Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An Organocatalytic method for Constructing Pyrroles via Cycloisomerisation of Z-1-iodo-4-N-methylbenzenesulfonyl-1,6-enynes

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Supporting Information

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I. General Information

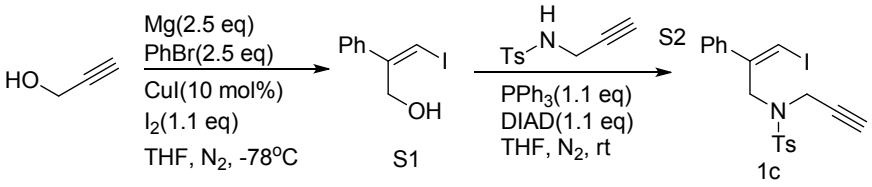
Organic solvents (Aldrich) were used without further purification. Purifications of reactions productswere carried out by flash chromatography using Merck silica gel (40-63 μm). Infrared spectra (IR) were obtained on a PerkinElmer system 2000 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were collected by preparing a KBr pellet containing the title compound.

NMR spectra were recorded on a AVANCE Ⅲ HD 400MHz spectrometer [^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz)]. Chemical shifts for 1H NMR are reported in parts per million (δ) relative to methylbenzenesulfonyl as the internal standard. Coupling constant (*J*) are reported in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. Chemical shifts for ^{13}C NMR are reported in parts per million (δ) relative to the solvent ($CDCl_3$, δ 77.16).

All commercially available reagents were bought from Macklin, Aladdin and used without further purification. Dry THF was steamed with metal sodium. Potassium tert-butoxide was directly purchased from Aladdin. Structure **1a-1j** are known compounds and were prepared according to reported procedures.

Reactions were conducted in dry solvents under Nitrogen atmosphere unless otherwise stated. The abbreviation “rt” refers to reactions carried out approximately at 23-27ºC. Reaction mixtures were stirred using Teflon-coated Magnetic stirring rotor. Thin-layer chromatography (tlc) was performed on silica gel plates and components were visualized by observation under UV light, flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4 or $MgSO_4$. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator, followed by residual solvent removal under high vacuum. The reactions were monitored by tlc or **GC-MS**.

II. General procedure for the synthesis of propynamide starting materials by Mitsunobu



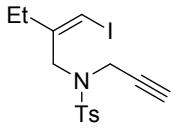
General Procedure:

Firstly, prepare phenyl Grignard reagent.In a 250 ml three-necked flask, weighed 3 g (2.5 equiv, 125 mmol) of magnesium shavings.Anhydrous tetrahydrofuran was added until it just exceeded the magnesium turnings.0.3 ml bromobenzene was injected once with a syringe and heated by a hair dryer until the solution became cloudy and bubbles appeared, indicating that the format reagent was successfully initiated.13 ml (2.5 equiv, 125 mmol) of bromobenzene in 100 ml of THF was slowly added dropwise through a 150 ml dropping funnel, and the reaction solution was kept under reflux by adjusting the dropping rate.After the completion of the dropwise addition, stir at room temperature for 2 h until the magnesium turnings reaction is complete, and a clear solution is obtained. At this time, the Grignard reagent has been prepared, waiting for the next step.In another 500 ml three-necked flask, 2.8 g of propargyl alcohol (1.0 equiv, 50 mmol) was dissolved in 70 ml THF, and 0.95 g of CuI (10 mol%, 5 mmol) was added under stirring, and the whole system was operated under nitrogen atmosphere. The suspension was then cooled to -78 °C. At this time, the freshly prepared Grignard reagent was transferred to a constant pressure dropping funnel under nitrogen protection.With vigorous stirring, the Grignard reagent was added dropwise and the reaction temperature was kept below -60°C. After the completion of the dropwise addition, stir at low temperature for 1 h, warm to room temperature and stir for 18 h.Then, the reaction system was again cooled to -78 °C, and 13 g (1.1 equiv, 55 mmol) I_2 in 40 ml dry THF was added dropwise with vigorous stirring, keeping the temperature below -60 °C. After the drop. Stir for 0.5 h, then stir at room temperature for 1 h.The system was cooled to 0 °C and the reaction was quenched by slow dropwise addition of saturated NH_4Cl solution.After liquid separation, the aqueous phase was extracted with ethyl acetate (3×50 ml) and the organic phases were combined. The organic phase was washed with a saturated $Na_2S_2O_3$ solution. Finally, the organic phase was washed with a saturated NaCl solution and dried over

anhydrous Na_2SO_4 .The crude product was purified by column chromatography using petroleum Petroleum ether/ethyl acetate (10:1) as eluent to afford a yellow liquid(68% yield).

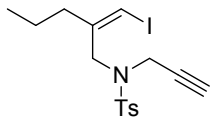
Synthetic material **1c** according to the general operation method of Mitsunobu.In a 100 ml round bottom flask, 2.6 g (1.0 equiv, 10 mmol) of **S1** was dissolved in 30 ml of THF, followed by 2.3 g (1.1 equiv, 11 mmol) of **S2**, 2.9 g (1.1 equiv, 11 mmol) of PPh_3 and 2.2 ml (1.1 equiv, 11 mmol) DIAD. Stir at room temperature overnight. The reaction was followed by TLC. After the material was consumed, ethyl acetate (3 × 50 ml) was combined and the organic phase was combined and purified by column chromatography to give a white solid **1c**(3.74 g, 8.3 mmol).

(Z) -N-(2-(iodomethylene)butyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1a



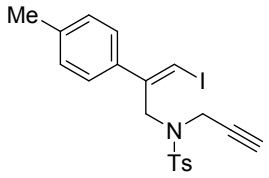
following the general procedure described above, compound **1a** (3.47 g, 8.6 mmol) was obtained in 86 % yield.

(Z)-N-(2-(iodomethylene)pentyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1b



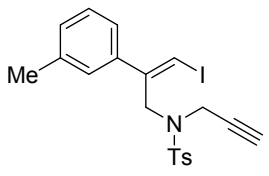
following the general procedure described above, compound **1b** (3.67 g, 8.8 mmol) was obtained in 88 % yield.

(Z)-N-(3-iodo-2-(p-tolyl)allyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1d



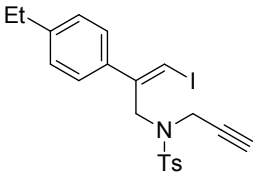
following the general procedure described above, compound **1d** (3.95 g, 8.5 mmol) was obtained in 85 % yield.

(Z)-N-(3-iodo-2-(m-tolyl)allyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1e



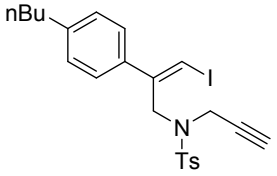
following the general procedure described above, compound **1e** (4.00 g, 8.6 mmol) was obtained in 86 % yield.

(Z)-N-(2-(4-ethylphenyl)-3-iodoallyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1f



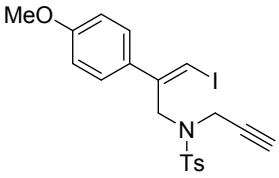
following the general procedure described above, compound **1f** (3.93 g, 8.2 mmol) was obtained in 82 % yield.

(Z)-N-(2-(4-butylphenyl)-3-iodoallyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1g



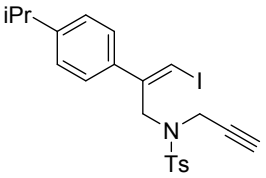
following the general procedure described above, compound **1g** (4.41 g, 8.7 mmol) was obtained in 87 % yield.

(Z)-N-(3-iodo-2-(4-methoxyphenyl)allyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1h



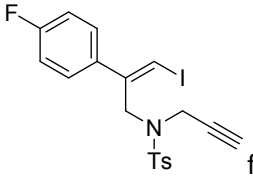
following the general procedure described above, compound **1h** (4.09 g, 8.5 mmol) was obtained in 85 % yield.

(Z)-N-(3-iodo-2-(4-isopropylphenyl)allyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1i



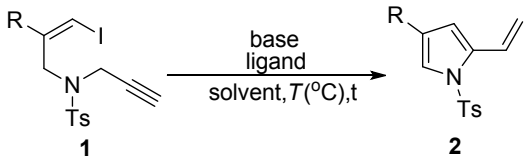
following the general procedure described above, compound **1i** (4.34 g, 8.8 mmol) was obtained in 88 % yield.

(Z)-N-(2-(4-fluorophenyl)-3-iodoallyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide,1j



following the general procedure described above, compound **1j**(4.03 g, 8.6 mmol) was obtained in 86 % yield.

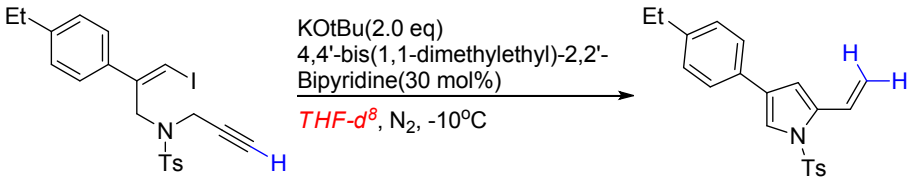
III. Optimization of reaction conditions.



1 **2**

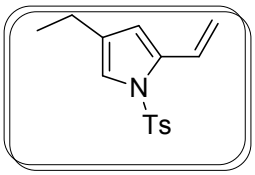
entry	base(equiv)	ligand(mol%)	solvent	temp(°C)	time(min)	yield(%)
1	KOtBu(1.2)		THF	-20	30	5
2	KOtBu(1.2)		THF	-10	30	19
3	KOtBu(1.2)		THF	0	30	4
4	KOtBu(1.2)		THF	rt	30	14
5	KOtBu(1.2)	1,10-phenanthroline(20 mol%)	THF	-10	30	0
6	KOtBu(2)	1,10-phenanthroline(20 mol%)	THF	-10	10	0
7	KOtBu(2)		benzene	-10	30	0
8	KOtBu(2)		pyridin	-10	30	11
9	KOtBu(2)		THF	-10	10	0
10	KOtBu(1.2)	2,2'-Bipyridine(20 mol%)	THF	rt	30	10
11	KOtBu(1.2)	2,2'-Bipyridine(20 mol%)	THF	0	30	12
12	KOtBu(2)	2,2'-Bipyridine(20 mol%)	THF	-10	30	35
13	KOtBu(1.2)	2,2'-Bipyridine(20 mol%)	THF	-10	30	22
14	KOtBu(2)	2,2'-Bipyridine(20 mol%)	THF	-20	30	30
15	KOtBu(2)	2,2'-Bipyridine(20 mol%)	THF	-10	10	54
16	KOtBu(2)	4-Methoxy-2-(4-methoxypyridin-2-yl)pyridine(20 mol%)	THF	-10	10	32
17	KOtBu(2)	4,4'-Dimethyl-2,2'-dipyridyl(20 mol%)	THF	-10	10	39
18	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(20 mol%)	THF	0	10	60
19	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(20 mol%)	THF	-10	10	62
20	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	THF	-10	10	77
21	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(40 mol%)	THF	-10	10	70
22	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	THF:tBuOH(10:1)	-10	10	23
23	LiOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	THF	-10	10	0
24	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	THF:tBuOH(1:1)	-10	10	17
25	NaOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	THF	-10	10	0
26	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	triethylamine	-10	10	0
27	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	acetonitrile	-10	10	0
28	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	anisole	-10	10	0
29	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	dioxane	-10	10	0
30	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	DCM	-10	10	0
31	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	ether	-10	10	0
32	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	DMSO	rt	10	0
33	KOtBu(2)	4,4'-bis(1,1-dimethylethyl)-2,2'-Bipyridine(30 mol%)	DMF	rt	10	0

IV. Mechanism exploration



Using **THF-d^8** as D source solvent to investigate the transfer of hydrogen at the terminal olefin.The results show that the use of D source solvent will reduce the reaction yield and hinder the reaction, and finally product was isolated in 67% without deuterium erosion.

