Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Grob-type fragmentation of oxonium ylide generated from α-imino rhodium carbene

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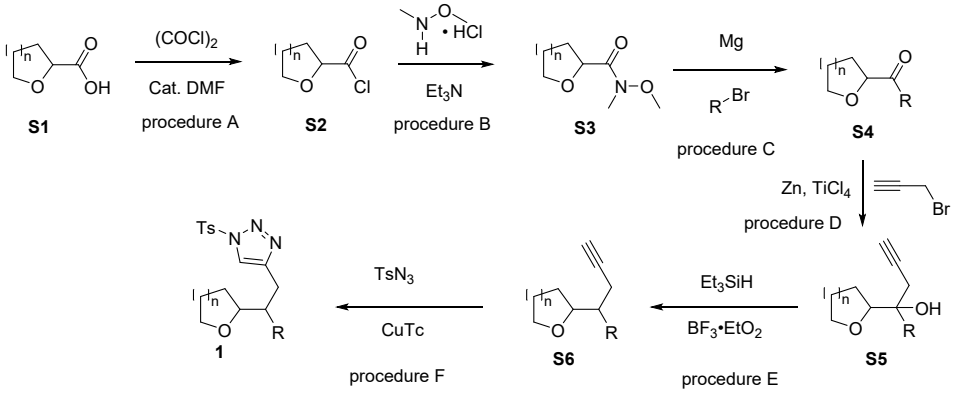
1. General information

All reactions were carried out under nitrogen atmosphere with anhydrous solvents in oven-dried glassware, unless otherwise noted. 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 (^{1}H-NMR) spectra were recorded using Brucker Avance II DMX 400MHz spectrometer. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or Chloroform-*d* (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 Brucker Avance II DMX 400 spectrometer at 101 MHz. Chemical shift is reported in ppm relative to the carbon resonance of Chloroform-*d* (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University from Waters TOFMS GCT Premier Instrument. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M+) or a suitable fragment ion.

2. Procedure for synthesis of 1



Procedure A: A 100 mL round-bottom flask was charged with acid **S1** (977 mg, 8 mmol), dry CH_2Cl_2 (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 min. Then $(COCl)_2$ (0.89 mL, 1.3 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride **S2** quantitatively which was used directly without further purification for the next step.

Procedure B: To a solution of N-methoxy-N-methylamine hydrochloride (2.0 g, 20 mmol) in CH_2Cl_2 (40 mL) were sequentially added triethylamine (5.6 mL, 40 mmol) and **S2** (2.3 mL, 20 mmol) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 13 h. The reaction was quenched with sat. aq. $NaHCO_3$, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford amides **S3** quantitatively which was used directly without further purification for the next step.

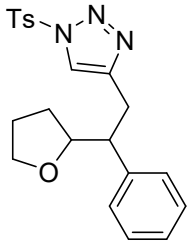
Procedure C: To a stirred solution of magnesium (5.0 mmol) in dry THF (5 mL) and a single crystal of iodine under a nitrogen atmosphere, was added bromobenzene (5.0 mmol) and the solution was heated under a gentle reflux for 0.5 h. The solution was allowed to cool to room temperature, was

added dropwise to the amides **S3** and stirred at 0 °C for 30 min before quenched with saturated aqueous NH_4Cl (20 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continuously washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **S4**.

Procedure D: Under N_2 atmosphere, activated zinc (981 mg, 15 mmol) was suspended in dry THF (10 mL) and was cooled to 0 ºC. Propargyl bromide (0.9 mL, 10 mmol) was added, followed by $TiCl_4$ (1 M in CH_2Cl_2, 0.25 mL, 0.25 mmol). The reaction mixture was stirred for 5 min before a solution of **S4** (5 mmol) in dry THF (10 mL) was added. The mixture was stirred for 1 h before quenched with saturated aqueous NH_4Cl (20 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continuously washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **S5**.

Procedure E: Add Et_3SiH (18 mmol, 2.0 equiv) to a solution of **S5** (9 mmol, 1.0 equiv) in CH_2Cl_2 (27 mL) at 0 °C under N_2 atmosphere. Stir the reaction at this temperature for 30 min. Add TFA or $BF_3{\cdot}Et_2O$ (36 mmol, 4.0 equiv) dropwise via syringe. Warm the mixture slowly to room temperature and stir until substrate disappeared. Quench with sat aq. $NaHCO_3$. Wash the solution with brine solution and extract with CH_2Cl_2 (3×10 mL). Dry over the combined organic layers with anhydrous Na_2SO_4. Filter and concentrate under reduced pressure. Purify the crude product by chromatography on silica gel using petroleum ether/EtOAc (80:1) as the eluent giving alkyne **S6**.

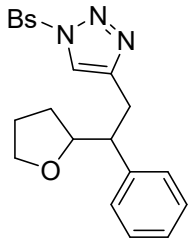
Procedure F: Under N_2 atmosphere, dry toluene (4 mL) was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTc, 0.3 mmol, 0.1 equiv) and alkyne **S6** (3 mmol, 1 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, sulfonyl azide (3.3 mmol, 1.1 equiv) was added 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 purified by flash column chromatography with petroleum ether/ethyl acetate (5:1 to 2:1, volume ratio) as eluent to give the corresponding triazole **1**.



1a 5.4:1

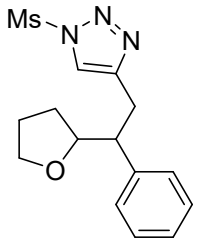
4-(2-phenyl-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 361 mg, yield: 60%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.13 (m, 8H), 4.19 – 4.07 (m, 1H), 3.83 – 3.66 (m, 2H), 3.28 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.14 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.05 (dt, *J* = 10.2, 5.2 Hz, 1H).2.48 (s, 3H), 1.99 – 1.88 (m, 1H), 1.88 – 1.74 (m, 1H), 1.71 – 1.52 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.10 (m, 8H), 4.19 – 4.07 (m, 1H),3.96 – 3.80 (m, 2H), 3.56 (dd, *J* = 14.4, 3.7 Hz, 1H), 3.08 – 2.97 (m, 1H) 2.96 – 2.87 (m, 1H). 2.48 (s, 3H), 1.99 – 1.88 (m, 1H), 1.88 – 1.74 (m,

1H), 1.71 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.8, 146.4, 146.1, 141.0, 140.5, 133.3, 130.3, 130.2, 128.9, 128.4, 128.3, 128.3, 128.2, 128.2, 126.8, 126.7, 121.3, 121.3, 82.4, 81.4, 68.2, 68.2, 51.1, 50.0, 29.4, 29.2, 25.8, 25.6, 21.8, 21.7. HRMS (ESI) m/z calcd for $C_{21}H_{24}N_3O_3S^+$ $[M + H]^+$ 398.1533, found 398.1533.



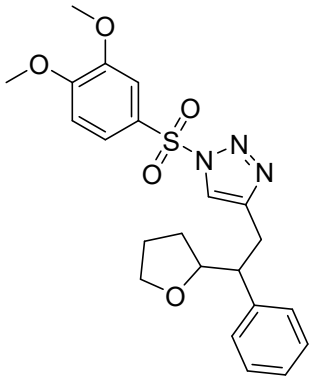
1a-1 single isomer

1-((4-bromophenyl)sulfonyl)-4-(2-phenyl-2-(tetrahydrofuran-2-yl)ethyl)-1H-1,2,3-triazole: white solid, m.p.: 122.6-123.3 ºC, 196 mg, yield: 43%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.37 (s, 1H), 7.25 – 7.17 (m, 5H), 4.21 – 4.09 (m, 1H), 3.81 – 3.68 (m, 2H), 3.30 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.16 (dd, *J* = 14.4, 10.1 Hz, 1H), 3.06 (dt, *J* = 10.2, 5.2 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.87 – 1.79 (m, 1H), 1.66 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.5, 140.4, 135.2, 133.1, 131.1, 129.6, 128.9, 128.2, 126.8, 121.4, 81.4, 68.3, 50.0, 29.4, 29.1, 25.8. HRMS (ESI) m/z calcd for $C_{20}H_{21}BrN_3O_3S^+$ $[M + H]^+$ 462.0482, found 462.0482.



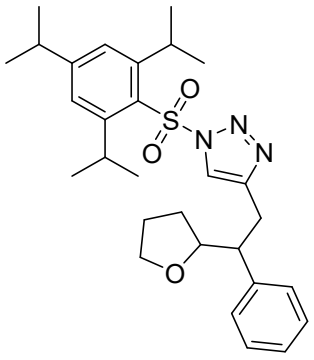
1a-2 2.6:1

1-(methylsulfonyl)-4-(2-phenyl-2-(tetrahydrofuran-2-yl)ethyl)-1H-1,2,3-triazole: clear oil, 424 mg, yield: 60%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (s, 1H), 7.33 – 7.22 (m, 5H), 4.20 – 4.10 (m, 1H), 3.84 – 3.70 (m, 2H), 3.39 (s, 3H), 3.37 – 3.33 (m, 1H), 3.22 (dd, *J* = 14.4, 9.9 Hz, 1H), 3.15 (dt, *J* = 9.9, 4.8 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.89 – 1.75 (m, 1H), 1.70 – 1.42 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ7.41 (s, 1H), 7.33 – 7.22 (m, 5H), 4.15 – 4.09 (m, 1H), 4.01 – 3.84 (m, 2H), 3.68 – 3.58 (m, 1H), 3.39 (s, 3H), 3.12 – 3.06 (m, 1H), 3.06 – 2.97 (m, 1H). 2.06 – 1.95 (m, 1H), 1.89 – 1.75 (m, 1H), 1.70 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 146.3, 140.9, 140.4, 128.9, 128.6, 128.3, 128.2, 127.0, 126.9, 121.1, 121.0, 82.5, 81.4, 68.3, 68.2, 51.1, 49.9, 42.5, 42.5, 30.3, 29.4, 29.2, 29.1, 25.8, 25.6. HRMS (ESI) m/z calcd for $C_{15}H_{20}N_3O_3S^+$ $[M + H]^+$ 322.1220, found 322.1224.



1a-3 3:1

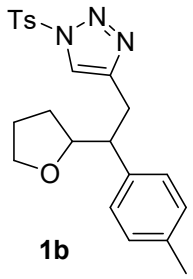
1-((3,4-dimethoxyphenyl)sulfonyl)-4-(2-phenyl-2-(tetrahydrofuran-2-yl)ethyl)-1H-1,2,3-triazole: clear oil, 350.4 mg, yield: 40%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 6.84 (m, 9H), 4.24 – 4.05 (m, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.80 – 3.64 (m, 2H), 3.34 – 3.25 (m, 1H), 3.14 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.05 (dt, *J* = 10.2, 5.2 Hz, 1H), 2.10 – 1.93 (m, 1H), 1.87 – 1.77 (m, 1H), 1.67 – 1.50 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 6.84 (m, 9H), 4.11 – 4.05 (m, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.92 – 3.79 (m, 2H), 3.60 – 3.51 (m, 1H), 3.03 – 2.98 (m, 1H), 2.98 – 2.89 (m, 1H), 2.10 – 1.93 (m, 1H), 1.87 – 1.77 (m, 1H), 1.67 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 154.8, 149.4, 146.3, 146.1, 141.0, 140.5, 128.9, 128.4, 128.3, 128.2, 127.3, 127.2, 126.8, 126.7, 123.1, 123.1, 121.1, 121.0, 110.8, 110.7, 110.1, 82.4, 81.4, 68.3, 68.2, 56.4, 56.4, 51.1, 49.9, 30.2, 29.4, 29.2, 29.1, 25.8, 25.6. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_5S^+$ $[M + H]^+$ 444.1588, found 444.1590.



1a-4 5:1

4-(2-phenyl-2-(tetrahydrofuran-2-yl)ethyl)-1-((2,4,6-triisopropylphenyl) sulfonyl)-1H-1,2,3-triazole: clear oil, 418 mg, yield: 41%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.28 – 7.20 (m, 7H), 4.10 – 3.98 (m, 3H), 3.81 – 3.71 (m, 2H), 3.33 (dd, *J* = 14.6, 5.4 Hz, 1H), 3.22 (dd, *J* = 14.6, 9.8 Hz, 1H), 3.13 (dt, *J* = 10.1, 5.3 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.10 – 1.93 (m, 1H), 1.91 – 1.75 (m, 1H), 1.67 – 1.52 (m, 2H), 1.36 – 1.04 (m, 18H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.28 – 7.20 (m, 7H), 4.17 – 4.11 (m, 3H), 3.95 – 3.82 (m, 2H), 3.60 (dd, *J* = 14.5, 3.5 Hz, 1H), 3.10 – 2.82 (m, 3H), 2.10 – 1.93 (m, 1H), 1.91 –

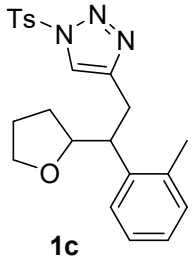
1.75 (m, 1H), 1.67 – 1.52 (m, 2H), 1.36 – 1.04 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 155.9, 152.7, 152.7, 145.9, 145.6, 141.0, 140.5, 128.9, 128.9, 128.5, 128.3, 128.2, 126.9, 126.8, 124.5, 124.5, 120.2, 120.0, 82.6, 81.5, 68.3, 68.2, 51.0, 49.8, 34.3, 30.2, 29.8, 29.3, 29.0, 25.8, 25.6, 24.5, 24.5, 23.4. HRMS (ESI) m/z calcd for $C_{29}H_{40}N_3O_3S^+$ $[M + H]^+$ 510.2785, found 510.2787.



1b

6.6:1

4-(2-(tetrahydrofuran-2-yl)-2-(p-tolyl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 1245 mg, yield: 80%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 5.4 Hz, 2H), 7.36 (s, 1H), 7.10 – 7.06 (m, 4H), 4.15 – 4.06 (m, 1H), 3.80 – 3.62 (m, 2H), 3.26 (dd, *J* = 14.5, 5.3 Hz, 1H), 3.11 (dd, *J* = 14.5, 10.0 Hz, 1H), 3.01 (dt, *J* = 10.2, 5.2 Hz, 1H), 2.48 (s, 3H), 2.35 (s, 3H), 2.05 – 1.88 (m, 1H), 1.87 – 1.75 (m, 1H), 1.72 – 1.48 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 5.4 Hz, 2H), 7.36 (s, 1H), 7.10 – 7.06 (m, 4H), 4.09 – 4.04 (m, 1H), 3.95 – 3.80 (m, 2H), 3.54 (dd, *J* = 14.6, 3.8 Hz, 1H), 3.02–2.96 (m, 1H), 2.93 – 2.84 (m, 1H), 2.48 (s, 3H), 2.35 (s, 3H), 2.05 – 1.88 (m, 1H), 1.87 – 1.75 (m, 1H), 1.72 – 1.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.3, 137.9, 137.4, 136.3, 136.2, 133.3, 130.2, 130.2, 129.1, 128.9, 128.7, 128.3, 128.3, 128.1, 121.3, 121.3, 82.5, 81.5, 68.2, 68.2, 50.7, 49.6, 30.2, 29.4, 29.2, 29.2, 25.8, 25.6, 21.8, 21.2. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_3S^+$ $[M + H]^+$ 412.1689, found 412.1690.

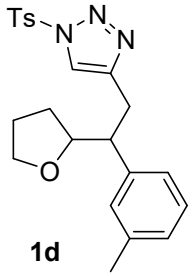


1c

5.5:1

4-(2-(tetrahydrofuran-2-yl)-2-(o-tolyl)ethyl)-1-tosyl-1H-1,2,3-triazole: clear oil ， 260.6 mg, yield: 41%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.36 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.12 – 6.94 (m, 2H), 4.14 (dt, *J* = 8.4, 6.2 Hz, 1H), 3.84 – 3.70 (m, 2H), 3.38 (dt, *J* = 10.7, 5.4 Hz, 1H), 3.28 (dd, *J* = 14.5, 5.0 Hz, 1H), 3.07 (dd, *J* = 14.4, 10.5 Hz, 1H), 2.49 (s, 3H), 2.09 – 2.00 (m, 1H), 1.98 (s, 3H), 1.87 – 1.81 (m, 1H), 1.80 – 1.55 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.40

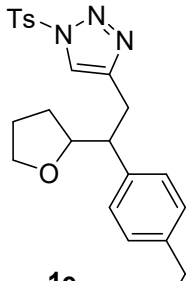
(d, *J* = 7.8 Hz, 2H), 7.36 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.12 – 6.94 (m, 2H), 4.24 – 4.12(m, 1H), 4.01 – 3.82 (m, 2H), 3.59 (dd, *J* = 14.4, 4.1 Hz, 1H),3.29 – 3.15(m, 1H), 2.93 (dd, *J* = 14.4, 10.9 Hz, 1H), 2.49 (s, 3H), 2.09 – 2.00 (m, 1H), 1.98 (s, 3H), 1.87 – 1.81 (m, 1H), 1.80 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.2, 139.0, 136.9, 133.3, 130.3, 130.2, 130.0, 128.3, 128.2, 127.0, 126.4, 126.3, 126.1, 121.2, 82.8, 81.7, 68.1, 44.2, 29.5, 29.2, 26.0, 21.8, 19.8. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_3S^+$ $[M + H]^+$ 412.1689, found 412.1695.



1d

11:1

4-(2-(tetrahydrofuran-2-yl)-2-(m-tolyl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 596 mg, yield: 61%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 3.5 Hz, 2H), 7.36 (s, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 4.20 – 4.00 (m, 1H), 3.80 – 3.69 (m, 2H), 3.26 (dd, *J* = 14.5, 5.2 Hz, 1H), 3.11 (dd, *J* = 14.5, 9.9 Hz, 1H), 3.00 (dt, *J* = 10.4, 5.5 Hz, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 2.05 – 1.95 (m, 1H), 1.85 – 1.83 (m, 1H), 1.74 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.2, 140.5, 137.7, 133.2, 130.3, 129.6, 128.3, 128.1, 127.5, 125.8, 121.3, 81.5, 68.2, 49.9, 29.5, 29.2, 25.8, 21.8, 21.5. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_3S^+$ $[M + H]^+$ 412.1689, found 412.1693.

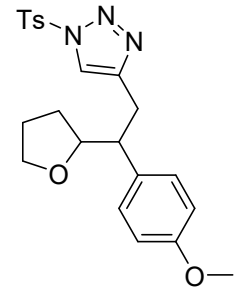


1e

3.1:1

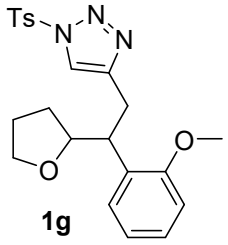
4-(2-(4-ethylphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: clear oil, 450 mg, yield: 96%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.79 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.12 – 7.05 (m, 4H), 4.19 – 4.06 (m, 1H), 3.80 – 3.67 (m, 2H), 3.26 (dd, *J* = 14.5, 5.3 Hz, 1H), 3.11 (dd, *J* = 14.5, 9.9 Hz, 1H), 3.01 (dd, *J* = 10.2, 4.9 Hz, 1H), 2.71 – 2.63 (m, 2H), 2.48 (s, 3H), 2.03 – 1.92 (m, 1H), 1.89 – 1.76 (m, 1H), 1.71 – 1.44 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.79 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.12 – 7.05 (m, 4H), 4.09 – 4.04 (m, 1H), 3.94 – 3.80 (m, 2H), 3.54 (dd, *J* = 14.6, 3.9 Hz, 1H), 3.00 – 2.96 (m, 1H), 2.93 – 2.86 (m, 1H), 2.71 – 2.63 (m,

2H), 2.48 (s, 3H), 2.03 – 1.92 (m, 1H), 1.89 – 1.76 (m, 1H), 1.71 – 1.44 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.8, 146.5, 146.2, 142.7, 142.5, 138.1, 137.6, 133.3, 133.3, 130.2, 130.2, 128.7, 128.3, 128.3, 128.1, 127.9, 127.7, 121.3, 121.3, 82.5, 81.5, 68.2, 68.2, 50.7, 49.6, 30.3, 29.4, 29.5, 28.4, 25.8, 25.6, 21.8, 15.4. HRMS (ESI) m/z calcd for $C_{23}H_{28}N_3O_3S^+$ $[M + H]^+$ 426.1846, found 426.1848.



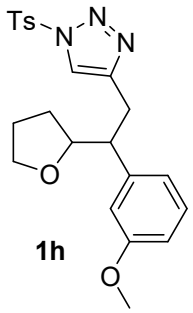
1f single isomer

4-(2-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p.: 95.6-97.3 ºC, 1051.5 mg, yield: 59%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 1H), 7.40 – 7.34 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.14 – 4.06 (m, 1H), 3.84 (s, 3H), 3.79 – 3.60 (m, 2H), 3.26 (dd, *J* = 14.7, 5.1 Hz, 1H), 3.11 (dd, *J* = 14.5, 10.0 Hz, 1H), 3.00 (dt, *J* = 10.1, 5.1 Hz, 1H), 2.48 (s, 3H), 2.05 – 1.90 (m, 1H), 1.86 – 1.75 (m, 1H), 1.65 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 146.9, 146.3, 133.3, 132.4, 130.3, 129.8, 128.3, 121.3, 113.6, 81.6, 68.2, 55.1, 49.1, 29.4, 29.3, 25.8, 21.7. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_4S^+$ $[M + H]^+$ 428.1639, found 428.1644.



1g

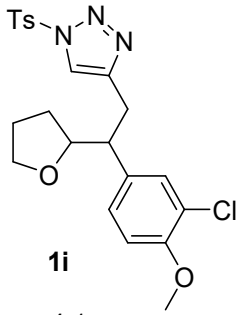
4-(2-(2-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p.: 101.6-102.7 ºC, 1051.5 mg ,yield: 45%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.43 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.16 (m, 2H), 6.89 – 6.81 (m, 2H), 4.25 – 4.05 (m, 1H), 3.84 – 3.73 (m, 2H), 3.71 (s, 3H), 3.69 – 3.59 (m, 1H), 3.23 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.15 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.47 (s, 3H), 2.08 – 1.94 (m, 1H), 1.93 – 1.85 (m, 1H), 1.76 – 1.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 146.9, 146.6, 133.3, 130.3, 128.9, 128.8, 128.3, 127.6, 121.1, 120.6, 110.5, 80.8, 68.1, 55.3, 41.4, 29.3, 28.2, 25.9, 21.7. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_4S^+$ $[M + H]^+$ 428.1639, found 428.1642.



1h

3:1

4-(2-(3-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: clear oil, 626 mg, yield: 73%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.40 – 7.32 (m, 2H), 7.24 – 7.14 (m, 1H), 6.83 – 6.75 (m, 2H), 6.74 – 6.69 (m, 1H), 4.07 – 4.16 (m, 1H), 3.79 – 3.68 (m, 5H), 3.26 (dd, *J* = 14.4, 5.2 Hz, 1H), 3.11 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.06 – 2.93 (m, 1H), 2.47 (s, 3H), 2.04 – 1.94 (m, 1H), 1.88 – 1.78 (m, 1H), 1.74 – 1.59 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.40 – 7.32 (m, 2H), 7.24 – 7.14 (m, 1H), 6.83 – 6.75 (m, 2H), 6.74 – 6.69 (m, 1H), 4.10 – 4.05 (m, 1H), 3.96 – 3.81 (m, 2H), 3.79 – 3.68 (s, 3H), 3.55 (dd, *J* = 14.5, 3.8 Hz, 1H), 3.00 – 2.95 (m, 1H), 2.92 – 2.87 (m, 1H), 2.47 (s, 3H), 2.04 – 1.94 (m, 1H), 1.88 – 1.78 (m, 1H), 1.74 – 1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.4, 146.9, 146.8, 146.3, 146.0, 142.7, 142.2, 133.2, 130.3, 130.2, 129.4, 129.1, 128.3, 128.2, 121.4, 121.3, 121.2, 120.5, 114.5, 114.1, 112.1, 111.8, 82.3, 81.4, 68.3, 68.2, 55.1, 55.1, 51.2, 50.1, 29.5, 29.2, 25.7, 25.6, 21.8, 21.7. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_4S^+$ $[M + H]^+$ 428.1639, found 428.1637.

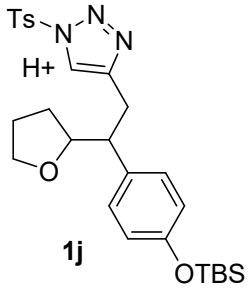


1i

4:1

4-(2-(3-chloro-4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: clear oil, 1772 mg, yield: 83%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.91 (s, 3H), 3.79 – 3.65 (m, 2H), 3.23 (dd, *J* = 14.5, 5.3 Hz, 1H), 3.08 (dd, *J* = 14.5, 9.9 Hz, 1H), 2.99 (dt, *J* = 10.7, 5.6 Hz, 1H), 2.47 (s, 3H), 2.02 – 1.96 (m, 1H), 1.87 – 1.78 (m, 1H), 1.65 – 1.42 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.90 (s, 3H) 3.88 – 3.77 (m, 2H), 3.49 (dd, *J* = 13.8, 3.1 Hz, 1H), 3.00 – 2.94 (m, 1H), 2.94 – 2.87

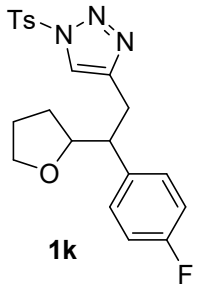
(m, 1H), 2.47 (s, 3H), 2.02 – 1.96 (m, 1H), 1.87 – 1.78 (m, 1H), 1.65 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 147.0, 147.0, 146.1, 145.9, 134.2, 133.6, 133.2, 133.1, 130.5, 130.3, 130.3, 129.8, 129.6, 128.3, 128.2, 128.1, 127.4, 126.4, 122.1, 121.9, 121.3, 121.2, 112.1, 111.8, 82.3, 81.2, 68.3, 68.2, 56.0, 49.9, 48.9, 29.5, 29.3, 25.8, 25.6, 21.8. HRMS (ESI) m/z calcd for $C_{22}H_{25}ClN_3O_4S^+$ $[M + H]^+$ 462.1249, found 462.1254.



1j

6.5:1

4-(2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: clear oil, 1003 mg, yield: 95%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.30 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 4.17 – 4.08 (m, 1H), 3.80 – 3.79 (m, 2H), 3.25 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.11 (dd, *J* = 14.6, 10.0 Hz, 1H), 2.98 (dt, *J* = 10.0, 5.0 Hz, 1H), 2.47 (s, 3H), 1.99 – 1.91 (m, 1H), 1.86 – 1.66 (m, 1H), 1.63 – 1.54 (m, 2H), 1.03 (s, 9H), 0.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 146.9, 146.3, 133.3, 133.0, 130.3, 130.2, 129.8, 129.1, 128.3, 128.3, 121.3, 120.1, 119.8, 82.6, 81.4, 68.3, 68.2, 50.3, 49.1, 30.2, 29.3, 25.8, 25.7, 21.8, 18.2, -4.3. HRMS (ESI) m/z calcd for $C_{27}H_{38}N_3O_4SSi^+$ $[M + H]^+$ 528.2347, found 528.2358.

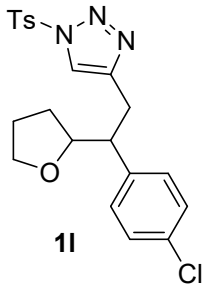


1k

3.8:1

4-(2-(4-fluorophenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 602 mg, yield: 58%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.75 (m, 2H), 7.43 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.07 (m, 2H), 6.94 – 6.85 (m, 2H), 4.24 – 4.04 (m, 1H), 3.78 – 3.69 (m, 2H), 3.28 – 3.20 (m, 1H), 3.14 – 3.00 (m, 2H), 2.49 (s, 3H), 2.05 – 1.96 (m, 1H), 1.82 – 1.74(m, 1H), 1.64 – 1.41 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.75 (m, 2H), 7.43 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.07 (m, 2H), 6.94 – 6.85 (m, 2H), 4.08 – 4.02 (m, 1H), 3.95 – 3.81 (m, 2H), 3.60 – 3.47 (m, 1H), 3.20 – 3.14 (m, 1H), 3.01 –

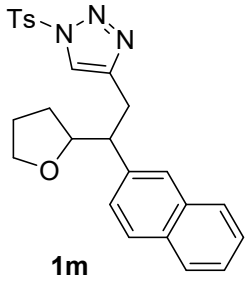
2.91 (m, 1H), 2.49 (s, 3H), 2.05 – 1.96 (m, 1H), 1.82 – 1.74(m, 1H), 1.64 –1.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245.0 Hz), 161.6 (d, *J* = 245.0 Hz) 162.8, 160.3, 147.1, 147.0, 146.3, 146.0, 136.8 (d, *J* = 3.1 Hz), 136.2 (d, *J* = 3.2 Hz), 130.4, 130.3 (d, *J* = 7.7 Hz), 129.6 (d, *J* = 7.7 Hz),121.4, 115.2 (d, *J* = 21.0 Hz), 115.0 (d, *J* = 21.1 Hz), 82.4, 81.3, 68.3, 50.3, 49.3, 30.2, 29.5, 25.8, 25.7, 21.8. HRMS (ESI) m/z calcd for $C_{21}H_{23}FN_3O_3S^+$ $[M + H]^+$ 416.1439, found 416.1440.



1l

3.4:1

4-(2-(4-chlorophenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 422.5 mg, yield: 50%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.42 – 7.36 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.12 – 4.01 (m, 1H), 3.79-3.70 (m, 2H), 3.24 (m, 1H), 3.12 – 3.06 (m, 1H), 3.03 – 2.94 (m, 1H) 2.48 (s, 3H), 2.08 – 1.93 (m, 1H), 1.87 – 1.71 (m, 1H), 1.69 – 1.38 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.42 – 7.36 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.07 – 4.01 (m, 1H), 3.96 – 3.79 (m, 2H), 3.49 (dd, *J* = 12.3, 7.6 Hz, 1H), 3.20 – 3.06 (m, 1H), 3.04 – 2.94 (m, 1H), 2.48 (s, 3H), 2.08 – 1.93 (m, 1H), 1.87 – 1.71 (m, 1H), 1.69 – 1.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 147.0, 139.5, 139.0, 133.2, 133.1, 132.3, 130.3, 130.3, 130.2, 129.6, 129.5, 128.5, 128.2, 128.2, 126.4, 121.4, 82.1, 81.2, 68.3, 50.4, 49.4, 30.2, 29.5, 29.3, 25.8, 25.6, 21.9, 21.8. HRMS (ESI) m/z calcd for $C_{21}H_{23}ClN_3O_3S^+$ $[M + H]^+$ 432.1143, found 432.1142.

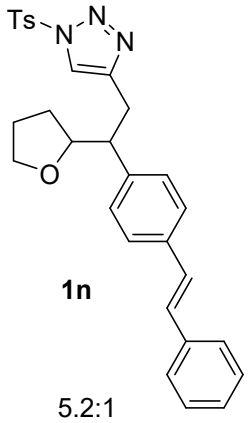


1m

5.2:1

4-(2-(naphthalen-2-yl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 761.5 mg, yield: 69%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.06 (m, 12H), 4.33 – 4.14 (m, 1H), 3.80 – 3.75 (m, 2H), 3.46 – 3.34 (m, 1H), 3.38 – 3.30 (m, 1H), 3.29 – 3.22 (m, 1H), 2.41 (s, 3H), 2.10 – 2.01 (m,

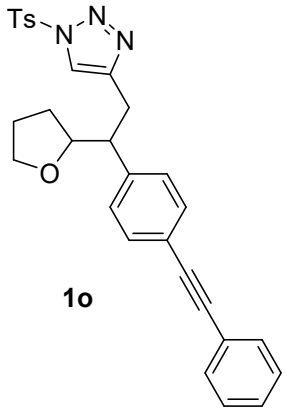
1H), 1.90 – 1.82 (m, 1H), 1.68 – 1.60 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.06 (m, 12H), 4.21 – 4.17 (m, 1H), 4.02 – 3.82 (m, 2H), 3.68 – 3.59 (m, 1H), 3.36 – 3.31 (m, 1H), 3.21 – 3.10 (m, 1H). 2.41 (s, 3H), 2.10 – 2.01 (m, 1H), 1.90 – 1.82 (m, 1H), 1.68 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 146.6, 146.4, 146.1, 138.4, 137.9, 133.3, 133.2, 133.1, 132.4, 132.4, 130.2, 130.1, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.6, 127.3, 126.8, 126.0, 125.8, 125.6, 125.5, 121.4, 121.4, 82.5, 81.5, 68.3, 68.2, 51.2, 50.1, 30.3, 29.5, 29.1, 29.0, 25.8, 25.7, 21.8. HRMS (ESI) m/z calcd for $C_{25}H_{26}N_3O_3S^+$ $[M + H]^+$ 448.1689, found 448.1695.



1n

5.2:1

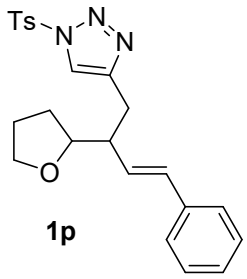
E)-4-(2-(4-styrylphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 612.5 mg, yield: 74%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.51 (m, 2H), 7.48 (s, 1H), 7.45 – 7.25 (m, 7H), 7.18 – 7.11 (m, 4H), 4.19 – 4.11 (m, 1H), 3.84 – 3.65 (m, 2H), 3.30 (dd, *J* = 14.3, 5.1 Hz, 1H), 3.23 – 3.16 (m, 1H), 3.14 – 3.04 (m, 1H), 2.43 (s, 3H), 2.05 – 1.95 (m, 1H), 1.91 – 1.76 (m, 1H), 1.72 – 1.52 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.51 (m, 2H), 7.48 (s, 1H), 7.45 – 7.25 (m, 7H), 7.18 – 7.11 (m, 4H), 4.12 – 4.04 (m, 1H), 3.97 – 3.79 (m, 2H), 3.64 – 3.50 (m, 1H), 3.10 – 3.03 (m, 1H), 3.03 – 2.94 (m, 1H). 2.43 (s, 3H), 2.05 – 1.95 (m, 1H), 1.91 – 1.76 (m, 1H), 1.72 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.8, 146.4, 146.1, 140.5, 140.1, 137.3, 137.2, 135.8, 135.8, 133.3, 133.2, 130.3, 130.2, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 127.7, 127.6, 126.6, 126.4, 126.3, 121.4, 121.3, 82.4, 81.4, 68.3, 50.8, 49.7, 29.5, 29.1, 25.8, 25.7, 21.8, 21.7. HRMS (ESI) m/z calcd for $C_{29}H_{29}N_3NaO_3S^+$ $[M + Na]^+$ 522.1822, found 522.1791.



1o

3.2:1

4-(2-(4-(phenylethynyl)phenyl)-2-(tetrahydrofuran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 470.5 mg, yield: 65%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.45 (s, 1H), 7.42 – 7.32 (m, 7H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.15 (dt, *J* = 10.1, 5.1 Hz, 1H), 3.89 – 3.64 (m, 2H), 3.29 (dd, *J* = 13.3, 4.1 Hz, 1H), 3.22 – 3.10 (m, 1H), 3.11 – 3.04 (m, 1H), 2.47 (s, 3H), 2.13 – 1.96 (m, 1H), 1.92 – 1.78 (m, 1H), 1.69 – 1.40 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.45 (s, 1H), 7.42 – 7.32 (m, 7H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.17– 4.10 (m, 1H), 3.97 – 3.80 (m, 2H), 3.64 – 3.51 (m, 1H), 3.10 – 3.05 (m, 1H), 3.04 – 2.95 (m, 1H), 2.47 (s, 3H), 2.13 – 1.96 (m, 1H), 1.92 – 1.78 (m, 1H), 1.69 – 1.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.9, 145.9, 141.4, 140.9, 133.2, 133.2, 131.6, 131.5, 131.4, 130.3, 130.3, 129.0, 128.4, 128.3, 128.3, 128.2, 128.2, 123.2, 123.1, 121.6, 121.5, 121.4, 89.5, 89.4, 89.3, 89.1, 82.2, 81.2, 68.3, 68.3, 51.0, 50.0, 30.2, 29.5, 29.2, 28.9, 25.8, 25.7, 21.9, 21.8. HRMS (ESI) m/z calcd for $C_{29}H_{28}N_3O_3S^+$ $[M + H]^+$ 498.1846, found 498.1850.

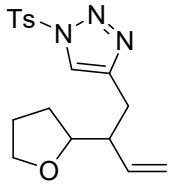


1p

2:3

(E)-4-(4-phenyl-2-(tetrahydrofuran-2-yl)but-3-en-1-yl)-1-tosyl-1H-1,2,3-triazole: white solid, 380.5 mg, yield: 37%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.03 (m, 10H), 6.22 (d, *J* = 6.7 Hz, 1H), 5.96 (dd, *J* = 15.9, 9.1 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.86 – 3.73 (m, 2H), 3.29 (dd, *J* = 14.8, 3.9 Hz, 1H), 2.85 (dd, *J* = 14.8, 9.7 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.42 (s, 3H), 2.02 – 1.85 (m, 3H), 1.75 – 1.59 (m, 1H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.03 (m, 10H), 6.26 (d, *J* = 6.6 Hz, 1H), 6.08 (dd, *J* = 16.0, 9.2 Hz, 1H). 3.93 – 3.86 (m, 1H), 3.86 – 3.73 (m, 2H), 3.11 (dd, *J* = 14.7, 5.3 Hz, 1H), 2.93 (dd, *J* = 14.7, 9.5 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.42 (s, 3H), 2.02 – 1.85 (m, 3H), 1.75 – 1.59 (m, 1H). ^{13}C NMR

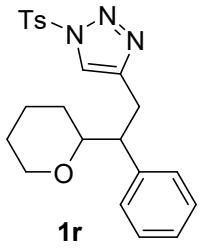
(101 MHz, $CDCl_3$) δ 146.9, 146.8, 146.3, 146.2, 137.0, 136.9, 133.2, 133.2, 133.1, 132.5, 130.3, 130.2, 129.1, 128.5, 128.5, 128.3, 127.4, 127.3, 126.1, 121.5, 81.1, 80.9, 68.5, 68.1, 48.4, 47.8, 29.6, 29.1, 28.5, 27.8, 26.0, 25.8, 21.8, 21.7. HRMS (ESI) m/z calcd for $C_{23}H_{26}N_3O_3S^+$ $[M + H]^+$ 424.1689, found 424.1695.



1q

5.8:1

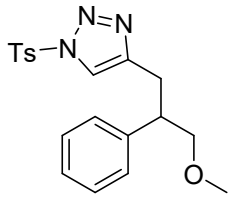
4-(2-(tetrahydrofuran-2-yl)but-3-en-1-yl)-1-tosyl-1H-1,2,3-triazole: clear oil, 83.4 mg, yield: 23%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.88 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 5.76 – 5.63 (m, 1H), 5.08 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.91 (dd, *J* = 17.2, 2.0 Hz, 1H), 3.90 – 3.81 (m, 2H), 3.79 – 3.70 (m, 1H), 3.00 (dd, *J* = 14.7, 5.1 Hz, 1H), 2.80 (dd, *J* = 14.8, 9.5 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.47 (s, 3H), 1.94 (m, 1H),1.92 – 1.83 (m, 2H), 1.69 – 1.63 (m, 1H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.61 – 5.52 (m, 1H), 5.03 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.92 (dd, *J* = 17.2, 2.0 Hz, 1H), 3.90 – 3.81 (m, 2H), 3.79 – 3.70 (m, 1H), 3.18 (dd, *J* = 14.8, 3.9 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.58 – 2.52 (m, 1H), 2.47 (s, 3H), 1.98 – 1.90 (m, 1H),1.92 – 1.83 (m, 2H), 1.69 – 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 147.0, 146.1, 137.4, 137.1, 133.2, 130.3, 129.6, 128.5, 126.4, 121.4, 118.0, 117.6, 80.7, 68.4, 68.0, 49.1, 48.5, 29.7, 29.5, 28.9, 27.9, 27.4, 25.9, 25.7, 21.8, 21.5. HRMS (ESI) m/z calcd for $C_{17}H_{22}N_3O_3S^+$ $[M + H]^+$ 348.1376, found 348.1378.



1r

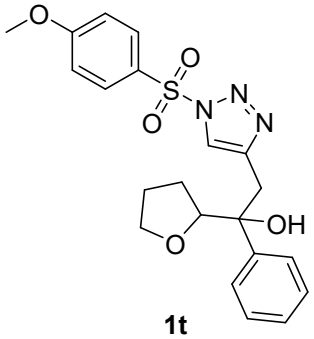
8:1

4-(2-phenyl-2-(tetrahydro-2H-pyran-2-yl)ethyl)-1-tosyl-1H-1,2,3-triazole: white solid, 110.5 mg, yield: 12%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 9.7 Hz, 2H), 7.37 (s, 1H), 7.32 – 7.11 (m, 5H), 4.16 – 3.93 (m, 1H), 3.49 – 3.42 (m, 1H), 3.39 – 3.34 (m, 1H), 3.32 – 3.24 (m, 1H), 3.12 (dd, *J* = 14.5, 9.5 Hz, 1H), 3.05 – 2.95 (m, 1H), 2.49 (s, 3H), 1.83 – 1.72 (m, 1H), 1.55 – 1.37 (m, 4H), 1.28 – 1.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.9, 146.5, 140.8, 133.4, 130.3, 129.1, 128.4, 128.0, 126.5, 121.3, 79.5, 68.9, 50.6, 29.2, 28.3, 26.0, 23.5, 21.7. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_3O_3S^+$ $[M + H]^+$ 412.1689, found 412.1696.



1s

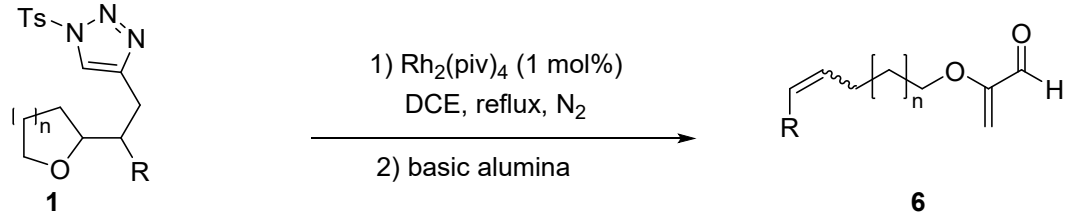
4-(3-methoxy-2-phenylpropyl)-1-tosyl-1H-1,2,3-triazole: white solid, m.p.: 88.6-91.3 ºC, 787.5 mg yield: 60%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.43 – 7.36 (m, 2H), 7.32 – 7.07 (m, 5H), 3.60 (d, *J* = 6.1 Hz, 2H), 3.34 (s, 3H), 3.33 – 3.21 (m, 2H), 3.06 – 2.98 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.0, 146.0, 141.3, 133.3, 130.3, 128.5, 128.4, 127.8, 126.9, 121.3, 76.1, 58.8, 45.4, 28.7, 21.8. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_3O_5S^+$ [M + H]$^+$ 372.1376, found 372.1380.



