Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Cobalt-Catalyzed (*Z*)-Selective Semihydrogenation of Alkynes with Molecular Hydrogen

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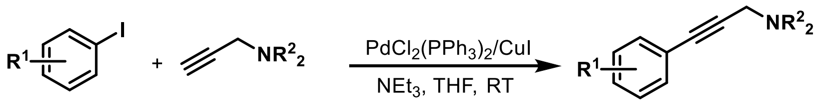
General Remarks

All reactions were performed in the argon-filled glovebox or under nitrogen using standard Schlenk techniques, unless otherwise noted. Solvents were degassed through three freeze-pump-thaw cycles. Column chromatography was performed using 400 mesh silica gel. Thin layer chromatography (TLC) was performed on EM reagents 0.25 mm silica 60-F plates. ^{1}H, ^{13}C spectrum were recorded on Bruker-400, with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in ppm, upfield to TMS (0.00 ppm) for and relative to $CDCl_3$ (7.26 ppm, 77.3 ppm) for ^{1}H NMR and ^{13}C NMR. GC analysis was carried out on SHIMADZU Lab Solution using achiral capillary columns. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. Substrates **1a** and **1f** are commercially available. Substrates **2b-2d** were prepared according to the literature procedures[1].

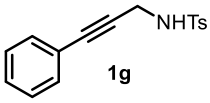
Synthesis of the alkynes

1. Synthesis of the 3-substituted propargyl amines 1g-1l and 1w



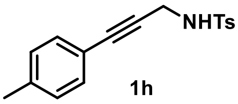
This is a modified procedure based on the literature report [2]: To an oven dried schlenk flask was added phenyl iodides (5 mmol), $PdCl_2(PPh_3)_2$ (0.1 mmol, 70.2 mg), CuI (0.15 mmol, 28.6 mg), and a mixture of dry THF and NEt_3 (THF/NEt_3 = 6 mL/1.5 mL) under N_2 atmosphere. To the resulting solution was added the solution of the terminal alkynes (4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide, or N,N-dimethylprop-2-yn-1-amine, 6 mmol) in the mixture of dry THF and NEt_3 (THF/NEt_3 = 6 mL/1.5 mL) dropwise. After the addition, the reaction was stirred at room temperature for 12 h. Saturated aqueous solution of NH_4Cl (30 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (30 mL) three times. The combined organic phases were dried and concentrated under reduced pressure.

The residue was purified by silica gel column chromatography to give the desired products.



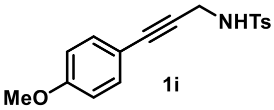
1g

White solid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.29-7.22 (m, 5H), 7.13 (dd, *J* = 8.1, 1.4 Hz, 2H), 4.67 (t, *J* = 5.9 Hz, 1H), 4.08 (d, *J* = 6.1 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.07, 137.05, 131.81, 129.99, 128.82, 128.44, 127.77, 122.26, 85.00, 83.43, 34.09, 21.76 ppm.



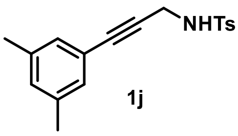
1h

White solid, 75% yield; ^{1}H NMR (400 MHz, CDCl3): δ 7.87 – 7.73 (m, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.10 – 6.93 (m, 4H), 4.79 (t, *J* = 5.9 Hz, 1H), 4.06 (d, *J* = 6.1 Hz, 2H), 2.36 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.97, 138.94, 137.04, 131.70, 129.95, 129.17, 127.75, 119.17, 85.08, 82.74, 34.09, 21.74, 21.72 ppm.



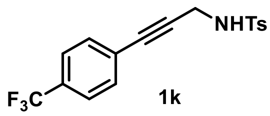
1i

White solid, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.80 – 6.74 (m, 2H), 4.69 (t, *J* = 6.0 Hz, 1H), 4.05 (d, *J* = 6.1 Hz, 2H), 3.79 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.97, 143.98, 137.05, 133.30, 129.96, 127.76, 114.32, 114.04, 84.93, 82.03, 55.55, 34.15, 21.78 ppm.



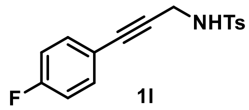
1j

White solid, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 6.75 (s, 2H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 6.1 Hz, 2H), 2.37 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.68, 137.73, 136.86, 130.45, 129.73, 129.25, 127.54, 121.65, 85.03, 82.46, 33.83, 21.54, 21.10 ppm.



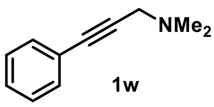
1k

White solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.19 (m, 4H), 4.95 (t, *J* = 5.3 Hz, 1H), 4.10 (d, *J* = 5.8 Hz, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.88, 136.81, 131.82, 130.25 (q, *J* = 32.7 Hz), 129.74, 127.54, 125.88, 125.10 (q, *J* = 3.8 Hz), 123.73 (q, *J* = 272.2 Hz), 85.83, 83.36, 33.65, 21.47 ppm.



1l

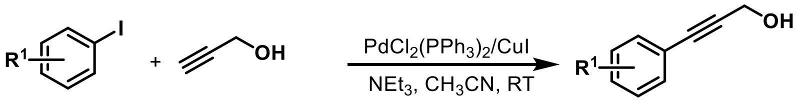
White solid, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.75 (m, 2H), 7.32 – 7.25 (m, 2H), 7.18 – 7.05 (m, 2H), 6.99 – 6.87 (m, 2H), 4.93 (t, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 6.2 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.54 (d, *J* = 250.0 Hz), 143.77, 136.83, 133.50 (d, *J* = 8.4 Hz), 129.72, 127.53, 118.15 (d, *J* = 3.5 Hz), 115.48 (d, *J* = 22.1 Hz), 83.66, 83.00 (d, *J* = 1.4 Hz), 33.72, 21.51 ppm.



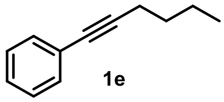
1w

White solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.32 – 7.27 (m, 3H), 3.47 (s, 2H), 2.37 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.94, 128.49, 128.26, 123.46, 85.45, 84.87, 48.83, 44.54 ppm.

2. Synthesis of the 3-substituted propargyl alcohols 1e, 1m-1v and 1x

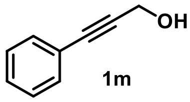


This is a modified procedure based on the literature report [3]: To an oven dried schlenk flask was added phenyl iodides (5 mmol), $PdCl_2(PPh_3)_2$ (0.05 mmol, 35.5 mg), CuI (0.1 mmol, 19.1 mg), and a mixture of dry CH_3CN and NEt_3 (CH_3CN/NEt_3 = 3 mL/3 mL) under N_2 atmosphere. To the resulting solution was added prop-2-yn-1-ol (5.5 mmol, 308.6 mg) or hex-1-yne (6 mmol, 492 mg) dropwise. After the addition, the reaction was stirred at room temperature for 12 h. Saturated aqueous solution of NH_4Cl (30 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (30 mL) three times. The combined organic phases were dried and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired products.



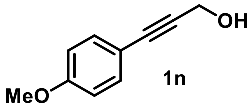
1e

Yellow oil, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.35 (m, 2H), 7.31 – 7.23 (m, 3H), 2.40 (t, J = 7.0 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.42 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.56, 128.21, 127.49, 124.10, 90.45, 80.56, 30.88, 22.06, 19.14, 13.71 ppm.



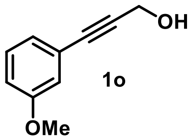
1m

Yellow oil, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.40 (m, 2H), 7.37 – 7.27 (m, 3H), 4.50 (s, 2H), 1.87 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.72, 128.55, 128.36, 122.52, 87.21, 85.72, 51.67 ppm.



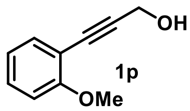
1n

White solid, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.36 (m, 2H), 6.86 – 6.83 (m, 2H), 4.48 (s, 2H), 3.81 (s, 3H), 1.93 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.73, 133.21, 114.60, 113.96, 85.89, 85.65, 55.31, 51.72 ppm.



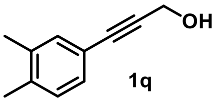
1o

White solid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.18 (m, 1H), 7.03 (dt, J = 7.6, 1.1 Hz, 1H), 6.97 (dd, J = 2.5, 1.4 Hz, 1H), 6.88 (ddd, J = 8.4, 2.6, 0.9 Hz, 1H), 4.49 (s, 2H), 3.79 (s, 3H), 2.09 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.25, 129.44, 124.23, 123.52, 116.54, 115.09, 87.09, 85.59, 55.29, 51.61 ppm.



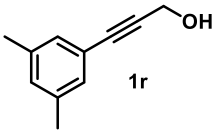
1p

White solid, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.6, 1.7 Hz, 1H), 7.35 – 7.27 (m, 1H), 6.96 – 6.82 (m, 2H), 4.55 (s, 2H), 3.88 (s, 3H), 2.37 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.94, 133.78, 130.02, 120.53, 111.61, 110.57, 91.49, 81.87, 55.79, 51.83 ppm.



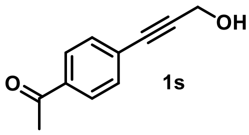
1q

White solid, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 4.48 (s, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.81 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.50, 136.70, 132.75, 129.65, 129.15, 119.72, 86.28, 85.99, 51.73, 19.80, 19.61 ppm.



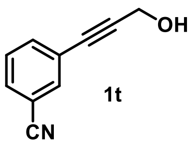
1r

White solid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 2H), 6.95 (s, 1H), 4.48 (s, 2H), 2.27 (s, 6H), 2.17 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.92, 130.44, 129.39, 122.15, 86.57, 85.99, 51.63, 21.12 ppm.



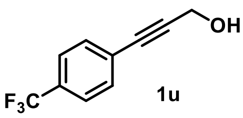
1s

Yellow oil, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.53 (s, 2H), 2.61 (s, 3H), 2.00 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.52, 136.42, 131.82, 128.27, 127.47, 90.58, 84.86, 51.61, 26.69 ppm.



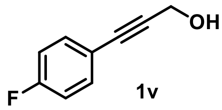
1t

Yellow oil, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (t, *J* = 1.4 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.60 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.43 (td, *J* = 7.8, 0.4 Hz, 1H), 4.52 (s, 2H), 2.32 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.84, 134.98, 131.72, 129.33, 124.24, 118.05, 112.72, 89.91, 83.16, 51.34 ppm.



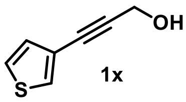
1u

Yellow solid, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (q, *J* = 8.4 Hz, 4H), 4.53 (s, 2H), 2.15 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.91, 130.24 (q, *J* = 32.7 Hz), 126.33 (q, *J* = 1.3 Hz), 125.28 (q, *J* = 3.8 Hz), 123.85 (q, *J* = 272.2 Hz), 89.61, 84.35, 51.51 ppm.



1v

Yellow solid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.36 (m, 2H), 7.07 – 6.93 (m, 2H), 4.49 (s, 2H), 2.09 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.62 (d, *J* = 249.7 Hz), 133.63 (d, *J* = 8.4 Hz), 118.60 (d, *J* = 3.6 Hz), 115.65 (d, *J* = 22.1 Hz), 86.91 (d, *J* = 1.4 Hz), 84.66, 51.56 ppm.



1x

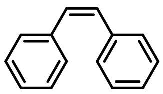
Yellow oil, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.21 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.50 (s, 2H), 2.35 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.45, 127.49, 127.03, 122.43, 91.22, 79.02, 51.65 ppm.

General procedure for the semihydrogenation of alkynes

In an argon-filled glove box, $Co(OAc)_2{\cdot}(H_2O)_4$ and $NaBH_4$ were dissolved in degassed EtOH and stirred for 10 min. Ethylenediamine (Ethylenediamine/Co/$NaBH_4$ = 8:2:1, the detailed amounts for each substrate were described in Table 2) was then added and the resulting suspension was stirred for another 10 min. The resulting suspension was transferred by syringe into the vials charged with different substrates (0.5 mmol for each). Additional degassed EtOH, THF, and water was added to bring the total reaction volume to 2.1 mL (EtOH/THF/H_2O = 1.0 : 1.0 : 0.1 mL). The vials were subsequently transferred into an autoclave which was purged with hydrogen three times and charged with hydrogen (3 bar). The reaction was then stirred at rt for different times (The reaction was monitored by GC-MS or ^{1}H NMR, prolonged reaction time would decrease the selectivity to give increased amount of (E)-alkenes and alkanes). The hydrogen gas was released slowly and carefully. The desired compounds **2** were then obtained by column chromatography.

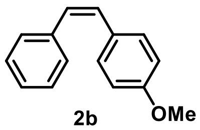
Characterization data of compounds 2a-2v

According to the above mentioned procedure, compounds **2a-2v** can be obtained. Characterization data are as follows.



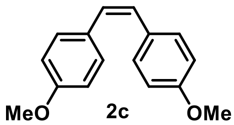
2a
S/C = 100, 24 h
> 99% Conv.
Z:E:A = 21 :1 : 3

>99% conv., colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.15 (m, 10H), 6.59 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.48, 130.50, 129.13, 128.47, 127.35.



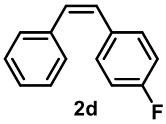
2b
S/C = 50, 16 h
> 99% Conv.
Z:E:A = 18 :1 : 1

>99% conv., colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.07 (m, 7H), 6.78 – 6.72 (m, 2H), 6.52 (d, J = 1.9 Hz, 2H), 3.78 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.90, 137.86, 130.41, 130.01, 129.89, 129.07, 129.01, 128.50, 127.16, 113.82, 55.46 ppm.



2c
S/C = 50, 24 h
> 99% Conv.
Z:E:A = 18 :1 : 1

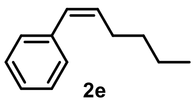
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 6.44 (s, 2H), 3.77 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.73, 130.29, 130.21, 128.60, 113.82, 55.42 ppm.



2d

S/C = 50, 16 h
> 99% Conv.
Z:E:A = 15 :1 : 1

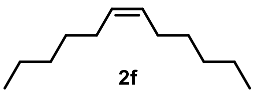
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.16 (m, 7H), 6.94 – 6.87 (m, 2H), 6.56 (q, J = 12.2 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.06 (d, *J* = 246.6 Hz), 137.28, 133.42 (d, *J* = 3.5 Hz), 130.79 (d, *J* = 7.9 Hz), 130.50 (d, *J* = 1.2 Hz), 129.33, 129.08, 128.58, 127.46, 115.42 (d, *J* = 21.4 Hz) ppm.



2e

S/C = 200, 24 h
> 99% Conv.
Z:E:A = 10 :1 : 2

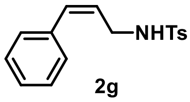
>99% conv., colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.24 (m, 4H), 7.24 – 7.16 (m, 1H), 6.40 (d, *J* = 11.6 Hz, 1H), 5.66 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.33 (q, *J* = 7.3 Hz, 2H), 1.46 – 1.33 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.85, 133.29, 128.79, 128.69, 128.13, 126.44, 32.22, 28.41, 22.48, 14.04 ppm.



2f

S/C = 100, 12 h
> 99% Conv.
Z:E:A = 20 :1 : 1

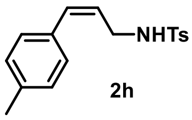
>99% conv., colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.35 (ddd, *J* = 5.5, 4.4, 1.0 Hz, 2H), 2.02 (dd, *J* = 12.6, 6.9 Hz, 4H), 1.44 – 1.17 (m, 12H), 1.01 – 0.78 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.19, 31.82, 29.75, 27.46, 22.88, 14.38 ppm.



2g

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 33 :1 : 3

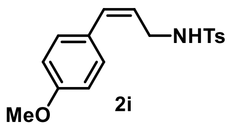
>99% conv, white solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.20 (m, 6H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.52 (d, *J* = 11.5 Hz, 1H), 5.56 (dt, *J* = 13.3, 6.8 Hz, 1H), 4.63 (t, *J* = 5.6 Hz, 1H), 3.85 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.79, 137.02, 136.04, 132.92, 130.00, 128.84, 128.61, 127.71, 127.45, 126.70, 41.57, 21.82 ppm.



2h

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 25 :1 : 2

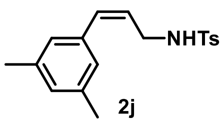
>99% conv. white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 11.5 Hz, 1H), 5.50 (dt, *J* = 11.6, 6.8 Hz, 1H), 4.64 (t, *J* = 5.9 Hz, 1H), 3.85 (td, *J* = 6.9, 1.7 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.53, 137.34, 136.81, 132.94, 132.59, 129.77, 129.08, 128.56, 127.22, 125.68, 41.41, 21.59, 21.23 ppm.



2i

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 51 :1 : 3

>99% conv., white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.44 (d, *J* = 11.5 Hz, 1H), 5.45 (dt, *J* = 11.5, 6.8 Hz, 1H), 4.73 (t, *J* = 5.7 Hz, 1H), 3.91 – 3.81 (m, 2H), 3.80 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.11, 143.76, 136.99, 132.44, 130.18, 129.98, 128.64, 127.44, 124.88, 113.99, 55.52, 41.63, 21.80 ppm.

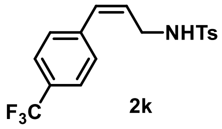


2j

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 65 :1 : 5

>99% conv., white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.23 (m, 2H), 6.88 (s, 1H), 6.72 (s, 2H), 6.44 (d, *J* = 11.6 Hz, 1H), 5.49

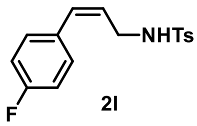
(dt, J = 11.6, 6.9 Hz, 1H), 4.78 (t, J = 5.7 Hz, 1H), 3.95 – 3.77 (m, 2H), 2.41 (s, 3H), 2.26 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.70, 138.10, 137.05, 135.96, 133.04, 129.95, 129.34, 127.40, 126.62, 126.27, 41.64, 21.77, 21.49 ppm.



2k

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 33 :1 : 3

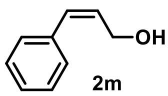
>99% conv., white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.55 (d, J = 11.6 Hz, 1H), 5.70 (dt, J = 11.6, 6.9 Hz, 1H), 4.93 (s, 1H), 3.88 – 3.71 (m, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.02, 139.59, 136.71, 131.64, 130.04, δ 129.59 (q, J = 32.5 Hz), 129.07, 128.82, 127.44, 125.51 (q, J = 3.8 Hz), 124.27 (q, J = 272.0 Hz), 41.36, 21.75 ppm.



2l

S/C = 50, 24 h
> 99% Conv.
Z:E:A = 72 :1 : 4

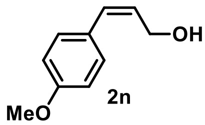
>99% conv., white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.70 (m, 2H), 7.30 – 7.25 (m, 2H), 7.09 – 7.02 (m, 2H), 6.99 – 6.92 (m, 2H), 6.46 (d, J = 11.5 Hz, 1H), 5.55 (dt, J = 11.6, 6.9 Hz, 1H), 4.93 (t, J = 5.6 Hz, 1H), 3.87 – 3.73 (m, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.17 (d, J = 247.4 Hz), 143.86, 136.83, 132.09 (d, J = 3.4 Hz), 131.80, 130.51 (d, J = 8.1 Hz), 129.99, 127.42, 126.58 (d, J = 1.2 Hz), 115.52 (d, J = 21.5 Hz), 41.40, 21.78 ppm.



2m

S/C = 50, 24 h
> 99% Conv.
Z:E:A = 53 :1 : 1

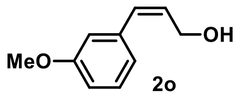
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (ddd, J = 7.6, 4.4, 1.2 Hz, 2H), 7.26 (ddd, J = 7.4, 3.9, 2.4 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.56 (d, J = 11.7 Hz, 1H), 5.86 (dt, J = 11.8, 6.4 Hz, 1H), 4.43 (dd, J = 6.4, 1.6 Hz, 2H), 1.77 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.74, 131.41, 131.22, 129.03, 128.52, 127.51, 59.93 ppm.



2n

S/C = 20, 24 h
> 99% Conv.
Z:E:A = 50 :1 : 2

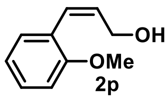
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.93 – 6.85 (m, 2H), 6.50 (d, *J* = 11.7 Hz, 1H), 5.86 – 5.68 (m, 1H), 4.43 (d, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 1.79 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.79, 130.58, 130.13, 129.47, 129.21, 113.70, 59.77, 55.31 ppm.



2o

S/C = 20, 24 h
> 99% Conv.
Z:E:A = > 99 :1 : 1

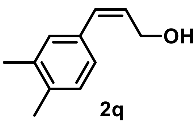
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 7.9 Hz, 1H), 6.81 (dd, *J* = 13.2, 5.0 Hz, 2H), 6.77 – 6.71 (m, 1H), 6.53 (d, *J* = 11.7 Hz, 1H), 5.94 – 5.80 (m, 1H), 4.44 (d, *J* = 6.3 Hz, 2H), 3.81 (s, 3H), 1.79 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66, 138.13, 131.72, 131.08, 129.51, 121.53, 114.58, 113.00, 59.98, 55.48 ppm.



2p

S/C = 20, 24 h
> 99% Conv.
Z:E:A = > 99 :1 : 1

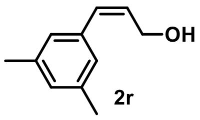
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 1H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.00 – 6.83 (m, 2H), 6.68 (d, *J* = 11.6 Hz, 1H), 5.92 (dt, *J* = 11.7, 6.7 Hz, 1H), 4.31 (d, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 1.71 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.08, 131.18, 130.51, 129.13, 127.08, 125.55, 120.46, 110.68, 60.14, 55.72 ppm.



2q

S/C = 200, 12 h
> 99% Conv.
Z:E:A = 25 :1 : 1

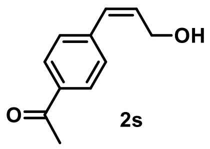
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.89 (m, 2H), 6.51 (d, *J* = 11.7 Hz, 1H), 5.80 (dt, *J* = 11.8, 6.4 Hz, 1H), 4.44 (dd, *J* = 6.4, 1.3 Hz, 2H), 2.26 (s, 6H), 1.68 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.69, 136.06, 134.37, 131.20, 130.55, 130.34, 129.78, 126.48, 60.09, 20.08, 19.78 ppm.



2r

S/C = 200, 12 h
> 99% Conv.
Z:E:A = 18 :1 : 2

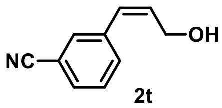
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (s, 1H), 6.82 (s, 2H), 6.50 (d, *J* = 11.8 Hz, 1H), 5.82 (dt, *J* = 11.8, 6.4 Hz, 1H), 4.44 (dd, *J* = 6.4, 1.6 Hz, 2H), 2.31 (d, *J* = 0.5 Hz, 6H), 1.65 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.02, 136.68, 131.33, 131.11, 129.20, 126.84, 60.08, 21.58 ppm.



2s

S/C = 200, 12 h
> 99% Conv.
Z:E:A = 11 :1 : 1

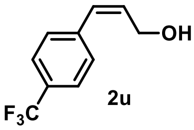
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 11.8 Hz, 1H), 6.00 (dt, *J* = 11.9, 6.4 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 2.61 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.83, 141.33, 135.66, 133.55, 129.93, 128.95, 128.40, 59.64, 26.68 ppm.



2t

S/C = 100, 24 h
> 99% Conv.
Z:E:A = 17 :1 : 1

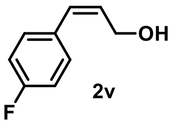
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.53 (m, 1H), 7.50 (s, 1H), 7.47 – 7.43 (m, 2H), 6.54 (d, *J* = 11.8 Hz, 1H), 6.01 (dt, *J* = 11.8, 6.5 Hz, 1H), 4.39 (dd, *J* = 6.5, 1.6 Hz, 2H), 1.97 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.87, 133.79, 133.32, 132.34, 130.94, 129.39, 129.09, 118.96, 112.65, 59.43 ppm.



2u

S/C = 100, 12 h
> 99% Conv.
Z:E:A = 18 :1 : 1

>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 11.8 Hz, 1H), 5.99 (dt, *J* = 11.8, 6.5 Hz, 1H), 4.42 (dd, *J* = 6.5, 1.5 Hz, 2H), 1.80 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.23 (q, *J* = 1.3 Hz), 133.44, 130.04, 129.46 (q, *J* = 32.4 Hz), 129.24, 125.47 (q, *J* = 3.8 Hz), 124.38 (q, *J* = 271.9 Hz), 59.71 ppm.

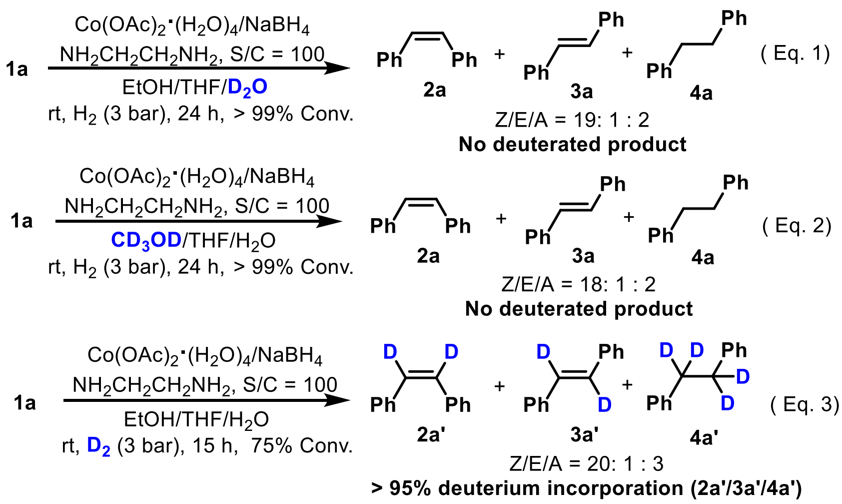


2v

S/C = 50, 24 h
> 99% Conv
Z:E:A = 28 :1 :1

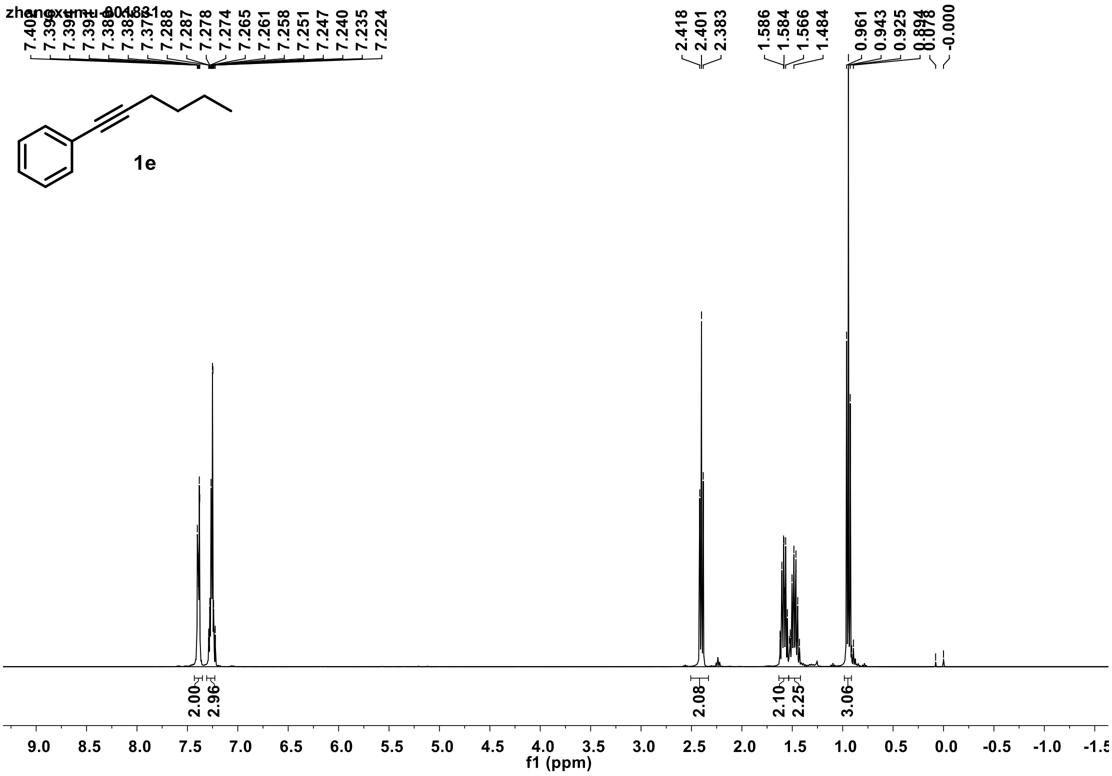
>99% conv., colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.14 (m, 2H), 7.07 – 6.98 (m, 2H), 6.52 (d, *J* = 11.7 Hz, 1H), 5.93 – 5.78 (m, 1H), 4.40 (dd, *J* = 6.5, 1.5 Hz, 2H), 1.78 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96 (d, *J* = 247.0 Hz), 132.55 (d, *J* = 3.4 Hz), 130.89 (d, *J* = 1.2 Hz), 130.44 (d, *J* = 8.0 Hz), 130.08, 115.23 (d, *J* = 21.5 Hz), 59.52 ppm.

Control experiments

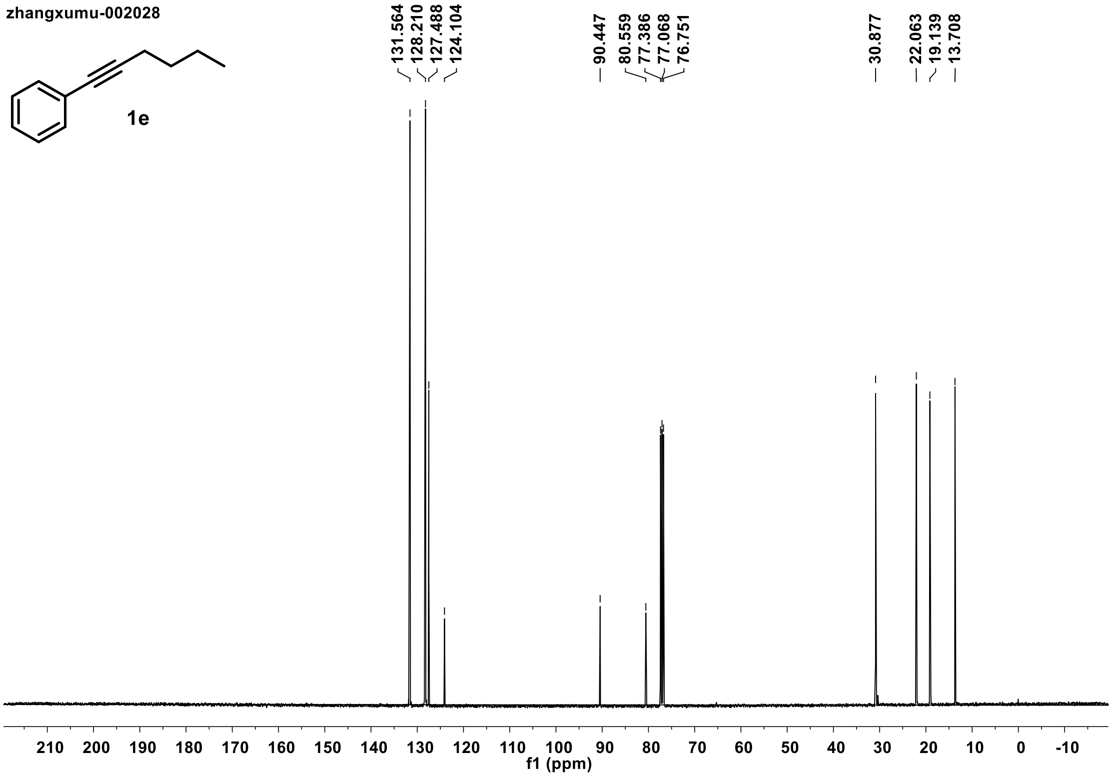


The reaction procedure was the same as the general procedure described for the semihydrogenaion of alkynes except using MeOD, D_2O or D_2.

