Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Divergent Synthesis of Functionalized Pyrrolidines and γ-Amino Ketones by Rhodium-Catalyzed Switchable Reactions of Vinyl Aziridines and Silyl Enol Ethers

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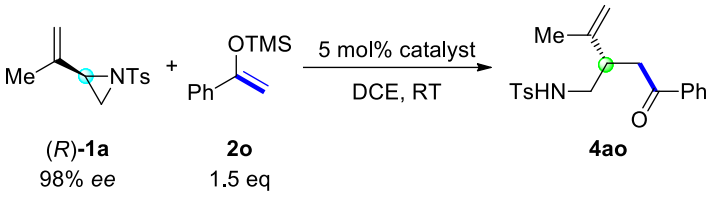
1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H NMR, ^{13}C NMR spectra were measured at 400 MHz (or 500 MHz) and 100 MHz (or 125 MHz) in $CDCl_3$ (or $(CD_3)_2CO$, C_6D_6) using TMS signal, δ 0.00 ppm ($(CD_3)_2CO$: δ 2.05 ppm; C_6D_6: δ 7.16 ppm), and the residual signals from $CHCl_3$, δ 77.0 ppm ($(CH_3)_2CO$: δ 206.8 ppm; C_6H_6: δ 128.7 ppm), as internal references for ^{1}H and ^{13}C NMR respectively. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane (DCE) was distilled from CaH_2 prior to use.

The catalysts $[Rh(\eta^6\text{-}C_{10}H_8)(COD)]SbF_6$,[1] $[Rh(dnCOT)(MeCN)_2]SbF_6$,[2] RhCl(IPr)(COD)[3] and chiral vinylaziridines[4] were synthesized according to the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

2. Table S1. Optimization of the Ring-Opening Reaction Conditions[a]



(*R*)-**1a** 98% *ee* | **2o** 1.5 eq | **4ao**

entry	catalyst	time (h)	Conversion (%)	Yield (%)[b]	*ee* (%)
1	IPrRh(COD)Cl/$AgSbF_6$	0.25	100	66	98
2	[Rh(η^6-$C_{10}H_8$)(COD)]SbF_6	0.25	100	55	97
3	[Rh(COD)$_2$]BF_4	18	60	30	98
4	[Rh(NBD)$_2$]BF_4	18	100	50	82
5	[Rh(NBD)Cl]$_2$/$AgClO_4$	0.25	100	62	94
6	[Rh(NBD)Cl]$_2$/$AgSbF_6$	0.25	100	82	94
7	[Rh(NBD)Cl]$_2$/$AgPF_6$	0.25	100	91	95
8[c]	**[Rh(NBD)Cl]$_2$/$AgPF_6$**	**3**	**100**	**95(86)**	**98**
9	[Rh(NBD)Cl]$_2$/AgOTf	0.25	100	61	68
10	[Rh(NBD)Cl]$_2$/AgOMs	18	50	20	25

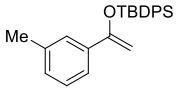
[a] Reaction conditions: To a solution of catalyst (5 mol%, the mole ratio of [Rh]:[Ag] = 1:1) in 1,2-dichloroethane (DCE) (0.5 mL) was added a mixture of (*R*)-**1a** (0.1 mmol), **2o** (1.5 equiv) in DCE (1 mL) dropwise over a period of 3 mins at room temperature. [b] Determined by H^1-NMR with CH_2Br_2 as an internal standard. [c] The reaction was run at 0 °C, the value in the parentheses was isolated yield.

3. Experimental Procedures and Characterization Data

3.1 Preparation of Enol Silyl Ethers[5].

Enol silyl ethers **2** were facilely synthesized according to the known procedure and the physical data are identical in all respects to those previously reported.[5] The new enolsilane substrates were also prepared from corresponding ketones according to the reported procedure and the physical data are showed as following:

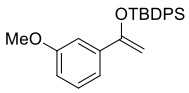
***tert*-butyldiphenyl((1-(m-tolyl)vinyl)oxy)silane: 2b**



Colorless oil. 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 4H), 7.58-7.56 (m, 2H), 7.44-7.36 (m, 6H), 7.29-7.25 (m, 1H), 7.16-7.14 (m, 1H), 4.73 (s, 1H), 4.00 (s, 1H), 2.38 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 137.7, 137.5, 135.5, 132.5, 129.9, 129.1, 128.2, 127.8, 126.0, 122.4, 92.1, 26.6, 21.6, 19.5. HRMS (EI) calcd for $C_{25}H_{28}OSi$: 372.1909, found: 372.1907.

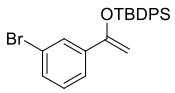
***tert*-butyl((1-(3-methoxyphenyl)vinyl)oxy)diphenylsilane: 2c**



Colorless oil. 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 4H), 7.43-7.26 (m, 9H), 6.90-6.88 (m, 1H), 4.75 (s, 1H), 4.03 (s, 1H), 3.83 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 154.8, 139.1, 135.5, 132.4, 129.9, 129.2, 127.8, 117.8, 114.1, 110.7, 92.5, 55.2, 26.6, 19.5. HRMS (EI) calcd for $C_{25}H_{28}O_2Si$: 388.1859, found: 388.1860.

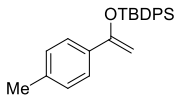
((1-(3-bromophenyl)vinyl)oxy)(*tert*-butyl)diphenylsilane: 2d



Colorless oil. 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.87 (m, 1H), 7.77-7.74 (m, 4H), 7.67-7.65 (m, 1H), 7.46-7.37 (m, 7H), 7.26-7.22 (m, 1H), 4.73 (d, *J* = 2.8 Hz, 1H), 4.05 (d, *J* = 2.4 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 139.7, 135.5, 132.2, 131.2, 130.0, 129.8, 128.4, 127.8, 123.8, 122.5, 93.3, 26.6, 19.5. HRMS (EI) calcd for $C_{24}H_{25}OSiBr$: 436.0858, found: 436.0856.

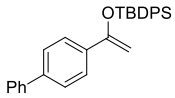
***tert*-butyldiphenyl((1-(p-tolyl)vinyl)oxy)silane: 2e**



Colorless oil. 65% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.87 (m, 4H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.43-7.35 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.70 (d, *J* = 2.0 Hz, 1H), 3.97 (d, *J* = 2.5 Hz, 1H), 2.47 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 138.2, 135.6, 134.8, 132.6, 129.9, 129.0, 127.8, 125.2, 91.5, 26.7, 21.3, 19.6. HRMS (EI) calcd for $C_{25}H_{28}OSi$: 372.1909, found: 372.1912.

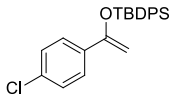
((1-([1,1'-biphenyl]-4-yl)vinyl)oxy)(*tert*-butyl)diphenylsilane: 2f



White solid. 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.79 (m, 6H), 7.64-7.61 (m, 4H), 7.44-7.33 (m, 9H), 4.80 (s, 1H), 4.05 (s, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 141.0, 140.7, 136.4, 135.5, 132.4, 129.9, 128.8, 127.8, 127.4, 127.0, 126.9, 125.6, 92.3, 26.6, 19.5. HRMS (EI) calcd for $C_{30}H_{30}OSi$: 434.2066, found: 434.2063.

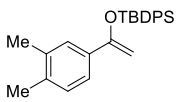
***tert*-butyl((1-(4-chlorophenyl)vinyl)oxy)diphenylsilane: 2g**



Colorless oil. 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.75 (m, 4H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.46-7.37 (m, 6H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.72 (d, *J* = 2.4 Hz, 1H), 4.03 (d, *J* = 2.0 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 136.0, 135.4, 134.0, 132.2, 129.9, 128.3, 127.8, 126.5, 92.6, 26.5, 19.5. HRMS (EI) calcd for $C_{24}H_{25}OSiCl$: 392.1363, found: 392.1362.

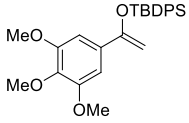
***tert*-butyl((1-(3,4-dimethylphenyl)vinyl)oxy)diphenylsilane: 2h**



Colorless oil. 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 4H), 7.39-7.36 (m, 2H), 7.27-7.23 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 1H), 4.57 (s, 1H), 3.82 (s, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 136.9, 136.3, 135.5, 135.2, 132.6, 129.8, 129.6, 127.7, 126.6, 122.8, 91.3, 26.6, 20.0, 19.6, 19.5. HRMS (EI) calcd for $C_{26}H_{30}OSi$: 386.2066, found: 386.2065.

***tert*-butyldiphenyl((1-(3,4,5-trimethoxyphenyl)vinyl)oxy)silane: 2i**

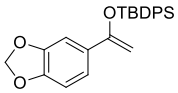


Colorless oil. 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 4H), 7.46-7.38 (m, 6H), 7.00 (s, 2H), 4.70 (s, 1H), 4.04 (s, 1H), 3.88 (s, 3H), 3.87 (s, 6H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 152.9, 138.2, 135.5, 133.1, 132.3, 129.9, 127.8, 102.5, 91.7, 60.9, 56.0, 26.6, 19.5. HRMS (EI) calcd for $C_{27}H_{32}O_4Si$: 448.2070, found: 448.2073.

((1-(benzo[d][1,3]dioxol-5-yl)vinyl)oxy)(*tert*-butyl)diphenylsilane: 2j

Colorless oil. 68% yield.

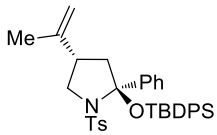


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.76 (m, 4H), 7.45-7.37 (m, 6H), 7.30-7.28 (m, 1H), 7.20 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 4.60 (s, 1H), 3.93 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 147.7, 147.6, 135.5, 132.4, 132.0, 129.9, 127.8, 119.2, 108.0, 105.9, 101.2, 91.1, 26.6, 19.5. HRMS (EI) calcd for $C_{25}H_{26}O_3Si$: 402.1651, found: 402.1653.

3.2 General Procedure for $[Rh(NBD)_2]BF_4$ Catalyzed Intermolecular [3+2] Cycloaddition Reaction of Vinyl Aziridines and Enol Silyl Ethers.

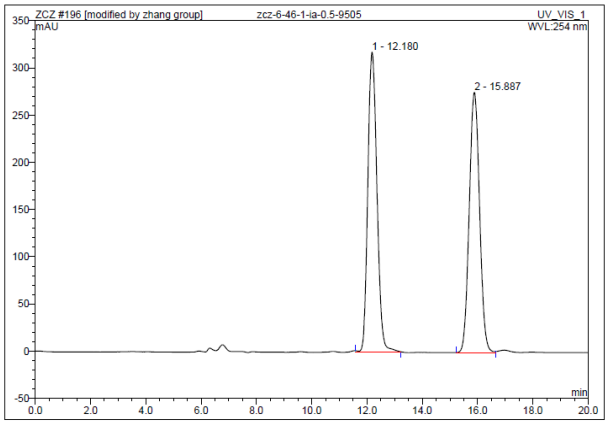
To a stirred solution of $[Rh(NBD)_2]BF_4$ in DCE (0.5 mL) at room temperature under argon atmosphere was added a solution of vinylaziridine **1** (0.20 mmol) and enol silyl ether **2** (0.3 mmol) in DCE (1.5 mL) via syringe. The resulting mixture was then stirred at room temperature for about 0.25-19 h. Upon complete consumption of **1** (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography on a triethylamine-deactivated silica gel column, eluting with hexane:ethyl acetate:triethylamine (200:10:1) to afford the desired [3+2] cycloadduct **3**.

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-2-phenyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3aa

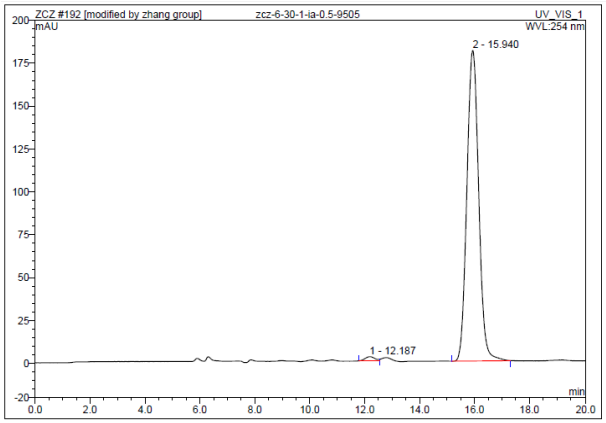


Colorless oil. 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.71-7.69 (m, 2H), 7.49-7.38 (m, 6H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.21-7.18 (m, 2H), 7.00 (s, 4H), 4.51 (s, 1H), 4.23 (s, 1H), 3.60 (t, *J* = 8.0 Hz, 1H), 2.88 (dd, *J* = 10.5 and 8.5 Hz, 1H), 2.40 (dd, *J* = 14.0 and 7.5 Hz, 1H), 2.34 (s, 3H), 2.22 (dd, *J* = 14.0 and 12.0 Hz, 1H), 1.87-1.79 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 143.1, 142.2, 136.9, 136.5, 136.0, 134.0, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.2, 127.1, 126.8, 110.4, 96.1, 53.4, 49.5, 40.0, 27.1, 21.4, 20.7, 20.1. HRMS (ESI) calcd for $C_{36}H_{41}NNaO_3SSi$ [$(M+Na^+)$]: 618.2469, found: 618.2475. $[\alpha]^{27}_D$ = -5.0 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.19 min (minor), 15.94 min (major).

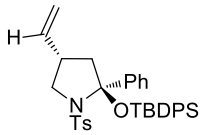


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.18	n.a.	317.204	121.100	50.40	n.a.	MB*
2	15.89	n.a.	275.430	119.186	49.60	n.a.	BM *
Total:			592.634	240.286	100.00	0.000	



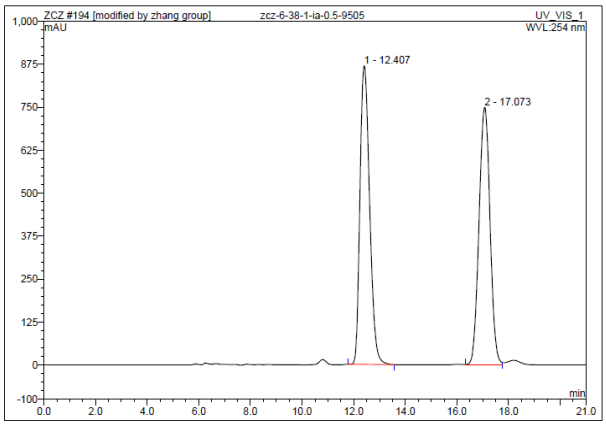
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.19	n.a.	2.482	1.012	1.11	n.a.	BM *
2	15.94	n.a.	181.201	90.268	98.89	n.a.	BMB*
Total:			183.683	91.280	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-2-phenyl-1-tosyl-4-vinylpyrrolidine: 3ba

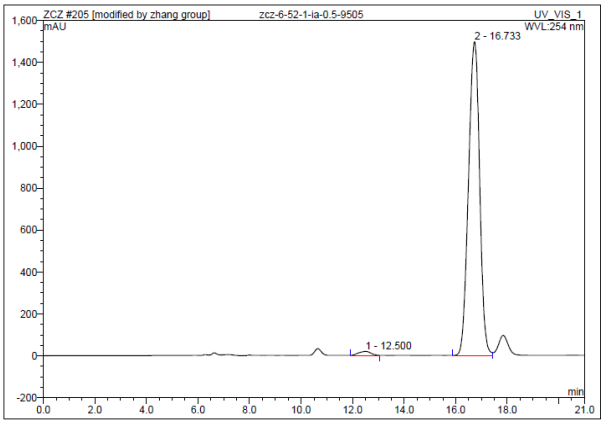


White solid. 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.06 (m, 2H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.50-7.18 (m, 11H), 6.99 (s, 4H), 5.31-5.22 (m, 1H), 4.74 (d, *J* = 10.4 Hz, 1H), 4.49 (d, *J* = 17.2 Hz, 1H), 3.55 (t, *J* = 8.4 Hz, 1H), 2.80 (t, *J* = 9.6 Hz, 1H), 2.44 (dd, *J* = 14.8 and 8.0 Hz, 1H), 2.34 (s, 3H), 2.11 (dd, *J* = 14.4 and 12.0 Hz, 1H), 1.77-1.65 (m, 1H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 142.3, 137.1, 136.8, 136.5, 136.0, 133.98, 133.96, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.3, 127.1, 126.8, 116.4, 96.0, 54.3, 51.4, 38.1, 27.1, 21.4, 20.1. HRMS (ESI) calcd for $C_{35}H_{39}NNaO_3SSi$ [(M+Na$^+$)]: 604.2312, found: 604.2319. $[\alpha]^{27}_D$ = +11.3 (*c* 1.0, $CHCl_3$). 97% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.50 min (minor), 16.73 min (major).

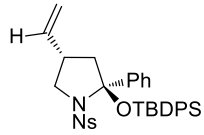


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.41	n.a.	869.355	376.191	50.44	n.a.	BMB*
2	17.07	n.a.	749.068	369.675	49.56	n.a.	BM *
Total:			1618.423	745.866	100.00	0.000	



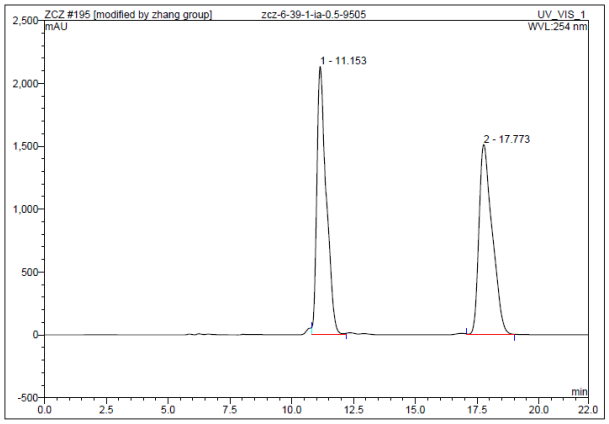
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.50	n.a.	18.957	10.240	1.35	n.a.	BMB*
2	16.73	n.a.	1496.613	750.351	98.65	n.a.	BM *
Total:			1515.570	760.591	100.00	0.000	

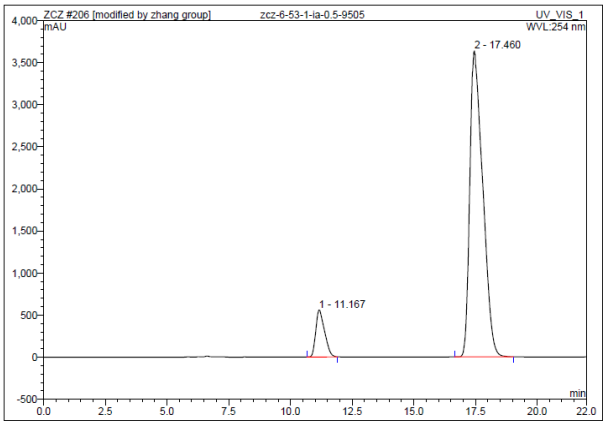
(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-1-((4-nitrophenyl)sulfonyl)-2-phenyl-4-vinylpyrrolidine: 3ca



White solid. 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 3H), 7.43-7.28 (m, 6H), 7.20-7.16 (m, 4H), 5.31-5.22 (m, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.52 (d, *J* = 17.2 Hz, 1H), 3.63 (t, *J* = 8.4 Hz, 1H), 2.80 (t, *J* = 10.4 Hz, 1H), 2.48 (dd, *J* = 14.4 and 8.0 Hz, 1H), 2.14 (dd, *J* = 14.4 and 11.6 Hz, 1H), 1.79-1.69 (m, 1H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 143.5, 149.3, 136.5, 136.4, 136.0, 133.7, 133.6, 130.3, 129.6, 128.1, 128.0, 127.9, 127.8, 127.7, 126.8, 123.4, 116.9, 96.1, 54.7, 50.8, 38.1, 27.1, 20.1. HRMS (ESI) calcd for $C_{34}H_{36}N_2NaO_5SSi$ [(M+Na$^+$)]: 635.2006, found: 635.2011. $[\alpha]^{27}_D$ = +23.6 (*c* 1.0, $CHCl_3$). 81% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.17 min (minor), 17.46 min (major).

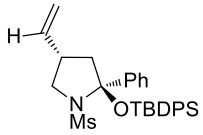




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.15	n.a.	2133.598	944.091	50.20	n.a.	M *
2	17.77	n.a.	1508.398	936.715	49.80	n.a.	MB*
Total:			3641.996	1880.807	100.00	0.000	

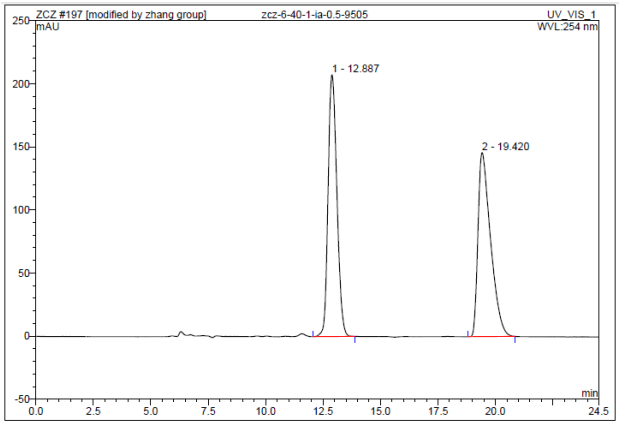
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.17	n.a.	558.209	229.603	9.41	n.a.	BMB*
2	17.46	n.a.	3638.288	2211.437	90.59	n.a.	BMB*
Total:			4196.497	2441.040	100.00	0.000	

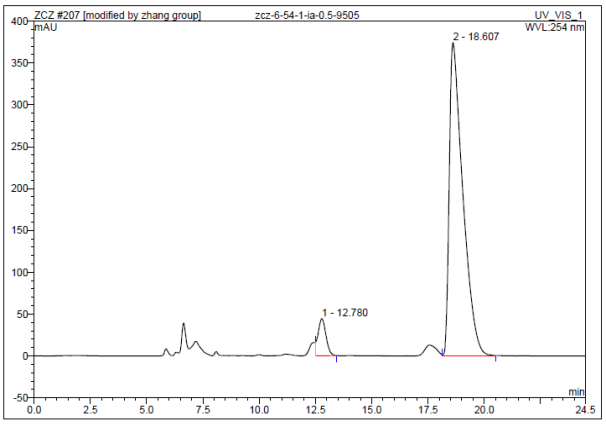
(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-1-(methylsulfonyl)-2-phenyl-4-vinylpyrrolidine: 3da



Yellow oil. 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.74-7.73 (m, 2H), 7.69-7.67 (m, 2H), 7.48-7.40 (m, 6H), 7.36-7.33 (m, 3H), 5.44-5.37 (m, 1H), 4.82 (d, *J* = 9.5 Hz, 1H), 4.60-4.57 (m, 1H), 3.46 (t, *J* = 8.5 Hz, 1H), 2.98 (t, *J* = 9.5 Hz, 1H), 2.52 (dd, *J* = 14.5 and 8.0 Hz, 1H), 2.30 (dd, *J* = 14.5 and 11.5 Hz, 1H), 2.26 (s, 3H), 1.83-1.74 (m, 1H), 1.31 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 136.9, 136.4, 136.0, 133.9, 133.8, 130.1, 129.5, 128.0, 127.9, 127.8, 127.6, 126.6, 116.5, 95.7, 54.1, 50.7, 38.3, 37.7, 27.1, 20.0. HRMS (ESI) calcd for $C_{29}H_{35}NNaO_3SSi$ [(M+Na^+)]: 528.1999, found: 528.2009. $[\alpha]^{28}_D$ = +11.6 (*c* 1.0, $CHCl_3$). 87% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 12.78 min (minor), 18.61 min (major).

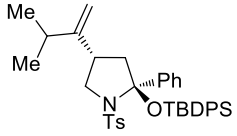




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.89	n.a.	207.534	92.329	49.94	n.a.	BMB*
2	19.42	n.a.	145.910	92.557	50.06	n.a.	BMB*
Total:			353.444	184.886	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.78	n.a.	44.297	17.894	6.43	n.a.	MB*
2	18.61	n.a.	373.953	260.265	93.57	n.a.	MB*
Total:			418.249	278.159	100.00	0.000	

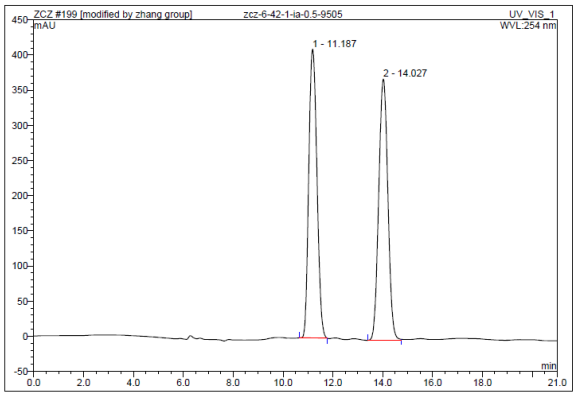
(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(3-methylbut-1-en-2-yl)-2-phenyl-1-tosylpyrrolidine: 3ea



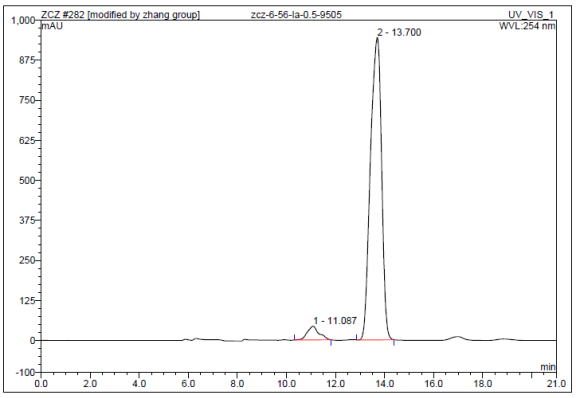
White solid. 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.73-7.71 (m, 2H), 7.47-7.31 (m, 8H), 7.26-7.24 (m, 1H), 7.20-7.18 (m, 2H), 7.01 (s, 4H), 4.61 (s, 1H), 4.38 (s, 1H), 3.73 (t, *J* = 8.4 Hz, 1H), 2.92-2.87 (m, 1H), 2.45 (dd, *J* = 13.6 and 6.8 Hz, 1H), 2.34 (s, 3H), 2.25-2.08

(m, 2H), 1.71-1.64 (m, 1H), 1.20 (s, 9H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.63 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 144.2, 142.2, 137.1, 136.4, 136.1, 134.1, 133.9, 130.0, 129.5, 128.8, 127.8, 127.7, 127.6, 127.2, 127.1, 126.9, 106.4, 96.0, 55.0, 51.1, 38.0, 33.3, 27.1, 21.9, 21.8, 20.1. HRMS (ESI) calcd for $C_{38}H_{45}NNaO_3SSi$ [$(M+Na^+)$]: 646.2782, found: 646.2791. $[\alpha]^{27}_D$ = -4.0 (*c* 1.0, $CHCl_3$). 91% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.09 min (minor), 13.70 min (major).

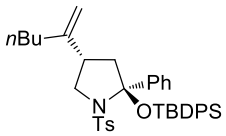


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.19	n.a.	410.639	155.168	49.52	n.a.	BMB*
2	14.03	n.a.	371.540	158.178	50.48	n.a.	BM *
Total:			782.179	313.346	100.00	0.000	



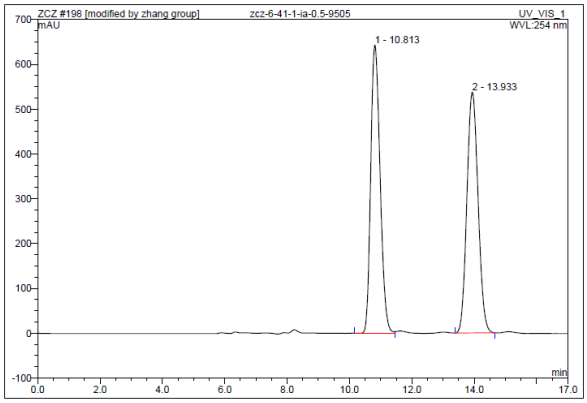
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.09	n.a.	42.520	23.421	4.51	n.a.	BMB*
2	13.70	n.a.	944.862	495.428	95.49	n.a.	BMB*
Total:			987.381	518.849	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(hex-1-en-2-yl)-2-phenyl-1-tosylpyrrolidine: 3fa

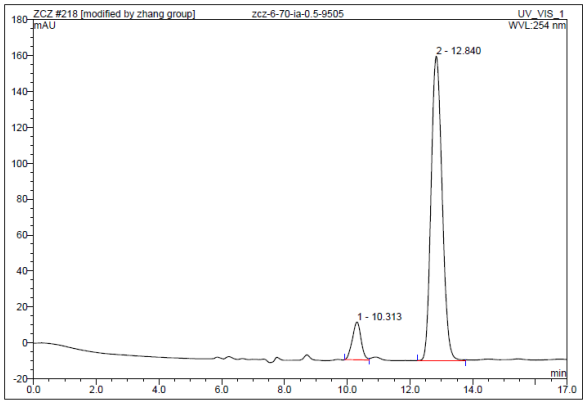


Colorless oil. 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.31 (m, 8H), 7.25-7.16 (m, 3H), 7.00 (s, 4H), 4.54 (s, 1H), 4.32 (s, 1H), 3.70 (t, *J* = 8.0 Hz, 1H), 2.89 (dd, *J* = 10.4 and 8.8 Hz, 1H), 2.43 (dd, *J* = 14.0 and 7.2 Hz, 1H), 2.33 (s, 3H), 2.24-2.17 (m, 1H), 2.08-1.99 (m, 1H), 1.56-1.53 (m, 2H), 1.21 (s, 9H), 1.12-1.05 (m, 2H), 0.99-0.93 (m, 2H), 0.79 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 144.0, 142.2, 137.0, 136.4, 136.0, 134.0, 133.8, 130.0, 129.5, 128.7, 127.7, 127.64, 127.59, 127.2, 127.0, 126.8, 108.5, 96.0, 54.1, 49.9, 38.5, 35.2, 29.7, 27.1, 22.2, 21.3, 20.1, 13.8. HRMS (ESI) calcd for $C_{39}H_{47}NNaO_3SSi$ [$(M+Na^+)$]: 660.2938, found: 660.2945. $[\alpha]^{27}_D$ = -1.4 (*c* 1.0, $CHCl_3$). 82% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 10.31 min (minor), 12.84 min (major).

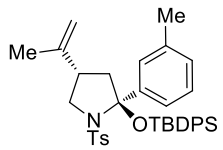


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.81	n.a.	642.443	223.500	50.07	n.a.	BM *
2	13.93	n.a.	537.028	222.892	49.93	n.a.	BMB*
Total:			1179.472	446.392	100.00	0.000	



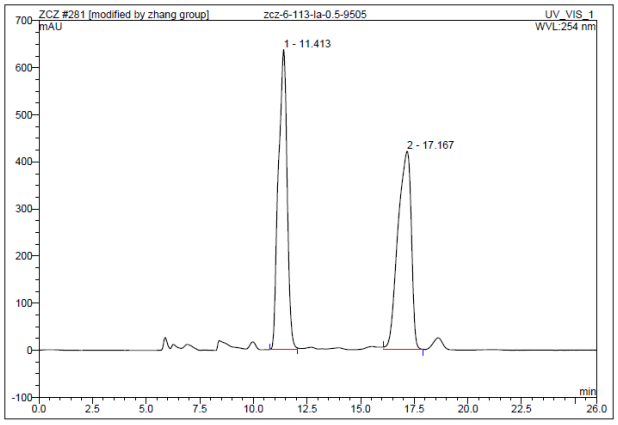
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.31	n.a.	21.023	6.755	8.91	n.a.	BM *
2	12.84	n.a.	169.533	69.037	91.09	n.a.	BM *
Total:			190.555	75.792	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(*m*-tolyl)-1-tosylpyrrolidine: 3ab

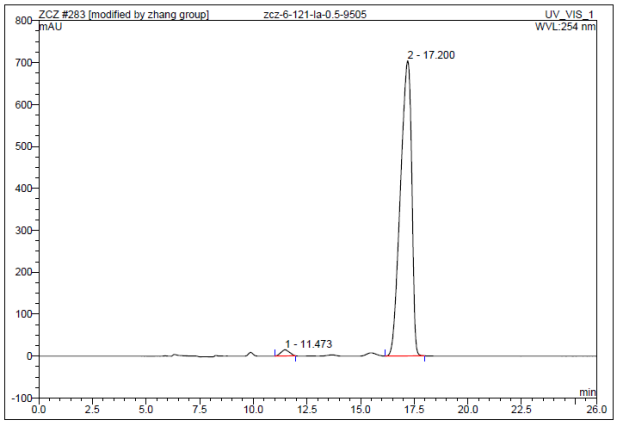


Whtie solid. 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.05 (m, 2H), 7.73-7.71 (m, 2H), 7.47-7.45 (m, 4H), 7.39-7.32 (m, 3H), 7.18-7.14 (m, 1H), 7.06-7.01 (m, 5H), 6.87 (s, 1H), 4.51 (s, 1H), 4.24 (s, 1H), 3.64 (t, *J* = 8.0 Hz, 1H), 2.89 (dd, *J* = 10.4 and 8.4 Hz, 1H), 2.40-2.37 (m, 1H), 2.34 (s, 3H), 2.21-2.14 (m, 1H), 2.11 (s, 3H), 1.93-1.83 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.2, 142.1, 137.0, 136.9, 136.5, 136.1, 134.13, 134.07, 130.0, 129.4, 128.7, 128.0, 127.8, 127.7, 127.6, 127.5, 127.1, 124.1, 110.3, 96.1, 53.6, 49.6, 40.0, 27.2, 21.4, 21.3, 20.8, 20.1. HRMS (ESI) calcd for $C_{37}H_{43}NNaO_3SSi$ [(M+Na$^+$)]: 632.2625, found: 632.2623. $[\alpha]^{28}_D$ = +15.8 (*c* 1.0, $CHCl_3$). 97% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.47 min (minor), 17.20 min (major).

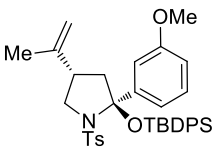


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.41	n.a.	636.818	299.441	49.71	n.a.	BM *
2	17.17	n.a.	420.304	302.910	50.29	n.a.	MB*
Total:			1057.123	602.350	100.00	0.000	



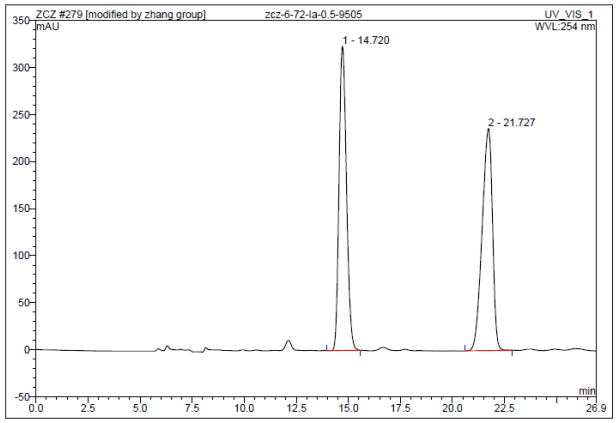
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.47	n.a.	14.664	6.696	1.54	n.a.	BMB*
2	17.20	n.a.	703.915	427.385	98.46	n.a.	BMB*
Total:			718.579	434.081	100.00	0.000	

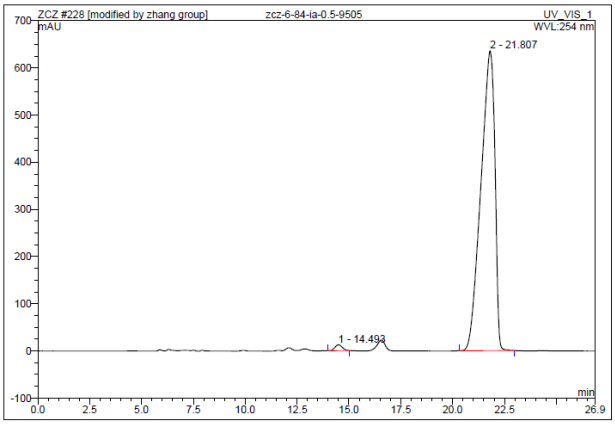
(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-2-(3-methoxyphenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ac



Colorless oil. 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.05 (m, 2H), 7.73-7.71 (m, 2H), 7.49-7.44 (m, 3H), 7.40-7.32 (m, 3H), 7.11-7.07 (m, 1H), 7.03 (s, 4H), 6.97-6.92 (m, 2H), 6.81-6.79 (m, 1H), 4.51 (s, 1H), 4.23 (s, 1H), 3.63-3.58 (m, 4H), 2.87 (dd, *J* = 10.4 and 8.8 Hz, 1H), 2.40 (dd, *J* = 14.4 and 8.0 Hz, 1H), 2.35 (s, 3H), 2.24-2.17 (m, 1H), 1.87-1.78 (m, 1H), 1.31 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 145.8, 143.1, 142.3, 136.8, 136.5, 136.0, 133.95, 133.86, 130.0, 129.5, 128.7, 128.6, 127.8, 127.6, 127.1, 119.2, 113.4, 112.2, 110.5, 95.9, 54.9, 53.5, 49.6, 39.9, 27.1, 21.3, 20.6, 20.1. HRMS (ESI) calcd for $C_{37}H_{44}NO_4SSi$ [(M+H$^+$)]: 626.2755, found: 626.2757. $[\alpha]^{27}_D$ = +8.5 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 14.49 min (minor), 21.81 min (major).