1t

2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-1-phenyl-1-(tetrahydrofuran-2-yl)ethan-1-ol: clear oil, 511 mg, yield: 61%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 9.0 Hz, 2H), 7.47 (s, 1H), 7.37 – 7.15 (m, 5H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.25 (dd, *J* = 8.3, 6.8 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.95 – 3.91 (m, 1H), 3.90 (s, 3H), 3.59 (dd, *J* = 15.2, 0.8 Hz, 1H), 3.36 (d, *J* = 15.2 Hz, 1H), 3.07 (s, 1H), 1.95 – 1.76 (m, 2H), 1.69 – 1.63 (m, 1H), 1.52 – 1.46 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 143.9, 141.6, 130.8, 128.1, 127.3, 126.9, 125.3, 122.0, 114.9, 84.8, 76.7, 69.6, 55.9, 37.1, 26.4, 26.1. HRMS (ESI) m/z calcd for $C_{21}H_{24}N_3O_5S^+$ [M + H]$^+$ 430.1431, found 430.1439.

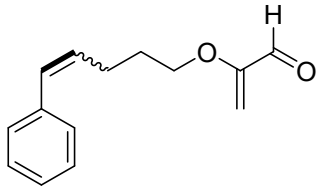
3. Procedure for synthesis of 6



1 **6**

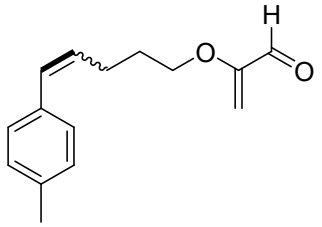
General procedure: Under N_2 atmosphere, dry DCE (2.0 mL) was added to an oven-dried reaction flask charged with triazole **1** (0.2 mmol), $Rh_2(piv)_4$ (0.002 mmol, 1

mol%) and a stirring bar, then the reaction mixture was stirred at reflux in an oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and basic alumina (5 g per mmol of triazole) was added to the crude reaction mixture and stirred at ambient temperature for 10 min. The reaction mixture was purified directly by flash column chromatography (10% ethyl acetate in petrol) to yield the aldehyde.



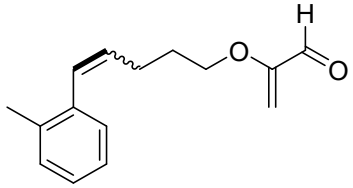
6a, 7 min, 93%, 1.5 mmol, 90%
Z/E = 5.4:1

(Z)-2-((5-phenylpent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 40.2 mg, yield: 93%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.44 – 7.13 (m, 5H), 6.52 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.70 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.18 (d, *J* = 2.9 Hz, 1H), 5.08 (d, *J* = 2.9 Hz, 1H), 3.84 (t, *J* = 6.5 Hz, 2H), 2.53 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.10 – 1.92 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.50 – 7.18 (m, 5H), 6.46 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.23 (d, *J* = 2.9 Hz, 1H), 5.11 (d, *J* = 2.9 Hz, 1H), 3.96 – 3.86 (m, 2H), 2.42 (qd, *J* = 7.3, 1.5 Hz, 2H), 2.05 – 2.01 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.1, 158.6, 158.6, 137.5, 137.3, 131.2, 130.8, 130.0, 129.3, 128.7, 128.5, 128.2, 127.0, 126.7, 126.0, 125.5, 103.0, 102.7, 67.6, 29.3, 28.7, 28.1, 24.9. HRMS (ESI) m/z calcd for $C_{14}H_{17}O_2^+$ $[M + H]^+$ 217.1223, found 217.1226.



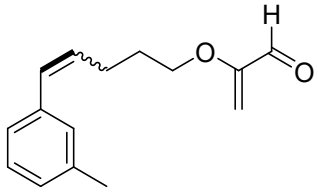
6b, 10 min, 78%
Z/E = 6.6:1

(Z/E)-2-((5-(p-tolyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 36.0 mg, yield: 78%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.24 – 7.14 (m, 4H), 6.48 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.66 (dt, *J* = 11.7, 7.3 Hz, 1H), 5.20 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.54 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.39 (s, 3H), 2.01-1.95 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.34 – 7.7.16 (m, 4H), 6.44 (d, *J* = 16.6 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.45 – 2.41 (m, 2H), 2.38 (s, 3H), 2.03 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 188.2, 158.6, 158.6, 136.8, 136.4, 134.7, 134.5, 130.6, 130.5, 129.8, 129.2, 128.9, 128.6, 128.2, 125.9, 102.9, 29.3, 28.7, 28.2, 24.9, 21.2. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2^+$ $[M + H]^+$ 231.1380, found 231.1380.



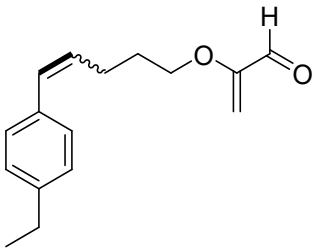
6c, 7 min, 84%
Z/E = 5.4:1

(Z/E)-2-((5-(o-tolyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 38.7 mg, yield: 84%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.28 – 7.02 (m, 4H), 6.54 (dt, *J* = 11.5, 1.7 Hz, 1H), 5.76 (dt, *J* = 11.5, 7.4 Hz, 1H), 5.16 (d, *J* = 2.9 Hz, 1H), 5.08 (d, *J* = 2.9 Hz, 1H), 3.79 (t, *J* = 6.6 Hz, 2H), 2.38 – 2.31 (m, 2H), 2.29 (s, 3H), 1.99 – 1.87 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.29-7.05 (m, 4H), 6.66 (dt, *J* = 15.7, 1.6 Hz, ^{1}H), 6.13 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.13 (d, *J* = 2.9 Hz, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.49 – 2.40 (m, 2H), 2.36 (s, 3H), 2.04 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 188.1, 158.7, 158.5, 136.7, 136.4, 136.1, 135.0, 131.1, 130.6, 130.2, 129.8, 129.2, 128.9, 128.7, 127.0, 126.9, 126.1, 125.4, 125.3, 103.1, 102.6, 67.6, 67.5, 28.5, 28.2, 24.7, 24.6, 19.9, 19.8. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2^+$ $[M + H]^+$ 231.1380, found 231.1384.



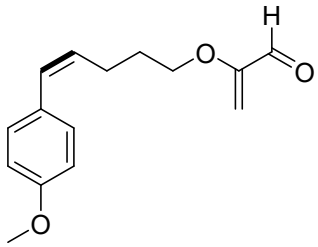
6d, 10 min, 80%
Z/E = 11:1

(Z/E)-2-((5-(m-tolyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 36.7 mg, yield: 80%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.35 – 7.00 (m, 4H), 6.48 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.68 (dt, *J* = 11.7, 7.3 Hz, 1H), 5.19 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.85 (t, *J* = 6.6 Hz, 2H), 2.53 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.39 (s, 3H), 2.04– 1.92 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 158.6, 137.7, 137.3, 131.1, 130.0, 129.4, 128.1, 127.4, 125.7, 102.8, 67.6, 28.7, 24.9, 21.5. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2^+$ $[M + H]^+$ 231.1380, found 231.1375.



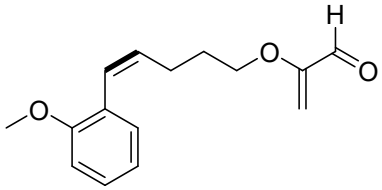
6e, 5 min, 73%
Z/E = 3.1:1

(Z/E)-2-((5-(4-ethylphenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 36.0 mg, yield: 73%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.38 – 7.07 (m, 4H), 6.49 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.66 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.21 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.72 – 2.64 (m, 2H), 2.55 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.11 – 1.89 (m, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.36 – 7.05 (m, 4H), 6.47 – 6.37 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.65 – 2.73 (m, 2H), 2.41 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.26 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 188.2, 158.6, 158.6, 143.2, 142.8, 135.0, 134.7, 130.7, 130.5, 129.8, 128.7, 128.3, 128.0, 127.7, 125.9, 125.6, 103.2, 102.9, 67.6, 67.5, 29.3, 28.7, 28.6, 28.2, 24.9, 15.6, 15.6. HRMS (ESI) m/z calcd for $C_{16}H_{21}O_2^+$ $[M + H]^+$ 245.1536, found 245.1529.



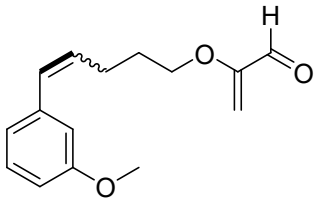
6f, 6 min, 88%

(Z)-2-((5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 43.7 mg, yield: 88%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.29 – 7.17 (m, 2H), 6.96 – 6.84 (m, 2H), 6.44 (dt, *J* = 11.6, 2.0 Hz, 1H), 5.60 (dt, *J* = 11.6, 7.2 Hz, 1H), 5.19 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.90 – 3.79 (m, 5H), 2.52 (qd, *J* = 7.3, 1.8 Hz, 2H), 2.06 – 1.88 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.1, 158.6, 158.3, 129.9, 129.9, 129.6, 129.4, 113.6, 102.8, 67.6, 55.2, 28.7, 24.9. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_3^+$ $[M + H]^+$ 247.1329, found 247.1332.



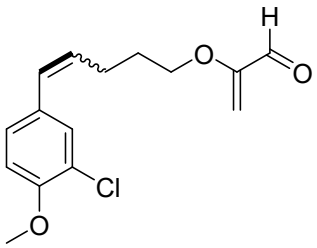
6g, 7 min, 73%

(Z/E)-2-((5-(2-methoxyphenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 36.1 mg, yield: 73%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.04 – 6.82 (m, 2H), 6.61 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.75 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.17 (d, *J* = 2.9 Hz, 1H), 5.07 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.44 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.05 – 1.84 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 158.6, 156.9, 131.1, 129.9, 128.2, 125.5, 120.1, 110.4, 102.4, 67.6, 55.4, 28.6, 24.9. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_3^+$ $[M + H]^+$ 247.1329, found 247.1333.



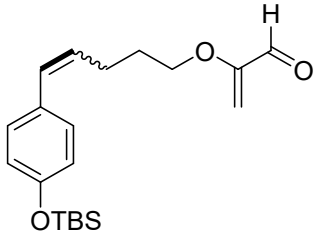
6h, 4 h, 23%
Z/E = 1.4:1

(Z/E)-2-((5-(3-methoxyphenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 11.7 mg, yield: 23%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.28 (s, 1H), 7.40 – 6.75 (m, 4H), 6.48 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.3 Hz, 1H), 5.18 (d, *J* = 2.9 Hz, 1H), 5.08 (d, *J* = 2.9 Hz, 1H), 3.99 – 3.63 (m, 5H), 2.53 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.07 – 1.85 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.43 – 6.67 (m, 4H), 6.45 – 6.38 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.11 (d, *J* = 2.9 Hz, 1H), 3.85 – 3.83 (m, 5H), 2.45 – 2.28 (m, 2H), 2.06 – 1.99 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.2, 159.8, 159.4, 158.6, 158.5, 139.0, 138.7, 131.6, 130.7, 129.8, 129.7, 129.5, 129.2, 121.2, 118.6, 114.4, 112.6, 112.0, 111.3, 103.1, 102.8, 67.6, 67.5, 55.2, 29.3, 28.7, 28.1, 25.0. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_3^+$ $[M + H]^+$ 247.1329, found 247.1332.



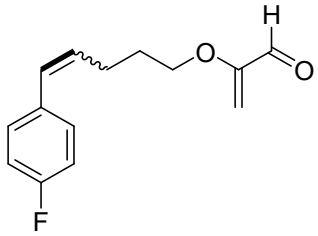
6i, 8 min, 82%
Z/E = 4:1

(Z/E)-2-((5-(3-chloro-4-methoxyphenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 46.2 mg, yield: 82%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.37 (dt, *J* = 11.7, 2.0 Hz, 1H), 5.64 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.19 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.93 (s, 3H), 3.83 (t, *J* = 6.5 Hz, 2H), 2.49 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.10 – 1.89 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.33 (d, *J* = 18.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.23 (d, *J* = 2.9 Hz, 1H), 5.11 (d, *J* = 2.9 Hz, 1H), 3.92 (s, 3H), 3.88 (t, *J* = 6.4 Hz, 2H), 2.42 – 2.31 (m, 2H), 2.03 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.1, 158.6, 158.5, 154.0, 153.6, 131.3, 131.0, 130.9, 130.4, 129.0, 128.6, 128.3, 128.1, 127.4, 125.5, 122.5, 122.0, 112.0, 111.8, 103.1, 102.9, 67.5, 67.4, 56.1, 29.2, 28.6, 28.1, 24.8. HRMS (ESI) m/z calcd for $C_{15}H_{17}ClNaO_3^+$ $[M + Na]^+$ 303.0758, found 303.0766.



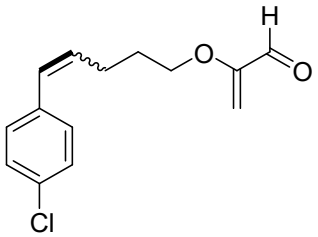
6j, 6 min, 81%
Z/E = 6.5:1

(Z/E)-2-((5-(4-((tert-butyldimethylsilyl)oxy)phenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 56.1 mg, yield: 81%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.43 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.59 (dt, *J* = 11.6, 7.2 Hz, 1H), 5.20 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.52 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.10 – 1.89 (m, 2H), 1.03 (s, 9H), 0.25 (s, 6H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.11 (d, *J* = 2.9 Hz, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.43 – 2.32 (m, 2H), 2.05 – 1.95 (m, 2H), 1.02 (s, 9H), 0.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.2, 158.6, 158.6, 154.9, 154.4, 130.9, 130.6, 130.3, 129.9, 129.6, 129.5, 127.2, 127.0, 120.1, 119.8, 103.0, 102.9, 67.7, 29.2, 28.8, 28.2, 25.7, 24.9, 18.2, -4.3. HRMS (ESI) m/z calcd for $C_{20}H_{31}O_3Si^+$ $[M + H]^+$ 347.2037, found 347.2048.



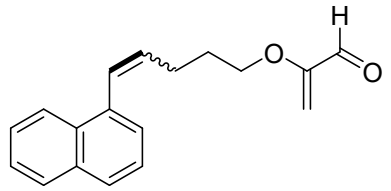
6k, 5 min, 85%
Z/E = 3.8:1

(Z/E)-2-((5-(4-fluorophenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 40.1 mg, yield: 85%, major isomer: 1H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.54 – 6.83 (m, 4H), 6.46 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.20 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.84 (t, *J* = 6.4 Hz, 2H), 2.49 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.03 – 1.80 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.33 – 6.92 (m, 4H), 6.39 (d, *J* = 18.9 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.88 (t, *J* = 6.5 Hz, 2H), 2.43 – 2.34 (m, 2H), 2.05 – 2.00 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 188.1, 162.0 (d, *J* = 246.0 Hz), 161.6 (d, *J* = 246.1 Hz), 158.7, 158.6, 131.1, 133.7 (d, *J* = 3.2 Hz), 133.4 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 7.9 Hz), 129.6, 129.1, 128.9, 127.4 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 21.7 Hz), 115.1 (d, *J* = 21.3 Hz), 103.1, 103.0, 67.6, 67.5, 29.3, 28.7, 28.2, 24.8. HRMS (ESI) m/z calcd for $C_{14}H_{16}FO_2^+$ $[M + H]^+$ 235.1129, found 235.1132.



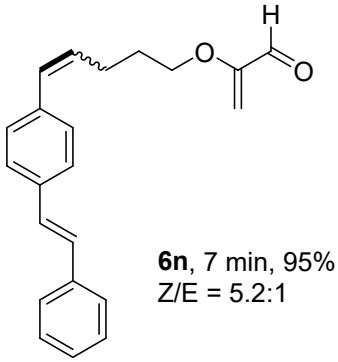
6l, 7 min, 94%
Z/E = 3.4:1

(Z/E)-2-((5-(4-chlorophenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 47.0 mg, yield: 94%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.44 (dt, *J* = 11.9, 2.0 Hz, 2H), 5.71 (dt, *J* = 11.6, 7.4 Hz, 1H), 5.19 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 3.0 Hz, 1H), 3.84 (t, *J* = 6.4 Hz, 2H), 2.50 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.03 – 1.88 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.50 – 6.81 (m, 4H), 6.38 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.88 (t, *J* = 6.4 Hz, 2H), 2.44 – 2.36 (m, 2H), 2.05 – 2.00 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.1, 158.6, 158.5, 136.0, 135.7, 132.5, 132.4, 131.9, 130.1, 130.0, 129.6, 128.8, 128.6, 128.3, 127.2, 103.1, 102.9, 67.5, 67.4, 29.3, 28.6, 28.0, 24.9. HRMS (ESI) m/z calcd for $C_{14}H_{16}ClO_2^+$ $[M + H]^+$ 251.0833, found 251.0816.



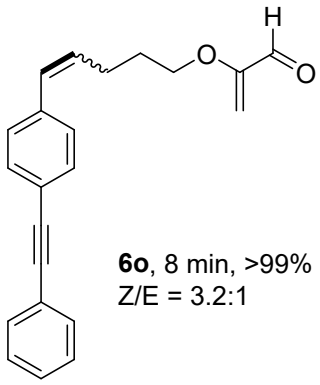
6m, 10 min, >99%
Z/E = 5.2:1

(Z/E)-2-((5-(naphthalen-1-yl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 54.6 mg, yield: >99%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.26 (s, 1H), 7.88 – 7.32 (m, 7H), 6.67 (dt, *J* = 11.6, 2.0 Hz, 1H), 5.79 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.17 (d, *J* = 2.9 Hz, 1H), 5.06 (d, *J* = 2.9 Hz, 1H), 3.84 (t, *J* = 6.5 Hz, 3H), 2.62 (qd, *J* = 7.4, 1.8 Hz, 3H), 2.09 – 2.01 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.99 – 7.19 (m, 7H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.40 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.53 – 2.42 (m, 2H), 2.10 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 188.2, 158.6, 158.5, 135.0, 134.9, 133.7, 133.3, 132.7, 132.2, 131.7, 130.9, 130.0, 129.8, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 127.1, 126.2, 126.1, 125.8, 125.6, 125.5, 123.5, 103.2, 102.9, 29.4, 28.7, 28.2, 25.0. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_2^+$ $[M + H]^+$ 267.1380, found 267.1384.



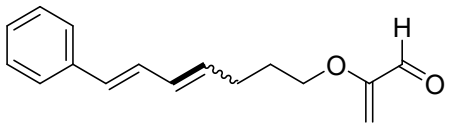
6n, 7 min, 95%
Z/E = 5.2:1

2-(((Z/E)-5-(4-((E)-styryl)phenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 60.8 mg, yield: 95%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.71 – 7.12 (m, 11H), 6.51 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.72 (dt, *J* = 11.7, 7.3 Hz, 1H), 5.21 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H), 3.87 (t, *J* = 6.4 Hz, 2H), 2.59 (qd, *J* = 7.4, 1.8 Hz, 2H), 2.07 – 1.93 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.71 – 6.98 (m, 11H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.13 (d, *J* = 2.9 Hz, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.49 – 2.36 (m, 2H), 2.04 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 188.2, 158.6, 158.6, 137.3, 136.9, 136.8, 136.1, 135.7, 131.4, 130.5, 129.6, 129.4, 129.1, 128.7, 128.5, 128.3, 128.2, 127.6, 126.7, 126.5, 126.4, 126.3, 103.2, 103.0, 67.6, 29.4, 28.7, 28.1, 25.1. HRMS (ESI) m/z calcd for $C_{22}H_{23}O_2^+$ $[M + H]^+$ 319.1693, found 319.1698.



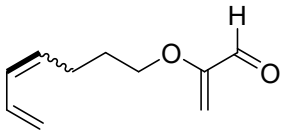
6o, 8 min, >99%
Z/E = 3.2:1

(Z/E)-2-((5-(4-(phenylethynyl)phenyl)pent-4-en-1-yl)oxy)acrylaldehyde: clear oil, 64.7 mg, yield: >99 %, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 7.63 – 7.24 (m, 9H), 6.50 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.75 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.20 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 3H), 2.55 (qd, *J* = 7.4, 1.9 Hz, 3H), 2.05 – 1.98(m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.62 – 7.25 (m, 9H), 6.46 (d, *J* = 16.1 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.8 Hz, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 2.46 – 2.39 (m, 2H), 2.08 – 1.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.1, 158.6, 158.5, 137.5, 137.4, 132.2, 131.8, 131.6, 131.6, 131.5, 130.5, 130.3, 129.4, 128.7, 128.3, 128.2, 125.9, 125.6, 123.3, 123.3, 121.7, 121.4, 103.1, 102.9, 89.8, 89.7, 89.6, 89.5, 67.5, 29.4, 28.7, 28.1, 25.1. HRMS (ESI) m/z calcd for $C_{22}H_{20}NaO_2^+$ $[M + Na]^+$ 339.1356, found 339.1364.



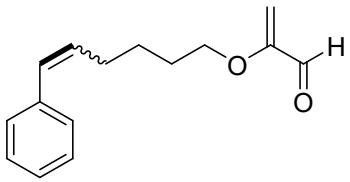
6p, 8 min, 95%
Z/E = 1:1.5

2-(((4Z/E,6E)-7-phenylhepta-4,6-dien-1-yl)oxy)acrylaldehyde: clear oil, 46.3 mg, yield: 95%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.54 – 7.17 (m, 5H), 6.86 – 6.74 (m, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.31 – 6.25 (m, 1H), 5.91 – 5.80 (m, 1H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.35 (qd, *J* = 7.2, 1.4 Hz, 2H), 2.03 – 1.94 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 7.50 – 7.20 (m, 5H), 7.08 (ddd, *J* = 15.5, 11.1, 1.2 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.30 – 6.24 (m, 1H), 5.65 – 5.49 (m, 1H), 5.22 (d, *J* = 2.9 Hz, 1H), 5.07 (d, *J* = 2.9 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.51 (qd, *J* = 7.3, 1.5 Hz, 2H), 2.05 – 1.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 188.2, 158.6, 137.5, 137.4, 133.8, 132.7, 131.5, 131.0, 130.6, 130.1, 129.0, 128.6, 127.5, 127.2, 126.4, 126.2, 123.9, 103.2, 103.0, 67.5, 67.1, 29.1, 28.3, 28.1, 24.2. HRMS (ESI) m/z calcd for $C_{16}H_{19}O_2^+$ $[M + H]^+$ 243.1380, found 243.1381.



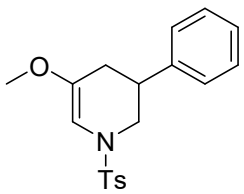
6q, 10 min, 72%
Z/E = 5.8:1

(Z/E)-2-(hepta-4,6-dien-1-yloxy)acrylaldehyde: clear oil, 24 mg, yield: 72%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 6.64 (dddd, *J* = 16.8, 11.2, 10.2, 1.1 Hz, 1H), 6.21 – 6.01 (m, 1H), 5.55 – 5.40 (m, 1H), 5.33 – 5.18 (m, 2H), 5.17 – 5.05 (m, 2H), 3.83 (t, *J* = 6.4 Hz, 2H), 2.39 (qd, *J* = 7.4, 1.5 Hz, 2H), 2.03 – 1.82 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 6.35 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.20 – 6.00 (m, 1H) 5.73 (dt, *J* = 14.6, 6.9 Hz, 1H). 5.31 – 5.17 (m, 2H), 5.13 – 5.00 (m, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.32 – 2.24 (m, 2H), 2.03 – 1.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 158.6, 137.0, 133.5, 131.9, 131.8, 130.8, 130.4, 117.5, 115.4, 103.1, 67.5, 67.3, 28.2, 27.9, 23.9, 23.8. HRMS (ESI) m/z calcd for $C_{10}H_{15}O_2^+$ $[M + H]^+$ 167.1067, found 167.1063.



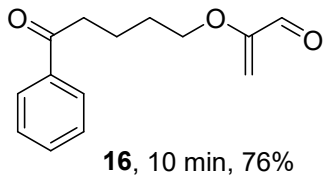
6r, 10 min, 50%
Z/E = 8:1

(Z/E)-2-((6-phenylhex-5-en-1-yl)oxy)acrylaldehyde: clear oil, 23 mg, yield: 50%, major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 7.62 – 7.17 (m, 5H), 6.50 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.71 (dt, *J* = 11.6, 7.2 Hz, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 5.09 (d, *J* = 2.9 Hz, 1H), 3.81 (t, *J* = 6.5 Hz, 3H), 2.43 (qd, *J* = 7.4, 1.9 Hz, 2H), 1.93 – 1.77 (m, 2H), 1.71 – 1.60 (m, 2H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.45 – 7.16 (m, 5H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.23 (d, *J* = 2.9 Hz, 1H), 5.12 (d, *J* = 2.9 Hz, 1H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.31 (qd, *J* = 7.3, 1.4 Hz, 2H), 1.90 – 1.78 (m, 2H), 1.69 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.2, 158.6, 137.6, 132.2, 129.3, 128.7, 128.1, 126.5, 102.7, 68.0, 28.1, 28.0, 26.2. HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2^+$ $[M + H]^+$ 231.1380, found 231.1384.



12, 4 h, 31%

5-methoxy-3-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine: clear oil, 21 mg, yield: 31%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.24 (m, 5H), 7.23 – 7.17 (m, 2H), 5.11 (t, *J* = 1.5 Hz, 1H), 4.40 (dd, *J* = 8.6, 7.0 Hz, 1H), 4.06 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.55 – 3.46 (m 1H), 3.07 (s, 3H), 2.98 (ddd, *J* = 15.5, 7.8, 1.4 Hz, 1H), 2.70 (ddd, *J* = 15.5, 7.7, 1.7 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.3, 143.0, 140.5, 135.1, 129.3, 128.8, 127.5, 127.1, 126.9, 98.2, 42.9, 37.1, 36.2, 21.5. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_3S^+$ $[M + Na]^+$ 366.1134, found 366.1138.

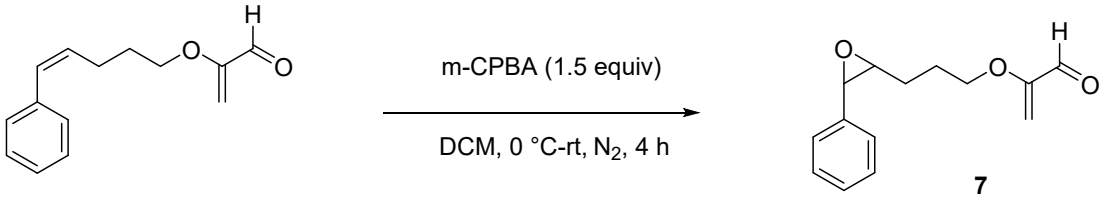


16, 10 min, 76%

2-((5-oxo-5-phenylpentyl)oxy)acrylaldehyde: white solid, m.p.: 80.6-85.3 ºC, 35.3 mg, yield: 76%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 8.09 – 7.88 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 5.23 (d, *J* = 2.9 Hz, 1H), 5.11 (d, *J* = 2.9 Hz, 1H), 4.15 – 3.76 (m, 2H), 3.20 – 2.97 (m, 2H), 2.01 – 1.86 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.9, 188.1, 158.6, 136.9, 133.0, 128.6, 128.0, 102.9, 68.2, 38.0, 28.1, 20.8. HRMS (ESI) m/z calcd for $C_{14}H_{17}O_3^+$ $[M + H]^+$ 233.1172, found 233.1170.

4. Procedure for derivations of 6

4.1 Synthesis of 2-(3-(3-phenyloxiran-2-yl)propoxy)acrylaldehyde

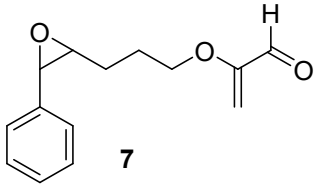


6a, 0.18 mmol

7

73% yield

Procedure: **6a** (0.18 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and *m*-CPBA (62.1 mg, 0.27 mmol) was added carefully to the mixture. Stirred the reaction mixture until the starting material disappeared monitored by TLC. After filtration, the solvent was removed under reduced pressure. Purify the crude on flash chromatography with petroleum ether /ethyl acetate 10:1 as eluent to obtain product **7** as a clear oil (30.0 mg, 73% yield).



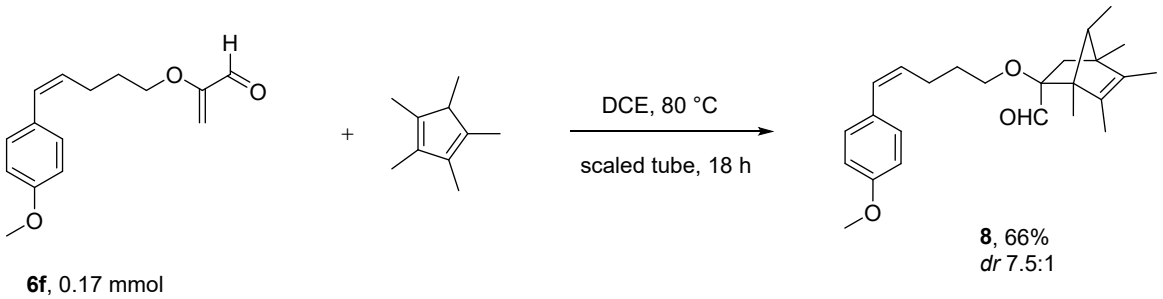
7

dr 5:1

5:1

2-(3-(3-phenyloxiran-2-yl)propoxy)acrylaldehyde: clear oil, 30.0 mg, yield: 73%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.26 (s, 1H), 7.49 – 7.17 (m, 5H), 5.12 (d, *J* = 2.9 Hz, 1H), 5.06 (d, *J* = 2.9 Hz, 1H), 4.13 (d, *J* = 4.2 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.32 – 3.23 (m, 2H), 2.02 – 1.86 (m, 2H), 1.57 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.0, 158.4, 135.3, 128.1, 127.6, 126.4, 102.8, 67.5, 58.8, 57.3, 25.2, 23.3. HRMS (ESI) m/z calcd for $C_{14}H_{17}O_3^+$ $[M + H]^+$ 233.1172, found 233.1177.

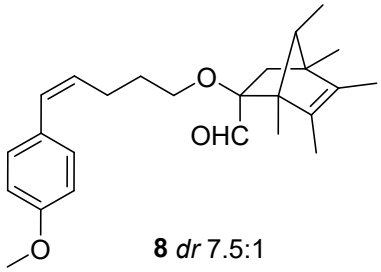
4.2 Synthesis of (2S,4S)-2-(((Z)-5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde



6f, 0.17 mmol

8, 66%
dr 7.5:1

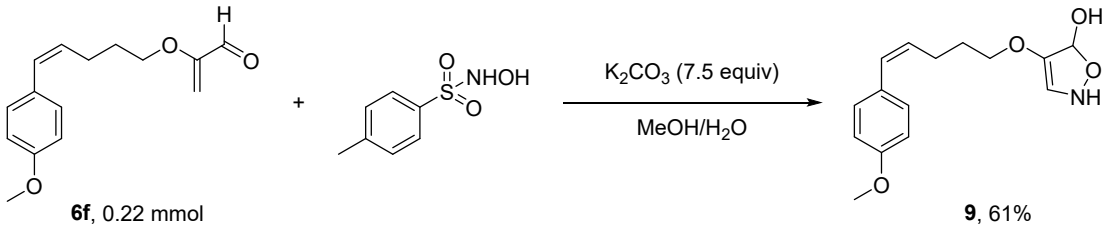
Procedure: In a nitrogen-protected round-bottom flask with a stirring bar, **6f** (0.17 mmol, 42 mg), 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (0.68 mmol, 90.1 mg), and dry DCE (2 mL) were added. The reaction mixture was heated at 80°C for 14 h. The resulting mixture was cooled to room temperature, and filtered through a short plug of silica gel. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (10:1) as eluent to give the corresponding product **8** as a colorless oil (43.2 mg, 66% yield).



8 *dr* 7.5:1

2-(((Z)-5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde: clear oil, 43.2 mg, yield: 66% ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.43 (s, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.40 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.61 (dt, *J* = 11.6, 7.4 Hz, 1H), 3.82 (s, 3H), 3.47 – 3.28 (m, 2H), 2.56 – 2.46 (m, 2H), 2.03 – 1.94 (m, 1H), 1.85 (d, *J* = 12.1 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.53 (d, *J* = 1.3 Hz, 3H), 1.44 (d, *J* = 12.0 Hz, 1H), 1.38 (d, *J* = 1.5 Hz, 3H), 1.13 – 1.04 (m, 6H), 0.59 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 203.7, 158.5, 138.9, 130.4, 130.1, 129.9, 128.7, 127.0, 113.5, 92.3, 64.9, 63.1, 58.5, 54.6, 51.9, 38.3, 30.5, 25.1, 14.4, 10.6, 9.5, 9.4, 6.6. HRMS (ESI) m/z calcd for $C_{25}H_{35}O_3^+$ $[M + H]^+$ 383.2581, found 383.2596.

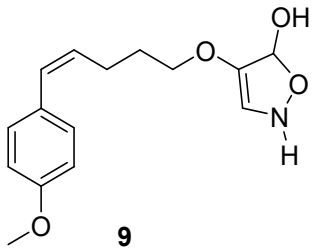
4.3 Synthesis of (Z)-4-((5-phenylpent-4-en-1-yl)oxy)-2,5-dihydroisoxazol-5-ol



6f, 0.22 mmol

9, 61%

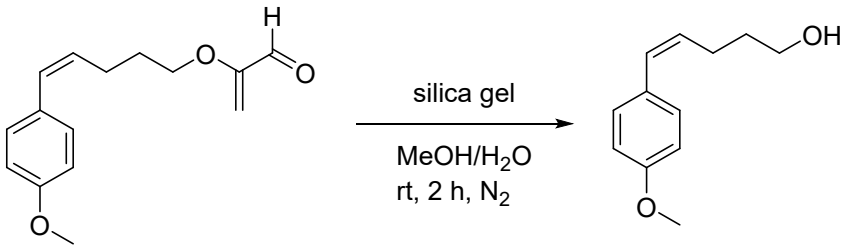
Procedure: To a solution of N-hydroxyl-4-toluenesulfonamide (149.8 mg, 0.8 mmol) in 1.4 mL methanol/water (vol: vol = 6: 1) was added K_2CO_3 (138.2 mg, 1.0 mmol) in portions. Then solution of **6f** (50 mg, 0.23 mmol) in 0.6 mL methanol was added, and the reaction mixture was stirred for 10 h at room temperature and monitored by TLC till all of the starting material was consumed. Then additional K_2CO_3 (69.1 mg, 0.5 mmol) was added and the mixture was stirred for 24 h at 60 °C. On completion, the reaction mixture was diluted with EtOAc (40 mL) and the mixture was washed with water (20 mL) and brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4.After filtration, the filtrate was concentratedon rotary evaporation under reduced pressure gave a residue, which was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 2:1) to afford **9** as a white solid (38.3 mg, 61% yield).



9

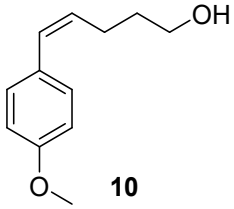
(Z)-4-((5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)-2,5-dihydroisoxazol-5-ol: white solid, m.p.: 106.9-107.2 ºC, 38.3 mg, yield: 61%, ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.95 (s, 1H), 7.26 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.38 (dd, J = 11.7, 2.0 Hz, 1H) , 5.58 (dt, J = 11.6, 7.1 Hz, 1H), 5.01 (d, J = 2.0 Hz, 1H), 4.44 (d, J = 2.0 Hz, 1H), 3.82 – 3.75 (m, 5H), 2.45 (qd, J = 7.3, 1.8 Hz, 2H), 1.91 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 158.4, 154.0, 130.5, 130.3, 130.1, 129.1, 114.2, 89.5, 67.9, 55.5, 28.9, 25.3. HRMS (ESI) m/z calcd for $C_{15}H_{20}NO_4^+$ $[M + H]^+$ 278.1387, found 278.1395.

4.4 Synthesis of (Z)-5-phenylpent-4-en-1-ol



6f, 0.2 mmol **10**, 99%

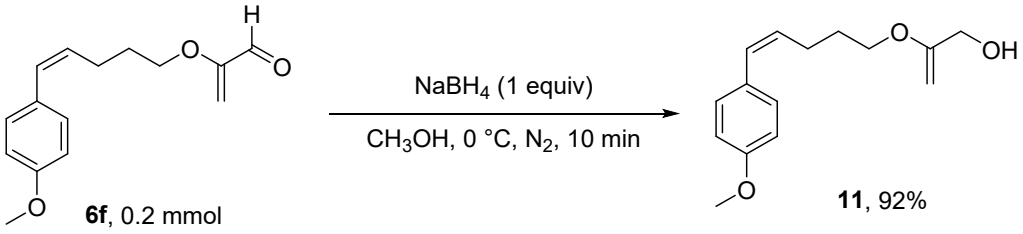
Procedure: **6f** was dissolved in MeOH (6 mL) and wet silica gel was added, the mixture was stirred at room temperature for 2 h. After filtration, MeOH was removed under reduced pressure, and the residue was purified by flash chromatography to give **10** as a clear oil (38.2 mg, 99%).



10

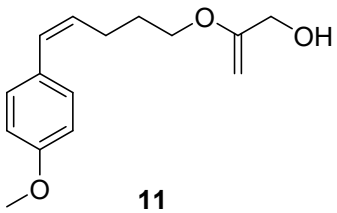
(Z)-5-(4-methoxyphenyl)pent-4-en-1-ol: clear oil, 38.2 mg, yield: 99%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.20 (m, 2H), 7.03 – 6.80 (m, 2H), 6.42 (dd, *J* = 11.6, 1.9 Hz, 1H), 5.61 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.84 (s, 3H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.45 (qt, *J* = 7.4, 1.7 Hz, 2H), 1.95 – 1.67 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.3, 130.5, 130.2, 129.9, 128.9, 113.6, 62.4, 55.3, 32.9, 24.9. HRMS (ESI) m/z calcd for $C_{12}H_{17}O_2^+$ [M + H]$^+$ 193.1223, found 193.1234.

4.5 Synthesis of (Z)-2-((5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)prop-2-en-1-ol



6f, 0.2 mmol **11**, 92%

Procedure: Under N_2 atmosphere, MeOH (2.0 mL) was added to a reaction flask charged with **6f** (0.2 mmol) and a stirring bar; with stirring, $NaBH_4$ (7.6 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature for 10 min. Upon completion of the reaction, and the residue was purified by flash column chromatography giving **11** as a clear oil (46.2 mg, 92% yield).



11

(Z)-2-((5-(4-methoxyphenyl)pent-4-en-1-yl)oxy)prop-2-en-1-ol: clear oil, 46.2 mg, yield: 92%, ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.28 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.41 (dt, J = 11.7, 2.0 Hz, 1H), 5.61 (dt, J = 11.6, 7.3 Hz, 1H), 4.20 (s, 1H), 4.05 – 3.90 (m, 4H), 3.82 (s, 3H), 3.78 (t, J = 6.3 Hz, 2H), 2.47 (qd, J = 7.4, 1.8 Hz, 2H), 1.93 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.2, 163.7, 135.3, 135.2, 135.1, 135.1, 134.1, 118.8, 85.0, 71.6, 67.4, 59.8, 30.2. HRMS (ESI) m/z calcd for $C_{15}H_{21}O_3^+$ $[M + H]^+$ 249.1485, found 249.1490.

5. References

[1] D. Yadagiri and P. Anbarasan, Rhodium-catalyzed denitrogenative [2,3] sigmatropic rearrangement: an efficient entry to sulfur-containing quaternary centers, *Chem.-Eur. J.*, 2013, **19**, 15115-15119.

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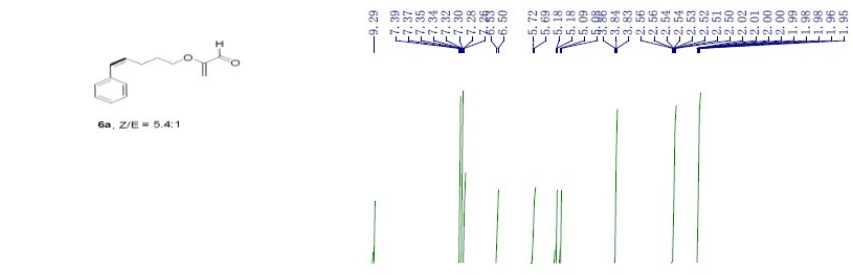
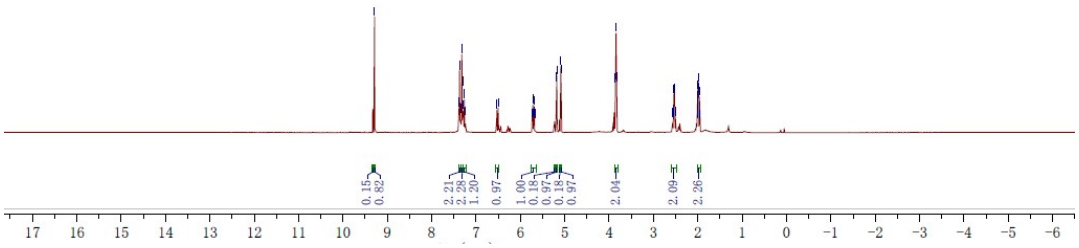
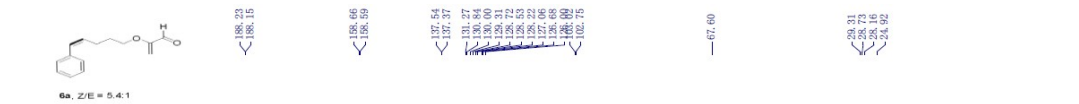
[3] A. Boyer, Rhodium(II)-catalyzed stereocontrolled synthesis of 2-tetrasubstituted saturated heterocycles from 1-sulfonyl-1,2,3-triazoles, *Org. Lett.*, 2014, **16**, 5878-5881.

