Supporting Information

Diastereo-, and enantioselective copper-catalyzed decarboxylative ring-opening [3+2] annulation of tertiary propargylic carbamates through regioselective α-attack of γ-butenolides

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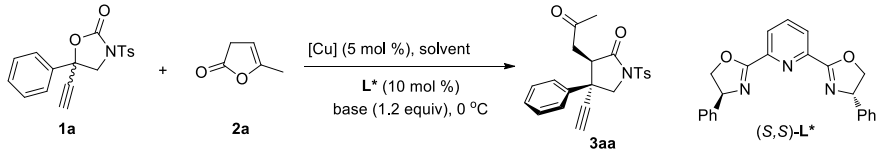
I. General Information

All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel 200-300. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 101 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Enantiomeric ratios were determined by chiral HPLC with *n*-hexane and *i*-PrOH as solvents. γ-Substituted butenolides **2b**-**2k** were prepared according to the known methods.[1]

II. Details for Condition Optimization

Table S1. Optimization of Reaction Conditions[a]

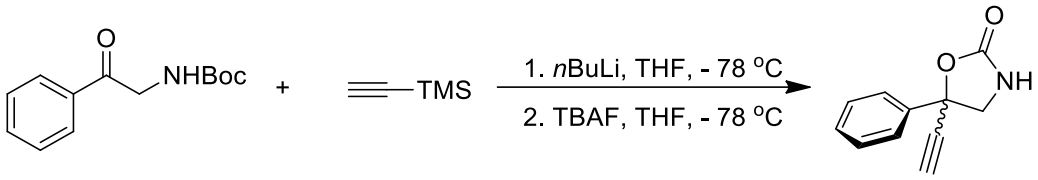


Entry	[Cu]	Solvent (mL)	Base	Yield (%)[b]	*ee* (%)[c]	dr[d]
1	$Cu(OAc)\cdot H_2O$	MeOH (3)	*i*Pr_2NEt	55	91	10:1
2	$CuOTf\cdot 1/2C_6H_6$	MeOH (3)	*i*Pr_2NEt	64	67	14:1
3	CuI	MeOH (3)	*i*Pr_2NEt	45	93	20:1
4	$Cu(MeCN)_4BF_4$	MeOH (3)	*i*Pr_2NEt	51	94	15:1
5	***Cu(OTf)$_2$***	MeOH (3)	*i*Pr_2NEt	65	94	10:1
6	$Cu(MeCN)_4PF_6$	MeOH (3)	*i*Pr_2NEt	33	87.5	8:1
7 [e]	$Cu(OTf)_2$	DCM (3)	*i*Pr_2NEt	5 <	-	-
8[e]	$Cu(OTf)_2$	DCM (2.9)/MeOH (0.1)	*i*Pr_2NEt	5 <	-	-
9	$Cu(OTf)_2$	DCM (2)/MeOH (1)	*i*Pr_2NEt	25	95	12:1
10	$Cu(OTf)_2$	***DCM (1)/MeOH (2)***	*i*Pr_2NEt	79	95	15:1
11[e]	$Cu(OTf)_2$	THF	*i*Pr_2NEt	5 <	-	-
12	$Cu(OTf)_2$	THF (1)/MeOH (2)	*i*Pr_2NEt	65	95	15:1
13[f]	$Cu(OTf)_2$	Toluene	*i*Pr_2NEt	5 <	-	-
14	$Cu(OTf)_2$	DCM (1)/MeOH (2)	Et_3N	50	96	8:1
15	$Cu(OTf)_2$	DCM (1)/MeOH (2)	*i*$PrNMe_2$	26	-	-
16[f]	$Cu(OTf)_2$	DCM (1)/MeOH (2)	DBU	5 <	-	-
17[f]	$Cu(OTf)_2$	DCM (1)/MeOH (2)	DABCO	5 <	-	-
18[f]	$Cu(OTf)_2$	DCM (1)/MeOH (2)	Cs_2CO_3	5 <	-	-
19[f]	$Cu(OTf)_2$	DCM (1)/MeOH (2)		5 <	-	-

20	$Cu(OTf)_2$	DCM (1)/MeOH (2)	$n Pr_3N$	52	94	12:1
21	$Cu(OTf)_2$	DCM (1)/MeOH (2)	***Cy_2NMe***	85	96	14:1
22	$Cu(OTf)_2$	DCM (1)/MeOH (2)	$CyNMe_2$	30	88	5:1

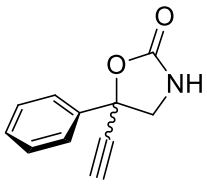
[a] **1a** (68.2 mg, 0.2 mmol), **2a** (58.9 mg, 0.6 mmol), [Cu] (5 mol %), **L*** (10 mol %), and base (0.24 mmol), were stirred in solvent (3 mL) at 0 °C for 12 h. [b] Isolated yield of the target product and its diastereoisomer. [c] Enantiomeric excess was determined by chiral HPLC analysis. [d] Diastereoselectivity was determined by ^{1}H NMR. [e] Enthynyl oxazolidinone was recovered in more than 80% yield. [f] Enthynyl oxazolidinone was decomposed and no major product was obtained.

III. General Procedure for Preparation of Enthynyl Oxazolidinones



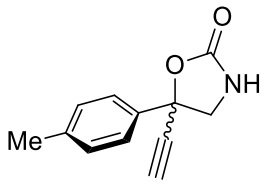
Enthynyl oxazolidinones were preopared according to the methods reported in the literature with some modifications.[2] Trimethylsilylacetylene (2.95 g, 30 mmol) was dissolved into 50 mL THF and cooled to 0 °C, then *n*-BuLi (30 mmol, 2.5 M in Hexane, 12 mL) was added and stirred at this temperature for 1 h under argon atmosphere. The mixture was then cooled to -78 °C, and *tert*-butyl (2-oxo-2-phenylethyl) carbamate (10 mmol) in 10 mL THF was added. The mixture was allowed to stir at this temperature for further 10 min before warmed to room temperature and stirred overnight. A saturated solution of NH_4Cl (20 mL) was added and the aqueous phase was extracted with EtOAc (3×20 mL). The combined extracts were dried by Na_2SO_4 and the solvent removed under vaccum. The crude product was used next step directly without further purification.

The crude product was dissolved in THF (30 mL) and cooled to -78 °C. TBAF (1.0 M in THF, 10 mL) was added and stirred 1 h at this temperature before quenched with saturated solution of NH_4Cl (10 mL). The mixture was extracted with EtOAc (3×20 mL), and the organic mixture was dried by Na_2SO_4 and concentrated under reduced pressure. The concentrate was purified by silica gel flash chromatography (PE/EtOAc = 2:1) to give the product as white solid.



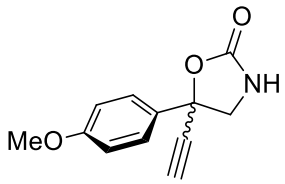
5-Ethynyl-5-phenyloxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 2:1, 1.40 g, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.44 – 7.37 (m, 3H), 6.54 – 6.25 (m, 1H), 4.08 (d, J = 8.8 Hz, 1H), 3.80 (d, J = 8.8 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 139.1, 129.1, 128.8, 124.9, 81.9, 78.3, 76.6, 55.6. HRMS calc. for $C_{11}H_9NO_2$ $[M+H]^+$: 188.0706, found: 188.0704.



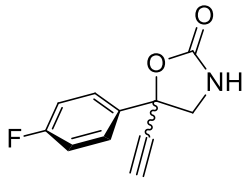
5-Ethynyl-5-(*p*-tolyl)oxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 2:1, 1.20 g, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 6.3 Hz, 2H), 7.11 (d, J = 6.3 Hz, 2H), 6.72 (brs, 1H), 3.96 (d, J = 8.1 Hz, 1H), 3.69 (d, J = 8.2 Hz, 1H), 2.75 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 139.1, 136.2, 129.4, 124.9, 122.9, 82.0, 78.3, 76.4, 55.6, 21.1. HRMS calc. for $C_{12}H_{11}NO_2$ $[M+H]^+$: 202.0863, found: 202.0860.



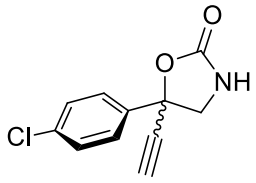
5-Ethynyl-5-(4-methoxyphenyl)oxazolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 1:1, 1.17g, yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 6.45 (brs, 1H), 3.90 (d, J = 8.6 Hz, 1H), 3.68 – 3.65 (m, 4H), 2.73 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.6, 131.0, 126.6, 114.0, 82.0, 78.3, 76.5, 55.6, 55.3. HRMS calc. for $C_{12}H_{11}NO_3$ $[M+H]^+$: 218.0812, found: 218.0809.



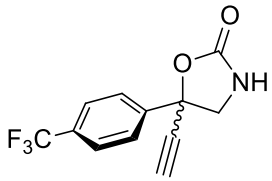
5-Ethynyl-5-(4-fluorophenyl)oxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 2:1, 1.46 g, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.8, 5.3 Hz, 2H), 7.09 (t, J = 8.4 Hz, 2H), 6.86 (brs, 1H), 4.07 (d, J = 8.9 Hz, 1H), 3.77 (d, J = 9.0 Hz, 1H), 2.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 248.8 Hz), 158.6, 134.9 (d, $J_{C\text{-}F}$ = 3.1 Hz), 127.1 (d, $J_{C\text{-}F}$ = 8.5 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.0 Hz), 81.6, 77.8, 76.9, 55.6. HRMS calc. for $C_{11}H_8FNO_2$ $[M+H]^+$: 206.0612, found: 206.0609.



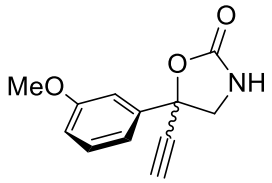
5-(4-Chlorophenyl)-5-ethynyloxazolidin-2-one

Yellow solid, purified by silica gel chromatography using PE/EA 2:1, 1.95 g, yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.46 (brs, 1H), 4.07 (d, J = 8.8 Hz, 1H), 3.75 (d, J = 8.9 Hz, 1H), 2.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 137.7, 135.2, 129.0, 126.5, 81.4, 77.7, 77.0, 55.5. HRMS calc. for $C_{11}H_8ClNO_2$ $[M+H]^+$: 222.0316, found: 222.0315..



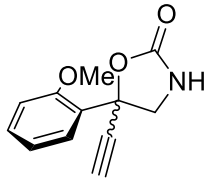
5-Ethynyl-5-(4-(trifluoromethyl)phenyl)oxazolidin-2-one

Brown oil, purified by silica gel chromatography using PE/EA 2:1, 2,17 g, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 6.96 (brs, 1H), 4.11 (d, J = 9.1 Hz, 1H), 3.76 (d, J = 9.1 Hz, 1H), 2.90 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.1, 131.30 (q, $J_{C\text{-}F}$ = 32.7 Hz), 125.84 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.4, 123.7 (q, $J_{C\text{-}F}$ = 272.3 Hz), 81.2, 77.6, 77.2, 55.4. HRMS calc. for $C_{12}H_8F_3NO_2$ $[M+H]^+$: 256.0580, found: 256.0575.



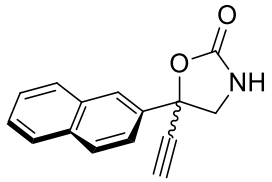
5-Ethynyl-5-(3-methoxyphenyl)oxazolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 1:1, 1.37 g, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 8.0 Hz, 1H), 7.15 – 7.12 (m, 2H), 6.91 (dd, J = 8.1, 2.1 Hz, 1H), 6.58 (brs, 1H), 4.06 (d, J = 8.8 Hz, 1H), 3.82 (s, 3H), 3.78 (d, J = 8.9 Hz, 1H), 2.85 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 158.5, 140.7, 130.0, 117.0, 114.5, 110.7, 81.9, 78.1, 76.4, 55.6, 55.4. HRMS calc. for $C_{12}H_{11}NO_3$ $[M+H]^+$: 218.0812, found: 218.0809.



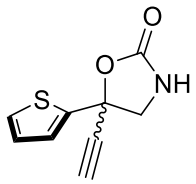
5-Ethynyl-5-(2-methoxyphenyl)oxazolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 1:1, 0.89 g, yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.7, 1.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.19 (brs, 1H), 4.15 (d, J = 9.0 Hz, 1H), 3.91 – 3.82 (m, 4H), 2.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.0, 130.3, 127.3, 126.2, 120.6, 111.6, 82.3, 76.8, 74.4, 55.7, 53.9. HRMS calc. for $C_{12}H_{11}NO_3$ $[M+H]^+$: 218.0812, found: 218.0808.



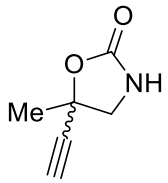
5-Ethynyl-5-(naphthalen-2-yl)oxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 2:1, 1.66 g, yield: 70%. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.00 – 7.98 (m, 2H), 7.90 – 7.88 (m, 2H), 7.51 (d, J = 8.3 Hz, 1H), 7.45 – 7.44 (m, 2H), 4.02 (brs, 1H), 3.89 (d, J = 9.4 Hz, 1H), 3.70 (d, J = 9.4 Hz, 1H), 2.37 (s, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 158.1, 137.8, 133.8, 133.3, 129.8, 129.3, 128.5, 127.9, 127.8, 124.8, 123.7, 83.7, 80.1, 78.1, 55.3. HRMS calc. for $C_{15}H_{11}NO_2$ $[M+H]^+$: 238.0863, found: 238.0858.



5-Ethynyl-5-(thiophen-2-yl)oxazolidin-2-one

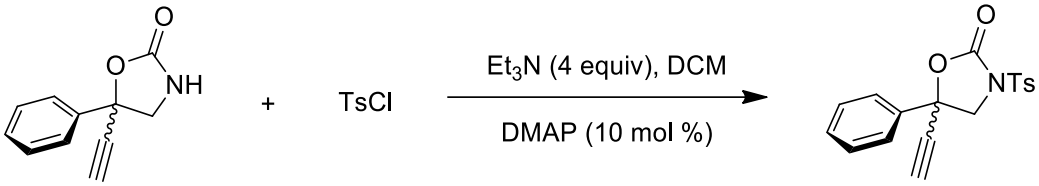
Yellow solid, purified by silica gel chromatography using PE/EA 3:1, 0.81 g, yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.10 – 7.05 (m, 1H), 6.84 (brs, 1H), 4.16 (d, J = 8.4 Hz, 1H), 4.06 (d, J = 8.5 Hz, 1H), 2.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 142.0, 127.3, 127.0, 126.9, 81.0, 76.4, 75.5, 55.6. HRMS calc. for $C_9H_7NO_2S$ $[M+H]^+$: 194.0270, found: 194.0269.



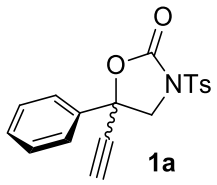
5-Ethynyl-5-methyloxazolidin-2-one

Yellow solid, purified by silica gel chromatography using PE/EA 1:1, 1.14 g, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (brs, 1H), 3.79 (d, J = 8.7 Hz, 1H), 3.50 (d, J = 8.7 Hz, 1H), 2.65 (s, 1H), 1.74 – 1.73 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 82.7, 74.6, 74.3, 53.3, 27.4. HRMS calc. for $C_6H_7NO_2$ $[M+H]^+$: 126.0550, found: 126.0549.

IV. General Procedure for Preparation of Ts-Protected Enthynyl Oxazolidinones

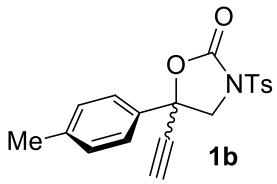


The enthynyl oxazolidinones (2 mmol), DMAP (24.4 mg, 0.2 mmol) and TsCl (572 mg, 3 mmol) were dissolved in DCM (5 mL). The mixture was then cooled to 0 °C, and Et_3N (810 mg, 8 mmol) was added dropwise. The mixture was warmed to room temperature and stirred 2 hours before quenched with saturated solution of NaCl (5 mL). The mixture was extracted with DCM (2×10 mL) and the organic mixture was dried by Na_2SO_4 and concentrated under reduced pressure. The concentrate was purified by silica gel flash chromatography (PE/EtOAc = 5:1) to give the product as white solid.



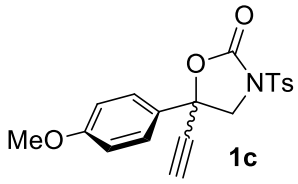
1a **5-Ethynyl-5-phenyl-3-tosyloxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 5:1, 615 mg, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.35 (m, 5H), 4.49 (d, J = 9.4 Hz, 1H), 4.13 (d, J = 9.5 Hz, 1H), 2.87 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 146.0, 137.1, 133.8, 130.0, 129.7, 129.0, 128.3, 124.9, 80.2, 77.8, 76.1, 58.4, 21.7. HRMS calc. for $C_{18}H_{15}NO_4S$ $[M+H]^+$: 342.0795, found: 342.0788.



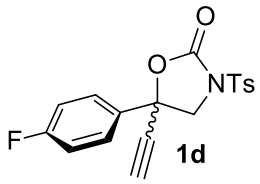
5-Ethynyl-5-(*p*-tolyl)-3-tosyloxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 5:1, 647 mg, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.37 – 7.34 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 4.46 (d, J = 9.4 Hz, 1H), 4.12 (d, J = 9.4 Hz, 1H), 2.86 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 145.9, 139.8, 134.1, 133.8, 129.9, 129.6, 128.3, 124.9, 80.3, 77.7, 76.2, 58.4, 21.7, 21.1. HRMS calc. for $C_{19}H_{17}NO_4S$ $[M+H]^+$: 356.0951, found: 356.0945.



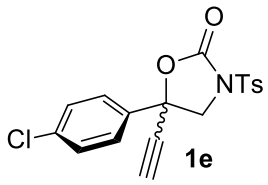
5-Ethynyl-5-(4-methoxyphenyl)-3-tosyloxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 3:1, 706 mg, yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 6.3 Hz, 2H), 7.42 – 7.37 (m, 4H), 6.90 (d, J = 6.8 Hz, 2H), 4.46 (d, J = 8.7 Hz, 1H), 4.15 (d, J = 8.7 Hz, 1H), 3.81 (s, 3H), 2.91 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 150.3, 145.9, 133.7, 129.9, 128.6, 128.1, 126.6, 114.2, 80.1, 77.9, 76.2, 58.3, 55.3, 21.6. HRMS calc. for $C_{19}H_{17}NO_5S$ $[M+H]^+$: 372.0900, found: 372.0893.



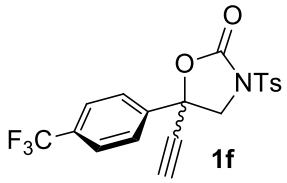
5-Ethynyl-5-(4-fluorophenyl)-3-tosyloxazolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 10:1, 467 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 8.8, 5.0 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.08 (t, J = 8.5 Hz, 2H), 4.47 (d, J = 9.5 Hz, 1H), 4.10 (d, J = 9.5 Hz, 1H), 2.89 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 250.0 Hz), 150.2, 146.1, 133.7, 133.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.0, 128.3, 127.13 (d, $J_{C\text{-}F}$ = 8.7 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.1 Hz), 79.9, 78.1, 75.7, 58.4, 21.7. HRMS calc. for $C_{18}H_{14}FNO_4S$ $[M+H]^+$: 360.0700, found: 360.0693.



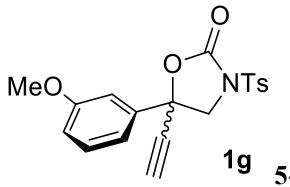
5-(4-Chlorophenyl)-5-ethynyl-3-tosyloxazolidin-2-one

White solid, purified by silica gel chromatography using PE/EA 5:1, 579 mg, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.36 (dt, J = 8.3, 6.8 Hz, 6H), 4.47 (d, J = 9.6 Hz, 1H), 4.08 (d, J = 9.6 Hz, 1H), 2.90 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 146.1, 135.7, 135.7, 133.6, 129.9, 129.2, 128.2, 126.4, 79.7, 78.3, 75.6, 58.2, 21.7. HRMS calc. for $C_{18}H_{14}ClNO_4S$ $[M+H]^+$: 376.0405, found: 376.0399.



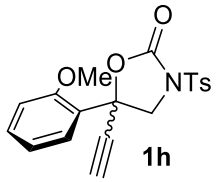
1f **5-Ethynyl-3-tosyl-5-(4-(trifluoromethyl)phenyl)oxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 10:1, 598 mg, yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.52 (d, J = 9.6 Hz, 1H), 4.10 (d, J = 9.6 Hz, 1H), 2.93 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 146.2, 141.1, 133.5, 131.8 (q, $J_{C\text{-}F}$ = 32.9 Hz), 130.0, 128.2, 126.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.4, 123.6 (q, $J_{C\text{-}F}$ = 281.7 Hz), 79.5, 78.5, 75.4, 58.1, 21.6. HRMS calc. for $C_{19}H_{14}F_3NO_4S$ $[M+H]^+$: 410.0668, found: 410.0661.



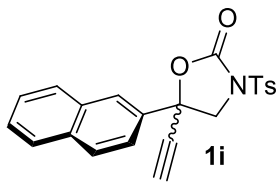
1g **5-Ethynyl-5-(3-methoxyphenyl)-3-tosyloxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 3:1, 557 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.02 (ddd, J = 7.8, 1.7, 0.8 Hz, 1H), 6.98 – 6.97 (m, 1H), 6.93 – 6.90 (m, 1H), 4.47 (d, J = 9.4 Hz, 1H), 4.11 (d, J = 9.4 Hz, 1H), 3.79 (s, 3H), 2.86 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 150.3, 146.0, 138.7, 133.7, 130.2, 129.9, 128.3, 116.9, 115.0, 110.6, 80.2, 77.7, 76.0, 58.4, 55.4, 21.7. HRMS calc. for $C_{19}H_{17}NO_5S$ $[M+H]^+$: 372.0900, found: 372.0894.



1h **5-Ethynyl-5-(2-methoxyphenyl)-3-tosyloxazolidin-2-one**

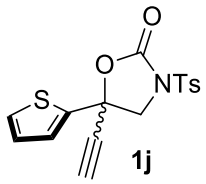
White solid, purified by silica gel chromatography using PE/EA 3:1, 579 mg, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.62 (dd, J = 7.7, 1.6 Hz, 1H), 7.39 – 7.35 (m, 3H), 6.96 (td, J = 7.6, 0.9 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 4.55 (d, J = 9.2 Hz, 1H), 4.24 (d, J = 9.2 Hz, 1H), 3.60 (s, 3H), 2.86 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 150.6, 145.7, 134.3, 131.3, 129.8, 128.4, 127.4, 124.8, 120.6, 111.7, 80.4, 77.1, 75.0, 56.8, 55.4, 21.7. HRMS calc. for $C_{19}H_{17}NO_5S$ $[M+H]^+$: 372.0900, found: 372.0894.



1i **5-Ethynyl-5-(naphthalen-2-yl)-3-tosyloxazolidin-2-one**

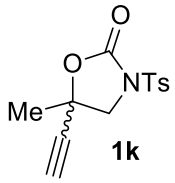
White solid, purified by silica gel chromatography using PE/EA 5:1, 689 mg, yield: 88%. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.95 – 7.80 (m, 6H), 7.55 – 7.53 (m, 2H), 7.46 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 4.57 (d, J = 9.5 Hz, 1H), 4.23 (d, J = 9.5 Hz, 1H), 2.94 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.0, 134.2, 133.7, 133.3, 132.5, 129.9, 129.3, 128.4, 128.2, 127.6, 127.3, 127.0, 124.5, 121.7, 80.1, 78.1, 76.2, 58.3, 21.6. HRMS calc. for $C_{22}H_{17}NO_4S$ $[M+H]^+$: 392.0951, found: 392.0945.



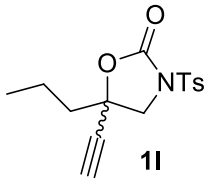
1j **5-Ethynyl-5-(thiophen-2-yl)-3-tosyloxazolidin-2-one**

Brown oil, purified by silica gel chromatography using PE/EA 10:1, 500 mg, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.39 – 7.37 (m, 3H), 7.27 (d, J = 3.6 Hz, 1H), 6.99 (dd, J = 4.9, 3.8 Hz, 1H), 4.47 (d, J = 9.7 Hz, 1H), 4.33 (d, J = 9.7 Hz, 1H), 2.92 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 146.1, 139.8, 133.7, 130.0, 128.4, 128.0, 127.6, 127.2, 79.4, 77.7, 73.4, 58.3, 21.7. HRMS calc. for $C_{16}H_{13}NO_4S_2$ $[M+H]^+$: 348.0359, found: 348.0351.



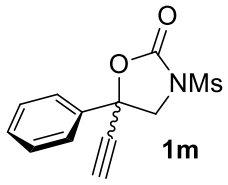
1k **5-Ethynyl-5-methyl-3-tosyloxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 4:1, 531 mg, yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.17 (d, J = 9.2 Hz, 1H), 3.88 (d, J = 9.2 Hz, 1H), 2.68 (s, 1H), 2.45 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 145.9, 133.7, 129.9, 128.3, 80.8, 75.8, 72.6, 56.3, 26.8, 21.7. HRMS calc. for $C_{13}H_{13}NO_4S$ $[M+H]^+$: 280.0638, found: 280.0632.



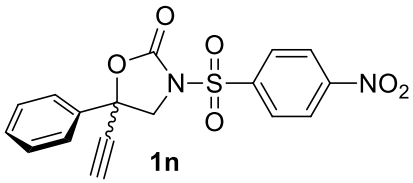
1l **5-Ethynyl-5-propyl-3-tosyloxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 4:1, 584 mg, yield: 95%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.13 (d, J = 9.3 Hz, 1H), 3.87 (d, J = 9.3 Hz, 1H), 2.68 (s, 1H), 2.44 (s, 3H), 1.89 – 1.74 (m, 2H), 1.57 – 1.46 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 145.9, 133.8, 129.9, 128.2, 80.1, 76.5, 75.7, 55.4, 41.5, 21.7, 17.0, 13.6. HRMS calc. for $C_{15}H_{18}NO_4S$ $[M+H]^+$: 308.0951, found: 308.0954.



1m **5-Ethynyl-3-(methylsulfonyl)-5-phenyloxazolidin-2-one**

White solid, purified by silica gel chromatography using PE/EA 3:1, 377 mg, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.48 – 7.44 (m, 3H), 4.47 (d, J = 9.5 Hz, 1H), 4.17 (d, J = 9.5 Hz, 1H), 3.37 (s, 3H), 2.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 136.9, 129.9, 129.2, 124.9, 80.1, 78.1, 76.9, 57.7, 40.4. HRMS calc. for $C_{12}H_{11}NO_4S$ $[M+H]^+$: 266.0482, found: 266.0477.

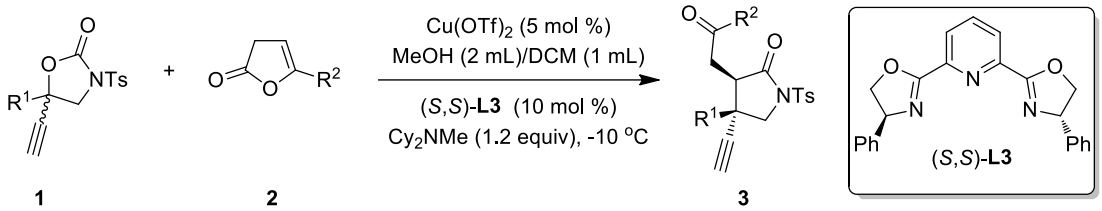


1n

5-Ethynyl-3-((4-nitrophenyl)sulfonyl)-5-phenyloxazolidin-2-one

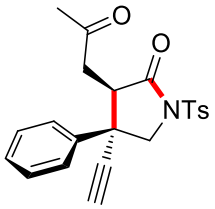
Yellow solid, purified by silica gel chromatography using PE/EA 5:1, 492 mg, yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.39 (m, 2H), 8.27 – 8.24 (m, 2H), 7.49 – 7.45 (m, 2H), 7.44 – 7.40 (m, 3H), 4.54 (d, J = 9.5 Hz, 1H), 4.19 (d, J = 9.5 Hz, 1H), 2.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 150.0, 142.1, 136.6, 130.0, 129.8, 129.2, 124.9, 124.5, 79.8, 78.3, 76.9, 58.5. HRMS calc. for $C_{17}H_{12}N_2O_6S$ $[M+H]^+$: 373.0489, found: 373.0488.

V. General Procedure for Preparation of Optical Active Pyrrolidinone



1 **2** **3**

General procedure for the synthesis of optical active pyrrolidinone: $Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*,*S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of enthynyl oxazolidinones (**1**, 0.2 mmol) and γ-substituted butenolides (**2**, 0.6 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 10:1 to 5:1) to afford the pyrrolidinone (**3**), and chemical yields are total of the diastereomers.

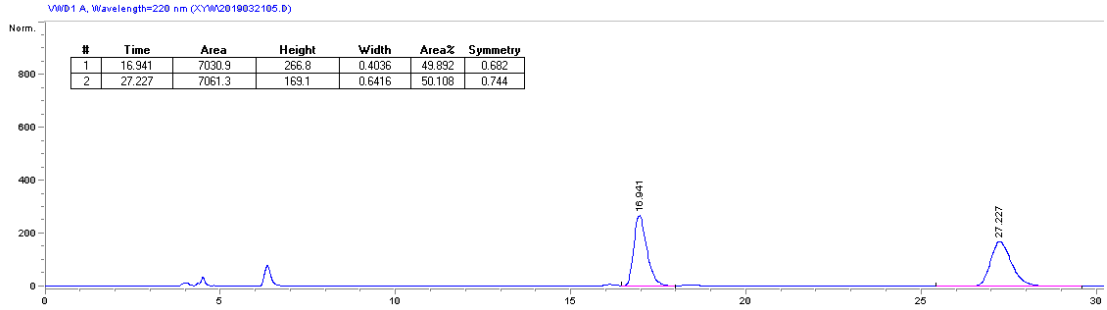


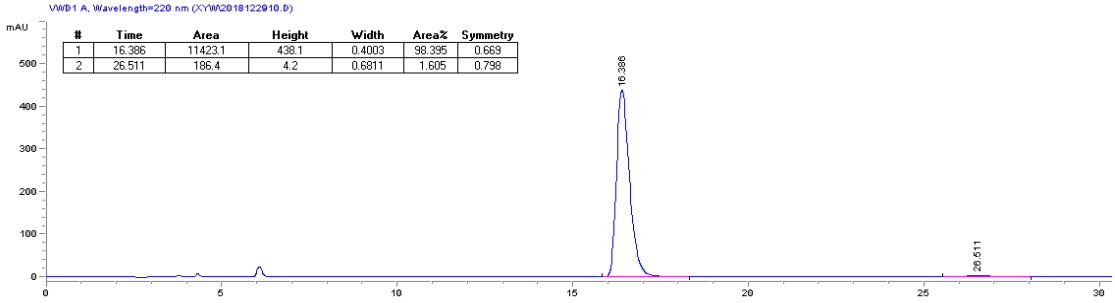
3aa

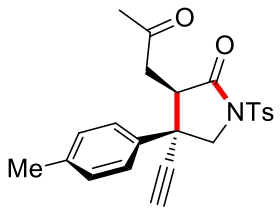
(3*R*,4*S*)-4-Ethynyl-3-(2-oxopropyl)-4-phenyl-1-tosylpyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 71.1 mg, 90% yield, dr > 25:1. 97% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.4 min, t_R (minor) = 26.5 min. $[\alpha]_D^{25}$ = -24.1 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.24 – 7.14 (m, 5H), 4.27 (d, J

= 10.4 Hz, 1H), 4.19 (d, *J* = 10.4 Hz, 1H), 3.77 (dd, *J* = 7.0, 5.0 Hz, 1H), 2.50 (s, 1H), 2.40 (s, 3H), 2.34 (dd, *J* = 17.9, 7.2 Hz, 1H), 2.01 (dd, *J* = 17.9, 5.0 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 171.7, 145.6, 137.9, 134.5, 129.8, 128.9, 128.2, 128.1, 126.0, 83.7, 74.3, 57.8, 50.5, 42.7, 39.2, 30.1, 21.6. HRMS calc. for $C_{22}H_{21}NO_4S$ $[M+H]^+$: 396.1264, found: 396.1259.

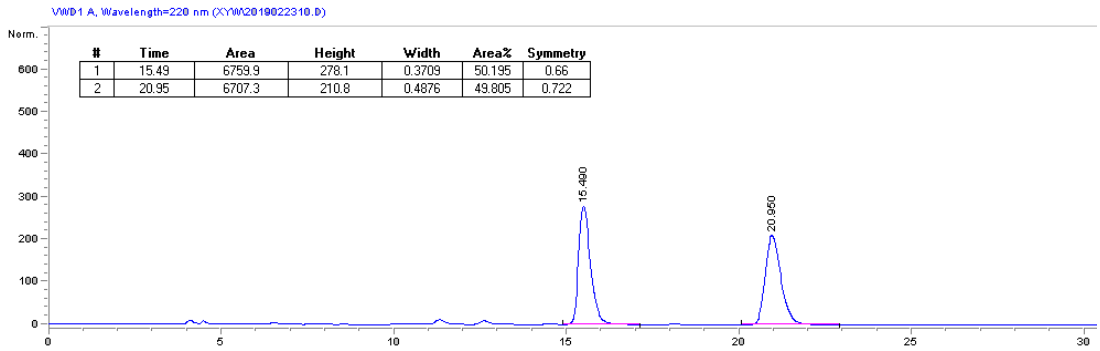






3ba **(3*R*,4*S*)-4-Ethynyl-3-(2-oxopropyl)-4-(*p*-tolyl)-1-tosylpyrrolidin-2-one**

Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 66.7 mg, 81% yield, dr = 20:1. 97% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 15.4 min, t_R (minor) = 20.8 min. $[\alpha]_D^{25}$ = -35.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 4.31 (d, *J* = 10.3 Hz, 1H), 4.24 (d, *J* = 10.3 Hz, 1H), 3.81 (dd, *J* = 7.0, 5.0 Hz, 1H), 2.54 (s, 1H), 2.47 (s, 3H), 2.41 (dd, *J* = 17.9, 7.0 Hz, 1H), 2.31 (s, 3H), 2.08 (dd, *J* = 17.8, 5.1 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 171.9, 145.5, 138.0, 134.9, 134.5, 129.8, 129.5, 128.1, 125.9, 83.9, 74.1, 58.0, 50.5, 42.4, 39.2, 30.1, 21.7, 20.8. HRMS calc. for $C_{23}H_{23}NO_4S$ $[M+H]^+$: 410.1421, found: 410.1414.



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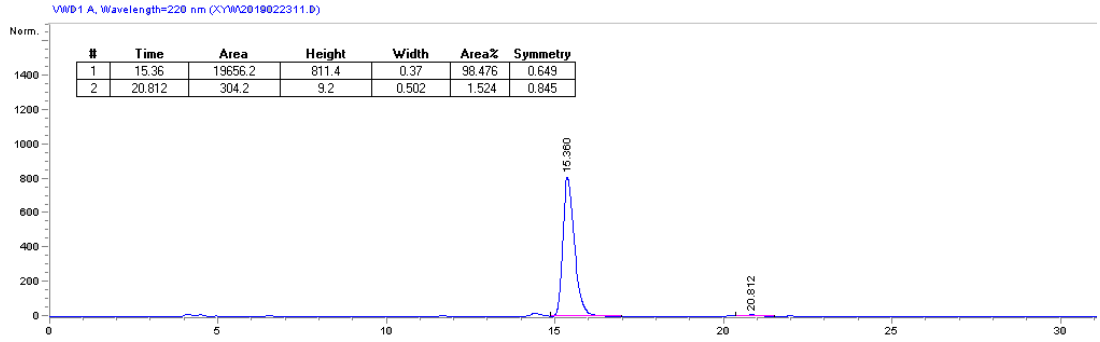

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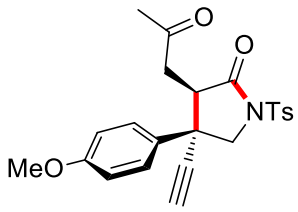
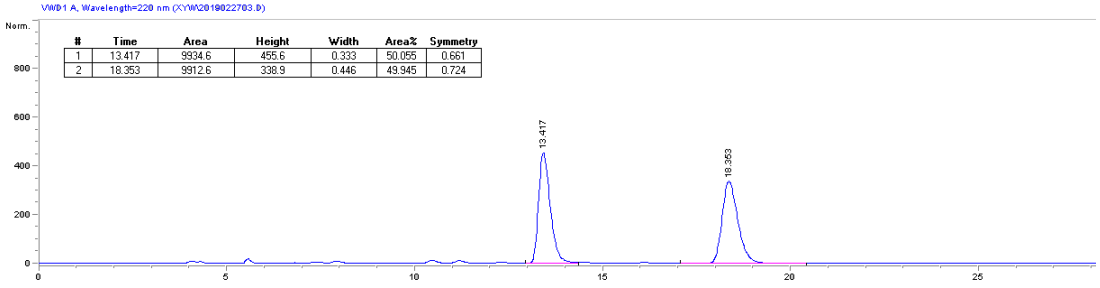


3ca

(3*R*,4*S*)-4-Ethynyl-4-(4-methoxyphenyl)-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 5:1, 68.6 mg, yield: 81%, dr = 14:1. 96% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 13.6 min, t_R (minor) = 18.6 min. $[\alpha]_D^{25}$ = -32.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.12 (m, 2H), 6.75 – 6.71 (m, 2H), 4.30 (d, *J* = 10.3 Hz, 1H), 4.23 (d, *J* = 10.3 Hz, 1H), 3.81 – 3.76 (m, 4H), 2.54 (s, 1H), 2.47 – 2.37 (m, 4H), 2.09 (dd, *J* = 17.9, 5.0 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 171.9, 159.2, 145.6, 134.5, 129.8, 129. 8, 128.1, 127.3, 114.1, 84.0, 74.1, 58.0, 55.2, 50.6, 42.2, 39.2, 30.2, 21.7. HRMS calc. for $C_{23}H_{23}NO_5S$ $[M+H]^+$: 426.1370, found: 426.1362.



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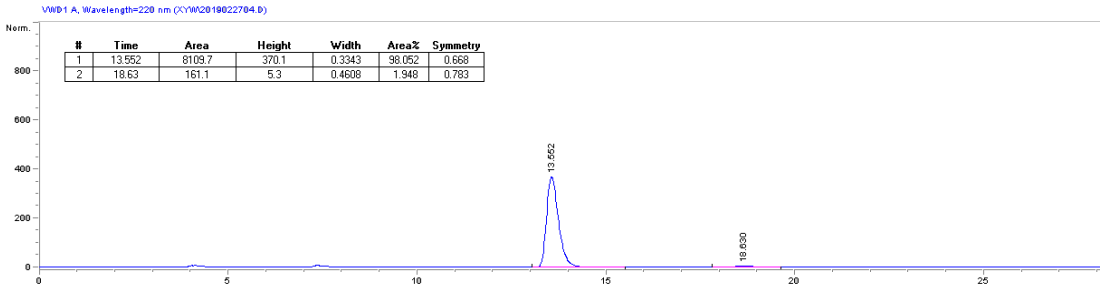
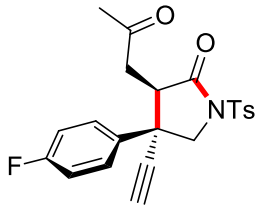
2	18.353	9912.6	338.9	0.446	49.945	0.724

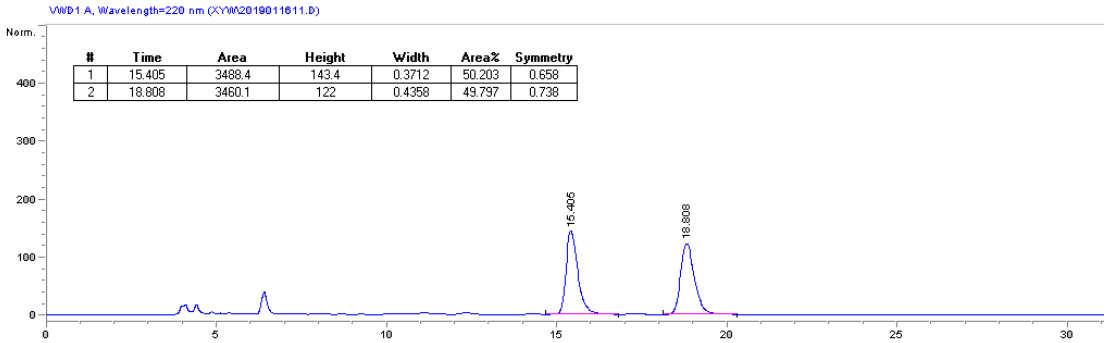


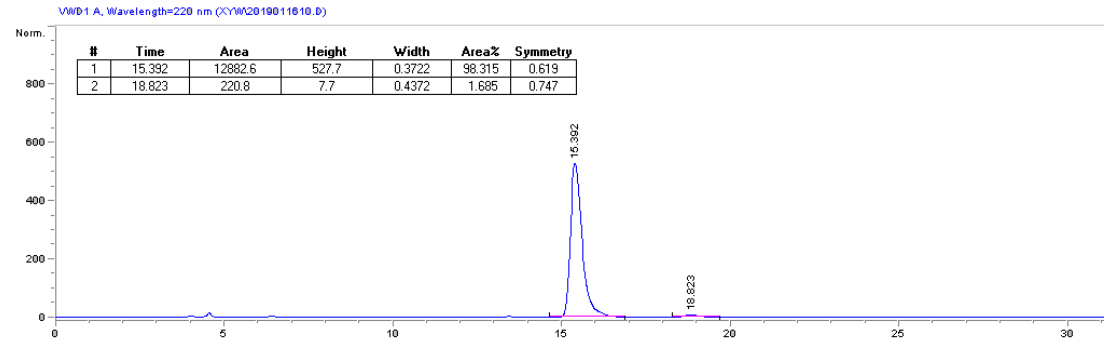


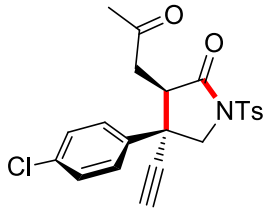
3da

(3*R*,4*S*)-4-Ethynyl-4-(4-fluorophenyl)-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 65.2 mg, 79% yield, dr = 14:1. 97% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 15.4 min, t_R (minor) = 18.8 min. $[\alpha]_D^{25}$ = -26.9 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 8.7, 5.1 Hz, 2H), 6.90 (t, *J* = 8.5 Hz, 2H), 4.29 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 3.82 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.71 (dd, *J* = 6.9, 4.0 Hz, 1H), 2.58 (s, 1H), 2.49 – 2.38 (m, 4H), 2.11 – 2.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 171.6, 162.2 (d, $J_{C\text{-}F}$ = 248.7 Hz), 145.7, 134.4, 133.8 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.8, 128.1, 128.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 83.5, 74.7, 57.9, 50.5, 42.3, 39.1, 30.1, 21.7. HRMS calc. for $C_{22}H_{20}FNO_4S$ $[M+H]^+$: 414.1170, found: 414.1162.



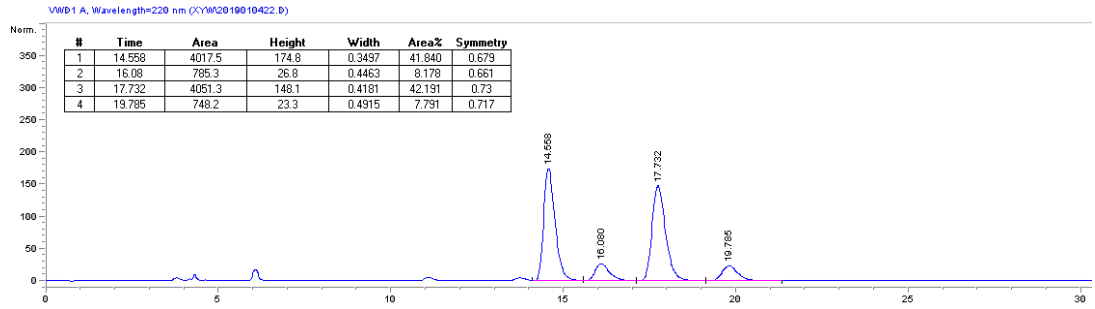


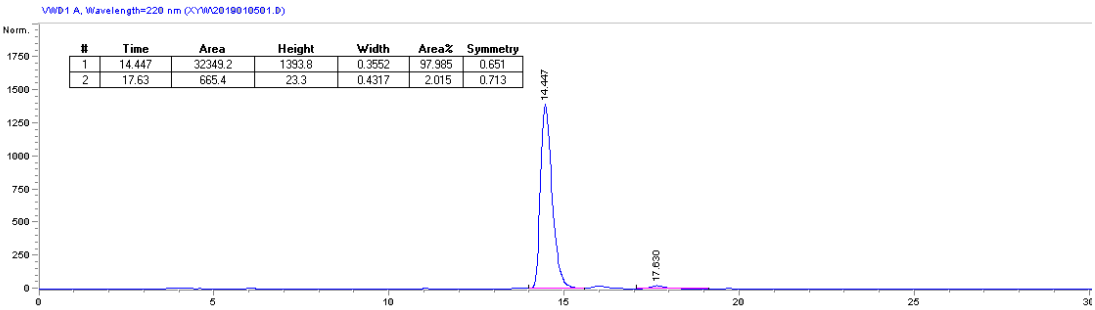


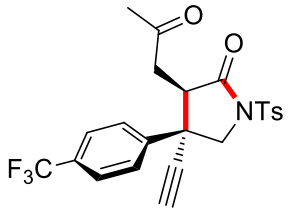
3ea

(3*R*,4*S*)-4-(4-Chlorophenyl)-4-ethynyl-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 5:1, 64.2 mg, 75% yield, dr = 25:1. 96% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 14.4 min, t_R (minor) = 17.6 min. $[\alpha]_D^{25}$ = -40.0 (*c* = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.05 – 7.01 (m, 4H), 4.14 – 4.08 (m, 2H), 3.69 (dd, *J* = 7.0, 4.9 Hz, 1H), 2.44 (s, 1H), 2.33 – 2.26 (m, 4H), 1.96 – 1.90 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 171.5, 145.8, 136.5, 134.4, 134.3, 129.8, 129.0, 128.1, 127.5, 83.2, 74.8, 57.8, 50.3, 42.5, 39.1, 30.1, 21.7. HRMS calc. for $C_{22}H_{20}ClNO_4S$ $[M+H]^+$: 430.0874, found: 430.0869.



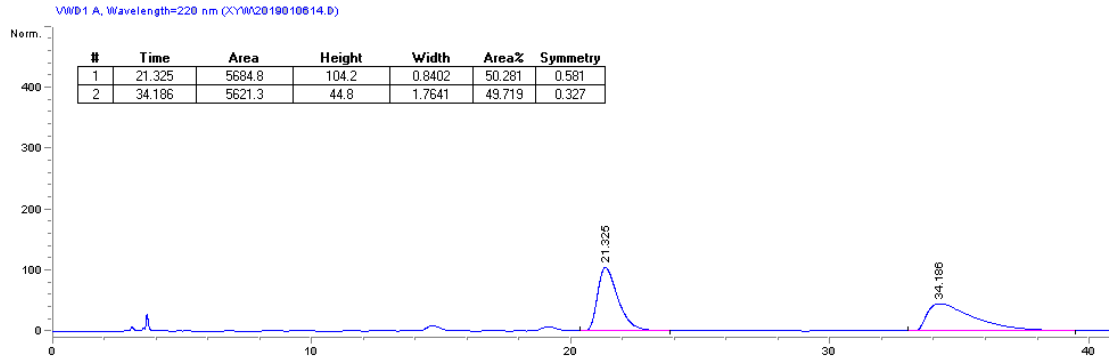




3fa

(3*R*,4*S*)-4-Ethynyl-3-(2-oxopropyl)-1-tosyl-4-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 72.7 mg, 78% yield, dr = 5:1(The diastereomers cannot be fully separated, and only the major isomer was shown in follows). 91.5% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 ml/min, 220 nm, 40 °C): t_R (minor) = 21.4 min, t_R (major) = 33.1 min. $[\alpha]_D^{25}$ = 29.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.31 (d, *J* = 10.2 Hz, 1H), 3.95 (d, *J* = 10.2 Hz, 1H), 3.77 (dd, *J* = 6.8, 4.3 Hz, 1H), 2.98 (dd, *J* = 18.2, 7.0 Hz, 1H), 2.48 – 2.43 (m, 4H), 2.42 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 171.2, 145.5, 140.6, 134.8, 130.9 (q, J_{C-F} = 32.8 Hz), 129.7, 128.3, 127.1, 126.0 (q, J_{C-F} = 3.7 Hz), 123.7 (q, J_{C-F} = 272.2 Hz), 81.6, 76.0, 58.7, 48.5, 46.6, 39.7, 30.2, 21.7. HRMS calc. for $C_{23}H_{20}F_3NO_4S$ $[M+H]^+$: 464.1138, found: 464.1132.



#	Time	Area	Height	Width	Area%	Symmetry
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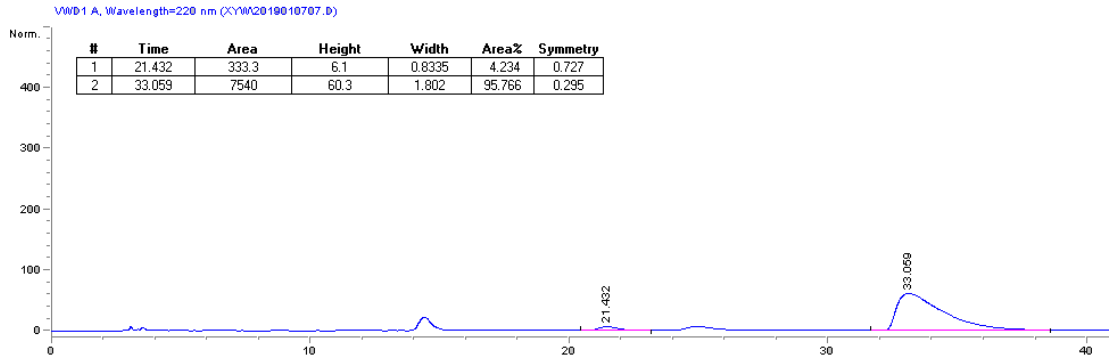
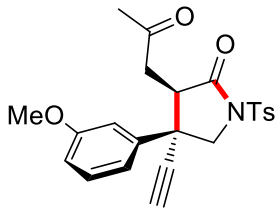
2	34.186	5621.3	44.8	1.7641	49.719	0.327



#	Time	Area	Height	Width	Area%	Symmetry
1	21.432	333.3	6.1	0.8335	4.234	0.727
2	33.059	7540	60.3	1.802	95.766	0.295

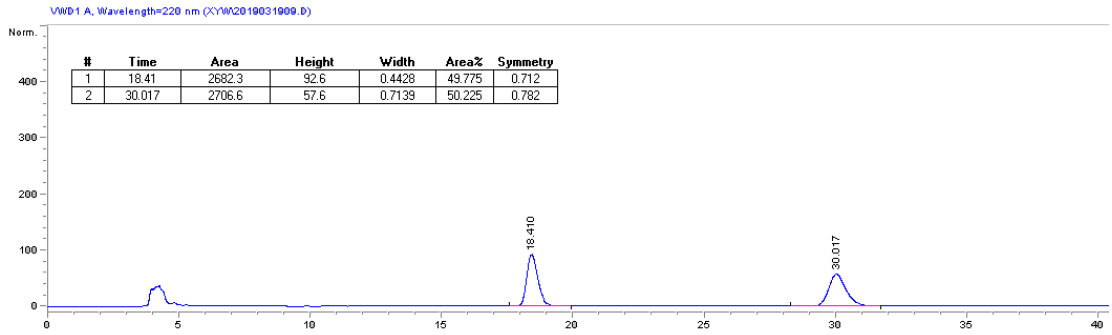


3ga

(3*R*,4*S*)-4-Ethynyl-4-(3-methoxyphenyl)-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 4:1, 57.3 mg, yield: 67%, dr = 20:1. 96% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 18.3 min, t_R (minor) = 29.8 min. $[\alpha]_D^{25}$ = -28.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.74 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.4 Hz, 1H), 3.83 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.73 (s, 3H), 2.56 (s, 1H), 2.45 – 2.39 (m, 4H),

2.09 (dd, J = 17.9, 5.0 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 171.8, 159.9, 145.7, 139.6, 134.6, 130.1, 129.9, 128.2, 118.0, 113.5, 112.5, 83.8, 74.5, 57.9, 55.2, 50.6, 42.8, 39.3, 30.2, 21.8. HRMS calc. for $C_{23}H_{23}NO_5S$ $[M+H]^+$: 426.1370, found: 426.1361.



#	Time	Area	Height	Width	Area%	Symmetry
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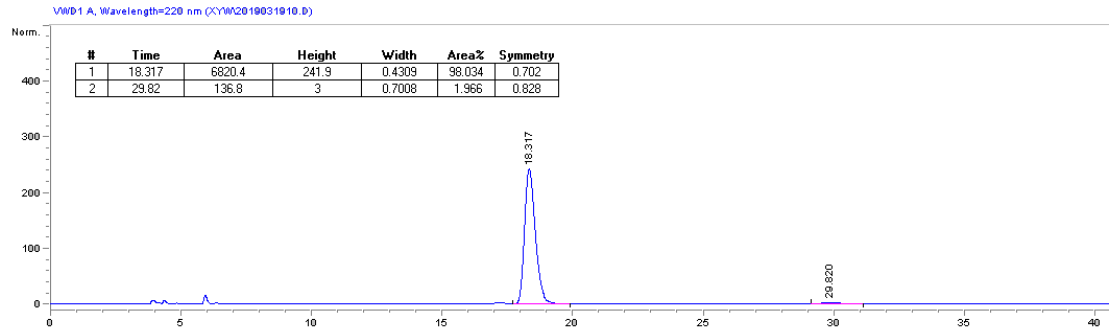
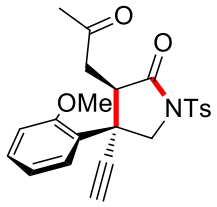
2	30.017	2706.6	57.6	0.7139	50.225	0.782



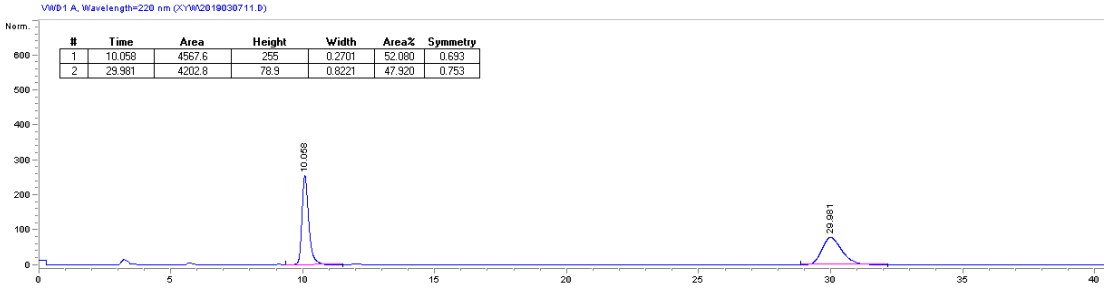
#	Time	Area	Height	Width	Area%	Symmetry
1	18.317	6820.4	241.9	0.4309	98.034	0.702
2	29.82	136.8	3	0.7008	1.966	0.828

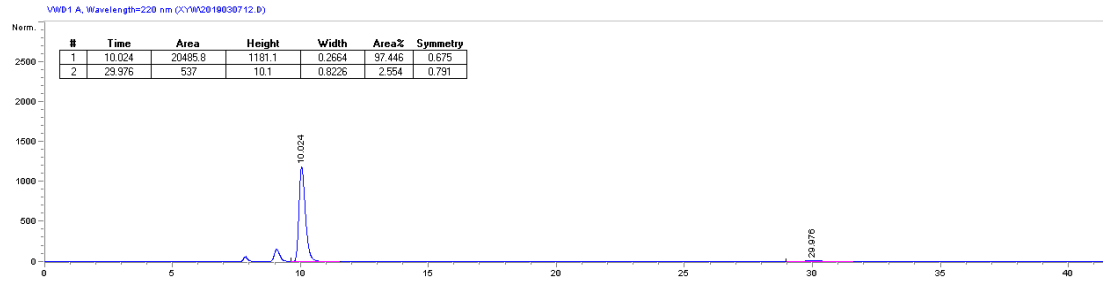


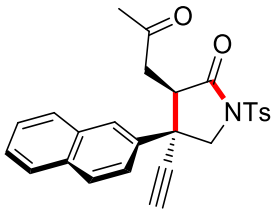
3ha

(3*R*,4*S*)-4-Ethynyl-4-(2-methoxyphenyl)-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 4:1, 51.4 mg, yield: 60%, dr = 3:1(The diastereomers cannot be fully separated, and only the major isomer was shown in follows). 95% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 1.0 ml/min, 220 nm, 40 °C): t_R (major) = 10.0 min, t_R (minor) = 30.0 min. $[\alpha]_D^{25}$ = -5.7 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.72 (dd, J = 7.7, 1.4 Hz, 1H), 7.36 – 7.29 (m, 3H), 6.95 (td, J = 7.6, 0.9 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 4.37 (d, J = 10.1 Hz, 1H), 4.16 (d, J = 10.1 Hz, 1H), 3.89 (t, J = 6.2 Hz, 1H), 3.40 (s, 3H), 2.68 (s, 1H), 2.55 (dd, J = 17.9, 5.9 Hz, 1H), 2.44 (s, 3H), 2.01 (dd, J = 17.9, 6.6 Hz, 1H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 172.6, 156.4, 145.1, 135.4, 130.0, 129.9, 129.6, 128.5, 126.1, 120.8, 110.8, 86.8, 74.3, 58.5, 54.3, 49.3, 40.9, 39.9, 29.9, 21.6. HRMS calc. for $C_{23}H_{23}NO_5S$ $[M+H]^+$: 426.1370, found: 426.1363.