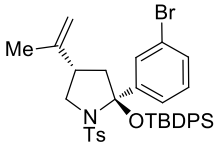




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.72	n.a.	323.475	133.736	49.58	n.a.	BMB*
2	21.73	n.a.	236.106	136.003	50.42	n.a.	BMB*
Total:			559.581	269.739	100.00	0.000	

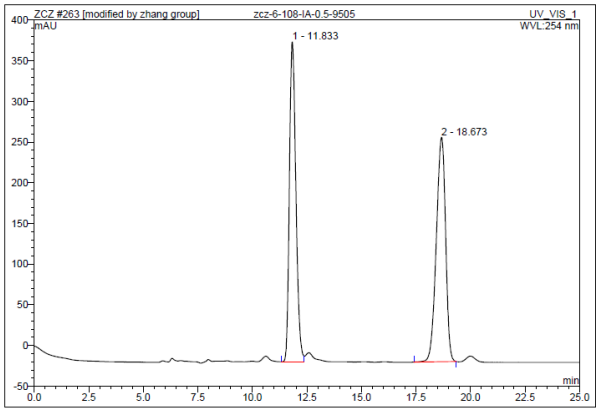
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.49	n.a.	12.321	5.037	1.00	n.a.	BMB*
2	21.81	n.a.	635.444	496.886	99.00	n.a.	BMB*
Total:			647.765	501.923	100.00	0.000	

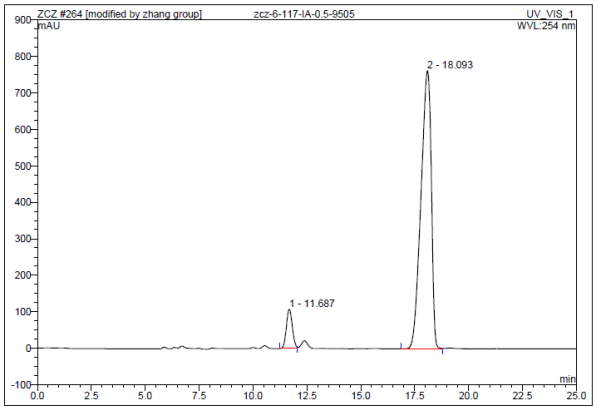
(2*S*,4*S*)-2-(3-bromophenyl)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ad



White solid. 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06-8.04 (m, 2H), 7.70-7.68 (m, 2H), 7.65-7.64 (m, 1H), 7.49-7.46 (m, 3H), 7.41-7.33 (m, 4H), 7.18-7.15 (m, 2H), 7.09-7.06 (m, 4H), 4.53 (s, 1H), 4.24 (s, 1H), 3.64 (t, *J* = 8.5 Hz, 1H), 2.89 (dd, *J* = 10.5 and 8.5 Hz, 1H), 2.40-2.36 (m, 4H), 2.12-2.06 (m, 1H), 1.95-1.88 (m, 1H), 1.30 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 142.9, 142.8, 136.7, 136.5, 136.0, 133.8, 133.7, 130.4, 130.1, 129.9, 129.6, 129.3, 129.1, 127.8, 127.7, 126.7, 125.7, 121.9, 110.5, 95.3, 53.4, 49.4, 39.9, 27.1, 21.4, 20.8, 20.1. HRMS (ESI) calcd for $C_{36}H_{40}BrNNaO_3SSi$ [$(M+Na^+)$]: 696.1574, found: 696.1591. $[\alpha]^{26}_D$ = +26.2 (*c* 1.0, $CHCl_3$). 85% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.69 min (minor), 18.09 min (major).

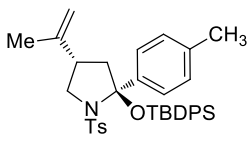




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.83	n.a.	393.242	135.113	49.81	n.a.	BM *
2	18.67	n.a.	275.760	136.160	50.19	n.a.	BMB*
Total:			669.003	271.273	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.69	n.a.	107.826	34.518	7.55	n.a.	BM *
2	18.09	n.a.	762.929	422.544	92.45	n.a.	BM *
Total:			870.755	457.062	100.00	0.000	

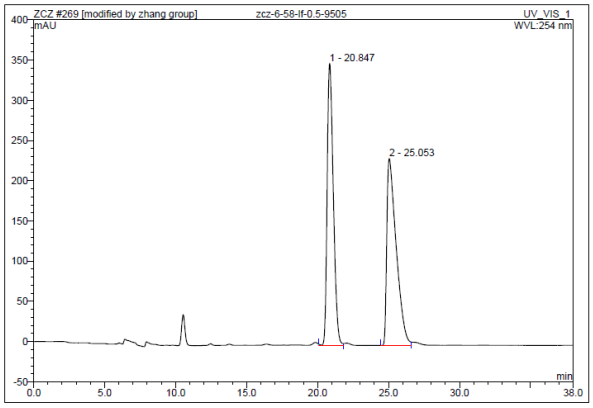
(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(*p*-tolyl)-1-tosylpyrrolidine: 3ae



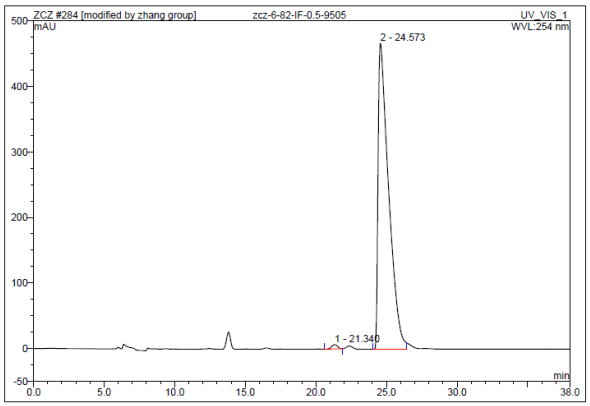
Colorless oil. 60% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 6.5 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.46-7.44 (m, 3H), 7.40-7.29 (m, 5H), 7.04-6.98 (m, 6H), 4.50 (s, 1H), 4.23 (s, 1H), 3.58 (t, *J* = 8.0 Hz, 1H), 2.88 (t, *J* = 9.5 Hz, 1H), 2.41-2.35 (m, 7H), 2.23-2.17 (m, 1H), 1.85-1.78 (m,

1H), 1.30 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 142.2, 141.3, 137.1, 136.9, 136.5, 136.1, 134.1, 130.0, 129.4, 128.6, 128.3, 127.8, 127.6, 127.2, 126.7, 110.4, 96.1, 53.4, 49.4, 40.0, 27.1, 21.4, 21.0, 20.7, 20.1. HRMS (ESI) calcd for $C_{37}H_{43}NNaO_3SSi$ [(M+Na^+)]: 632.2625, found: 632.2631. $[\alpha]^{28}_D$ = -9.4 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 21.34 min (minor), 24.57 min (major).

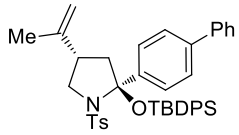


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.85	n.a.	350.131	175.581	49.58	n.a.	M *
2	25.05	n.a.	232.382	178.562	50.42	n.a.	BM *
Total:			582.513	354.143	100.00	0.000	



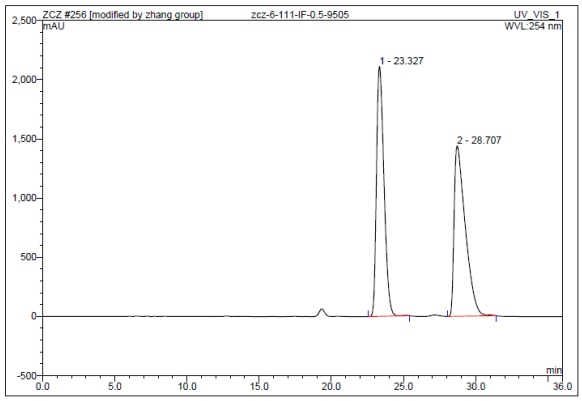
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.34	n.a.	6.634	3.223	0.79	n.a.	BMB*
2	24.57	n.a.	466.937	404.468	99.21	n.a.	BM *
Total:			473.571	407.692	100.00	0.000	

(2*S*,4*S*)-2-([1,1'-biphenyl]-4-yl)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1 tosylpyrrolidine: 3af

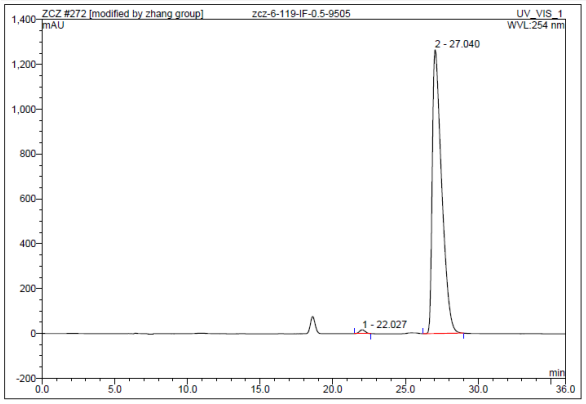


White solid. 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.07 (m, 2H), 7.73-7.72 (m, 2H), 7.62-7.60 (m, 2H), 7.49-7.46 (m, 7H), 7.42-7.32 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.53 (s, 1H), 4.26 (s, 1H), 3.65 (t, *J* = 8.0 Hz, 1H), 2.95 (dd, *J* = 10.4 and 8.8 Hz, 1H), 2.44 (dd, *J* = 14.0 and 7.6 Hz, 1H), 2.31 (s, 3H), 2.27-2.23 (m, 1H), 1.90-1.80 (m, 1H), 1.33 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 143.1, 142.2, 140.6, 140.1, 137.1, 136.5, 136.0, 134.01, 133.97, 130.0, 129.5, 128.81, 128.76,127.8, 127.6, 127.4, 127.3, 127.1, 126.9, 126.2, 110.5, 95.9, 53.6, 49.3, 40.0, 27.2, 21.3, 20.7, 20.1. HRMS (ESI) calcd for $C_{42}H_{45}NNaO_3SSi$ [(M+Na^+)]: 694.2782, found: 694.2785. $[\alpha]^{27}_D$ = -46.2 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 22.03 min (minor), 27.04 min (major).

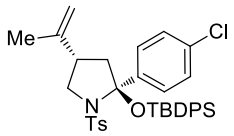


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.33	n.a.	2111.184	1273.317	49.61	n.a.	BMB*
2	28.71	n.a.	1439.221	1293.293	50.39	n.a.	BMB*
Total:			3550.406	2566.611	100.00	0.000	



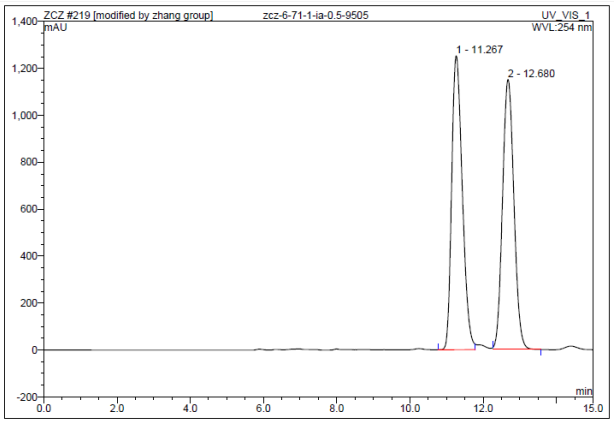
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.03	n.a.	17.263	8.279	0.87	n.a.	BMB*
2	27.04	n.a.	1265.382	946.346	99.13	n.a.	BMB*
Total:			1282.646	954.625	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-2-(4-chlorophenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ag

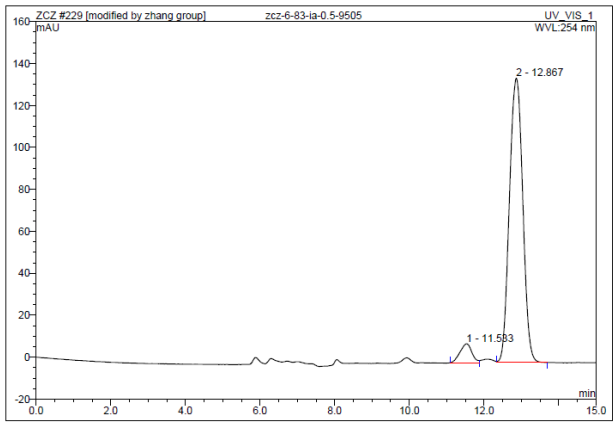


Colorless oil. 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H), 7.67-7.65 (m, 2H), 7.49-7.33 (m, 8H), 7.15-7.13 (m, 2H), 7.06 (s, 4H), 4.52 (s, 1H), 4.23 (s, 1H), 3.60 (t, *J* = 8.0 Hz, 1H), 2.90 (dd, *J* = 10.4 and 9.2 Hz, 1H), 2.42-2.40 (m, 1H), 2.37 (s, 3H), 2.17-2.10 (m, 1H), 1.88-1.79 (m, 1H), 1.31 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 142.8, 142.6, 137.0, 136.4, 135.9, 133.8, 133.7, 133.2, 130.1, 129.6, 128.9, 128.2, 127.8, 127.70, 127.68, 126.9, 110.5, 95.5, 53.4, 49.2, 39.9, 27.1, 21.4, 20.7, 20.1. HRMS (ESI) calcd for $C_{36}H_{41}ClNO_3SSi$ [(M+H$^+$)]: 630.2259, found: 630.2270. $[\alpha]^{28}_D$ = -20.1 (*c* 1.0, $CHCl_3$). 89% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.53 min (minor), 12.87 min (major).

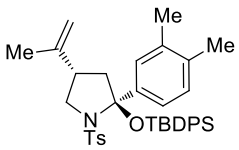


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.27	n.a.	1252.161	421.651	50.39	n.a.	BM *
2	12.68	n.a.	1151.090	415.149	49.61	n.a.	MB*
Total:			2403.251	836.800	100.00	0.000	



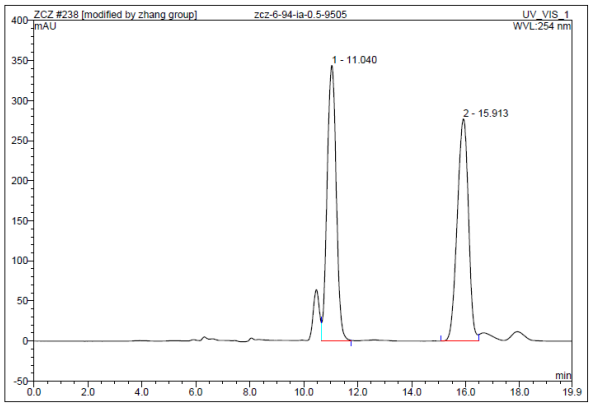
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.53	n.a.	8.998	3.297	5.55	n.a.	BM *
2	12.87	n.a.	135.534	56.133	94.45	n.a.	MB*
Total:			144.532	59.430	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-2-(3,4-dimethylphenyl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ah

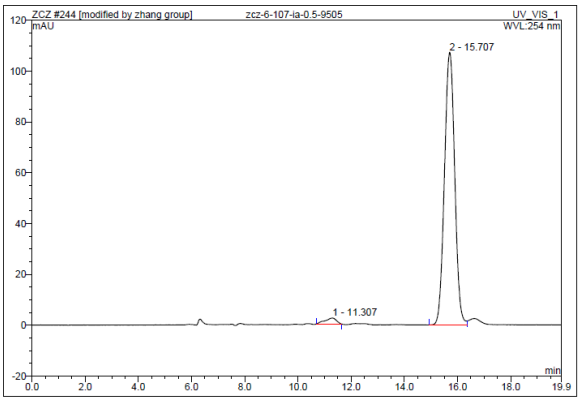


Colorless oil. 44% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.44 (m, 3H), 7.40-7.31 (m, 4H), 7.04-6.98 (m, 5H), 6.81 (s, 1H), 4.51 (s, 1H), 4.24 (s, 1H), 3.62 (t, *J* = 8.0 Hz, 1H), 2.90 (dd, *J* = 10.4 and 8.4 Hz, 1H), 2.38-2.33 (m, 4H), 2.26 (s, 3H), 2.20-2.13 (m, 1H), 2.00 (s, 3H), 1.91-1.82 (m, 1H), 1.31 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.0, 141.5, 137.2, 136.5, 136.1, 135.6, 135.3, 134.2, 134.1, 130.0, 129.4, 128.9, 128.6, 128.0, 127.8, 127.6, 127.1, 124.4, 110.3, 96.1, 53.6, 49.5, 40.0, 27.1, 21.3, 20.8, 20.2, 19.8, 19.4. HRMS (ESI) calcd for $C_{38}H_{45}NNaO_3SSi$ [(M+Na$^+$)]: 646.2782, found: 646.2791. $[\alpha]^{27}_D$ = +9.1 (*c* 1.0, $CHCl_3$). 95% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 11.31 min (minor), 15.71 min (major).

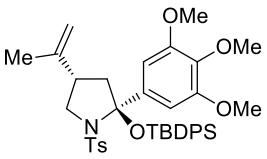


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.04	n.a.	343.358	133.786	50.03	n.a.	M *
2	15.91	n.a.	277.019	133.625	49.97	n.a.	BM *
Total:			620.377	267.411	100.00	0.000	



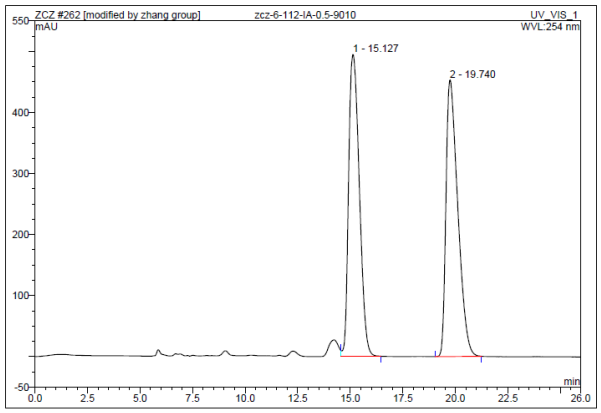
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.31	n.a.	2.387	1.194	2.43	n.a.	MB*
2	15.71	n.a.	107.337	47.882	97.57	n.a.	BM *
Total:			109.724	49.076	100.00	0.000	

(2*S*,4*S*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosyl-2-(3,4,5-trimethoxyphenyl)pyrrolidine: 3ai

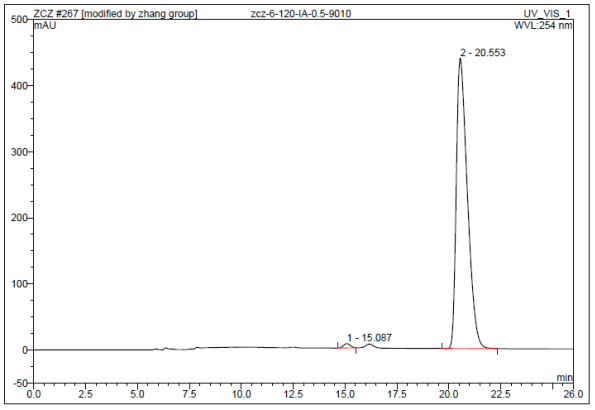


White solid. 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07-8.05 (m, 2H), 7.76-7.74 (m, 2H), 7.50-7.36 (m, 6H), 7.08 (s, 4H), 6.55 (s, 2H), 4.53 (s, 1H), 4.25 (s, 1H), 3.91 (s, 3H), 3.64 (t, *J* = 8.5 Hz, 1H), 3.53 (s, 6H), 2.90 (dd, *J* = 10.5 and 9.0 Hz, 1H), 2.42 (dd, *J* = 14.0 and 7.5 Hz, 1H), 2.35 (s, 3H), 2.20 (dd, *J* = 14.0 and 12.0 Hz, 1H), 1.86-1.78 (m, 1H), 1.33 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 143.1, 142.4, 139.6, 136.9, 136.8, 136.5, 136.0, 133.9, 133.6, 130.1, 129.5, 128.7, 127.9, 127.6, 127.0, 110.5, 104.0, 95.8, 60.8, 55.4, 53.6, 49.7, 39.9, 27.0, 21.3, 20.6, 20.1. HRMS (ESI) calcd for $C_{39}H_{47}NNaO_6SSi$ [(M+Na^+)]: 708.2786, found: 708.2780. $[\alpha]^{26}_D$ = +44.4 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 15.09 min (minor), 20.55 min (major).

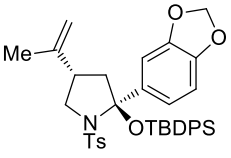


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.13	n.a.	494.353	292.057	49.75	n.a.	MB*
2	19.74	n.a.	453.285	294.939	50.25	n.a.	BMB*
Total:			947.638	586.996	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.09	n.a.	6.484	2.460	0.90	n.a.	BMB*
2	20.55	n.a.	439.372	271.632	99.10	n.a.	BMB*
Total:			445.856	274.093	100.00	0.000	

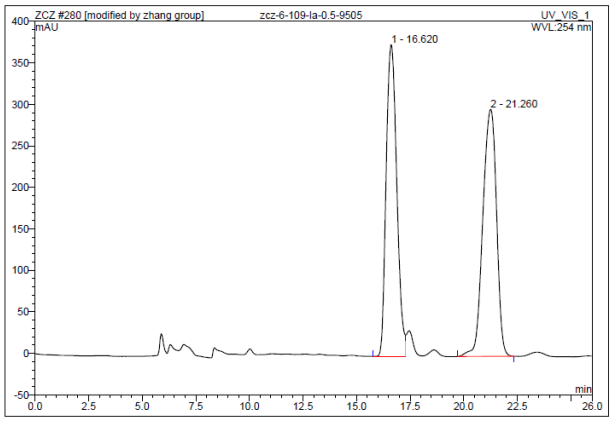
(2*S*,4*S*)-2-(benzo[*d*][1,3]dioxol-5-yl)-2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3aj



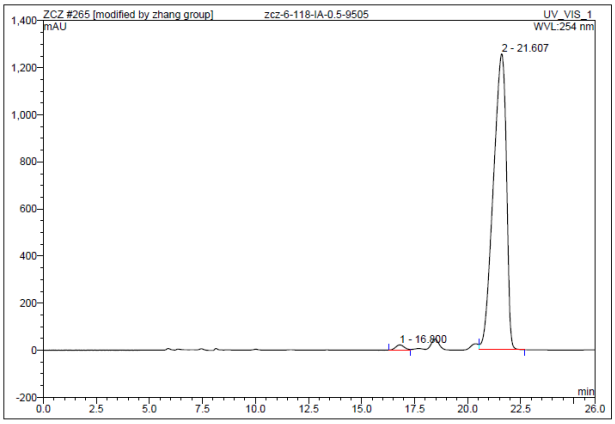
White solid. 71% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06-8.04 (m, 2H), 7.70-7.69 (m, 2H), 7.48-7.44 (m, 3H), 7.40-7.38 (m, 1H), 7.36-7.33 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.5

Hz, 2H), 7.02 (dd, *J* = 8.0 and 2.0 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.95-5.92 (m, 2H), 4.51 (s, 1H), 4.23 (s, 1H), 3.59 (t, *J* = 8.5 Hz, 1H), 2.88 (dd, *J* = 10.5 and 8.5 Hz, 1H), 2.38 (dd, *J* = 14.0 and 7.5 Hz, 1H), 2.35 (s, 3H), 2.15 (dd, *J* = 14.0 and 12.5 Hz, 1H), 1.82-1.74 (m, 1H), 1.30 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 146.7, 143.1, 142.3, 138.3, 137.1, 136.5, 136.0, 133.93, 133.89, 130.0, 129.5, 128.7, 127.8, 127.6, 127.0, 120.44, 120.41, 107.7, 107.1, 101.0, 95.8, 53.5, 49.4, 39.8, 27.1, 21.4, 20.7, 20.1. HRMS (ESI) calcd for $C_{37}H_{41}NNaO_5SSi$ [(M+Na$^+$)]: 662.2367, found: 662.2366. $[\alpha]^{27}_D$ = -1.3 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 16.80 min (minor), 21.61 min (major).

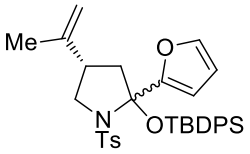


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.62	n.a.	375.360	215.262	49.43	n.a.	BM *
2	21.26	n.a.	297.729	220.215	50.57	n.a.	BMB*
Total:			673.088	435.477	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.80	n.a.	21.677	10.235	1.13	n.a.	BM *
2	21.61	n.a.	1256.685	895.586	98.87	n.a.	MB*
Total:			1278.362	905.822	100.00	0.000	

2-((*tert*-butyldiphenylsilyl)oxy)-2-(furan-2-yl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3ak

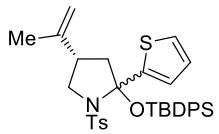


Colorless oil. 71% yield. *d.r.* = 5:1. (The diastereomers can not be separated by chromatography)

^{1}H NMR (the major product, 500 MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.73-7.71 (m, 2H), 7.48-7.34 (m, 6H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 2H), 6.96 (s, 1H), 6.80-6.79 (m, 1H), 6.37-6.36 (m, 1H), 4.51 (s, 1H), 4.25 (s, 1H), 3.54 (t, *J* = 8.0 Hz, 1H), 2.84 (dd, *J* = 11.0 and 8.5 Hz, 1H), 2.37 (s, 3H), 2.29-2.24 (m, 1H), 2.13 (dd, *J* = 13.5 and 6.5 Hz, 1H), 1.87-1.80 (m, 1H), 1.30 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (the major product, 125 MHz, $CDCl_3$): δ 154.8, 142.9, 142.4, 141.1, 136.8, 136.5, 135.9, 133.9, 133.6, 130.0, 129.5, 129.0, 127.8, 127.6, 127.2, 110.6, 110.4, 109.3, 92.1, 52.8, 45.1, 40.0, 26.8, 21.4, 20.5, 19.8; ^{1}H NMR (the minor product, 500 MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.69-7.68 (m, 2H), 7.48-7.34 (m, 6H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 2H), 7.03 (s, 1H), 6.78-6.77 (m, 1H), 6.40-6.39 (m, 1H), 4.51 (s, 1H), 4.25 (s, 1H), 3.29 (t, *J* = 8.0 Hz, 1H), 2.70 (dd, *J* = 11.0 and 9.0 Hz, 1H), 2.37 (s, 3H), 2.23-2.20 (m, 1H), 2.07 (dd, *J* = 13.0 and 6.0 Hz, 1H), 2.03-2.00 (m, 1H), 1.20 (s, 3H), 1.16 (s, 9H).^{13}C NMR (the minor product, 125 MHz, $CDCl_3$): δ 156.2, 142.9, 142.4, 141.0, 136.8, 136.3, 135.8, 134.0, 133.6, 129.9, 129.5, 129.0, 127.7, 127.5, 127.1, 111.4, 110.2, 108.0, 92.8, 51.5, 46.9, 42.6, 26.8, 21.4, 20.0, 19.5. HRMS (ESI) calcd for $C_{34}H_{40}NO_4SSi$ [(M+H$^+$)]: 586.2442, found: 586.2450. $[\alpha]^{26}_D$ = +27.2 (*c* 1.0, $CHCl_3$).

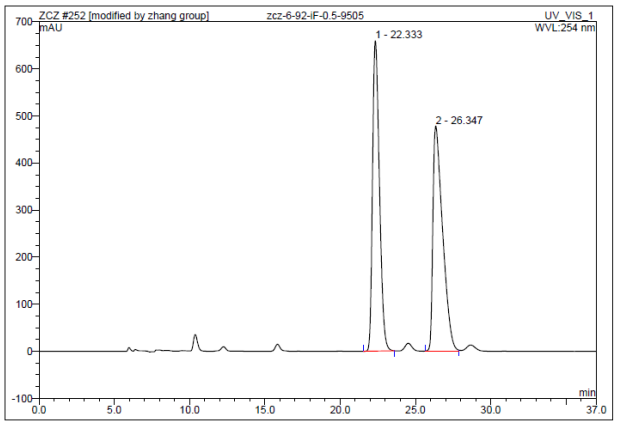
*Note: the ee value of **3ak** can not be determined by HPLC analysis using a chiral stationary phase.*

2-((*tert*-butyldiphenylsilyl)oxy)-4-(prop-1-en-2-yl)-2-(thiophen-2-yl)-1-tosylpyrrolidine: 3al

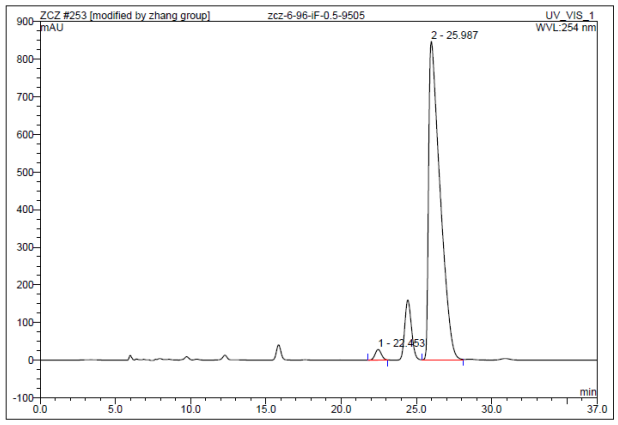


Colorless oil. 56% yield. *d.r.* = 10:1

^{1}H NMR (the major product, 400 MHz, $CDCl_3$): δ 8.05-8.04 (m, 2H), 7.75-7.73 (m, 2H), 7.47-7.33 (m, 6H), 7.21-7.19 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.81-6.79 (m, 1H), 6.67-6.66 (m, 1H), 4.52 (s, 1H), 4.24 (s, 1H), 3.51 (t, *J* = 8.0 Hz, 1H), 2.81 (dd, *J* = 10.8 and 9.2 Hz, 1H), 2.51 (dd, *J* = 14.0 and 7.2 Hz, 1H), 2.34 (s, 3H), 2.23-2.16 (m, 1H), 1.83-1.73 (m, 1H), 1.30 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (the major product,100 MHz, $CDCl_3$): δ 148.9, 142.8, 142.3, 136.8, 136.6, 136.0, 133.8, 133.5, 130.0, 129.5, 128.8, 127.8, 127.6, 127.0, 126.3, 125.2, 124.6, 110.6, 94.1, 52.9, 50.2, 39.7, 26.9, 21.4, 20.6, 20.0. HRMS (ESI) calcd for $C_{34}H_{40}NO_3S_2Si$ [$(M+H^+)$]: 602.2213, found: 602.2221. $[\alpha]^{27}_D$ = +5.9 (*c* 1.0, $CHCl_3$). 96% *ee* (the major product). HPLC analysis of the major product: Daicel Chiralpak IF column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 22.45 min (minor), 25.99 min (major).

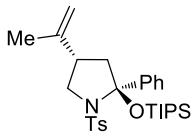


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.33	n.a.	659.010	349.348	49.49	n.a.	BMB*
2	26.35	n.a.	477.974	356.517	50.51	n.a.	BM *
Total:			1136.984	705.866	100.00	0.000	



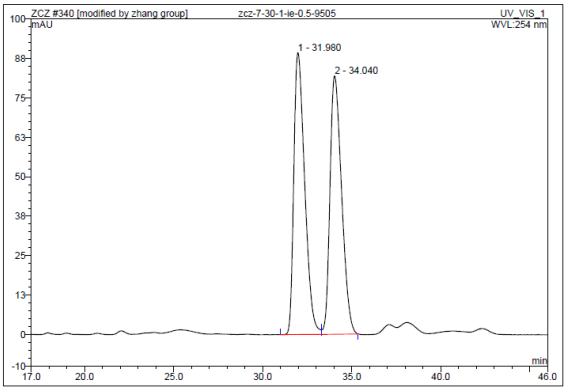
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.45	n.a.	28.109	13.542	1.79	n.a.	BMB*
2	25.99	n.a.	846.664	744.433	98.21	n.a.	BM *
Total:			874.773	757.975	100.00	0.000	

(2*S*,4*S*)-2-phenyl-4-(prop-1-en-2-yl)-1-tosyl-2-((triisopropylsilyl)oxy)pyrrolidine: 3am

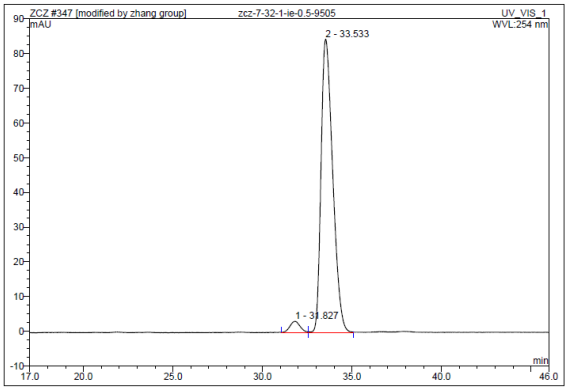


Colorless oil. 25% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H), 7.22-7.19 (m, 1H), 7.16-7.13 (m, 2H), 7.05-7.01 (m, 4H), 4.84 (s, 1H), 4.73 (s, 1H), 4.14 (t, *J* = 8.5 Hz, 1H), 3.33-3.26 (m, 1H), 3.17 (dd, *J* = 11.0 and 9.0 Hz, 1H), 2.48-2.44 (m, 2H), 2.37 (s, 3H), 1.79 (s, 3H), 1.34-1.28 (m,



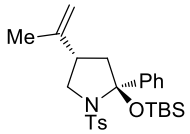
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	31.98	n.a.	89.357	63.373	50.52	n.a.	BM *
2	34.04	n.a.	81.909	62.070	49.48	n.a.	MB*
Total:			171.266	125.442	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	31.83	n.a.	3.196	2.080	3.16	n.a.	BM *
2	33.53	n.a.	84.487	63.750	96.84	n.a.	M *
Total:			87.683	65.830	100.00	0.000	

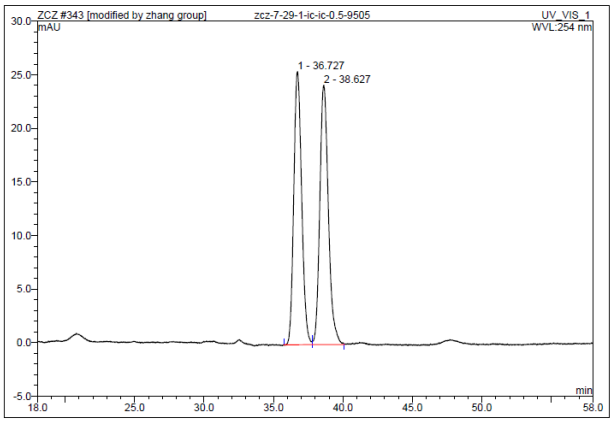
3H), 1.24-1.21 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 143.3, 142.2, 137.3, 128.8, 127.4, 127.2, 127.0, 126.8, 111.0, 95.8, 53.4, 50.6, 41.3, 21.40, 21.37, 18.53, 18.48, 14.0. HRMS (ESI) calcd for $C_{29}H_{43}NNaO_3SSi$ [(M+Na$^+$)]: 536.2625, found: 536.2631. $[\alpha]^{28}_D$ = -29.7 (*c* 1.0, $CHCl_3$). 94% *ee*. HPLC analysis of the product: Daicel Chiralpak IE column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 31.83 min (minor), 33.53 min (major).

(2*S*,4*S*)-2-((*tert*-butyldimethylsilyl)oxy)-2-phenyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine: 3an

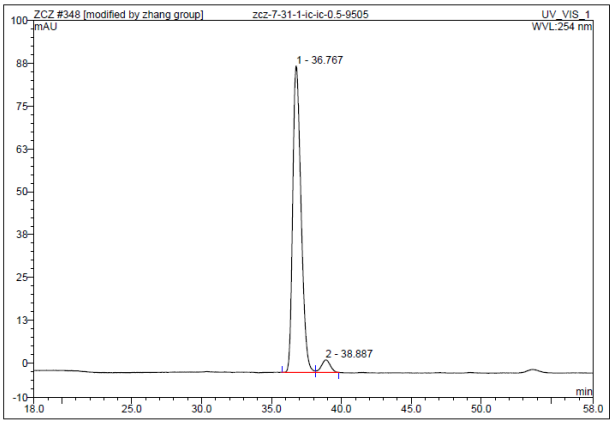


Colorless oil. 15% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-7.19 (m, 3H), 7.13-7.11 (m, 2H), 7.04 (s, 4H), 4.84 (s, 1H), 4.74 (s, 1H), 4.19-4.13 (m, 1H), 3.29-3.23 (m, 2H), 2.41-2.30 (m, 5H), 1.77 (s, 3H), 1.04 (s, 9H), 0.42 (s, 3H), 0.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 142.8, 142.4, 137.5, 128.8, 127.5, 127.2, 127.0, 126.9, 111.0, 95.4, 53.5, 51.2, 41.4, 26.1, 21.42, 21.41, 18.8, -2.9, -3.0. HRMS (ESI) calcd for $C_{26}H_{37}NNaO_3SSi$ [(M+Na$^+$)]: 494.2156, found: 494.2153. $[\alpha]^{28}_D$ = -45.0 (*c* 0.5, $CHCl_3$). 92% *ee*. HPLC analysis of the product: Daicel Chiralpak IC column; hexane/2-propanol = 95/05, 0.5 mL/min. Retention times: 36.77 min (major), 38.89 min (minor).



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	36.73	n.a.	25.524	16.851	49.25	n.a.	BM *
2	38.63	n.a.	24.232	17.362	50.75	n.a.	M *
Total:			49.756	34.214	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	36.77	n.a.	89.463	61.719	95.85	n.a.	BM *
2	38.89	n.a.	3.670	2.674	4.15	n.a.	MB*
Total:			93.133	64.392	100.00	0.000	

3.3 General Procedure for Ring-Opening Reaction of Vinyl Aziridines and Enol Silyl Ethers.

(*R*)-**1** **2** **4**

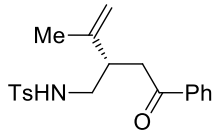
Condition A:

A mixture of $[Rh(NBD)Cl]_2$ (5.0 mg, 5 mol%) and $AgPF_6$ (5.5 mg, 10 mol%) in DCE (0.5 mL) was stirred at room temperature under argon atmosphere for 30 min. Then a solution of vinylaziridine **1** (0.20 mmol) and enol silyl ethers **2** (0.3 mmol) in DCE (1.5 mL) was added dropwisely to this mixture at 0 °C. The resulting mixture was then stirred at 0 °C for about 1-4 h. Upon complete consumption of **1** (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography, eluting with hexane:ethyl acetate:dichloromethane (7:1:1) to afford the desired cycloadduct **4**.

