Supporting Information

NHC Ligand–Enabled Ni–Catalyzed Reductive Coupling of Alkyne and Imine Using Isopropanol as Reductant

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1. General Information

All reactions and manipulations that are sensitive to moisture or air were performed in an argon-filled glove box or using standard Schlenk techniques. Unless otherwise noted, commercially available reagents were received from commercial sources without further purification. Anhydrous tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen before use. The other solvents were all purified according to the standard procedures. Melting points were measured on X-4B microscope melting point apparatus and uncorrected. NMR spectra were recorded on Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on an Agilent6520 Q-TOF LC/MS with Electron Spray Ionization (ESI) resource.

2. Preparation of Imines

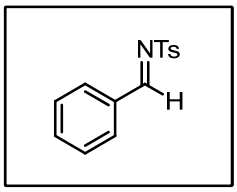
General procedure A[1]: A mixture of aldehyde (10 mmol), *p*-toluenesulfonamide and sodium *p*-toluenesulfinate (10 mmol) in formic acid (15 mL) and H_2O (15 mL) was stirred over night at room temperature. The resulting white precipitate was collected through filtration, washed with H_2O and pentane, and then dissolved in CH_2Cl_2 (100 mL). Saturated aqueous $NaHCO_3$ (70 mL) was added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to yield the corresponding crude imines, which was crystallized with EA/hexane to afford the pure imine.

General procedure B[2]: A mixture of aldehyde (1.0 equiv), *p*-toluenesulfonamide (1.0 equiv) and tetraethoxysilane (1.05 equiv) was heated at 160 °C for 6 h, and then cooled to room temperature. The resulting mixture was crystallized from ethyl acetate and *n*-hexane to afford the pure imine.

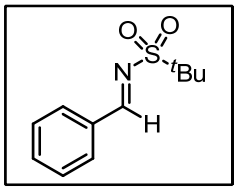
General procedure C[3]: To a solution of amine (1 equiv) in CH_2Cl_2 (0.32 M) were added 4Å molecular sieves (1 g/mmol), the corresponding aldehyde and 10 mol% of pyrrolidine (stock solution in CH_2Cl_2). The mixture was stirred in a sealed vial at 60 ºC, cooled and filtered through either a short pad of silica gel or Celite. The corresponding crude imines were crystallized from ethyl acetate and hexane to afford the pure imine.

General procedure D[4]: To the solution of *p*-toluenesulfonamide (1 equiv), triethylamine (4 equiv) and the corresponding aldehyde (1 equiv) in anhydrous CH_2Cl_2 (20 mL) at 0 °C was added titanium tetrachloride (0.5 equiv) dropwise. The mixture was stirred at 0°C for 30 min and the resulting precipitate was filtered off. The filtrate was concentrated under vacuum, dissolved in toluene (50 mL). After discarding the resulting triethylamine hydrochloride through filtration, the crude imine was obtained by concentration and recrystallized from acetone to give the pure

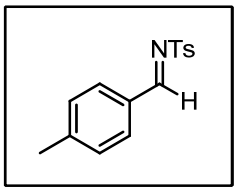
imine.



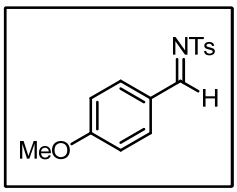
1a: *N*-Benzylidene-4-methylbenzenesulfonamide.[5]
Procedure A. White solid (78% yield). m.p. 111-112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 144.7, 135.2, 135.1, 132.4, 131.4, 129.9, 129.2, 128.2, 21.8.



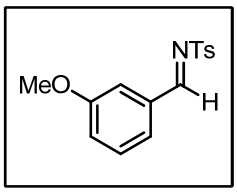
1b: (*E*)-*N*-Benzylidene-2-methylpropane-2-sulfonamide.[6]
Procedure C. White solid (68% yield). m.p. 76-77 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 1.50 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 135.1, 132.7, 131.3, 129.4, 58.6, 24.2.



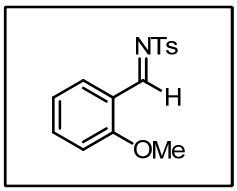
1c: 4-Methyl-*N*-(4-methylbenzylidene)benzenesulfonamide.[7]
Procedure C. White solid (77% yield). m.p. 115-116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.43 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 146.5, 144.5, 135.4, 131.5, 130.0, 129.9, 129.8, 128.1, 22.1, 21.7.



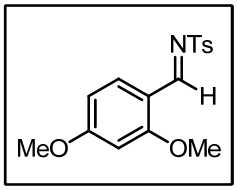
1d: *N*-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide.[5]
Procedure A. White solid (66% yield). m.p. 124-125 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.88 (d, J = 8.0 Hz, 4H), 7.33 (d, J = 7.6 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 165.4, 144.4, 135.9, 133.9, 129.9, 128.0, 125.4, 114.8, 55.8, 21.8.



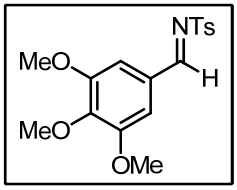
1e: *N*-(3-Methoxybenzylidene)-4-methylbenzenesulfonamide.[8]
Procedure C. White solid (61% yield). m.p. 56-58 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.50-7.42 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.16 (ddd, J = 8.0, 2.4, 1.2 Hz, 1H), 3.84 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 160.1, 144.8, 135.1, 133.7, 130.2, 129.9, 128.2, 125.4, 122.3, 113.4, 55.6, 21.8.



1f: *N*-(2-Methoxybenzylidene)-4-methylbenzenesulfonamide.[7]
Procedure C. White solid (85% yield). m.p. 105-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.05 (dd, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.04-6.93 (m, 2H), 3.92 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 161.7, 144.3, 137.1, 135.7, 129.8, 129.3, 128.0, 120.9, 120.8, 111.6, 55.8, 21.7.

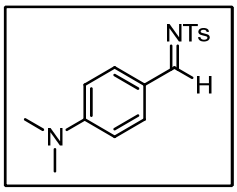


1g: *N*-(2,4-dimethoxybenzylidene)-4-methylbenzenesulfonamide.[9]
Procedure C. White solid (81% yield). m.p. 143-145 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.51 (dd, J = 8.8, 2.0 Hz, 1H), 6.40 (d, J = 2.0 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 165.6, 163.8, 144.0, 136.4, 131.4, 129.7, 127.8, 114.3, 106.9, 97.6, 55.9, 55.8, 21.7.

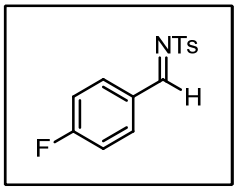


1h: 4-Methyl-*N*-(3,4,5-trimethoxybenzylidene)benzenesulfonamide.[3]
Procedure C. White solid (63% yield). m.p. 119-120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.16 (s, 2H), 3.93 (s, 3H), 3.89 (s, 6H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 153.5, 144.6,

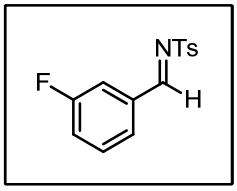
144.1, 135.3, 129.9, 128.1, 127.4, 108.5, 61.1, 56.4, 21.7.



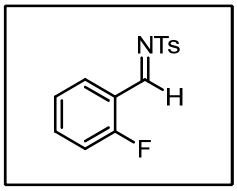
1i: *N*-(4-(dimethylamino)benzylidene)-4-methylbenzenesulfonamide.[5]
Procedure B. Light yellow solid (80% yield). m.p. 171-172 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.09 (s, 6H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 155.0, 143.6, 136.9, 134.0, 129.6, 127.6, 119.7, 111.4, 40.1, 21.6.



1j: *N*-(4-Fluorobenzylidene)-4-methylbenzenesulfonamide.[5]
Procedure B. White solid (63% yield). m.p. 103-105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.99-7.91 (m, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 8.4 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 166.9 (d, J = 256.8 Hz), 144.8, 135.1, 133.9 (d, J = 9.6 Hz), 129.9, 128.9 (d, J = 2.9 Hz), 128.2, 116.7 (d, J = 22.3 Hz), 21.8.

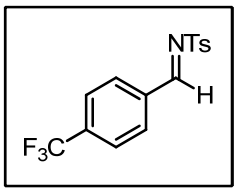


1k: *N*-(3-Fluorobenzylidene)-4-methylbenzenesulfonamide.[10]
Procedure B. White solid (87% yield). m.p. 82-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.72-7.62 (m, 2H), 7.53-7.45 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.33-7.28 (m, 1H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 162.9 (d, J = 247.6 Hz), 145.0, 134.7, 134.5 (d, J = 7.5 Hz), 130.9 (d, J = 7.8 Hz), 130.0, 128.2, 128.0, 122.0 (d, J = 21.5 Hz), 116.6 (d, J = 22.2 Hz), 21.7.

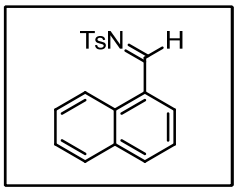


1l: *N*-(2-Fluorobenzylidene)-4-methylbenzenesulfonamide.[7]
Procedure B. White solid (75% yield). m.p. 135-137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.08 (t, J = 7.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.68-7.56 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 9.2 Hz, 1H), 2.45 (s,

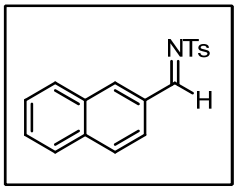
3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4 (d, J = 258.4 Hz), 163.7 (d, J = 6.1 Hz), 144.9, 137.2 (d, J = 9.2 Hz), 134.8, 130.0, 129.4, 128.3, 125.0 (d, J = 3.6 Hz), 120.5 (d, J = 8.7 Hz), 116.5 (d, J = 20.5 Hz), 21.8.



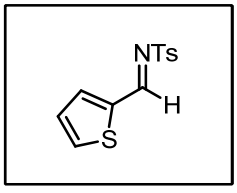
1m: 4-Methyl-*N*-(4-(trifluoromethyl)benzylidene)benzenesulfonamide.[11]
Procedure B. White solid (45% yield). m.p. 154-156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 145.2, 135.9 (q, J = 32.6 Hz), 135.5, 134.6, 131.5, 130.1, 128.4, 126.2 (q, J = 3.6 Hz), 123.4 (q, J = 271.3 Hz), 21.8.



1n: 4-Methyl-*N*-(naphthalen-1-ylmethylene)benzenesulfonamide.[5]
Procedure C. White solid (81% yield). m.p. 133-134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 9.00 (d, J = 8.8 Hz, 1H), 8.13 (dd, J = 20.4, 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.72-7.64 (m, 1H), 7.59 (q, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 144.5, 136.1, 135.4, 135.2, 133.7, 131.7, 129.8, 129.0, 128.9, 128.0, 127.5, 126.9, 125.1, 124.2, 21.6.

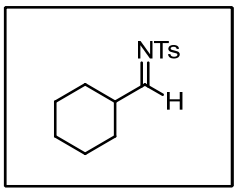


1o: 4-Methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide.[11]
Procedure C. White solid (59% yield). m.p. 112-113 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.34 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.98-7.85 (m, 5H), 7.64 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 144.7, 136.6, 136.2, 135.3, 132.7, 130.2, 129.9, 129.6, 129.3, 128.2, 128.2, 127.3, 124.2, 21.8.



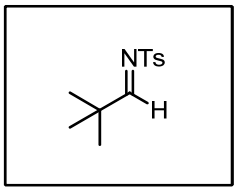
1p: 4-Methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide.[5]

Procedure B. Purple solid (82% yield). m.p. 118-119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.2 (t, J = 4.4 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 144.5, 139.3, 138.1, 136.9, 135.4, 129.8, 129.0, 127.9, 21.7.



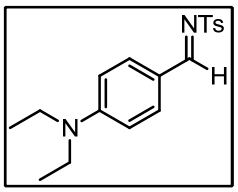
1q: *N*-(Cyclohexylmethylene)-4-methylbenzenesulfonamide.[4]

Procedure A. White solid (70% yield). m.p. 106-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, J = 4.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 1.93-1.59 (m, 5H), 1.39-1.12 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2, 144.7, 134.9, 129.9, 128.2, 43.8, 28.5, 25.7, 25.2, 21.8.



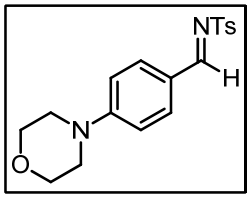
1r: *N*-(2,2-dimethylpropylidene)-4-methylbenzenesulfonamide.[4]

Procedure D. White solid (49% yield). m.p. 104-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.9, 144.7, 134.8, 129.9, 128.1, 37.9, 25.9, 21.7.



1s: *N*-(4-(diethylamino)benzylidene)-4-methylbenzenesulfonamide.

Procedure B. Orange solid (80% yield). m.p. 107-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 6.8 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.43 (q, J = 7.2 Hz, 4H), 2.41 (s, 3H), 1.20 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 153.0, 143.4, 137.1, 134.3, 129.5, 127.4, 119.1, 111.0, 44.8, 21.6, 12.5. **HRMS** (ESI) calcd. for $C_{18}H_{23}N_2O_2S$ ($[M+H]^+$) 331.1475, Found 331.1478.

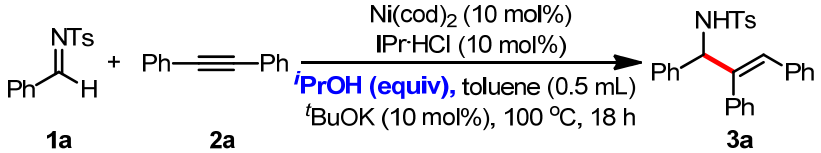


1t: 4-Methyl-*N*-(4-morpholinobenzylidene)benzenesulfonamide.

Procedure B. Orange solid (63% yield). m.p. 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 9.2 Hz, 2H), 3.84 (t, J = 4.8 Hz, 4H), 3.37 (t, J = 4.8 Hz, 4H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 155.5, 143.9, 136.3, 133.8, 129.7, 127.7, 122.2, 113.3, 66.4, 46.9, 21.6. **HRMS** (ESI) calcd. for $C_{18}H_{20}N_2NaO_3S$ ($[M+H]^+$) 367.1087, Found 367.1077.

3. Reaction Optimization

Table S1. Loading Effects of Alcohol

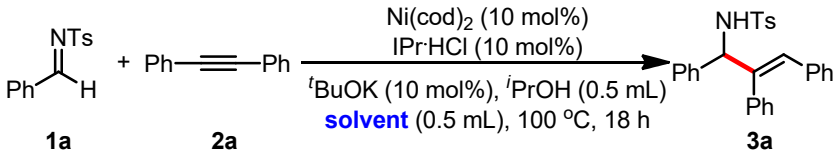


1a **2a** **3a**

entry	^{i}PrOH (equiv)	yield (%)[a,b]
1	5	7
2	20	13
3	40	25
4	65	**47**
5	80	32
6	100	33

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR with TCE as the internal standard.

Table S2. Solvent Effects

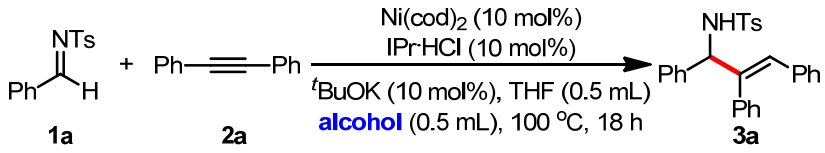


1a **2a** **3a**

entry	solvent	yield (%)[a,b]
1	toluene	47
2	benzene	62
3	*p*-xylene	8
4	DMF	19
5	CH_3CN	trace
6	dioxane	trace
7	**THF**	**72**
8	DCM	0
9	only ^{i}PrOH (0.5 mL)	52

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR with TCE as the internal standard.

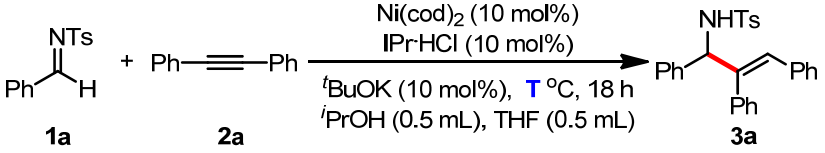
Table S3. Alcohol Effects



entry	alcohol	yield (%)[a,b]
1	^{i}PrOH	72
2	^{n}PrOH	trace
3	HFIP	0
4	EtOH	trace
5	MeOH	trace
6	BnOH	44
7	MBA	61

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR with TCE as the internal standard. MBA = 1-methylbenzyl alcohol.

Table S4. Temperature Effects

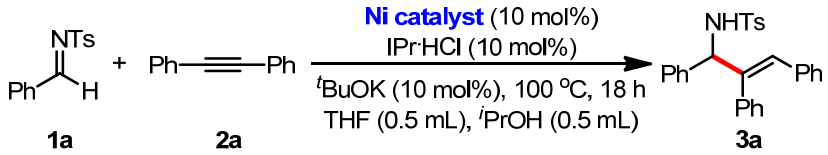


entry	T (°C)	yield (%)[a,b]
1	80	54
2	90	65
3	100	72
4	110	69
5	120	68
6	130	73

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR with TCE as the internal standard.

At 100 °C, the yield can be kept well every time. Above 100 °C, the yield will vary a little, but still less than 5%.

Table S5. Ni Catalyst Effects

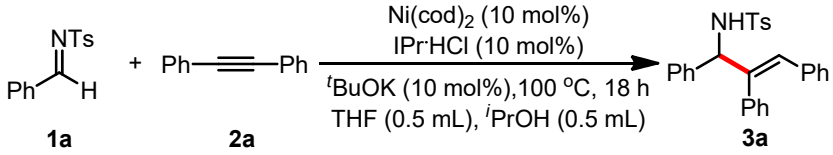


1a **2a** **3a**

entry	Ni catalyst	additive	yield (%)[a,b]
1	$Ni(cod)_2$	-	**72**
2	$Ni(OAc)_2{\cdot}4H_2O$	-	0
3	$Ni(PPh_3)_2Cl_2$	-	0
4	$NiBr_2$	-	0
5	$NiCl_2$·glyme	-	0
6	$NiCl_2$·glyme	Zn	0
7	$NiCl_2$·glyme	Mn	0
8	$Ni(acac)_2$	-	trace

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^1H NMR with TCE as the internal standard.

Table S6. Substrate Loading Effects

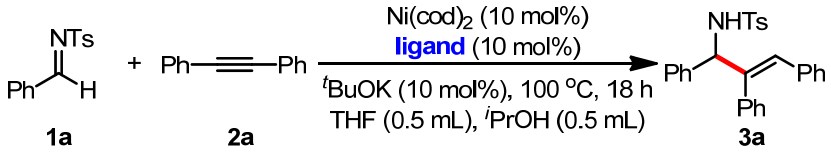


1a **2a** **3a**

entry	**1a** (mmol)	**2a** (mmol)	yield (%)[a,b]
1	0.2	0.1	13
2	0.15	0.1	37
3	0.12	0.1	**72**
4	0.1	0.1	44
5	0.1	0.12	30
6	0.1	0.15	15
7	0.1	0.2	16

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^1H NMR with TCE as the internal standard.

Table S7. Ligand Effects



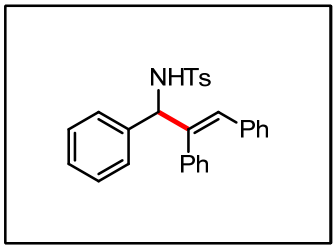
1a **2a** **3a**

entry	ligand	yield (%)[a,b]
1	PPh_3	0
2	PCy_3	0
3	BINAP	trace
4	dcype	0
5	SIPr·HCl	trace
6	ICy·HCl	39
7	IPr·HCl	72
8	IPr*·HCl	40
9	IPr^{Me}·HCl	54
10	IPr^{NQ}·HCl	15
11	AnIPr·HCl	86
12[c]	**AnIPr·HCl**	**91**
13[d]	AnIPr·HCl	86
14[e]	AnIPr·HCl	87

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR with TCE as the internal standard. [c]AnIPr·HCl (5 mol%). [d]AnIPr·HCl (2.5 mol%).[e]AnIPr·HCl (5 mol%) and $Ni(cod)_2$ (5 mol%).

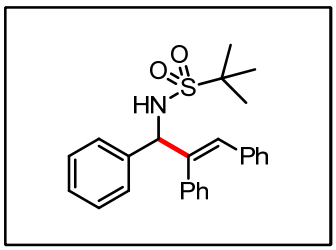
4. General Procedure for Reductive Coupling Reaction

To a 15 mL pressure tube were added $Ni(cod)_2$ (5.5 mg, 0.02 mmol), AnIPr·HCl (5.5 mg, 0.01 mmol), KO^{t}Bu (2.3 mg, 0.02 mmol), THF (1 mL), ^{i}PrOH (1 mL), alkynes (0.2 mmol) and imines (0.24 mmol) in a glove box. The tube was sealed with a Teflon cap and the mixture was stirred at 100 °C for 18 h. After cooled to room temperature, the crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum. The resulting residue was obtained by chromatography on silica gel column with petroleum ether/ethyl acetate as the eluent. The analytic data for reductive coupling products are listed below.

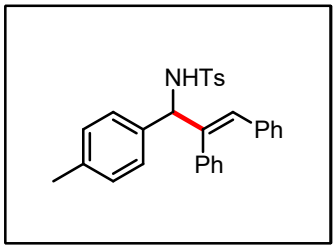


3a: **(*E*)-4-Methyl-*N*-(1,2,3-triphenylallyl)benzenesulfonamide**.
White solid (81% yield). m.p. 186-188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J =

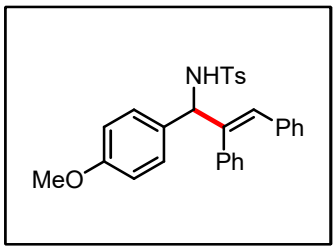
8.4 Hz, 2H), 7.29-7.24 (m, 5H), 7.24-7.17 (m, 3H), 7.13 (t, J = 7.6 Hz, 2H), 7.09-6.99 (m, 3H), 6.78-6.72 (m, 2H), 6.8 (d, J = 6.8 Hz, 2H), 6.48 (s, 1H), 5.36 (d, J = 7.6 Hz, 1H), 4.83 (d, J = 7.6 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 139.8, 139.2, 137.7, 137.3, 136.0, 130.1, 129.6, 129.5, 129.3, 128.8, 128.7, 128.0, 127.9, 127.9, 127.5, 127.4, 127.2, 64.4, 21.6. **HRMS** (ESI) calcd. for $C_{28}H_{29}N_2O_2S$ ($[M+NH_4]^+$) 457.1944, Found 457.1942.



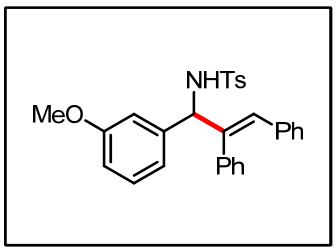
3b: **(*E*)-2-Methyl-*N*-(1,2,3-triphenylallyl)propane-2-sulfonamide.**
White solid (65% yield). m.p. 189-191 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 4H), 7.32-7.27 (m, 1H), 7.26-7.19 (m, 3H), 7.15-7.06 (m, 3H), 6.98-6.91 (m, 2H), 6.89 (d, J = 6.8 Hz, 2H), 6.78 (s, 1H), 5.52 (d, J = 10.0 Hz, 1H), 4.29 (d, J = 9.6 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 140.2, 137.4, 136.1, 129.7, 129.6, 129.4, 128.9, 128.8, 128.1, 128.0, 127.8, 127.3, 127.1, 65.5, 60.3, 24.3. **HRMS** (ESI) calcd. for $C_{25}H_{31}N_2O_2S$ ($[M+NH_4]^+$) 423.2101, Found 423.2101.



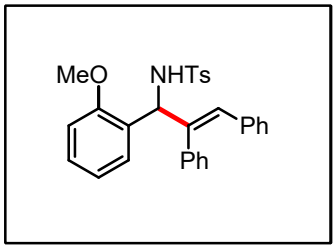
3c:**(*E*)-*N*-(2,3-diphenyl-1-(*p*-tolyl)allyl)-4-methylbenzenesulfonamide.**
White solid (79% yield). m.p. 120-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.24-7.17 (m, 3H), 7.17-7.10 (m, 4H), 7.10-7.01 (m, 5H), 6.79-6.72 (m, 2H), 6.69 (d, J = 6.8 Hz, 2H), 6.48 (s, 1H), 5.31 (d, J = 8.0 Hz, 1H), 4.77 (d, J = 8.0 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 139.9, 137.7, 137.6, 137.5, 136.2, 136.1, 129.8, 129.6, 129.4, 129.4, 129.3, 128.8, 127.9, 127.8, 127.5, 127.3, 127.1, 64.2, 21.6, 21.2. **HRMS** (ESI) calcd. for $C_{29}H_{31}N_2O_2S$ ($[M+NH_4]^+$) 471.2101, Found 471.2100.



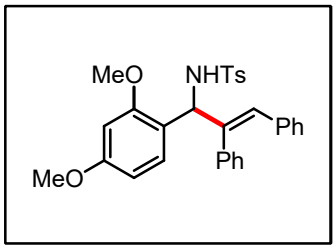
3d: (*E*)-*N*-(1-(4-Methoxyphenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide. White solid (82% yield). m.p. 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.23-7.11 (m, 7H), 7.08-7.01 (m, 3H), 6.80 (d, J = 8.8 Hz, 2H), 6.77-6.72 (m, 2H), 6.70 (d, J = 6.8 Hz, 2H), 6.47 (s, 1H), 5.30 (d, J = 7.6 Hz, 1H), 4.76 (d, J = 7.6 Hz, 1H), 3.79 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 143.5, 140.0, 140.0, 137.8, 137.5, 136.0, 131.2, 129.6, 129.4, 129.3, 128.8, 128.6, 128.0, 127.8, 127.5, 127.1, 114.0, 63.9, 55.4, 21.6. **HRMS** (ESI) calcd. for $C_{29}H_{31}N_2O_3S$ ($[M+NH_4]^+$) 487.2050, Found 487.2047.



3e: (*E*)-*N*-(1-(3-Methoxyphenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide. White solid (77% yield). m.p. 110-112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.24-7.18 (m, 4H), 7.17-7.10 (m, 2H), 7.09-7.00 (m, 3H), 6.88 (d, J = 7.6 Hz, 1H), 6.82-6.73 (m, 4H), 6.70 (d, J = 7.2 Hz, 2H), 6.48 (s, 1H), 5.32 (d, J = 8.0 Hz, 1H), 4.79 (d, J = 8.0 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 143.5, 140.8, 139.7, 137.7, 137.3, 136.0, 130.1, 129.7, 129.6, 129.5, 129.3, 128.8, 128.0, 127.9, 127.5, 127.2, 119.7, 113.4, 112.9, 64.4, 55.3, 21.6. **HRMS** (ESI) calcd. for $C_{29}H_{31}N_2O_3S$ ($[M+NH_4]^+$) 487.2050, Found 487.2046.

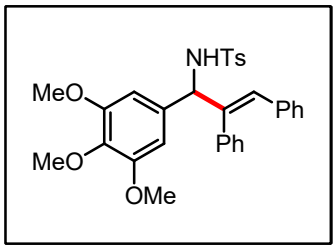


3f: **(*E*)-*N*-(1-(2-Methoxyphenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide**. White solid (68% yield). m.p. 142-144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.23-7.10 (m, 4H), 7.08-6.99 (m, 5H), 6.96 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 7.2 Hz, 2H), 6.79-6.72 (m, 3H), 6.70 (d, J = 8.0 Hz, 1H), 6.48 (s, 1H), 5.47 (s, 2H), 3.66 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 142.9, 140.4, 138.7, 137.7, 136.5, 129.3, 129.2, 128.9, 128.5, 128.4, 127.8, 127.3, 127.1, 126.8, 126.8, 120.5, 110.9, 61.1, 55.4, 21.5. **HRMS** (ESI) calcd. for $C_{29}H_{31}N_2O_3S$ ($[M+NH_4]^+$) 487.2050, Found 487.2047.



3g:

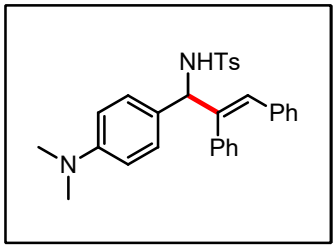
(*E*)-*N*-(1-(2,4-Dimethoxyphenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide. White solid (87% yield). m.p. 129-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.23-7.12 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 7.05-6.98 (m, 3H), 6.93-6.83 (m, 3H), 6.80-6.69 (m, 2H), 6.48 (s, 1H), 6.31-6.24 (m, 2H), 5.41 (d, J = 8.4 Hz, 1H), 5.36 (d, J = 8.4 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 157.7, 142.8, 140.6, 138.8, 137.8, 136.5, 129.9, 129.3, 129.2, 128.5, 128.2, 127.8, 127.2, 127.1, 126.7, 119.4, 104.0, 98.8, 60.6, 55.4, 55.4, 21.5. **HRMS** (ESI) calcd. for $C_{30}H_{29}NNaO_4S$ ($[M+Na]^+$) 522.1710, Found 522.1700.



3h:

(*E*)-*N*-(2,3-Diphenyl-1-(3,4,5-trimethoxyphenyl)allyl)-4-methylbenzenesulfonamide

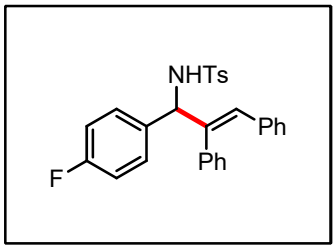
White solid (89% yield). m.p. 163-165 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.24-7.20 (m, 3H), 7.17 (t, J = 7.4 Hz, 2H), 7.11-7.02 (m, 3H), 6.80-6.70 (m, 4H), 6.48 (s, 1H), 6.43 (s, 2H), 5.29 (d, J = 7.6 Hz, 1H), 4.85 (d, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 6H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 143.5, 139.8, 137.8, 137.4, 137.3, 136.0, 134.7, 129.8, 129.5, 129.5, 129.3, 128.8, 128.0, 127.9, 127.4, 127.2, 104.5, 64.5, 60.9, 56.1, 21.5. **HRMS** (ESI) calcd. for $C_{31}H_{35}N_2O_5S$ ($[M+NH_4]^+$) 547.2261, Found 547.2257.



3i:

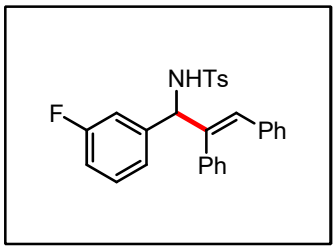
(*E*)-*N*-(1-(4-(Dimethylamino)phenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide.

White solid (87% yield). m.p. 151-153 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.18-7.11 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 7.07-7.01 (m, 3H), 6.81-6.69 (m, 4H), 6.61 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 5.24 (d, J = 7.2 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 2.93 (s, 6H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.2, 143.2, 140.3, 138.1, 138.0, 136.3, 129.6, 129.5, 129.3, 129.1, 128.6, 128.4, 127.9, 127.6, 127.5, 126.9, 126.5, 112.5, 64.0, 40.6, 21.6. **HRMS** (ESI) calcd. for $C_{30}H_{31}N_2O_2S$ ($[M+H]^+$) 483.2101, Found 483.2100.



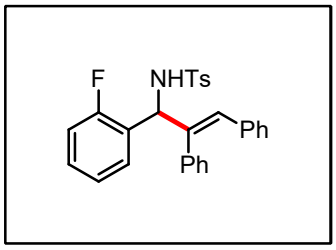
3j: **(*E*)-*N*-(1-(4-Fluorophenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide.**

White solid (74% yield). m.p. 166-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 2H), 7.24-7.18 (m, 5H), 7.18-7.12 (m, 2H), 7.10-7.01 (m, 3H), 6.95 (t, J = 8.6 Hz, 2H), 6.77-6.71 (m, 2H), 6.68 (d, J = 7.2 Hz, 2H), 6.45 (s, 1H), 5.34 (d, J = 8.0 Hz, 1H), 4.90 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245.1 Hz), 143.6, 139.7, 137.6, 137.2, 135.8, 135.0 (d, J = 3.0 Hz), 130.1, 129.6, 129.4, 129.3, 129.1 (d, J = 8.0 Hz), 128.9, 128.0, 128.0, 127.4, 127.3, 115.5 (d, J = 21.4 Hz), 63.8, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.9. **HRMS** (ESI) calcd. for $C_{28}H_{28}FN_2O_2S$ ($[M+NH_4]^+$) 475.1850, Found 475.1858.

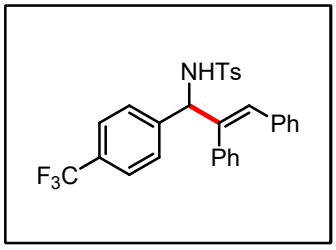


3k: **(*E*)-*N*-(1-(3-Fluorophenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide.**

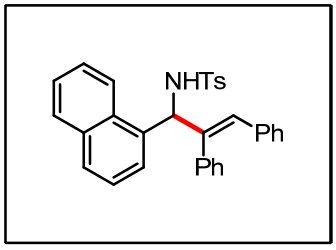
White solid (64% yield). m.p. 173-175 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.26-7.19 (m, 4H), 7.15 (t, J = 7.4 Hz, 2H), 7.12-7.02 (m, 4H), 7.02-6.91 (m, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 7.2 Hz, 2H), 6.45 (s, 1H), 5.35 (d, J = 8.0 Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0 (d, J = 245.0 Hz), 143.7, 142.1, 142.0, 139.3, 137.6, 136.8, 135.7, 130.7, 130.2 (d, J = 8.2 Hz), 129.7, 129.4 (d, J = 5.8 Hz), 129.0, 128.1, 128.0, 127.5, 127.4, 123.0 (d, J = 2.6 Hz), 114.8 (d, J = 21.1 Hz), 114.4 (d, J = 22.5 Hz), 64.0, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.9. **HRMS** (ESI) calcd. for $C_{28}H_{28}FN_2O_2S$ ($[M+NH_4]^+$) 475.1850, Found 475.1856.



3l: **(*E*)-*N*-(1-(2-Fluorophenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide.** White solid (48% yield). m.p. 180-182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 2H), 7.24-7.12 (m, 5H), 7.11 (d, J = 7.6 Hz, 2H), 7.07-6.97 (m, 4H), 6.92 (t, J = 9.4 Hz, 1H), 6.87-6.80 (m, 2H), 6.78-6.69 (m, 2H), 6.42 (s, 1H), 5.55 (d, J = 7.6 Hz, 1H), 5.04 (d, J = 7.6 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2 (d, J = 245.7 Hz), 143.3, 139.4, 137.6, 137.1, 135.9, 129.7, 129.5, 129.5, 129.3, 129.2 (d, J = 3.6 Hz), 128.8, 127.9, 127.8, 127.2, 126.7, 126.6, 124.1 (d, J = 3.4 Hz), 115.6 (d, J = 21.4 Hz), 59.0, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.7. **HRMS** (ESI) calcd. for $C_{28}H_{28}FN_2O_2S$ ($[M+NH_4]^+$) 475.1850, Found 475.1851.

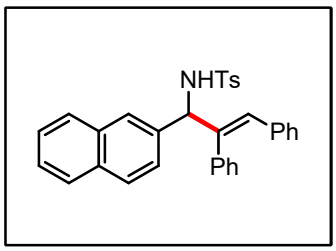


3m:
(*E*)-*N*-(2,3-Diphenyl-1-(4-(trifluoromethyl)phenyl)allyl)-4-methylbenzenesulfonamide.
White solid (29% yield). m.p. 134-136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.25-7.13 (m, 5H), 7.11-7.00 (m, 3H), 6.74 (d, J = 7.6 Hz, 2H), 6.66 (d, J = 7.2 Hz, 2H), 6.44 (s, 1H), 5.41 (d, J = 8.0 Hz, 1H), 4.92 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 143.3, 139.2, 137.3, 136.8, 135.6, 130.7, 129.9 (q, J = 32.4 Hz), 129.7, 129.3, 129.0, 128.1, 128.0, 127.8, 127.5, 127.4, 125.5 (q, J = 3.6 Hz), 124.1 (q, J = 270.5 Hz), 64.1, 21.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3. **HRMS** (ESI) calcd. for $C_{29}H_{28}F_3N_2O_2S$ ($[M+NH_4]^+$) 525.1818, Found 525.1820.

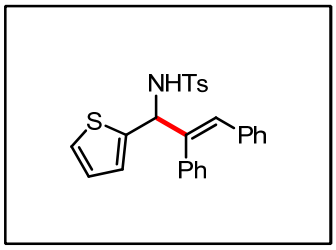


3n: (*E*)-4-Methyl-*N*-(1-(naphthalen-1-yl)-2,3-diphenylallyl)benzenesulfonamide. White solid (65% yield). m.p. 180-182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-8.05

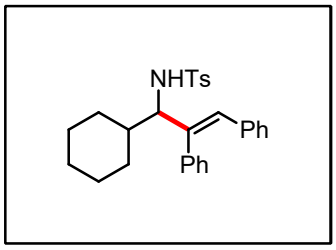
(m, 1H), 7.88-7.80 (m, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.56-7.43 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.21-7.11 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 7.06-6.98 (m, 3H), 6.96 (d, J = 6.8 Hz, 2H), 6.69 (d, J = 6.8 Hz, 2H), 6.44 (s, 1H), 6.14 (d, J = 6.4 Hz, 1H), 4.98 (d, J = 6.4 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.1, 138.5, 137.7, 136.1, 134.1, 134.1, 131.1, 130.5, 129.5, 129.3, 129.1, 129.0, 128.9, 128.8, 127.9, 127.7, 127.3, 127.1, 126.8, 126.2, 125.9, 125.2, 123.3, 60.7, 21.5. **HRMS** (ESI) calcd. for $C_{32}H_{31}N_2O_2S$ ($[M+NH_4]^+$) 507.2101, Found 507.2094.



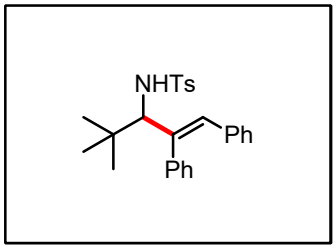
3o: **(*E*)-4-Methyl-*N*-(1-(naphthalen-2-yl)-2,3-diphenylallyl)benzenesulfonamide**. White solid (78% yield). m.p. 149-151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.79 (m, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.74-7.64 (m, 4H), 7.52-7.44 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 7.22-7.14 (m, 3H), 7.14-7.02 (m, 5H), 6.77 (d, J = 6.8 Hz, 2H), 6.69 (d, J = 7.6 Hz, 2H), 6.55 (s, 1H), 5.52 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 139.7, 137.6, 137.4, 136.4, 135.9, 133.2, 132.8, 130.2, 129.5, 129.4, 129.3, 128.8, 128.5, 128.2, 127.9, 127.8, 127.6, 127.4, 127.2, 126.4, 126.3, 126.2, 125.2, 64.5, 21.5. **HRMS** (ESI) calcd. for $C_{32}H_{31}N_2O_2S$ ($[M+NH_4]^+$) 507.2101, Found 507.2099.



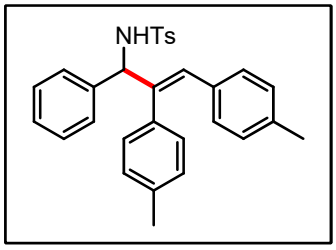
3p: **(*E*)-*N*-(2,3-Diphenyl-1-(thiophen-2-yl)allyl)-4-methylbenzenesulfonamide.** White solid (65% yield). m.p. 148-150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.25-7.20 (m, 4H), 7.16 (t, J = 7.4 Hz, 2H), 7.12-7.03 (m, 3H), 6.97-6.89 (m, 2H), 6.84-6.78 (m, 2H), 6.76 (d, J = 6.8 Hz, 2H), 6.56 (s, 1H), 5.59 (d, J = 8.4 Hz, 1H), 4.89 (d, J = 8.4 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 143.7, 139.6, 137.7, 136.7, 135.8, 130.0, 129.7, 129.5, 129.4, 128.9, 128.1, 128.0, 127.5, 127.4, 127.3, 125.9, 125.8, 60.8, 21.6. **HRMS** (ESI) calcd. for $C_{26}H_{27}N_2O_2S_2$ ($[M+NH_4]^+$) 463.1508, Found 463.1507.



3q: **(*E*)-*N*-(1-Cyclohexyl-2,3-diphenylallyl)-4-methylbenzenesulfonamide.**
White solid (83% yield). m.p. 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.30-7.24 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.09-6.96 (m, 3H), 6.88-6.78 (m, 2H), 6.68-6.59 (m, 2H), 6.19 (s, 1H), 4.43 (d, J = 9.6 Hz, 1H), 3.92 (t, J = 9.0 Hz, 1H), 2.30 (s, 3H), 1.96 (d, J = 12.4 Hz, 1H), 1.86-1.68 (m, 3H), 1.64 (s, 1H), 1.43-1.29 (m, 1H), 1.24-1.02 (m, 4H), 1.01-0.84 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 138.8, 138.4, 137.7, 136.1, 130.1, 129.6, 129.4, 129.1, 128.9, 127.8, 127.7, 127.4, 126.8, 66.8, 40.1, 31.0, 28.9, 26.4, 26.1, 21.5. **HRMS** (ESI) calcd. for $C_{28}H_{35}N_2O_2S$ ($[M+NH_4]^+$) 463.2414, Found 463.2410.

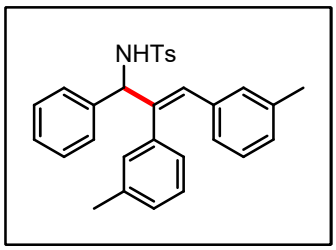


3r:
(*E*)-*N*-(4,4-Dimethyl-1,2-diphenylpent-1-en-3-yl)-4-methylbenzenesulfonamide.
White solid (23% yield). m.p. 167-169 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.23-7.15 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 7.06-6.96 (m, 5H), 6.62-6.52 (m, 2H), 6.24 (s, 1H), 5.00 (d, J = 9.2 Hz, 1H), 4.10 (d, J = 9.2 Hz, 1H), 2.18 (s, 3H), 0.84 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 140.0, 139.1, 138.2, 136.6, 131.5, 129.8, 129.6, 129.2, 128.6, 127.7, 127.4, 126.6, 68.8, 36.5, 27.3, 21.4. **HRMS** (ESI) calcd. for $C_{26}H_{29}NNaO_2S$ ($[M+Na]^+$) 442.1811, Found 442.1815.

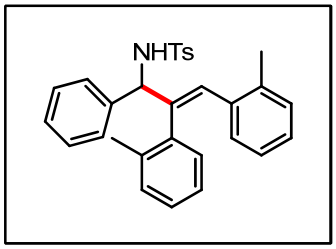


4a: **(*E*)-4-Methyl-*N*-(1-phenyl-2,3-di-p-tolylallyl)benzenesulfonamide.**
White solid (81% yield). m.p. 168-170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.33-7.26 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.0 Hz, 2H), 6.38 (s, 1H), 5.33 (d, J = 8.0 Hz, 1H), 4.83 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 2.22

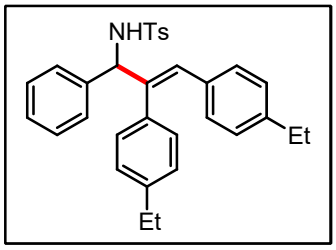
(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 139.5, 138.8, 137.8, 137.5, 136.9, 134.2, 133.2, 129.9, 129.5, 129.5, 129.3, 129.2, 128.7, 128.6, 127.7, 127.5, 127.4, 64.5, 21.6, 21.3, 21.2. **HRMS** (ESI) calcd. for $C_{30}H_{33}N_2O_2S$ ($[M+NH_4]^+$) 485.2257, Found 485.2253.



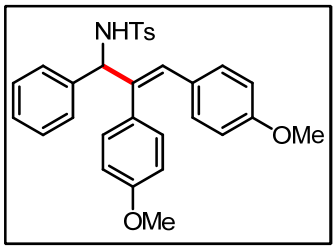
4b: **(*E*)-4-Methyl-*N*-(1-phenyl-2,3-di-m-tolylallyl)benzenesulfonamide.**
White solid (77% yield). m.p. 116-117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.33-7.26 (m, 5H), 7.21 (d, J = 8.0 Hz, 2H), 7.04-6.97 (m, 2H), 6.95-6.84 (m, 2H), 6.60 (s, 1H), 6.52 (d, J = 7.2 Hz, 1H), 6.48-6.41 (m, 2H), 6.40 (s, 1H), 5.34 (d, J = 7.6 Hz, 1H), 4.81 (d, J = 7.6 Hz, 1H), 2.37 (s, 3H), 2.14 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.8, 139.4, 138.3, 137.8, 137.3, 137.2, 135.9, 130.3, 130.0, 129.9, 129.6, 128.6, 128.5, 128.5, 127.9, 127.8, 127.7, 127.4, 127.4, 126.5, 126.2, 64.5, 21.6, 21.4, 21.4. **HRMS** (ESI) calcd. for $C_{30}H_{33}N_2O_2S$ ($[M+NH_4]^+$) 485.2257, Found 485.2255.



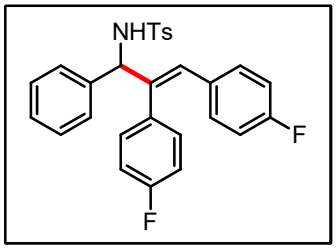
4c: (*E*)-4-Methyl-*N*-(1-phenyl-2,3-di-o-tolylallyl)benzenesulfonamide.
White solid (64% yield, *Z*/*E* = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.25-7.17 (m, 8H), 7.17-7.11 (m, 4H), 7.10-7.00 (m, 7H), 6.99-6.80 (m, 7H), 6.75-6.65 (m, 3H), 6.62 (d, J = 7.6 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.33 (d, J = 6.8 Hz, 1H), 5.10 (d, J = 6.0 Hz, 1H), 5.07-4.98 (m, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 1.78 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 143.2, 140.2, 139.7, 139.3, 139.2, 137.5, 137.3, 136.9, 136.7, 136.4, 136.4, 136.3, 136.2, 135.5, 135.4, 130.5, 130.3, 130.0, 129.7, 129.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.8, 127.6, 127.6, 127.3, 127.3, 127.2, 127.2, 127.0, 125.7, 125.4, 125.1, 64.3, 64.3, 21.5, 21.5, 20.0, 19.9, 19.3, 19.0. **HRMS** (ESI) calcd. for $C_{30}H_{33}N_2O_2S$ ($[M+NH_4]^+$) 485.2257, Found 485.2252.



4d: **(*E*)-*N*-(2,3-bis(4-ethylphenyl)-1-phenylallyl)-4-methylbenzenesulfonamide.** White solid (72% yield). m.p. 139-141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.35-7.24 (m, 5H), 7.21 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.0 Hz, 2H), 6.37 (s, 1H), 5.33 (d, J = 8.0 Hz, 1H), 4.79 (d, J = 8.0 Hz, 1H), 2.59 (q, J = 7.6 Hz, 2H), 2.52 (q, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H), 1.14 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 143.4, 143.3, 139.6, 138.7, 137.8, 134.4, 133.4, 130.0, 129.6, 129.3, 129.3, 128.6, 128.3, 127.7, 127.5, 127.4, 64.6, 28.6, 28.6, 21.6, 15.4, 15.3. **HRMS** (ESI) calcd. for $C_{32}H_{37}N_2O_2S$ ($[M+NH_4]^+$) 513.2570, Found 513.2564.

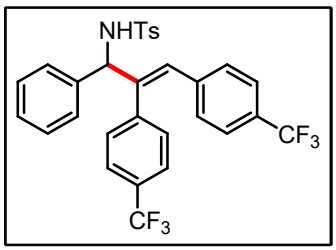


4e:
(*E*)-*N*-(2,3-bis(4-methoxyphenyl)-1-phenylallyl)-4-methylbenzenesulfonamide.
White solid (74% yield). m.p. 127-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.31-7.23 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 6.73-6.64 (m, 4H), 6.63-6.54 (m, 4H), 6.35 (s, 1H), 5.31 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 8.0 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 158.7, 143.4, 139.6, 137.8, 137.4, 137.3, 130.7, 130.6, 129.6, 129.3, 128.7, 128.6, 127.7, 127.5, 127.3, 114.3, 113.4, 64.6, 55.3, 21.6. **HRMS** (ESI) calcd. for $C_{30}H_{29}NNaO_4S$ ($[M+Na]^+$) 522.1710, Found 522.1713.

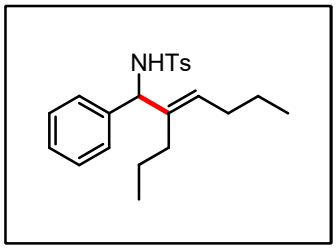


4f: **(*E*)-*N*-(2,3-bis(4-fluorophenyl)-1-phenylallyl)-4-methylbenzenesulfonamide**.
White solid (73% yield). m.p. 139-141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.33-7.15 (m, 8H), 6.85 (t, J = 8.0 Hz, 2H), 6.80-6.63 (m, 5H), 6.52 (s,

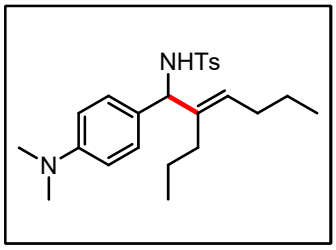
1H), 5.31 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, J = 246.0 Hz), 161.8 (d, J = 246.2 Hz), 143.6, 139.0, 138.8, 137.7, 133.2 (d, J = 3.3 Hz), 131.9 (d, J = 3.3 Hz), 131.2 (d, J = 7.8 Hz), 130.9 (d, J = 7.8 Hz), 129.6, 129.0, 128.8, 128.0, 127.4, 127.3, 115.9 (d, J = 21.3 Hz), 115.0 (d, J = 21.1 Hz), 64.4, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.4, -114.0. **HRMS** (ESI) calcd. for $C_{28}H_{27}F_2N_2O_2S$ ($[M+NH_4]^+$) 493.1756, Found 493.1752.



4g:
(*E*)-4-Methyl-*N*-(1-phenyl-2,3-bis(4-(trifluoromethyl)phenyl)allyl)benzenesulfonamide.
White solid (53% yield). m.p. 177-179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30-7.26 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.18-7.13 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.71 (s, 1H), 5.32 (d, J = 6.8 Hz, 1H), 4.89 (d, J = 6.8 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 141.6, 141.4, 139.1, 138.1, 137.4, 130.1 (q, J = 32.4 Hz), 129.7, 129.7, 129.4, 129.2 (q, J = 32.2 Hz), 129.1, 129.0, 128.3, 127.4, 127.3, 125.8 (q, J = 3.6 Hz), 125.0 (q, J = 3.6 Hz), 124.0 (q, J = 270.6 Hz), 124.1 (q, J = 270.3 Hz), 64.1, 21.5. **HRMS** (ESI) calcd. for $C_{30}H_{27}F_6N_2O_2S$ ($[M+NH_4]^+$) 593.1692, Found 593.1691.



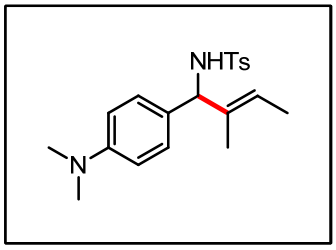
4h: **(*E*)-4-Methyl-*N*-(1-phenyl-2-propylhex-2-en-1-yl)benzenesulfonamide**.
White solid (52% yield). m.p. 69-71 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.23-7.16 (m, 5H), 7.12-7.06 (m, 2H), 5.24 (t, J = 7.2 Hz, 1H), 4.88 (d, J = 7.6 Hz, 1H), 4.72 (d, J = 7.6 Hz, 1H), 2.39 (s, 3H), 1.97-1.84 (m, 3H), 1.76-1.64 (m, 1H), 1.25 (q, J = 7.2 Hz, 2H), 1.20 (q, J = 7.2 Hz, 2H), 0.83 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.0, 140.0, 137.9, 137.9, 129.4, 128.9, 128.4, 127.4, 127.4, 127.3, 62.0, 31.0, 29.8, 22.8, 22.1, 21.5, 14.3, 14.0. **HRMS** (ESI) calcd. for $C_{22}H_{29}NNaO_2S$ ($[M+Na]^+$) 394.1811, Found 394.1815.



4i:

(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-propylhex-2-en-1-yl)-4-methylbenzenesulfonamide.

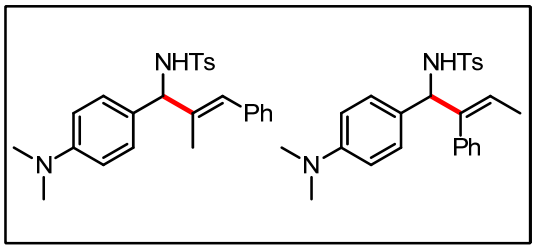
White solid (78% yield). m.p. 83-85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 5.33 (t, J = 7.0 Hz, 1H), 4.77 (d, J = 6.8 Hz, 1H), 4.64 (d, J = 6.8 Hz, 1H), 2.90 (s, 6H), 2.39 (s, 3H), 2.00-1.83 (m, 3H), 1.70-1.56 (m, 1H), 1.34-1.13 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 142.8, 138.1, 138.0, 129.3, 128.3, 127.7, 127.6, 127.4, 112.4, 61.5, 40.6, 31.2, 29.8, 22.9, 22.0, 21.6, 14.3, 14.0. **HRMS** (ESI) calcd. for $C_{24}H_{35}N_2O_2S$ ($[M+H]^+$) 415.2414, Found 415.2413.



4j:

(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide.

White solid (55% yield). m.p. 121-123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 5.45 (q, J = 6.8 Hz, 1H), 4.75 (d, J = 7.2 Hz, 1H), 4.64 (d, J = 7.2 Hz, 1H), 2.90 (s, 6H), 2.40 (s, 3H), 1.49 (d, J = 6.8 Hz, 3H), 1.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 142.9, 137.9, 134.0, 129.3, 127.8, 127.5, 127.2, 122.5, 112.4, 64.0, 40.6, 21.6, 13.3, 13.0. **HRMS** (ESI) calcd. for $C_{20}H_{27}N_2O_2S$ ($[M+H]^+$) 359.1788, Found 359.1784.

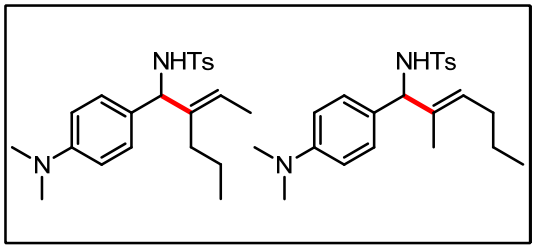


4k:

(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-methyl-3-phenylallyl)-4-methylbenzenesulfonamide

(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-phenylbut-2-en-1-yl)-4-methylbenzenesulfonamide (2.6 : 1 mixture).