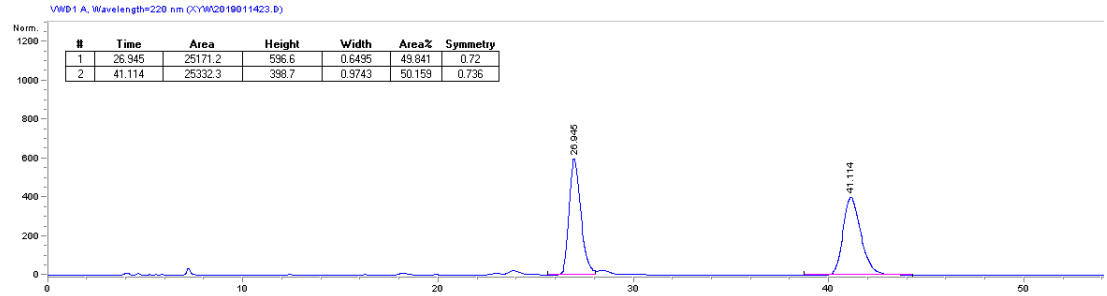


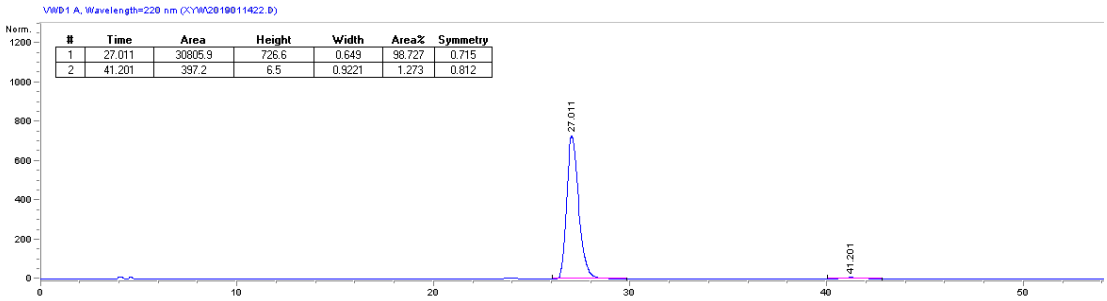


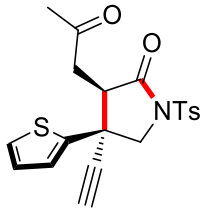
3ia

(3*R*,4*S*)-4-Ethynyl-4-(naphthalen-2-yl)-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 5:1, 67.7 mg, 76% yield, dr = 14:1. 97.5% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 27.0 min, t_R (minor) = 41.2 min. $[\alpha]_D^{25}$ = -26.5 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.65 (s, 1H), 7.60 – 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 3H), 4.43 – 4.36 (m, 2H), 3.96 (dd, *J* = 7.0, 5.0 Hz, 1H), 2.66 (s, 1H), 2.50 – 2.43 (m, 4H), 2.13 (dd, *J* = 18.0, 4.9 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 171.8, 145.6, 135.2, 134.5, 132.8, 132.6, 129.8, 128.9, 128.2, 128.1, 127.4, 126.7, 126.6, 125.3, 123.5, 83.7, 74.6, 58.0, 50.4, 42.9, 39.2, 30.1, 21.7. HRMS calc. for $C_{26}H_{23}NO_4S$ $[M+H]^+$: 446.1421, found: 446.1414.

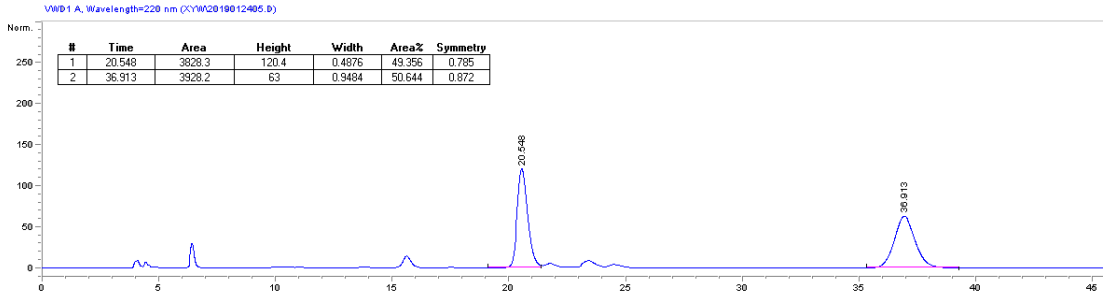


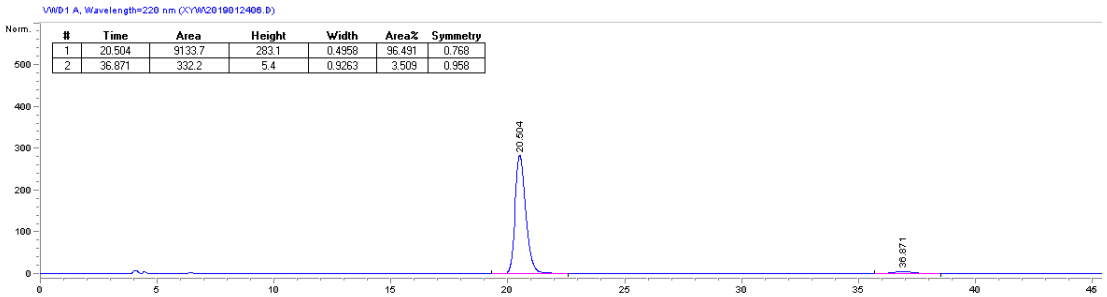


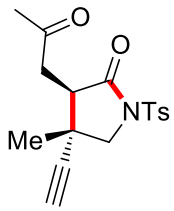


3ja **(3*R*,4*R*)-4-Ethynyl-3-(2-oxopropyl)-4-(thiophen-2-yl)-1-tosylpyrrolidin-2-one**

Brown oil, purified by silica gel chromatography using PE/EA 5:1, 56.4 mg, yield: 70%, dr = 20:1. 93% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 20.5 min, t_R (minor) = 36.9 min. $[\alpha]_D^{25}$ = -47.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 1H), 6.89 – 6.85 (m, 2H), 4.32 (d, *J* = 10.1 Hz, 1H), 4.18 (d, *J* = 10.1 Hz, 1H), 3.76 (dd, *J* = 7.0, 4.8 Hz, 1H), 2.57 (s, 1H), 2.52 – 2.44 (m, 4H), 2.19 (dd, *J* = 17.9, 4.7 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 171.1, 145.6, 141.2, 134.5, 129.7, 128.2, 126.9, 125.7, 125.3, 82.2, 74.2, 58.2, 51.1, 41.2, 38.8, 30.2, 21.7. HRMS calc. for $C_{20}H_{19}NO_4S_2$ $[M+H]^+$: 402.0828, found: 402.0822.



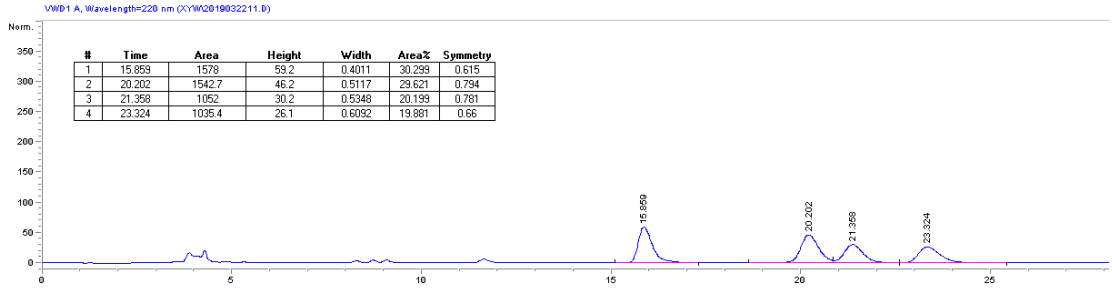




3ka

(3*R*,4*S*)-4-Ethynyl-4-methyl-3-(2-oxopropyl)-1-tosylpyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 4:1, 30.9 mg, yield: 46%, dr = 5:1(The diastereomers cannot be fully separated, and only the major isomer was shown in follows). 88% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 15.8 min, t_R (minor) = 20.2 min. $[\alpha]_D^{25}$ = -21.0 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.88 (d, *J* = 10.0 Hz, 1H), 3.84 (d, *J* = 10.0 Hz, 1H), 3.39 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.70 (dd, *J* = 17.1, 8.3 Hz, 1H), 2.44 (s, 3H), 2.39 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.27 (s, 1H), 2.24 (d, *J* = 9.1 Hz, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 171.5, 145.5, 134.8, 129.9, 128.0, 84.1, 72.1, 57.0, 49.3, 37.6, 34.7, 30.5, 21.7, 21.1. HRMS calc. for $C_{17}H_{19}NO_4S$ $[M+H]^+$: 334.1108, found: 334.1098.



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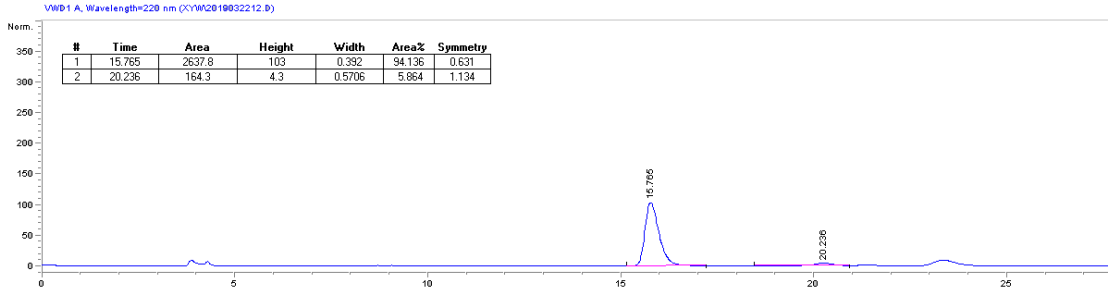
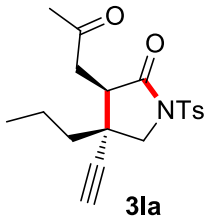
2	20.202	1542.7	46.2	0.5117	29.621	0.794
3	21.358	1052	30.2	0.5348	20.199	0.781
4	23.324	1035.4	26.1	0.6092	19.881	0.66



#	Time	Area	Height	Width	Area%	Symmetry
1	15.765	2637.8	103	0.392	94.136	0.631
2	20.236	164.3	4.3	0.5706	5.864	1.134

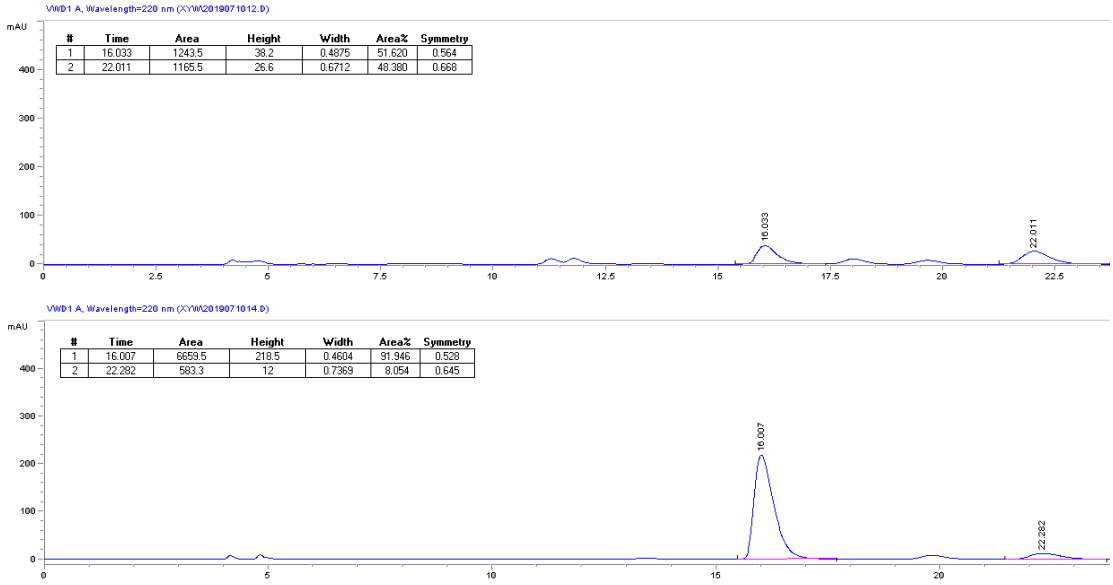


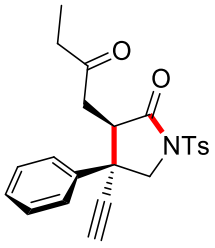
3la

(3*R*,4*S*)-4-Ethynyl-3-(2-oxopropyl)-4-propyl-1-tosylpyrrolidin-2-one

Colorless oil, purified by silica gel chromatography using PE/EA 4:1, 30.4 mg, yield: 42%, dr = 5:1(The diastereomers cannot be fully separated, and only the major isomer was shown in follows). 84% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 ml/min, 220 nm,

40 °C): t_R (major) = 16.0 min, t_R (minor) = 22.3 min. $[\alpha]_D^{25}$ = -18.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.03 (d, J = 10.3 Hz, 1H), 3.73 (d, J = 10.5 Hz, 1H), 3.44 (dd, J = 8.6, 4.1 Hz, 1H), 2.69 (dd, J = 17.1, 8.6 Hz, 1H), 2.43 – 2.37 (m, 4H), 2.22 (s, 3H), 1.55 – 1.49 (m, 1H), 1.27 – 1.25 (m, 1H), 1.08 – 1.03 (m, 1H), 0.95 – 0.91 (m, 1H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 171.8, 145.4, 134.8, 129.8, 127.9, 83.3, 72.6, 53.4, 49.9, 39.1, 37.3, 34.3, 30.5, 21.7, 18.1, 14.0. HRMS calc. for $C_{19}H_{24}NO_4S$ $[M+H]^+$: 362.1421, found: 362.1425.

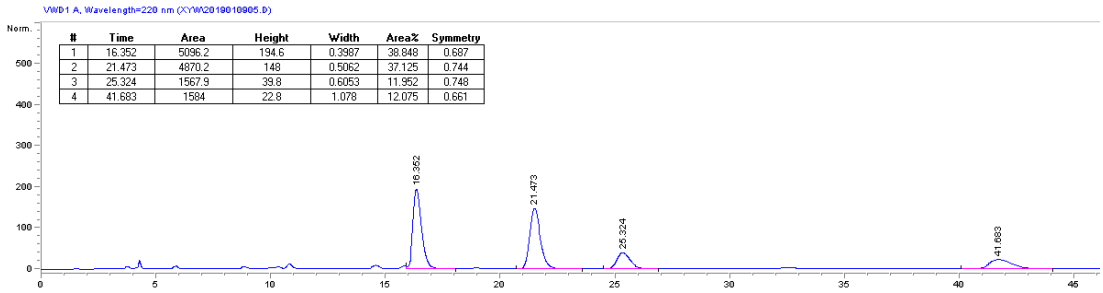




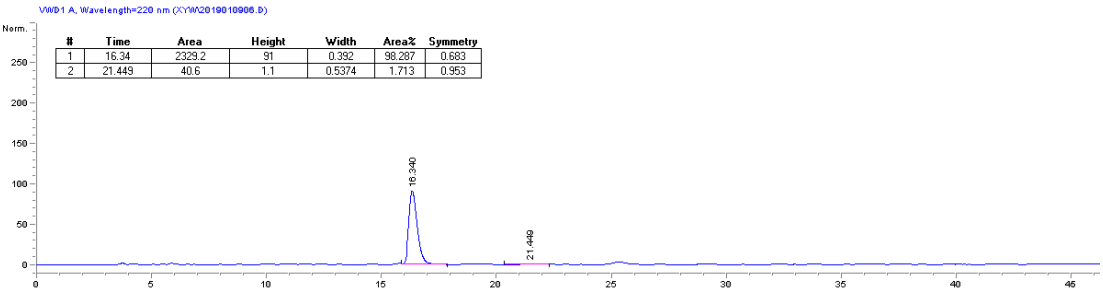
3ab

(3*R*,4*S*)-4-Ethynyl-3-(2-oxobutyl)-4-phenyl-1-tosylpyrrolidin-2-one

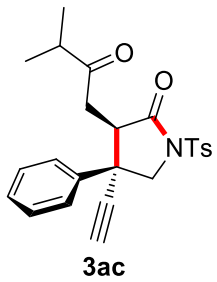
Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 58.5 mg, yield: 71%, dr > 25:1. 97% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.3 min, t_R (minor) = 21.4 min. $[\alpha]_D^{25}$ = -23.3 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.30 – 7.24 (m, 5H), 4.37 (d, J = 10.3 Hz, 1H), 4.29 (d, J = 10.4 Hz, 1H), 3.89 (t, J = 6.0 Hz, 1H), 2.58 (s, 1H), 2.49 (s, 3H), 2.43 – 2.29 (m, 2H), 2.26 – 2.17 (m, 1H), 2.07 (dd, J = 17.6, 5.0 Hz, 1H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 171.9, 145.6, 138.0, 134.5, 129.8, 128.9, 128.2, 128.1, 126.1, 83.8, 74.3, 57.9, 50.6, 42.7, 38.1, 36.2, 21.7, 7.5. HRMS calc. for $C_{23}H_{23}NO_4S$ $[M+H]^+$: 410.1421, found: 410.1412.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.352	5096.2	194.6	0.3987	38.848	0.687
2	21.473	4870.2	148	0.5062	37.125	0.744
3	25.324	1567.9	39.8	0.6053	11.952	0.748
4	41.683	1584	22.8	1.078	12.075	0.661



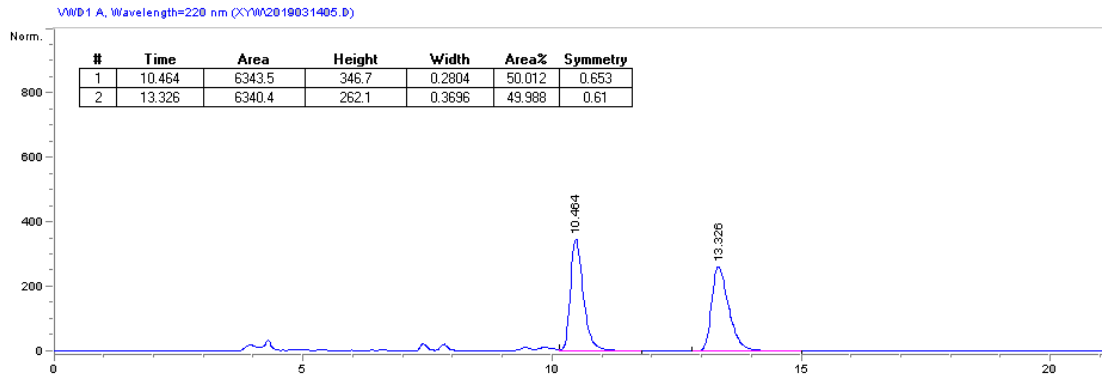
#	Time	Area	Height	Width	Area%	Symmetry
1	16.34	2329.2	91	0.392	98.287	0.683
2	21.449	40.6	1.1	0.5374	1.713	0.953



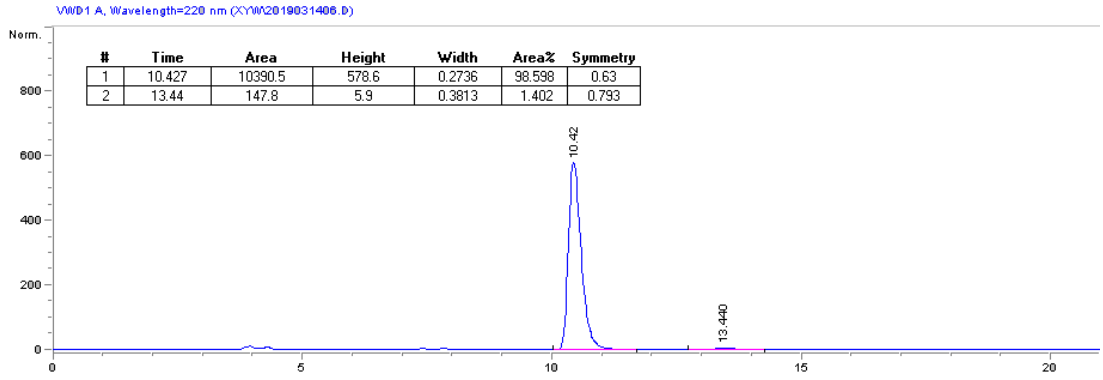
3ac

(3*R*,4*S*)-4-Ethynyl-3-(3-methyl-2-oxobutyl)-4-phenyl-1-tosylpyrrolidin-2-one

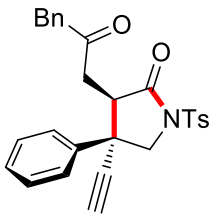
Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 63.9 mg, yield: 75%, dr > 25:1. 97% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 15.8 min, t_R (minor) = 20.2 min. $[\alpha]_D^{25}$ = -18.7 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.12 (m, 5H), 4.27 (d, *J* = 10.3 Hz, 1H), 4.20 (d, *J* = 10.3 Hz, 1H), 3.80 (t, *J* = 5.9 Hz, 1H), 2.49 (s, 1H), 2.45 – 2.37 (m, 4H), 2.35 – 2.28 (m, 1H), 2.04 (dd, *J* = 18.0, 5.6 Hz, 1H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 171.9, 145.5, 138.0, 134.5, 129.8, 128.8, 128.2, 128.1, 126.1, 83.9, 74.2, 57.9, 50.3, 42.7, 40.8, 36.4, 21.6, 18.0, 17.9. HRMS calc. for $C_{24}H_{25}NO_4S$ $[M+H]^+$: 424.1577, found: 424.1568.



#	Time	Area	Height	Width	Area%	Symmetry
1	10.464	6343.5	346.7	0.2804	50.012	0.653
2	13.326	6340.4	262.1	0.3696	49.988	0.61



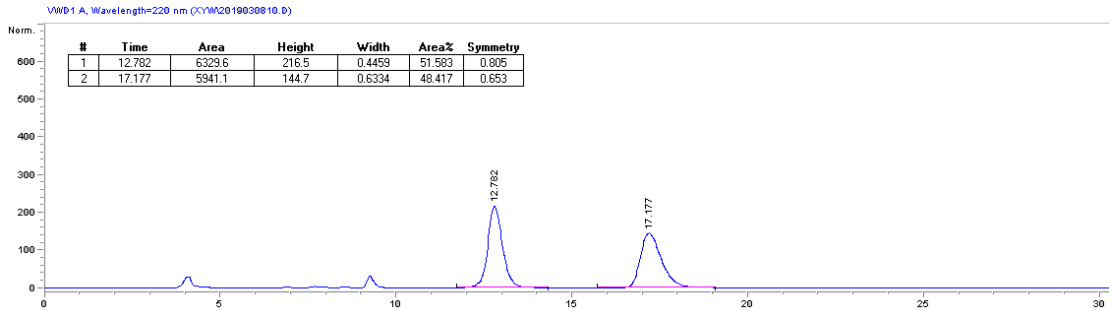
#	Time	Area	Height	Width	Area%	Symmetry
1	10.427	10390.5	578.6	0.2736	98.598	0.63
2	13.44	147.8	5.9	0.3813	1.402	0.793



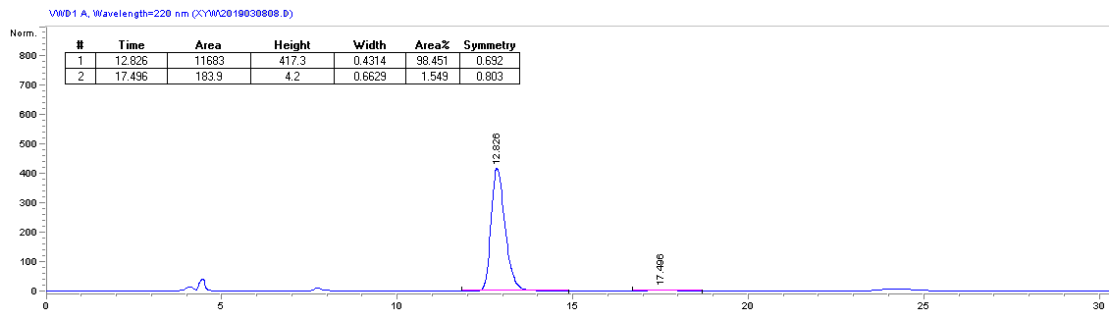
3ad

(3*R*,4*S*)-4-Ethynyl-3-(2-oxo-3-phenylpropyl)-4-phenyl-1-tosylpyrrolidin-2-one

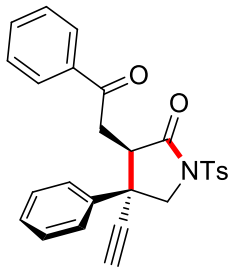
Colorless oil, purified by silica gel chromatography using PE/EA 5:1, 54.1 mg, yield: 57%, dr = 12:1. 97% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 12.8 min, t_R (minor) = 17.5 min. $[\alpha]_D^{25}$ = -15.9 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.12 (m, 4H), 7.11 – 7.06 (m, 4H), 6.93 (dd, *J* = 7.6, 1.7 Hz, 2H), 4.27 (d, *J* = 10.4 Hz, 1H), 4.17 (d, *J* = 10.4 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 1H), 3.48 (d, *J* = 15.8 Hz, 1H), 3.42 (d, *J* = 15.8 Hz, 1H), 2.45 (s, 1H), 2.41 – 2.35 (m, 4H), 2.03 (dd, *J* = 17.9, 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 171.7, 145.6, 137.7, 134.5, 133.3, 129.8, 129.3, 128.9, 128.5, 128.2, 128.1, 127.0, 126.1, 83.8, 74.3, 57.8, 50.6, 49.9, 42.6, 38.0, 21.7. HRMS calc. for $C_{28}H_{25}NO_4S$ $[M+H]^+$: 472.1577, found: 472.1568.



#	Time	Area	Height	Width	Area%	Symmetry
1	12.782	6329.6	216.5	0.4459	51.583	0.805
2	17.177	5941.1	144.7	0.6334	48.417	0.653



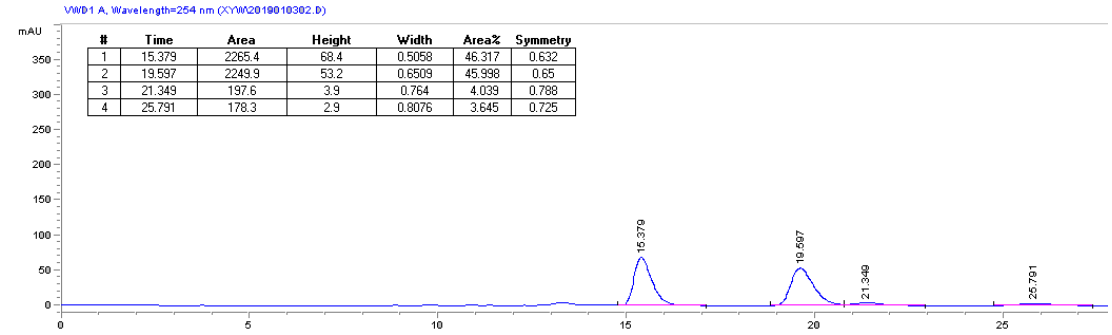
#	Time	Area	Height	Width	Area%	Symmetry
1	12.826	11683	417.3	0.4314	98.451	0.692
2	17.496	183.9	4.2	0.6629	1.549	0.803



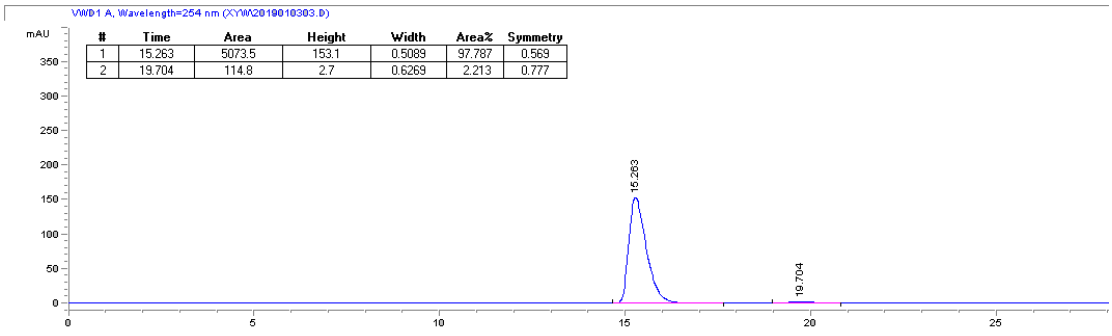
3ae

(3*R*,4*S*)-4-Ethynyl-3-(2-oxo-2-phenylethyl)-4-phenyl-1-tosylpyrrolidin-2-one

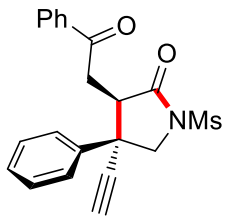
Red oil, purified by silica gel chromatography using PE/EA 10:1, 82.8 mg, yield: 90%, dr = 13:1. 95.5% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 15.3 min, t_R (minor) = 19.7 min. $[\alpha]_D^{25}$ = -29.7 (*c* = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.09 (m, 9H), 4.31 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.4 Hz, 1H), 4.04 (t, *J* = 5.7 Hz, 1H), 2.95 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.57 – 2.49 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 171.9, 145.5, 138.0, 136.1, 134.5, 133.2, 129.7, 128.9, 128.4, 128.2, 128.1, 127.9, 126.1, 83.8, 74.4, 57.9, 50.4, 42.9, 34.7, 21.6. HRMS calc. for $C_{27}H_{23}NO_4S$ $[M+H]^+$: 458.1421, found: 458.1411.



#	Time	Area	Height	Width	Area%	Symmetry
1	15.379	2265.4	68.4	0.5058	46.317	0.632
2	19.597	2249.9	53.2	0.6509	45.998	0.65
3	21.349	197.6	3.9	0.764	4.039	0.788
4	25.791	178.3	2.9	0.8076	3.645	0.725



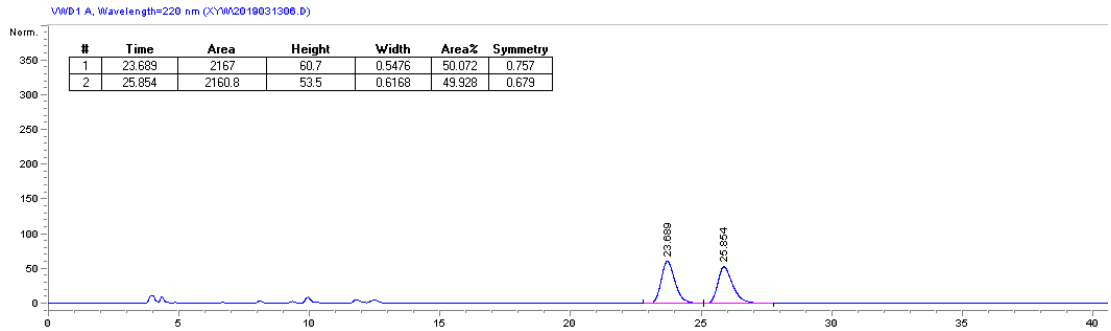
#	Time	Area	Height	Width	Area%	Symmetry
1	15.263	5073.5	153.1	0.5089	97.787	0.569
2	19.704	114.8	2.7	0.6269	2.213	0.777

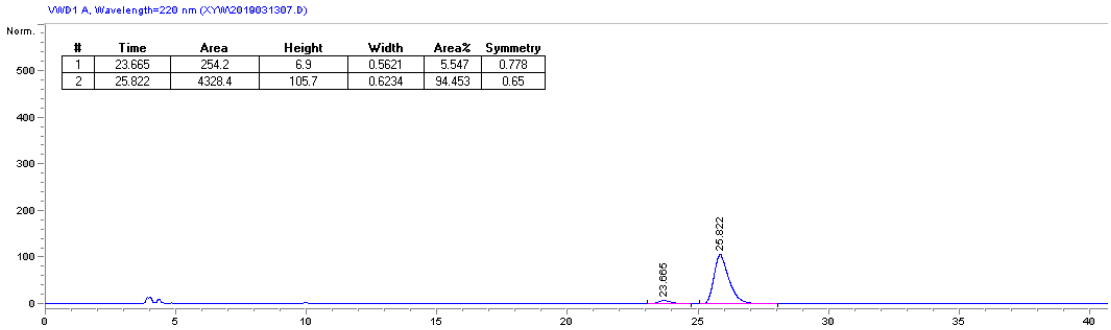


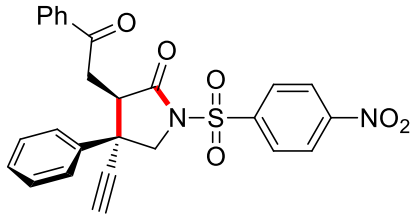
3a'e

(3*R*,4*S*)-4-Ethynyl-1-(methylsulfonyl)-3-(2-oxo-2-phenylethyl)-4-phenylpyrrolidin-2-one

Red oil, purified by silica gel chromatography using PE/EA 10:1, 74.3 mg, yield: 97%, dr = 10:1. 89% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (minor) = 23.7 min, t_R (major) = 25.8 min. $[\alpha]_D^{25}$ = -6.6 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.53 – 7.45 (m, 3H), 7.39 – 7.31 (m, 5H), 4.44 (d, *J* = 10.2 Hz, 1H), 4.33 (d, *J* = 10.2 Hz, 1H), 4.20 (t, *J* = 5.8 Hz, 1H), 3.35 (s, 3H), 3.12 (dd, *J* = 18.1, 6.1 Hz, 1H), 2.82 (dd, *J* = 18.1, 5.5 Hz, 1H), 2.60 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 173.3, 137.6, 136.0, 133.3, 129.1, 128.5, 128.4, 127.9, 126.3, 84.4, 74.0, 56.9, 50.8, 43.1, 40.5, 35.1. HRMS calc. for $C_{21}H_{19}NO_4S$ $[M+H]^+$: 382.1108, found: 382.1102.





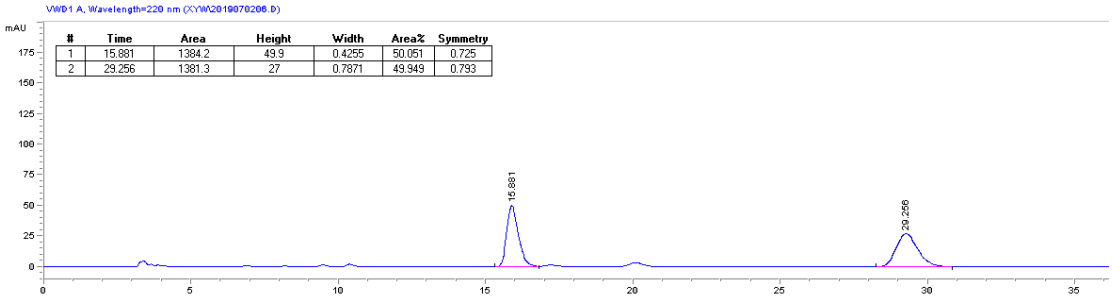


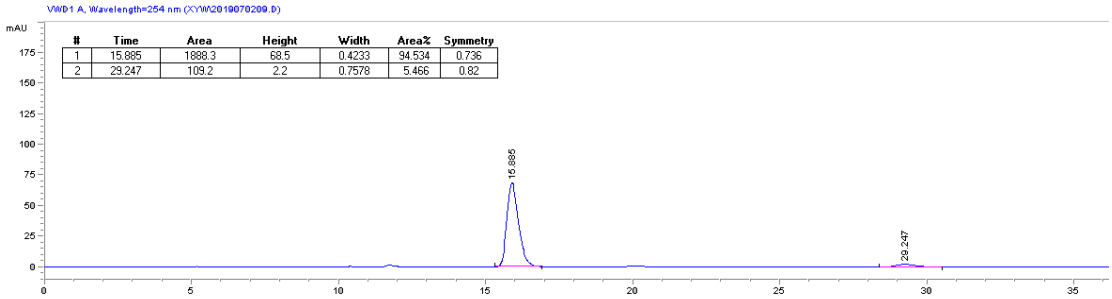
3a"e

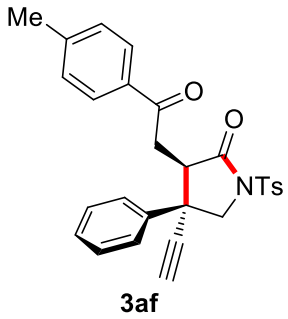
(3*R*,4*S*)-4-Ethynyl-1-((4-nitrophenyl)sulfonyl)-3-(2-oxo-2-phenylethyl)-4-phenylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 10:1, 87.0 mg, yield: 89%, dr = 12:1. 89% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 ml/min, 254 nm, 40 °C): t_R (minor) = 15.9 min, t_R (major) = 29.2 min. $[\alpha]_D^{25}$ = -26.8 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.9 Hz, 2H), 8.24 (d, *J* = 8.9 Hz, 2H), 7.69 – 7.67 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.21 (m, 5H), 4.43 (d, *J* = 10.3 Hz, 1H), 4.38 (d, *J* = 10.3 Hz, 1H), 4.13 (t, *J* = 5.7 Hz, 1H), 3.07 (dd, *J* = 18.2, 6.2 Hz, 1H), 2.73 (dd, *J* = 18.1, 5.2 Hz, 1H), 2.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 172.4, 151.0, 142.8, 137.5, 135.9, 133.4, 129.8, 129.1,

128.5, 128.0, 126.2, 124.3, 83.8, 74.5, 58.1, 50.3, 43.4, 34.9 (one signal missing due to overlap). HRMS calc. for $C_{26}H_{21}N_2O_6S$ $[M+H]^+$: 489.1115, found: 489.1114.



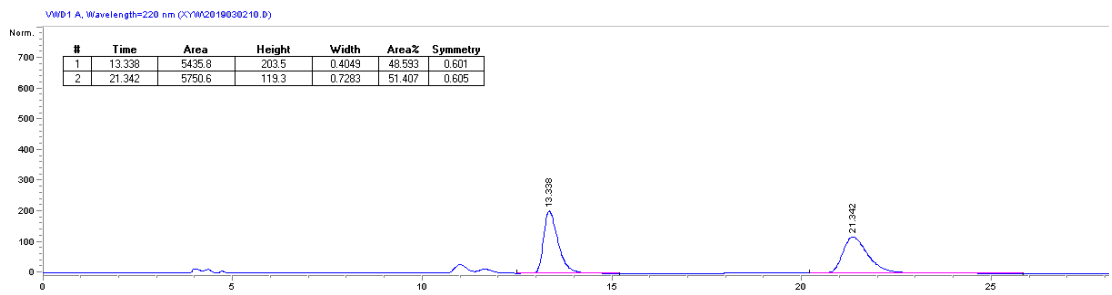


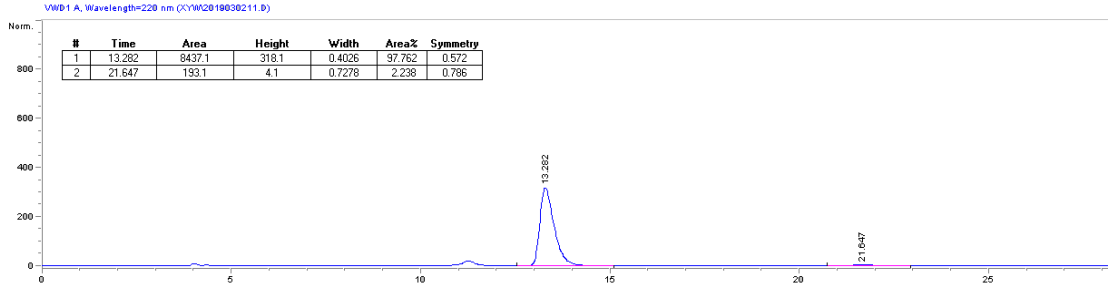


3af

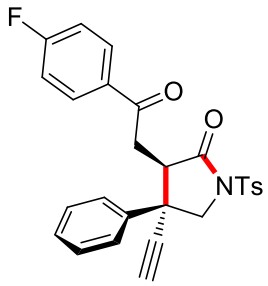
(3*R*,4*S*)-4-Ethynyl-3-(2-oxo-2-(*p*-tolyl)ethyl)-4-phenyl-1-tosylpyrrolidin-2-one

Yellow oil, purified by silica gel chromatography using PE/EA 10:1, 78.0 mg, yield: 83%, dr = 13:1. 95.5% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 13.3 min, t_R (minor) = 21.6 min. $[\alpha]_D^{25}$ = -27.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.20 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 4.14 (t, *J* = 5.8 Hz, 1H), 3.05 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.66 – 2.59 (m, 2H), 2.50 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 171.9, 145.5, 144.0, 138.0, 134.5, 133.6, 129.7, 129.1, 128.9, 128.2 (two signals overlapped), 128.1, 126.2, 83.9, 74.3, 57.9, 50.4, 43.0, 34.6, 21.6, 21.5. HRMS calc. for $C_{28}H_{25}NO_4S$ $[M+H]^+$: 472.1577, found: 472.1565.





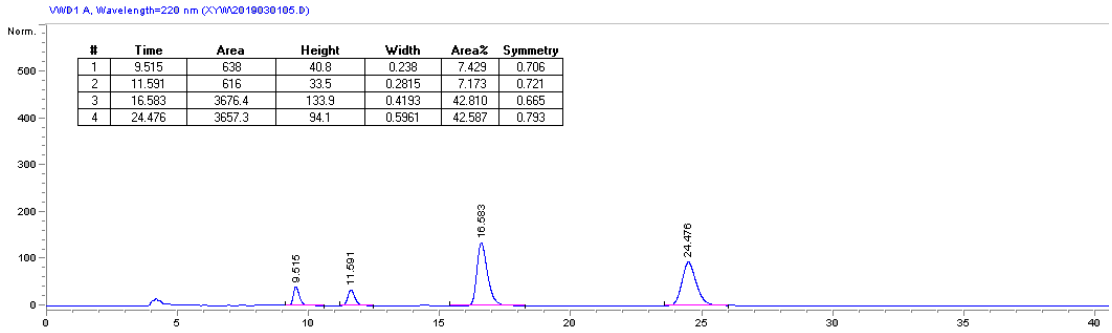
#	Time	Area	Height	Width	Area%	Symmetry
1	13.282	8437.1	318.1	0.4026	97.762	0.572
2	21.647	193.1	4.1	0.7278	2.238	0.786



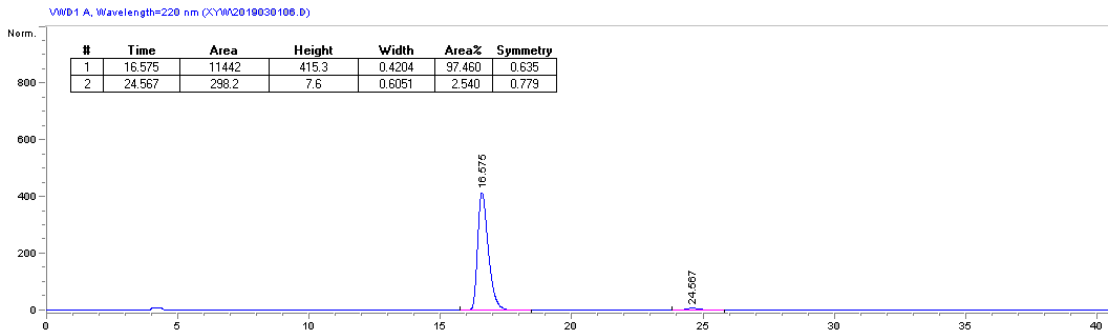
3ag

(3*R*,4*S*)-4-Ethynyl-3-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenyl-1-tosylpyrrolidin-2-one

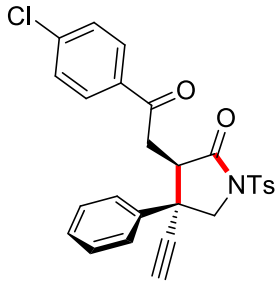
Yellow oil, purified by silica gel chromatography using PE/EA 10:1, 90.4 mg, yield: 95%, dr = 12:1. 95% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.6 min, t_R (minor) = 24.6 min. $[\alpha]_D^{25}$ = -31.5 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.75 – 7.72 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.19 (m, 5H), 7.07 – 7.01 (m, 2H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 4.12 (t, *J* = 5.9 Hz, 1H), 3.01 (dd, *J* = 17.9, 6.2 Hz, 1H), 2.63 – 2.57 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 171.8, 165.7 (d, $J_{C\text{-}F}$ = 255.2 Hz), 145.6, 137.9, 134.5, 132.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.6 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.8, 128.9, 128.2, 128.1, 126.1, 115.5 (d, $J_{C\text{-}F}$ = 21.9 Hz), 83.8, 74.4, 57.9, 50.4, 42.9, 34.6, 21.6. HRMS calc. for $C_{27}H_{22}FNO_4S$ $[M+H]^+$: 476.1326, found: 476.1316.



#	Time	Area	Height	Width	Area%	Symmetry
1	9.515	638	40.8	0.238	7.429	0.706
2	11.591	616	33.5	0.2815	7.173	0.721
3	16.583	3676.4	133.9	0.4193	42.810	0.665
4	24.476	3657.3	94.1	0.5961	42.587	0.793



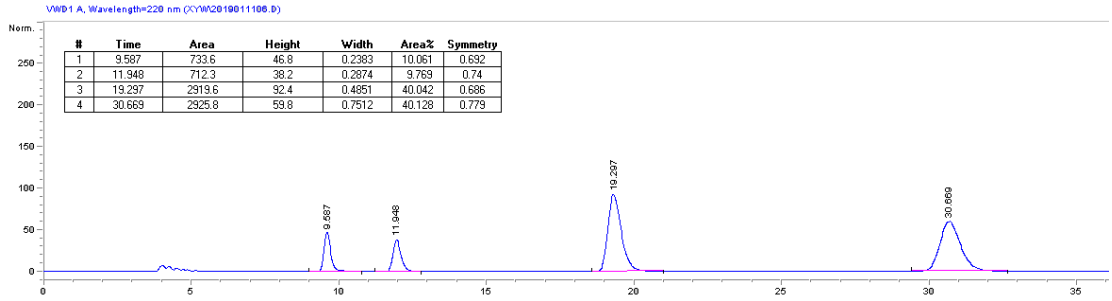
#	Time	Area	Height	Width	Area%	Symmetry
1	16.575	11442	415.3	0.4204	97.460	0.635
2	24.567	298.2	7.6	0.6051	2.540	0.779

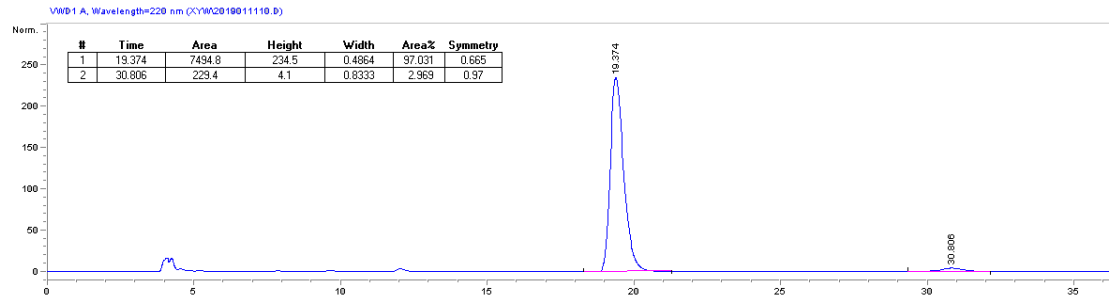


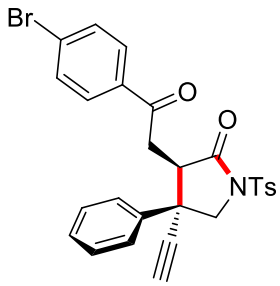
3ah

(3*R*,4*S*)-3-(2-(4-Chlorophenyl)-2-oxoethyl)-4-ethynyl-4-phenyl-1-tosylpyrrolidin-2-one

Yellow solid, purified by silica gel chromatography using PE/EA 10:1, 93.6 mg, yield: 95%, dr = 13:1. 94% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 19.4 min, t_R (minor) = 30.8 min. $[\alpha]_D^{25}$ = -32.4 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.16 (m, 5H), 4.38 (d, *J* = 10.4 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 4.08 (t, *J* = 5.9 Hz, 1H), 2.97 (dd, *J* = 18.0, 6.2 Hz, 1H), 2.59 – 2.53 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 171.7, 145.6, 139.6, 137.9, 134.5, 134.4, 129.8, 129.4, 128.9, 128.7, 128.3, 128.2, 126.1, 83.8, 74.4, 57.9, 50.4, 42.9, 34.7, 21.6. HRMS calc. for $C_{27}H_{22}ClNO_4S$ $[M+H]^+$: 492.1031, found: 492.1024.



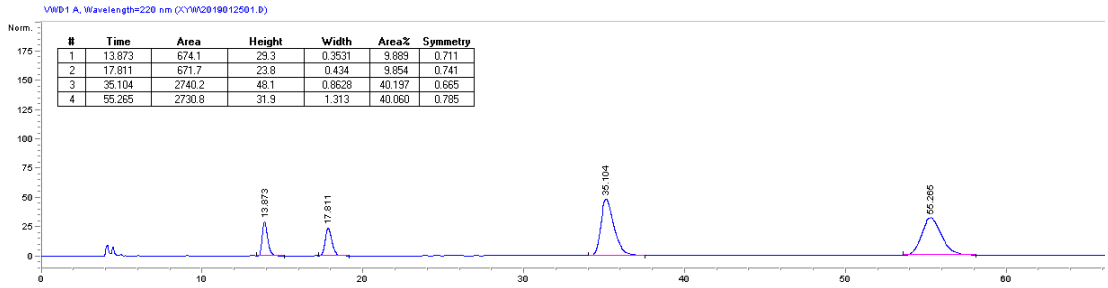


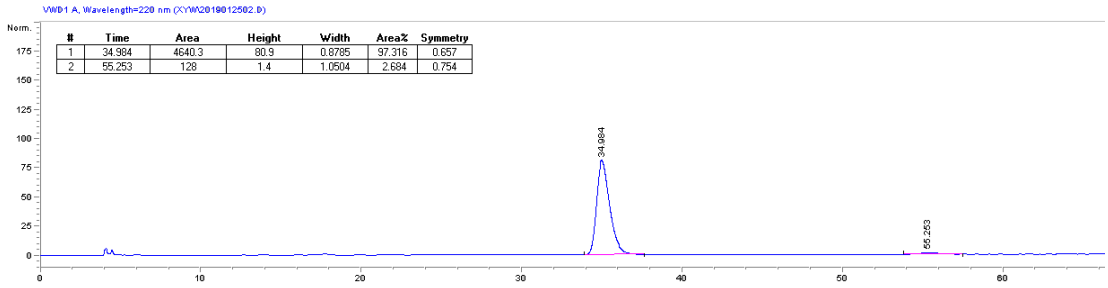


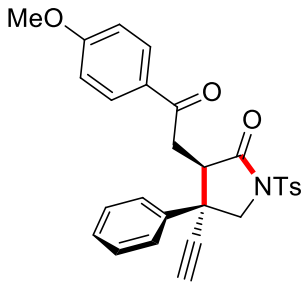
3ai

(3*R*,4*S*)-3-(2-(4-Bromophenyl)-2-oxoethyl)-4-ethynyl-4-phenyl-1-tosylpyrrolidin-2-one

Red solid, purified by silica gel chromatography using PE/EA 8:1, 98.1 mg, yield: 92%, dr = 10:1. 95% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 35.0 min, t_R (minor) = 55.3 min. $[\alpha]_D^{25}$ = -35.7 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.19 (m, 5H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 4.11 (t, *J* = 5.8 Hz, 1H), 3.00 (dd, *J* = 18.0, 6.1 Hz, 1H), 2.59 (q, *J* = 5.6 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 171.7, 145.6, 137.9, 134.8, 134.5, 131.7, 129.8, 129.5, 128.9, 128.4, 128.3, 128.1, 126.1, 83.8, 74.4, 57.9, 50.4, 42.9, 34.7, 21.6. HRMS calc. for $C_{27}H_{22}BrNO_4S$ $[M+H]^+$: 536.0526, found: 536.0519.





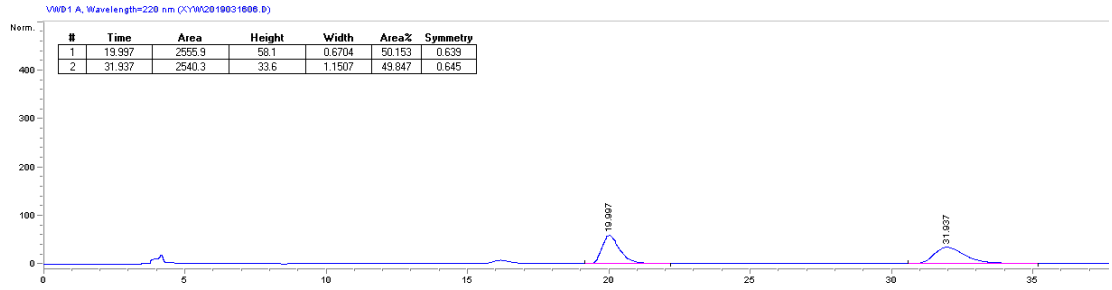


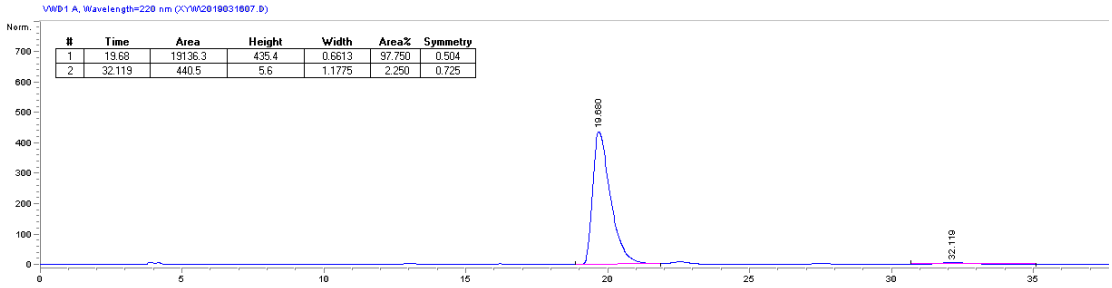
3aj

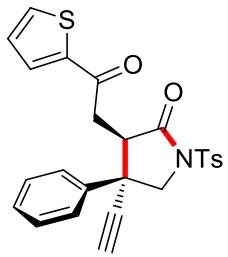
(3*R*,4*S*)-4-Ethynyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-4-phenyl-1-tosylpyrrolidin-2-one

Red solid, purified by silica gel chromatography using PE/EA 5:1, 88.5 mg, yield: 91%, dr = 13:1. 95.5% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 19.7 min, t_R (minor) = 32.1 min. $[\alpha]_D^{25}$ = -20.6 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.13 – 7.09 (m, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 4.31 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.4 Hz, 1H), 4.03 (t, *J* = 5.8 Hz, 1H), 3.71 (s, 3H), 2.91 (dd, *J* = 17.9, 6.0 Hz, 1H), 2.52 – 2.46 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 172.0, 163.5, 145.5, 138.0, 134.5, 130.2, 129.7, 129.1,

128.9, 128.1, 126.2, 113.5, 83.9, 74.3, 57.9, 55.3, 50.4, 43.0, 34.3, 21.6. HRMS calc. for $C_{28}H_{25}NO_5S$ $[M+H]^+$: 488.1526, found: 488.1516.



