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Photocatalytic intramolecular carboazidation of *N*-arylacrylamides into 3-(azidomethyl)indolin-2-ones

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Contents

General Experimental

All of the manipulations were performed under N_2 atmosphere, using standard Schlenk techniques. Chemicals were used as received without special purification unless stated otherwise. Olefinic amides were prepared according to the published procedure.[S1] ^{1}H NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 ppm) as the internal standard. NMR analysis was carried out at 298 K unless noted otherwise. All the products are known compounds and their ^{1}H NMR spectrums are consistent with the literature reports.

Photoreactor (blue LEDs, light intensity = 32.8 mW/cm^2, 1 W for every light bulb; every Schlenk tube was irradiated by six light bulbs from the side.): The photoreactors used in this research were bought from GeAo Chem. The pictures of the photoreactors in Figure S1-S3 were cited from the following literatures.[S1,S2]

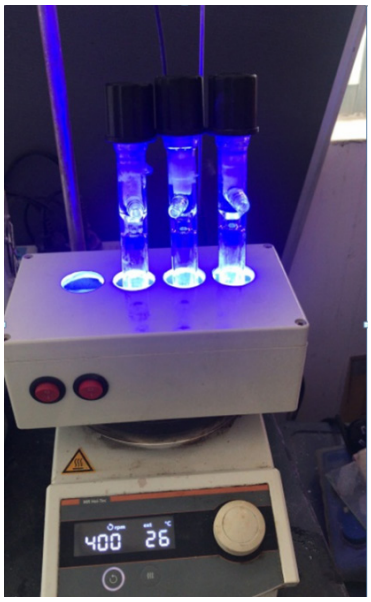


Figure S1

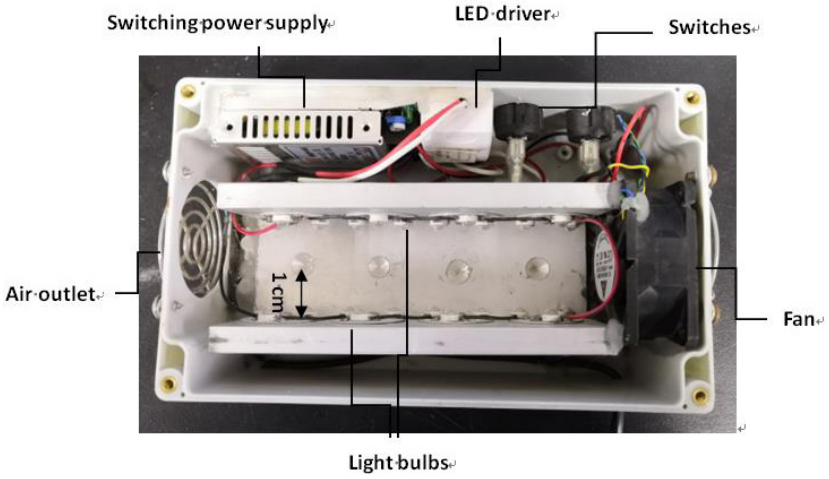


Figure S2

Figure S3

Photocatalyst structures

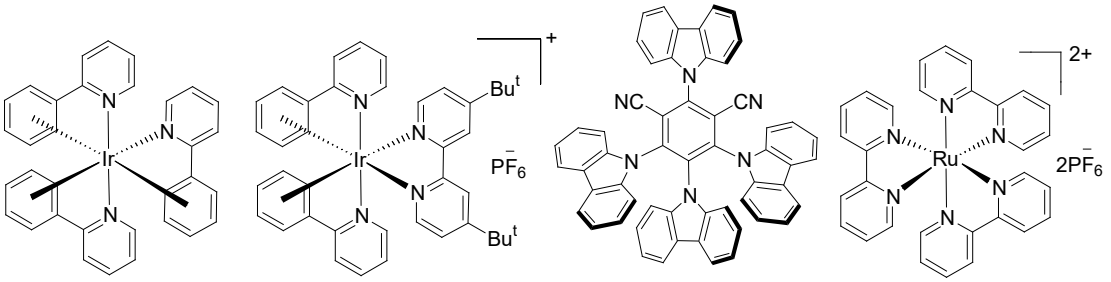


Figure S4

The structures of photocatalysts used

PC1: *fac*-Ir(ppy)$_3$, tris(2-phenylpyridine)iridium; cas: 693794-98-8;

PC2: Ir(ppy)$_2$(dtbbpy)PF$_6$, (4,4-di-*tert*-butyl-2,2-bipyridine)bis(2-phenylpyridine)iridium(III) hexafluorophosphate, cas: 676525-77-2;

PC3: 4CzIPN, 2,4,5,6-tetra(carbazol-9-yl)-1,3-dicyanobenzene; cas: 1416881-52-1;

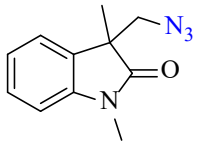
PC4: Ru(bpy)$_3$·2PF$_6$, tris(2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate), cas: 60804-74-2

Experimental Procedure

*General procedure for the synthesis of **3***

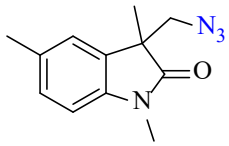
Under air, to an over-dried 20 mL Schlenk tube equipped with a Teflon cap was sequentially added arylacrylamide **1** (0.2 mmol), 1-azido-λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one **2** (0.4 mmol, 115.6 mg), **PC3** (4CzIPN, 2 mol %, 3.2 mg), K_2CO_3 (0.4 mmol, 55.3 mg) and 1,2-dichloroethane (2.0 mL). The reaction vessel was evacuated to about 0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm) three times. Then, the Schlenk tube was stirred at room temperature under 2 × 3 W blue LEDs irradiation for 12 h. After that, the reaction mixture was washed with saturated brine and extracted with ethyl acetate for at least 6 times (2 mL × 6). Subsequently, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to give the desired product.