Yellow oil (48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 0.78H), 7.23-7.26 (m, 1.95H), 7.24-7.15 (m, 5H), 7.07 (d, J = 7.6 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 0.78H), 6.80-6.74 (m, 0.78H), 6.61 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.8 Hz, 0.78H), 6.46 (s, 1H), 5.66 (q, J = 6.6 Hz 0.39H), 5.11 (d, J = 7.2 Hz, 0.39H), 4.94 (d, J = 7.2 Hz, 1H), 4.81 (d, J = 7.2 Hz, 1H), 4.63 (d, J = 7.2 Hz, 0.39H), 2.92 (s, 6H), 2.91 (s, 2.34H), 2.41 (s, 1.17H), 2.37 (s, 3H), 1.58 (s, 3H), 1.43 (d, J = 7.2 Hz, 1.17H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.1, 150.0, 143.1, 142.9, 140.3, 138.0, 137.9, 137.4, 136.2, 129.5, 129.4, 129.3, 129.0, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 127.1, 127.0, 126.7, 126.5, 125.0, 112.5, 112.4, 64.4, 63.1, 40.6, 40.6, 21.6, 21.5, 15.2, 14.5. **HRMS** (ESI) calcd. for $C_{25}H_{29}N_2O_2S$ ($[M+H]^+$) 421.1944, Found 421.1948.



4l:

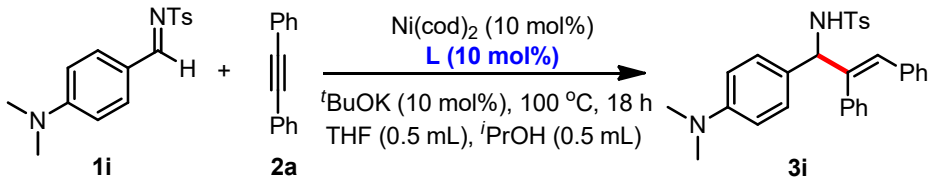
(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-ethylidenepentyl)-4-methylbenzenesulfonamide

(*E*)-*N*-(1-(4-(dimethylamino)phenyl)-2-methylhex-2-en-1-yl)-4-methylbenzenesulfonamide (1.4 : 1 mixture).

Yellow oil (49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1.42H), 7.62 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.2 Hz, 1.42H), 7.19 (d, J = 7.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 1.42H), 6.89 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.8 Hz, 1.42H), 6.54 (d, J = 8.8 Hz, 2H), 5.40 (q, J = 6.8 Hz, 1H), 5.36 (t, J = 6.8 Hz, 0.71H), 4.79-4.71 (m, 2.42H), 4.65 (d, J = 6.8 Hz, 1H), 2.90 (s, 4.26H), 2.90 (s, 6H), 2.40 (s, 2.13H), 2.39 (s, 3H), 2.00-1.83 (m, 2H), 1.74-1.62 (m, 1H), 1.52 (d, J = 6.4 Hz, 3H), 1.35 (s, 2.13H), 1.32-1.17 (m, 3.84H), 0.85 (t, J = 7.2 Hz, 2.13H), 0.79 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.9, 142.8, 142.7, 138.9, 138.0, 133.3, 129.9, 129.6, 129.5, 129.3, 129.2, 128.2, 128.0, 127.8, 127.6, 127.3, 126.4, 121.9, 112.4, 112.4, 63.9, 61.6, 40.6, 30.7, 29.8, 22.5, 21.6, 21.5, 14.2, 13.9, 13.3. **HRMS** (ESI) calcd. for $C_{22}H_{31}N_2O_2S$ ($[M+H]^+$) 387.2101, Found 387.2090.

5. Reaction Optimization for Asymmetric Control

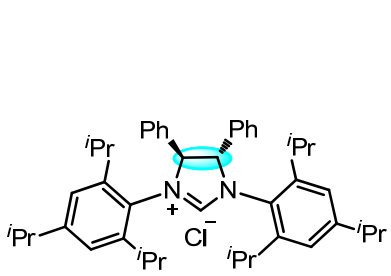
Table S8. Chiral Ligand Examination



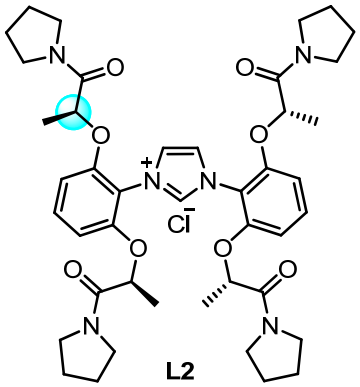
1i **2a** **3i**

entry	L	yield (%)[a,b]	ee (%)[c]
1	**L1**	37	-5
2	**L2**	0	--
3	**L3**	12	-42
4	**L4**	8	12
5	**L5**	53	70
6	**AnIPe-1**	**67**	**76**

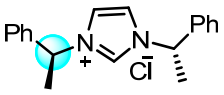
[a]Reaction conditions: **1i** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR analysis with TCE as the internal standard. [c]Determined by chiral HPLC.



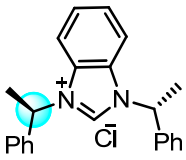
L1



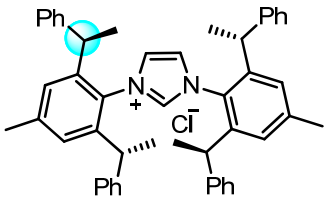
L2



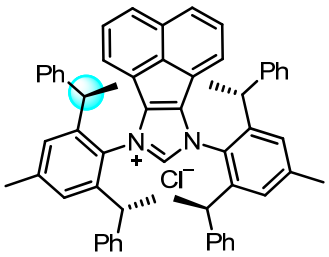
L3



L4

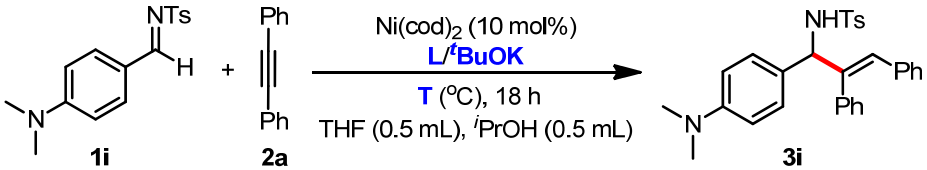


L5



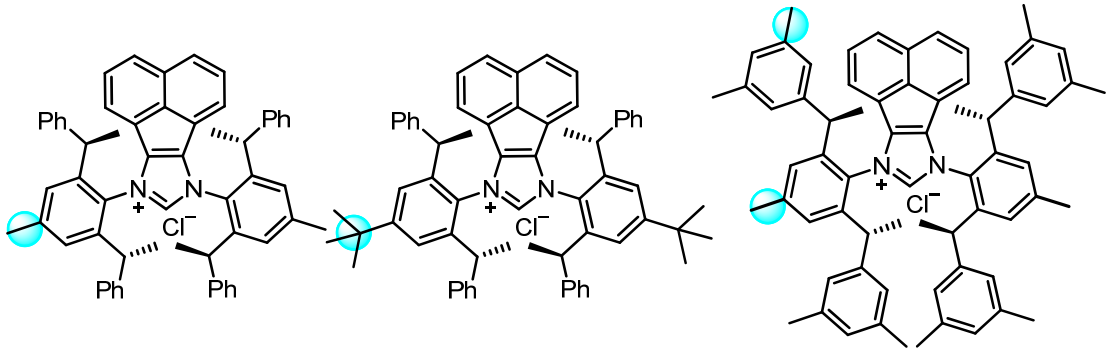
AnIPe-1

Table S9. Conditions Optimization



entry	L (mol%)	*t*-BuOK (mol%)	T (°C)	yield (%)[a,b]	ee (%)[c]
1	**AnIPe-1** (5)	5	100	66	62
2	**AnIPe-1** (10)	10	100	67	76
3	**AnIPe-1** (15)	15	100	64	76
4	**AnIPe-1** (10)	10	80	63	77
5	**AnIPe-2** (10)	10	80	52	82
6	**AnIPe-3** (10)	10	80	59	87
7[d]	**AnIPe-3** (10)	10	60	**57**	**91**

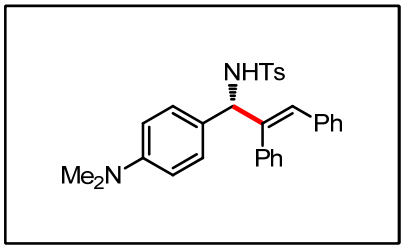
[a]Reaction conditions: **1i** (0.12 mmol), **2a** (0.1 mmol). [b]Determined by ^{1}H NMR analysis with TCE as the internal standard. [c]Determined by chiral HPLC. [d]THF (1.5 mL), ^{i}PrOH (1.5 mL) .



AnIPe-1 **AnIPe-2** **AnIPe-3**

6. General Procedure for Asymmetric Control

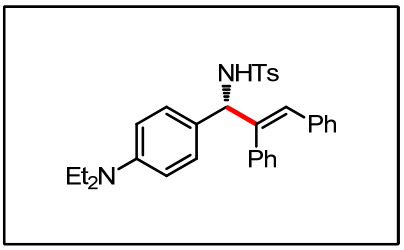
To a 15 mL pressure tube were added Ni(cod)$_2$ (2.75 mg, 0.01 mmol), AnIPe-3 (9.4 mg, 0.01 mmol), KO^{t}Bu (1.3 mg, 0.012 mmol), THF (1.5 mL), ^{i}PrOH (1.5 mL), alkynes (0.1 mmol) and imines (0.12 mmol) in a glove box. The tube was sealed with a Teflon cap and the mixture was stirred at 60 °C for 18 h. After cooled to room temperature, the crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum. The resulting residue was obtained by chromatography on silica gel column with petroleum ether/ethyl acetate as the eluent. The analytic data for asymetric reductive coupling products are listed below.



3i:

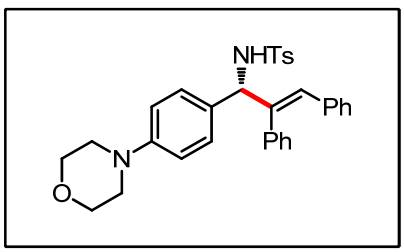
(*S*,*E*)-*N*-(1-(4-(Dimethylamino)phenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide.

White solid (55% yield). **HPLC condition:** Chiralpak AD-H column, *n*-hexane/ *i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 19.7 min, $t_{r\text{-minor}}$ = 23.5 min, 91% ee. $[\alpha]_D^{26}$ +43.0 (c 0.2, $CHCl_3$).



5a:

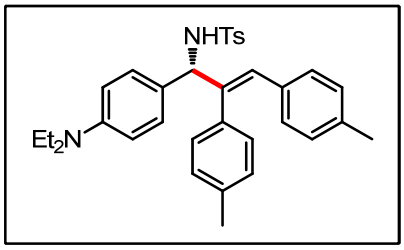
(*S*,*E*)-*N*-(1-(4-(Diethylamino)phenyl)-2,3-diphenylallyl)-4-methylbenzenesulfonamide. White solid (60% yield). m.p. 146-148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.23-7.11 (m, 5H), 7.09-7.02 (m, 5H), 6.79 (d, J = 8.0 Hz, 2H), 6.77-6.73 (m, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.51 (s, 1H), 5.22 (d, J = 7.2 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 3.32 (q, J = 7.2 Hz, 4H), 2.35 (s, 3H), 1.14 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 143.2, 140.3, 138.2, 137.9, 136.4, 129.5, 129.4, 129.3, 128.9, 128.6, 128.6, 127.8, 127.5, 127.4, 126.8, 125.2, 111.7, 63.9, 44.4, 21.5, 12.6. **HRMS** (ESI) calcd. for $C_{32}H_{35}N_2O_2S$ ($[M+H]^+$) 511.2414, Found 511.2417. **HPLC condition:** Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 12.5 min, $t_{r\text{-minor}}$ = 16.2 min, 95% ee. $[\alpha]_D^{26}$ +50.6 (c 1.0, $CHCl_3$).



5b:

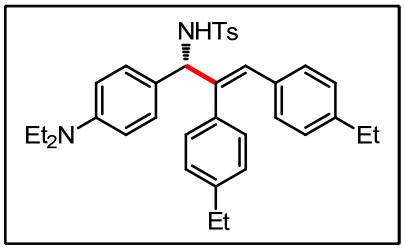
(*S*,*E*)-4-Methyl-*N*-(1-(4-morpholinophenyl)-2,3-diphenylallyl)benzenesulfonamide.

White solid (35% yield). m.p. 149-151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.23-7.10 (m, 7H), 7.08-7.00 (m, 3H), 6.81 (d, J = 8.0 Hz, 2H), 6.78-6.68 (m, 4H), 6.47 (s, 1H), 5.28 (d, J = 7.6 Hz, 1H), 4.81 (d, J = 7.6 Hz, 1H), 3.86 (t, J = 4.4 Hz, 4H), 3.14 (t, J = 4.4 Hz, 4H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 143.3, 140.0, 137.8, 137.7, 136.1, 130.3, 129.5, 129.4, 129.4, 129.3, 128.7, 128.4, 127.9, 127.7, 127.4, 127.0, 115.5, 66.9, 63.9, 49.2, 21.6. **HRMS** (ESI) calcd. for $C_{32}H_{33}N_2O_3S$ ($[M+H]^+$) 525.2206, Found 525.2211. **HPLC condition:** Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 23.3 min, $t_{r\text{-minor}}$ = 46.1 min, 51% ee. $[\alpha]_D^{26}$ +32.4 (c 0.5, $CHCl_3$).



5c:
(*S*,*E*)-*N*-(1-(4-(Diethylamino)phenyl)-2,3-di-p-tolylallyl)-4-methylbenzenesulfonamide.

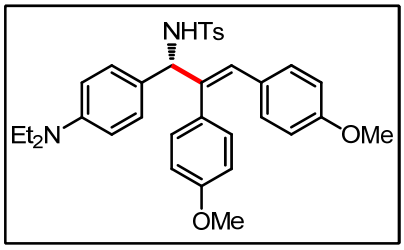
White solid (37% yield). m.p. 63-64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 4H), 6.55 (d, J = 8.4 Hz, 2H), 6.40 (s, 1H), 5.20 (d, J = 7.2 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 3.32 (q, J = 7.2 Hz, 4H), 2.35 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H), 1.14 (t, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 143.1, 139.2, 138.0, 137.1, 136.5, 135.0, 133.5, 129.4, 129.3, 129.3, 129.1, 128.8, 128.6, 127.4, 125.6, 111.7, 64.0, 44.4, 21.5, 21.3, 21.2, 12.6. **HRMS** (ESI) calcd. for $C_{34}H_{39}N_2O_2S$ ($[M+H]^+$) 539.2727, Found 539.2730. **HPLC condition:** Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 10.9 min, $t_{r\text{-minor}}$ = 16.1 min, 87% ee. $[\alpha]_D^{26}$ +62.4 (c 0.5, $CHCl_3$).



5d:
(*S*,*E*)-*N*-(1-(4-(Diethylamino)phenyl)-2,3-bis(4-ethylphenyl)allyl)-4-methylbenzenesulfonamide.

White solid (60% yield). m.p. 59-61 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 6.89 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 7.6 Hz, 4H), 6.56 (d, J = 8.0 Hz, 2H), 6.41 (s, 1H), 5.22 (d, J = 7.6 Hz, 1H), 4.77 (d, J = 7.2 Hz, 1H), 3.33 (q, J = 6.8 Hz, 4H),

2.59 (q, J = 7.6 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 2.35 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H), 1.18-1.10 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 143.5, 143.1, 142.9, 139.2, 138.0, 135.3, 133.8, 129.5, 129.4, 129.3, 129.0, 128.6, 128.1, 127.5, 127.4, 125.7, 111.8, 64.1, 44.4, 28.6, 28.6, 21.6, 15.4, 15.4, 12.6. **HRMS** (ESI) calcd. for $C_{36}H_{43}N_2O_2S$ ($[M+H]^+$) 567.3040, Found 567.3044. **HPLC condition:** Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 8.5 min, $t_{r\text{-minor}}$ = 10.6 min, 90% ee. $[\alpha]_D^{26}$ +62.4 (c 1.0, $CHCl_3$).



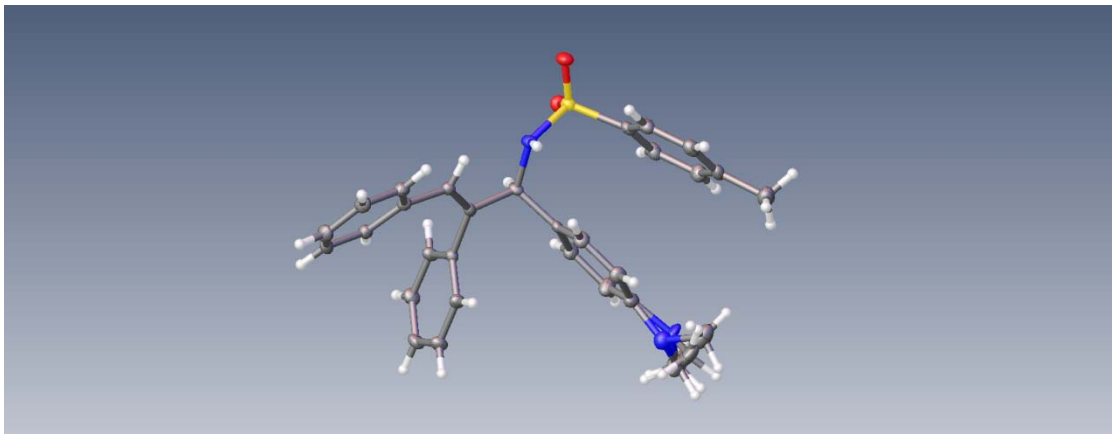
5e:

(*S*,*E*)-*N*-(1-(4-(Diethylamino)phenyl)-2,3-bis(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide.

White solid (28% yield). m.p. 160-162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.69 (s, 4H), 6.60 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 6.37 (s, 1H), 5.18 (d, J = 7.2 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.32 (q, J = 7.2 Hz, 4H), 2.35 (s, 3H), 1.14 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 158.3, 147.3, 143.1, 138.0, 137.8, 130.7, 130.5, 130.3, 129.4, 129.1, 128.5, 128.4, 127.5, 125.6, 114.1, 113.3, 111.7, 64.1, 55.2, 44.4, 21.6, 12.6. **HRMS** (ESI) calcd. for $C_{34}H_{39}N_2O_4S$ ($[M+H]^+$) 571.2625, Found 571.2628. **HPLC condition:** Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 254 nm, $t_{r\text{-major}}$ = 13.8 min, $t_{r\text{-minor}}$ = 19.5 min, 75% ee. $[\alpha]_D^{26}$ +50.8 (c 0.5, $CHCl_3$).

Absolute Configuration Determination:

A single crystal of (*S*)-**3i** (91% ee) was obtained in Hexane/EtOAc. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC 1870018, Unit Cell Parameters:a5.72050(10)b19.9636(3)c21.5679(3) P212121



Stereochemical Model

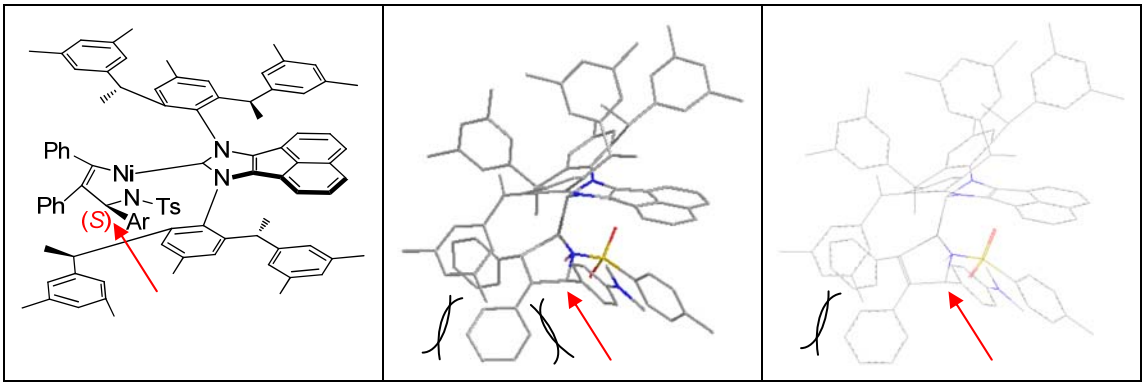
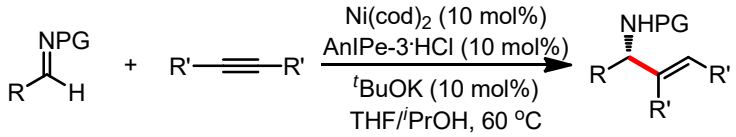
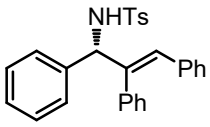
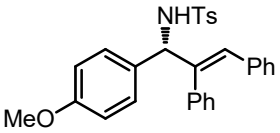


Table S10. Unsuccessful Substrates

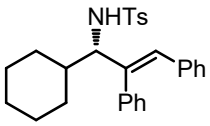




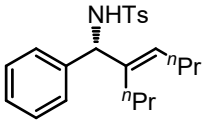
3a, 37%, 0% ee



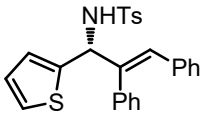
3d, 38%, 19% ee



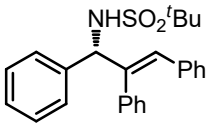
3q, 29%, 12% ee



4h, 32%, 2% ee



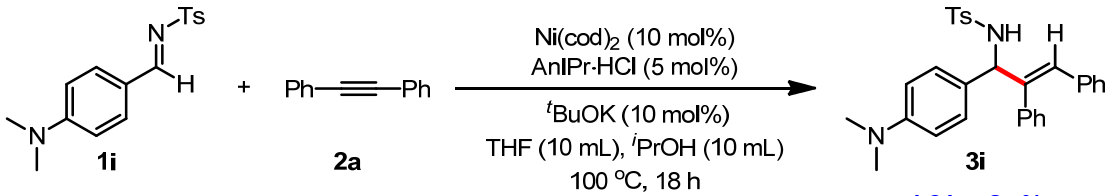
3p, trace



3b, 0%

7. Gram-Scale Reaction and Deuterium-Labeling Experiment

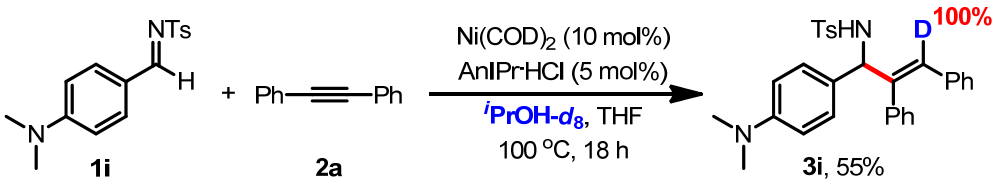
7.1 Gram-Scale Reaction



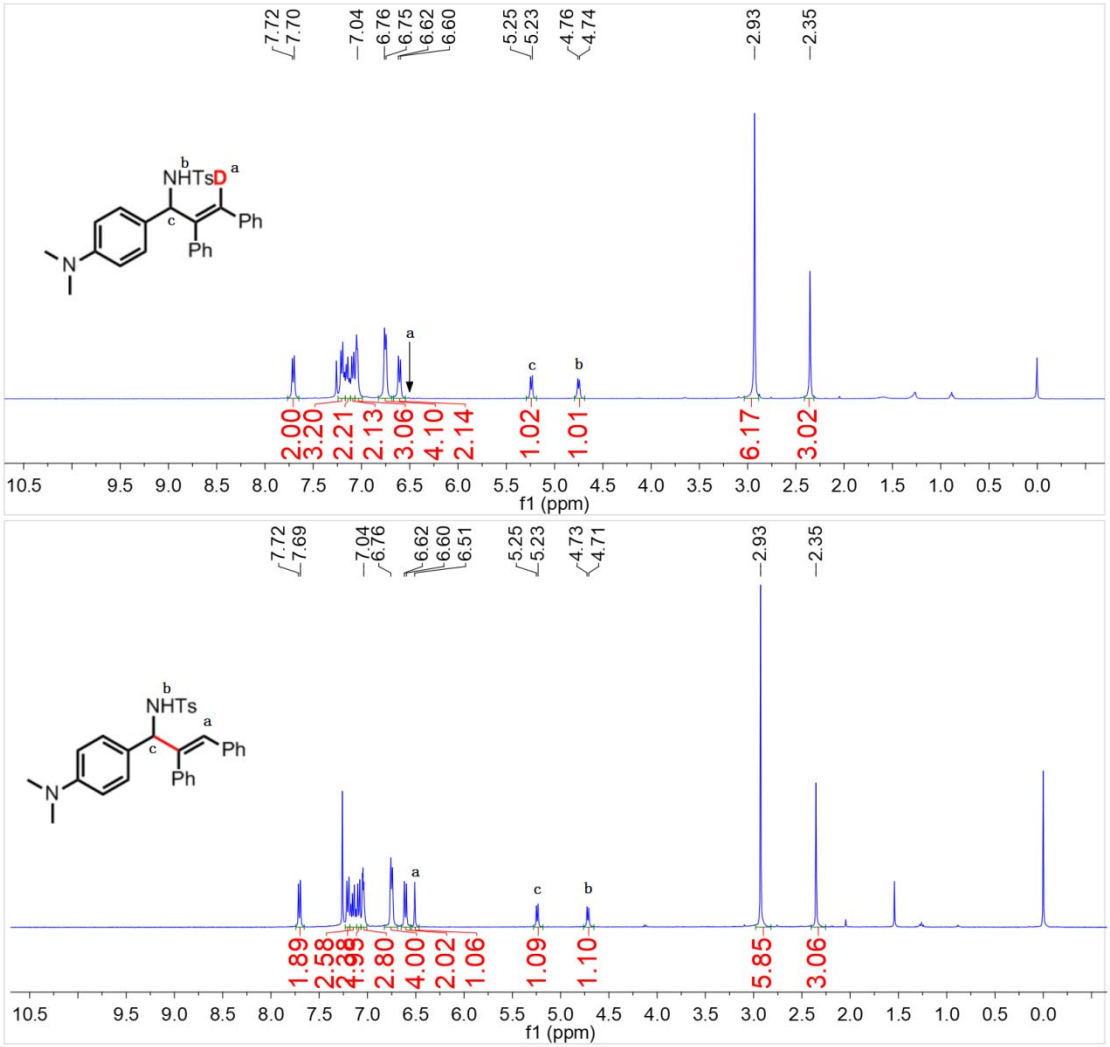
To a 48 mL pressure tube were added $Ni(cod)_2$ (82.5 mg, 0.3 mmol), AnIPr·HCl (82.2 mg, 0.15 mmol), KO^{t}Bu (33.7 mg, 0.3 mmol), THF (10 mL), ^{i}PrOH (10 mL), alkynes (3 mmol) and imines (3.6 mmol) in a glove box. The tube was sealed with a Teflon cap and the mixture was stirred at 100 °C for 18 h. After cooled to room temperature, the crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum. The resulting residue was obtained by chromatography on silica gel column with petroleum ether/ethyl acetate as the eluent

to afford pure product **3i** (84% yield, 1.21 g).

7.2 Deuterium-Labeling Experiment



To a 15 mL pressure tube were added $Ni(cod)_2$ (5.5 mg, 0.02 mmol), AnIPr·HCl (5.5 mg, 0.01 mmol), KO^{t}Bu (2.3 mg, 0.02 mmol), THF (1 mL), ^{i}PrOH-d_8 (1 mL), **2a** (0.2 mmol) and **1i** (0.24 mmol) in a glove box. The tube was sealed with a Teflon cap and the mixture was stirred at 100 °C for 18 h. After cooled to room temperature, the crude product was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum. The resulting residue was obtained by chromatography on silica gel column with petroleum ether/ethyl acetate as the eluent to afford pure product **3i** (55% yield, 52.8 mg). ***Note:*** *the (N-)D was almost completely exchanged with the H of water during the process of column purification.*



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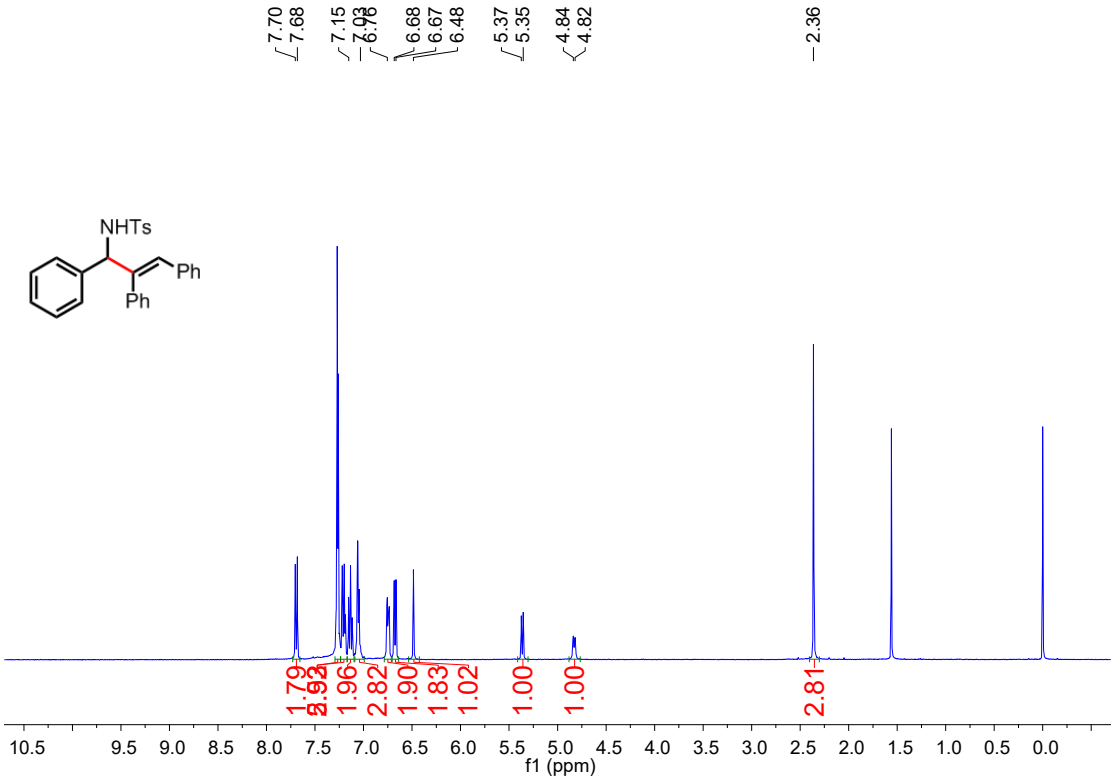
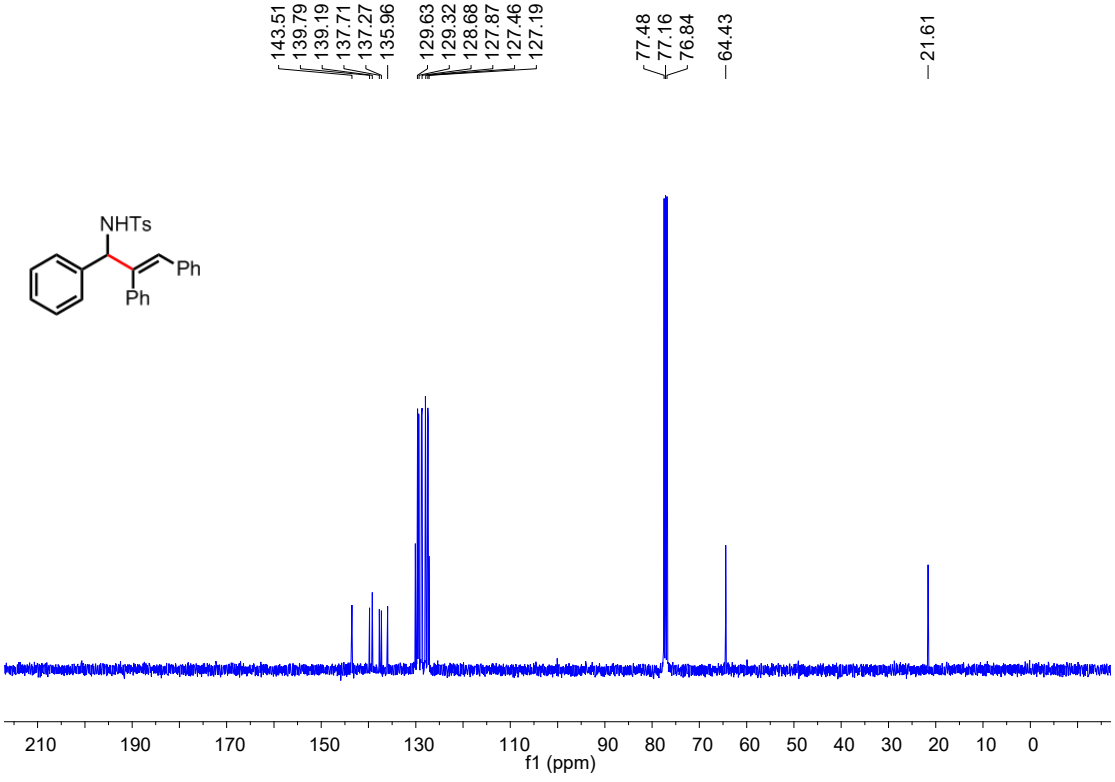
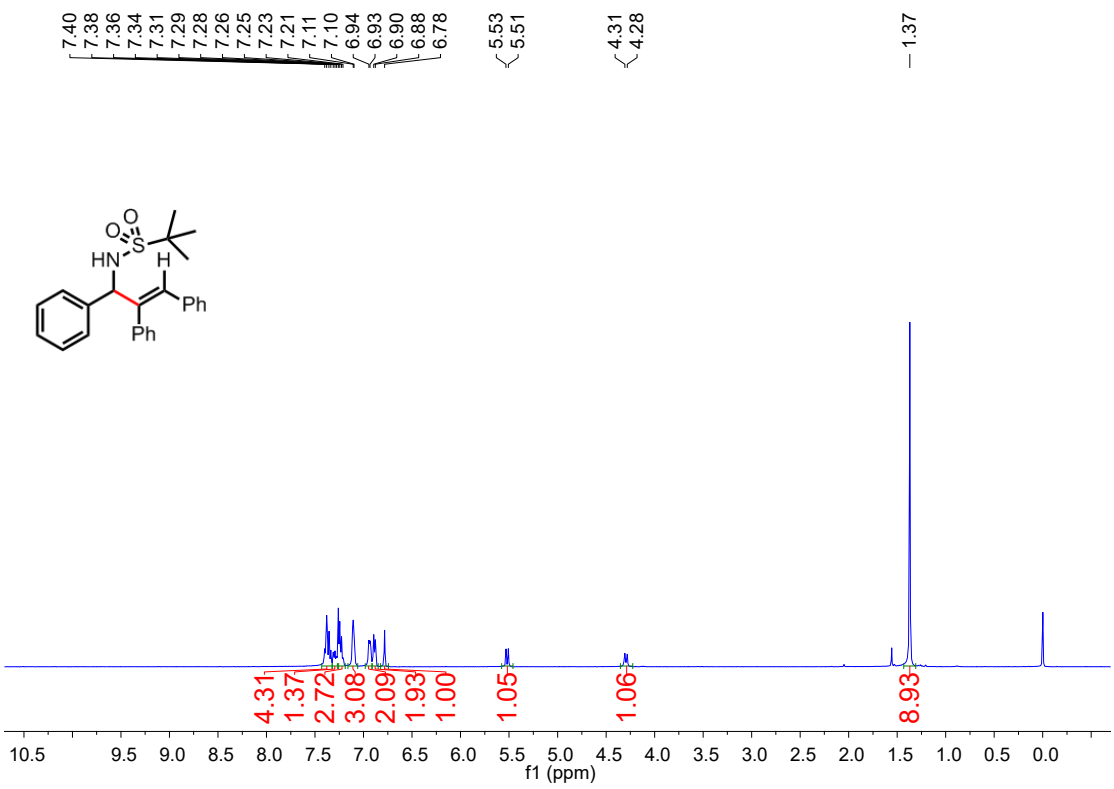
8. NMR Spectra



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7.29
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7.23
7.21
7.11
7.10
6.94
6.93
6.90
6.88
6.78
5.53
5.51
4.31
4.28
1.37
O
O
S
HN
H
Ph
Ph
4.31
1.37
2.72
3.08
2.09
1.93
1.00
1.05
1.06
8.93
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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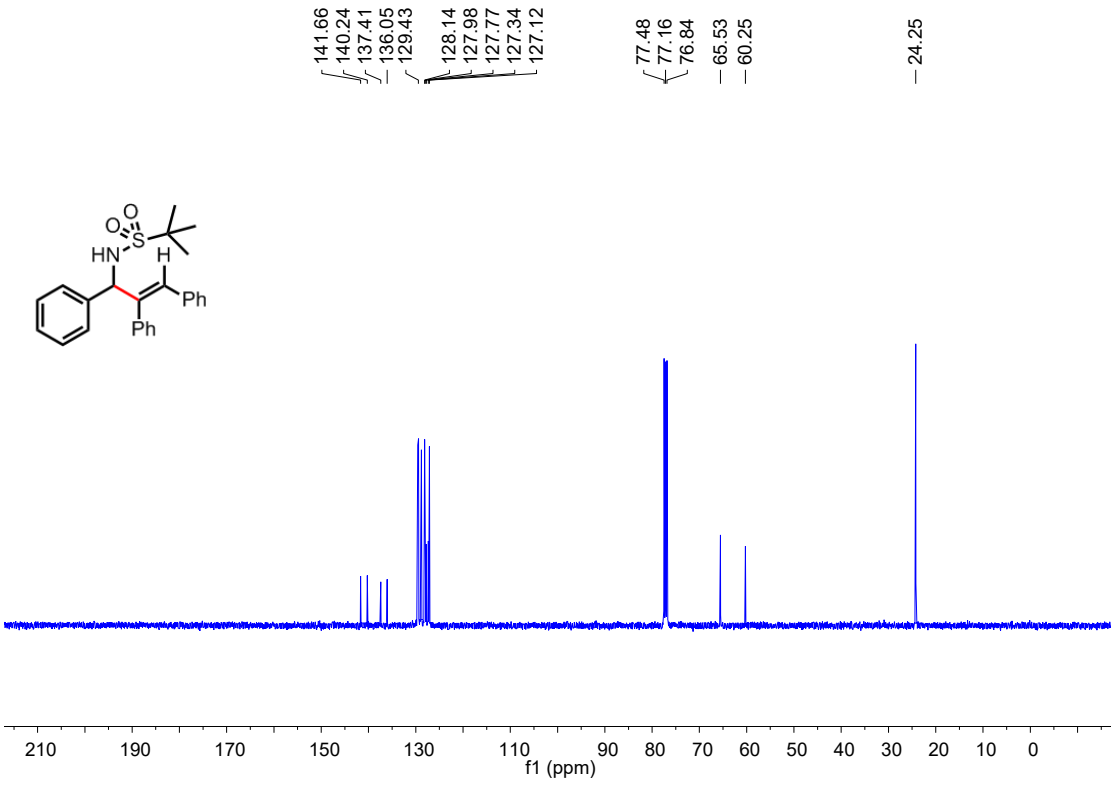
0.0
f1 (ppm)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24.25
O
O
S
HN
H
Ph
Ph
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170
150
130
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90
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50
40
30
20
10
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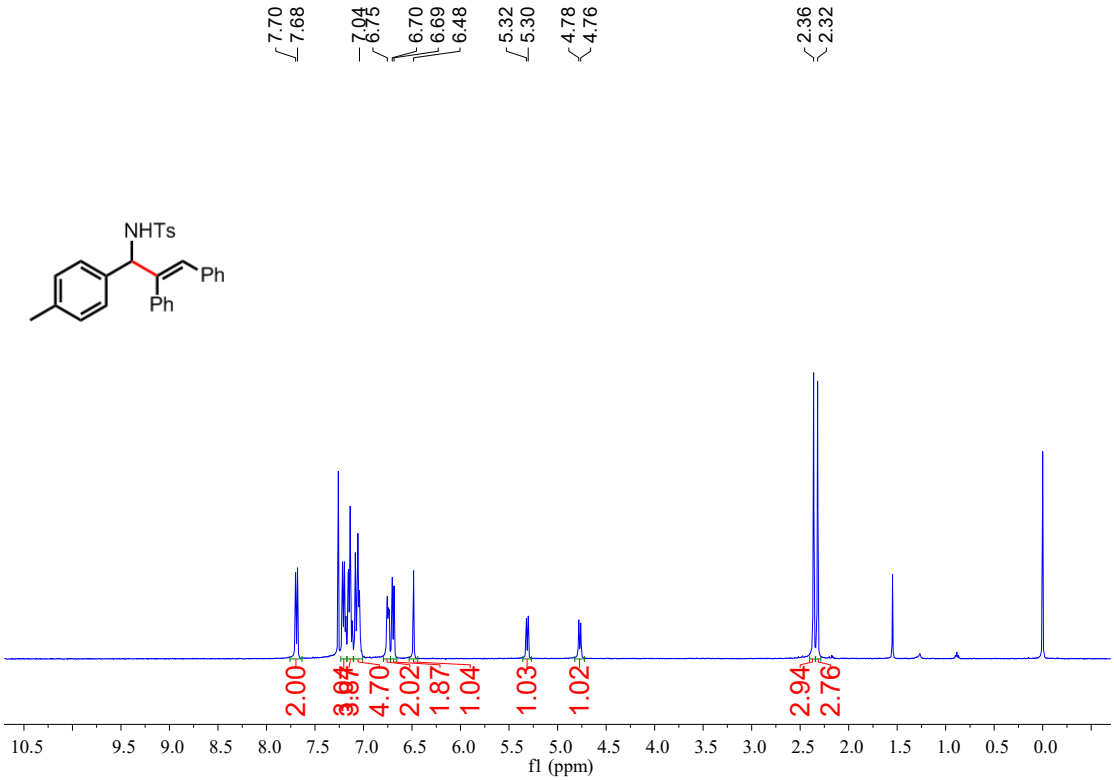
f1 (ppm)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2.32
NHTs
Ph
Ph
2.00
3.04
3.01
4.70
2.02
1.87
1.04
1.03
1.02
2.94
2.76
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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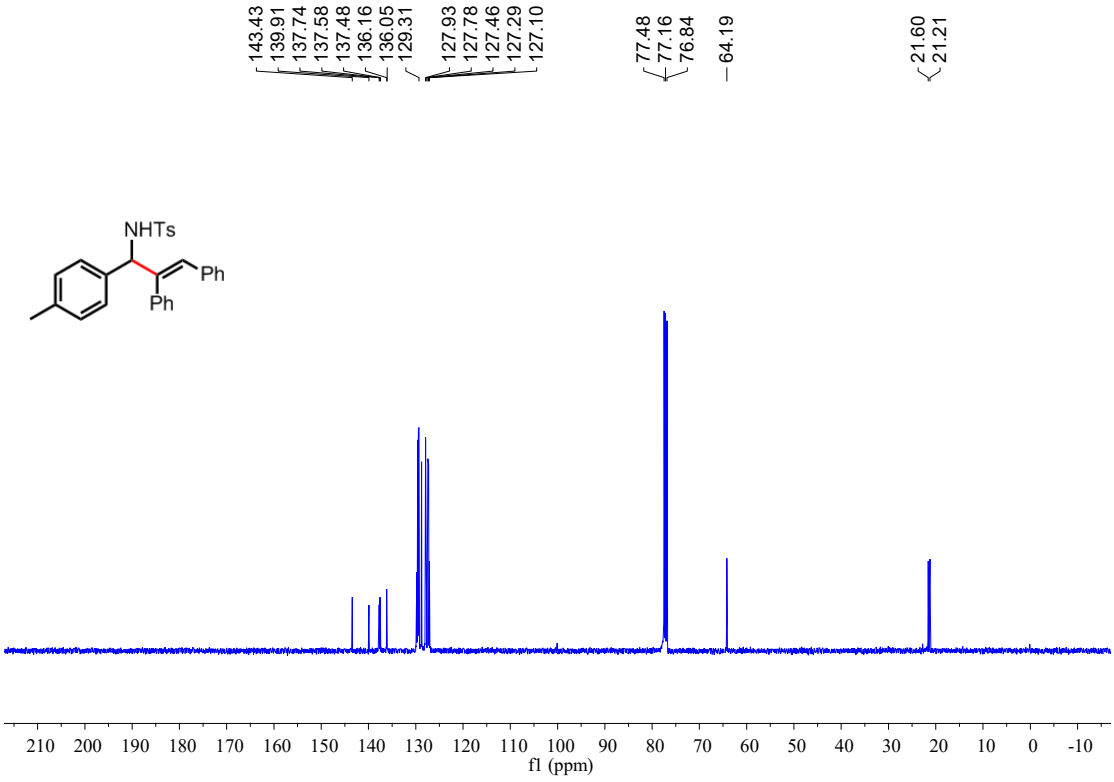
f1 (ppm)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77.48
77.16
76.84
64.19
21.60
21.21
NHTs
Ph
Ph
210
200
190
180
170
160
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120
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100
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80
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40
30
20
10
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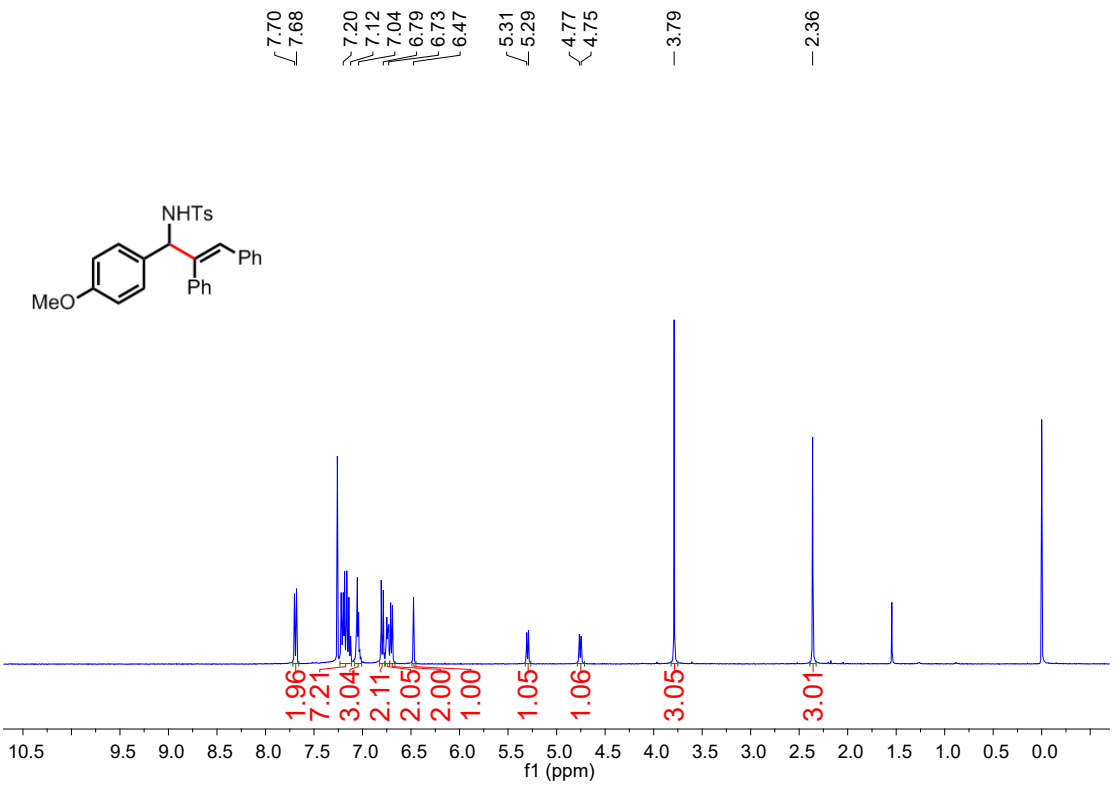
f1 (ppm)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NHTs
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MeO
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2.11
2.05
2.00
1.00
1.05
1.06
3.05
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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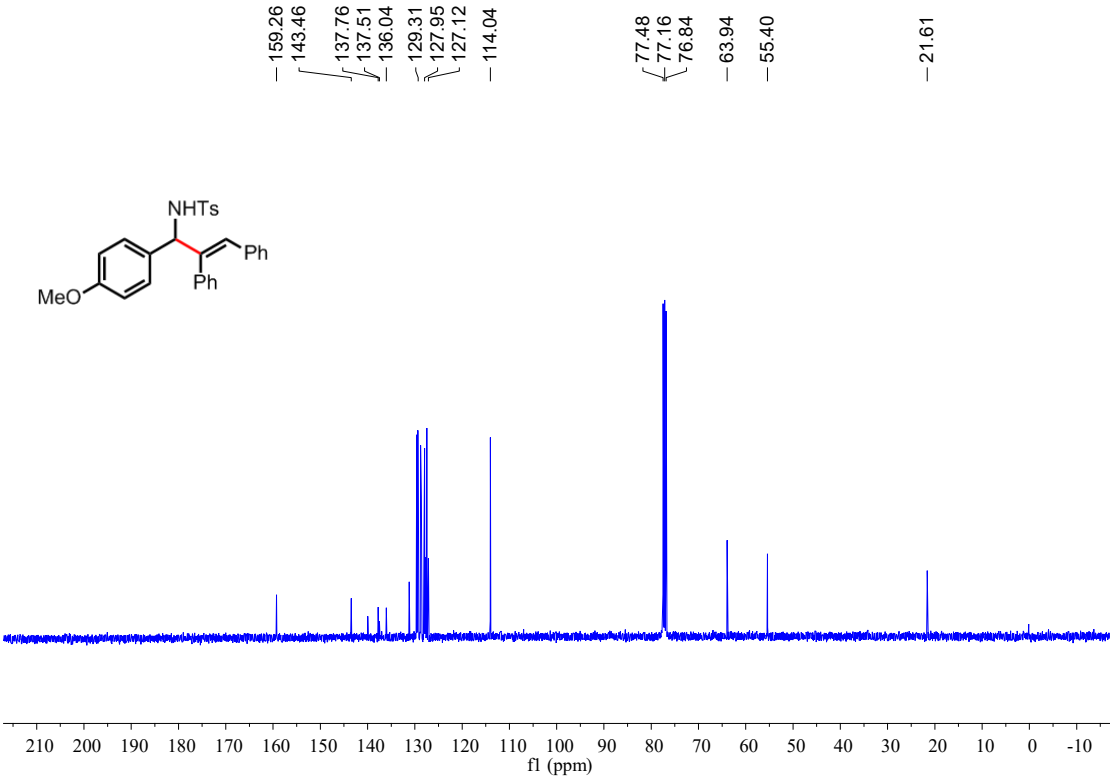
0.0
f1 (ppm)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63.94
55.40
21.61
NHTs
Ph
Ph
MeO
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
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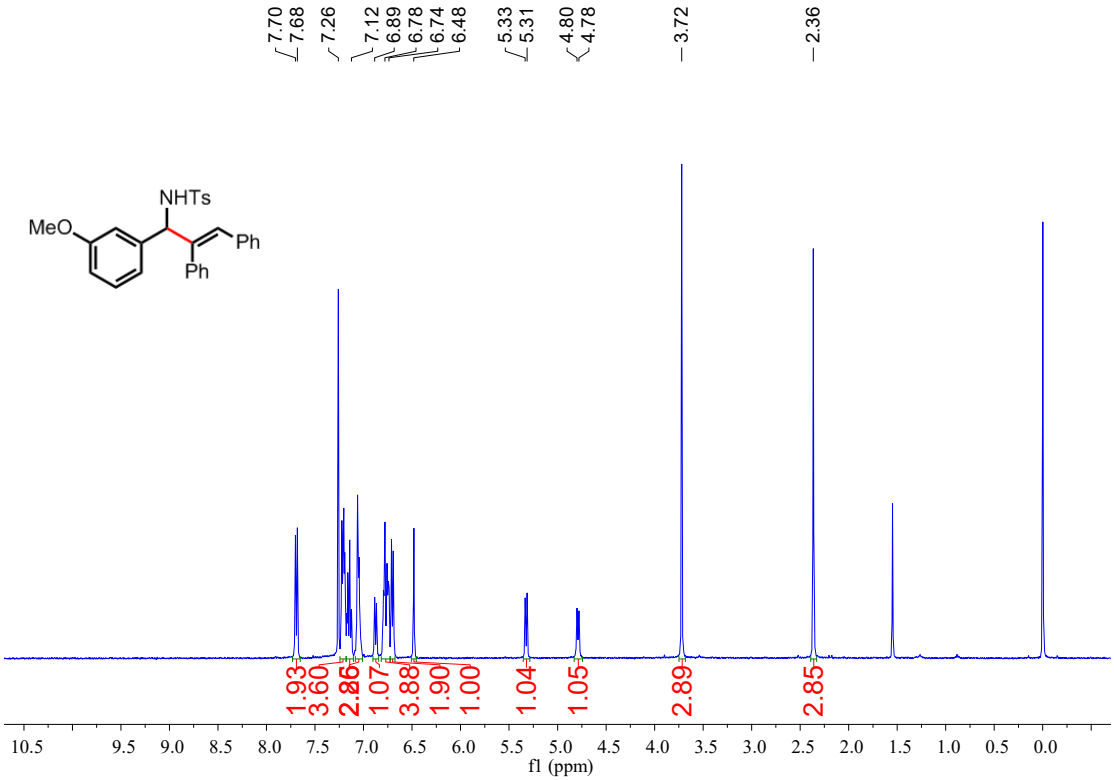
10
0
-10
f1 (ppm)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7.12
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6.48
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5.31
4.80
4.78
3.72
2.36
NHTs
MeO
Ph
Ph
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1.90
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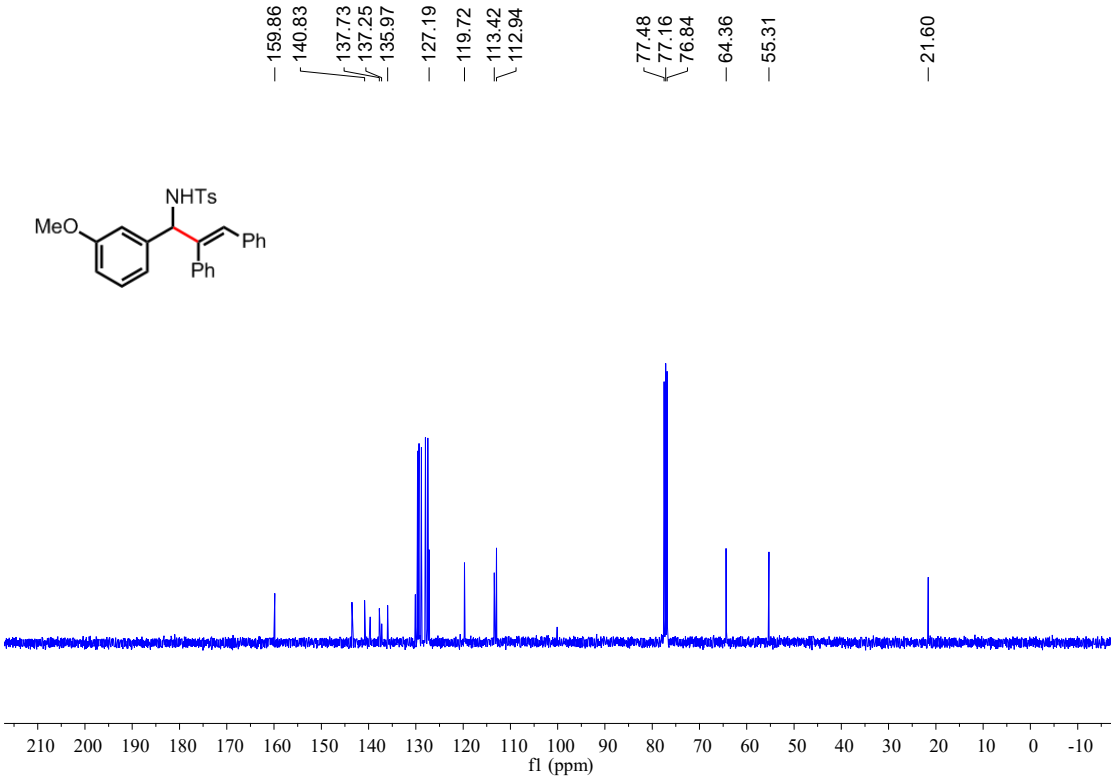
2.85
fl (ppm)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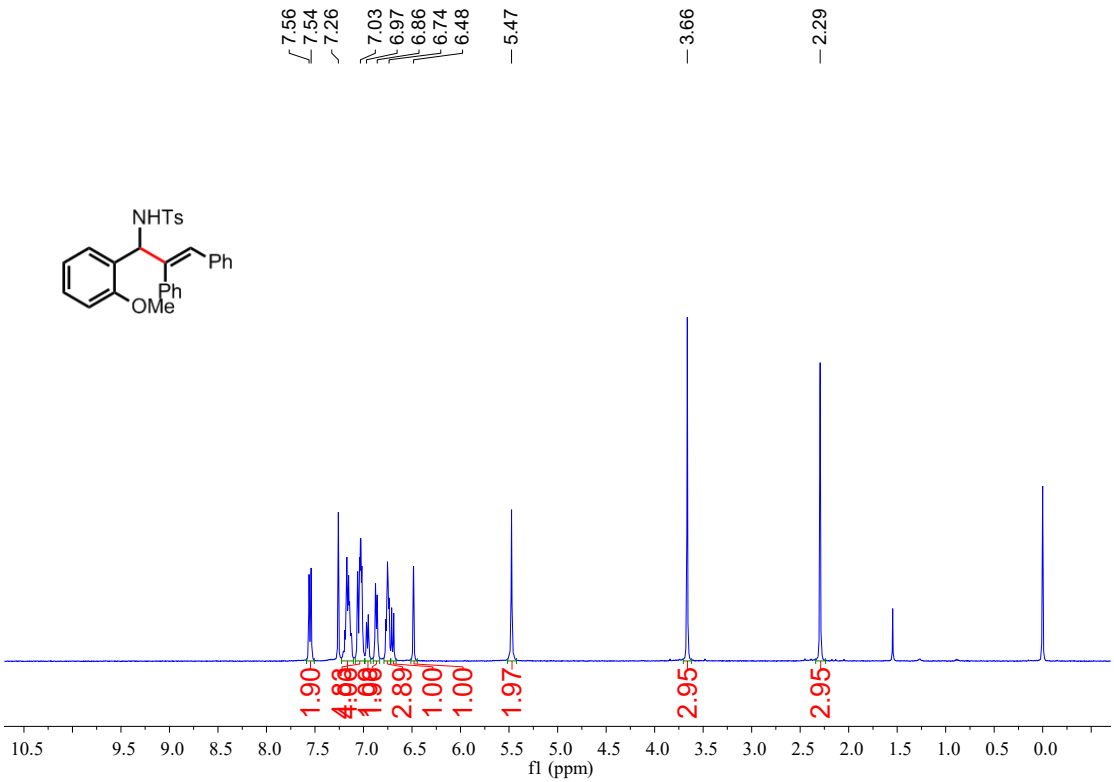
64.36
55.31
21.60
NHTs
MeO
Ph
Ph
fl (ppm)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Ph
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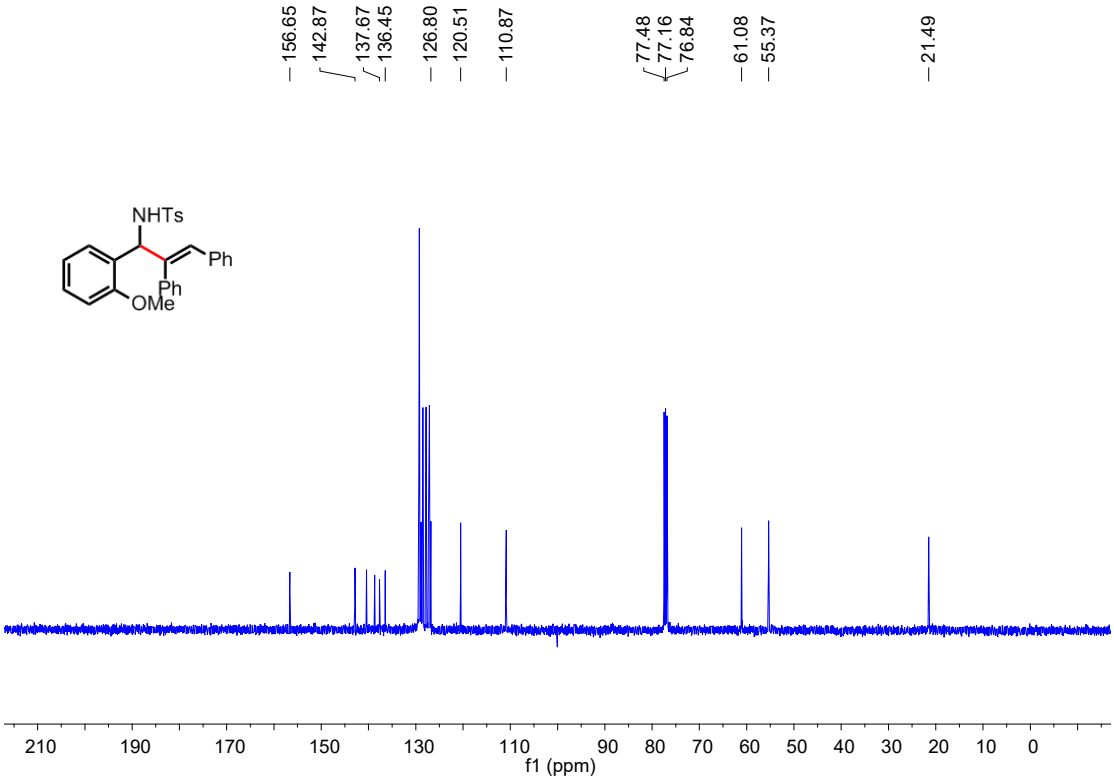
f1 (ppm)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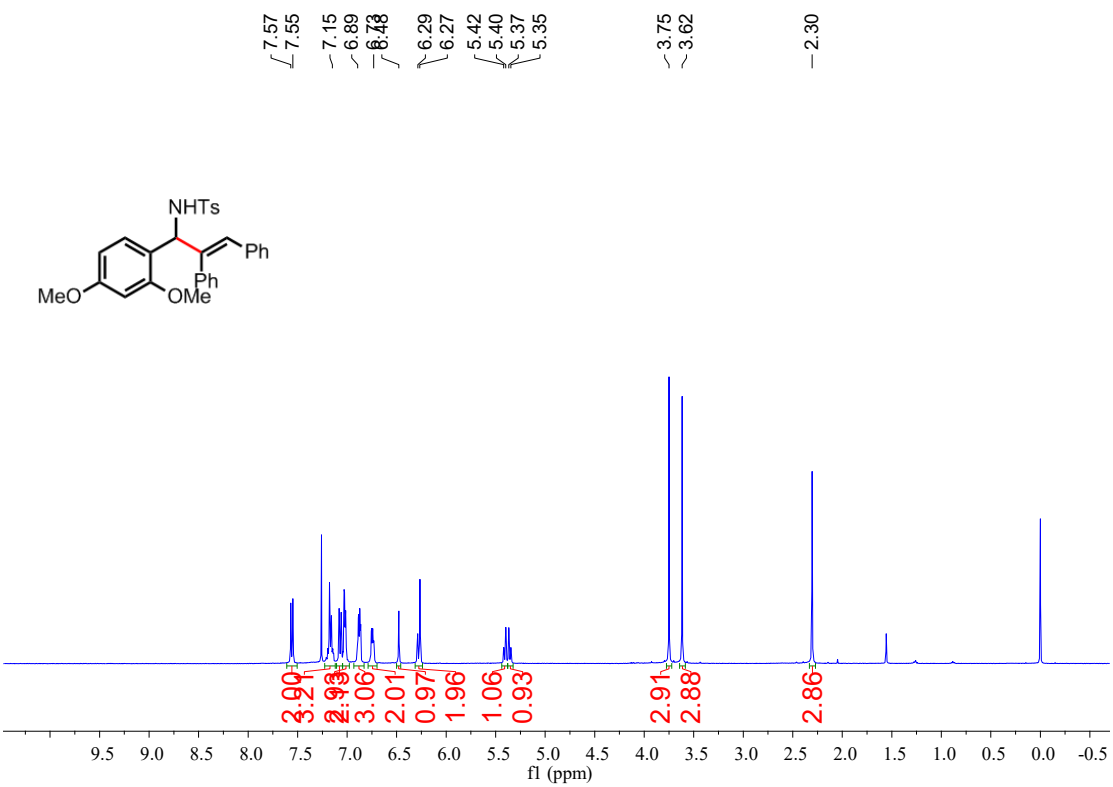
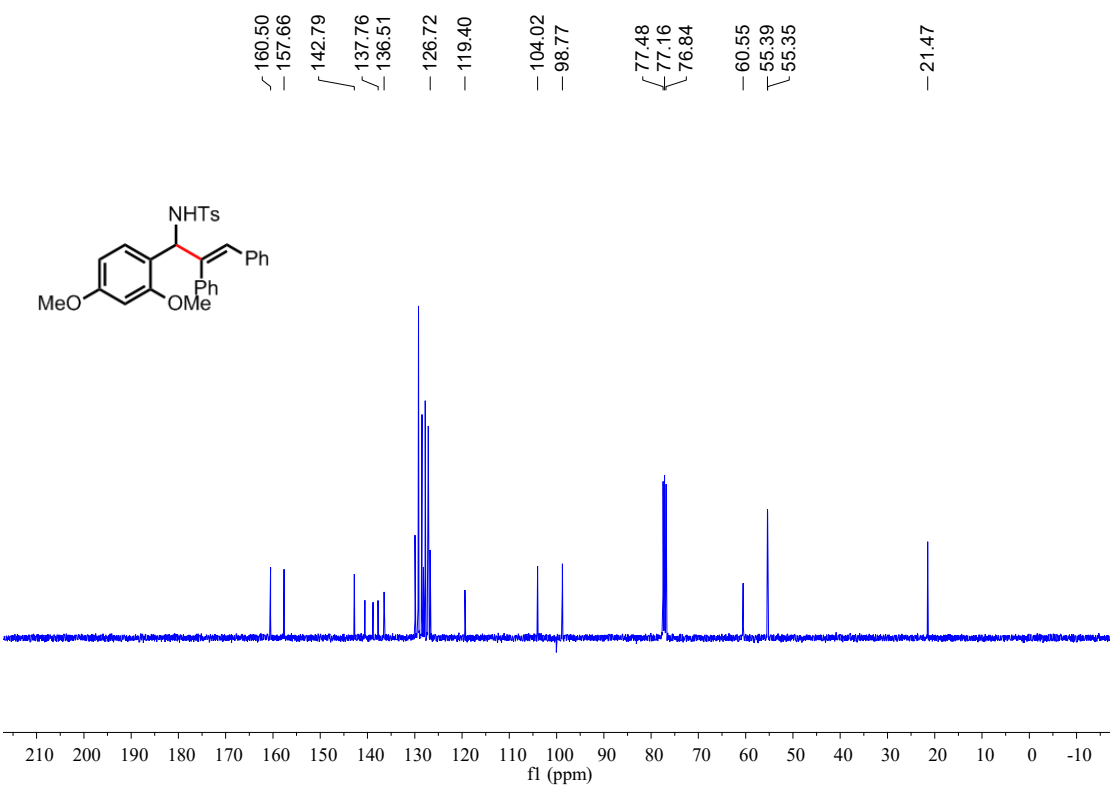
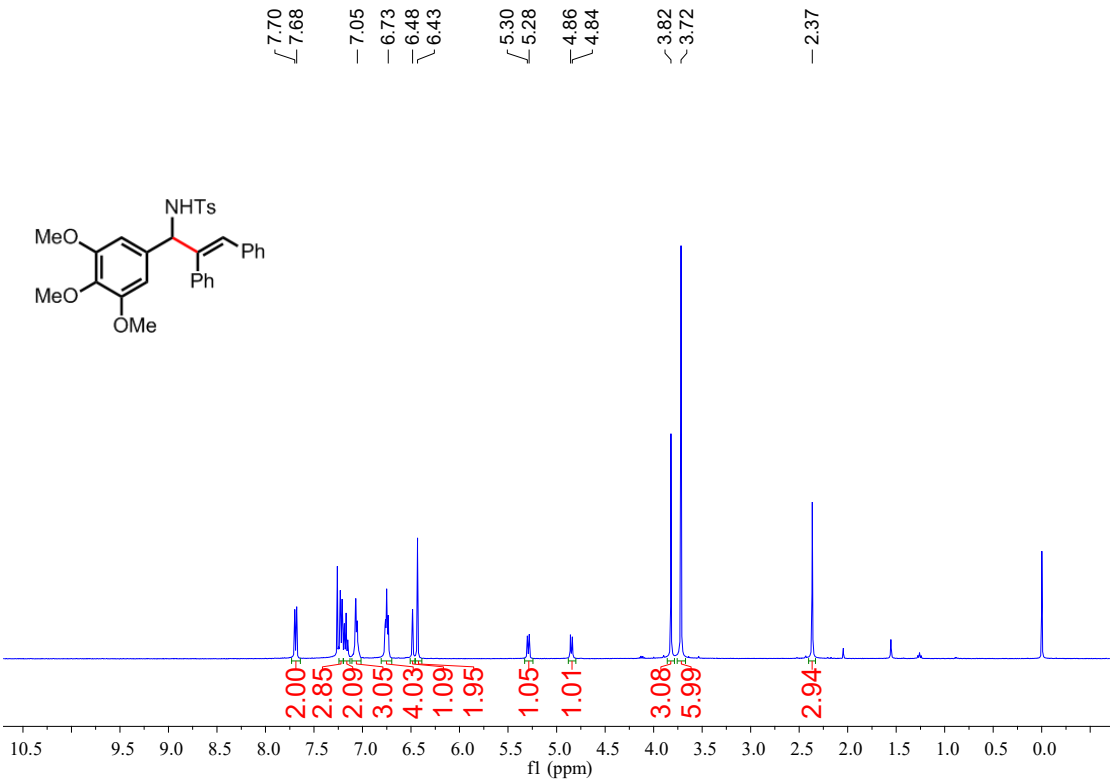
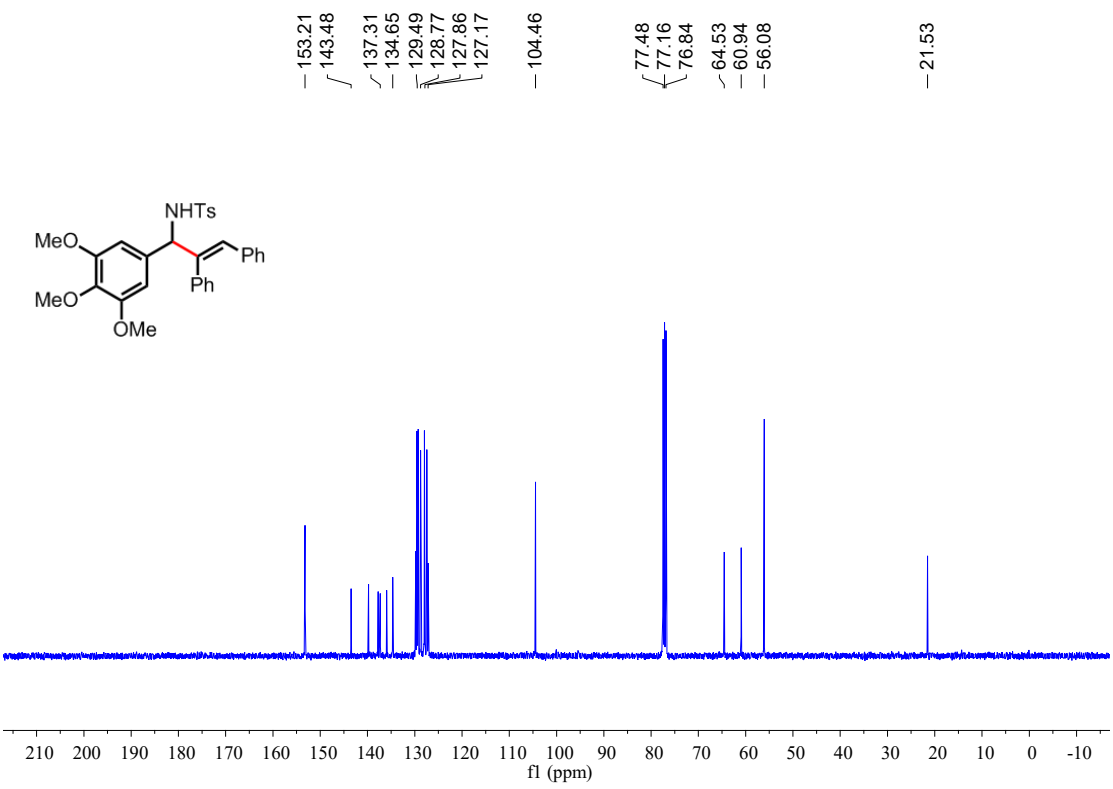
76.84
61.08
55.37
21.49
NHTs
Ph
Ph
OMe
f1 (ppm)


