Supporting Information

Synthesis of Indolizine Derivatives Containing Eight-membered Ring by a Gold-catalyzed Two-fold Hydroarylation of Diynes

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CONTENTS

(A) Additional References

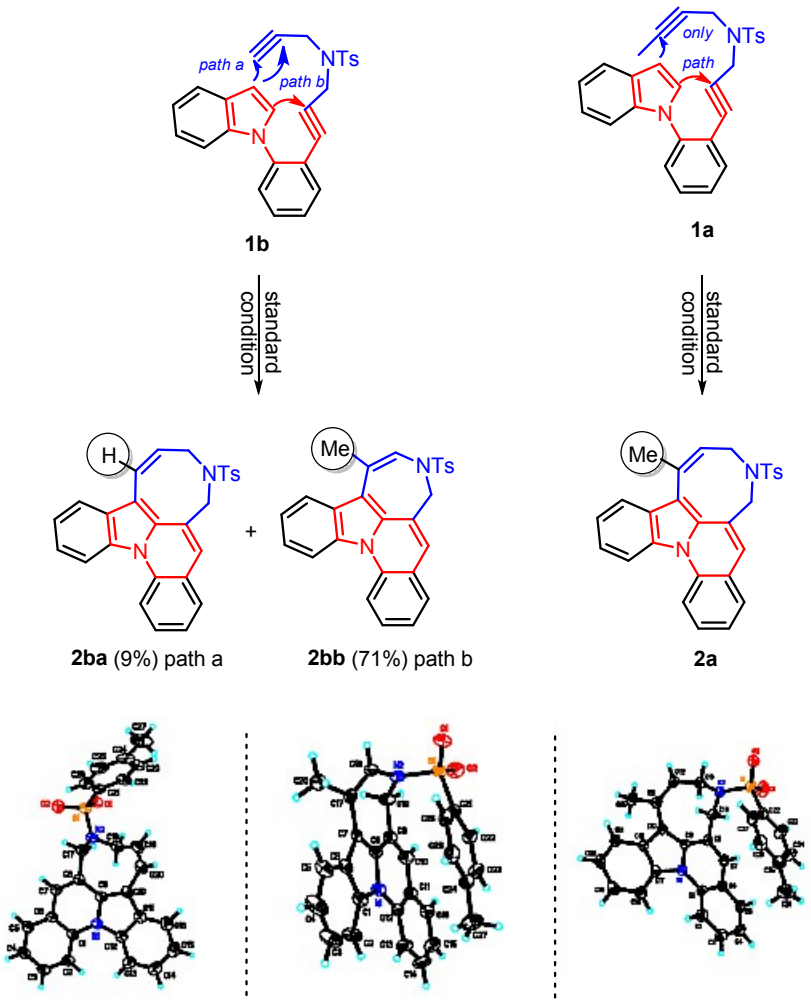
Additiona citation for ref 9 (c) Zi, W.; Wu, H,; Toste, F., Dean; *J. Am. Chem. Soc*. **2015**, *137*, 3225. (d) Hashmi, A. S. K.; Rominger, R. *Adv. Synth. Catal.* **2012**, *354*, 1273. (e) Jha, M.; Dhiman, S.; Kumar, A. *Org. Lett.* **2017**, *19*, 2038. (d) England, D., B.; Padwa, A. *Org. Lett.* **2008**, *10*, 3631. (f) Liu, Y.; Xu, W.; Wang, X, *Org. Lett.* **2010**, *12*, 1448. (g) Huang, L.; Yang, H.-B.; Zhang, D.-H.; Shi, M. *Angew. Chem. Int. Ed*. **2013**, *52* 6767. (h) Zhang, Z.; Shi, M. *Chem. Eur. J*. **2013**, *19*, 10625. (i) Naoe, S.; Saito, T.; Uchiyama, M.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2015**, *17*, 1774. (j) Matsuda, Y.; Naoe, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. Eur. J*. **2015**, *21*, 1463. (k) Lu, Y.; Du, X.; Jia, X.; Liu, Y. *Adv. Synth. Catal.* **2009**, *351*, 1517. (l) Xu, S.; Zhou, Y.; Xu, J.; Jiang, H.; Liu, H. *Green Chem*. **2013**, *15*, 718. (m) Wurm, Y.; Bucher, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Adv. Synth. Catal.* **2017**, *359*, 1637. (n) Hamada, N.; Yoshida, Y.; Oishi, S.; Ohno, H. *Org. Lett*. **2017**, *19*, 3875.

(B) General Remarks

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, respectively. HRMS spectra were recorded by ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, HRMS was measured on a Agilent 6224 TOF instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure.

(C) More experimental details.

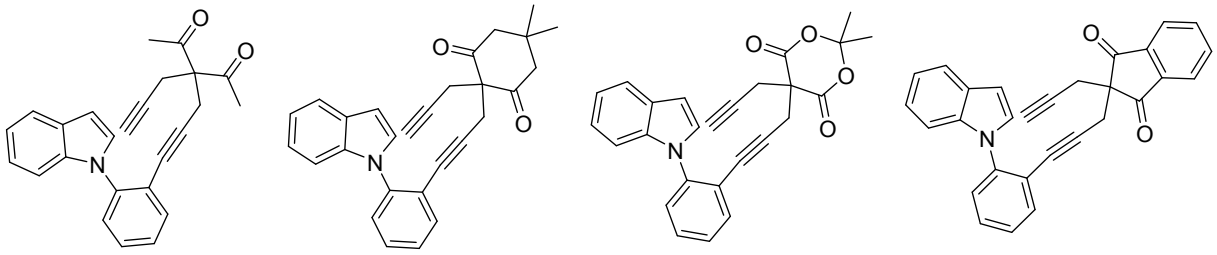
We credited that this essence of π-π stacking interaction is derived from the conformation of eight-membered ring. In product **2a**, diene (C9-C10-C11-C12) of eight-membered ring is nearly in the same plane with aromatic ring. However, without methyl group, diene of **2ba** (C9-C10-C20-C19) is completely deviated from the aromatic plane.



Scheme S1. Different reaction pathways for **1b** and **1a** as well as their X-ray crystal structures

We also synthesized four substrates shown in Scheme S1 for this gold(I)-catalyzed tandem cyclization under the standard conditions, but all these attempts failed to give pure cyclized products. Under the combination of JohnPhos/$AgNTf_2$, similar results were obtained and only complex mixtures were formed. We speculated that the eight-membered ring structure having two conjugated double bonds is twisted and the carbon atom connected by two carbonyl groups would stretch the conformation of this eight-membered ring, rendering that the corresponding product is

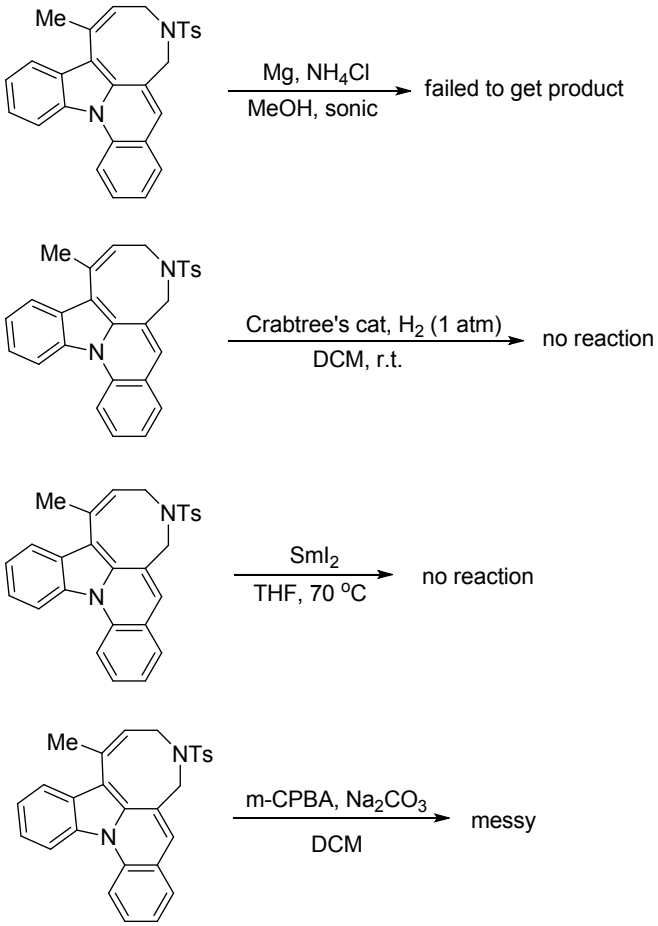
not stable upon heating for a long time.



S1 **S2** **S3** **S4**

Scheme S2. Unsuccessful substrates **S1**-**S4**.

We also tried to perform further transformation to test product's photonic properties. We tried to remove Ts protecting group under $Mg/NH_4Cl/MeOH$, but failed to get product due to the instability of the desired product with silica gel. SmI_2 seemed not be able to remove Ts group successfully. Thus, we did not try other condition to remove the protecting group because the desired product can not tolerate acidic condition. We also attempted to hydrogenate the double bond of eight-membered ring with Pd/C and H_2. However, all of these examinations are also unsuccessful even with Crabtree's catalyst. Epoxidation has also been tried, but TLC showed that complex product mixture was formed.



Scheme S3. Unsuccessful transformation of product **2a**.

UV/FL spectra and quantum yields of 2a and 2c

Sample preparation: To a 25 mL of volumetric flask was added **2a** or **2c** (0.01 mmol) and diluted with CH_2Cl_2 to 25 mL. The flask with solution was shaken several times and then 1.0 mL of this solution was moved to another 25 mL of volumetric flask, which was further diluted with CH_2Cl_2 to 25 mL. The flask with solution was shaken several times and then 1.6 mL of this solution was moved to another 25 mL of volumetric flask and the flask with solution was shaken several times for using. **2n** was excited at 365 nm, the others was excited at 254 nm.

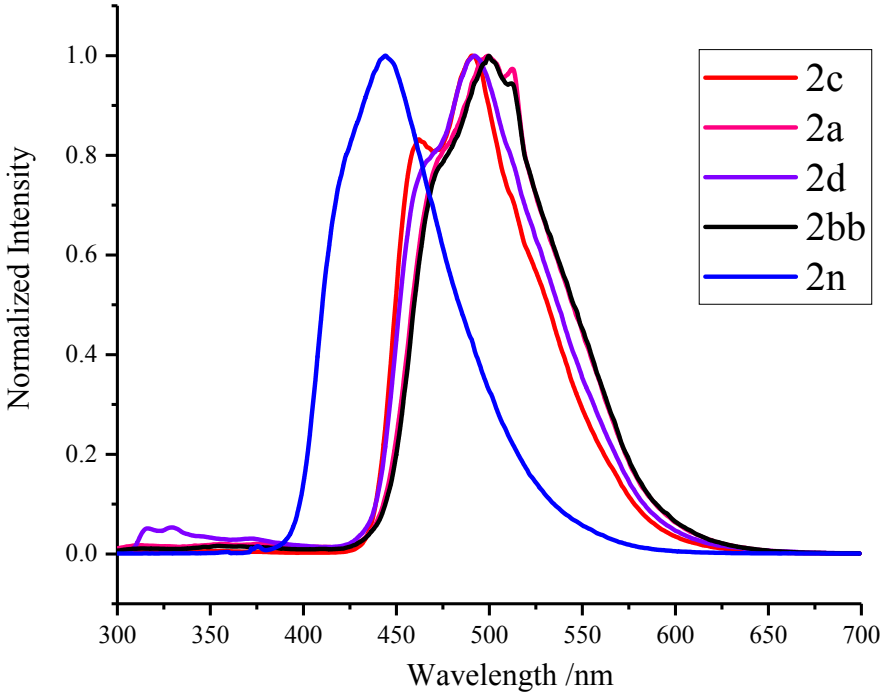


Figure S1. Fluorescence emission spectra of **2c 2a 2d 2bb** and **2n**

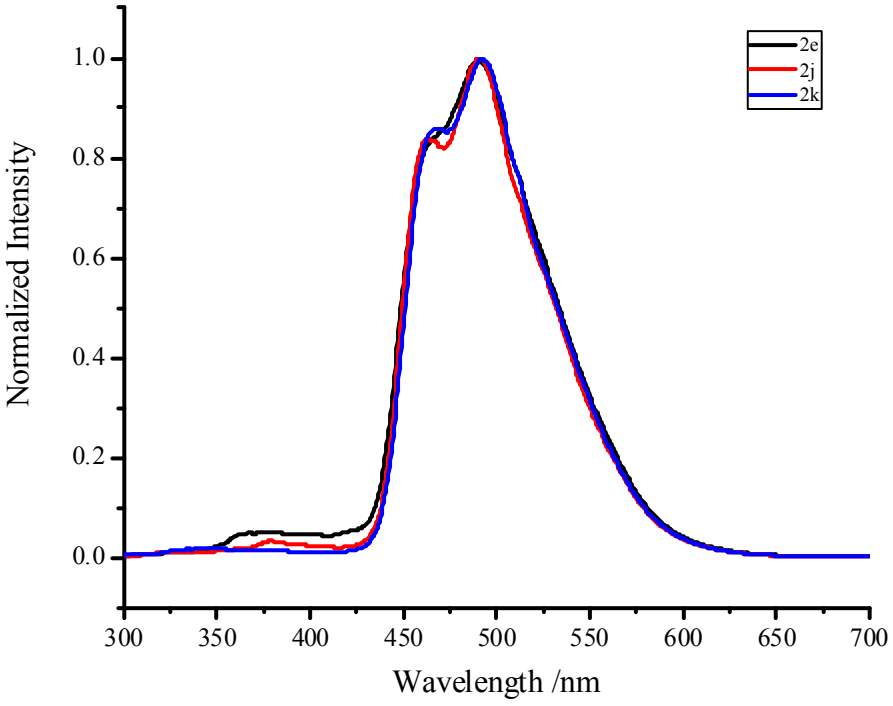
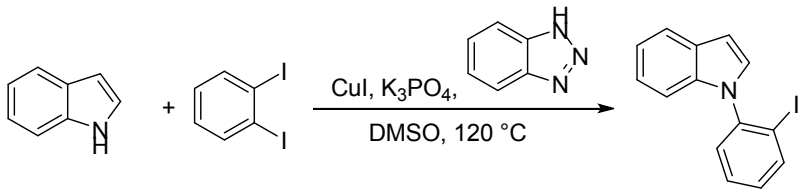


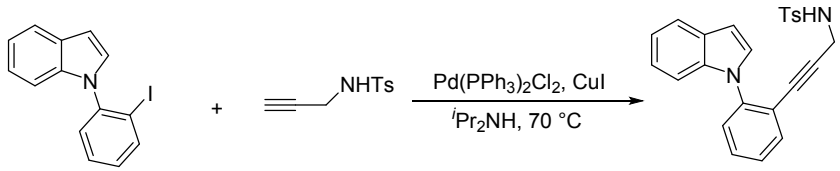
Figure S2. Fluorescence emission spectra of **2e 2j** and **2k**

Quantum yield determination: All the quantum yields of samples were determined based on 1.0 x 10^{-5} mol/L Quinine in 0.5 M H_2SO_4 (Φ = 0.55). Fluorescence emission of all the samples were measured in CH_2Cl_2, c = 1.0 μM. excitation at 254 nm with 2.5 nm EX slit and 10.0 EM slit.

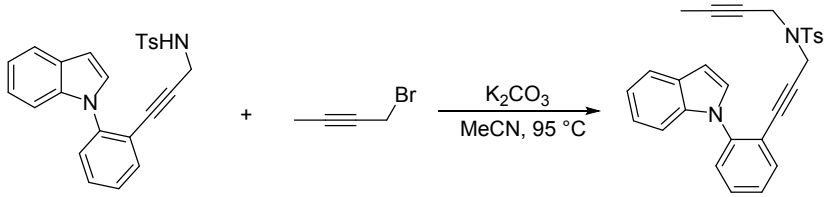
(B) General Procedure for the Preparation of Substrates 1a-1t



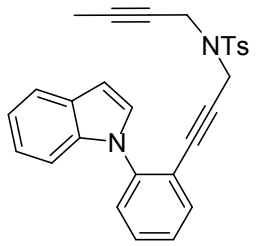
To a Schlenk tube was added indole (11 mmol), 1,2-diiodobenzene (10 mmol), copper(I) iodide (1.0 mmol), benzotriazole (2.0 mmol) and tripotassium phosphate (20 mmol). Then, the flask was evacuated under reduced pressure and was charged with argon. 25 mL of DMSO was injected into the flask. The reaction mixture was stirred and then was heated at 120 °C for 24 to 48 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered on a Celite, washed by water and extracted with ethyl acetate. The residues concentrated in vacuo were purified by chromatography on silica gel using petroleum ether to give the corresponding aryl iodide.



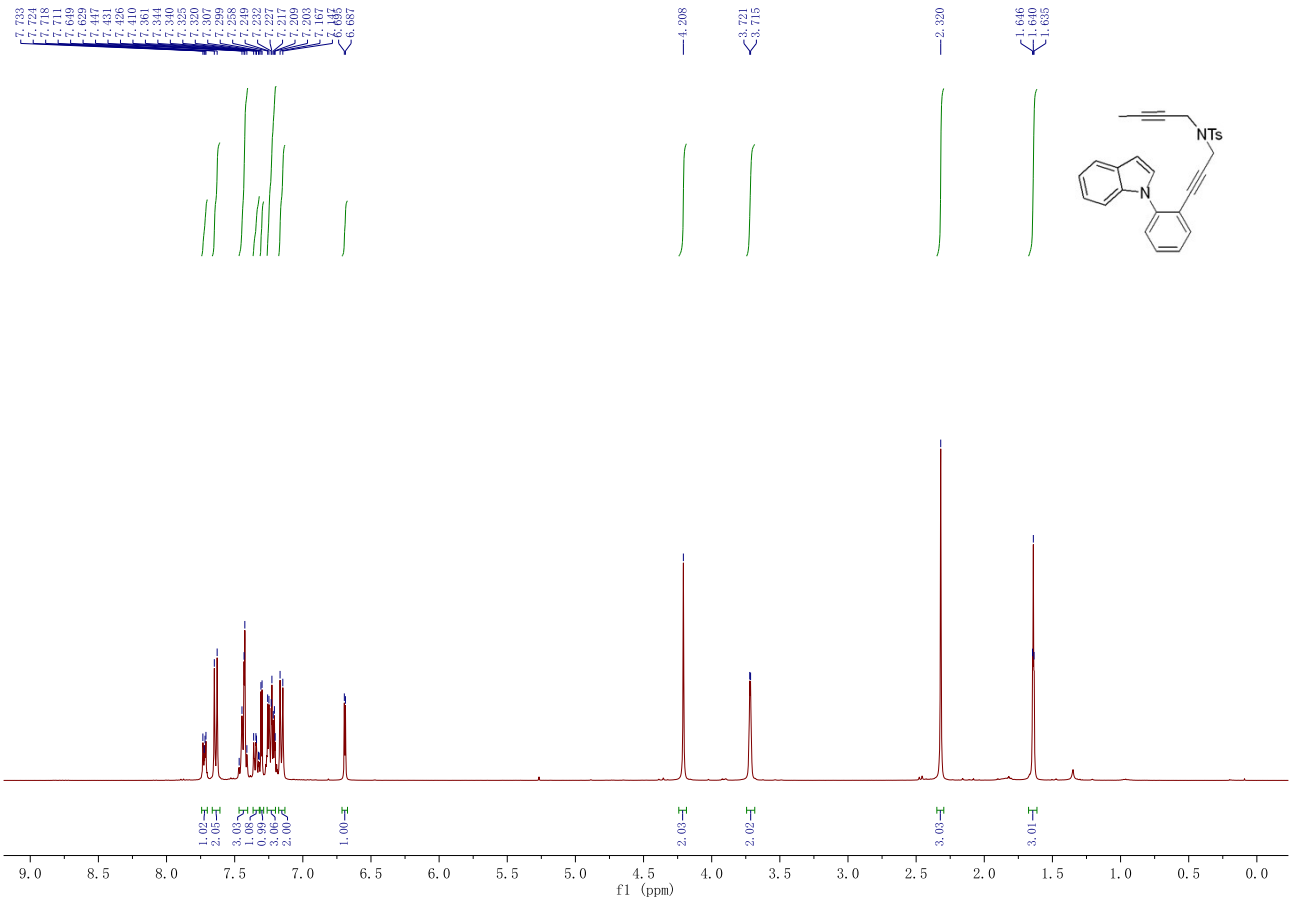
To a Schlenk tube was added aryl iodide (1.0 mmol), propargylamine derivative (1.0 mmol), copper(I) iodide (0.01 mmol) and triphenylphosphine palladium dichloride (0.02 mmol). Then the flask was evacuated and was charged with argon. 5 mL of diisopropylamine was injected into the flask. The reaction mixture was stirred and heated at 80 °C for 10 h. After the reaction mixture was cooled to room temperature, the residues concentrated in vacuo were purified by chromatography on silica gel using petroleum ether and ethyl acetate (4:1) to give the corresponding aryl alkyne derivative.



To an open round bottle was added aryl alkyne (1.0 mmol), 1-bromo-2-butyne (1.5 mmol) and potassium carbonate (2.0 mmol). The mixture was stirred and was heated at 90 °C for 5 h. Then the residues filtered through a Celite were purified by chromatography on silica gel using petroleum ether and ethyl acetate (10:1) to give the corresponding substrate.



Compound 1a: yellow oil (527.1 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.64 (t, *J* = 2.4 Hz, 3H), 2.32 (s, 3H), 3.72 (d, *J* = 2.4 Hz, 2H), 4.21 (s, 2H), 6.69 (d, *J* = 3.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.20-7.26 (m, 3H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.40-7.47 (m, 3H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.70-7.74 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.5, 36.8, 37.0, 71.5, 81.8, 82.2, 87.0, 103.1, 110.7, 119.8, 120.4, 121.0, 122.2, 127.0, 127.2, 127.9, 128.80, 128.83, 129.4, 129.6, 133.9, 135.3, 136.3, 140.6, 143.7. IR (neat) ν 3054, 2914, 2846, 2223, 1595, 1512, 1493, 1458, 1347, 1329, 1300, 1240, 1209, 1160, 1092, 1012, 945 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_2O_2S$ requires (M^++H): 453.1631, Found: 453.1628.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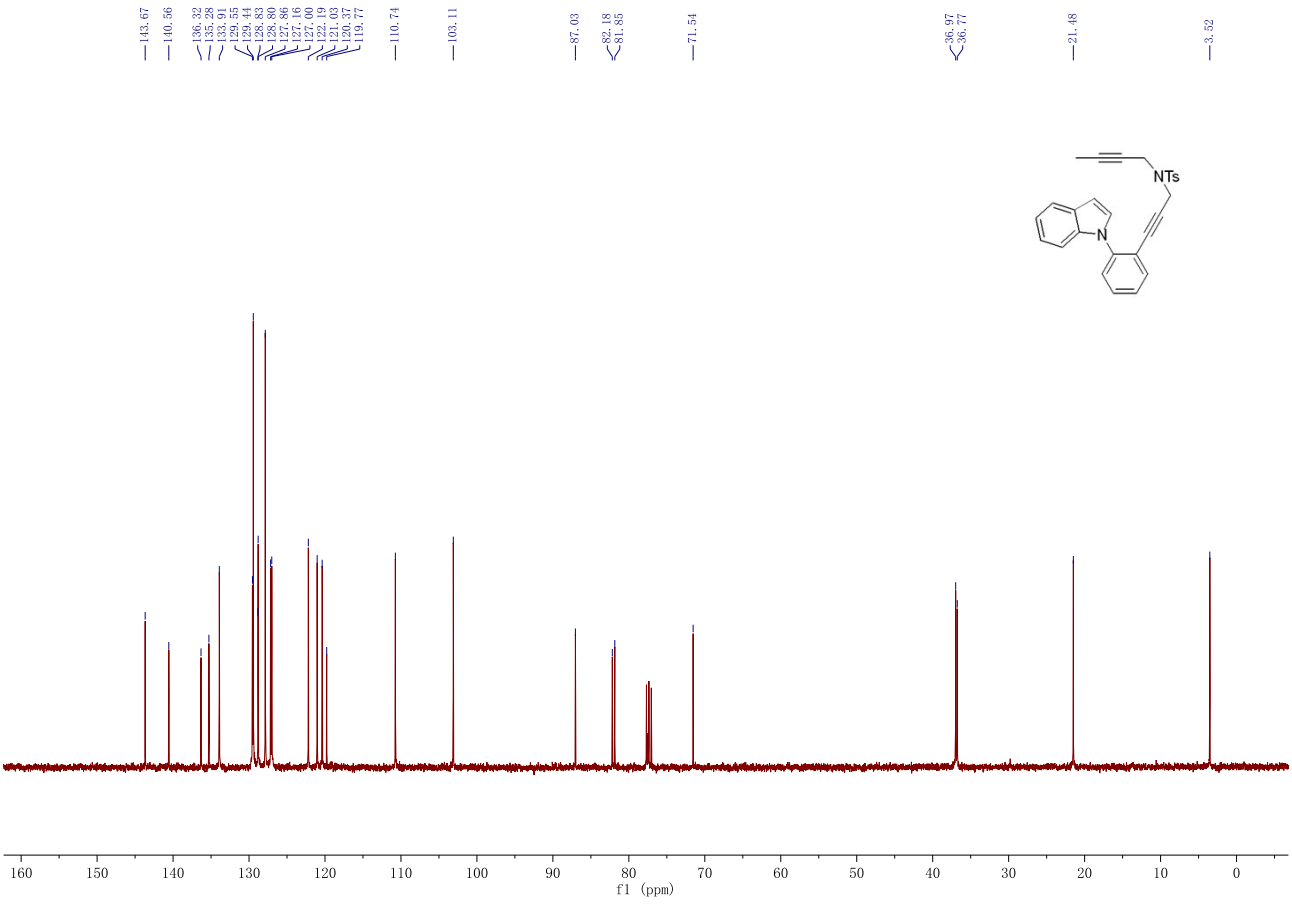
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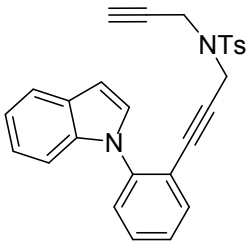
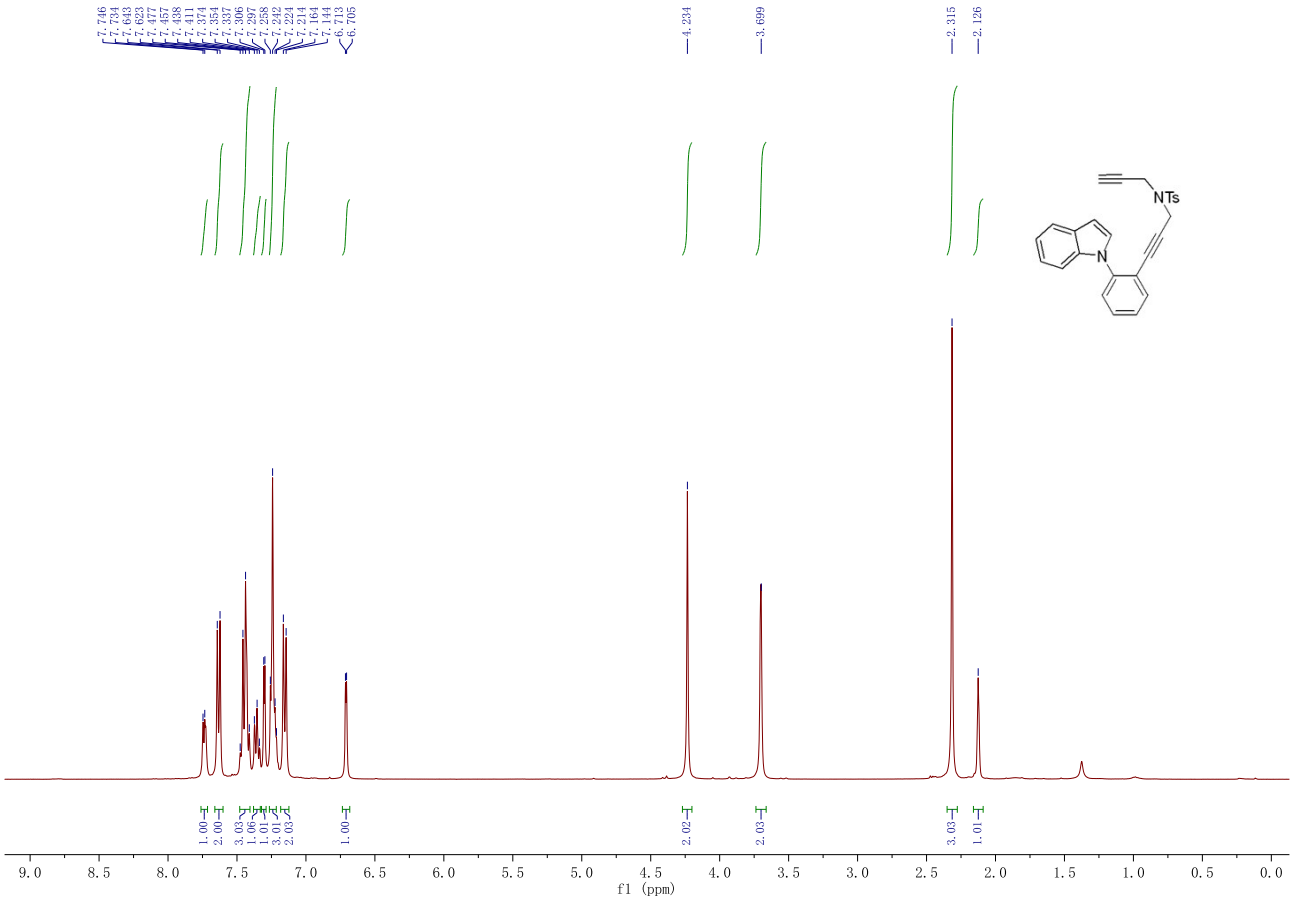
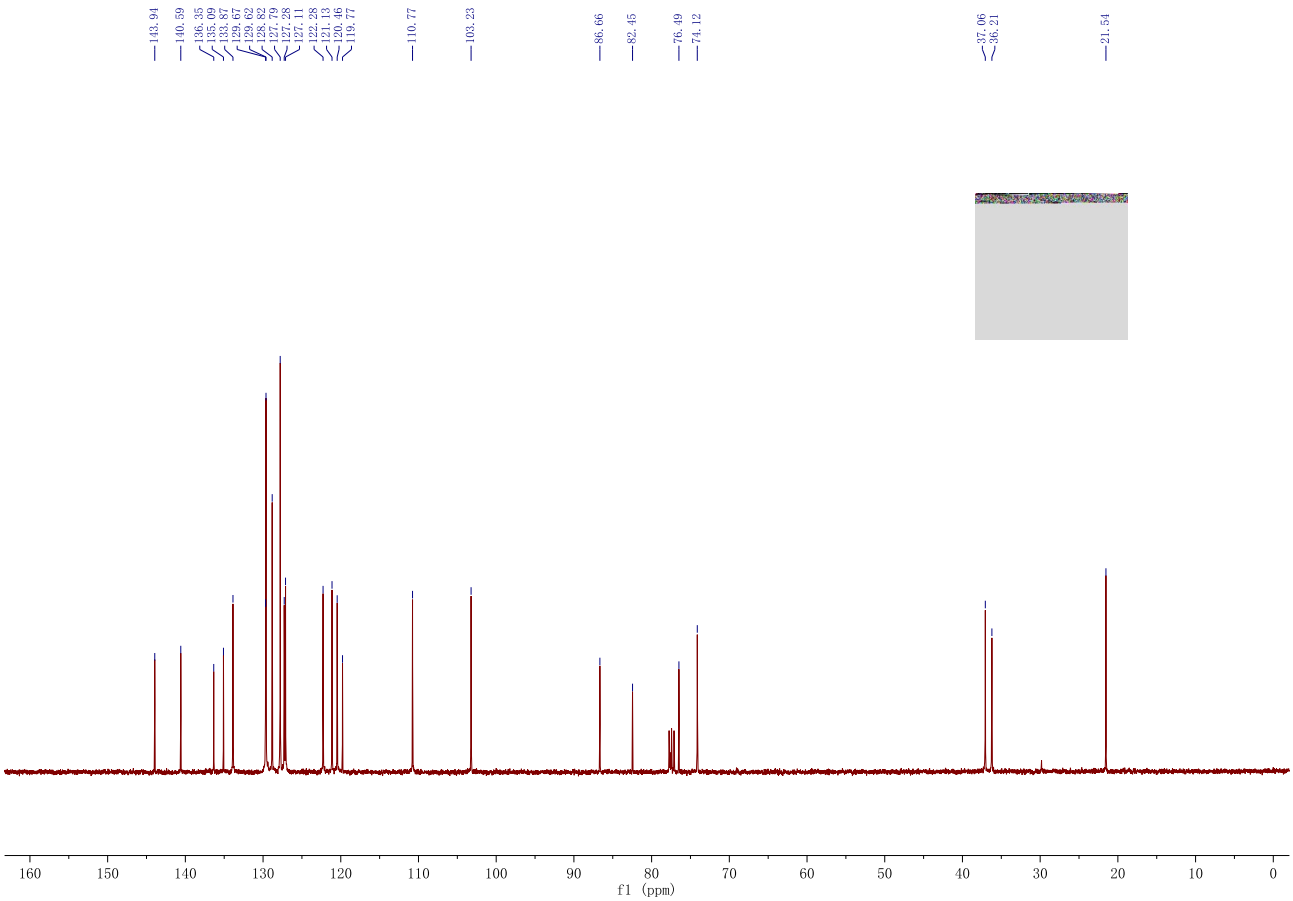
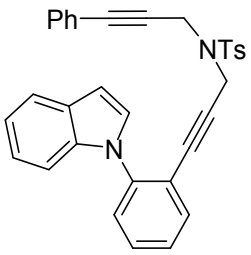


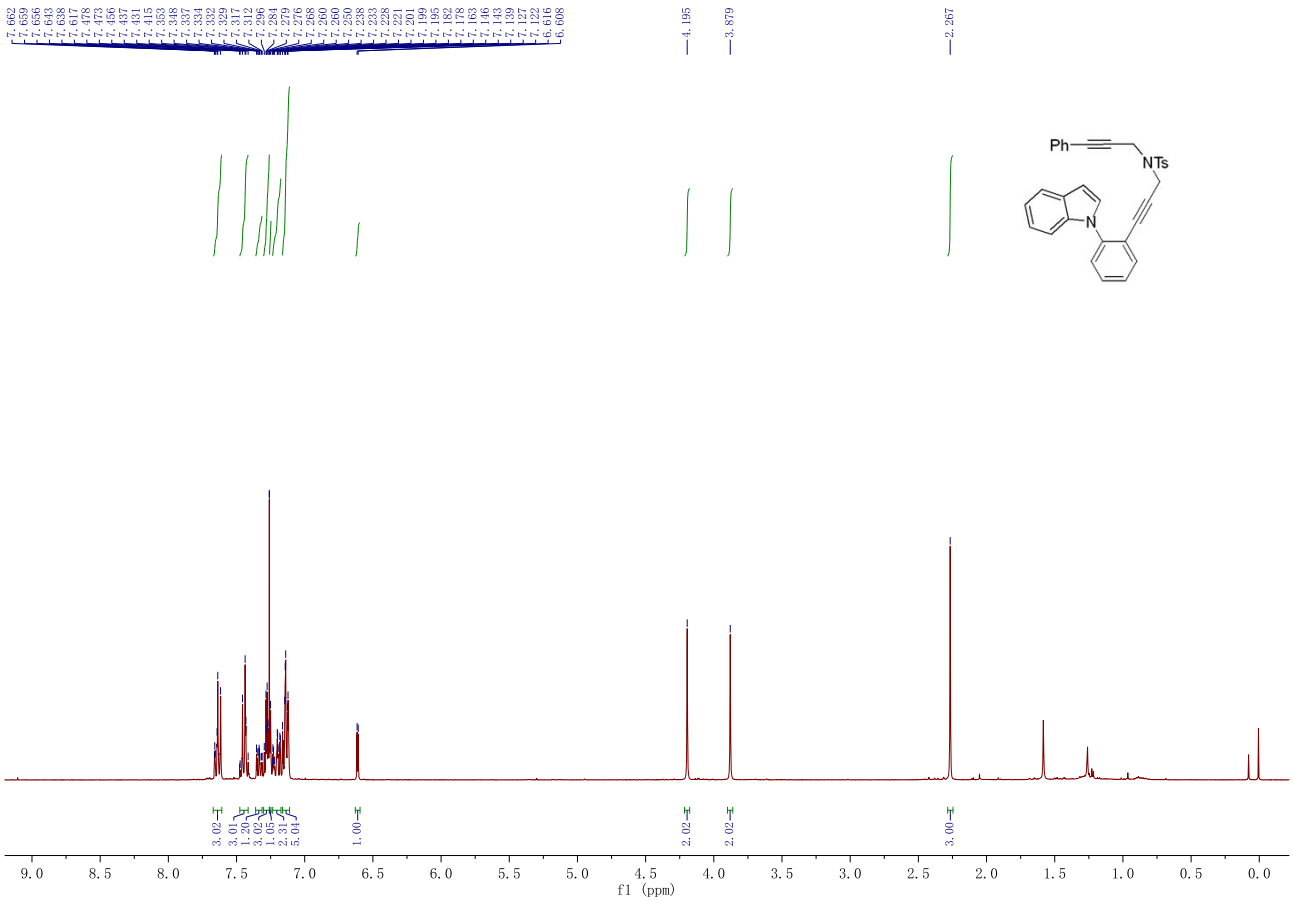
Compound 1b: yellow oil (491 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.13 (s, 1H), 2.32 (s, 3H), 3.70 (s, 2H), 4.23 (s, 2H), 6.71 (d, *J* = 3.2 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.22-7.26 (m, 3H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.36 (dd, *J* = 7.2 Hz, 1H), 7.31-7.37 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.5, 36.2, 37.1, 74.1, 76.5, 82.5, 86.7, 103.2, 110.8, 119.8, 120.5, 121.1, 122.3, 127.1, 127.3, 127.8, 128.8, 129.6, 129.7, 133.9, 135.1, 136.3, 140.6, 143.9. IR (neat) ν 3279, 3046, 2922, 2841, 1624, 1595, 1517, 1494, 1458, 1348, 1329, 1306, 1209, 1160, 1137, 1092, 892 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{23}N_2O_2S$ requires (M^++H): 439.1475, Found: 439.1472.







Compound 1c: yellow oil (712 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.27 (s, 3H), 3.88 (s, 2H), 4.20 (s, 2H), 6.61 (d, *J* = 3.3 Hz, 1H), 7.11-7.16 (m, 5H), 7.17-7.24 (m, 2H), 7.25 (s, 1H), 7.26-7.30 (m, 3H), 7.31-7.36 (m, 1H), 7.42-7.48 (m, 3H), 7.61-7.67 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 37.0, 37.3, 81.6, 82.3, 85.7, 86.9, 103.1, 110.7, 119.9, 120.4, 121.0, 122.2, 122.3, 127.1, 127.2, 127.8, 128.2, 128.5, 128.7, 129.5, 131.7, 133.8, 135.1, 136.3, 140.6, 143.8. IR (neat) ν 2960, 2919, 2849, 2219, 1598, 1492, 1459, 1354, 1331, 1222, 1158, 1139, 1110, 1091, 1064 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{27}N_2O_2S$ requires (M^++H): 515.1788, Found: 515.1784.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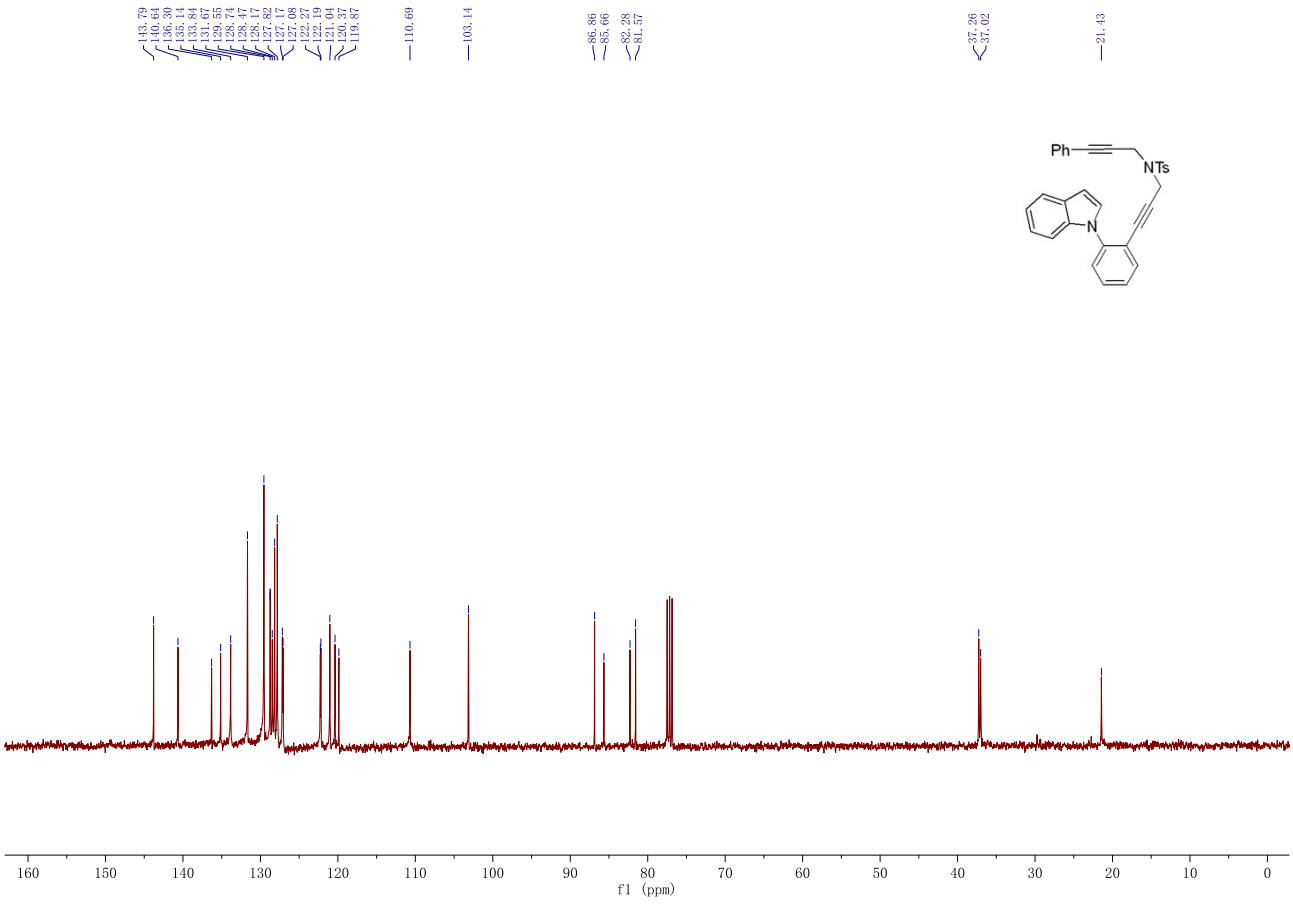
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37.26
37.02
21.43
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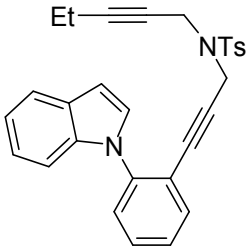
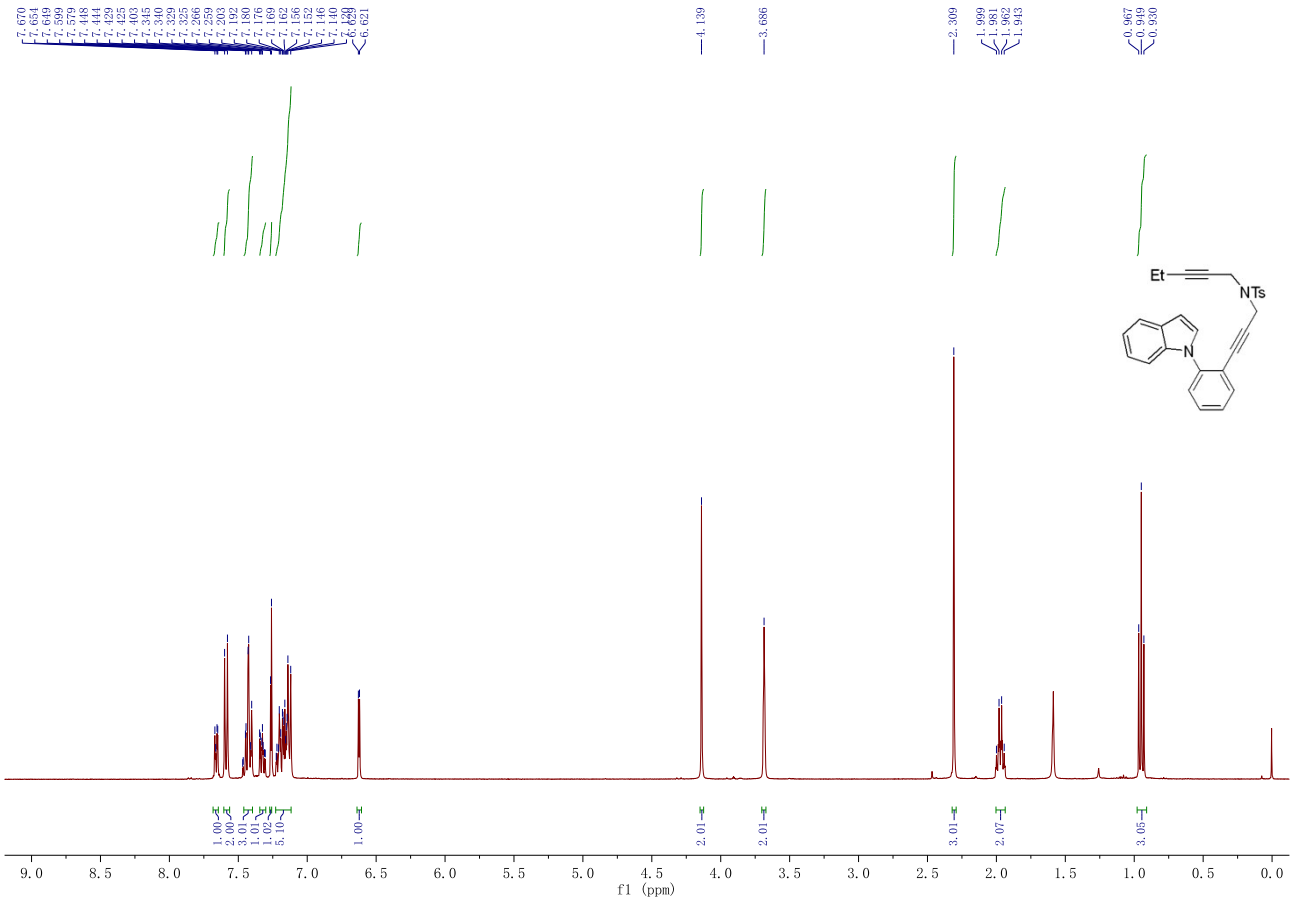
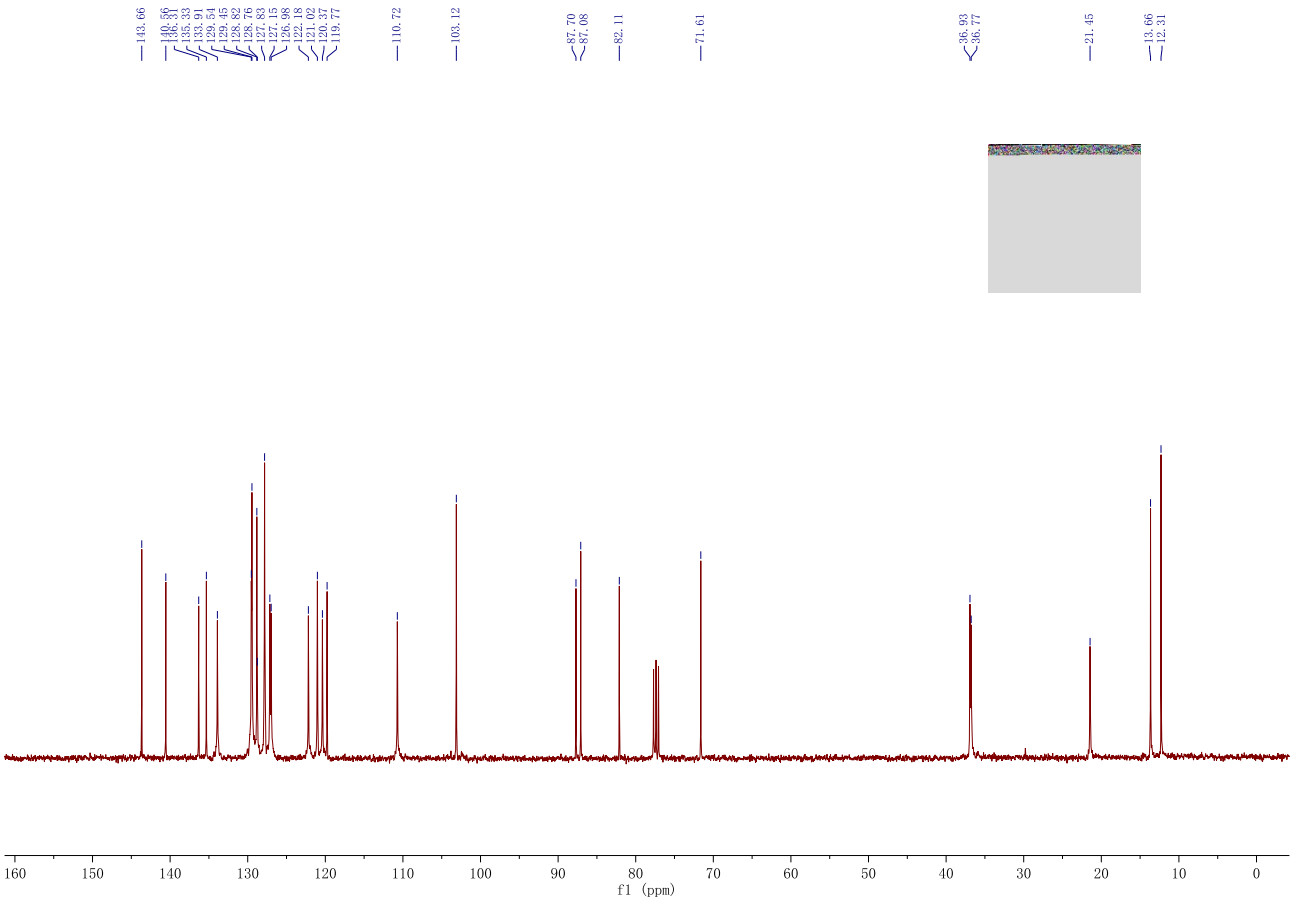
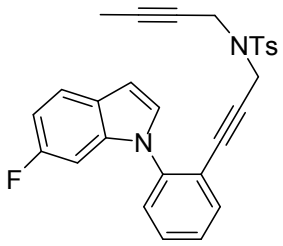


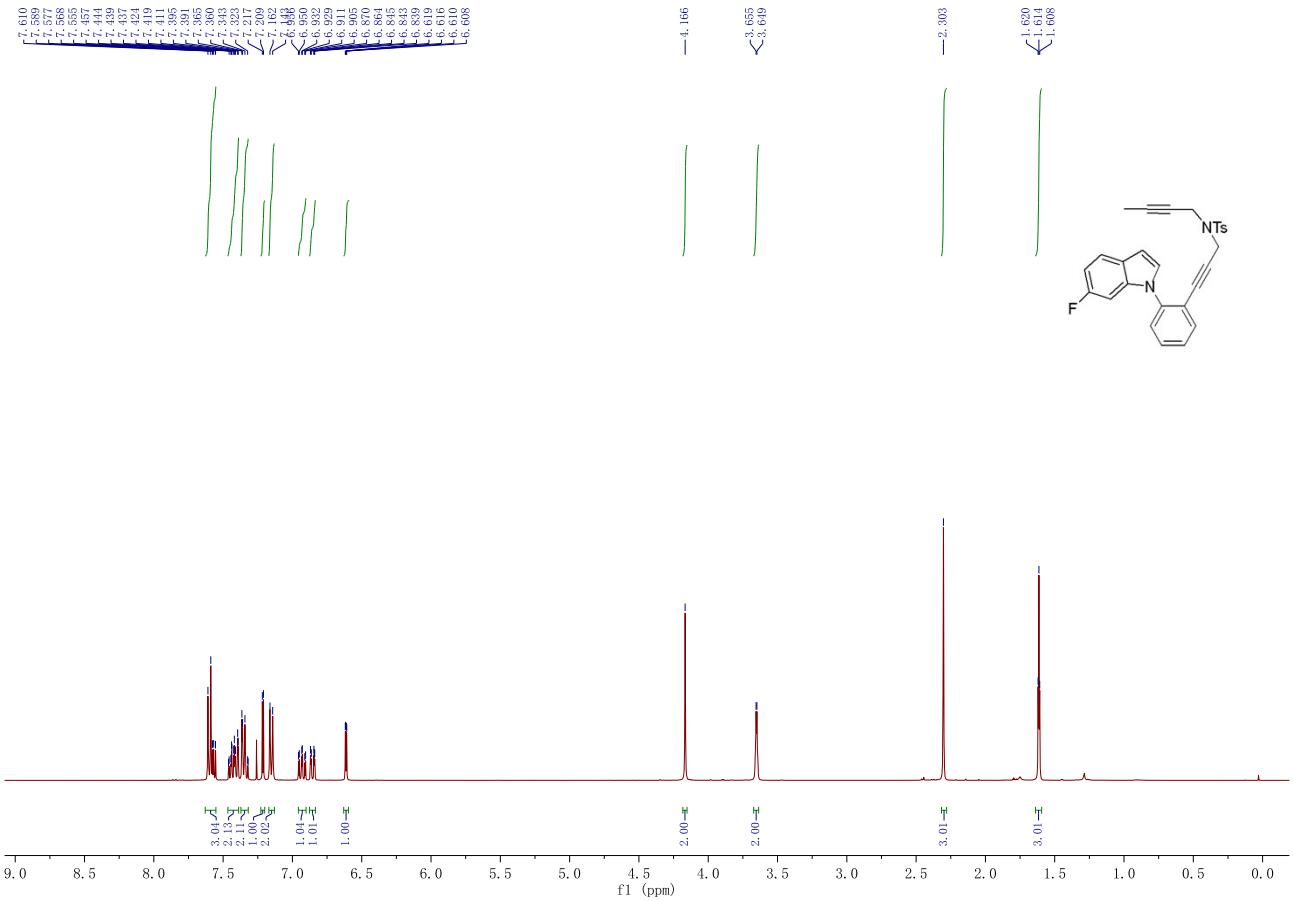
Compound 1d: yellow oil (592.1 mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.97 (q, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 3.69 (s, 2H), 4.14 (s, 2H), 6.62 (d, *J* = 3.2 Hz, 1H), 7.12-7.23 (m, 5H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.30-7.34 (m, 1H), 7.40-7.46 (m, 3H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.65-7.67 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 12.3, 13.7, 21.4, 36.8, 36.9, 71.6, 82.1, 87.1, 87.7, 103.1, 110.7, 119.8, 120.4, 121.0, 122.2, 127.0, 127.1, 127.8, 128.76, 128.82, 129.45, 129.54, 133.9, 135.3, 136.3, 140.6, 143.7. IR (neat) ν 2973, 2919, 2844, 2238, 1595, 1512, 1494, 1458, 1348, 1330, 1209, 1160, 1092, 897 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_2S$ requires (M^++H): 467.1788, Found: 467.1784.