Characterization data



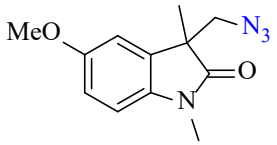
3-Azidomethyl-1,3-dimethylindolin-2-one (3a) was prepared as a clear liquid from *N*-methyl-*N*-phenylmethacrylamide **1a** (35.0 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate =10:1) in 85% yield (36.7 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.67 – 3.61 (m, 2H), 3.24 (s, 3H), 1.38 (s, 3H).



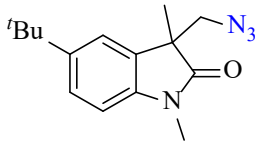
3-Azidomethyl-1,3,5-trimethylindolin-2-one (3b) was prepared as a clear liquid from *N*-methyl-*N*-(*p*-tolyl)methacrylamide **1b** (37.8 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate =10:1) in 73% yield (33.5 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 3.63 (s, 2H), 3.22 (s, 3H), 2.36 (s, 3H), 1.36 (s, 3H).



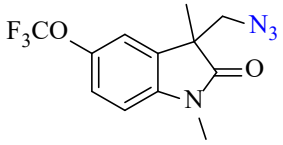
3-Azidomethyl-5-methoxy-1,3-dimethylindolin-2-one (3c) was prepared as a clear liquid from *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide **1c** (41.0 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 69% yield (34.0 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 2.5 Hz, 1H), 6.85 – 6.76 (m, 2H), 3.80 (s, 3H), 3.62 (s, 2H), 3.21 (s, 3H), 1.36 (s, 3H).



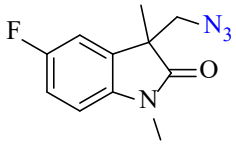
3-Azidomethyl-5-*tert*-butyl-1,3-dimethylindolin-2-one (3d) was prepared as a clear liquid from *N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide **1d** (46.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 68% yield (37.0 mg). This is a known compound.[S4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 6.83 – 6.81 (m, 1H), 3.66 – 3.57 (m, 2H), 3.22 (s, 3H), 1.38 (s, 3H), 1.33 (s, 9H).



3-Azidomethyl-1,3-dimethyl-5-(trifluoromethoxy)indolin-2-one (3e) was prepared as a clear liquids from *N*-methyl-*N*-(4-(trifluoromethoxy)phenyl)methacrylamide **1e** (51.8 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 72% yield (43.2 mg). This is a known compound.[S3]

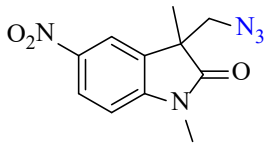
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.64 (d, *J* = 0.9 Hz, 2H), 3.24 (s, 3H), 1.39 (s, 3H).



3-Azidomethyl-5-fluoro-1,3-dimethylindolin-2-one (3f) was prepared as a clear liquid from

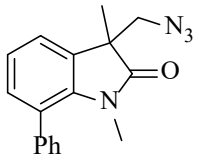
N-(4-fluorophenyl)-*N*-methylmethacrylamide **1f** (38.6 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 66% yield (24.8 mg). This is a known compound.[S5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.99 (m, 2H), 6.80 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.63 (s, 2H), 3.22 (s, 3H), 1.37 (s, 3H).



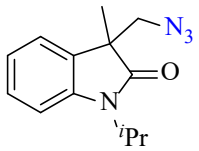
3-Azidomethyl-1,3-dimethyl-5-nitroindolin-2-one (3g) was prepared as a clear liquid from *N*-methyl-*N*-(4-nitrophenyl)methacrylamide **1g** (44.1 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 64% yield (33.4 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 3.73 (s, 2H), 3.31 (s, 3H), 1.43 (s, 3H).



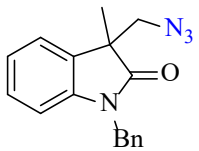
3-Azidomethyl-1,3-dimethyl-7-phenylindolin-2-one (3h) was prepared as a clear liquid from *N*-([1,1'-biphenyl]-2-yl)-*N*-methylmethacrylamide **1h** (50.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 41% yield (23.9 mg). This is a known compound.[S6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 5H), 7.28 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.17 – 7.09 (m, 2H), 3.67 (s, 2H), 2.75 (s, 3H), 1.42 (s, 3H).



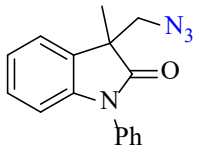
3-Azidomethyl-1-isopropyl-3-methylindolin-2-one (3i) was prepared as a clear liquid from *N*-isopropyl-*N*-phenylmethacrylamide **1i** (40.6 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 87% yield (42.4 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H + overlapped with $CDCl_3$), 7.10 – 7.04 (m, 2H), 4.65 (hept, *J* = 7.0 Hz, 1H), 3.61 (d, *J* = 7.5 Hz, 2H), 1.50 (d, *J* = 7.0 Hz, 6H), 1.35 (s, 3H).



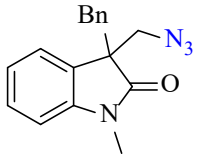
3-Azidomethyl-1-benzyl-3-methylindolin-2-one (3j) was prepared as a clear liquid from *N*-benzyl-*N*-phenylmethacrylamide **1j** (50.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 70% yield (40.9 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 6H + overlapped with $CDCl_3$), 7.23 (td, *J* = 7.8, 1.3 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.06 (d, *J* = 15.7 Hz, 1H), 4.89 (d, *J* = 15.8 Hz, 1H), 3.75 (s, 2H), 1.46 (s, 3H).



3-Azidomethyl-3-methyl-1-phenylindolin-2-one (3k) was prepared as a clear liquid from *N*,*N*-diphenylmethacrylamide **1k** (47.4 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 75% yield (41.7 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.43 – 7.40 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.15 (q, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 3.79 – 3.69 (m, 2H), 1.49 (s, 3H).