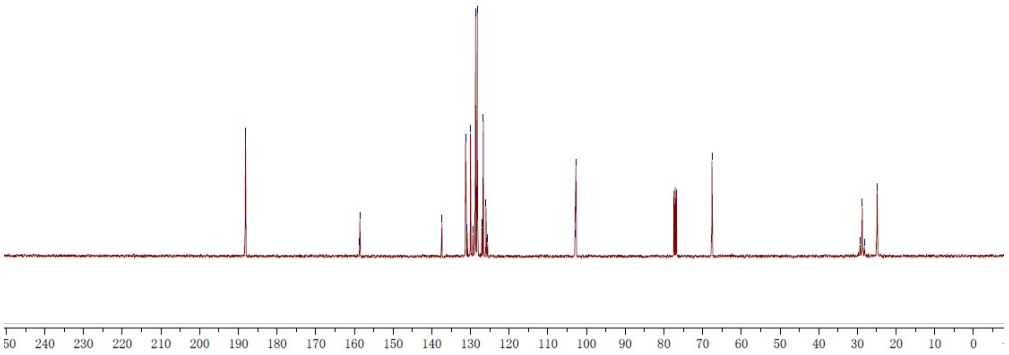
[4] Z.-F. Xu, W. Wang, M. Cen, Z. Feng, S. Duan and C.-Y. Li, Synthesis of α-(2-Hydroxyphenyl)-α-Aminoketones by Rhodium-Catalyzed Tandem Reaction of 1-Sulfonyl-1,2,3-Triazoles and Benzoquinone-Derived Alcohols, *Adv. Synth. Catal.*, 2020, **362**, 2888-2893.

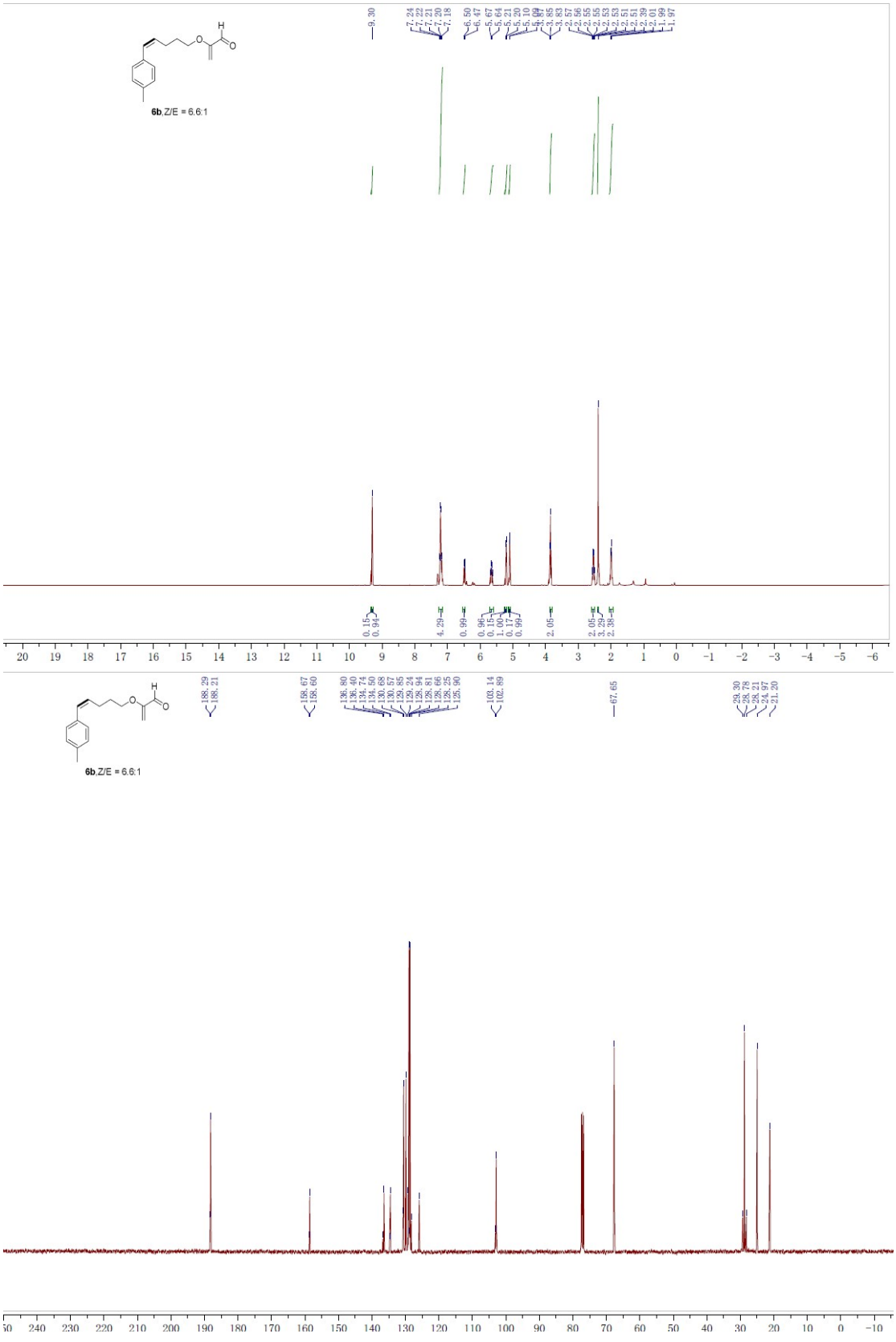
6. NMR spectra










6b, Z/E = 6.6:1
8.30
7.24
7.22
7.21
7.20
7.18
6.50
6.47
5.67
5.64
5.21
5.20
5.10
5.08
3.85
3.83
2.57
2.56
2.55
2.55
2.53
2.53
2.51
2.51
2.39
2.01
1.99
1.97
0.15
0.94
4.29
0.99
0.96
0.15
1.00
0.17
0.99
2.05
2.05
3.29
2.38
6b, Z/E = 6.6:1
188.29
188.21
158.67
158.60
136.80
136.40
134.74
134.69
130.68
130.57
129.85
129.24
128.94
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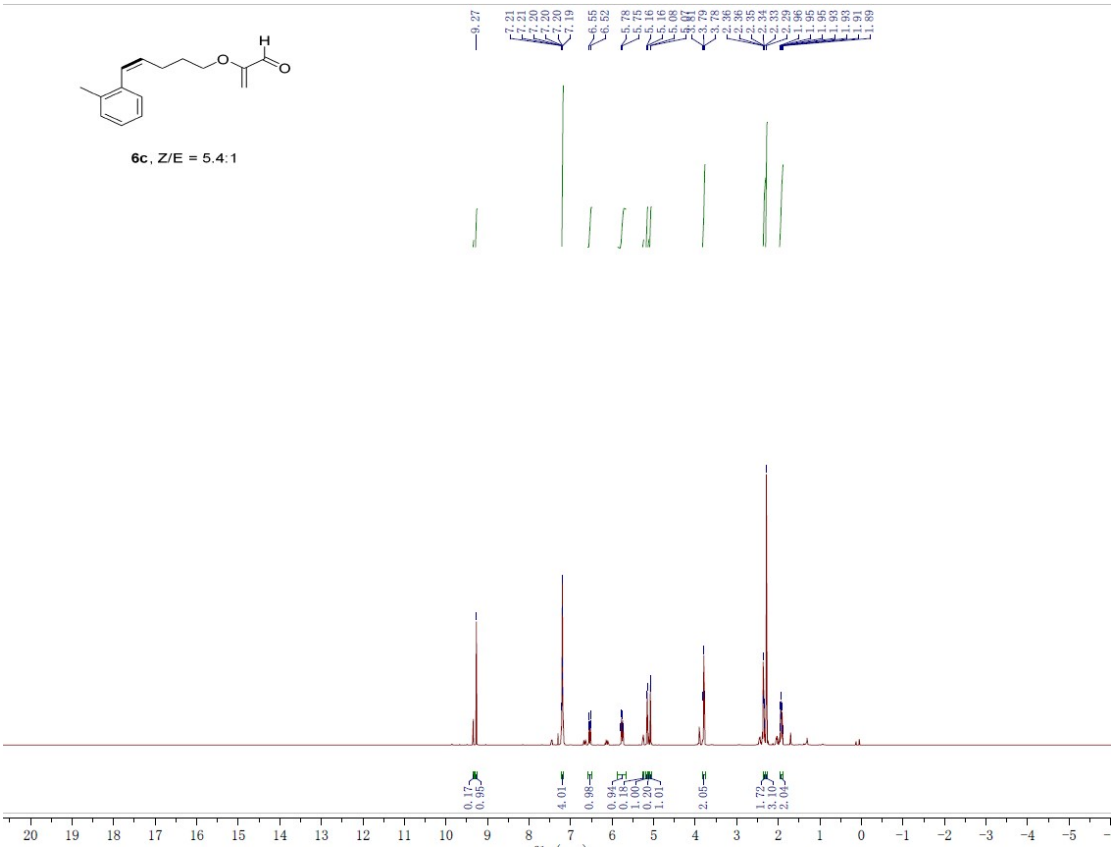
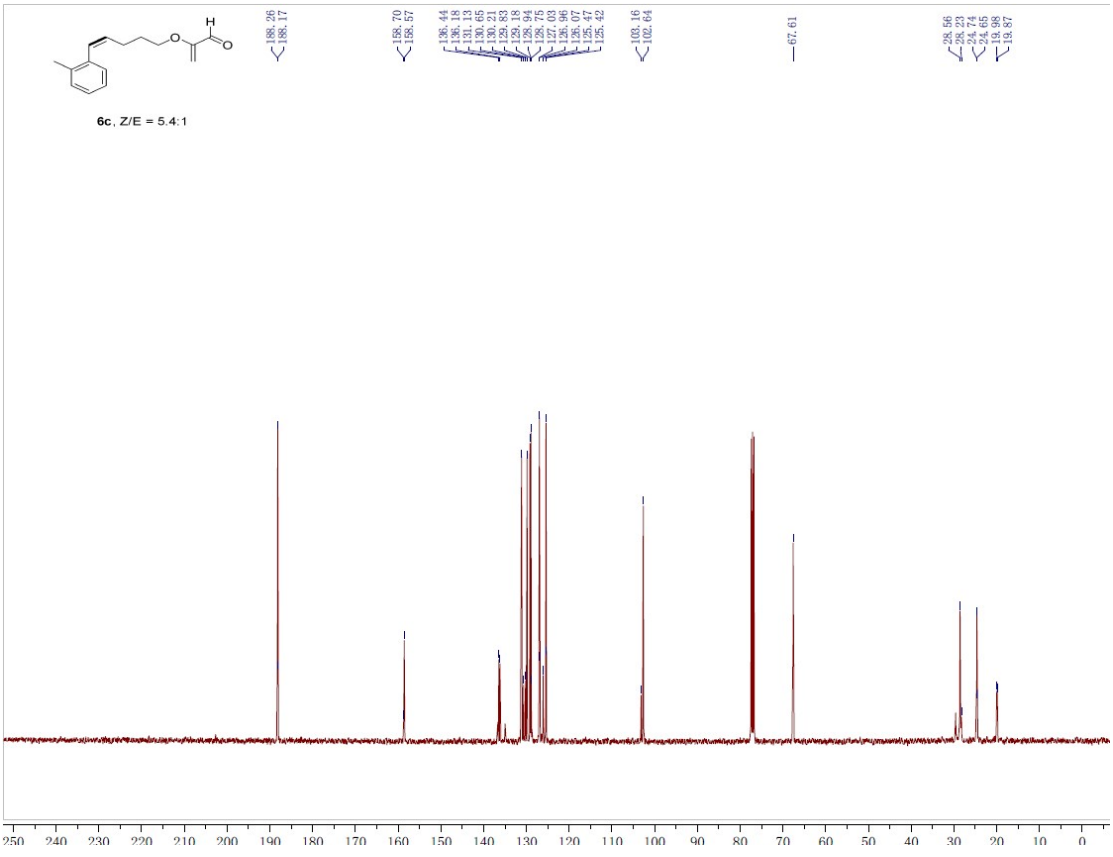
67.65
29.30
28.78
24.71
24.57
21.20


6c, Z/E = 5.4:1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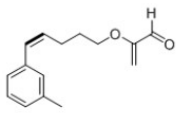
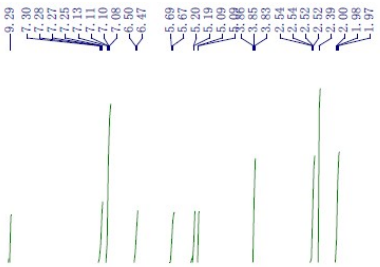
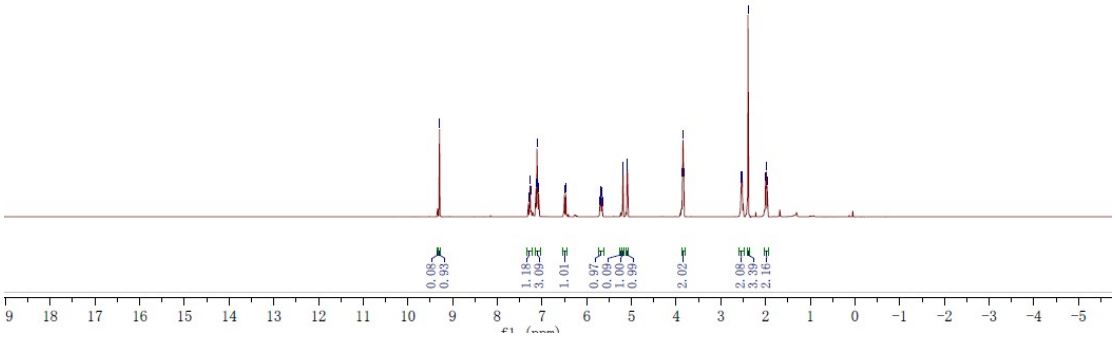
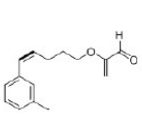


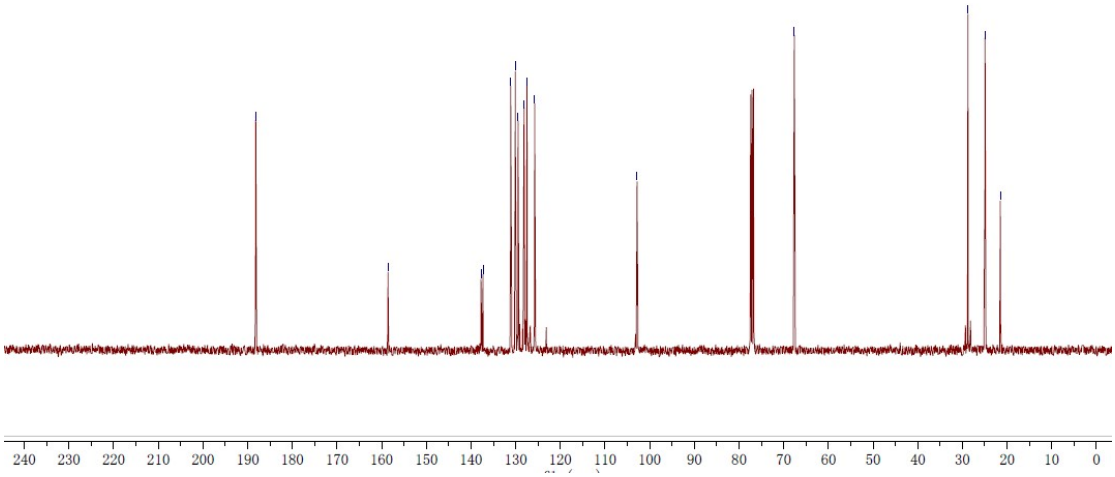
6d, Z/E = 11:1

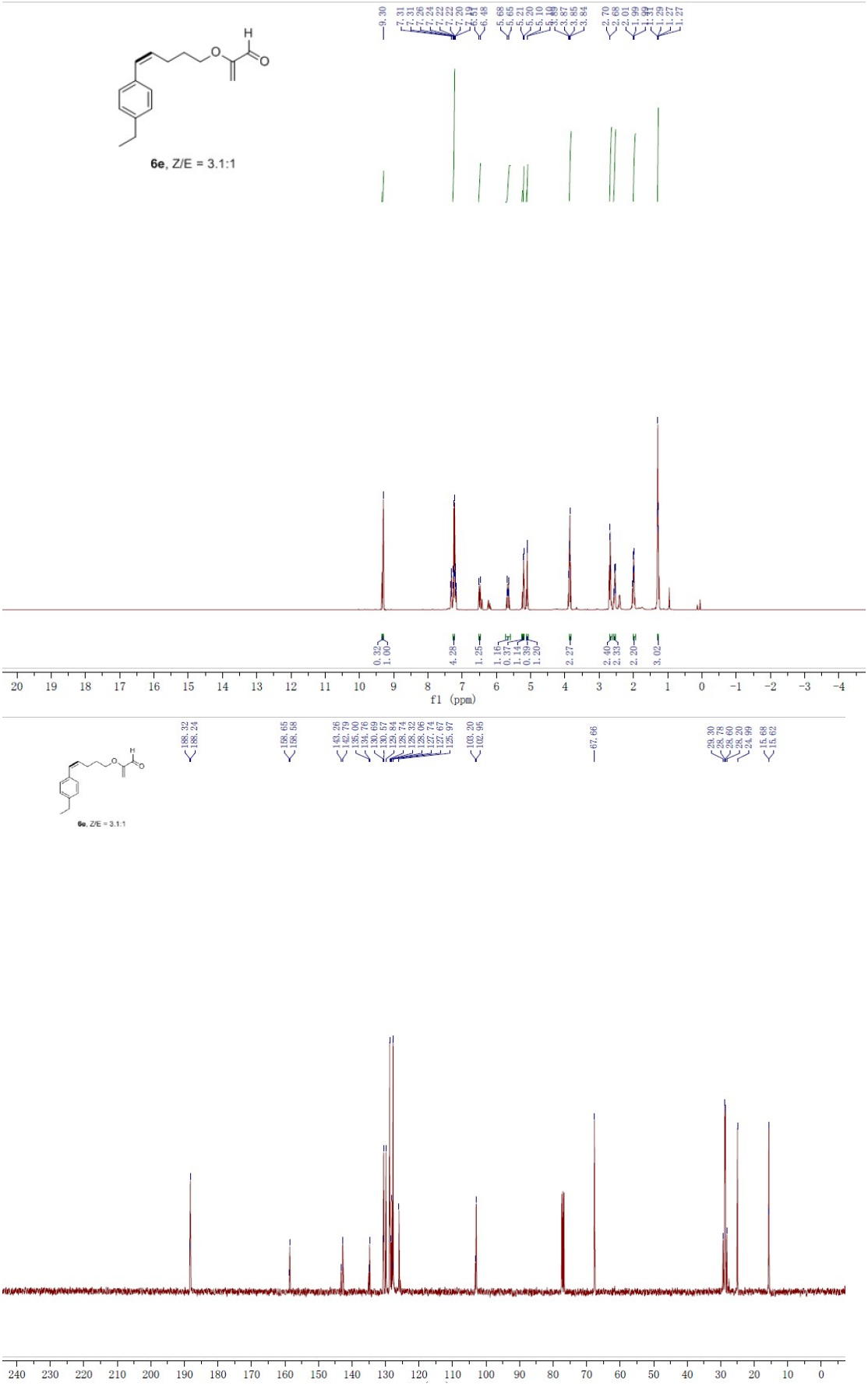


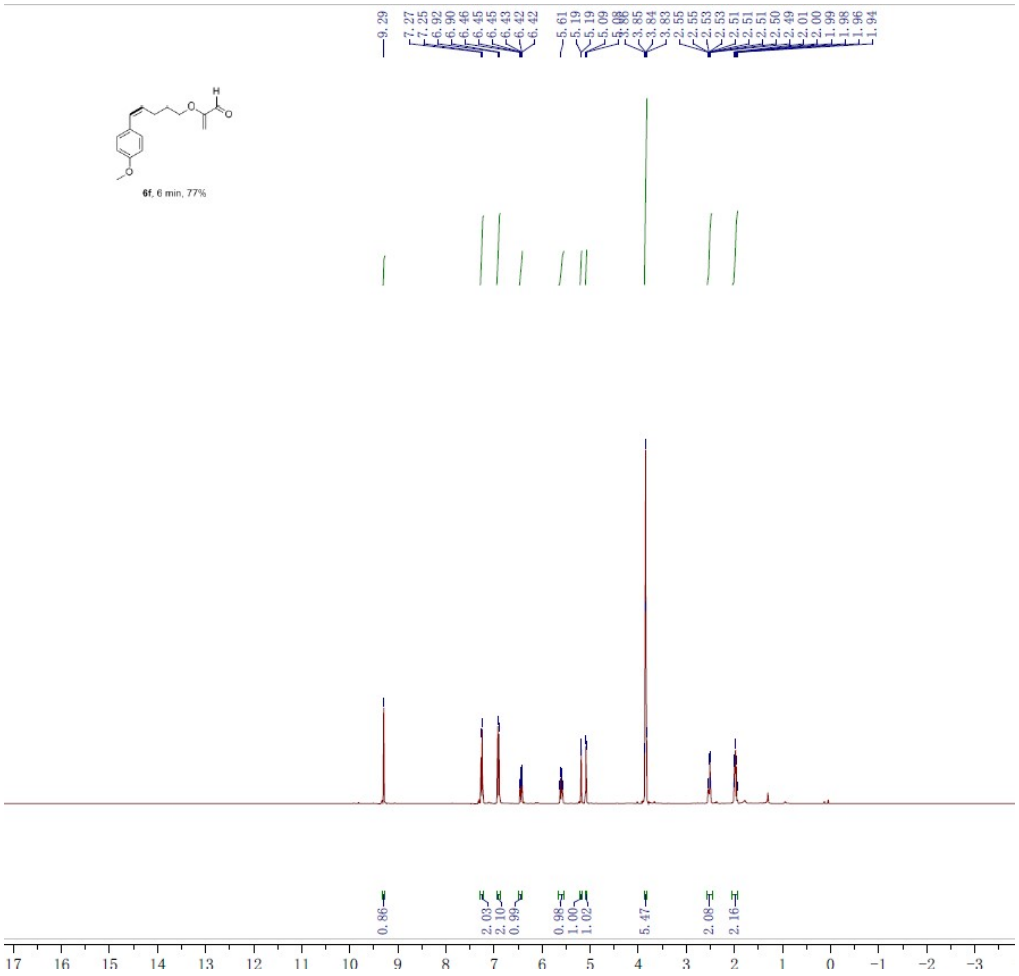


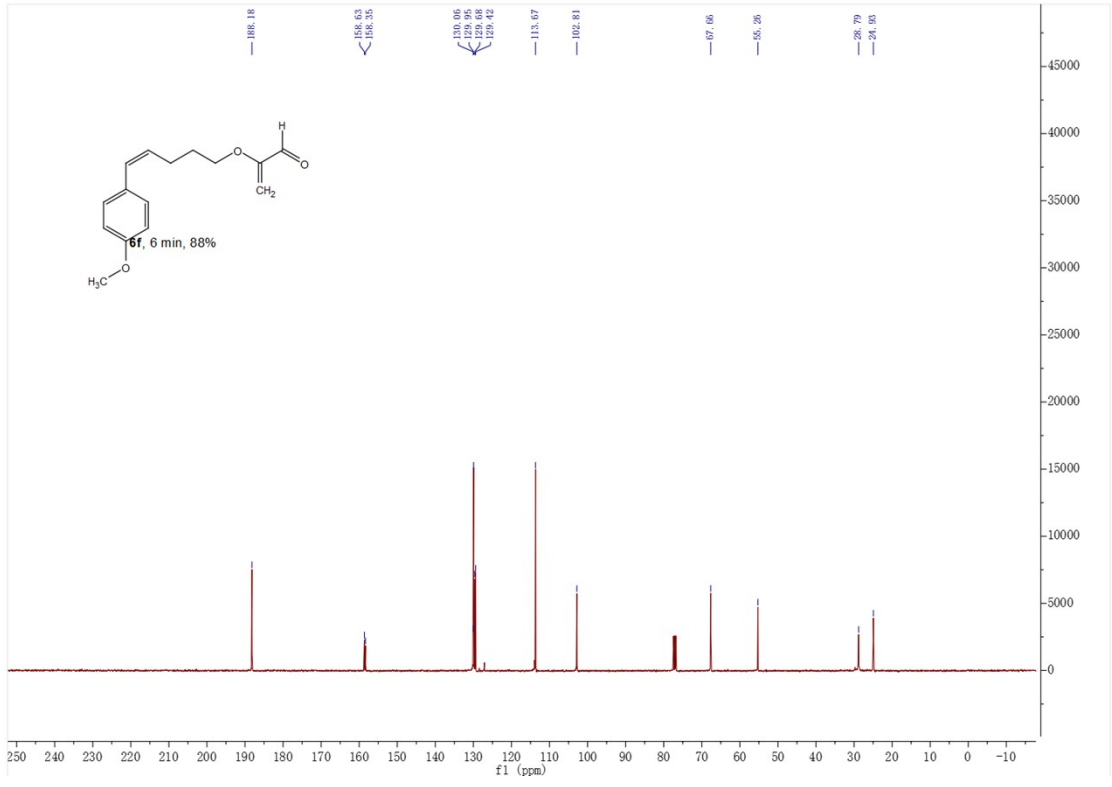


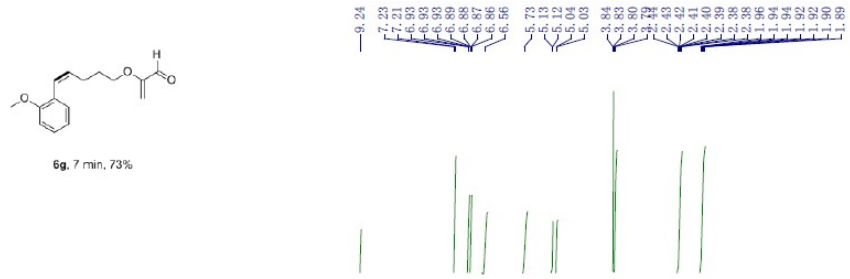
6d, Z/E = 11:1



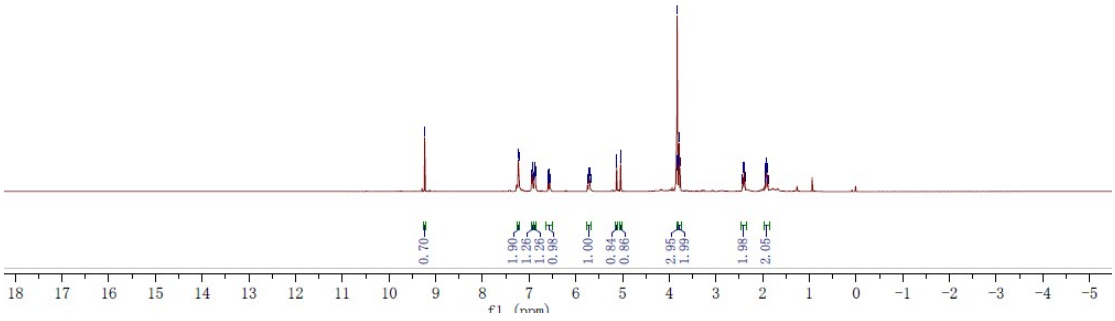

6e, Z/E = 3.1:1
f1 (ppm)

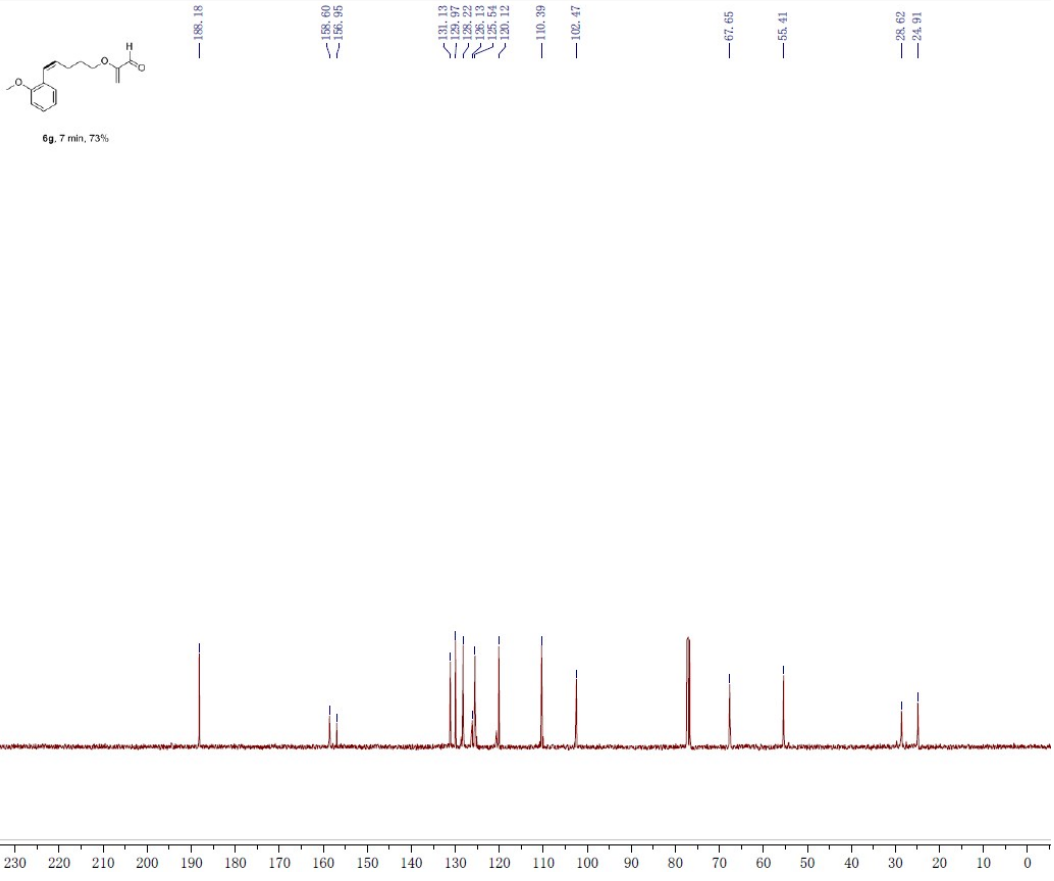

6f, 6 min, 77%

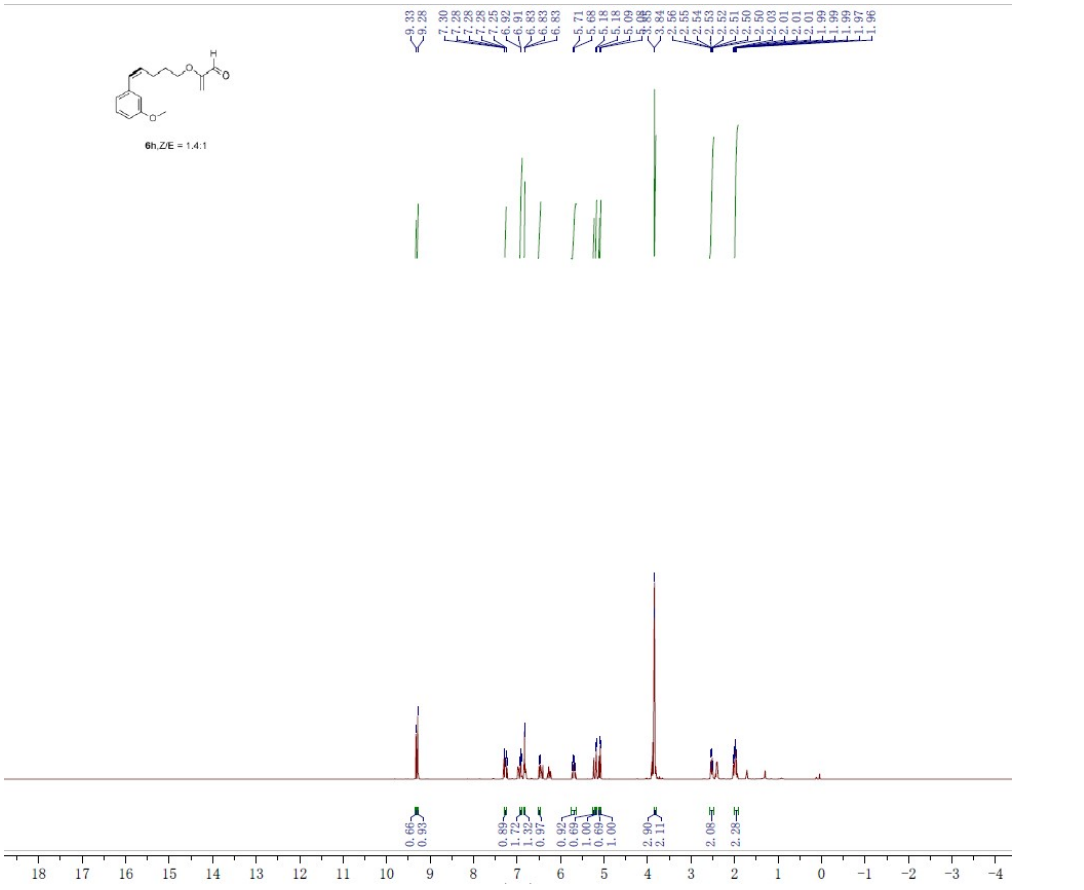

6f, 6 min, 88%
f1 (ppm)

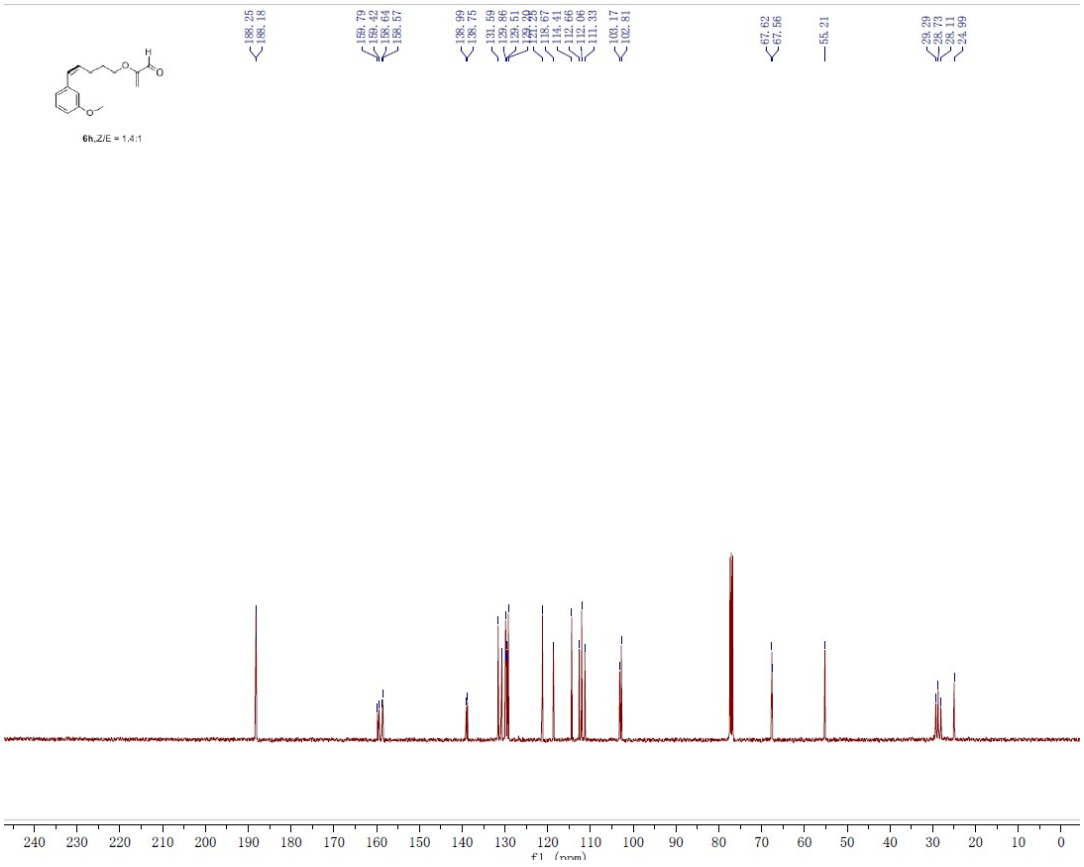

9.24
7.23
7.21
6.93
6.93
6.93
6.89
6.88
6.87
6.86
6.56
5.73
5.13
5.12
5.04
5.03
3.84
3.83
3.80
2.43
2.42
2.41
2.40
2.39
2.38
2.38
1.96
1.94
1.94
1.92
1.92
1.90
1.89

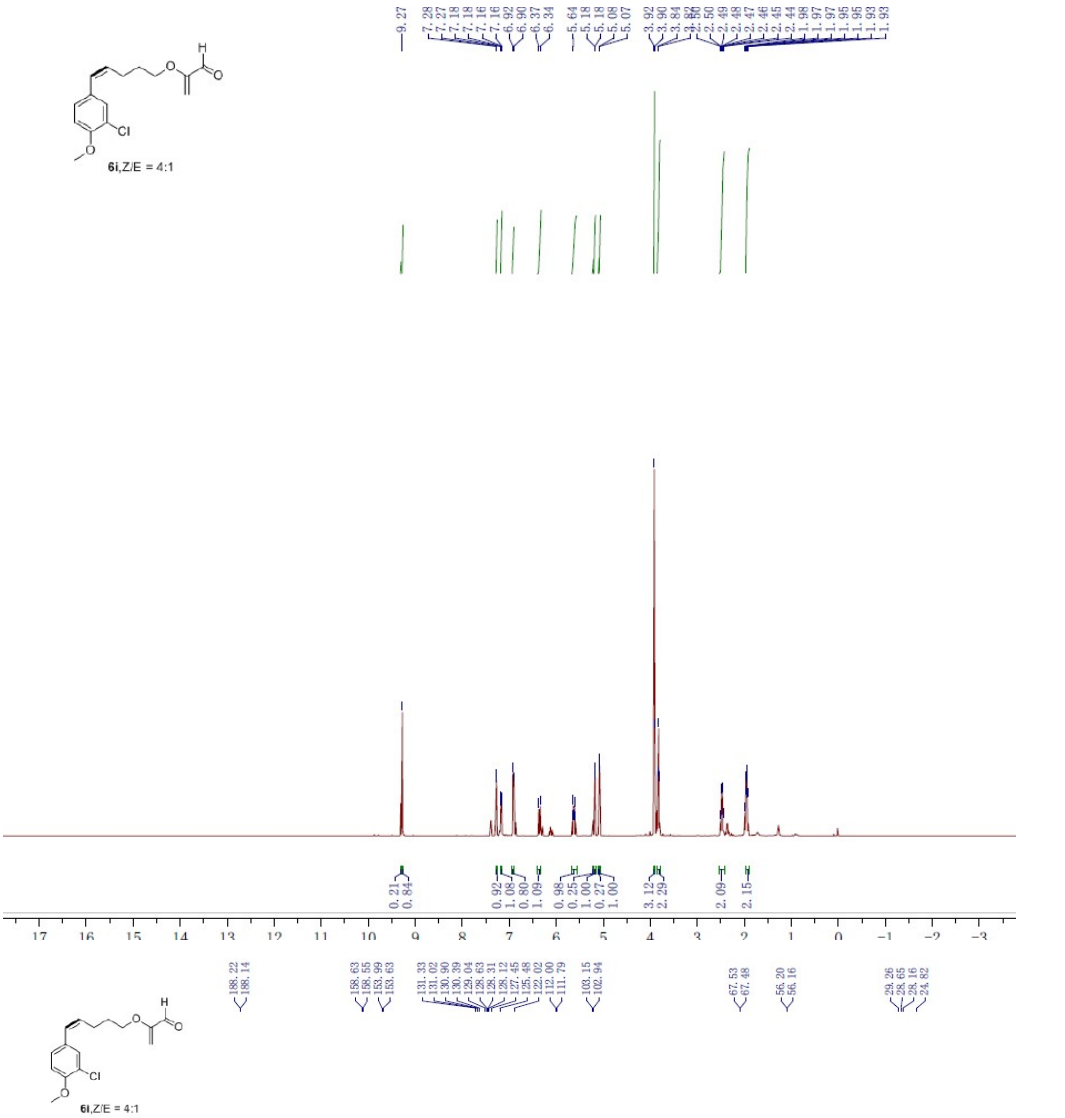
6g, 7 min, 73%

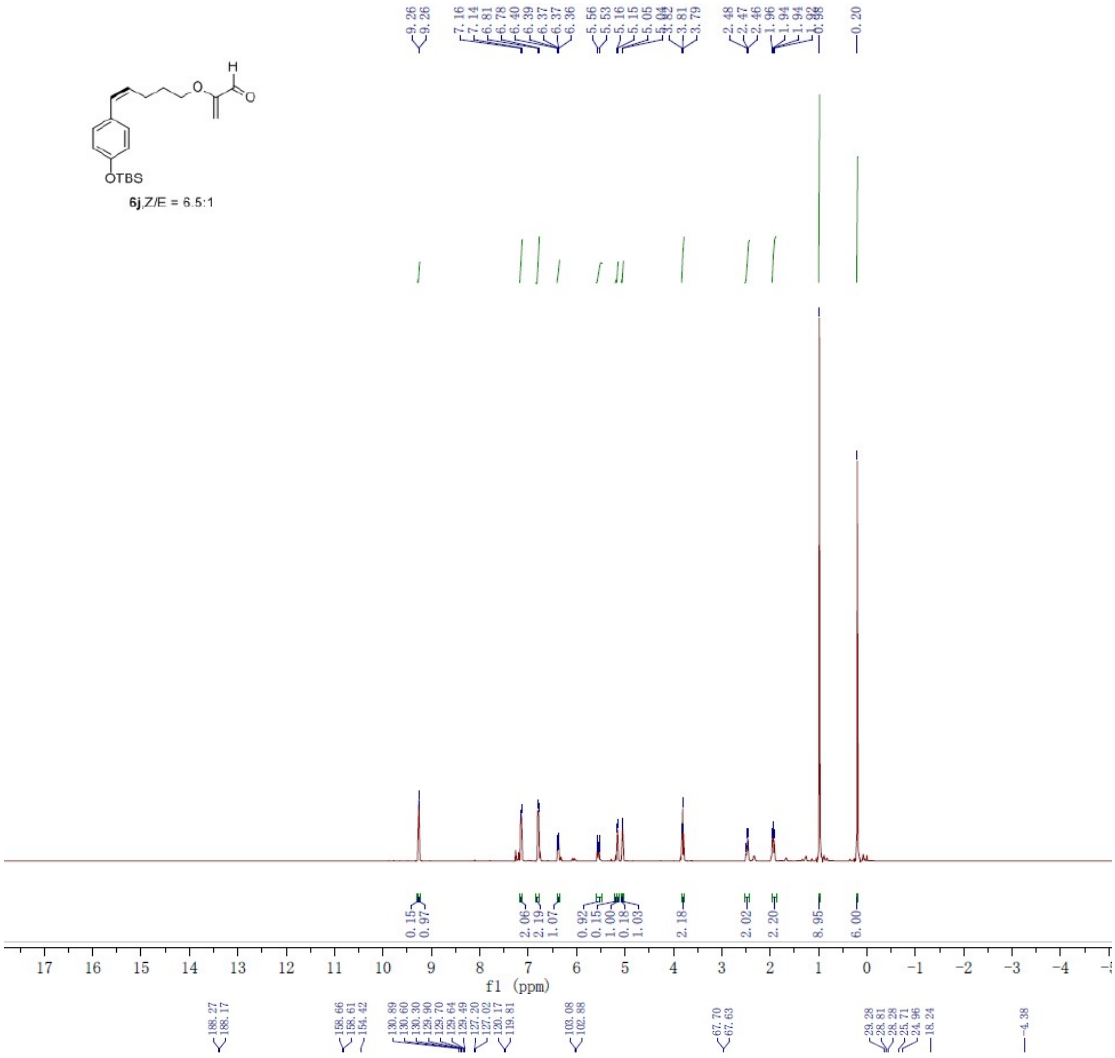

0.70
1.90
1.26
1.26
0.98
1.00
0.84
0.86
2.95
1.99
1.98
2.05
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 −5
f1 (ppm)