V. Copies of the ^{1}H NMR, ^{13}C NMR,^{19}F NMR



$C_{15}H_{17}NO_2S$

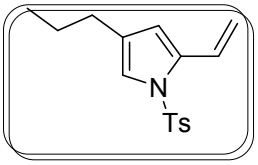
MW：275.10 g • mol^{-1}

Non-white liquid

Isolated Amount:34.1mg **Yield:**62%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.65 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 1.7 Hz, 1H), 6.97 – 6.79 (m, 1H), 6.48 (d, *J* = 1.8 Hz, 1H), 5.47 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.08 (dd, *J* = 11.2, 1.5 Hz, 1H), 2.35 – 2.20 (m, 5H), 1.03 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 145.8, 135.8, 133.6, 130.7, 130.1, 127.0, 125.3, 119.8, 113.3, 31.6, 30.3, 21.52, 2.71, 14.6.

MS (EI) m/z 275 (M+)； **HRMS (SI)** Calcd for $C_{15}H_{17}NO_2S$+H 276.3739，Found 276.3741.



$C_{16}H_{19}NO_2S$

MW：289.39 g • mol^{-1}

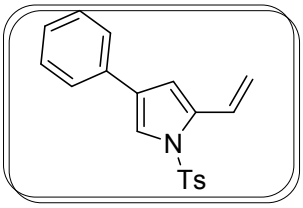
Non-white liquid

Isolated Amount:30.1mg **Yield:**52%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.66 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.31 (d, *J* = 1.5 Hz, 1H), 5.43 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.10 (dd, *J* = 11.2, 1.3 Hz, 1H), 2.38 (s, 3H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.57 – 1.51 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 144.7, 136.2, 134.0, 129.8, 128.2, 126.8, 125.7, 119.92, 114.5, 113.0, 31.5, 30.2, 28.72, 23.1, 21.6, 13.8.

MS (EI) m/z 289 (M+)； **HRMS (SI)** Calcd for $C_{16}H_{19}NO_2S$+H 290.4005，Found 290.4007.



$C_{19}H_{17}NO_2S$

MW：323.41 g • mol^{-1}

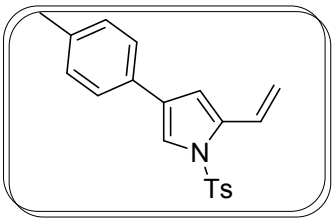
Non-white liquid

Isolated Amount: 49.8 mg **Yield:**77%

^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.91 (d, *J* = 1.7 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 1.3 Hz, 1H), 7.05 (dd, *J* = 17.5, 11.3 Hz, 1H), 5.70 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.28 – 5.24 (m, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 146.1, 135.4, 133.0, 130.8, 129.2, 127.7, 127.6, 127.2, 125.9, 125.1, 119.6, 116.6,110.67, 21.5.

MS (EI) m/z 323 (M+)； **HRMS (SI)** Calcd for $C_{19}H_{17}NO_2S$+H 324.4167，Found 324.4169.



$C_{20}H_{19}NO_2S$

MW：337.44 g • mol^{-1}

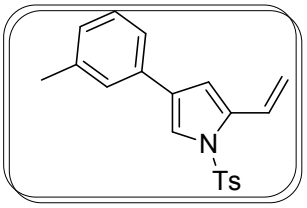
Non-white liquid

Isolated Amount:50.7mg **Yield:**75%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (dd, *J* = 17.5, 11.2 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 5.54 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.19 (dd, *J* = 11.1, 1.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 146.1, 135.4, 134.5, 133.0, 130.8, 129.2, 127.7, 127.6, 127.2, 125.9, 125.1, 119.6, 116.6, 110.67, 21.5.

MS (EI) m/z 337 (M+)； **HRMS (SI)** Calcd for $C_{20}H_{19}NO_2S$+H 338.4433，Found 338.4435.



$C_{20}H_{19}NO_2S$

MW：337.44 g • mol^{-1}

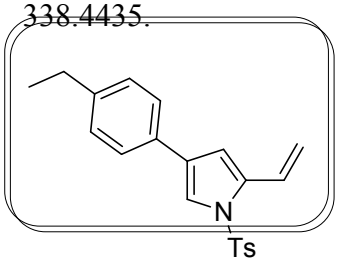
Non-white liquid

Isolated Amount:33.7mg **Yield:**50%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.34 – 7.22 (m, 6H), 7.15 – 7.06 (m, 2H), 6.74 (d, *J* = 1.8 Hz, 1H), 5.55 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.19 (dd, *J* = 11.2, 1.1 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 145.1, 138.4, 135.9, 134.8, 133.1, 130.0, 128.7, 127.9, 127.0, 126.3, 125.5, 122.6, 118.7, 115.5, 110.2, 21.7, 21.5.

MS (EI) m/z 337 (M+)； **HRMS (SI)** Calcd for $C_{20}H_{19}NO_2S$+H 338.4433，Found 338.4435.



$C_{21}H_{21}NO_2S$

MW：351.46 g • mol^{-1}

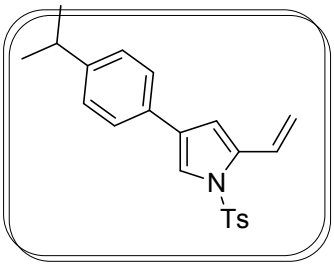
Non-white liquid

Isolated Amount:35.8mg **Yield:**51%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.70 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 1.5 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 17.4, 11.1 Hz, 1H), 6.73 (d, *J* = 1.6 Hz, 1H), 5.57 – 5.51 (m, 1H), 5.20 – 5.16 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 145.1, 143.4, 135.9, 134.8, 130.6, 130.0, 128.3, 127.9, 127.0, 125.5, 118.5, 115.5, 110.2, 31.5, 30.2, 29.8, 28.6, 21.7, 15.7.

MS (EI) m/z 351 (M+)； **HRMS (SI)** Calcd for $C_{21}H_{21}NO_2S$+H 352.4699，Found 352.4701.



$C_{22}H_{23}NO_2S$

MW：365.49 g • mol^{-1}

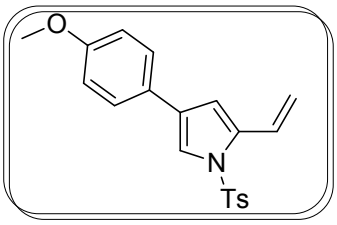
Non-white liquid

Isolated Amount:32.2mg **Yield:**44%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.62 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.12 (m, 4H), 7.04 (dd, *J* = 17.4, 11.1 Hz, 1H), 6.67 – 6.63 (m, 1H), 5.47 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.14 – 5.09 (m, 1H), 2.83 (p, *J* = 6.9 Hz, 1H), 2.30 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 148.0, 145.0, 135.9, 130.8, 129.9, 127.9, 126.9, 126.9, 125.5, 125.5, 118.5, 115.5, 110.2, 33.9, 24.0, 21.6.

MS (EI) m/z 365 (M+)； **HRMS (SI)** Calcd for $C_{22}H_{23}NO_2S$+H 366.4965，Found 366.4966.



$C_{20}H_{19}NO_3S$

MW：353.43 g • mol^{-1}

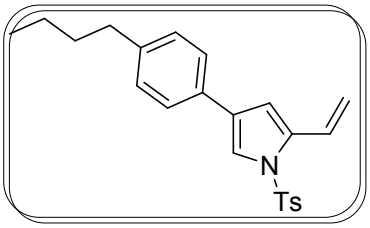
Non-white liquid

Isolated Amount:48.8mg **Yield:**69%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.11 (dd, *J* = 17.5, 11.2 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 1.4 Hz, 1H), 5.54 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.19 (dd, *J* = 11.1, 1.2 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 158.9, 145.0, 135.9, 134.7, 129.9, 127.6, 126.9, 126.7, 125.9, 125.5, 117.9, 115.4, 114.2, 110.1, 55.4, 21.7.

MS (EI) m/z 353 (M+)； **HRMS (SI)** Calcd for $C_{20}H_{19}NO_3S$+H 354.4427，Found 354.4429.



$C_{23}H_{25}NO_2S$

MW：379.52 g • mol^{-1}

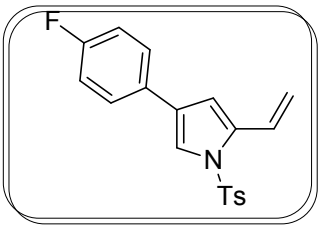
Non-white liquid

Isolated Amount:53.9mg **Yield:**71%

^{1}H NMR (400 MHz, Chloroform-*d*,δ ppm): 7.70 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 12.7, 4.6 Hz, 1H), 6.73 (s, 1H), 5.57 – 5.51 (m, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 1.61 – 1.57 (m, 2H), 1.34 (s, 2H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*,δ ppm): 145.1, 142.0, 136.0, 134.8, 130.6, 130.0, 128.9, 126.96, 125.6, 125.4, 118.5, 115.5, 110.2, 35.4, 33.7, 22.4, 21.6, 14.0.

MS (EI) m/z 379 (M+)； **HRMS (SI)** Calcd for $C_{23}H_{25}NO_2S$+H 380.5230，Found 380.5232.