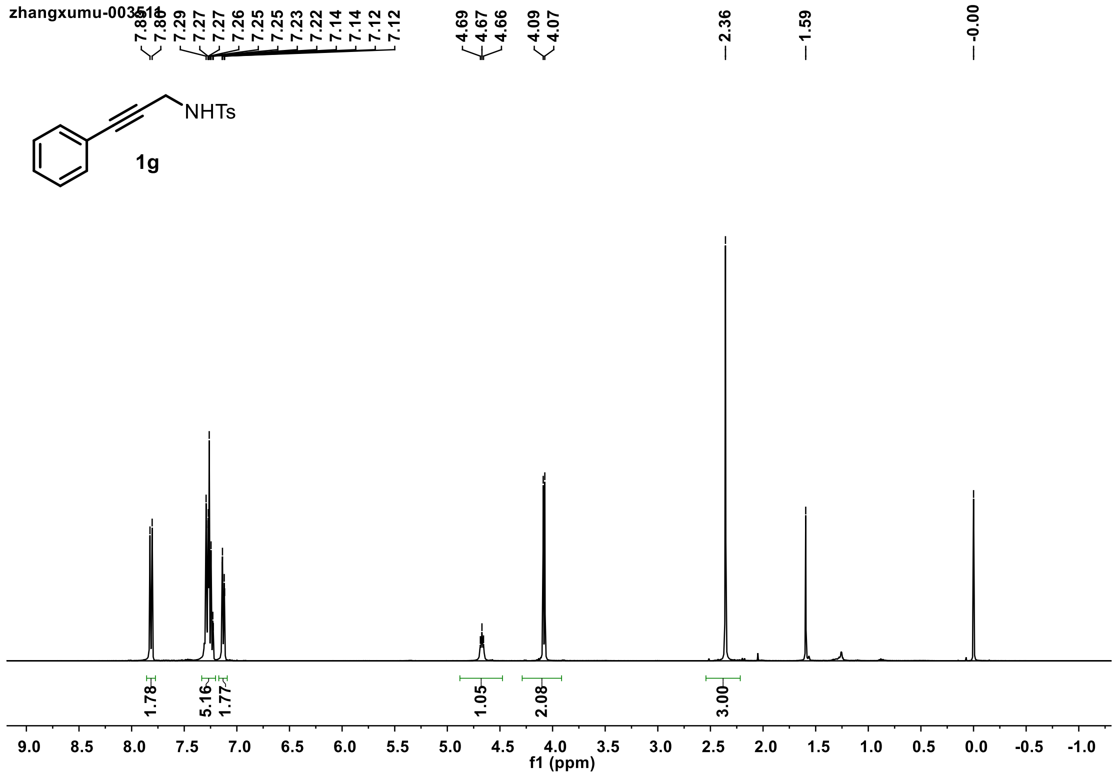
NMR Spectra

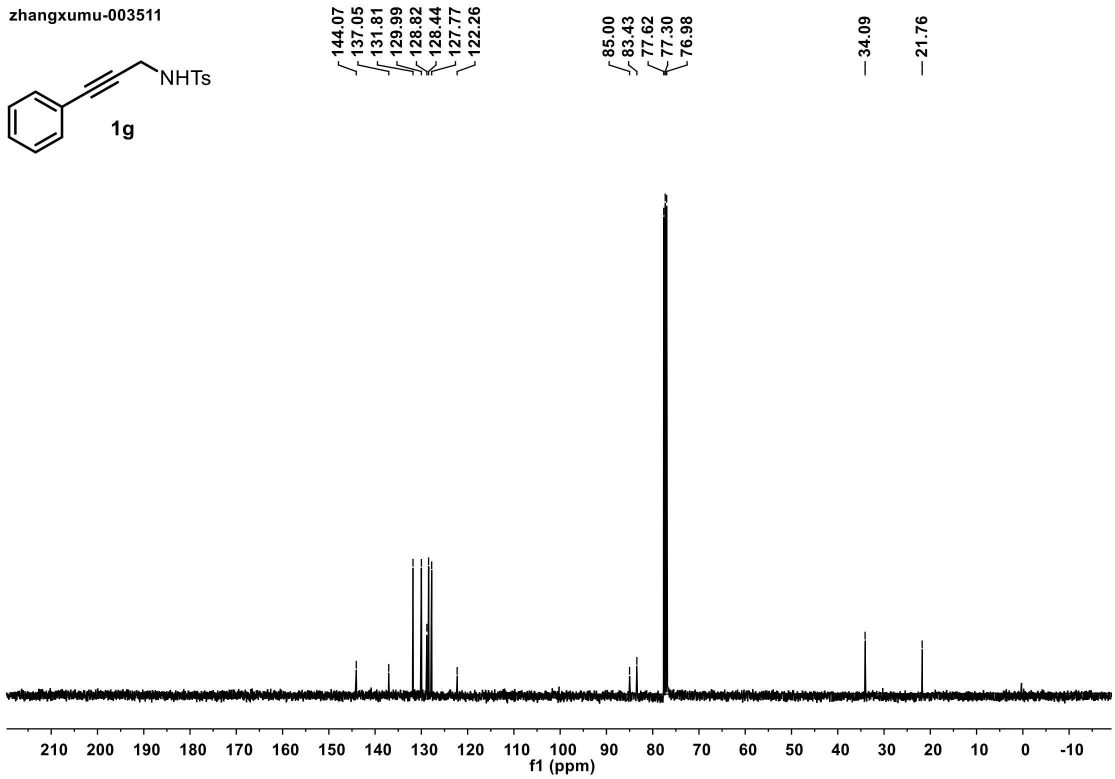


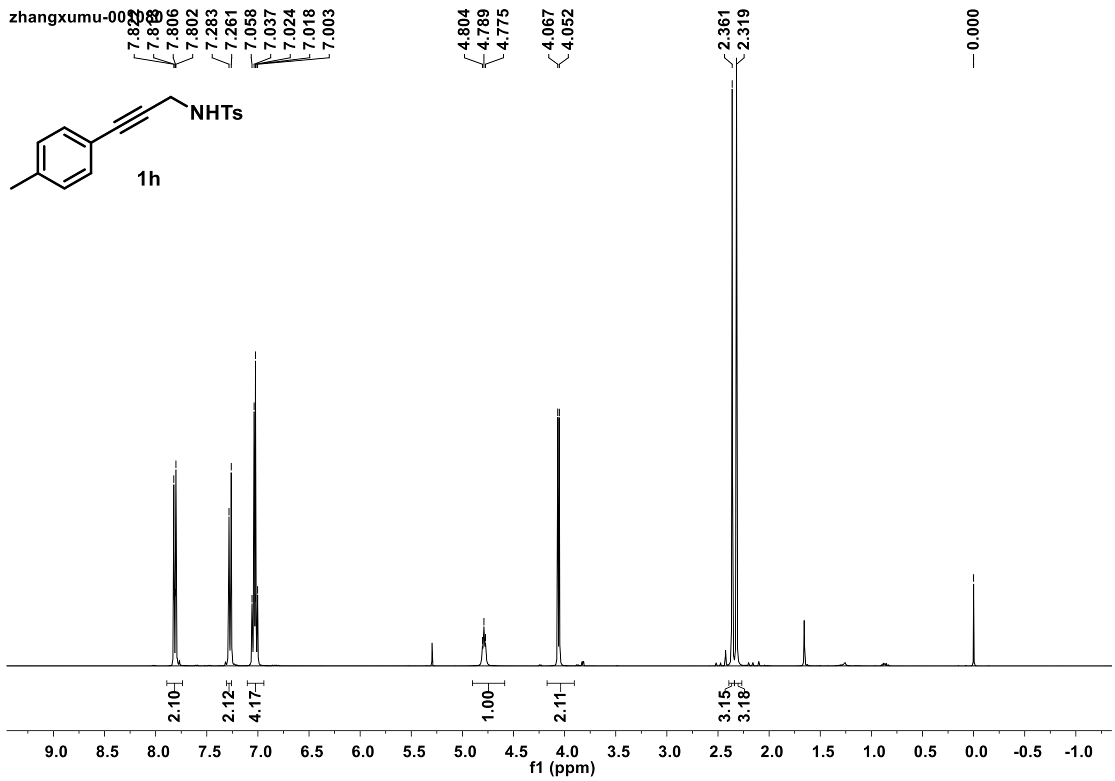
zhangxumu-001831
1e
2.418
2.401
2.383
1.586
1.584
1.566
1.484
0.961
0.943
0.925
-0.000
2.00
2.96
2.08
2.10
2.25
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

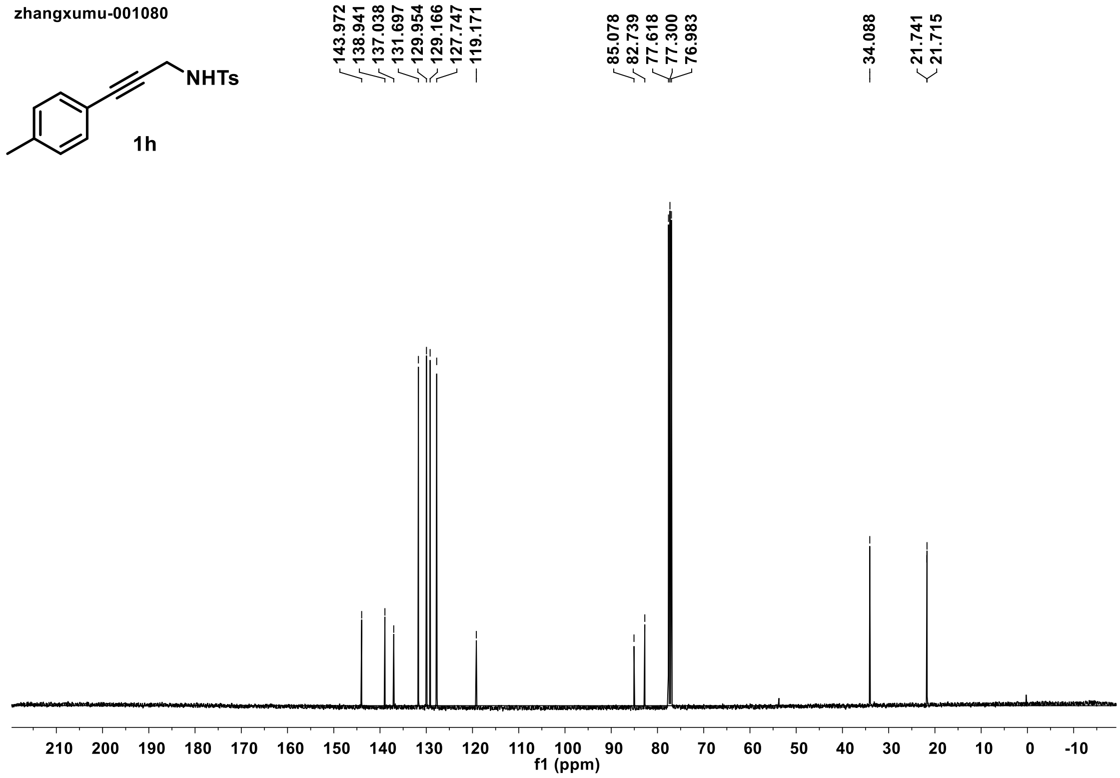


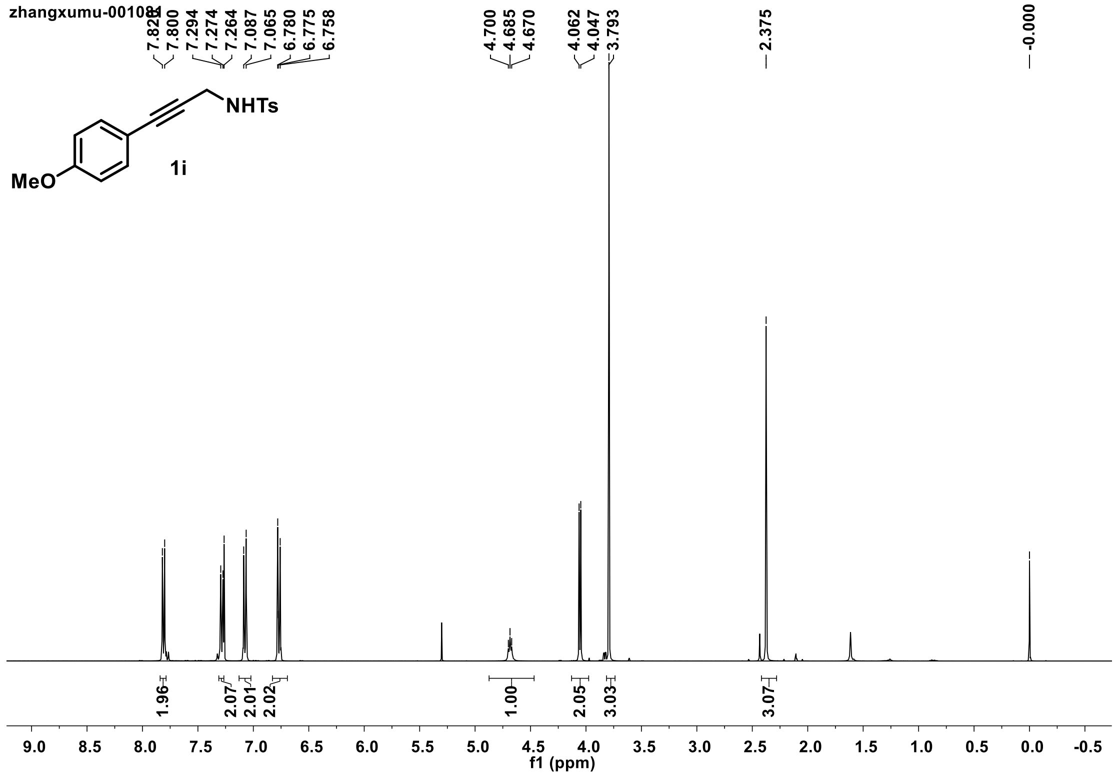
zhangxumu-002028
1e
131.564
128.210
127.488
124.104
90.447
80.559
77.386
77.068
76.751
30.877
22.063
19.139
13.708
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

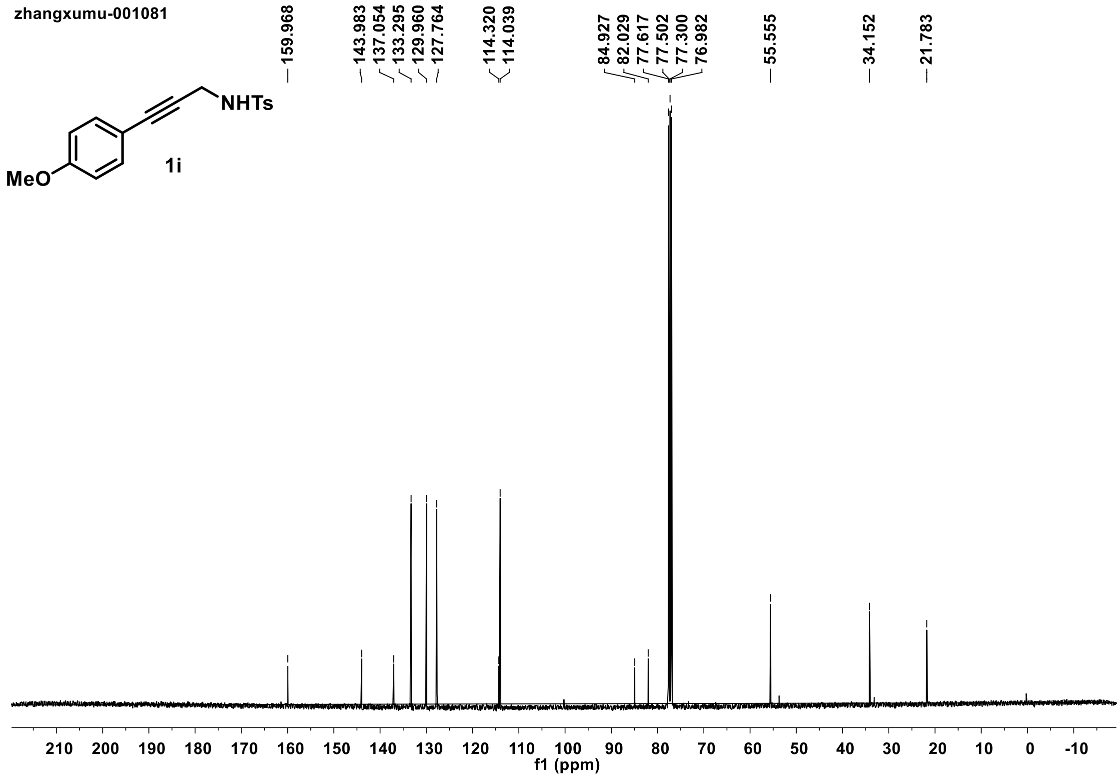

zhangxumu-003511
7.81
7.80
7.29
7.27
7.27
7.26
7.25
7.25
7.23
7.22
7.14
7.14
7.12
7.12
4.69
4.67
4.66
4.09
4.07
2.36
1.59
-0.00
NHTs
1g
1.78
5.16
1.77
1.05
2.08
3.00
f1 (ppm)

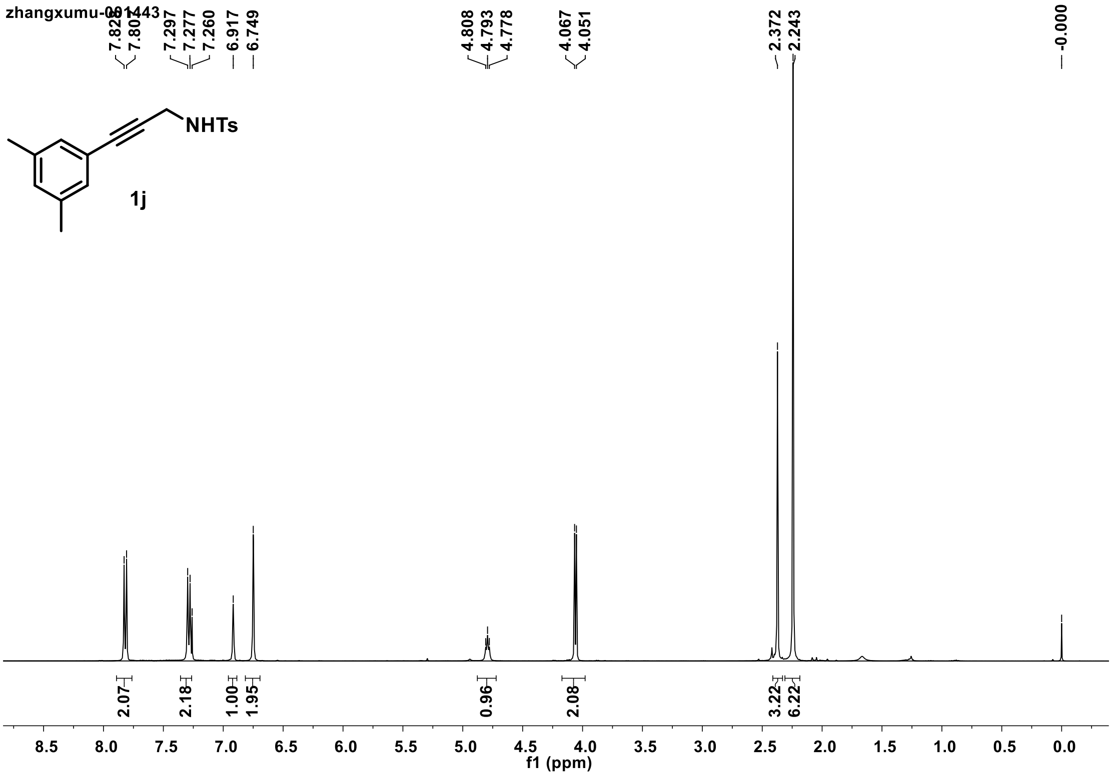

zhangxumu-003511
144.07
137.05
131.81
129.99
128.82
128.44
127.77
122.26
85.00
83.43
77.62
77.30
76.98
34.09
21.76
NHTs
1g
f1 (ppm)

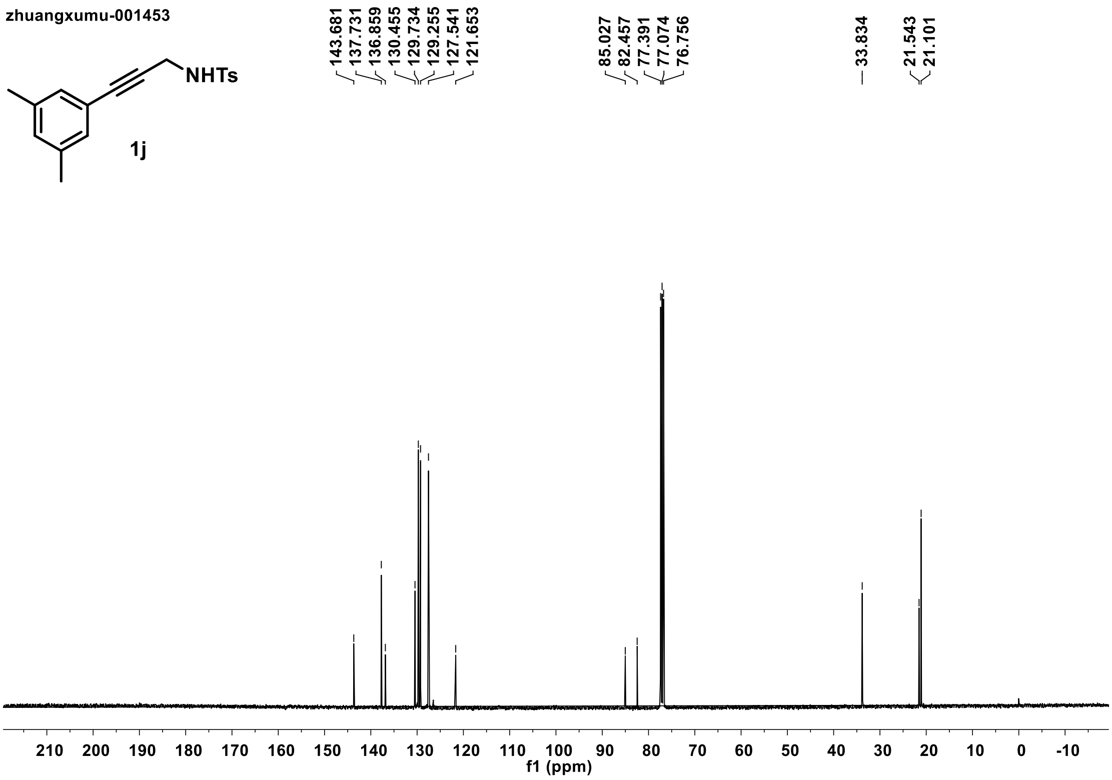


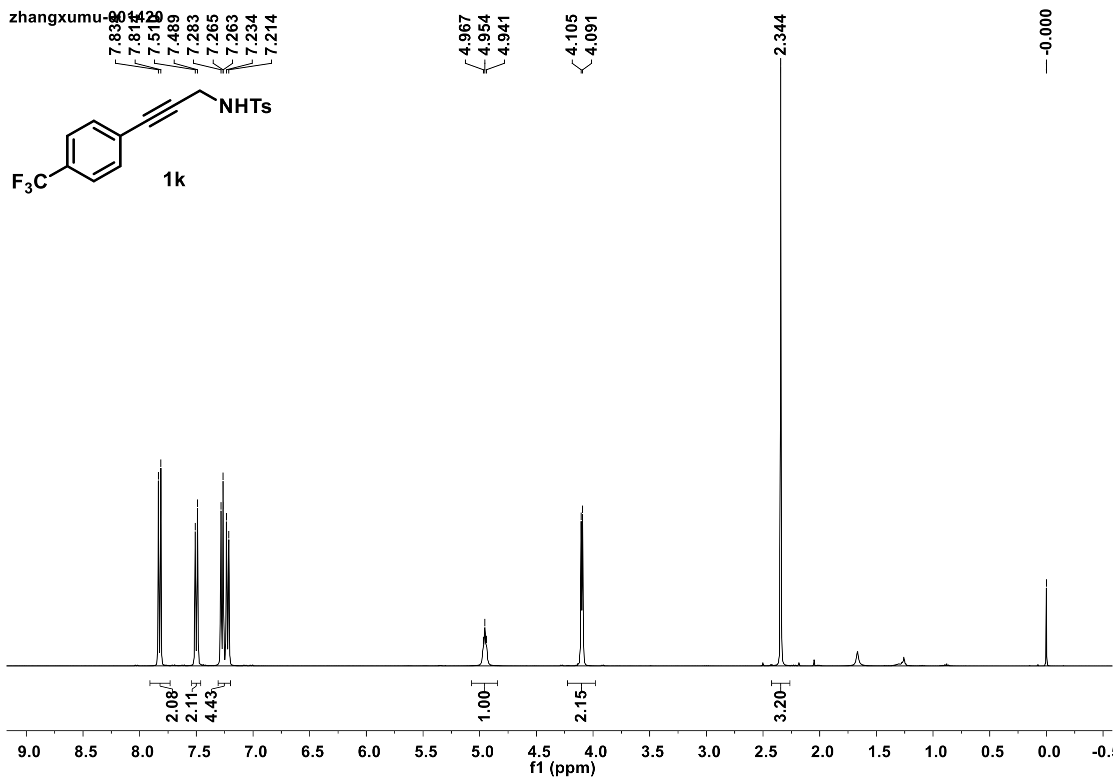



zhangxumu-001081
7.821
7.800
7.294
7.274
7.264
7.087
7.065
6.780
6.775
6.758
4.700
4.685
4.670
4.062
4.047
3.793
2.375
-0.000
NHTs
MeO
1i
1.96
2.07
2.01
2.02
1.00
2.05
3.03
3.07
f1 (ppm)

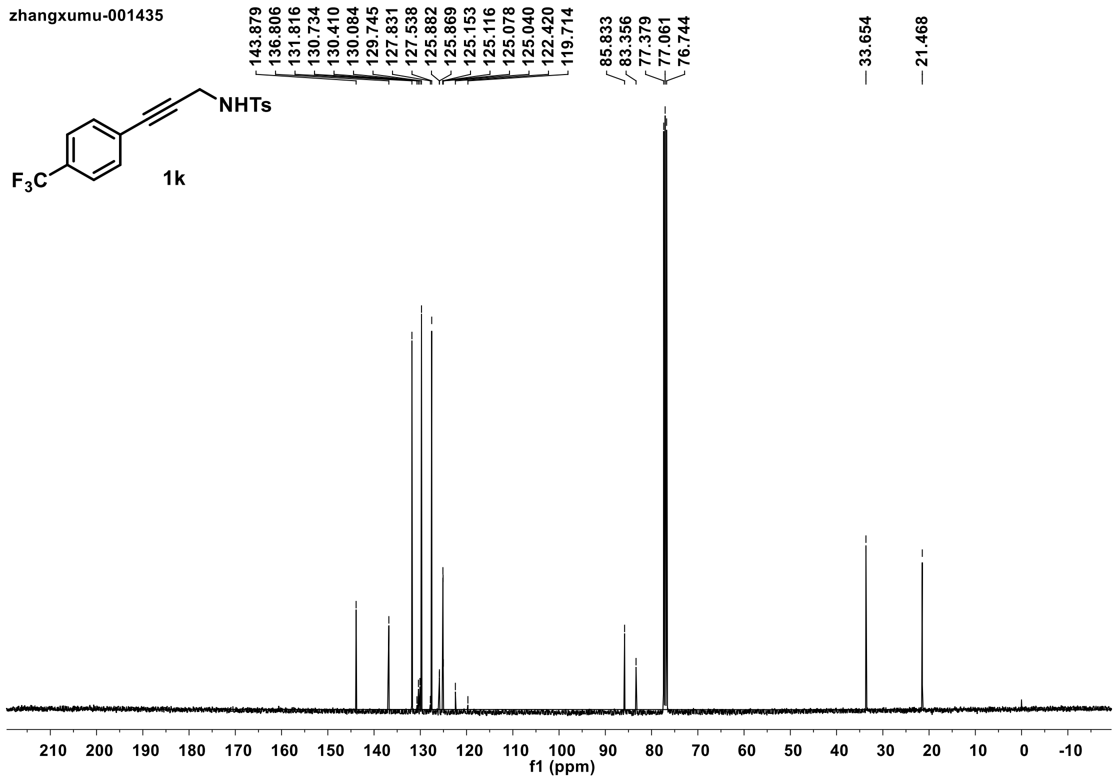

zhangxumu-001081
159.968
143.983
137.054
133.295
129.960
127.764
114.320
114.039
84.927
82.029
77.617
77.502
77.300
76.982
55.555
34.152
21.783
NHTs
MeO
1i
f1 (ppm)


zhangxumu-001443
7.821
7.801
7.297
7.277
7.260
6.917
6.749
4.808
4.793
4.778
4.067
4.051
2.372
2.243
-0.000
NHTs
1j
2.07
2.18
1.00
1.95
0.96
2.08
3.22
6.22
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

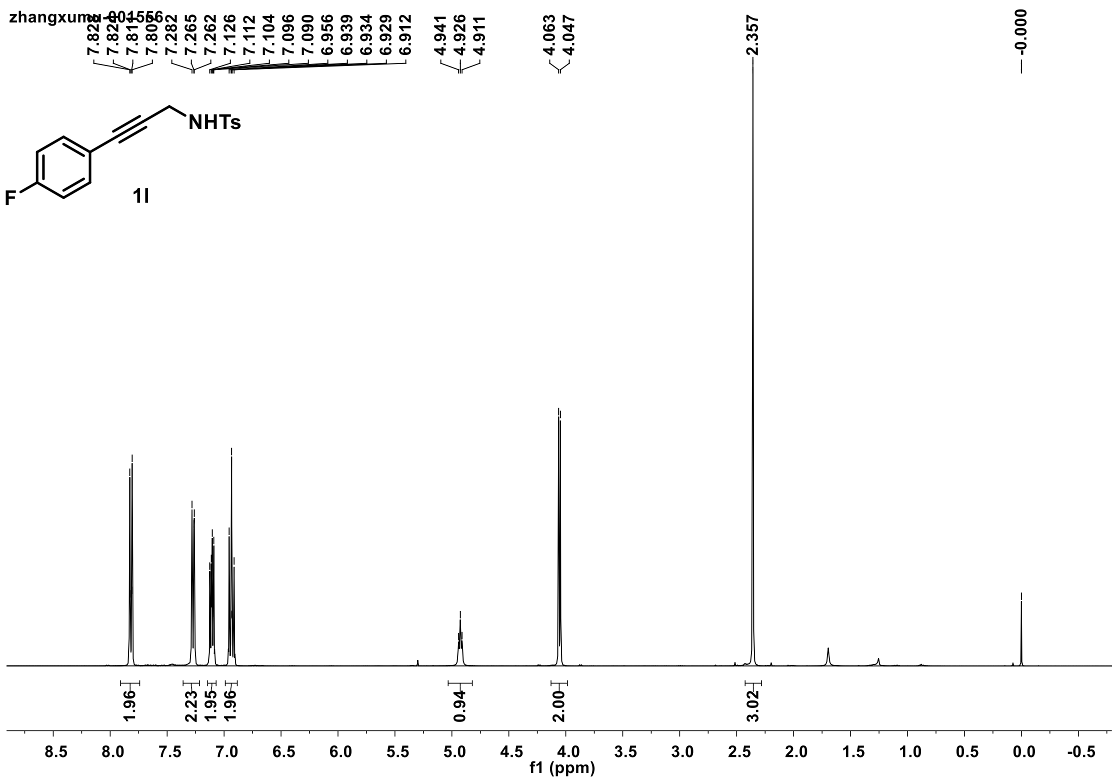

zhuangxumu-001453
143.681
137.731
136.859
130.455
129.734
129.255
127.541
121.653
85.027
82.457
77.391
77.074
76.756
33.834
21.543
21.101
NHTs
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

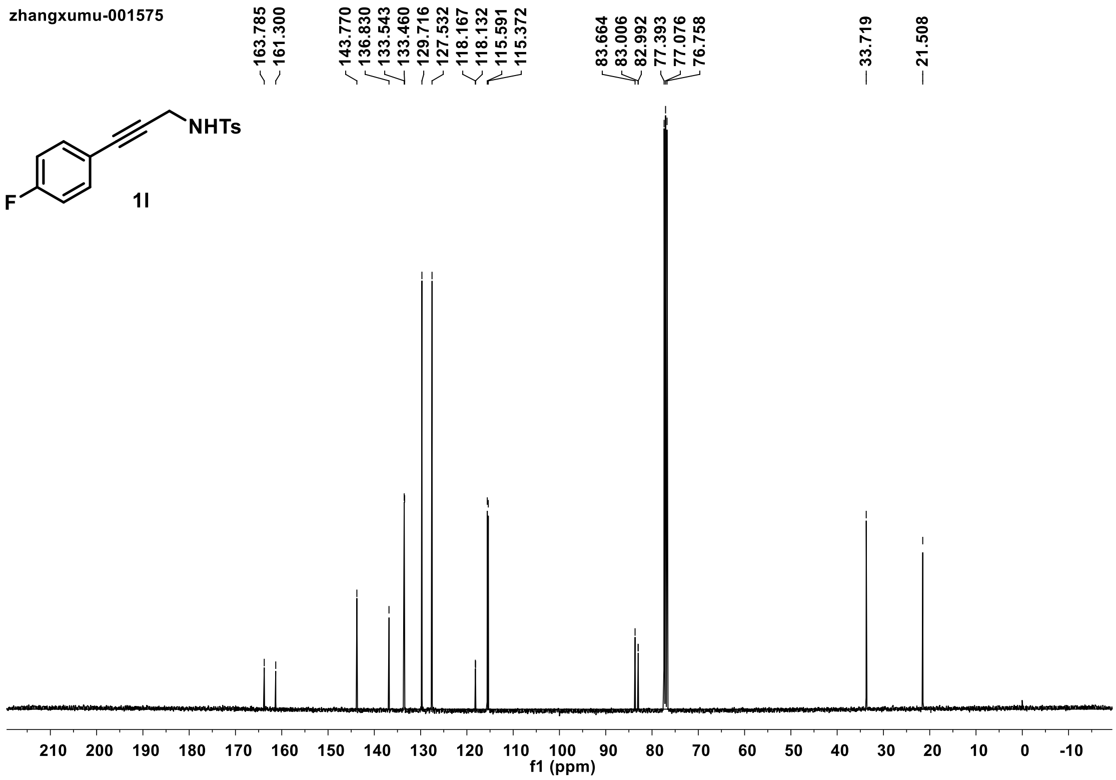


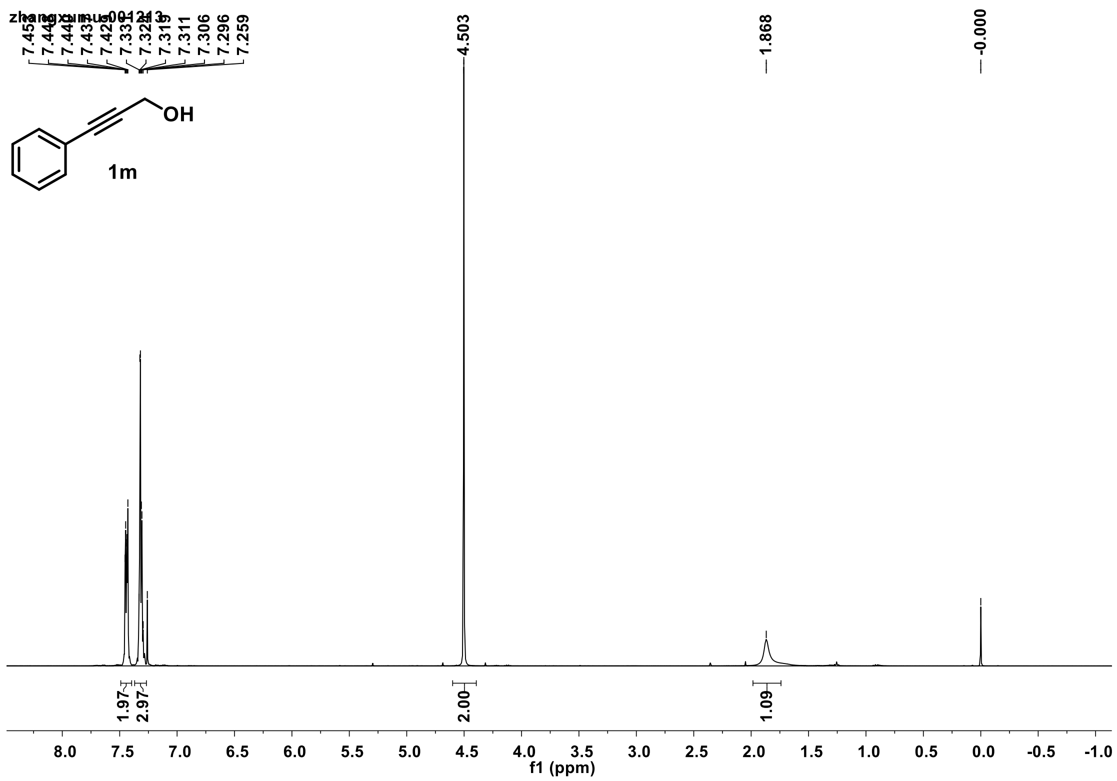
7.510
7.489
7.283
7.265
7.263
7.234
7.214
4.967
4.954
4.941
4.105
4.091
2.344
-0.000
NHTs
F3C
1k
2.08
2.11
4.43
1.00
2.15
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