Compound 1e: brown oil (111.9 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.61 (t, *J* = 2.4 Hz, 3H), 2.30 (s, 3H), 3.65 (d, *J* = 2.4 Hz, 2H), 4.17 (s, 2H), 6.61 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.83-6.88 (m, 1H), 6.90-6.96 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 3.2 Hz, 1H), 7.32-7.37 (m, 2H), 7.39-7.47 (m, 2H), 7.55-7.63 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.4, 21.4, 36.6, 36.8, 71.3, 81.80, 81.82, 87.2, 97.2 (d, *J* = 26.7 Hz), 103.1, 109.0 (d, *J* = 24.5 Hz), 119.9, 121.7 (d, *J* = 10.0 Hz), 125.1, 126.9, 127.5, 127.8, 129.2 (d, *J* = 3.7 Hz), 129.4, 129.6, 133.8, 135.2, 136.4 (d, *J* = 12.2 Hz), 140.1, 143.6, 160.0 (d, *J* = 237.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.4. IR (neat) ν 2919, 2846, 2232, 1618, 1595, 1512, 1494, 1482, 1453, 1346, 1325, 1300, 1210, 1160, 1113, 1091, 932 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}FN_2O_2S$ requires (M^++H): 471.1537, Found: 471.1533.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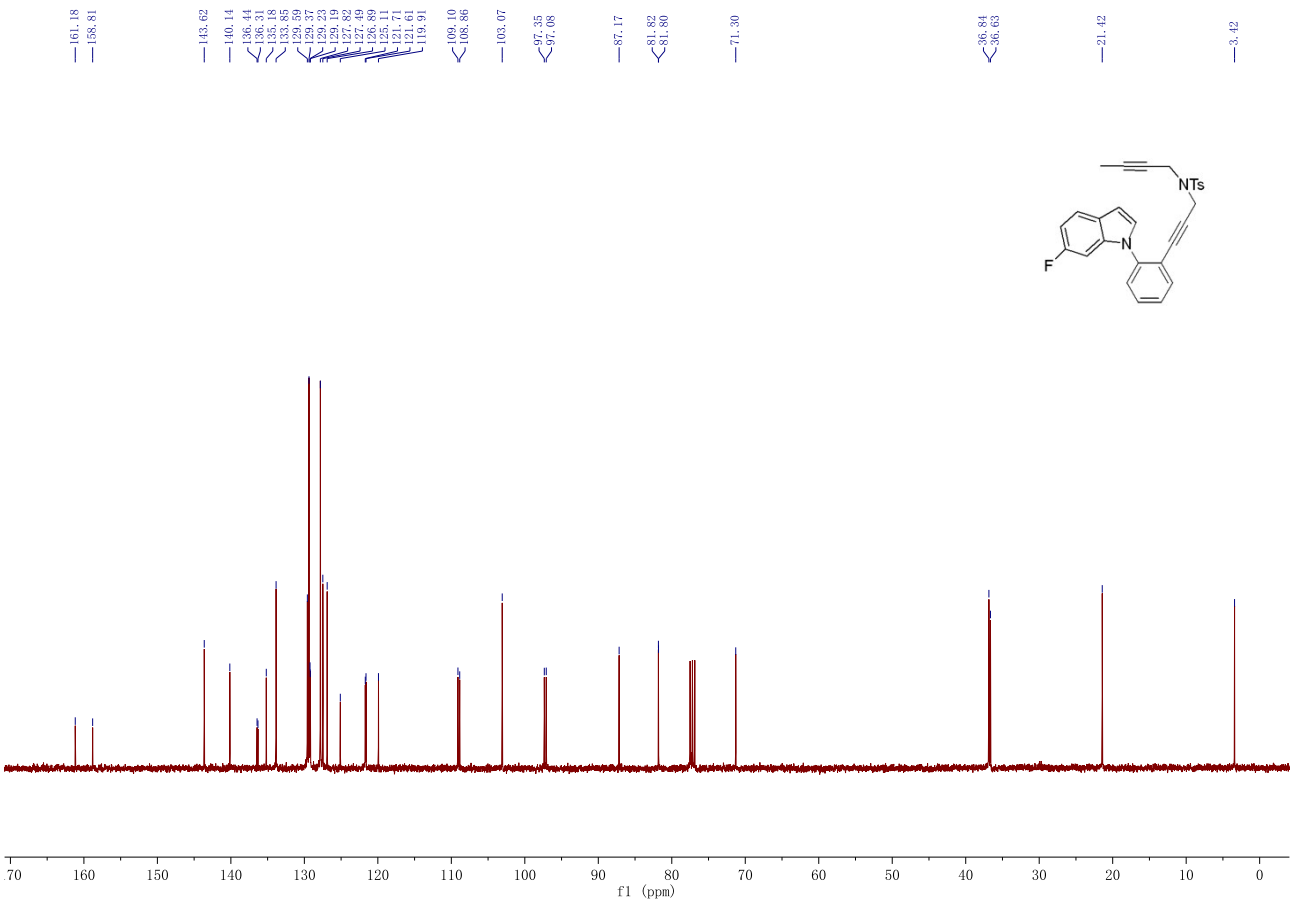
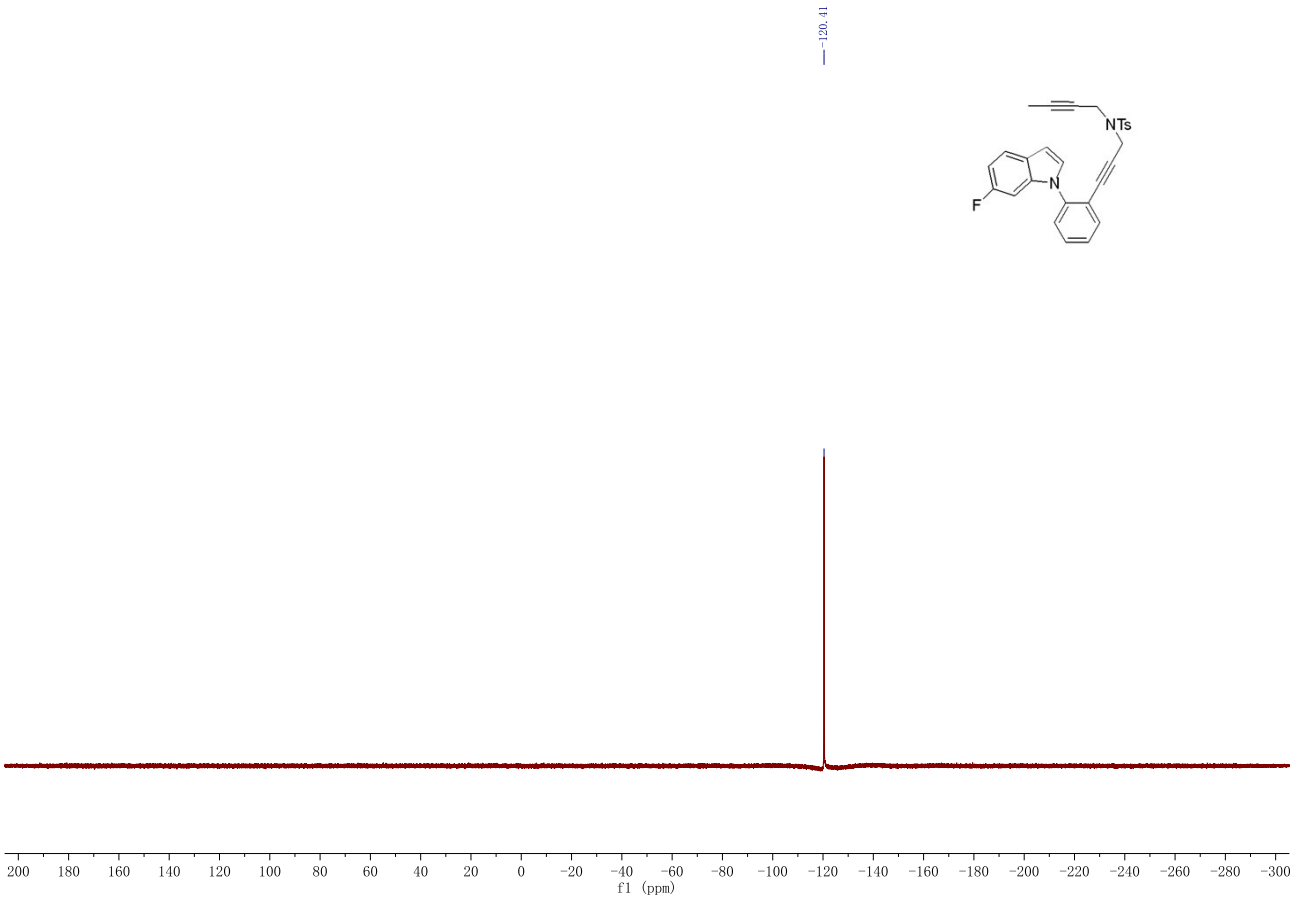
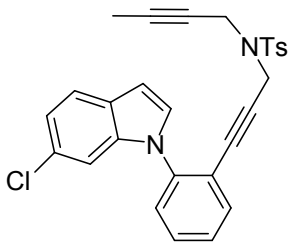
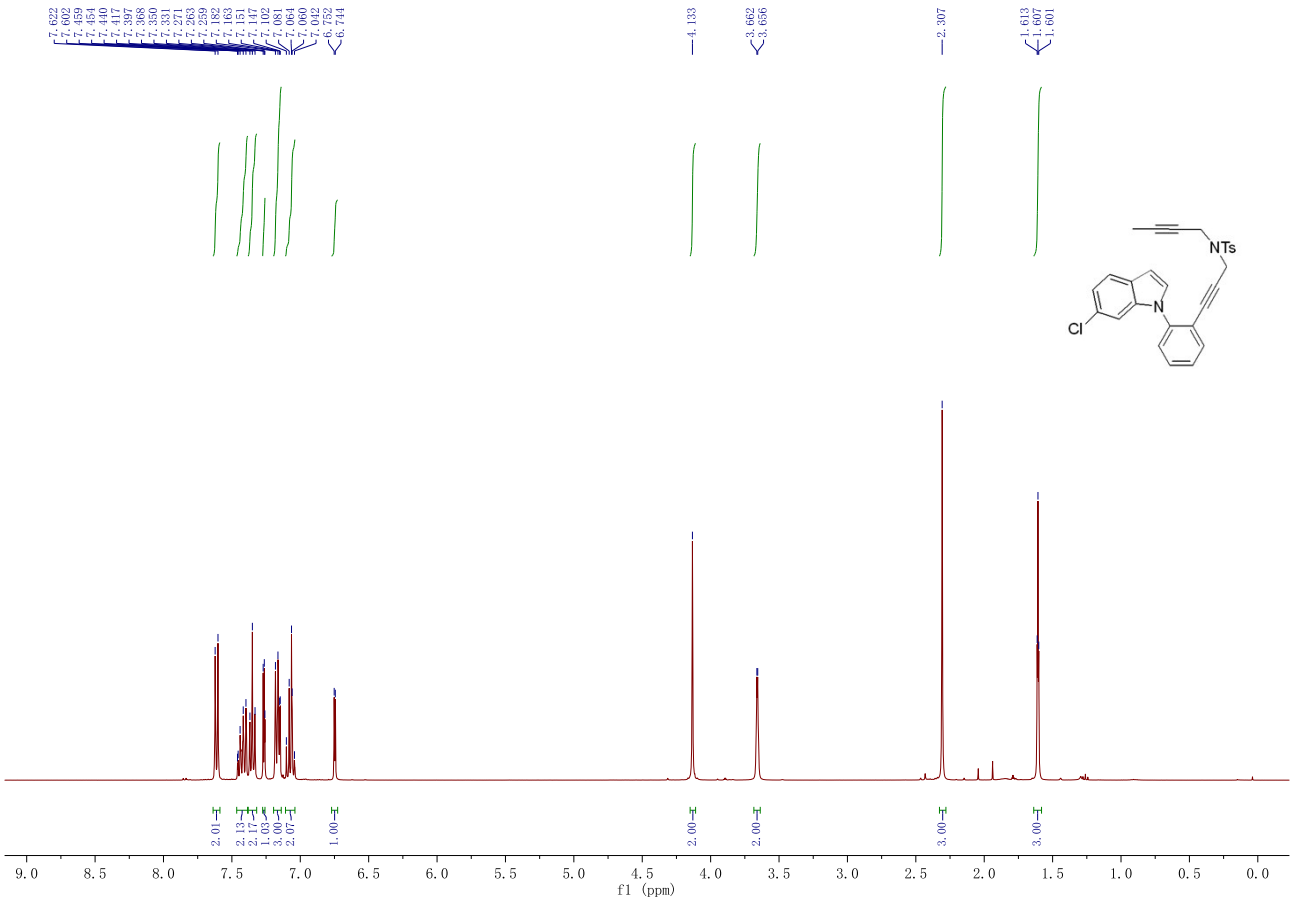
7.599
7.577
7.568
7.555
7.457
7.444
7.439
7.437
7.424
7.419
7.411
7.395
7.391
7.365
7.360
7.343
7.323
7.217
7.209
7.162
7.143
6.958
6.950
6.932
6.909
6.911
6.905
6.870
6.864
6.845
6.843
6.839
6.619
6.616
6.610
6.608
4.166
3.655
3.649
2.303
1.620
1.614
1.608
NTs
F
N
3.04
2.13
2.11
1.00
2.02
1.04
1.01
1.00
2.00
2.00
3.01
3.01
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)


161.18
158.81
143.62
140.14
136.44
136.31
135.18
133.85
129.59
129.37
129.23
129.19
127.82
127.49
126.89
125.11
121.71
121.61
119.91
109.10
108.86
103.07
97.35
97.08
87.17
81.82
81.80
71.30
36.84
36.63
21.42
3.42
NTs
F
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)





Compound 1f: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.61 (t, *J* = 2.4 Hz, 3H), 2.31 (s, 3H), 3.66 (d, *J* = 2.4 Hz, 2H), 4.13 (s, 2H), 6.75 (d, *J* = 3.2 Hz, 1H), 7.04-7.11 (m, 2H), 7.14-7.19 (m, 3H), 7.26-7.28 (m, 1H), 7.32-7.38 (m, 2H), 7.39-7.46 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.4, 36.7, 36.8, 71.3, 81.7, 81.8, 87.2, 103.1, 110.6, 120.0, 121.0, 121.9, 127.0, 127.2, 127.6, 127.8, 128.1, 129.4, 129.5, 129.6, 133.9, 135.2, 136.7, 139.9, 143.6. IR (neat) ν 2922, 2844, 2232, 1594, 1510, 1493, 1482, 1453, 1346, 1326 1300, 1210, 1160, 1182, 1092, 898 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}ClN_3O_2S$ requires ($M+NH_4^+$): 504.1507, Found: 504.1504.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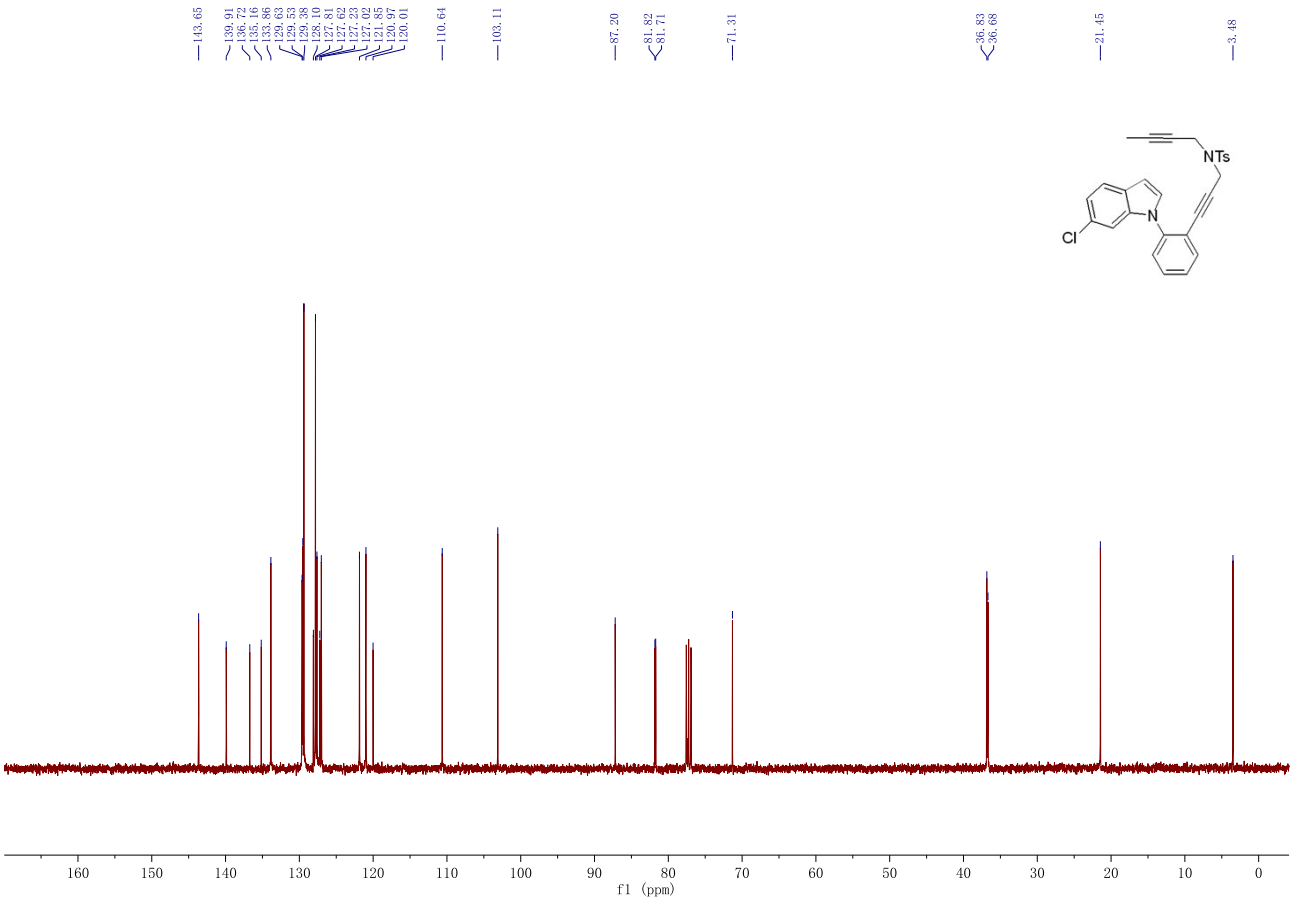
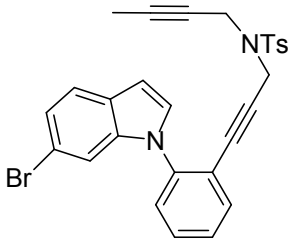
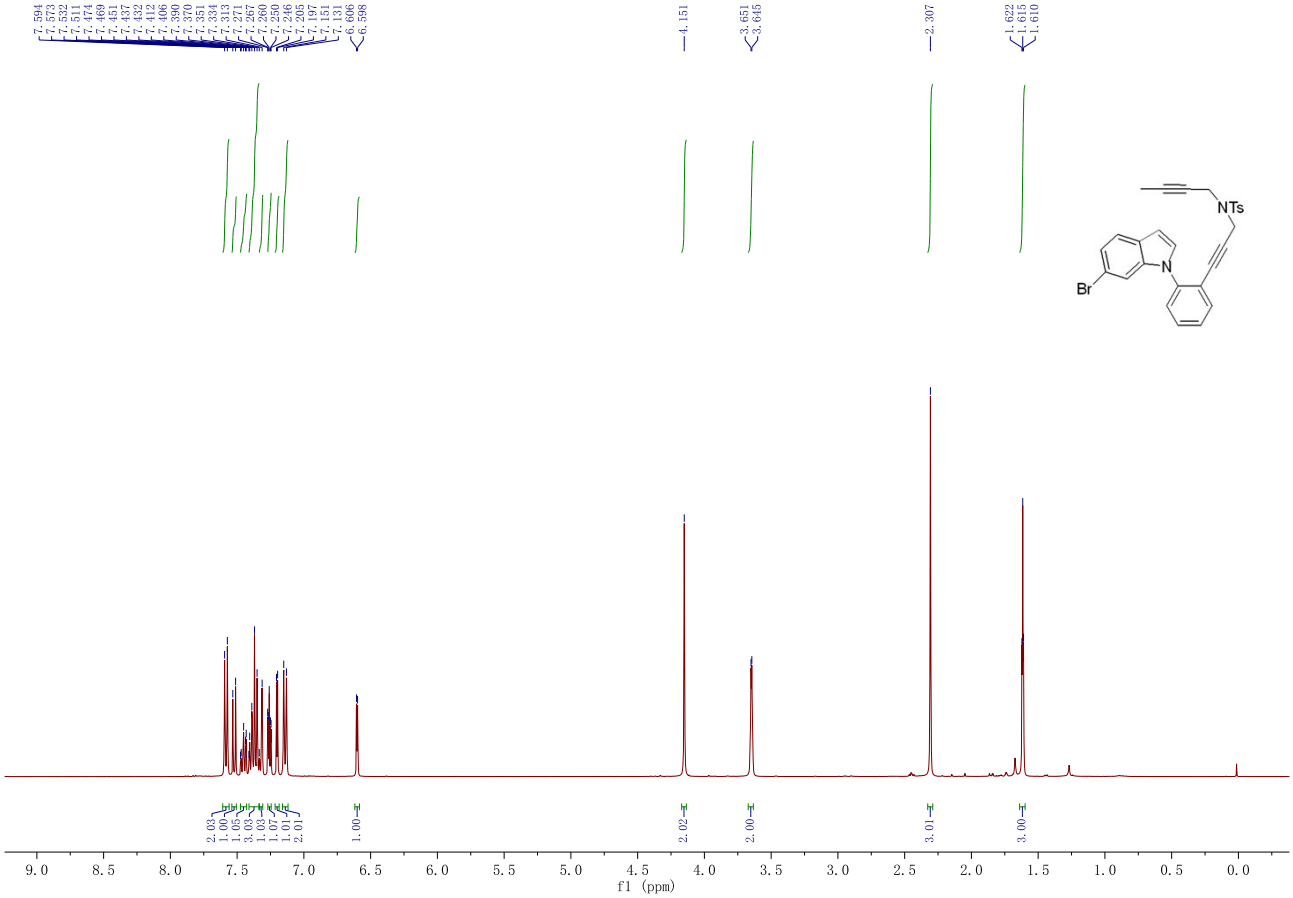
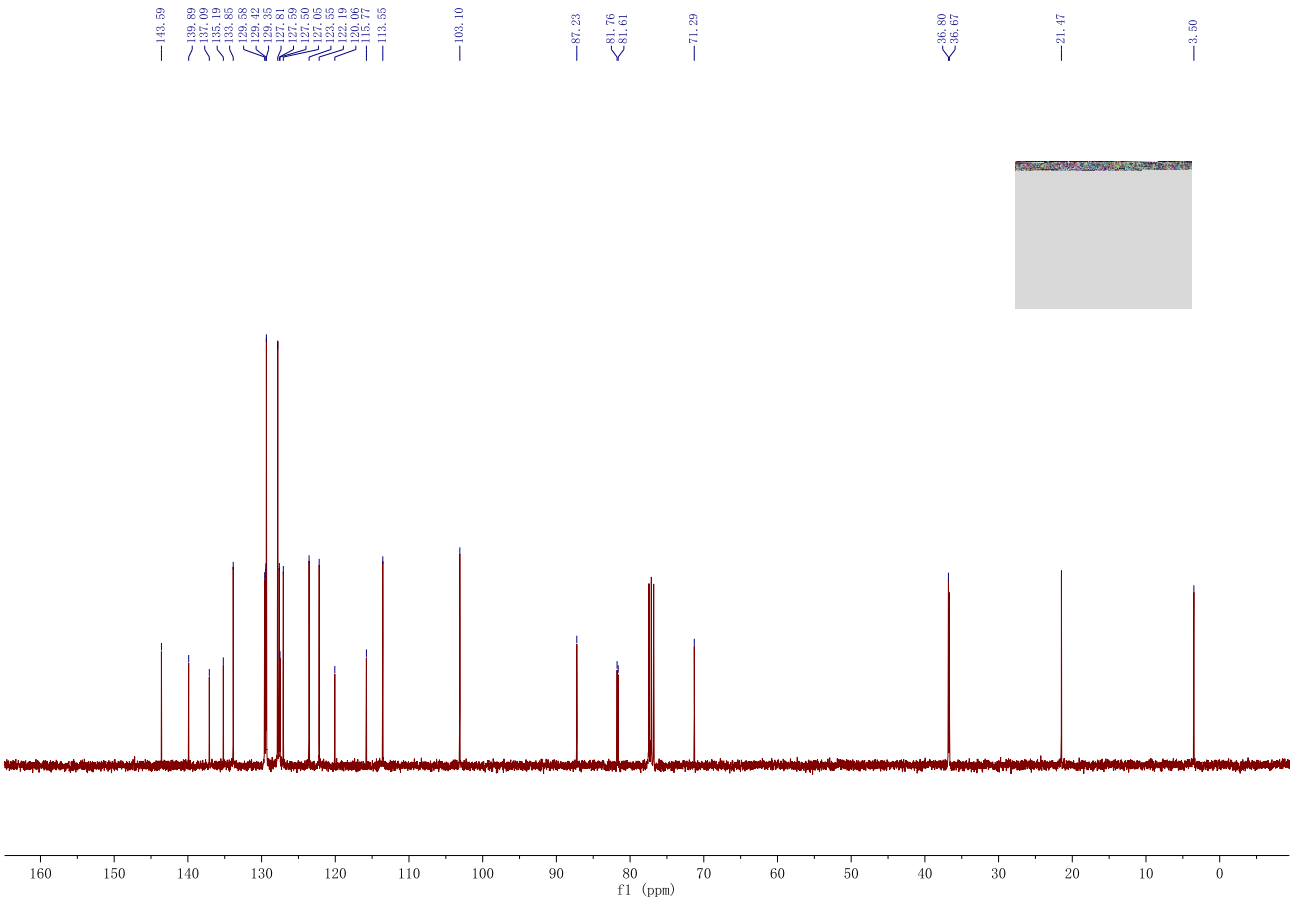
7.602
7.459
7.451
7.440
7.417
7.397
7.368
7.350
7.331
7.271
7.263
7.189
7.182
7.163
7.151
7.147
7.102
7.081
7.064
7.000
6.942
6.752
6.744
4.133
3.662
3.656
2.307
1.613
1.607
1.601
NTs
N
Cl
2.01
2.13
2.17
1.03
3.00
2.07
1.00
2.00
2.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

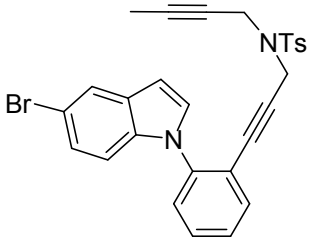

143.65
139.91
136.72
135.16
133.86
129.63
129.53
129.38
128.10
127.81
127.62
127.23
127.02
121.85
120.97
120.01
110.64
103.11
87.20
81.82
81.71
71.31
36.83
36.68
21.45
3.48
NTs
N
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



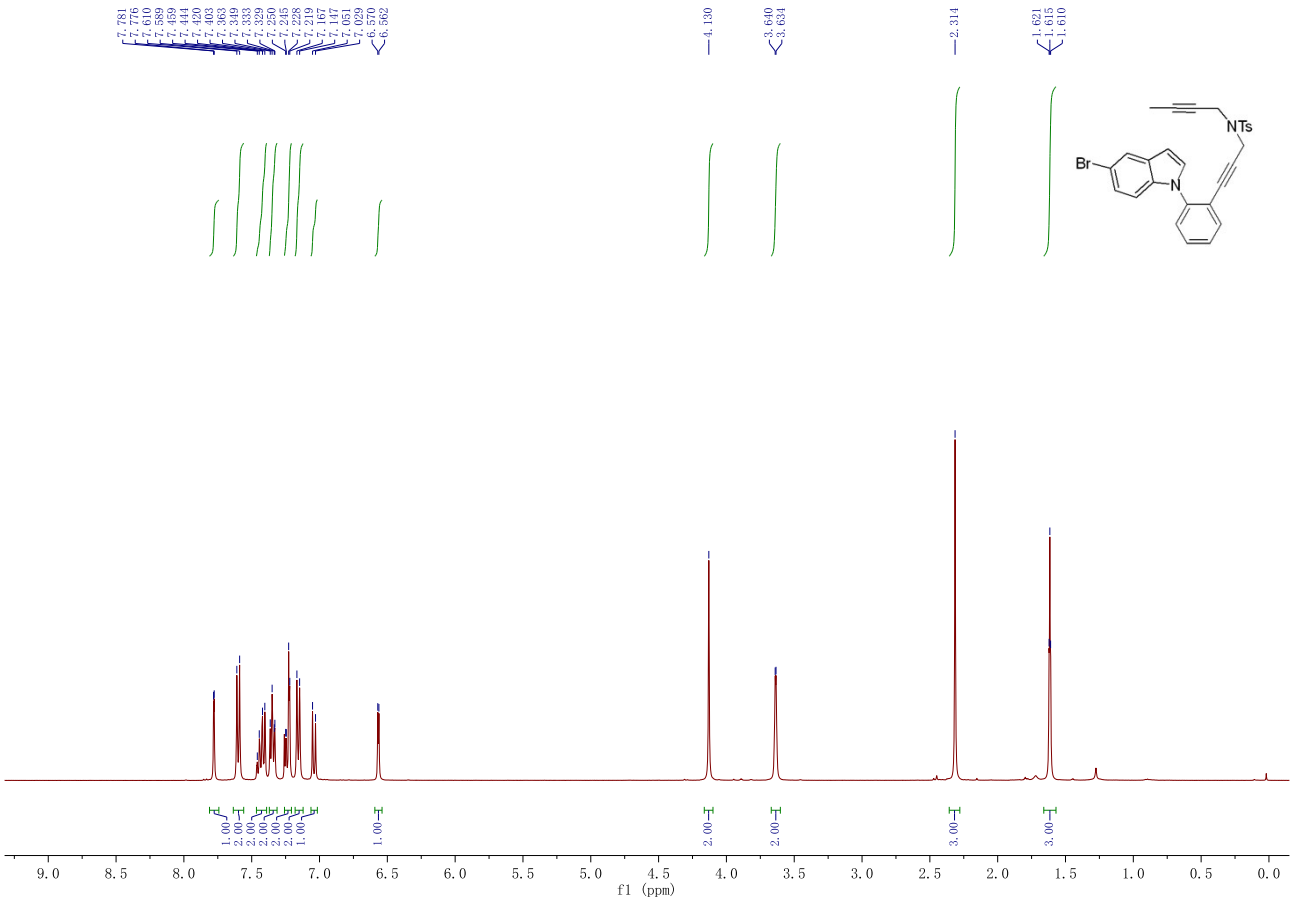
Compound 1g: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.62 (t, *J* = 2.4 Hz, 3H), 2.31 (s, 3H), 3.65 (d, *J* = 2.4 Hz, 2H), 4.15 (s, 2H), 6.60 (d, *J* = 3.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 3.2 Hz, 1H), 7.26 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.31 (s, 1H), 7.34-7.41 (m, 3H), 7.45 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.5, 36.7, 36.8, 71.3, 81.6, 81.8, 87.2, 103.1, 113.6, 115.8, 120.1, 122.2, 123.6, 127.1, 127.5, 127.6, 127.8, 129.3, 129.4, 129.6, 133.8, 135.2, 137.1, 139.9, 143.6. IR (neat) ν 3148, 3117, 2916, 2852, 2234, 1597, 1566, 1510, 1494, 1461, 1441, 1345, 1328, 1240, 1207, 1160, 1113, 1065, 889 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}BrN_3O_2S$ requires ($M+NH_4^+$): 548.1002, Found: 548.0999.

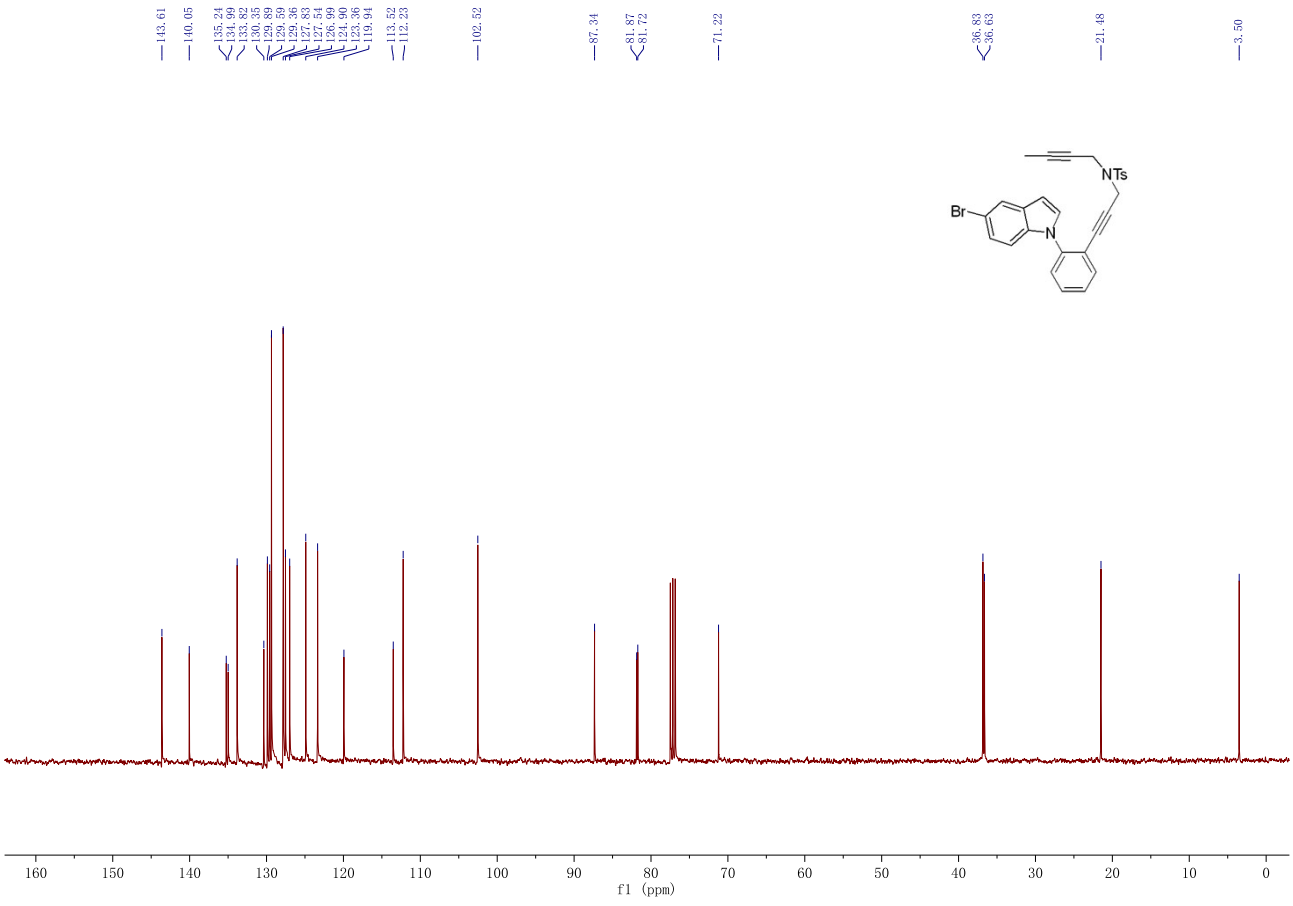


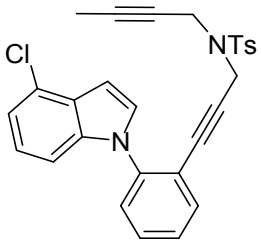




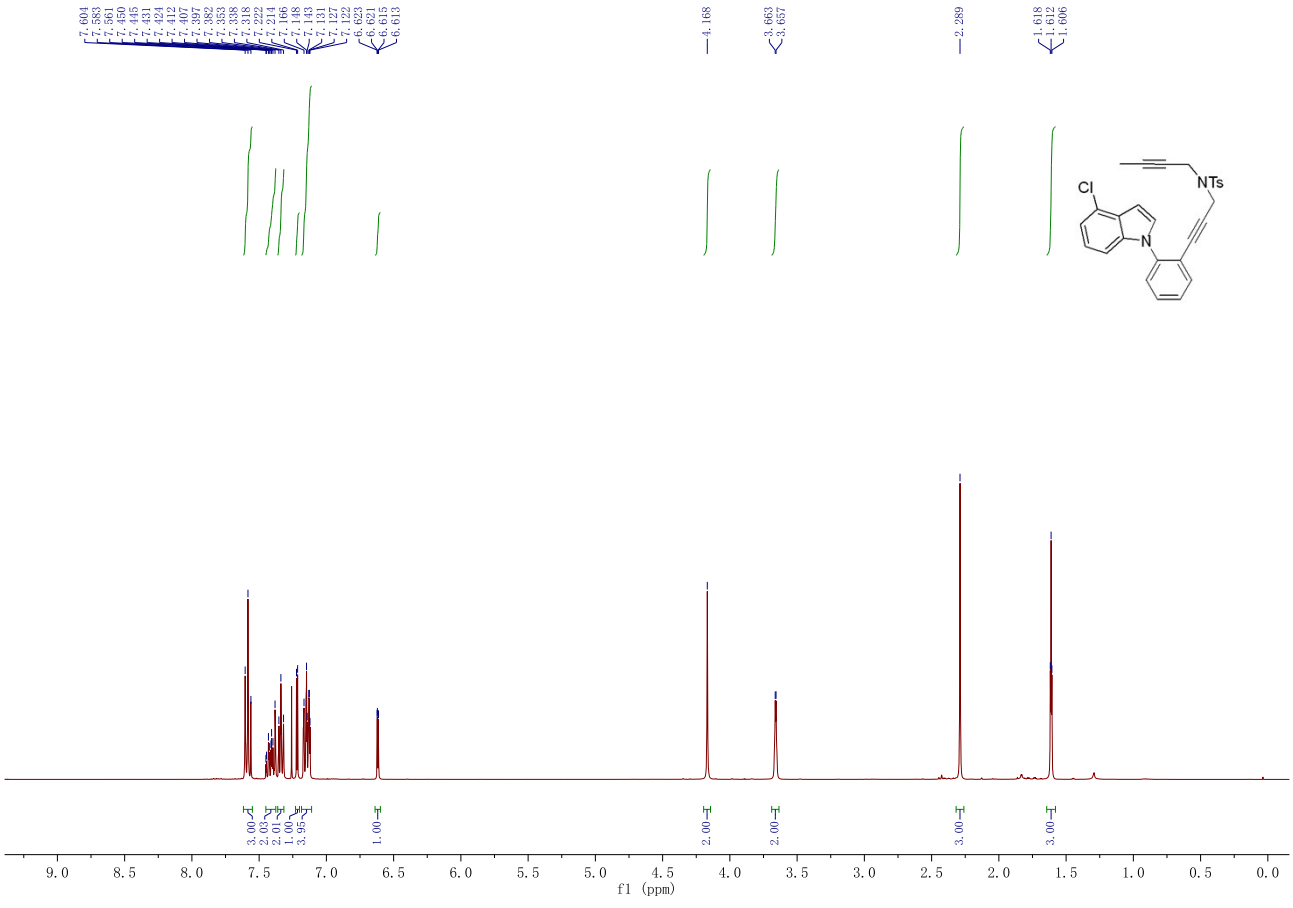
Compound 1h: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.62 (t, *J* = 2.4 Hz, 3H), 2.31 (s, 3H), 3.64 (d, *J* = 2.4 Hz, 2H), 4.13 (s, 2H), 6.57 (d, *J* = 3.2 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.21-7.26 (m, 2H), 7.31-7.37 (m, 2H), 7.39-7.47 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.5, 36.6, 36.8, 71.2, 81.7, 81.9, 87.3, 102.5, 112.2, 113.5, 119.9, 123.4, 124.9, 127.0, 127.5, 127.8, 129.4, 129.6, 129.9, 130.4, 133.8, 135.0, 135.2, 140.0, 143.6. IR (neat) ν 2919, 2850, 2223, 1600, 1508, 1493, 1456, 1348, 1325, 1159, 1092 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}BrN_3O_2S$ requires ($M+NH_4^+$): 548.1002, Found: 548.1000.

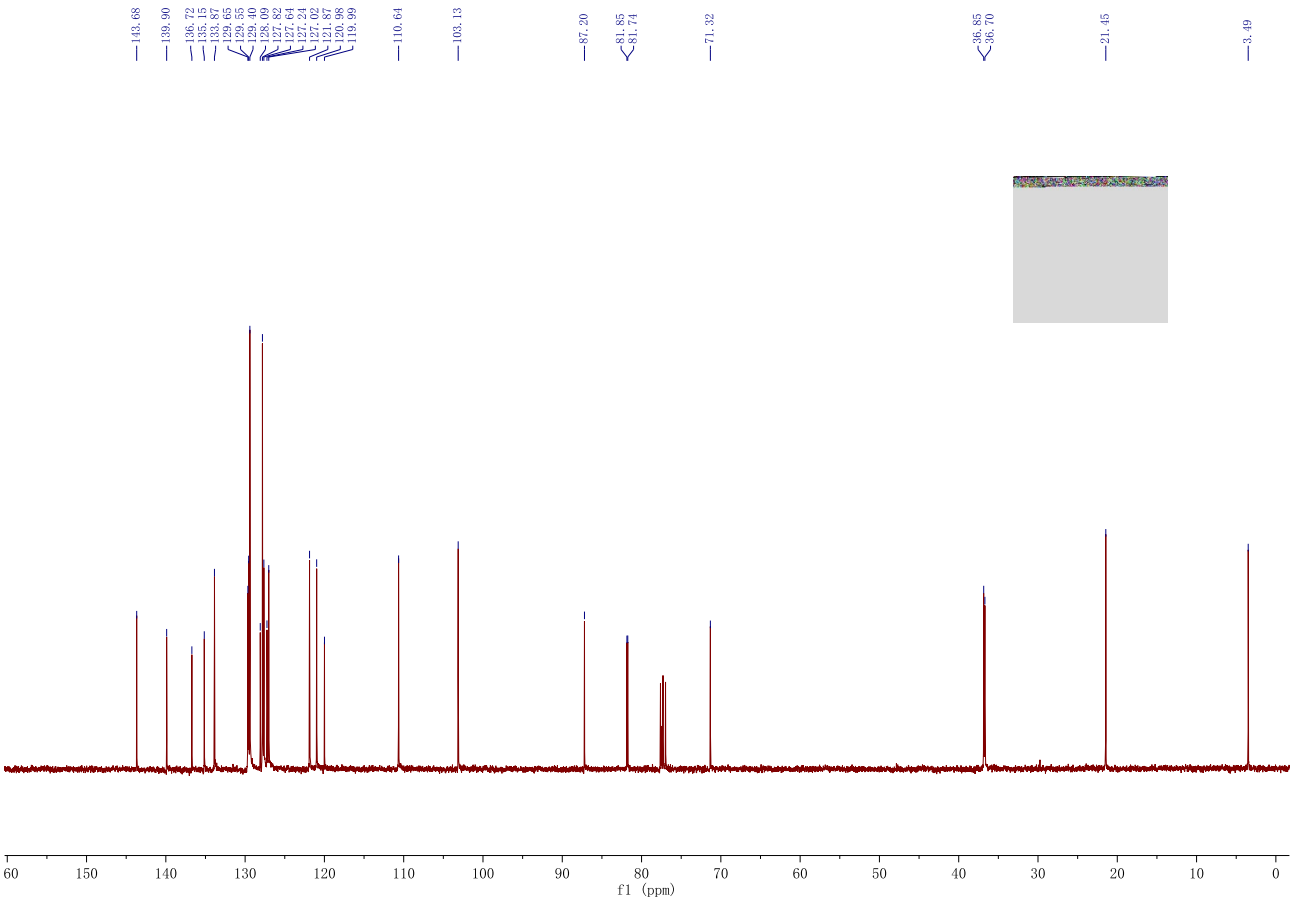

7.781
7.776
7.610
7.589
7.459
7.444
7.420
7.403
7.363
7.349
7.333
7.299
7.250
7.245
7.228
7.219
7.167
7.147
7.051
7.029
6.570
6.562
4.130
3.640
3.634
2.314
1.621
1.615
1.610
NTs
Br
N
1.00
2.00
2.00
2.00
2.00
2.00
1.00
1.00
2.00
2.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

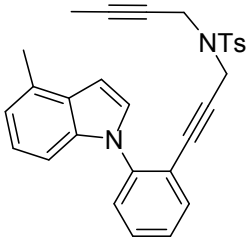

143.61
140.05
135.24
134.49
133.82
130.35
129.89
129.59
129.36
127.83
127.54
126.99
124.90
123.98
119.94
113.52
112.23
102.52
87.34
81.87
81.72
71.22
36.83
36.63
21.48
3.50
NTs
Br
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



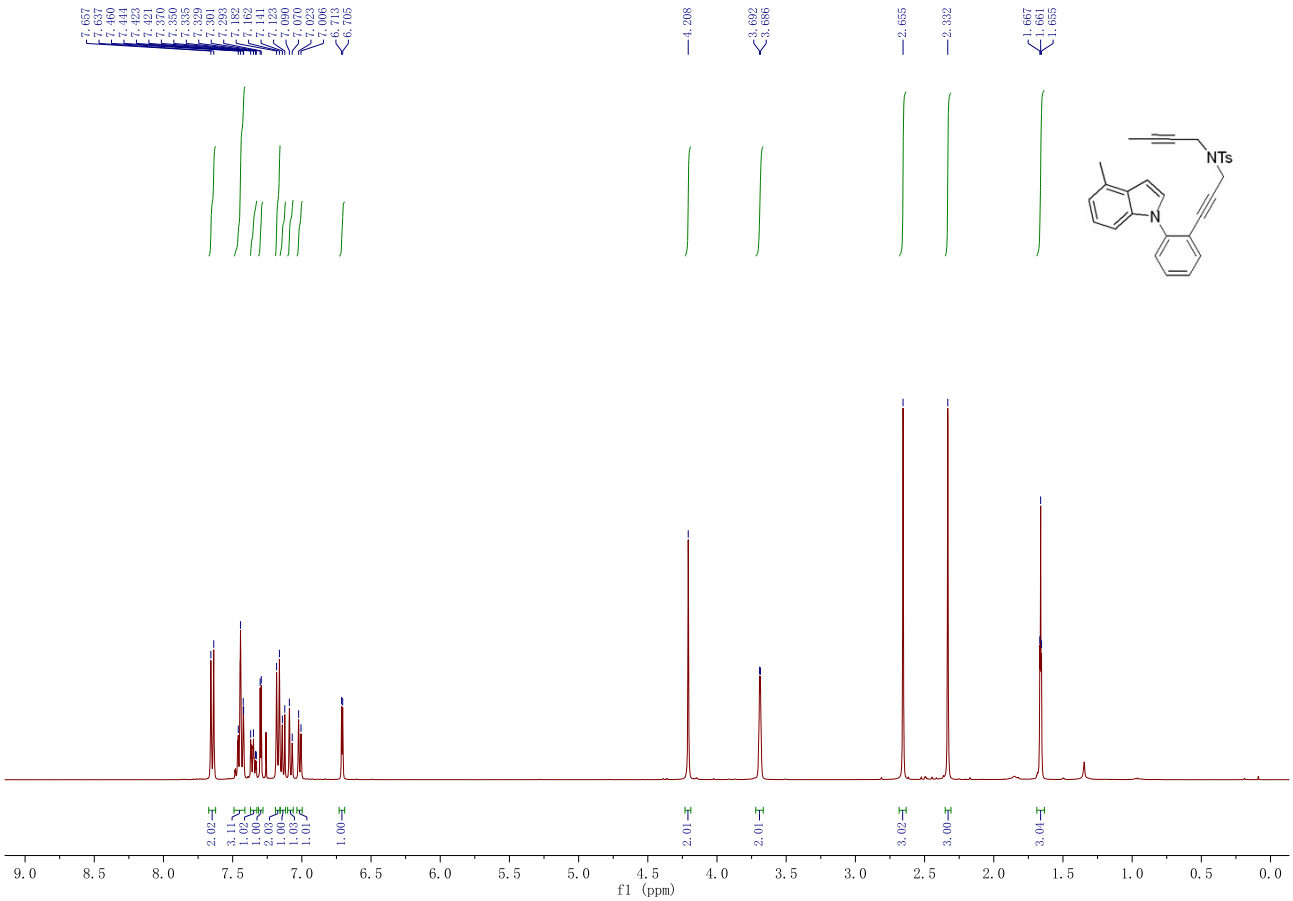
Compound 1i: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.61 (t, *J* = 2.4 Hz, 3H), 2.29 (s, 3H), 3.66 (d, *J* = 2.4 Hz, 2H), 4.17 (s, 2H), 6.62 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.11-7.19 (m, 4H), 7.22 (d, *J* = 3.2 Hz, 1H), 7.32-7.36 (m, 2H), 7.38-7.45 (m, 2H), 7.58 (dd, *J* = 8.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.4, 36.7, 36.8, 71.3, 81.7, 81.8, 87.2, 103.1, 110.6, 120.0, 121.0, 121.9, 127.0, 127.2, 127.6, 127.8, 128.1, 129.4, 129.6, 129.7, 133.9, 135.2, 136.7, 139.9, 143.7. IR (neat) ν 2916, 2850, 2229, 1594, 1510, 1493, 1469, 1364, 1350, 1288, 1165, 1133, 1091, 1064, 1051, 1014, 1004, 976 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}ClN_3O_2S$ requires ($M+NH_4^+$): 504.1507, Found: 504.1505.