$C_{19}H_{16}FNO_2S$

MW：341.40 g • mol^{-1}

Non-white liquid

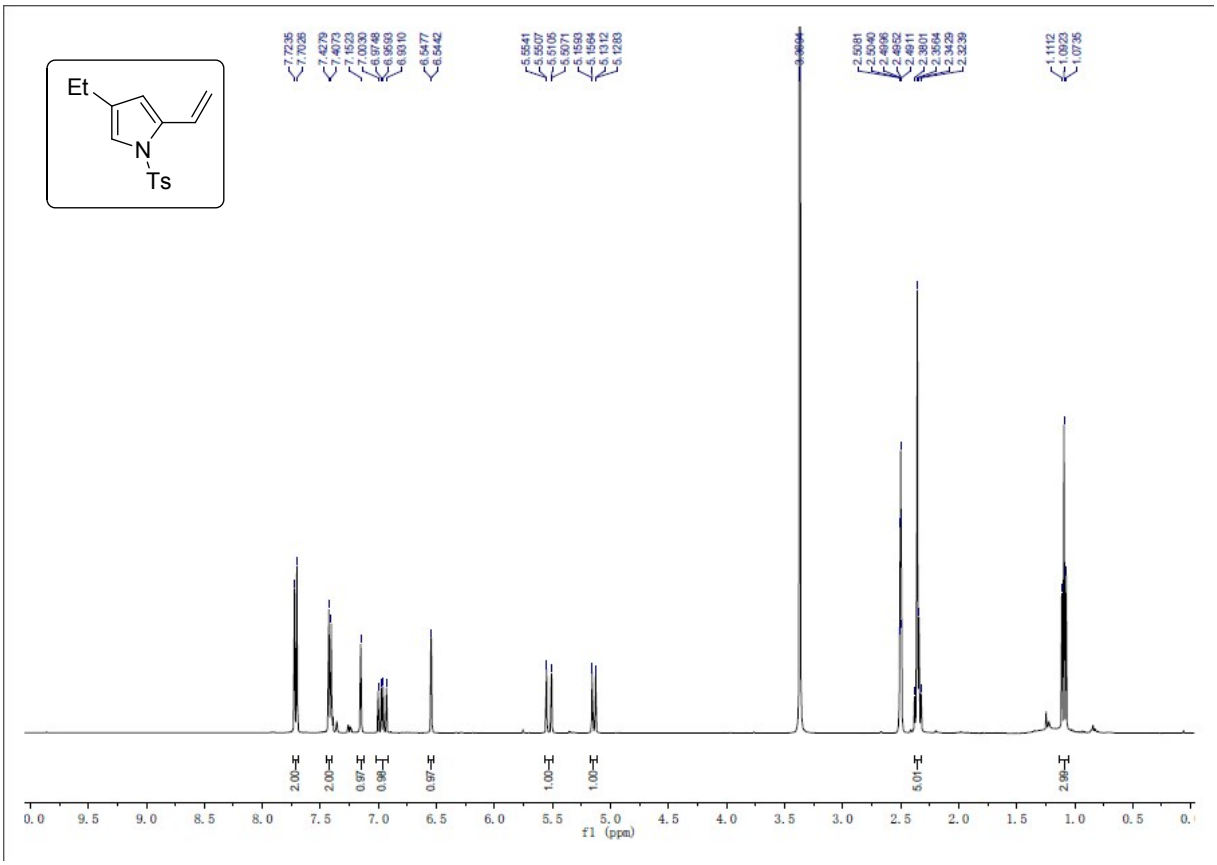
Isolated Amount:53.9mg **Yield:**79%

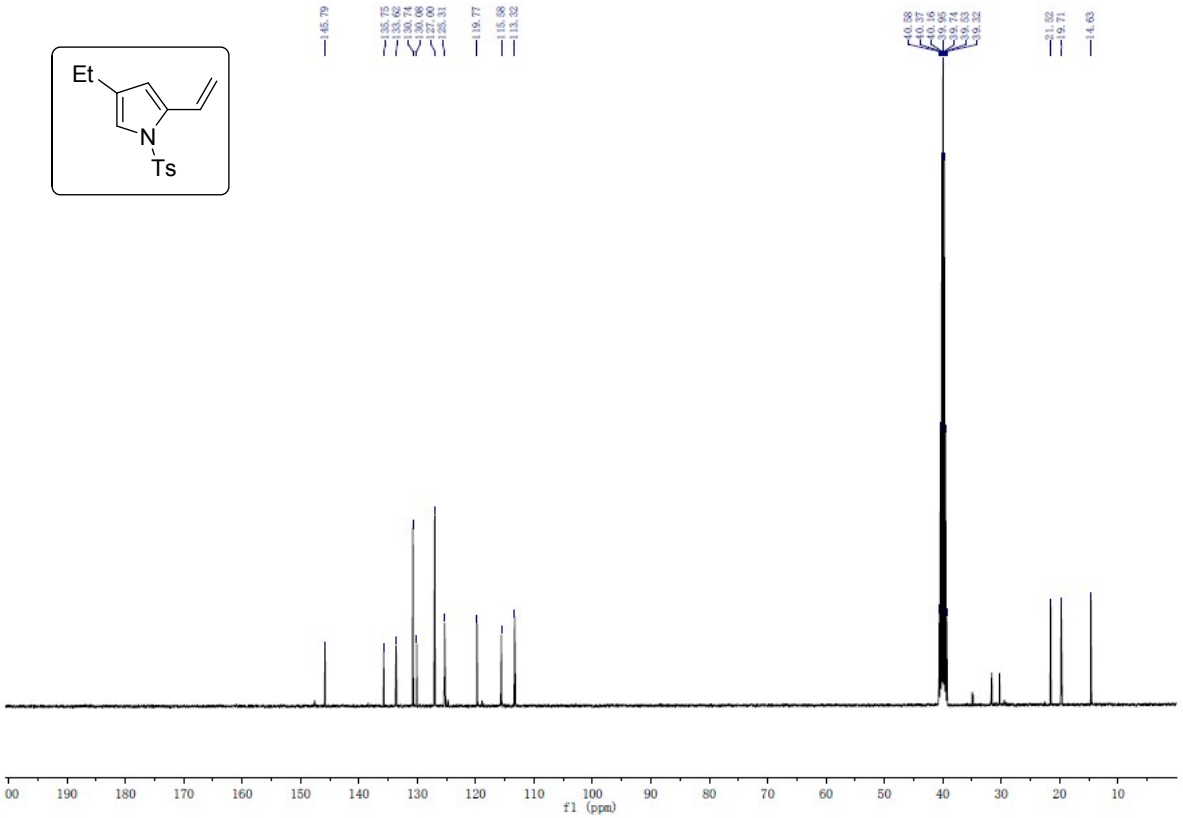
^{1}H NMR (400 MHz, DMSO-d_6,δ ppm): 7.90 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.74 (dd, *J* = 8.9, 5.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 1.6 Hz, 1H), 7.03 (dd, *J* = 17.5, 11.3 Hz, 1H), 5.69 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.26 (dd, *J* = 11.2, 1.2 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6,δ ppm): 163.1, 160.6, 146.1, 135.4, 134.5, 130.9, 129.6 (d, J = 15.0 Hz), 127.9 (d, J = 30.1 Hz), 127.2, 126.7, 125.1, 119.5, 116.6, 116.0 (d, J = 82.7 Hz), 110.7, 21.6.

^{19}F NMR (377 MHz, Chloroform-d,δ ppm): 115.22 (ddd, J = 13.7, 8.7, 5.4 Hz).

MS (EI) m/z 341 (M+)； **HRMS (SI)** Calcd for $C_{19}H_{16}FNO_2S$+H 342.4072，Found 342.4074.