7.57
7.55
7.15
6.89
6.73
6.48
6.29
6.27
5.42
5.40
5.37
5.35
3.75
3.62
2.30
NHTs
Ph
Ph
MeO
OMe
2.00
3.21
2.93
3.06
2.01
0.97
1.96
1.06
0.93
2.91
2.88
2.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


160.50
157.66
142.79
137.76
136.51
126.72
119.40
104.02
98.77
77.48
77.16
76.84
60.55
55.39
55.35
21.47
NHTs
Ph
Ph
MeO
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.70
7.68
7.05
6.73
6.48
6.43
5.30
5.28
4.86
4.84
3.82
3.72
2.37
NHTs
MeO
MeO
OMe
Ph
Ph
2.00
2.85
2.09
3.05
4.03
1.09
1.95
1.05
1.01
3.08
5.99
2.94
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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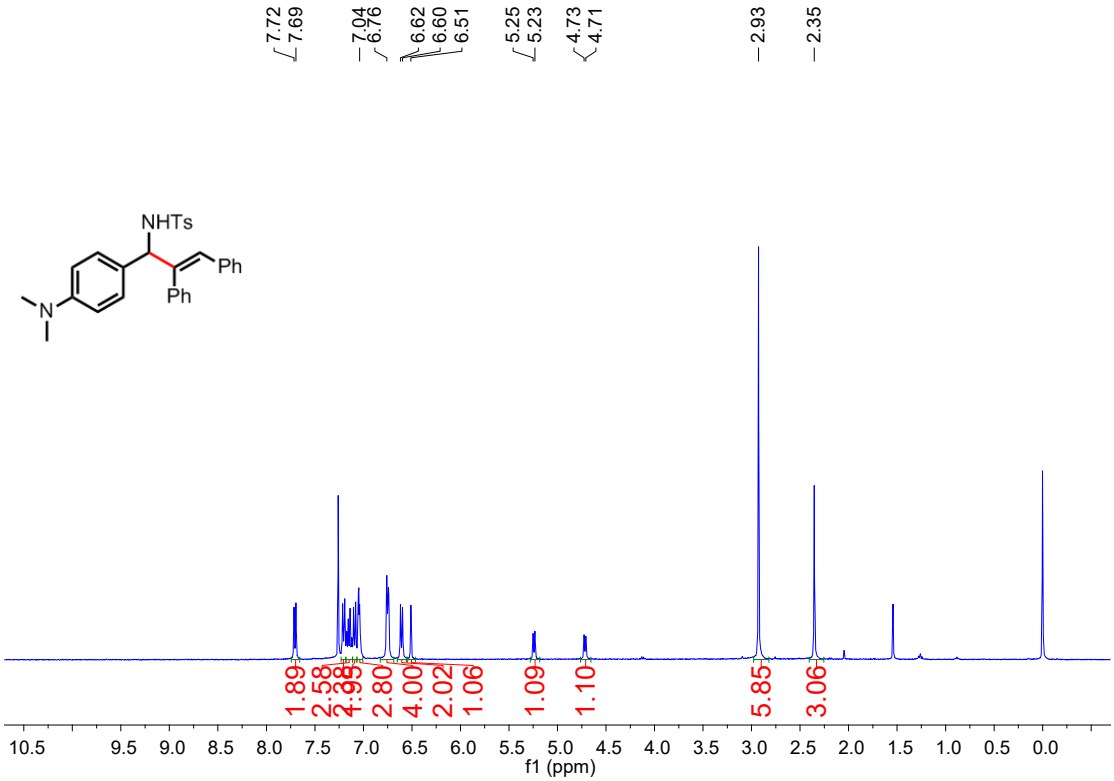
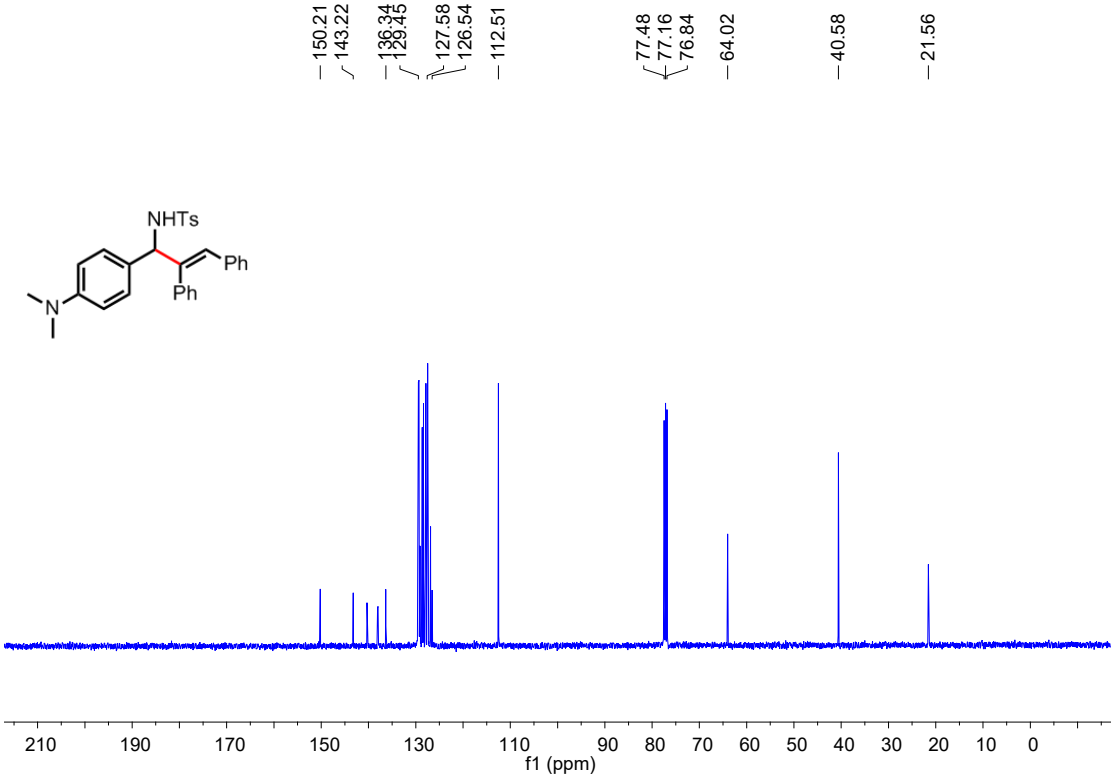
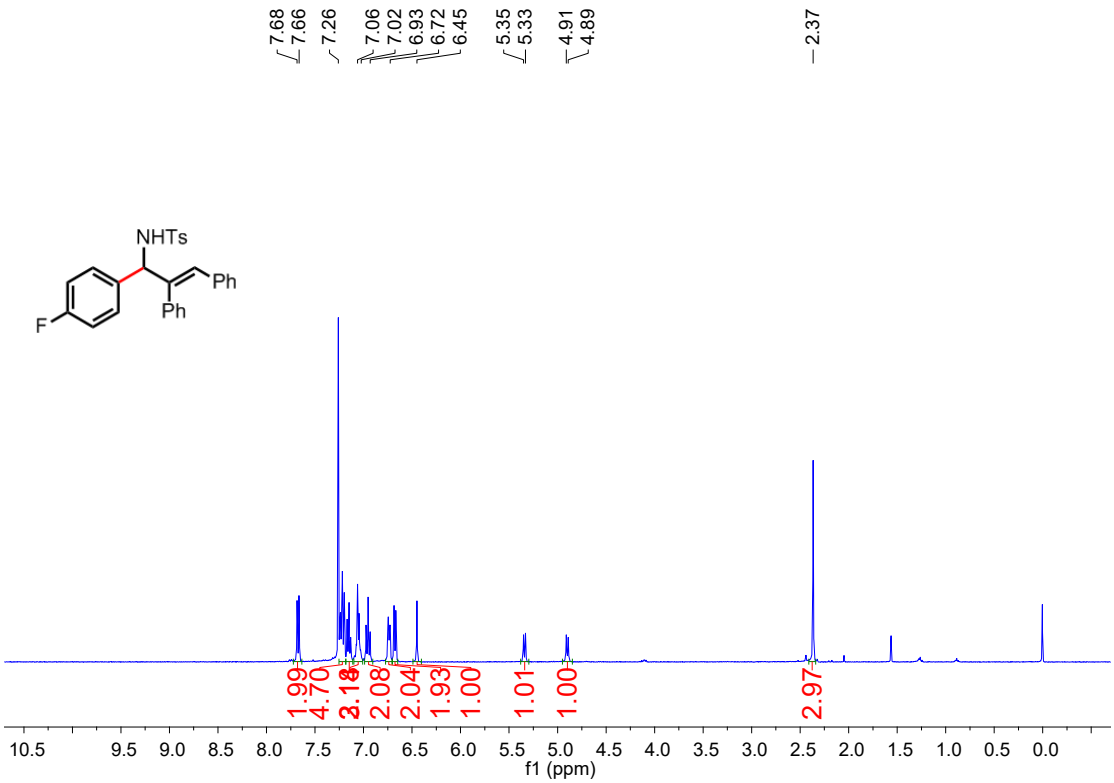
143.48
137.31
134.65
129.49
128.77
127.86
127.17
104.46
77.48
77.16
76.84
64.53
60.94
56.08
21.53
NHTs
MeO
MeO
OMe
Ph
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.72
7.69
7.04
6.76
6.62
6.60
6.51
5.25
5.23
4.73
4.71
2.93
2.35
NHTs
Ph
Ph
N
1.89
2.58
2.80
4.00
2.02
1.06
1.09
1.10
5.85
3.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.21
143.22
136.34
129.45
127.58
126.54
112.51
77.48
77.16
76.84
64.02
40.58
21.56
NHTs
Ph
Ph
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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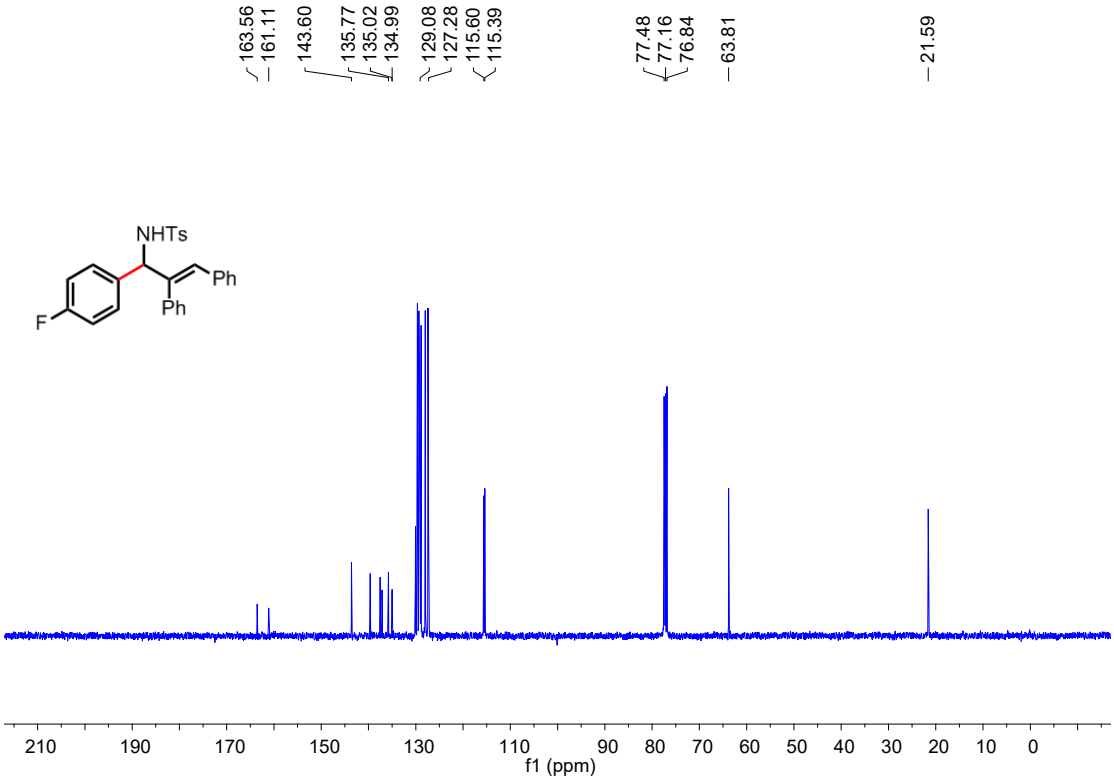
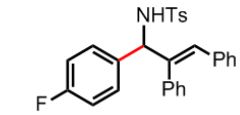
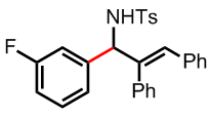
7.66
7.26
7.06
7.02
6.93
6.72
6.45
5.35
5.33
4.91
4.89
2.37
NHTs
Ph
Ph
F
1.99
4.70
2.08
2.04
1.93
1.00
1.01
1.00
2.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

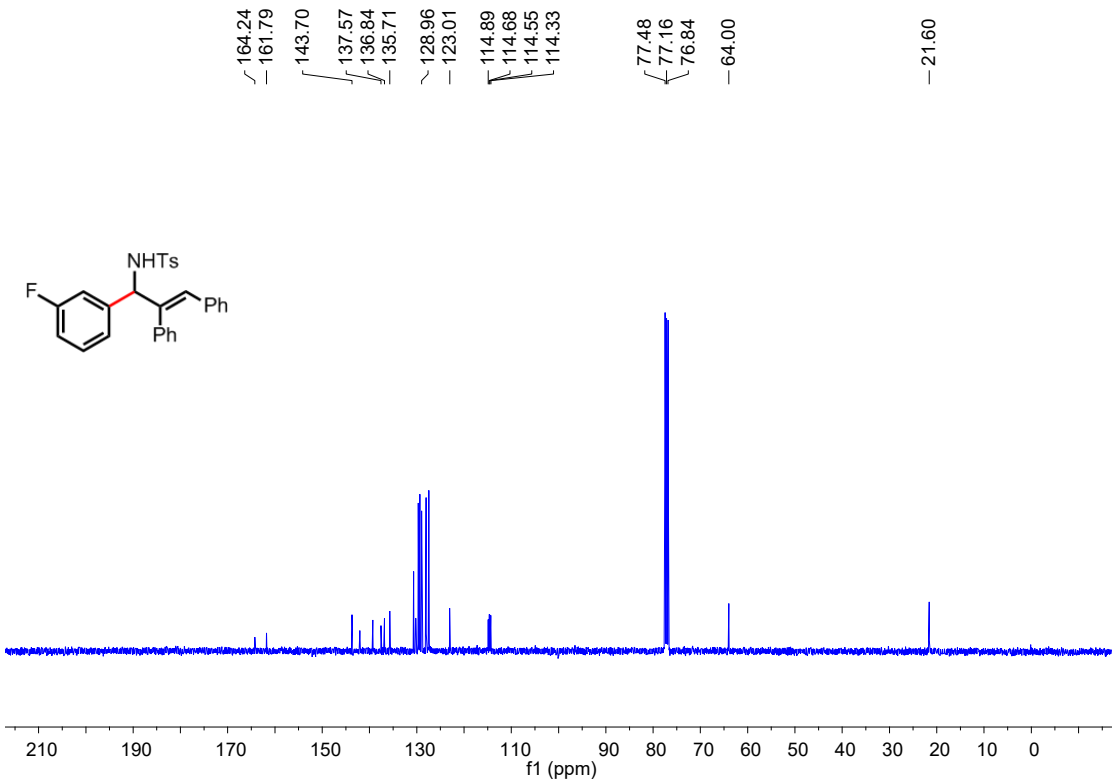

163.56
161.11
143.60
135.77
135.02
134.99
129.08
127.28
115.60
115.39
77.48
77.16
76.84
63.81
21.59
NHTs
Ph
Ph
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

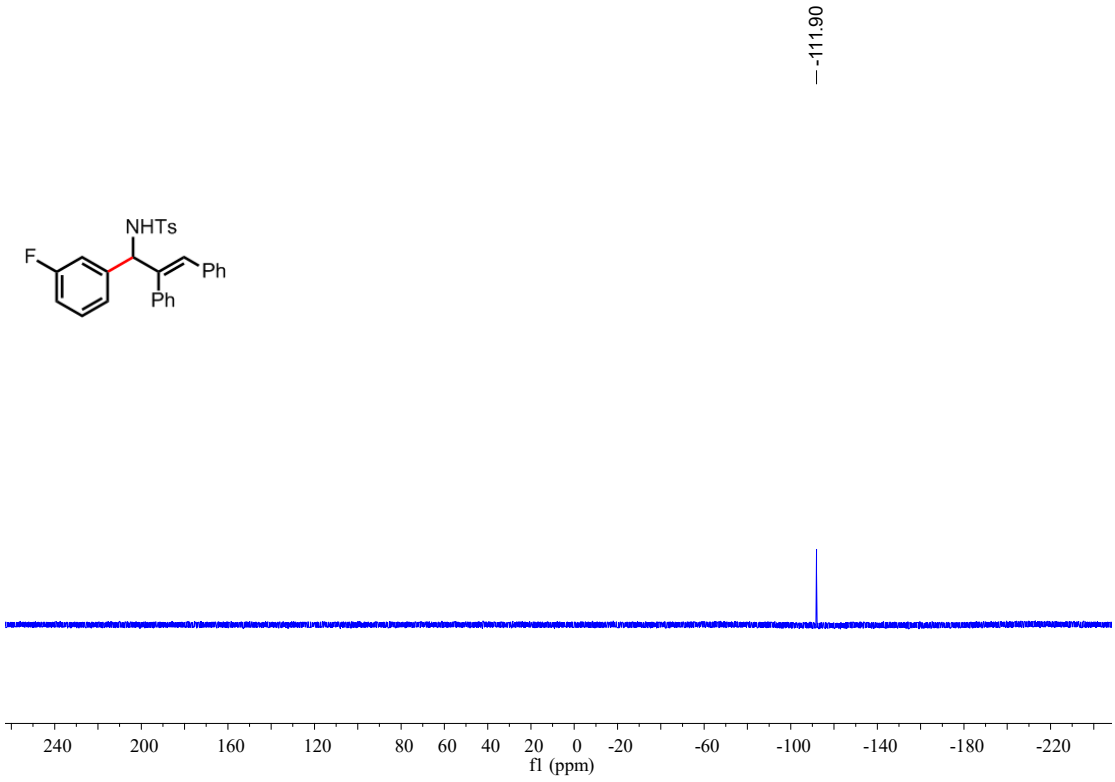

NHTs
Ph
Ph
F

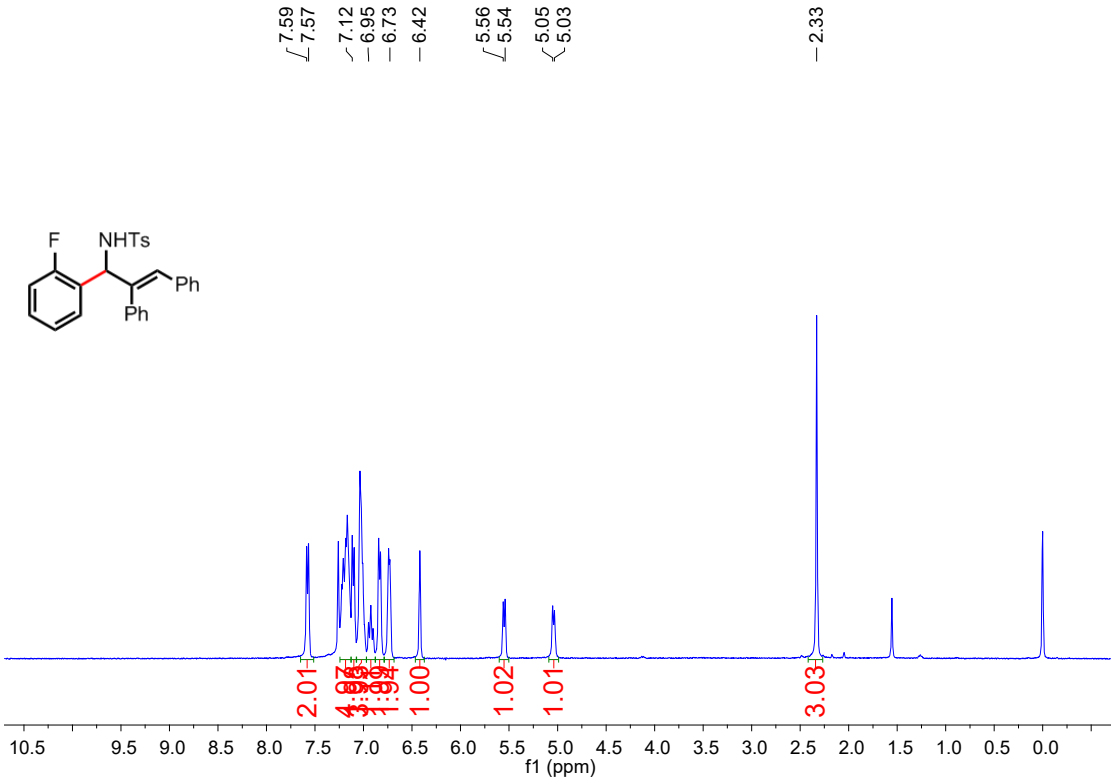
-114.85
240
200
160
120
80
60
40
20
0
-20
-60
-100
-140
-180
-220
f1 (ppm)

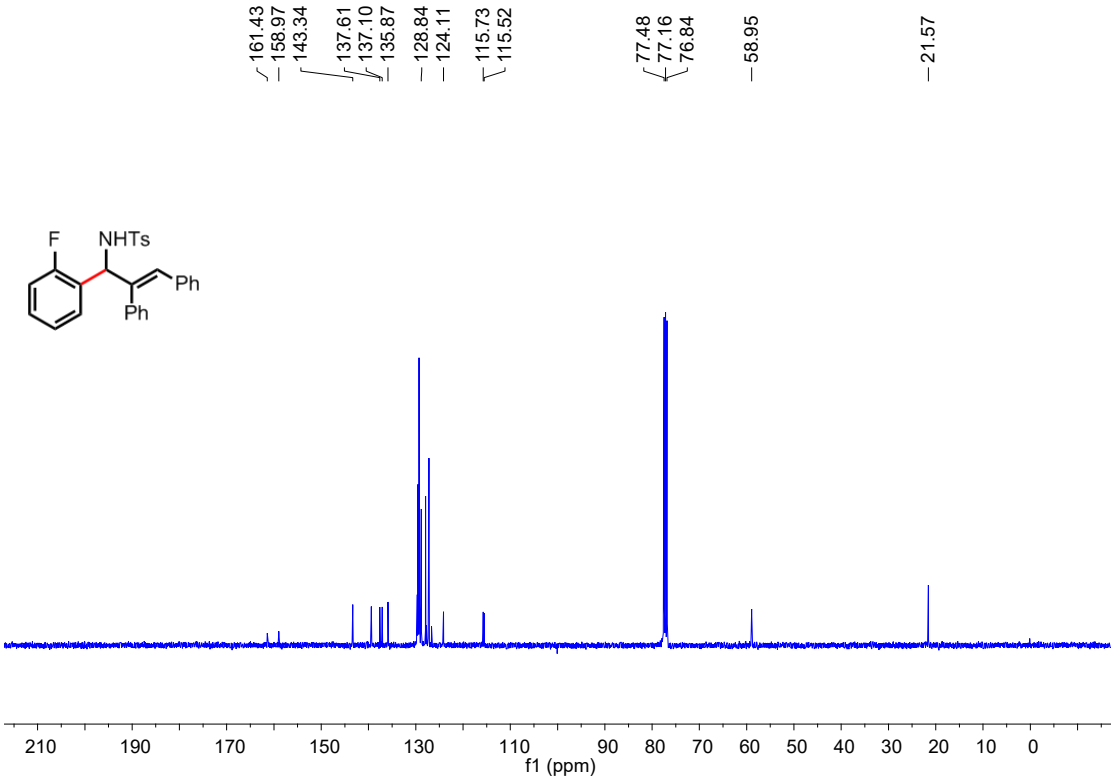

NHTs
F
Ph
Ph

7.69
7.67
7.26
7.07
7.00
6.93
6.74
6.45
5.36
5.34
4.87
4.85
2.37
1.95
3.06
2.05
2.02
1.92
1.00
0.99
1.00
2.98
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.24
161.79
143.70
137.57
136.84
135.71
128.96
123.01
114.89
114.68
114.55
114.33
77.48
77.16
76.84
64.00
21.60
NHTs
F
Ph
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-111.90
NHTs
F
Ph
Ph
240
200
160
120
80
60
40
20
0
-20
-60
-100
-140
-180
-220
f1 (ppm)


7.59
7.57
7.12
6.95
6.73
6.42
5.56
5.54
5.05
5.03
2.33
F
NHTs
Ph
Ph
2.01
1.00
1.02
1.01
3.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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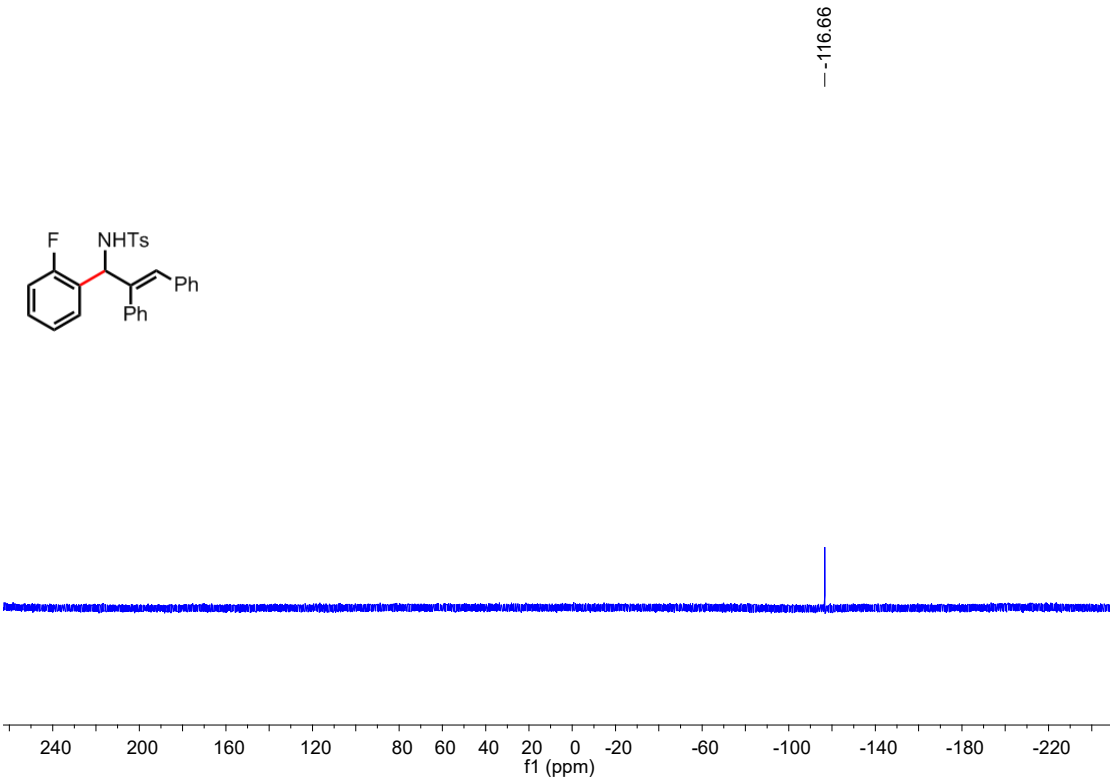
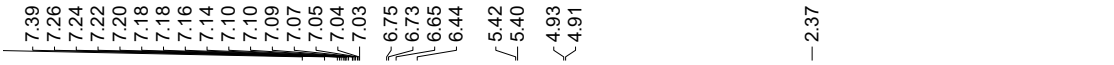
158.97
143.34
137.61
137.10
135.87
128.84
124.11
115.73
115.52
77.48
77.16
76.84
58.95
21.57
F
NHTs
Ph
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-116.66
F
NHTs
Ph
Ph
240
200
160
120
80
60
40
20
0
-20
-60
-100
-140
-180
-220
f1 (ppm)


7.39
7.26
7.24
7.22
7.20
7.18
7.18
7.16
7.14
7.10
7.10
7.09
7.07
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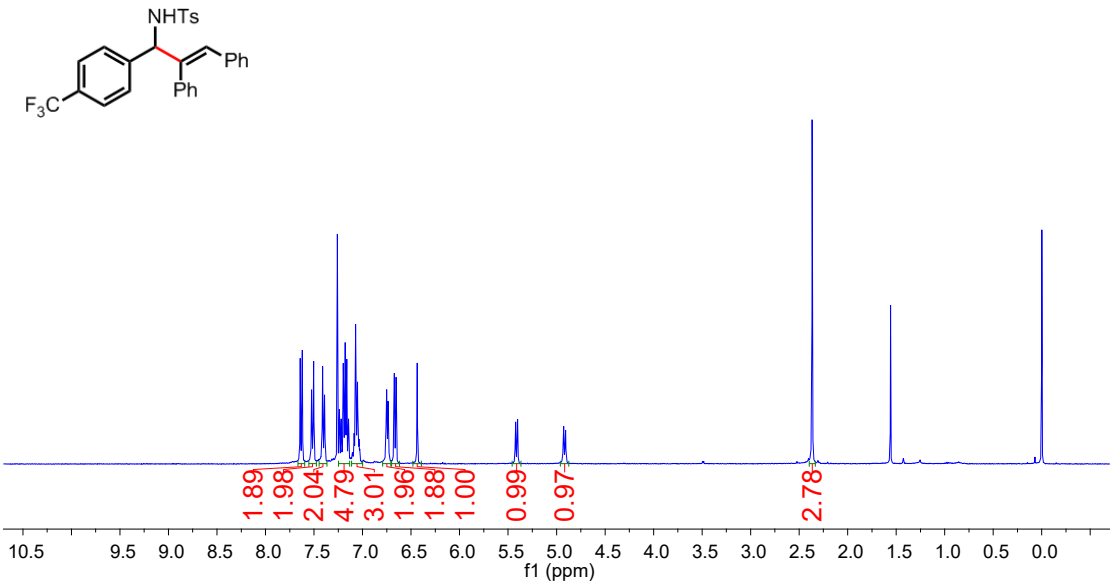
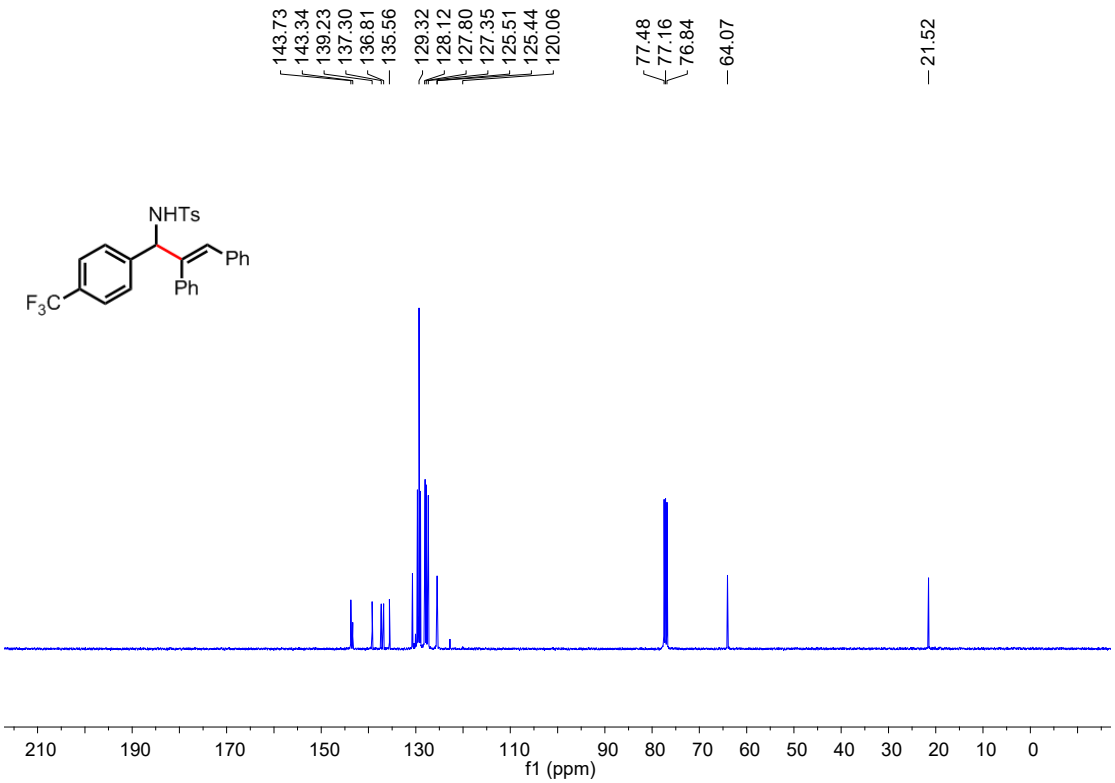
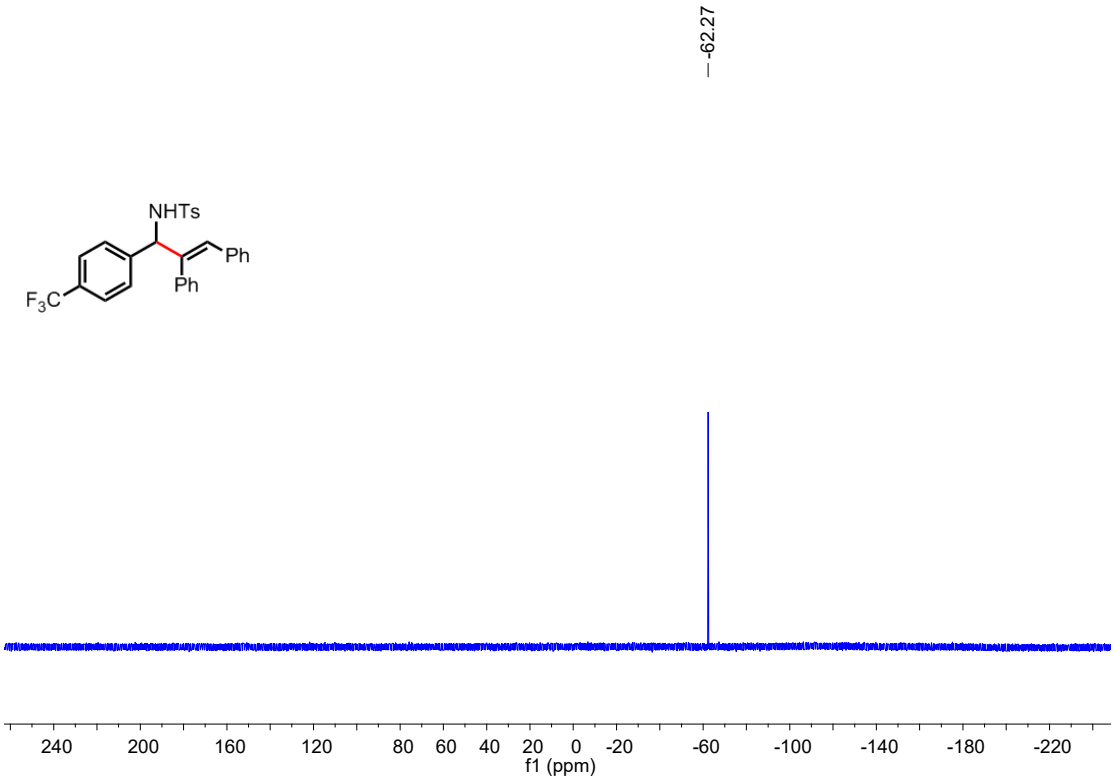
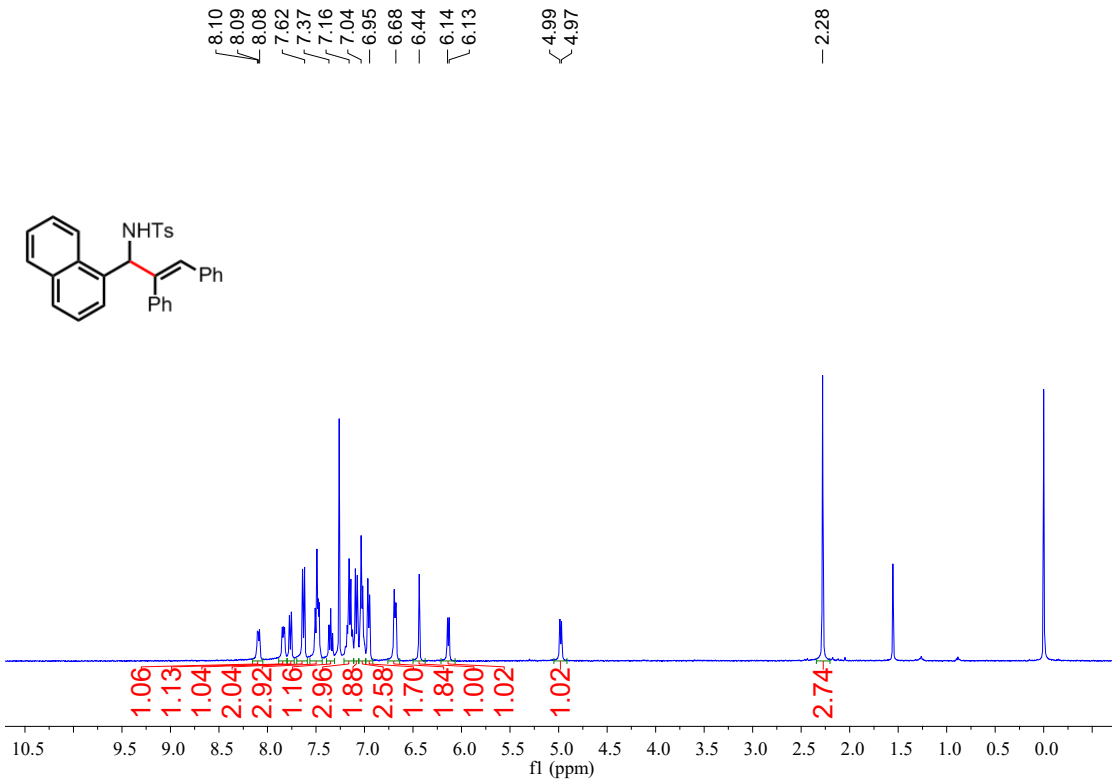
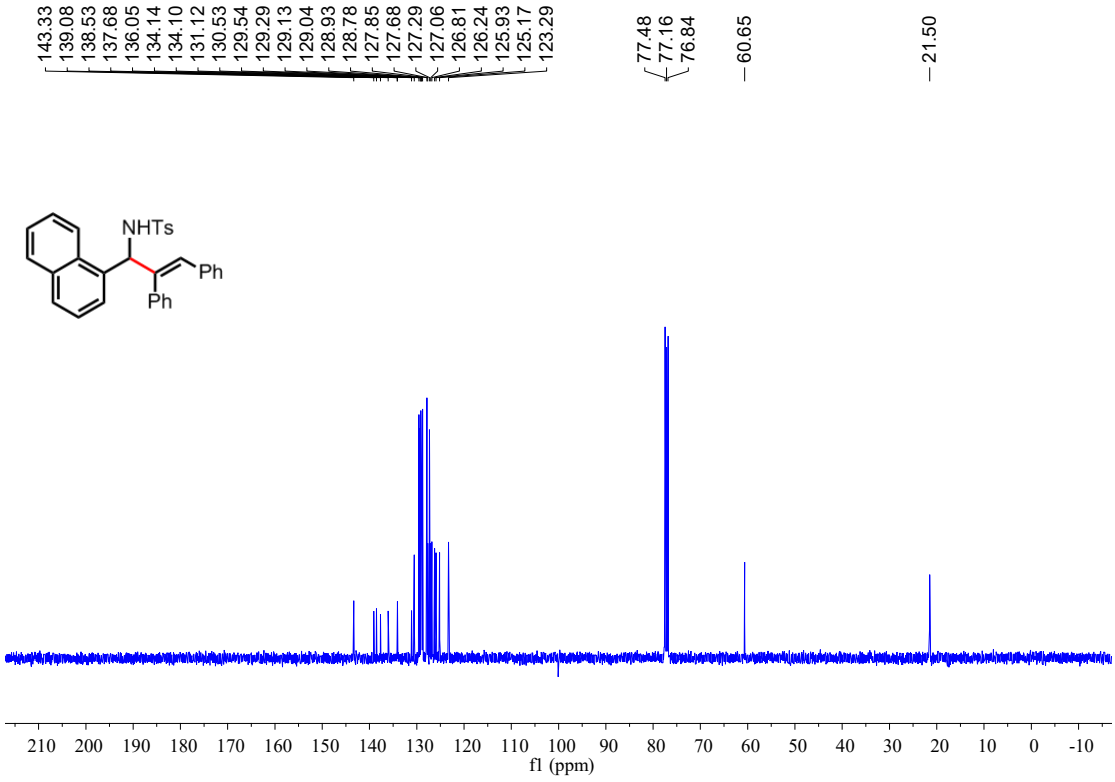
6.44
5.42
5.40
4.93
4.91
2.37


