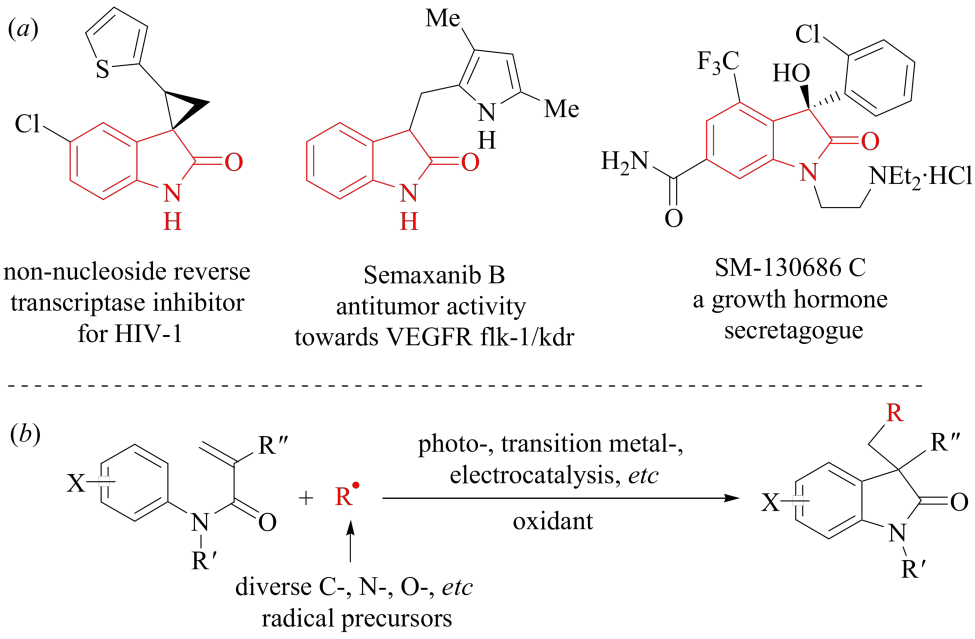
Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 717–719

Photocatalytic radical arylation/cyclization of *N*-arylacrylamides to 3-benzyl oxindoles

Jue Wang, Wenkai Lai, Mei Hong, Chengxian Liu and Liang Wang

Contents



Scheme S1 (*a*) Selected biologically active oxindoles and (*b*) previous syntheses of substituted oxindoles from *N*-arylacrylamides.

General Experimental

All 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]

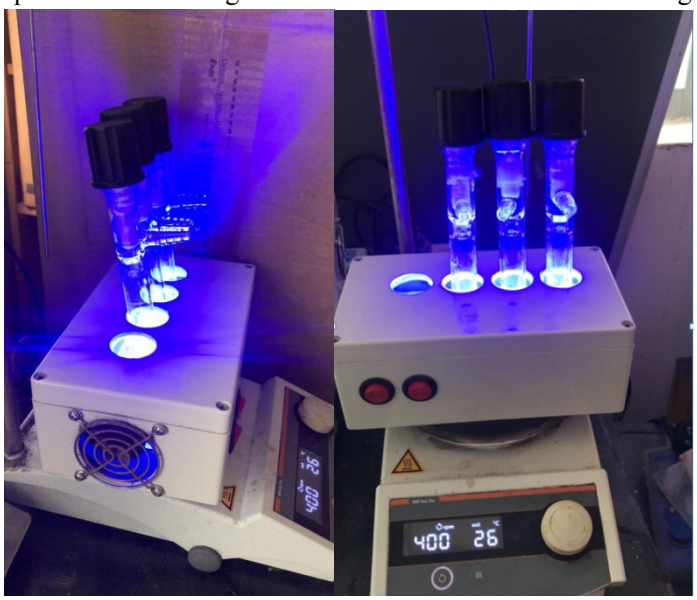


Figure S1

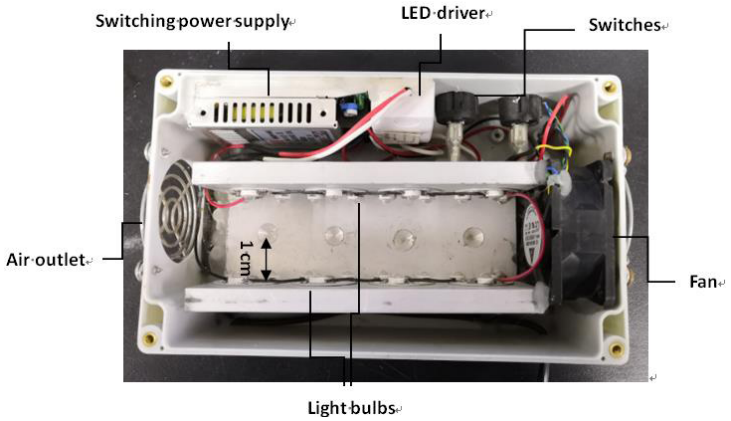


Figure S2

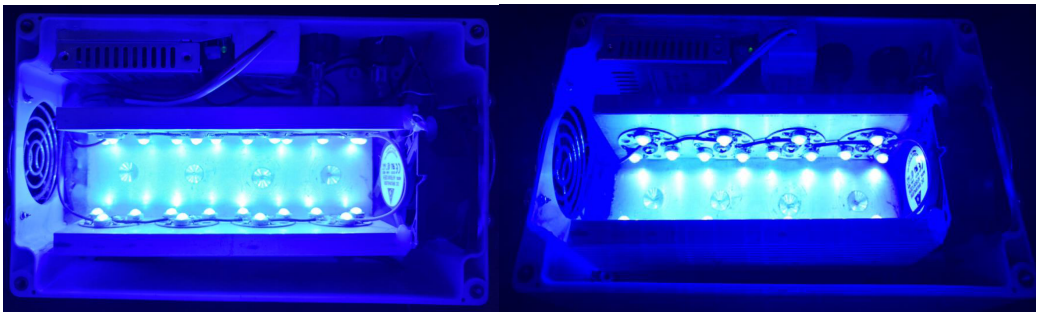


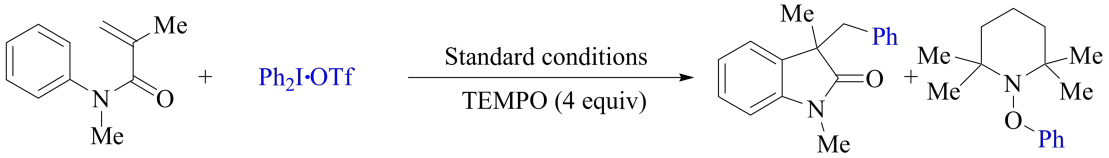
Figure S3

Experimental Procedure

General procedure for the synthesis of **3**

To an over-dried 20 mL Schlenk tube equipped with a Teflon cap was sequentially added *N*-arylacrylamide **1** (0.2 mmol), diaryliodonium triflate **2** (0.3 mmol, 64.5 mg), **PC4** (2 mol %, 3.6 mg) and acetonitrile (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 3 times (3 mL × 3). 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 using petroleum ether/ethyl acetate (5:1, *v*/*v*) as eluent to give the desired product **3**.