Et
N
Ts
145.79
135.75
133.62
130.74
130.08
127.00
125.31
119.77
115.88
113.32
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39.95
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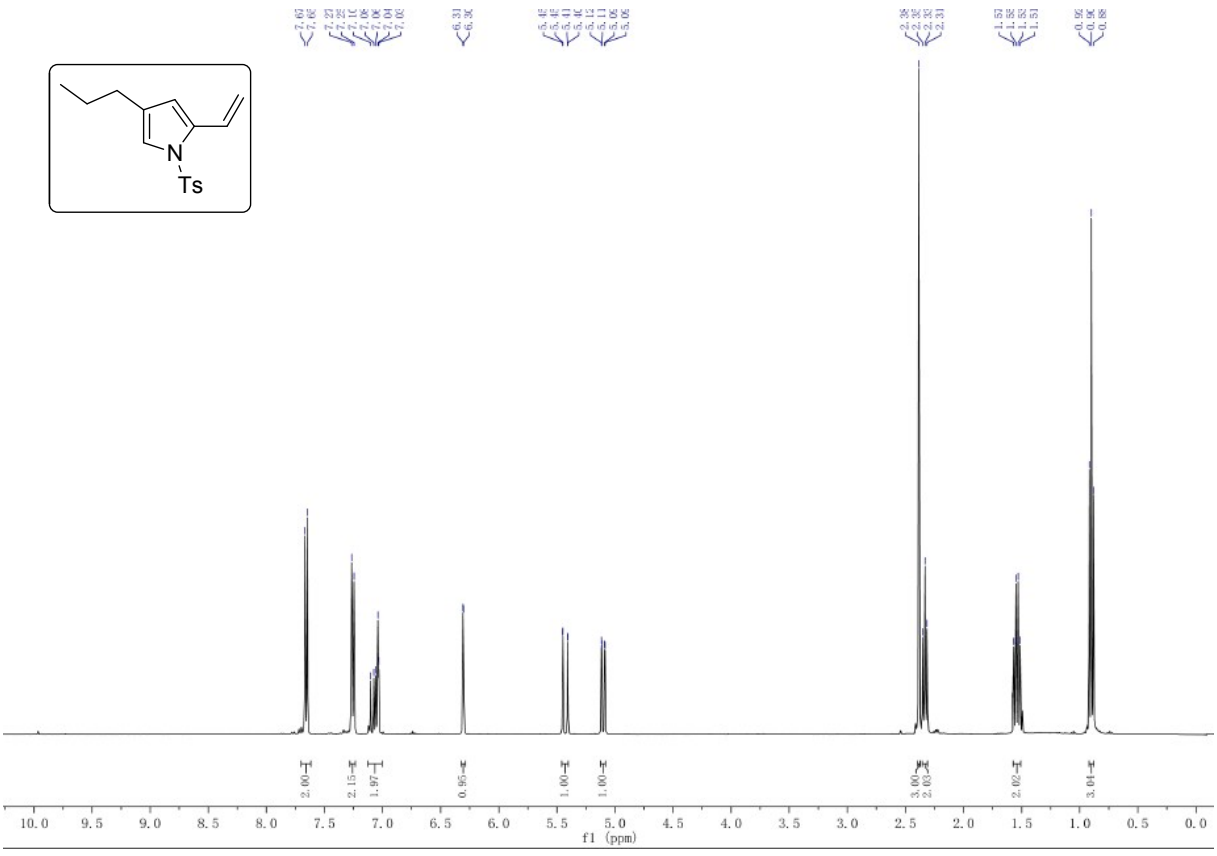
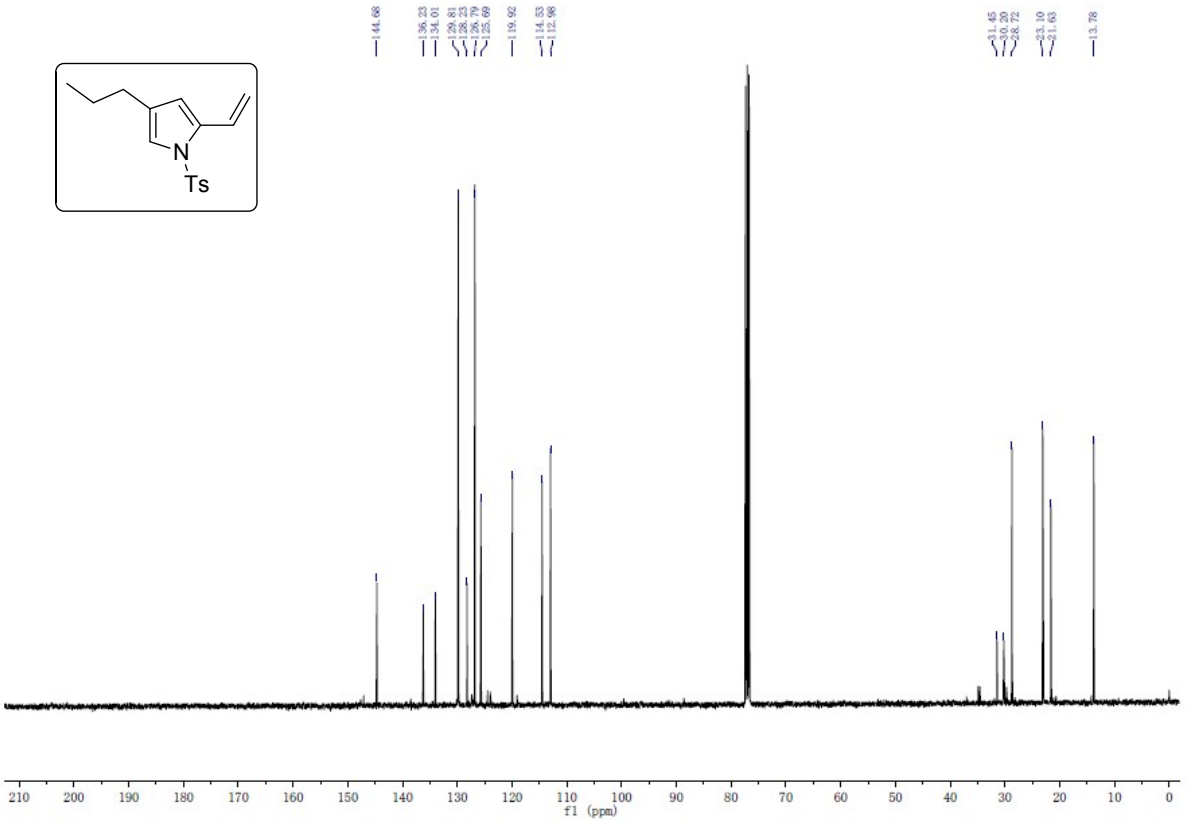
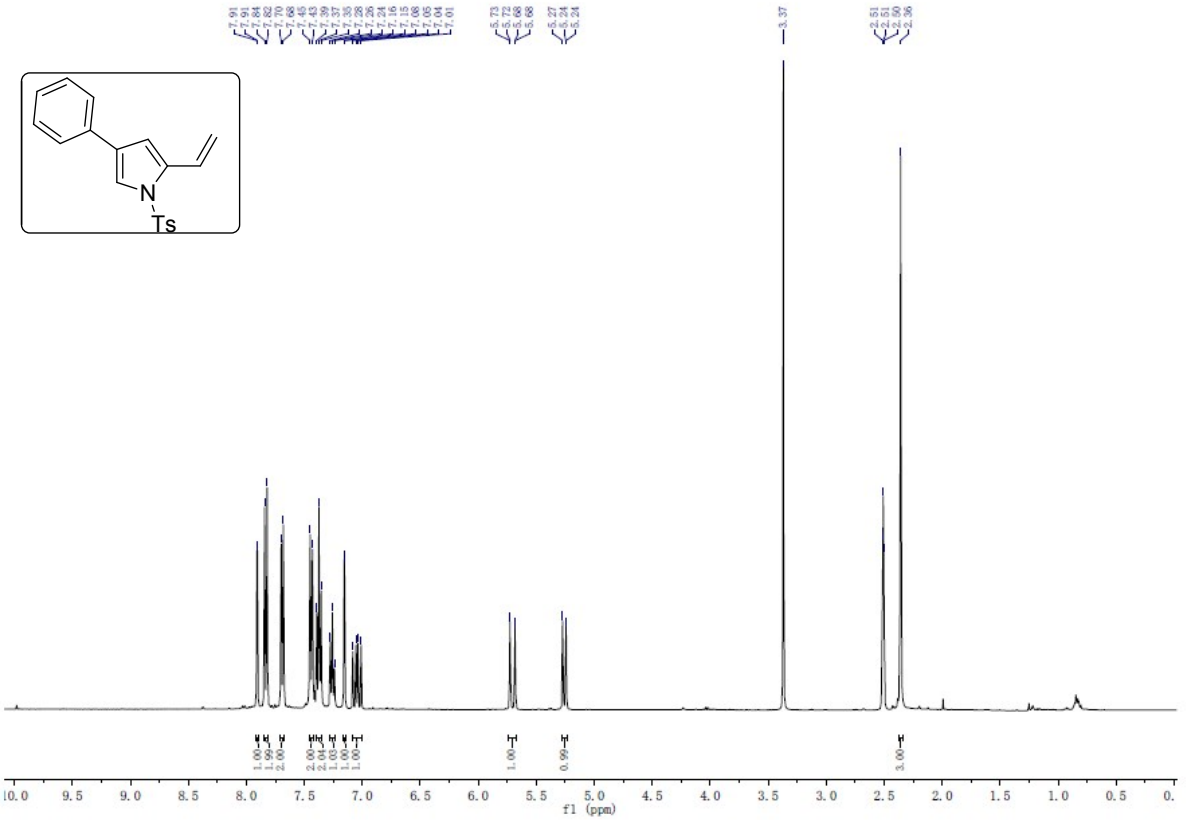
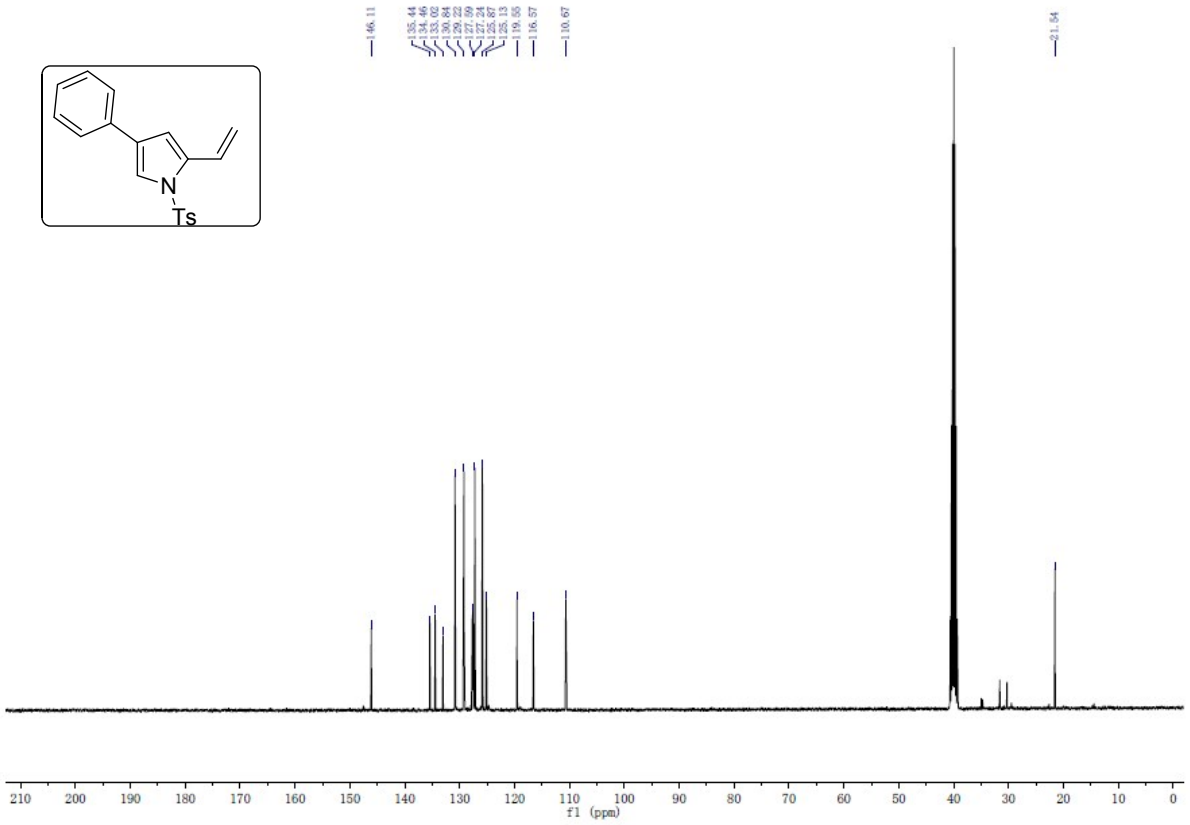
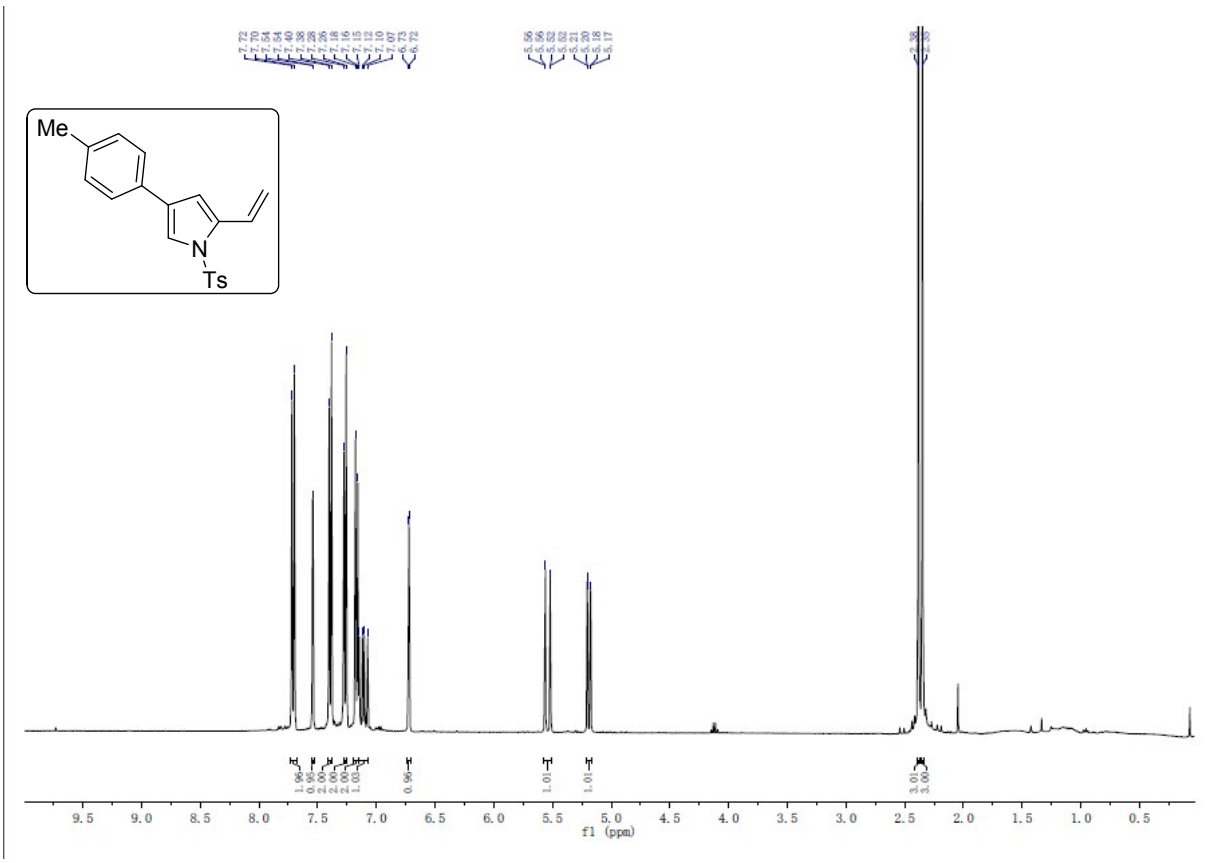
39.53
39.32
21.52
19.71
14.63
f1 (ppm)

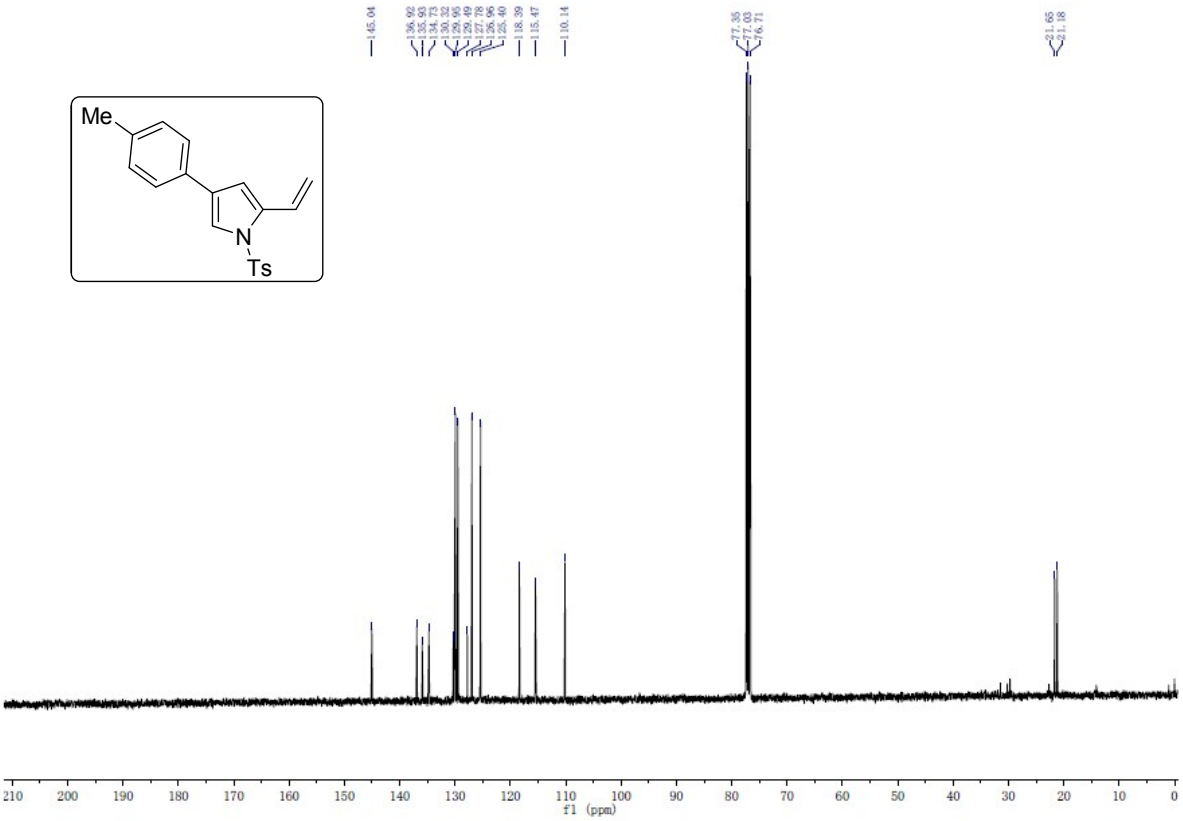

N
Ts
7.69
7.68
7.23
7.22
7.11
7.08
7.06
7.04
7.03
7.02
6.31
6.30
5.46
5.45
5.43
5.41
5.15
5.13
5.06
5.05
2.38
2.33
2.32
2.31
1.53
1.52
1.51
0.92
0.91
0.88
2.60
2.15
1.97
0.95
1.00
1.00
3.00
2.03
2.02
3.04
f1 (ppm)