Condition B:

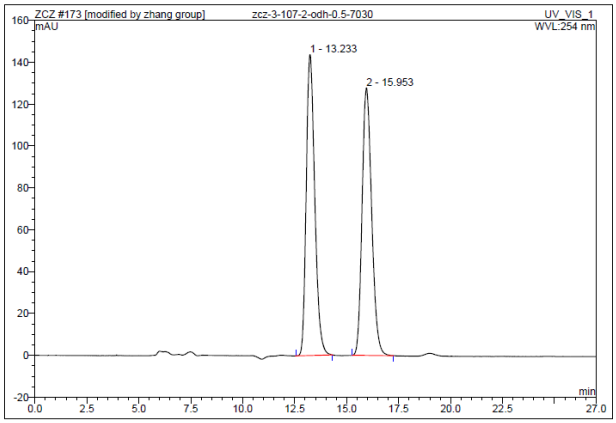
A mixture of $[Rh(NBD)Cl]_2$ (5.0 mg, 5 mol%) and $AgSbF_6$ (7.5 mg, 10 mol%) in DCE (0.5 mL) was stirred at room temperature under argon atmosphere for 30 min. Then a solution of vinylaziridine **1** (0.20 mmol) and enol silyl ethers **2** (0.3 mmol) in DCE (1.5 mL) was added dropwisely to this mixture at room temperature. The resulting mixture was then stirred at room temperature for about 0.5-2.5 h. Upon complete consumption of **1** (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography, eluting with hexane:ethyl acetate:dichloromethane (7:1:1) to afford the desired cycloadduct **4**.

(*S*)-4-methyl-*N*-(3-methyl-2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4ao

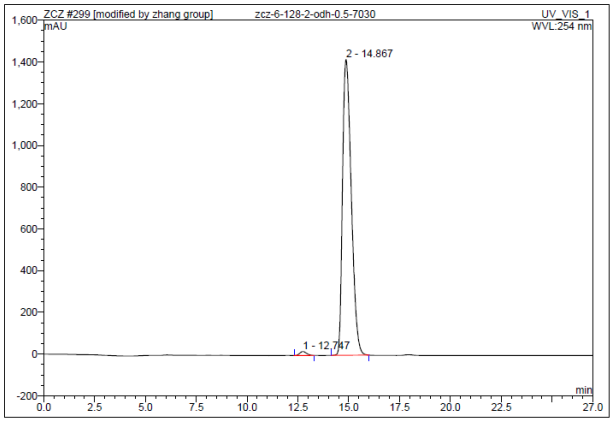


Colorless oil. 86% yield. Conditon A.

The enantiomer of this compound has already been reported.[4a] $[\alpha]^{28}_D$ = -2.8 (*c* 1.0, $CHCl_3$). 98% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.75 min (minor), 14.87 min (major).

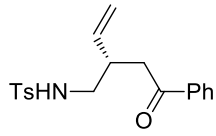


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.23	n.a.	143.804	68.277	49.93	n.a.	BMB*
2	15.95	n.a.	127.823	68.477	50.07	n.a.	BMB*
Total:			271.627	136.753	100.00	0.000	



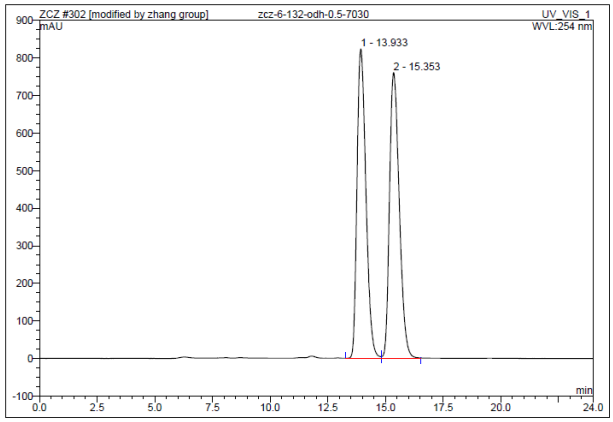
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.75	n.a.	18.849	7.243	1.01	n.a.	BMB*
2	14.87	n.a.	1417.548	707.256	98.99	n.a.	BMB*
Total:			1436.397	714.499	100.00	0.000	

(*S*)-4-methyl-*N*-(2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4bo

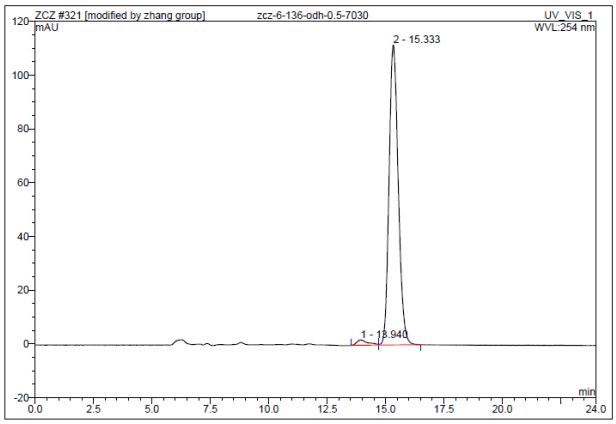


Colorless oil. 70% yield. Conditon A.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.58-7.55 (m, 1H), 7.46-7.43 (m, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 5.69-5.62 (m, 1H), 5.10-5.04 (m, 2H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.11-2.91 (m, 5H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 143.4, 137.8, 136.8, 136.7, 133.2, 129.7, 128.6, 128.0, 127.0, 117.4, 46.3, 40.3, 38.5, 21.4. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_3S$ [$(M+Na^+)$]: 366.1134, found: 366.1128. $[\alpha]^{27}_D$ = +1.7 (*c* 1.0, $CHCl_3$). 96% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 13.94 min (minor), 15.33 min (major).

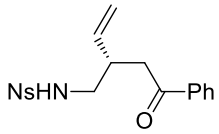


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.93	n.a.	823.318	369.232	49.74	n.a.	BM *
2	15.35	n.a.	760.379	373.059	50.26	n.a.	M *
Total:			1583.697	742.291	100.00	0.000	



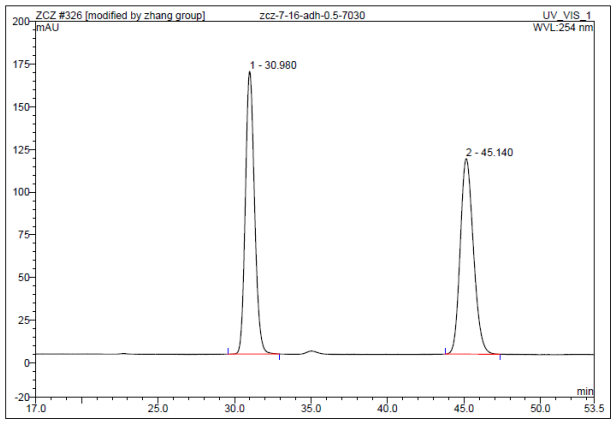
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.94	n.a.	1.961	1.080	2.08	n.a.	BM *
2	15.33	n.a.	111.626	50.908	97.92	n.a.	MB*
Total:			113.587	51.987	100.00	0.000	

(*S*)-4-nitro-*N*-(2-(2-oxo-2-phenylethyl)but-3-en-1-yl)benzenesulfonamide: 4co

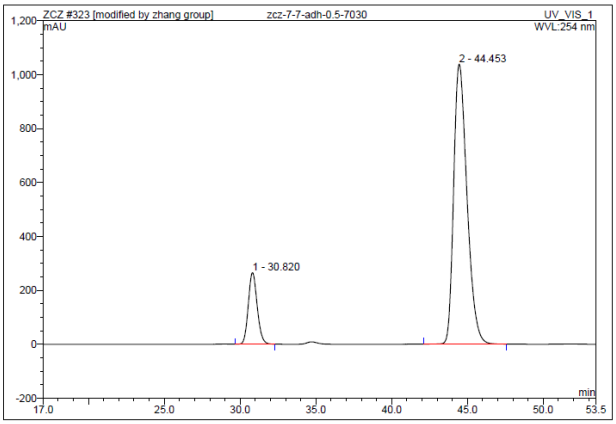


Yellow oil. 67% yield. Conditon A.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29-8.27 (m, 2H), 8.04-8.01 (m, 2H), 7.88-7.86 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.43 (m, 2H), 5.72-5.65 (m, 1H), 5.28 (t, *J* = 6.0 Hz, 1H), 5.13-5.07 (m, 2H), 3.22-3.18 (m, 1H), 3.11-3.06 (m, 3H), 2.98-2.92 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 149.9, 145.8, 137.5, 136.4, 133.5, 128.7, 128.2, 128.0, 124.3, 117.6, 46.3, 40.2, 38.5. HRMS (ESI) calcd for $C_{18}H_{18}N_2NaO_5S$ [(M+Na$^+$)]: 397.0829, found: 397.0832. $[\alpha]^{27}_D$ = +4.0 (*c* 1.0, $CHCl_3$). 71% *ee*. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 30.82 min (minor), 44.45 min (major).

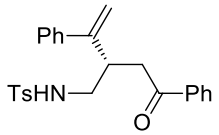


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.98	n.a.	165.620	114.818	50.11	n.a.	BMB*
2	45.14	n.a.	114.484	114.330	49.89	n.a.	BMB*
Total:			280.105	229.148	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.82	n.a.	265.657	180.235	14.56	n.a.	BMB*
2	44.45	n.a.	1038.652	1057.306	85.44	n.a.	BMB*
Total:			1304.309	1237.541	100.00	0.000	

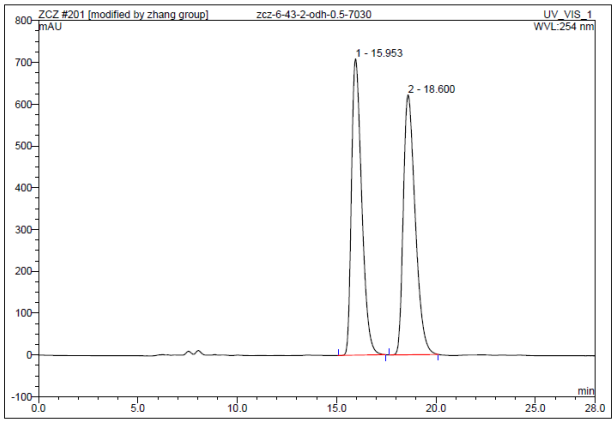
(*S*)-4-methyl-*N*-(2-(2-oxo-2-phenylethyl)-3-phenylbut-3-en-1-yl)benzenesulfonamide: 4go

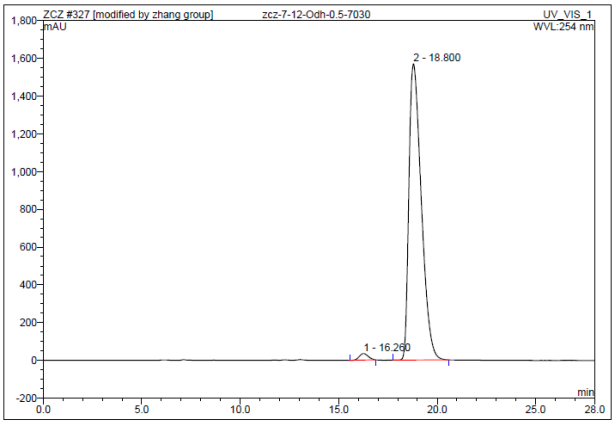


Colorless oil. 87% yield. Conditon A.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.56-7.52 (m, 1H), 7.44-7.40 (m, 2H), 7.29-7.24 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.30 (s, 1H), 5.04 (s, 1H), 4.90 (t, *J* = 6.4 Hz, 1H), 3.59-3.53 (m, 1H), 3.25-3.12 (m, 3H), 3.06-2.99 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 149.0, 143.2, 141.0, 136.8, 136.7, 133.1, 129.6, 128.5, 128.4, 128.0, 127.8, 126.9, 126.6, 113.9, 45.5, 40.2, 38.5, 21.4. HRMS (ESI) calcd for

$C_{25}H_{25}NNaO_3S$ [(M+Na^+)]: 442.1447, found: 442.1454. $[\alpha]^{28}_D$ = -29.3 (*c* 1.0, $CHCl_3$). 97% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 16.26 min (minor), 18.80 min (major).

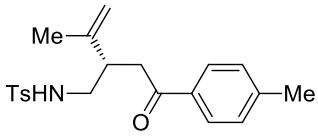




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.95	n.a.	708.762	422.581	49.46	n.a.	BMB*
2	18.60	n.a.	621.644	431.812	50.54	n.a.	BMB*
Total:			1330.406	854.394	100.00	0.000	

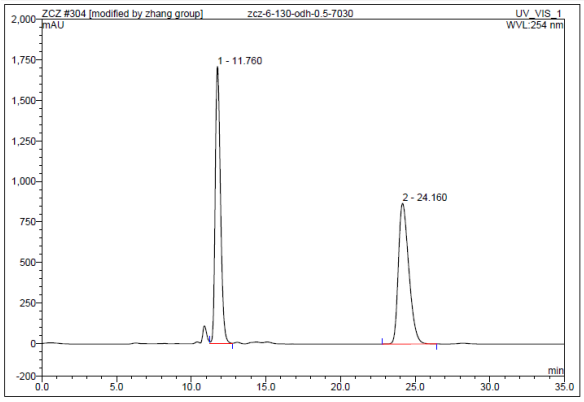
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.26	n.a.	34.706	18.117	1.56	n.a.	BMB*
2	18.80	n.a.	1570.100	1143.975	98.44	n.a.	BMB*
Total:			1604.806	1162.092	100.00	0.000	

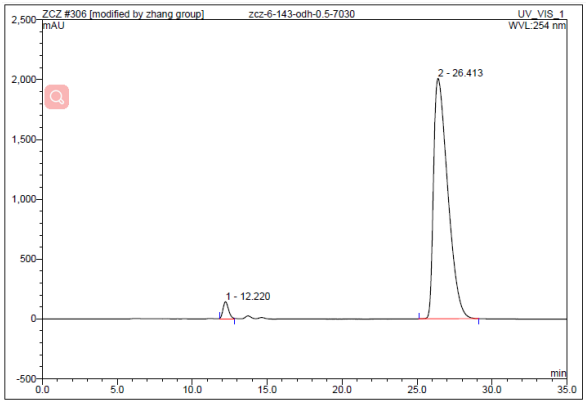
(*S*)-4-methyl-*N*-(3-methyl-2-(2-oxo-2-(*p*-tolyl)ethyl)but-3-en-1-yl)benzenesulfonamide: 4ap



Yellow oil. 96% yield. Conditon A.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 4H), 4.85 (s, 1H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.71 (s, 1H), 3.10-2.95 (m, 4H), 2.91-2.85 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 144.2, 143.9, 143.2, 136.8, 134.2, 129.6, 129.2, 128.1, 127.0, 113.3, 44.9, 41.2, 39.8, 21.5, 21.4, 20.2. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_3S$ [(M+Na^+)]: 394.1447, found: 394.1450. $[\alpha]^{27}_D$ = -1.7 (*c* 1.0, $CHCl_3$). 95% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.22 min (minor), 26.41 min (major).

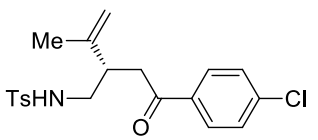




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.76	n.a.	1707.753	698.822	49.82	n.a.	MB*
2	24.16	n.a.	867.780	703.861	50.18	n.a.	BMB*
Total:			2575.533	1402.683	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.22	n.a.	142.314	60.692	2.68	n.a.	M*
2	26.41	n.a.	2010.164	2204.567	97.32	n.a.	BMB*
Total:			2152.478	2265.259	100.00	0.000	

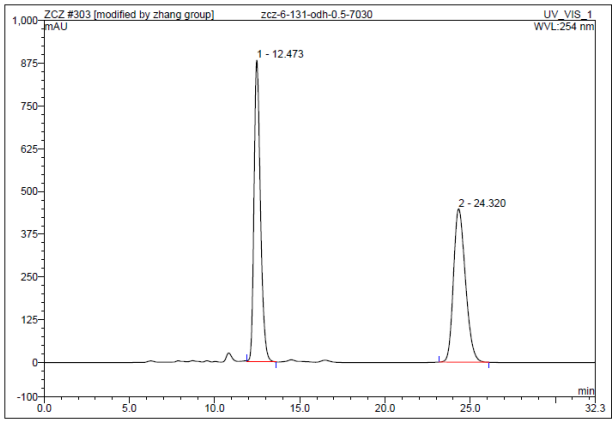
(*S*)-*N*-(2-(2-(4-chlorophenyl)-2-oxoethyl)-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide: 4aq



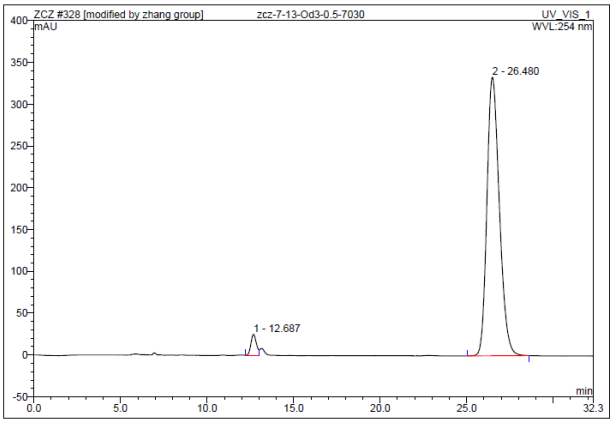
Yellow oil. 62% yield. Conditon B.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.87 (s, 1H), 4.72 (s,

1H), 4.70-4.67 (m, 1H), 3.11-2.97 (m, 4H), 2.91-2.86 (m, 1H), 2.39 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 144.0, 143.4, 139.6, 136.8, 135.0, 129.7, 129.4, 128.9, 127.0, 113.5, 44.8, 41.1, 39.8, 21.4, 20.4. HRMS (ESI) calcd for $C_{20}H_{22}ClNNaO_3S$ [(M+Na$^+$)]: 414.0901, found: 414.0900. $[\alpha]^{28}_D$ = +0.1 (*c* 1.0, $CHCl_3$). 94% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-3 column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 12.69 min (minor), 26.48 min (major).

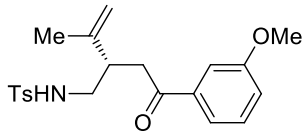


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.47	n.a.	882.191	386.192	51.43	n.a.	MB*
2	24.32	n.a.	448.473	364.651	48.57	n.a.	BMB*
Total:			1330.664	750.843	100.00	0.000	



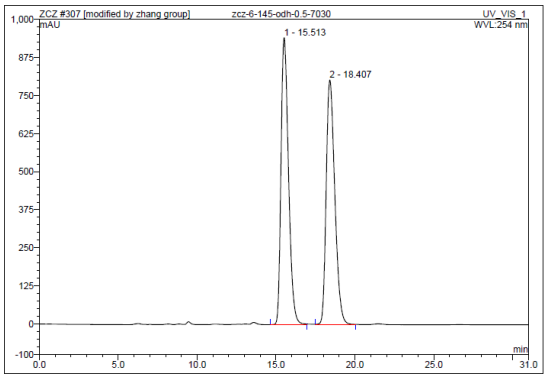
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.69	n.a.	24.922	9.013	3.15	n.a.	BM *
2	26.48	n.a.	333.225	277.309	96.85	n.a.	BMB*
Total:			358.147	286.322	100.00	0.000	

(*S*)-*N*-(2-(2-(3-methoxyphenyl)-2-oxoethyl)-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide: 4ar

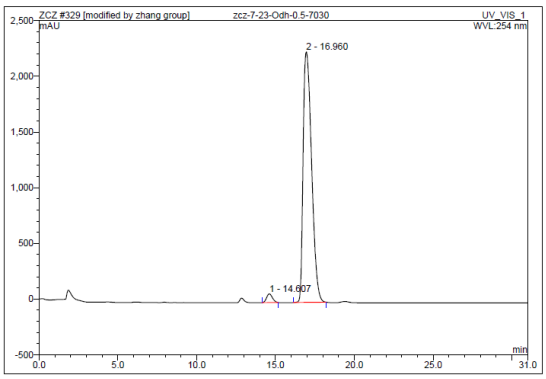


Yellow oil. 83% yield. Conditon B.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.47-7.45 (m, 1H), 7.42-7.41 (m, 1H), 7.36-7.32 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12-7.09 (m, 1H), 4.86 (s, 1H), 4.72 (s, 1H), 4.69 (t, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.12-2.96 (m, 4H), 2.92-2.85 (m, 1H), 2.39 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 159.8, 144.1, 143.3, 138.1, 136.9, 129.65, 129.55, 127.0, 120.6, 119.6, 113.5, 112.3, 55.4, 44.9, 41.3, 40.0, 21.4, 20.2. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_4S$ [(M+Na$^+$)]: 410.1396, found: 410.1403. $[\alpha]^{27}_D$ = -2.0 (*c* 1.0, $CHCl_3$). 95% *ee*. HPLC analysis of the product: Daicel Chiralpak OD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 14.61 min (minor), 16.96 min (major).



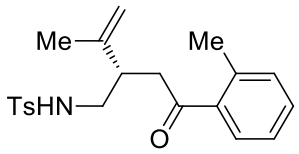
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.51	n.a.	942.462	519.597	50.61	n.a.	BM *
2	18.41	n.a.	802.580	507.068	49.39	n.a.	MB*
Total:			1745.043	1026.665	100.00	0.000	



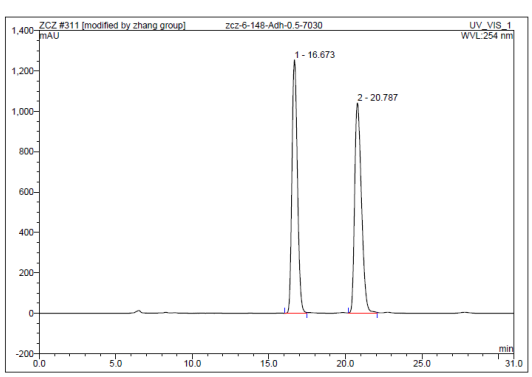
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.61	n.a.	77.513	33.030	2.31	n.a.	BMB*
2	16.96	n.a.	2249.380	1397.780	97.69	n.a.	BMB*
Total:			2326.893	1430.811	100.00	0.000	

(*S*)-4-methyl-*N*-(3-methyl-2-(2-oxo-2-(*o*-tolyl)ethyl)but-3-en-1-yl)benzenesulfonamide: 4as

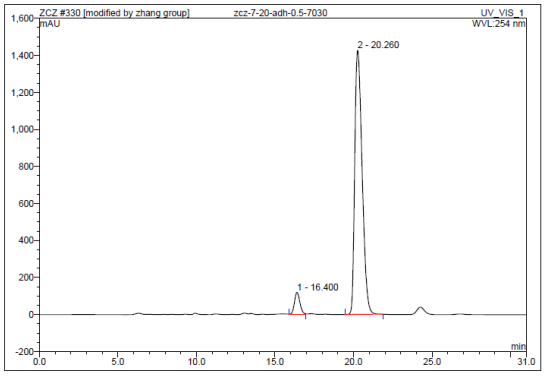
Yellow oil. 55% yield. Conditon B.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.56-7.54 (m, 2H), 7.38-7.34 (m, 1H), 7.28-7.22 (m, 4H), 4.86 (s, 1H), 4.70 (s, 1H), 4.57 (t, *J* = 6.4 Hz, 1H), 3.09-2.95 (m, 4H), 2.88-2.84 (m, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 144.0, 143.4, 138.1, 137.7, 136.9, 131.9, 131.3, 129.7, 128.3, 127.1, 125.7, 113.7, 44.8, 42.8, 41.5, 21.4, 21.1, 20.1. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_3S$ [(M+Na$^+$)]: 394.1447, found: 394.1457. $[\alpha]^{28}_D$ = -3.1 (*c* 1.0, $CHCl_3$). 89% *ee*. HPLC analysis of the product: Daicel Chiralpak AD-H column; hexane/2-propanol = 70/30, 0.5 mL/min. Retention times: 16.40 min (minor), 20.26 min (major).

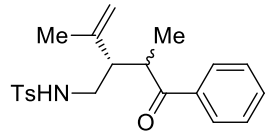


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.67	n.a.	1254.089	519.101	49.21	n.a.	BM *
2	20.79	n.a.	1040.122	535.680	50.79	n.a.	BM *
Total:			2294.211	1054.781	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.40	n.a.	117.486	46.340	5.63	n.a.	BM *
2	20.26	n.a.	1426.399	776.674	94.37	n.a.	BMB*
Total:			1543.885	823.014	100.00	0.000	

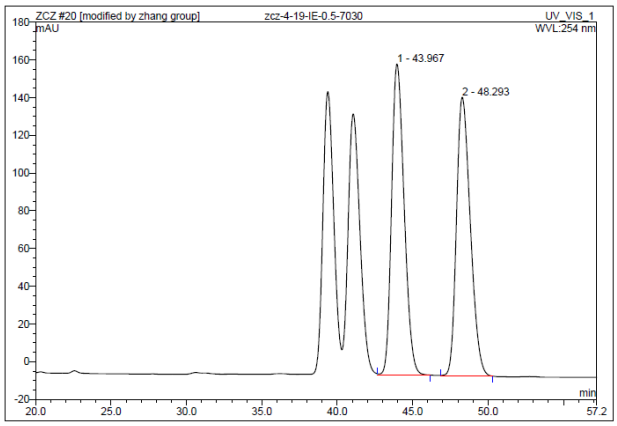
4-methyl-*N*-(3-methyl-2-(1-oxo-1-phenylpropan-2-yl)but-3-en-1-yl)benzenesulfonamide: 4at



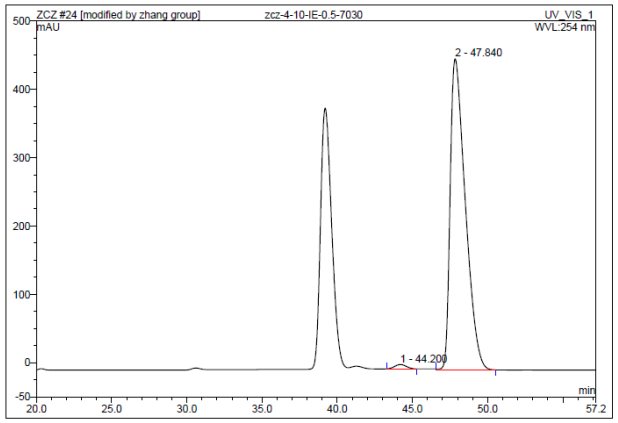
Colorless oil. 84% yield. *d.r.* = 1.5:1. (*Z*)-**2t** was used. Conditon A (10 mol% $AgClO_4$ was used) (The diastereomers can not be separated by chromatography). ^{1}H NMR (the major product, 500 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.80 (s, 1H), 4.66 (s, 1H), 4.61 (s, 1H), 3.76-3.70 (m, 1H), 3.10 (t, *J* = 6.0 Hz, 2H), 2.64-2.60 (m, 1H), 2.42 (s, 3H), 1.57 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (the major product, 125 MHz, $CDCl_3$): δ 203.1, 144.0, 141.8, 136.6, 136.1, 133.1, 129.7, 128.7, 128.1, 127.0, 113.9, 46.9, 41.5, 40.4, 21.6, 21.4, 15.2; ^{1}H NMR (the minor product, 500 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.59-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.98 (s, 1H), 4.80 (s, 1H), 4.50 (s, 1H), 3.46-3.40 (m, 1H), 2.97-2.92 (m, 1H), 2.84-2.78 (m, 1H), 2.72-2.67 (m, 1H), 2.39 (s, 3H), 1.59 (s, 3H), 1.05 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (the minor product, 125 MHz, $CDCl_3$): δ 202.6, 143.4, 143.2, 136.7, 136.4, 133.2, 129.5, 128.7, 128.2, 127.0, 116.7, 49.0, 43.4, 40.7, 21.4, 18.4, 16.7. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_3S$ [(M+H$^+$)]: 394.1448, found: 394.1447. $[\alpha]^{27}_D$ = -15.0 (*c* 1.0, $CHCl_3$).

HPLC analysis of the product: Daicel Chiralpak IE column; hexane/2-propanol = 70/30, 0.5 mL/min.

The major product: 98% *ee*: Retention times: 44.20 min (minor), 47.84 min (major);

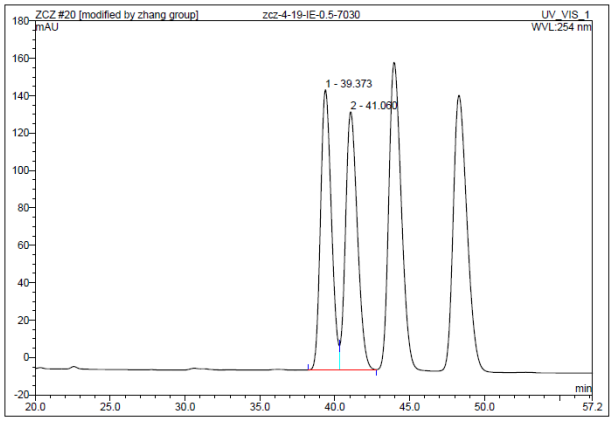


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	43.97	n.a.	164.896	159.500	50.22	n.a.	MB*
2	48.29	n.a.	147.916	158.122	49.78	n.a.	MB*
Total:			312.812	317.622	100.00	0.000	

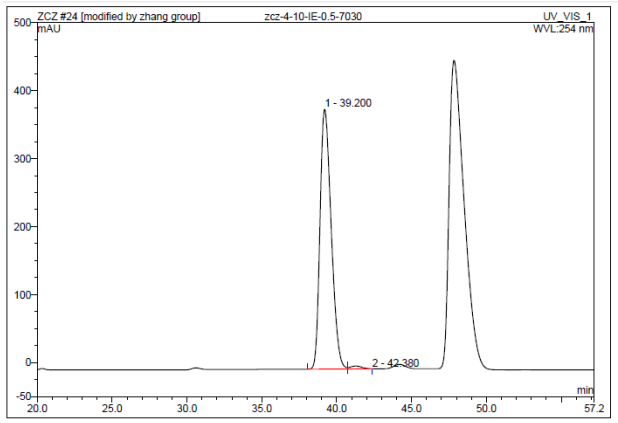


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.20	n.a.	6.303	5.561	1.04	n.a.	BMB*
2	47.84	n.a.	455.122	530.578	98.96	n.a.	MB*
Total:			461.425	536.139	100.00	0.000	

The minor product: 98% *ee*: Retention times: 39.20 min (major), 42.38 min (minor).



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	39.37	n.a.	149.786	125.061	49.72	n.a.	BM *
2	41.06	n.a.	138.020	126.474	50.28	n.a.	M *
Total:			287.806	251.535	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	39.20	n.a.	382.052	330.135	98.88	n.a.	BM *
2	42.38	n.a.	0.000	3.728	1.12	n.a.	MB*
Total:			382.052	333.863	100.00	0.000	

4. References:

[1] Wender, P. A.; Williams, T. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4550.

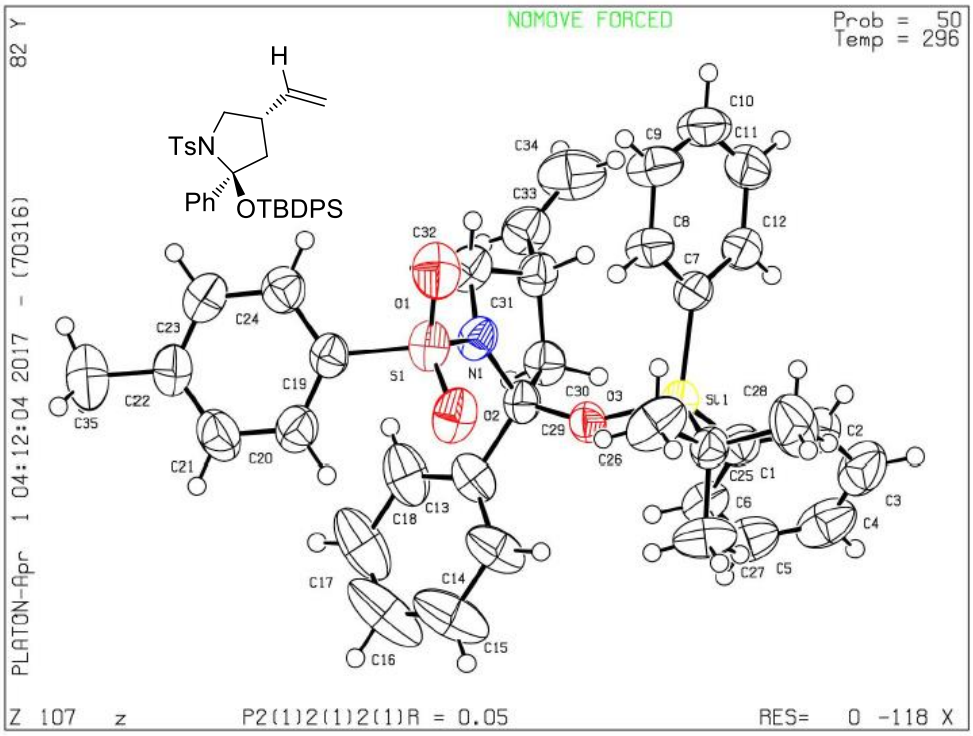
[2] Wender, P. A.; Lesser, A. B.; Sirois, L. E. *Angew. Chem. Int. Ed.* **2012**, *51*, 2736.

[3] Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem*. **2006**, *71*, 91.

[4] a) Feng, J.-J.; Lin, T.-Y.; Zhu, C.-Z.; Wang, H.; Wu, H.-H.; Zhang, J. *J. Am. Chem. Soc.* **2016**, *138*, 2178. b) Zuo, G.; Zhang, K.; Louie, J. *Tetrahedron Lett*. **2008**, *49*, 6797. c) Brichacek, M.; Lee, D.; Njardarson, J. T. *Org. Lett*. **2008**, *10*, 5023. d) Lam, S. K.; Lam, S.; Wong, W.-T.; Chiu, P. *Chem. Comm*. **2014**, *50*, 1738.

[5] a) Xu, H.; Qu, J.-P.; Liao, S.; Hu, X.; Tang, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 4004.; b) Zhao, J.-F.; Tan, B.-H.; Loh, T.-P. *Chem. Sci.* **2011**, *2*, 349. c) Ventura, D. L.; Li, Z.; Coleman, M. G.; Davies, Huw M.L. *Tetrahedron*, **2009**, *65*, 3052. d) Eames, J; Coumbarides, G. S.; Suggate, M. J.; Weerasooriya, N. *Eur. J. Org. Chem.* **2003**, *2003*, 634. e) Ren, X.; Li, G.; Wei, S.; Du, H. *Organic Letters*, **2015**, *17*, 990.