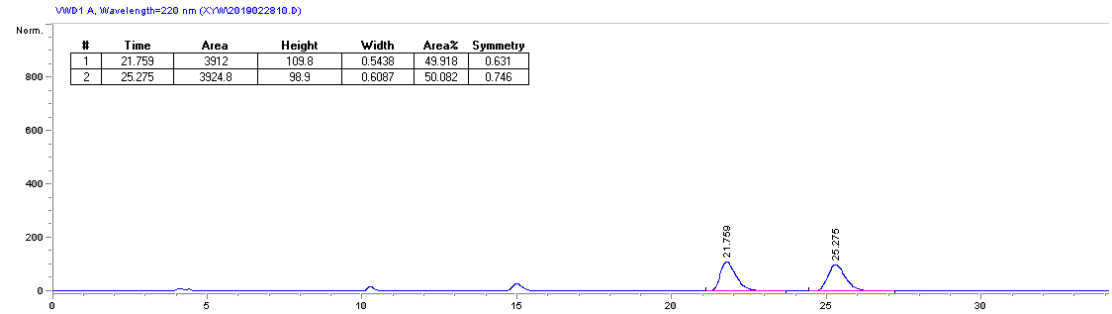


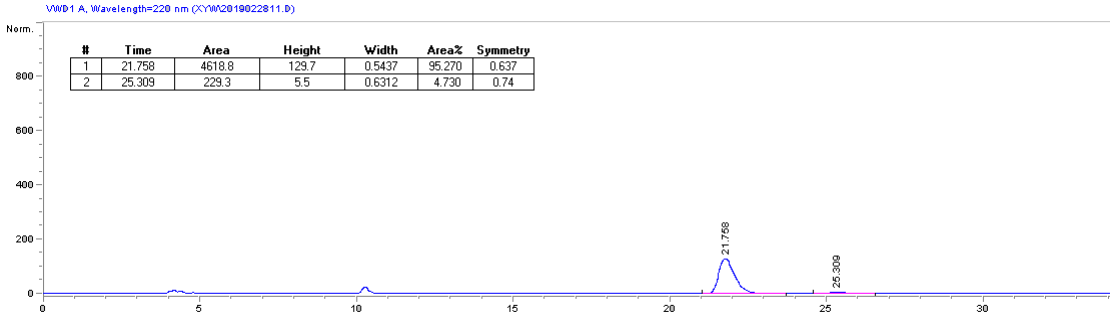


3ak

(3*R*,4*S*)-4-Ethynyl-3-(2-oxo-2-(thiophen-2-yl)ethyl)-4-phenyl-1-tosylpyrrolidin-2-one

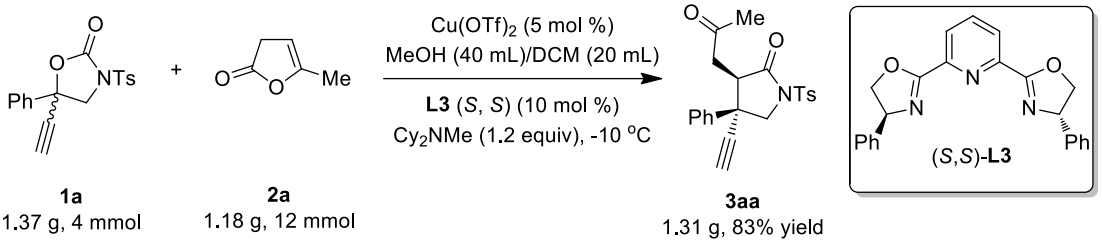
Red solid, purified by silica gel chromatography using PE/EA 10:1, 76.6 mg, yield: 83%, dr = 13:1. 90.5% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 75/25, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 21.8 min, t_R (minor) = 25.3 min. $[\alpha]_D^{25}$ = -33.2 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 4.9, 0.7 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.31 – 7.20 (m, 5H), 7.01 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.33 (d, *J* = 10.4 Hz, 1H), 4.07 (t, *J* = 6.0 Hz, 1H), 2.99 (dd, *J* = 17.5, 5.9 Hz, 1H), 2.62 – 2.56 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 171.6, 145.6, 143.1, 137.8, 134.5, 134.0, 132.1, 129.8, 128.9, 128.2, 128.1, 127.9, 126.1, 83.7, 74.5, 57.8, 50.5, 42.8, 35.2, 21.6. HRMS calc. for $C_{25}H_{21}NO_4S_2$ $[M+H]^+$: 464.0985, found: 464.0976.





VI. Gram-Scale Preparation and Transformations

(a) Gram-Scale Preparation of **3aa**

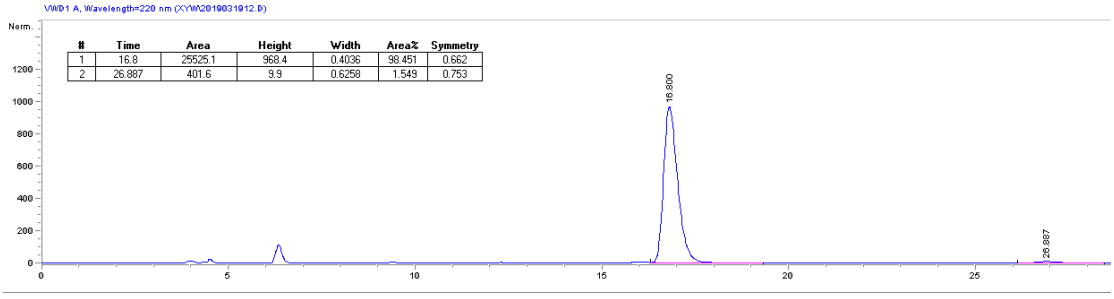


1a
1.37 g, 4 mmol

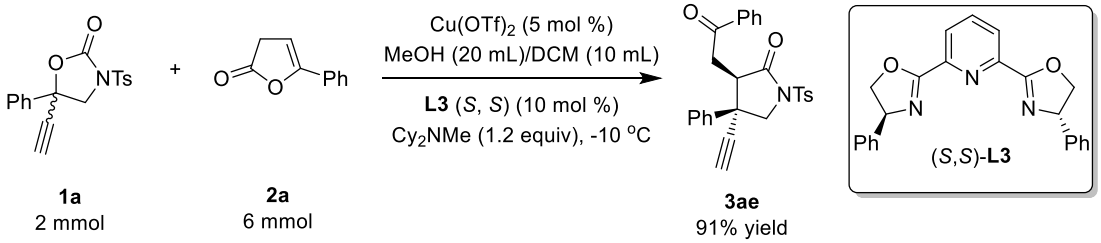
2a
1.18 g, 12 mmol

3aa
1.31 g, 83% yield

$Cu(OTf)_2$ (72.3 mg, 0.2 mmol) and **L3** (*S*, *S*) (47.8 mg, 0.4 mmol) were stirred at 60 °C in 20 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of enthynyl oxazolidinones (**1a**, 1.37 g, 4 mmol) and γ-substituted butenolides (**2a**, 1.18 g, 12 mmol) and Cy_2NMe (0.94 g, 4.8 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 40 mL) was added. The mixture was stirred at -10 °C for 72 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 10:1 to 5:1) to afford the pyrrolidinone (**3aa**), yield: 83%, dr = 13:1. 97% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.8 min, t_R (minor) = 26.9 min.



(b) Large-Scale Preparation of **3ae**



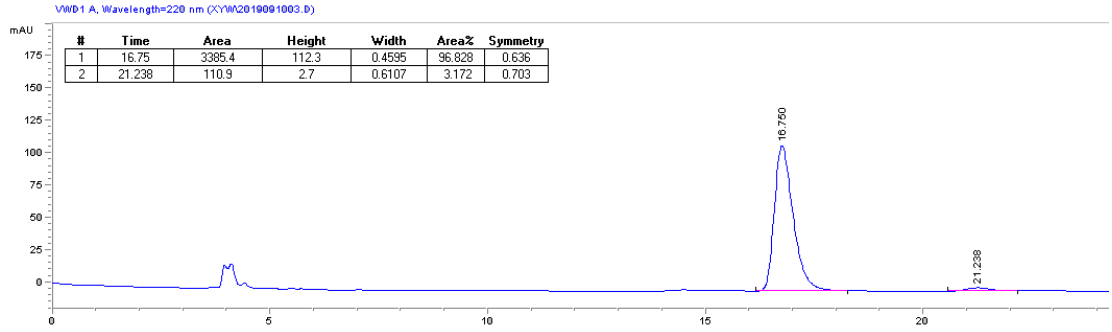
1a
2 mmol

2a
6 mmol

3ae
91% yield

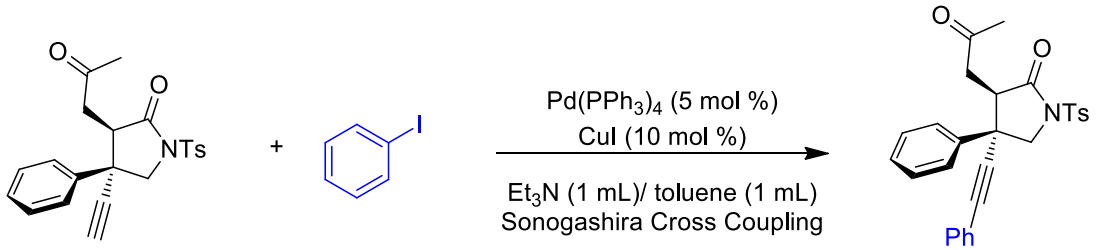
$Cu(OTf)_2$ (36.1 mg, 0.1 mmol) and **L3** (*S*, *S*) (74.0 mg, 0.4 mmol) were stirred at 60 °C in 10 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a

solution of enthynyl oxazolidinones (**1a**, 683 mg, 2 mmol) and γ-substituted butenolides (**2a**, 961 mg, 6 mmol) and Cy_2NMe (469 mg, 2.4 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 20 mL) was added. The mixture was stirred at -10 °C for 24 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 10:1 to 5:1) to afford the pyrrolidinone (**3ae**), yield: 91%, dr = 13:1. 94% *ee* was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.8 min, t_R (minor) = 21.2 min.



#	Time	Area	Height	Width	Area%	Symmetry
1	16.75	3385.4	112.3	0.4595	96.828	0.636
2	21.238	110.9	2.7	0.6107	3.172	0.703

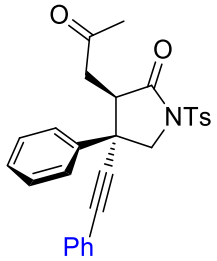
(c) Sonogashira Coupling Reaction



3aa

4, 96% yield
97% *ee*, 13:1 dr

3aa (79.1 mg, 0.2 mmol), iodobenzene (49.0 mg, 0.24 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (1.0 mL) and toluene (1.0 mL) were added to a pressure tube. The reaction mixture was stirred under N_2 condition for overnight. The solvent was removed under reduced pressure to get the crude product, which was purified by flash column chromatography on silica gel to afford the pure product **4**, yield: 96%.

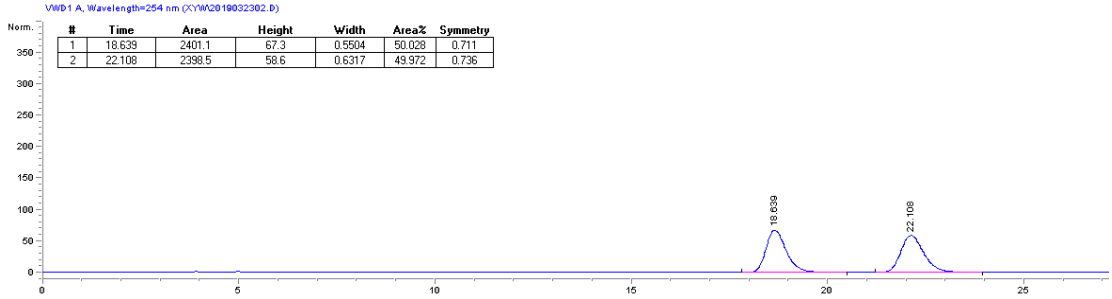


4

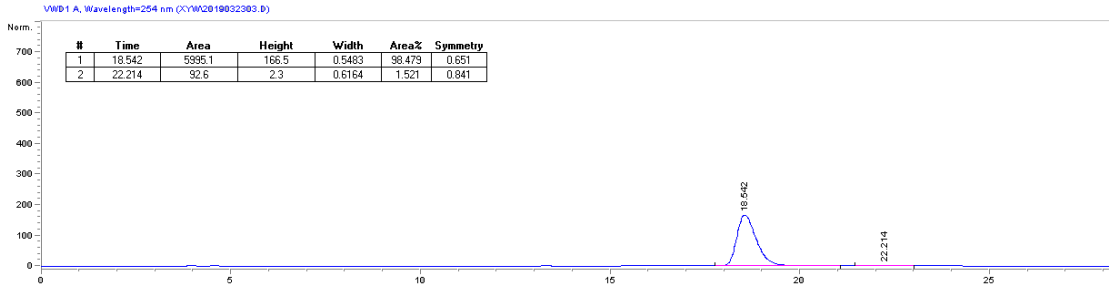
(3*R*,4*R*)-3-(2-Oxopropyl)-4-phenyl-4-(phenylethynyl)-1-tosylpyrrolidin-2-one

Colorless oil, 90.4 mg, yield: 96%, dr = 13:1. 97% *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 18.5 min, t_R (minor) = 22.2 min. $[\alpha]_D^{25}$ = 14.4 (*c* = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.36 (m,

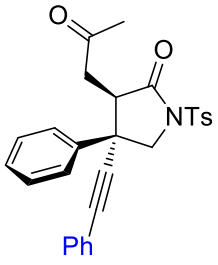
2H), 7.29 – 7.16 (m, 10H), 4.37 (d, *J* = 10.3 Hz, 1H), 4.27 (d, *J* = 10.3 Hz, 1H), 3.87 (dd, *J* = 6.9, 5.2 Hz, 1H), 2.43 – 2.37 (m, 4H), 2.08 (dd, *J* = 17.8, 5.2 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 172.1, 145.6, 138.6, 134.6, 131.7, 129.8, 129.0, 128.7, 128.4, 128.22, 128.18, 126.3, 122.1, 89.0, 86.0, 58.0, 50.9, 43.5, 39.4, 30.2, 21.7. HRMS calc. for $C_{28}H_{25}NO_4S$ $[M+H]^+$: 472.1577, found: 472.1568.



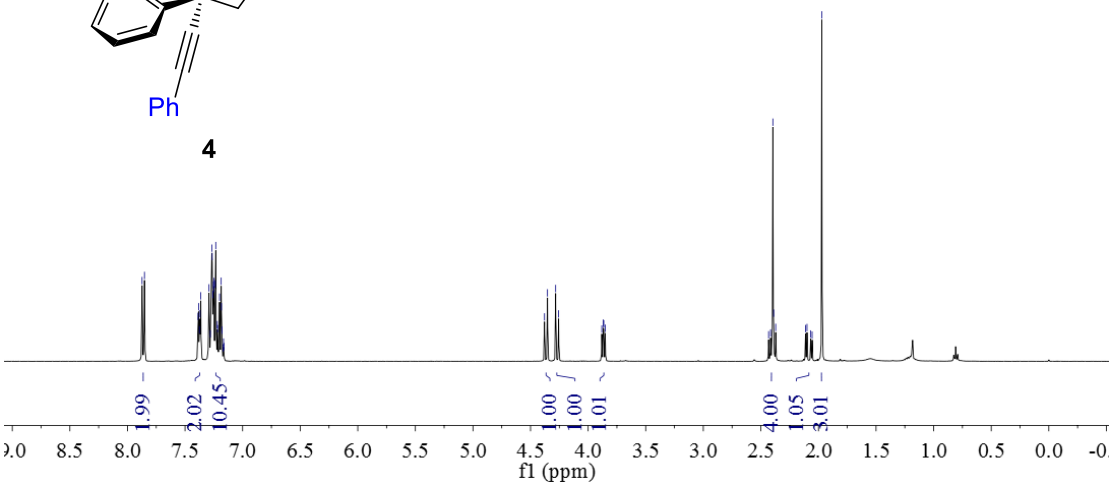
#	Time	Area	Height	Width	Area%	Symmetry
1	18.639	2401.1	67.3	0.5504	50.028	0.711
2	22.108	2398.5	58.6	0.6317	49.972	0.736

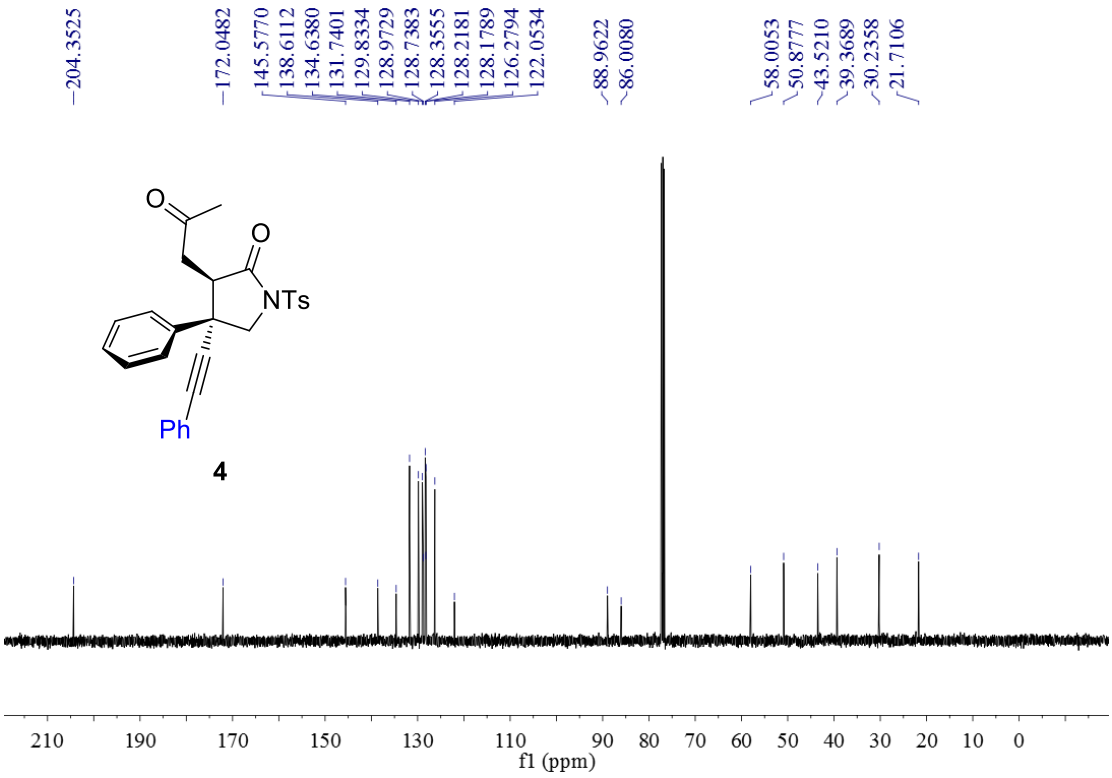


#	Time	Area	Height	Width	Area%	Symmetry
1	18.542	5995.1	166.5	0.5483	98.479	0.651
2	22.214	92.6	2.3	0.6164	1.521	0.841

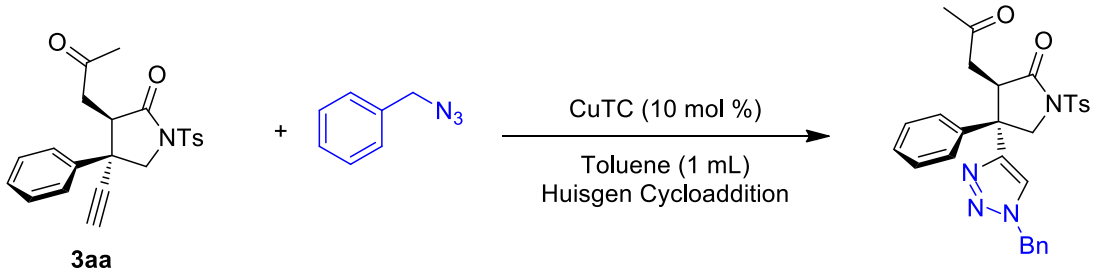


4



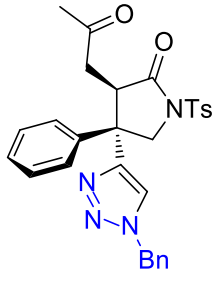


(d) Copper-Catalyzed Huisgen Cycloaddition Reaction



5, 81% yield
95% *ee*, 10:1 d.r.

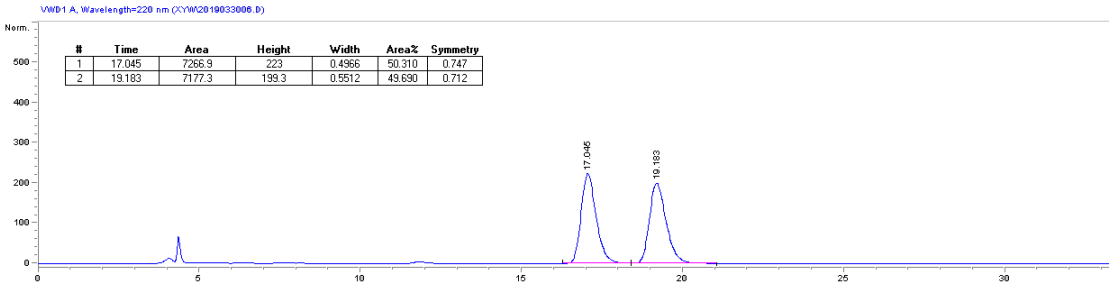
3aa (79.1 mg, 0.2 mmol), azides (49.0 mg, 0.24 mmol), CuTC (3.8 mg, 0.02 mmol) and toluene (1 mL) were added to a pressure tube. The reaction mixture was stirred under N_2 condition for 2h. The reaction was quenched by saturated NH_4Cl aqueous solution, extracted with DCM, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the pure product **5**, yield: 81%.

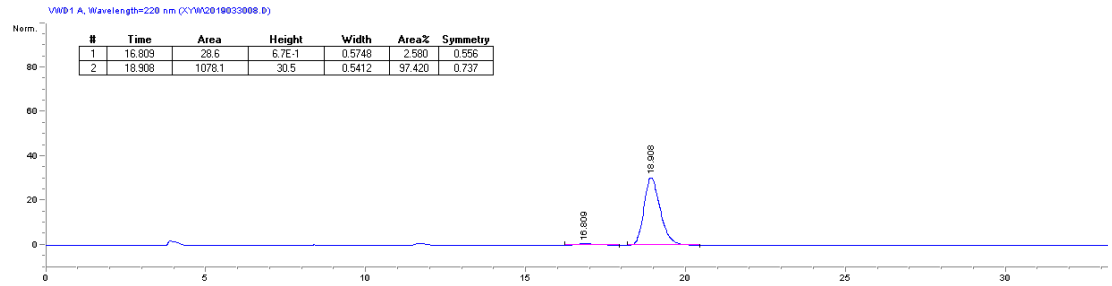


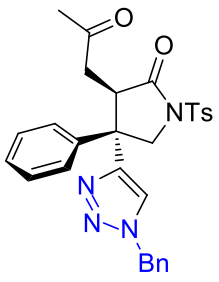
5

(3*R*,4*S*)-4-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-3-(2-oxopropyl)-4-phenyl-1-tosylpyrrolidin-2-one

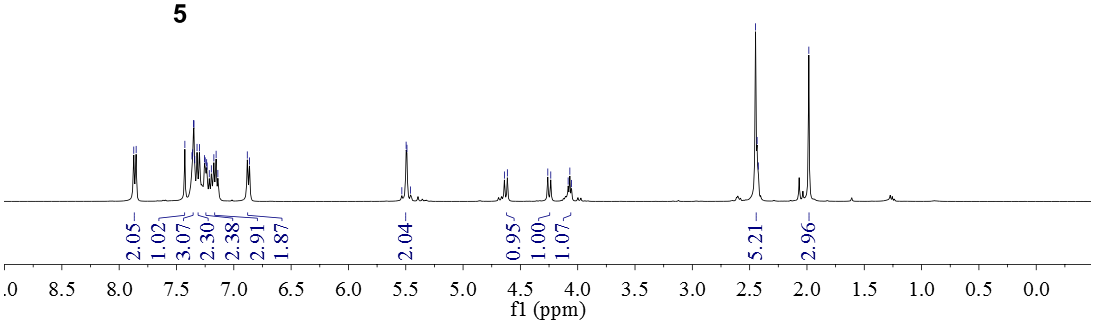
Colorless oil, 85.8 mg, yield: 81%, dr = 10:1. 95% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 0.8 ml/min, 220 nm, 40 °C): t_R (minor) = 16.8 min, t_R (major) = 18.9 min. $[\alpha]_D^{25}$ = 24.7 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.43 (s, 1H), 7.37 – 7.32 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.17 – 7.14 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 2H), 5.53 – 5.46 (m, 2H), 4.63 (d, *J* = 10.4 Hz, 1H), 4.25 (d, *J* = 10.4 Hz, 1H), 4.07 (t, *J* = 5.9 Hz, 1H), 2.45 – 2.42 (m, 5H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 172.6, 150.6, 145.3, 140.1, 134.5, 134.3, 129.6, 129.0, 128.9, 128.6 , 127.9, 127.8, 127.6, 126.7, 121.3, 56.8, 54.0, 48.4, 46.2, 40.1, 30.0, 21.5. HRMS calc. for $C_{29}H_{28}N_4O_4S$ $[M+H]^+$: 529.1904, found: 529.1892.

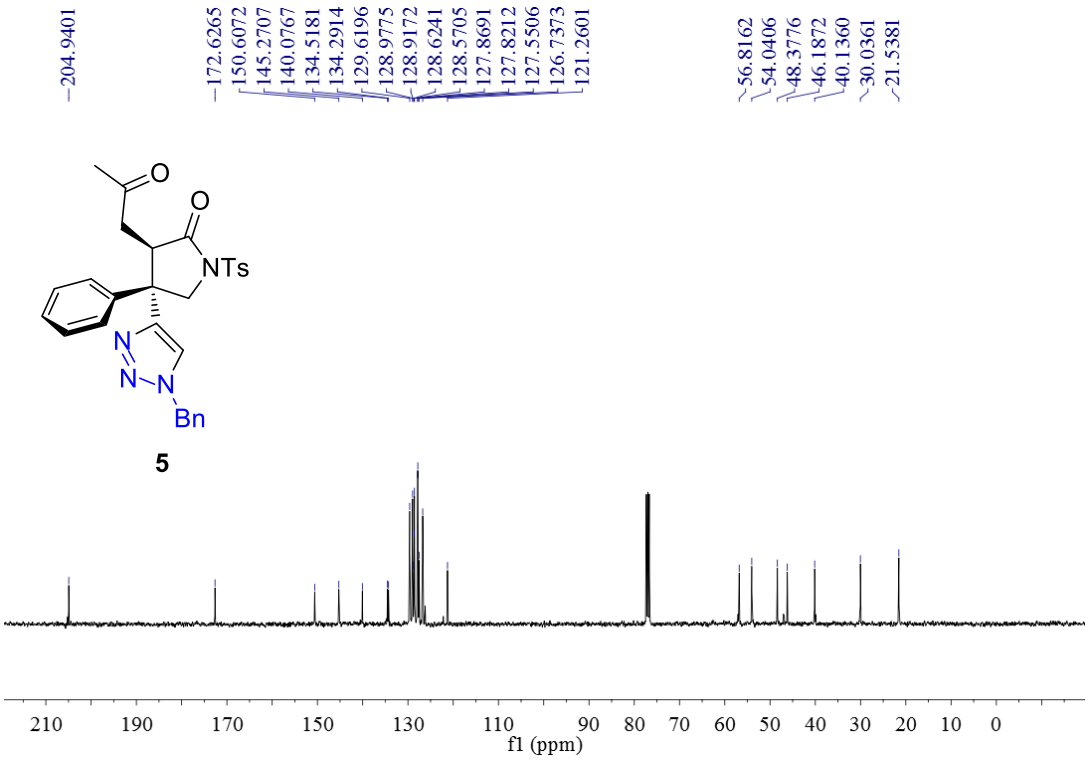




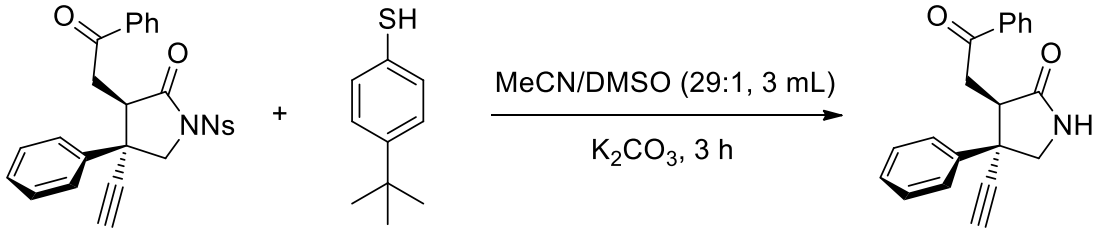


5





(e) Removal of protecting group

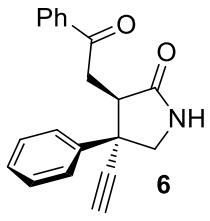


3a"e

6

88% yield, 87% *ee*

3a''e (48.8 mg, 0.1 mmol), 4-(*tert*-butyl)benzenethiol (50.0 mg, 0.3 mmol), K_2CO_3 (55.3 mg, 0.4 mmol) and MeCN/DMSO (29:1, 3 mL) were added to a pressure tube. The reaction mixture was stirred under air condition for 3 h. The reaction was quenched by saturated NH_4Cl aqueous solution, extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the pure product **6**, yield: 88%.

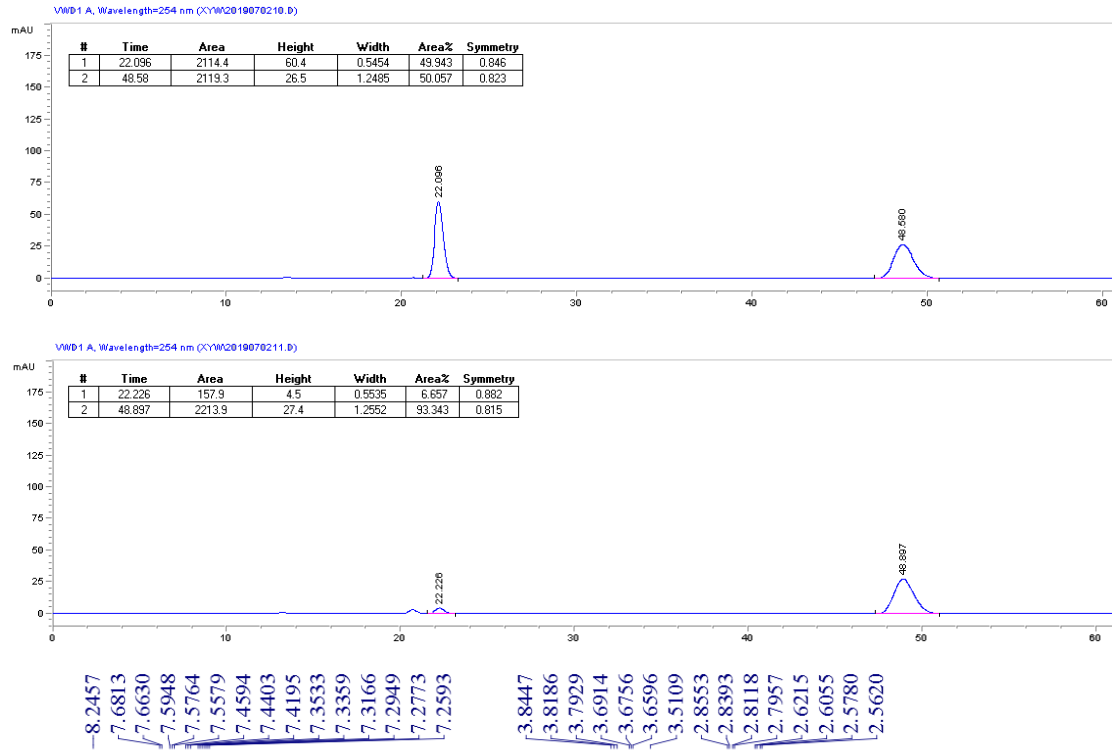


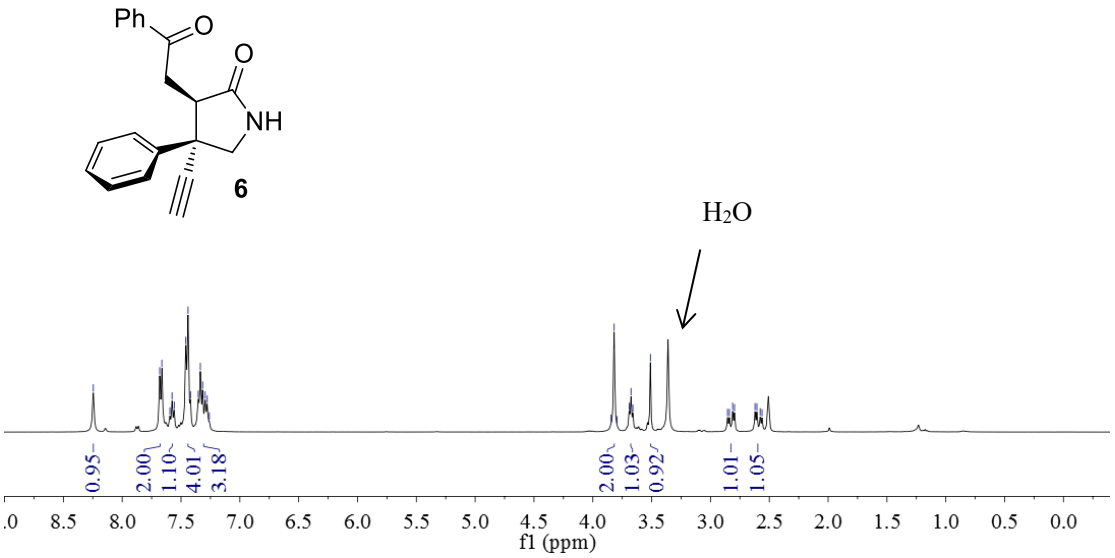
6

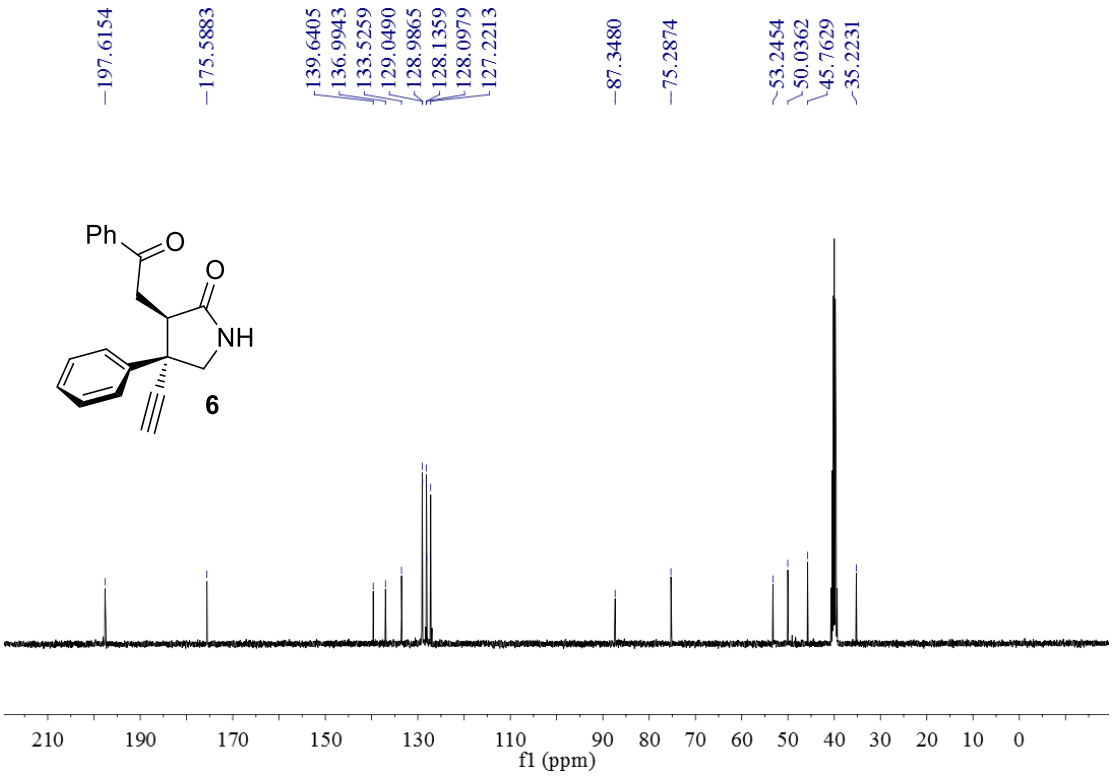
(3*R*,4*S*)-4-Ethynyl-3-(2-oxo-2-phenylethyl)-4-phenylpyrrolidin-2-one

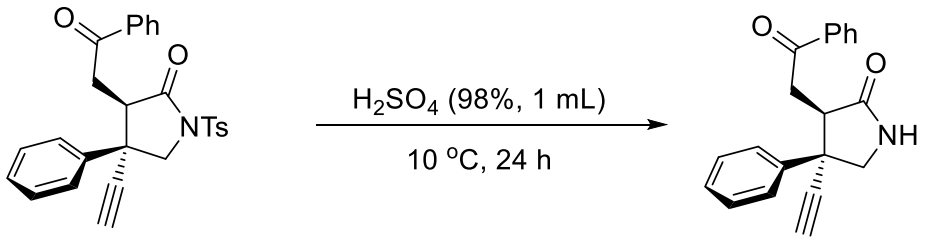
White solid, 26.7 mg, yield: 88%, dr = 12:1. 87% *ee* was determined by chiral HPLC (Chiralpak IC-H, *n*-hexane/*i*-PrOH = 60/40, 0.8 ml/min, 254 nm, 40 °C): t_R (minor) = 22.2 min, t_R (major) = 48.9 min. $[\alpha]_D^{25}$ = -18.3 (*c* = 1.0, CH_2Cl_2).^{1}H NMR (400 MHz, d_6-DMSO) δ 8.25 (brs, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.42 (m, 4H), 7.35 – 7.26 (m, 3H), 3.84 – 3.79 (m, 2H), 3.68 (t, *J* = 6.4 Hz, 1H), 3.51 (s, 1H), 2.83 (dd, *J* = 17.4, 6.4 Hz, 1H), 2.59 (dd, *J* = 17.4, 6.4 Hz, 1H). ^{13}C NMR

(101 MHz, d_6-DMSO) δ 197.6, 175.6, 139.6, 137.0, 133.5, 129.1, 129.0, 128.2, 128.1, 127.2, 87.4, 75.3, 53.3, 50.0, 45.8, 35.2. HRMS calc. for $C_{20}H_{19}N_2O$ $[M+H]^+$: 304.1332, found: 304.1330.







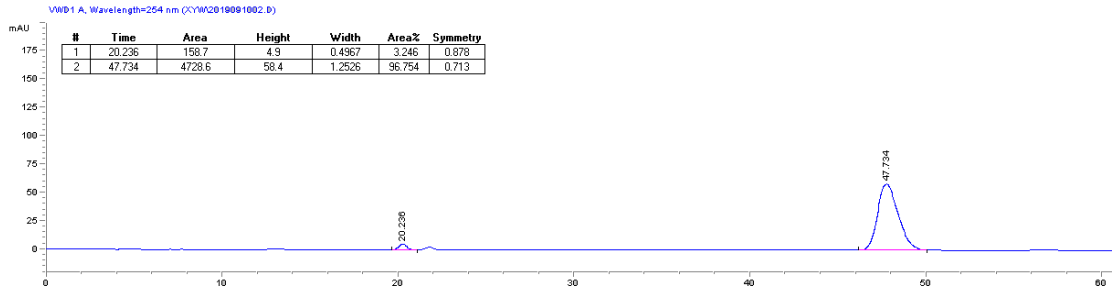


3ae

6

55% yield, 93.5% *ee*

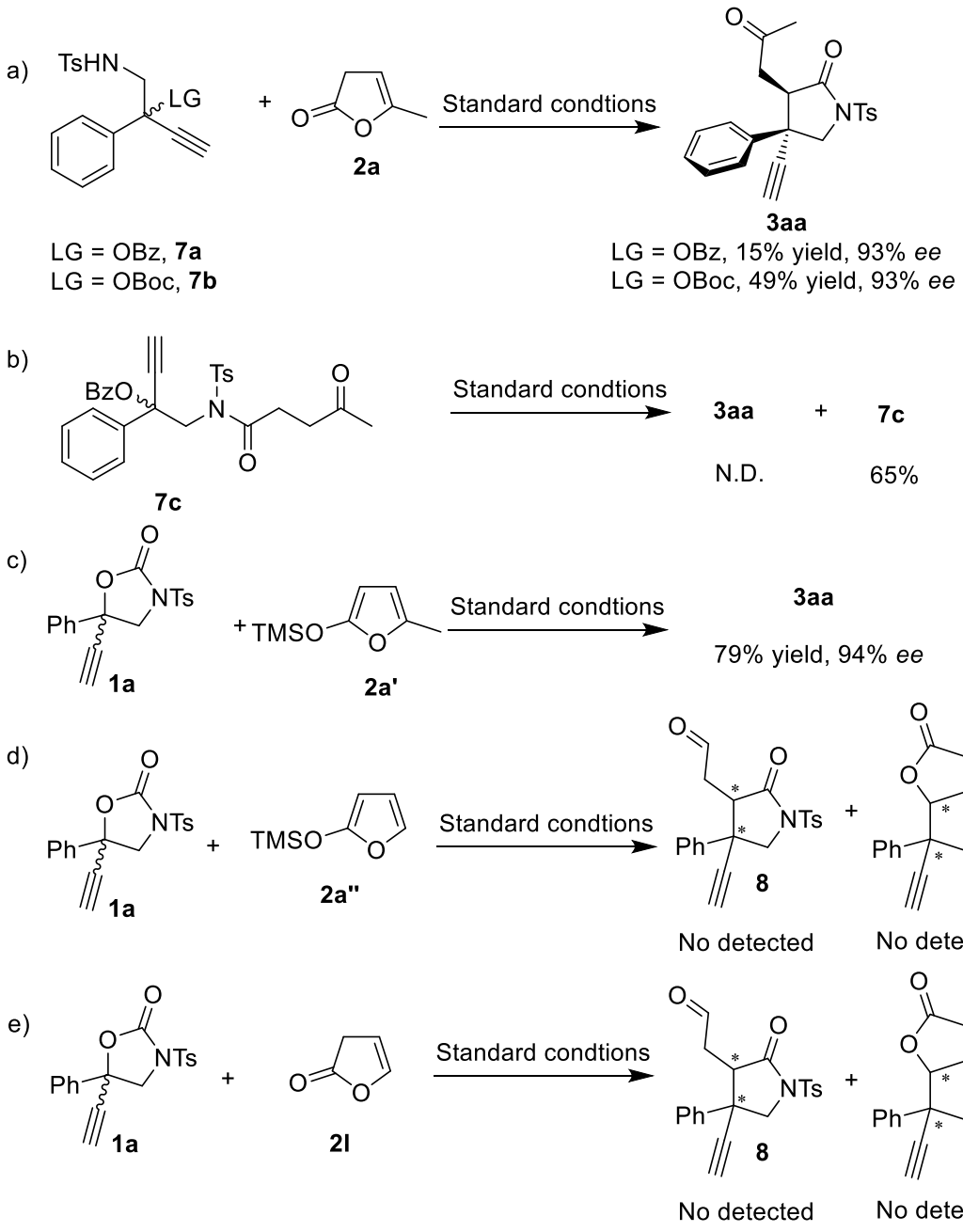
3ae (45.8 mg, 0.1 mmol) and concentrated H_2SO_4 (1 mL) were added to a pressure tube. The reaction mixture was stirred at 10 ºC for 24 h. Then the solution was added dropwise into Et_2O with stirring, and ice−water was added to the solution. The aqueous layer was made alkaline by addition of NaOH(aq) and was then extracted with EA. The combined organic layer was dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the pure product **6**, yield: 55%, dr = 13:1. 93.5% *ee* was determined by chiral HPLC (Chiralpak IC-H *n*-hexane/*i*-PrOH = 60/40, 0.8 ml/min, 254 nm, 40 ºC): t_R (minor) = 20.2 min, t_R (major) = 47.7 min.



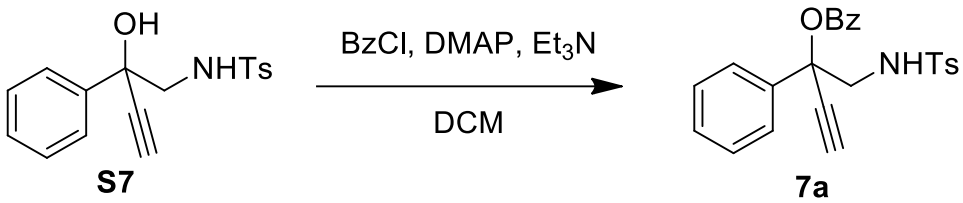
#	Time	Area	Height	Width	Area%	Symmetry
1	20.236	158.7	4.9	0.4967	3.246	0.878
2	47.734	4728.6	58.4	1.2526	96.754	0.713

VII. Mechanistic Studies

We have conducted preliminary mechanistic studies by performing some control experiments. First, linear propargylic esters **7a** and **7b** were prepared and submitted to the coupling with **1a** under standard conditions, giving the desirable cycloadducts. Although both the yield and enantioselectivity not so satisfactory, the result suggested that the reaction should proceed through the decarboxylative ring-opening of **1a** to form the copper allenylidene complex zwitterionic pairs B, following by the attack of **2a**. The treatment of **7c** under standard conditions was not afforded target product 3aa, suggesting that the ammonolysis should be intramolecular. Siloxyfuran (**2a'**) was also a suitable participant, although a decreased yield of **3aa** was achieved. Surprisingly, the expected pyrrolidinone (**8**) was not observed under the standard conditions using **2a"** or **2l** as the coupling reagent, and Michael adduct (**9**) was also not observed.

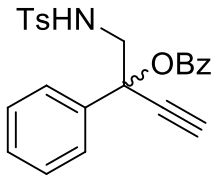


(a) Synthesis of Linear Propargylic Esters[3]



S7 **7a**

To a solution of amino alcohol **S7** (631 mg, 2 mmol) and DMAP (24.4 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added BzCl (351 mg, 2.5 mmol) and Et_3N (304 mg, 3 mmol). The reaction mixtures was allowed to warm to room temperature and stirred for 24 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: PE:EtOAc = 7:1) to give the desired product **7a**.

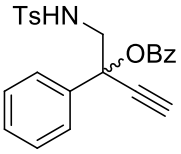


7a

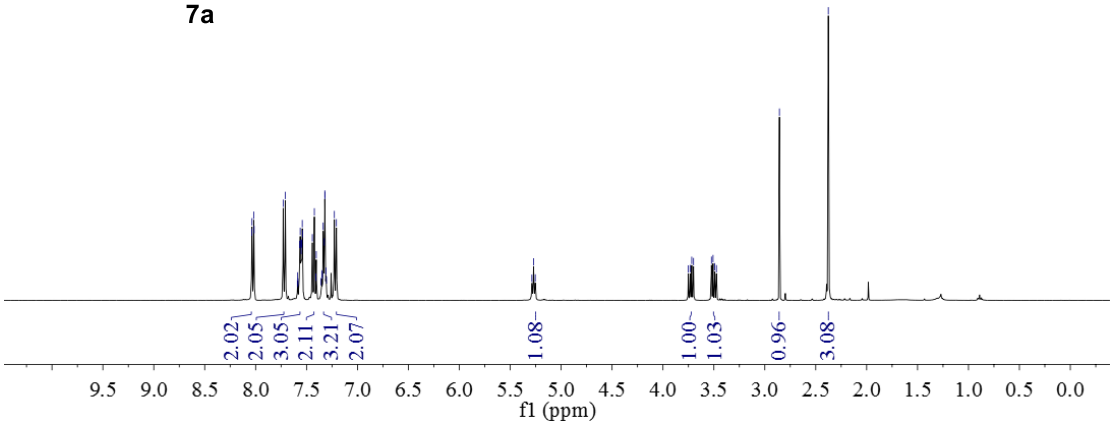
1-(4-Methylphenylsulfonamido)-2-phenylbut-3-yn-2-yl benzoate

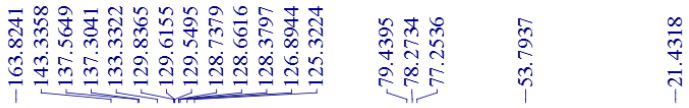
White solid, 210 mg, yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.3, 1.2 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.59 – 7.54 (m, 3H), 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 5.27 (t, J = 6.7 Hz, 1H), 3.73 (dd, J = 13.3, 7.1 Hz, 1H), 3.50 (dd, J = 13.3, 6.4 Hz, 1H), 2.86 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 143.3, 137.6, 137.3, 133.3, 129.8, 129.6, 129.6, 128.7, 128.6, 128.4, 126.9, 125.3, 79.4, 78.3, 77.3, 53.8, 21.4. HRMS calc. for $C_{24}H_{21}NO_4S$ $[M+H]^+$: 418.1119, found: 418.1114.

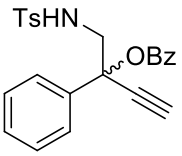

8.0385
8.0359
8.0181
8.0148
7.7293
7.7086
7.5871
7.5840
7.5684
7.5622
7.5569
7.5532
7.5497
7.5465
7.5420
7.5382
7.4432
7.4233
7.4084
7.4044
7.3591
7.3501
7.3455
7.3368
7.3261
7.3207
7.3184
7.3086
7.3041
7.2269
7.2069
5.2874
5.2708
5.2540
3.7509
3.7332
3.7177
3.7001
3.5242
3.5083
3.4911
3.4751
2.8565
2.3764


TsHN
OBz

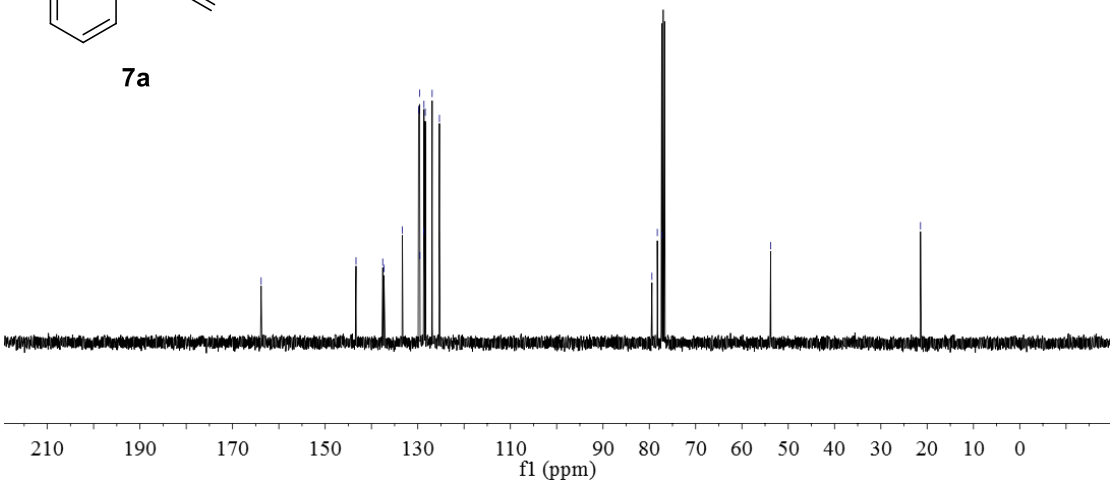
7a

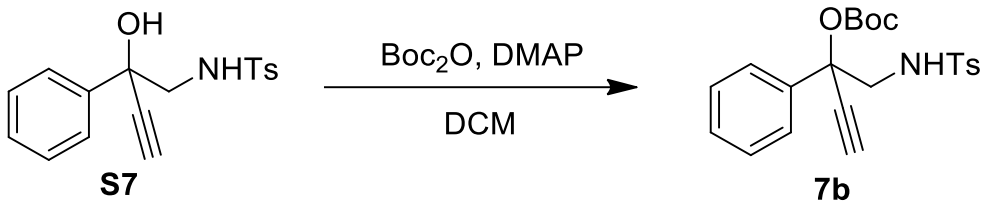

2.02
2.05
3.05
2.11
3.21
2.07
1.08
1.00
1.03
0.96
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.8241
143.3358
137.5649
137.3041
133.3322
129.8365
129.6155
129.5495
128.7379
128.6616
128.3797
126.8944
125.3224
79.4395
78.2734
77.2536
53.7937
21.4318


TsHN
OBz

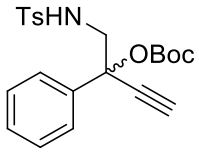
7a


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



S7 7b

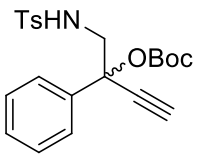
To a solution of amino alcohol **S7** (631 mg, 2 mmol) and DMAP (24.4 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added Boc_2O (873 mg, 4 mmol). The reaction mixtures was allowed to warm to room temperature and stirred for 24 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: PE:EtOAc = 7:1) to give the desired product **7b**.