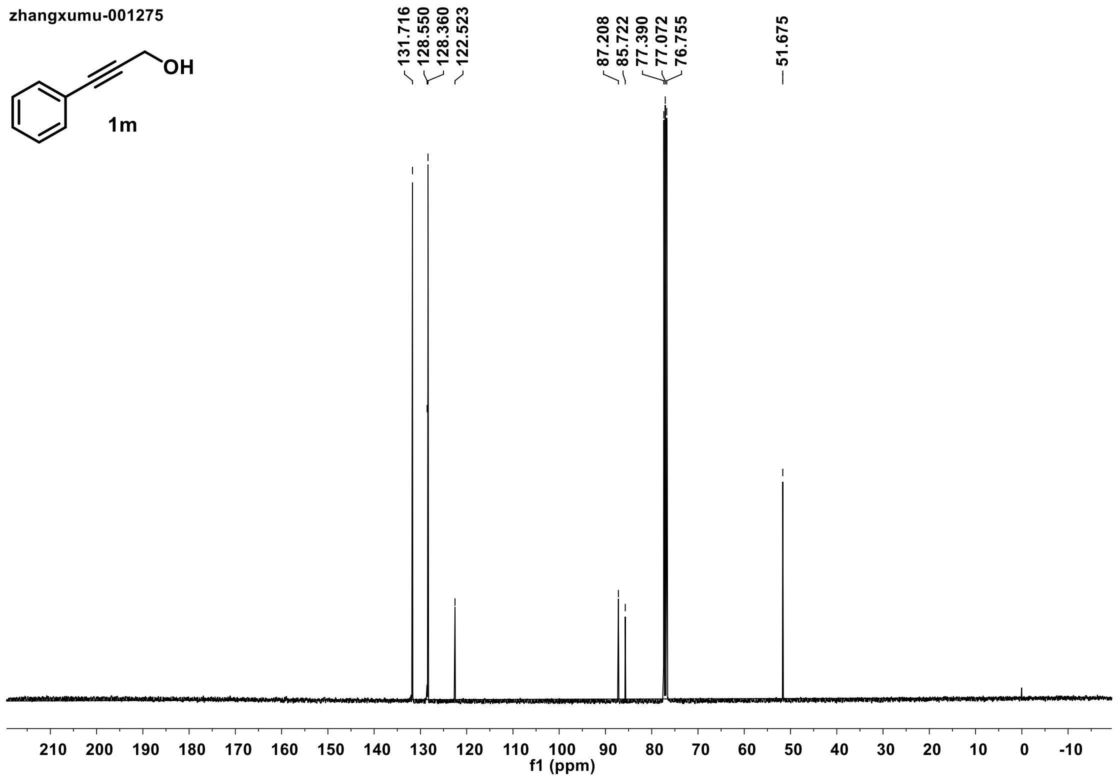


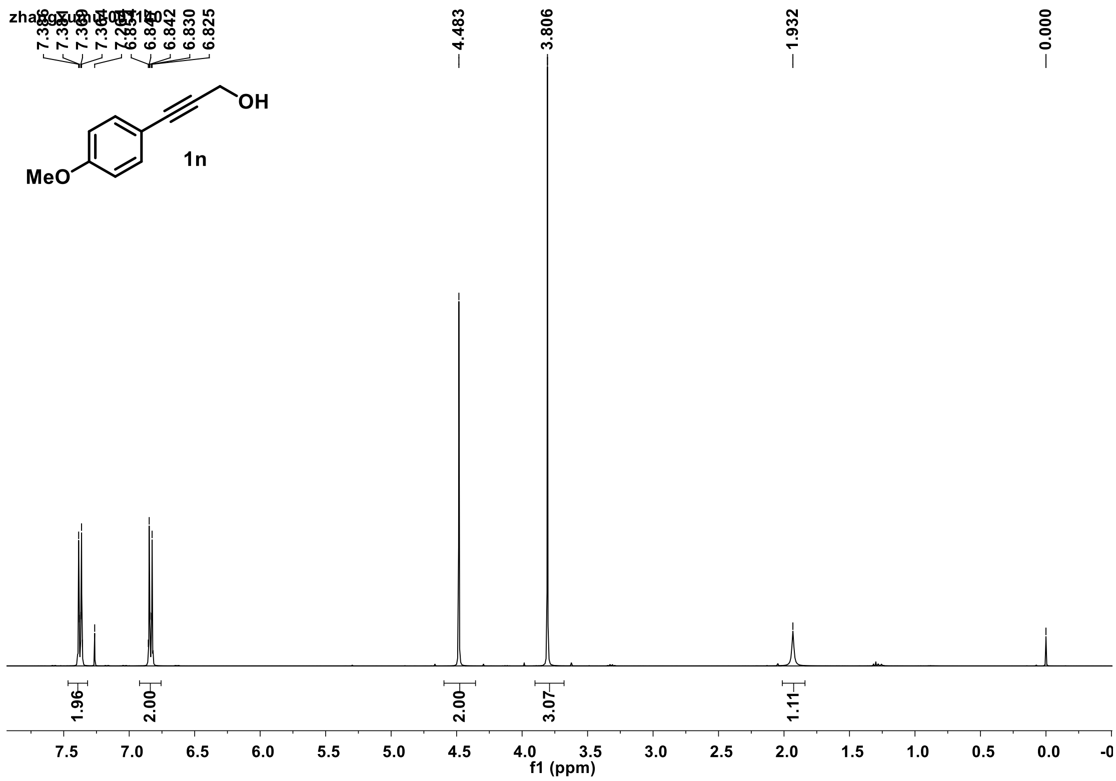
zhangxumu-001435
143.879
136.806
131.816
130.734
130.410
130.084
129.745
127.831
127.538
125.882
125.869
125.153
125.116
125.078
125.040
122.420
119.714
85.833
83.356
77.379
77.061
76.744
33.654
21.468
NHTs
F3C
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

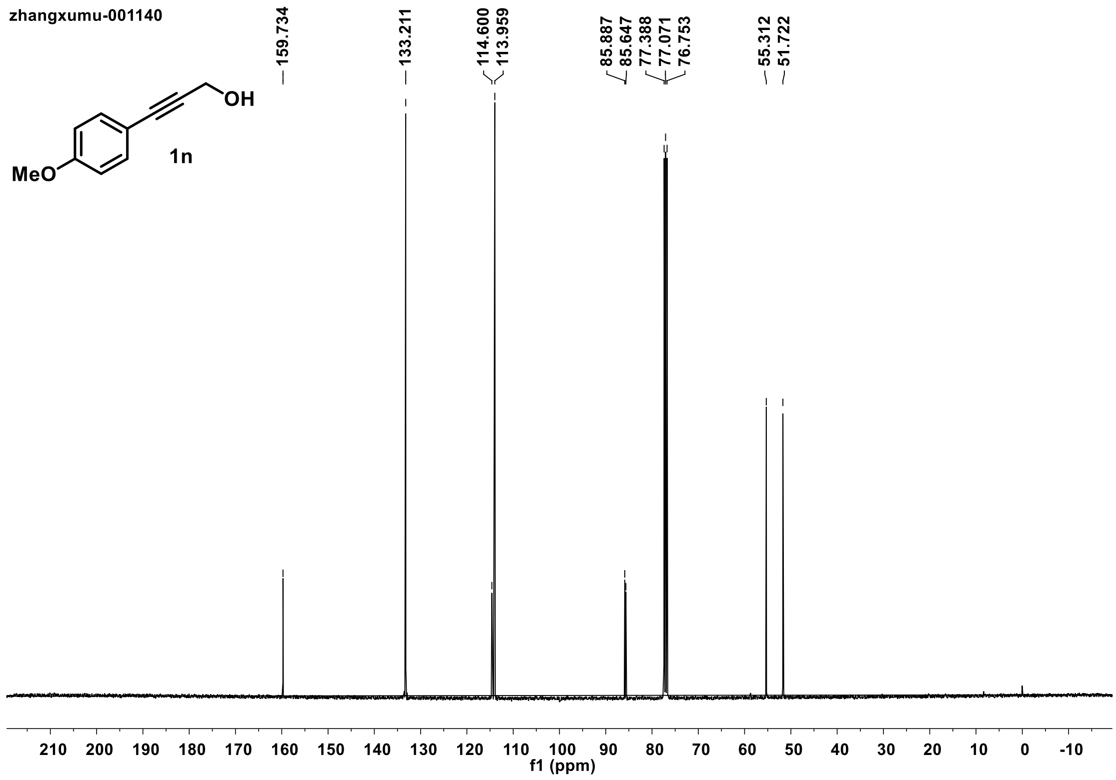

zhangxumu-001556
7.822
7.820
7.813
7.806
7.282
7.265
7.262
7.126
7.112
7.104
7.096
7.090
6.956
6.939
6.934
6.929
6.912
4.941
4.926
4.911
4.063
4.047
2.357
-0.000
NHTs
F
1l
1.96
2.23
1.95
1.96
0.94
2.00
3.02
f1 (ppm)

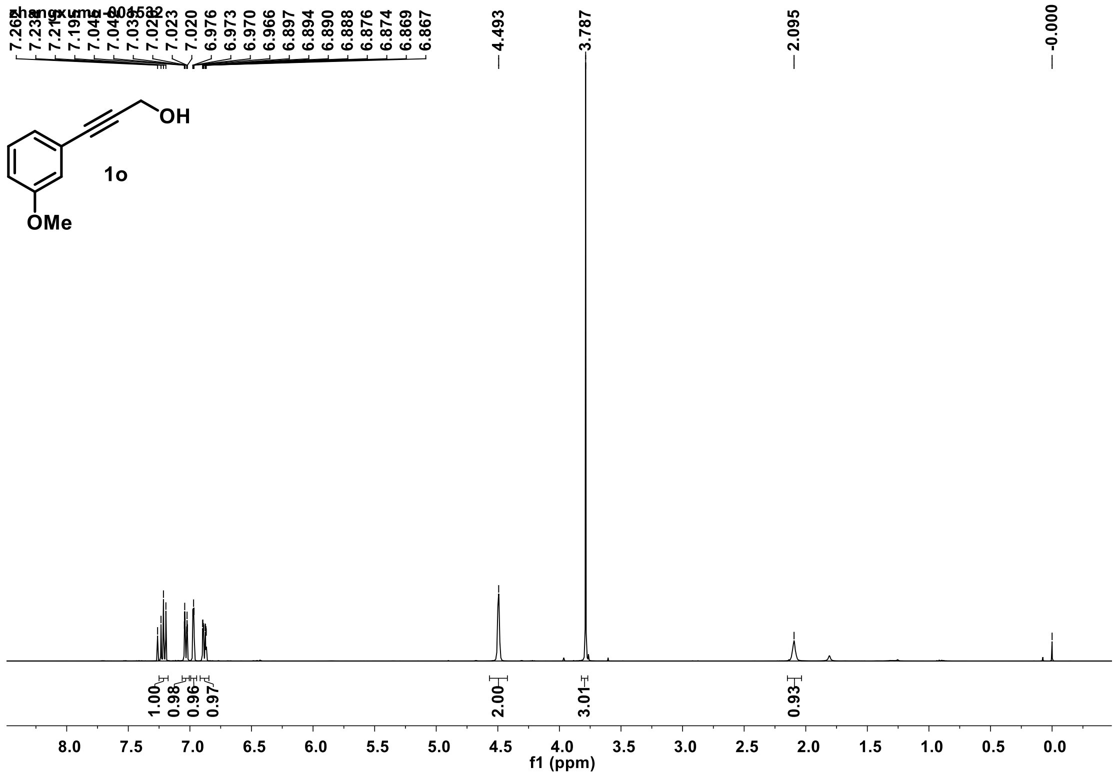

zhangxumu-001575
163.785
161.300
143.770
136.830
133.543
133.460
129.716
127.532
118.167
118.132
115.591
115.372
83.664
83.006
82.992
77.393
77.076
76.758
33.719
21.508
NHTs
F
1l
f1 (ppm)

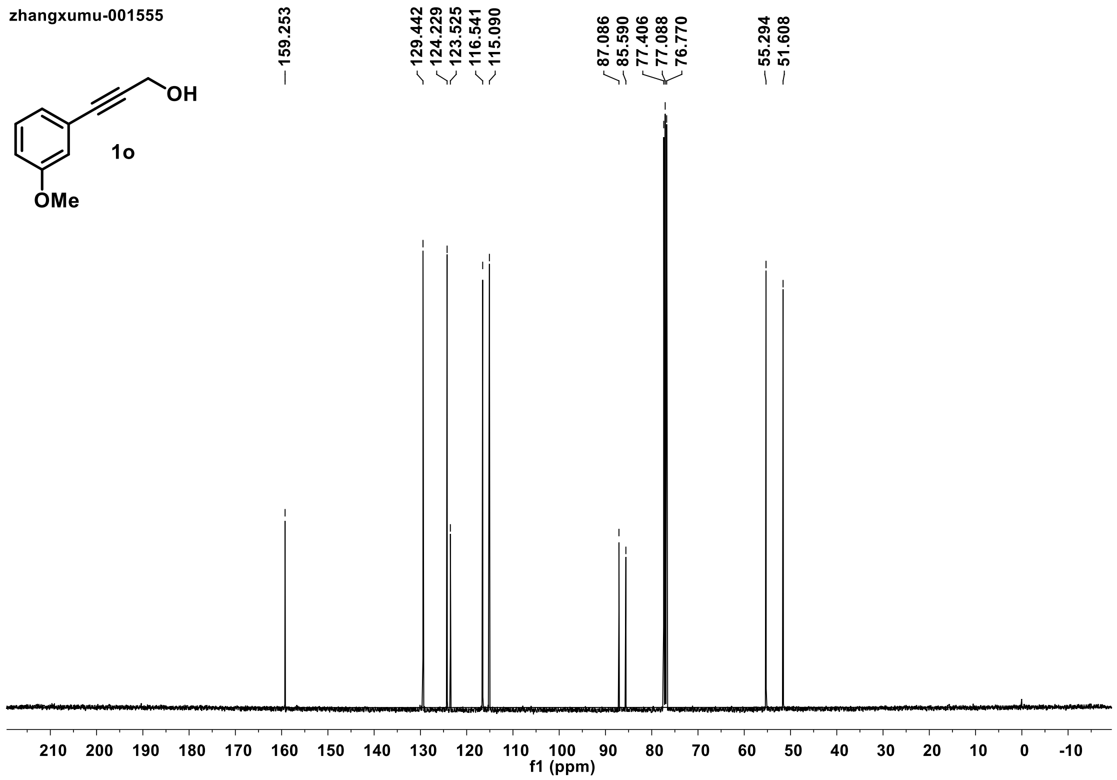

zhangxumu-001213
7.453
7.448
7.440
7.431
7.426
7.333
7.324
7.319
7.311
7.306
7.296
7.259
4.503
1.868
-0.000
OH
1m
1.97
2.97
2.00
1.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

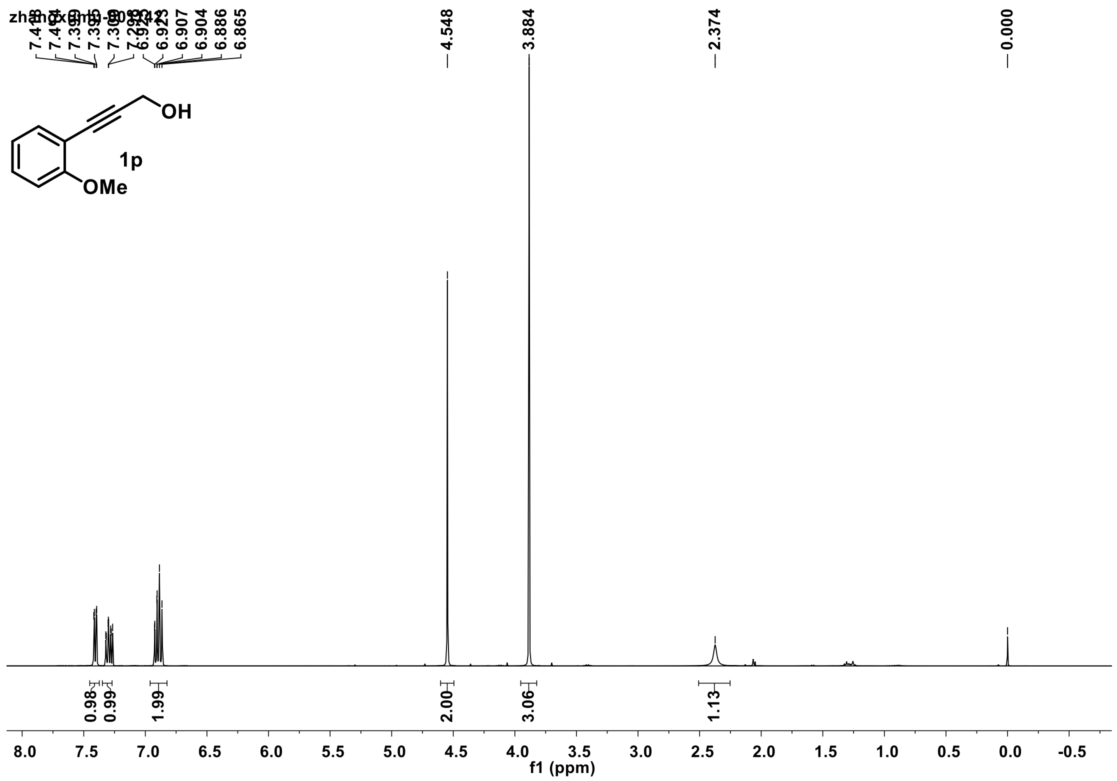

zhangxumu-001275
131.716
128.550
128.360
122.523
87.208
85.722
77.390
77.072
76.755
51.675
OH
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

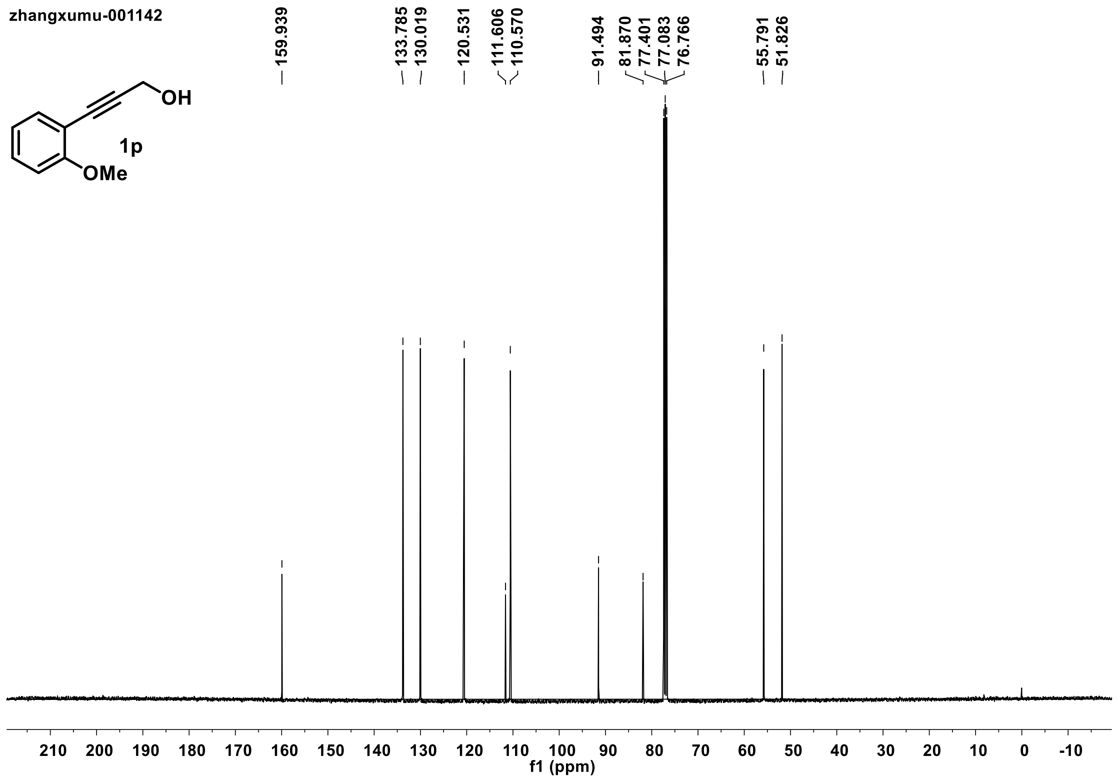

4.483
3.806
1.932
0.000
6.842
6.830
6.825
OH
MeO
1n
1.96
2.00
2.00
3.07
1.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

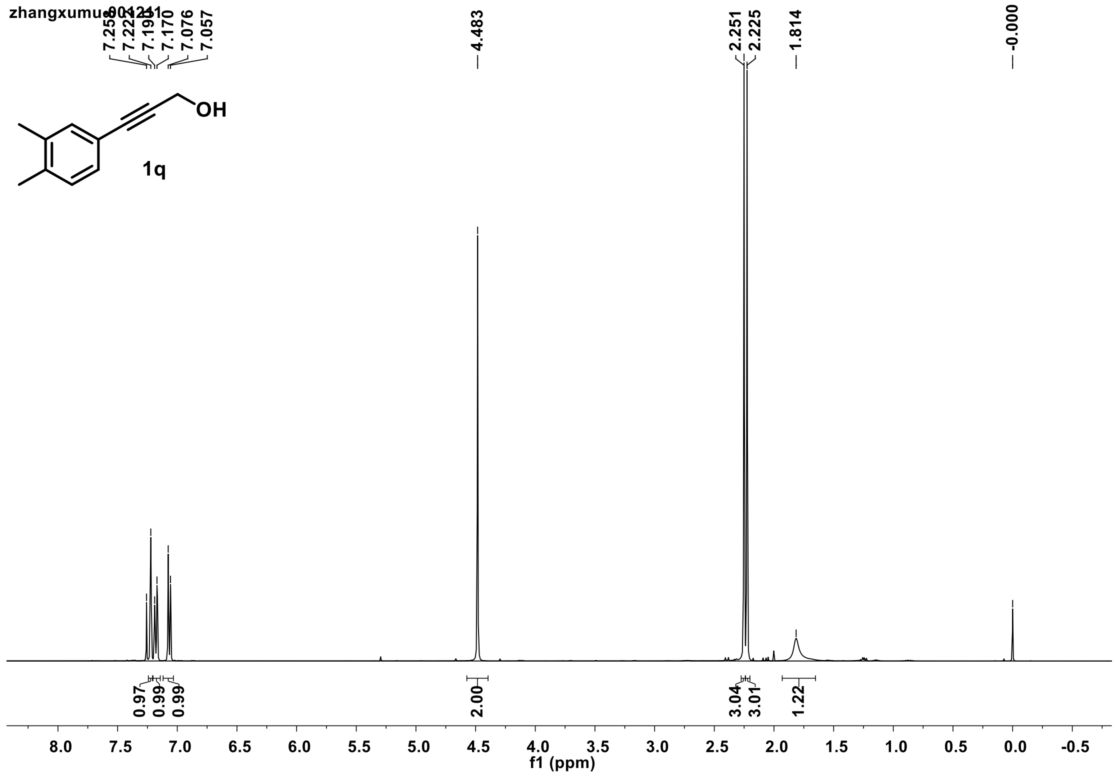

zhangxumu-001140
159.734
133.211
114.600
113.959
85.887
85.647
77.388
77.071
76.753
55.312
51.722
OH
MeO
1n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

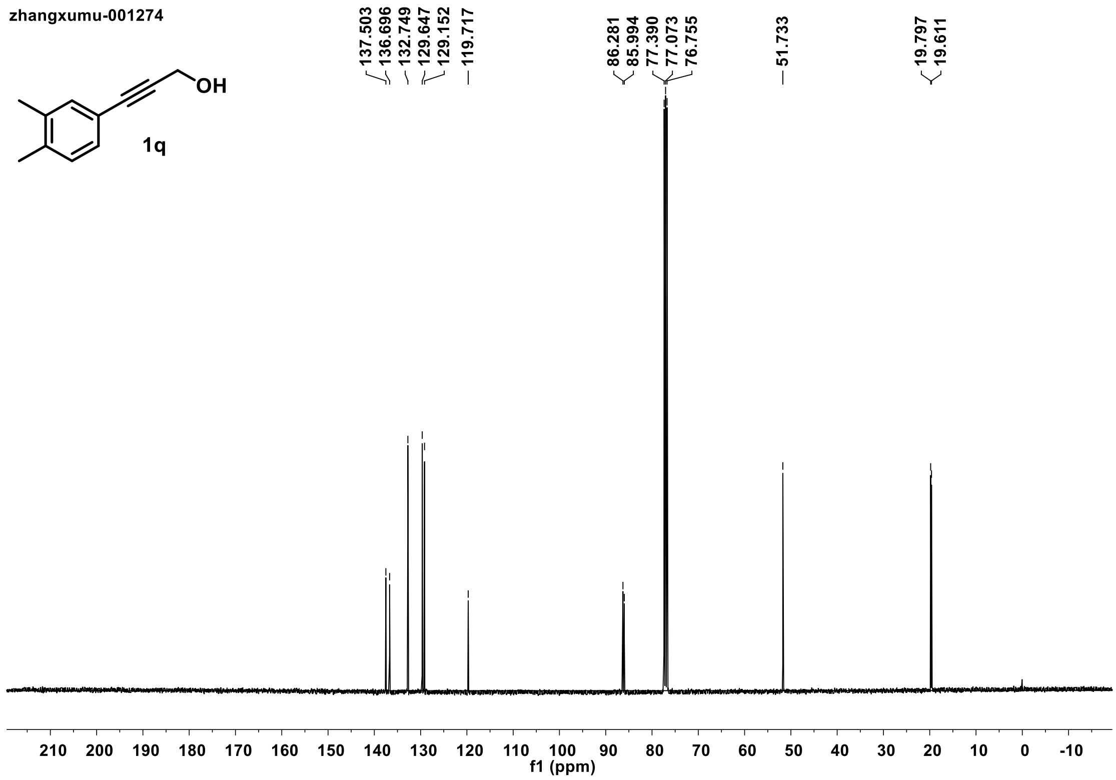


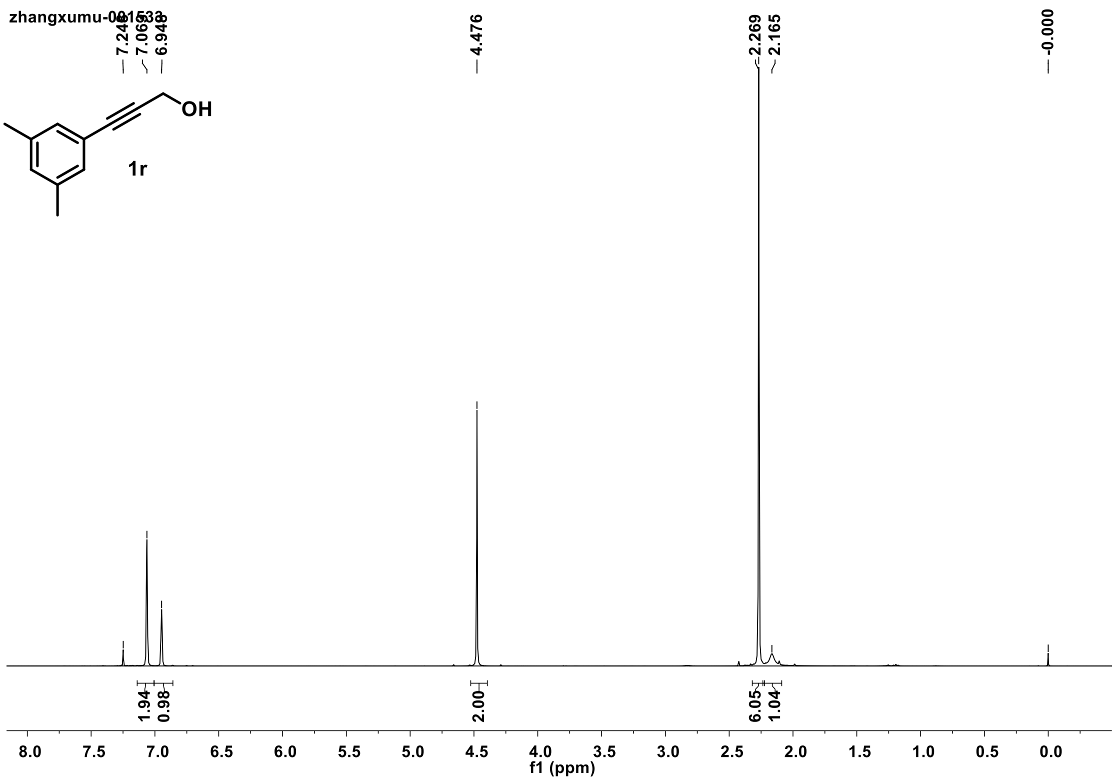


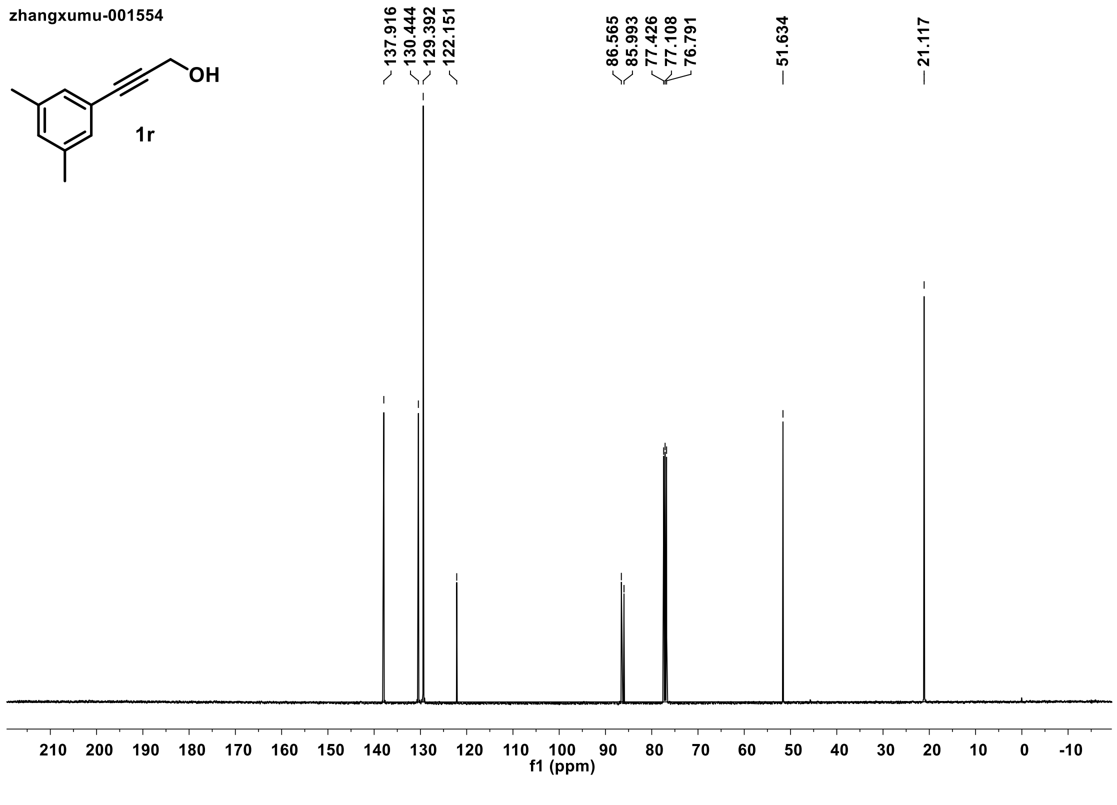

zhangxumu-001142
7.418
7.414
7.399
7.395
7.304
7.299
6.927
6.923
6.907
6.904
6.886
6.865
4.548
3.884
2.374
0.000
OH
1p
OMe
0.98
0.99
1.99
2.00
3.06
1.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

