Supporting Information for

Silver(I) and Base-Mediated [3+3] Cycloaddition of *C,N*-Cyclic Azomethine Imines with Aza-oxyallyl Cations

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1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from K under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The starting materials were synthesized according to literature procedures.

TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light or dipping into a solution of $KMnO_4$ (1.5 g in 400mL H_2O, 5 g $NaHCO_3$), followed by heating.

Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 μm) applying a pressure of about 0.2 bar.

^{1}H NMR and **^{13}C NMR** spectra were recorded on a *DPX 300*, *AV 400* or *DD2 600* at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR).

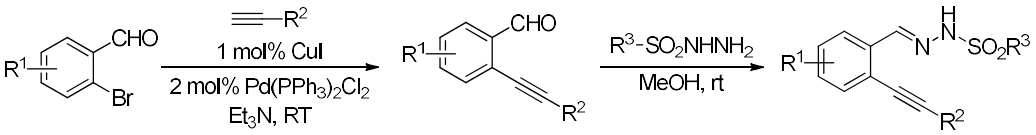
Mass spectra were recorded on a Finnigan MAT 4200S, a *Bruker Daltonics Micro Tof,* a *Waters-Micromass Quatro LCZ* (ESI); peaks are given in m/z (% of basis peak).

IR spectra were recorded on a *Digilab FTS 4000* with a Specac MKII Golden Gate Single Refelxtion ART System. IR signals are described as *w* (weak), *m* (middle), *s* (strong).

Melting points (MP) were determined by *Stuart SMP10* and are uncorrected.

2. Preparation and Spectral Data of starting materials

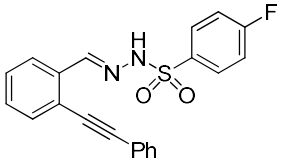
The hydrazide **1**[1] were prepared according to the following 2 steps (***GP1***) and the spectral data of unknown structures were list as bellow. All of the α-halohydroxamate **2** are known compounds and synthesized according to the literature methods. [2-4]



Step I: Under the protection of argon, $Pd(PPh_3)_2Cl_2$ (0.02 equiv) was added to a solution of 2-bromobenzaldehyde (1.0 equiv), alkyne (1.2 equiv) in Et_3N (0.25 M). The mixture was stirred for 5 min and then CuI (0.01 equiv) was added. The resulting system was then stirred at room temperature until full consumption of the 2-bromobenzaldehyde as monitored by TLC. The formed ammonium salt was removed by filtration and washed with Et_2O several times. The filtrate was then washed with brine and the aqueous layer was extracted with Et_2O for 3 times. The combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the corresponding coupling product.

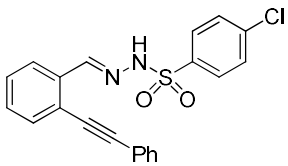
Step II: A solution of 2-ethynylbenzaldehyde (1.0 equiv), hydrazine (1.2 equiv) and MeOH (0.5 M) was stirred in a dried round flask at room temperature until full consumption of the 2-ethynylbenzaldehyde as monitored by TLC. The reaction mixture was diluted with dichloromethane. The resulting mixture was chromatographed on silica gel to give the final adduct.

(*E*)-4-fluoro-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1c)



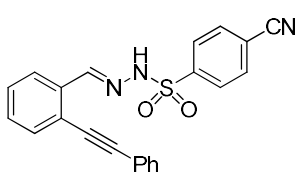
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.42 (s, 1H), 8.36 (s, 1H), 8.12 – 8.00 (m, 2H), 7.99 – 7.90 (m, 1H), 7.61 – 7.49 (m, 3H), 7.37 (dd, *J* = 6.1, 2.9 Hz, 5H), 7.20 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.5 (d, *J* = 254.3), 146.3, 134.3 (d, *J* = 3.2), 133.8, 132.5, 131.6, 130.8 (d, *J* = 9.5), 130.1, 128.8, 128.6, 128.5, 125.4, 123.4, 122.5, 116.4 (d, *J* = 22.6), 95.3, 85.9; **HRMS** (ESI) exact mass calculated for $C_{21}H_{15}FN_2O_2S$: 401.0736, found: 401.0730 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1592*m*, 1493*s*, 1443*w*, 1364*w*, 1293*w*, 1171*s*, 1155*s*, 1091*m*, 1053*w*, 836*m*, 756*s*, 690*m*, 600*w*; **Mp**: 179 – 180 °C.

(*E*)-4-chloro-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1d)



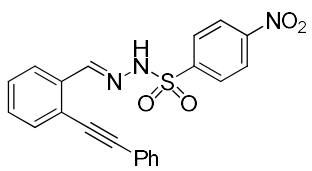
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.42 (s, 1H), 8.35 (s, 1H), 8.04 – 7.86 (m, 3H), 7.62 – 7.45 (m, 5H), 7.43 – 7.30 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.4, 140.0, 136.7, 133.7, 132.5, 131.6, 130.2, 129.4, 129.4, 128.8, 128.6, 128.5, 125.4, 123.4, 122.5, 95.3, 85.9; **HRMS** (ESI) exact mass calculated for $C_{21}H_{15}ClN_2O_2S$: 417.0440, found: 417.0435 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1493*m*, 1442*w*, 1362*m*, 1323*m*, 1168*s*, 1093*s*, 1015*m*, 944*m*, 821*m*, 754*s*, 732*w*, 636*w* 596*w*; **Mp**: 180 – 181 °C.

(*E*)-4-cyano-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1e)



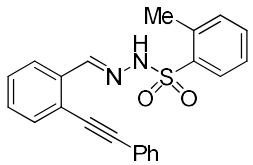
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.88 (s, 1H), 8.43 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.41 – 7.30 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.9, 142.5, 133.5, 132.8, 132.5, 131.5, 130.3, 128.9, 128.6, 128.5, 125.3, 123.4, 122.4, 117.2, 116.8, 95.3, 85.8; **HRMS** (ESI) exact mass calculated for $C_{22}H_{15}N_3O_2S$: 408.0783, found: 408.0777 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1493*m*, 1443*w*, 1368*m*, 1328*m*, 1184*s*, 1169*s*, 1091*m*, 946*m*, 910*w*, 757*s*, 731*w*, 644*s*, 598*m*; **Mp**: 135 – 136 °C.

(*E*)-4-nitro-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1f)



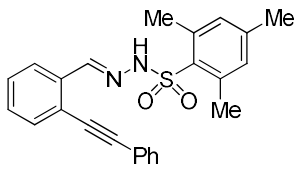
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.31 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.18 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.90 – 7.78 (m, 1H), 7.51 – 7.37 (m, 3H), 7.35 – 7.20 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.5, 147.1, 143.9, 133.3, 132.6, 131.5, 130.5, 129.3, 129.0, 128.7, 128.5, 125.4, 124.3, 123.6, 122.4, 95.4, 85.8; **HRMS** (ESI) exact mass calculated for $C_{21}H_{15}N_3O_4S$: 428.0681, found: 428.0675 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1607*w*, 1530*s*, 1493*m*, 1348*s*, 1311*m*, 1171*s*, 1091*w*, 1053*s*, 853*s*, 758*s*, 737*s*, 683*m*, 592*m*; **Mp**: 162 – 163 °C.

(*E*)-2-methyl-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1g)



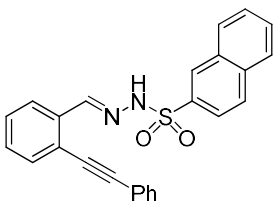
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.31 (s, 1H), 8.04 (d, *J* = 9.1 Hz, 2H), 7.81 – 7.73 (m, 1H), 7.50 – 7.37 (m, 4H), 7.32 – 7.21 (m, 7H), 2.68 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.2, 138.0, 136.6, 134.0, 133.4, 132.6, 132.4, 131.6, 130.5, 129.9, 128.8, 128.6, 128.5, 126.4, 125.4, 123.3, 122.6, 95.2, 85.9, 20.8; **HRMS** (ESI) exact mass calculated for $C_{22}H_{18}N_2O_2S$: 397.0987, found: 397.0981 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1350*w*, 1326*m*, 1163*s*, 1098*w*, 956*w*, 868*w*, 822*w*, 762*m*, 749*s*, 686*s*, 606*s*, 585*s*; **Mp**: 191 – 192 °C.

(*E*)-2,4,6-trimethyl-*N*'-(2-(phenylethynyl)benzylidene)benzenesulfonohydrazide (1h)



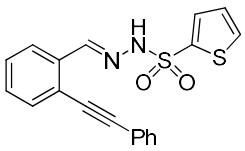
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.59 (s, 1H), 8.41 (s, 1H), 7.93 – 7.79 (m, 1H), 7.65 – 7.46 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 5H), 7.00 (s, 2H), 2.79 (s, 6H), 2.32 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.7, 143.1, 140.3, 134.2, 132.4, 132.3, 132.0, 131.6, 129.7, 128.7, 128.5, 128.4, 125.2, 123.2, 122.6, 95.2, 86.0, 23.3, 21.0; **HRMS** (ESI) exact mass calculated for $C_{24}H_{22}N_2O_2S$: 425.1300, found: 425.1294 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1601*w*, 1491*w*, 1442*w*, 1320*s*, 1203*w*, 1157*s*, 1098*w*, 1052*m,* 1035*w*, 937*m*, 852*m*, 820*m*, 747*s*, 683*m*, 657*s*, 604*m*, 574*m*; **Mp**: 192 – 193 °C.

(*E*)-*N*'-(2-(phenylethynyl)benzylidene)naphthalene-2-sulfonohydrazide (1i)



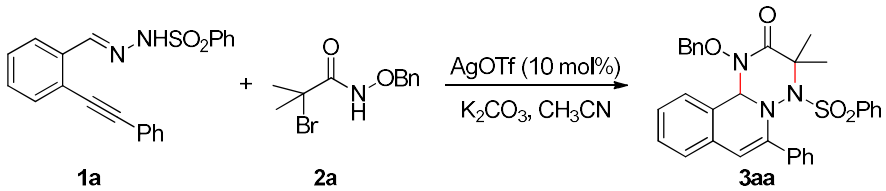
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.63 (s, 1H), 8.47 (d, *J* = 10.2 Hz, 2H), 8.10 – 7.83 (m, 5H), 7.71 – 7.45 (m, 5H), 7.43 – 7.25 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.1, 135.2, 135.1, 133.9, 132.3, 132.1, 131.5, 129.9, 129.6, 129.4, 129.3, 129.0, 128.7, 128.5, 128.4, 127.9, 127.5, 125.4, 123.3, 122.8, 122.5, 95.3, 85.9; **HRMS** (ESI) exact mass calculated for $C_{25}H_{18}N_2O_2S$: 433.0987, found: 433.0981 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 1591*w*, 1493*m*, 1443*w*, 1354*m*, 1322*m*, 1165*s*, 1132*m*, 1057*m,* 908*w*, 860*m*, 814*m*, 755*s*, 659*s*, 617*w*; **Mp**: 171 – 172 °C.

(*E*)-*N*'-(2-(phenylethynyl)benzylidene)thiophene-2-sulfonohydrazide (1j)



^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.47 (s, 1H), 8.23 (s, 1H), 8.10 – 8.00 (m, 1H), 7.80 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.65 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.45 – 7.34 (m, 5H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.6, 138.4, 133.8, 133.6, 133.3, 132.4, 131.6, 130.2, 128.8, 128.6, 128.5, 127.4, 125.6, 123.5, 122.5, 95.4, 85.9; **HRMS** (ESI) exact mass calculated for $C_{19}H_{14}N_2O_2S_2$: 389.0394, found: 389.0389 ([M+Na]$^+$); **IR** (neat, cm^{-1}): 1493*m*, 1442*w*, 1403*w*, 1325*m*, 1227*w*, 1165*s*, 1057*w*, 1017*s*, 912*w*, 855*w*, 757*s*, 691*m*, 675*m*, 596*m*; **Mp**: 157 – 158 °C.

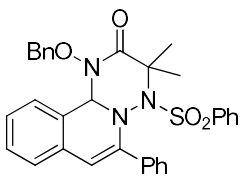
3. General Procedure and Spectral Data of Products



1a **2a** **3aa**

General procedure (*GP2*): A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (1.0 equiv, 0.1 mmol), AgOTf (0.1 equiv, 0.01 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times). Then, CH_3CN (1.5 mL) was added under a flow of argon. The reaction mixture was then stirred at 80 °C for 3 h. After cooling to room temperature, **2a** (2.0 equiv, 0.2 mmol) and K_2CO_3 (4.0 equiv, 0.4 mmol) were added and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure product **3aa** as a white solid in 88% yield.

1-(benzyloxy)-3,3-dimethyl-6-phenyl-4-(phenylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11b*H*)-one (3aa)

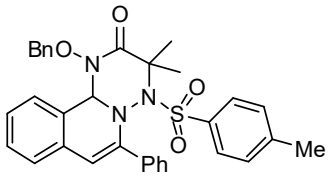


According to ***GP2*** with **1a** (36.0 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3aa** as a white solid in 88% yield (48.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H),

77.42 – 7.34 (m, 3H), 7.31 – 7.21 (m, 5H), 7.19 – 7.08 (m, 5H), 6.84 – 6.71 (m, 3H), 5.86 (s, 1H), 5.65 (s, 1H), 4.69 (d, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 1.73 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.7, 147.0, 139.4, 135.3, 134.1, 133.4, 132.2, 130.4, 130.2, 129.7, 129.1, 128.9, 128.7, 128.6, 128.6, 128.2, 127.8, 126.2, 124.6, 123.2, 108.6, 77.6, 75.9, 70.9, 26.4, 25.4; **HRMS** (ESI) exact mass calculated for $C_{32}H_{29}N_3O_4S$: 552.1957, found: 552.1952 ($[M+H]^+$); **IR** (neat, cm^{-1}):1686*s*, 1492*m*, 1447*m*, 1356*s*, 1286*w*, 1089*m*, 972*w*, 753*s*, 725*s*, 699*m*, 642*w*, 578*s*; **Mp**: 162 – 163 °C.

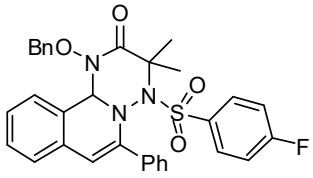
1-(benzyloxy)-3,3-dimethyl-6-phenyl-4-tosyl-3,4-dihydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11b*H*)-one (**3ba**)



According to ***GP2*** with **1b** (37.4 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ba** as a white solid in 92% yield (52.2 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.62 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.24 (m, 7H), 7.20 – 7.09 (m, 7H), 6.84 – 6.71 (m, 3H), 5.85 (s, 1H), 5.70 (s, 1H), 4.69 (d, *J* = 9.2 Hz, 1H), 4.10 (d, *J* = 9.2 Hz, 1H), 2.39 (s, 3H), 1.71 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.8, 147.0, 144.5, 136.6, 135.4, 134.2, 132.3, 130.3, 130.2, 129.7, 129.5, 129.3, 129.1, 128.6, 128.6, 128.2, 127.7, 126.1, 124.6, 123.2, 120.2, 108.4, 77.6, 75.8, 70.8, 26.3, 25.4, 21.6; **HRMS** (ESI) exact mass calculated for $C_{33}H_{31}N_3O_4S$: 566.2114, found: 566.2108 ($[M+H]^+$); **IR** (neat, cm^{-1}):167*s* 1682*s*, 1492*m*, 1355*s*, 1286*w*, 1164*s*, 1089*m*, 971*m*, 909*s*, 815*w*, 729*s*, 699*s*, 668*s*, 655*m*, 610*w*, 567*s*; **Mp**: 163 – 164 °C.

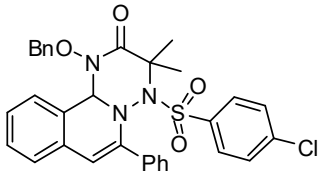
1-(benzyloxy)-4-((4-fluorophenyl)sulfonyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11b*H*)-one (**3ca**)



According to ***GP2*** with **1c** (37.8 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ba** as a white solid in 93% yield (53.1 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 – 7.63 (m, 2H), 7.48 – 6.95 (m, 14H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.3 Hz, 2H), 5.84 (s, 1H), 5.73 (s, 1H), 4.68 (d, *J* = 9.3 Hz, 1H), 4.14 (d, *J* = 9.3 Hz, 1H), 1.75 (s, 3H), 1.18 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.5, 165.6 (d, *J* = 255.4), 146.6, 135.3, 135.2 (d, *J* = 3.1), 134.1, 132.1, 132.0, 131.9, 130.4, 130.1, 129.7, 128.7, 128.7, 128.6, 128.6, 128.2, 127.7, 126.3, 124.7, 123.1, 116.2 (d, *J* =22.4), 108.7, 77.7, 75.8, 70.8, 26.4, 25.2; **HRMS** (ESI) exact mass calculated for $C_{32}H_{28}FN_3O_4S$: 570.1863, found: 570.1857 ($[M+H]^+$); **IR** (neat, cm^{-1}): 1684*s*, 1591*m*, 1492*s*, 1291*m*, 1238*m*, 1168*s*, 1155*s*, 1068*m*, 972*m*, 910*m*, 754*s*, 700*s*, 626*w*, 563*s*; **Mp**: 161 – 162 °C.

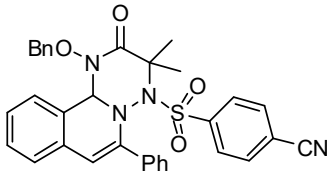
1-(benzyloxy)-4-((4-chlorophenyl)sulfonyl)-3,3-dimethyl-6-phenyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11*b*H)-one (**3da**)



According to ***GP2*** with **1d** (39.4 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3da** as a white solid in 97% yield (56.7 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.06 (m, 14H), 6.83 – 6.74 (m, 3H), 5.84 (s, 1H), 5.74 (s, 1H), 4.68 (d, *J* = 9.3 Hz, 1H), 4.15 (d, *J* = 9.3 Hz, 1H), 1.75 (s, 3H), 1.19 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.5, 146.5, 140.2, 137.7, 135.1, 134.1, 132.1, 130.5, 130.4, 130.1, 129.7, 129.2, 128.7, 128.7, 128.6, 128.2, 127.7, 126.3, 124.7, 123.1, 108.8, 77.7, 75.8, 70.9, 26.5, 25.2; **HRMS** (ESI) exact mass calculated for $C_{32}H_{28}ClN_3O_4S$: 586.1567, found: 586.1561 ($[M+H]^+$); **IR** (neat, cm^{-1}): 1684*s*,1492*w*, 1476*w*, 1396*w*, 1359*s*, 1282*w*, 1165*s*, 1091*m*, 972*m*, 91*0m*, 755*s*, 700*s*, 644*m*, 630*w*; **Mp**: 140 – 141 °C.