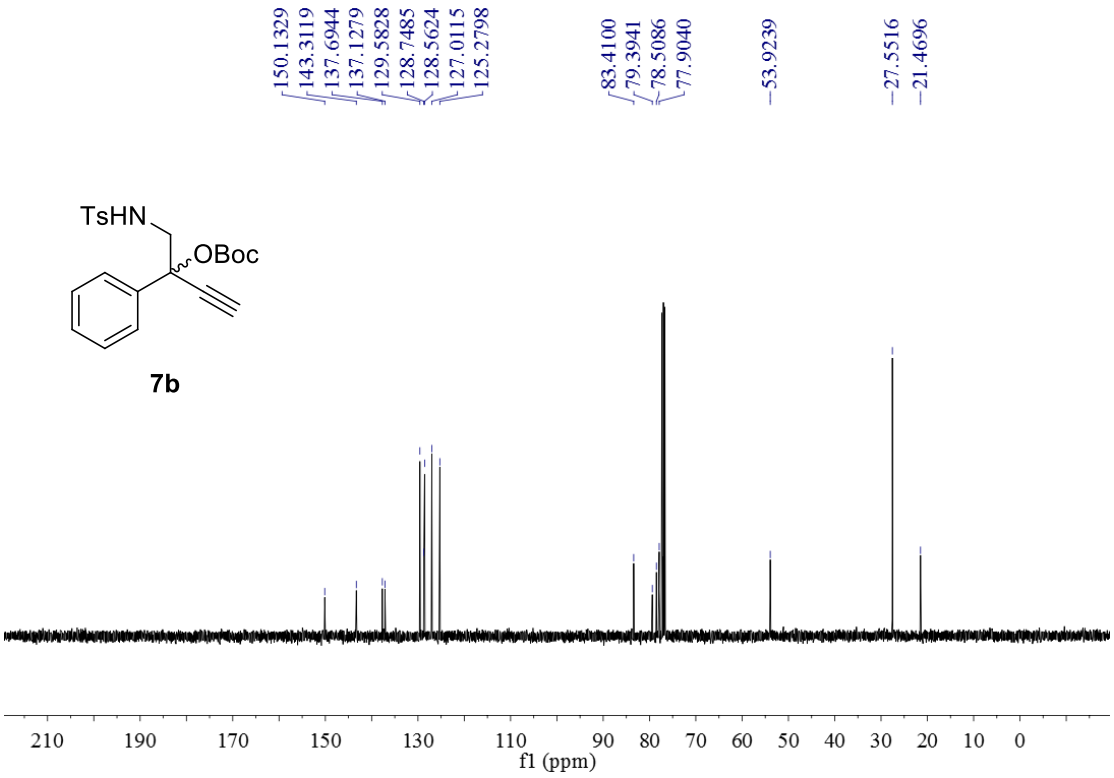
7b

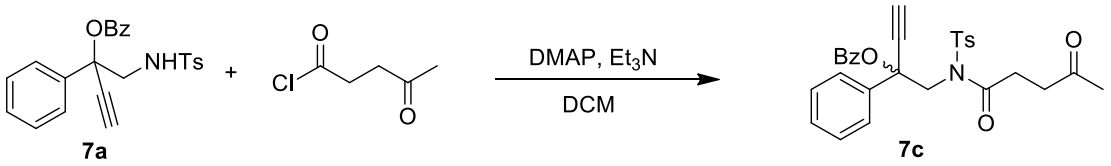
***tert*-Butyl (1-(4-methylphenylsulfonamido)-2-phenylbut-3-yn-2-yl) carbonate**

White solid, 125 mg, yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.36 – 7.31 (m, 3H), 7.24 (d, J = 8.0 Hz, 2H), 4.93 (t, J = 6.6 Hz, 1H), 3.48 – 3.37 (m, 2H), 2.80 (s, 1H), 2.40 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 143.3, 137.7, 137.1, 129.6, 128.8, 128.6, 127.0, 125.3, 83.4, 79.4, 78.5, 77.9, 53.9, 27.6, 21.5. HRMS calc. for $C_{22}H_{25}NO_5S$ $[M+H]^+$: 414.1381, found: 414.1375.

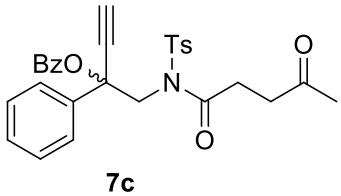


7b



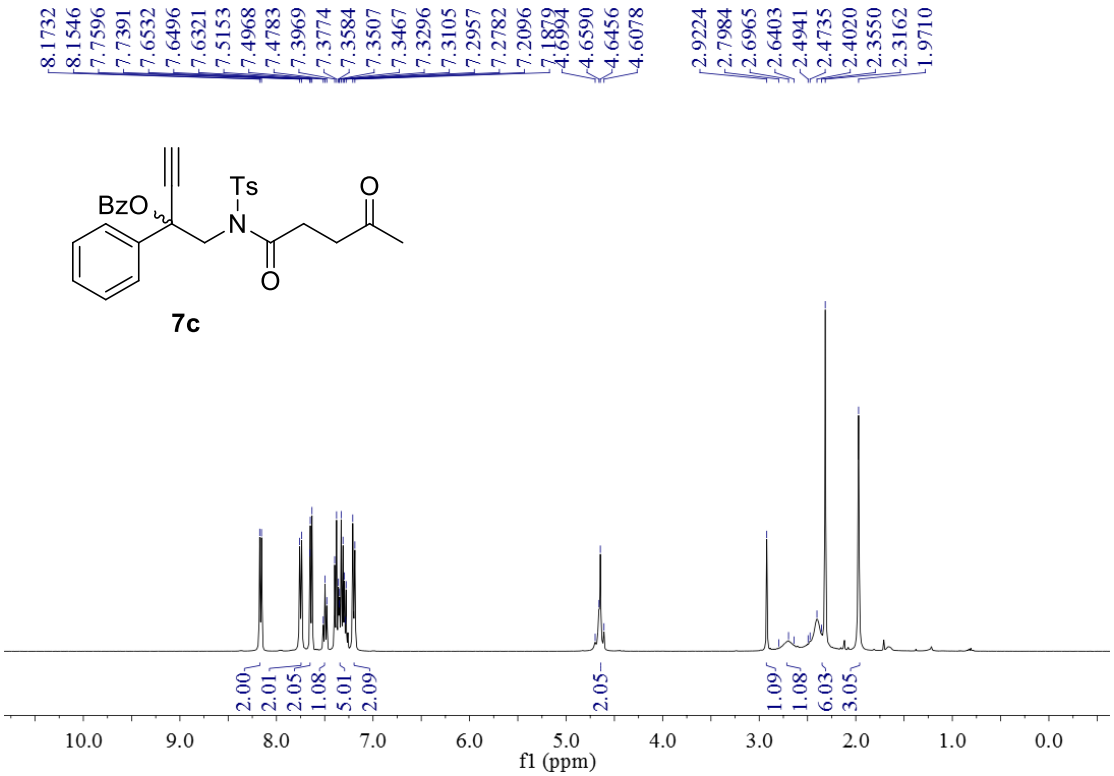


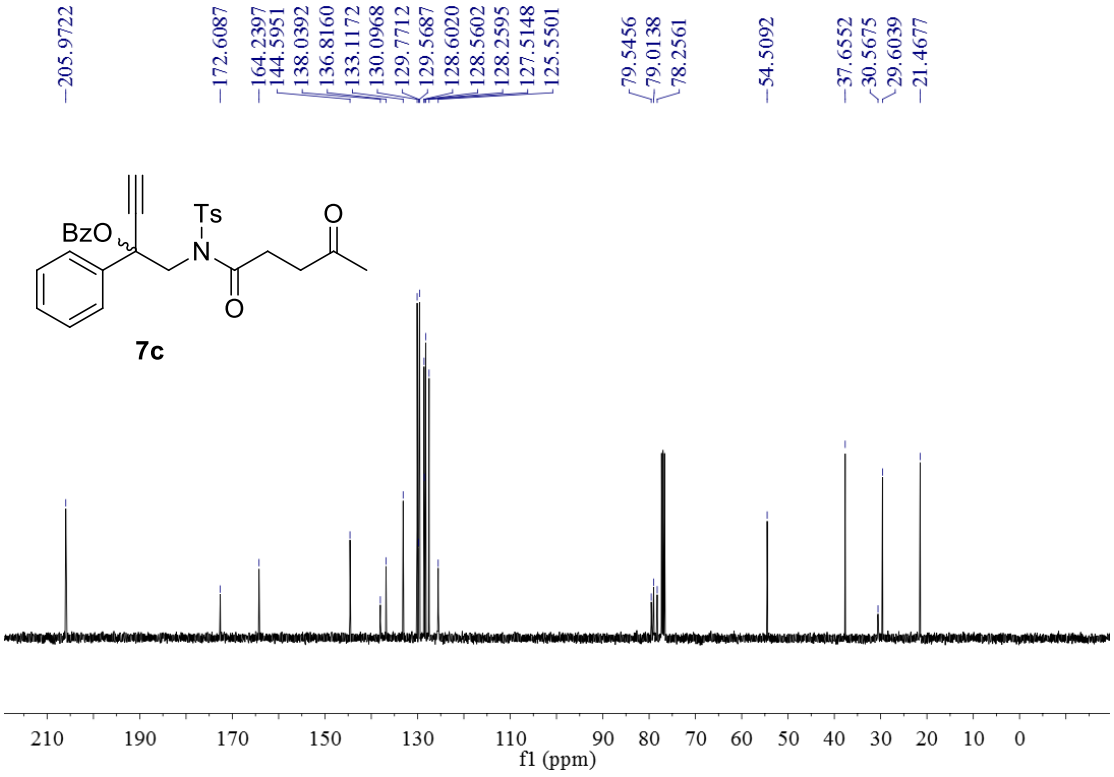
To a solution of propargylic ester **7a** (210 mg, 0.5 mmol) and DMAP (6.1 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added 4-oxopentanoyl chloride (87.5 mg, 0.65 mmol) and Et_3N (75.9 mg, 0.75 mmol). The reaction mixtures was allowed to warm to room temperature and stirred for 24 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: PE:EtOAc = 10:1) to give the desired product **7c**.



1-(4-Oxo-*N*-tosylpentanamido)-2-phenylbut-3-yn-2-yl benzoate

Colorless oil, 176 mg, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.65 – 7.63 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.20 (d, J = 8.7 Hz, 2H), 4.70 – 4. 61 (m, 2H), 2.92 (s, 1H), 2.80 – 2.64 (m, 1H), 2.49 – 2.32 (m, 6H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 172.6, 164.2, 144.6, 138.0, 136.8, 133.1, 130.1, 129.8, 129.6, 128.6, 128.6, 128.3, 127.5, 125.6, 79.6, 79.0, 78.3, 54.5, 37.7, 30.6, 29.6, 21.5. HRMS calc. for $C_{29}H_{27}NO_6S$ $[M+H]^+$: 535.1897, found: 535.1889.





(b)Transformation of Linear Propargylic Esters

LG = OBz, **7a**
LG = OBoc,7**b**

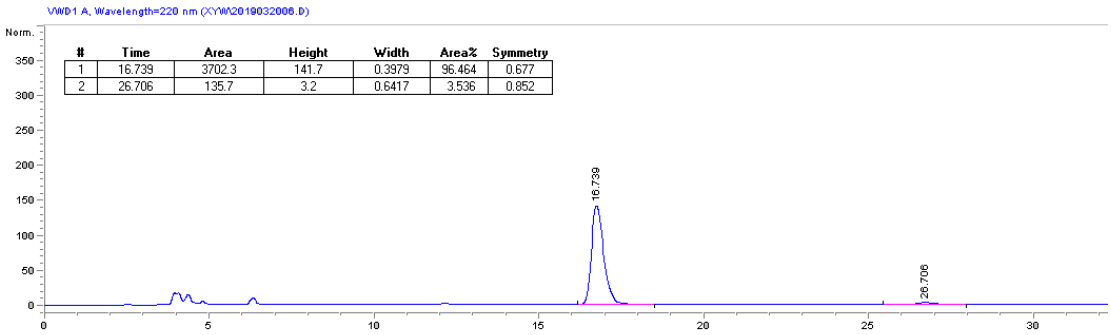
2a

3aa

LG = OBz, 15% yield, 93% *ee*
LG = OBoc, 49% yield, 93% *ee*

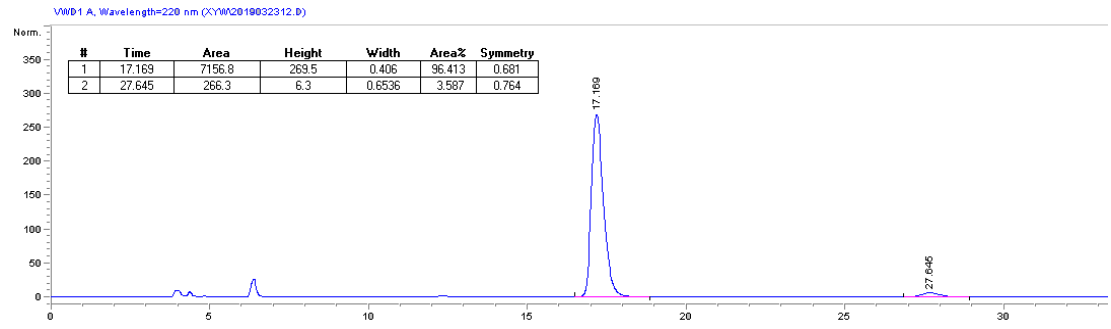
$Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*, *S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of **7a** or **7b** (0.2 mmol), **2a** (58.9 mg, 0.6 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 10:1 to 5:1) to afford the pyrrolidinone (**3aa**).

When LG = OBz, 11.9 mg, 15% yield of **3aa**. 93% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.7 min, t_R (major) = 26.7 min.

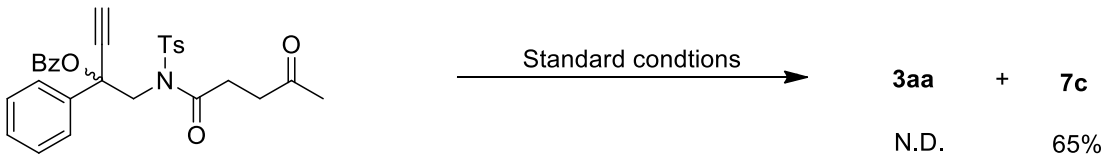


#	Time	Area	Height	Width	Area%	Symmetry
1	16.739	3702.3	141.7	0.3979	96.464	0.677
2	26.706	135.7	3.2	0.6417	3.536	0.852

When LG = OBoc, 38.8 mg, 49% yield of **3aa**. 93% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 17.2 min, t_R (major) = 27.6 min.



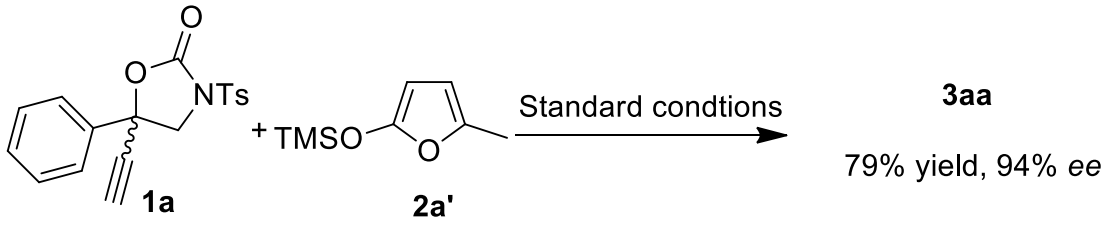
#	Time	Area	Height	Width	Area%	Symmetry
1	17.169	7156.8	269.5	0.406	96.413	0.681
2	27.645	266.3	6.3	0.6536	3.587	0.764



7c

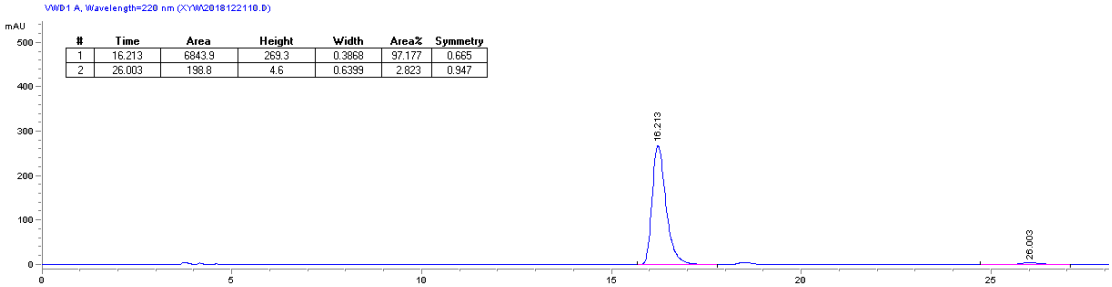
$Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*, *S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of **7c** (103.5 mg, 0.2 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 8:1) to recover **6c**.

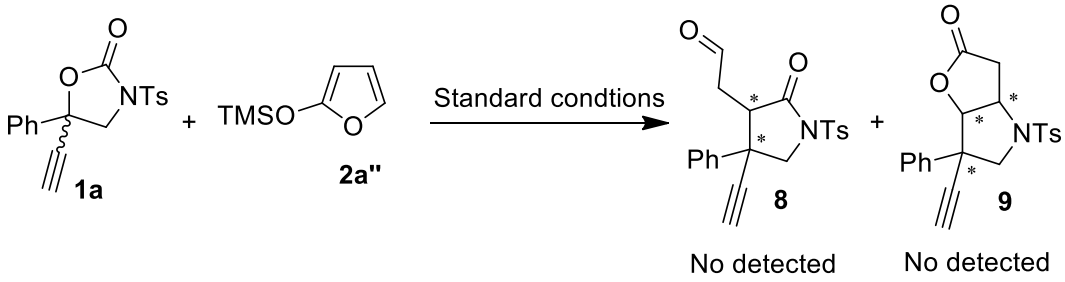
(c) Siloxyfuran as the Coupling Reagent



$Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*, *S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of **1a** (68.3 mg, 0.2 mmol), **2a'** (102.2 mg, 0.6 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, filtered through a pad of celite, and concentrated in vaccum. The concentrate was then purified by silica gel chromatography (PE/EtOAc, 10:1 to 5:1) to afford the pyrrolidinone (**3aa**).

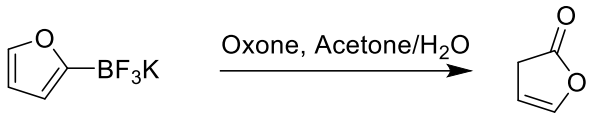
94% *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 ml/min, 220 nm, 40 °C): t_R (major) = 16.2 min, t_R (major) = 26.0 min.



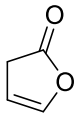


$Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*, *S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of **1a** (68.3 mg, 0.2 mmol), **2a'** (93.8 mg, 0.6 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, and a complex mixture was observed by TLC.

(d) Synthesis of furan-2(3*H*)-one[4]

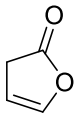


To a 50 mL round-bottom flask containing a mixture of potassium furan-2-yltrifluoroborate (174 mg, 1.0 mmol) and acetone (5 mL, 0.2 M) was added Oxone (5 mL of a 0.2 M solution in H_2O, 1 equiv) in one portion. The reaction mixture was stirred at room temperature until 11B NMR indicated completion of the reaction (~2 min). To the crude mixture was added H_2O (5 mL) and aqueous HCl (0.1 M, 3 mL), and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, concentrated, and dried in vacuo. The crude extract was filtered through a small plug of silica topped with charcoal, with CH_2Cl_2 as eluent, to afford the desired pure product in 98% yield (0.1 g) as yellow oil.

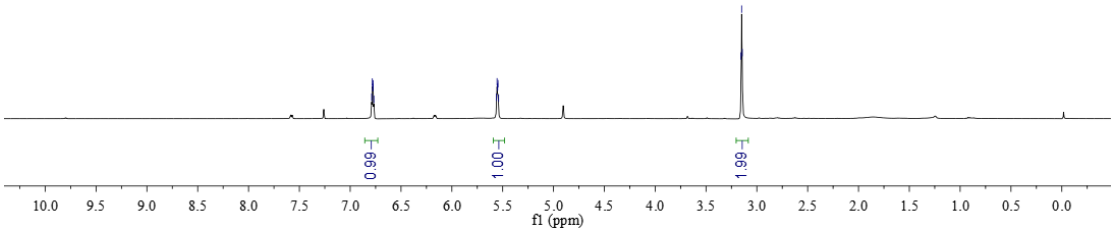


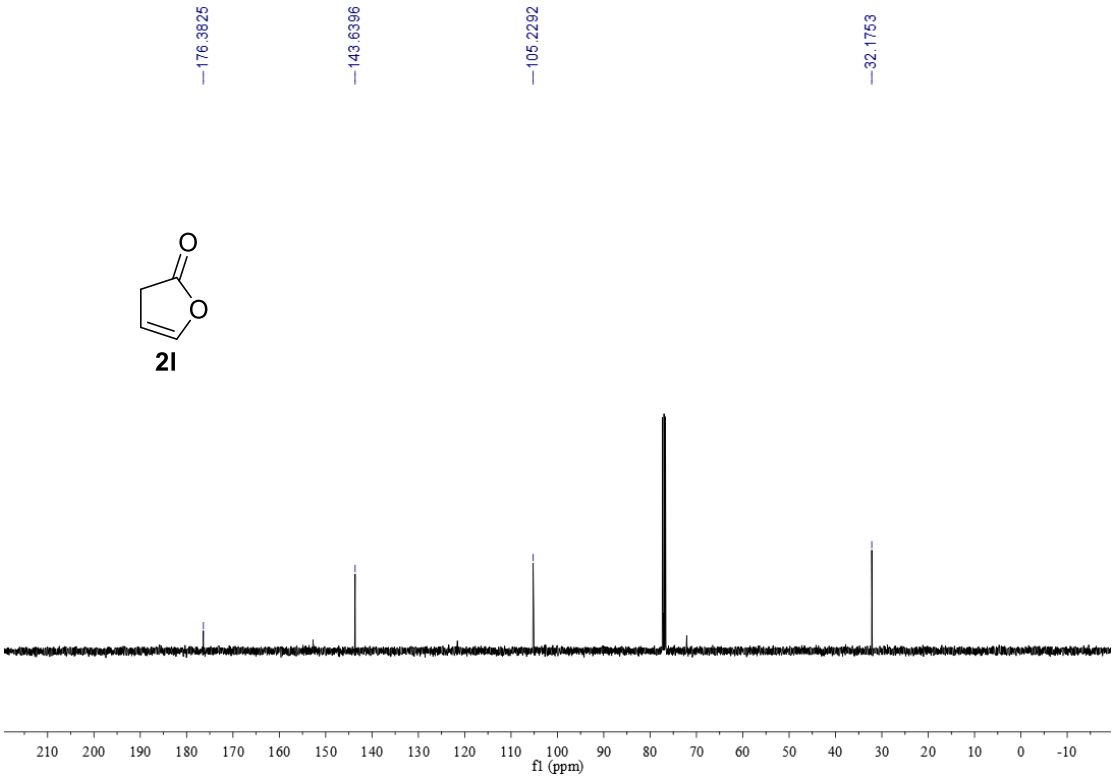
2l

Yellow oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dt, J = 3.6, 2.5 Hz, 1H), 5.55 (dt, J = 3.6, 2.4 Hz, 1H), 3.15 (t, J = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 143.6, 105.2, 32.2.

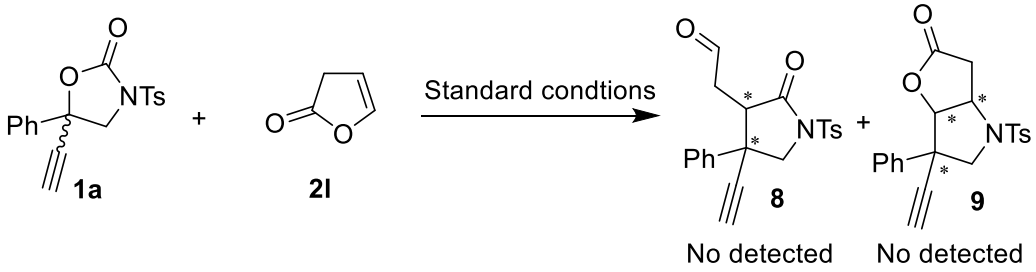


2l





(e) Furan-2(3*H*)-one as the Coupling Reagent



$Cu(OTf)_2$ (3.6 mg, 0.010 mmol) and **L3** (*S*, *S*) (7.4 mg, 0.020 mmol) were stirred at 60 °C in 1 mL of anhydrous methanol under nitrogen atmosphere for 1 h. Then, the mixture was cooled to -10 °C and a solution of **1a** (68.3 mg, 0.2 mmol), **2l** (50.5 mg, 0.6 mmol) and Cy_2NMe (46.9 mg, 0.24 mmol) in a mixture of anhydrous DCM and MeOH (1:1, 2 mL) was added. The mixture was stirred at -10 °C for 24 h, and a complex mixture was observed by TLC.

VIII. X-ray Data for Compounds 3ak

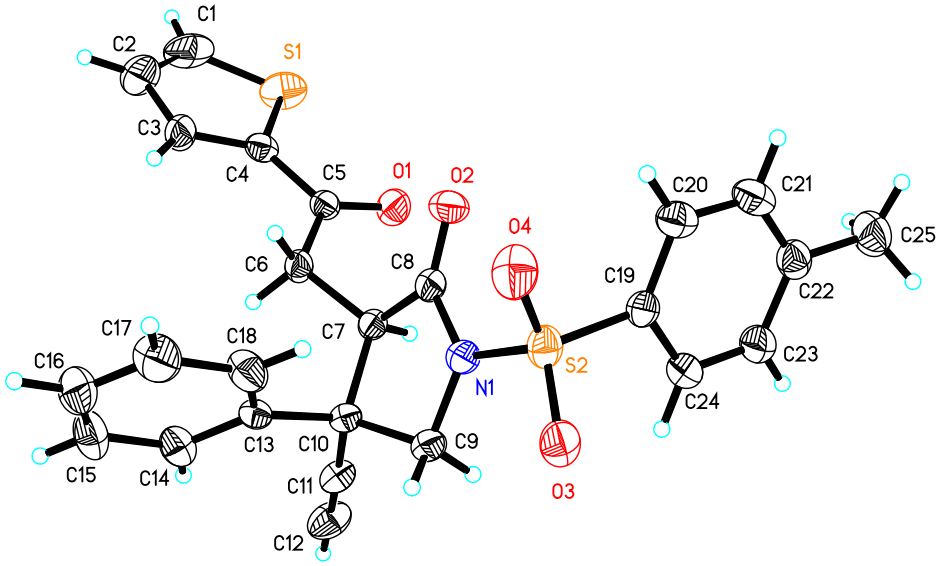


Table S2. Crystal data and structure refinement for **3ak**

CCDC number	1906833	
Empirical formula	$C_{25}H_{21}NO_4S_2$	
Formula weight	463.55	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.3448(3) Å	α= 90°.
	b = 13.4995(4) Å	β= 90°.
	c = 16.1640(5) Å	γ = 90°.
Volume	2257.30(12) $Å^3$	
Z	4	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	0.268 mm^{-1}	
F(000)	968	
Crystal size	0.190 x 0.160 x 0.140 mm^3	
Theta range for data collection	2.480 to 26.000°.	
Index ranges	-12<=h<=11, -16<=k<=13, -19<=l<=19	
Reflections collected	11335	
Independent reflections	4398 [R(int) = 0.0253]	

Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6070
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4398 / 0 / 291
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0834
R indices (all data)	R1 = 0.0433, wR2 = 0.0899
Absolute structure parameter	0.03(3)
Largest diff. peak and hole	0.148 and -0.168 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3ak**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	10918(1)	5819(1)	7380(1)	75(1)
S(2)	4066(1)	2729(1)	5909(1)	52(1)
O(1)	9340(2)	4438(2)	6364(1)	62(1)
O(2)	6274(2)	3726(2)	6827(1)	64(1)
O(3)	3259(2)	2596(2)	5204(2)	66(1)
O(4)	3519(2)	3034(2)	6676(2)	76(1)
N(1)	5135(2)	3591(2)	5614(2)	49(1)
C(1)	10929(4)	6967(3)	7810(2)	86(1)
C(2)	9821(5)	7450(3)	7690(2)	87(1)
C(3)	8918(4)	6906(2)	7215(2)	60(1)
C(4)	9396(3)	5997(2)	6987(2)	44(1)
C(5)	8808(2)	5230(2)	6479(2)	40(1)
C(6)	7534(2)	5481(2)	6075(2)	43(1)
C(7)	6934(3)	4628(2)	5593(2)	40(1)
C(8)	6116(3)	3944(2)	6116(2)	45(1)
C(9)	5179(3)	3983(2)	4769(2)	49(1)
C(10)	6032(3)	4924(2)	4860(2)	41(1)
C(11)	6786(3)	5080(2)	4103(2)	50(1)
C(12)	7402(3)	5229(3)	3502(2)	68(1)
C(13)	5242(2)	5859(2)	5080(2)	40(1)
C(14)	5533(3)	6755(2)	4716(2)	56(1)
C(15)	4939(3)	7619(3)	4973(3)	72(1)
C(16)	4036(4)	7597(3)	5578(2)	77(1)
C(17)	3695(4)	6709(3)	5932(2)	78(1)
C(18)	4296(3)	5842(3)	5681(2)	60(1)
C(19)	4995(3)	1665(2)	6064(2)	45(1)
C(20)	5201(3)	1296(2)	6846(2)	58(1)
C(21)	5882(3)	424(3)	6933(2)	62(1)
C(22)	6385(3)	-78(2)	6261(2)	56(1)
C(23)	6192(3)	326(2)	5487(2)	61(1)
C(24)	5499(3)	1182(2)	5379(2)	56(1)
C(25)	7143(4)	-1027(3)	6372(3)	80(1)

IX. Reference

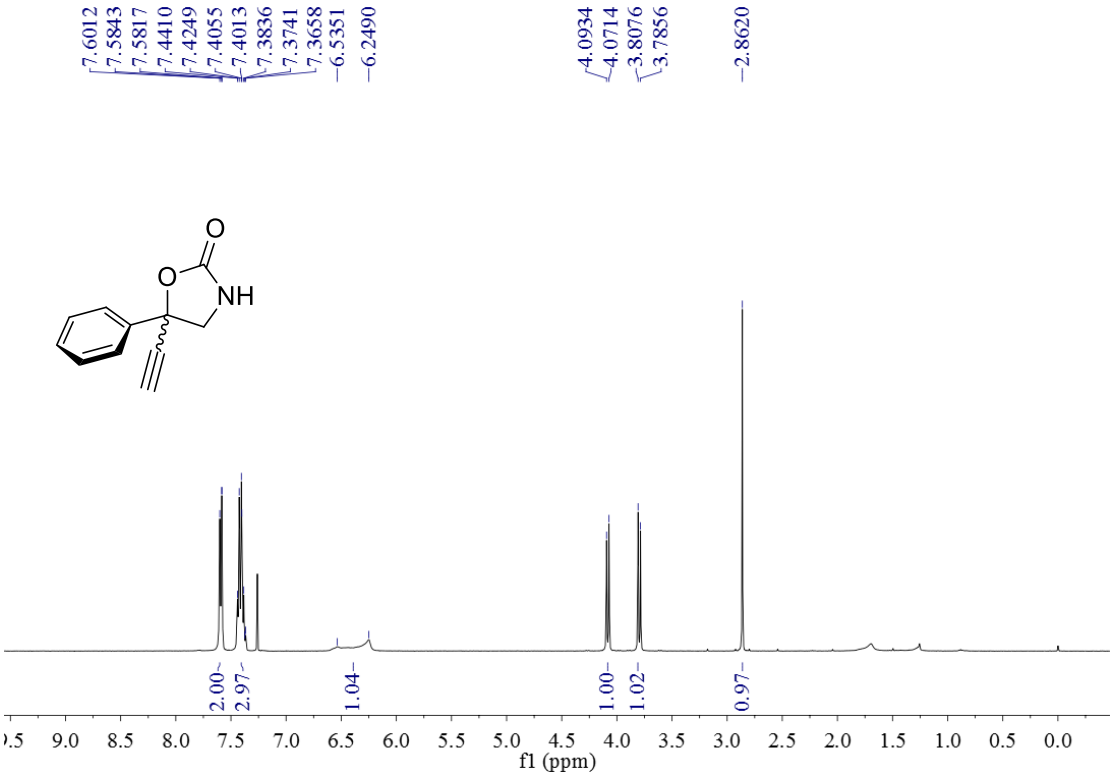
(1) (a) Muratore, M. E.; Holloway, C. A.; Pilling, A. W.; Storer, R. I.; Trevitt, G.; Dixon, D. J. *J. Am. Chem. Soc.* **2009**, *131*, 10796-10797. (b) Wu, Y.; Singh, R. P.; Deng, L. *J. Am. Chem. Soc.* **2011**, *133*, 12458-12461.

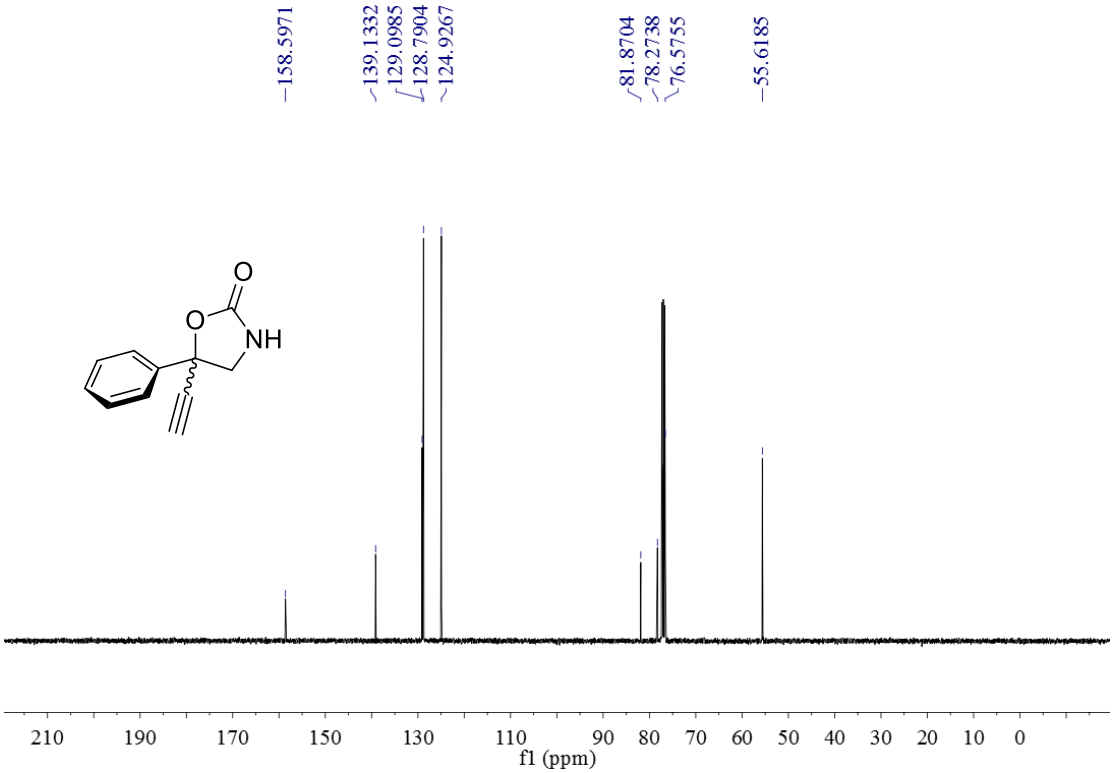
(2) (a) Yang, Y.; Yang, W. *Chem. Comm.* **2018**, *54*, 12182-12185. (b) Wang, Q.; Li, T.-R.; Lu, L.-Q.; Li, M.-M.; Zhang, K.; Xiao, W.-J. *J. Am. Chem. Soc.* **2016**, *138*, 8360−8363.

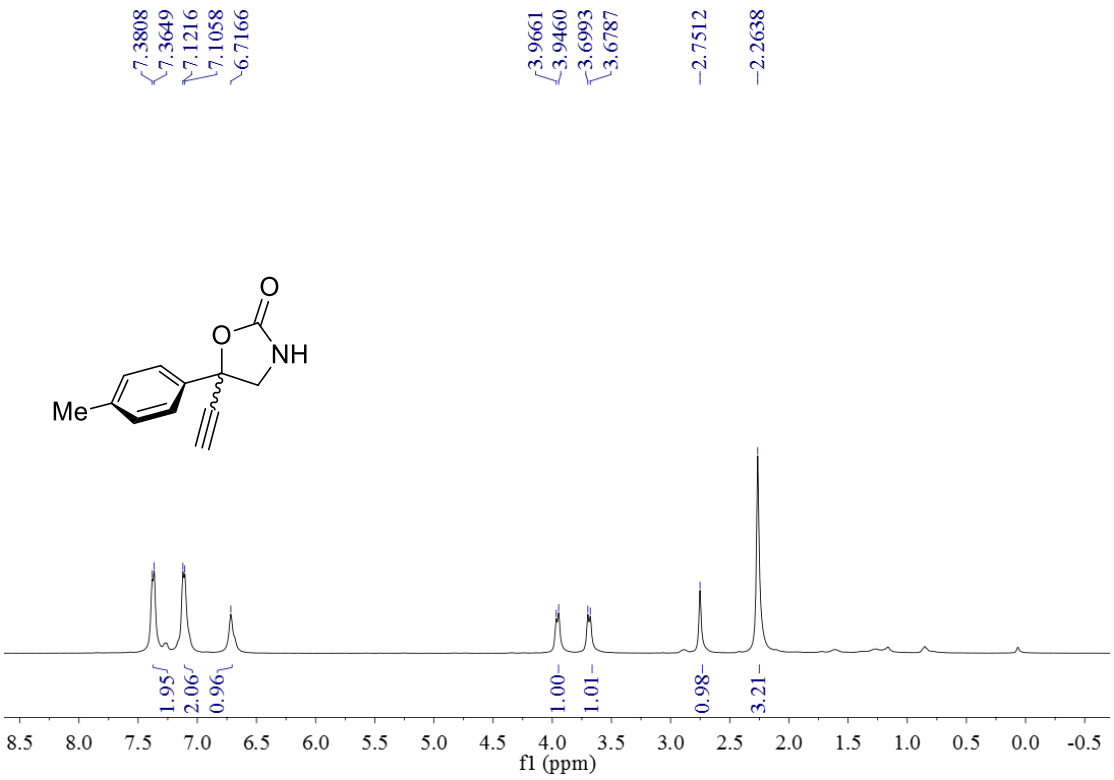
(3) Rao, W.; Koh, M. J.; Kothandaraman, P.; Chan, P. W. H. *J. Am. Chem. Soc*. **2012**, *134*, 10811–10814.

(4) Molander, G. A.; Cavalcanti, L.N. *J. Org. Chem.* **2011**, *76*, 623–630.