3-Azidomethyl-3-benzyl-1-methylindolin-2-one (3l) was prepared as a clear liquid from 2-benzyl-*N*-methyl-*N*-phenylacrylamide **1l** (50.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 10:1) in 63% yield (36.8 mg). This is a known compound.[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H + overlapped with $CDCl_3$), 7.10 – 7.04 (m, 4H), 6.85 – 6.83 (m, 2H), 6.65 (dt, *J* = 7.5, 0.9 Hz, 1H), 3.80 (d, *J* = 1.2 Hz, 2H), 3.09 (s, 2H), 3.00 (s, 3H).

References

S1. Y. Wei, S. Liu, M.-M. Li, Y. Li, Y. Lan, L.-Q. Lu and W.-J. Xiao, *J. Am. Chem. Soc.*, 2019, **141**, 133.

S2. S. Sun, C. Zhou, J.-T. Yu and J. Cheng, *Org. Lett.*, 2019, **21**, 6579.

S3. C. Pei, Y. Liu, X. Chen, J. Li, D. Zou, Y. J. Wu and Y. S. Wu, *Adv. Synth. Catal.*, 2023, **365**, 860.

S4. K. Matcha, R. Narayan and A. P. Antonchick, *Angew. Chem. Int. Ed.*, 2013, **52**, 7985.

S5. D. Maiti, K. Mahanty and S. De Sarkar, *Chem Asian J.*, 2021, **16**, 748.

S6. X. H. Wei, Y. M. Li, A. X. Zhou, T. T. Yang and S. D. Yang, *Org. Lett.*, 2013, **15**, 4158.

S7. Y. Yuan, T. Shen, K. Wang and N. Jiao, *Chem. Asian J.*, 2013, **8**, 2932.

