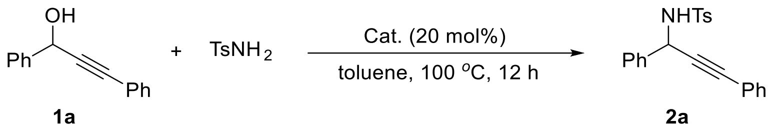
Supporting Information

Alkynyl Borrowing: Silver Catalyzed Amination of Secondary Propargylic Alcohols via C(sp^3)-C(sp) Bond Cleavage

Xin Zhuang, Min Zhu, Chuan-Ming Hong, Zhen Luo, Wan-Fang Li, Qing-Hua Li, Qun-Li Luo* and Tang-Lin Liu*

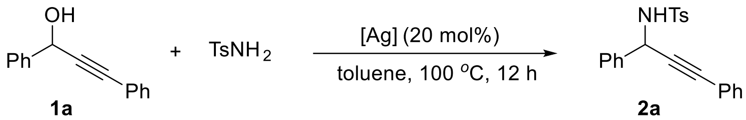
1. Optimization of reaction conditions

Table S1. Screening of different metals.



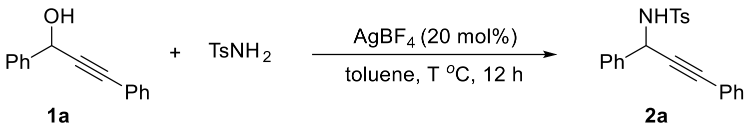
Entry[ ]	Cat.	Yield (%)
1	$Pd(acac)_2$	Trace
2	$[Rh(OH)(COD)]_2$	Trace
3	$Cu(OAc)_2{\cdot}H_2O$	33
4	$\mathbf{AgBF_4}$	**76**

Table S2. Screening of different silver.



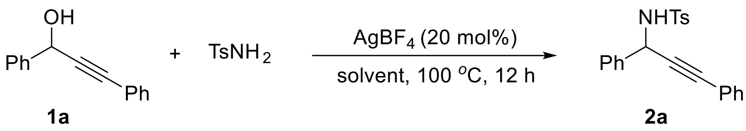
Entry	[Ag]	Yield (%)
1	$AgSbF_6$	ND
2	AgOTf	ND
3	AgOAc	NR
4	Ag_2CO_3	NR
5	$AgCO_2CF_3$	27
6	$AgPF_6$	65
7	$\mathbf{AgBF_4}$	**76**

Table S3. Screening of the temperature.



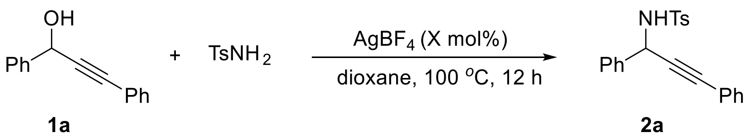
Entry	T (^oC)	Yield (%)
1	**100**	**76**
2	70	60
3	50	49

Table S4. Screening of the solvent.



Entry	Solvent	Yield (%)
1	HFIP	ND
2	DMF	trace
3	*p*-xylene	trace
4	*o*-xylene	78
5	MeCN	19
6	THF	50
7	**dioxane**	**86**

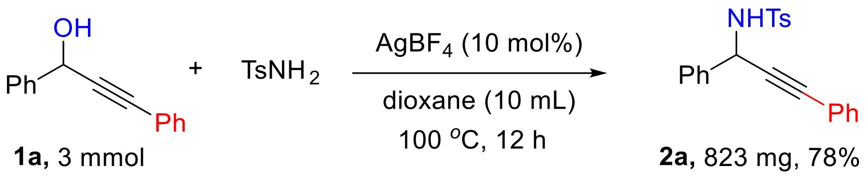
Table S5. Screening of different amounts of catalyst.



Entry	X(mol%)	Yield (%)
1	**10**	**82**
2	5	75
3	2	70

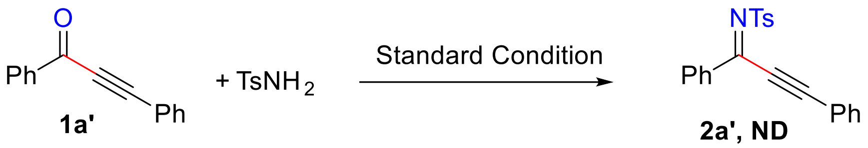
2. Mechanistic Studies

a. Gram-scale reaction



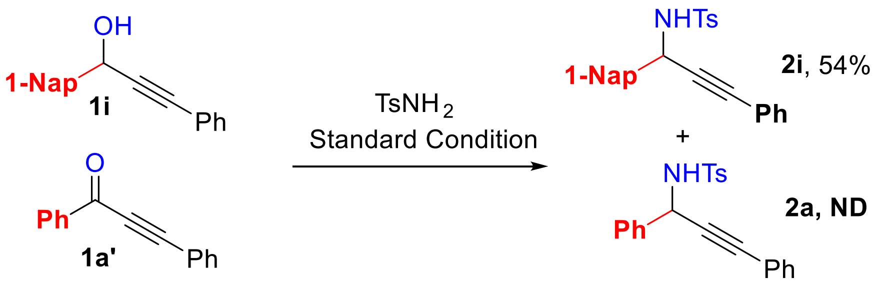
To a vial equipped with a dried stir bar was added **1a** (3 mmol), $TsNH_2$ (3.6 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (10 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C for 12 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to give **2a** with the yield of 78%.

b. Rule out the mechanism of hydron borrowing



To a vial equipped with a dried stir bar was added **1a’** (0.1 mmol), $TsNH_2$ (0.12 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C for 12 hours. The desired product **2a’** was not detected.

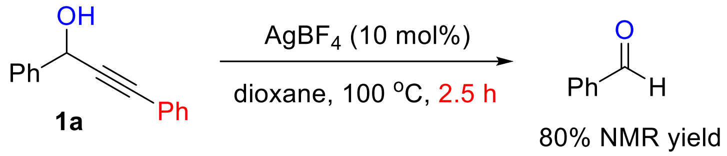
c. Rule out the mechanism of hydrogen borrowing



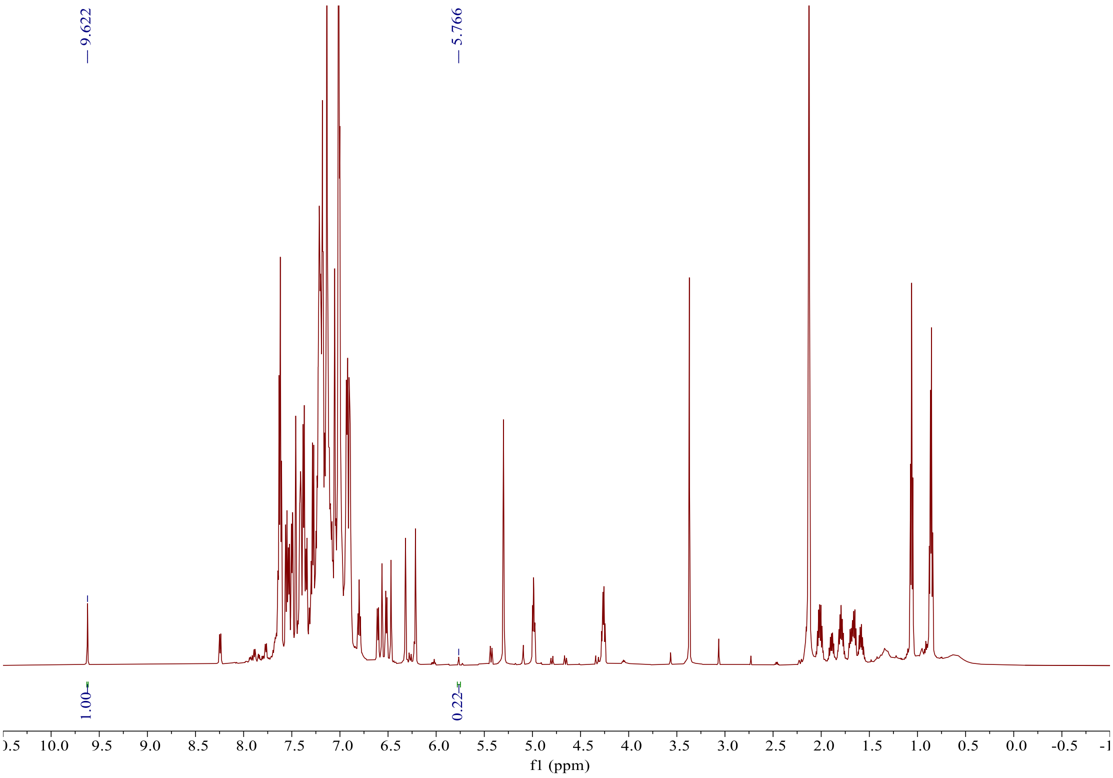
To a vial equipped with a dried stir bar was added **1i** (0.1 mmol) and **1a’** (0.1 mmol), $TsNH_2$ (0.12 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C for 12 hours. **2i** and **2a** was used to contrast with the reaction mixture by TLC. The desired product **2a** was not detected and **2i** was isolated with the yield of 54%.

Reactions b. and c. could rule out the mechanism of hydrogen borrowing.

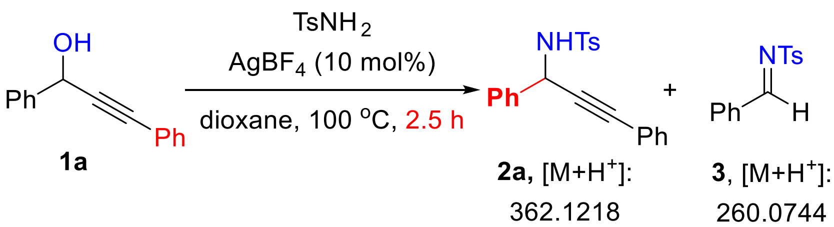
d. To verify the cleavage of Csp^3-Csp bond



To a vial equipped with a dried stir bar was added **1a** (0.1 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C for 2.5 hours. The ratio of aldehyde and **1a** was 1.00:0.22, which proved the cleavage of Csp^3-Csp bond could taken place with silver.



e. Monitor the existence of imine



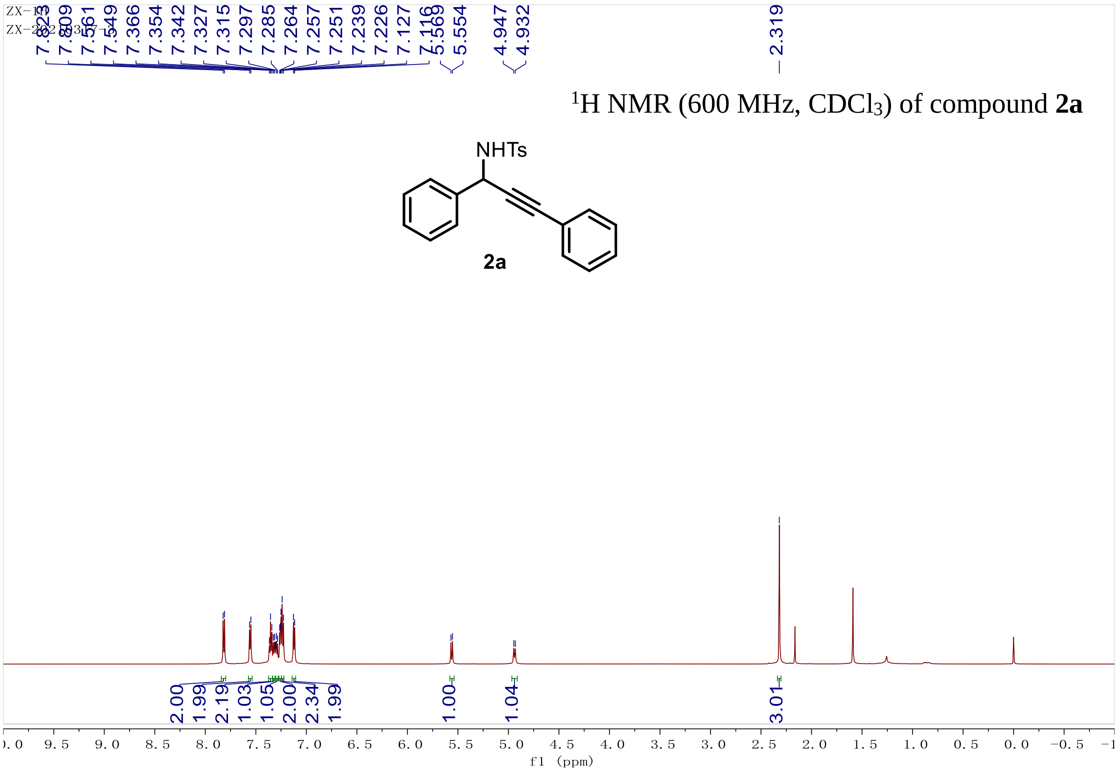
To a vial equipped with a dried stir bar was added **1a** (0.1 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 °C for 2.5 hours. **2a** and **3** were detected by HRMS.

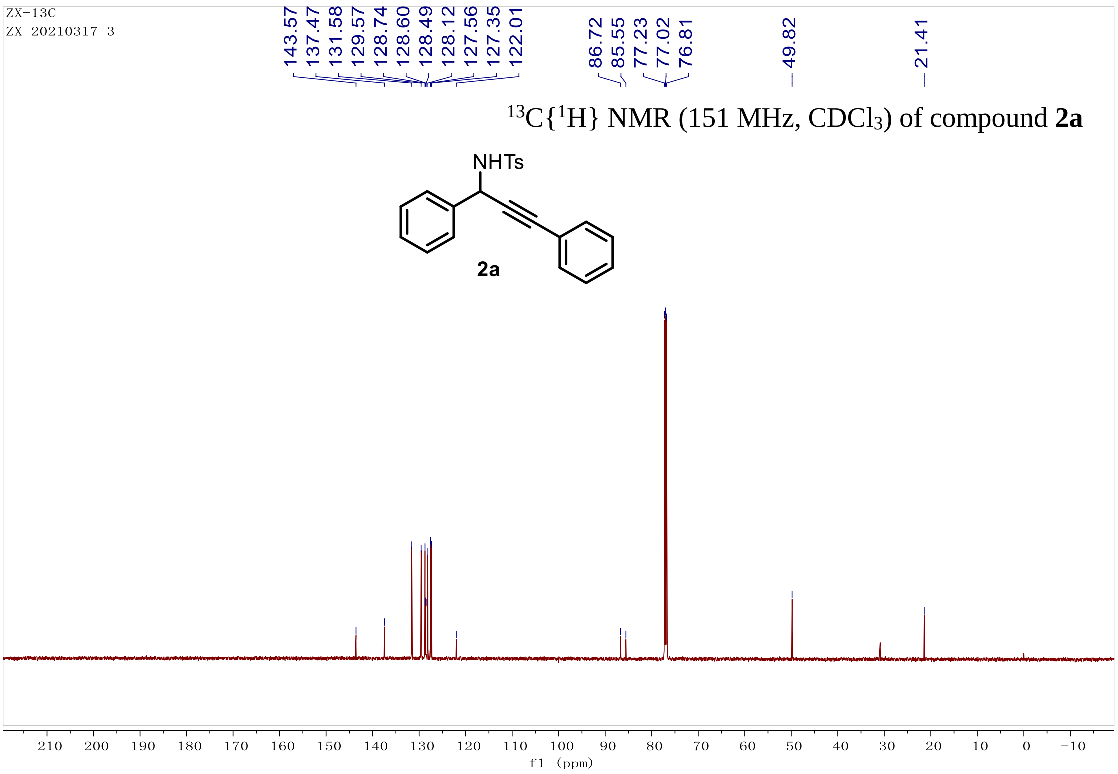
m/z	Res.	S/N	I	I%	FWHM
260.0744	23932	906.5	69809	0.9	0.0109
362.1218	23564	642.3	70598	0.9	0.0154

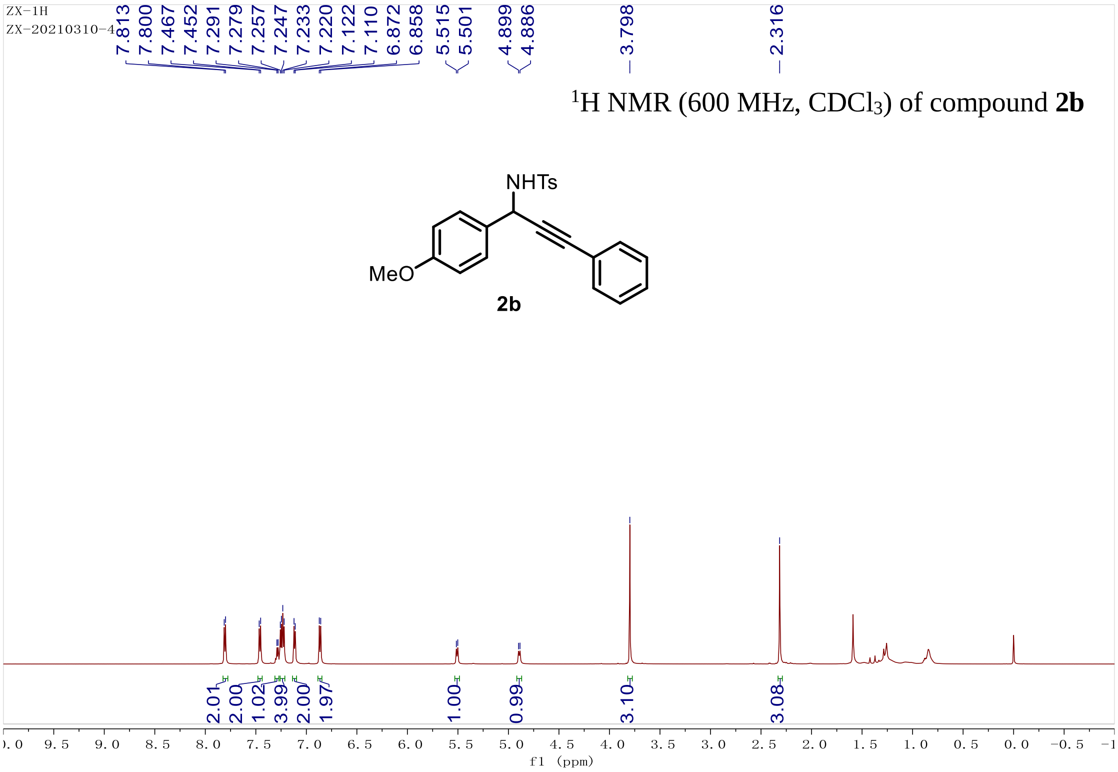
f. Cross-over reaction

To a vial equipped with a dried stir bar was added **1a** (0.1 mmol), **3** (0.1 mmol), $AgBF_4$ (10 mol%), 1,4-dioxane (0.5 mL) in the glovebox. The reaction mixture was taken outside the glovebox and allowed to stir at 100 ^{o}C for 12 hours. The desired product was isolated with the yield of 52%, which proved the process that imine was added by the alkynyl-silver intermediate.

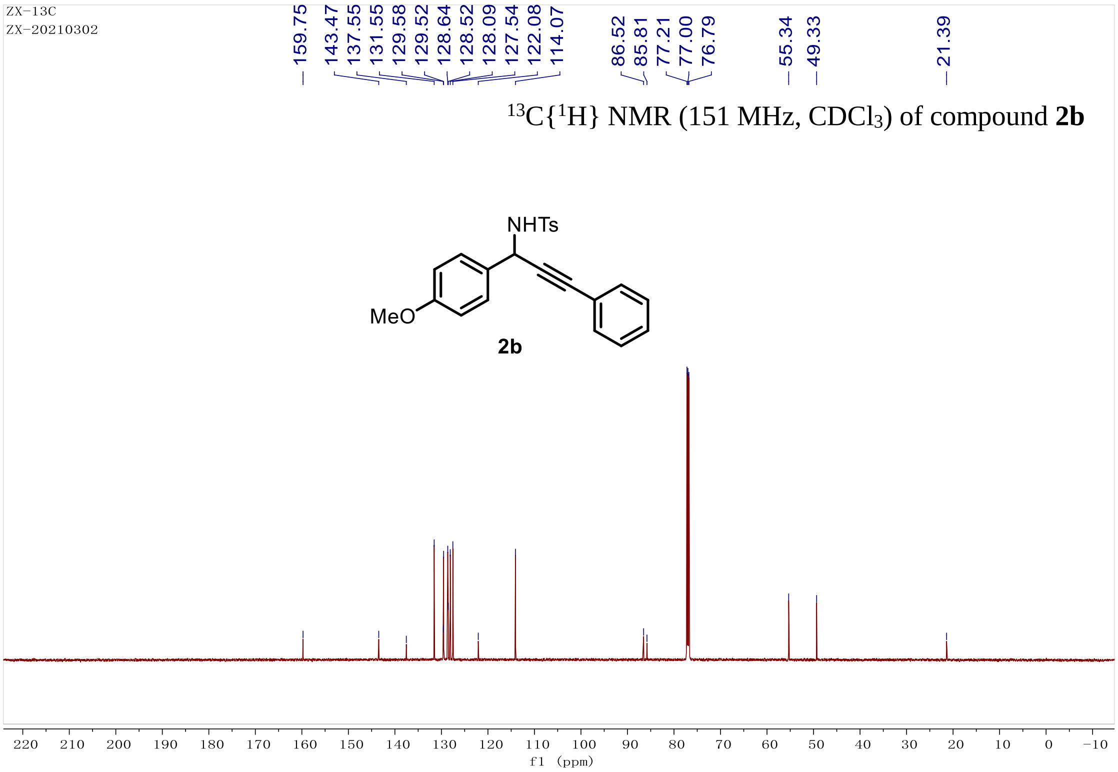
3. NMR Spectra of the Products



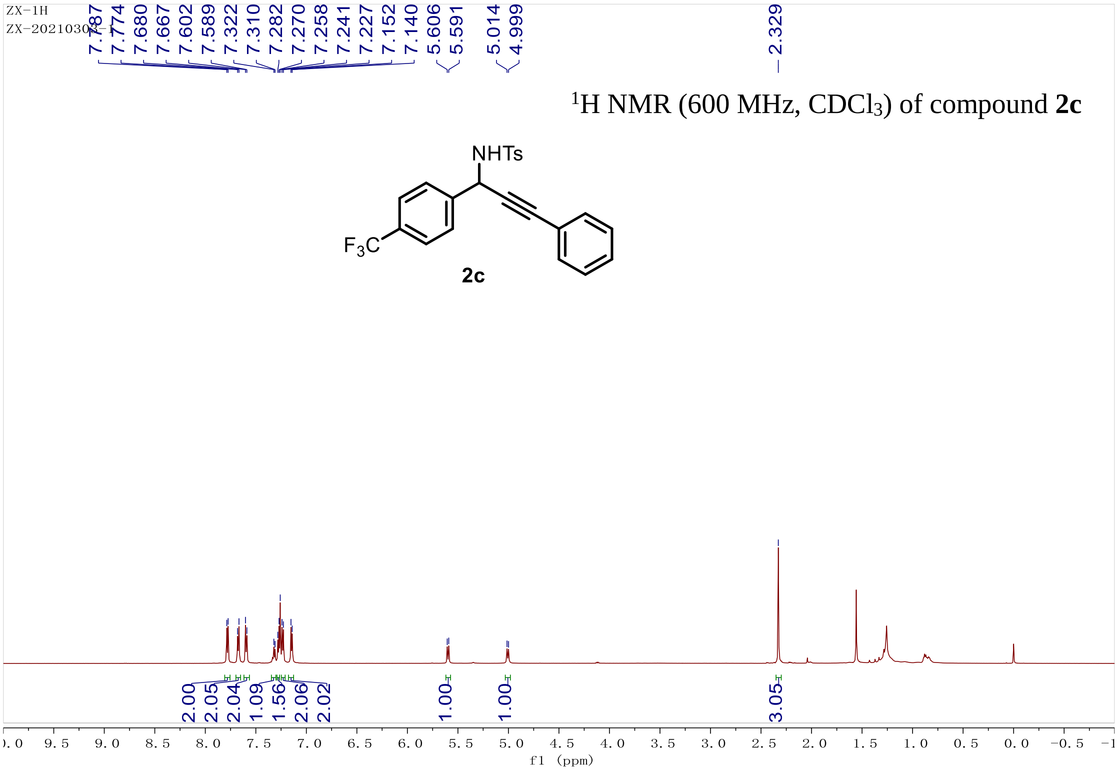




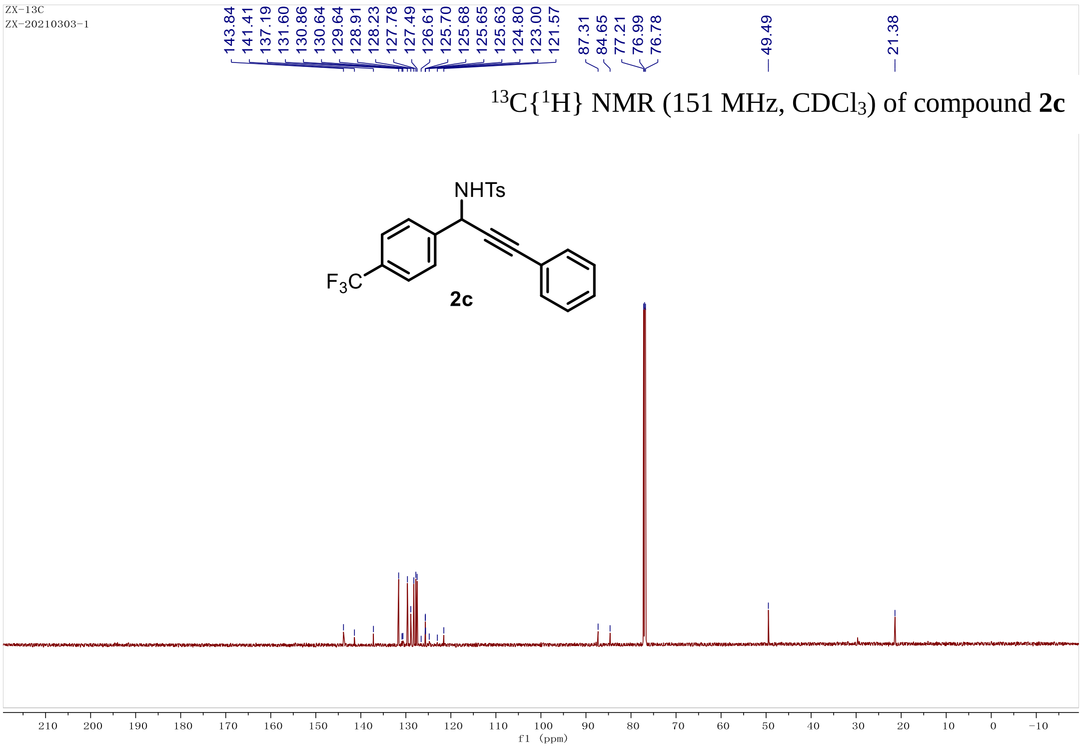
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2b**



