# An Efficient Approach to 1,2,3-Trisubstituted Indole Via Rhodium Catalyzed Carbene $C_{sp3}$-H Bond Insertion

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## Supporting Information Contents

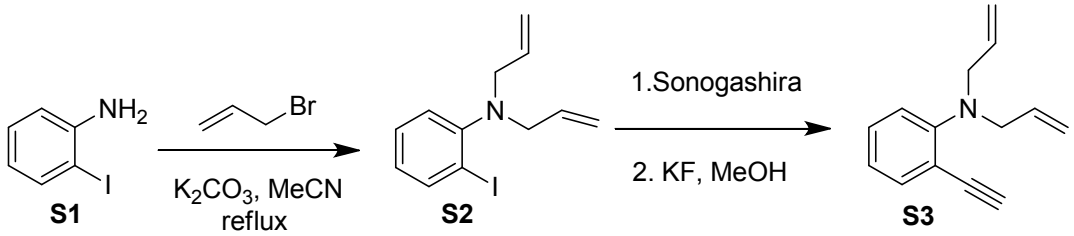


## General information and materials

$^{1}H$ NMR and $^{13}C$ NMR spectra were recorded using Bruker AV-400 / AV-500 spectrometers in $CDCl_3$. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectral analysis (HRMS) data were recorded by ElectroSpray Ionization (ESI). The parent ions $[M + H]^+$, $[M + Na]^+$ or $[M + K]^+$ are quoted. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 μm) mesh silica gel ($SiO_2$). All reactions were carried out with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

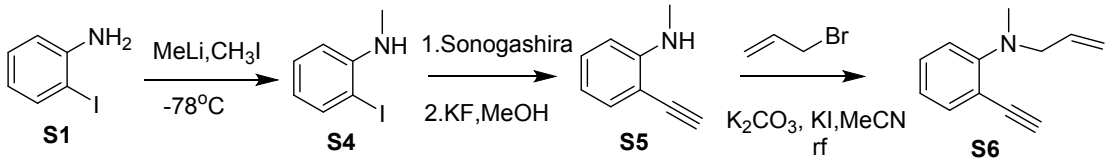
## I. Preparation of Triazole Substrates

### A. Alkyne Synthesis

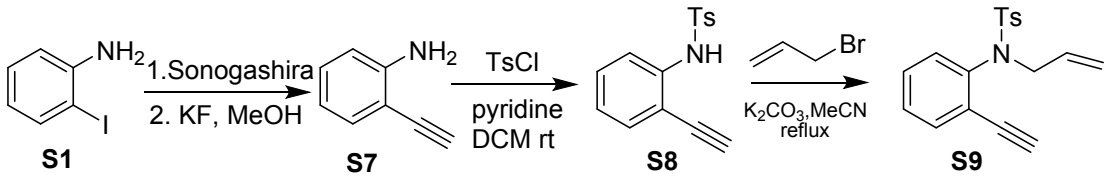



**Alkyne S3**. To a solution of **S1** (2.19 g, 10 mmol) in dry MeCN was added bromo alkyne (1.3 g, 11 mmol) and $K_2CO_3$ (1.6 g, 12 mmol) under nitrogen. The resulting mixture was heated to reflux overnight. The mixture was cooled to rt before quenched with $H_2O$ (5 ml). The resulting two phases were separated, and the aqueous phase was extracted with EtOAc (8 ml) for three times. The combined organic phases were washed with brine and dried over $Na_2SO_4$. Filtration and evaporation led to a residue. Purification of the residue by flash chromatography on silica gel using PE/EA as the eluent provided the desired product **S2:** 2.7 g, colorless oil, 90%. [1]

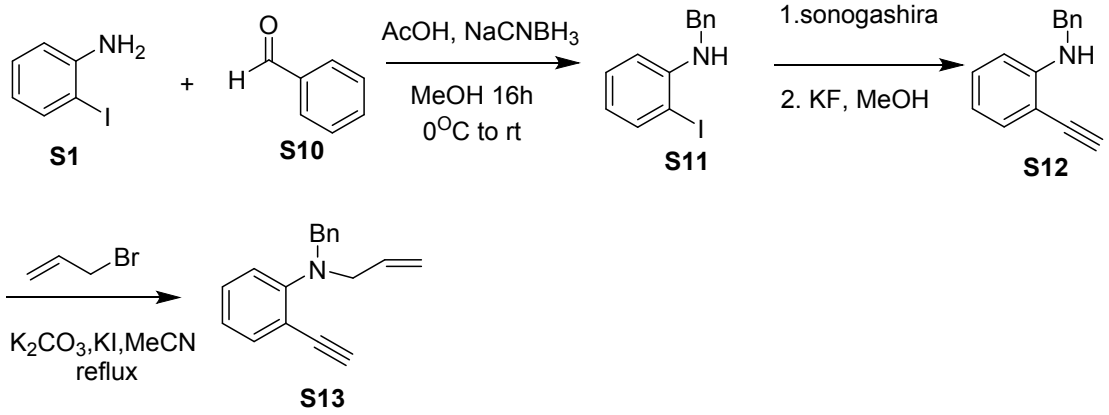
To a solution of the above prepared **S2** (2.7 g, 9 mmol) in $Et_3N$ (20 ml) under nitrogen were added TMS-acetylene (1 g, 11 mmol), $Pd(PPh_3)_4Cl_2$ (315 mg, 0.45 mmol) and CuI (171mg, 0.9mmol). The reaction mixture was stirred at room temperature for 24 h. $Et_2O$ (20 ml) and 1 N aqueous HCl (15 ml) were added, then the organic layer was separated, washed with brine, dried over $MgSO_4$, then evaporated. The residue was dissolved in MeOH (25 mL). KF (2.8 g, 30 mmol) was then added and the reaction mixture was stirred at room temperature. After 12 h, the organic layer was separated, washed with brine, dried over $MgSO_4$ and evaporated followed by a silica gel column chromatography to afford terminal alkyne **S3**: 1.59 g, 90%, yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22-6.87 (m, 3H), 5.86 (m, 2H), 5.20(d, *J*= 15.5 Hz, 2H), 5.17 (d, *J*= 8.7 Hz, 2H), 3.90 (d, *J* = 5.9 Hz, 4H), 3.37 (s, 1H). The $^1$H NMR matches the reported literature.[2]



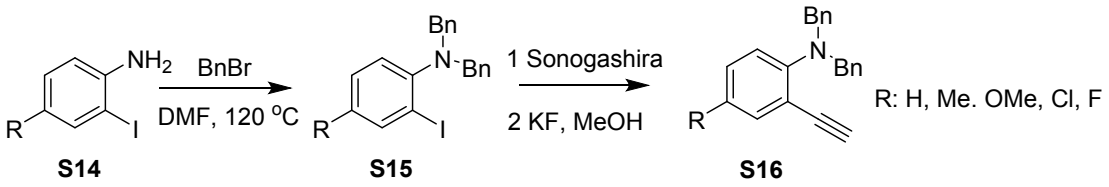

**Alkyne S6** was prepared from **S4**, which were prepared following the method reported by Nakamura and co-workers[3], by Sonogashira coupling followed by allylation with similar procedures as **S3**.



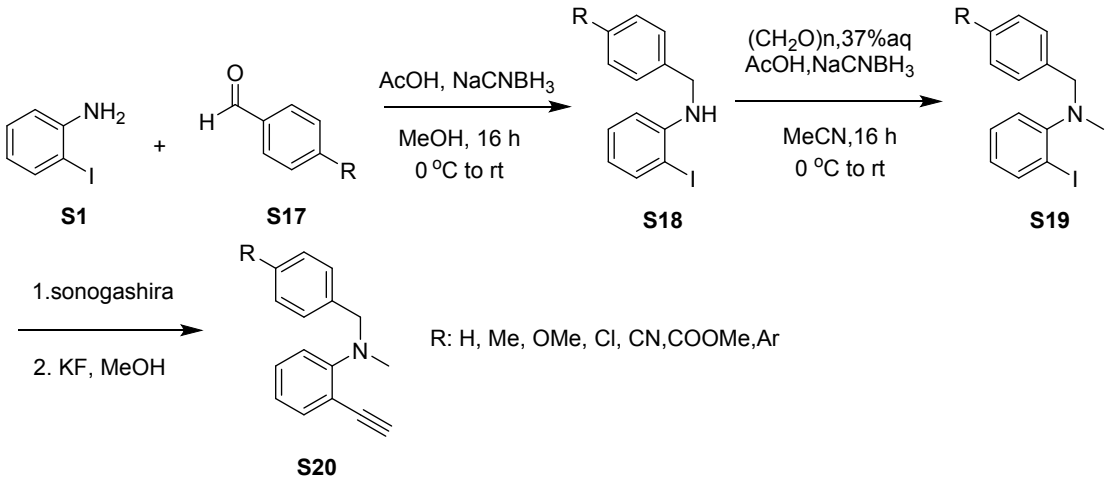
**Alkyne S9** was prepared from **S8**, which were prepared following the method reported by Swamy and co-workers[4], by allylation with similar procedures as **S3**.



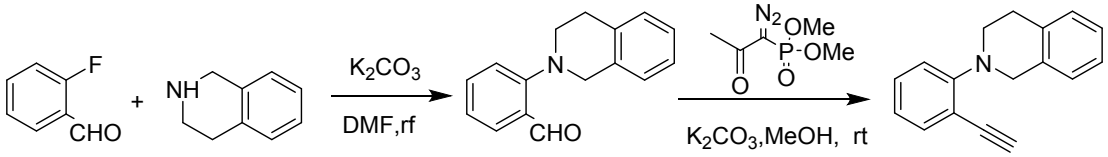

**Alkyne S13** was prepared from **S11**, which was prepared following the method reported by Roman and co-workers[5], by Sonogashira coupling followed by allylation with similar procedures as **S3**.




**Alkynes S16** were prepared from **S15**, which were prepared following the method reported by Zhu and co-workers[6], by Sonogashira coupling with similar procedures as **S3**.



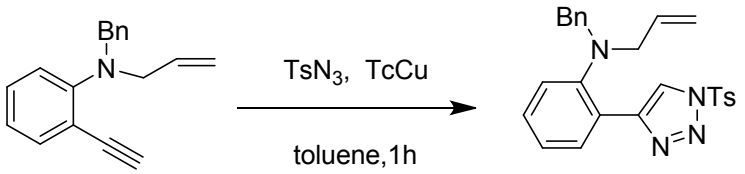

**Alkynes S20** were also prepared by reductive amination[5] and Sonogashira coupling[2] following the similar methods reported in literatures.




**S21** **S22** **S23** **S24**

**Alkyne S24** was prepared by aromatic substitution[7] and Ohira-Bestmann homologation[8] following the methods reported in literatures.

**B. Typical Procedure for Triazoles**

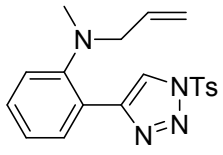



**S12** **3d**

CuTc (95.0 mg, 0.5 mmol) and $TsN_3$ (1.09 g, 5.5 mmol) were successively added to a solution of N-allyl-N-benzyl-2-ethynylaniline **S12** (1.23 g, 5.0 mmol) in toluene (20 mL) in a 50 mL flask equipped with a stirrer bar. The reaction mixture was stirred for 1 h at room temperature. The resulting mixture was quenched with saturated $NH_4Cl$ aq solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel using PE/EA (7:1) as the eluent to give triazole **3d** as a white solid (1.95 g, 88%)，mp = 140-143°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.17 (d, *J* = 7.3 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.26-7.23 (m, 4H), 7.18-7.10 (m, 4H), 5.84 – 5.66 (m, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.11(d, *J* = 17.2 Hz, 1H), 4.10 (s, 2H), 3.41 (d, *J* = 5.8 Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.2, 144.7, 137.3, 133.7, 133.4, 130.5, 129.2, 129.1, 129.0, 128.6, 128.3, 127.3, 125.2, 124.5, 123.6, 122.1, 118.8, 56.8, 55.9, 21.9. HRMS (ESI) m/z calcd for $C_{25}H_{25}N_4O_2S^+$([M+H]$^+$): 445.1693. Found: 445.1698.

**C. Triazoles**

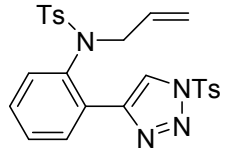
The following triazoles were prepared from the above corresponding alkynes following the typical procedure.




**3b**

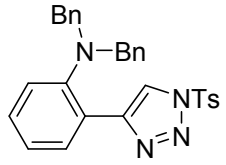
**3b**: 91%，white solid, mp = 79-82°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.14 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.22 – 7.11 (m, 2H), 5.75 (m, 1H), 5.18-5.13 (m, 2H), 3.42 (d, *J* = 6.2 Hz, 2H), 2.62 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.7,

134.5, 133.4, 130.4, 129.5, 129.2, 128.6, 124.3, 124.1, 122.1, 121.2, 118.3, 59.7, 41.1, 21.9. HRMS (ESI) m/z calcd for $C_{19}H_{21}N_4O_2S^+$([M+H]$^+$): 369.1380. Found: 369.1382.



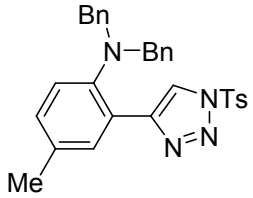

**3c**

**3c**: 91%; white solid, mp = 120-123°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.18 (dd, *J* = 7.9,1.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.40-7.36 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.25-7.21 (m, 1H), 6.69 (d, *J* = 7.3 Hz 1H), 5.41 (m, 1H), 4.89-4.82 (m, 2H), 4.29 (s, 1H), 3.83 (s, 1H), 2.43 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.3, 144.3, 143.8, 136.5, 135.2, 133.4, 131.3, 131.3, 130.5, 129.8, 129.7, 129.3, 129.1, 128.7, 128.6, 128.1, 123.1, 120.2, 54.9, 21.8, 21.6. HRMS (ESI) m/z calcd for $C_{25}H_{25}N_4O_4S_2^+$([M + H]$^+$): 509.1312. Found: 509.1315.



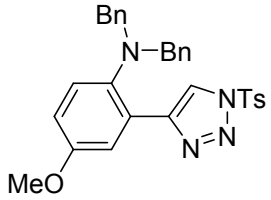

**3e**

**3e**: red oil, 40%. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.16 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 7H), 7.18-7.14 (m, 1H), 7.09-7.07 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 1H), 3.98 (s, 4H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.7, 147.2, 144.8, 137.0, 133.5, 130.5, 129.4, 129.3, 128.6, 128.3, 127.4, 127.1, 124.9, 124.4, 124.0, 122.1, 56.8, 21.9. HRMS (ESI) m/z calcd for $C_{29}H_{27}N_4O_2S^+$([M + H]$^+$): 495.1849. Found: 495.1843 .



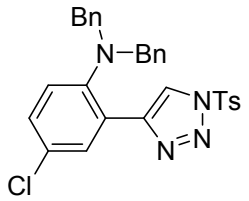

**3f**

**3f**: red oil, 30%. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.16 (m, 6H), 7.02-6.95 (m, 5H), 6.81 (d, *J* = 7.1 Hz, 1H), 3.89 (s, 4H), 2.35 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 147.1, 146.1, 144.8, 137.1, 134.0, 133. 5, 130.4, 129.9, 129.6, 129.3, 128.5, 128.3, 127.3, 124.7, 123.9, 122.1, 57.1, 21.9, 20.9. HRMS (ESI) m/z calcd for $C_{30}H_{29}N_4O_2S^+$([M + H]$^+$): 509.2006. Found: 509.2007



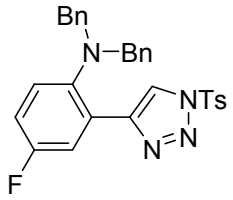

**3g**

**3g**: red oil, 28%. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.26-7.10 (m, 10H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.87 – 6.79 (m, 1H), 3.99 (s, 4H), 3.83 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.5, 147.1, 144.4, 141.5, 137.1, 133.5, 130.4, 129.4, 128. 6, 128.2, 127.3, 126.6, 125.6, 122.5, 115.7, 112.6, 57.9, 55.6, 21.8. HRMS (ESI) m/z calcd for $C_{30}H_{29}N_4O_3S^+$([M + H]$^+$): 525.1955. Found: 525.1957.



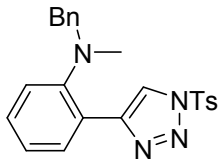

**3h**

**3h**: red oil, 29%. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.17 (d, *J* = 2.5 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 6H), 7.17-7.07 (m, 5H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 4H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.3, 147.0, 143.6, 136.6, 133.3, 130.5, 129.9, 129.2, 129.0, 128.6, 128.4, 127.6, 126.7, 125.5, 122.5, 57.0, 21.9. HRMS (ESI) m/z calcd for $C_{29}H_{26}N_4O_2SCl^+$([M + H]$^+$): 529.1460. Found: 529.1458.




**3i**

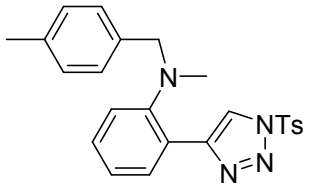
**3i**: red oil, 26%. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.95 – 7.90 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.21 (m, 6H), 7.10 – 7.05 (m, 4H), 6.97 – 6.91 (m, 2H), 3.99 (s, 4H), 2.44 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ$^{13}$C NMR (101 MHz, $CDCl_3$) δ 160.84, 158.42, 147.35, 144.31, 143.55, 136.66, 133.33, 130.52, 129.38, 128.61, 128.36, 126.0 (d, $J_{CF}$ = 8.51 Hz), 125.96, 122.61, 115.8 (d, $J_{CF}$ = 22.2 Hz), 115.4 (d, $J_{CF}$ = 24.3 Hz), 57.55, 21.87. HRMS (ESI) m/z calcd for $C_{29}H_{26}N_4O_2SF^+$([M + H]$^+$): 513.1755. Found: 513.1759.




**3j**

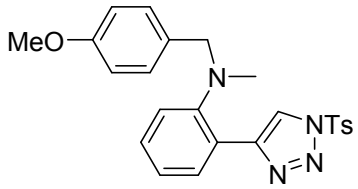
**3j**: 88%, white solid, mp = 91-94°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.19 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.26 (m, 6H), 7.22 – 7.14 (m, 4H), 4.04 (s, 2H), 2.51 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.2, 144.7, 137.6, 133.4, 130.5, 129.7, 129.2, 128.9, 128.5, 128.4, 127.4, 124.4, 124.2, 122.2, 121.6, 60.6, 41.8, 21.9.

HRMS (ESI) m/z calcd for $C_{23}H_{23}N_4O_2S^+$ ([M +H]$^+$): 419.1536. Found: 419.1540.



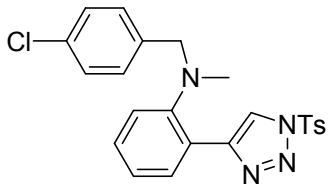

**3k**

**3k**: 89%, white solid, mp = 116-119°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.20-7.18 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.01 (s, 2H), 2.52 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.2, 144.7, 136.9, 134.5, 133.5, 130.5, 129.6, 129.1, 128.9, 128.5, 124.4, 124.2, 122.2, 121.7, 60.3, 41.7, 21.9, 21.2. HRMS (ESI) m/z for $C_{24}H_{25}N_4O_2S^+$ ([M + H]$^+$): 433.1693. Found: 433.1685.



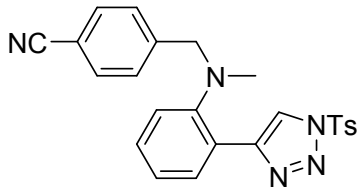

**3l**

**3l**: 92%, white solid, mp = 120-122°C. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.17 (d, *J* = 7.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.26-7.16 (m,3H), 7.13 (t, *J* = 7.1 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 2H), 3.77 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.5, 147.1, 144.4, 141.5, 137.1, 133.5, 130.4, 129.4, 128.6, 128.3, 127.3, 126.6, 125.6, 122.5, 115.7, 112.6, 57.9, 55.6, 41.6，21.8. HRMS (ESI) m/z for $C_{24}H_{25}N_4O_3S^+$ ([M + H]$^+$): 449.1642. Found: 449.1645.



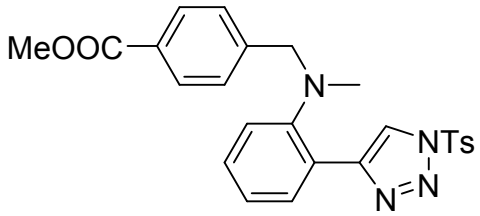

**3m**

**3m**: 91%, white solid, mp = 130-132°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32-7.27 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.15 (dd, *J* = 14.2, 7.6 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.99 (s, 2H), 2.52 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.3, 144.6, 135.9, 133.3, 133.1, 130.5, 130.2, 129.7, 129.4, 128.6, 128.5, 124.4, 122.0, 121.6, 59.9, 41.8, 21.9. HRMS (ESI) m/z calcd for $C_{23}H_{22}ClN_4O_2S^+$ ([M+H]$^+$): 453.1147. Found: 453.1136.



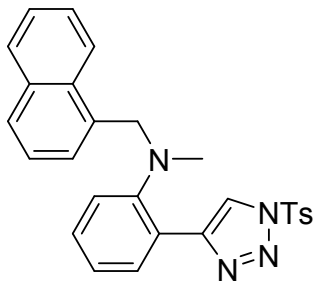
**3n**

**3m**: 71%, white solid, mp = 110-112°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.21 – 7.08 (m, 2H), 4.10 (s, 2H), 2.57 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.9, 147.4, 144.5, 143.0, 133.1, 132.2, 130.5, 129.8, 129.5, 129.3, 128.6, 124.6, 124.4, 121.9, 121. 5, 118.8, 111.2, 60.2, 42.2, 21.9. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_5O_2S^+$ ($[M+H]^+$):444.1489.Found: 444.1491.



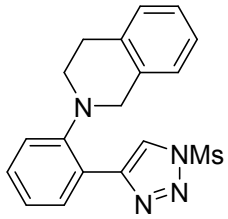
**3o**

**3o**: 65%, white solid, mp = 97-99°C. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.17 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.05 – 7.88 (m, 4H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.11 (m, 4H), 4.08 (s, 2H), 3.91 (s, 3H), 2.55 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.9, 150.3, 147.3, 144.5, 142.8, 133.3, 130.5, 129.7, 129.3, 129.2, 128.7, 128.6, 124.4, 124.4, 121.9, 121.5, 60.3, 52.3, 42.1, 21.9. HRMS (ESI) m/z calcd for $C_{25}H_{25}N_4O_4S^+$ ($[M+H]^+$): 447.1591. Found: 447.1590.



**3p**

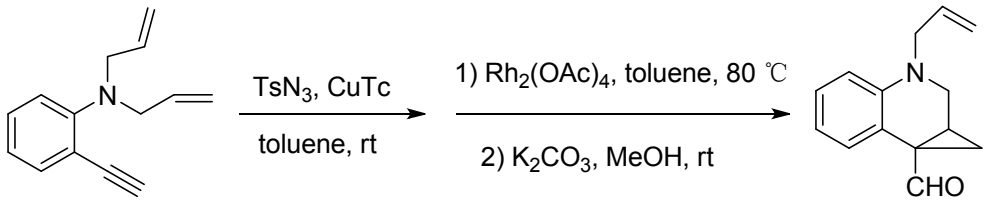
**3p**: 45%, white solid, mp = 111-113°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.21 (d, *J* = 7.3 Hz, 1H), 7.97 (t, *J* = 7.1 Hz, 2H), 7.88 (d, *J* = 6.0 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 3H), 7.50 – 7.36 (m, 5H), 7.26 – 7.13 (m, 3H), 4.53 (s, 2H), 2.35 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 146.9, 144.5,134.1, 133.6, 133.2, 132.1, 130.2, 129.9, 129.3, 128.9, 128.6, 128.4, 127.8, 126.3, 125.9, 125.3, 124.4, 124.3, 124.2, 122.4, 121.0, 57.9, 42.9, 21.8. HRMS (ESI) m/z calcd for $C_{27}H_{25}N_4O_2S^+$ ($[M+H]^+$): 469.1693. Found: 469.1690.




**3q**

**3q**: yellow oil, 25%. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.34 – 7.25 (m, 1H), 7.19 – 7.14 (m, 2H), 7.13-7.11 (m, 2H), 7.08 – 7.03 (m, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 3.95 (s, 2H), 3.28 (s, 3H), 3.19 (t, *J* = 5.9 Hz, 2H), 2.89 (t, *J* = 5.9 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 150.5, 144.8, 134.6, 134.0, 130.1, 129.2, 129.2, 126.7, 126.1, 125.9, 124.4, 124.2, 121.9, 120.8, 55.1, 50.1, 42.6, 29.2. HRMS (ESI) m/z for $C_{18}H_{19}N_4O_2S^+$([M+H]$^+$): 355.1223. Found: 355.1226.

## II. Syntesis of Tricyclic Aldehyde 7a

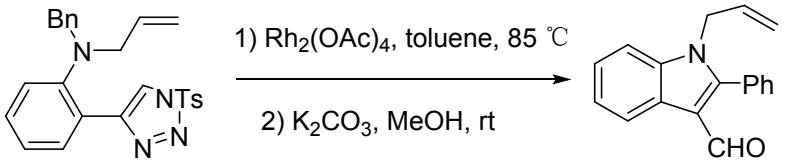



**S3** **7a**

CuTc (95.0 mg, 0.5 mmol) and $TsN_3$ (1.09 g, 5.5 mmol) were successively added to a solution of N,N-diallyl-2-ethynylaniline **S3** (985 mg, 5.0 mmol) in toluene (20 mL) in a 50 mL flask equipped with a stirrer bar. The reaction mixture was stirred for 1 h at room temperature.Then $Rh_2(OAc)_4$ (28 mg, 2 mol%) were added to the flask. The reaction mixture was stirred for 2 h at 80 $^o$C under nitrogen. Then it was cooled to room temperature and concentrated under reduced pressure. The resulting residue was diluted with methanol (4 mL), then $K_2CO_3$ (2.72 g, 20mmol) was added to the mixture. The new reaction mixture was stirred at room temperature overnight. Then the mixture was filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel using PE/EA as the eluent to give aldehyde **7a**: 630 mg, 60%, amorphous solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.17-7.11 (m, 1H), 6.84-6.78 (m, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.86 (m, 1H), 5.27–5.21 (m, 1H), 5.20-5.19 (m, 1H), 4.00–3.89 (m, 1H), 3.72 (m, 1H), 3.36–3.24 (m, 2H), 2.21-2.41 (m, 1H), 1.83 (dd, *J* = 8.6, 4.0 Hz, 1H), 1.76 (dd, *J* = 6.6, 4.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.3, 143.1, 133.2, 127.8, 127.3, 121.6, 118.0, 117. 7, 112.6, 53.5, 45.2, 32.1, 31.7, 19.5. HRMS (ESI) m/z for $C_{14}H_{16}NO^+$ ([M + H]$^+$): 214.1226. Found: 214.1227.