Copies of ^{1}H NMR spectrum

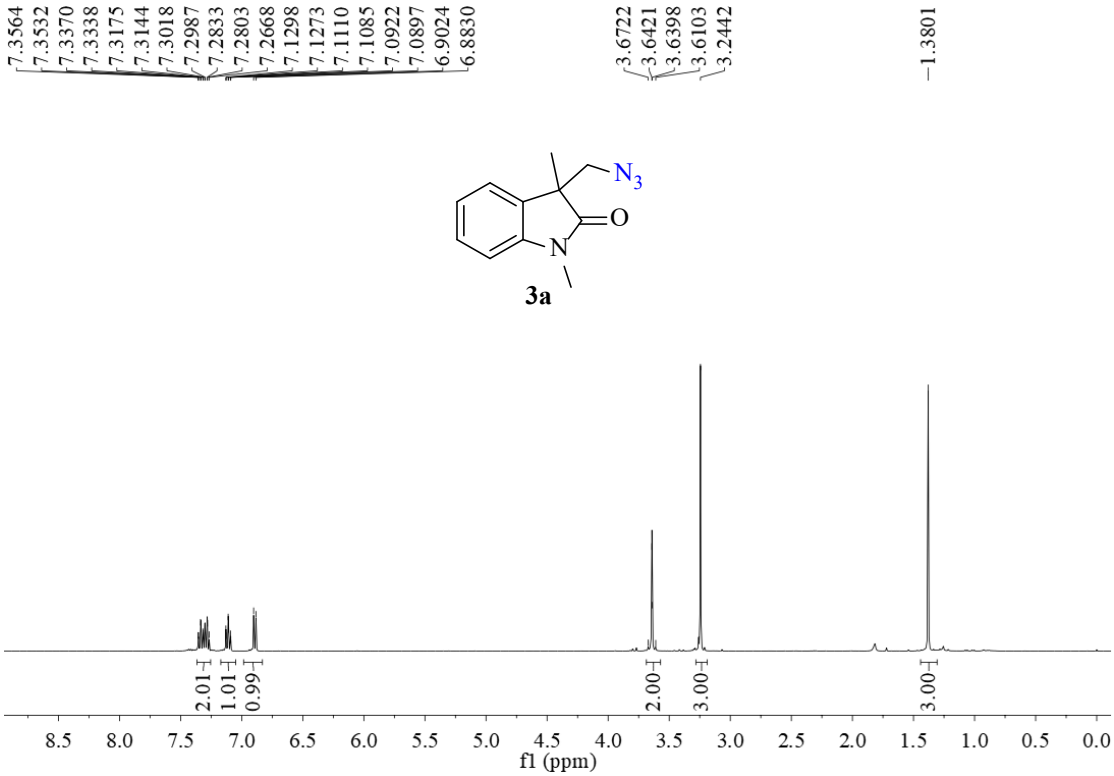


Figure S5. The ^{1}H NMR for compound **3a**

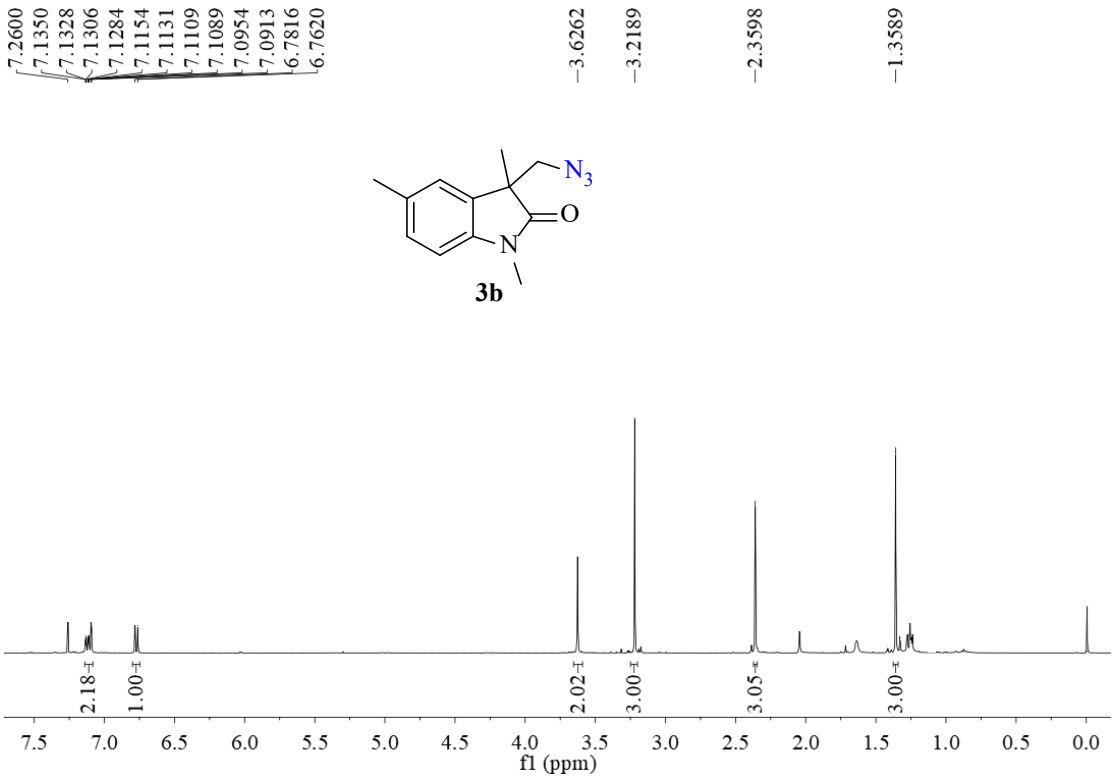


Figure S6. The ^{1}H NMR for compound **3b**