NHTs
Ph
Ph
F3C
1.89
1.98
2.04
4.79
3.01
1.96
1.88
1.00
0.99
0.97
2.78
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.73
143.34
139.23
137.30
136.81
135.56
129.32
128.12
127.80
127.35
125.51
125.44
120.06
77.48
77.16
76.84
64.07
21.52
NHTs
Ph
Ph
F3C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.27
NHTs
Ph
Ph
F3C
240
200
160
120
80
60
40
20
0
-20
-60
-100
-140
-180
-220
f1 (ppm)


8.10
8.09
8.08
7.62
7.37
7.16
7.04
6.95
6.68
6.44
6.14
6.13
4.99
4.97
2.28
NHTs
Ph
Ph
1.06
1.13
1.04
2.04
2.92
1.16
2.96
1.88
2.58
1.70
1.84
1.00
1.02
1.02
2.74
fl (ppm)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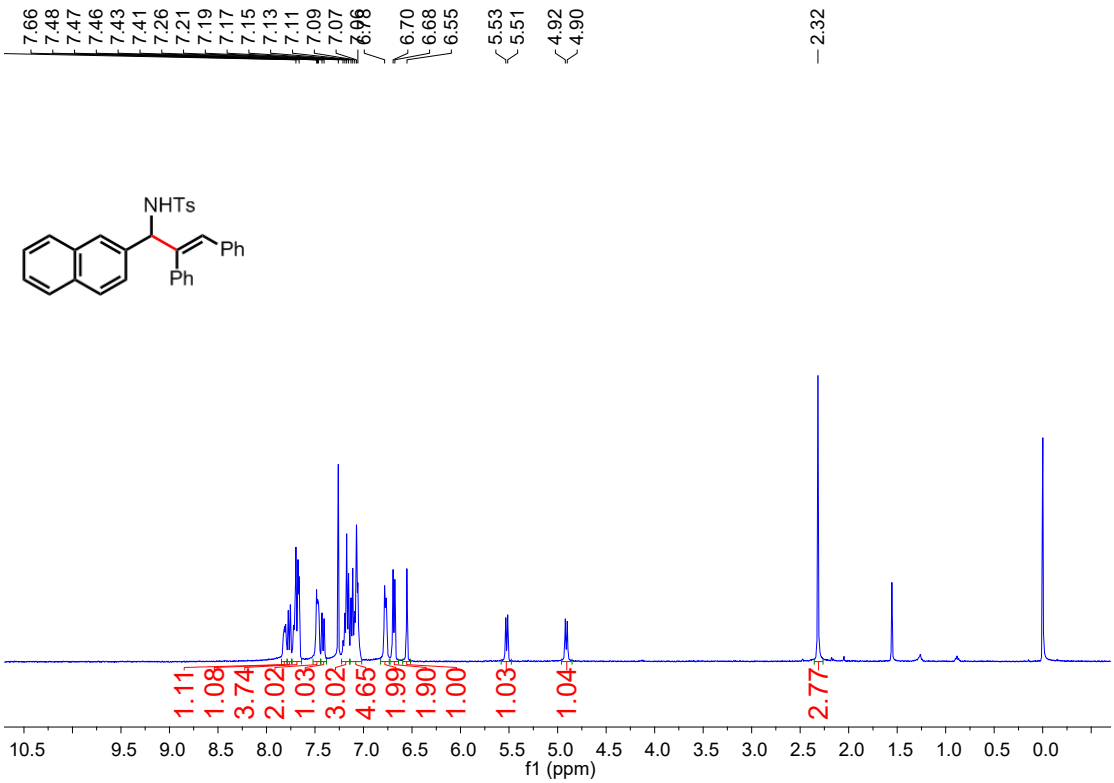
139.08
138.53
137.68
136.05
134.14
134.10
131.12
130.53
129.54
129.29
129.13
129.04
128.93
128.78
127.85
127.68
127.29
127.06
126.81
126.24
125.93
125.17
123.29
77.48
77.16
76.84
60.65
21.50
NHTs
Ph
Ph
fl (ppm)


