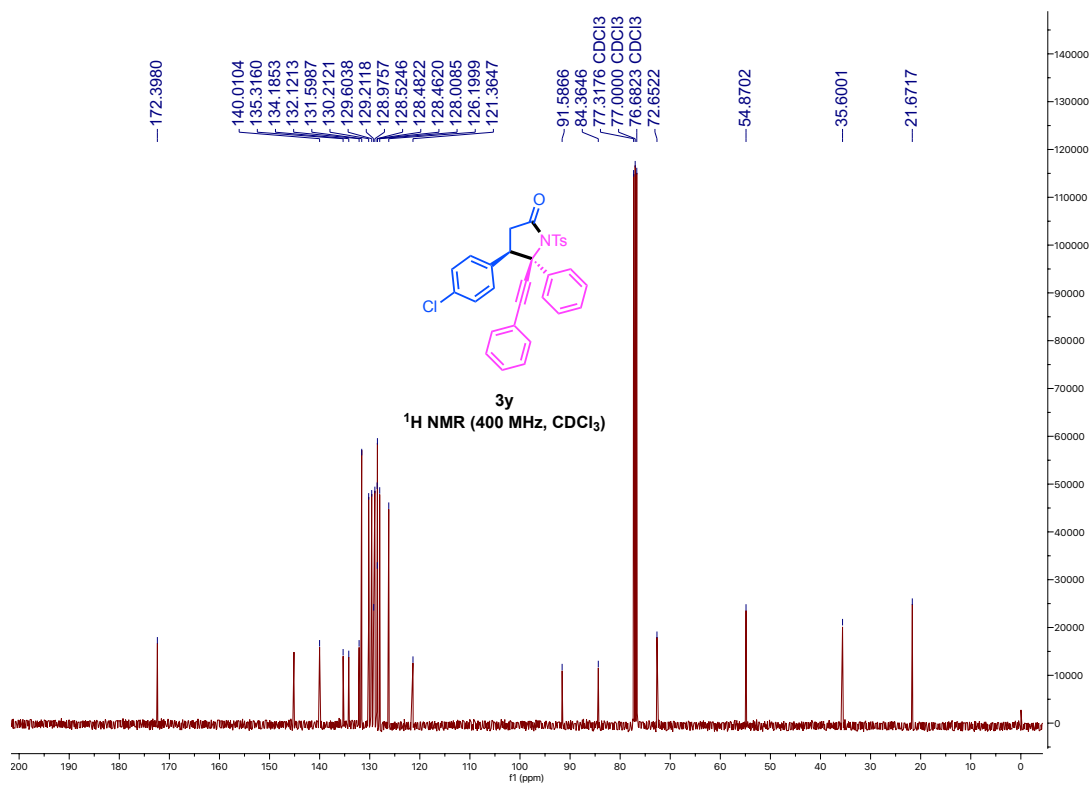
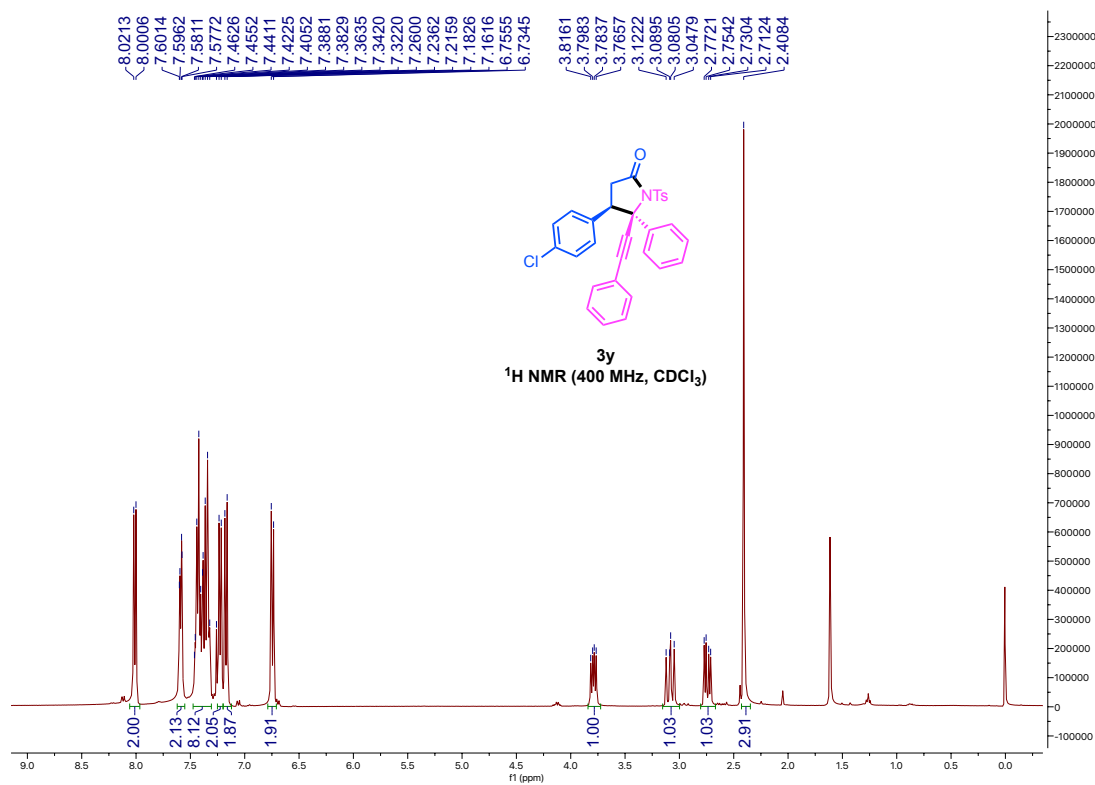


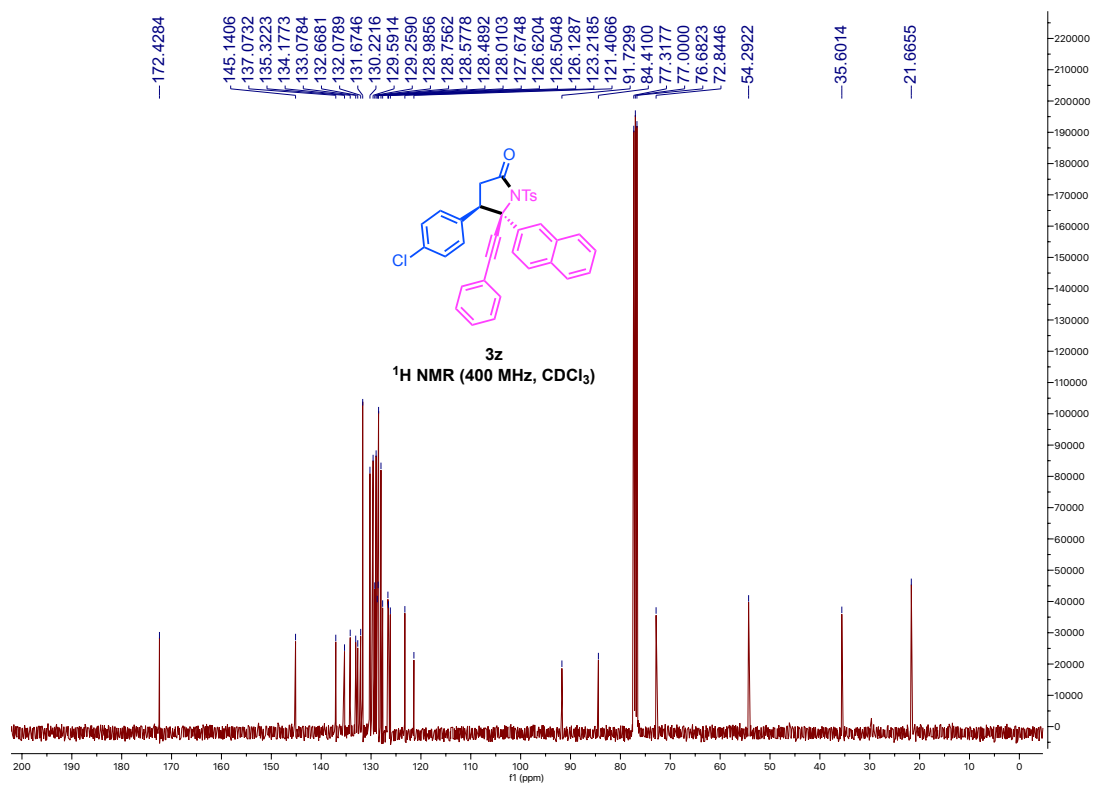
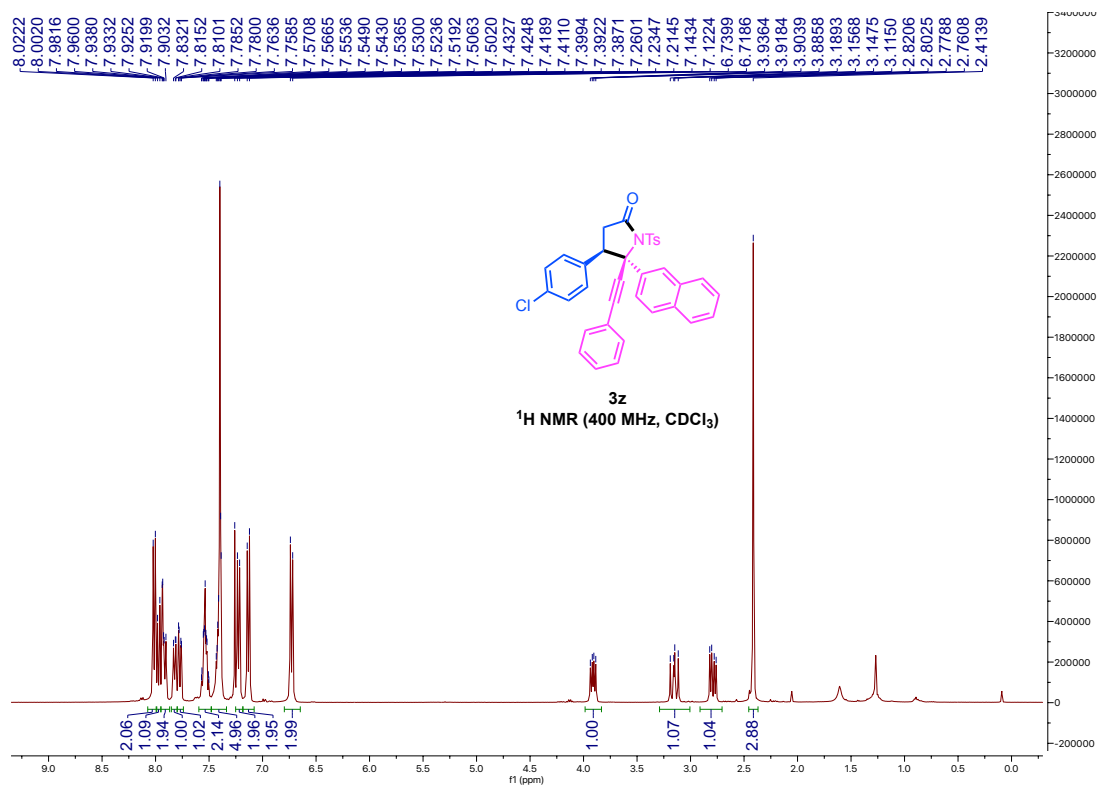


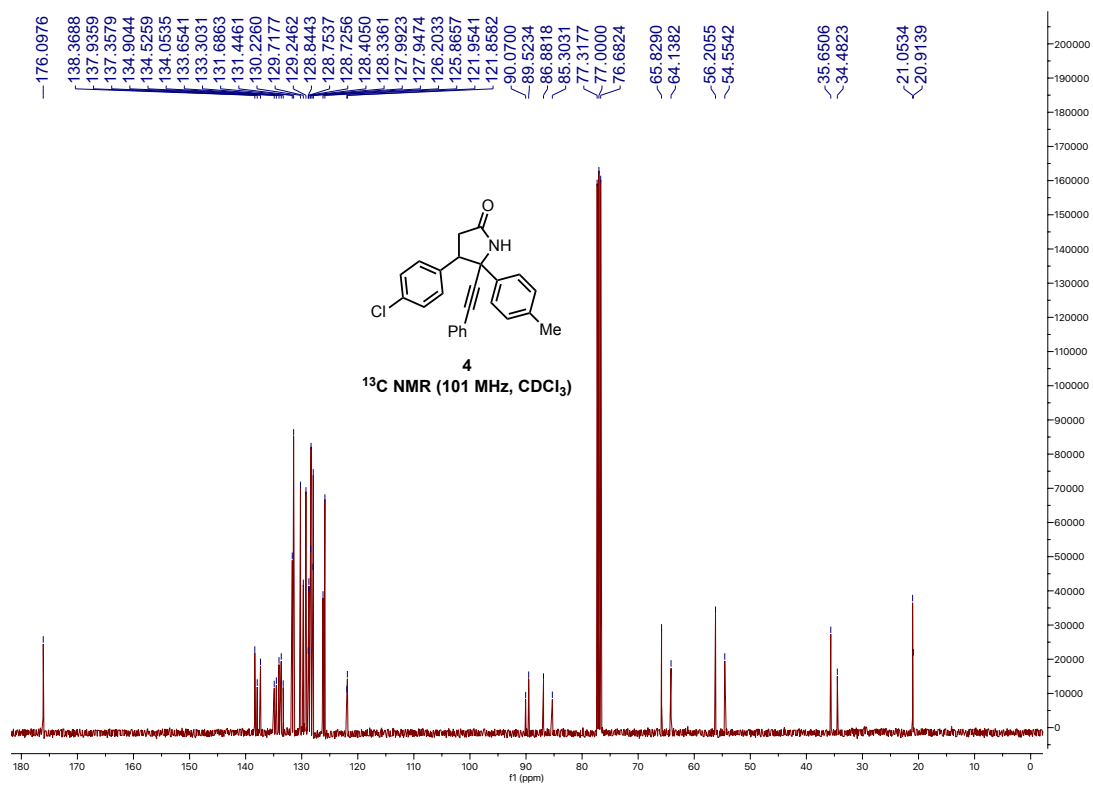
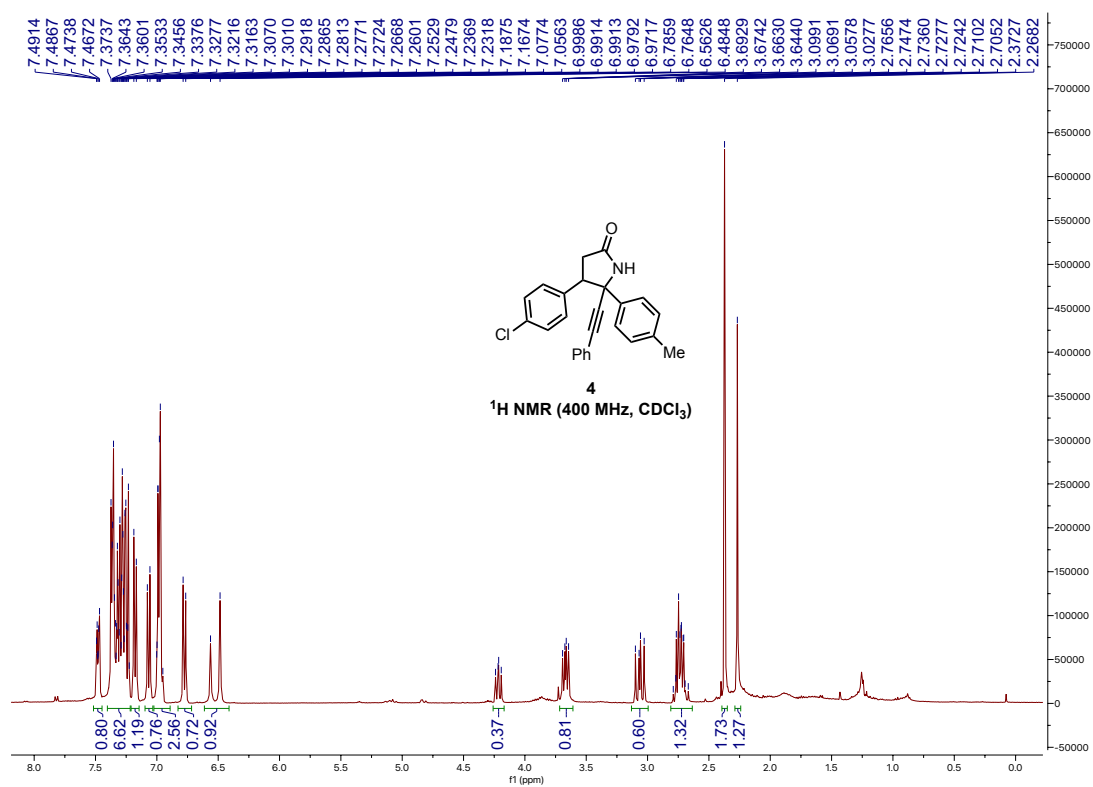