## III. Synthesis of 3-Formyl Indole and Benzofuran from Triazoles

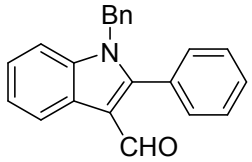
### A. Typical Procedure




**3d** **4d**

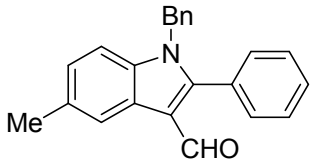
Triazole **3d**(177 mg, 0.4 mmol) and $Rh_2(OAc)_4$ (3 mg, 2 mol%) were added to a 25 mL round bottom flask equipped with a stirrer bar, then 4 mL of toluene was added to the flask. The reaction mixture was stirred for 2 h at 85 °C under nitrogen. Then it was cooled to room temperature and concentrated under reduced pressure. The resulting residue was diluted with methanol (4 mL), then $K_2CO_3$ (220 mg, 1.6 mmol) was added to the mixture. The new reaction mixture was stirred at room temperature overnight. Then the mixture was filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel using PE/EA as the eluent to give aldehyde **4d**: 49 mg, 47%, white solid, mp = 133-135°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.49 – 8.40 (m, 1H), 7.57 – 7.48 (m, 5H), 7.38-7.34 (m, 3H), 6.02 – 5.86 (m, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 4.97 (d, *J* = 17.1 Hz, 1H), 4.74 – 4.54 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.7, 151.7, 136.8, 132.4, 130.8, 130.1, 128.7, 128.5, 125.3, 124.2, 123.4, 122.3, 117.6, 116.0, 110.6, 46.6. The $^1$H NMR matches the reported literature.[9]

**B. 3-Formyl Indoles 4e-4n and Benzofuran 4o**



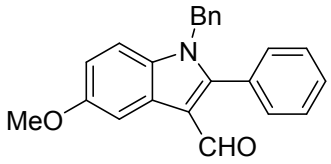

**4e**

**4e**: 65%, white solid, mp = 155-157°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.37 – 7.32 (m, 1H), 7.30 – 7.22 (m, 5H), 7.00 – 6.93 (m, 2H), 5.29 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.8, 152.0, 136.9, 136.4, 130.8, 130.1, 129.0, 128.7, 128.5, 127.8, 126.0, 125.5, 124.3, 123.5, 122.3, 116.2 110.9, 47.8. The $^1$H NMR matches the reported literature.[6]



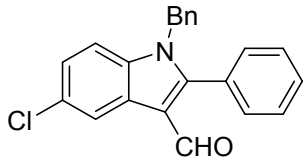

**4f**

**4f**: yellow oil, 72%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.27 (s, 1H), 7.54 – 7.38 (m, 5H), 7.27-7.24 (m, 3H), 7.11-7.10 (m, 2H), 6.97-6.95 (m, 2H), 5.26 (s, 2H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.8, 152.0, 136.5, 135.3, 133.4, 130.8, 130.0, 128.9, 128.7, 128.6, 127.7, 126.0, 125.8, 125.7, 122.1, 115.8, 110.5, 47.9, 21.5. HRMS (ESI) m/z for $C_{23}H_{20}NO^+$ ($[M+H]^+$): 326.1539. Found: 326.1544.



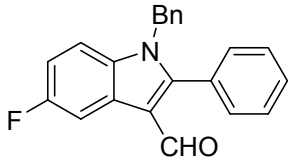

**4g**

**4g**: yellow oil, 74%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.96 (d, $J$ = 2.5 Hz, 1H), 7.54 – 7.40 (m, 5H), 7.28-7.26 (m, 3H), 7.11 (d, $J$ = 8.9 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.91 (dd, $J$ =8.9, 2.5 Hz, 1H), 5.26 (s, 2H), 3.92 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.9, 157.0, 151.6, 136.5, 131.7, 130.8, 129.9, 128.9, 128.7, 128.6, 127.7, 126.3, 126.0, 116.1, 114.6, 111.7, 103.5, 55.9, 47.9. HRMS (ESI) m/z for $C_{23}H_{20}NO_2^+$ ($[M + H]^+$):342.1489.Found:342.1484.



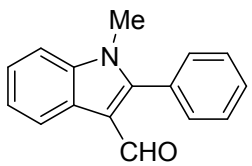

**4h**

**4h**: yellow oil, 55%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.45 (d, $J$ = 1.9 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.45 – 7.39 (m, 2H), 7.30 – 7.23 (m, 3H), 7.19 (dd, $J$ = 8.7, 2.0 Hz, 1H), 7.11 (d, $J$ = 8.7 Hz, 1H), 6.99 – 6.89 (m, 2H), 5.27 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.5, 152.4, 136.0, 135.3, 130.7, 130.3, 129.3, 129.1, 128.8, 128.1, 127.9, 126.5, 125.9, 124.6, 121.8, 115.6, 111.9, 47.9. The $^1$H NMR matches the reported literature.[6]



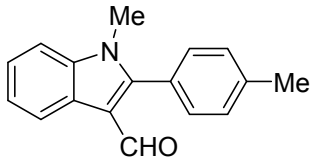

**4i**

**4i**: yellow oil, 52%. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.13 (dd, $J$ = 9.3, 2.5 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.44-7.41 (m, 2H), 7.29 – 7.24 (m, 3H), 7.13 (dd, $J$ = 8.9, 4.2 Hz, 1H), 7.02 – 6.94 (m, 3H), 5.27 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.6, 161.3, 158.9，152.7, 136.1, 133.4, 130.7, 130. 3, 129.0, 128.8, 128.2，127.9, 125.9, 116.2(d, $J_{CF}$ = 2.4 Hz), 112.5(d, $J_{CF}$ =26.1 Hz), 111.7(d, $J_{CF}$ =9.6 Hz), 107.7(d, $J_{CF}$ = 24.7 Hz), 48.2. The $^1$H NMR matches the reported literature.[6]



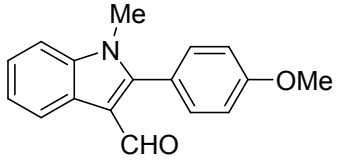

**4j**

**4j**: 38%, white solid, mp = 112-115°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.44-8.42 (m, 1H), 7.56-7.54 (m, 3H), 7.48-7.46 (m, 2H), 7.41 – 7.32 (m, 3H), 3.66 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.6, 151.7, 137.4, 130.9, 129.9, 128.7, 128.6, 125.2, 124.1, 123.4, 122.2, 115.7, 109.9, 31.1. The $^1$H NMR matches the reported literature.[10]



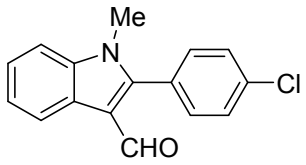

**4k**

**4k**: 47%, white solid, mp = 130-132°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.49 – 8.35 (m, 1H), 7.42 – 7.29 (m, 7H), 3.64 (s, 3H), 2.47 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.7, 151.9, 140.1, 137.4, 130.8, 129.4, 125.6, 125.3, 123.9, 123.3, 122.1, 115.6, 109.8, 31.0, 21.5. The $^1$H NMR matches the reported literature.[11]



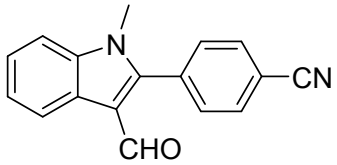

**4l**

**4l**: 55%, white solid, mp = 127-129°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.48 – 8.33 (m, 1H), 7.41 – 7.29 (m, 5H), 7.05 (d, $J$ = 8.6 Hz, 2H), 3.88 (s, 3H), 3.62 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.6, 160.9, 151.8, 137.4, 132.3, 125.3, 123.9, 123.2, 122.0, 120.5, 115.6, 114.2, 109.9, 55.5, 31.0. The $^1$H NMR matches the reported literature.[11]



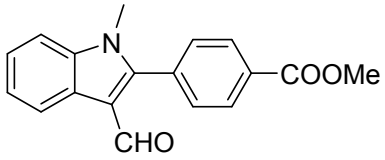

**4m**

**4m**: 33%, white solid, mp = 142-144°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.47 – 8.36 (m, 1H), 7.60 – 7.49 (m, 2H), 7.44 – 7.33 (m, 5H), 3.65 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.1, 149.9, 137.4, 136.4, 132.2, 129.1, 127.1, 125.1, 124.3, 123.5, 122.2, 115.9, 109.9, 31.1. HRMS (ESI) m/z for $C_{16}H_{13}ClNO^+$([M+H]$^+$): 270.0680. Found: 270.0681.



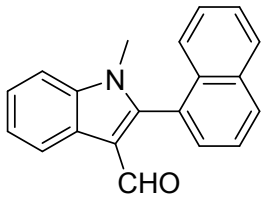

**4n**

**4n**: 32%, white solid, mp = 122-124°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.42 (d, *J* = 7.1 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.46-7.36 (m, 3H), 3.69 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.7, 148.1, 137.6, 133.4, 132.4, 131.7, 125.1, 124.8, 123.8, 122.4, 118.0, 116.2, 113.9, 110.0, 31.3. HRMS (ESI) m/z for $C_{17}H_{13}N_2O^+$([M+H]$^+$): 261.1022. Found: 261.1019.



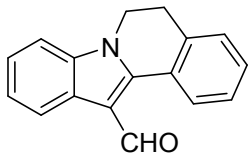

**4o**

**4o**: 25%, white solid, mp = 108-110°C. $^1$H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.50 – 8.39 (m, 1H), 8.28 – 8.17 (m, 2H), 7.65 – 7.55 (m, 2H), 7.49 – 7.35 (m, 3H), 3.99 (s, 3H), 3.69 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 186.2, 166.3, 149.7, 137.5, 133.2, 131.4, 131.0, 129.8, 125.1, 124.4, 123.6, 122.3, 116.1, 109.9, 52.6, 31.2. HRMS (ESI) m/z for $C_{18}H_{16}NO_3^+$([M+H]$^+$): 294.1125. Found: 294.1126.




**4p**

**4p**: 63%, white solid, mp = 118-120°C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.57 – 8.44 (m, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.54 (m, 3H), 7.50 – 7.38 (m, 5H), 3.50 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.5, 150.2, 137.5, 133.5, 132.8, 130.6, 130.2, 128.7, 127.6, 126.8, 126.2, 125.4, 125.3, 125.1, 124.1, 123.4, 122.3, 117.0, 109.9, 31.0. HRMS (ESI) m/z for $C_{20}H_{16}NO^+$([M+H]$^+$): 286.1226. Found: 286.1225.



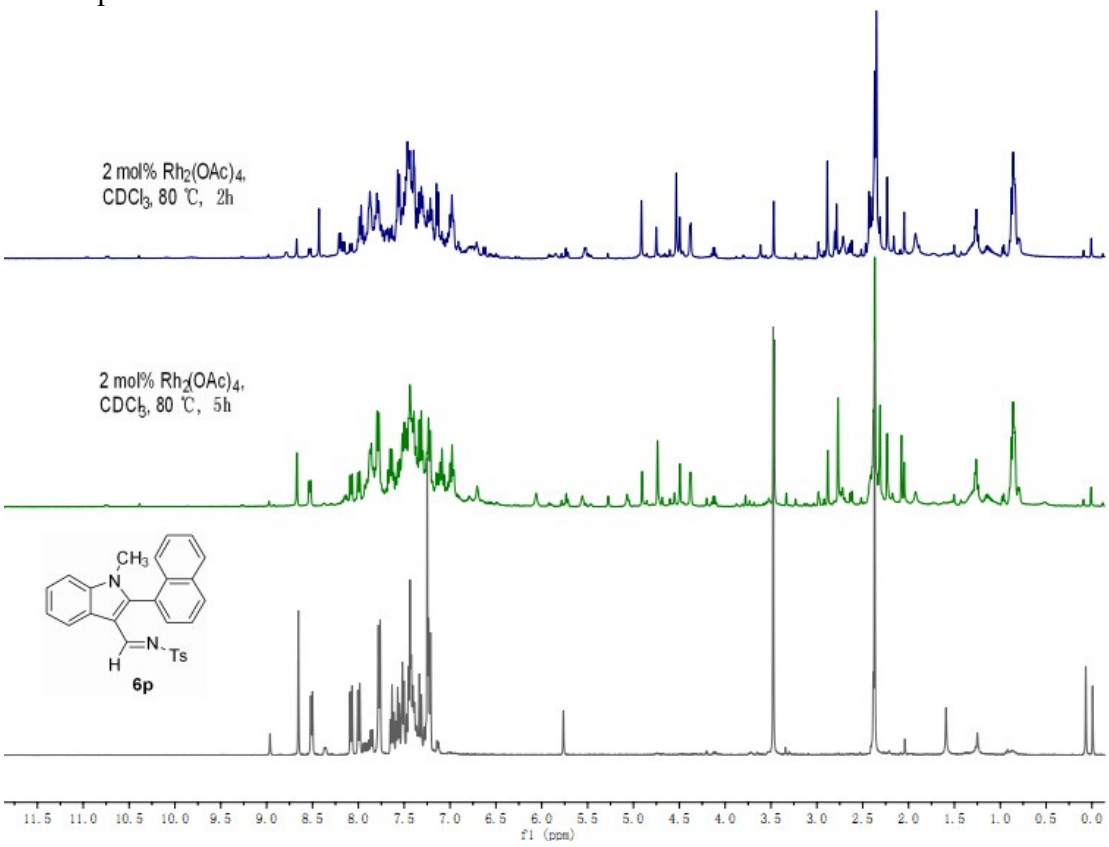

**4q**

**4q**: 61%, white solid, mp = 120-123°C. $^1$H NMR (300 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.53 – 8.34 (m, 1H), 7.96-7.93 (m, 1H), 7.46–7.27 (m, 6H), 4.31–4.14 (m, 2H), 3.17 (t, *J* = 6.5 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 185.6, 143.1, 135.8, 135.0, 129.9, 129.0, 128.5, 127.8, 127.1, 126. 7, 124.0, 123.3, 122.4, 113.4, 109.2, 40.1, 29.2. The $^1$H NMR matches the reported literature.[12]

**IV Monitoring the reaction of triazole 3p via proton NMR.**

Triazole **3p** (30 mg, 0.04 mmol) and $Rh_2(OAc)_4$ (0.6 mg, 2 mol%) were added to a NMR tube, then 0.4ml of $CDCl_3$ was added to the tube. The tube was capped with a

small plug and the solution was bubbled with nitrogen for 20 minutes. Then the NMR tube was heated at 80 °C for 2 hours and then subjected to NMR experiment at room temperature; after that, the reaction was heated to 80 °C for 3 hours before a second NMR experiment. The resulting residue was directly purified by a short silica gel using PE/EA (4:1) as the eluent to give the semi-purified product **6p** (20mg)**.** These NMR spectra were shown below.




## V. Reference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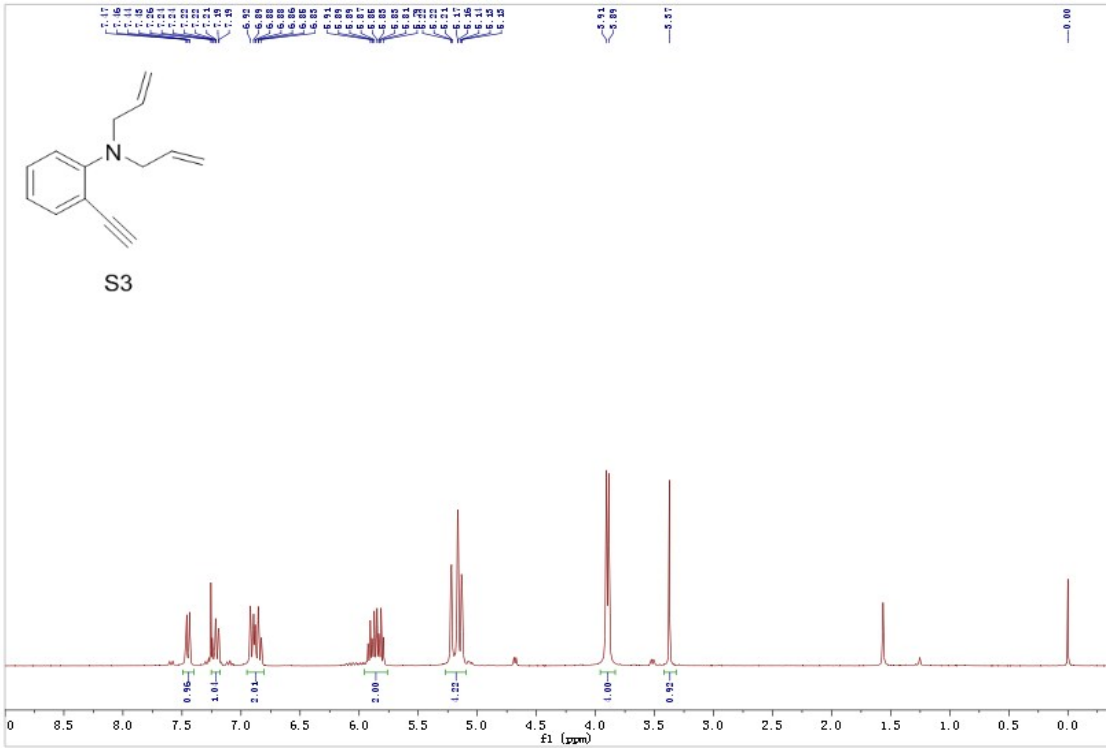
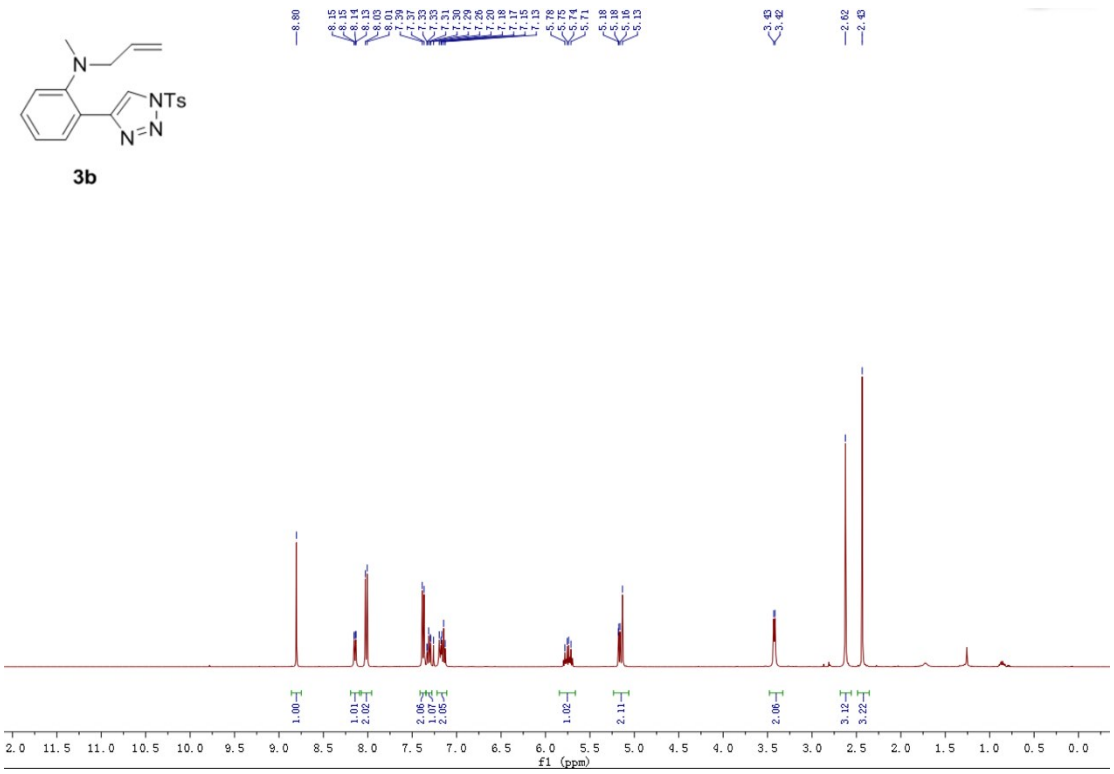
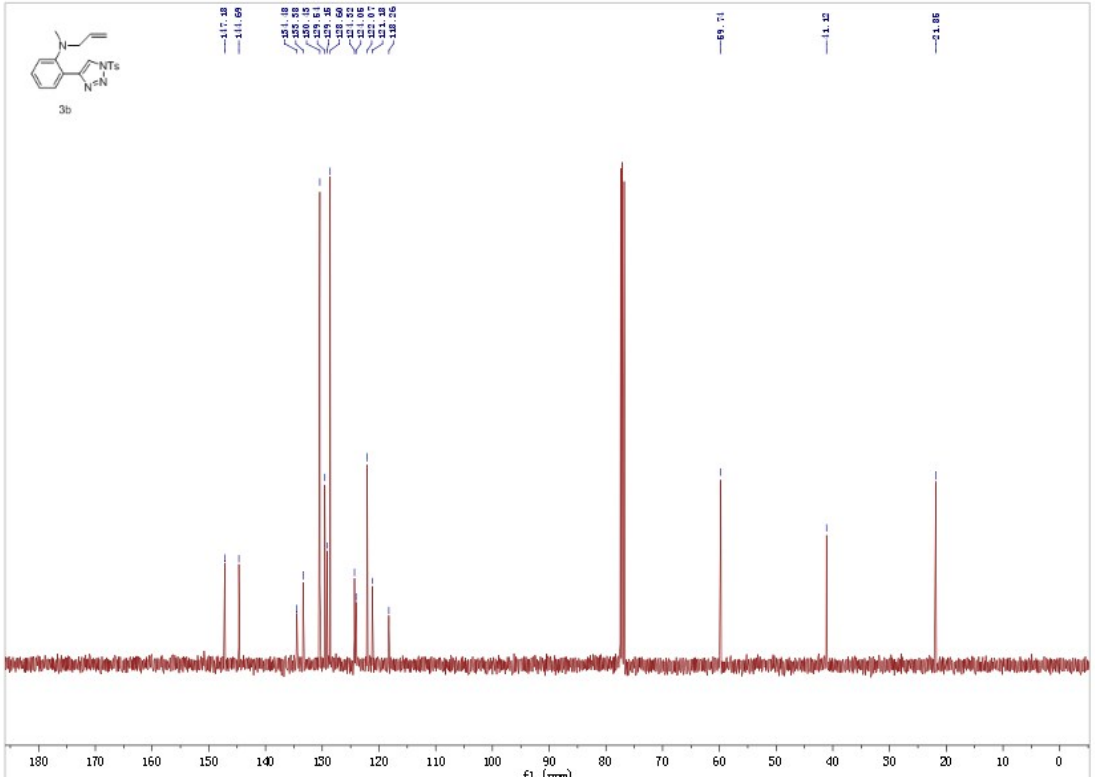
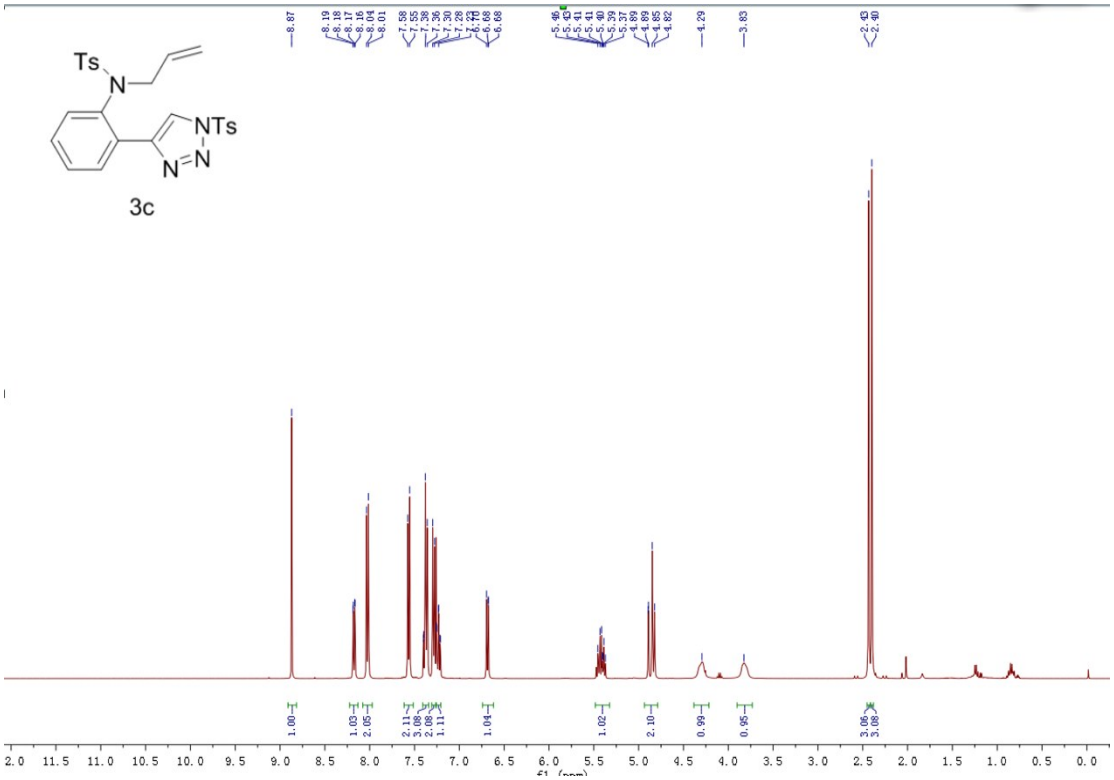
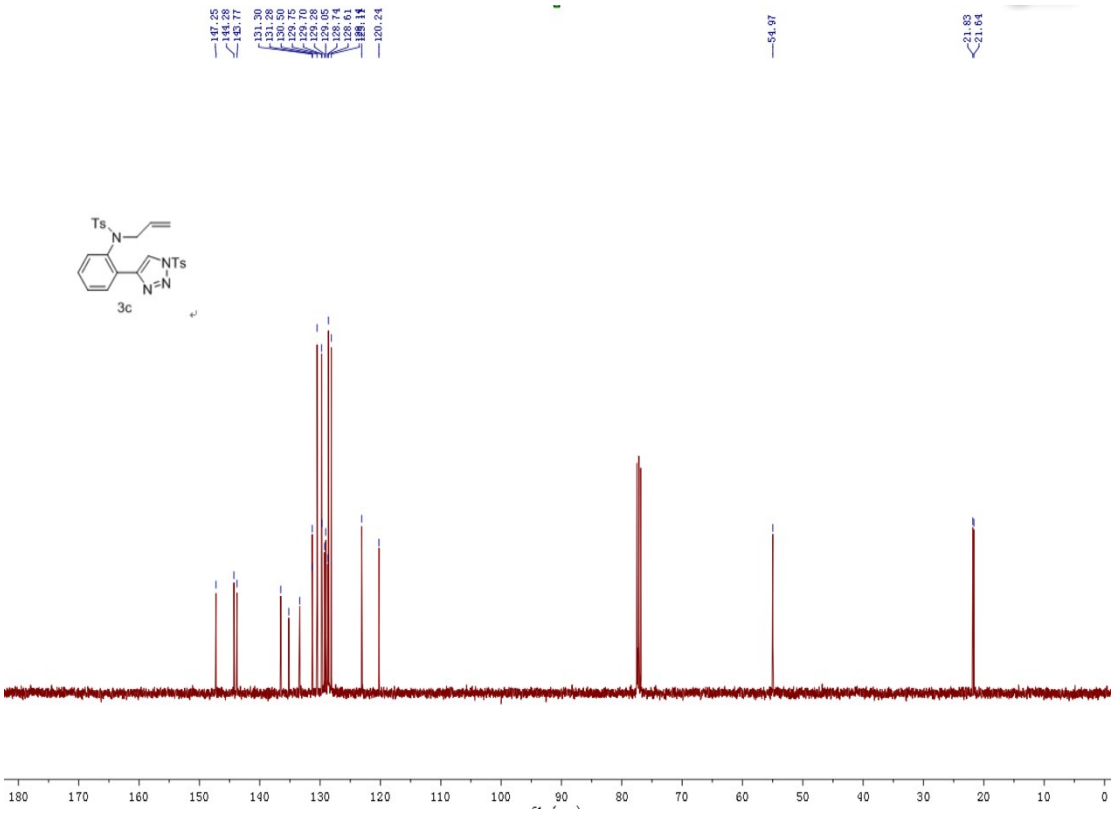
## VII. $^{1}$H NMR and $^{13}$C NMR spectra of compounds

