

Supporting Information

Metal-Free Synthesis of (*E*)-Monofluoroenamine from 1-Sulfonyl-1,2,3-Triazole and Et₂O·BF₃ via Stereospecific Fluorination of α-Diazoimine

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1. General comments

Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF254 pre-coated plates. Flash column chromatography was performed using 200 - 300 Mesh Silica Gel. Proton nuclear magnetic resonance (^1H -NMR) spectra were recorded using Bruker Avance IIDMX 400MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or CDCl_3 (7.26 ppm). Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectra were recorded using a Bruker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of CDCl_3 (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University and a Waters TOFMS GCT Premier instrument for HRMS. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion.

2. Detailed optimization of reaction conditions

Table S1 Optimization of Reaction Conditions.^a

CN1C=NC(=C1c2ccccc2)S(=O)(=O)C + CCOC(F)(F)F $\xrightarrow[\text{solvent, temp 40-50 min}]{\text{additive}}$ CN1C=NC(=C1c2ccccc2)C=O

1a, 1.0 equiv x equiv **8a**

entry	x	Additive (equiv)	solvent	temp (°C)	yield (%) ^b
1	1.0	--	DCE	rt	44
2	1.0	--	DCE	reflux	54
3	0.5	--	DCE	reflux	52
4	1.5	--	DCE	reflux	59
5	2.0	--	DCE	reflux	55
6	1.5	--	CHCl ₃	reflux	36
7	1.5	--	DCM	reflux	47
8	1.5	--	toluene	90	20
9	1.5	--	dioxane	90	0
10	1.5	--	TCE	90	46
11	1.5	H ₂ O (1.0)	DCE	reflux	28
12	1.5	TsOH (1.0)	DCE	reflux	0
13	1.5	NH ₄ Cl (1.0)	DCE	reflux	49
14 ^d	1.5	--	DCE	reflux	68
15 ^{d,e}	1.5	AcOH (1.0)	DCE	reflux	51
16 ^{d,e}	1.5	TFA (1.0)	DCE	reflux	68
17 ^{d,e}	1.5	TsOH (1.0)	DCE	reflux	60
18 ^{d,e}	1.5	TfOH (1.0)	DCE	reflux	0
19 ^d	1.5	PhB(OH) ₂ (0.5)	DCE	reflux	71
20 ^d	1.5	HBF ₄ (1.0)	DCE	reflux	20
21 ^d	1.5	pyridine·HF (1.0)	DCE	reflux	0
22 ^d	1.5	TsONa (1.0)	DCE	reflux	0
23 ^d	1.5	Ph ₃ P (1.0)	DCE	reflux	20
24 ^d	1.5	Ph ₂ S (1.0)	DCE	reflux	45
25 ^d	1.5	TBAF·3H ₂ O (1.0)	DCE	reflux	51
26 ^d	1.5	TBAF·3H ₂ O (0.3)	DCE	reflux	70
27 ^d	1.5	TBAF·3H ₂ O (0.2)	DCE	reflux	80(71 ^c)
28 ^d	1.5	TBAF·3H ₂ O (0.1)	DCE	reflux	75
29	1.5	TBAF·3H ₂ O (0.2)	DCE	reflux	78
30 ^f	1.5	TBAF·3H ₂ O (0.2)	DCE	reflux	--(70 ^c)

^a General reaction conditions: **1a** (44.6 mg, 0.2 mmol), Et₂O·BF₃, additive, solvent (2.0-2.5 mL), N₂ atmosphere. ^b Determined by ¹H NMR with 1,3,5-trimethoxylbenzene as the internal standard. ^c Isolated yield. ^d 4 Å molecular sieve was added. ^e The additive was added after disappearance of **1a**. ^f The reaction was carried out in 1.0 mmol scale. Ms = methylsulfonyl, Ts = tosyl, AcO = acetate, TFA = trifluoroacetic acid, TfOH = triflic acid, TBAF = tetrabutylammonium fluoride, DCE = 1,2-dichloroethane, DCM = dichloromethane, TCE = 1,1,2-trichloroethane.

Detailed optimization of reaction conditions was displayed above in Table S1. Elevating the temperature from rt to reflux promoted the yield of **8a** to 54% in the presence of 1.0 equiv Et₂O·BF₃ in DCE (entries 1-2); dosage of Et₂O·BF₃ influenced the yield of the product slightly (entries 3-5) and 1.5 equiv should be the best (59%, entry 4). DCE was proved to be the most efficient solvent (entries 6-10). Several hydrogen sources were added to the reaction to

promote the formation of the desired product, however, giving no positive results (entries 11-13). Interestingly, 4 Å molecular sieves could improve the yield to 68% (entry 14). Accordingly, many other additives were tested along with the addition of 4 Å molecular sieves; for instance, most of protonic acids tested in this work displayed negative effect (entries 15-18) except for PhB(OH)₂ which led to the formation of **8a** in a slightly increased yield (71%, entry 19); however, no further improvement was achieved by using other boronic acids. HBF₄ and pyridine·HF were introduced to the reactions respectively attempting to provide both fluorine and hydrogen, but very poor yields were obtained (entries 20-21). According to Sander and co-workers, migration of F from boron to diazo-linked carbon was reversible (Costa, P.; Mieres-Perez, J.; Ozkan, N.; Sander, W. *Angew. Chem., Int. Ed.* **2017**, *56*, 1760.), and in hence, Lewis bases were utilized in the purpose of coordinating with the newly formed -BF₂ group to stop F migrating back to boron (entries 22-28). Fortunately, 0.2 equiv of TBAF·3H₂O could increase the yield of the desired product to 80% (71% isolated yield, entry 27). Surprisingly, in the presence of TBAF·3H₂O, 4 Å molecular sieves was not necessary (78%, entry 29) and furthermore, when the reaction was carried in a larger scale (1.0 mmol), the yield of **8a** was also reserved (70% isolated yield, entry 30). Eventually, conditions of entry 30 were selected as the optimal conditions utilized in further examination of substrate scope.

3 Evaluation of other 1-sulfonyl-1,2,3-triazoles

Several other triazoles were also tested under the standard conditions, and the results were summarized in the following Table S2.

Table S2 Evaluation of other 1-sulfonyl-1,2,3-triazoles.^a

entry	1	R ¹	R ²	8	yield (%) ^b	note
1	1z	Ph	<i>p</i> -MeOC ₆ H ₄	8z	0	decomposed
2	1aa	<i>p</i> -MeO-C ₆ H ₄	Me	8aa	0	decomposed
3	1ab	<i>p</i> -O ₂ N-C ₆ H ₄	Me	8ab	0	decomposed
4	1ac	<i>p</i> -F ₃ C-C ₆ H ₄	Me	8ac	trace	decomposed
5	1ad	<i>o</i> -NC-C ₆ H ₄	Me	8ad	8	
6 ^c	1ae	<i>n</i> Bu	<i>p</i> -MeC ₆ H ₄	8ae	0	decomposed

^a The reactions were carried out under standard conditions in 1.0 mmol scale. ^b Isolated yield. ^c The reaction time was 4 h.

Alkoxy group was not compatible at all in the reaction. When **1z** and **1aa** was treated under standard conditions, no desired products were monitored or isolated and the starting materials were decomposed very fast (entries 1-2).

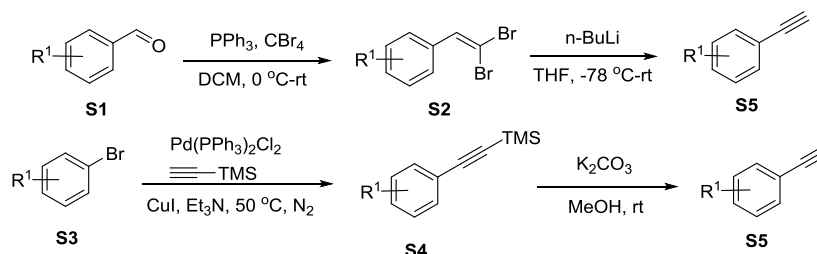
For strong electron-withdrawing groups, a complicated mixture was obtained when *p*-NO₂ substituted **1ab**

was used (entry 3). Trace amount of *p*-CF₃ substituted **8ac** was detected from the ¹H NMR of the reaction mixture (entry 4), and *o*-cyano **8ad** was isolated in only 8% yield after twice flash column chromatograph and then recrystallization (entry 5).

Triazole **1ae** was not reactive under the standard conditions as 4-aryl triazoles, and after 4 h, it was decomposed without any desired **8ae** generated (entry 6).

4. Synthetic procedures and spectra data of 1-sulfonyl-1,2,3-triazoles

4.1 General procedures for preparation of S5



4.1.1 Synthesis of polysubstituted (2,2-dibromovinyl)benzenes (**S2**)^[1]

General Procedure: To a solution of **S1** (10 mmol) and CBr₄ (6.63 g, 20 mmol) in CH₂Cl₂ (10 mL) was added the solution of PPh₃ (10.48 g, 40 mmol) in CH₂Cl₂ (10 mL) via cannula at 0 °C. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S2**.

4.1.2 Synthesis of polysubstituted trimethyl(phenylethynyl)silane (**S4**)^[1]

General Procedure: Under a nitrogen atmosphere, to a triethylamine solution (20 mL) of Pd(PPh₃)₂Cl₂ (213 mg, 0.3 mmol) and CuI (190 mg, 1.0 mmol) was added **S3** (10.0 mmol) and stirred for 10 min, then trimethylsilylacetylene (1.80 mL, 12.0 mmol) was added dropwise over 30 min. The resulting suspension was allowed to be stirred for 4.0 h at 50 °C. After completion of the reaction, the mixture was filtered through a short celite bed and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford compound **S4**.

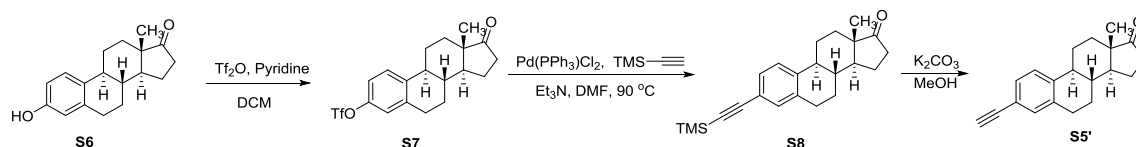
4.1.3 Synthesis of polysubstituted-ethynylbenzene (**S5**)^[1]

General Procedure 1: To a solution of **S2** (10 mmol) in THF (10 mL) *n*-BuLi (20 mmol, 8.3 mL, 2.4 M in hexane) was added dropwise at -78 °C. After stirring for 4.0 h, MeOH (8 mL) was added and the mixture was stirred for an additional 1.0 h, then the reaction was quenched with saturated aqueous NH₄Cl solution at 0 °C, and the aqueous phase

was extracted with Et₂O. The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S5**.

General Procedure 2: To polysubstituted-trimethyl(phenylethynyl)silane **S4** (5 mmol) a solution of K₂CO₃ (0.276 g, 2 mmol) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S4** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S5**.

4.2 Synthesis of **S5'**



4.2.1 Synthesis of **S7** ^[2]

To a solution of **S6** (2.7 g, 10.0 mmol) and pyridine (1.62 mL, 20.0 mmol) in 20 mL dry DCM was added Tf₂O (2.0 mL, 12.0 mmol) dropwise at 0 °C. After that, the mixture was warmed to rt, and stirred overnight. The mixture was then quenched with HCl (10%) and extracted with CH₂Cl₂, washed with saturated NaHCO₃ and saturated brine. The organic layer was dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to give the corresponding product **S7**.

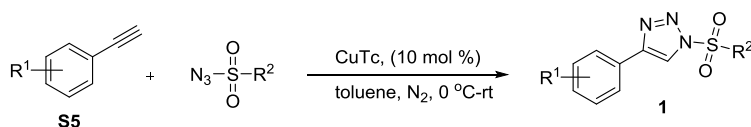
4.2.2 Synthesis of **S8** ^[3]

A mixture of **S7** (1.61 g, 4.0 mmol), ethynyltrimethylsilane (0.79 mL, 5.6 mmol), triethylamine (3.0 mL), and Pd(PPh₃)₂Cl₂ (84 mg, 0.12 mmol) in 15 mL DMF was stirred at 90 °C for 4 h under nitrogen. The reaction mixture was then diluted with water, extracted with 1:1 petroleum ether/ether, washed with water until neutral, and dried (Na₂SO₄), after filtration the filtrate was evaporated. Chromatography of the residue on silica gel provided the corresponding product **S8**.

4.2.3 Synthesis of **S5'**

To **S8** (1.16 g, 3.3 mmol) a solution of K₂CO₃ (0.52 g, 4.95 mmol) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S4** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S5'** (726.5 mg, overall 54% yield from **S6**).

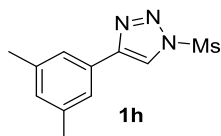
4.3 General procedure for synthesis of 1-sulfonyl-1,2,3-triazoles



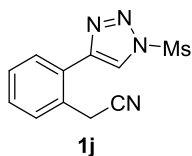
Under a nitrogen atmosphere, dry toluene was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 equiv in regards to alkyne) and the alkyne (1 equiv, 0.33 M). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography with PE/EtOAc (3:1) as eluent to give the corresponding product **1**.

1a-e and **1ae** were reported in ref 4, **1f**, **1k**, **1m** and **1r** were reported in ref 5, **1g** was reported in ref 6, **1i** was reported in ref 7, **1l** and **1z** was reported in ref 8, **1o** and **1s** were reported in ref 9, **1t** was reported in ref 10, and **1x** was reported in ref 11, **1aa-ac** were reported in ref 12.

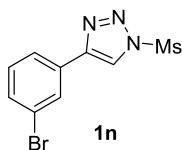
The corresponding alkynes of **1h**, **1v** and **1w** were synthesized through **S4** from **S3**, and the corresponding alkynes of **1j**, **1n**, **1p**, **1q** and **1u** were synthesized through **S2** from **S1**, **1y** was prepared from **S5'**.



4-(3,5-dimethylphenyl)-1-(methylsulfonyl)-1H-1,2,3-triazole (1h): white solid, yield: 80%, m.p.: 89-91 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.49 (s, 2H), 7.06 (s, 1H), 3.58 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 138.7, 131.0, 128.4, 123.9, 118.9, 42.7, 21.3. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_3\text{O}_2\text{S}^+$ 252.0801, found 252.0804.

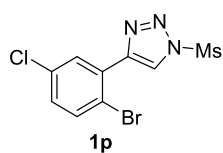


2-(2-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)phenyl)acetonitrile (1j): white solid, yield: 83%, m.p.: 135-137 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.57 – 7.43 (m, 3H), 4.19 (s, 2H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 130.2, 130.1, 129.9, 128.83, 128.76, 127.6, 121.5, 117.8, 42.8, 22.9. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{N}_4\text{O}_2\text{S}^+$ 263.0597, found 263.0602.

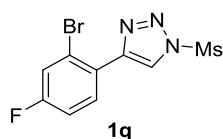


4-(3-bromophenyl)-1-(methylsulfonyl)-1H-1,2,3-triazole (1n): white solid, yield: 68%, m.p.: 102-104 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 8.01 (s, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.54 – 7.50 (m, 1H), 7.32 (t, $J = 7.9$ Hz, 1H),

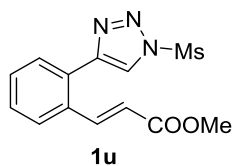
3.60 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 132.2, 130.64, 130.59, 129.1, 124.7, 123.1, 119.6, 42.8. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{BrN}_3\text{O}_2\text{S}^+$ 301.9593, found 301.9609.



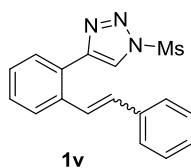
4-(2-bromo-5-chlorophenyl)-1-(methylsulfonyl)-1H-1,2,3-triazole (1p): white solid, yield: 27%, m.p.: 115-117 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.83 (s, 1H), 8.20 – 8.12 (m, 1H), 7.66 – 7.61 (m, 1H), 7.30 – 7.23 (m, 1H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 134.9, 134.1, 130.8, 130.5, 130.3, 122.5, 119.1, 42.8. HRMS (ESI) calcd for $\text{C}_9\text{H}_8\text{BrClN}_3\text{O}_2\text{S}^+$ 335.9204, found 335.9207.



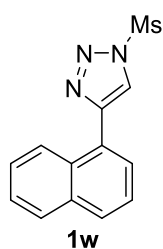
4-(2-bromo-4-fluorophenyl)-1-(methylsulfonyl)-1H-1,2,3-triazole (1q): white solid, yield: 30%, m.p.: 101-103 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.75 (s, 1H), 8.13 (dd, J = 8.8, 6.0 Hz, 1H), 7.46 (dd, J = 8.2, 2.6 Hz, 1H), 7.21 (td, J = 8.8, 8.2, 2.6 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.4 (d, J = 254.3 Hz), 144.3, 132.1 (d, J = 8.7 Hz), 125.9 (d, J = 3.6 Hz), 122.0, 121.7 (d, J = 9.5 Hz), 121.0 (d, J = 24.8 Hz), 115.4 (d, J = 21.3 Hz), 42.8. HRMS (ESI) calcd for $\text{C}_9\text{H}_8\text{BrFN}_3\text{O}_2\text{S}^+$ 319.9499, found 319.9505.



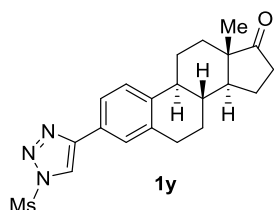
methyl (E)-3-(2-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)phenyl)acrylate (1u): white solid, yield: 67%, m.p.: 114-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 7.98 (d, J = 16.0 Hz, 1H), 7.78 (d, J = 7.1 Hz, 1H), 7.72 (d, J = 7.1 Hz, 1H), 7.55 – 7.45 (m, 2H), 6.48 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 145.6, 142.5, 133.3, 130.2, 130.0, 129.6, 128.6, 127.4, 122.1, 120.9, 51.9, 42.8. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}_3\text{O}_4\text{S}^+$ 308.0700, found 308.0706.



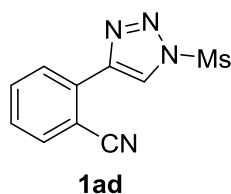
1-(methylsulfonyl)-4-(2-styrylphenyl)-1H-1,2,3-triazole (1v): yellow oil, yield: 60%; ^1H NMR (400 MHz, CDCl_3) δ 8.34 8.20 (1H), 8.12 – 8.10 7.78 – 7.73 (2H), 7.53 – 7.35 (m, 6H), 7.32 – 7.30 (m, 1H), 7.19 – 7.08 6.73 – 6.72 (2H), 3.59 3.53 (3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 137.1, 136.5, 131.9, 129.7, 129.6, 128.8, 128.1, 127.9, 127.2, 126.9, 126.8, 126.5, 121.8, 42.7. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2\text{S}^+$ 326.0958, found 326.0960.



1-(methylsulfonyl)-4-(naphthalen-1-yl)-1H-1,2,3-triazole (1w): white solid, yield: 46%, m.p.: 116-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 8.30 – 8.23 (m, 1H), 8.00 – 7.89 (m, 2H), 7.78 (d, J = 7.0 Hz, 1H), 7.60 – 7.55 (m, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 133.8, 130.9, 130.0, 128.7, 127.9, 127.2, 126.4, 126.0, 125.3, 124.8, 121.9, 42.8. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_2\text{S}^+$ 274.0645, found 274.0651.



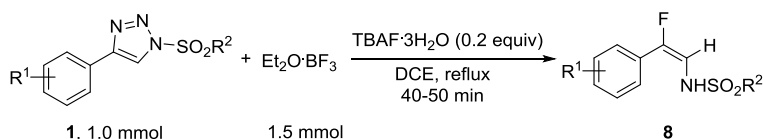
(8R,9S,13S,14S)-13-methyl-3-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1y): yellow solid, yield: 53%, m.p.: 155-157 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.67 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 3.59 (s, 3H), 3.01 (dd, J = 10.1, 4.6 Hz, 2H), 2.62 – 2.43 (m, 2H), 2.42 – 2.26 (m, 1H), 2.24 – 1.91 (m, 4H), 1.73 – 1.39 (m, 6H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 220.8, 147.5, 141.2, 137.4, 126.7, 126.14, 126.06, 123.5, 118.6, 50.5, 48.0, 44.5, 42.7, 38.0, 35.9, 31.6, 29.4, 26.4, 25.7, 21.6, 13.9. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}_3\text{S}^+$ 400.1689, found 400.1698.



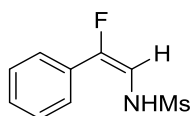
2-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)benzonitrile (1ad): yellow oil, yield: 80%; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.21 (s, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 143.7, 134.9, 134.3, 131.9, 130.1, 129.4, 123.9, 118.6, 109.4, 42.9. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_9\text{N}_4\text{O}_2\text{S}^+$ 249.0441, found 249.0443.

5. Reaction scope

Procedure for the preparation of 8

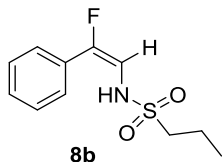


General procedure: Under a nitrogen atmosphere, a solution of $\text{Et}_2\text{O}\cdot\text{BF}_3$ (0.19 mL, 1.5 mmol) in DCE (4.0 mL) was added to a reaction flask charged with $\text{TBAF}\cdot 3\text{H}_2\text{O}$ (50.5 mg, 0.2 mmol) and a stirring bar, and then the solution of 1-sulfonyl-1,2,3-triazoles (**1**, 1.0 mmol) in DCE (4.0 mL) was added. The reaction mixture was stirred at reflux for 40-50 min, then was cooled to room temperature and filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (4:1) as eluent to give the corresponding product **8**.



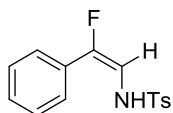
8a

(*E*)-N-(2-fluoro-2-phenylvinyl)methanesulfonamide (8a): yellow oil, 149.0 mg, yield: 70%; ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.33 (m, 5H), 6.59 (d, J = 10.7 Hz, 1H), 6.47 (dd, J = 25.4, 10.7 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.1 (d, J = 240.7 Hz), 130.2 (d, J = 24.8 Hz), 128.72 (d, J = 2.0 Hz), 128.65, 122.8 (d, J = 6.7 Hz), 104.0 (d, J = 13.9 Hz), 41.1. HRMS (ESI) calcd for $\text{C}_9\text{H}_{11}\text{FNO}_2\text{S}^+$ 216.0489, found 216.0497.



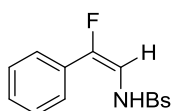
8b

(*E*)-N-(2-fluoro-2-phenylvinyl)propane-1-sulfonamide (8b): yellow oil, 166.2 mg, yield: 68%; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 7.1 Hz, 1H), 7.02 (d, J = 10.2 Hz, 1H), 6.49 (dd, J = 26.3, 10.2 Hz, 1H), 3.19 (t, J = 7.5 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5 (d, J = 240.0 Hz), 130.4 (d, J = 24.7 Hz), 128.7, 128.4, 122.7 (d, J = 6.6 Hz), 104.5 (d, J = 13.6 Hz), 55.5, 17.3, 12.9. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{15}\text{FNO}_2\text{S}^+$ 244.0802, found 244.0809.



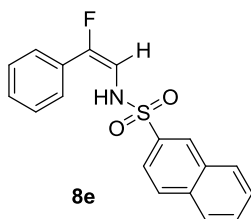
8c

(*E*)-N-(2-fluoro-2-phenylvinyl)-4-methylbenzenesulfonamide (8c): yellow oil, 168.0 mg, yield: 58%; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.3 Hz, 2H), 7.37 – 7.25 (m, 7H), 6.70 (d, J = 9.4 Hz, 1H), 6.45 (dd, J = 25.7, 9.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.1 (d, J = 240.5 Hz), 144.2, 136.7, 130.3 (d, J = 24.8 Hz), 130.0, 128.6 (d, J = 1.8 Hz), 128.5, 126.8, 122.8 (d, J = 6.6 Hz), 104.2 (d, J = 13.9 Hz), 21.6. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{FNO}_2\text{S}^+$ 292.0802, found 292.0791.



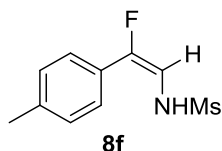
8d

(*E*)-4-bromo-N-(2-fluoro-2-phenylvinyl)benzenesulfonamide (8d): yellow solid, 243.4 mg, yield: 69%, m.p.: 94–96 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 6.81 (d, J = 10.6 Hz, 1H), 6.43 (dd, J = 25.6, 10.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.6 (d, J = 241.7 Hz), 138.6, 132.7, 130.0 (d, J = 24.6 Hz), 128.8, 128.7, 128.4, 128.3, 122.9 (d, J = 6.5 Hz), 103.6 (d, J = 14.0 Hz). HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{BrFNO}_2\text{S}^+$ 355.9751, found 355.9763.

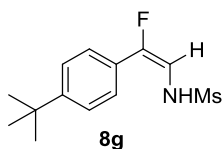


8e

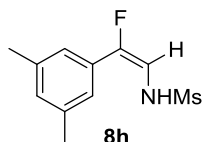
(E)-N-(2-fluoro-2-phenylvinyl)naphthalene-2-sulfonamide (8e): yellow oil, 157.0 mg, yield: 48%; ^1H NMR (400 MHz, CDCl_3) δ 8.51 (s, 1H), 7.98 (d, $J = 8.0$ Hz, 2H), 7.90 (t, $J = 8.0$ Hz, 2H), 7.68 – 7.60 (m, 2H), 7.42 – 7.28 (m, 5H), 6.94 (d, $J = 10.4$ Hz, 1H), 6.55 (dd, $J = 25.7, 10.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.2 (d, $J = 240.7$ Hz), 136.5, 135.0, 132.1, 130.3, 129.8, 129.4, 129.1, 128.6 (d, $J = 1.8$ Hz), 128.5, 128.3 (d, $J = 4.2$ Hz), 128.0, 127.7, 122.8 (d, $J = 6.6$ Hz), 121.8, 104.1 (d, $J = 14.1$ Hz). HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{FNO}_2\text{S}^+$ 328.0802, found 328.0811.



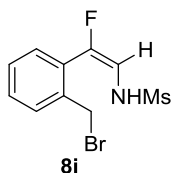
(E)-N-(2-fluoro-2-(p-tolyl)vinyl)methanesulfonamide (8f): yellow oil, 140.1 mg, yield: 62%; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 6.67 (d, $J = 10.4$ Hz, 1H), 6.40 (dd, $J = 25.9, 10.4$ Hz, 1H), 3.11 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.5 (d, $J = 241.9$ Hz), 138.7, 129.4, 127.4 (d, $J = 25.8$ Hz), 122.9 (d, $J = 6.5$ Hz), 103.2 (d, $J = 14.2$ Hz), 40.9, 21.3. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{FNNaO}_2\text{S}^+$ 252.0465, found 252.0480.



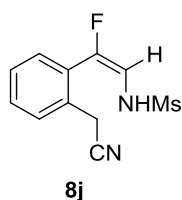
(E)-N-(2-(4-(tert-butyl)phenyl)-2-fluorovinyl)methanesulfonamide (8g): yellow oil, 145.4 mg yield: 54%; ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.36 (m, 4H), 6.82 (d, $J = 10.3$ Hz, 1H), 6.43 (dd, $J = 26.0, 10.3$ Hz, 1H), 3.13 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.0, 147.5 (d, $J = 240.9$ Hz), 127.3 (d, $J = 24.9$ Hz), 125.7 (d, $J = 1.8$ Hz), 122.7 (d, $J = 6.5$ Hz), 103.3 (d, $J = 14.1$ Hz), 40.9, 34.7, 31.2. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{FNNaO}_2\text{S}^+$ 294.0934, found 294.0933.



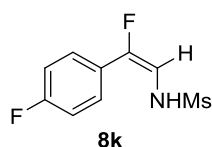
(E)-N-(2-(3,5-dimethylphenyl)-2-fluorovinyl)methanesulfonamide (8h): yellow oil, 134.0 mg, yield: 55%; ^1H NMR (400 MHz, CDCl_3) δ 7.07 (s, 2H), 7.02 – 6.92 (m, 2H), 6.45 (dd, $J = 26.2, 9.4$ Hz, 1H), 3.13 (s, 3H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.4 (d, $J = 241.6$ Hz), 138.3, 130.4, 130.1 (d, $J = 24.4$ Hz), 120.7 (d, $J = 6.5$ Hz), 103.7 (d, $J = 14.1$ Hz), 40.9, 21.3. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{FNNaO}_2\text{S}^+$ 266.0621, found 266.0617.



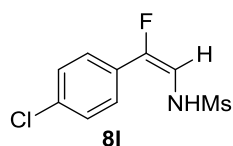
(E)-N-(2-(2-(bromomethyl)phenyl)-2-fluorovinyl)methanesulfonamide (8i): yellow oil, 177.6 mg, yield: 59%; ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.30 (m, 4H), 7.18 (d, $J = 10.6$ Hz, 1H), 6.37 (dd, $J = 25.5, 10.6$ Hz, 1H), 4.62 (s, 2H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.1 (d, $J = 244.2$ Hz), 135.5, 131.4, 130.1, 129.8 (d, $J = 22.4$ Hz), 129.0, 128.9, 108.0 (d, $J = 14.4$ Hz), 41.3, 31.8. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{BrFNNaO}_2\text{S}^+$ 329.9570, found 329.9576.



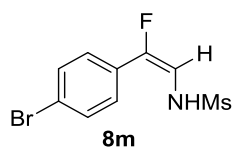
(E)-N-(2-(2-(cyanomethyl)phenyl)-2-fluorovinyl)methanesulfonamide (8j): yellow oil, 139.8 mg, yield: 55%; ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H), 7.24 (d, J = 10.7 Hz, 1H), 6.23 (dd, J = 25.7, 10.7 Hz, 1H), 3.83 (s, 2H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.9 (d, J = 243.5 Hz), 130.4, 129.8, 129.6 (d, J = 22.5 Hz), 129.0 (d, J = 4.9 Hz), 128.6, 128.5, 117.5, 108.4 (d, J = 14.1 Hz), 41.3, 22.5. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{12}\text{FN}_2\text{O}_2\text{S}^+$ 255.0598, found 255.0600.



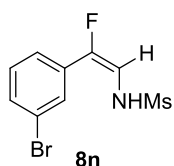
(E)-N-(2-fluoro-2-(4-fluorophenyl)vinyl)methanesulfonamide (8k): yellow oil, 153.7 mg, yield: 66%; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, J = 8.8, 5.2 Hz, 2H), 7.07 (t, J = 8.8 Hz, 2H), 6.89 (d, J = 8.9 Hz, 1H), 6.41 (dd, J = 26.0, 8.9 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.8 (d, J = 249.0 Hz), 146.4 (d, J = 240.6 Hz), 126.4 (dd, J = 25.7, 3.5 Hz), 124.9 (dd, J = 8.1, 6.6 Hz), 115.9 (dd, J = 22.1, 1.7 Hz), 103.8 (dd, J = 14.1, 1.7 Hz), 41.1. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{F}_2\text{NO}_2\text{S}^+$ 234.0395, found 234.0396.



(E)-N-(2-(4-chlorophenyl)-2-fluorovinyl)methanesulfonamide (8l): yellow oil, 168.6 mg, yield: 68%; ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.30 (m, 4H), 6.97 (d, J = 10.1 Hz, 1H), 6.47 (dd, J = 26.0, 10.1 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.0 (d, J = 240.1 Hz), 134.4, 129.0, 128.7 (d, J = 25.6 Hz), 124.1 (d, J = 6.4 Hz), 104.5 (d, J = 14.0 Hz), 41.23. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{ClFNO}_2\text{S}^+$ 250.0099, found 250.0127.

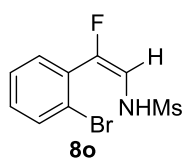


(E)-N-(2-(4-bromophenyl)-2-fluorovinyl)methanesulfonamide (8m): yellow oil, 217.0 mg, yield: 74%; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 10.4 Hz, 1H), 6.50 (dd, J = 26.1, 10.4 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.9 (d, J = 240.0 Hz), 131.9, 129.4, 124.3 (d, J = 6.2 Hz), 122.4, 104.7 (d, J = 13.6 Hz), 41.3. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{BrFNO}_2\text{S}^+$ 293.9594, found 293.9592.

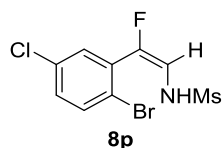


(E)-N-(2-(3-bromophenyl)-2-fluorovinyl)methanesulfonamide (8n): yellow oil, 226.1 mg, yield: 77%; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.51 (dd, J = 26.1, 10.7 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.2 (d, J = 240.4 Hz), 132.3 (d, J = 24.8 Hz), 131.4,

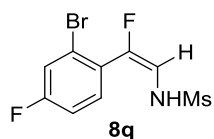
130.3 (d, $J = 2.1$ Hz), 125.7 (d, $J = 7.0$ Hz), 122.9 (d, $J = 2.1$ Hz), 121.2 (d, $J = 6.5$ Hz), 105.3 (d, $J = 13.2$ Hz), 41.4. HRMS (ESI) calcd for $C_9H_{10}BrFNO_2S^+$ 293.9594, found 293.9604.



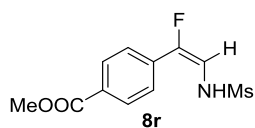
(E)-N-(2-(2-bromophenyl)-2-fluorovinyl)methanesulfonamide (8o): yellow oil, 250.0 mg, yield: 85%; 1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, $J = 7.9$ Hz, 1H), 7.46 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 6.61 (d, $J = 11.4$ Hz, 1H), 6.53 (dd, $J = 24.4, 11.4$ Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (d, $J = 242.2$ Hz), 133.8, 131.2 (d, $J = 23.5$ Hz), 130.5, 129.9 (d, $J = 5.4$ Hz), 127.5, 121.1 (d, $J = 1.6$ Hz), 109.1 (d, $J = 13.9$ Hz), 41.2. HRMS (ESI) calcd for $C_9H_{10}BrFNO_2S^+$ 293.9594, found 293.9604.



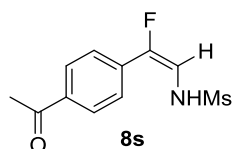
(E)-N-(2-(2-bromo-5-chlorophenyl)-2-fluorovinyl)methanesulfonamide (8p): white solid, 256.2 mg, m.p.: 132-134 °C, yield: 78%; 1H NMR (400 MHz, DMSO- d_6) δ 10.14 (d, $J = 10.2$ Hz, 1H), 7.70 (d, $J = 8.6$ Hz, 1H), 7.63 (d, $J = 2.5$ Hz, 1H), 7.38 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.51 (dd, $J = 28.3, 10.2$ Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 141.7 (d, $J = 241.0$ Hz), 135.6, 133.8 (d, $J = 23.2$ Hz), 133.1, 130.7, 130.0, 119.2, 111.6 (d, $J = 12.3$ Hz), 41.5. HRMS (ESI) calcd for $C_9H_9BrClFNO_2S^+$ 327.9204, found 327.9210.