Radical trapping experiment



1a **2a** **3a**, not detected **IM-A** *m/z* = 233.1

Scheme S2

Under air, to an over-dried 20 mL Schlenk tube equipped with a Teflon cap was sequentially added *N*-methyl-*N*-phenylmethacrylamide **1a** (35.0 mg, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate **2a** (0.3 mmol, 64.5 mg), **PC4** (2 mol%, 3.6 mg), MeCN (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) in 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 analyzed by GC-MS. The desired product **3a** can not be detected, however, the radical adduct **IM-A** with the molecular weight of 233.1 could be detected by GC-MS. Thus, a radical pathwaymight be involved in this reaction.

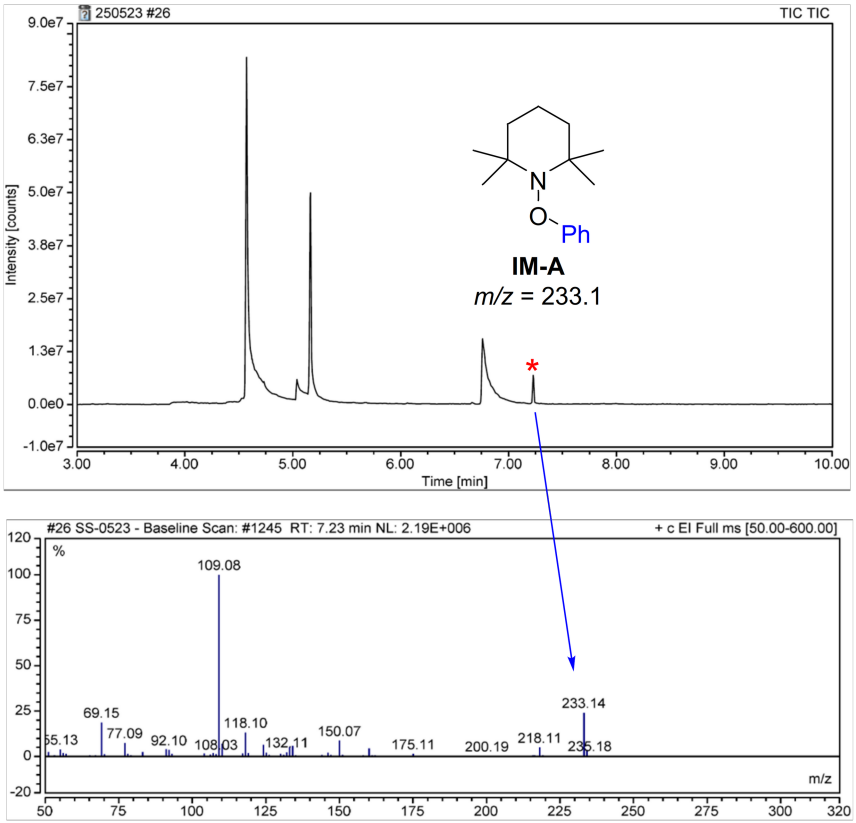
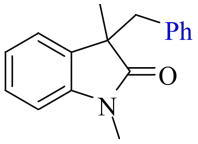


Figure S4

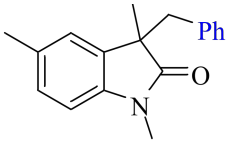
Characterization data



3a

3-Benzyl-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 = 5:1) in 75% yield (37.7 mg). This is a known compound.[S3]

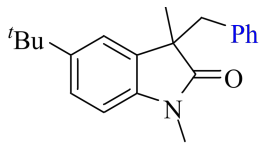
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.07 – 7.01 (m, 4H), 6.86 – 6.83 (m, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 3.02 – 2.98 (m, 4H), 1.47 (s, 3H).



3b

3-Benzyl-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 = 5:1) in 67% yield (35.5 mg). This is a known compound.[S3]

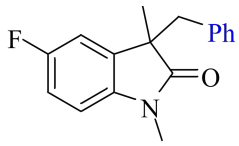
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.04 (m, 3H), 7.00 – 6.97 (m, 1H), 6.94 (s, 1H), 6.86 – 6.83 (m, 2H), 6.50 (d, *J* = 7.8 Hz, 1H), 3.09 (d, *J* = 13.0 Hz, 1H), 3.11 – 2.96 (m, 4H), 2.34 (s, 3H), 1.45 (s, 3H).



3c

3-Benzyl-5-*tert*-butyl-1,3-dimethylindolin-2-one (3c) was prepared as a clear liquid from *N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide **1c** (46.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 72% yield (44.2 mg). This is a known compound.[S3]

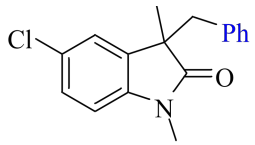
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.12 – 7.05 (m, 3H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.57 (d, *J* = 8.1 Hz, 1H), 3.02 (brs, 5H), 1.46 (s, 3H), 1.30 (s, 9H).



3d

3-Benzyl-5-fluoro-1,3-dimethylindolin-2-one (3d) was prepared as a clear liquid from *N*-(4-fluorophenyl)-*N*-methylmethacrylamide **1d** (38.6 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 61% yield (32.8 mg). This is a known compound.[S3]

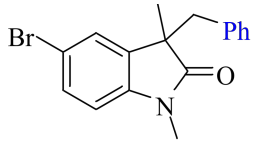
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.06 (m, 3H), 6.90 – 6.85 (m, 4H), 6.52 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 2.99 – 2.96 (m, 4H), 1.47 (s, 3H).



3e

3-Benzyl-5-chloro-1,3-dimethylindolin-2-one (3e) was prepared as a clear liquid from *N*-(4-chlorophenyl)-*N*-methylmethacrylamide **1e** (41.8 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 70% yield (39.9 mg). This is a known compound.[S3]

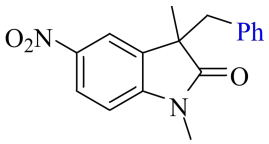
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.87 – 6.84 (m, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 13.1 Hz, 1H), 2.98 (d, *J* = 13.8 Hz, 4H), 1.47 (s, 3H).



3f

3-Benzyl-5-bromo-1,3-dimethylindolin-2-one (3f) was prepared as a clear liquid from *N*-(4-bromophenyl)-*N*-methylmethacrylamide **1f** (50.6 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 65% yield (42.8 mg). This is a known compound.[S3]

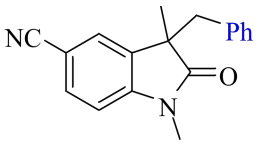
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 5.0, 2.0 Hz, 3H), 6.85 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.48 (d, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 2.99 – 2.96 (m, 4H), 1.47 (s, 3H).



3g

3-Benzyl-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 = 5:1) in 51% yield (30.2 mg). This is a known compound.[S4]

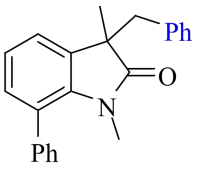
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.06 (d, *J* = 2.3 Hz, 1H), 7.10 – 7.03 (m, 3H), 6.82 – 6.79 (m, 2H), 6.66 (d, *J* = 8.6 Hz, 1H), 3.21 (d, *J* = 13.1 Hz, 1H), 3.06 – 3.03 (m, 4H), 1.54 (s, 3H).



3h

3-Benzyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3h) was prepared as a clear liquid from *N*-(4-cyanophenyl)-*N*-methylmethacrylamide **1h** (40.0 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 58% yield (32.0 mg). This is a known compound.[S5]

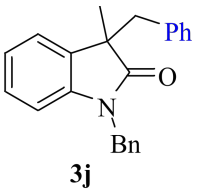
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.81 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 3.15 (d, *J* = 13.1 Hz, 1H), 3.01 – 2.98 (m, 4H), 1.50 (s, 3H).