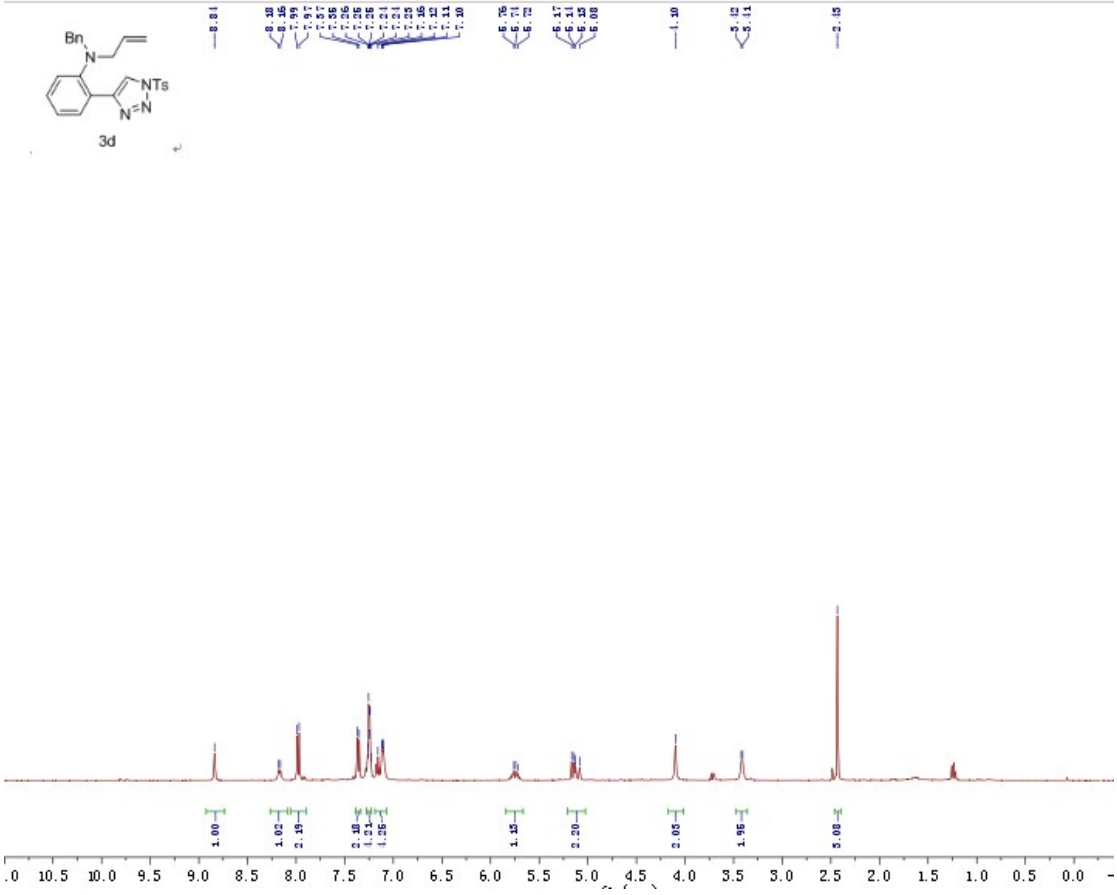



NTs
N
N
3b
f1 (ppm)


NTs
N
N
3b


Ts
N
NTs
N=N
3c


Ts
N
NTs
N=N
3c


Bn
N
NTs
N=N
3d
8.84
8.18
8.16
7.99
7.97
7.57
7.56
7.56
7.55
7.55
7.54
7.21
7.21
7.20
7.19
7.12
7.11
7.10
6.75
6.71
6.72
6.17
6.14
6.13
6.08
4.10
3.82
3.81
2.45
1.00
1.02
2.19
2.18
1.21
1.26
1.15
2.20
2.05
1.96
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
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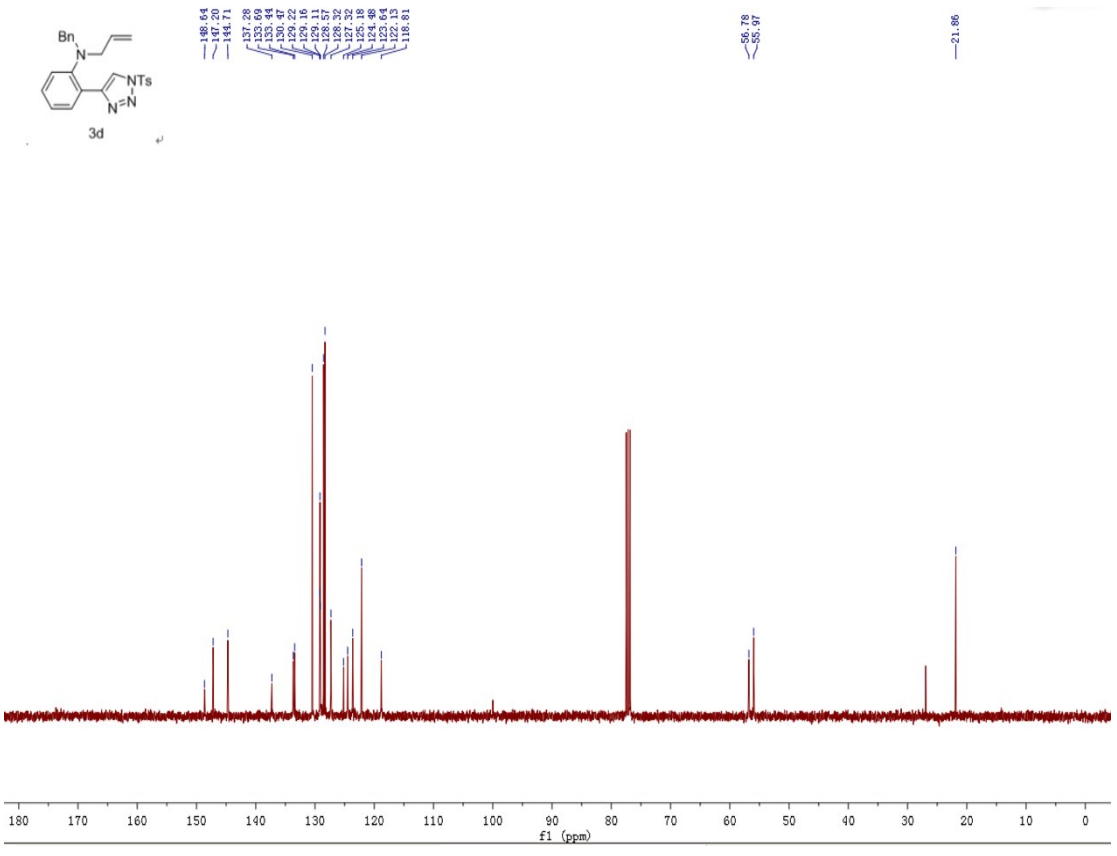
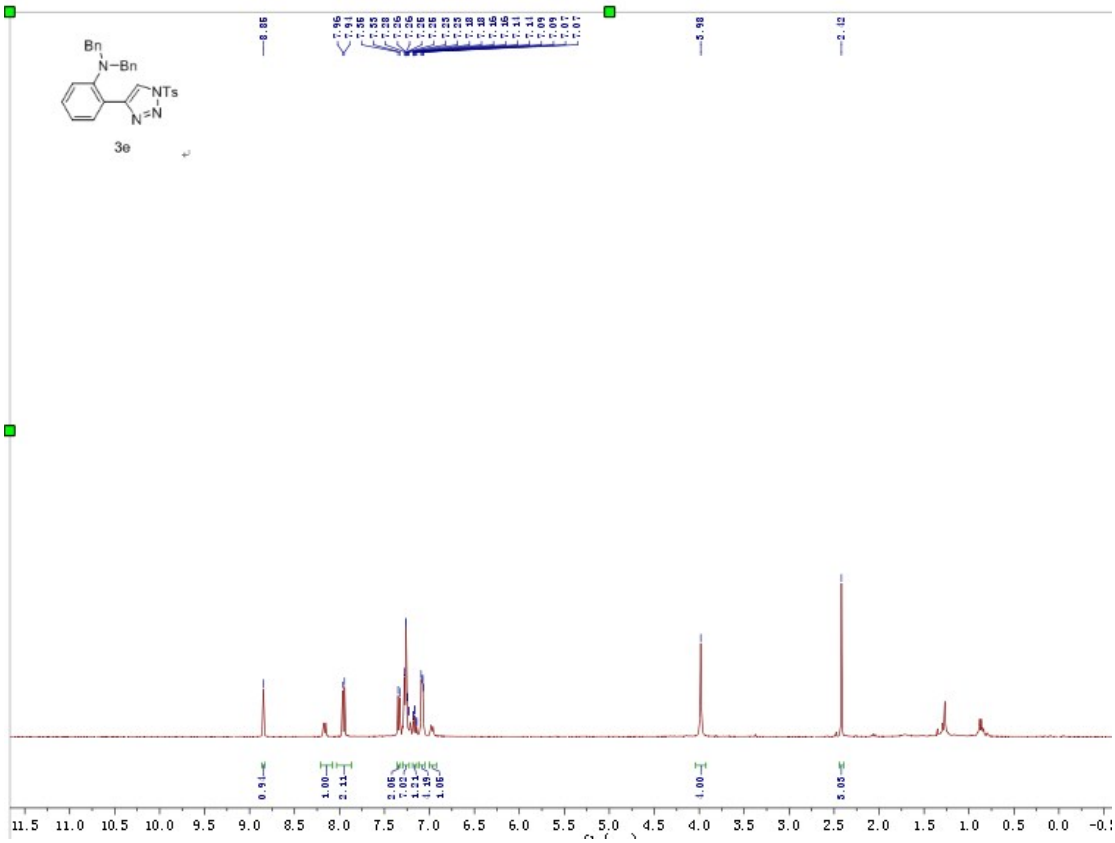
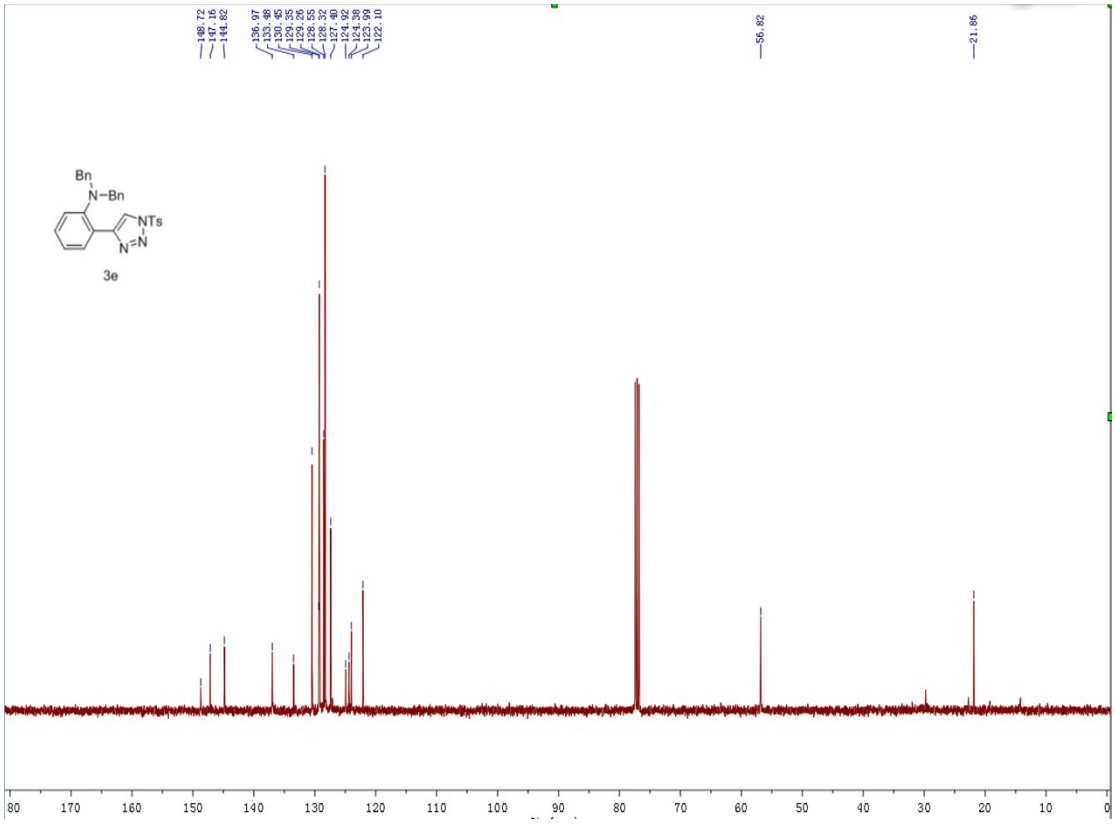
1.0
0.5
0.0


Bn
N
NTs
N=N
3d
148.64
147.20
144.71
137.28
133.69
133.44
130.47
129.22
129.16
129.11
128.57
128.32
127.32
125.18
124.48
123.64
122.13
118.81
56.78
56.97
21.86
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Bn
N–Bn
NTs
N=N
3e
8.85
7.96
7.91
5.98
2.12
0.91
1.00
2.11
2.05
7.02
1.21
1.19
1.05
1.00
5.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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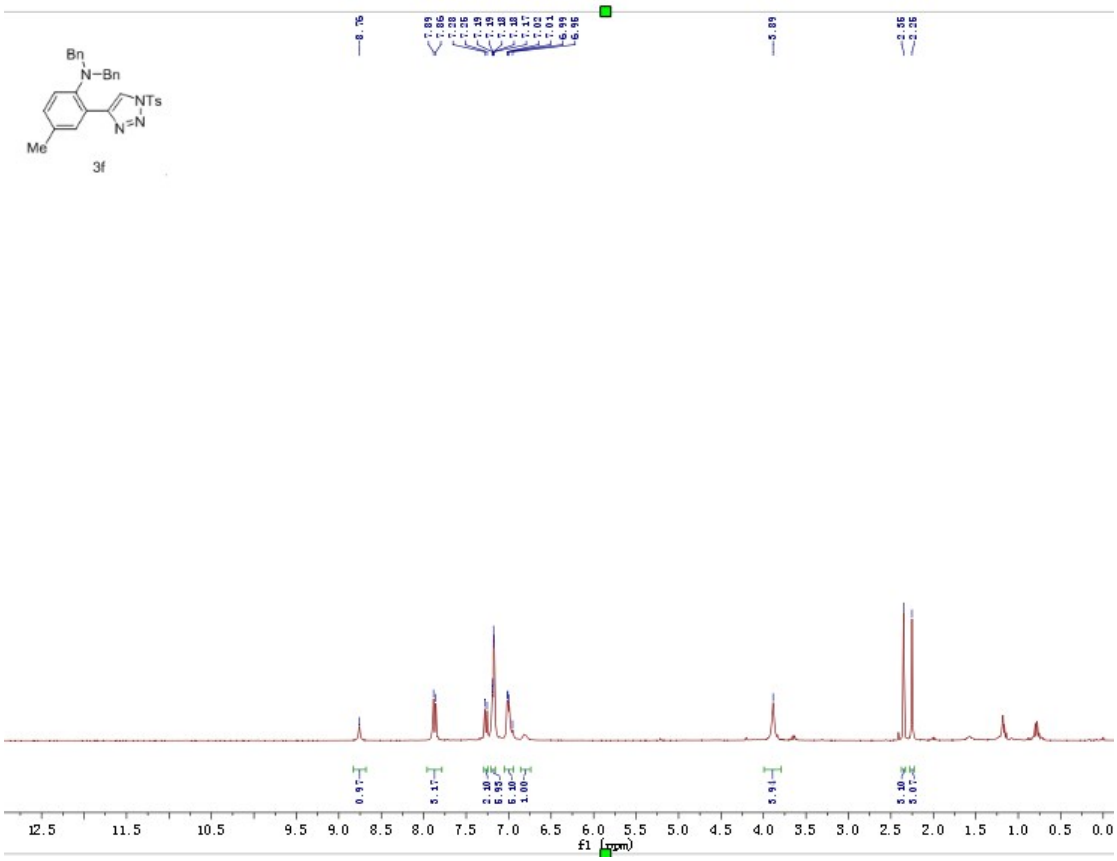
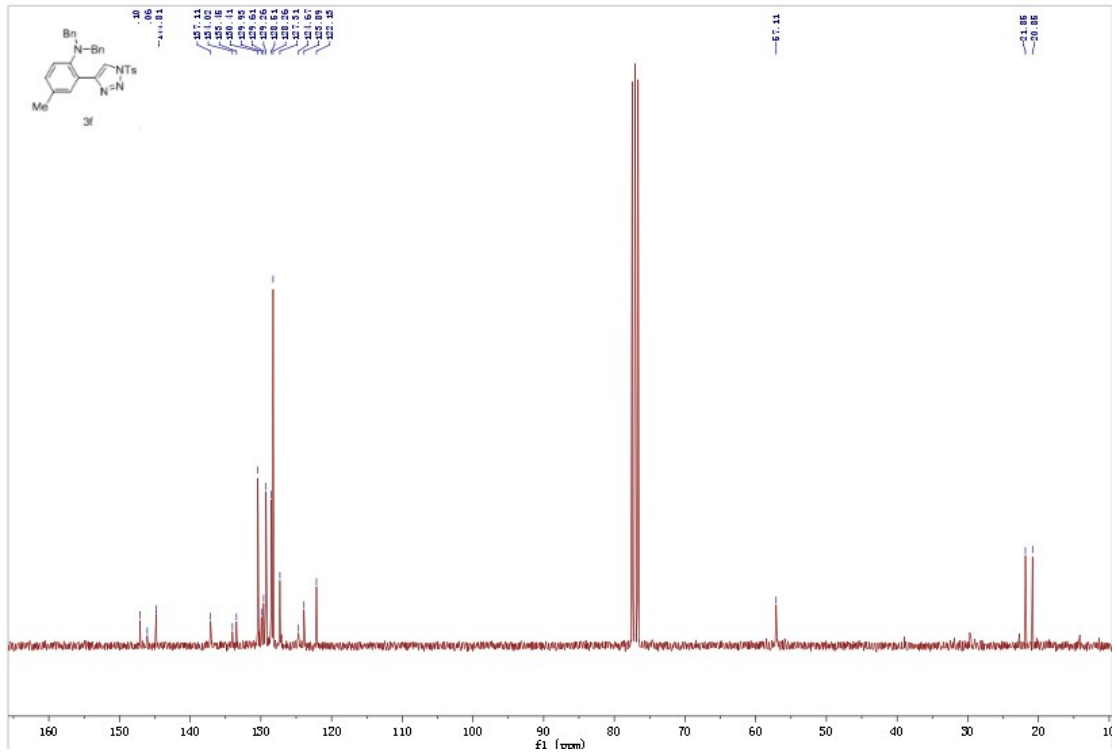
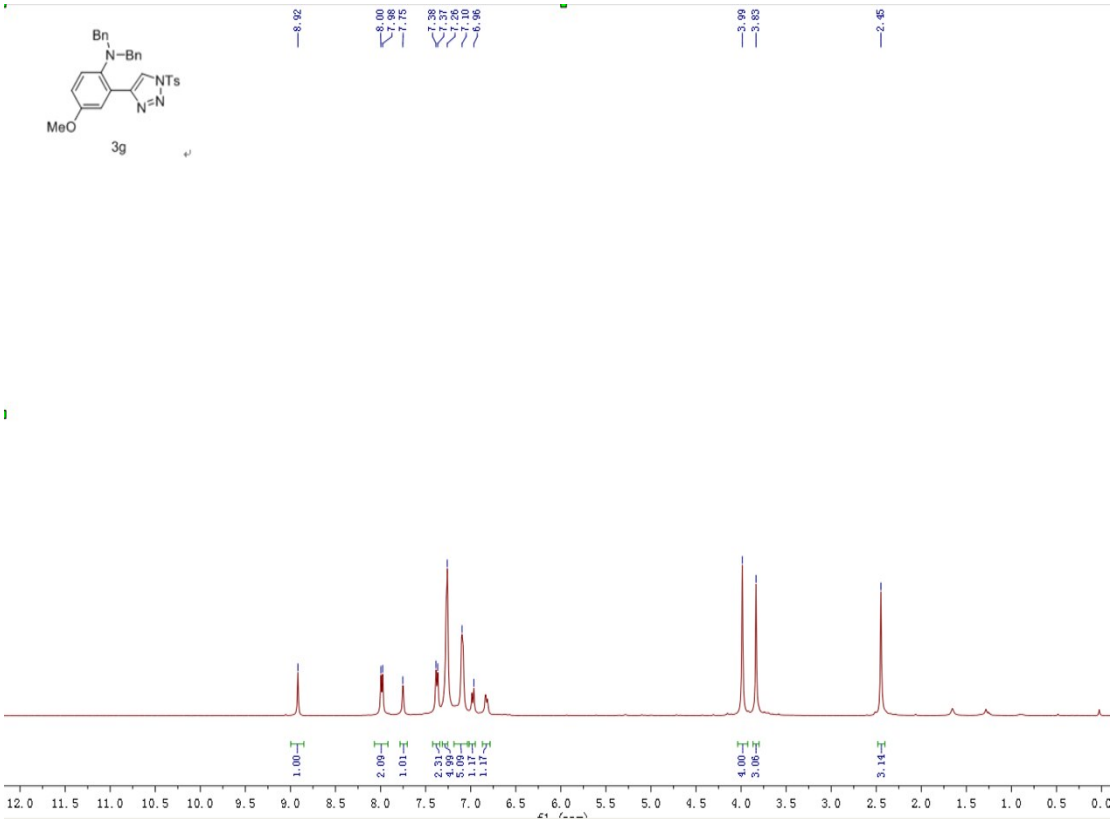
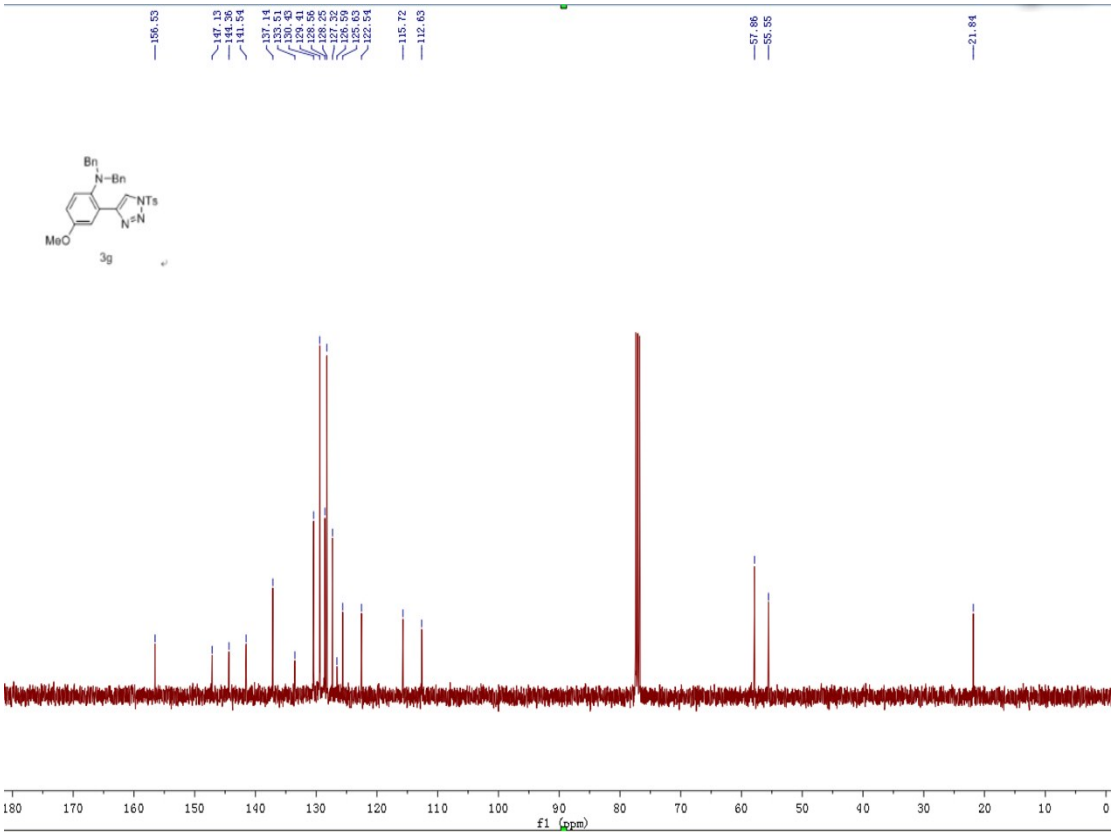
147.15
141.82
136.97
133.98
130.45
129.35
129.26
128.55
128.32
127.40
124.92
124.38
123.99
122.10
56.82
21.86
Bn
N–Bn
NTs
N=N
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Bn
N–Bn
NTs
N=N
Me
3f
f1 (ppm)


Bn
N–Bn
NTs
N=N
Me
3f
f1 (ppm)