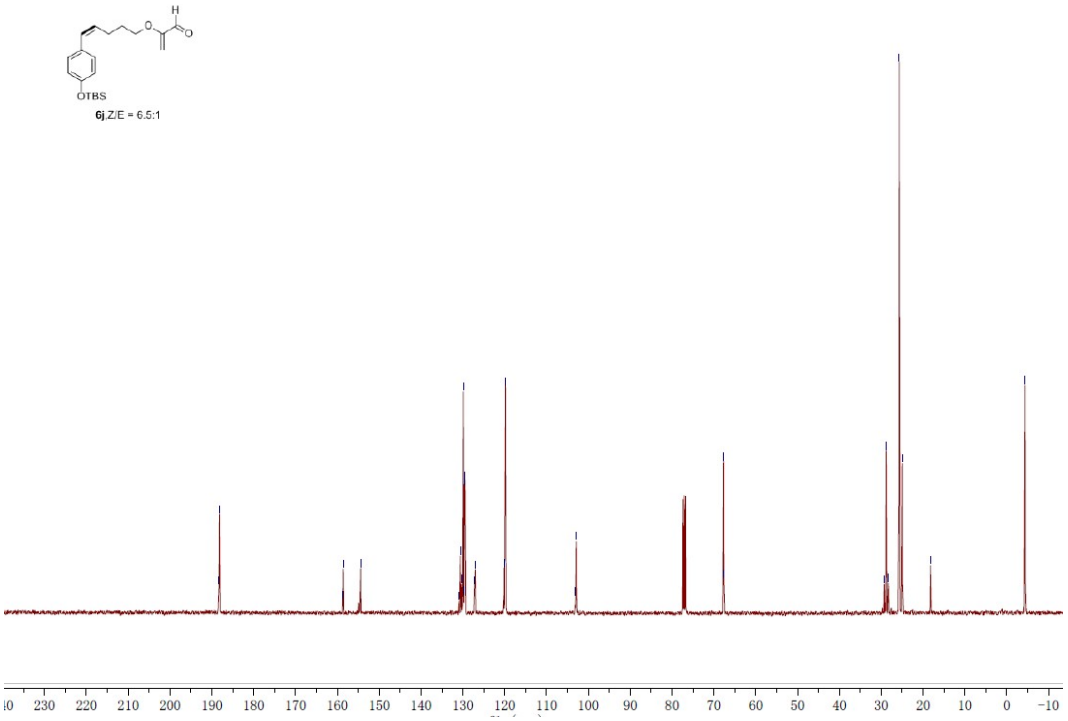

188.18
168.60
166.95
131.13
129.97
128.22
126.13
125.54
120.12
110.39
102.47
67.65
55.41
28.62
24.91
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

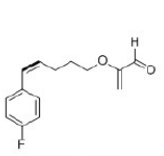

6h,Z/E = 1.4:1


6h,Z/E = 1.4:1

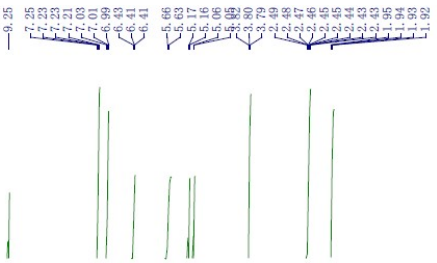

6i,Z/E = 4:1
6i,Z/E = 4:1

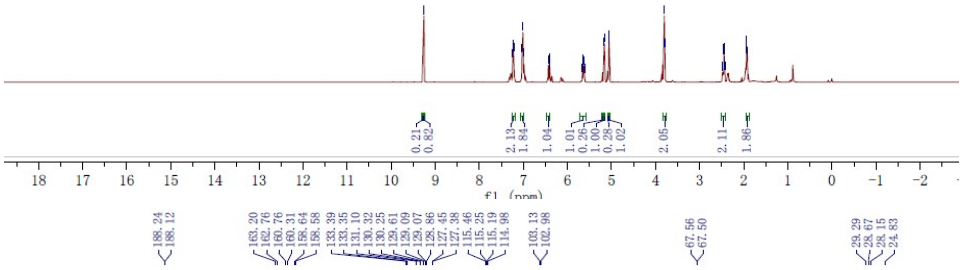

OTBS
6j,Z/E = 6.5:1
f1 (ppm)

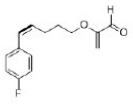

OTBS
6j,Z/E = 6.5:1



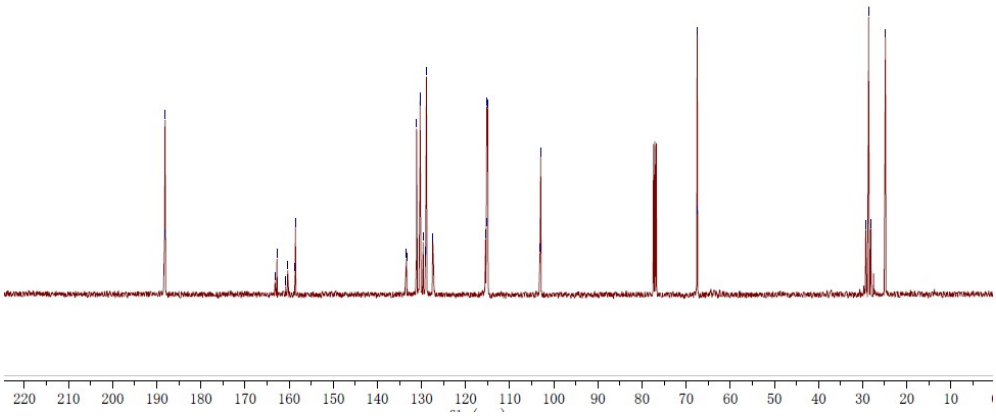
6k,Z/E = 3.8:1

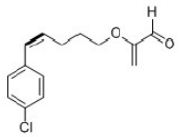




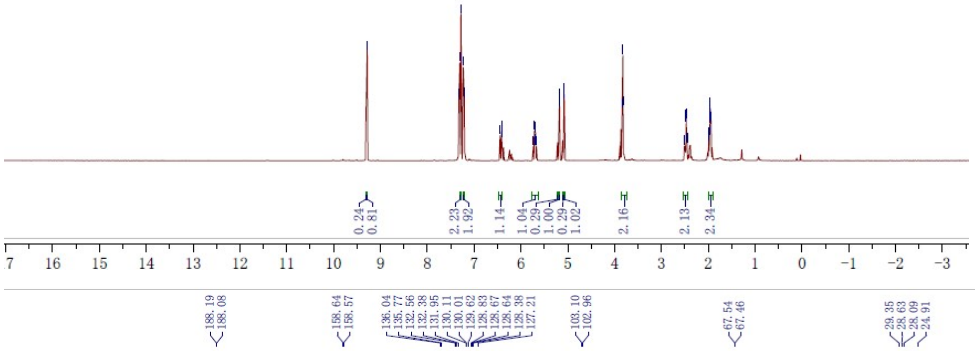


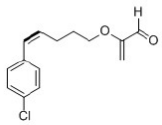
6k,Z/E = 3.8:1



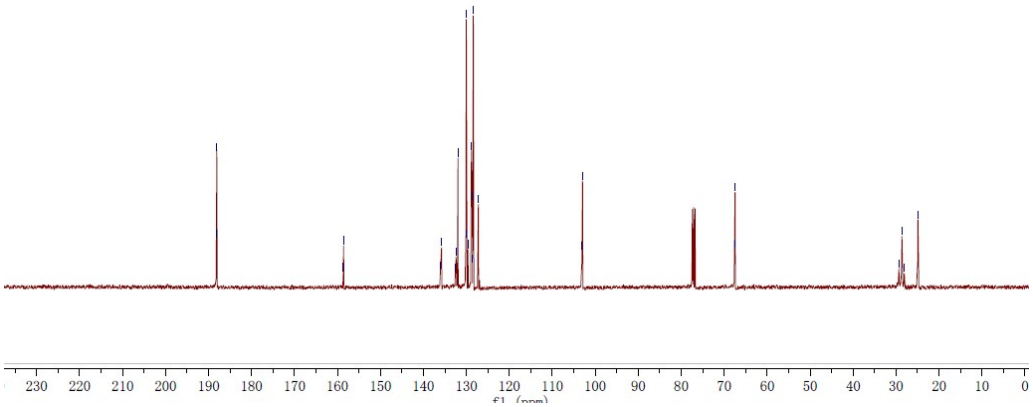


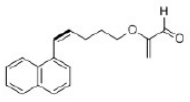
6l,Z/E = 3.4:1



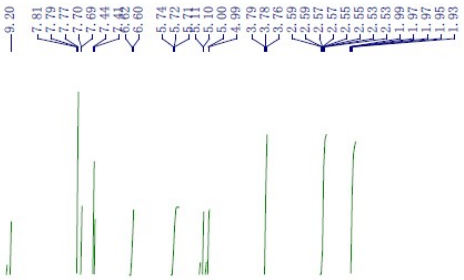


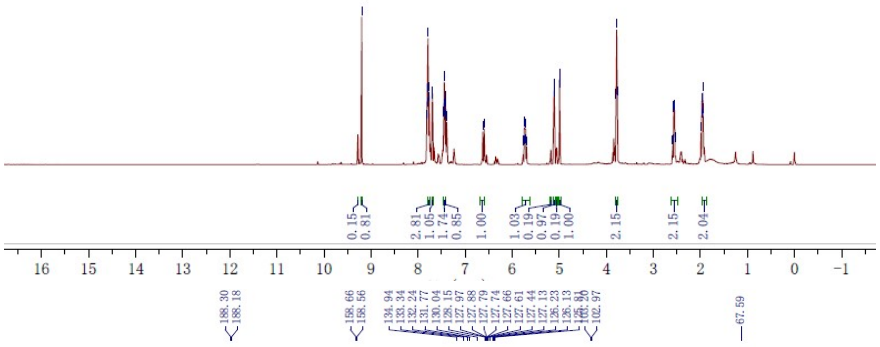
6l,Z/E = 3.4:1

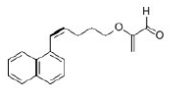




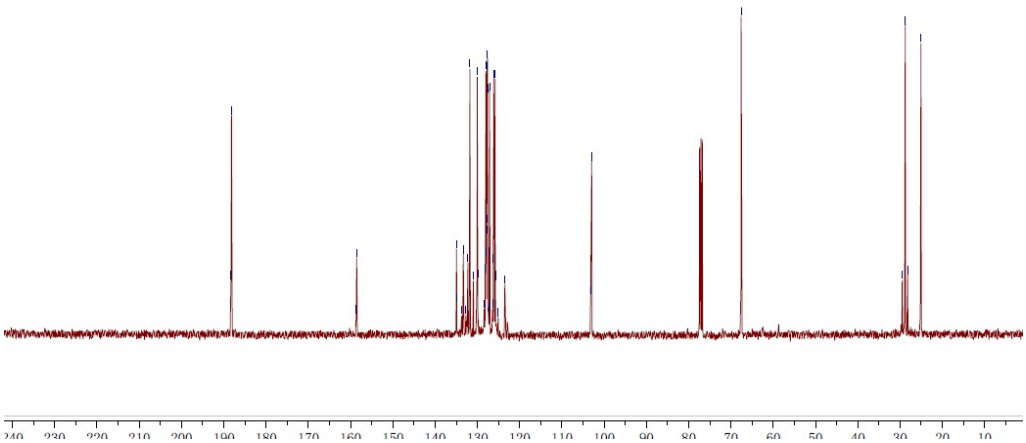
6m, 10 min,Z/E = 5.2:1

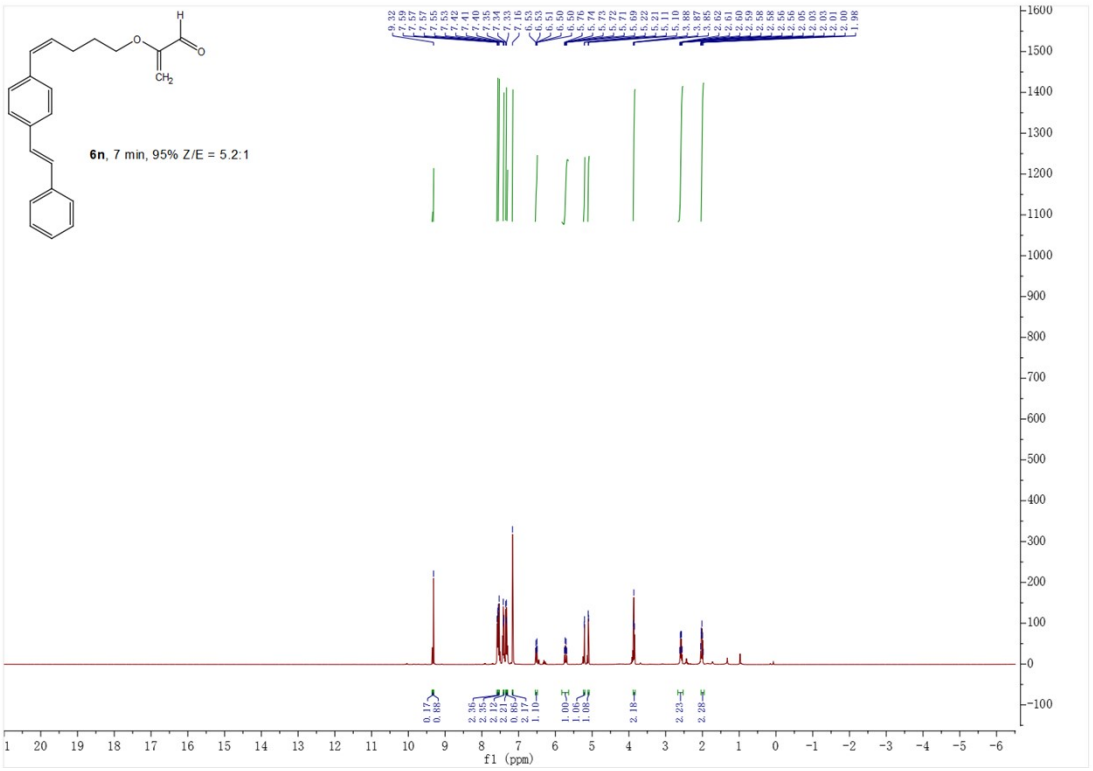


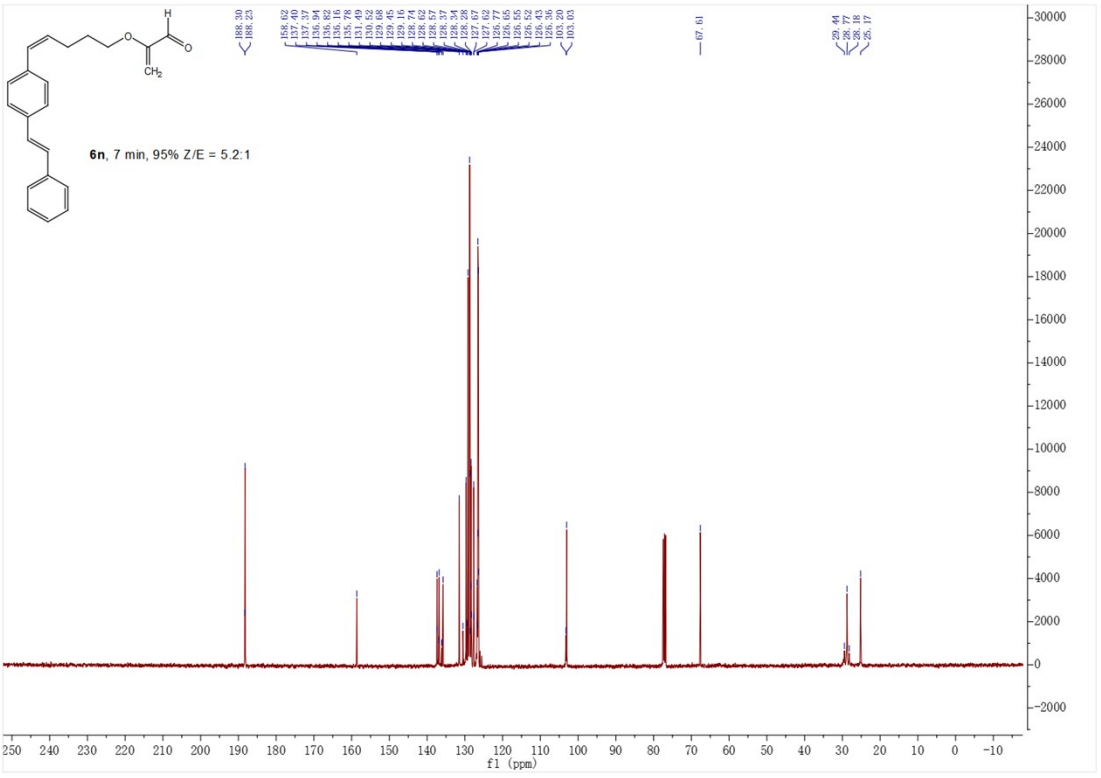


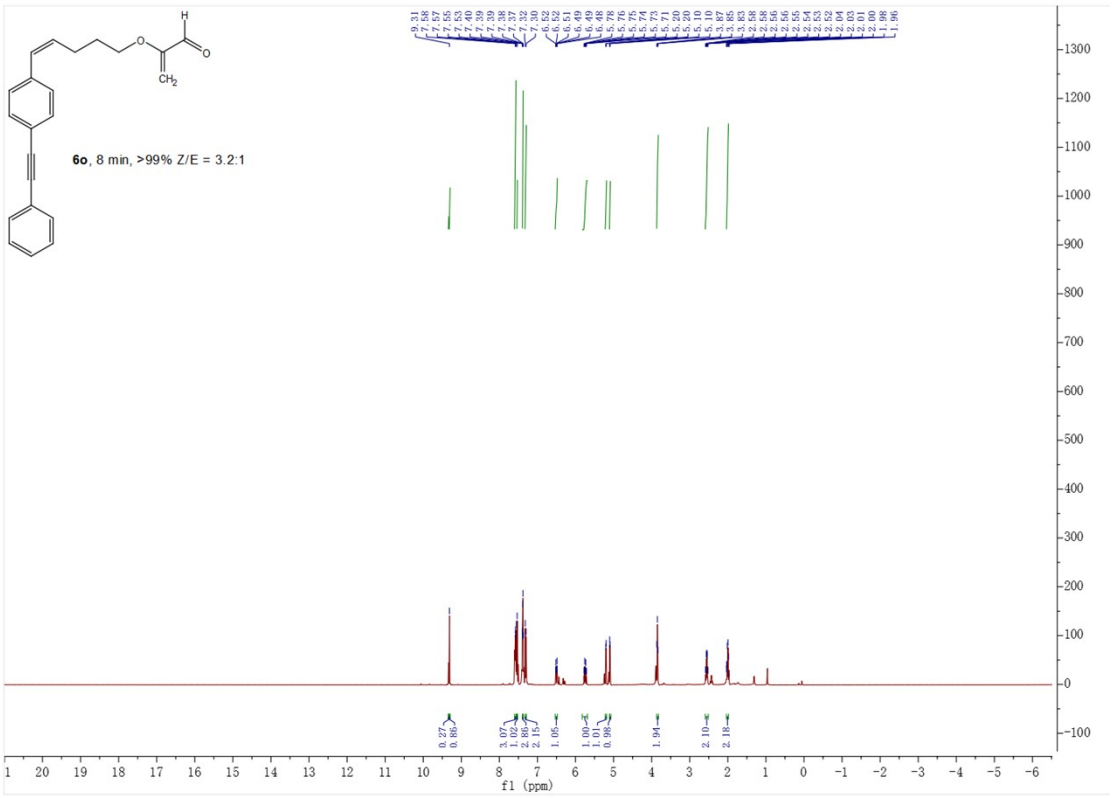


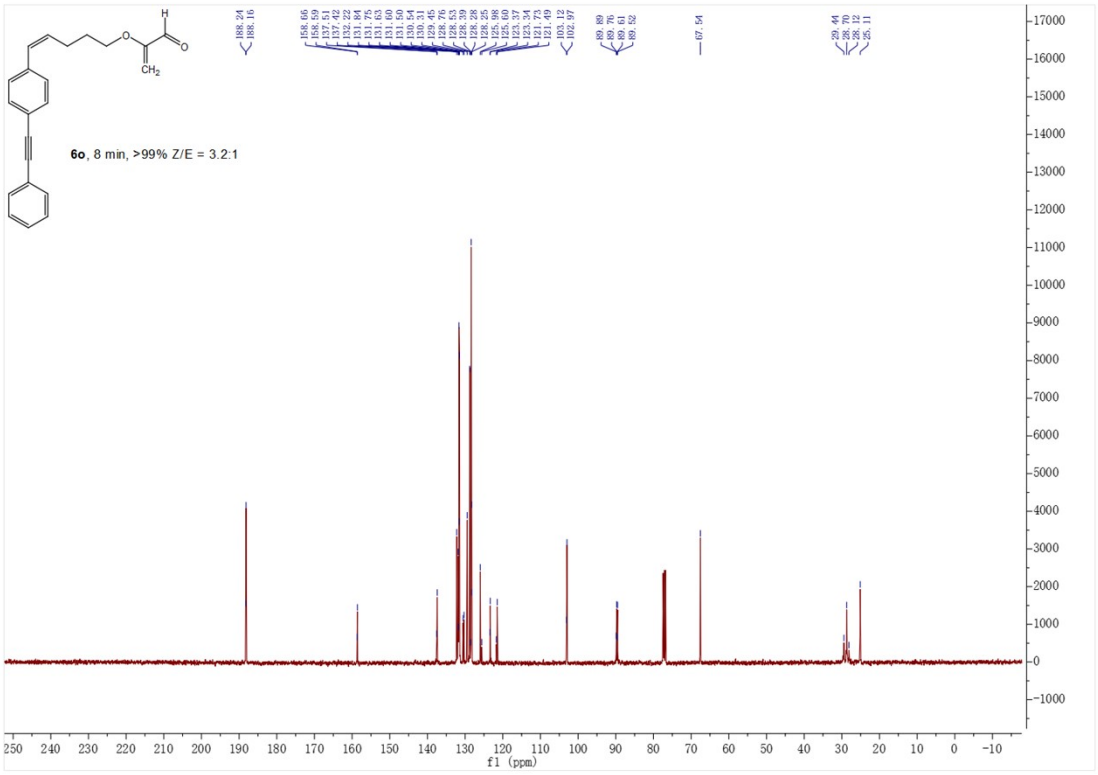
6m, 10 min,Z/E = 5.2:1

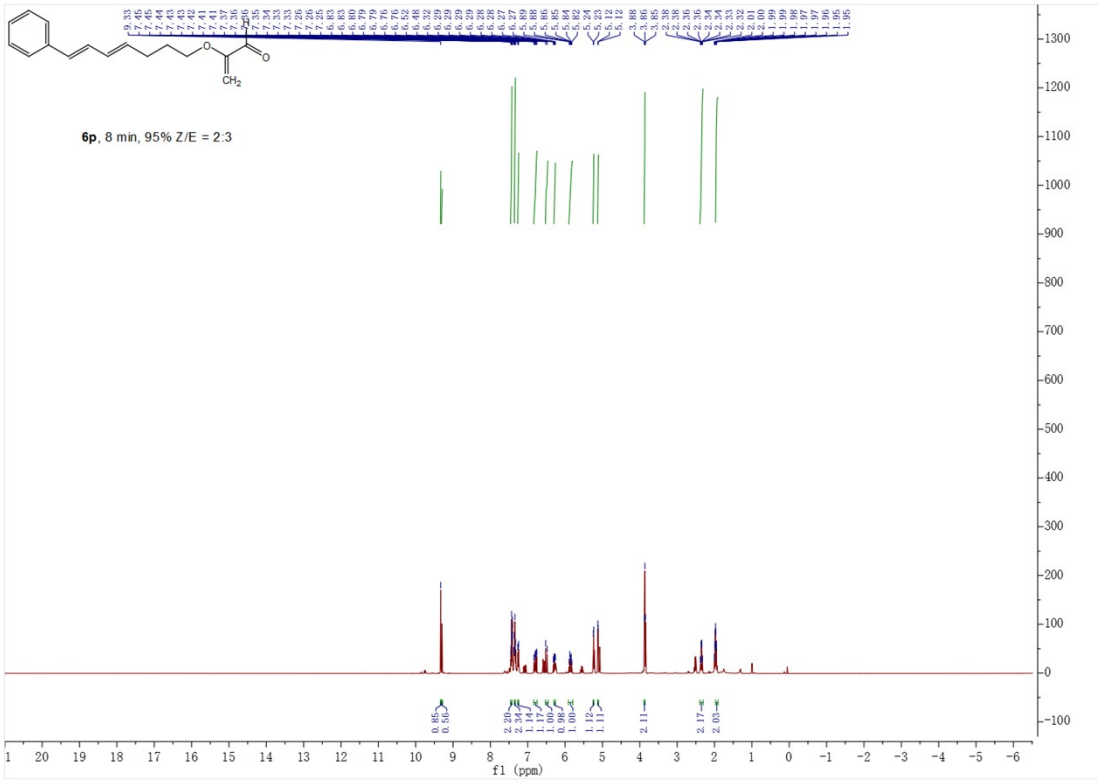


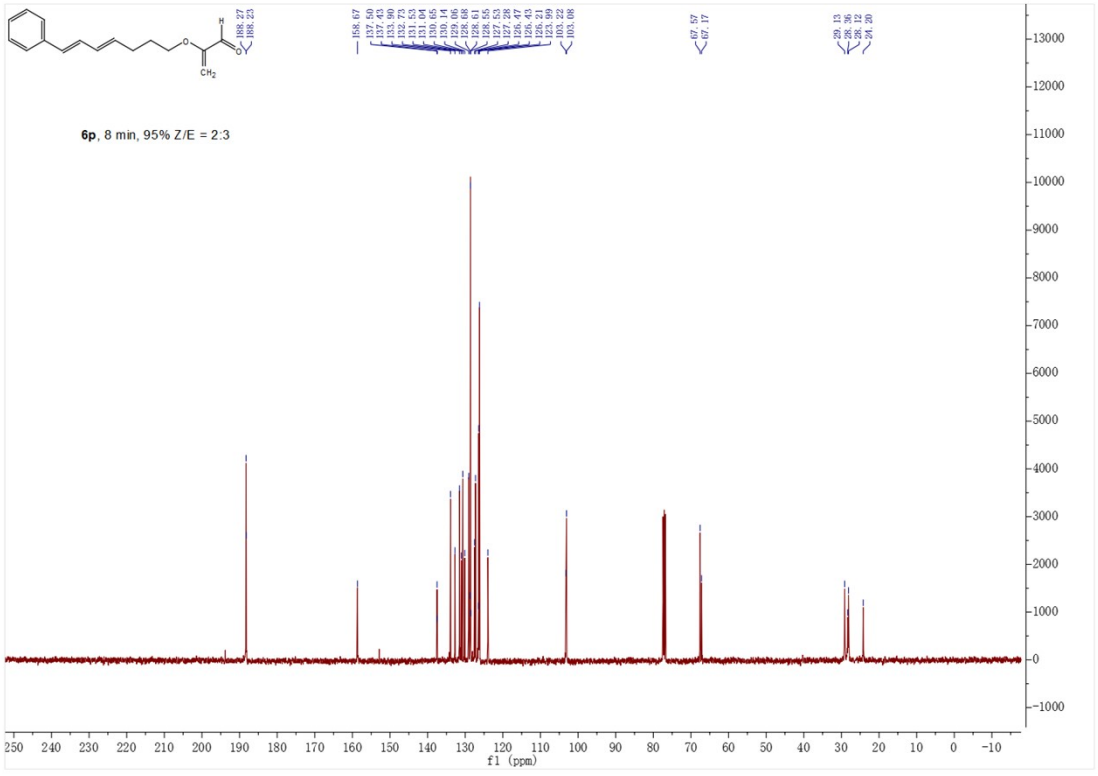

6n, 7 min, 95% Z/E = 5.2:1
f1 (ppm)

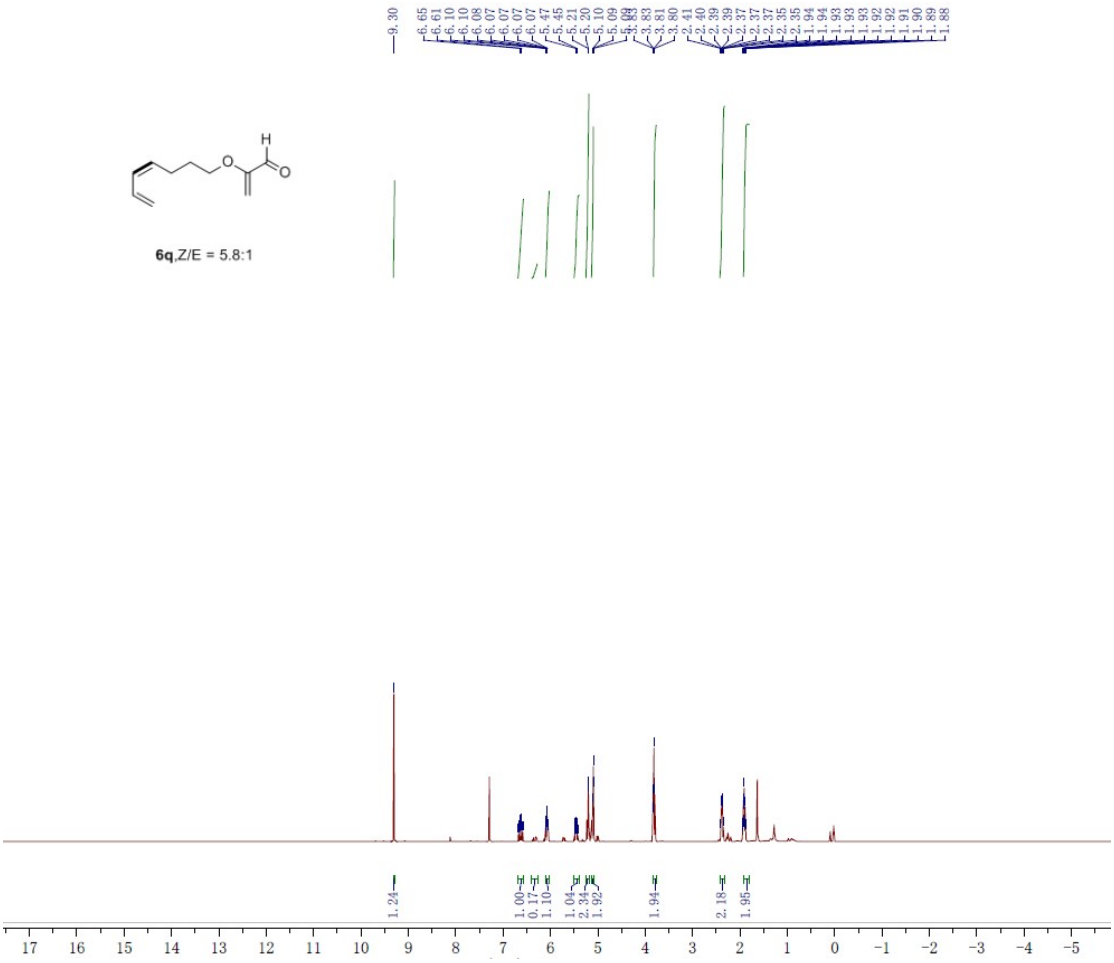

6n, 7 min, 95% Z/E = 5.2:1
f1 (ppm)

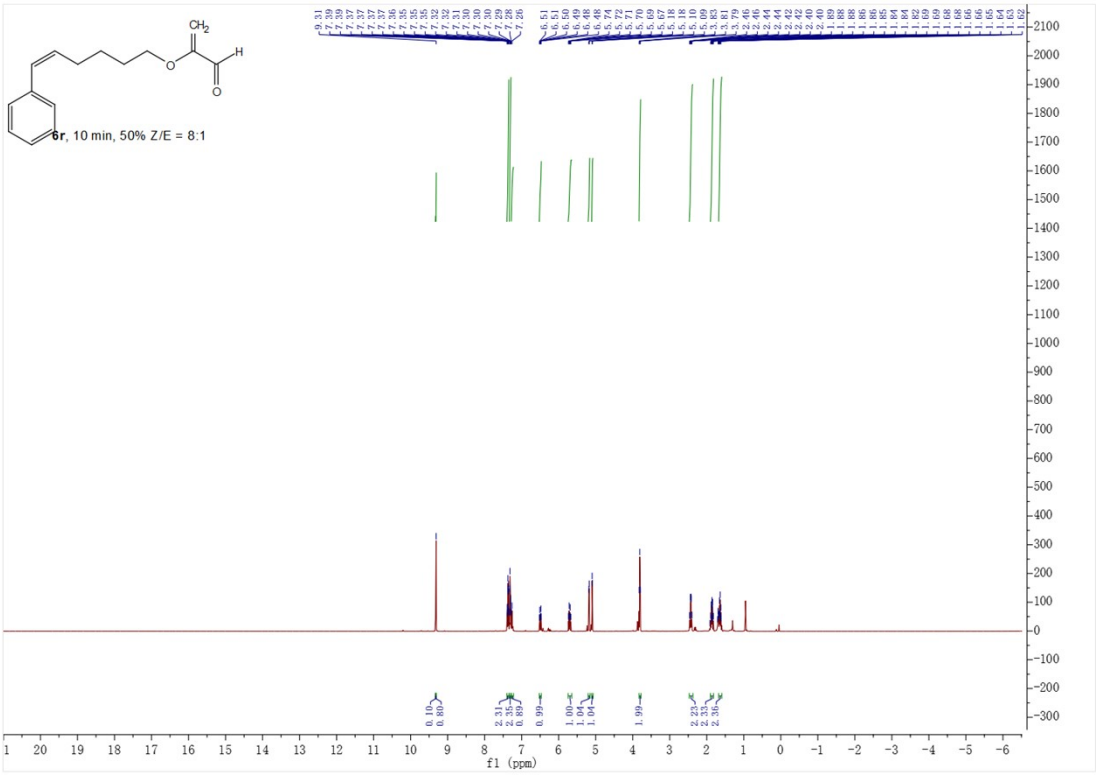

6o, 8 min, >99% Z/E = 3.2:1
f1 (ppm)

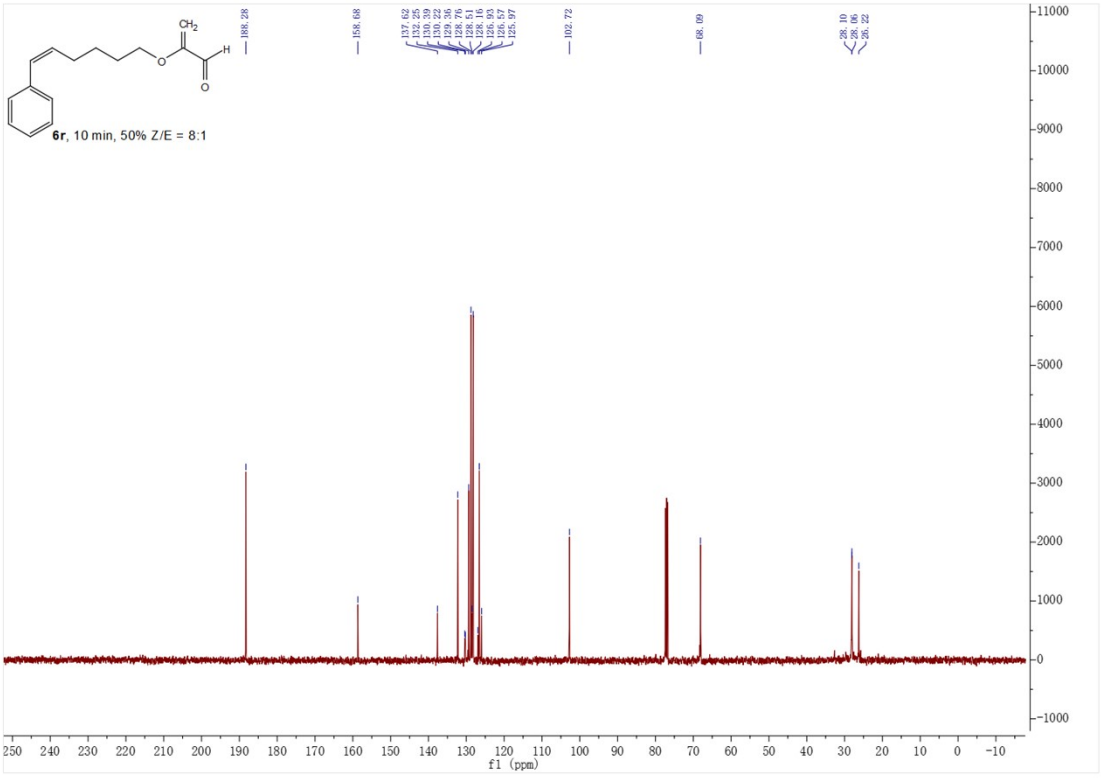

6o, 8 min, >99% Z/E = 3.2:1
f1 (ppm)

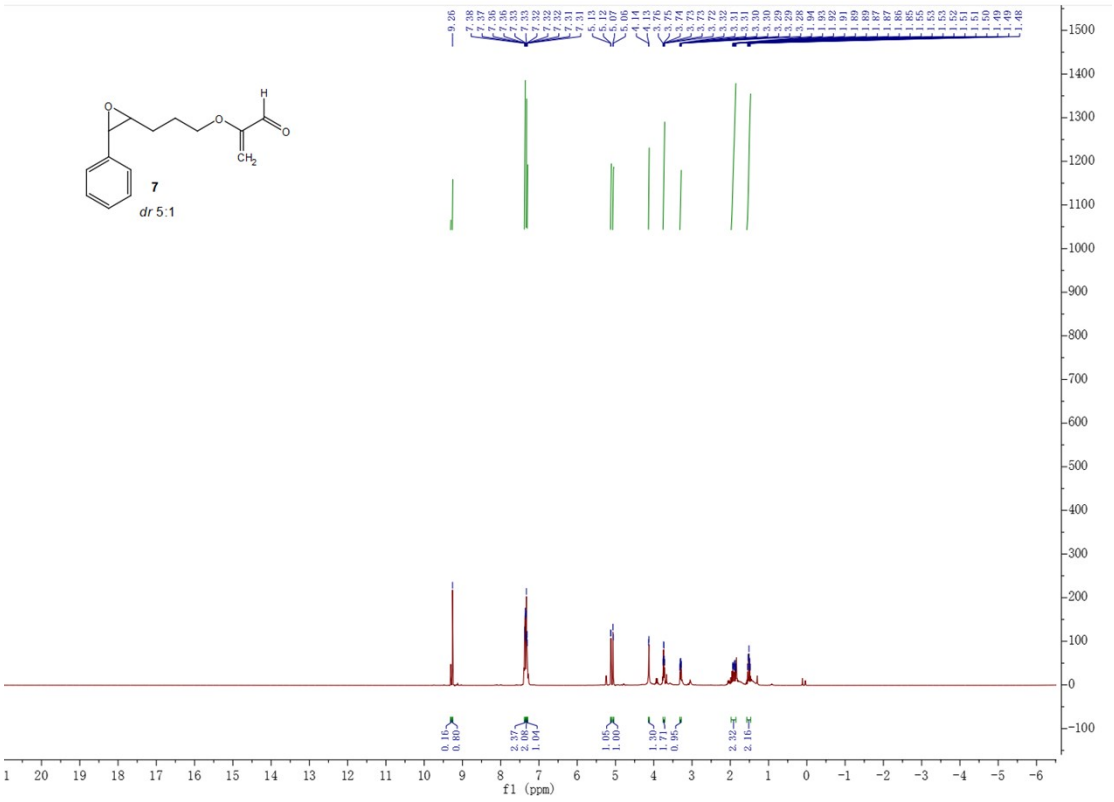

6p, 8 min, 95% Z/E = 2:3
f1 (ppm)

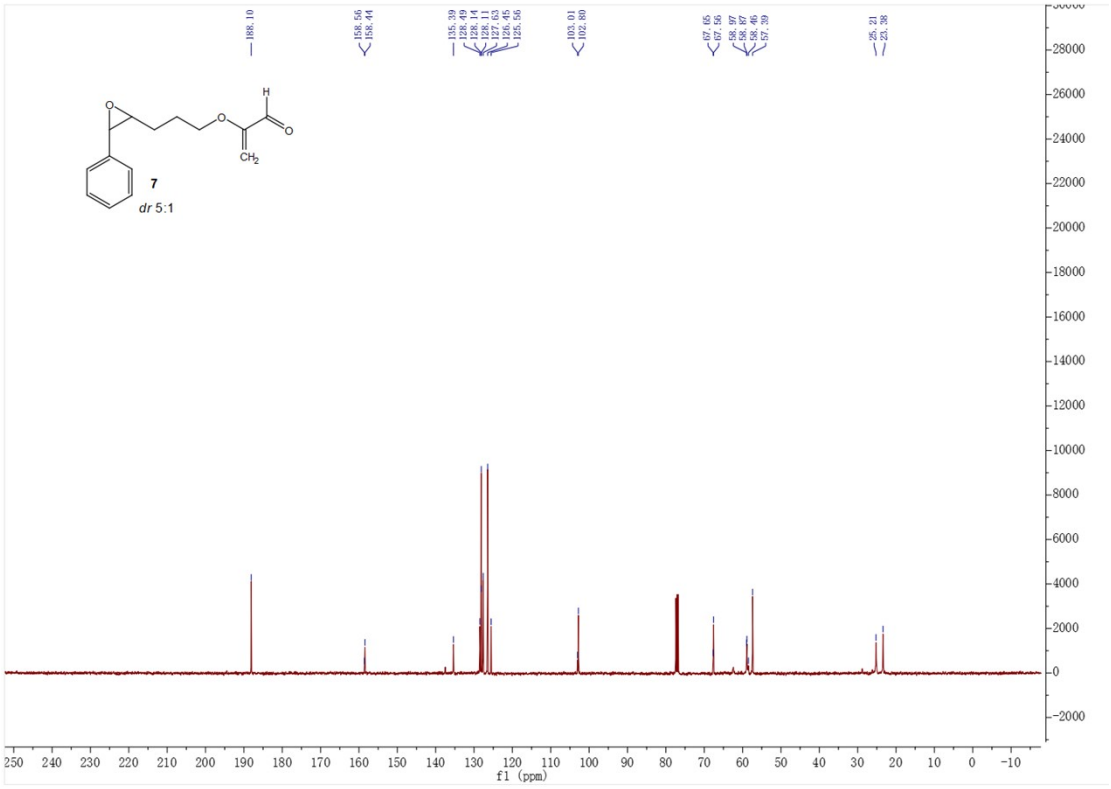

6p, 8 min, 95% Z/E = 2:3
f1 (ppm)