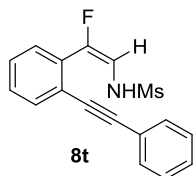
(E)-N-(2-(2-bromo-4-fluorophenyl)-2-fluorovinyl)methanesulfonamide (8q): yellow oil, 237.3 mg, yield: 76%; 1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 2H), 7.11 – 6.98 (m, 2H), 6.43 (dd, $J = 25.3, 10.7$ Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J = 255.4$ Hz), 144.3 (d, $J = 242.4$ Hz), 131.4 (dd, $J = 8.8, 4.8$ Hz), 127.6 (dd, $J = 24.3, 3.7$ Hz), 122.1 (d, $J = 9.8$ Hz), 121.1 (d, $J = 24.8$ Hz), 114.9 (d, $J = 21.4$ Hz), 109.0 (d, $J = 14.3$ Hz), 41.2. HRMS (ESI) calcd for $C_9H_9BrF_2NO_2S^+$ 311.9500, found 311.9511.



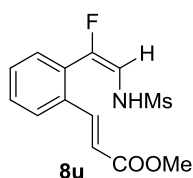
methyl (E)-4-(1-fluoro-2-(methanesulfonamido)vinyl)benzoate (8r): white solid, 138.1 mg, yield: 51%, m.p.: 127-129 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 10.5$ Hz, 1H), 6.63 (dd, $J = 25.8, 10.5$ Hz, 1H), 3.94 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 145.5 (d, $J = 239.5$ Hz), 130.0 (d, $J = 2.1$ Hz), 129.8 (d, $J = 20.8$ Hz), 125.1, 122.3 (d, $J = 6.8$ Hz), 106.3 (d, $J = 13.5$ Hz), 52.3, 41.6. HRMS (ESI) calcd for $C_{11}H_{13}FNO_4S^+$ 274.0544, found 274.0542.



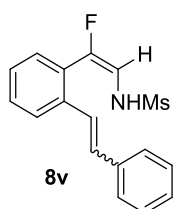
(E)-N-(2-(4-acetylphenyl)-2-fluorovinyl)methanesulfonamide (8s): yellow oil, 72.4 mg, yield: 28%; ^1H NMR (400 MHz, DMSO- d_6) δ 10.20 (d, J = 10.0 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 6.90 (dd, J = 29.3, 10.0 Hz, 1H), 3.18 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 197.5, 143.5 (d, J = 236.8 Hz), 135.9, 135.7 (d, J = 24.0 Hz), 129.1 (d, J = 1.8 Hz), 122.4 (d, J = 6.8 Hz), 109.1 (d, J = 12.5 Hz), 41.4, 27.1. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{FNO}_3\text{S}^+$ 258.0595, found 258.0603.



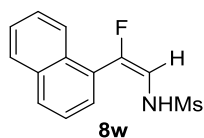
(E)-N-(2-fluoro-2-(2-(phenylethynyl)phenyl)vinyl)methanesulfonamide (8t): yellow oil, 239.6 mg, yield: 76%; ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.60 (m, 3H), 7.55 (d, J = 7.9 Hz, 1H), 7.52 – 7.35 (m, 5H), 7.35 – 7.27 (m, 1H), 7.07 – 6.93 (m, 1H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.9 (d, J = 237.2 Hz), 134.1, 131.7, 130.9 (d, J = 23.7 Hz), 128.9, 128.5, 127.9, 125.1, 125.0, 122.5, 118.0 (d, J = 4.7 Hz), 108.7 (d, J = 13.3 Hz), 95.6, 88.3, 41.1. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{FNO}_2\text{S}^+$ 316.0802, found 316.0796.



methyl (E)-3-(2-((E)-1-fluoro-2-(methanesulfonamido)vinyl)phenyl)acrylate (8u): yellow oil, 194.4 mg, yield: 65%; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, J = 15.9, 2.4 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.46 – 7.37 (m, 3H), 7.27 (d, J = 11.0 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 25.4, 11.0 Hz, 1H), 3.82 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 144.7 (d, J = 243.5 Hz), 142.6, 132.7, 130.5 (d, J = 22.6 Hz), 129.9, 129.6, 128.3 (d, J = 4.3 Hz), 127.4, 120.0, 109.5 (d, J = 14.0 Hz), 51.9, 41.1. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FNO}_4\text{S}^+$ 300.0700, found 300.0710.

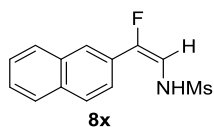


N-((1E)-2-fluoro-2-(2-styrylphenyl)vinyl)methanesulfonamide (8v): yellow oil, 113.8 mg, yield: 37%; ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.48 (m, 3H), 7.47 – 7.36 (m, 3H), 7.36 – 7.28 (m, 2H), 7.28 – 7.02 (m, 2H), 6.93 – 6.64 (m, 2H), 6.48 – 6.14 (m, 1H), 3.12 3.05 (3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5 (d, J = 243.6 Hz), 146.3 (d, J = 242.4 Hz), 137.1, 136.3 (d, J = 8.3 Hz), 135.1, 131.3, 130.4, 129.7, 129.0, 128.9, 128.8, 128.4 (d, J = 4.8 Hz), 128.2, 128.1, 127.6, 127.5 (d, J = 6.1 Hz), 126.7, 126.6, 126.4 (d, J = 2.2 Hz), 108.4 (d, J = 14.8 Hz), 108.1 (d, J = 13.9 Hz), 41.1, 41.0. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{FNO}_2\text{S}^+$ 318.0959, found 318.0959.

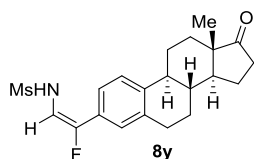


(E)-N-(2-fluoro-2-(naphthalen-1-yl)vinyl)methanesulfonamide (8w): yellow oil, 119.4 mg, yield: 49%; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 7.5 Hz, 1H), 7.91 (t, J = 7.1 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.46 (t, J = 7.5 Hz, 1H),

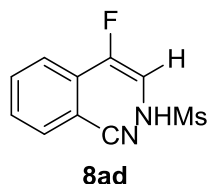
6.92 (d, $J = 10.3$ Hz, 1H), 6.32 (dd, $J = 24.7, 10.3$ Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.7 (d, $J = 245.6$ Hz), 133.6, 130.9, 130.6, 128.6, 127.7 (d, $J = 21.8$ Hz), 127.2 (d, $J = 4.8$ Hz), 127.0, 126.4, 125.12, 125.06 (d, $J = 2.2$ Hz), 107.8 (d, $J = 15.1$ Hz), 41.2. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{FNNaO}_2\text{S}^+$ 288.0465, found 288.0468.



(E)-N-(2-fluoro-2-(naphthalen-2-yl)vinyl)methanesulfonamide (8x): yellow oil, 82.0 mg, yield: 31%; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.86 – 7.79 (m, 3H), 7.54 – 7.45 (m, 3H), 6.90 (d, $J = 10.5$ Hz, 1H), 6.62 (dd, $J = 25.9, 10.5$ Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.1 (d, $J = 240.2$ Hz), 133.1, 128.62, 128.60, 128.3, 127.8, 127.4 (d, $J = 24.3$ Hz), 126.9, 126.6, 122.0 (d, $J = 6.9$ Hz), 120.2 (d, $J = 6.5$ Hz), 104.6 (d, $J = 13.7$ Hz), 41.2. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{FNO}_2\text{S}^+$ 266.0646, found 266.0632.



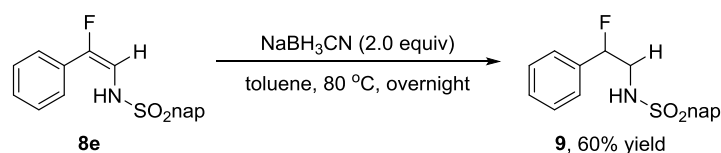
N-((E)-2-fluoro-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)vinyl)methanesulfonamide (8y): yellow oil, 160.3 mg, yield: 53%; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 8.3$ Hz, 1H), 7.21 (d, $J = 8.3$ Hz, 1H), 7.17 (s, 1H), 7.05 – 6.81 (m, 1H), 6.41 (dd, $J = 26.2, 10.1$ Hz, 1H), 3.12 (s, 3H), 2.96 – 2.86 (m, 2H), 2.60 – 1.92 (m, 8H), 1.71 – 1.42 (m, 5H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 221.2, 147.2 (d, $J = 241.1$ Hz), 140.6, 137.0, 127.7 (d, $J = 24.6$ Hz), 125.8, 123.4 (d, $J = 6.4$ Hz), 120.4 (d, $J = 6.4$ Hz), 103.5 (d, $J = 14.0$ Hz), 50.4, 48.0, 44.4, 41.0, 38.0, 35.9, 31.5, 29.4, 26.3, 25.6, 21.6, 13.8. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{FNO}_3\text{S}^+$ 392.1690, found 392.1676.



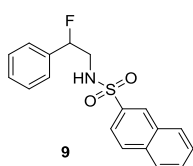
(E)-N-(2-(2-cyanophenyl)-2-fluorovinyl)methanesulfonamide (8ad): white solid, 17.3 mg, yield: 8%, m.p.: 128–130 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 10.37 (d, $J = 10.2$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.75 (d, $J = 4.0$ Hz, 2H), 7.57 – 7.50 (m, 1H), 6.87 (dd, $J = 28.9, 10.2$ Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.5 (d, $J = 238.2$ Hz), 134.9, 134.1 (d, $J = 22.9$ Hz), 133.9, 129.1, 126.4 (d, $J = 5.5$ Hz), 118.6, 111.3 (d, $J = 11.8$ Hz), 106.7, 41.6. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{10}\text{FN}_2\text{O}_2\text{S}^+$ 241.0442, found 241.0445.

6. Procedure for derivation of products

6.1 Synthesis of N-(2-fluoro-2-phenylethyl)naphthalene-2-sulfonamide (9)^[13]

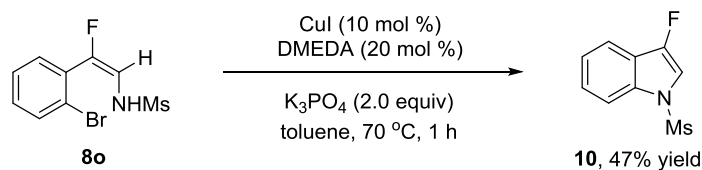


(*E*)-N-(2-fluoro-2-phenylvinyl)naphthalene-2-sulfonamide (**8e**) (0.30 mmol, 100 mg) was dissolved in toluene (2.0 mL) and added to an oven-dried tube equipped with NaBH₃CN (0.60 mmol, 36.9 mg) and a stir bar. The reaction mixture was stirred overnight at 80 °C. Then the reaction mixture was filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **9** (60.5 mg, 60%) as a yellow oil.

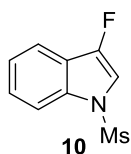


N-(2-fluoro-2-phenylethyl)naphthalene-2-sulfonamide (9): yellow oil, 60.5 mg, yield: 60%; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.01 – 7.90 (m, 3H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.37 – 7.30 (m, 3H), 7.27 – 7.21 (m, 2H), 5.54 (ddd, *J* = 48.0, 8.2, 3.2 Hz, 1H), 5.34 – 5.19 (m, 1H), 3.58 – 3.26 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 136.7, 136.3 (d, *J* = 19.4 Hz), 134.9, 132.2, 129.7, 129.3, 129.1, 129.0, 128.7 (d, *J* = 2.7 Hz), 128.4, 127.9, 127.7, 125.5 (d, *J* = 6.9 Hz), 122.2, 92.8 (d, *J* = 174.0 Hz), 48.7 (d, *J* = 25.2 Hz). HRMS (ESI) calcd for C₁₈H₁₇FNO₂S⁺ 330.0959, found 330.0956.

6.2 Synthesis of 3-fluoro-1-(methylsulfonyl)-1H-indole (**10**)^[13]

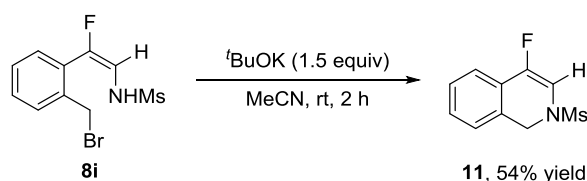


To a solution of **8o** (146 mg, 0.50 mmol) in toluene (4.0 mL), CuI (9.5 mg, 0.05 mmol), *N,N'*-dimethylethylenediamine (DMEDA, 88.0 mg, 0.1 mmol) and K₃PO₄ (212 mg, 1.0 mmol) were added and the reaction mixture was stirred at 70 °C for 1 h. After evaporation of the solvent, the corresponding product **10** (49.0 mg, 47%) was purified by silica gel column chromatography using PE/EtOAc (10:1) as eluent.

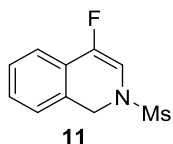


3-fluoro-1-(methylsulfonyl)-1H-indole (10): yellow oil, 49.0 mg, yield: 47%; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 9.3$ Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.48 – 7.43 (m, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 2.9$ Hz, 1H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.7 (d, $J = 255.6$ Hz), 132.8 (d, $J = 5.1$ Hz), 126.3, 124.0, 121.5 (d, $J = 19.2$ Hz), 118.0 (d, $J = 2.6$ Hz), 113.6, 108.6 (d, $J = 28.9$ Hz), 40.2. HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{FNO}_2\text{S}^+$ 214.0333, found 214.0324.

6.3 Synthesis of 4-fluoro-2-(methylsulfonyl)-1,2-dihydroisoquinoline (11)^[14]

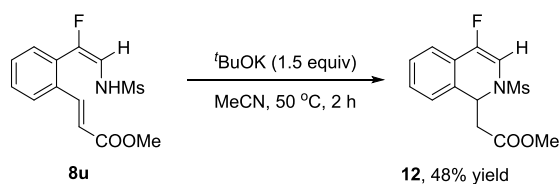


A solution of **8i** (120 mg, 0.40 mmol), *t*-BuOK (67.2 mg, 0.6 mmol) in MeCN (2 mL) was stirred at room temperature for 2 h. After the reaction completed (checked by TLC), the mixture was concentrated under vacuum and filtered through a plug of silica gel. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (PE/EtOAc=10:1) to give pure product **11** (48.0 mg, 54%).



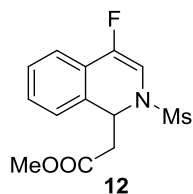
4-fluoro-2-(methylsulfonyl)-1,2-dihydroisoquinoline (11): yellow oil, 48.2 mg, yield: 54%; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.34 (m, 3H), 7.24 – 7.17 (m, 1H), 6.62 (d, $J = 5.6$ Hz, 1H), 4.77 (s, 2H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3 (d, $J = 247.0$ Hz), 129.8, 128.7 (d, $J = 5.7$ Hz), 128.4, 125.9 (d, $J = 23.6$ Hz), 125.4, 120.0, 110.1 (d, $J = 39.6$ Hz), 47.9, 37.7. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{FNO}_2\text{S}^+$ 228.0489, found 228.0500.

6.4 Synthesis of methyl 2-(4-fluoro-2-(methylsulfonyl)-1,2-dihydroisoquinolin-1-yl) acetate (12)^[14]



A solution of **8u** (81.0 mg, 0.27 mmol), *t*-BuOK (44.8 mg, 0.40 mmol) in MeCN (2 mL) was stirred at room temperature for 2 h. After the reaction completed (checked by TLC), the mixture was concentrated under vacuum and

filtered through a plug of silica gel. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (PE/EtOAc=10:1) to give pure product **12** (39.0 mg, 48%).

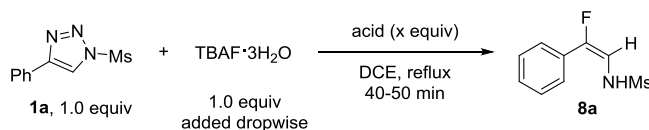


methyl 2-(4-fluoro-2-(methylsulfonyl)-1,2-dihydroisoquinolin-1-yl)acetate (12**):** yellow oil, 39.0 mg, yield: 48%; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 6.9 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.33 – 7.27 (m, 1H), 6.54 (d, J = 5.2 Hz, 1H), 5.57 (t, J = 7.3 Hz, 1H), 3.69 (s, 3H), 2.84 (dd, J = 15.0, 7.3 Hz, 1H), 2.70 (s, 3H), 2.69 – 2.63 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 152.0 (d, J = 248.3 Hz), 131.5 (d, J = 5.6 Hz), 130.0, 128.8, 126.0 (d, J = 2.8 Hz), 124.1 (d, J = 23.0 Hz), 120.6 (d, J = 3.3 Hz), 107.3 (d, J = 39.3 Hz), 54.5, 52.0, 40.6, 38.3. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FNO}_4\text{S}^+$ 300.0700, found 300.0699.

7. Protonic acid catalyzed/mediated reaction

We used protonic acid to catalyze the reaction with TBAF as the fluoride source, no **8a** was obtained. The results were summarized as follows:

Table S3 Protonic Acid Catalyzed/Mediated Reaction.



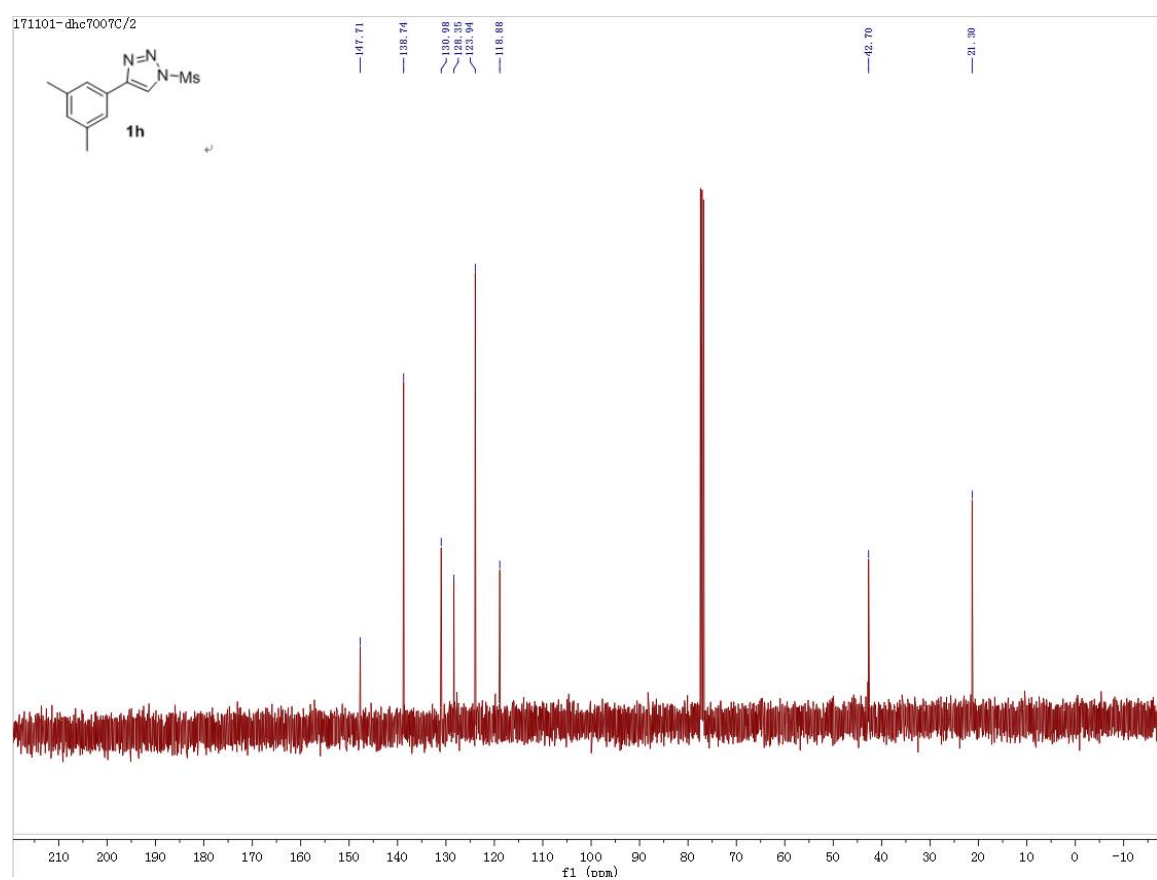
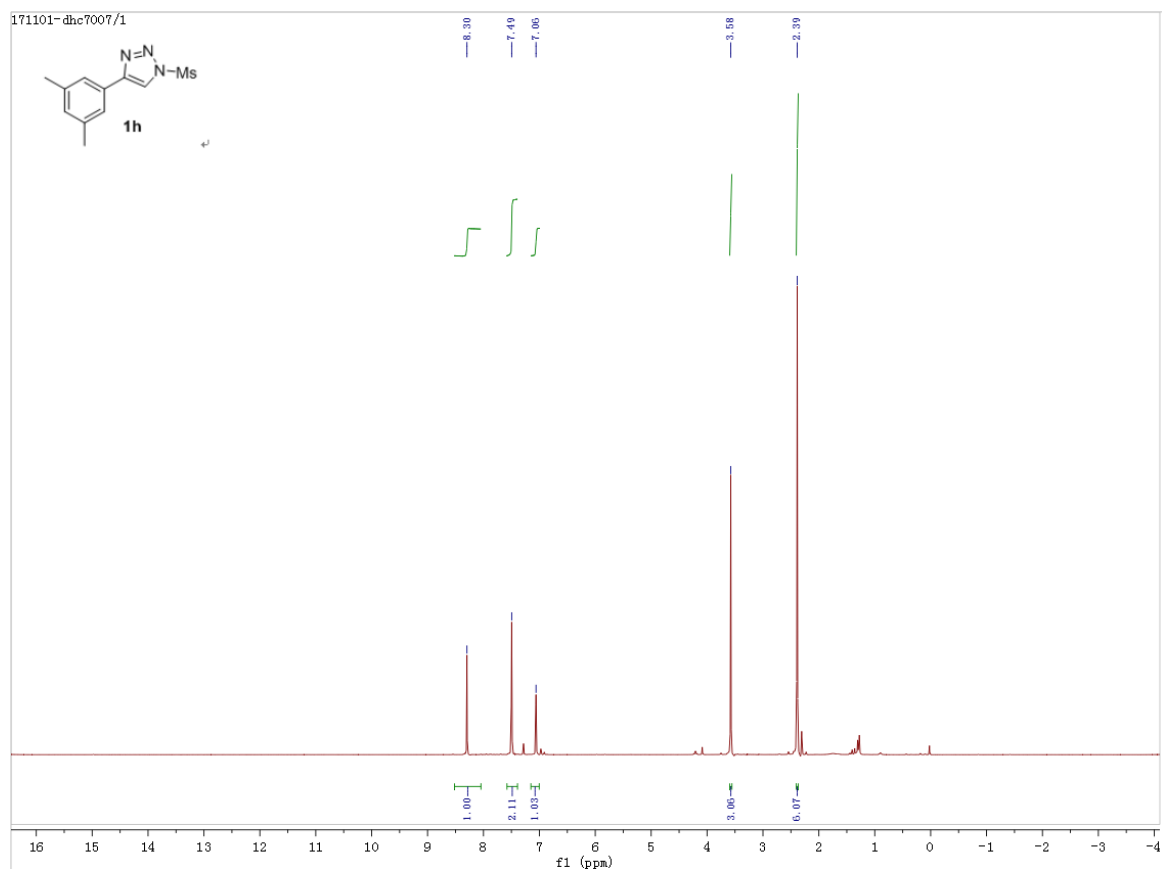
entry	acid	x	yield of 8a (%)	note
1	HBF_4	1.0	0	desulfonylation
2	TsOH	1.0	0	desulfonylation
3	HBF_4	0.2	0	desulfonylation
4	TsOH	0.2	0	desulfonylation

Thus, under strong acidic conditions, desulfonylation was the major reaction. Since it is difficult to mimic the reaction condition without adding $\text{Et}_2\text{O} \cdot \text{BF}_3$, and we do not know the exact amount of protonic acid under the optimized conditions, the mechanism of path c in the manuscript cannot be excluded at this stage. However, on the basis of the above experiments, we thought the participation of $\text{Et}_2\text{O} \cdot \text{BF}_3$ in the activation of triazole is necessary.

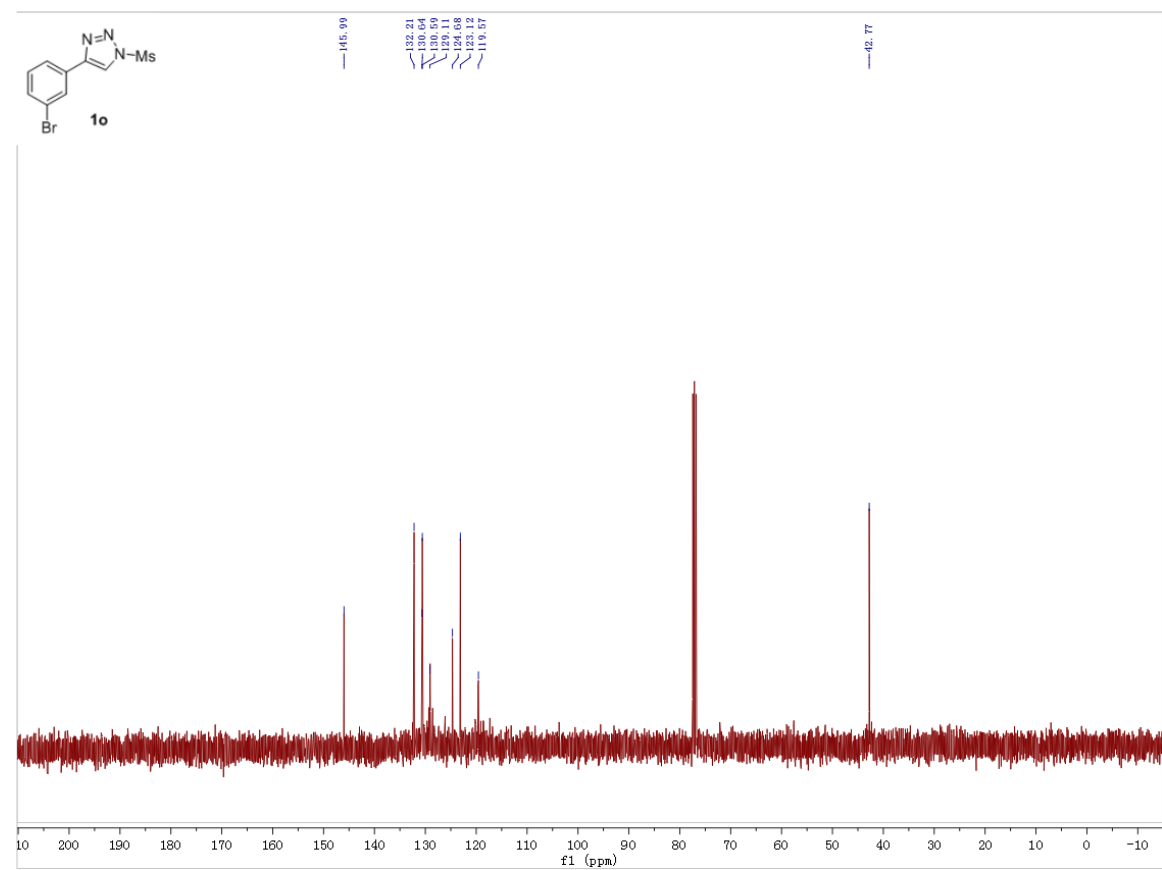
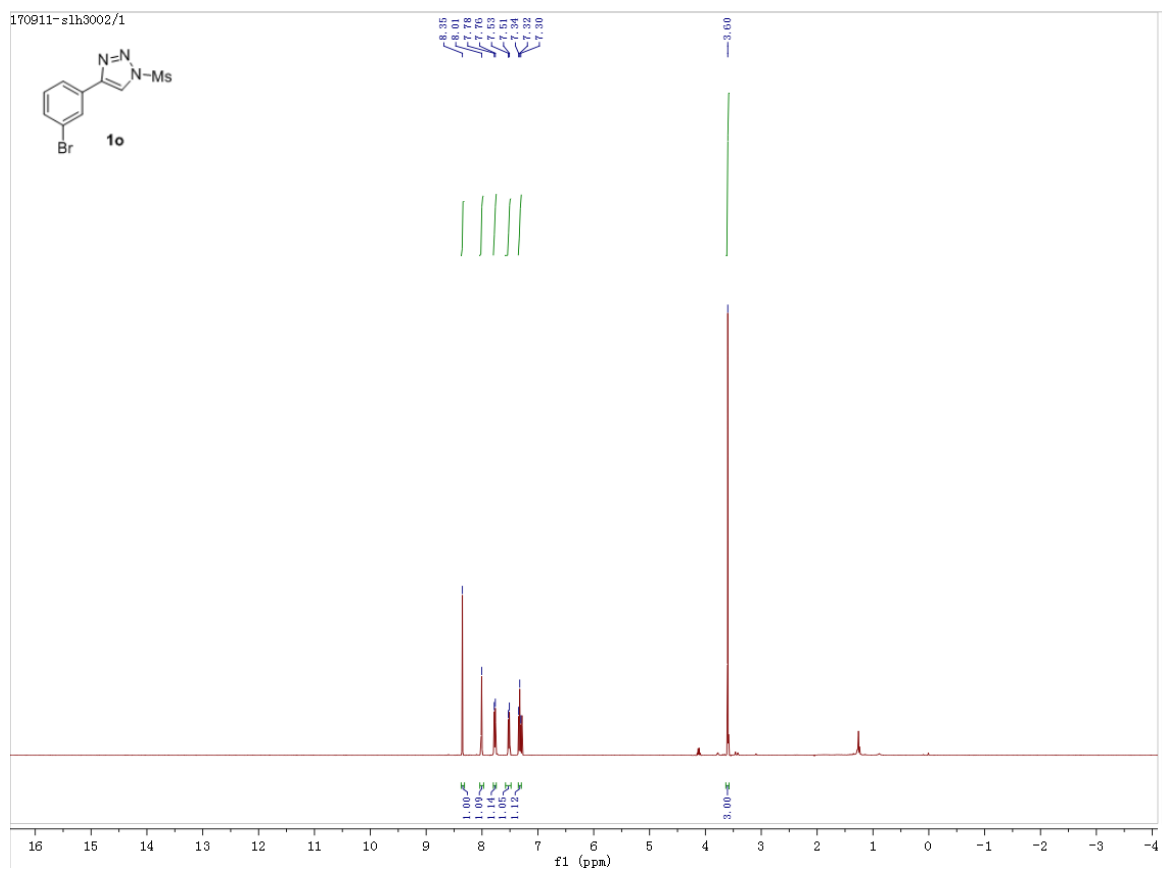
8. References