X. NMR Spectra



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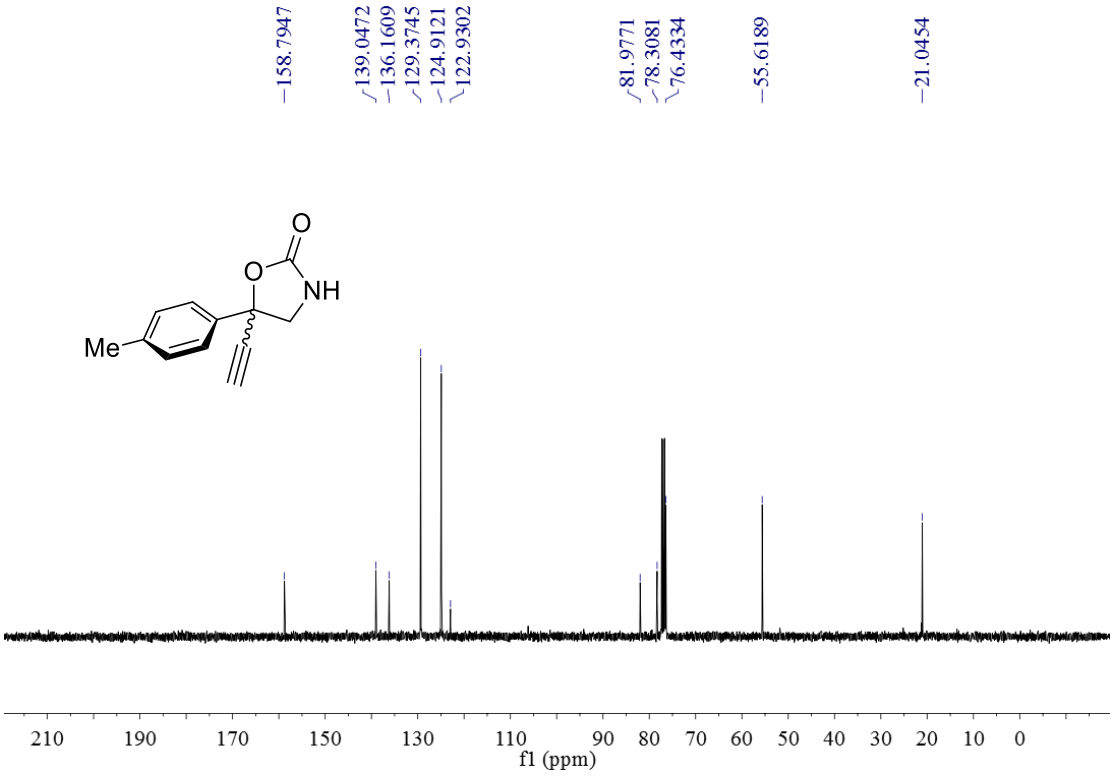
2.2638
O
O
NH
Me
1.95
2.06
0.96
1.00
1.01
0.98
3.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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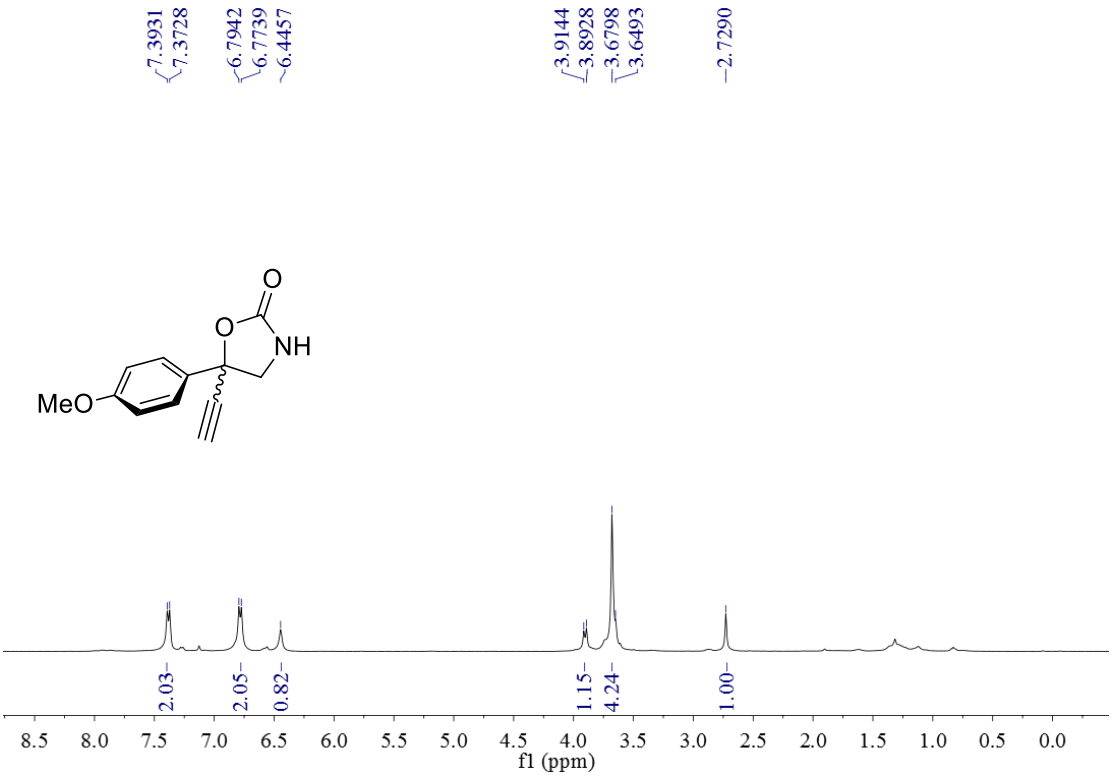
O
O
NH
Me
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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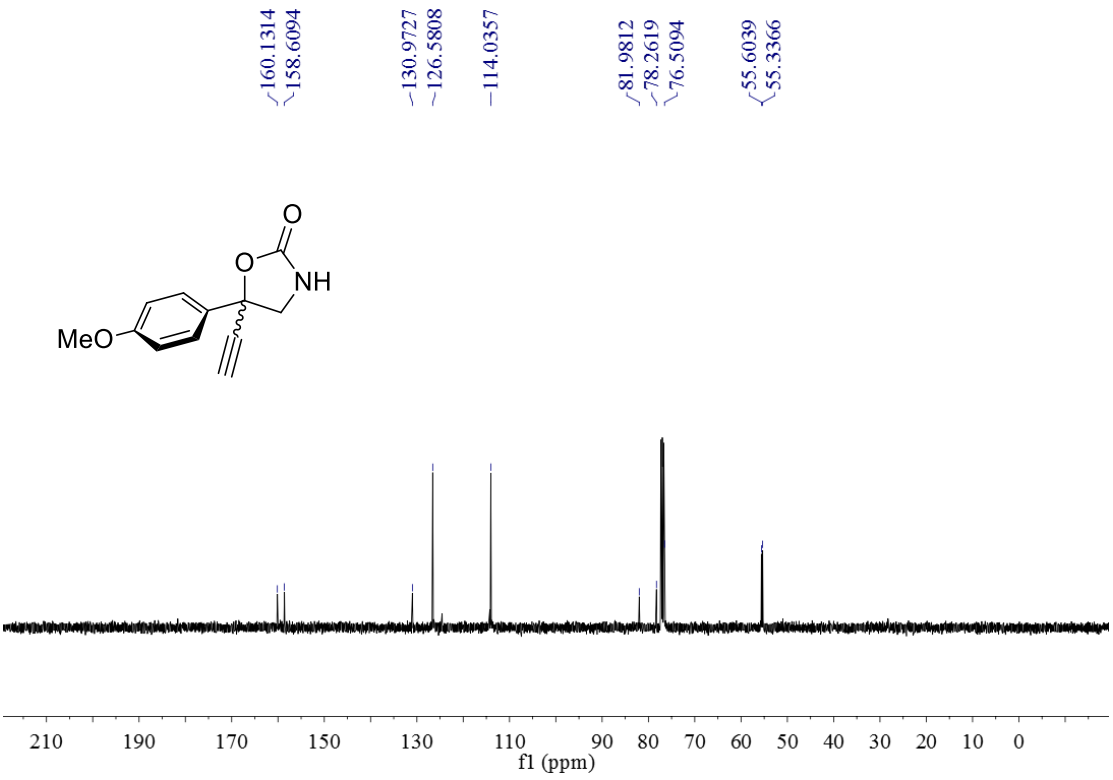
O
NH
MeO
2.03
2.05
0.82
1.15
4.24
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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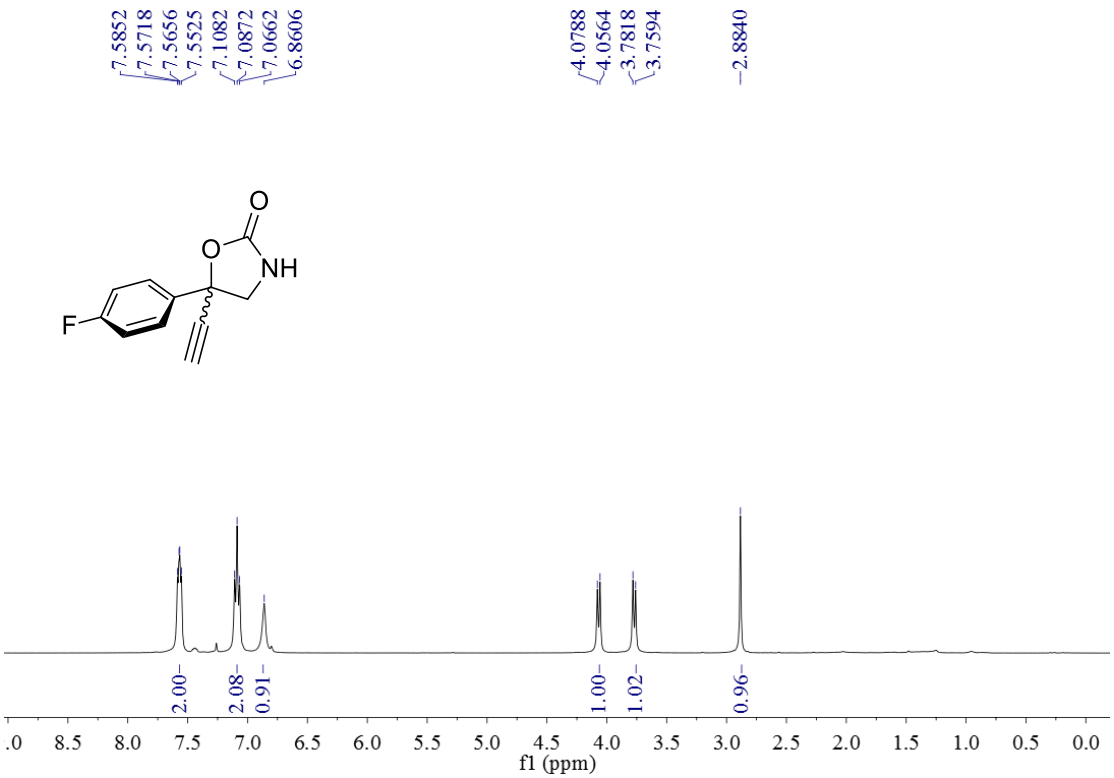
130.9727
126.5808
114.0357
81.9812
78.2619
76.5094
55.6039
55.3366
O
O
NH
MeO
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.7818
3.7594
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O
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F
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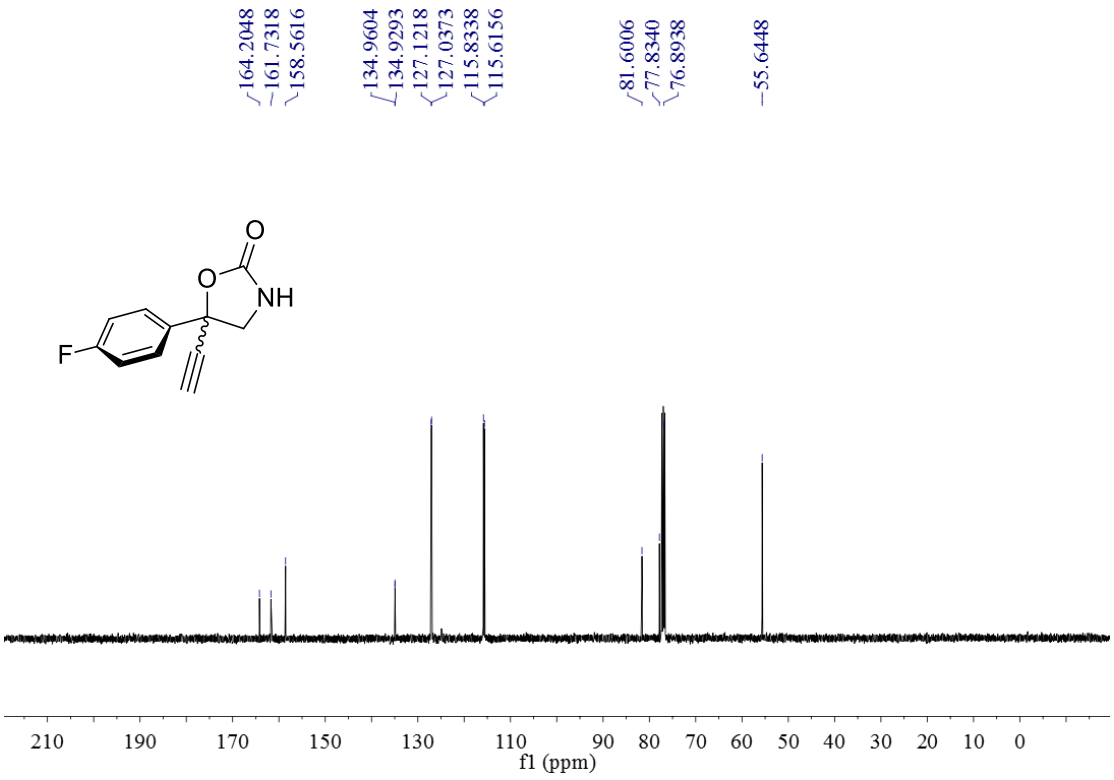
1.00
1.02
0.96
f1 (ppm)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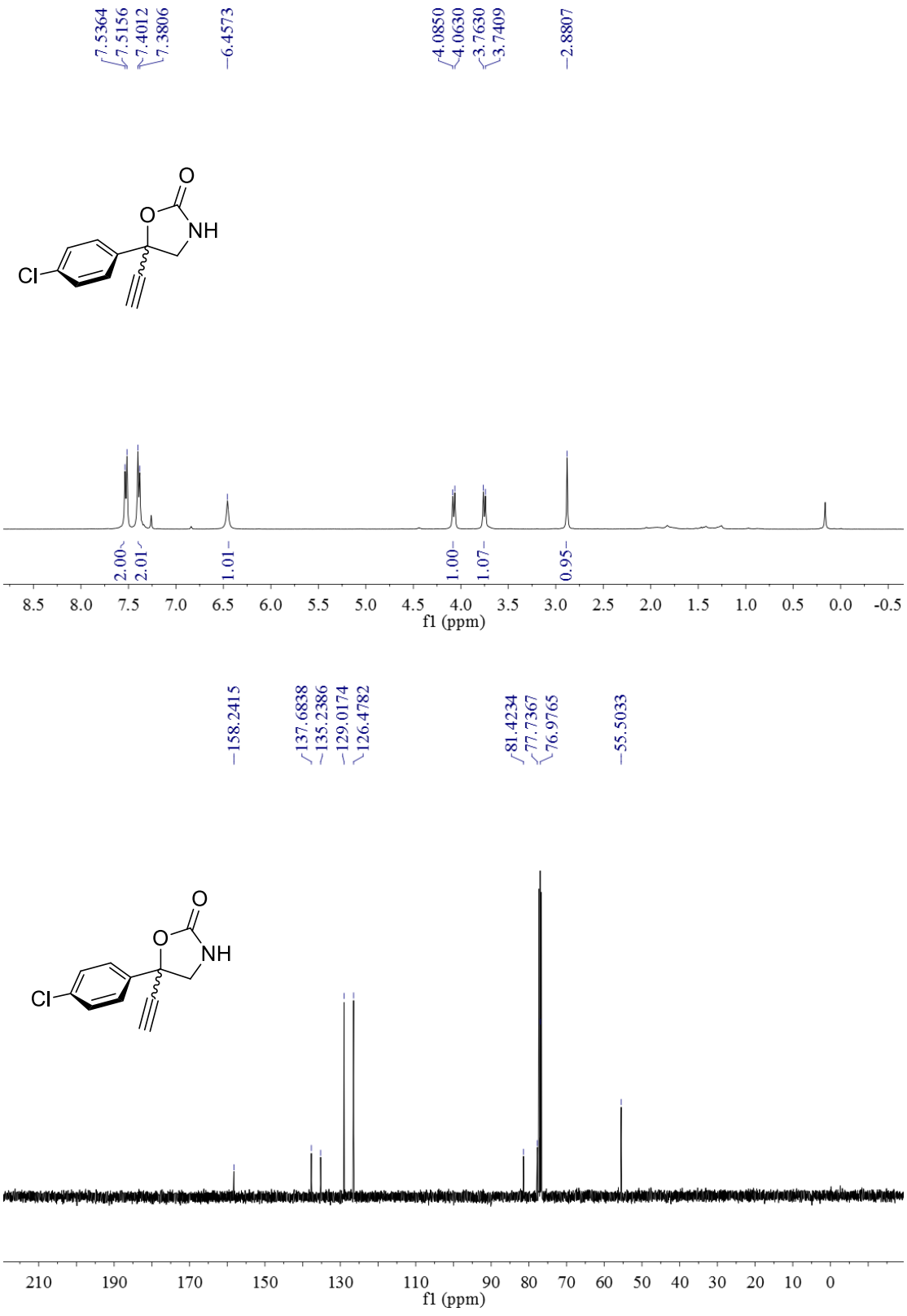
55.6448
O
O
NH
F
f1 (ppm)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O
O
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Cl
2.00
2.01
1.01
1.00
1.07
0.95
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f1 (ppm)
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137.6838
135.2386
129.0174
126.4782
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76.9765
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O
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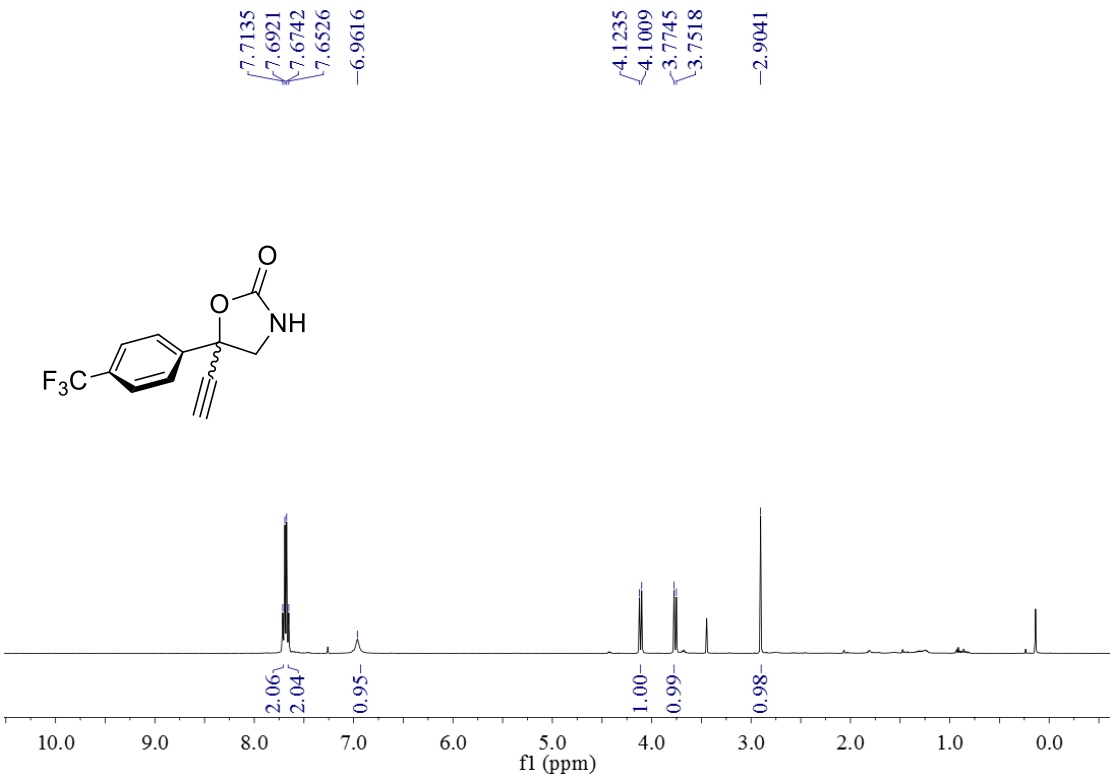
NH
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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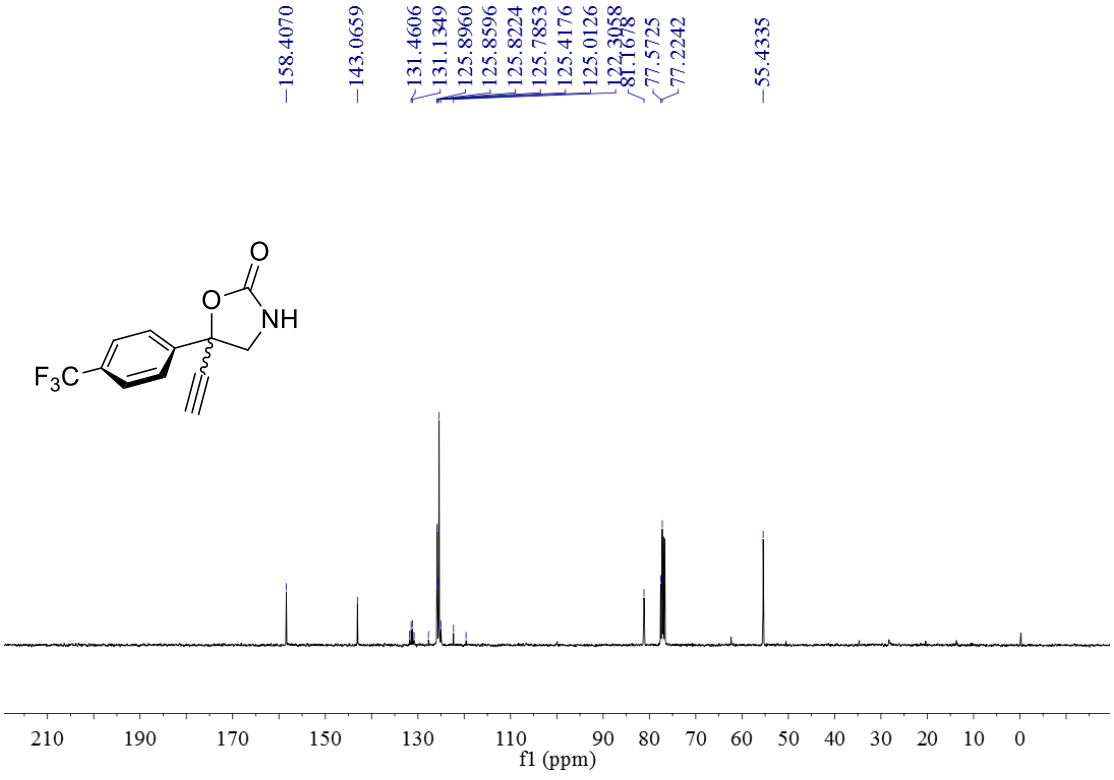
O
O
NH
F3C
2.06
2.04
0.95
1.00
0.99
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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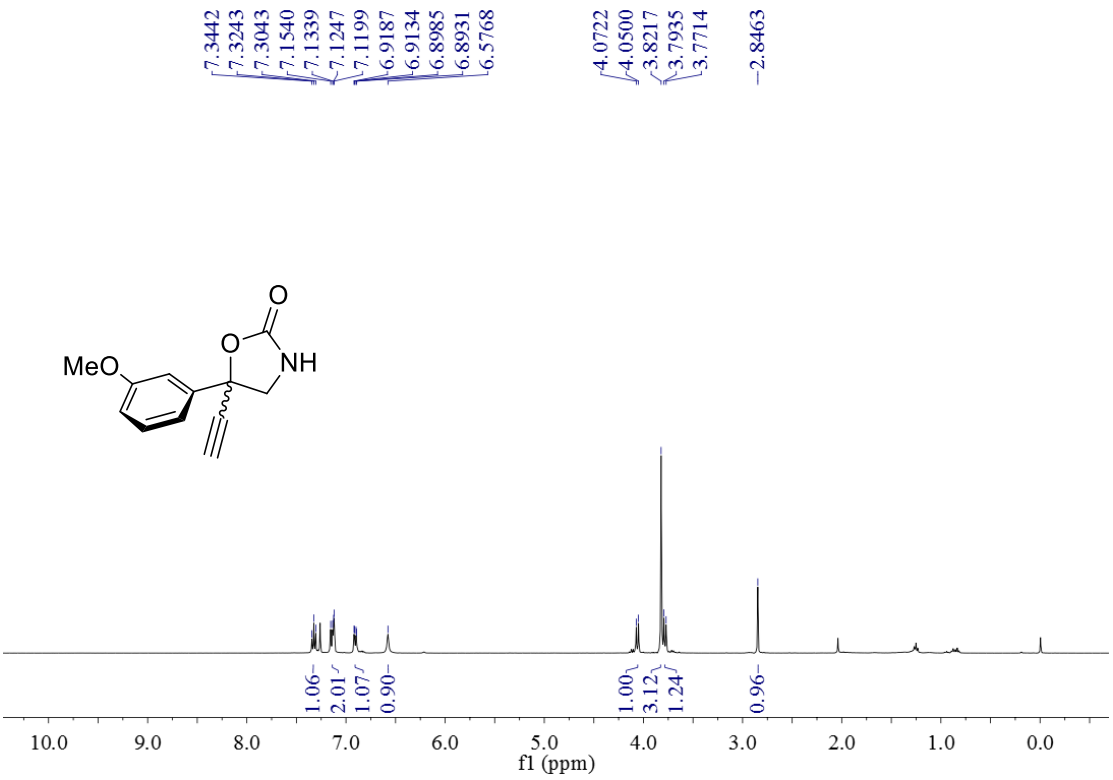
122.3058
81.7678
77.5725
77.2242
55.4335
O
O
NH
F3C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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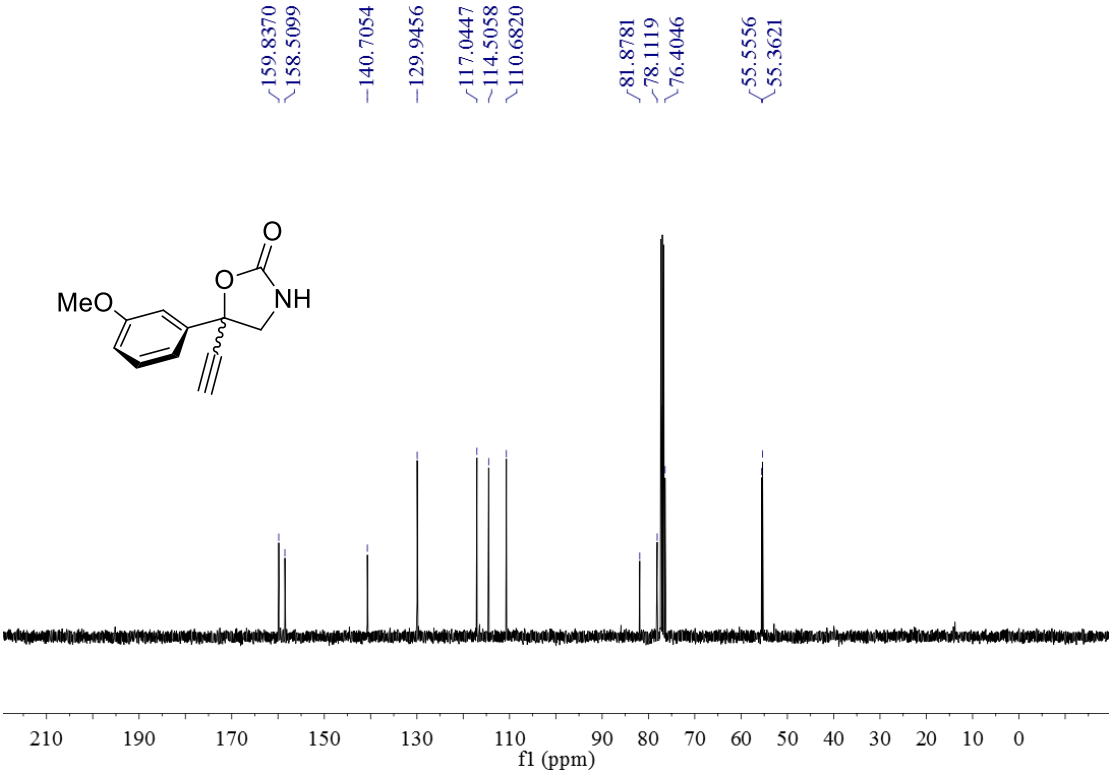
3.7714
2.8463
MeO
O
O
NH
1.06
2.01
1.07
0.90
1.00
3.12
1.24
0.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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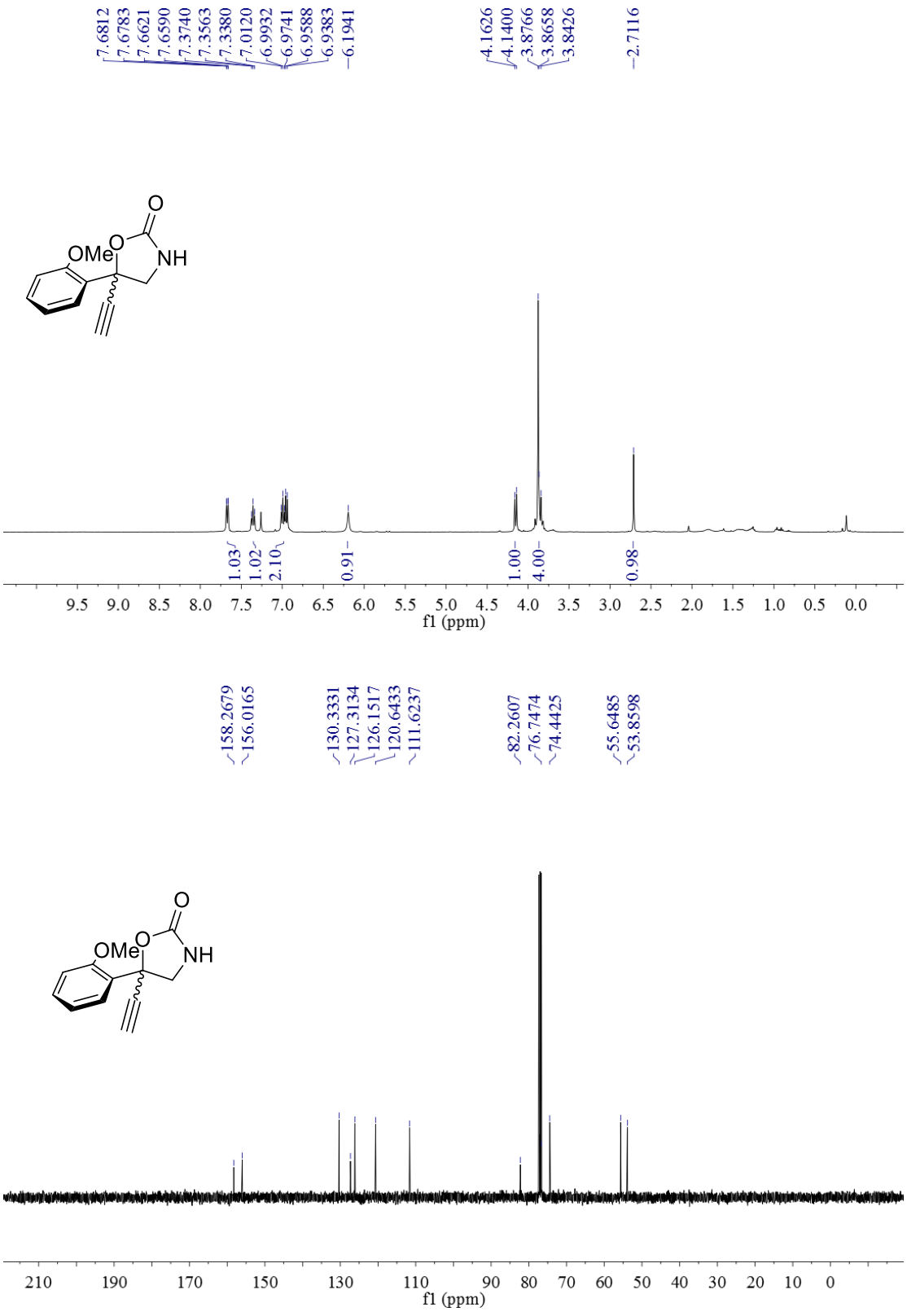
140.7054
129.9456
117.0447
114.5058
110.6820
81.8781
78.1119
76.4046
55.5556
55.3621
MeO
O
O
NH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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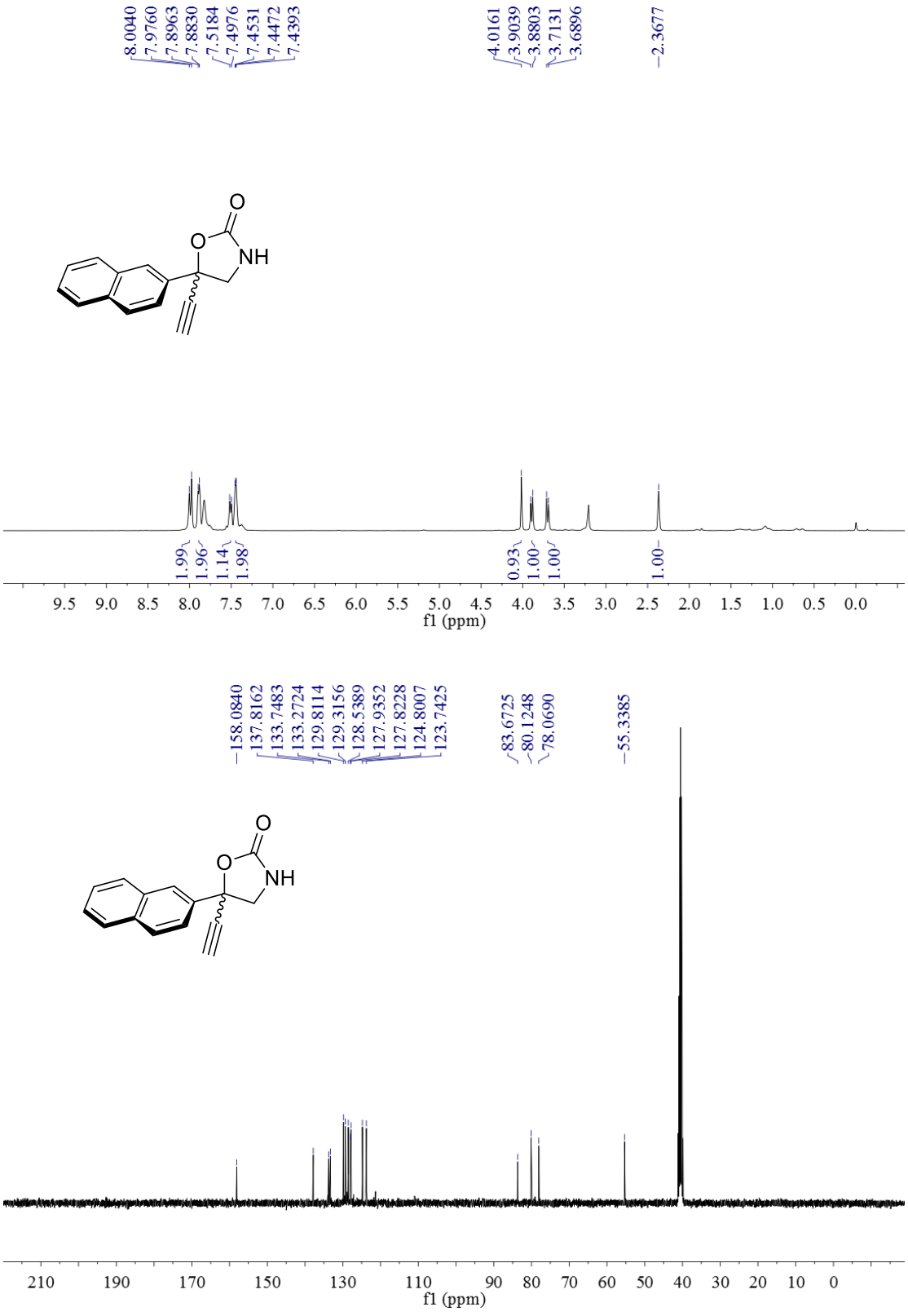
7.6783
7.6621
7.6590
7.3740
7.3563
7.3380
7.0120
6.9932
6.9741
6.9588
6.9383
6.1941
4.1626
4.1400
3.8766
3.8658
3.8426
2.7116
O
O
OMe
NH
1.03
1.02
2.10
0.91
1.00
4.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
158.2679
156.0165
130.3331
127.3134
126.1517
120.6433
111.6237
82.2607
76.7474
74.4425
55.6485
53.8598
O
O
OMe
NH
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.9760
7.8963
7.8830
7.5184
7.4976
7.4531
7.4472
7.4393
4.0161
3.9039
3.8803
3.7131
3.6896
2.3677
O
O
NH
1.99
1.96
1.14
1.98
0.93
1.00
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
158.0840
137.8162
133.7483
133.2724
129.8114
129.3156
128.5389
127.9352
127.8228
124.8007
123.7425
83.6725
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78.0690
55.3385
O
O
NH
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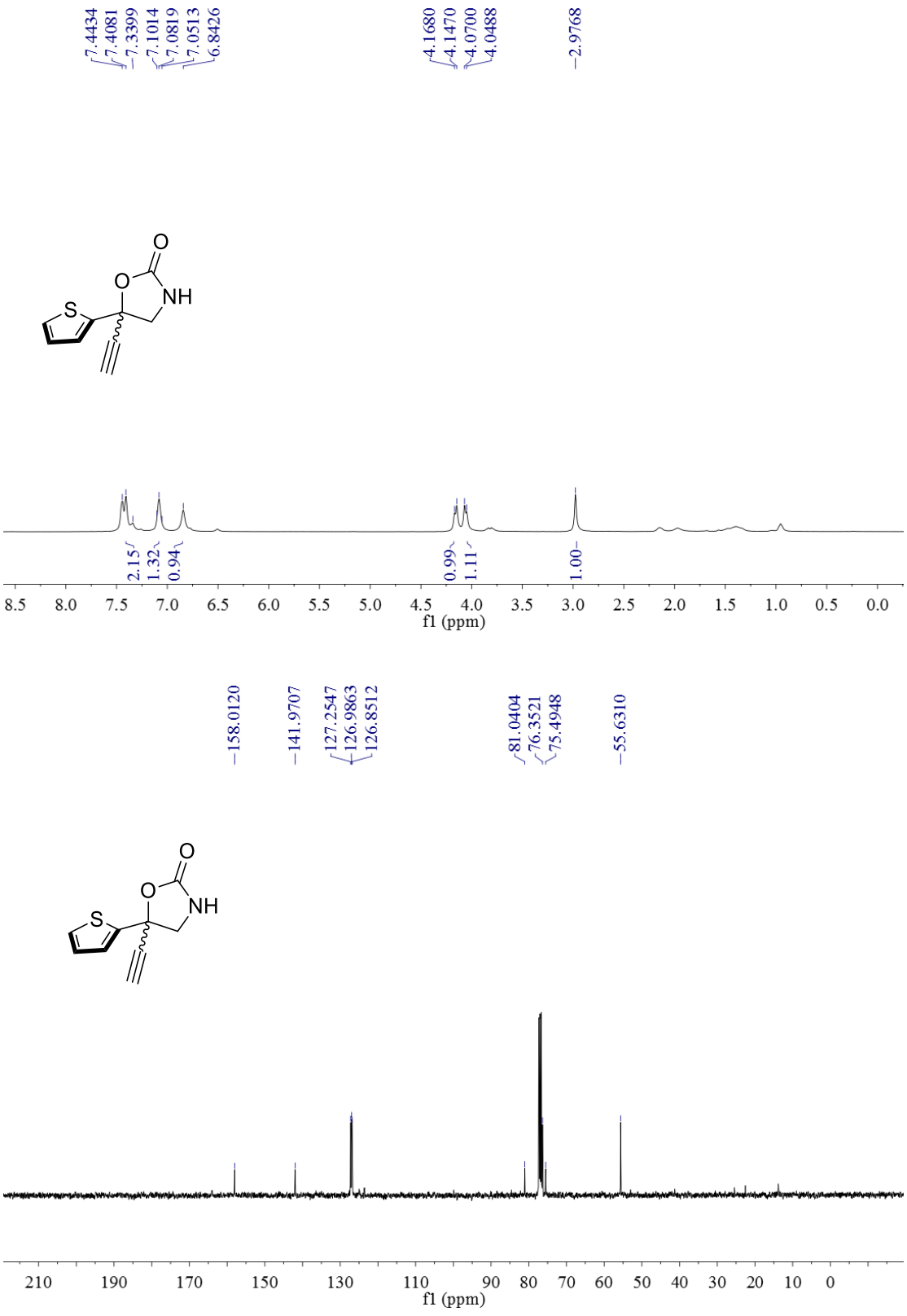
f1 (ppm)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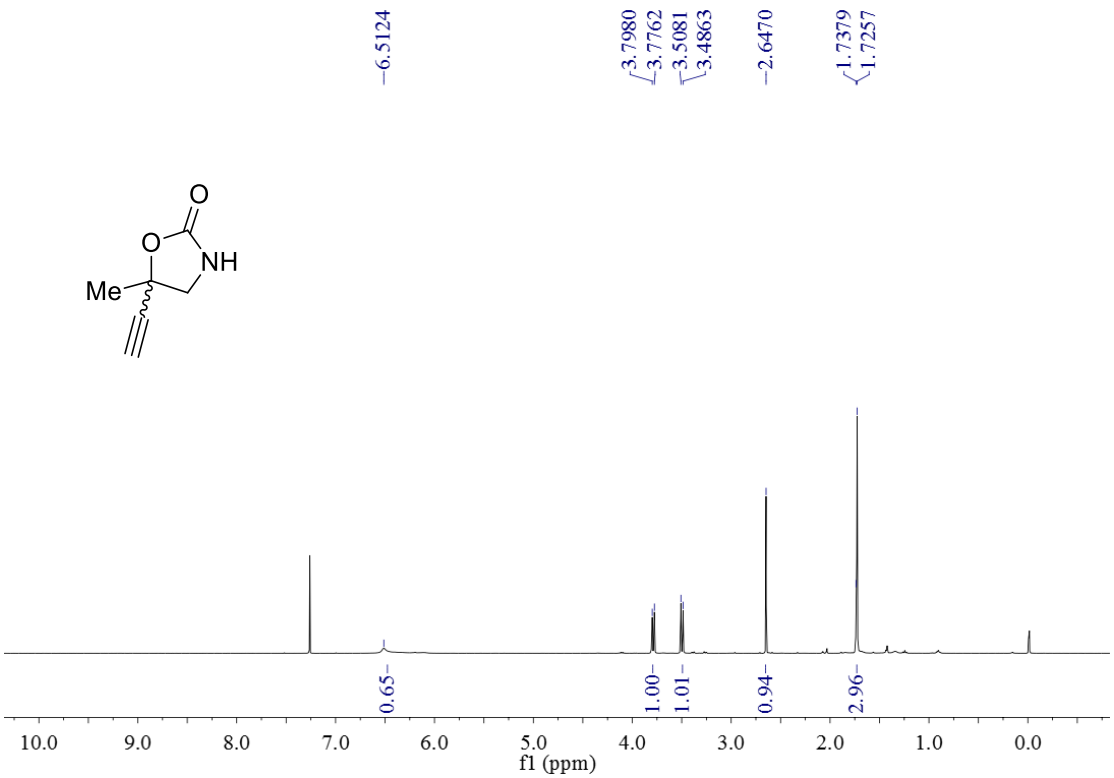
7.4081
7.3399
7.1014
7.0819
7.0513
6.8426
4.1680
4.1470
4.0700
4.0488
2.9768
O
O
NH
S
2.15
1.32
0.94
0.99
1.11
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
158.0120
141.9707
127.2547
126.9863
126.8512
81.0404
76.3521
75.4948
55.6310
O
O
NH
S
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.7762
3.5081
3.4863
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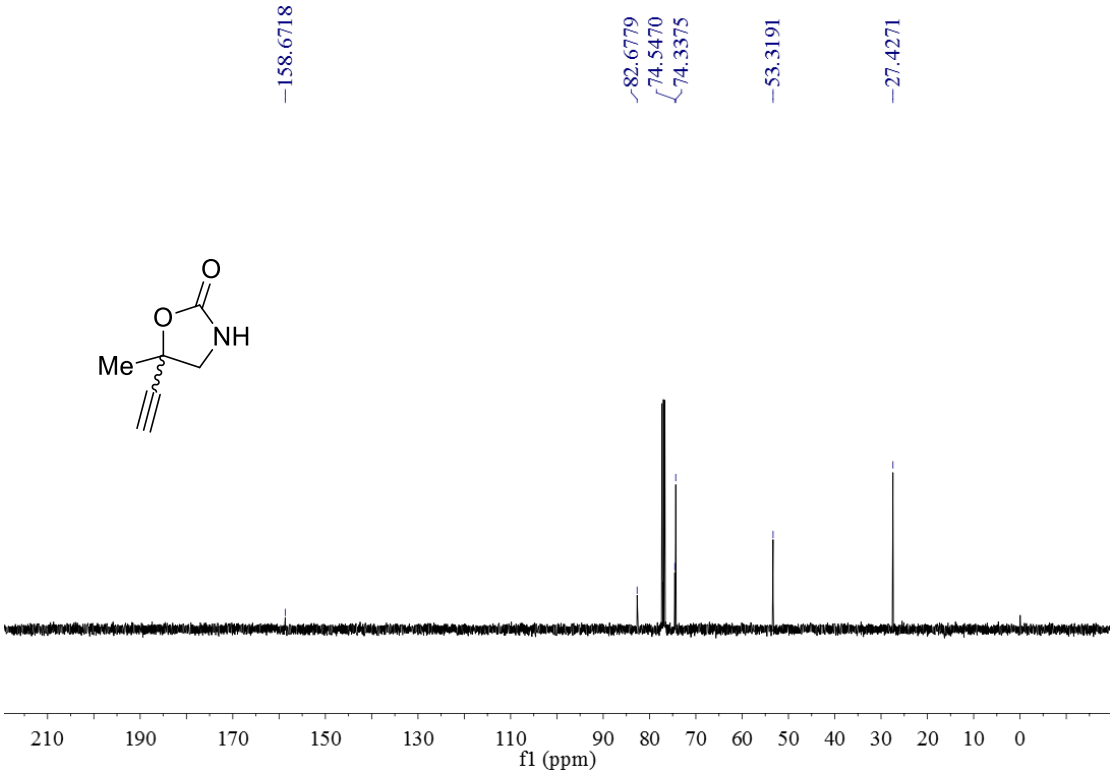
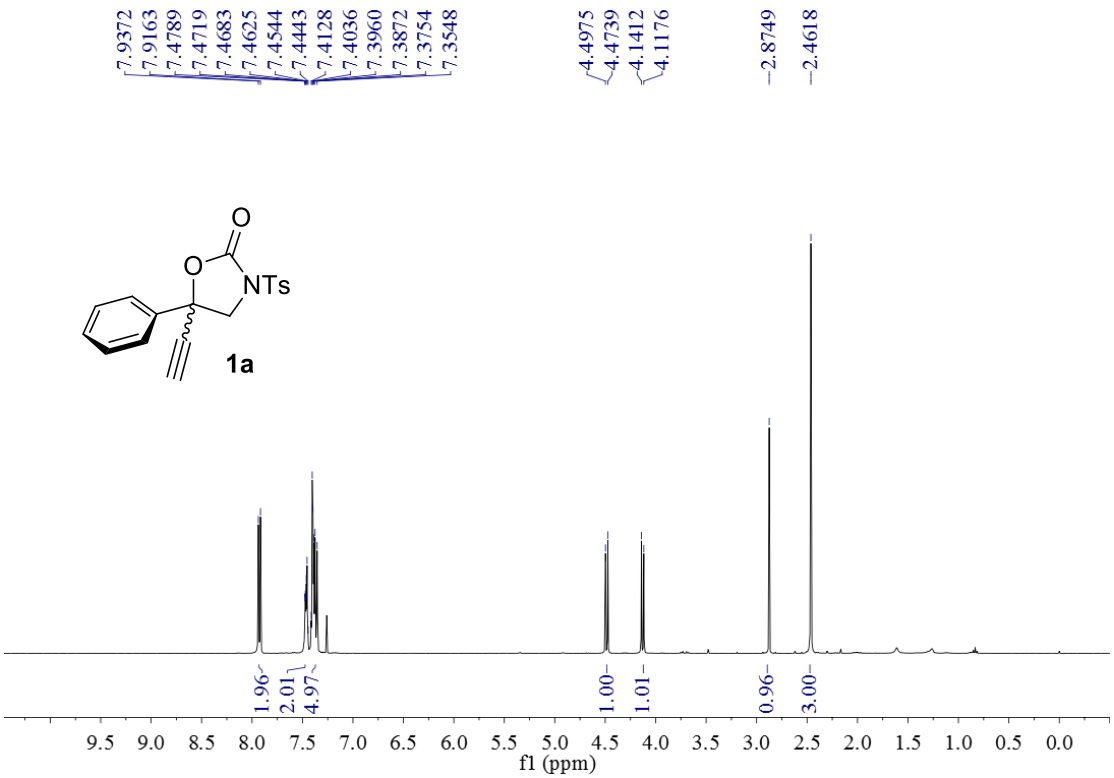
1.7379
1.7257
O
O
NH
Me
0.65
1.00
1.01
0.94
2.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