5. Crystal Structure of (*S*,*S*)-3ba



Datablock: z

Bond precision: C-C = 0.0055 A Wavelength=0.71073

Cell: a=8.4929(13) b=9.8371(16) c=39.949(6)
alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	3337.6(9)	3337.6(9)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C35 H39 N O3 S Si	?
Sum formula	C35 H39 N O3 S Si	C35 H39 N O3 S Si
Mr	581.82	581.82
Dx,g cm-3	1.158	1.158
Z	4	4
Mu (mm-1)	0.166	0.166
F000	1240.0	1240.0
F000'	1241.28	
h,k,lmax	10,11,47	10,11,47
Nref	5894[3383]	5892
Tmin,Tmax	0.938,0.958	0.924,0.958
Tmin'	0.923	

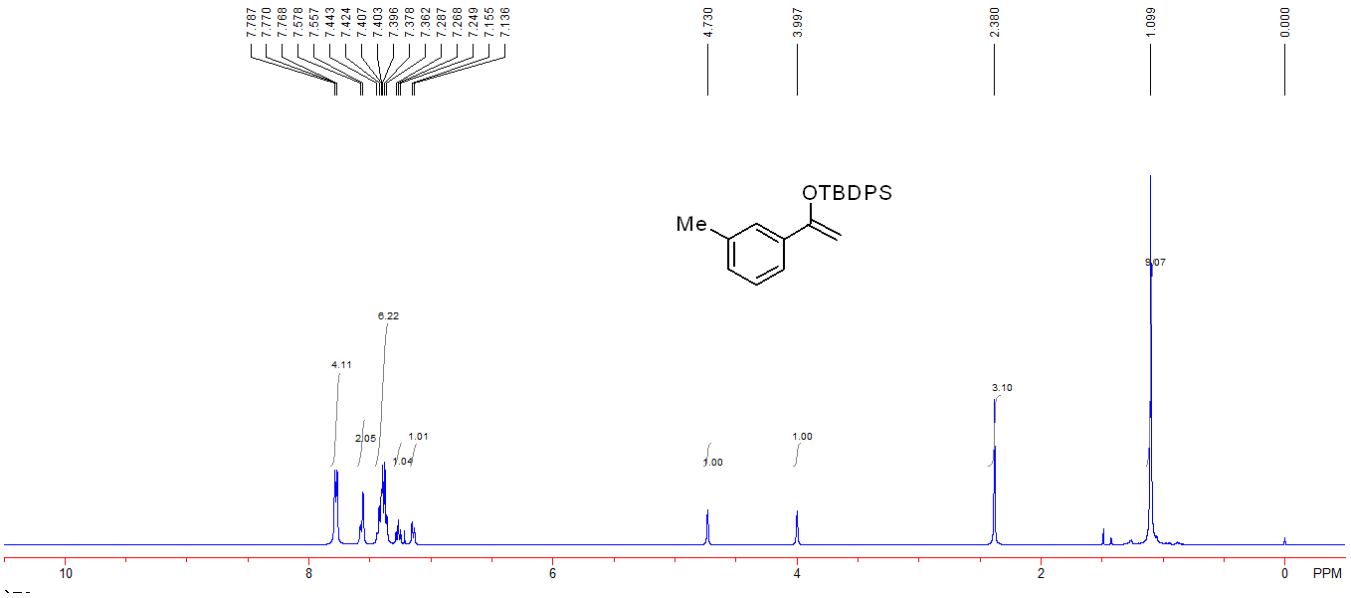
Correction method= # Reported T Limits: Tmin=0.924 Tmax=0.958
AbsCorr = MULTI-SCAN

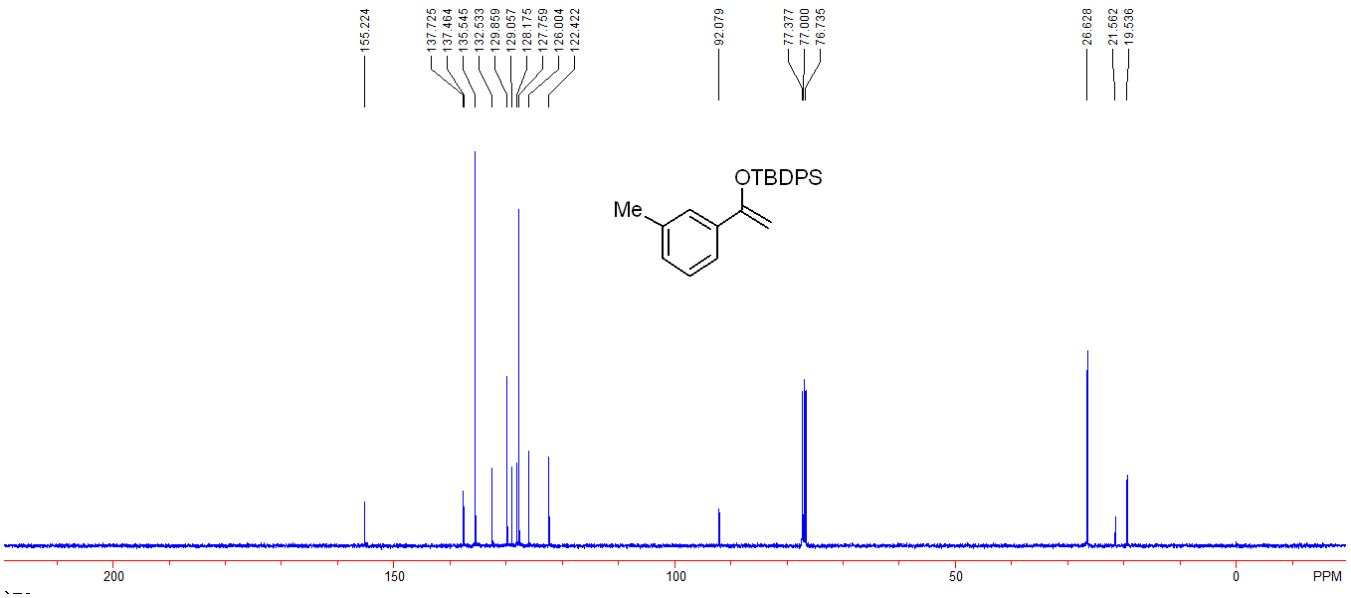
Data completeness= 1.74/1.00 Theta(max)= 25.010

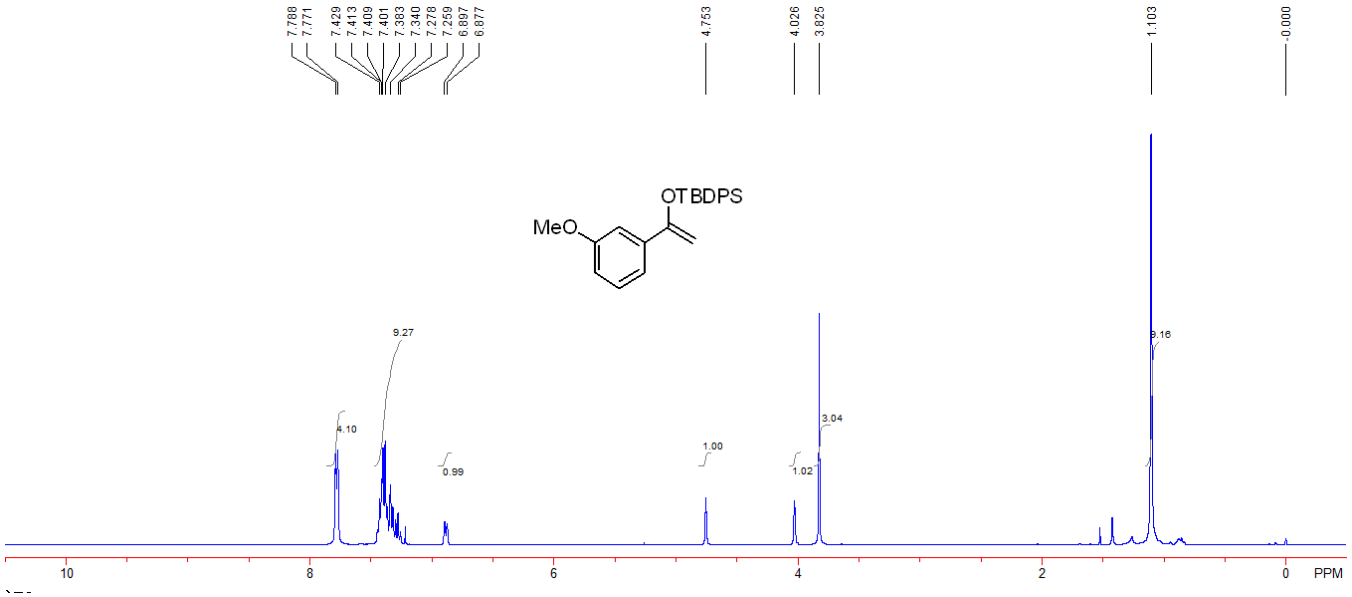
R(reflections)= 0.0470(4014) wR2(reflections)= 0.1086(5892)