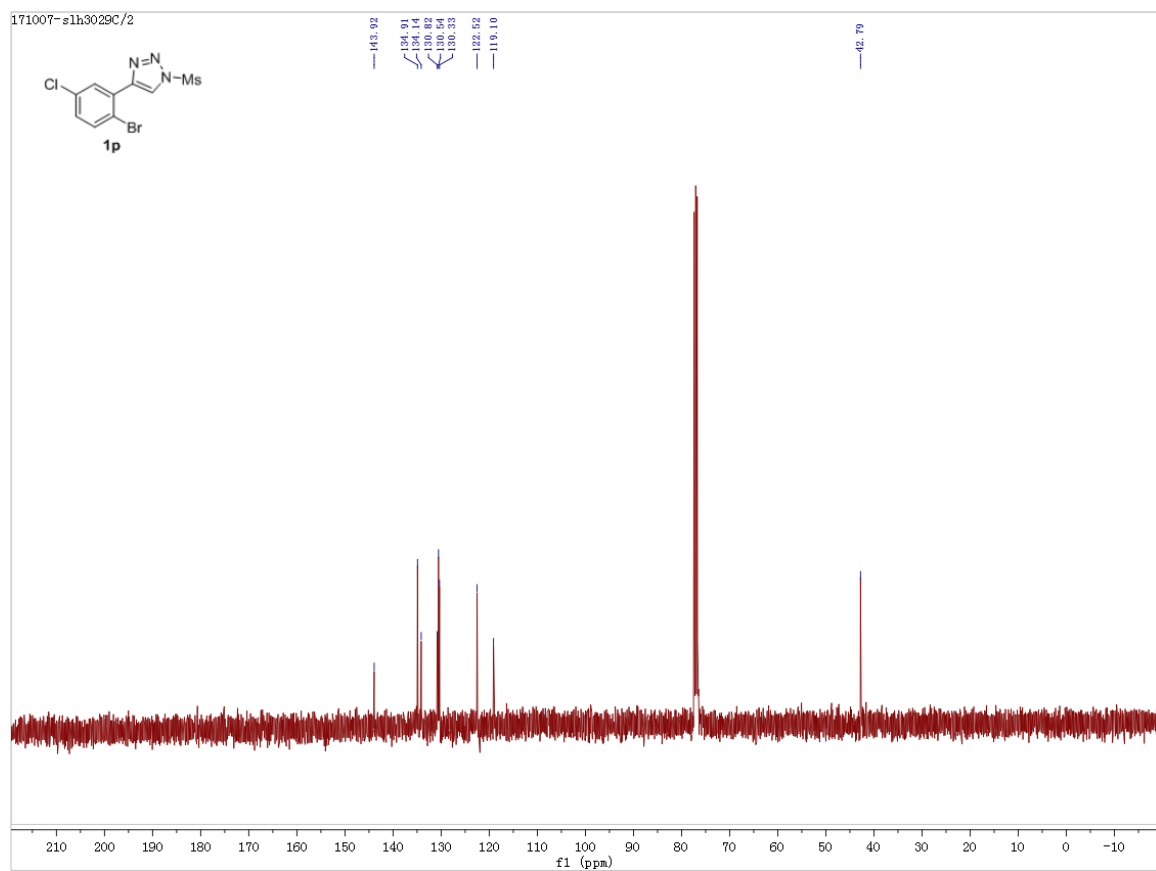
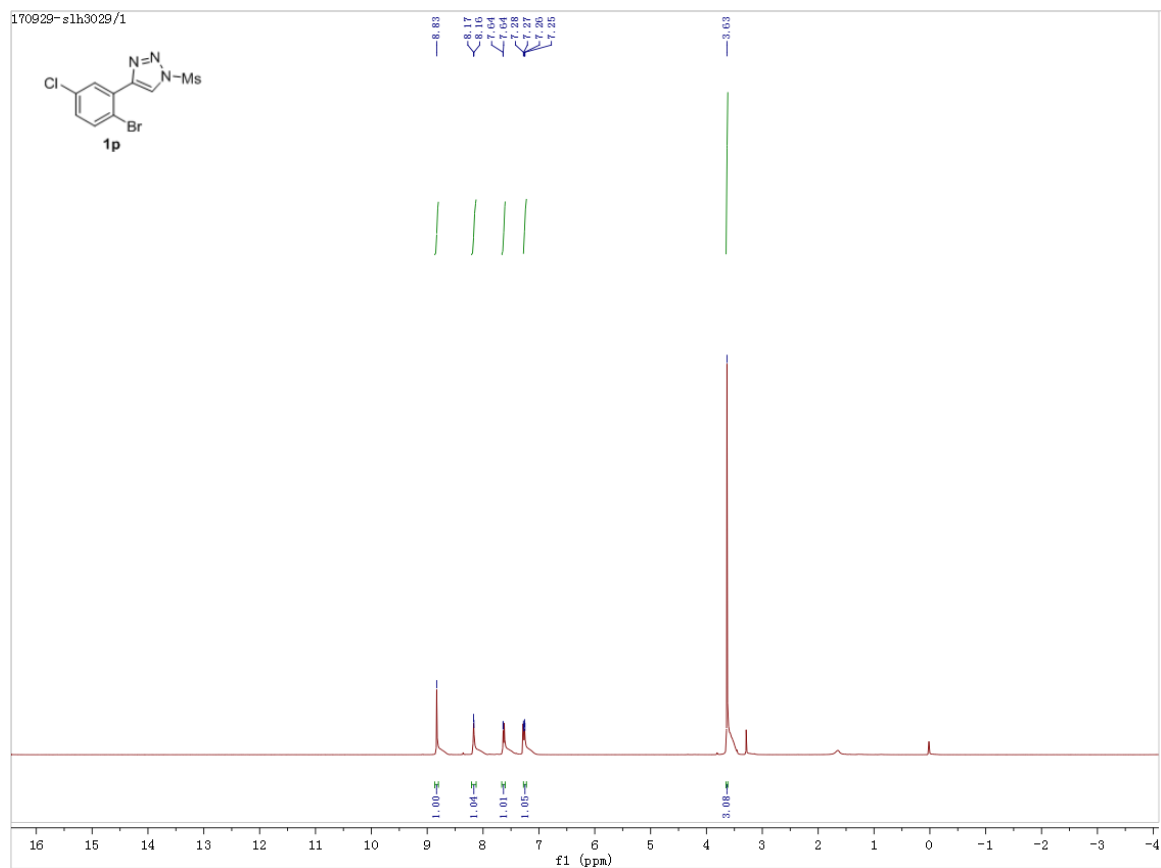
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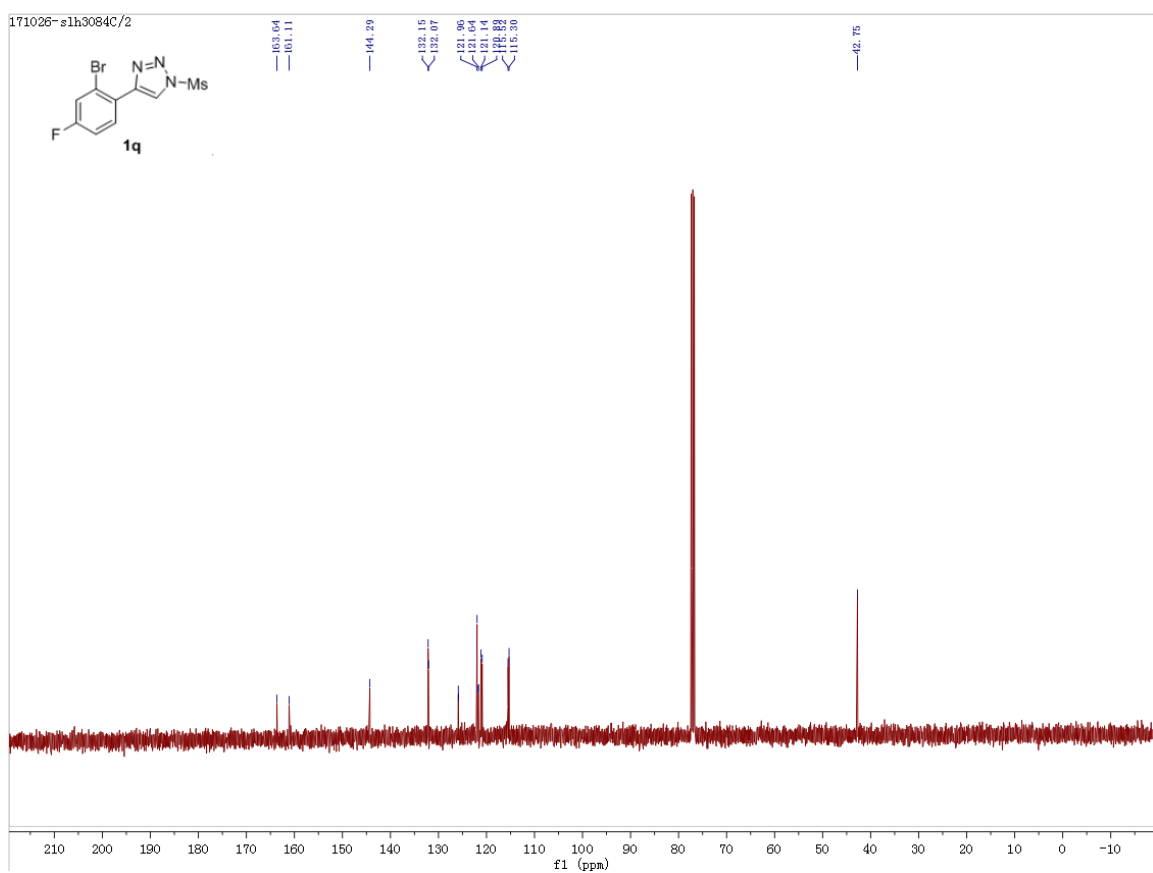
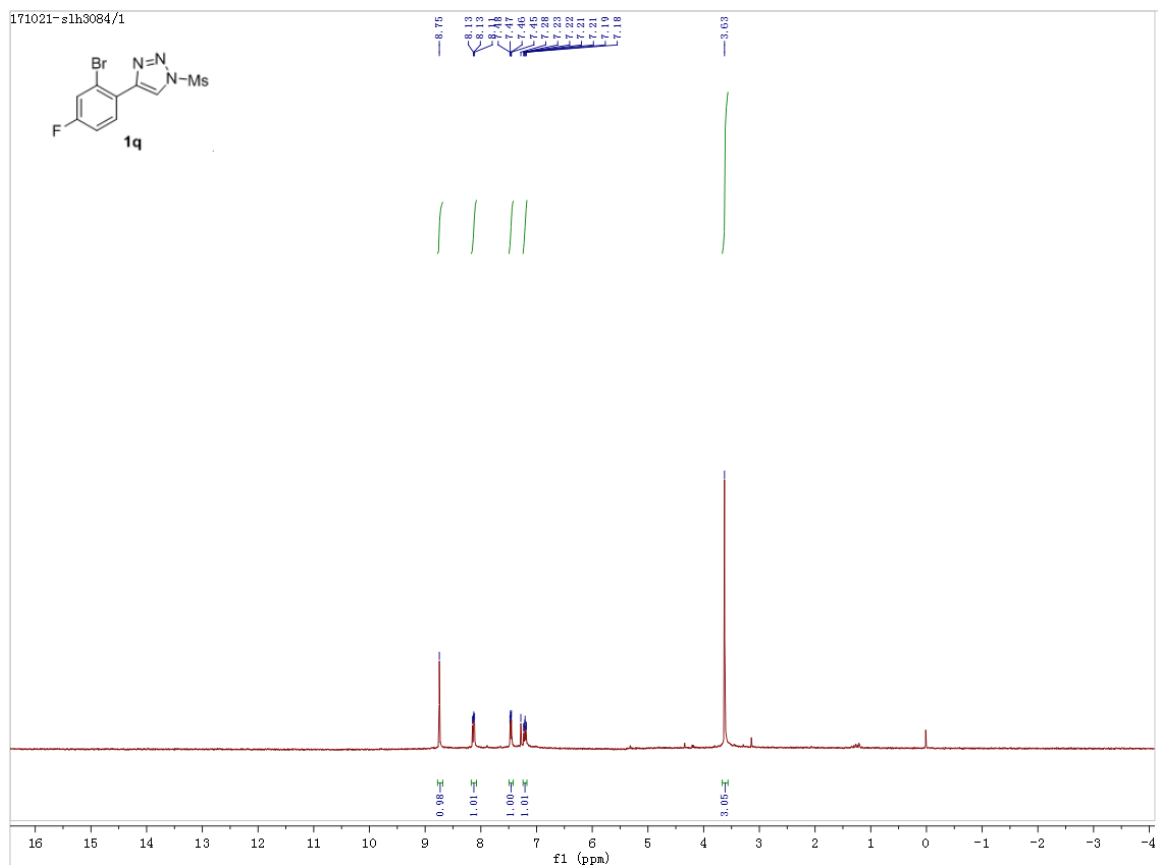
9. ^1H and ^{13}C NMR spectra for new compounds

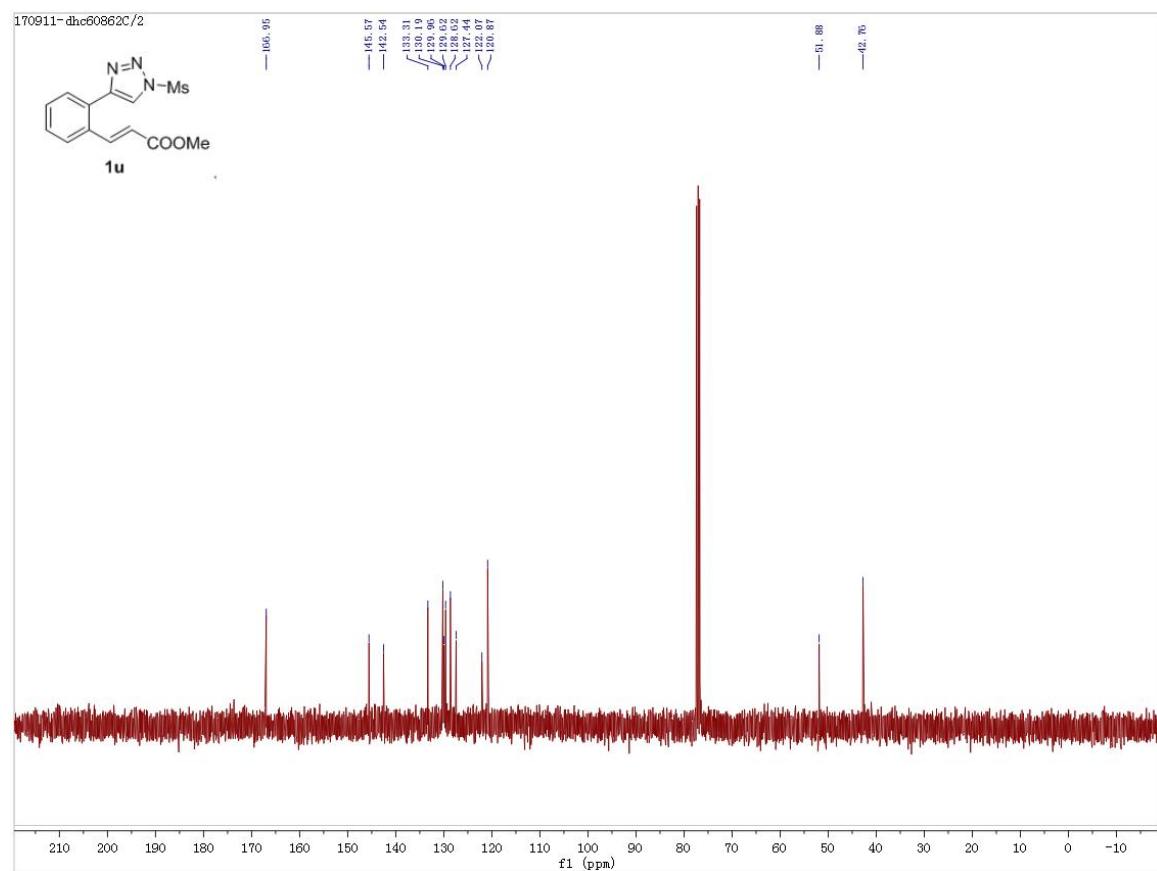
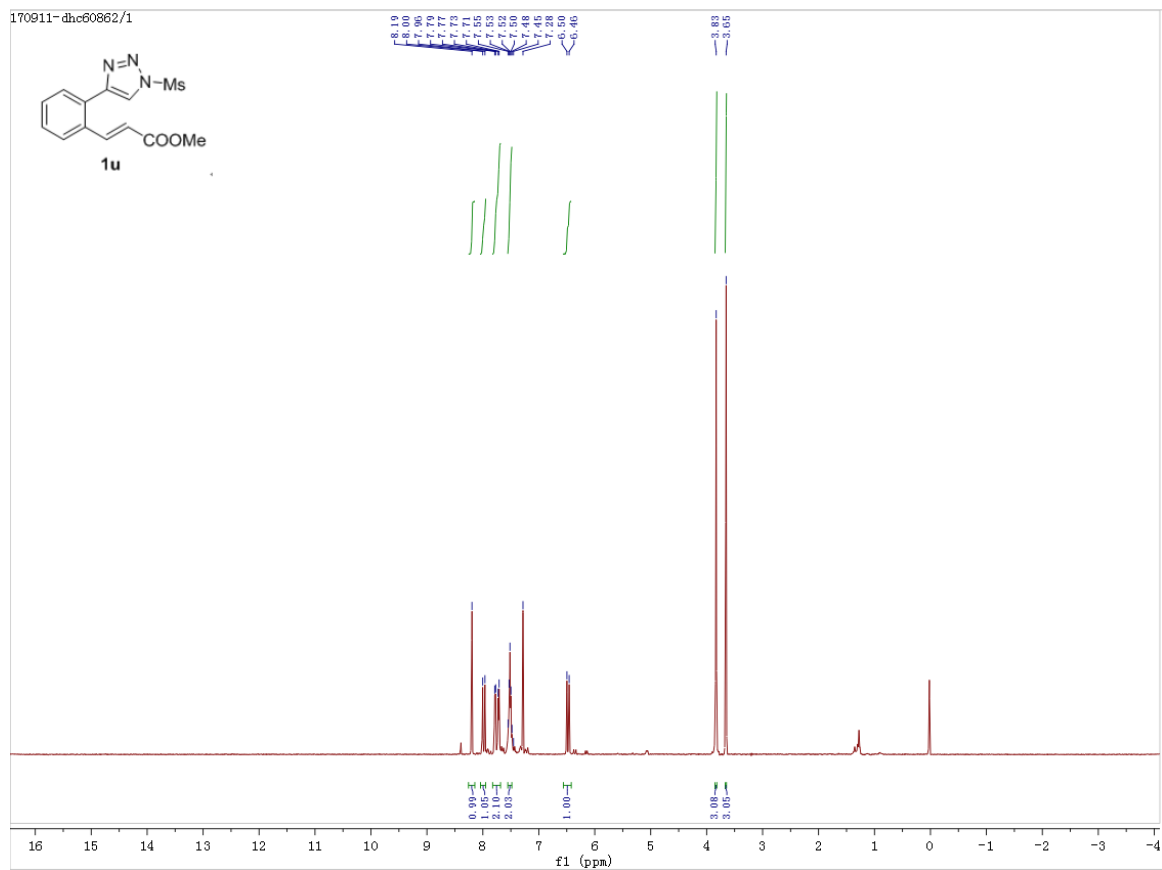


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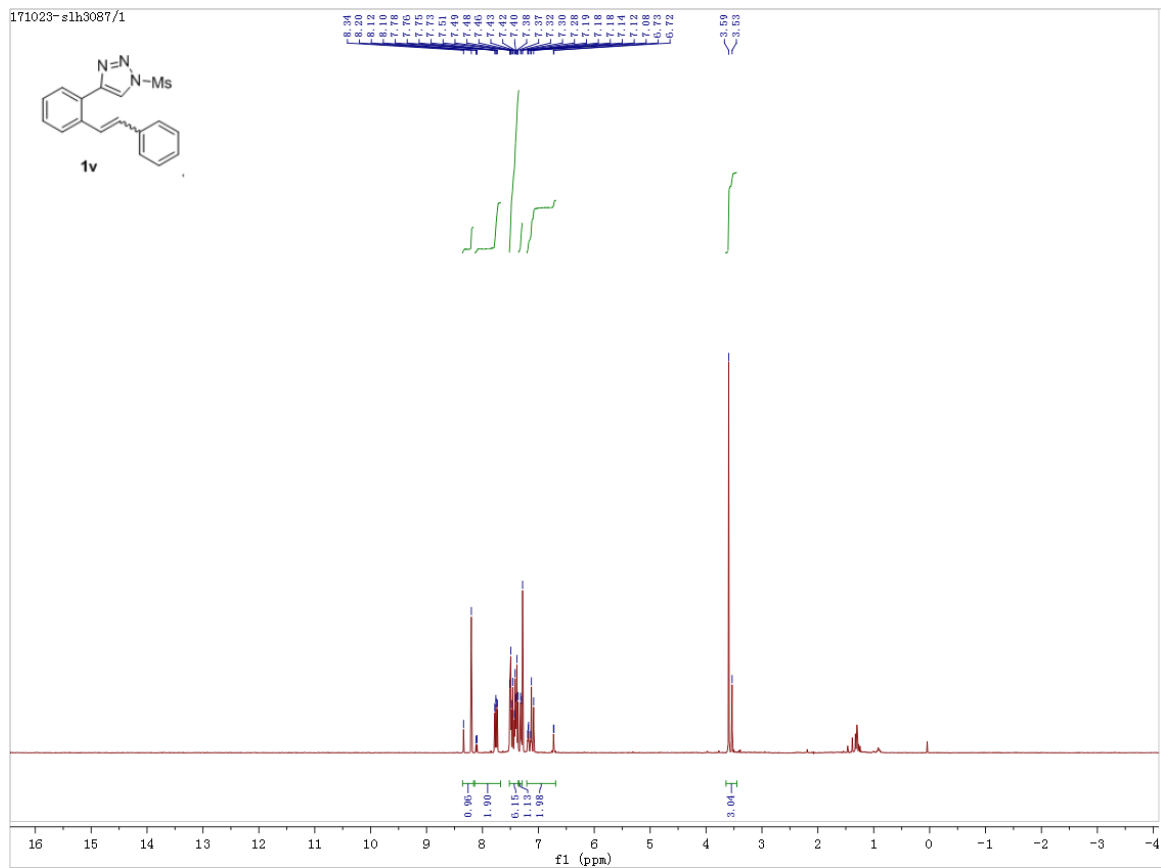




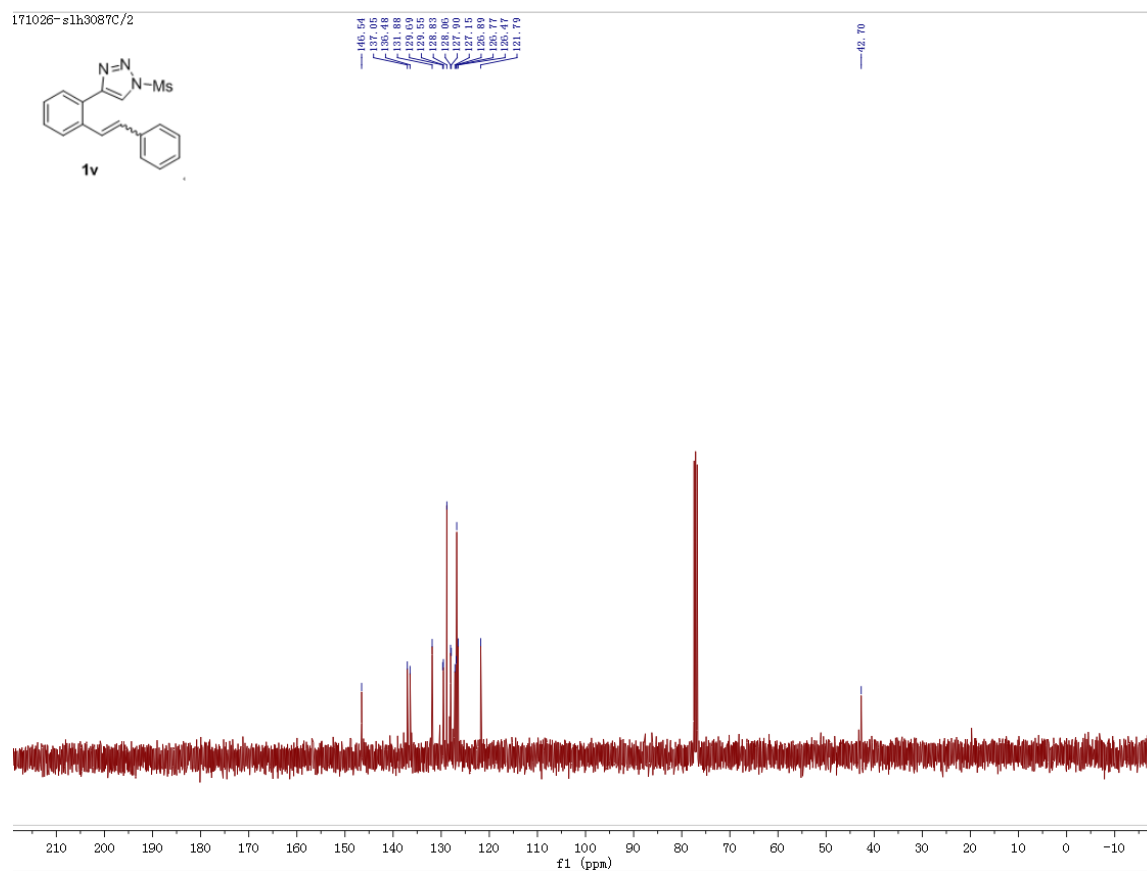


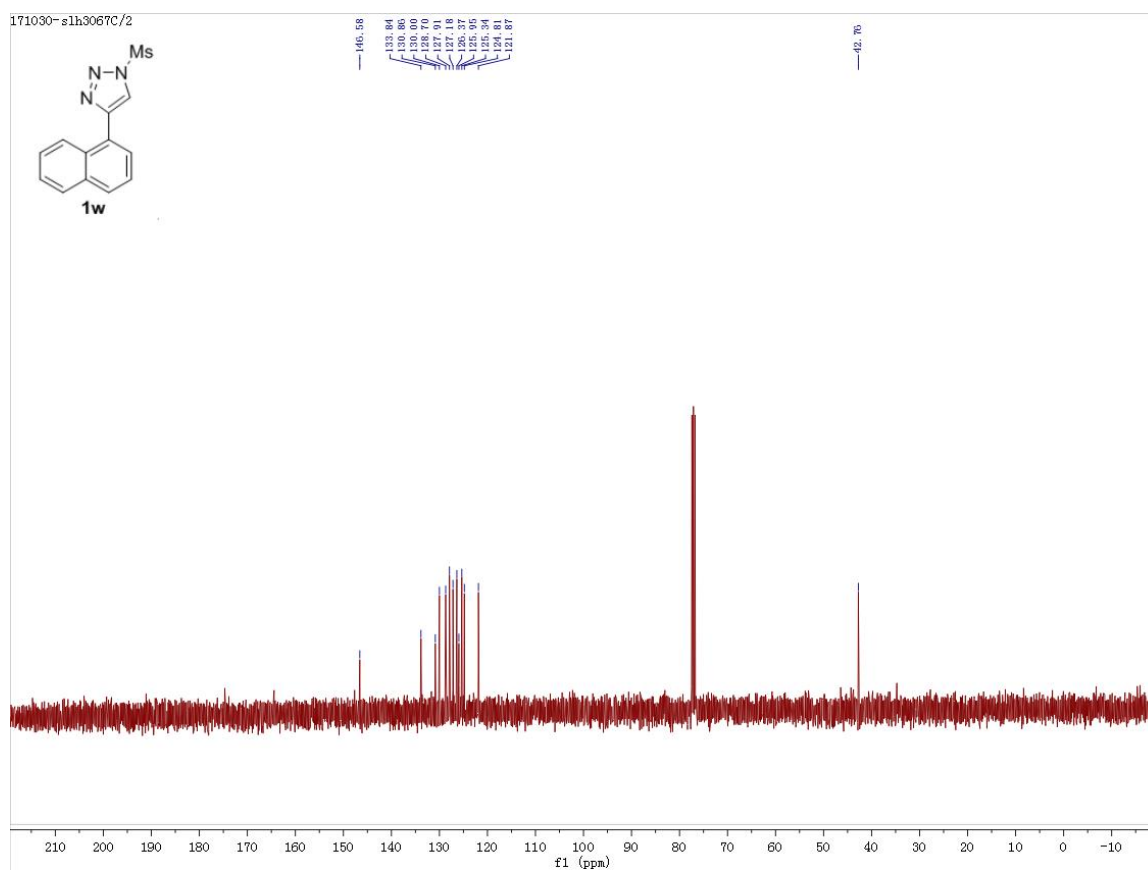
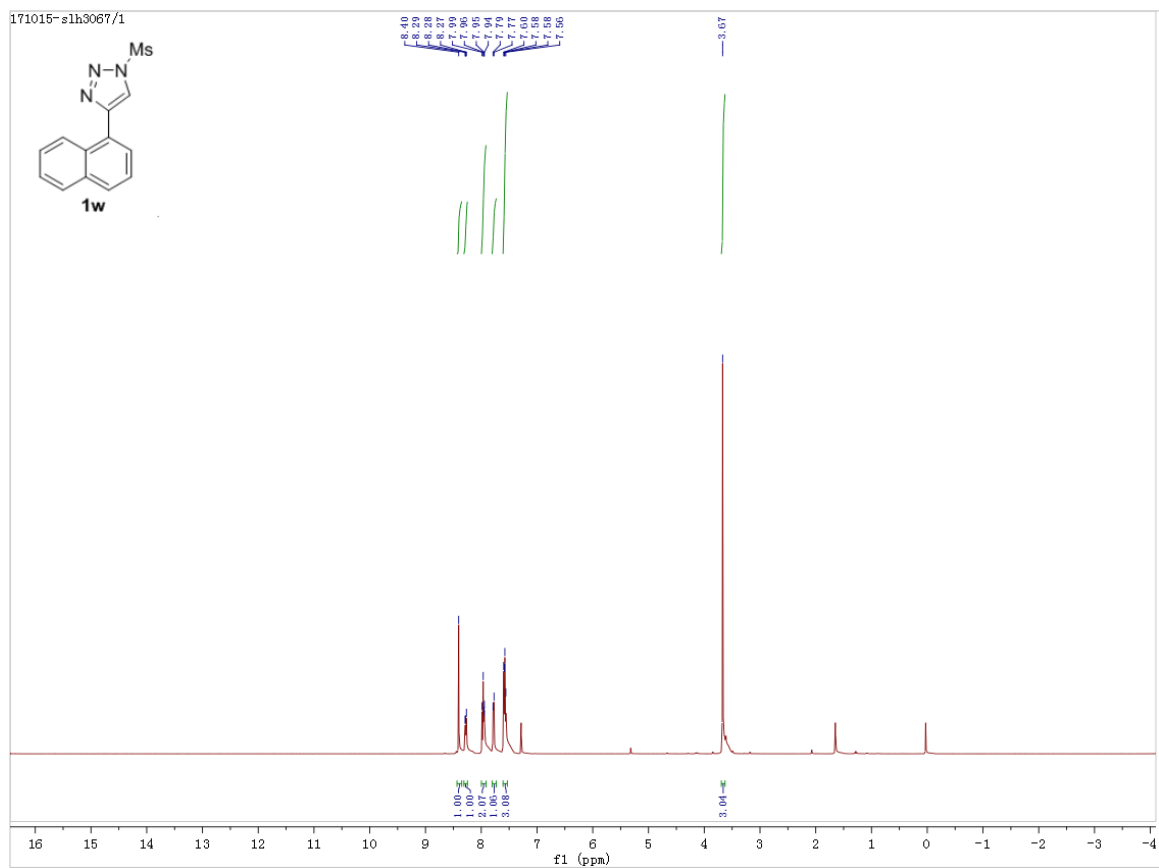


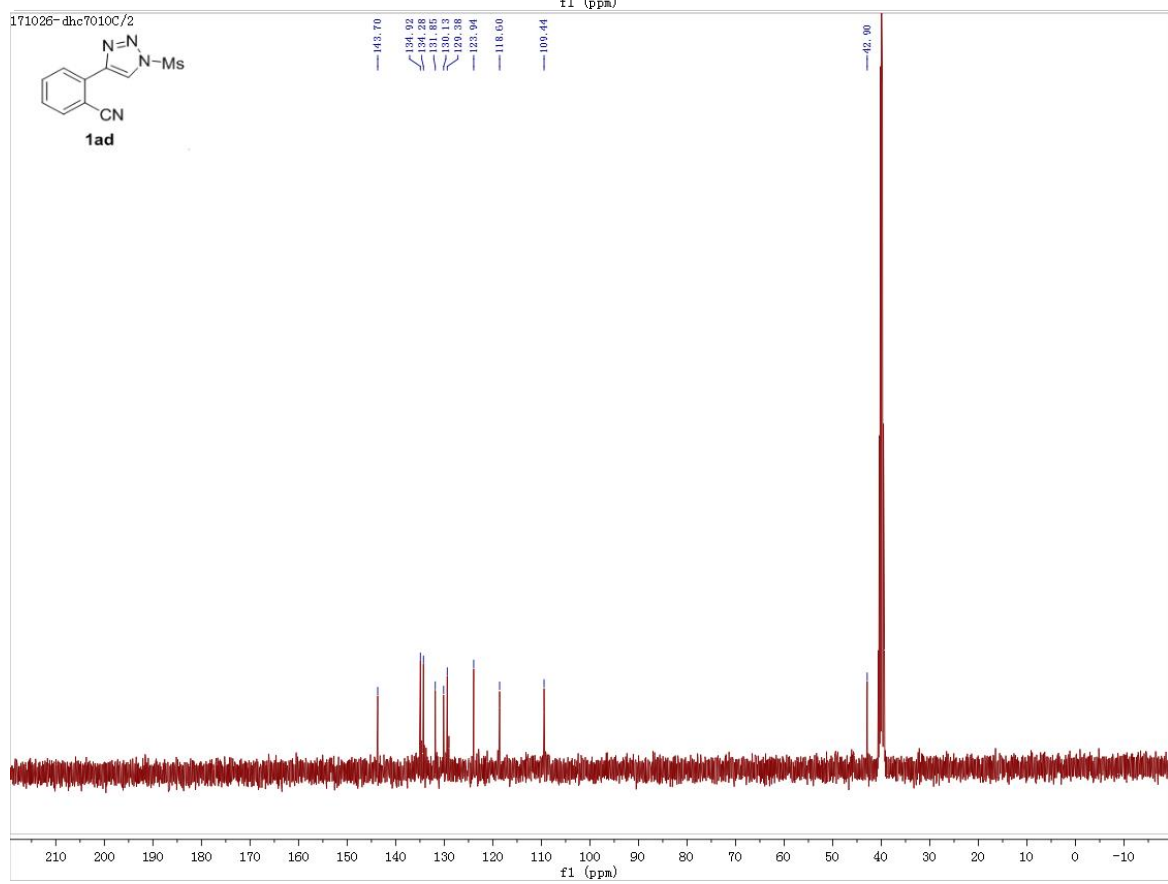
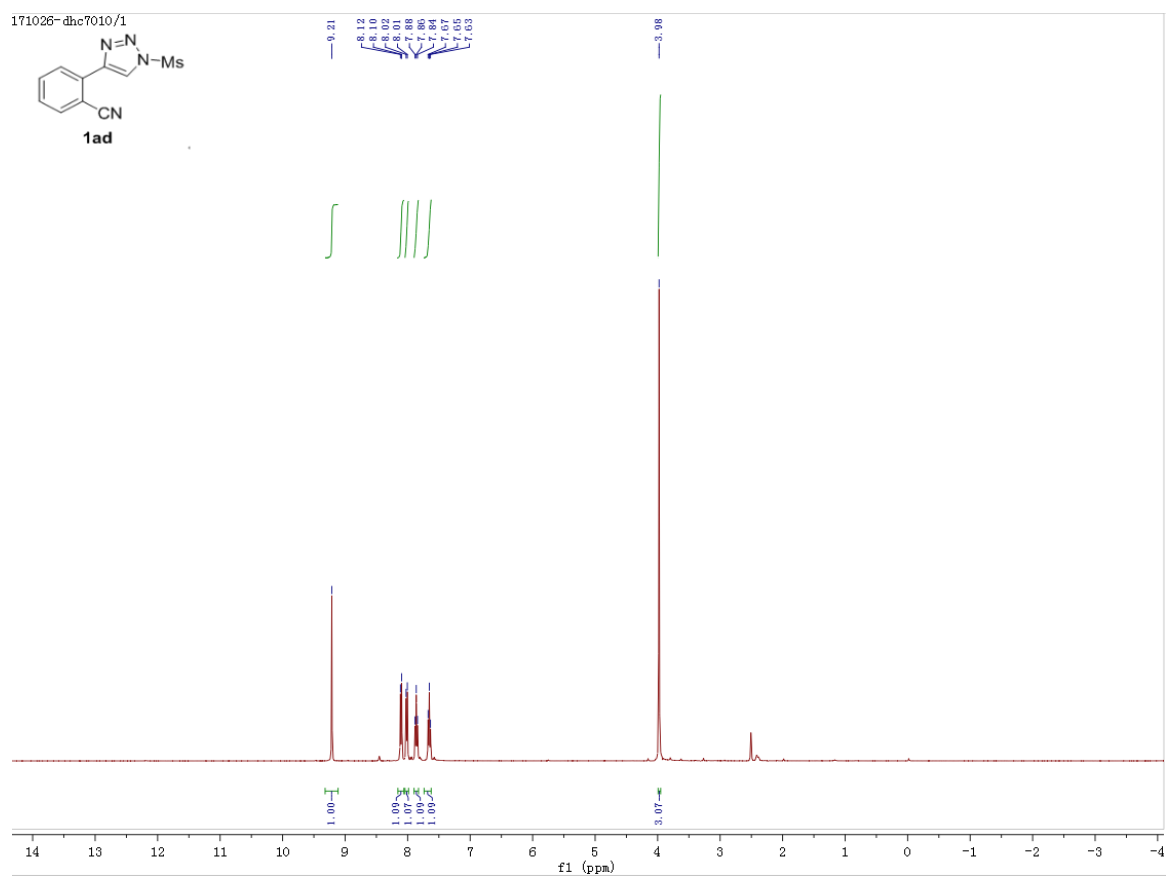
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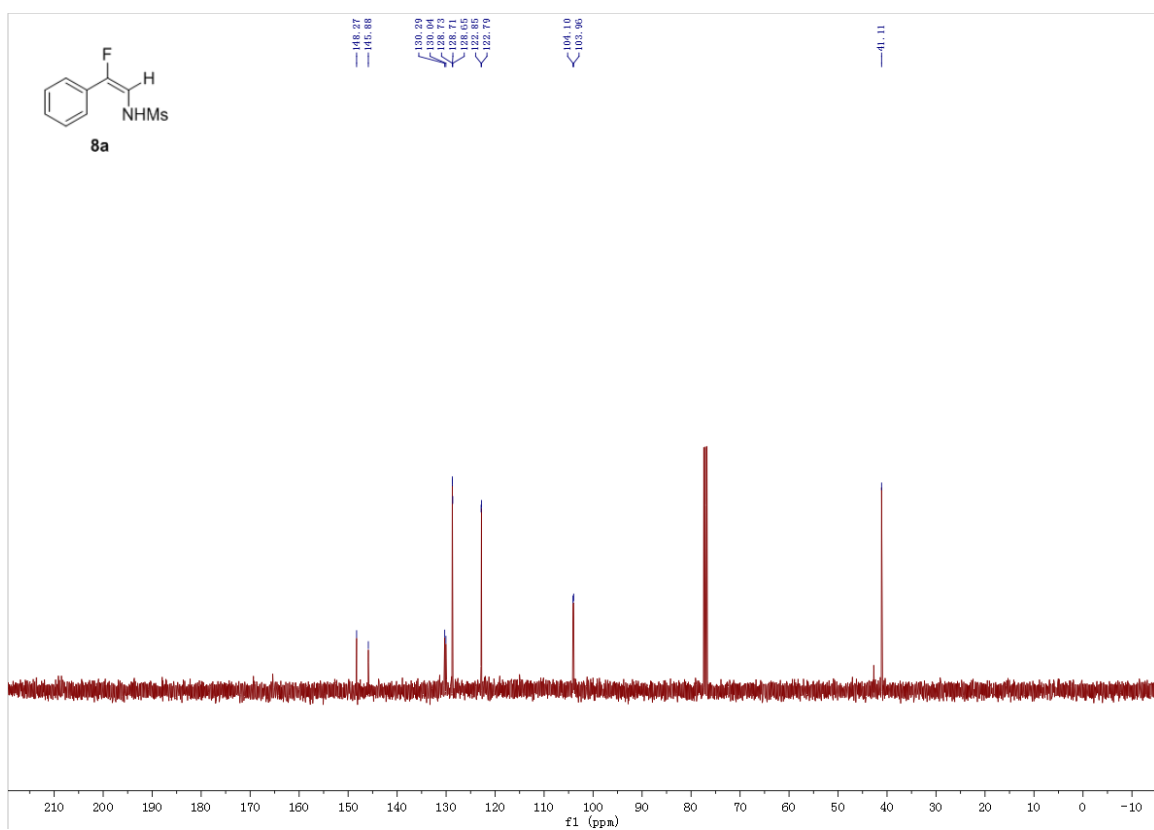
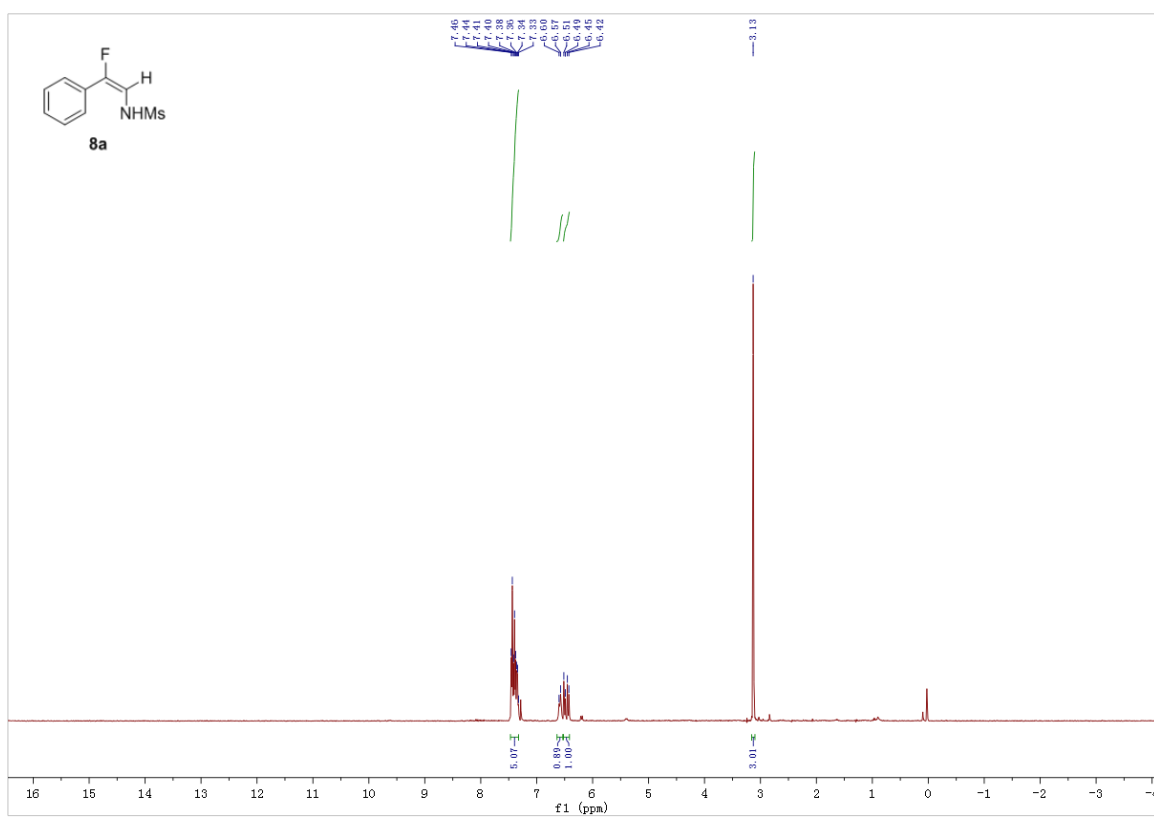