Bn
N–Bn
NTs
MeO
3g
8.92
8.00
7.98
7.75
7.38
7.37
7.26
7.10
6.96
3.99
3.83
2.45
1.00
2.09
1.01
2.31
4.00
5.09
1.17
1.17
4.00
3.06
3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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141.54
137.14
133.51
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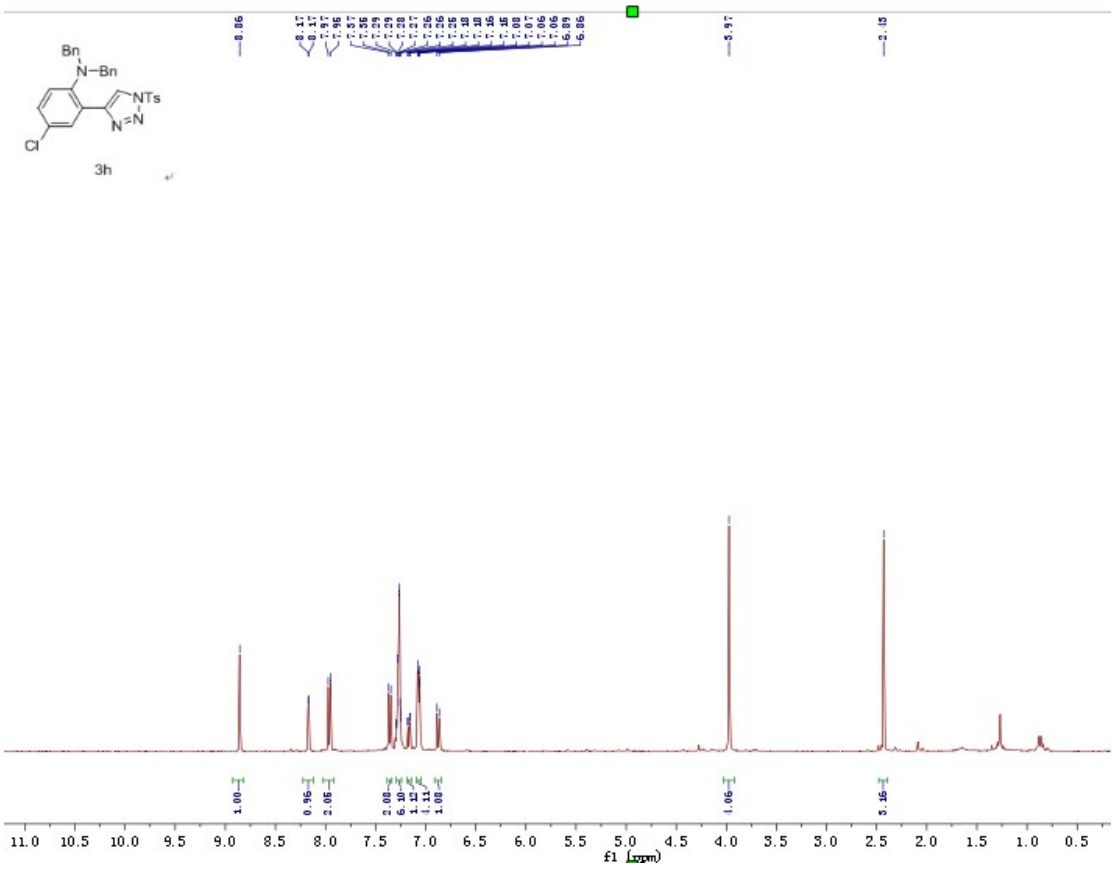
129.41
128.56
128.25
127.32
126.59
125.63
122.54
115.72
112.63
57.86
55.55
21.84
Bn
N–Bn
NTs
MeO
3g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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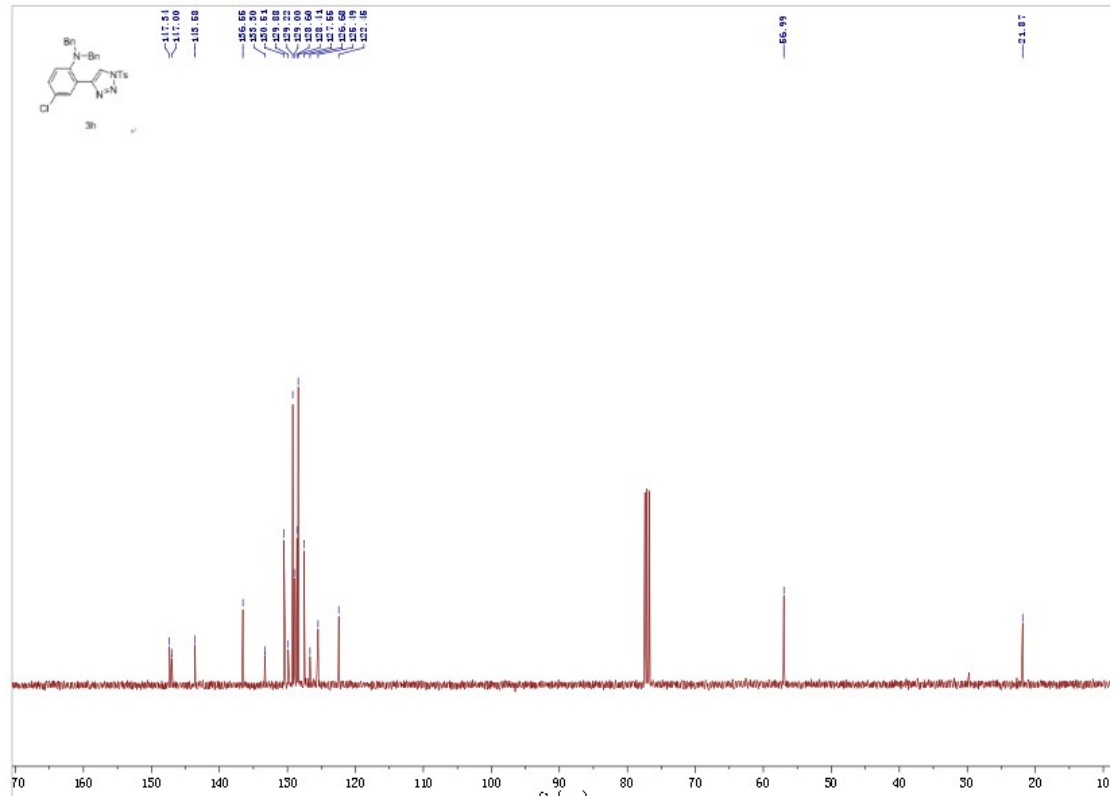
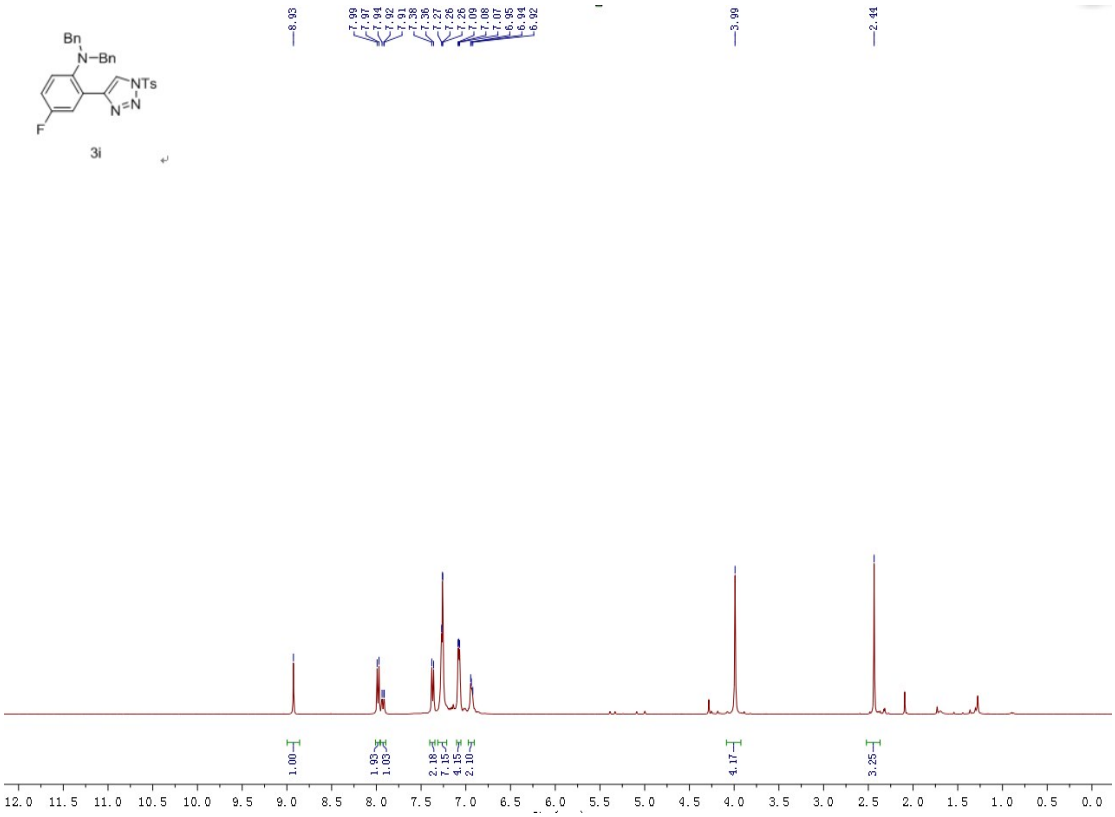
N–Bn
NTs
N
N
Cl
3h
f1 (ppm)


Bn
N–Bn
NTs
N
N
Cl
3h


Bn
N–Bn
NTs
N=N
F
3i
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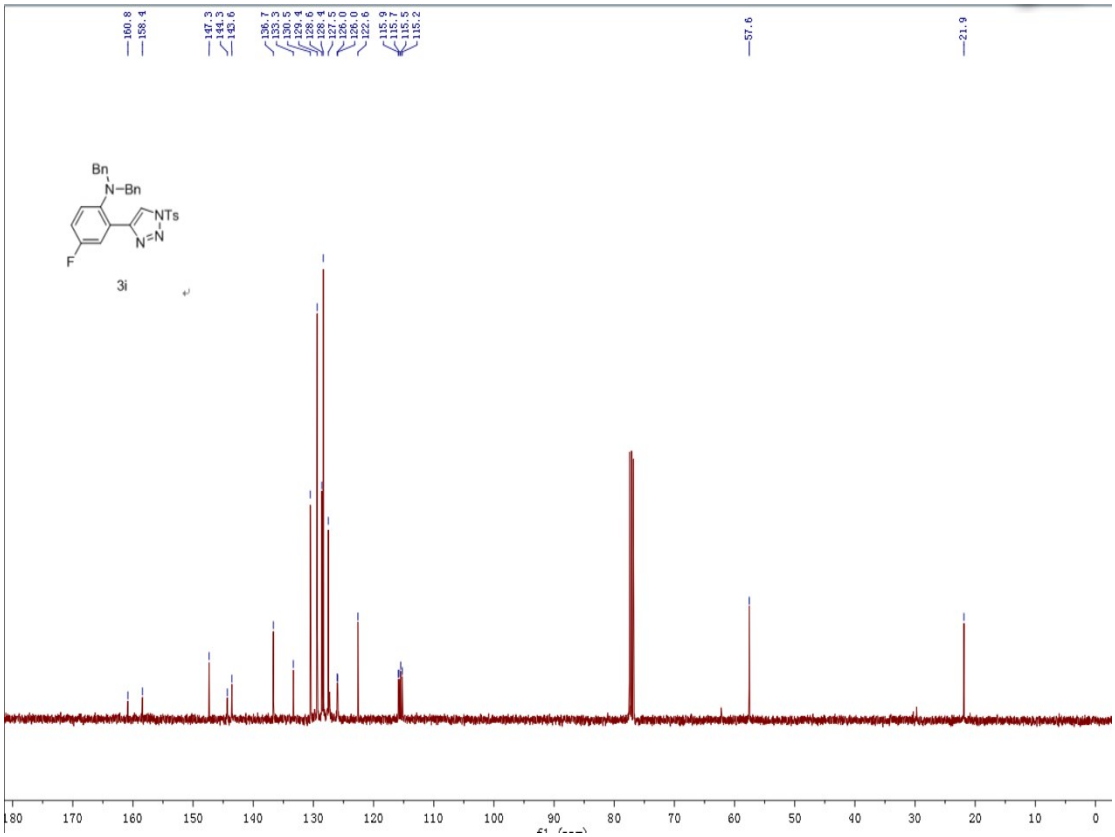
7.99
7.97
7.94
7.92
7.91
7.38
7.36
7.27
7.26
7.09
7.08
7.07
6.95
6.94
6.92
3.99
2.44
1.00
1.93
1.03
2.18
7.15
4.15
2.10
4.17
3.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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144.3
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133.3
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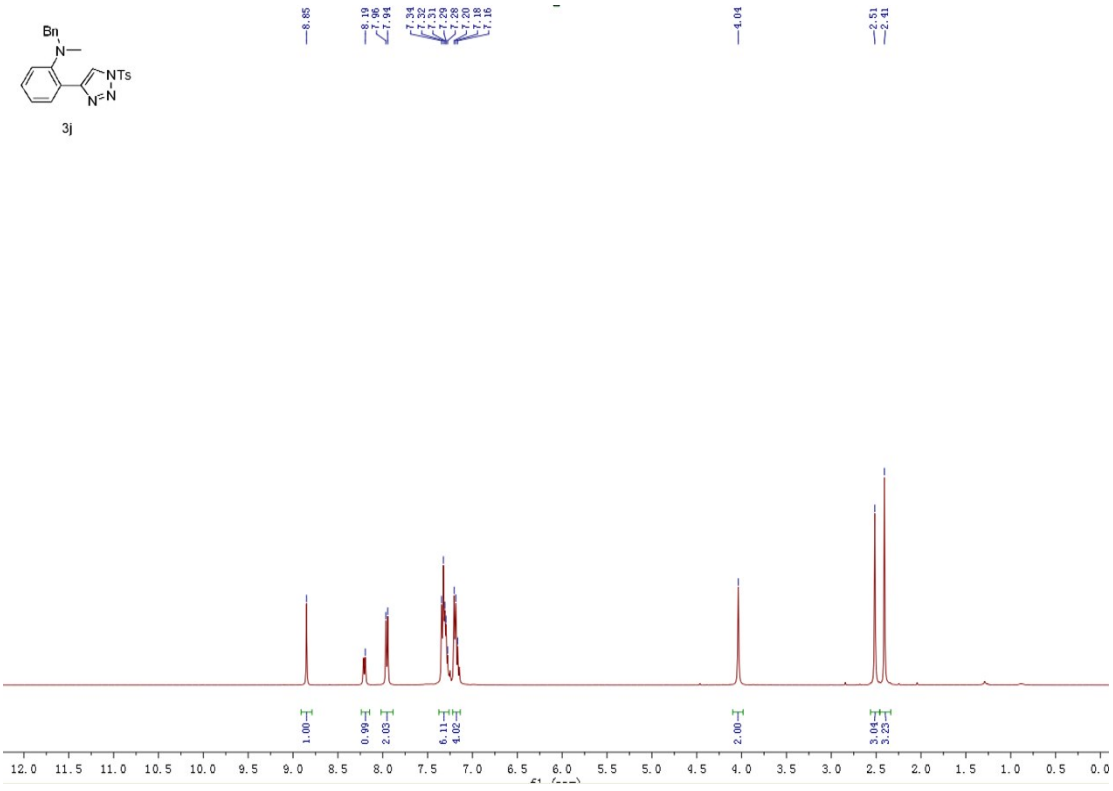
129.4
128.6
128.4
127.5
126.0
126.0
122.6
115.9
115.7
115.5
115.2
57.6
21.9
Bn
N–Bn
NTs
N=N
F
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Bn
N
NTs
N
N
3j
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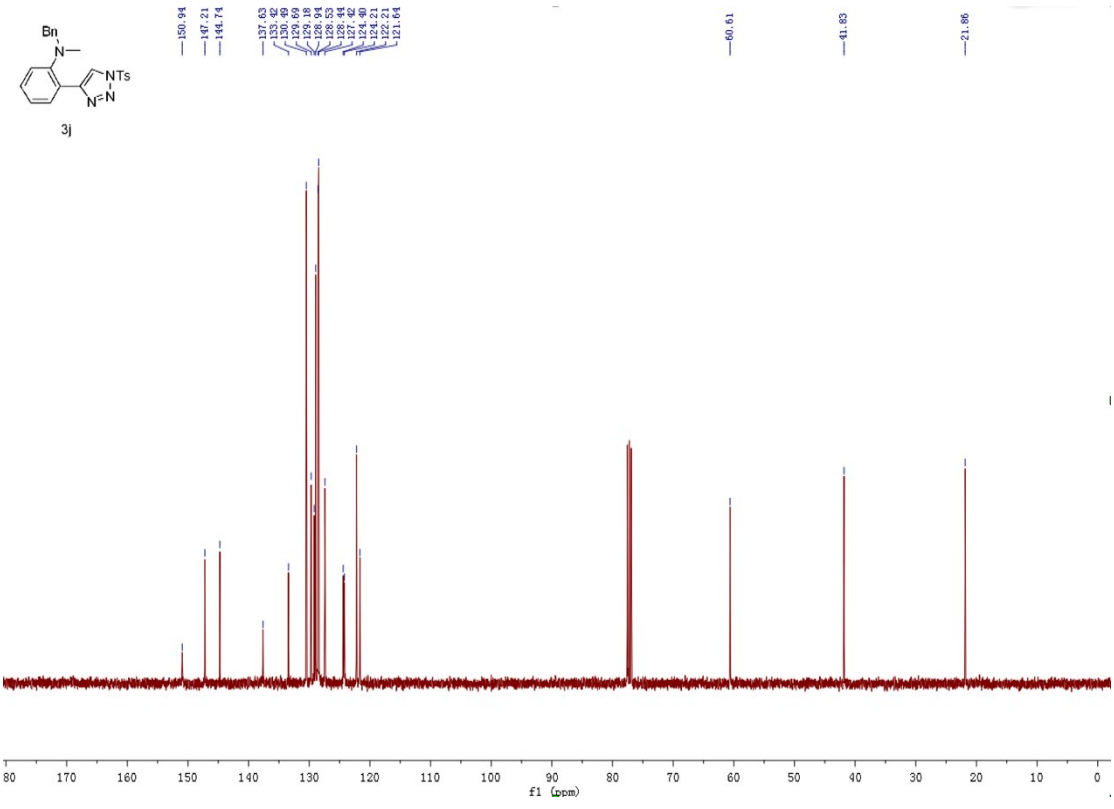
8.19
7.96
7.94
7.34
7.32
7.31
7.29
7.28
7.20
7.18
7.16
4.04
2.51
2.41
1.00
0.99
2.03
6.11
4.02
2.00
3.04
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


Bn
N
NTs
N
N
3j
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144.74
137.63
133.42
130.49
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128.94
128.53
128.44
127.46
124.40
124.21
122.21
121.64
60.61
41.83
21.86
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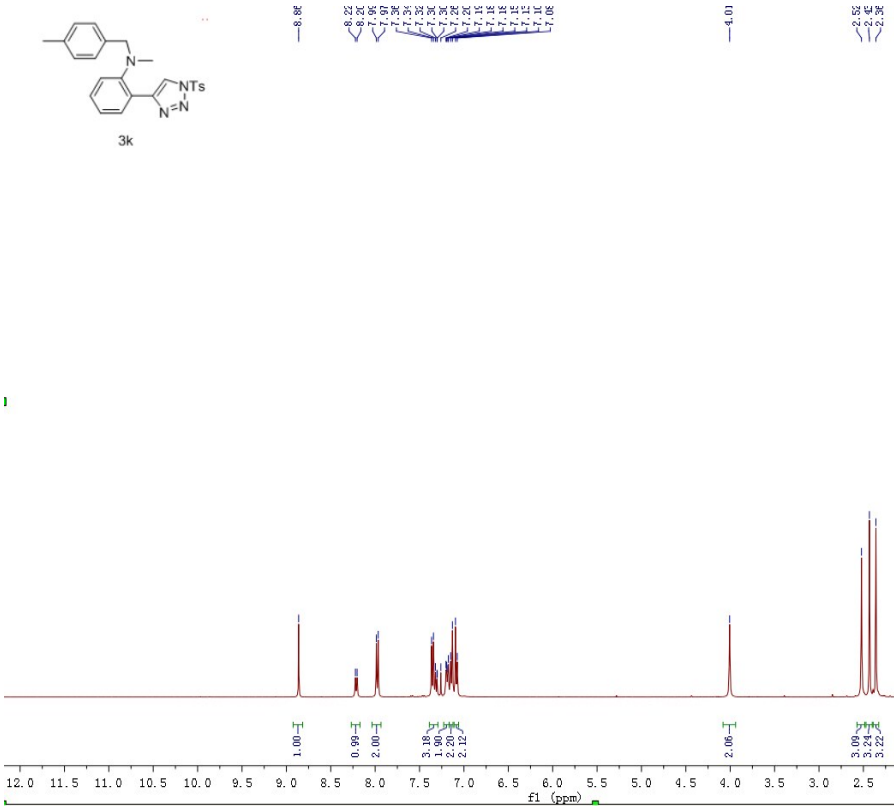
f1 (ppm)


NTs
N=N
3k
1.00
0.99
2.00
3.18
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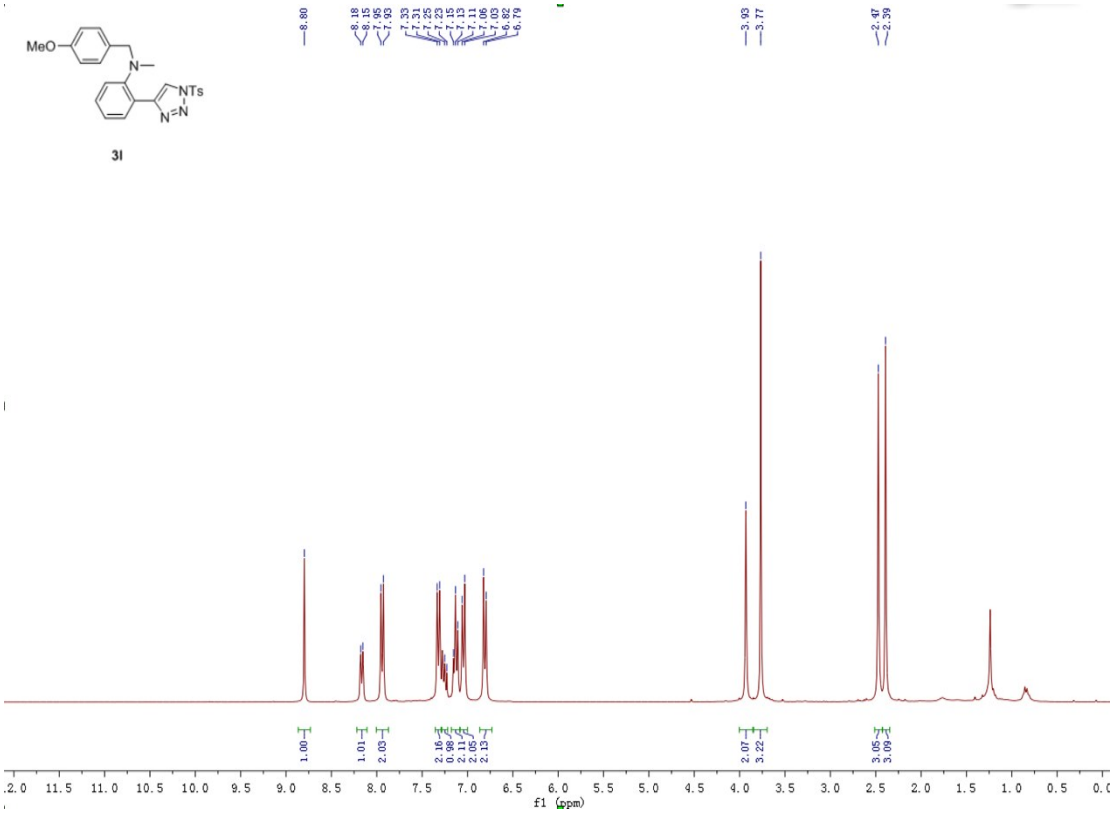
2.20
2.12
2.06
3.09
3.24
3.22
f1 (ppm)
NTs
N=N
3k