$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) of compound **2b**

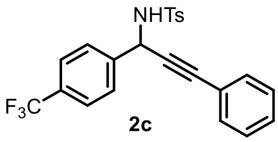


^{1}H NMR (600 MHz, $CDCl_3$) of compound **2c**

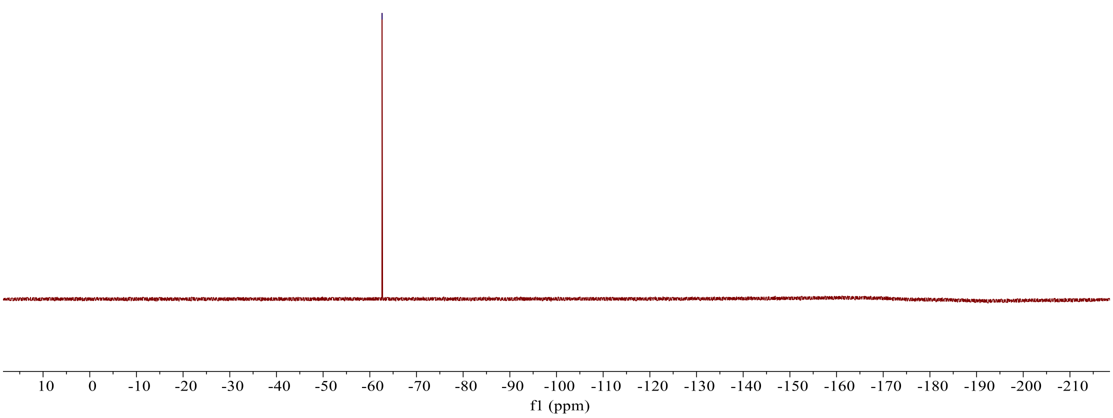


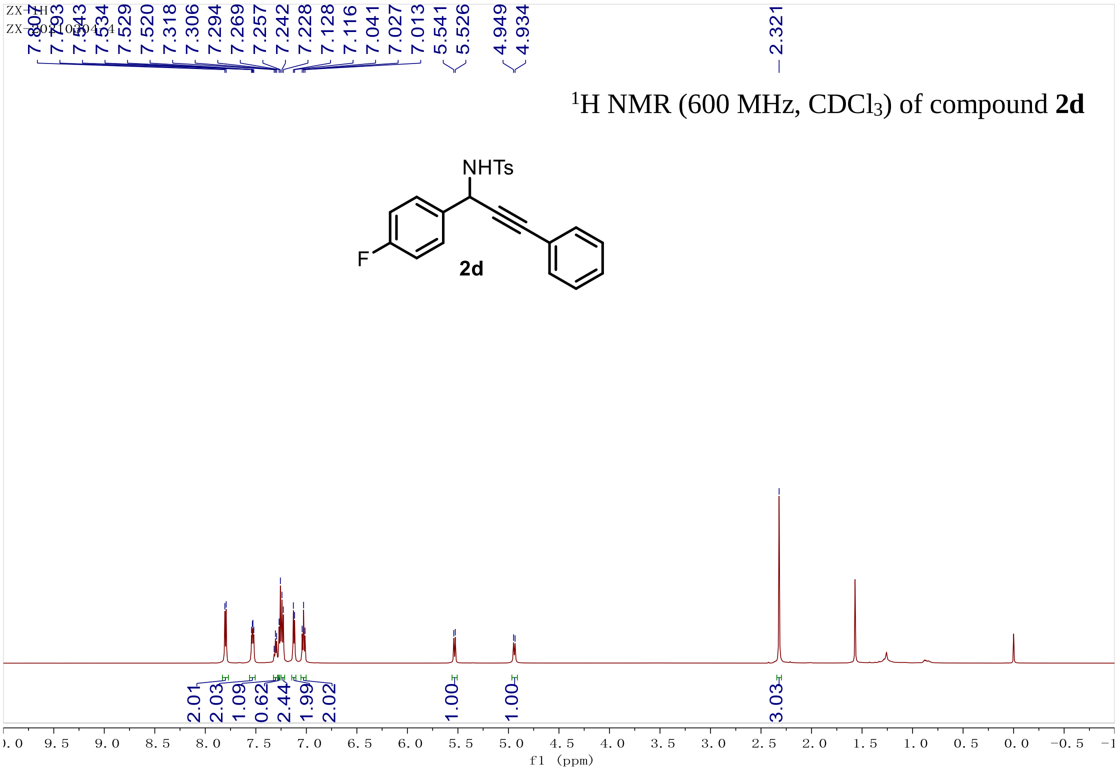
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2c**

$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$) of compound **2c**

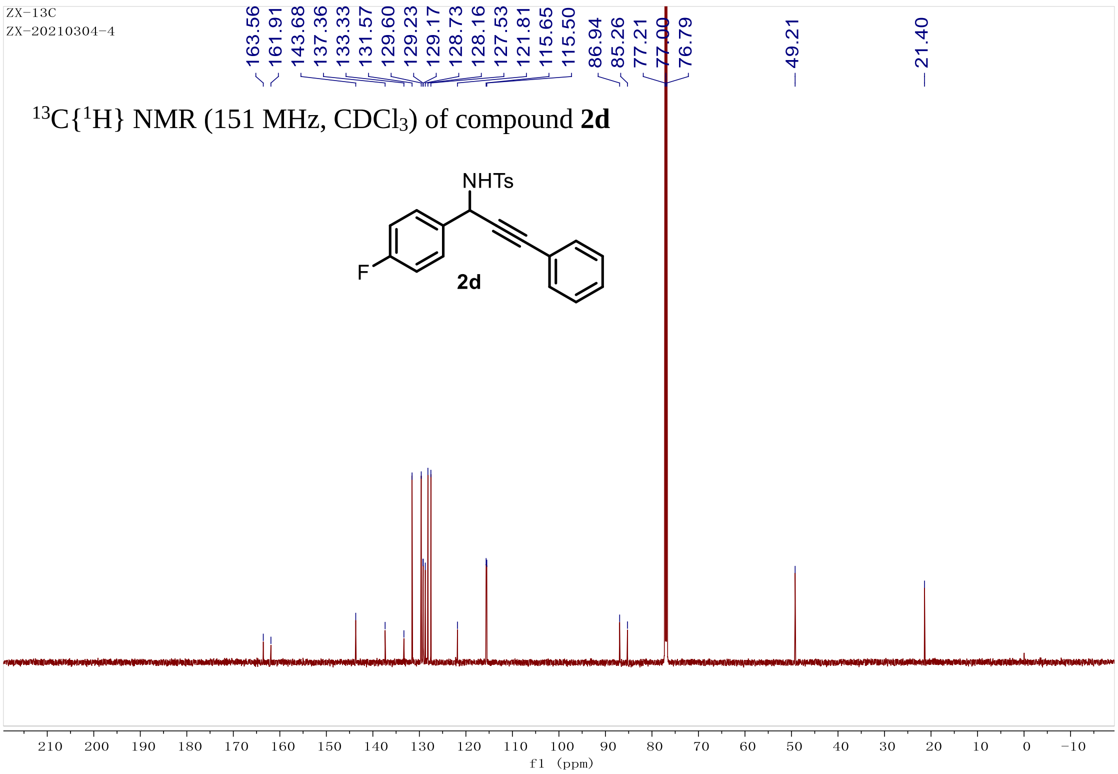


2c



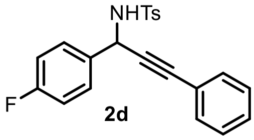


^{1}H NMR (600 MHz, CDCl$_3$) of compound **2d**
NHTs
F
2d

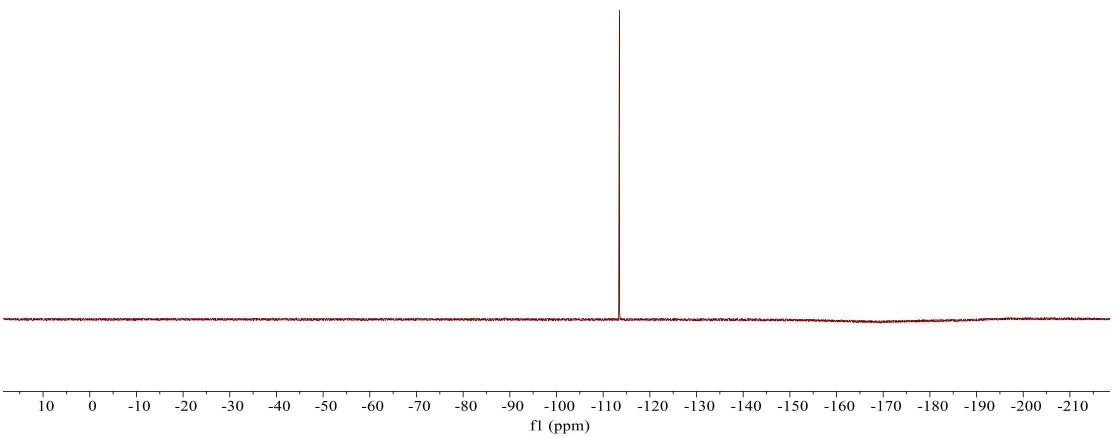


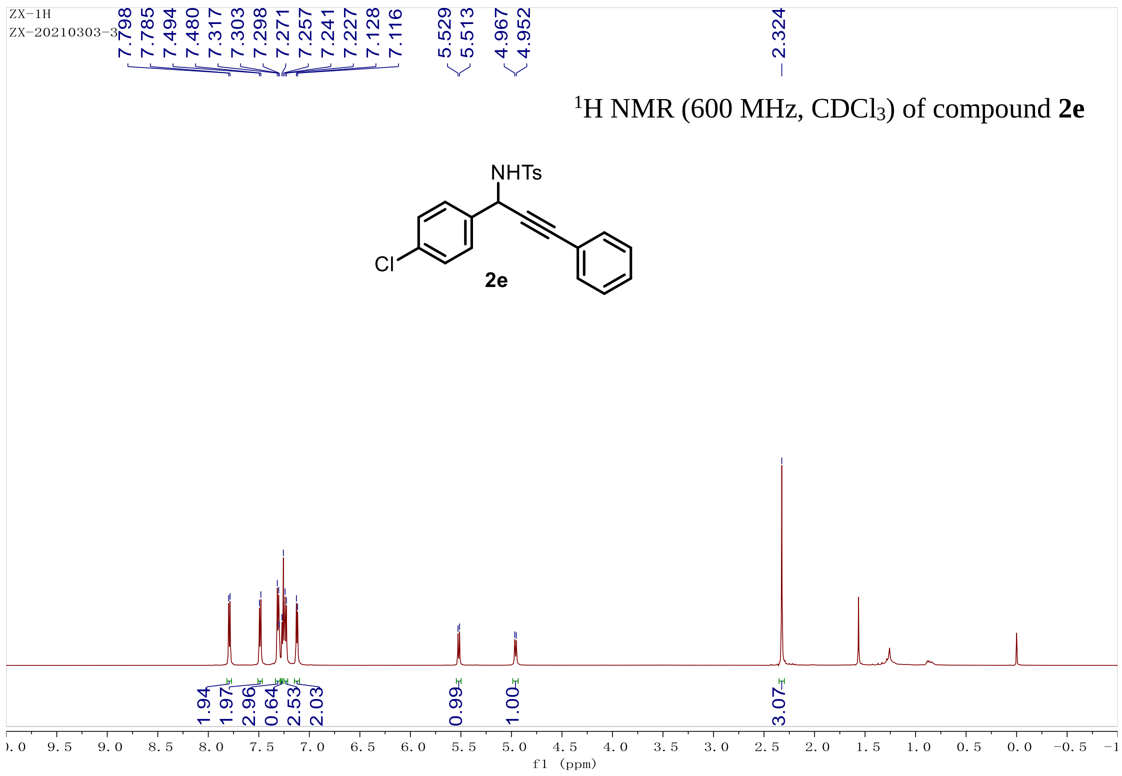
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2d**
NHTs
F
2d

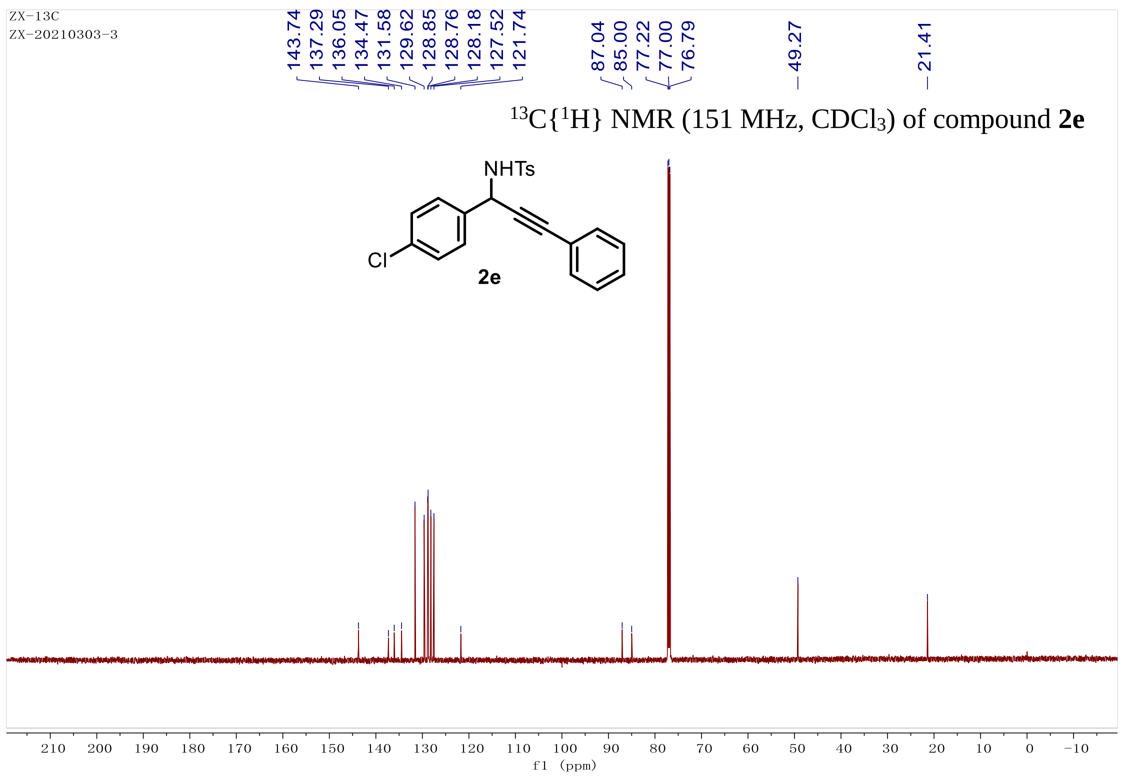
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$) of compound **2d**

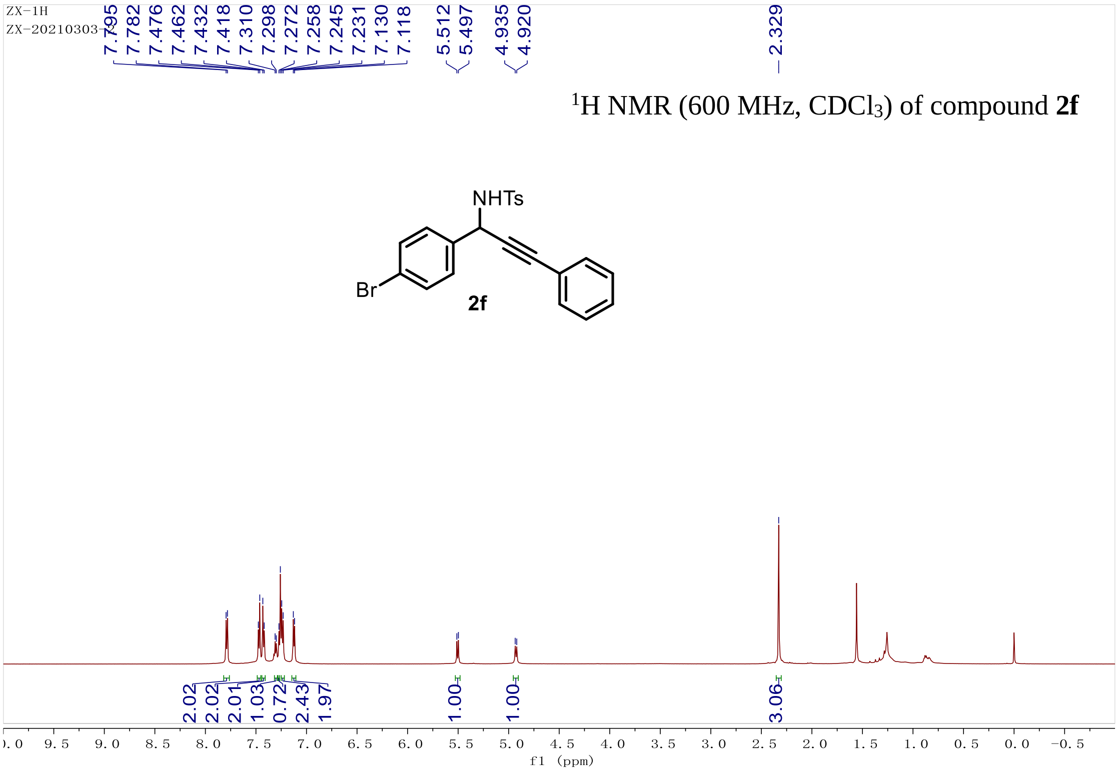


2d

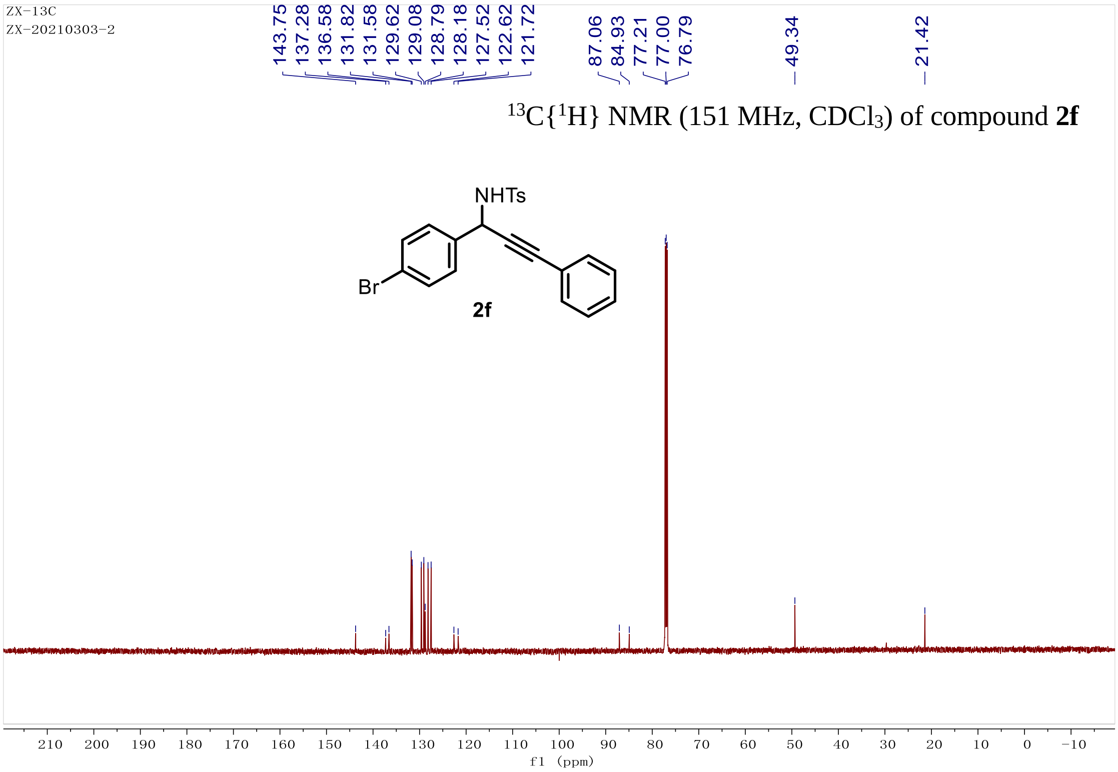



ZX-1H
ZX-20210303-3
7.798
7.785
7.494
7.480
7.317
7.303
7.298
7.271
7.257
7.241
7.227
7.128
7.116
5.529
5.513
4.967
4.952
2.324
1H NMR (600 MHz, CDCl3) of compound 2e
NHTs
Cl
2e
1.94
1.97
2.96
0.64
2.53
2.03
0.99
1.00
3.07
f1 (ppm)

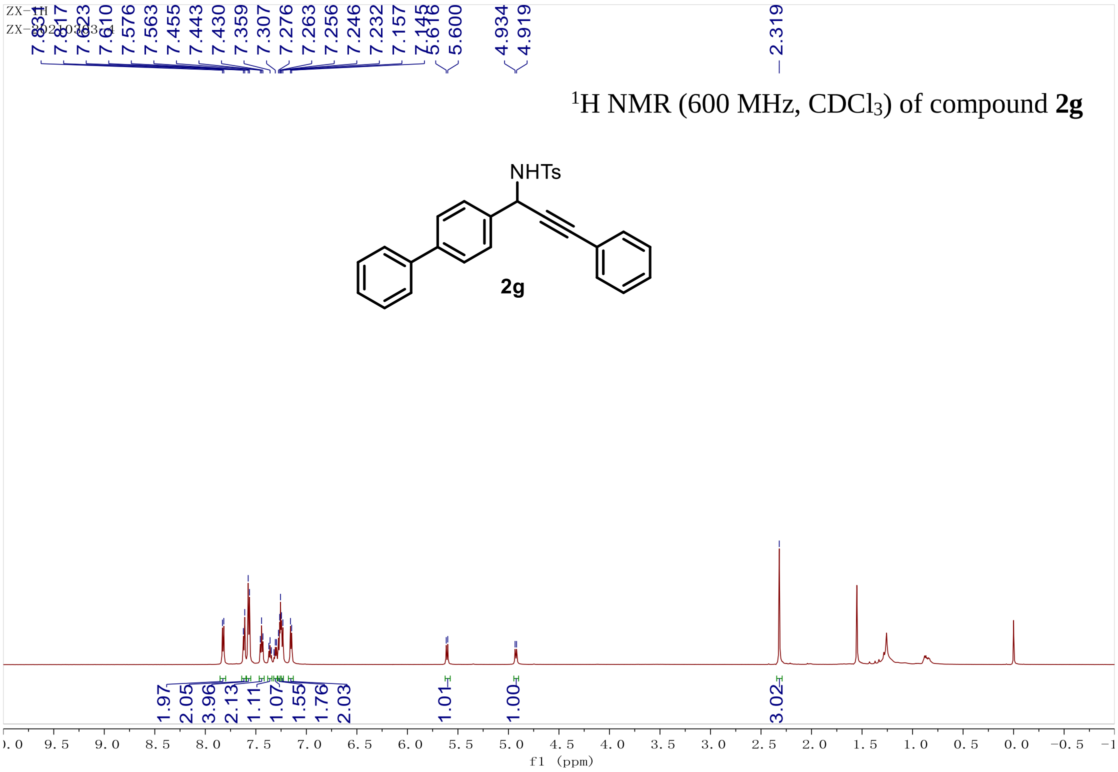

ZX-13C
ZX-20210303-3
143.74
137.29
136.05
134.47
131.58
129.62
128.85
128.76
128.18
127.52
121.74
87.04
85.00
77.22
77.00
76.79
49.27
21.41
13C{1H} NMR (151 MHz, CDCl3) of compound 2e
NHTs
Cl
2e
f1 (ppm)



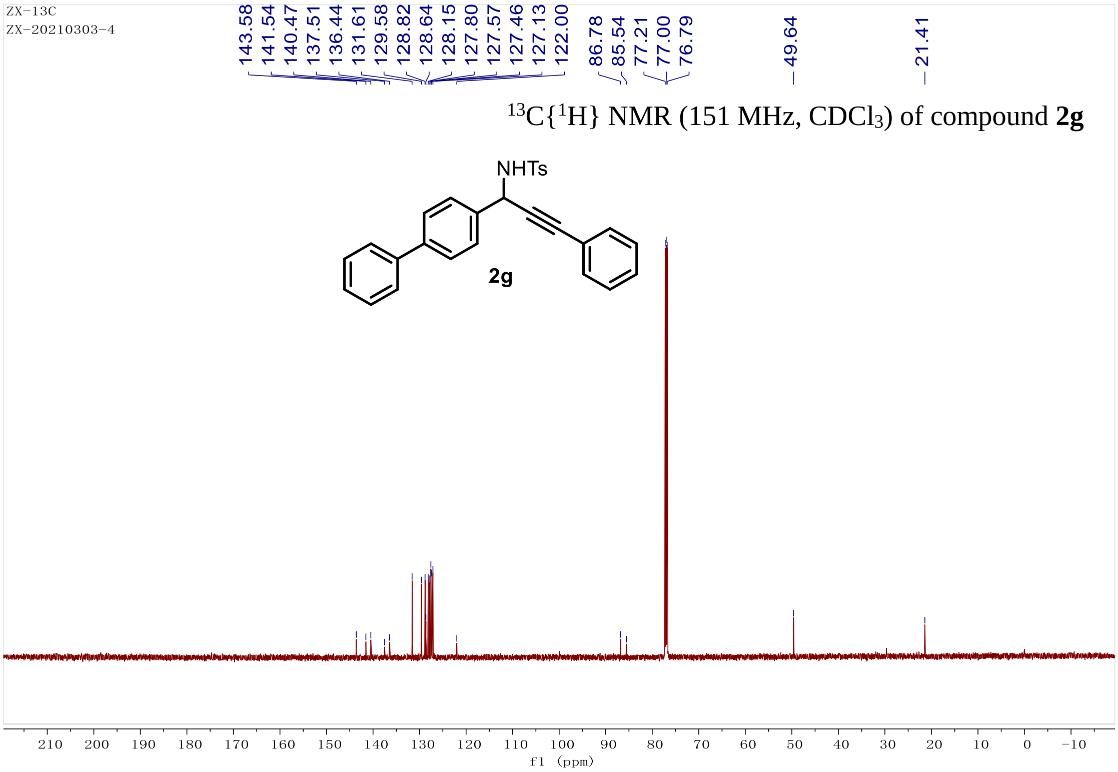
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2f**



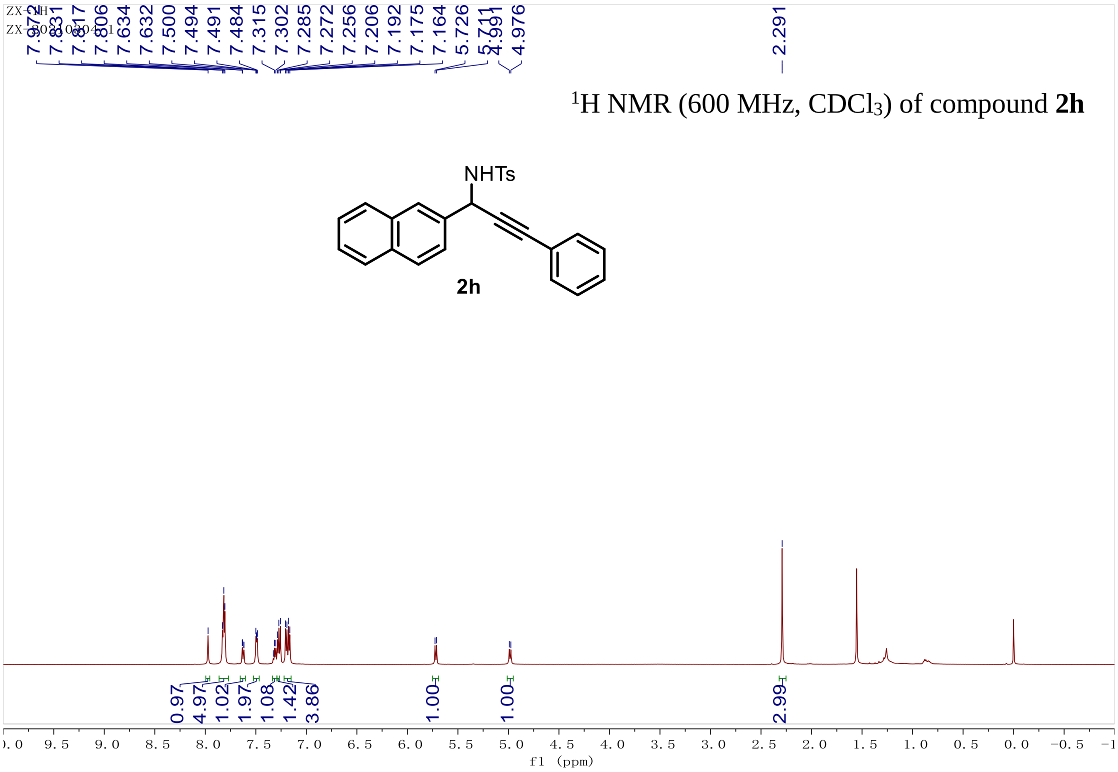
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2f**