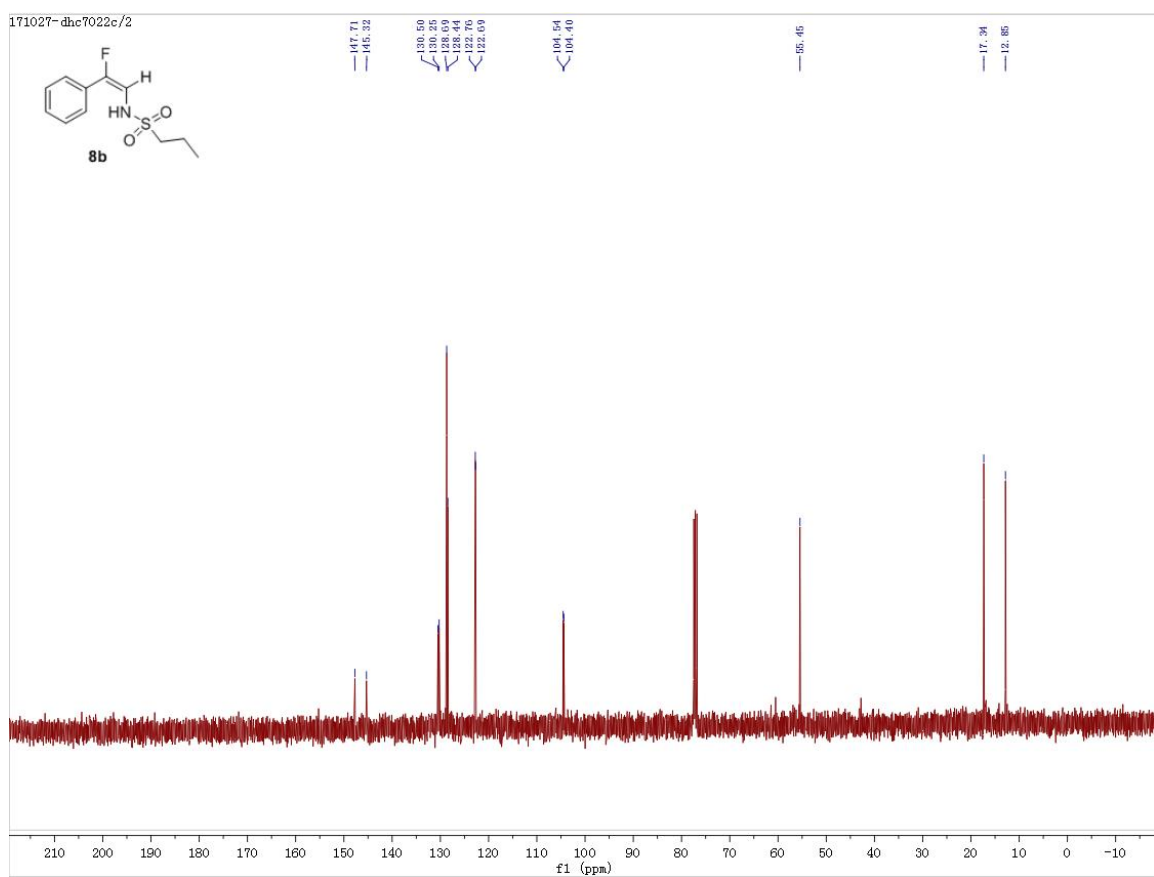
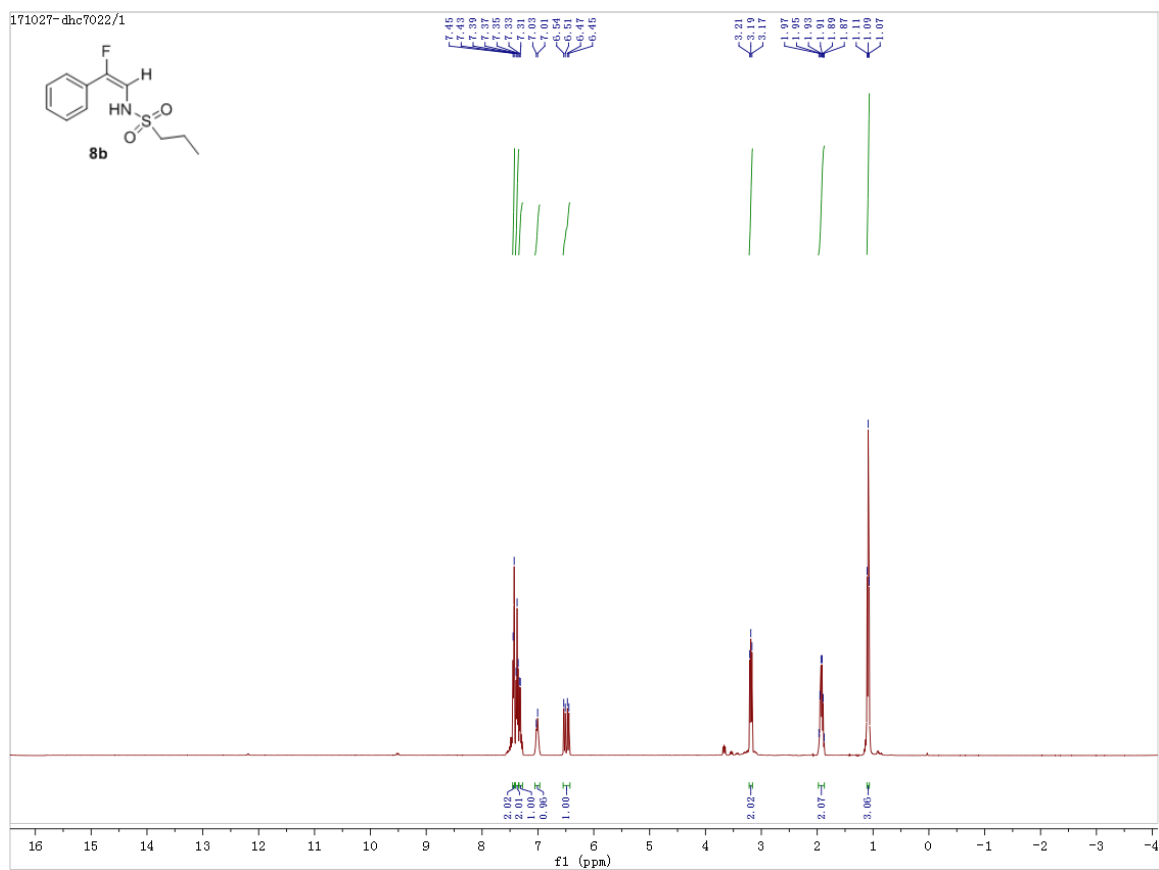
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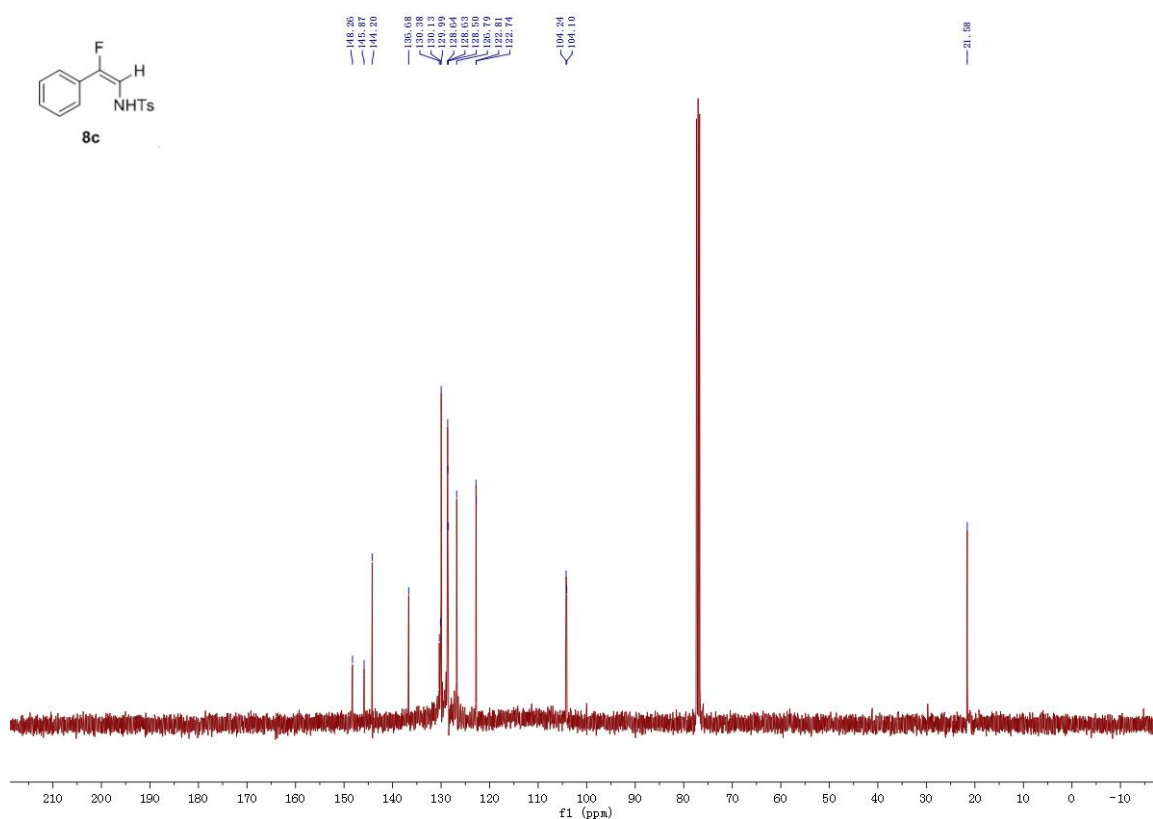
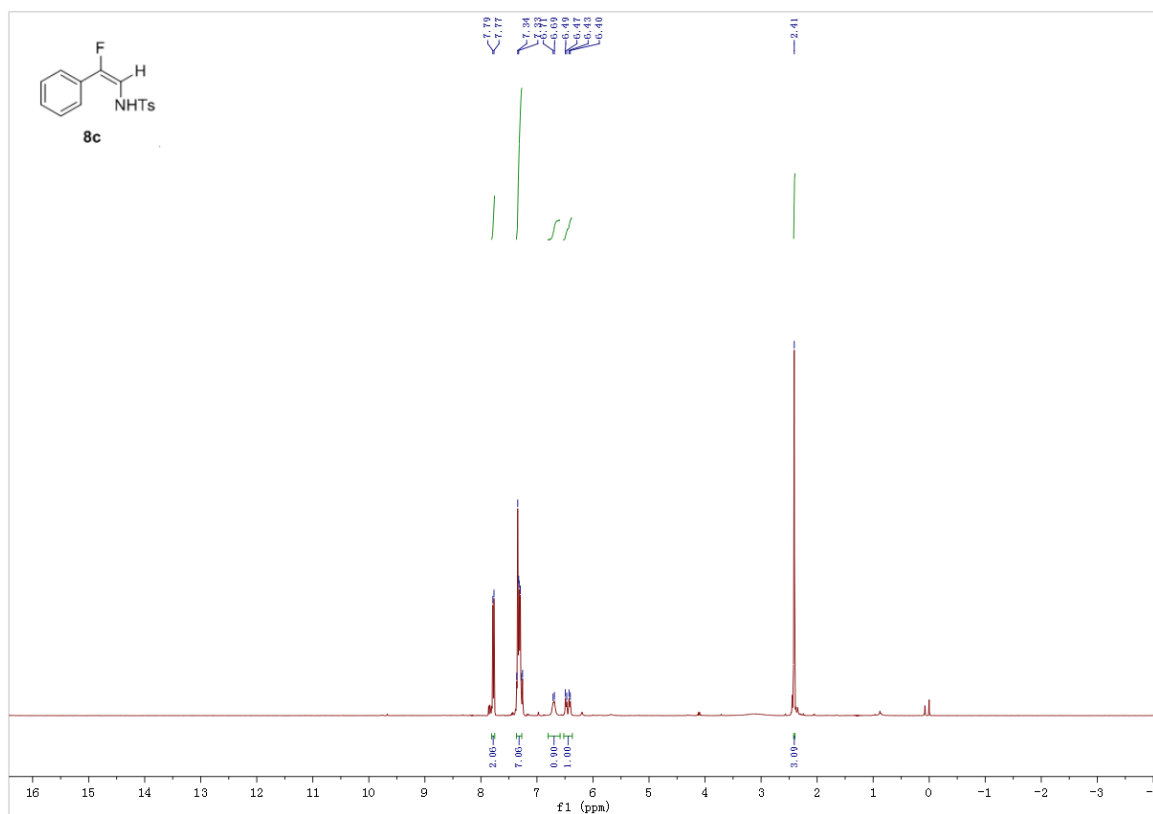


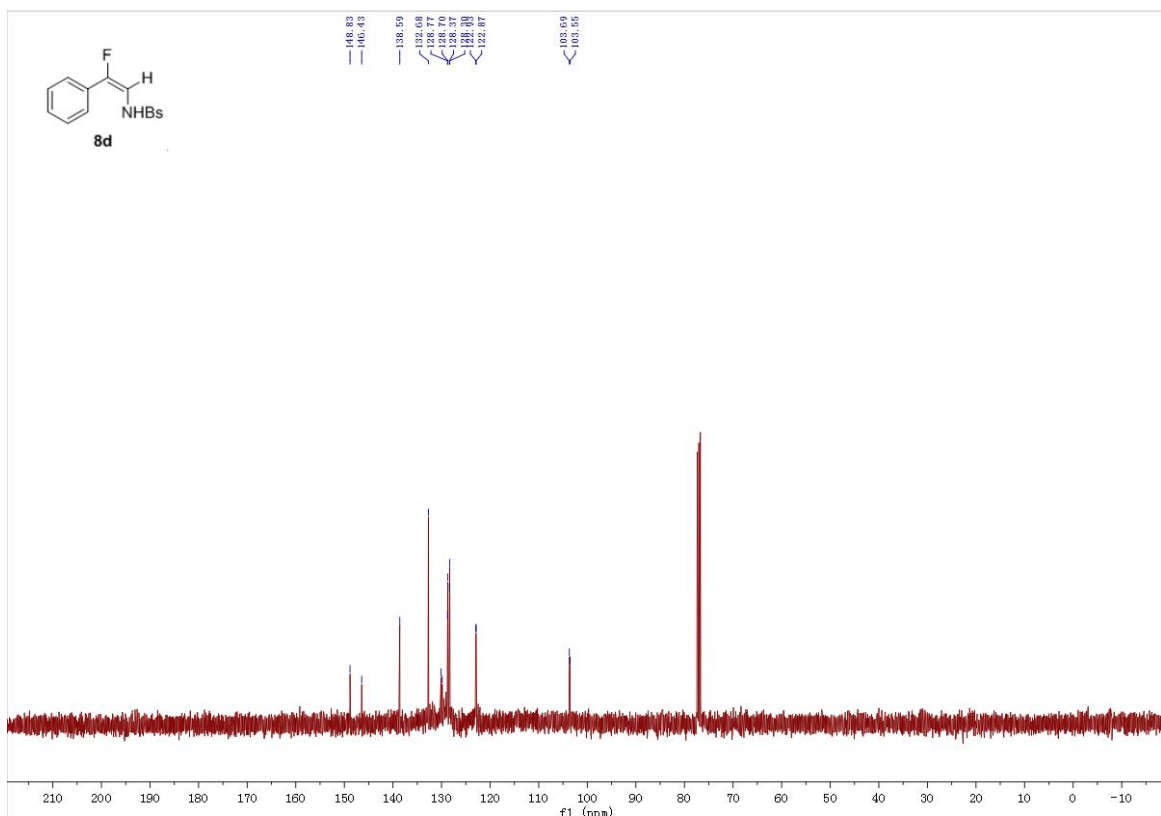
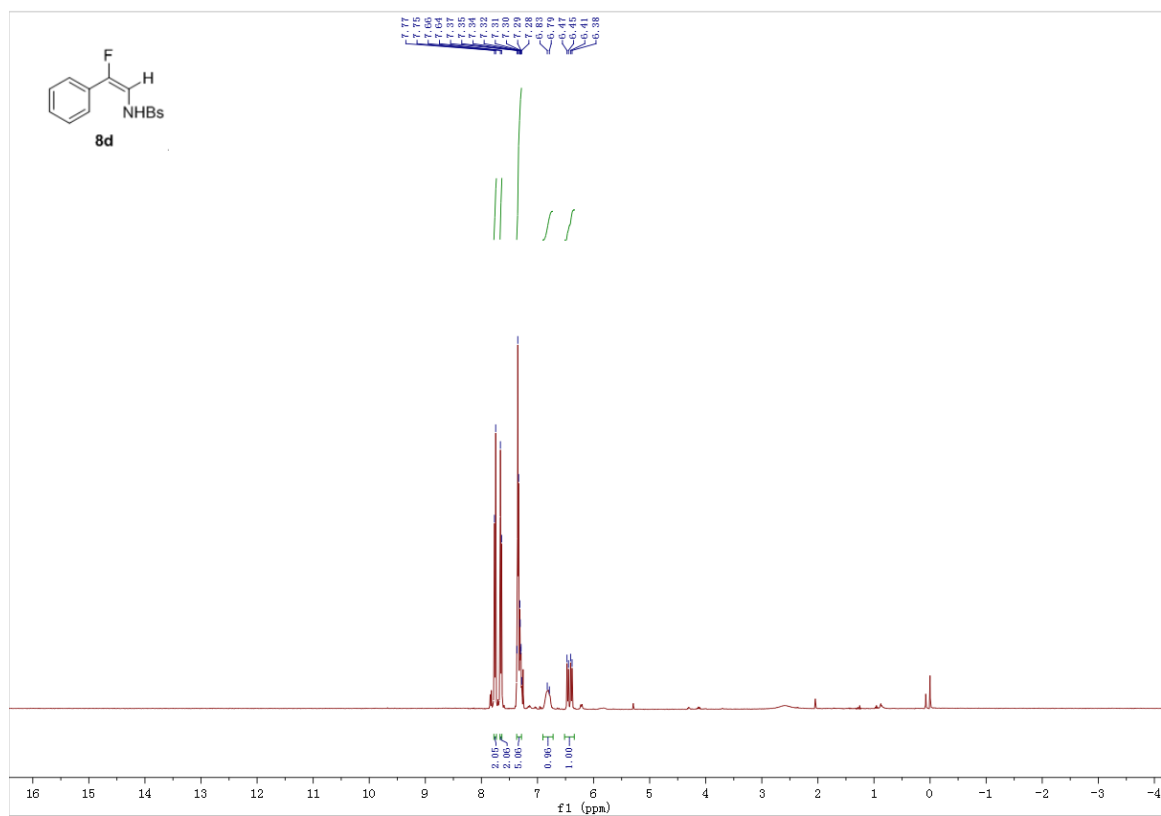


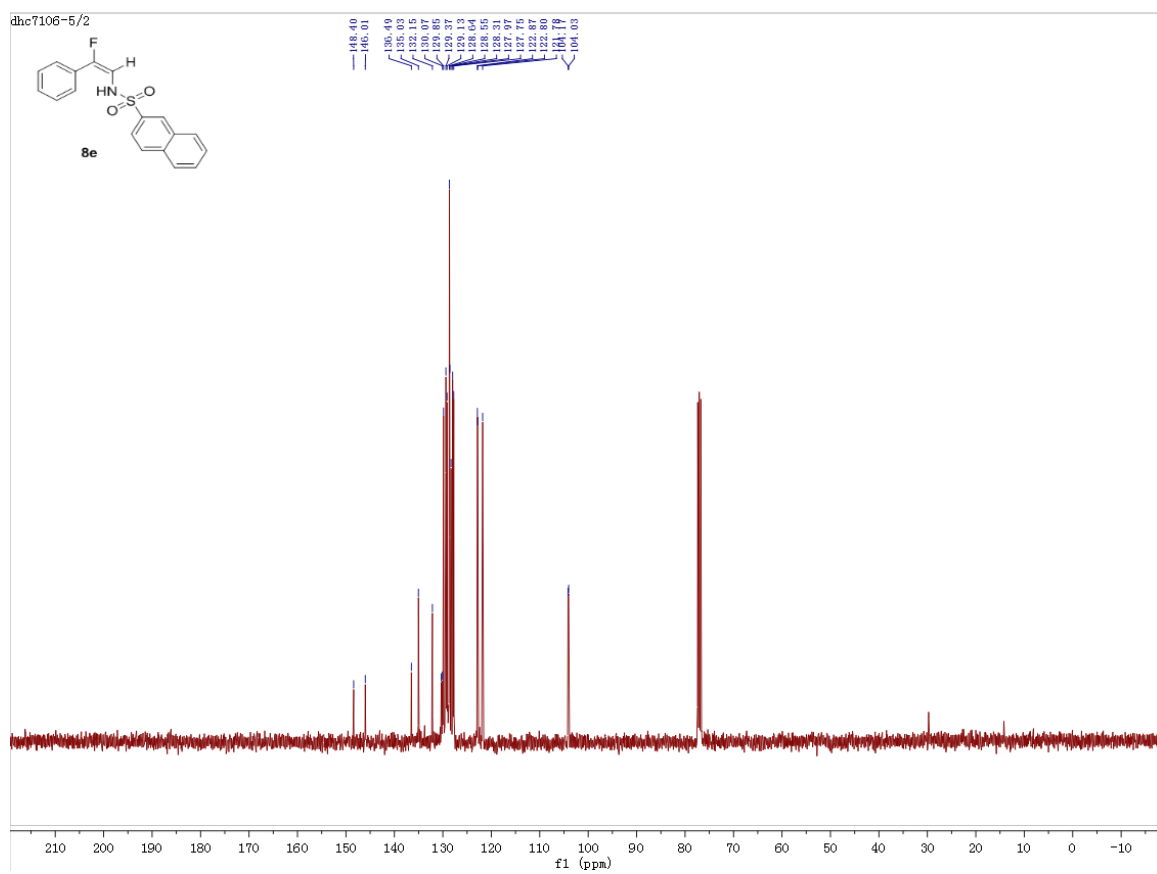
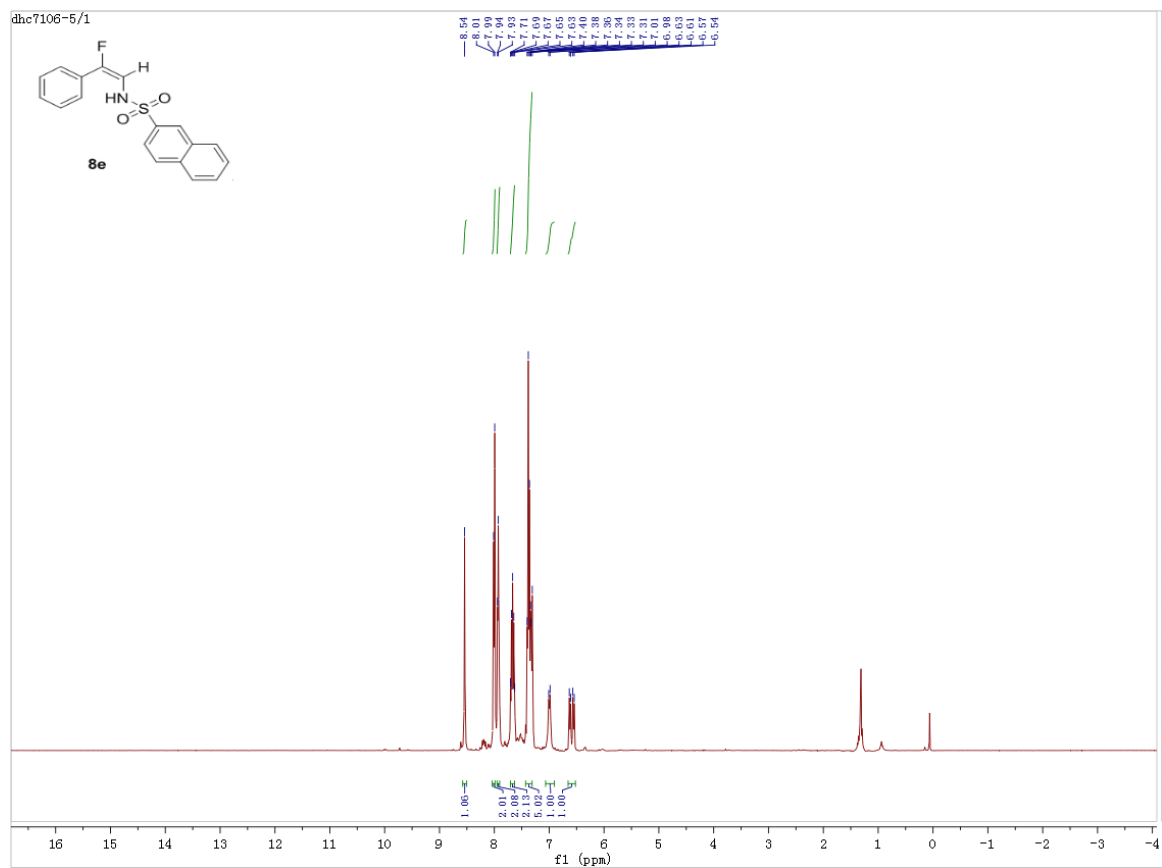


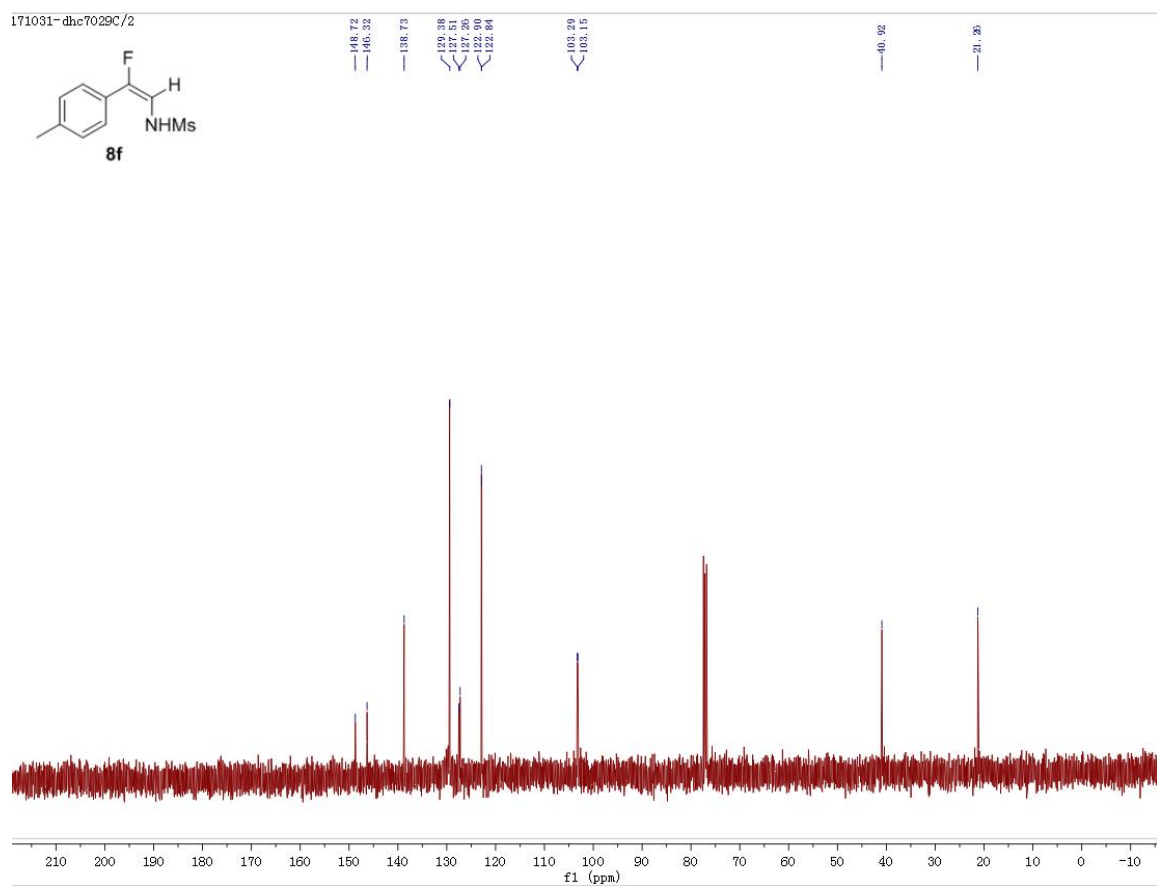
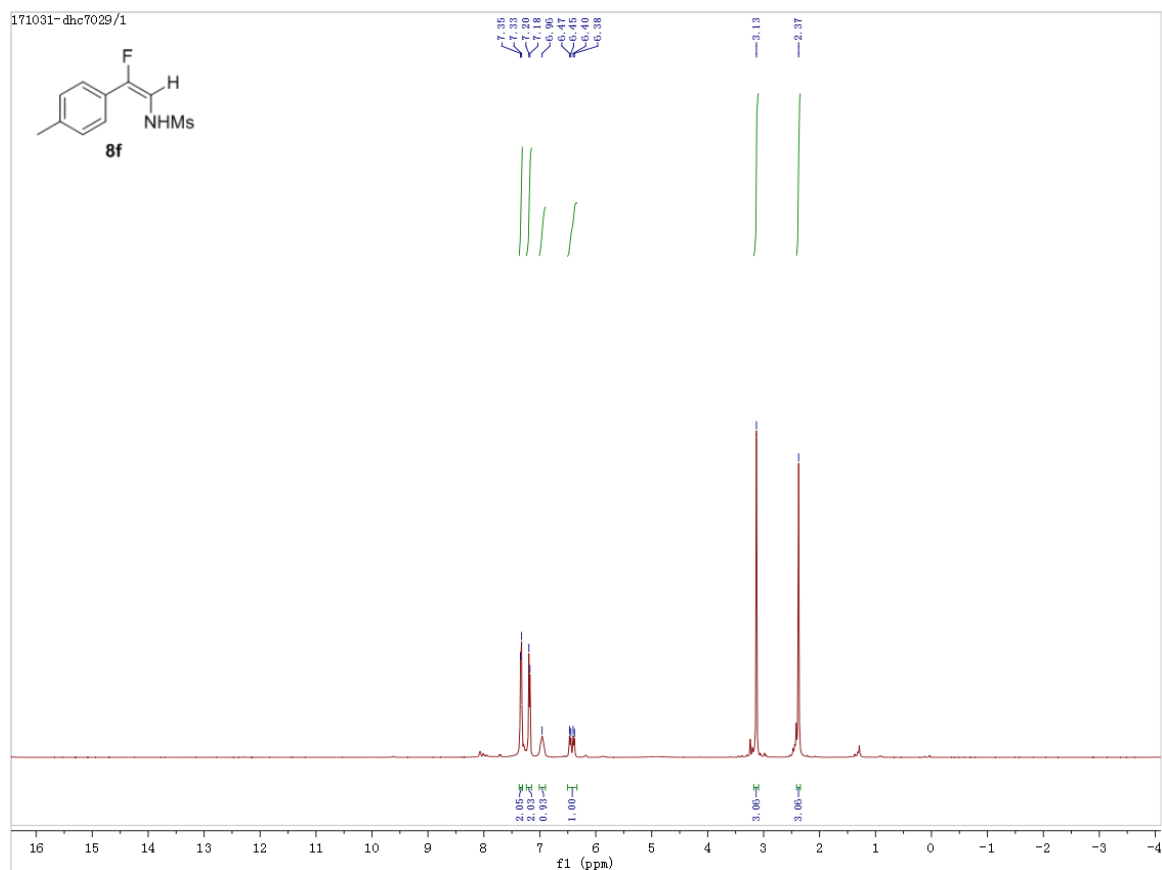