S = 1.014 Npar= 370

6. ^{1}H and ^{13}C NMR Spectra for New Compounds



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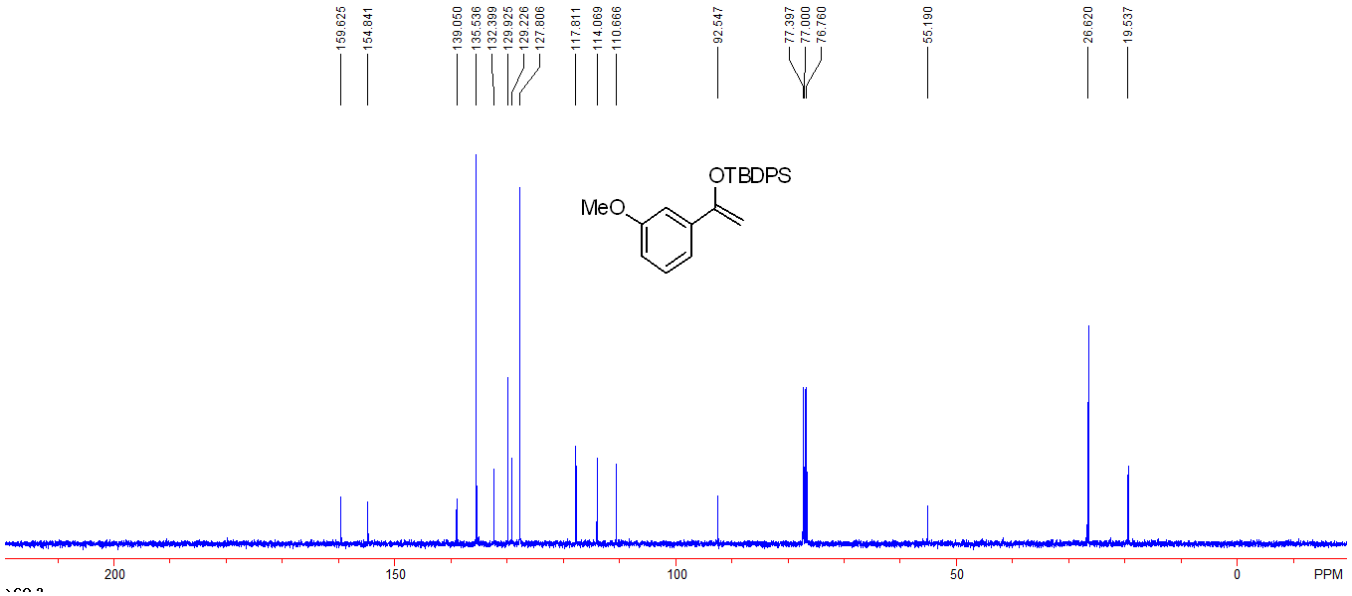
7.413
7.409
7.401
7.383
7.340
7.278
7.259
6.897
6.877
4.753
4.026
3.825
1.103
0.000
OTBDPS
MeO
9.27
4.10
0.99
1.00
1.02
3.04
9.16
10
8
6
4
2
0
PPM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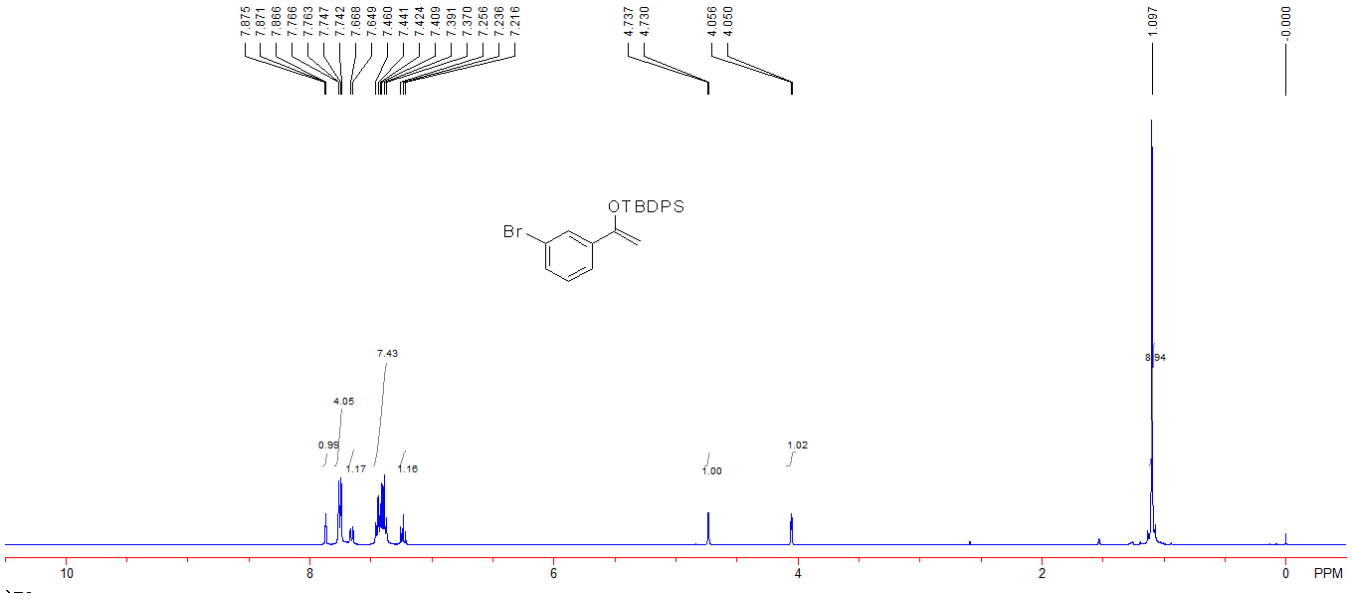
154.841
139.050
135.536
132.399
129.925
129.226
127.806
117.811
114.069
110.666
92.547
77.397
77.000
76.760
55.190
26.620
19.537
OTBDPS
MeO
200
150
100
50
0
PPM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7.747
7.742
7.668
7.649
7.460
7.441
7.424
7.409
7.391
7.370
7.256
7.236
7.216
4.737
4.730
4.056
4.050
1.097
0.000
OTBDPS
Br
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10
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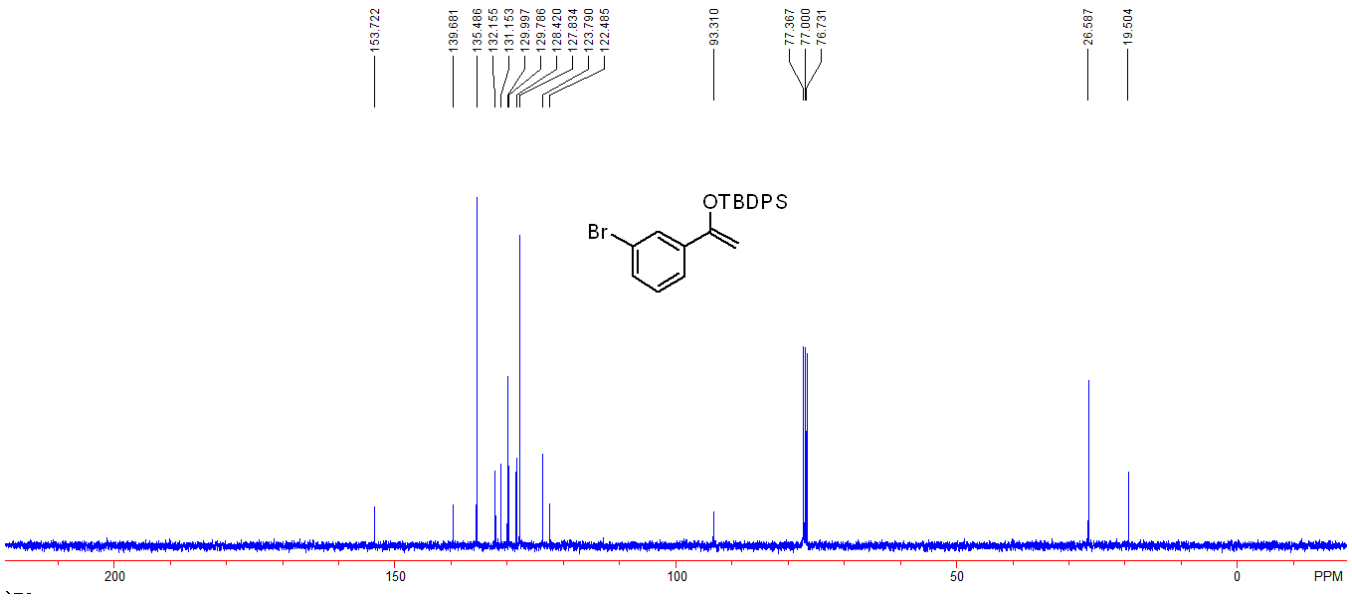
PPM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128.420
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123.790
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77.000
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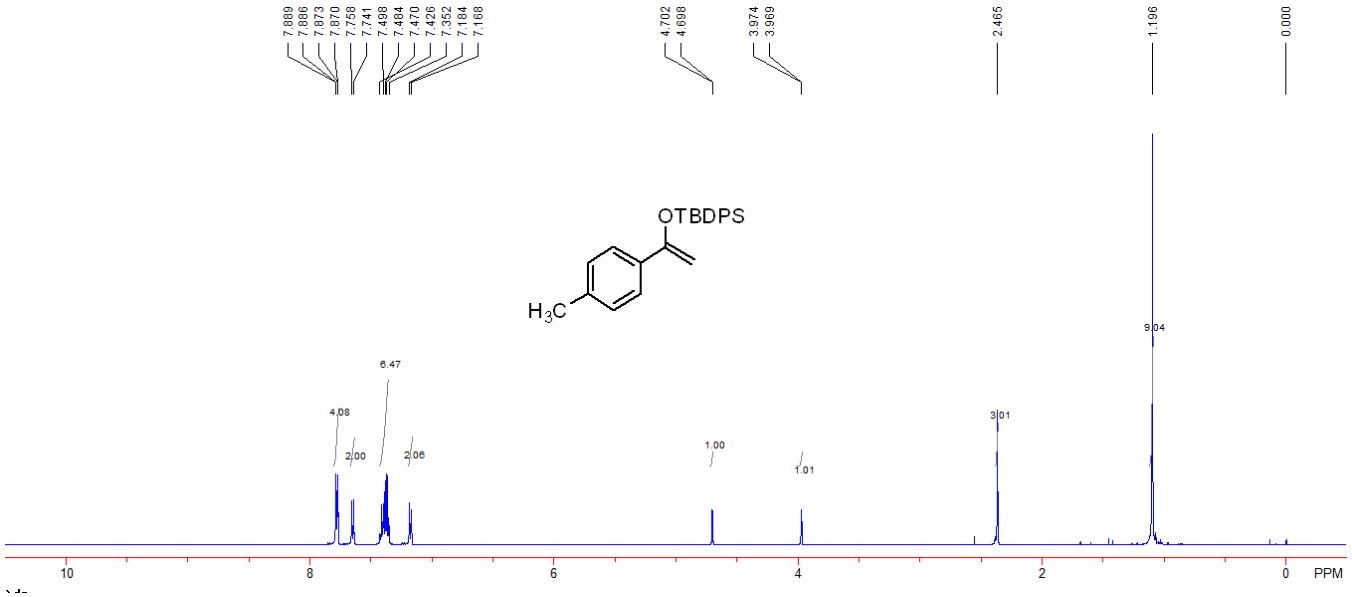
Br
200
150
100
50
0
PPM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7.873
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7.484
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7.426
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7.168
4.702
4.698
3.974
3.969
2.465
1.196
0.000
OTBDPS
H3C
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2.06
1.00
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10
8
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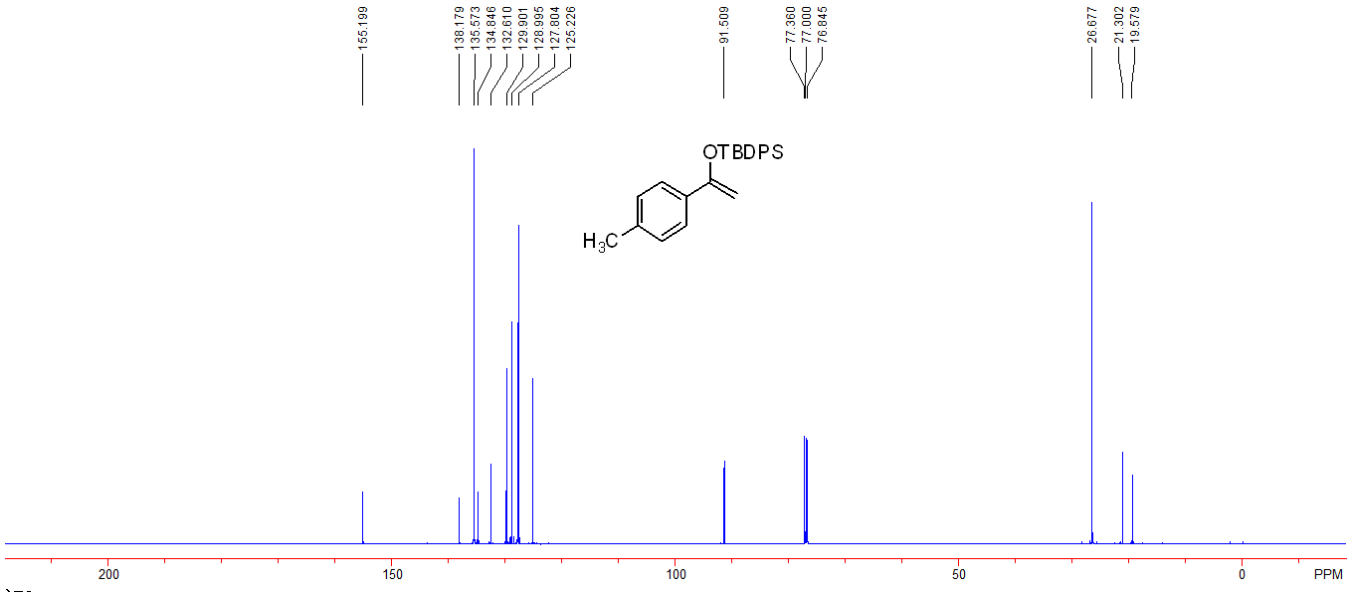
PPM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132.610
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127.804
125.226
91.509
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26.677
21.302
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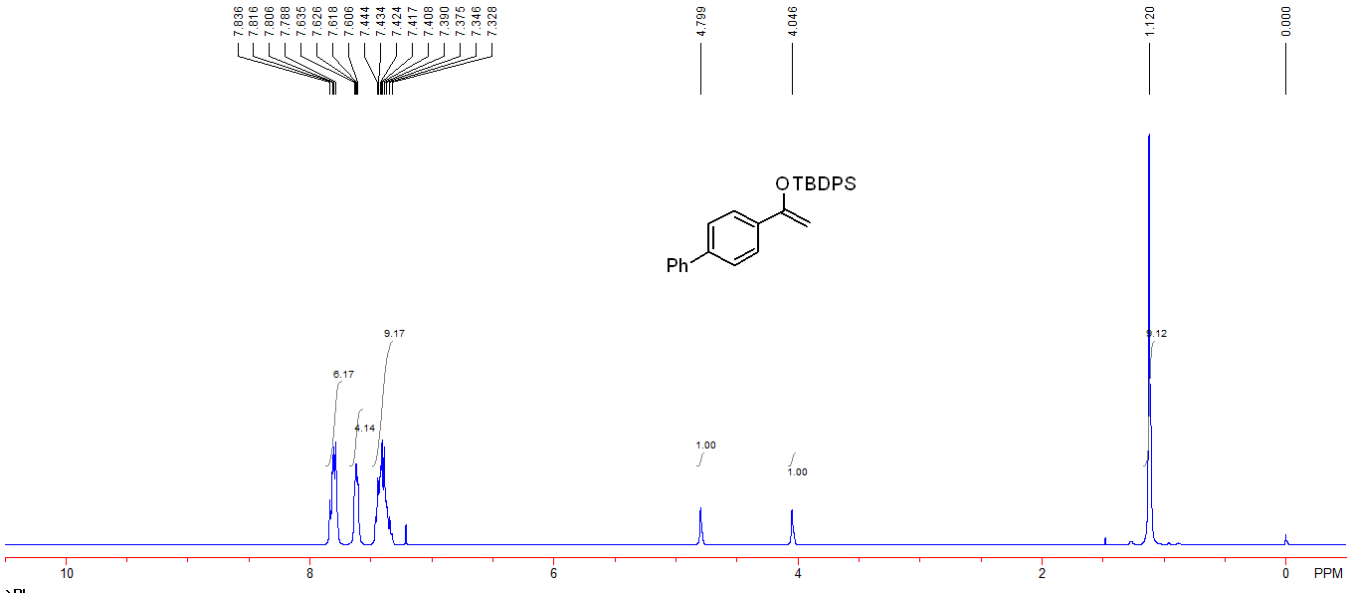
H3C
200
150
100
50
0
PPM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7.417
7.408
7.390
7.375
7.346
7.328
4.799
4.046
1.120
0.000
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10
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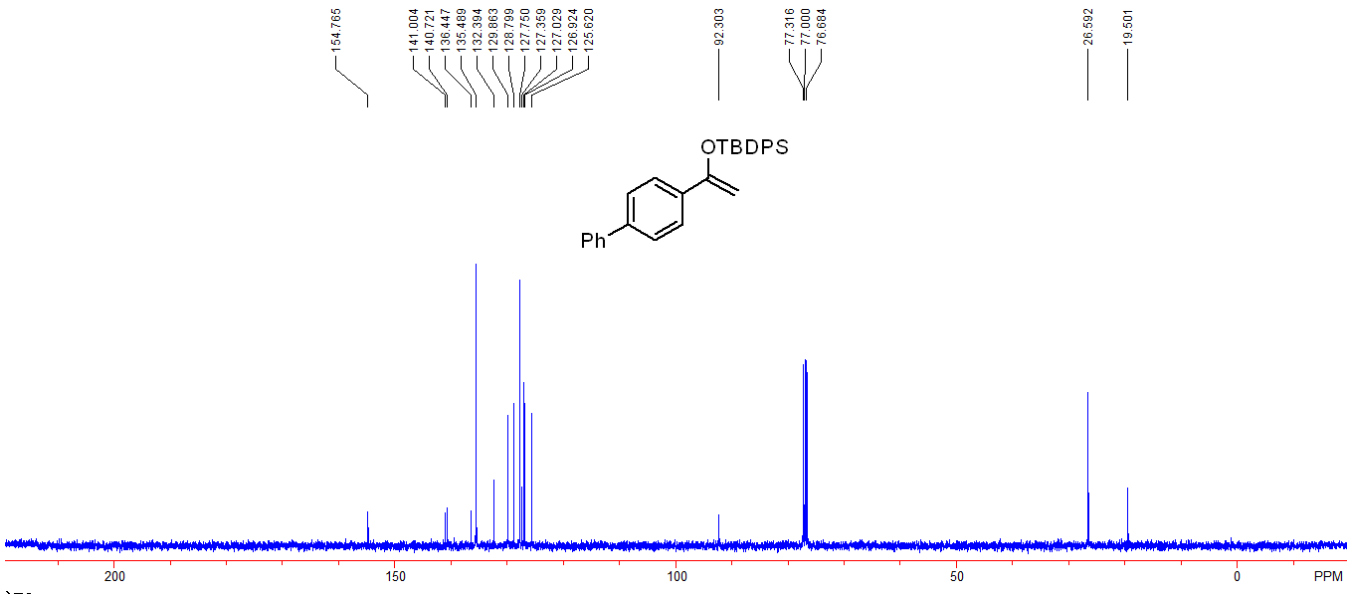
PPM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126.924
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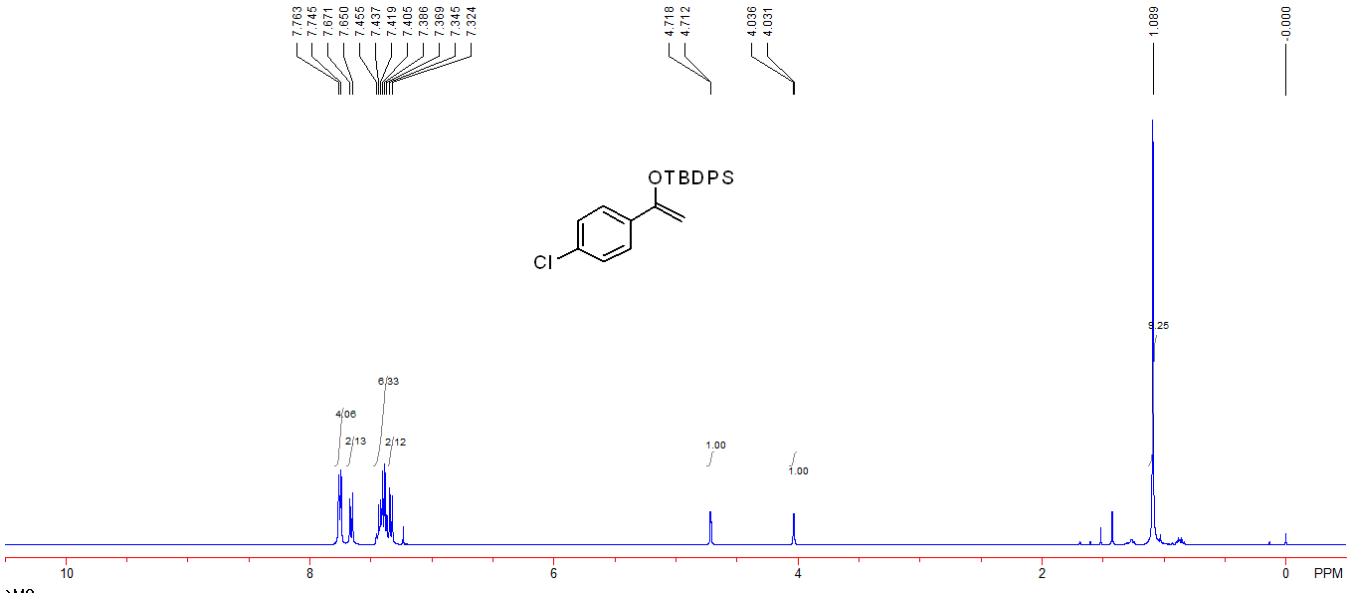
Ph
200
150
100
50
0
PPM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7.405
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7.324
4.718
4.712
4.036
4.031
1.089
0.000
OTBDPS
Cl
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2.13
2.12
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1.00
10
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6