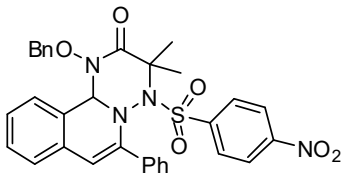
4-((1-(benzyloxy)-3,3-dimethyl-2-oxo-6-phenyl-2,3-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11b*H*)-yl)sulfonyl)benzonitrile (3ea)



According to ***GP2*** with **1e** (38.5 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ea** as a white solid in 82% yield (47.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.32 – 7.19 (m, 6H), 7.13 (t, *J* = 7.3 Hz, 5H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.74 (m, 2H), 5.85 (s, 1H), 5.70 (s, 1H), 4.68 (d, *J* = 9.3 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 1.76 (s, 3H), 1.24 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.2, 146.1, 143.1, 134.9, 134.0, 132.6, 132.0, 130.6, 130.0, 129.7, 129.7, 128.8, 128.5, 128.2, 127.8, 126.6, 124.9, 123.0, 117.1, 117.0, 109.2, 77.8, 75.9, 71.1, 26.6, 25.2; **HRMS** (ESI) exact mass calculated for $C_{33}H_{28}N_4O_4S$: 599.1729, found: 599.1723 ($[M+Na^+]$); **IR** (neat, cm^{-1}):1685*s*, 1571*w*, 1492*m*, 1362*s*, 1285*m*, 1086*s*, 972*m*, 908*s*, 791*w*, 720*s*, 699*s*, 666*s*, 645*s*, 606*w*, 569*s*; **Mp**: 112 – 113 °C.

1-(benzyloxy)-3,3-dimethyl-4-((4-nitrophenyl)sulfonyl)-6-phenyl-3,4-dihydro-1H-[1,2,*4*]triazino[3,2-a]isoquinolin-2(11b*H*)-one (3fa)

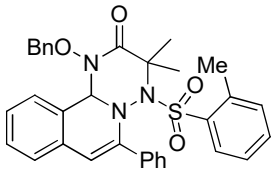


According to ***GP2*** with **1f** (40.5 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3fa** as a white solid in 86% yield (50.7 mg)

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.17 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.43 (td, *J* = 7.6, 1.1 Hz, 1H), 7.34 – 7.19 (m, 5H), 7.17 – 7.08 (m, 5H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.80 – 6.70 (m, 2H), 4.68 (d, *J* = 9.3 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 1.78 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.2, 150.5, 146.0, 144.6, 134.8, 134.0, 132.0, 130.6, 130.4, 130.0, 129.7, 128.9, 128.8, 128.5, 128.2, 127.9, 126.6, 124.9, 124.0, 123.0, 109.3, 77.8, 76.0, 71.1, 26.6, 25.2; **HRMS** (ESI) exact mass calculated for $C_{32}H_{28}N_4O_6S$: 597.1808, found: 597.1803 ($[M+H]^+$); **IR** (neat, cm^{-1}):1687*s*, 1606*w*, 1562*s*, 1492*w*, 1364*s*, 1349*s*, 1312*w*,

1167*s*, 1087*w*, 911*w*, 738*s*, 700*m*, 643*w*, 598*m*; **Mp**: 134 – 135 °C.

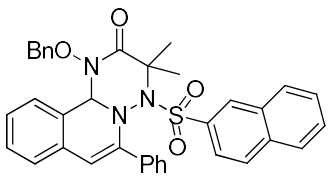
1-(benzyloxy)-3,3-dimethyl-6-phenyl-4-(o-tolylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*] isoquinolin-2(11b*H*)-one (**3ga**)



According to ***GP2*** with **1d** (37.4 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ga** as a white solid in 96% yield (54.6 mg)

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.68 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.22 – 7.09 (m, 6H), 7.04 (t, *J* = 7.6 Hz, 5H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.52 (s, 1H), 6.42 (d, *J* = 7.1 Hz, 2H), 5.52 (s, 1H), 4.71 (d, *J* = 9.4 Hz, 1H), 4.25 (d, *J* = 9.4 Hz, 1H), 2.08 (s, 3H), 1.89 (s, 3H), 1.60 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.9, 145.5, 140.9, 135.7, 134.8, 134.2, 133.5, 132.9, 132.2, 132.1, 130.1, 129.7, 129.6, 128.9, 128.7, 128.4, 128.2, 127.4, 126.1, 126.1, 124.4, 123.1, 108.0, 77.7, 75.3, 70.9, 27.3, 24.6, 20.1; **HRMS** (ESI) exact mass calculated for $C_{33}H_{31}N_3O_4S$: 566.2114, found: 566.2108 ($[M+H]^+$); **IR** (neat, cm^{-1}):1685*s*, 1574*w*, 1492*m*, 1368*w*, 1330*s*, 1031*w*, 910*s*, 807*w*, 754*s*, 731*s*, 721*s*, 701*s*, 647*m*, 619*m*, 593*s*; **Mp**: 137 – 138 °C.

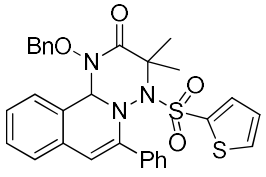
1-(benzyloxy)-3,3-dimethyl-4-(naphthalen-2-ylsulfonyl)-6-phenyl-3,4-dihydro-1H-[1,2,4]triaz ino[3,2-*a*]isoquinolin-2(11b*H*)-one (**3ia**)



According to ***GP2*** with **1i** (41.1 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.60 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ia** as a white solid in 80% yield (48.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.28 (s, 1H), 7.90 – 7.68 (m, 4H), 7.66 – 7.49 (m, 2H), 7.42 – 7.34 (m, 1H), 7.29 – 6.99 (m, 10H), 6.78 – 6.67 (m, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.85 (s, 1H), 5.69 (s, 1H), 4.64 (d, *J* = 9.3 Hz, 1H), 4.10 (d, *J* = 9.3 Hz, 1H), 1.74 (s, 3H), 1.17 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.7, 146.9, 136.3, 135.3, 135.1, 134.1, 132.2, 132.1, 130.5, 130.4, 130.1, 129.6, 129.4, 129.4, 128.9, 128.7, 128.6, 128.1, 127.8, 127.7, 127.6, 126.1, 124.6, 124.0, 123.0, 108.6, 77.6, 75.9, 70.9, 26.4, 25.4; **HRMS** (ESI) exact mass calculated for $C_{36}H_{31}N_3O_4S$: 602.2114, found: 602.2108 ($[M+H]^+$); **IR** (neat, cm^{-1}):1685*s*, 1626*w*, 1492*m*, 1352*s*, 1285*w*, 1163*s*, 1073*m*, 972*m*, 910*m*, 752*s*, 732*s*, 669*s*, 615*w*; **Mp**: 160 – 161 °C.

1-(benzyloxy)-3,3-dimethyl-6-phenyl-4-(thiophen-2-ylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazin o[3,2-*a*]isoquinolin-2(11b*H*)-one (**3ja**)

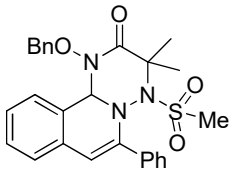


According to ***GP2*** with **1j** (36.6 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ja** as a white solid in 83% yield (46.2 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.60 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.54 (dd, *J* = 3.8,

1.3 Hz, 1H), 7.41 – 7.25 (m, 7H), 7.17 – 7.09 (m, 4H), 7.03 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.3 Hz, 2H), 5.92 (s, 1H), 5.70 (s, 1H), 4.71 (d, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 1.79 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.5, 146.9, 139.8, 135.3, 134.6, 134.1, 133.8, 132.1, 130.4, 130.2, 129.7, 129.3, 128.7, 128.6, 128.6, 128.2, 127.8, 127.2, 126.2, 124.7, 123.4, 120.2, 109.0, 77.7, 75.9, 71.2, 25.9, 25.4; **HRMS** (ESI) exact mass calculated for $C_{30}H_{27}N_3O_4S_2$: 558.1521, found: 558.1516 ($[M+H]^+$); **IR** (neat, cm^{-1}):1681*s*, 1492*w*, 1359*s*, 1285*w*, 1161*s*, 1010*m*, 910*m*, 790*w*, 727*s*, 699*s*, 670*s*, 610*w*, 581*s*; **Mp**: 123 – 124 °C.

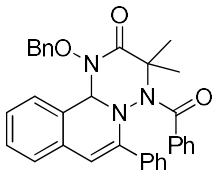
1-(benzyloxy)-3,3-dimethyl-4-(methylsulfonyl)-6-phenyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11b*H*)-one (3ka)



According to ***GP2*** with **1k** (29.8 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ka** as a white solid in 62% yield (30.1 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.40 – 7.29 (m, 6H), 7.22 – 7.14 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.92 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.44 (s, 1H), 5.80 (s, 1H), 4.73 (d, *J* = 9.2 Hz, 1H), 4.21 (d, *J* = 9.3 Hz, 1H), 2.87 (s, 3H), 1.84 (s, 3H), 1.33 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.3, 146.0, 135.5, 134.2, 132.0, 130.3, 129.9, 129.8, 129.1, 128.8, 128.7, 128.3, 127.9, 126.3, 124.6, 123.5, 107.7, 77.7, 76.4, 69.6, 41.6, 25.8, 25.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{27}N_3O_4S$: 490.1801, found: 490.1795 ($[M+H]^+$); **IR** (neat, cm^{-1}):1684*s*, 1492*m*, 1400*w*, 1348*s*, 1332*s*, 1156*s*, 957*m*, 909*s,* 754*s*, 727*s*, 699*s*, 646*w*, 577*w*; **Mp**: 163 – 164 °C.

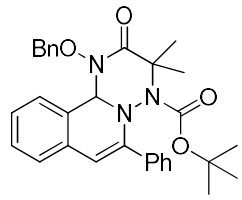
4-benzoyl-1-(benzyloxy)-3,3-dimethyl-6-phenyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11bH)-one (3la)



According to ***GP2*** with **1l** (32.4 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3la** as a white solid in 69% yield (35.8 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 – 7.60 (m, 2H), 7.43 – 7.19 (m, 12H), 7.07 (dd, *J* = 7.5, 2.0 Hz, 3H), 6.91 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.30 (s, 1H), 5.81 (s, 1H), 4.83 (d, *J* = 9.2 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 1.80 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.4, 169.3, 146.2, 135.8, 135.1, 134.2, 131.9, 130.8, 130.6, 129.9, 129.1, 129.0, 129.0, 128.8, 128.3, 128.2, 128.1, 126.3, 124.5, 122.6, 108.1, 78.0, 77.8, 69.4, 26.4, 20.9; **HRMS** (ESI) exact mass calculated for $C_{33}H_{29}N_3O_3$: 516.2287, found: 516.2282 ($[M+H]^+$); **IR** (neat, cm^{-1}):1676*s*, 1654*s*, 1492*w*, 1364*m*, 1285*w*, 1242*w*, 1126*w*, 980*m*, 909*m*, 833*w*, 753*m*, 731*s*, 699*s*, 676*s*, 597*w*; **Mp**: 204 – 205 °C.

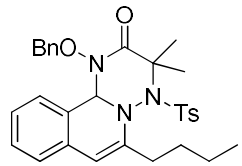
***tert*-butyl 1-(benzyloxy)-3,3-dimethyl-2-oxo-6-phenyl-2,3-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinoline-4(11bH)-carboxylate (3ma)**



According to ***GP2*** with **1m** (29.8 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ma** as a white solid in 64% yield (32.6 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.35 (td, *J* = 7.7, 1.7 Hz, 3H), 7.30 – 7.22 (m, 3H), 7.21 – 7.06 (m, 6H), 6.89 (dd, *J* = 7.4, 1.9 Hz, 2H), 6.12 (s, 1H), 5.85 (s, 1H), 4.79 (d, *J* = 9.1 Hz, 1H), 3.97 (d, *J* = 9.1 Hz, 1H), 1.66 (s, 3H), 1.45 (s, 9H), 0.88 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.1, 153.8, 146.7, 136.1, 134.3, 132.4, 130.2, 129.8, 129.3, 128.7, 128.6, 128.3, 128.2, 128.0, 125.6, 124.2, 122.9, 106.5, 82.2, 77.6, 76.9, 67.8, 28.4, 28.0, 21.8; **HRMS** (ESI) exact mass calculated for $C_{31}H_{33}N_3O_4$: 512.2549, found: 512.2544 ($[M+H]^+$); **IR** (neat, cm^{-1}):1710*s*, 1678*s*, 1492*w*, 1455*w*, 1367*m*, 1324*m*, 1281*w*, 1157*s*, 982*m*, 910*m*, 806*w*, 730*s*, 700*s*, 647*w*; **Mp**: 108 – 109 °C.

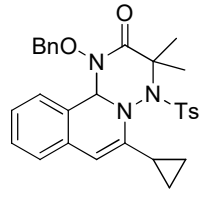
1-(benzyloxy)-6-butyl-3,3-dimethyl-4-tosyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11bH)-one (**3na**)



According to ***GP2*** with **1n** (35.4 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3na** as a white solid in 87% yield (47.3 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 8.4 Hz, 2H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23 – 6.99 (m, 7H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 7.9, 1.4 Hz, 2H), 5.63 (d, *J* = 5.2 Hz, 2H), 4.58 (d, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 2.17 (t, *J* = 7.4 Hz, 2H), 1.87 (s, 3H), 1.85 (s, 3H), 1.45 – 1.17 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.4, 146.4, 144.5, 135.9, 134.0, 132.6, 130.2, 129.6, 129.4, 128.8, 128.8, 128.6, 128.1, 125.1, 123.8, 121.9, 102.2, 77.8, 74.9, 70.4, 29.5, 29.1, 26.6, 26.2, 22.5, 21.5, 14.0; **HRMS** (ESI) exact mass calculated for $C_{31}H_{35}N_3O_4S$: 546.2427, found: 546.2421 ($[M+H]^+$); **IR** (neat, cm^{-1}):1686*s*, 1634*w*, 1493*w*, 1407*w*, 1353*s*, 1292*w*, 1164*s*, 1089*m*, 980*w*, 910*w*, 817*w*, 752*m*, 672*s*, 628*w*; **Mp**: 115 – 116 °C.

1-(benzyloxy)-6-cyclopropyl-3,3-dimethyl-4-tosyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-*a*]isoquinolin-2(11bH)-one (**3oa**)

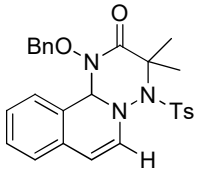


According to ***GP2*** with **1o** (33.8 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3oa** as a white solid in 88% yield (46.8 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.20 – 6.96 (m, 7H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.69 (dd, *J* = 7.9, 1.3 Hz, 2H), 5.58 (s, 1H), 5.37 (s, 1H), 4.55 (d, *J* = 9.0 Hz, 1H), 3.81 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 1.92 (s, 3H), 1.87 (s, 3H), 1.77 (td, *J* = 8.3, 5.4 Hz, 1H), 0.93 – 0.78 (m, 1H), 0.76 – 0.55 (m, 2H), 0.46 – 0.33 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.4, 148.4, 144.4, 135.9, 133.9, 132.5,

130.2, 129.6, 129.4, 129.2, 128.8, 128.7, 128.6, 128.1, 125.0, 123.8, 121.6, 120.1, 98.8, 77.7, 77.4, 70.6, 26.9, 26.1, 21.5, 11.3, 10.7, 7.7; **HRMS** (ESI) exact mass calculated for $C_{30}H_{31}N_3O_4S$: 530.2114, found: 530.2108 ($[M+H]^+$); **IR** (neat, cm^{-1}):1683*s*, 1631*w*, 1493*w*, 1407*w*, 1351*s*, 1293*w*, 1163*s*, 1089*m*, 981*w*, 816*w*, 753*m*, 713*s*, 661*s*, 631*w*; **Mp**: 138 – 139 °C.

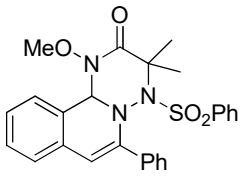
1-(benzyloxy)-3,3-dimethyl-4-tosyl-3,4-dihydro-1H-[1,2,4]triazino[3,2-a]isoquinolin-2(11bH)-one (**3pa**)



According to ***GP2*** with **1p** (29.8 mg, 0.100 mmol, 1.0 equiv), **2a** (54.3 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3pa** as a white solid in 72% yield (35.1 mg)

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.67 (d, *J* = 8.3 Hz, 2H), 7.34 (qd, *J* = 6.9, 6.2, 1.9 Hz, 2H), 7.19 – 6.97 (m, 8H), 6.86 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.28 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.73 (d, *J* = 7.8 Hz, 1H), 5.56 (d, *J* = 1.5 Hz, 1H), 4.63 (d, *J* = 8.8 Hz, 1H), 3.52 (d, *J* = 8.8 Hz, 1H), 2.34 (s, 3H), 1.93 (s, 3H), 1.85 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.8, 144.2, 136.9, 136.3, 133.9, 131.0, 130.4, 130.0, 129.7, 129.6, 128.7, 128.2, 127.7, 126.0, 124.4, 123.1, 105.2, 77.9, 74.2, 70.9, 27.2, 26.1, 21.6; **HRMS** (ESI) exact mass calculated for $C_{27}H_{27}N_3O_4S$: 490.1801, found: 490.1795 ($[M+H]^+$); **IR** (neat, cm^{-1}):1678*s*, 1629*m*, 1493*w*, 1455*w*, 1353*m*, 1275*m*, 1165*s*, 1091*m*, 999*m*, 933*w*, 773*m*, 684*s*, 653*w*; **Mp**: 139 – 140 °C.