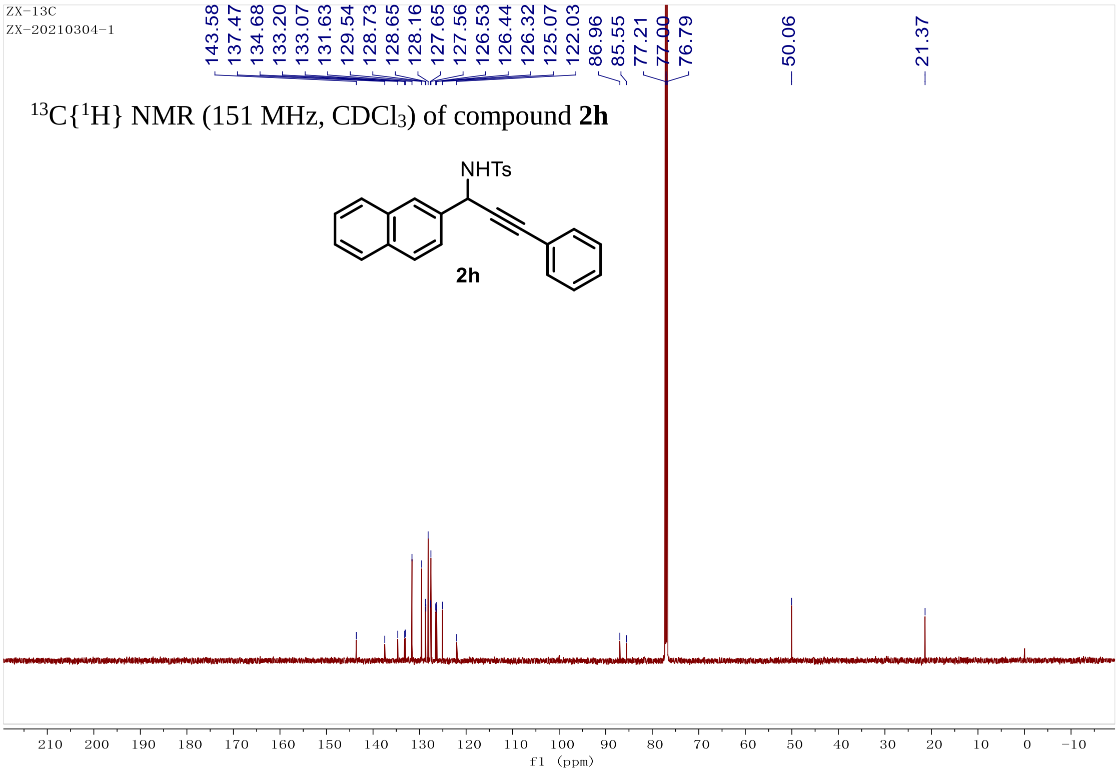
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2g**



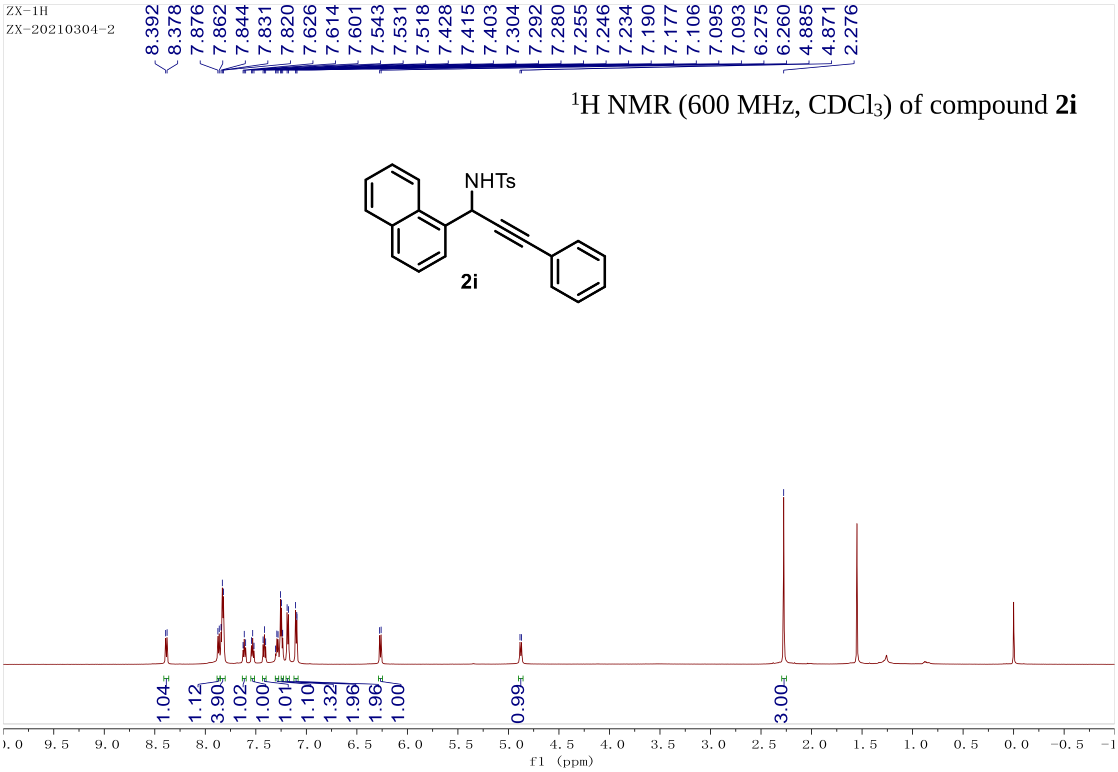
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2g**

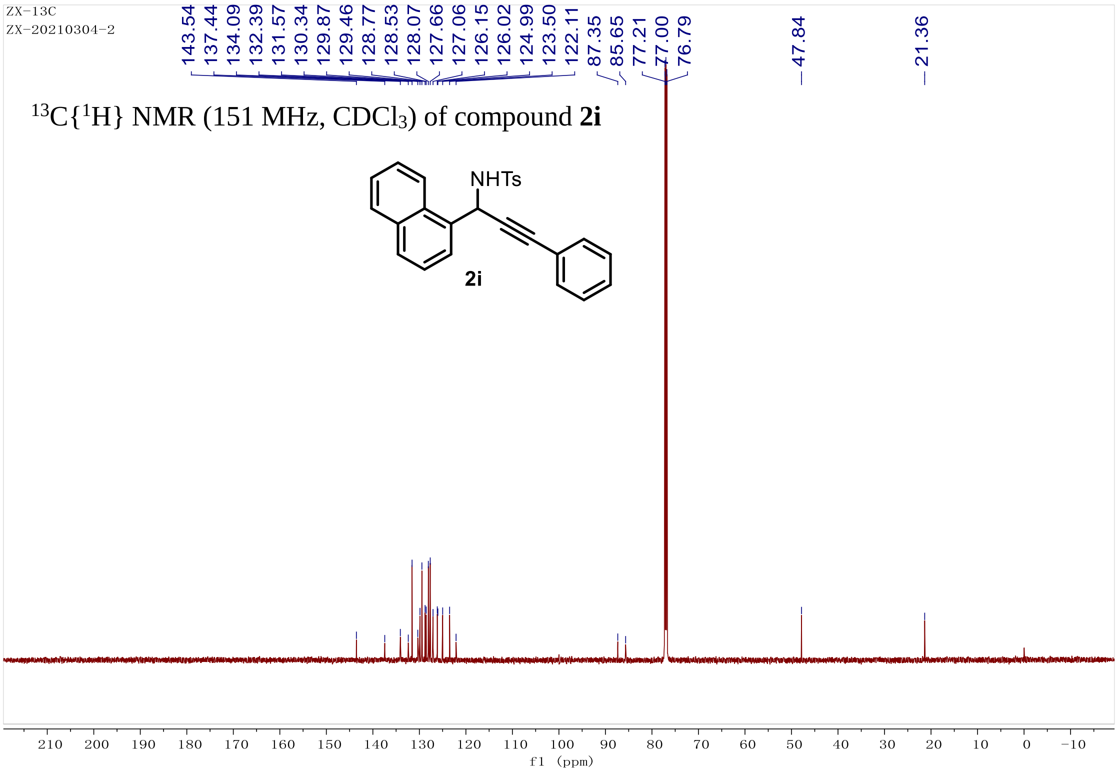


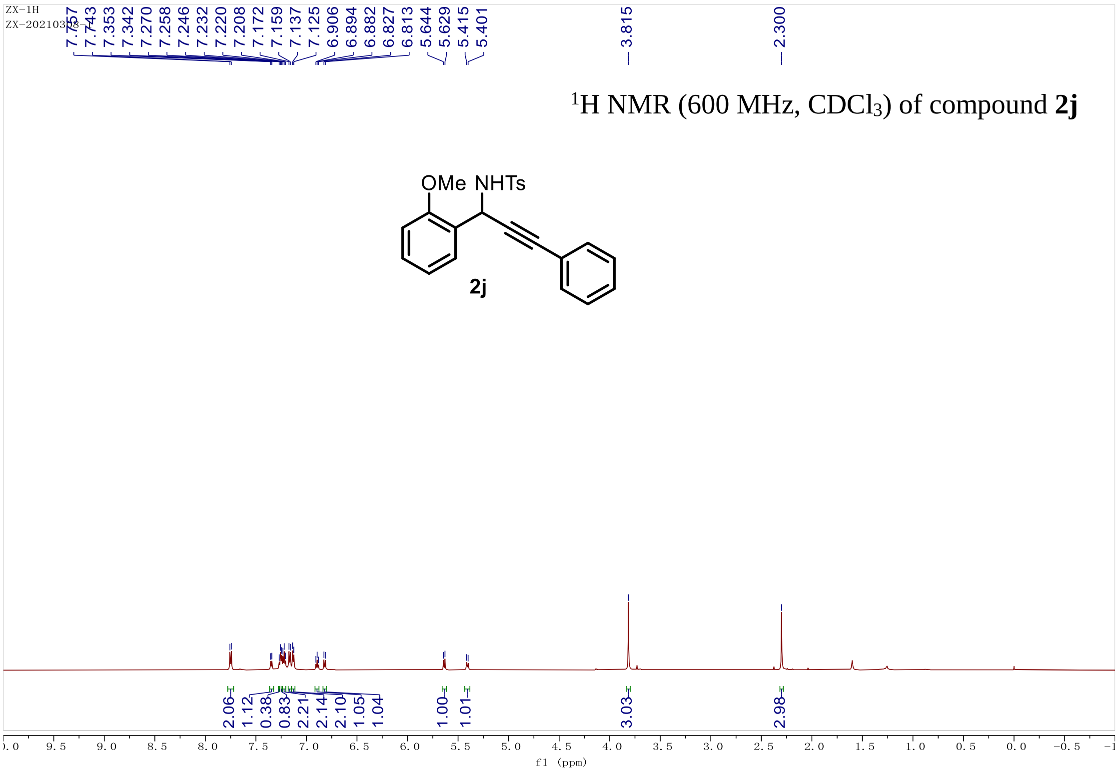
[1]H NMR (600 MHz, $CDCl_3$) of compound **2h**

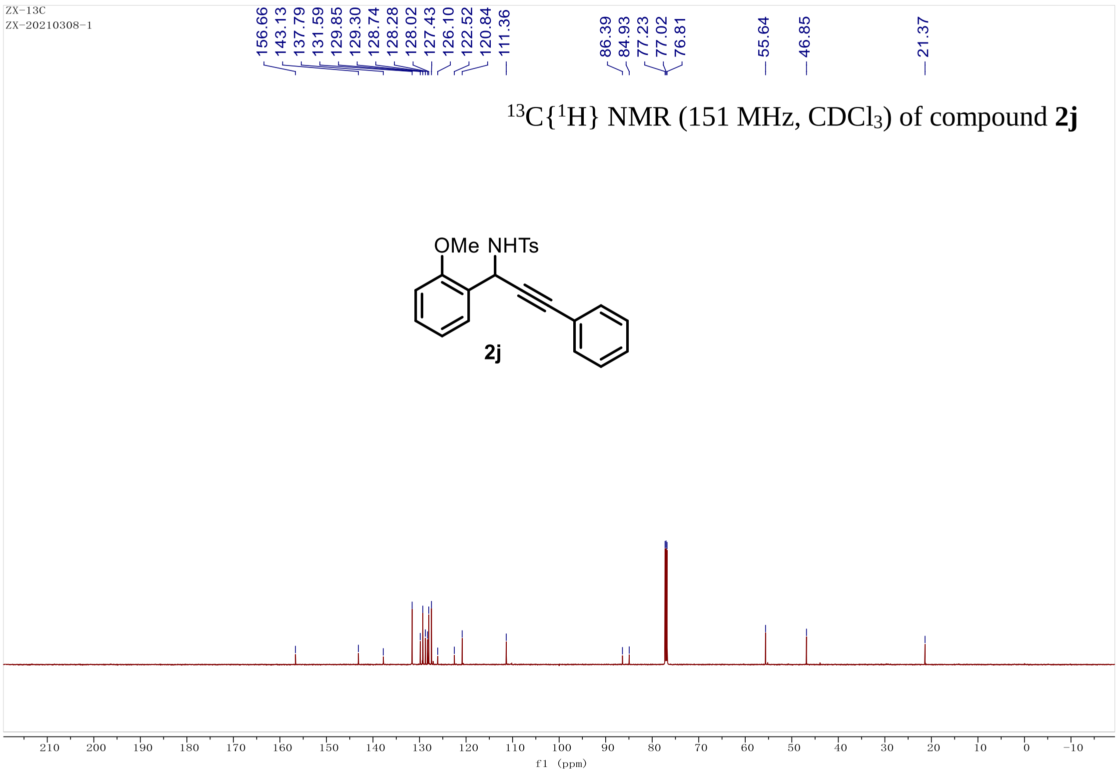


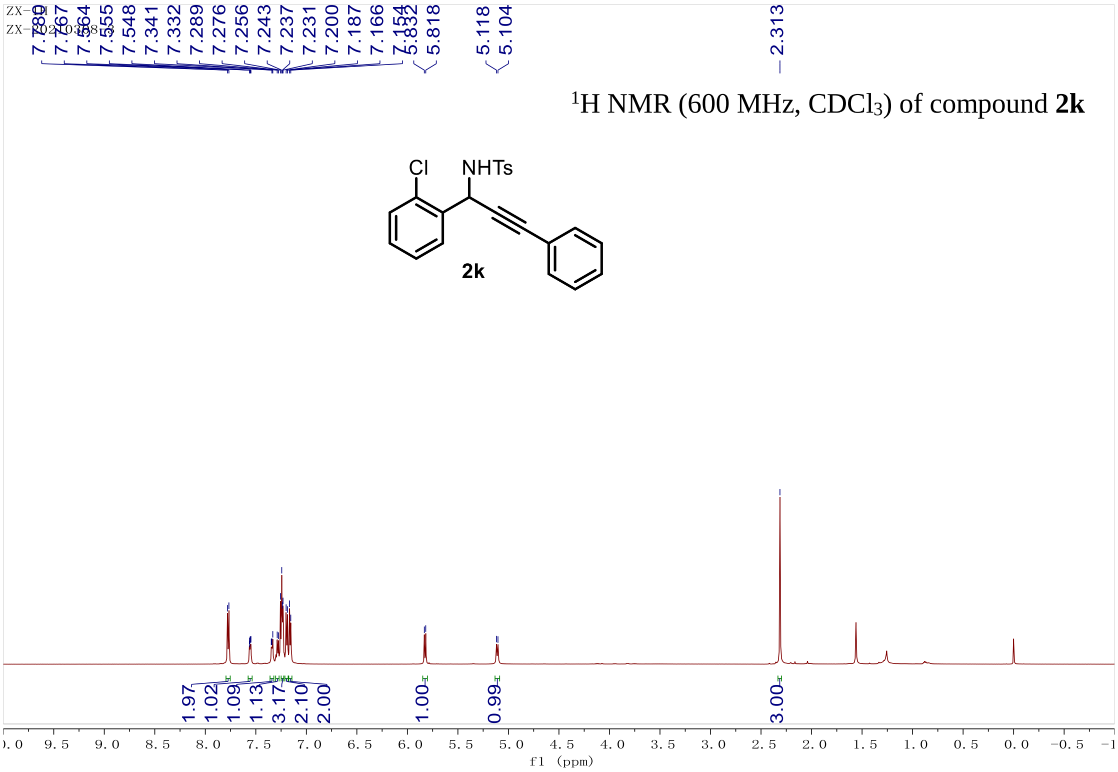
[13]C{[1]H} NMR (151 MHz, $CDCl_3$) of compound **2h**


ZX-1H
ZX-20210304-2
8.392 8.378 7.876 7.862 7.844 7.831 7.820 7.626 7.614 7.601 7.543 7.531 7.518 7.428 7.415 7.403 7.304 7.292 7.280 7.255 7.246 7.234 7.190 7.177 7.106 7.095 7.093 6.275 6.260 4.885 4.871 2.276
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2i**
NHTs
2i
1.04 1.12 3.90 1.02 1.00 1.01 1.10 1.32 1.96 1.96 1.00 0.99 3.00
f1 (ppm)

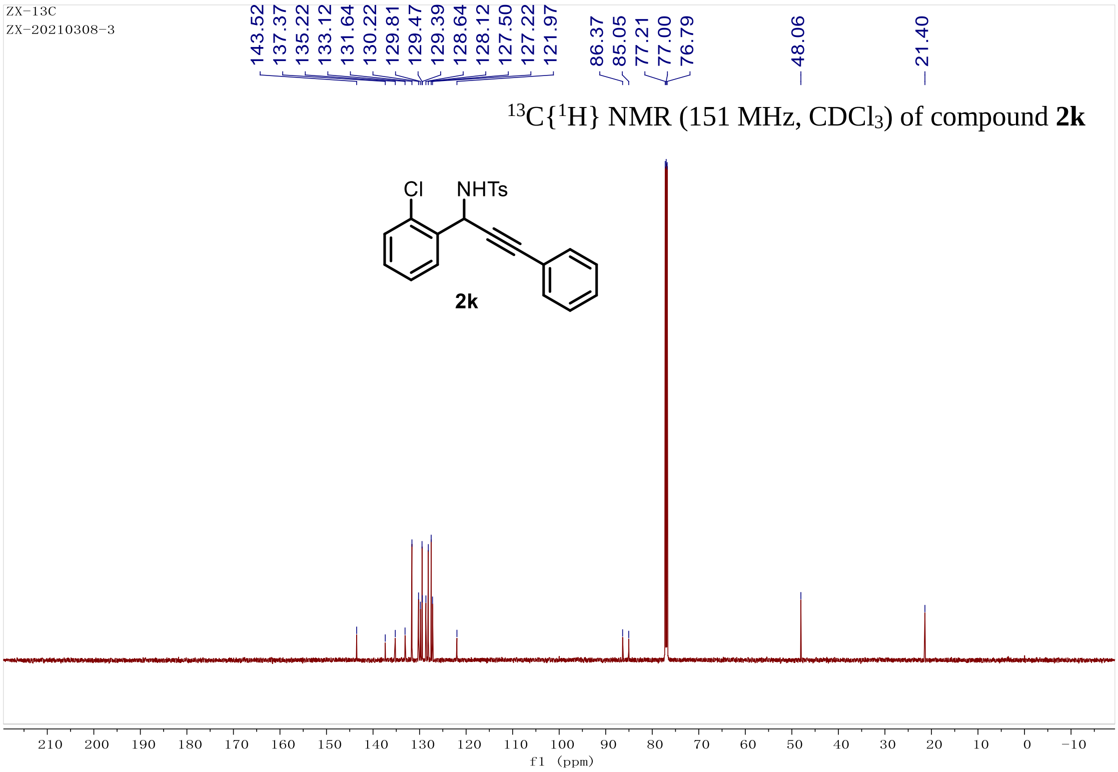

ZX-13C
ZX-20210304-2
143.54 137.44 134.09 132.39 131.57 130.34 129.87 129.46 128.77 128.53 128.07 127.66 127.06 126.15 126.02 124.99 123.50 122.11 87.35 85.65 77.21 77.00 76.79 47.84 21.36
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2i**
NHTs
2i
f1 (ppm)


ZX-1H
ZX-20210308-1
7.757
7.743
7.353
7.342
7.270
7.258
7.246
7.232
7.220
7.208
7.172
7.159
7.137
7.125
6.906
6.894
6.882
6.827
6.813
5.644
5.629
5.415
5.401
3.815
2.300
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2j**
OMe NHTs
2j
2.06
1.12
0.38
0.83
2.21
2.14
2.10
1.05
1.04
1.00
1.01
3.03
2.98
f1 (ppm)

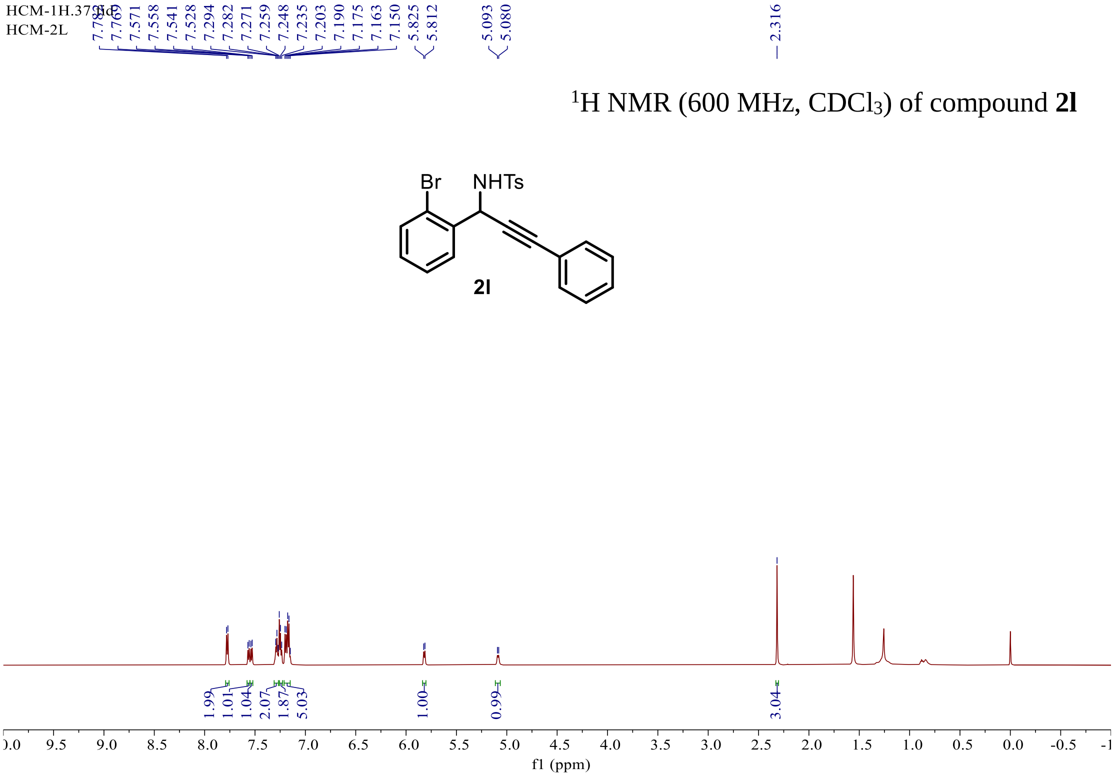

ZX-13C
ZX-20210308-1
156.66
143.13
137.79
131.59
129.85
129.30
128.74
128.28
128.02
127.43
126.10
122.52
120.84
111.36
86.39
84.93
77.23
77.02
76.81
55.64
46.85
21.37
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2j**
OMe NHTs
2j
f1 (ppm)



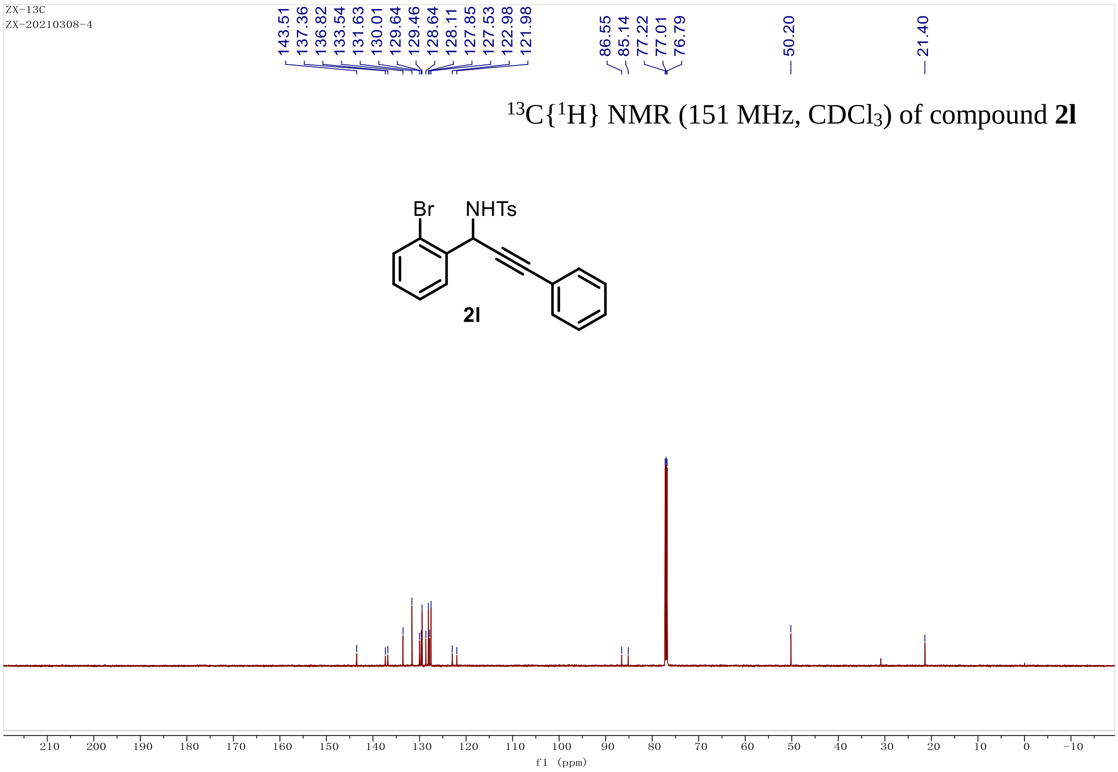
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2k**