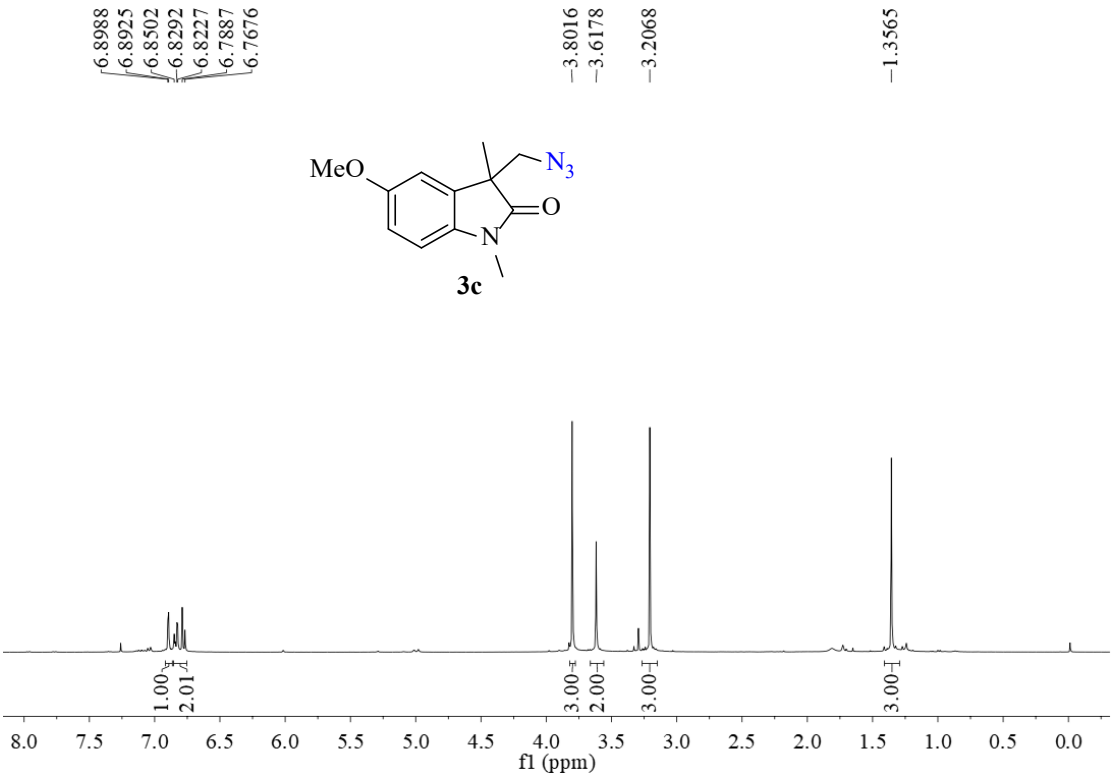


Figure S7. The ^{1}H NMR for compound **3c**

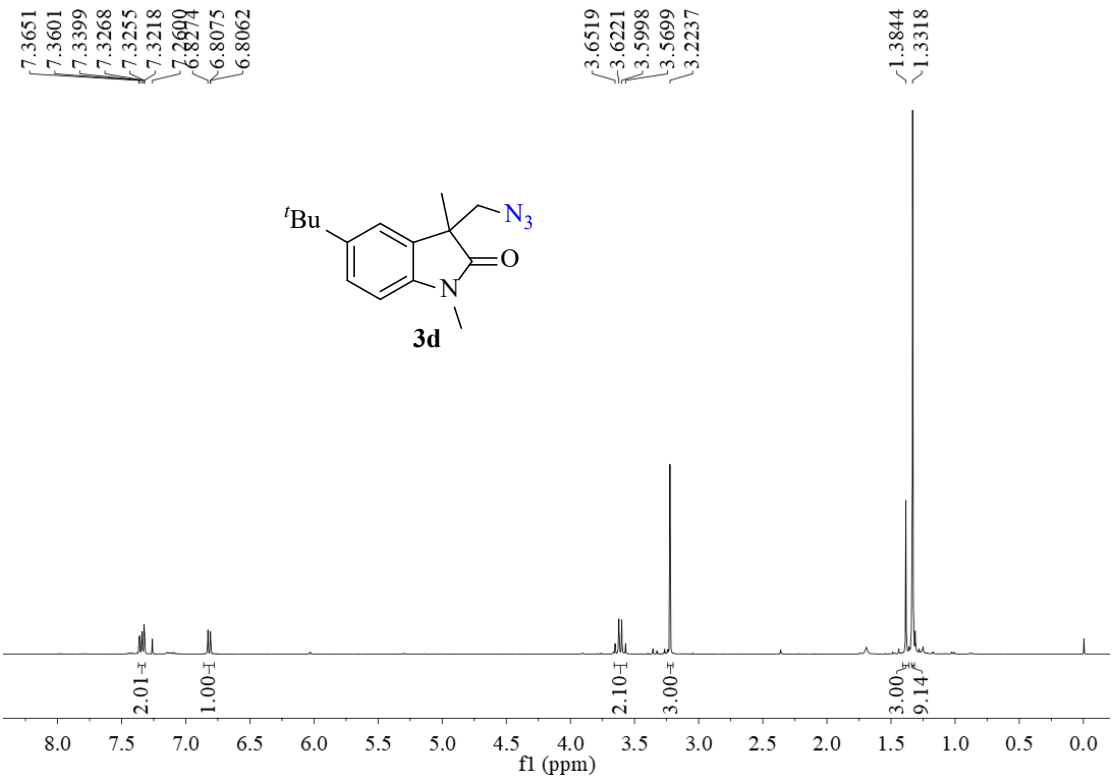


Figure S8. The ^{1}H NMR for compound **3d**