4
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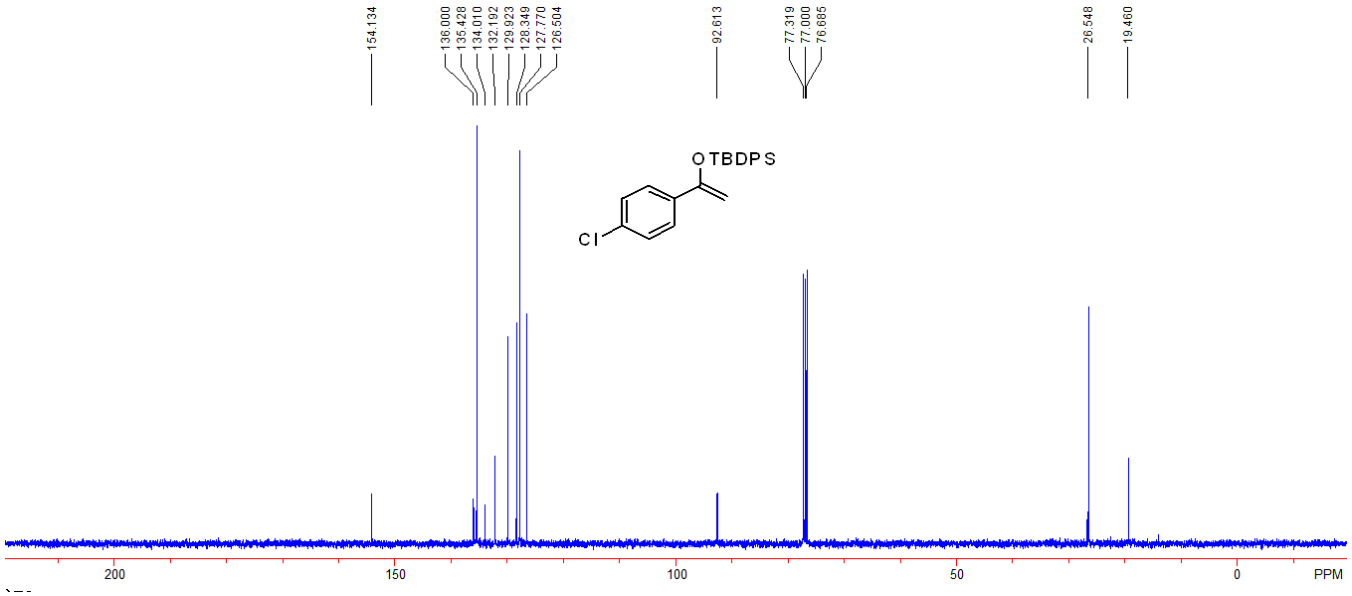
PPM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129.923
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77.000
76.685
26.548
19.460
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Cl
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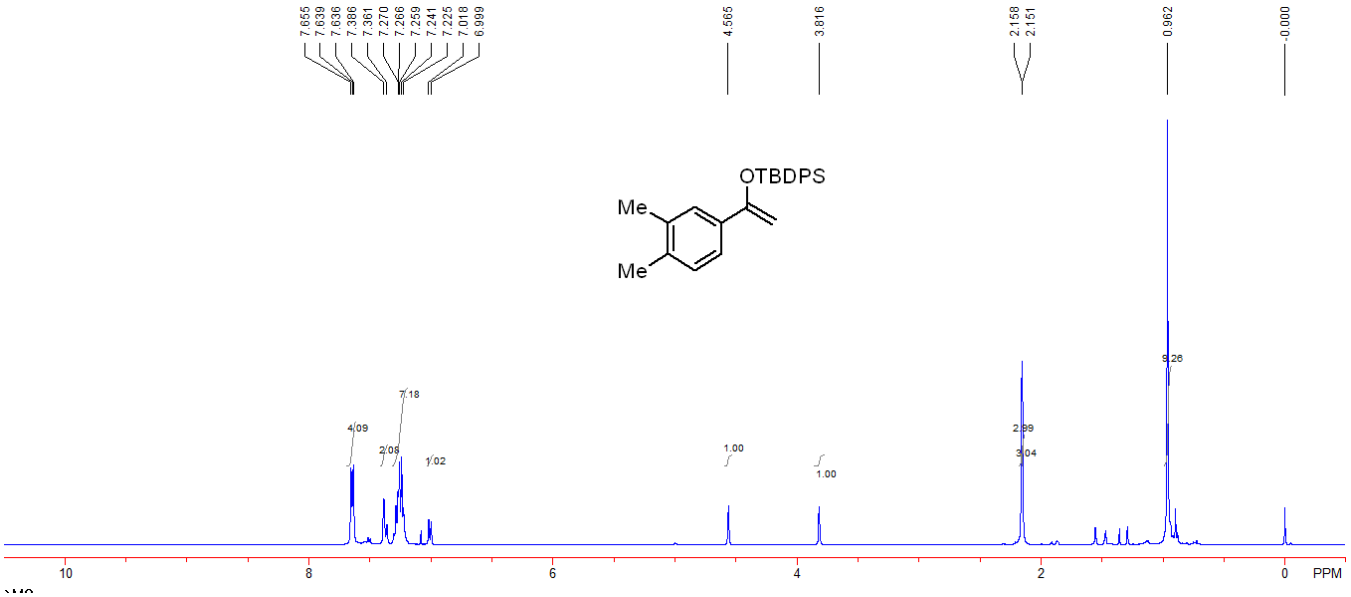
100
50
0
PPM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7.259
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7.225
7.018
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4.565
3.816
2.158
2.151
0.962
0.000
OTBDPS
Me
Me
4.09
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1.00
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10
8
6
4
2
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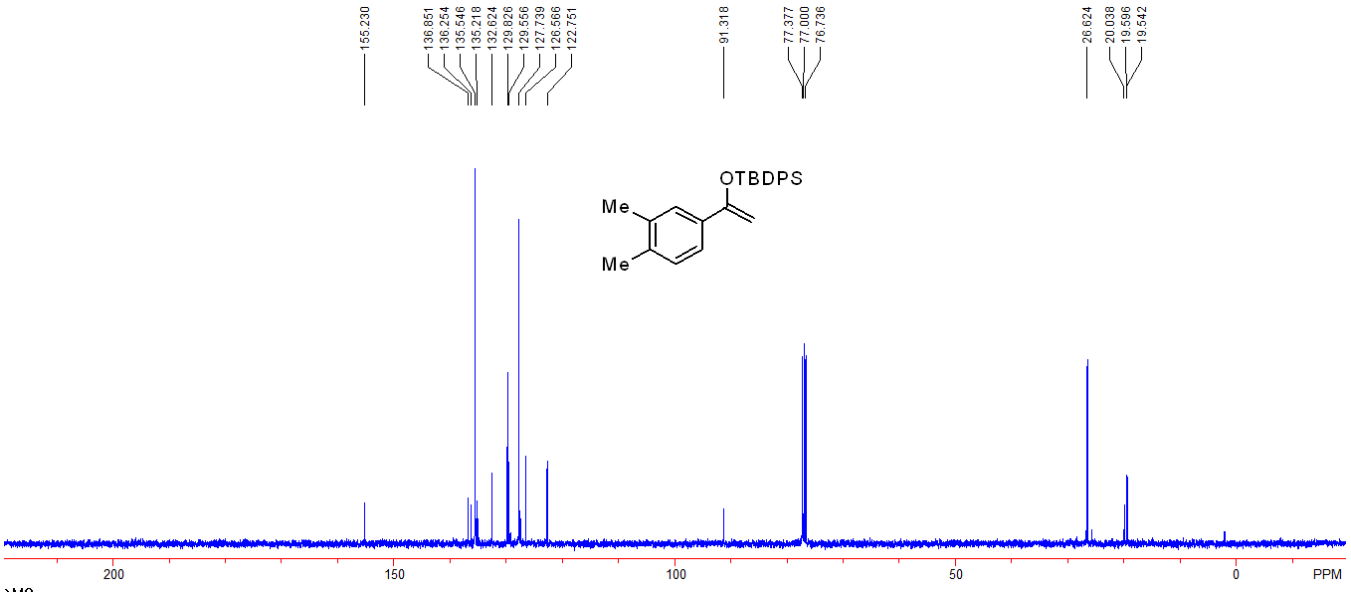
PPM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Me
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150
100
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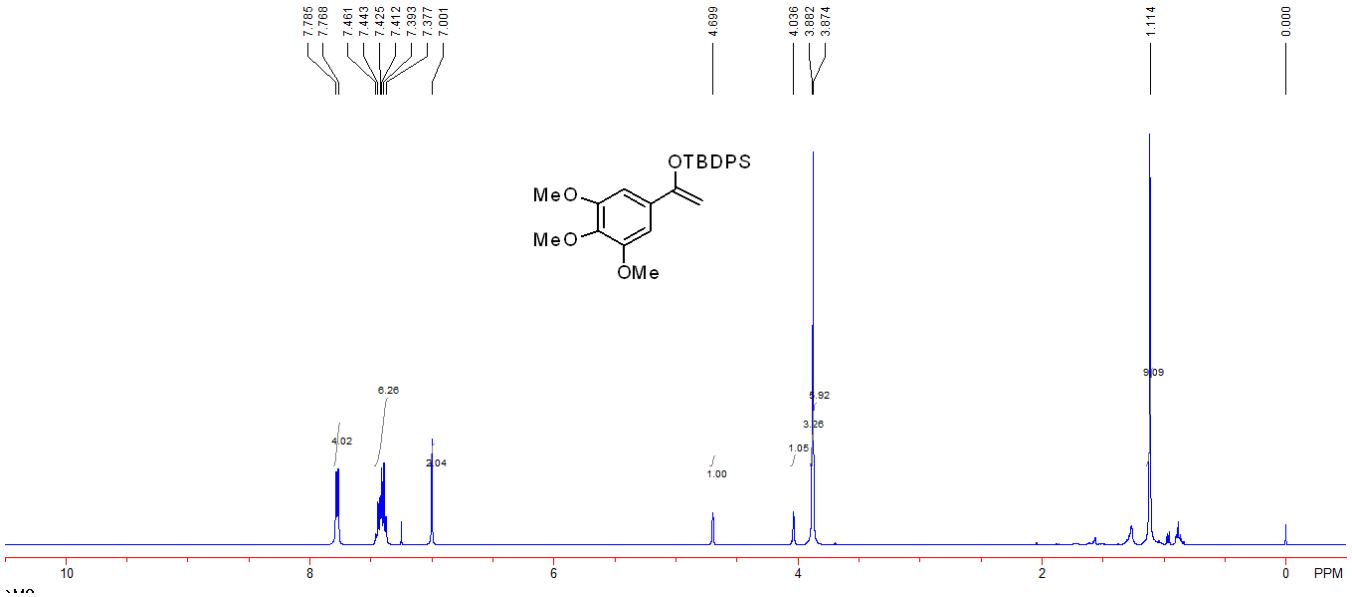
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3.874
1.114
0.000
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MeO
MeO
OMe
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1.00
1.05
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10
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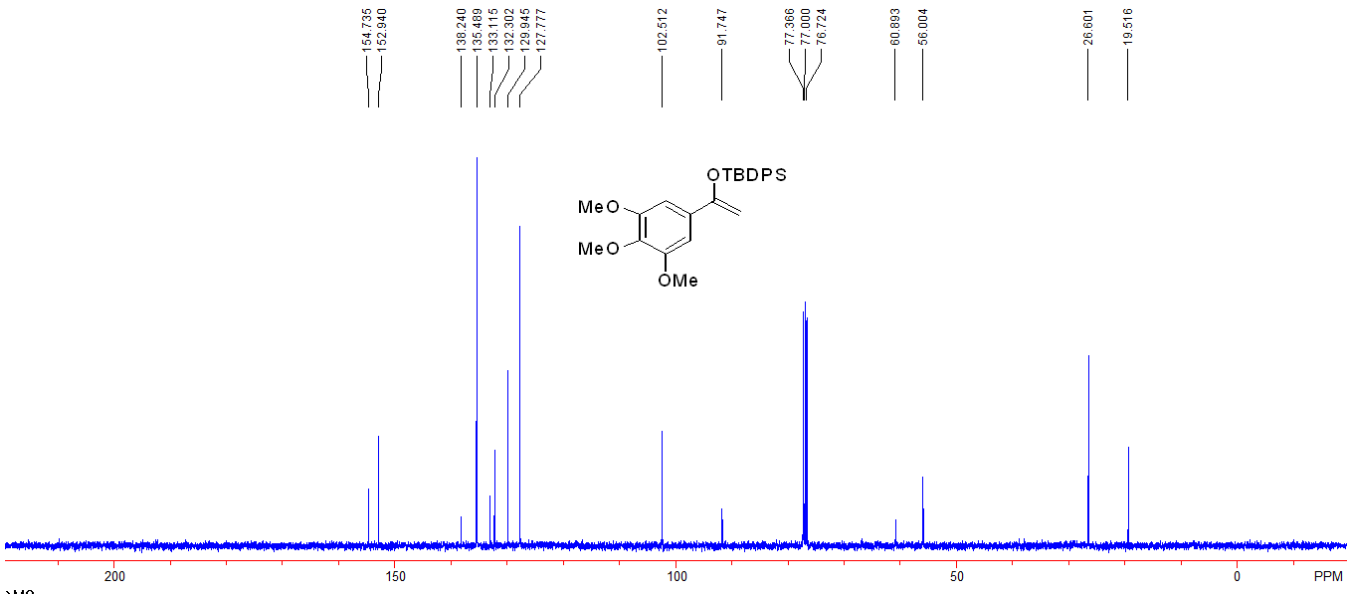
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26.601
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MeO
OMe
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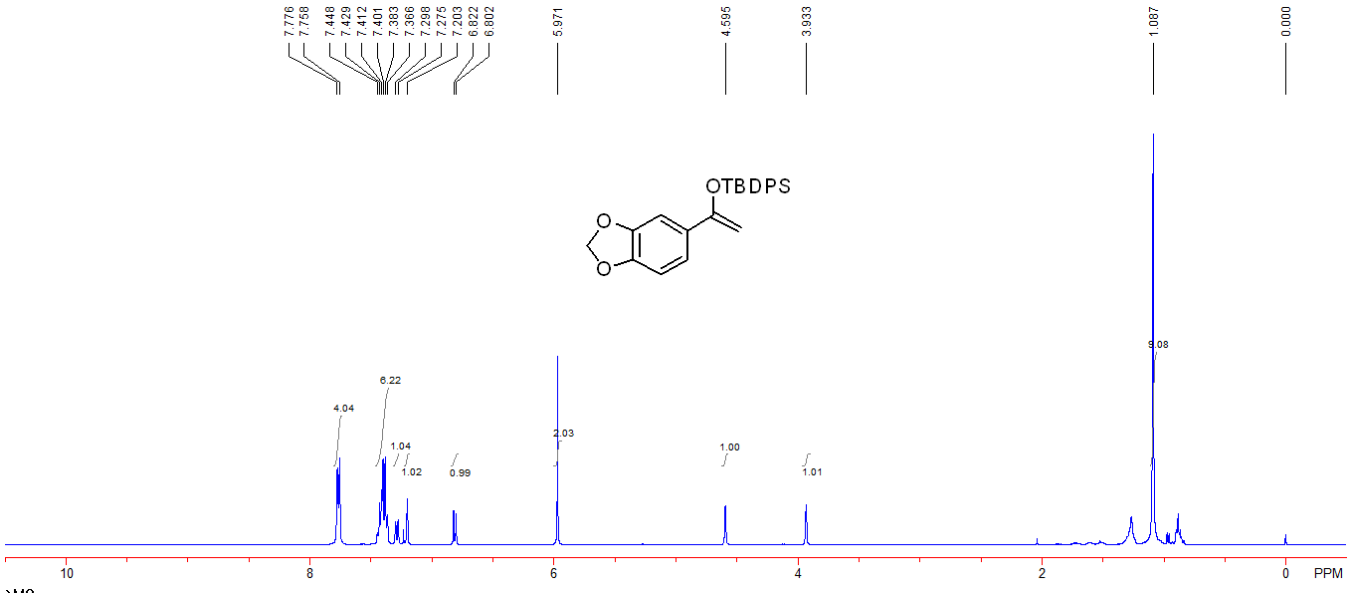
PPM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6.802
5.971
4.595
3.933
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OTBDPS
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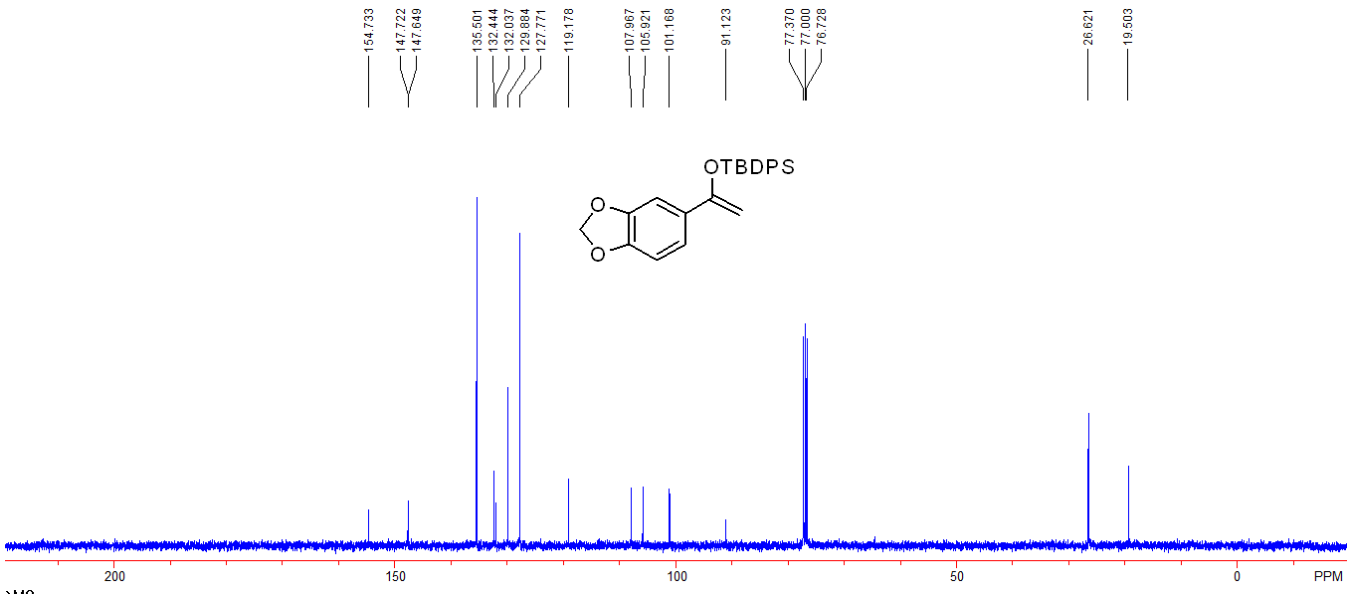
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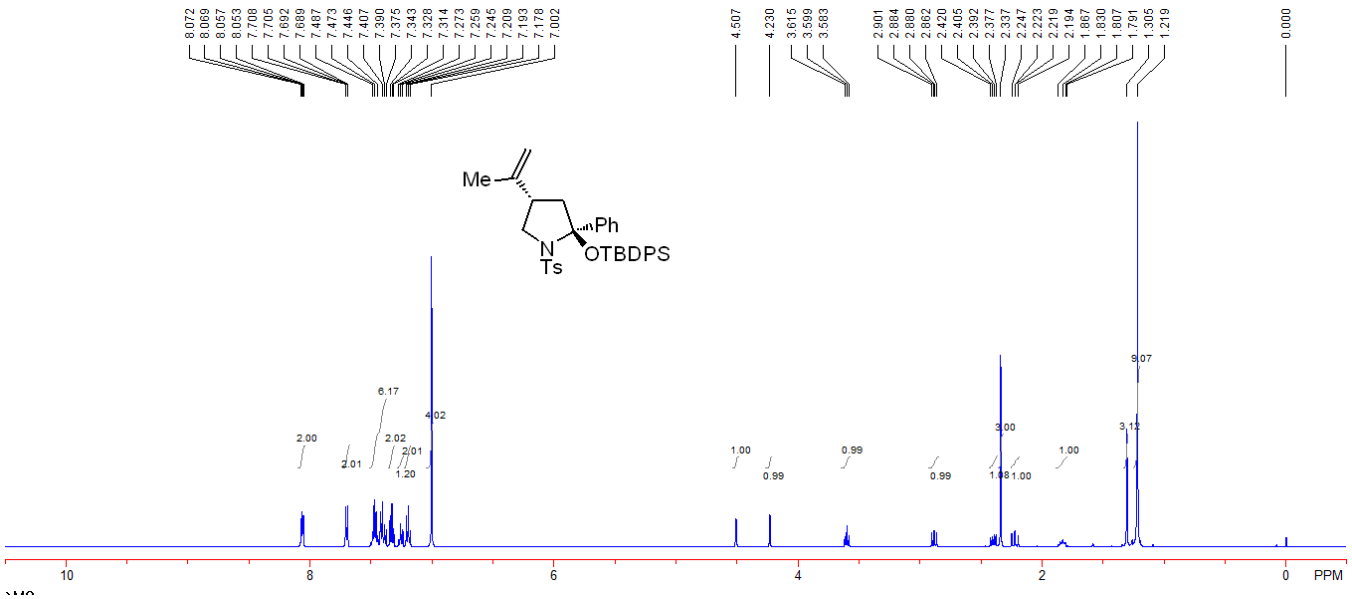
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1.791
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Me
Ph
N
Ts
OTBDPS
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2.02
2.01
1.20
4.02
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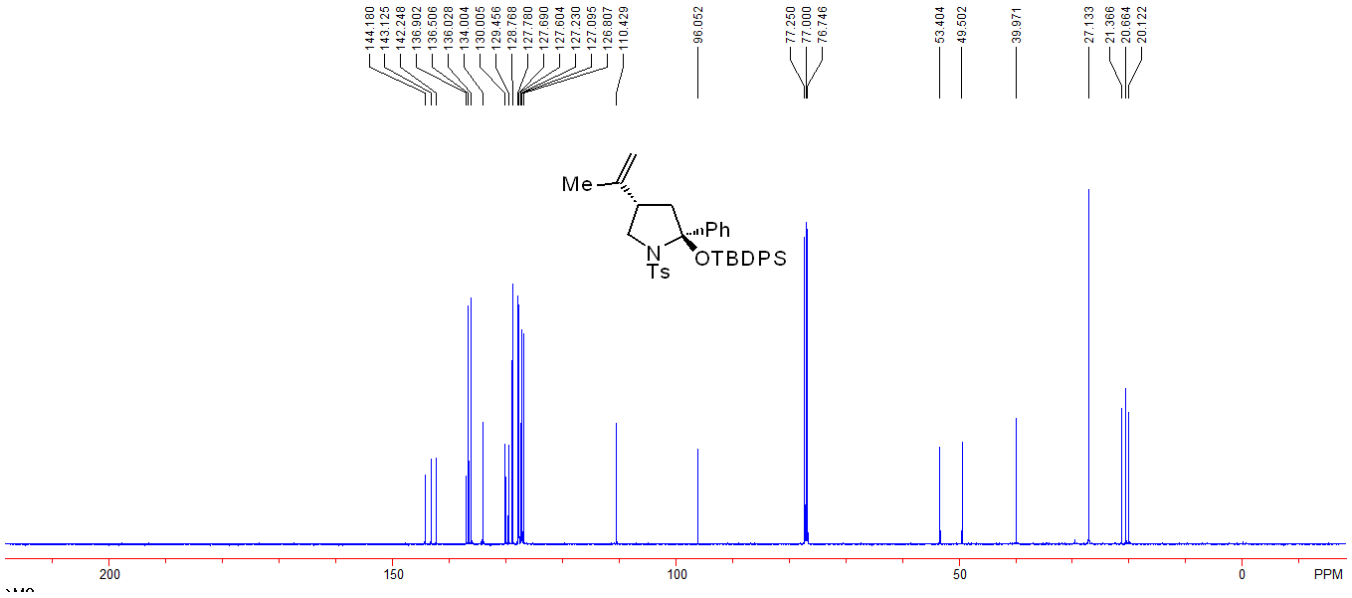
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127.095
126.807
110.429
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77.250
77.000
76.746
53.404
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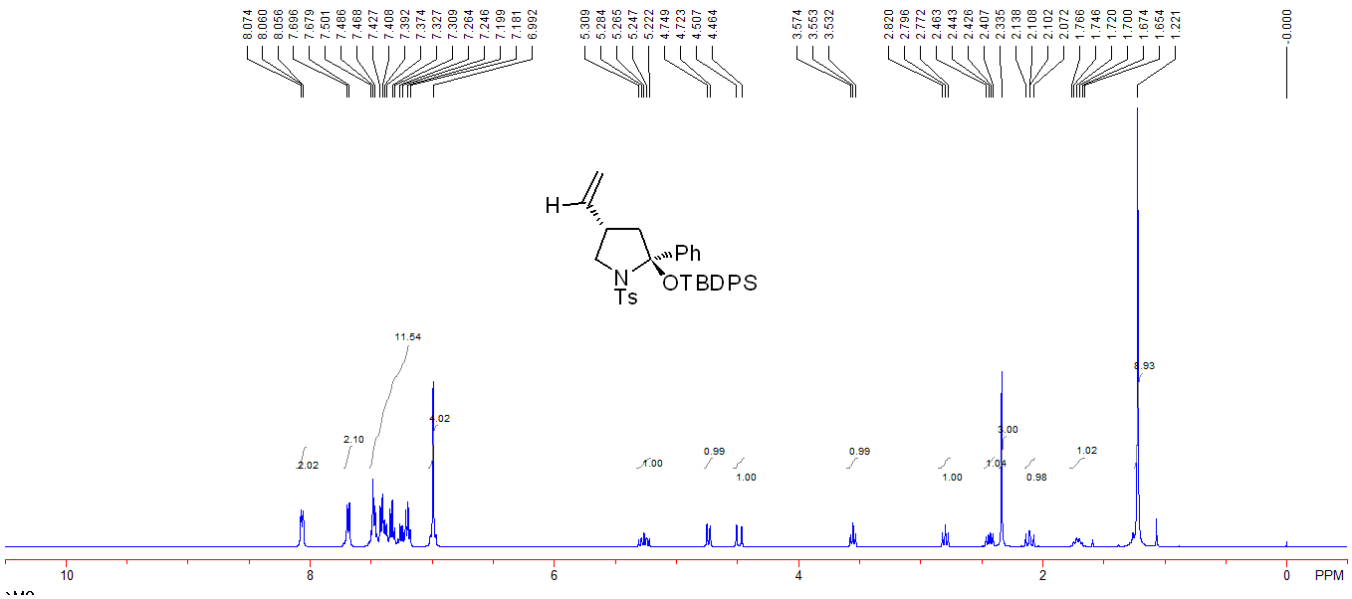
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4.723
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2.102
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1.746
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0.000
H
Ph
N
Ts
OTBDPS