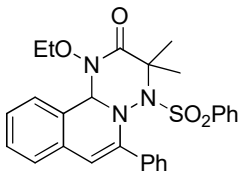
1-methoxy-3,3-dimethyl-6-phenyl-4-(phenylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazino[3,2-a]isoquinolin-2(11bH)-one (**3ab**)



According to ***GP2*** with **1a** (36.0 mg, 0.100 mmol, 1.0 equiv), **2b** (39.2 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ab** as a white solid in 79% yield (37.3 mg)

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80 – 7.67 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.15 (m, 9H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.82 (s, 1H), 5.75 (s, 1H), 3.23 (s, 3H), 1.70 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = δ 168.6, 146.8, 139.4, 135.3, 133.5, 132.0, 130.4, 130.2, 129.0, 129.0, 128.6, 128.1, 127.7, 126.2, 124.6, 123.1, 108.4, 75.7, 70.6, 63.2, 26.2, 25.4; **HRMS** (ESI) exact mass calculated for $C_{26}H_{25}N_3O_4S$: 476.1644, found: 476.1639 ($[M+H]^+$); **IR** (neat, cm^{-1}):1685*s*, 1492*w*, 1447*w*, 1355*s*, 1286*w*, 1165*s*, 1089*m*, 1021*m*, 908*s*, 754*m*, 724*s*, 690*m*, 637*s*, 610*w*; **Mp**: 157 – 158 °C.

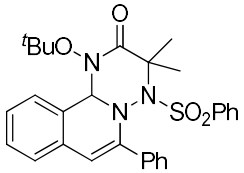
1-ethoxy-3,3-dimethyl-6-phenyl-4-(phenylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazino[3,2-a]isoquinolin-2(11bH)-one (**3ac**)



According to ***GP2*** with **1a** (36.0 mg, 0.100 mmol, 1.0 equiv), **2c** (42.0 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ac** as a white solid in 86% yield (42.1 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 – 7.71 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.16 (m, 9H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 5.81 (s, 1H), 5.73 (s, 1H), 3.71 – 3.58 (m, 1H), 3.31 – 3.15 (m, 1H), 1.71 (s, 3H), 1.12 (s, 3H), 0.69 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.8, 146.8, 139.4, 135.4, 133.4, 132.1, 130.3, 130.2, 129.1, 128.9, 128.6, 128.3, 127.7, 126.0, 124.6, 123.3, 108.4, 75.7, 71.6, 70.7, 26.3, 25.4, 13.0; **HRMS** (ESI) exact mass calculated for $C_{27}H_{27}N_3O_4S$: 490.1801, found: 490.1795 ($[M+H]^+$); **IR** (neat, cm^{-1}):1684*s*, 1492*w*, 1447*w*, 1355*s*, 1286*w*, 1165*s*, 1088*m*, 1031*m*, 911*m*, 753*m*, 724*s*, 690*s*, 638*m,* 610*w*; **Mp**: 163 – 164 °C.

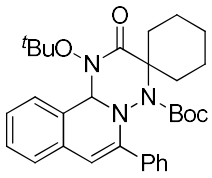
1-(tert-butoxy)-3,3-dimethyl-6-phenyl-4-(phenylsulfonyl)-3,4-dihydro-1H-[1,2,4]triazino[3,2-a]isoquinolin-2(11bH)-one (3ad)



According to ***GP2*** with **1a** (36.0 mg, 0.100 mmol, 1.0 equiv), **2d** (47.6 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3ad** as a white solid in 89% yield (46.2 mg).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.19 (m, 3H), 7.19 – 7.03 (m, 5H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.81 (s, 1H), 5.78 (s, 1H), 1.79 (s, 3H), 1.07 (s, 3H), 0.83 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 173.0, 145.9, 139.3, 135.2, 133.4, 132.9, 130.2, 130.0, 129.2, 128.9, 128.3, 127.5, 125.4, 124.4, 123.7, 109.8, 84.4, 78.2, 77.4, 77.0, 76.6, 71.4, 27.4, 26.5, 25.3; **HRMS** (ESI) exact mass calculated for $C_{29}H_{31}N_3O_4S$: 518.2114, found: 518.2108 ($[M+H]^+$); **IR** (neat, cm^{-1}): 1700*s*, 1492*w*, 1447*w*, 1356*s*, 1165*s*, 1089*m*, 970*w*, 911*m*, 753*s*, 725*s*, 637*s*, 610*w*; **Mp**: 166 – 167 °C.

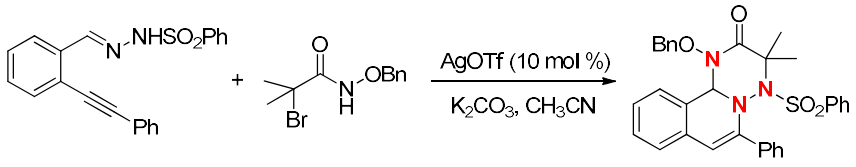
***tert*-butyl**
1-(tert-butoxy)-2-oxo-6-phenyl-1,11b-dihydrospiro[[1,2,4]triazino[3,2-a]isoquinoline-3,1'-cyclohexane]-4(2H)-carboxylate (3mf)



According to ***GP2*** with **1m** (32.1 mg, 0.100 mmol, 1.0 equiv), **2f** (54.0 mg, 0.200 mmol, 2.0 equiv), AgOTf (2.40 mg, 0.100 mmol, 0.1 equiv) and K_2CO_3 (55.2 mg, 0.400 mmol, 4.0 equiv) in 1.0 mL CH_3CN. Purification by silica gel chromatography afforded the desired **3mf** as a white solid in 76% yield (41.7 mg).

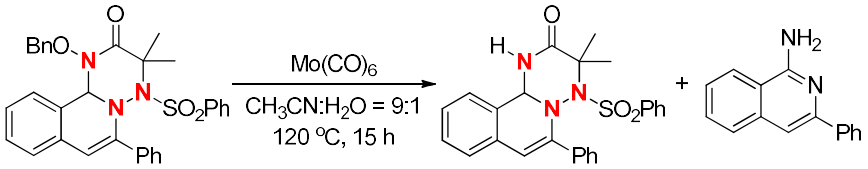
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.40 – 7.29 (m, 3H), 7.29 – 7.15 (m, 7H), 7.08 (q, *J* = 7.5 Hz, 2H), 7.02 – 6.89 (m, 3H), 6.12 (s, 1H), 5.75 (s, 1H), 4.65 (d, *J* = 9.9 Hz, 1H), 4.18 (d, *J* = 9.8 Hz, 1H), 2.62 (td, *J* = 12.8, 3.8 Hz, 1H), 2.01 – 1.84 (m, 1H), 1.80 – 1.53 (m, 4H), 1.45 (s, 9H), 1.42 – 1.29 (m, 2H), 1.17 – 0.96 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 154.0, 146.3, 136.0, 134.9, 132.7, 129.8, 129.8, 128.9, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 127.9, 125.3, 124.3, 123.1, 105.7, 82.3, 77.7, 77.5, 71.3, 32.6, 30.5, 28.4, 24.4, 23.5, 22.9; **HRMS** (ESI) exact mass calculated for $C_{34}H_{37}N_3O_4$: 552.2862, found: 552.2857 ($[M+H]^+$); **IR** (neat, cm^{-1}): 1704*s*, 1492*w,* 1454*w*, 1369*m*, 1283*w*, 1159*s*, 1115*w*, 1027*w*, 911*m*, 815*w*, 763*m*, 731*s*, 700*s*, 576*w*; **Mp**: 173 – 171 °C.

4. Follow-Up Chemistry



1a (3 mmol, 1.08 g) **2a** (6 mmol, 1.63 g) **3aa** 1.18 g, (71%)

General procedure: A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (1.0 equiv, 3.0 mmol, 1.08 g), AgOTf (0.1 equiv, 0.3 mmol, 77.1 mg), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times). Then, CH_3CN (45 mL) was added under a flow of argon. The reaction mixture was then stirred at 80 °C for 3 h. After cooling to room temperature, **2a** (2.0 equiv, 6.0 mmol, 1.63 g) and K_2CO_3 (4.0 equiv, 12 mmol, 1.66 g) were added and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure product **3aa** as a white solid in 71% yield (1.18 g).



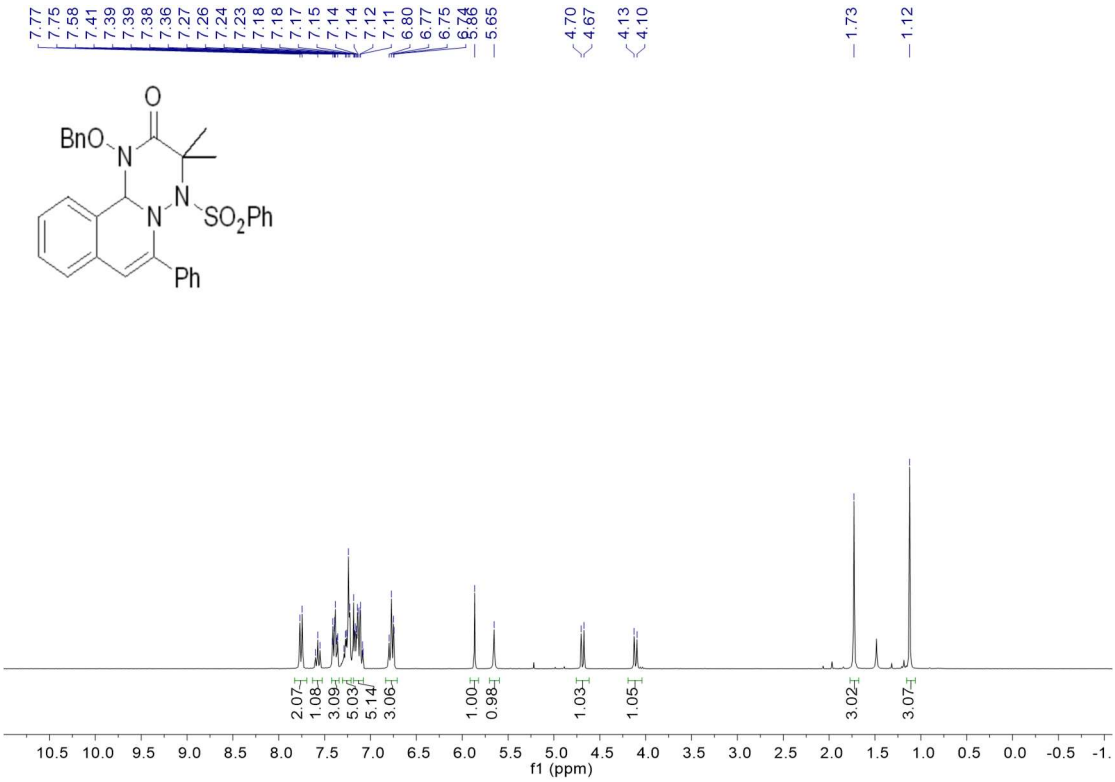
3aa **4**, (0%) **5**, (63%)

General procedure: To a solution of **3aa** (1.0 equiv, 0.2 mmol, 110 mg) in acetonitrile/water (9:1, 2.0 mL), $Mo(CO)_6$ (1.2 equiv, 0.24 mmol, 63.4 mg) was added. The reaction was stirred at 120 °C under argon for 12 h. After cooling to room temperature, the mixture was the filtered through celite and washed with ethyl acetate. Then, filtrate was concentrated under rotary evaporation, and the resulting residue was purified by silica gel chromatography to afford **5** as a light yellow oil in 63% yield (27.8 mg).

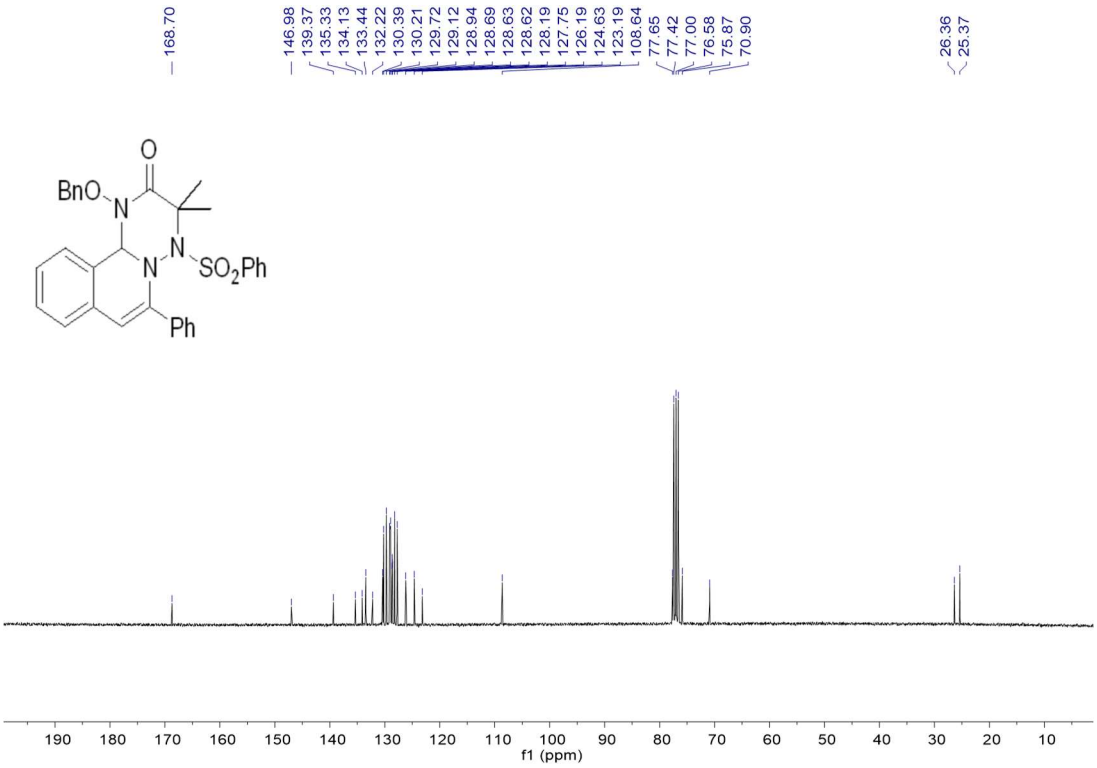
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 – 7.91 (m, 2H), 7.76 – 7.63 (m, 2H), 7.60 – 7.47 (m, 1H), 7.43 – 7.34 (m, 4H), 7.29 (dd, *J* = 7.6, 5.4 Hz, 1H), 5.19 (s, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.9, 149.6, 139.9, 138.2, 130.2, 128.5, 128.2, 127.5, 126.8, 125.9, 122.6, 117.0, 108.9; **HRMS** (ESI) exact mass calculated for $C_{15}H_{12}N_2$: 221.1079, found: 221.1074 ($[M+Na]^+$); **IR** (neat, cm^{-1}): 1662*s*, 1564*s*, 1500*s*, 1426*s*, 1342*w*, 1154*w*, 1032*w*, 923*w*, 833*w*, 770*m*, 695*m*. 586*w*.