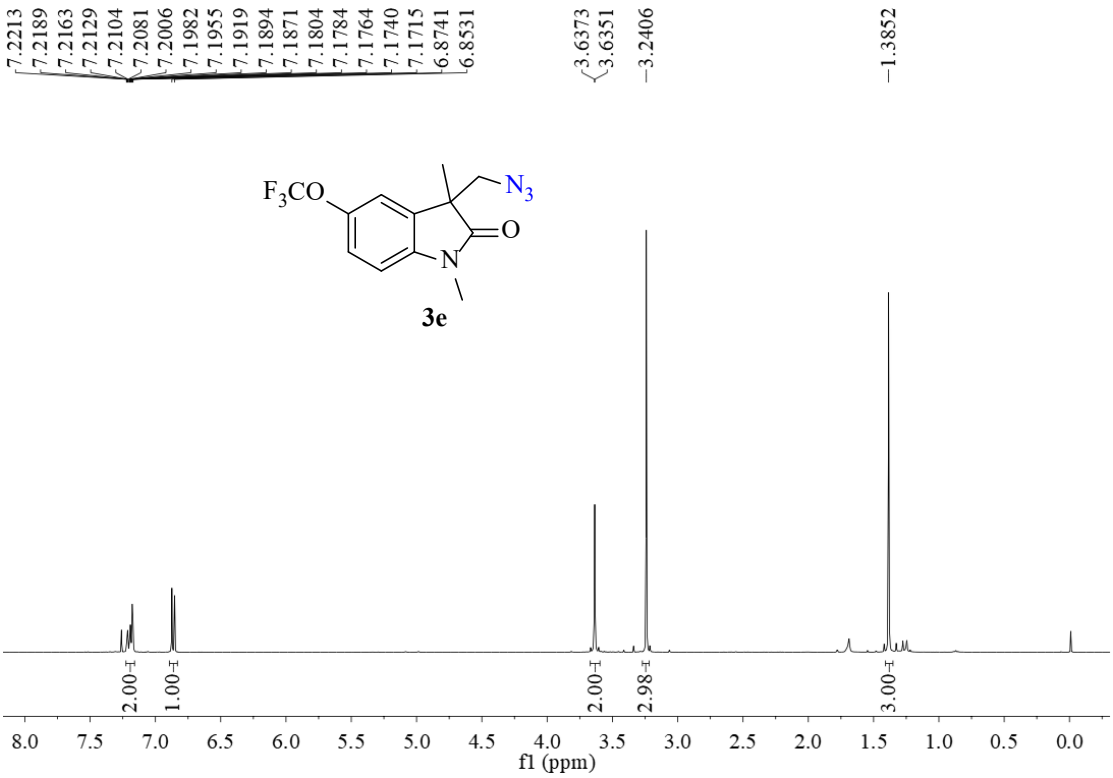


Figure S9. The ^{1}H NMR for compound **3e**

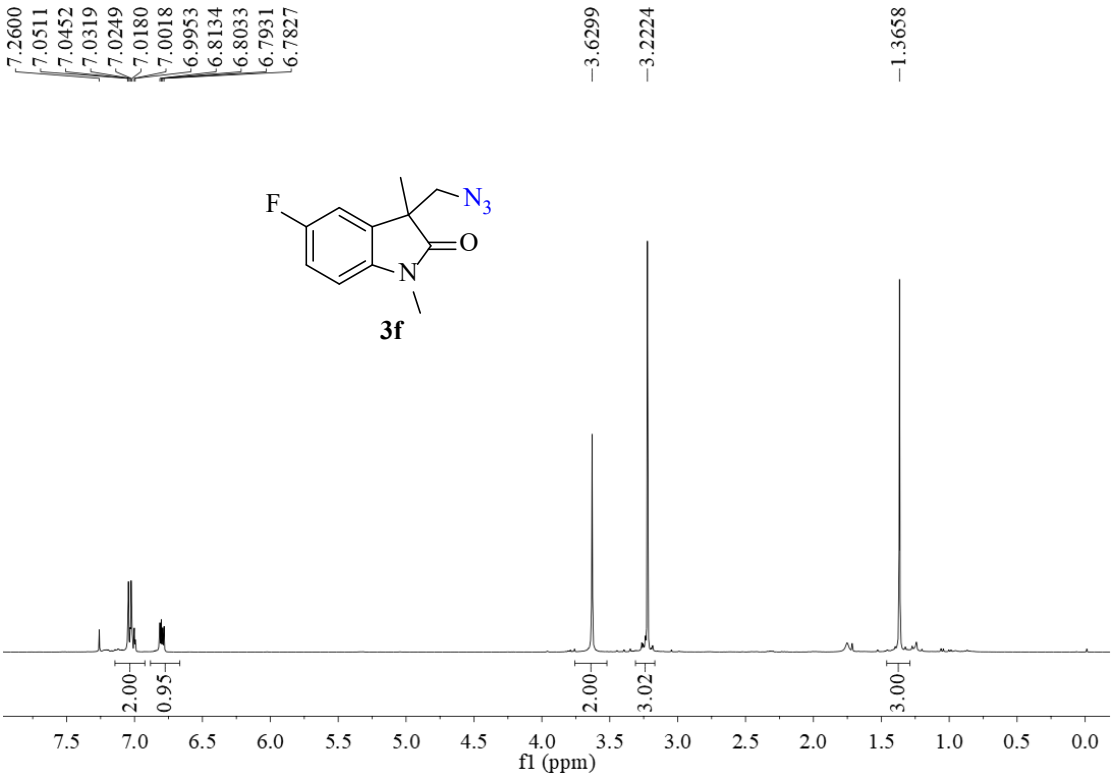


Figure S10. The ^{1}H NMR for compound **3f**