3i

3-Benzyl-1,3-dimethyl-7-phenylindolin-2-one (3i) was prepared as a clear liquid from *N*-([1,1'-biphenyl]-2-yl)-*N*-methylmethacrylamide **1i** (50.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 45% yield (29.4 mg). This is a known compound.[S5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.13 – 7.04 (m, 5H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.90 – 6.85 (m, 2H), 6.52 – 6.47 (m, 1H), 3.27 (d, *J* = 12.8 Hz, 1H), 3.08 (d, *J* = 12.8 Hz, 1H), 1.63 (s, 3H).

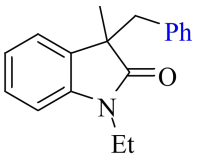


3j

1,3-Dibenzyl-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 = 5:1) in 68% yield (44.5 mg). This is a known compound.[S4]

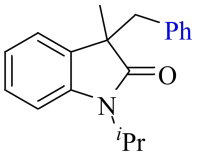
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 1H), 7.16 – 7.10 (m, 4H), 7.08 – 7.04 (m, 4H), 6.89 (dd, *J* = 8.2, 1.3 Hz, 2H), 6.64 (dd, *J* = 7.5, 1.8 Hz, 2H), 6.42 – 6.40 (m, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 3.25 (d, *J* = 13.0 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 1.55 (s, 3H).



3k

3-Benzyl-1-ethyl-3-methylindolin-2-one (3k) was prepared as a clear liquid from *N*-ethyl-*N*-phenylmethacrylamide **1k** (37.8 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 63% yield (33.4 mg). This is a known compound.[S6]

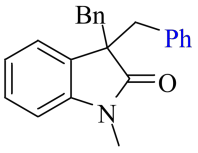
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2H), 7.06 – 7.00 (m, 4H), 6.81 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 3.70 (dq, *J* = 14.5, 7.3 Hz, 1H), 3.36 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.14 (d, *J* = 12.9 Hz, 1H), 3.01 (d, *J* = 12.9 Hz, 1H), 1.48 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H)



3l

3-Benzyl-1-isopropyl-3-methylindolin-2-one (3l) was prepared as a clear liquid from *N*-isopropyl-*N*-phenylmethacrylamide **1l** (40.6 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 70% yield (39.1 mg). This is a known compound.[S5]

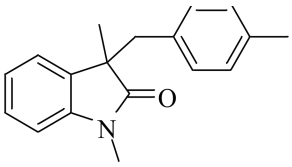
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.15 (td, *J* = 7.8, 1.4 Hz, 1H), 7.06 – 6.98 (m, 4H), 6.79 – 6.76 (m, 3H), 4.43 (hept, *J* = 7.1 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.98 (d, *J* = 12.8 Hz, 1H), 1.48 (s, 3H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H).



3m

3,3-Dibenzyl-1-methylindolin-2-one (3m) was prepared as a clear liquid from 2-benzyl-*N*-methyl-*N*-phenylacrylamide **1m** (50.2 mg, 0.2 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 56% yield (36.6 mg). This is a known compound.[S4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.08 – 6.98 (m, 8H), 6.91 – 6.88 (m, 4H), 6.38 – 6.36 (m, 1H), 3.31 (d, *J* = 13.0 Hz, 2H), 3.15 (d, *J* = 13.0 Hz, 2H), 2.77 (s, 3H).



3n

1,3-Dimethyl-3-(4-methylbenzyl)indolin-2-one (**3n**) was prepared as a clear liquid from *N*-methyl-*N*-phenylmethacrylamide **1a** (35.0 mg, 0.2 mmol) and di-*p*-tolyliodonium trifluoromethanesulfonate **2b** (137.4 mg, 0.3 mmol) according to the General Procedure (eluent: petroleum ether/ethyl acetate = 5:1) in 63% yield (33.4 mg). This is a known compound.[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.7 Hz, 1H), 3.10 – 2.96 (m, 5H), 2.21 (s, 3H), 1.45 (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; https://doi.org/10.1021/jacs.8b12095.

S2. S. Sun, C. Zhou, J.-T. Yu and J. Cheng, *Org. Lett.*, 2019, **21**, 6579; https://doi.org/10.1021/acs.orglett.9b02700.

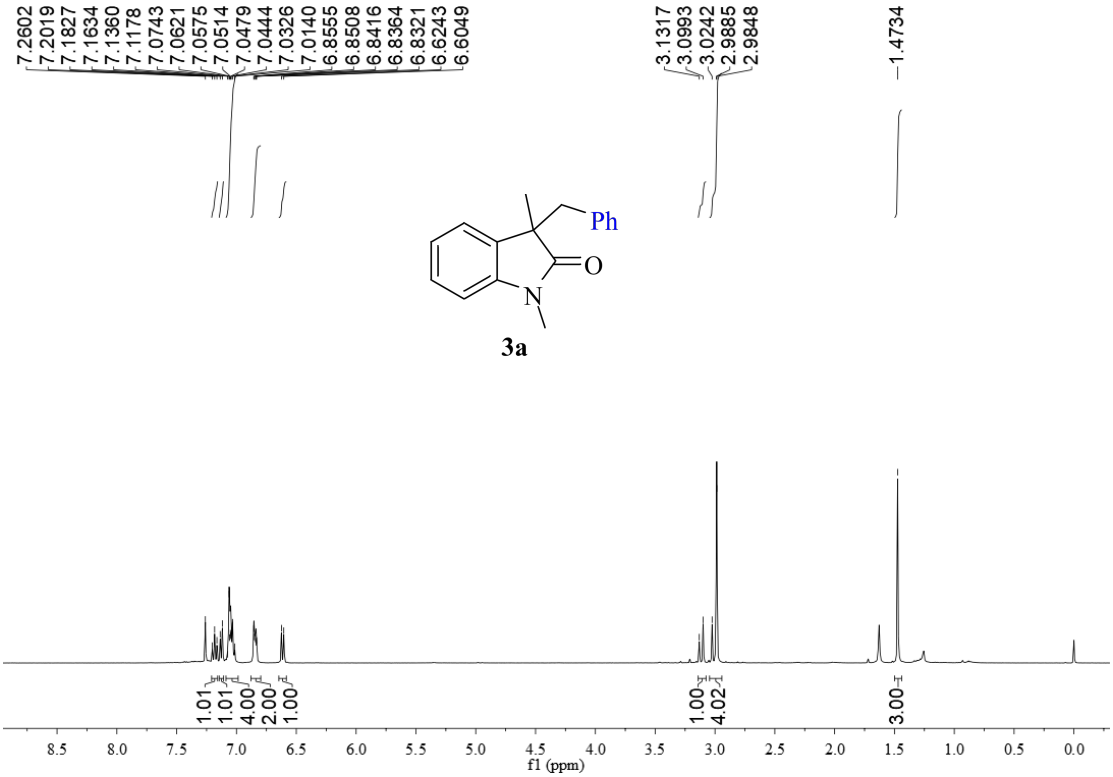
S3. L. Shi, Y. Wang, H. Yang and H. Fu, *Org. Biomol. Chem.*, 2014, **12**, 4070; https://doi.org/10.1039/c4ob00576g.

S4. X. Li, J. Xu, P. Zhang, Y. Gao, J. Wu, G. Tang and Y. Zhao, *Synlett*, 2014, **25**, 2009; https://doi.org/10.1055/s-0034-1378354.