Compound 1j: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.66 (t, *J* = 2.4 Hz, 3H), 2.33 (s, 3H), 2.66 (s, 3H), 3.69 (d, *J* = 2.5 Hz, 2H), 4.21 (s, 2H), 6.71 (d, *J* = 3.2 Hz, 1H), 7.01 (d, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.32-7.37 (m, 1H), 7.41-7.49 (m, 3H), 7.65 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 18.9, 21.5, 36.7, 37.0, 71.6, 81.7, 82.2, 86.9, 101.5, 108.3, 119.9, 120.6, 122.3, 127.08, 127.13, 127.9, 128.2, 128.6, 129.4, 129.5, 130.4, 133.8, 135.3, 136.1, 140.8, 143.6. IR (neat) ν 3033, 2964, 2919, 2844, 1603, 1586, 1564, 1493, 1454, 1350, 1236, 1205, 1158, 1092, 898 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_2S$ requires (M^++H): 467.1788, Found: 467.1783.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7.444
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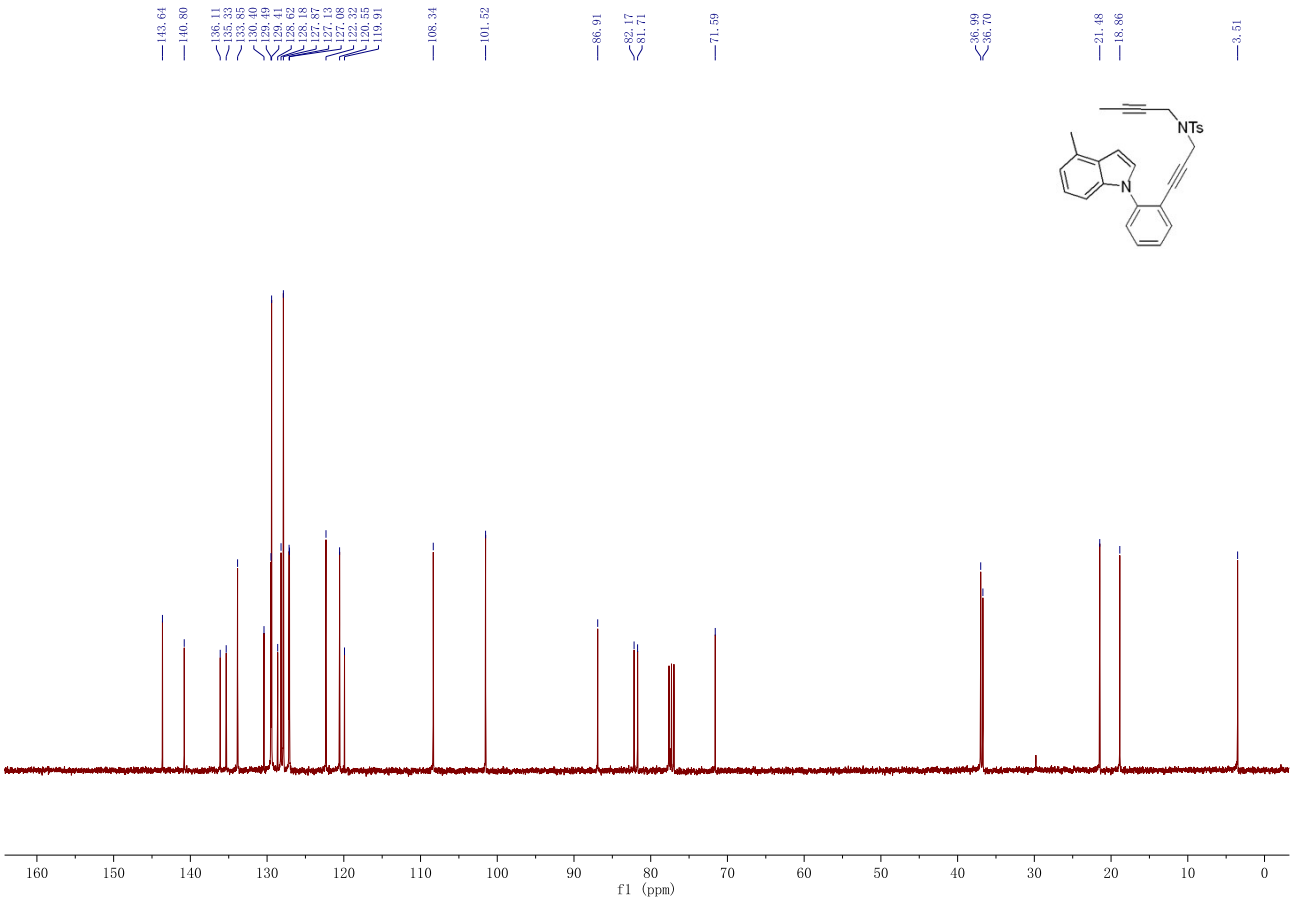
7.421
7.370
7.360
7.335
7.329
7.301
7.293
7.182
7.162
7.141
7.123
7.090
7.070
7.023
7.006
6.713
6.705
4.208
3.692
3.686
2.655
2.332
1.667
1.661
1.655
NTs
N
2.02
3.11
1.02
1.00
2.03
1.00
1.03
1.01
1.00
2.01
2.01
3.02
3.00
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.64
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135.33
133.85
130.40
129.49
129.41
128.62
128.18
127.87
127.43
127.08
122.32
120.55
119.91
108.34
101.52
86.91
82.17
81.71
71.59
36.99
36.70
21.48
18.86
3.51
NTs
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130
120
110
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90
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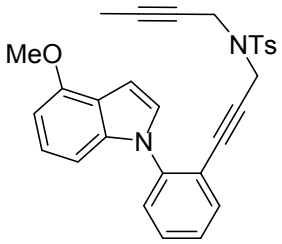
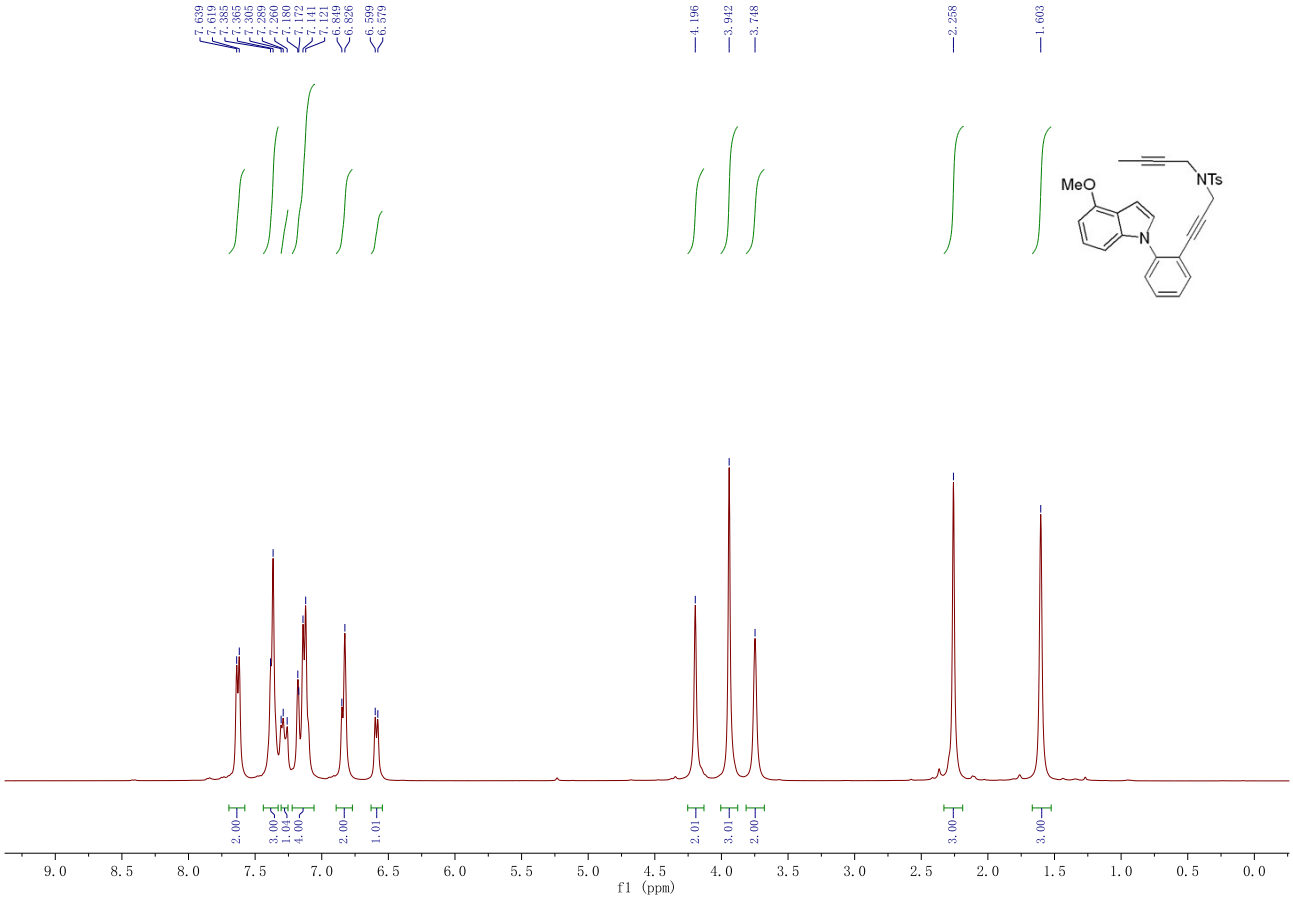
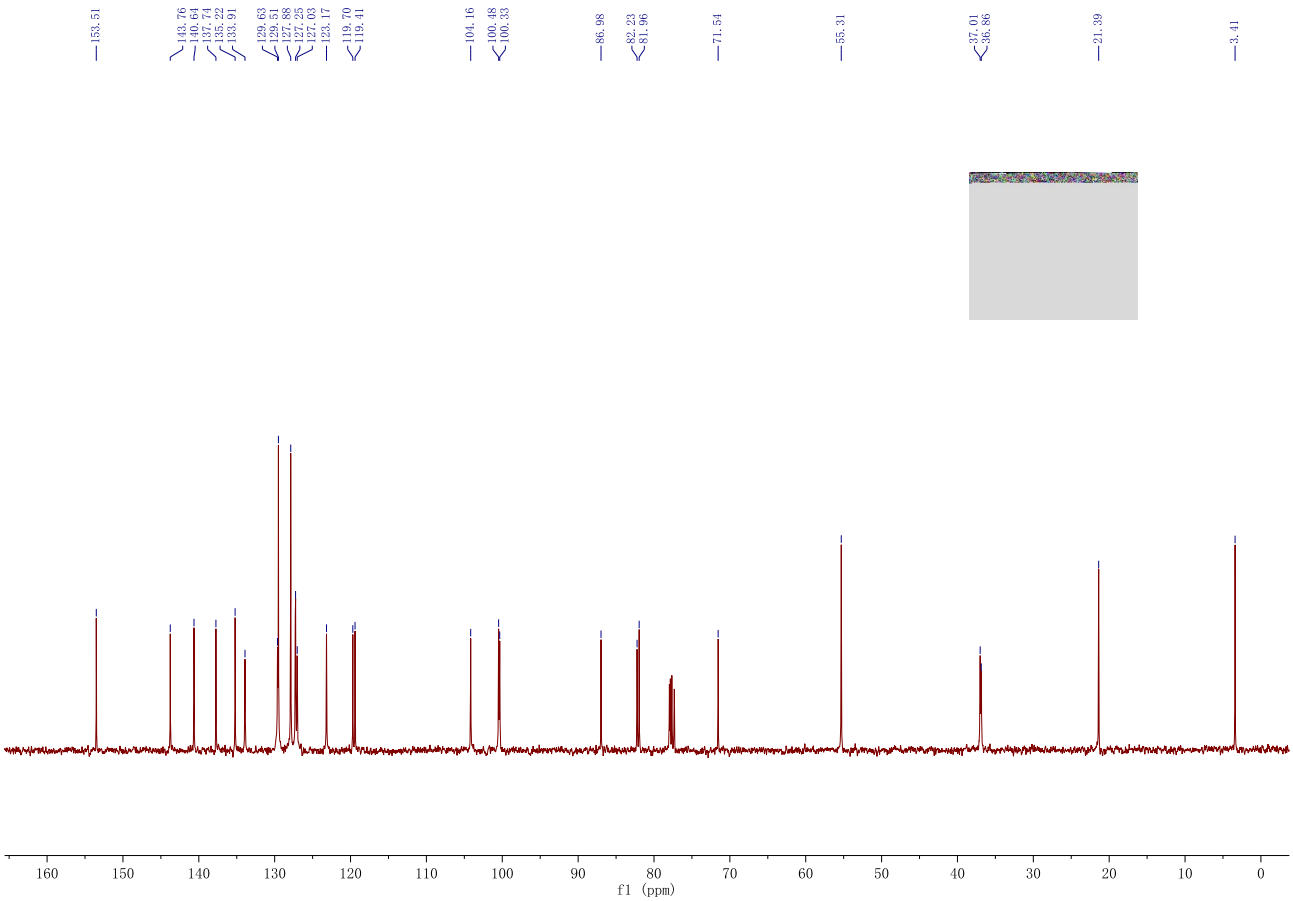
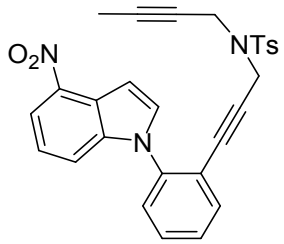
50
40
30
20
10
0
f1 (ppm)



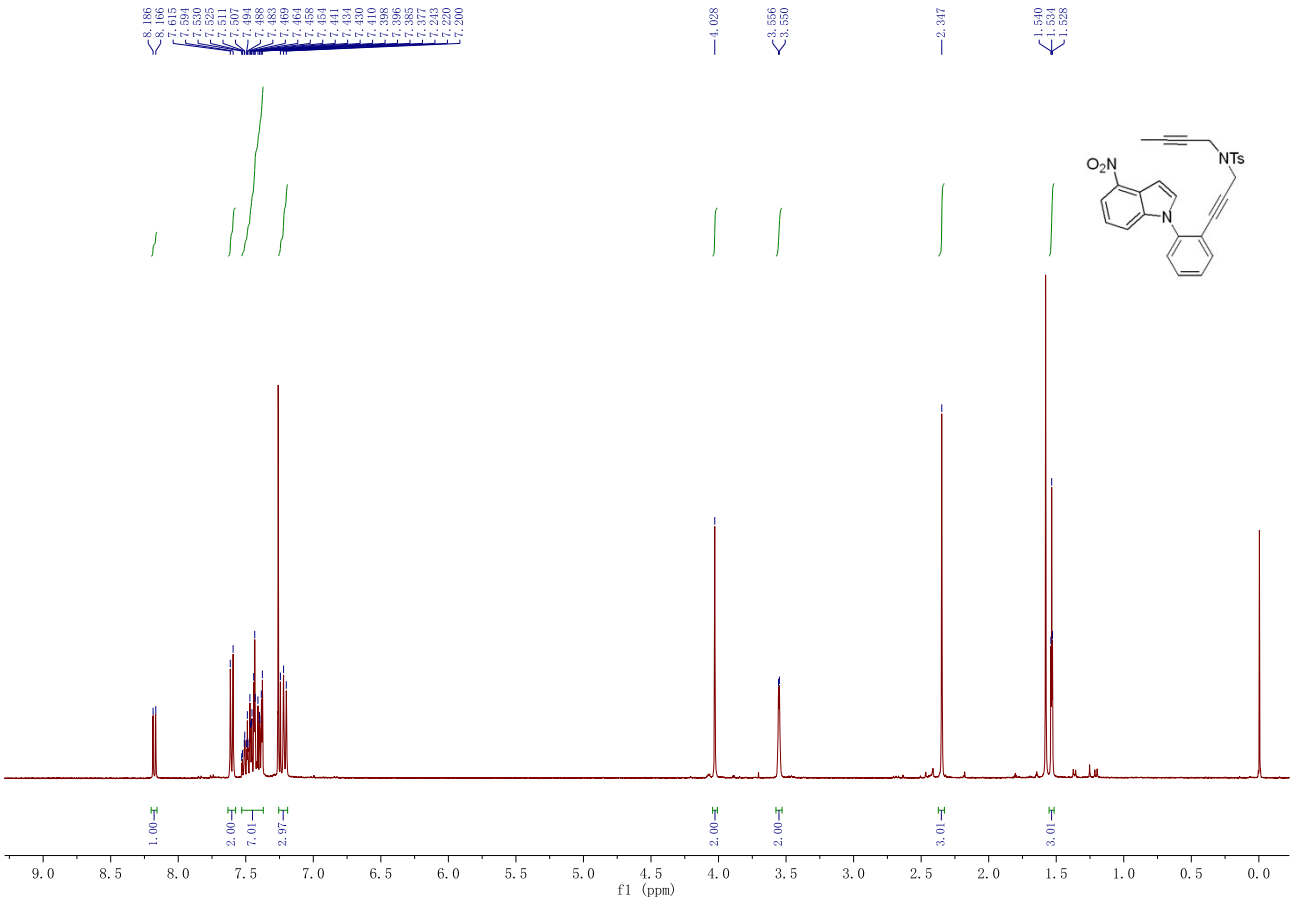
Compound 1k: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.60 (s, 3H), 2.26 (s, 3H), 3.75 (s, 2H), 3.94 (s, 3H), 4.20 (s, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.83-6.85 (m, 2H), 7.06-7.22 (m, 4H), 7.25-7.30 (m, 1H), 7.37-7.38 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.4, 21.4, 36.9, 37.0, 55.3, 71.5, 82.0, 82.2, 87.0, 100.3, 100.5, 104.2, 119.4, 119.7, 123.2, 127.0, 127.2, 127.9, 129.5, 129.6, 133.9, 135.2, 137.7, 140.6, 143.8, 153.5. IR (neat) ν 3134, 2839, 2232, 1732, 1580, 1491, 1447, 1434, 1347, 1297, 1260, 1162, 1150, 1091, 1061 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_3S$ requires (M^++H): 483.1737, Found: 483.1733.







Compound 1l: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.53 (t, *J* = 2.4 Hz, 3H), 2.35 (s, 3H), 3.55 (d, *J* = 2.4 Hz, 2H), 4.03 (s, 2H), 7.19-7.26 (m, 3H), 7.37-7.53 (m, 7H), 7.60 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.2, 21.4, 36.5, 36.7, 70.8, 82.0, 87.4, 103.2, 117.7, 117.9, 120.4, 121.1, 122.6, 127.4, 127.8, 128.5, 129.4, 133.1, 133.7, 134.9, 138.4, 139.2, 140.3, 143.8. IR (neat) ν 2973, 2898, 1592, 1501, 1450, 1429, 1347, 1322, 1291, 1243, 1209, 1183，1157，1094，1066，904 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}N_4O_4S$ requires ($M+NH_4^+$): 515.1748, Found: 515.1744.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7.511
7.507
7.494
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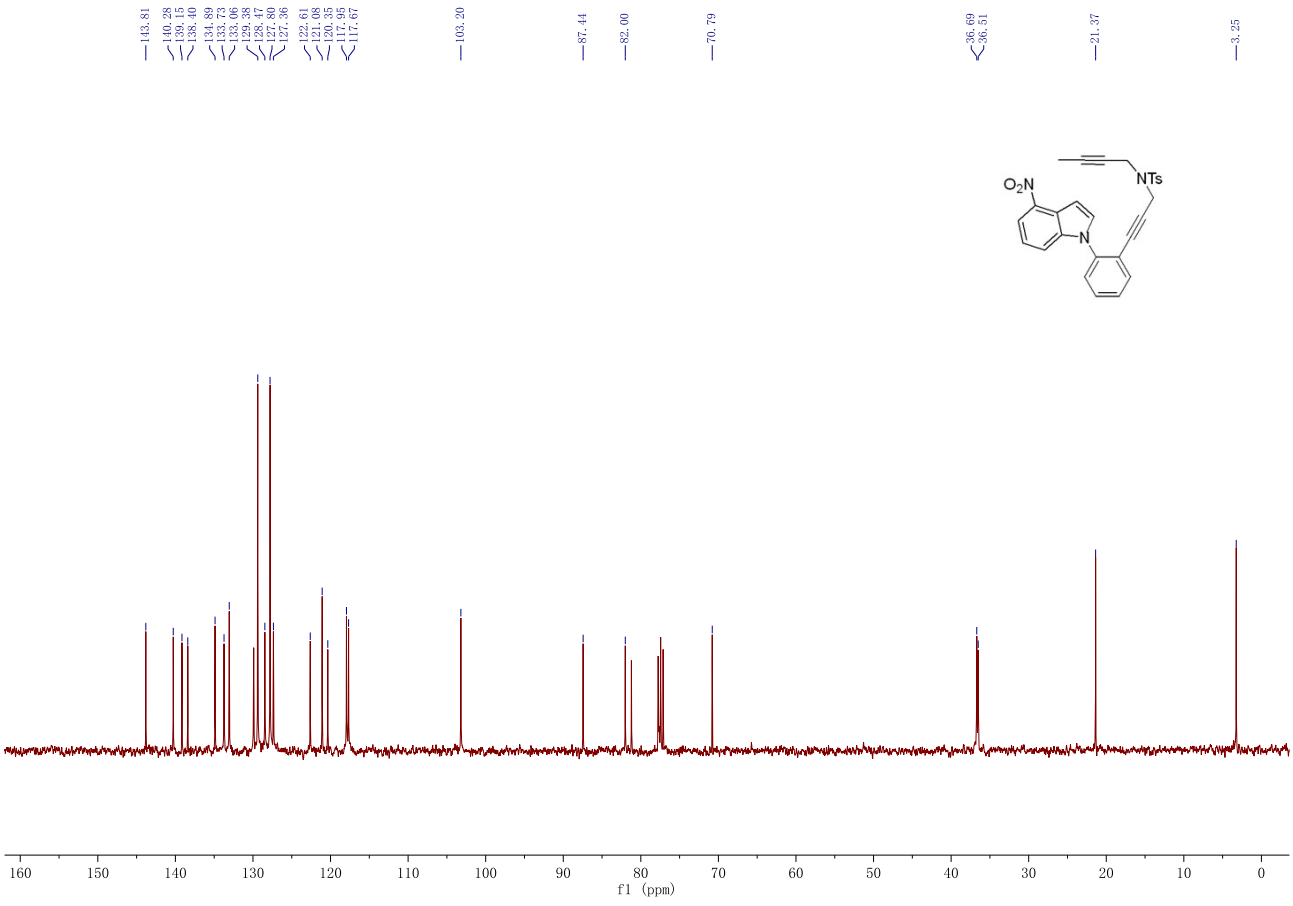
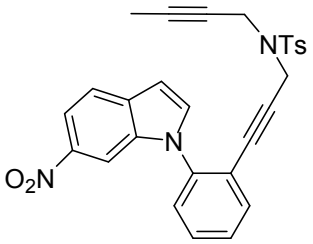
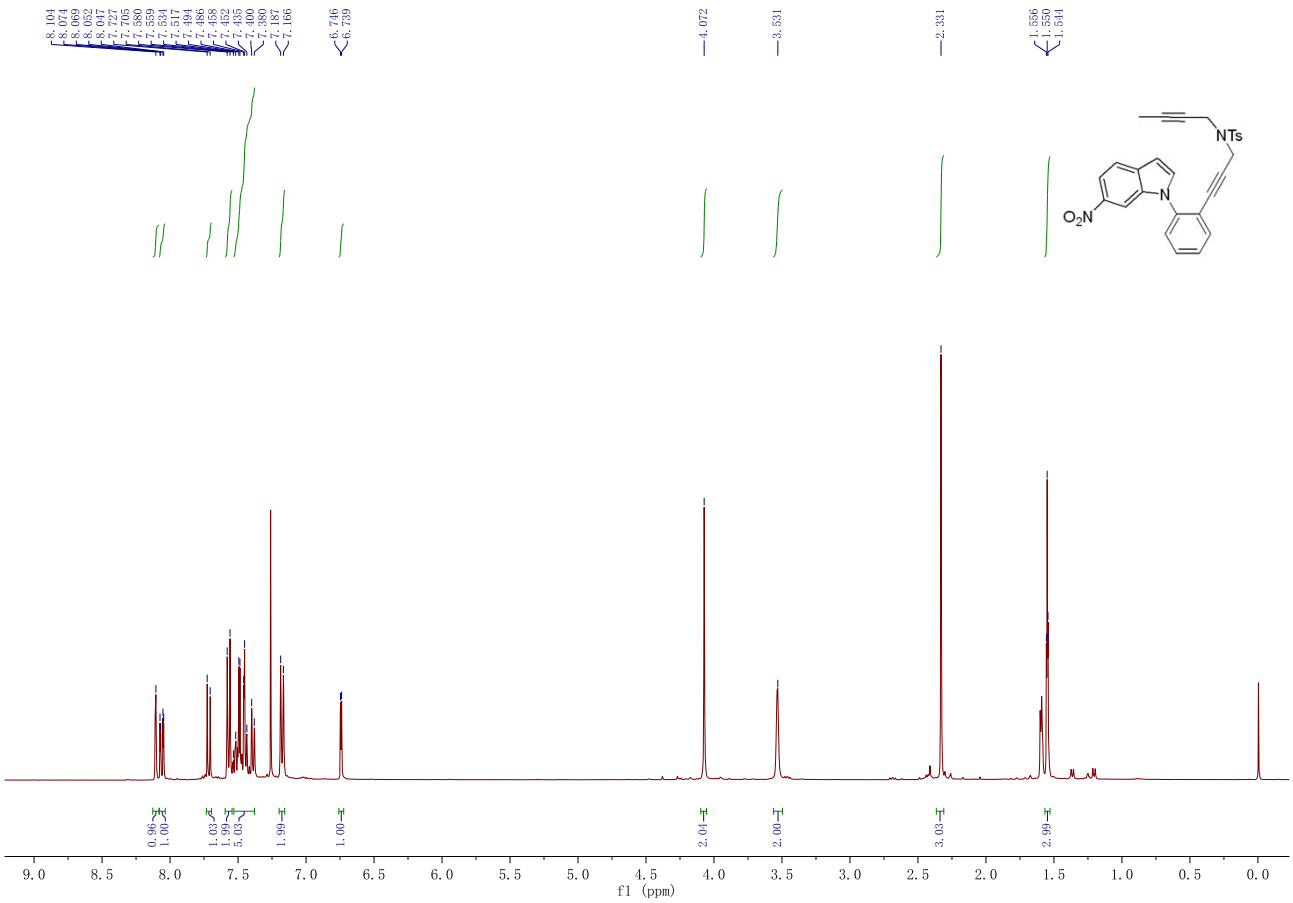
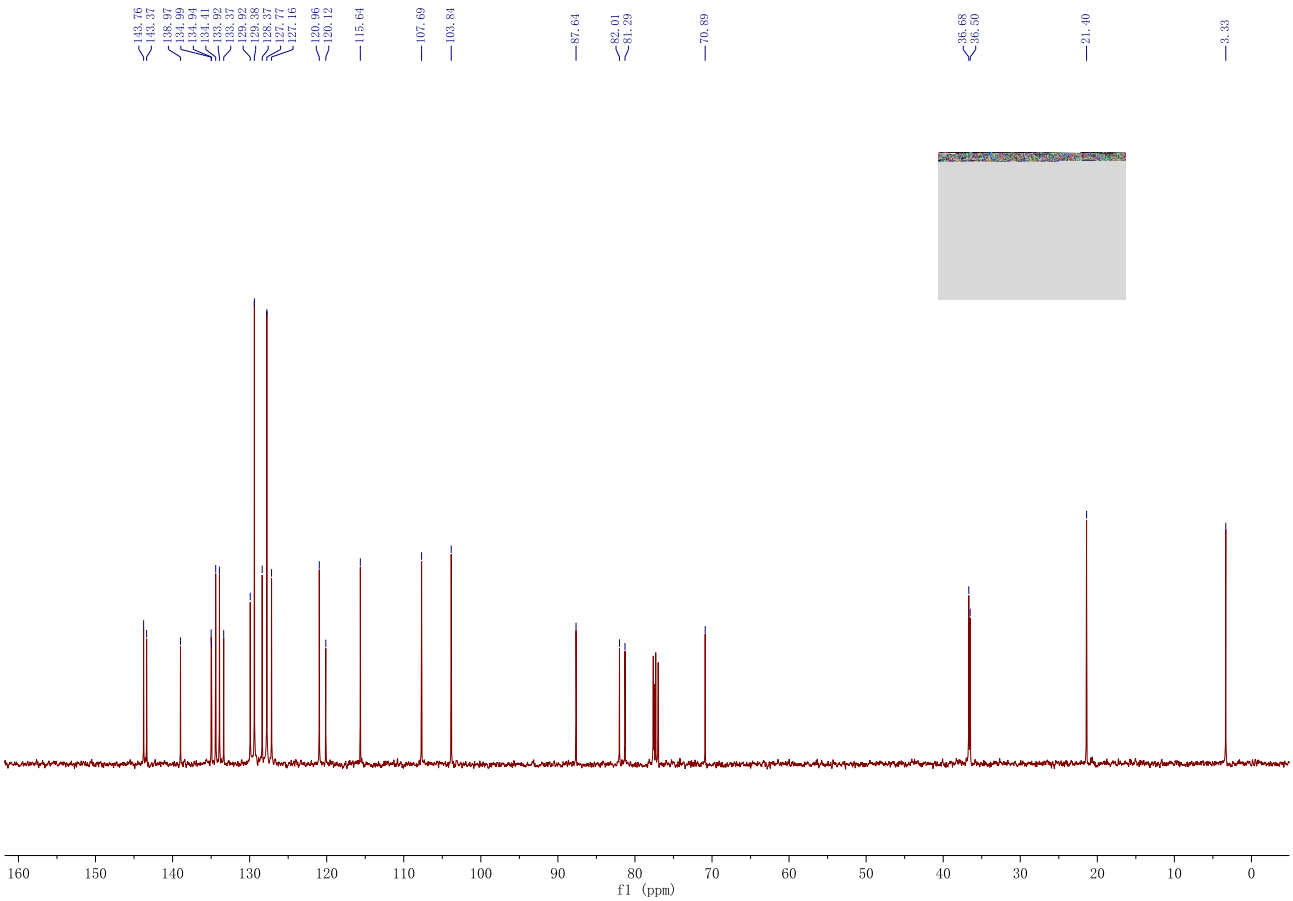
7.485
7.468
7.464
7.458
7.454
7.441
7.434
7.430
7.410
7.398
7.396
7.385
7.377
7.243
7.220
7.200
4.028
3.556
3.550
2.347
1.540
1.534
1.528
O2N
NTs
N
1.00
2.00
7.01
2.97
2.00
2.00
3.01
3.01
f1 (ppm)

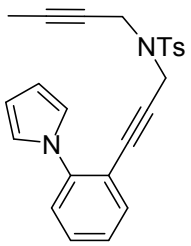

143.81
140.28
139.15
138.40
134.89
133.73
133.06
129.38
128.47
128.40
127.36
122.61
121.98
120.55
117.95
117.67
103.20
87.44
82.00
70.79
36.69
36.51
21.37
3.25
O2N
NTs
N
f1 (ppm)



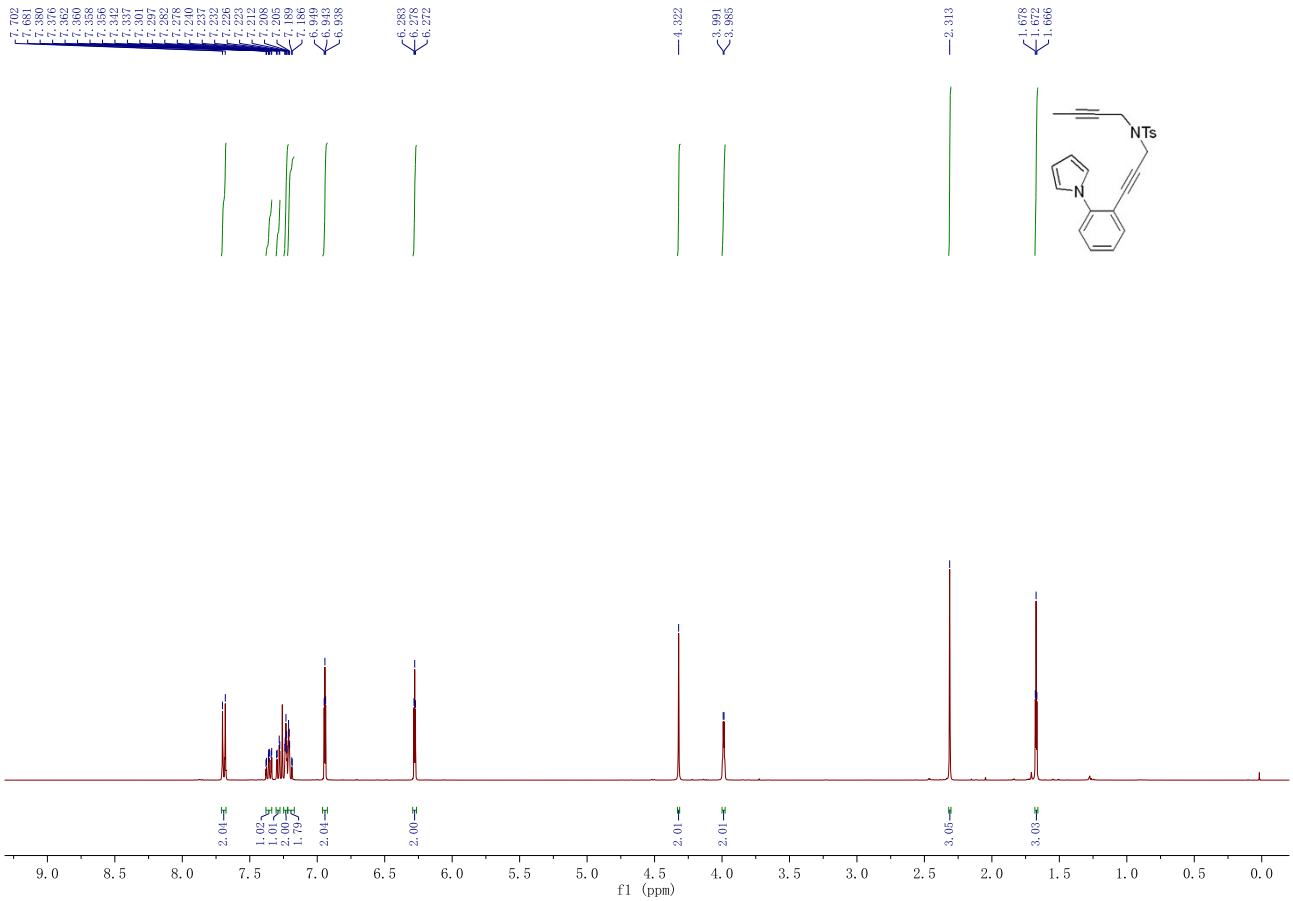
Compound 1m: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.55 (t, *J* = 2.4 Hz, 3H), 2.33 (s, 3H), 3.53 (s, 2H), 4.07 (s, 2H), 6.74 (dd, *J* = 3.2, 0.9 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.38-7.53 (m, 5H), 7.57 (d, *J* = 8.8 Hz, 2H), 8.06 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.10 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.3, 21.4, 36.5, 36.7, 70.9, 81.3, 82.0, 87.6, 103.8, 107.7, 115.6, 120.1, 121.0, 127.2, 127.8, 128.4, 129.4, 129.9, 133.4, 133.9, 134.4, 134.9, 135.0, 139.0, 143.4, 143.8. IR (neat) ν 2981, 2973, 2893, 1592, 1501, 1463, 1429, 1347, 1322, 1291, 1243, 1209, 1183, 1157, 1094, 1066 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{27}N_4O_4S$ requires ($M+NH_4^+$): 515.1748, Found: 515.1745.







Compound 1n: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.67 (t, *J* = 2.4 Hz, 3H), 2.31 (s, 3H), 3.99 (d, *J* = 2.4 Hz, 2H), 4.32 (s, 2H), 6.28 (dd, *J* = 2.0 Hz, 2H), 6.94 (dd, *J* = 2.0 Hz, 2H), 7.17-7.22 (m, 2H), 7.22-7.25 (m, 2H), 7.29 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.5, 21.5, 37.06, 37.11, 71.6, 82.0, 82.6, 86.4, 109.5, 117.0, 121.4, 124.8, 126.1, 127.9, 129.4, 129.5, 133.9, 135.3, 141.9, 143.7. IR (neat) ν 3061, 2919, 2846, 2232, 1595, 1500, 1476, 1442, 1421, 1344, 1331, 1250, 1166, 1111, 1091, 1067, 1012, 899 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_2S$ requires (M^++H): 403.1475, Found: 403.1472.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7.360
7.358
7.356
7.342
7.337
7.301
7.297
7.282
7.278
7.240
7.237
7.232
7.226
7.223
7.212
7.208
7.205
7.189
7.186
6.949
6.943
6.938
6.283
6.278
6.272
4.322
3.991
3.985
2.913
1.678
1.672
1.666
NTs
N
2.04
1.02
1.01
2.00
1.79
2.04
2.00
2.01
2.01
3.05
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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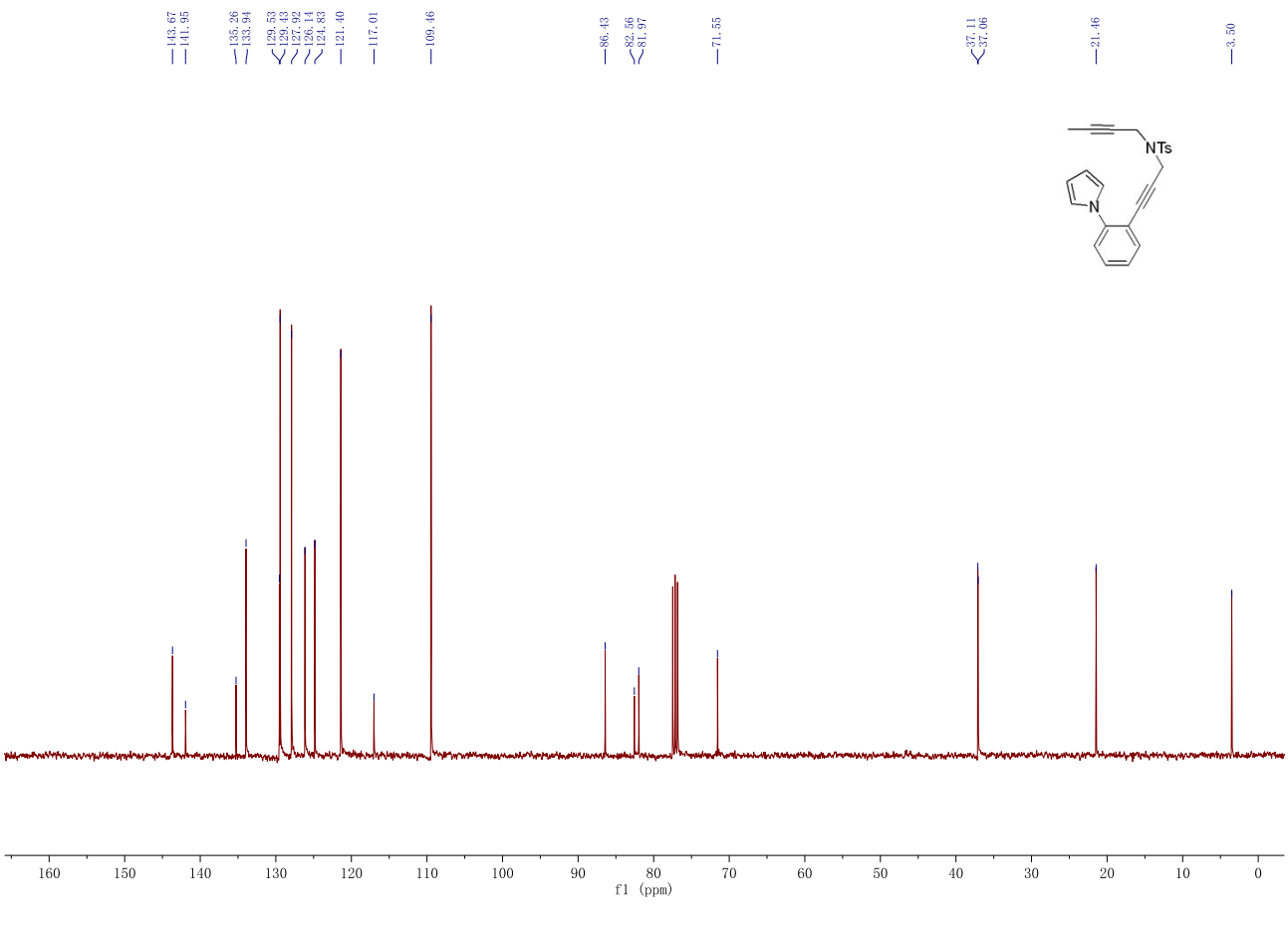
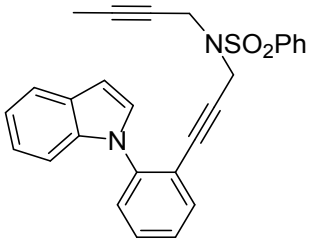
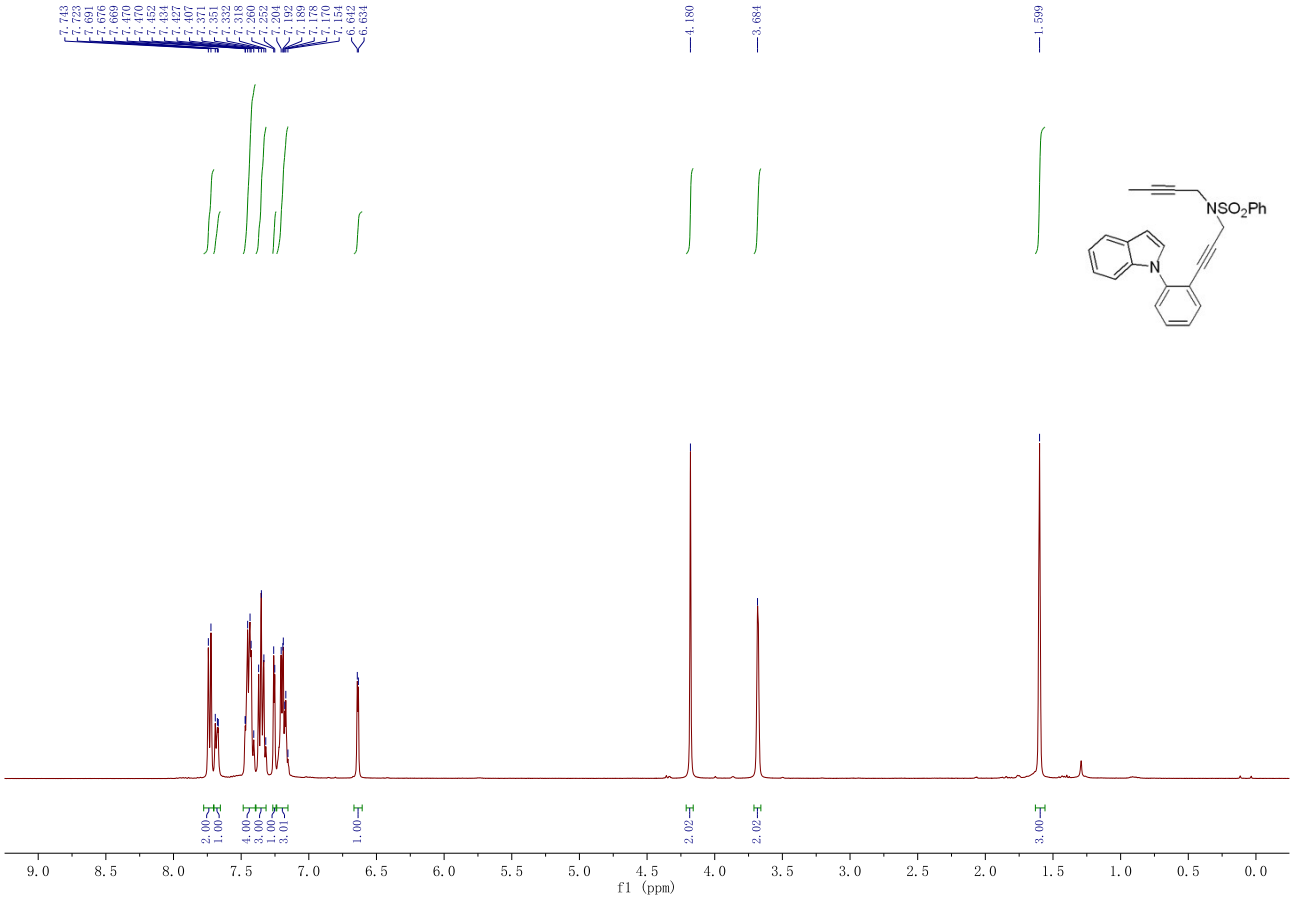
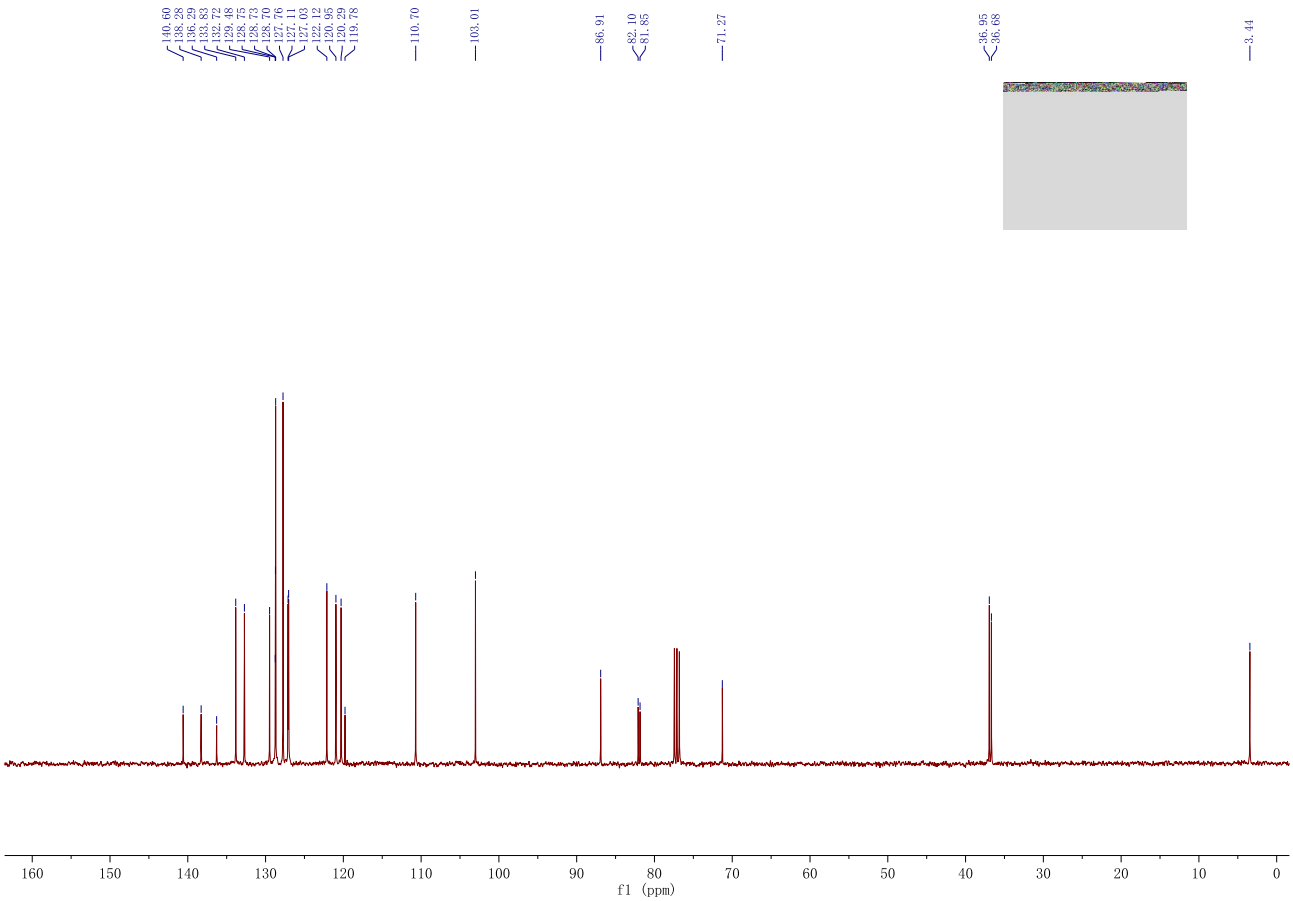
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

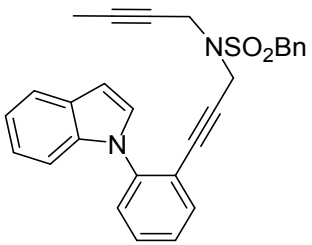

143.67
141.95
135.26
133.94
129.53
129.43
127.92
126.14
124.83
121.40
117.01
109.46
86.43
82.56
81.97
71.55
37.11
37.06
21.46
3.50
NTs
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



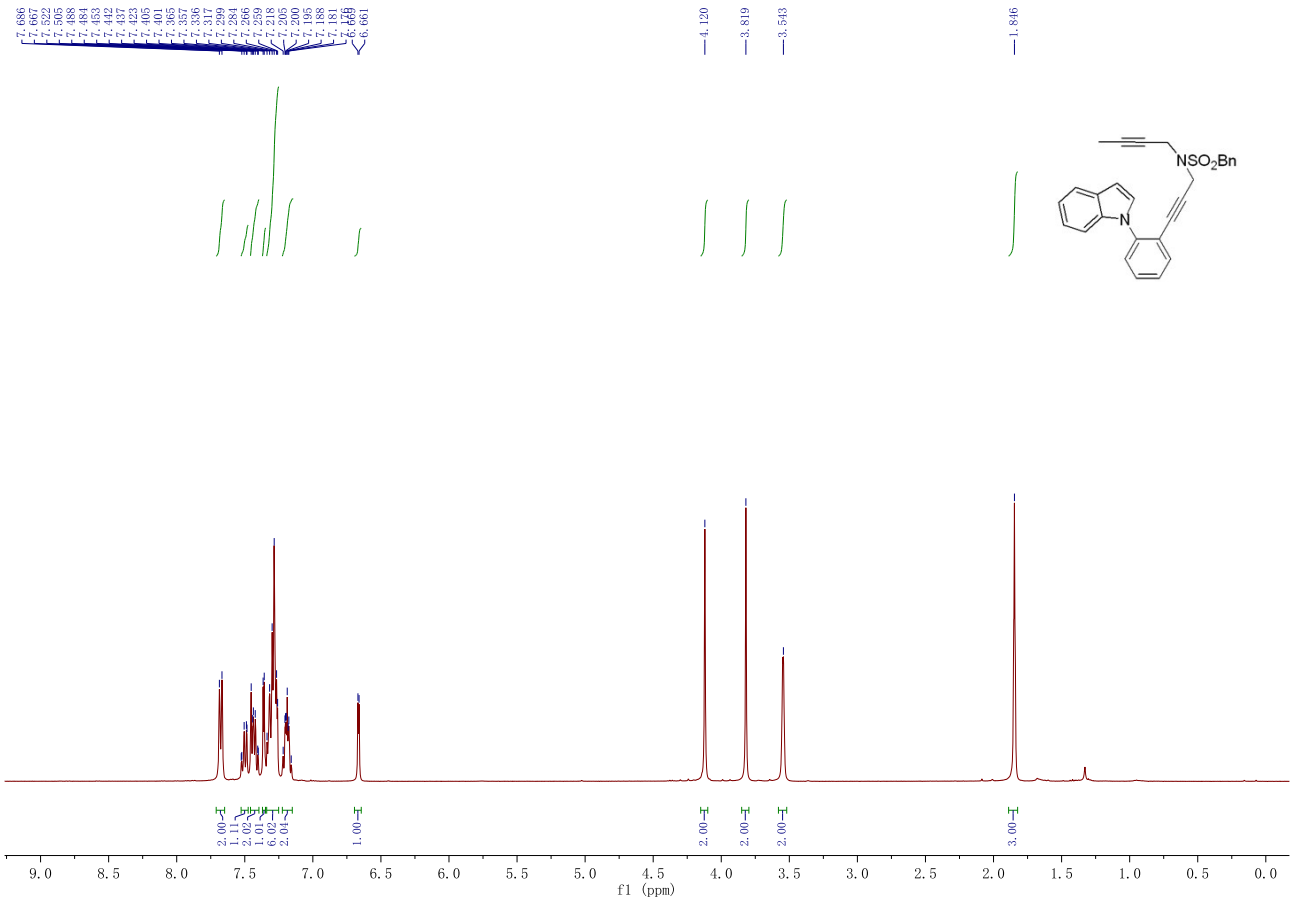
Compound 1o: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.60 (s, 3H), 3.68 (s, 2H), 4.18 (s, 2H), 6.64 (d, *J* = 3.2 Hz, 1H), 7.15-7.24 (m, 3H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.32-7.37 (m, 3H), 7.40-7.49 (m, 4H), 7.65-7.70 (m, 1H), 7.73 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.4, 36.7, 36.9, 71.3, 81.9, 82.1, 86.9, 103.0, 110.7, 119.8, 120.3, 121.0, 122.1, 127.0, 127.1, 127.8, 128.70, 128.73, 128.8, 129.5, 132.7, 133.8, 136.3, 138.3, 140.6. IR (neat) ν 3056, 2916, 2217, 1595, 1517, 1494, 1458, 1442, 1347, 1330, 1212, 1159, 1092 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{23}N_2O_2S$ requires (M^++H): 439.1475, Found: 439.1471.