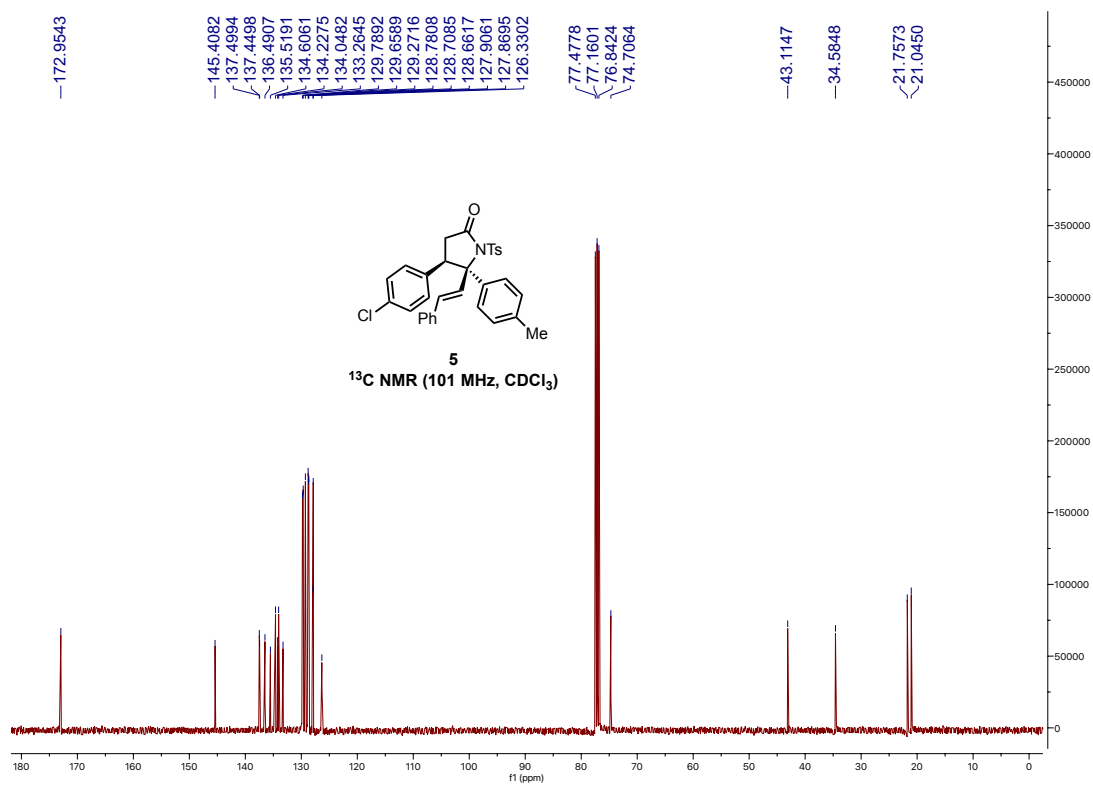
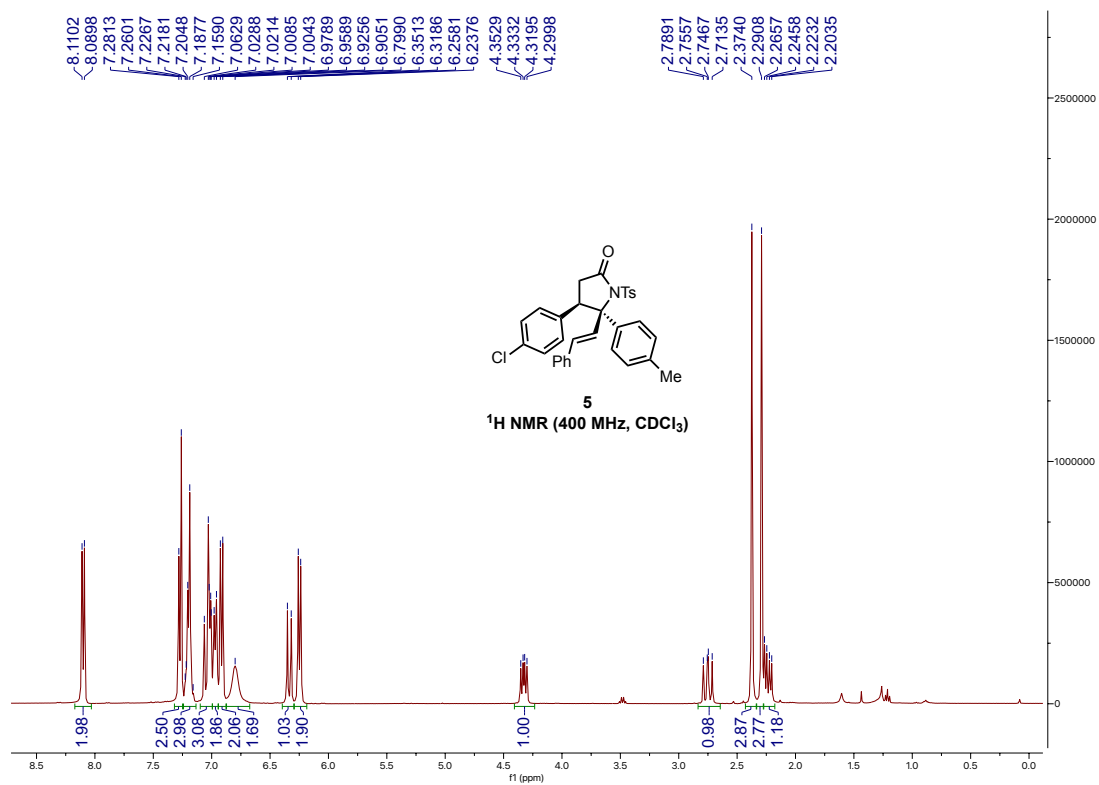




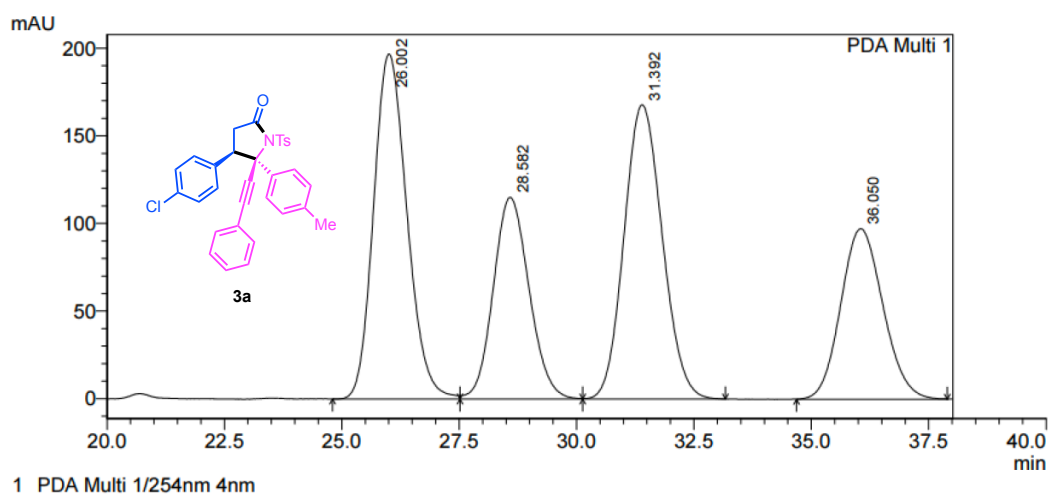








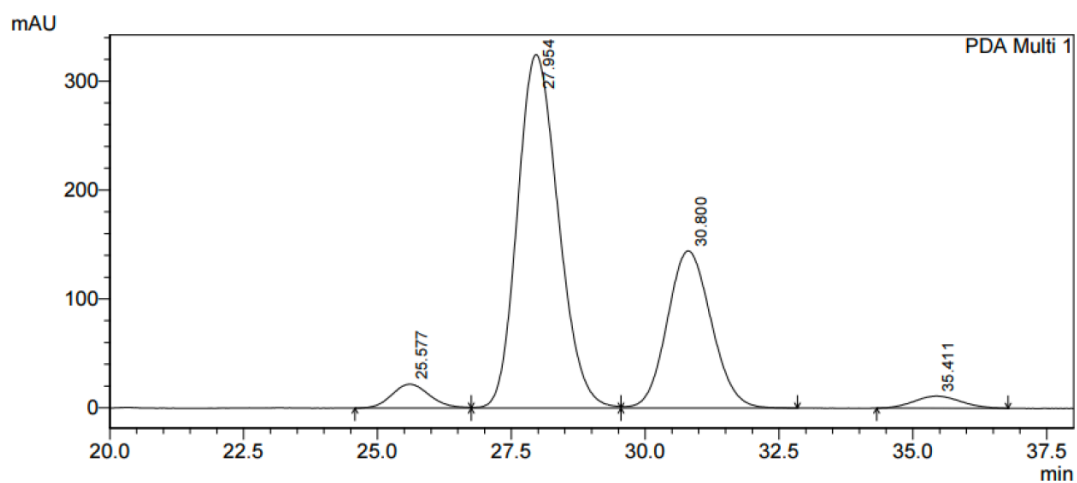
VII. HPLC Spectra



PeakTable

PDA Ch1 254nm 4nm

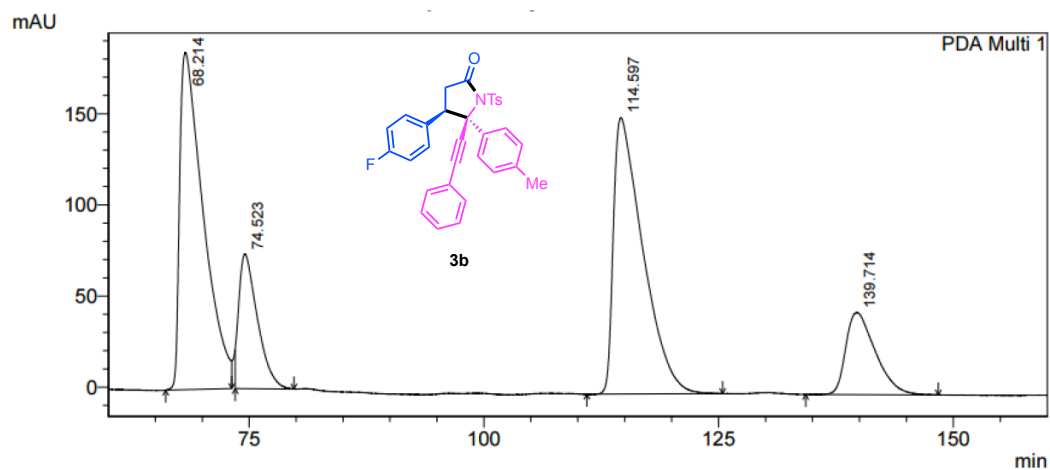
Peak#	Ret. Time	Area	Height	Area %
1	26.002	9748073	197021	30.967
2	28.582	6112647	115183	19.419
3	31.392	9527359	168009	30.266
4	36.050	6090325	97351	19.348
Total		31478404	577564	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	25.577	1080060	21924	3.960
2	27.954	17255766	324450	63.268
3	30.800	8255774	144254	30.270
4	35.411	682439	11183	2.502
Total		27274037	501810	100.000

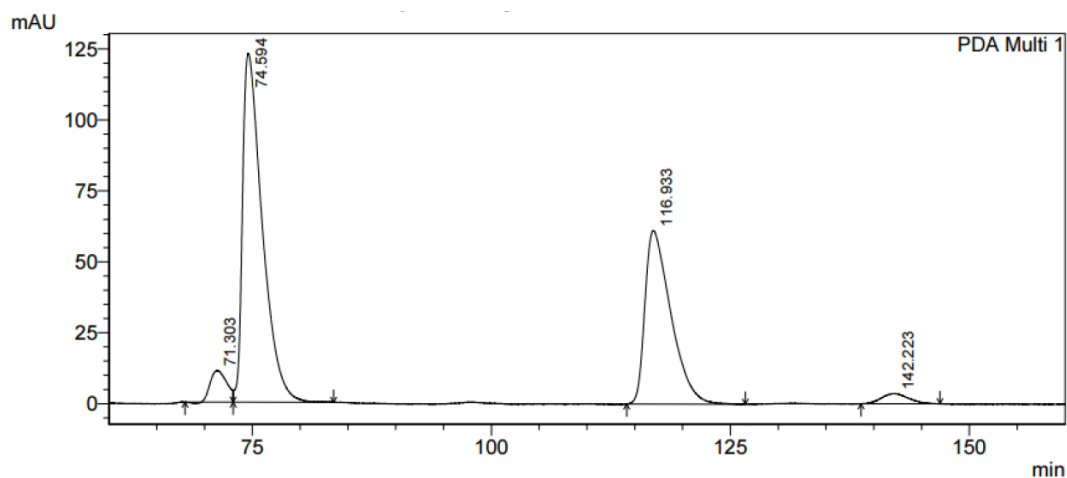


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	68.214	32273191	184953	37.783
2	74.523	10249365	73891	11.999
3	114.597	33055156	151647	38.698
4	139.714	9840597	45055	11.520
Total		85418309	455546	100.000

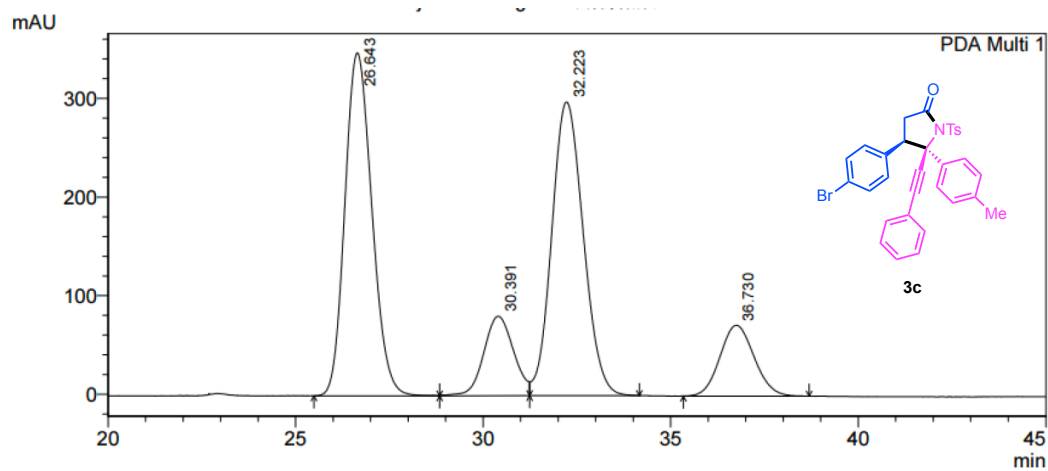


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	71.303	1317654	11171	4.214
2	74.594	17692513	122962	56.581
3	116.933	11546027	61191	36.924
4	142.223	713183	3632	2.281
Total		31269377	198956	100.000