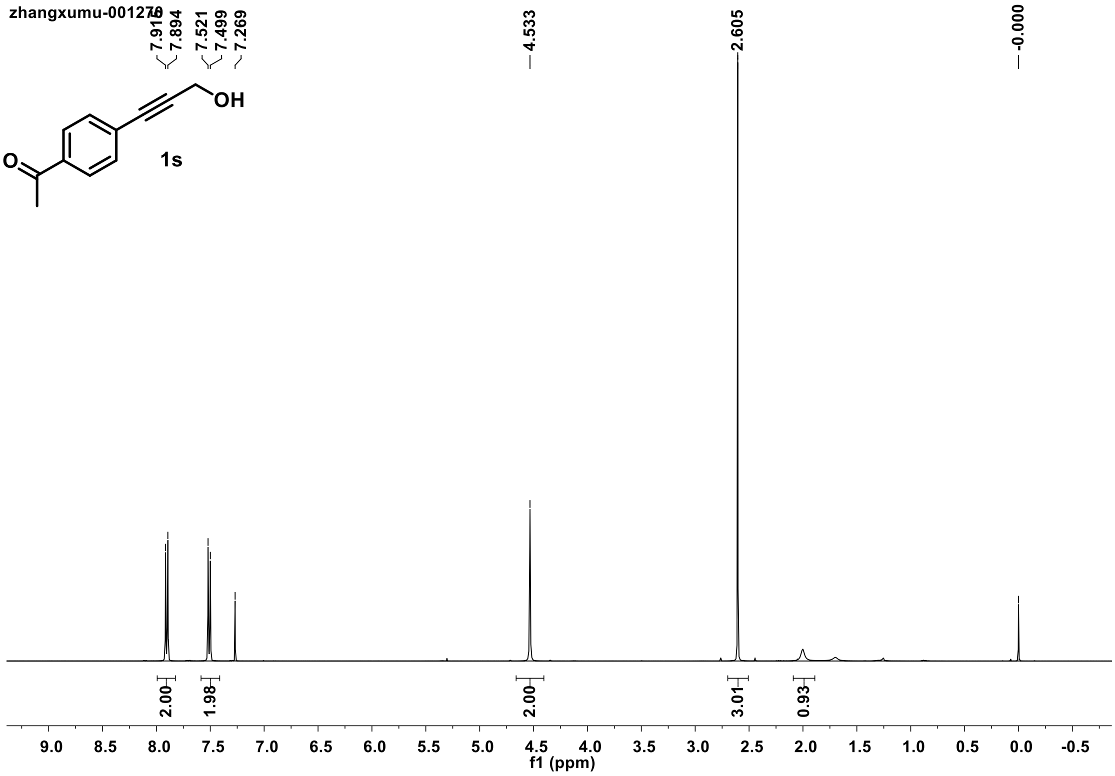

zhangxumu-001142
159.939
133.785
130.019
120.531
111.606
110.570
91.494
81.870
77.401
77.083
76.766
55.791
51.826
OH
1p
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

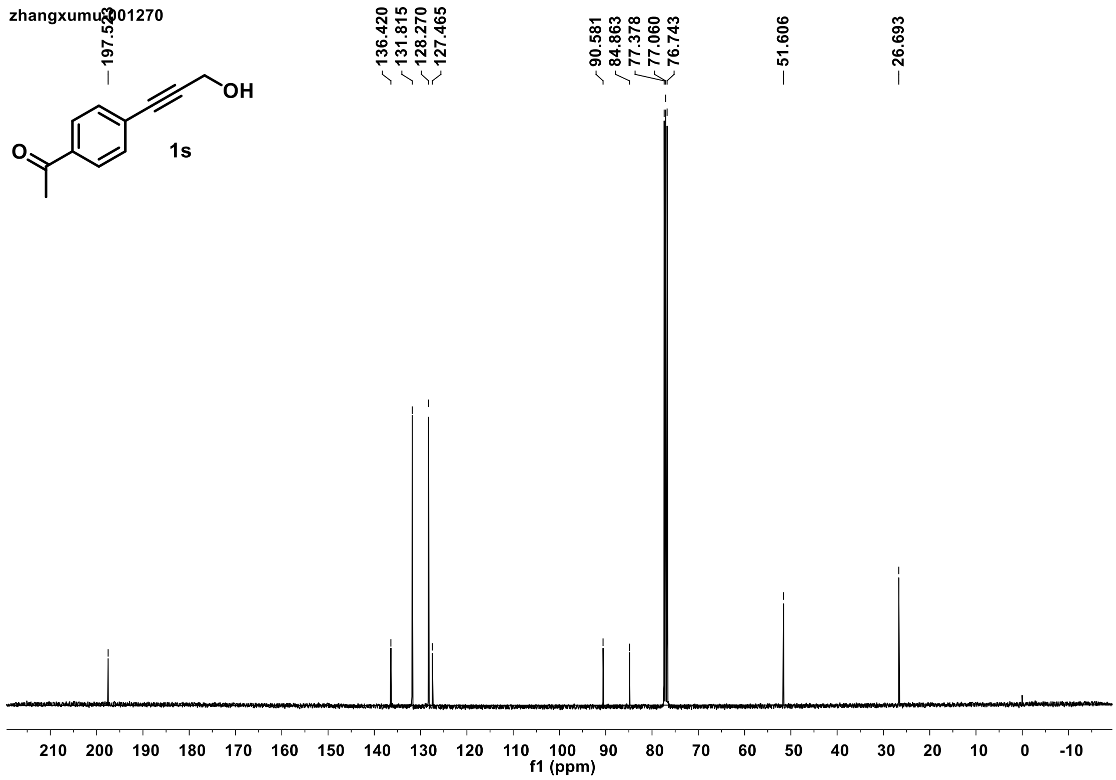

zhangxumu-001241
7.253
7.222
7.191
7.170
7.076
7.057
4.483
2.251
2.225
1.814
-0.000
OH
1q
0.97
0.99
0.99
2.00
3.04
3.01
1.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

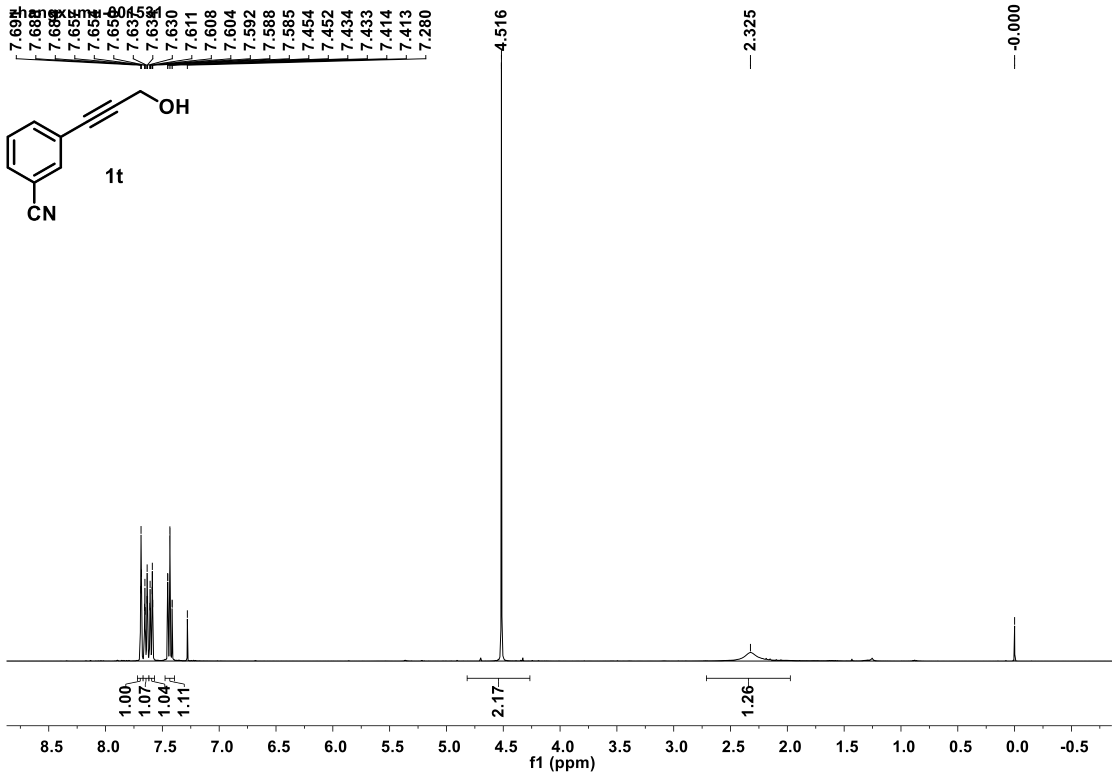

zhangxumu-001274
137.503
136.696
132.749
129.647
129.152
119.717
86.281
85.994
77.390
77.073
76.755
51.733
19.797
19.611
OH
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


zhangxumu-001533
7.246
7.063
6.948
4.476
2.269
2.165
-0.000
OH
1r
1.94
0.98
2.00
6.05
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

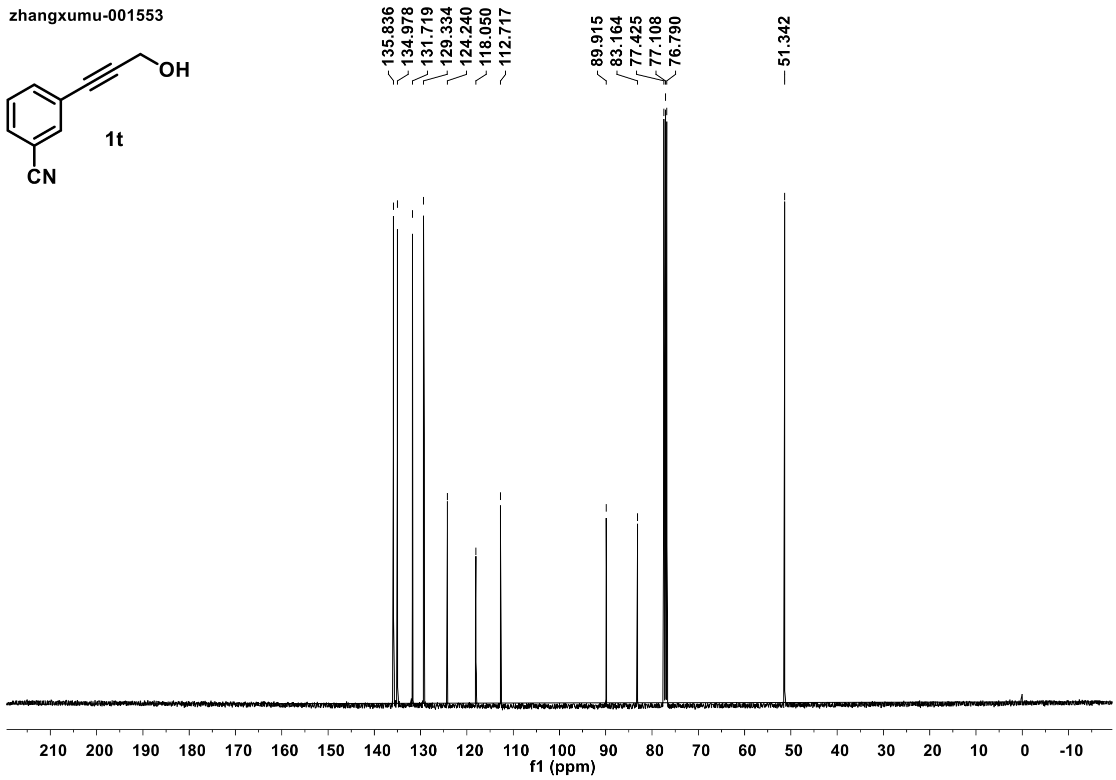

zhangxumu-001554
137.916
130.444
129.392
122.151
86.565
85.993
77.426
77.108
76.791
51.634
21.117
OH
1r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


zhangxumu-001270
7.910
7.894
7.521
7.499
7.269
4.533
2.605
-0.000
OH
O
1s
2.00
1.98
2.00
3.01
0.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

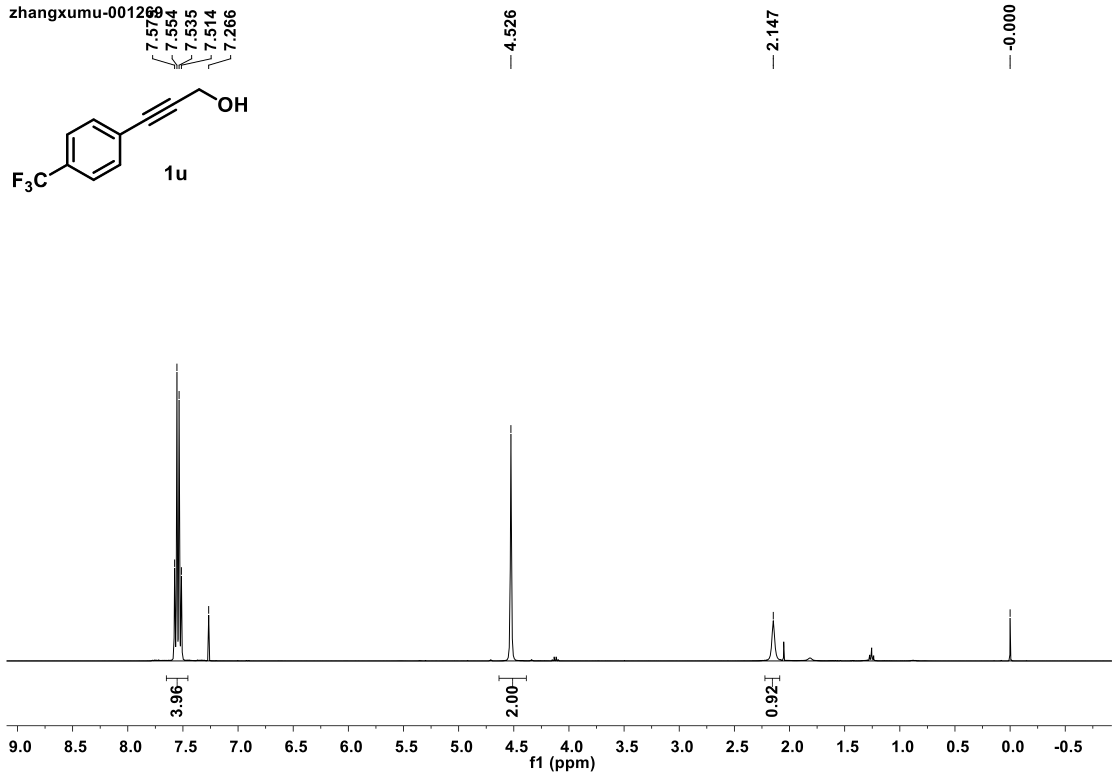

zhangxumu-001270
197.523
136.420
131.815
128.270
127.465
90.581
84.863
77.378
77.060
76.743
51.606
26.693
OH
O
1s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

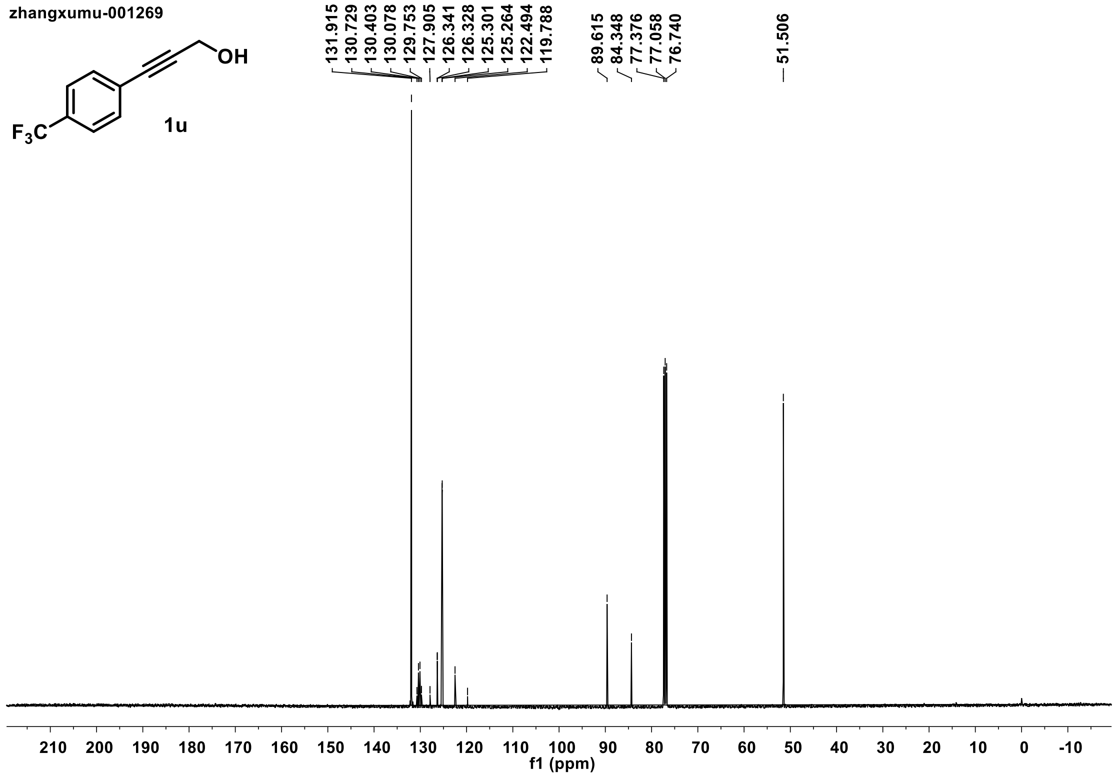


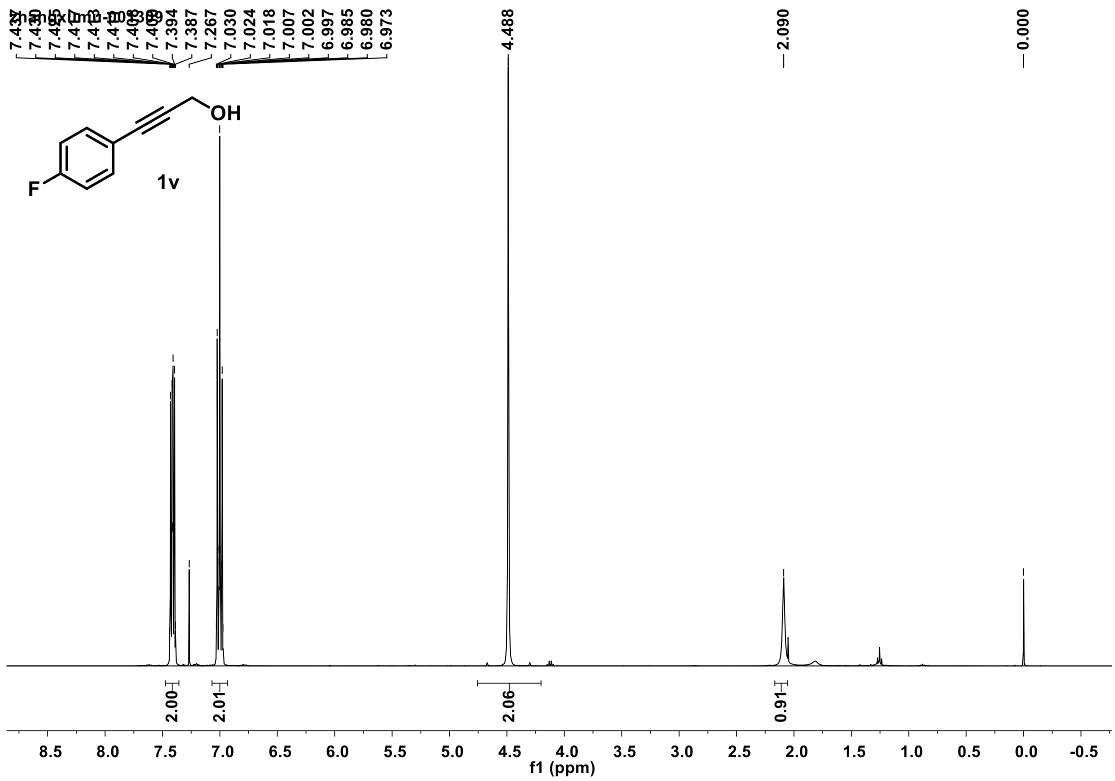
7.630
7.611
7.608
7.604
7.592
7.588
7.585
7.454
7.452
7.434
7.433
7.414
7.413
7.280
4.516
2.325
-0.000
OH
1t
CN
1.00
1.07
1.04
1.11
2.17
1.26
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



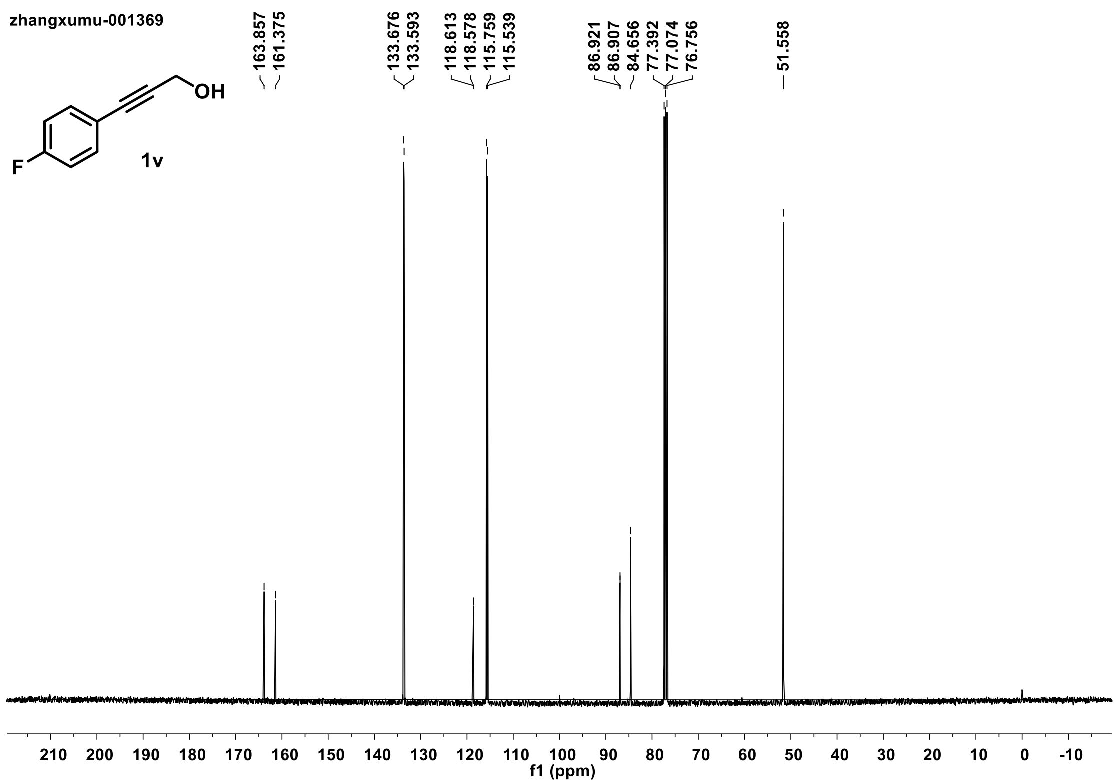
zhangxumu-001553
135.836
134.978
131.719
129.334
124.240
118.050
112.717
89.915
83.164
77.425
77.108
76.790
51.342
OH
1t
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


zhangxumu-001269
7.579
7.554
7.535
7.514
7.266
4.526
2.147
-0.000
OH
F3C
1u
3.96
2.00
0.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

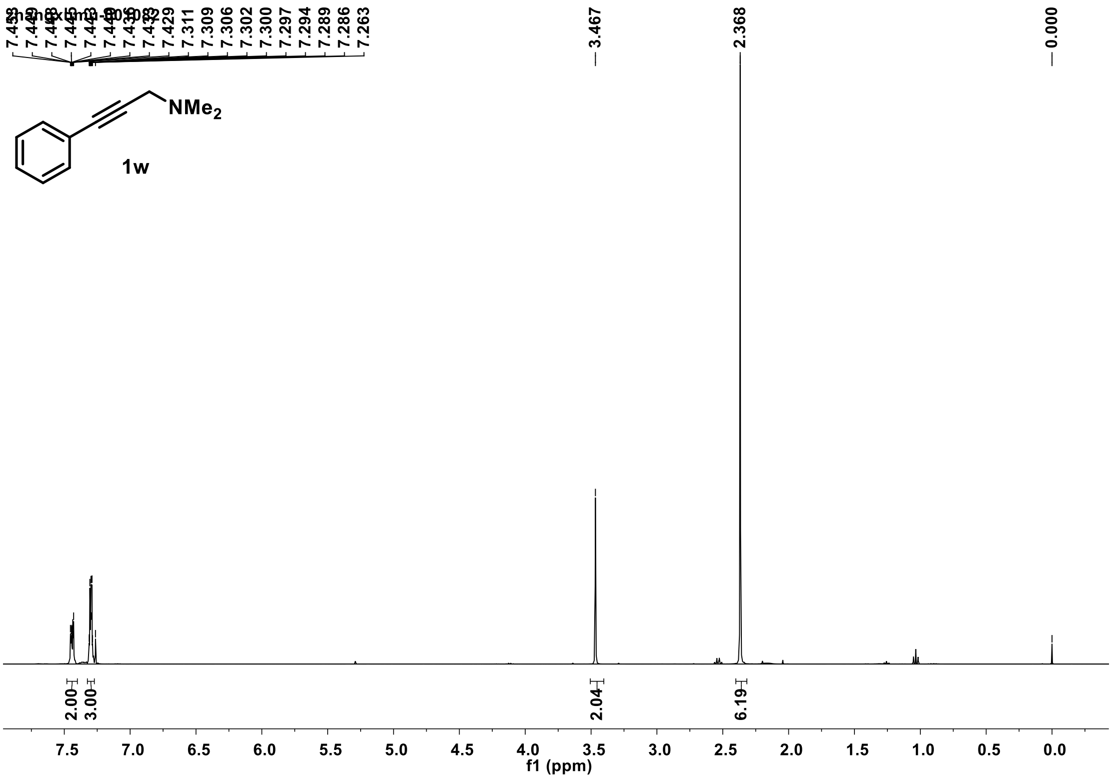

zhangxumu-001269
131.915
130.729
130.403
130.078
129.753
127.905
126.341
126.328
125.301
125.264
122.494
119.788
89.615
84.348
77.376
77.058
76.740
51.506
OH
F3C
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

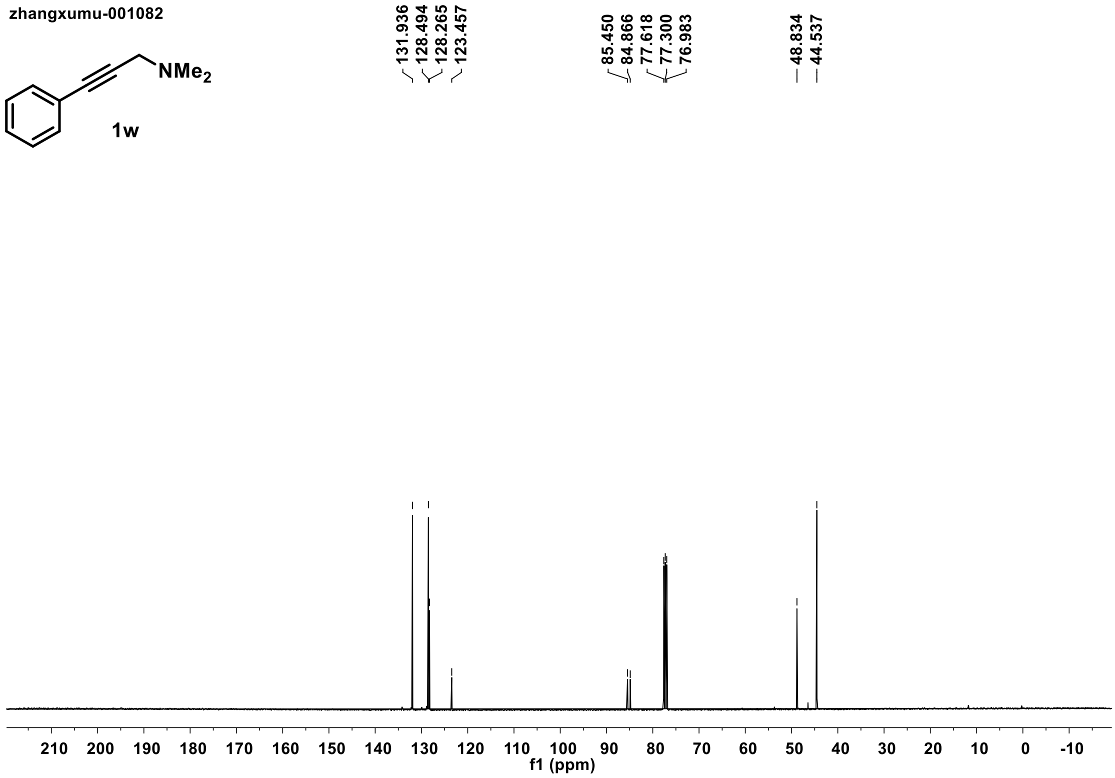


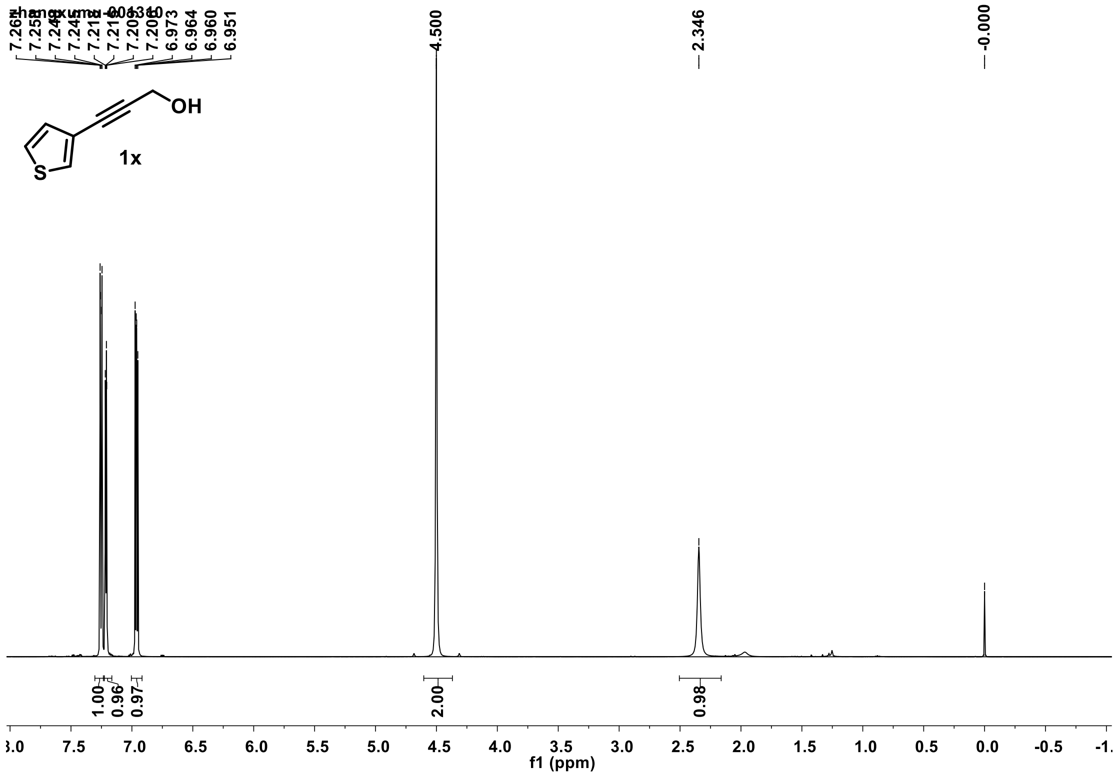
zhangxumu-001369
7.437
7.430
7.425
7.417
7.413
7.408
7.403
7.400
7.394
7.387
7.267
7.030
7.024
7.018
7.007
7.002
6.997
6.985
6.980
6.973
4.488
2.090
0.000
OH
F
1v
2.00
2.01
2.06
0.91
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