7.66
7.48
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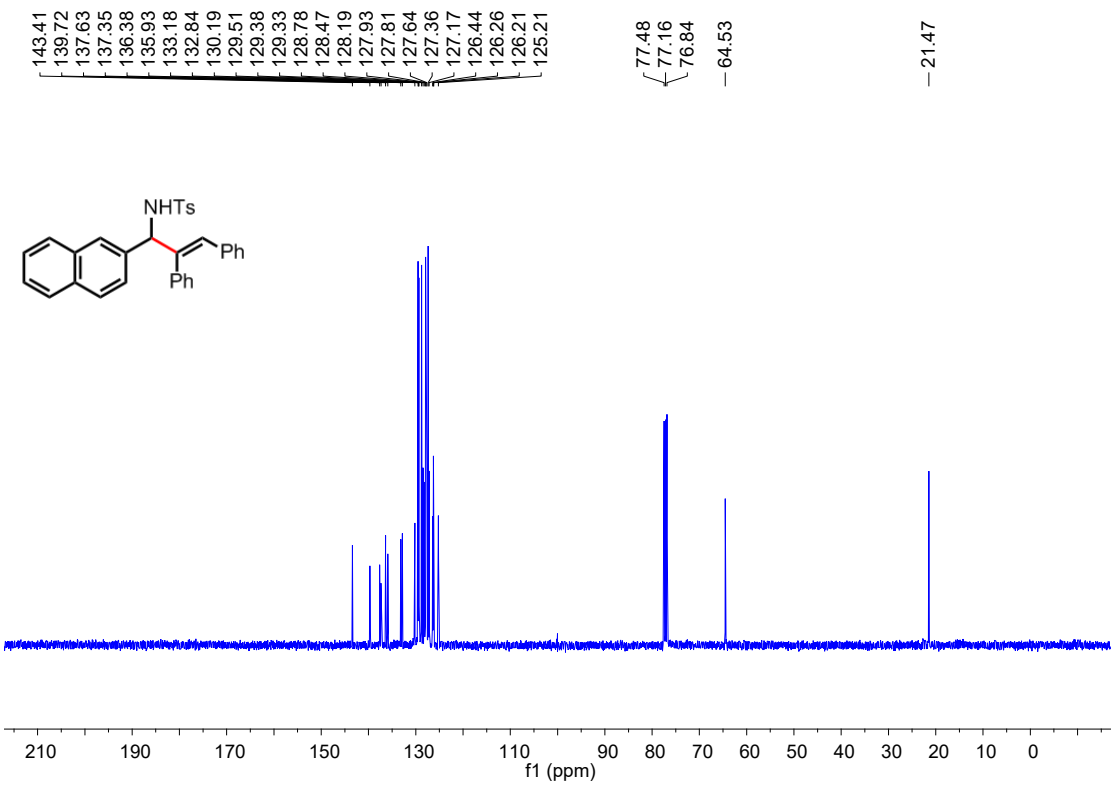
7.46
7.43
7.41
7.26
7.21
7.19
7.17
7.15
7.13
7.11
7.09
7.07
6.70
6.68
6.55
5.53
5.51
4.92
4.90
2.32
NHTs
Ph
Ph
1.11
1.08
3.74
2.02
1.03
3.02
4.65
1.99
1.90
1.00
1.03
1.04
2.77
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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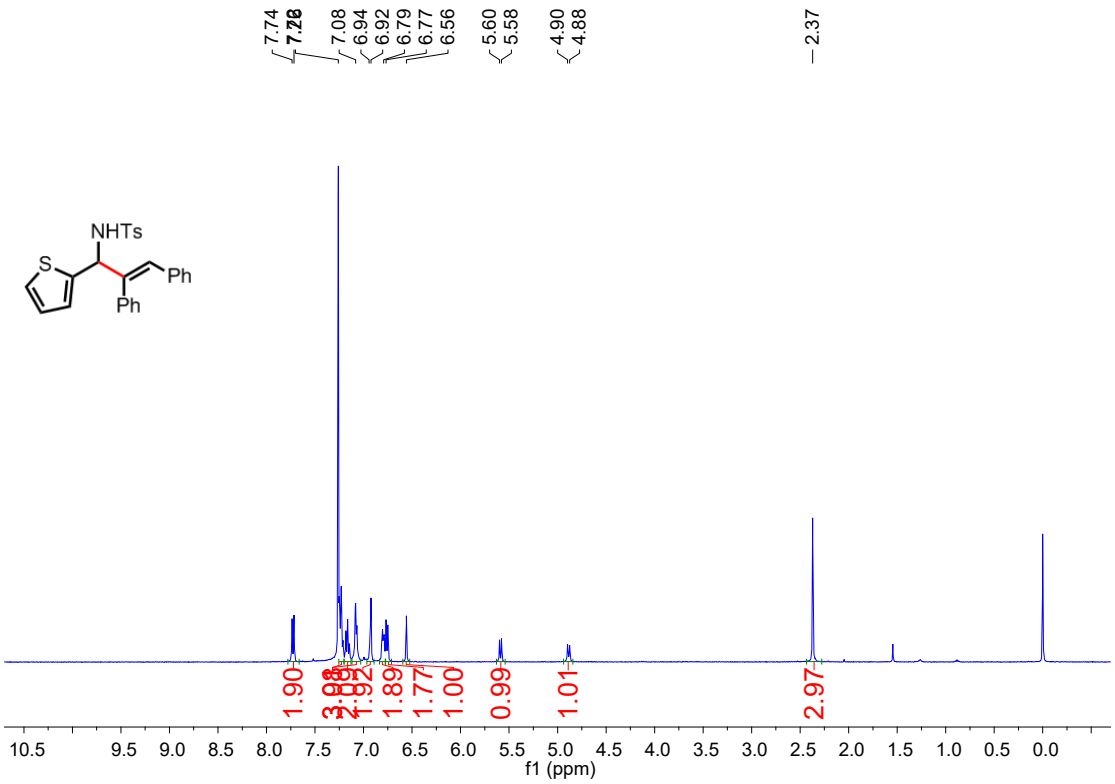
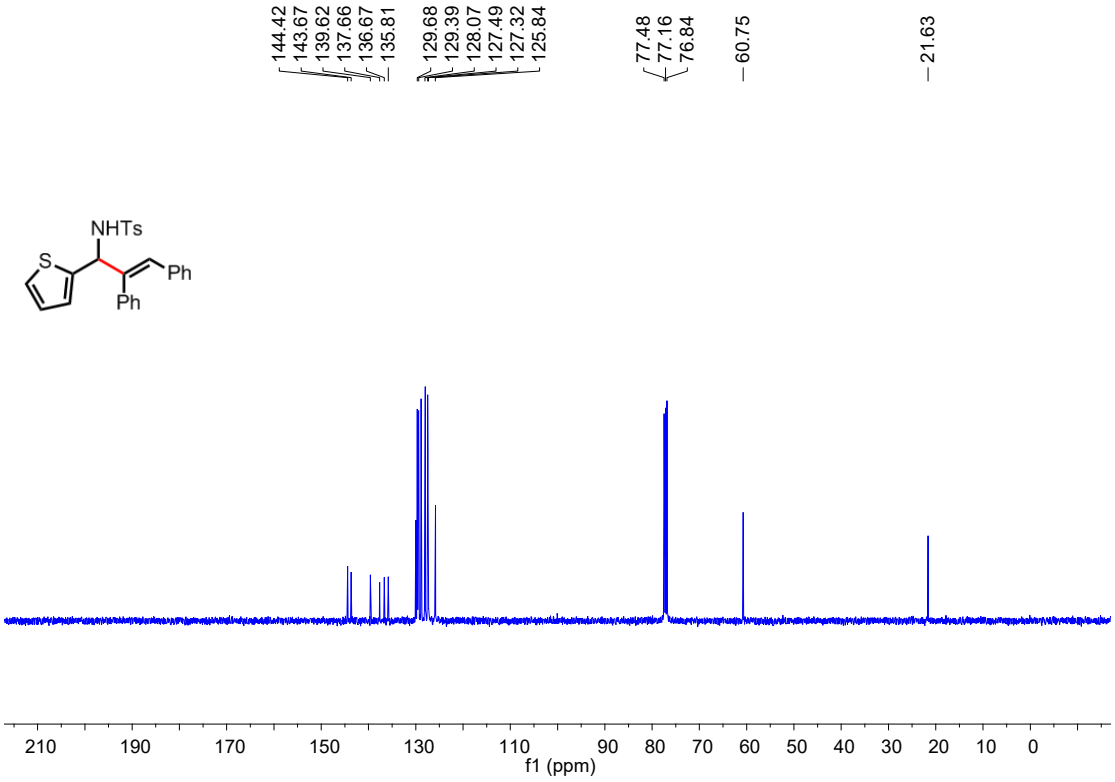
139.72
137.63
137.35
136.38
135.93
133.18
132.84
130.19
129.51
129.38
129.33
128.78
128.47
128.19
127.93
127.81
127.64
127.36
127.17
126.44
126.26
126.21
125.21
77.48
77.16
76.84
64.53
21.47
NHTs
Ph
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.74
7.26
7.08
6.94
6.92
6.79
6.77
6.56
5.60
5.58
4.90
4.88
2.37
NHTs
S
Ph
Ph
1.90
3.08
1.92
1.89
1.77
1.00
0.99
1.01
2.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.42
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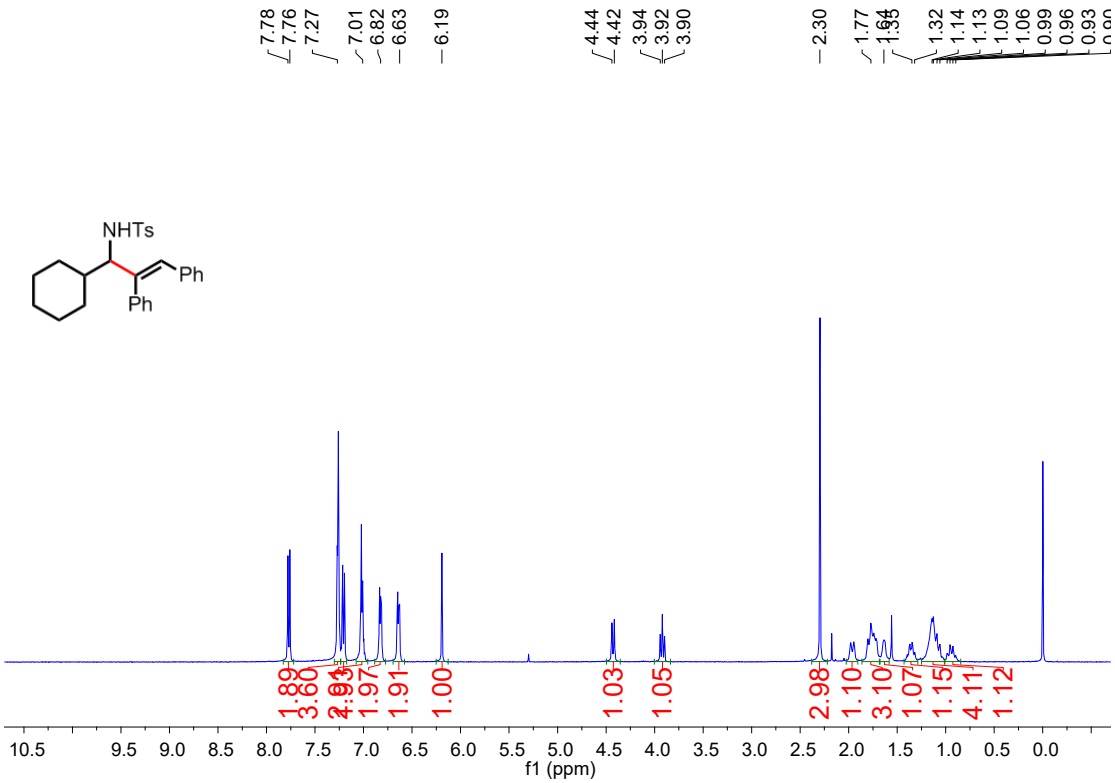
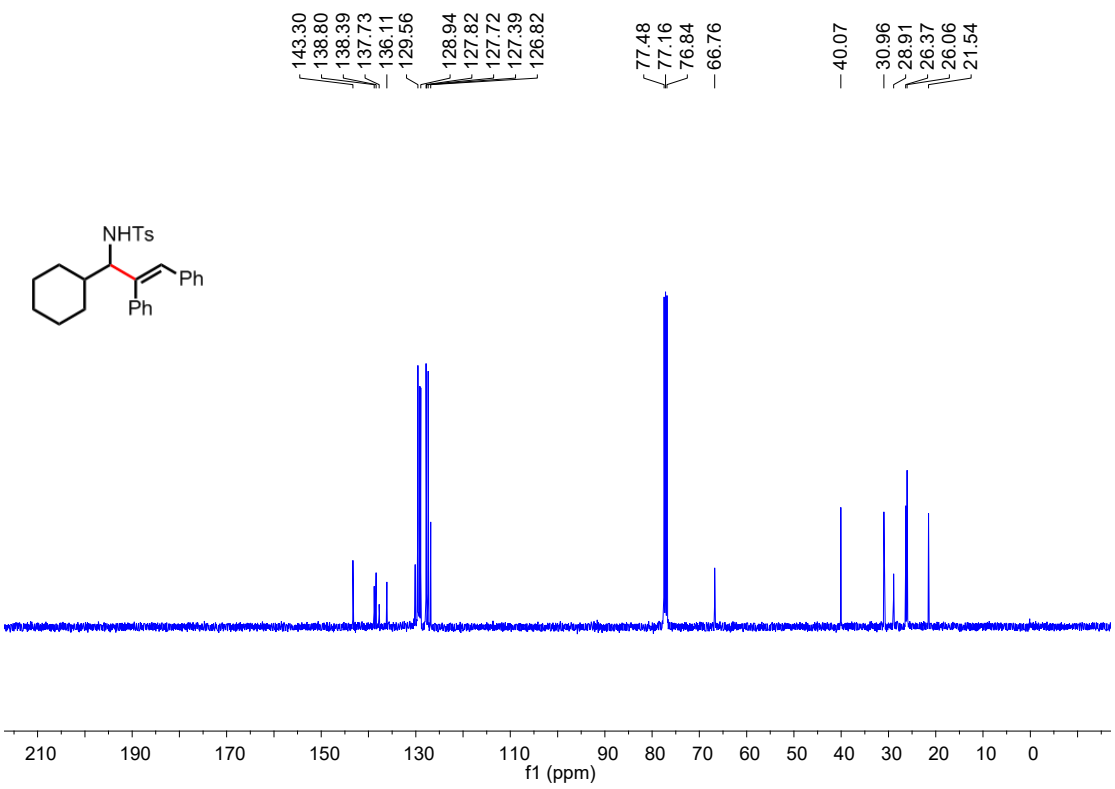
139.62
137.66
136.67
135.81
129.68
129.39
128.07
127.49
127.32
125.84
77.48
77.16
76.84
60.75
21.63
NHTs
S
Ph
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.78
7.76
7.27
7.01
6.82
6.63
6.19
4.44
4.42
3.94
3.92
3.90
2.30
1.77
1.32
1.14
1.13
1.09
1.06
0.99
0.96
0.93
NHTs
Ph
Ph
1.89
3.60
1.97
1.91
1.00
1.03
1.05
2.98
1.10
3.10
1.07
1.15
4.11
1.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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66.76
40.07
30.96
28.91
26.37
26.06
21.54
NHTs
Ph
Ph
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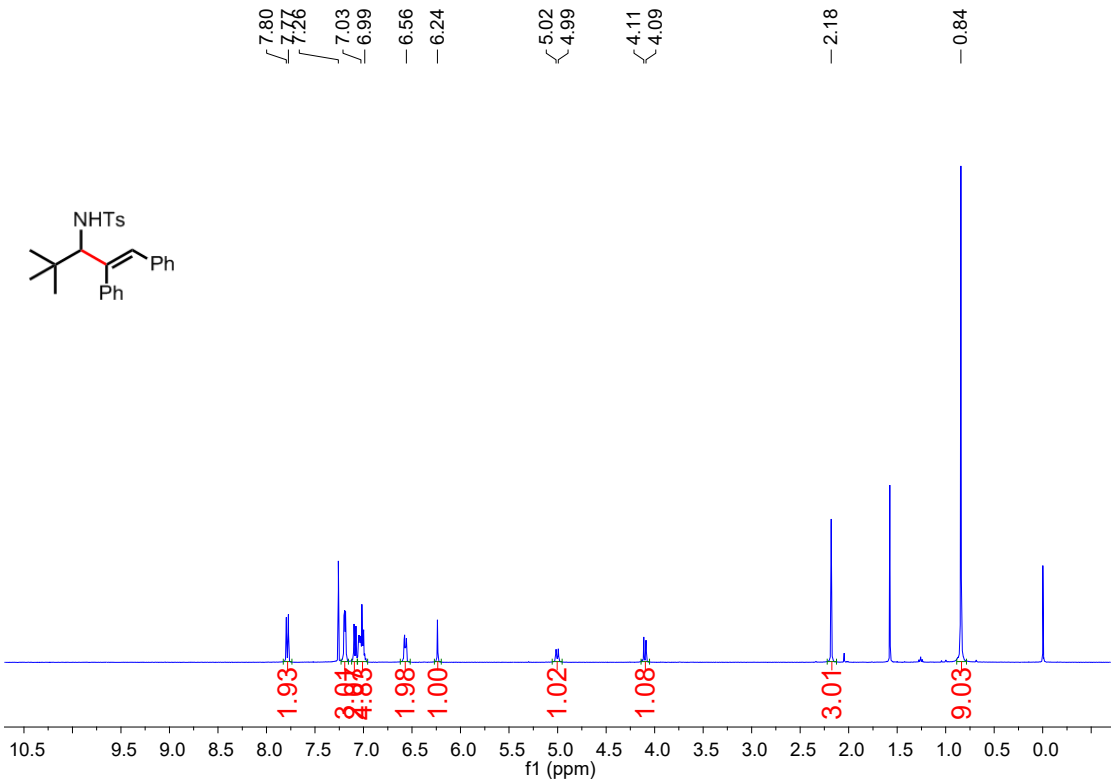
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6.24
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4.11
4.09
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0.84
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Ph
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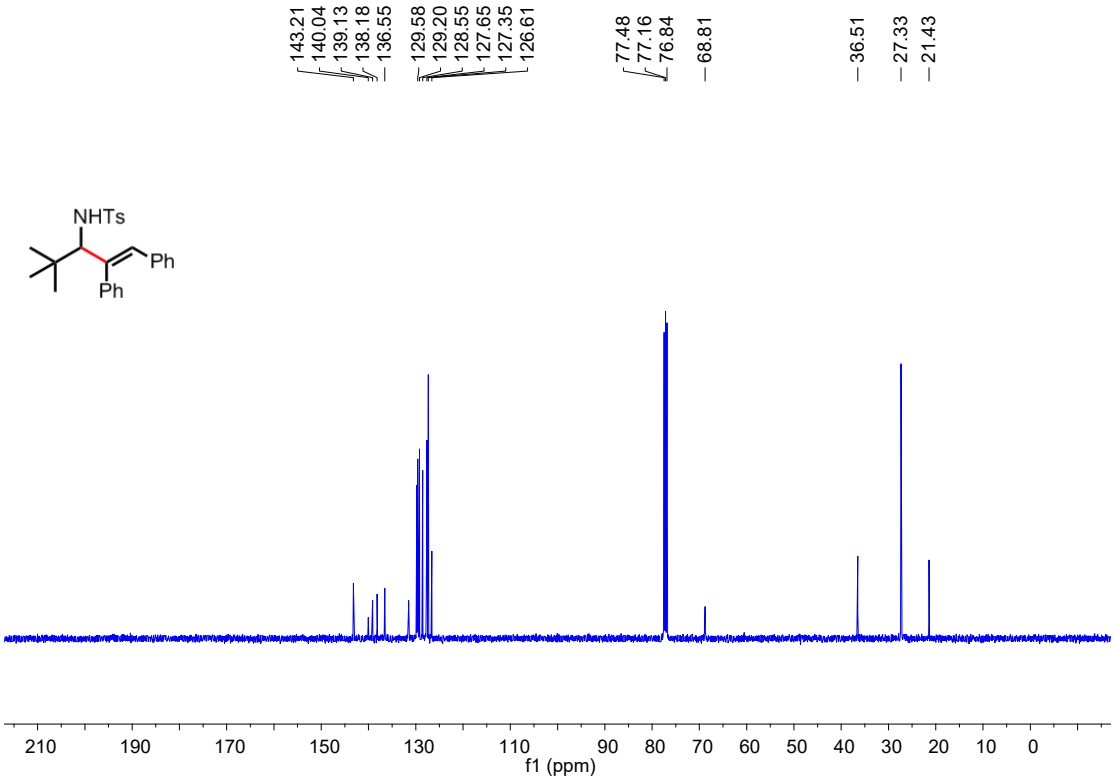
1.08
3.01
9.03
f1 (ppm)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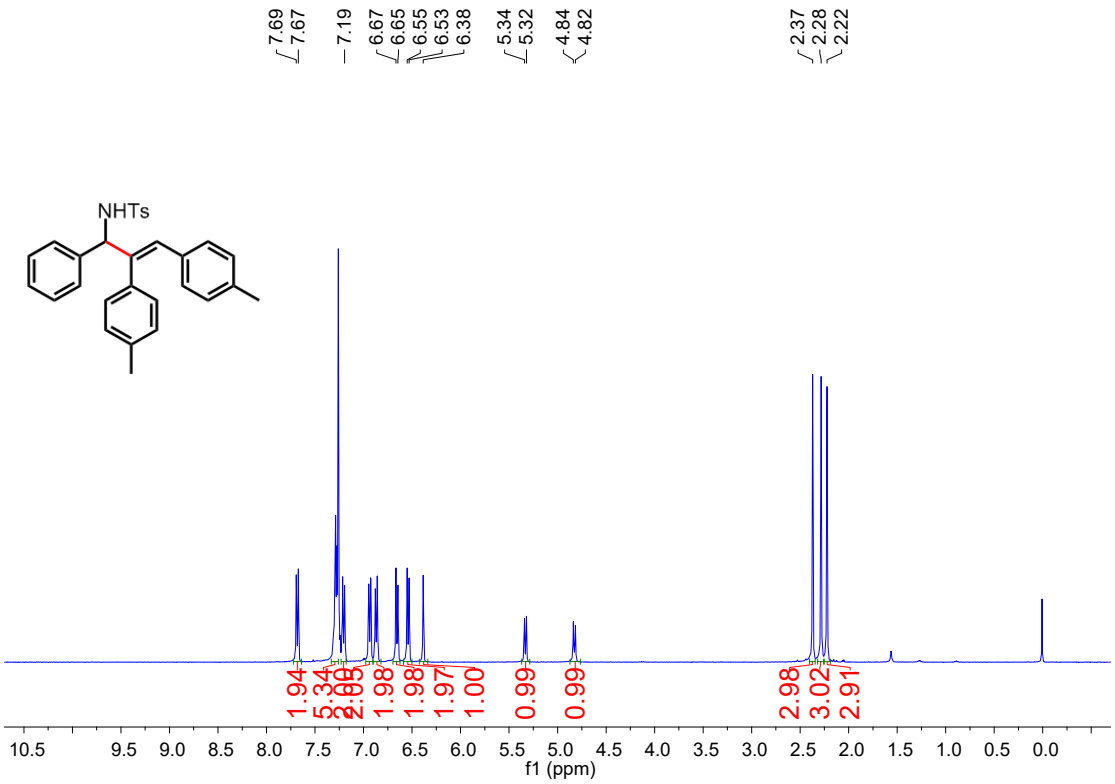
21.43
NHTs
Ph
Ph
f1 (ppm)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2.28
2.22
NHTs
1.94
5.34
2.05
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1.98
1.97
1.00
0.99
0.99
2.98
3.02
2.91
10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
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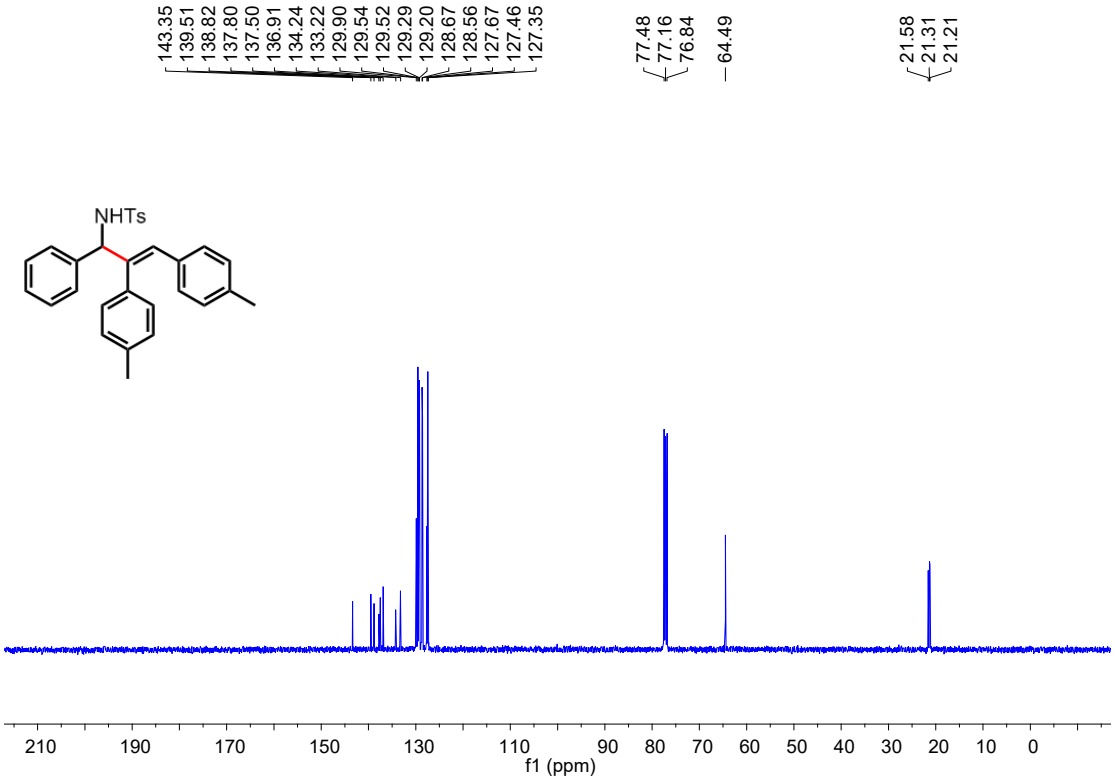
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127.67
127.46
127.35
77.48
77.16
76.84
64.49
21.58
21.31
21.21
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170
150
130
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90
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30
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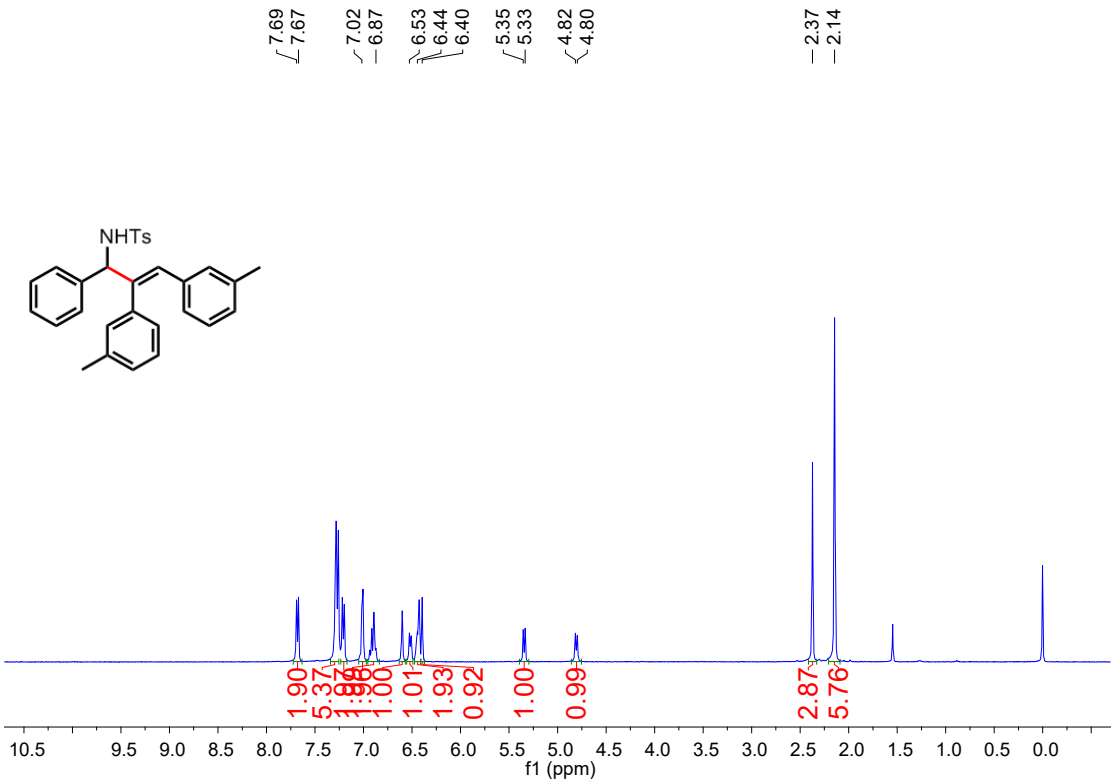
f1 (ppm)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NHTs
1.90
5.37
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1.01
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0.92
1.00
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5.76
10.5
9.5
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7.0
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5.5
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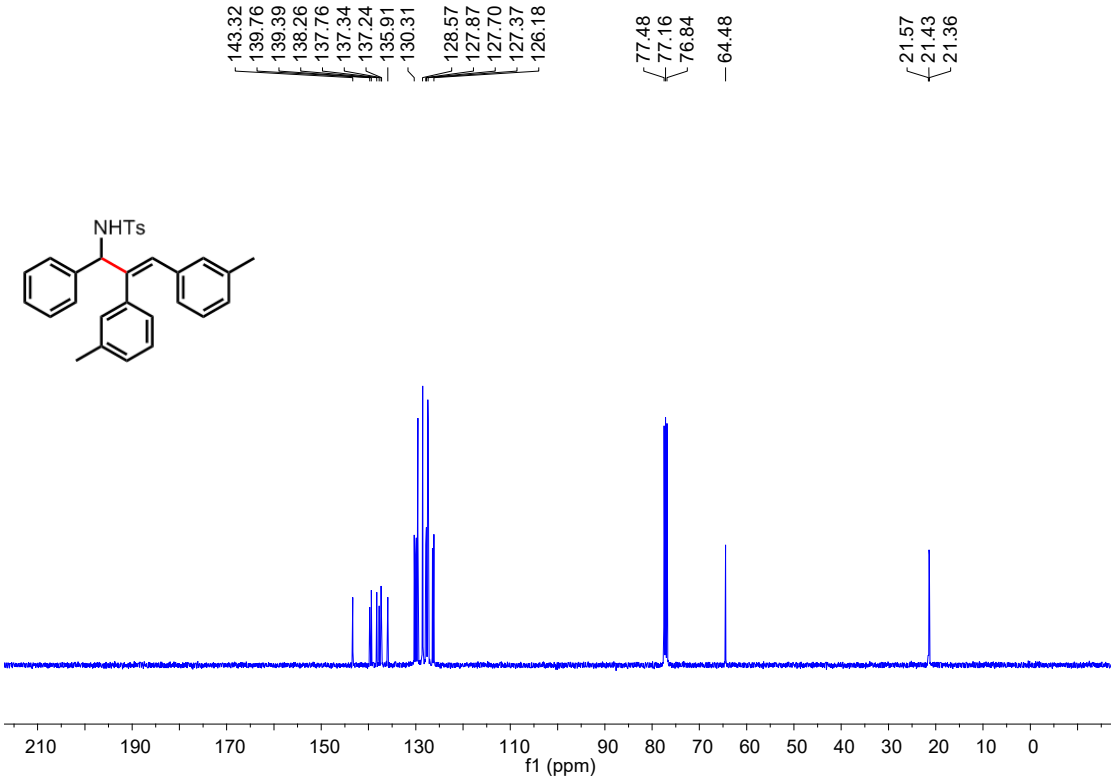
f1 (ppm)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127.37
126.18
77.48
77.16
76.84
64.48
21.57
21.43
21.36
NHTs
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170
150
130
110
90
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10
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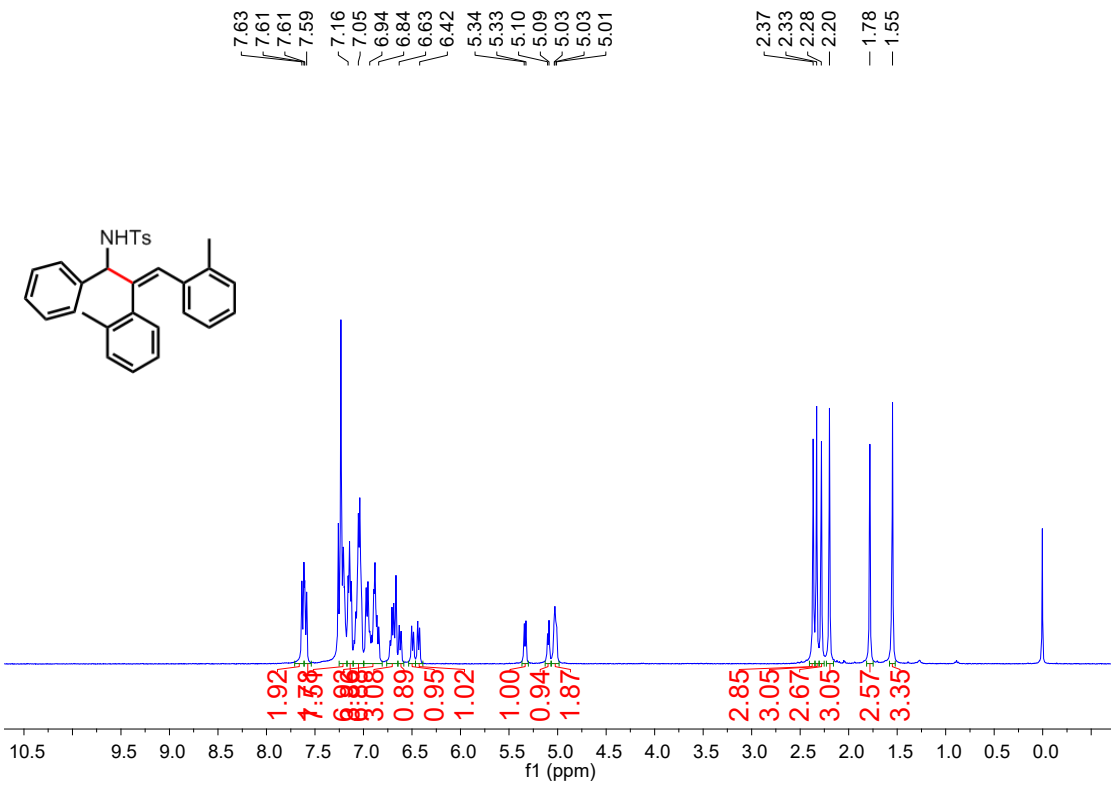
f1 (ppm)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5.10
5.09
5.03
5.03
5.01
2.37
2.33
2.28
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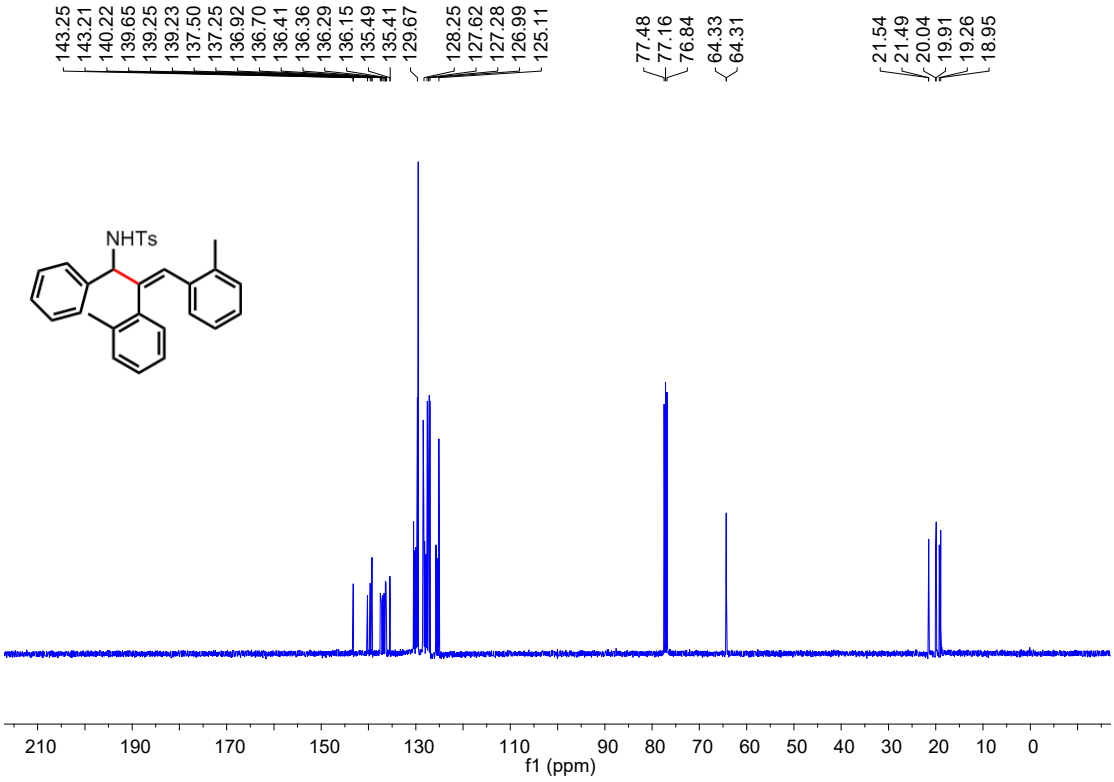
NHTs
1.92
2.85
3.05
2.67
3.05
2.57
3.35
f1 (ppm)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135.41
129.67
128.25
127.62
127.28
126.99
125.11
77.48
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64.31
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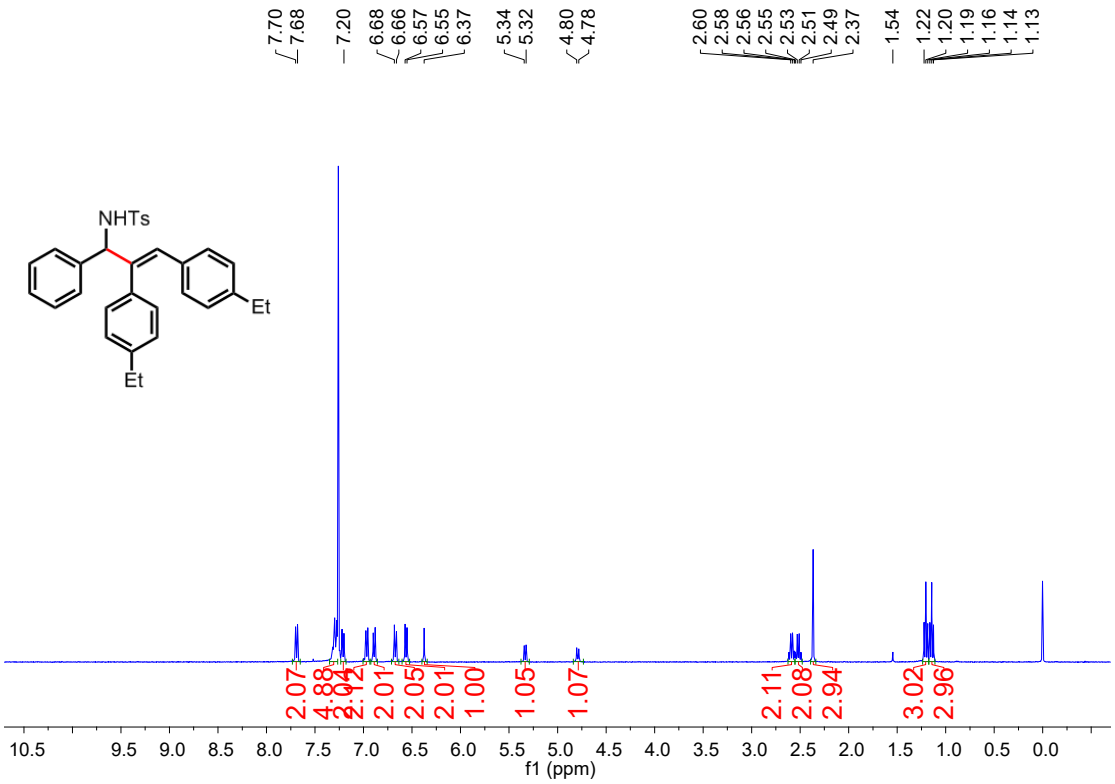
19.26
18.95
NHTs
f1 (ppm)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4.80
4.78
2.60
2.58
2.56
2.55
2.53
2.51
2.49
2.37
1.54
1.22
1.20
1.19
1.16
1.14
1.13
NHTs
Et
Et
2.07
4.88
2.12
2.01
2.05
2.01
1.00
1.05
1.07
2.11
2.08
2.94
3.02
2.96
10.5
9.5
9.0
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8.0
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7.0
6.5
6.0
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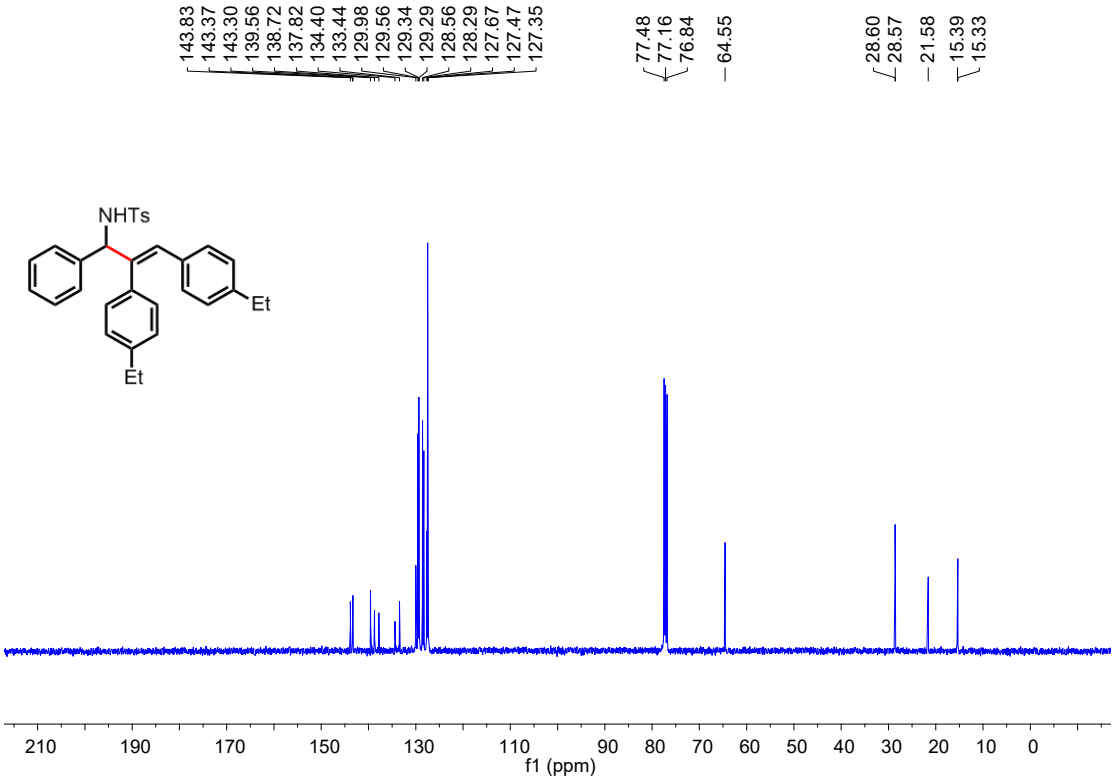
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127.47
127.35
77.48
77.16
76.84
64.55
28.60
28.57
21.58
15.39
15.33
NHTs
Et
Et
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150
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90
80
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50
40
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10
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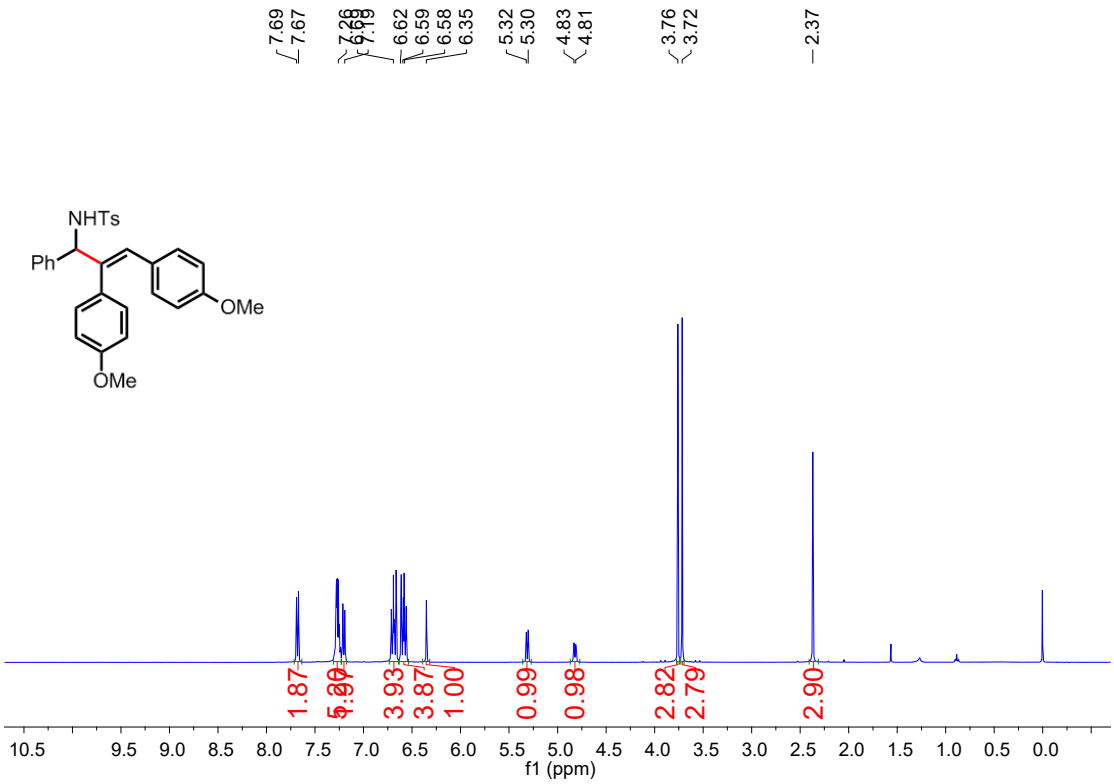
f1 (ppm)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4.83
4.81
3.76
3.72
2.37
NHTs
Ph
OMe
OMe
1.87
5.00
3.93
3.87
1.00
0.99
0.98
2.82
2.79
2.90
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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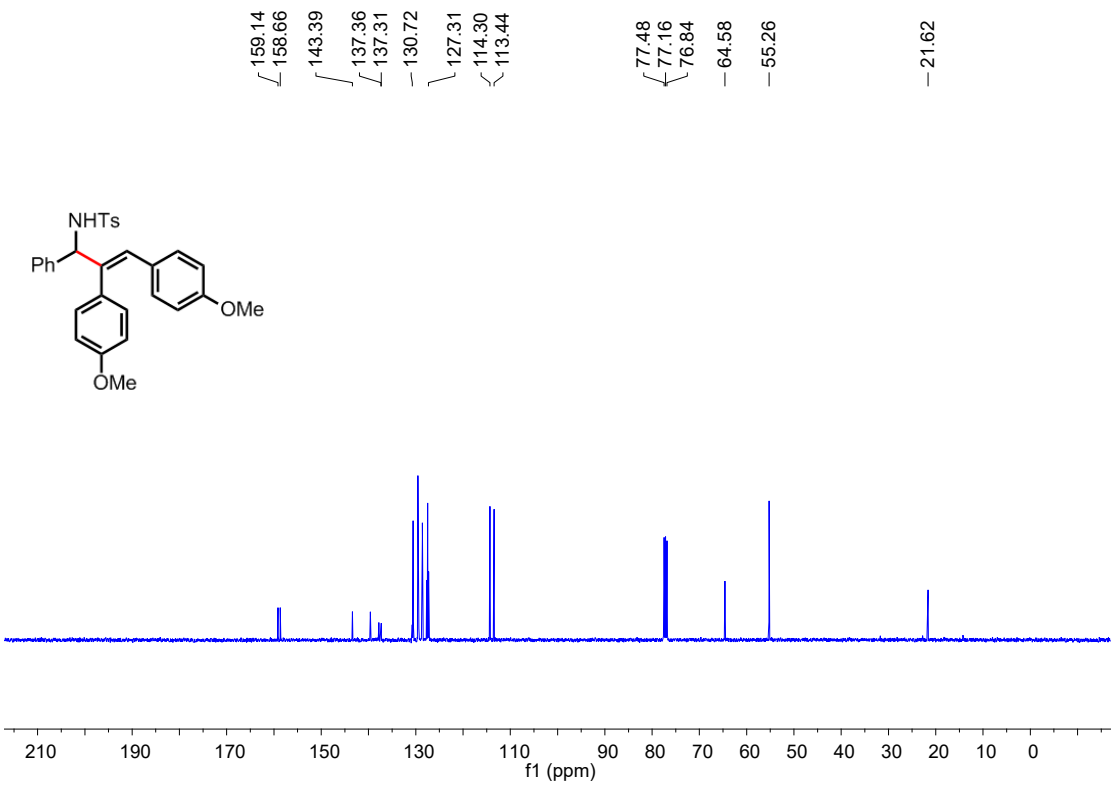
f1 (ppm)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76.84
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55.26
21.62
NHTs
Ph
OMe
OMe
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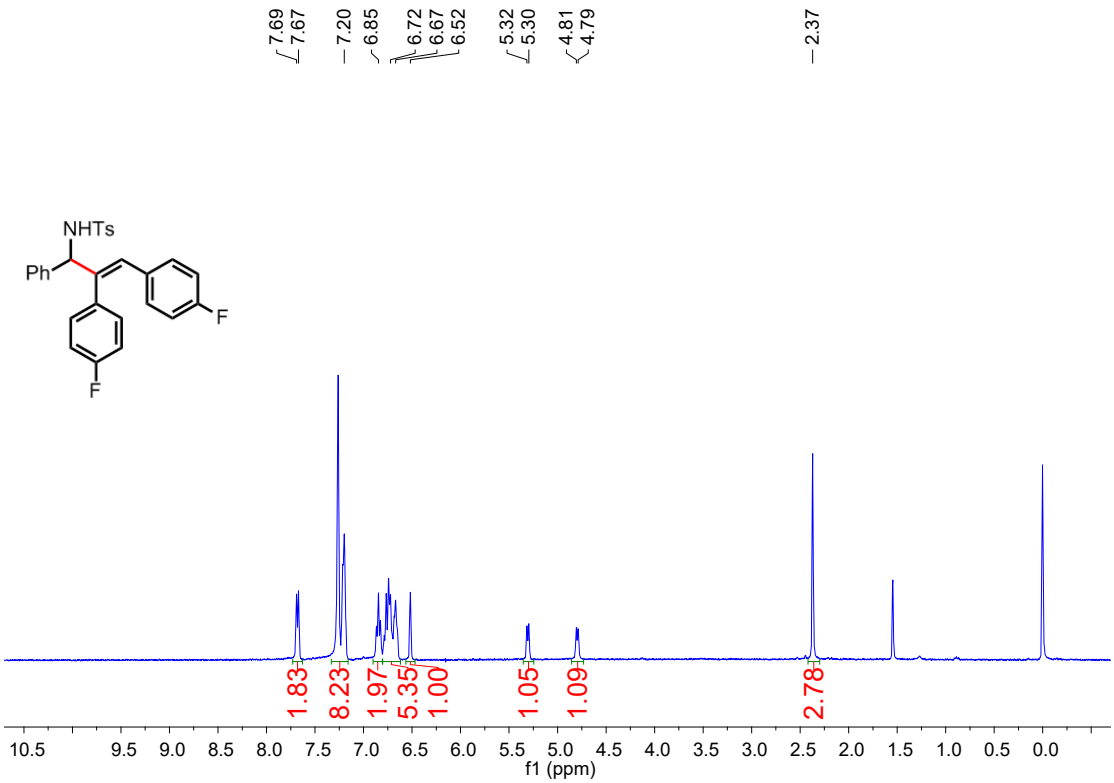
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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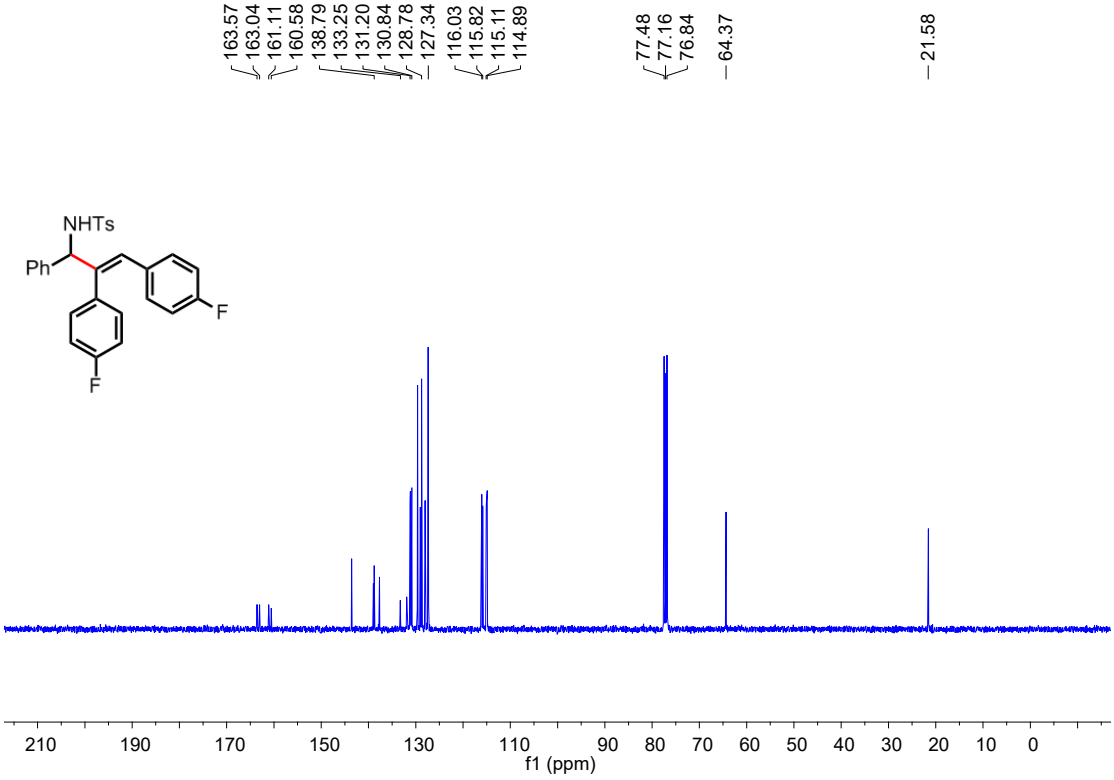
6.52
5.32
5.30
4.81
4.79
2.37
NHTs
Ph
F
F
1.83
8.23
1.97
5.35
1.00
1.05
1.09
2.78
f1 (ppm)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128.78
127.34
116.03
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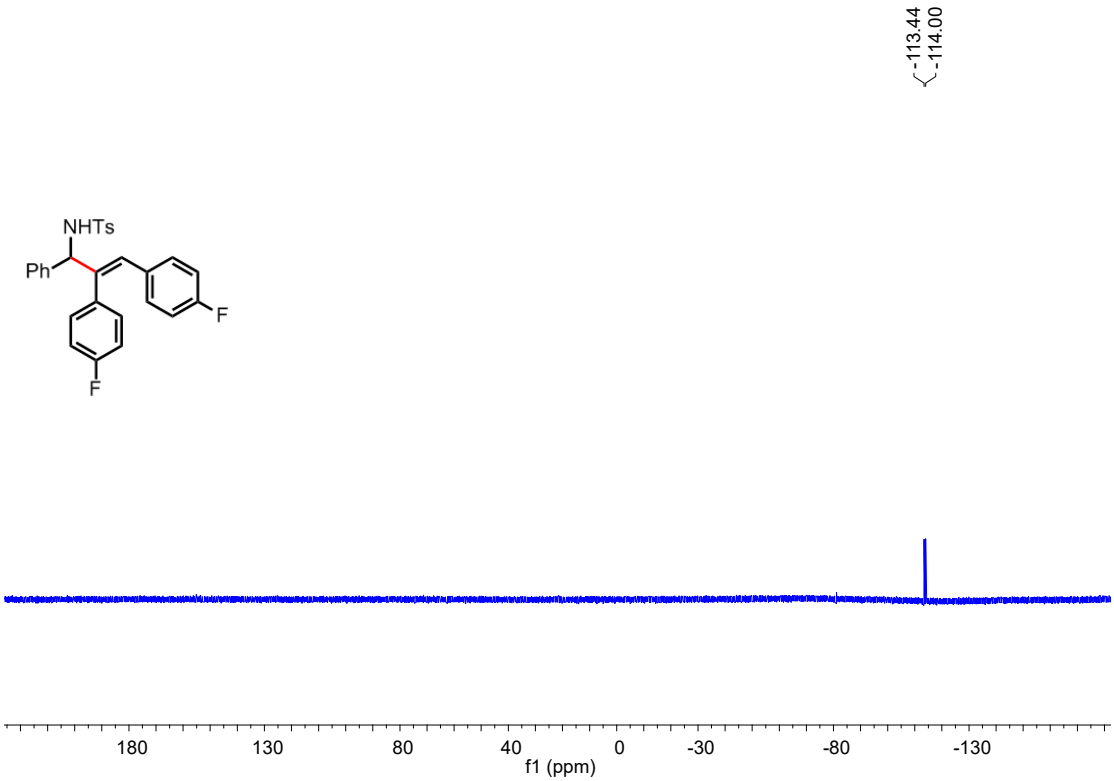
77.48
77.16
76.84
64.37
21.58
NHTs
Ph
F
F
f1 (ppm)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Ph
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F
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130
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40
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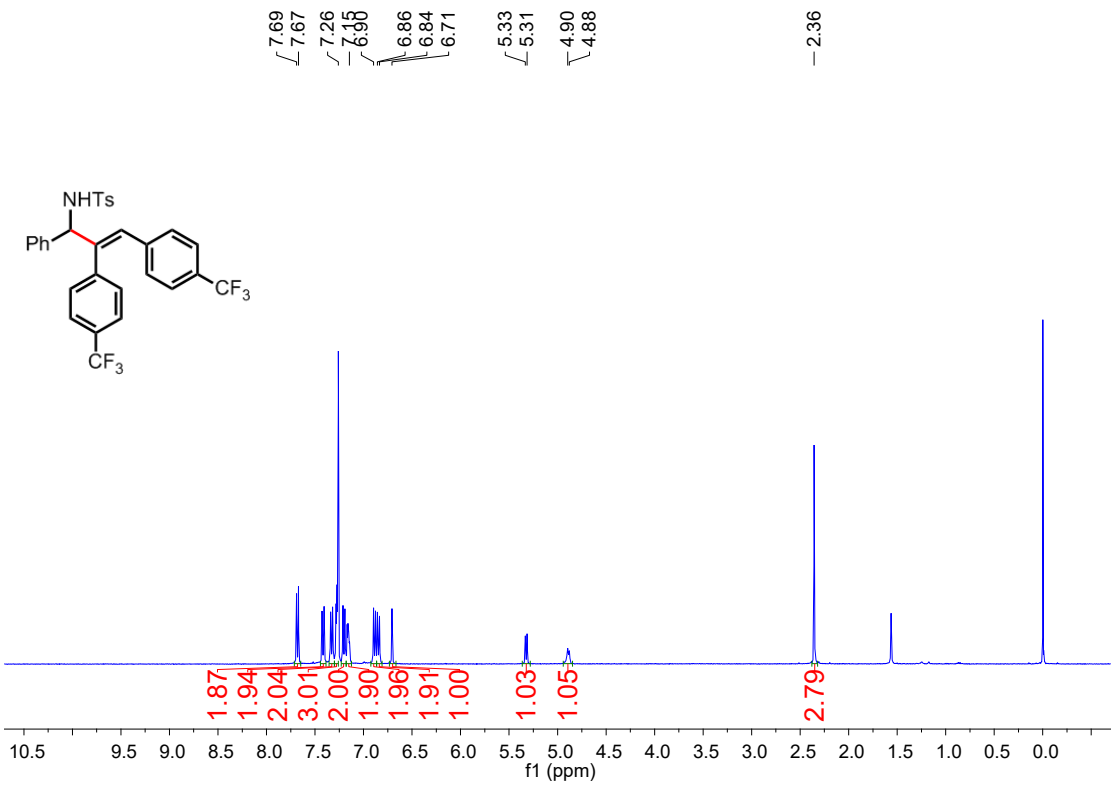
-80
-130
f1 (ppm)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6.71
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5.31
4.90
4.88
2.36
NHTs
Ph
CF3
CF3
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1.94
2.04
3.01
2.00
1.90
1.96
1.91
1.00
1.03
1.05
2.79
10.5
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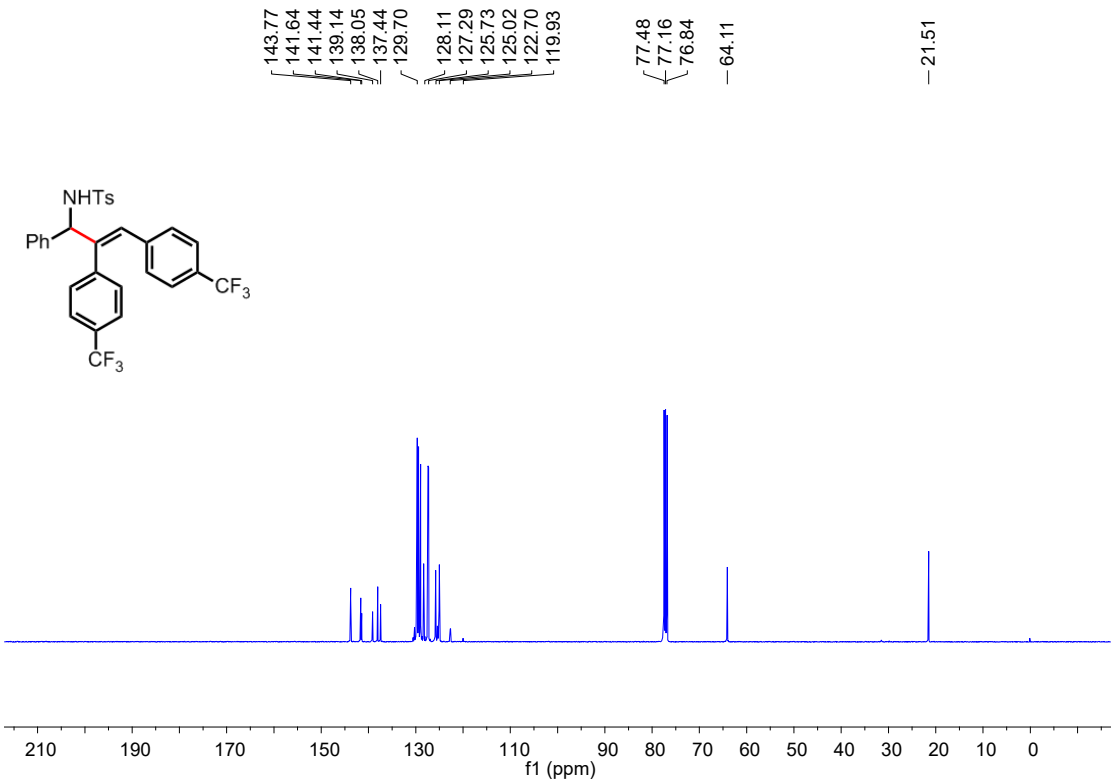
f1 (ppm)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125.02
122.70
119.93
77.48
77.16
76.84
64.11
21.51
NHTs
Ph
CF3
CF3
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130
110
90
80
70
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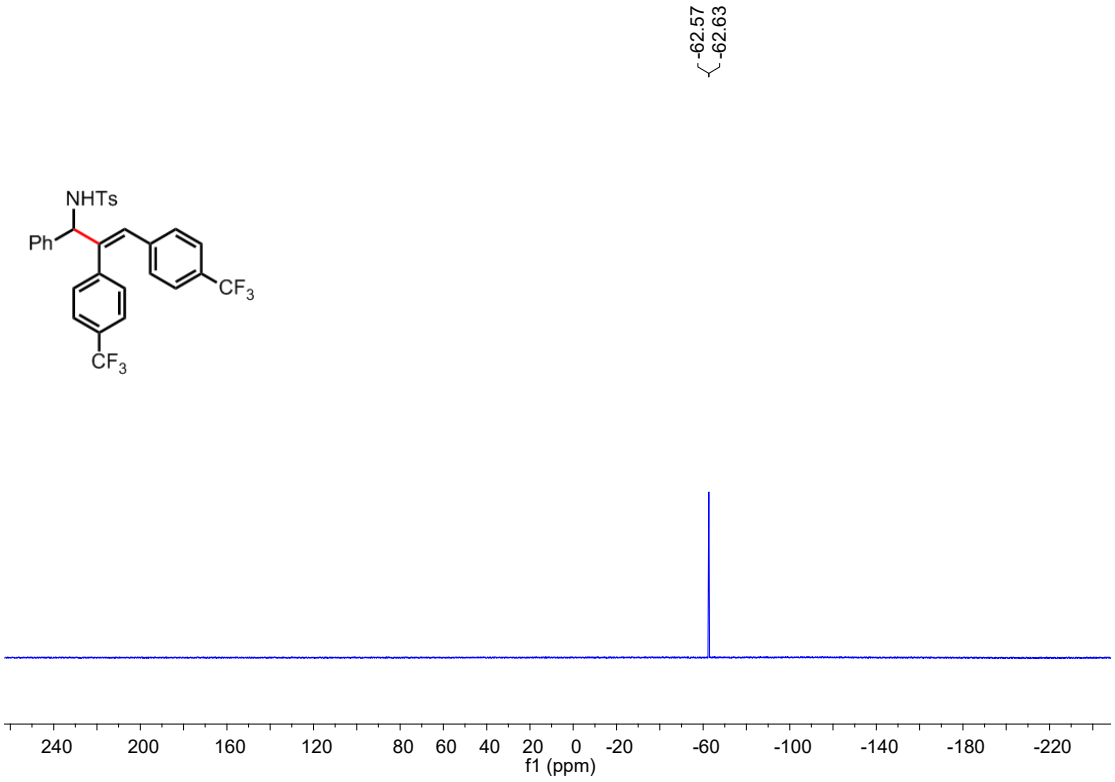
50
40
30
20
10
0
f1 (ppm)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NHTs
Ph
CF3
CF3
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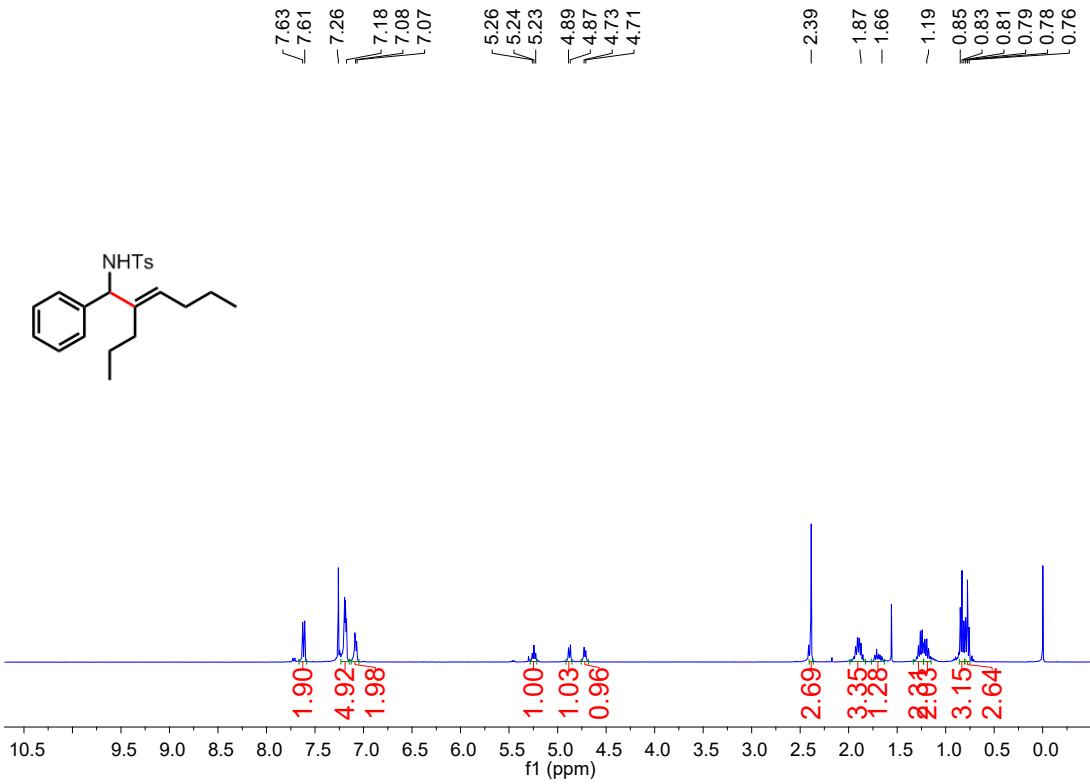
40
20
0
-20
-60
-100
-140
-180
-220
f1 (ppm)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2.39
1.87
1.66
1.19
0.85
0.83
0.81
0.79
0.78
0.76
NHTs
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4.92
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1.00
1.03
0.96
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1.28
2.03
3.15
2.64
10.5
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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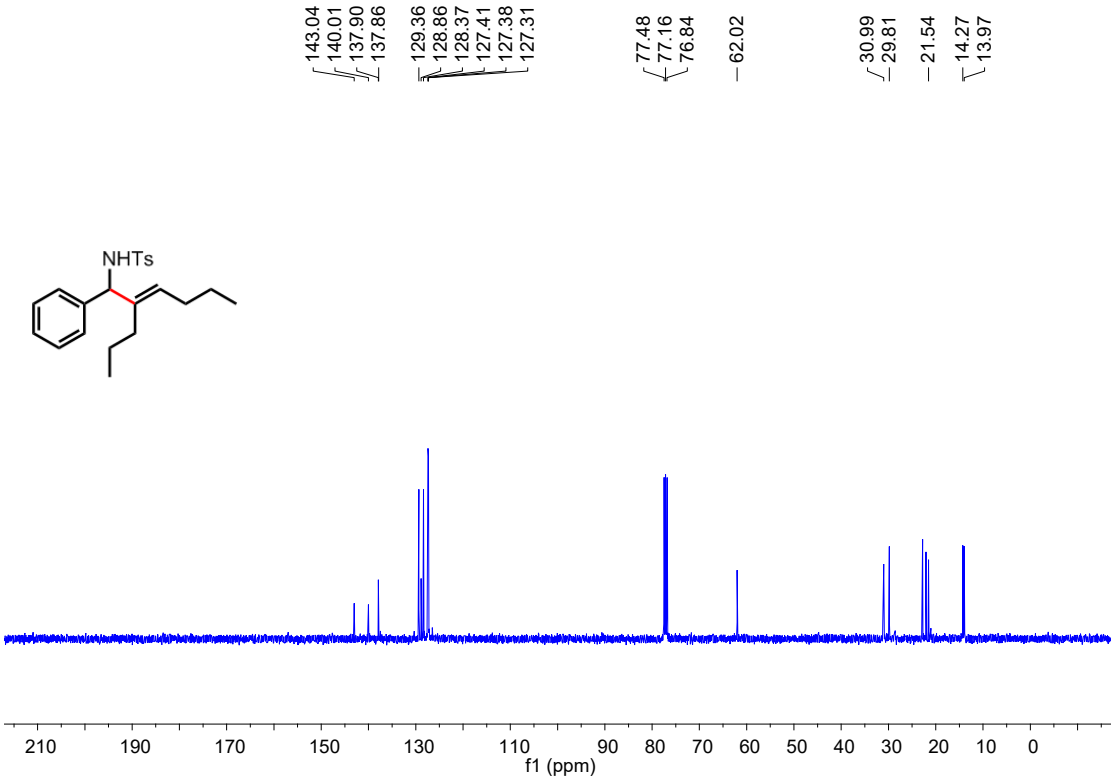
0.0
f1 (ppm)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127.31
77.48
77.16
76.84
62.02
30.99
29.81
21.54
14.27
13.97
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130
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50
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30
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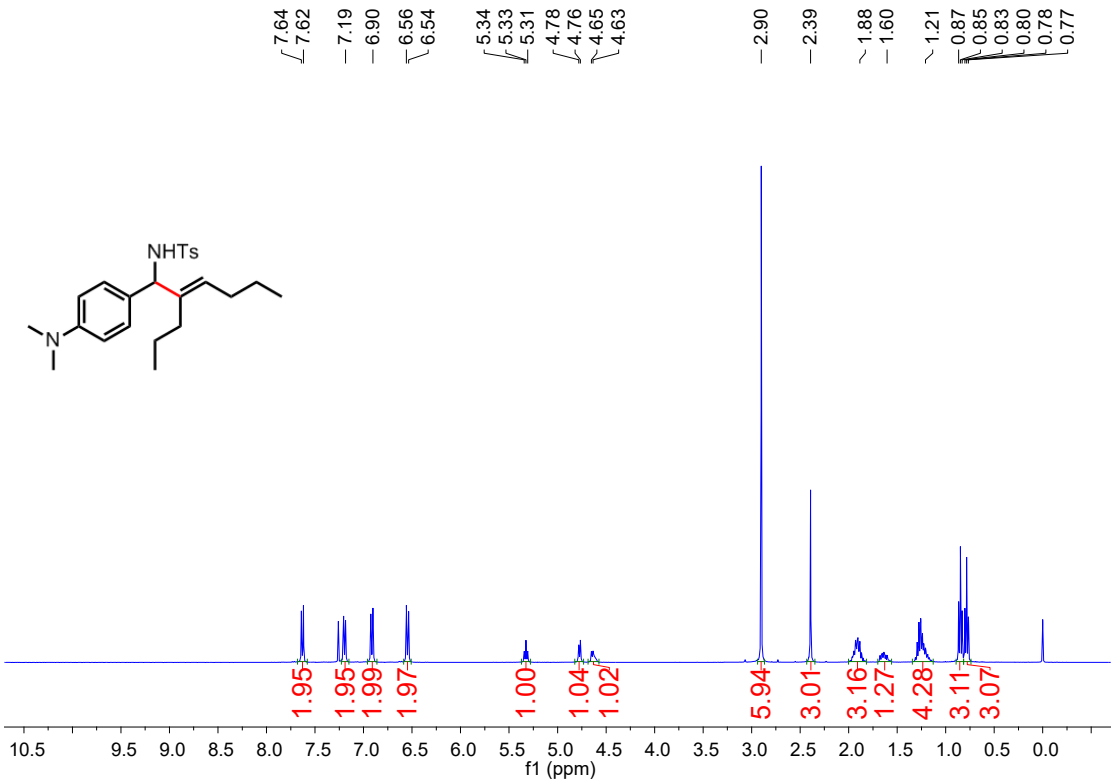
10
0
f1 (ppm)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4.78
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4.65
4.63
2.90
2.39
1.88
1.60
1.21
0.87
0.85
0.83
0.80
0.78
0.77
NHTs
N
1.95
1.95
1.99
1.97
1.00
1.04
1.02
5.94
3.01
3.16
1.27
4.28
3.11
3.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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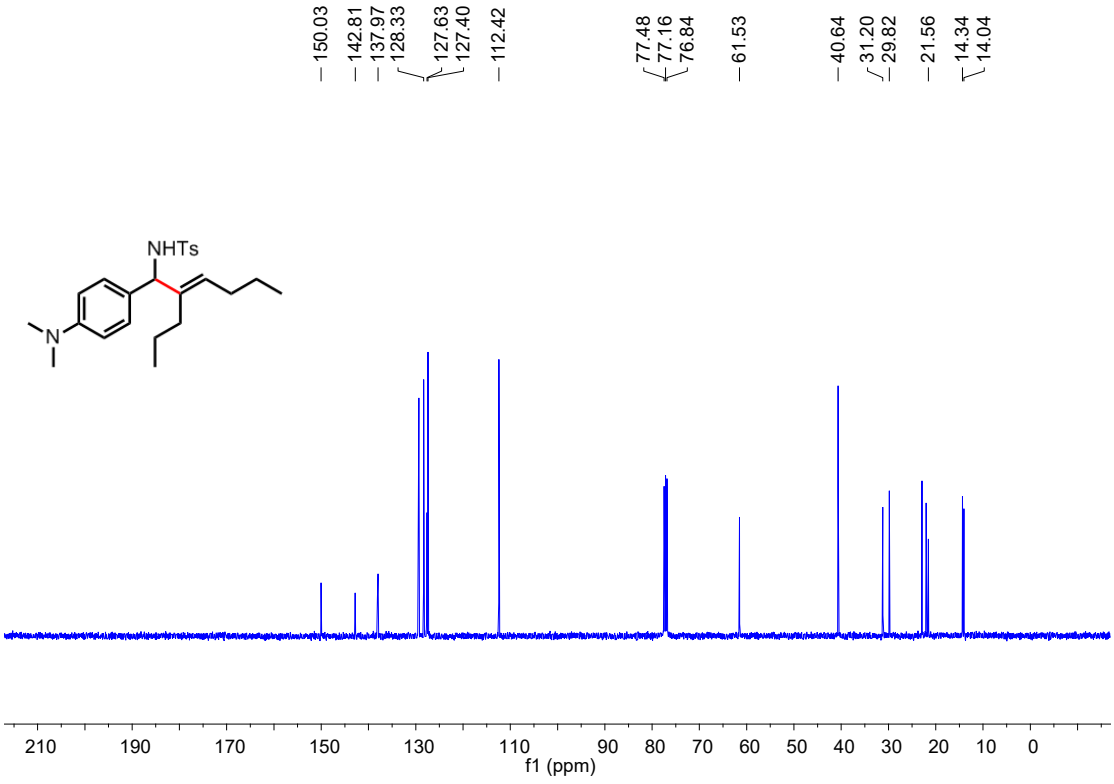
0.0
f1 (ppm)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61.53
40.64
31.20
29.82
21.56
14.34
14.04
NHTs
N
210
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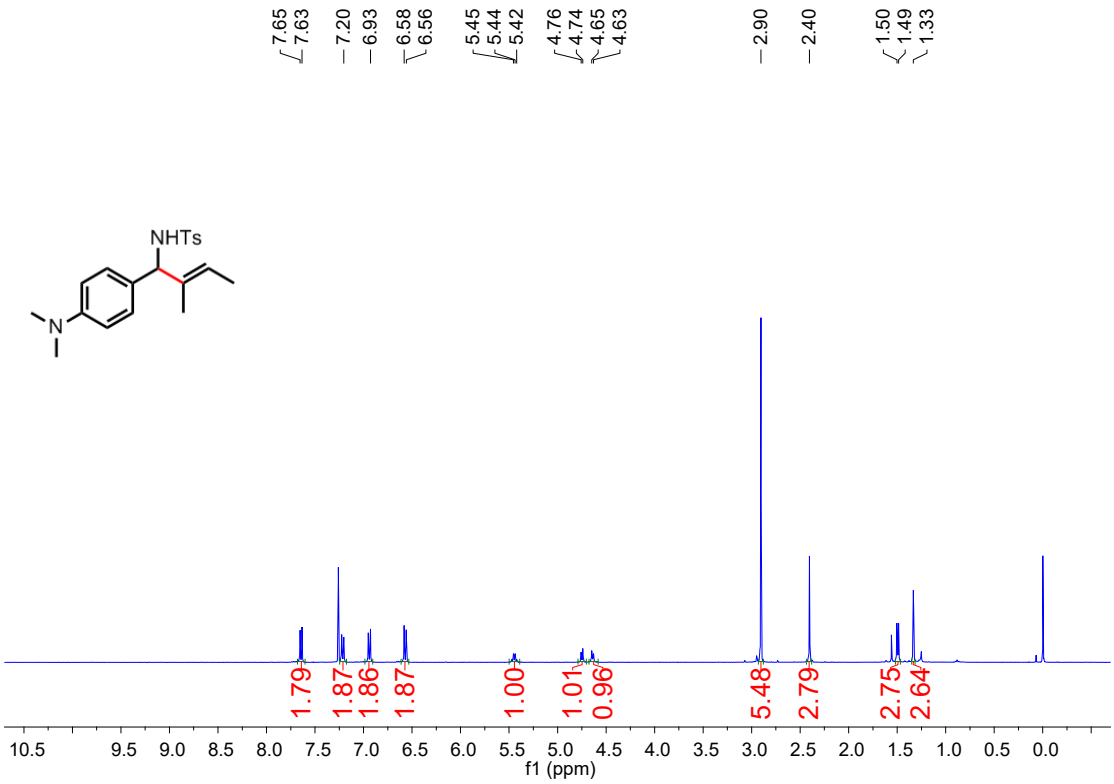
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.74
4.65
4.63
2.90
2.40
1.50
1.49
1.33
NHTs
N
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1.87
1.86
1.87
1.00
1.01
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2.75
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7.5
7.0
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6.0
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3.0
2.5
2.0
1.5
1.0
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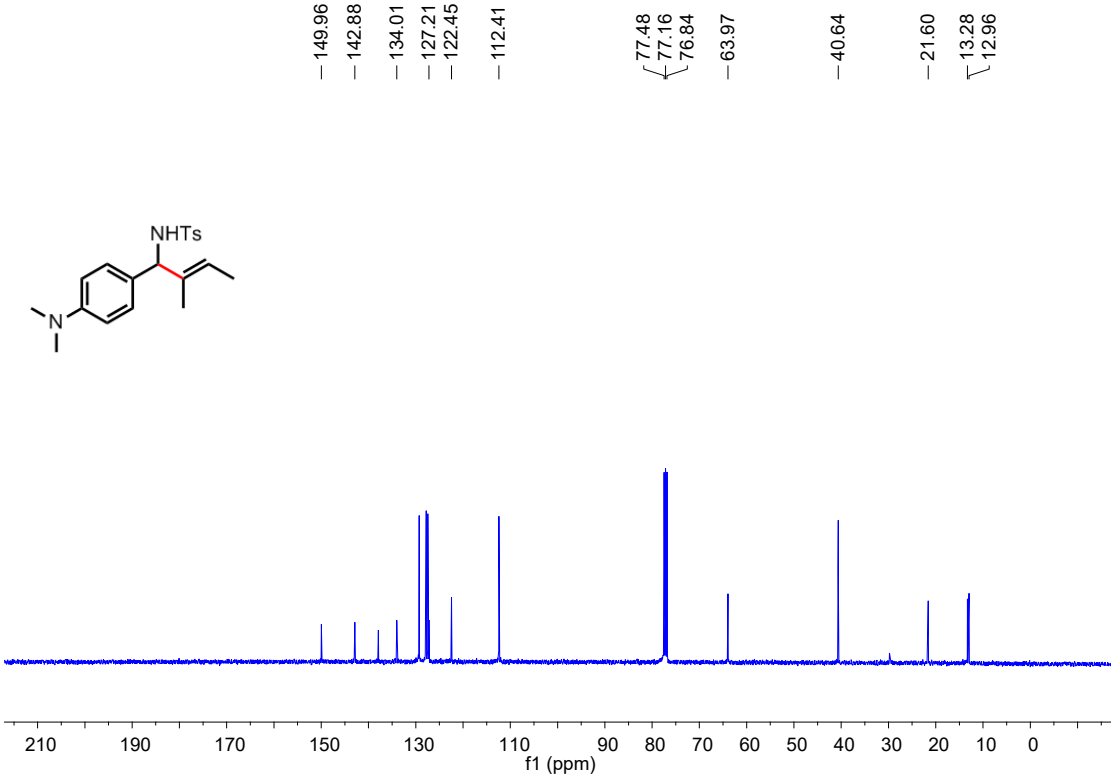
0.0
f1 (ppm)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40.64
21.60
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12.96
NHTs
N
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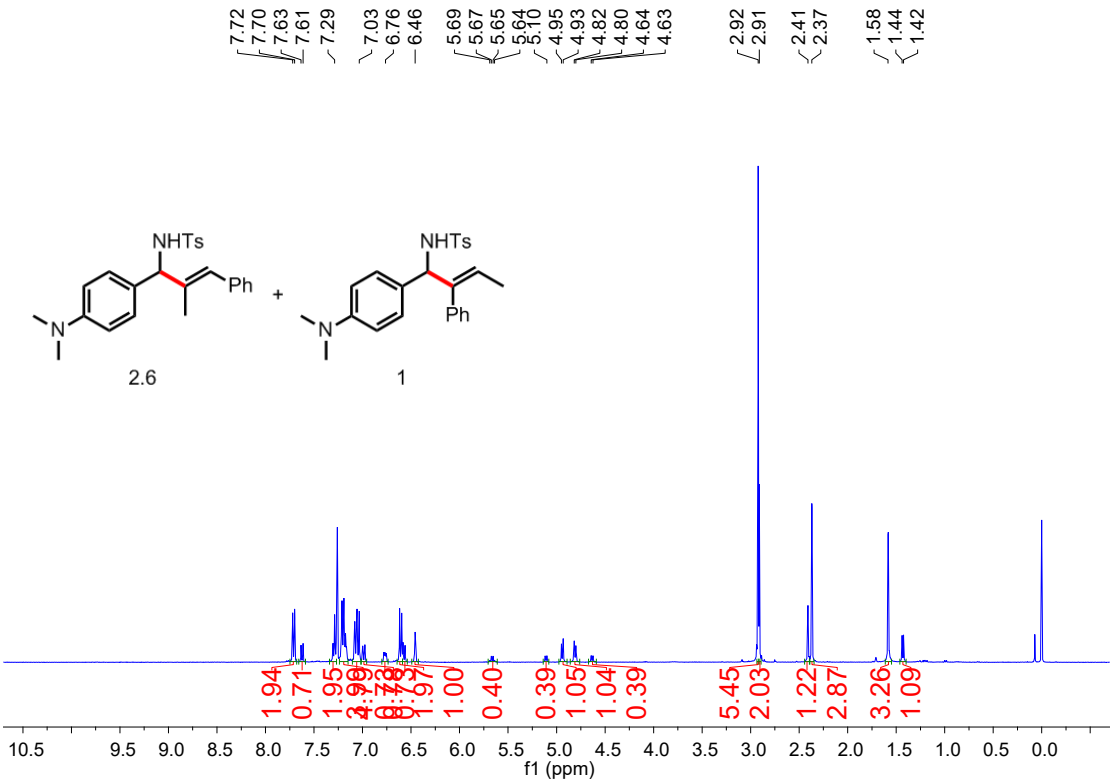
10
0
f1 (ppm)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4.82
4.80
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4.63
2.92
2.91
2.41
2.37
1.58
1.44
1.42
NHTs
Ph
N
2.6
NHTs
Ph
N
1
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0.71
1.95
1.97
1.00
0.40
0.39
1.05
1.04
0.39
5.45
2.03
1.22
2.87
3.26
1.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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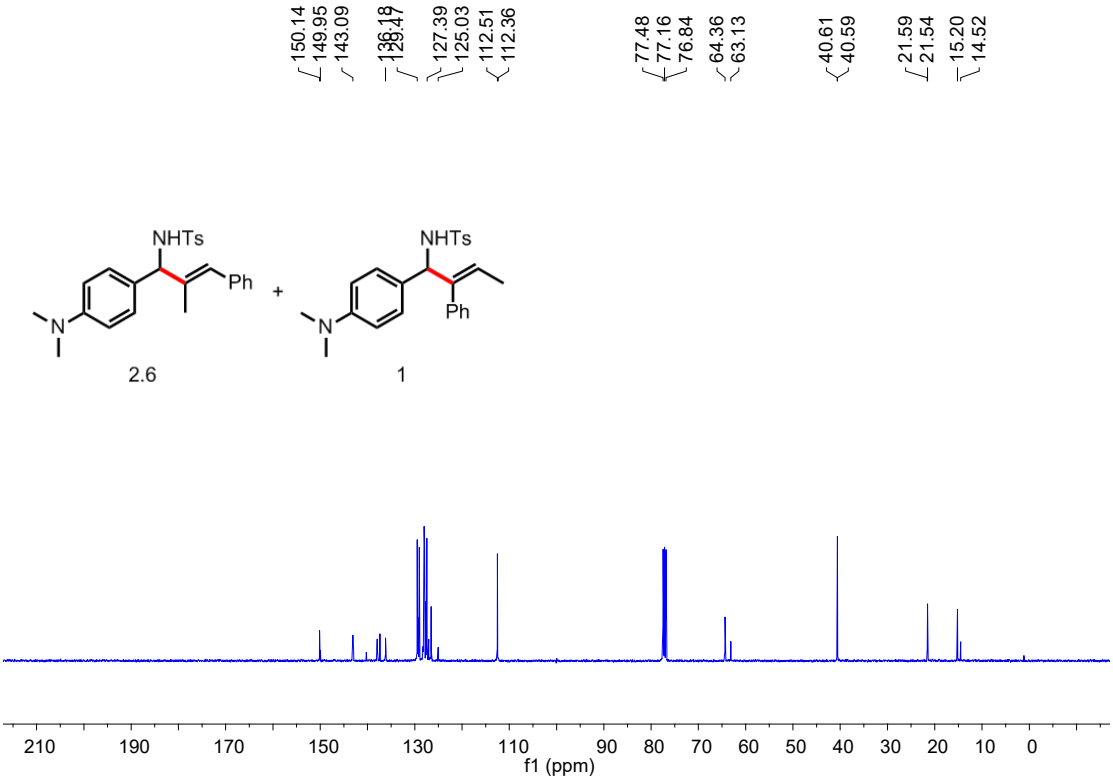
f1 (ppm)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112.51
112.36
77.48
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76.84
64.36
63.13
40.61
40.59
21.59
21.54
15.20
14.52
NHTs
Ph
N
2.6
NHTs
Ph
N
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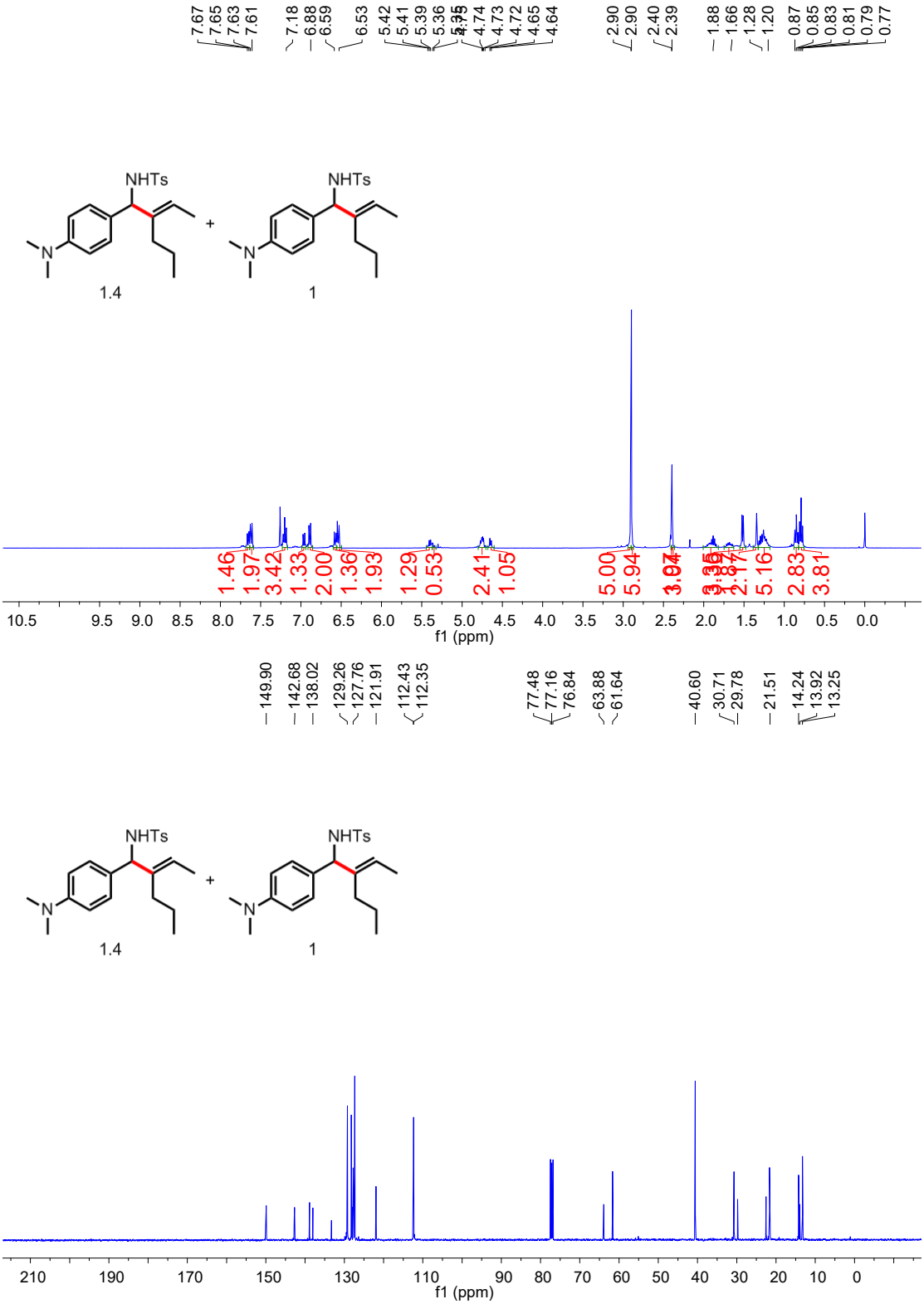
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.59
6.53
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5.41
5.39
5.36
4.74
4.73
4.72
4.65
4.64
2.90
2.90
2.40
2.39
1.88
1.66
1.28
1.20
0.87
0.85
0.83
0.81
0.79
0.77
NHTs
NHTs
1.4
1
1.46
1.97
3.42
1.33
2.00
1.36
1.93
1.29
0.53
2.41
1.05
5.00
5.94
5.16
2.83
3.81
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
149.90
142.68
138.02
129.26
127.76
121.91
112.43
112.35
77.48
77.16
76.84
63.88
61.64
40.60
30.71
29.78
21.51
14.24
13.92
13.25
NHTs
NHTs
1.4
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170
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130
110
90
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50
40
30
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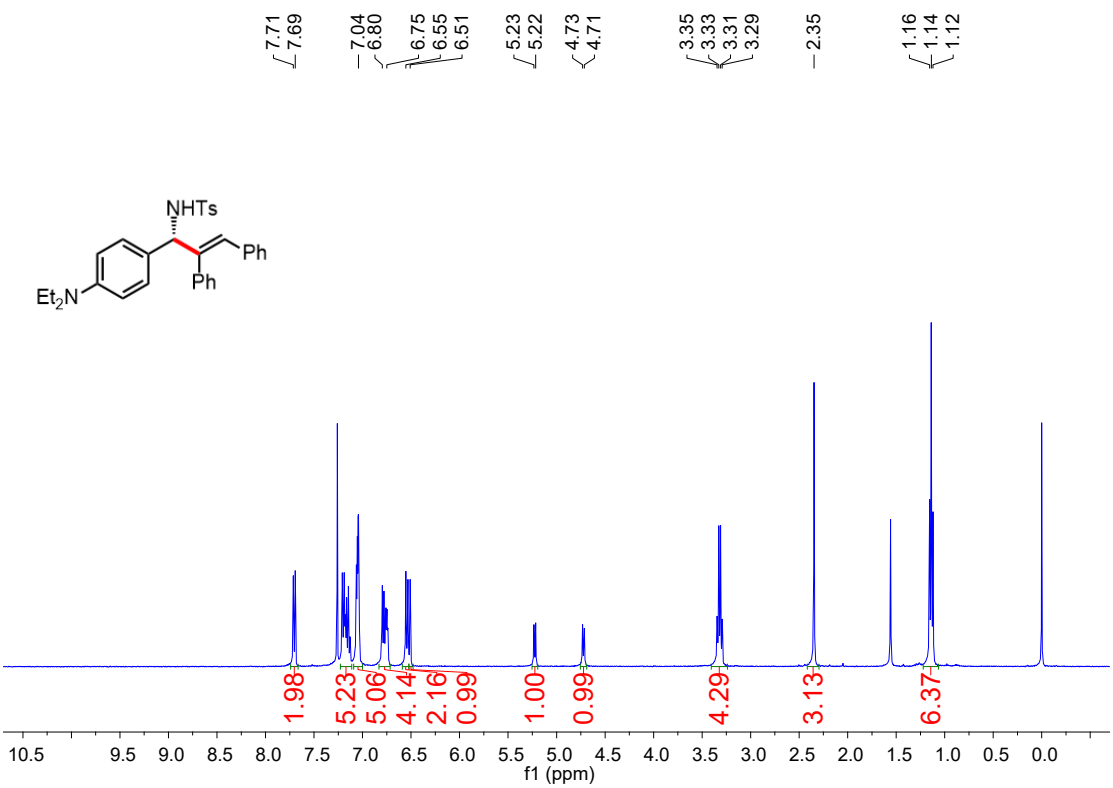
0
f1 (ppm)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6.51
5.23
5.22
4.73
4.71
3.35
3.33
3.31
3.29
2.35
1.16
1.14
1.12
NHTs
Ph
Ph
Et2N
1.98
5.23
5.06
4.14
2.16
0.99
1.00
0.99
4.29
3.13
6.37
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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2.5
2.0
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1.0
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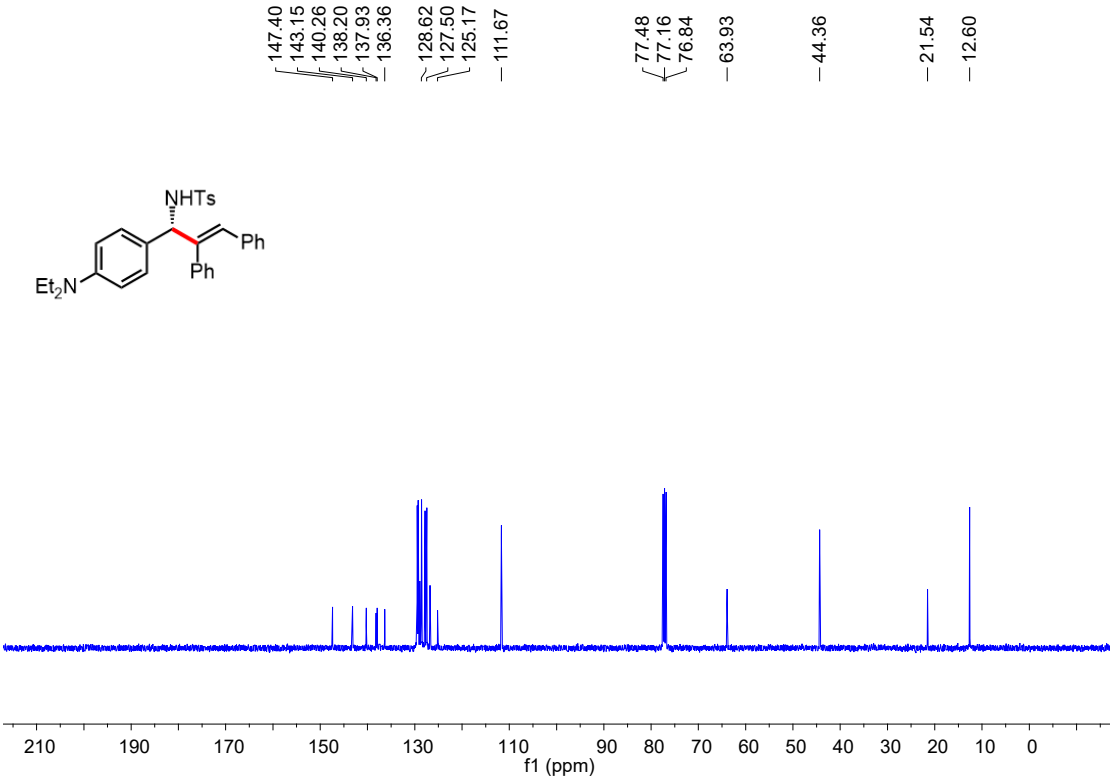
0.0
f1 (ppm)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143.15
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138.20
137.93
136.36
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127.50
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111.67
77.48
77.16
76.84
63.93
44.36
21.54
12.60
NHTs
Ph
Ph
Et2N
210
190
170
150
130
110
90
80
70
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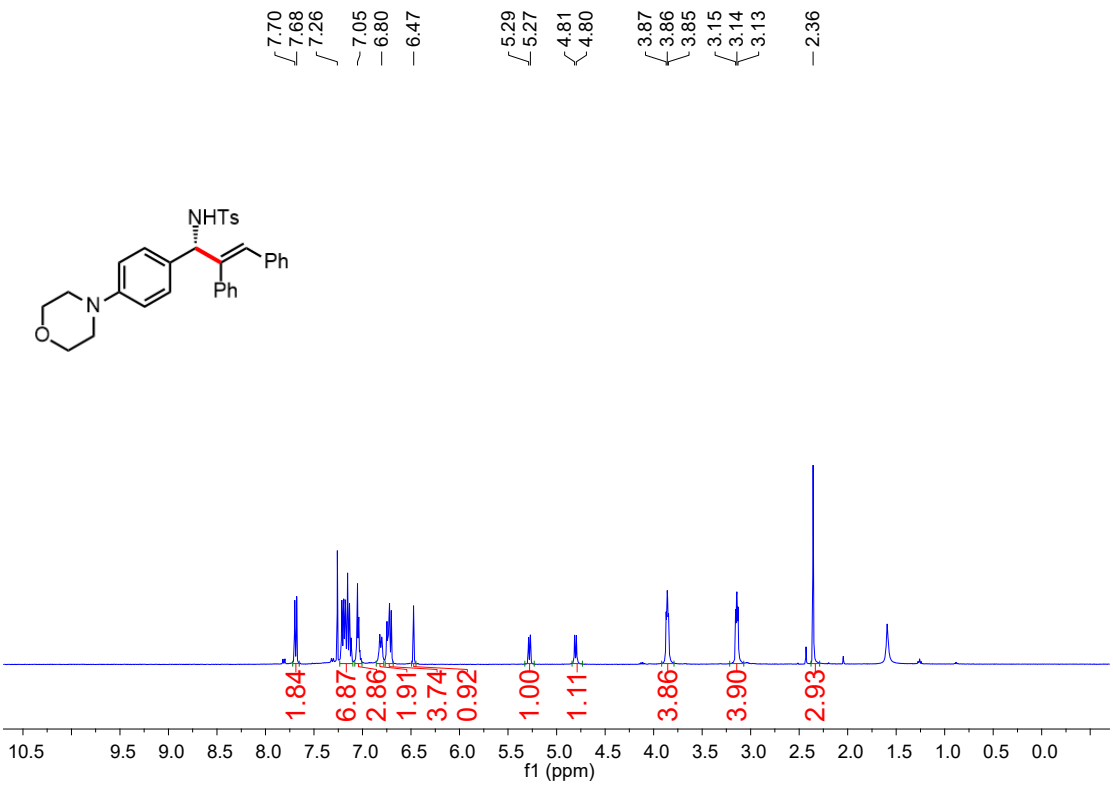
50
40
30
20
10
0
f1 (ppm)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7.68
7.26
7.05
6.80
6.47
5.29
5.27
4.81
4.80
3.87
3.86
3.85
3.15
3.14
3.13
2.36
NHTs
Ph
Ph
N
O
1.84
6.87
2.86
1.91
3.74
0.92
1.00
1.11
3.86
3.90
2.93
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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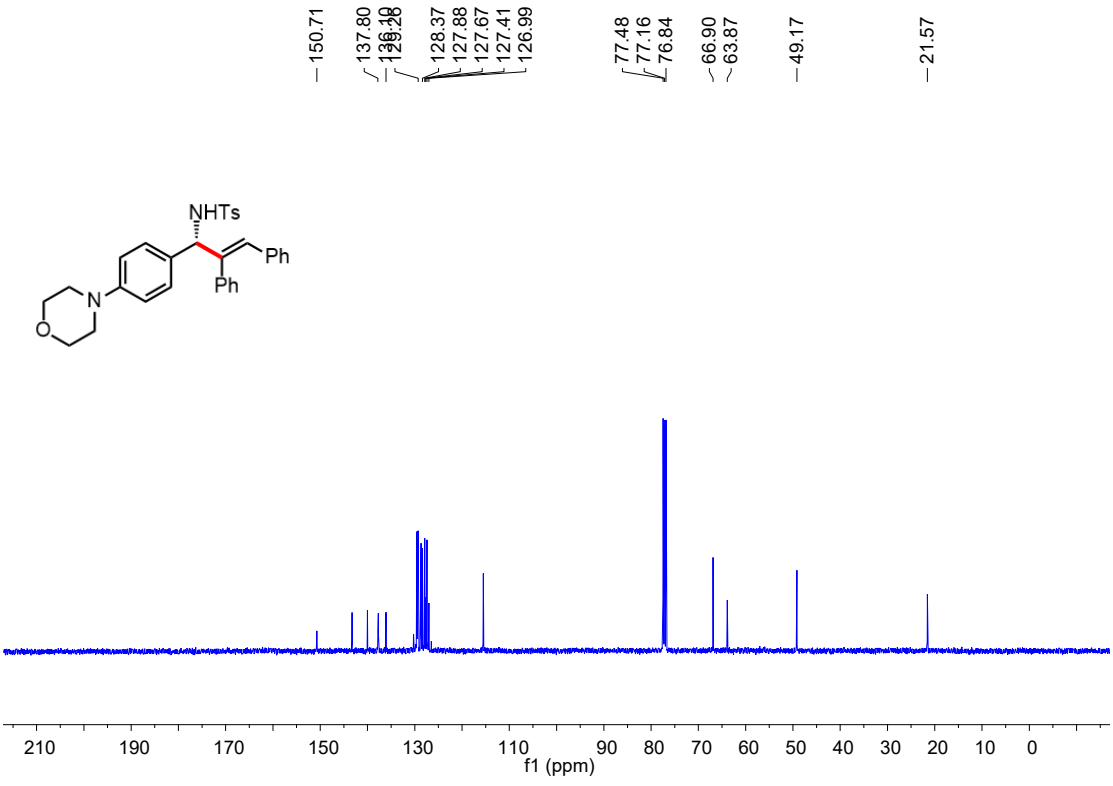
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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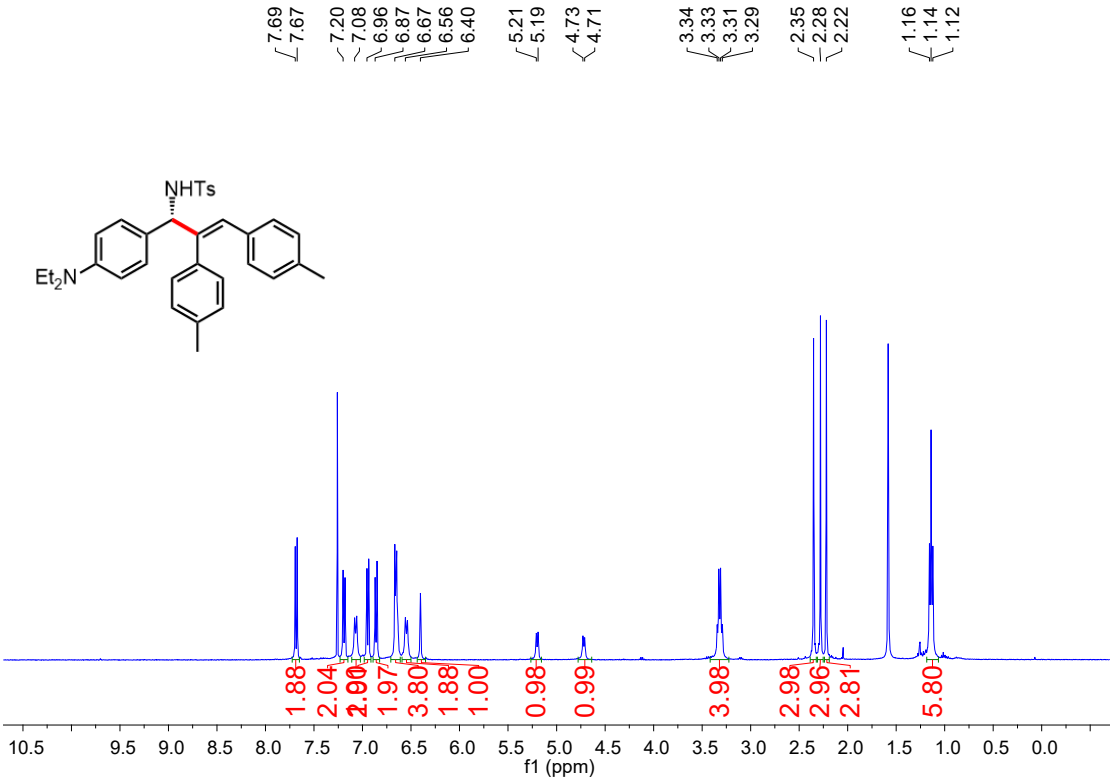
137.80
128.37
127.88
127.67
127.41
126.99
77.48
77.16
76.84
66.90
63.87
49.17
21.57
NHTs
Ph
Ph
N
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.67
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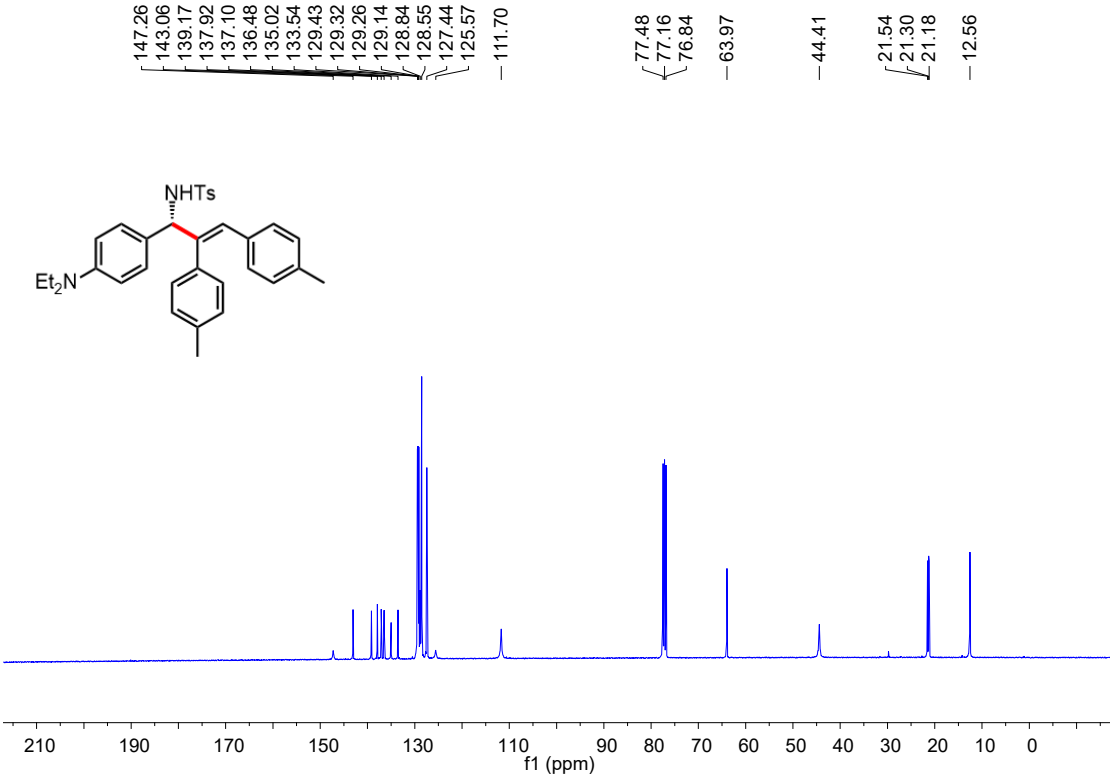
6.96
6.87
6.67
6.56
6.40
5.21
5.19
4.73
4.71
3.34
3.33
3.31
3.29
2.35
2.28
2.22
1.16
1.14
1.12
NHTs
Et2N
1.88
2.04
2.00
1.97
3.80
1.88
1.00
0.98
0.99
3.98
2.98
2.96
2.81
5.80
f1 (ppm)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129.32
129.26
129.14
128.84
128.55
127.44
125.57
111.70
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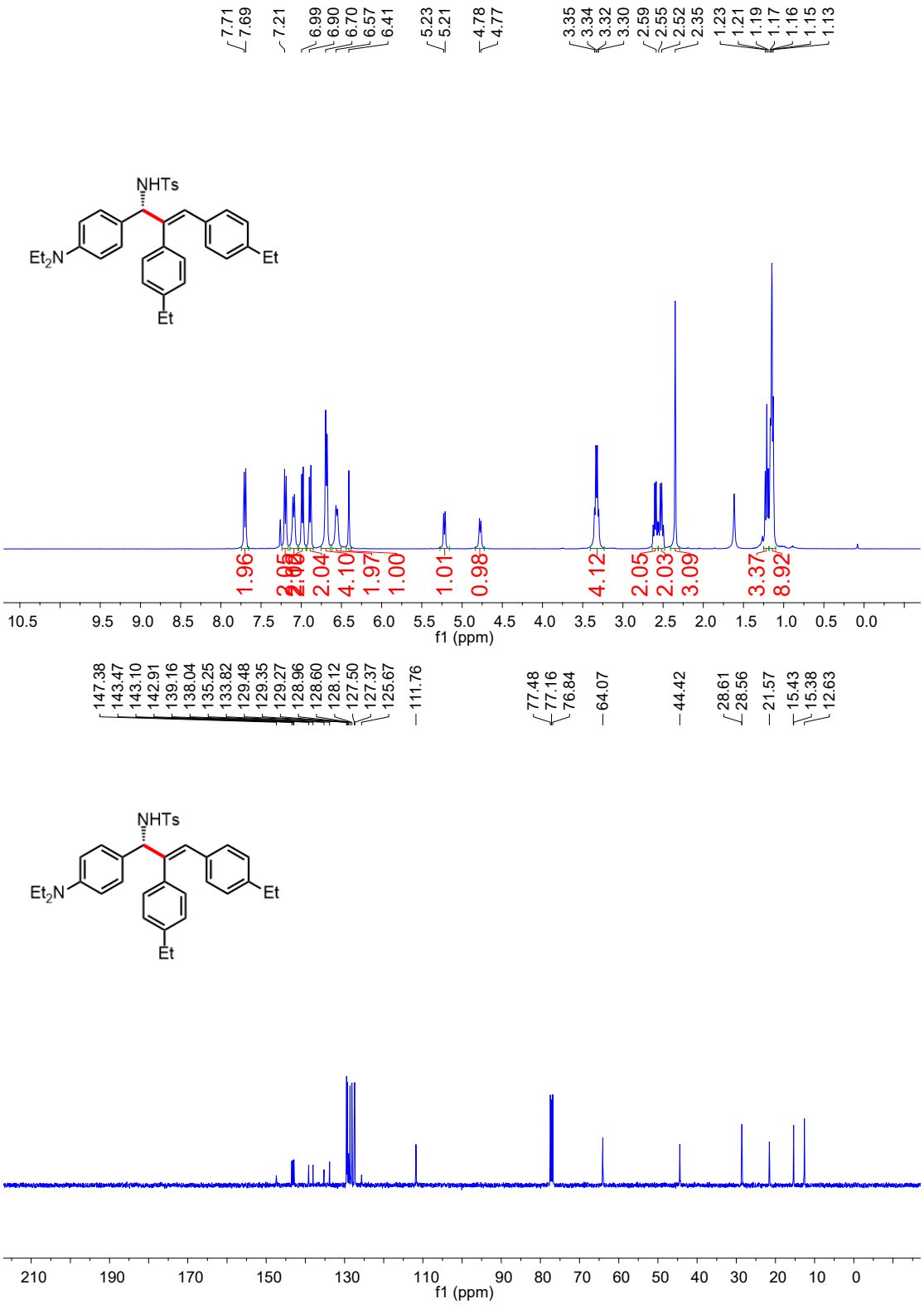
77.16
76.84
63.97
44.41
21.54
21.30
21.18
12.56
NHTs
Et2N
f1 (ppm)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6.99
6.90
6.70
6.57
6.41
5.23
5.21
4.78
4.77
3.35
3.34
3.32
3.30
2.59
2.55
2.52
2.35
1.23
1.21
1.19
1.17
1.16
1.15
1.13
NHTs
Et2N
Et
Et
1.96
2.04
4.10
1.97
1.00
1.01
0.98
4.12
2.05
2.03
3.09
3.37
8.92
f1 (ppm)
147.38
143.47
143.10
142.91
139.16
138.04
135.25
133.82
129.48
129.35
129.27
128.96
128.60
128.12
127.50
127.37
125.67
111.76
77.48
77.16
76.84
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28.56
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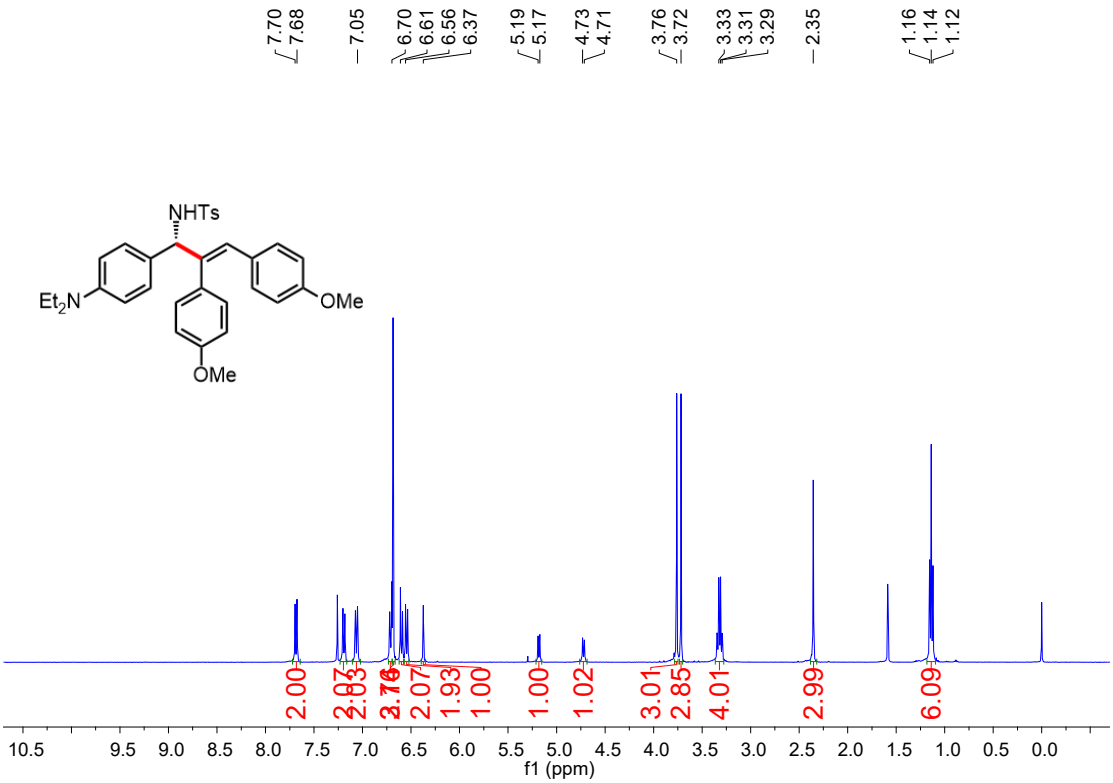
15.43
15.38
12.63
NHTs
Et2N
Et
Et
f1 (ppm)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7.68
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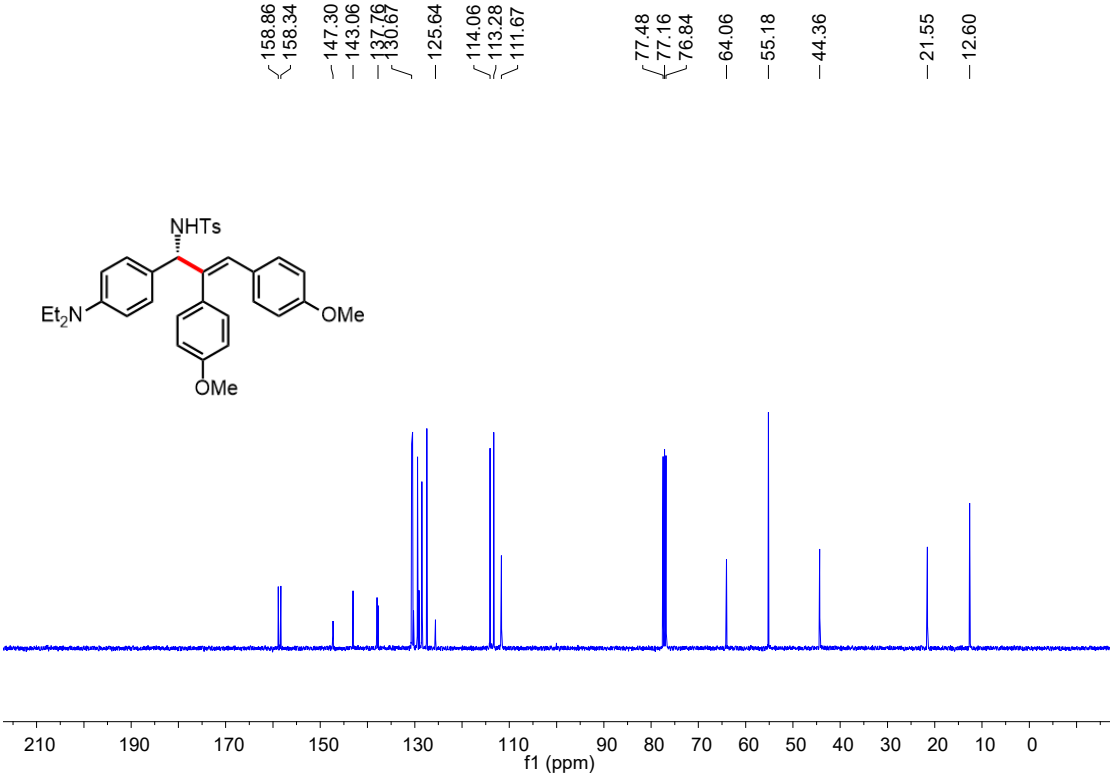
6.70
6.61
6.56
6.37
5.19
5.17
4.73
4.71
3.76
3.72
3.33
3.31
3.29
2.35
1.16
1.14
1.12
NHTs
Et2N
OMe
OMe
2.00
2.07
2.03
2.07
1.93
1.00
1.00
1.02
3.01
2.85
4.01
2.99
6.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.64
114.06
113.28
111.67
77.48
77.16
76.84
64.06
55.18
44.36
21.55
12.60
NHTs
Et2N
OMe
OMe
210
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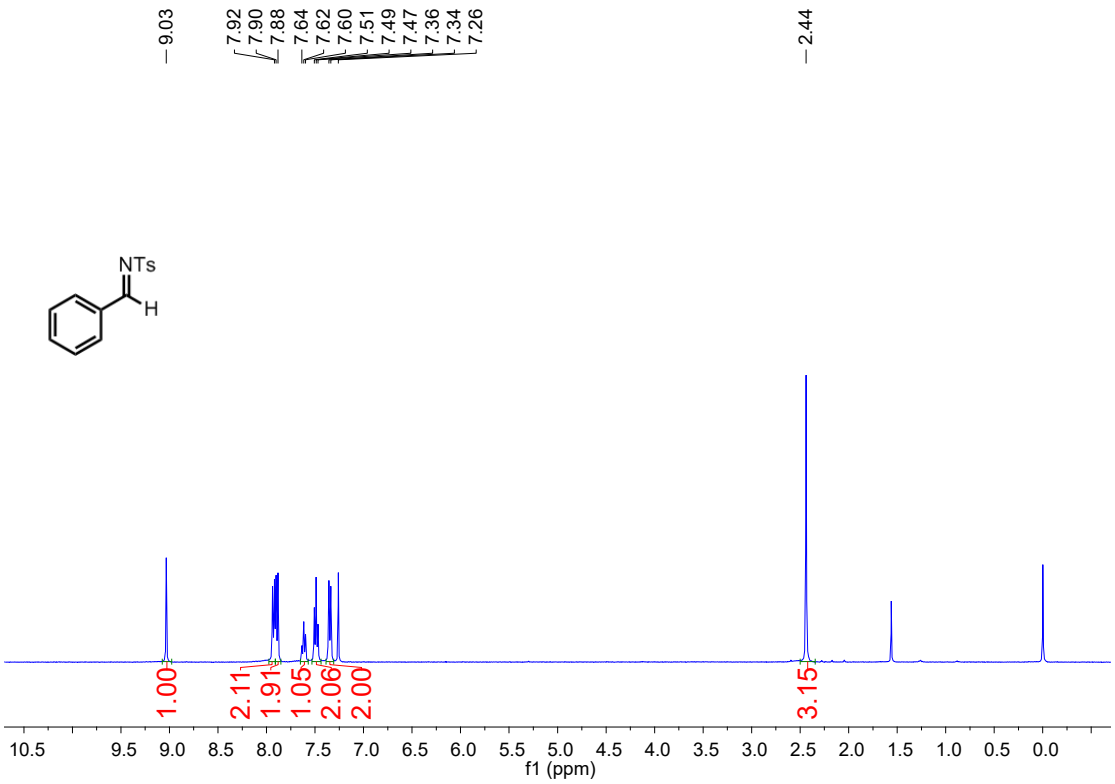
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.90
7.88
7.64
7.62
7.60
7.51
7.49
7.47
7.36
7.34
7.26
2.44
NTs
H
1.00
2.11
1.91
1.05
2.06
2.00
3.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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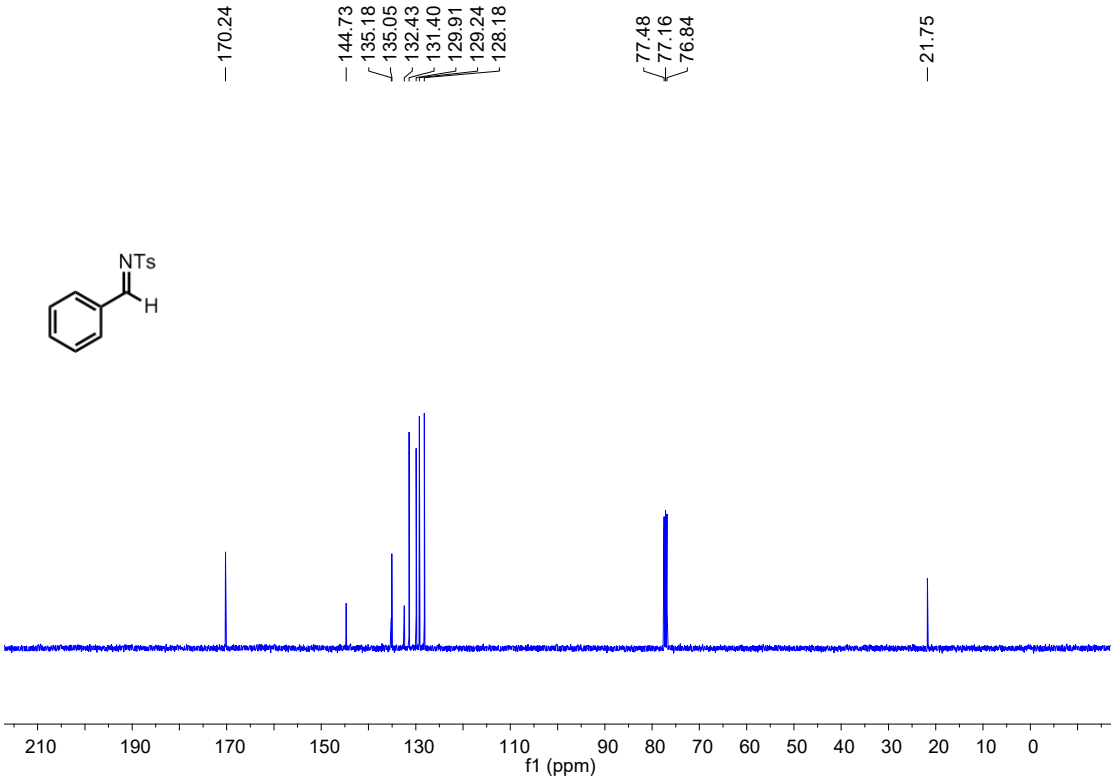
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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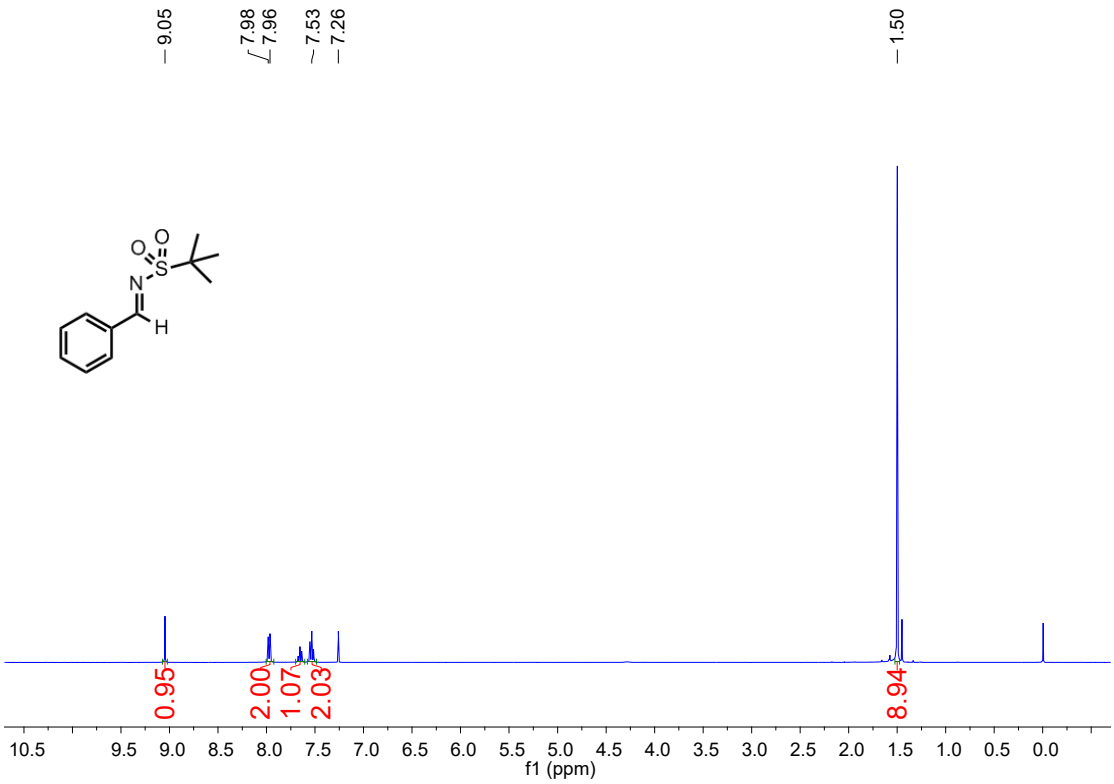
132.43
131.40
129.91
129.24
128.18
77.48
77.16
76.84
21.75
NTs
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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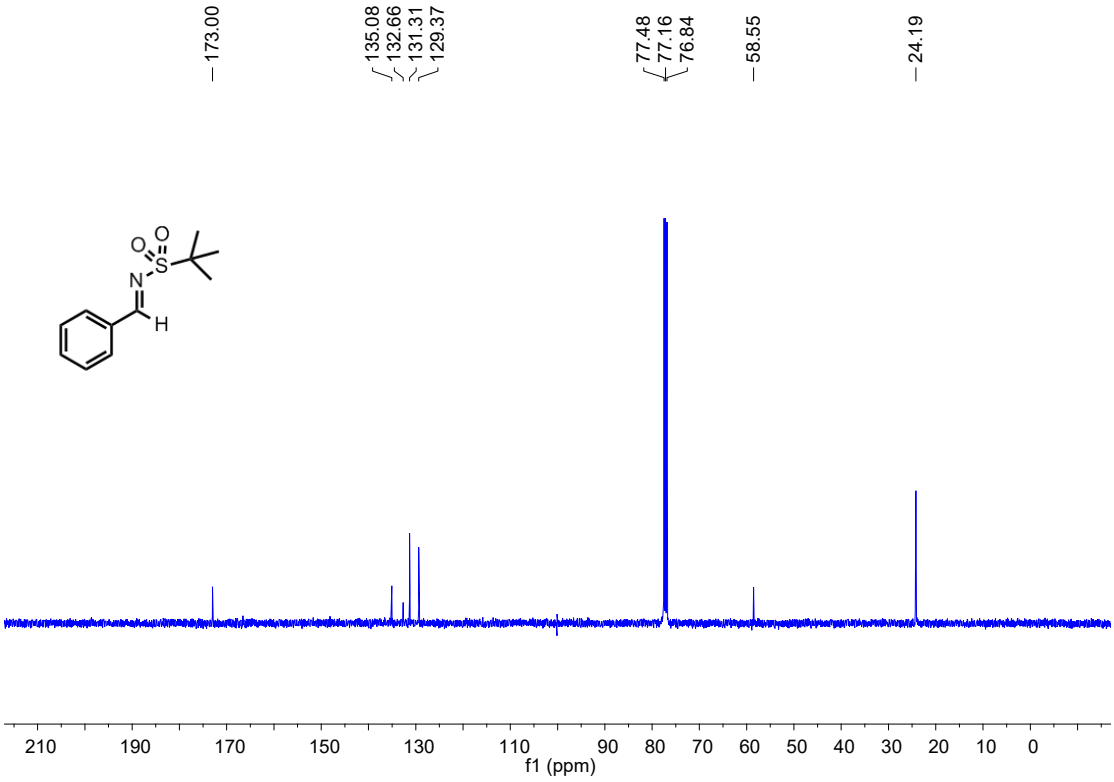
7.96
7.53
7.26
1.50
0.95
2.00
1.07
2.03
8.94
f1 (ppm)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77.48
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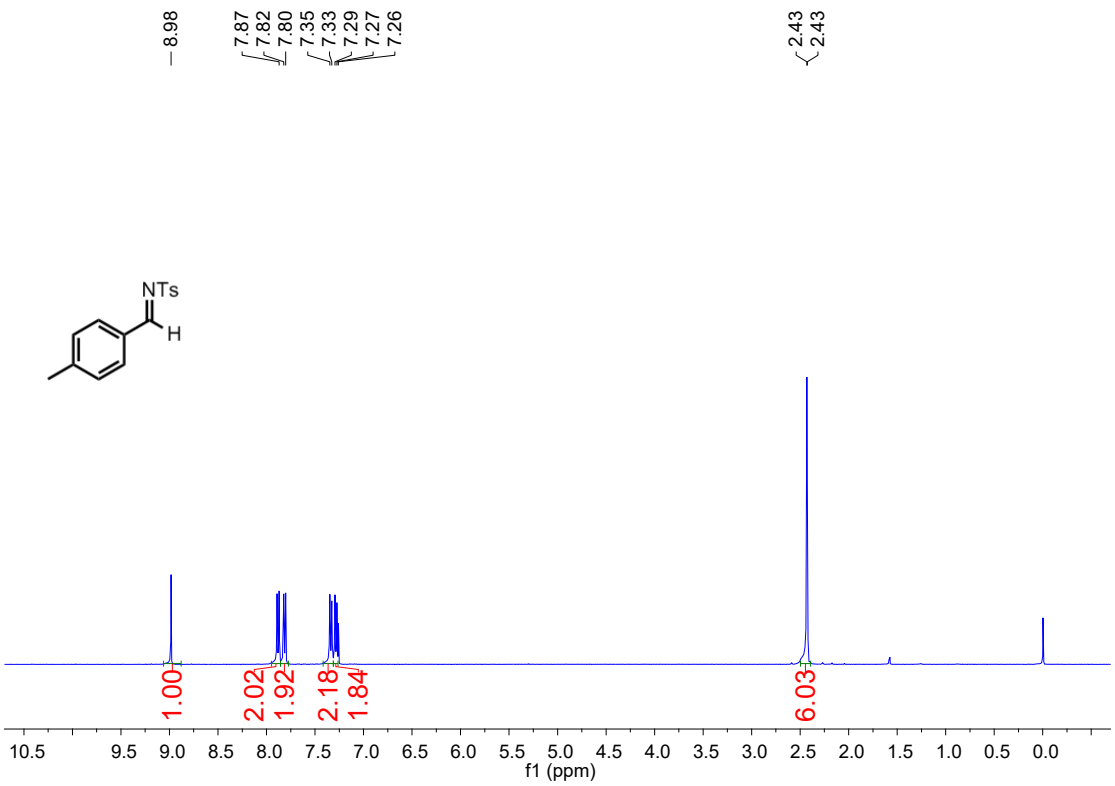
76.84
58.55
24.19
f1 (ppm)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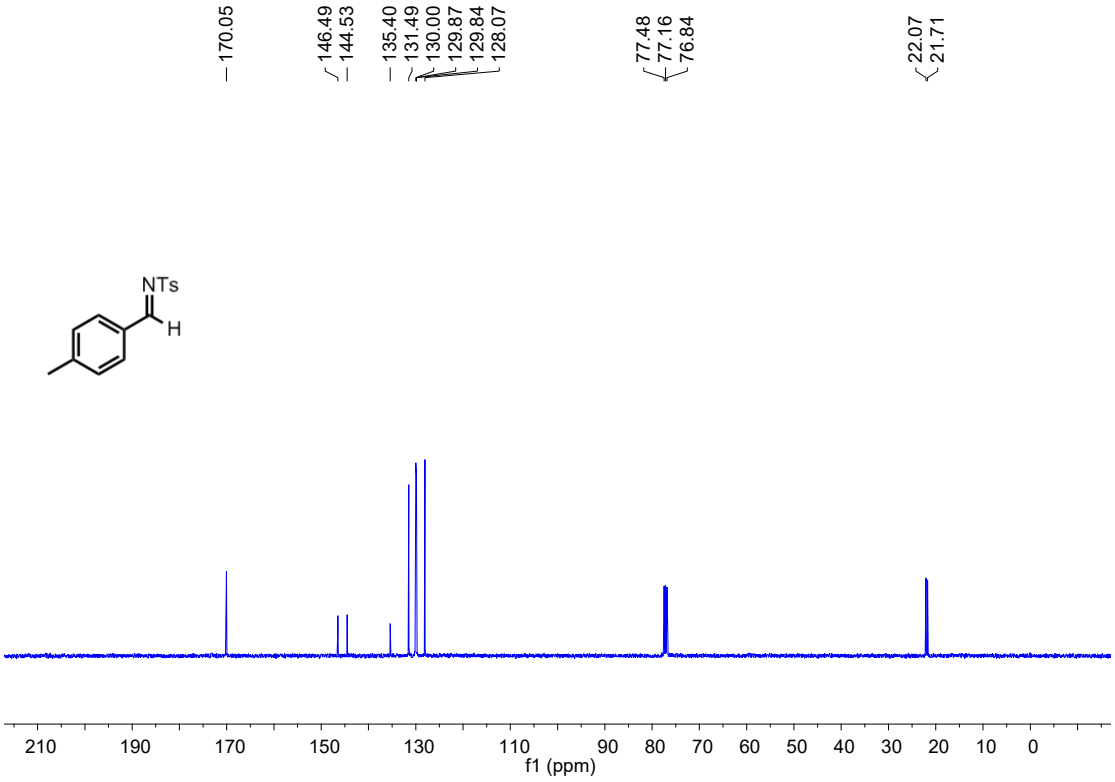
7.87
7.82
7.80
7.35
7.33
7.29
7.27
7.26
2.43
2.43
NTs
H
1.00
2.02
1.92
2.18
1.84
6.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.49
130.00
129.87
129.84
128.07
77.48
77.16
76.84
22.07
21.71
NTs
H
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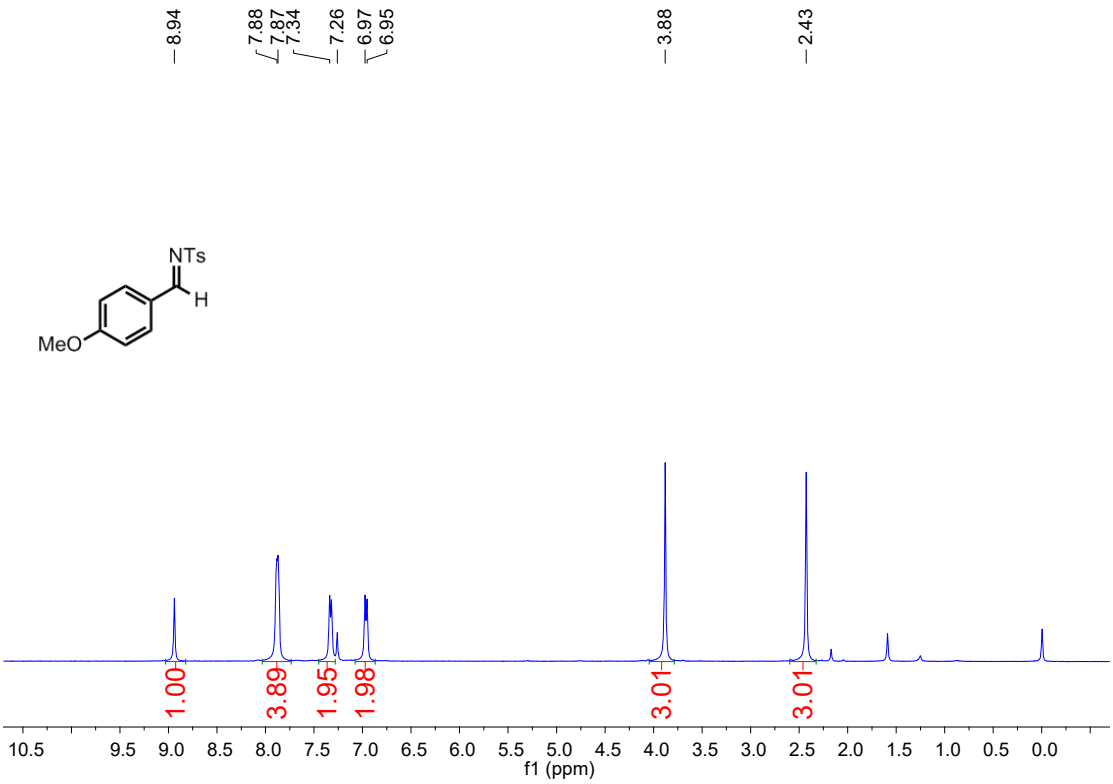
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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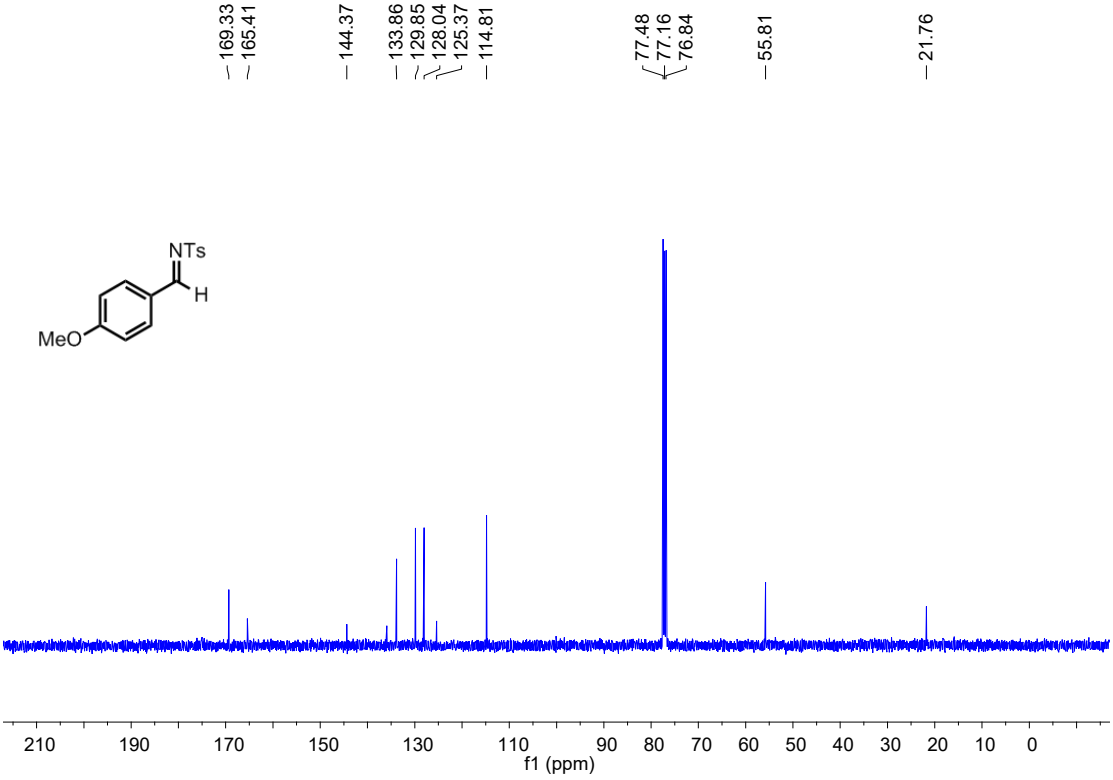
7.34
7.26
6.97
6.95
3.88
2.43
NTs
H
MeO
1.00
3.89
1.95
1.98
3.01
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.04
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114.81
77.48
77.16
76.84
55.81
21.76
NTs
H
MeO
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170
150
130
110
90
80
70
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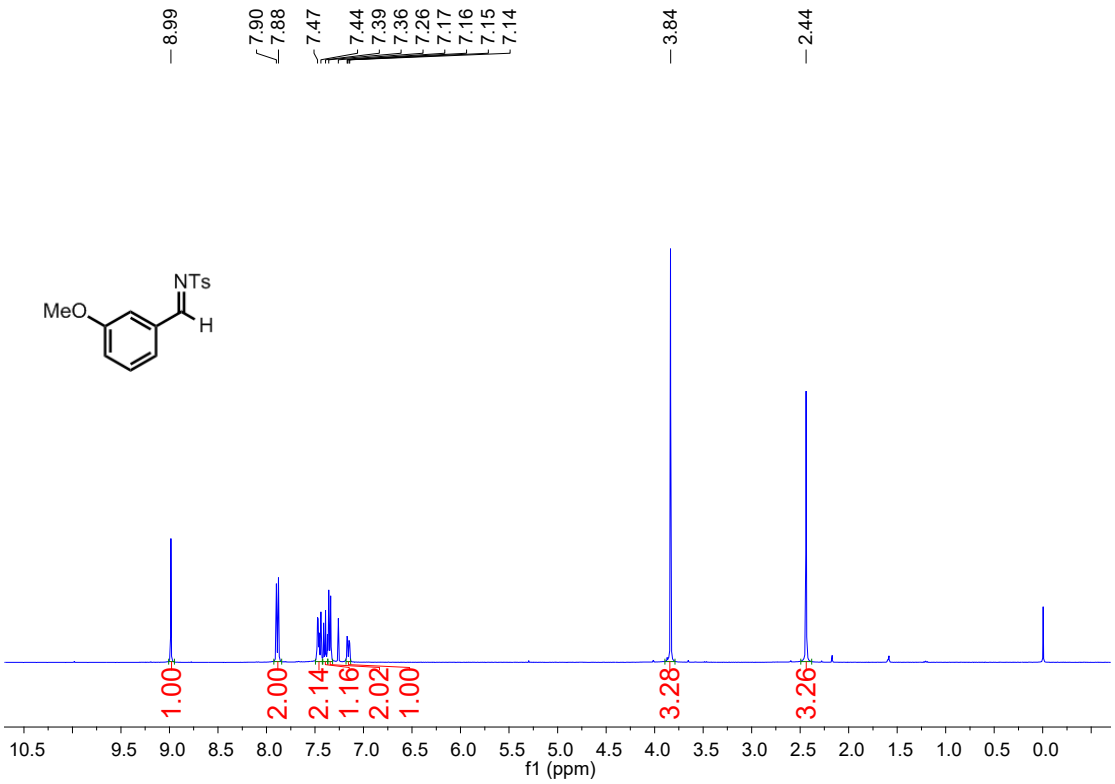
50
40
30
20
10
0
f1 (ppm)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7.26
7.17
7.16
7.15
7.14
3.84
2.44
NTs
MeO
H
1.00
2.00
2.14
1.16
2.02
1.00
3.28
3.26
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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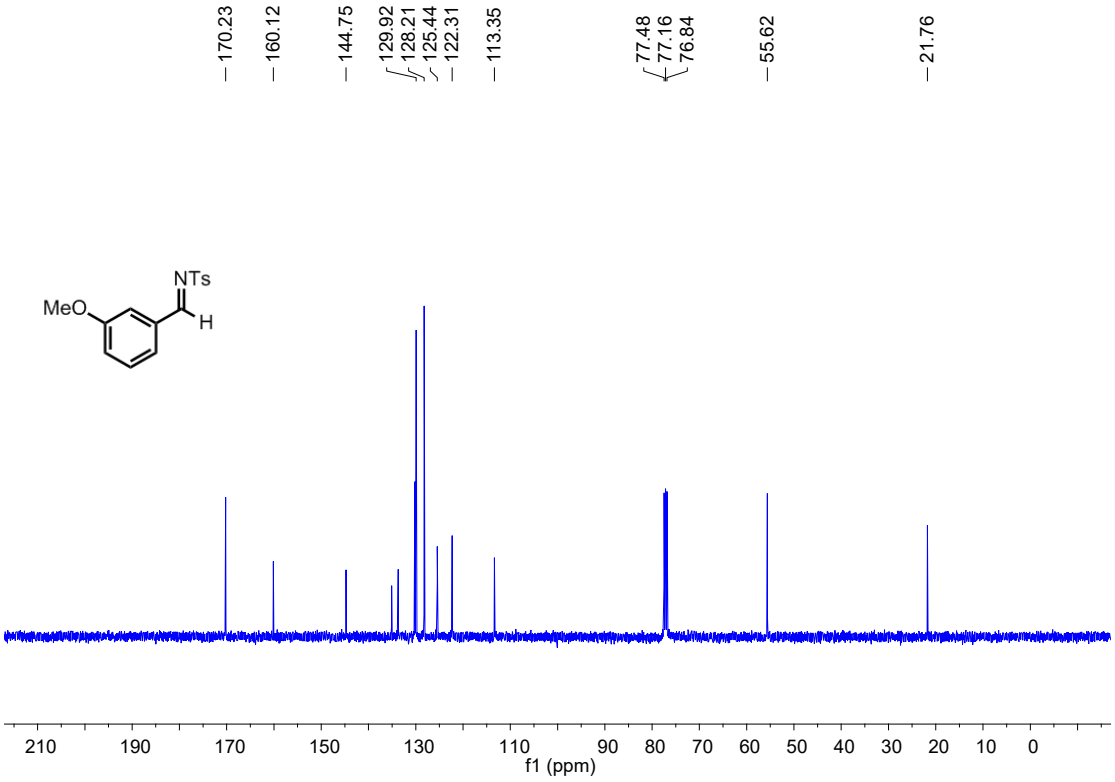
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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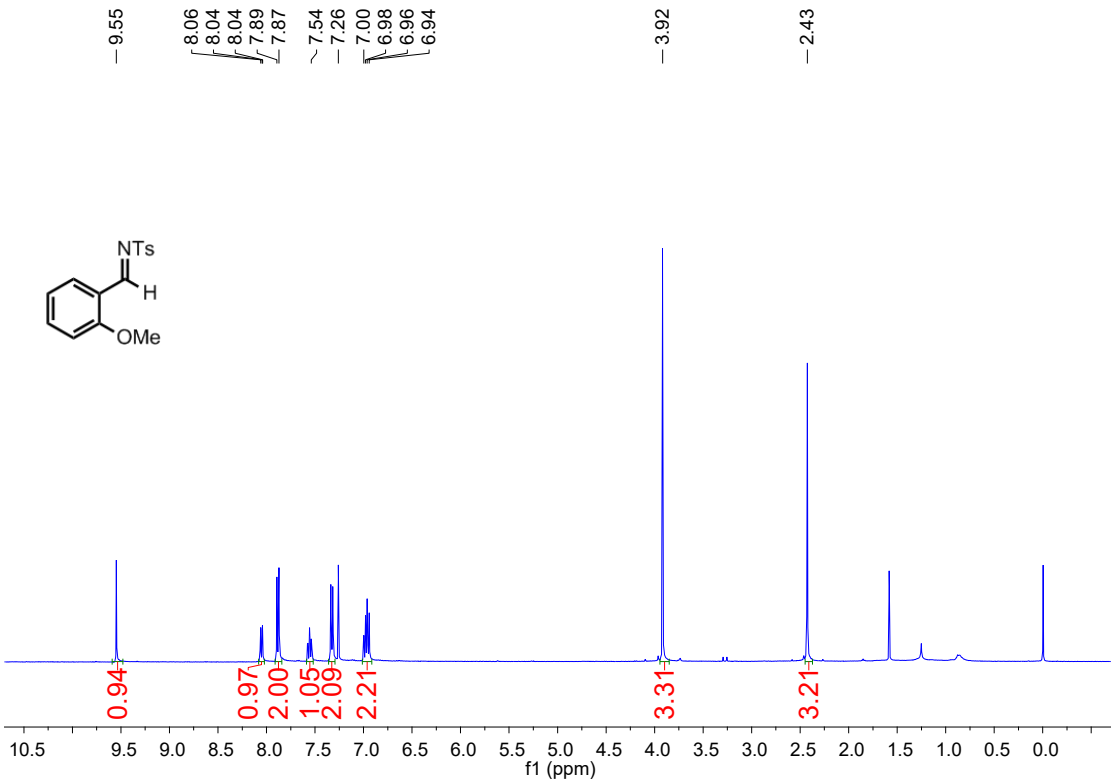
144.75
129.92
128.21
125.44
122.31
113.35
77.48
77.16
76.84
55.62
21.76
NTs
MeO
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.04
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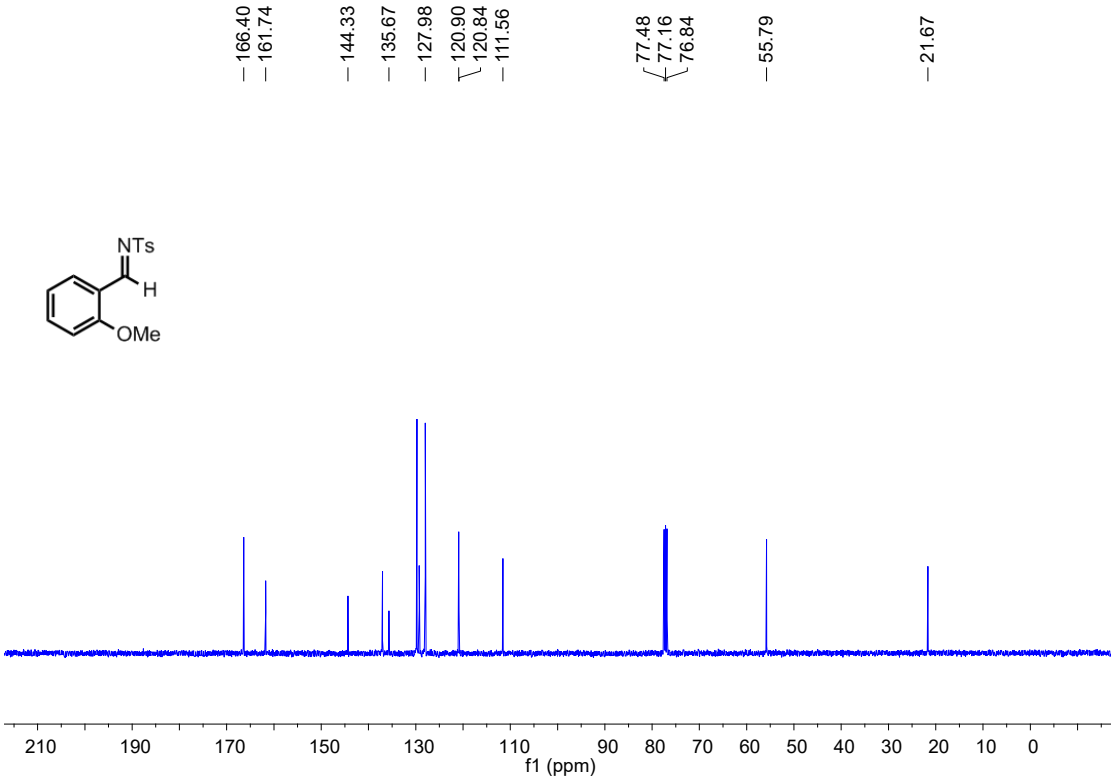
7.87
7.54
7.26
7.00
6.98
6.96
6.94
3.92
2.43
NTs
H
OMe
0.94
0.97
2.00
1.05
2.09
2.21
3.31
3.21
f1 (ppm)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111.56
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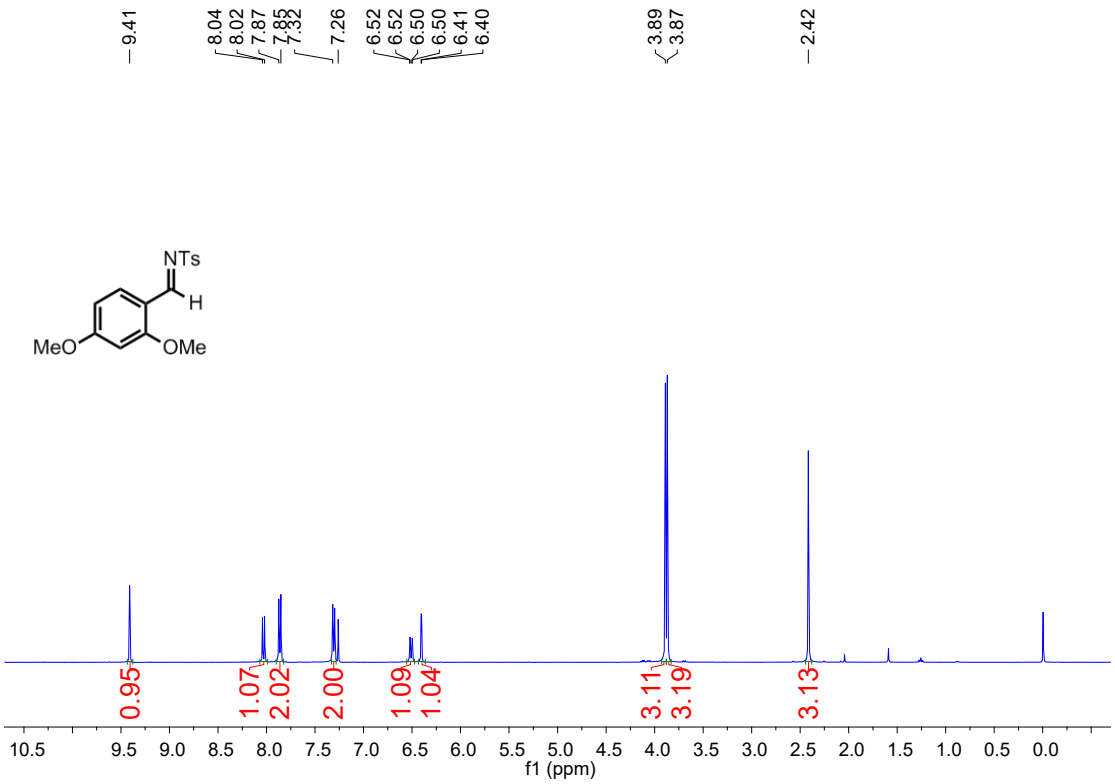
76.84
55.79
21.67
NTs
H
OMe
f1 (ppm)