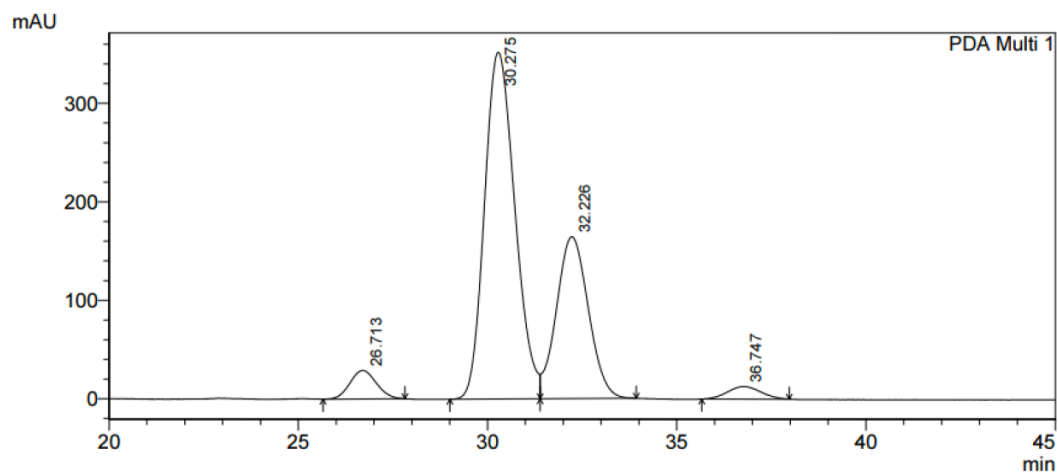


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	26.643	17397298	347732	39.690
2	30.391	4455754	80603	10.165
3	32.223	17411283	297688	39.722
4	36.730	4568243	71789	10.422
Total		43832577	797812	100.000

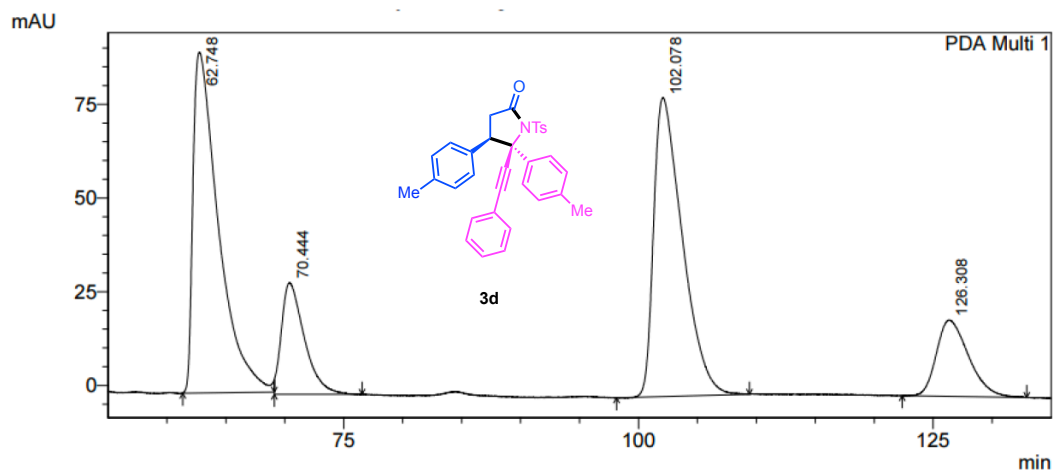


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	26.713	1410811	29026	4.479
2	30.275	19651125	351943	62.385
3	32.226	9648196	164470	30.629
4	36.747	789800	12792	2.507
Total		31499931	558231	100.000

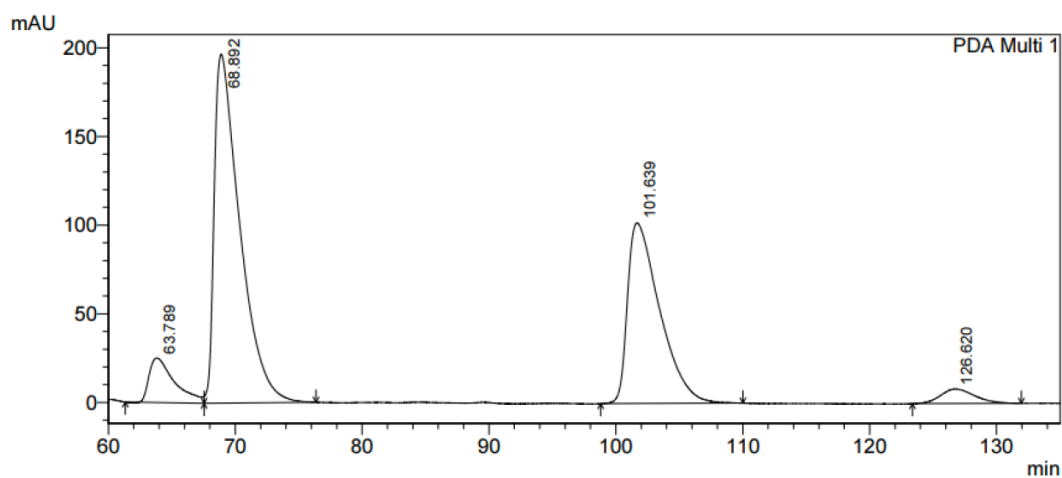


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	62.748	13692678	90981	39.053
2	70.444	4019310	29805	11.464
3	102.078	13500539	79792	38.505
4	126.308	3848942	20394	10.978
Total		35061469	220972	100.000

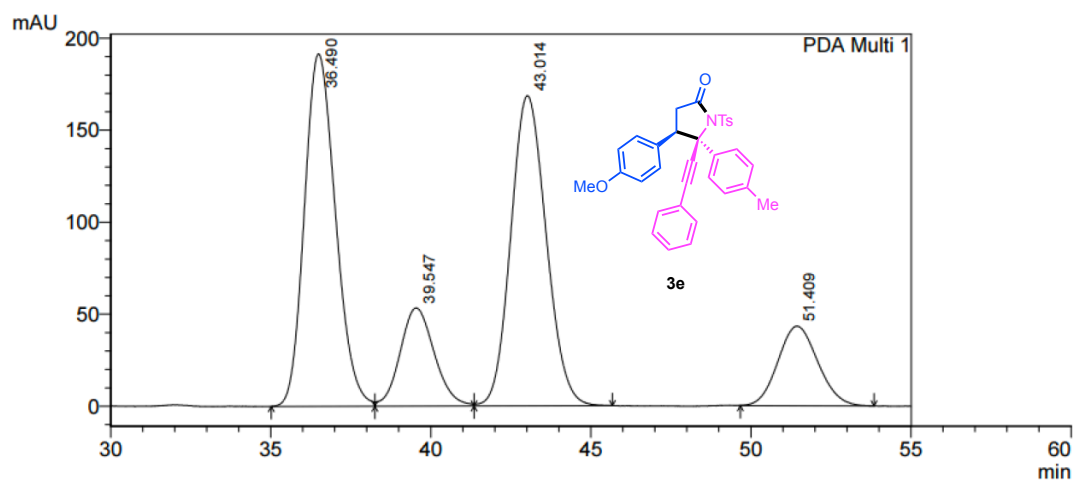


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	63.789	3486654	25114	6.889
2	68.892	27591949	196829	54.521
3	101.639	17995890	101831	35.559
4	126.620	1533815	8214	3.031
Total		50608309	331988	100.000

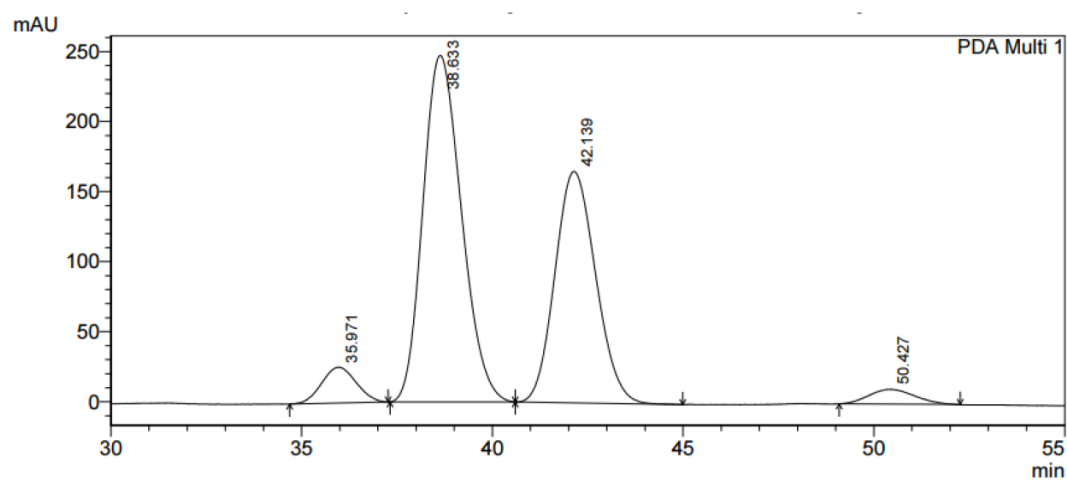


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	36.490	12953437	191582	38.473
2	39.547	3960530	53409	11.763
3	43.014	12983856	168600	38.563
4	51.409	3771004	43318	11.200
Total		33668827	456909	100.000

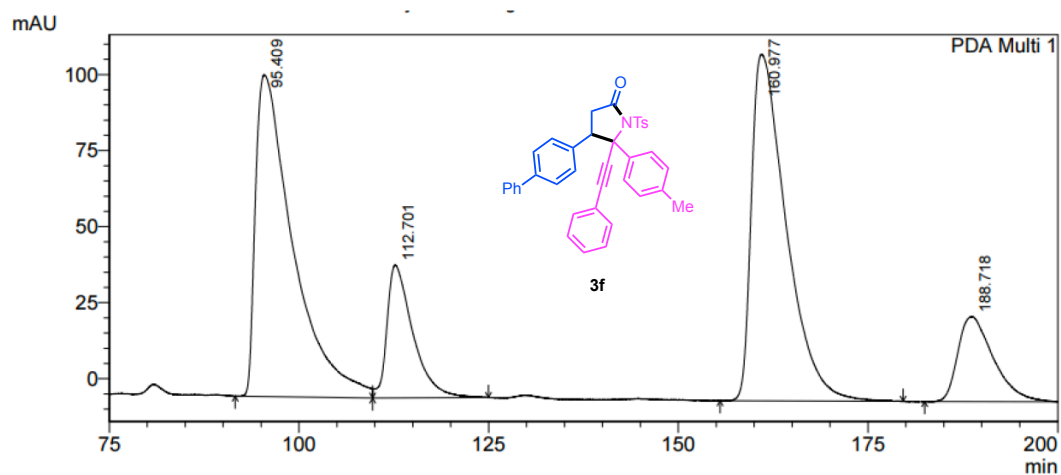


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	35.971	1608617	25597	5.003
2	38.633	17367504	247306	54.017
3	42.139	12300171	165320	38.257
4	50.427	875362	10558	2.723
Total		32151654	448781	100.000

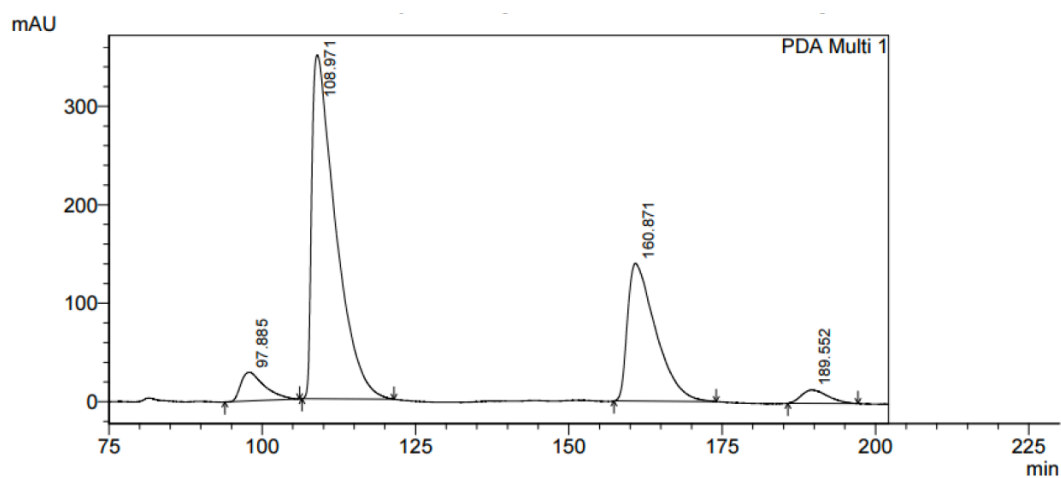


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	95.409	36334982	105821	39.455
2	112.701	10410911	43750	11.305
3	160.977	36236879	113984	39.349
4	188.718	9108819	27974	9.891
Total		92091592	291528	100.000

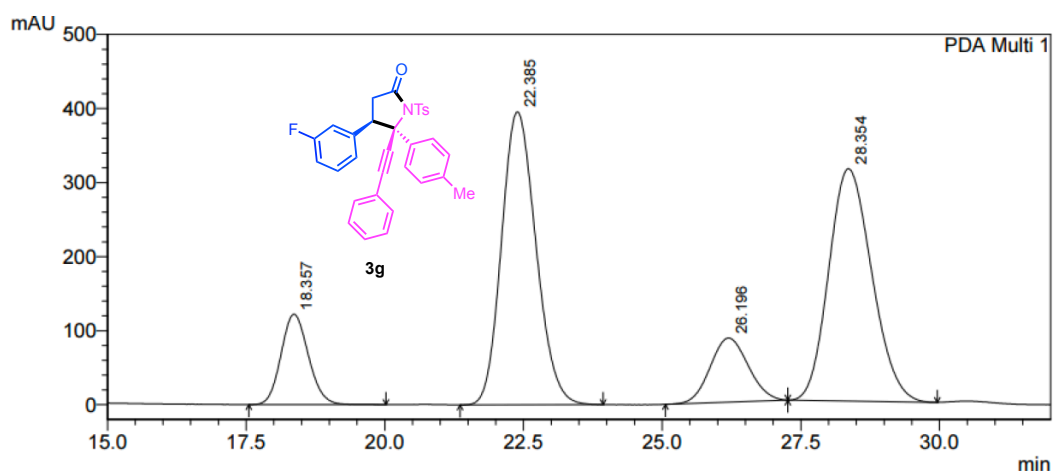


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	97.885	7846260	29224	5.200
2	108.971	94330764	349249	62.521
3	160.871	44602336	139988	29.562
4	189.552	4098625	13715	2.717
Total		150877986	532176	100.000

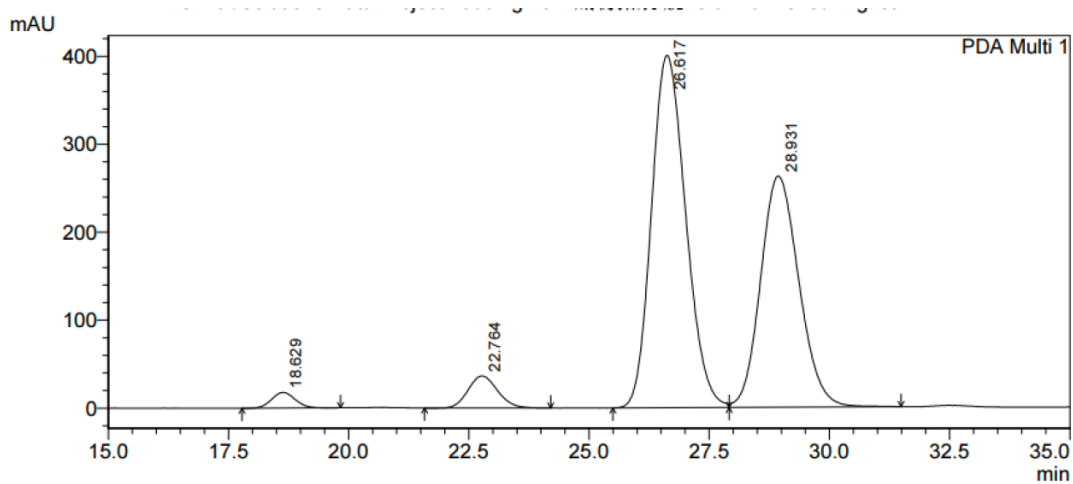


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	18.357	4201784	122064	9.905
2	22.385	17107702	395642	40.328
3	26.196	4137500	86687	9.753
4	28.354	16974576	313785	40.014
Total		42421561	918178	100.000