Compound 1p: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.85 (s, 3H), 3.54 (s, 2H), 3.82 (s, 2H), 4.12 (s, 2H), 6.66 (d, *J* = 3.2 Hz, 1H), 7.15-7.22 (m, 2H), 7.23-7.27 (m, 6H), 7.36 (d, *J* = 3.2 Hz, 1H), 7.40-7.46 (m, 2H), 7.47-7.53 (m, 1H), 7.68 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.7, 36.7, 37.0, 57.9, 72.7, 81.7, 82.0, 88.0, 103.3, 110.8, 120.2, 120.5, 121.1, 122.3, 127.5, 127.6, 128.4, 128.5, 128.7, 128.8, 129.8, 130.9, 133.8, 136.5, 140.7. IR (neat) ν 3025, 2914, 2225, 1592, 1515, 1494, 1458, 1347, 1330, 1209, 1151, 1074 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_2O_2S$ requires (M^++H): 453.1631, Found: 453.1627.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7.357
7.336
7.317
7.299
7.284
7.266
7.259
7.218
7.205
7.200
7.195
7.188
7.181
6.683
6.661
4.120
3.819
3.543
1.846
NSO2Bn
N
2.00
1.11
2.02
1.01
0.92
2.04
1.00
2.00
2.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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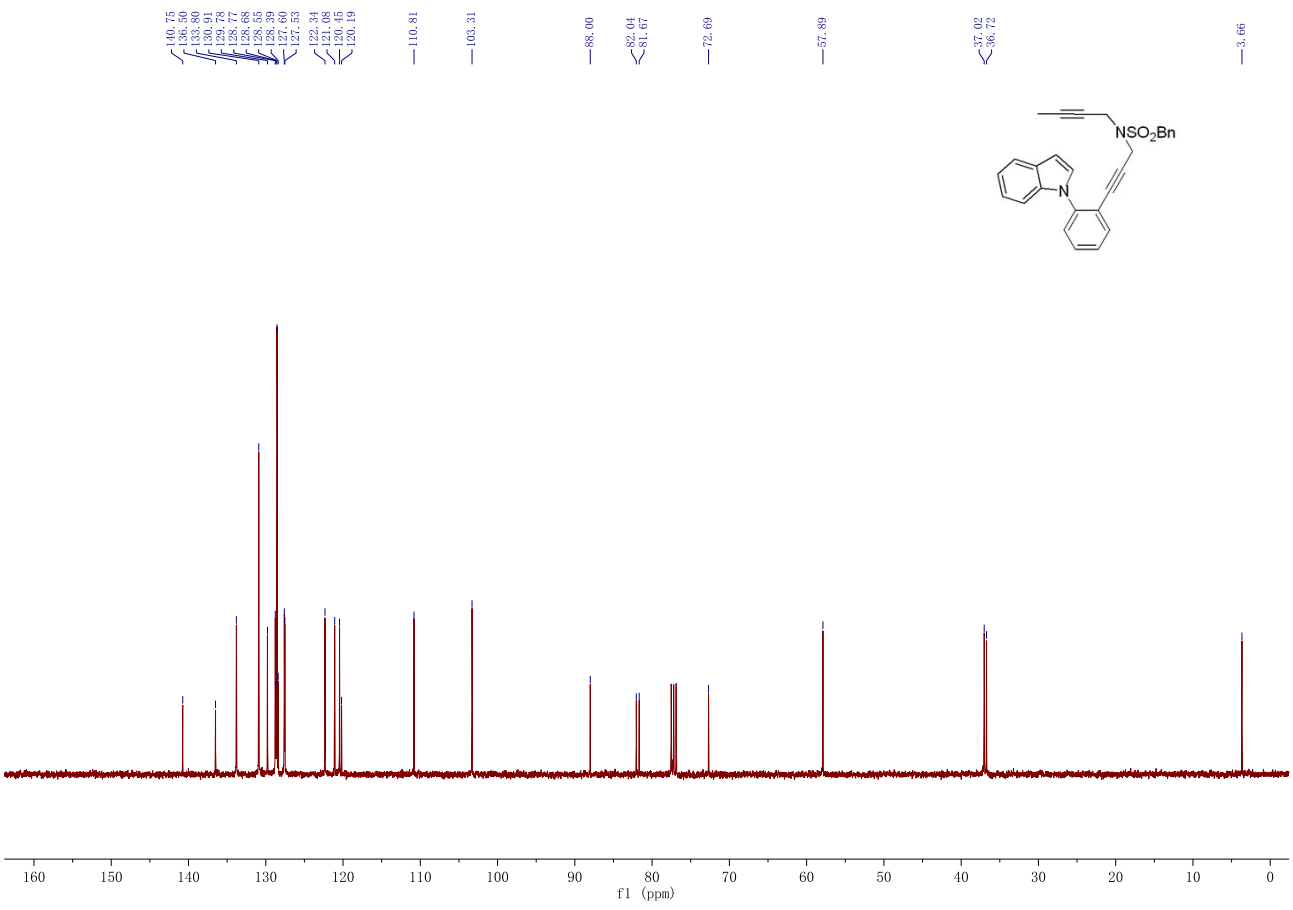
0.0
f1 (ppm)


140.75
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128.77
128.68
128.55
128.39
127.60
127.53
122.34
121.08
120.45
120.19
110.81
103.31
88.00
82.04
81.67
72.69
57.89
37.02
36.72
3.66
NSO2Bn
N
160
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130
120
110
100
90
80
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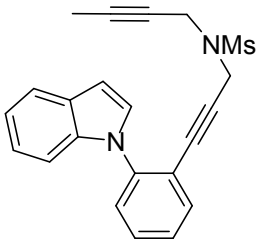
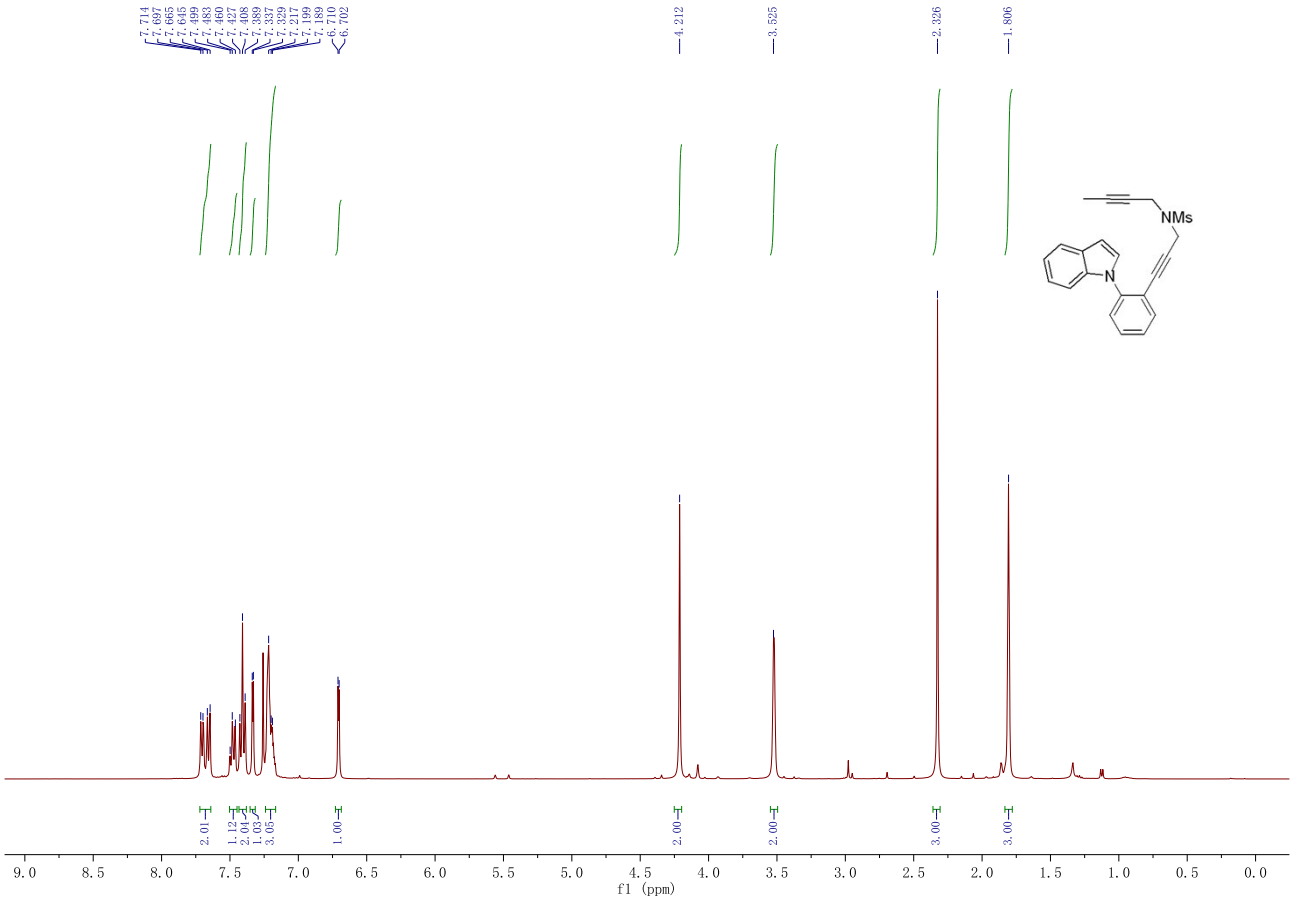
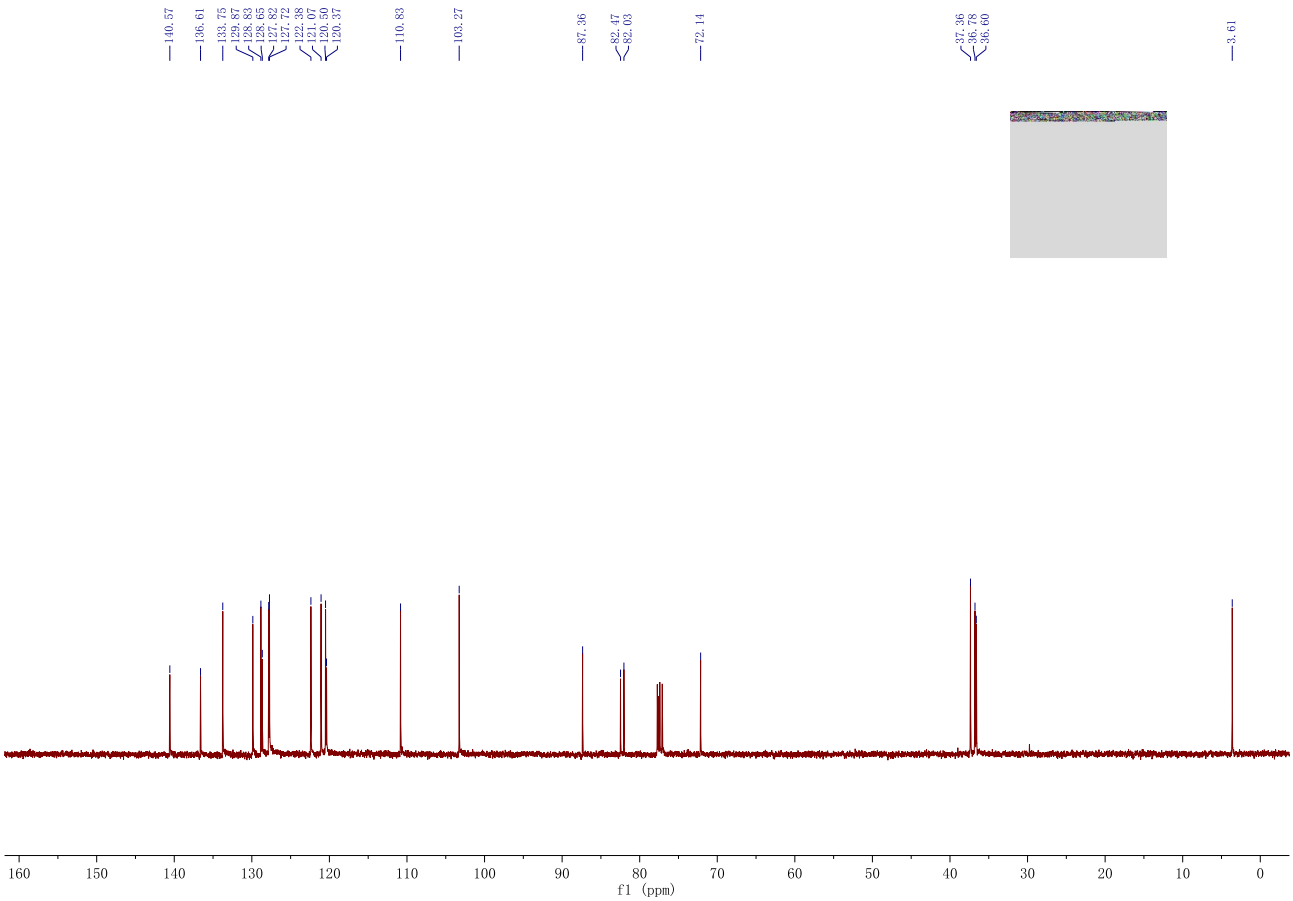
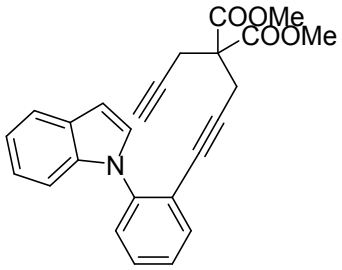
60
50
40
30
20
10
0
f1 (ppm)



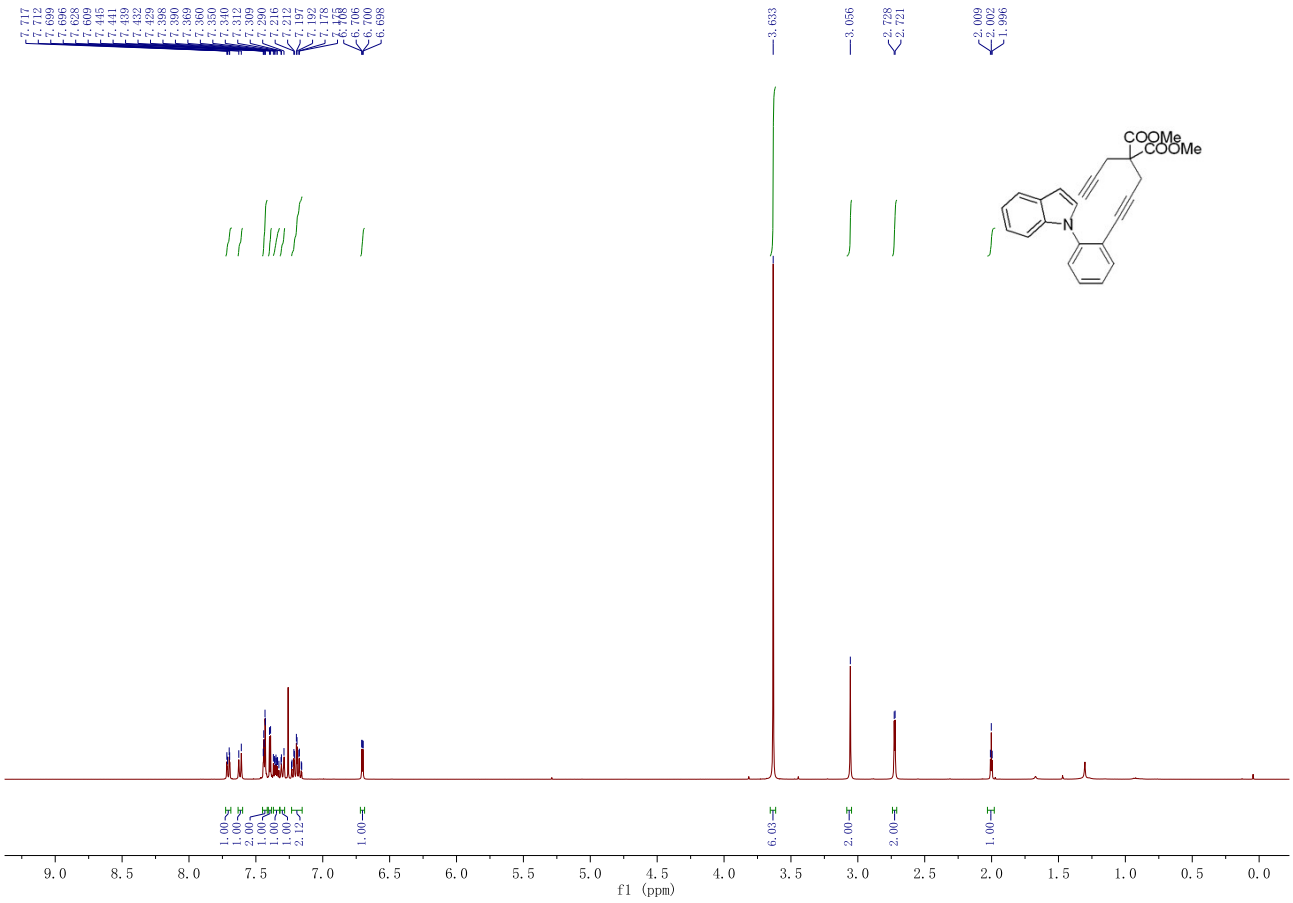
Compound 1q: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.81 (s, 3H), 2.33 (s, 3H), 3.53 (s, 2H), 4.21 (s, 2H), 6.71 (d, *J* = 3.2 Hz, 1H), 7.17-7.24 (m, 3H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.40 (dd, *J* = 7.6 Hz, 2H), 7.45-7.50 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.6, 36.6, 36.8, 37.4, 72.1, 82.0, 82.5, 87.4, 103.3, 110.8, 120.4, 120.5, 121.1, 122.4, 127.7, 127.8, 128.6, 128.8, 129.9, 133.7, 136.6, 140.6. IR (neat) ν 2965, 2931, 1621, 1556, 1502, 1458, 1384, 1360, 1327, 1302, 1261, 1231, 1131, 1098, 1065, 1054, 1041, 1016, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{21}N_2O_2S$ requires (M^++H): 377.1318, Found: 377.1314.







Compound 1r: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.00 (t, *J* = 2.8 Hz, 1H), 2.72 (d, *J* = 2.8 Hz, 2H), 3.06 (s, 2H), 3.63 (s, 6H), 6.70 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.15-7.23 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.32-7.37 (m, 1H), 7.39 (d, *J* = 3.2 Hz, 1H), 7.43-7.45 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.69-7.73 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 22.6, 23.7, 53.0, 56.5, 71.7, 78.5, 80.2, 88.9, 103.0, 110.7, 120.2, 120.5, 120.9, 122.1, 127.08, 127.13, 128.8, 129.0, 129.1, 134.2, 136.4, 140.5, 169.0. IR (neat) ν 3301, 3290, 3270, 3114, 2961, 2919, 2844, 2162, 1734, 1514, 1496, 1461, 1436, 1293, 1245, 1214 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{22}NO_4$ requires (M^++H): 400.1543, Found: 400.1540.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7.389
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7.350
7.340
7.312
7.309
7.290
7.216
7.212
7.197
7.192
7.178
6.706
6.700
6.698
3.633
3.056
2.728
2.721
2.009
2.002
1.996
COOMe
COOMe
N
1.00
1.00
2.00
1.00
1.00
2.12
1.00
6.03
2.00
2.00
1.00
9.0
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8.0
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6.0
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1.0
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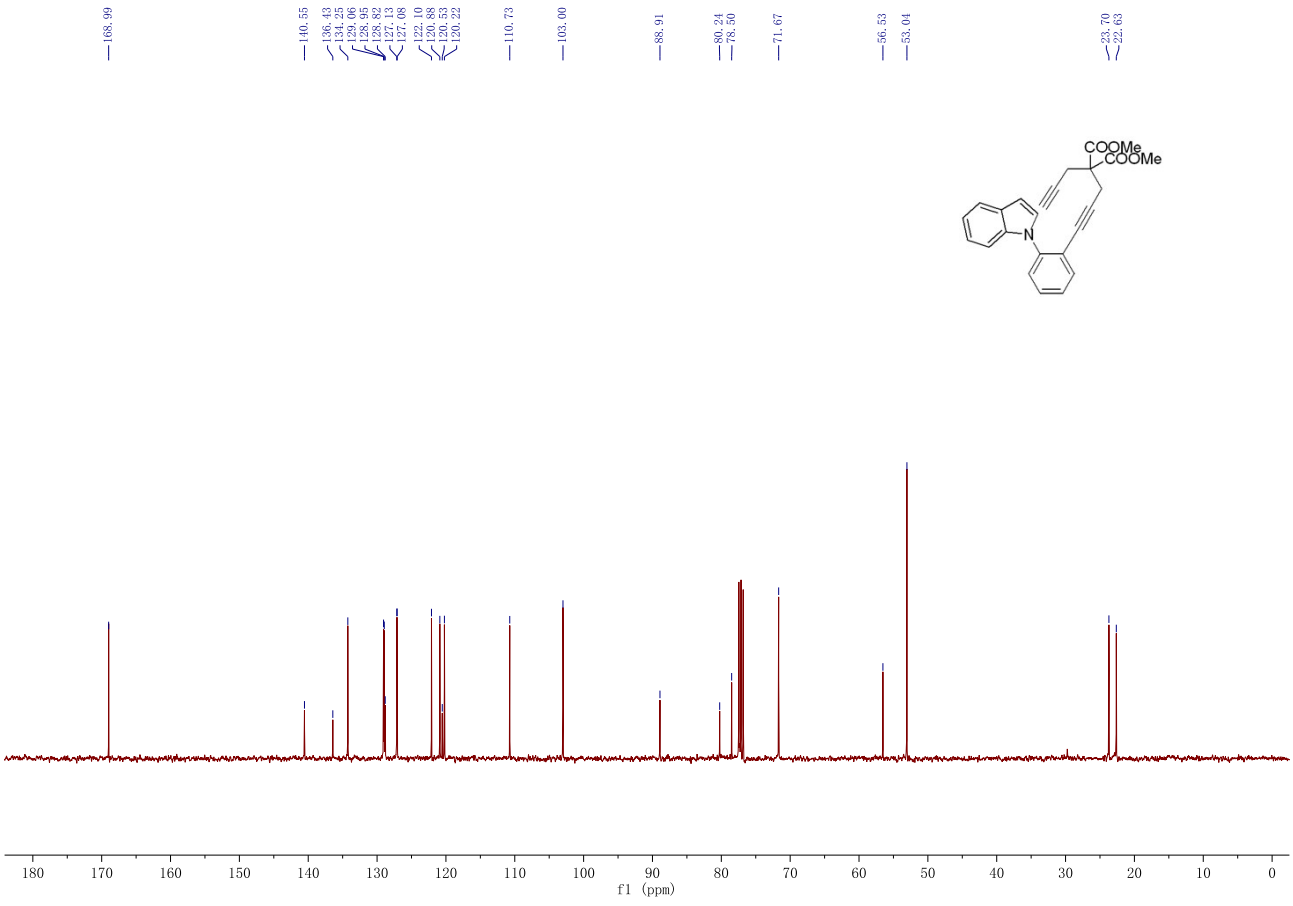
0.0
f1 (ppm)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127.13
127.08
122.10
120.88
120.53
120.22
110.73
103.00
88.91
80.24
78.50
71.67
56.53
53.04
23.70
22.63
COOMe
COOMe
N
180
170
160
150
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130
120
110
100
90
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50
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30
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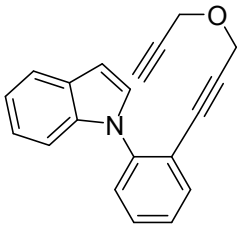
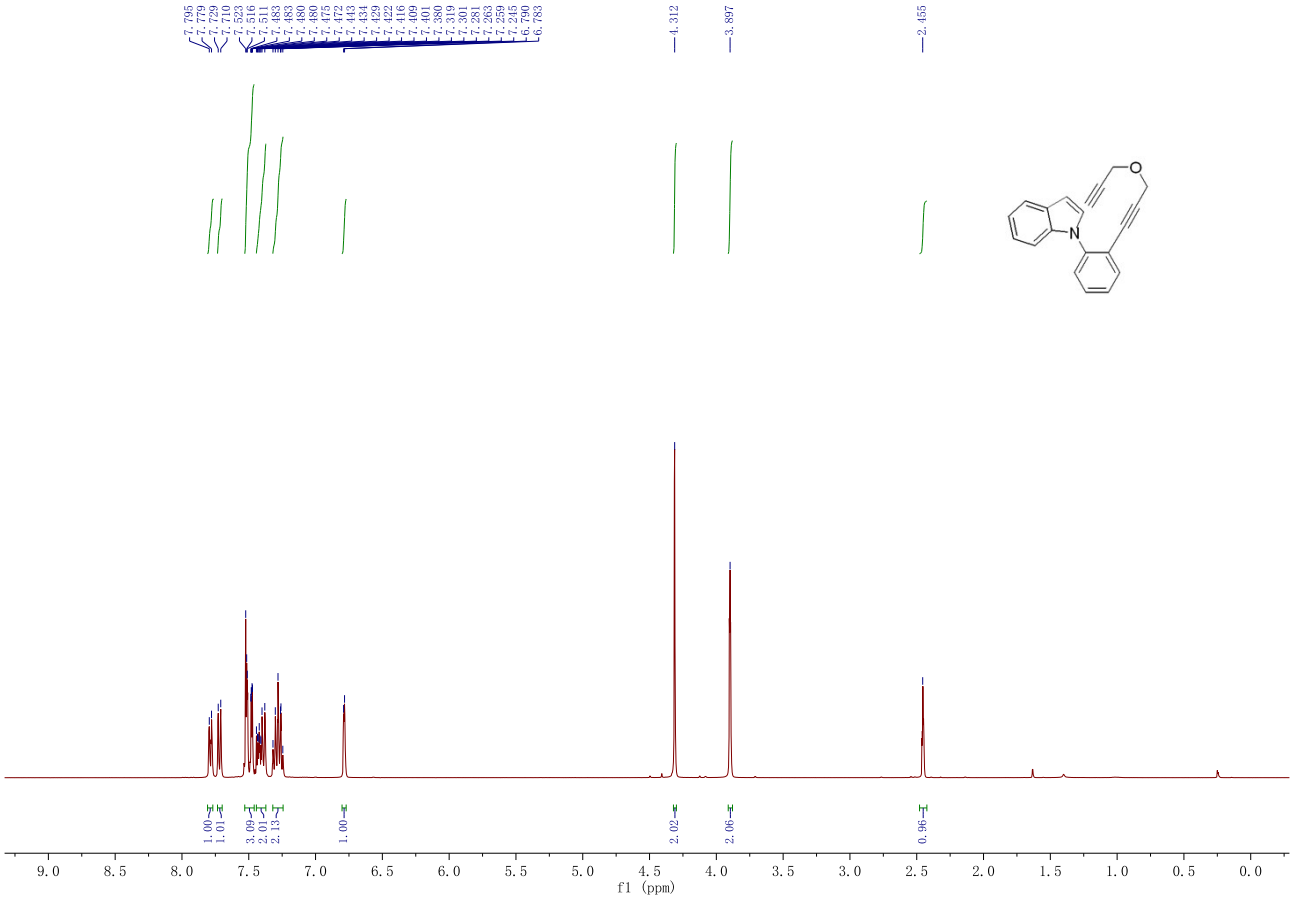
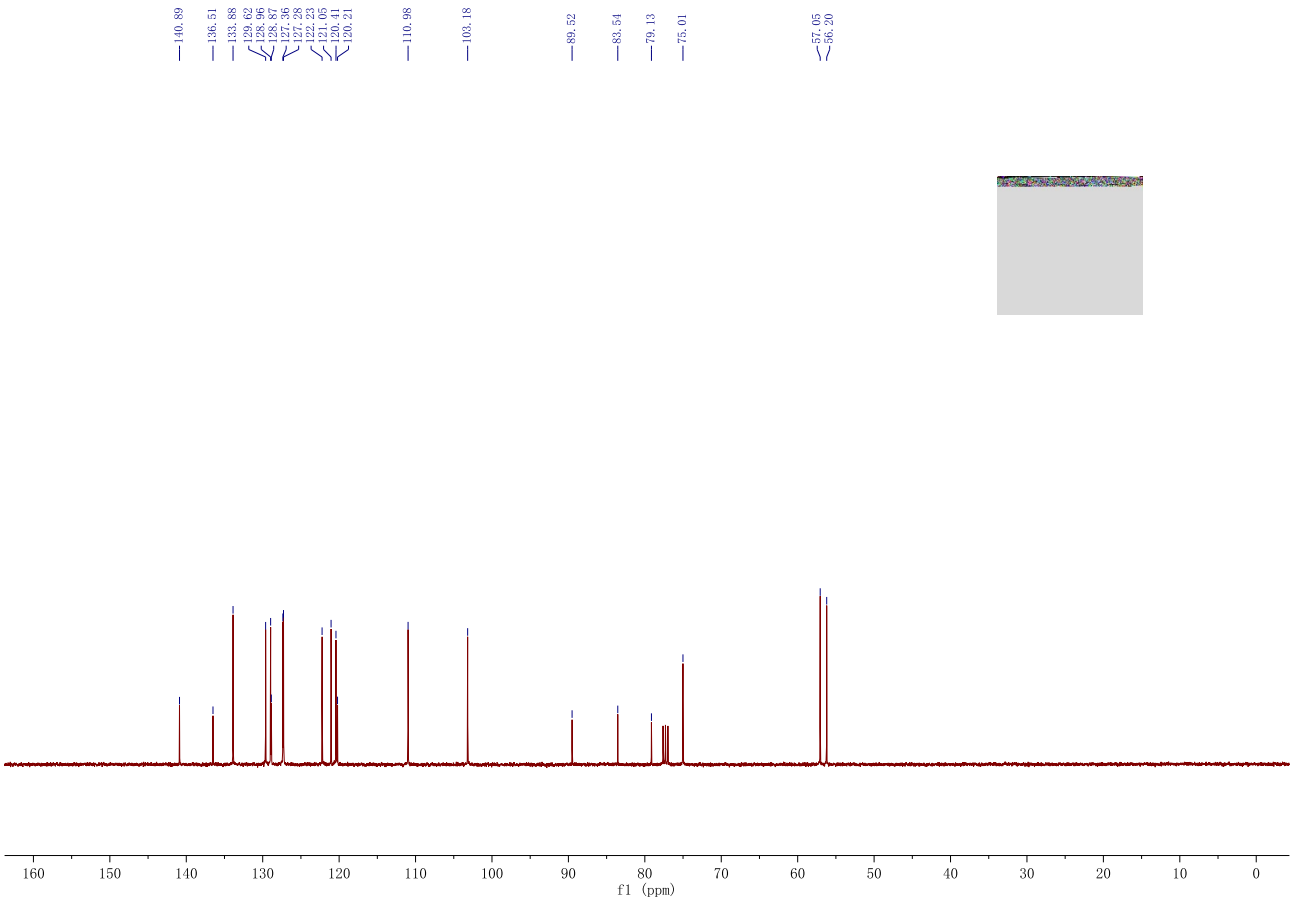
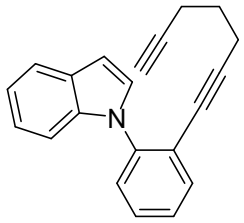
f1 (ppm)



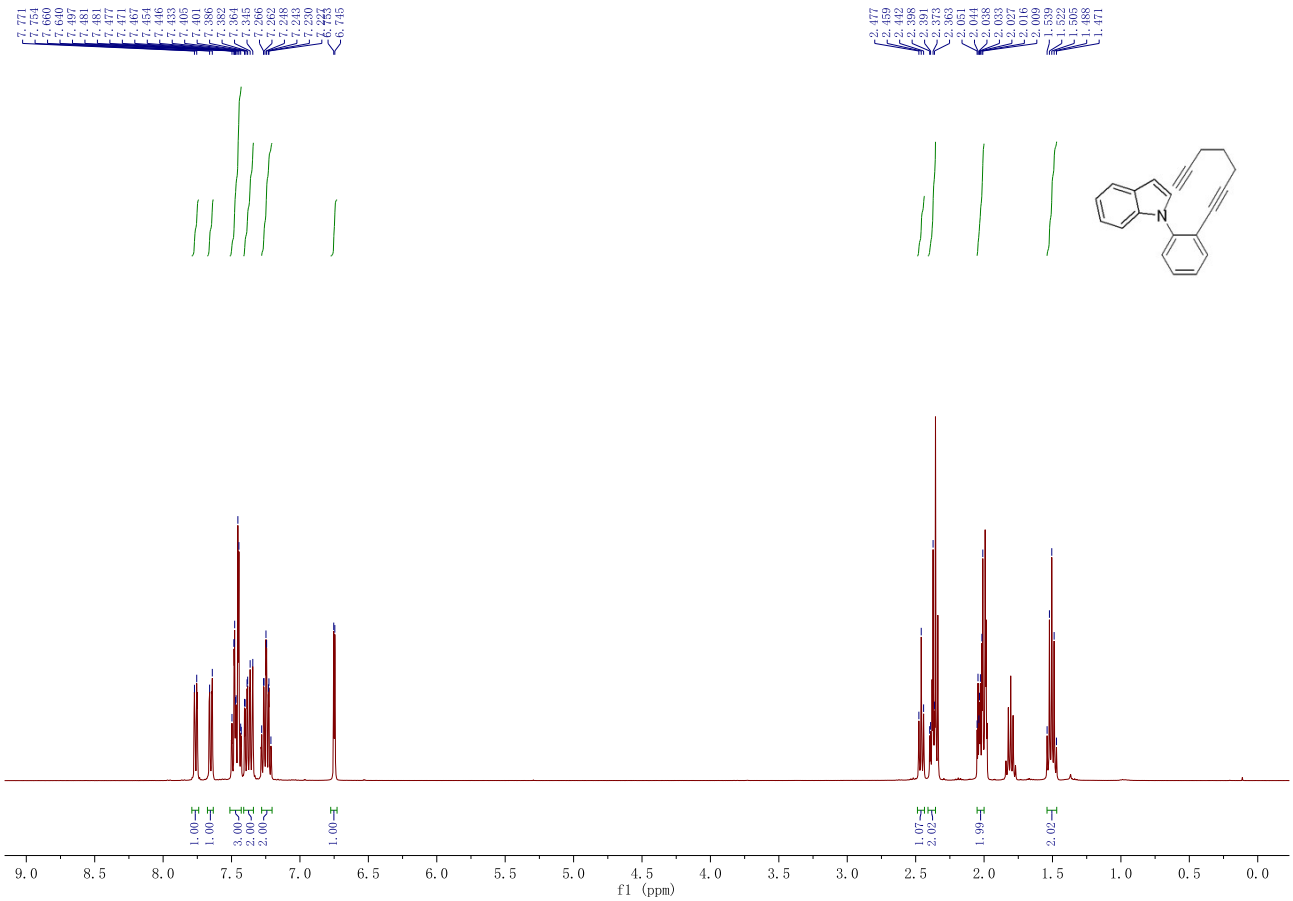
Compound 1s: yellow oil (183.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.45 (d, *J* = 1.1 Hz, 1H), 3.90 (s, 2H), 4.31 (d, *J* = 1.1 Hz, 2H), 6.78 (s, 1H), 7.24-7.32 (m, 2H), 7.37-7.44 (m, 2H), 7.46-7.53 (m, 3H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 56.2, 57.1, 75.0, 79.1, 83.5, 89.5, 103.2, 111.0, 120.2, 120.4, 121.1, 122.2, 127.3, 127.4, 128.9, 129.0, 129.6, 133.9, 136.5, 140.9. IR (neat) ν 3304, 2955, 2903, 2855, 2123, 1591, 1514, 1492, 1457, 1343, 1328, 1313, 1240, 1208 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{16}NO$ requires (M^{+}+H): 286.1226, Found: 286.1224.







Compound 1t: yellow oil (183.4 mg, 86%, containing a certain amount of inseparable 1,6-heptadiyne). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.51 (qu, *J* = 6.8 Hz, 2H), 2.00-2.05 (m, 2H), 2.38 (d, *J* = 7.3 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 1H), 6.75 (d, *J* = 3.2 Hz, 1H), 7.20-7.28 (m, 2H), 7.34-7.41 (m, 2H), 7.43-7.51 (m, 3H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 17.6, 18.3, 18.5, 27.0, 66.1, 69.3, 83.2, 94.6, 102.8, 111.1, 120.2, 120.9, 121.5, 122.0, 127.1, 127.2, 128.6, 128.8, 129.0, 133.6, 136.5, 140.7. IR (neat) ν 3296, 2932, 2235, 2111, 1513, 1493, 1475, 1458, 1428, 1330, 1308, 1241, 1170, 1113, 1090, 1038, 998 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}N$ requires (M^{+}+H): 284.1434, Found: 284.1432.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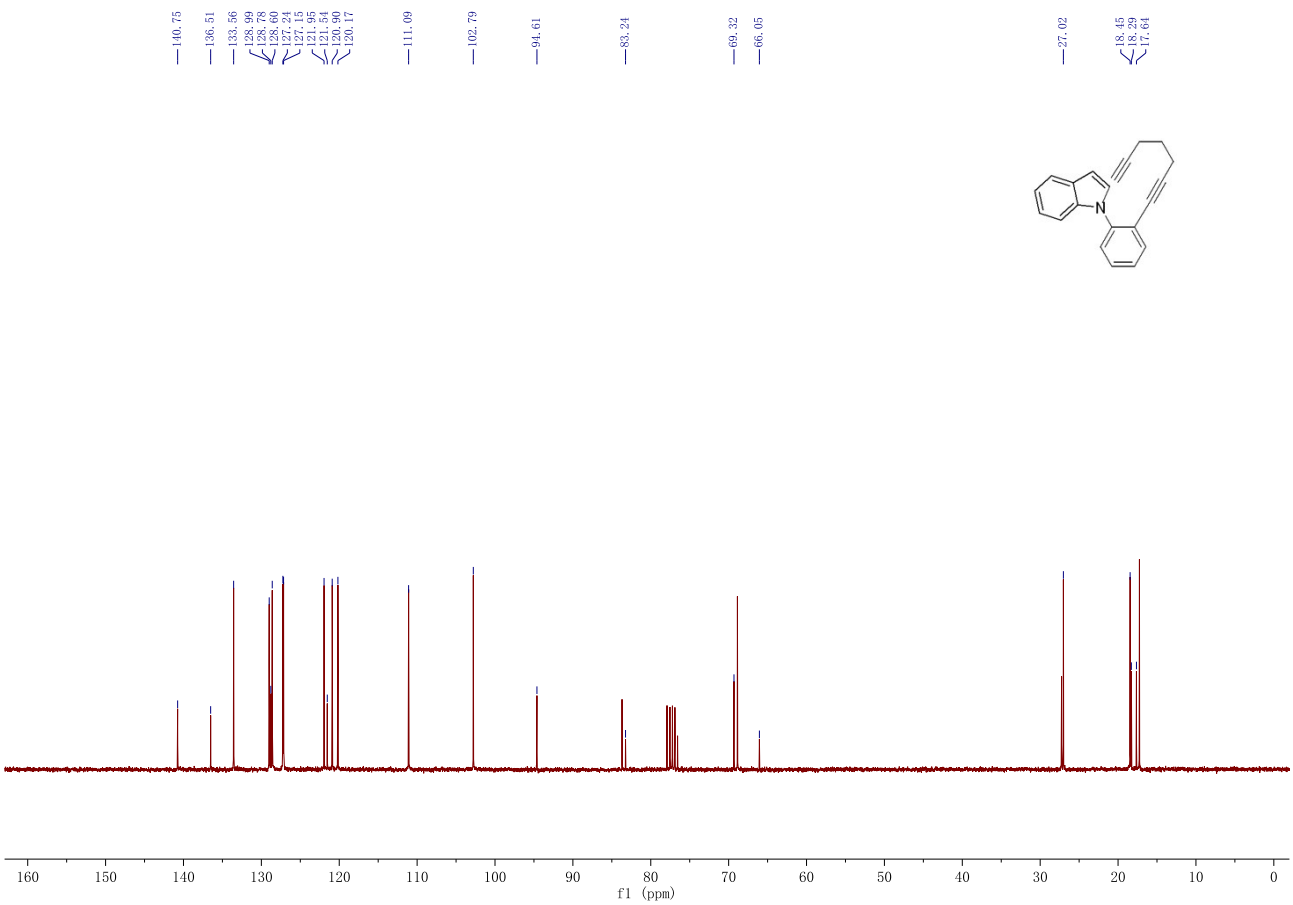
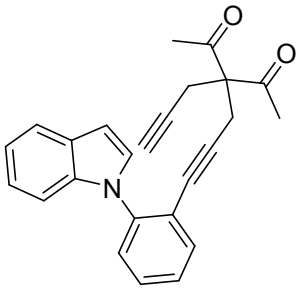
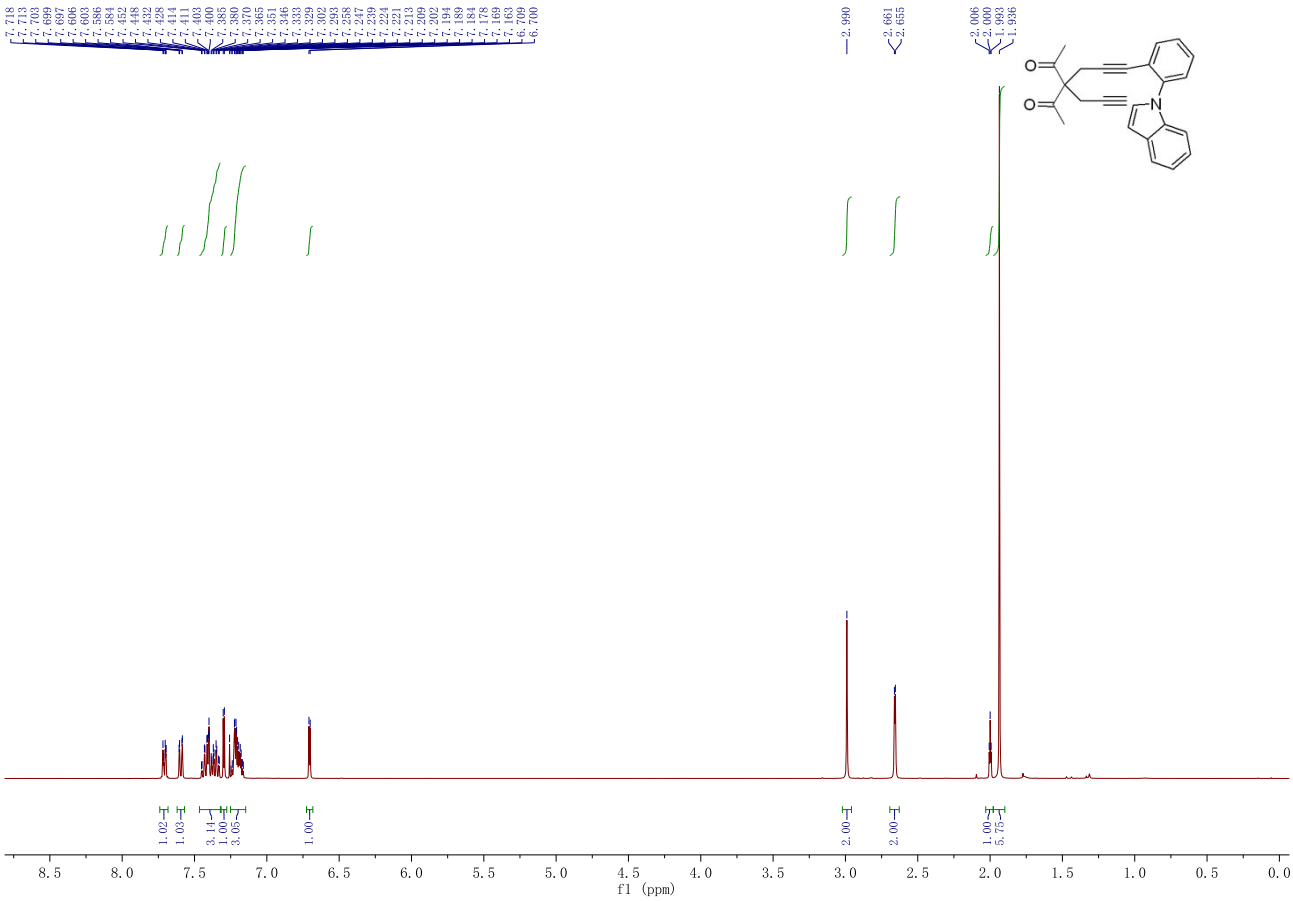
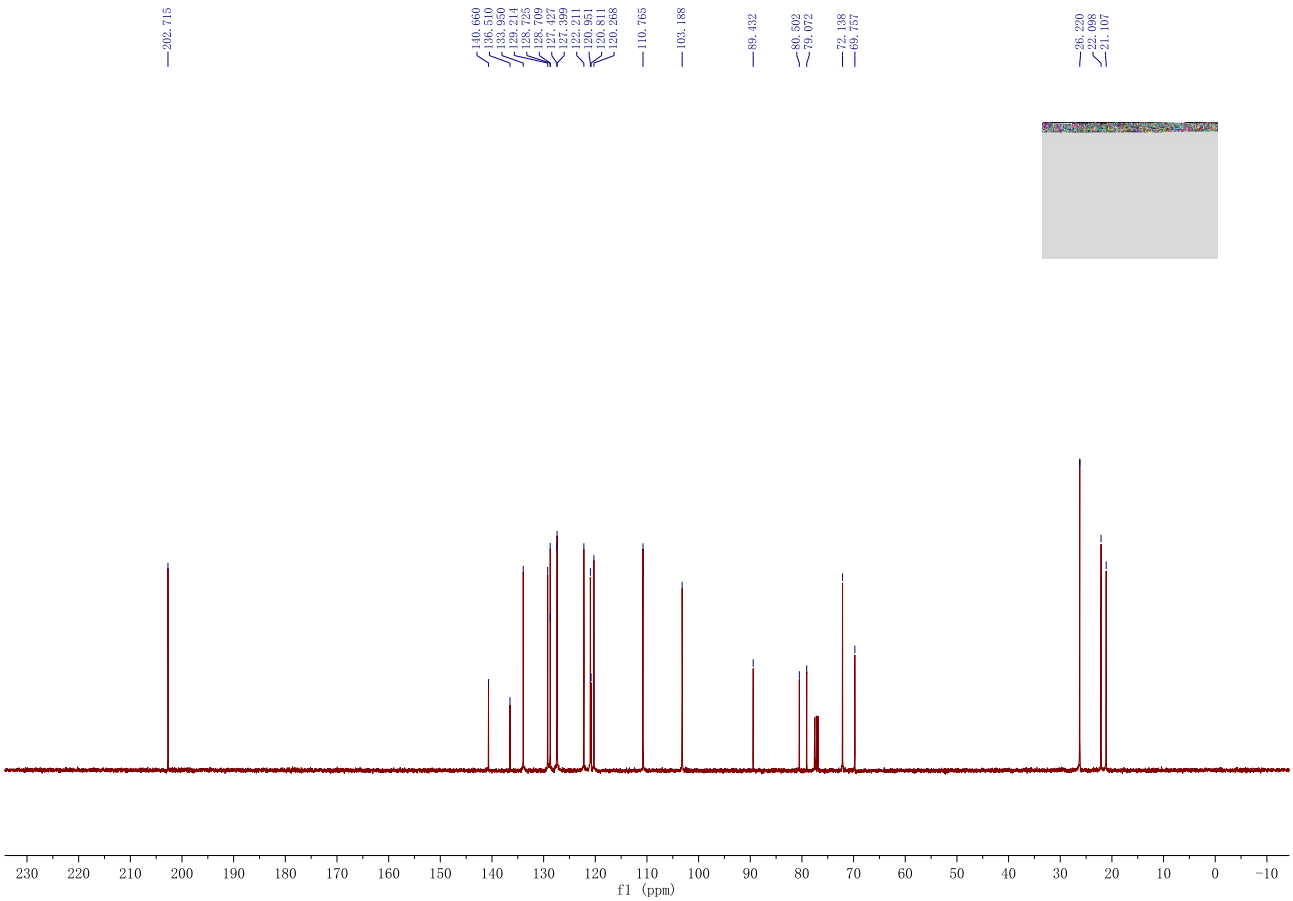
7.401
7.386
7.382
7.364
7.345
7.266
7.262
7.238
7.213
7.230
7.224
6.755
6.745
2.477
2.459
2.442
2.398
2.391
2.373
2.363
2.051
2.044
2.038
2.033
2.027
2.016
2.009
1.539
1.522
1.505
1.488
1.471
1.00
1.00
3.00
2.00
2.00
1.00
1.07
2.02
1.99
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

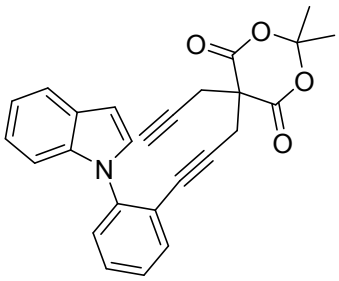

140.75
136.51
133.56
128.99
128.78
128.60
128.24
127.15
121.95
121.54
120.90
120.17
111.09
102.79
94.61
83.24
69.32
66.05
27.02
18.45
18.29
17.64
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



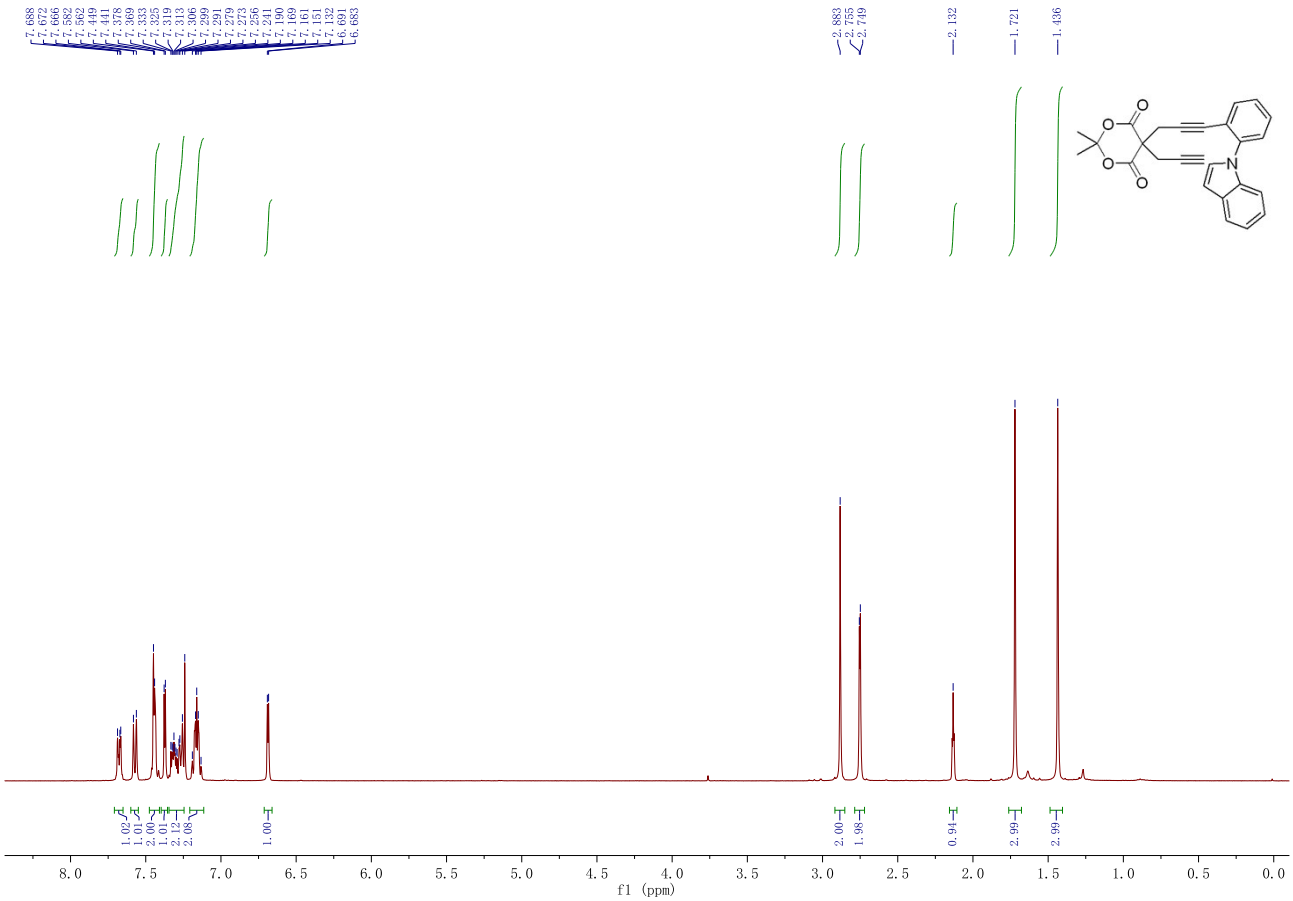
Compound 1u: yellow oil (362 mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.94 (s, 6H), 2.00 (t, *J* = 2.7 Hz, 1H), 2.66 (d, *J* = 2.7 Hz, 2H), 2.99 (s, 2H), 6.70 (d, *J* = 3.4 Hz, 1H), 7.15-7.25 (m, 3H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.32-7.47 (m, 3H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.68-7.74 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.1, 22.1, 26.2, 69.8, 72.1, 79.1, 80.5, 89.4, 103.2, 110.8, 120.3, 120.8, 121.0, 122.2, 127.4, 127.4, 128.7, 128.7, 129.2, 134.0, 136.5, 140.7, 202.7. IR (neat) ν 3284, 3054, 2915, 2230, 2114, 1722, 1700, 1596, 1513, 1494, 1475, 1458, 1418, 1356, 1331, 1307, 1271, 1242, 1226, 1211, 1177, 1153, 1137, 1117, 1100, 1064, 1011 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{22}NO_2$ requires (M^++H): 368.1645, Found: 368.1636.