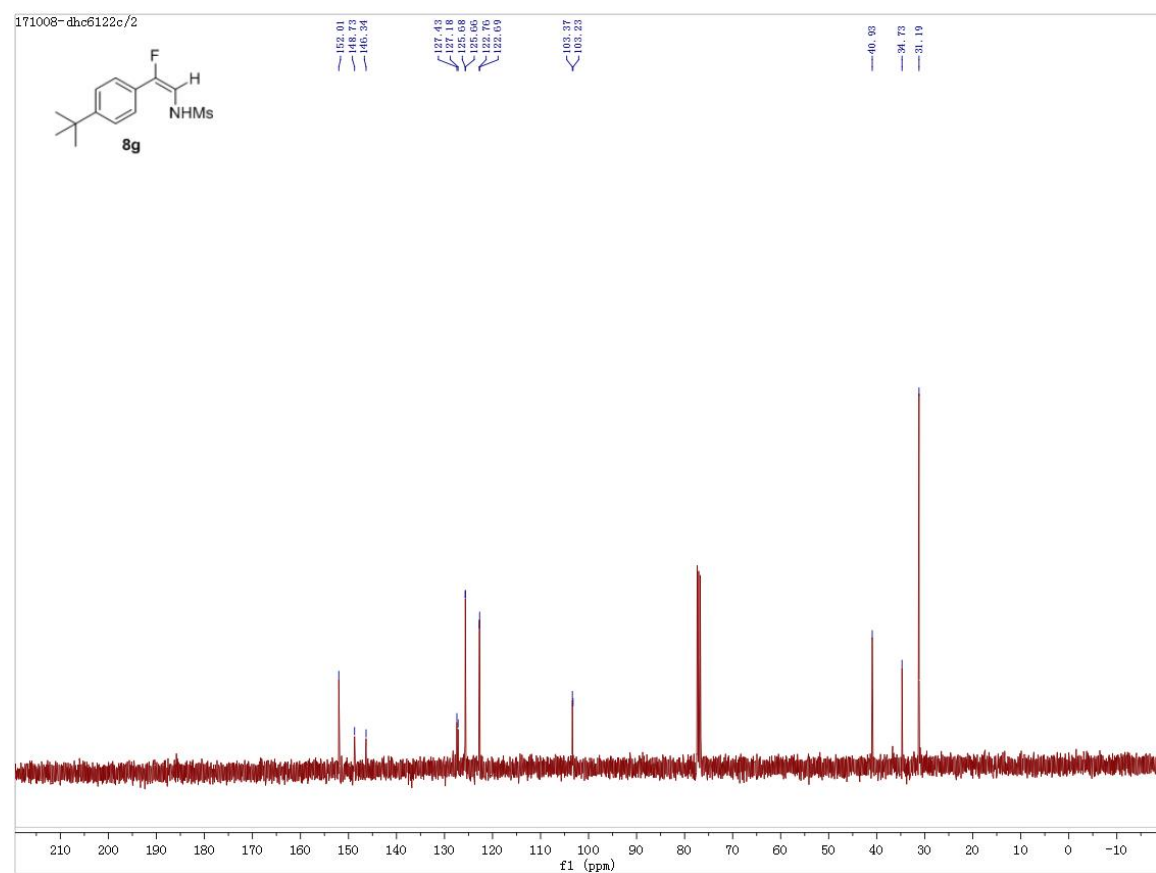
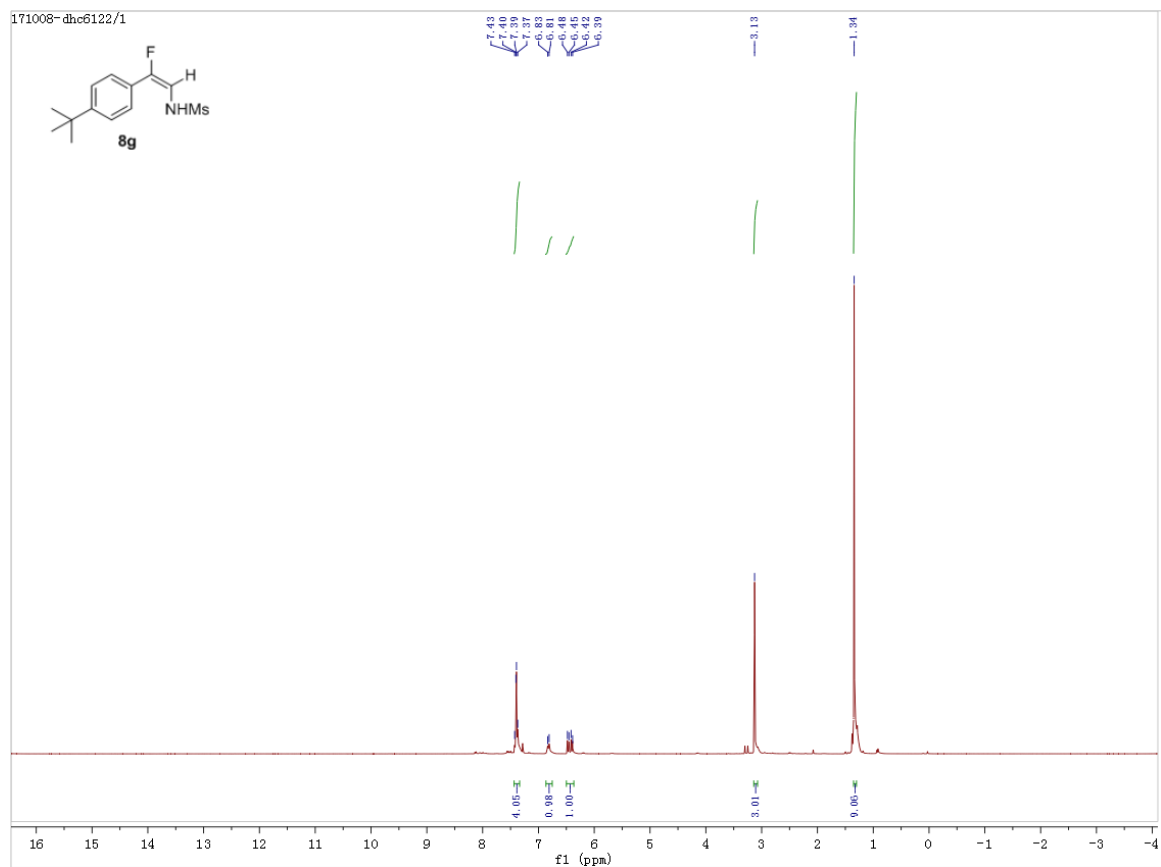


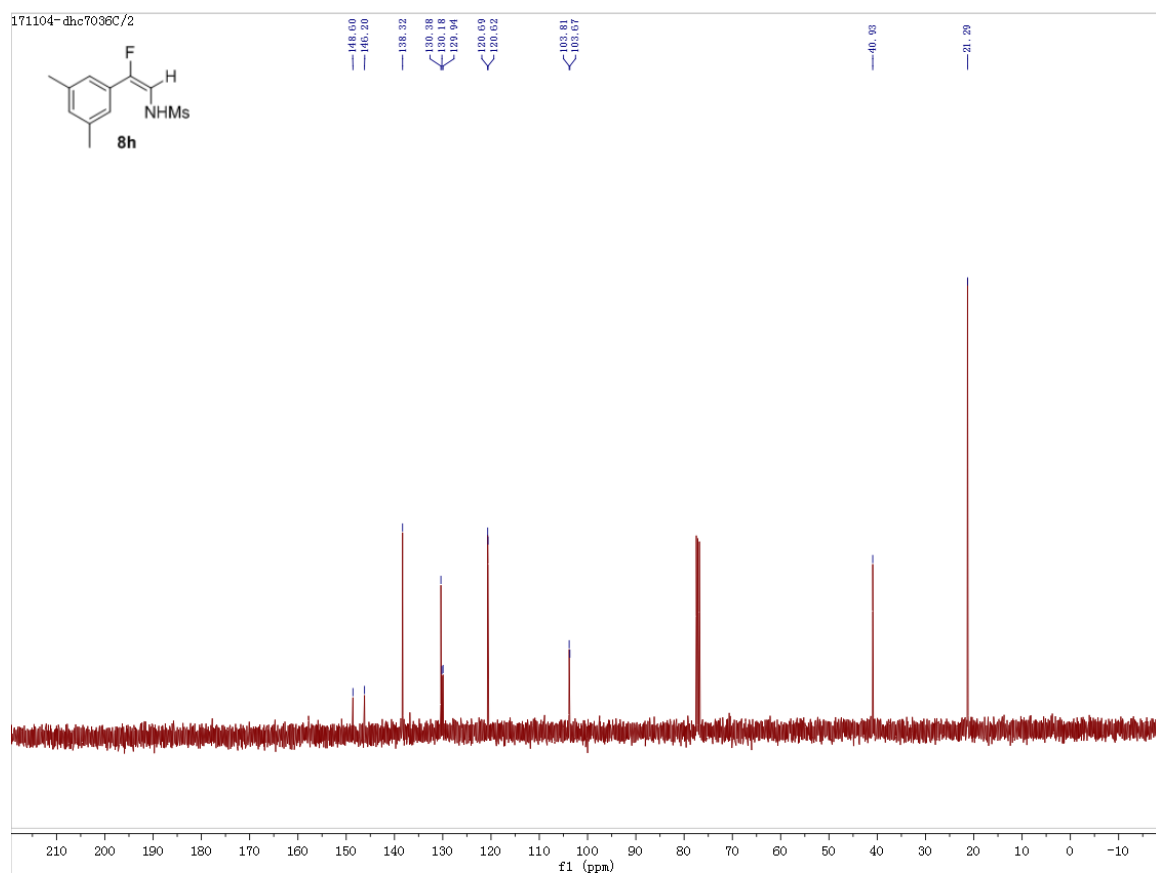
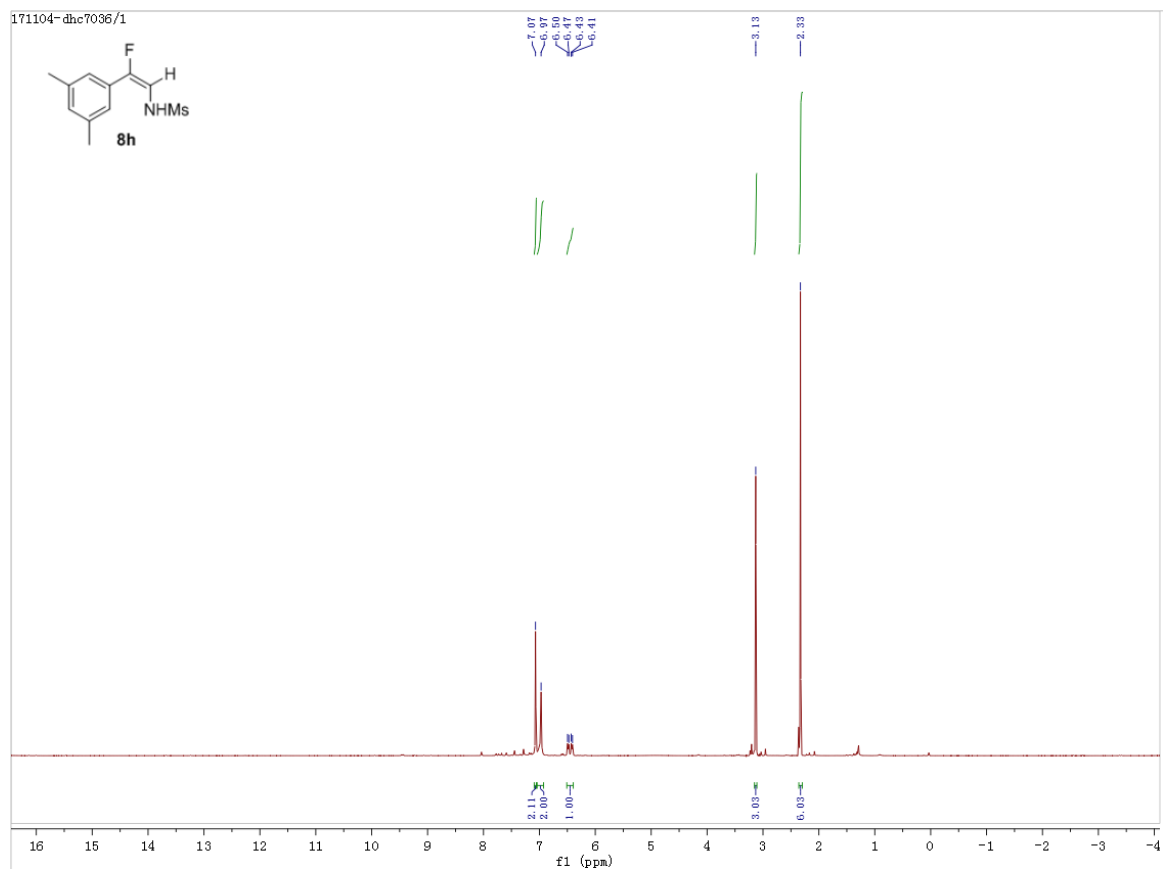




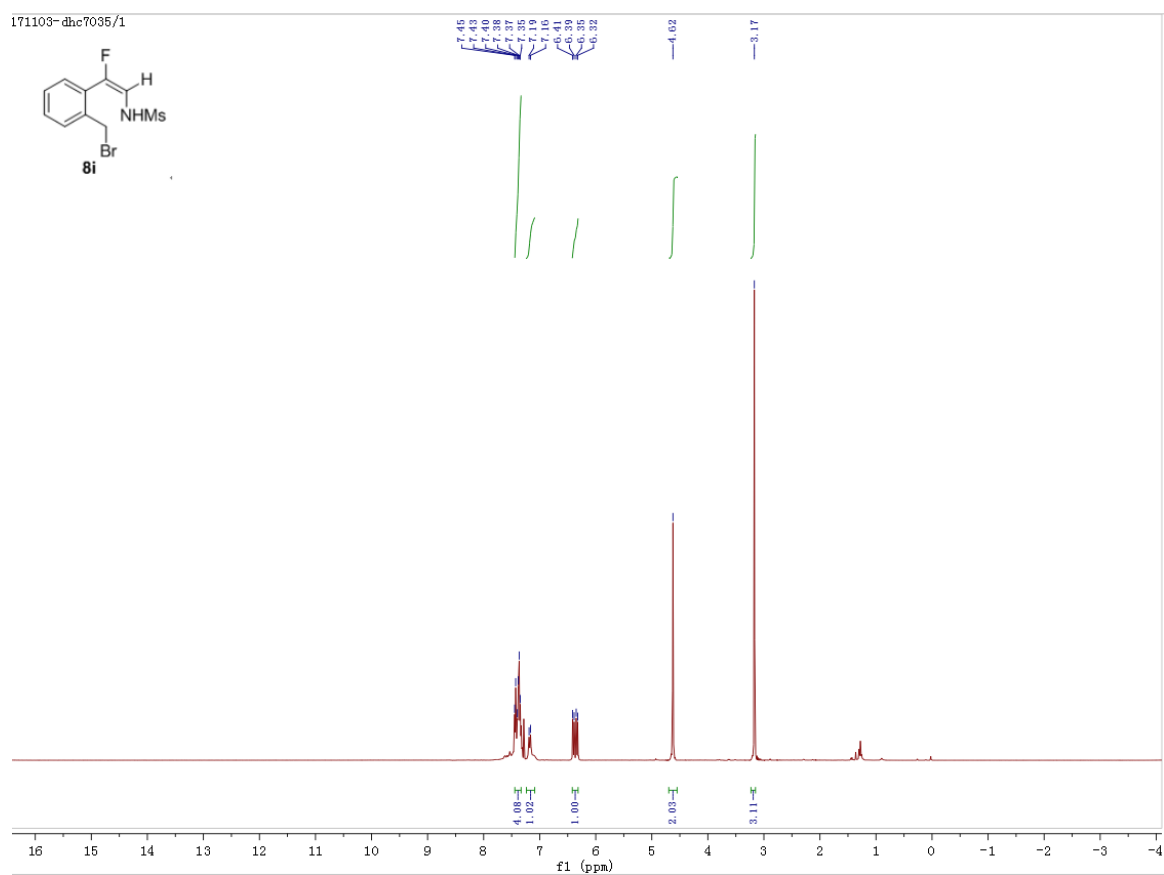




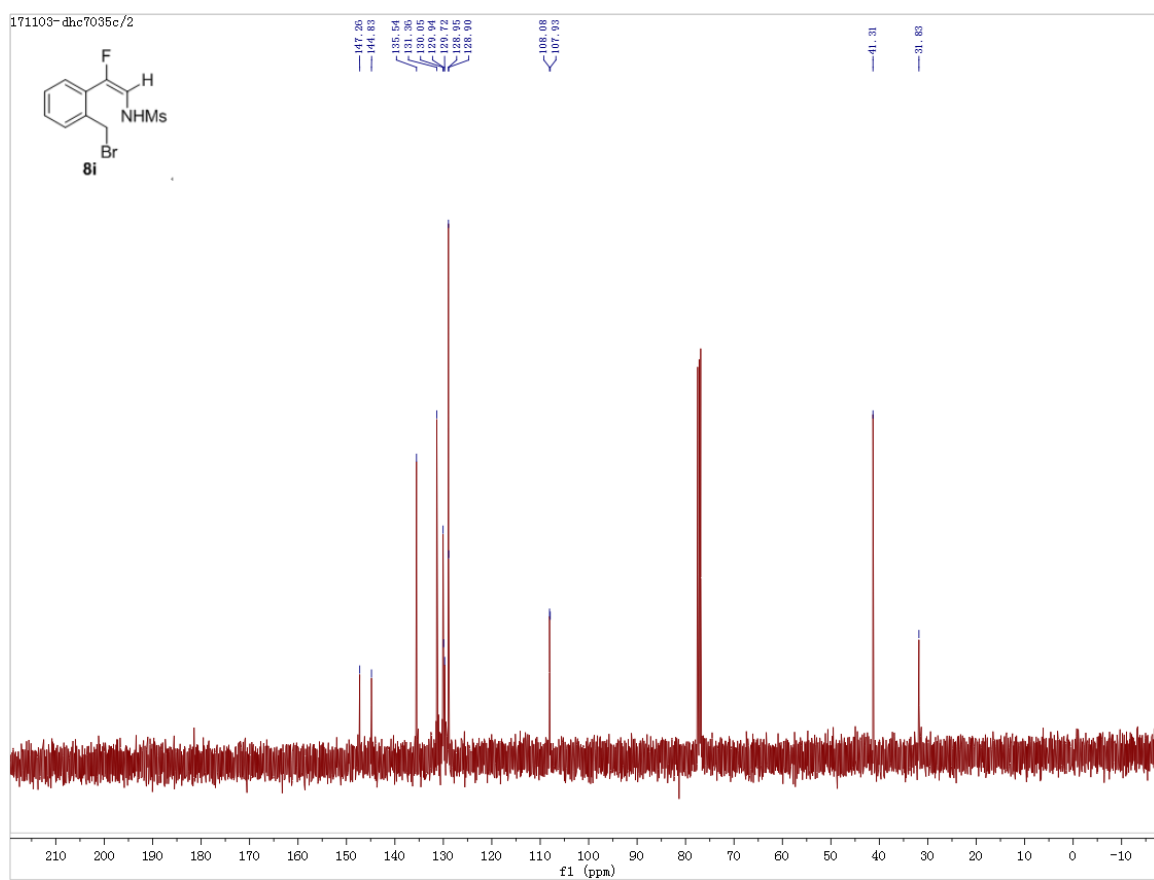


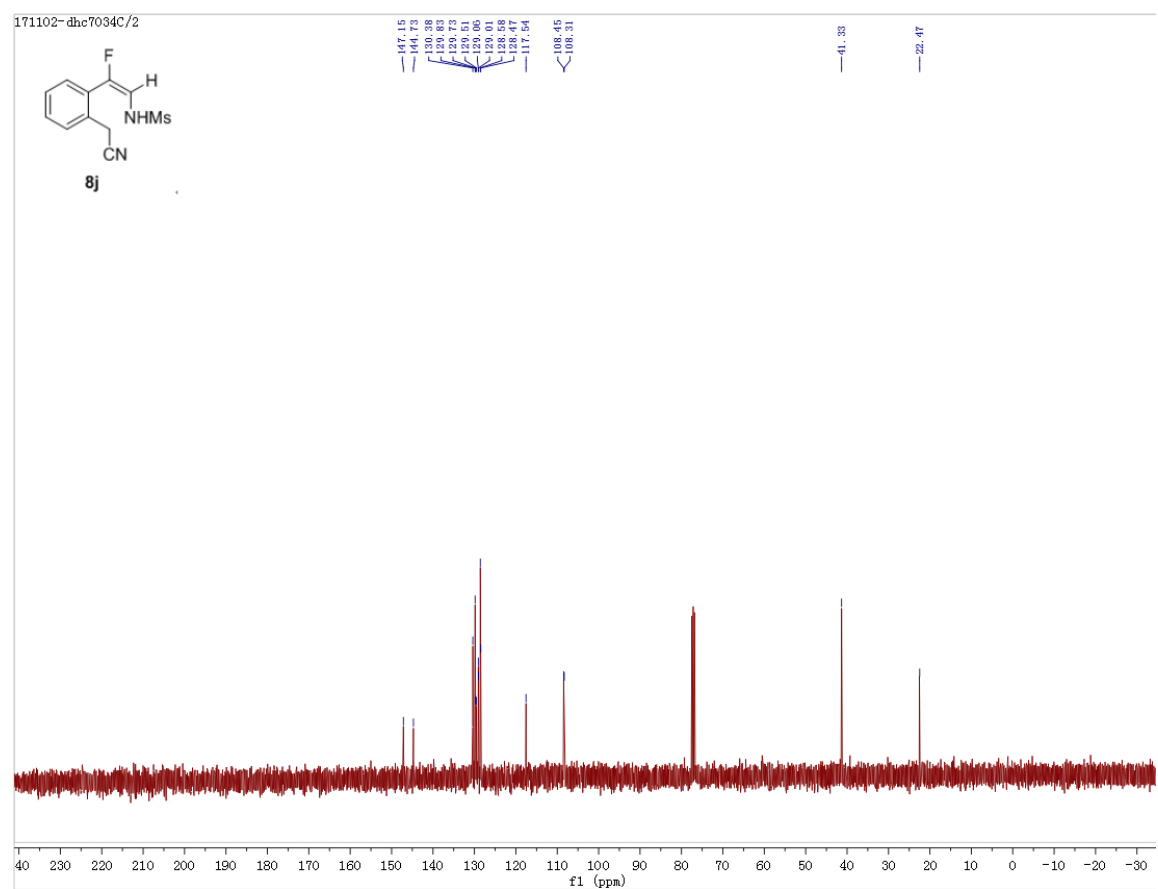
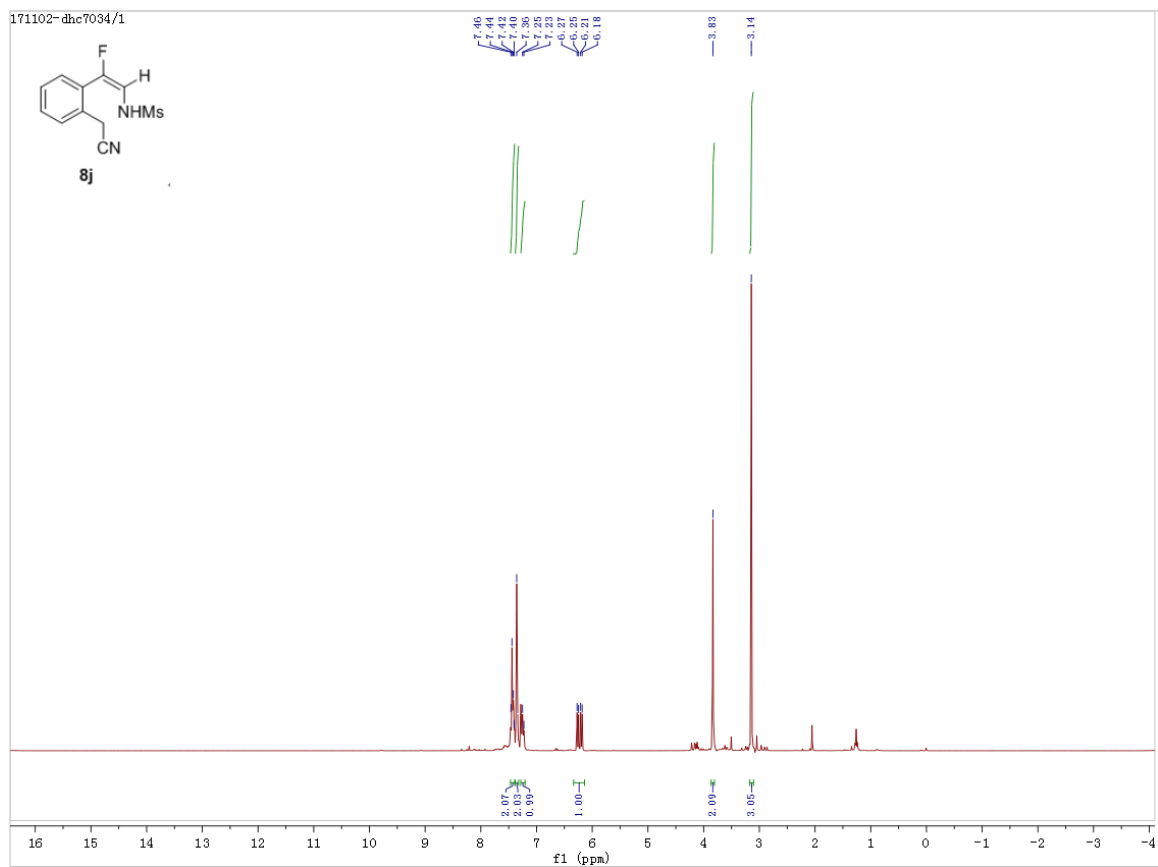


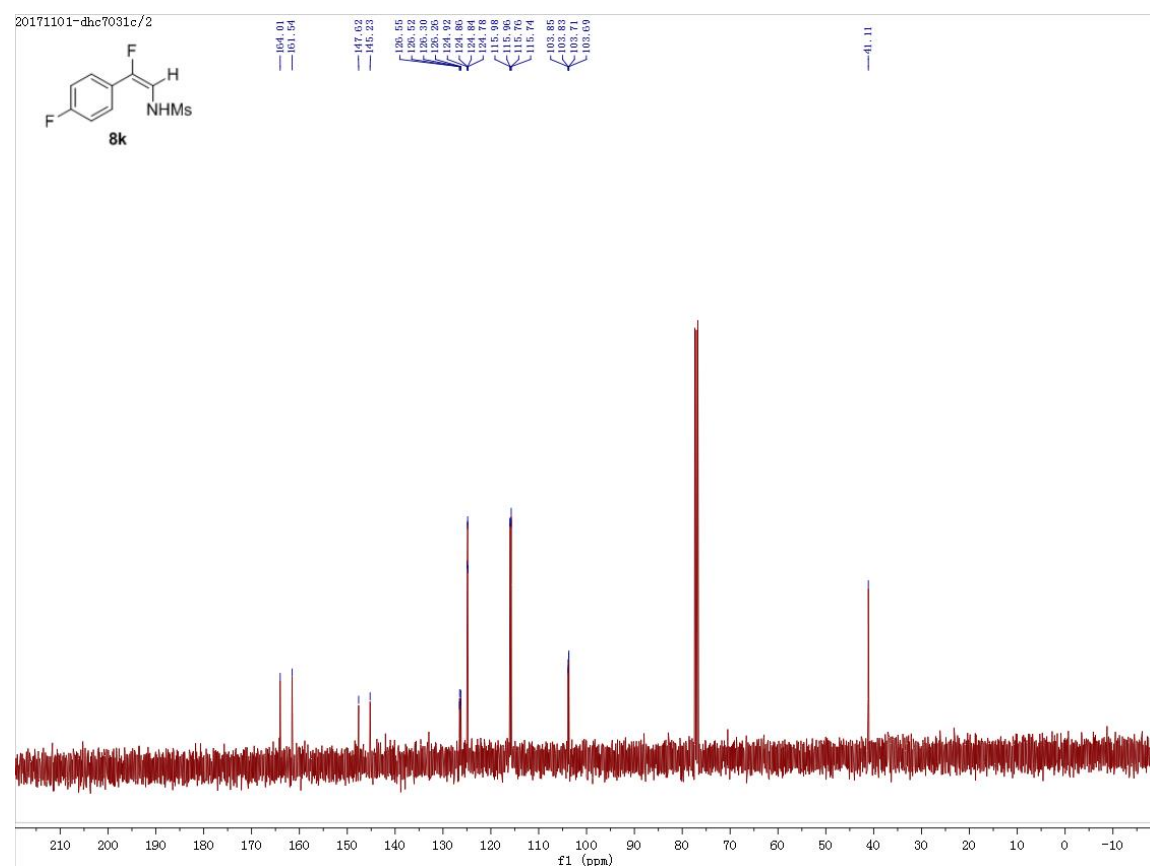
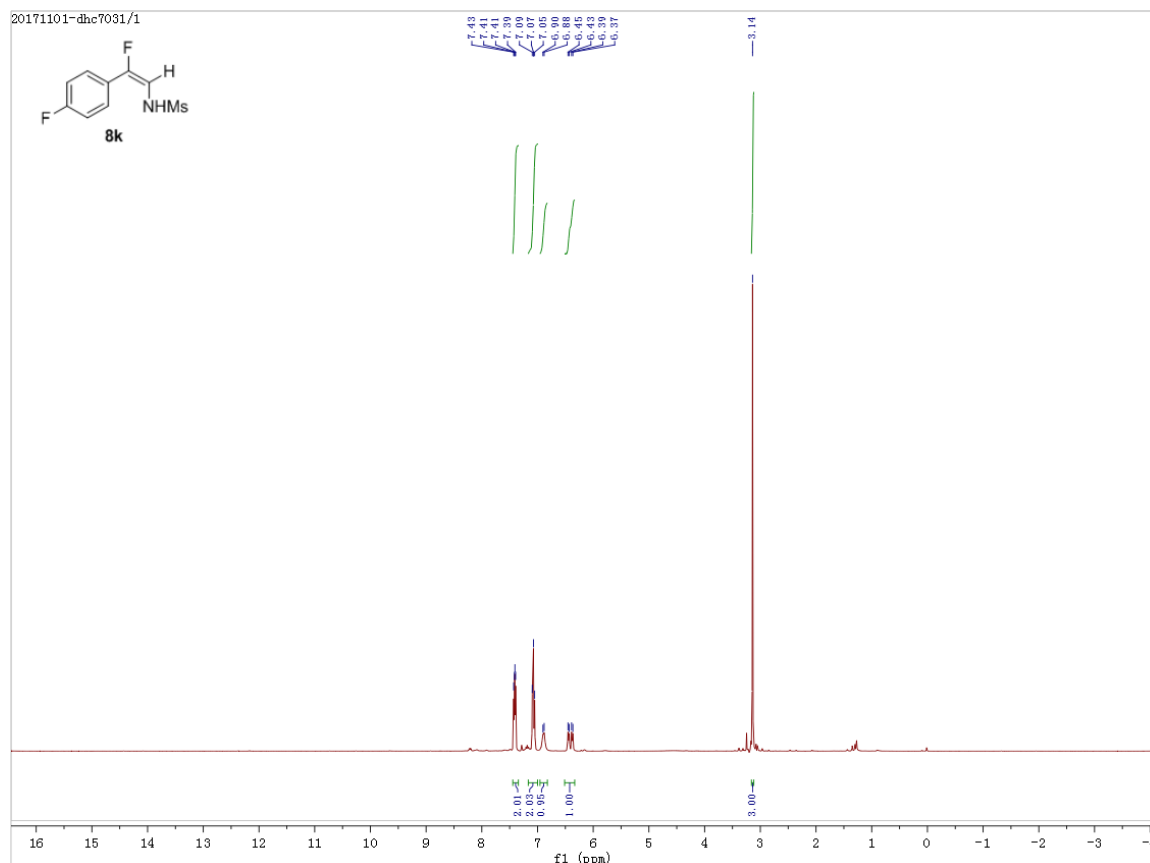
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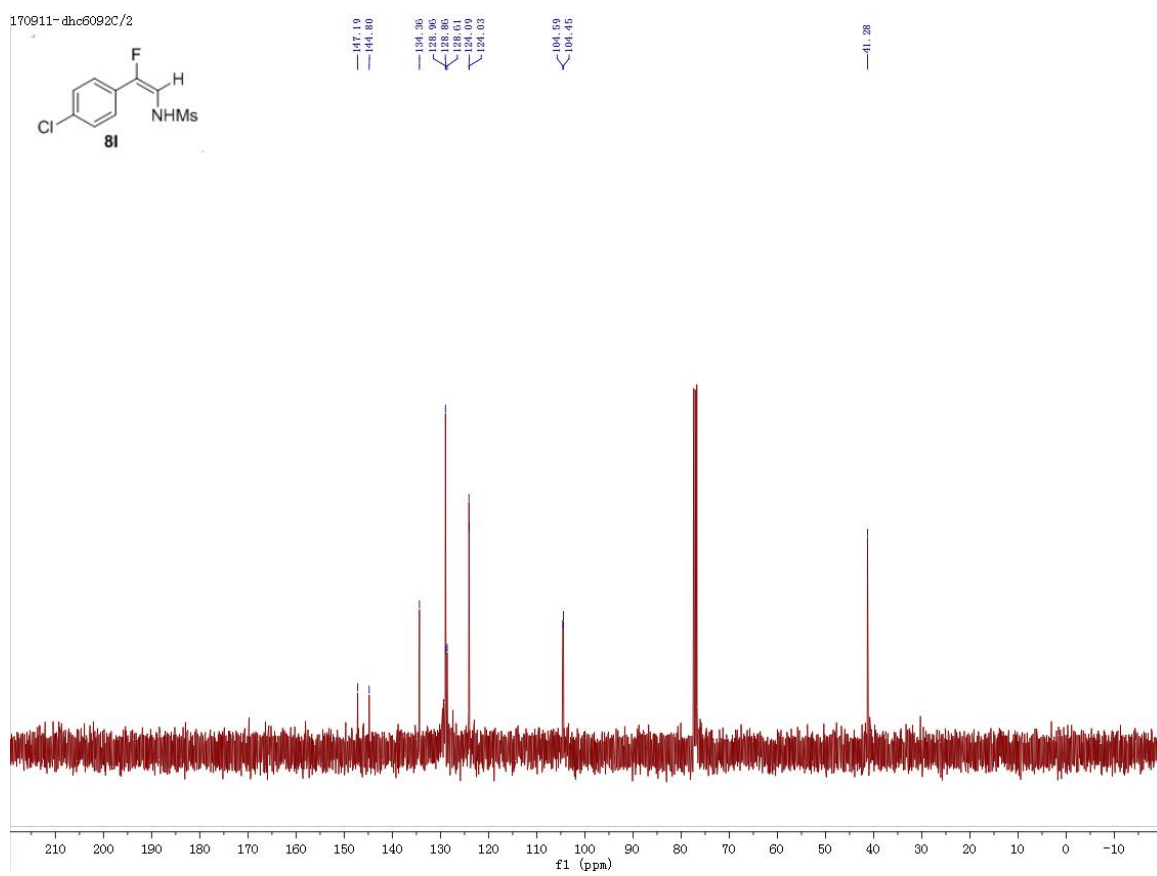
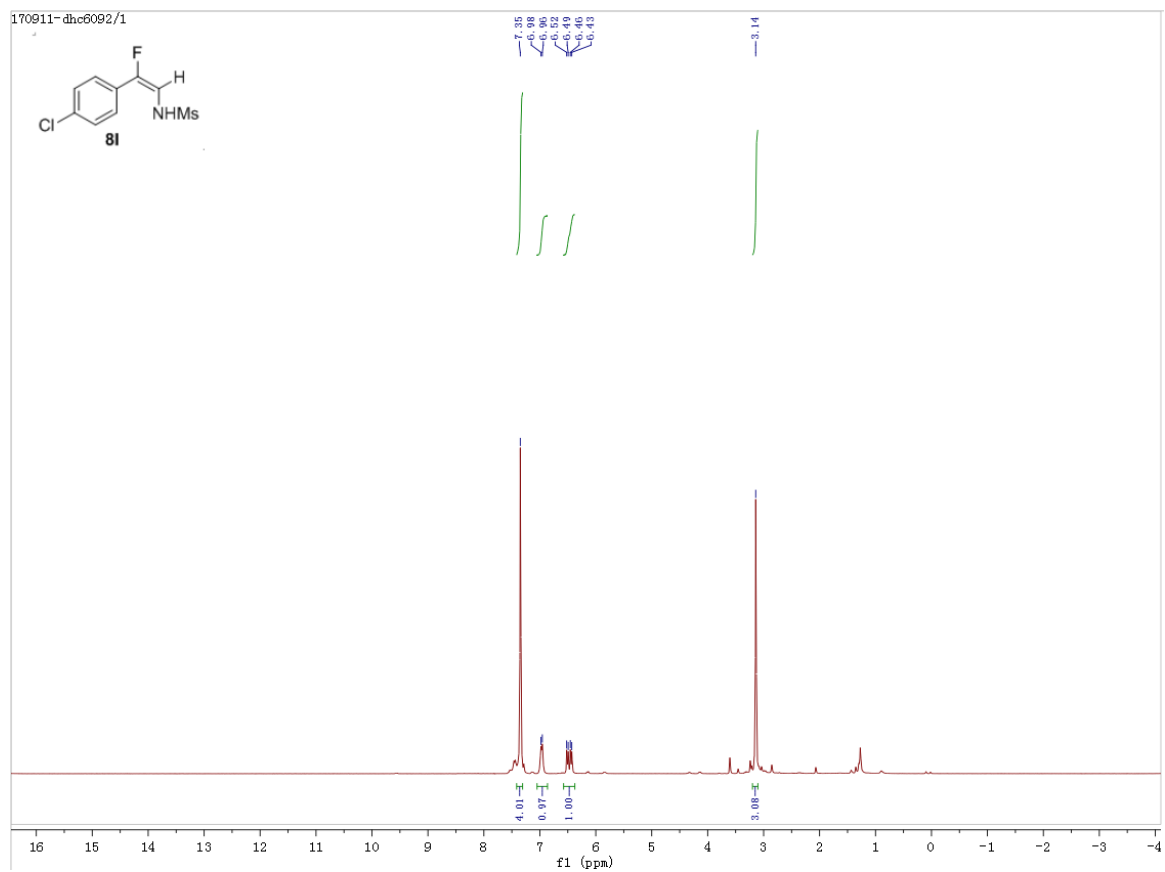