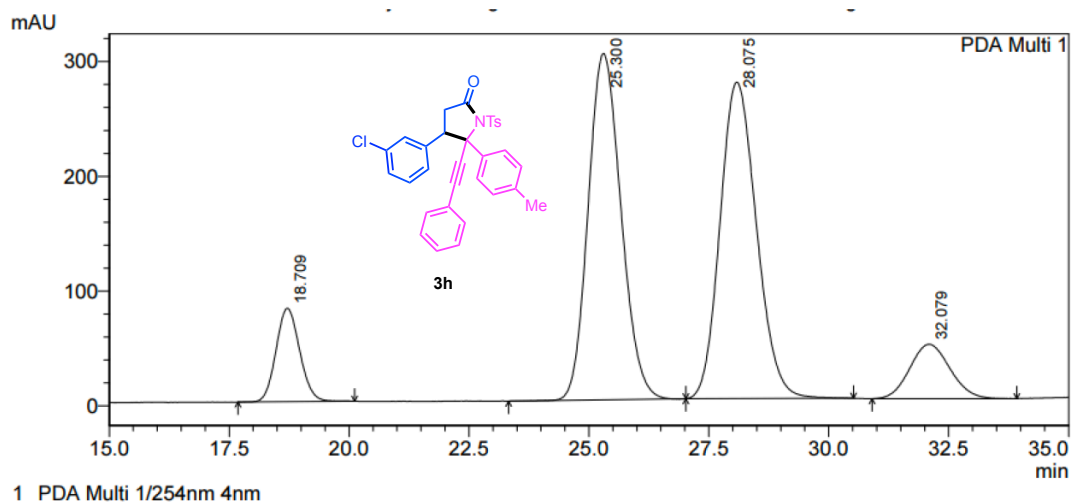


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

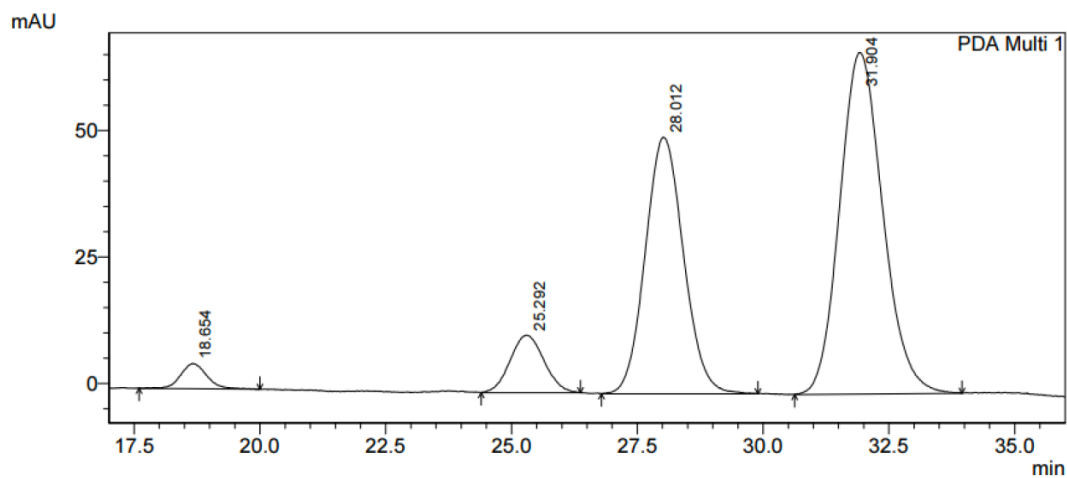
Peak#	Ret. Time	Area	Height	Area %
1	18.629	599779	17847	1.638
2	22.764	1562370	36566	4.267
3	26.617	19858347	400673	54.237
4	28.931	14593491	262951	39.858
Total		36613988	718037	100.000



PeakTable

PDA Ch1 254nm 4nm

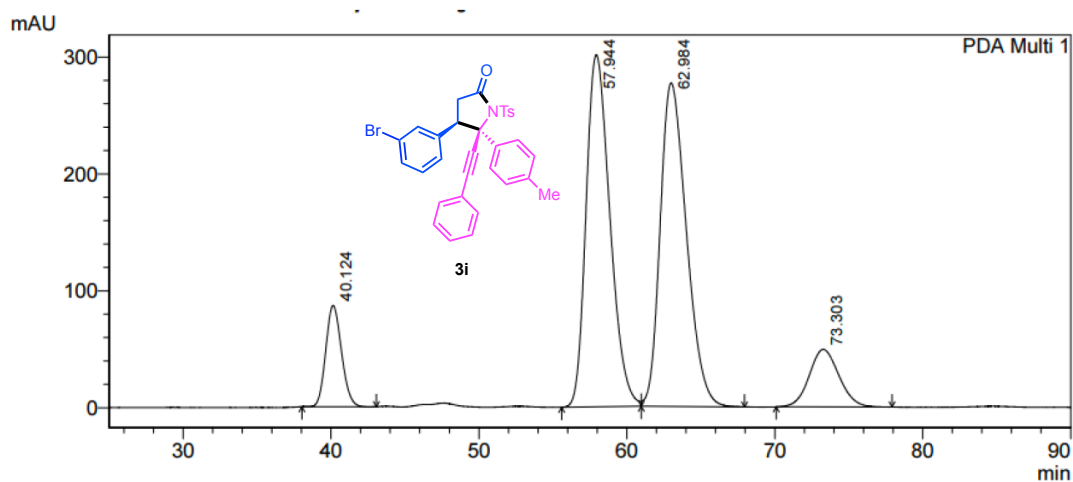
Peak#	Ret. Time	Area	Height	Area %
1	18.709	2791015	81383	8.087
2	25.300	14369834	301672	41.637
3	28.075	14575601	275687	42.234
4	32.079	2775408	47547	8.042
Total		34511858	706289	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	18.654	181335	5011	2.441
2	25.292	534152	11387	7.191
3	28.012	2684938	50728	36.145
4	31.904	4027881	67556	54.223
Total		7428305	134682	100.000

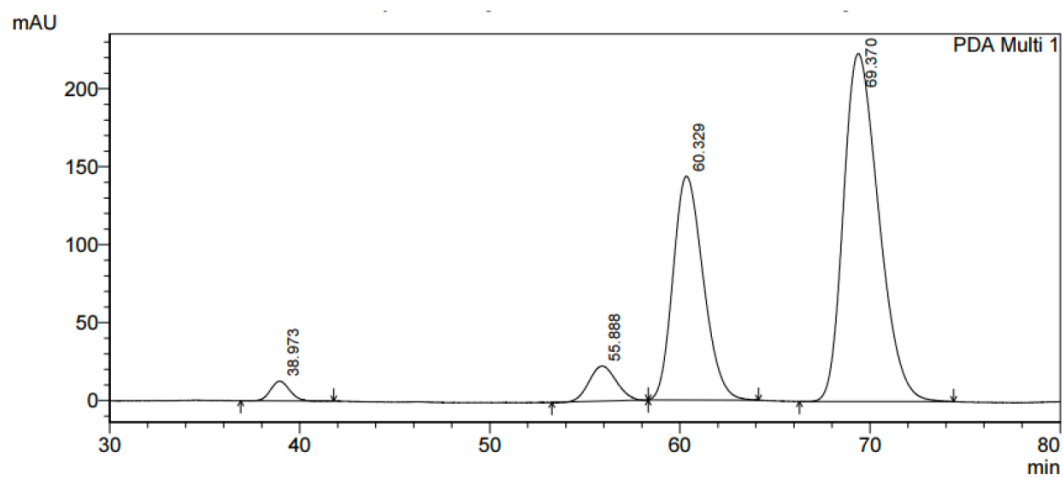


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	40.124	6405073	86568	7.898
2	57.944	33725058	301152	41.587
3	62.984	34087216	276793	42.034
4	73.303	6877019	49246	8.480
Total		81094366	713759	100.000

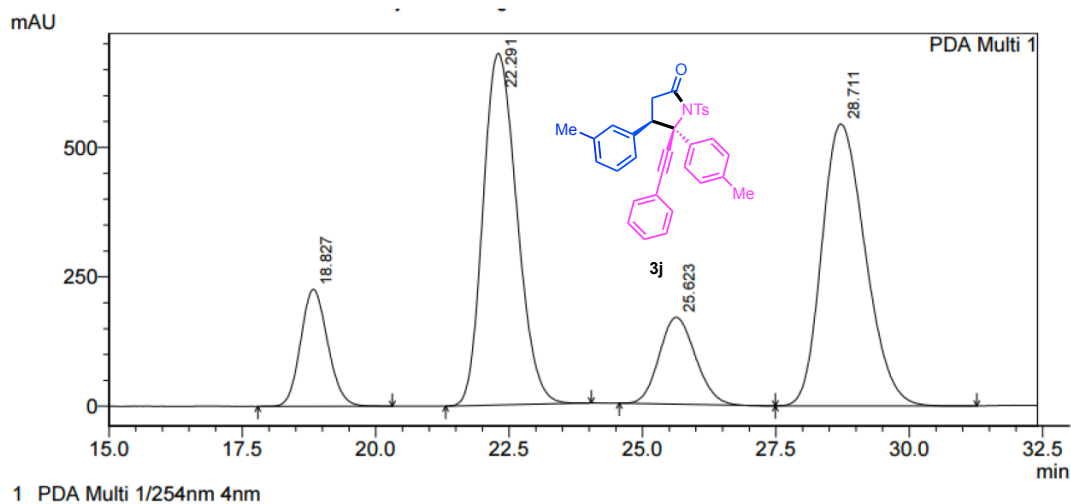


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

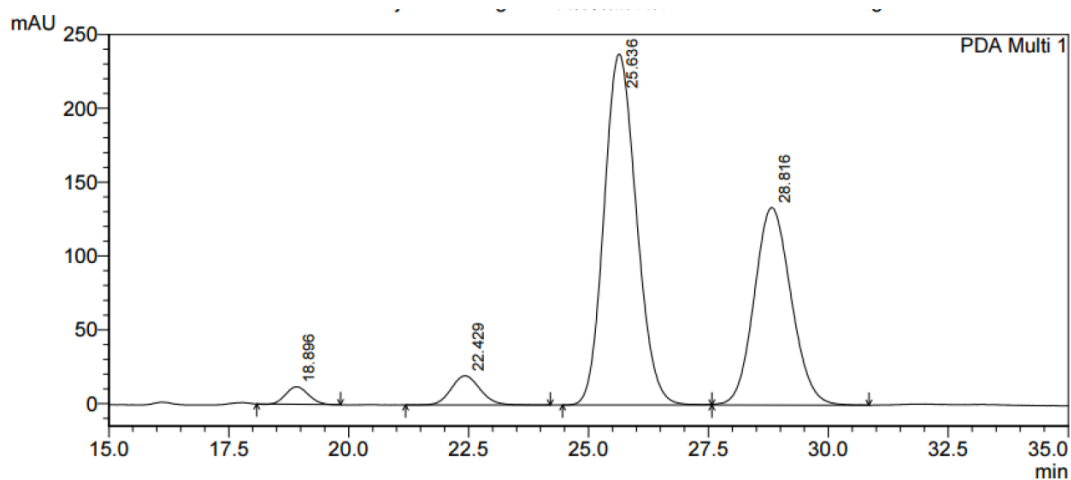
Peak#	Ret. Time	Area	Height	Area %
1	38.973	886439	12666	1.852
2	55.888	2241820	22560	4.683
3	60.329	15913340	143646	33.245
4	69.370	28825695	223273	60.220
Total		47867294	402145	100.000



PeakTable

PDA Ch1 254nm 4nm

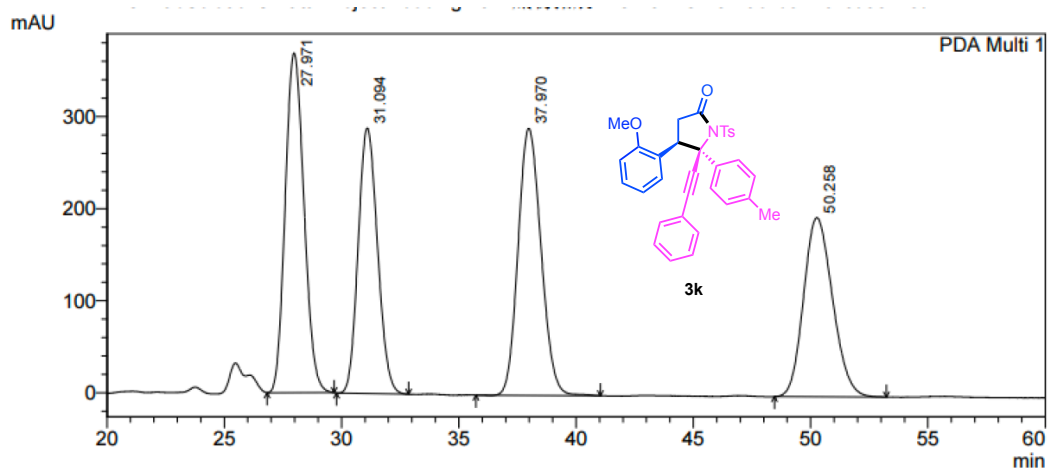
Peak#	Ret. Time	Area	Height	Area %
1	18.827	7969447	225533	10.377
2	22.291	30048322	679198	39.126
3	25.623	7942621	167758	10.342
4	28.711	30837841	544514	40.154
Total		76798231	1617003	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	18.896	390853	11882	1.999
2	22.429	831477	19739	4.252
3	25.636	11154427	237555	57.040
4	28.816	7178729	133738	36.710
Total		19555486	402914	100.000

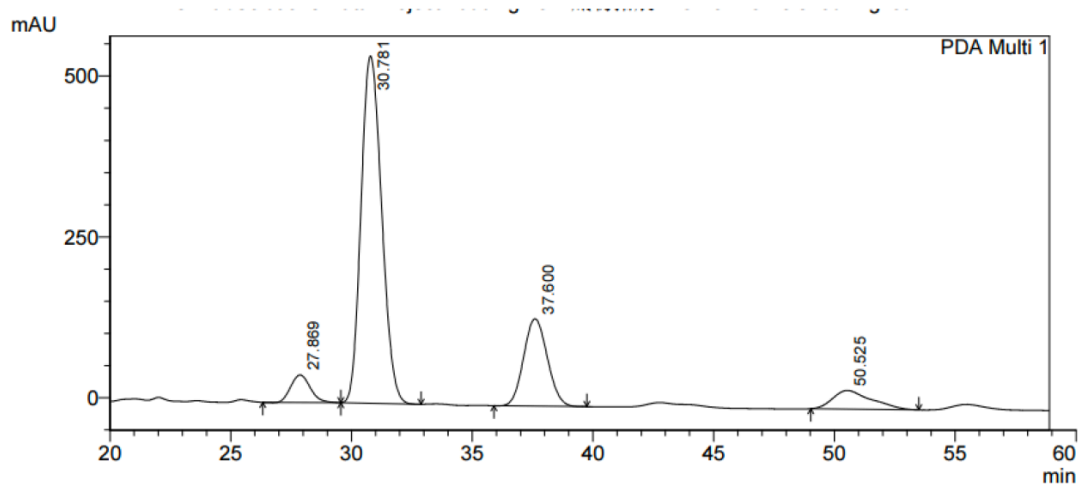


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	27.971	20546316	368948	27.917
2	31.094	16548936	288427	22.486
3	37.970	19767388	290026	26.859
4	50.258	16734907	194682	22.738
Total		73597547	1142083	100.000