MeO
N
NTs
N=N
3l
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8.18
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7.33
7.31
7.25
7.23
7.15
7.13
7.11
7.06
7.03
6.82
6.79
3.93
3.77
2.47
2.39
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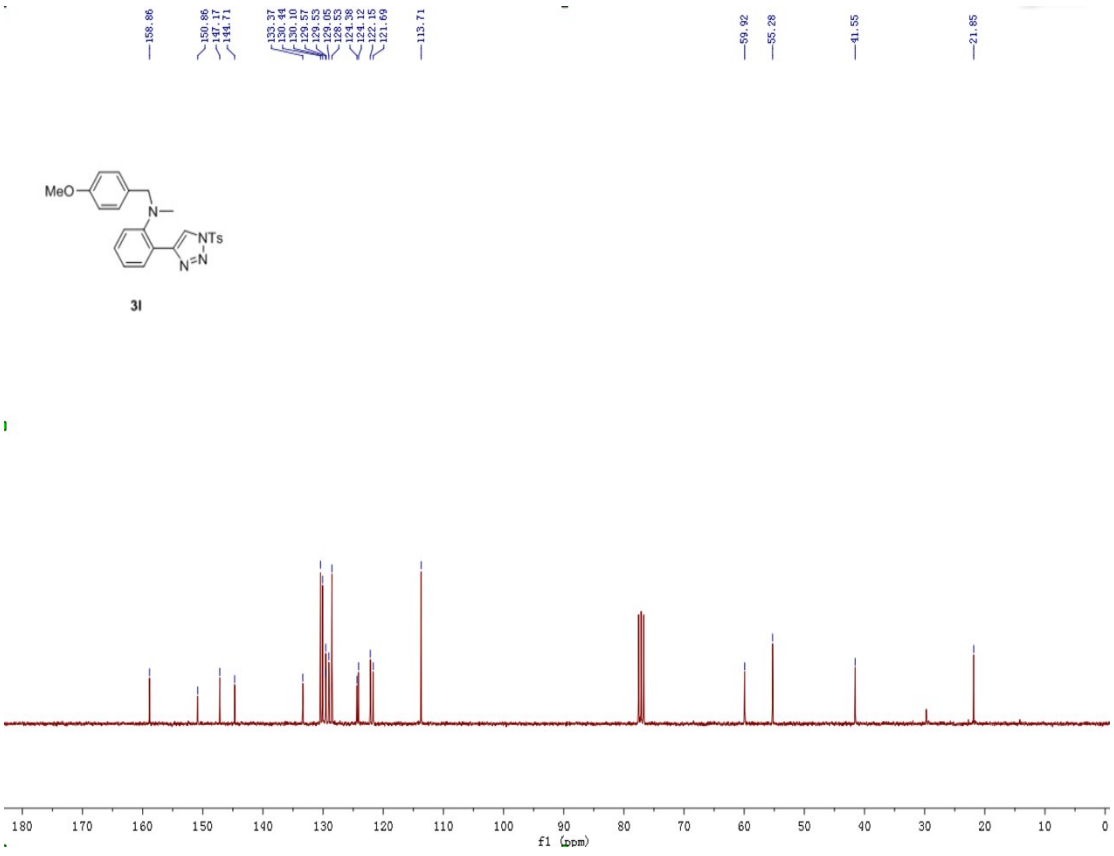
2.13
2.07
3.22
3.05
3.09
f1 (ppm)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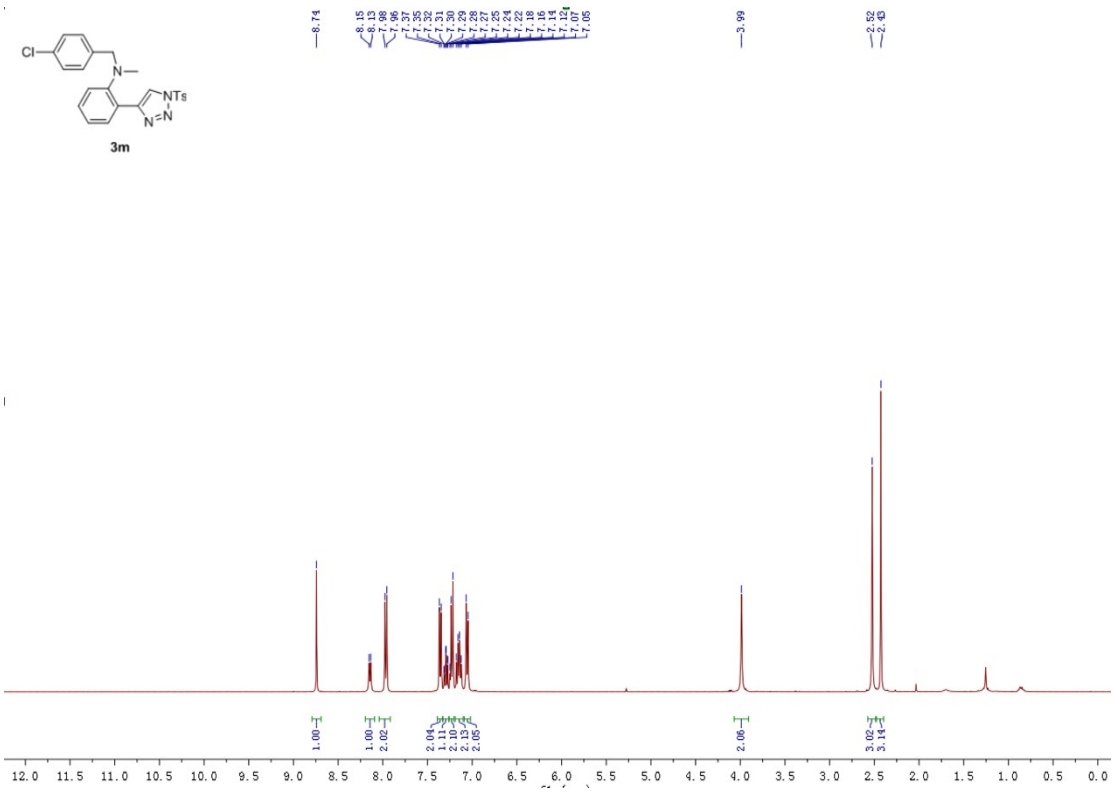
124.12
122.15
121.69
113.71
59.92
55.28
41.55
21.85
MeO
N
NTs
N=N
3l
f1 (ppm)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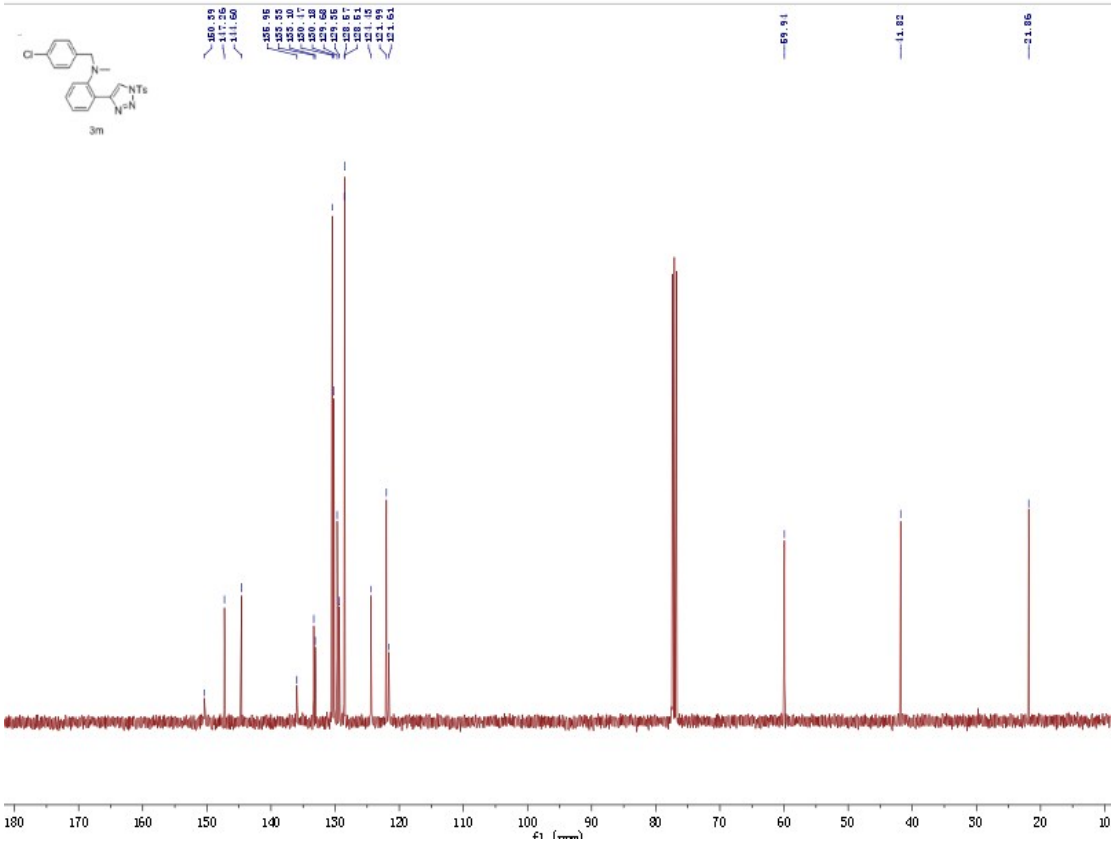
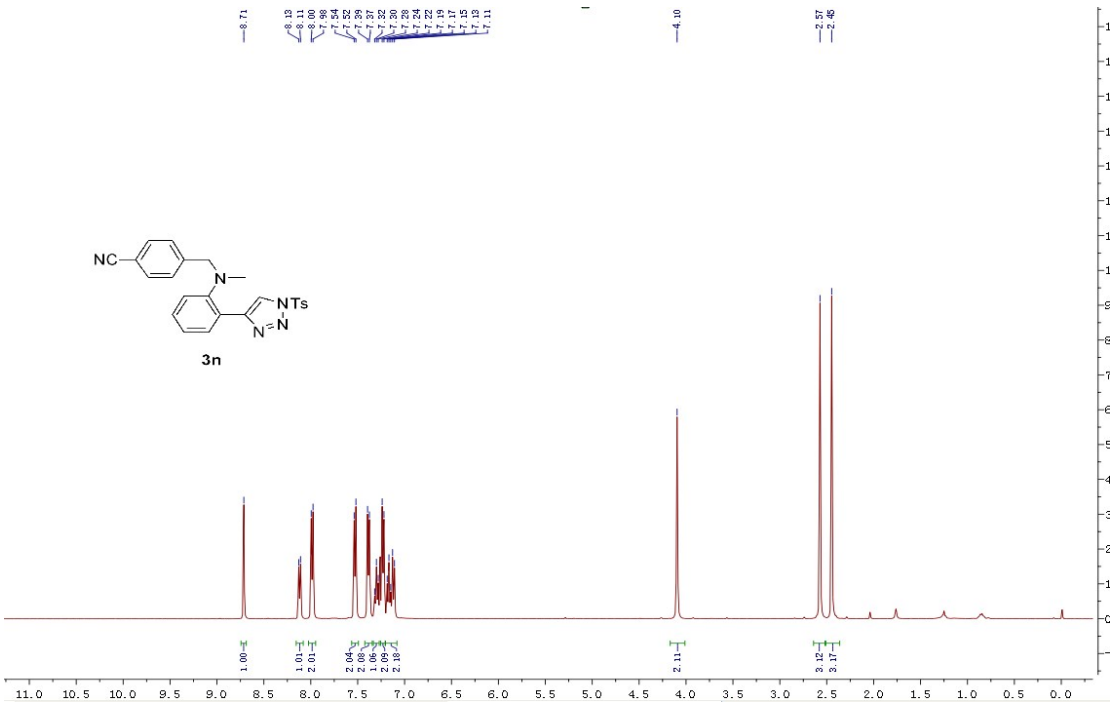

3m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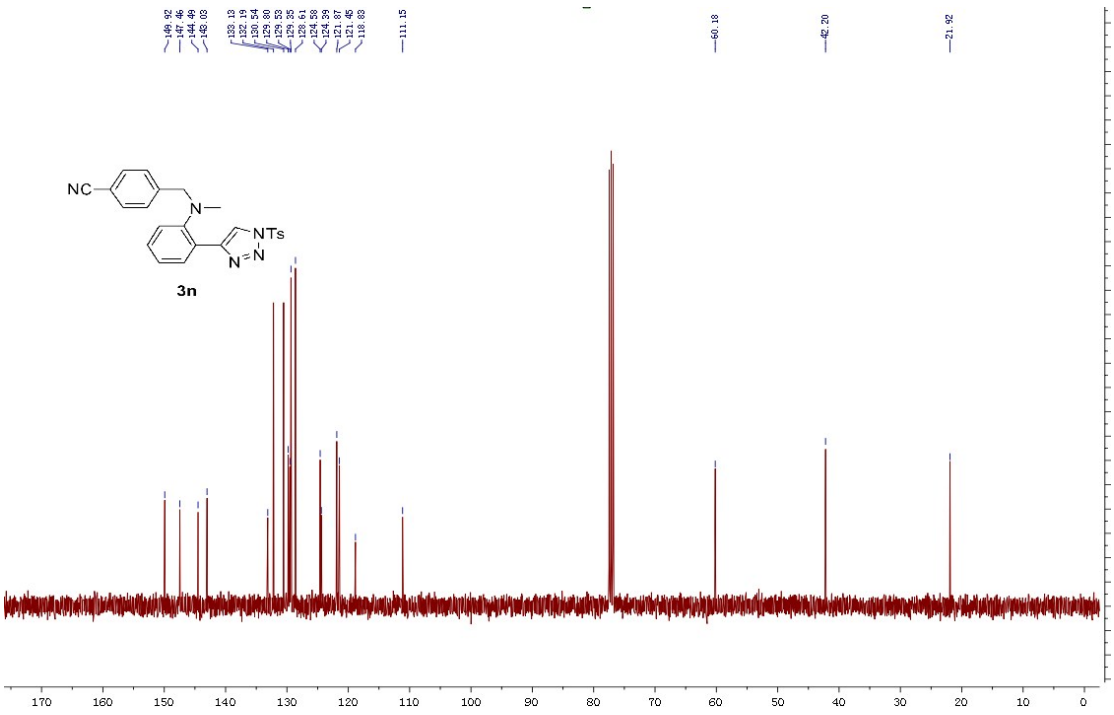
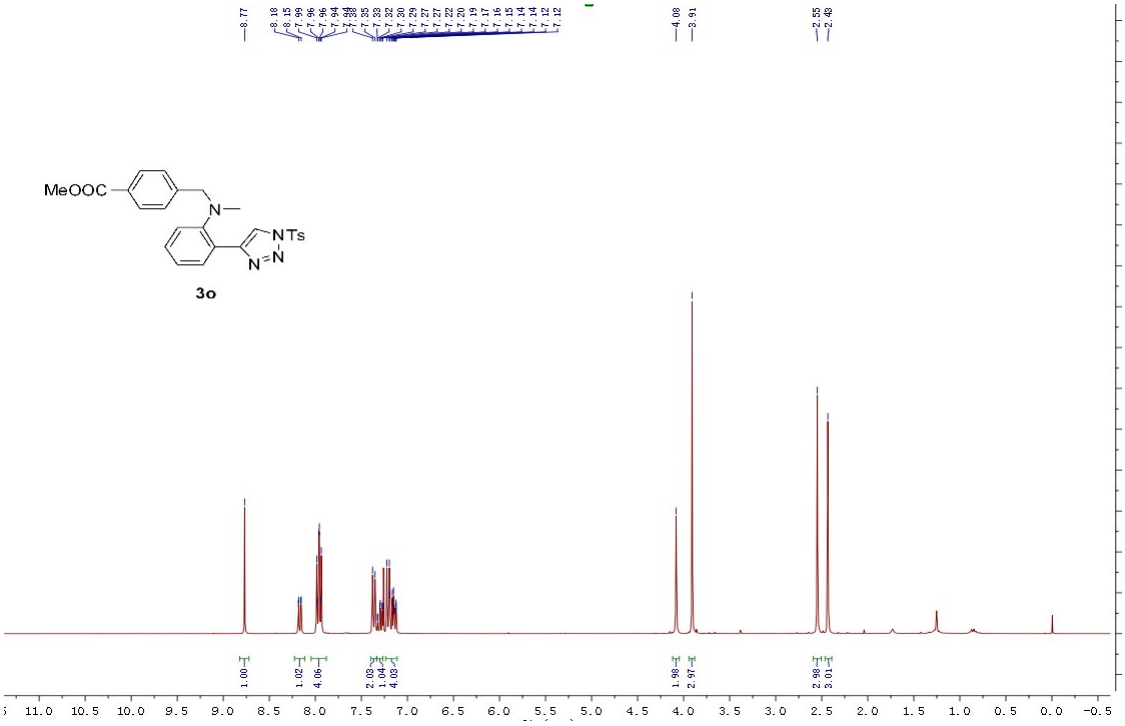
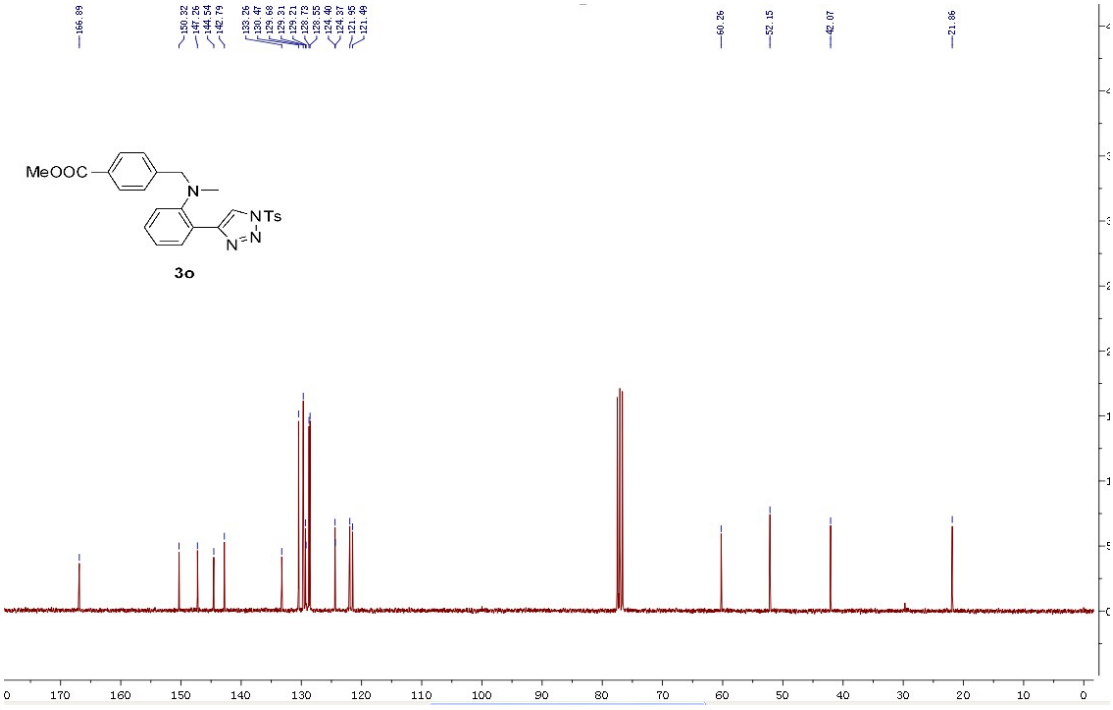
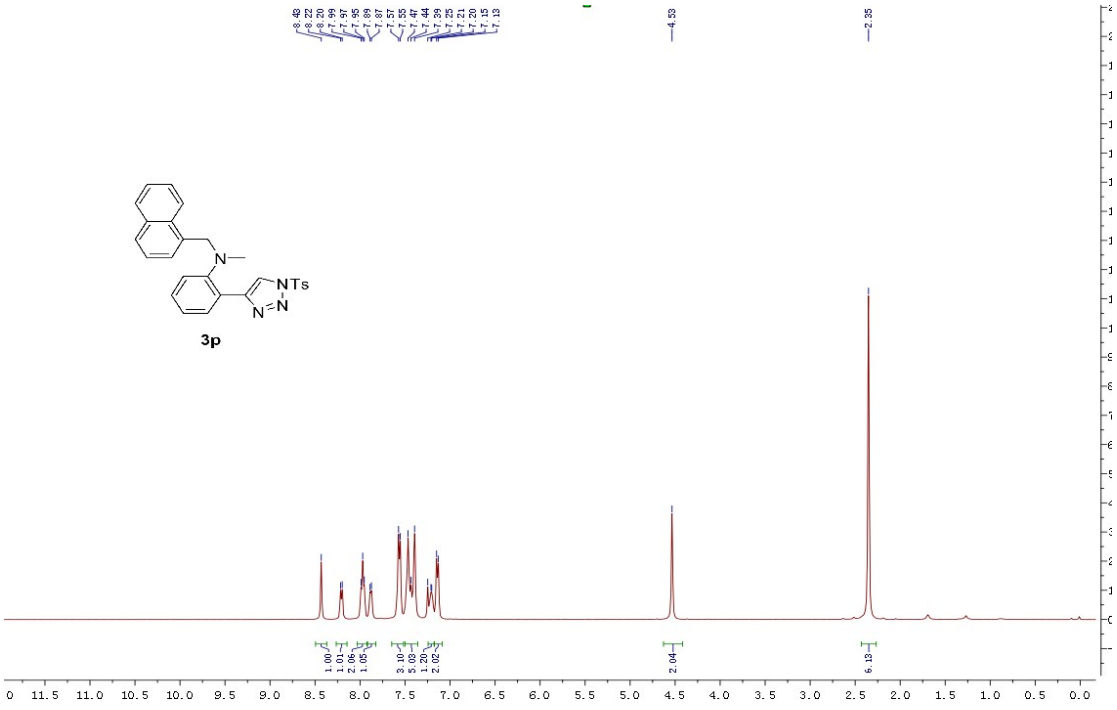
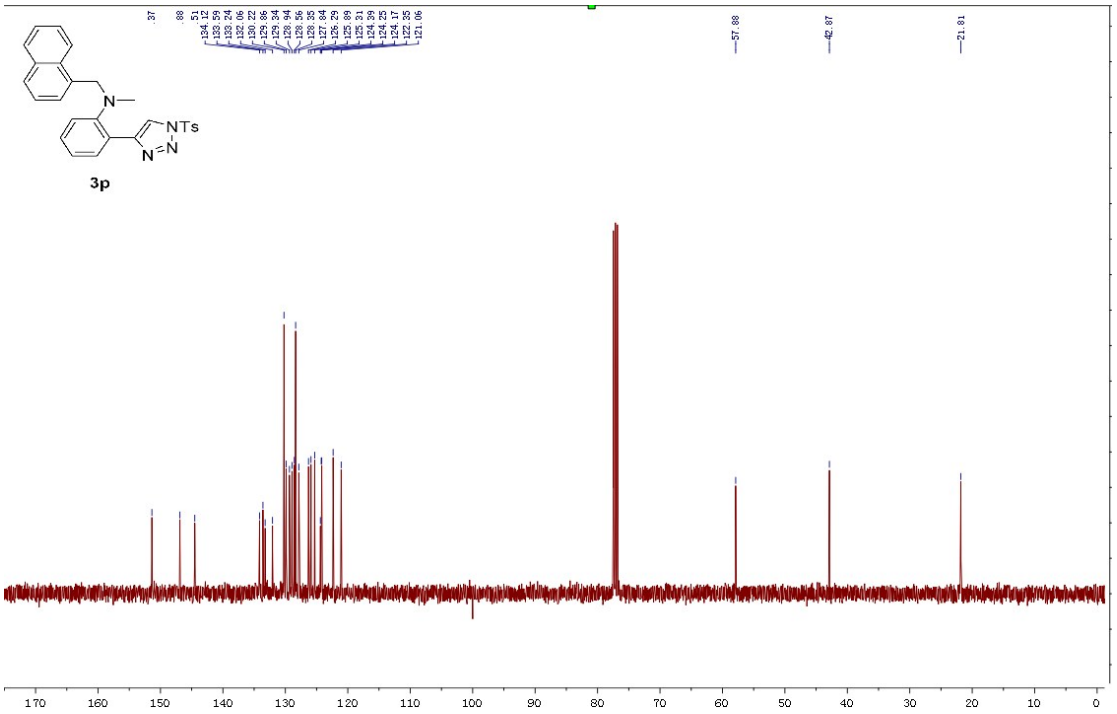
N
NTs
N
N
3n