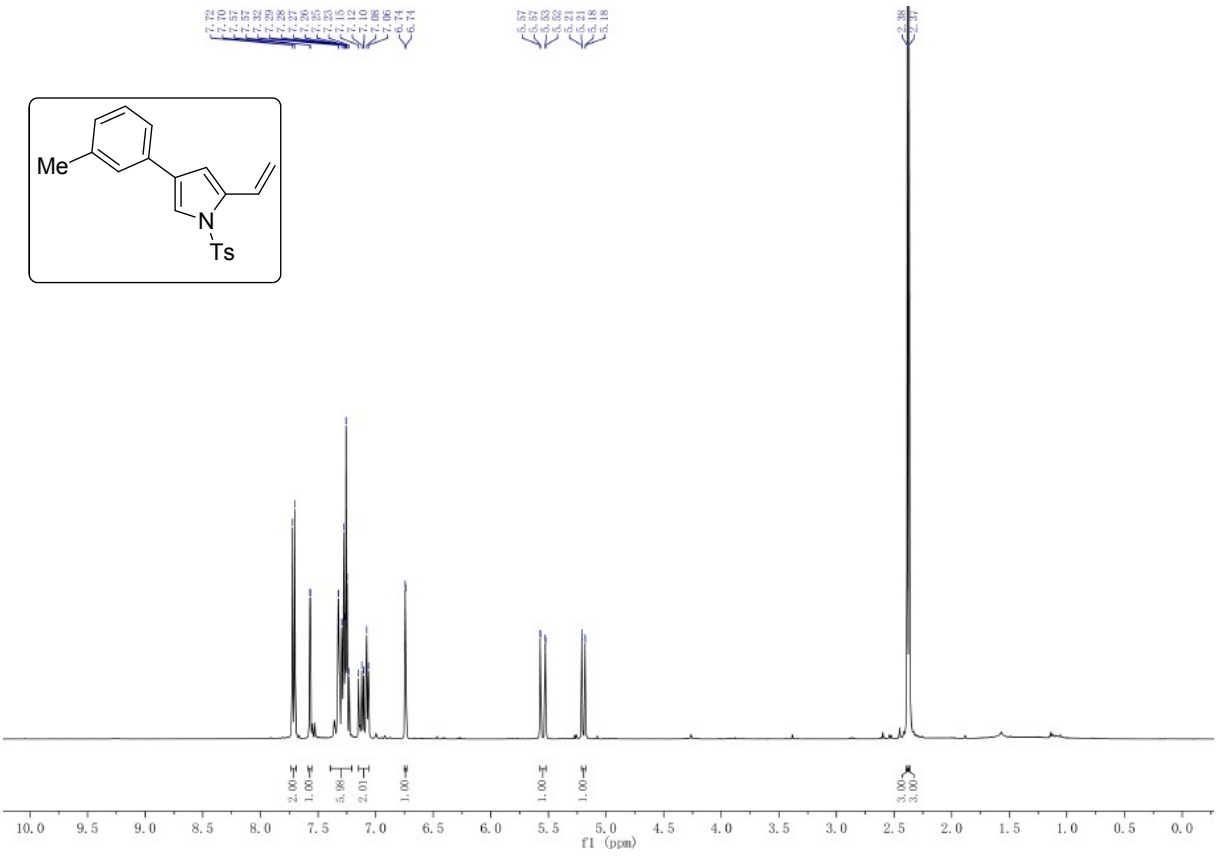

144.68
136.23
134.01
129.81
128.23
126.79
125.69
119.92
114.53
112.96
31.45
30.20
28.72
23.10
21.63
13.78
N
Ts
f1 (ppm)

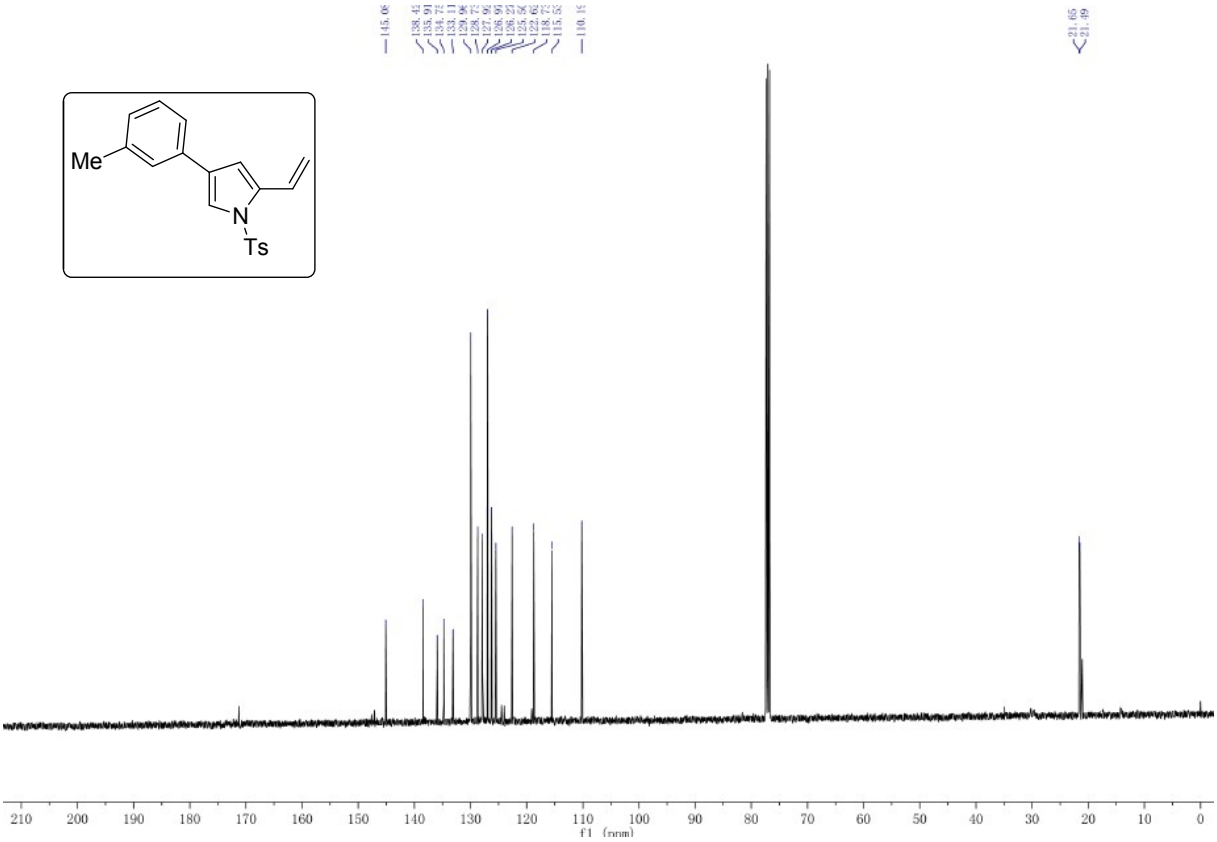

7.91
7.91
7.84
7.82
7.70
7.68
7.45
7.43
7.39
7.37
7.35
7.28
7.26
7.24
7.16
7.15
7.08
7.05
7.04
7.01
5.73
5.72
5.68
5.68
5.27
5.24
5.24
3.37
2.51
2.51
2.50
2.36
1.00
1.99
2.00
2.00
2.04
1.03
1.00
1.00
1.00
0.99
3.00
N
Ts
f1 (ppm)

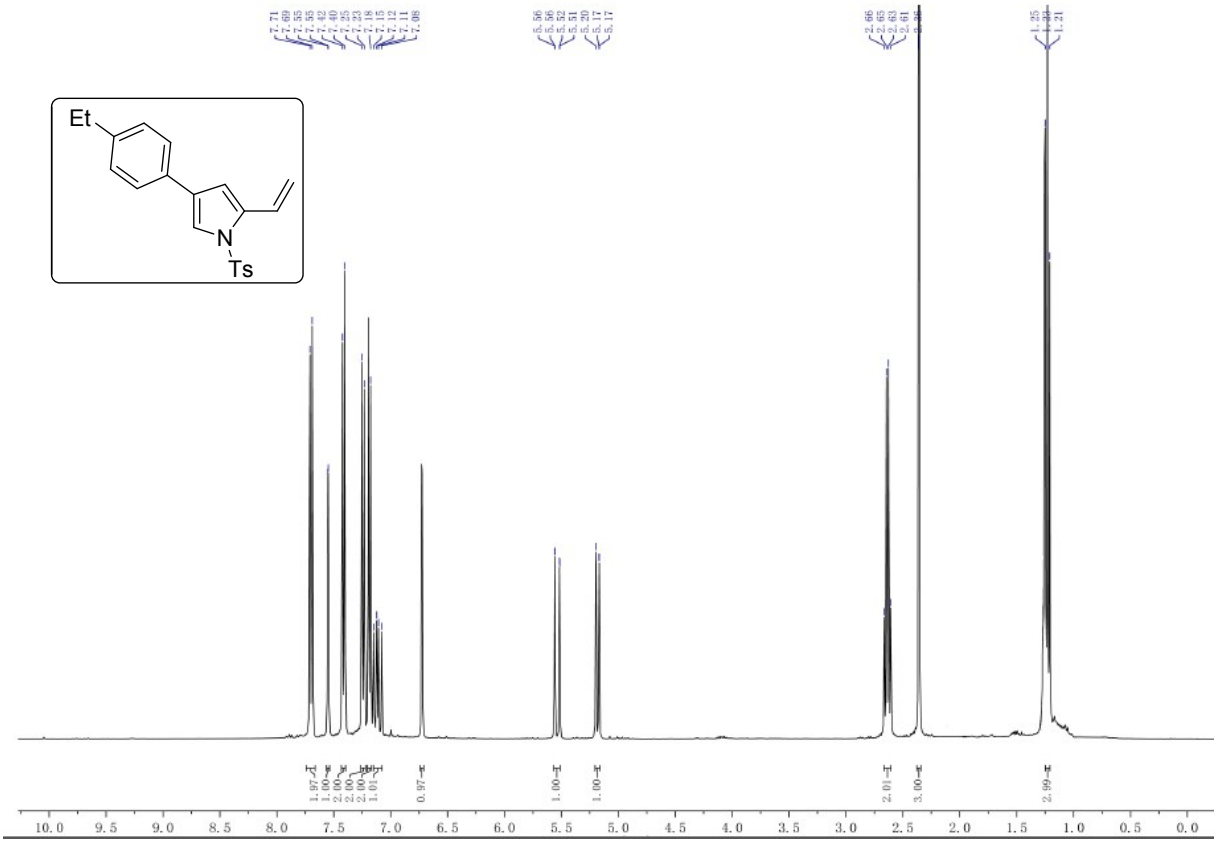

N
Ts
146.11
135.44
134.46
133.02
130.64
129.22
127.99
127.24
125.87
125.13
119.55
116.57
110.67
21.54
f1 (ppm)