158.6718
82.6779
74.5470
74.3375
53.3191
27.4271
O
O
NH
Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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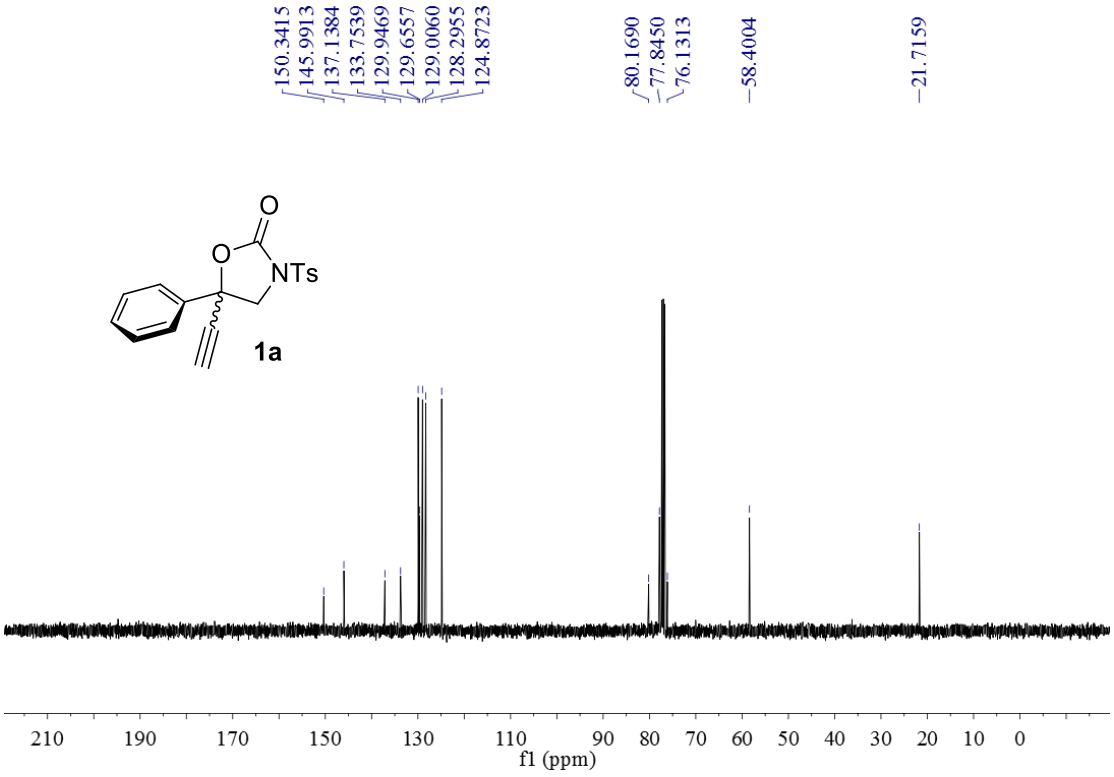
7.9163
7.4789
7.4719
7.4683
7.4625
7.4544
7.4443
7.4128
7.4036
7.3960
7.3872
7.3754
7.3548
4.4975
4.4739
4.1412
4.1176
2.8749
2.4618
O
O
NTs
1a
1.96
2.01
4.97
1.00
1.01
0.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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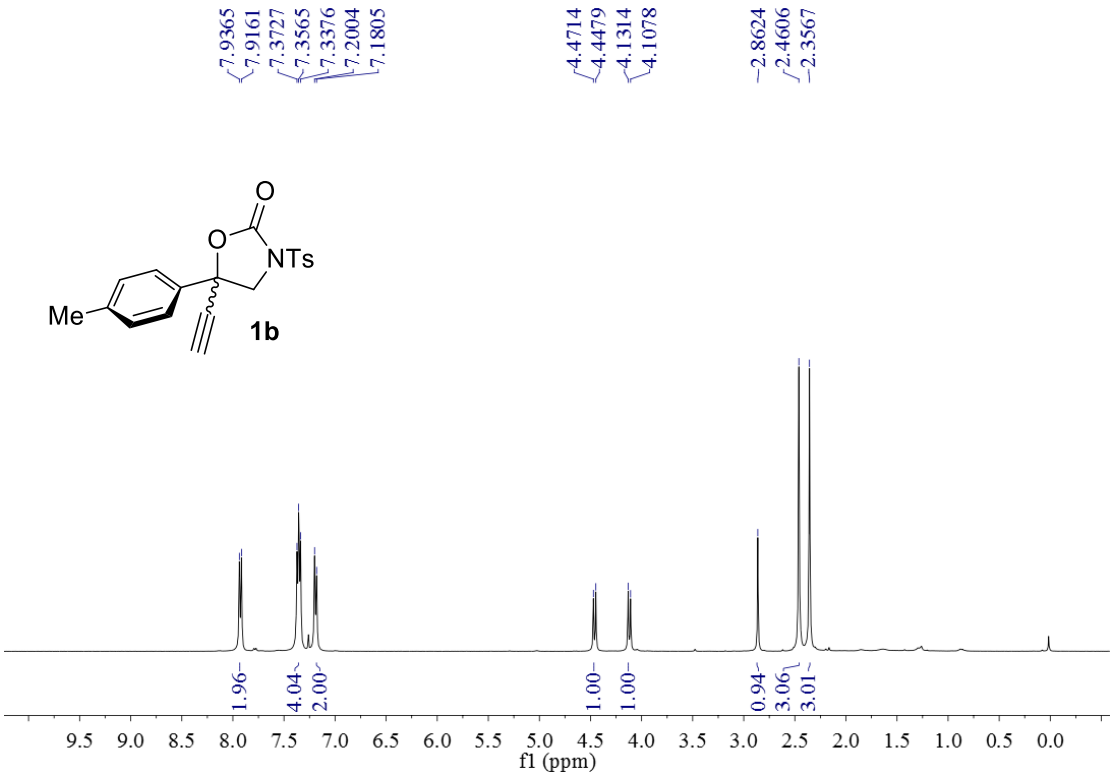
137.1384
133.7539
129.9469
129.6557
129.0060
128.2955
124.8723
80.1690
77.8450
76.1313
58.4004
21.7159
O
O
NTs
1a
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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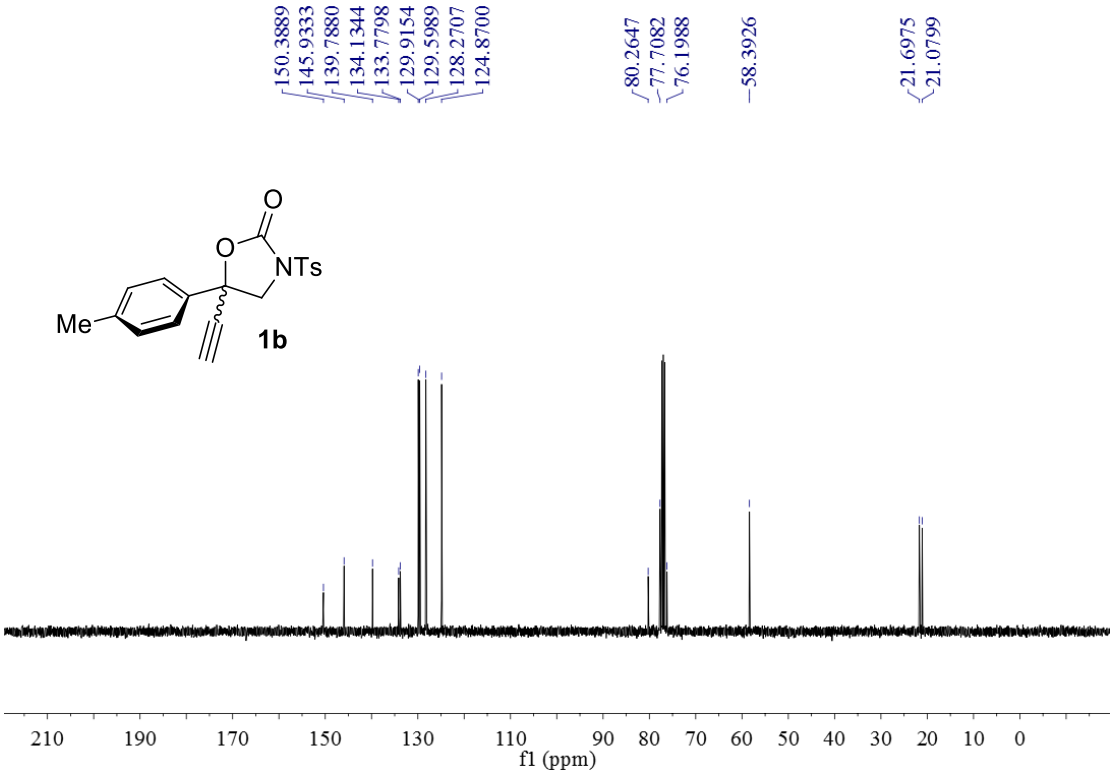
7.9161
7.3727
7.3565
7.3376
7.2004
7.1805
4.4714
4.4479
4.1314
4.1078
2.8624
2.4606
2.3567
O
O
NTs
Me
1b
1.96
4.04
2.00
1.00
1.00
0.94
3.06
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.1344
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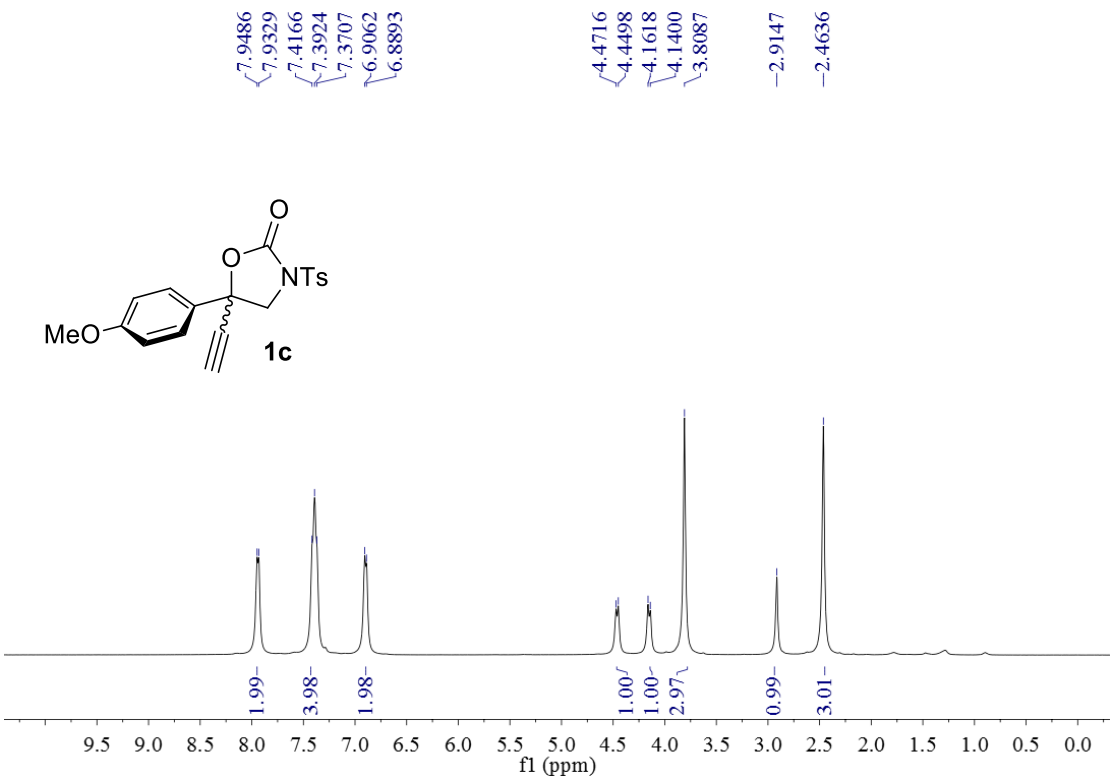
129.5989
128.2707
124.8700
80.2647
77.7082
76.1988
58.3926
21.6975
21.0799
O
O
NTs
Me
1b
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.9329
7.4166
7.3924
7.3707
6.9062
6.8893
4.4716
4.4498
4.1618
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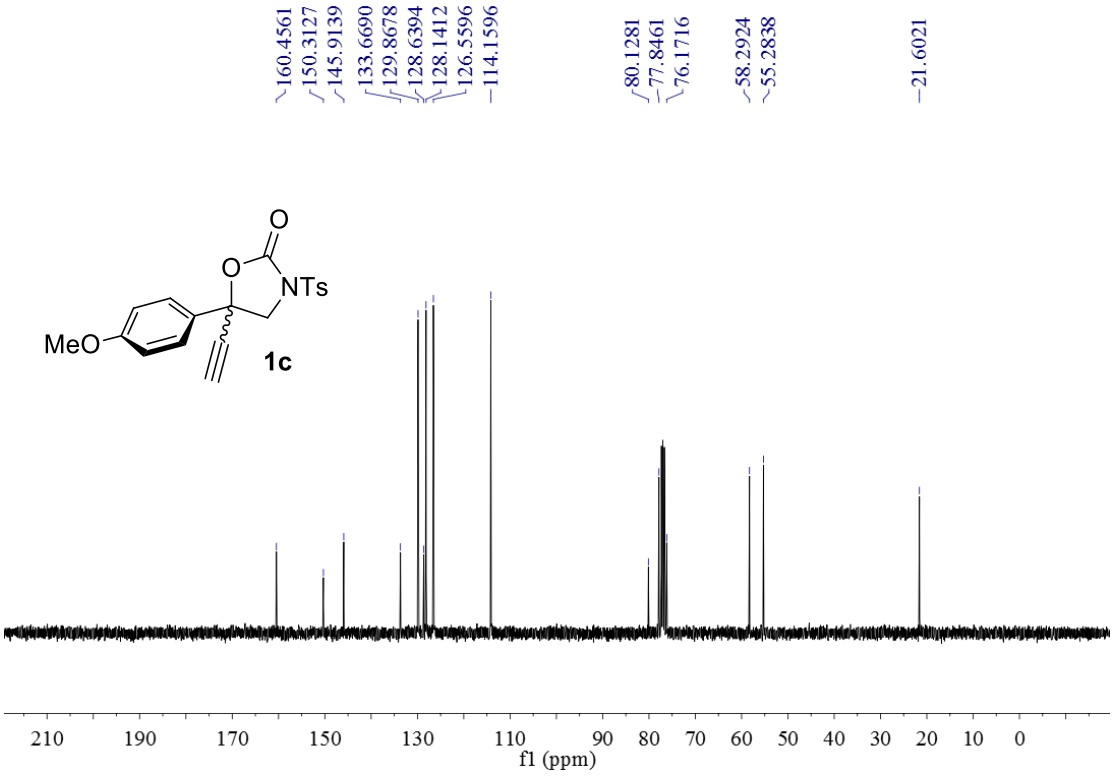
3.8087
2.9147
2.4636
O
O
NTs
MeO
1c
1.99
3.98
1.98
1.00
1.00
2.97
0.99
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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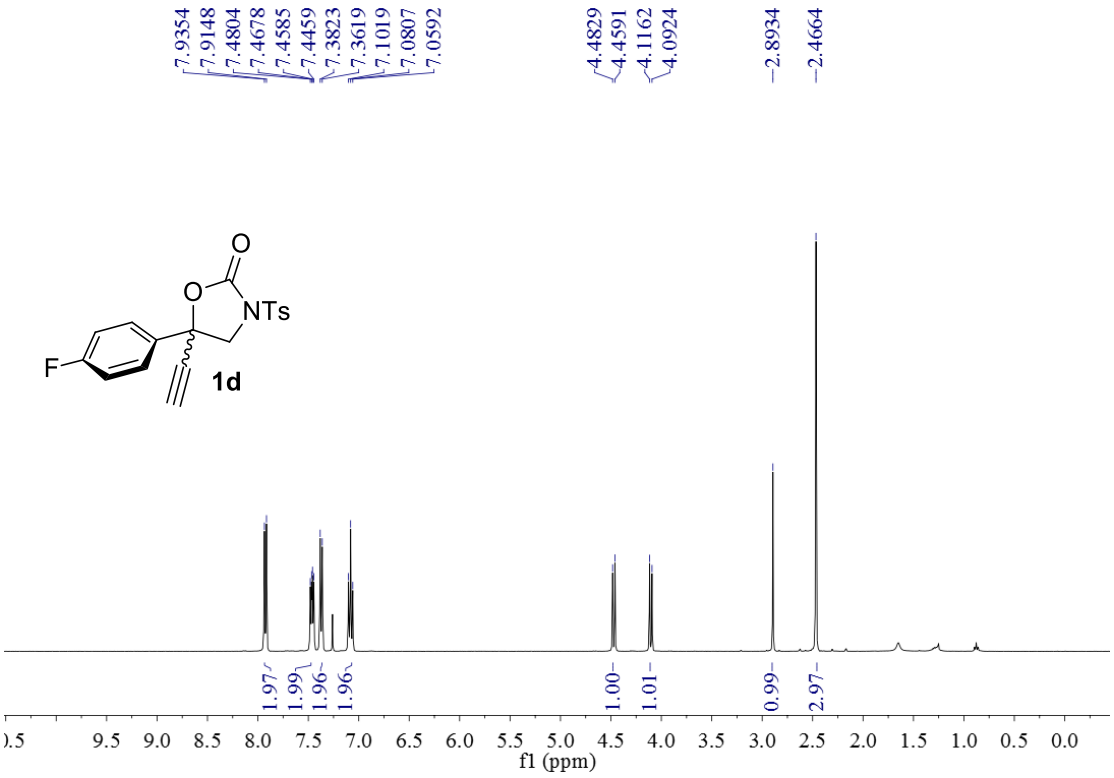
128.1412
126.5596
114.1596
80.1281
77.8461
76.1716
58.2924
55.2838
21.6021
O
O
NTs
MeO
1c
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4804
7.4678
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7.4459
7.3823
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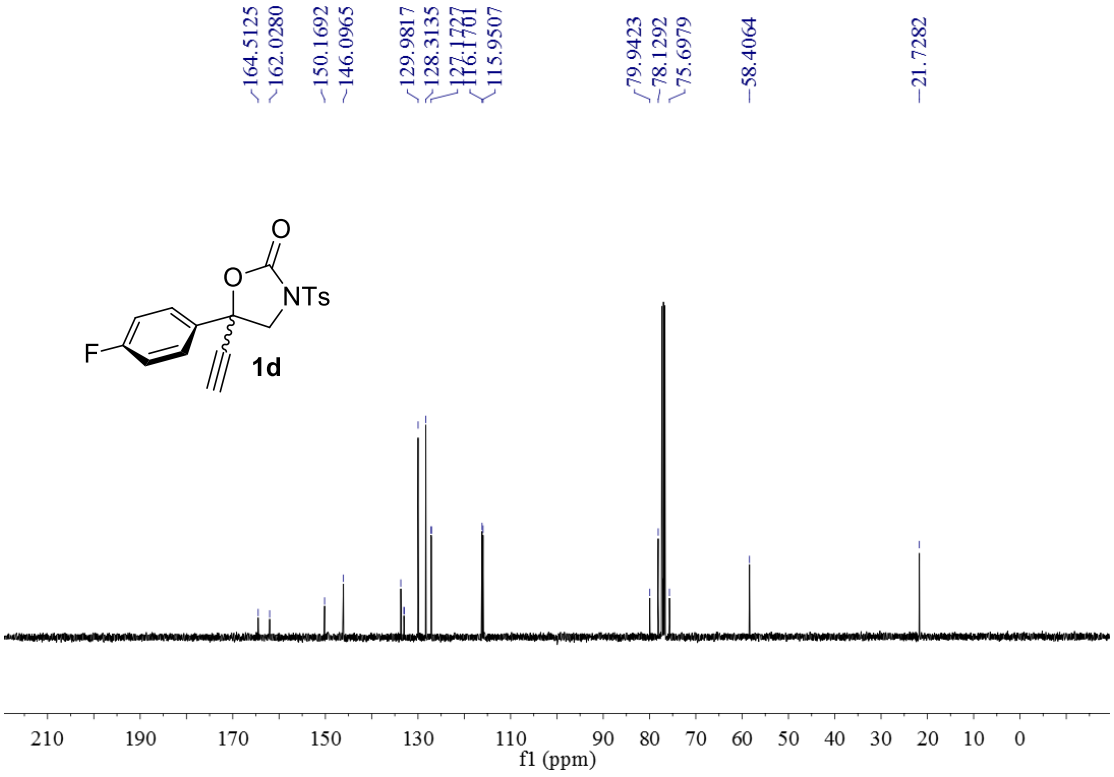
7.1019
7.0807
7.0592
4.4829
4.4591
4.1162
4.0924
2.8934
2.4664
O
O
NTs
F
1d
1.97
1.99
1.96
1.96
1.00
1.01
0.99
2.97
f1 (ppm)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127.1727
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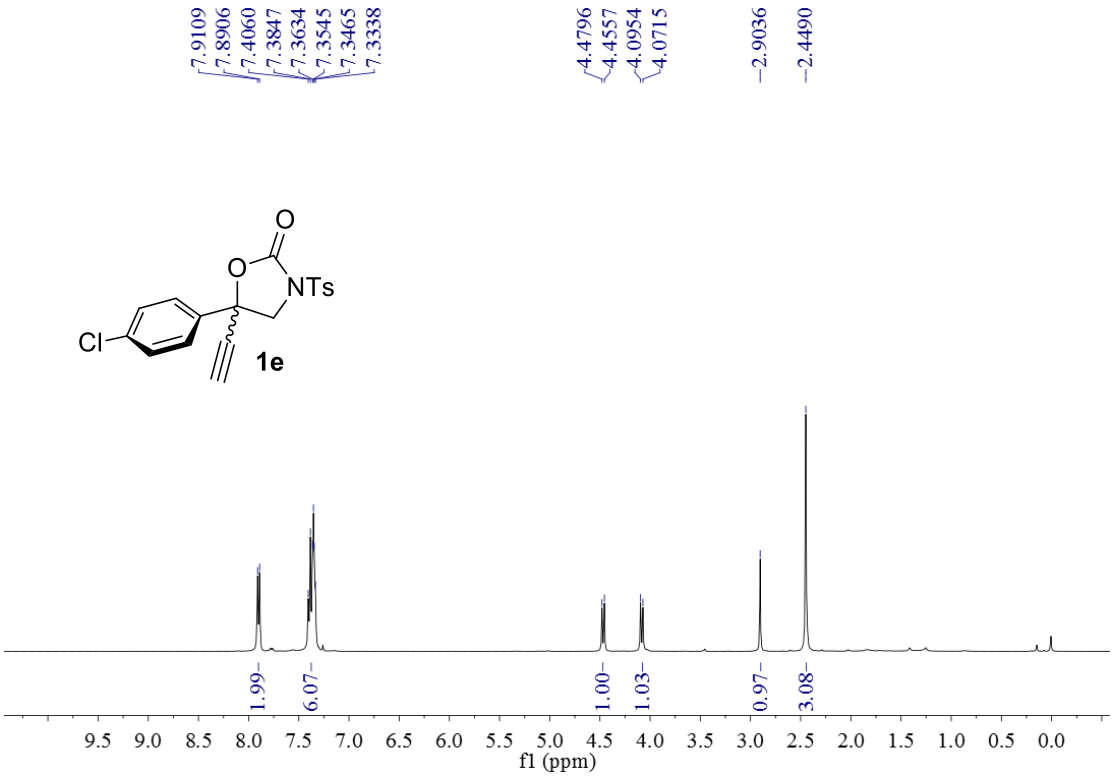
78.1292
75.6979
58.4064
21.7282
O
O
NTs
F
1d
f1 (ppm)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7.3465
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4.4796
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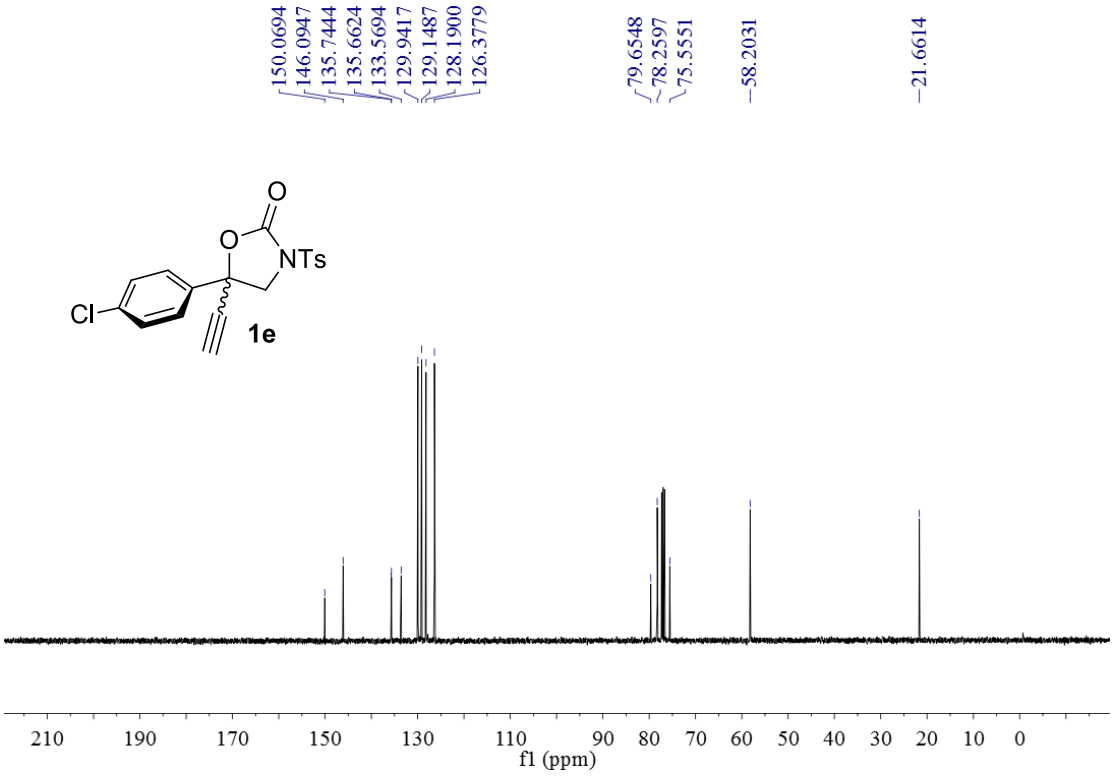
4.0954
4.0715
2.9036
2.4490
O
O
NTs
Cl
1e
1.99
6.07
1.00
1.03
0.97
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.5694
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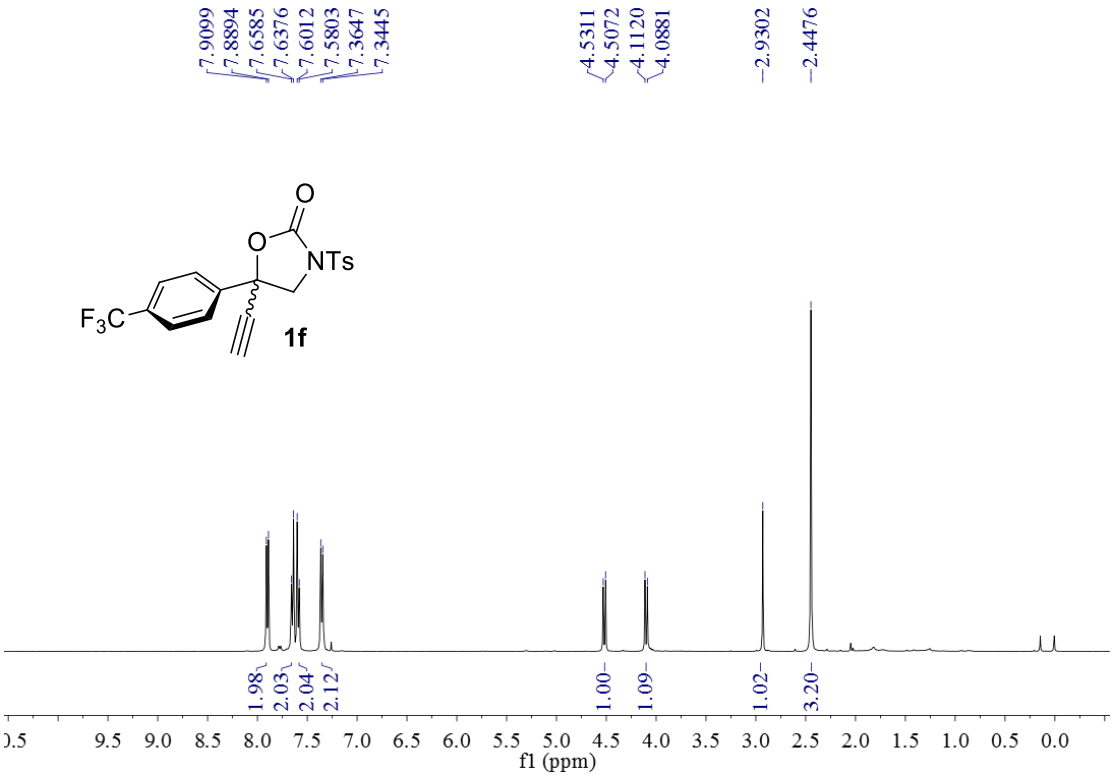
129.1487
128.1900
126.3779
79.6548
78.2597
75.5551
58.2031
21.6614
O
O
NTs
Cl
1e
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5803
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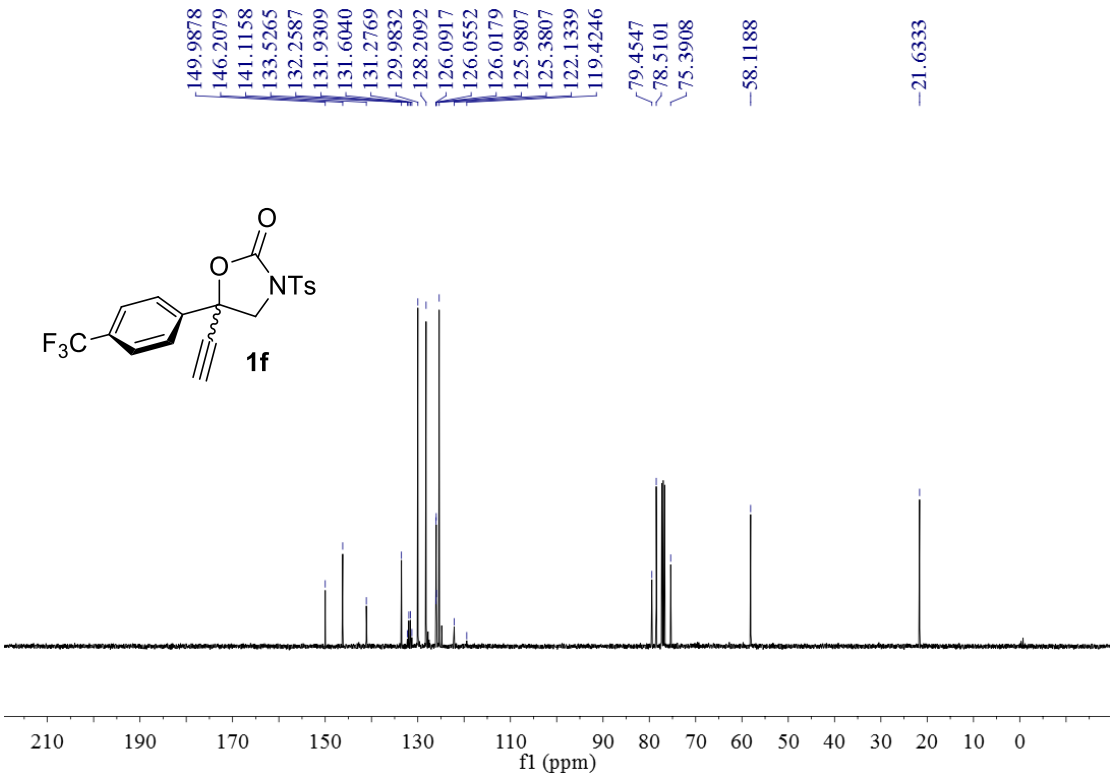
4.1120
4.0881
2.9302
2.4476
O
O
NTs
F3C
1f
1.98
2.03
2.04
2.12
1.00
1.09
1.02
3.20
f1 (ppm)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126.0917
126.0552
126.0179
125.9807
125.3807
122.1339
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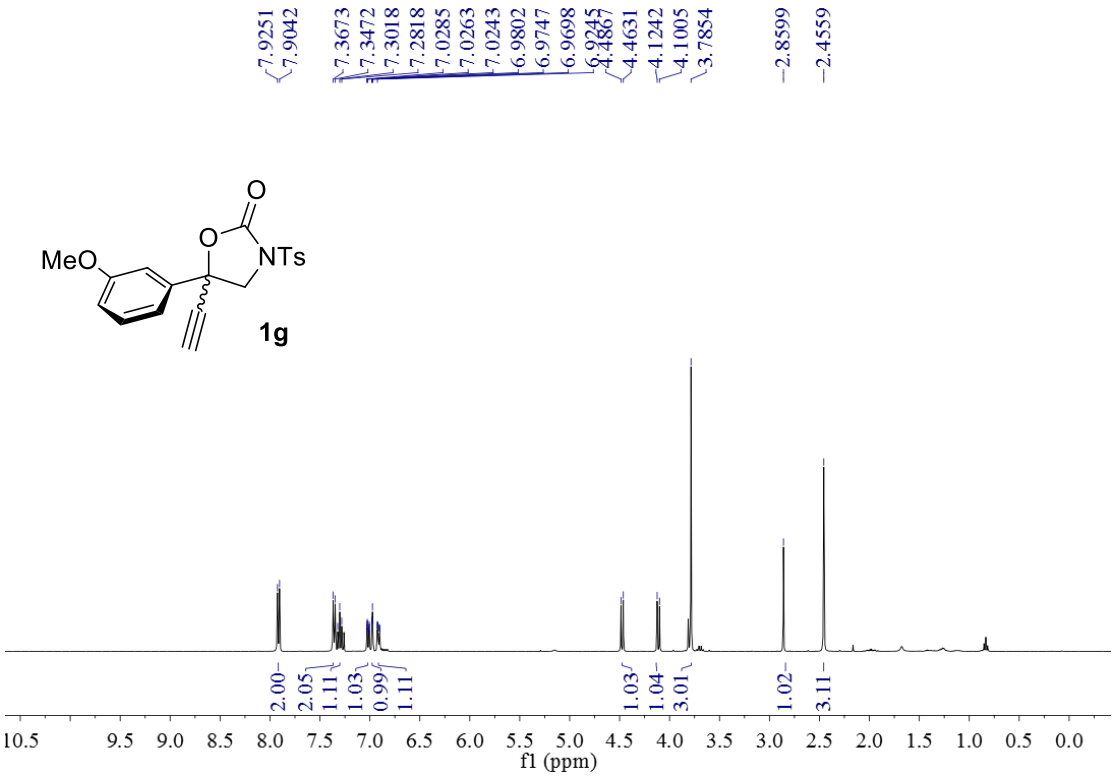
78.5101
75.3908
58.1188
21.6333
O
O
NTs
F3C
1f
f1 (ppm)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6.9698
6.9245
4.4867
4.4631
4.1242
4.1005
3.7854
2.8599
2.4559
MeO
O
O
NTs
1g
2.00
2.05
1.11
1.03
0.99
1.11
1.03
1.04
3.01
1.02
3.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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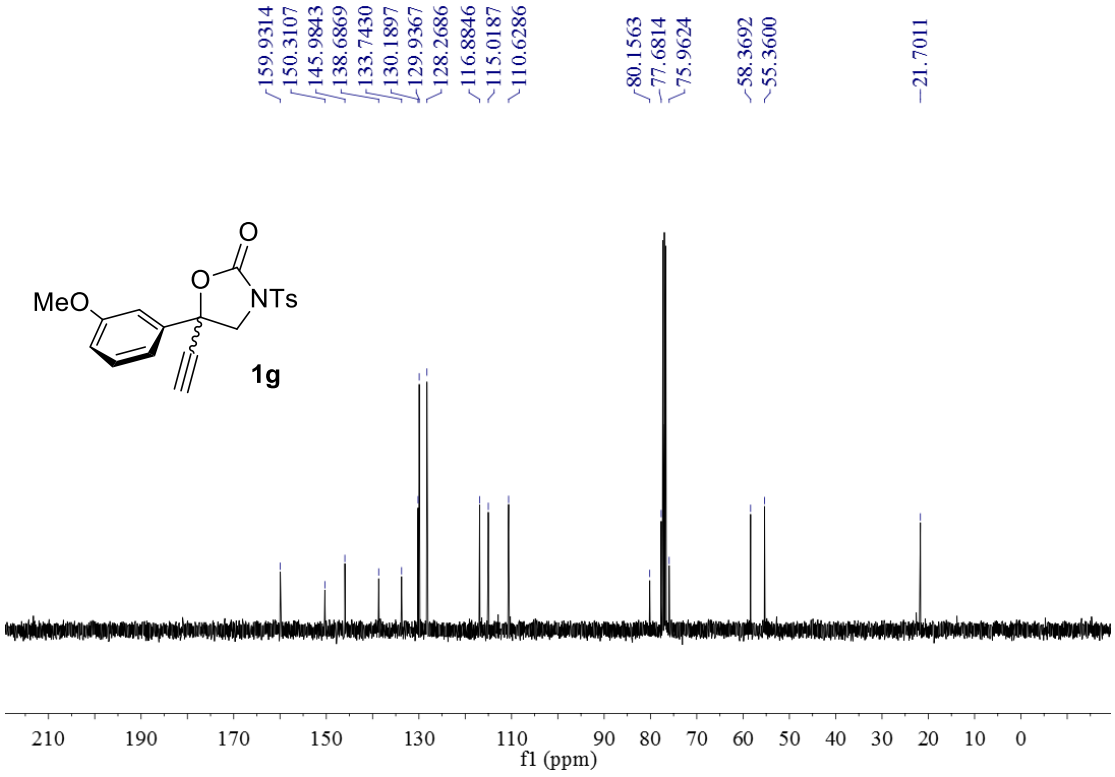
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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80.1563
77.6814
75.9624
58.3692
55.3600
21.7011
MeO
O
O
NTs
1g
210
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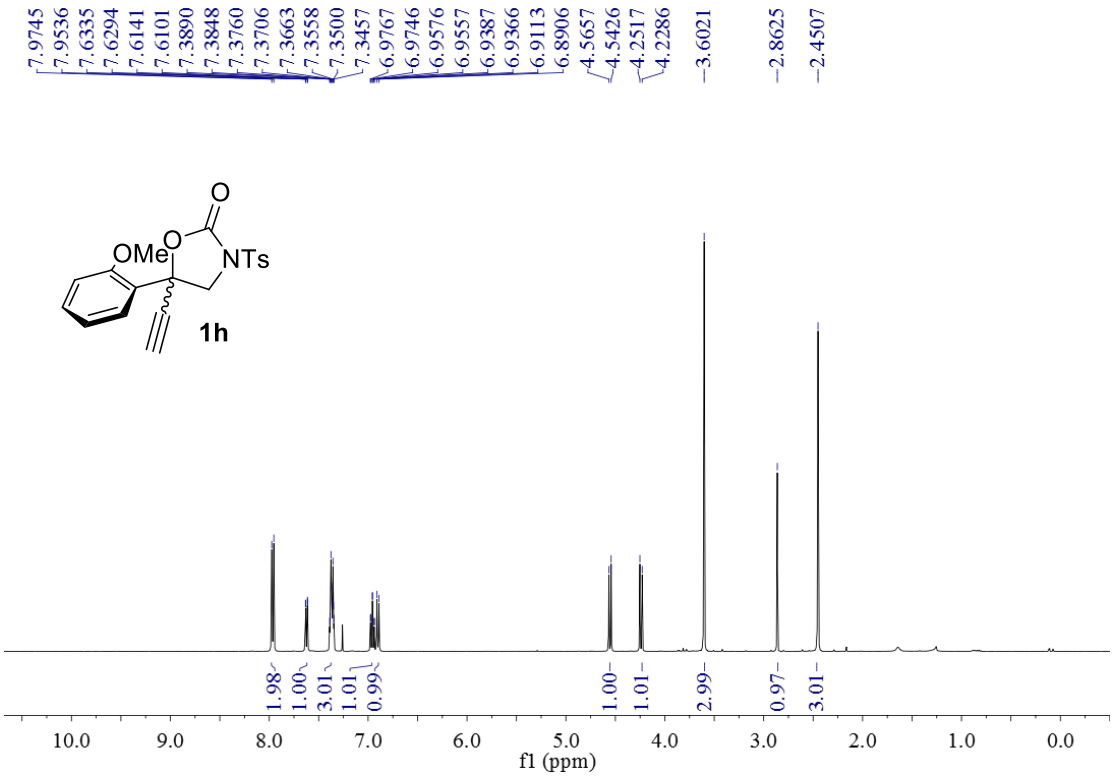
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3500
7.3457
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6.9746
6.9576
6.9557
6.9387
6.9366
6.9113
6.8906
4.5657
4.5426
4.2517
4.2286
3.6021
2.8625
2.4507
O
O
OMe
NTs
1h
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1.00
3.01
1.01
0.99
1.00
1.01
2.99
0.97
3.01
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9.0
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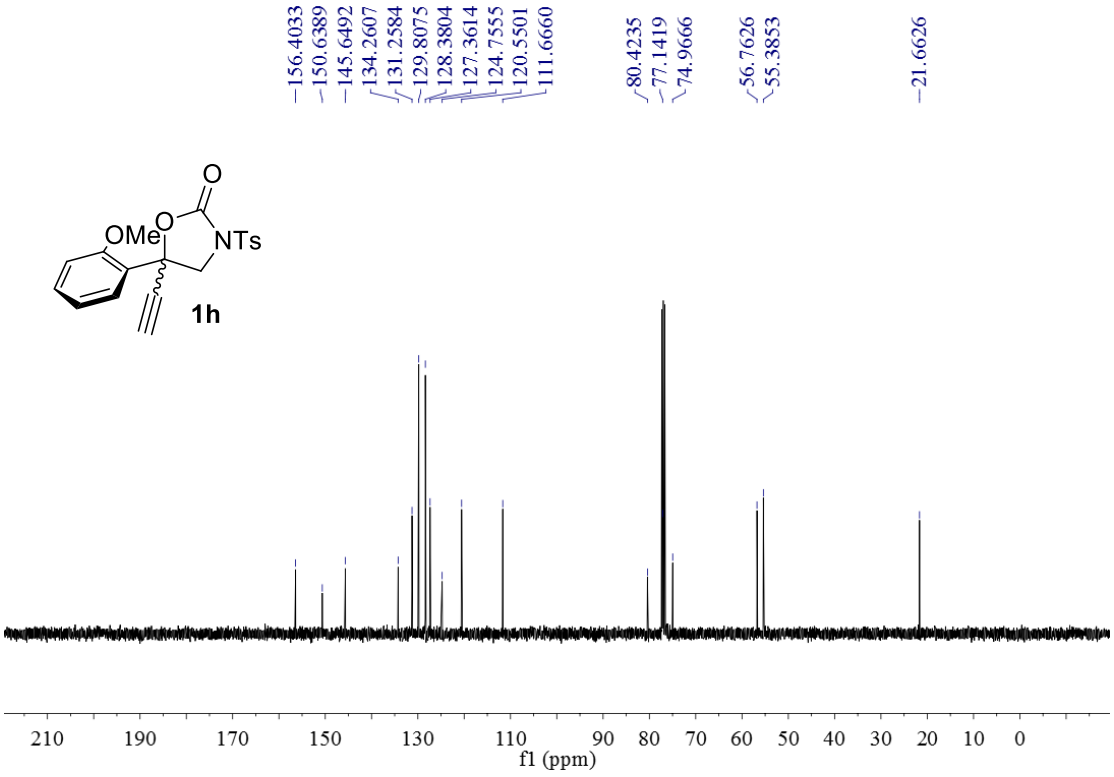
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.8075
128.3804
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124.7555
120.5501
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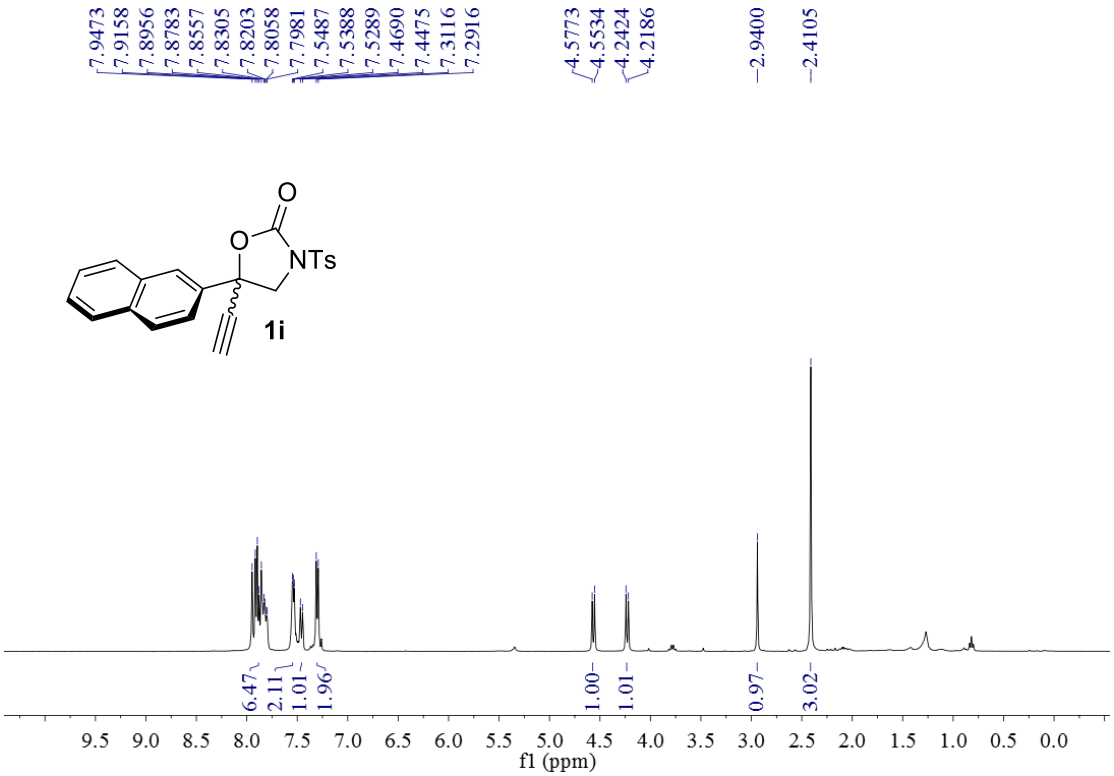
80.4235
77.1419
74.9666
56.7626
55.3853
21.6626
O
O
OMe
NTs
1h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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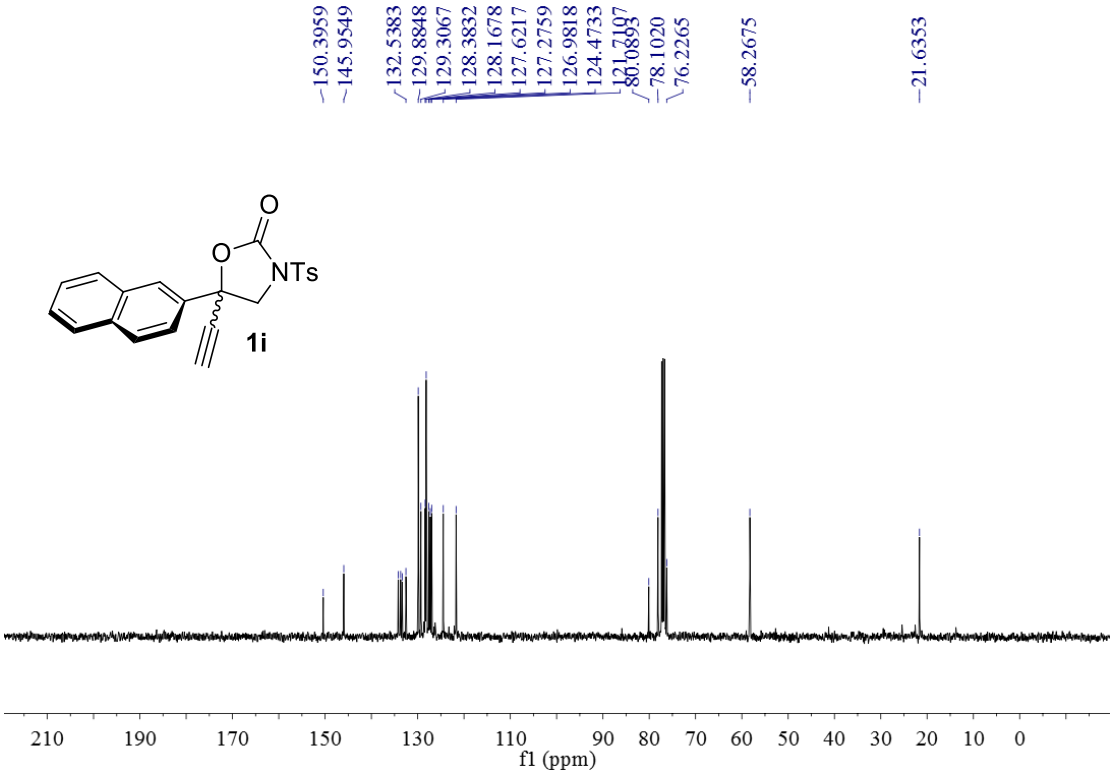
7.4690
7.4475
7.3116
7.2916
4.5773
4.5534
4.2424
4.2186
2.9400
2.4105
O
O
NTs
1i
6.47
2.11
1.01
1.96
1.00
1.01
0.97
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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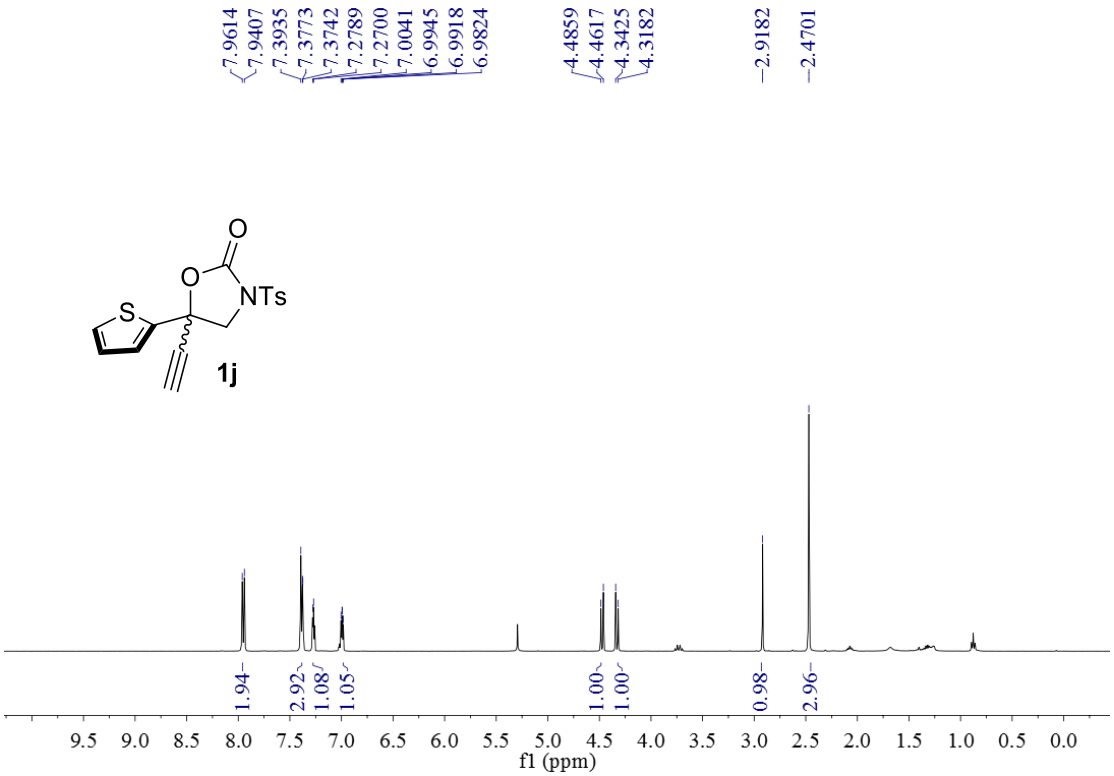
124.4733
121.7107
80.0893
78.1020
76.2265
58.2675
21.6353
O
O
NTs
1i
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2700
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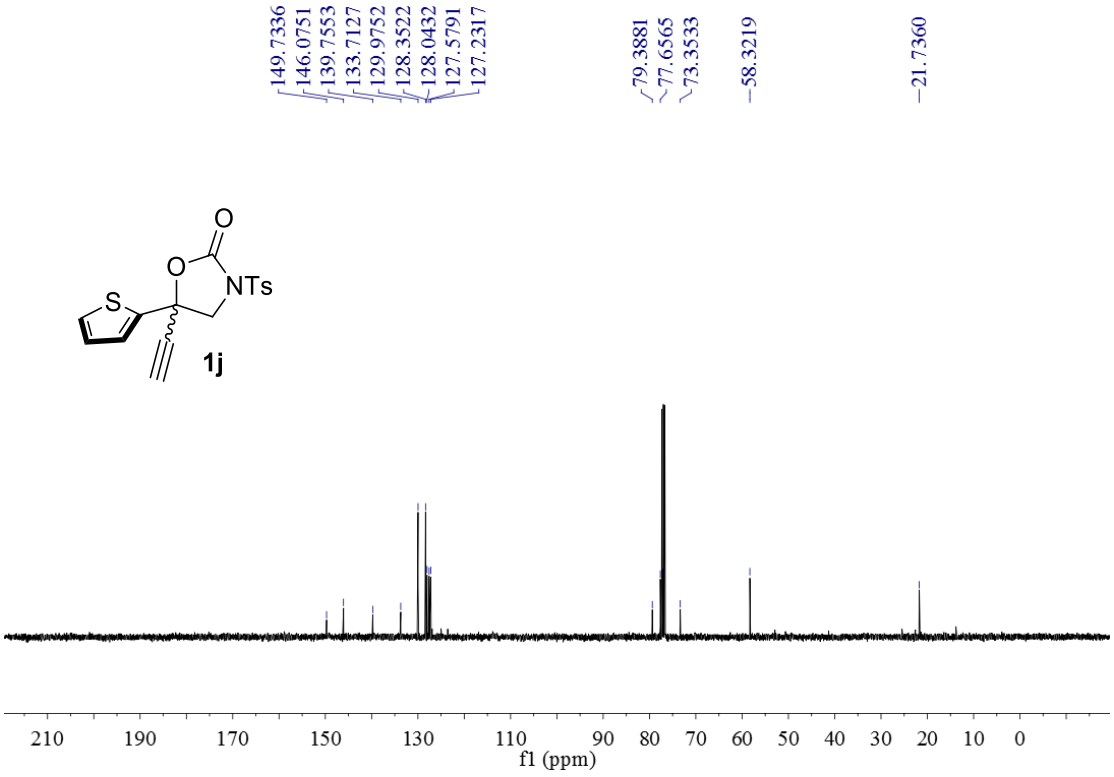
6.9824
4.4859
4.4617
4.3425
4.3182
2.9182
2.4701
O
O
NTs
S
1j
1.94
2.92
1.08
1.05
1.00
1.00
0.98
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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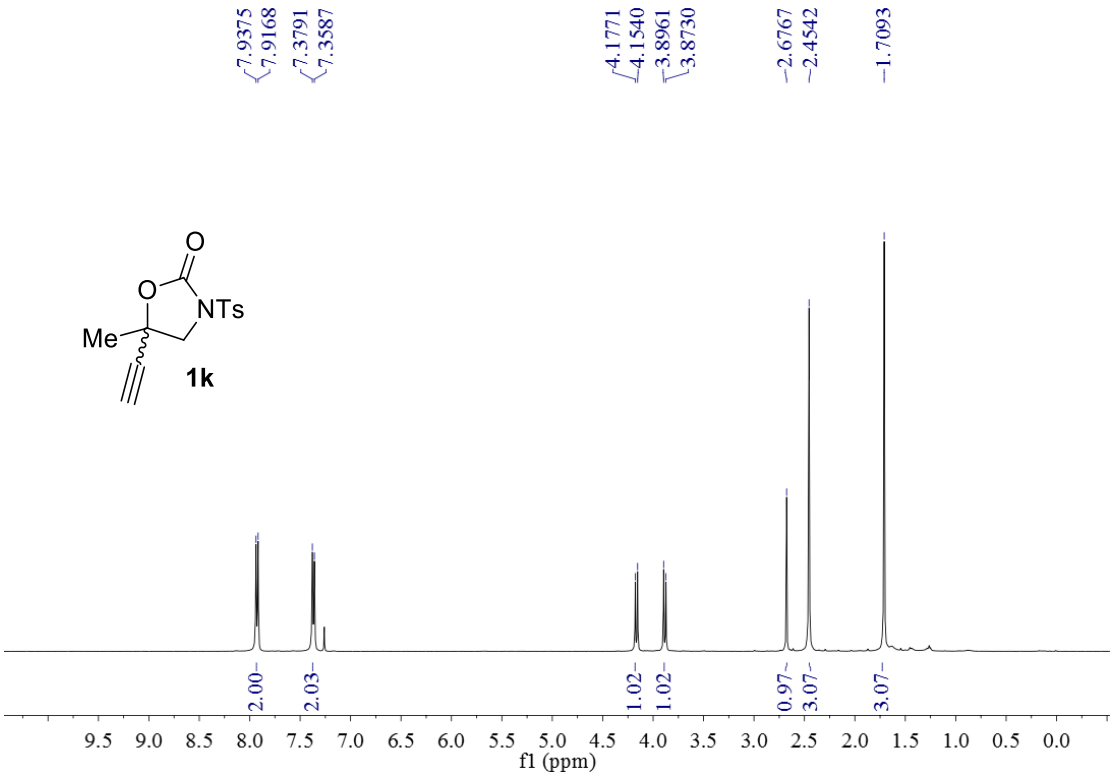
128.0432
127.5791
127.2317
79.3881
77.6565
73.3533
58.3219
21.7360
O
O
NTs
S
1j
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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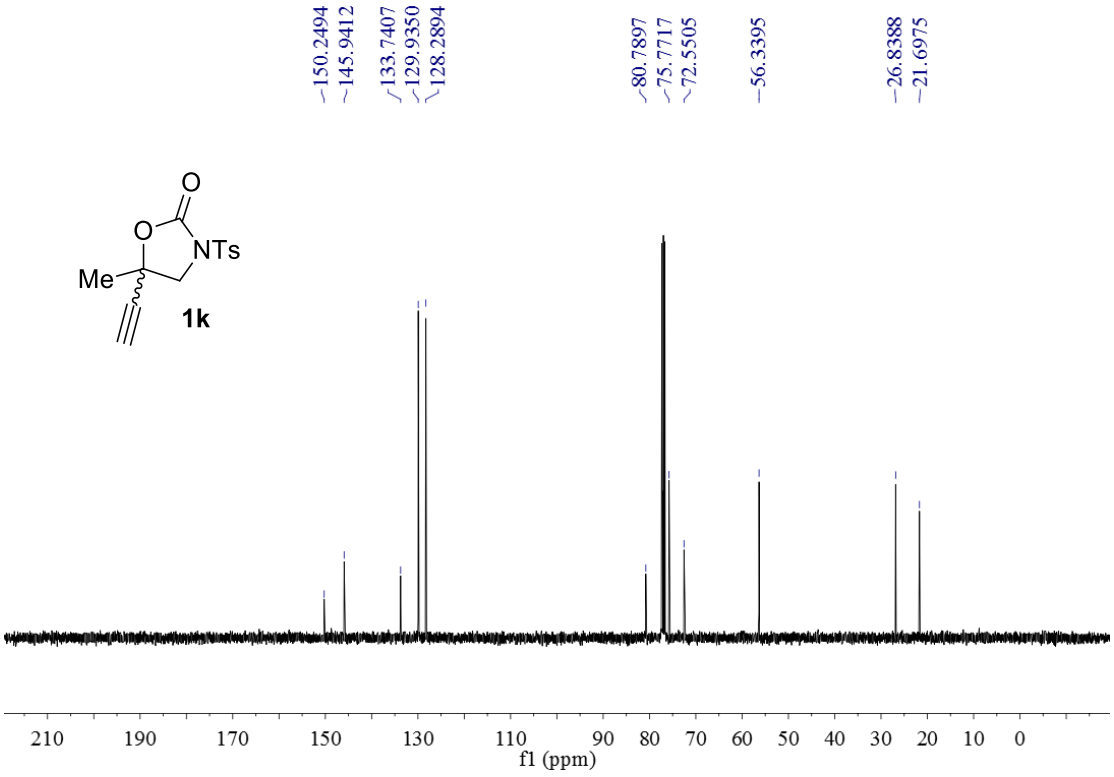
7.3587
4.1771
4.1540
3.8961
3.8730
2.6767
2.4542
1.7093
O
O
NTs
Me
1k
2.00
2.03
1.02
1.02
0.97
3.07
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.7407
129.9350
128.2894
80.7897
75.7717
72.5505
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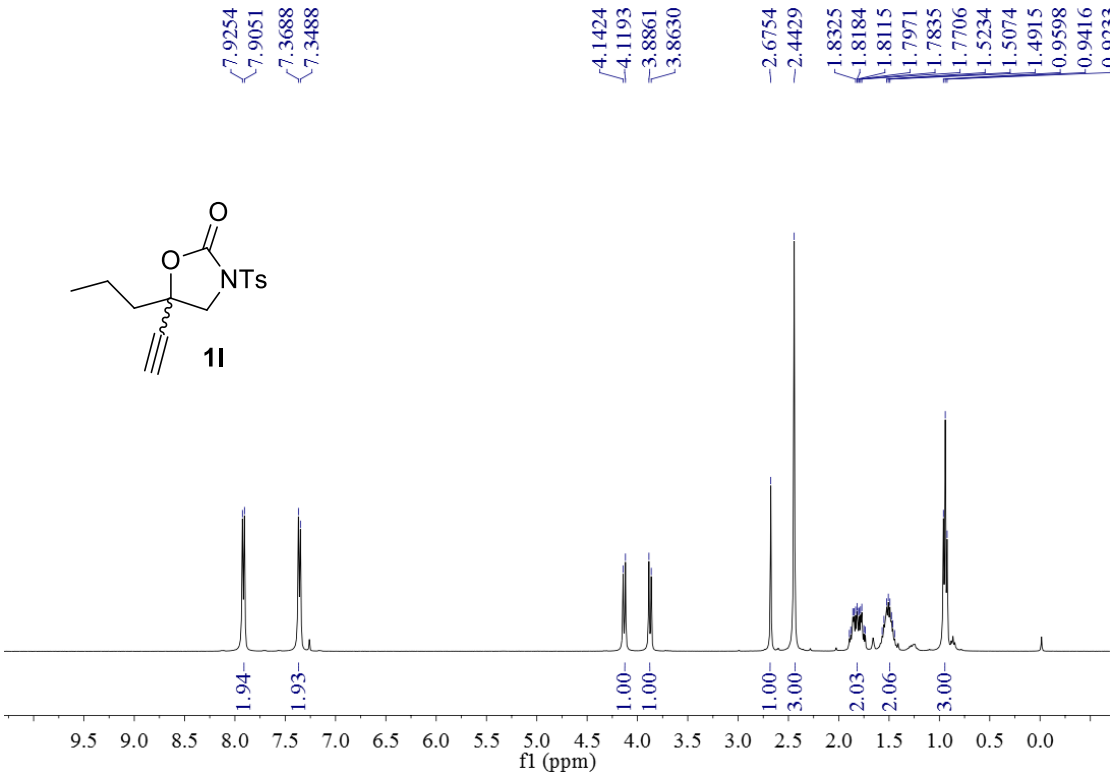
26.8388
21.6975
O
O
NTs
Me
1k
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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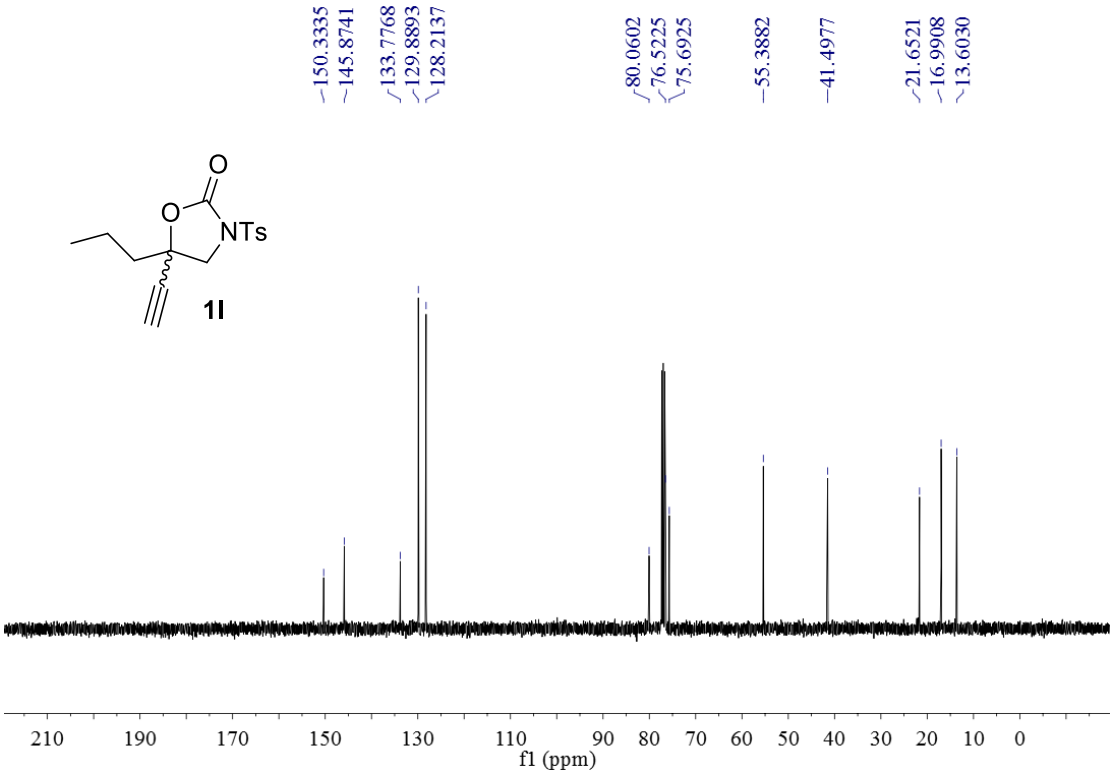
7.3688
7.3488
4.1424
4.1193
3.8861
3.8630
2.6754
2.4429
1.8325
1.8184
1.8115
1.7971
1.7835
1.7706
1.5234
1.5074
1.4915
0.9598
0.9416
O
O
NTs
1l
1.94
1.93
1.00
1.00
1.00
3.00
2.03
2.06
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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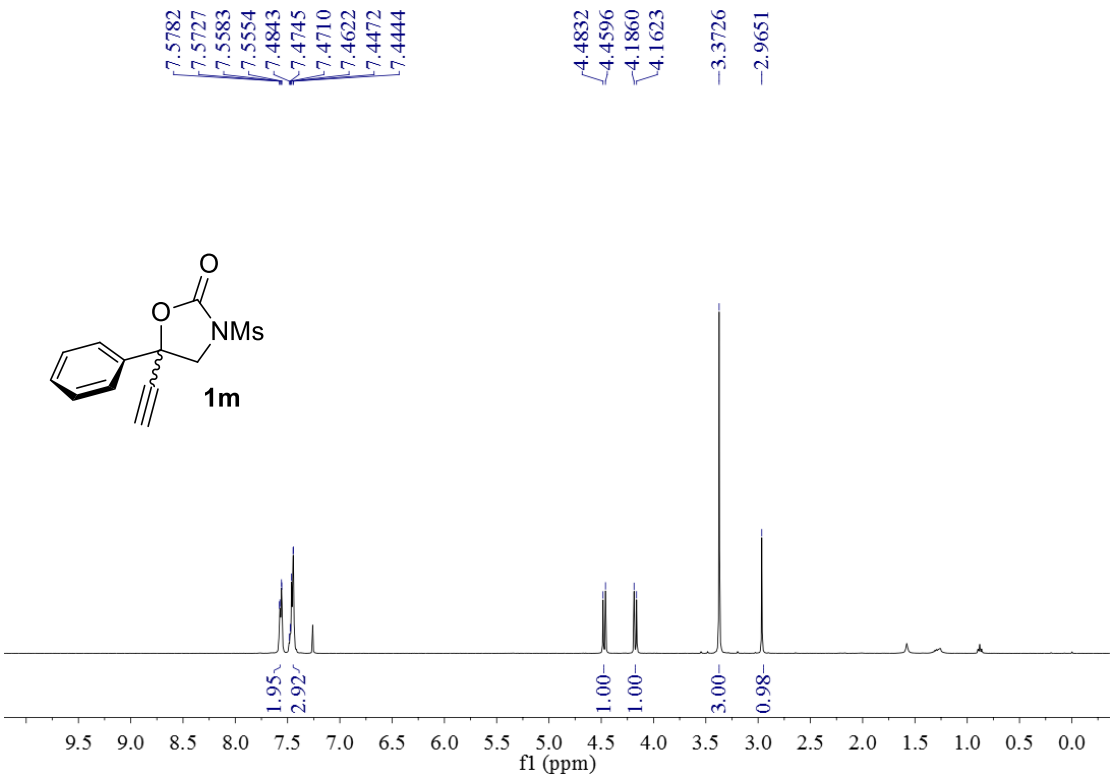
133.7768
129.8893
128.2137
80.0602
76.5225
75.6925
55.3882
41.4977
21.6521
16.9908
13.6030
O
O
NTs
1l
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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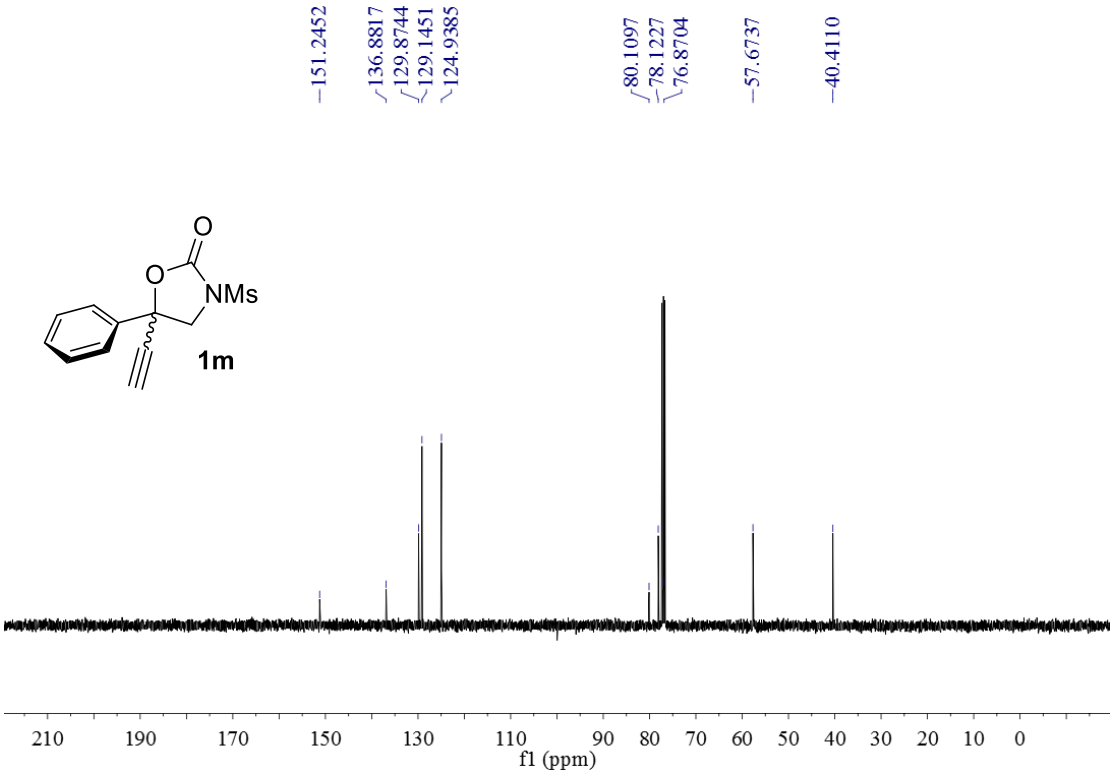
7.5727
7.5583
7.5554
7.4843
7.4745
7.4710
7.4622
7.4472
7.4444
4.4832
4.4596
4.1860
4.1623
3.3726
2.9651
O
O
NMs
1m
1.95
2.92
1.00
1.00
3.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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78.1227
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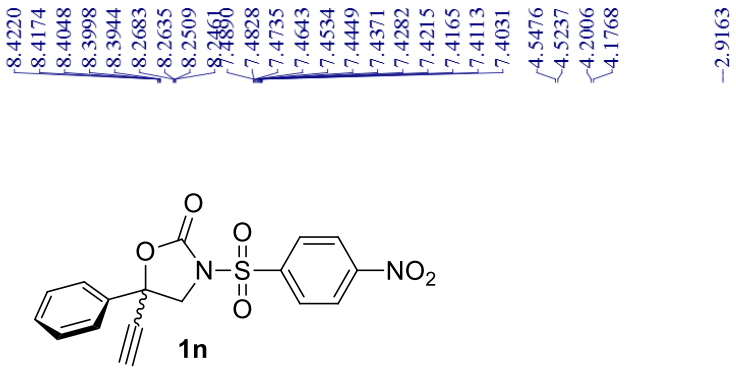
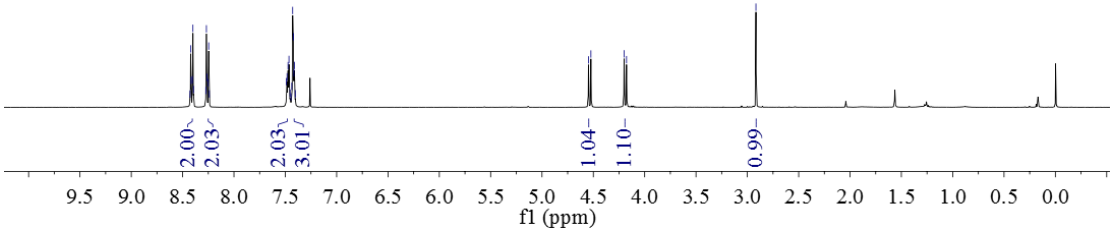
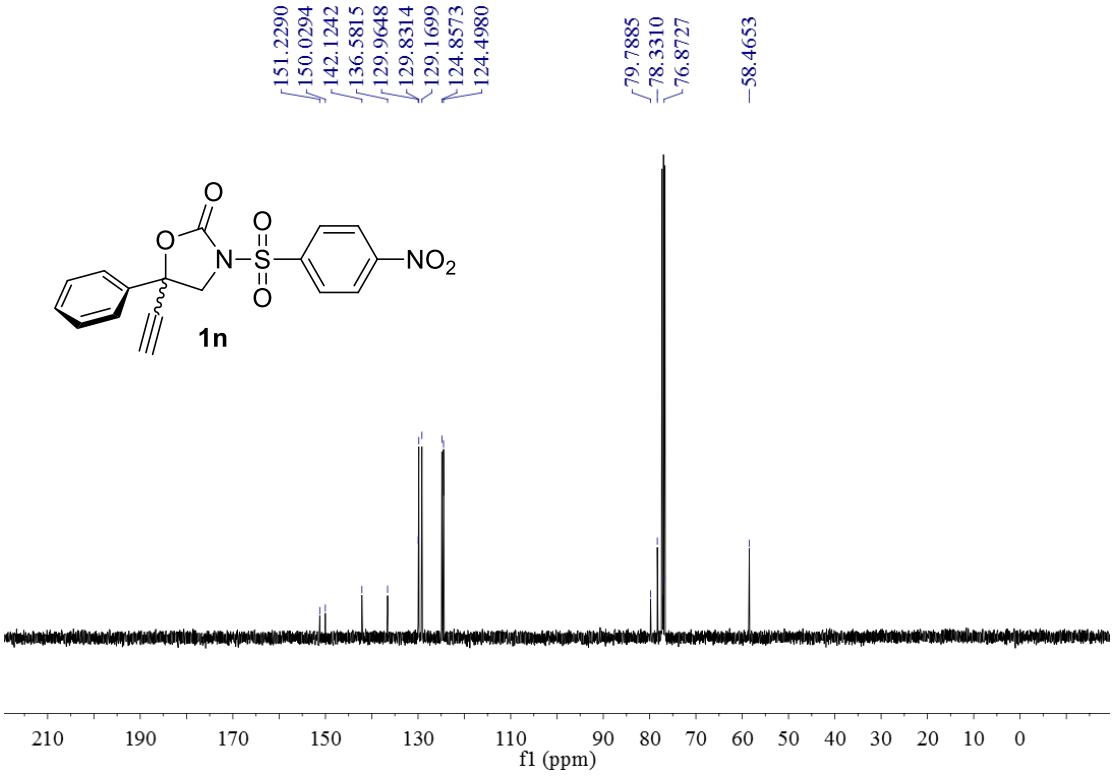
57.6737
40.4110
O
O
NMs
1m
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.4220
8.4174
8.4048
8.3998
8.3944
8.2683
8.2635
8.2509
7.4828
7.4735
7.4643
7.4534
7.4449
7.4371
7.4282
7.4215
7.4165
7.4113
7.4031
4.5476
4.5237
4.2006
4.1768
2.9163
O
O
N
S
O
O
NO2
1n