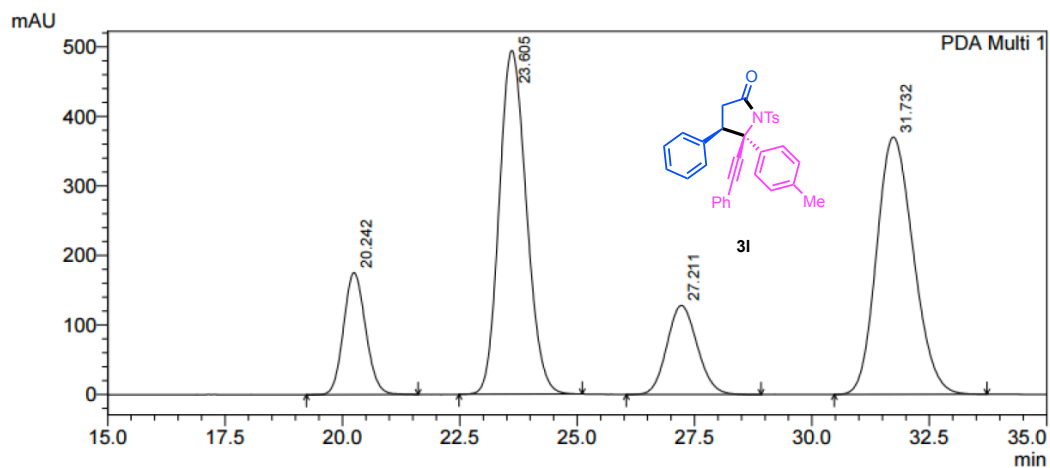


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	27.869	2403782	42937	5.115
2	30.781	32086970	539773	68.282
3	37.600	9280701	135853	19.750
4	50.525	3220328	29026	6.853
Total		46991781	747590	100.000

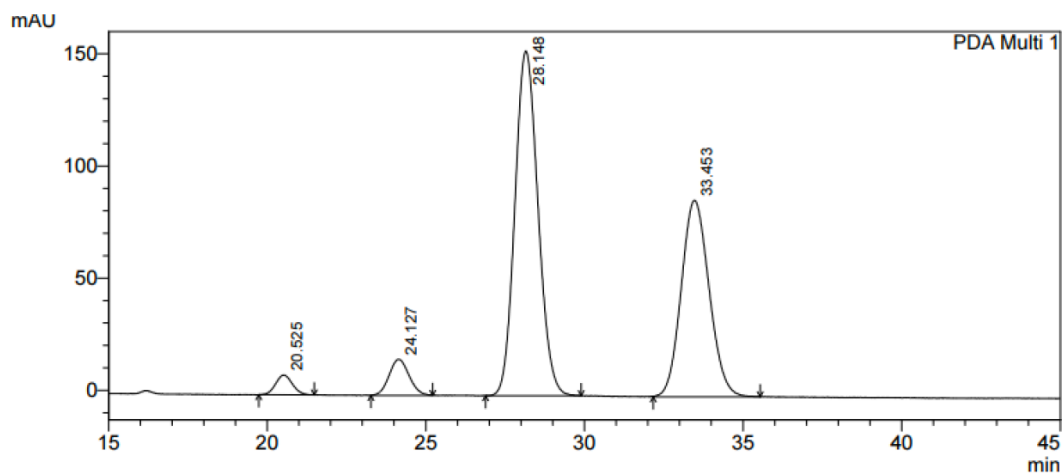


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.242	5731611	175320	11.108
2	23.605	19938313	494211	38.641
3	27.211	5756679	128017	11.157
4	31.732	20172413	370001	39.095
Total		51599015	1167548	100.000

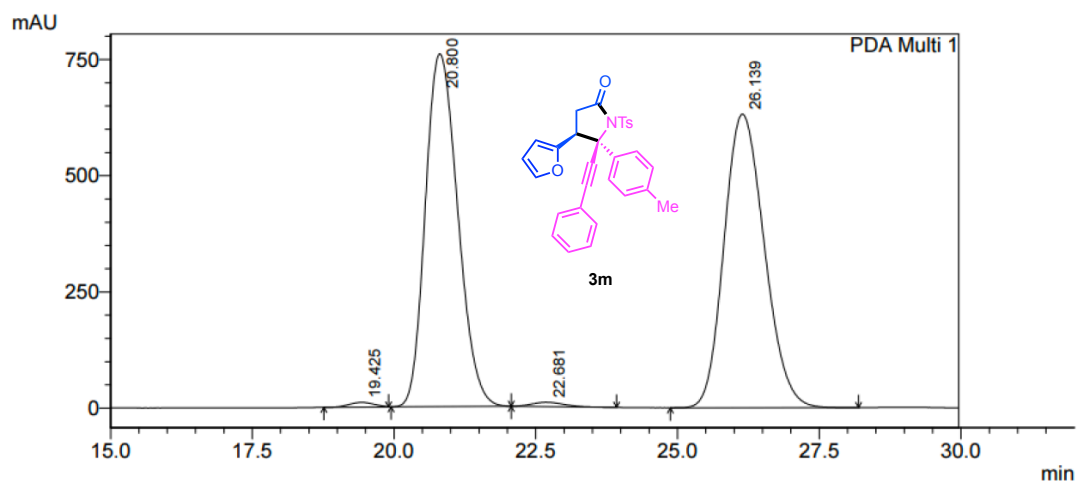


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.525	323145	8774	2.279
2	24.127	705561	16077	4.975
3	28.148	7798745	153675	54.995
4	33.453	5353415	87519	37.751
Total		14180866	266045	100.000

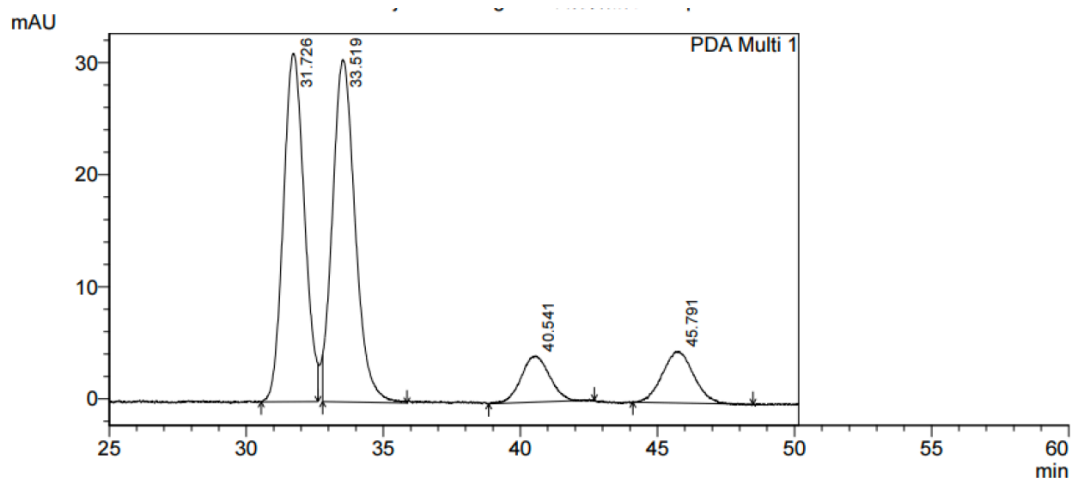


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	19.425	323082	10322	0.520
2	20.800	30170900	758955	48.576
3	22.681	371943	9498	0.599
4	26.139	31245200	632013	50.305
Total		62111125	1410788	100.000

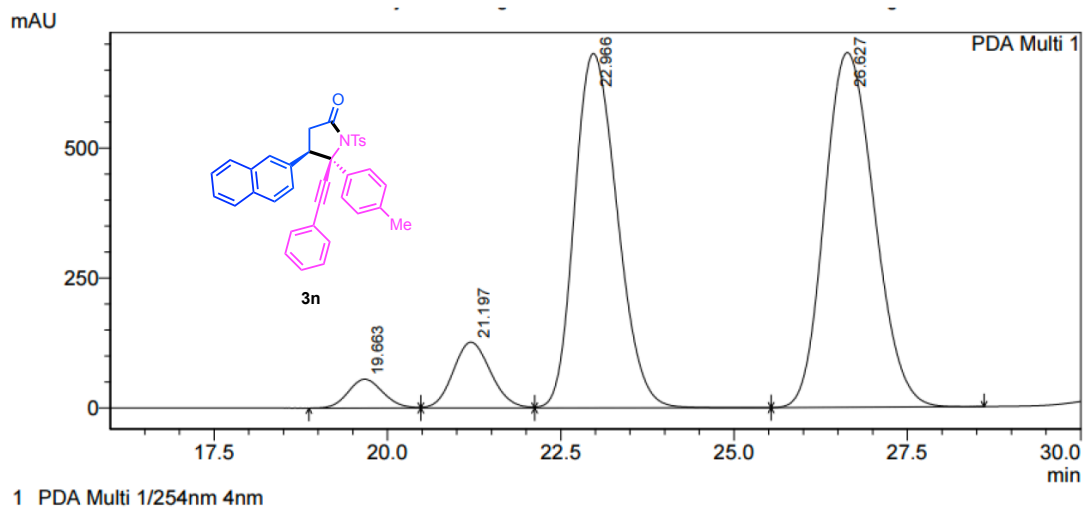


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

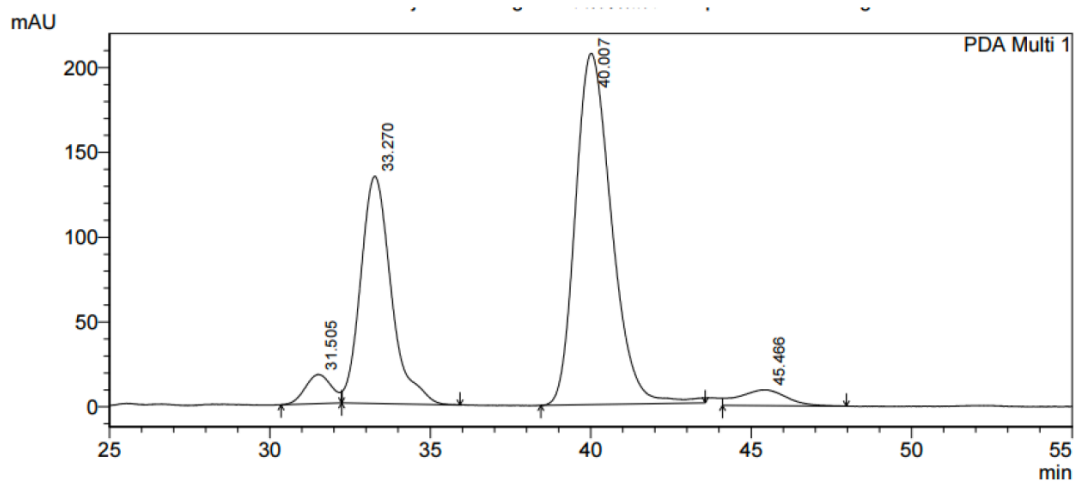
Peak#	Ret. Time	Area	Height	Area %
1	31.726	1648600	31083	40.599
2	33.519	1750280	30568	43.103
3	40.541	294862	4125	7.261
4	45.791	366953	4615	9.037
Total		4060695	70391	100.000



PeakTable

PDA Ch1 254nm 4nm

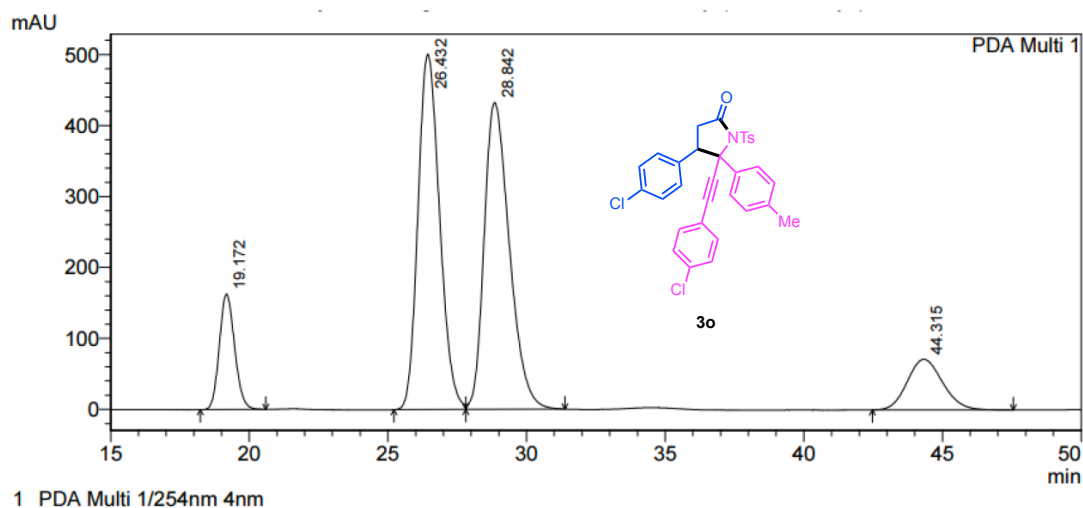
Peak#	Ret. Time	Area	Height	Area %
1	19.663	1936019	55495	2.766
2	21.197	4749467	126465	6.787
3	22.966	29193474	681516	41.716
4	26.627	34102143	682482	48.731
Total		69981104	1545959	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	31.505	987386	17281	3.648
2	33.270	8860556	133994	32.737
3	40.007	16254946	207124	60.057
4	45.466	963147	9345	3.559
Total		27066034	367745	100.000

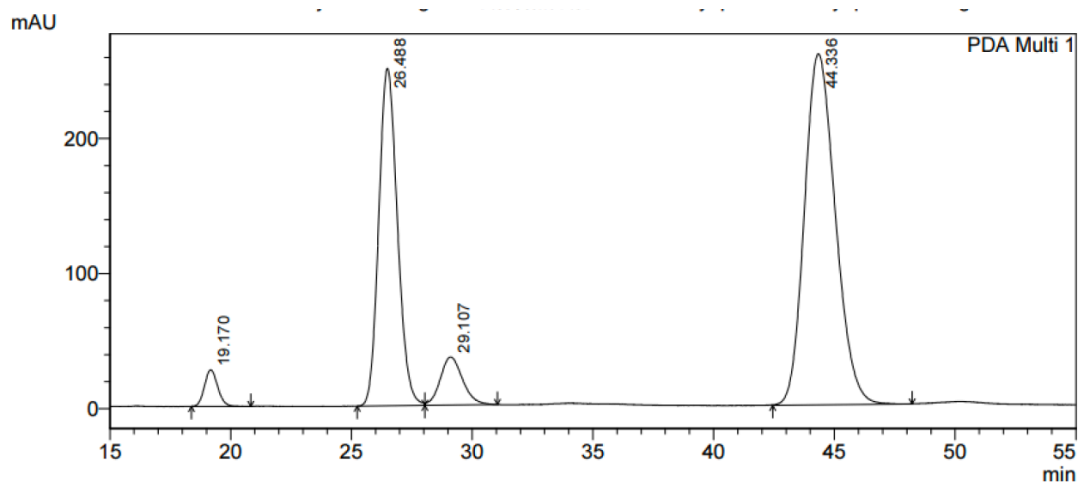


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	19.172	6257947	162867	9.319
2	26.432	27169452	500935	40.458
3	28.842	27402081	432464	40.804
4	44.315	6325935	71362	9.420
Total		67155415	1167628	100.000