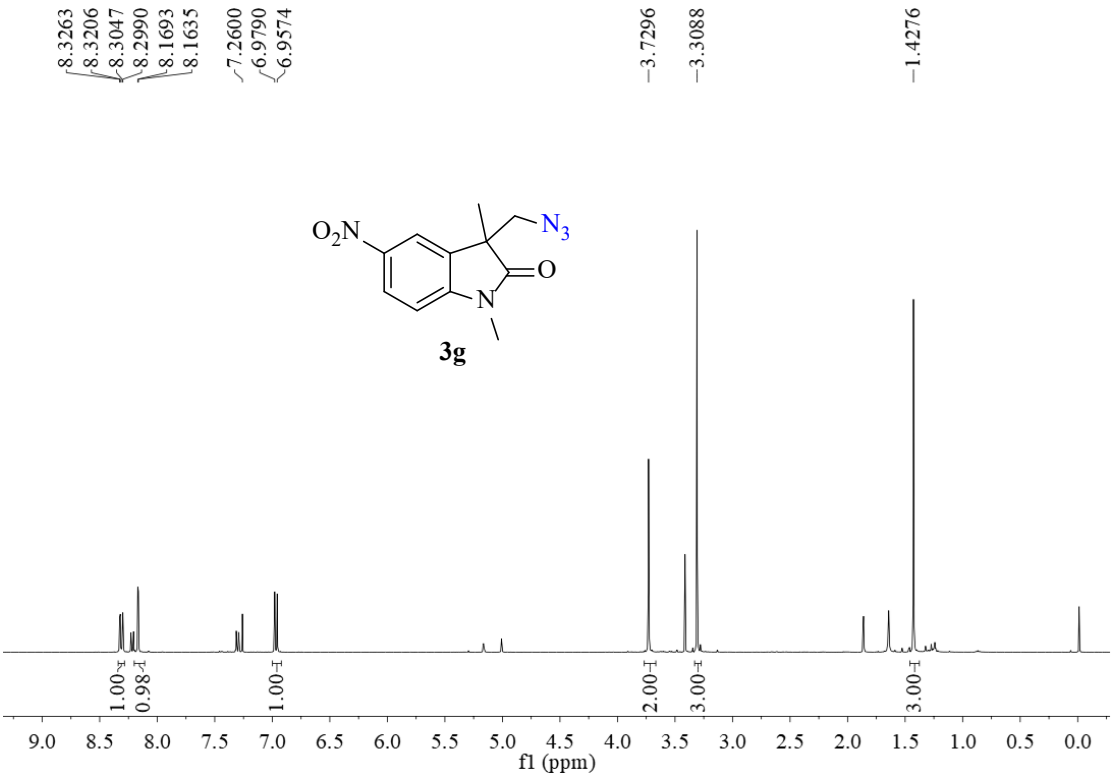


Figure S11. The ^{1}H NMR for compound **3g**

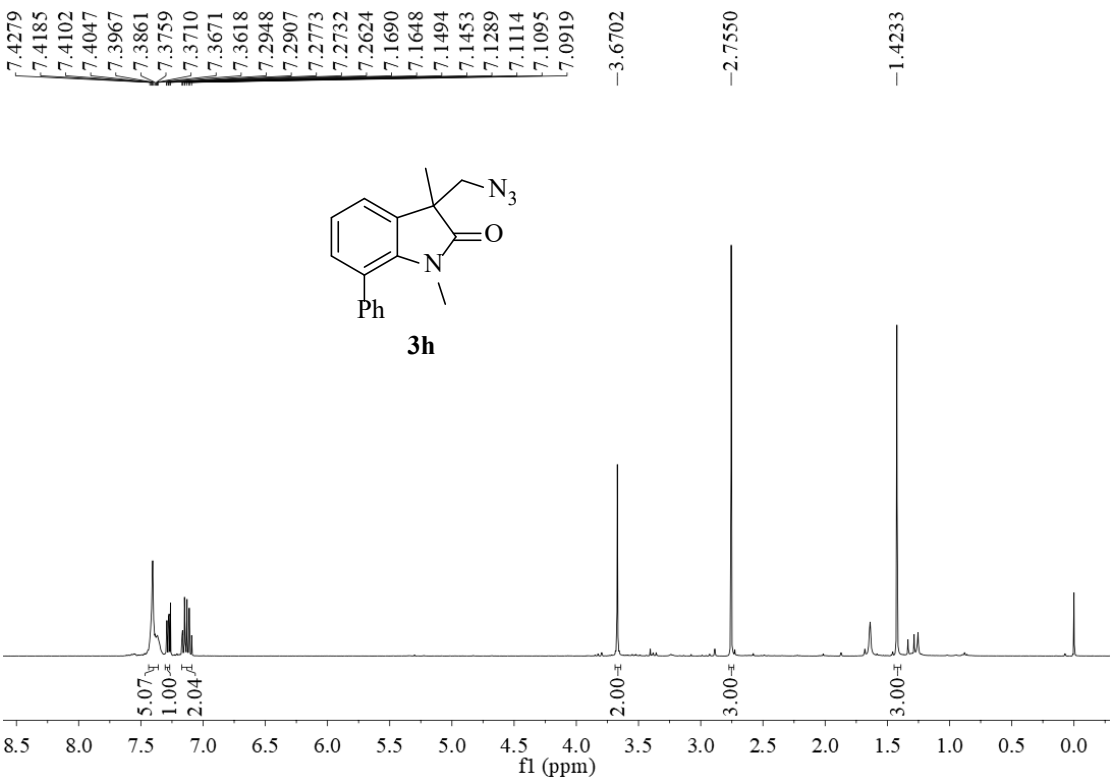
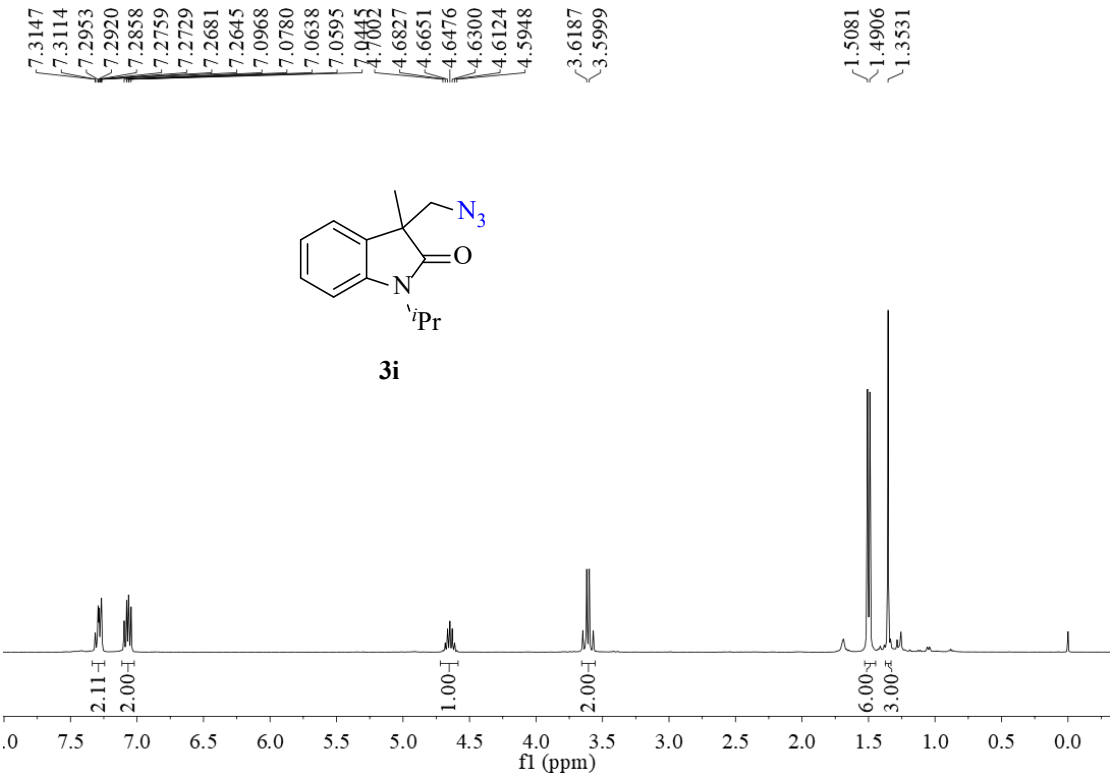
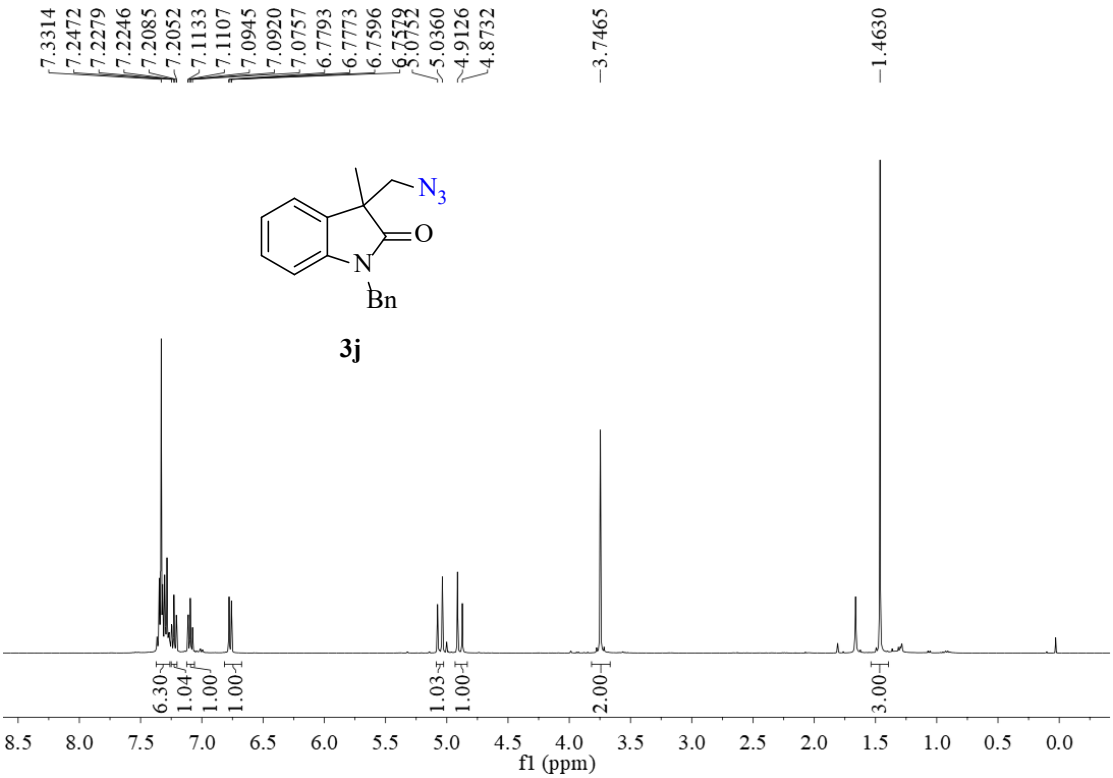