2.00
2.03
2.03
3.01
1.04
1.10
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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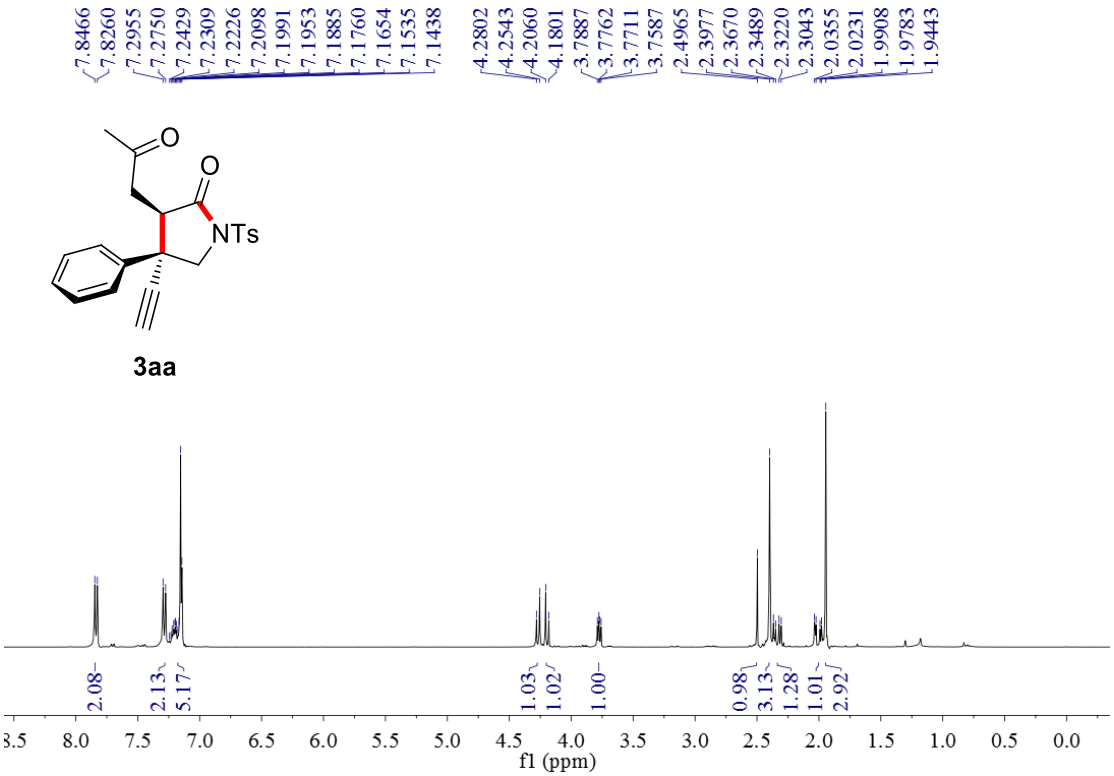
150.0294
142.1242
136.5815
129.9648
129.8314
129.1699
124.8573
124.4980
79.7885
78.3310
76.8727
58.4653
O
O
N
S
O
O
NO2
1n
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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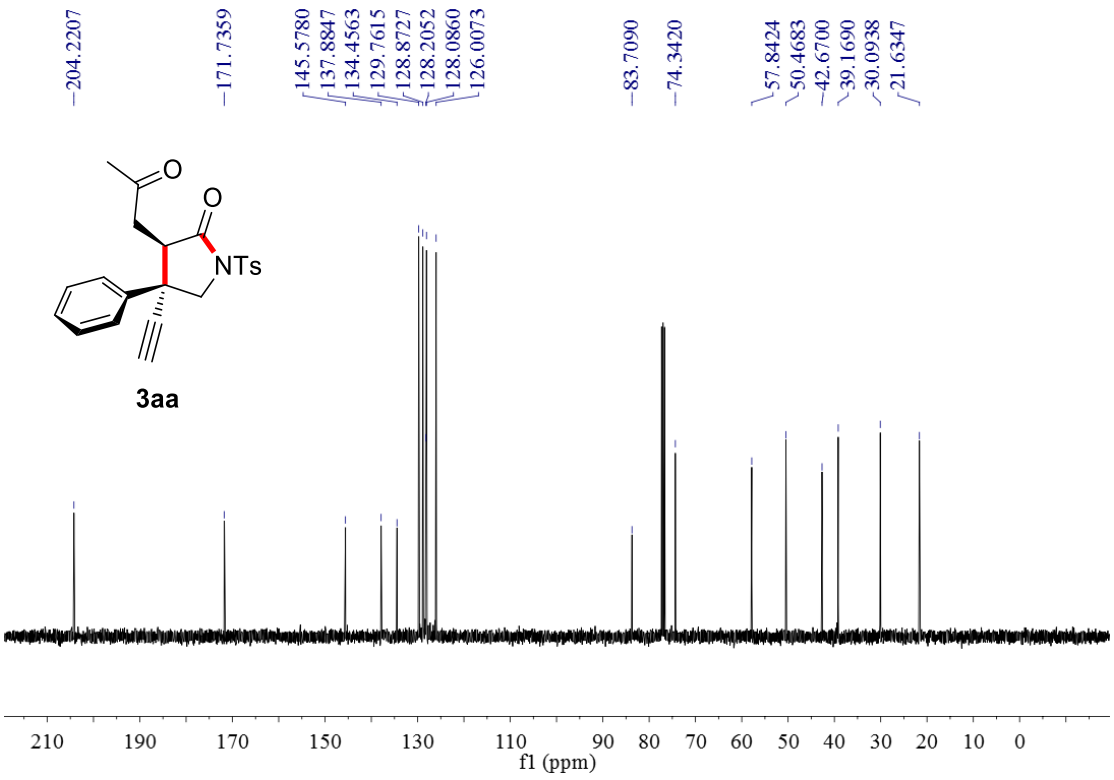
7.8260
7.2955
7.2750
7.2429
7.2309
7.2226
7.2098
7.1991
7.1953
7.1885
7.1760
7.1654
7.1535
7.1438
4.2802
4.2543
4.2060
4.1801
3.7887
3.7762
3.7711
3.7587
2.4965
2.3977
2.3670
2.3489
2.3220
2.3043
2.0355
2.0231
1.9908
1.9783
1.9443
O
O
NTs
3aa
2.08
2.13
5.17
1.03
1.02
1.00
0.98
3.13
1.28
1.01
2.92
f1 (ppm)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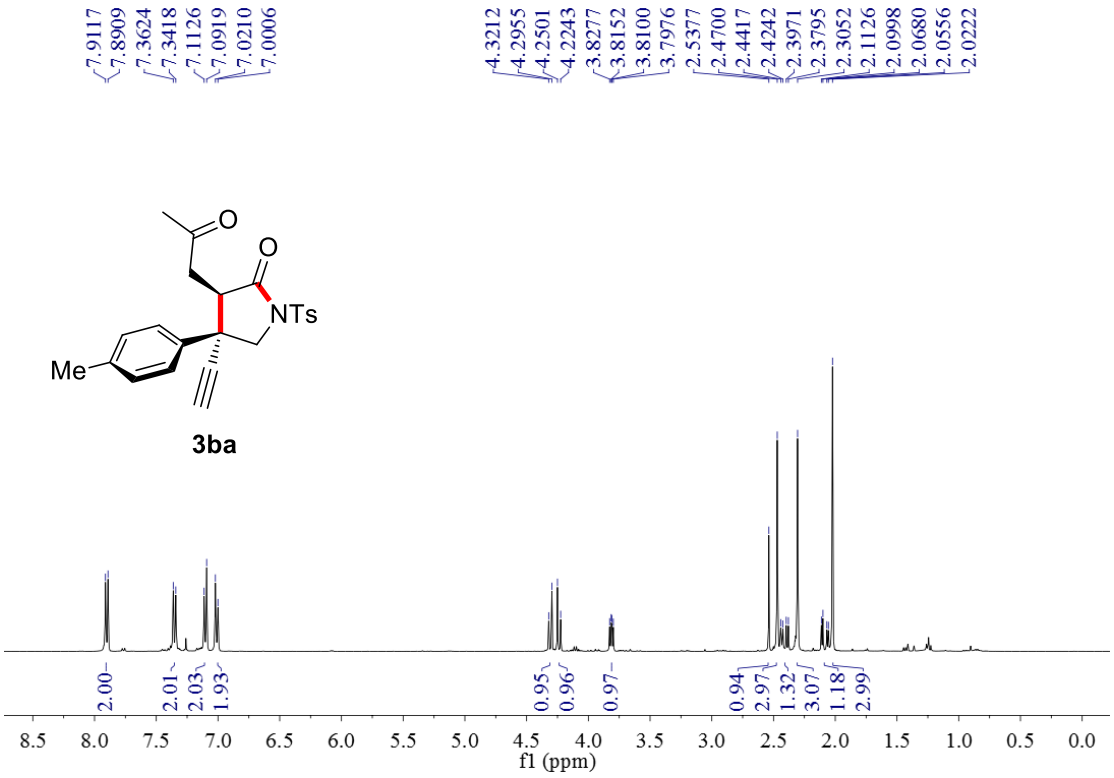
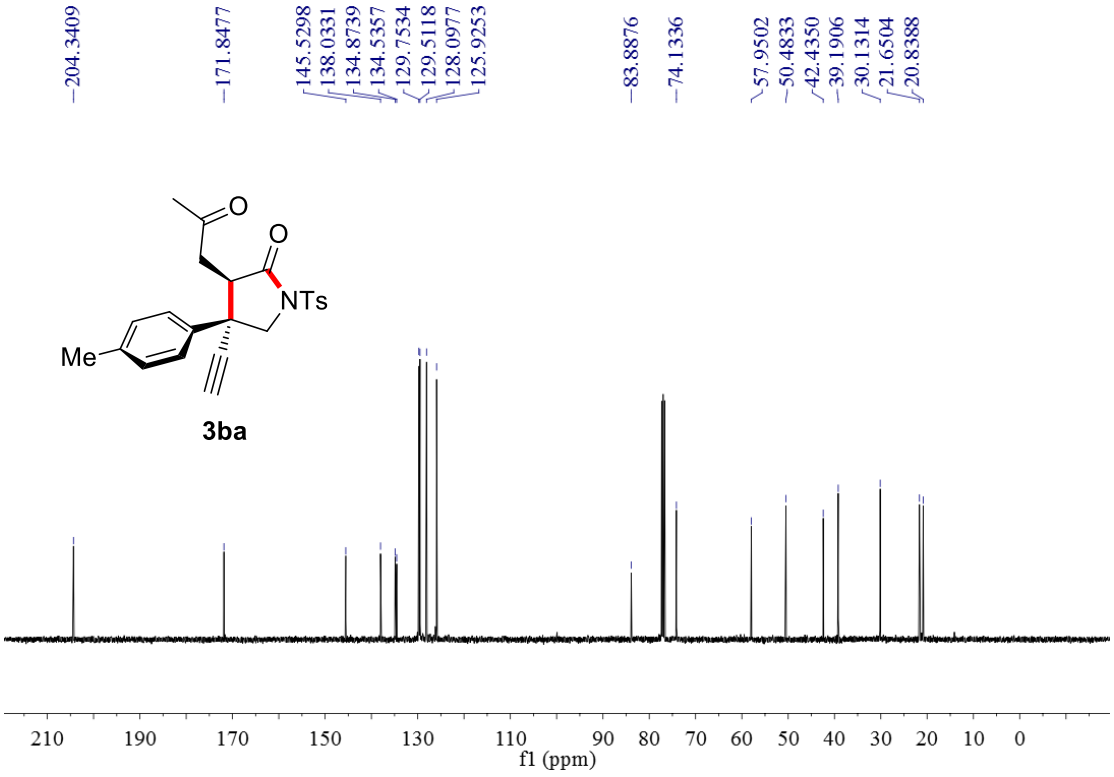
171.7359
145.5780
137.8847
134.4563
129.7615
128.8727
128.2052
128.0860
126.0073
83.7090
74.3420
57.8424
50.4683
42.6700
39.1690
30.0938
21.6347
O
O
NTs
3aa
f1 (ppm)


7.9117
7.8909
7.3624
7.3418
7.1126
7.0919
7.0210
7.0006
4.3212
4.2955
4.2501
4.2243
3.8277
3.8152
3.8100
3.7976
2.5377
2.4700
2.4417
2.4242
2.3971
2.3795
2.3052
2.1126
2.0998
2.0680
2.0556
2.0222
O
O
NTs
Me
2.00
2.01
2.03
1.93
0.95
0.96
0.97
0.94
2.97
1.32
3.07
1.18
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3ba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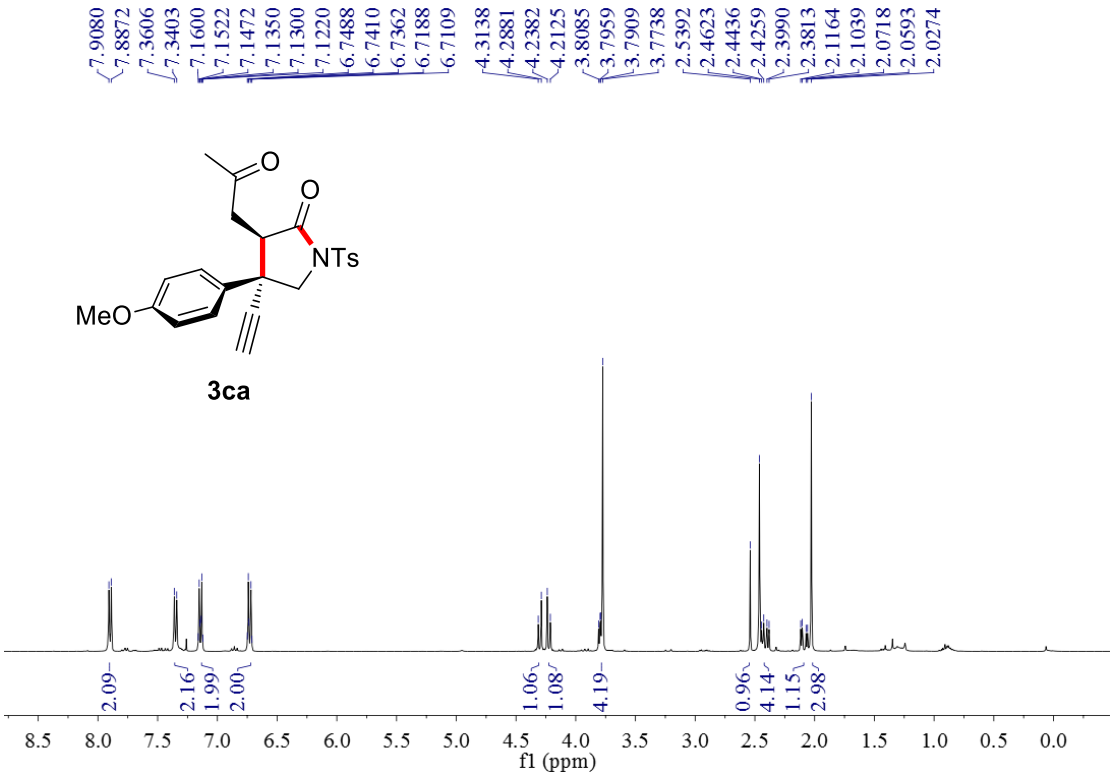
134.5357
129.7534
129.5118
128.0977
125.9253
83.8876
74.1336
57.9502
50.4833
42.4350
39.1906
30.1314
21.6504
20.8388
O
O
NTs
Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ba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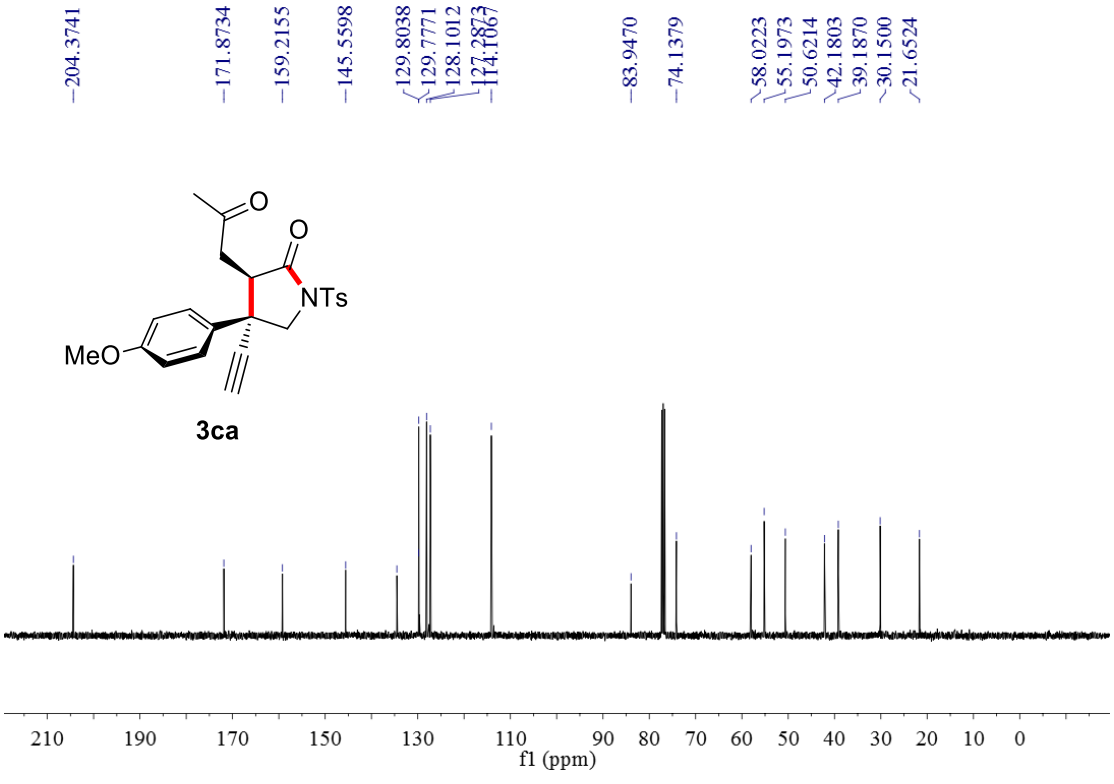
7.8872
7.3606
7.3403
7.1600
7.1522
7.1472
7.1350
7.1300
7.1220
6.7488
6.7410
6.7362
6.7188
6.7109
4.3138
4.2881
4.2382
4.2125
3.8085
3.7959
3.7909
3.7738
2.5392
2.4623
2.4436
2.4259
2.3990
2.3813
2.1164
2.1039
2.0718
2.0593
2.0274
O
O
NTs
MeO
3ca
2.09
2.16
1.99
2.00
1.06
1.08
4.19
0.96
4.14
1.15
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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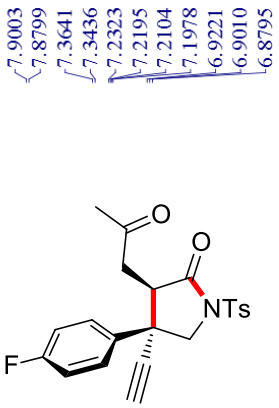
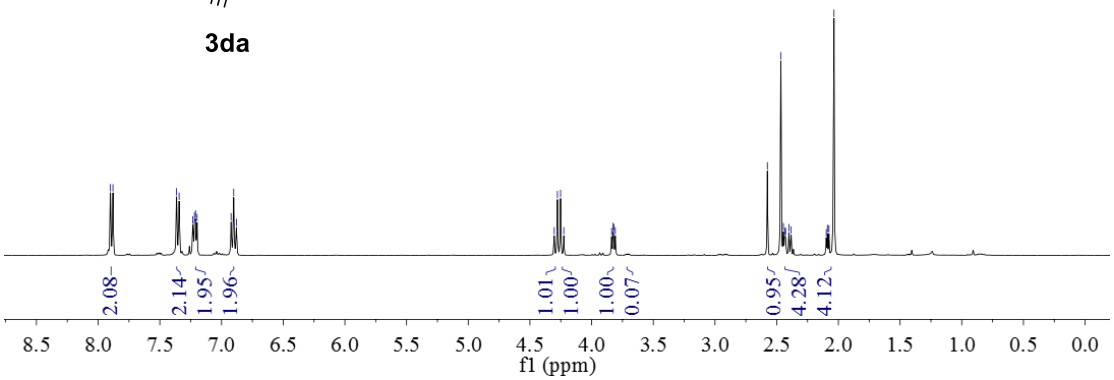
129.8038
129.7771
128.1012
127.2873
114.1067
83.9470
74.1379
58.0223
55.1973
50.6214
42.1803
39.1870
30.1500
21.6524
O
O
NTs
MeO
3ca
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
NTs
F

3da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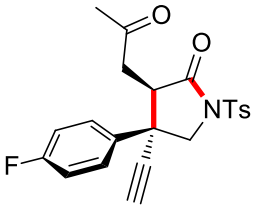
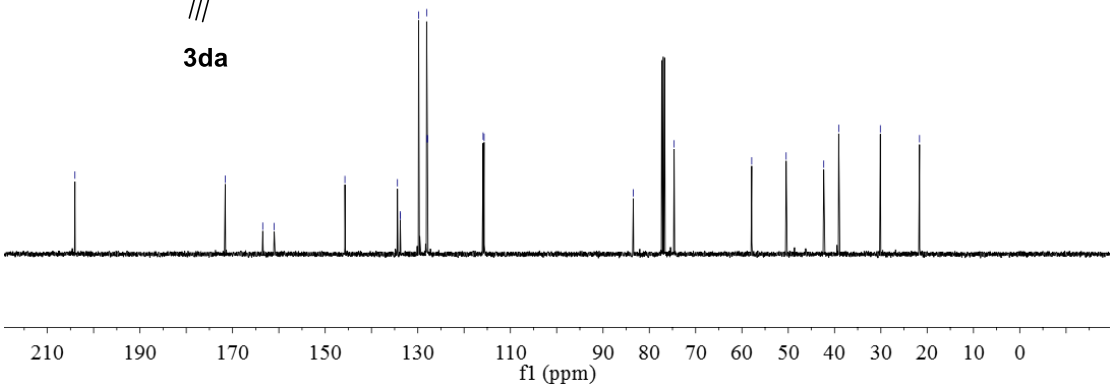
7.3641
7.3436
7.2323
7.2195
7.2104
7.1978
6.9221
6.9010
6.8795
4.3030
4.2771
4.2518
4.2257
3.8381
3.8255
3.8205
3.8081
2.5755
2.4665
2.4457
2.4355
2.4278
2.4008
2.3830
2.0983
2.0887
2.0764
2.0356
2.08
2.14
1.95
1.96
1.01
1.00
1.00
0.07
0.95
4.28
4.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
NTs
F

3da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129.8243
128.0899
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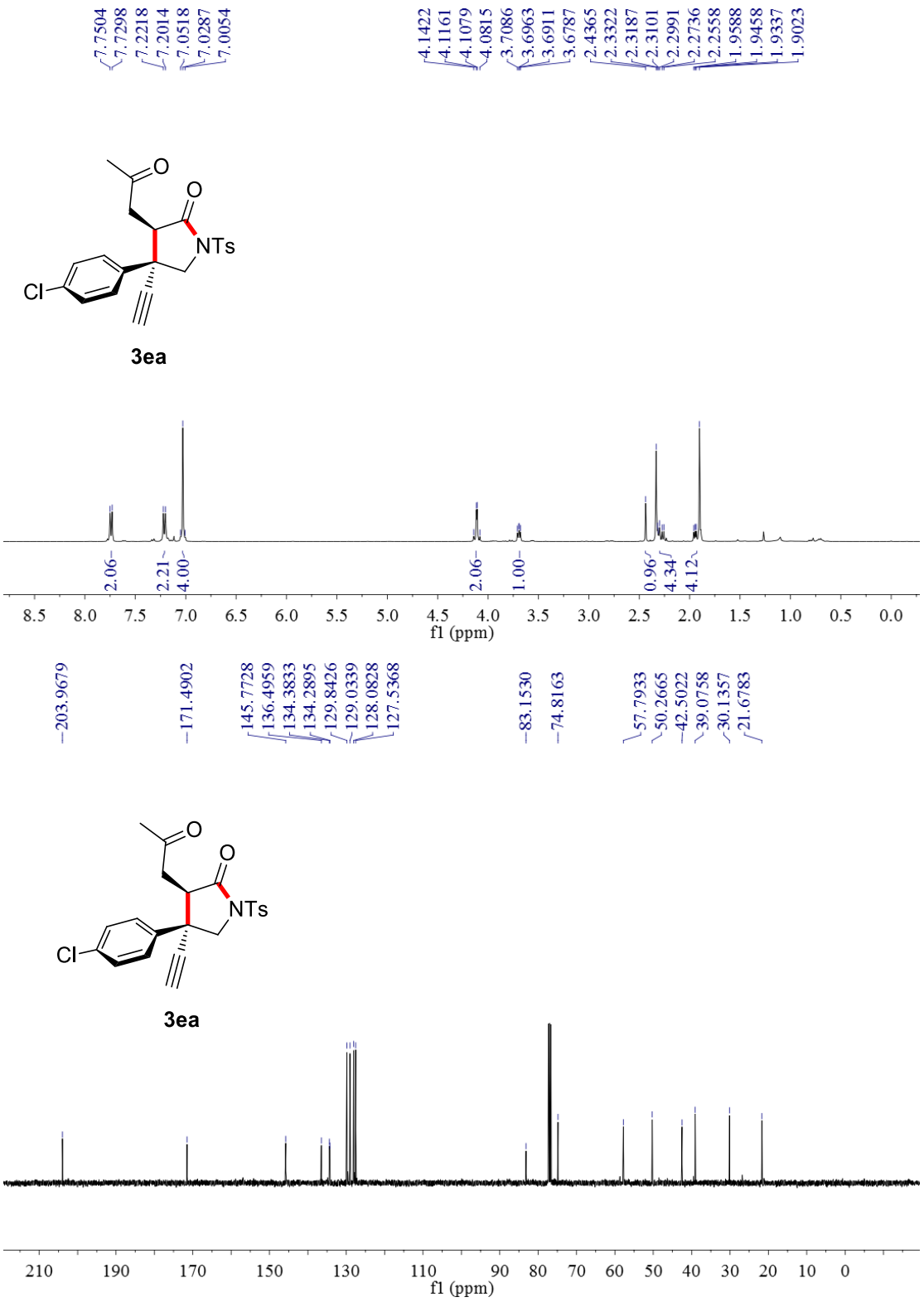
117.9161
115.8891
115.6754
83.4578
74.6478
57.8889
50.4551
42.3351
39.1017
30.1126
21.6498
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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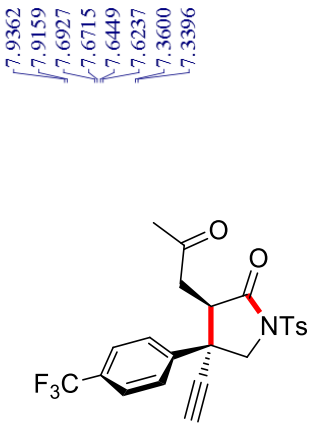
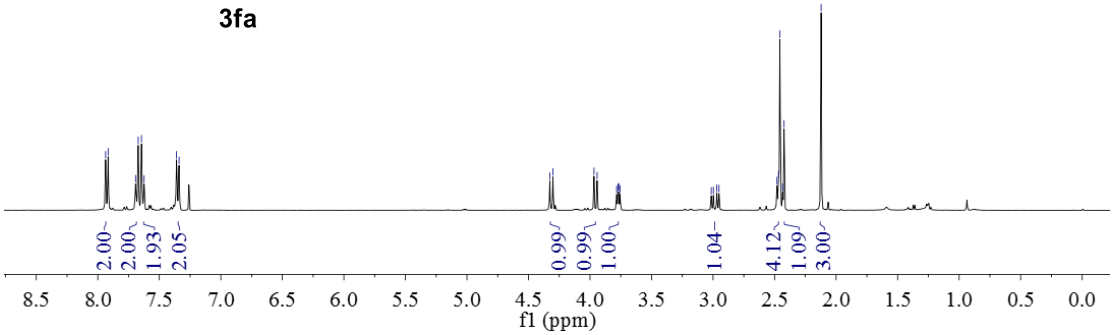
7.2218
7.2014
7.0518
7.0287
7.0054
4.1422
4.1161
4.1079
4.0815
3.7086
3.6963
3.6911
3.6787
2.4365
2.3322
2.3187
2.3101
2.2991
2.2736
2.2558
1.9588
1.9458
1.9337
1.9023
O
O
NTs
Cl
3ea
2.06
2.21
4.00
2.06
1.00
0.96
4.34
4.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
203.9679
171.4902
145.7728
136.4959
134.3833
134.2895
129.8426
129.0339
128.0828
127.5368
83.1530
74.8163
57.7933
50.2665
42.5022
39.0758
30.1357
21.6783
O
O
NTs
Cl
3ea
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
NTs
F3C

3fa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7.3600
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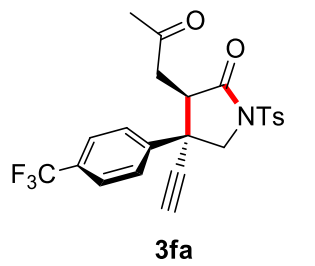
4.3012
3.9675
3.9420
3.7834
3.7726
3.7664
3.7556
2.9972
2.9692
2.4679
2.4571
2.4344
2.4228
2.1215
2.00
2.00
1.93
2.05
0.99
0.99
1.00
1.04
4.12
1.09
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
NTs
F3C

3fa

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171.1981
145.5033
140.5561
134.8258
131.0390
130.7130
129.7099
128.2555
127.0535
126.0958
126.0591
126.0218
125.9854
125.0684
122.3626
81.6268
75.9829
58.6644
48.4964
46.6349
39.7343
30.2019
21.7412
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9057
7.8850
7.3500
7.3297
7.1091
7.0890
6.8974
6.8924
6.8875
6.8206
6.7484
6.7459
6.7290
6.7264
6.3593
4.3334
4.2568
4.2309
3.8408
3.8284
3.8232
3.8107
3.7273
2.5560
2.4527
2.4302
2.4032
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2.1229
2.1104
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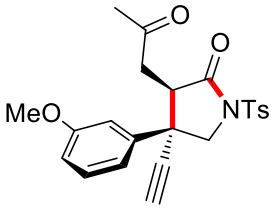
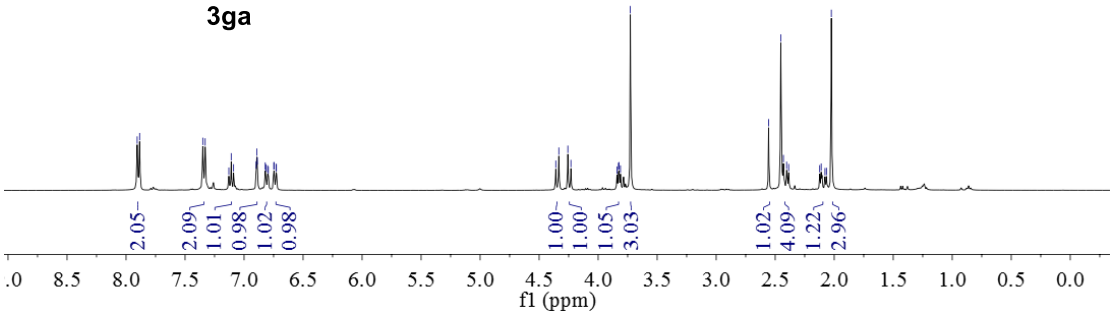
2.0658
2.0244


O
O
MeO
NTs

3ga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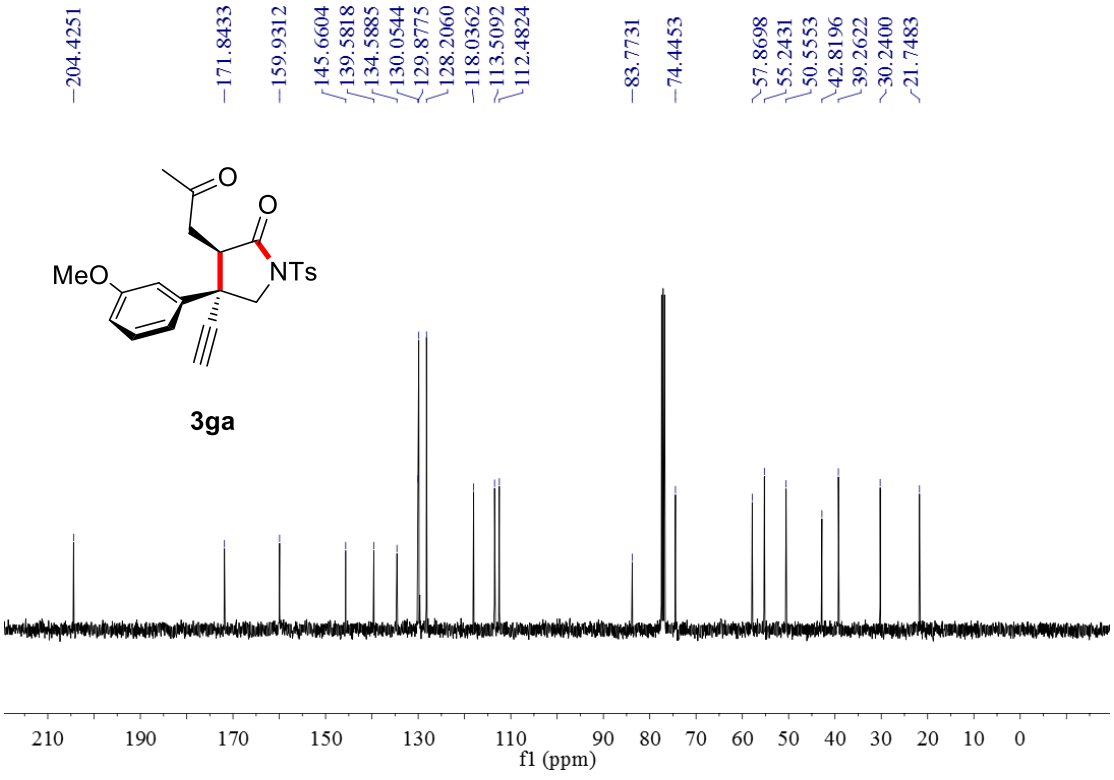
2.09
1.01
0.98
1.02
0.98
1.00
1.00
1.05
3.03
1.02
4.09
1.22
2.96
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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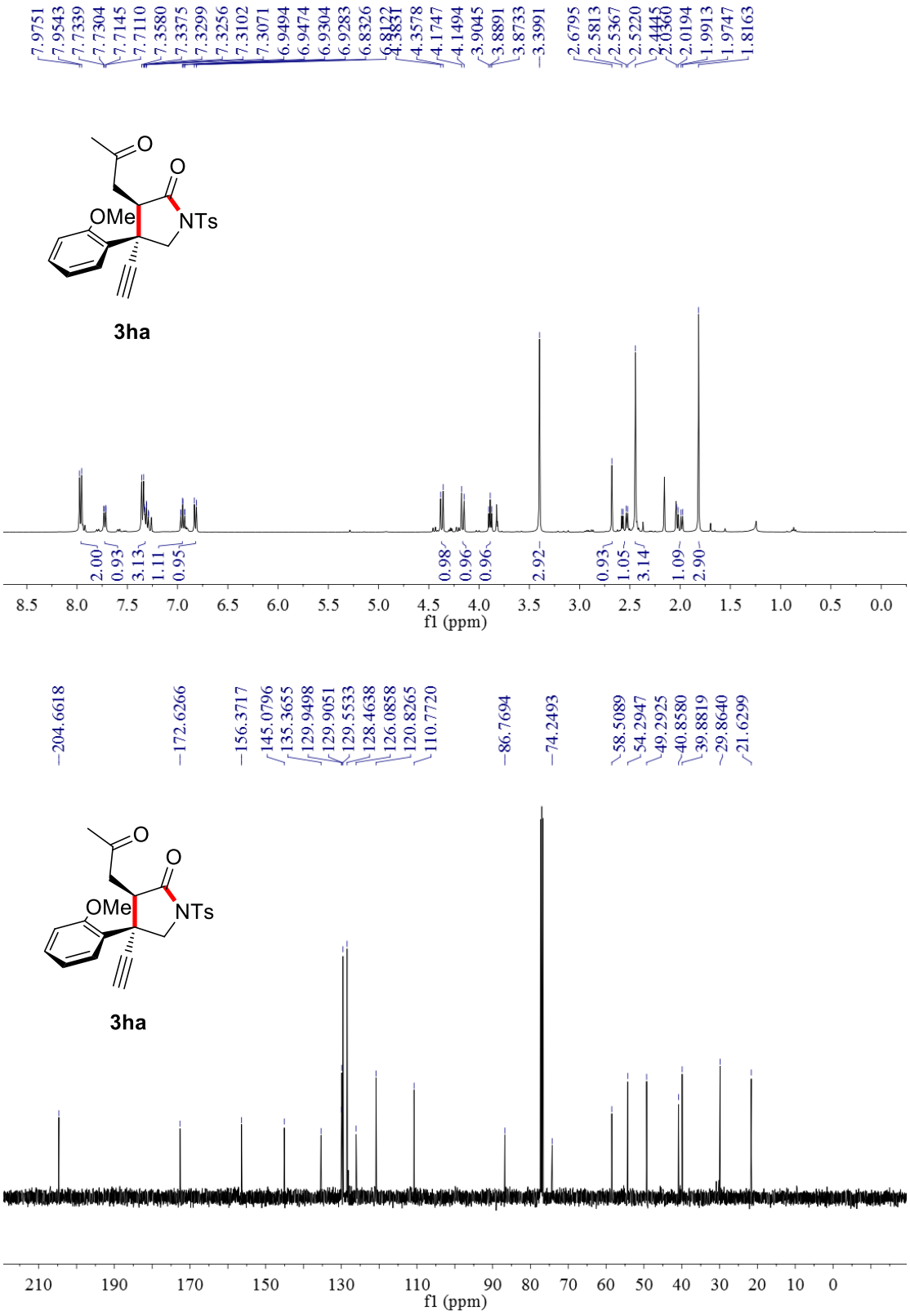
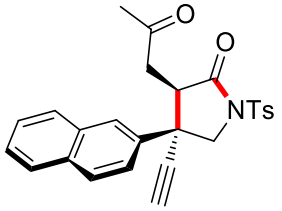
171.8433
159.9312
145.6604
139.5818
134.5885
130.0544
129.8775
128.2060
118.0362
113.5092
112.4824
83.7731
74.4453
57.8698
55.2431
50.5553
42.8196
39.2622
30.2400
21.7483
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

O
O
MeO
NTs

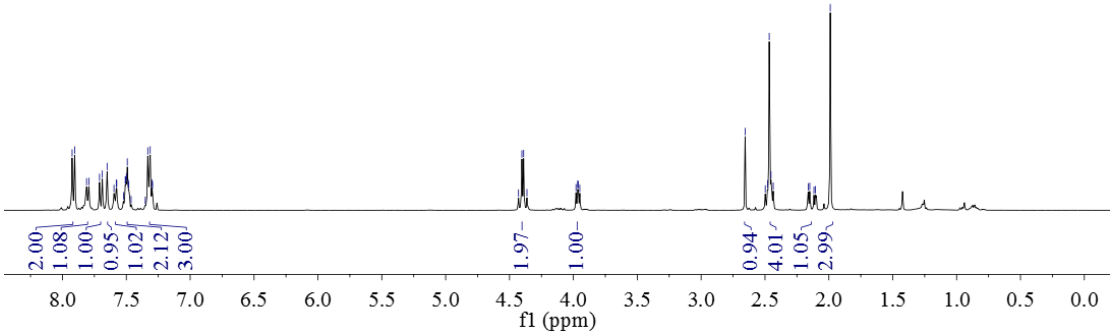
3ga


7.9751
7.9543
7.7339
7.7304
7.7145
7.7110
7.3580
7.3375
7.3299
7.3256
7.3102
7.3071
6.9494
6.9474
6.9304
6.9283
6.8326
4.3578
4.1747
4.1494
3.9045
3.8891
3.8733
3.3991
2.6795
2.5813
2.5367
2.5220
2.0360
2.0194
1.9913
1.9747
1.8163
O
O
OMe
NTs
3ha
2.00
0.93
3.13
1.11
0.95
0.98
0.96
0.96
2.92
0.93
1.05
3.14
1.09
2.90
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
204.6618
172.6266
156.3717
145.0796
135.3655
129.9498
129.9051
129.5533
128.4638
126.0858
120.8265
110.7720
86.7694
74.2493
58.5089
54.2947
49.2925
40.8580
39.8819
29.8640
21.6299
O
O
OMe
NTs
3ha
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

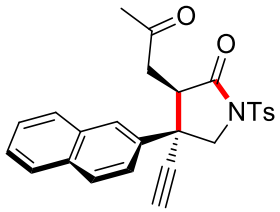

7.9244
7.9039
7.8112
7.7928
7.7097
7.6879
7.6504
7.5788
7.5750
7.5085
7.5047
7.4991
7.4924
7.4854
7.3321
7.3130
4.4035
4.3897
4.3635
3.9795
3.9670
3.9620
3.9497
2.6553
2.4980
2.4797
2.4669
2.4531
2.4355
2.1616
2.1494
2.1169
2.1044
1.9891


O
O
NTs

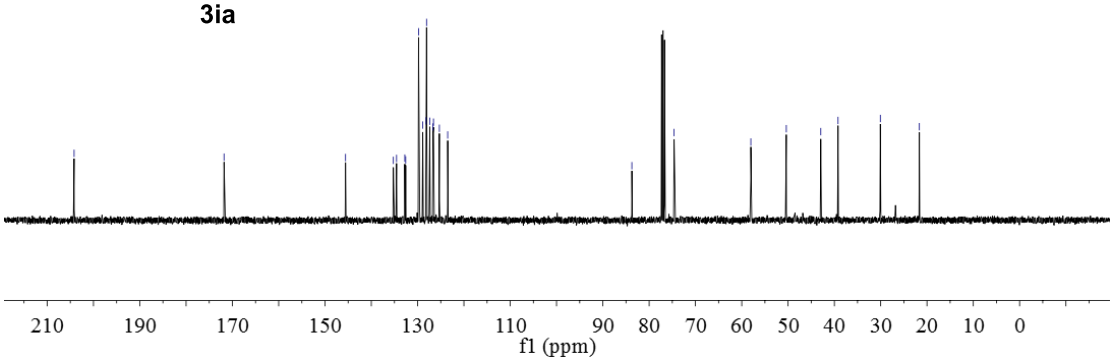
3ia

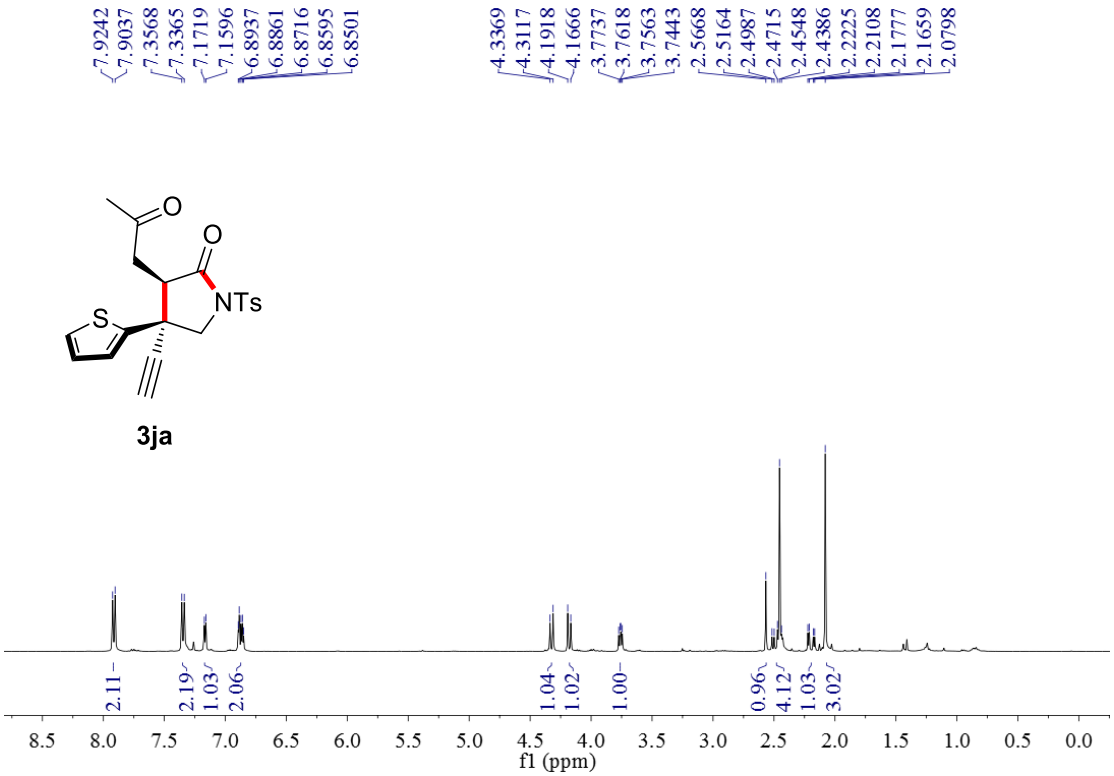

2.00
1.08
1.00
0.95
1.02
2.12
3.00
1.97
1.00
0.94
4.01
1.05
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

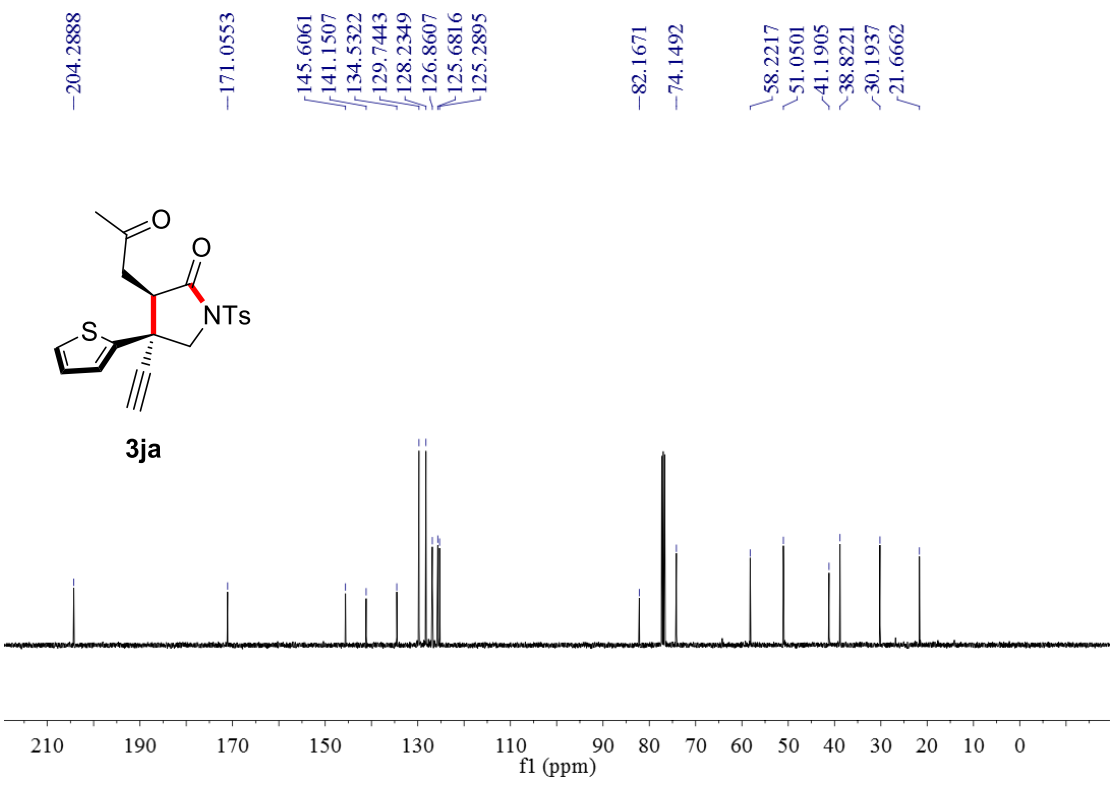

204.1781
171.8058
145.5610
135.2381
134.5433
132.7656
132.5706
129.8000
128.8840
128.1656
128.0688
127.3697
126.6921
126.5746
125.2988
123.5055
83.7349
74.6108
58.0364
50.3792
42.9344
39.2070
30.0785
21.6462

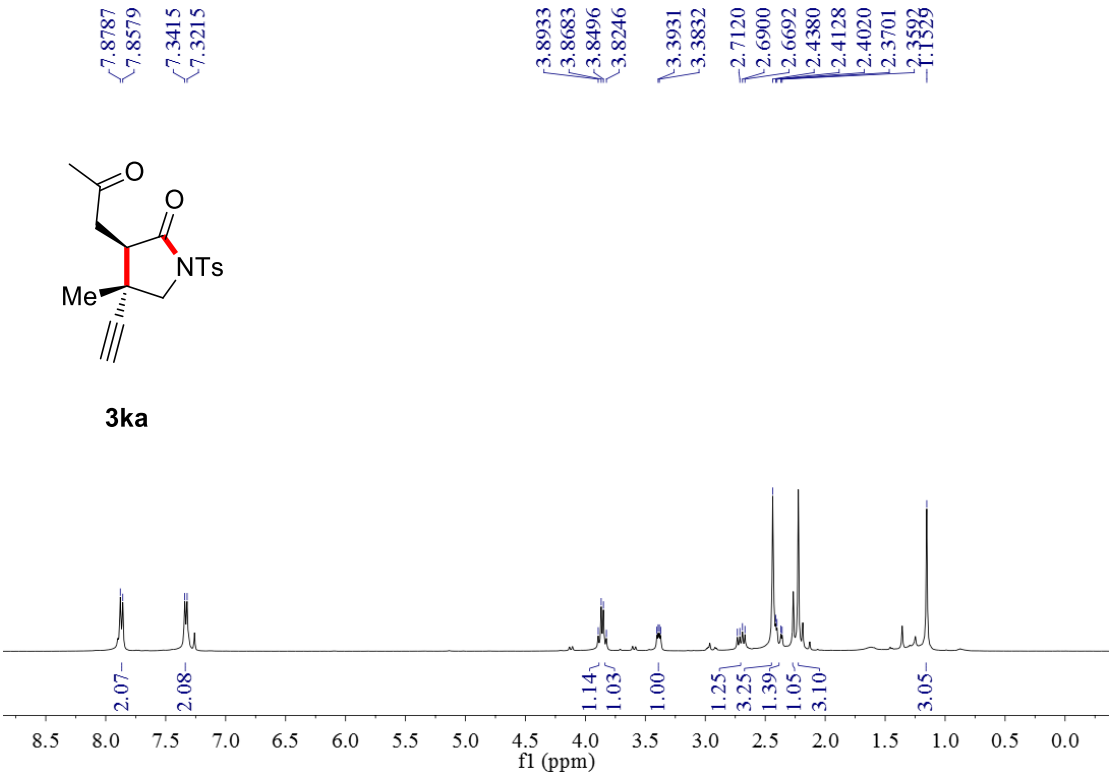

O
O
NTs

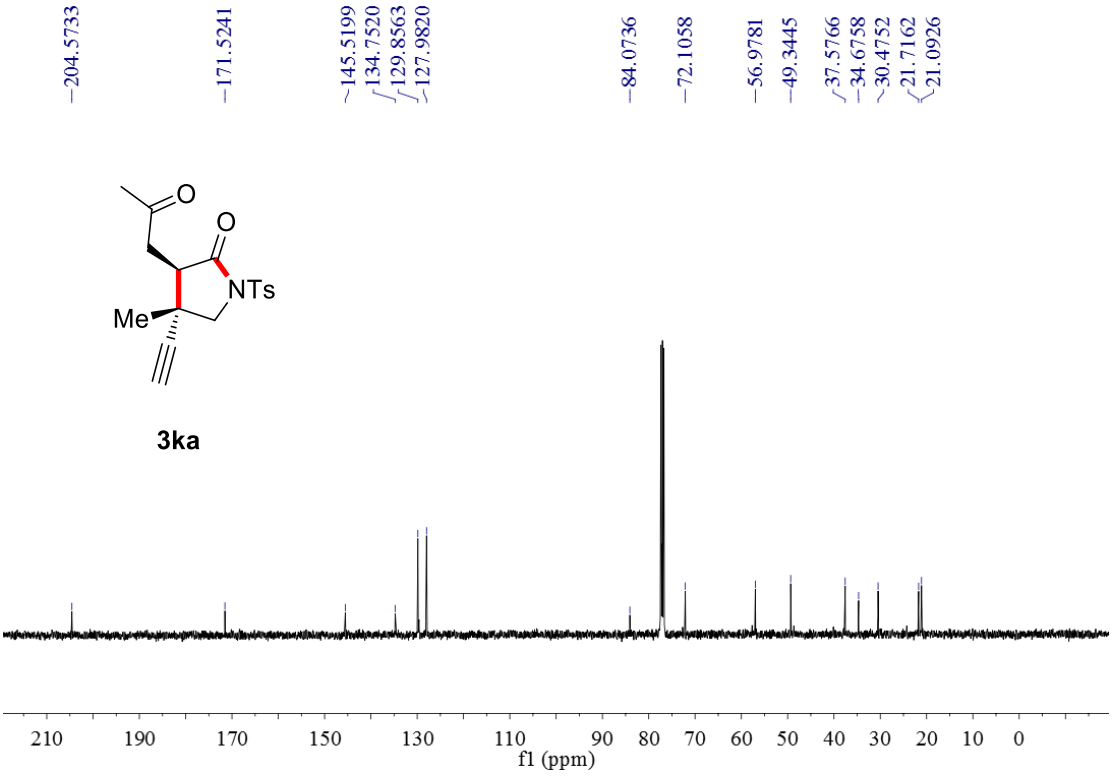
3ia

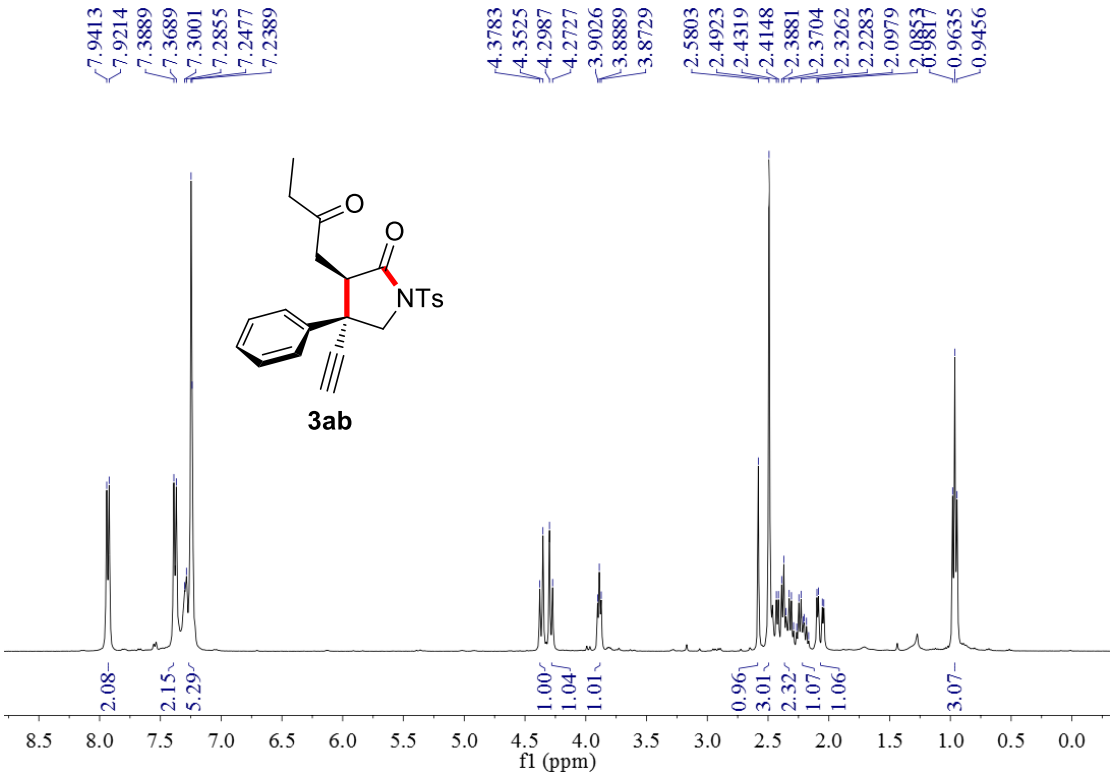

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

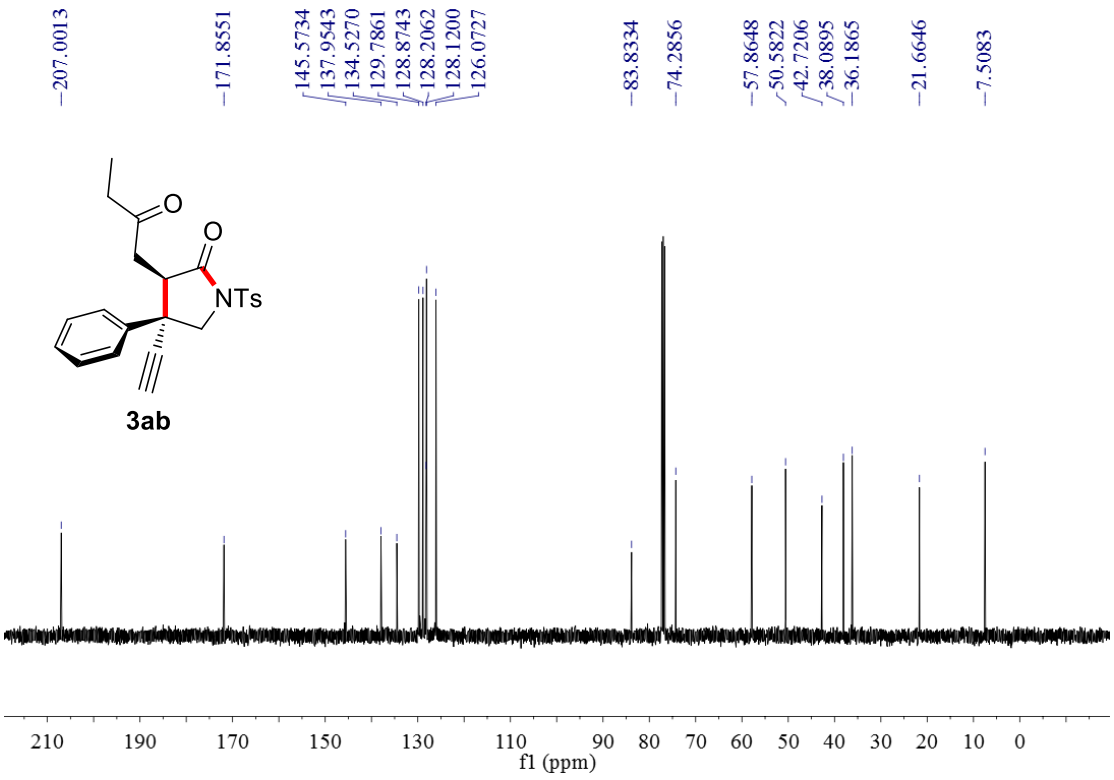

7.9242
7.9037
7.3568
7.3365
7.1719
7.1596
6.8937
6.8861
6.8716
6.8595
6.8501
4.3369
4.3117
4.1918
4.1666
3.7737
3.7618
3.7563
3.7443
2.5668
2.5164
2.4987
2.4715
2.4548
2.4386
2.2225
2.2108
2.1777
2.1659
2.0798
O
O
NTs
S
3ja
2.11
2.19
1.03
2.06
1.04
1.02
1.00
0.96
4.12
1.03
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