S5. W. Fu, F. Xu, Y. Fu, M. Zhu, J. Yu, C. Xu and D. Zou, *J. Org. Chem.*, 2013, **78**, 12202; https://doi.org/10.1021/jo401894b.

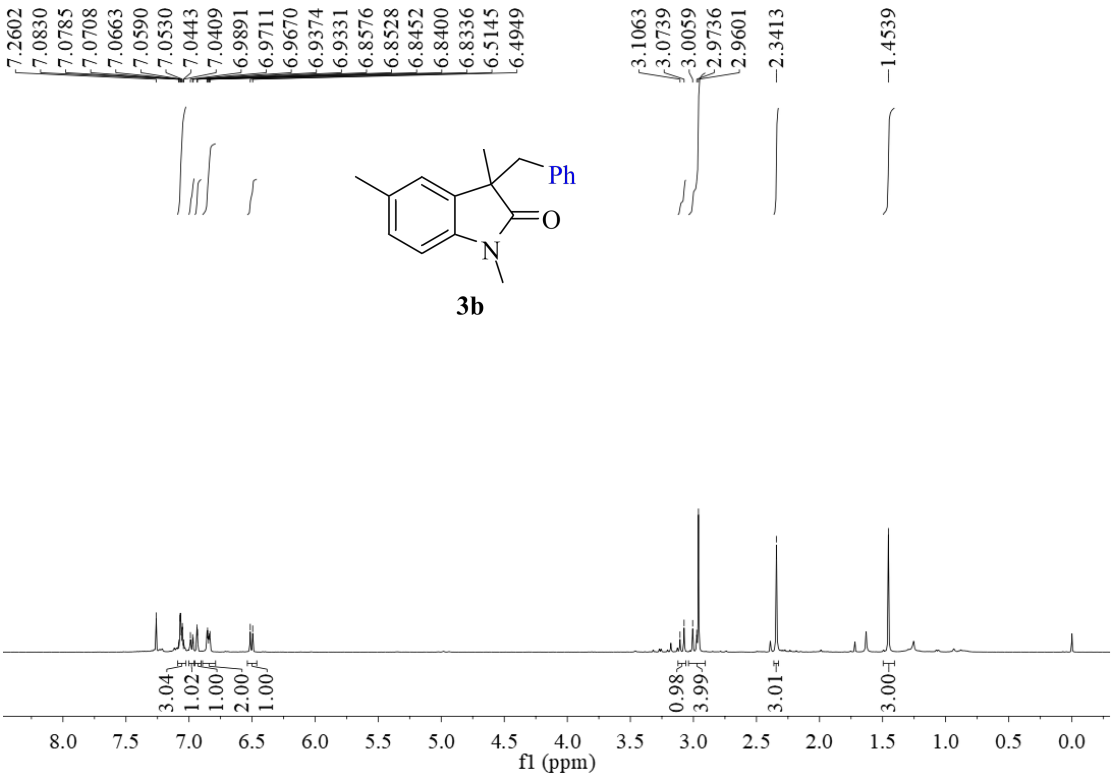
S6. Y. Yu, P. Zheng, Y. Wu and X. Ye, *Org. Biomol. Chem.*, 2018, **16**, 8917; https://doi.org/10.1039/c8ob02485e.