9.41
8.04
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7.87
7.85
7.32
7.26
6.52
6.52
6.50
6.50
6.41
6.40
3.89
3.87
2.42
NTs
H
MeO
OMe
0.95
1.07
2.02
2.00
1.09
1.04
3.11
3.19
3.13
10.5
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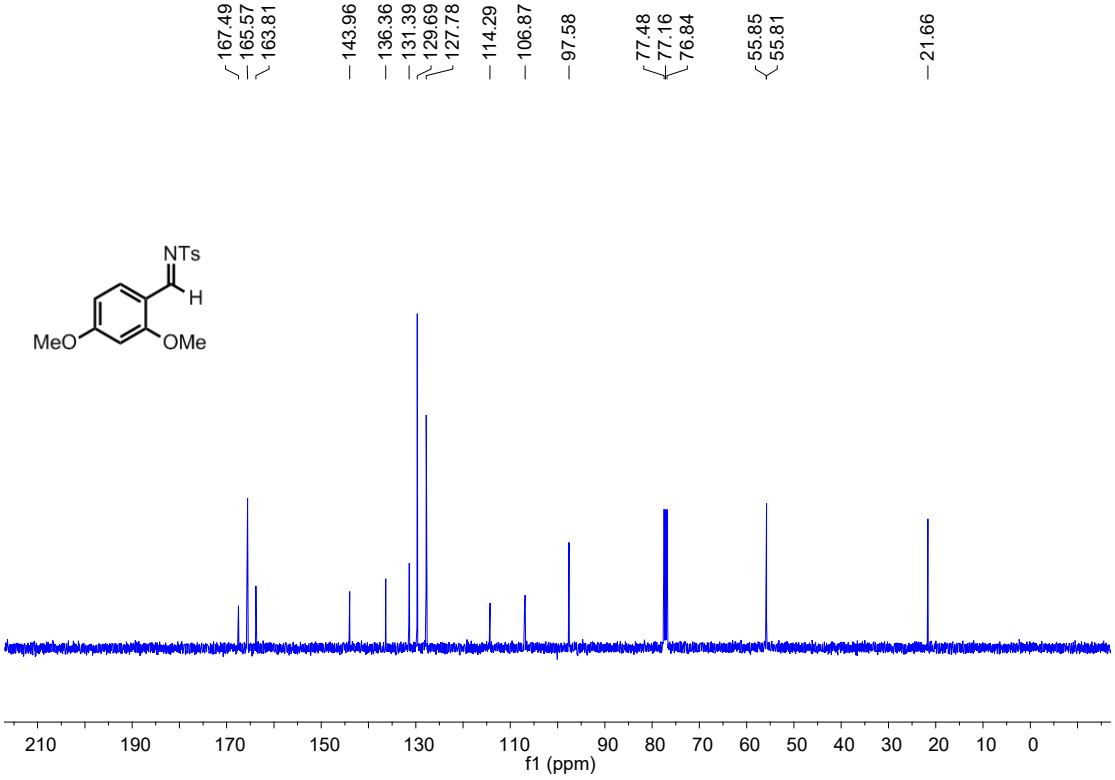
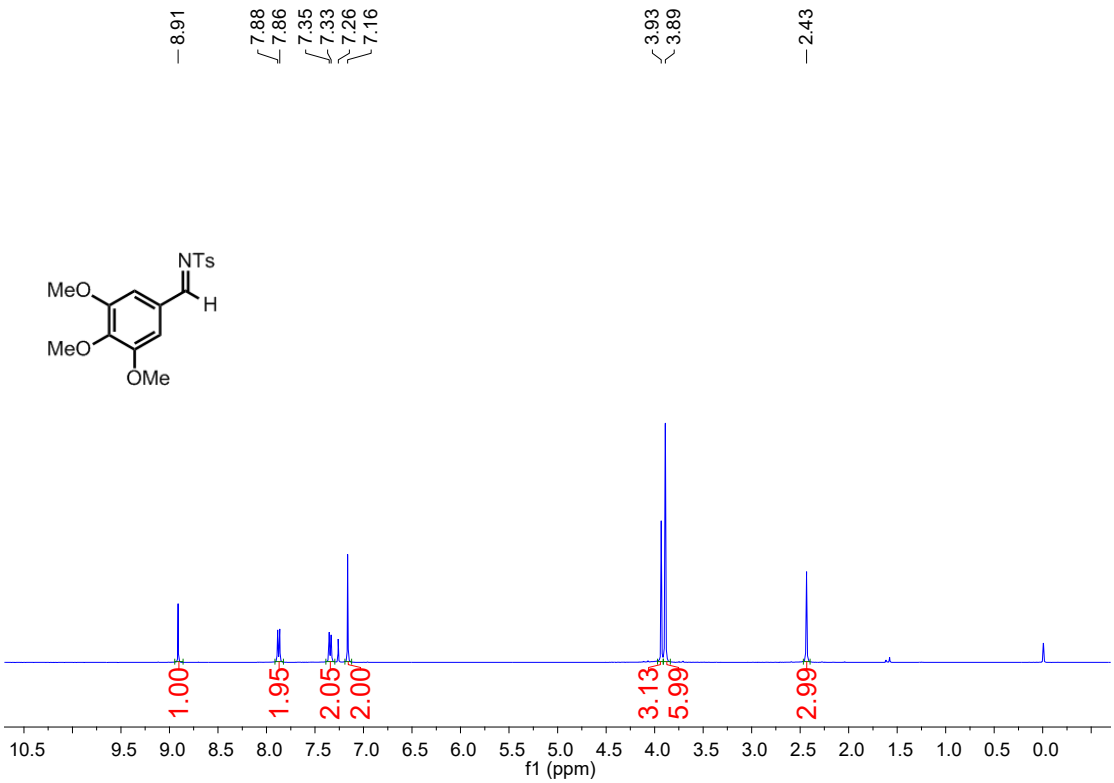
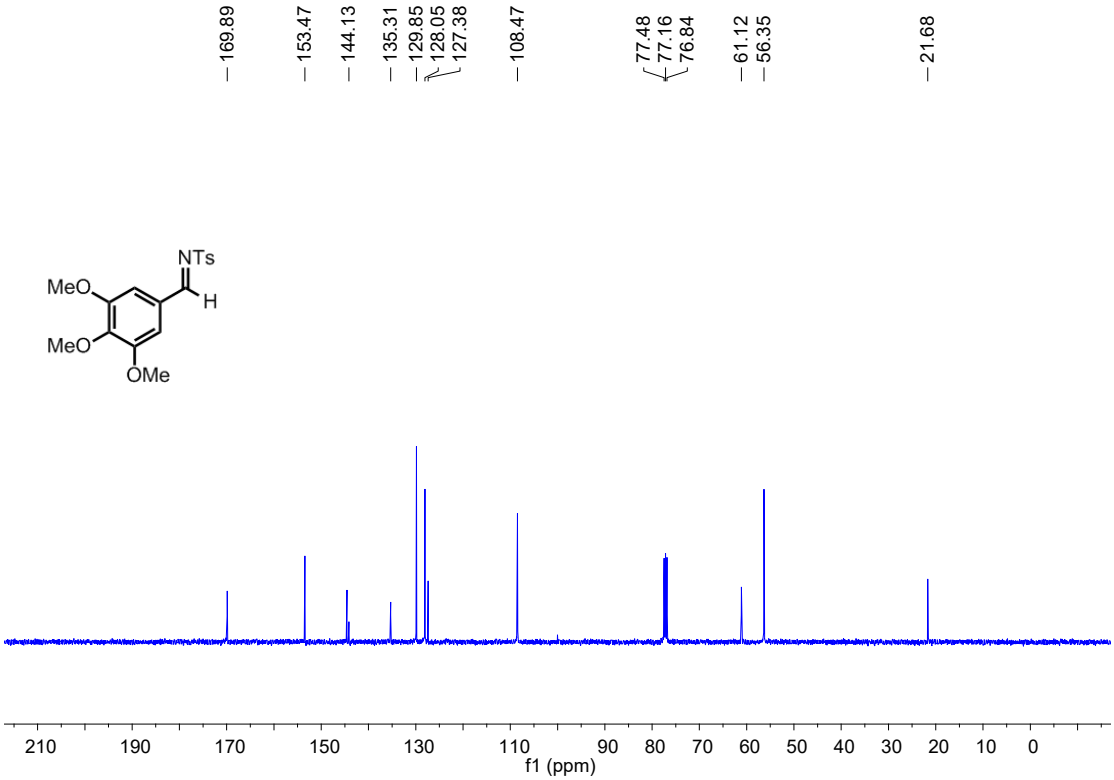
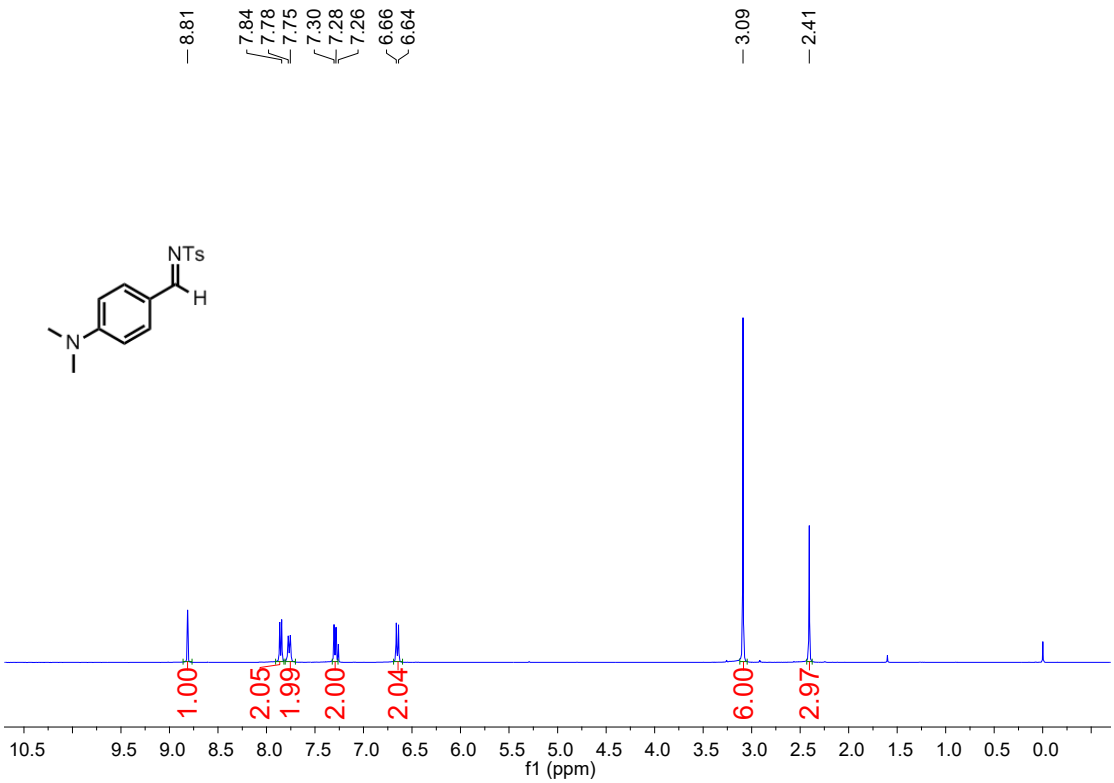
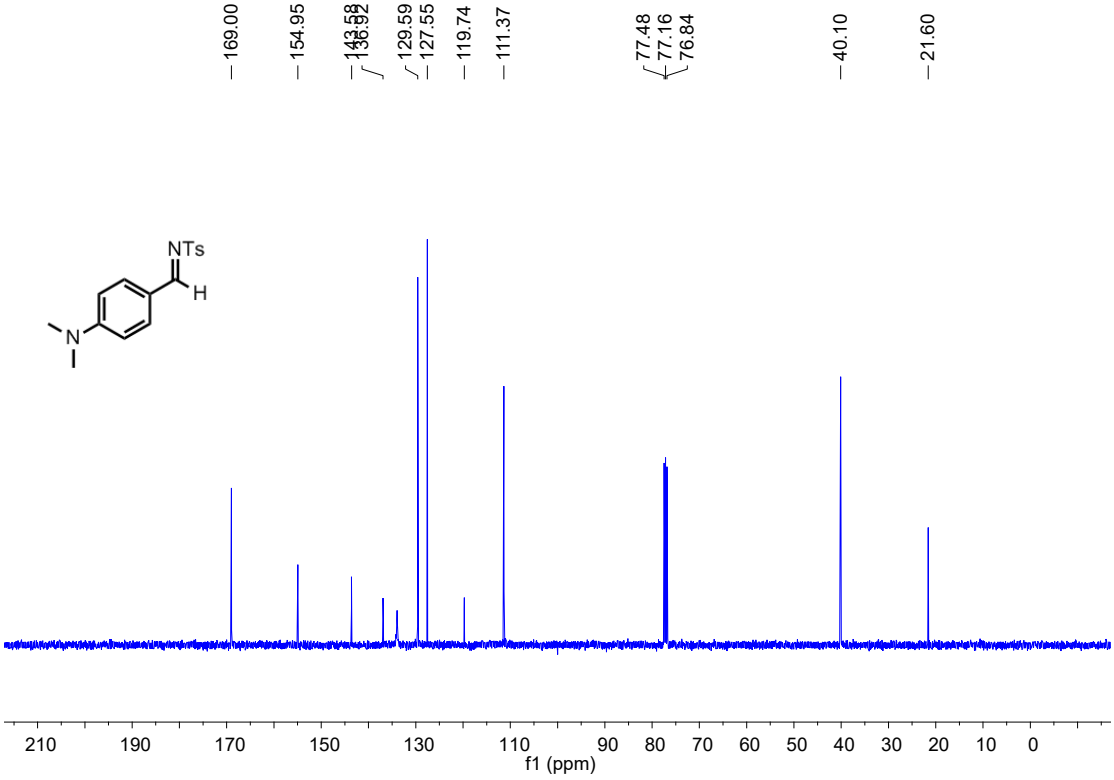
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