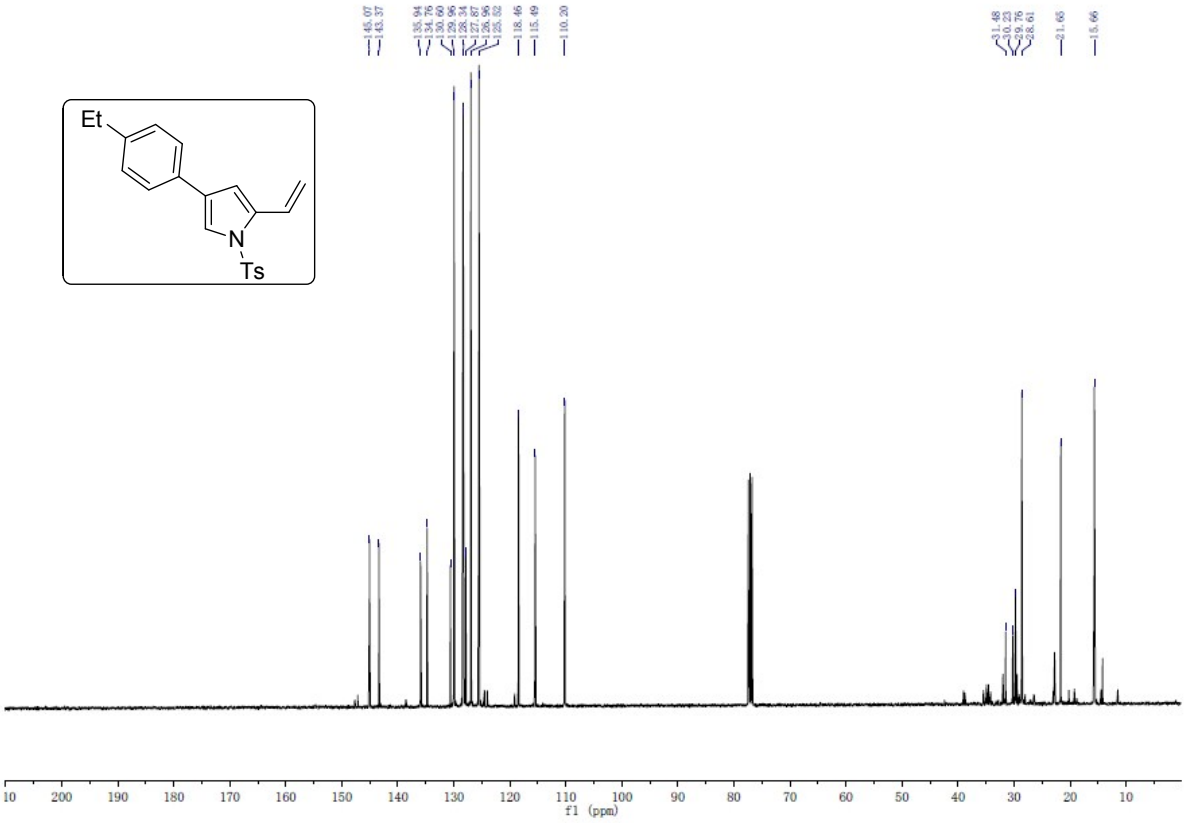

Me
N
Ts
f1 (ppm)

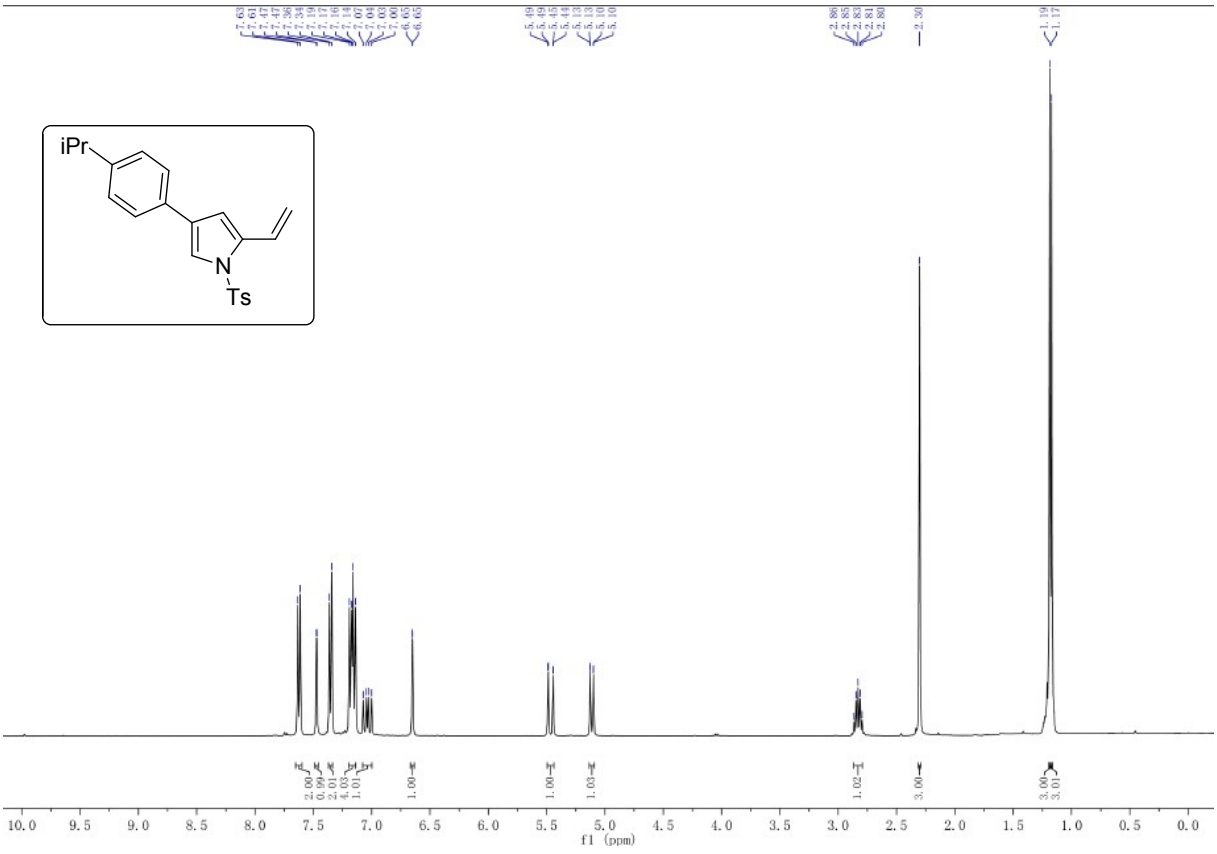

Me
N
Ts
145.04
136.92
135.93
134.73
130.32
129.95
129.49
127.78
125.96
125.40
118.39
115.47
110.14
77.35
77.03
76.71
21.65
21.18
f1 (ppm)

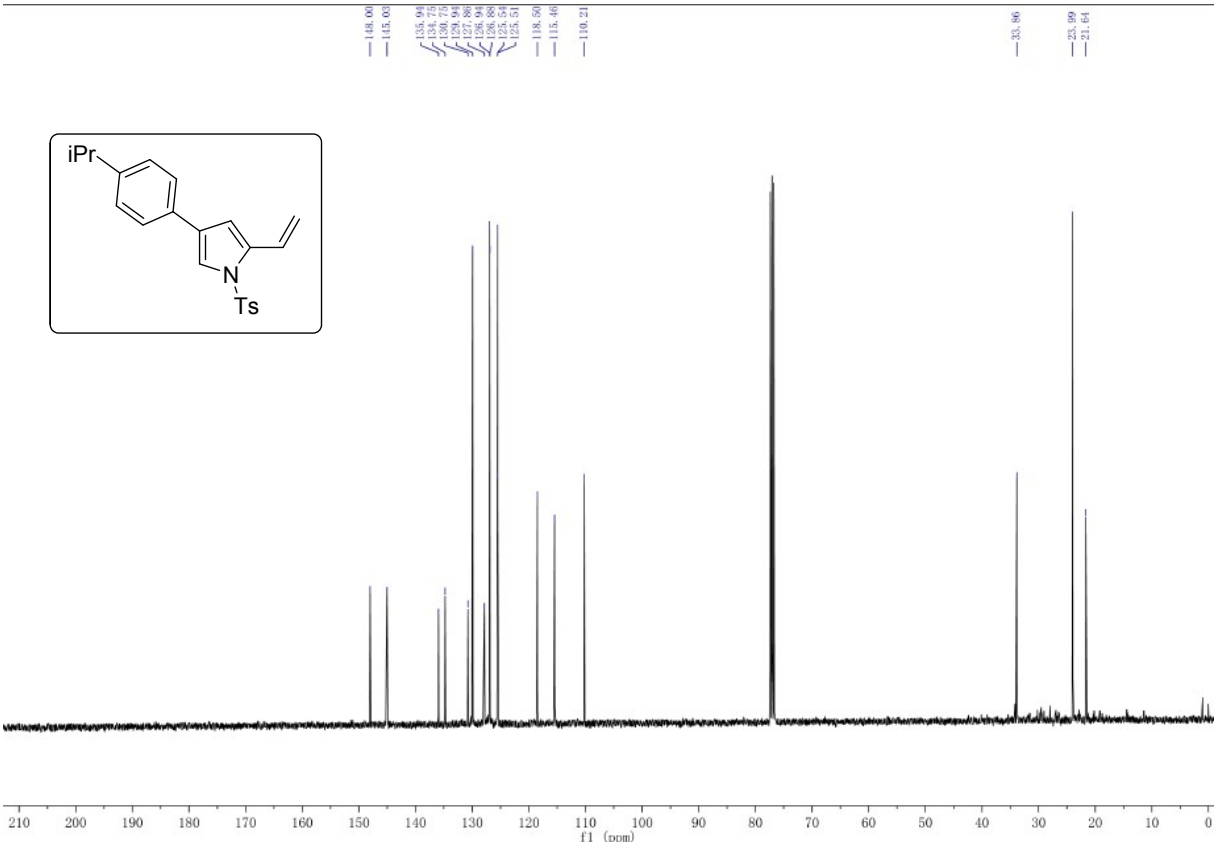

Me
N
Ts
7.72
7.70
7.57
7.57
7.32
7.29
7.28
7.27
7.26
7.25
7.23
7.15
7.12
7.10
7.08
7.06
6.74
6.74
5.57
5.57
5.53
5.52
5.21
5.21
5.18
5.18
2.38
2.37
2.00
1.00
5.08
2.01
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


Me
N
Ts
f1 (ppm)