5. Copies of ^{1}H NMR and ^{13}C NMR Spectra

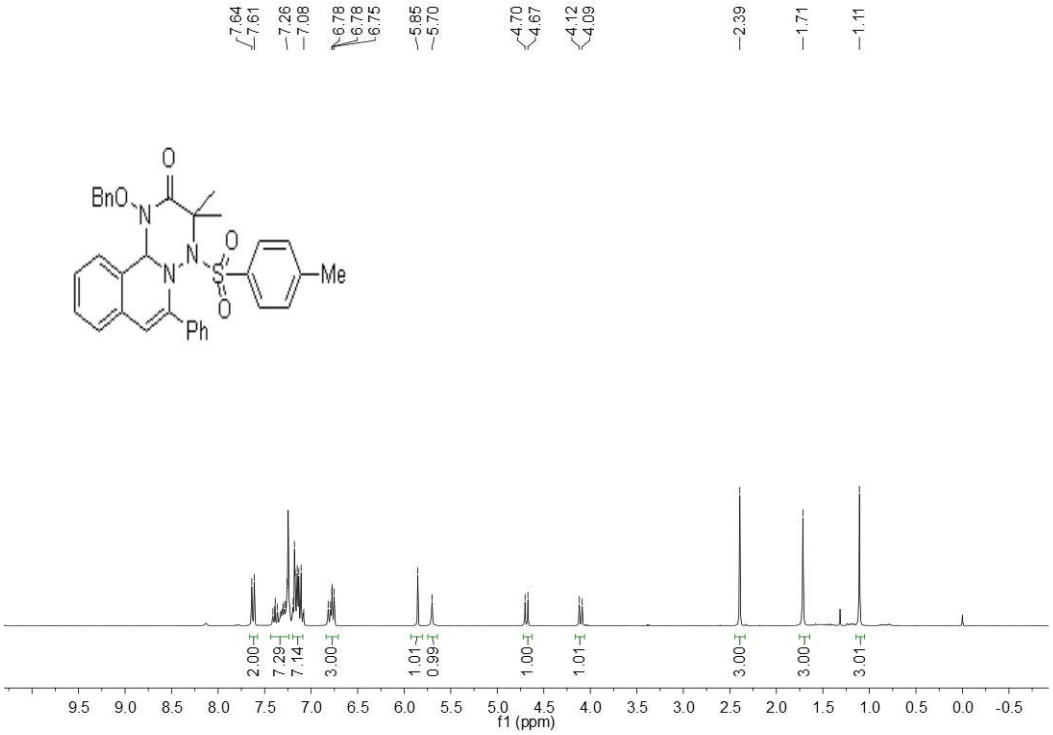
^{1}H NMR Spectrum of 3aa



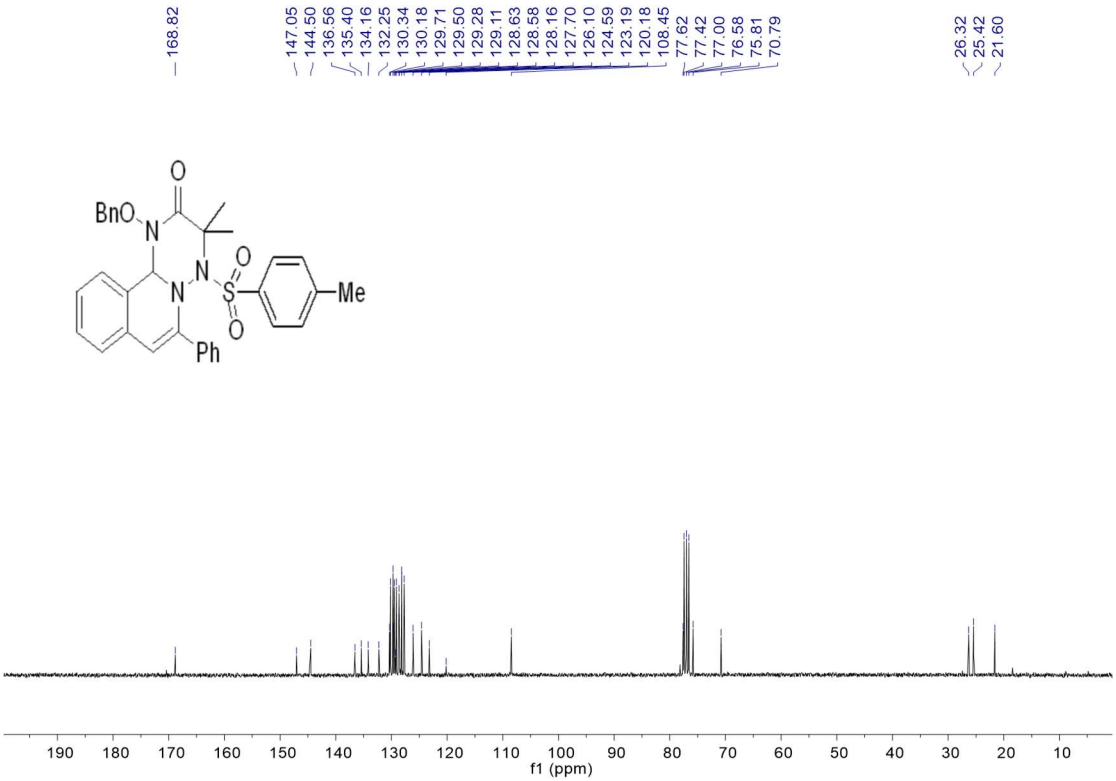
^{13}C NMR Spectrum of 3aa



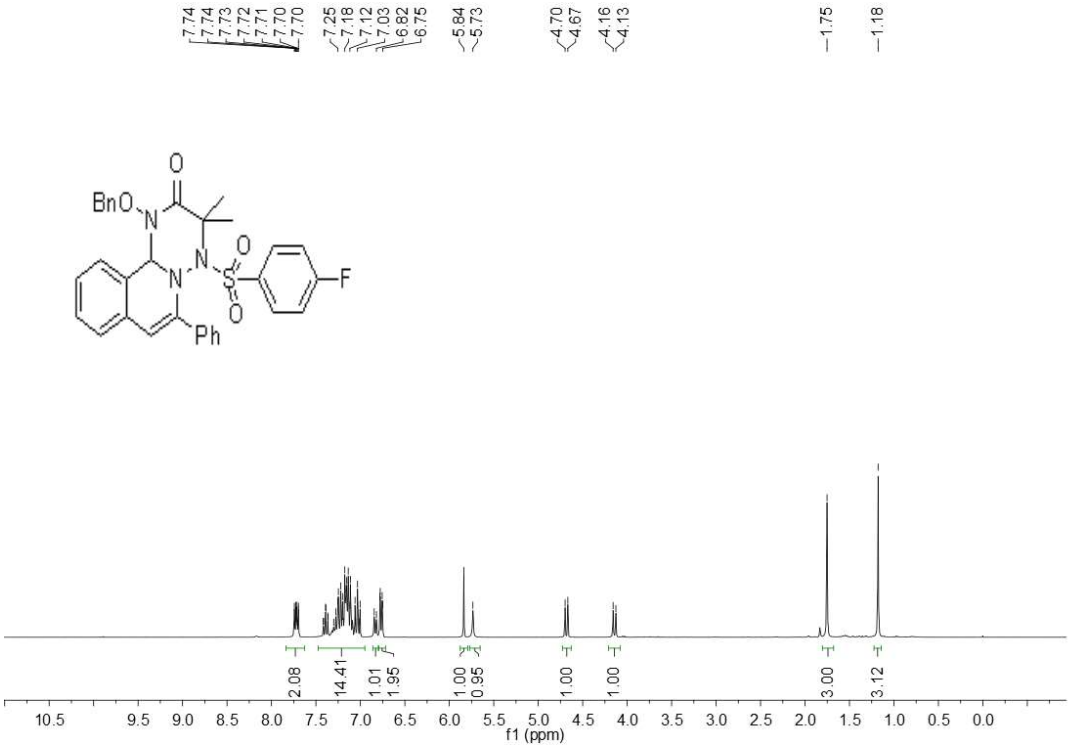
^{1}H NMR Spectrum of 3ba



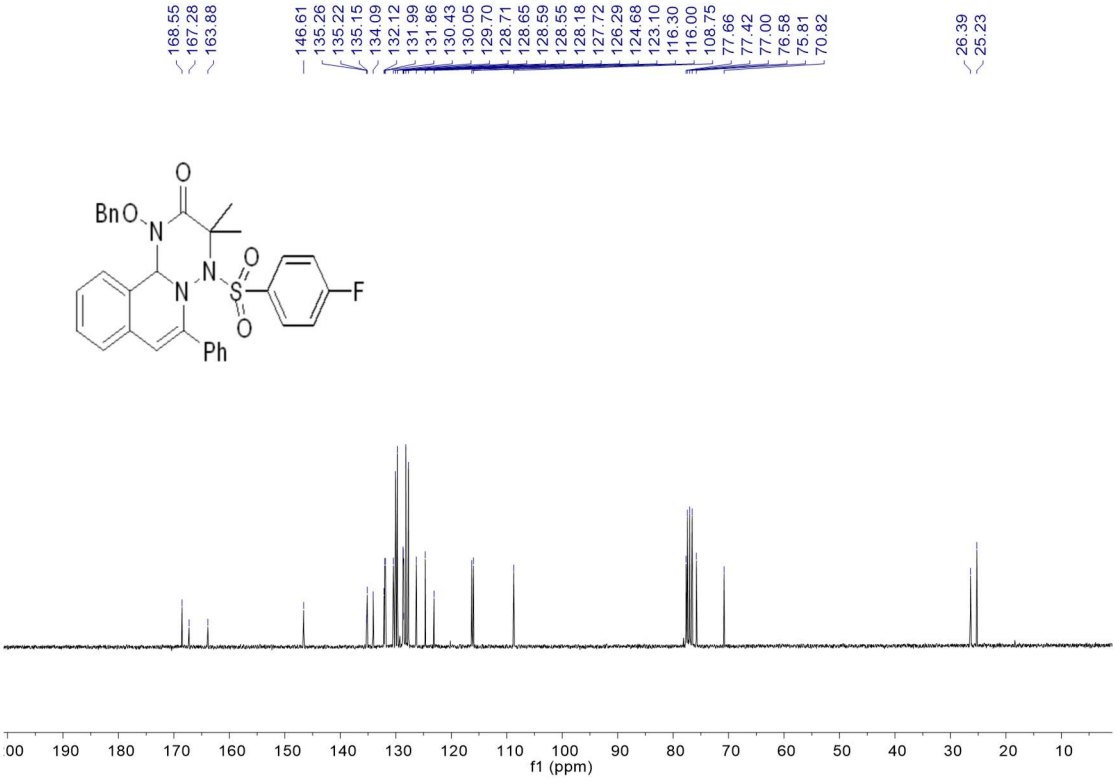
^{13}C NMR Spectrum of 3ba



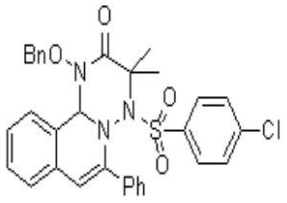
^{1}H NMR Spectrum of 3ca

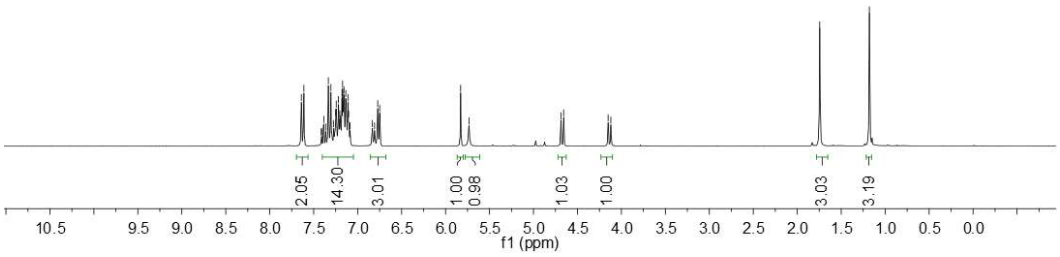


^{13}C NMR Spectrum of 3ca

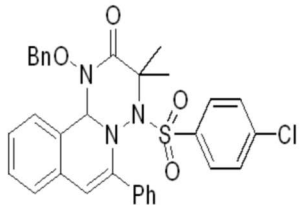


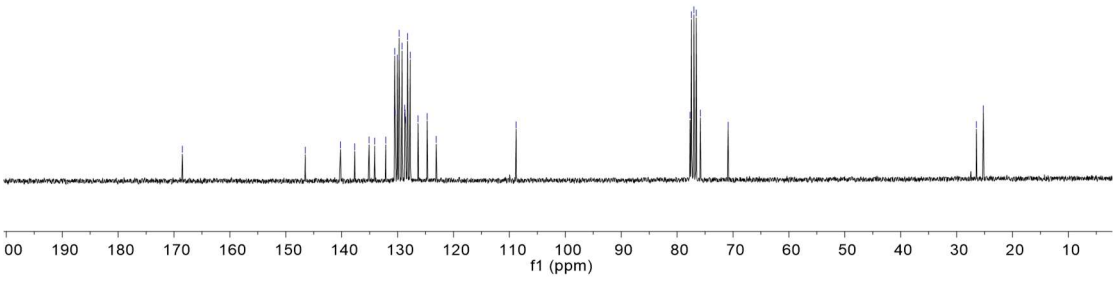
^{1}H NMR Spectrum of 3da



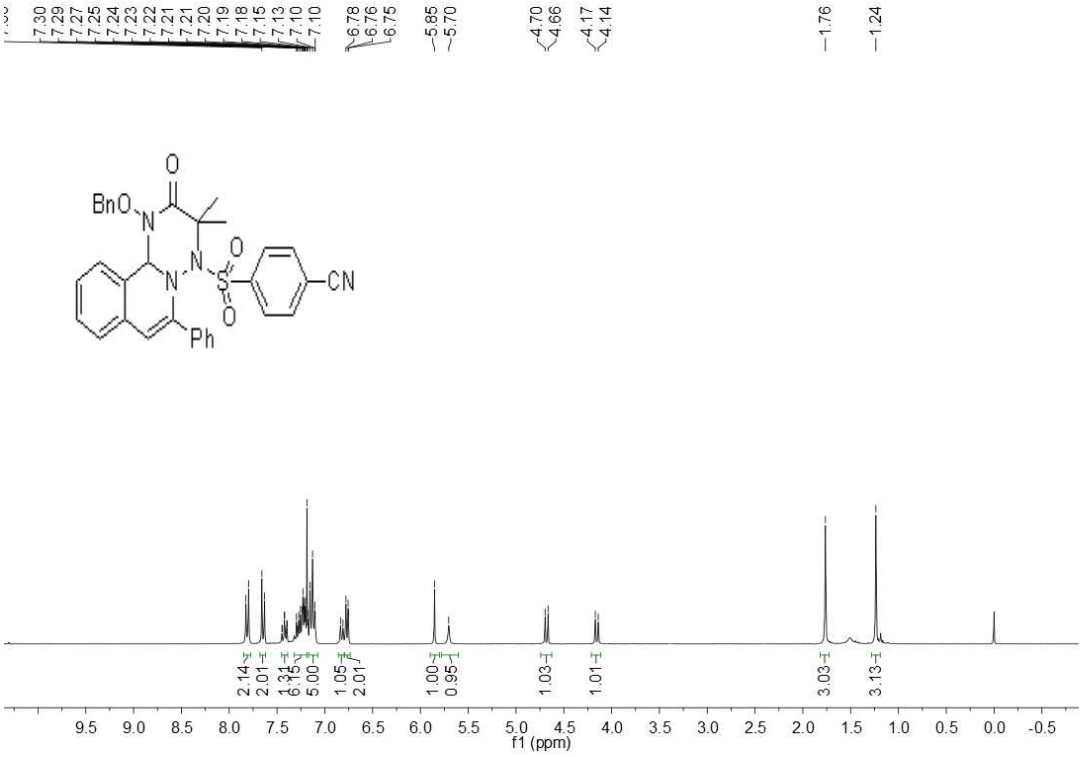


^{13}C NMR Spectrum of 3da

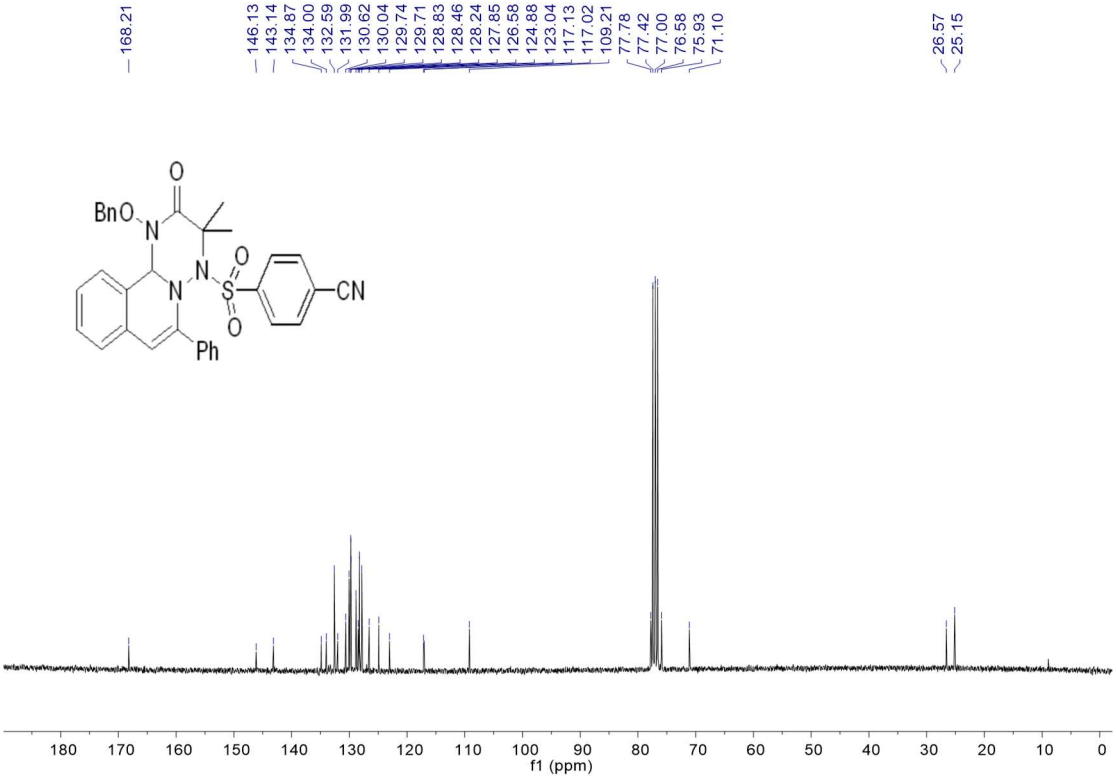