Compound 1v: yellow oil (373 mg, 61%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.44 (s, 3H), 1.72 (s, 3H), 2.13 (s, 1H), 2.75 (d, *J* = 2.6 Hz, 2H), 2.88 (s, 2H), 6.69 (d, *J* = 3.3 Hz, 1H), 7.11-7.21 (m, 2H), 7.25-7.35 (m, 2H), 7.37 (d, *J* = 3.3 Hz, 1H), 7.44 (d, *J* = 3.0 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.65-7.71 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 27.3, 29.0, 29.2, 29.8, 53.1, 73.4, 77.7, 81.9, 87.4, 103.3, 106.6, 110.6, 119.2, 120.3, 121.0, 122.1, 126.9, 127.0, 128.9, 129.0, 129.6, 134.2, 136.2, 140.8, 166.9. IR (neat) ν 3287, 3054, 3000, 2920, 2845, 2233, 2122, 1774, 1741, 1595, 1515, 1494, 1475, 1458, 1425, 1392, 1380, 1354, 1330, 1270, 1224, 1199, 1134, 1109, 1052, 1013 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{22}NO_4$ requires (M^++H): 412.1543, Found: 412.1537.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7.666
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7.378
7.369
7.333
7.325
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7.306
7.299
7.291
7.279
7.273
7.256
7.241
7.190
7.169
7.161
7.151
7.132
6.691
6.683
2.883
2.735
2.719
2.132
1.721
1.436
1.02
1.01
2.00
1.01
2.12
2.08
1.00
2.00
1.98
0.94
2.99
2.99
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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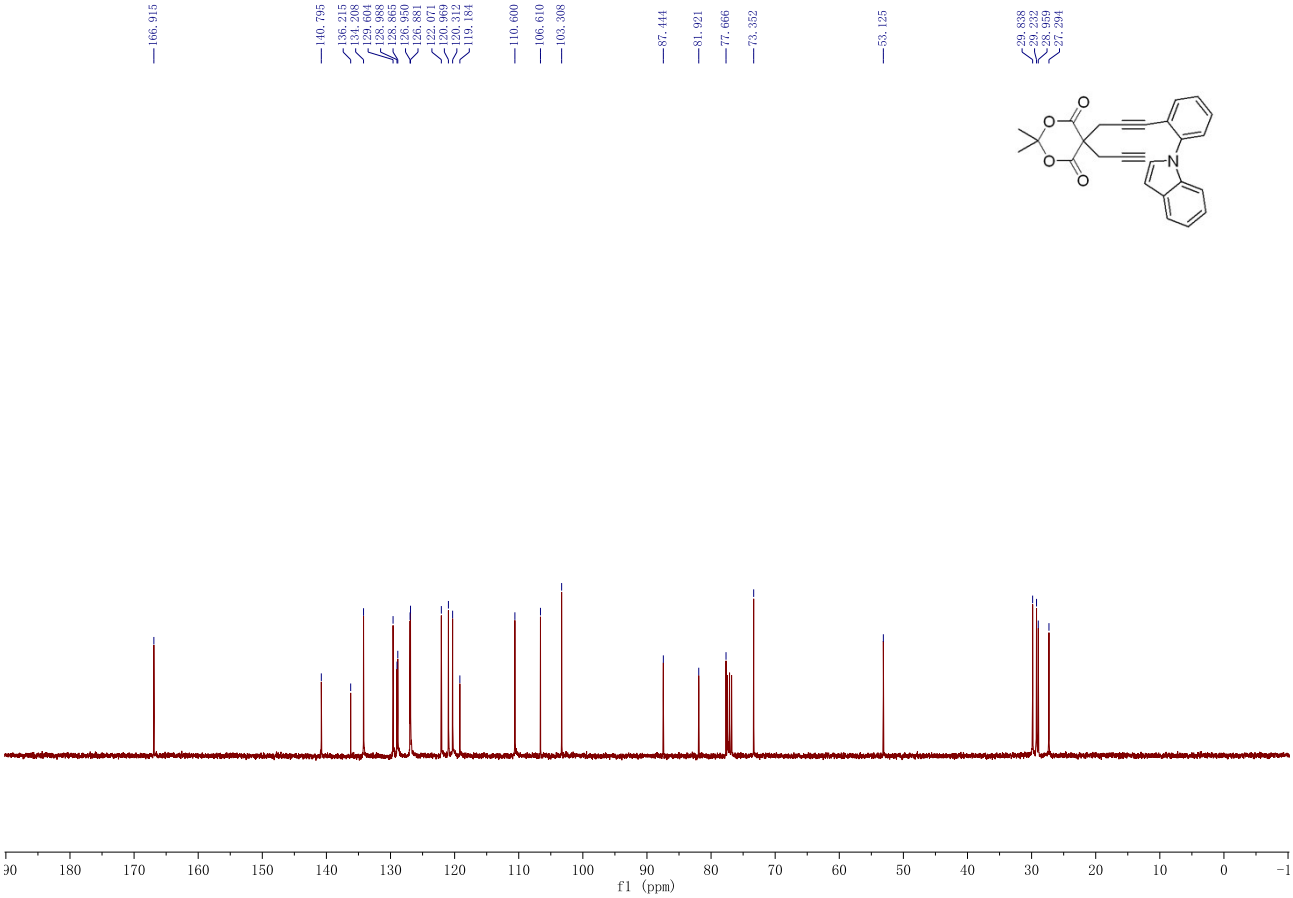
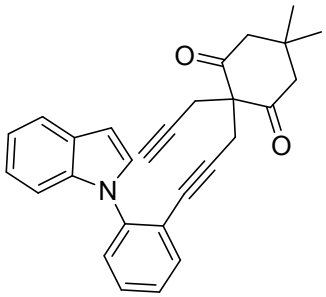
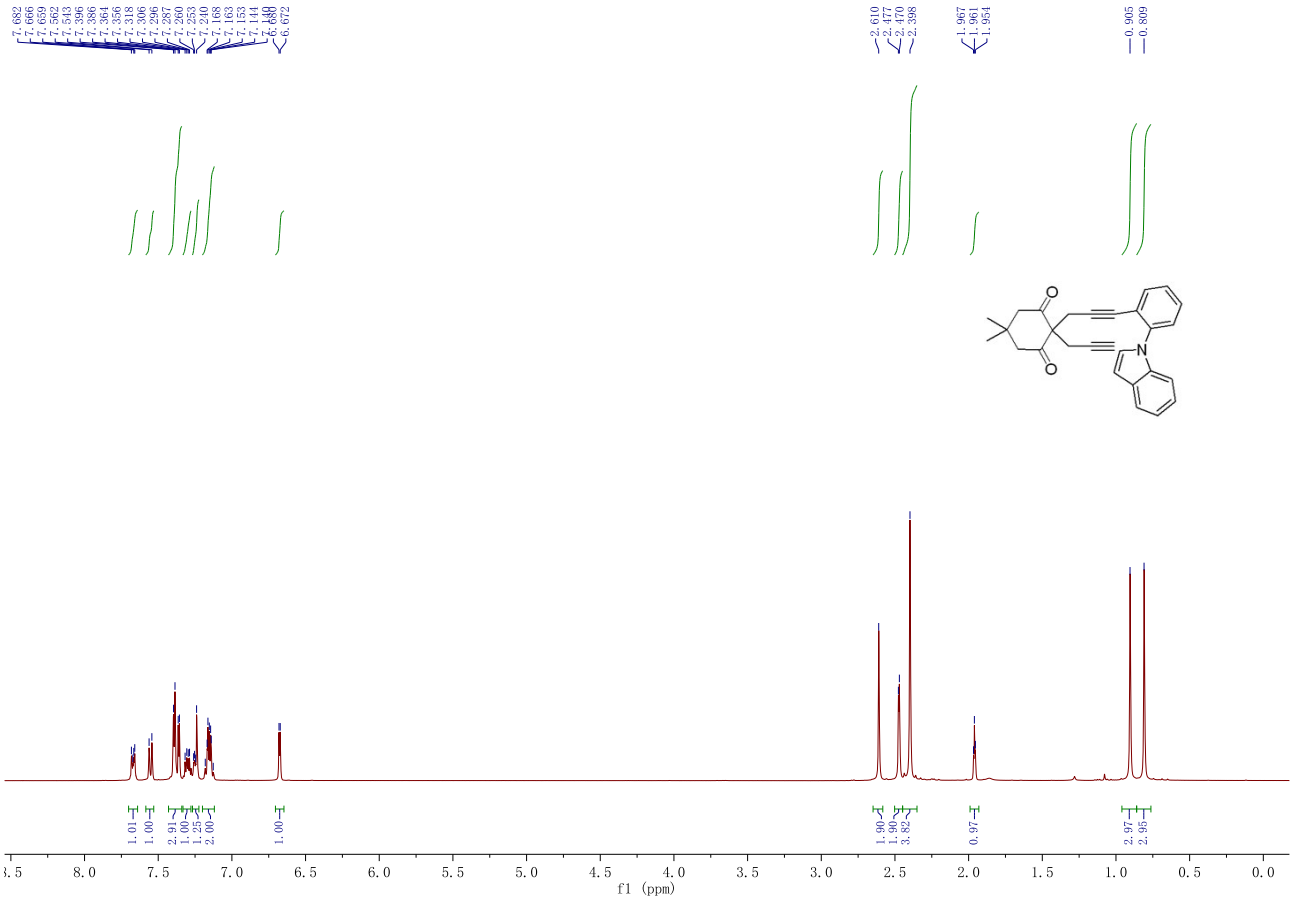
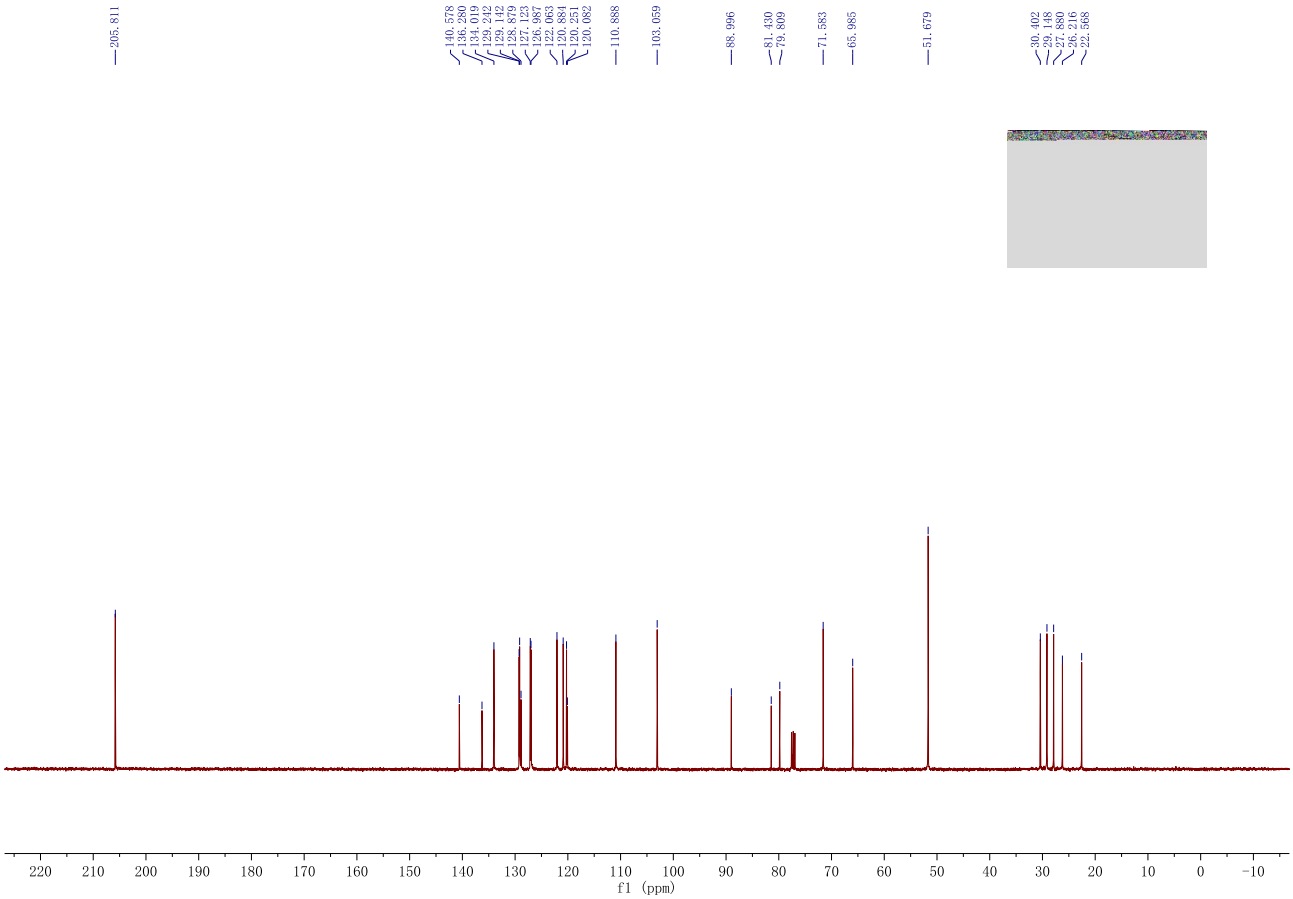
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

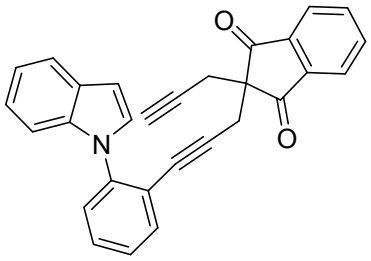

166.915
140.795
136.215
134.208
129.604
128.988
128.865
126.950
126.881
122.071
120.969
120.312
119.184
110.600
106.610
103.308
87.444
81.921
77.666
73.352
53.125
29.838
29.232
28.959
27.294
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



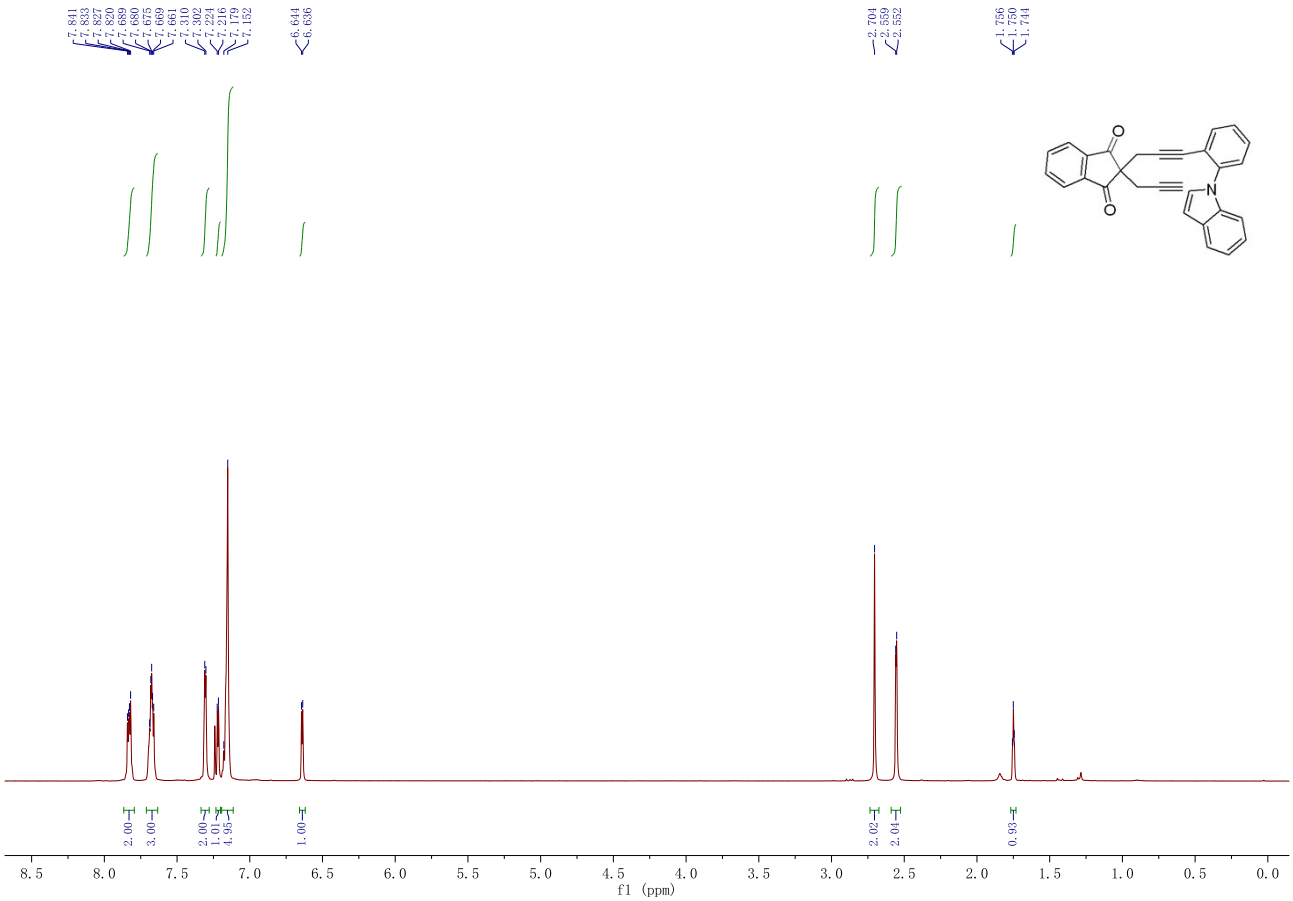
Compound 1w: yellow oil (426 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.81 (s, 3H), 0.90 (s, 3H), 1.96 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 4H), 2.47 (d, *J* = 2.6 Hz, 2H), 2.61 (s, 2H), 6.68 (d, *J* = 3.3 Hz, 1H), 7.12-7.20 (m, 2H), 7.22-7.27 (m, 1H), 7.30 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.38 (dd, *J* = 12.3, 3.6 Hz, 3H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.64-7.70 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 22.6, 26.2, 27.9, 29.1, 30.4, 51.7, 66.0, 71.6, 79.8, 81.4, 89.0, 103.1, 110.9, 120.1, 120.3, 120.9, 122.1, 127.0, 127.1, 128.9, 129.1, 129.2, 134.0, 136.3, 140.6, 205.8. IR (neat) ν 3287, 2948, 2928, 2860, 2236, 2114, 1731, 1698, 1595, 1559, 1514, 1494, 1474, 1458, 1411, 1372, 1330, 1308, 1243, 1224, 1210, 1135, 1116, 1089, 1068, 1013 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{26}NO_2$ requires (M^++H): 408.1958, Found: 408.1948.







Compound 1x: yellow oil (477 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.75 (t, *J* = 2.5 Hz, 1H), 2.56 (d, *J* = 2.6 Hz, 2H), 2.70 (s, 2H), 6.64 (d, *J* = 3.2 Hz, 1H), 7.11-7.19 (m, 5H), 7.22 (d, *J* = 3.3 Hz, 1H), 7.31 (d, *J* = 3.1 Hz, 2H), 7.63-7.71 (m, 3H), 7.79-7.87 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 22.4, 24.2, 55.2, 71.7, 78.0, 80.7, 88.5, 103.0, 110.7, 119.5, 120.3, 120.9, 122.0, 123.2, 126.5, 126.5, 126.7, 128.9, 129.0, 129.0, 134.1, 135.8, 136.1, 140.3, 142.0, 200.4. IR (neat) ν 3276, 3054, 2969, 2904, 2119, 1745, 1707, 1595, 1514, 1494, 1475, 1458, 1423, 1355, 1330, 1308, 1243, 1211, 1135, 1047, 933 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{20}NO_2$ requires (M^++H): 414.1489, Found: 414.1483.


7.841
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7.827
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7.680
7.675
7.669
7.661
7.310
7.302
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7.179
7.152
6.644
6.636
2.704
2.559
2.552
1.756
1.750
1.744
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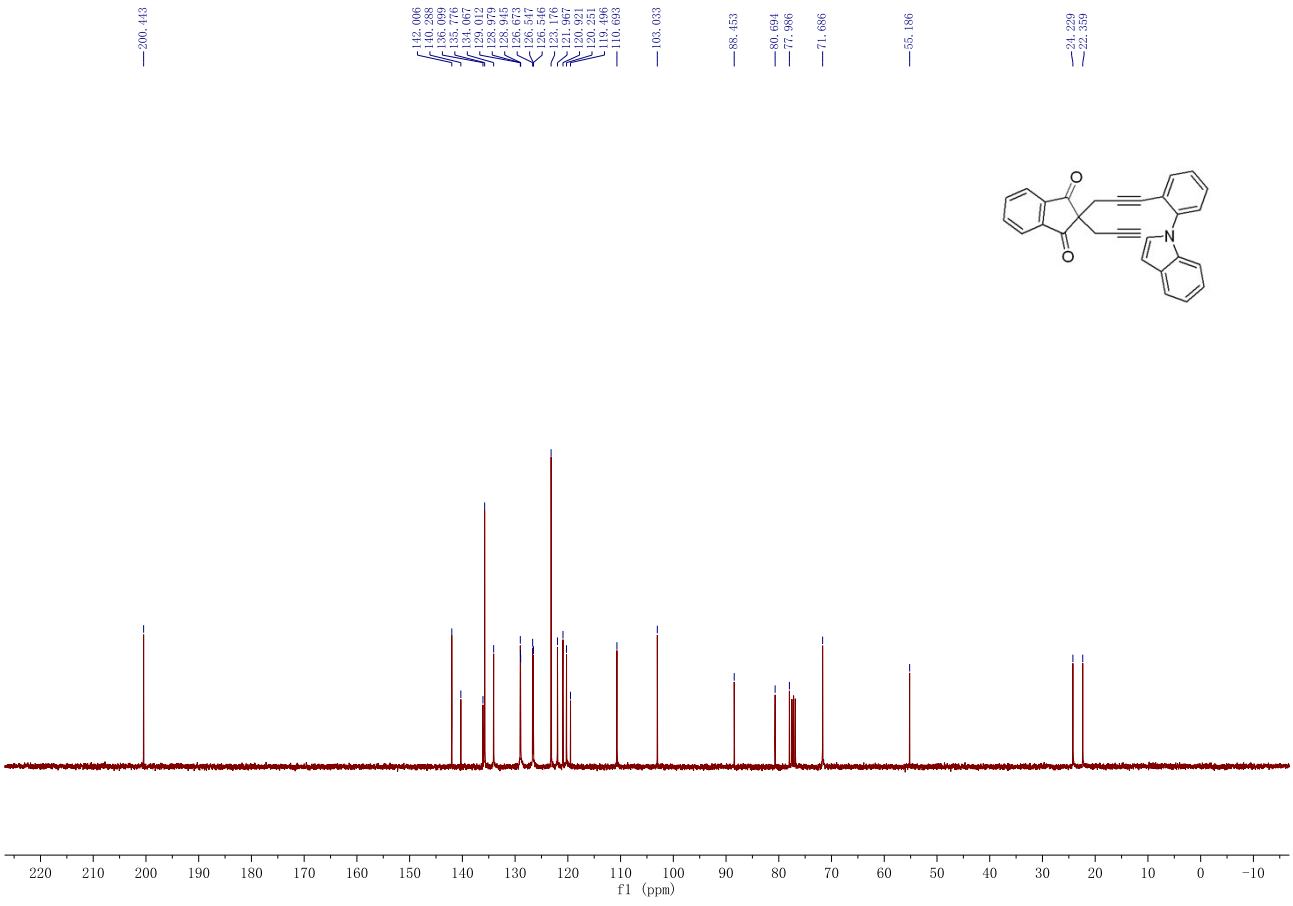
3.00
2.00
1.01
4.95
1.00
2.02
2.04
0.93
f1 (ppm)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134.067
129.012
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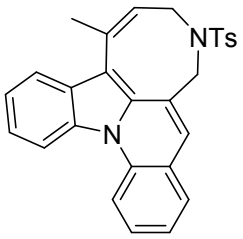
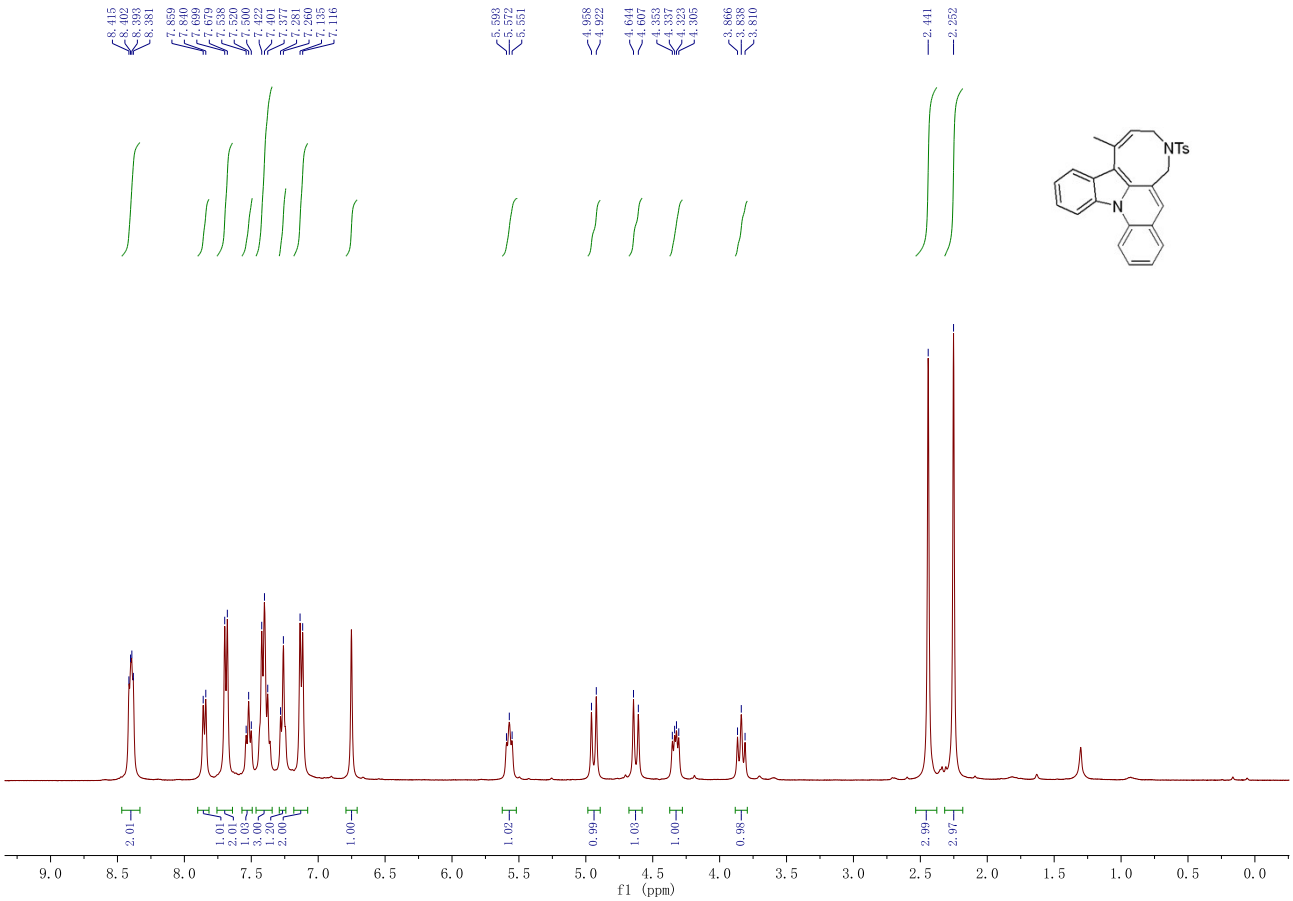
128.945
126.673
126.547
126.546
123.176
121.957
120.921
120.251
119.496
110.693
103.033
88.453
80.694
77.986
71.686
55.186
24.229
22.359
f1 (ppm)

(C) General Procedure for the Preparation of Products 2a-2t

To a Schlenk tube with magnetic stirring bar was added substrate (0.05 mmol), tri(1-adamantyl)phosphine coordinated gold complex (Ad_3PAuCl, 0.005 mmol) and silver salts (0.005 mmol). Then the flask was evacuated under reduced pressure and was charged with argon. 1.0 mL of DCE was injected to the reaction tube. The reaction mixture was stirred and heated at 80 °C for 48 h. The reaction mixture was cooled to room temperature, concentrated in vacuo and the residues were purified by chromatography on silica gel using petroleum ether to give the corresponding product.



Compound 2a: yellow oil (39.3 mg, 87%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.25 (s, 3H), 2.44 (s, 3H), 3.84 (dd, *J* = 12.8 Hz, 1H), 4.33 (dd, *J* = 12.8, 7.2 Hz, 1H), 4.63 (d, *J* = 14.4 Hz, 1H), 4.94 (d, *J* = 14.4 Hz, 1H), 5.57 (dd, *J* = 12.8, 7.2 Hz, 1H), 6.75 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.34-7.46 (m, 3H), 7.52 (dd, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 8.40 (dd, *J* = 8.4, 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.9, 45.4, 47.0, 108.3, 114.3, 115.4, 119.8, 121.0, 122.0, 122.5, 123.2, 123.7, 124.8, 127.28, 127.34, 128.5, 128.6, 129.1, 129.5, 133.1, 133.6, 135.9, 136.5, 139.7, 143.2. IR (neat) ν 2979, 2952, 2851, 1597, 1493, 1462, 1437, 1391, 1366, 1334, 1283, 1258, 1196, 1167, 1148, 1109, 1090, 1036 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_2O_2S$ requires (M^++H): 453.1631, Found: 453.1628.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7.679
7.538
7.520
7.500
7.422
7.401
7.377
7.281
7.260
7.135
7.116
5.593
5.572
5.551
4.958
4.922
4.644
4.607
4.353
4.337
4.323
4.305
3.866
3.838
3.810
2.441
2.252
NTs
N
2.01
1.01
2.01
1.00
1.20
2.00
1.00
1.02
0.99
1.03
1.00
0.98
2.99
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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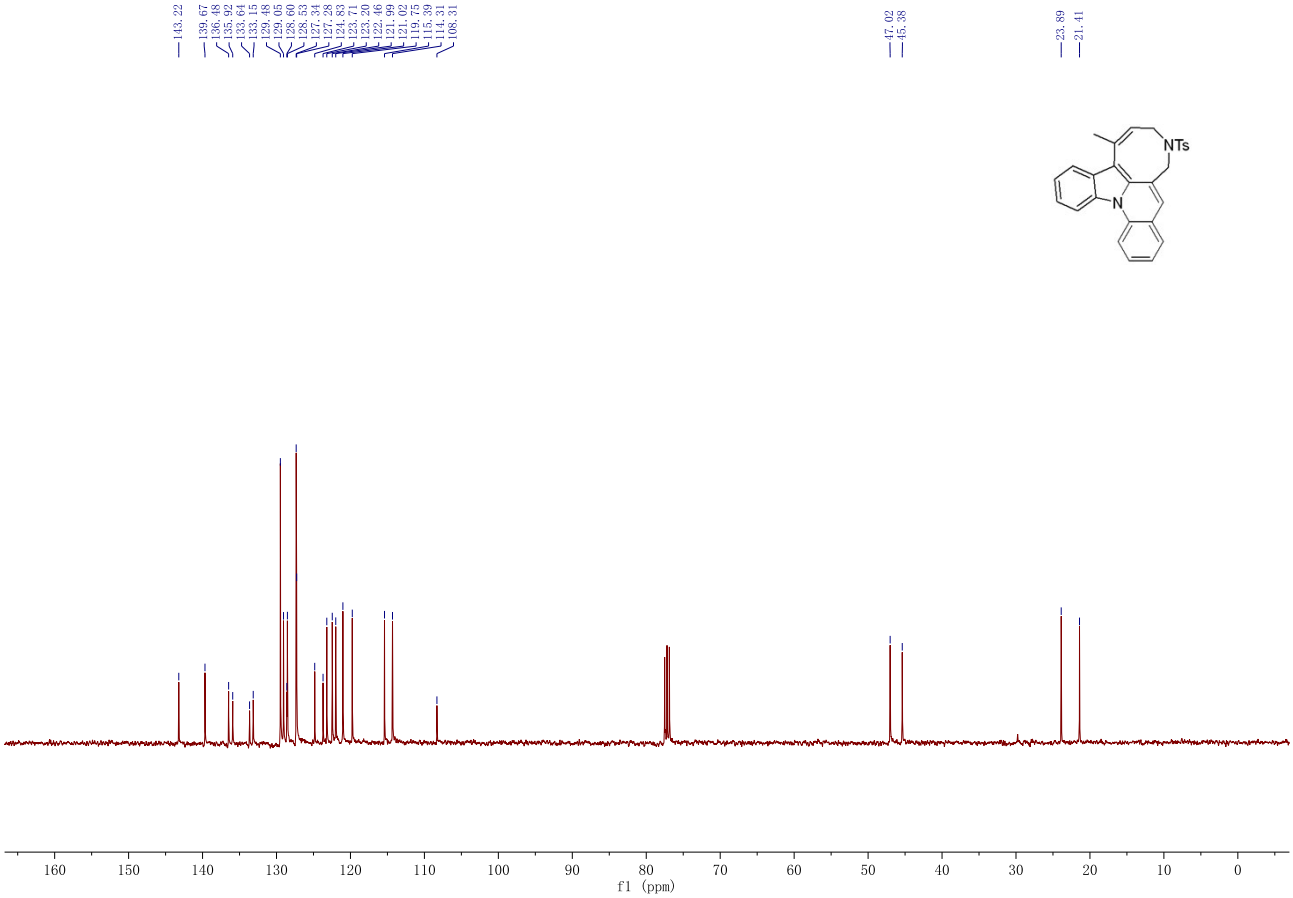
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.22
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133.15
129.48
129.05
128.60
128.33
127.94
127.38
124.83
123.71
123.20
122.46
121.99
121.02
119.75
115.39
114.31
108.31
47.02
45.38
23.89
21.41
NTs
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90
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50
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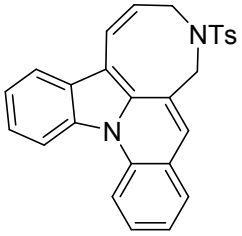
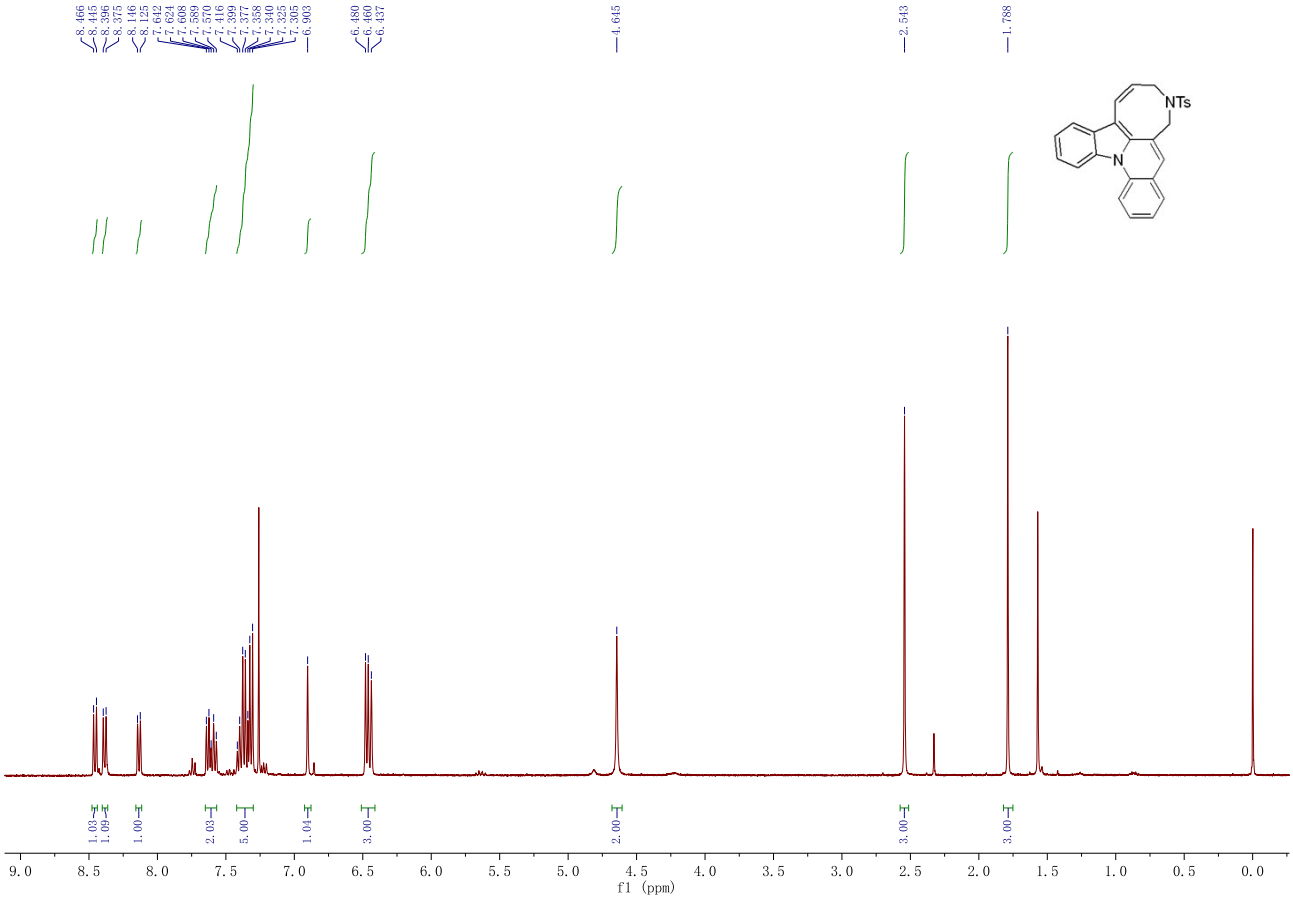
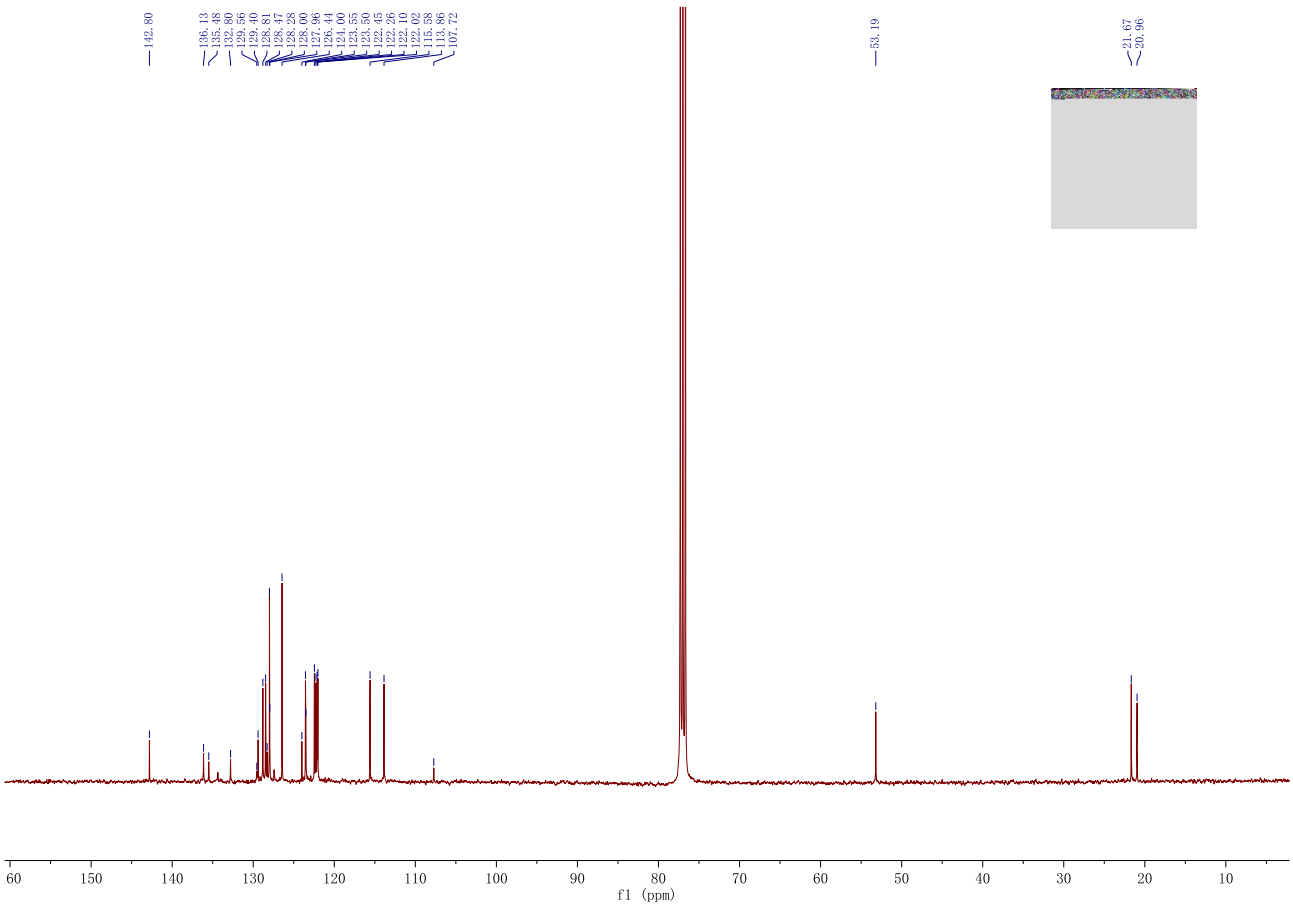
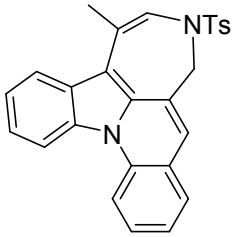
20
10
0
f1 (ppm)



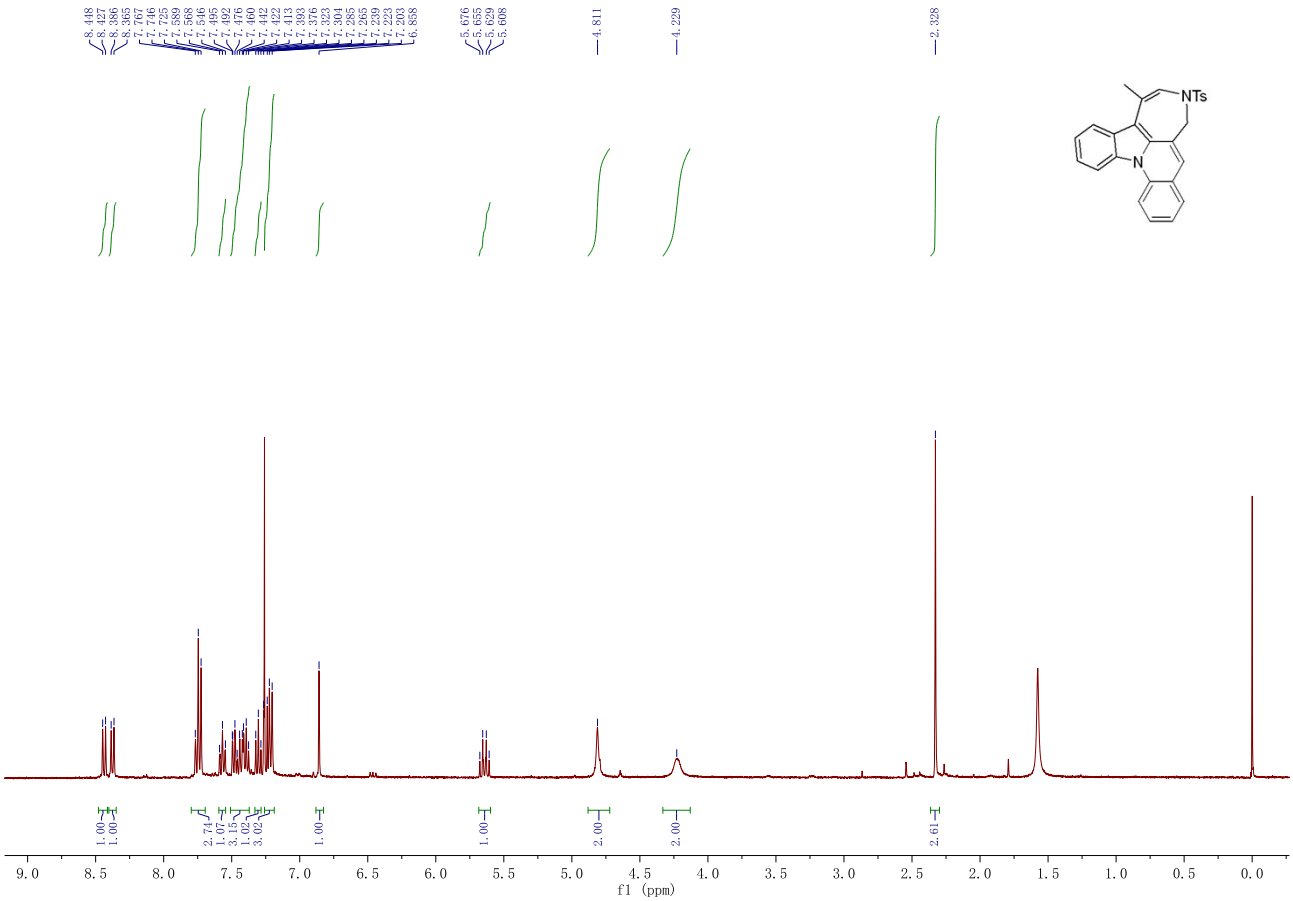
Compound 2ba: yellow oil (3.9 mg, 9%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.79 (s, 3H), 2.54 (s, 3H), 4.64 (s, 2H), 6.41-6.51 (m, 3H), 6.90 (s, 1H), 7.30-7.42 (m, 5H), 7.57-7.65 (m, 2H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.0, 21.7, 53.2, 107.7, 113.9, 115.6, 122.0, 122.1, 122.3, 122.5, 123.5, 123.6, 124.0, 126.4, 127.96, 128.0, 128.3, 128.5, 128.8, 129.4, 129.6, 132.8, 135.5, 136.1, 142.8. IR (neat) ν 3065, 2922, 2863, 1528, 1465, 1431, 1370, 1366, 1338, 1242, 1222, 1153, 1108, 1039, 999 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{23}N_2O_2S$ requires (M^++H): 439.1475, Found: 439.1471.