Et
N
Ts


Et
N
Ts
f1 (ppm)


iPr
N
Ts
f1 (ppm)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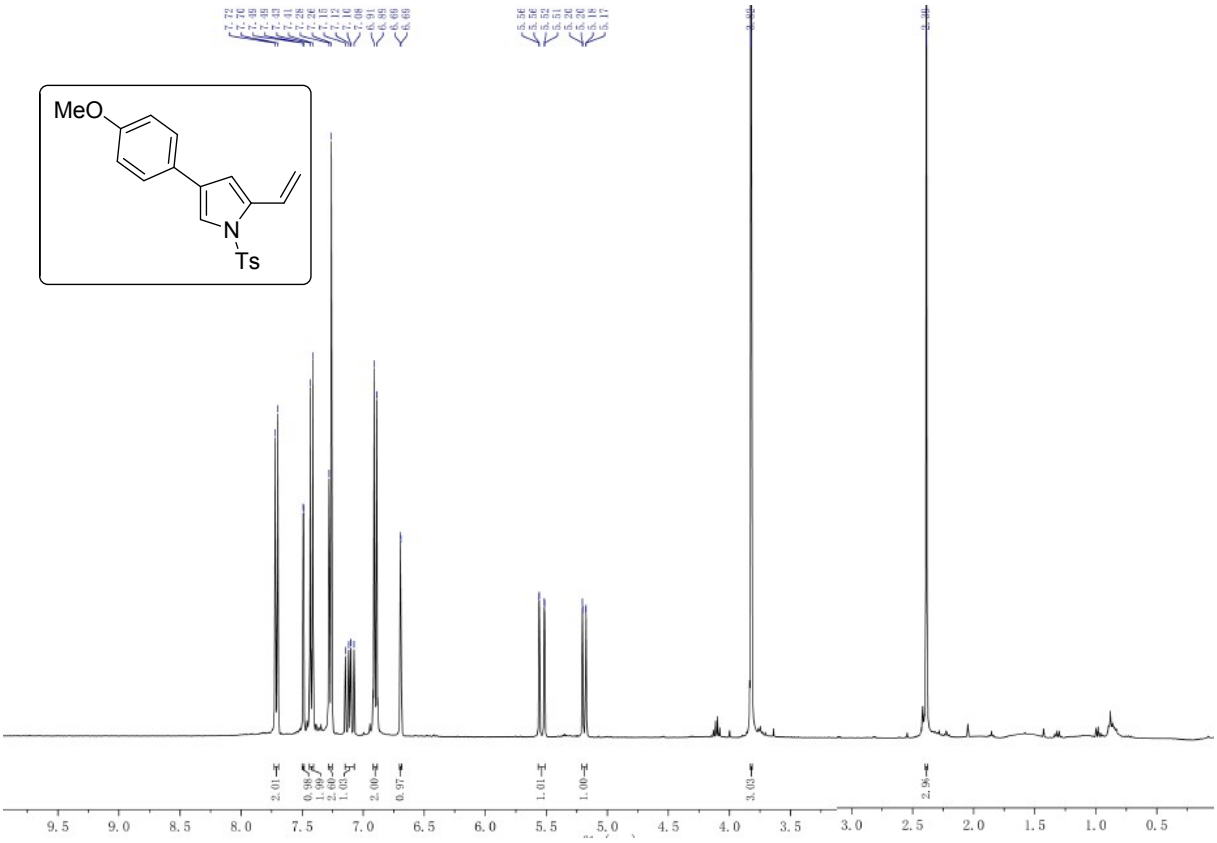
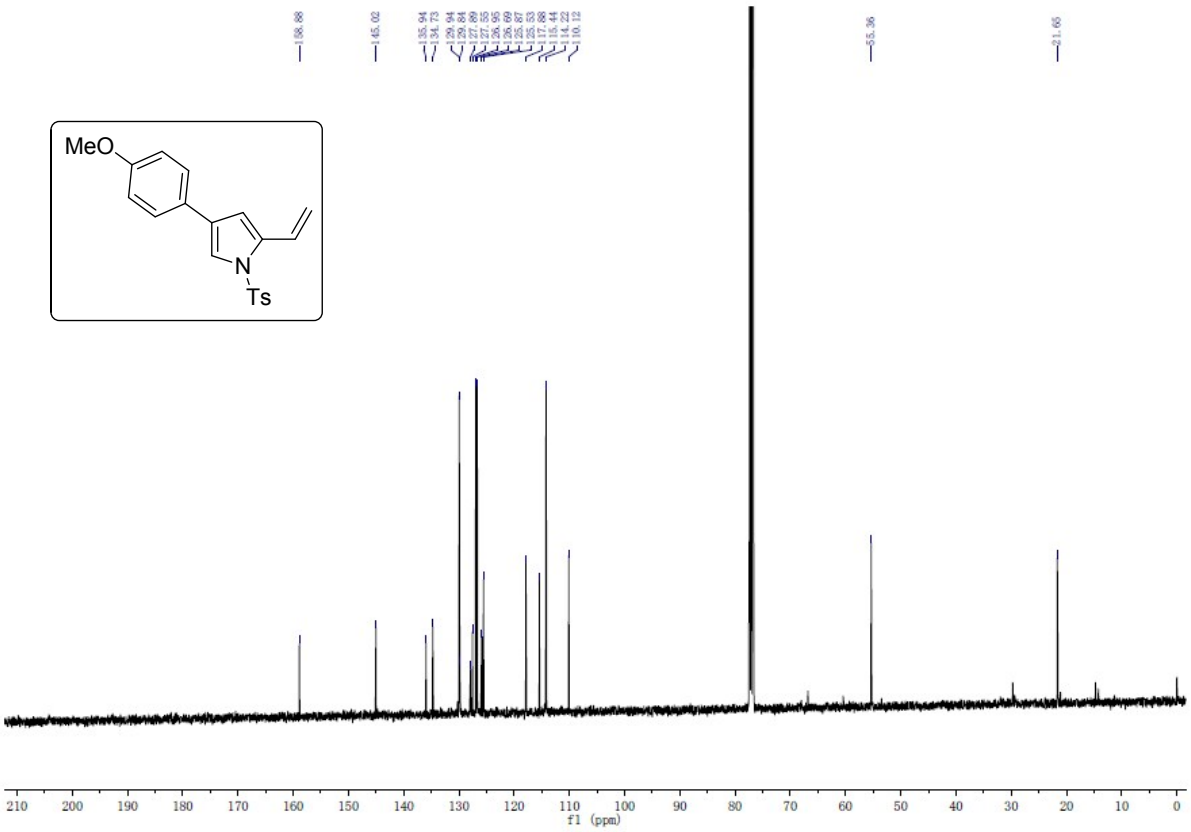
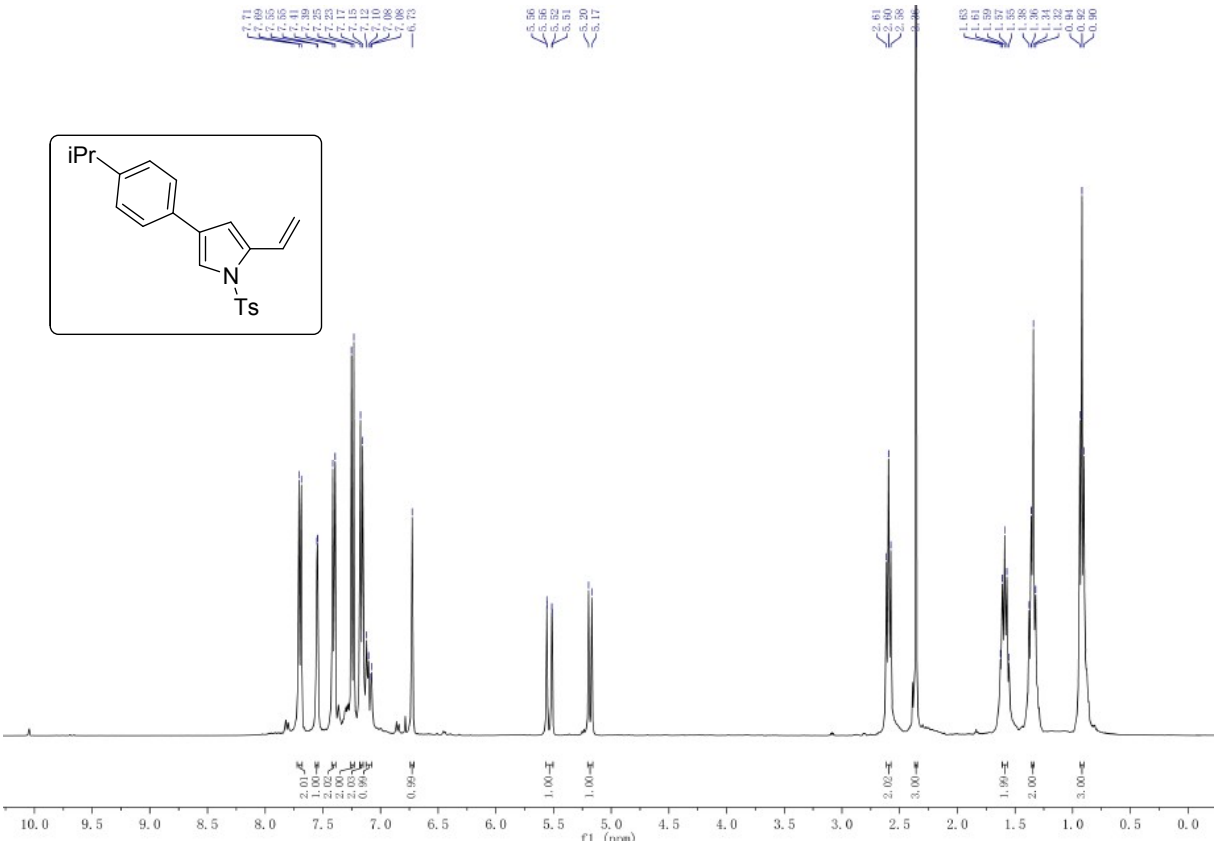
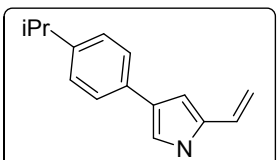
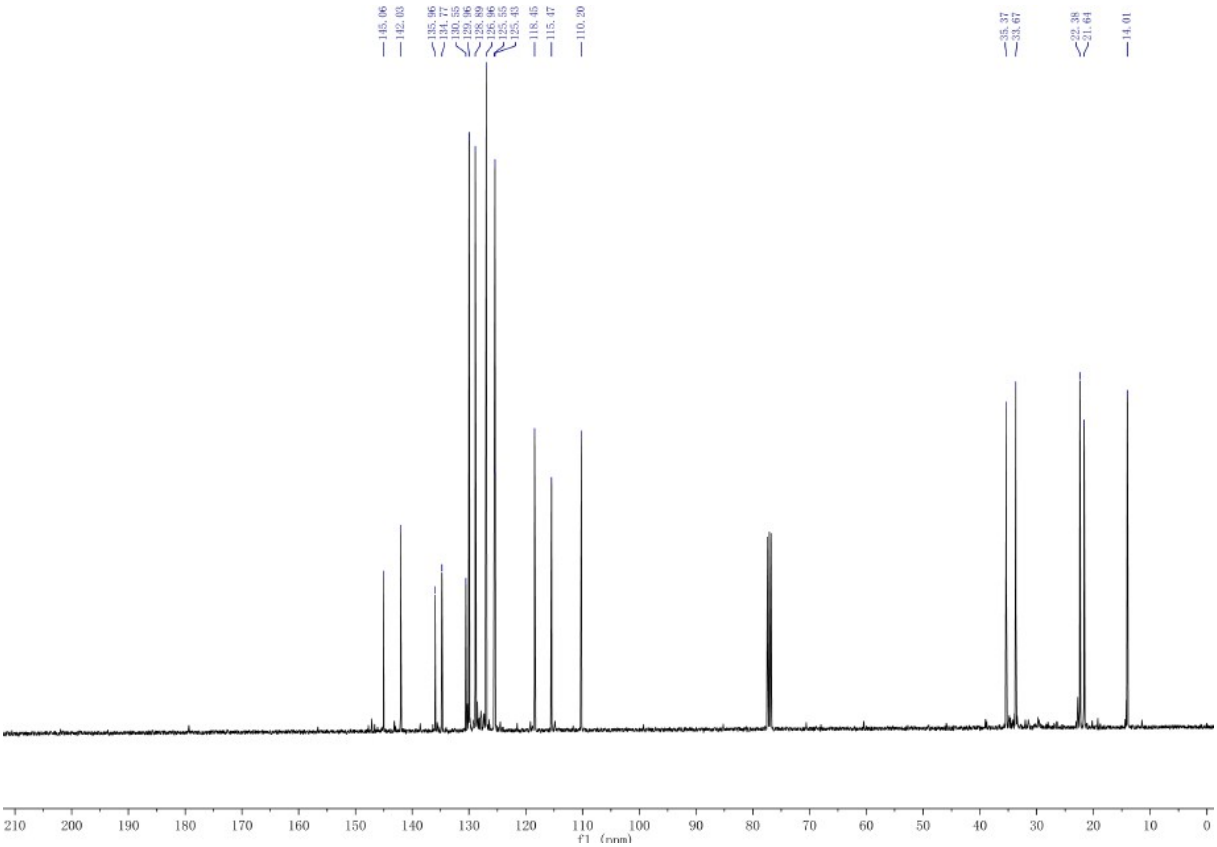
130.75
129.94
127.86
126.94
126.88
125.54
125.51
118.50
115.46
110.21
33.86
23.99
21.64
iPr
N
Ts
f1 (ppm)