Copies of ^{1}H NMR spectrum



3a

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



3b

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

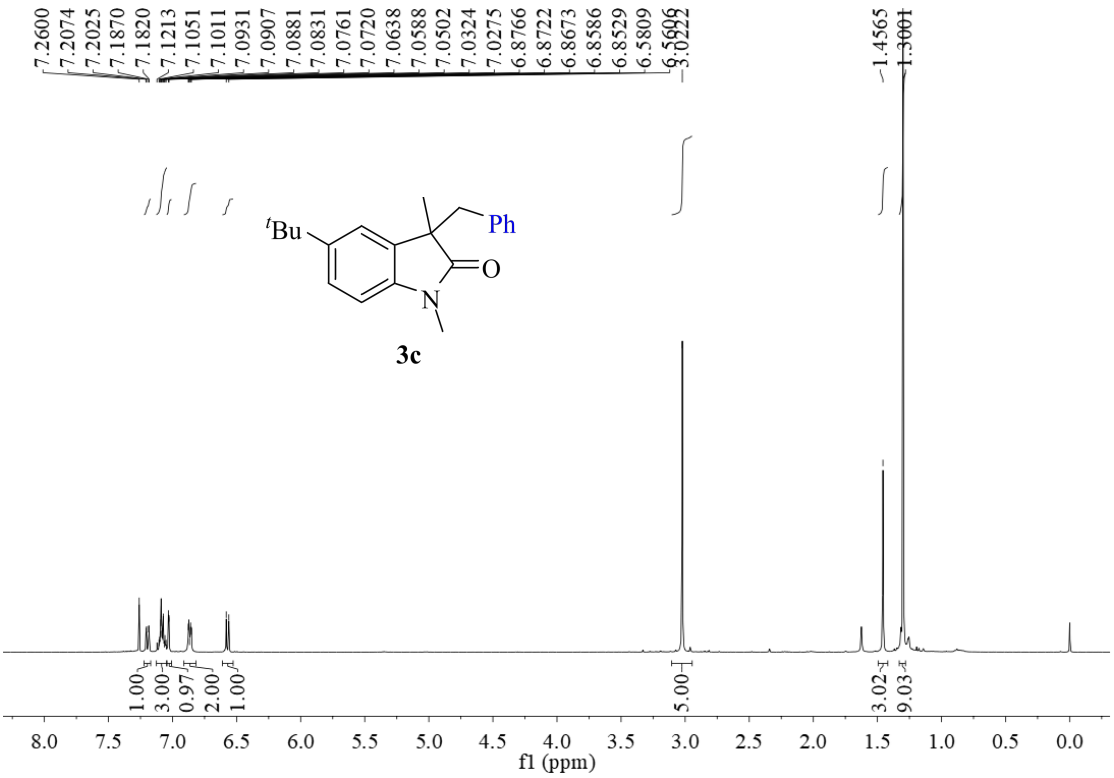


Figure S7. The ^{1}H NMR for compound **3c**

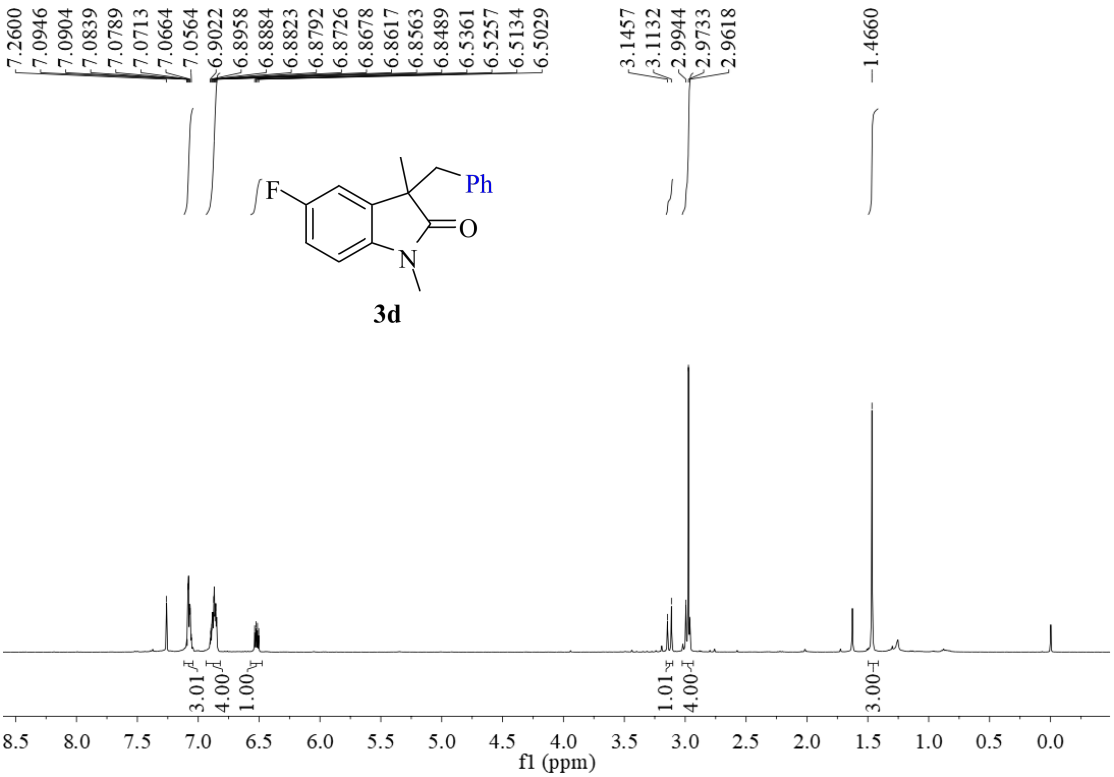