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4.02
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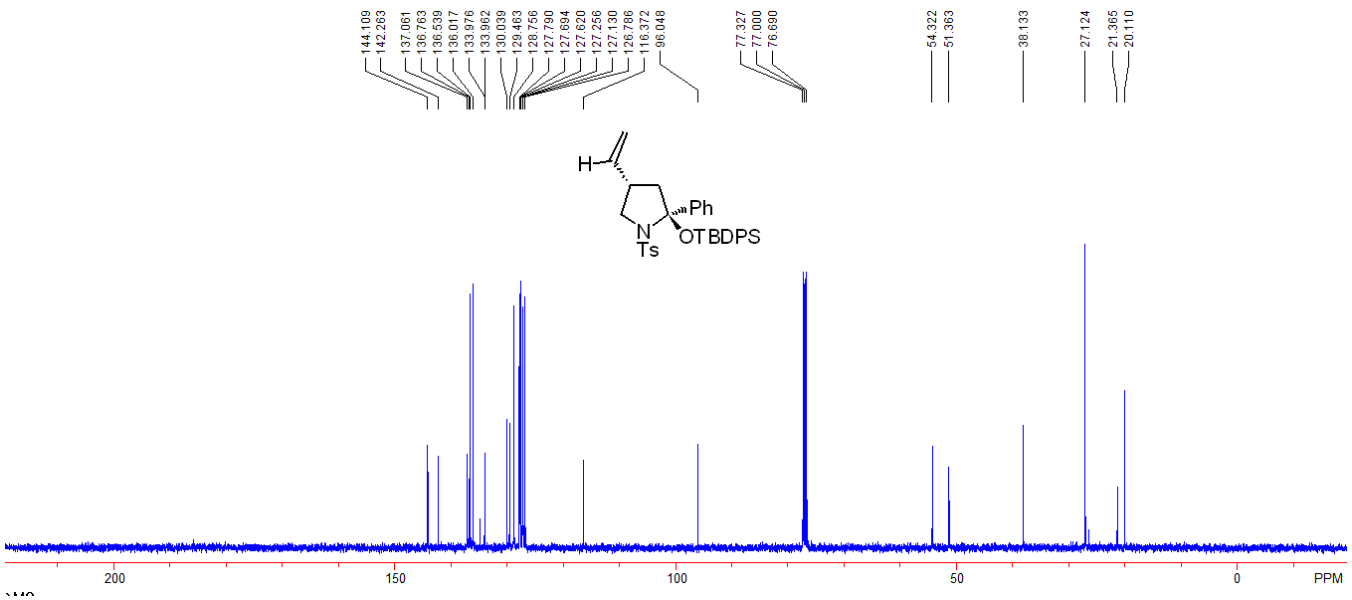
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96.048
77.327
77.000
76.690
54.322
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H
Ph
N
Ts
OTBDPS
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150
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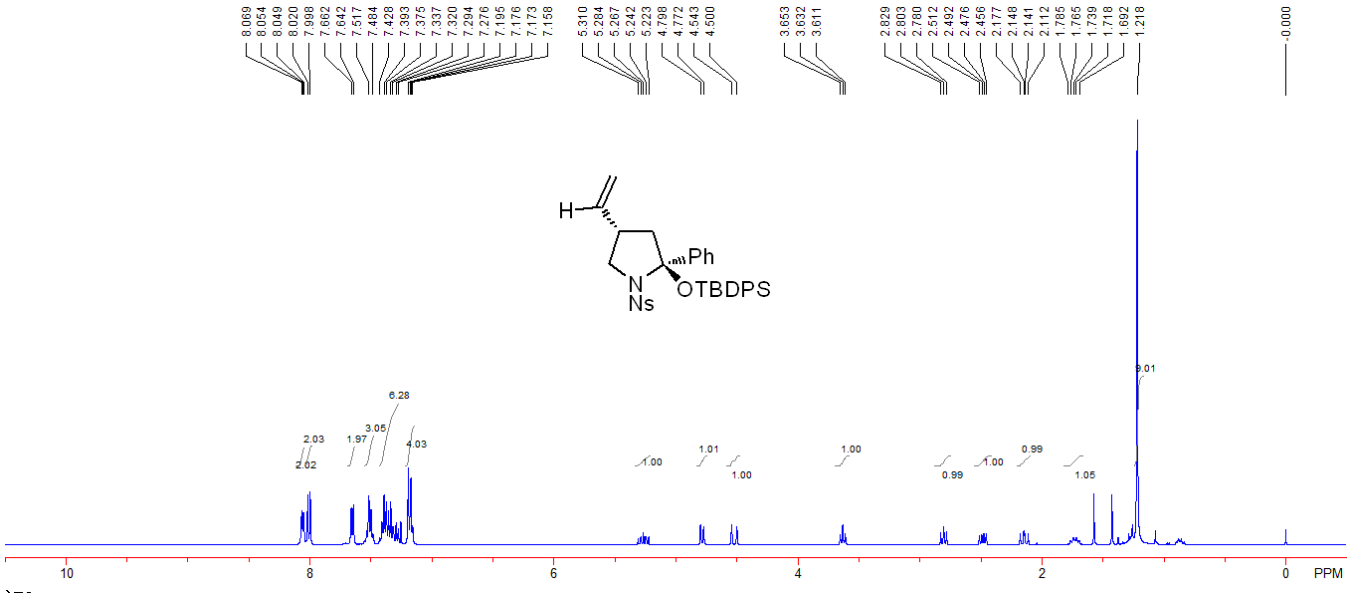
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5.267
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5.223
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Ph
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Ns
OTBDPS
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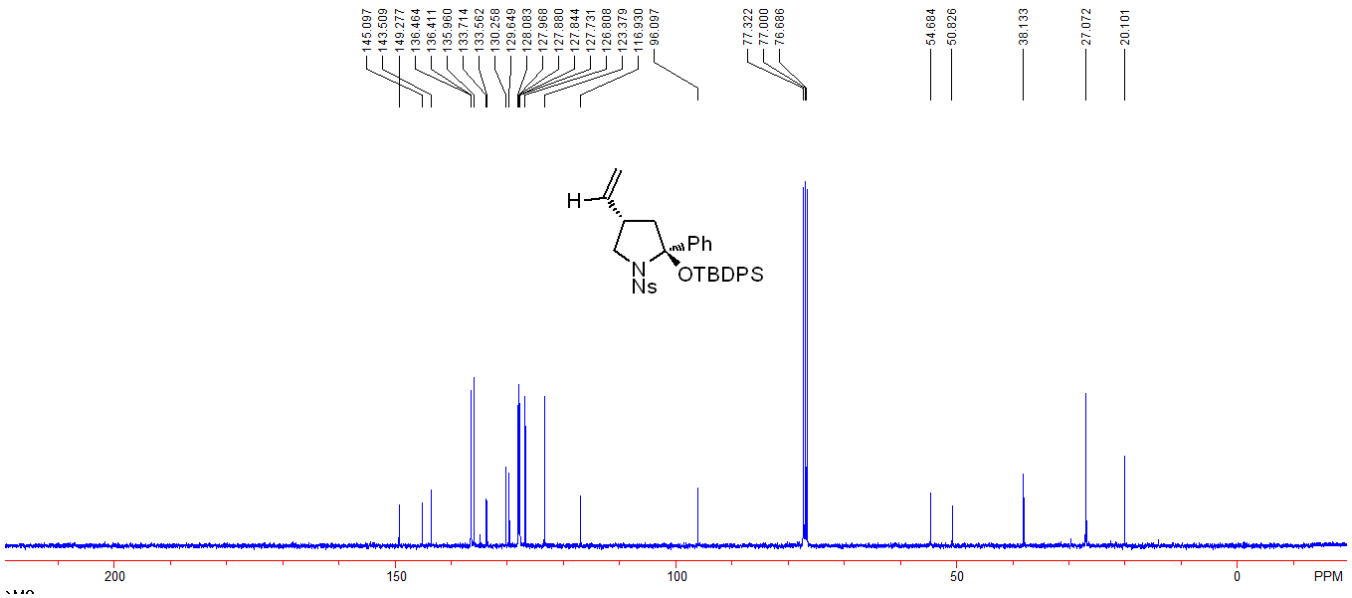
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126.808
123.379
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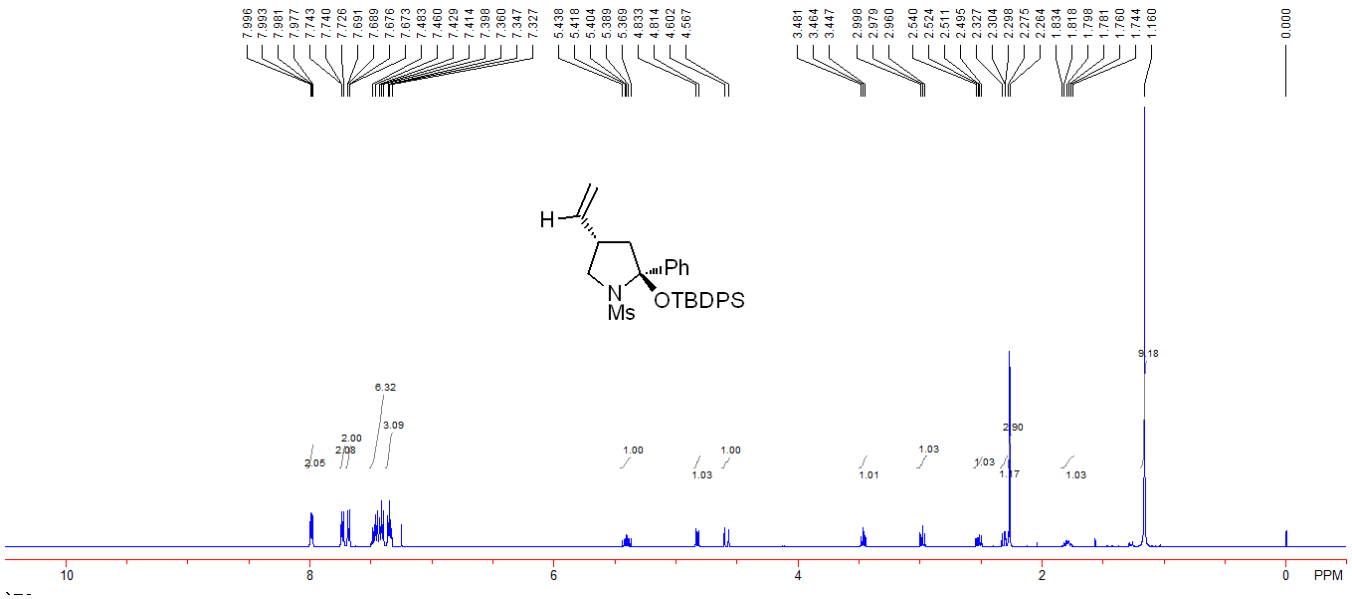
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4.833
4.814
4.602
4.567
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3.464
3.447
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Ph
N
Ms
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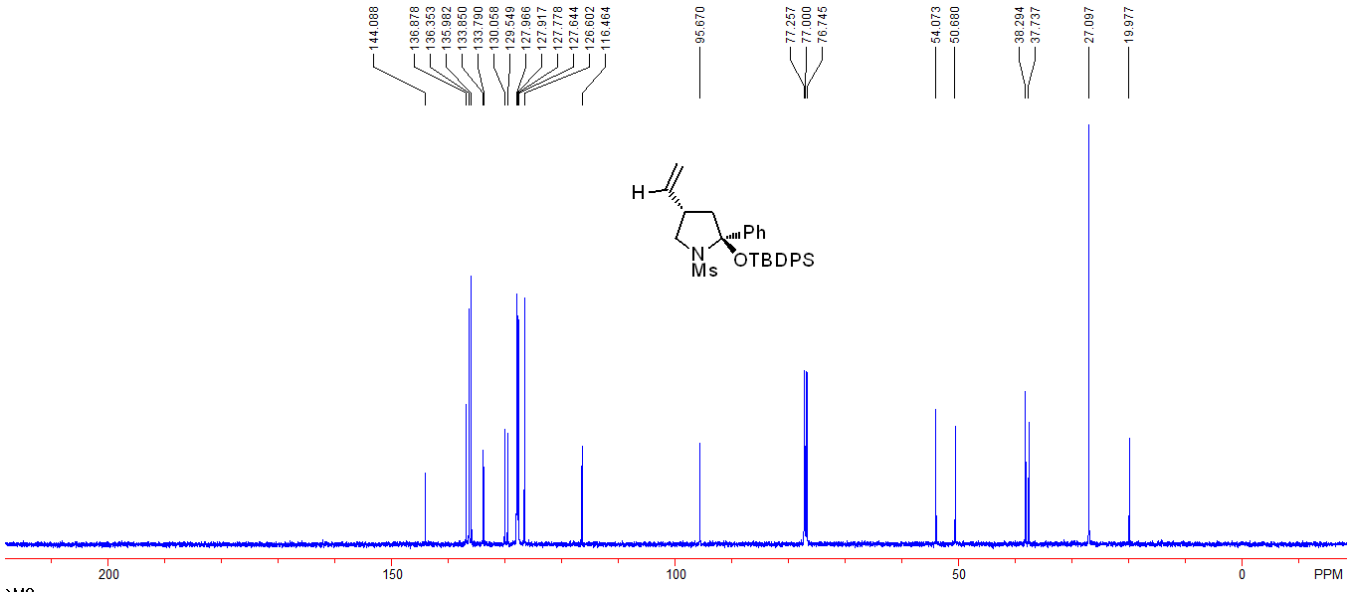
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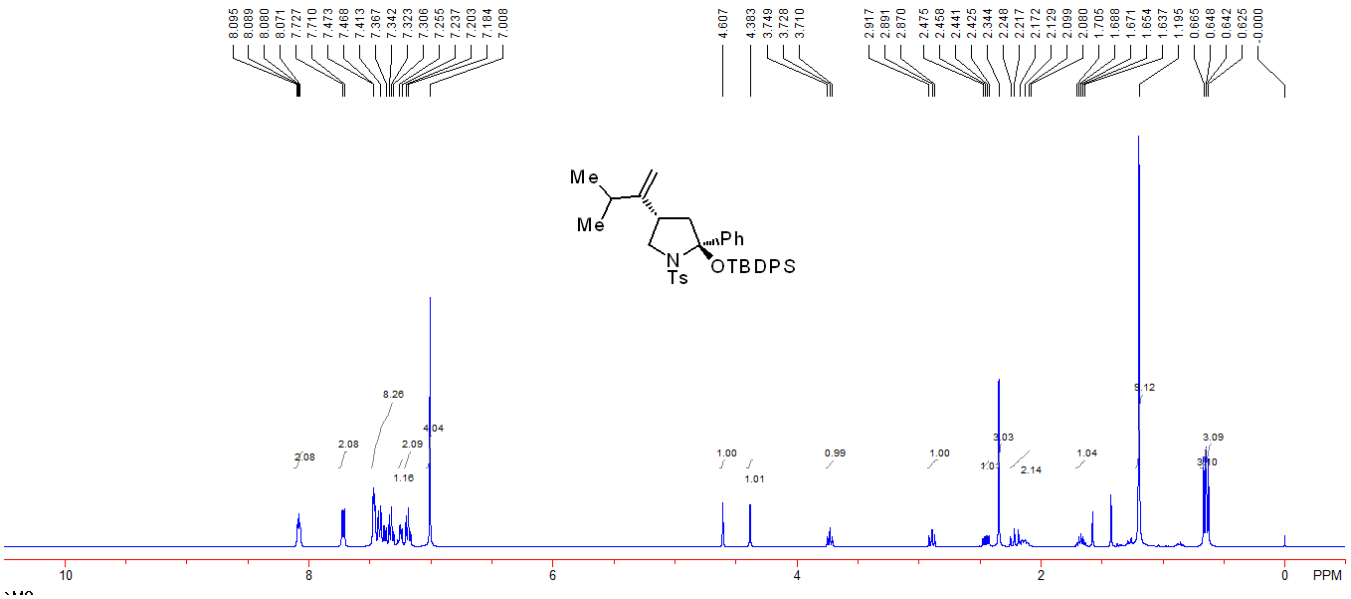
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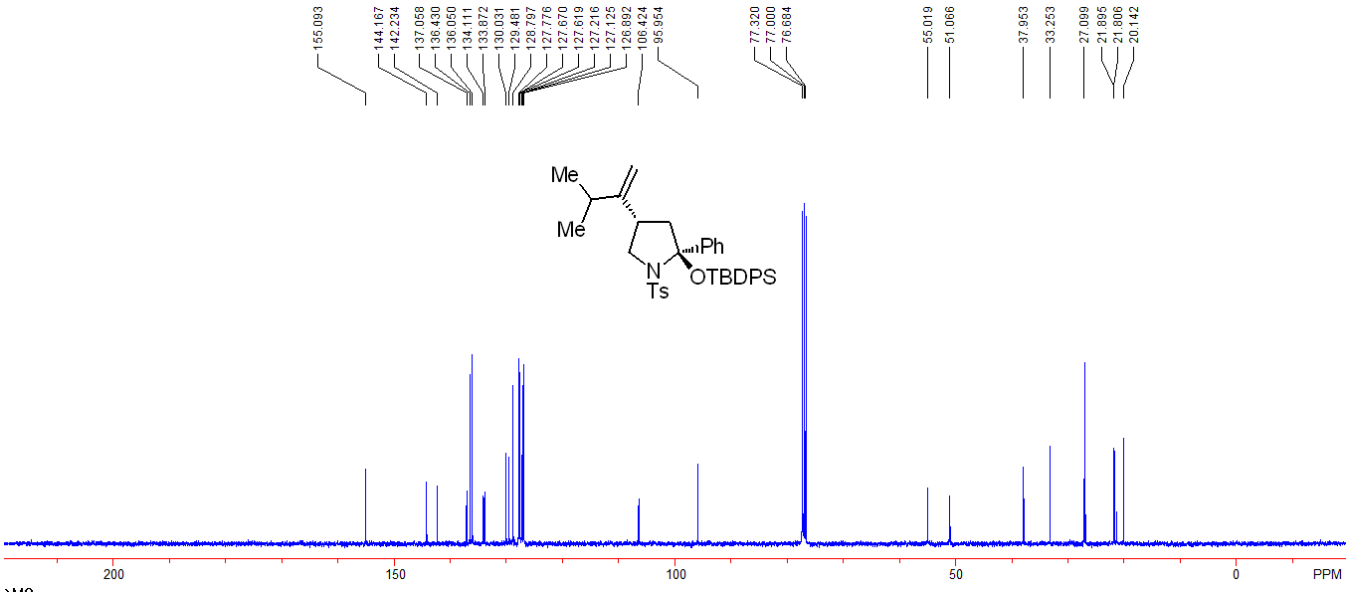
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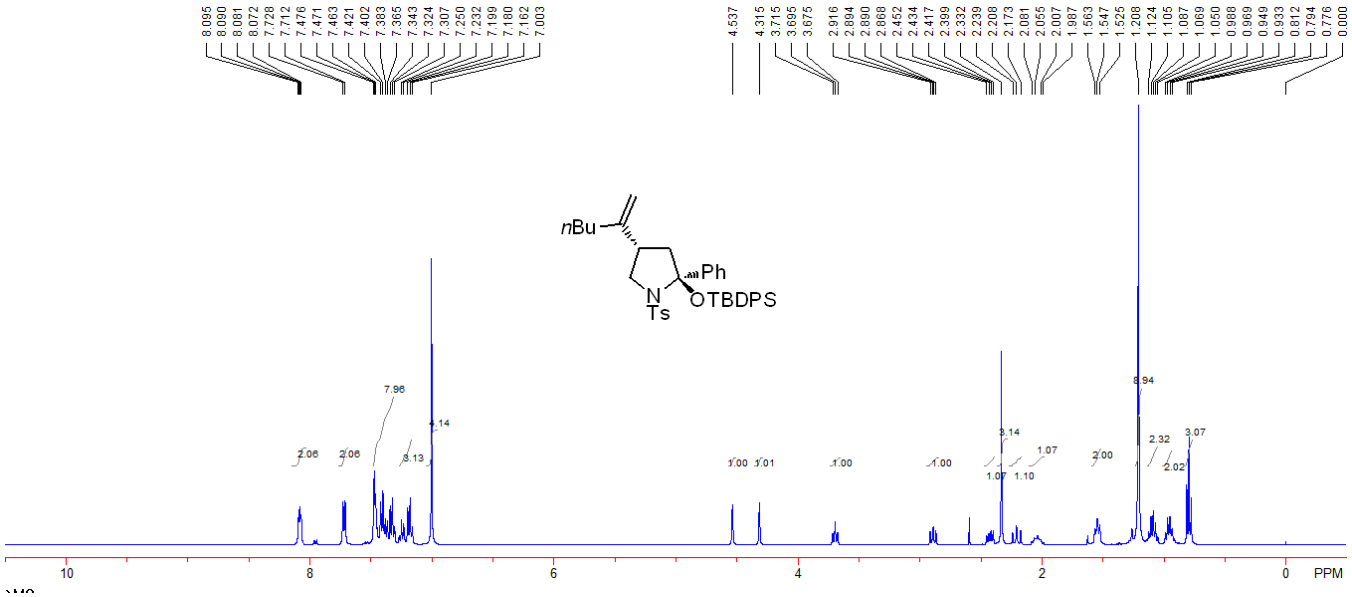
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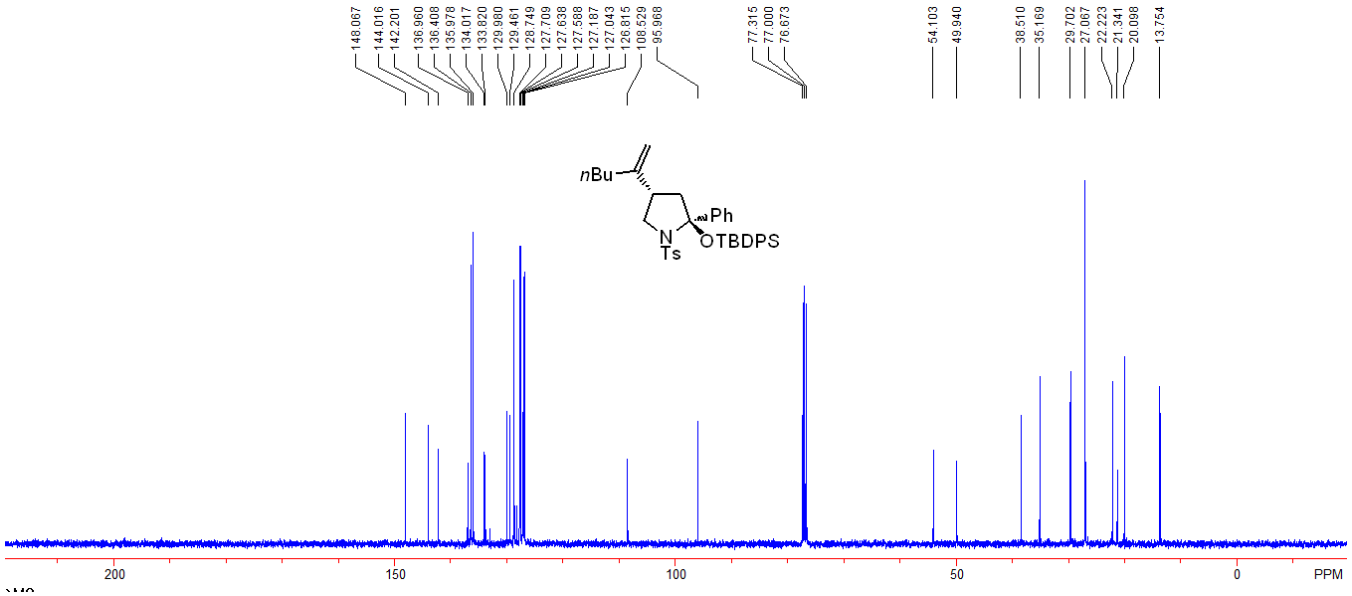
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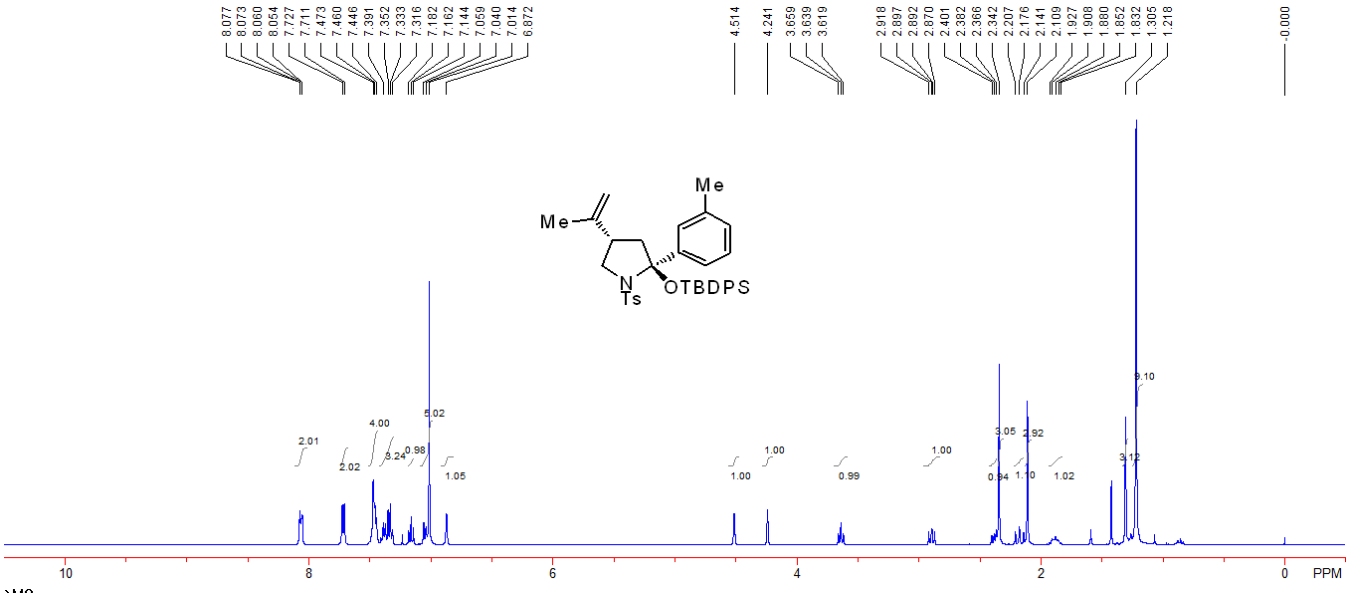
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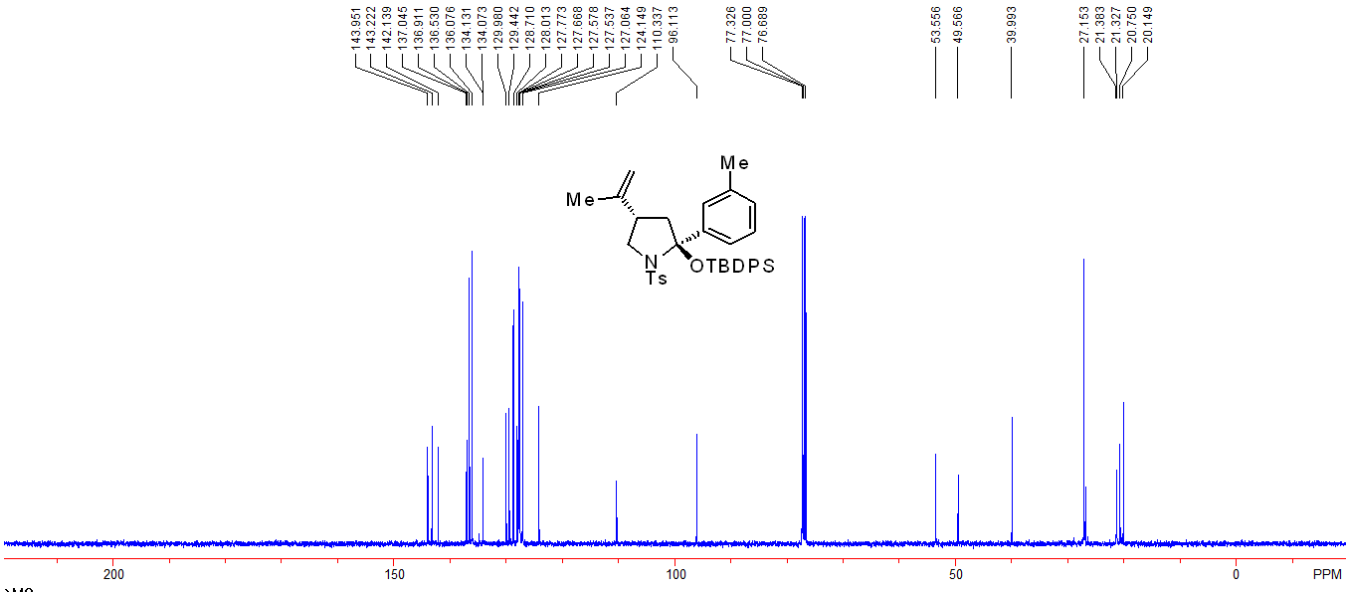
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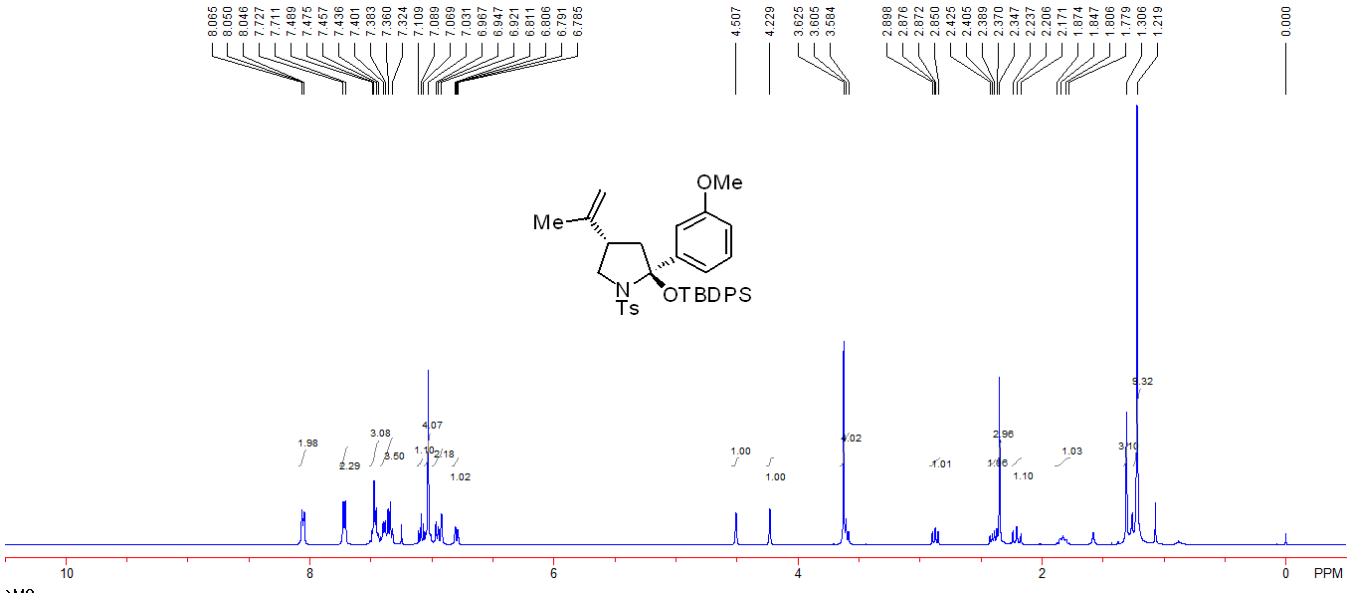
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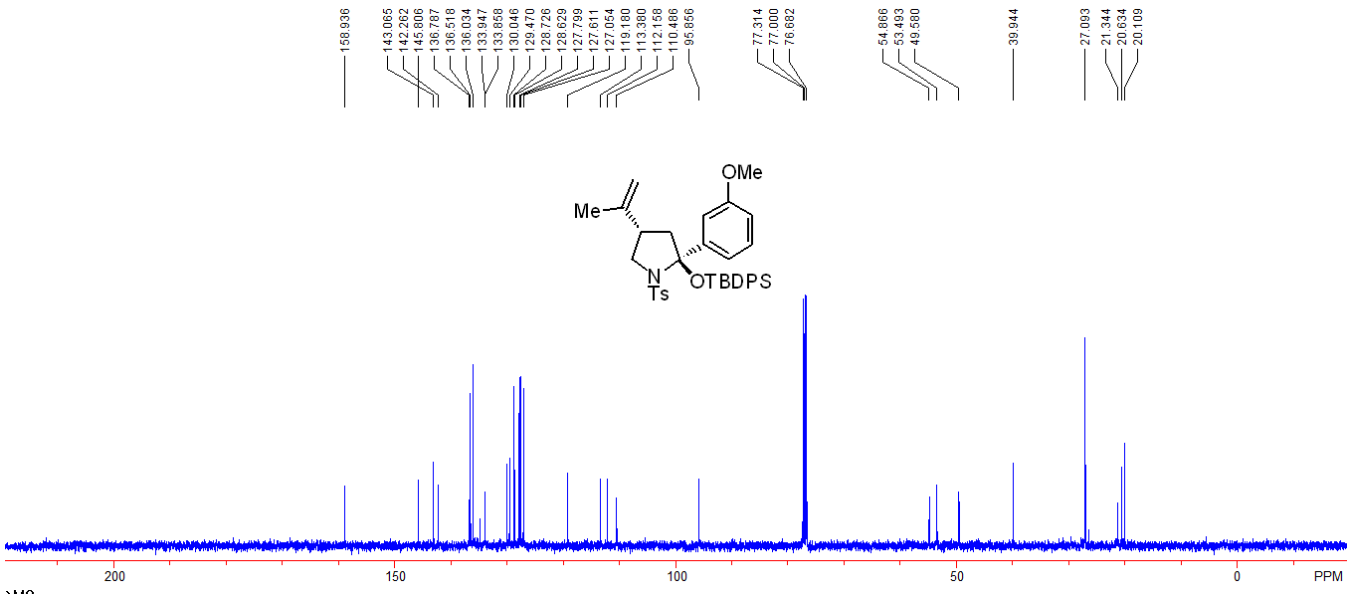
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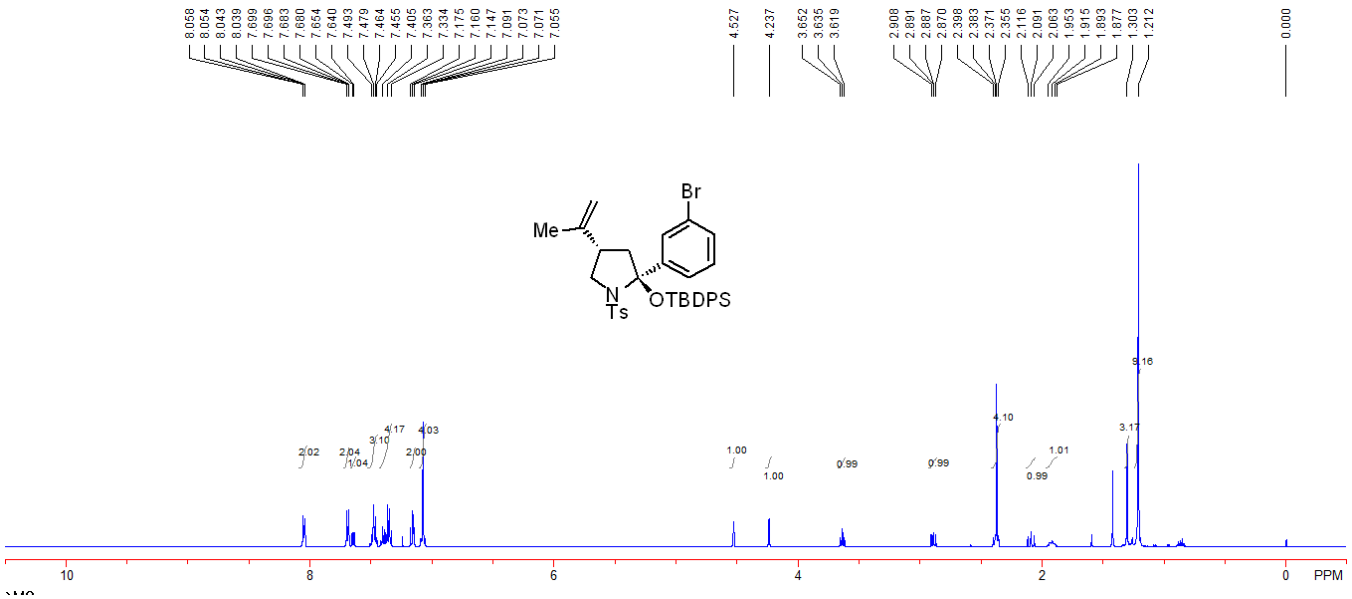
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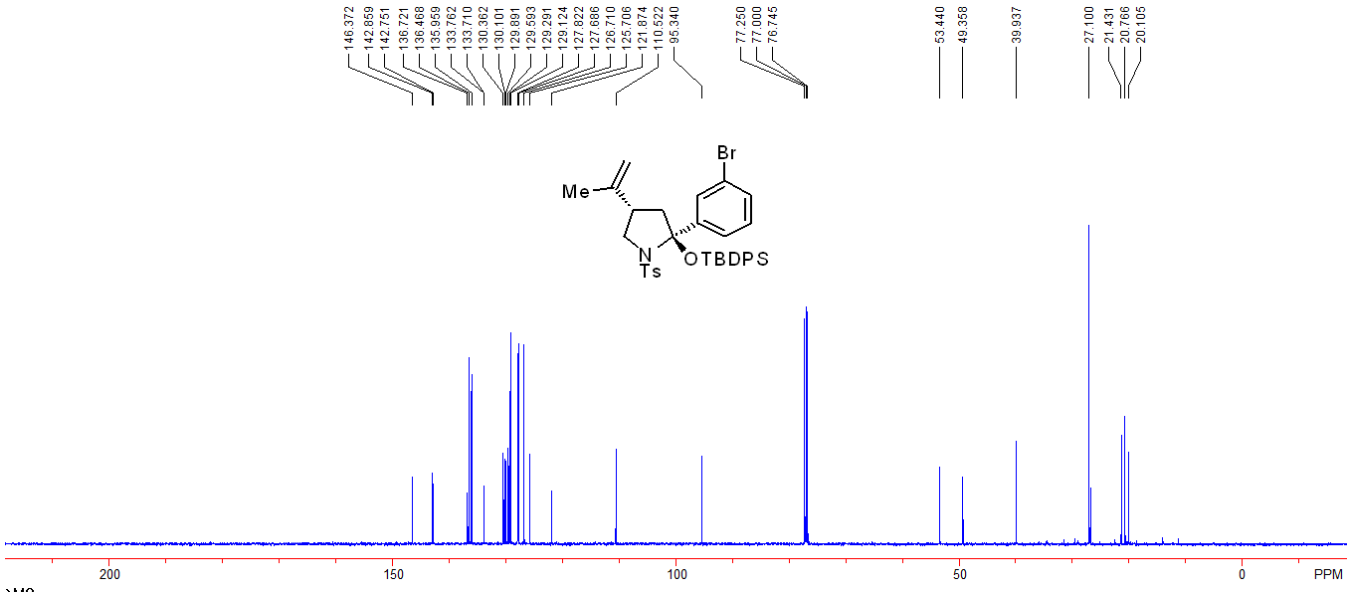
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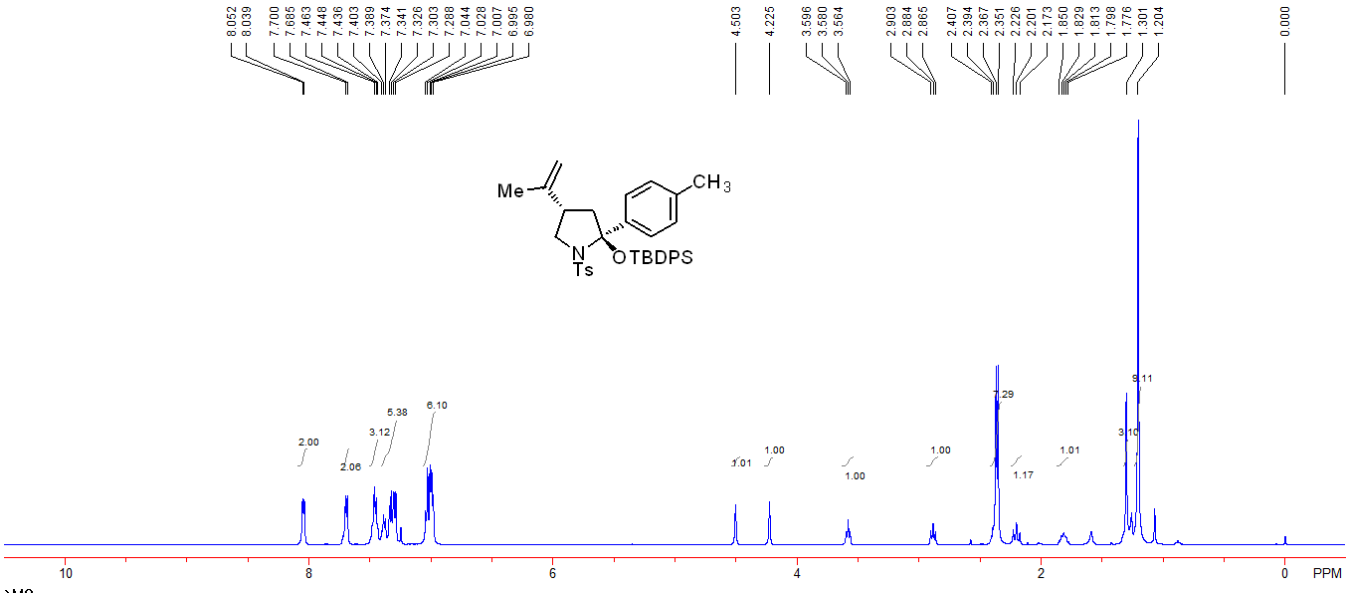
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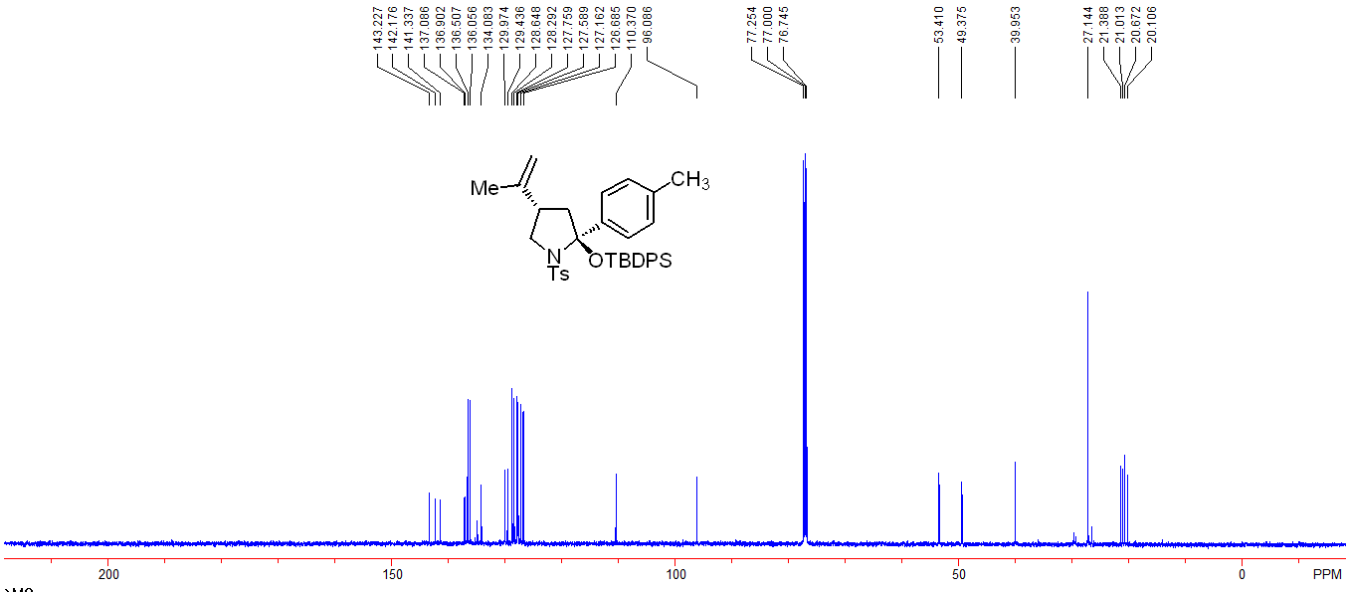
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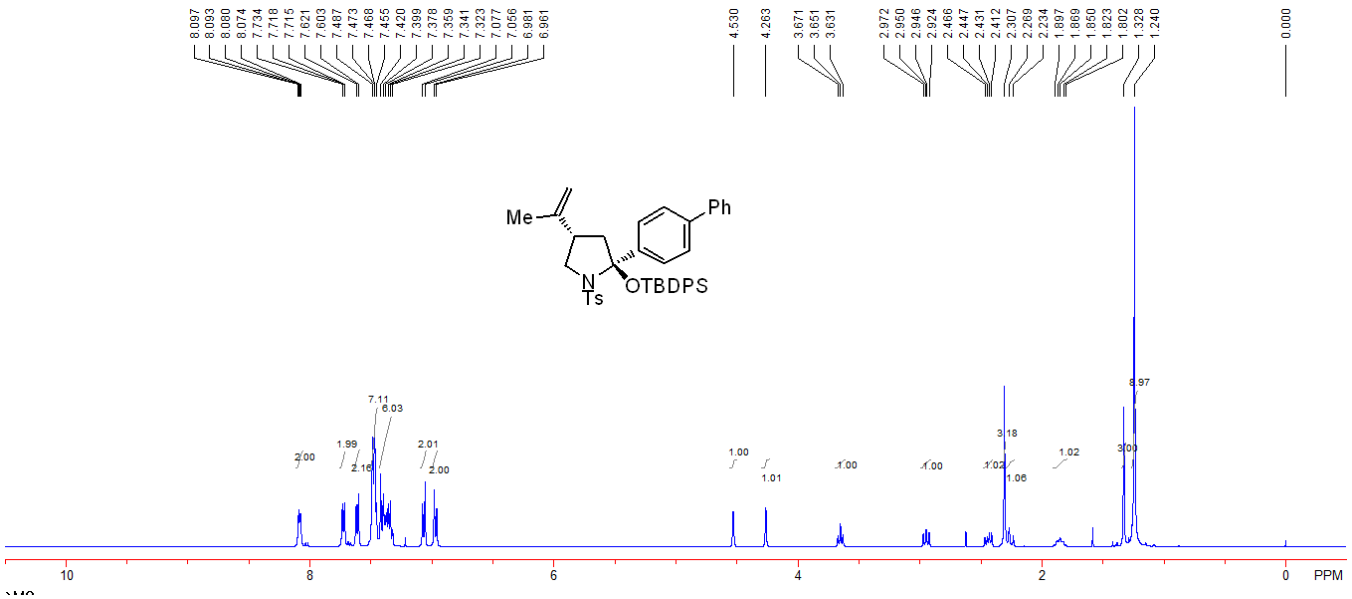
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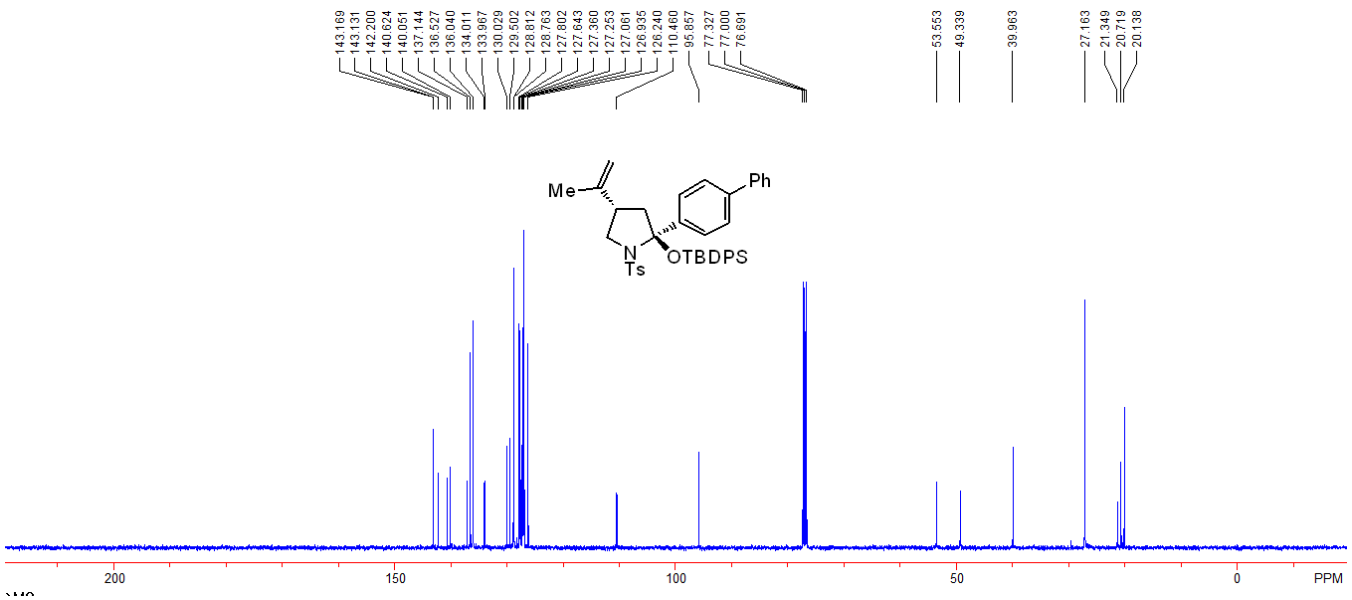
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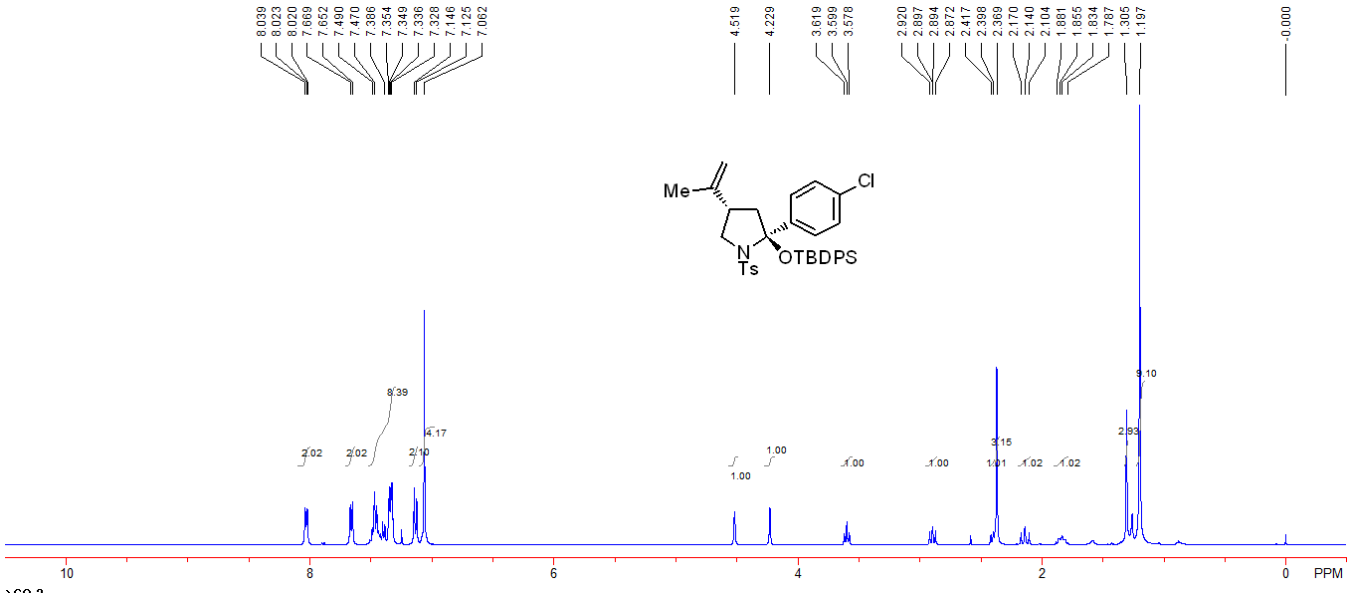
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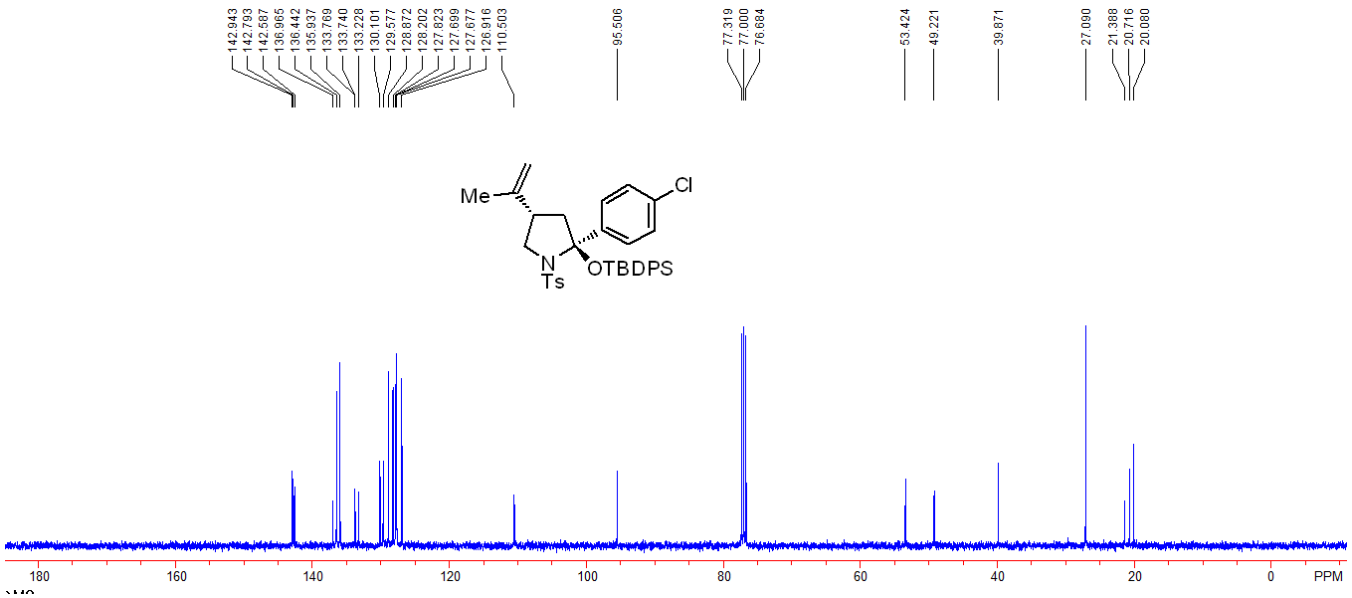
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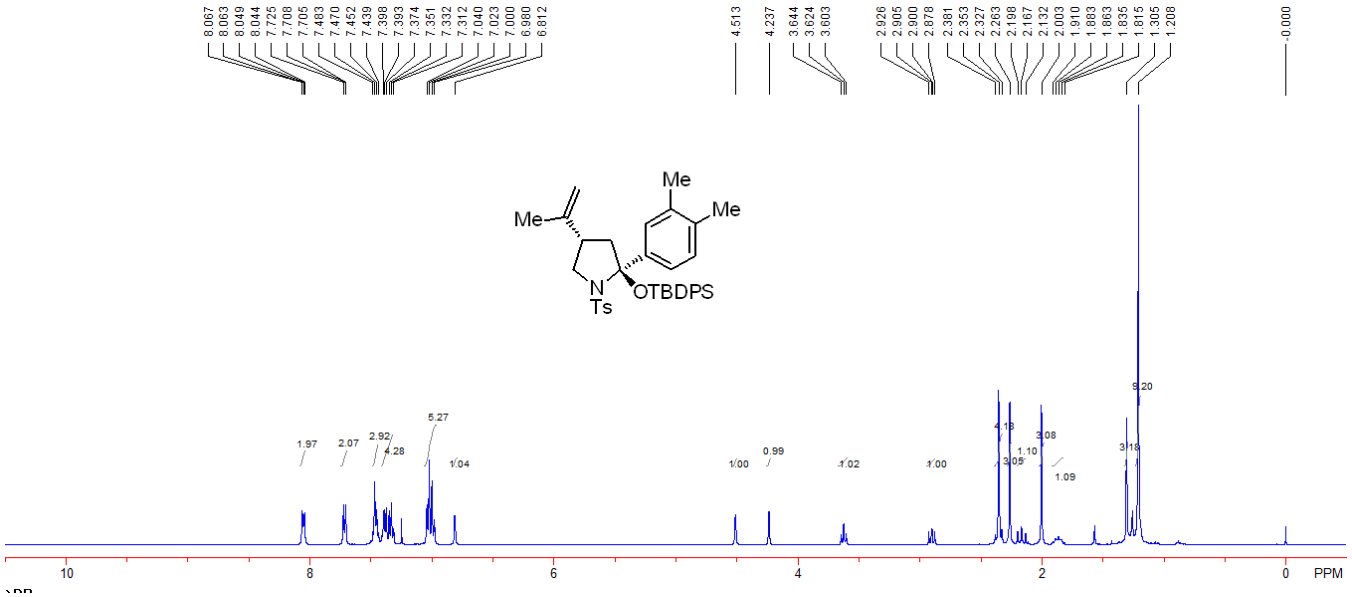