MeO
N
Ts


MeO
N
Ts
f1 (ppm)


iPr
N
Ts
f1 (ppm)


iPr
N


145.06
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134.77
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129.96
128.89
126.96
125.55
125.43
118.45
115.47
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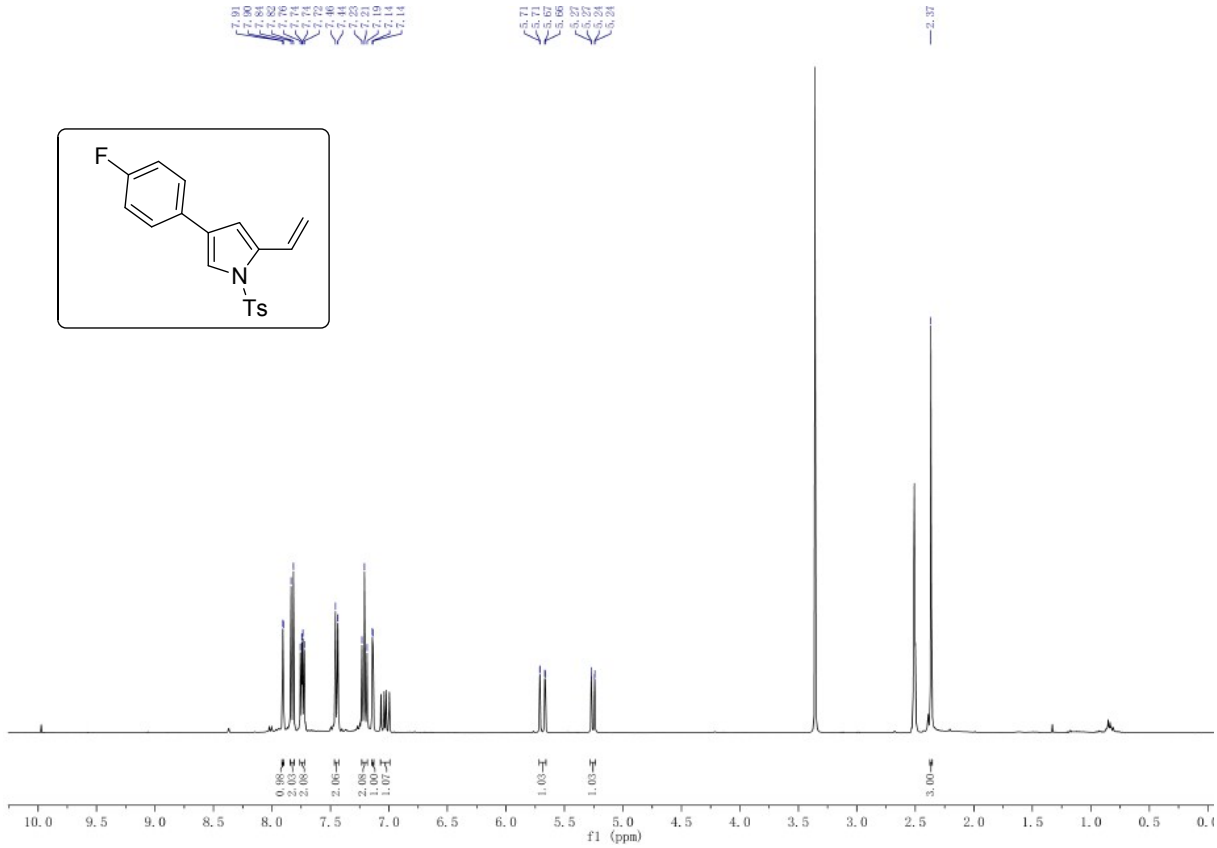
35.37
33.67
22.38
21.64
14.01
f1 (ppm)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7.44
7.23
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7.14
7.14
5.71
5.71
5.67
5.66
5.27
5.27
5.24
5.24
2.37
F
N
Ts
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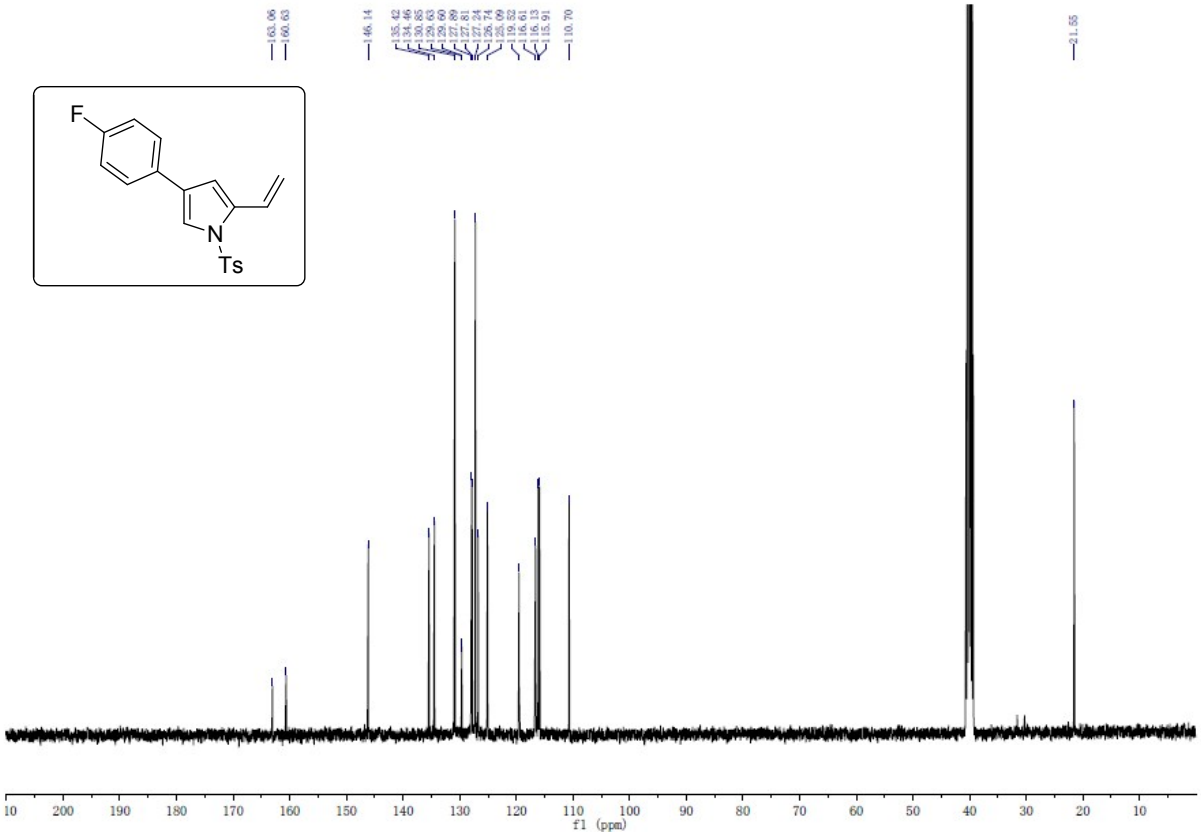
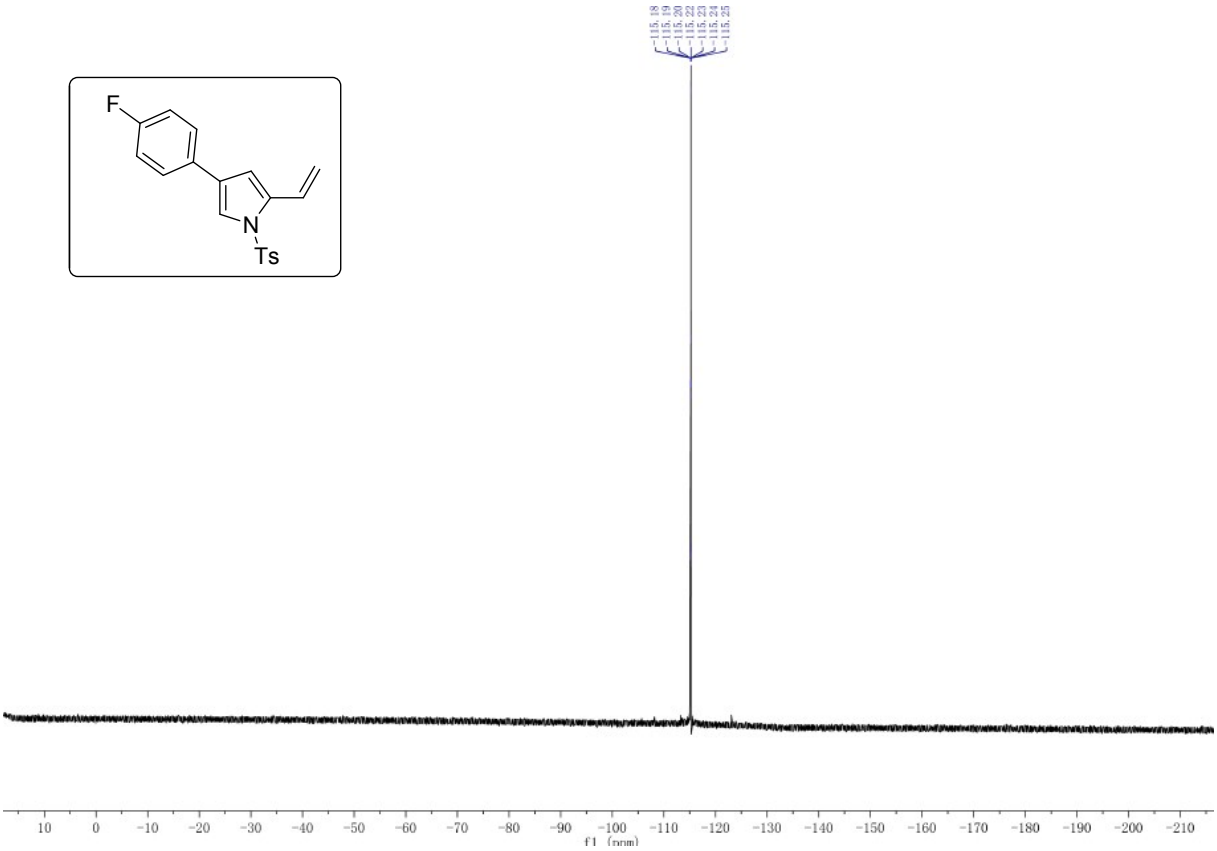
2.03
2.06
2.08
1.00
1.07
1.03
1.03
3.00
f1 (ppm)


F
N
Ts
f1 (ppm)


F
N
Ts
f1 (ppm)