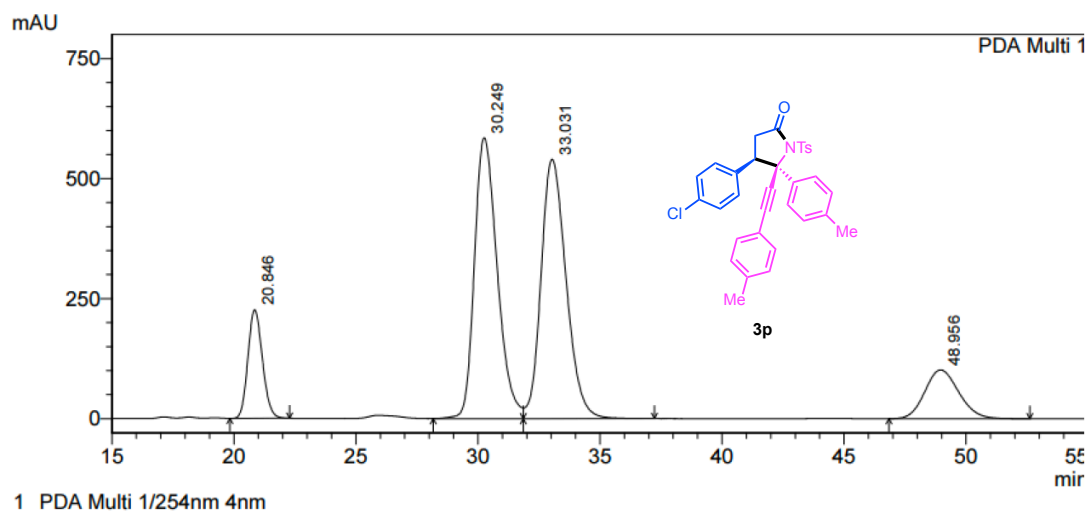


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

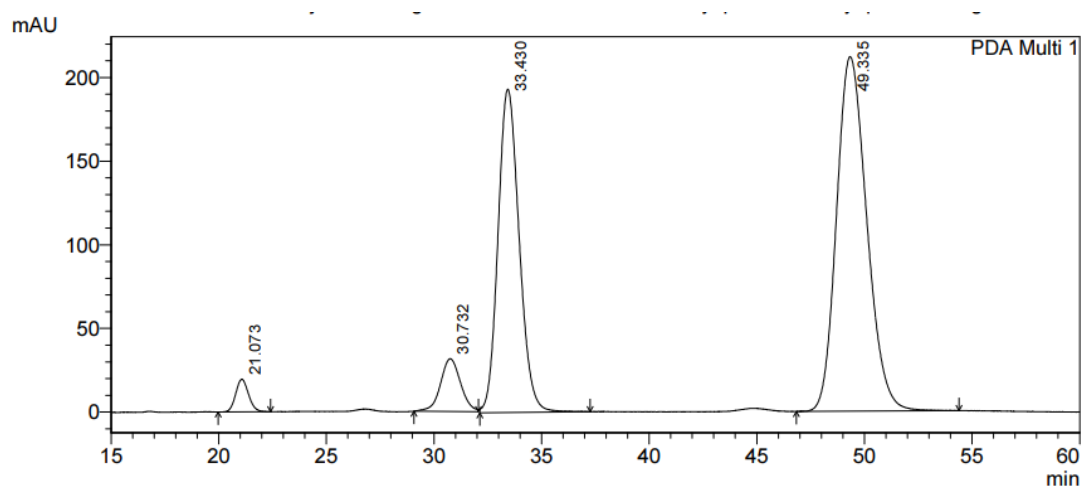
Peak#	Ret. Time	Area	Height	Area %
1	19.170	1030927	27118	2.584
2	26.488	13441463	249882	33.689
3	29.107	2287604	35558	5.734
4	44.336	23138120	259974	57.993
Total		39898113	572532	100.000



PeakTable

PDA Ch1 254nm 4nm

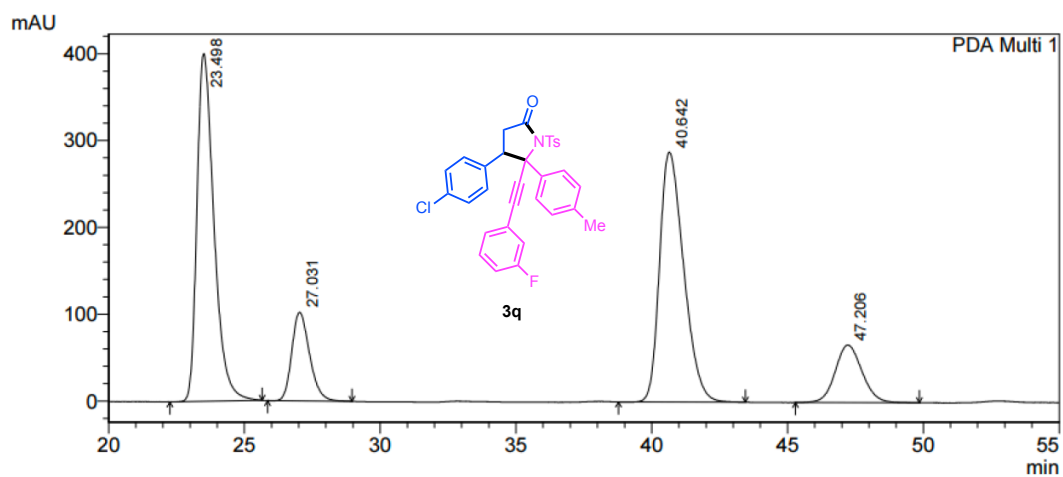
Peak#	Ret. Time	Area	Height	Area %
1	20.846	9366297	226288	9.782
2	30.249	37950045	584920	39.633
3	33.031	38569675	540249	40.280
4	48.956	9866868	101642	10.305
Total		95752885	1453100	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.073	801369	19513	2.180
2	30.732	2036555	31535	5.539
3	33.430	13216562	193345	35.948
4	49.335	20711051	211949	56.333
Total		36765538	456342	100.000

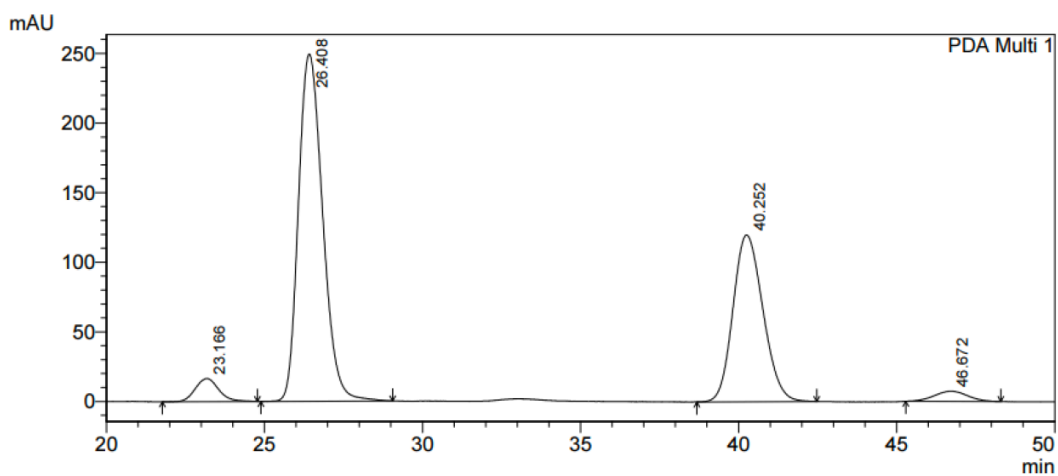


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	23.498	17425890	400430	39.226
2	27.031	4651659	102166	10.471
3	40.642	17790786	288052	40.047
4	47.206	4555961	66316	10.256
Total		44424296	856963	100.000

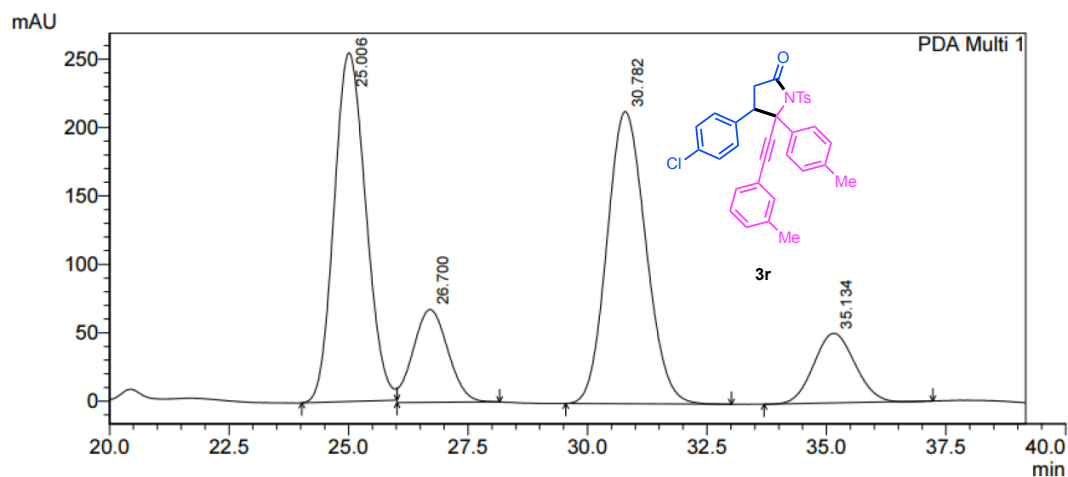


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	23.166	856246	16591	3.790
2	26.408	13285979	249417	58.806
3	40.252	7916717	119850	35.041
4	46.672	533885	7344	2.363
Total		22592827	393201	100.000

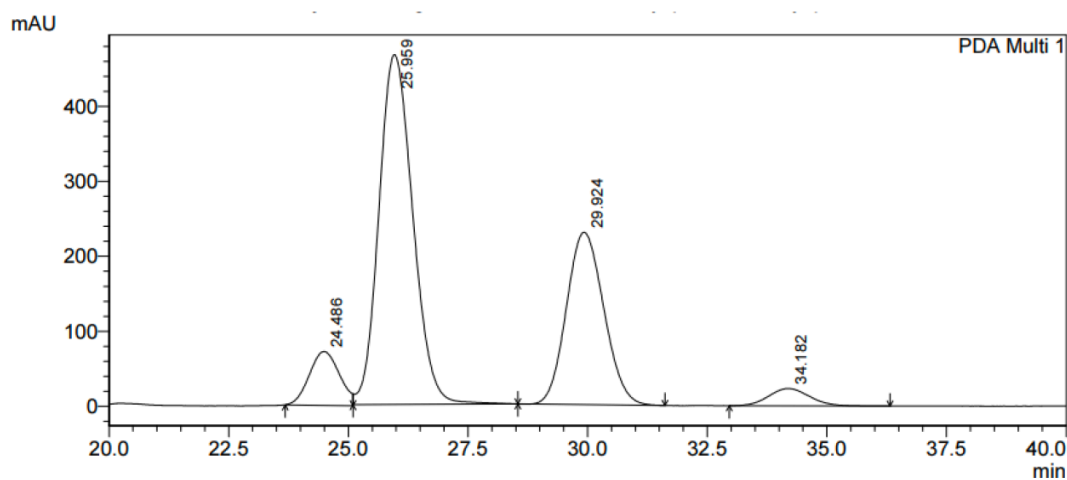


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	25.006	11767977	254855	38.857
2	26.700	3429976	67925	11.326
3	30.782	12049541	213534	39.787
4	35.134	3037840	50829	10.031
Total		30285334	587143	100.000

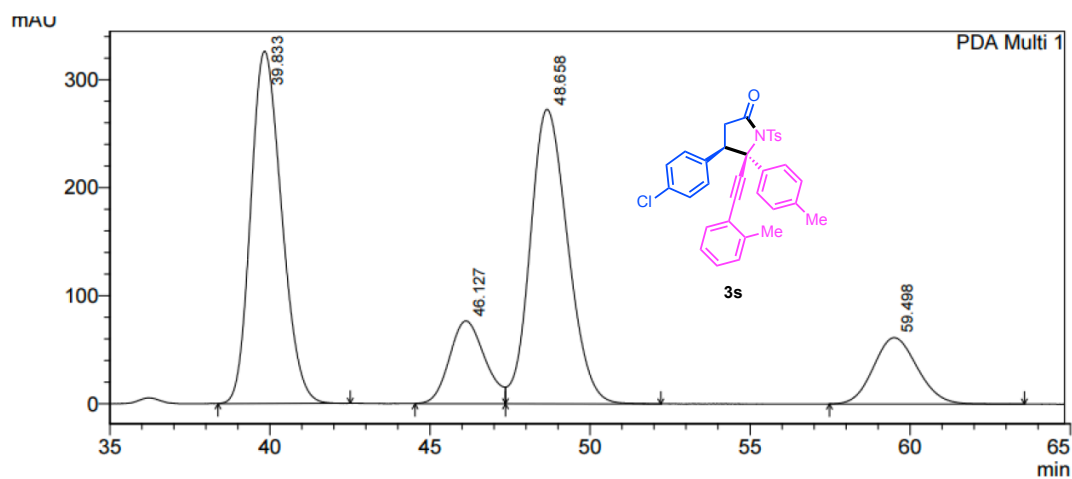


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	24.486	3130447	71843	7.822
2	25.959	23000714	466633	57.473
3	29.924	12537924	230021	31.329
4	34.182	1350835	23033	3.375
Total		40019919	791531	100.000

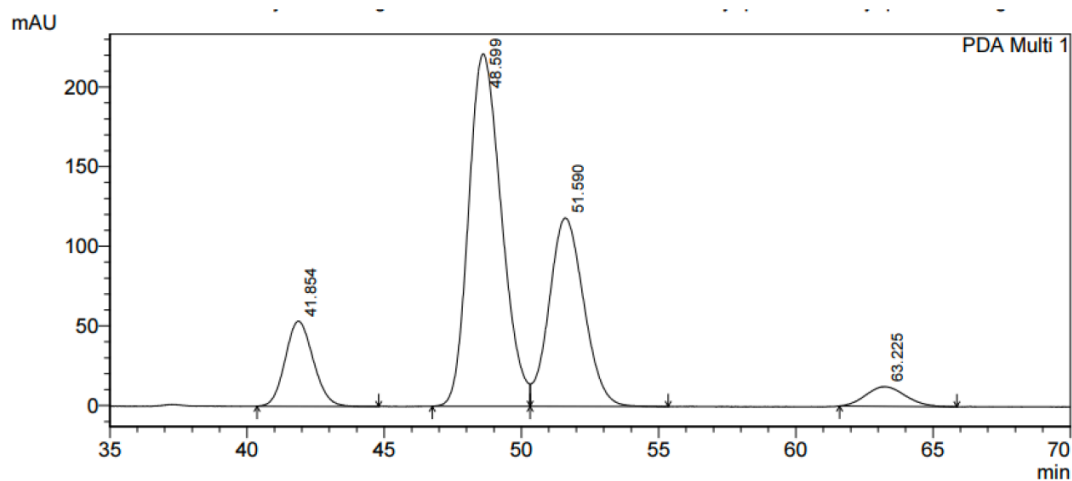


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	39.833	21921518	326307	39.154
2	46.127	5922612	76756	10.578
3	48.658	22284957	272743	39.803
4	59.498	5858652	61420	10.464
Total		55987739	737227	100.000

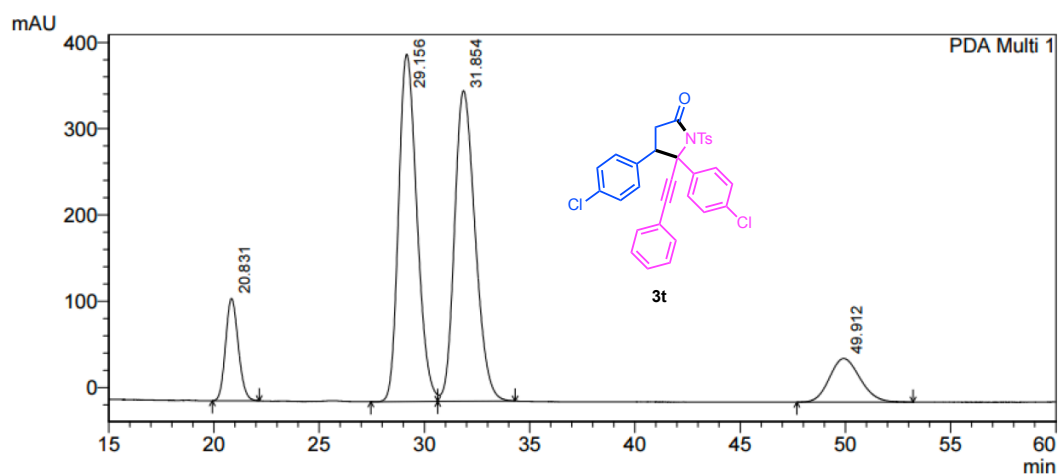


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	41.854	3794904	53447	11.210
2	48.599	18399239	221276	54.348
3	51.590	10434304	118405	30.821
4	63.225	1225822	12355	3.621
Total		33854269	405483	100.000