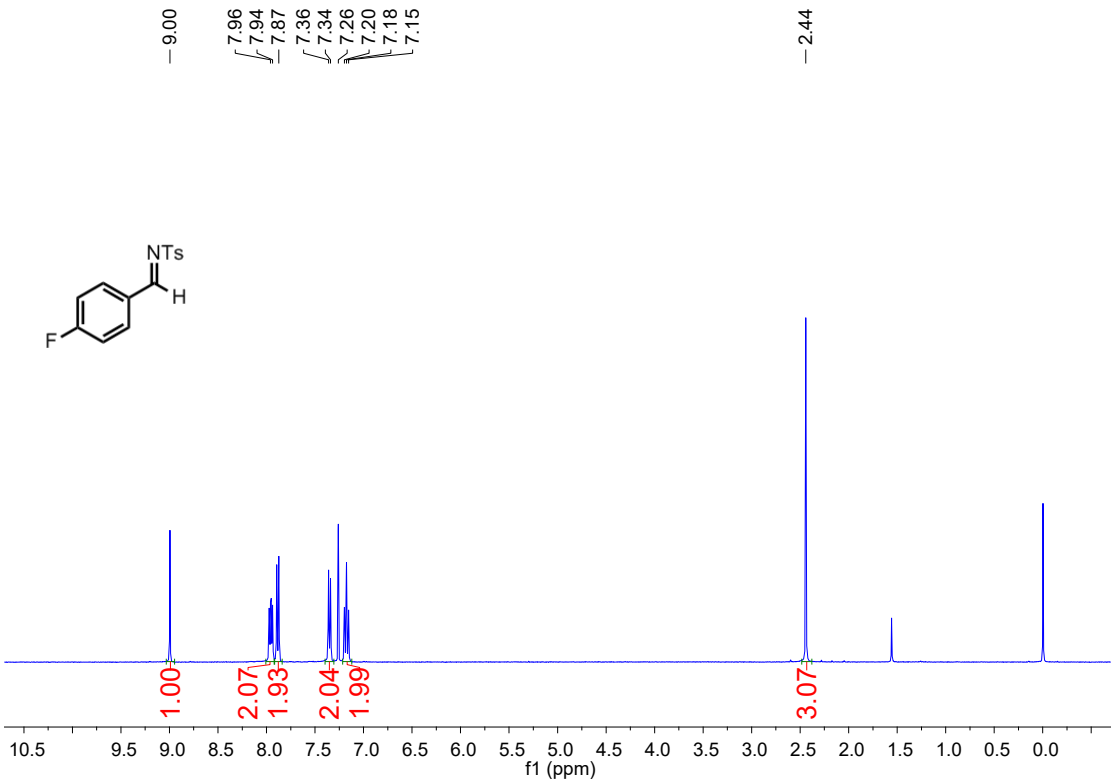

167.49
165.57
163.81
143.96
136.36
131.39
129.69
127.78
114.29
106.87
97.58
77.48
77.16
76.84
55.85
55.81
21.66
NTs
H
MeO
OMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

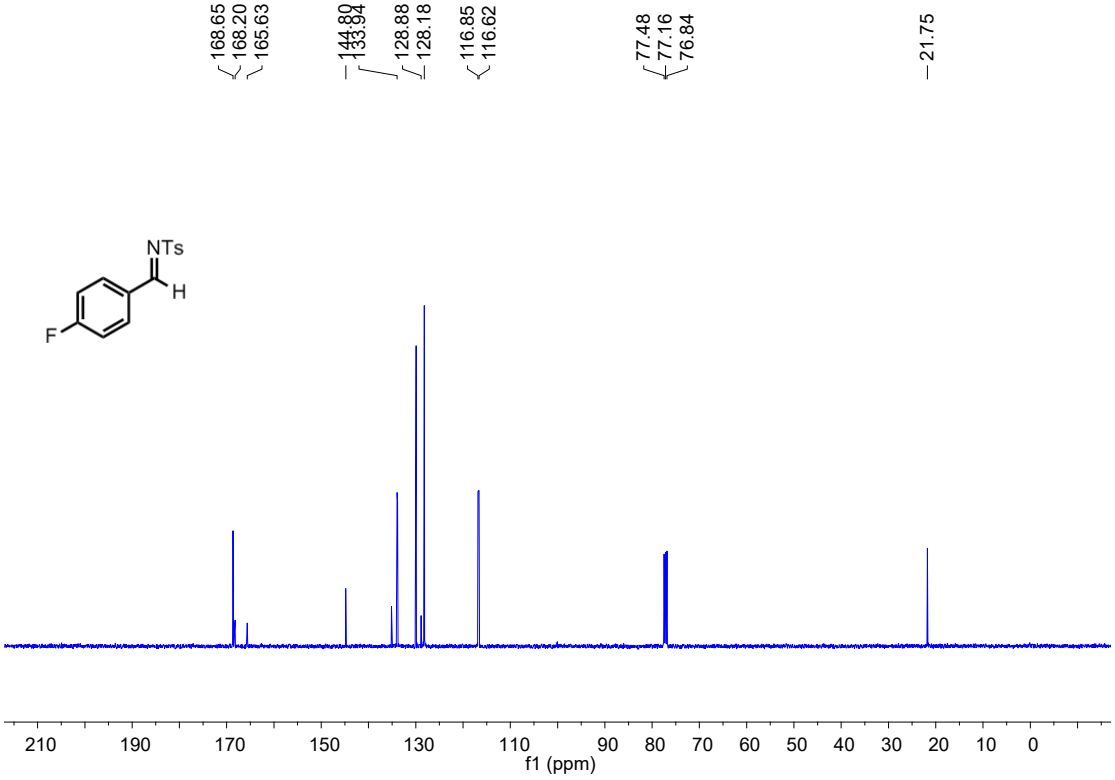

8.91
7.88
7.86
7.35
7.33
7.26
7.16
3.93
3.89
2.43
NTs
MeO
MeO
OMe
H
1.00
1.95
2.05
2.00
3.13
5.99
2.99
f1 (ppm)

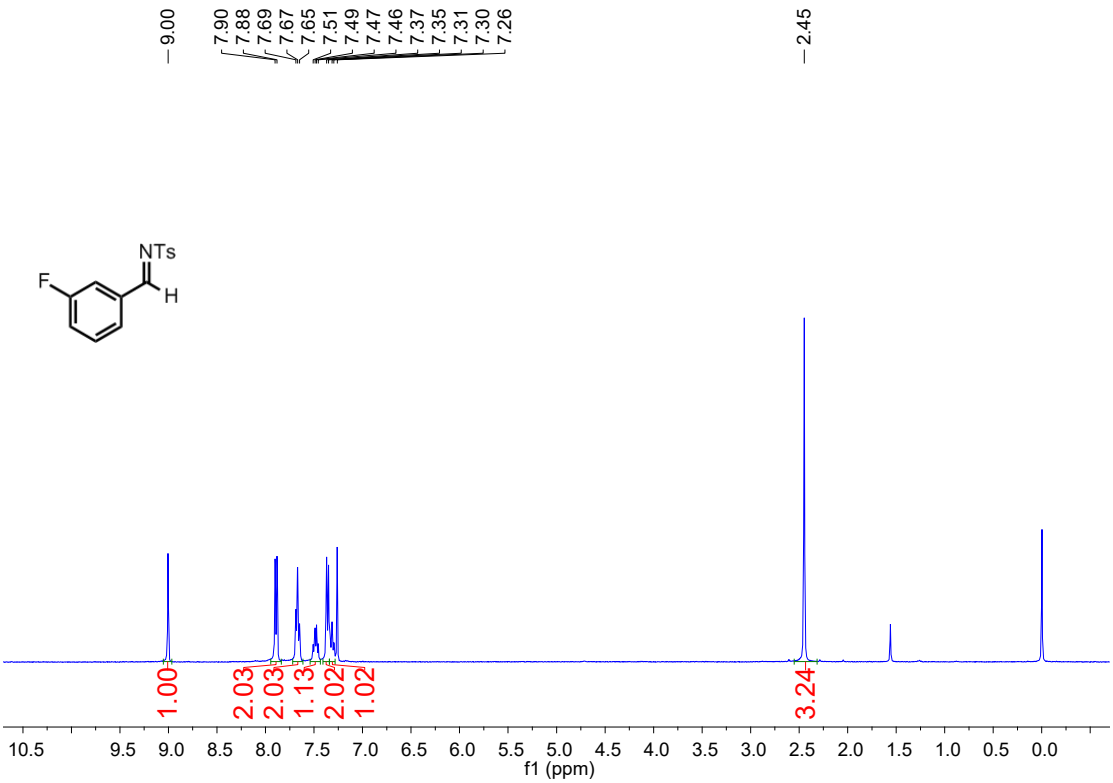

169.89
153.47
144.13
135.31
129.85
128.05
127.38
108.47
77.48
77.16
76.84
61.12
56.35
21.68
NTs
MeO
MeO
OMe
H
f1 (ppm)

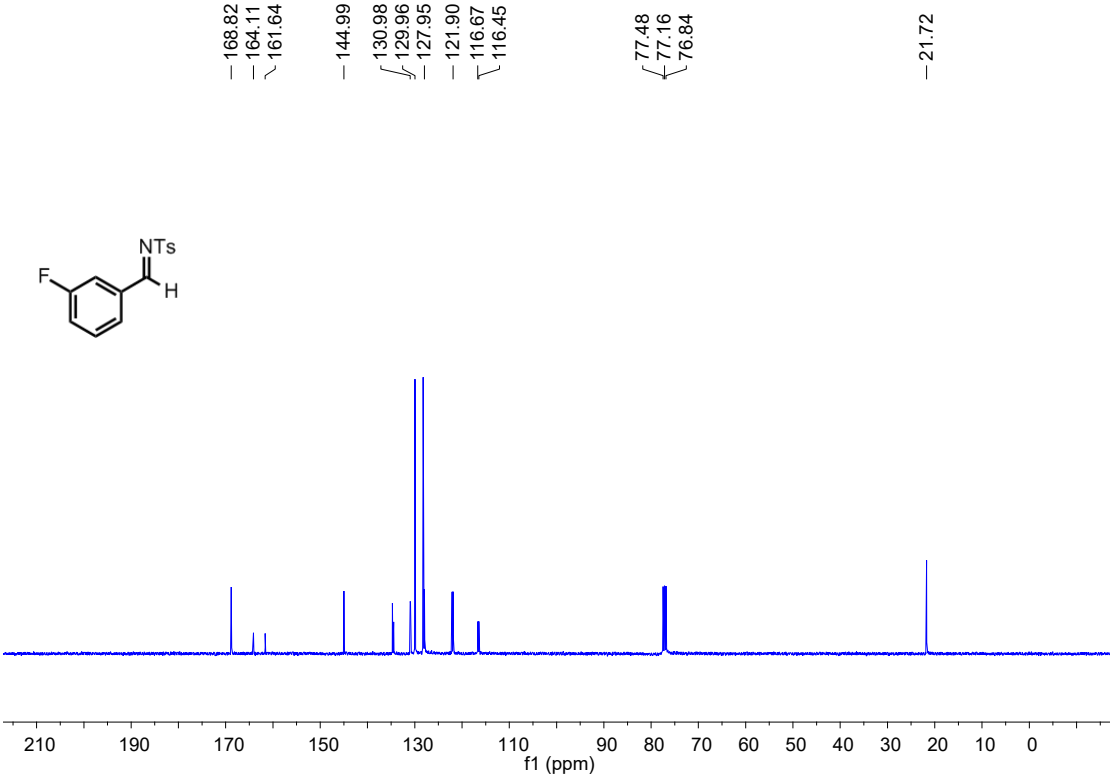

8.81
7.84
7.78
7.75
7.30
7.28
7.26
6.66
6.64
3.09
2.41
NTs
H
N
1.00
2.05
1.99
2.00
2.04
6.00
2.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

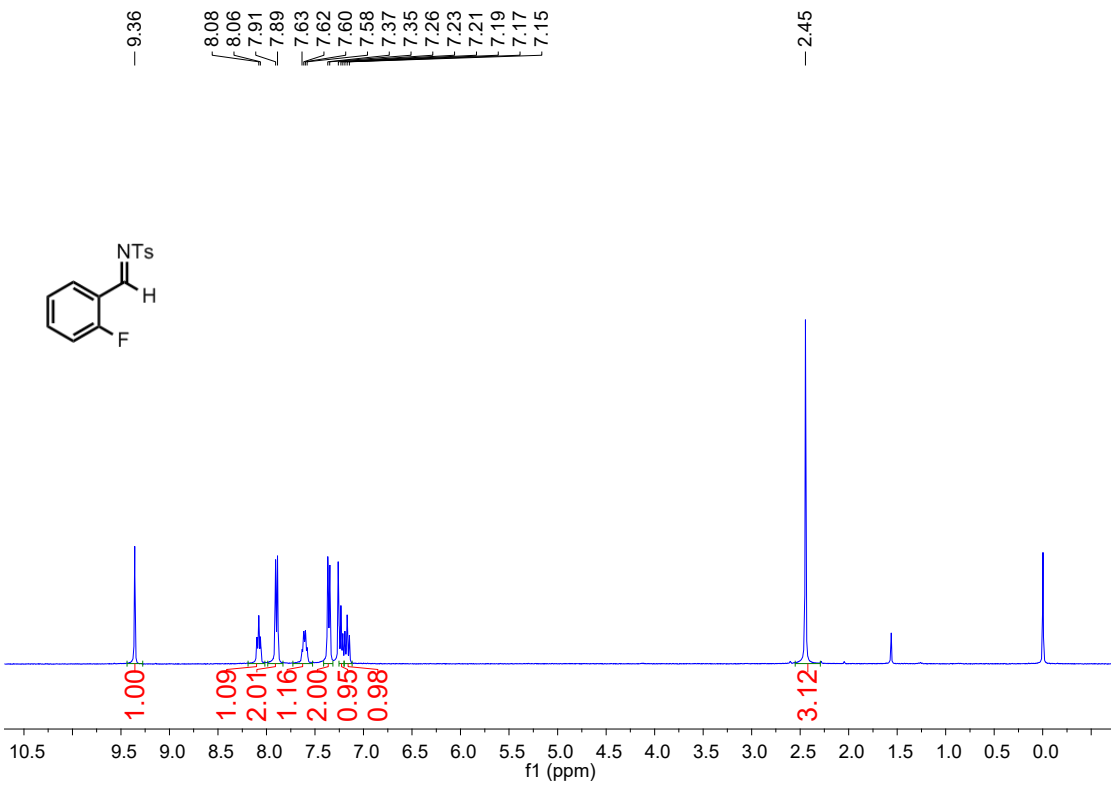

169.00
154.95
143.58
135.92
129.59
127.55
119.74
111.37
77.48
77.16
76.84
40.10
21.60
NTs
H
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

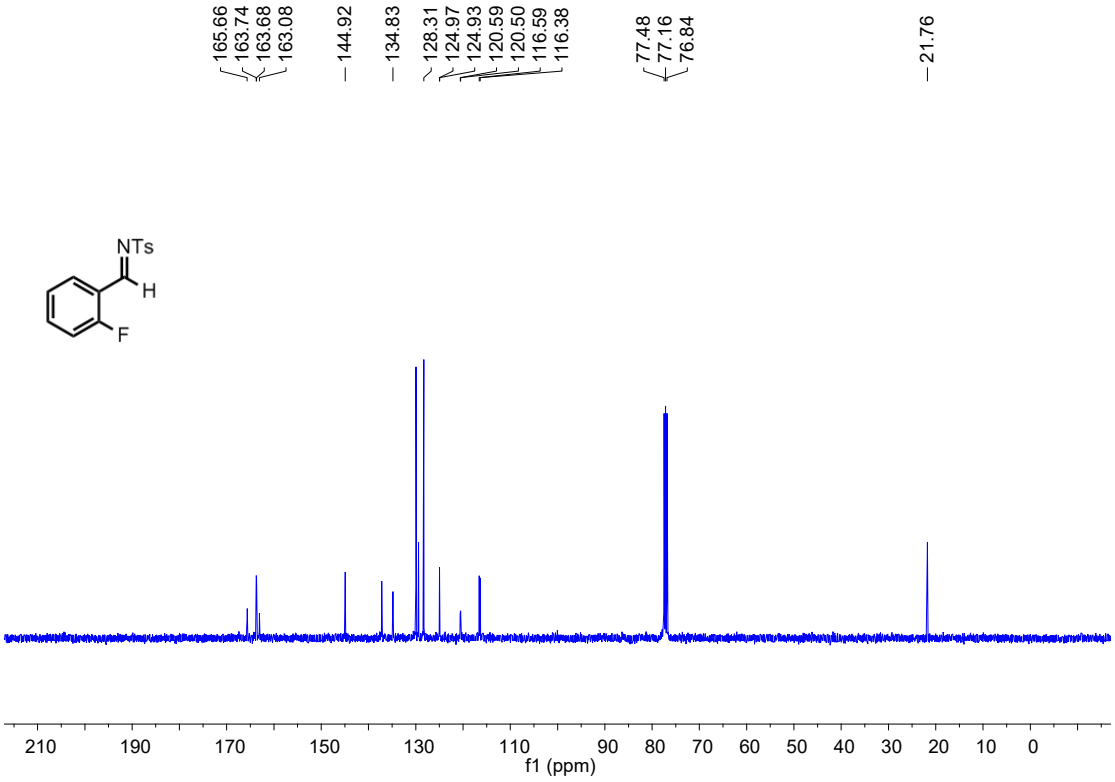

9.00
7.96
7.94
7.87
7.36
7.34
7.26
7.20
7.18
7.15
2.44
NTs
H
F
1.00
2.07
1.93
2.04
1.99
3.07
f1 (ppm)

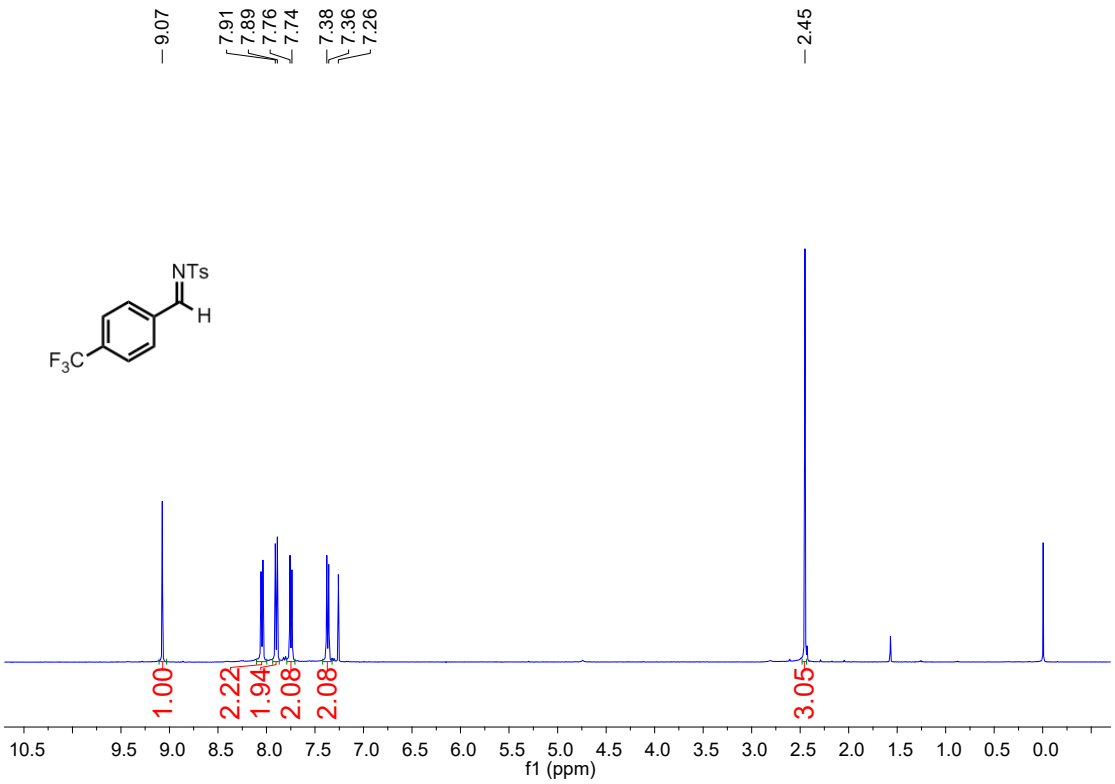

168.65
168.20
165.63
144.80
133.94
128.88
128.18
116.85
116.62
77.48
77.16
76.84
21.75
NTs
H
F
f1 (ppm)

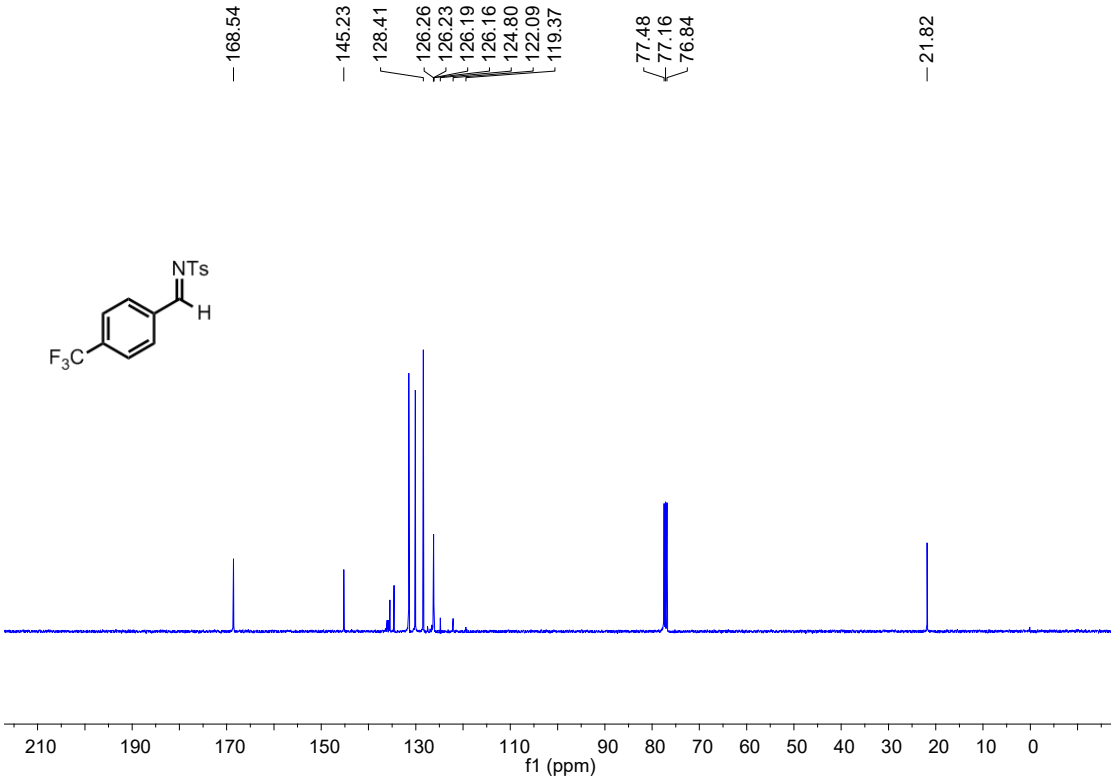

9.00
7.90
7.88
7.69
7.67
7.65
7.51
7.49
7.47
7.46
7.37
7.35
7.31
7.30
7.26
2.45
NTs
F
H
1.00
2.03
2.03
1.13
2.02
1.02
3.24
f1 (ppm)

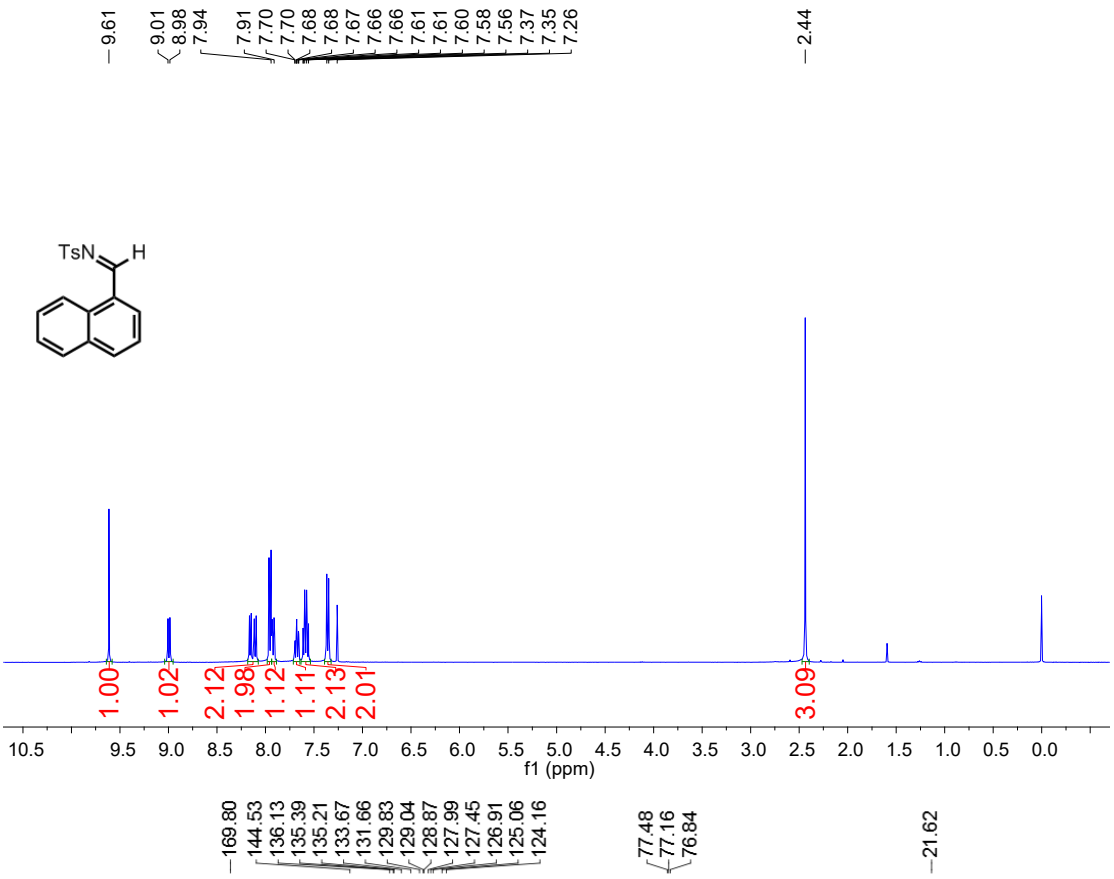

168.82
164.11
161.64
144.99
130.98
129.96
127.95
121.90
116.67
116.45
77.48
77.16
76.84
21.72
NTs
F
H
f1 (ppm)

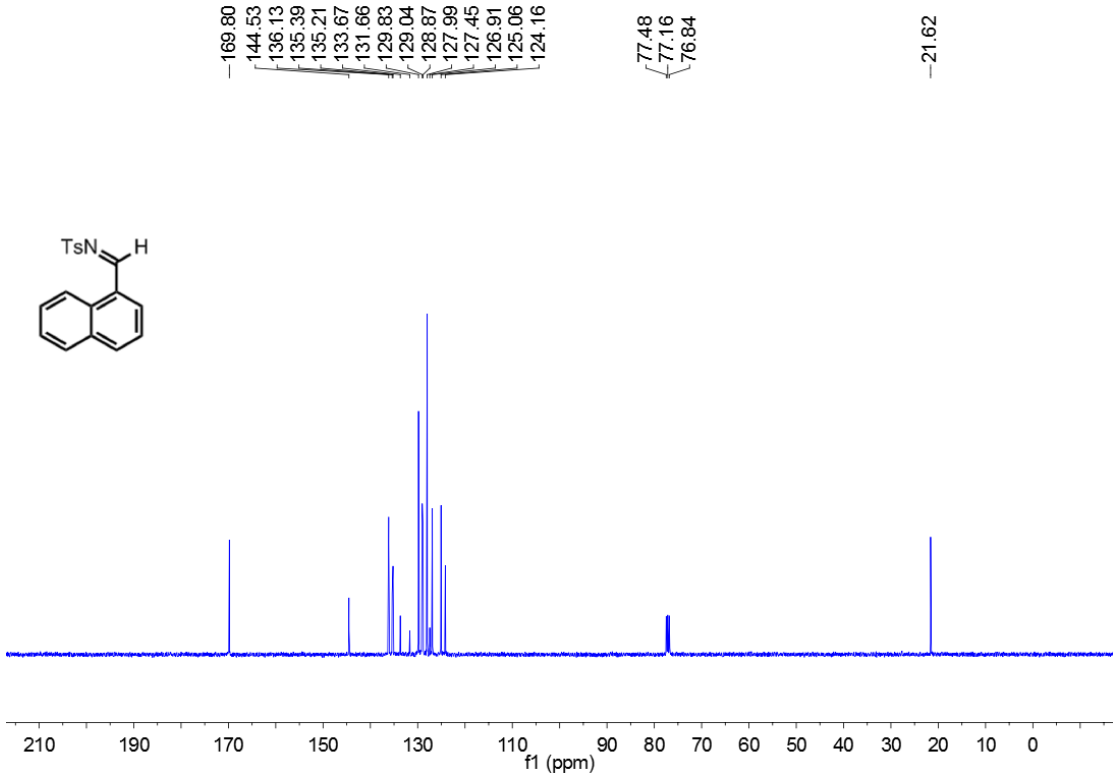

9.36
8.08
8.06
7.91
7.89
7.63
7.62
7.60
7.58
7.37
7.35
7.26
7.23
7.21
7.19
7.17
7.15
2.45
NTs
H
F
1.00
1.09
2.01
1.16
2.00
0.95
0.98
3.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

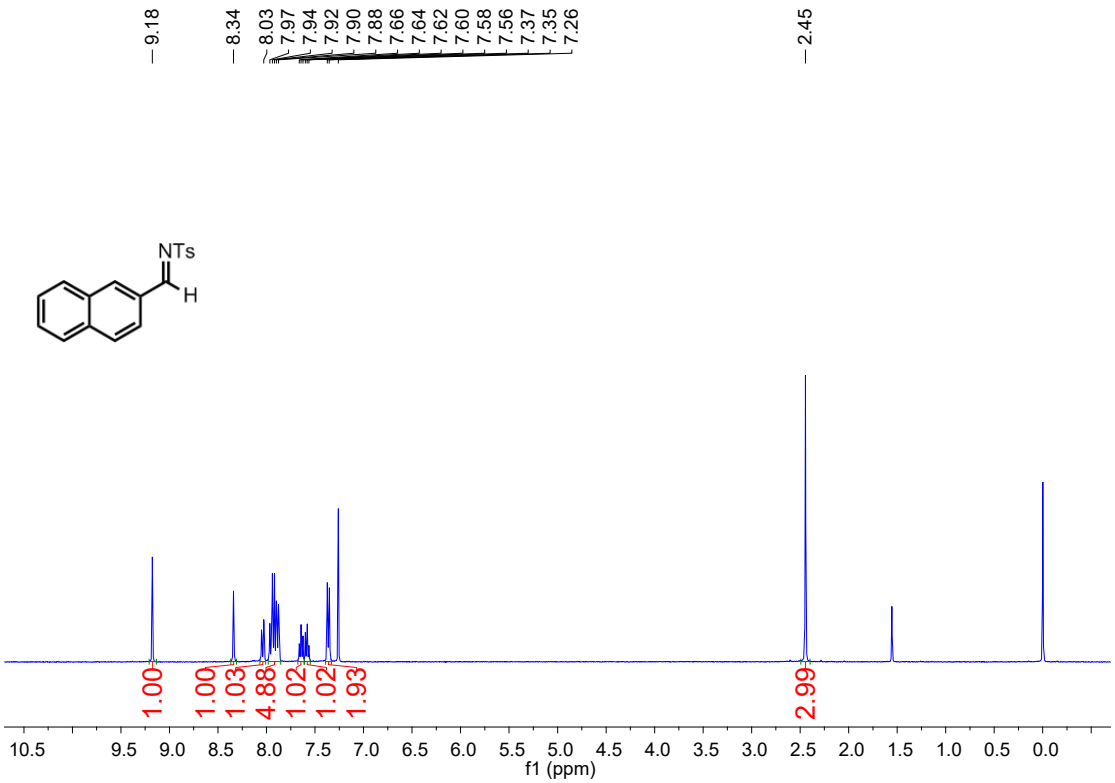

165.66
163.74
163.68
163.08
144.92
134.83
128.31
124.97
124.93
120.59
120.50
116.59
116.38
77.48
77.16
76.84
21.76
NTs
H
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

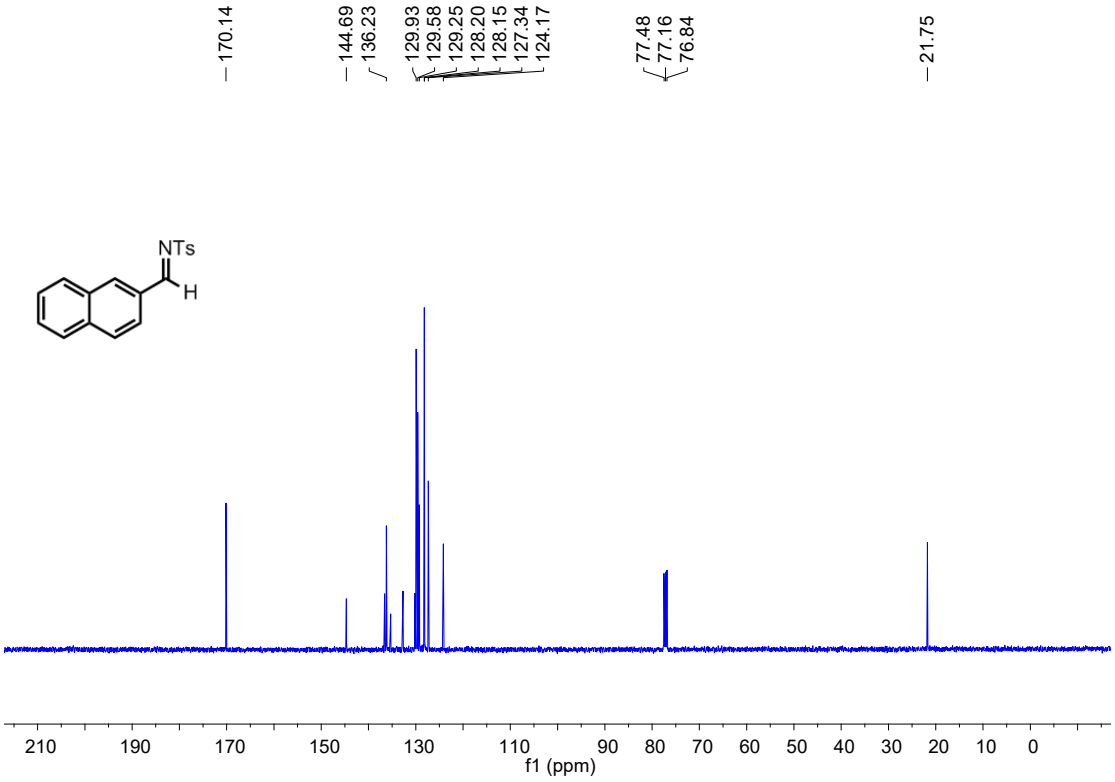

9.07
7.91
7.89
7.76
7.74
7.38
7.36
7.26
2.45
NTs
H
F3C
1.00
2.22
1.94
2.08
2.08
3.05
f1 (ppm)

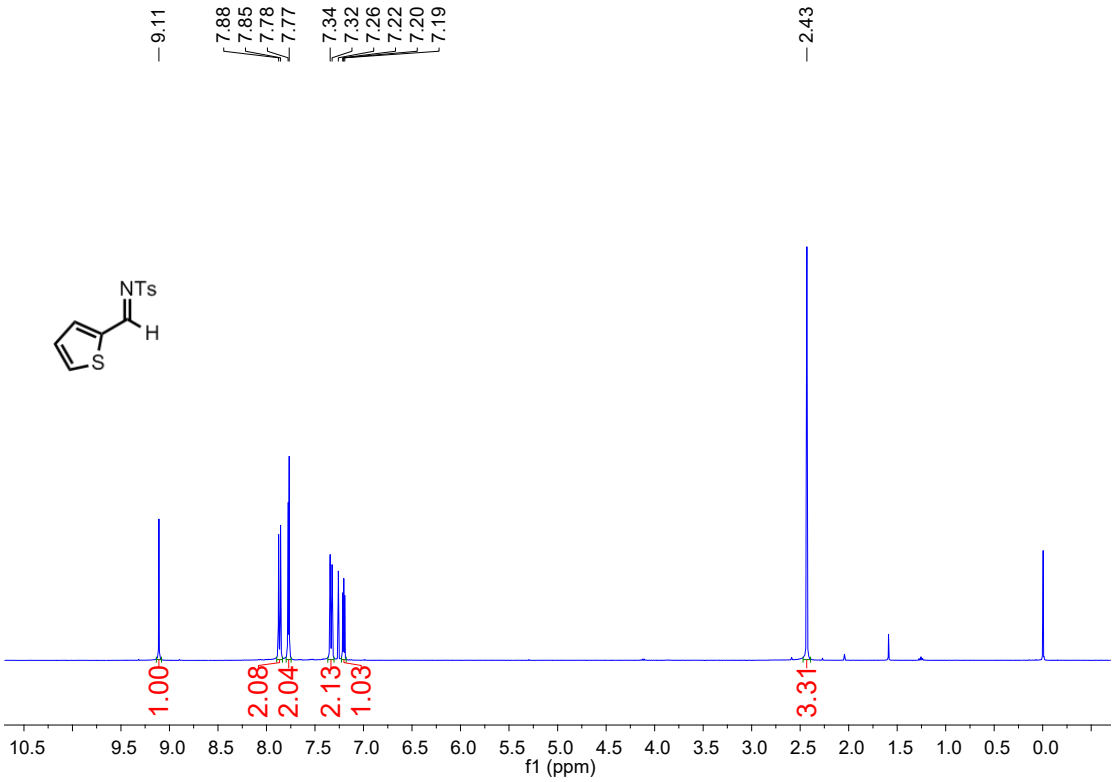

168.54
145.23
128.41
126.26
126.23
126.19
126.16
124.80
122.09
119.37
77.48
77.16
76.84
21.82
NTs
H
F3C
f1 (ppm)