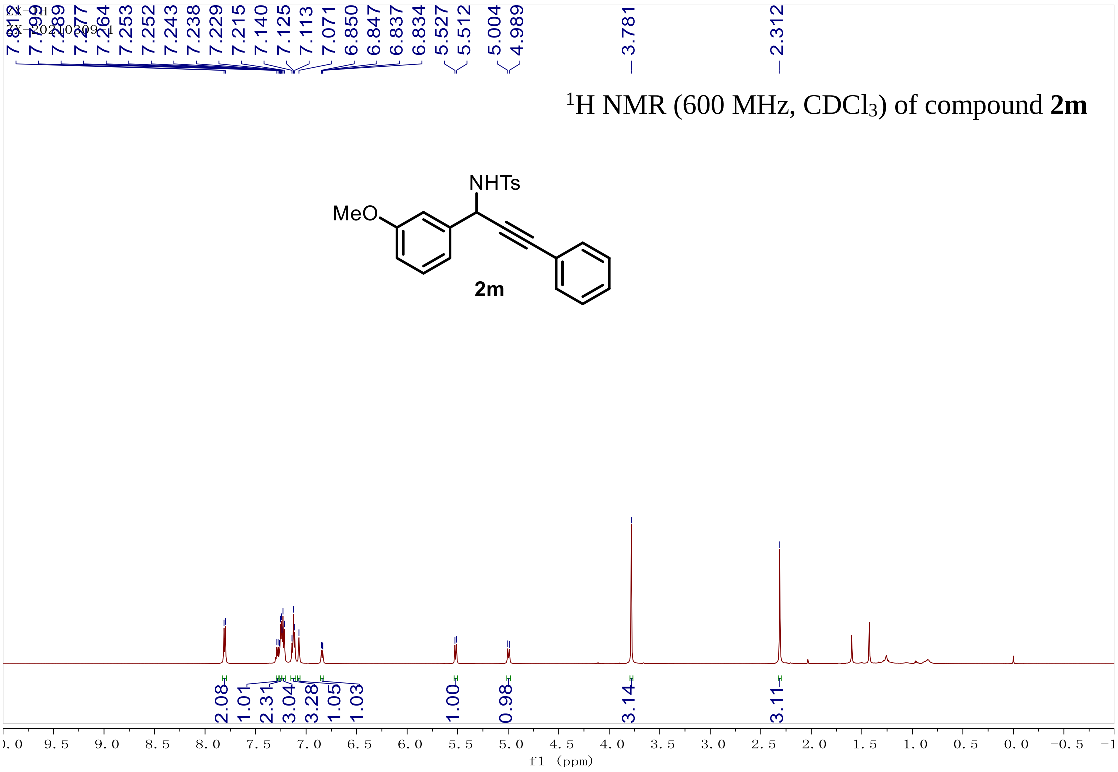
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2k**

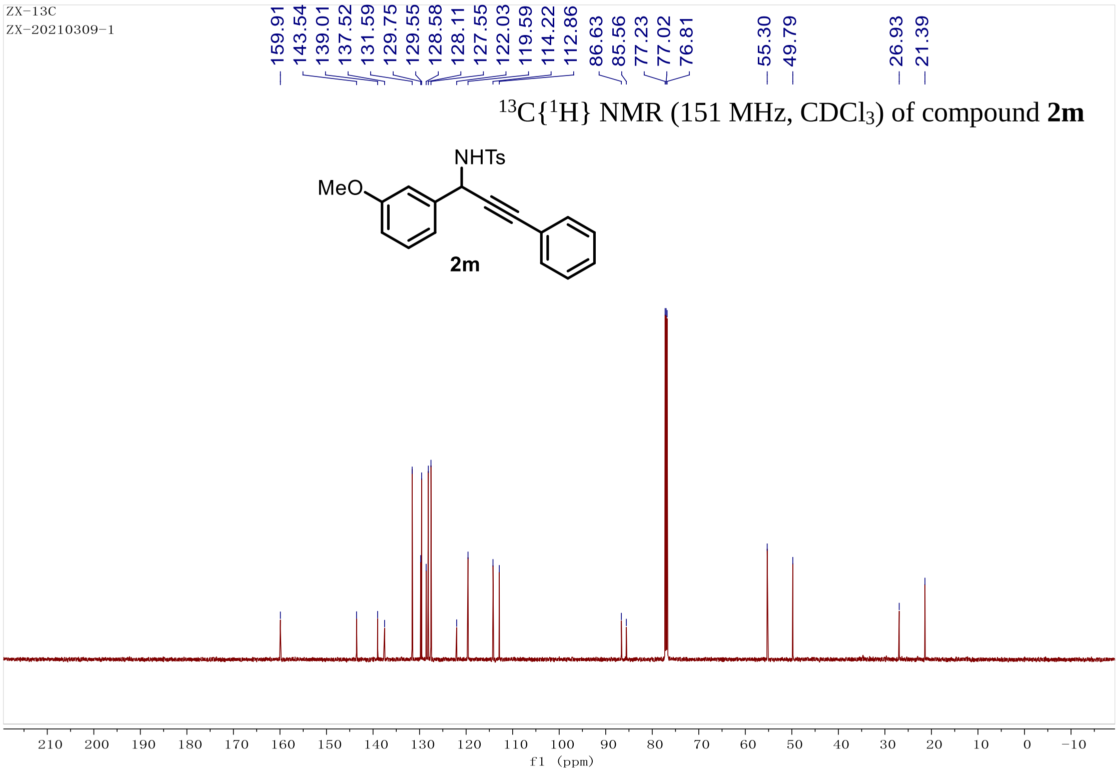


^{1}H NMR (600 MHz, $CDCl_3$) of compound **2l**

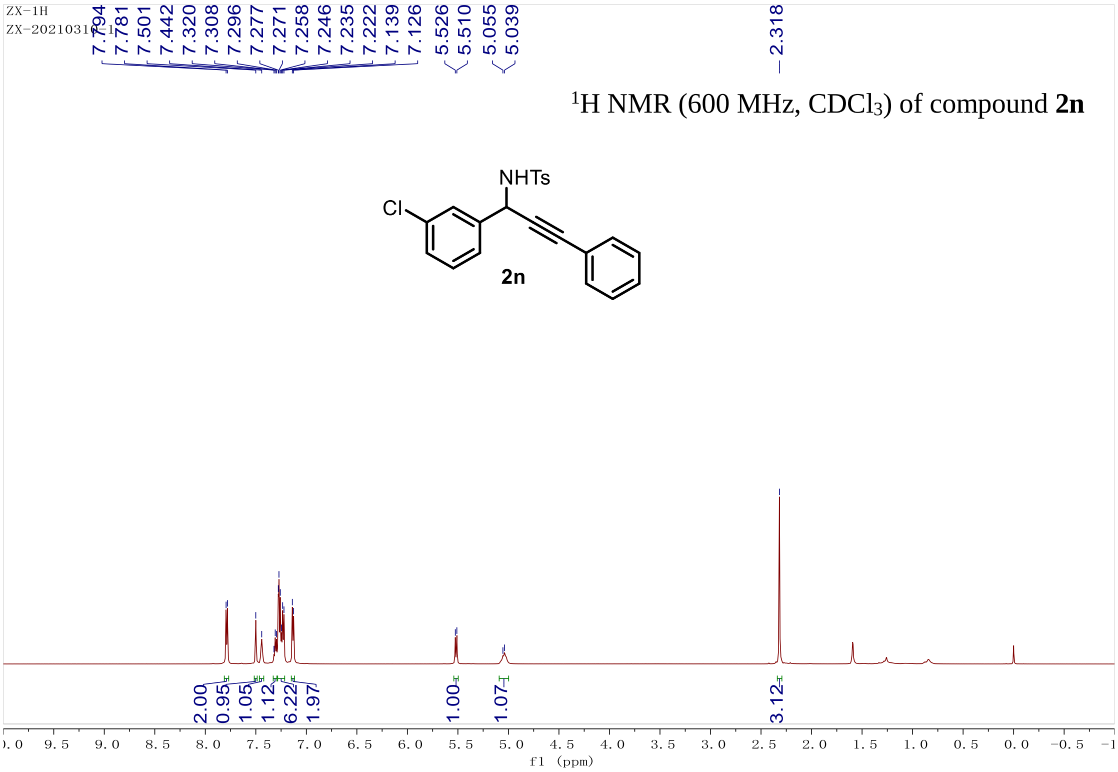


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2l**

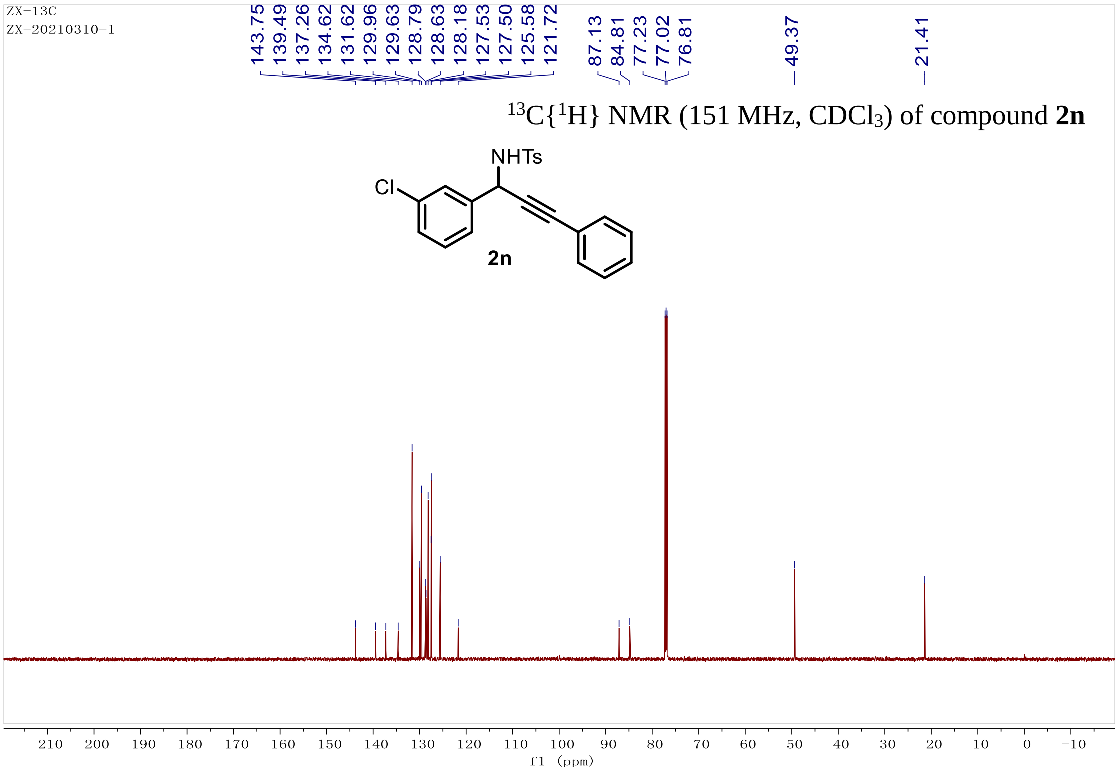

7.812
7.799
7.289
7.277
7.264
7.253
7.252
7.243
7.238
7.229
7.215
7.140
7.125
7.113
7.071
6.850
6.847
6.837
6.834
5.527
5.512
5.004
4.989
3.781
2.312
ZX-20210309-1
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2m**
NHTs
MeO
2m
2.08
1.01
2.31
3.04
3.28
1.05
1.03
1.00
0.98
3.14
3.11
f1 (ppm)

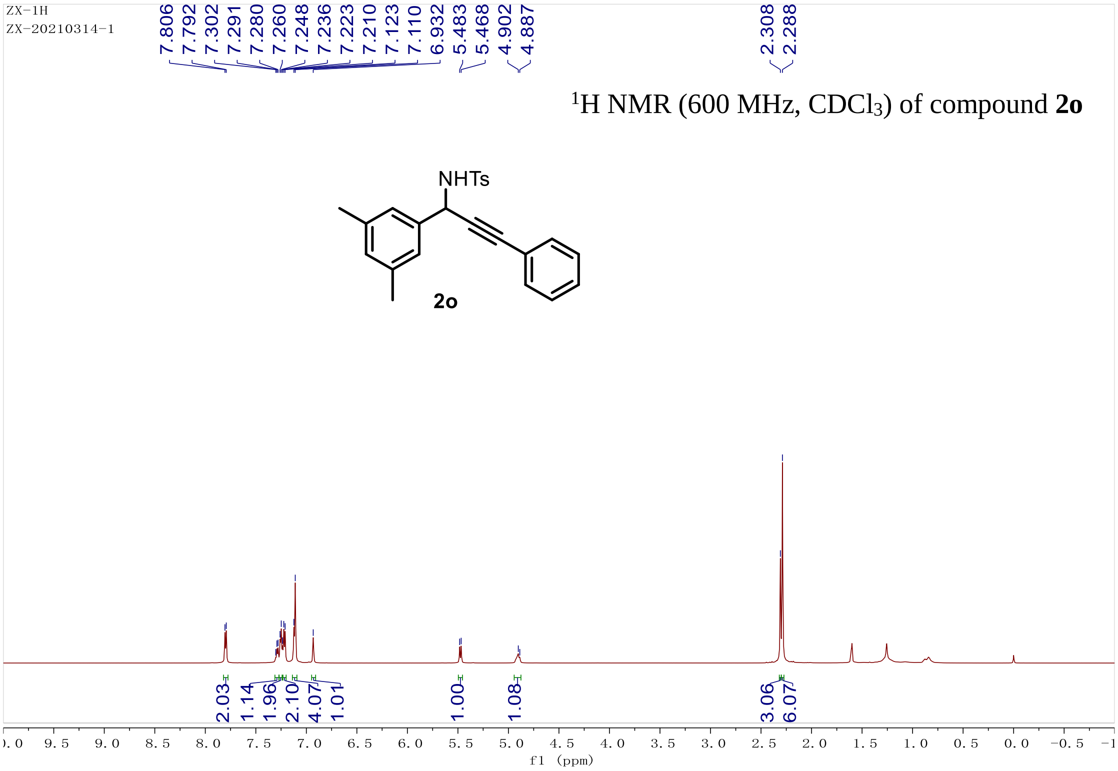

ZX-13C
ZX-20210309-1
159.91
143.54
139.01
137.52
131.59
129.75
129.55
128.58
128.11
127.55
122.03
119.59
114.22
112.86
86.63
85.56
77.23
77.02
76.81
55.30
49.79
26.93
21.39
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2m**
NHTs
MeO
2m
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$) of compound **2n**

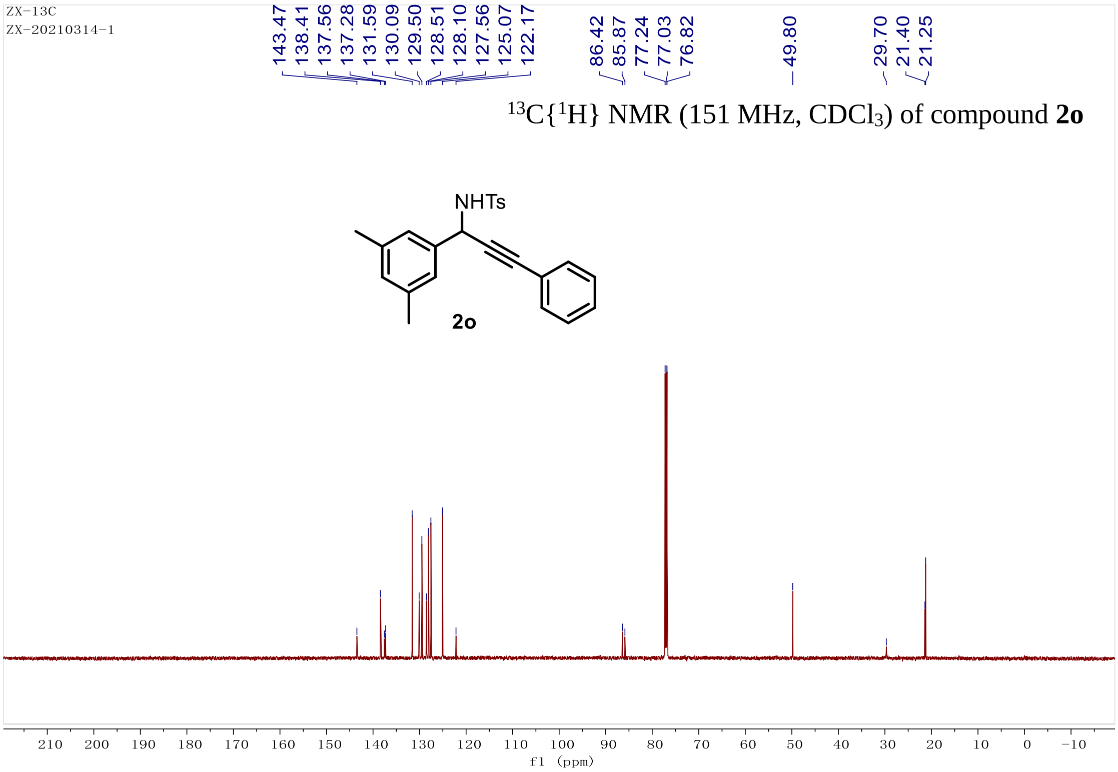


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2n**



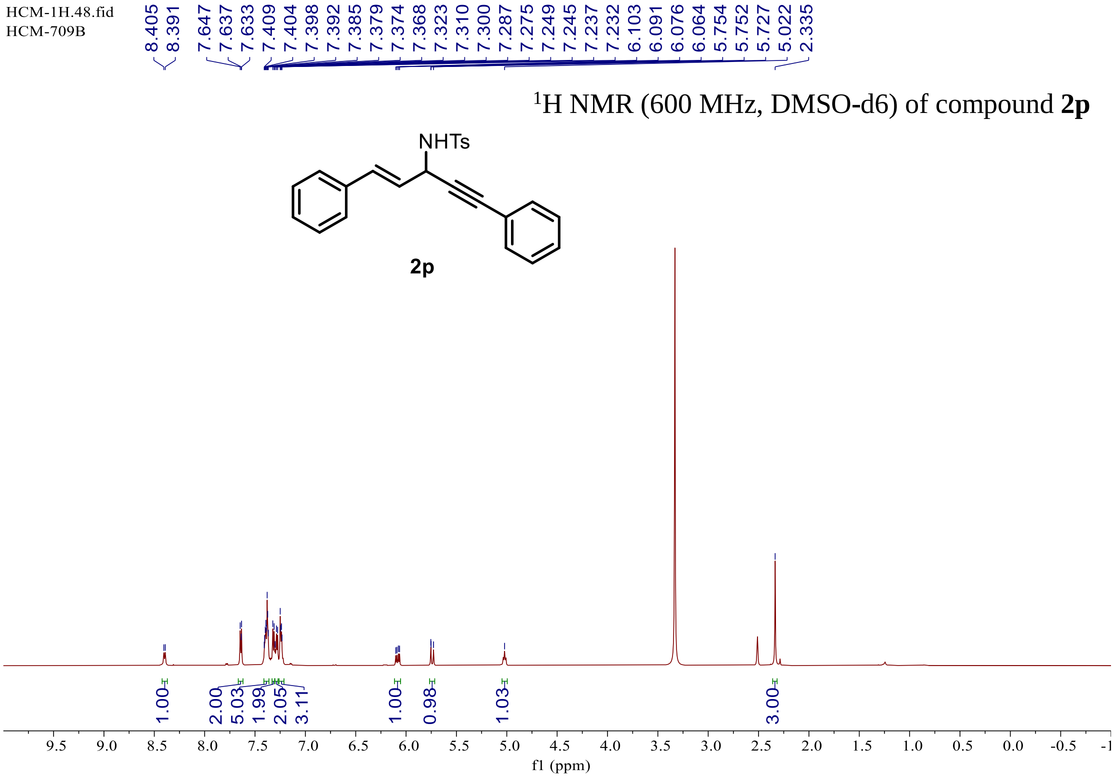


^{1}H NMR (600 MHz, $CDCl_3$) of compound **2o**



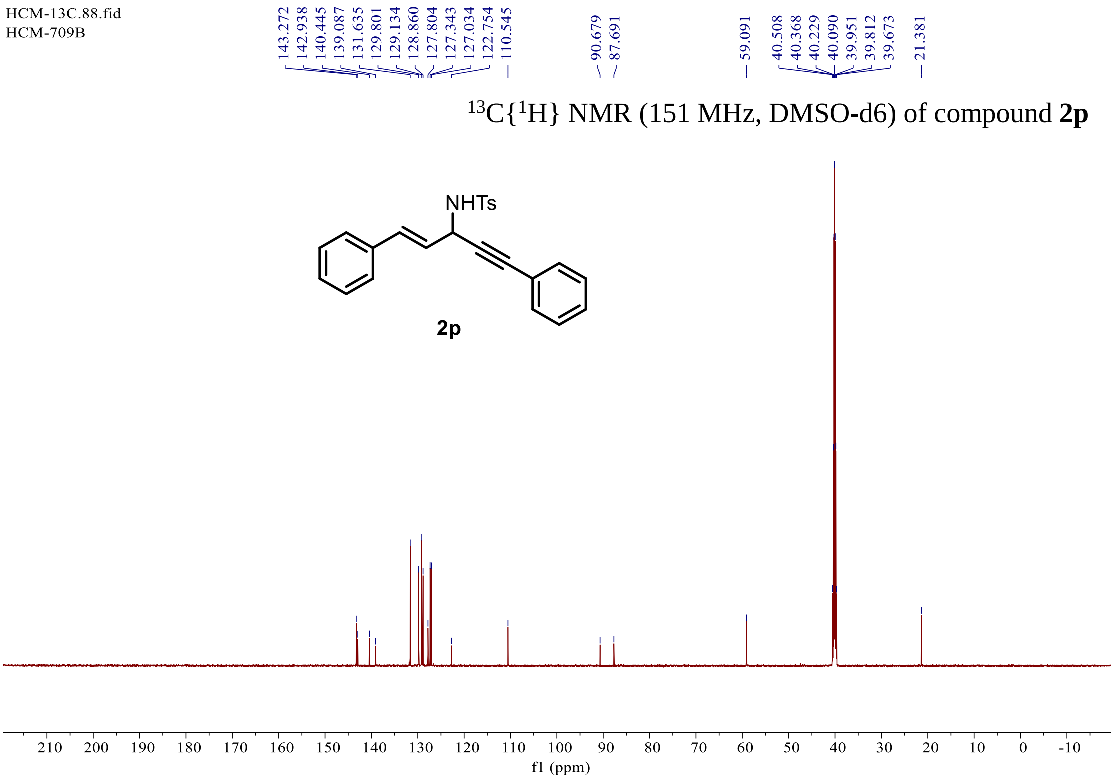
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2o**

HCM-1H.48.fid
HCM-709B

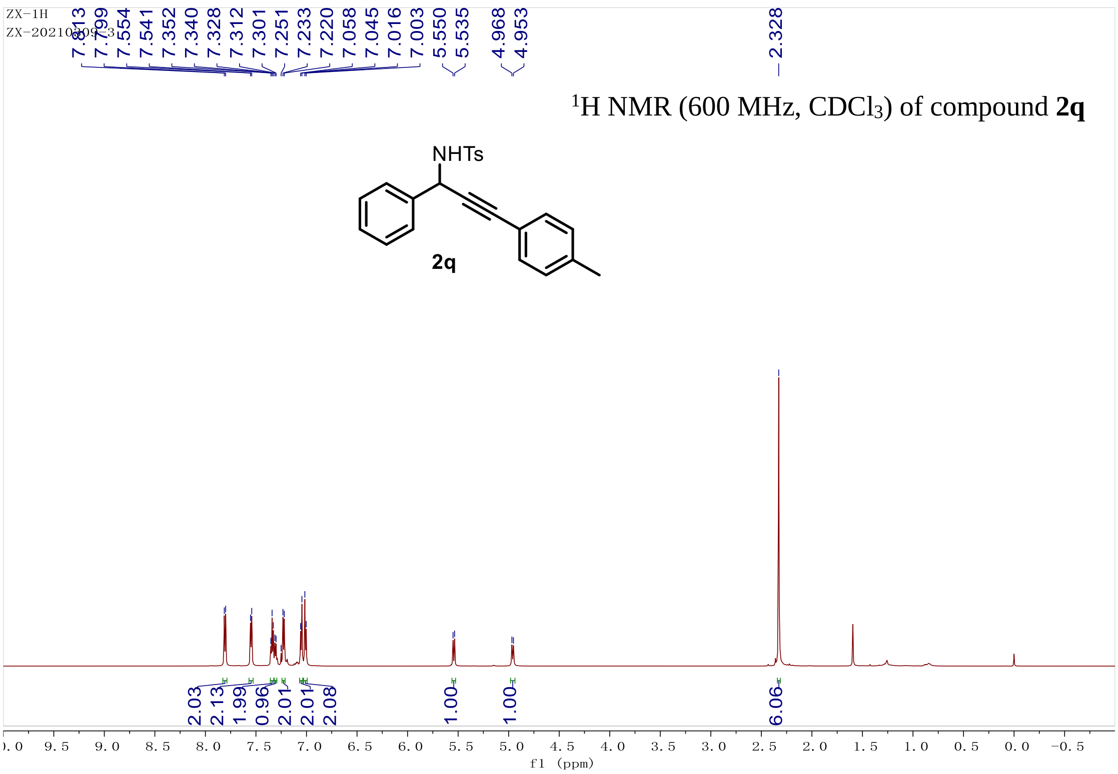


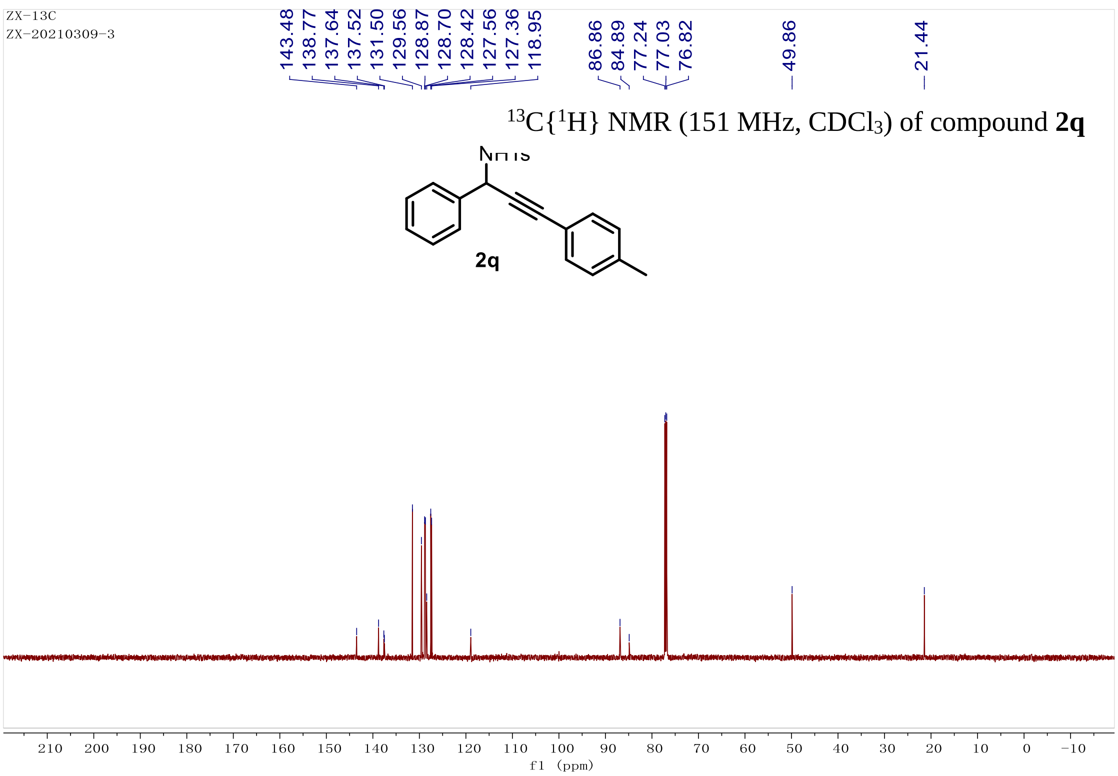
[1]H NMR (600 MHz, DMSO-d6) of compound **2p**