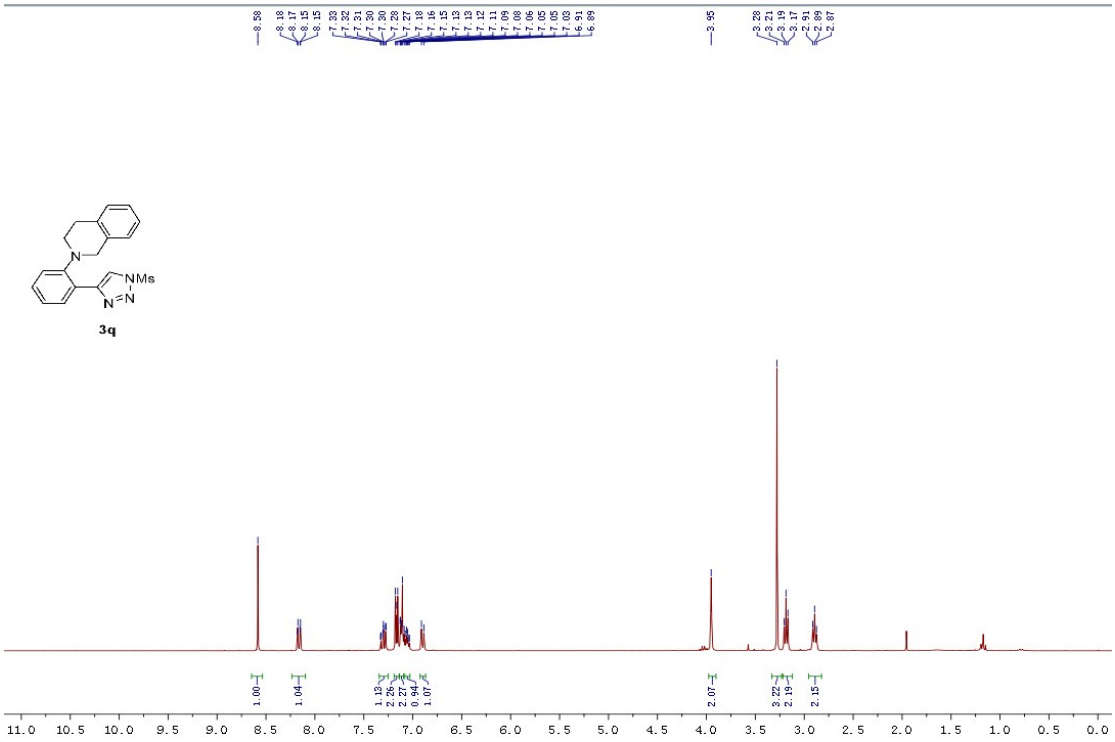

NC
N
NTs
N
N
3n


MeOOC
N
NTs
N
N
3o


MeOOC
N
NTs
N
N
3o


NTs
N
N
3p


NTs
N
N
3p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8.15
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7.31
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7.13
7.13
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7.03
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3.19
3.17
2.91
2.89
2.87
NMs
N=N
3q
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1.04
1.13
2.25
2.27
0.94
1.07
2.07
3.22
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2.15
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9.0
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8.0
7.5
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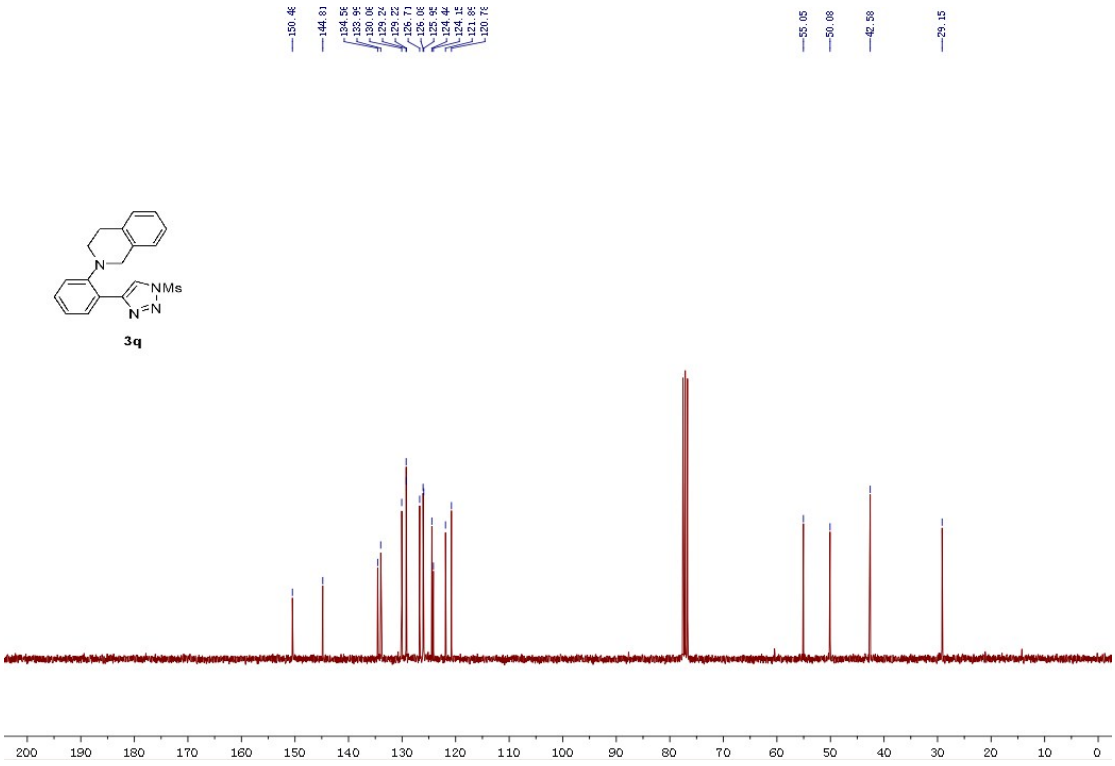
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126.08
125.95
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124.15
121.85
120.78
55.05
50.08
42.58
29.15
NMs
N=N
3q
200
190
180
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150
140
130
120
110
100
90
80
70
60
50
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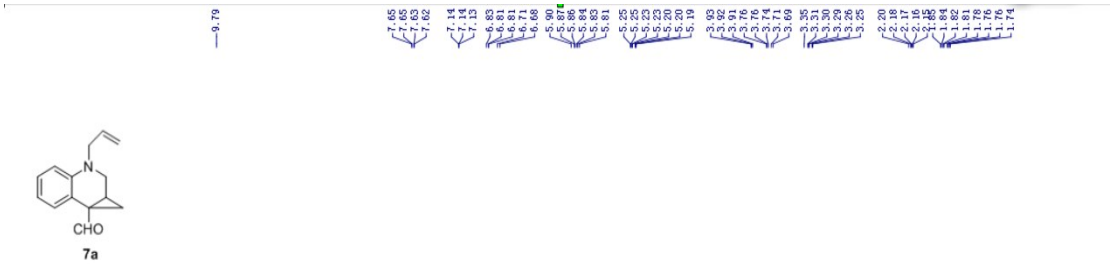
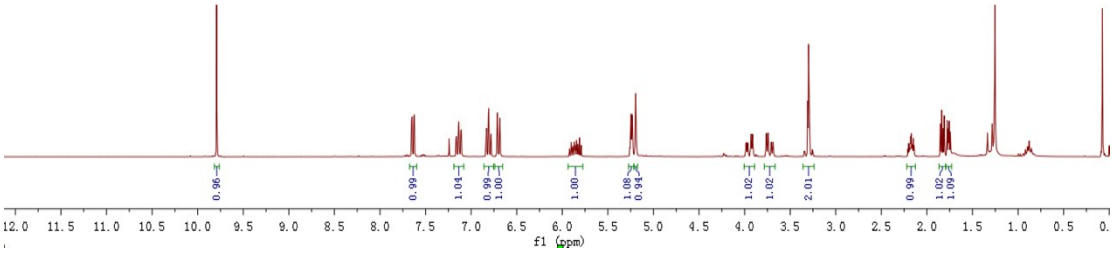
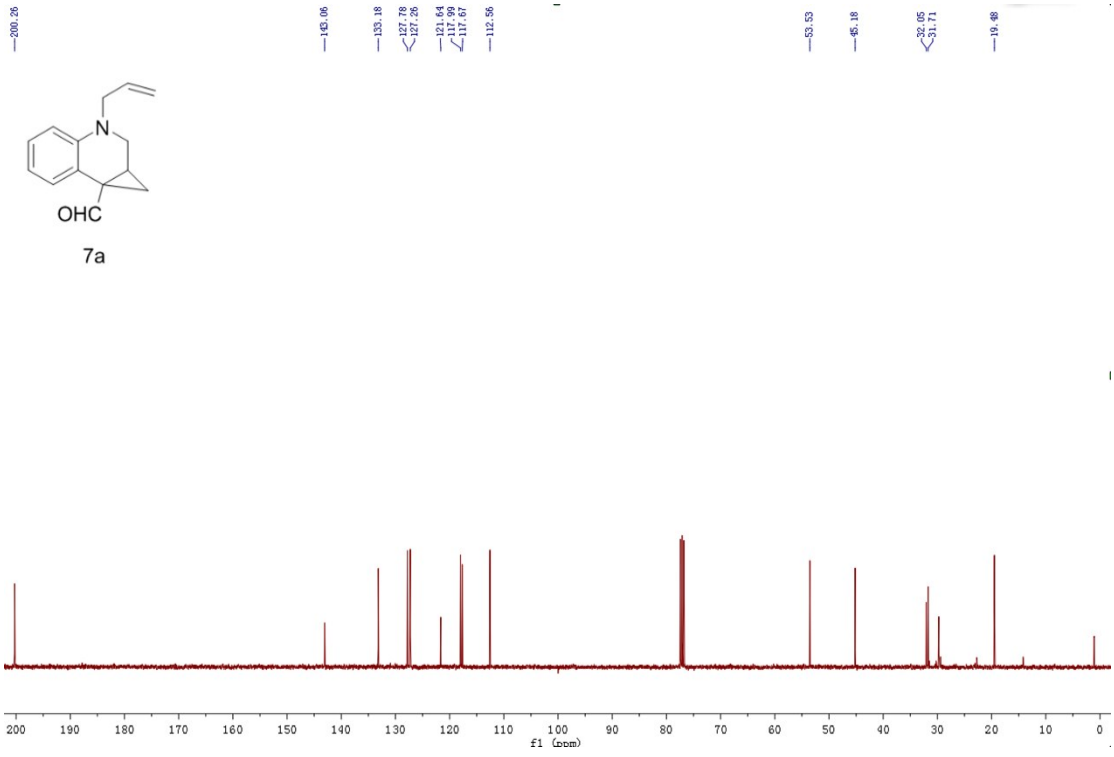
30
20
10
0

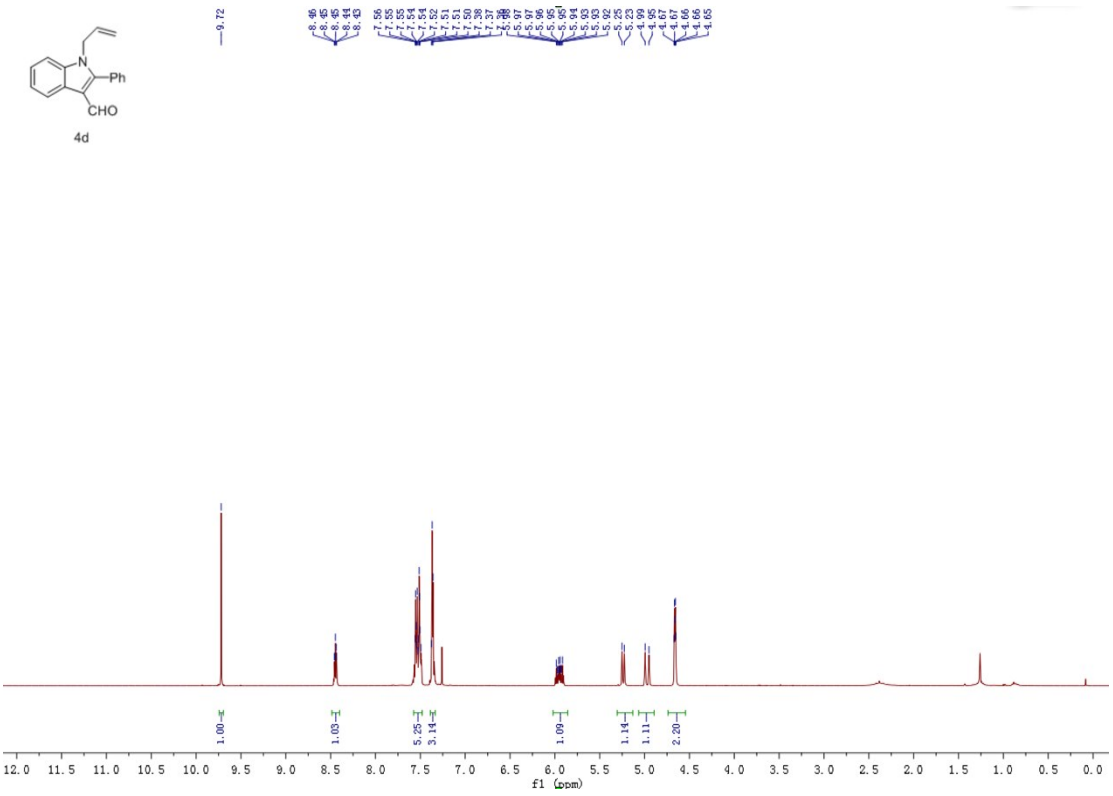

9.79
7.65
7.65
7.63
7.62
7.14
7.14
7.13
6.83
6.81
6.81
6.71
6.68
5.90
5.87
5.86
5.84
5.83
5.81
5.25
5.25
5.23
5.23
5.20
5.20
5.19
3.93
3.92
3.91
3.76
3.74
3.74
3.71
3.69
3.35
3.31
3.30
3.29
3.26
3.25
2.20
2.18
2.17
2.16
2.15
1.84
1.82
1.81
1.81
1.78
1.76
1.76
1.74
N
CHO

7a


0.96
0.99
1.04
0.99
1.00
1.00
1.08
0.94
1.02
1.02
2.01
0.99
1.02
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


200.26
143.06
133.18
127.78
127.26
121.64
117.99
117.67
112.56
53.53
45.18
32.05
31.71
19.48
N
OHC
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7a


Ph
CHO
4d
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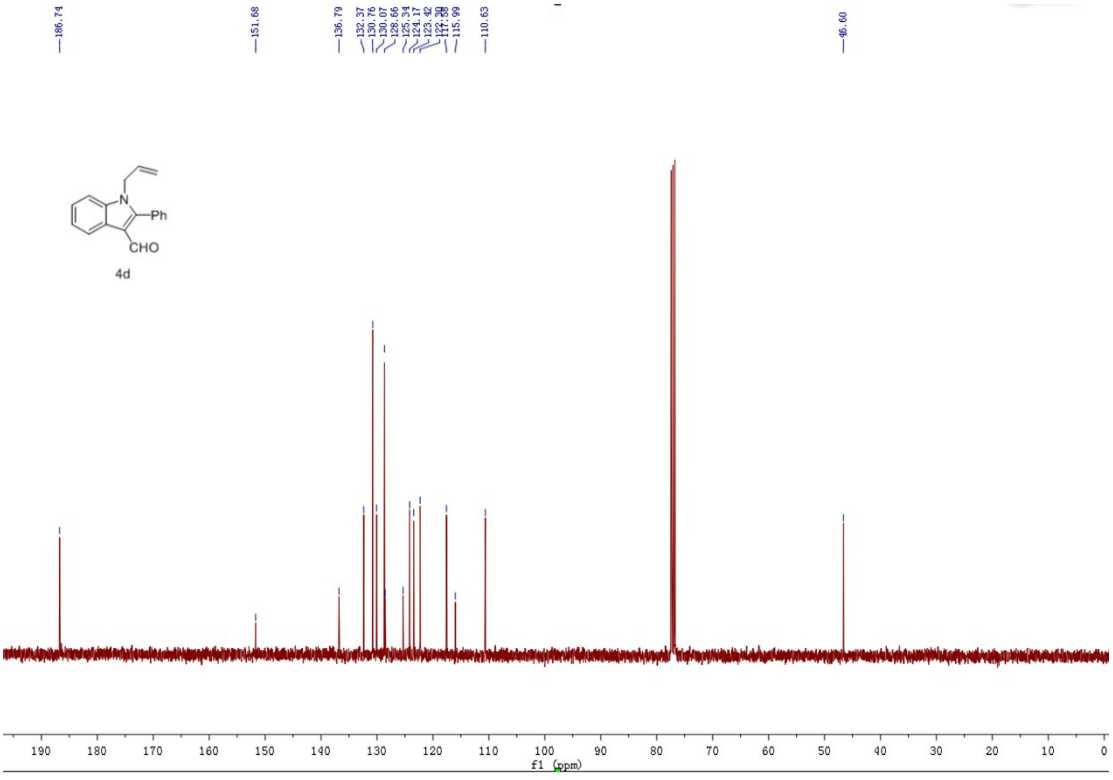
8.45
8.44
8.43
7.56
7.55
7.55
7.54
7.54
7.52
7.51
7.51
7.50
7.39
7.37
7.37
5.98
5.97
5.97
5.96
5.95
5.94
5.93
5.92
5.25
5.23
4.99
4.95
4.67
4.67
4.66
4.66
4.65
1.00
1.03
5.25
3.14
1.09
1.14
1.11
2.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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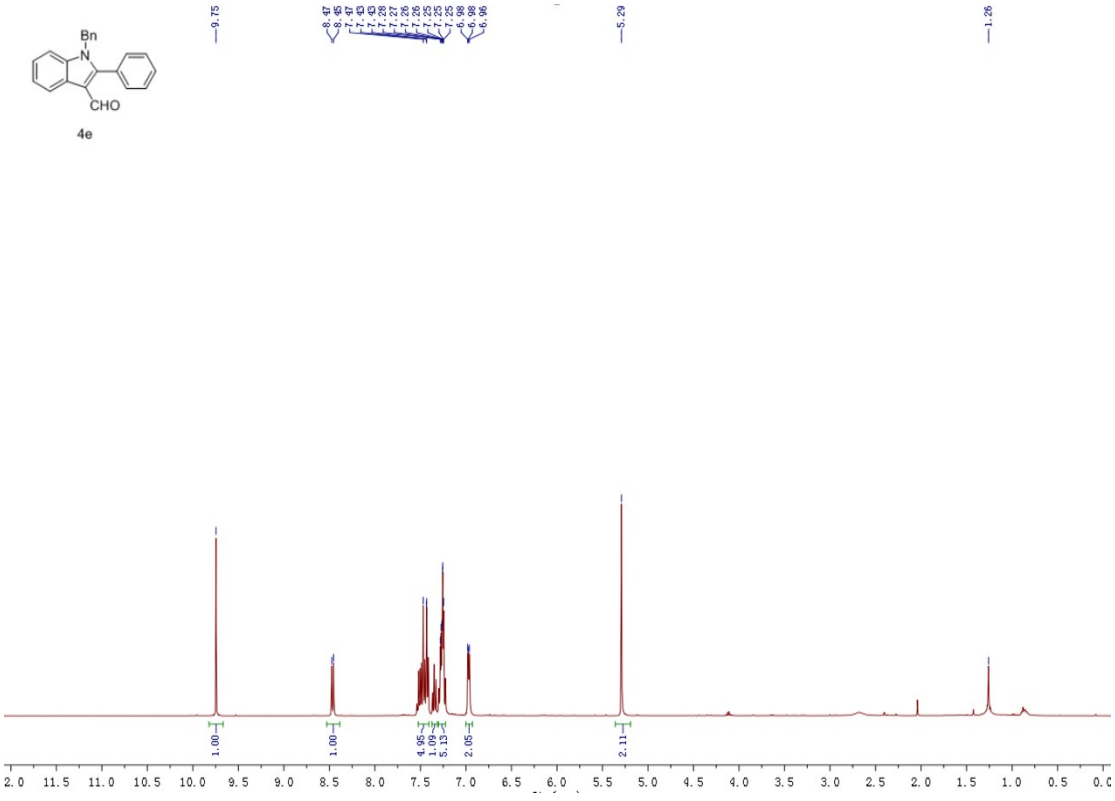
151.68
136.79
132.37
130.76
130.07
128.66
125.34
124.17
123.42
115.99
110.63
46.60
Ph
CHO
4d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Bn
N
CHO
4e
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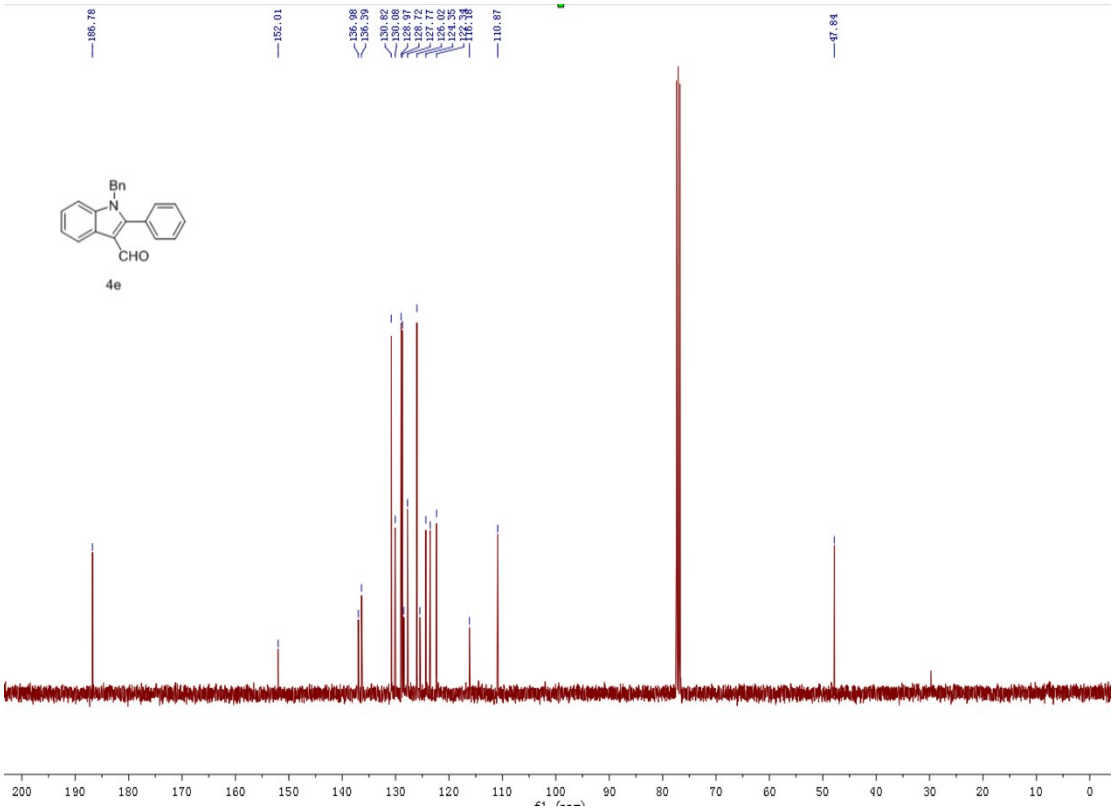
8.47
8.45
7.47
7.43
7.28
7.27
7.26
7.25
7.25
7.23
6.98
6.96
5.29
1.26
1.00
1.00
4.95
1.09
5.13
2.05
2.11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152.01
136.98
136.39
130.82
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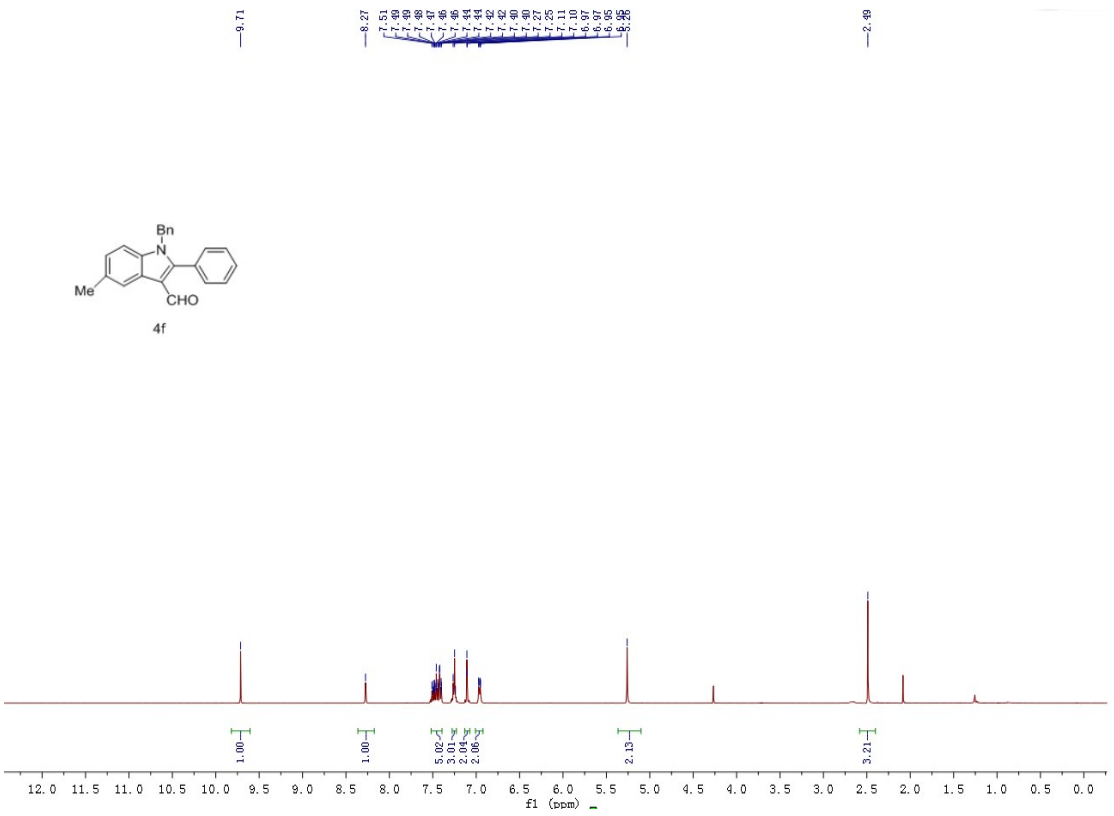
129.97
128.72
127.77
126.02
124.35
110.87
47.84
Bn
N
CHO
4e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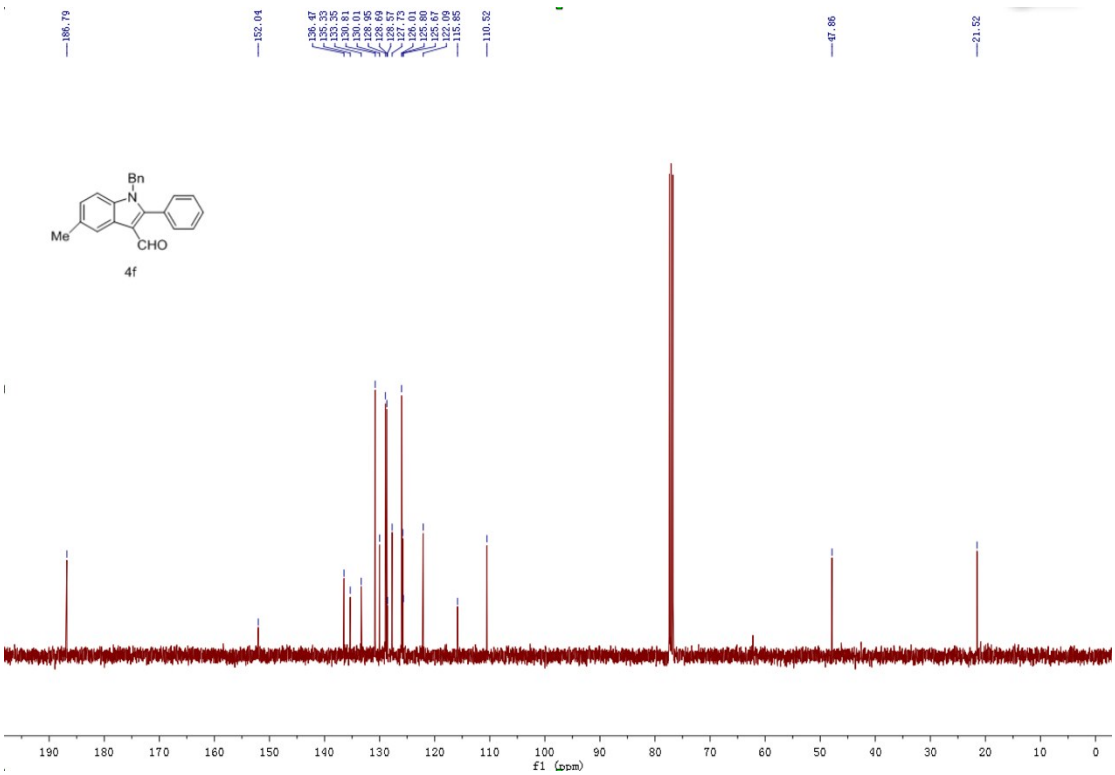
7.49
7.49
7.48
7.47
7.46
7.46
7.44
7.44
7.42
7.42
7.40
7.40
7.27
7.25
7.11
7.10
6.97
6.95
2.49
Bn
N
Me
CHO
4f
1.00
1.00
5.02
3.01
2.08
2.06
2.13
3.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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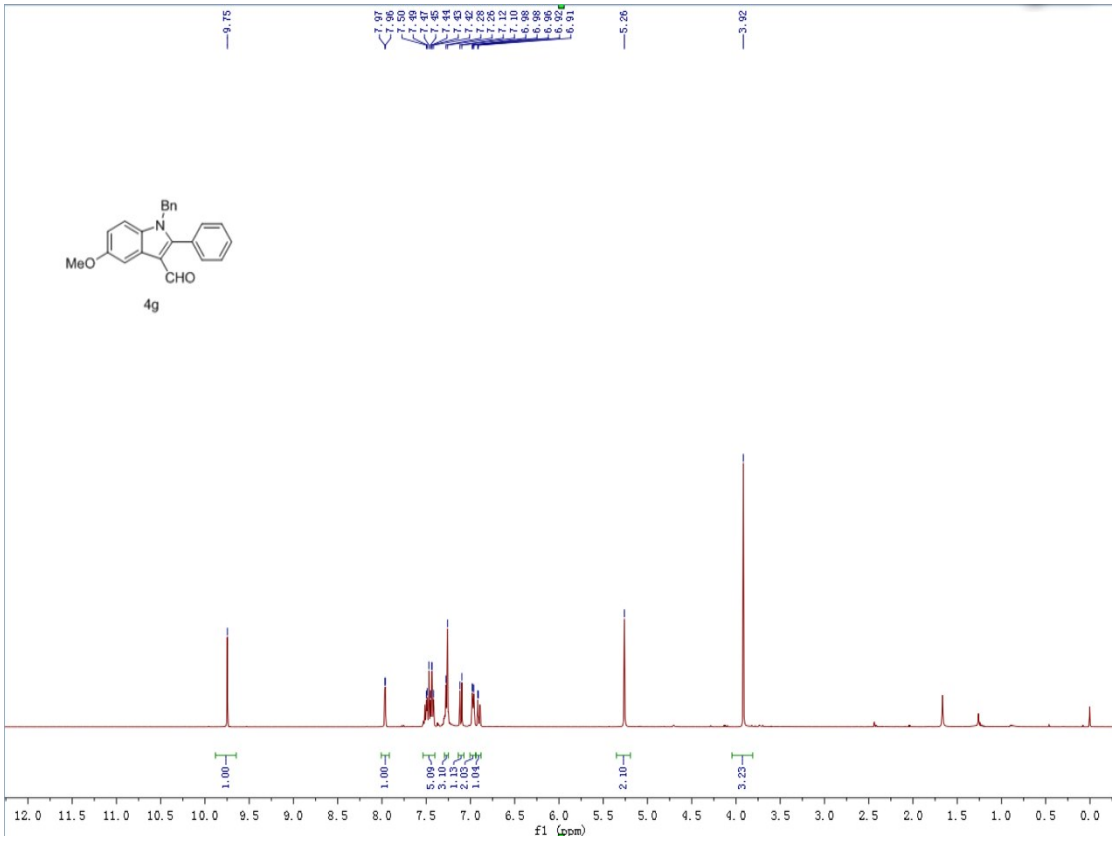
152.04
136.47
135.53
133.35
130.81
130.01
128.95
128.69
128.57
127.73
126.01
125.80
125.67
122.09
115.85
110.52
47.86
21.52
Bn
N
Me
CHO
4f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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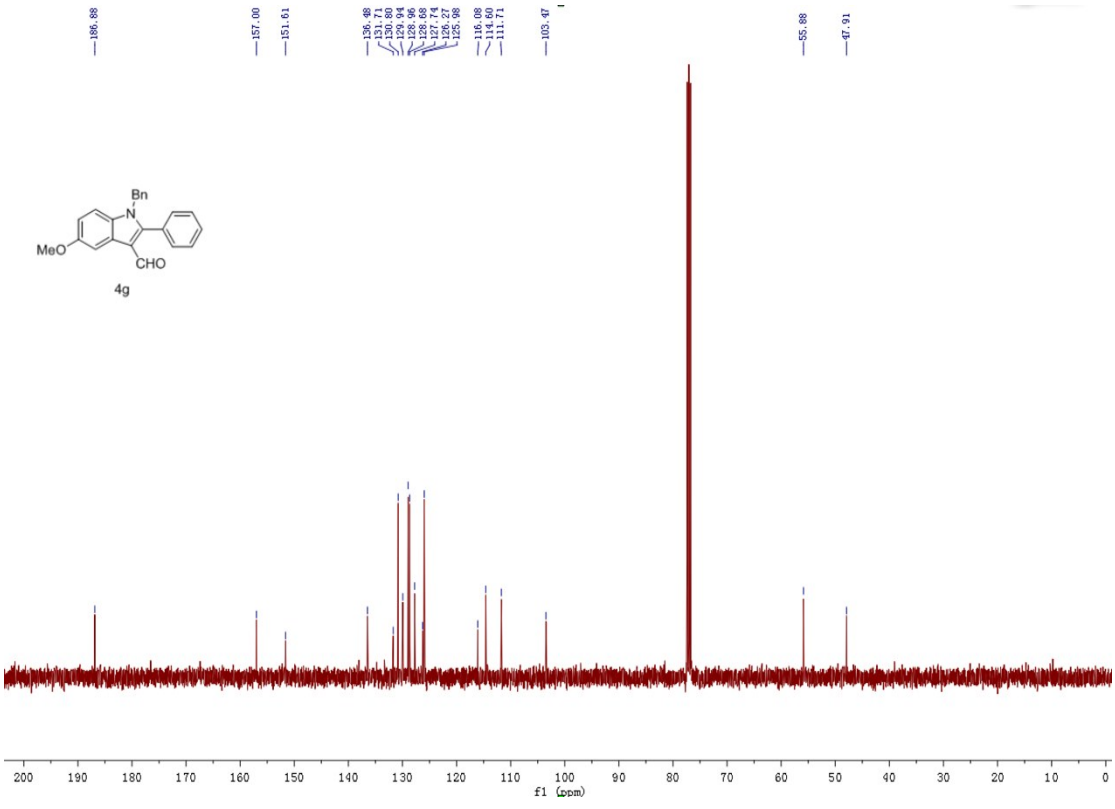
7.97
7.96
7.50
7.49
7.47
7.46
7.44
7.43
7.42
7.28
7.26
7.12
7.10
6.98
6.96
6.92
6.91
5.26
3.92
Bn
N
MeO
CHO
4g
1.00
1.00
5.09
3.10
1.13
2.03
1.04
2.10
3.23
f1 (ppm)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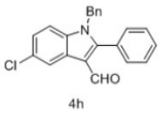
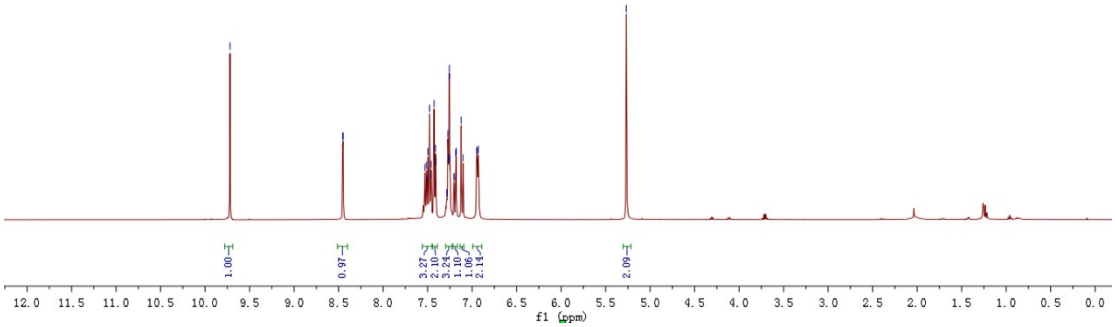
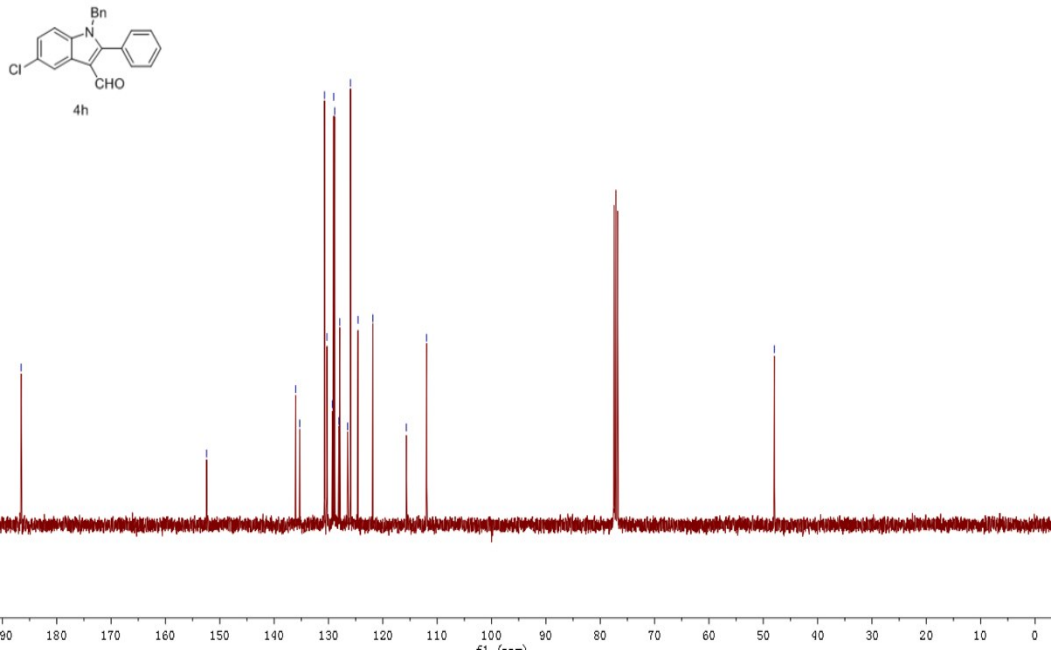
157.00
151.61
136.48
131.71
130.80
129.94
128.96
128.68
127.74
126.27
125.98
116.08
114.60
111.71
103.47
55.88
47.91
Bn
N
MeO
CHO
4g
f1 (ppm)