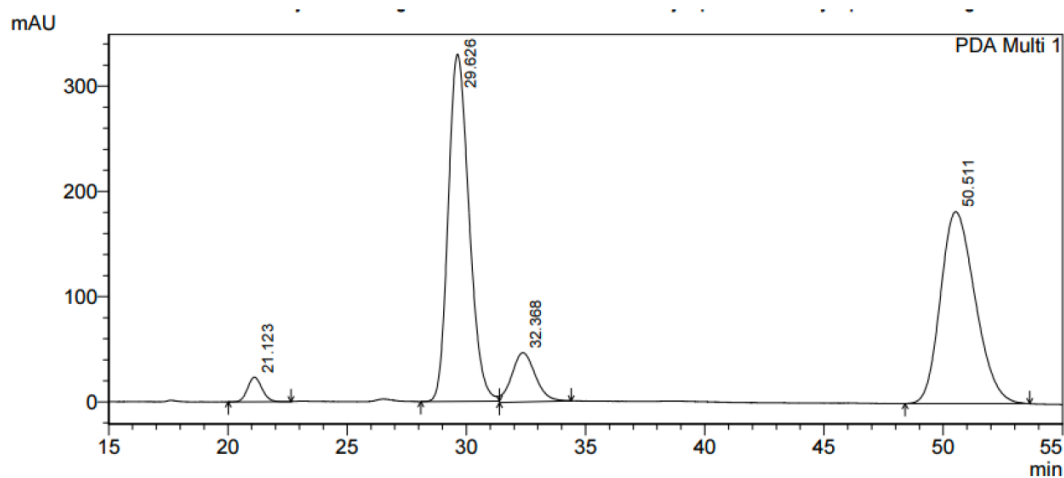


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.831	4970356	118556	8.423
2	29.156	24345322	402491	41.257
3	31.854	24574857	359970	41.646
4	49.912	5118288	50626	8.674
Total		59008823	931643	100.000

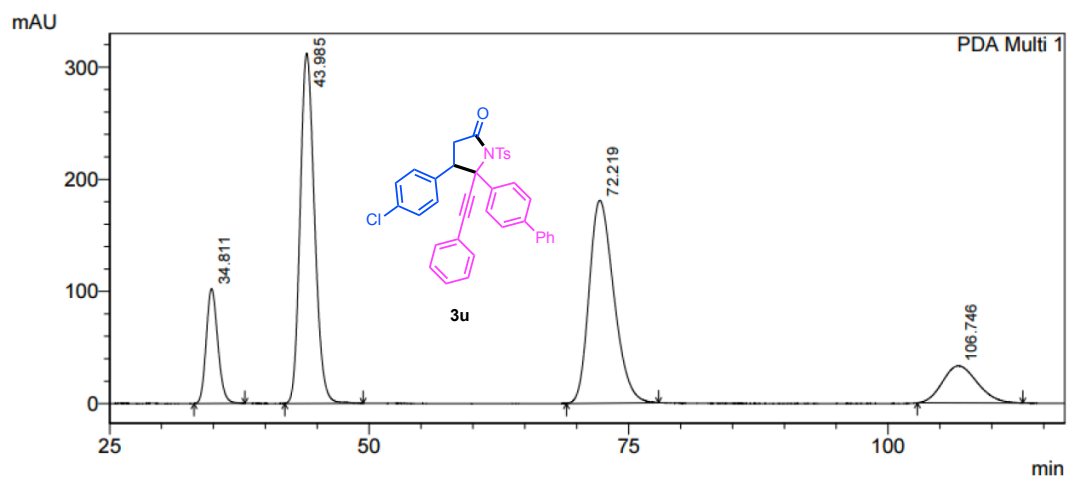


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.123	968227	23210	2.267
2	29.626	20044990	329928	46.939
3	32.368	3204155	46717	7.503
4	50.511	18486557	182271	43.290
Total		42703929	582127	100.000

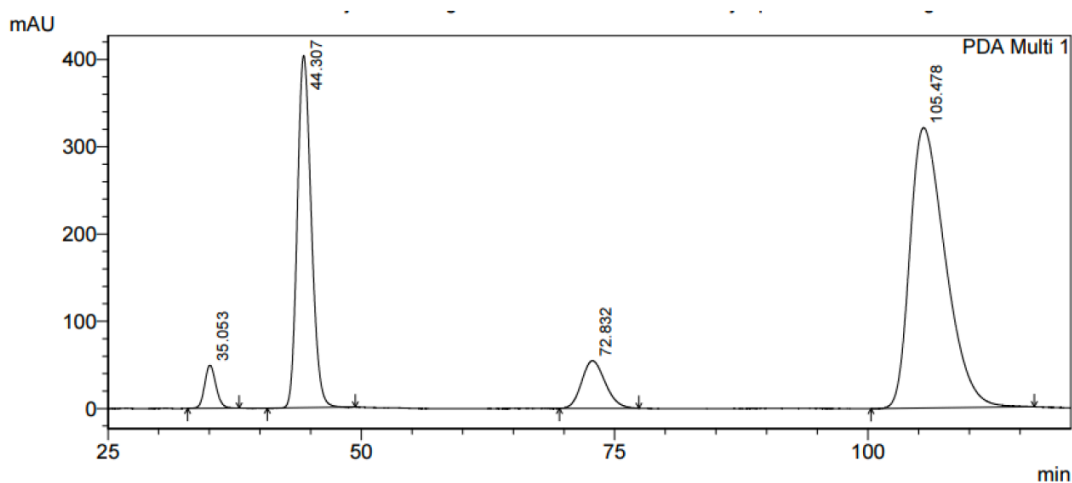


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	34.811	7960719	102489	10.518
2	43.985	30074023	312362	39.736
3	72.219	29922073	180889	39.535
4	106.746	7727519	33104	10.210
Total		75684334	628845	100.000

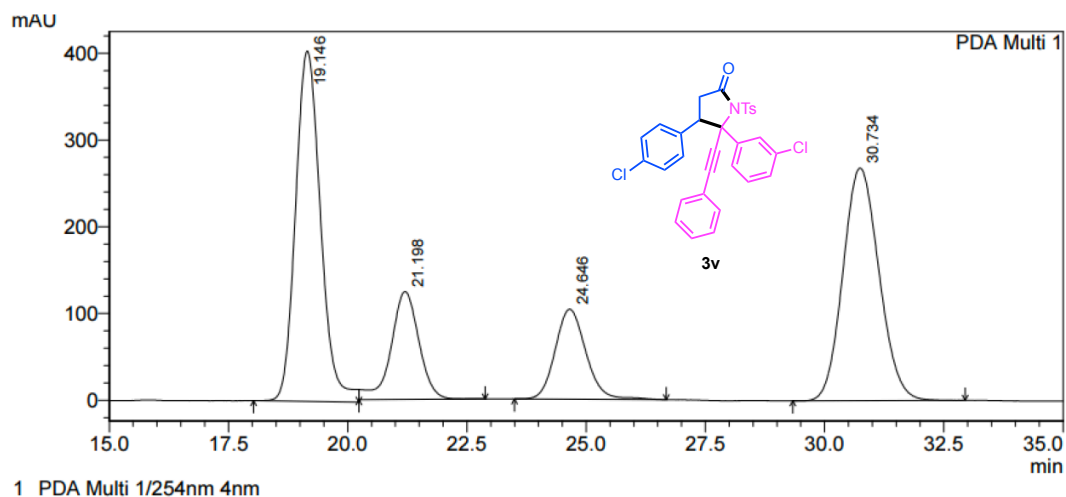


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

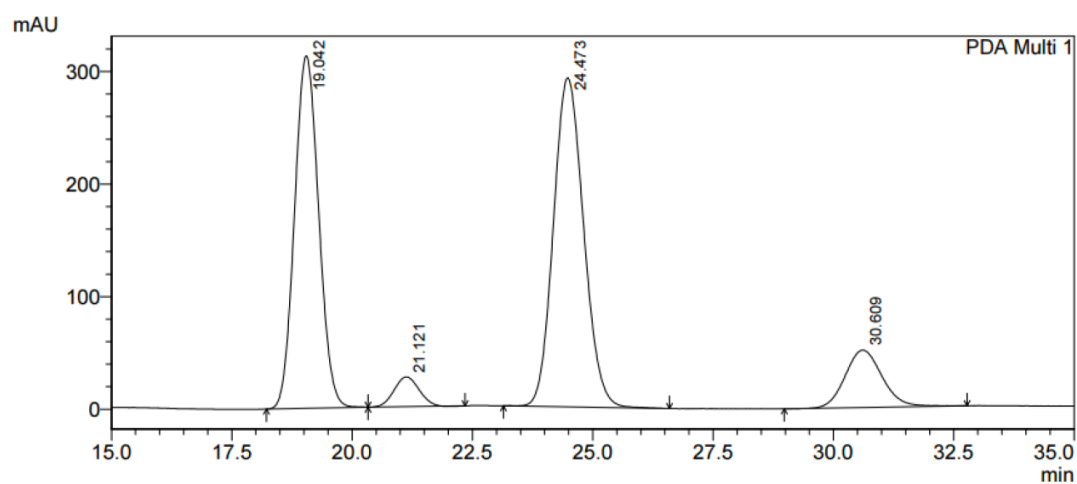
Peak#	Ret. Time	Area	Height	Area %
1	35.053	3804391	49212	2.935
2	44.307	38640422	403654	29.811
3	72.832	8813344	54504	6.800
4	105.478	78358908	321426	60.454
Total		129617064	828796	100.000



PeakTable

PDA Ch1 254nm 4nm

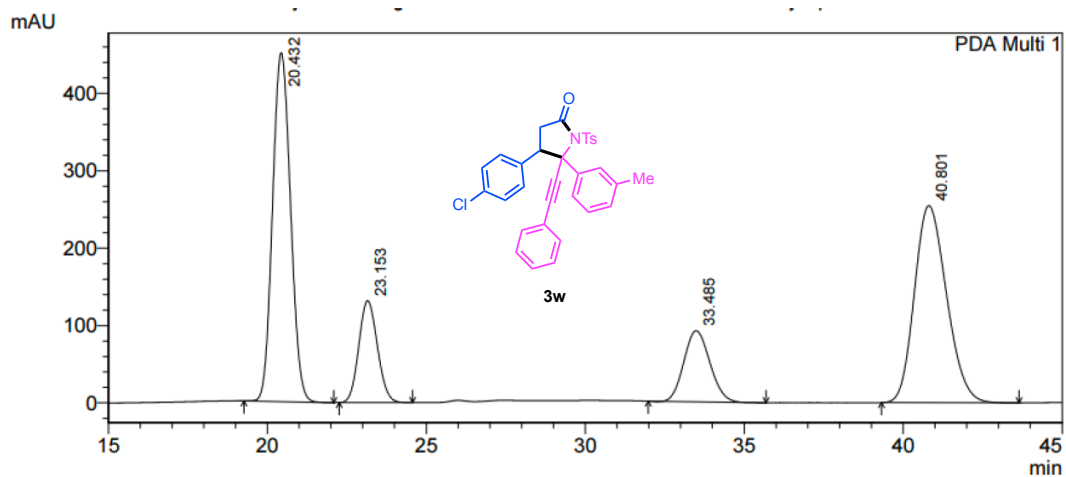
Peak#	Ret. Time	Area	Height	Area %
1	19.146	14759829	403882	38.172
2	21.198	5096782	124398	13.181
3	24.646	4662709	103809	12.059
4	30.734	14147621	268256	36.588
Total		38666941	900345	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	19.042	10934319	313084	39.958
2	21.121	948461	26421	3.466
3	24.473	12757387	292219	46.620
4	30.609	2724262	51025	9.955
Total		27364430	682749	100.000

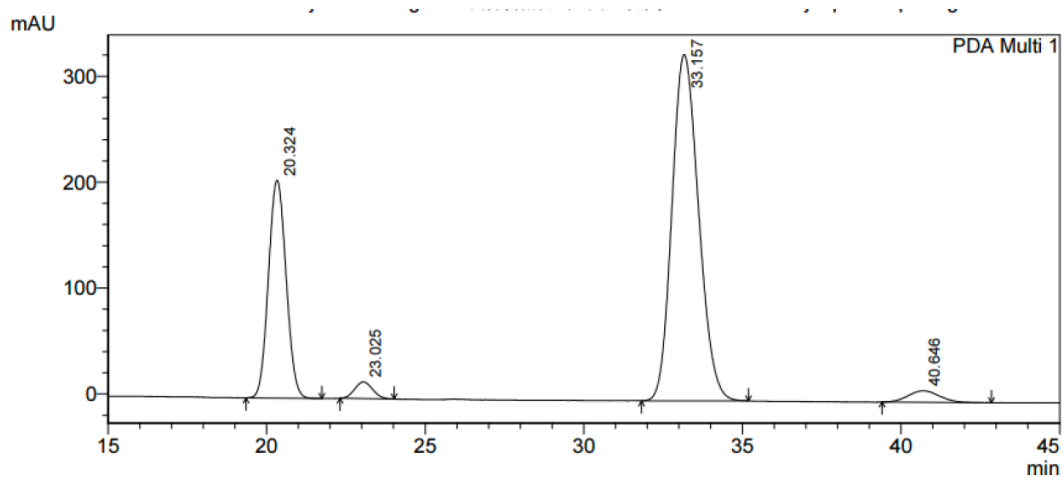


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.432	17718247	450681	38.335
2	23.153	5366635	131634	11.611
3	33.485	5227121	91876	11.309
4	40.801	17906939	254601	38.744
Total		46218941	928792	100.000

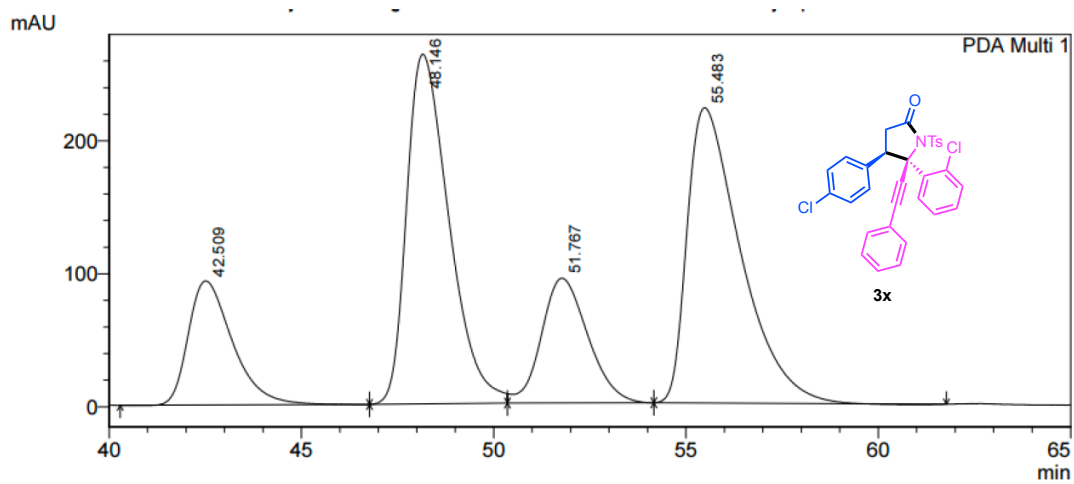


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.324	7972385	205866	28.016
2	23.025	627105	15728	2.204
3	33.157	19107371	327069	67.145
4	40.646	749997	10898	2.636
Total		28456858	559562	100.000