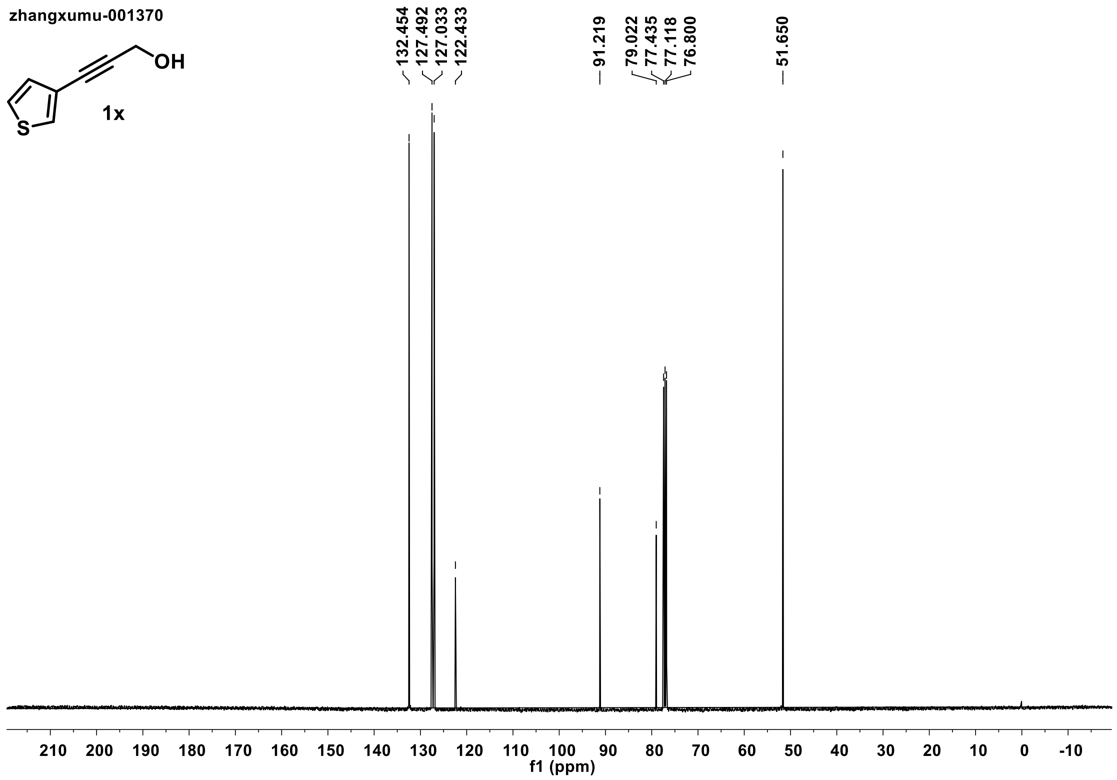


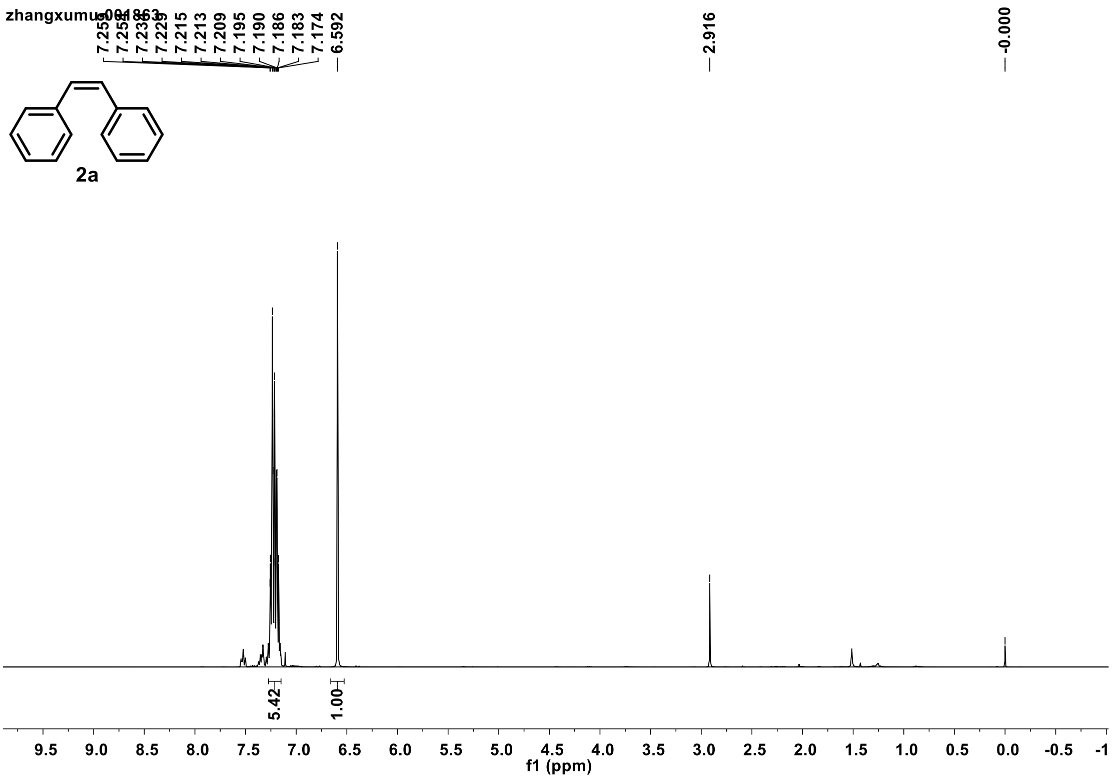
zhangxumu-001369
163.857
161.375
133.676
133.593
118.613
118.578
115.759
115.539
86.921
86.907
84.656
77.392
77.074
76.756
51.558
OH
F
1v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

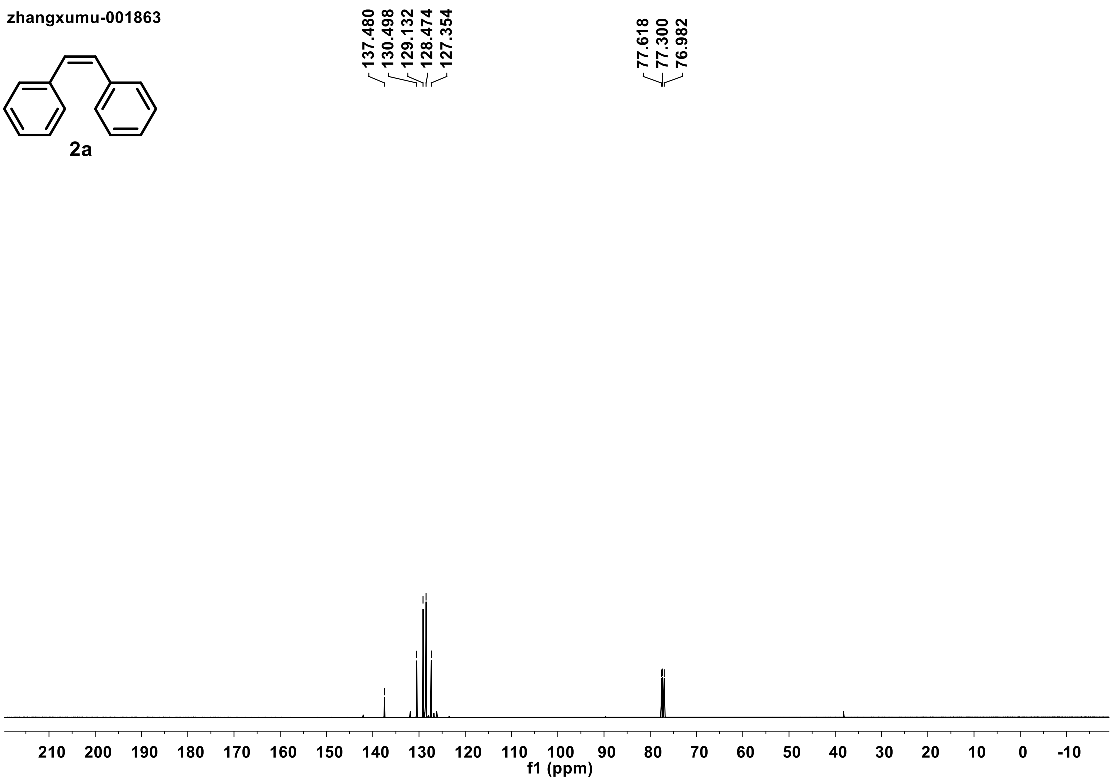

7.311
7.309
7.306
7.302
7.300
7.297
7.294
7.289
7.286
7.263
3.467
2.368
0.000
NMe$_2$
1w
2.00
3.00
2.04
6.19
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

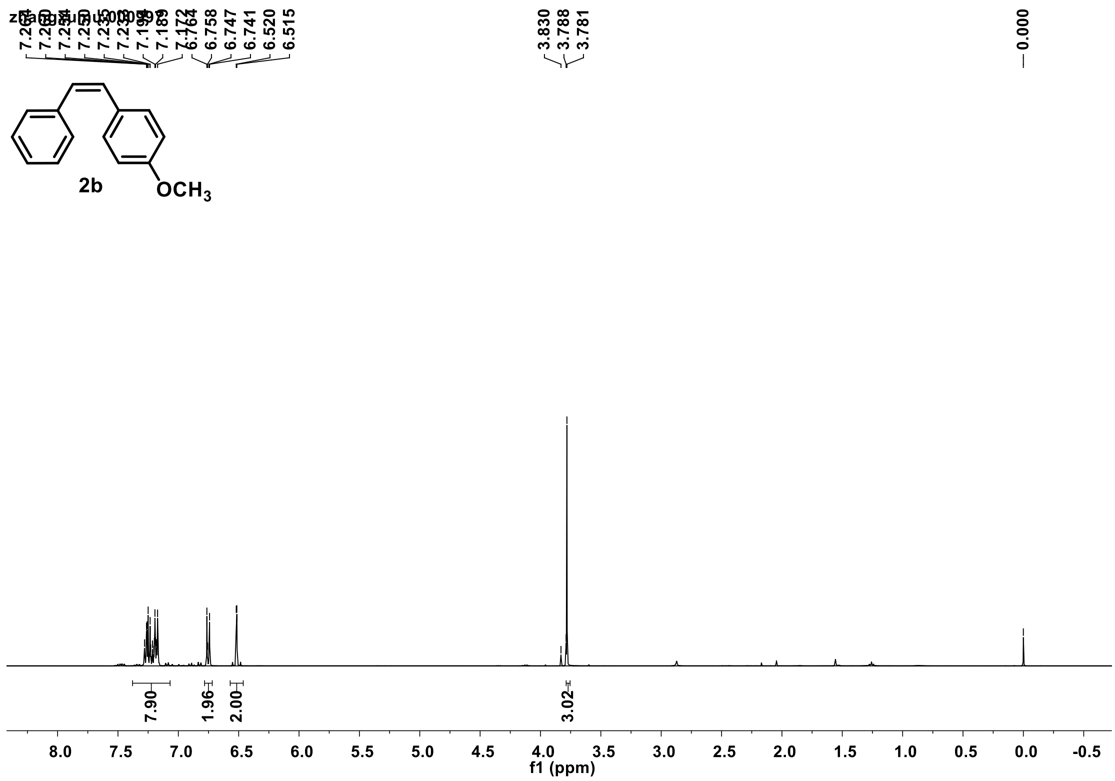

zhangxumu-001082
131.936
128.494
128.265
123.457
85.450
84.866
77.618
77.300
76.983
48.834
44.537
NMe$_2$
1w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

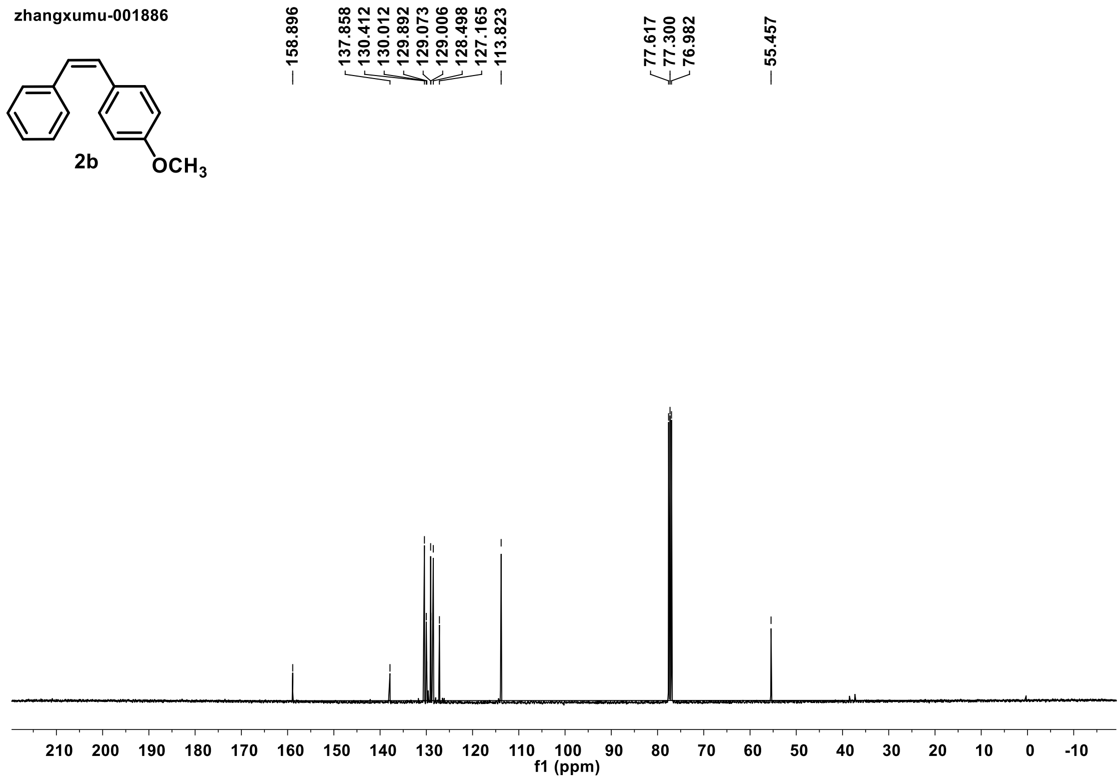

6.973
6.964
6.960
6.951
4.500
2.346
-0.000
OH
1x
S
1.00
0.96
0.97
2.00
0.98
f1 (ppm)

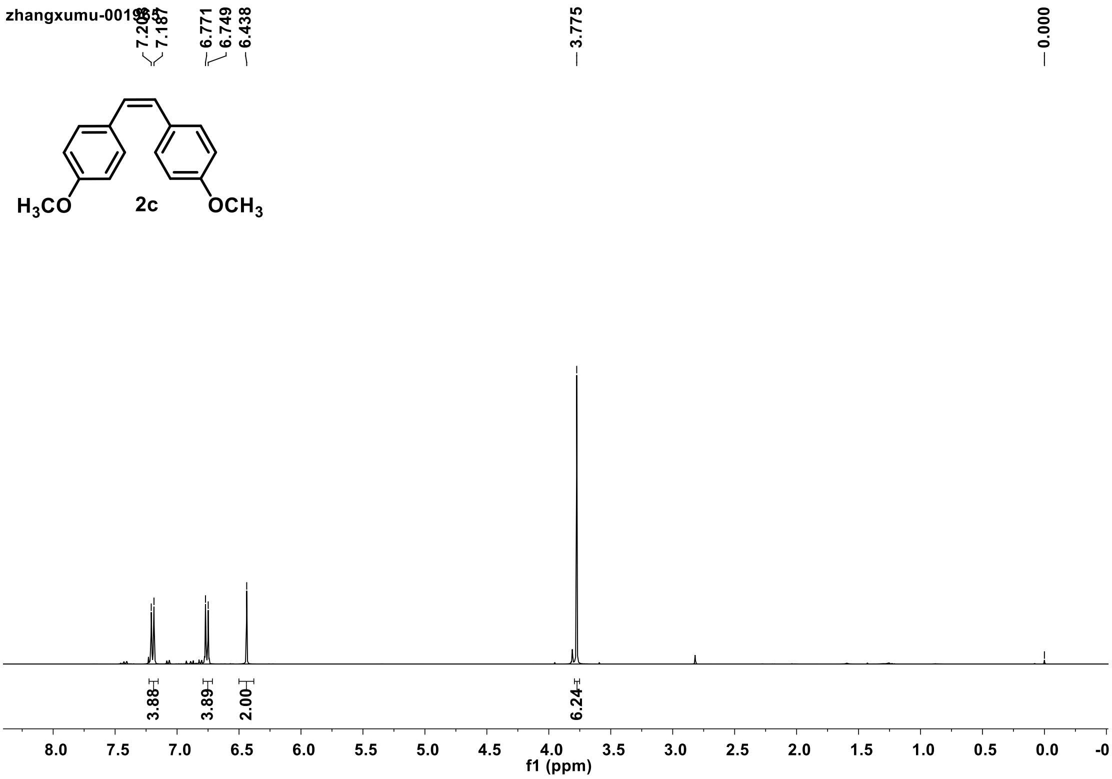

zhangxumu-001370
132.454
127.492
127.033
122.433
91.219
79.022
77.435
77.118
76.800
51.650
OH
1x
S
f1 (ppm)

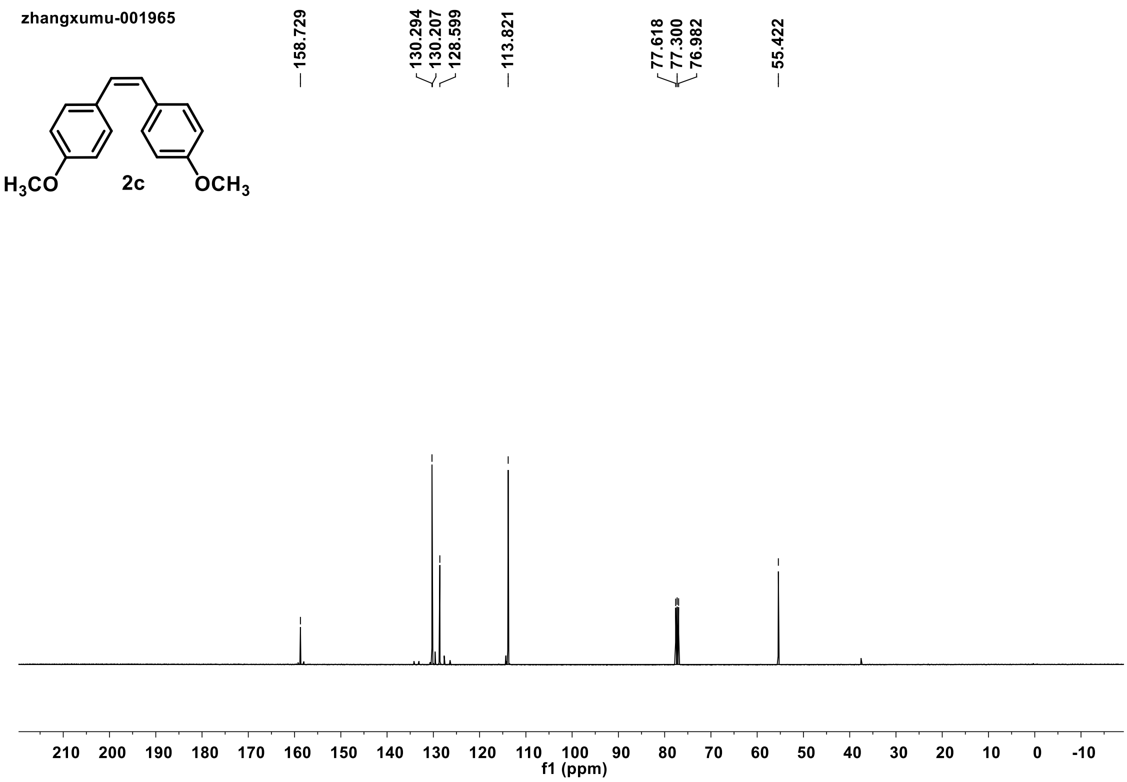

zhangxumu-001863
7.229
7.215
7.213
7.209
7.195
7.190
7.186
7.183
7.174
6.592
2.916
-0.000
2a
5.42
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

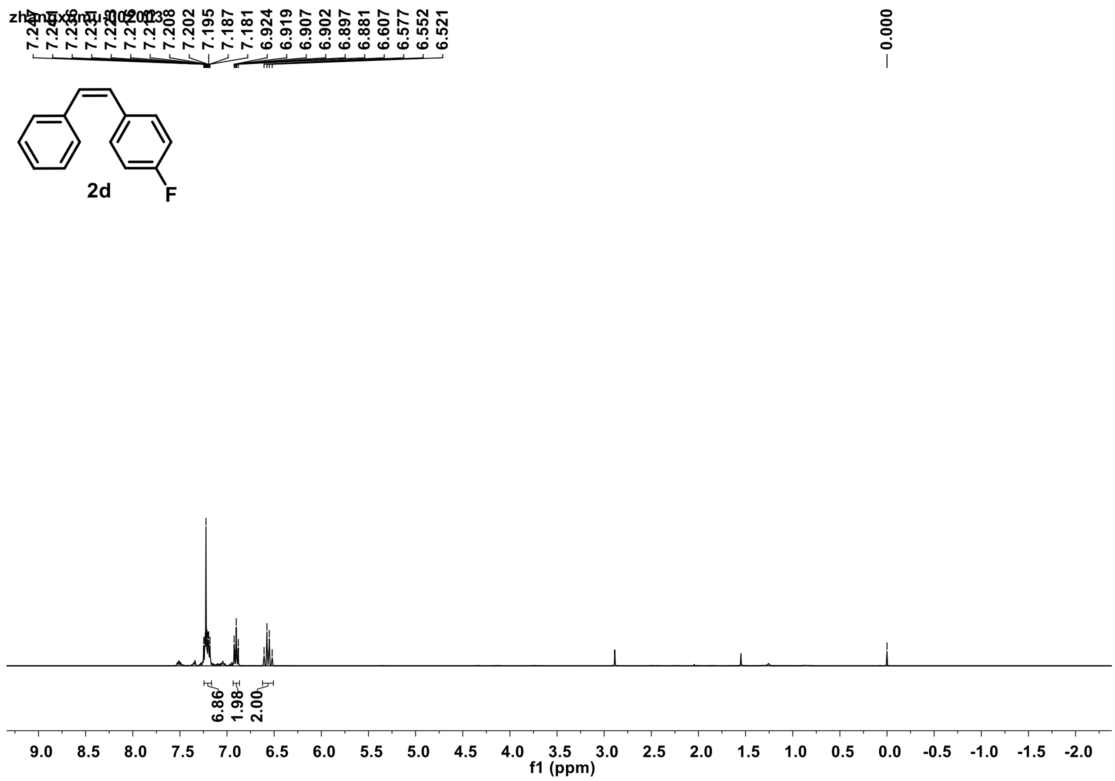

zhangxumu-001863
137.480
130.498
129.132
128.474
127.354
77.618
77.300
76.982
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

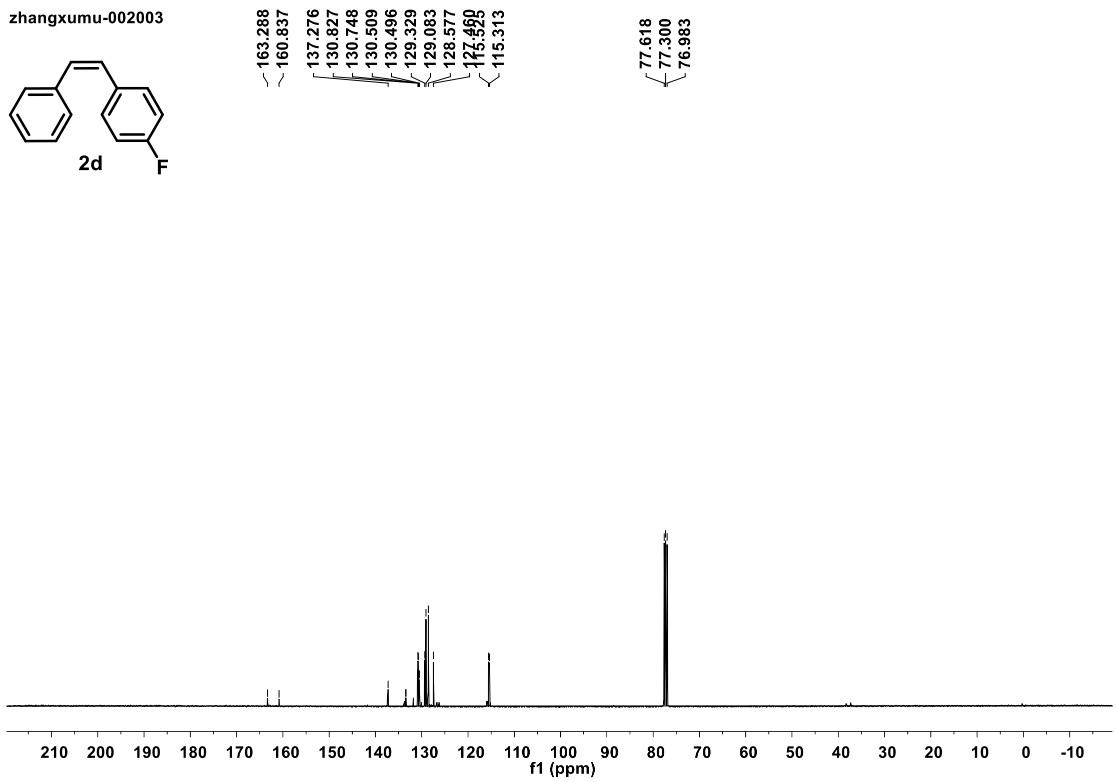

zhangxumu-
7.189
7.172
6.764
6.758
6.747
6.741
6.520
6.515
3.830
3.788
3.781
0.000
2b
OCH$_3$
7.90
1.96
2.00
3.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

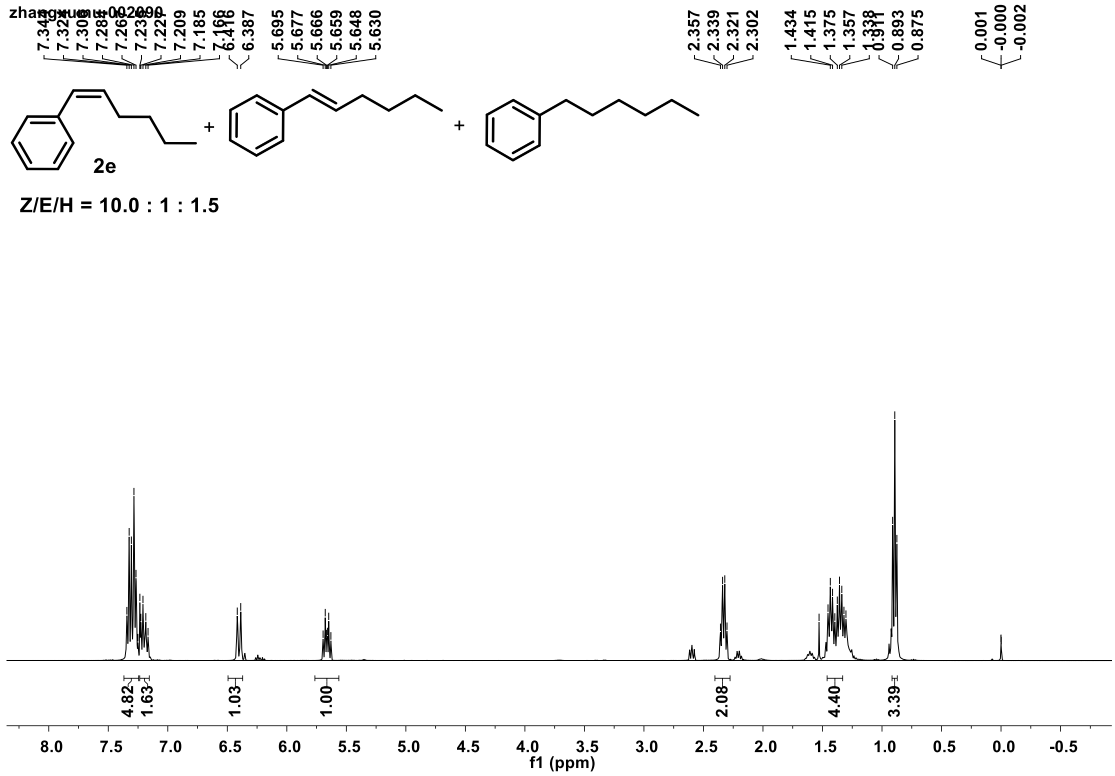

zhangxumu-001886
158.896
137.858
130.412
130.012
129.892
129.073
129.006
128.498
127.165
113.823
77.617
77.300
76.982
55.457
2b
OCH$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

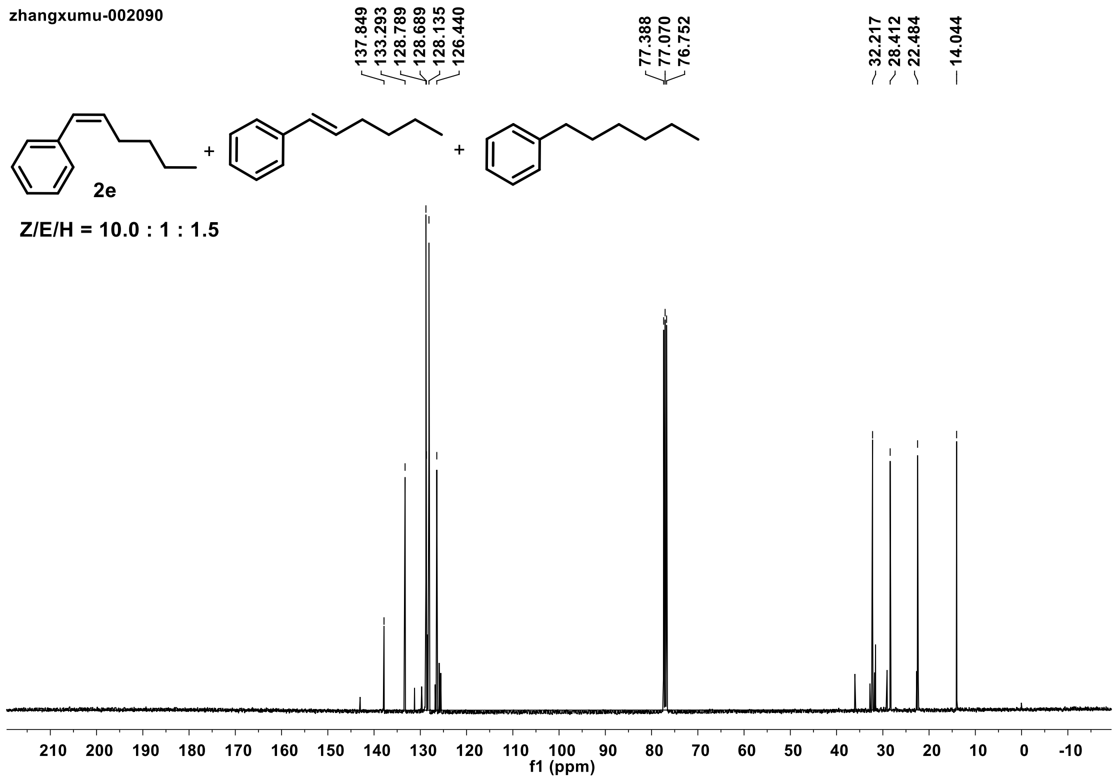

zhangxumu-001965
7.187
6.771
6.749
6.438
3.775
0.000
H3CO
2c
OCH3
3.88
3.89
2.00
6.24
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

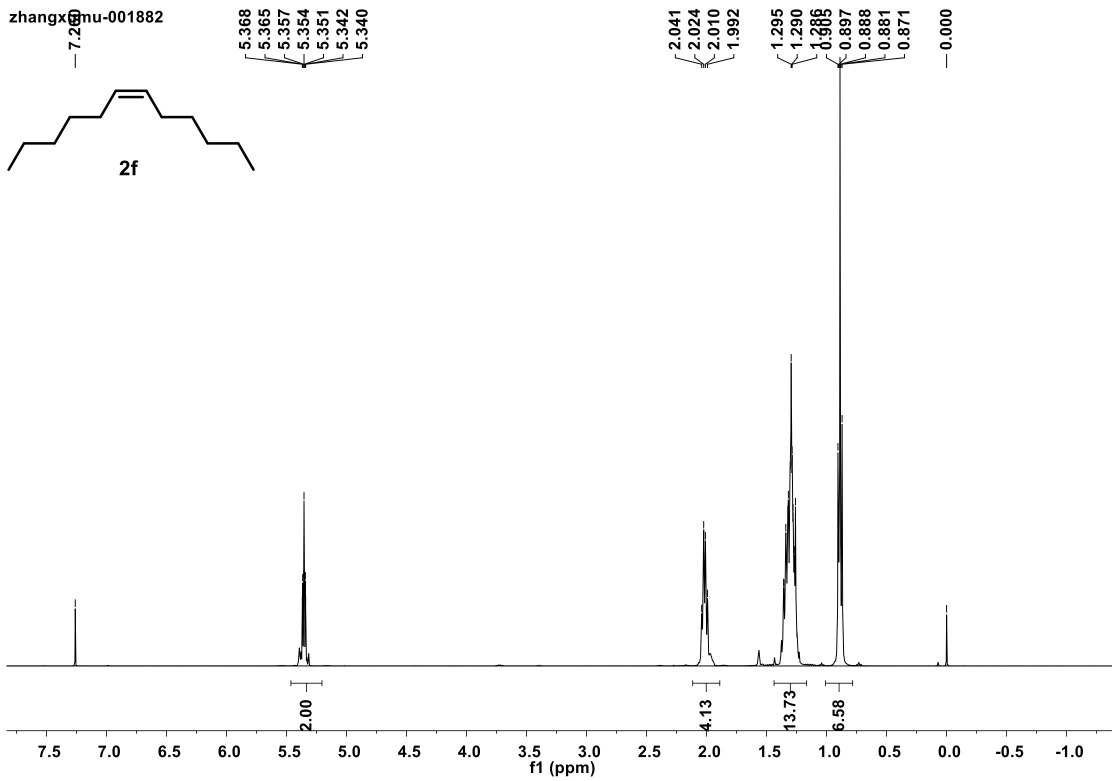

zhangxumu-001965
158.729
130.294
130.207
128.599
113.821
77.618
77.300
76.982
55.422
H3CO
2c
OCH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