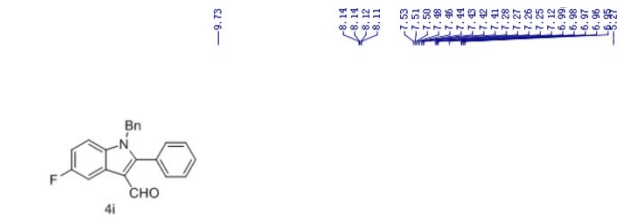

4h

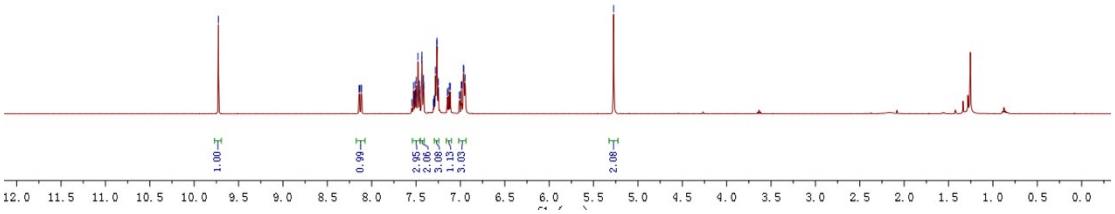


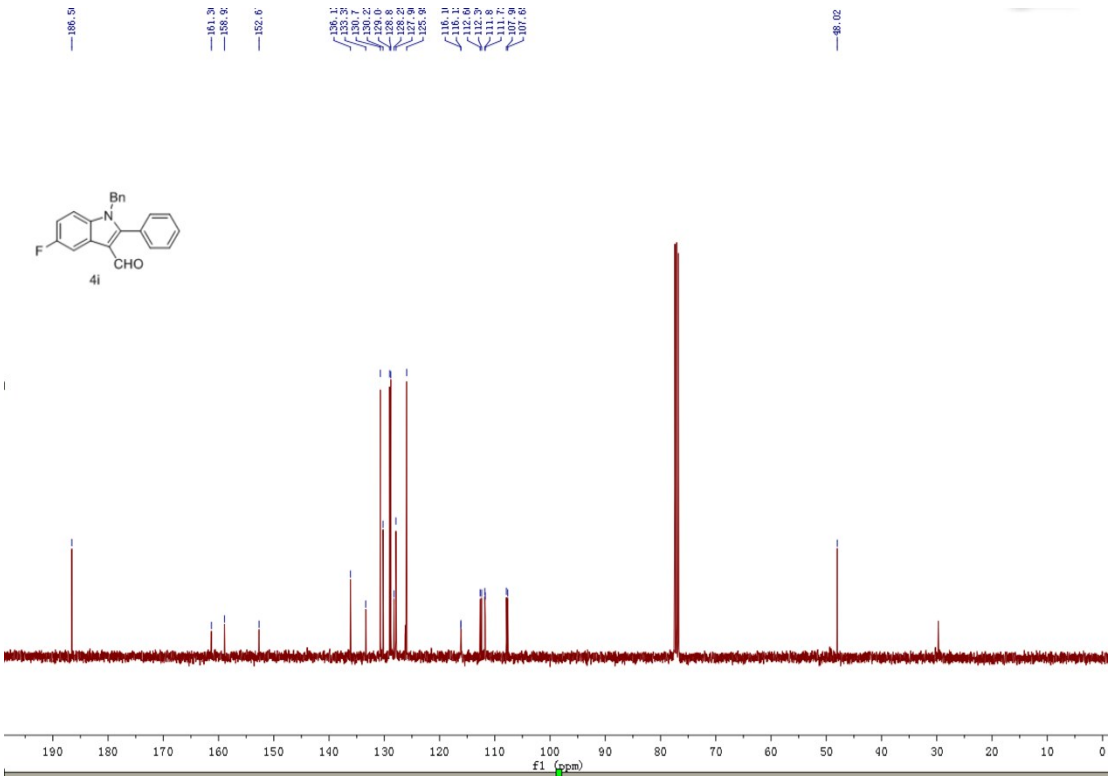






4h


9.73
8.14
8.12
8.11
7.53
7.51
7.50
7.48
7.46
7.44
7.43
7.42
7.41
7.29
7.27
7.26
7.25
7.12
6.98
6.97
6.96
Bn
N
F
CHO
4i


1.00
0.99
2.95
2.06
3.08
1.13
3.03
2.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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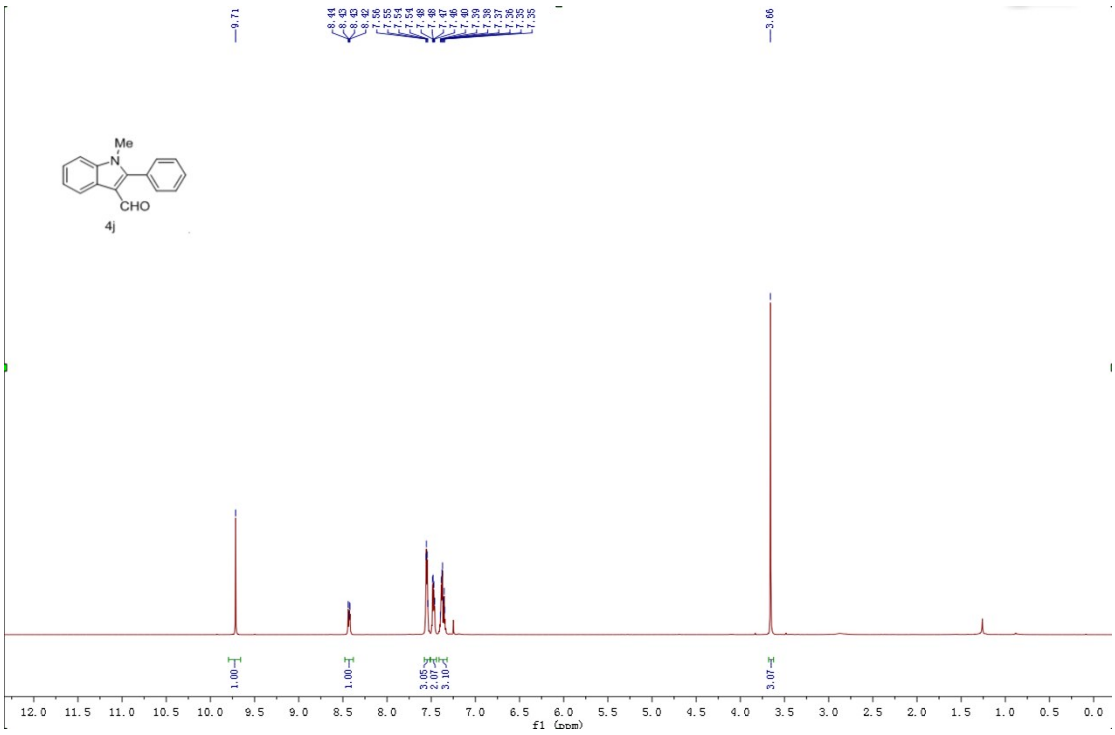
161.39
158.98
152.66
136.11
133.38
130.77
130.22
129.00
128.88
128.23
127.98
125.98
116.10
116.11
112.66
112.39
111.86
111.77
107.98
107.68
48.02
Bn
N
F
CHO
4i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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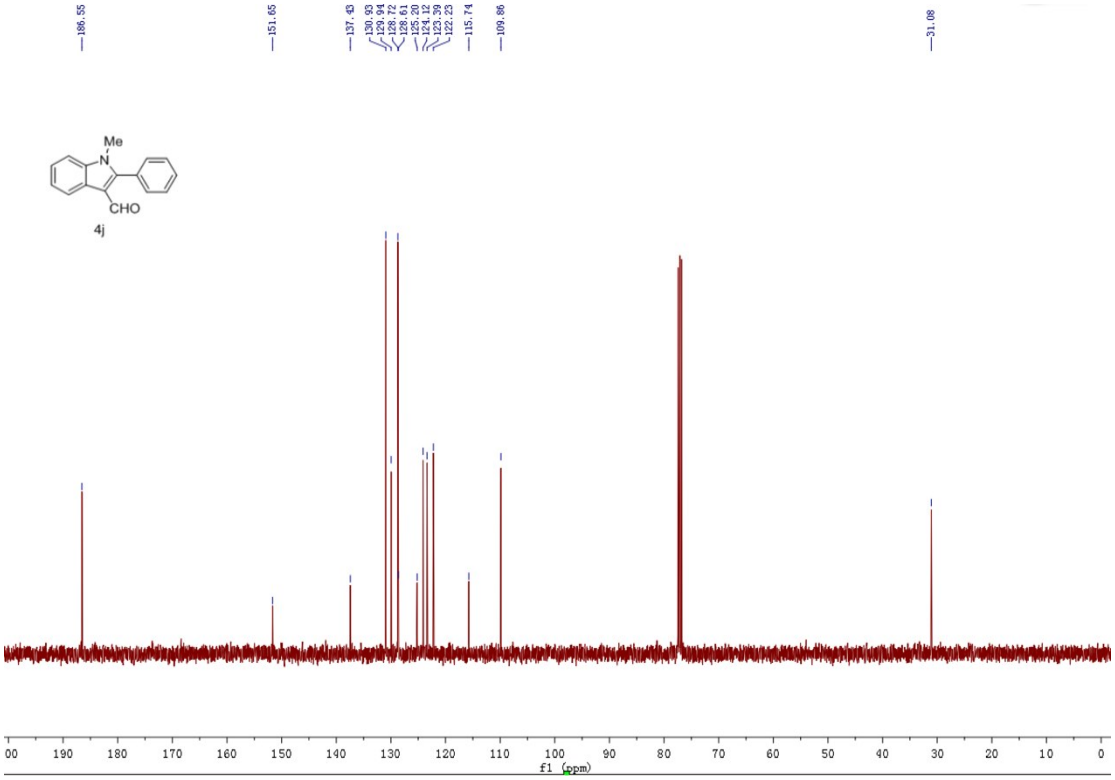
8.44
8.43
8.42
8.42
7.56
7.55
7.54
7.54
7.49
7.48
7.47
7.46
7.40
7.39
7.38
7.37
7.36
7.35
7.35
3.66
Me
N
CHO
4j
1.00
1.00
3.05
2.07
3.10
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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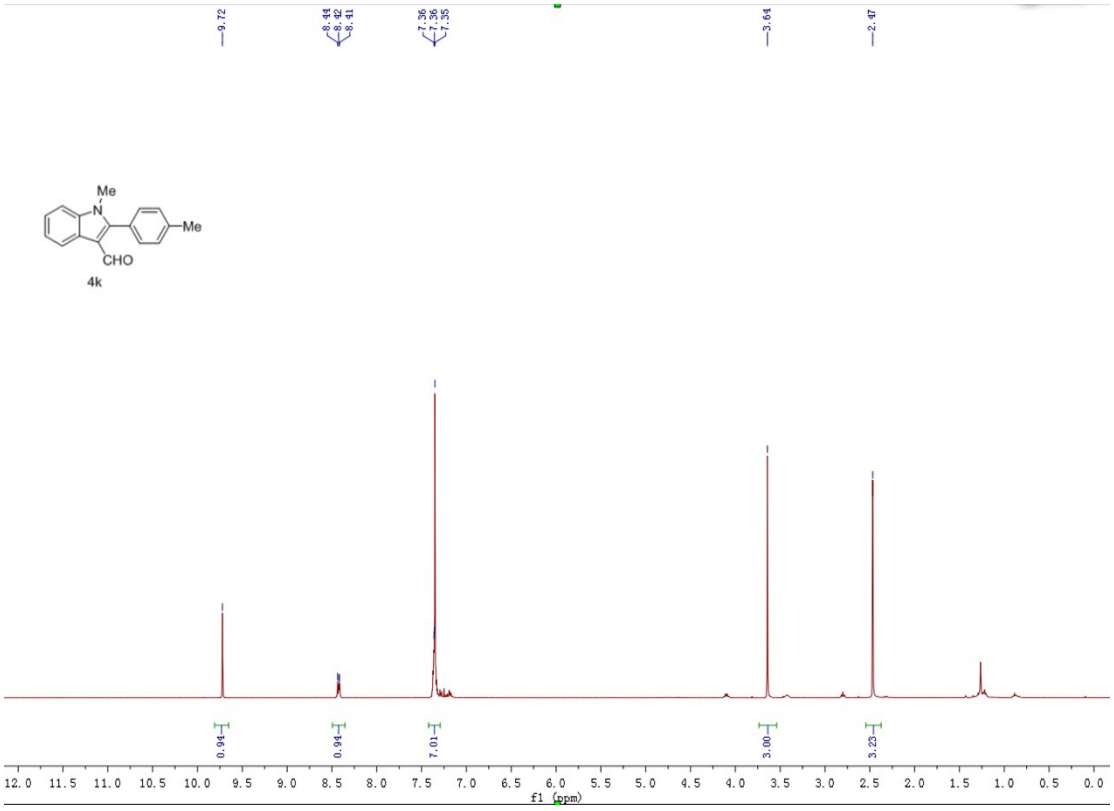
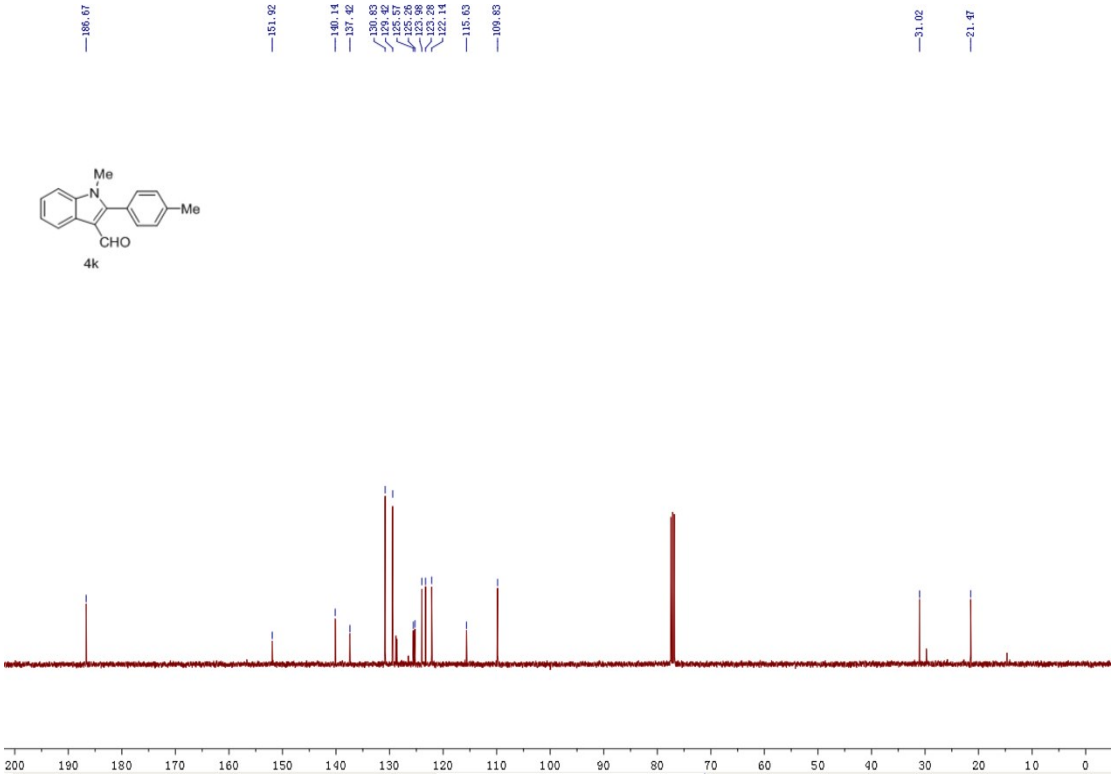
137.43
130.93
130.64
128.72
128.61
125.20
124.12
123.39
122.23
115.74
109.86
31.08
Me
N
CHO
4j
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.72
8.44
8.42
8.41
7.36
7.36
7.35
3.64
2.47
Me
N
Me
CHO
4k
0.94
0.94
7.01
3.00
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.42
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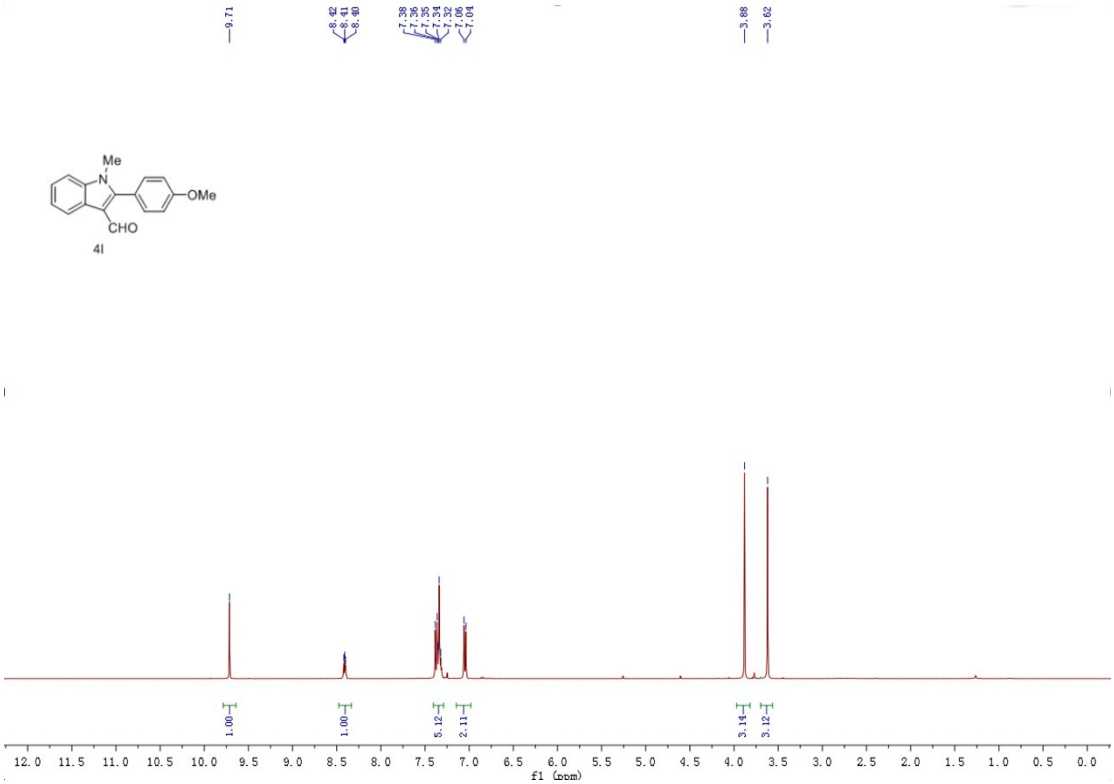
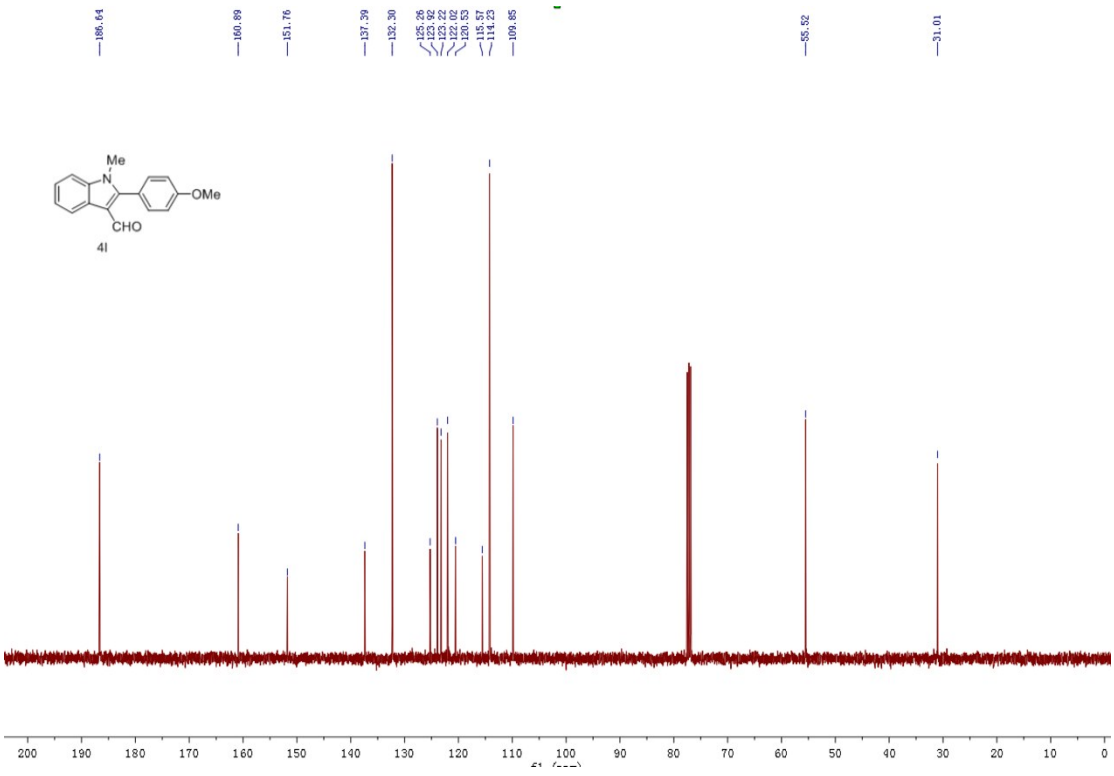
129.42
125.57
125.26
123.98
123.28
122.14
115.63
109.83
31.02
21.47
Me
N
Me
CHO
4k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