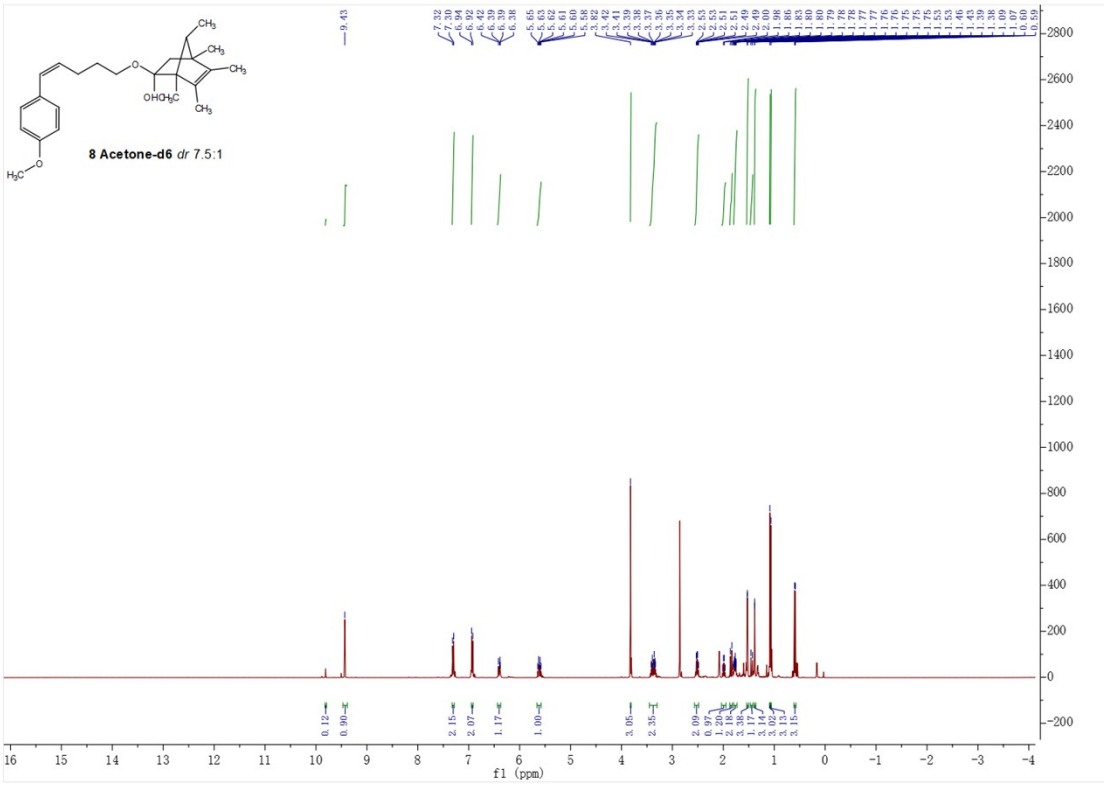

6q,Z/E = 5.8:1
6q, 10 min, 72% Z/E = 5.8:1
f1 (ppm)

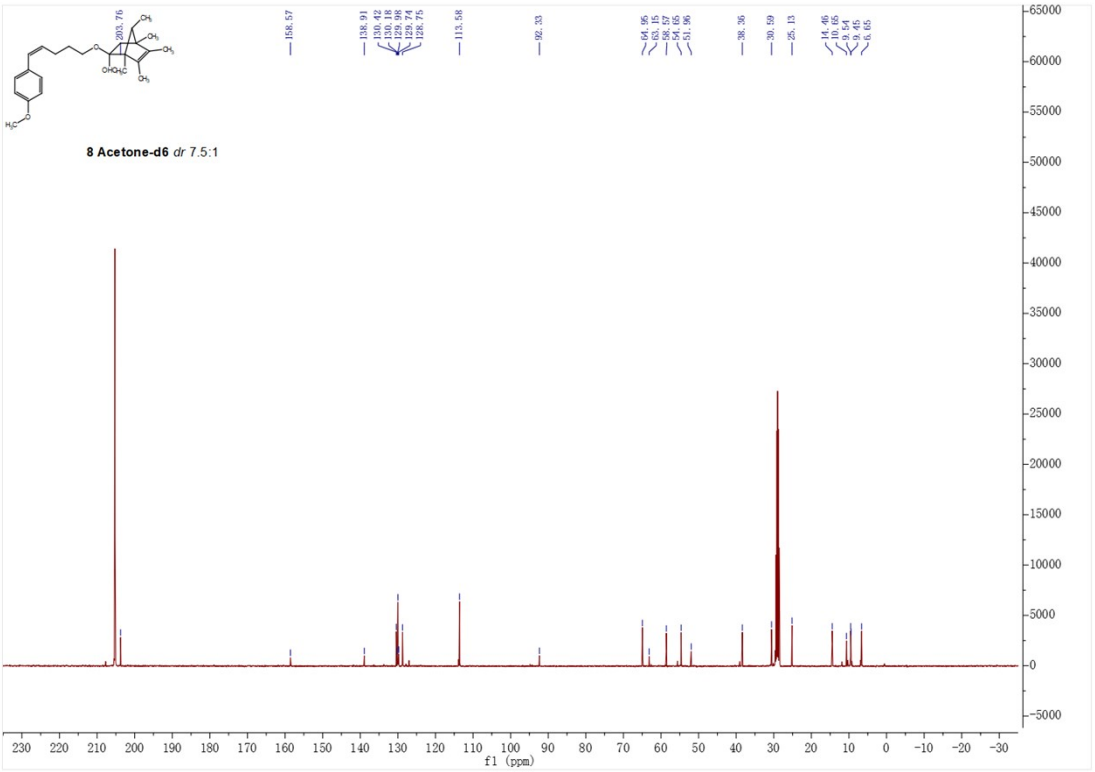

6r, 10 min, 50% Z/E = 8:1
f1 (ppm)

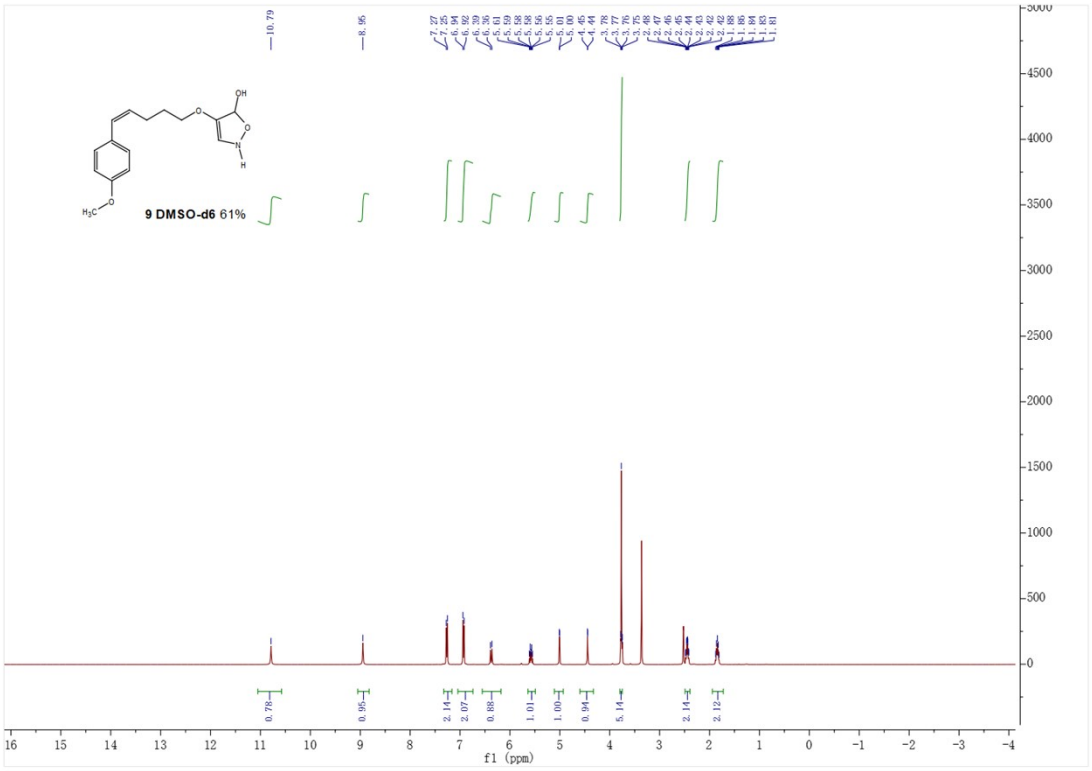

6r, 10 min, 50% Z/E = 8:1
f1 (ppm)

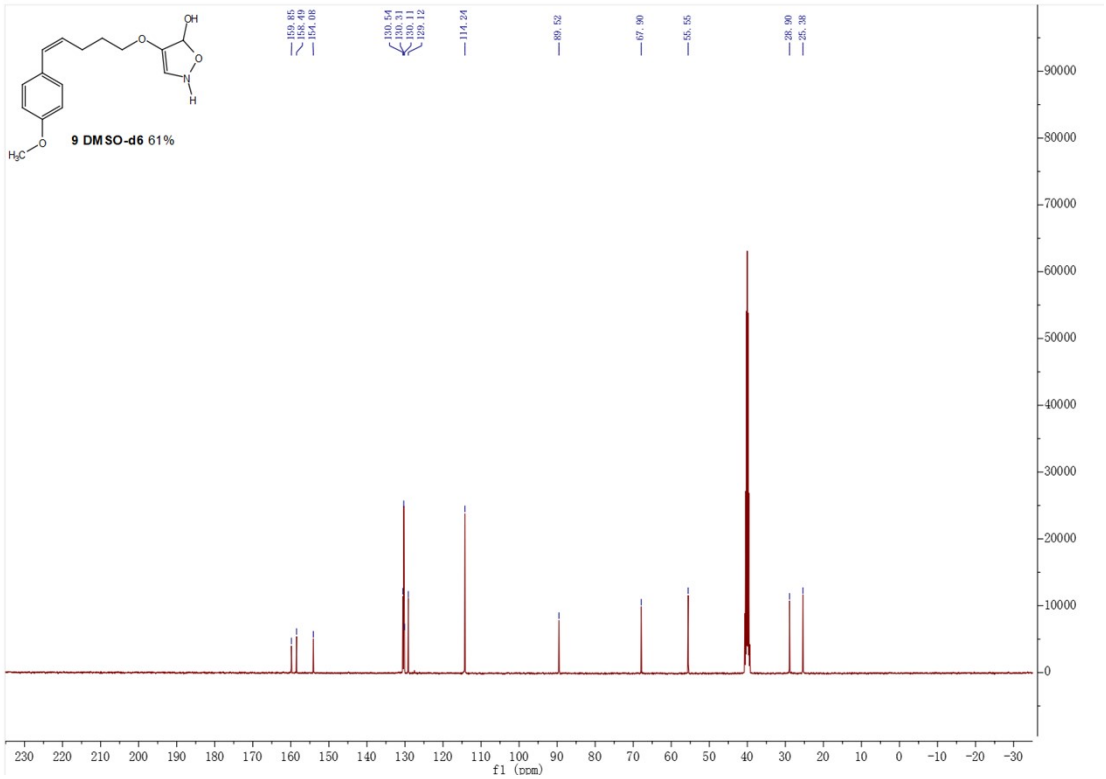

7
dr 5:1
f1 (ppm)

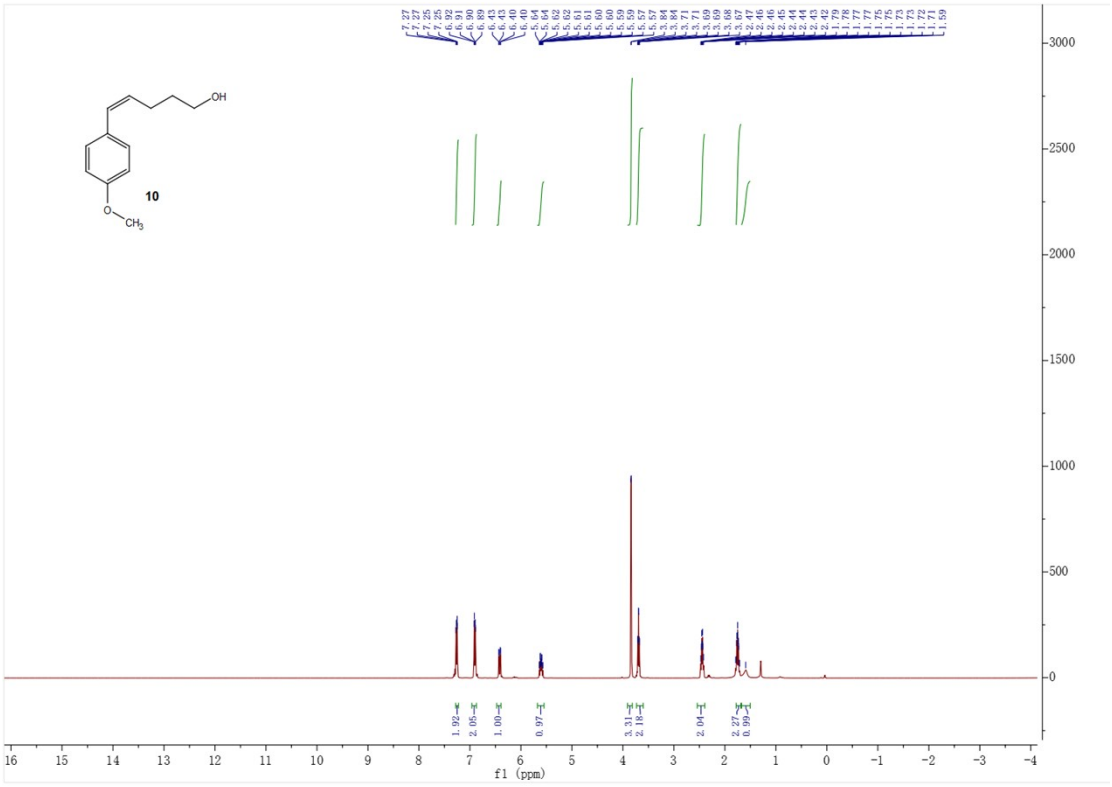

7
dr 5:1
f1 (ppm)

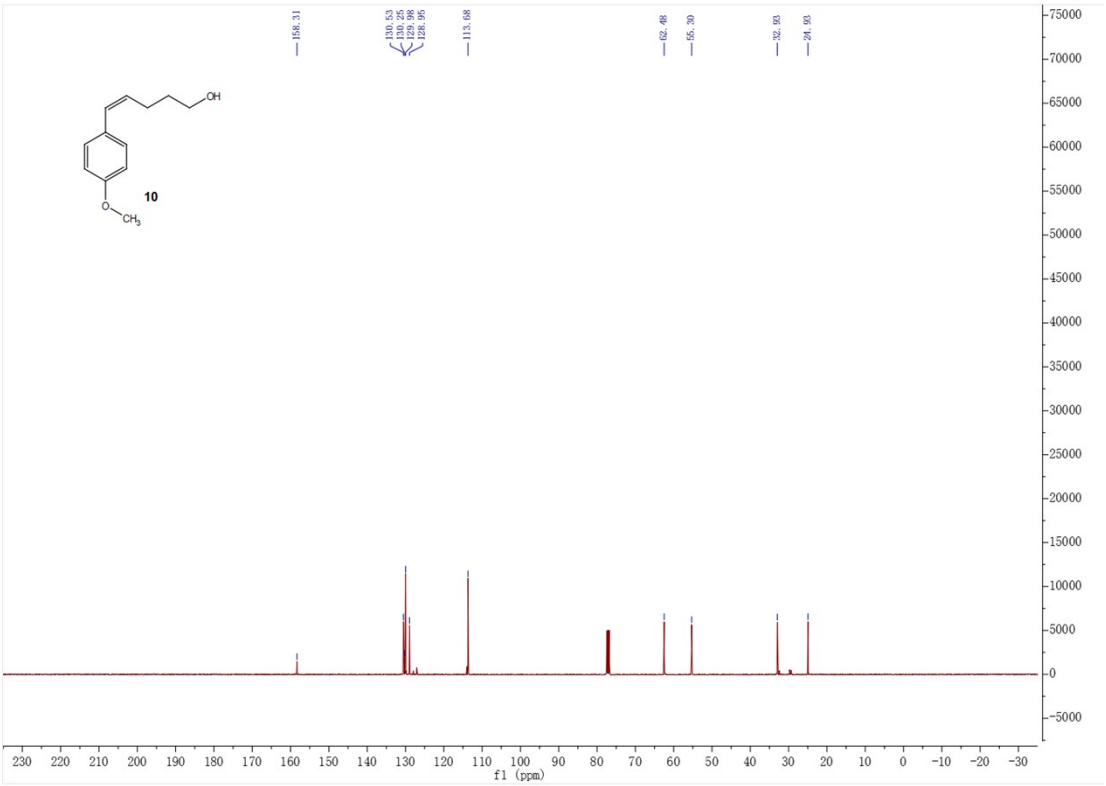

8 Acetone-d6 dr 7.5:1
f1 (ppm)

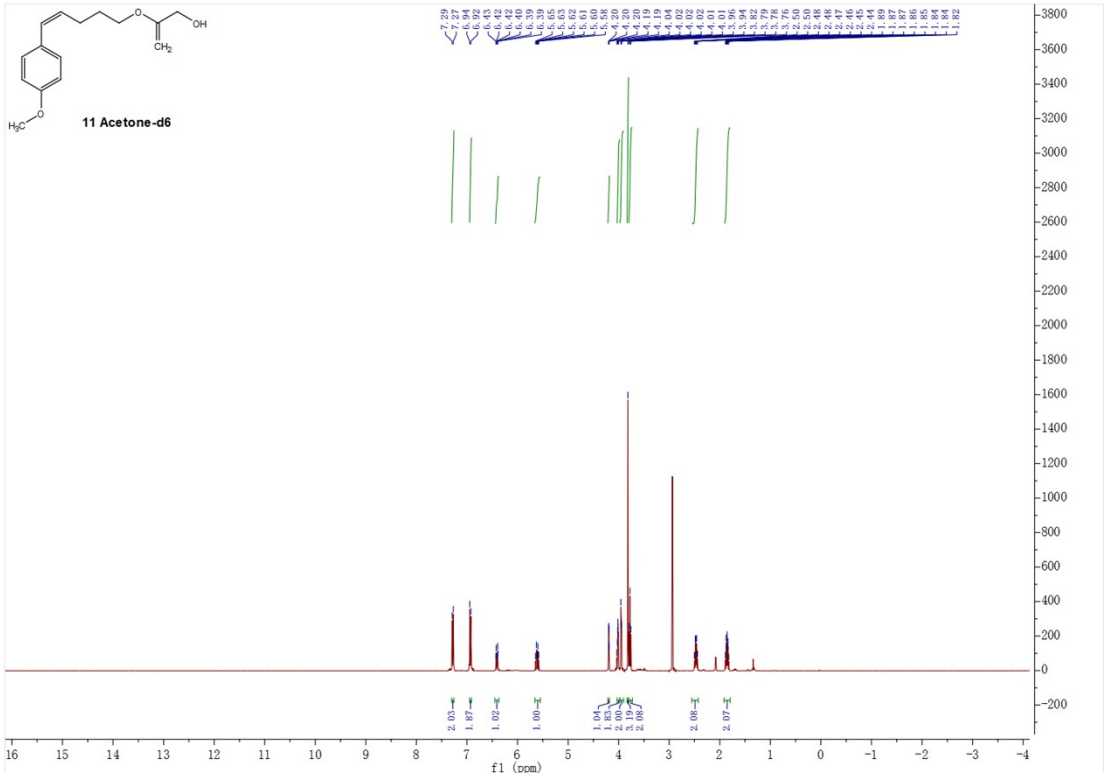

8 Acetone-d6 dr 7.5:1
f1 (ppm)

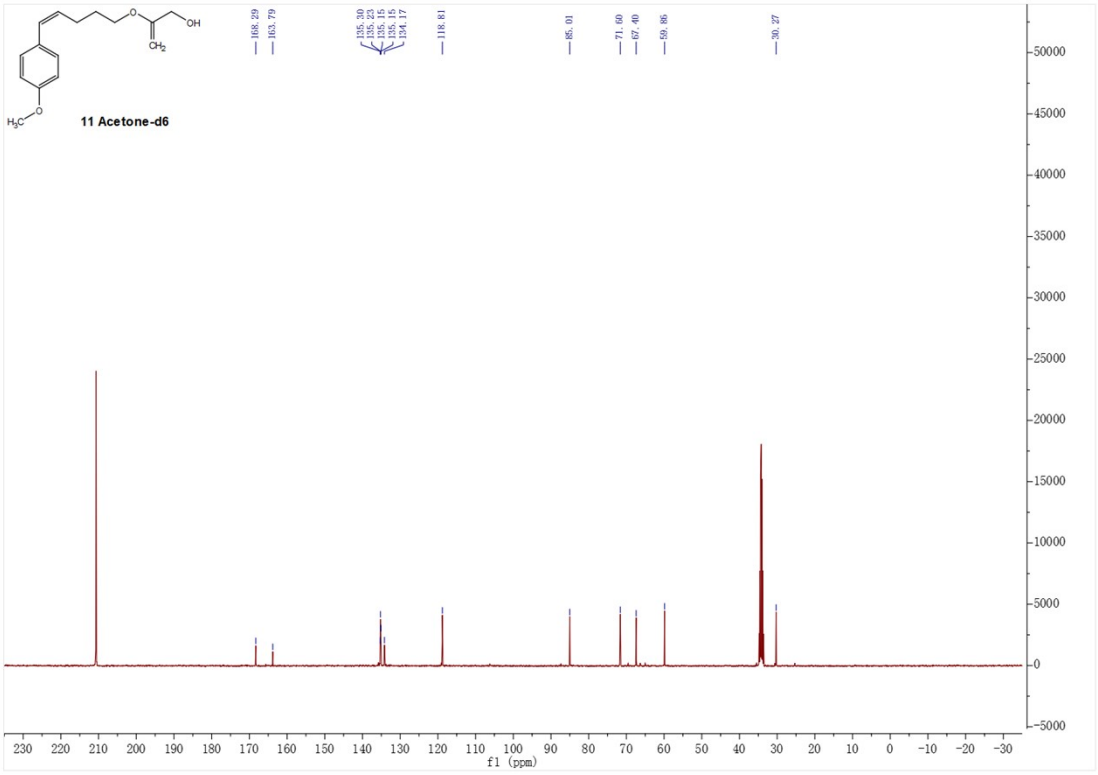

9 DMSO-d6 61%
f1 (ppm)

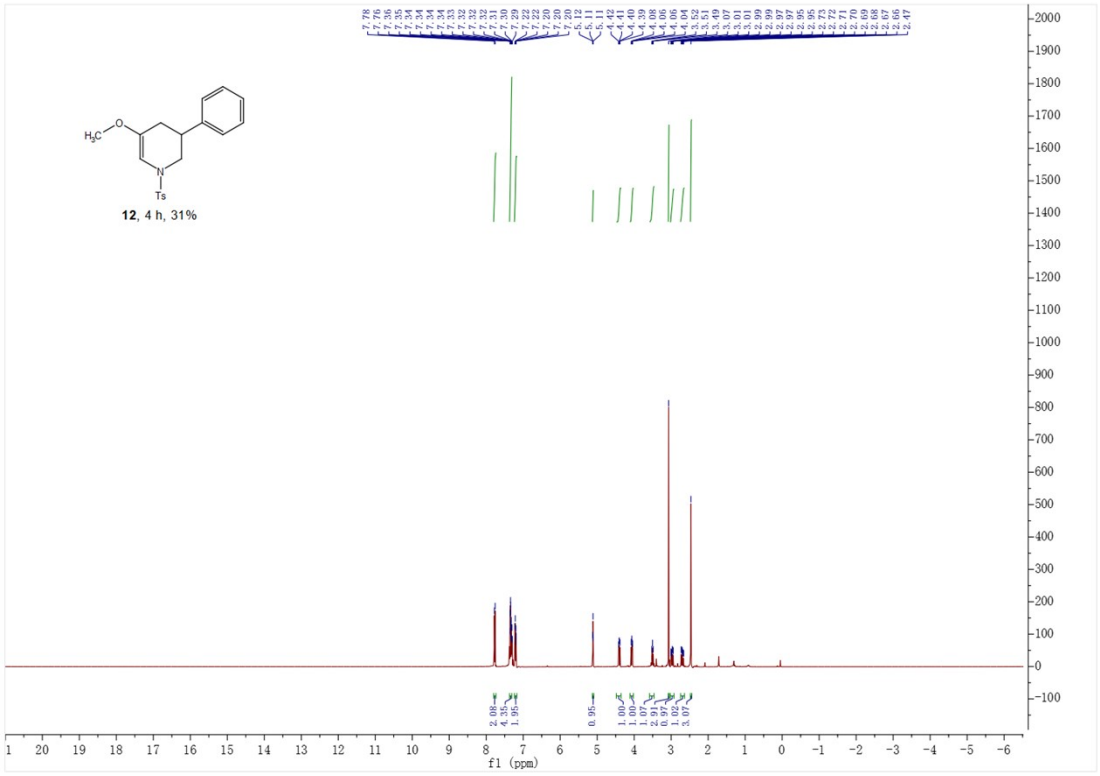

9 DMSO-d6 61%
f1 (ppm)

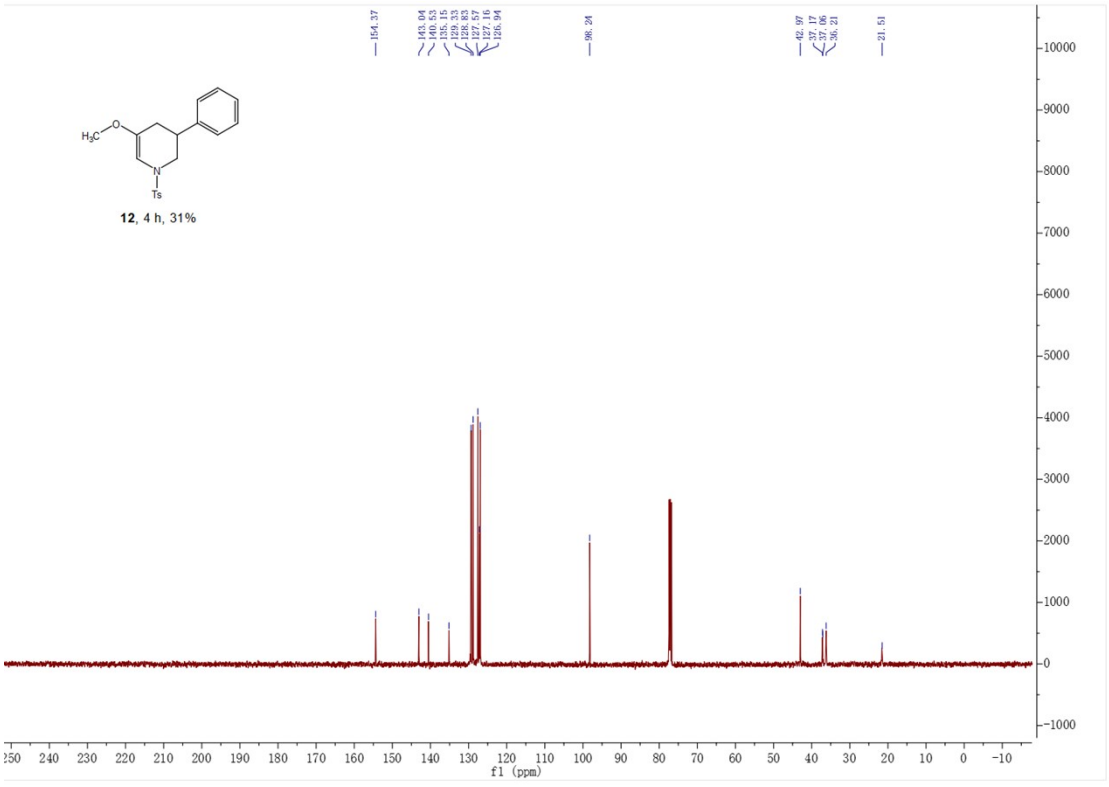

OH
10
O
CH3
f1 (ppm)

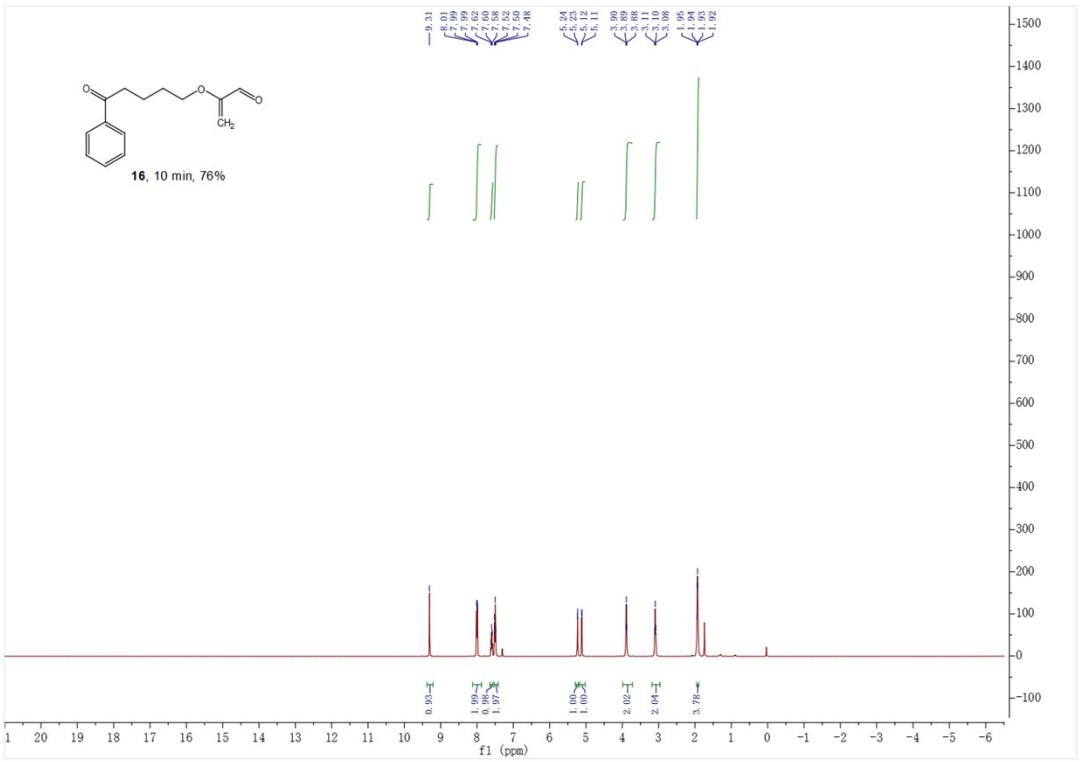

158.31
130.53
129.98
128.95
113.68
62.48
55.30
32.93
24.93
OH
10
O
CH3
f1 (ppm)

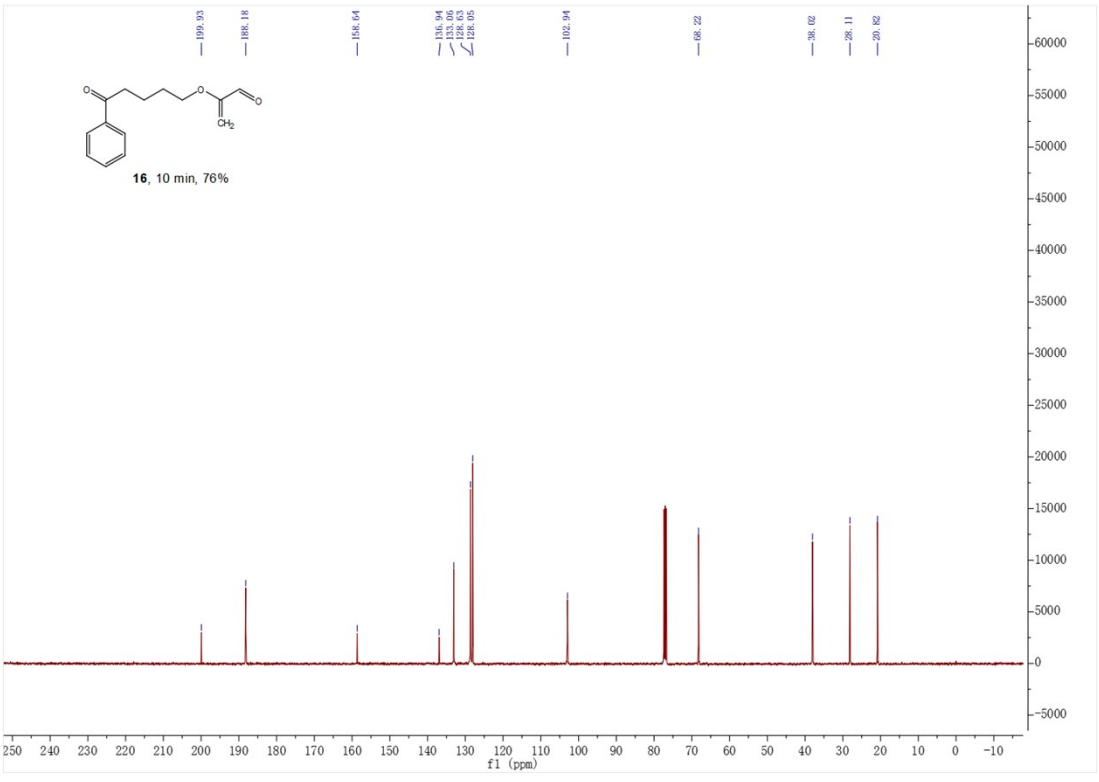

11 Acetone-d6
f1 (ppm)

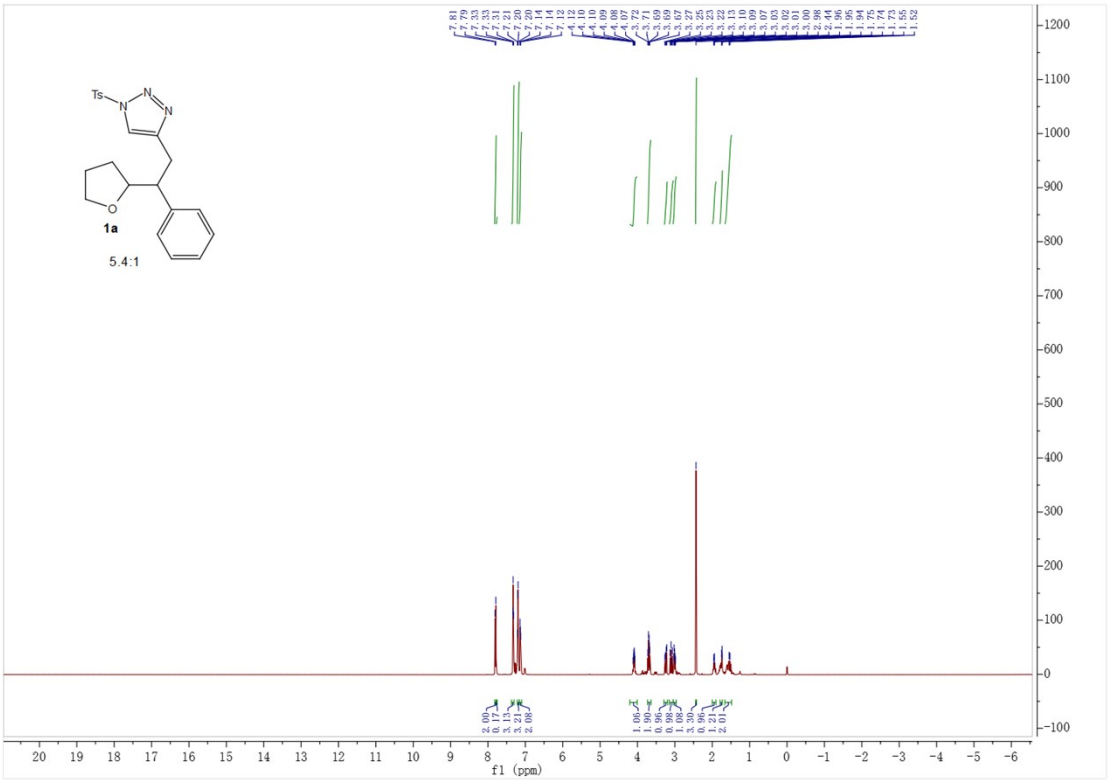

11 Acetone-d6
f1 (ppm)

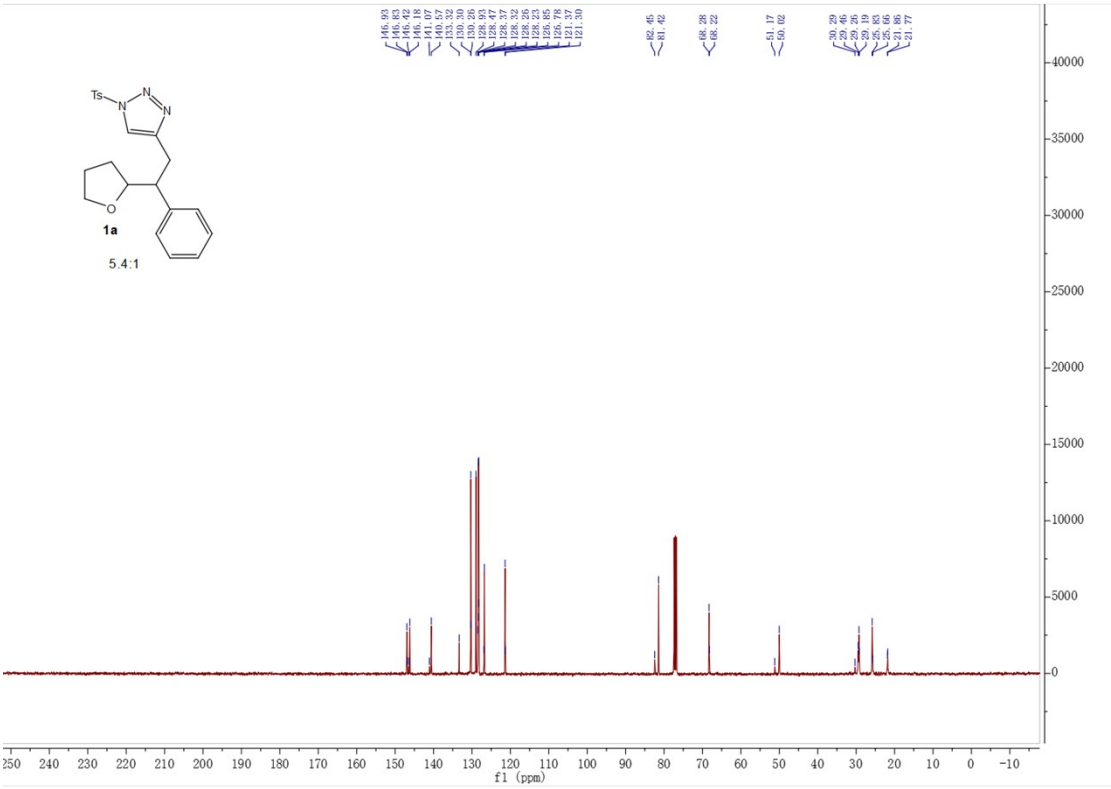

12, 4 h, 31%
f1 (ppm)

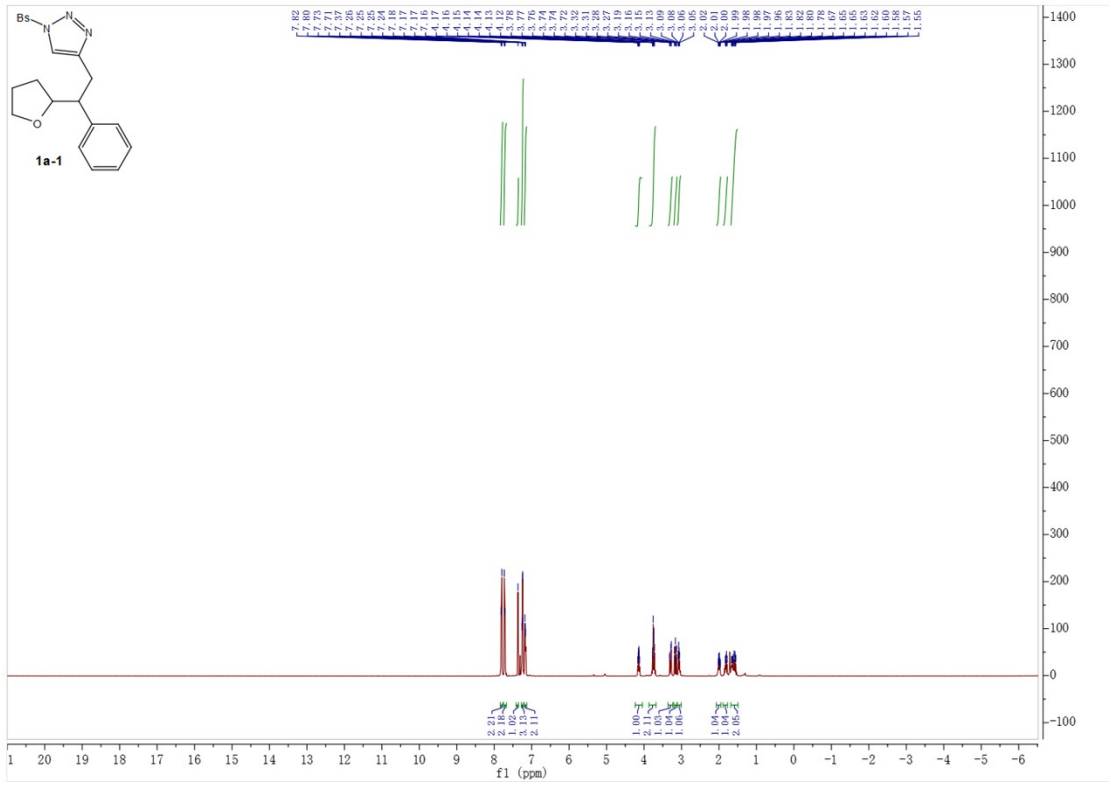

12, 4 h, 31%
f1 (ppm)