Figure S8. The ^{1}H NMR for compound **3d**

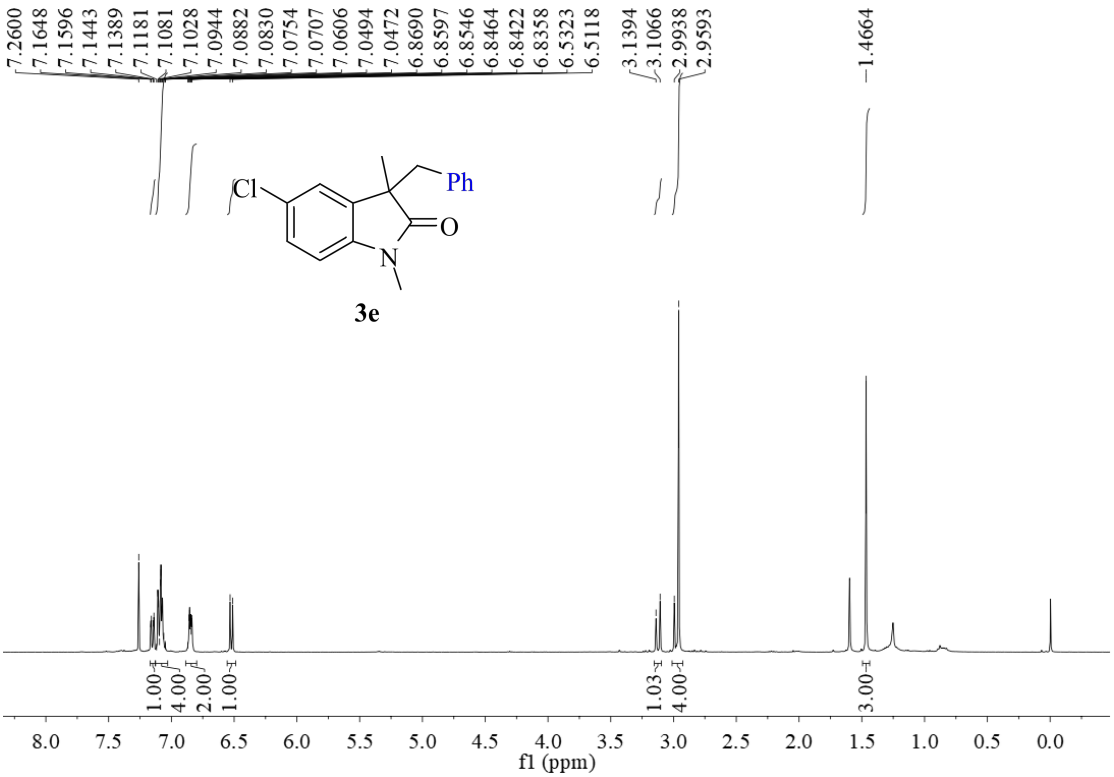


Figure S9. The ^{1}H NMR for compound **3e**

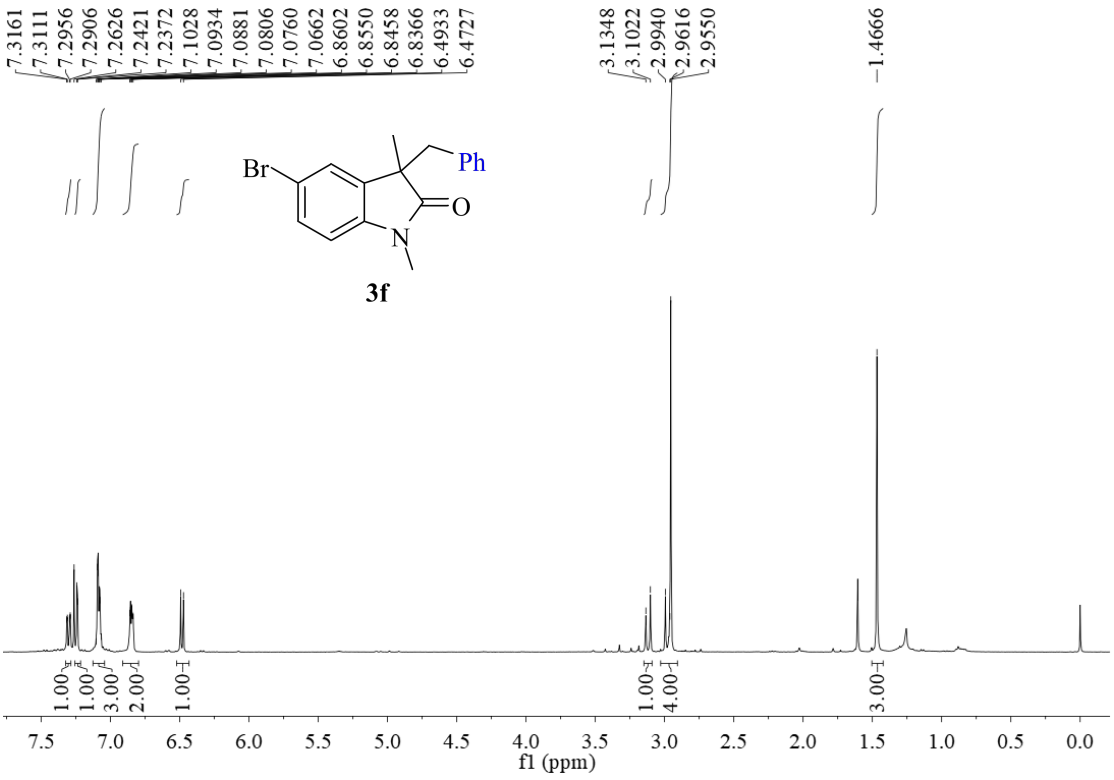


Figure S10. The ^{1}H NMR for compound **3f**

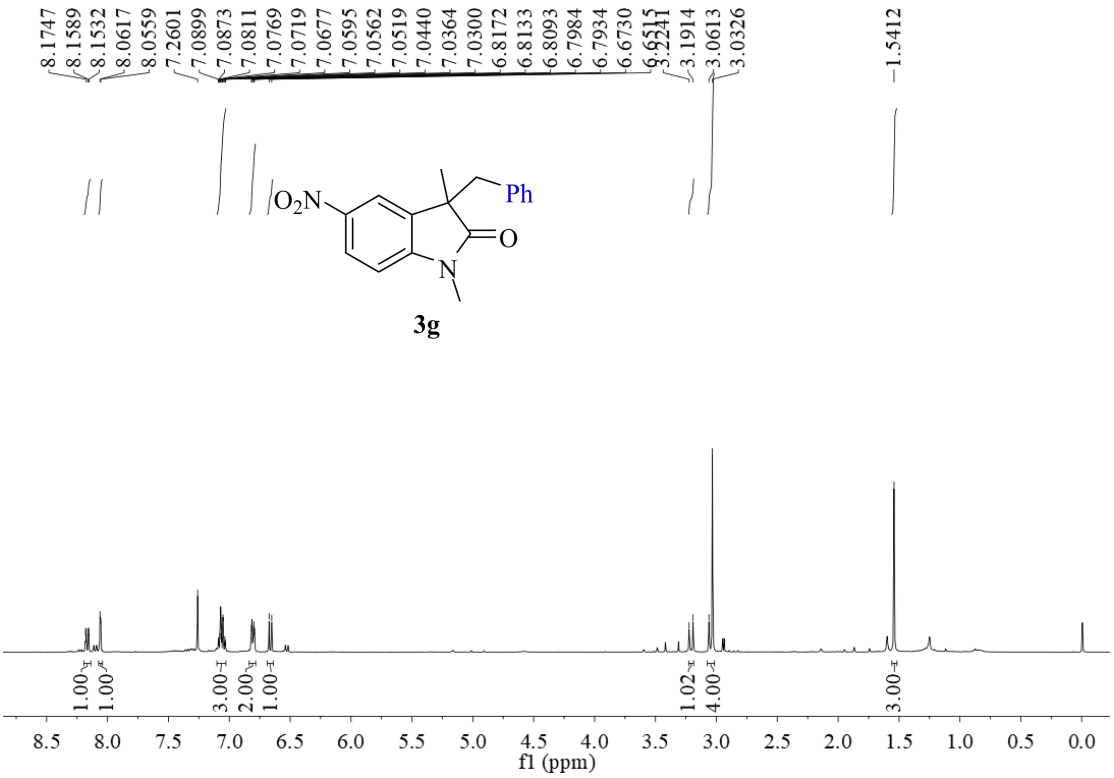


Figure S11. The ^{1}H NMR for compound **3g**