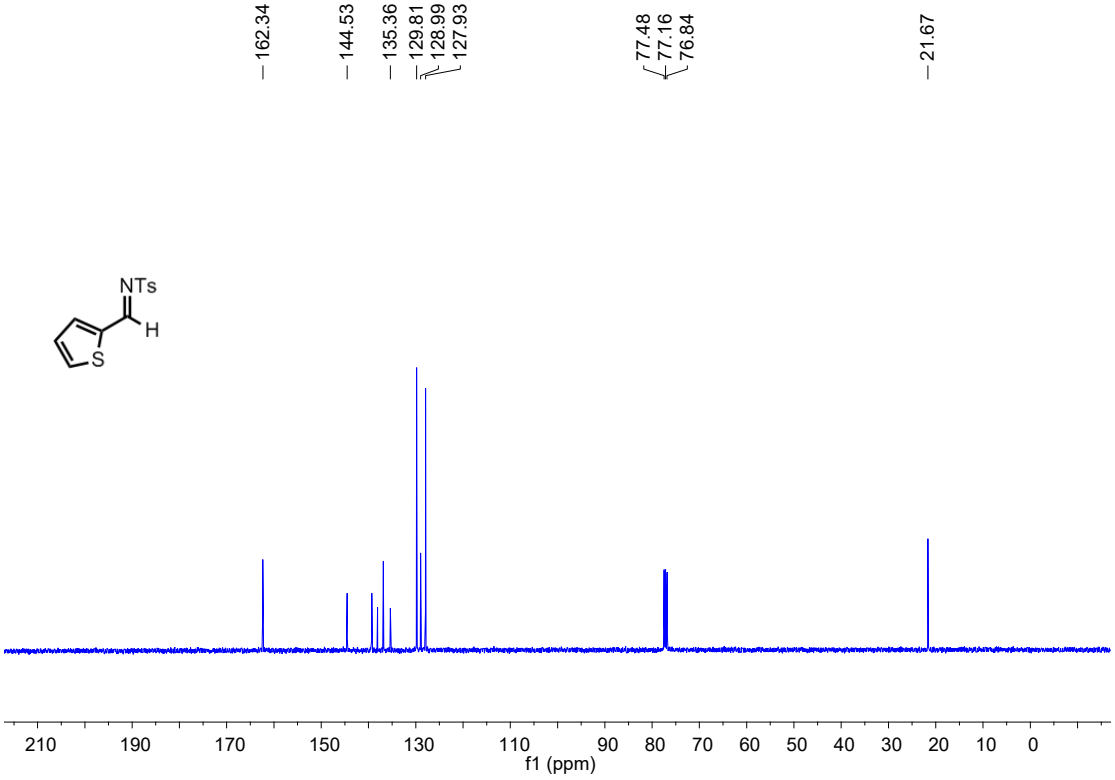

9.61
9.01
8.98
7.94
7.91
7.70
7.70
7.68
7.68
7.67
7.66
7.66
7.61
7.61
7.60
7.58
7.56
7.37
7.35
7.26
2.44
TsN
H
1.00
1.02
2.12
1.98
1.12
1.11
2.13
2.01
3.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

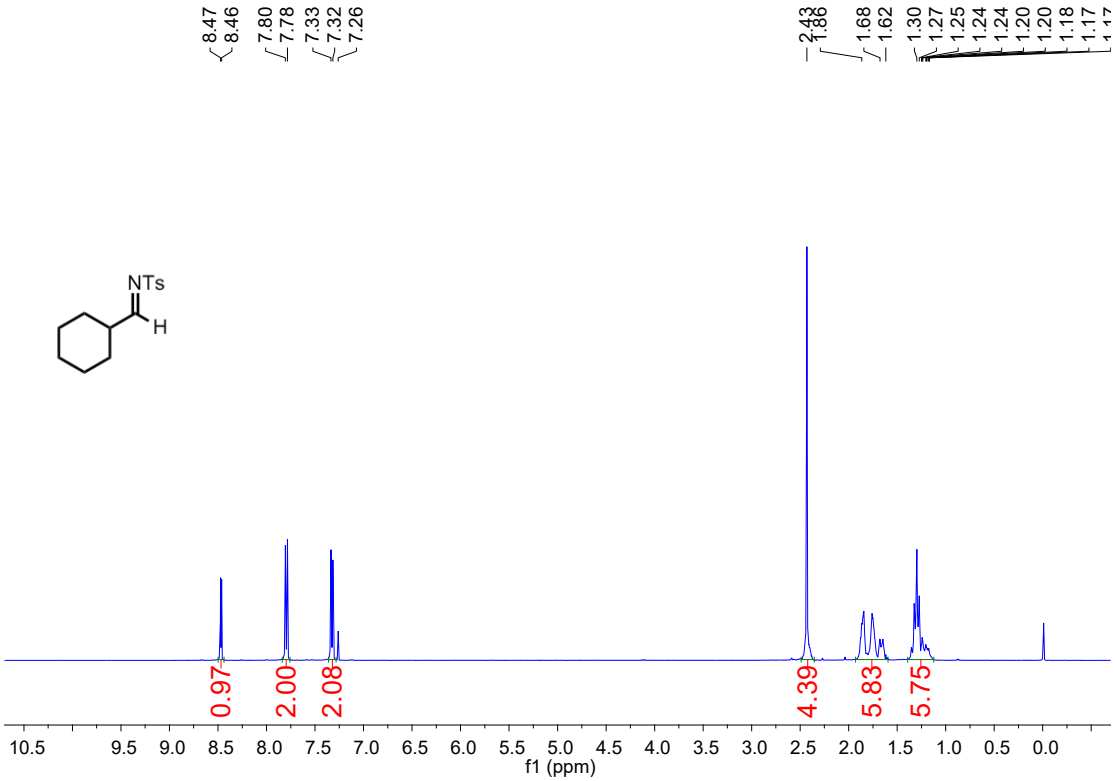

169.80
144.53
136.13
135.39
135.21
133.67
131.66
129.83
129.04
128.87
127.99
127.45
126.91
125.06
124.16
77.48
77.16
76.84
21.62
TsN
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

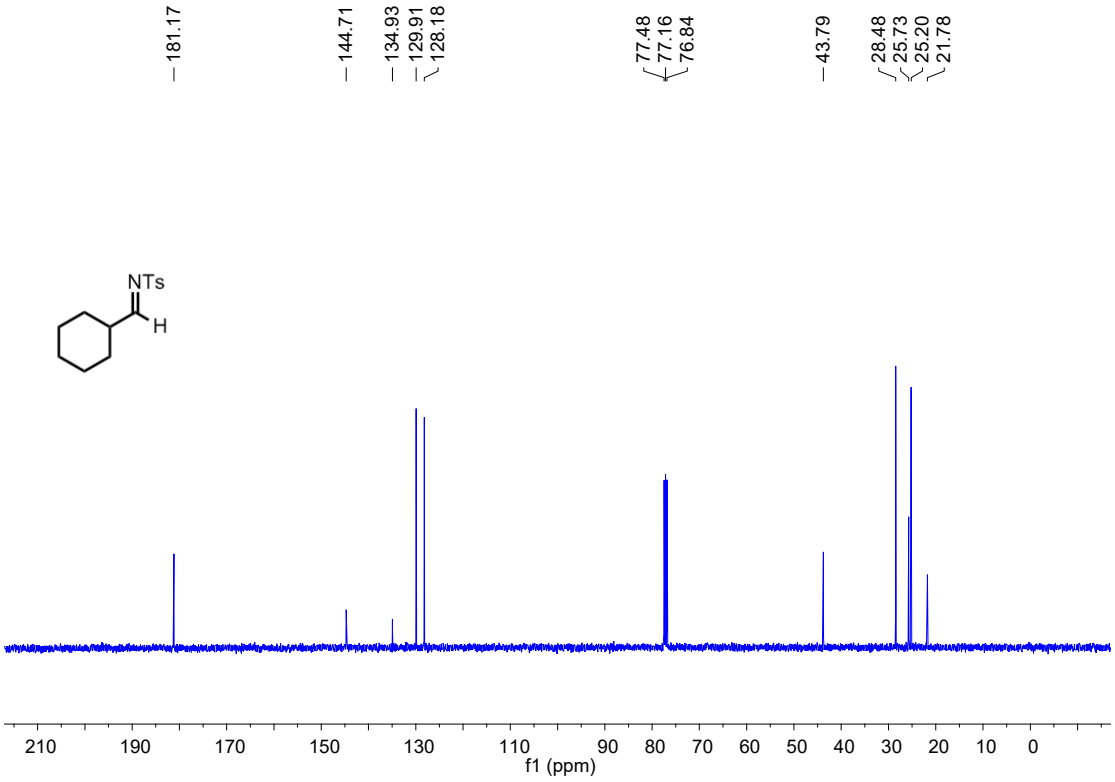

9.18
8.34
8.03
7.97
7.94
7.92
7.90
7.88
7.66
7.64
7.62
7.60
7.58
7.56
7.37
7.35
7.26
2.45
NTs
H
1.00
1.00
1.03
4.88
1.02
1.02
1.93
2.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

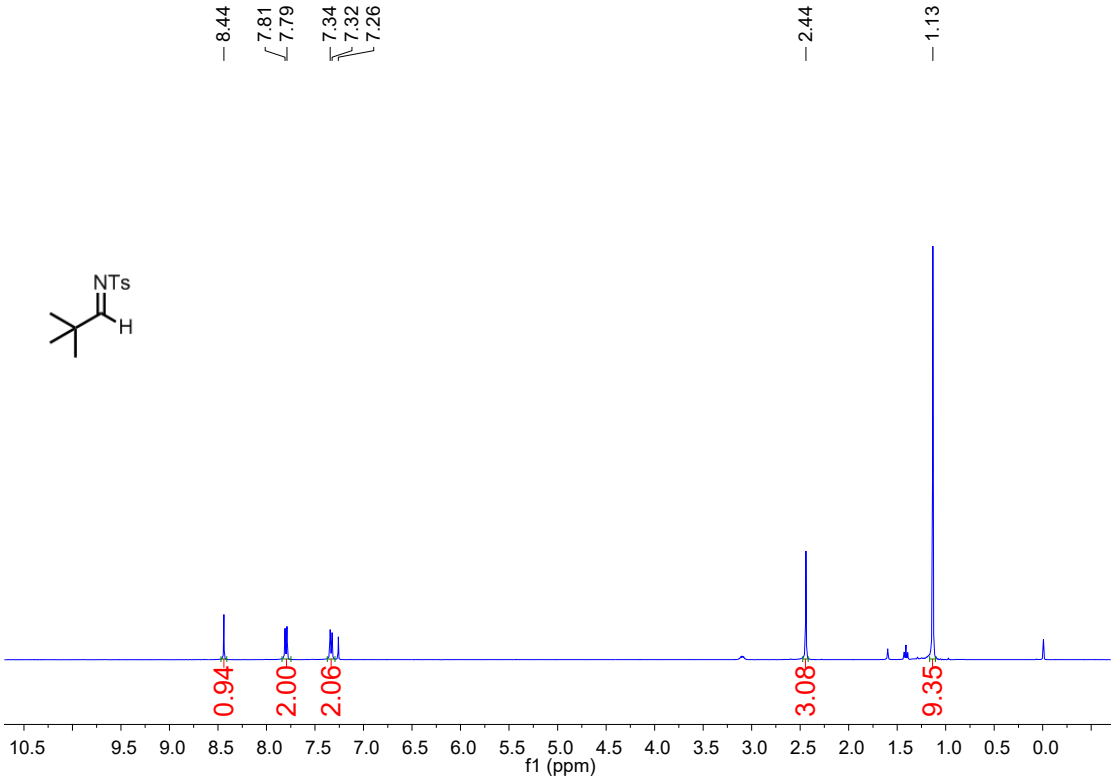

170.14
144.69
136.23
129.93
129.58
129.25
128.20
128.15
127.34
124.17
77.48
77.16
76.84
21.75
NTs
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

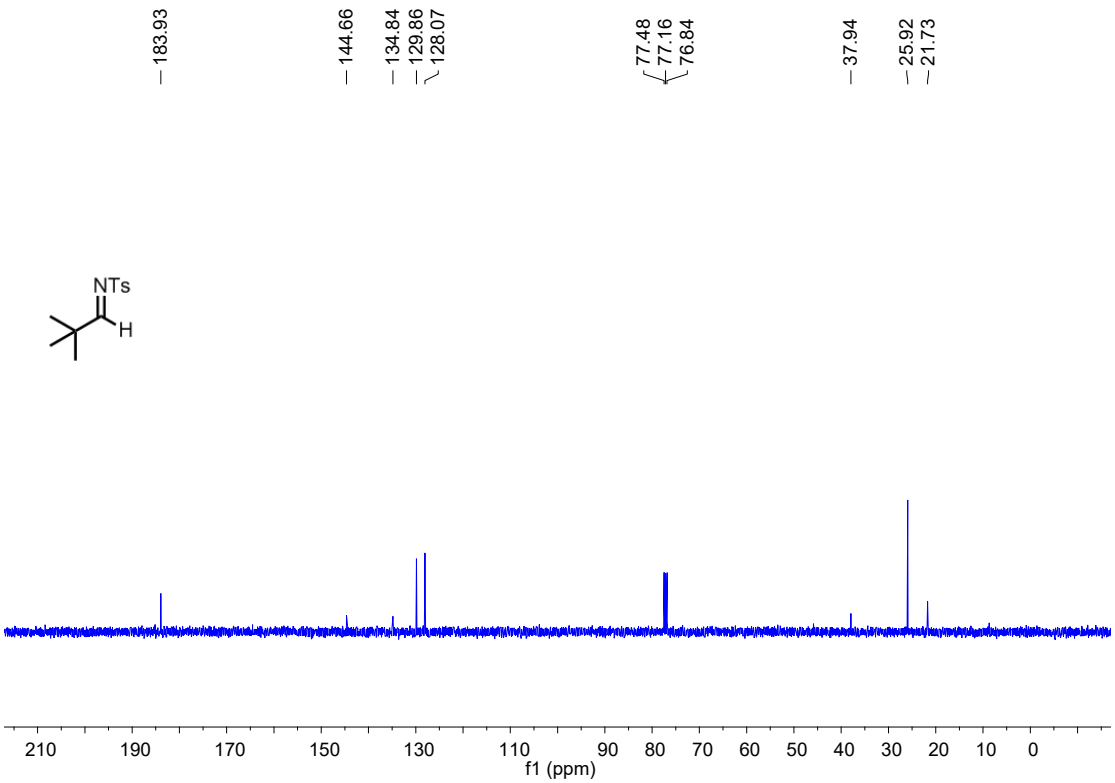

9.11
7.88
7.85
7.78
7.77
7.34
7.32
7.26
7.22
7.20
7.19
2.43
NTs
H
S
1.00
2.08
2.04
2.13
1.03
3.31
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

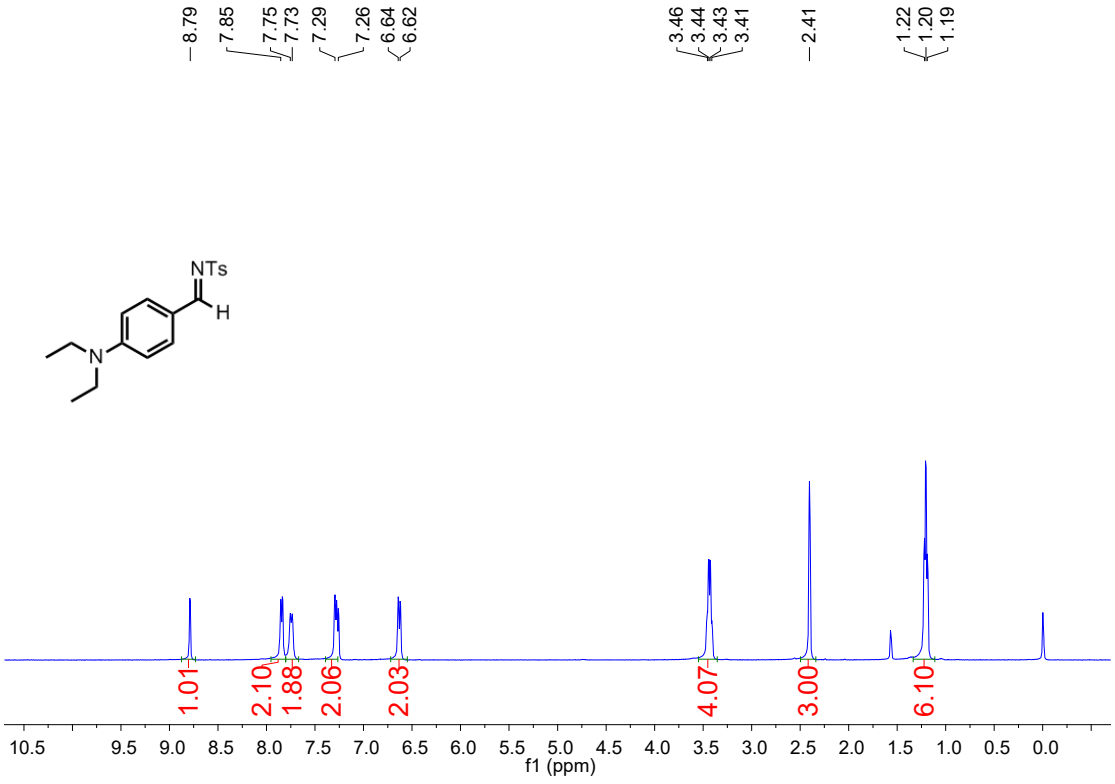

162.34
144.53
135.36
129.81
128.99
127.93
77.48
77.16
76.84
21.67
NTs
H
S
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

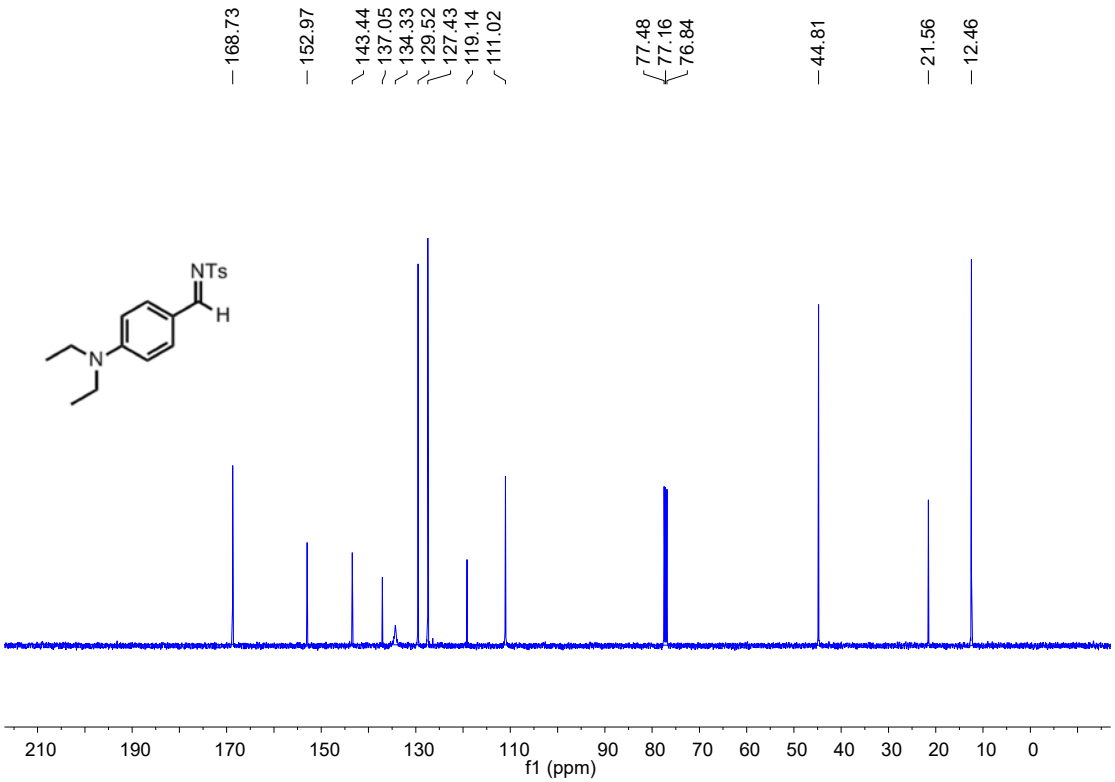

8.47
8.46
7.80
7.78
7.33
7.32
7.26
2.43
1.86
1.68
1.62
1.30
1.27
1.25
1.24
1.24
1.20
1.20
1.18
1.17
NTs
H
0.97
2.00
2.08
4.39
5.83
5.75
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

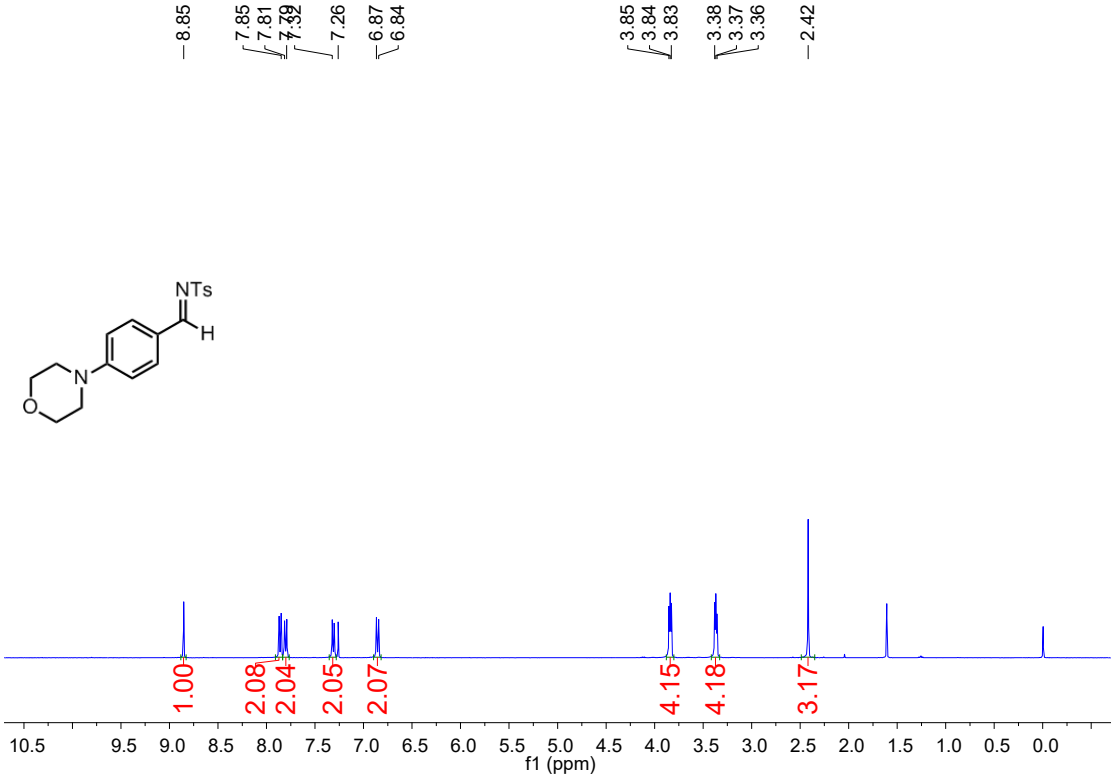

181.17
144.71
134.93
129.91
128.18
77.48
77.16
76.84
43.79
28.48
25.73
25.20
21.78
NTs
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

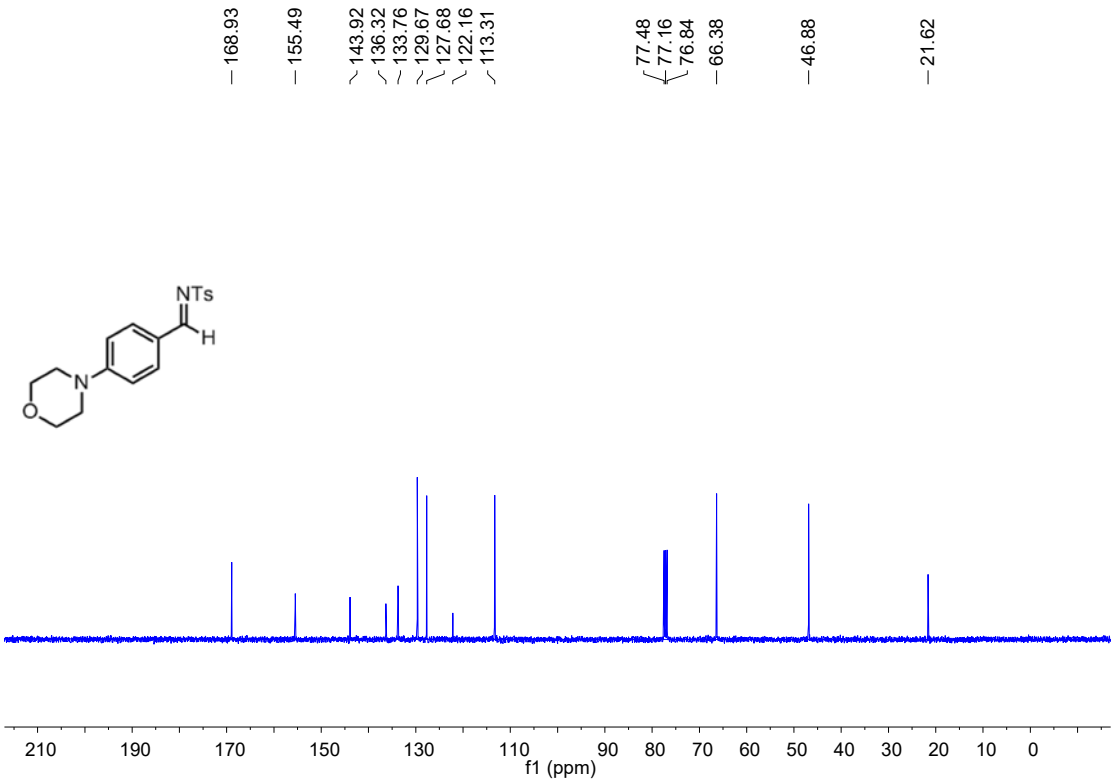

8.44
7.81
7.79
7.34
7.32
7.26
2.44
1.13
NTs
H
0.94
2.00
2.06
3.08
9.35
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


183.93
144.66
134.84
129.86
128.07
77.48
77.16
76.84
37.94
25.92
21.73
NTs
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

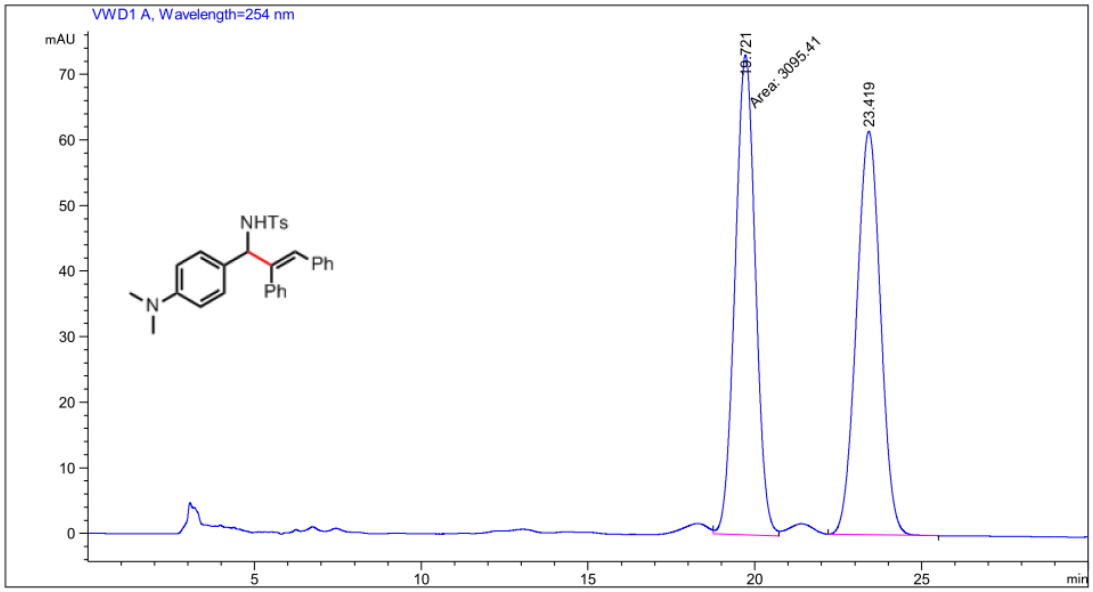

8.79
7.85
7.75
7.73
7.29
7.26
6.64
6.62
3.46
3.44
3.43
3.41
2.41
1.22
1.20
1.19
NTs
H
N
1.01
2.10
1.88
2.06
2.03
4.07
3.00
6.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.73
152.97
143.44
137.05
134.33
129.52
127.43
119.14
111.02
77.48
77.16
76.84
44.81
21.56
12.46
NTs
H
N
f1 (ppm)

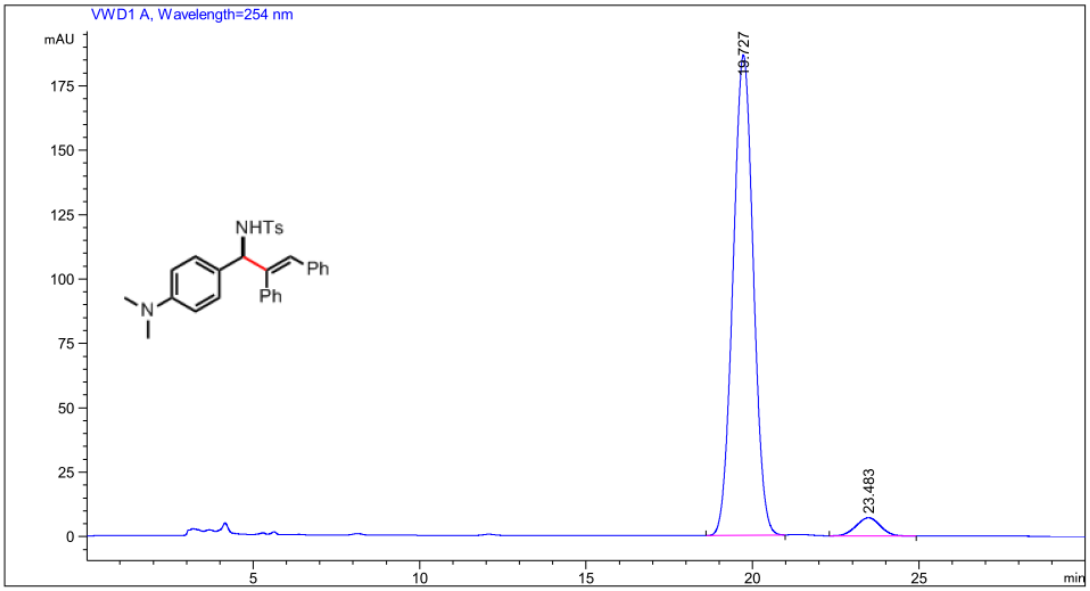

8.85
7.85
7.81
7.26
6.87
6.84
3.85
3.84
3.83
3.38
3.37
3.36
2.42
NTs
H
N
O
1.00
2.08
2.04
2.05
2.07
4.15
4.18
3.17
f1 (ppm)


168.93
155.49
143.92
136.32
133.76
129.67
127.68
122.16
113.31
77.48
77.16
76.84
66.38
46.88
21.62
NTs
H
N
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9. HPLC Charts

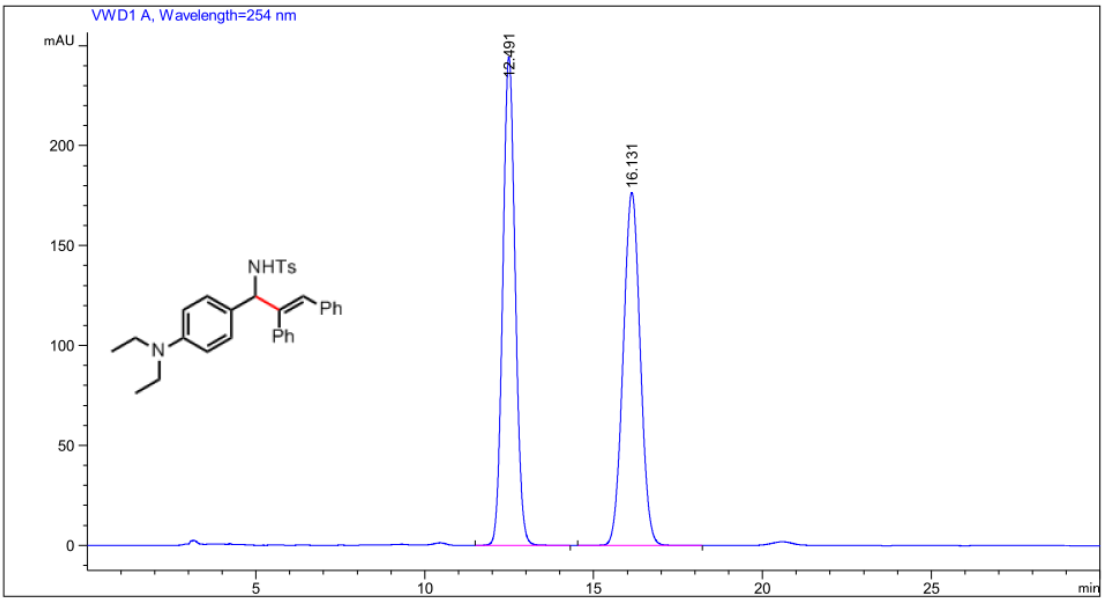


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.721	MM	0.7055	3095.40796	73.12049	50.0804
2	23.419	BB	0.7871	3085.46924	61.52321	49.9196

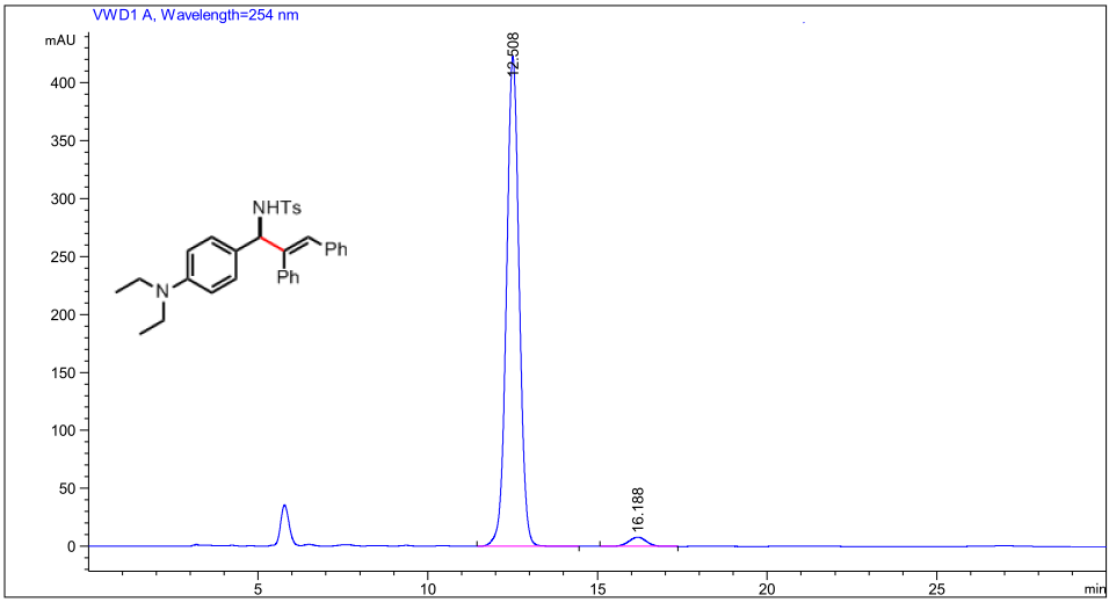


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.727	BB	0.6612	7897.06250	186.44078	95.6936
2	23.483	BB	0.7659	355.38577	7.04105	4.3064

Result: $t_{r\text{-major}}$ = 19.7 min (***S*-3i**), $t_{r\text{-minor}}$ = 23.5 min (***R*-3i**), 91% ee

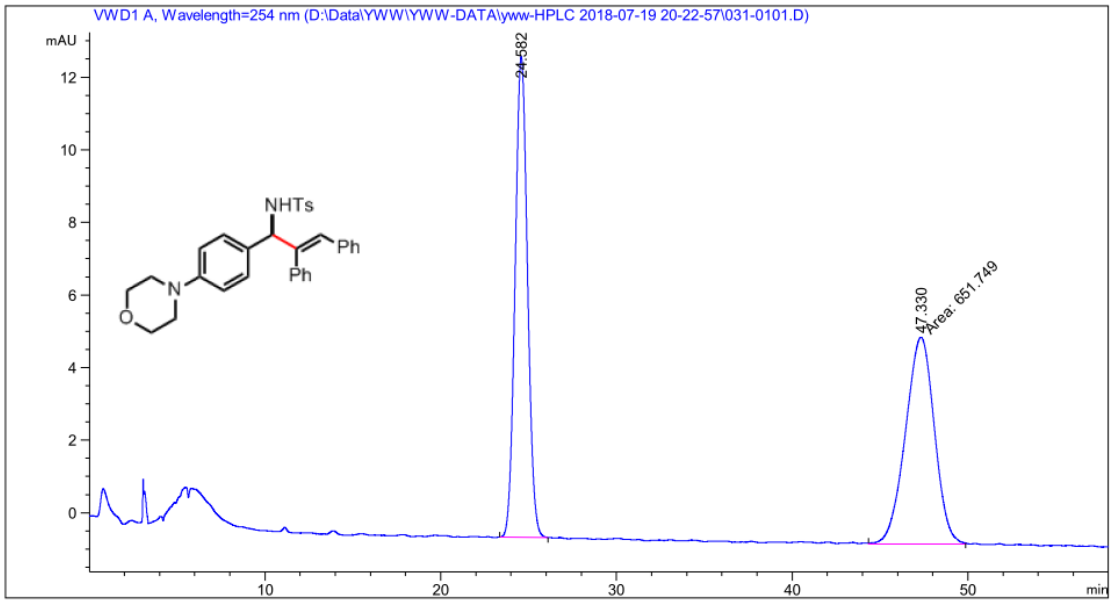


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.491	BB	0.3973	6254.65625	244.61754	50.1876
2	16.131	BB	0.5499	6207.90674	176.67084	49.8124

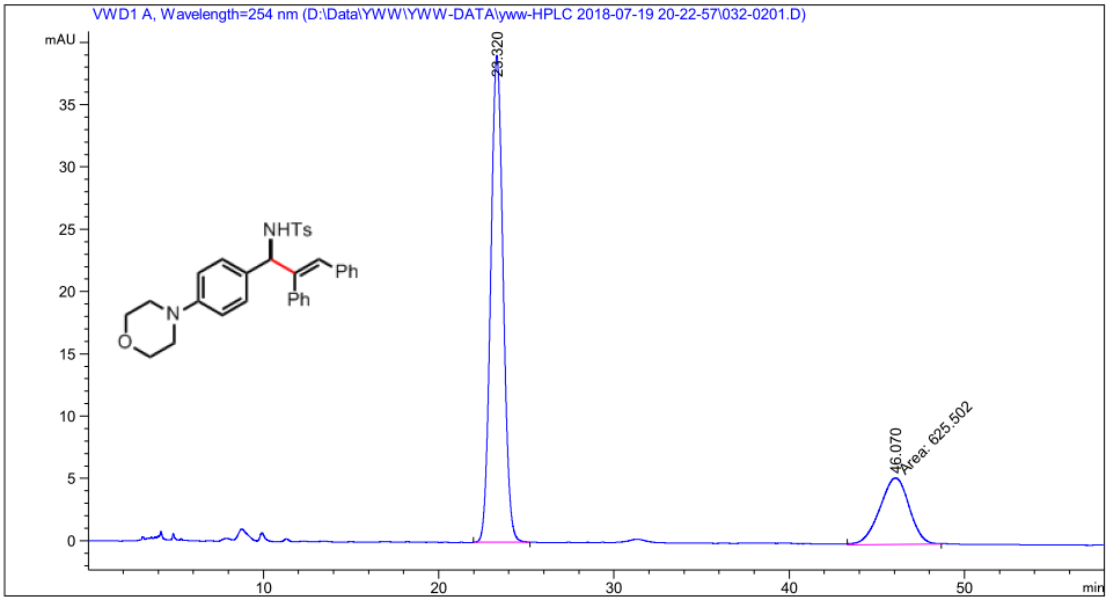


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.508	BB	0.4034	1.10350e4	422.87714	97.5027
2	16.188	BB	0.5575	282.63806	7.89850	2.4973

Result: $t_{r\text{-major}}$ = 12.5 min (***S*-5a**), $t_{r\text{-minor}}$ = 16.2 min (***R*-5a**), 95% ee

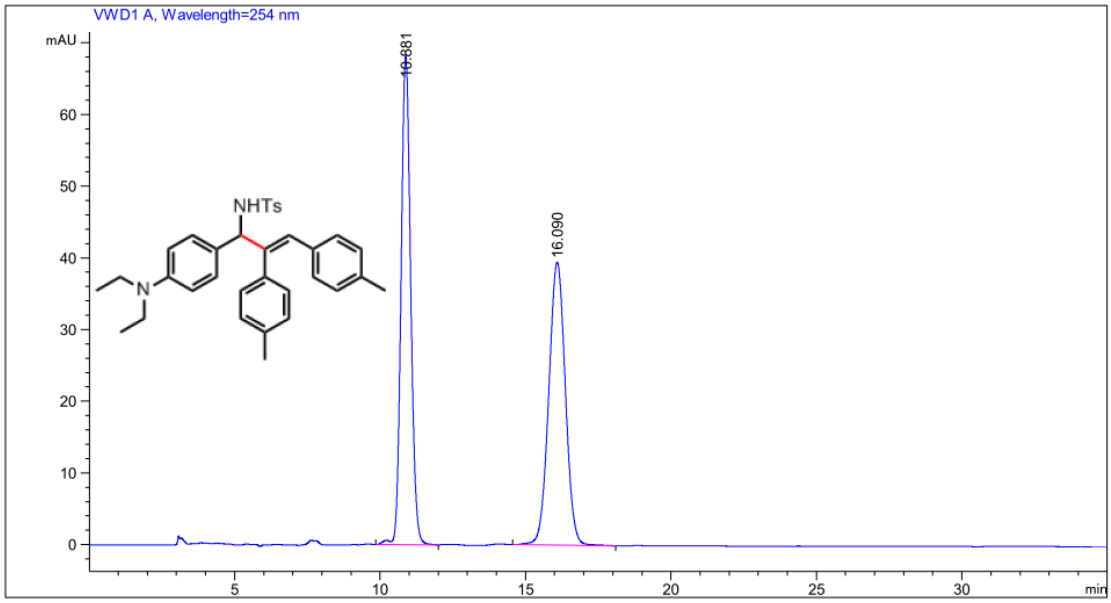


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.582	BB	0.7563	648.23309	13.23888	49.8648
2	47.330	MM	1.9071	651.74927	5.69591	50.1352

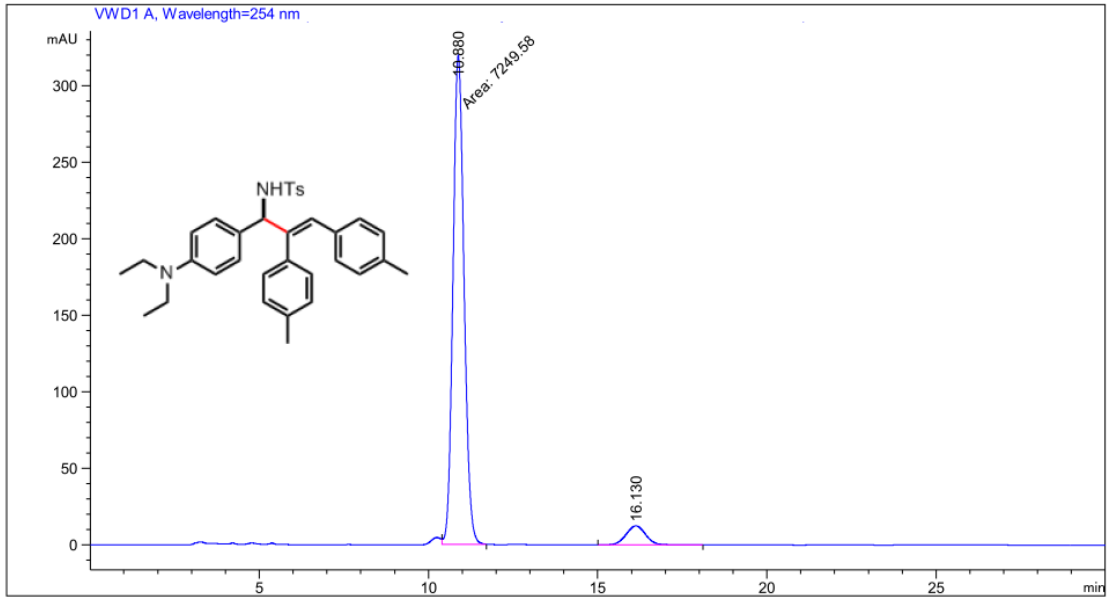


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.320	BB	0.7651	1925.49353	39.06065	75.4801
2	46.070	MM	1.9529	625.50177	5.33815	24.5199

Result: $t_{r\text{-major}}$ = 23.3 min (***S*-5b**) , $t_{r\text{-minor}}$ = 46.1 min (***R*-5b**), 51% ee.

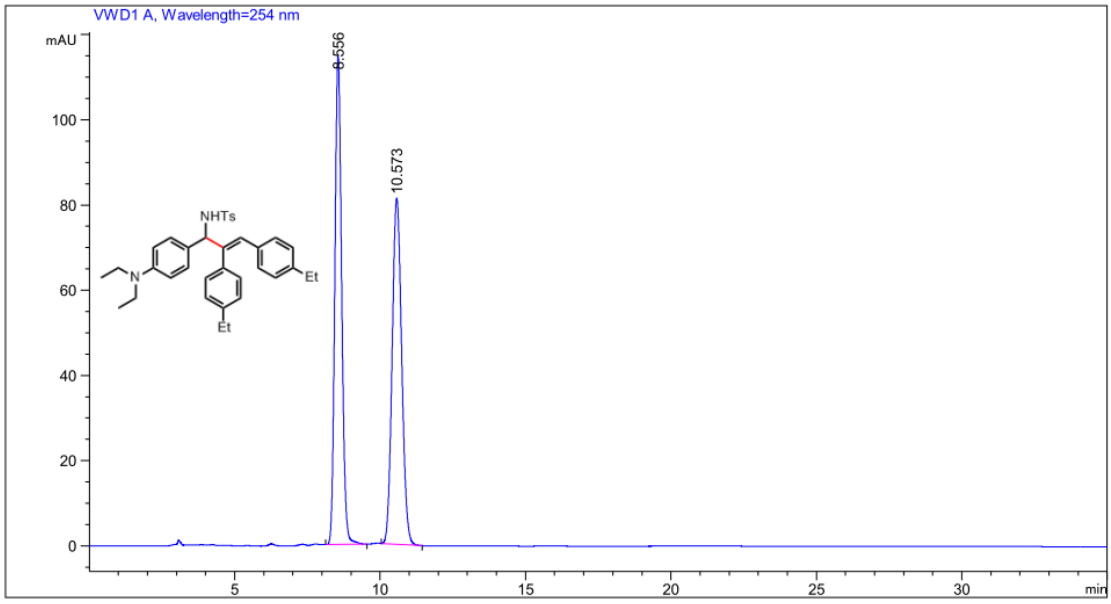


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.881	VB R	0.3577	1569.74707	68.14752	50.0422
2	16.090	BB	0.6190	1567.10046	39.49034	49.9578

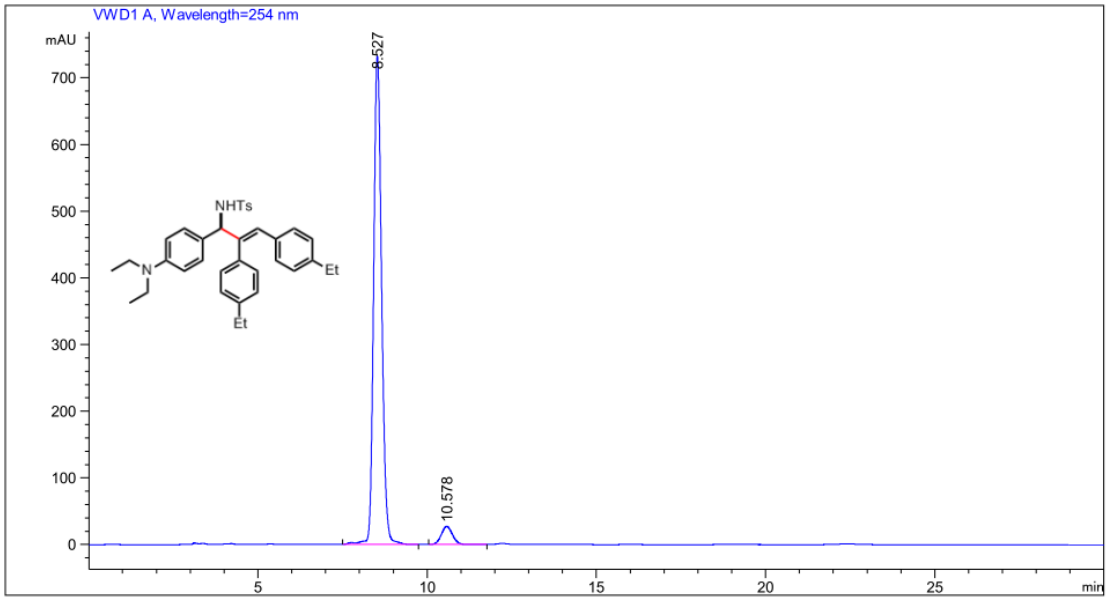


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.880	MM	0.3782	7249.57813	319.44031	93.5020
2	16.130	BB	0.6242	503.81717	12.44895	6.4980

Result: $t_{r\text{-major}}$ = 10.9 min (***S*-5c**), $t_{r\text{-minor}}$ = 16.1 min (***R*-5c**), 87% ee.

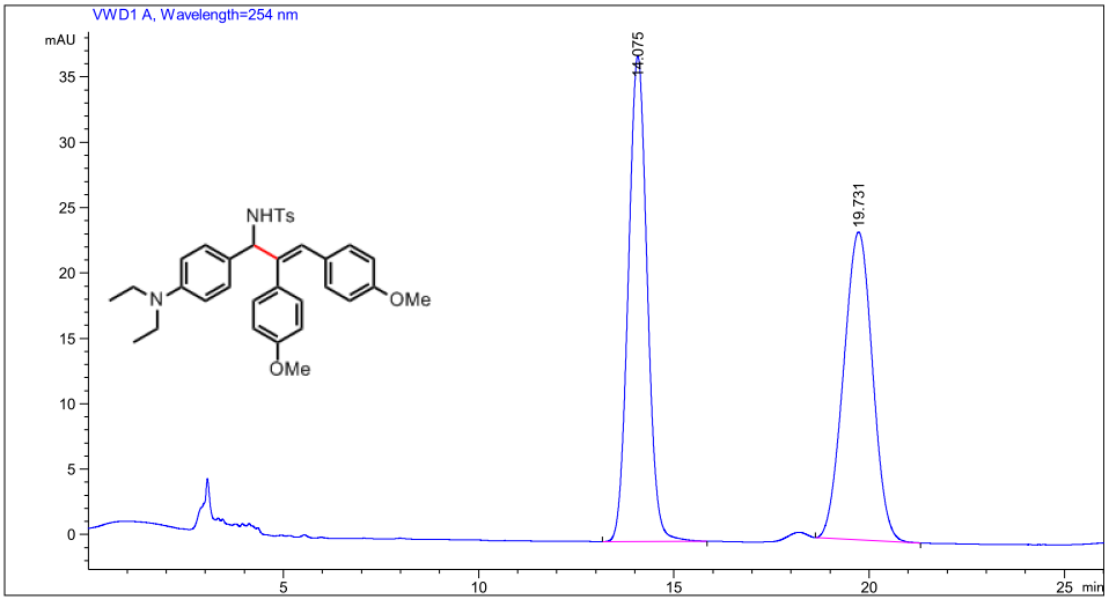


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.556	BB	0.2522	1868.02551	114.60315	50.2732
2	10.573	BB	0.3543	1847.72192	81.25831	49.7268

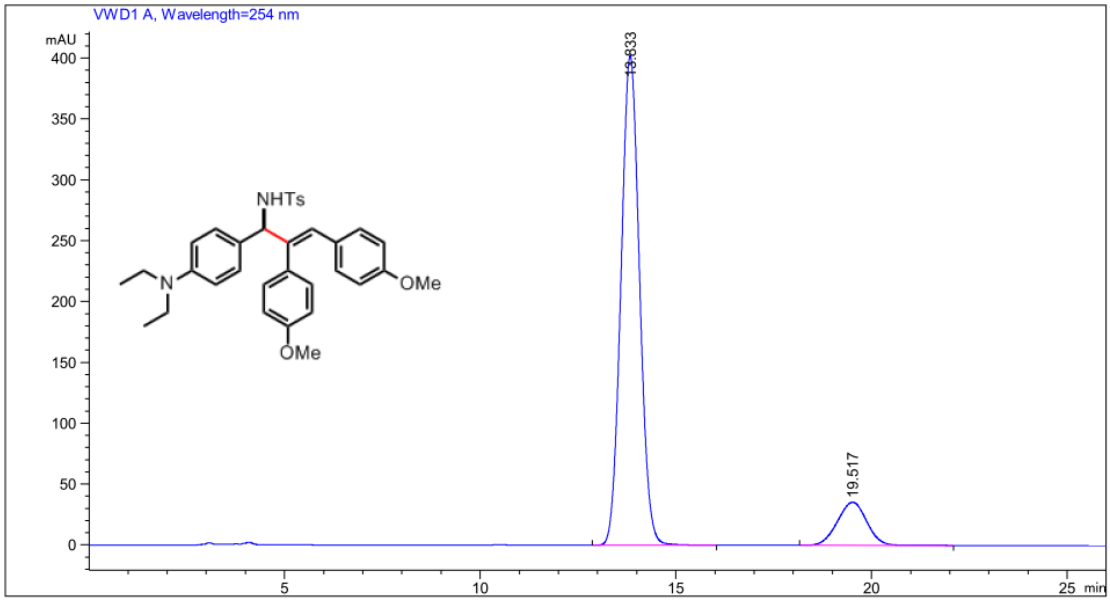


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.527	VB R	0.2534	1.20132e4	732.44592	95.1222
2	10.578	BB	0.3550	616.03235	27.01903	4.8778

Result: $t_{r\text{-major}}$ = 8.5 min (***S*-5d**), $t_{r\text{-minor}}$ = 10.6 min (***R*-5d**), 90% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.075	BB	0.5229	1247.04626	37.12828	50.7440
2	19.731	BB	0.7868	1210.48071	23.54608	49.2560



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.833	BB	0.5084	1.32154e4	402.12558	87.7878
2	19.517	BB	0.8038	1838.40222	35.40632	12.2122

Result: $t_{r\text{-major}}$ = 13.8 min (***S*-5e**), $t_{r\text{-minor}}$ = 19.5 min (***R*-5e**), 75% ee.