16, 10 min, 76%
f1 (ppm)


16, 10 min, 76%
f1 (ppm)


Ts
1a
5.4:1
f1 (ppm)


Ts
1a
5.4:1
f1 (ppm)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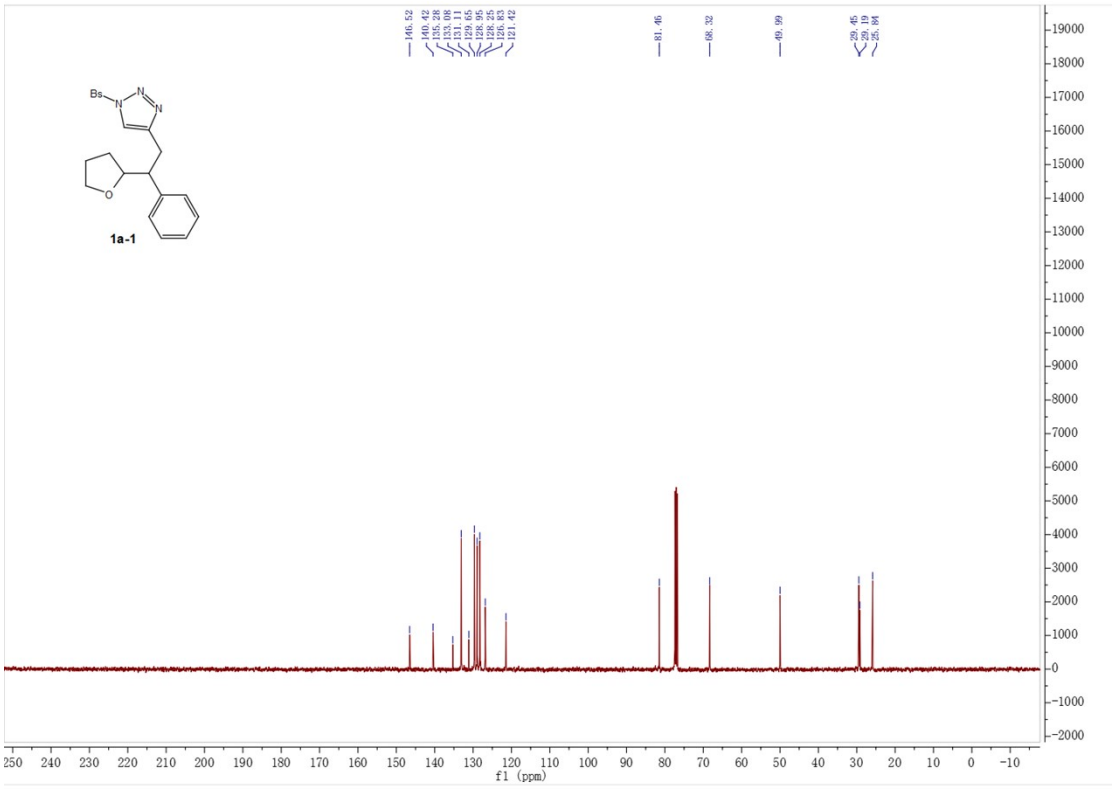
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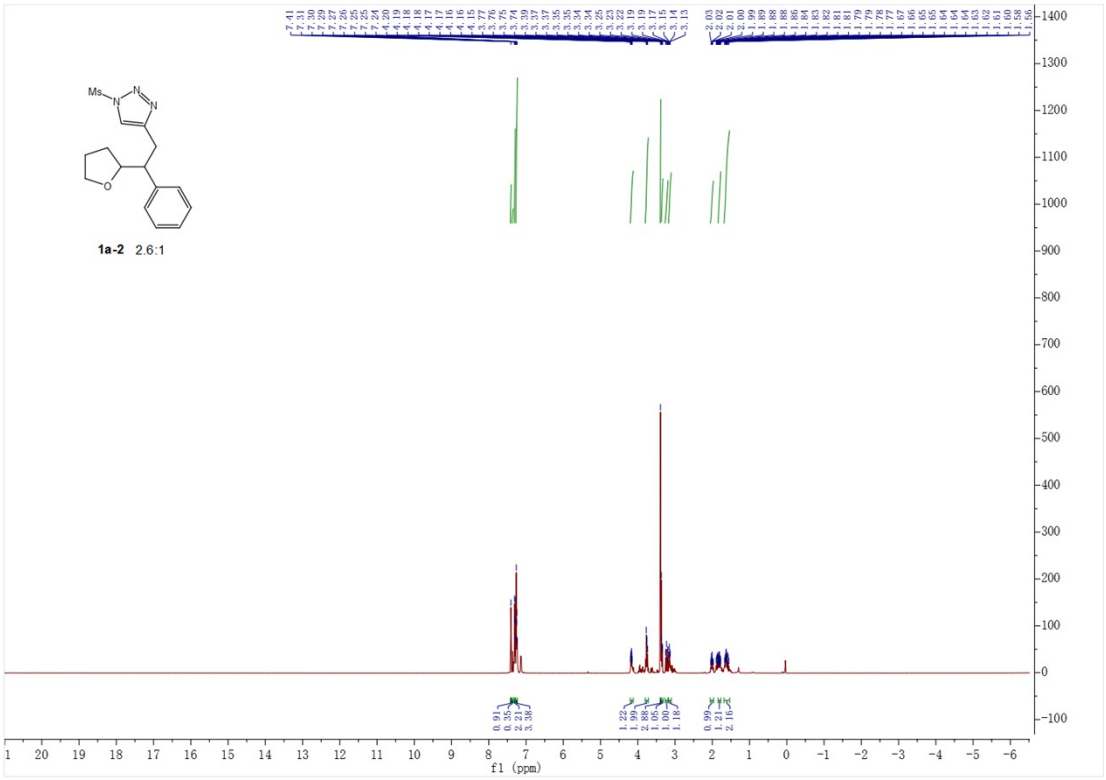
f1 (ppm)


Ms
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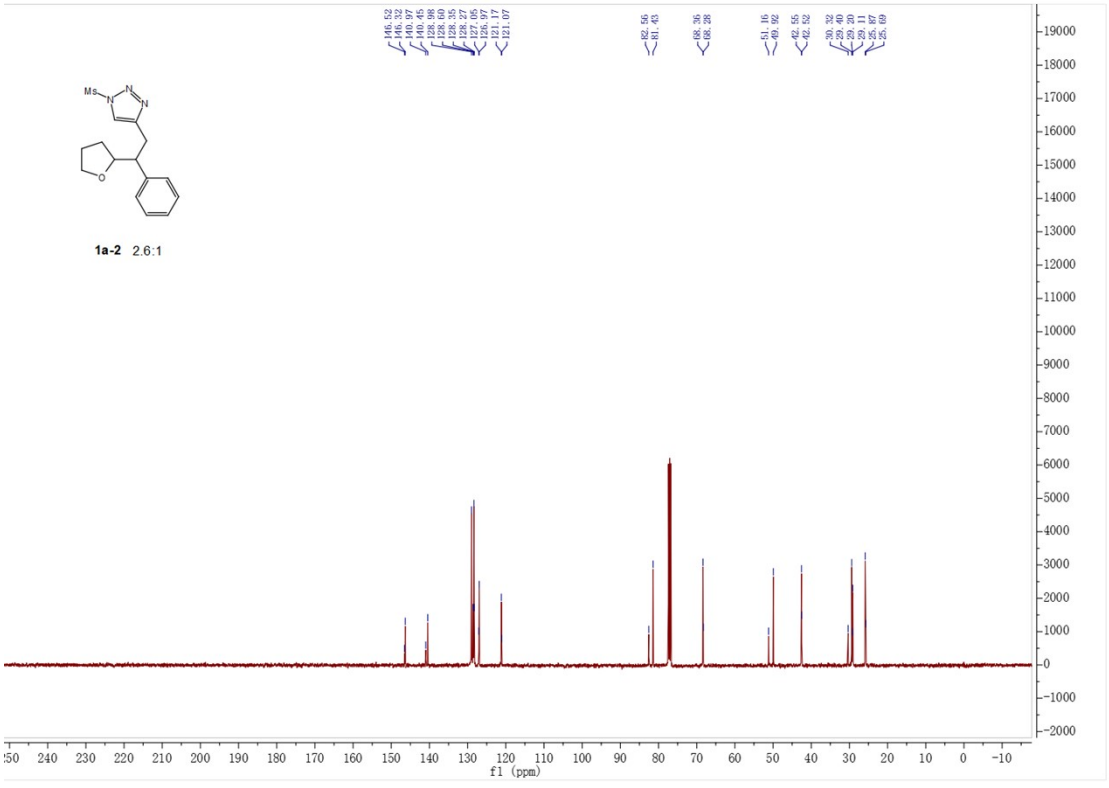
f1 (ppm)


Ms
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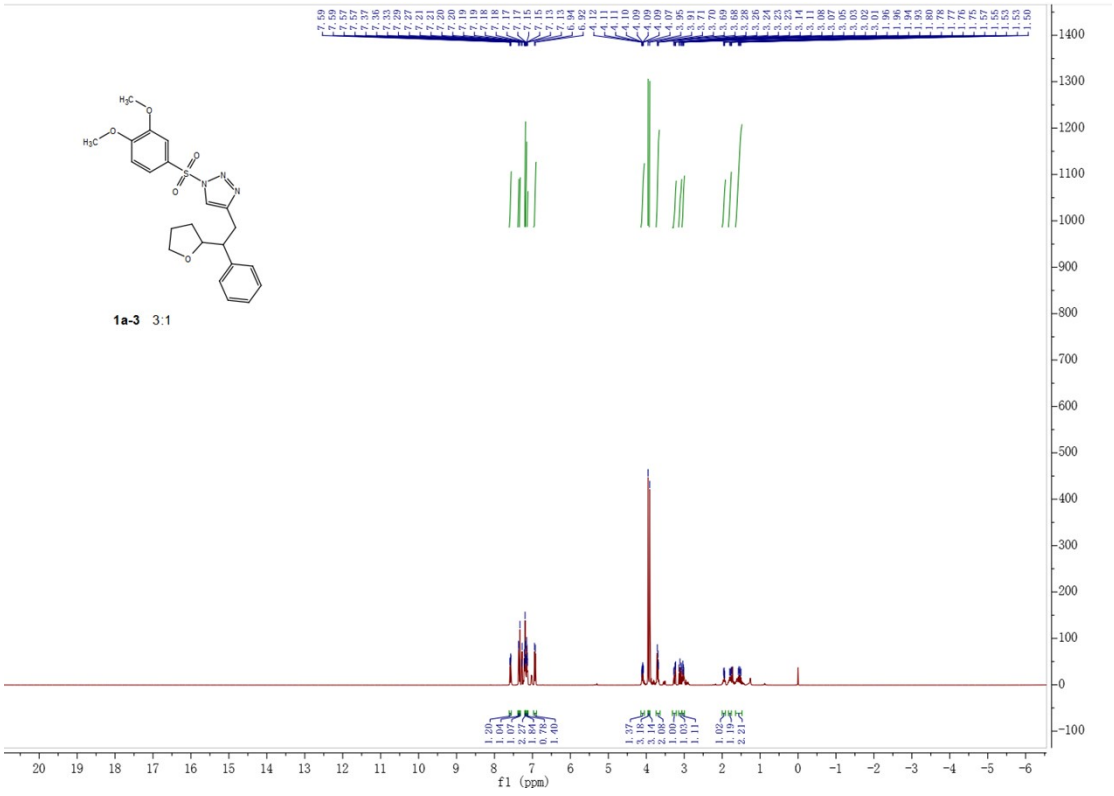
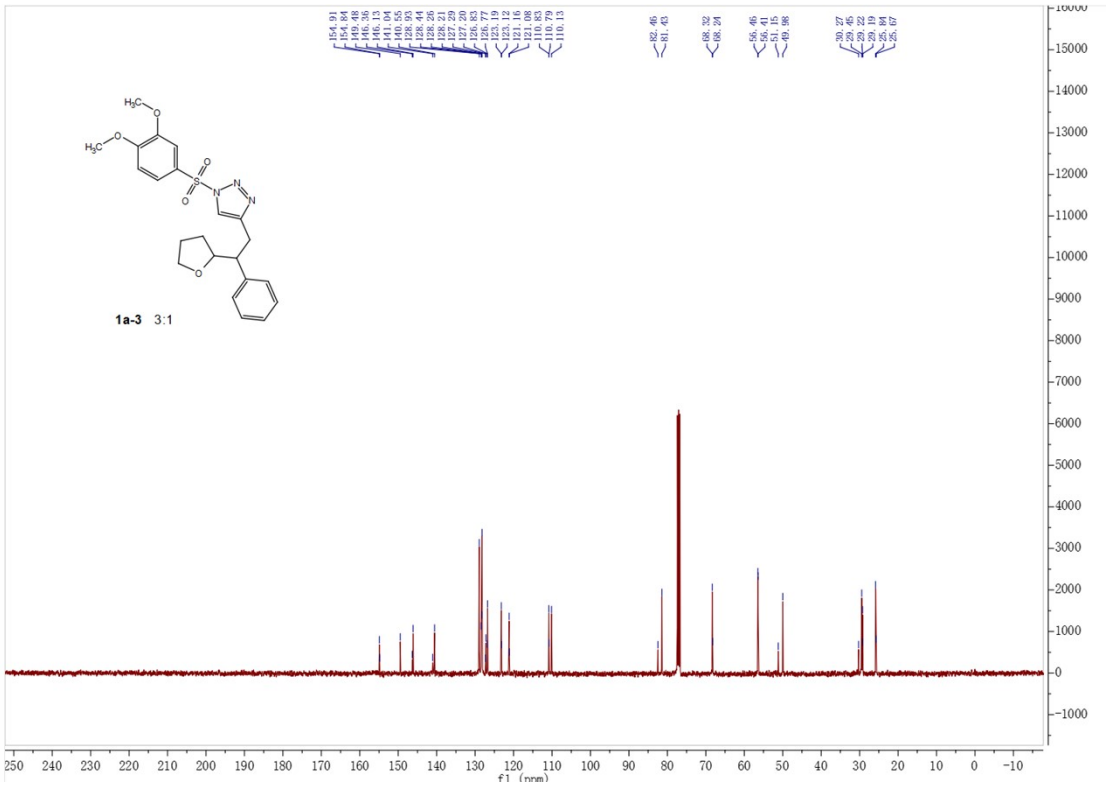
f1 (ppm)


1a-3 3:1
f1 (ppm)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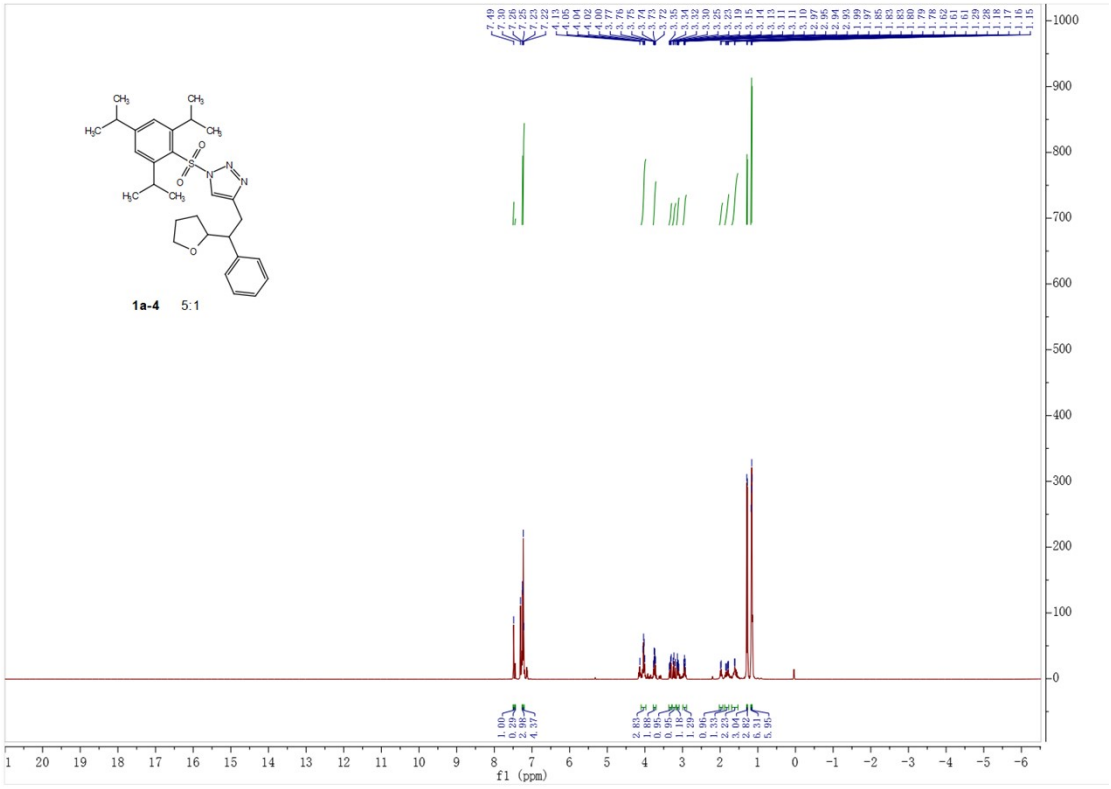
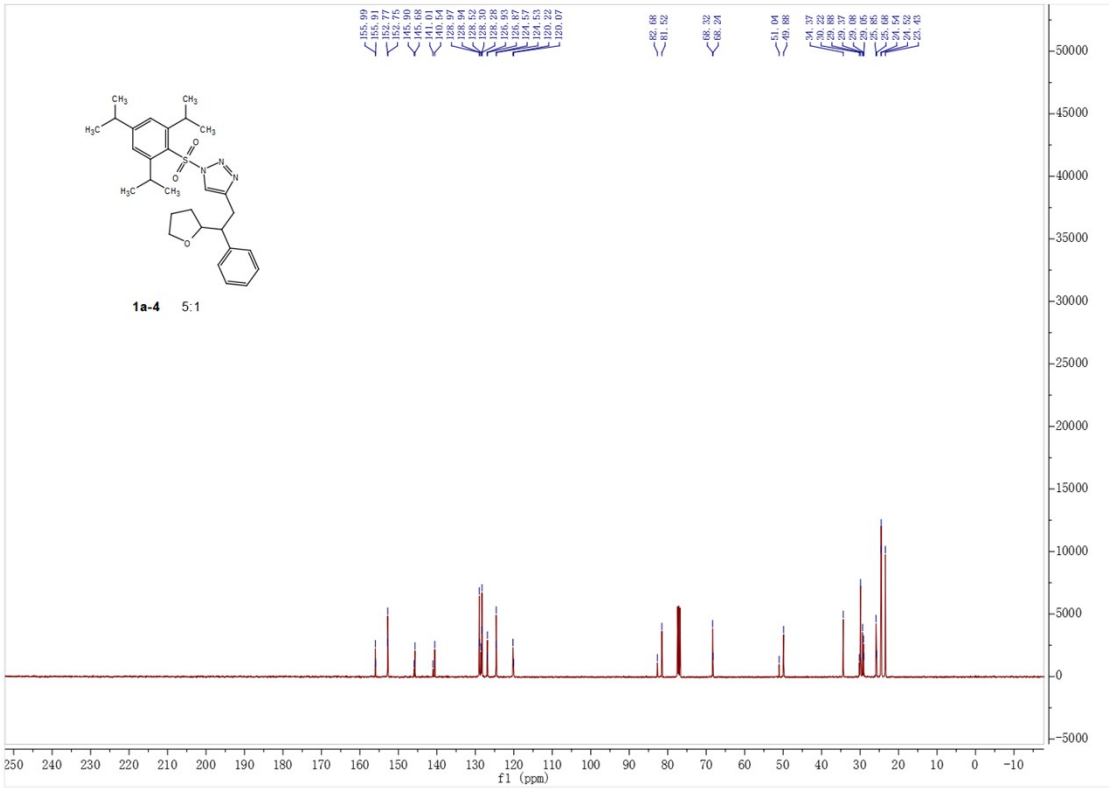
f1 (ppm)


1a-4 5:1
f1 (ppm)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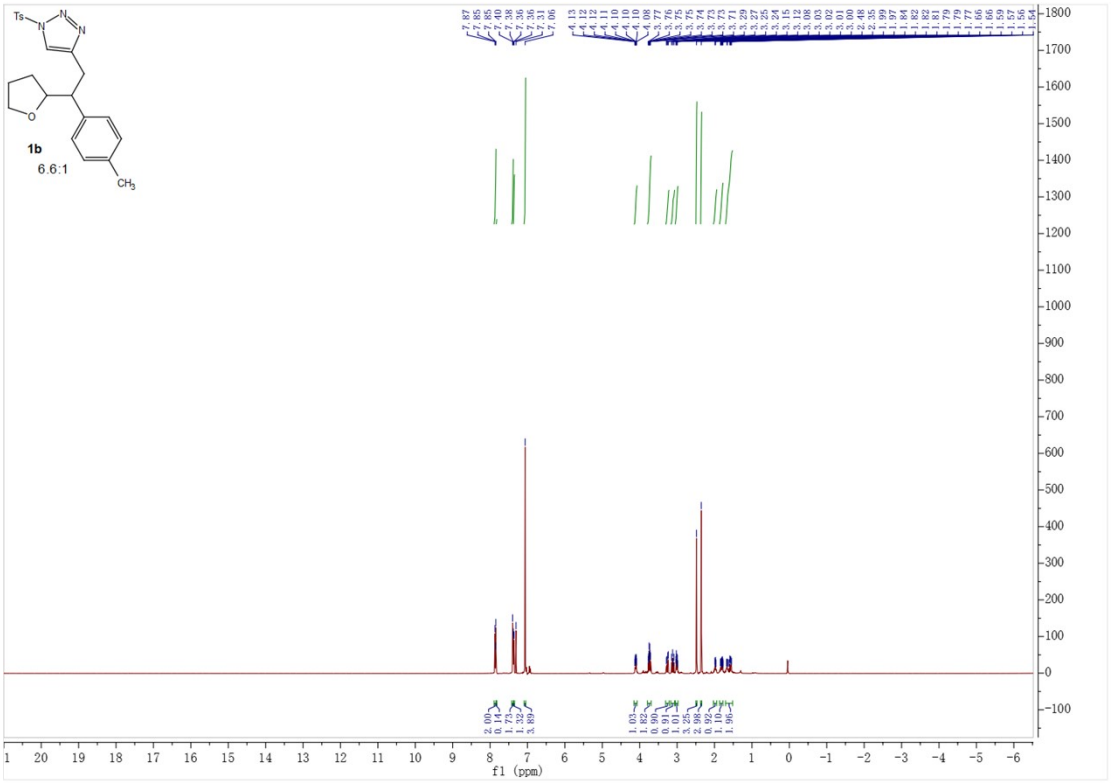
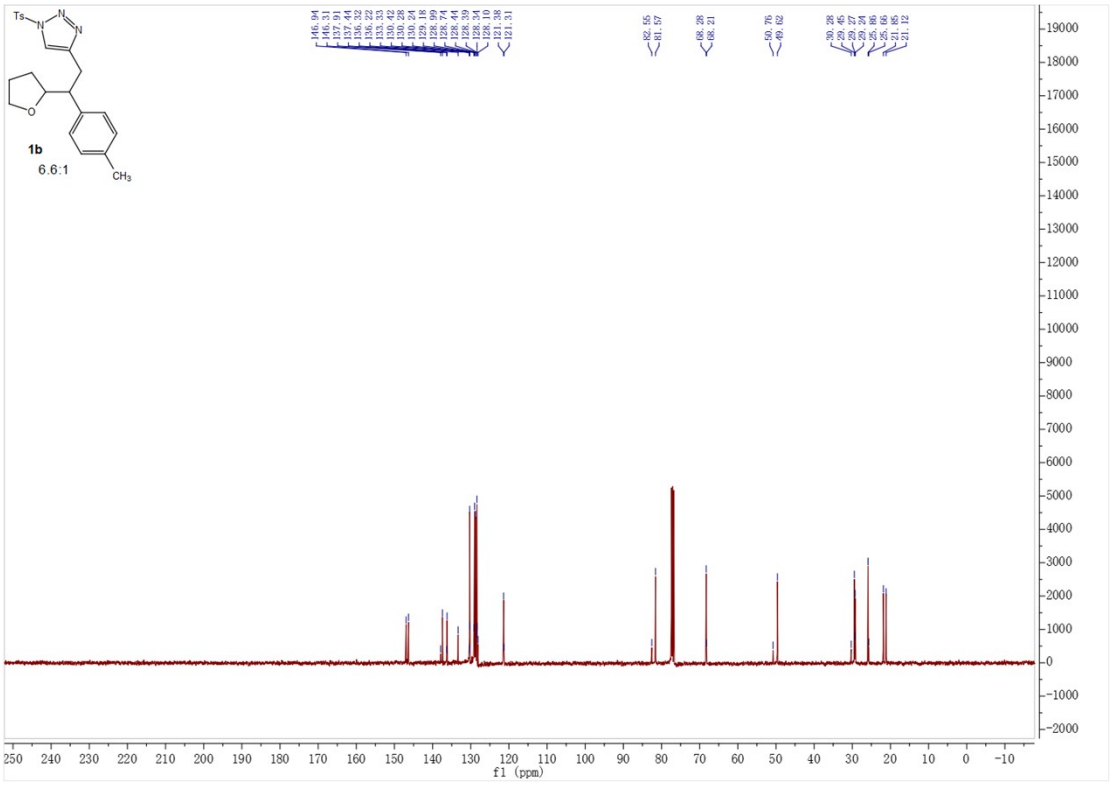
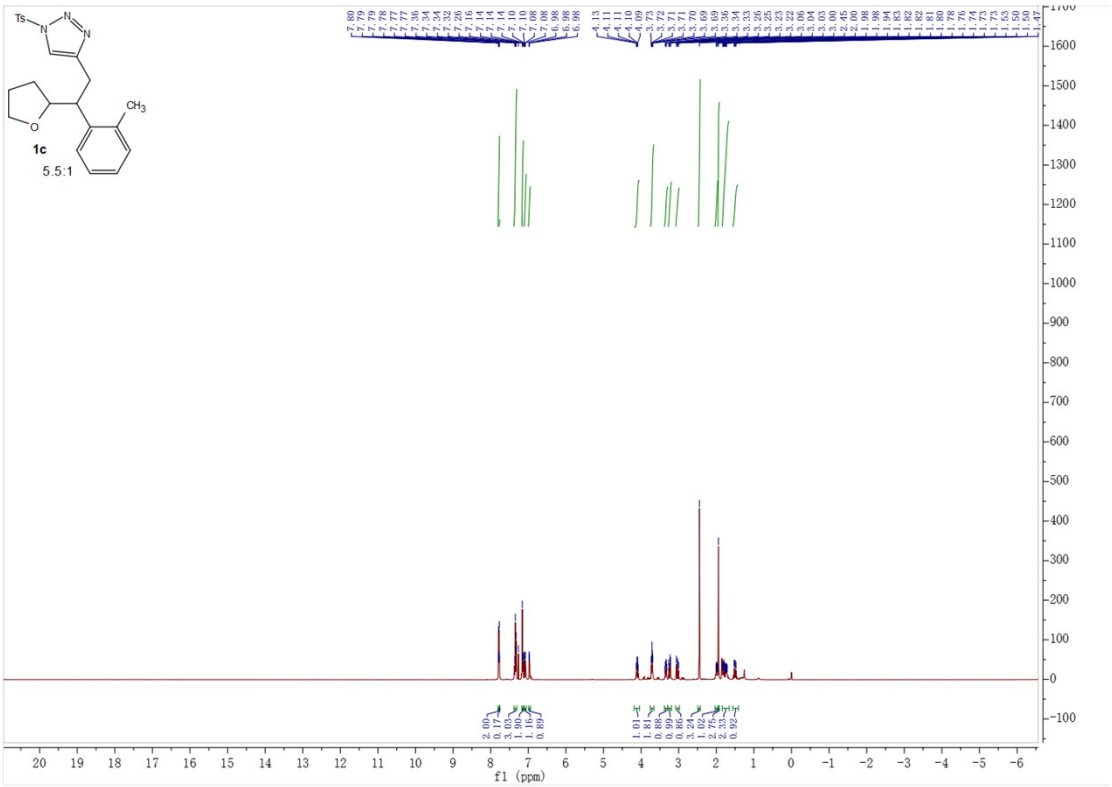
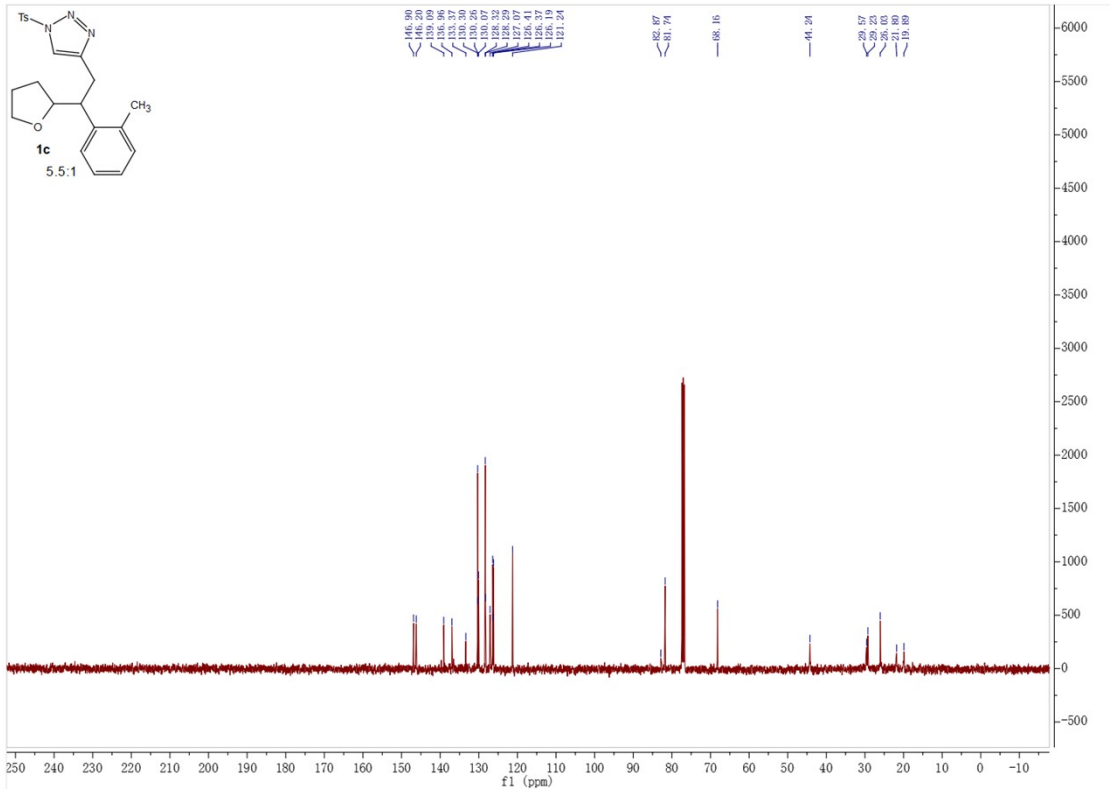
f1 (ppm)


Ts
1b
6.6:1
CH3
f1 (ppm)


Ts
1b
6.6:1
CH3
f1 (ppm)


Ts
CH3
1c
5.5:1
f1 (ppm)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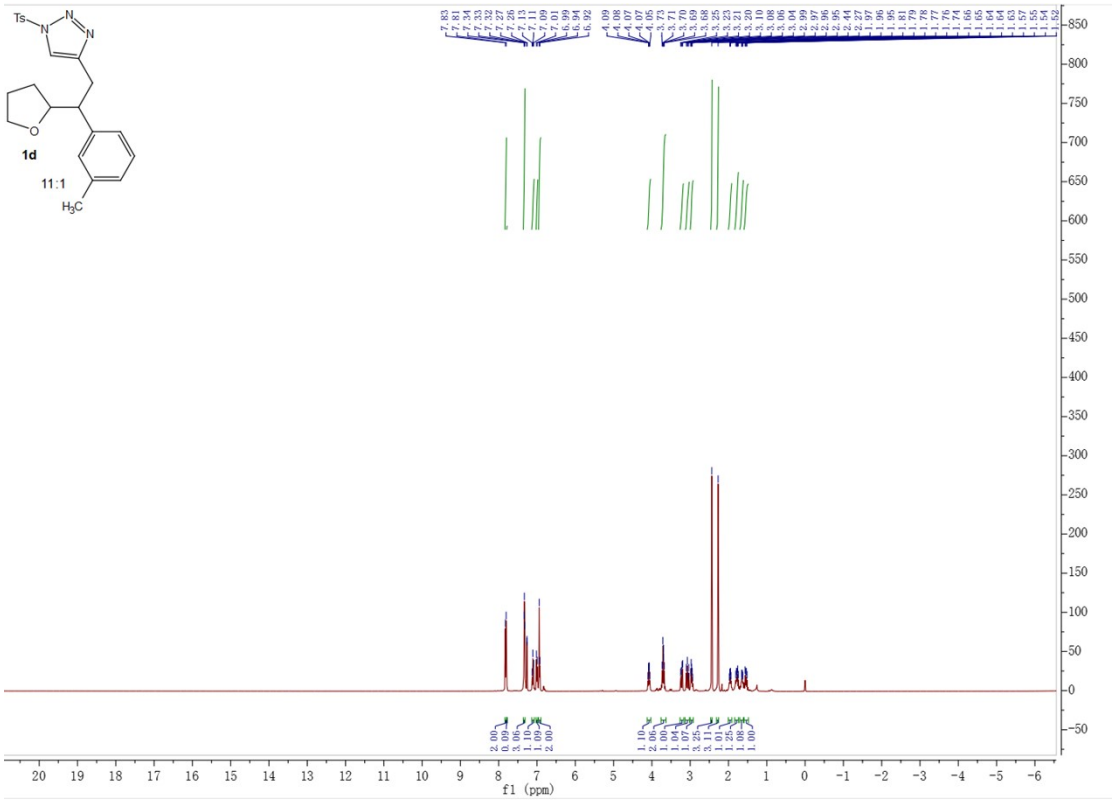
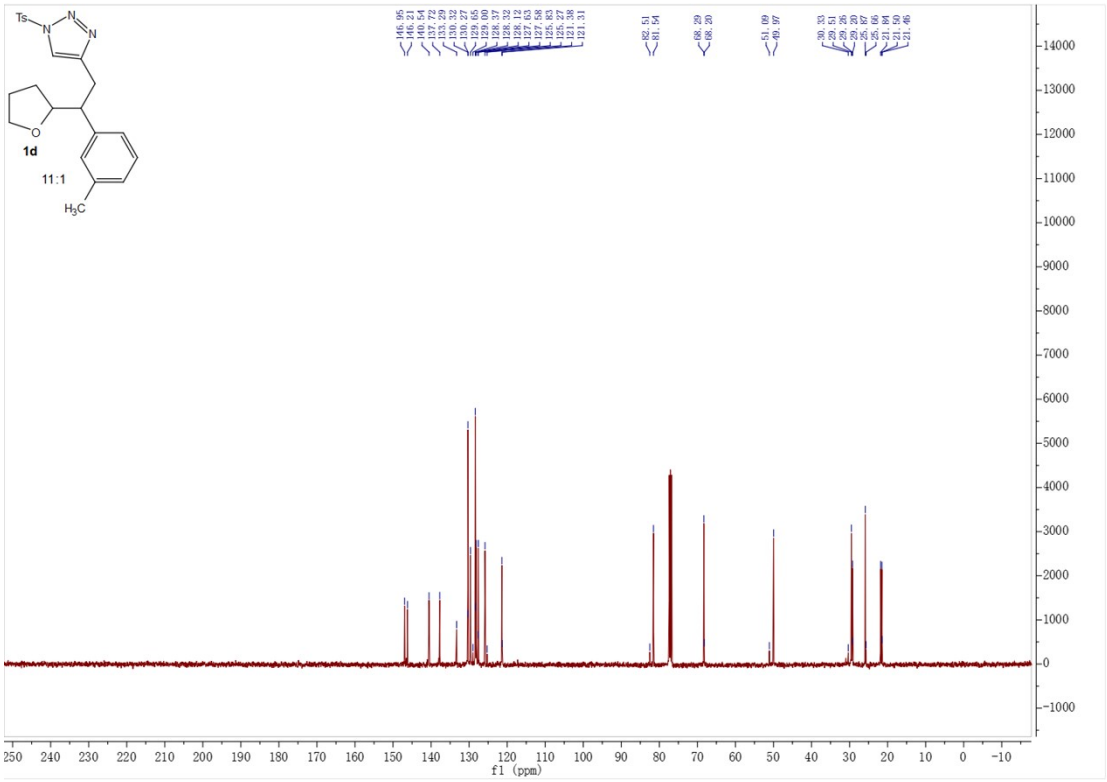
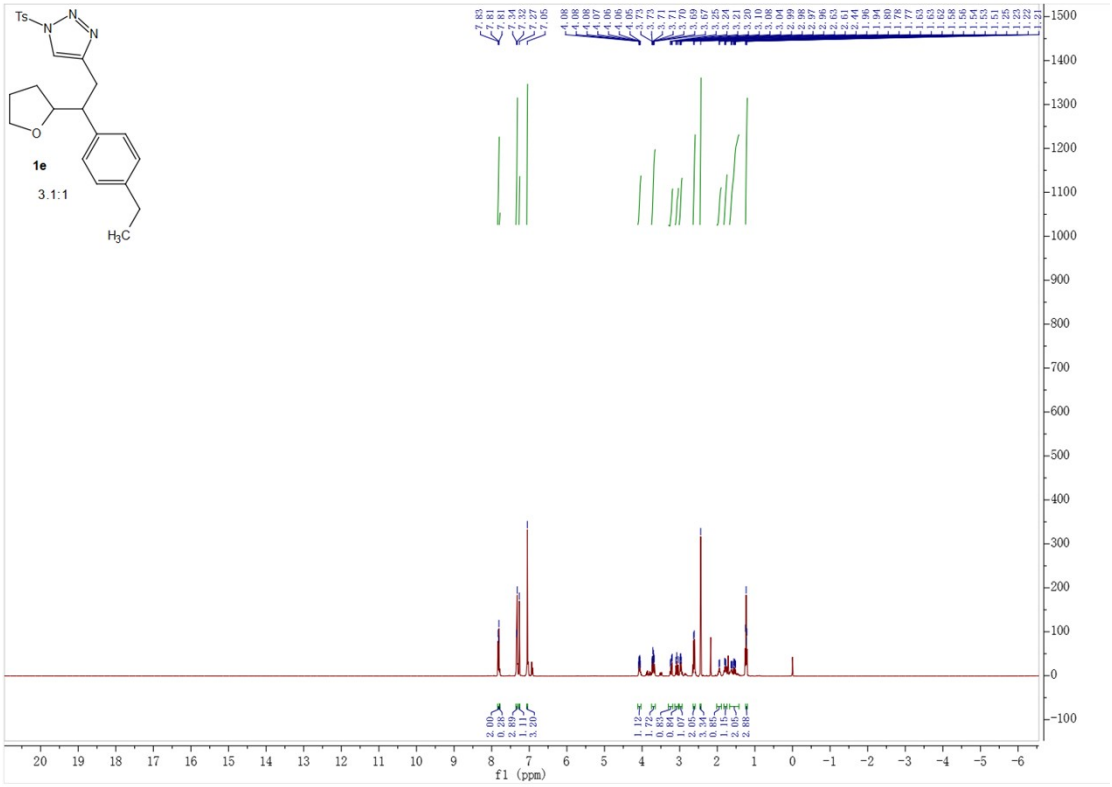
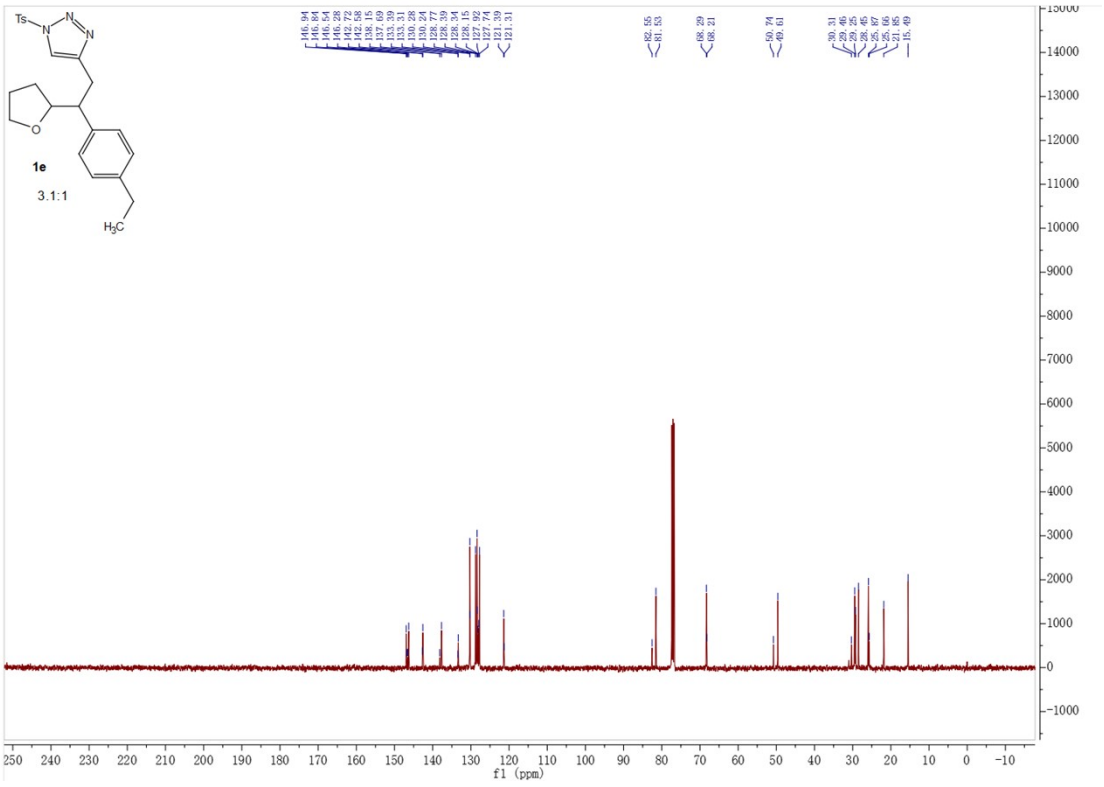
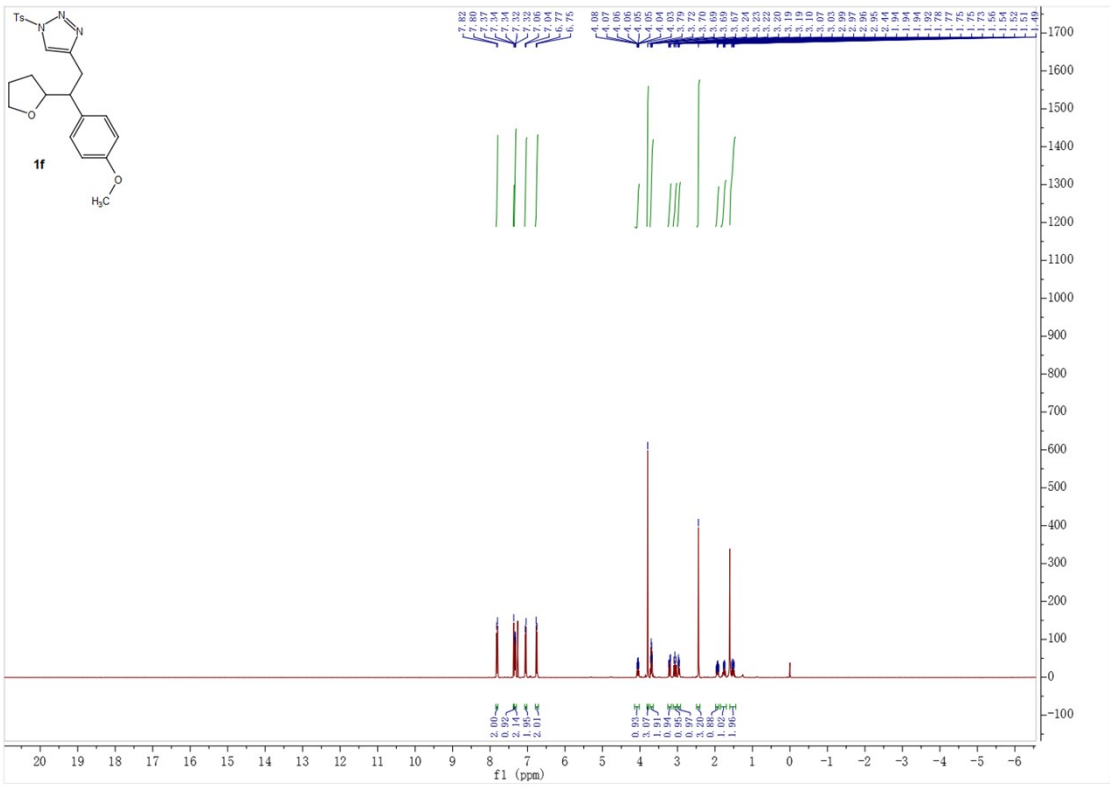
1c
5.5:1
f1 (ppm)