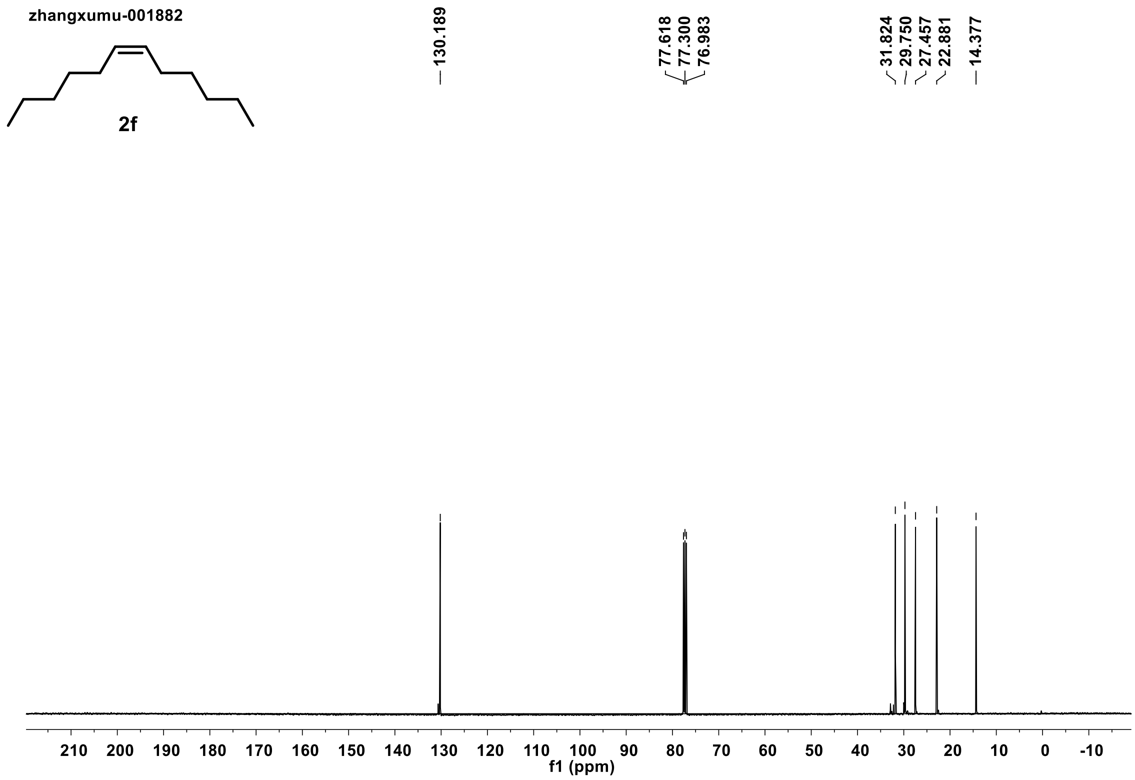

zhangxumu-002003
7.202
7.195
7.187
7.181
6.924
6.919
6.907
6.902
6.897
6.881
6.607
6.577
6.552
6.521
0.000
2d
F
6.86
1.98
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

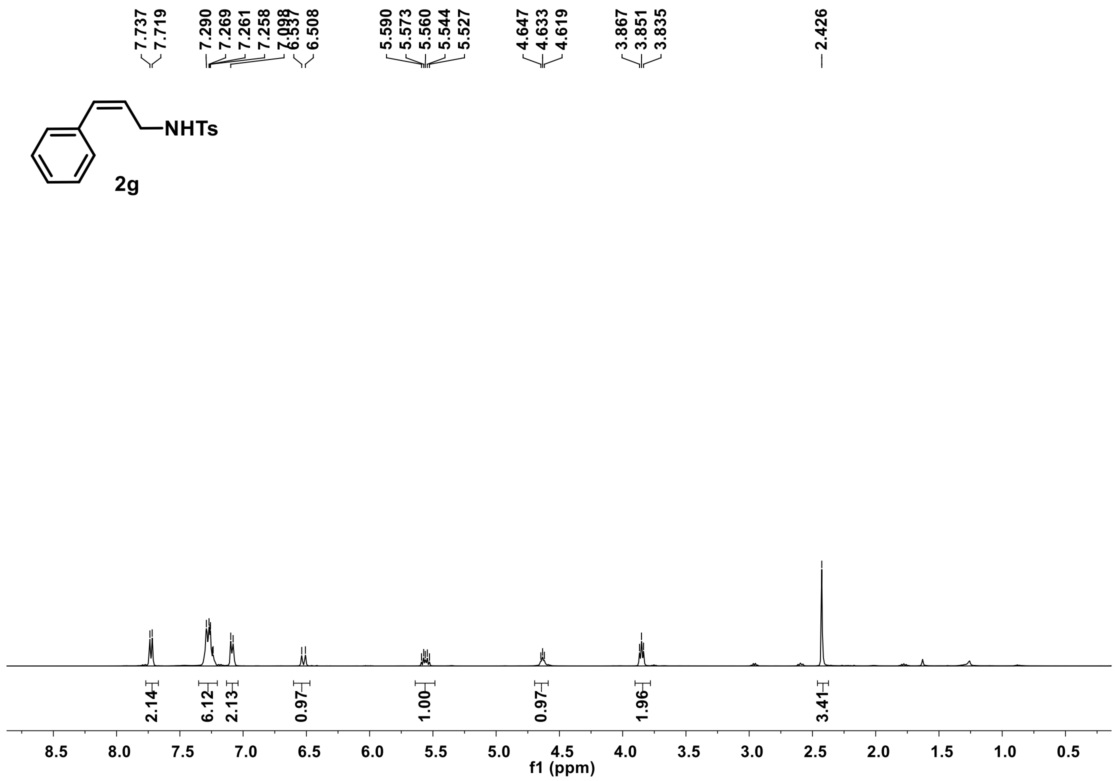

zhangxumu-002003
163.288
160.837
137.276
130.827
130.748
130.509
130.496
129.329
129.083
128.577
115.525
115.313
77.618
77.300
76.983
2d
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

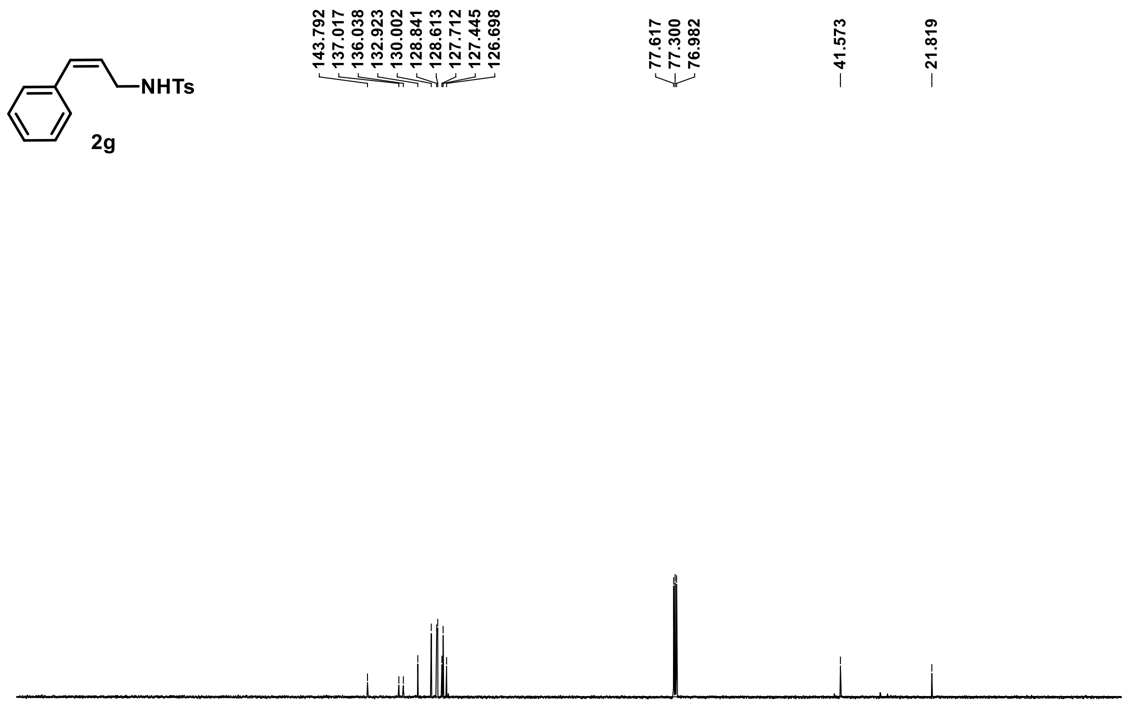

zhangxumu-002090
2e
Z/E/H = 10.0 : 1 : 1.5
f1 (ppm)

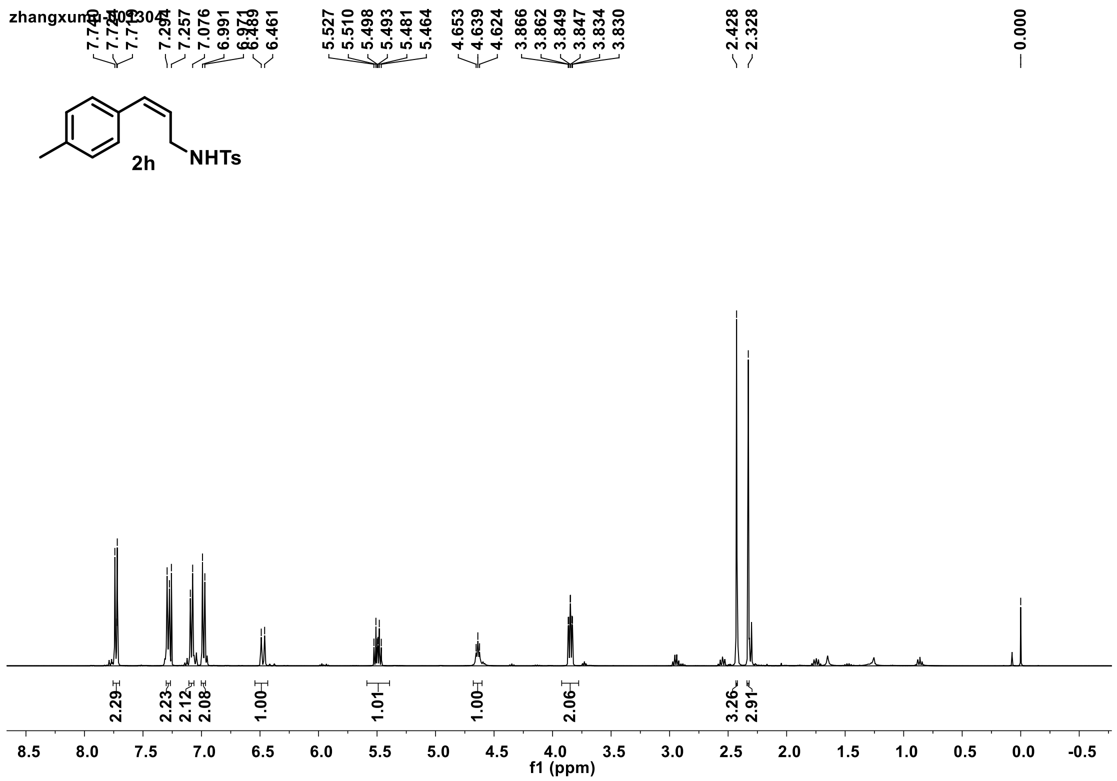

zhangxumu-002090
137.849
133.293
128.789
128.689
128.135
126.440
77.388
77.070
76.752
32.217
28.412
22.484
14.044
2e
Z/E/H = 10.0 : 1 : 1.5
f1 (ppm)

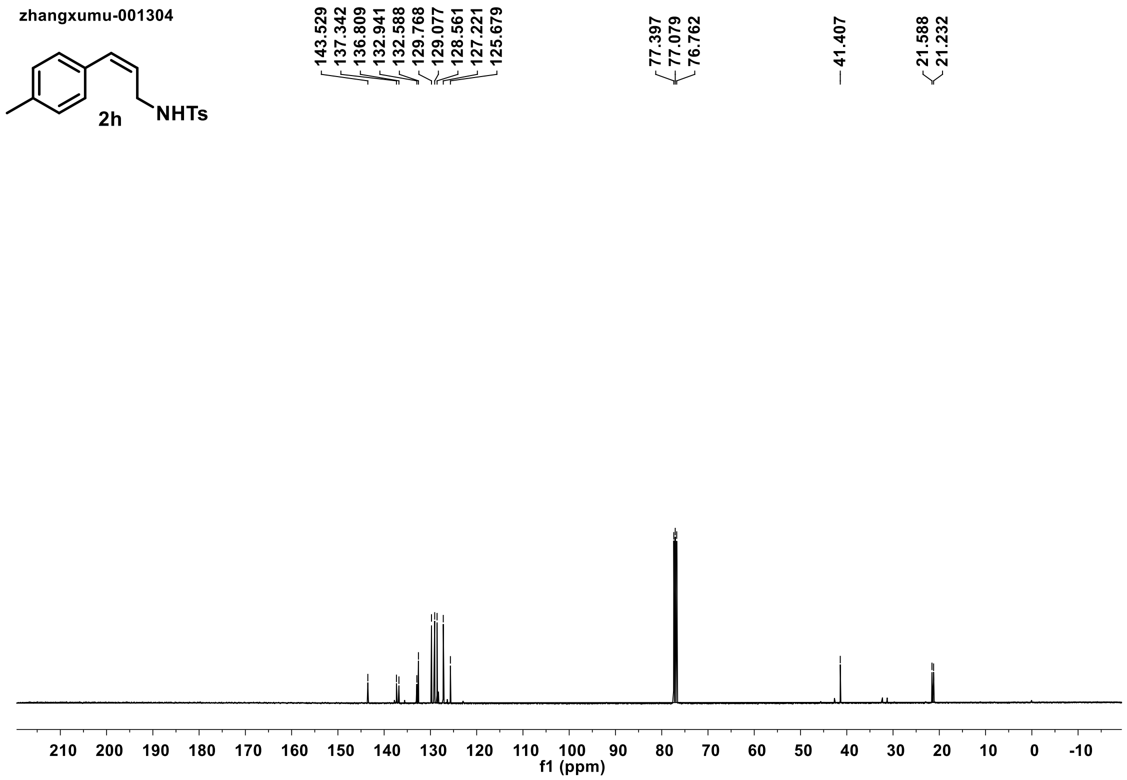

zhangxumu-001882
7.260
5.368
5.365
5.357
5.354
5.351
5.342
5.340
2.041
2.024
2.010
1.992
1.295
1.290
1.286
0.905
0.897
0.888
0.881
0.871
0.000
2f
2.00
4.13
13.73
6.58
f1 (ppm)

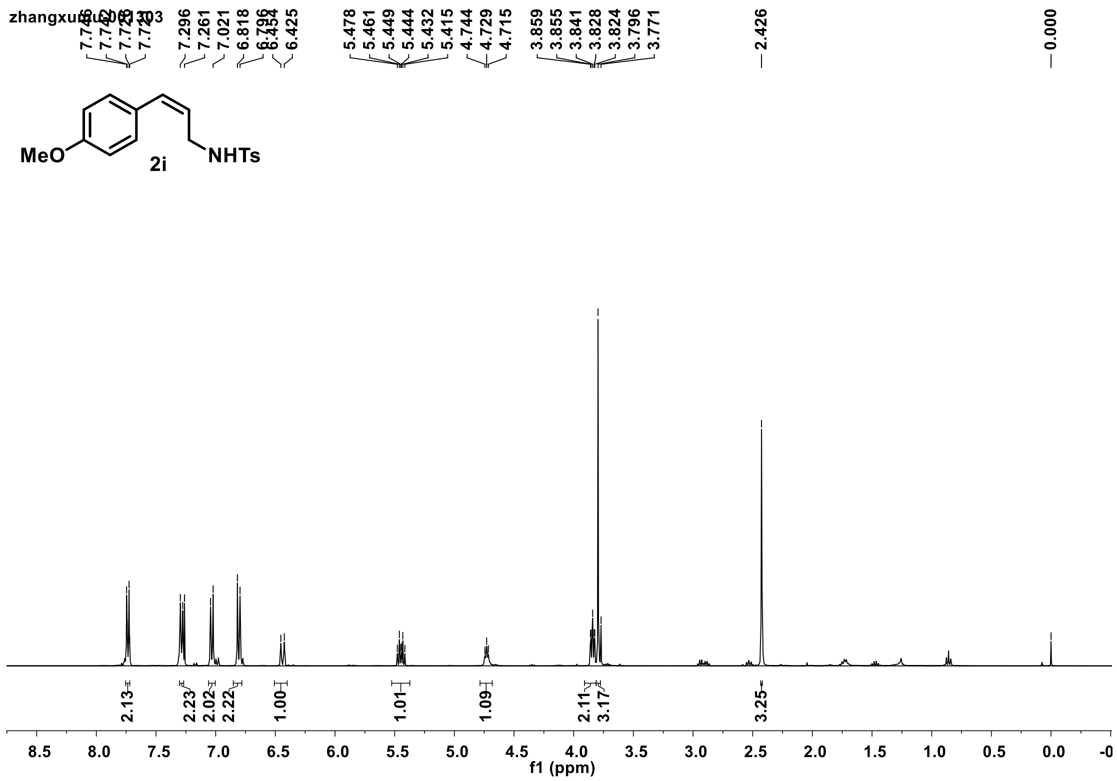

zhangxumu-001882
130.189
77.618
77.300
76.983
31.824
29.750
27.457
22.881
14.377
2f
f1 (ppm)

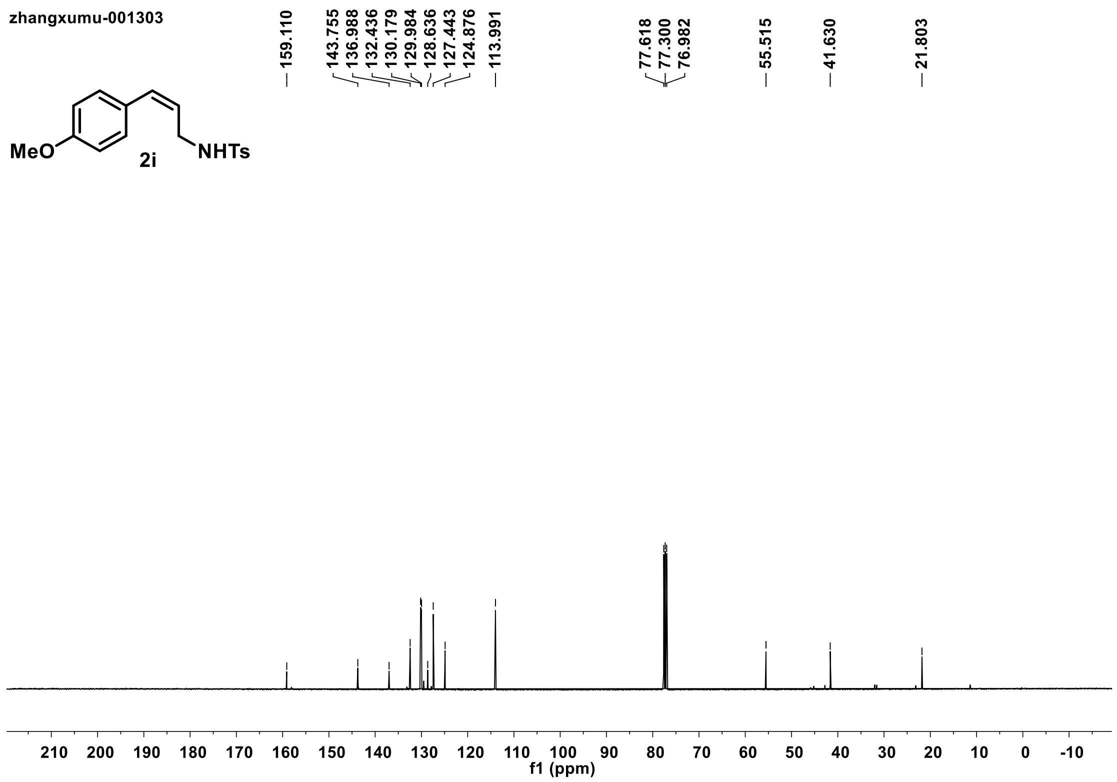


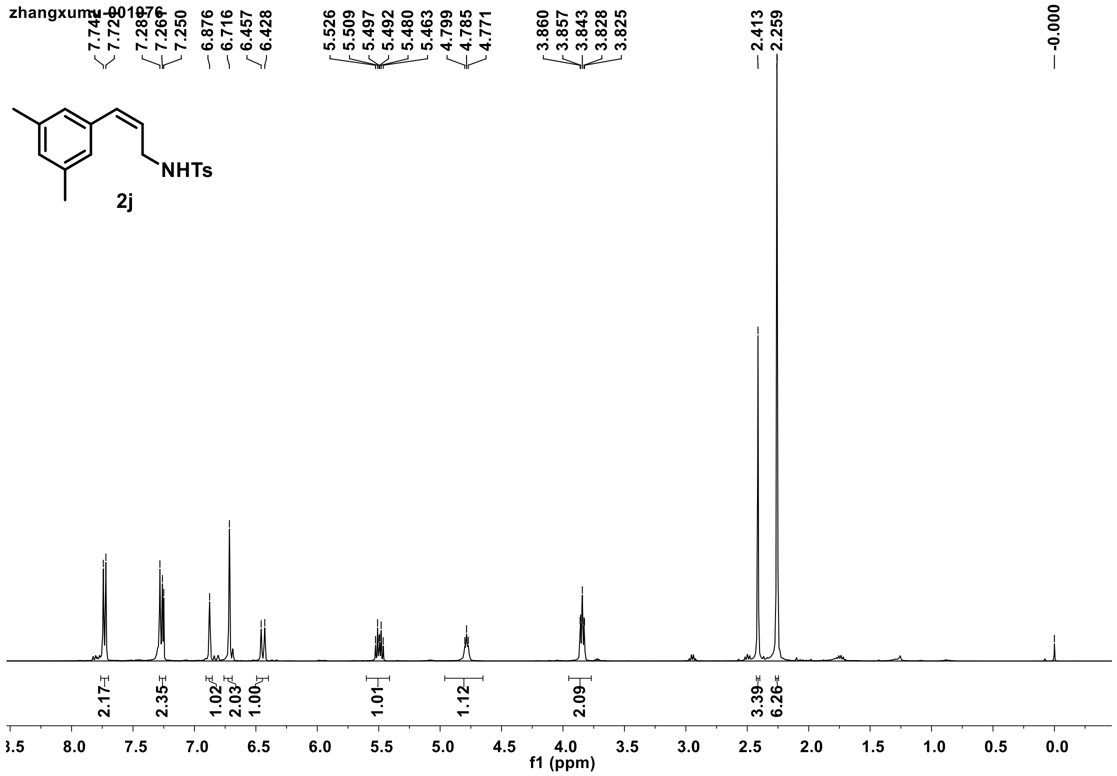


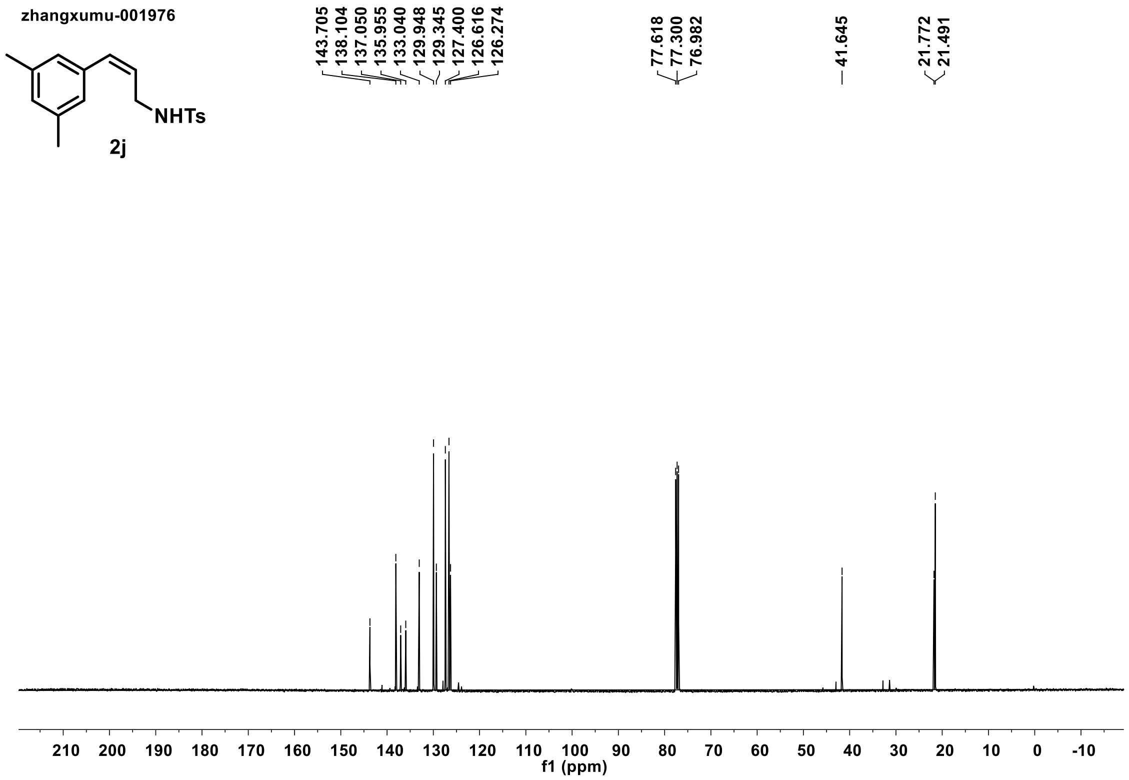

zhangxumu-001304
7.294
7.257
7.076
6.991
6.461
5.527
5.510
5.498
5.493
5.481
5.464
4.653
4.639
4.624
3.866
3.862
3.849
3.847
3.834
3.830
2.428
2.328
0.000
2h
NHTs
2.29
2.23
2.12
2.08
1.00
1.01
1.00
2.06
3.26
2.91
f1 (ppm)

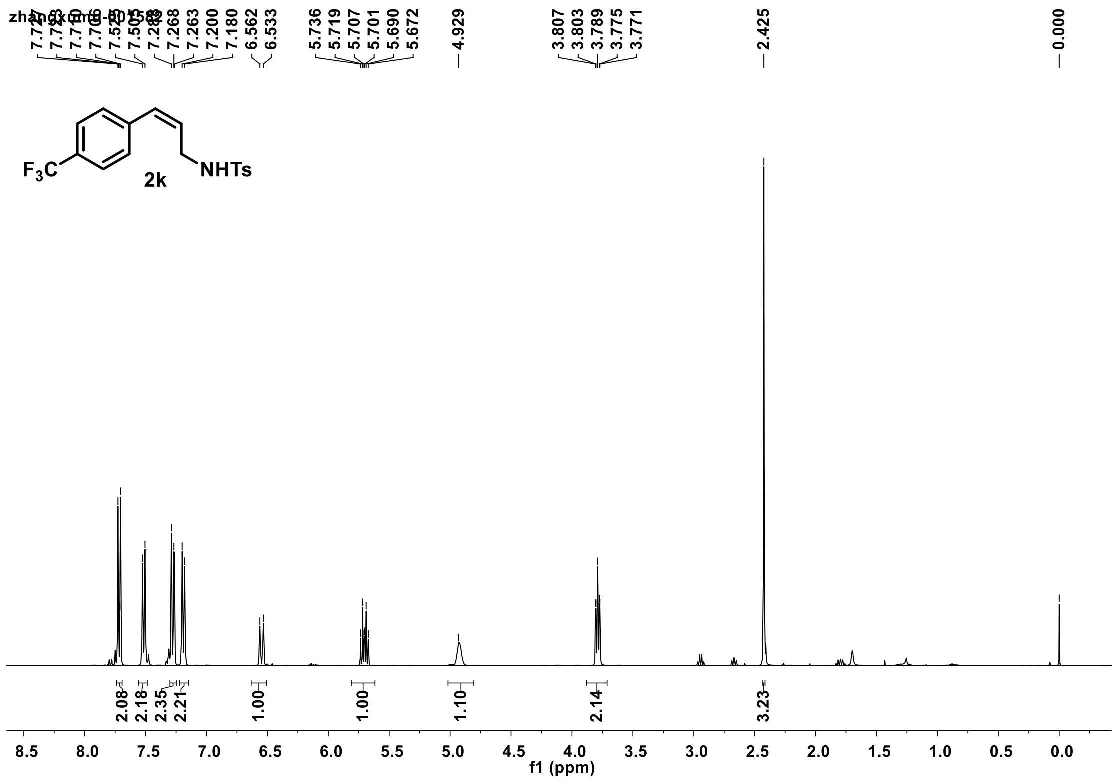

zhangxumu-001304
143.529
137.342
136.809
132.941
132.588
129.768
129.077
128.561
127.221
125.679
77.397
77.079
76.762
41.407
21.588
21.232
2h
NHTs
f1 (ppm)

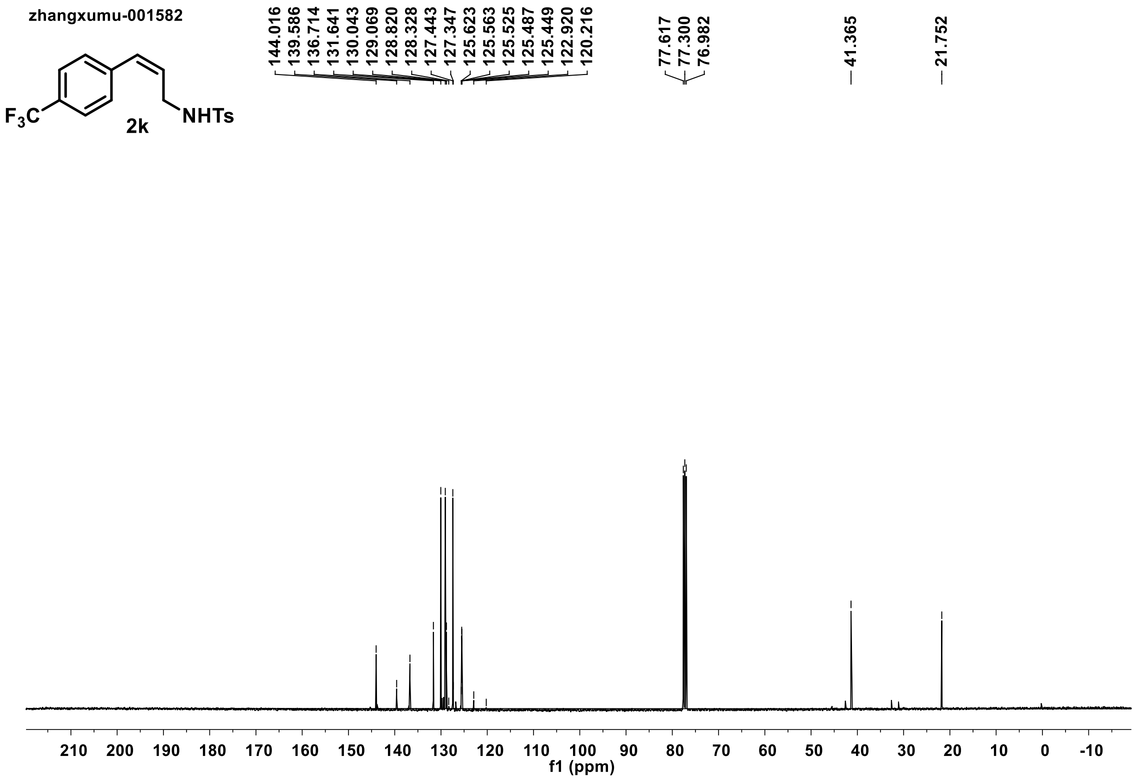

zhangxumu-001303
MeO
2i
NHTs
f1 (ppm)