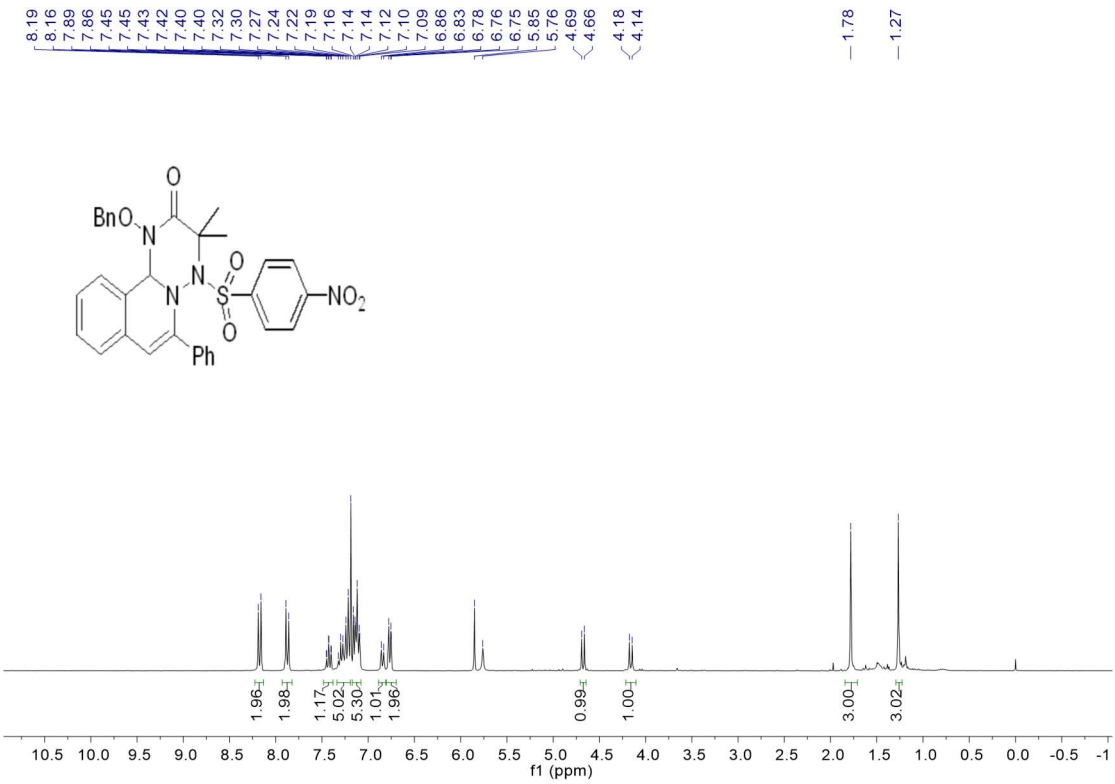
^{1}H NMR Spectrum of 3ea



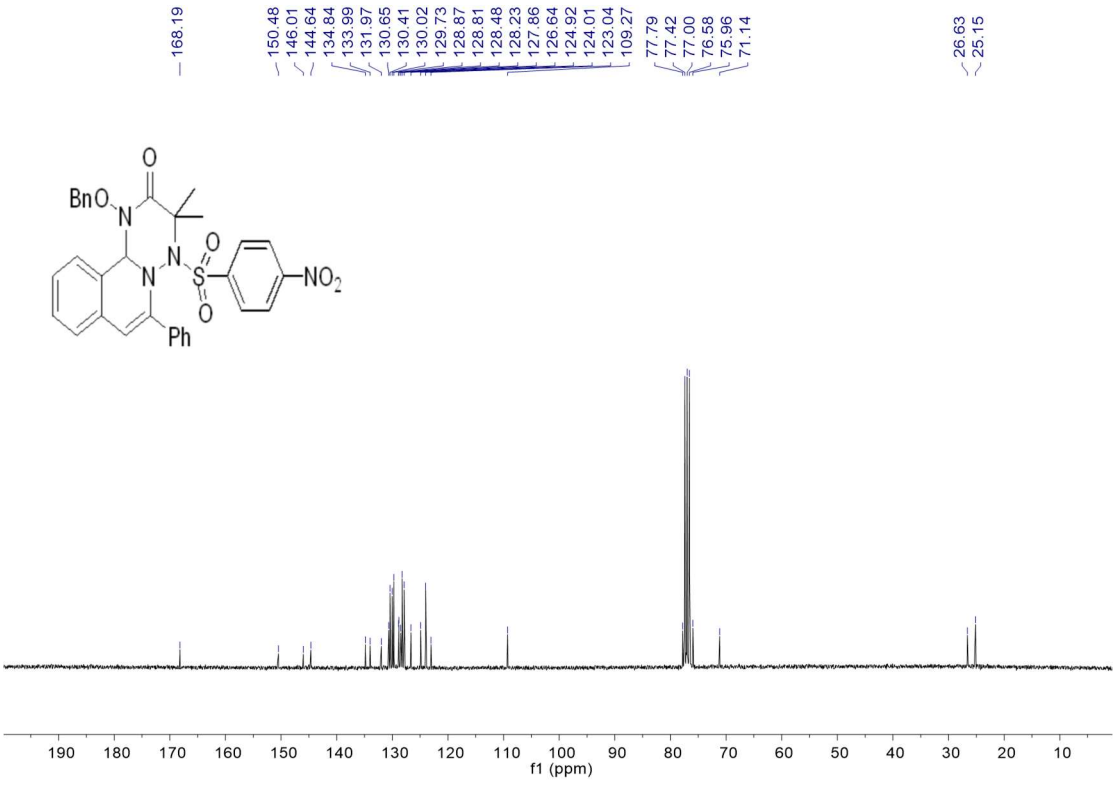
^{13}C NMR Spectrum of 3ea



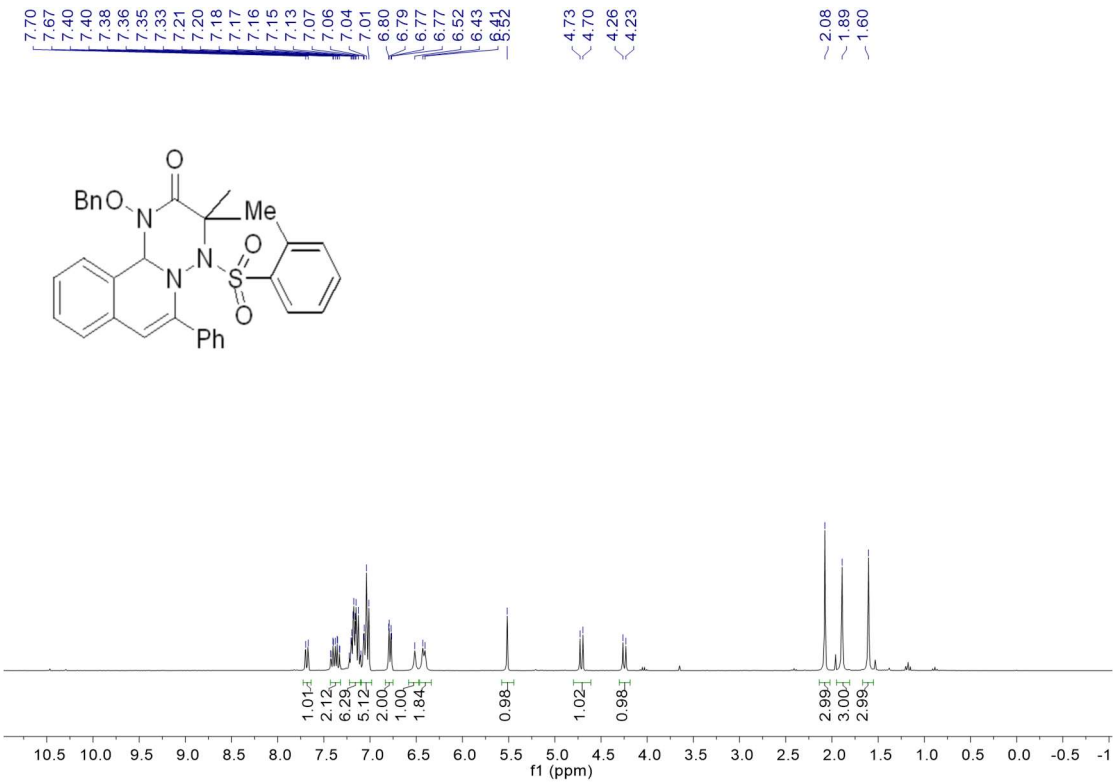
^{1}H NMR Spectrum of 3fa



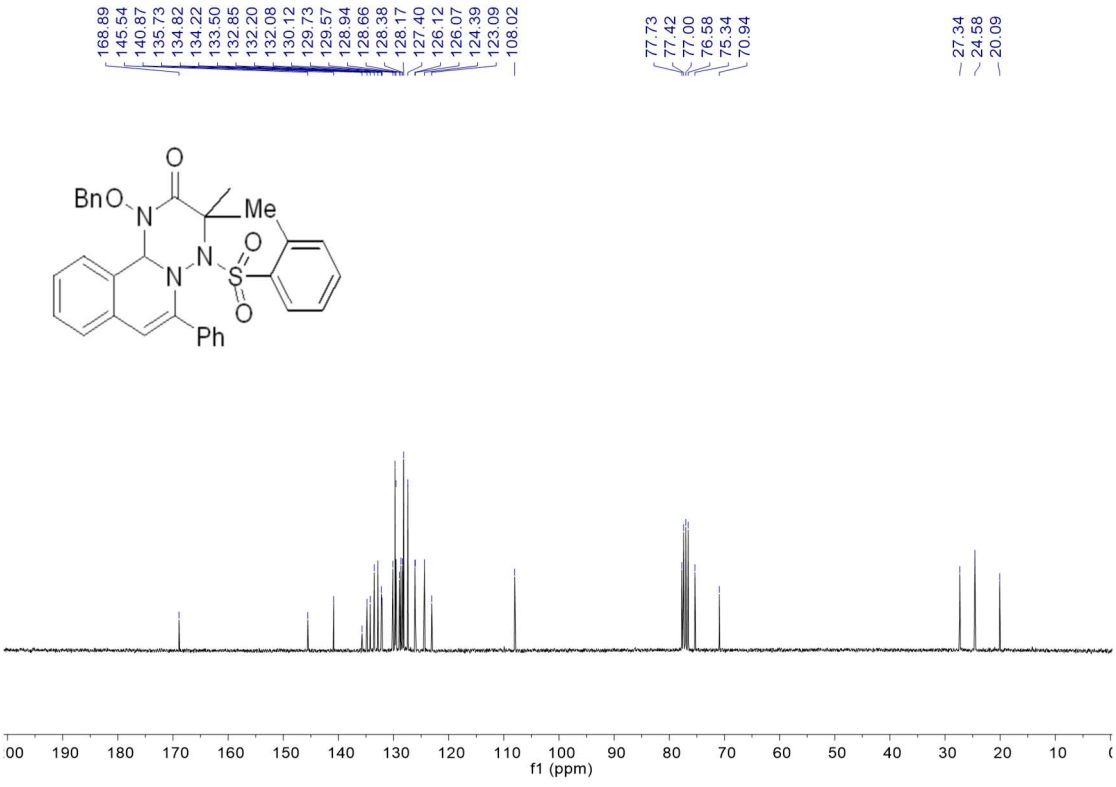
^{13}C NMR Spectrum of 3fa



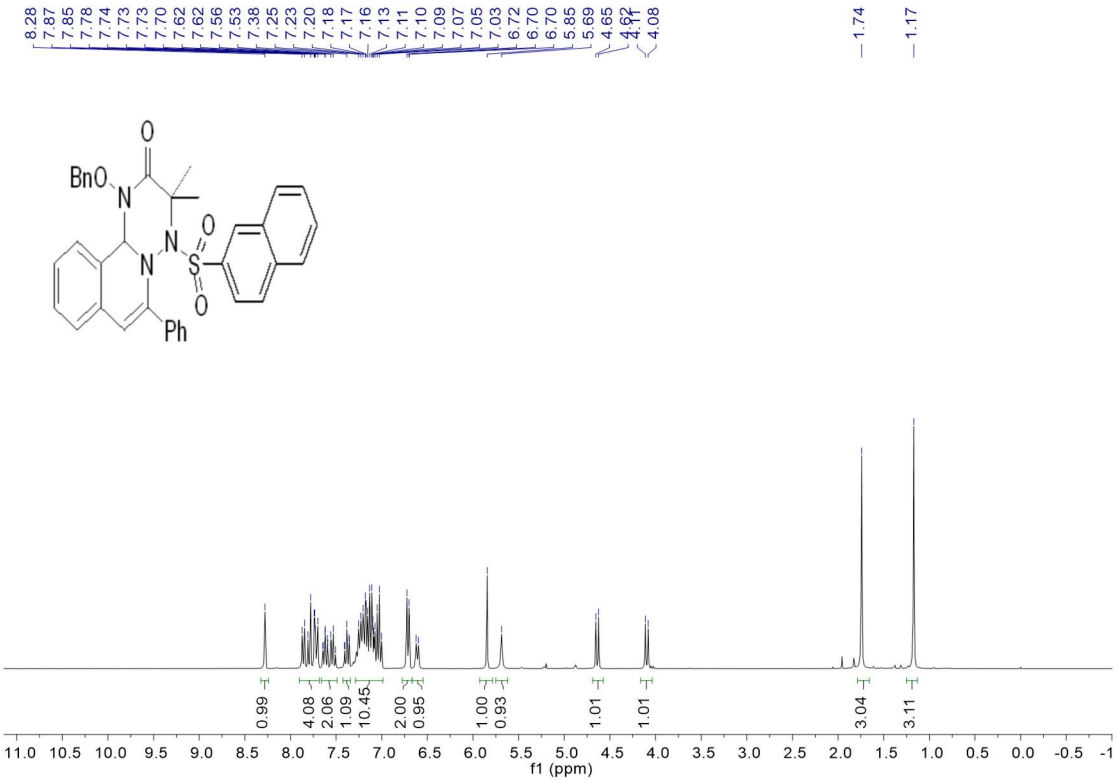
^{1}H NMR Spectrum of 3ga



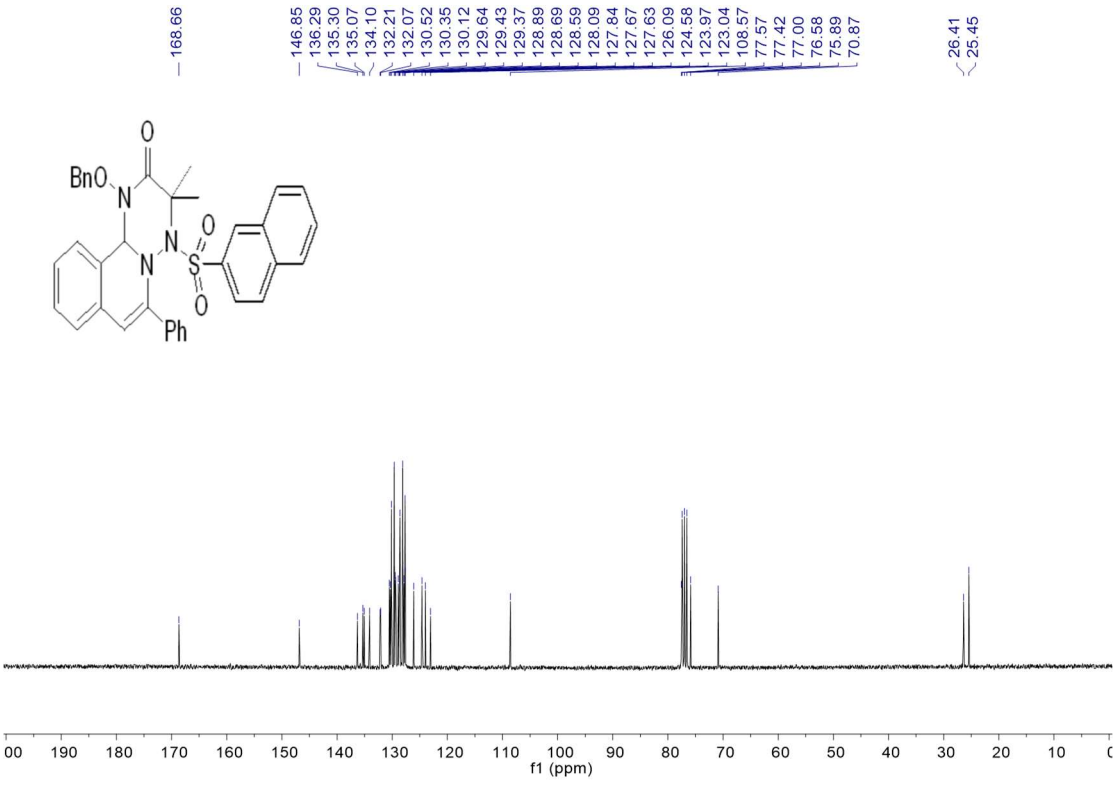
^{13}C NMR Spectrum of 3ga



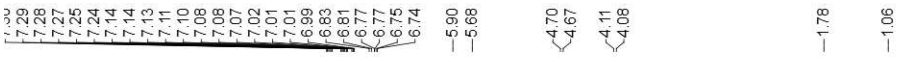
^{1}H NMR Spectrum of 3ia

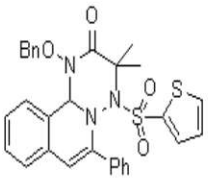


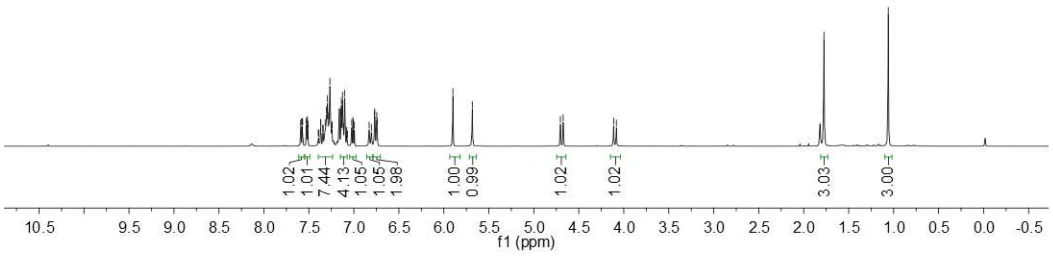
^{13}C NMR Spectrum of 3ia



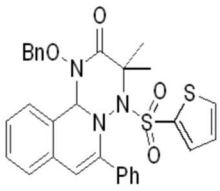
^{1}H NMR Spectrum of 3ja

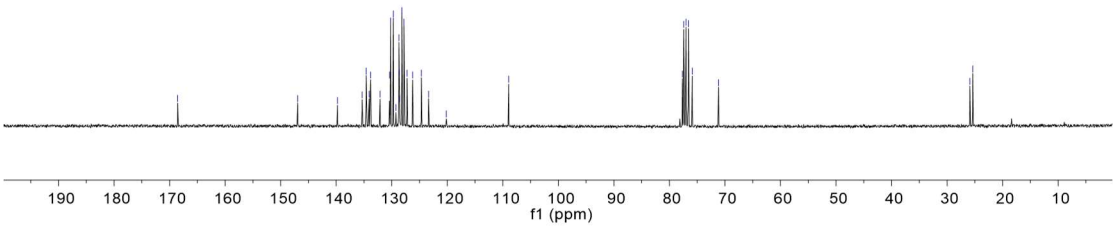