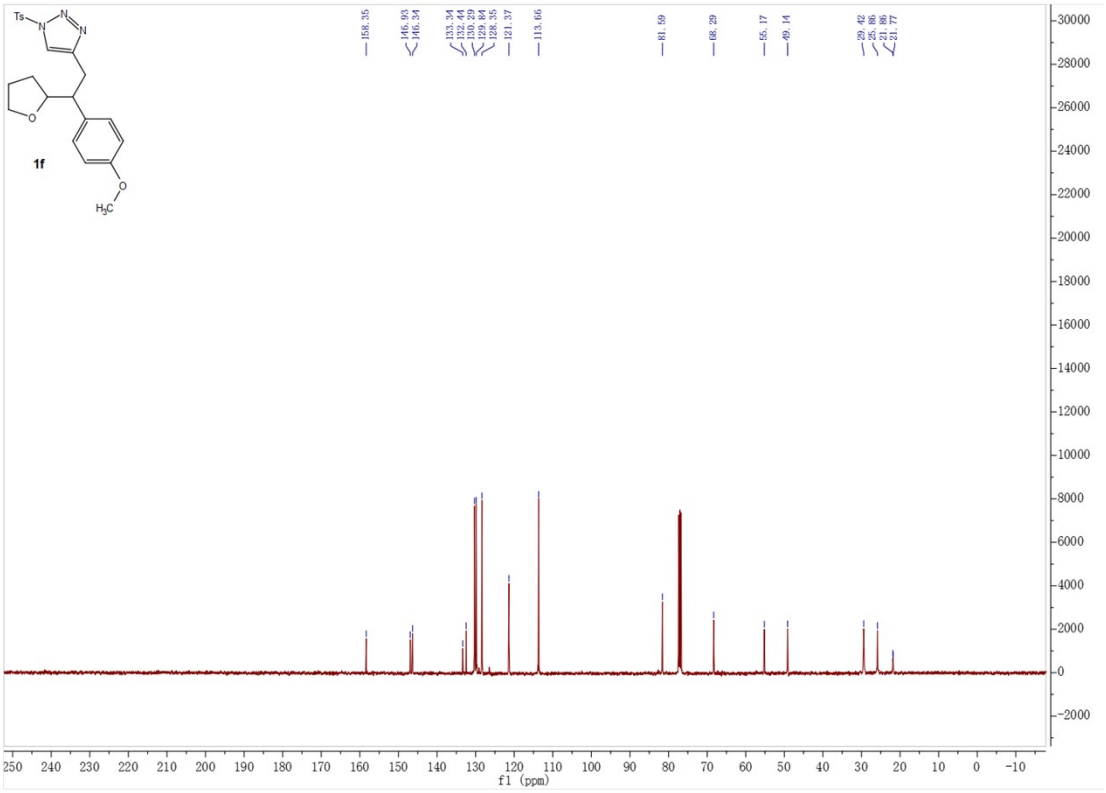

Ts
1d
11:1
H3C
f1 (ppm)

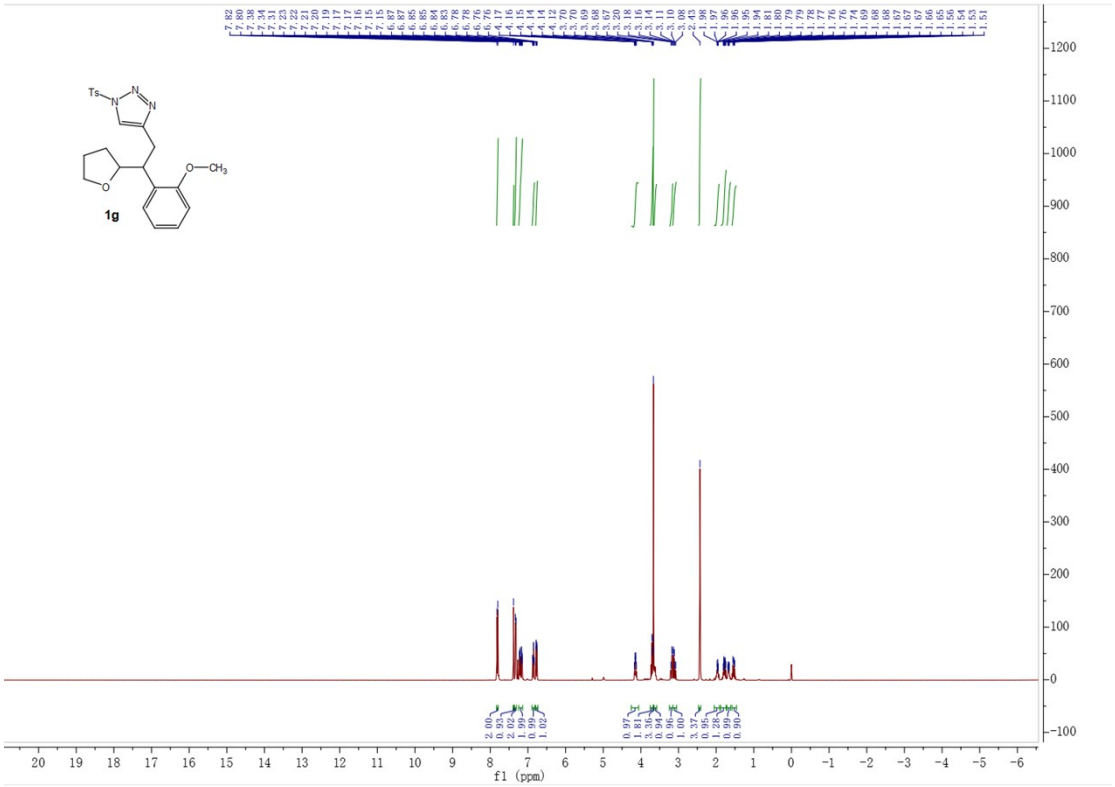

Ts
1d
11:1
H3C
f1 (ppm)

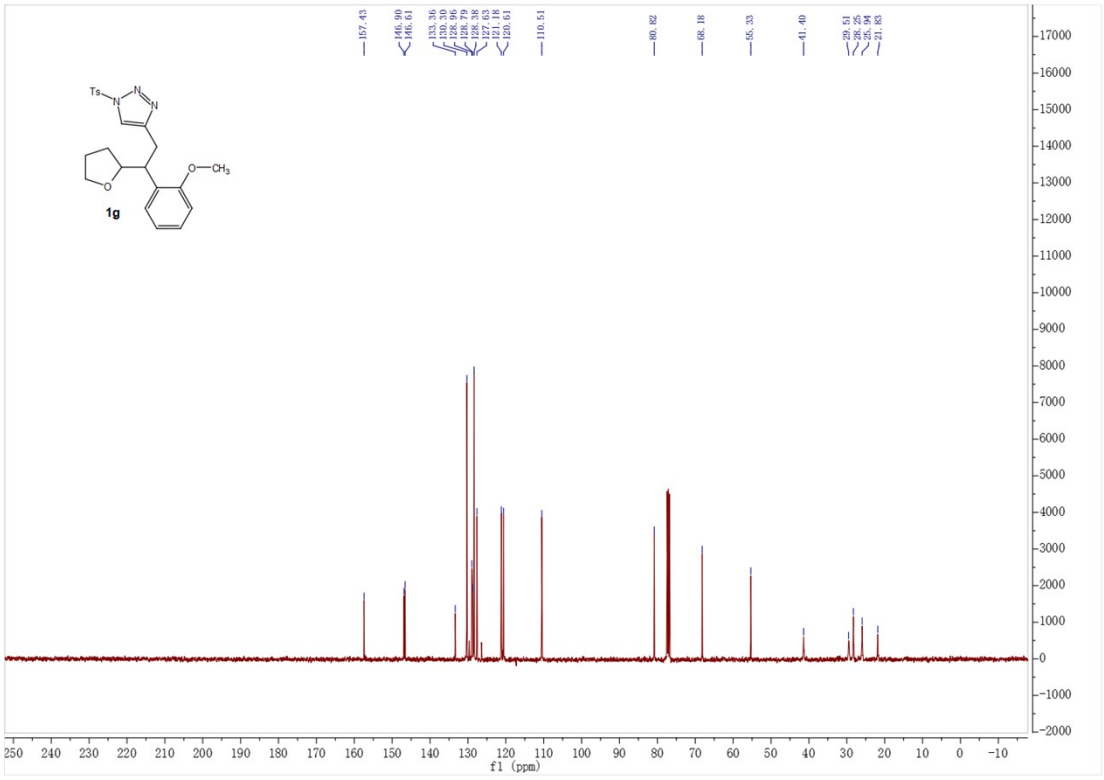

Ts
1e
3.1:1
H3C
f1 (ppm)

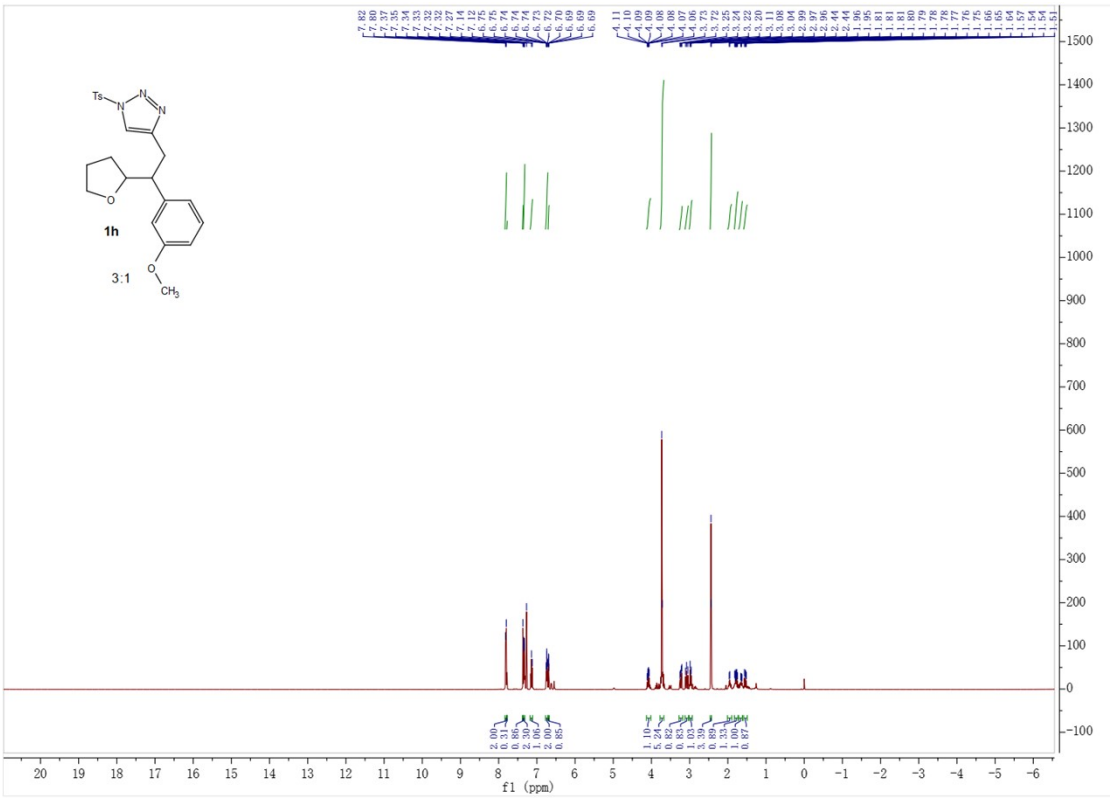

Ts
1e
3.1:1
H3C
f1 (ppm)

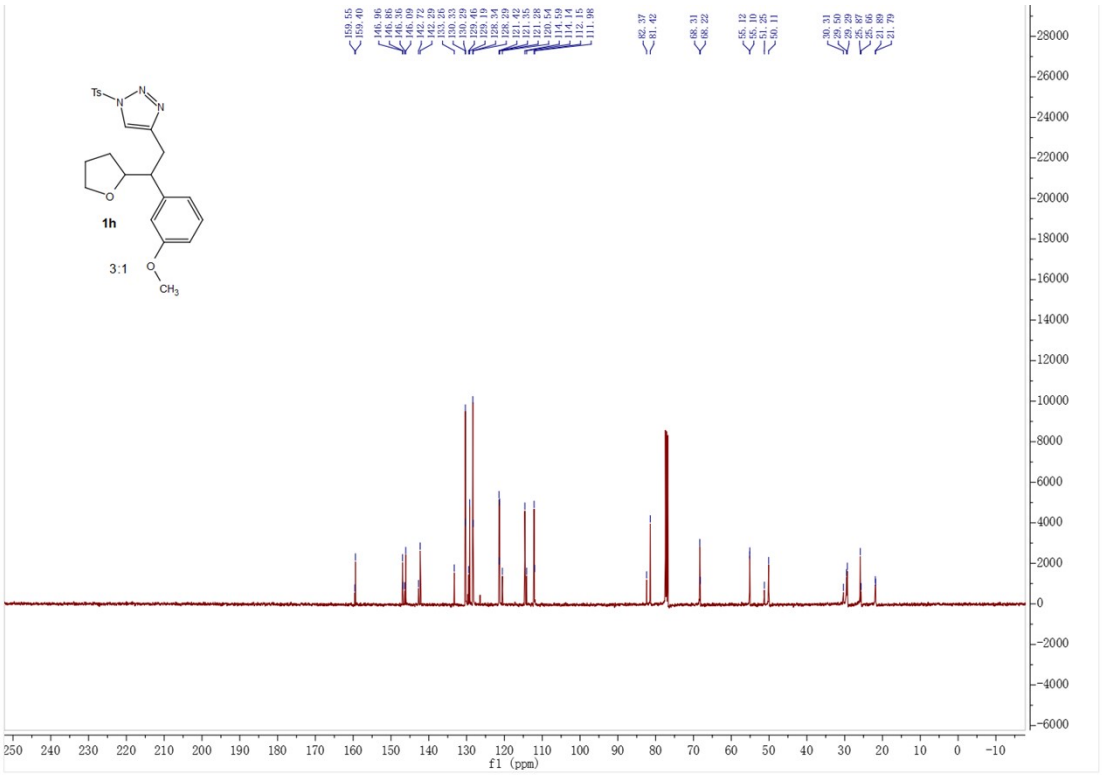

Ts
1f
H3C
f1 (ppm)


Ts
1f
H3C
158.35
146.93
146.34
133.34
132.44
130.89
129.84
128.35
121.37
113.66
81.59
68.29
55.17
49.14
29.42
25.86
21.86
21.77
f1 (ppm)


Ts
O—CH3
1g
f1 (ppm)


Ts
O—CH3
1g
f1 (ppm)


Ts
1h
3:1
O
CH3
f1 (ppm)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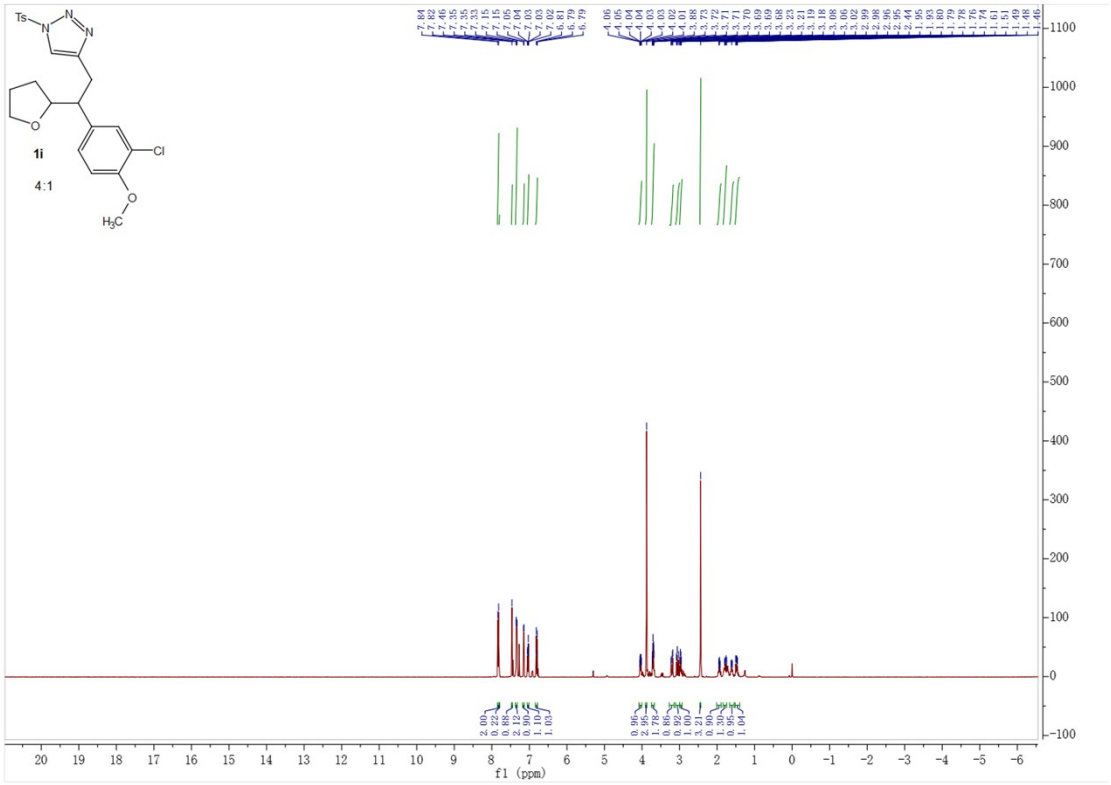
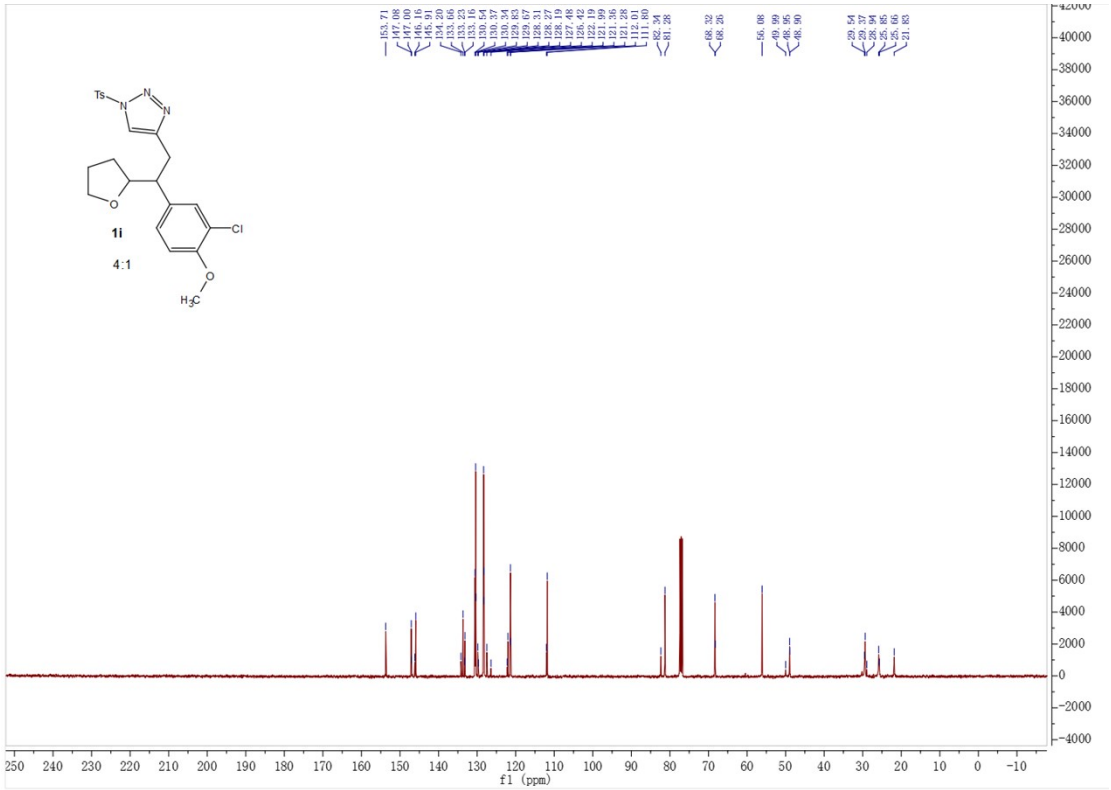
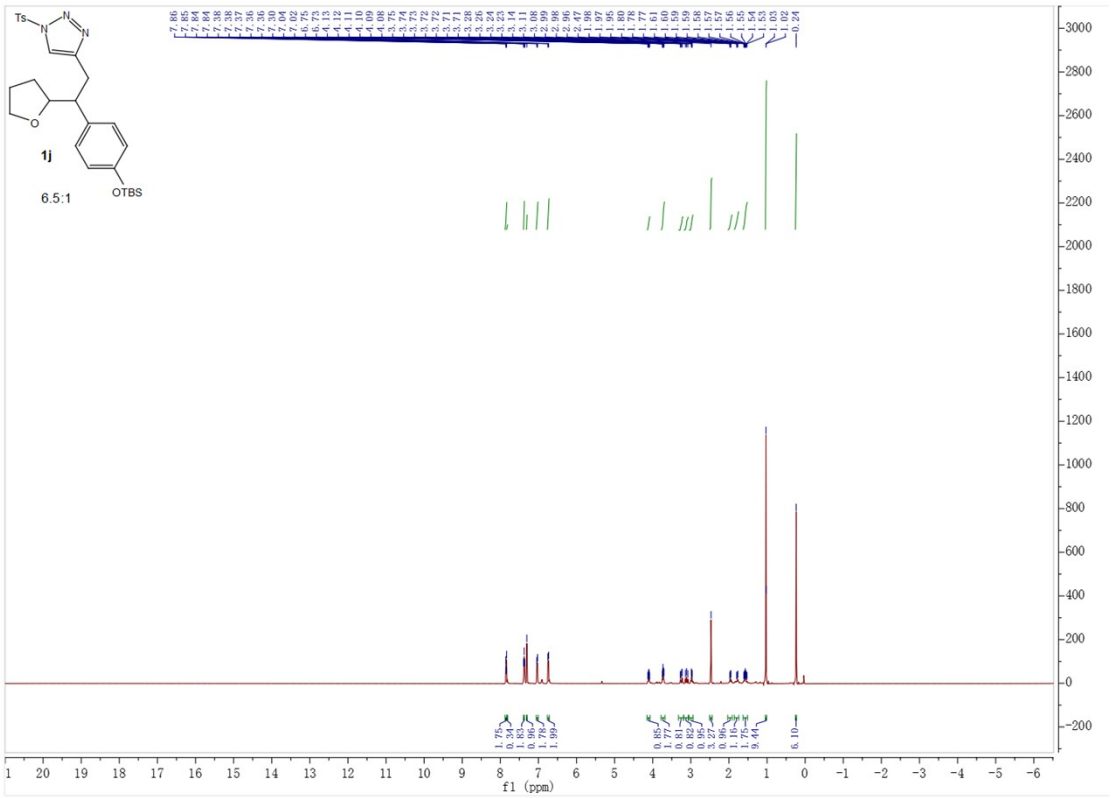
3:1
O
CH3
f1 (ppm)


Ts
1i
4:1
Cl
O
H3C
f1 (ppm)


Ts
1i
4:1
Cl
O
H3C
f1 (ppm)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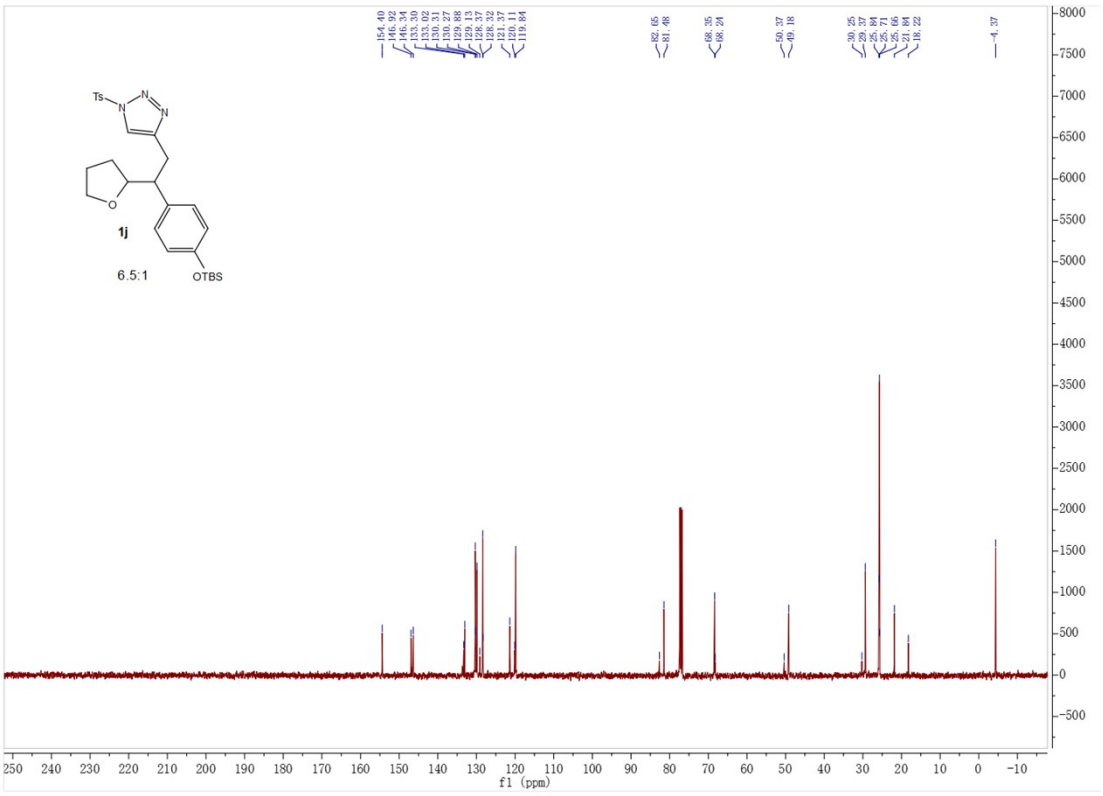
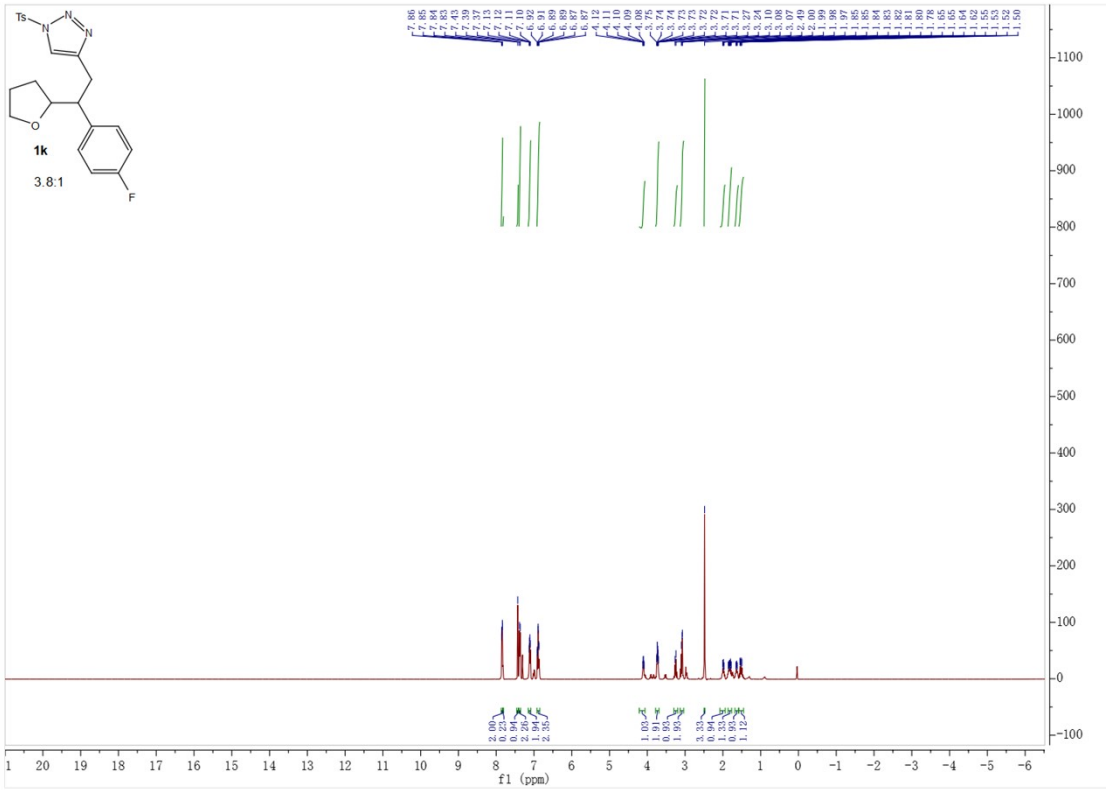
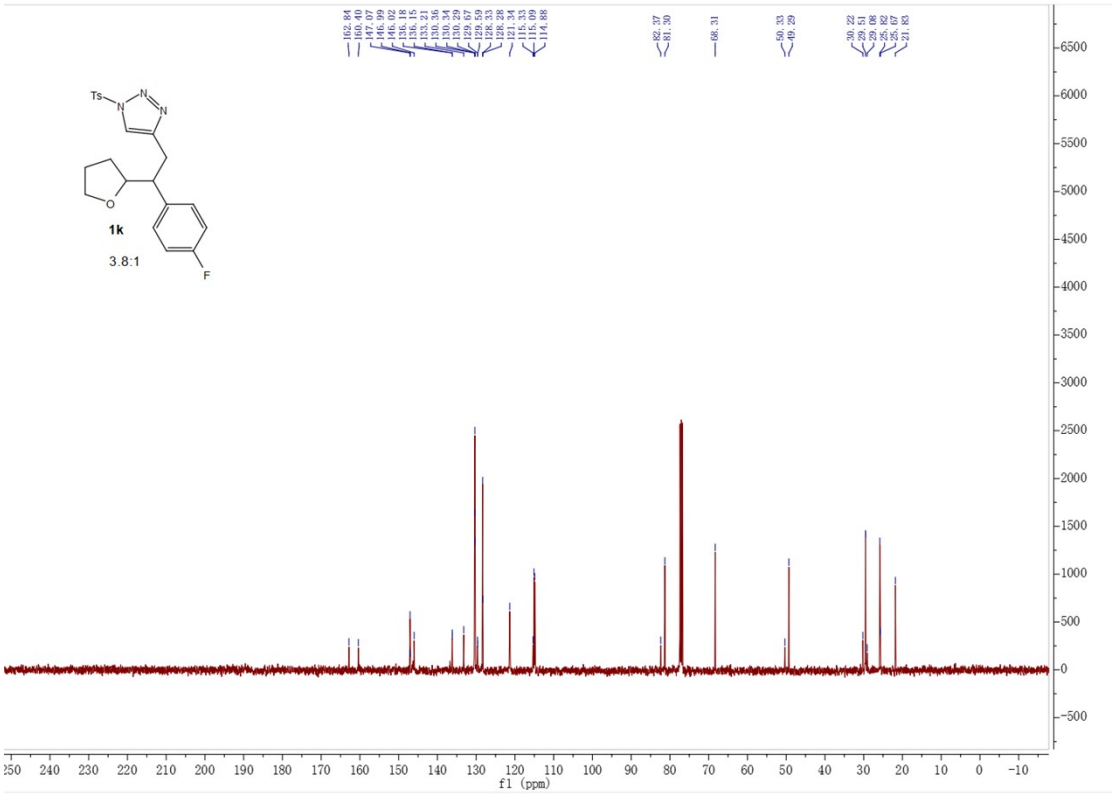
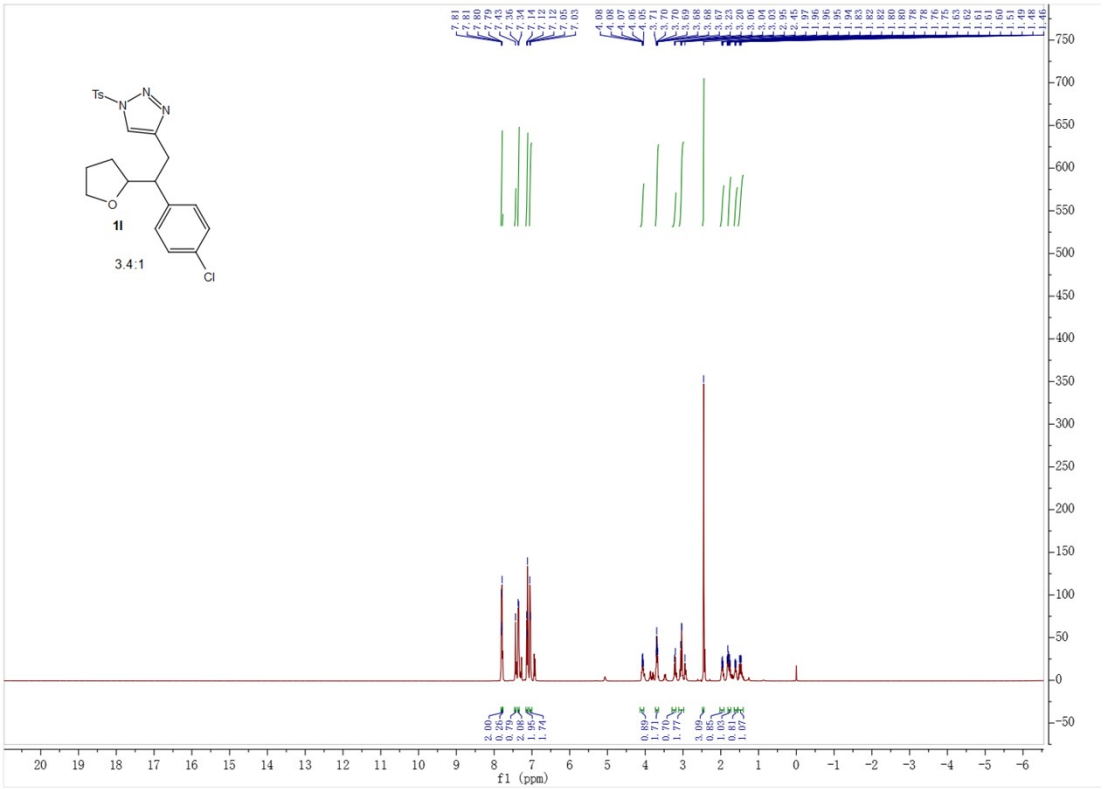
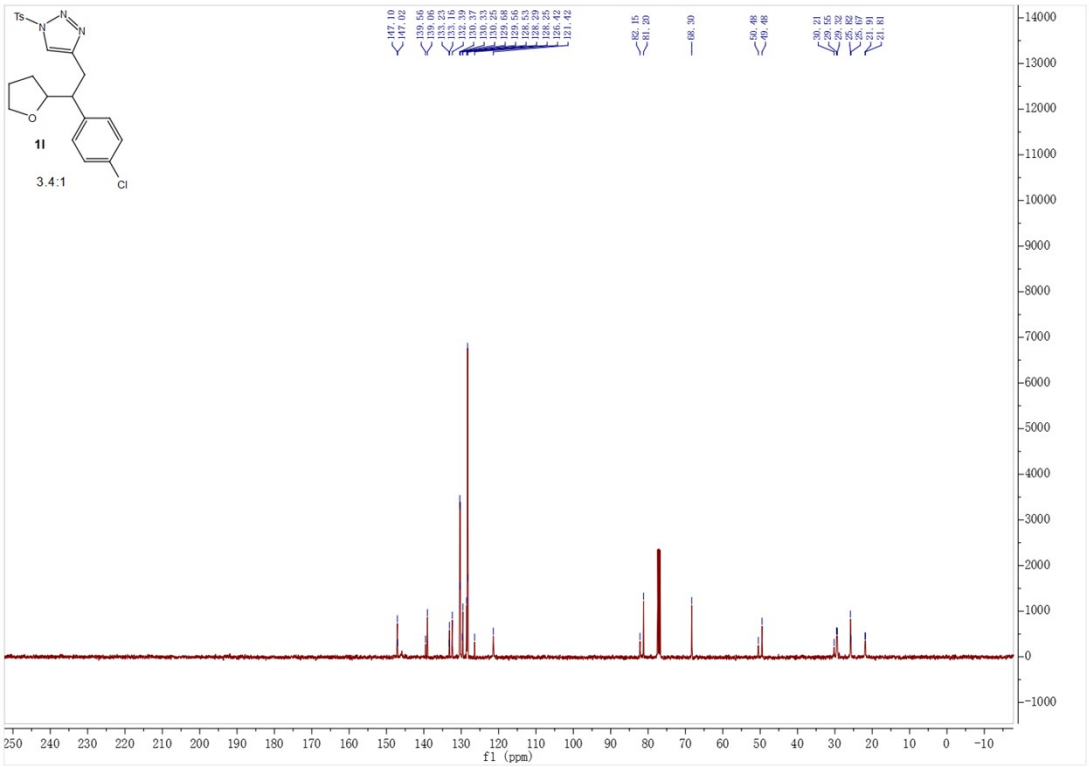
1j
6.5:1
OTBS
f1 (ppm)

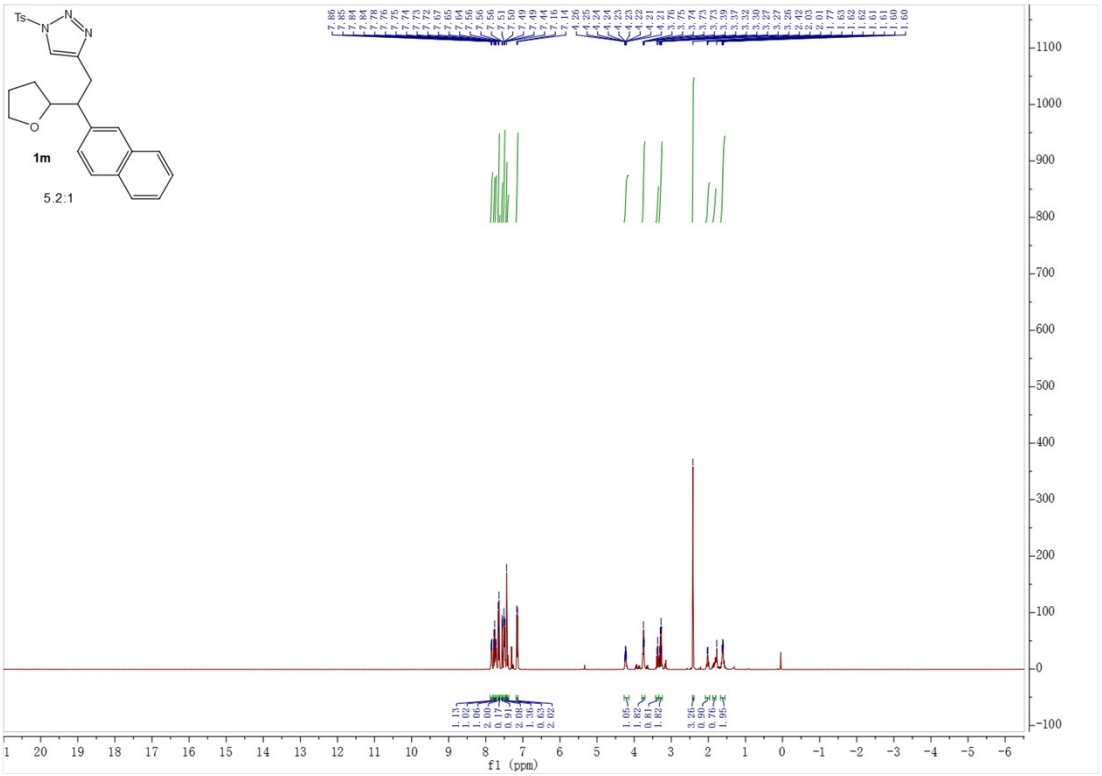

Ts
1j
6.5:1
OTBS
f1 (ppm)