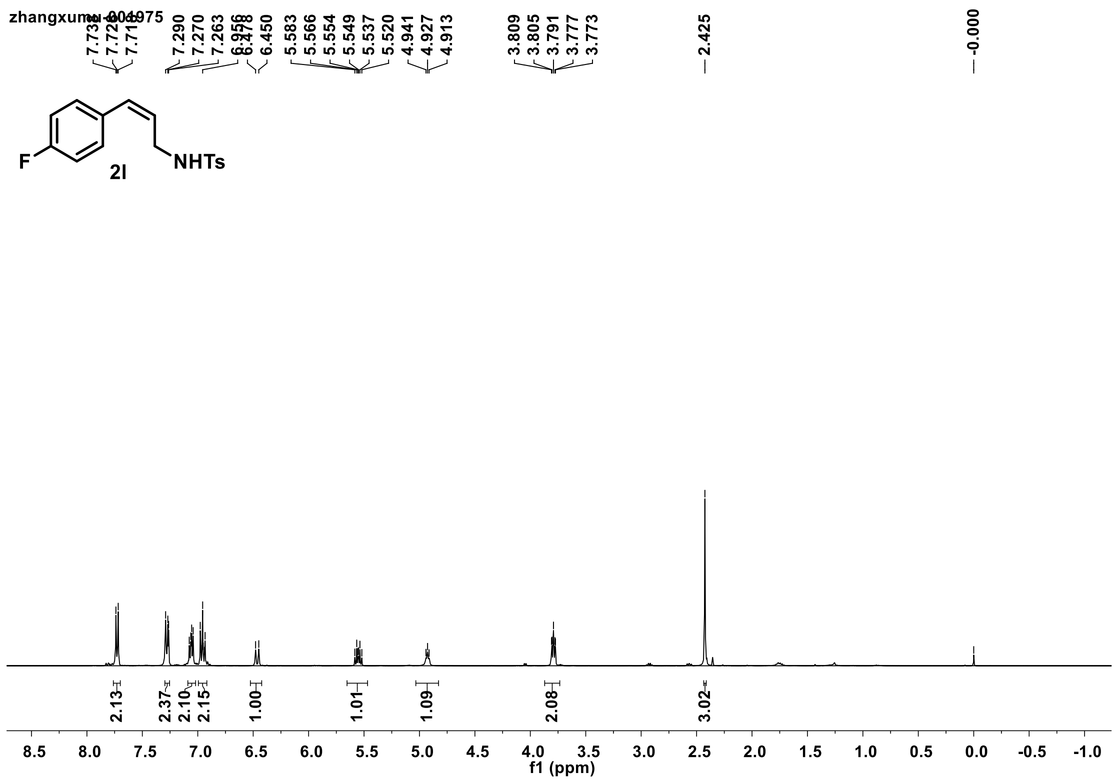

zhangxumu-001303
159.110
143.755
136.988
132.436
130.179
129.984
128.636
127.443
124.876
113.991
77.618
77.300
76.982
55.515
41.630
21.803
MeO
2i
NHTs
f1 (ppm)

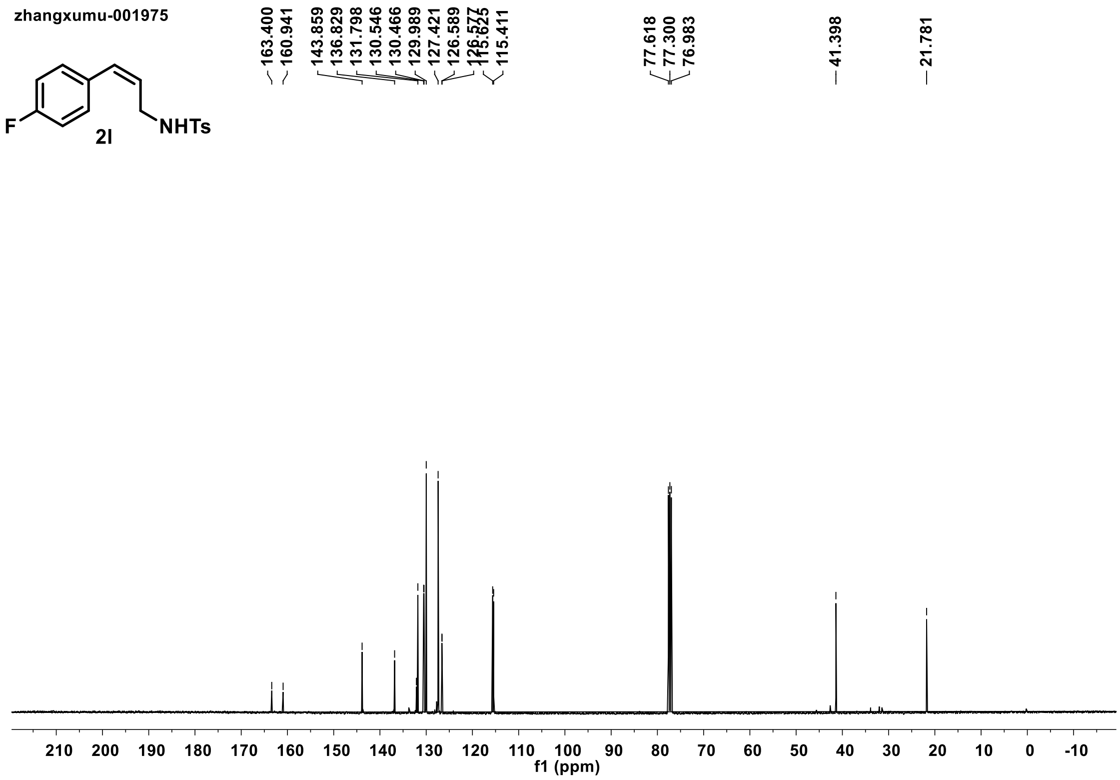

zhangxumu-001976
7.741
7.724
7.285
7.261
7.250
6.876
6.716
6.457
6.428
5.526
5.509
5.497
5.492
5.480
5.463
4.799
4.785
4.771
3.860
3.857
3.843
3.828
3.825
2.413
2.259
-0.000
NHTs
2j
2.17
2.35
1.02
2.03
1.00
1.01
1.12
2.09
3.39
6.26
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

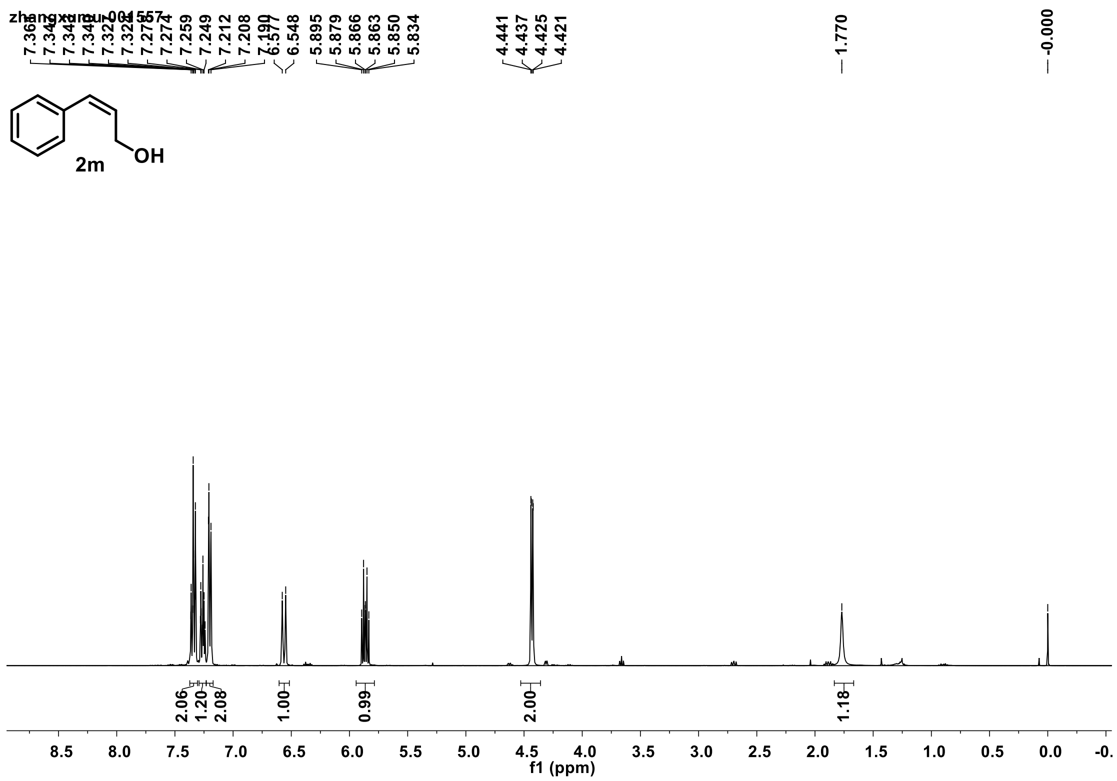

zhangxumu-001976
143.705
138.104
137.050
135.955
133.040
129.948
129.345
127.400
126.616
126.274
77.618
77.300
76.982
41.645
21.772
21.491
NHTs
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

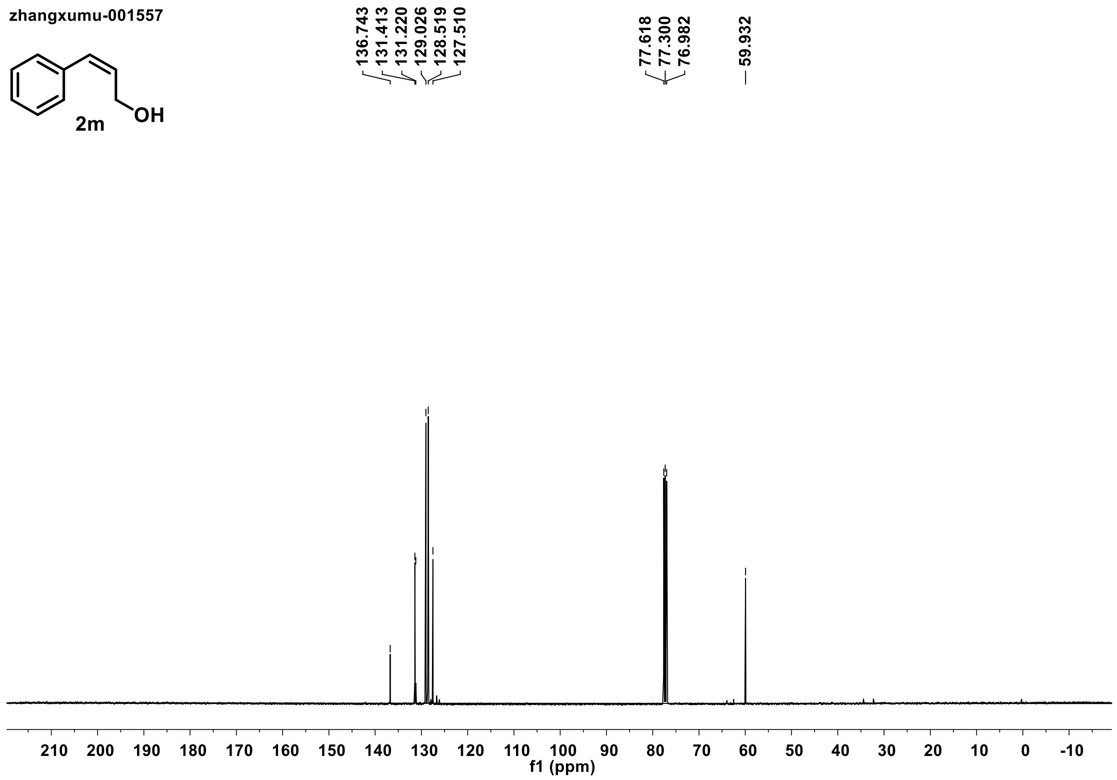

7.268
7.263
7.200
7.180
6.562
6.533
5.736
5.719
5.707
5.701
5.690
5.672
4.929
3.807
3.803
3.789
3.775
3.771
2.425
0.000
F_3C
2k
NHTs
2.08
2.18
2.35
2.21
1.00
1.00
1.10
2.14
3.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

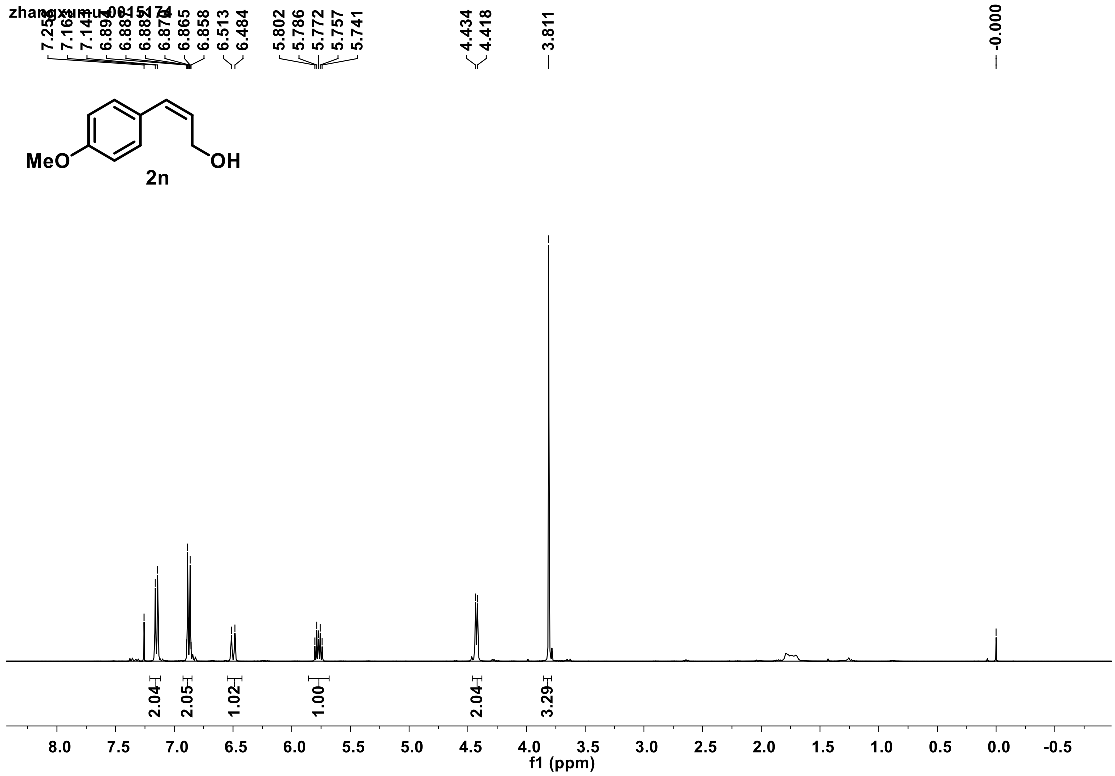

zhangxumu-001582
144.016
139.586
136.714
131.641
130.043
129.069
128.820
128.328
127.443
127.347
125.623
125.563
125.525
125.487
125.449
122.920
120.216
77.617
77.300
76.982
41.365
21.752
F_3C
2k
NHTs
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

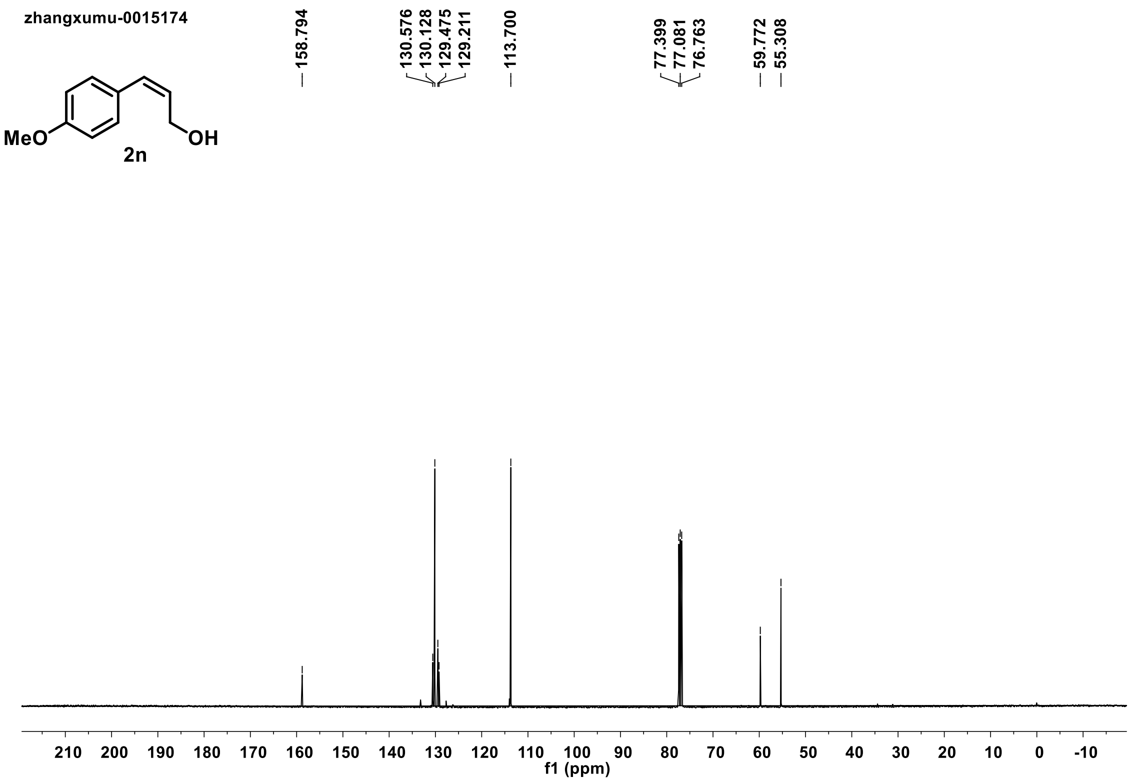

zhangxumu-001975
7.290
7.270
7.263
6.450
5.583
5.566
5.554
5.549
5.537
5.520
4.941
4.927
4.913
3.809
3.805
3.791
3.777
3.773
2.425
-0.000
F
NHTs
2l
2.13
2.37
2.10
2.15
1.00
1.01
1.09
2.08
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

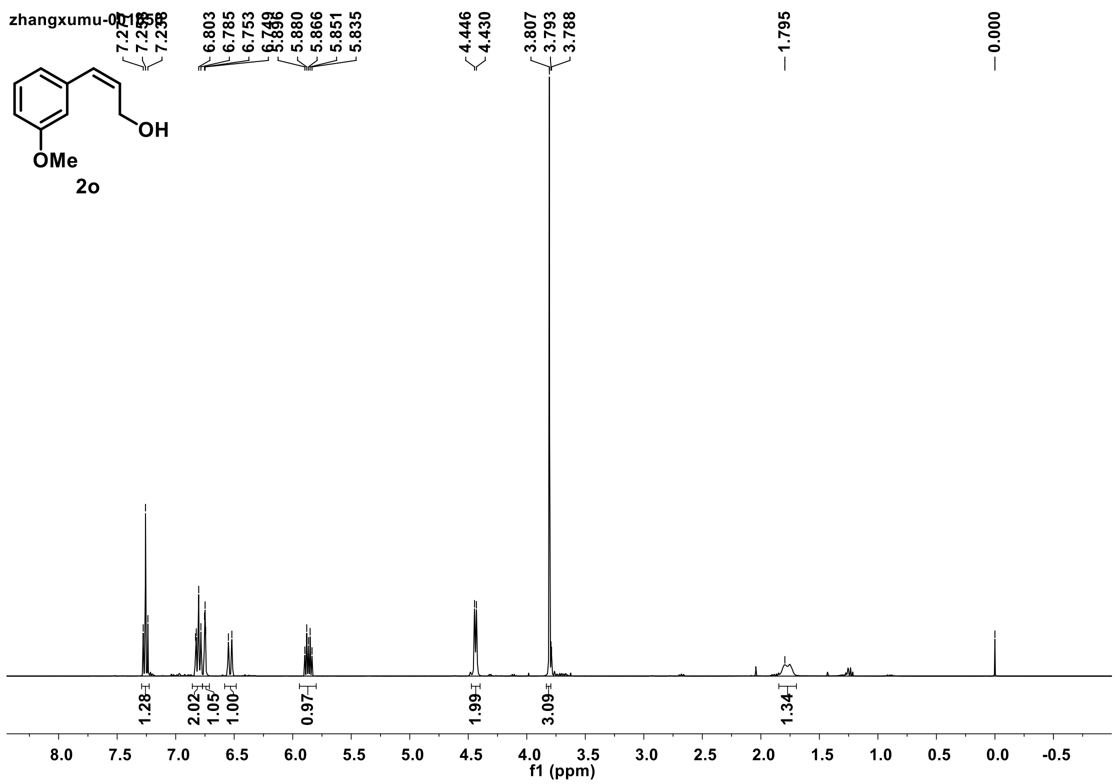

zhangxumu-001975
163.400
160.941
143.859
136.829
131.798
130.546
130.466
129.989
127.421
126.589
115.625
115.411
77.618
77.300
76.983
41.398
21.781
F
NHTs
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

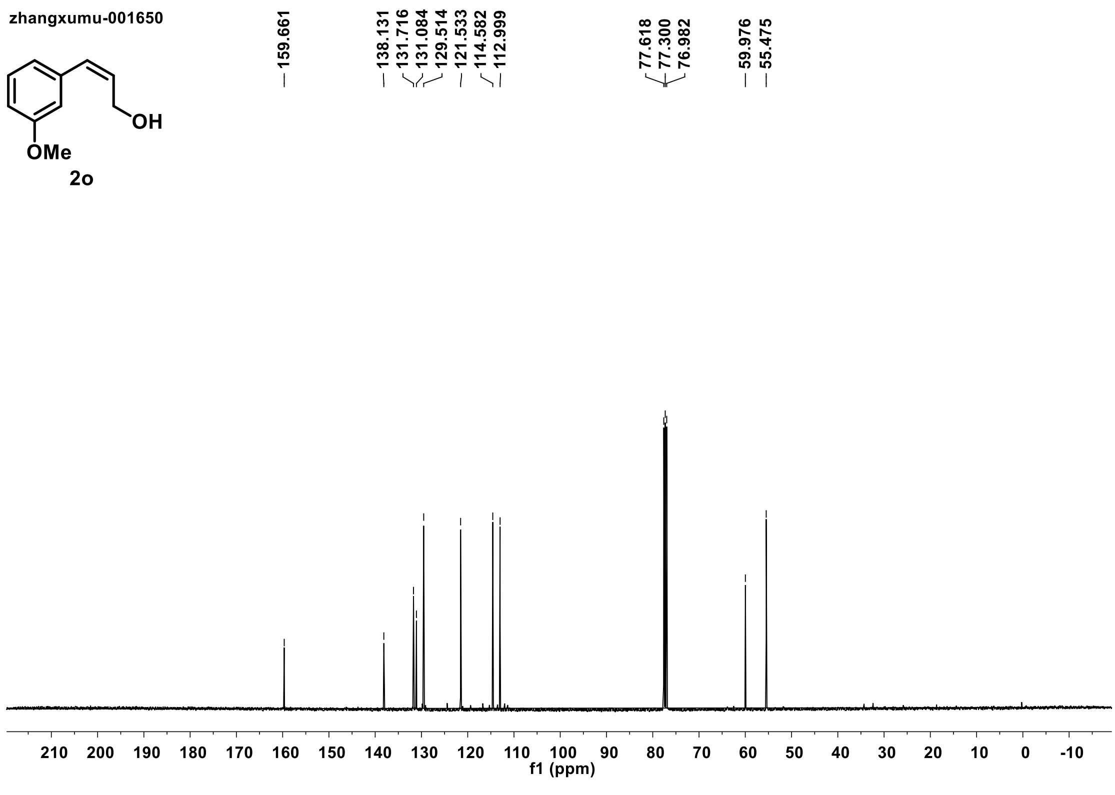

zhangxumu-001557
2m
OH
7.360
7.342
7.341
7.340
7.321
7.320
7.278
7.274
7.259
7.249
7.212
7.208
7.190
6.577
6.548
5.895
5.879
5.866
5.863
5.850
5.834
4.441
4.437
4.425
4.421
1.770
-0.000
2.06
1.20
2.08
1.00
0.99
2.00
1.18
f1 (ppm)

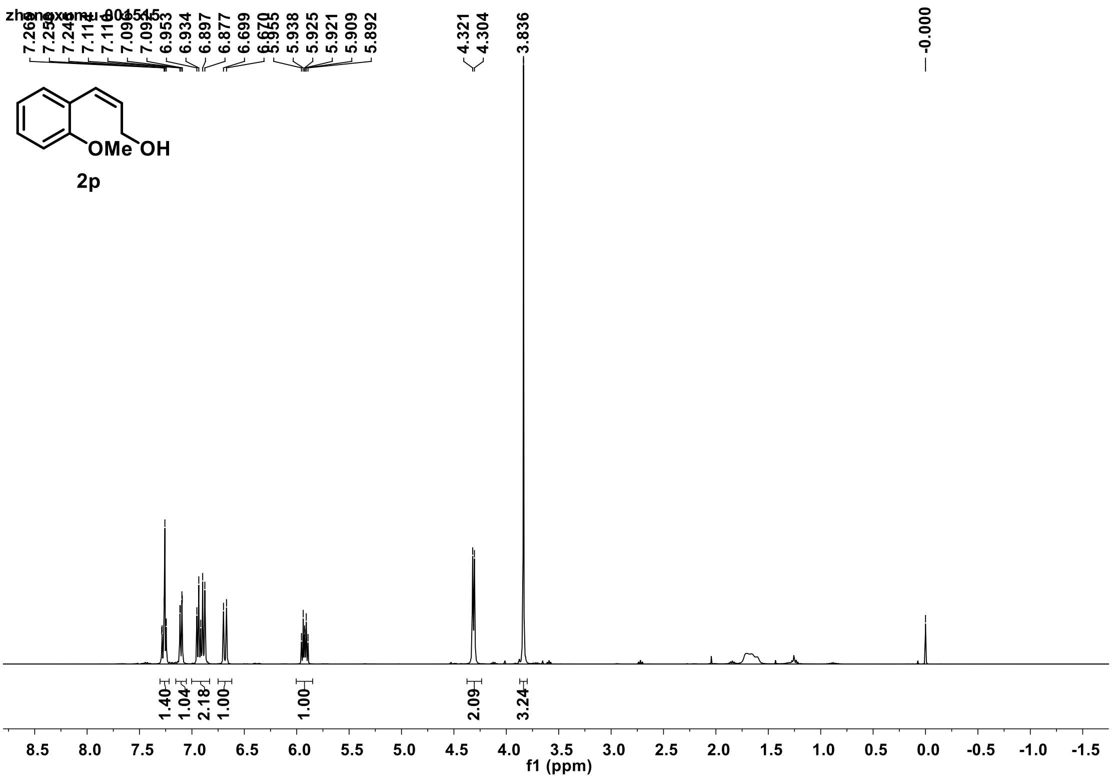

zhangxumu-001557
2m
OH
136.743
131.413
131.220
129.026
128.519
127.510
77.618
77.300
76.982
59.932
f1 (ppm)


zhangxumu-0015174
6.874
6.865
6.858
6.513
6.484
5.802
5.786
5.772
5.757
5.741
4.434
4.418
3.811
-0.000
MeO
OH
2n
2.04
2.05
1.02
1.00
2.04
3.29
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

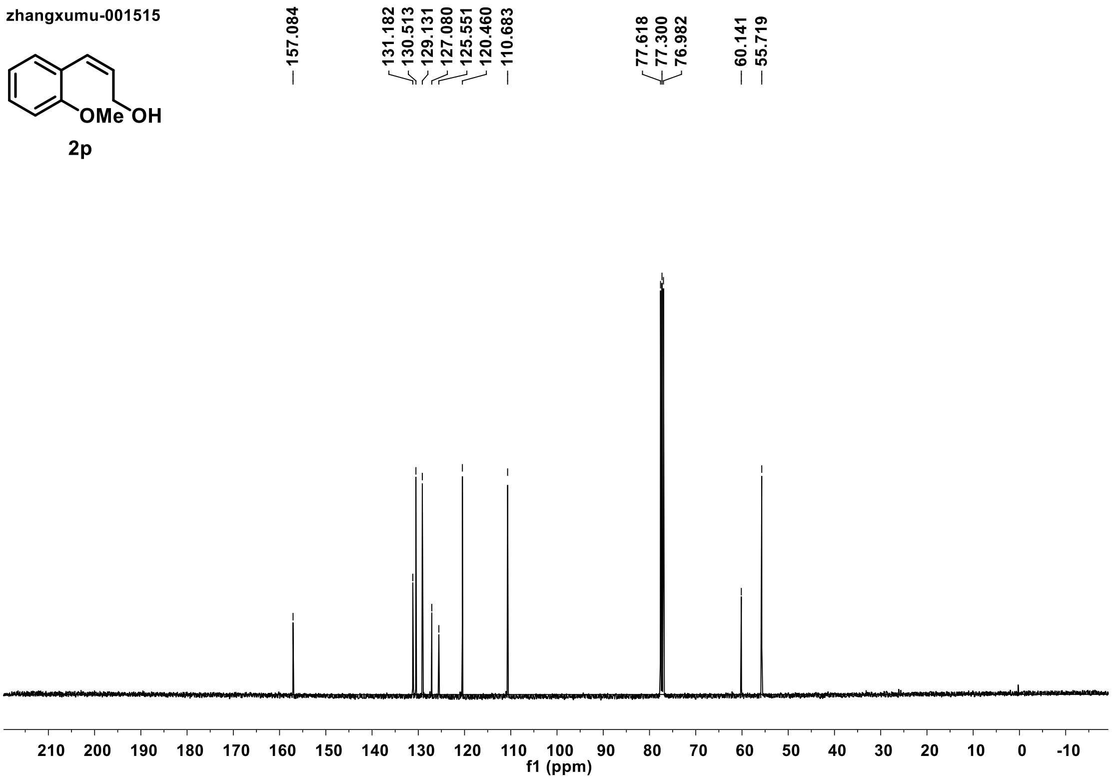

zhangxumu-0015174
158.794
130.576
130.128
129.475
129.211
113.700
77.399
77.081
76.763
59.772
55.308
MeO
OH
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


zhangxumu-001650
7.271
7.255
7.239
6.803
6.785
6.753
6.749
5.896
5.880
5.866
5.851
5.835
4.446
4.430
3.807
3.793
3.788
1.795
0.000
OH
OMe
2o
1.28
2.02
1.05
1.00
0.97
1.99
3.09
1.34
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

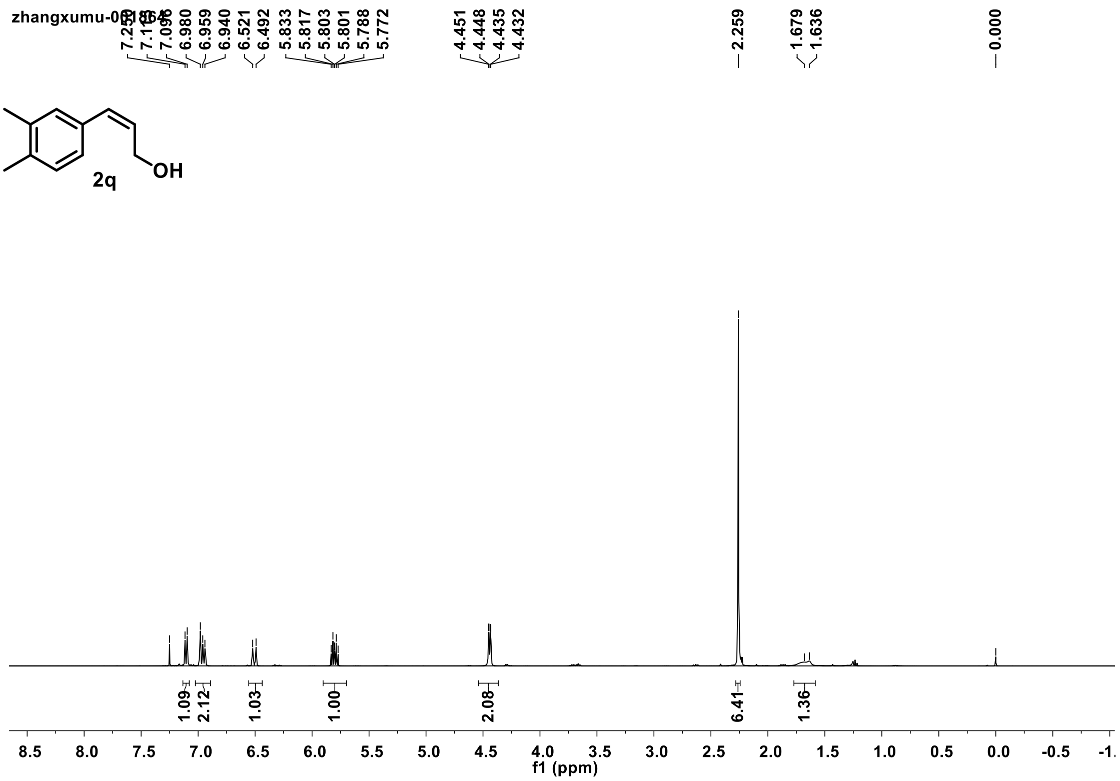

zhangxumu-001650
159.661
138.131
131.716
131.084
129.514
121.533
114.582
112.999
77.618
77.300
76.982
59.976
55.475
OH
OMe
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

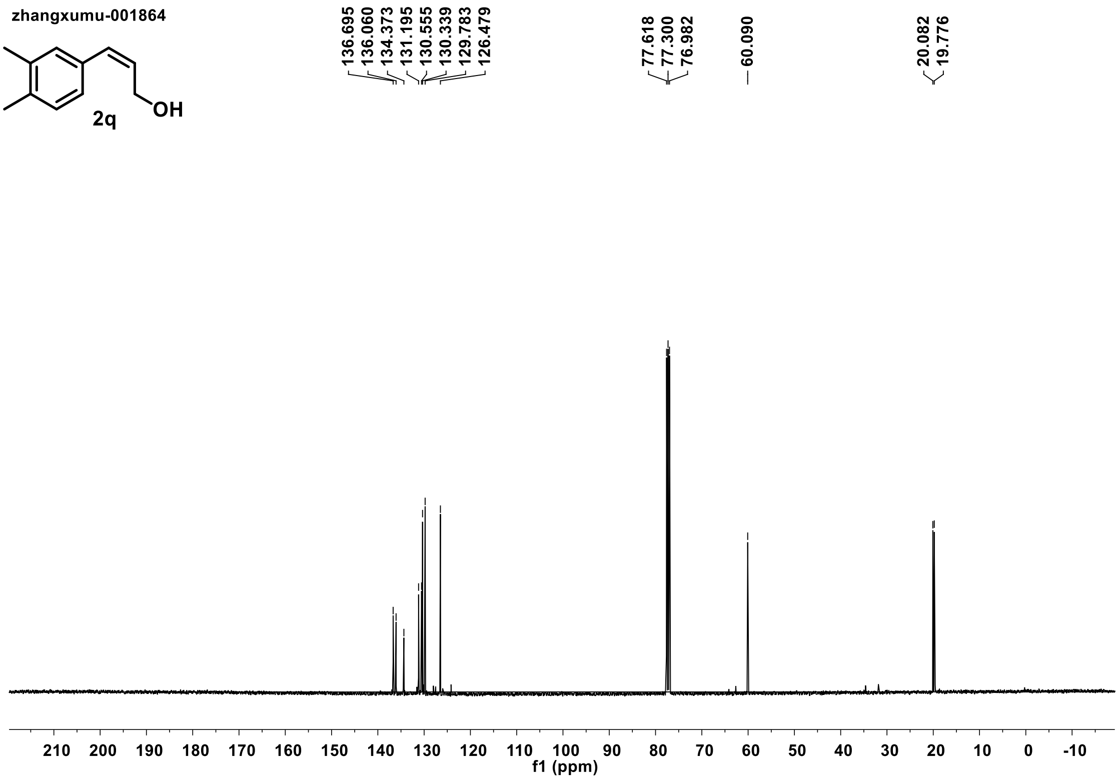

zhangxumu-001515
6.953
6.934
6.897
6.877
6.699
6.670
5.955
5.938
5.925
5.921
5.909
5.892
4.321
4.304
3.836
-0.000
OMe
OH
1.40
1.04
2.18
1.00
1.00
2.09
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