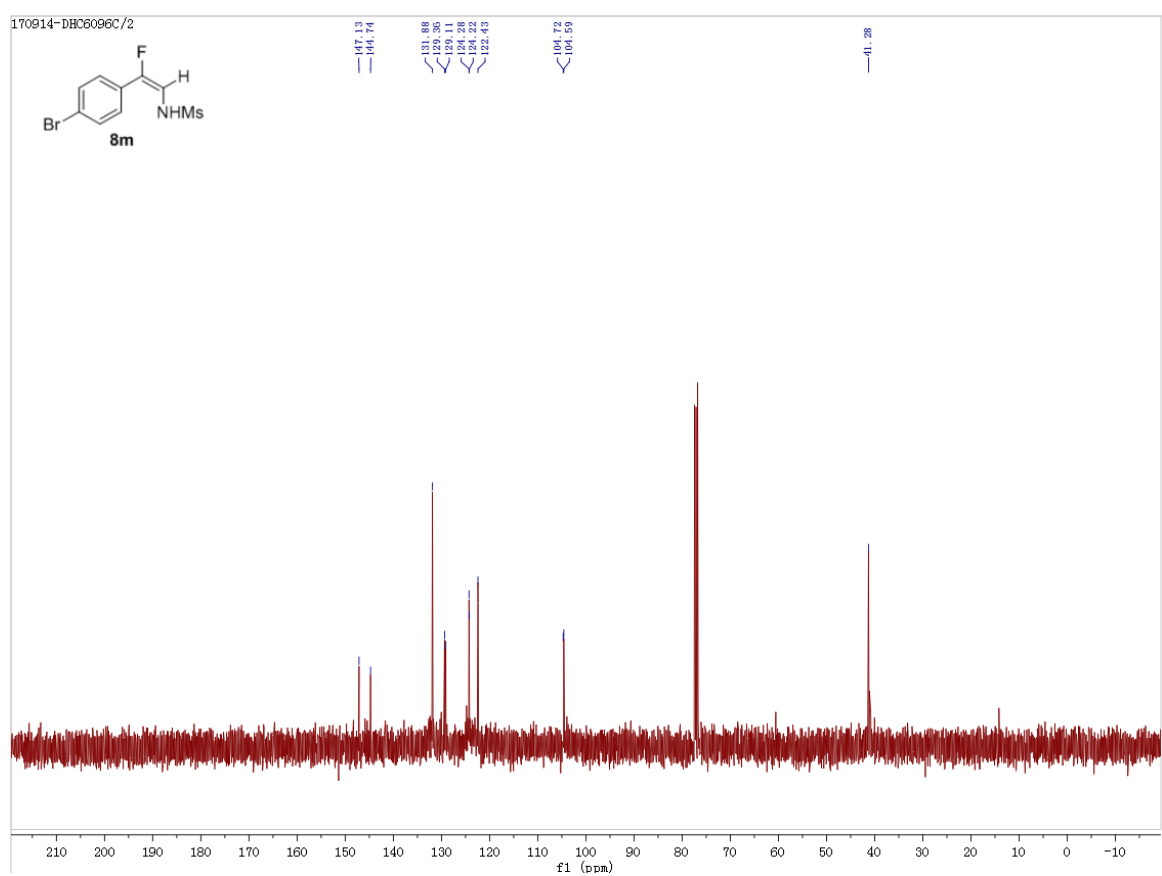
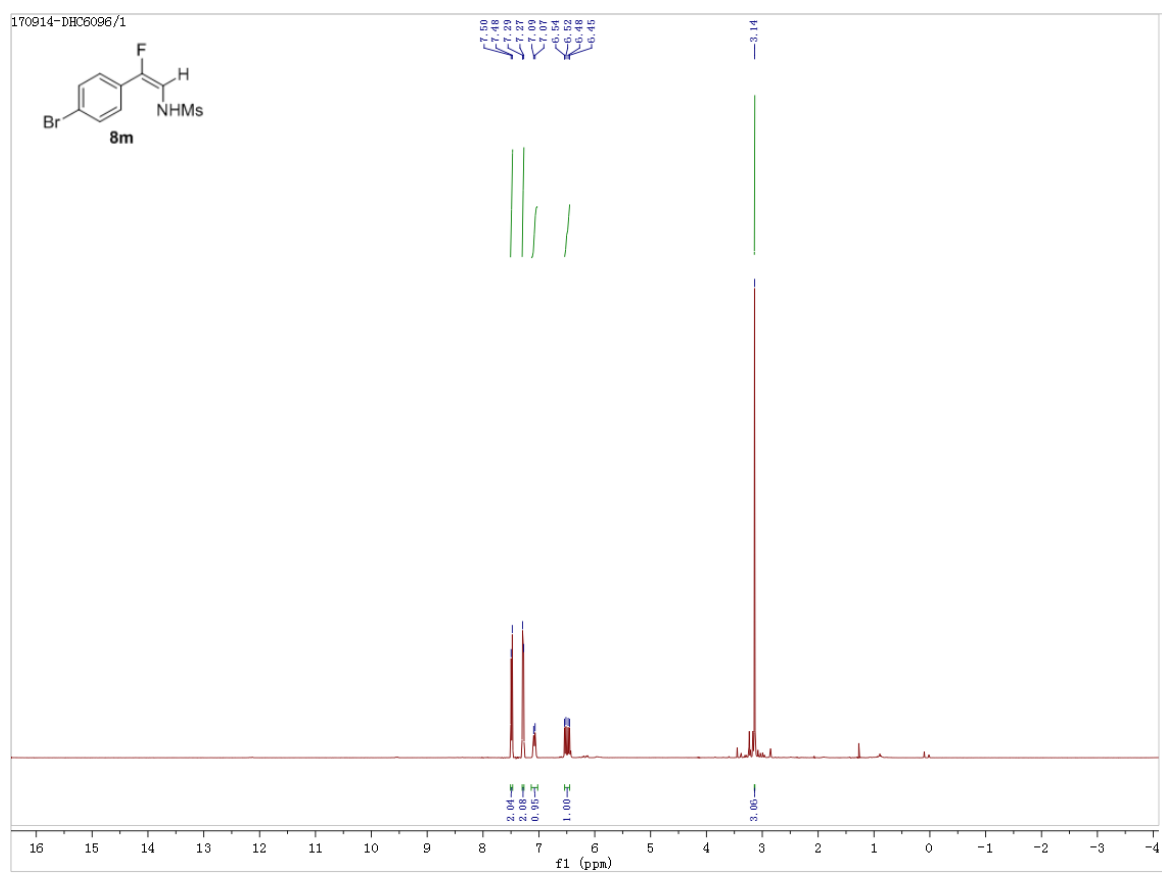
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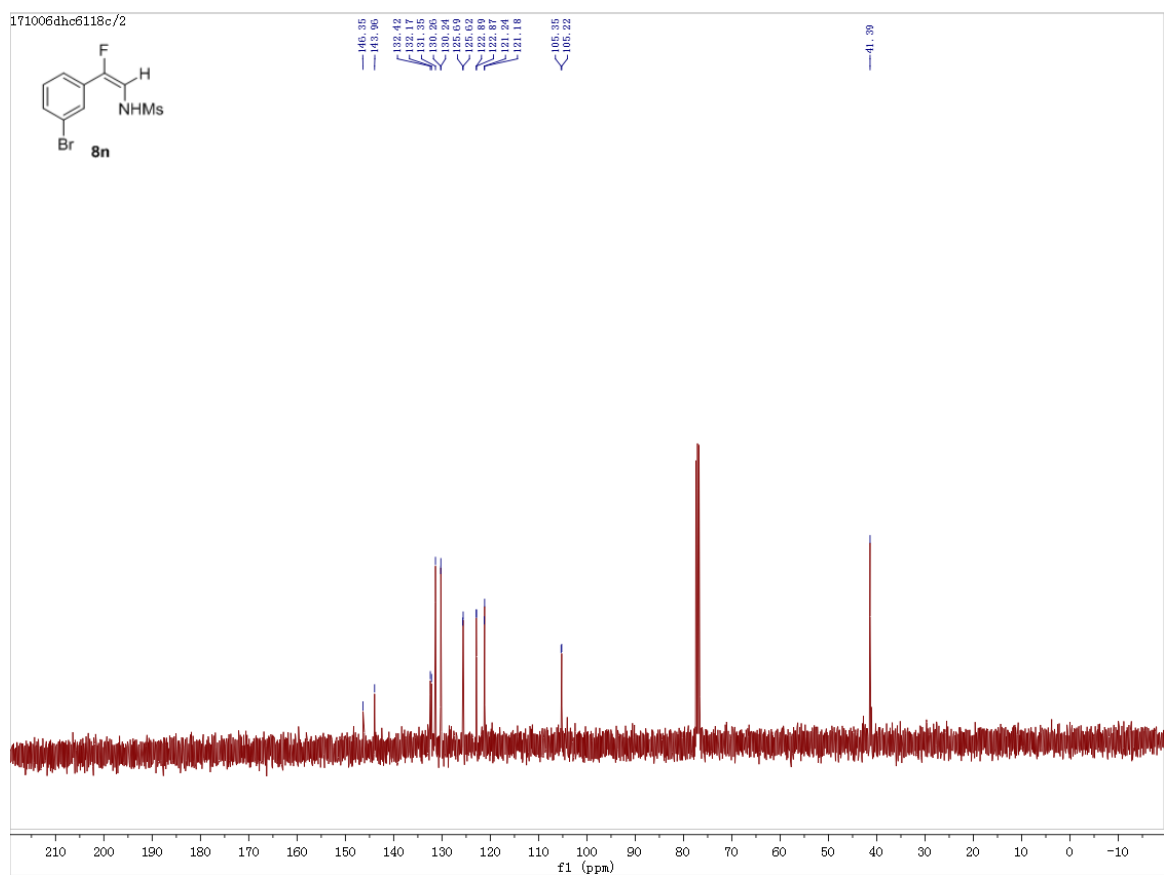
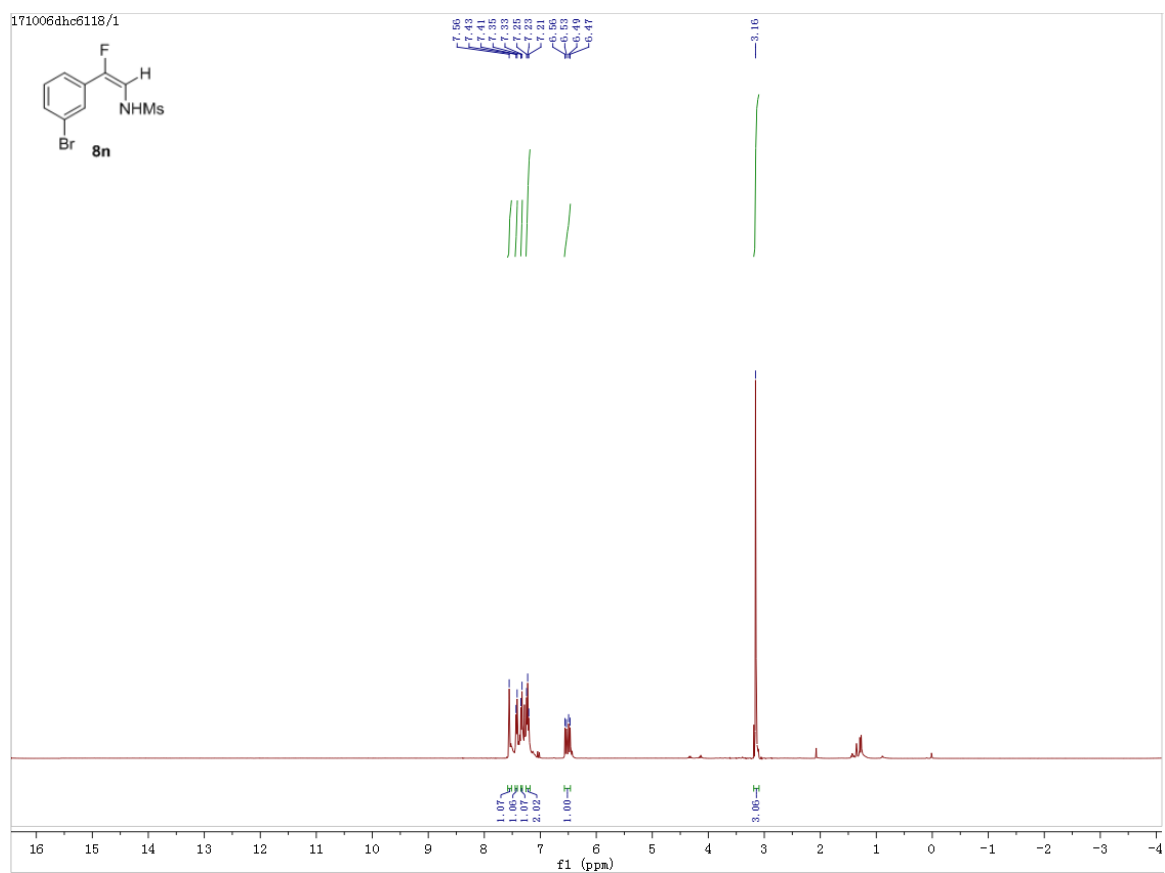


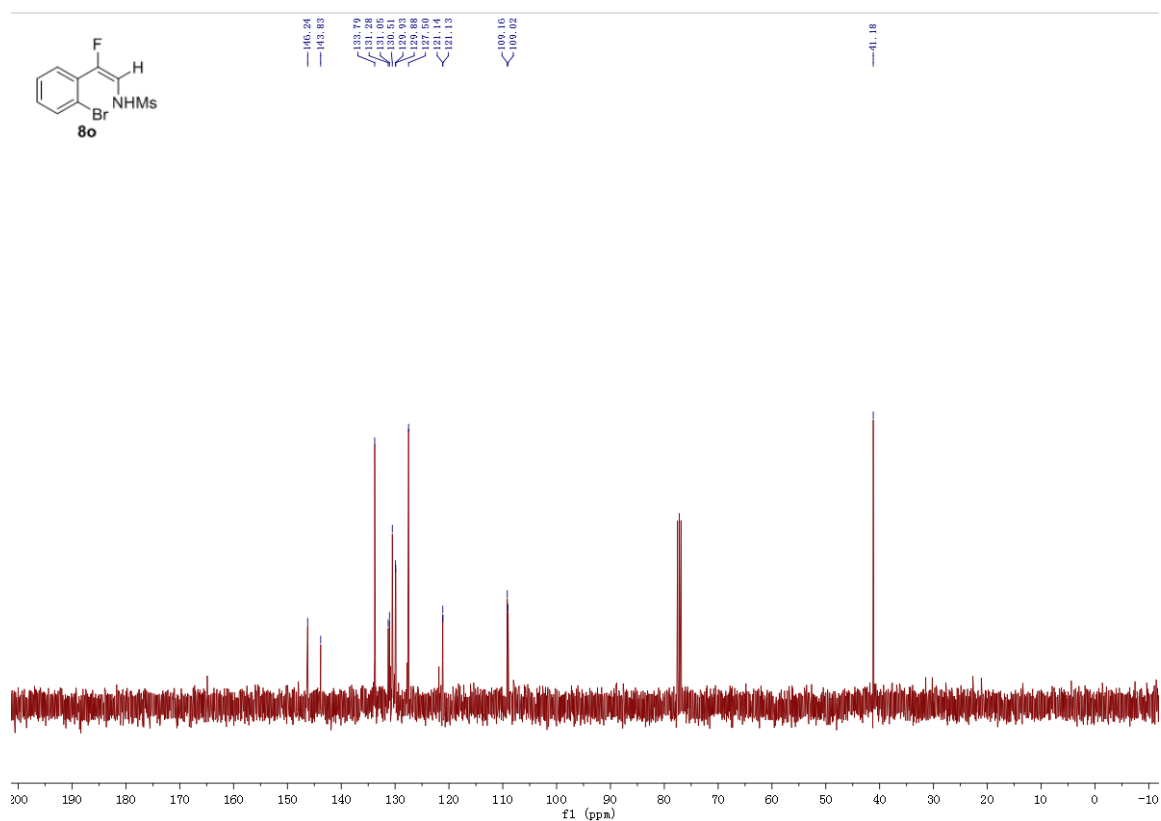
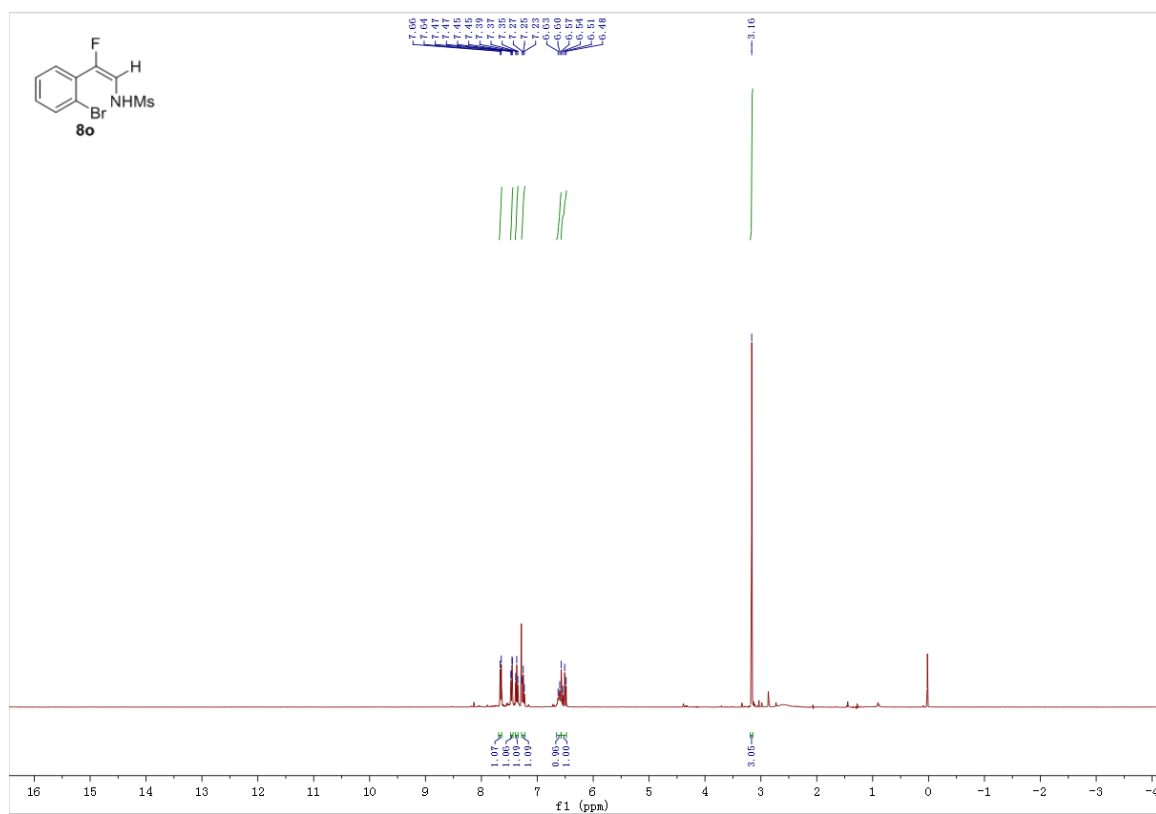


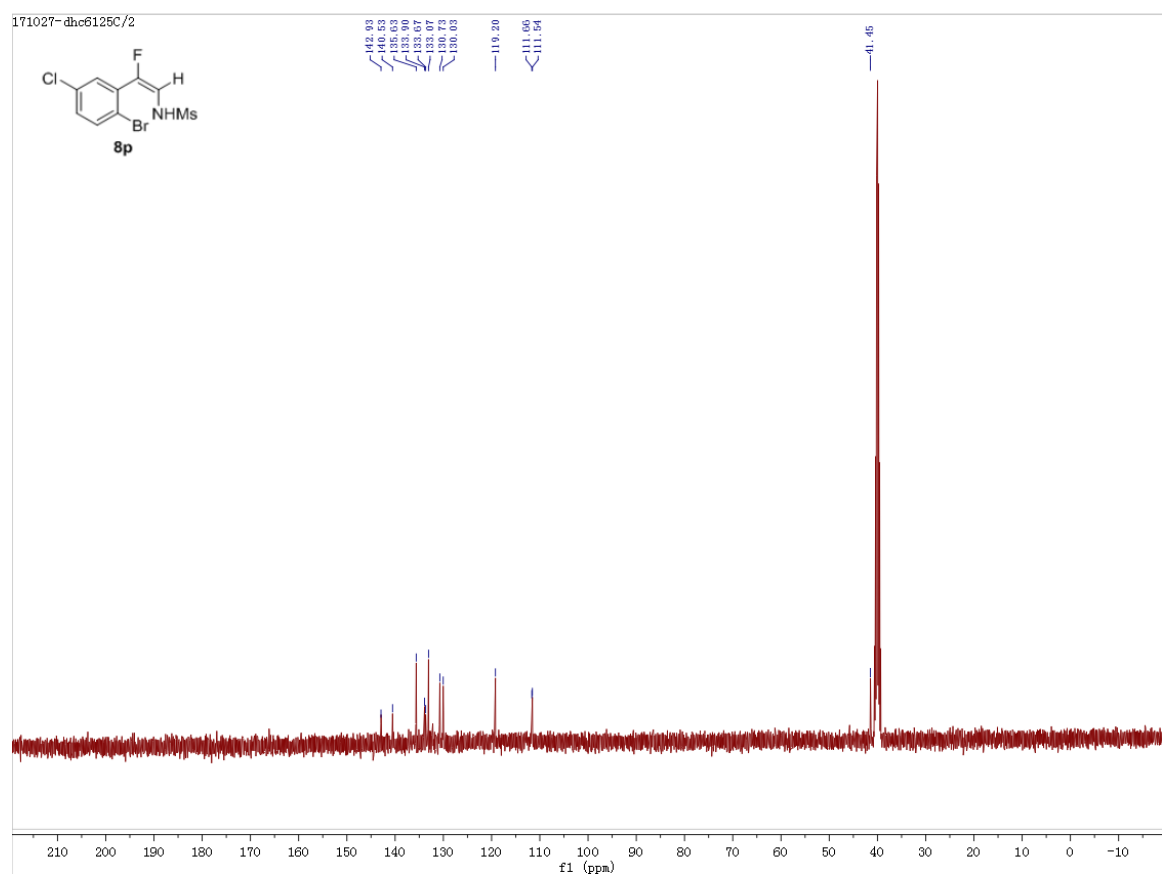
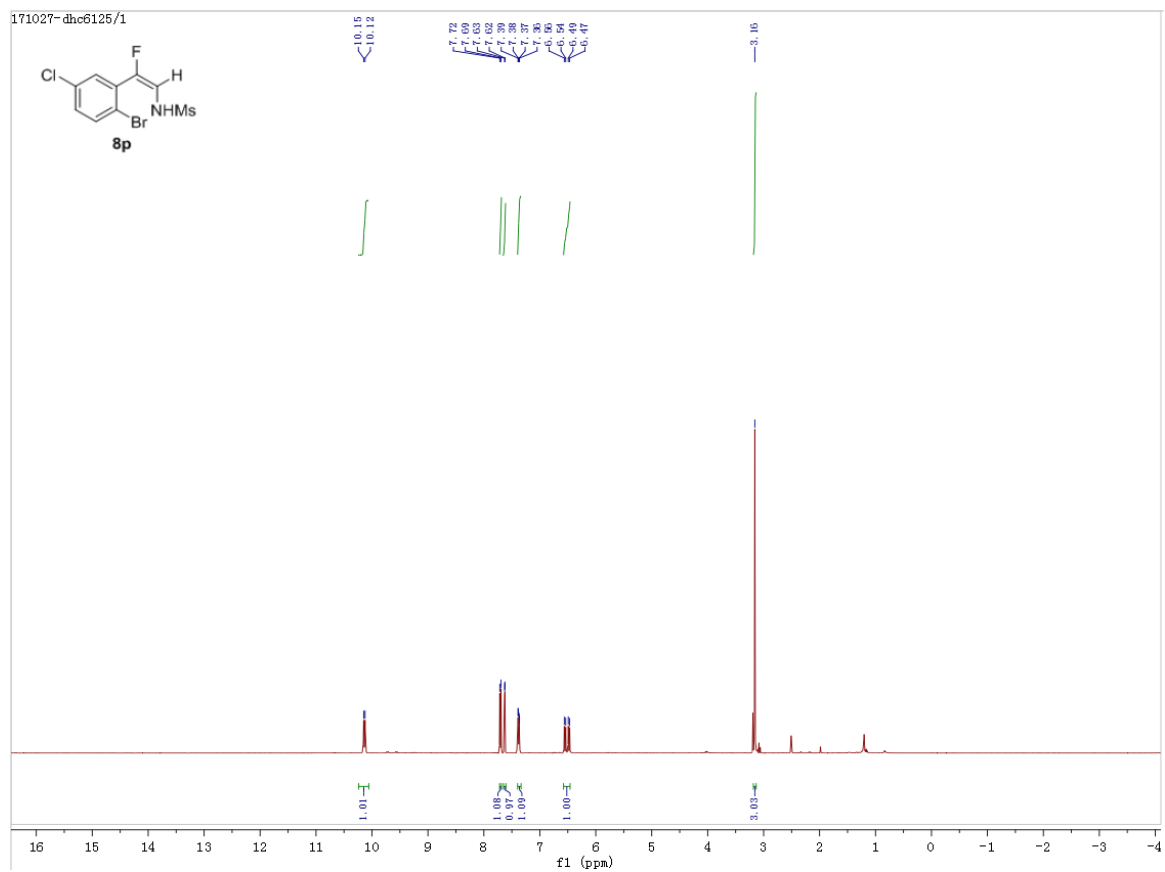


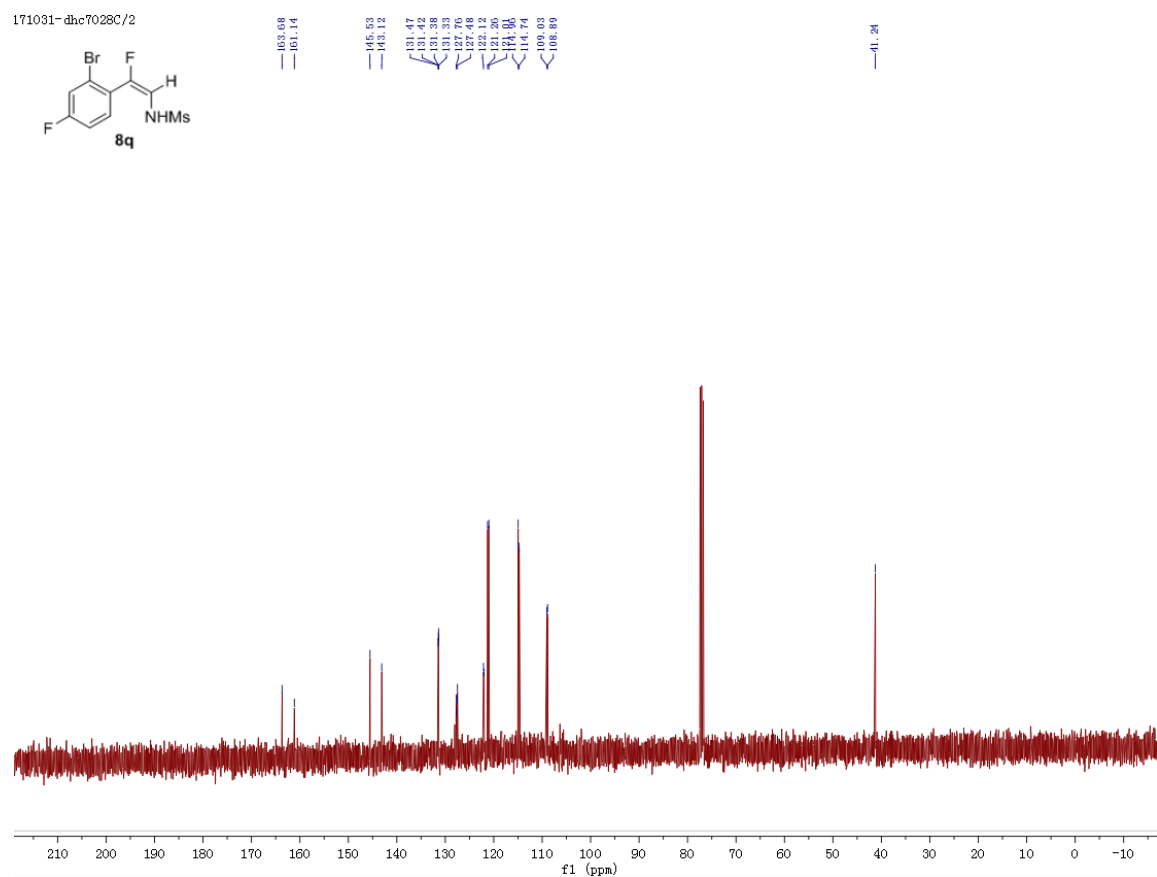
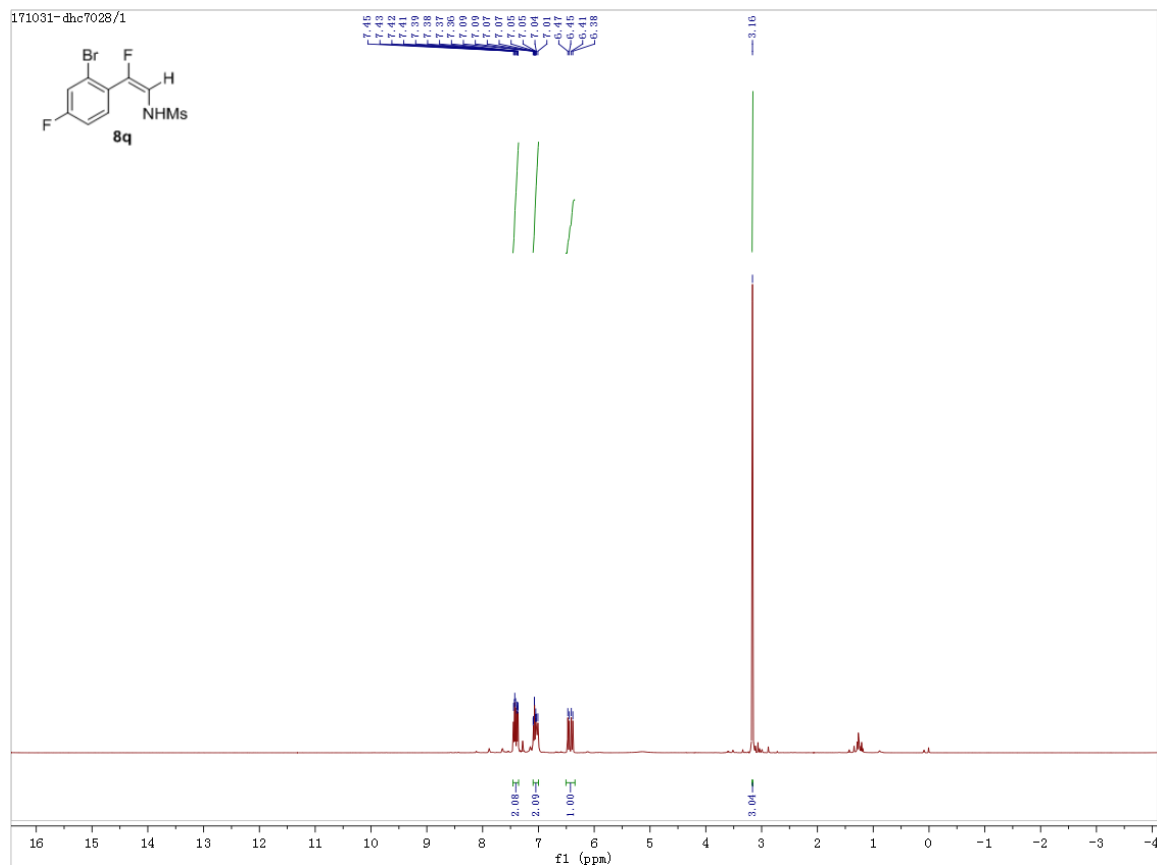