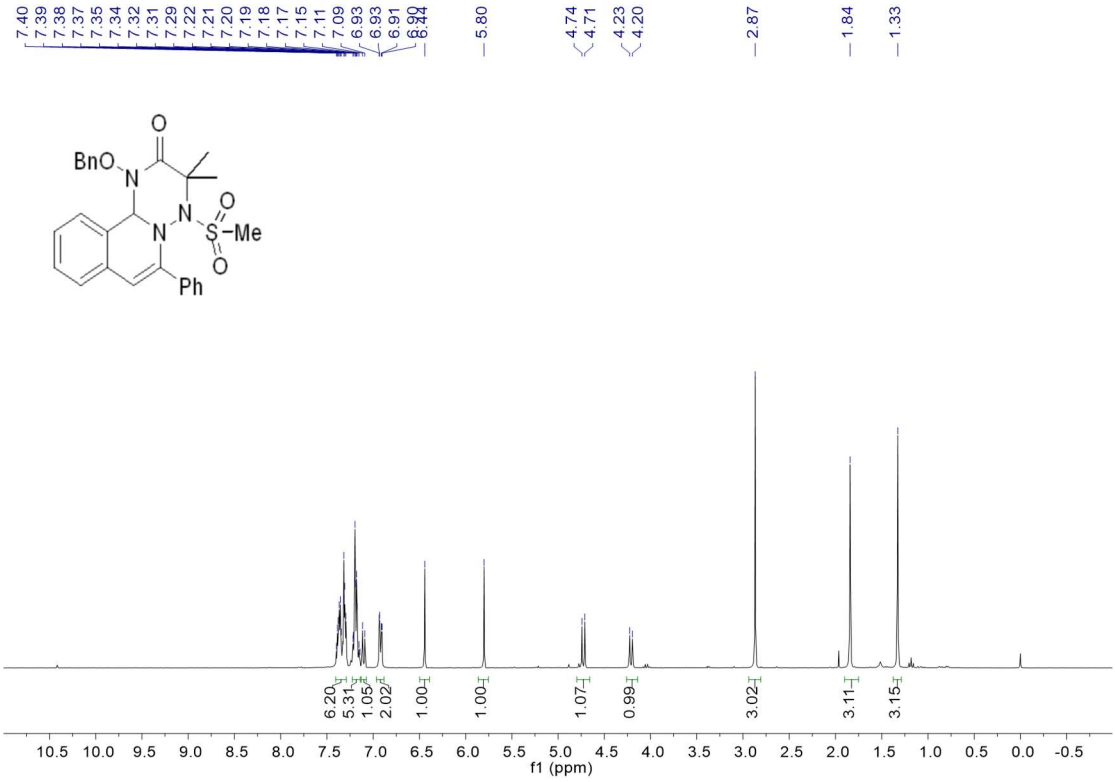


^{13}C NMR Spectrum of 3ja

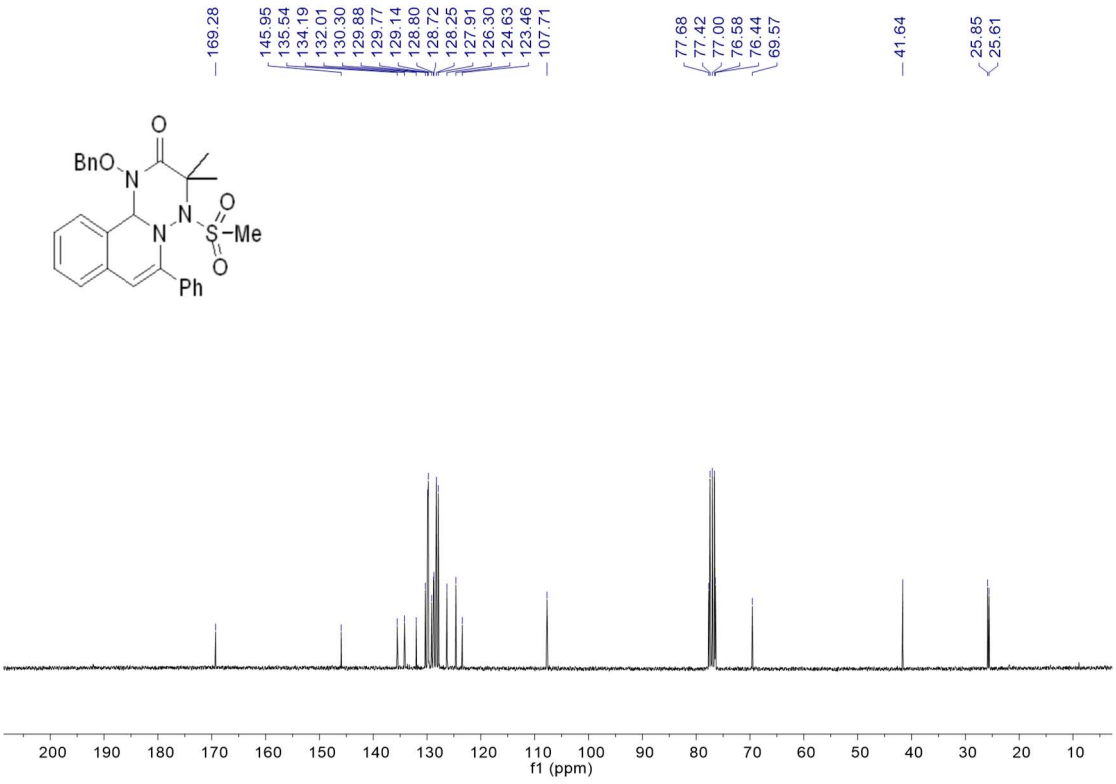




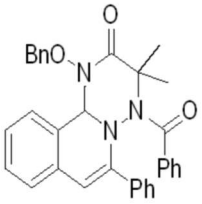
^{1}H NMR Spectrum of 3ka

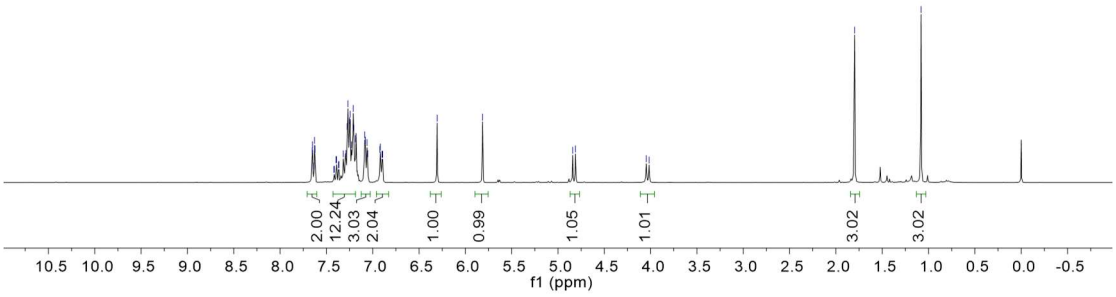


^{13}C NMR Spectrum of 3ka

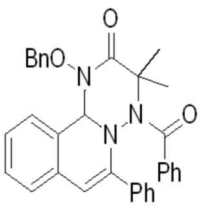


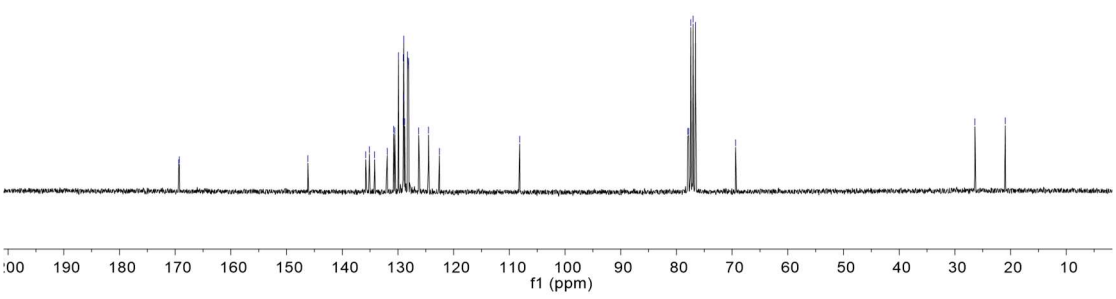
^{1}H NMR Spectrum of 3la



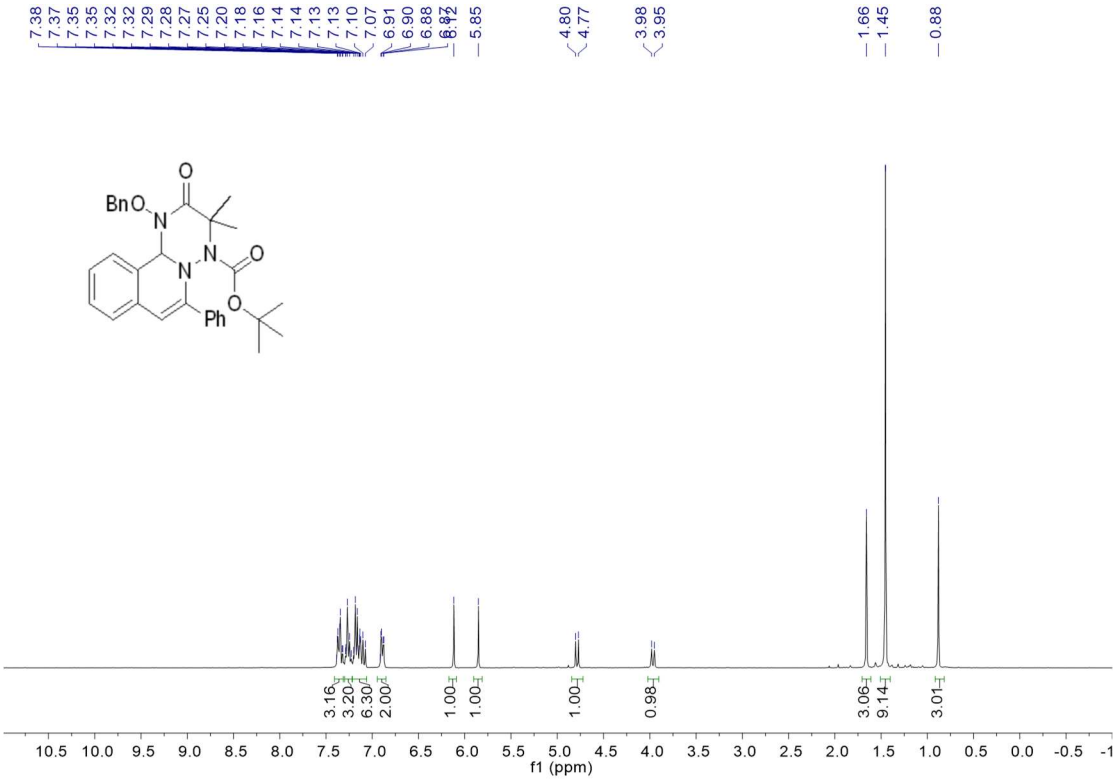


^{13}C NMR Spectrum of 3la

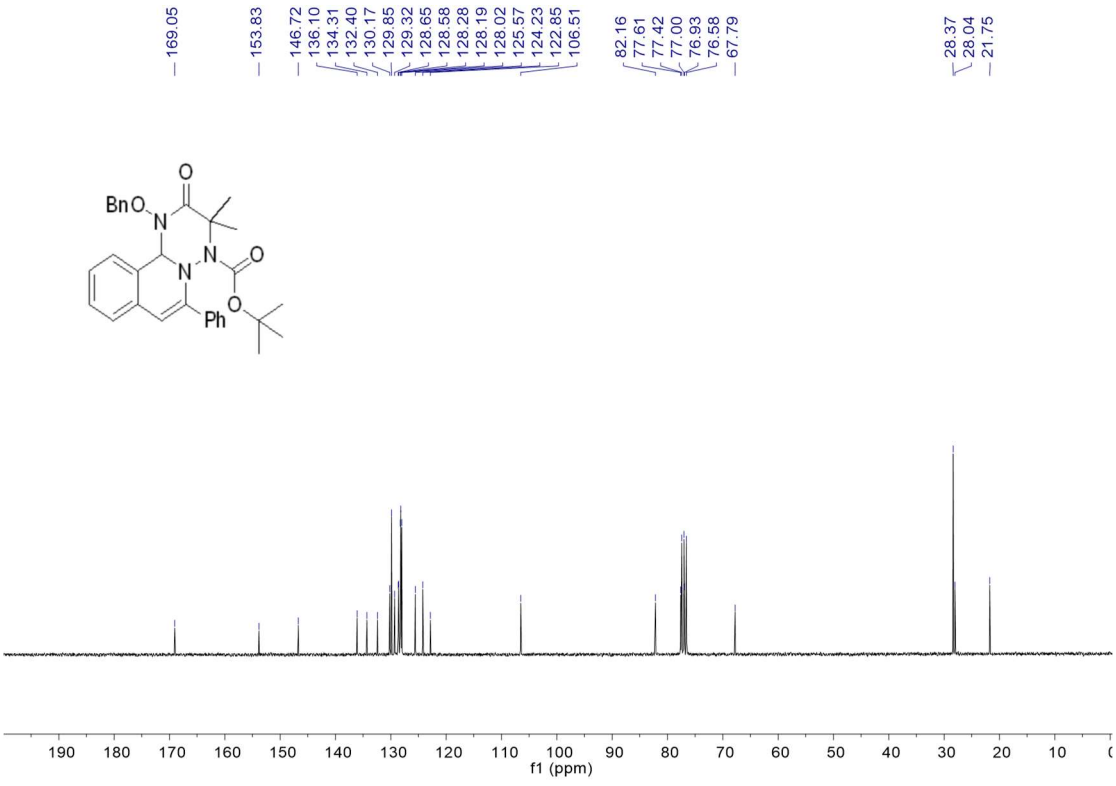




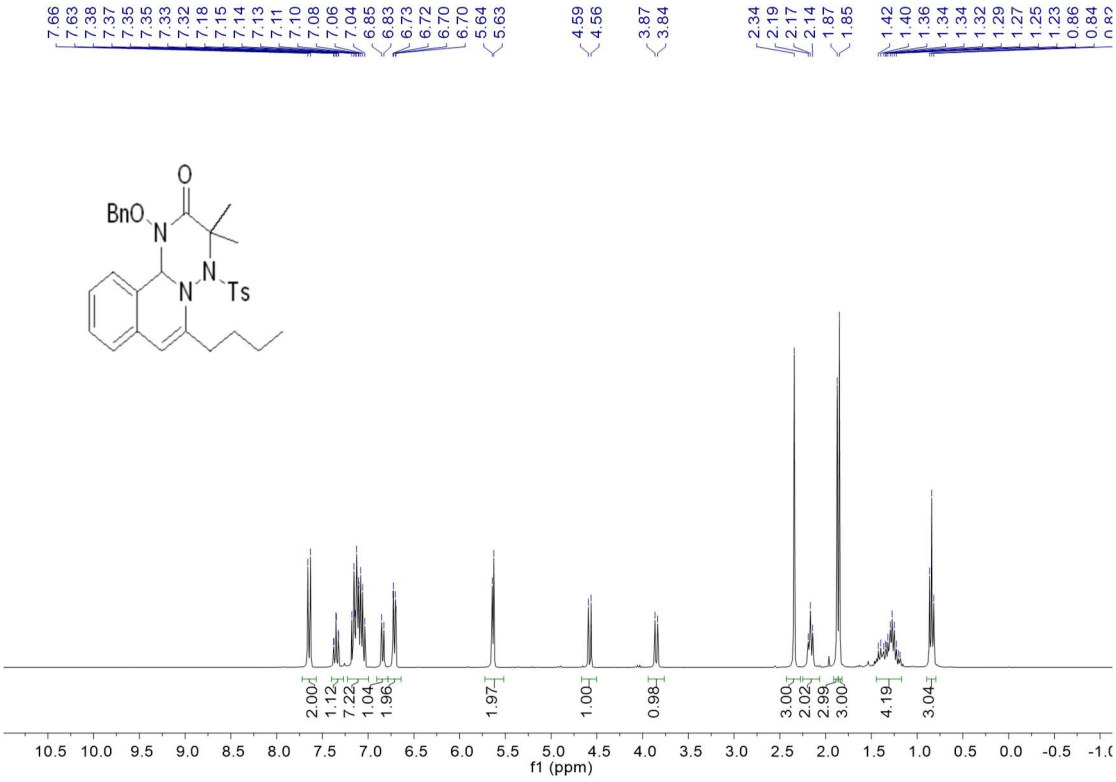
^{1}H NMR Spectrum of 3ma



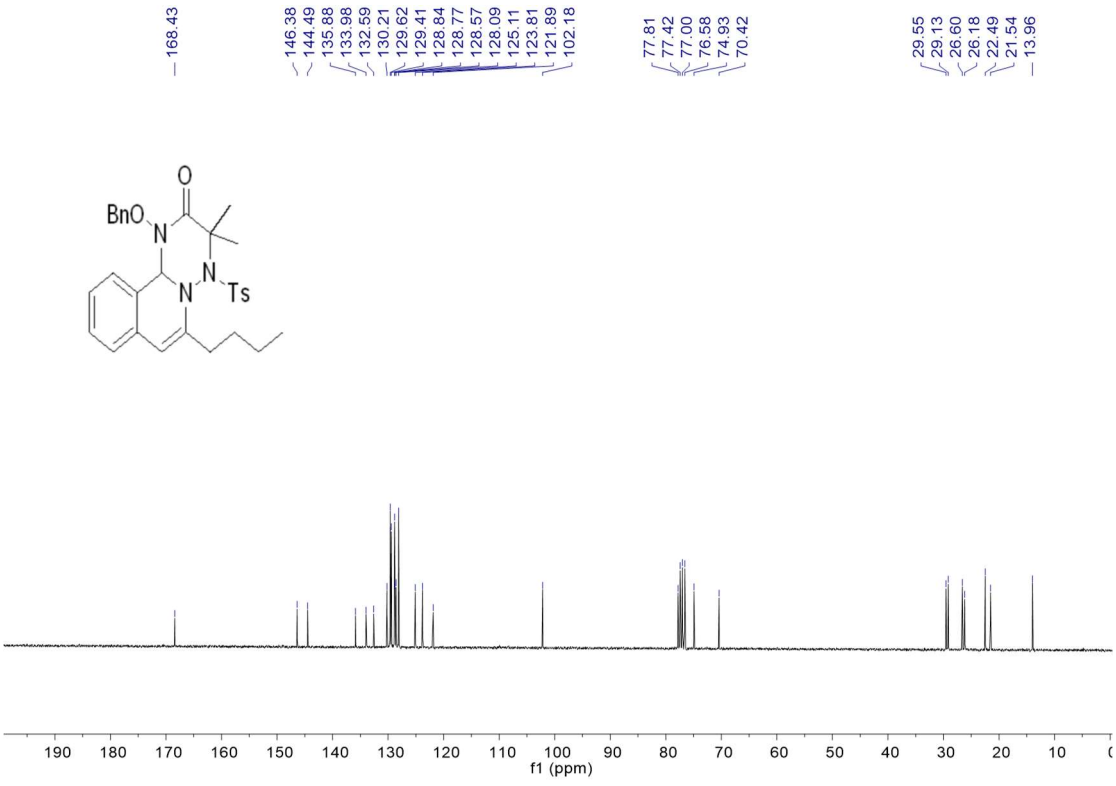
^{13}C NMR Spectrum of 3ma



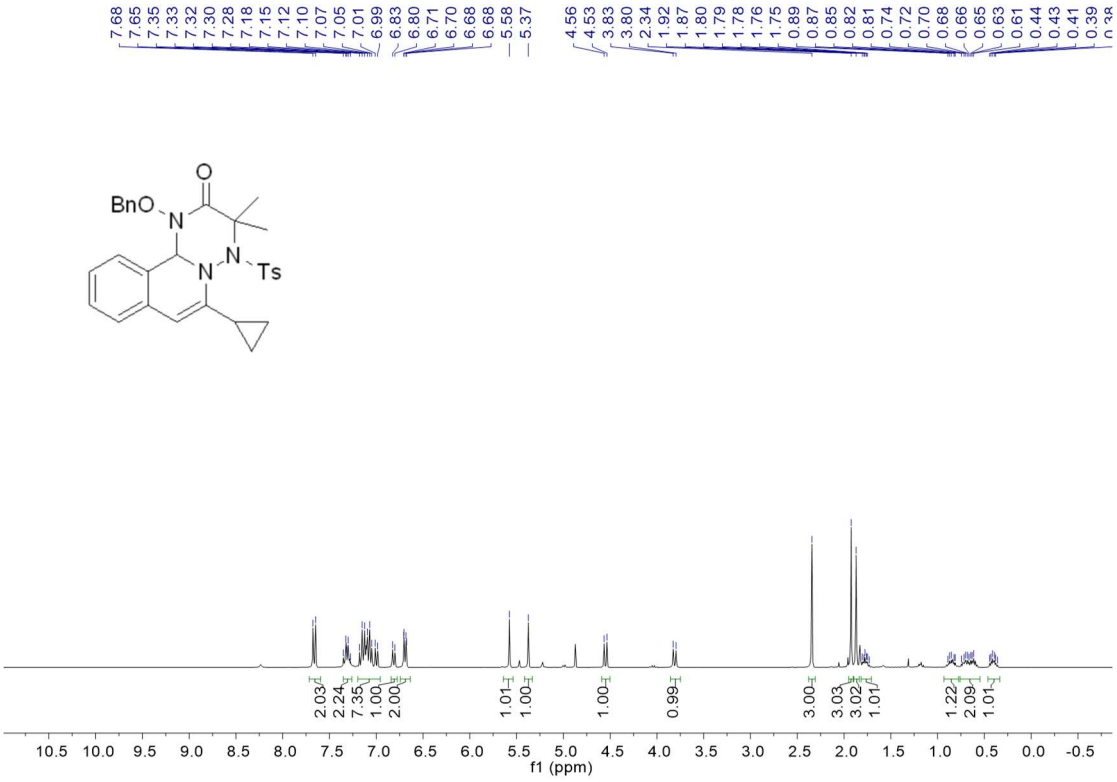
^{1}H NMR Spectrum of 3na