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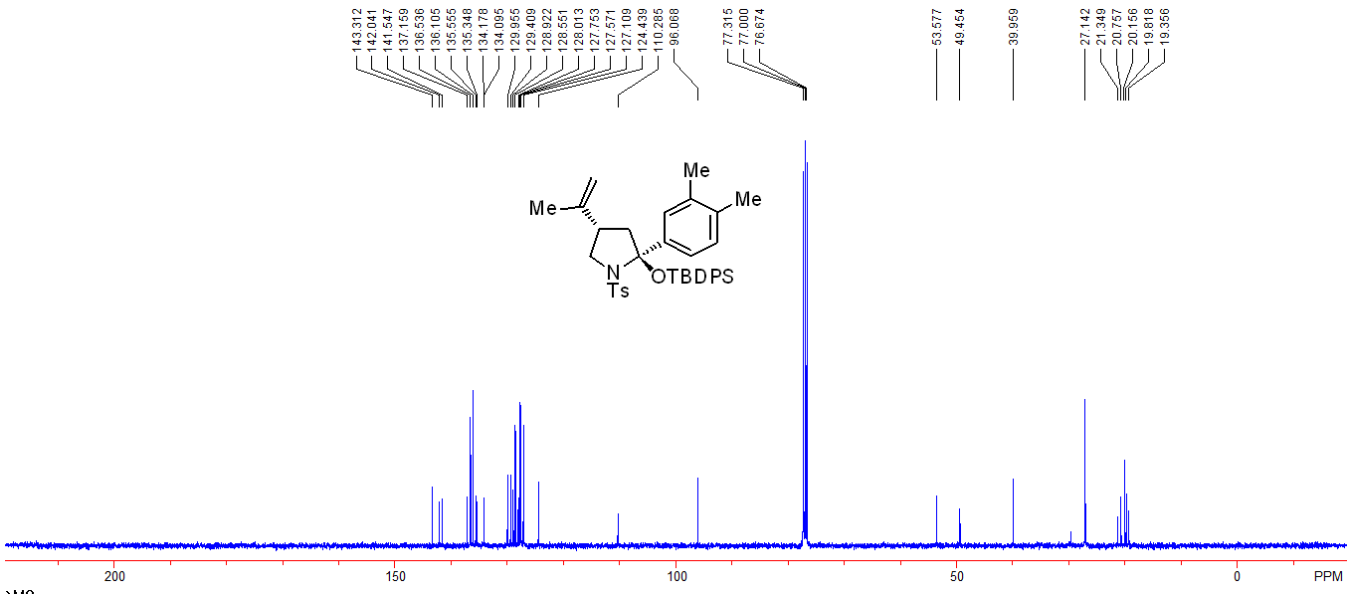
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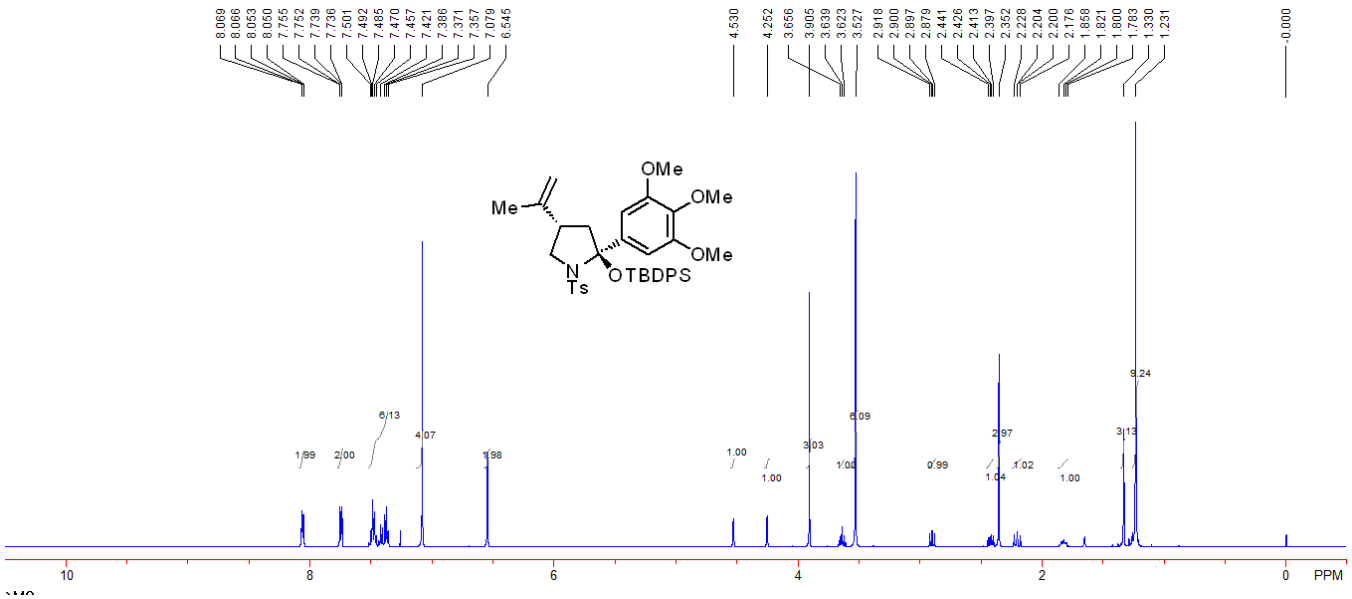
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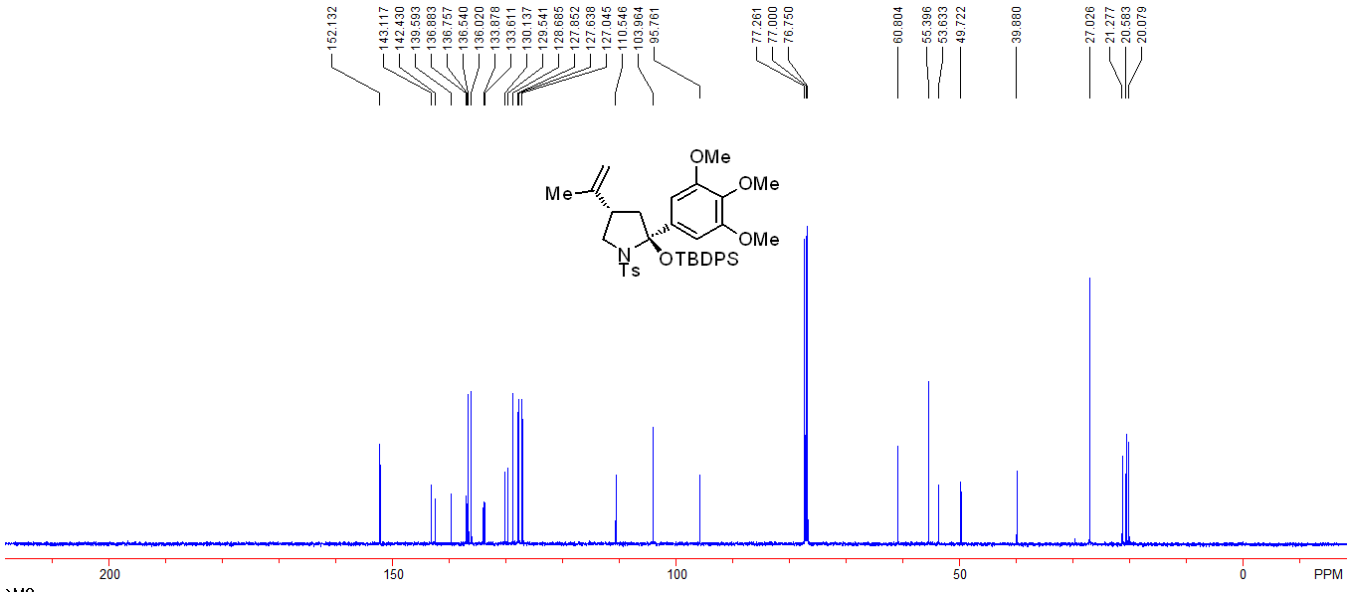
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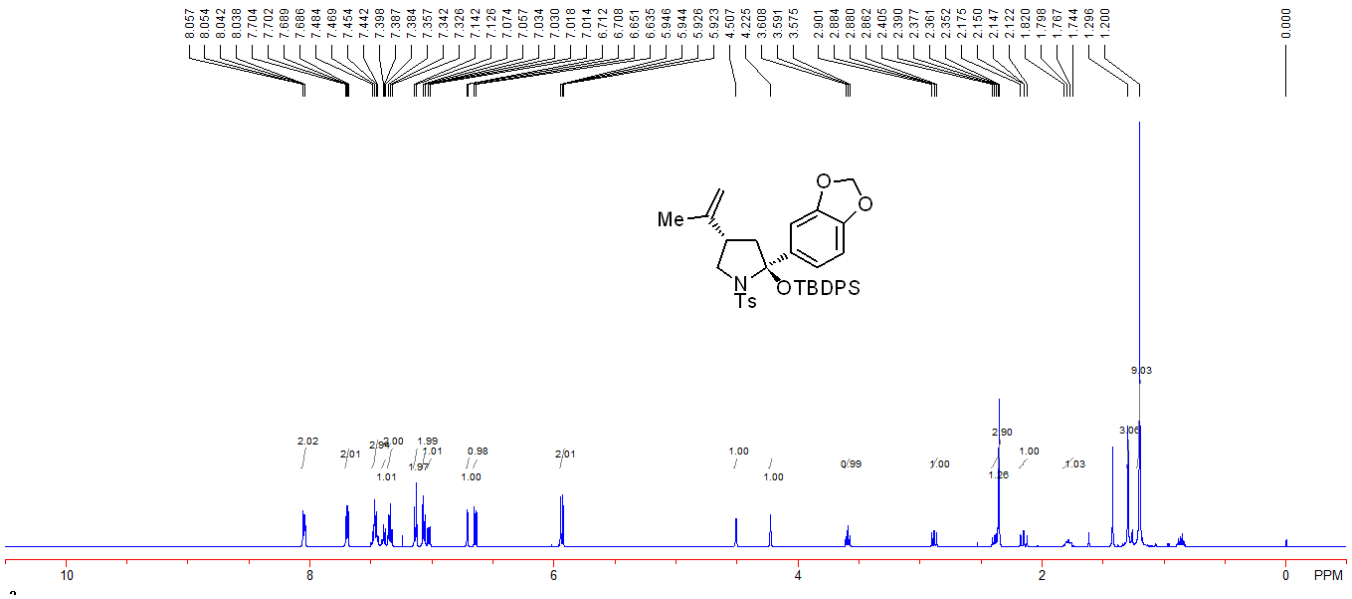
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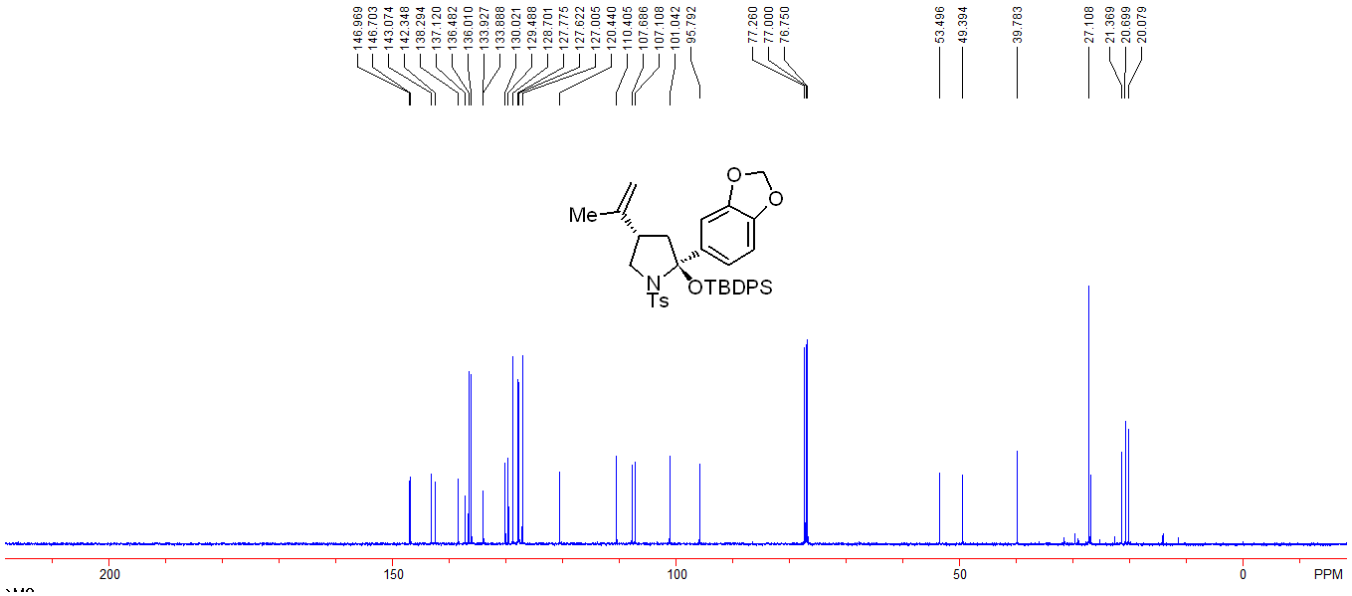
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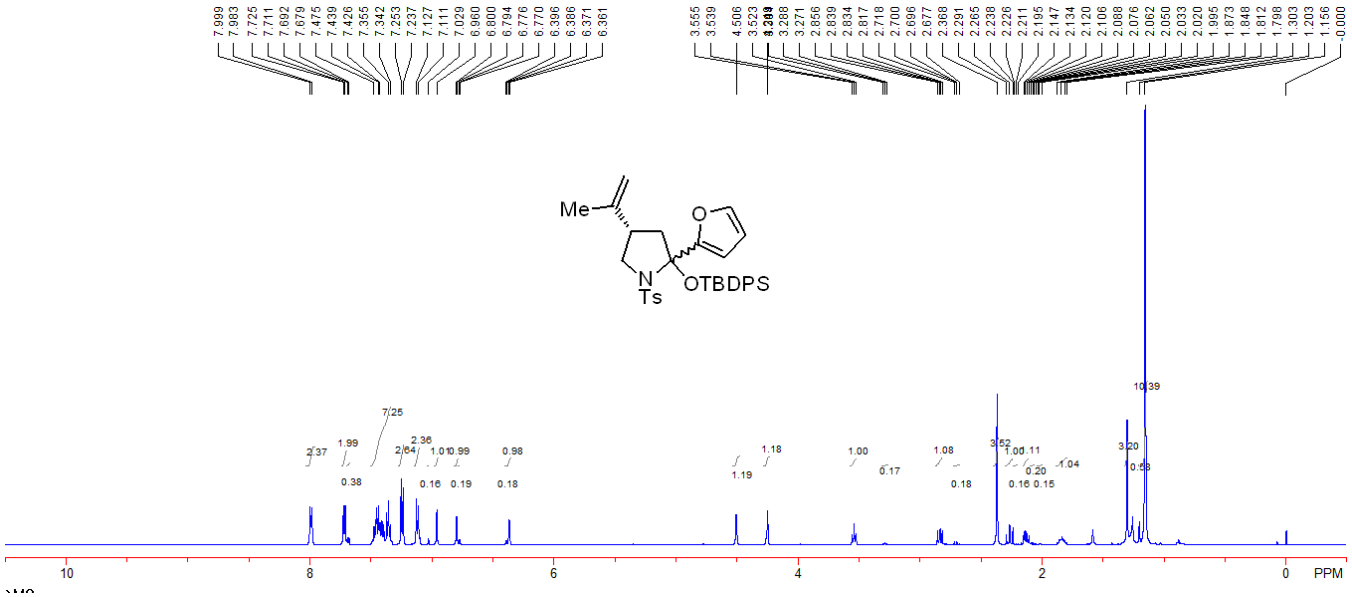
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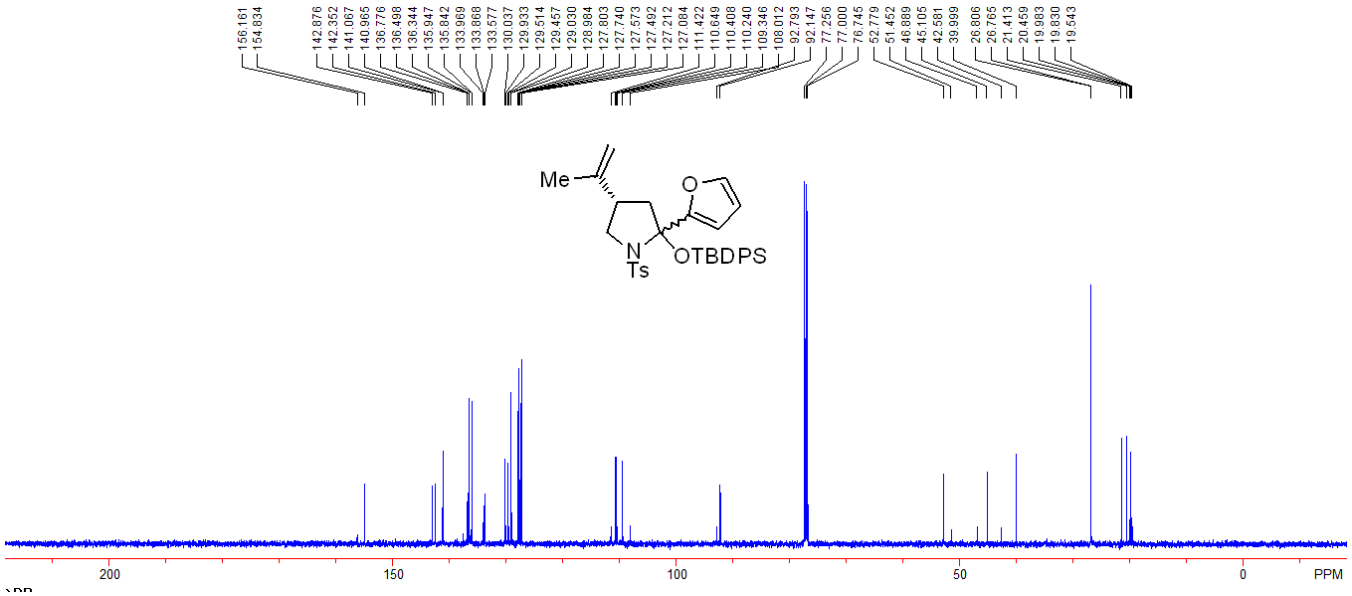
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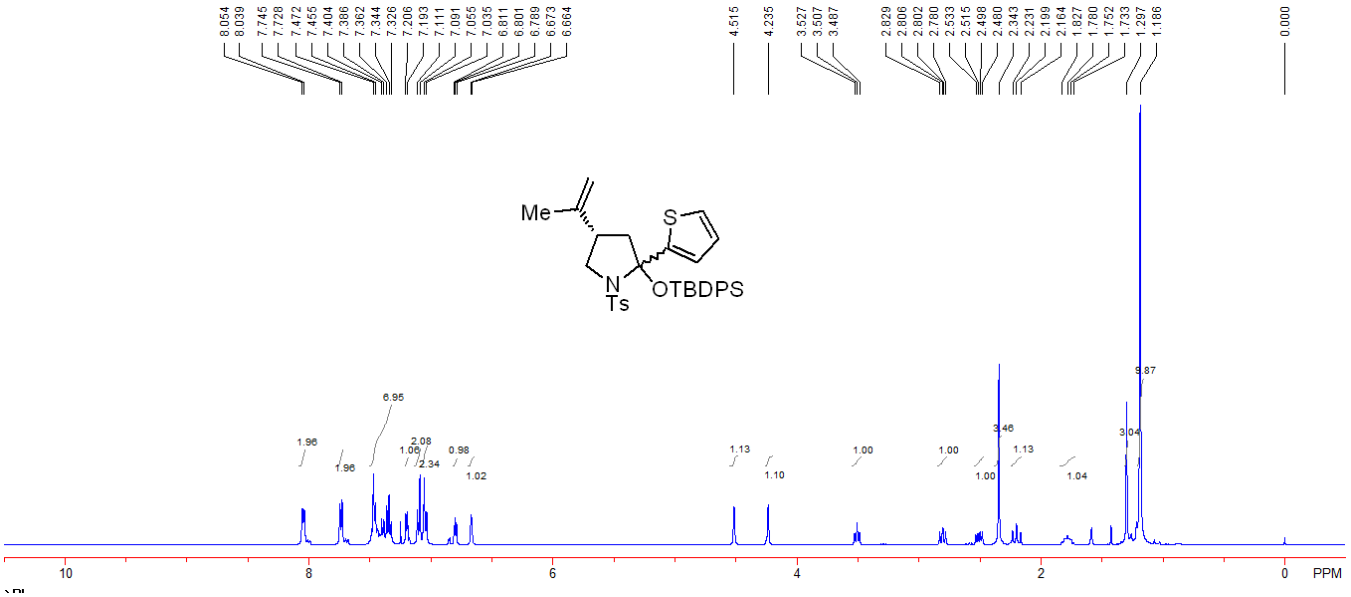
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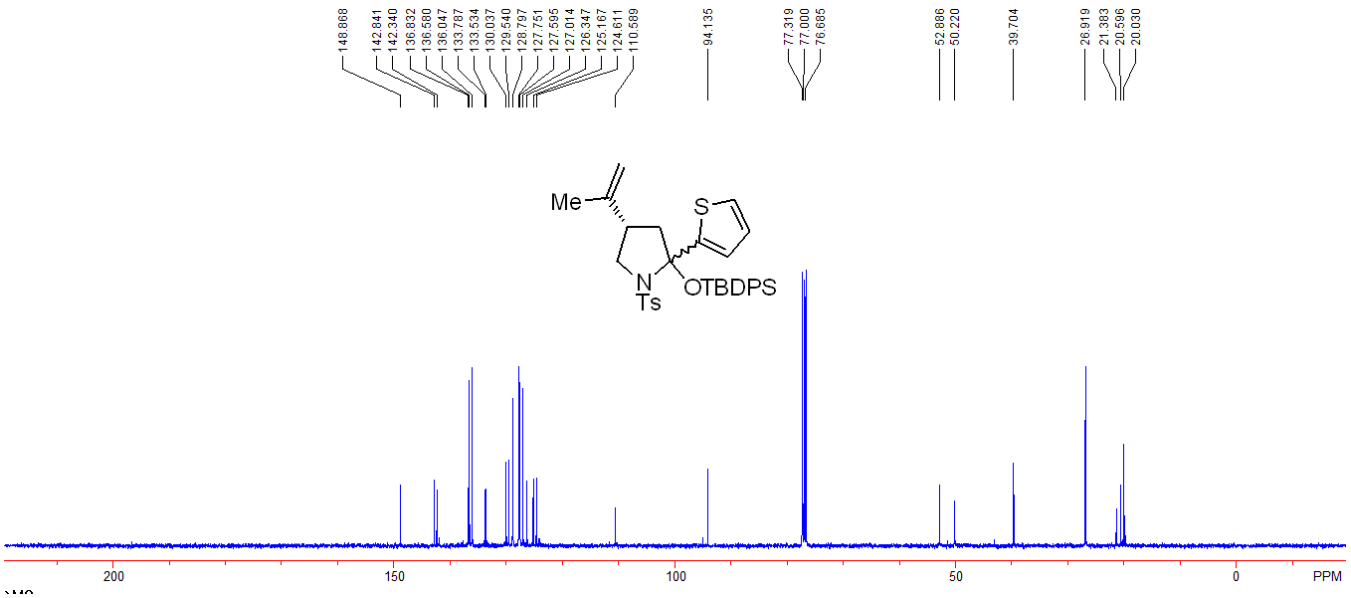
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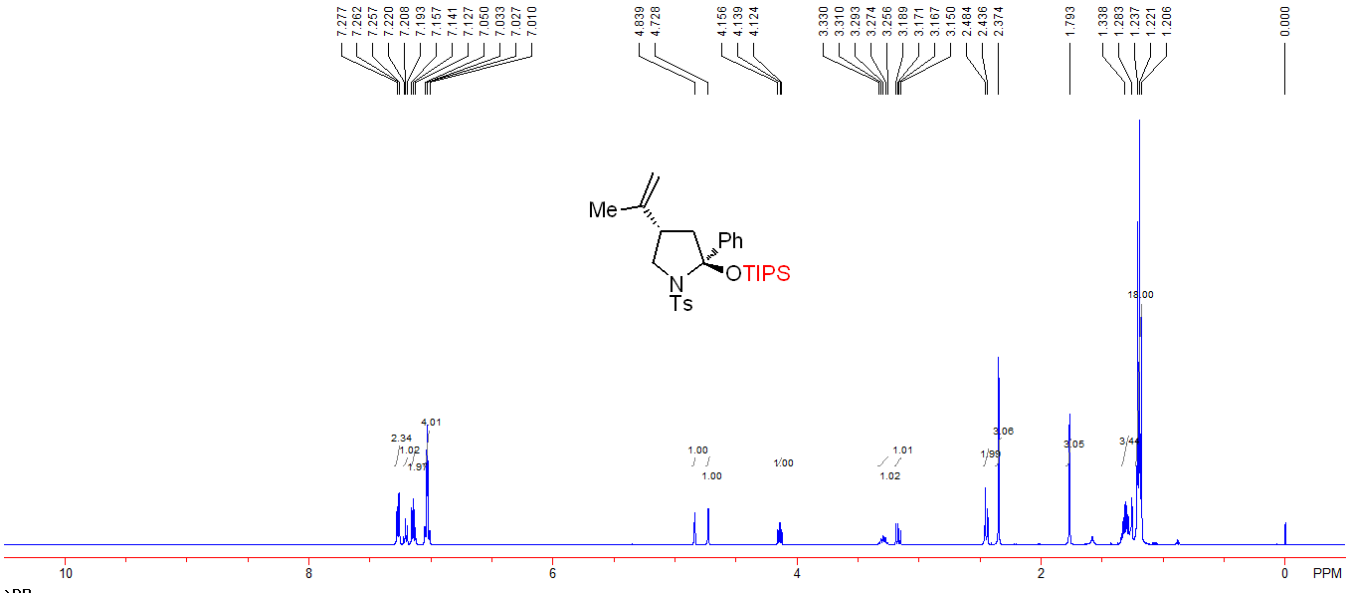
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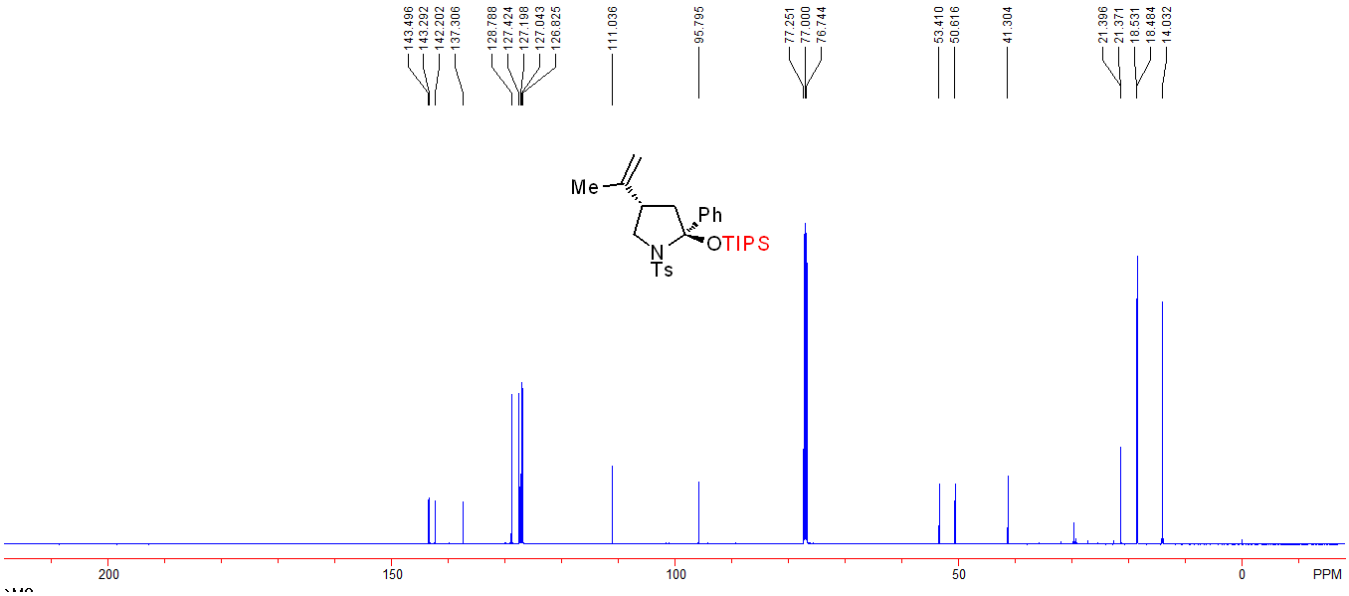
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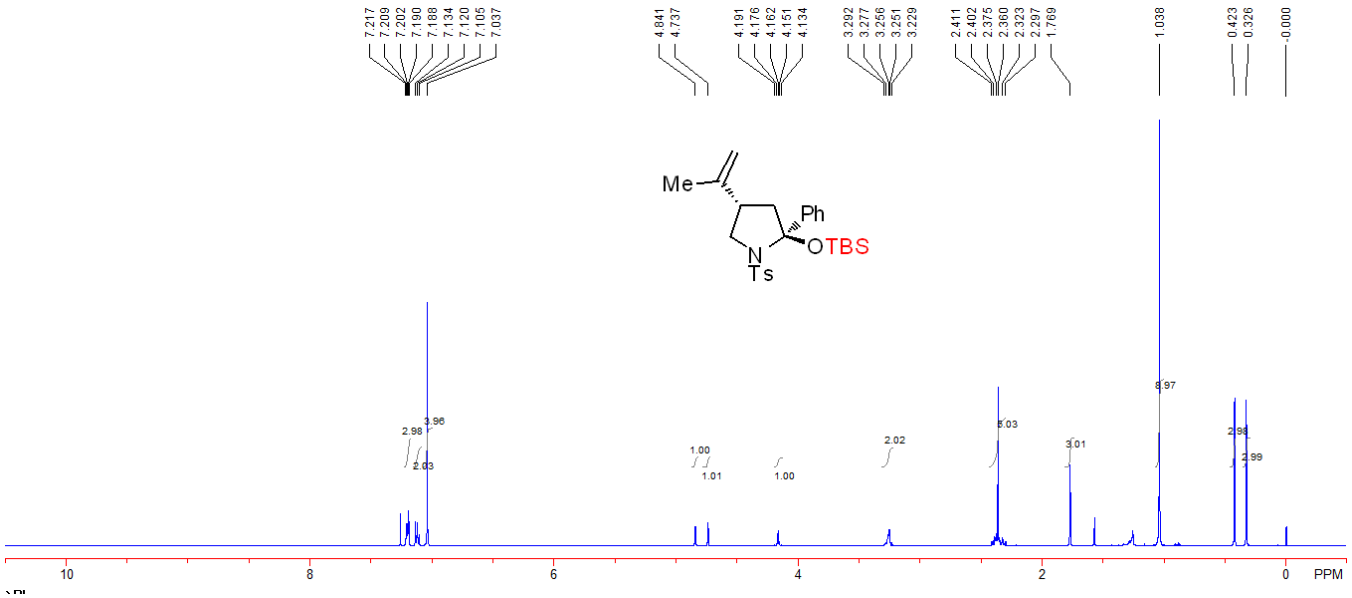
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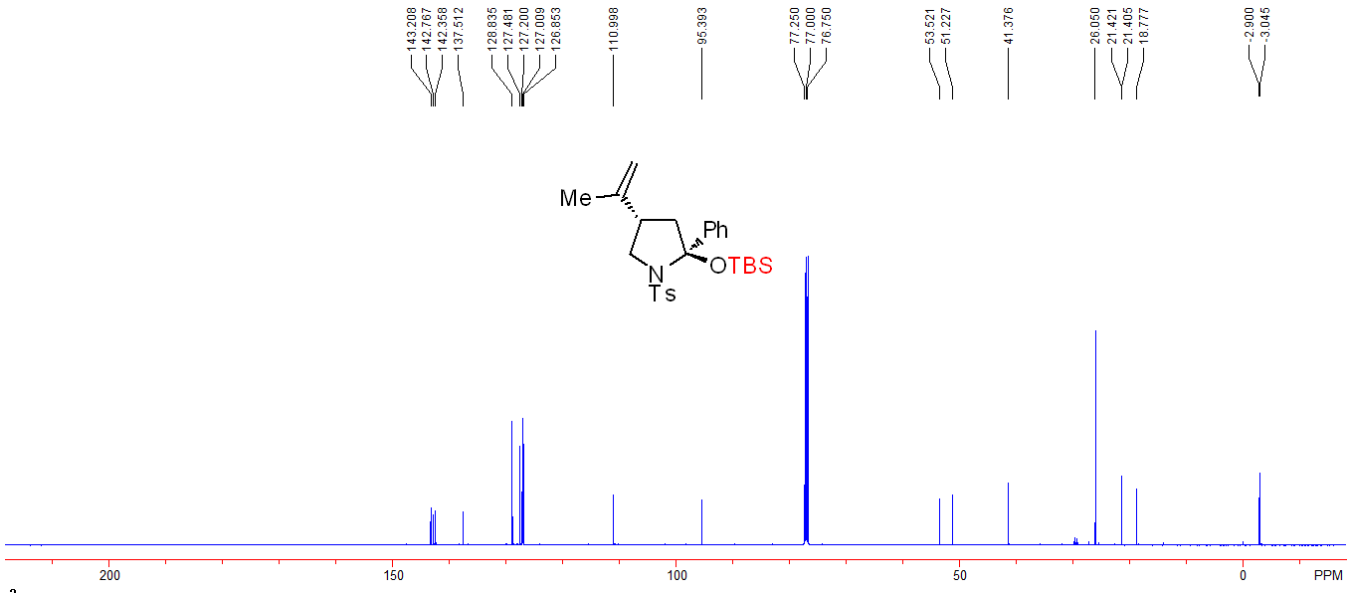
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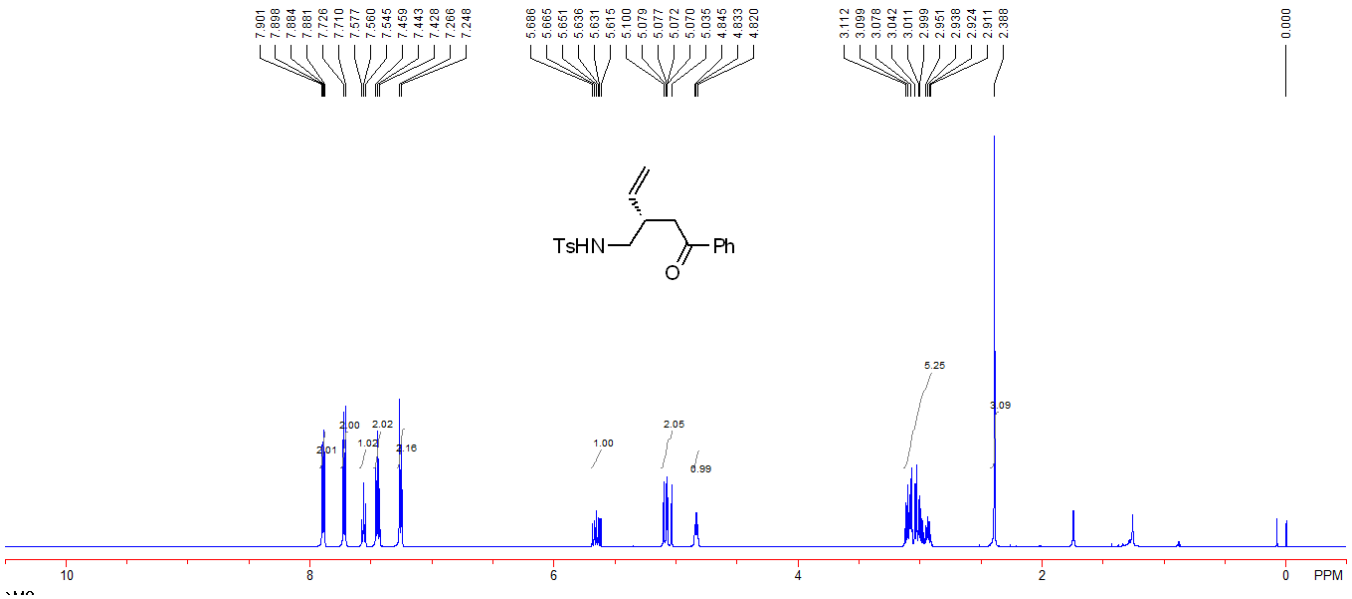
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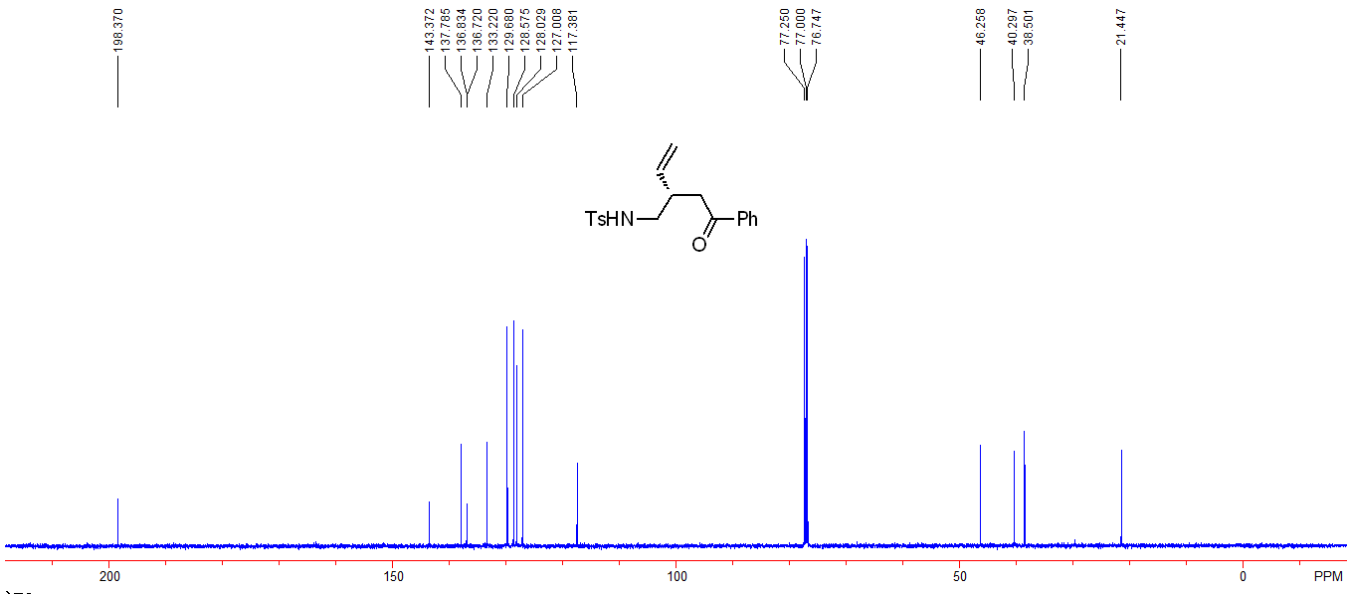
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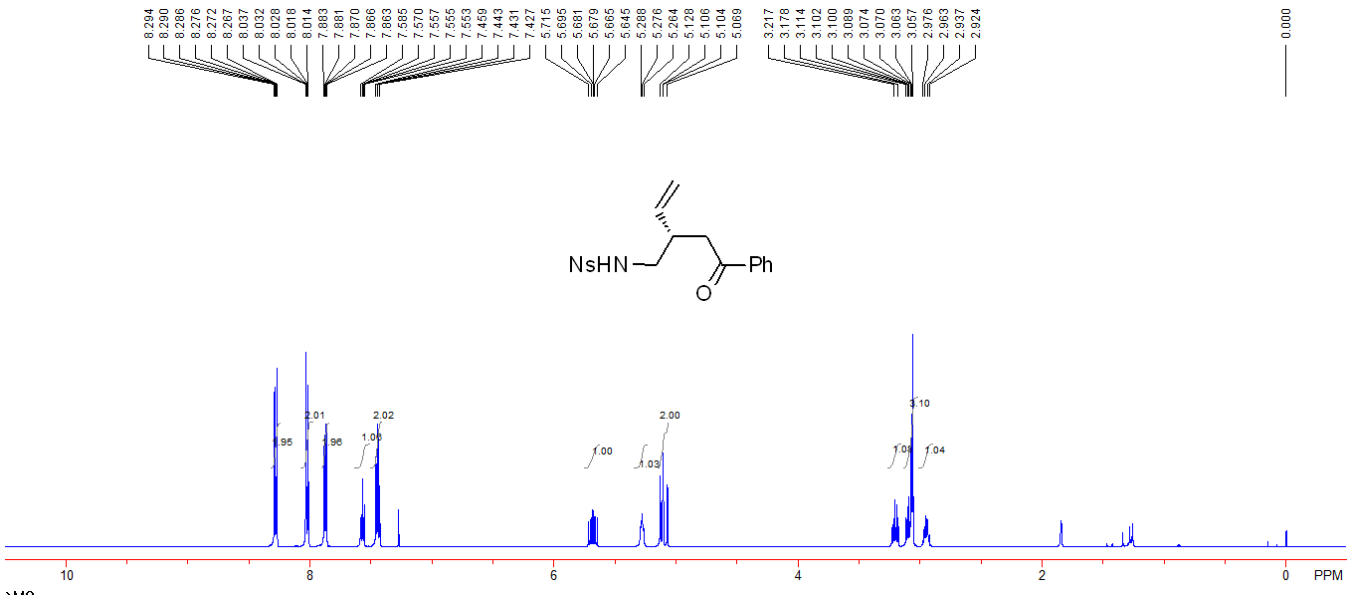
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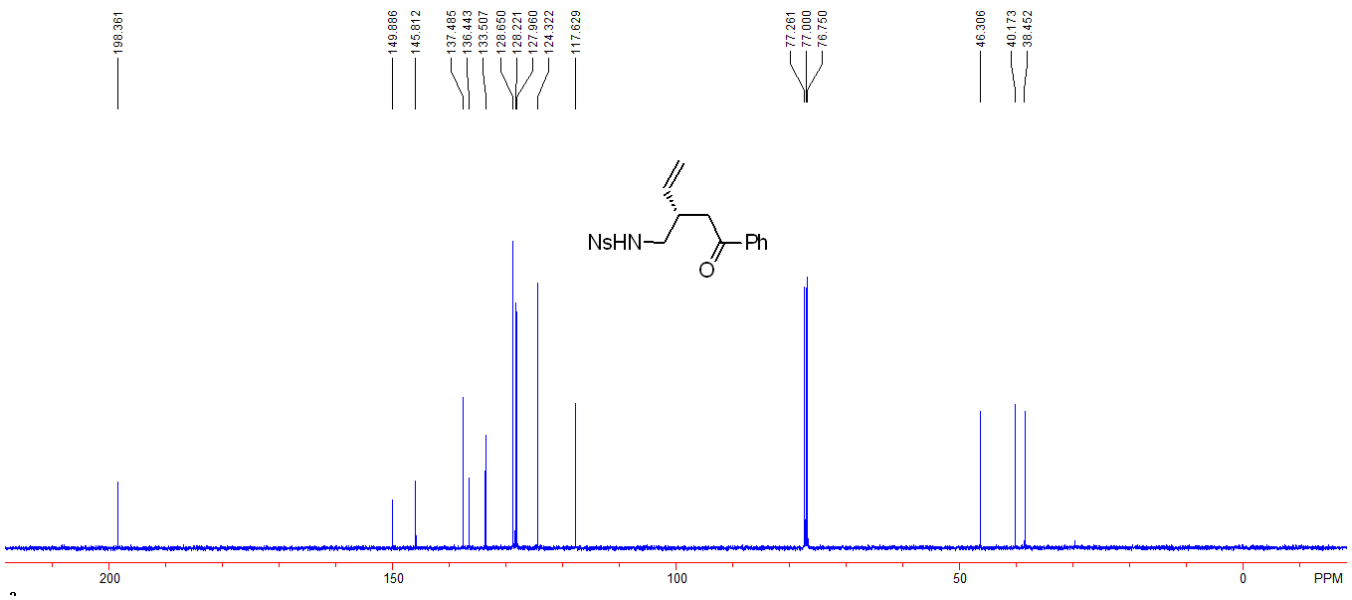
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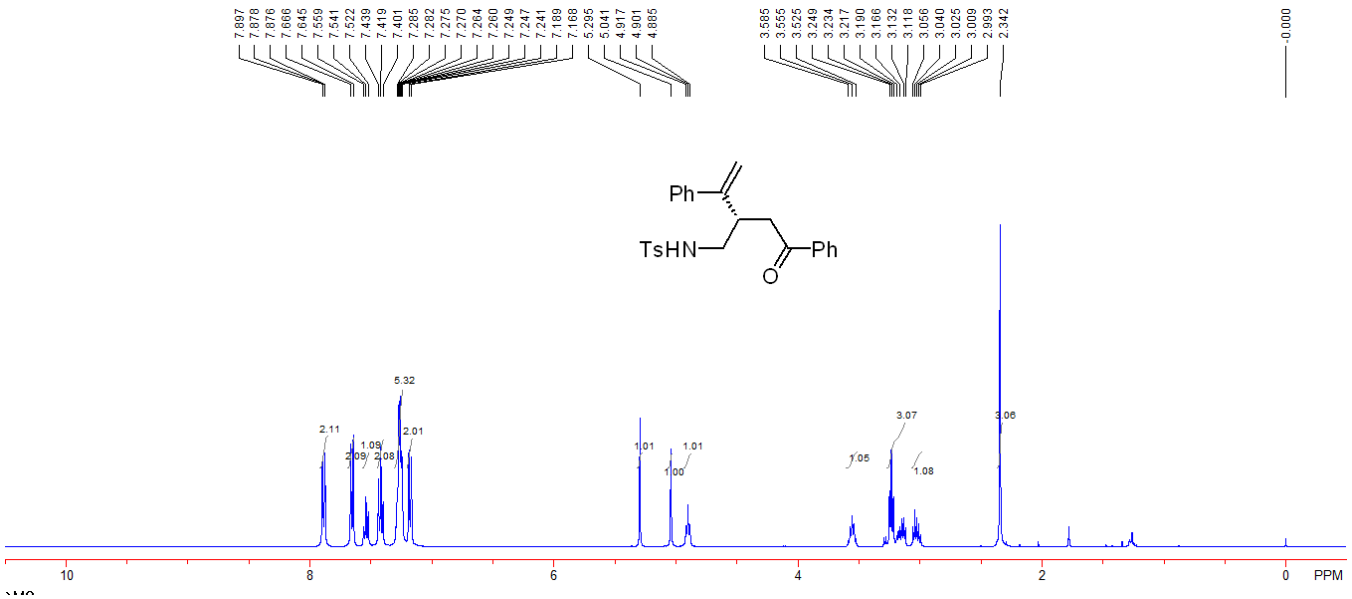
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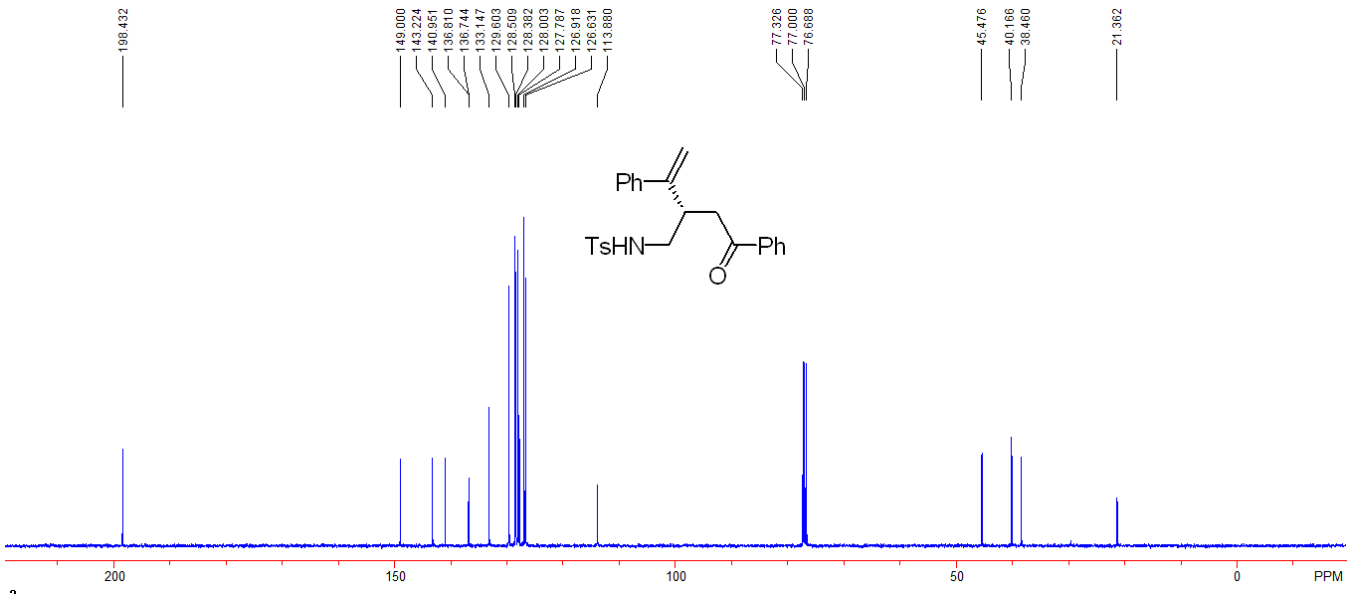
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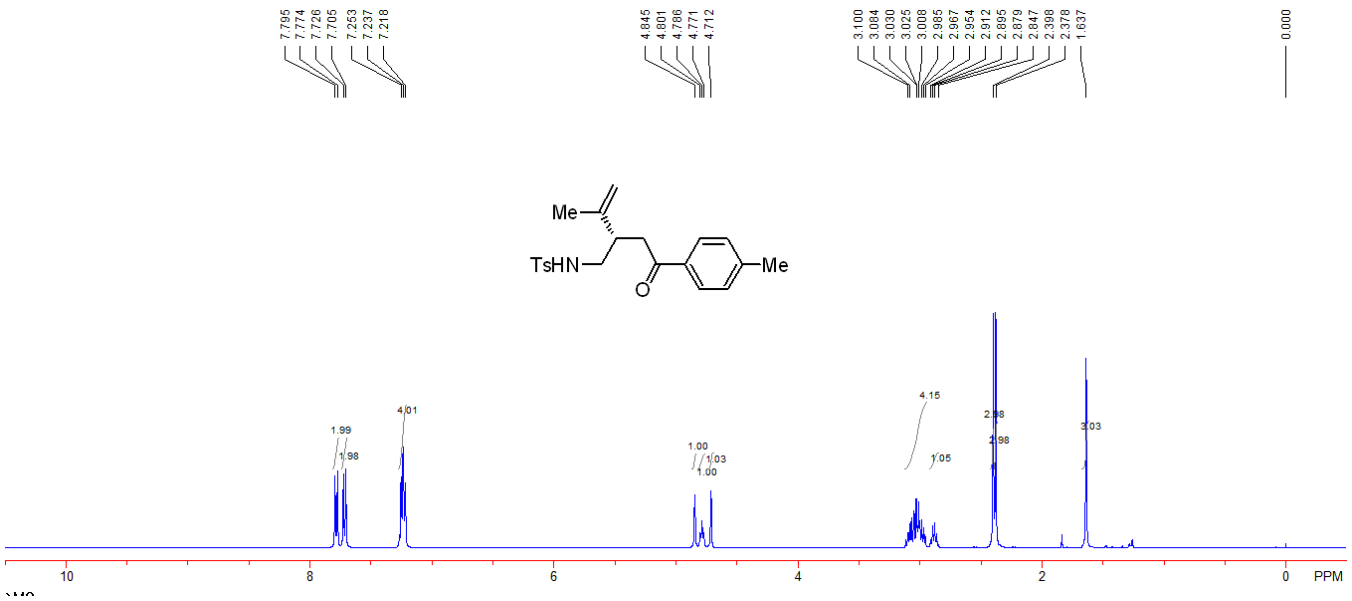
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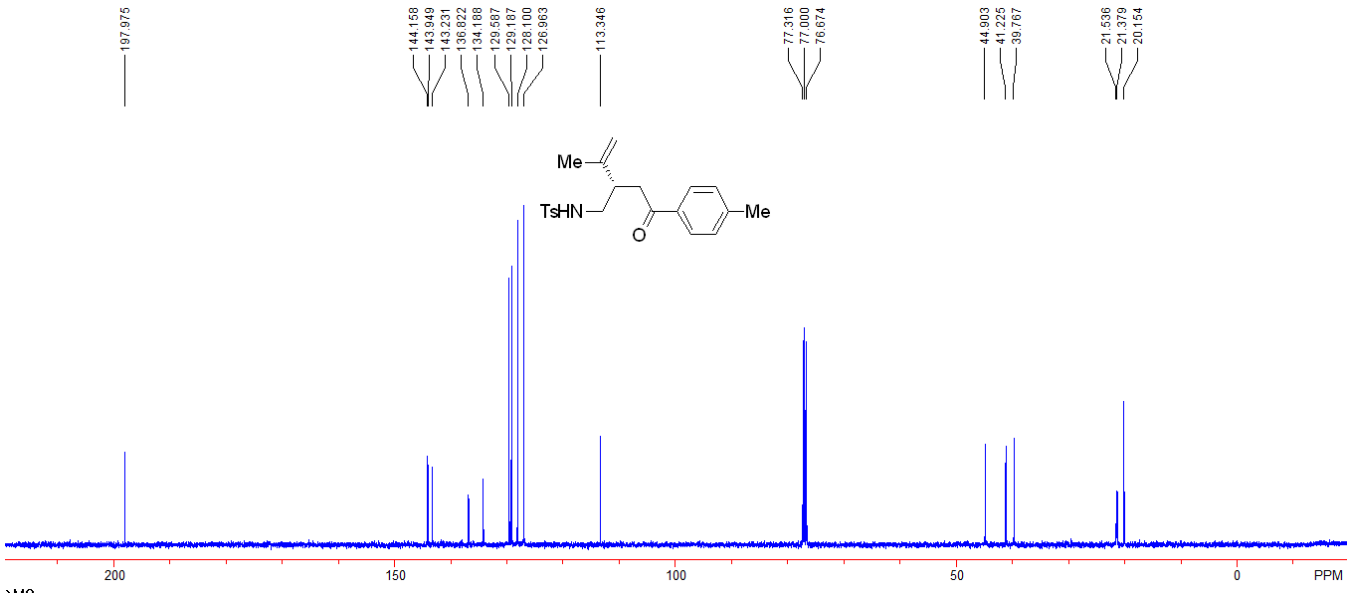
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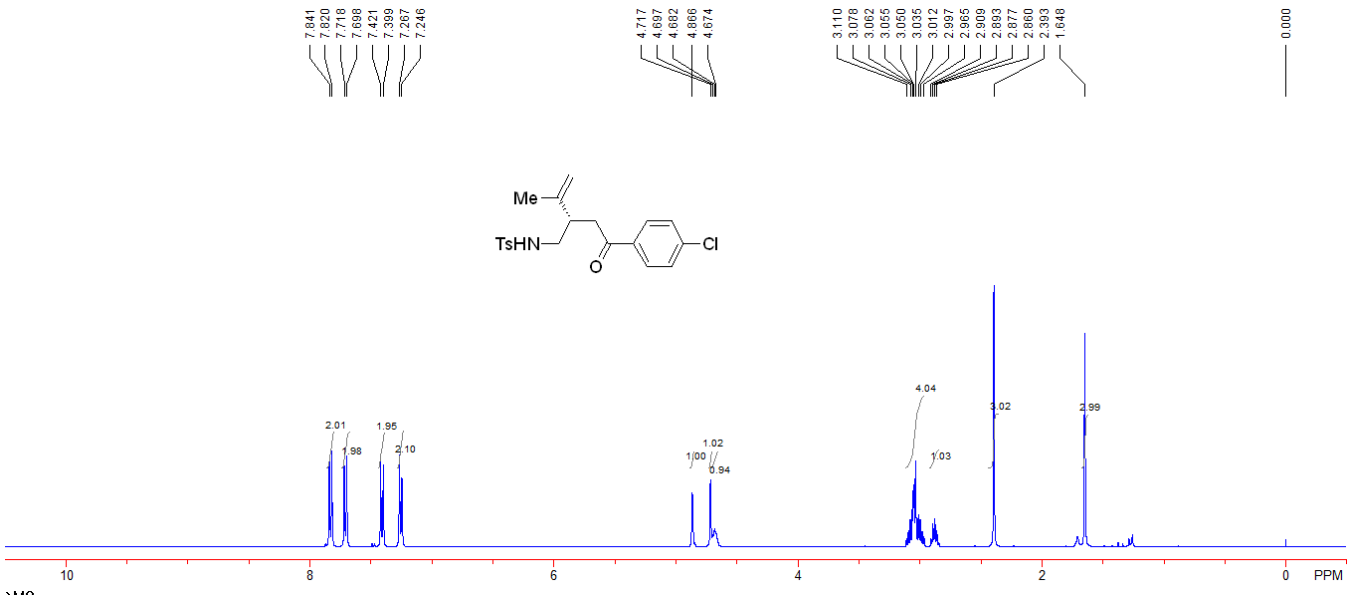
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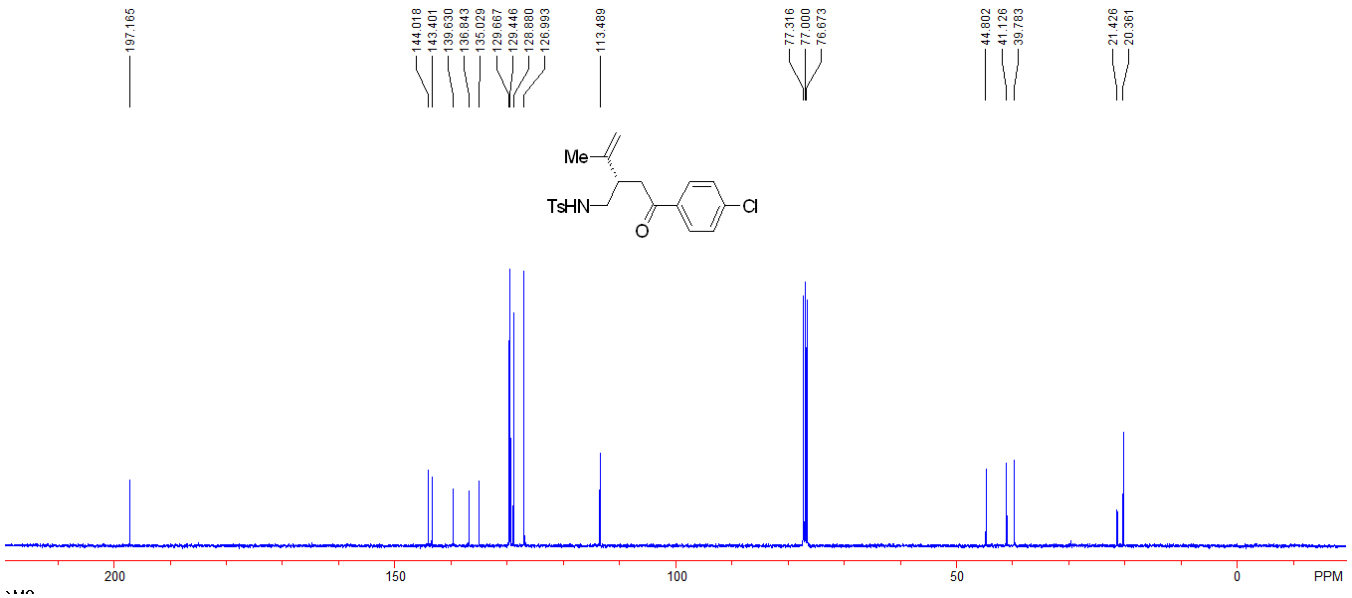
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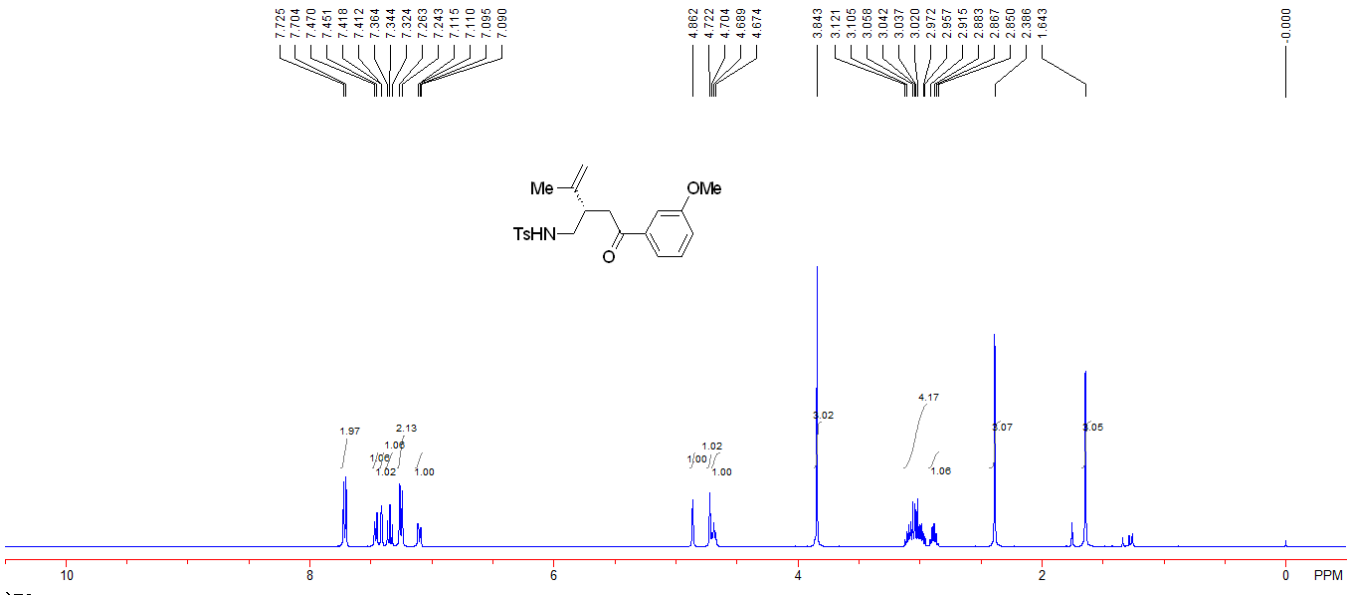
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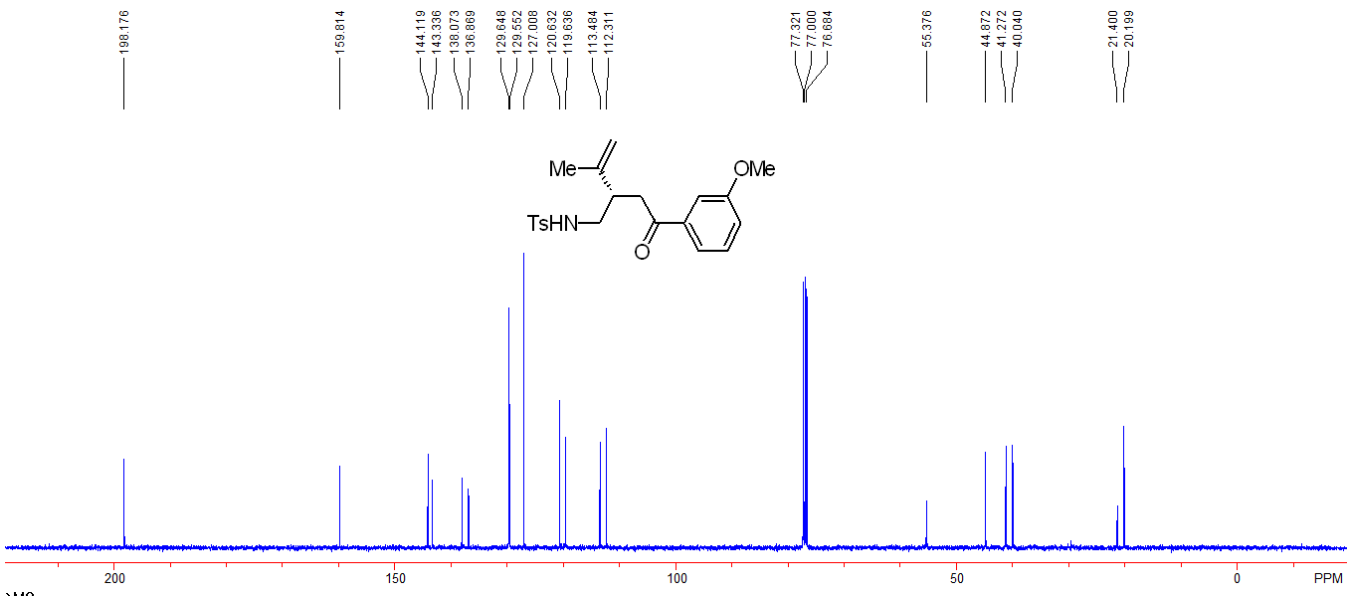
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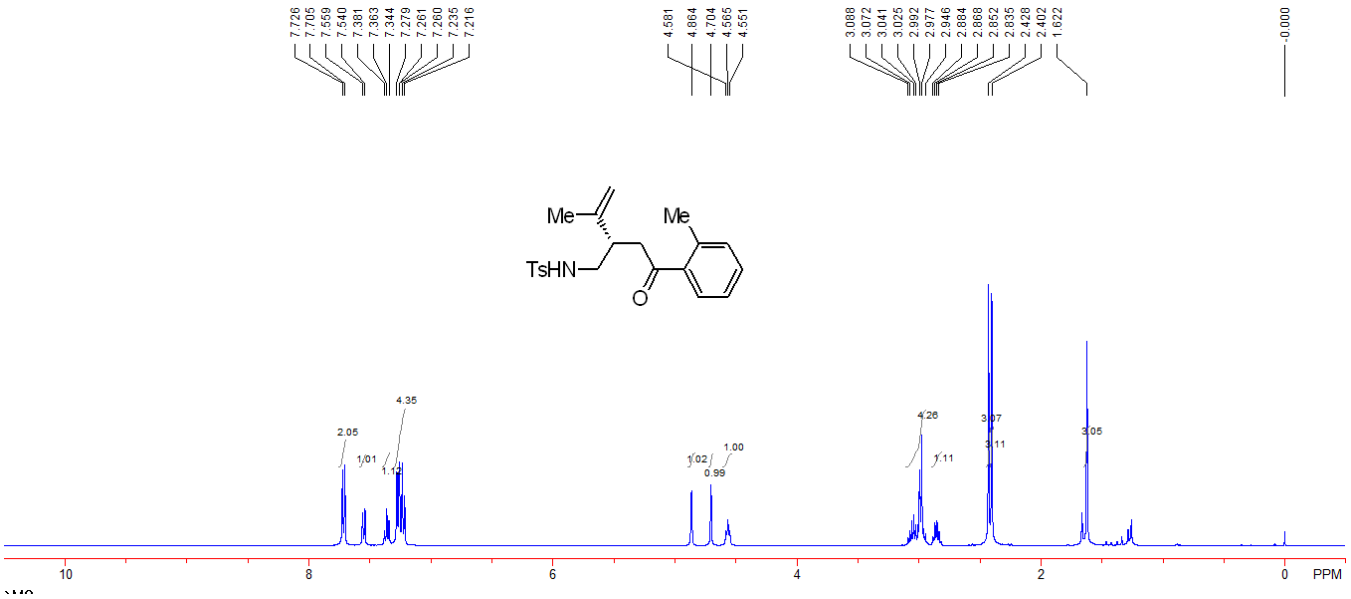
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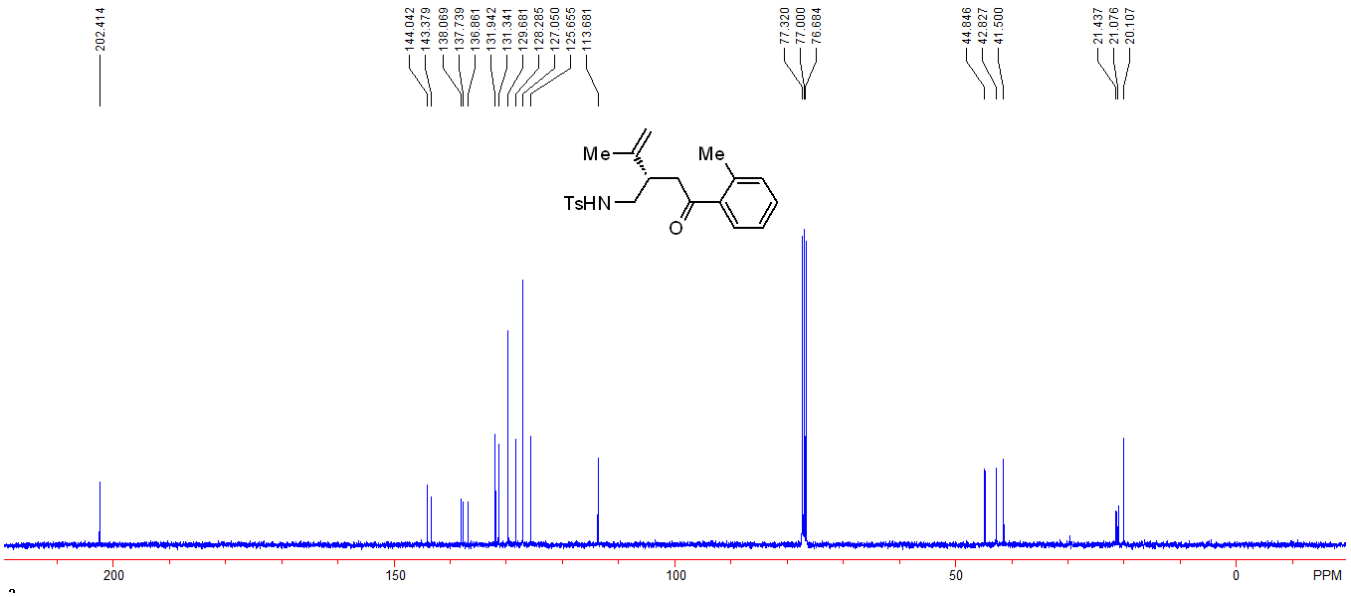
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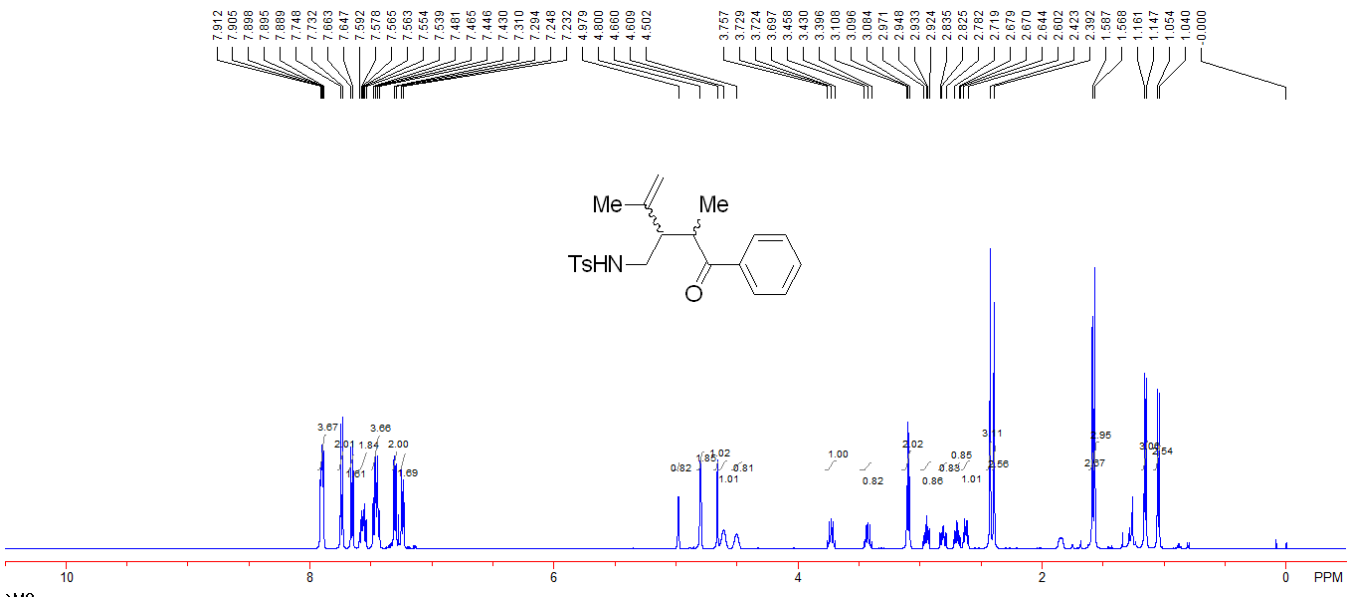
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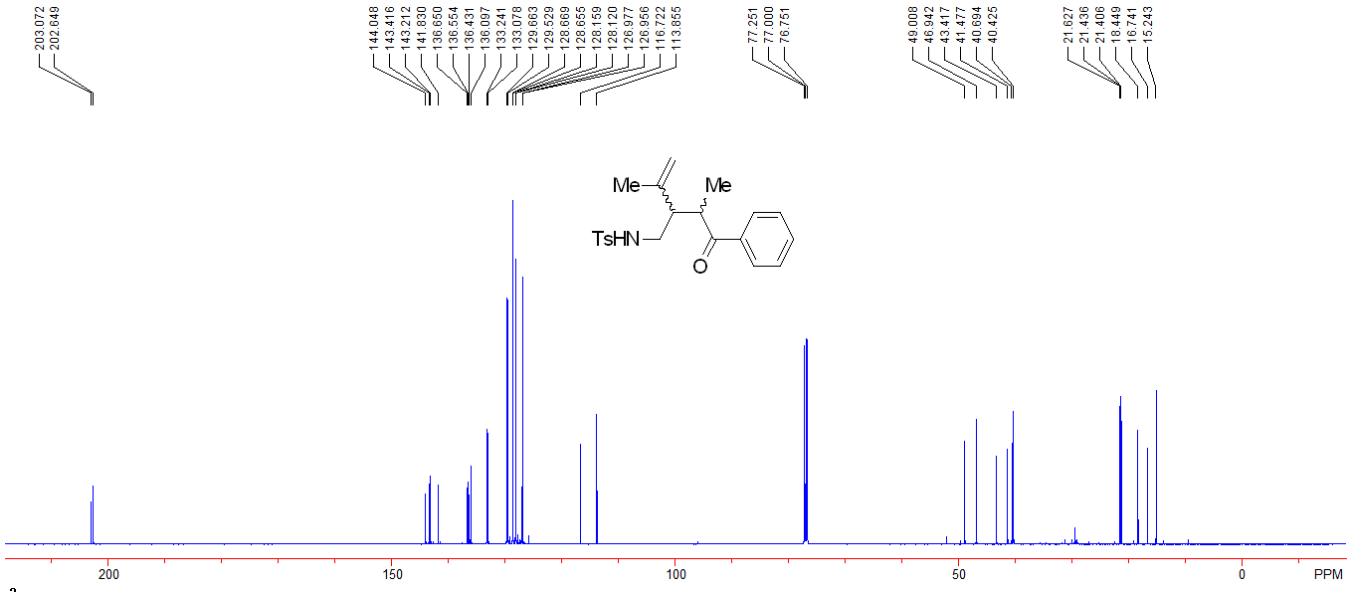
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