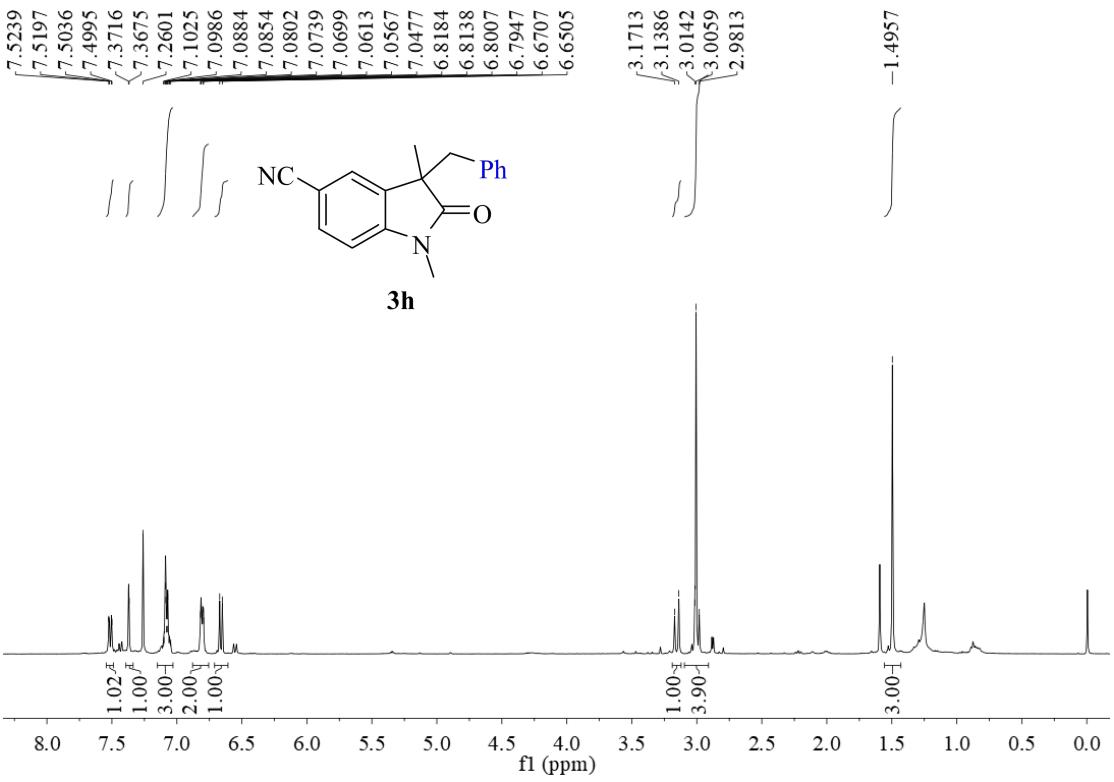


Figure S12. The ^{1}H NMR for compound **3h**

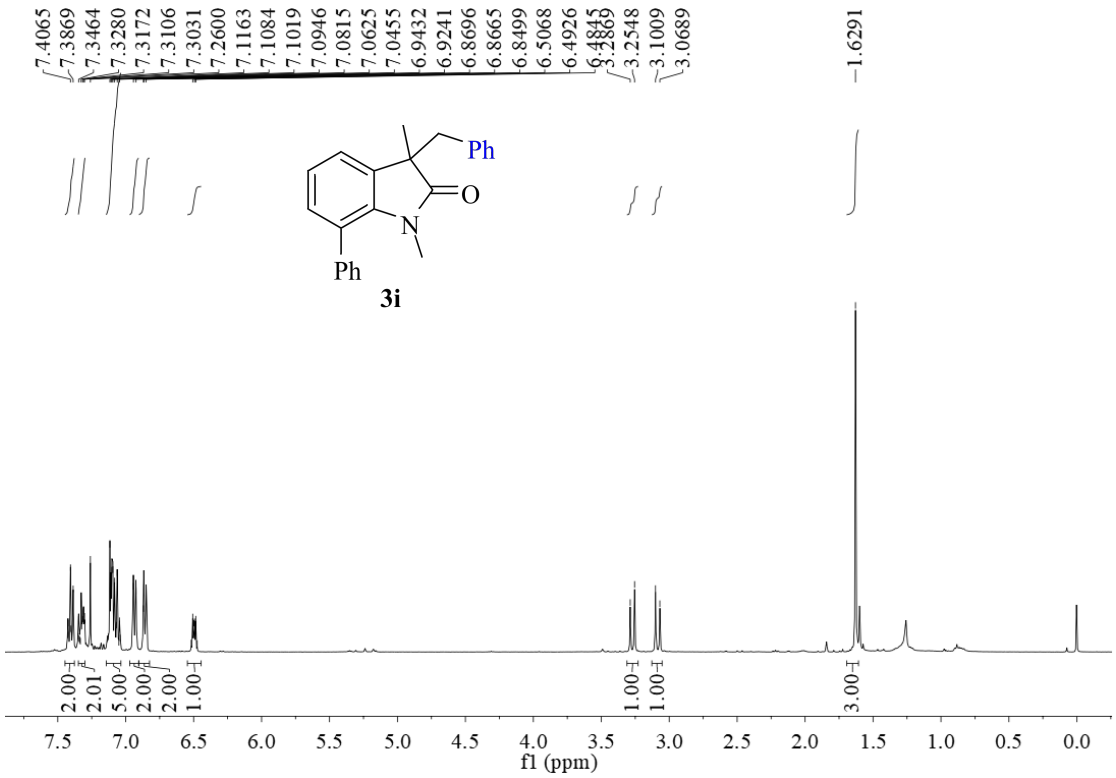


Figure S13. The ^{1}H NMR for compound **3i**

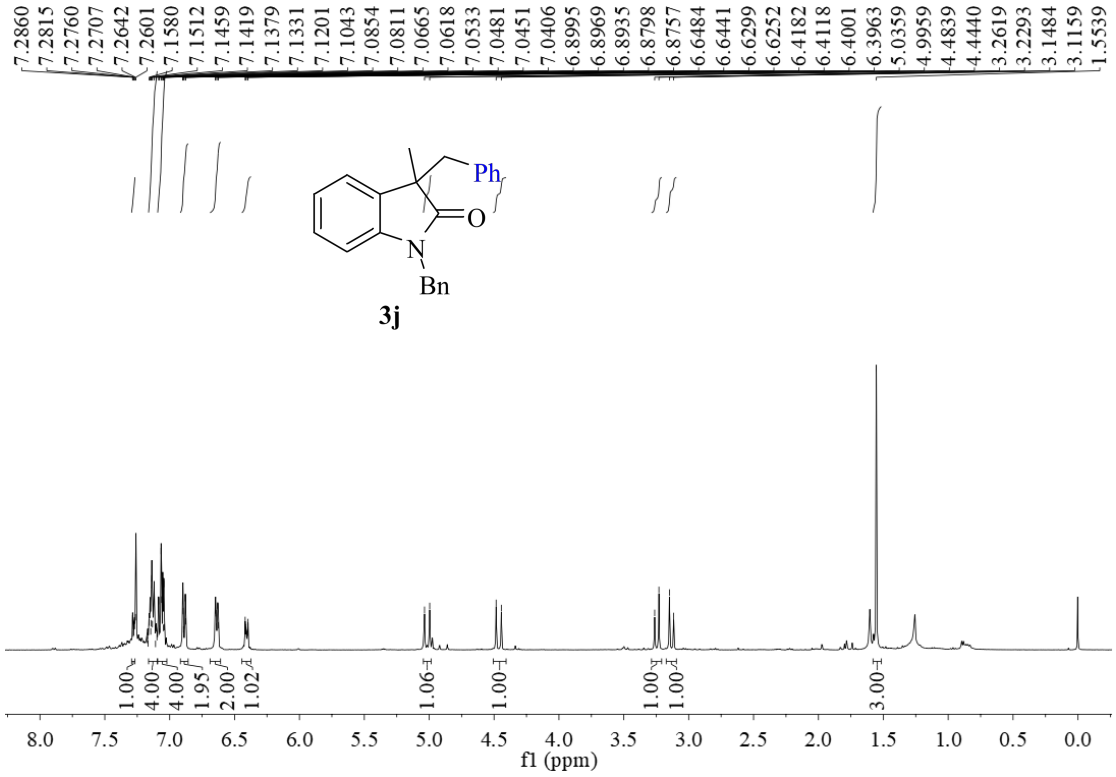


Figure S14. The ^{1}H NMR for compound **3j**

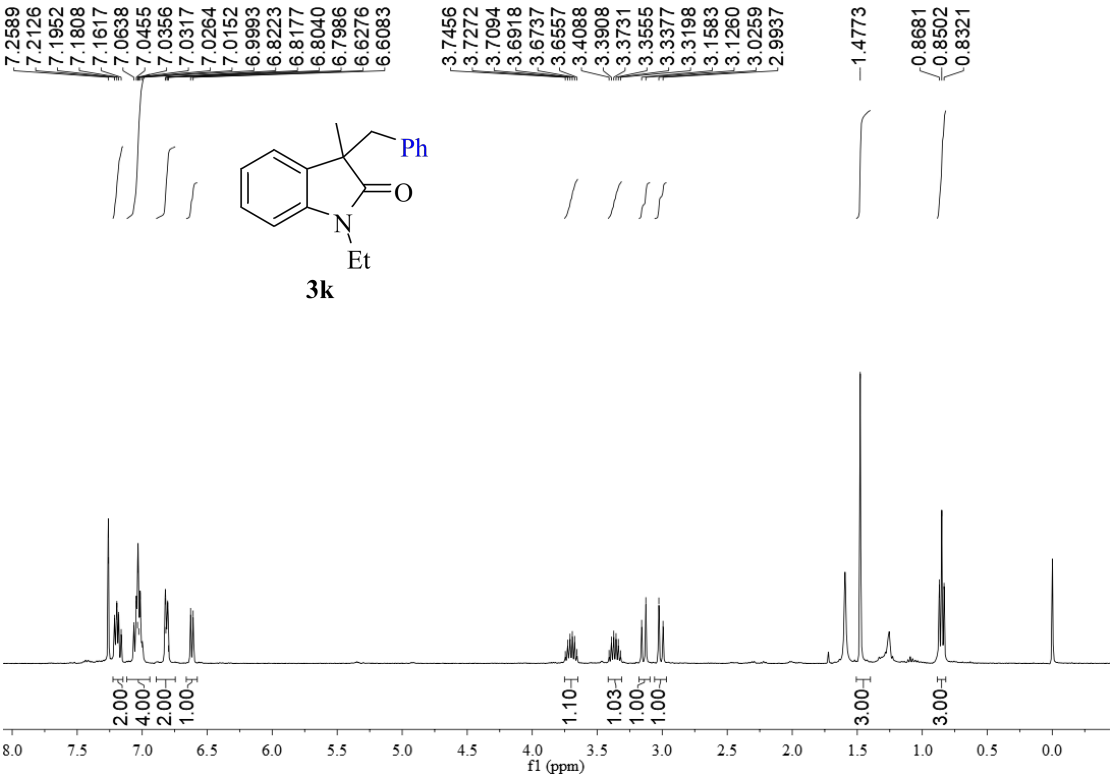