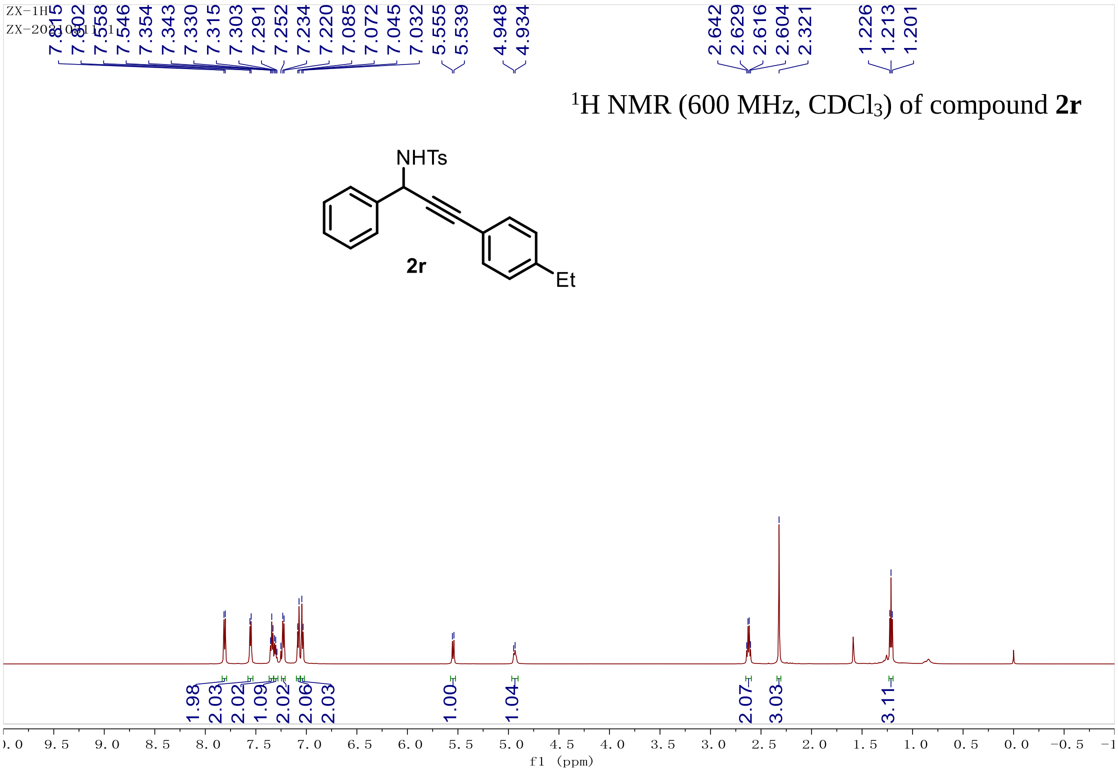
HCM-13C.88.fid
HCM-709B



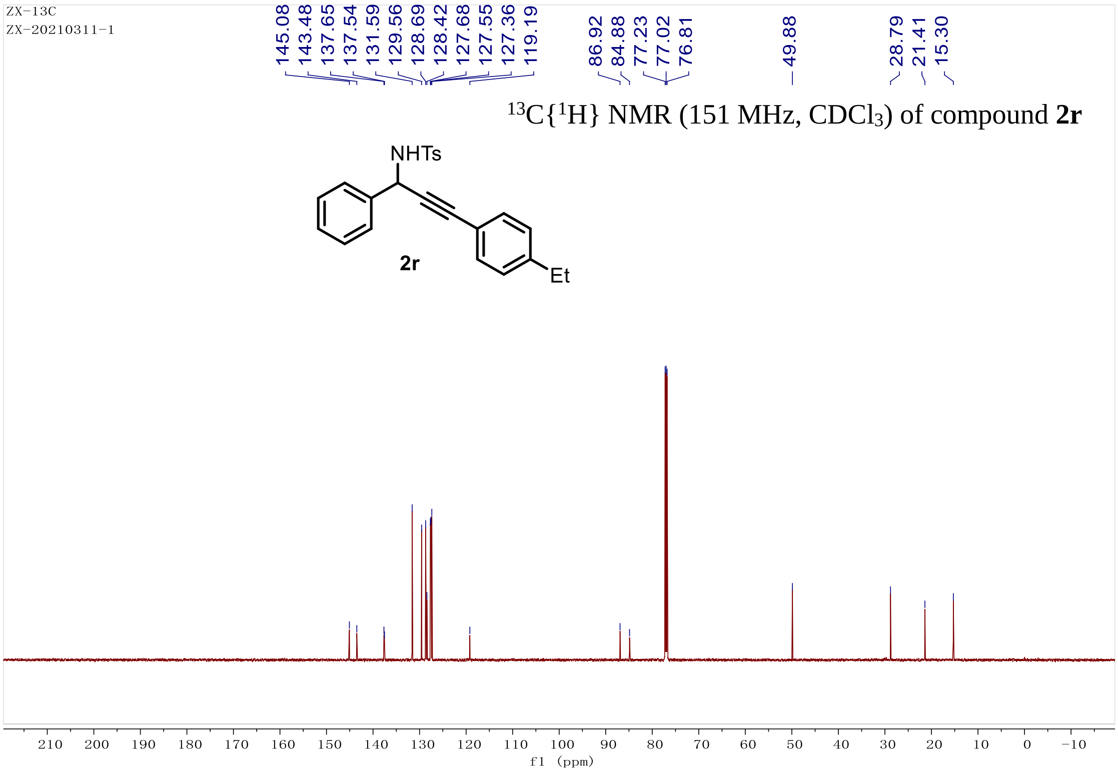
[13]C{[1]H} NMR (151 MHz, DMSO-d6) of compound **2p**


ZX-1H
ZX-20210309-3
7.813
7.799
7.554
7.541
7.352
7.340
7.328
7.312
7.301
7.251
7.233
7.220
7.058
7.045
7.016
7.003
5.550
5.535
4.968
4.953
2.328
1H NMR (600 MHz, CDCl3) of compound 2q
NHTs
2q
2.03
2.13
1.99
0.96
2.01
2.01
2.08
1.00
1.00
6.06
f1 (ppm)


ZX-13C
ZX-20210309-3
143.48
138.77
137.64
137.52
131.50
129.56
128.87
128.70
128.42
127.56
127.36
118.95
86.86
84.89
77.24
77.03
76.82
49.86
21.44
13C{1H} NMR (151 MHz, CDCl3) of compound 2q
NHTs
2q
f1 (ppm)

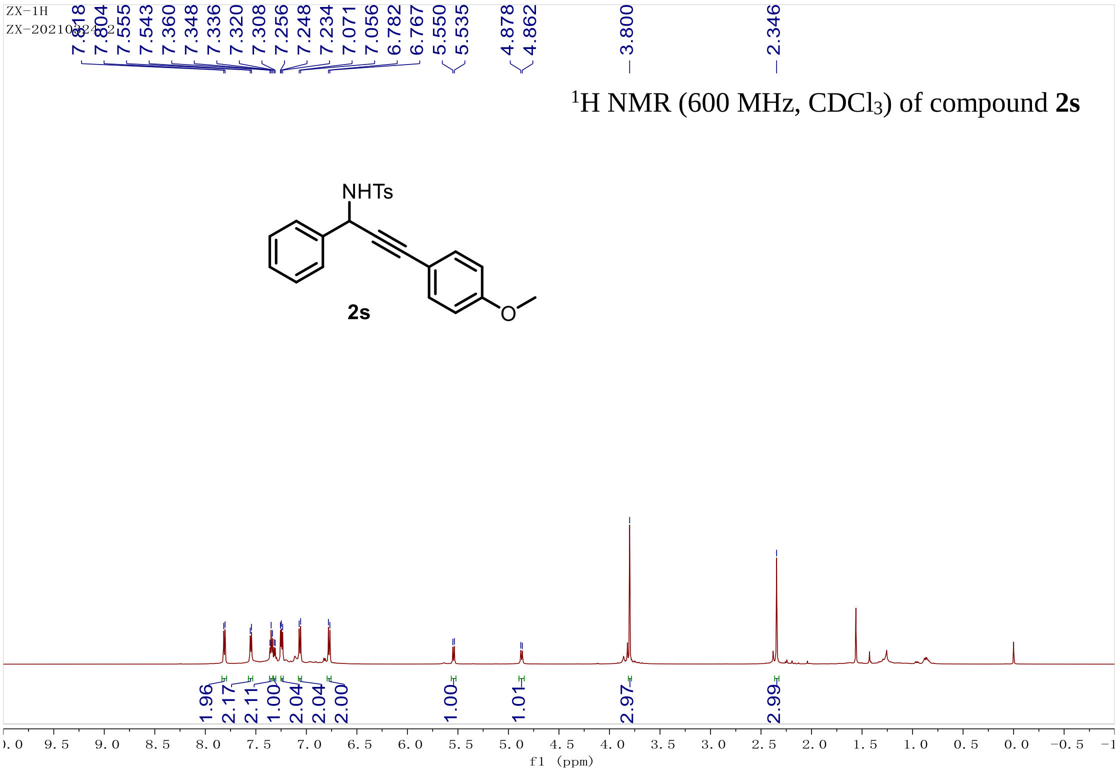


^{1}H NMR (600 MHz, $CDCl_3$) of compound **2r**

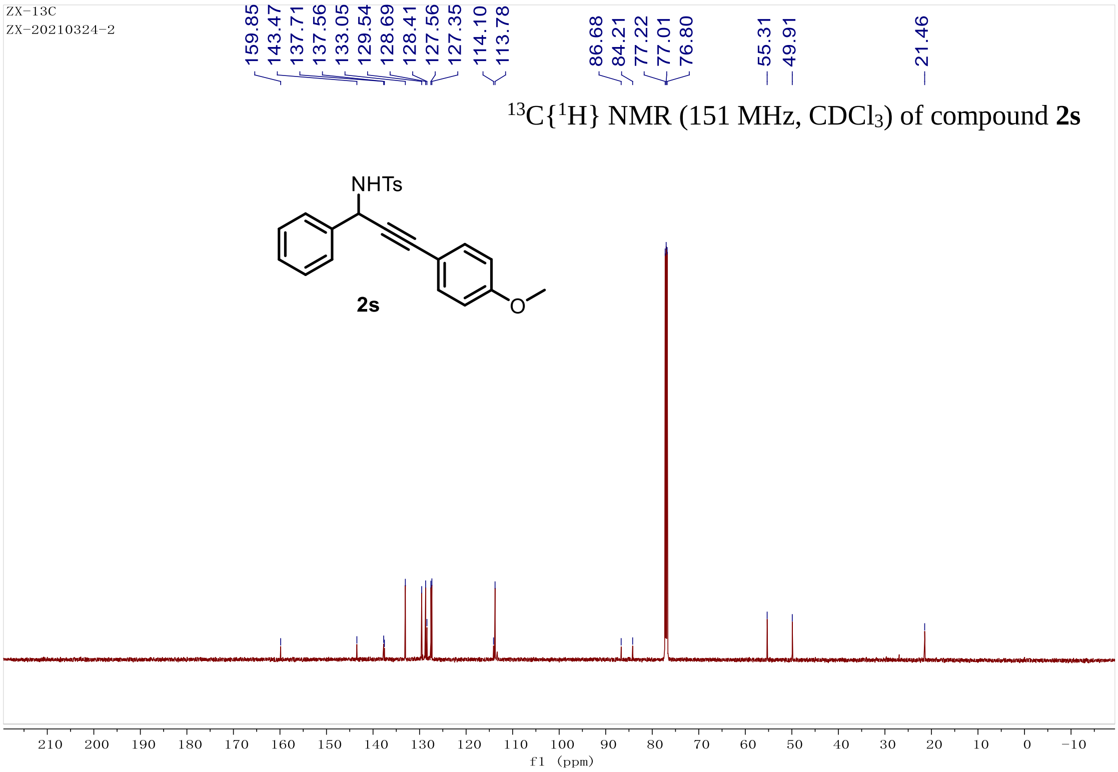


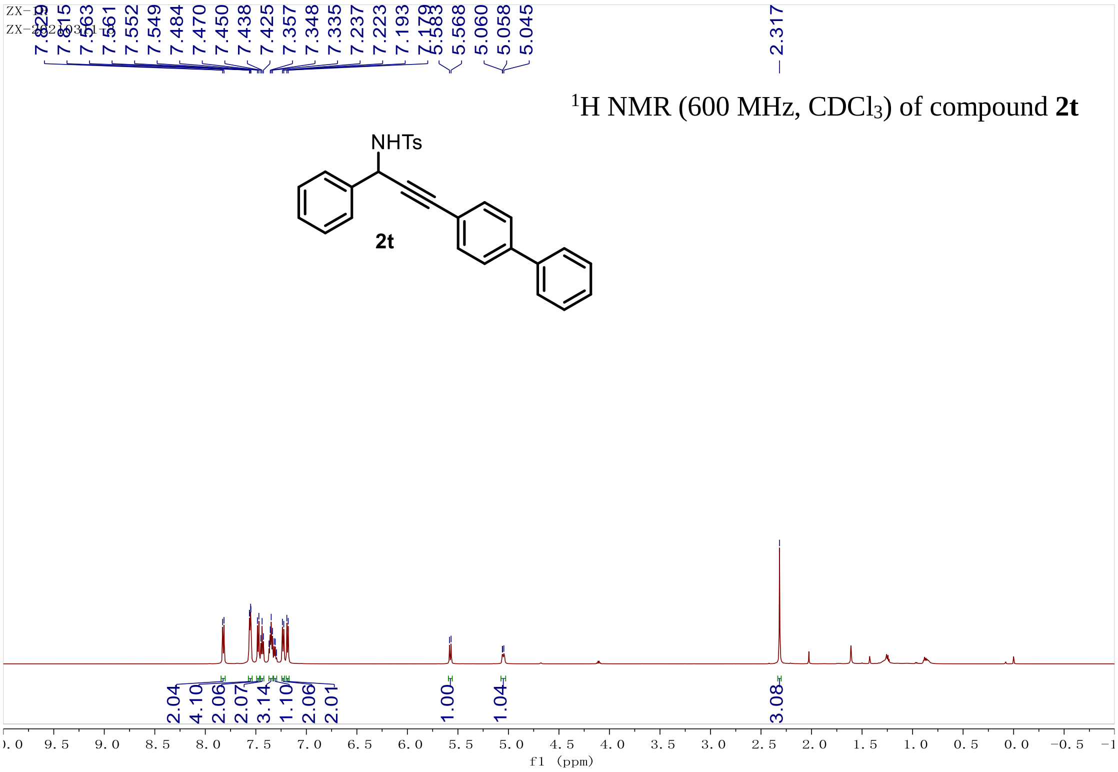
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2r**

[1]H NMR (600 MHz, $CDCl_3$) of compound **2s**

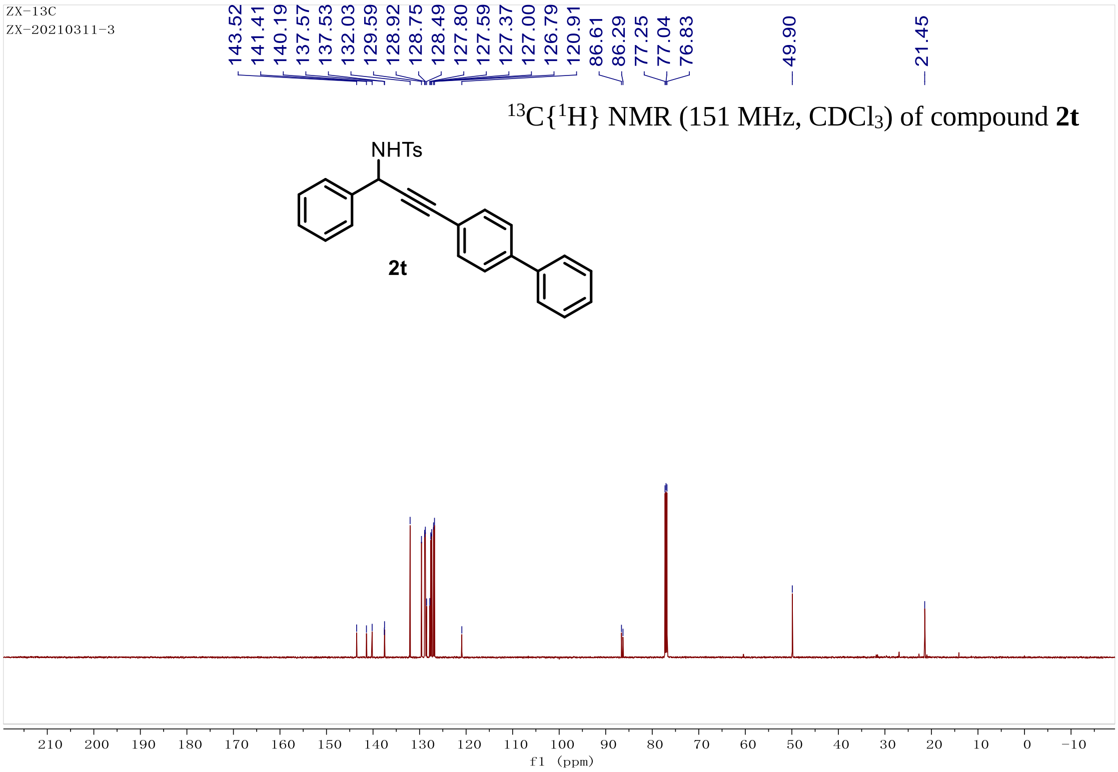


[13]C{[1]H} NMR (151 MHz, $CDCl_3$) of compound **2s**

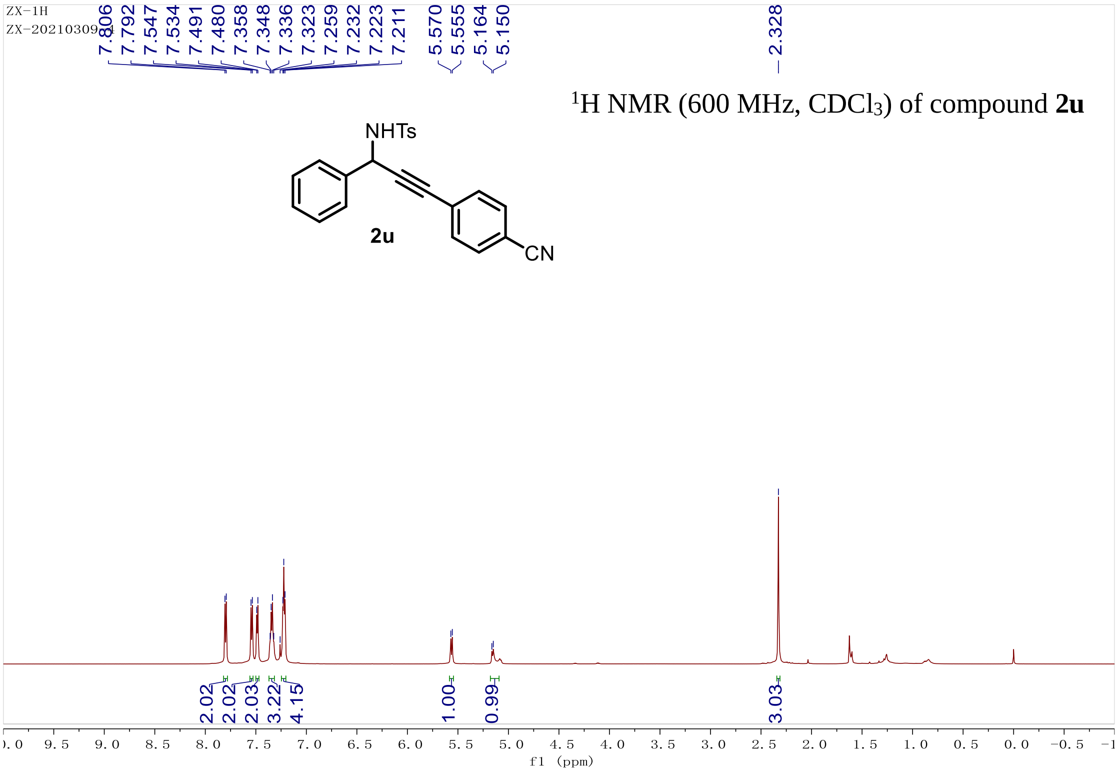


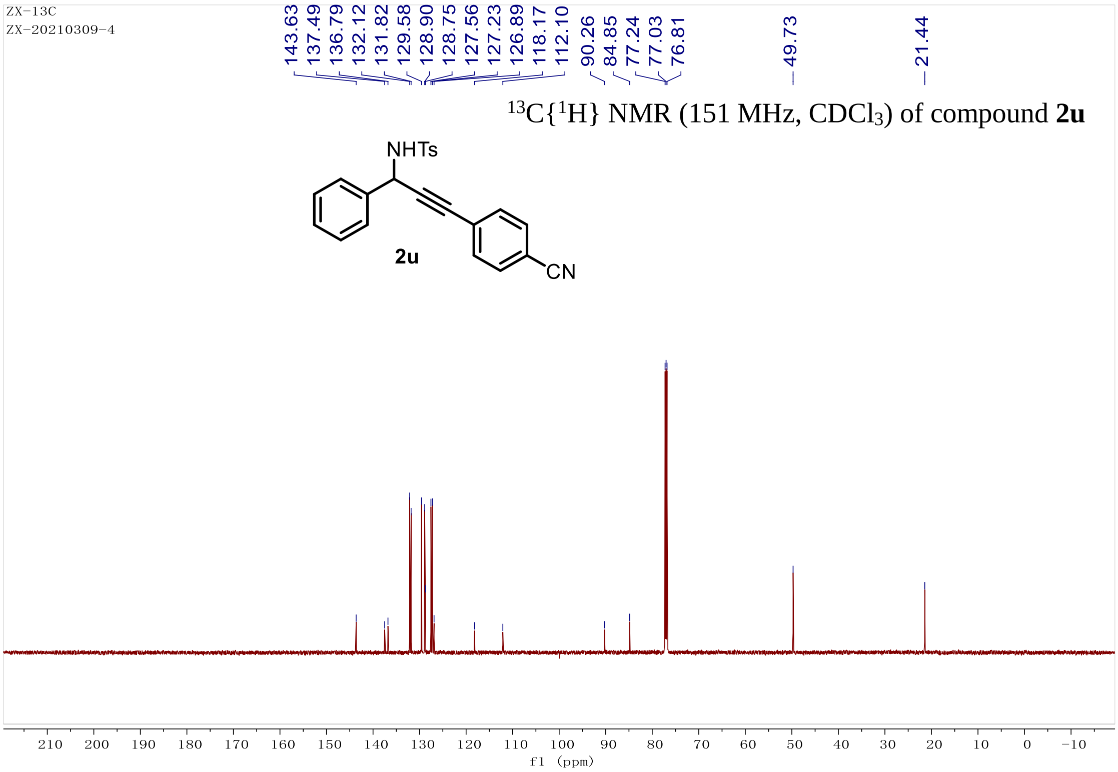


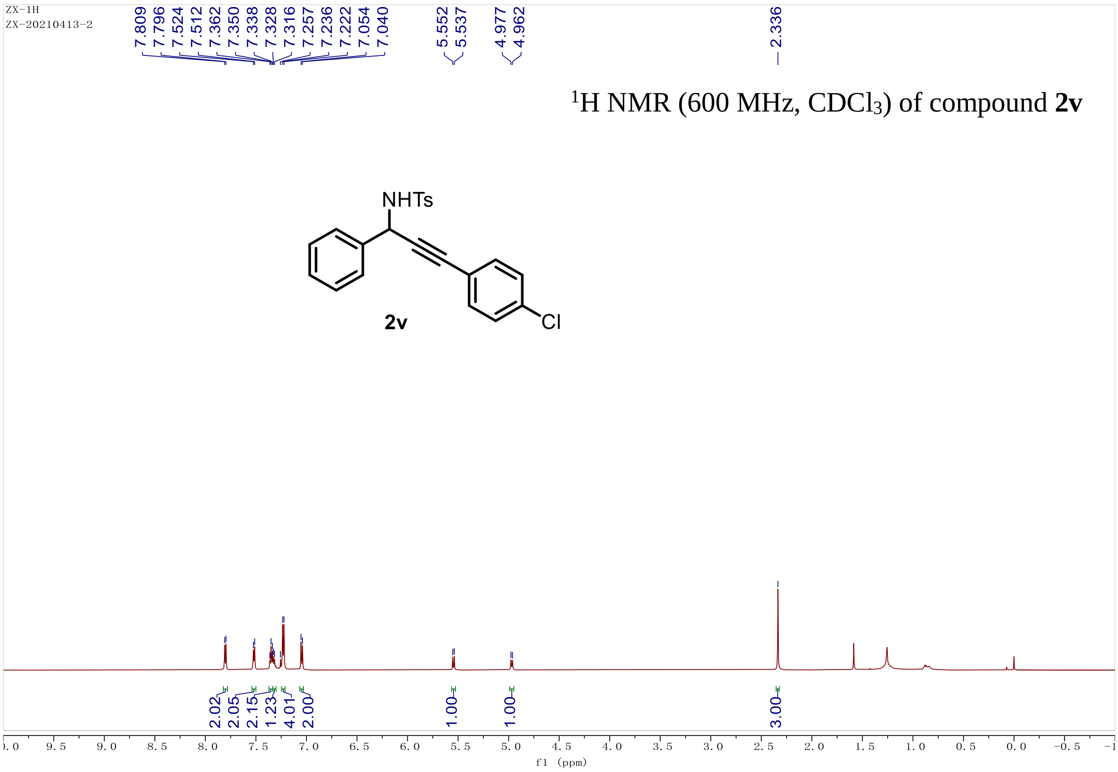
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2t**