Figure S12. The ^{1}H NMR for compound **3h**



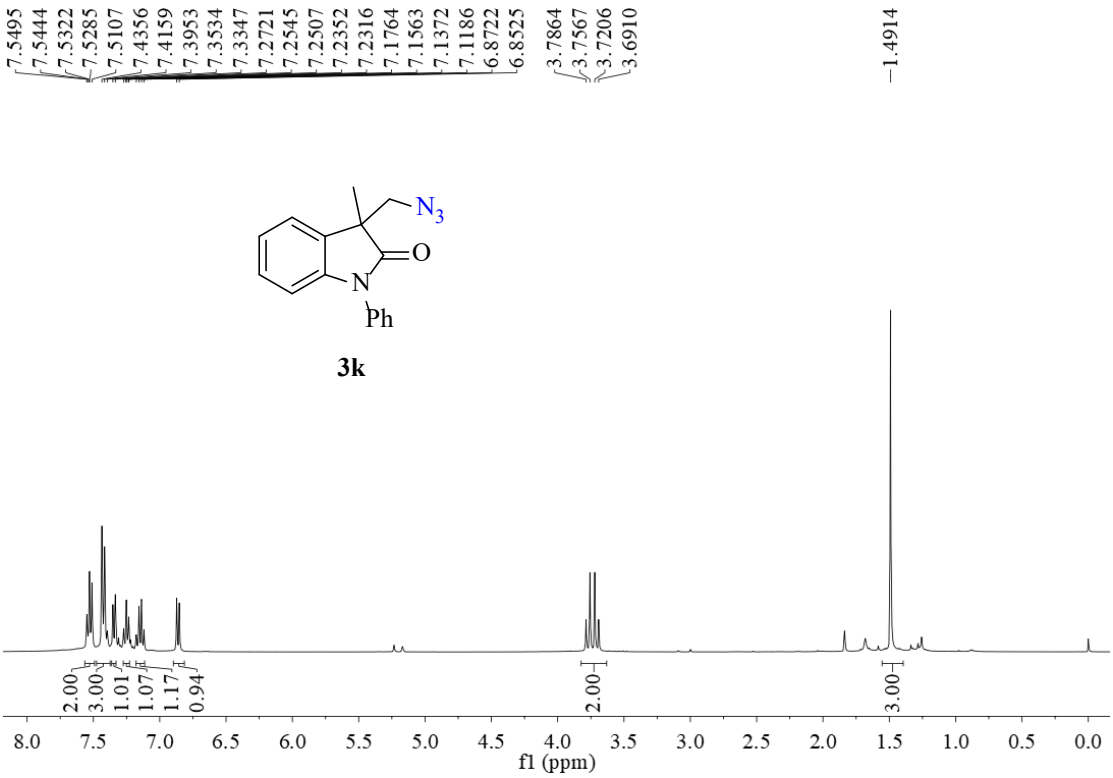
3i

Figure S13. The ^{1}H NMR for compound **3i**



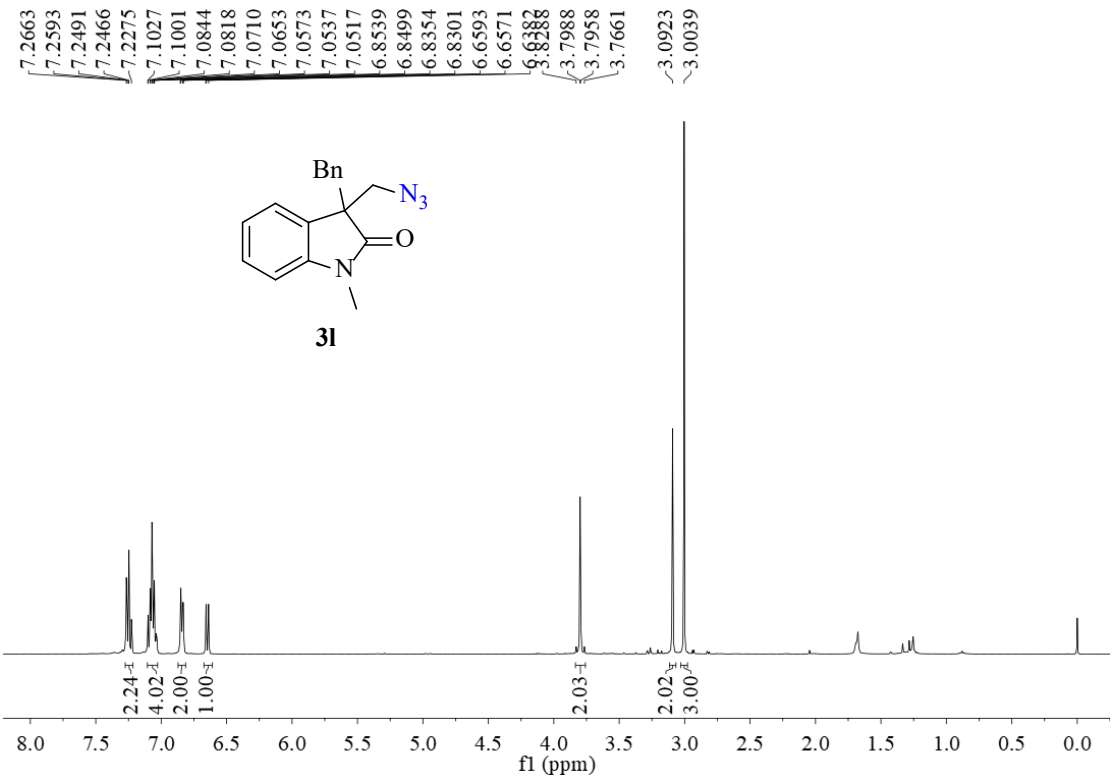
3j

Figure S14. The ^{1}H NMR for compound **3j**



3k

Figure S15. The ^{1}H NMR for compound **3k**



3l

Figure S16. The 1H NMR for compound **3l**