Compound 2bb: yellow oil (31.0 mg, 71%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.33 (s, 3H), 4.23 (s, 2H), 4.81 (s, 2H), 5.64 (dd, *J* = 18.8, 8.4 Hz, 1H), 6.86 (s, 1H), 7.19-7.26 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.37-7.51 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.69-7.80 (m, 3H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.5, 45.0, 47.2, 105.0, 114.1, 115.4, 119.0, 120.7, 122.3, 122.9, 123.3, 124.0, 125.2, 127.4, 127.5, 128.6, 129.0, 129.2, 129.6, 132.7, 134.7, 136.0, 136.2, 143.4. IR (neat) ν 2941, 2917, 2871, 1610, 1529, 1465, 1430, 1417, 1369, 1344, 1331, 1323, 1305, 1277, 1254, 1217, 1182, 1159, 1118, 1105 1038 cm^{-1} HRMS (ESI) Calcd. for $C_{27}H_{23}N_2O_2S$ requires (M^++H): 439.1475, Found: 439.1471.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7.546
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7.492
7.476
7.460
7.442
7.422
7.413
7.393
7.375
7.323
7.304
7.285
7.265
7.239
7.223
7.203
6.658
5.676
5.655
5.629
5.608
4.811
4.229
2.328
NTs
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1.00
2.74
1.07
3.15
1.02
3.02
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1.00
2.00
2.00
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6.5
6.0
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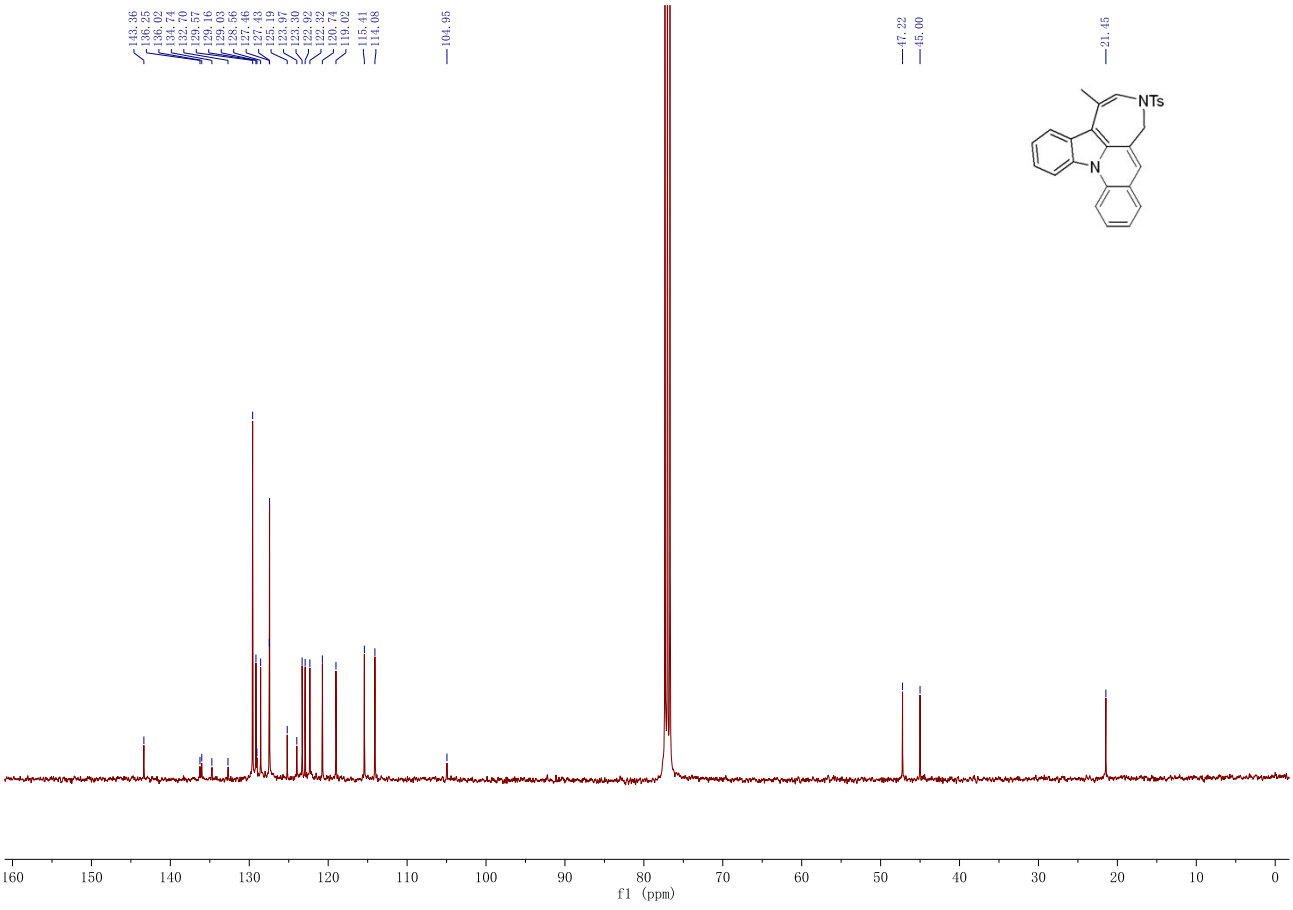
1.0
0.5
0.0
f1 (ppm)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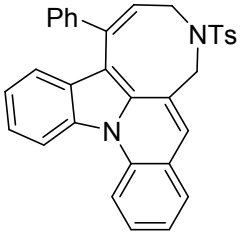
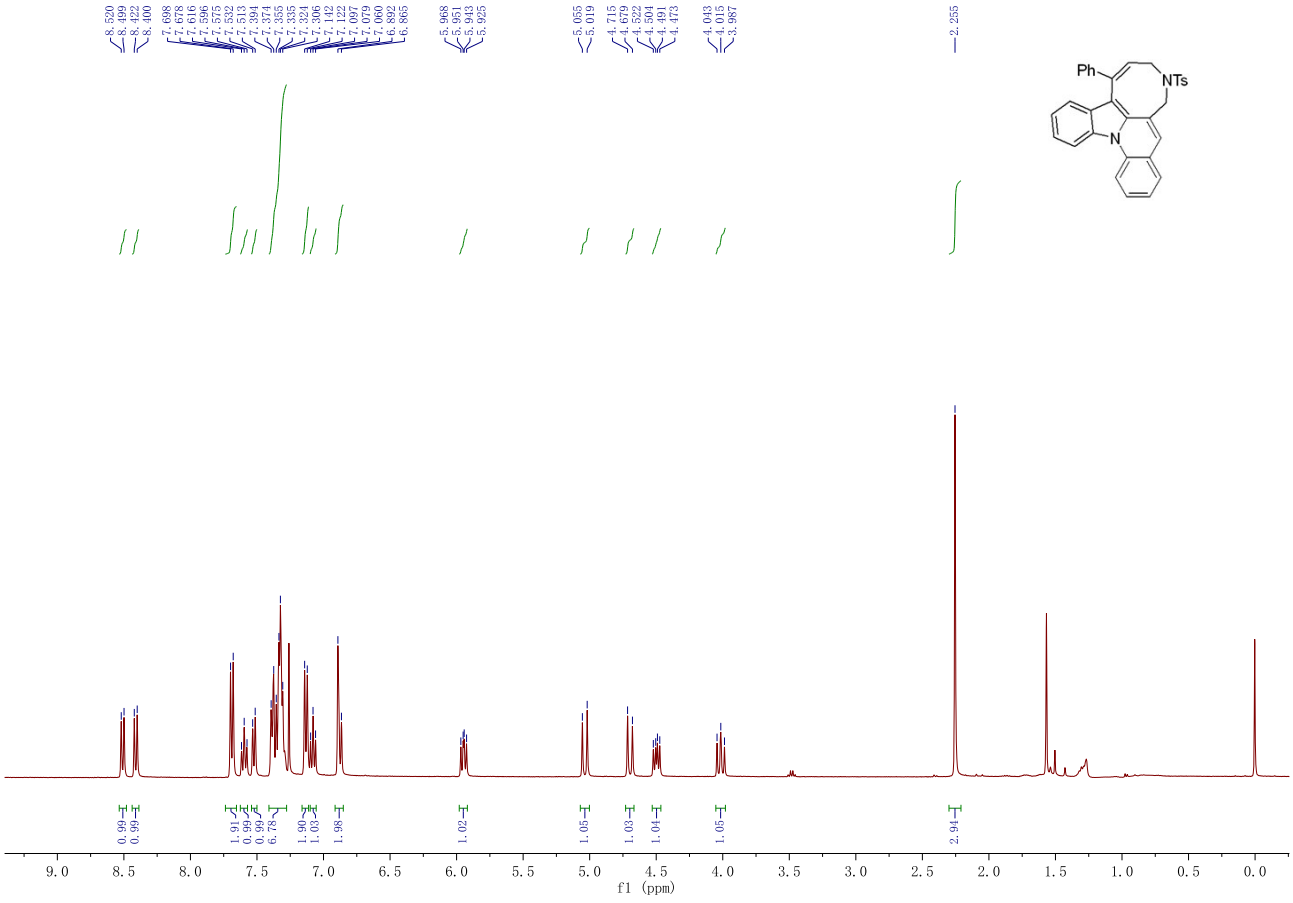
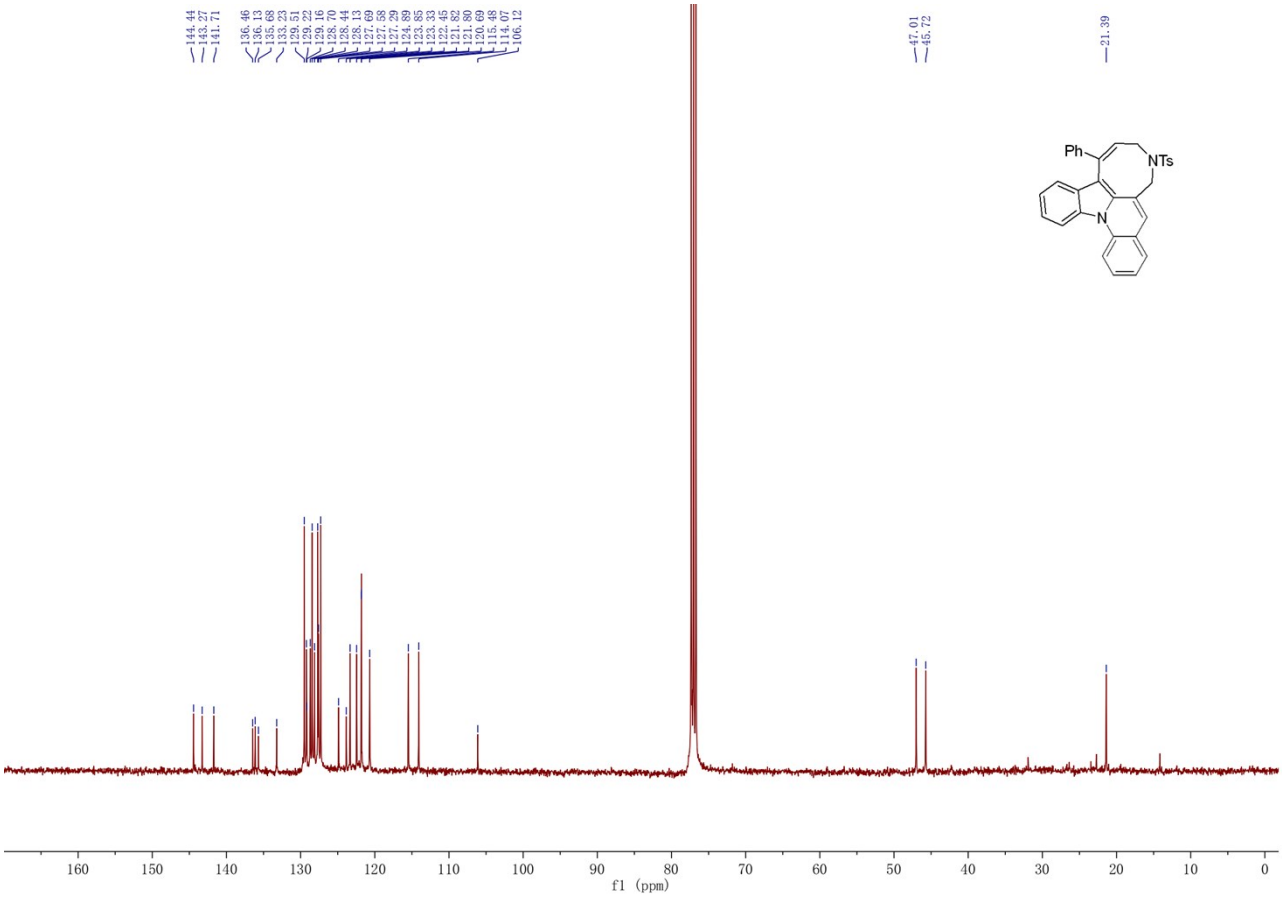
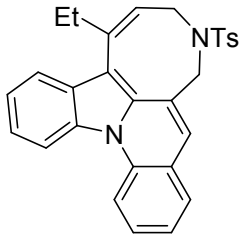
129.03
128.36
127.46
127.43
125.19
123.97
123.30
122.92
122.32
120.74
119.02
115.41
114.08
104.95
47.22
45.00
21.45
NTs
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



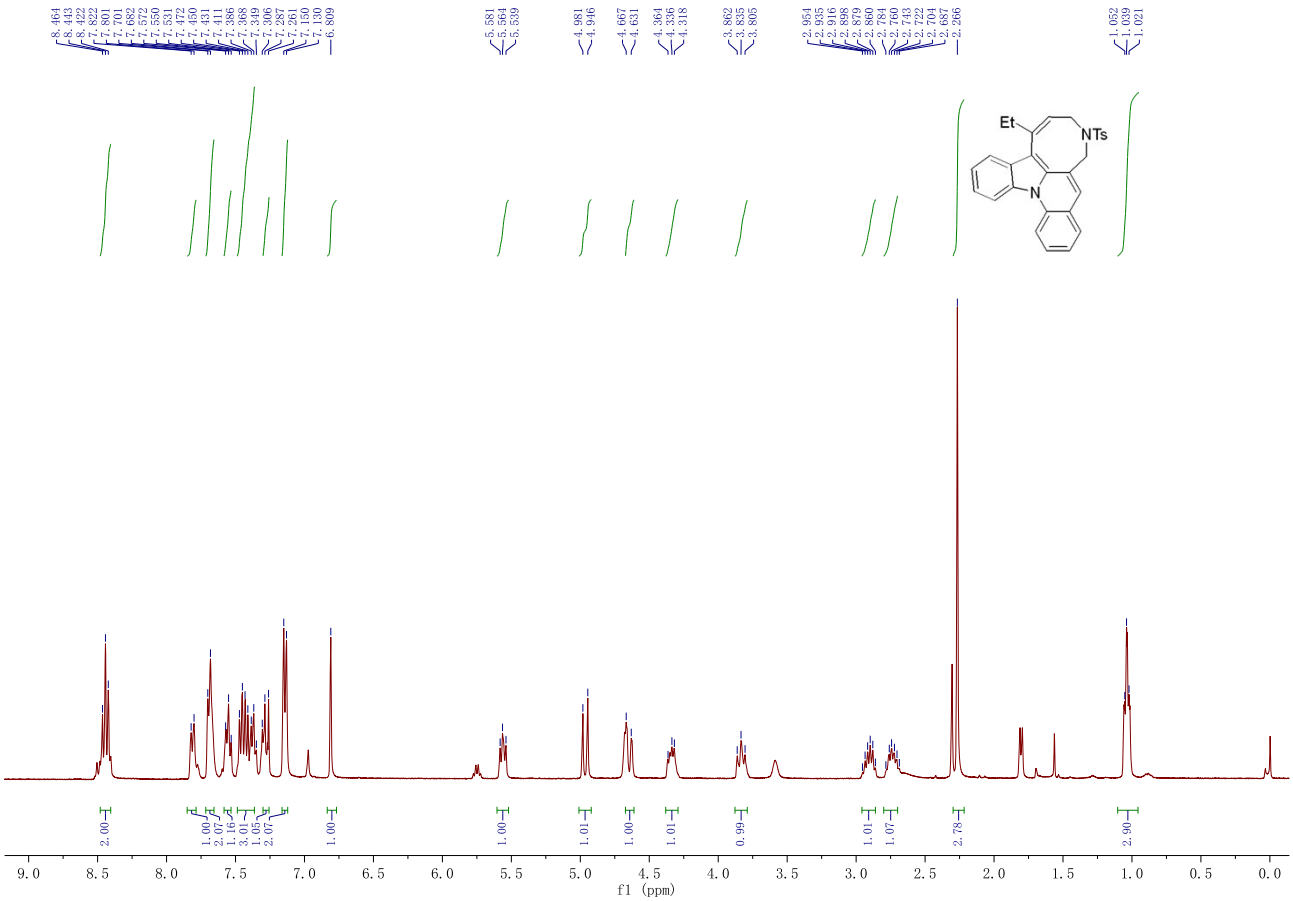
Compound 2c: yellow oil (38.5 g, 75%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.25 (s, 3H), 4.01 (dd, *J* = 12.4 Hz, 1H), 4.50 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.70 (d, *J* = 14.4 Hz, 1H), 5.04 (d, *J* = 14.4 Hz, 1H), 5.95 (dd, *J* = 12.4, 7.2 Hz, 1H), 6.85-6.91 (m, 2H), 7.08 (dd, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.30-7.39 (m, 7H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 45.7, 47.0, 106.1, 114.1, 115.5, 120.7, 121.80, 121.82, 122.5, 123.3, 123.8, 124.9, 127.3, 127.6, 127.7, 128.1, 128.4, 128.7, 129.16, 129.22, 129.5, 133.2, 135.7, 136.1, 136.5, 141.7, 143.3, 144.4. IR (neat) ν 3065, 2920, 2871, 1608, 1578, 1458, 1397, 1371, 1361, 1334, 1276, 1258, 1191, 1170, 1147, 1107, 992 cm^{-1}. HRMS (ESI) Calcd. for $C_{33}H_{27}N_2O_2S$ requires (M^++H): 515.1788, Found: 515.1784.







Compound 2d: yellow oil (35.4 g, 76%, containing impurity); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.04 (t, *J* = 6.1 Hz, 3H), 2.27 (s, 3H), 2.70-2.80 (m, 1H), 2.86-2.96 (m, 1H), 3.83 (dd, *J* = 12.0 Hz, 1H), 4.34 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.65 (d, *J* = 14.4 Hz, 1H), 4.96 (d, *J* = 14.4 Hz, 1H), 5.56 (dd, *J* = 12.0, 6.4 Hz, 1H), 6.81 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.26-7.30 (m, 1H), 7.36-7.49 (m, 3H), 7.56 (dd, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.44 (dd, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.4, 21.4, 30.4, 45.2, 46.9, 107.3, 114.3, 115.4, 118.1, 120.8, 122.0, 122.5, 123.2, 123.7, 124.8, 125.9, 127.3, 127.4, 128.6, 129.1, 129.5, 133.1, 134.4, 136.1, 136.4, 143.3, 146.3. IR (neat) ν 2925, 2845, 1610, 1588, 1465, 1392, 1363, 1341, 1278, 1260, 1196, 1146, 1112, 1093, 1051, 1018, 993 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_2S$ requires (M^++H): 467.1788, Found: 467.1784.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8.422
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7.701
7.682
7.572
7.550
7.531
7.472
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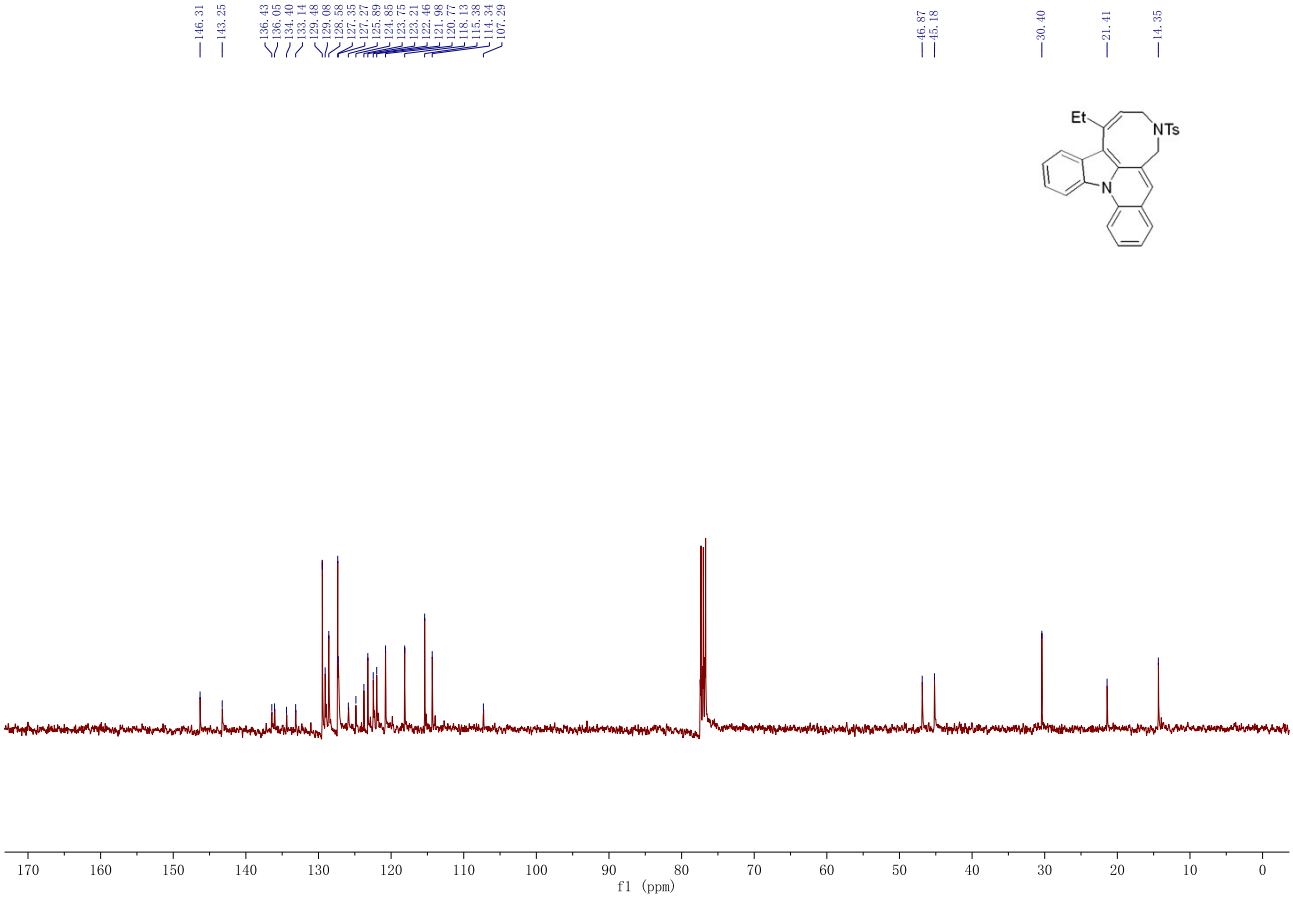
7.431
7.411
7.388
7.368
7.349
7.306
7.287
7.261
7.150
7.130
6.809
5.581
5.564
5.539
4.981
4.946
4.667
4.631
4.364
4.336
4.318
3.862
3.835
3.805
2.954
2.935
2.916
2.898
2.879
2.860
2.784
2.760
2.743
2.722
2.701
2.687
2.266
1.052
1.039
1.021
Et
NTs
N
2.00
1.00
2.07
1.16
3.01
1.05
2.07
1.00
1.00
1.01
1.00
1.01
0.99
1.01
1.07
2.78
2.90
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)


146.31
143.25
136.43
136.05
134.40
133.14
129.48
129.08
128.58
127.35
127.27
125.89
124.85
123.75
123.21
122.46
121.98
120.77
118.13
115.38
114.34
107.29
46.87
45.18
30.40
21.41
14.35
Et
NTs
N
170
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130
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90
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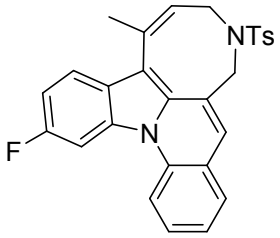
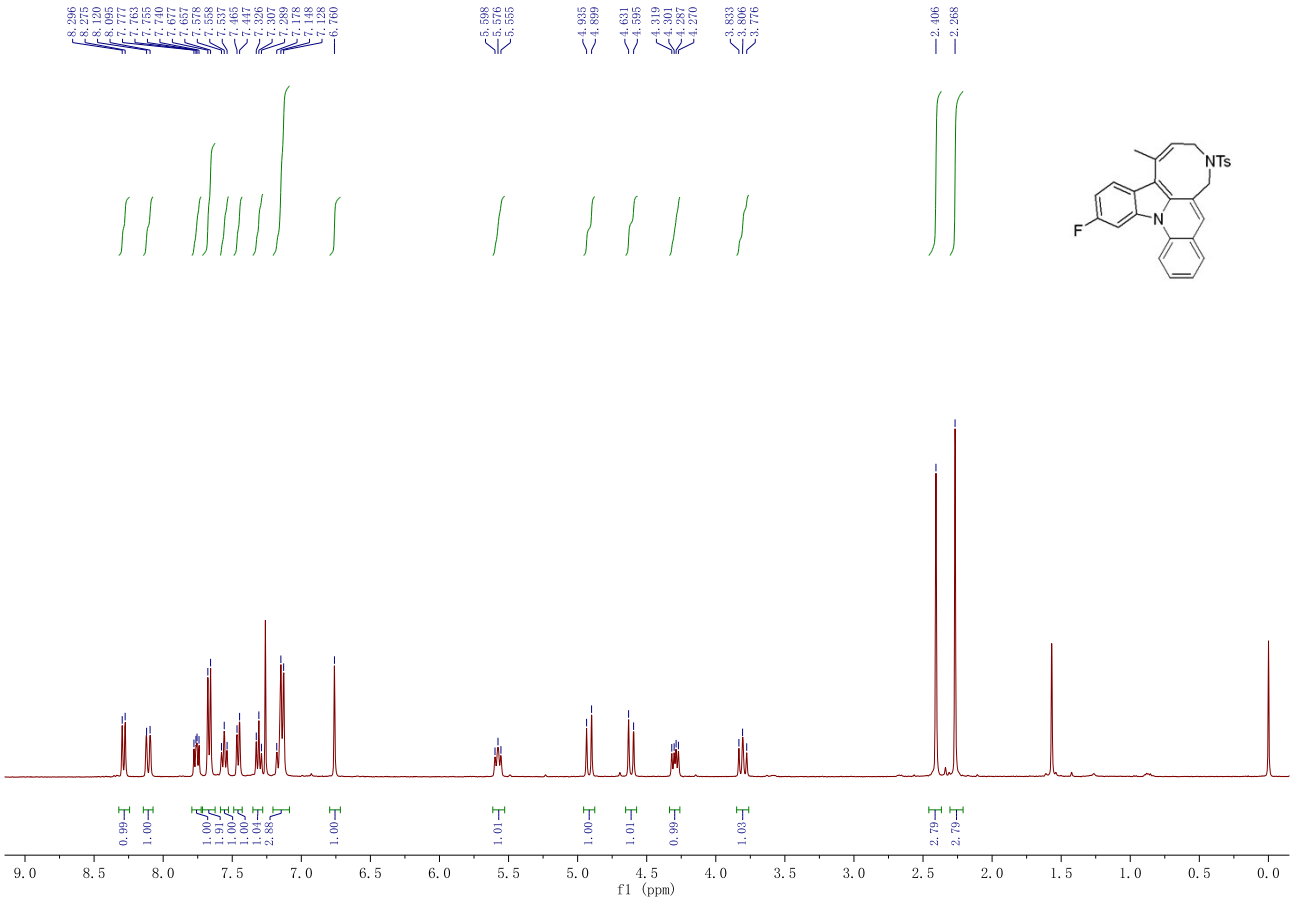
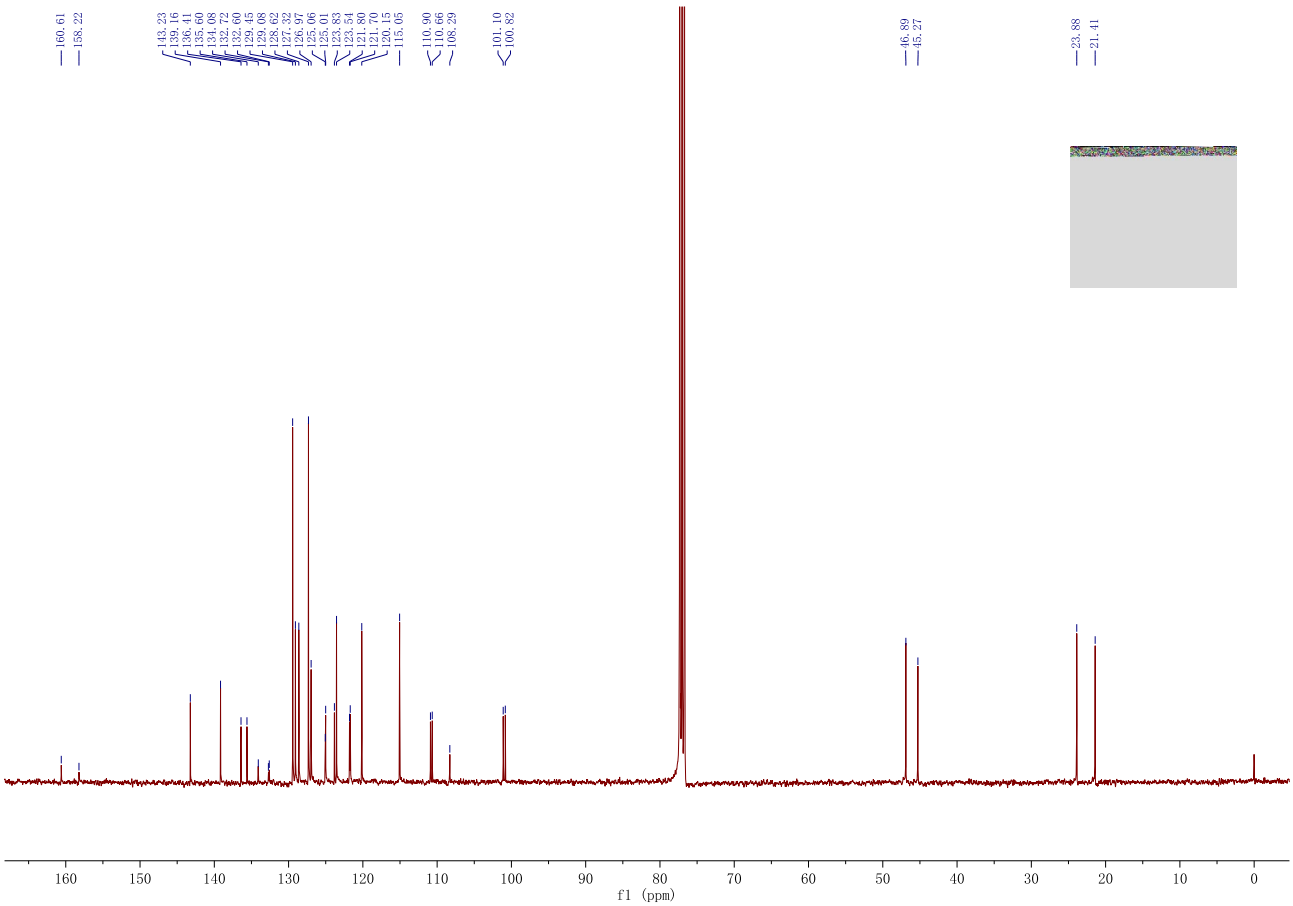
50
40
30
20
10
0
f1 (ppm)



Compound 2e: yellow oil (39.0 mg, 83%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.27 (s, 3H), 2.41 (s, 3H), 3.80 (dd, *J* = 12.4 Hz, 1H), 4.29 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.61 (d, *J* = 14.4 Hz, 1H), 4.92 (d, *J* = 14.4 Hz, 1H), 5.58 (dd, *J* = 12.4, 6.8 Hz, 1H), 6.76 (s, 1H), 7.09-7.21 (m, 3H), 7.31 (dd, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.76 (dd, *J* = 8.8, 6.0 Hz, 1H), 8.11 (d, *J* = 10.0 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.9, 45.3, 46.9, 101.0 (d, *J* = 28.3 Hz), 108.3, 110.8 (d, *J* = 24.3 Hz), 115.1, 120.1, 121.7 (d, *J* = 9.8 Hz), 123.5, 123.8, 125.0, 125.1, 127.0, 127.3, 128.6, 129.1, 129.5, 132.7 (d, *J* = 11.7 Hz), 134.1 (d, *J* = 3.5 Hz), 135.6, 136.4, 139.2, 143.2, 159.4 (d, *J* = 239.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.3. IR (neat) ν 2994, 2979, 2959, 2942, 1625, 1500, 1468, 1397, 1372, 1348, 1256, 1215, 1160, 1134, 1102, 1083, 1038, 1012, 990 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}FN_2O_2S$ requires (M^++H): 471.1537, Found: 471.1534.

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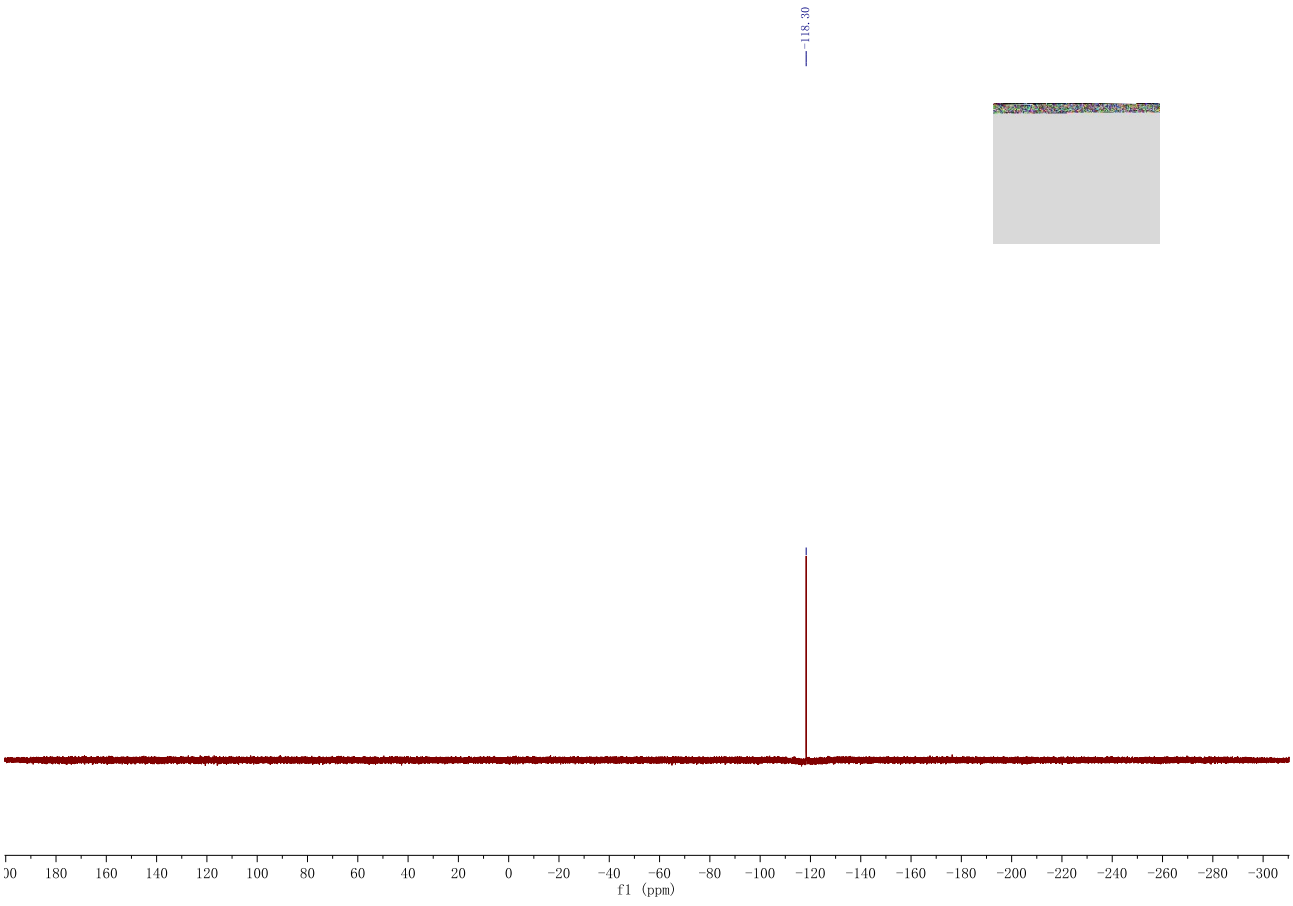
143.23
139.16
136.41
135.60
134.08
132.72
132.60
129.45
129.08
128.62
127.22
126.97
125.06
125.01
123.83
123.54
121.80
121.70
120.15
115.05
110.90
110.66
108.29
101.10
100.82
46.89
45.27
23.88
21.41
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


118.30
30
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
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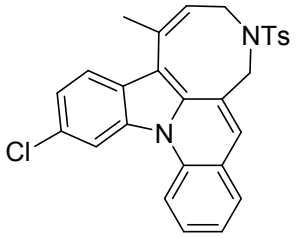
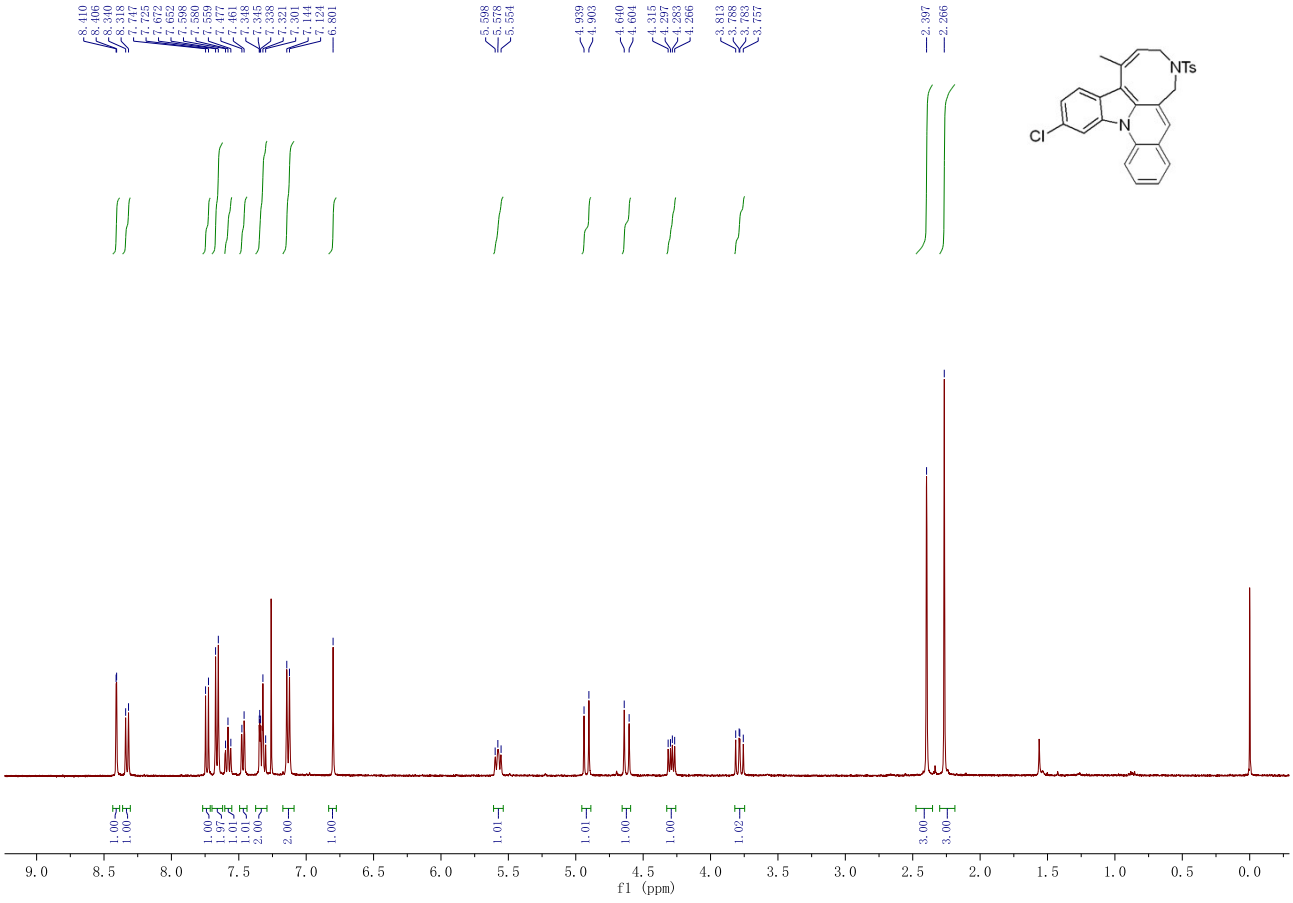
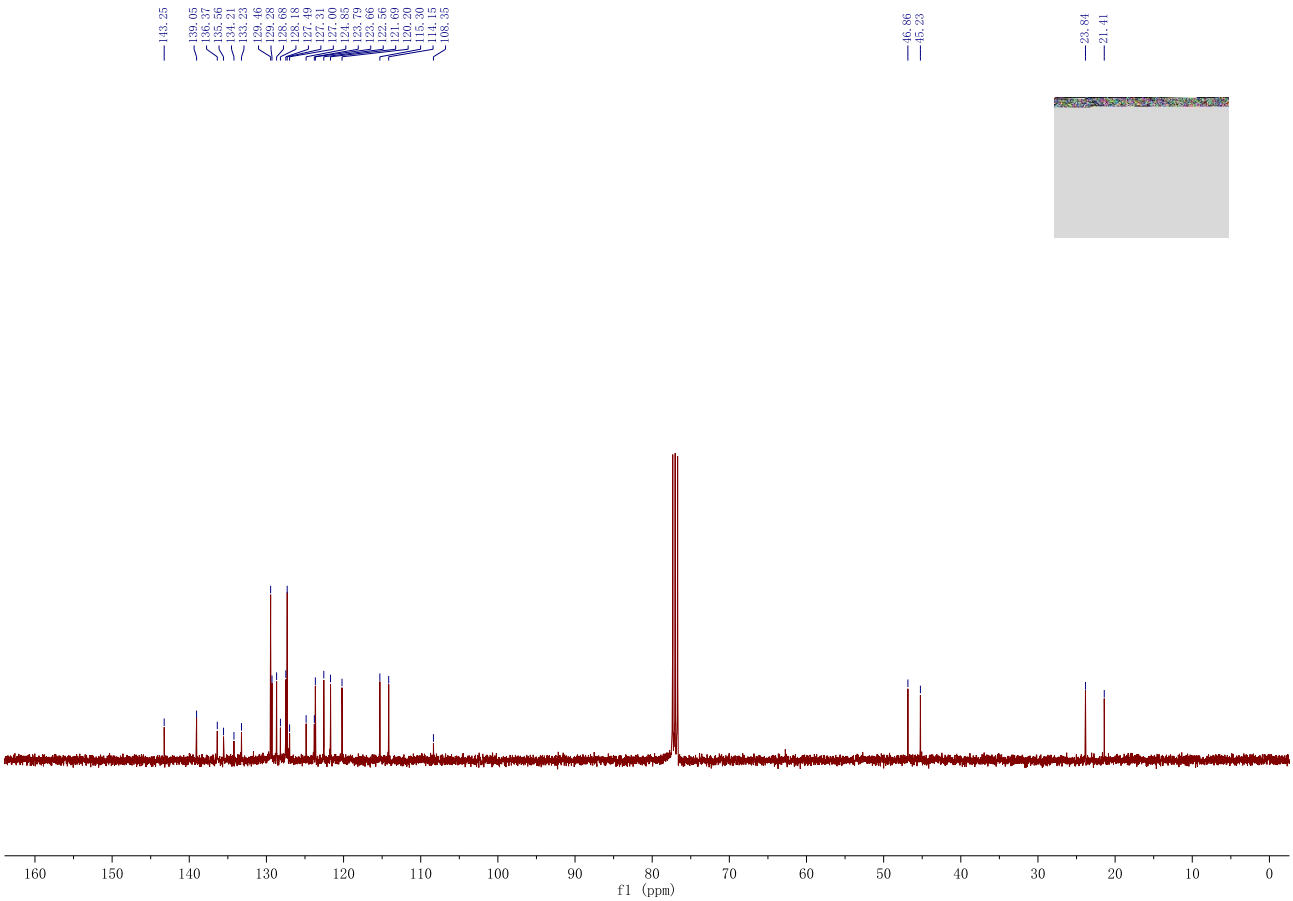
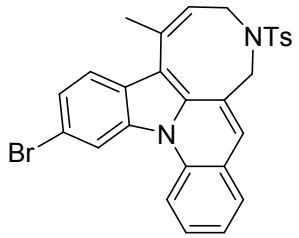
-200
-220
-240
-260
-280
-300
f1 (ppm)



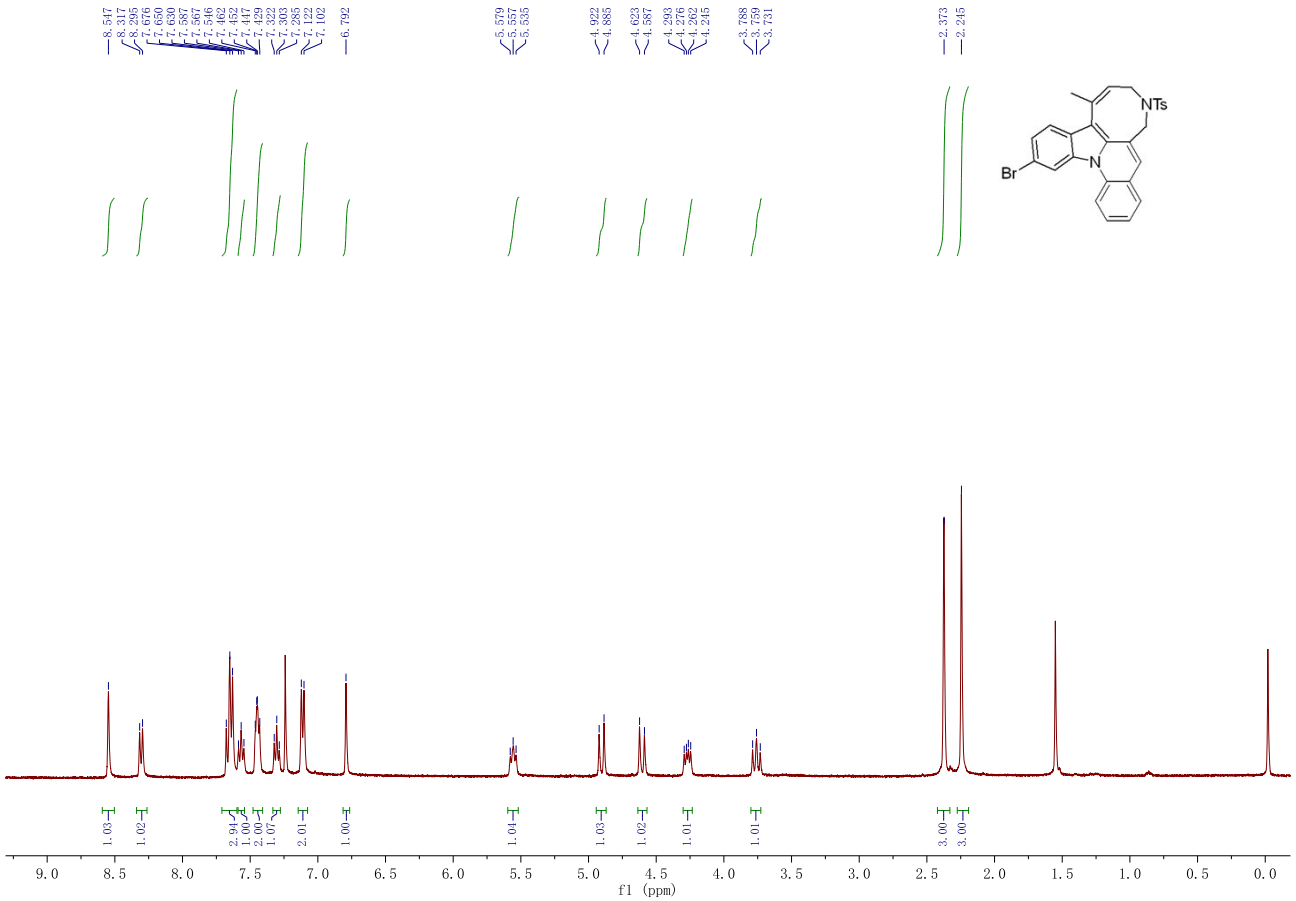
Compound 2f: yellow oil (46.1 mg, 95%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.27 (s, 3H), 2.40 (s, 3H), 3.79 (dd, *J* = 12.4, 11.2 Hz, 1H), 4.29 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.62 (d, *J* = 14.4 Hz, 1H), 4.92 (d, *J* = 14.4 Hz, 1H), 5.58 (dd, *J* = 11.2, 6.8 Hz, 1H), 6.80 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.29-7.37 (m, 2H), 7.47 (d, *J* = 6.4 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.41 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.8, 45.2, 46.9, 108.4, 114.2, 115.3, 120.2, 121.7, 122.6, 123.7, 123.8, 124.9, 127.0, 127.3, 127.5, 128.2, 128.7, 129.3, 129.5, 133.2, 134.2, 135.6, 136.4, 139.1, 143.2. IR (neat) ν 2916, 2844, 1620, 1596, 1467, 1421, 1396, 1372, 1342, 1324, 1285, 1261, 1201, 1170, 1146, 1115, 1092, 1060, 1036, 1018, 995 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}ClN_2O_2S$ requires (M^++H): 487.1242, Found: 487.1239.