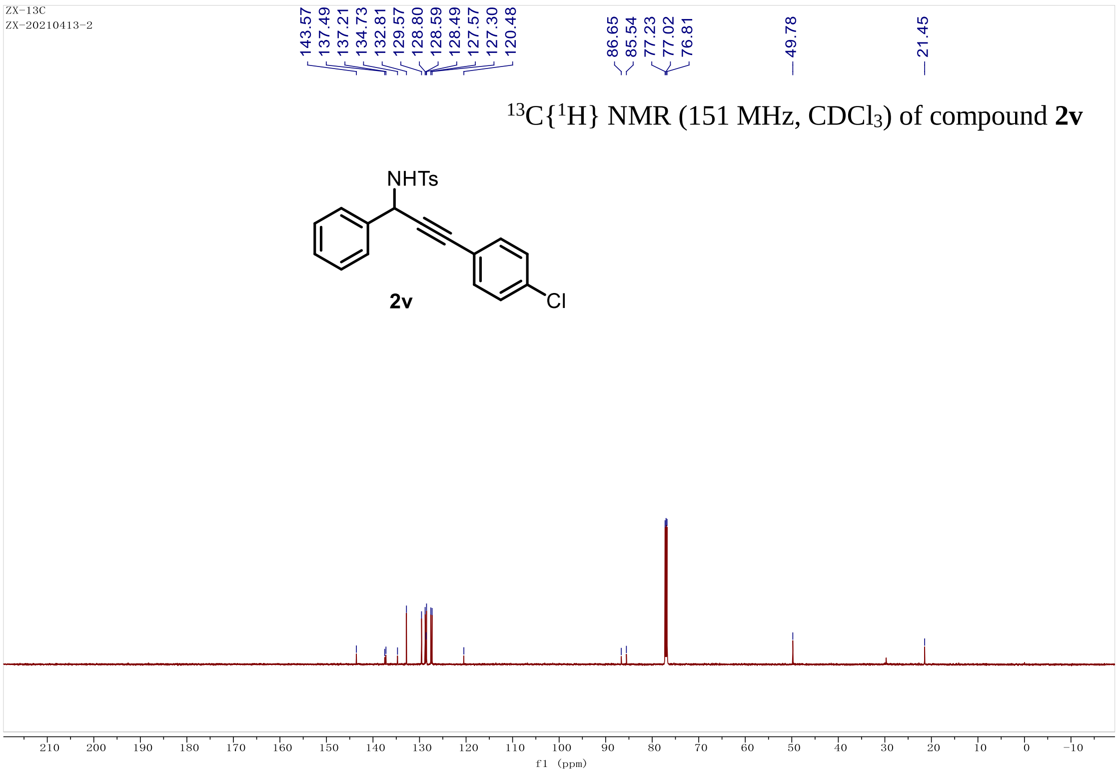


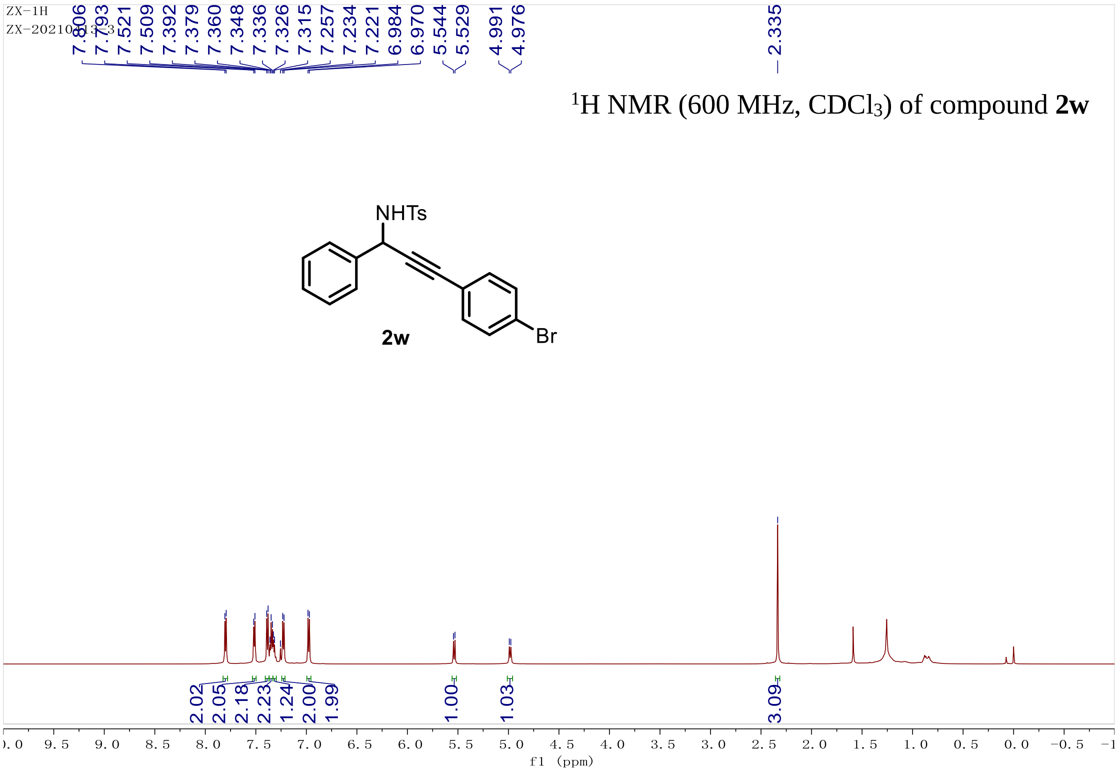
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2t**

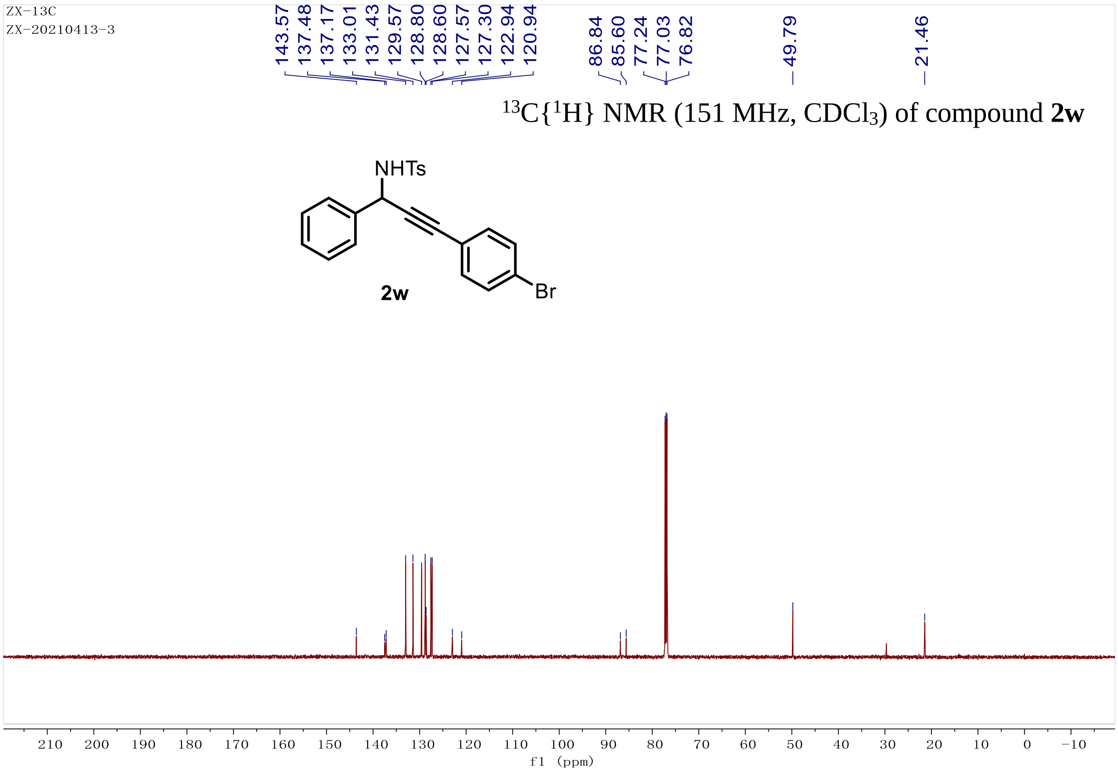

ZX-1H
ZX-20210309-4
7.806
7.792
7.547
7.534
7.491
7.480
7.358
7.348
7.336
7.323
7.259
7.232
7.223
7.211
5.570
5.555
5.164
5.150
2.328
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2u**
NHTs
2u
CN
2.02
2.02
2.03
3.22
4.15
1.00
0.99
3.03
f1 (ppm)

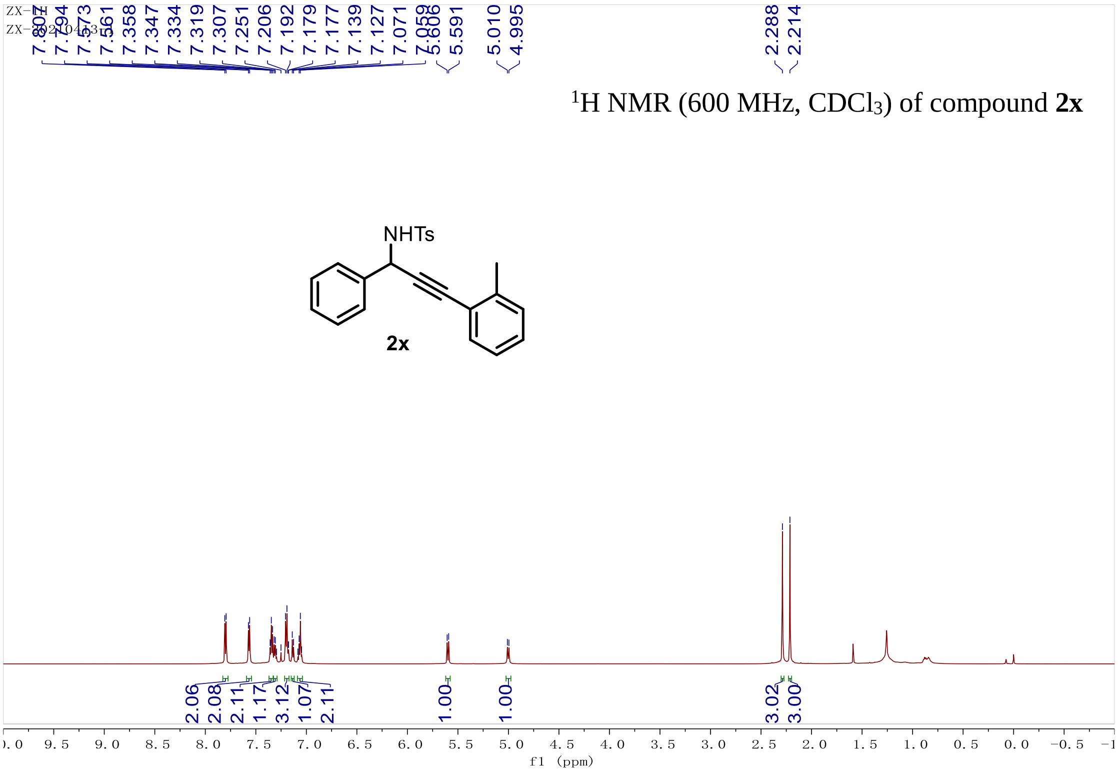

ZX-13C
ZX-20210309-4
143.63
137.49
136.79
132.12
131.82
129.58
128.90
128.75
127.56
127.23
126.89
118.17
112.10
90.26
84.85
77.24
77.03
76.81
49.73
21.44
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2u**
NHTs
2u
CN
f1 (ppm)


ZX-1H
ZX-20210413-2
7.809 7.796 7.524 7.512 7.362 7.350 7.338 7.328 7.316 7.257 7.236 7.222 7.054 7.040
5.552 5.537
4.977 4.962
2.336
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2v**
NHTs
Cl
2v
2.02 2.05 2.15 1.23 4.01 2.00
1.00
1.00
3.00
f1 (ppm)

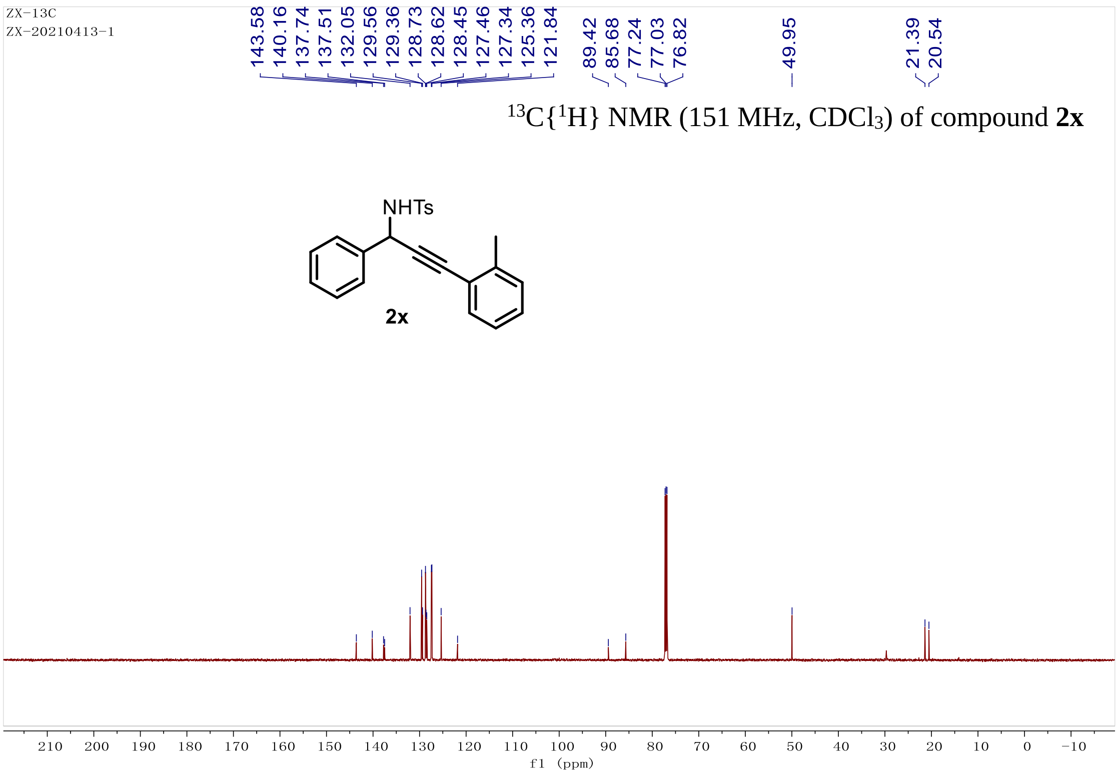

ZX-13C
ZX-20210413-2
143.57 137.49 137.21 134.73 132.81 129.57 128.80 128.59 128.49 127.57 127.30 120.48
86.65 85.54 77.23 77.02 76.81
49.78
21.45
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2v**
NHTs
Cl
2v
f1 (ppm)


ZX-1H
ZX-20210413-3
7.806
7.793
7.521
7.509
7.392
7.379
7.360
7.348
7.336
7.326
7.315
7.257
7.234
7.221
6.984
6.970
5.544
5.529
4.991
4.976
2.335
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2w**
NHTs
Br
2w
2.02
2.05
2.18
2.23
1.24
2.00
1.99
1.00
1.03
3.09
f1 (ppm)

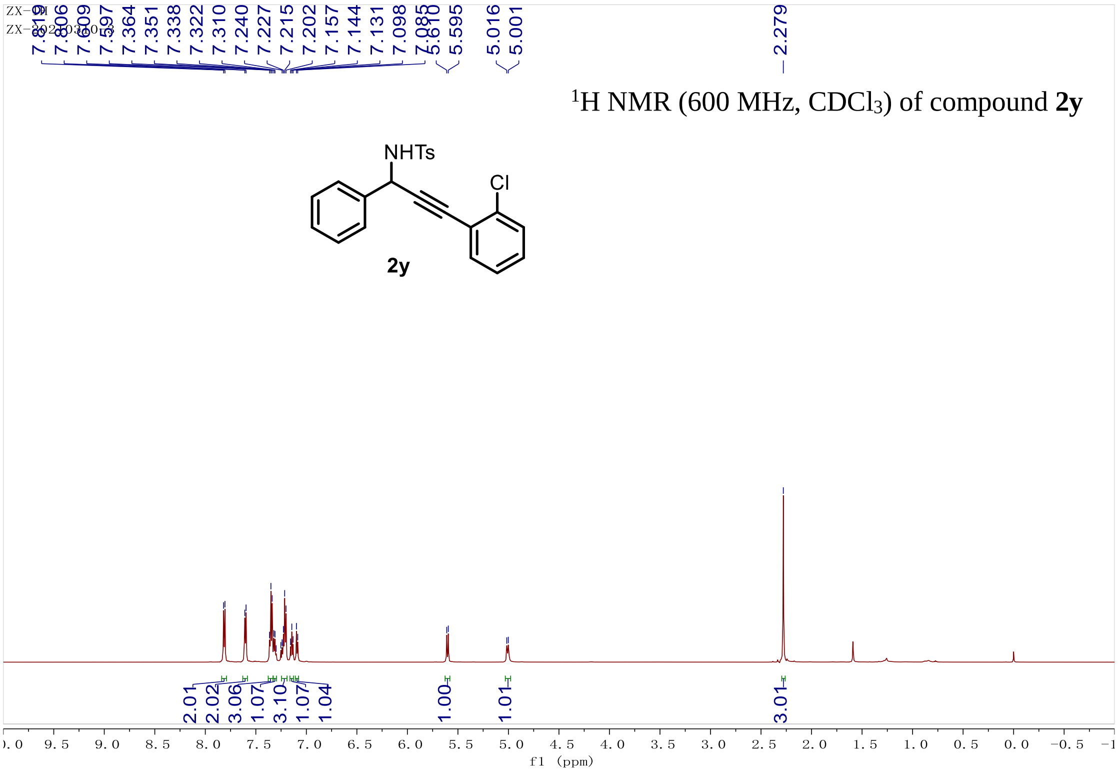

ZX-13C
ZX-20210413-3
143.57
137.48
137.17
133.01
131.43
129.57
128.80
128.60
127.57
127.30
122.94
120.94
86.84
85.60
77.24
77.03
76.82
49.79
21.46
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2w**
NHTs
Br
2w
f1 (ppm)



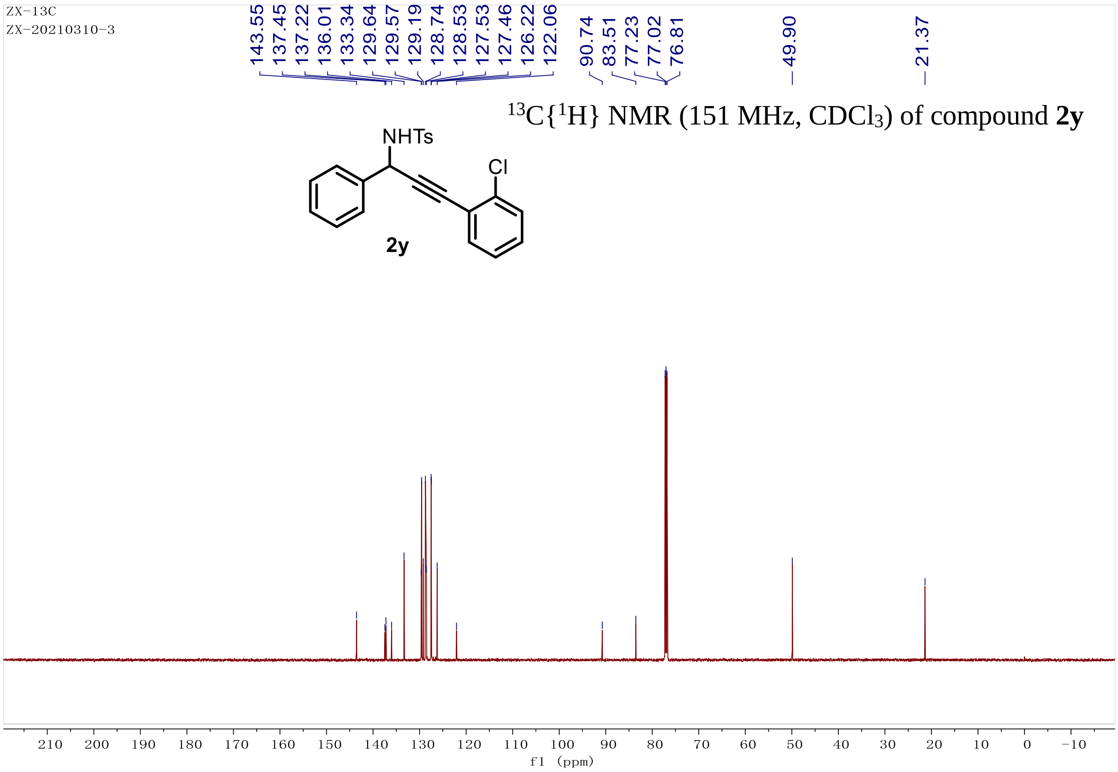
[1]H NMR (600 MHz, $CDCl_3$) of compound **2x**



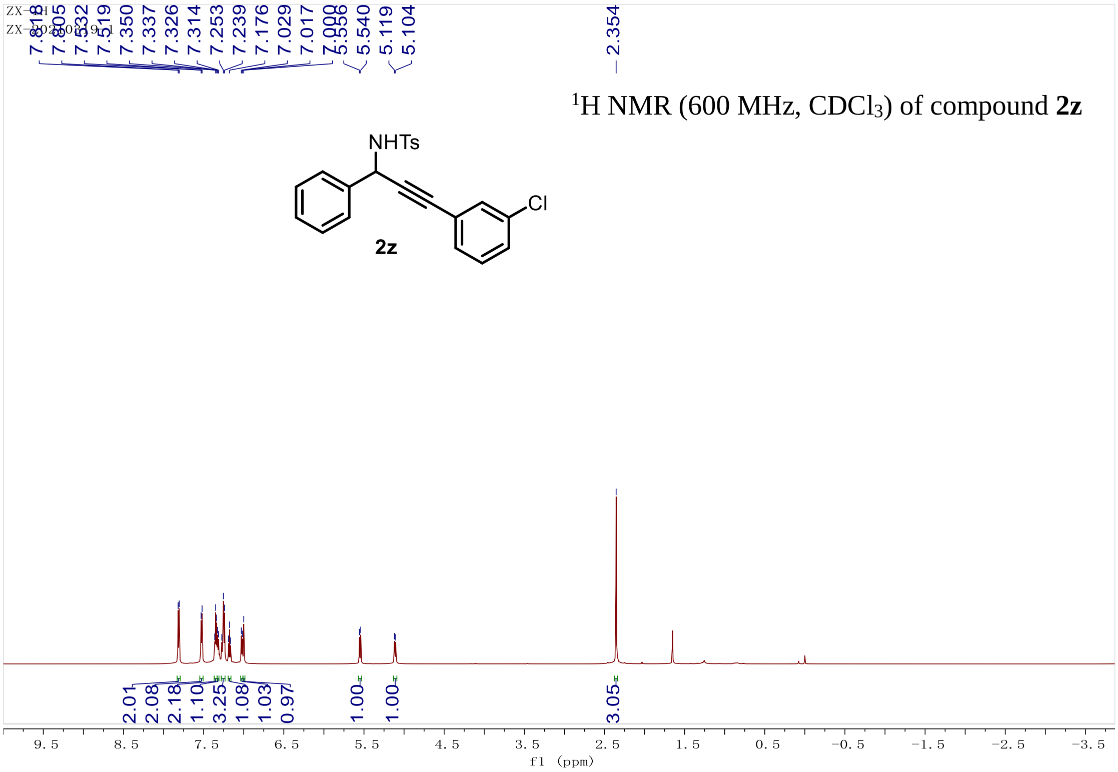
[13]C{[1]H} NMR (151 MHz, $CDCl_3$) of compound **2x**



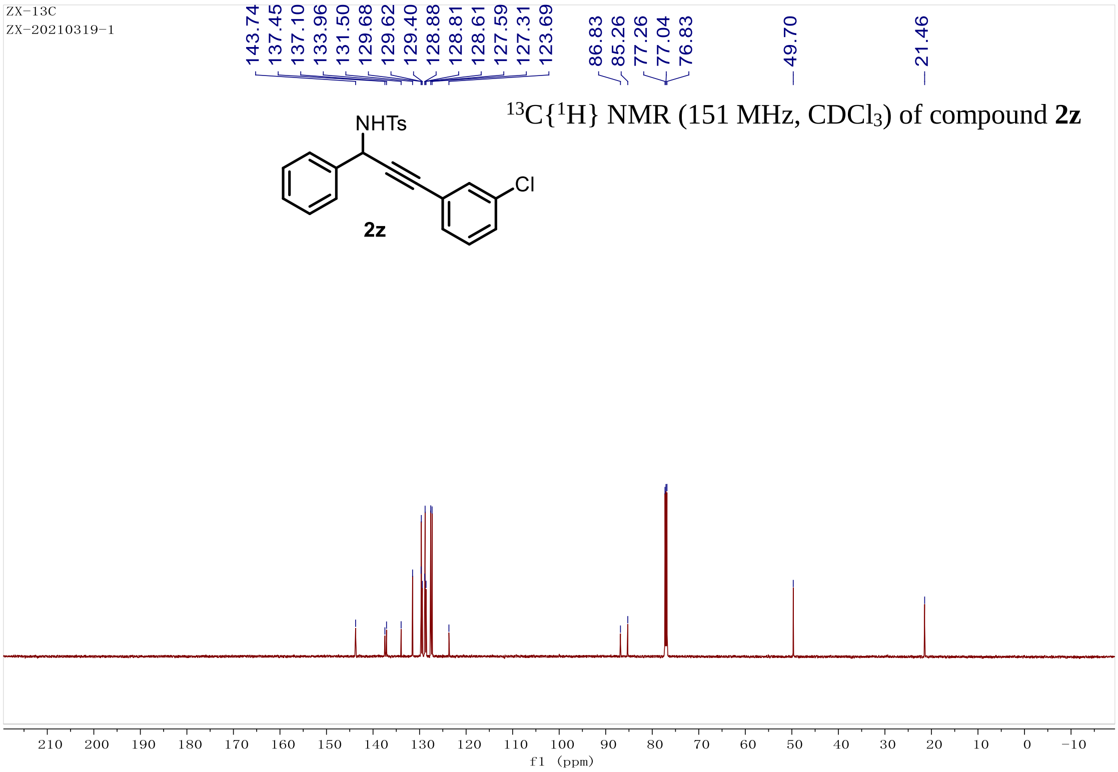
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2y**



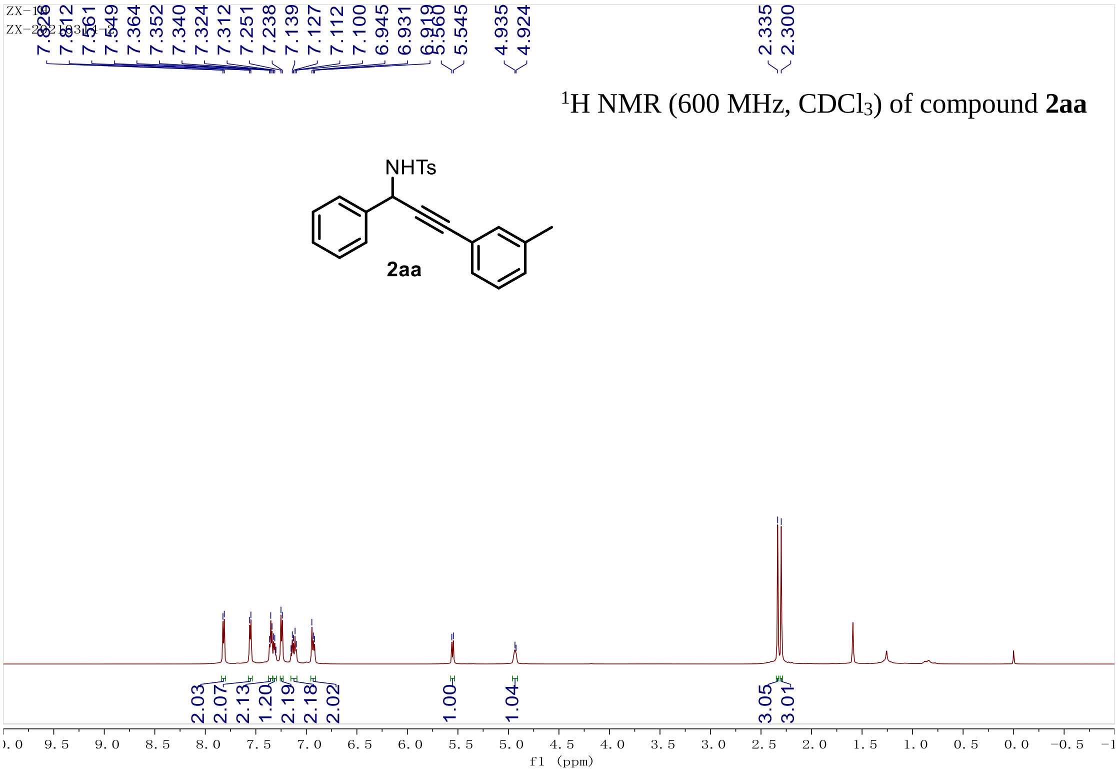
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2y**