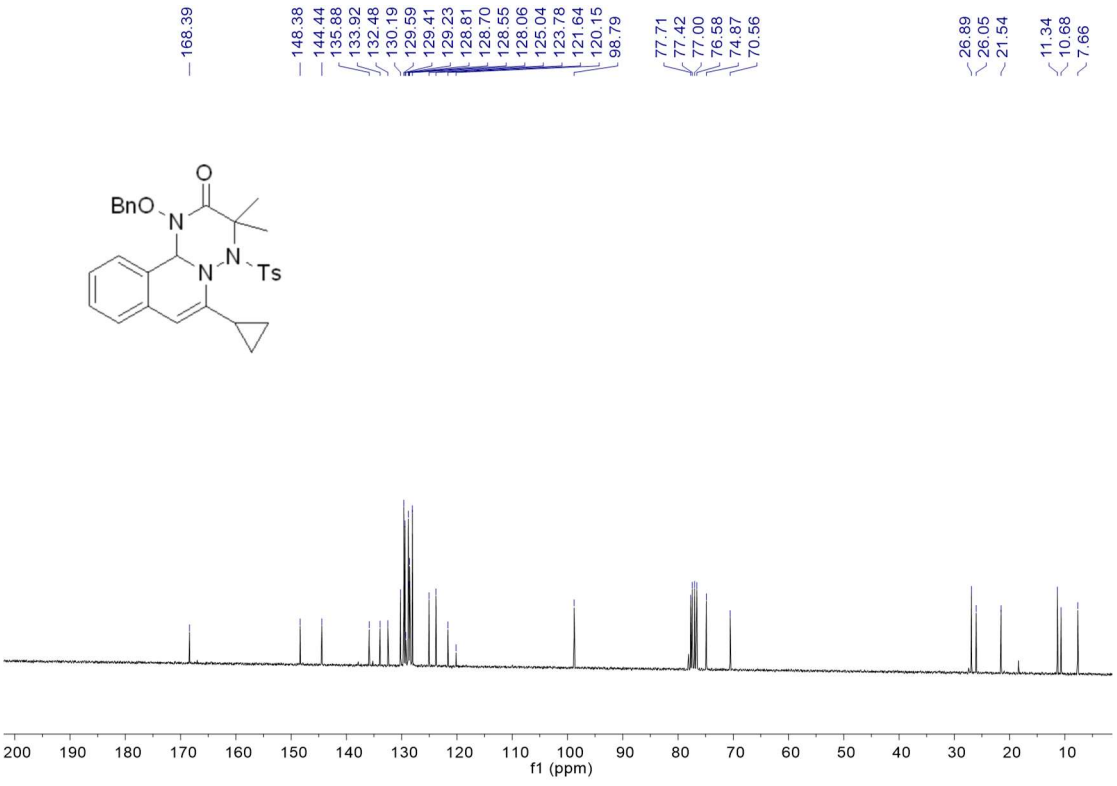
^{13}C NMR Spectrum of 3na



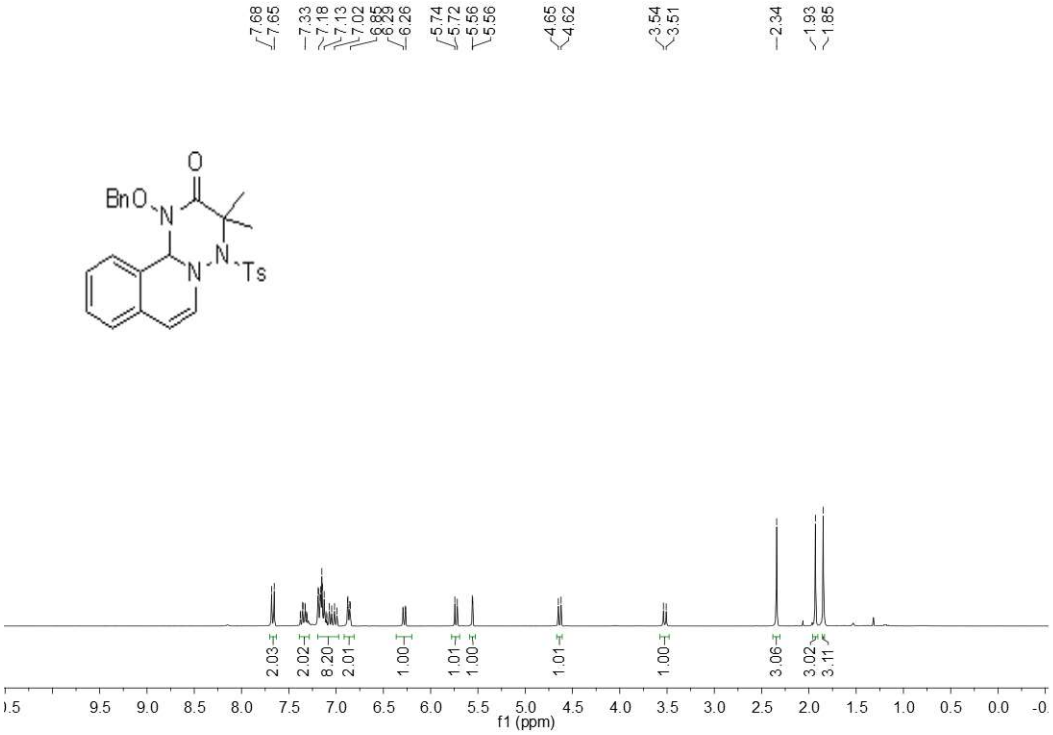
^{1}H NMR Spectrum of 3oa



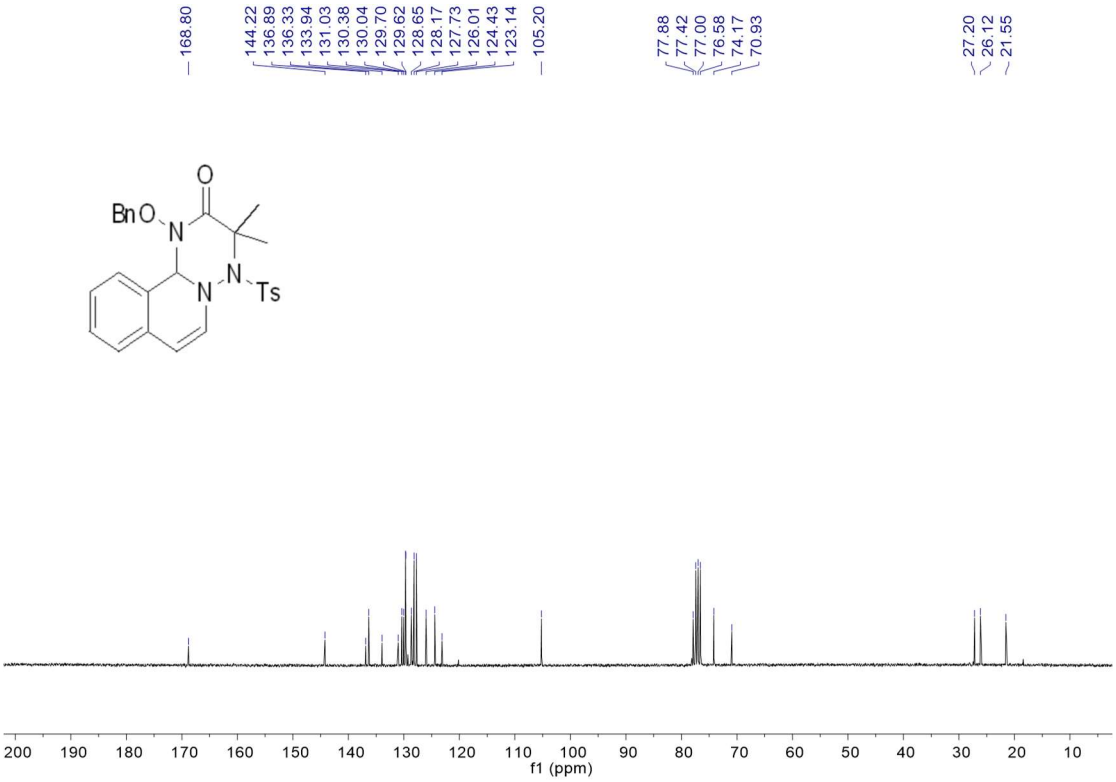
^{13}C NMR Spectrum of 3oa



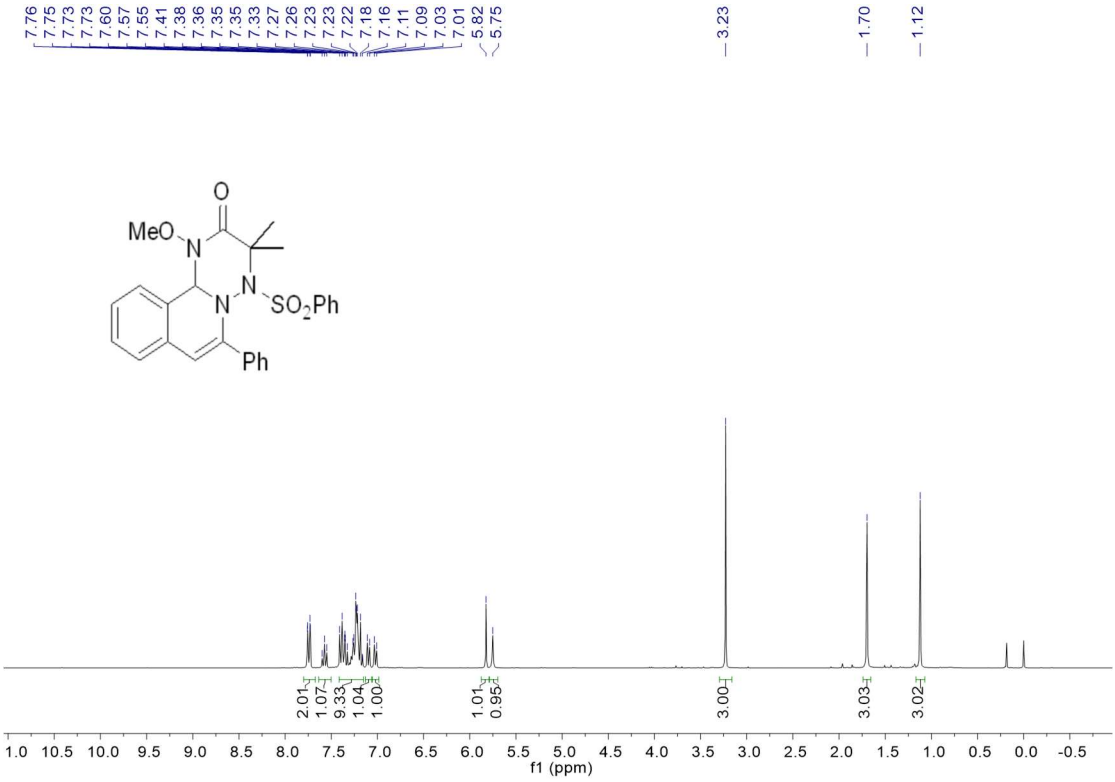
^{1}H NMR Spectrum of 3pa



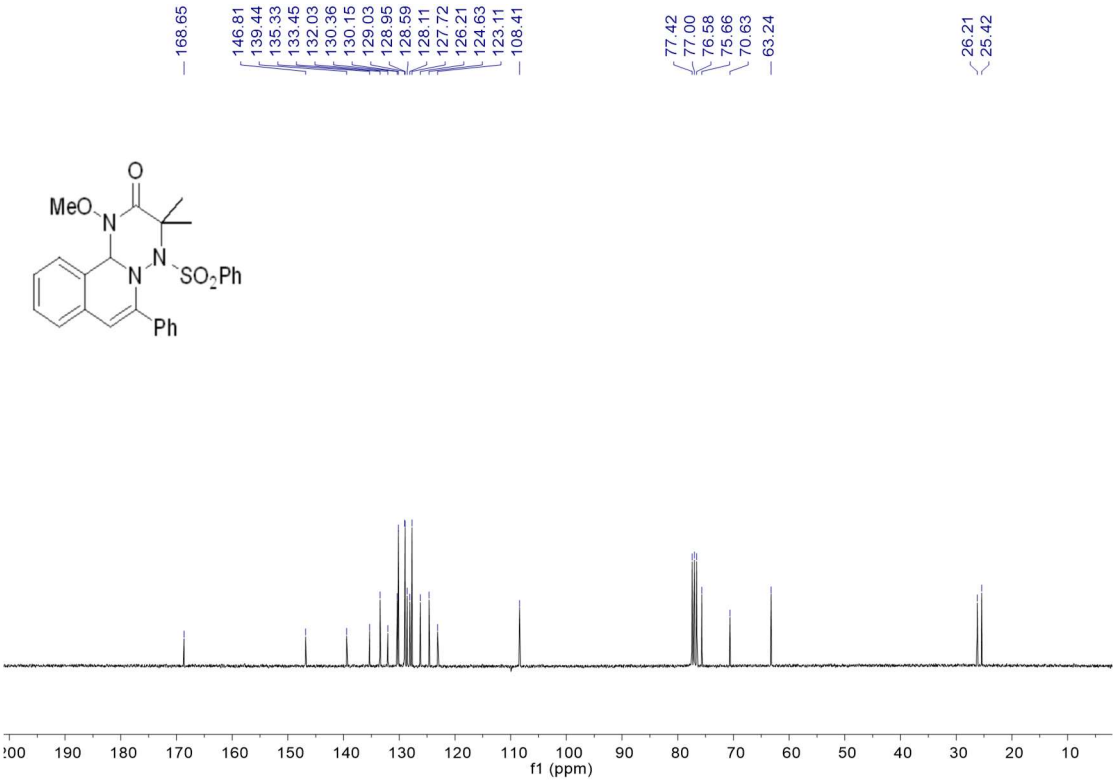
^{13}C NMR Spectrum of 3pa



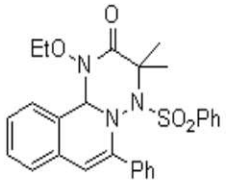
^{1}H NMR Spectrum of 3ab

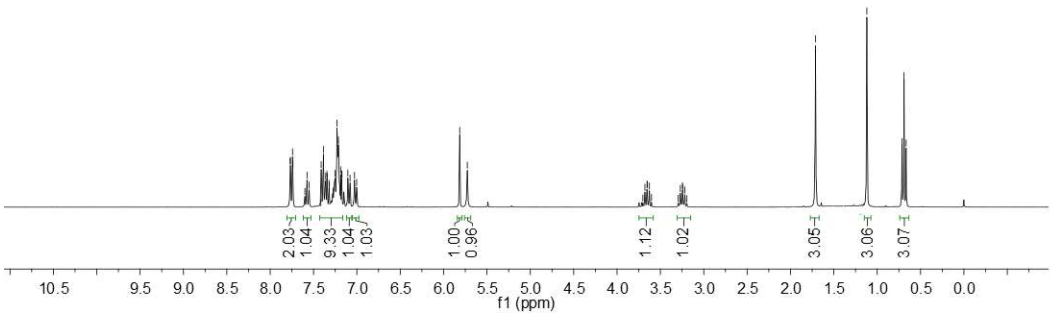


^{13}C NMR Spectrum of 3ab

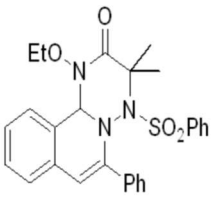


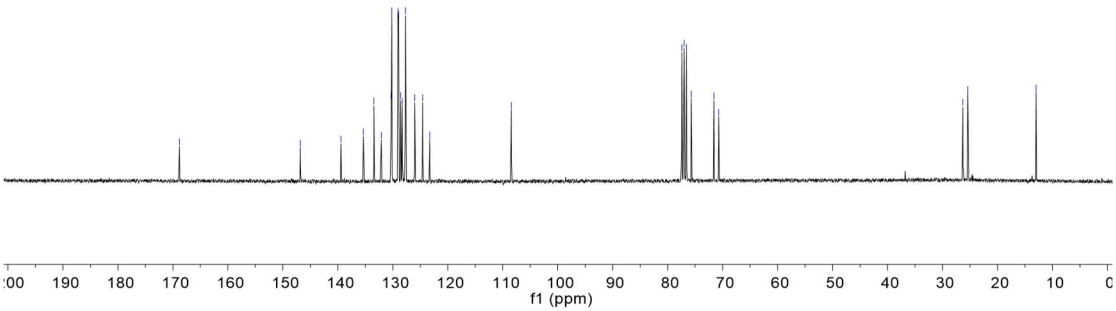
^{1}H NMR Spectrum of 3ac



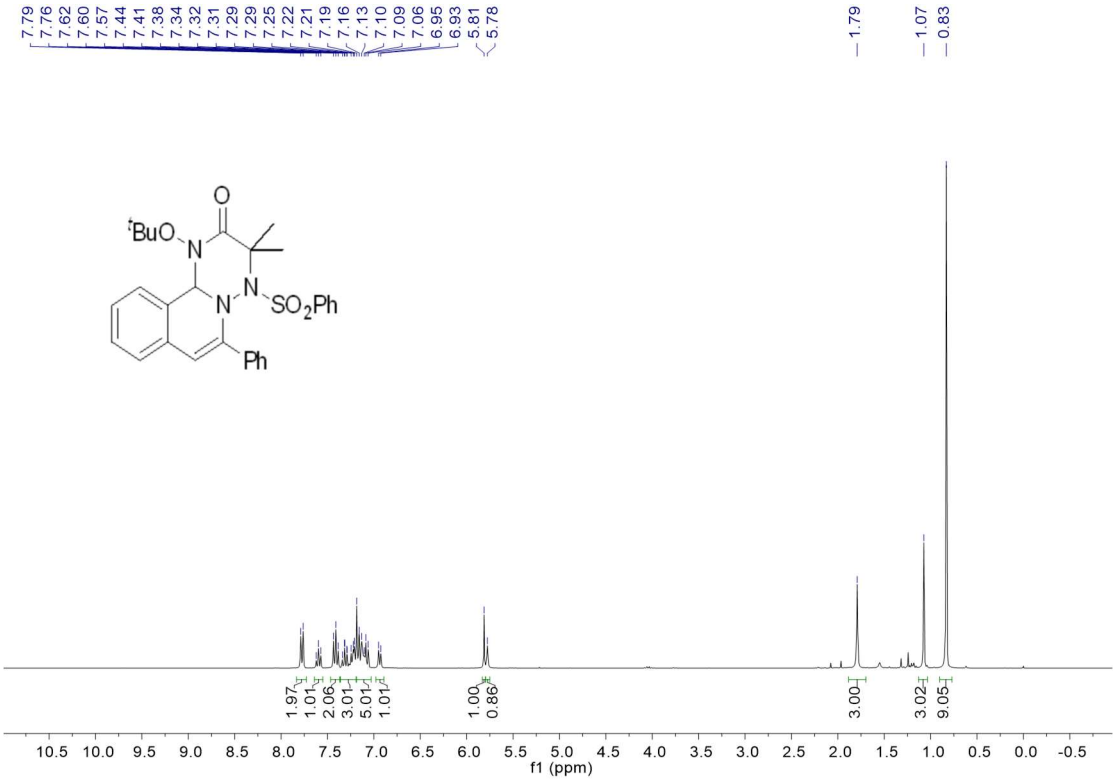


^{13}C NMR Spectrum of 3ac

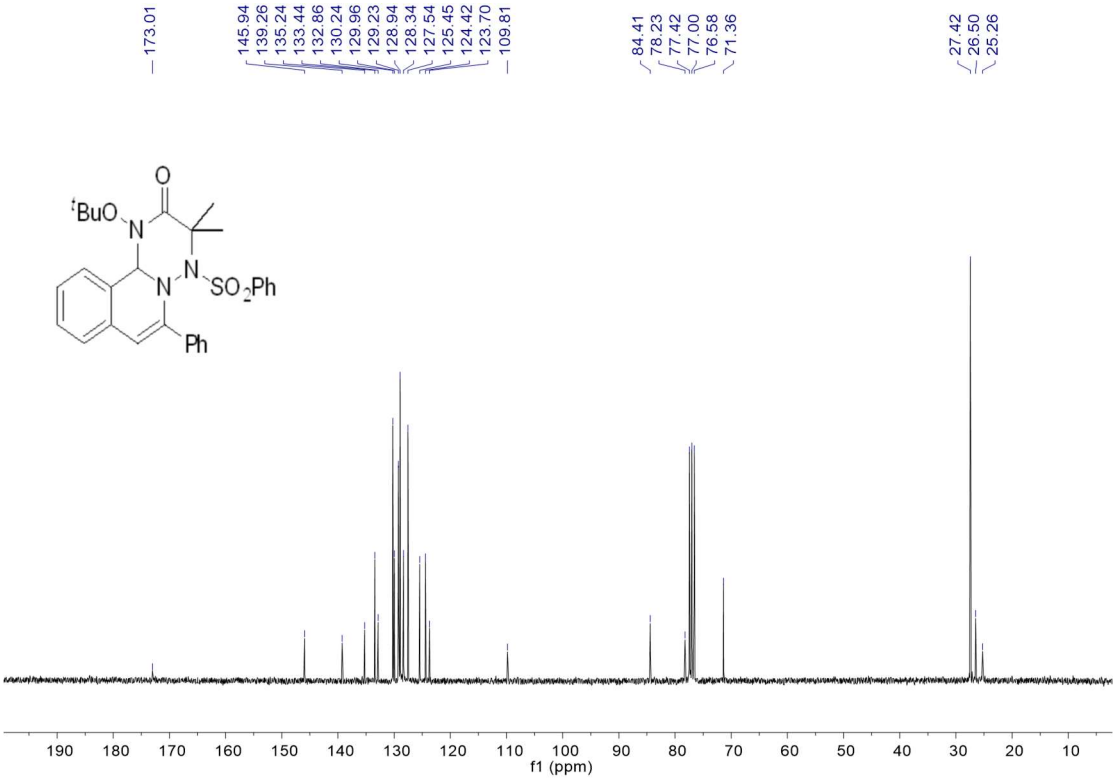