Figure S15. The ^{1}H NMR for compound **3k**

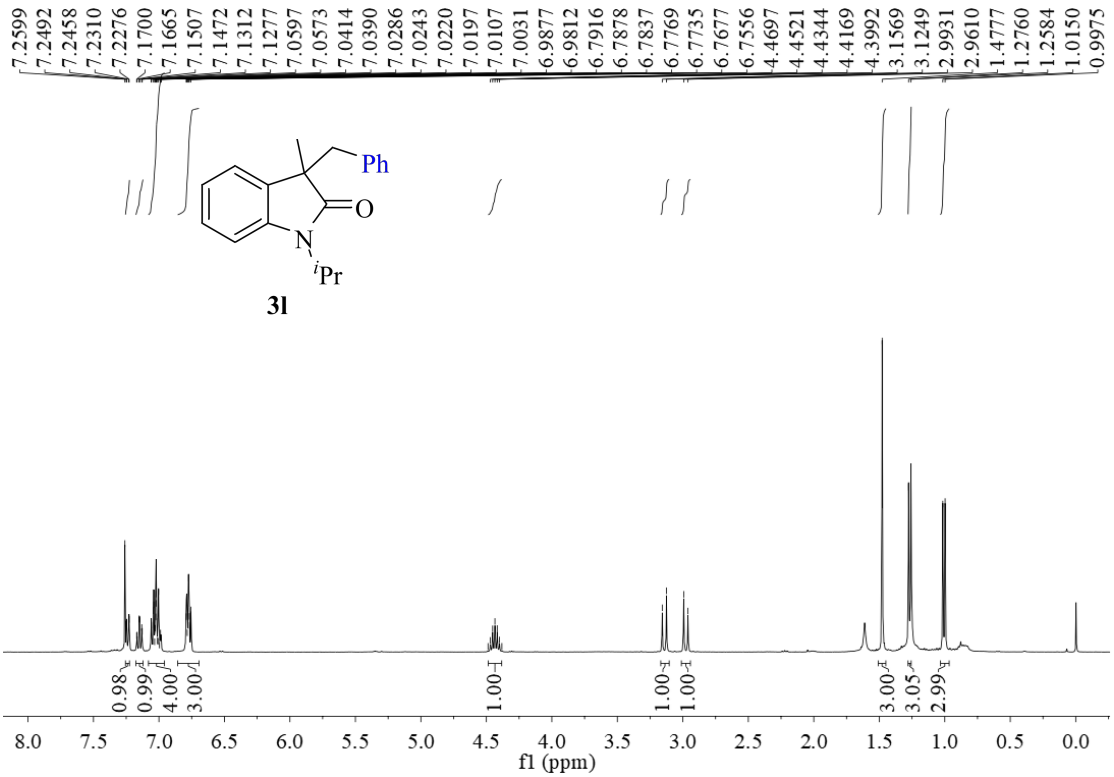


Figure S16. The ^{1}H NMR for compound **3l**

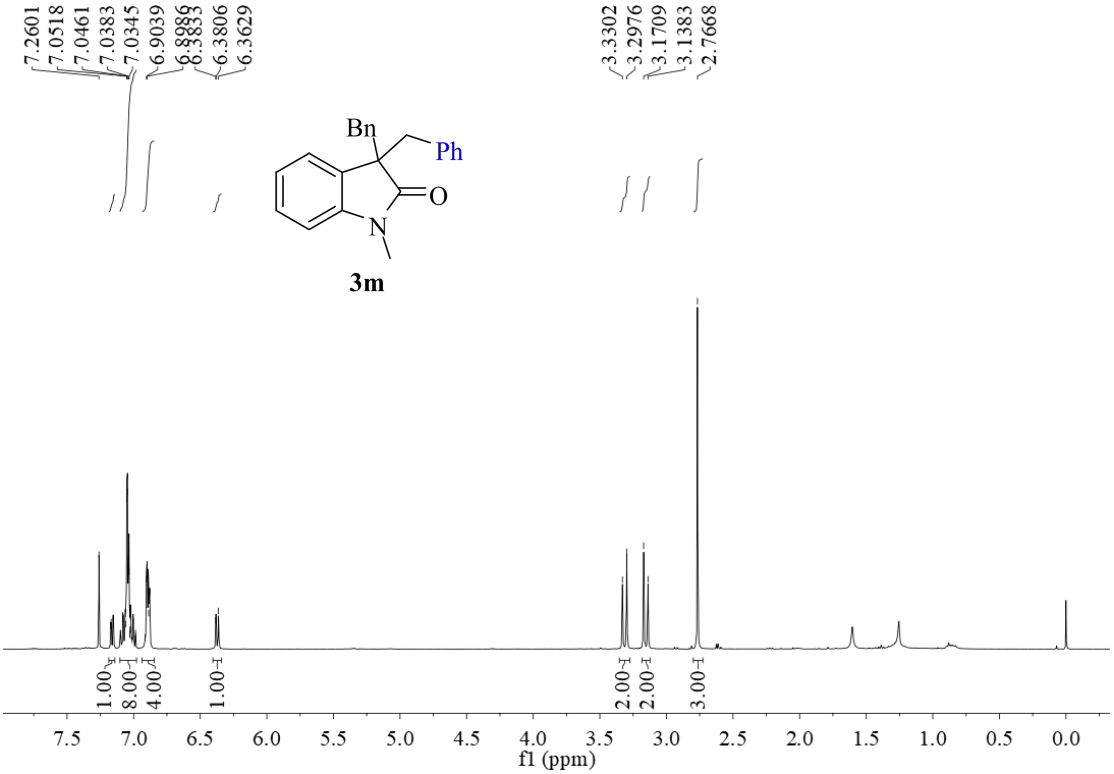


Figure S17. The ^{1}H NMR for compound **3m**

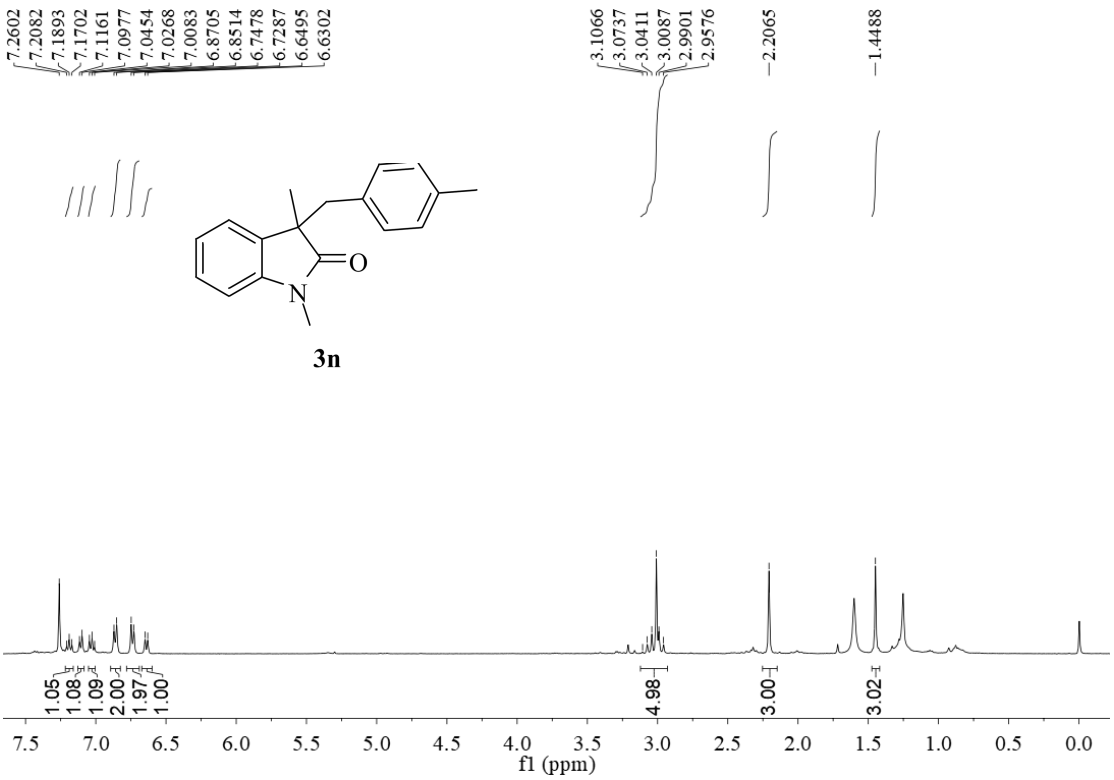


Figure S18. The ^{1}H NMR for compound **3n**