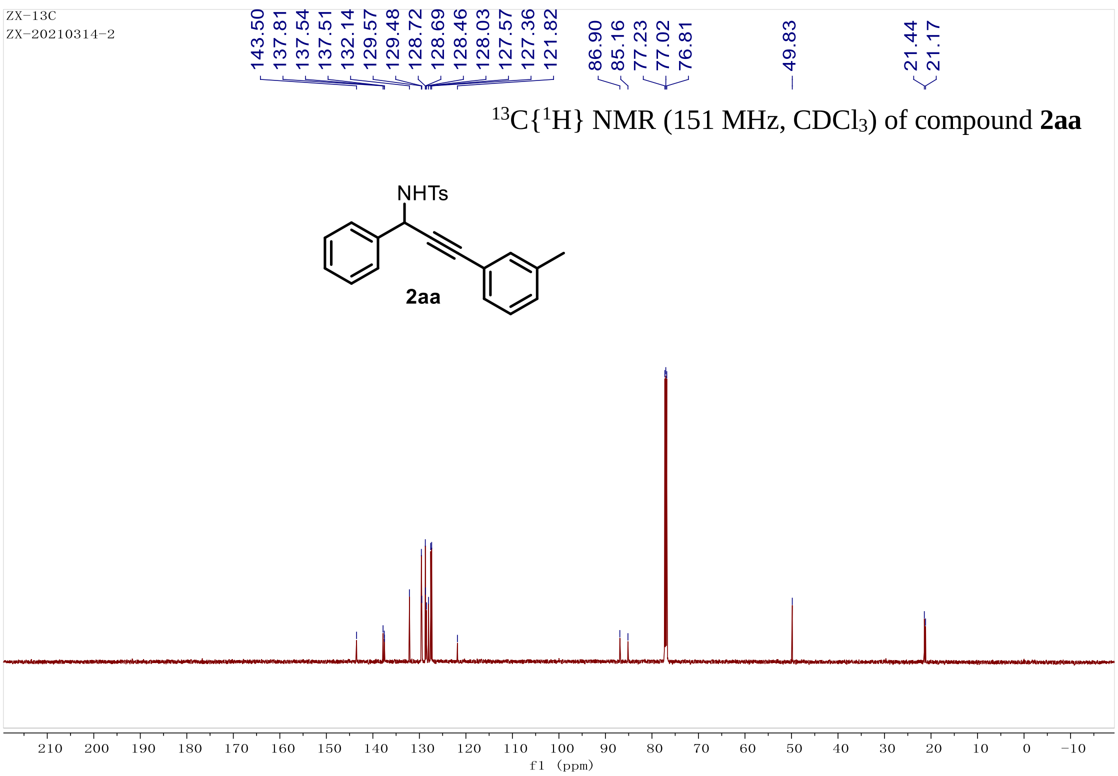
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2z**



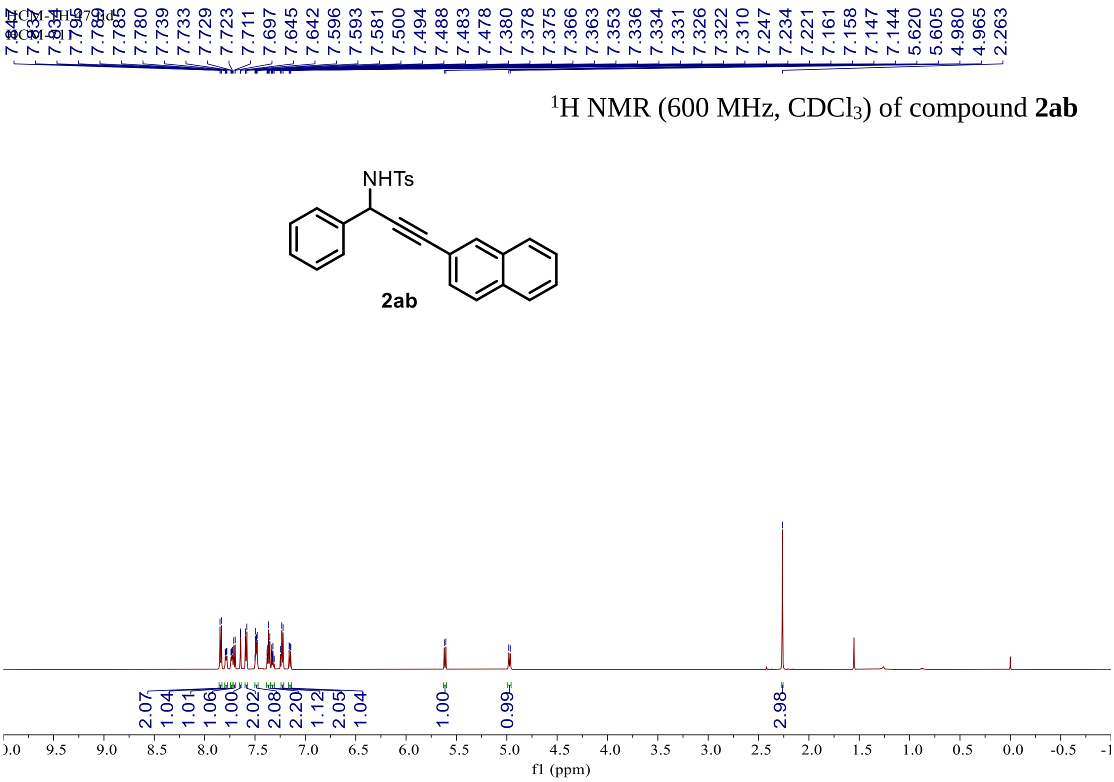
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2z**



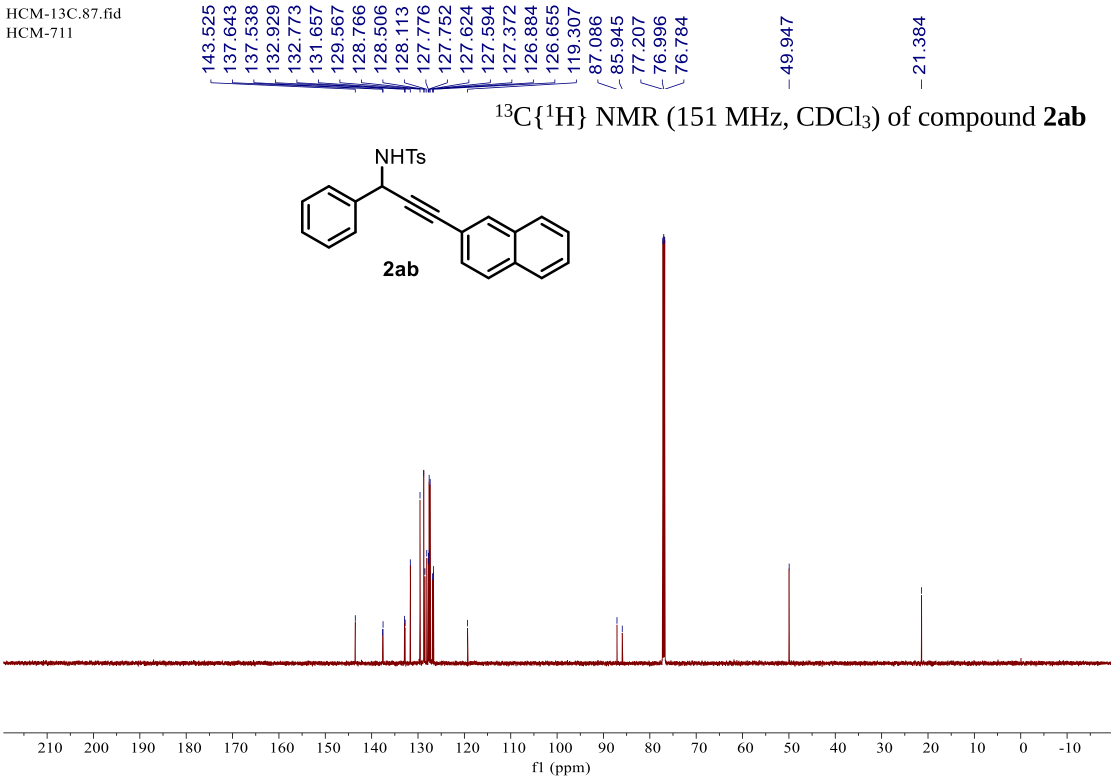
[1]H NMR (600 MHz, $CDCl_3$) of compound **2aa**



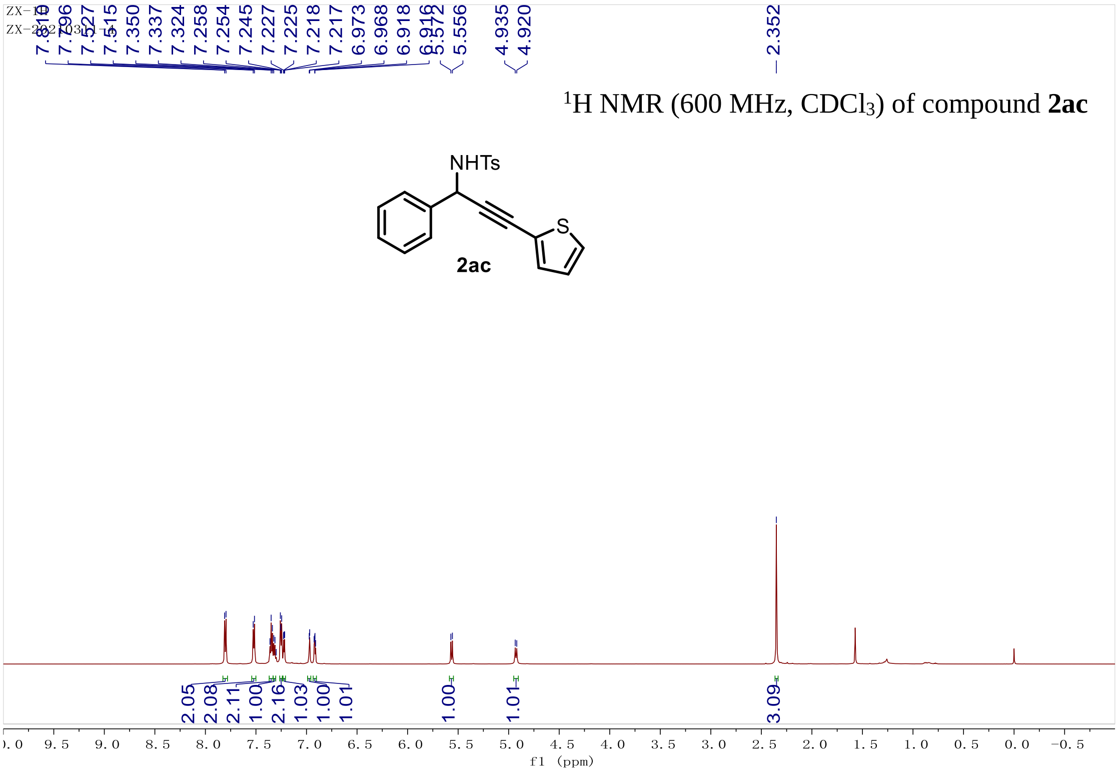
[13]C{[1]H} NMR (151 MHz, $CDCl_3$) of compound **2aa**

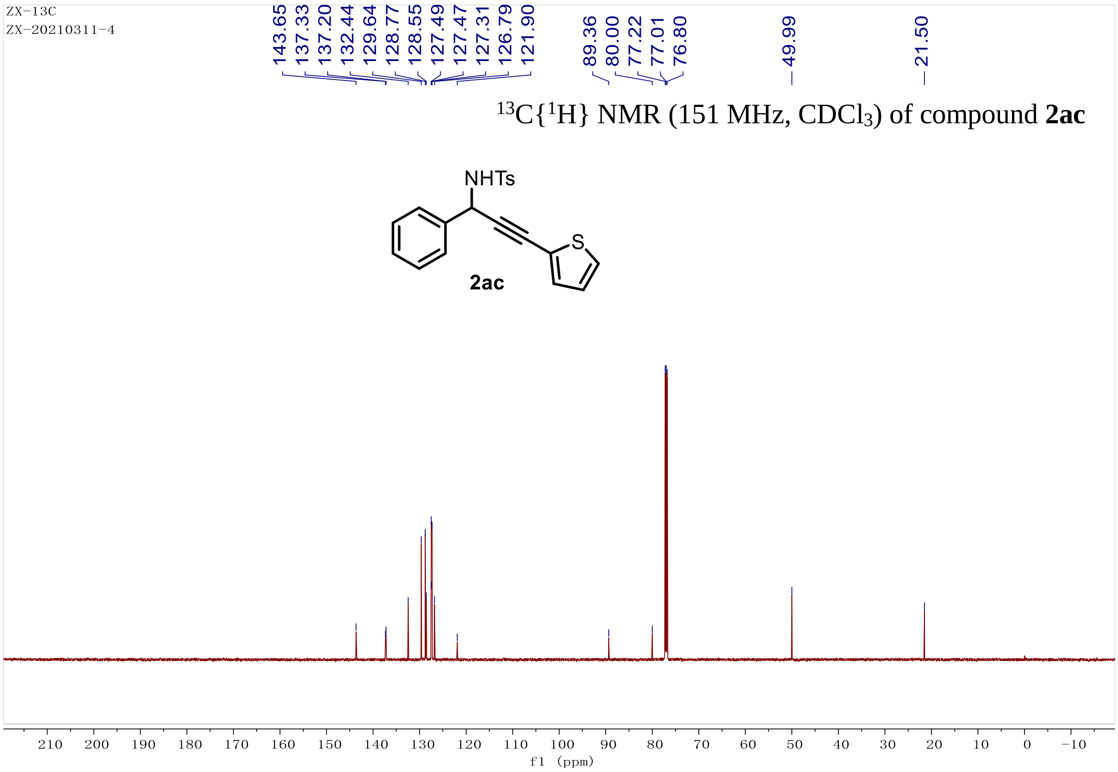


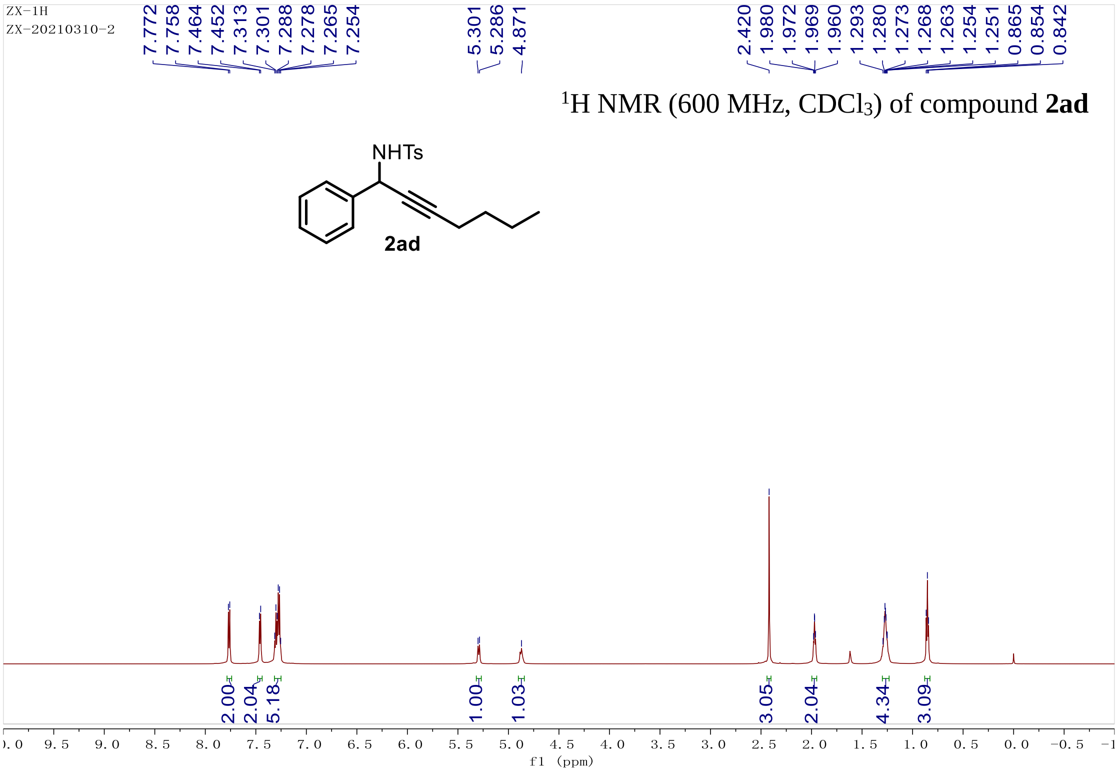
[1]H NMR (600 MHz, $CDCl_3$) of compound **2ab**

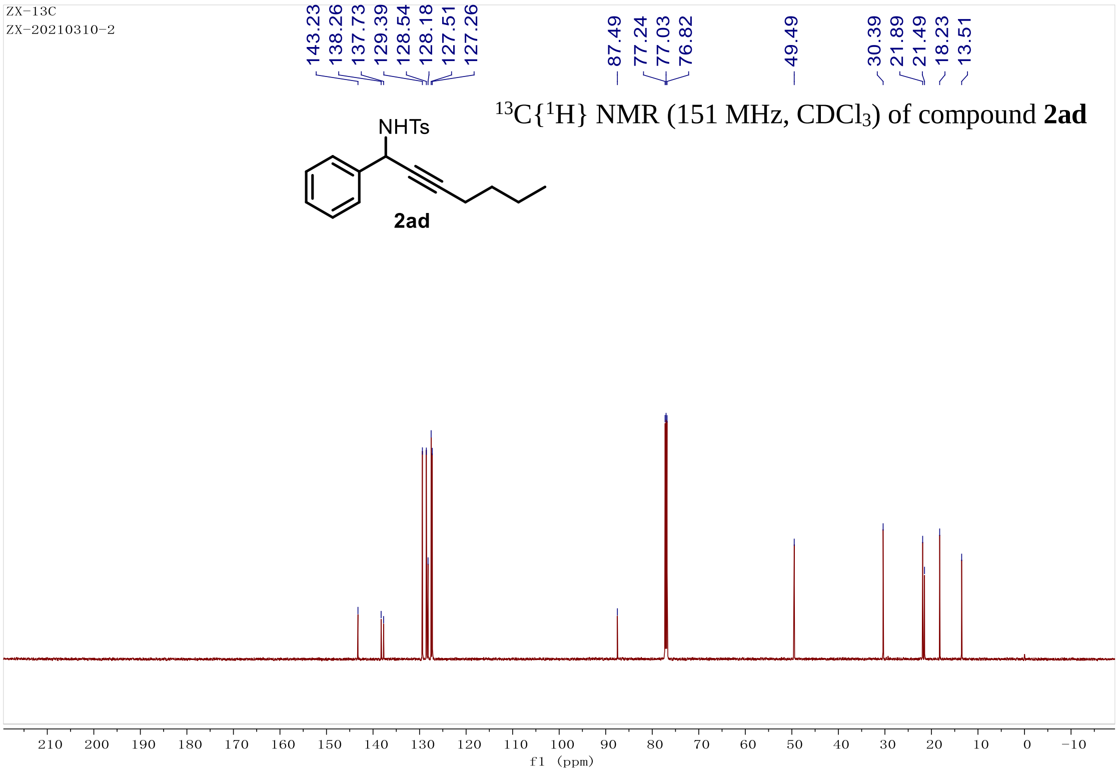


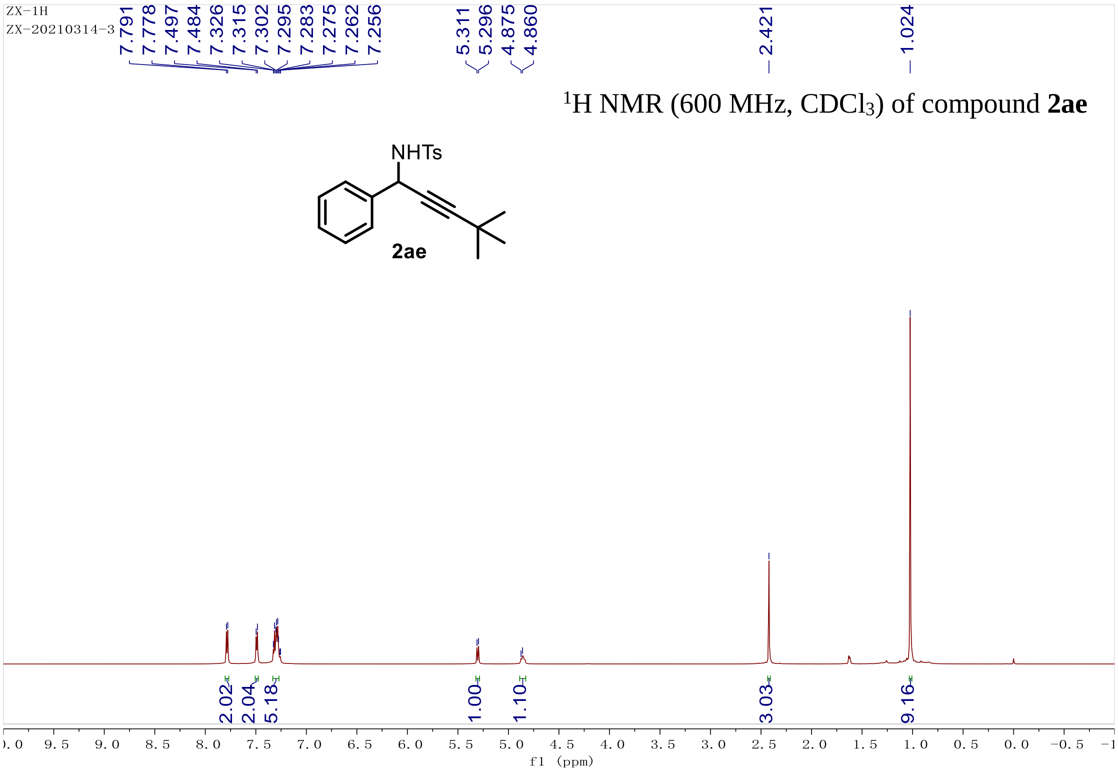
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) of compound **2ab**

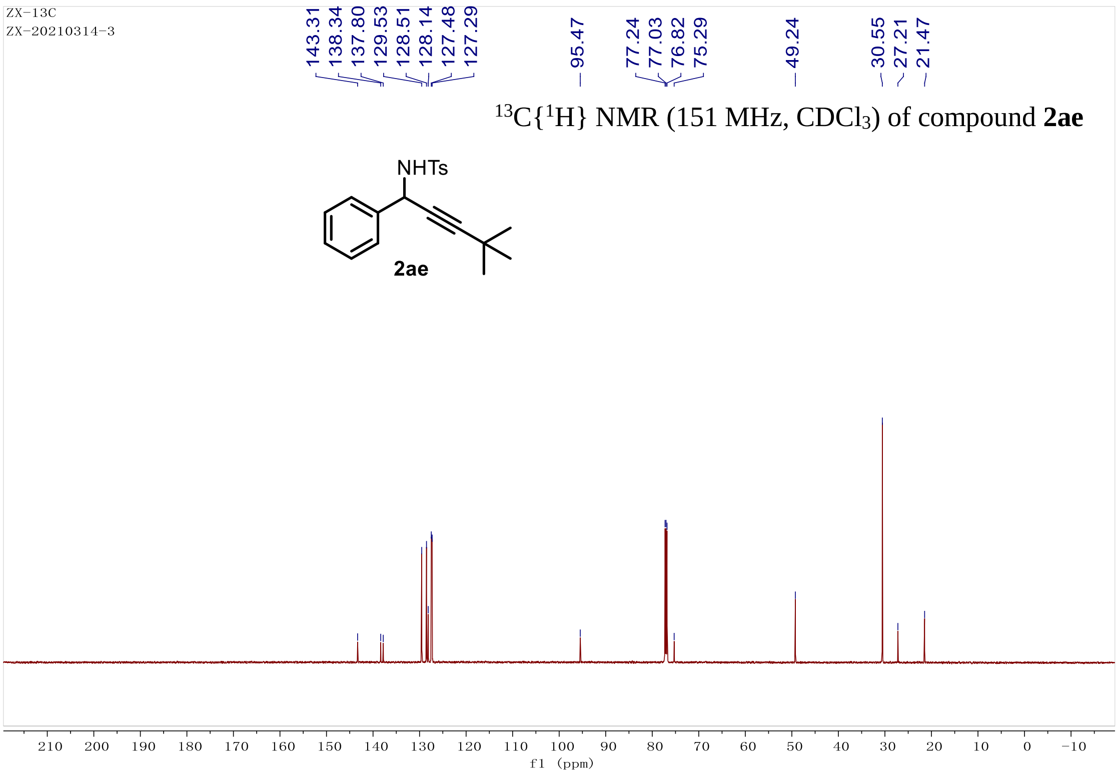

ZX-1H
ZX-20210311-4
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2ac**
NHTs
S
2ac
7.810
7.796
7.527
7.515
7.350
7.337
7.324
7.258
7.254
7.245
7.227
7.225
7.218
7.217
6.973
6.968
6.918
6.916
5.572
5.556
4.935
4.920
2.352
2.05
2.08
2.11
1.00
2.16
1.03
1.00
1.01
1.00
1.01
3.09
f1 (ppm)

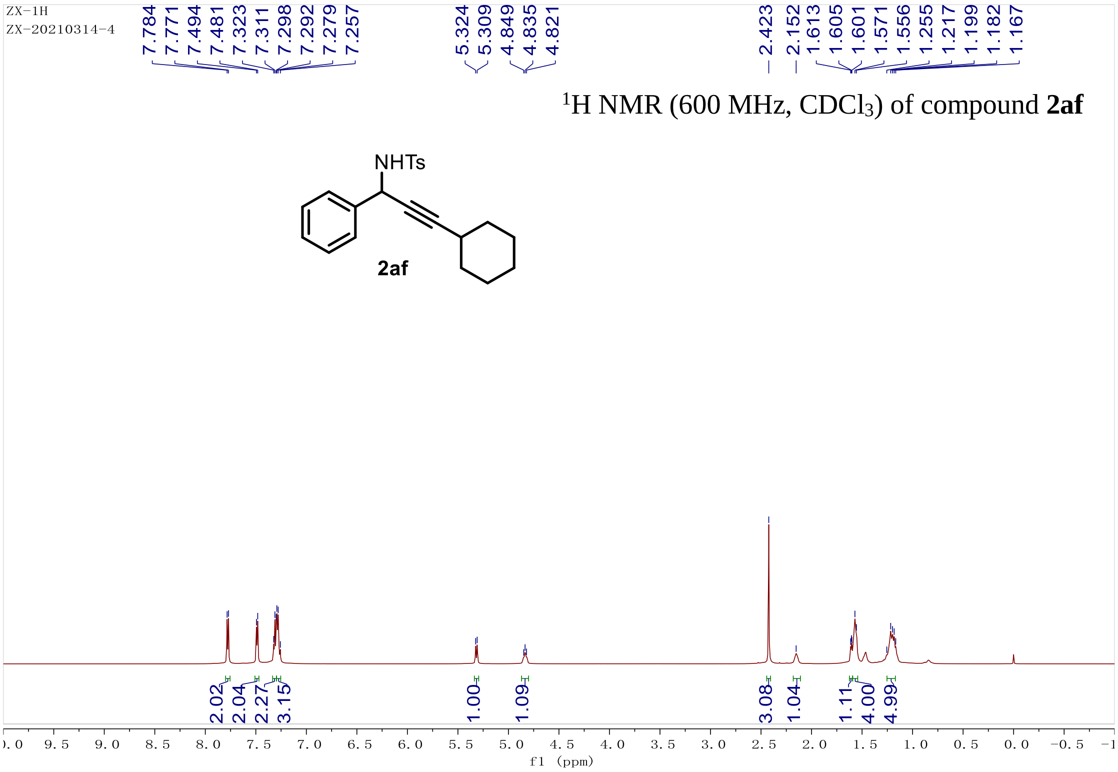

ZX-13C
ZX-20210311-4
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2ac**
NHTs
S
2ac
143.65
137.33
137.20
132.44
129.64
128.77
128.55
127.49
127.47
127.31
126.79
121.90
89.36
80.00
77.22
77.01
76.80
49.99
21.50
f1 (ppm)