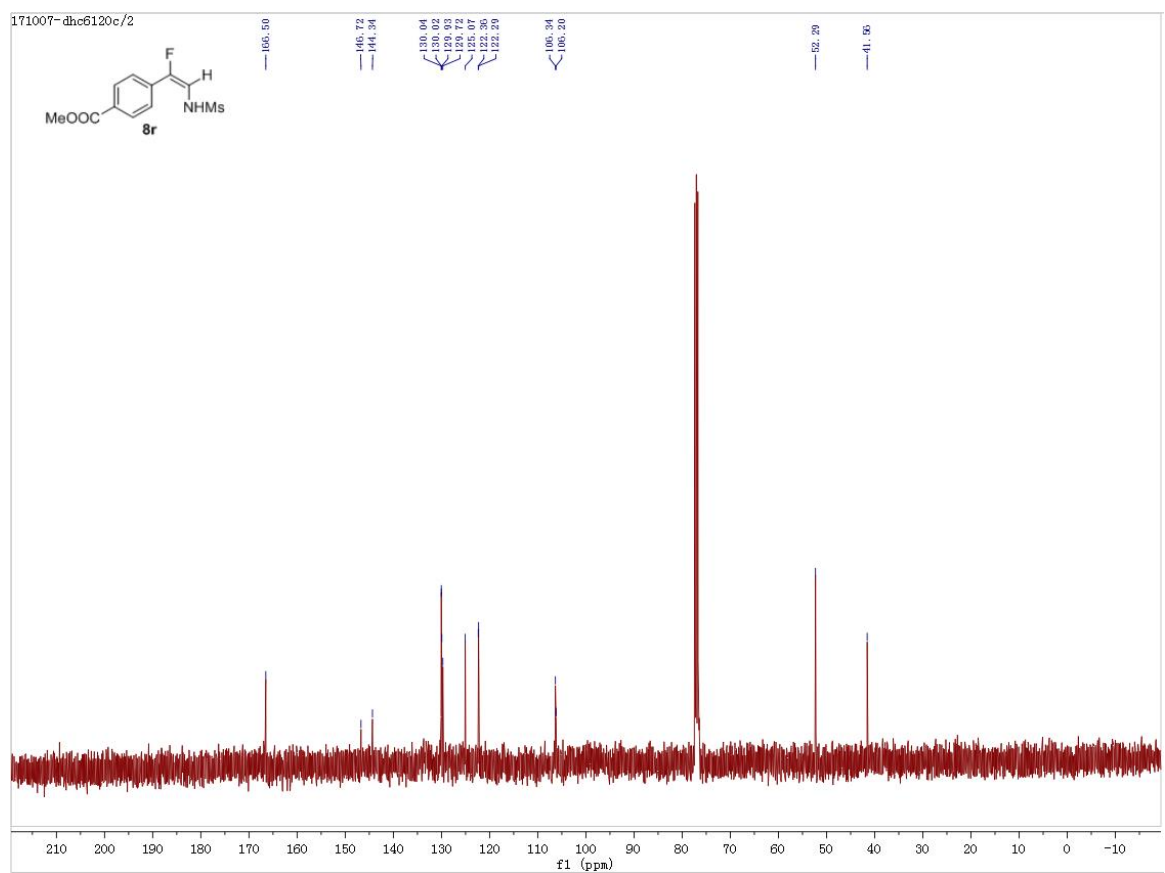
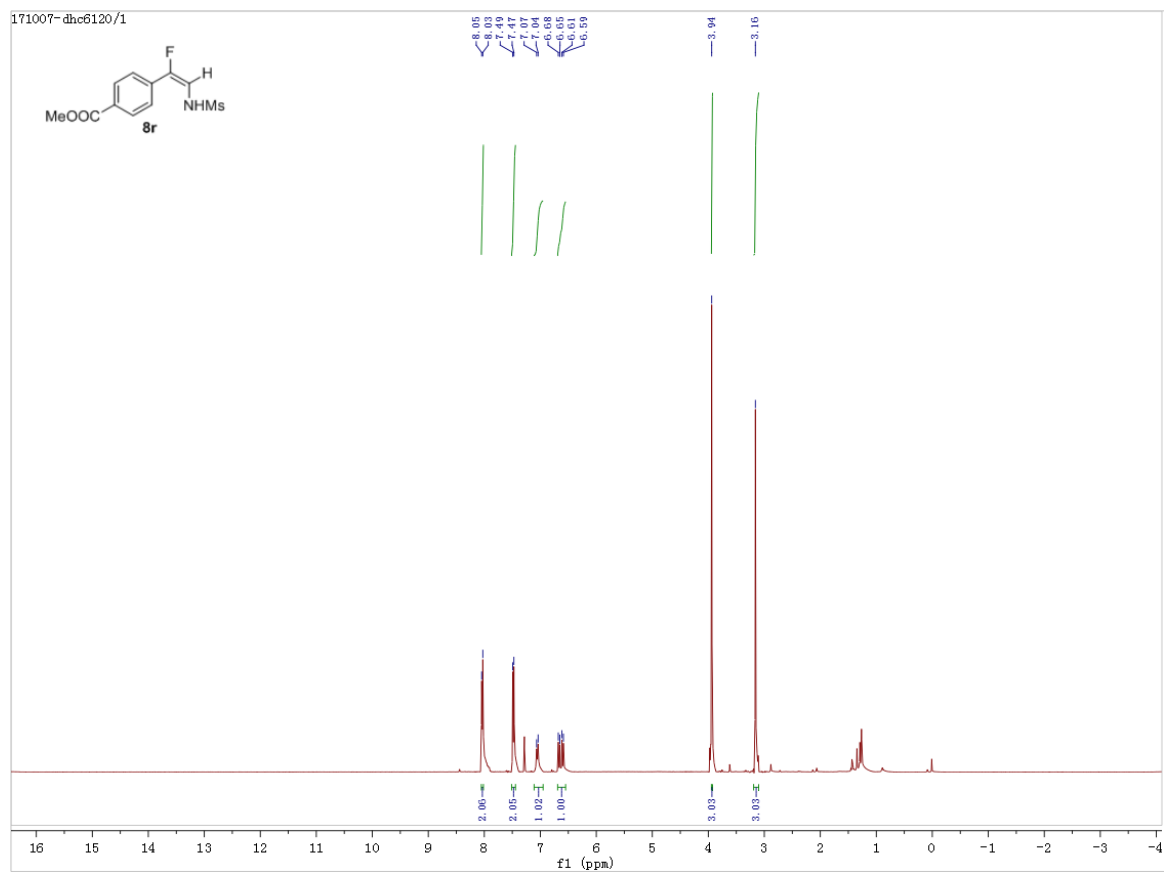


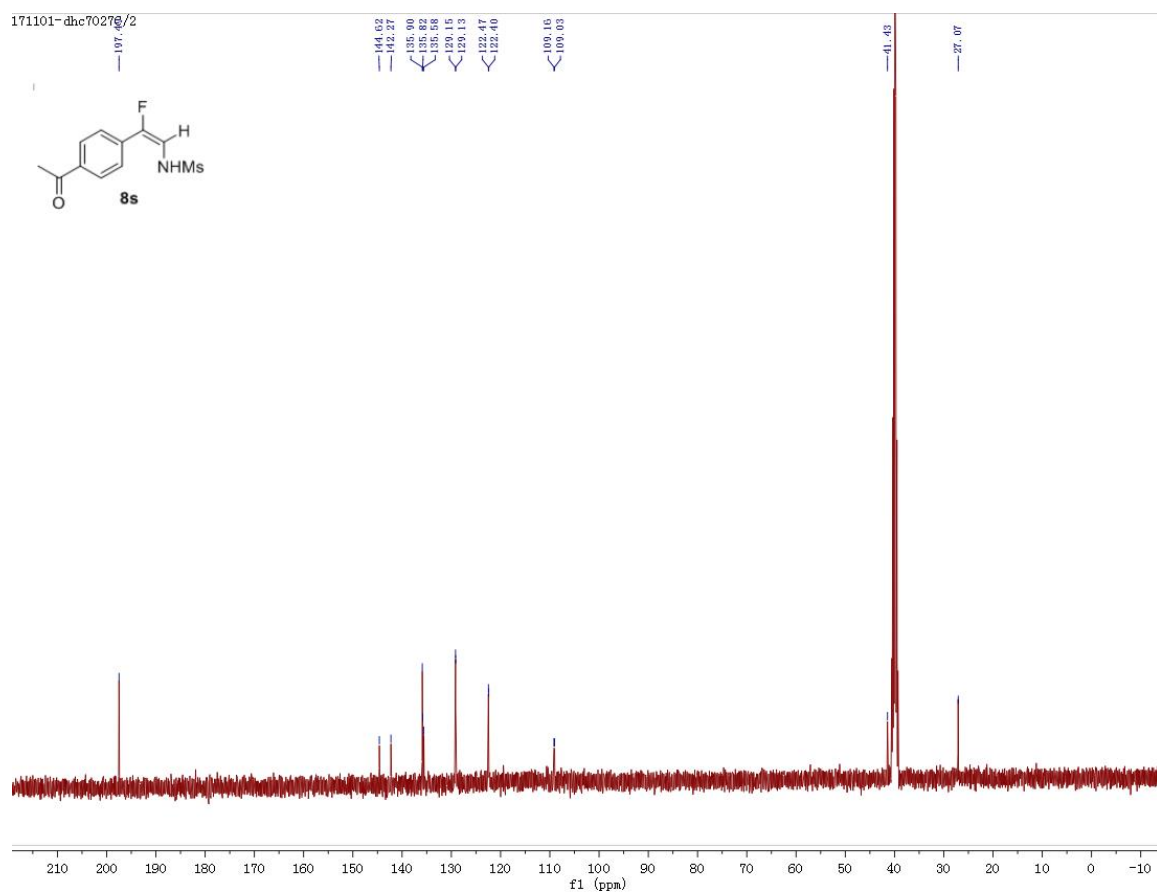
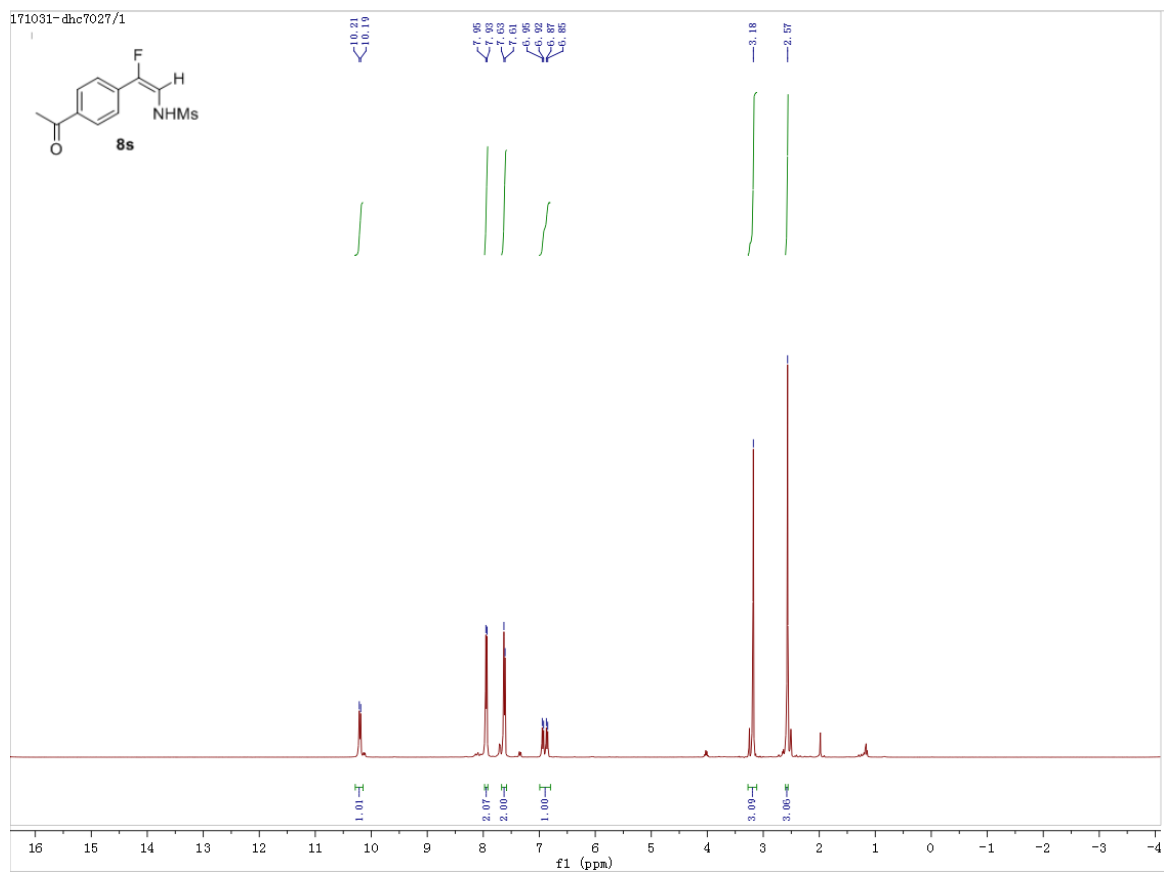


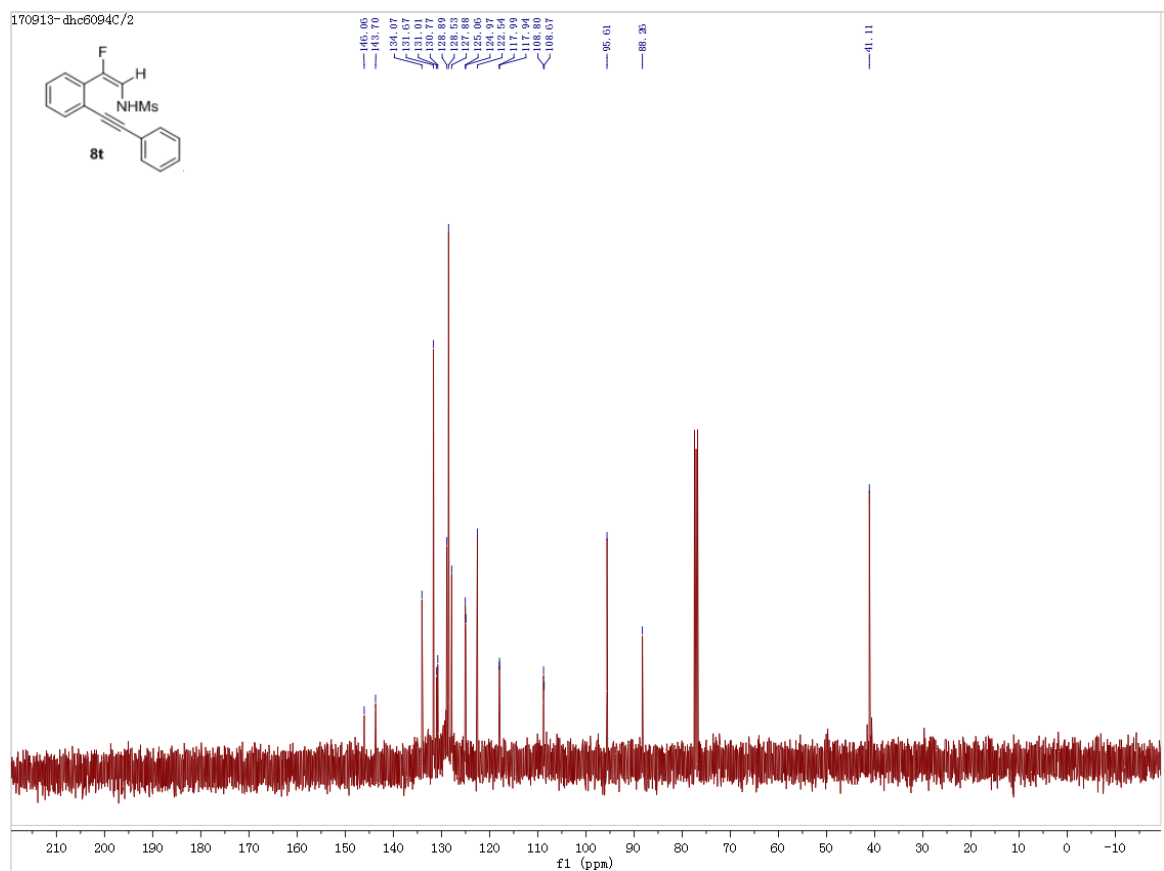
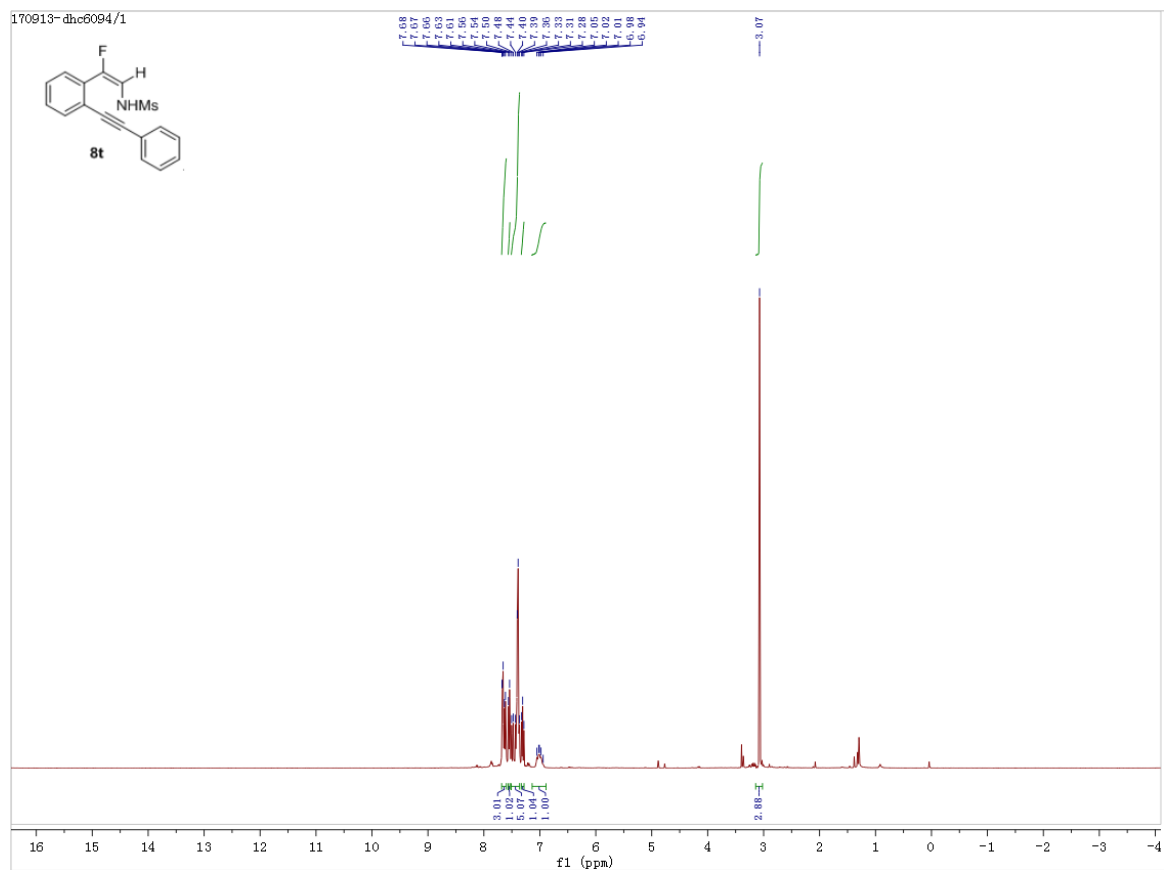


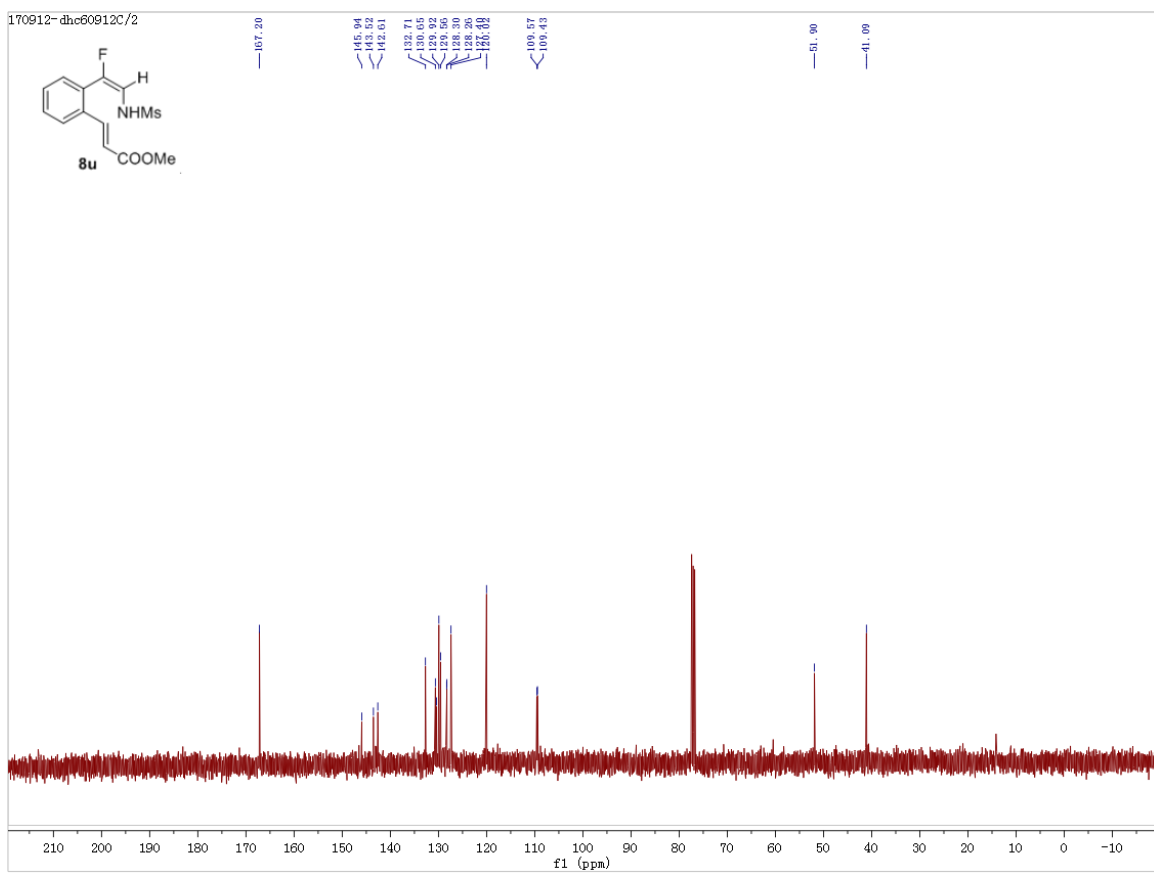
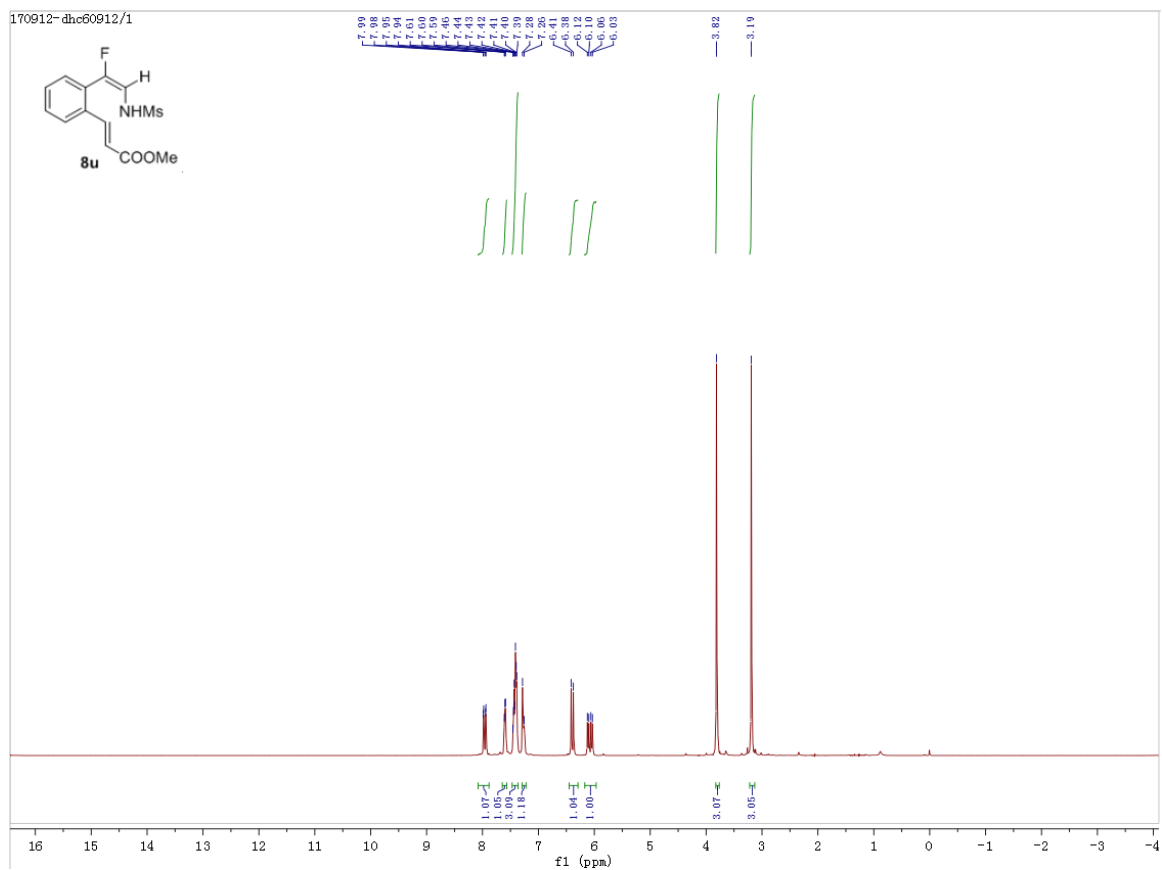