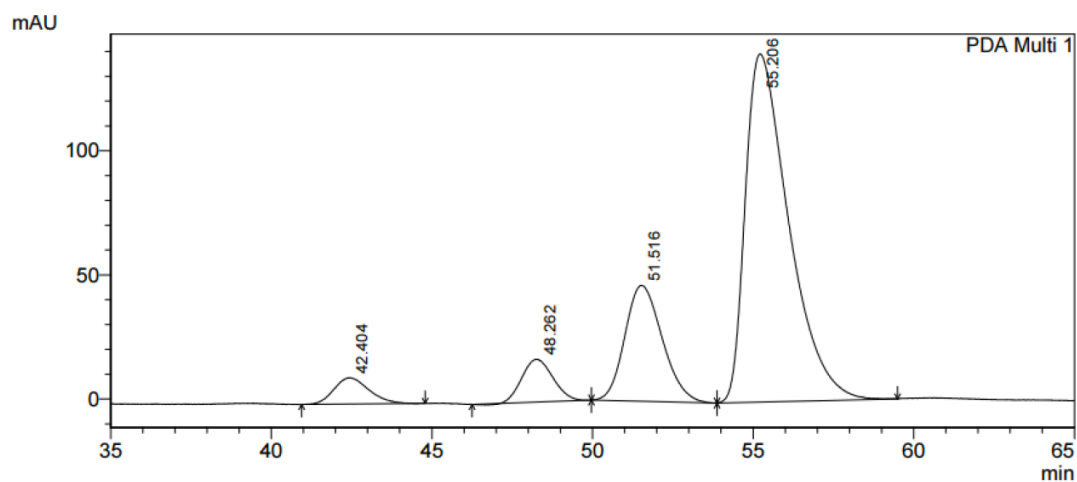


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	42.509	7441544	93353	13.084
2	48.146	20086591	263054	35.316
3	51.767	7889585	93828	13.872
4	55.483	21458270	222102	37.728
Total		56875989	672337	100.000

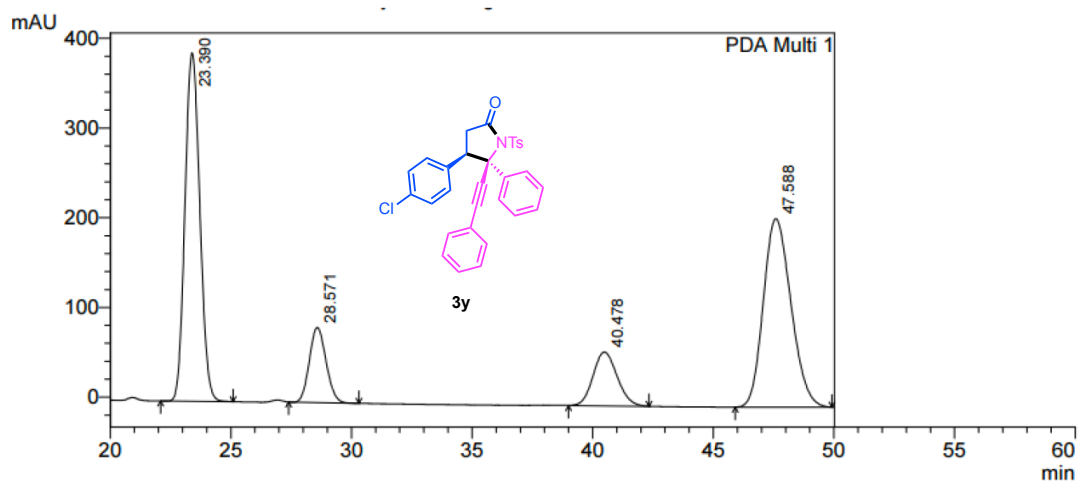


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	42.404	801837	10566	4.240
2	48.262	1150466	17266	6.084
3	51.516	3782965	46731	20.005
4	55.206	13174656	140218	69.671
Total		18909924	214782	100.000

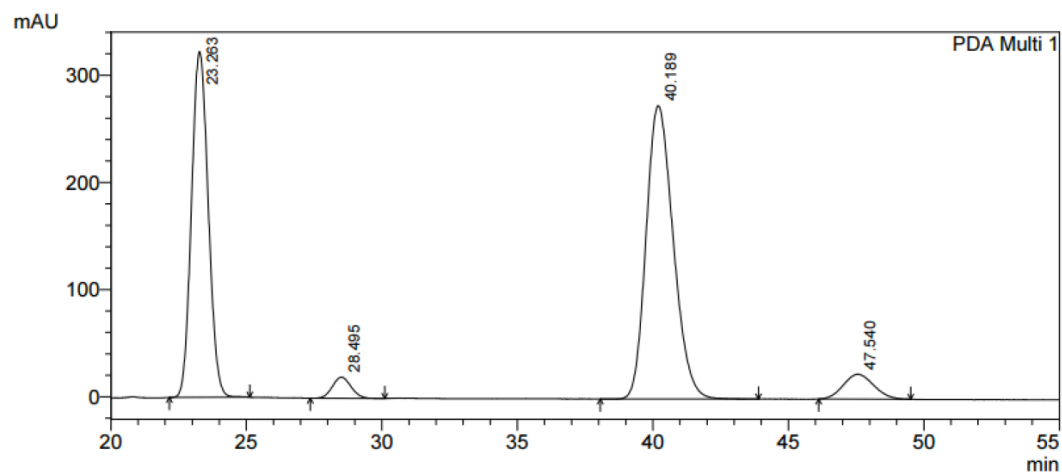


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	23.390	16618424	388305	39.926
2	28.571	4046308	83866	9.721
3	40.478	4172945	59968	10.026
4	47.588	16785320	210186	40.327
Total		41622997	742326	100.000

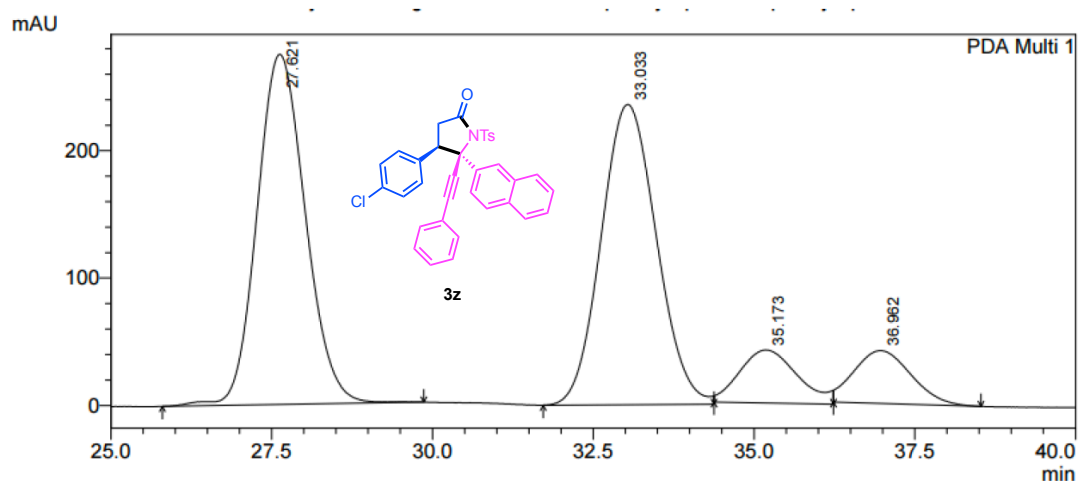


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	23.263	13885685	322653	38.875
2	28.495	941671	19719	2.636
3	40.189	19072017	273838	53.395
4	47.540	1819147	23239	5.093
Total		35718520	639449	100.000

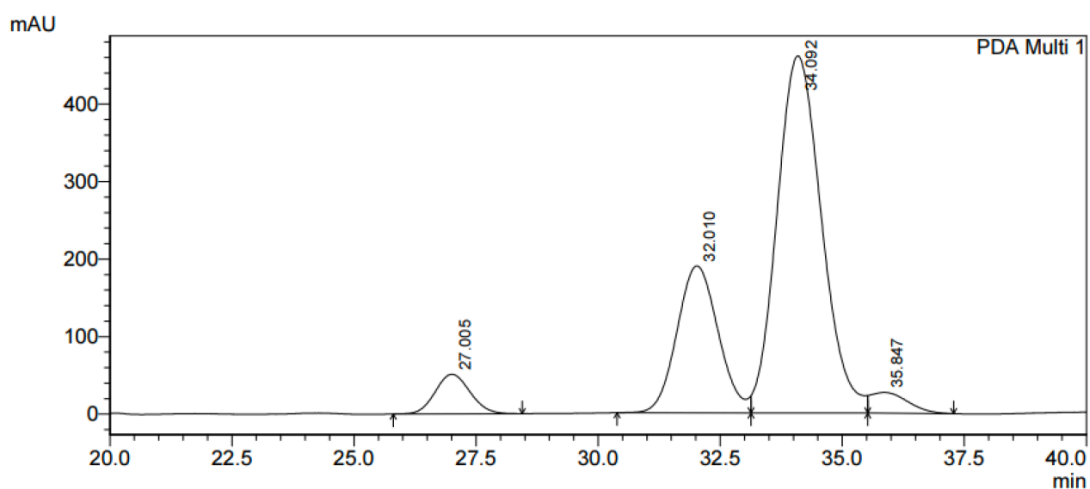


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	27.621	14344156	274843	42.673
2	33.033	14103919	235674	41.958
3	35.173	2603230	41608	7.744
4	36.962	2563156	41368	7.625
Total		33614461	593494	100.000

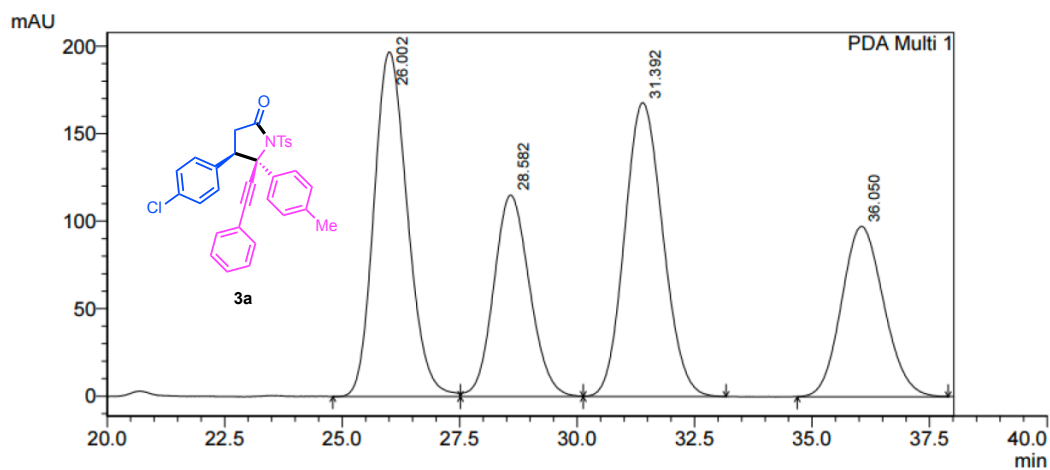


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	27.005	2534587	51116	5.718
2	32.010	11185077	189483	25.232
3	34.092	29197648	460609	65.866
4	35.847	1411557	26768	3.184
Total		44328870	727976	100.000

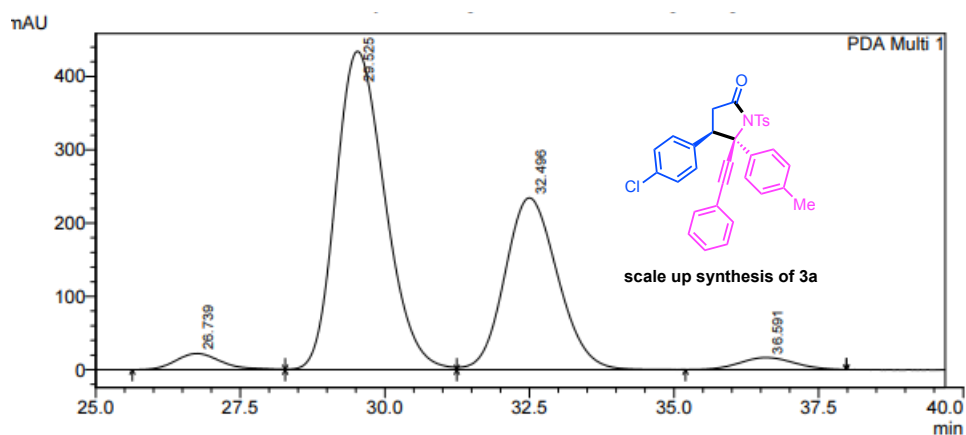


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	26.002	9748073	197021	30.967
2	28.582	6112647	115183	19.419
3	31.392	9527359	168009	30.266
4	36.050	6090325	97351	19.348
Total		31478404	577564	100.000

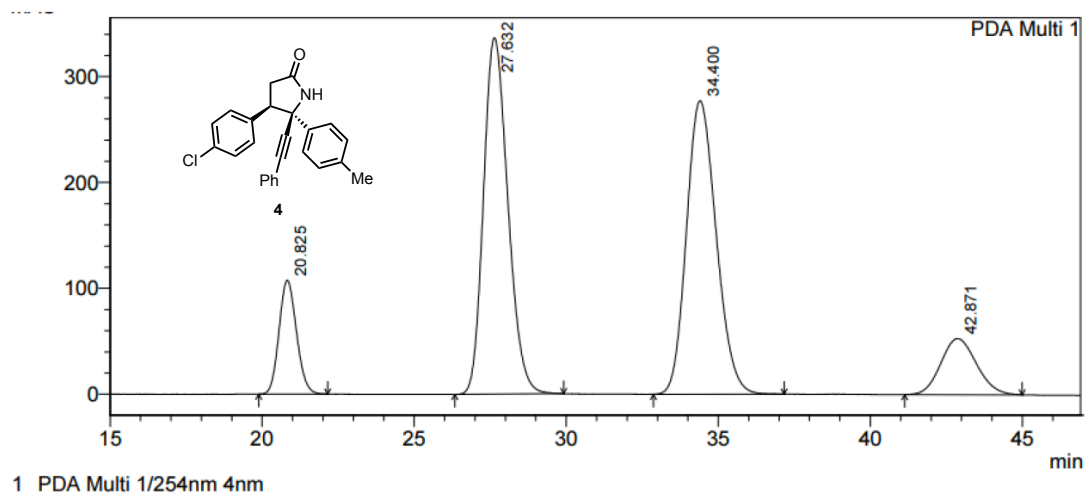


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

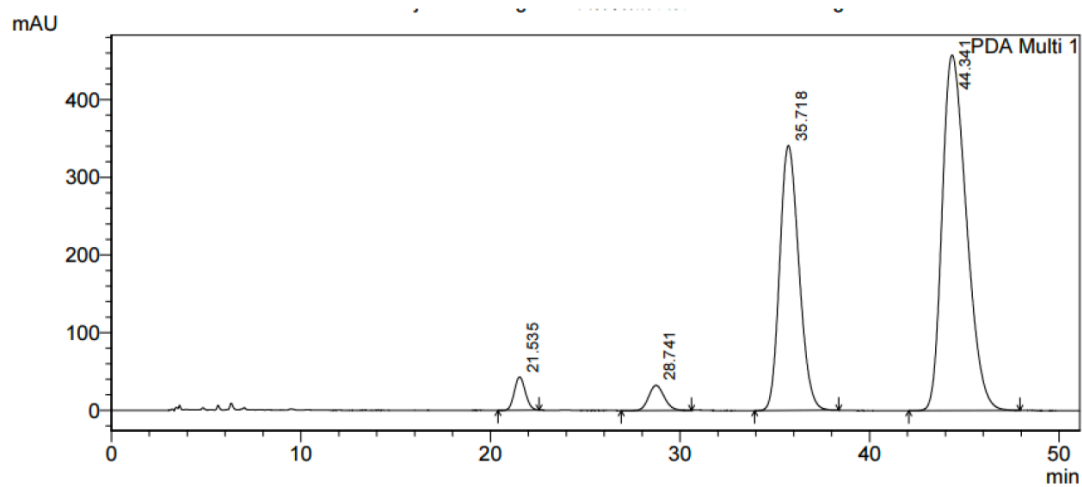
Peak#	Ret. Time	Area	Height	Area %
1	26.739	1214786	22005	2.844
2	29.525	25546729	434205	59.816
3	32.496	14865966	234260	34.808
4	36.591	1081527	16462	2.532
Total		42709008	706933	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	20.825	4312862	107595	9.305
2	27.632	18781818	336669	40.523
3	34.400	18913510	277285	40.807
4	42.871	4340660	53037	9.365
Total		46348850	774586	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.535	1739721	42911	2.547
2	28.741	1816022	32303	2.658
3	35.718	24048915	341186	35.201
4	44.341	40713411	457640	59.594
Total		68318069	874041	100.000