Compound 2g: yellow oil (50.3 mg, 95%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.24 (s, 3H), 2.37 (s, 3H), 3.76 (dd, *J* = 12.4 Hz, 1H), 4.27 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.60 (d, *J* = 14.4 Hz, 1H), 4.90 (d, *J* = 14.4 Hz, 1H), 5.56 (dd, *J* = 12.4, 6.8 Hz, 1H), 6.79 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.57 (dd, *J* = 8.0 Hz, 1H), 7.60-7.71 (m, 3H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.55 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.8, 45.2, 46.9, 108.4, 115.3, 115.9, 117.0, 120.2, 122.0, 123.7, 123.8, 124.8, 125.2, 127.3, 127.6, 128.7, 129.3, 129.5, 133.7, 134.1, 135.6, 136.4, 139.0, 143.3. IR (neat) ν 2955, 2919, 2852, 1592, 1507, 1488, 1467, 1435, 1394, 1371, 1280, 1258, 1186, 1166, 1117, 1090, 1038, 997 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}BrN_2O_2S$ requires (M^++H): 531.0736, Found: 531.0727.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7.567
7.546
7.462
7.432
7.417
7.322
7.303
7.285
7.122
7.102
6.792
5.579
5.557
5.535
4.922
4.885
4.623
4.587
4.293
4.276
4.262
4.245
3.788
3.759
3.731
2.373
2.245
NTs
Br
N
1.03
1.02
2.94
1.04
1.00
2.07
2.01
1.00
1.04
1.03
1.02
1.01
1.01
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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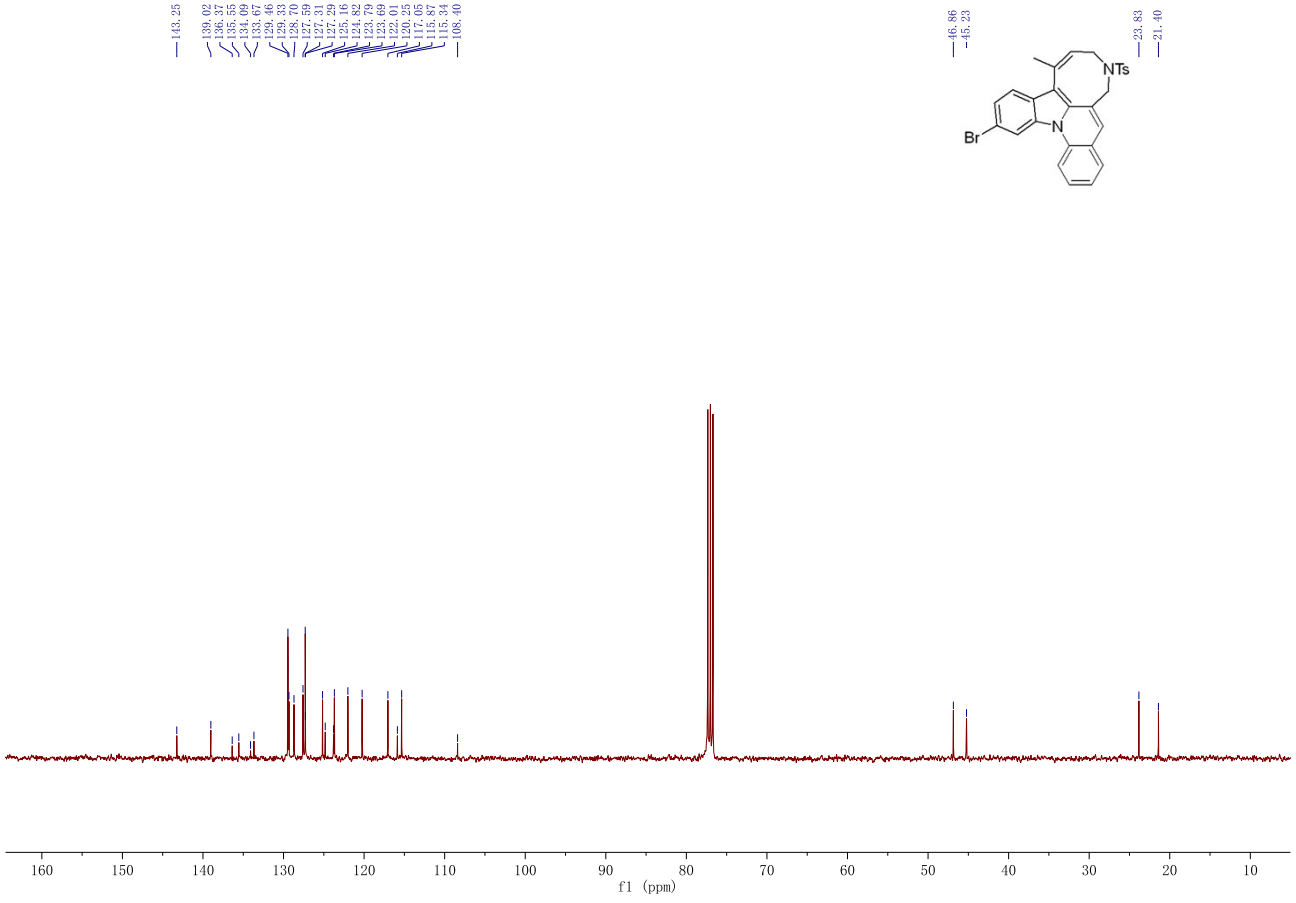
1.0
0.5
0.0
f1 (ppm)


143.25
139.02
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135.55
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133.67
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129.33
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127.59
127.31
127.29
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60
50
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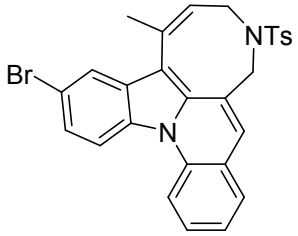
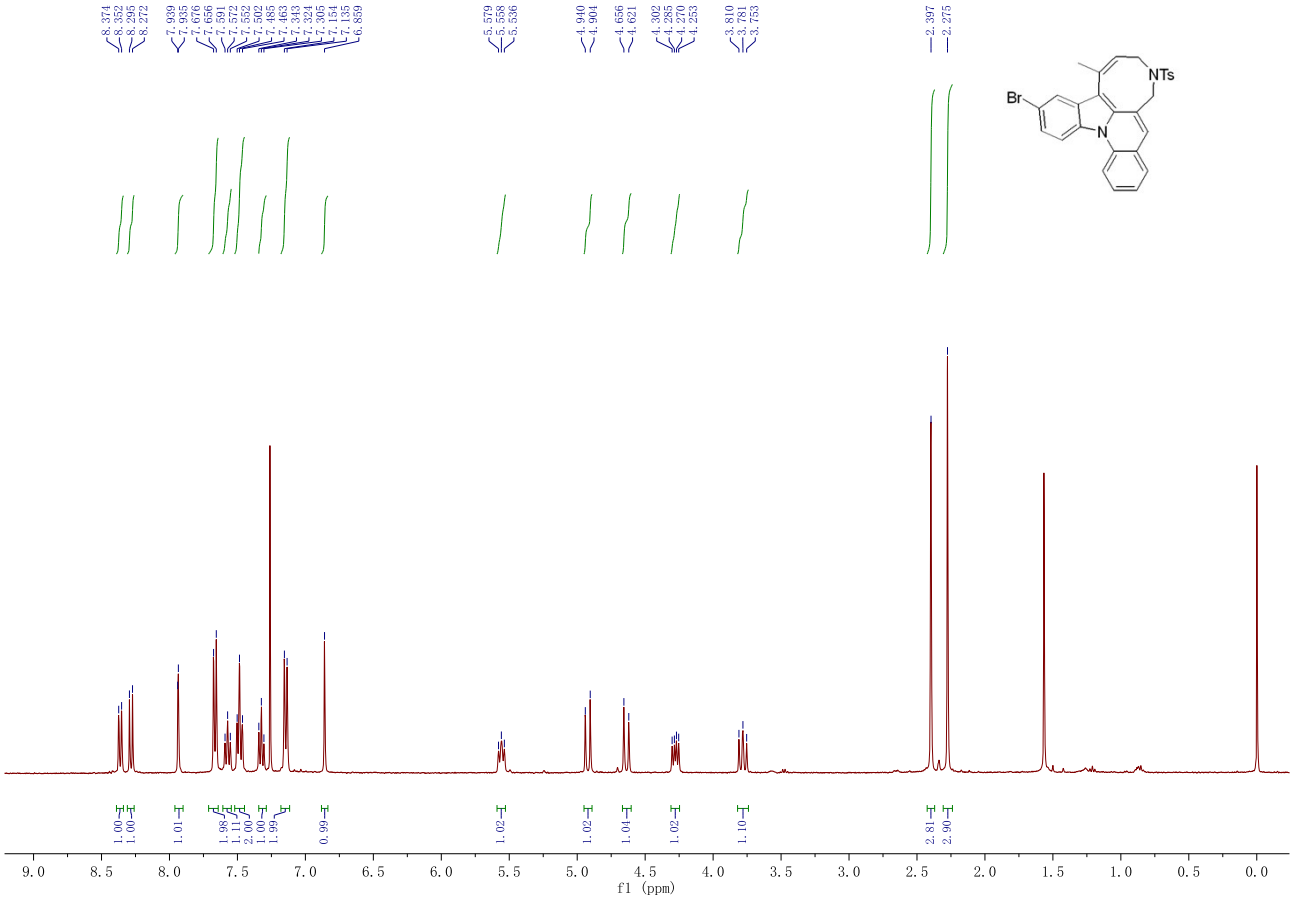
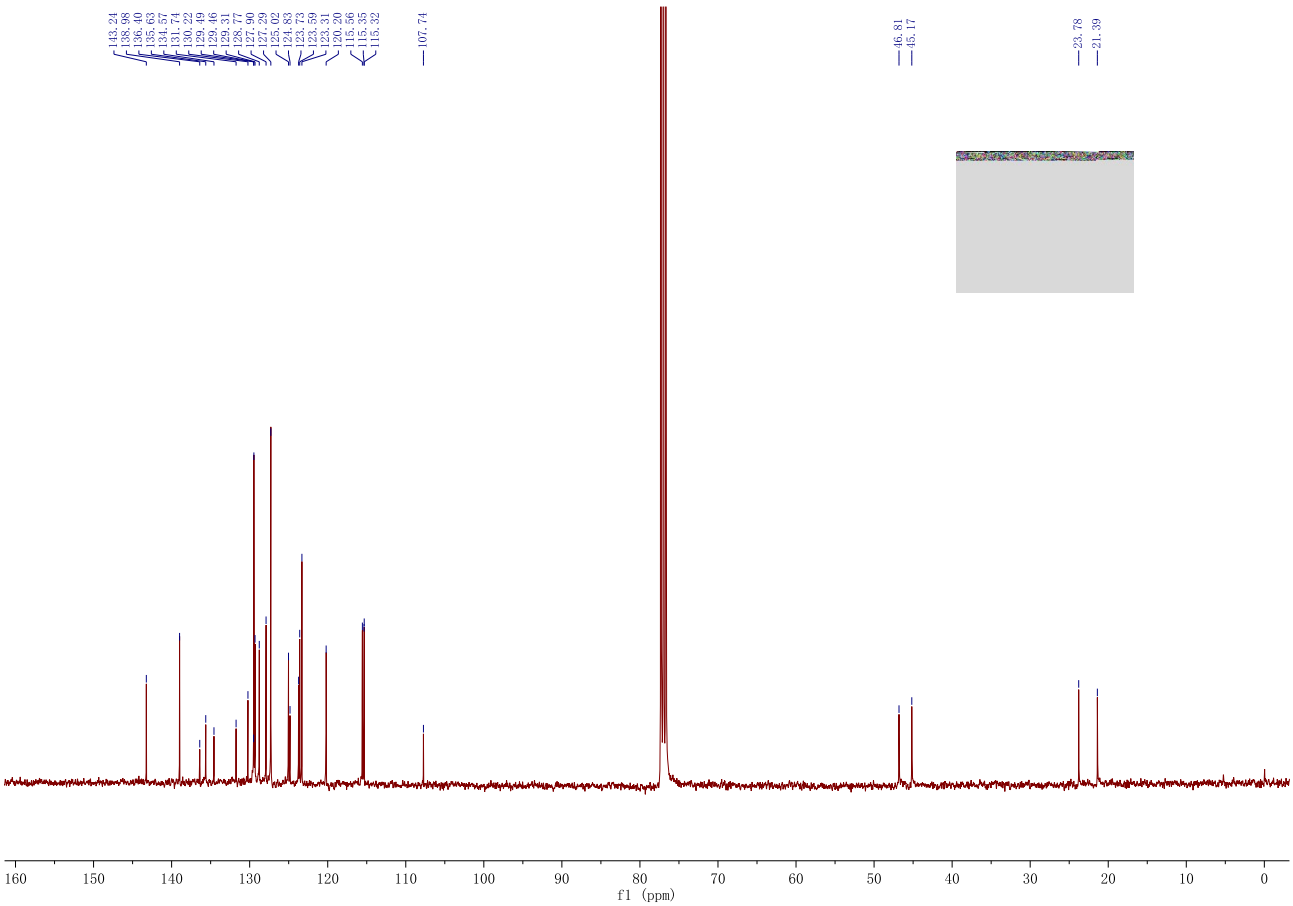
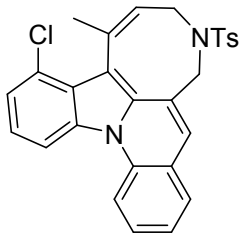
30
20
10
f1 (ppm)



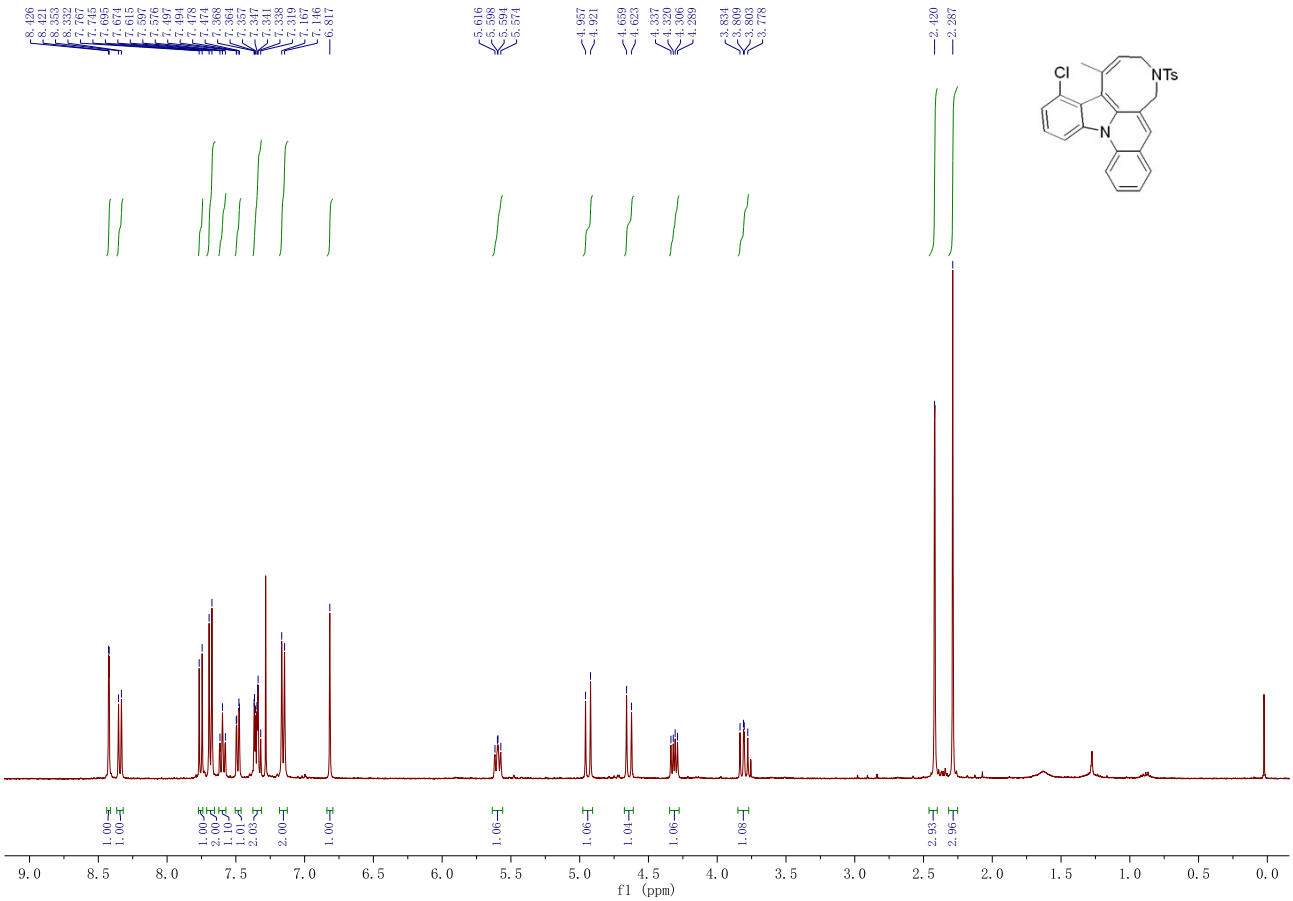
Compound 2h: yellow oil (46.6 mg, 88%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.28 (s, 3H), 2.40 (s, 3H), 3.78 (dd, *J* = 12.8 Hz, 1H), 4.28 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.64 (d, *J* = 14.4 Hz, 1H), 4.92 (d, *J* = 14.4 Hz, 1H), 5.56 (dd, *J* = 12.8, 6.8 Hz, 1H), 6.86 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 8.8 Hz, 2H), 7.57 (dd, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 1.6 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.8, 45.2, 46.8, 107.7, 115.32, 115.35, 115.6, 120.2, 123.3, 123.6, 123.7, 124.8, 125.0, 127.3, 127.9, 128.8, 129.3, 129.5, 130.2, 131.7, 134.6, 135.6, 136.4, 139.0, 143.2. IR (neat) ν 2919, 2846, 1608, 1484, 1432, 1395, 1372, 1352, 1328, 1280, 1261, 1181, 1114, 1098, 1070, 1055, 1040, 994 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}BrN_2O_2S$ requires (M^++H): 531.0736, Found: 531.0728.







Compound 2i: yellow oil (35.9 mg, 74%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.29 (s, 3H), 2.42 (s, 3H), 3.81 (dd, *J* = 12.4, 10.0 Hz, 1H), 4.31 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.64 (d, *J* = 14.5 Hz, 1H), 4.94 (d, *J* = 14.5 Hz, 1H), 5.60 (dd, *J* = 10.0, 6.8 Hz, 1H), 6.82 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.31-7.38 (m, 2H), 7.49 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.60 (dd, *J* = 7.9 Hz, 1H), 7.68 (dd, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 23.8, 45.2, 46.9, 108.3, 114.2, 115.3, 120.2, 121.7, 122.6, 123.7, 123.8, 124.8, 127.0, 127.3, 127.5, 128.2, 128.7, 129.3, 129.5, 133.2, 134.2, 135.6, 136.4, 139.1, 143.3. IR (neat) ν 3072, 2988, 2973, 2959, 2924, 2902, 1611, 1486, 1434, 1395, 1372, 1352, 1328, 1279, 1260, 1181, 1168, 1149, 1130, 1115, 1099, 1080, 1056, 1040, 995 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}ClN_2O_2S$ requires (M^++H): 487.1242, Found: 487.1238.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7.745
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7.494
7.478
7.474
7.398
7.364
7.357
7.347
7.341
7.338
7.319
7.167
7.146
6.817
5.616
5.598
5.594
5.574
4.957
4.921
4.659
4.623
4.337
4.320
4.306
4.289
3.834
3.809
3.803
3.778
2.420
2.287
Cl
NTs
N
1.00
1.00
1.00
2.00
1.10
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1.04
1.06
1.08
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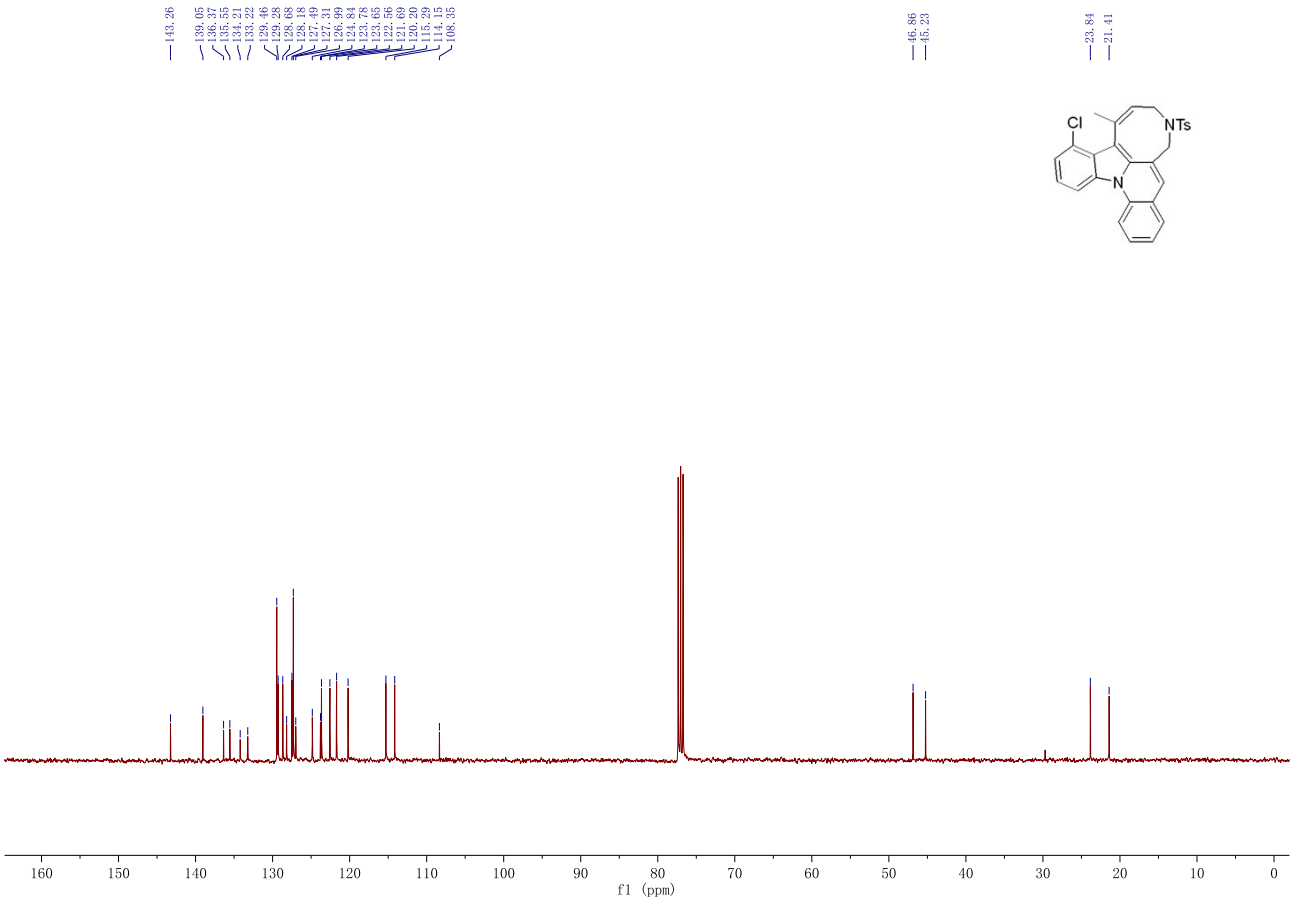
2.96
f1 (ppm)


143.26
139.05
136.37
135.55
134.21
133.22
129.46
129.28
128.68
128.18
127.49
127.31
126.99
124.84
123.78
123.65
122.56
121.69
120.29
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114.15
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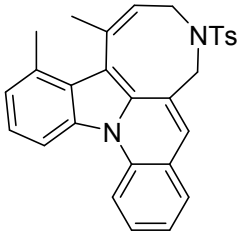
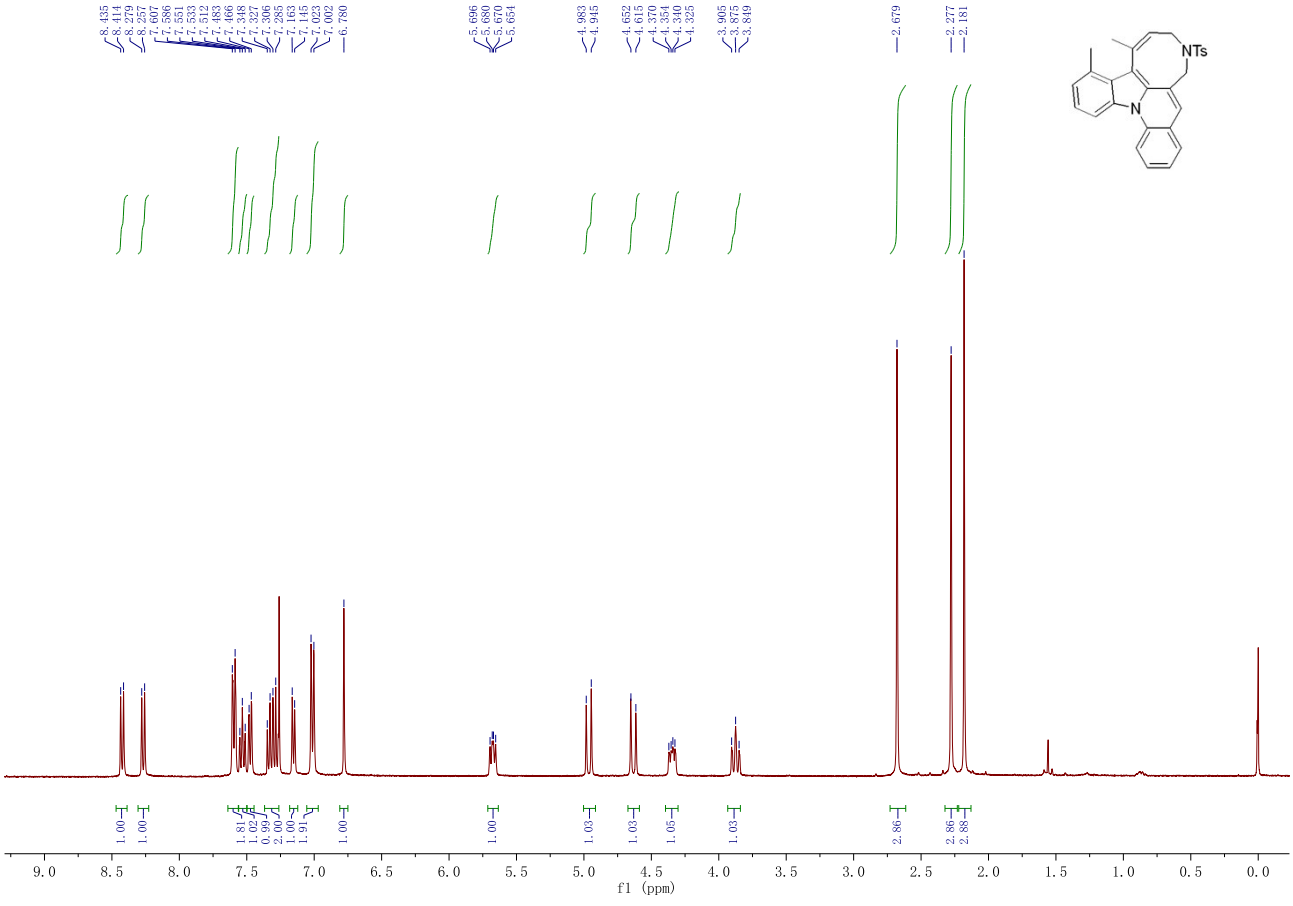
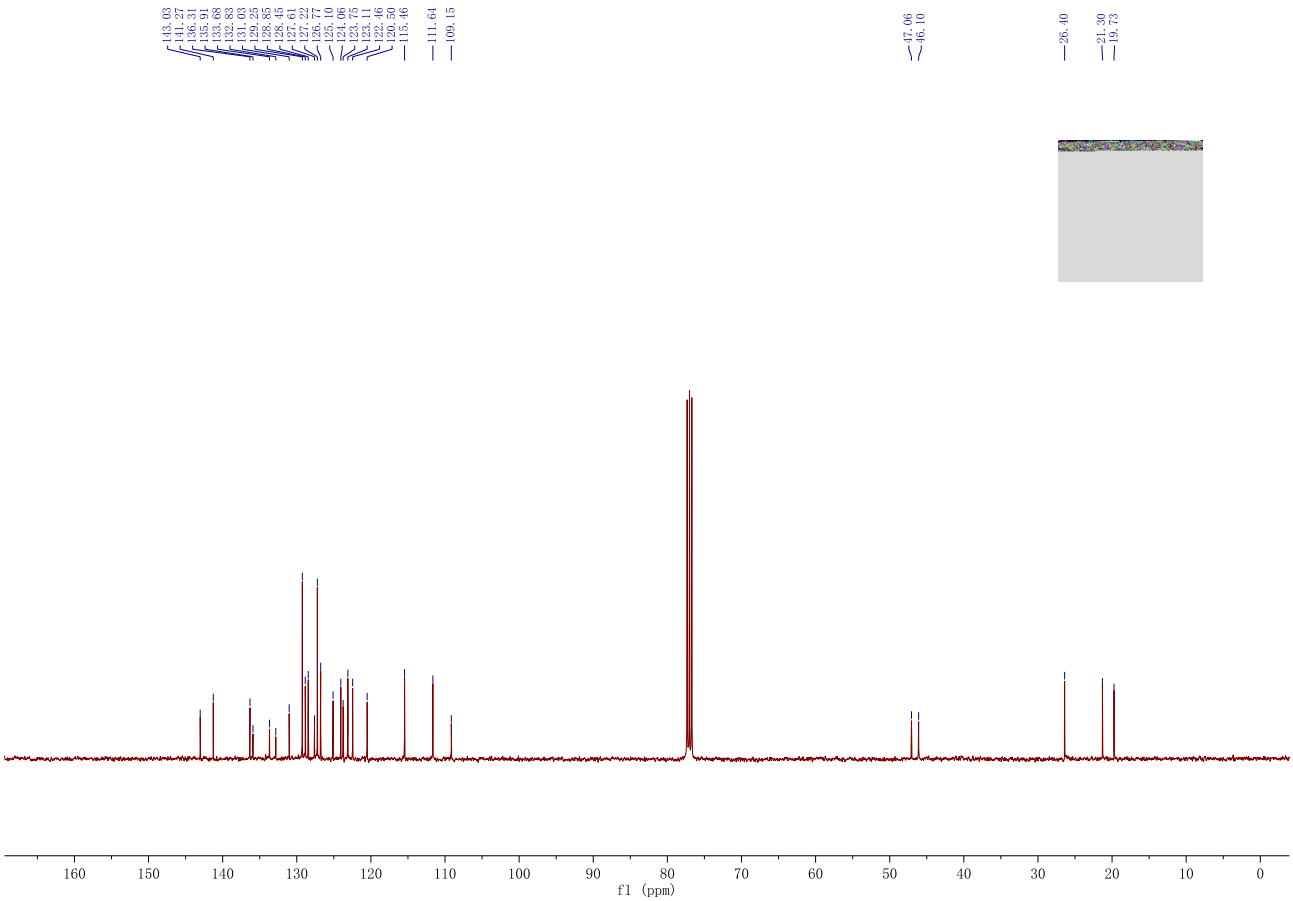
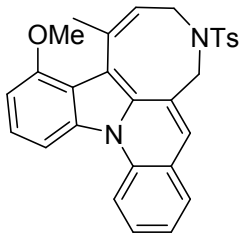
46.86
45.23
23.84
21.41
Cl
NTs
N
f1 (ppm)



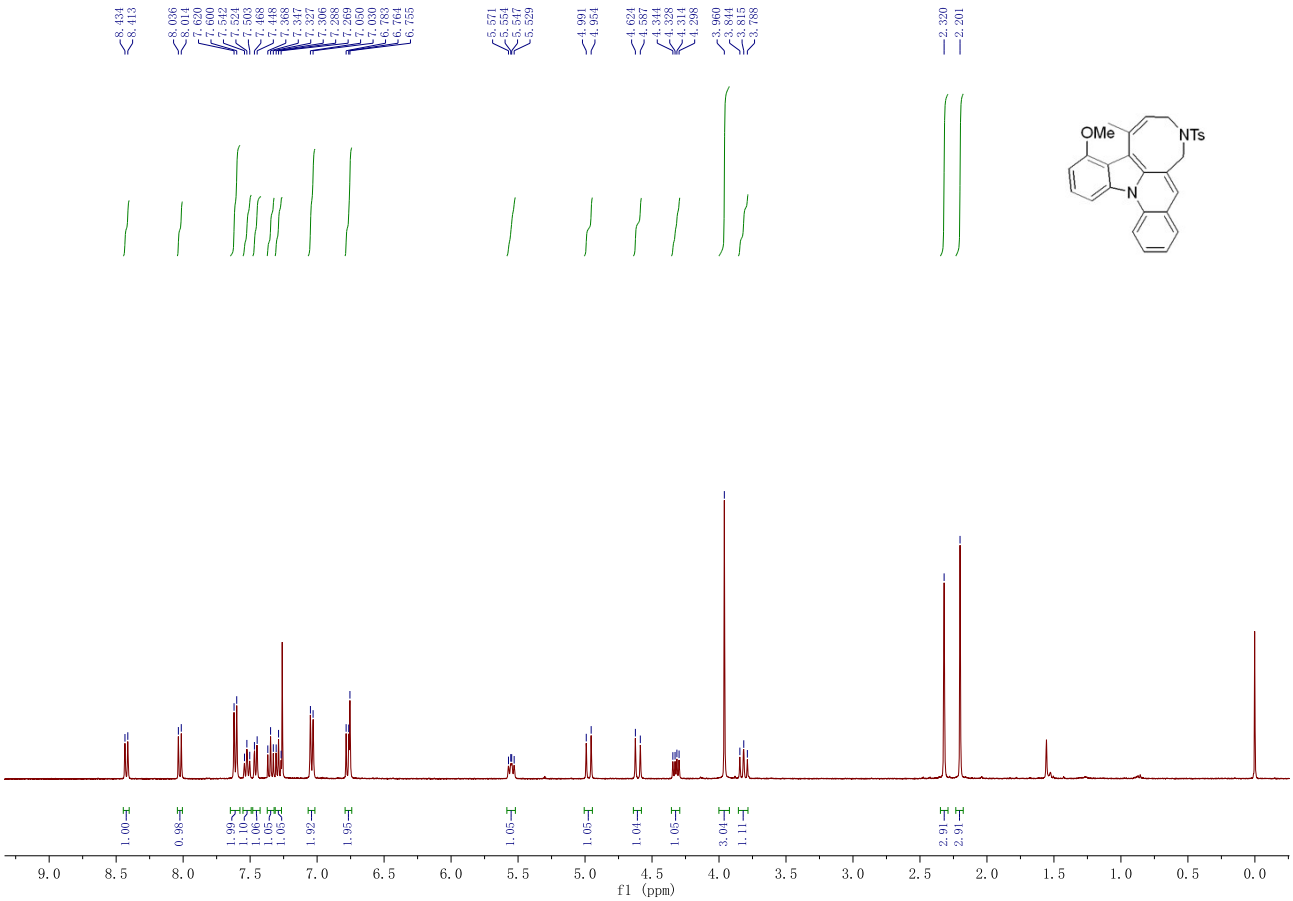
Compound 2j: yellow oil (44.3 mg, 95%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.18 (s, 3H), 2.28 (s, 3H), 2.68 (s, 3H), 3.88 (dd, *J* = 11.6 Hz, 1H), 4.35 (dd, *J* = 11.6, 6.0 Hz, 1H), 4.63 (d, *J* = 14.8 Hz, 1H), 4.96 (d, *J* = 14.8 Hz, 1H), 5.68 (dd, *J* = 11.6, 6.0 Hz, 1H), 6.78 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.26-7.37 (m, 2H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.53 (dd, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 19.7, 21.3, 26.4, 46.1, 47.1, 109.1, 111.6, 115.5, 120.5, 122.5, 123.1, 123.7, 124.1, 125.1, 126.8, 127.2, 127.6, 128.5, 128.9, 129.3, 131.0, 132.8, 133.7, 135.9, 136.3, 141.3, 143.0. IR (neat) ν 3025, 2924, 2846 1604, 1496, 1442, 1395, 1370, 1328, 1276, 1259, 1196, 1166, 1147, 1116, 1090, 996 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_2S$ requires (M^++H): 467.1788, Found: 467.1785.







Compound 2k: yellow oil (45.8 mg, 95%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.20 (s, 3H), 2.32 (s, 3H), 3.82 (dd, *J* = 12.0 Hz, 1H), 3.96 (s, 3H), 4.32 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.61 (d, *J* = 14.8 Hz, 1H), 4.97 (d, *J* = 14.8 Hz, 1H), 5.55 (dd, *J* = 12.0, 6.4 Hz, 1H), 6.74-6.79 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.3, 25.4, 46.0, 47.1, 55.4, 102.2, 107.2, 108.2, 115.6, 118.9, 119.1, 123.3, 123.4, 124.0, 125.2, 126.5, 127.3, 128.3, 128.7, 129.3, 132.2, 134.7, 135.8, 136.4, 141.8, 143.0, 153.9. IR (neat) ν 3046, 2999, 2982, 2933, 2915, 1613, 1491, 1468, 1441, 1396, 1365, 1334, 1282, 1262, 1195, 1184, 1162, 1116, 1100 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{27}N_2O_3S$ requires (M^++H): 483.1737, Found: 483.1731.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7.327
7.306
7.288
7.269
7.030
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6.761
6.755
5.571
5.554
5.547
5.529
4.991
4.954
4.624
4.587
4.344
4.328
4.314
4.298
3.960
3.844
3.815
3.788
2.320
2.201
OMe
NTs
N
1.00
0.98
1.99
1.10
1.06
1.05
1.05
1.92
1.95
1.05
1.05
1.04
1.05
3.04
1.11
2.91
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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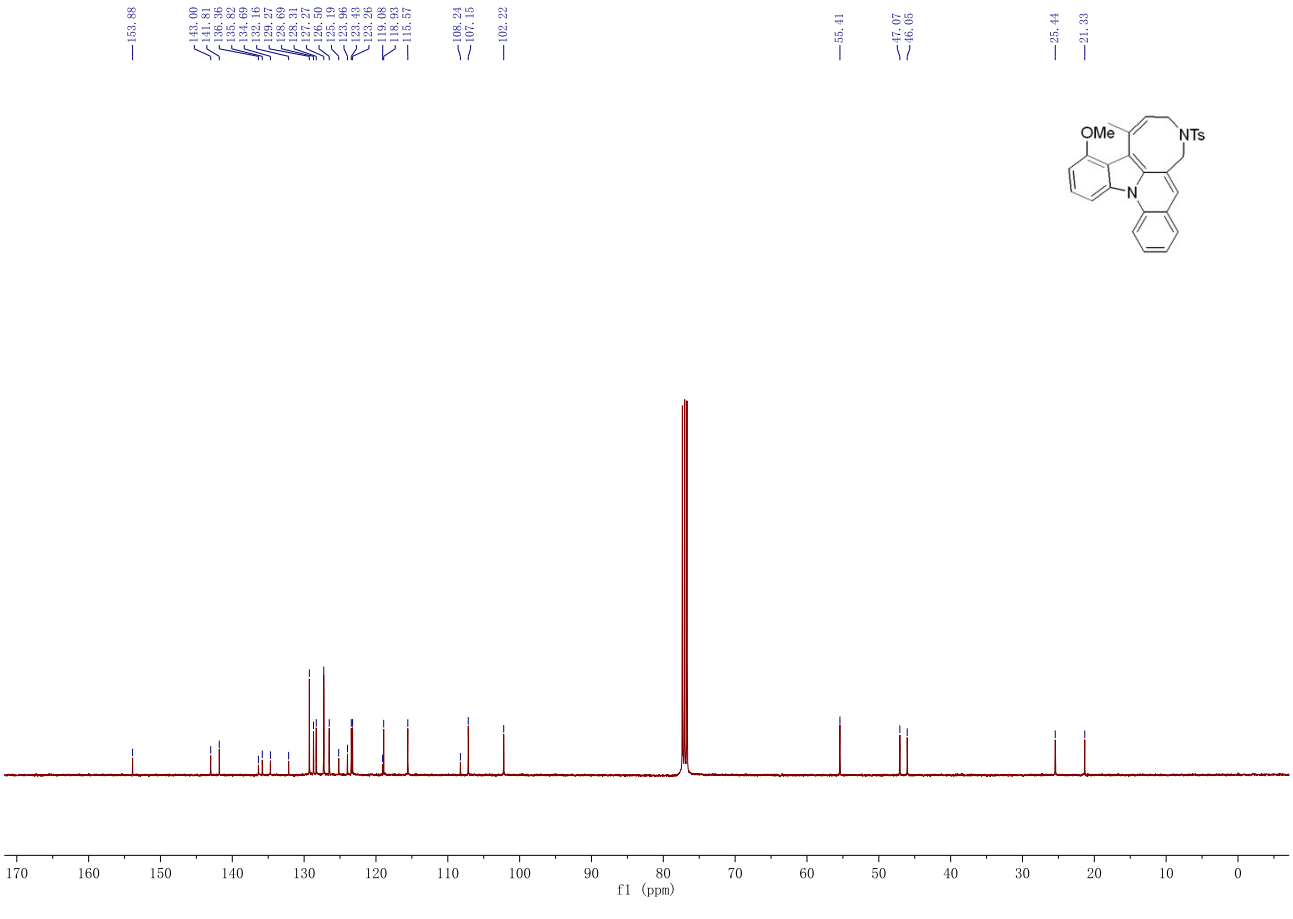
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.88
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135.92
134.69
132.16
129.27
128.69
128.31
127.27
126.50
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123.43
123.26
119.08
118.93
115.57
108.24
107.15
102.22
55.41
47.07
46.05
25.44
21.33
OMe
NTs
N
170
160
150
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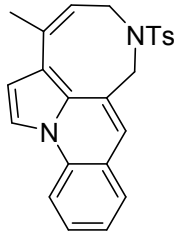
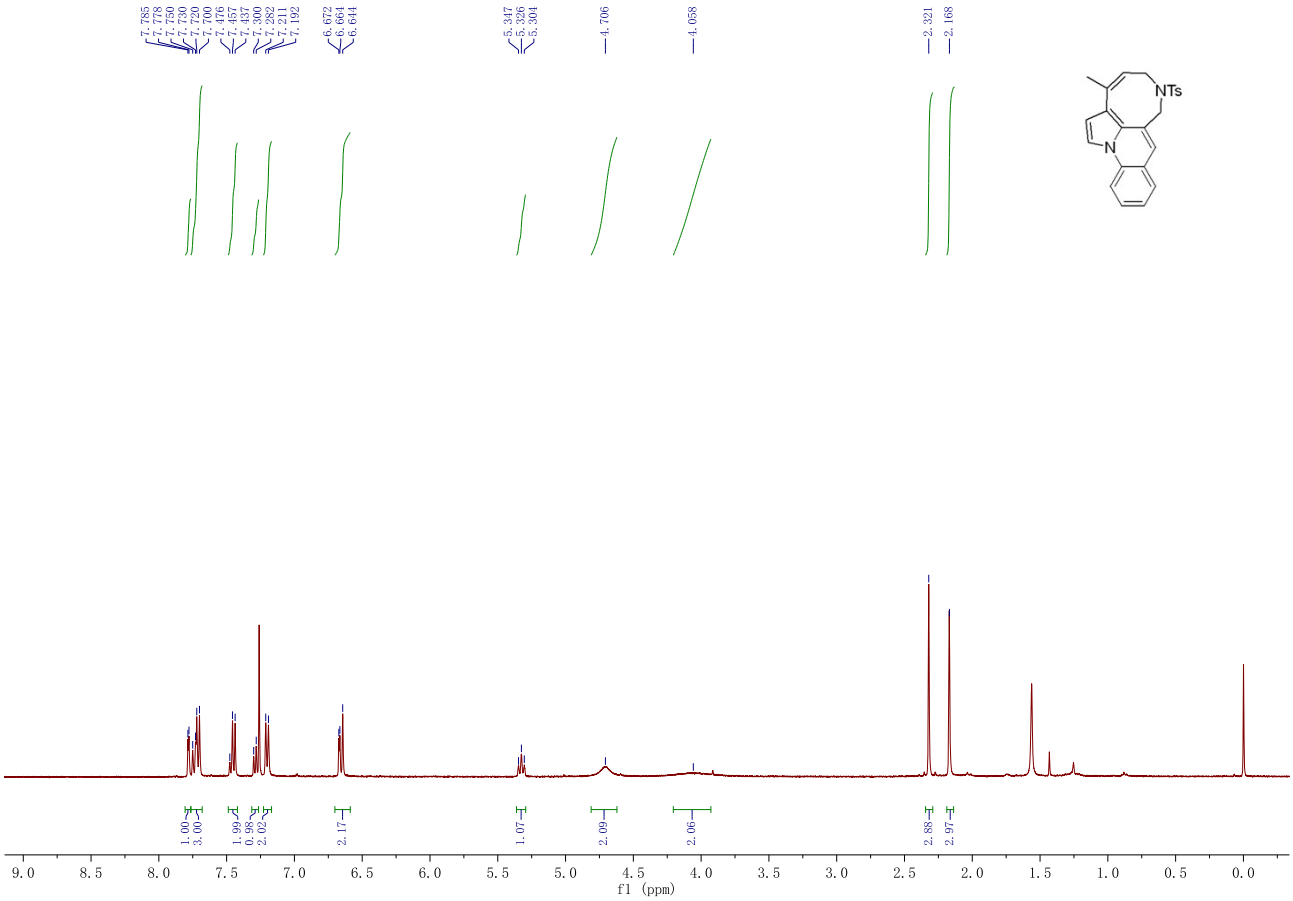
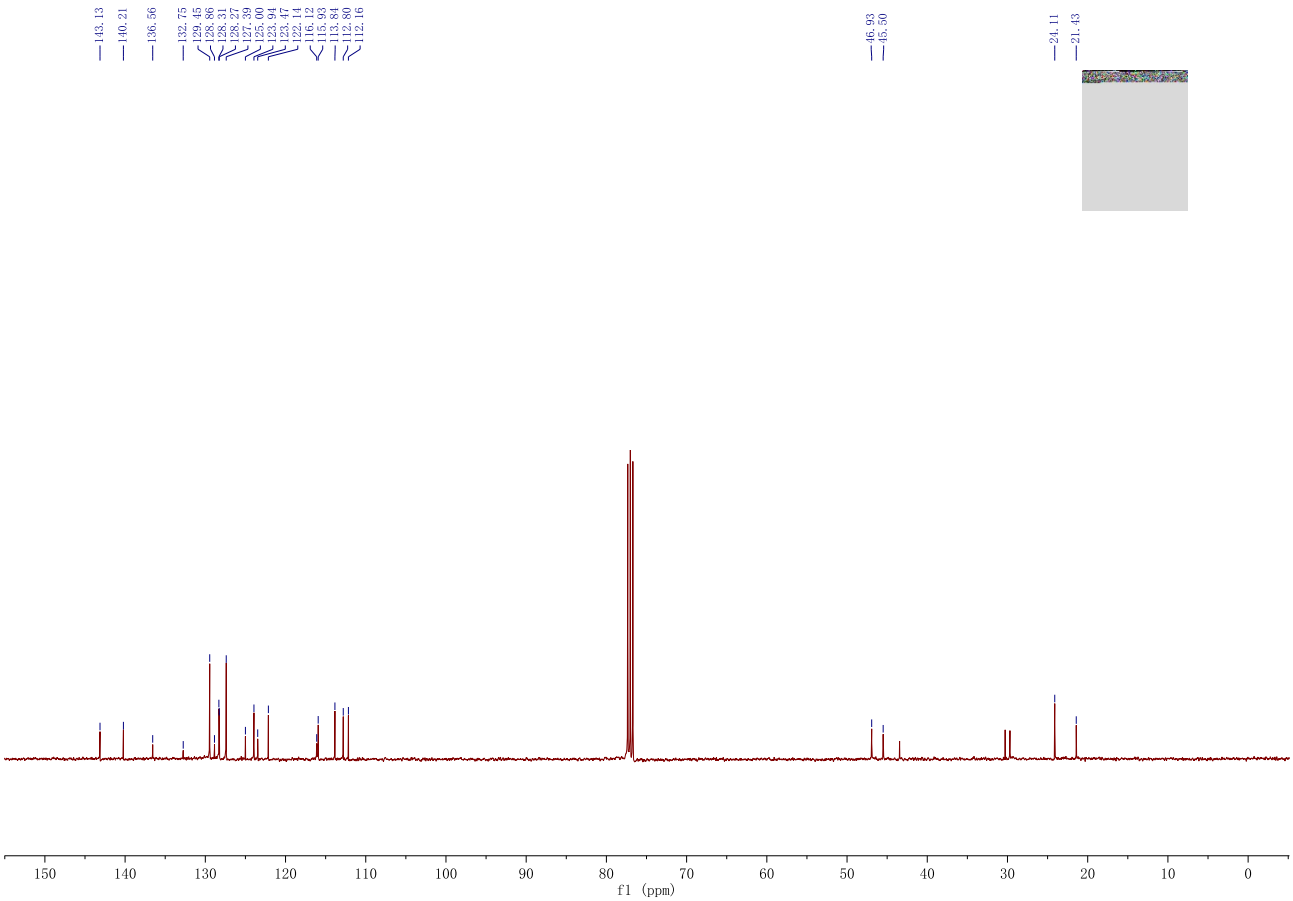
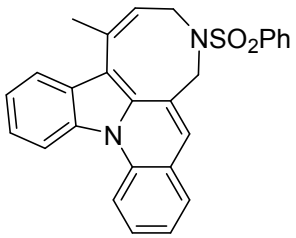
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



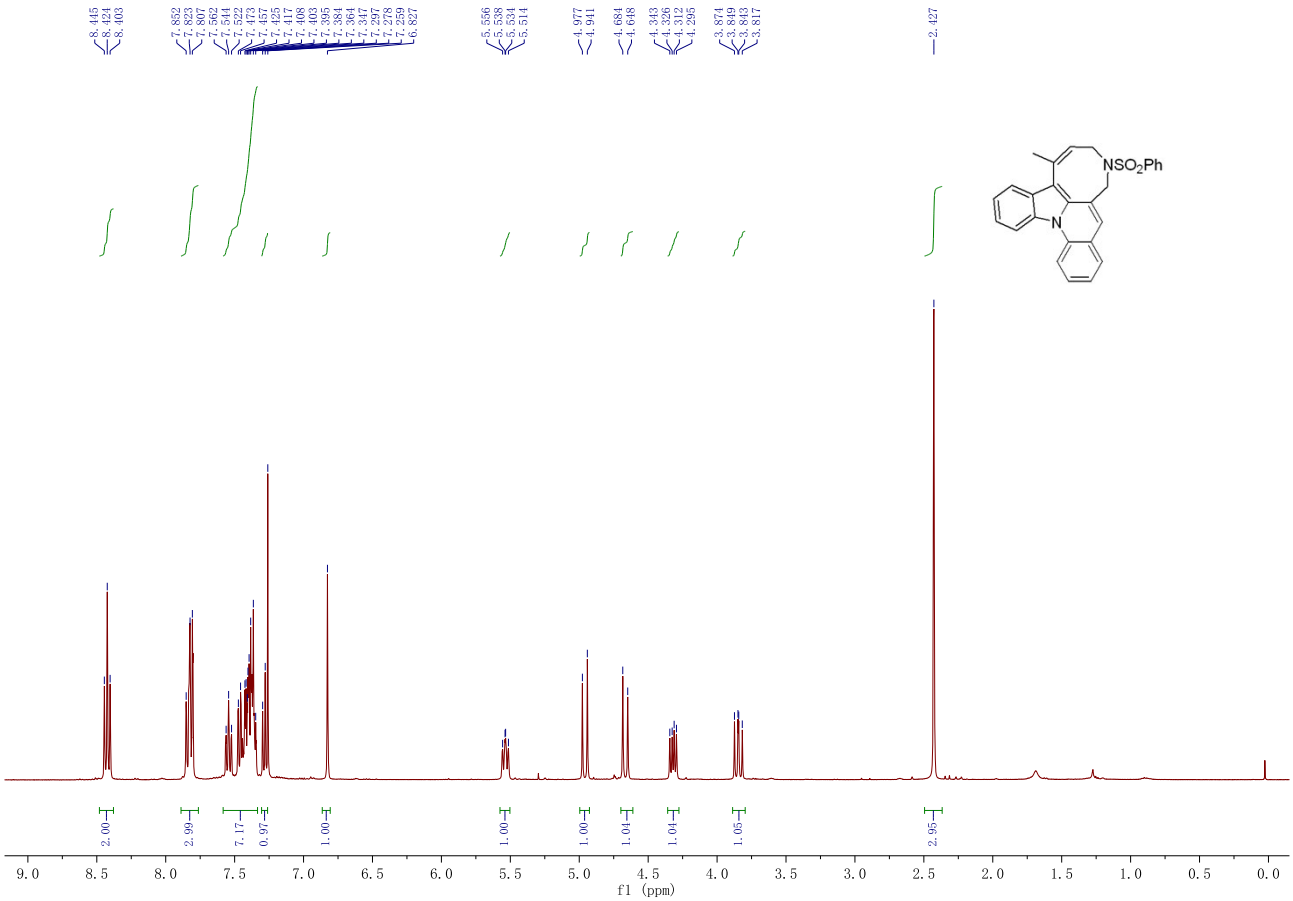
Compound 2o: pale white oil (26.9 mg, 67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.17 (s, 3H), 2.32 (s, 3H), 4.06 (s, 2H), 4.71 (s, 2H), 5.33 (d, *J* = 8.8 Hz, 1H), 6.59-6.70 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.42-7.49 (m, 2H), 7.68-7.76 (m, 3H), 7.78 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 21.4, 24.1, 45.5, 46.9, 112.2, 112.8, 113.8, 115.9, 116.1, 122.1, 123.5, 123.9, 125.0, 127.4, 128.27, 128.31, 128.9, 129.5, 132.8, 136.6, 140.2, 143.1. IR (neat) ν 2990, 2962, 2928, 1630, 1490, 1478, 1429, 1396, 1372, 1359, 1327, 1280, 1259, 1327, 1280, 1197, 1166, 1150, 1133, 1100, 1082, 1041, 995 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{23}N_2O_2S$ requires (M^++H): 403.1475, Found: 403.1475.