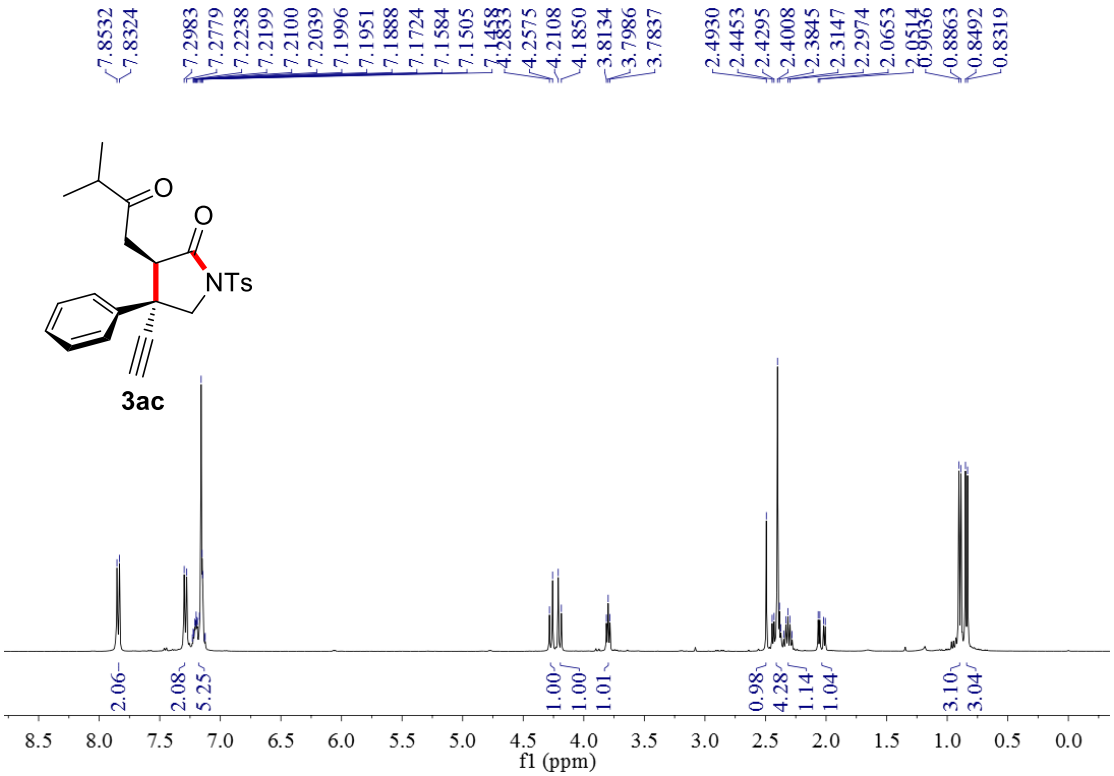

204.2888
171.0553
145.6061
141.1507
134.5322
129.7443
128.2349
126.8607
125.6816
125.2895
82.1671
74.1492
58.2217
51.0501
41.1905
38.8221
30.1937
21.6662
O
O
NTs
S
3ja
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

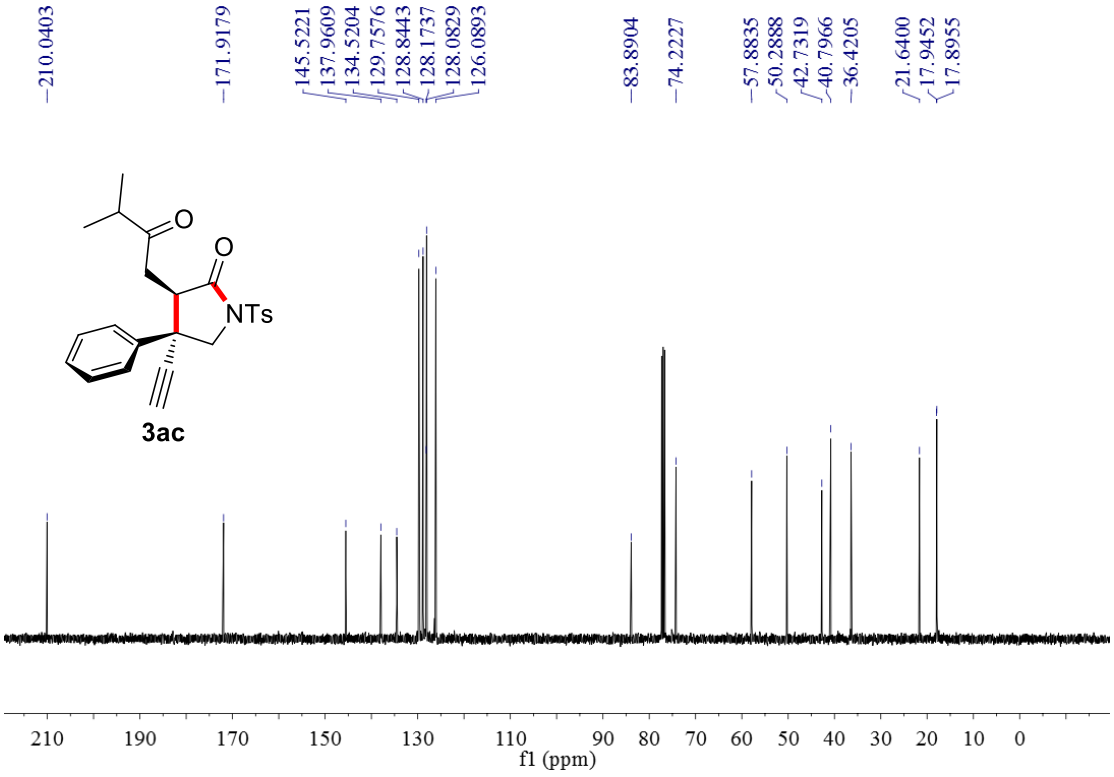

7.8787
7.8579
7.3415
7.3215
3.8933
3.8683
3.8496
3.8246
3.3931
3.3832
2.7120
2.6900
2.6692
2.4380
2.4128
2.4020
2.3701
2.3582
1.1529
O
O
NTs
Me
3ka
2.07
2.08
1.14
1.03
1.00
1.25
3.25
1.39
1.05
3.10
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


204.5733
171.5241
145.5199
134.7520
129.8563
127.9820
84.0736
72.1058
56.9781
49.3445
37.5766
34.6758
30.4752
21.7162
21.0926
O
O
NTs
Me
3ka
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9413
7.9214
7.3889
7.3689
7.3001
7.2855
7.2477
7.2389
4.3783
4.3525
4.2987
4.2727
3.9026
3.8889
3.8729
2.5803
2.4923
2.4319
2.4148
2.3881
2.3704
2.3262
2.2283
2.0979
0.9817
0.9635
0.9456
O
O
NTs
3ab
2.08
2.15
5.29
1.00
1.04
1.01
0.96
3.01
2.32
1.07
1.06
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


207.0013
171.8551
145.5734
137.9543
134.5270
129.7861
128.8743
128.2062
128.1200
126.0727
83.8334
74.2856
57.8648
50.5822
42.7206
38.0895
36.1865
21.6646
7.5083
O
O
NTs
3ab
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8532
7.8324
7.2983
7.2779
7.2238
7.2199
7.2100
7.2039
7.1996
7.1951
7.1888
7.1724
7.1584
7.1505
4.2575
4.2108
4.1850
3.8134
3.7986
3.7837
2.4930
2.4453
2.4295
2.4008
2.3845
2.3147
2.2974
2.0653
0.8863
0.8492
0.8319
O
O
NTs
3ac
2.06
2.08
5.25
1.00
1.00
1.01
0.98
4.28
1.14
1.04
3.10
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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145.5221
137.9609
134.5204
129.7576
128.8443
128.1737
128.0829
126.0893
83.8904
74.2227
57.8835
50.2888
42.7319
40.7966
36.4205
21.6400
17.9452
17.8955
O
O
NTs
3ac
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8462
7.8253
7.2863
7.2661
7.1930
7.1864
7.1825
7.1798
7.1728
7.1699
7.1648
7.1600
7.1560
7.1518
7.1458
7.1410
7.1360
7.1249
7.1093
7.1040
7.0874
7.0848
7.0737
7.0677
6.9468
6.9420
6.9272
6.9237
4.2828
4.2569
4.1801
4.1541
3.7671
3.7520
3.7368
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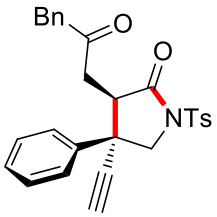
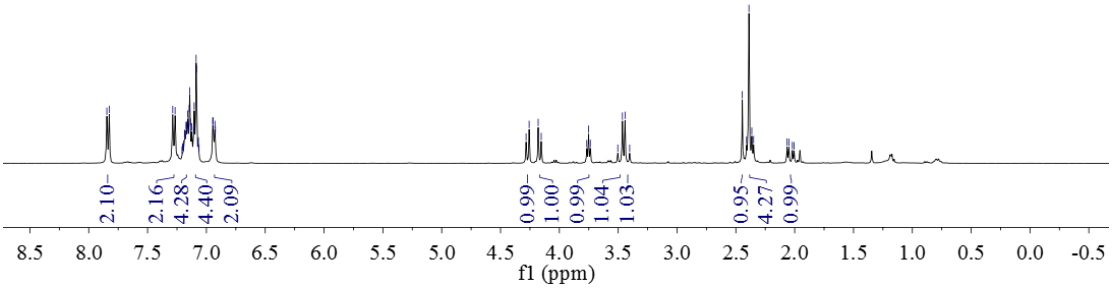
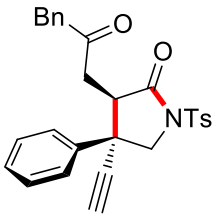
3.4419
2.4453
2.4091
2.3888
2.3643
2.3488
2.0644
2.0496


Bn
O
O
NTs

3ad

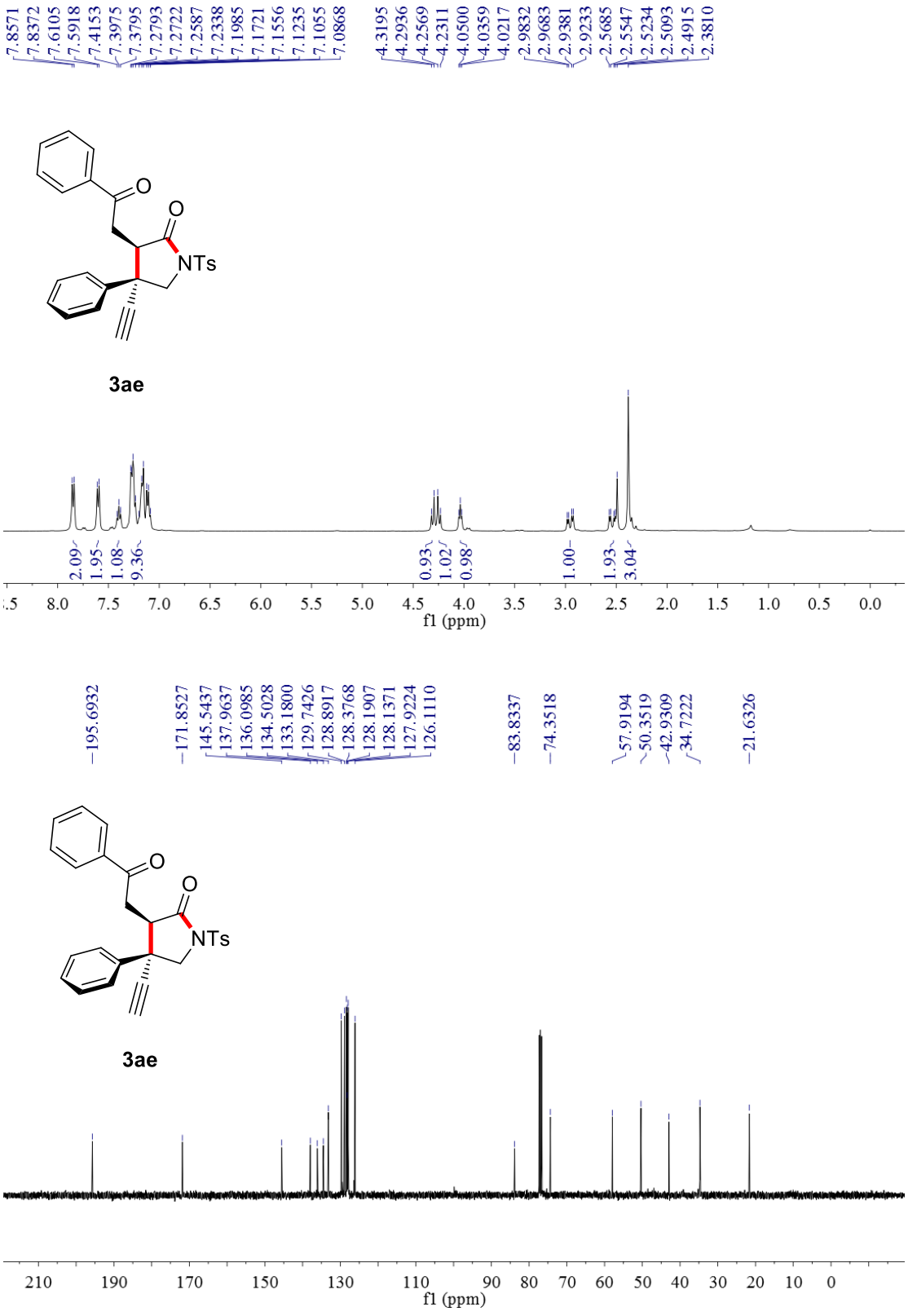

2.10
2.16
4.28
4.40
2.09
0.99
1.00
0.99
1.04
1.03
0.95
4.27
0.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


203.9582
171.7370
145.5943
137.7315
134.4828
133.3408
129.7862
129.3388
128.8662
128.5327
128.1618
128.1123
126.9460
126.0487
83.7838
74.2619
57.7679
50.6128
49.9288
42.6370
37.9883
21.6608

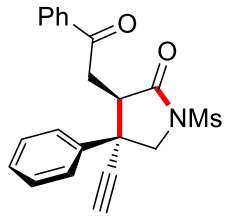

Bn
O
O
NTs

3ad

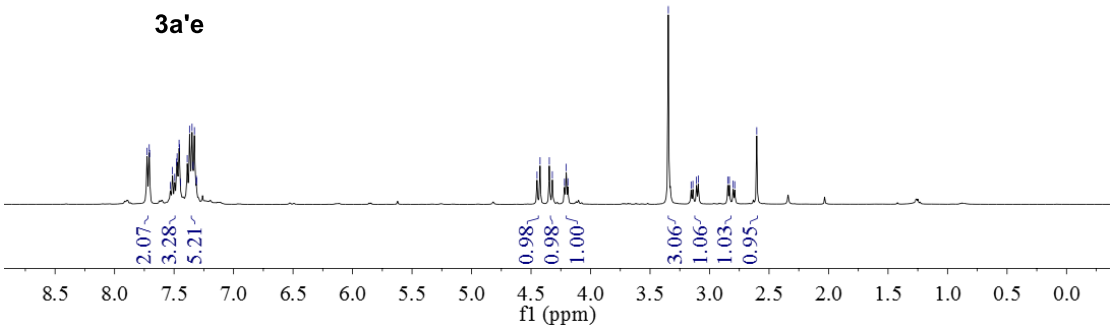
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8571
7.8372
7.6105
7.5918
7.4153
7.3975
7.3795
7.2793
7.2722
7.2587
7.2338
7.1985
7.1721
7.1556
7.1235
7.1055
7.0868
4.3195
4.2936
4.2569
4.2311
4.0500
4.0359
4.0217
2.9832
2.9683
2.9381
2.9233
2.5685
2.5547
2.5234
2.5093
2.4915
2.3810
O
O
NTs
3ae
2.09
1.95
1.08
9.36
0.93
1.02
0.98
1.00
1.93
3.04
f1 (ppm)
195.6932
171.8527
145.5437
137.9637
136.0985
134.5028
133.1800
129.7426
128.8917
128.3768
128.1907
128.1371
127.9224
126.1110
83.8337
74.3518
57.9194
50.3519
42.9309
34.7222
21.6326
O
O
NTs
3ae
f1 (ppm)

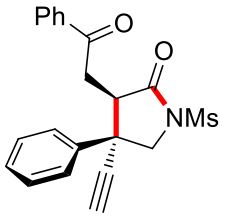

7.7268
7.7088
7.7056
7.5132
7.4946
7.4783
7.4740
7.4576
7.4545
7.4469
7.3893
7.3698
7.3489
7.3396
7.3286
7.3130
4.4242
4.3466
4.3210
4.2190
4.2048
4.1902
3.3465
3.1549
3.1396
3.1097
3.0945
2.8469
2.8333
2.8017
2.7881
2.6033


Ph
O
O
NMs

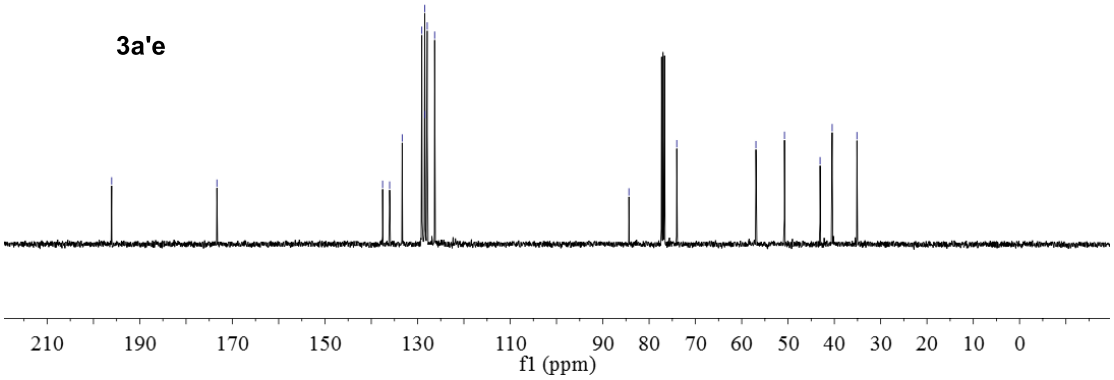
3a'e

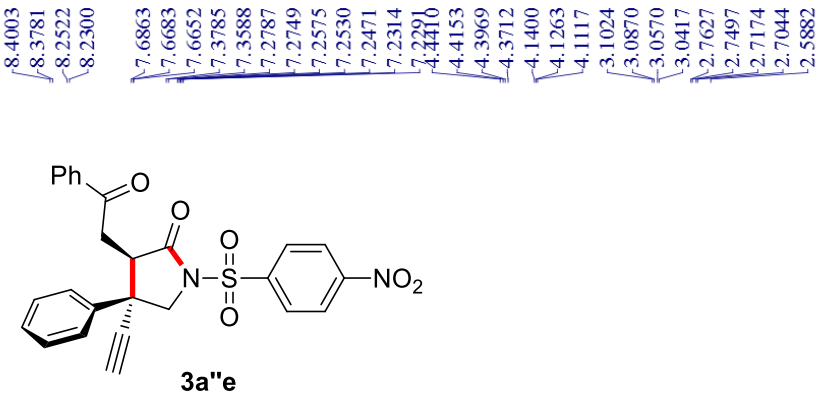

2.07
3.28
5.21
0.98
0.98
1.00
3.06
1.06
1.03
0.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.0629
173.3374
137.5543
136.0358
133.3276
129.0858
128.4571
128.4178
127.9238
126.3219
84.3653
74.0334
56.9341
50.7693
43.0820
40.4709
35.1241

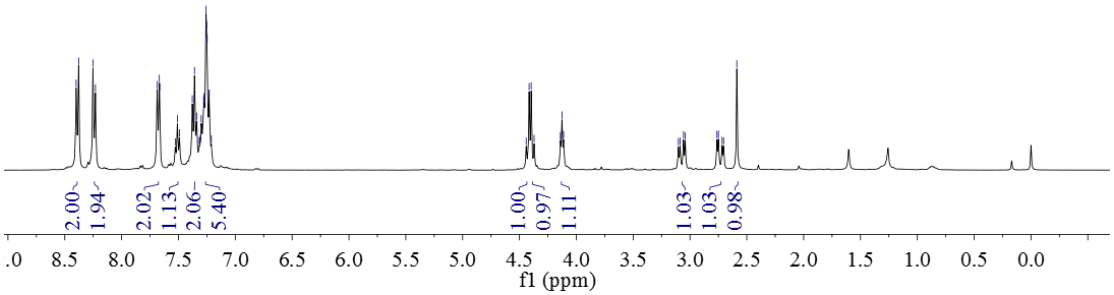

Ph
O
O
NMs

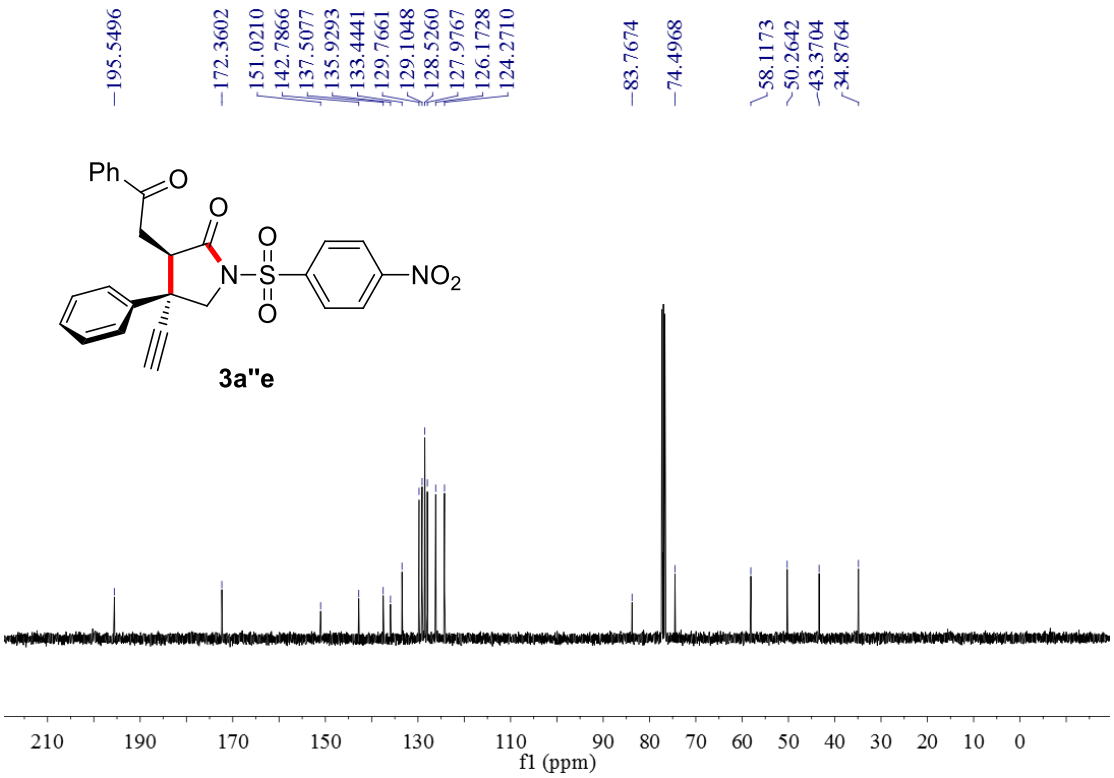
3a'e


210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.4003
8.3781
8.2522
8.2300
7.6863
7.6683
7.6652
7.3785
7.3588
7.2787
7.2749
7.2575
7.2530
7.2471
7.2314
7.2291
4.4410
4.4153
4.3969
4.3712
4.1400
4.1263
4.1117
3.1024
3.0870
3.0570
3.0417
2.7627
2.7497
2.7174
2.7044
2.5882
Ph
O
O
O
N
S
O
O
NO2

3a''e


2.00
1.94
2.02
1.13
2.06
5.40
1.00
0.97
1.11
1.03
1.03
0.98
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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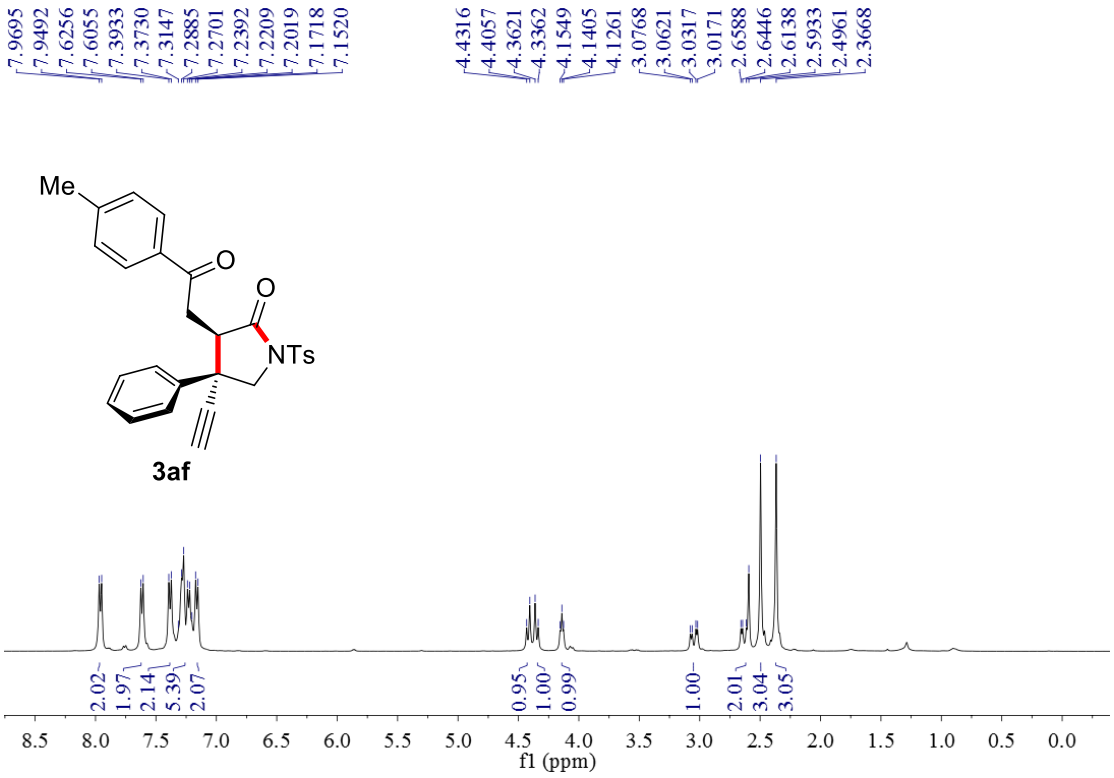
172.3602
151.0210
142.7866
137.5077
135.9293
133.4441
129.7661
129.1048
128.5260
127.9767
126.1728
124.2710
83.7674
74.4968
58.1173
50.2642
43.3704
34.8764
Ph
O
O
O
N
S
O
O
NO2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3a''e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7.6256
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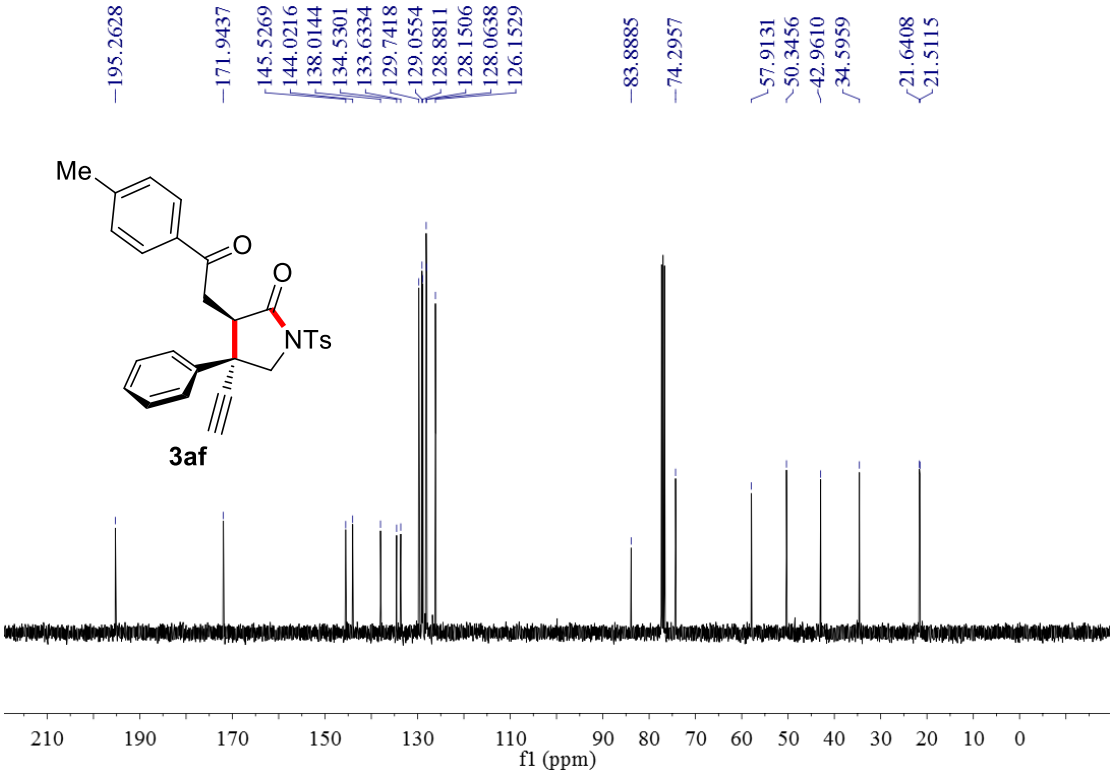
7.3730
7.3147
7.2885
7.2701
7.2392
7.2209
7.2019
7.1718
7.1520
4.4316
4.4057
4.3621
4.3362
4.1549
4.1405
4.1261
3.0768
3.0621
3.0317
3.0171
2.6588
2.6446
2.6138
2.5933
2.4961
2.3668
Me
O
O
NTs
3af
2.02
1.97
2.14
5.39
2.07
0.95
1.00
0.99
1.00
2.01
3.04
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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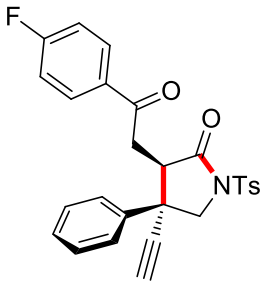
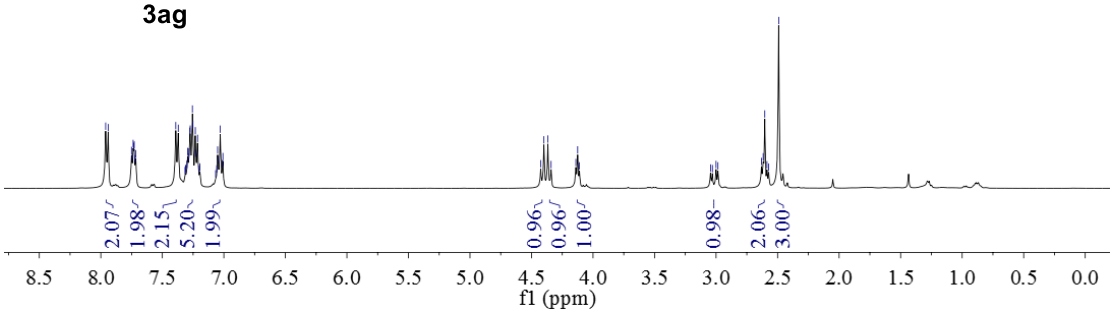
145.5269
144.0216
138.0144
134.5301
133.6334
129.7418
129.0554
128.8811
128.1506
128.0638
126.1529
83.8885
74.2957
57.9131
50.3456
42.9610
34.5959
21.6408
21.5115
Me
O
O
NTs
3af
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.9606
7.9398
7.7507
7.7454
7.7373
7.7330
7.7285
7.7204
7.7151
7.3910
7.3707
7.3005
7.2947
7.2891
7.2833
7.2764
7.2736
7.2557
7.2515
7.2321
7.2263
7.2138
7.1948
7.0507
7.0456
7.0293
7.0125
7.0076
4.4251
4.3991
4.3667
4.3407
4.1394
4.1249
4.1100
3.0451
3.0003
2.9848
2.6312
2.6172
2.6042
2.5864
2.5724
2.4911


F
O
O
NTs

3ag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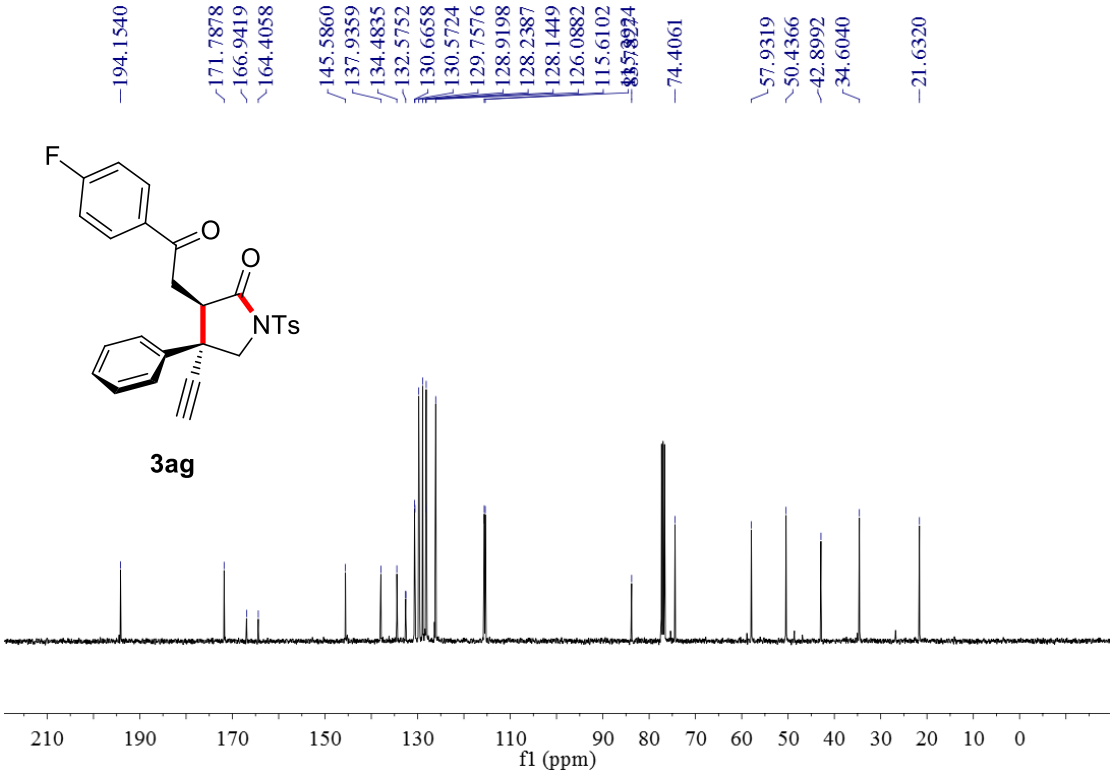
1.98
2.15
5.20
1.99
0.96
0.96
1.00
0.98
2.06
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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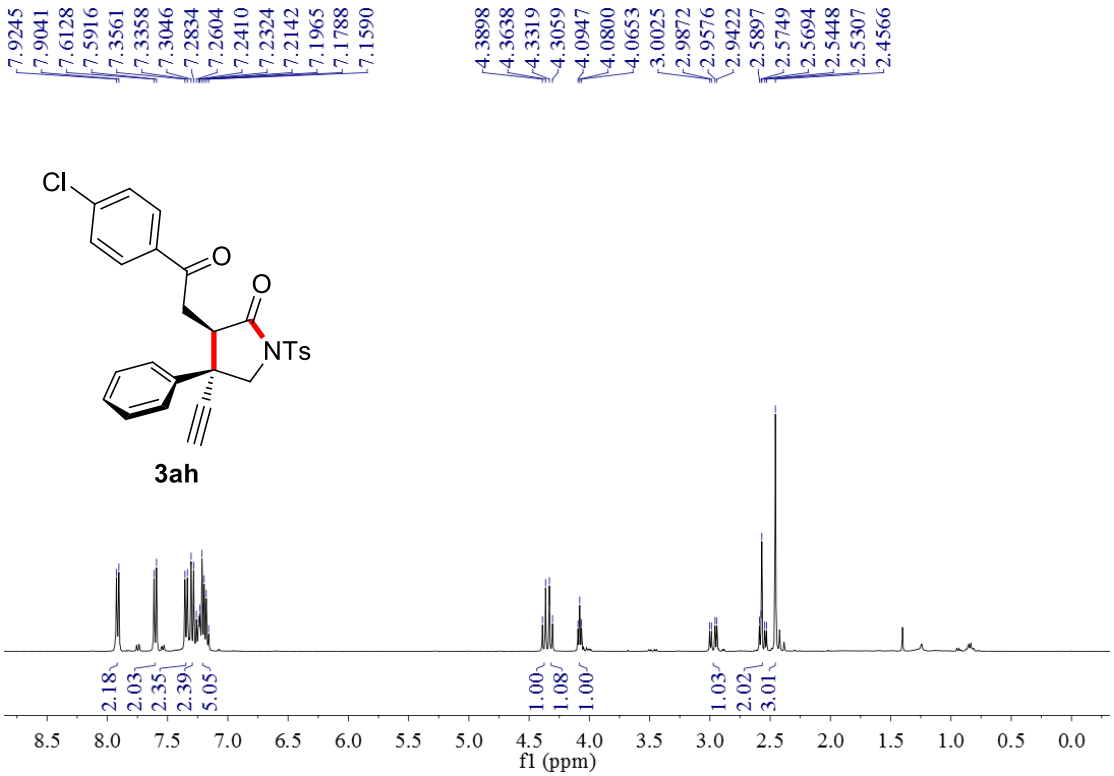
166.9419
164.4058
145.5860
137.9359
134.4835
132.5752
130.6658
130.5724
129.7576
128.9198
128.2387
128.1449
126.0882
115.6102
74.4061
57.9319
50.4366
42.8992
34.6040
21.6320
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

F
O
O
NTs

3ag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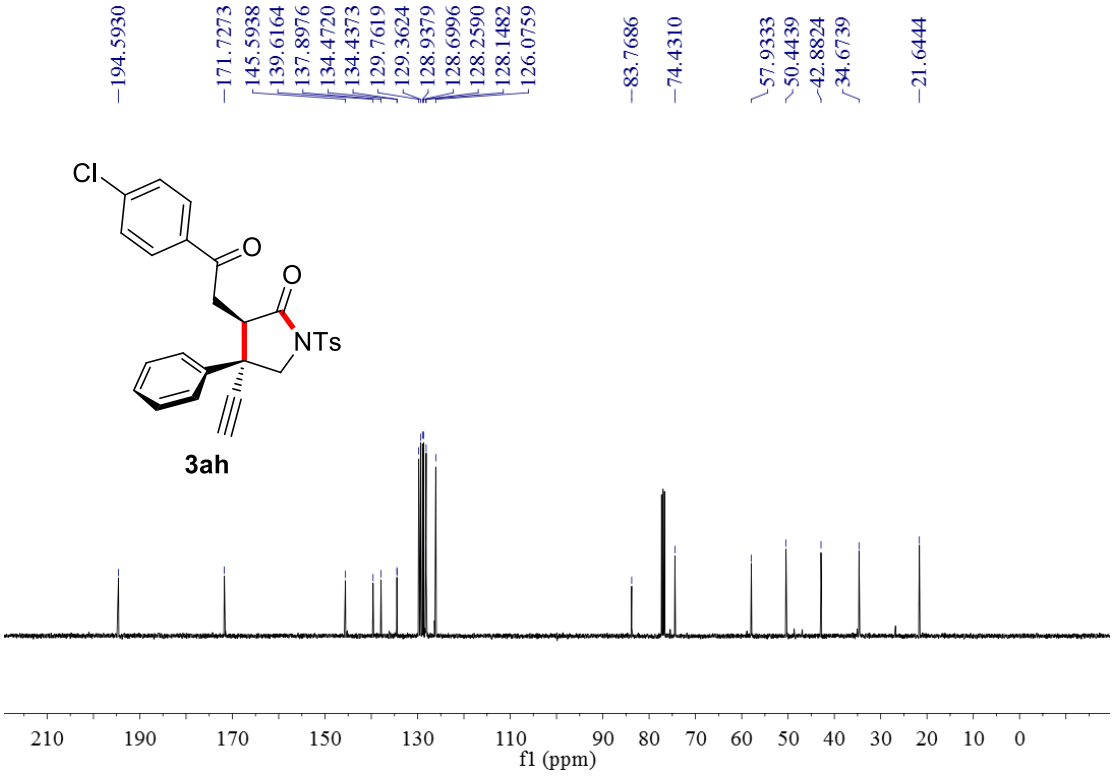
7.9041
7.6128
7.5916
7.3561
7.3358
7.3046
7.2834
7.2604
7.2410
7.2324
7.2142
7.1965
7.1788
7.1590
4.3898
4.3638
4.3319
4.3059
4.0947
4.0800
4.0653
3.0025
2.9872
2.9576
2.9422
2.5897
2.5749
2.5694
2.5448
2.5307
2.4566
Cl
O
O
NTs
3ah
2.18
2.03
2.35
2.39
5.05
1.00
1.08
1.00
1.03
2.02
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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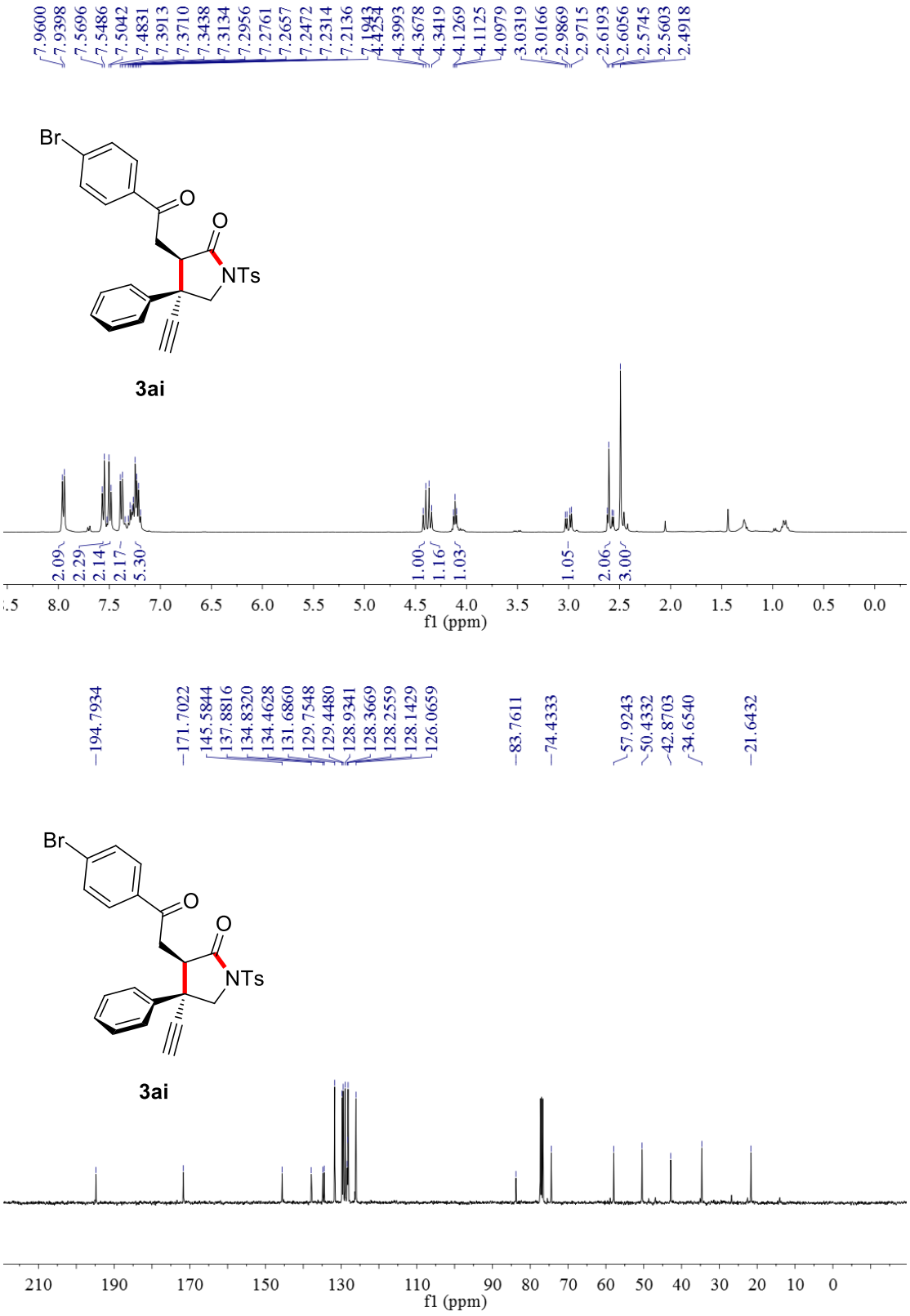
171.7273
145.5938
139.6164
137.8976
134.4720
134.4373
129.7619
129.3624
128.9379
128.6996
128.2590
128.1482
126.0759
83.7686
74.4310
57.9333
50.4439
42.8824
34.6739
21.6444
Cl
O
O
NTs
3ah
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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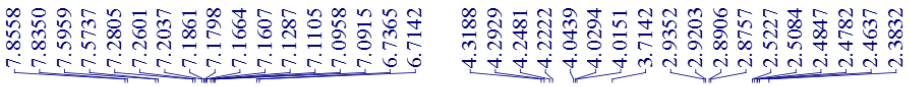
7.9398
7.5696
7.5486
7.5042
7.4831
7.3913
7.3710
7.3438
7.3134
7.2956
7.2761
7.2657
7.2472
7.2314
7.2136
4.3993
4.3678
4.3419
4.1269
4.1125
4.0979
3.0319
3.0166
2.9869
2.9715
2.6193
2.6056
2.5745
2.5603
2.4918
Br
O
O
NTs
3ai
2.09
2.29
2.14
2.17
5.30
1.00
1.16
1.03
1.05
2.06
3.00
f1 (ppm)
194.7934
171.7022
145.5844
137.8816
134.8320
134.4628
131.6860
129.7548
129.4480
128.9341
128.3669
128.2559
128.1429
126.0659
83.7611
74.4333
57.9243
50.4332
42.8703
34.6540
21.6432
Br
O
O
NTs
3ai
f1 (ppm)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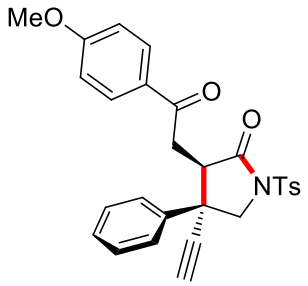
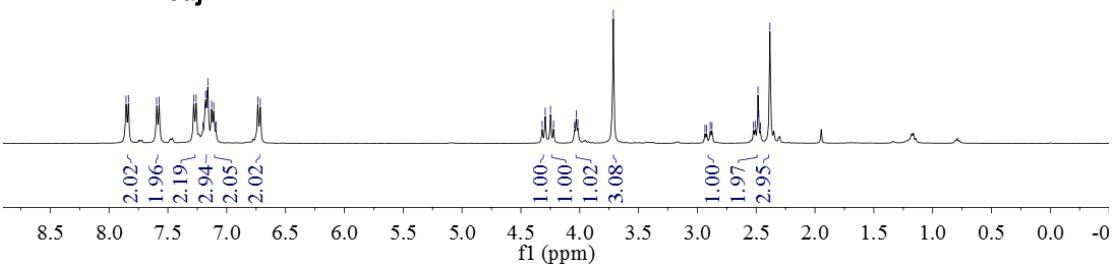
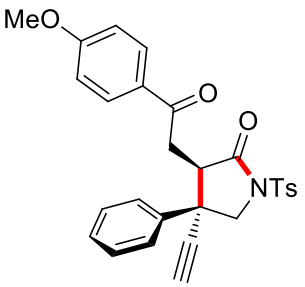
7.8350
7.5959
7.5737
7.2805
7.2601
7.2037
7.1861
7.1798
7.1664
7.1607
7.1287
7.1105
7.0958
7.0915
6.7365
6.7142
4.3188
4.2929
4.2481
4.2222
4.0439
4.0294
4.0151
3.7142
2.9352
2.9203
2.8906
2.8757
2.5227
2.5084
2.4847
2.4782
2.4637
2.3832


MeO
O
O
NTs

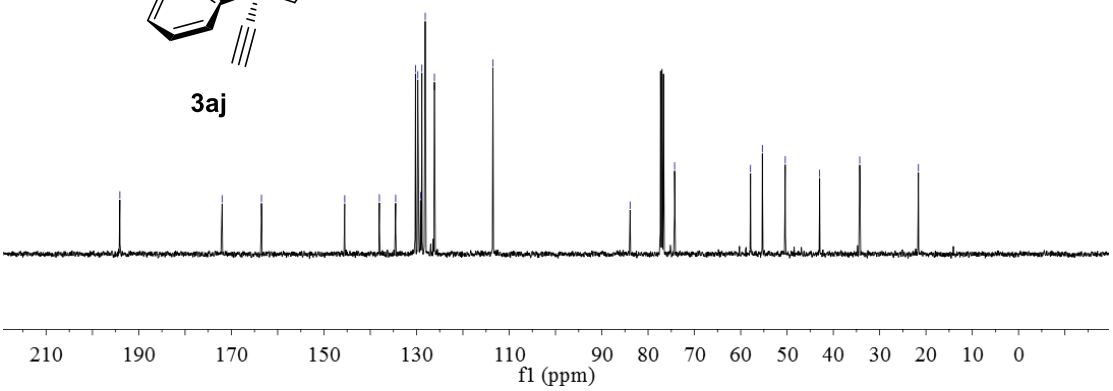
3aj


2.02
1.96
2.19
2.94
2.05
2.02
1.00
1.00
1.02
3.08
1.00
1.97
2.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


194.0756
171.9943
163.4959
138.0314
134.5155
130.2414
129.7290
129.1437
128.8524
128.1292
126.1503
115.5108
83.8937
74.2800
57.8833
55.3302
50.3826
42.9532
34.3011
21.6239


MeO
O
O
NTs

3aj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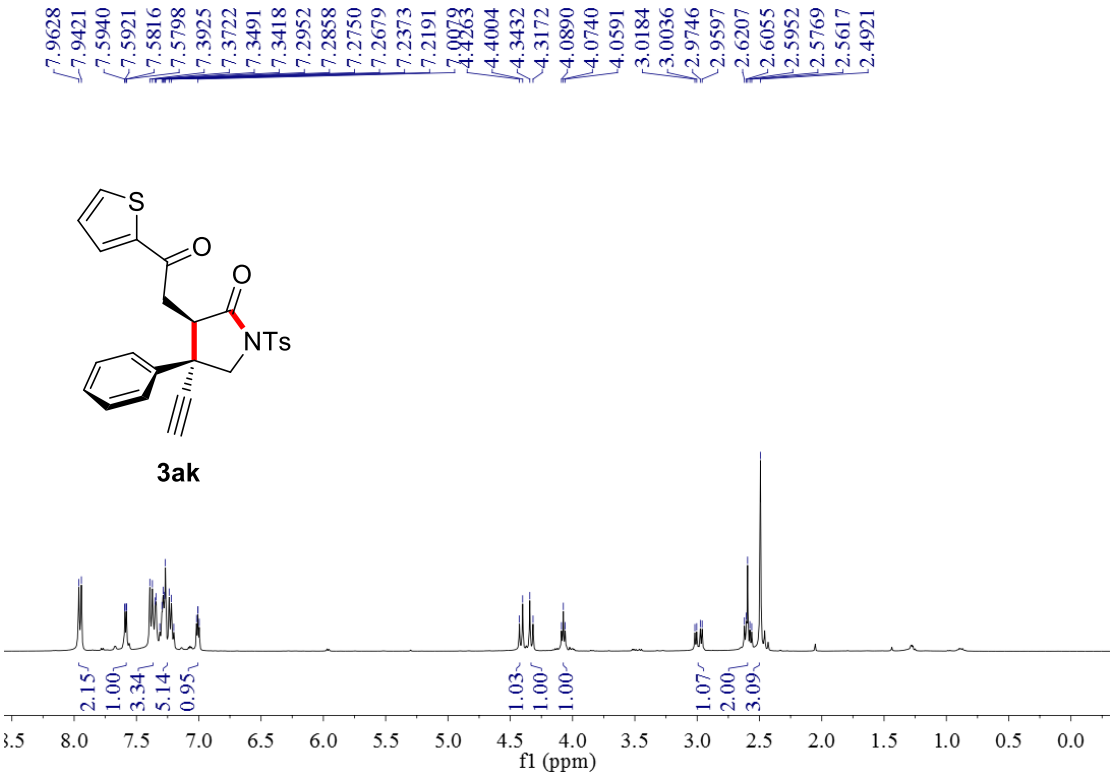
f1 (ppm)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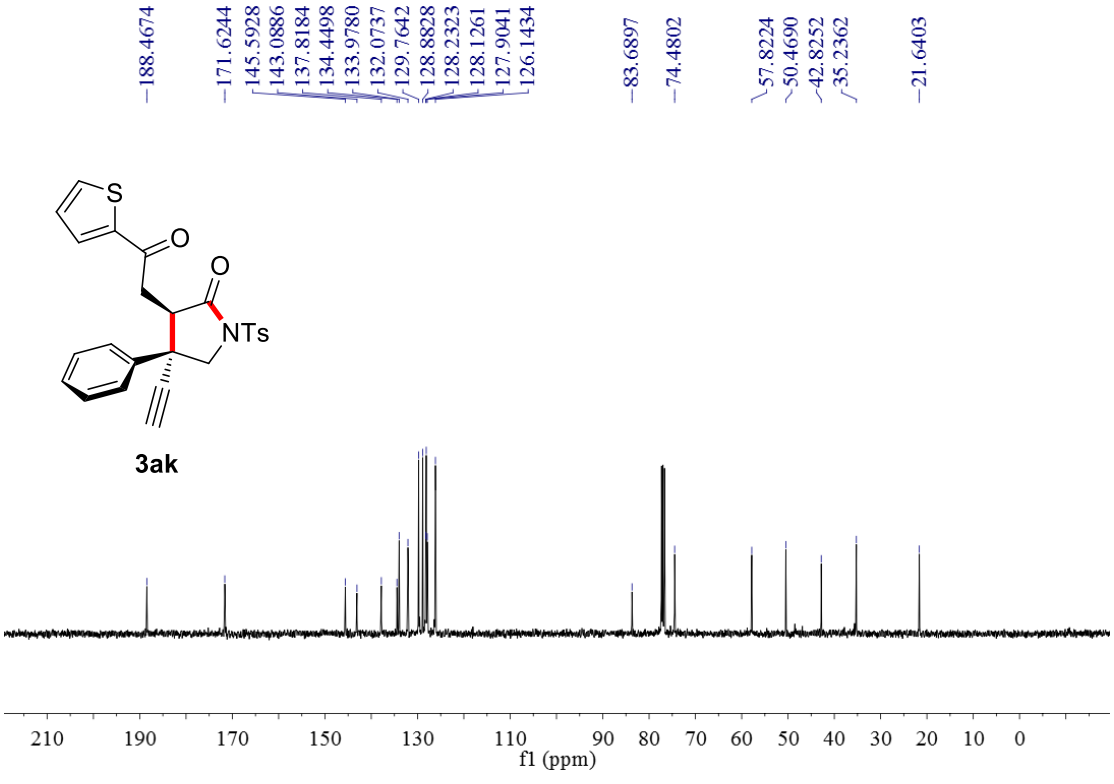
7.9421
7.5940
7.5921
7.5816
7.5798
7.3925
7.3722
7.3491
7.3418
7.2952
7.2858
7.2750
7.2679
7.2373
7.2191
4.4263
4.4004
4.3432
4.3172
4.0890
4.0740
4.0591
3.0184
3.0036
2.9746
2.9597
2.6207
2.6055
2.5952
2.5769
2.5617
2.4921
S
O
O
NTs
3ak
2.15
1.00
3.34
5.14
0.95
1.03
1.00
1.00
1.07
2.00
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.9780
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129.7642
128.8828
128.2323
128.1261
127.9041
126.1434
83.6897
74.4802
57.8224
50.4690
42.8252
35.2362
21.6403
S
O
O
NTs
3ak
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)