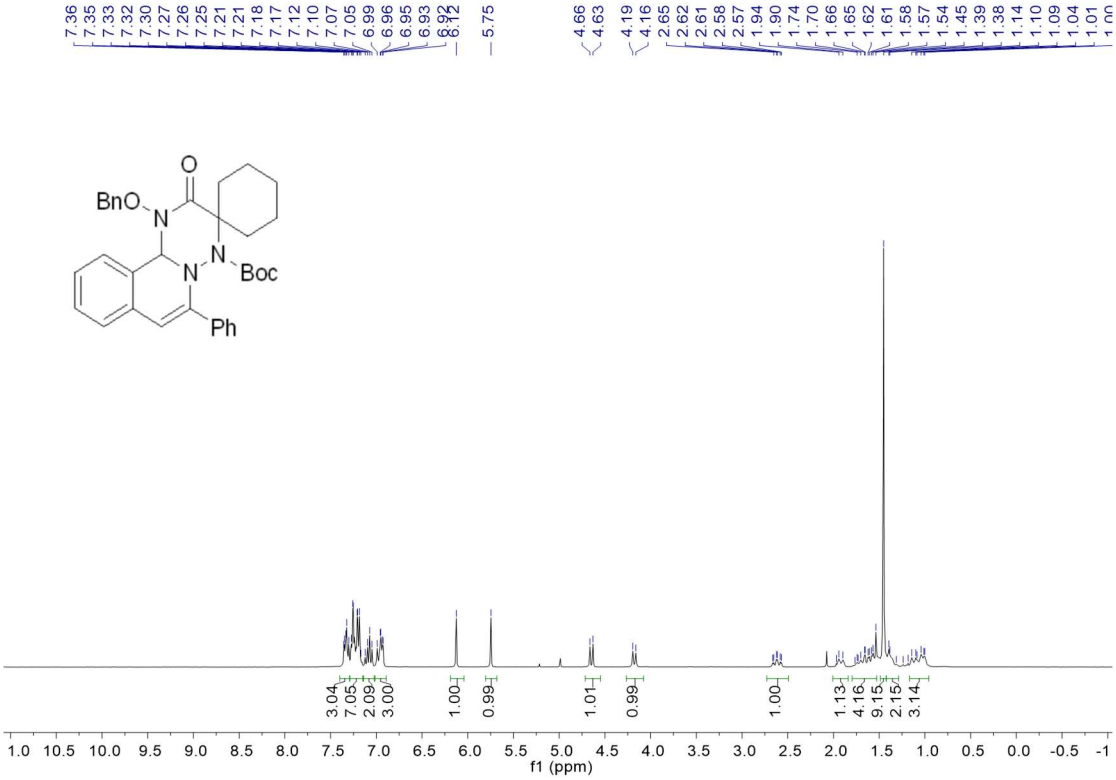
^{1}H NMR Spectrum of 3ad



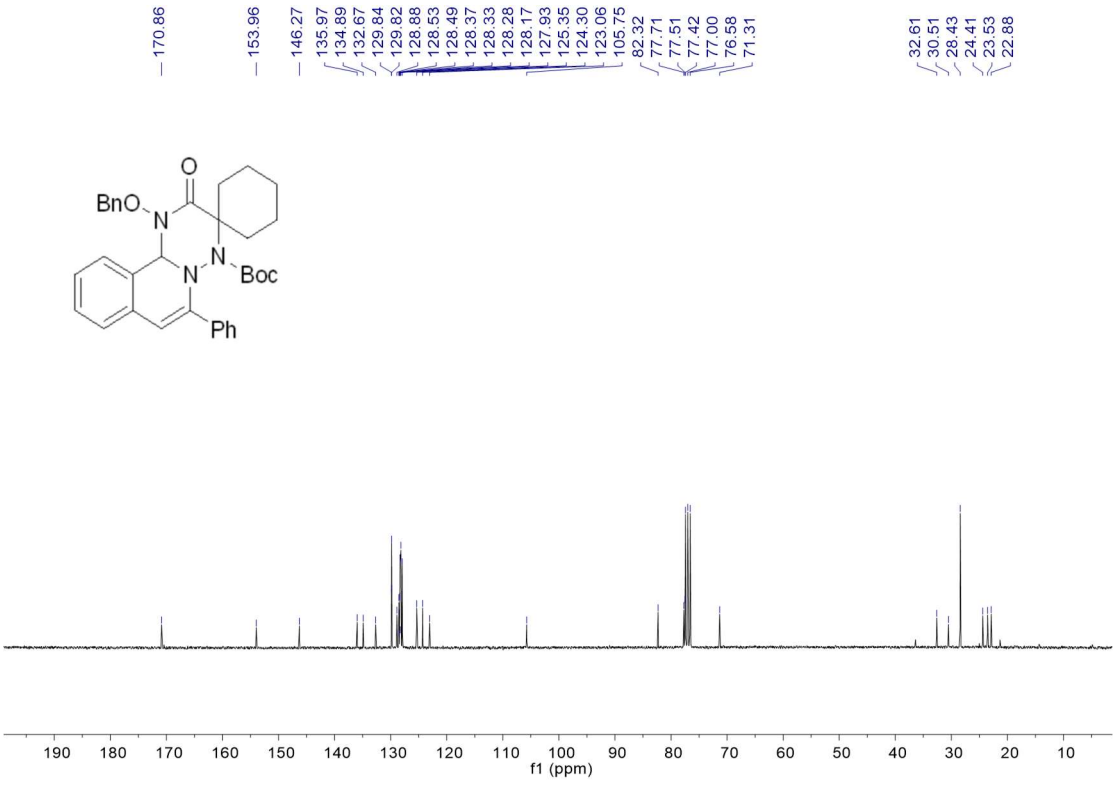
^{13}C NMR Spectrum of 3ad



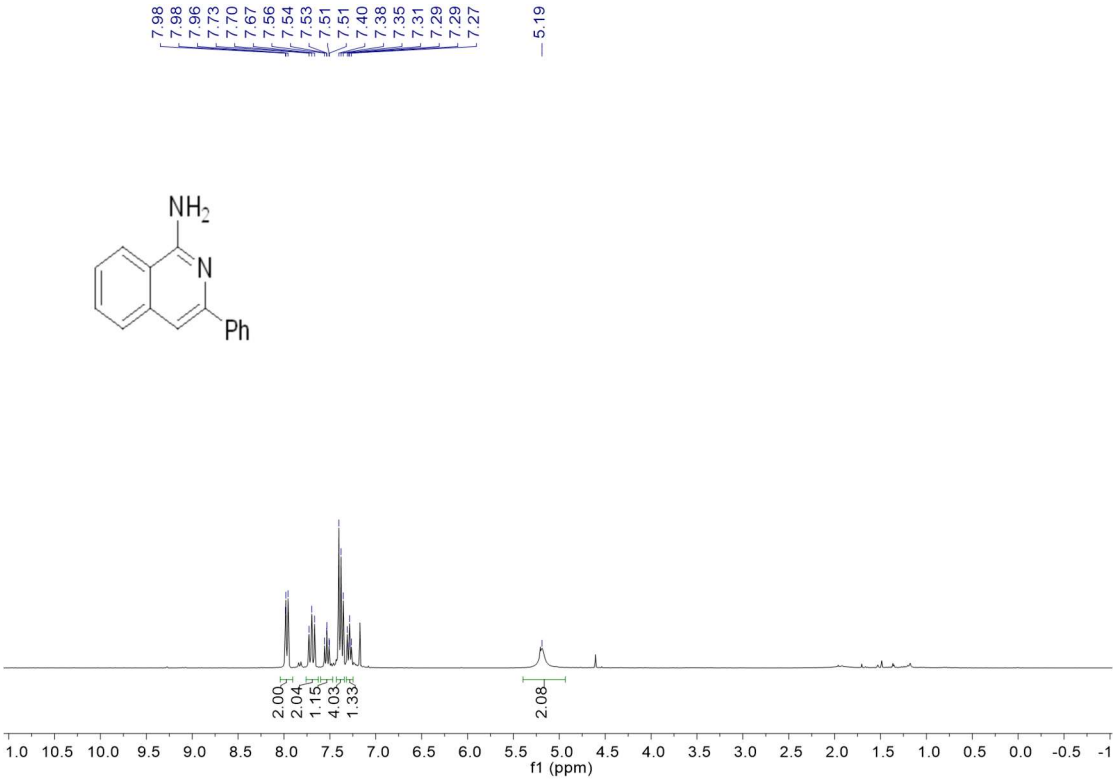
^{1}H NMR Spectrum of 3mf



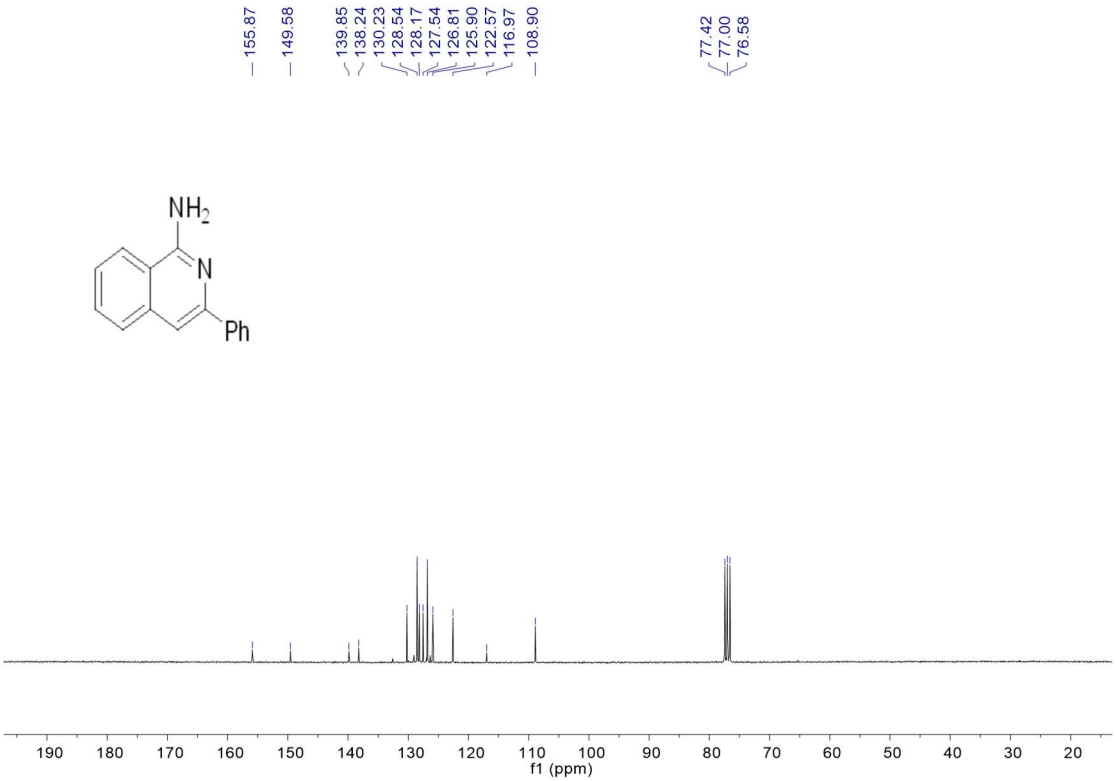
^{13}C NMR Spectrum of 3mf



^{1}H NMR Spectrum of 5



^{13}C NMR Spectrum of 5



6. References:

1. Z. Chen, X. Yang, J. Wu, *Chem. Commun*. **2009**, 3469-3471. And the references therein.
2. K. Zhang, C. Yang, H. Yao, A. Lin, *Org. Lett.* **2016**, *18*, 4618-4621.
3. A. Acharya, D. Anumandla, C. S. Jeffrey, *J. Am. Chem. Soc.* **2015**, *137*, 14858-14860.
3. W. Ji, L. Yao, X. Liao, *Org. Lett.* **2016**, *18*, 628-630.