Compound 3a: yellow oil (37.6 mg, 86%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.43 (s, 3H), 3.85 (dd, *J* = 12.8, 10.4 Hz, 1H), 4.32 (dd, *J* = 12.4, 6.8 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.96 (d, *J* = 14.4 Hz, 1H), 5.54 (dd, *J* = 10.4, 6.8 Hz, 1H), 6.83 (s, 1H), 7.29 (dd, *J* = 7.6 Hz, 1H), 7.33-7.58 (m, 7H), 7.76-7.89 (m, 3H), 8.42 (dd, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 23.9, 45.3, 47.0, 108.3, 114.3, 115.4, 119.6, 121.0, 122.0, 122.5, 123.3, 123.7, 124.9, 127.3, 127.4, 128.56, 128.59, 128.9, 129.1, 132.5, 133.2, 133.6, 136.0, 139.4, 139.8. IR (neat) ν 3065, 2968, 2857, 1621, 1596, 1456, 1439, 1396, 1371, 1331, 1285, 1259, 1195, 1168, 1121, 1091, 1042, 1021, 997 cm^{-1}. HRMS (ESI) Calcd. for $C_{27}H_{23}N_2O_2S$ requires (M^++H): 439.1475, Found: 439.1476.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7.408
7.403
7.395
7.384
7.364
7.347
7.297
7.278
7.259
6.627
5.556
5.538
5.524
5.514
4.977
4.941
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4.648
4.343
4.326
4.312
4.295
3.874
3.849
3.843
3.817
2.427
NSO2Ph
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1.00
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1.04
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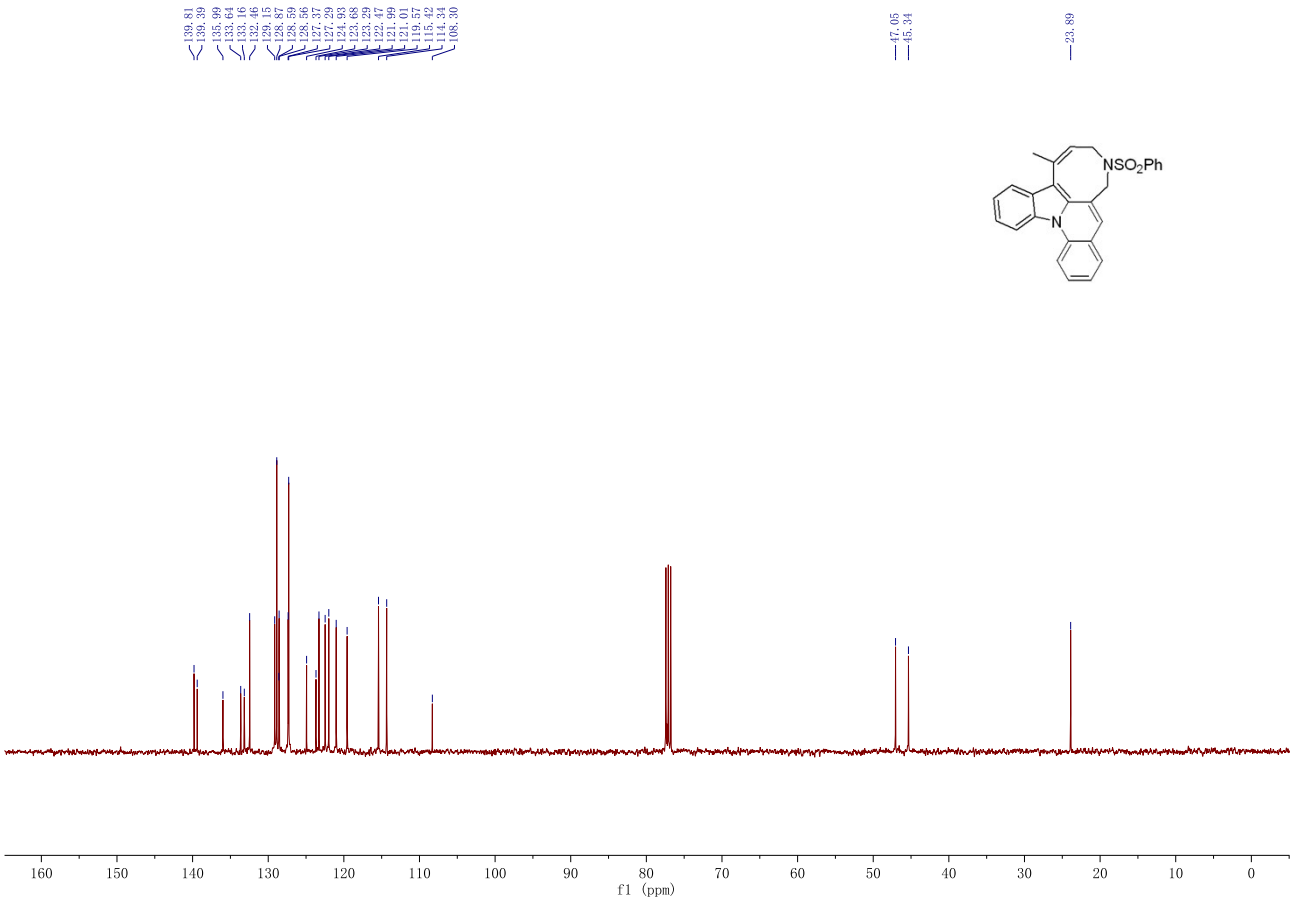
2.95
f1 (ppm)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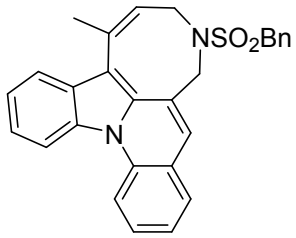
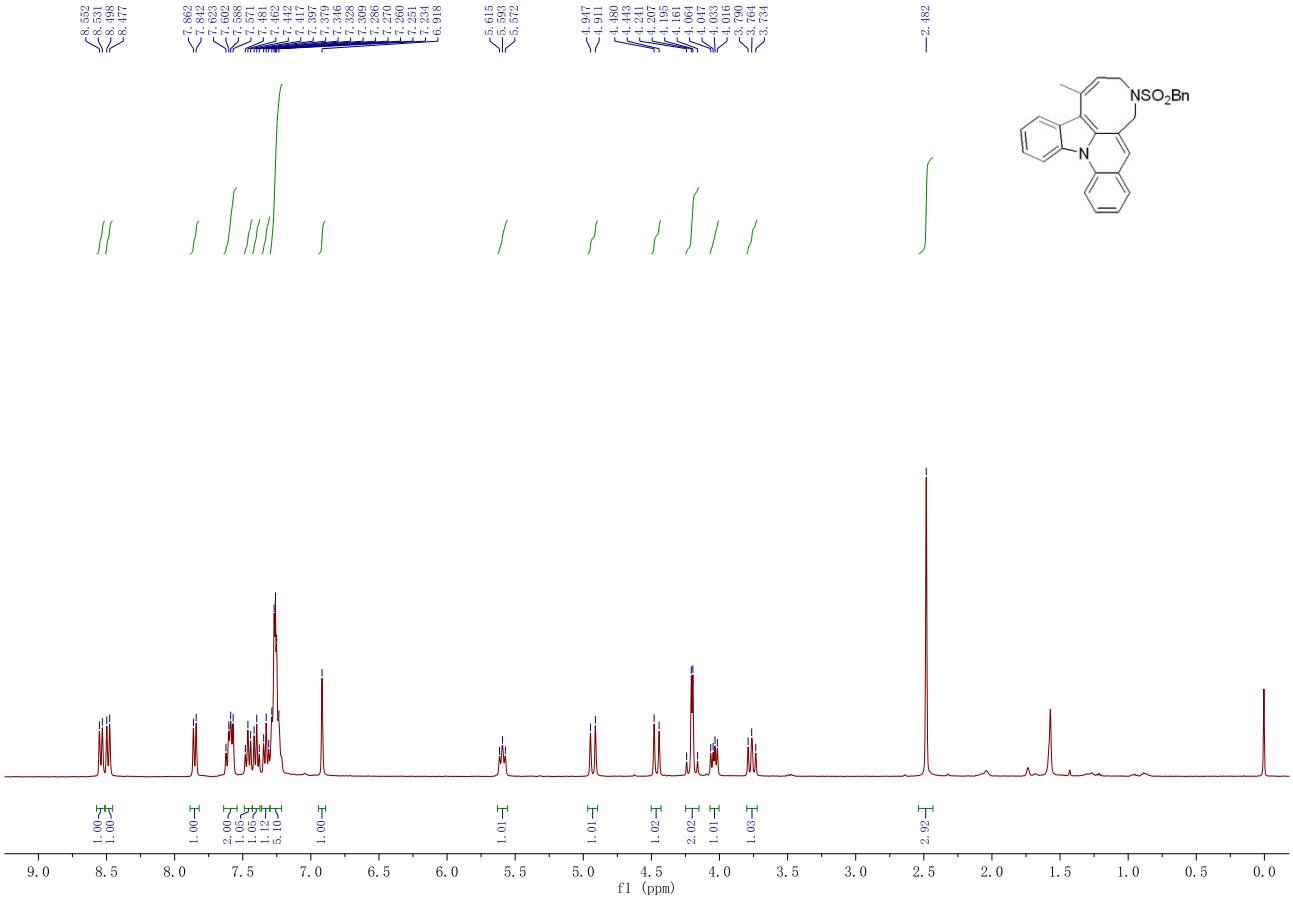
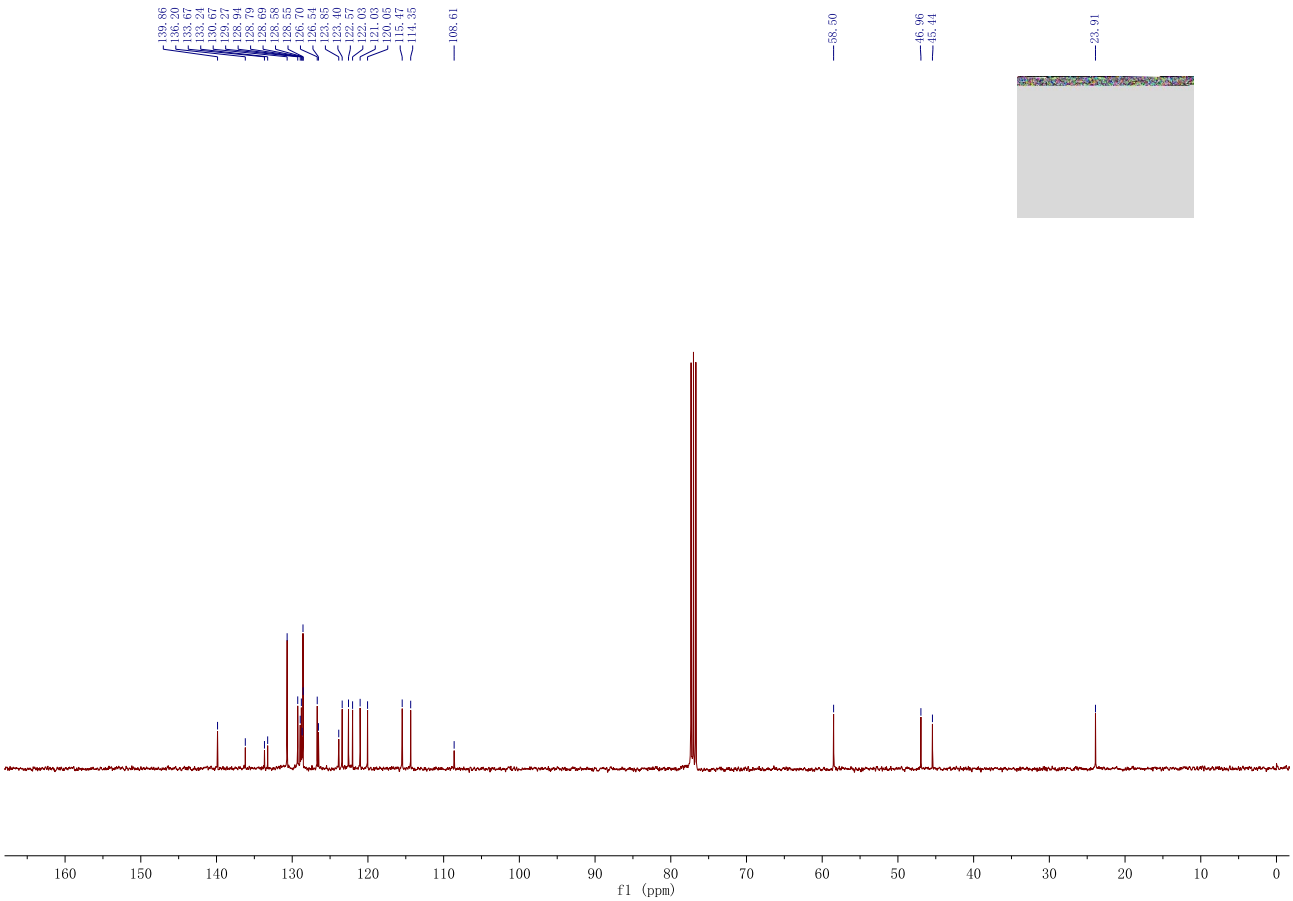
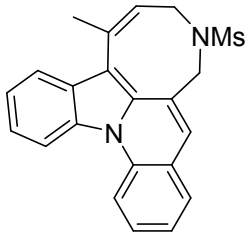
128.36
127.37
127.09
124.58
123.68
123.29
122.47
121.99
121.01
119.57
115.42
114.34
108.90
47.05
45.34
23.89
NSO2Ph
f1 (ppm)



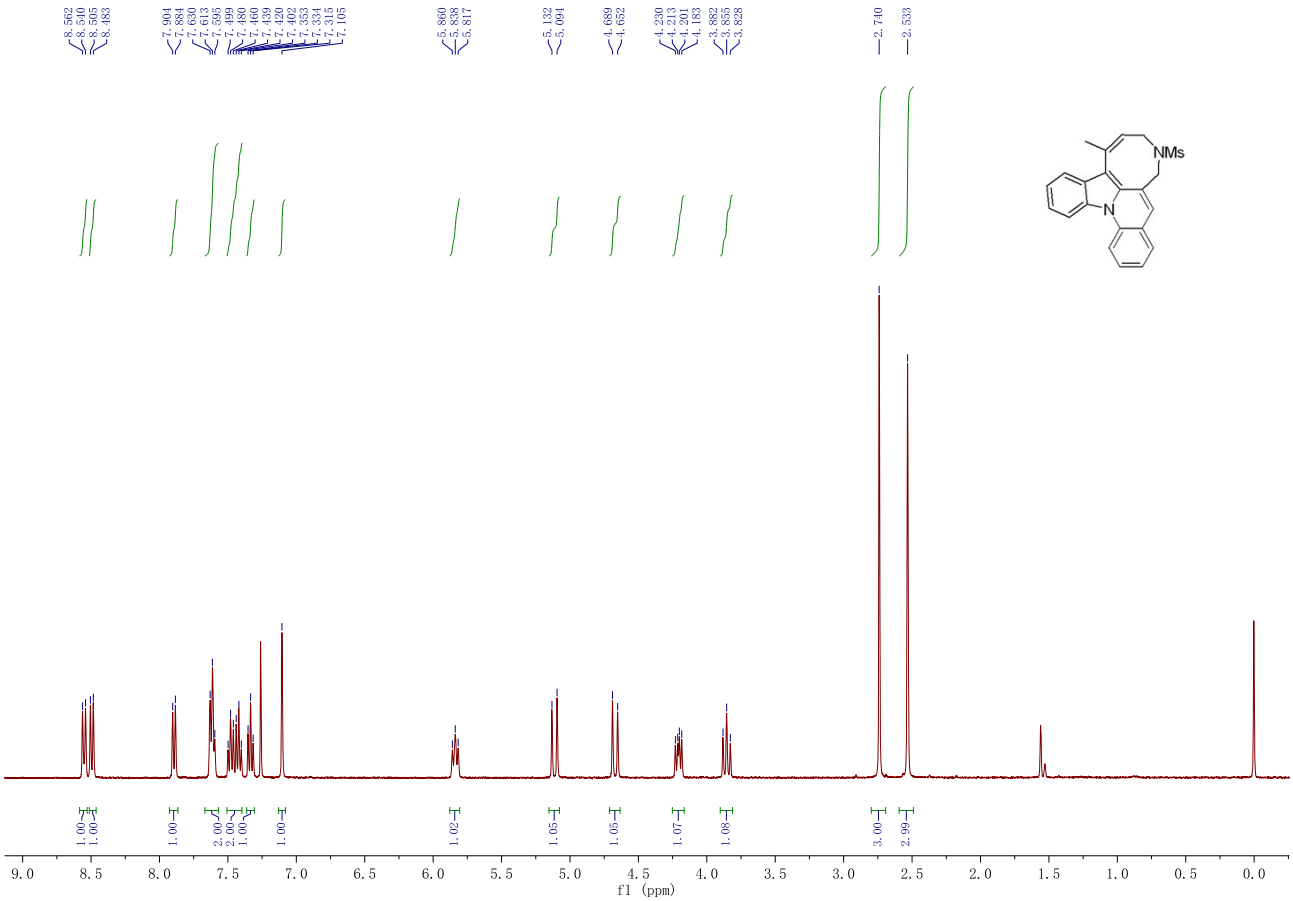
Compound 3b: yellow oil (41.1 mg, 91%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.48 (s, 3H), 3.76 (dd, *J* = 12.4 Hz, 1H), 4.04 (dd, *J* = 12.4, 7.0 Hz, 1H), 4.17 (d, *J* = 13.6 Hz, 1H), 4.22 (d, *J* = 13.6 Hz, 1H), 4.46 (d, *J* = 14.8 Hz, 1H), 4.93 (d, *J* = 14.8 Hz, 1H), 5.59 (dd, *J* = 12.4, 7.0 Hz, 1H), 6.92 (s, 1H), 7.22-7.30 (m, 5H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.40 (dd, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.54-7.64 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 23.9, 45.4, 47.0, 58.5, 108.6, 114.4, 115.5, 120.0, 121.0, 122.0, 122.6, 123.4, 123.9, 126.5, 126.7, 128.55, 128.58, 128.7, 128.8, 128.9, 129.3, 130.7, 133.2, 133.7, 136.2, 139.9. IR (neat) ν 2964, 2929, 2870, 1619, 1590, 1566, 1474, 1458, 1441, 1376, 1276, 1208, 1176, 1128, 1097, 1085, 1054, 1006, 978 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_2O_2S$ requires (M^++H): 453.1631, Found: 453.1627.







Compound 3c: A white solid (35.3 mg, 94%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.53 (s, 3H), 2.74 (s, 3H), 3.86 (dd, *J* = 12.0 Hz, 1H), 4.21 (dd, *J* = 12.0, 7.2 Hz, 1H), 4.67 (d, *J* = 14.8 Hz, 1H), 5.11 (d, *J* = 14.8 Hz, 1H), 5.84 (dd, *J* = 12.0, 7.2 Hz, 1H), 7.10 (s, 1H), 7.33 (dd, *J* = 7.6 Hz, 1H), 7.40-7.51 (m, 2H), 7.57-7.67 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 24.0, 37.7, 45.2, 47.1, 109.0, 114.5, 115.6, 119.9, 121.1, 122.2, 122.8, 123.5, 123.6, 125.8, 126.7, 128.69, 128.73, 129.5, 133.3, 133.6, 136.3, 140.3. IR (neat) ν 3044, 2946, 2925, 2858, 1614, 1581, 1466, 1454, 1425, 1396, 1372, 1354, 1336, 1281, 1261, 1240, 1213, 1155, 1129, 1089, 1070, 1024, 997 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{21}N_2O_2S$ requires (M^++H): 377.1318, Found: 377.1317.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7.420
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7.353
7.334
7.315
7.165
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5.838
5.817
5.132
5.094
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4.213
4.201
4.183
3.882
3.855
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1.00
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2.00
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1.00
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1.05
1.07
1.08
3.00
2.99
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6.0
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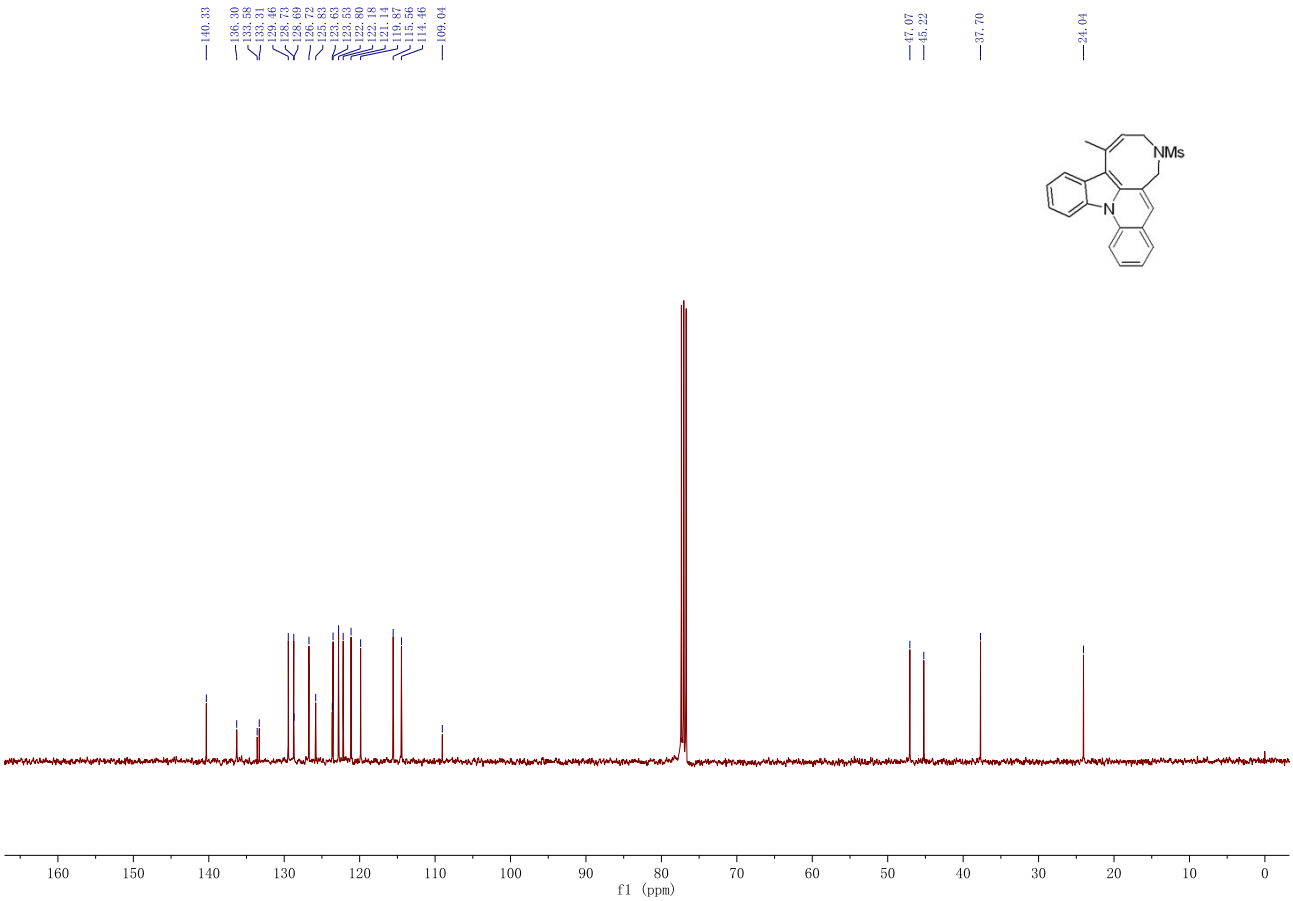
f1 (ppm)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114.46
109.04
47.07
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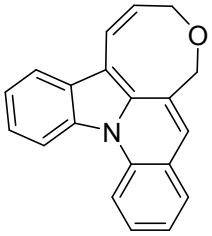
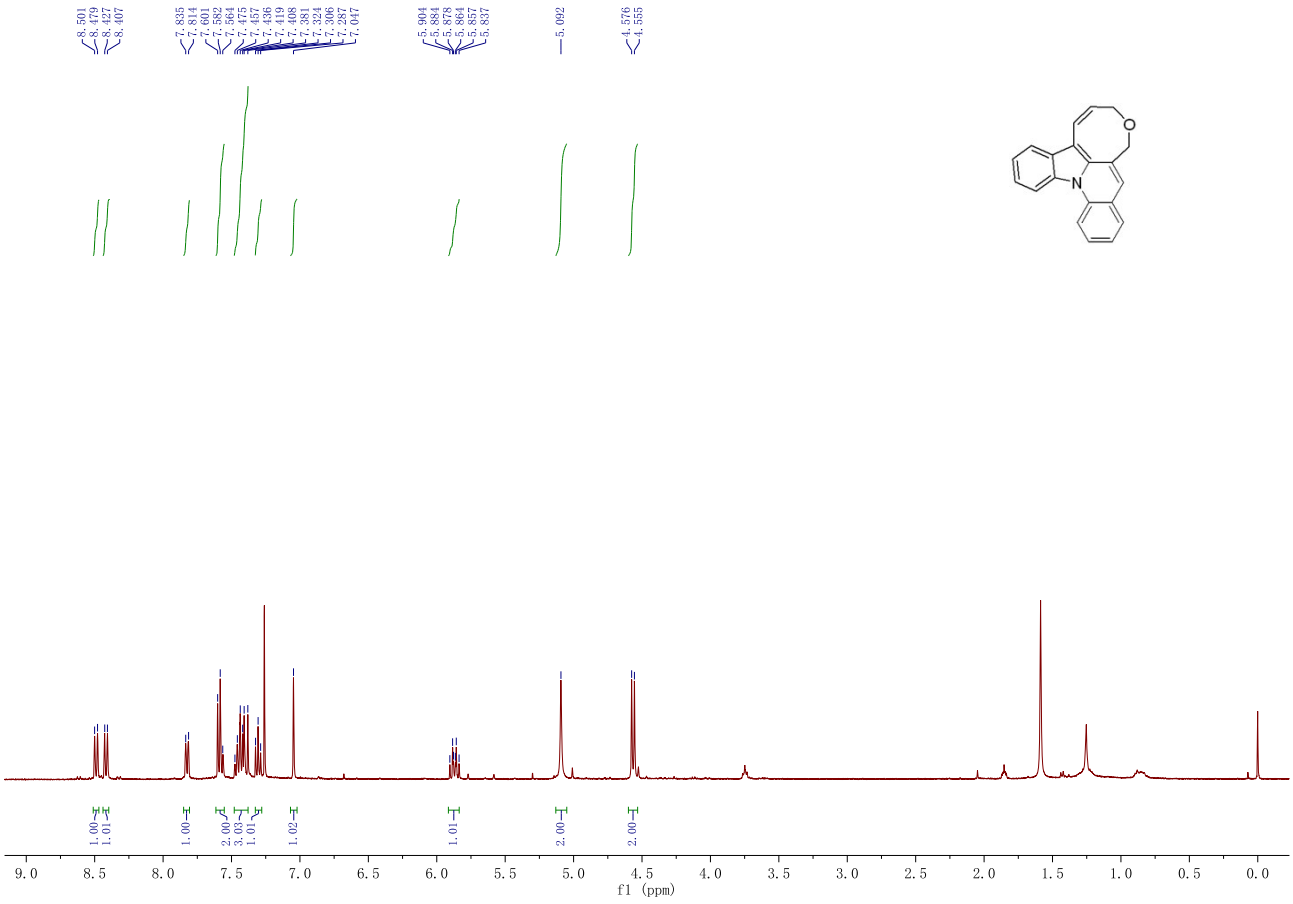
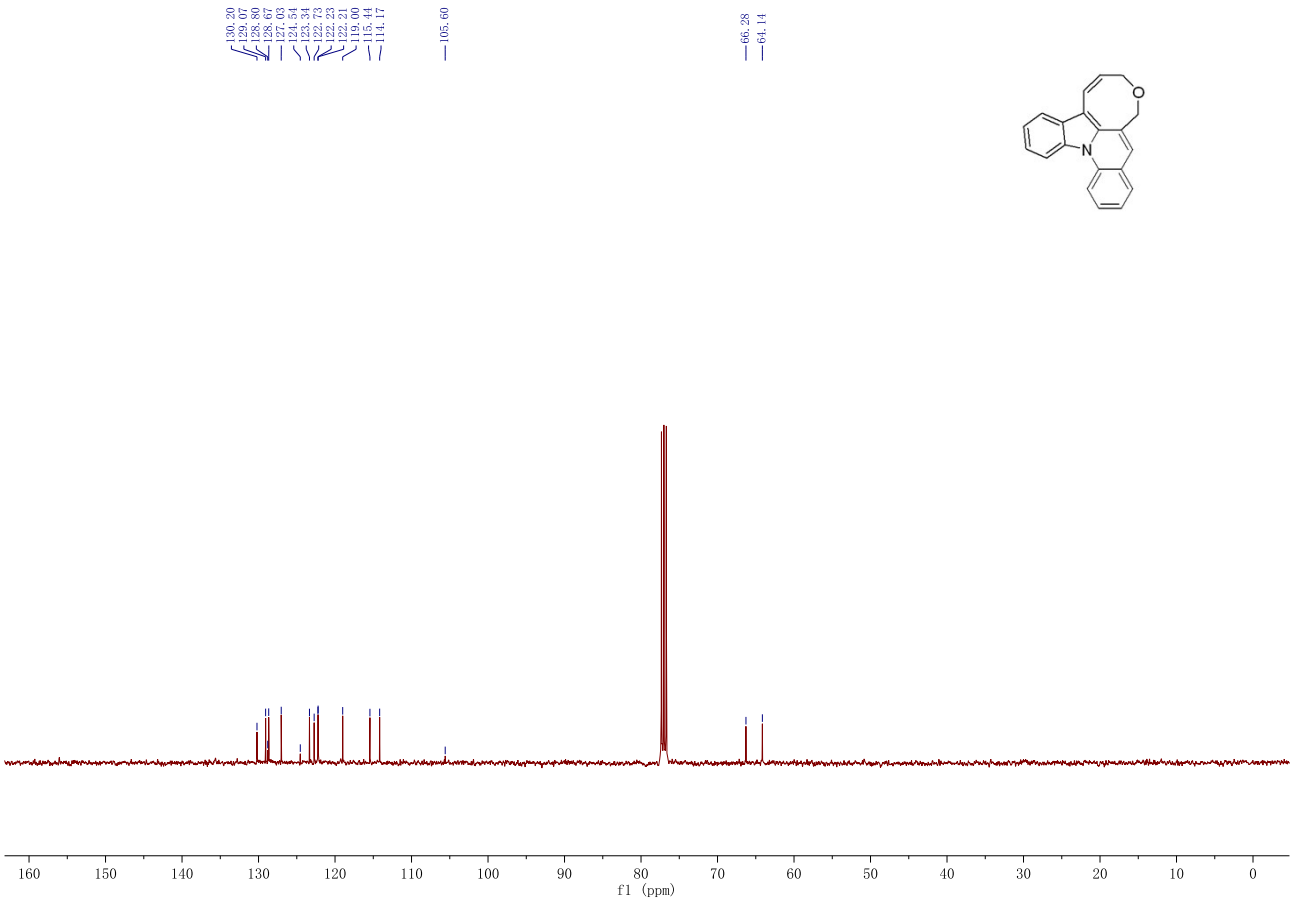
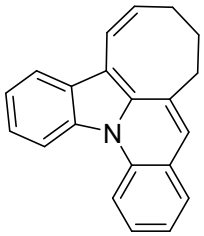
37.70
24.04
NMs
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



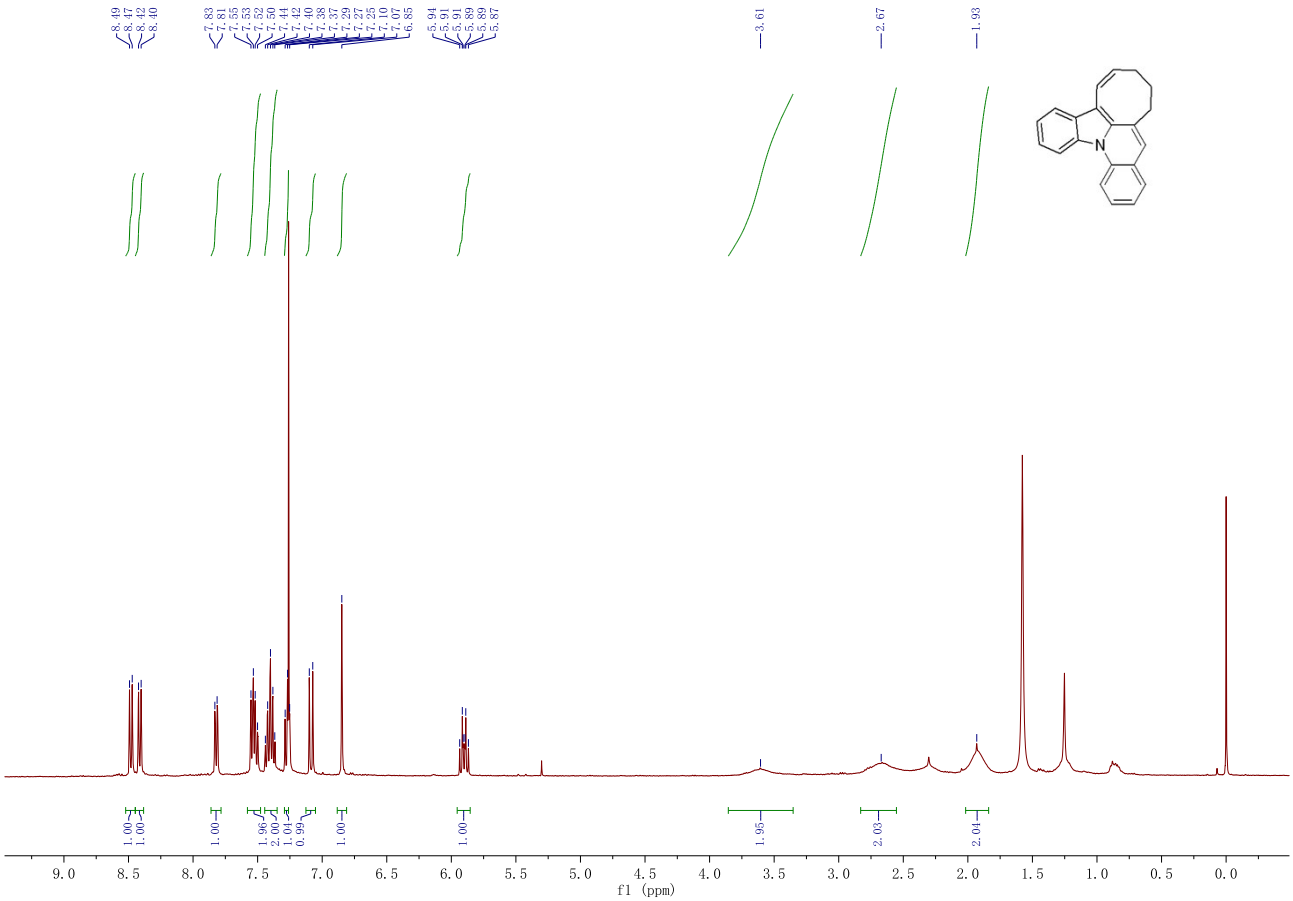
Compound 3e: yellow oil (23.3 mg, 82%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.56 (d, *J* = 8.4 Hz, 2H), 5.09 (s, 2H), 5.86 (dt, *J* = 10.8, 8.0 Hz, 1H), 7.05 (s, 1H), 7.30 (dd, *J* = 7.6 Hz, 1H), 7.38-7.48 (m, 3H), 7.56 (dd, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 64.1, 66.3, 105.6, 114.2, 115.4, 119.0, 122.21, 122.23, 122.7, 123.3, 124.5, 127.0, 128.7, 128.8, 129.1, 130.2. IR (neat) ν 2920, 2851, 1607, 1526, 1466, 1454, 1425, 1396, 1372, 1354, 1336, 1281, 1261, 1217, 1199, 1166, 1129, 1097, 1039, 1024, 995 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{16}NO$ requires (M^{+}+H): 286.1226, Found: 286.1229.

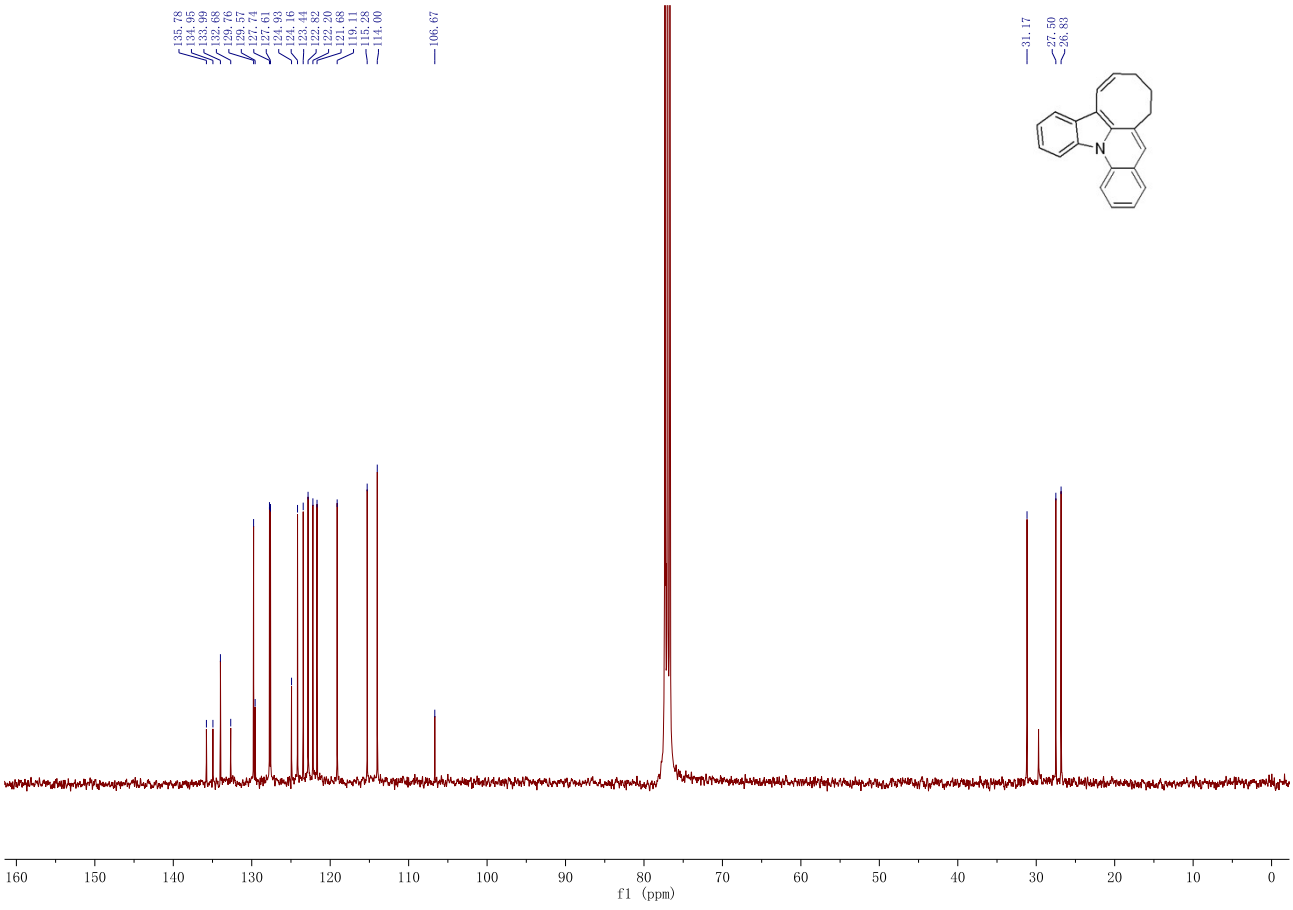




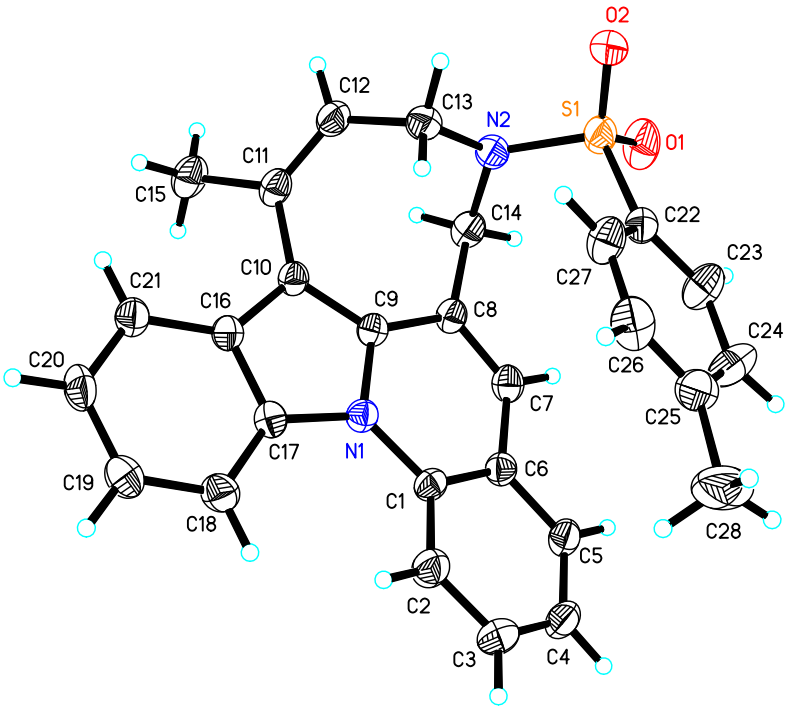


Compound 3f: green oil (12.1 mg, 43%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.93 (s, 2H), 2.67 (s, 2H), 3.61 (s, 2H), 5.90 (dt, *J* = 10.8, 8.2 Hz, 1H), 6.85 (s, 1H), 7.09 (d, *J* = 10.8 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.35-7.44 (m, 2H), 7.48-7.58 (m, 2H), 7.82 (d, *J* = 6.8 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 26.8, 27.5, 31.2, 106.7, 114.0, 115.3, 119.1, 121.7, 122.2, 122.8, 123.4, 124.2, 124.9, 127.6, 127.7, 129.6, 129.8, 132.7, 134.0, 134.9, 135.8. IR (neat) ν 2921, 2850, 1619, 1597, 1566, 1474, 1458, 1441, 1376, 1276, 1208, 1176, 1128, 1097, 1085, 1054, 1006, 978 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}N$ requires (M^{+}+H): 284.1434, Found: 284.1435.


8.49
8.47
8.42
8.40
7.83
7.81
7.55
7.53
7.52
7.50
7.44
7.42
7.40
7.38
7.37
7.29
7.27
7.25
7.10
7.07
6.85
5.94
5.91
5.89
5.87
3.61
2.67
1.93
N
1.00
1.00
1.00
1.96
2.00
1.04
0.99
1.00
1.00
1.95
2.03
2.04
f1 (ppm)

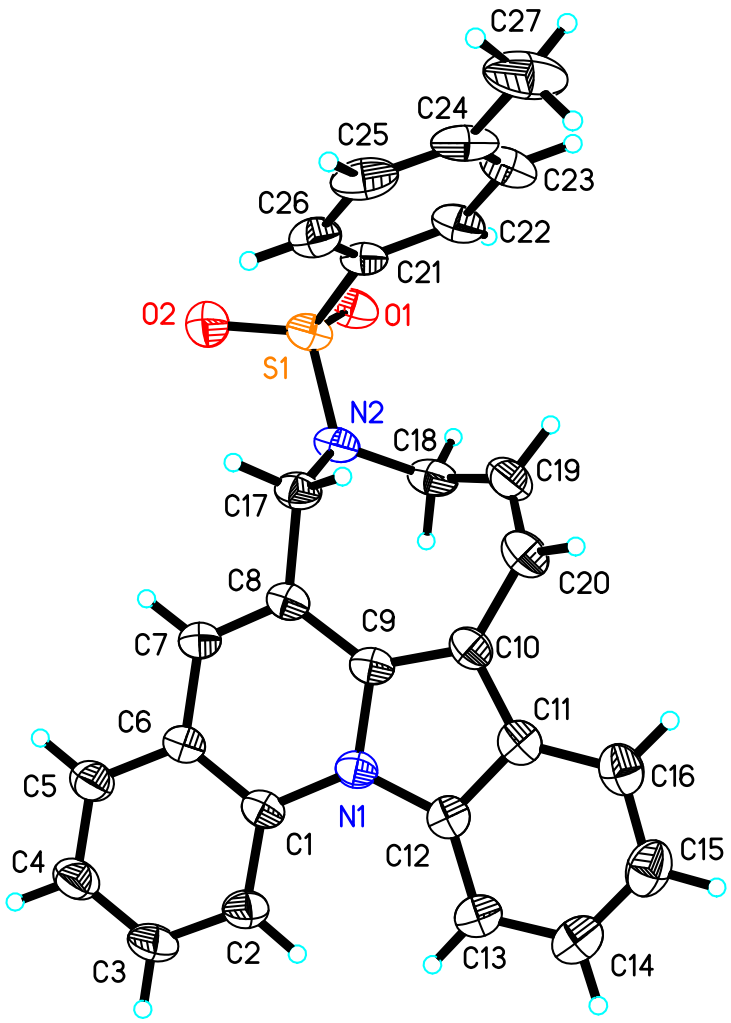

135.78
134.95
132.84
132.68
129.76
129.57
127.74
127.61
124.93
124.16
123.44
122.92
122.30
121.68
119.11
115.28
114.00
106.67
31.17
27.50
26.83
N
f1 (ppm)

(D) X-ray Crystal Data of Compounds 2a



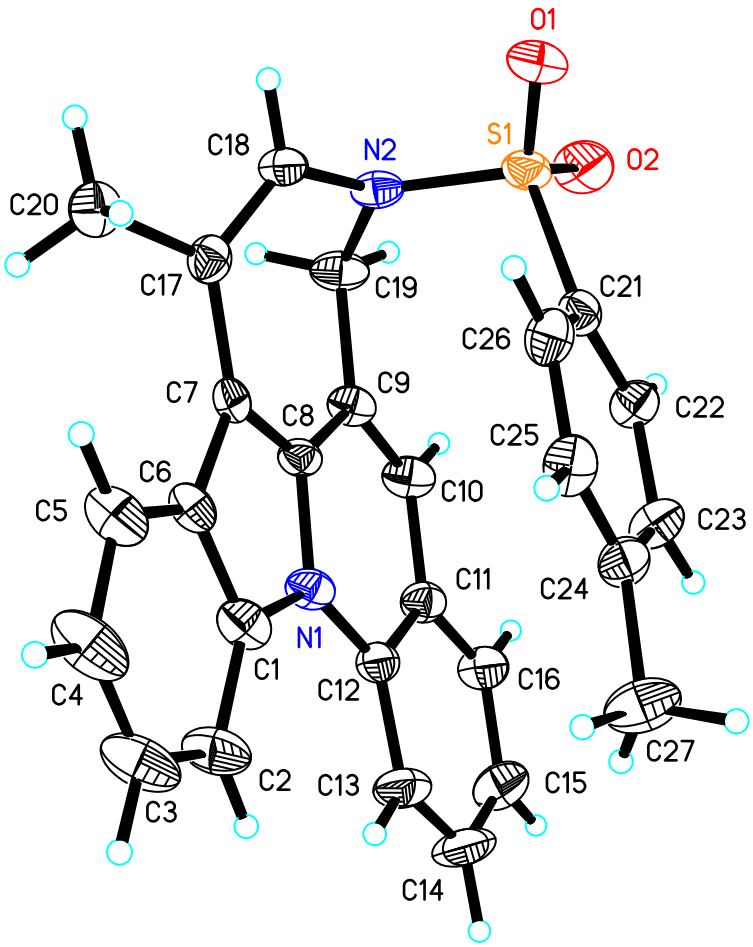
The crystal data of **2a** have been deposited in CCDC with number 1518151. Empirical formula: $C_{28}H_{24}N_2O_2S$, Formula weight: 452.55, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 11.2498(12) Å, α = 70.203(2)°; b = 12.7345(14) Å, β = 82.010(2)°; c = 16.7793(19) Å, γ = 81.806(3)°. Volume: 2228.0(4) $Å^3$, Z = 4, Density (calculated): 1.349 Mg/m^3, F(000) = 952, Crystal size: 0.200 x 0.170 x 0.140 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0634, wR2 = 0.1448.

X-ray Crystal Data of Compound 2ba



The crystal data of **2ba** have been deposited in CCDC with number 1544297. Empirical formula: $C_{27}H_{22}N_2O_2S$, Formula weight: 438.52, Crystal system: Orthorhombic, Space group: P -1, Unit cell dimensions: a = 9.219(2) Å, α = 91.398(4)°; b = 10.845(2) Å, β = 102.876(5)°; c = 10.965(2) Å, γ = 92.881(5)°. Volume: 1066.7(4) $Å^3$, Z = 2, Density (calculated): 1.365 Mg/m^3, F(000) = 460, Crystal size: 0.180 x 0.150 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0576, wR2 = 0.1330.

X-ray Crystal Data of Compound 2bb



The crystal data of **2bb** have been deposited in CCDC with number 1557465. Empirical formula: $C_{27}H_{22}N_2O_2S$, Formula weight: 438.52, Crystal system: Monoclinic, Space group: P 21/c, Unit cell dimensions: a = 14.938(5) Å, α = 90°; b = 7.167(2) Å, β = 90.970(7)°; c = 19.366(7) Å, γ = 90°. Volume: 2073.0(12) $Å^3$, Z = 4, Density (calculated): 1.405 Mg/m^3, F(000) = 920, Crystal size: 0.200 x 0.170 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0918, wR2 = 0.1966.