ZX-1H
ZX-20210310-2
7.772
7.758
7.464
7.452
7.313
7.301
7.288
7.278
7.265
7.254
5.301
5.286
4.871
2.420
1.980
1.972
1.969
1.960
1.293
1.280
1.273
1.268
1.263
1.254
1.251
0.865
0.854
0.842
¹H NMR (600 MHz, CDCl₃) of compound 2ad
NHTs
2ad
2.00
2.04
5.18
1.00
1.03
3.05
2.04
4.34
3.09
f1 (ppm)

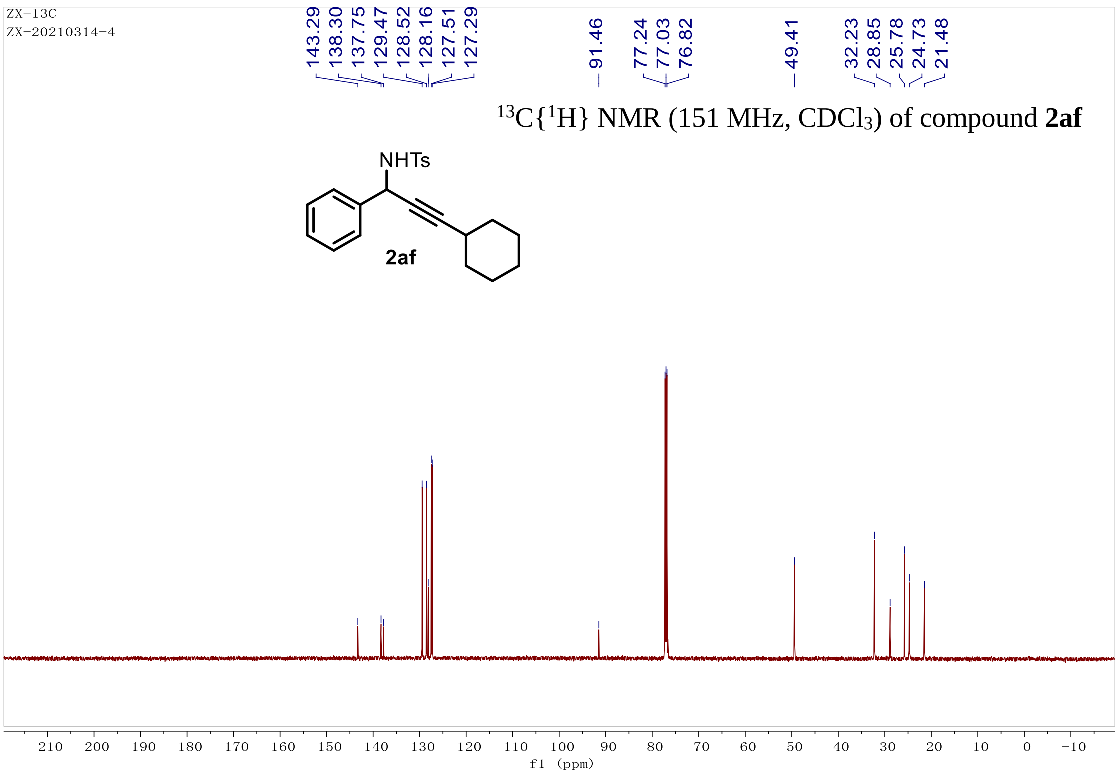

ZX-13C
ZX-20210310-2
143.23
138.26
137.73
129.39
128.54
128.18
127.51
127.26
87.49
77.24
77.03
76.82
49.49
30.39
21.89
21.49
18.23
13.51
¹³C{¹H} NMR (151 MHz, CDCl₃) of compound 2ad
NHTs
2ad
f1 (ppm)


ZX-1H
ZX-20210314-3
7.791
7.778
7.497
7.484
7.326
7.315
7.302
7.295
7.283
7.275
7.262
7.256
5.311
5.296
4.875
4.860
2.421
1.024
1H NMR (600 MHz, CDCl3) of compound 2ae
NHTs
2ae
2.02
2.04
5.18
1.00
1.10
3.03
9.16
f1 (ppm)

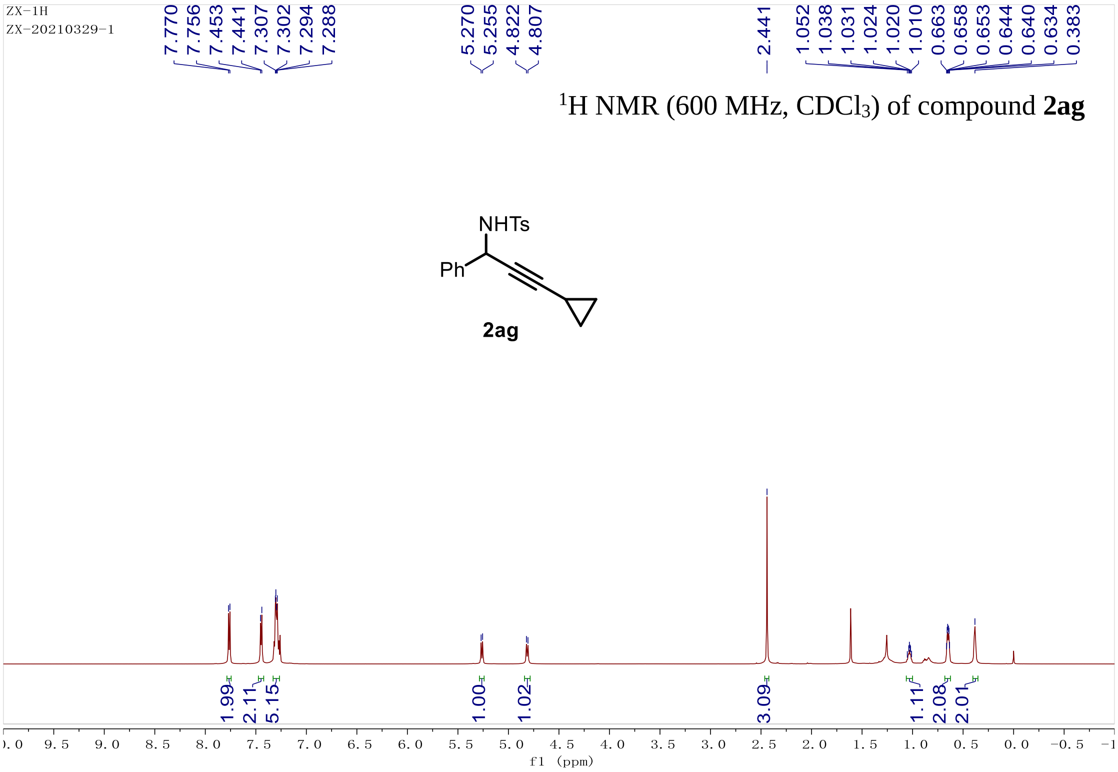

ZX-13C
ZX-20210314-3
143.31
138.34
137.80
129.53
128.51
128.14
127.48
127.29
95.47
77.24
77.03
76.82
75.29
49.24
30.55
27.21
21.47
13C{1H} NMR (151 MHz, CDCl3) of compound 2ae
NHTs
2ae
f1 (ppm)



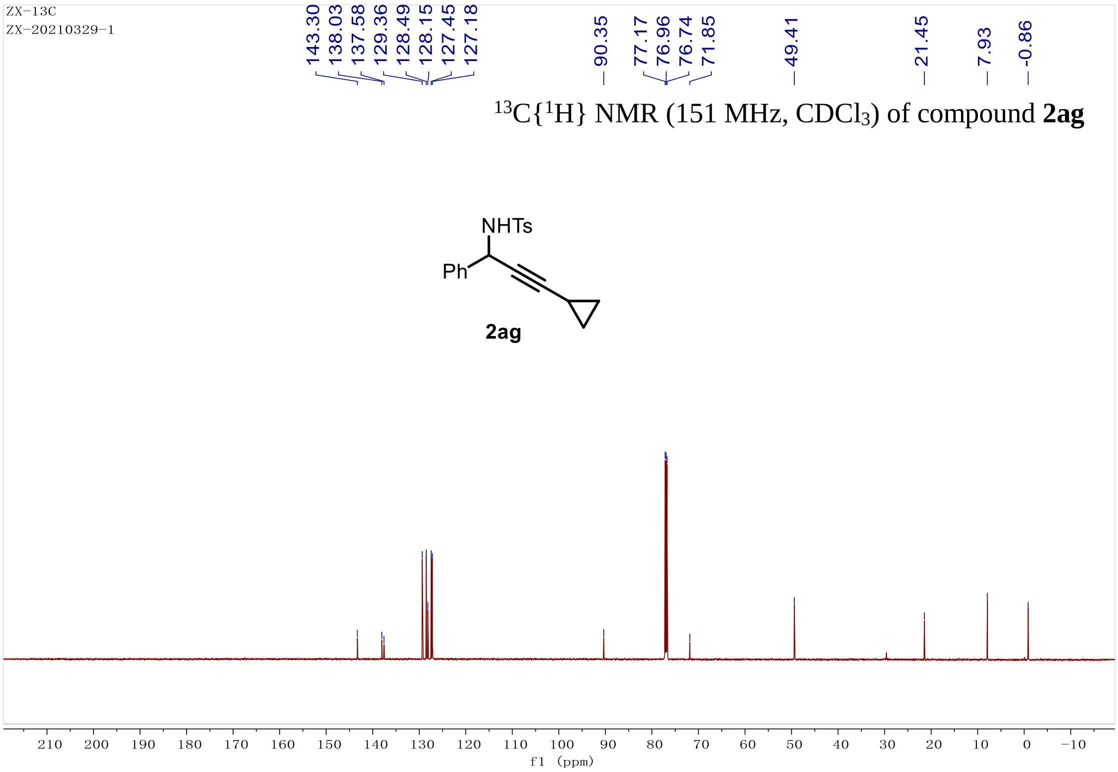
^{1}H NMR (600 MHz, CDCl$_3$) of compound **2af**



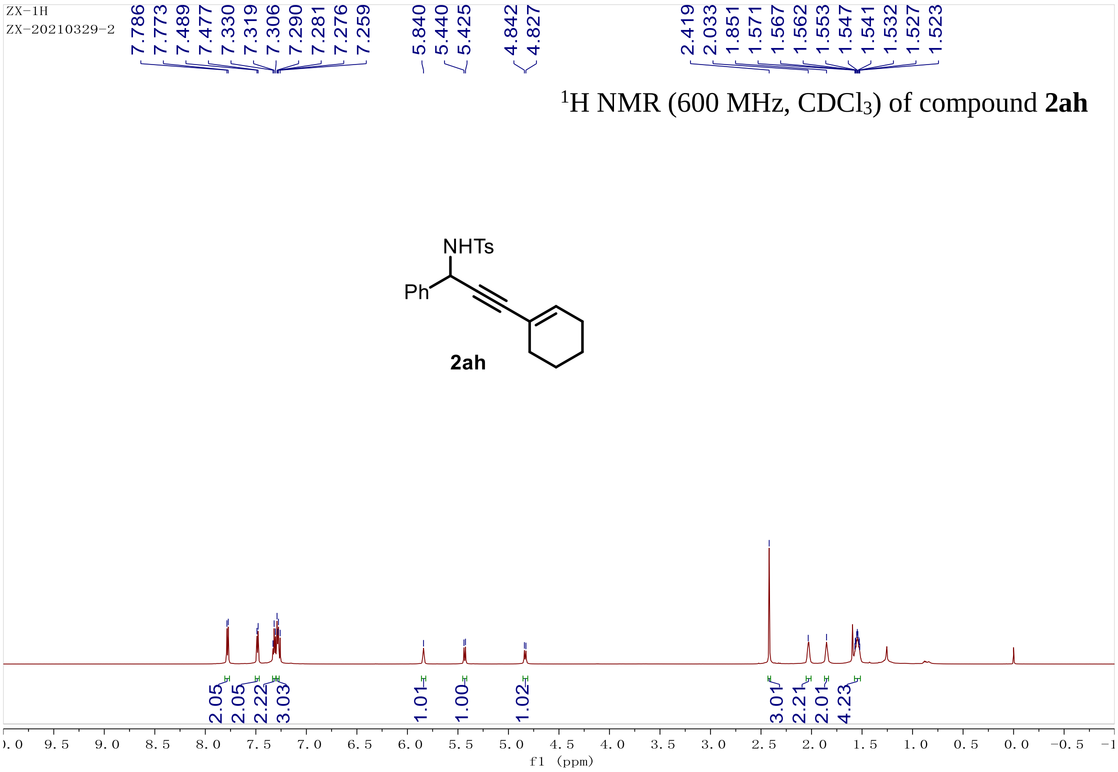
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) of compound **2af**



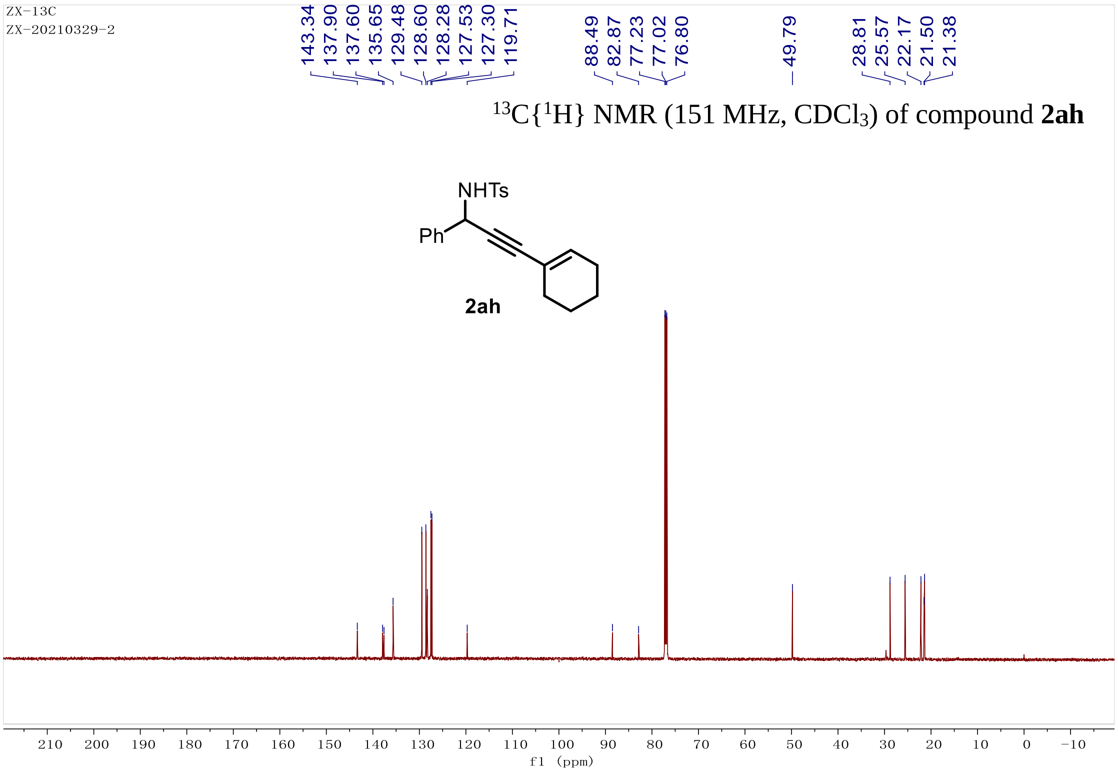
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2ag**



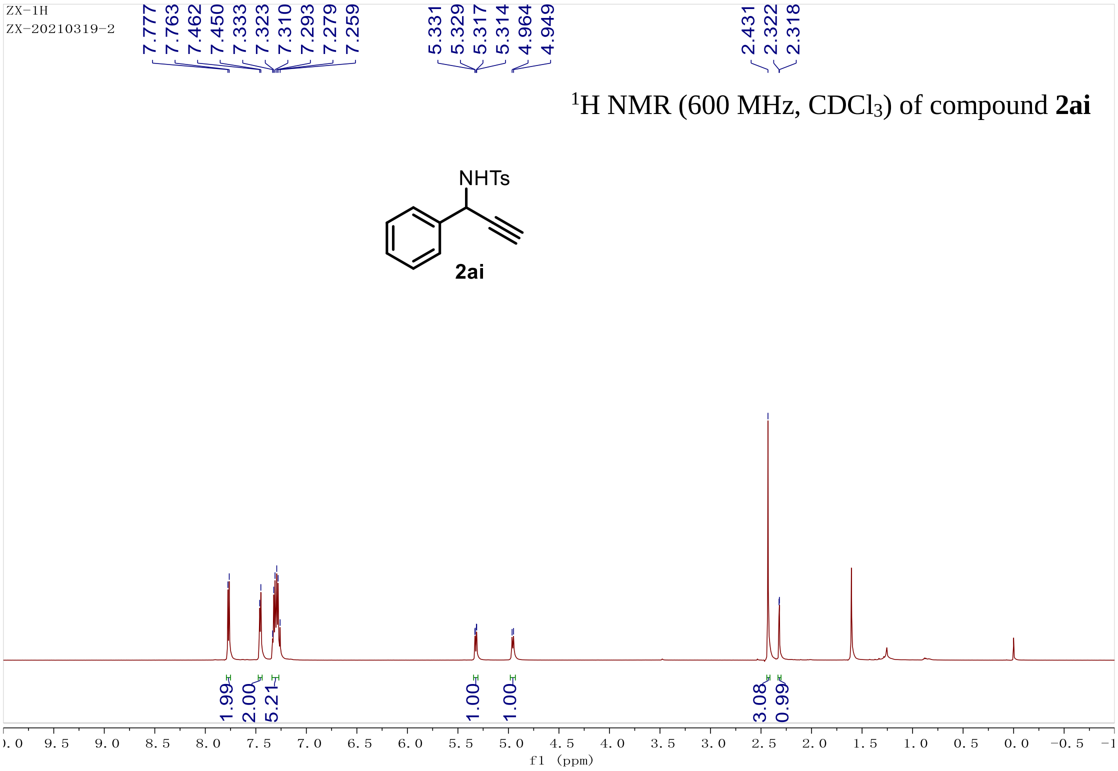
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2ag**

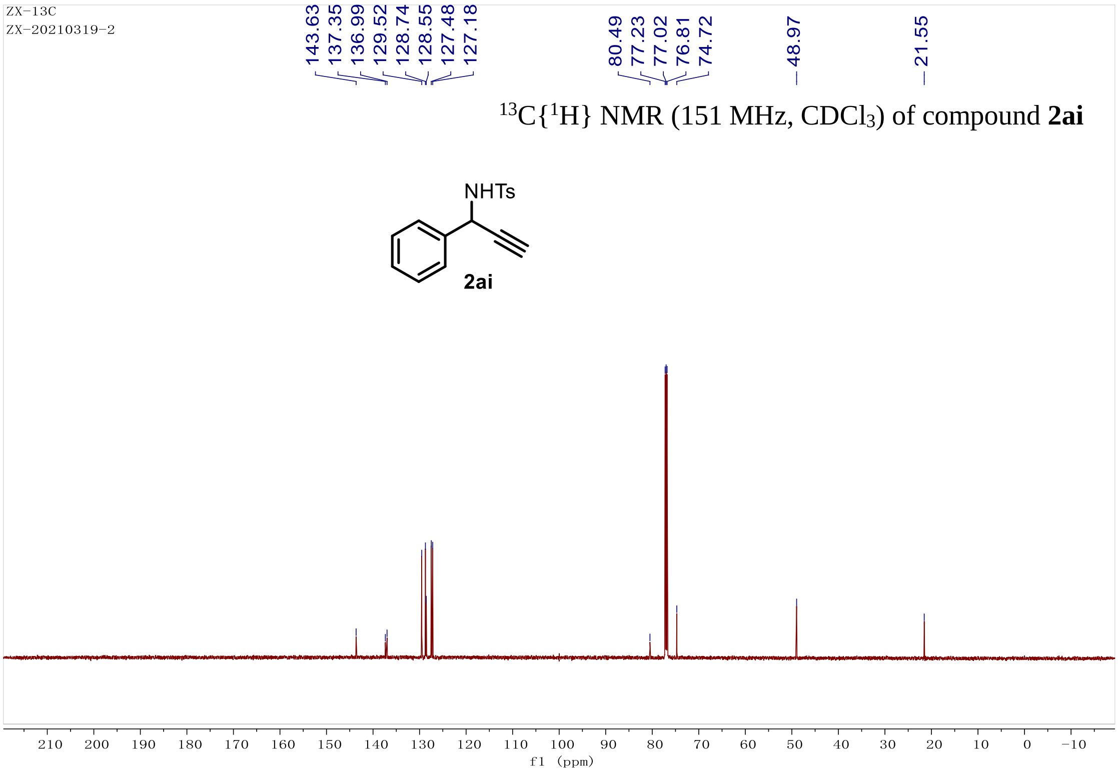


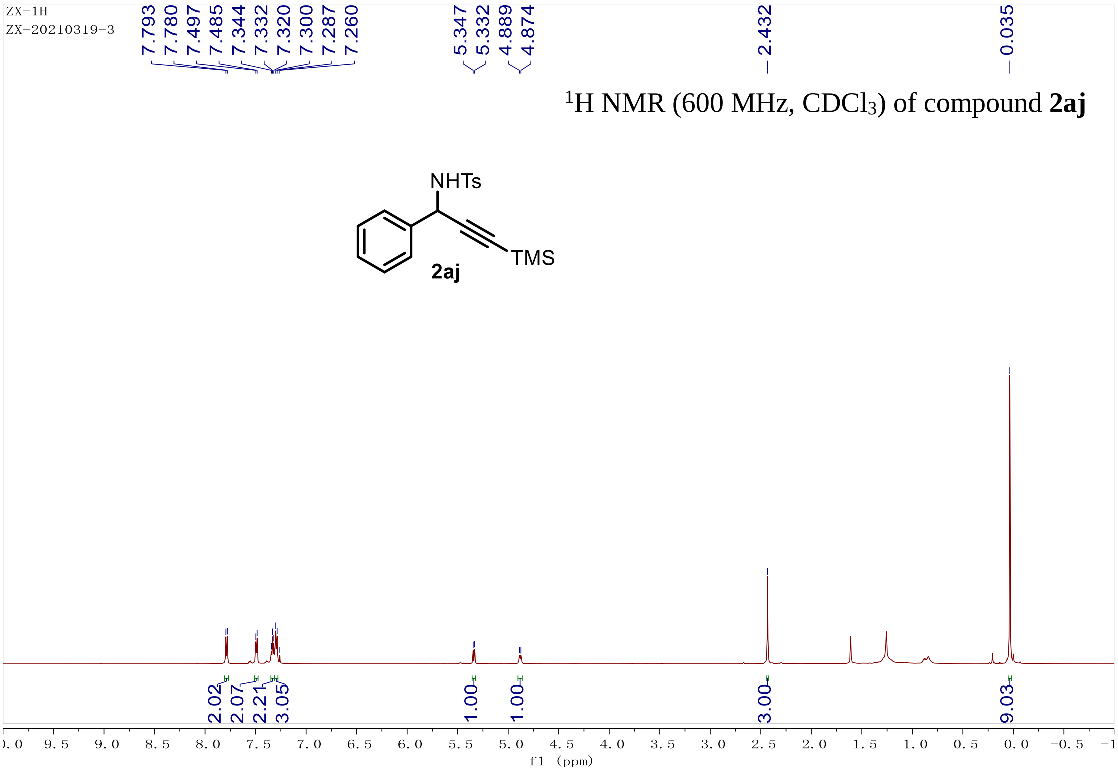
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2ah**



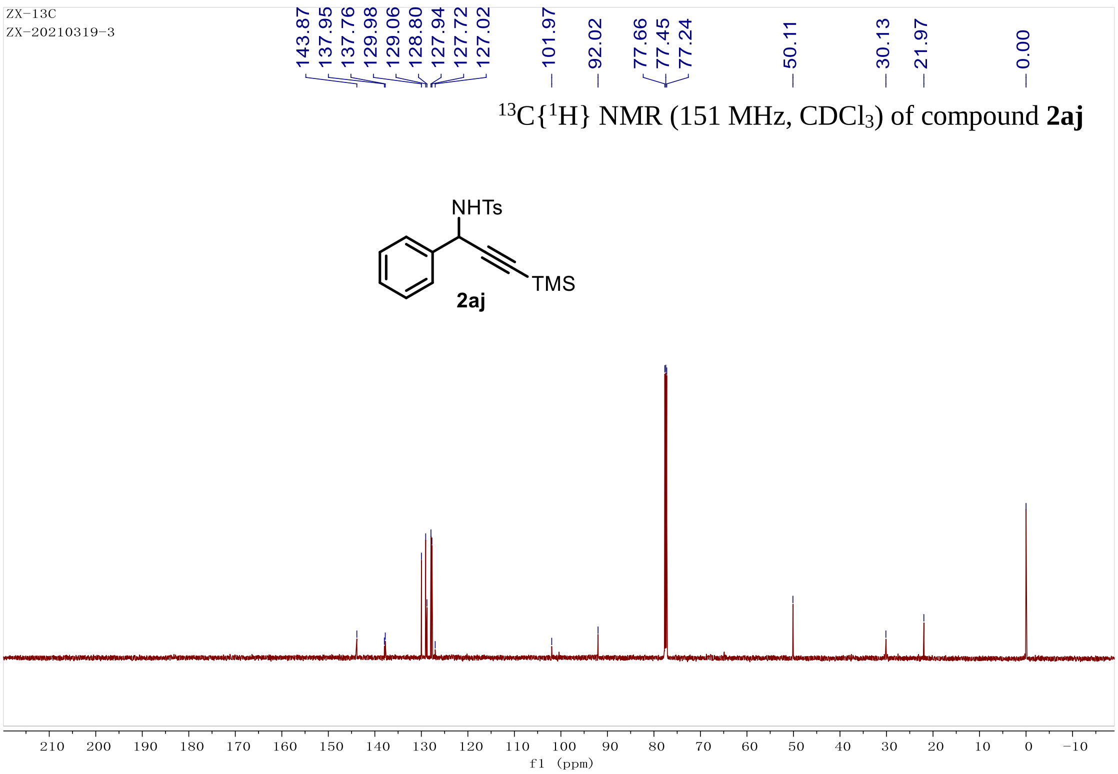
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) of compound **2ah**


ZX-1H
ZX-20210319-2
7.777
7.763
7.462
7.450
7.333
7.323
7.310
7.293
7.279
7.259
5.331
5.329
5.317
5.314
4.964
4.949
2.431
2.322
2.318
¹H NMR (600 MHz, CDCl₃) of compound **2ai**
NHTs
2ai
1.99
2.00
5.21
1.00
1.00
3.08
0.99
f1 (ppm)


ZX-13C
ZX-20210319-2
143.63
137.35
136.99
129.52
128.74
128.55
127.48
127.18
80.49
77.23
77.02
76.81
74.72
48.97
21.55
¹³C{¹H} NMR (151 MHz, CDCl₃) of compound **2ai**
NHTs
2ai
f1 (ppm)



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2aj**



$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **2aj**