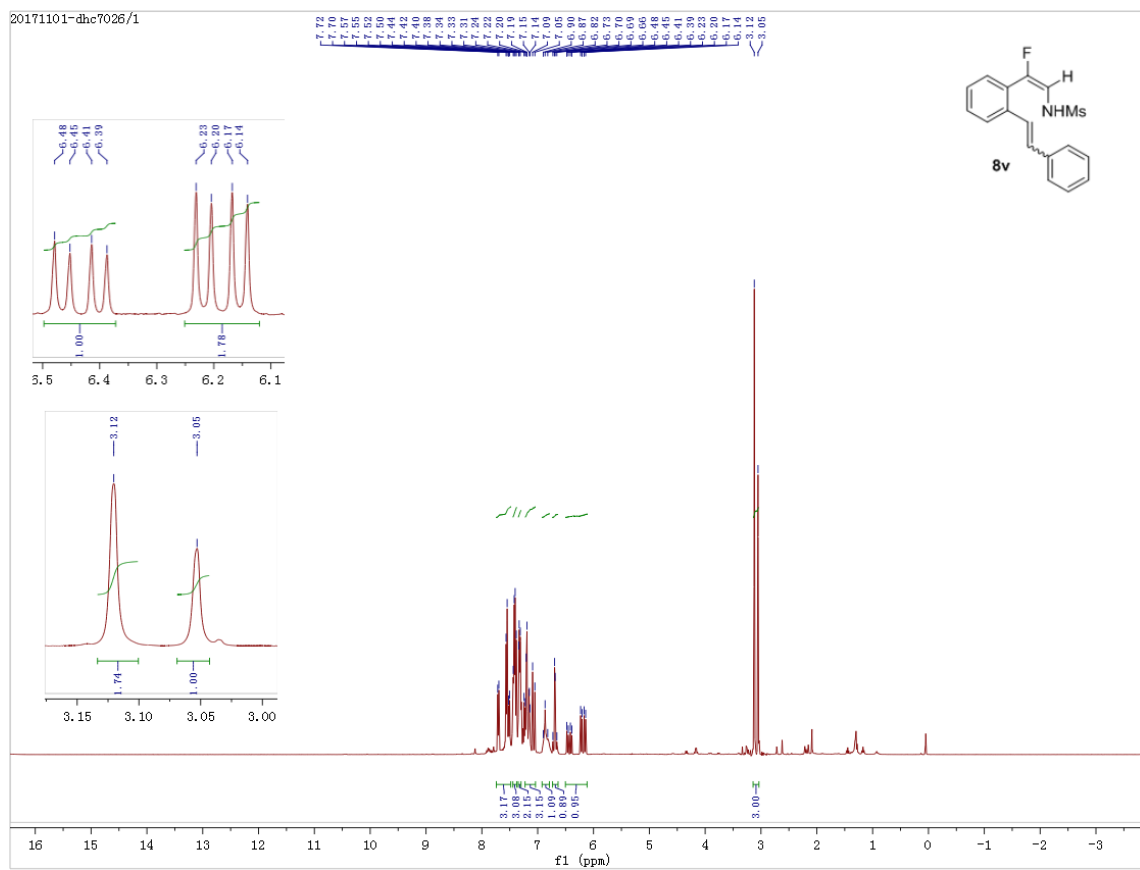




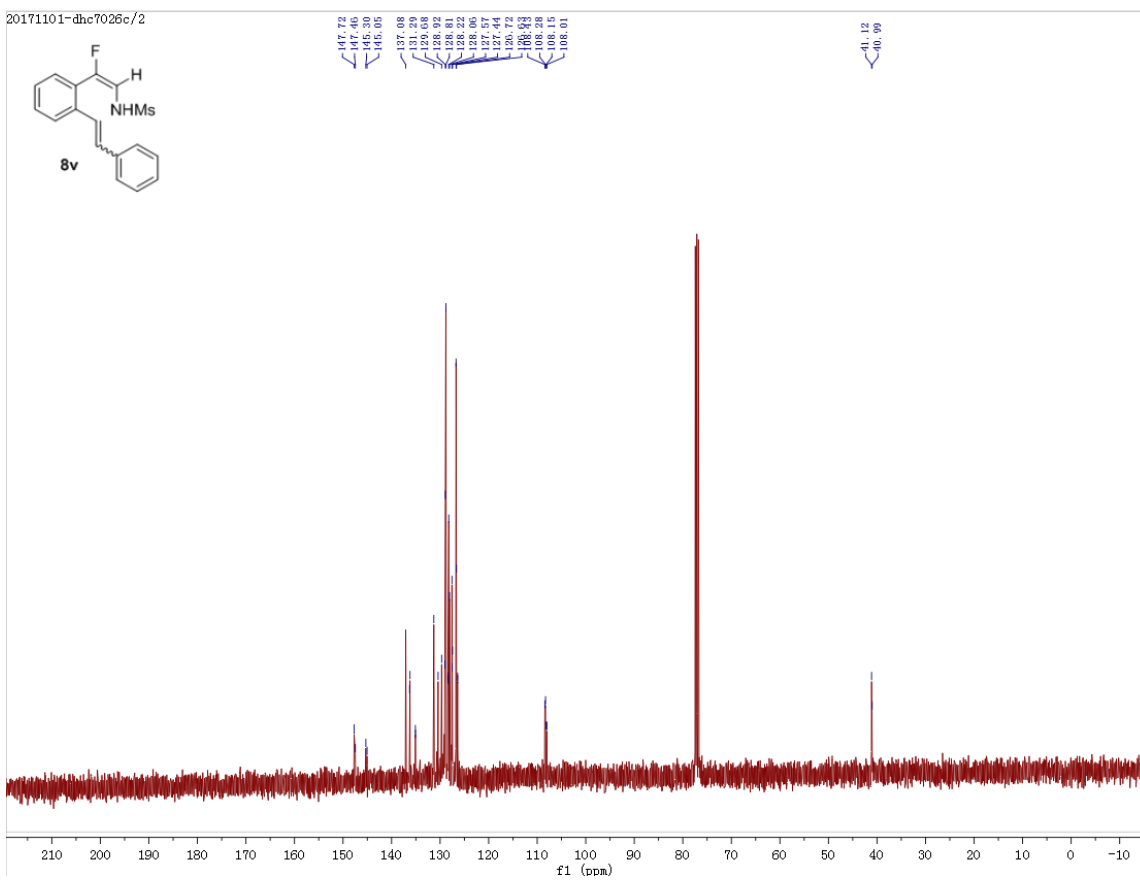


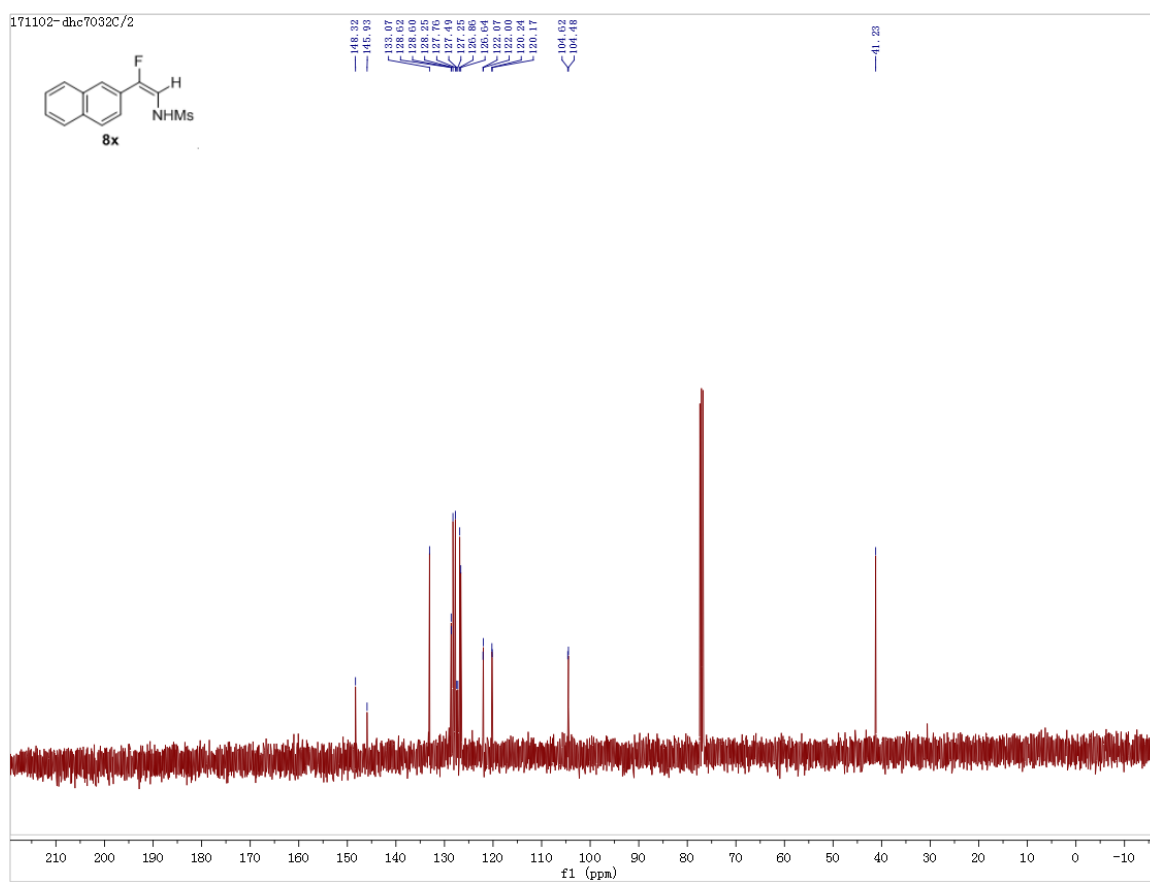
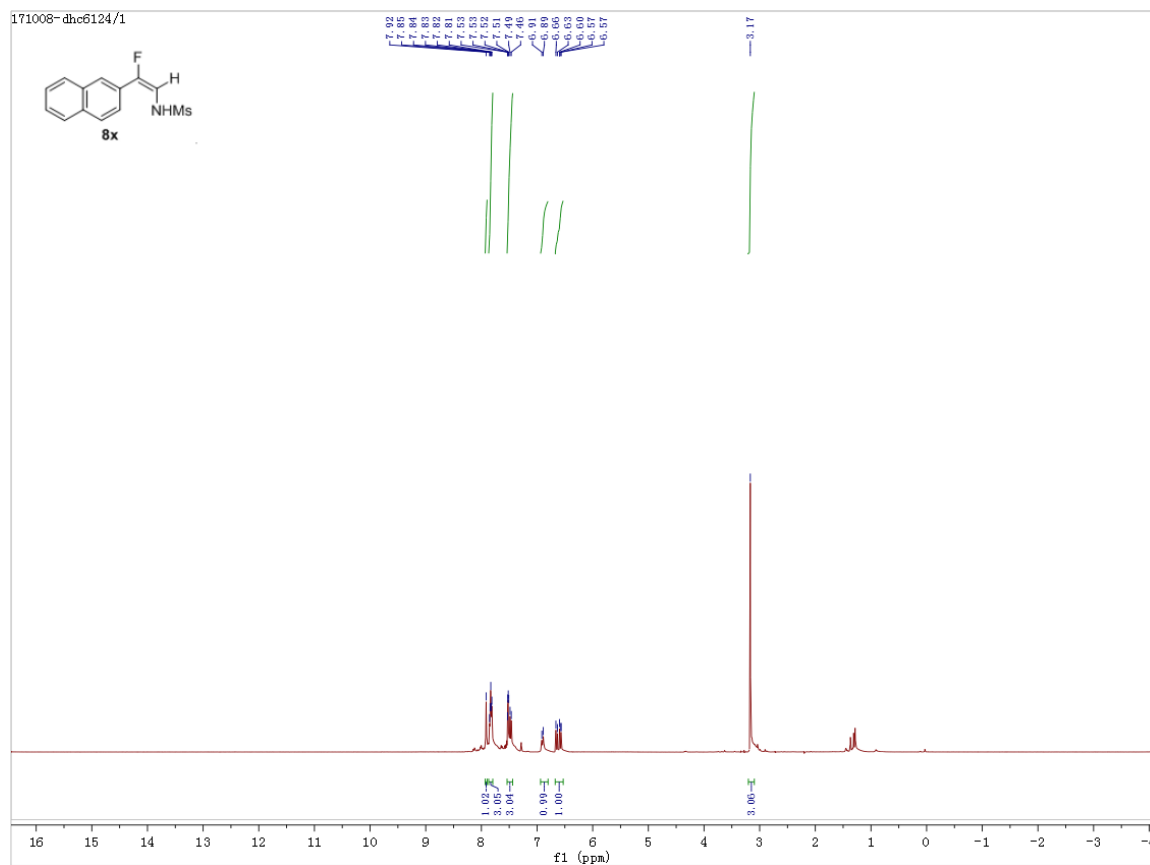


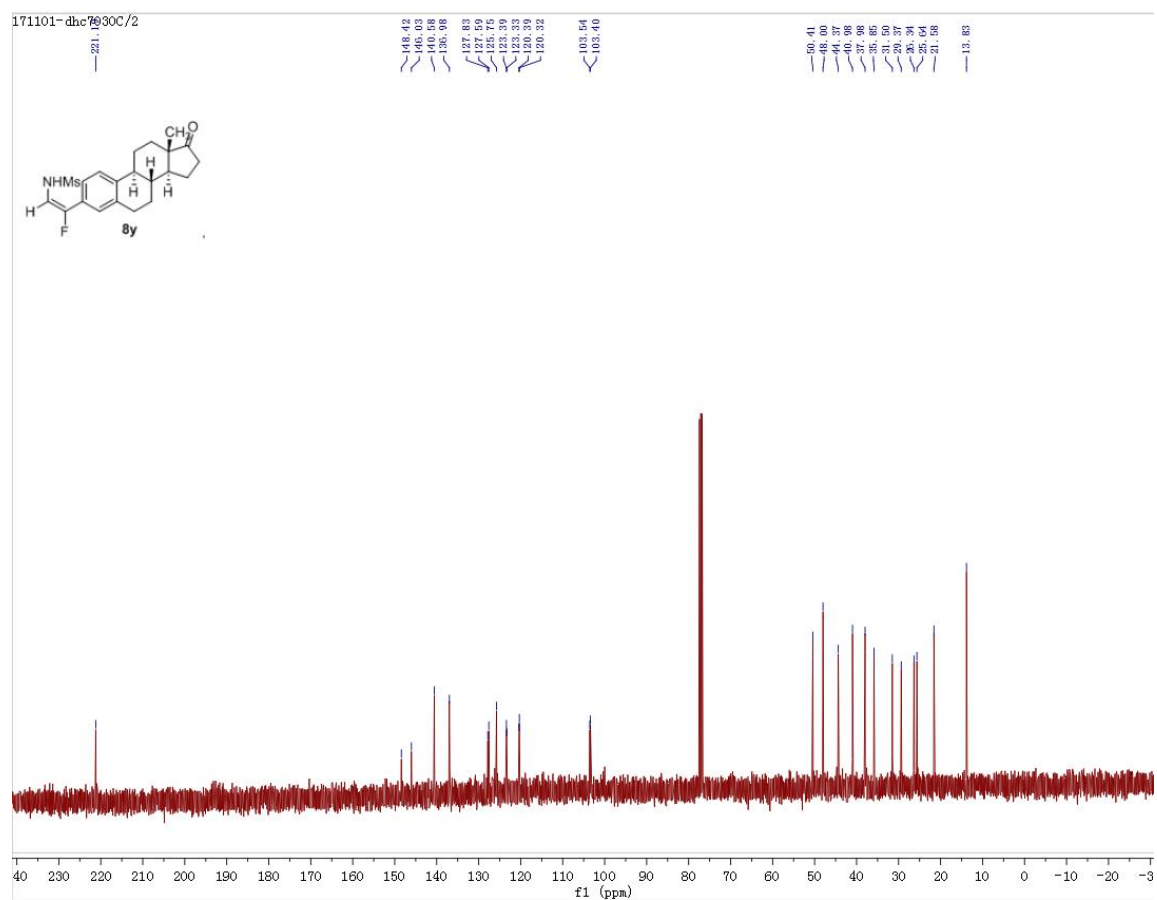
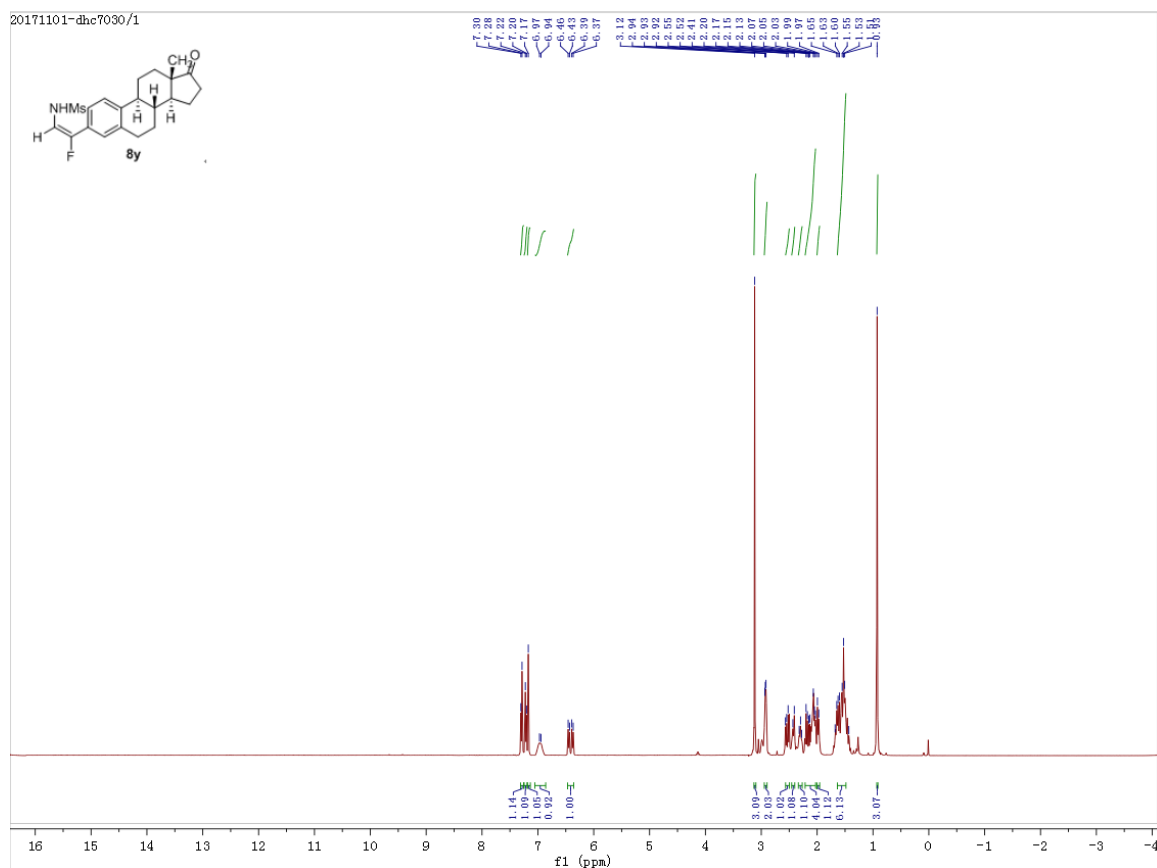
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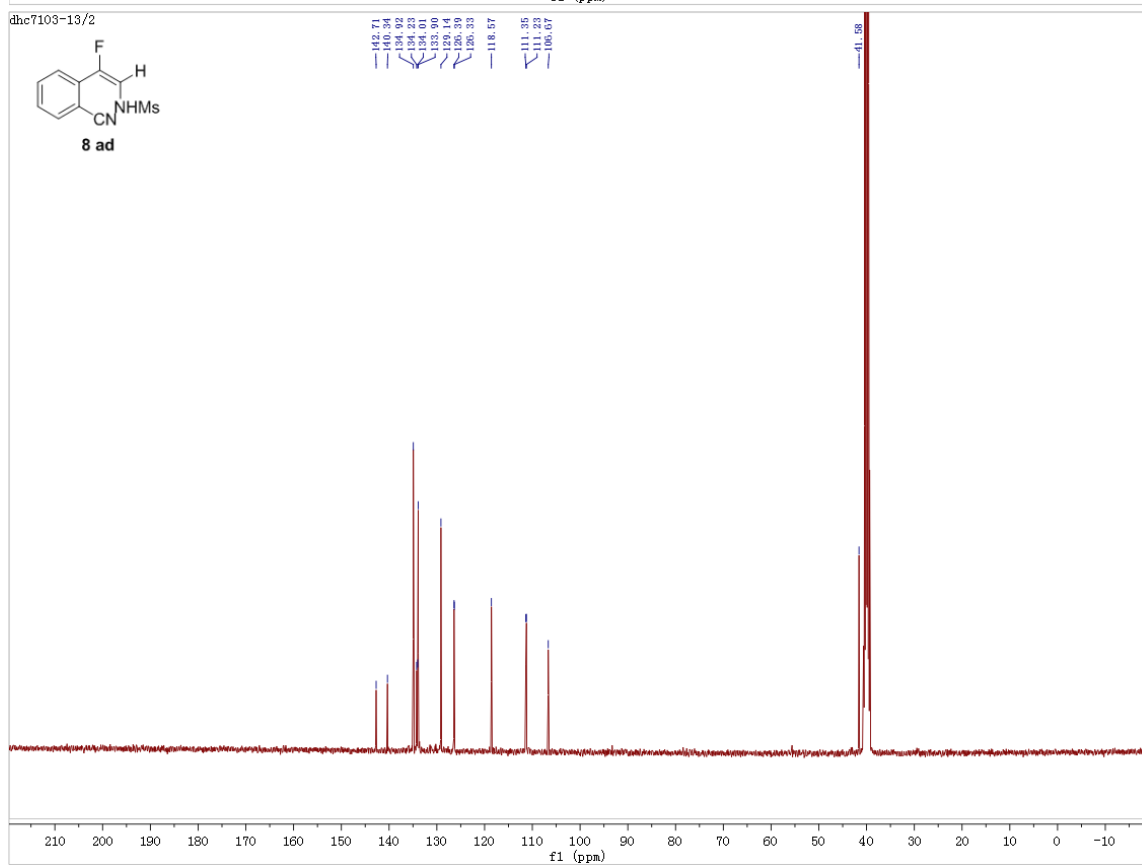
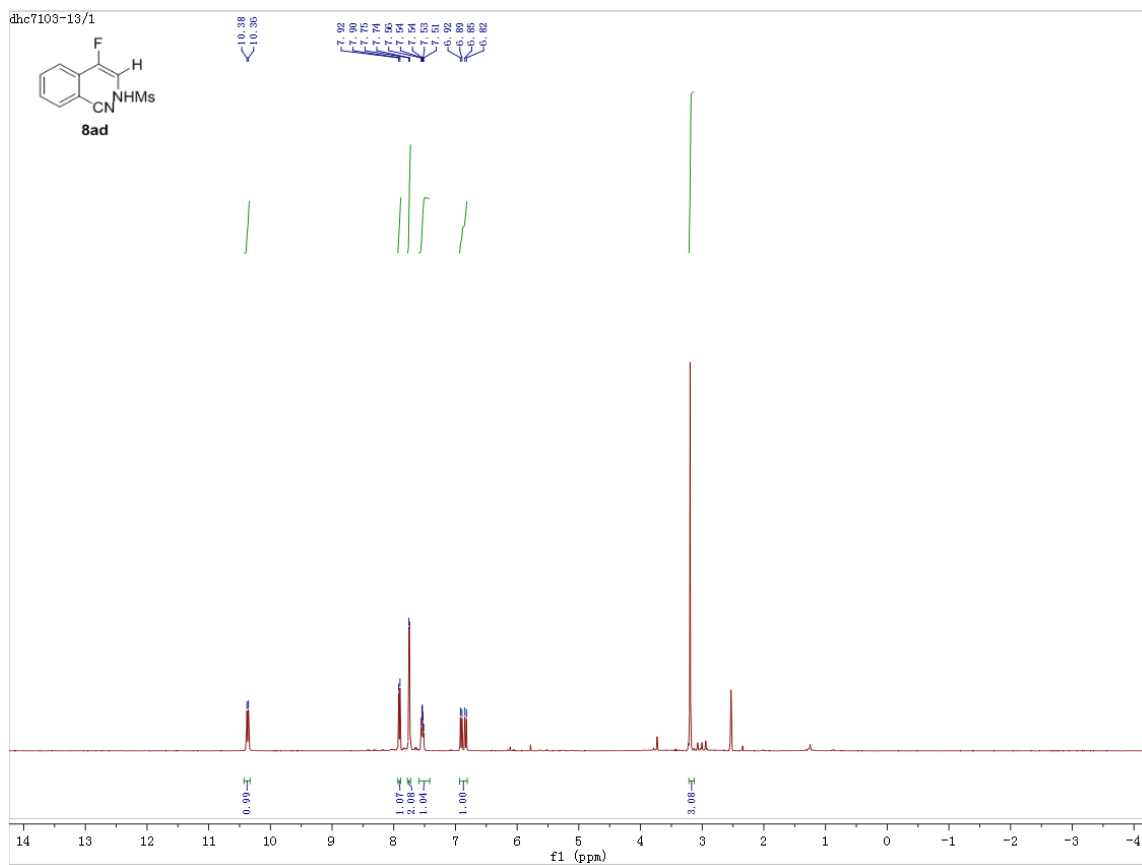


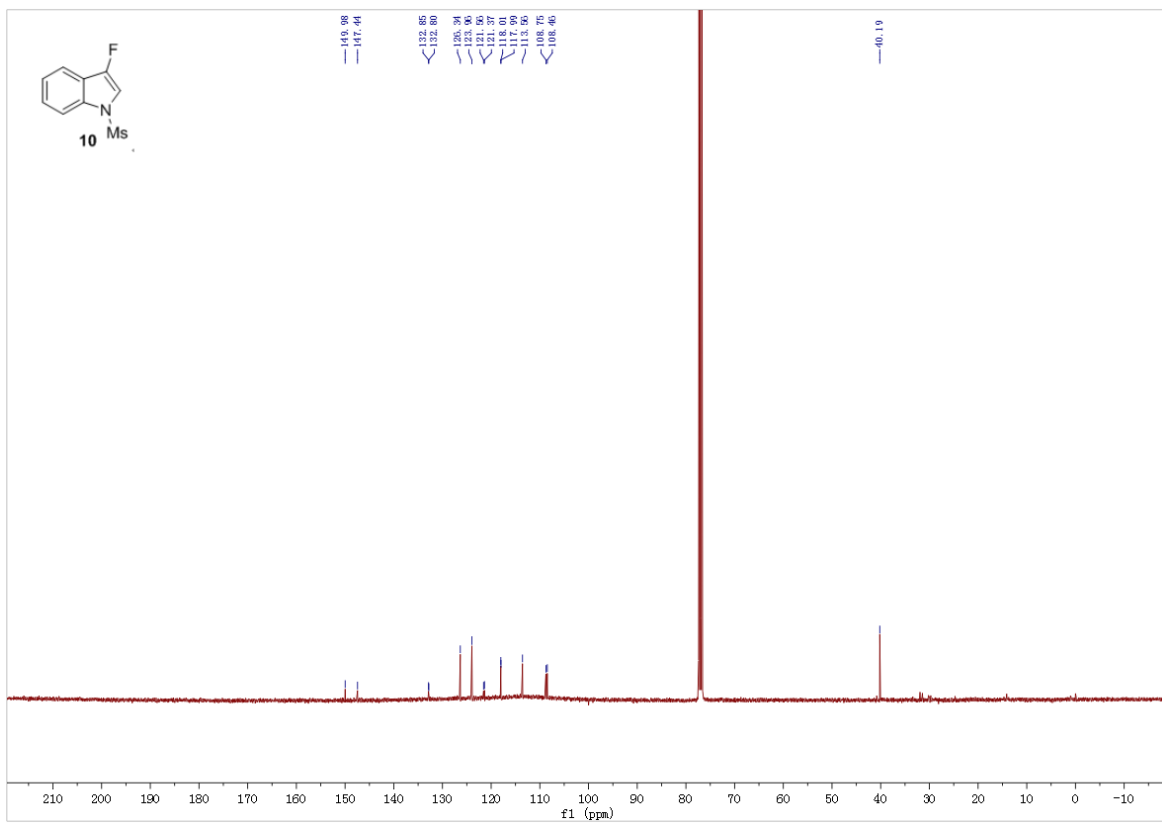
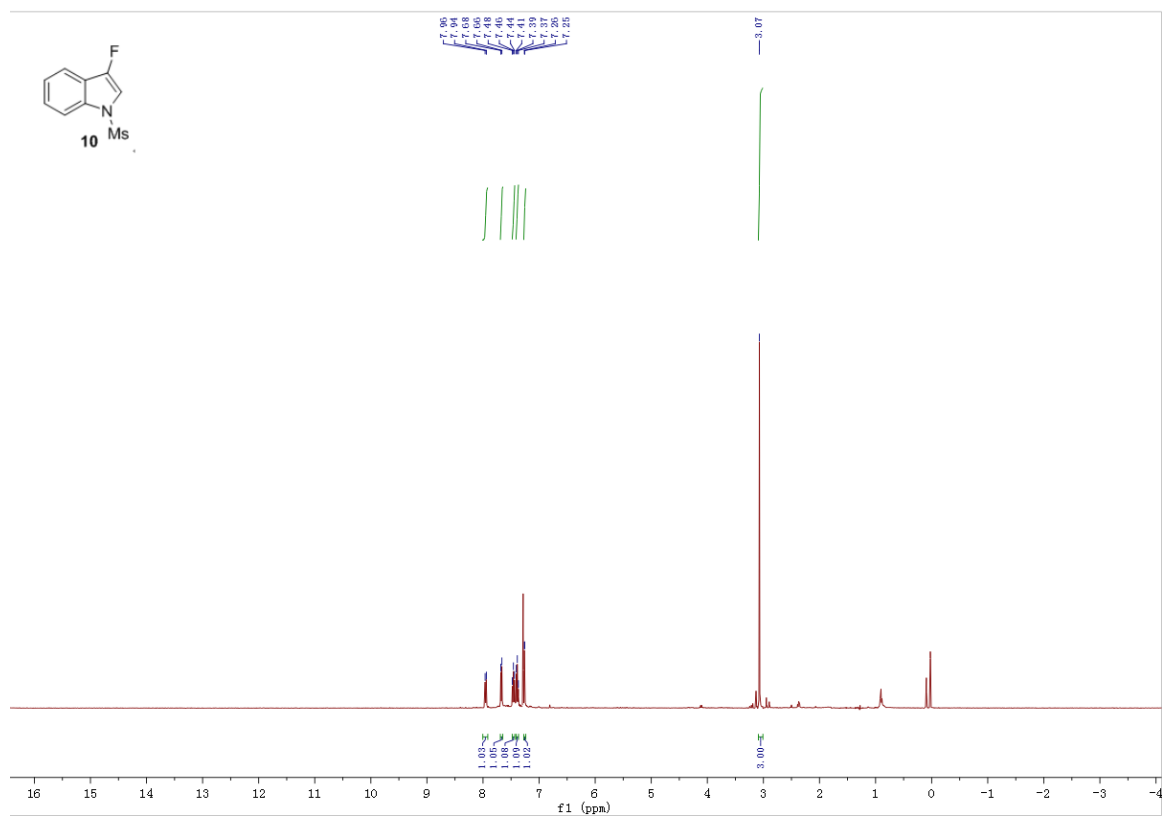
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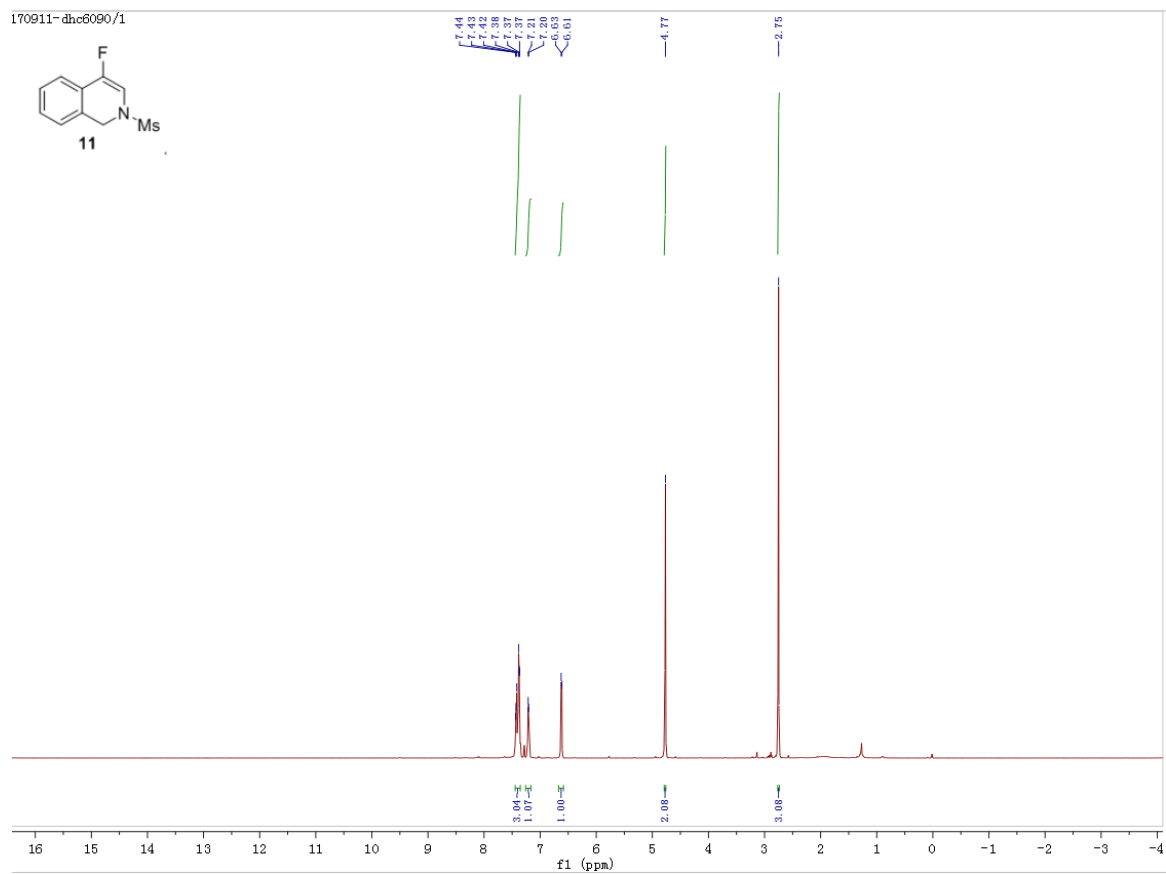
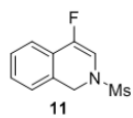




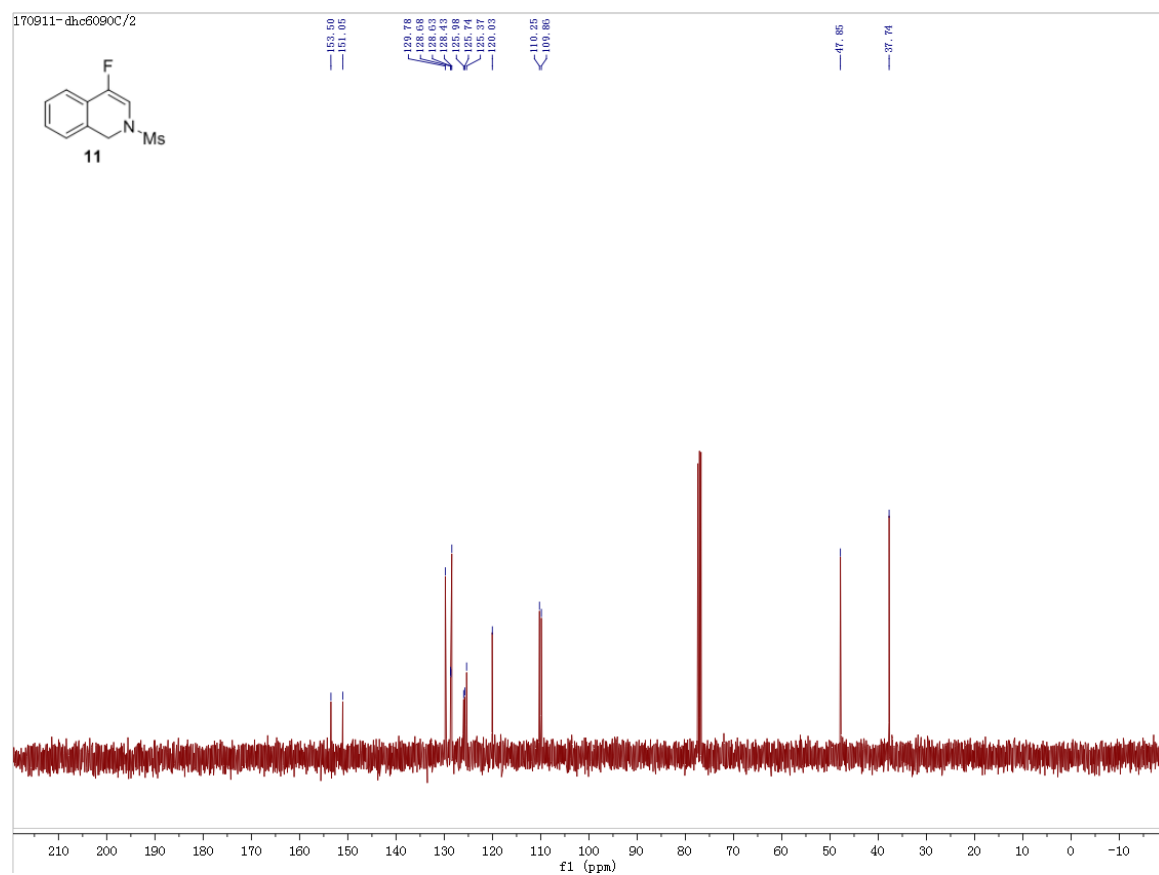
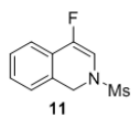




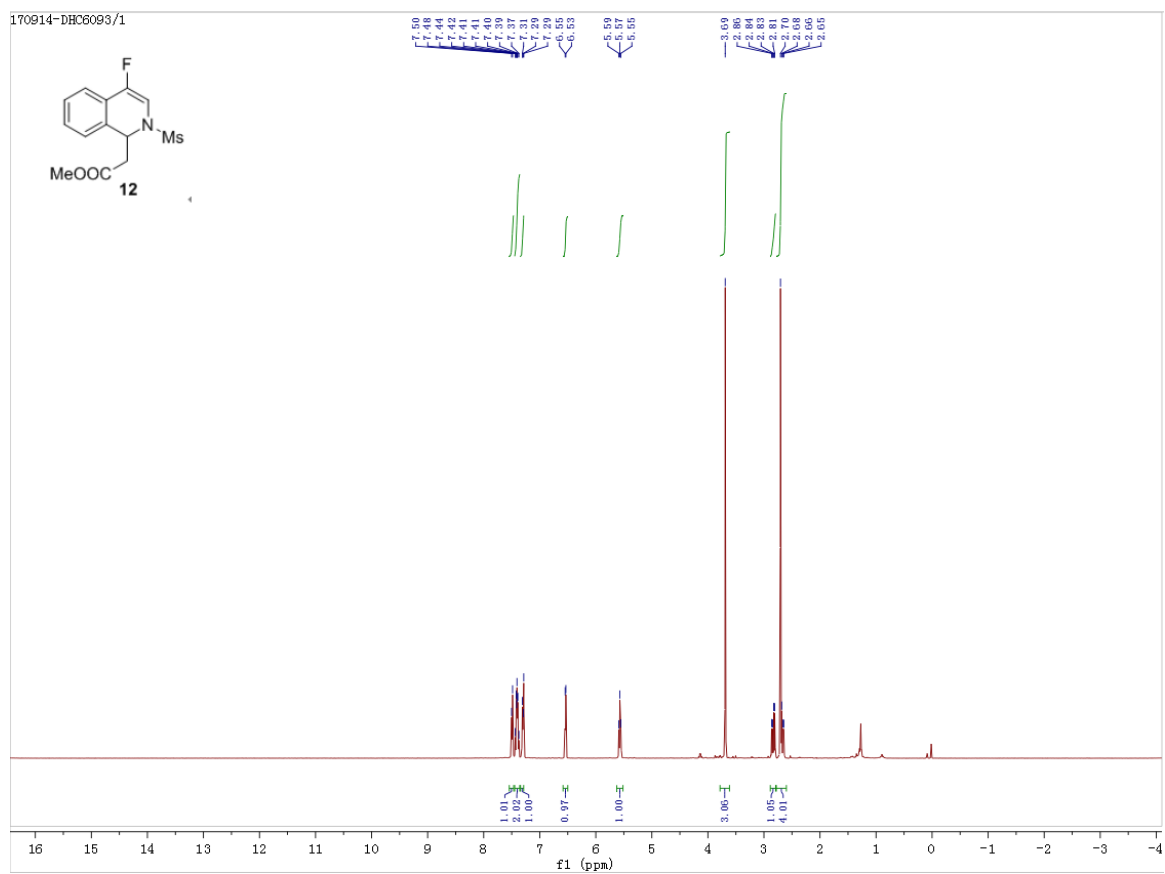
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