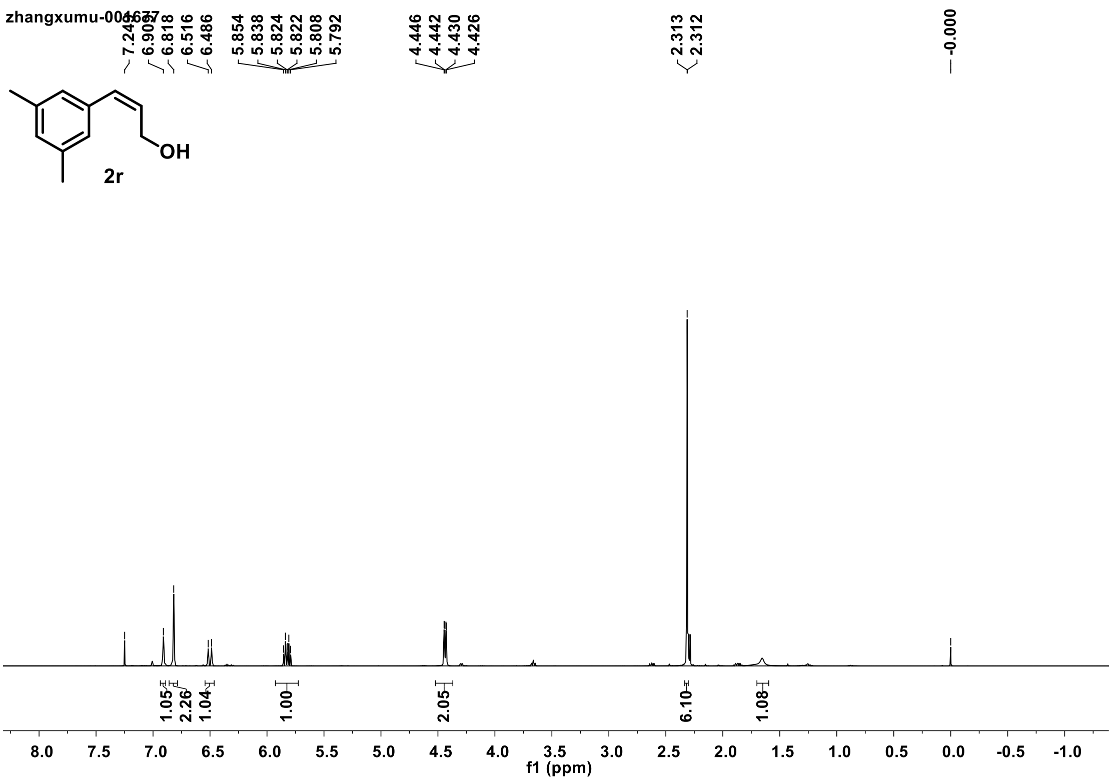
2p

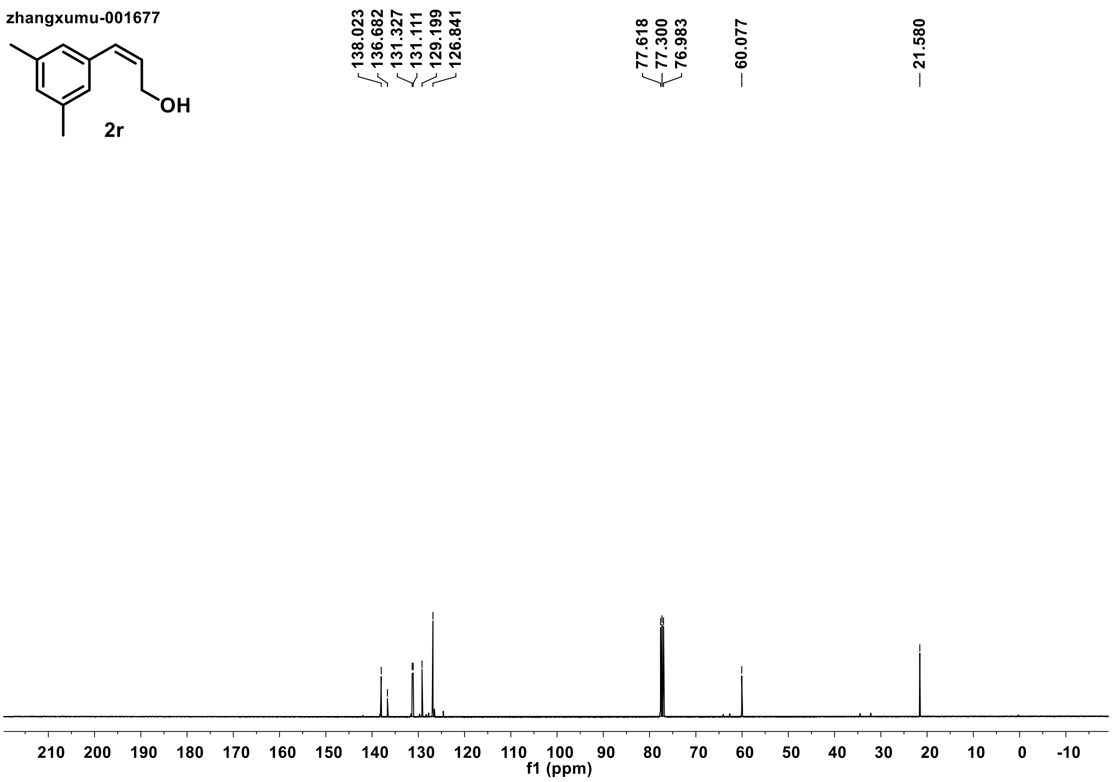

zhangxumu-001515
157.084
131.182
130.513
129.131
127.080
125.551
120.460
110.683
77.618
77.300
76.982
60.141
55.719
OMe
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

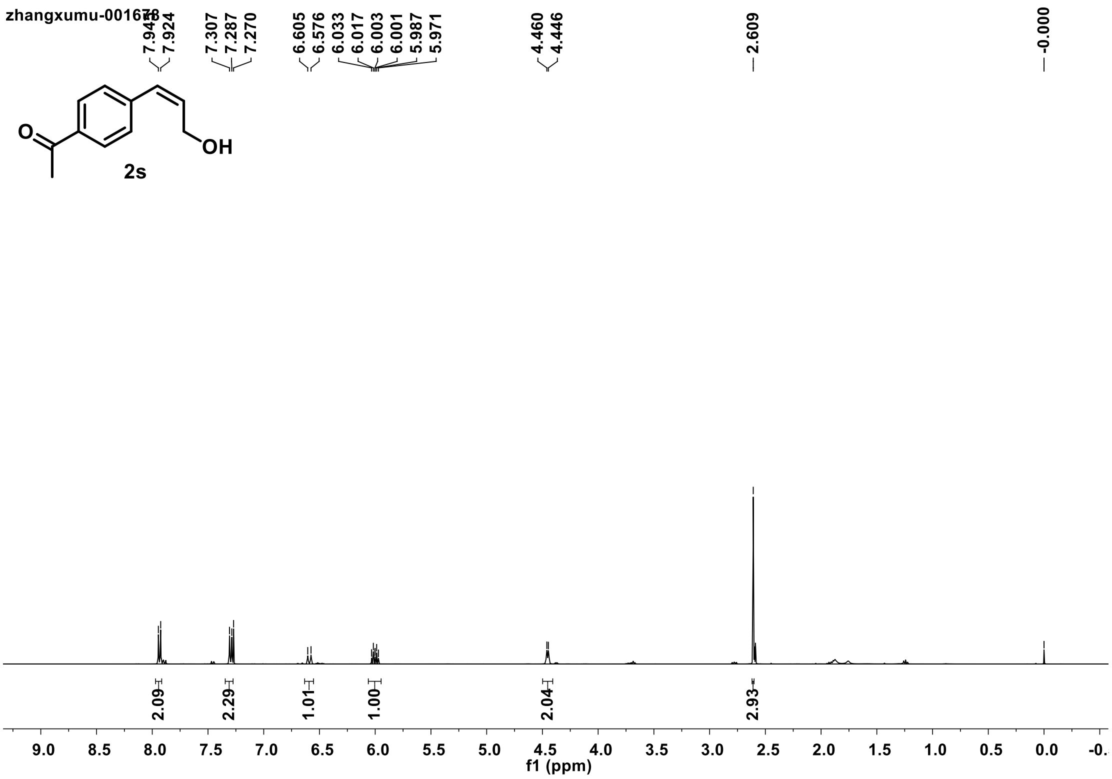
2p

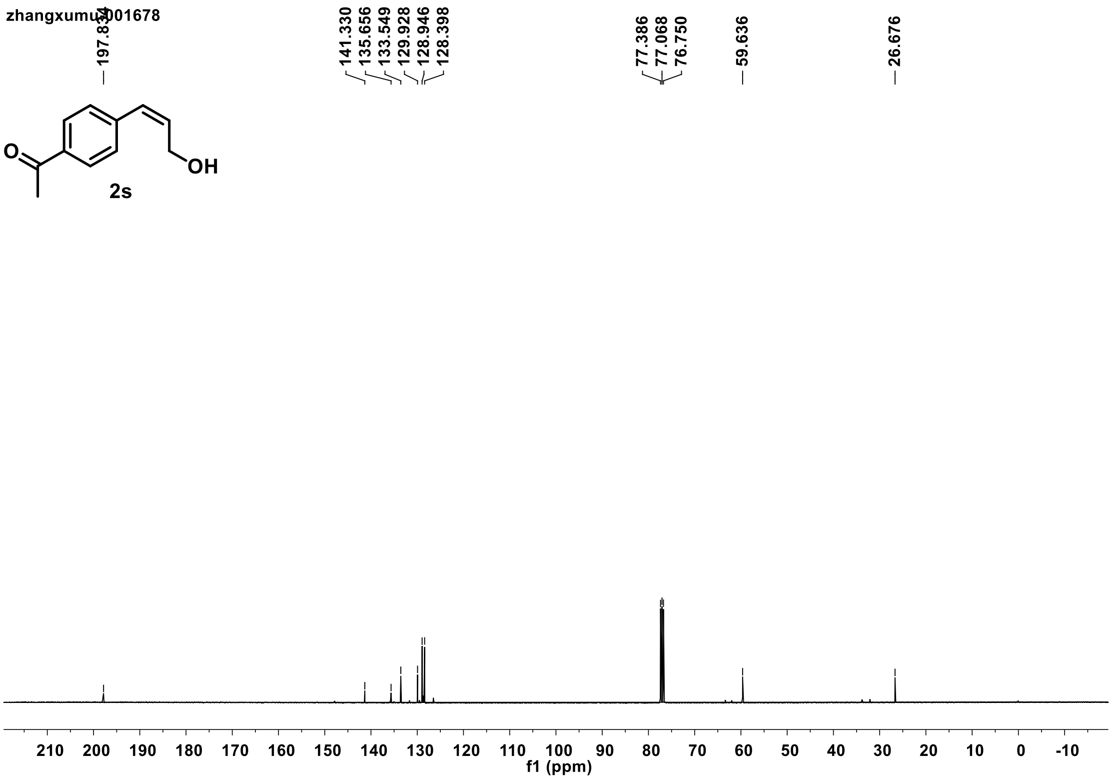

zhangxumu-001864
2q
OH
4.451
4.448
4.435
4.432
2.259
1.679
1.636
0.000
f1 (ppm)

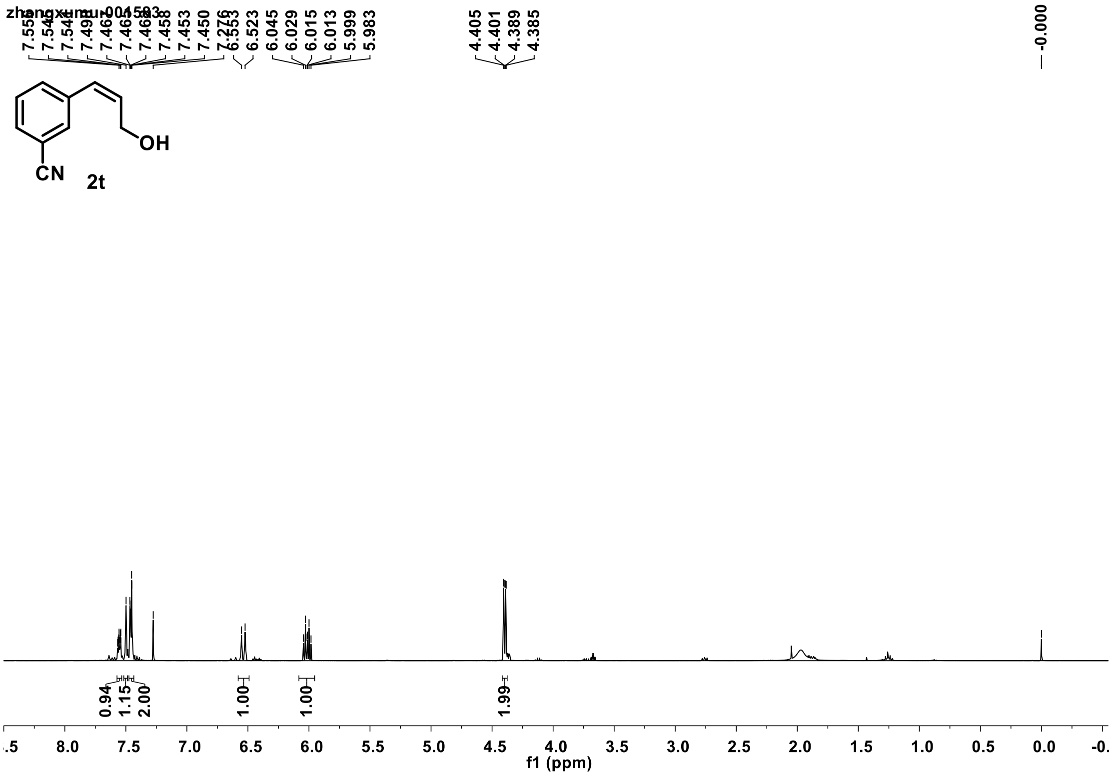

zhangxumu-001864
2q
OH
136.695
136.060
134.373
131.195
130.555
130.339
129.783
126.479
77.618
77.300
76.982
60.090
20.082
19.776
f1 (ppm)

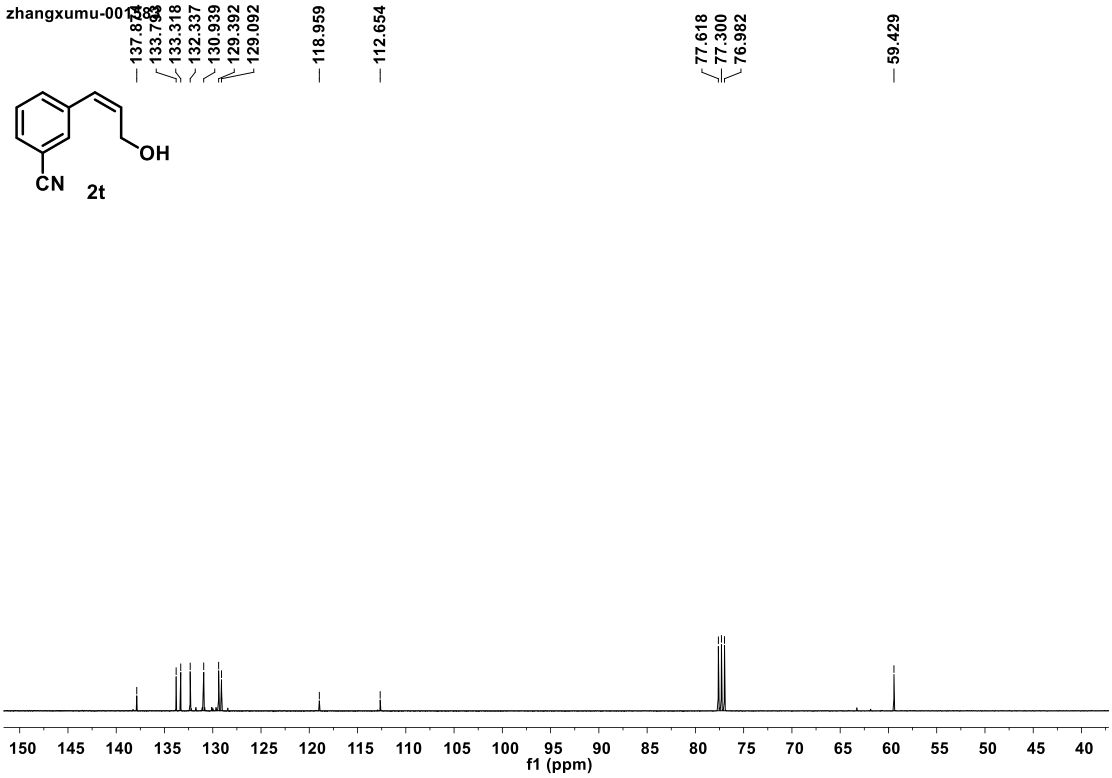

zhangxumu-001677
7.249
6.909
6.818
6.516
6.486
5.854
5.838
5.824
5.822
5.808
5.792
4.446
4.442
4.430
4.426
2.313
2.312
-0.000
OH
2r
1.05
2.26
1.04
1.00
2.05
6.10
1.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


zhangxumu-001677
138.023
136.682
131.327
131.111
129.199
126.841
77.618
77.300
76.983
60.077
21.580
OH
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

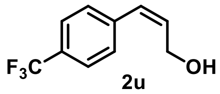

zhangxumu-001678
7.940
7.924
7.307
7.287
7.270
6.605
6.576
6.033
6.017
6.003
6.001
5.987
5.971
4.460
4.446
2.609
-0.000
O
OH
2s
2.09
2.29
1.01
1.00
2.04
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


zhangxumu-001678
197.834
141.330
135.656
133.549
129.928
128.946
128.398
77.386
77.068
76.750
59.636
26.676
O
OH
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

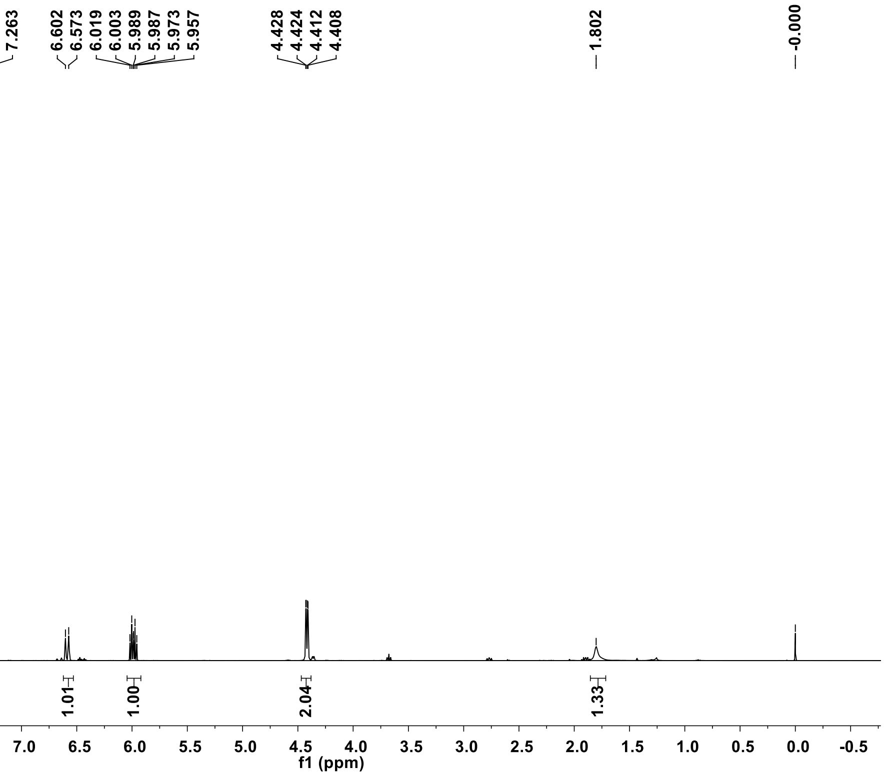

zhangxumu-001593
7.458
7.453
7.450
7.276
6.553
6.523
6.045
6.029
6.015
6.013
5.999
5.983
4.405
4.401
4.389
4.385
-0.000
OH
CN
2t
0.94
1.15
2.00
1.00
1.00
1.99
f1 (ppm)


137.874
133.318
132.337
130.939
129.392
129.092
118.959
112.654
77.618
77.300
76.982
59.429
OH
CN
2t
f1 (ppm)

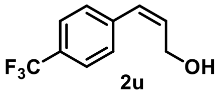
zhangxumu-001649



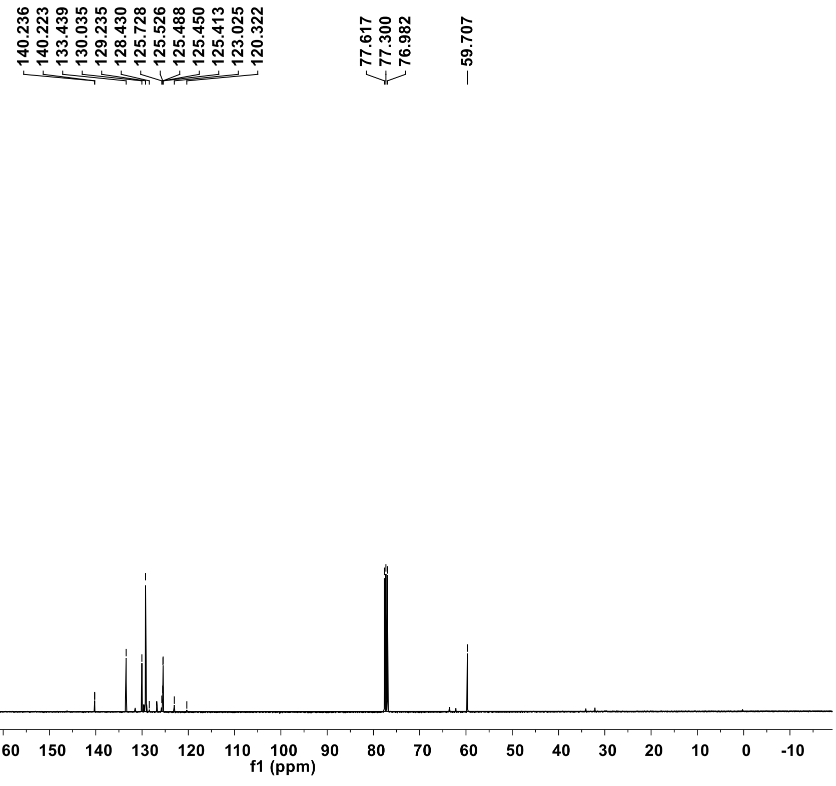
2u

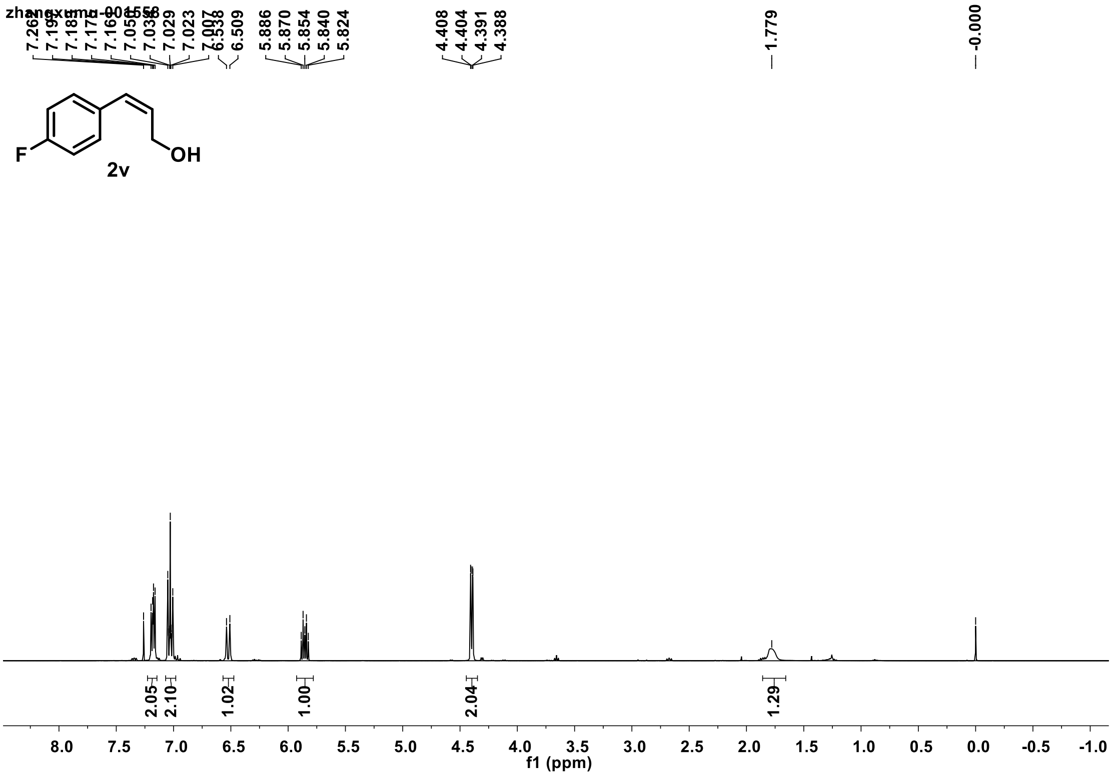


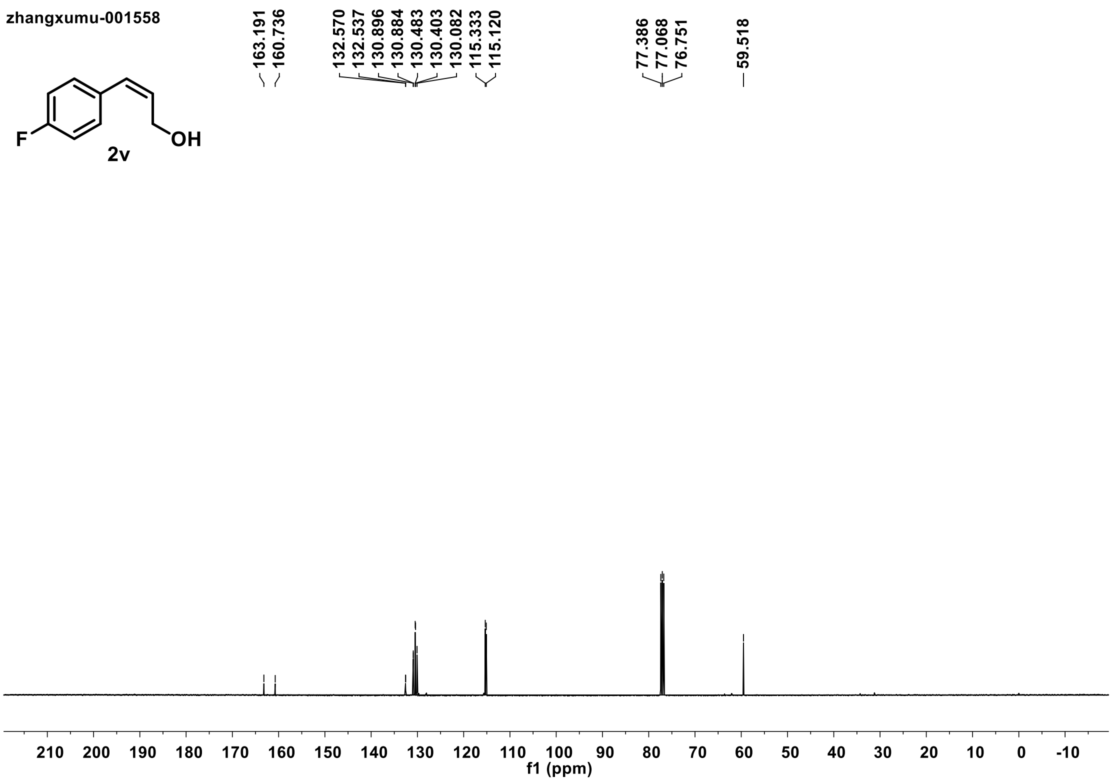
zhangxumu-001649

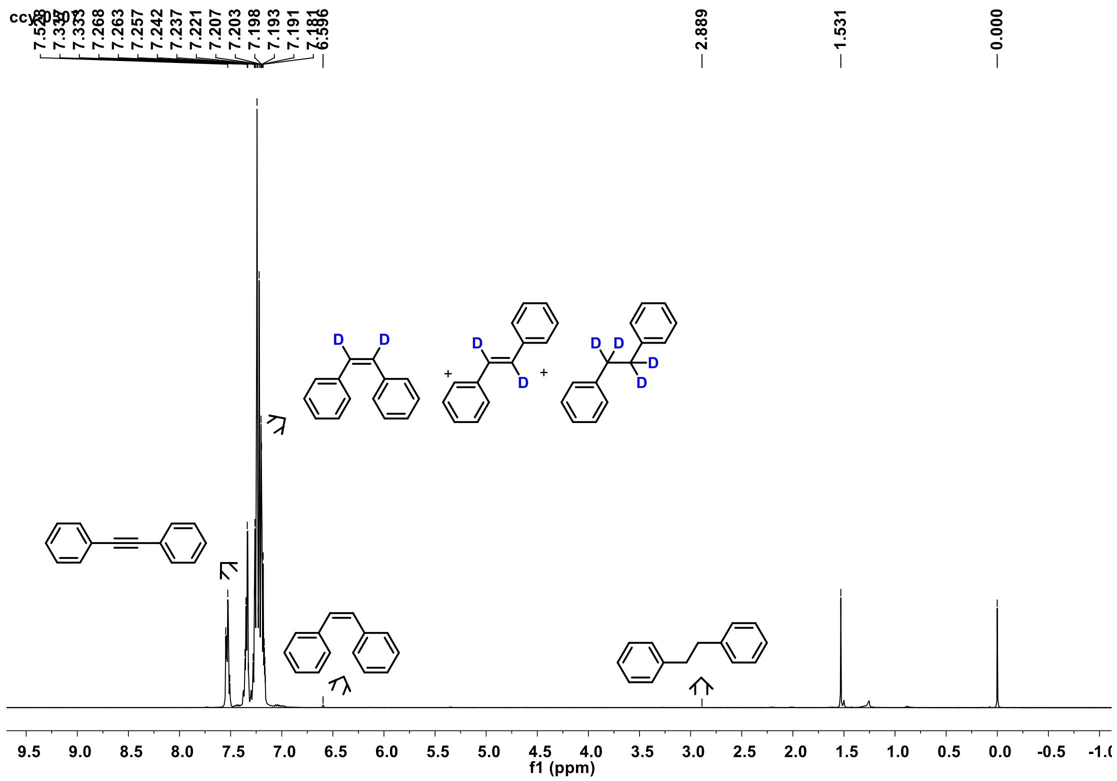


2u




zhangxumu-001558
7.029
7.023
6.538
6.509
5.886
5.870
5.854
5.840
5.824
4.408
4.404
4.391
4.388
1.779
-0.000
F
OH
2v
2.05
2.10
1.02
1.00
2.04
1.29
f1 (ppm)


zhangxumu-001558
163.191
160.736
132.570
132.537
130.896
130.884
130.483
130.403
130.082
115.333
115.120
77.386
77.068
76.751
59.518
F
OH
2v
f1 (ppm)


ccy0301
7.537
7.527
7.337
7.333
7.268
7.263
7.257
7.242
7.237
7.221
7.207
7.203
7.198
7.193
7.191
7.181
6.596
2.889
1.531
0.000
D
D
+
D
D
+
D
D
D
D
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

References

1. Z. Zhang, Q. Wang, C. Chen, Z. Han, X.-Q. Dong, X. Zhang, *Org. Lett.*, **2016**, *18* 3290–3293.
2. B. Prabagar, S. Nayak, R. Prasad, A. K. Sahoo, *Org. Lett.*, **2016**, *18*, 3066–3069.
3. Y.-F. Qiu, F. Yang, Z.-H. Qiu, M.-J. Zhong, L.-J. Wang, Y.-Y. Ye, B. Song, Y.-M. Liang, *J. Org. Chem.*, **2013**, *78*, 12018–12028.