9.71
8.42
8.41
8.40
7.38
7.36
7.35
7.34
7.32
7.06
7.04
3.68
3.62
Me
N
OMe
CHO
4l
1.00
1.00
5.12
2.11
3.14
3.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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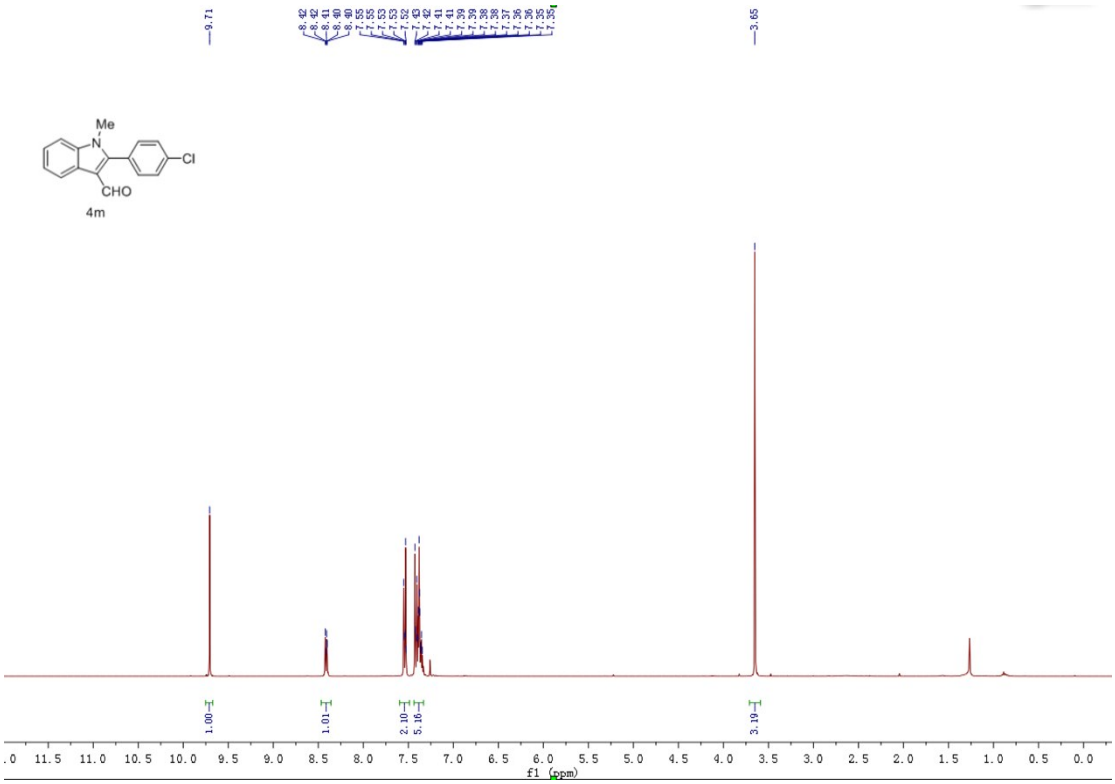
137.39
132.30
125.26
123.92
123.22
122.02
120.53
115.57
114.23
109.85
55.52
31.01
Me
N
OMe
CHO
4l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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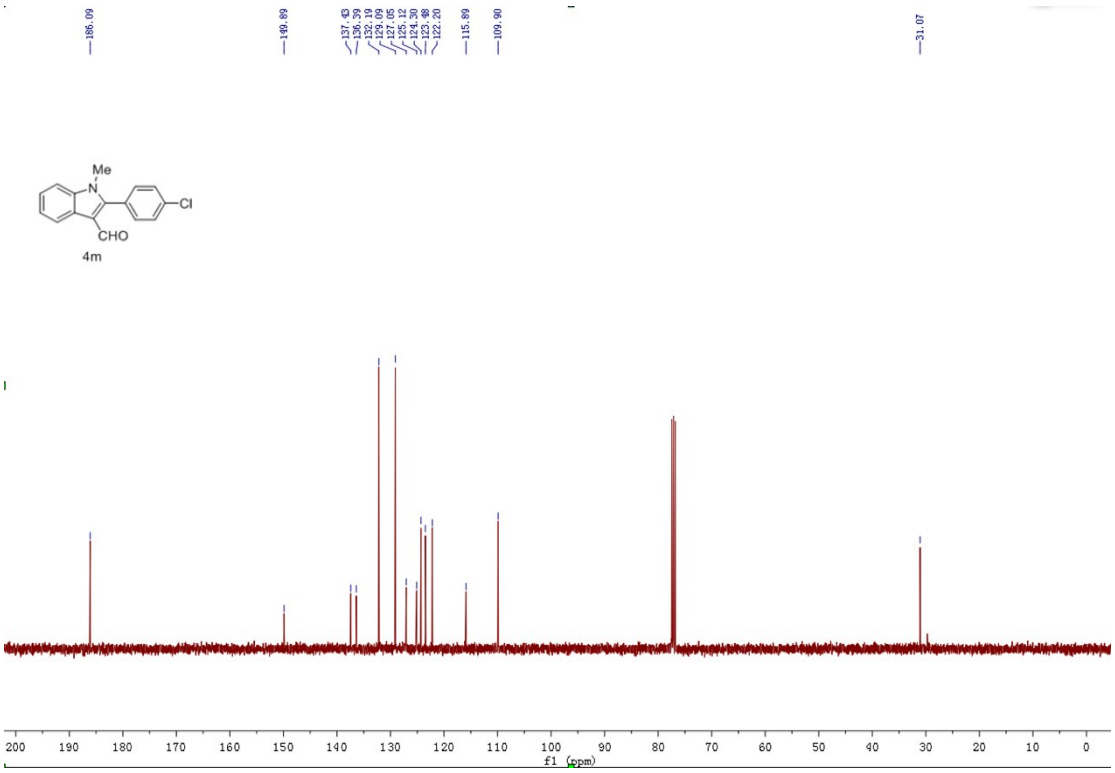
8.42
8.41
8.40
8.40
7.55
7.53
7.53
7.52
7.43
7.42
7.41
7.41
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
3.65
Me
N
Cl
CHO
4m
1.00
1.01
2.10
5.16
3.19
f1 (ppm)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132.19
129.88
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125.12
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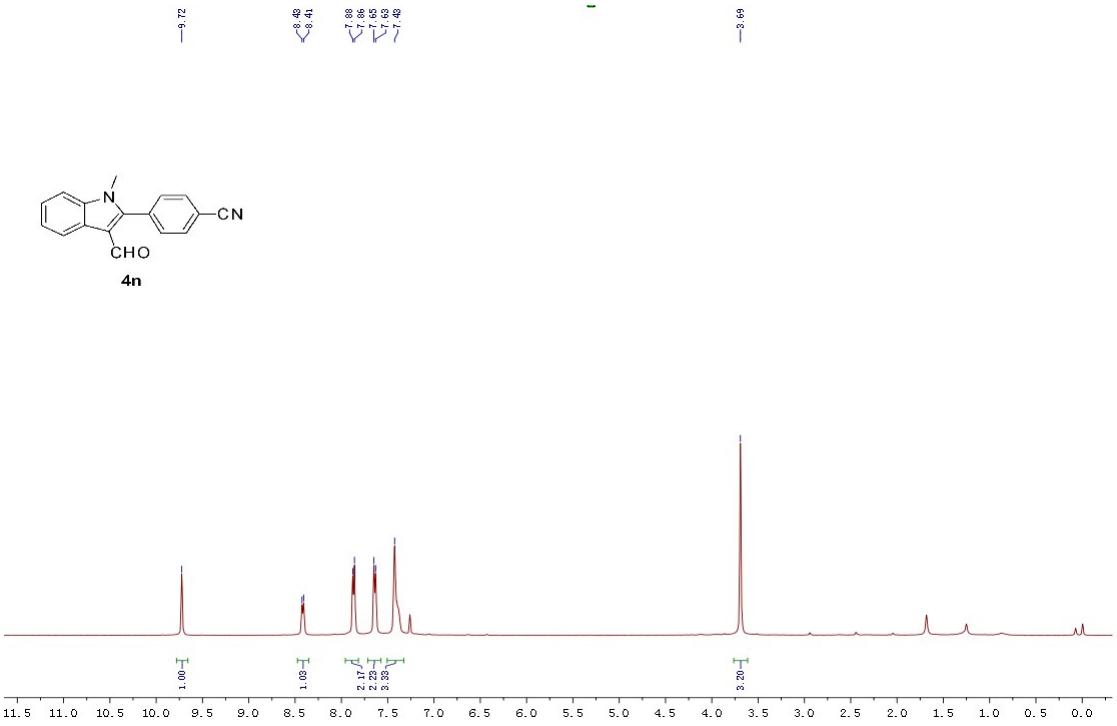
123.48
122.20
115.89
109.90
31.07
Me
N
Cl
CHO
4m
f1 (ppm)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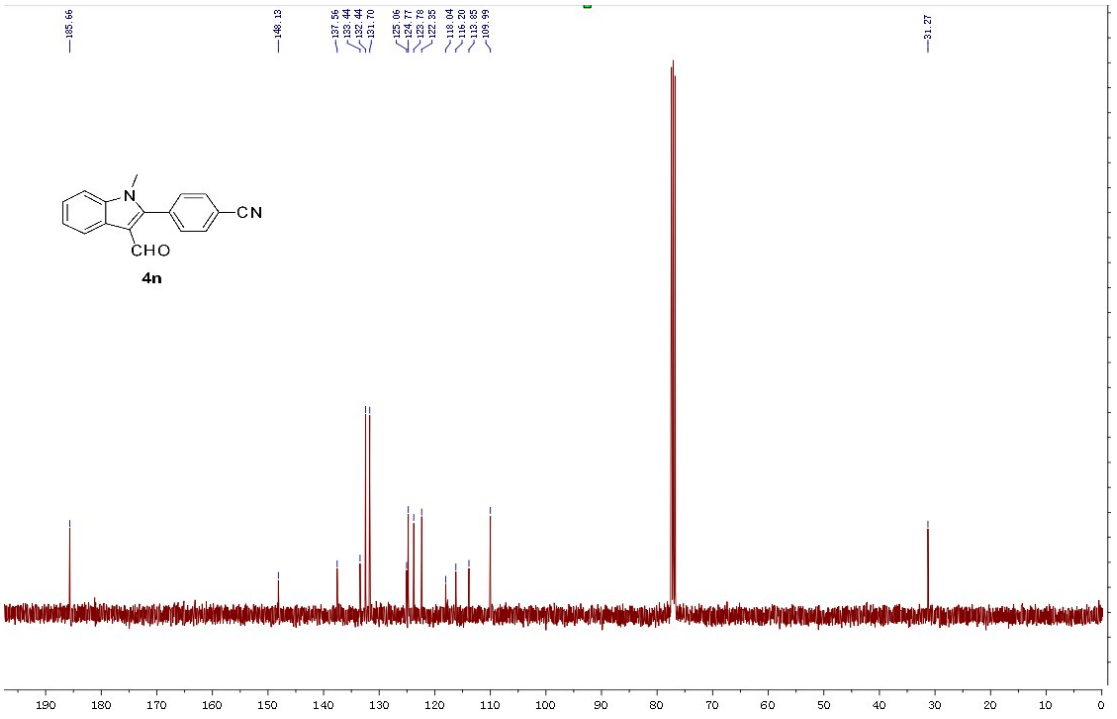
8.48
8.41
7.88
7.86
7.65
7.63
7.48
3.69
CN
CHO
4n
1.00
1.03
2.17
2.23
3.33
3.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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148.13
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133.44
132.44
131.70
125.06
124.17
123.78
122.35
118.04
116.20
113.85
109.99
31.27
CN
CHO
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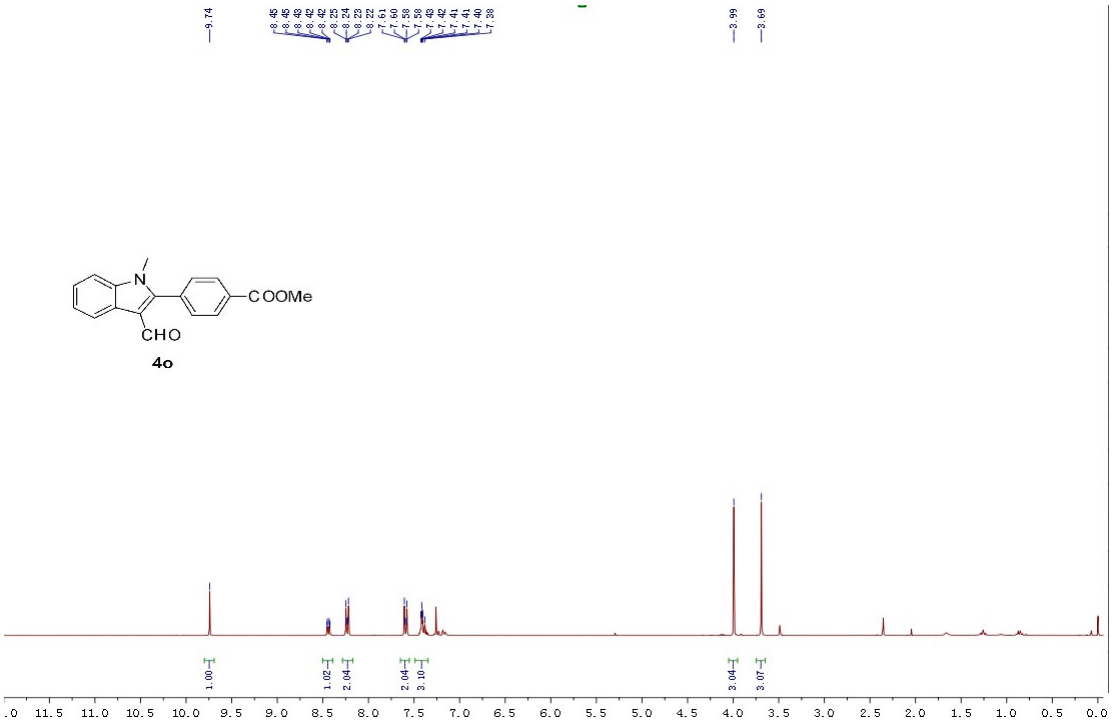
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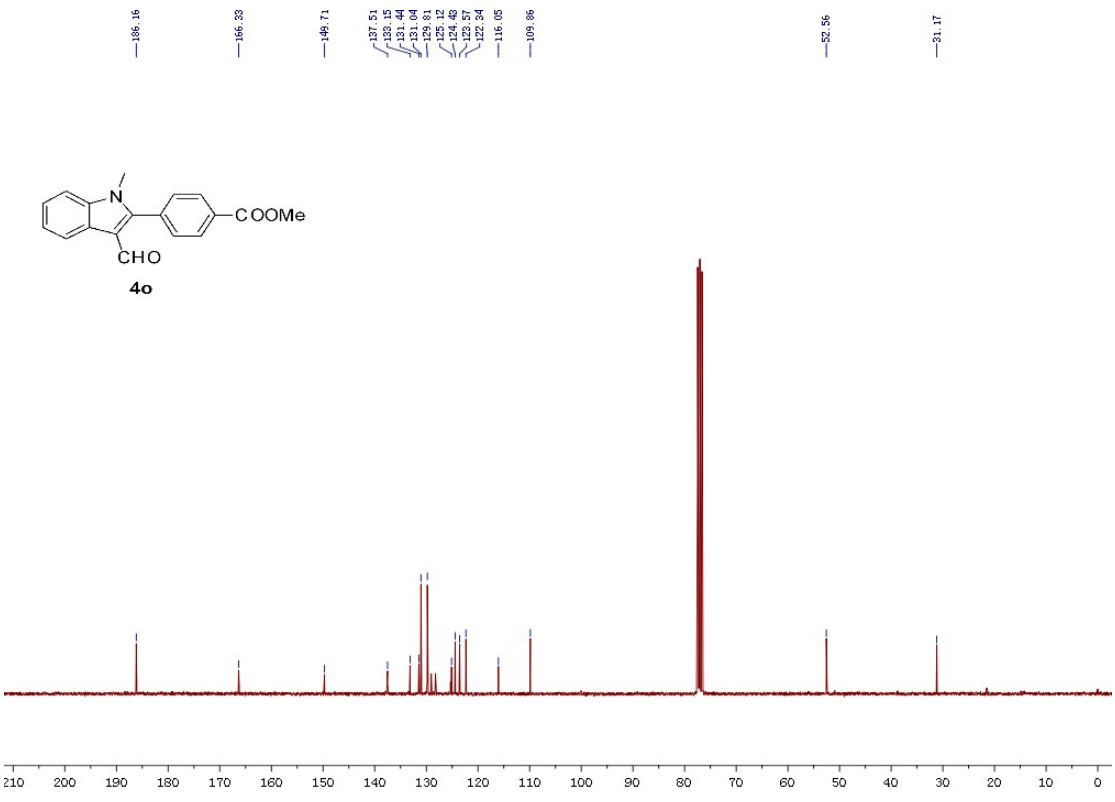
8.45
8.43
8.42
8.42
8.25
8.24
8.23
8.22
7.61
7.60
7.59
7.58
7.48
7.42
7.41
7.41
7.40
7.39
3.99
3.69
N
COOMe
CHO
1.00
1.02
2.04
2.04
3.10
3.04
3.07

4o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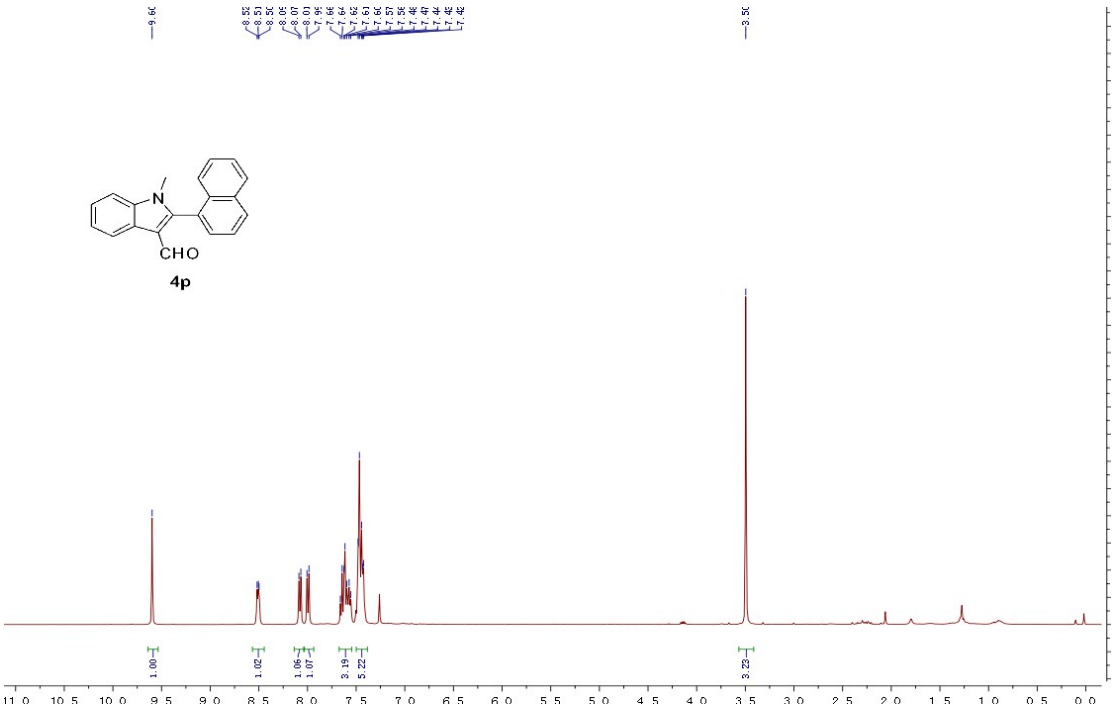
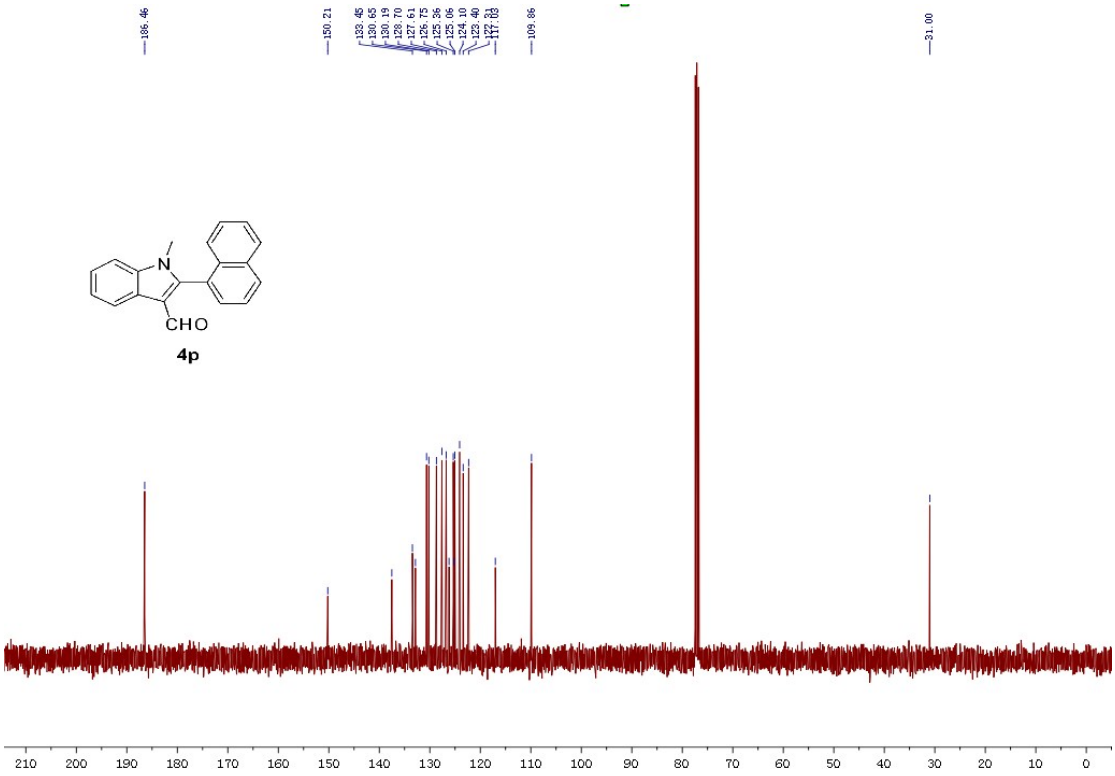
137.51
133.15
131.44
131.04
129.81
125.12
124.48
123.57
122.34
116.05
109.86
52.56
31.17
N
COOMe
CHO

4o


CHO
4p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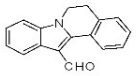

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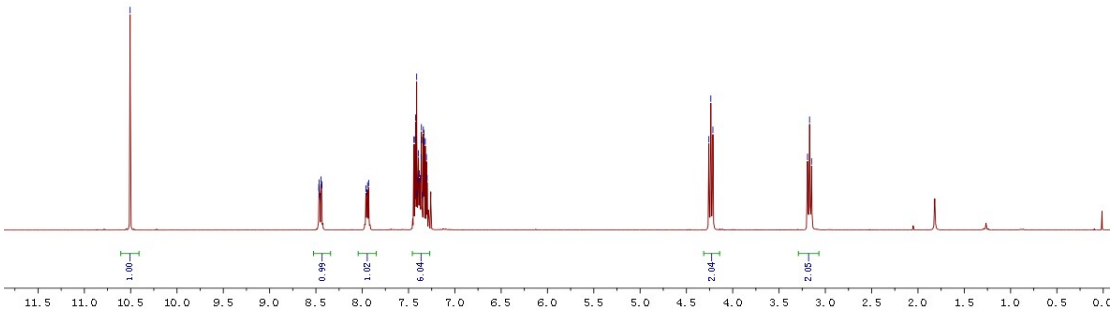

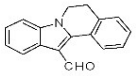

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