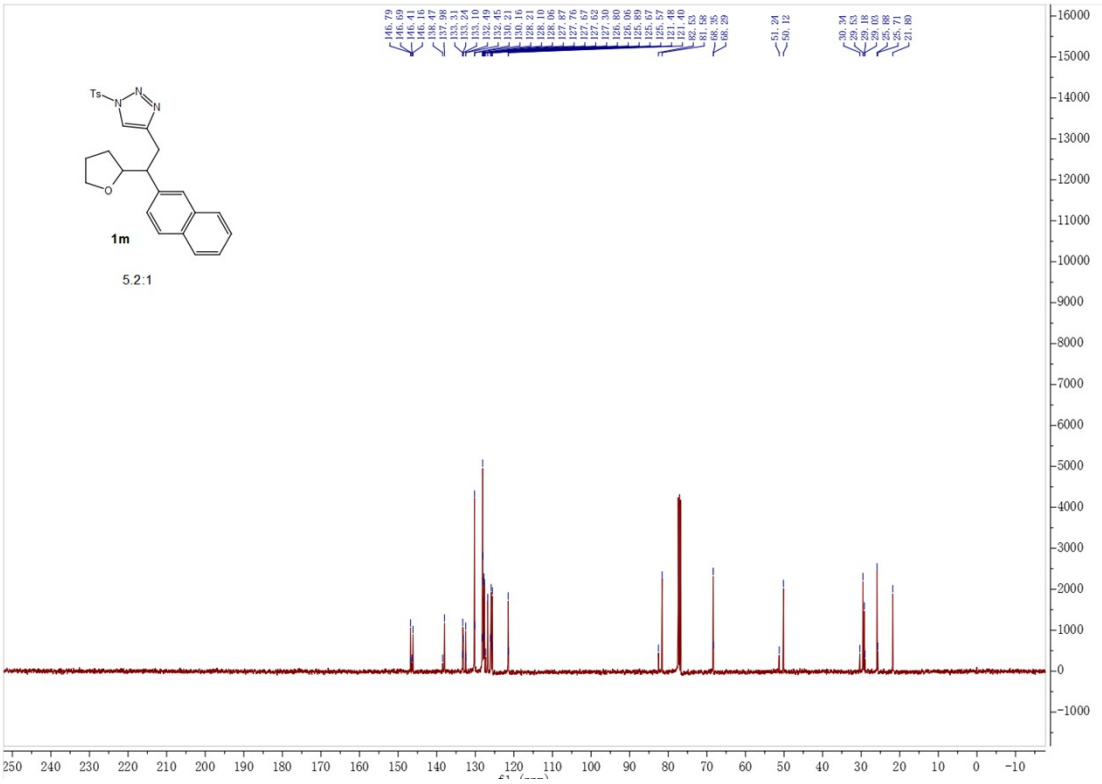

Ts
1k
3.8:1
F
f1 (ppm)

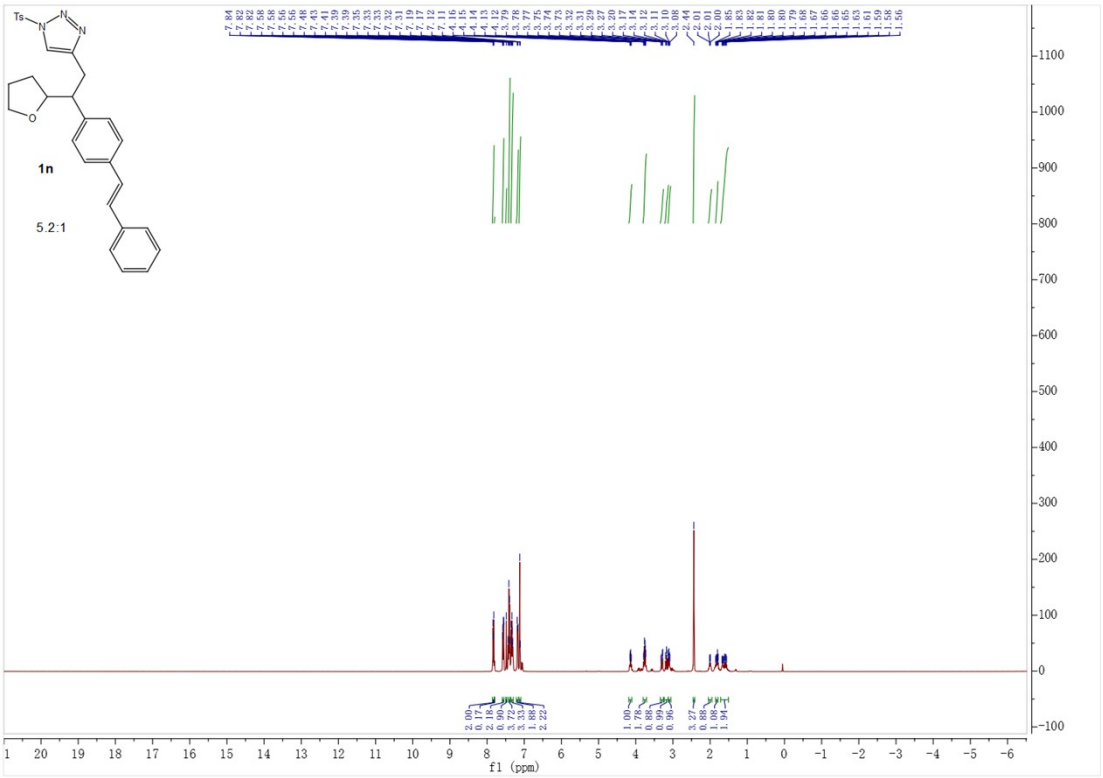

Ts
1k
3.8:1
F
f1 (ppm)


1l
3.4:1
f1 (ppm)


1l
3.4:1
f1 (ppm)


Ts
1m
5.2:1
f1 (ppm)


Ts
1m
5.2:1


1n
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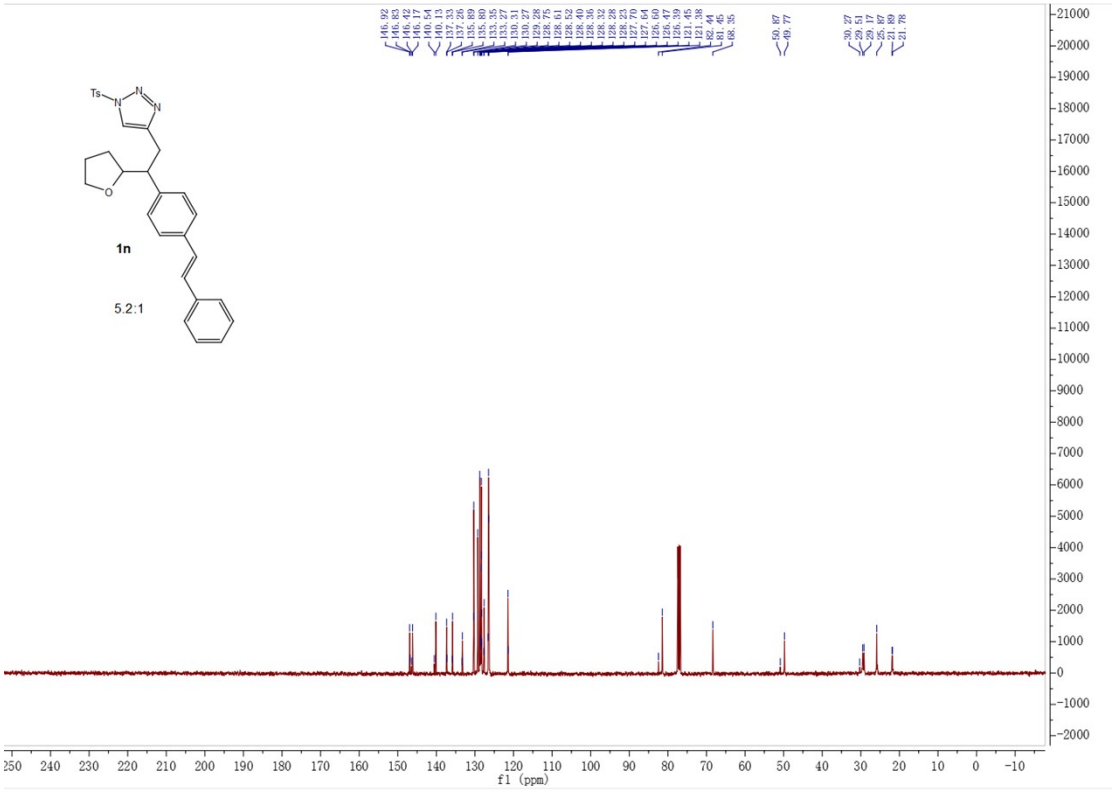
f1 (ppm)


1n
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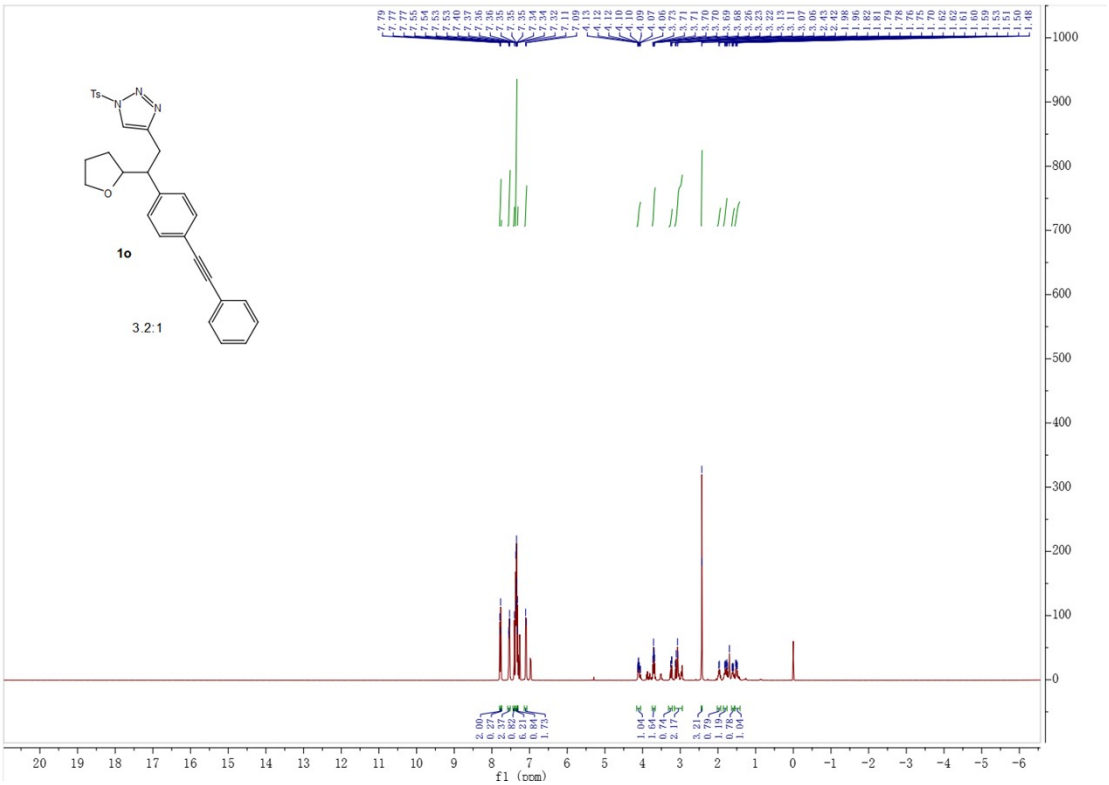
Ts
1o
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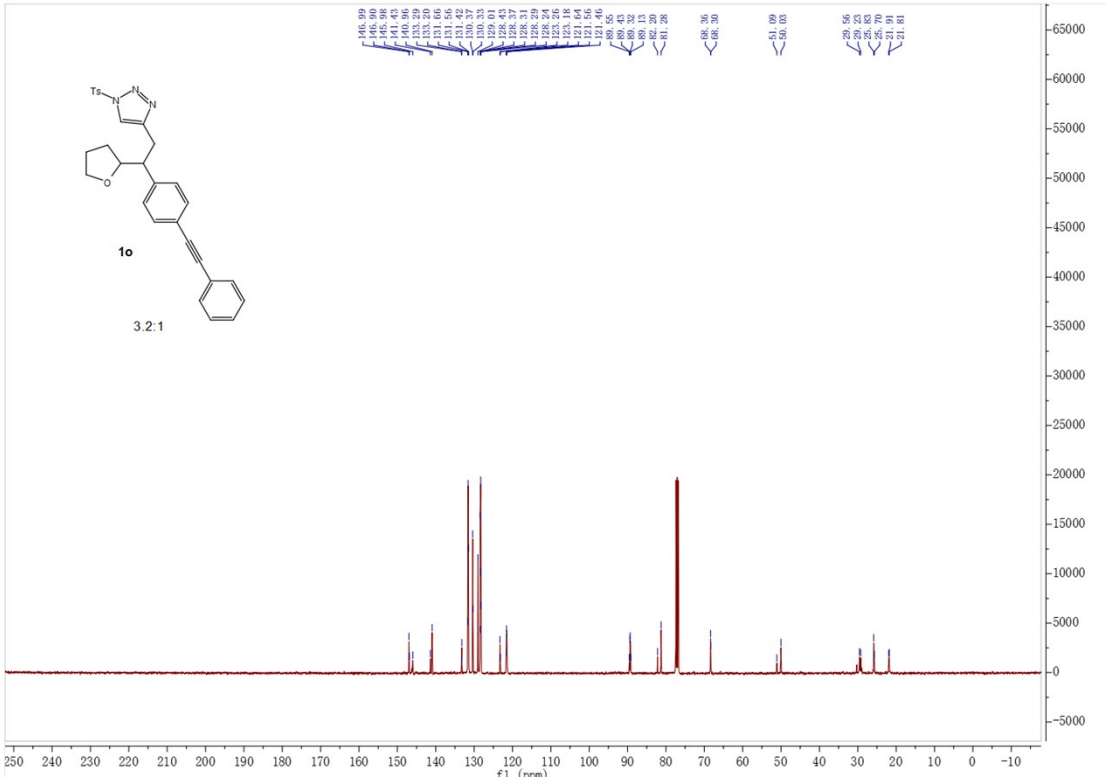
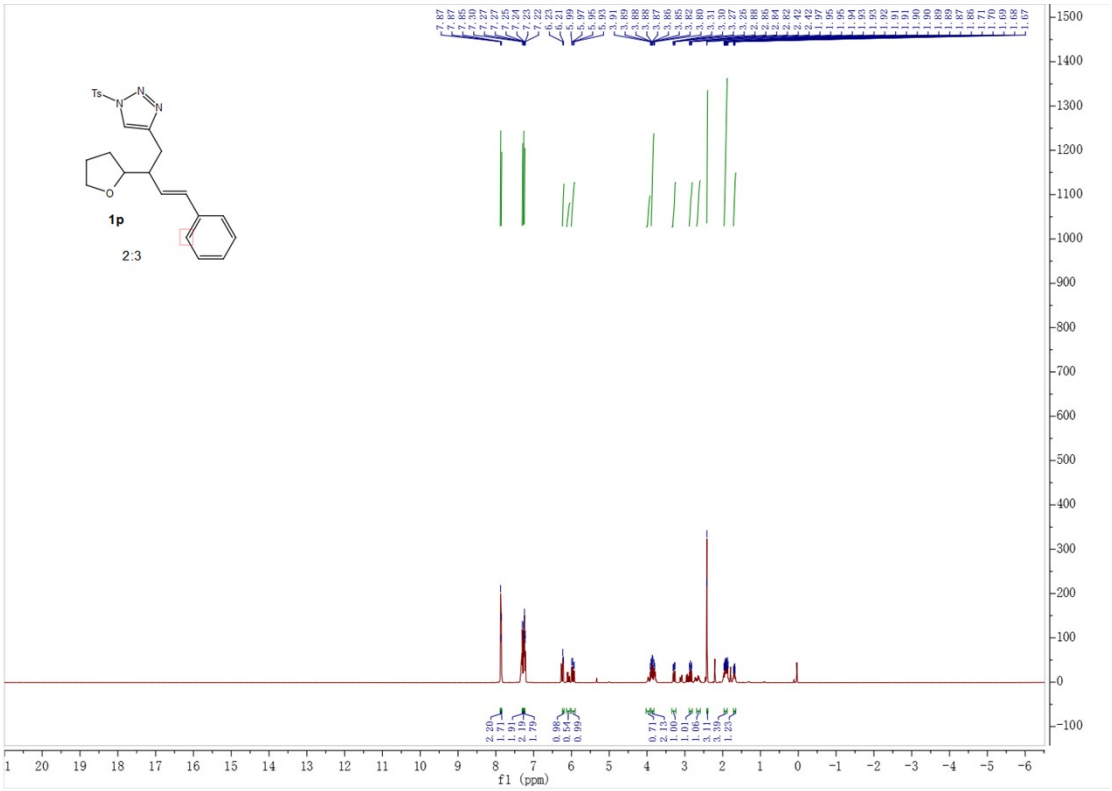
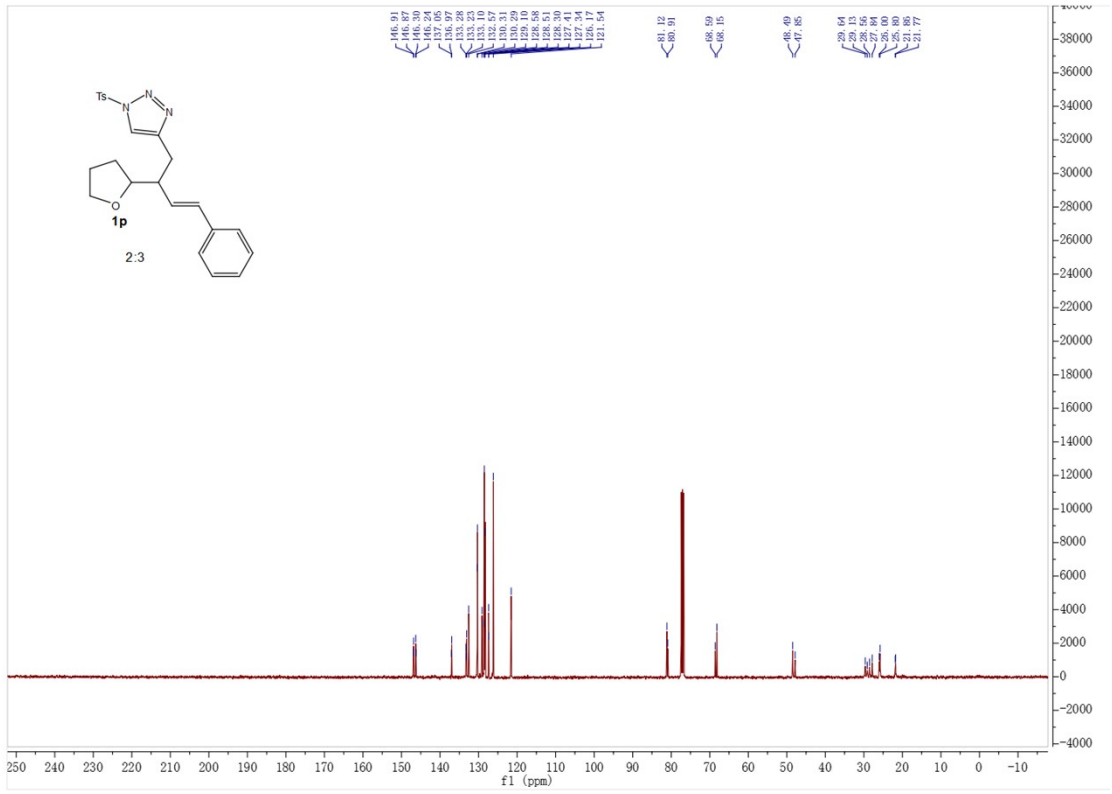
f1 (ppm)


Ts
1o
3.2:1
f1 (ppm)


Ts
1p
2:3
f1 (ppm)


Ts
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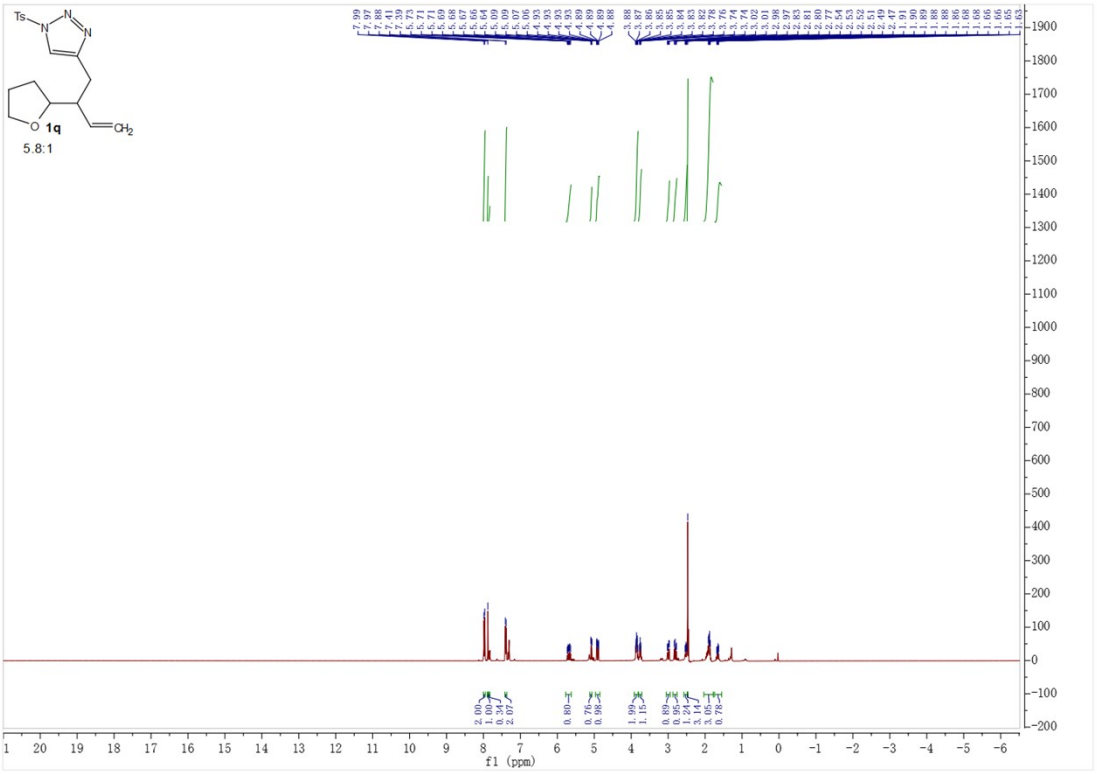
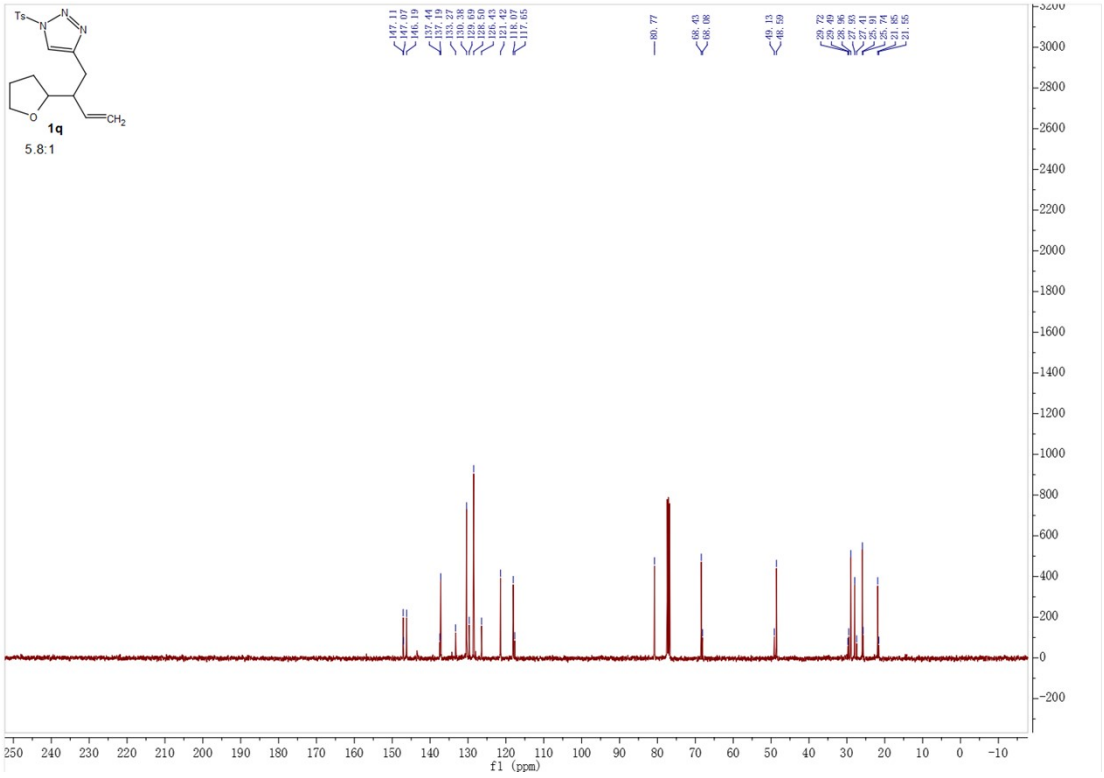
f1 (ppm)


Ts
1q
5.8:1
f1 (ppm)


Ts
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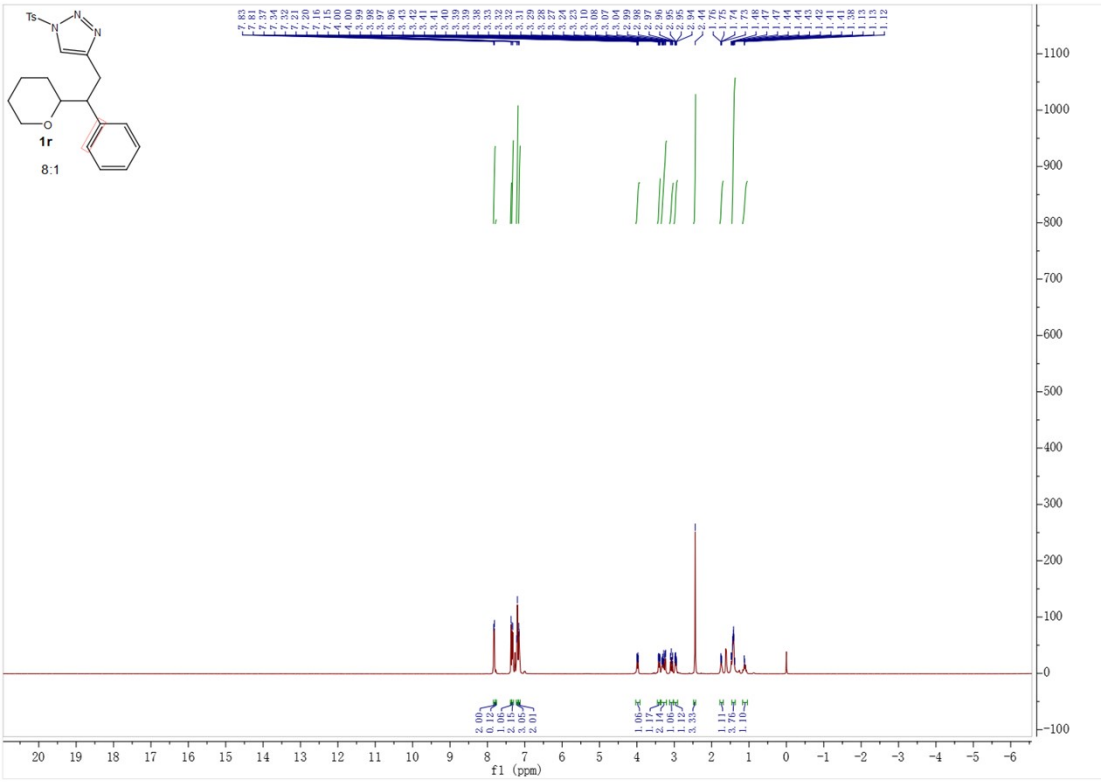
f1 (ppm)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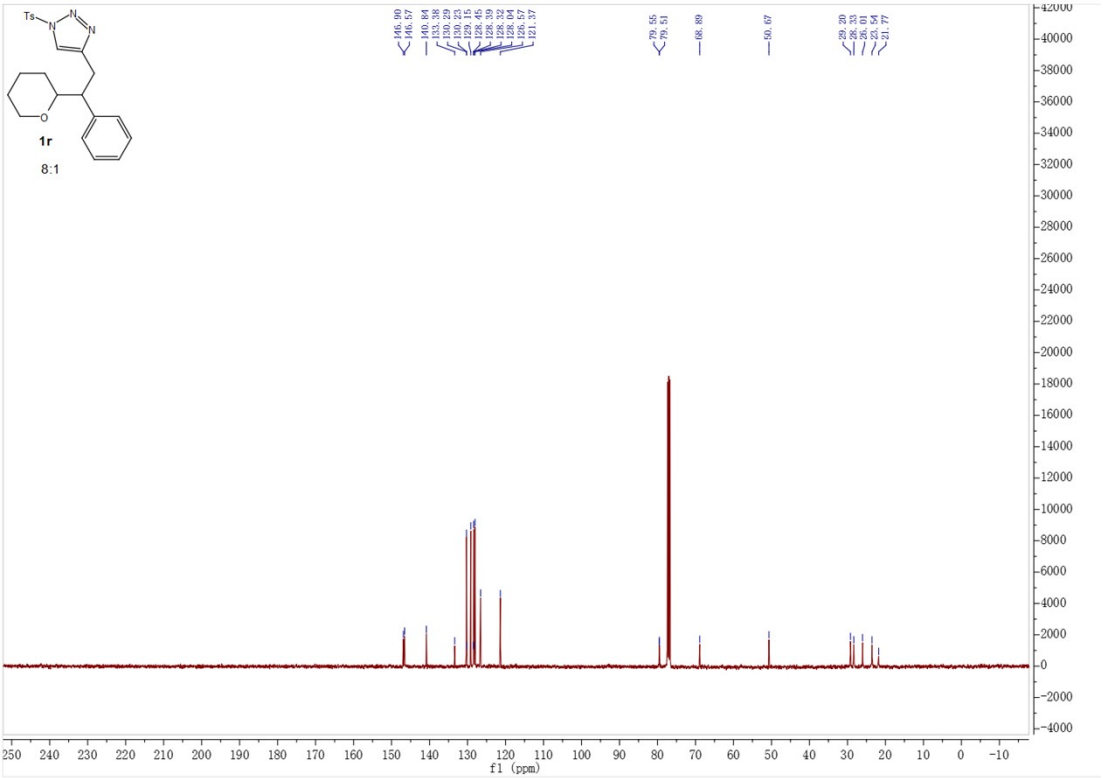
Ts
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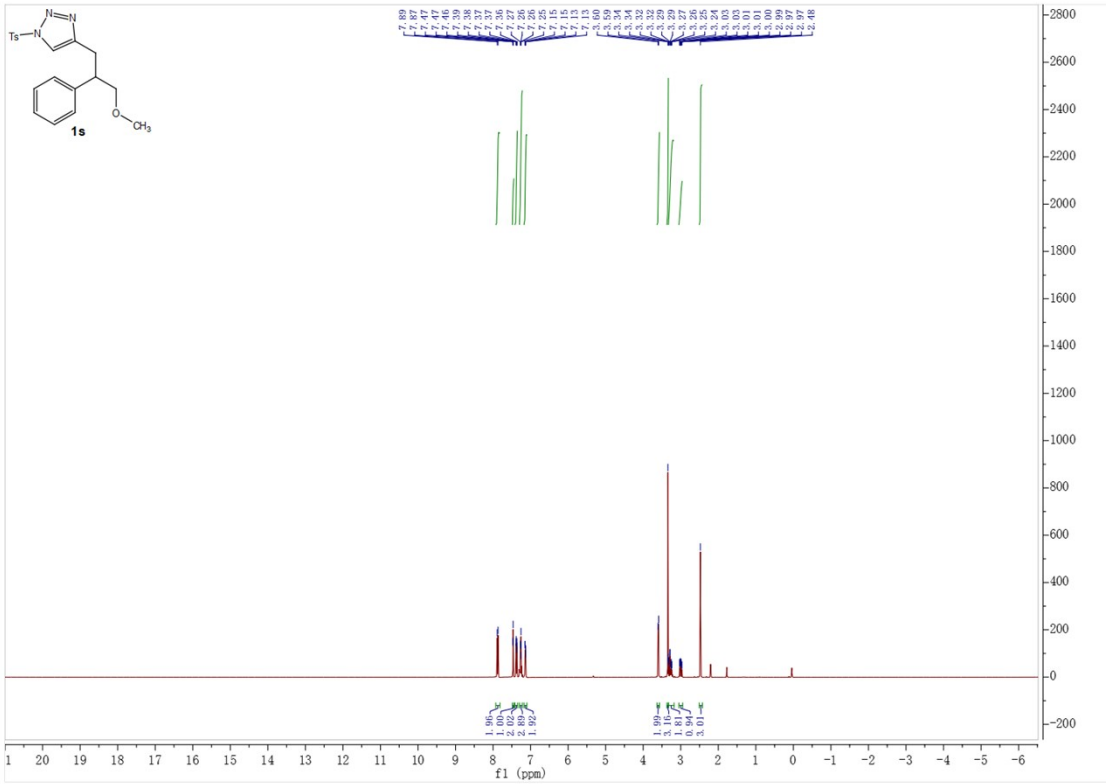
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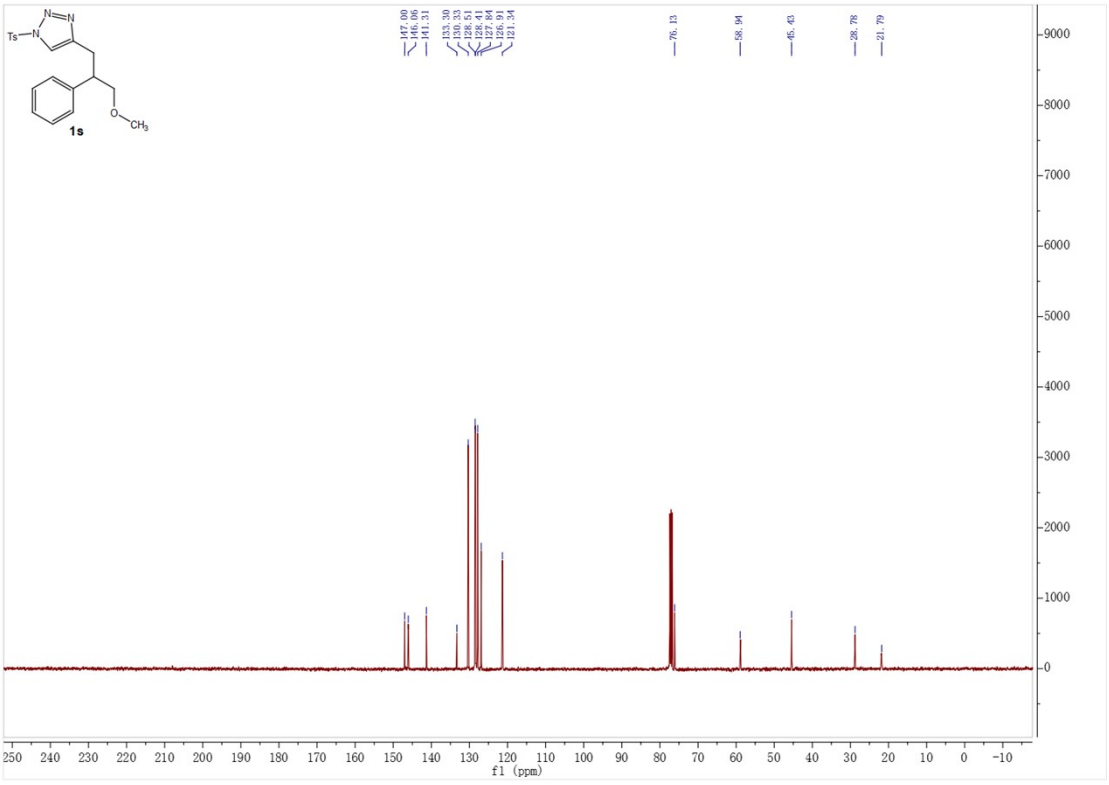
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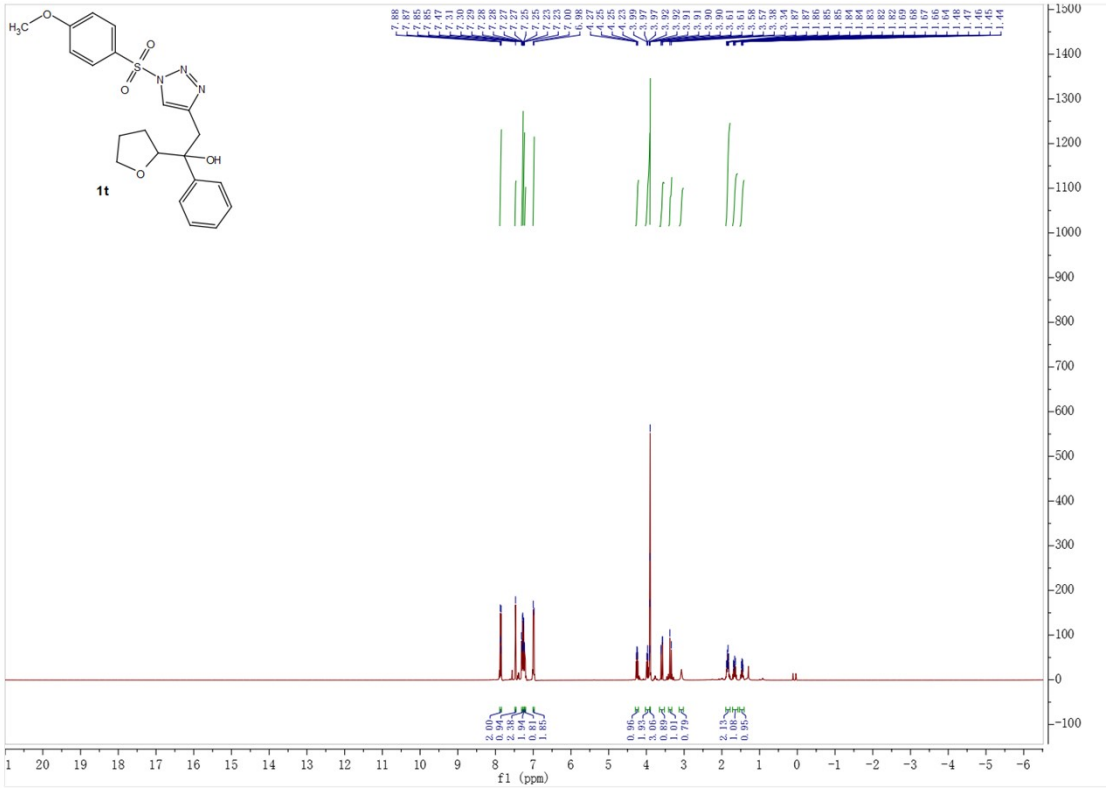
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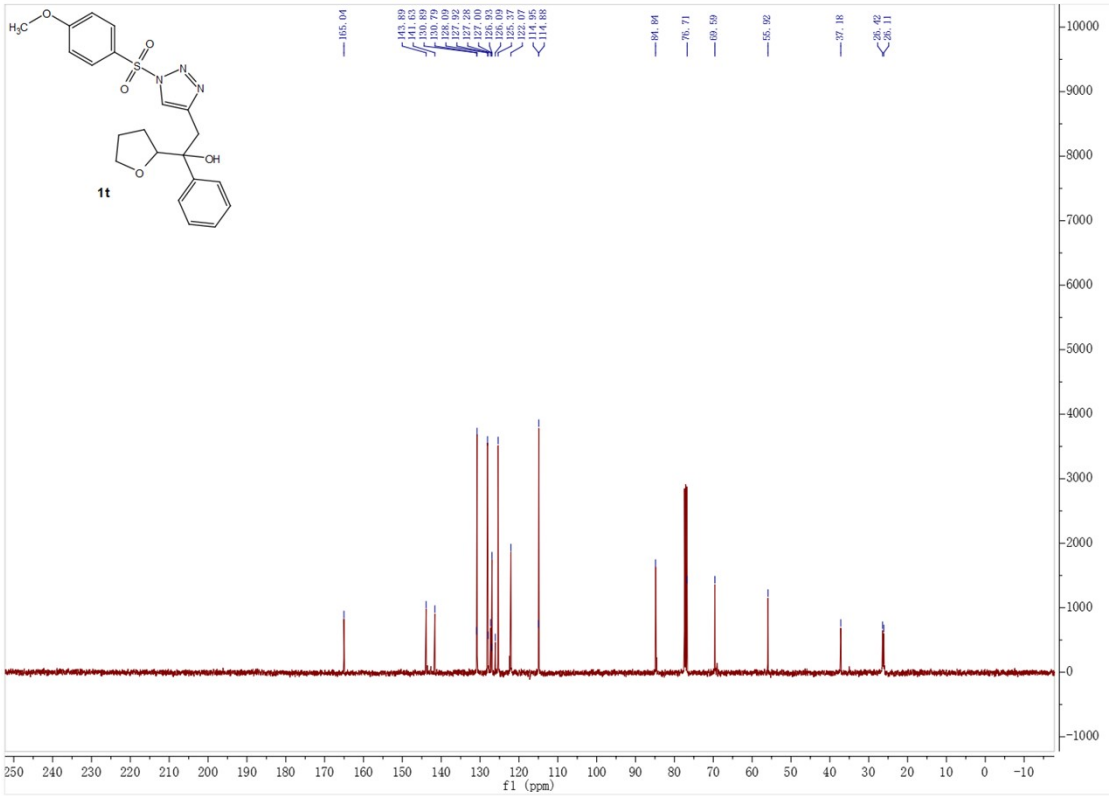
1t
f1 (ppm)