Supporting Information

Construction of multifunctionalized (oxo)indoles via

O-Selective interception of the zwitterionic intermediate with N=O

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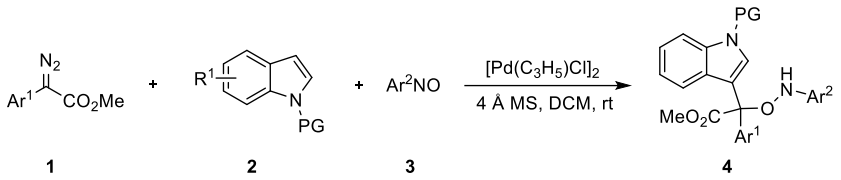
1. General information & materials

All ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Bruker spectrometers in $CDCl_3$; Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). Single crystal X-ray diffraction data were recorded on a Bruker-AXS SMART APEX II single crystal X-ray diffractometer. HRMS (ESI) Mass Spectra were recorded on IonSpec FT-ICR mass spectrometer.

All solvents were purified and dried using standard procedures. 4 Å molecular sieves was dried in a Muffle furnace at 250 ℃ over 5 h. Nitrosoarenes 3 [1], diazo compounds 1 [2] and diazo compounds 6 [3] were prepared according to the literature methods. All reactions and manipulations were carried out under N_2 atmosphere in a flame-dried or oven-dried flask containing a magneticstir bar.

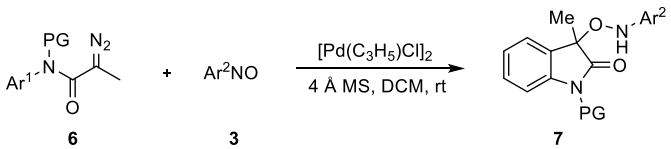
2. Experimental procedures

General procedure for multi-component reaction



1 2 3 4

To a tube charged with 1 mol % $[Pd(C_3H_5)Cl]_2$, 4Å molecular sieves, indole 2 (0.3 mmol) in DCM (1 mL) was added to the tube. Phenyl diazo compound 1 (0.3 mmol) and nitrosobenzene 3 (0.2mmol) in DCM (1mL) was introduced by syringe pump over 1 h at room temperature. After the completion of the pumping, the reaction mixture was filtrated, and the filtrate was evaporated in vacuo to give the crude product. Then the crude product was purified by flash chromatography on silica gel to give the pure product.

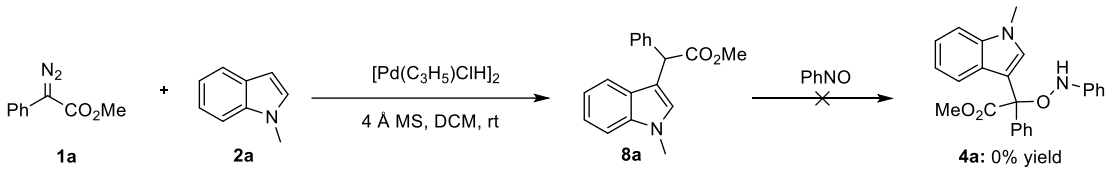


6 3 7

To a tube charged with 1 mol % $[Pd(C_3H_5)Cl]_2$, 4Å molecular sieves, and nitrosobenzene 3 (0.2 mmol) in DCM (1 mL) was added to the tube. Phenyl diazo compound 1 (0.3 mmol) in DCM (1mL) was introduced by syringe pump over 1 h at room temperature. After the completion of the pumping, the reaction mixture was filtrated, and the filtrate was evaporated in vacuo to give the crude product. Then the crude product was purified by flash chromatography on silica gel to give the pure product.

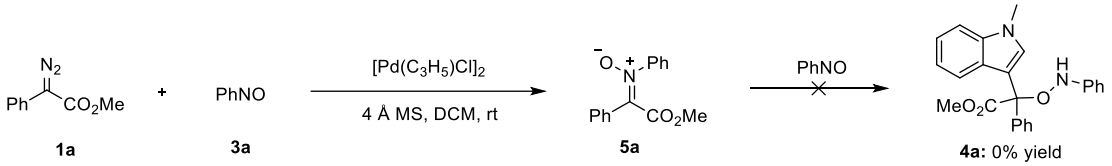
3. Control experiments

Scheme S1. *Control reaction with C-H insertion product*



Scheme S1: To a tube charged with 1 mol % $[Pd(C_3H_5)Cl]_2$, 4Å molecular sieves, insertion 8a (0.3 mmol) and nitrosobenzene 3a (0.2 mmol) in DCM (1 mL) was added to the tube. The reaction mixture was stirred for 3 h at room temperature. Most of the material **8a** remained intact and no desired product was detected.

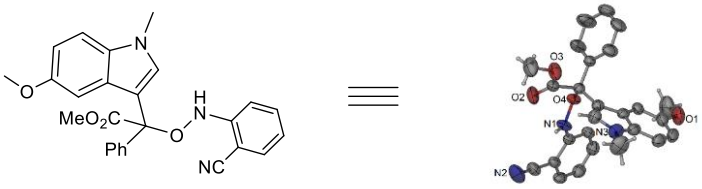
Scheme S2. *Control reaction with N-H insertion product*



Scheme S2: To a tube charged with 1 mol % $[Pd(C_3H_5)Cl]_2$, 4Å molecular sieves, insertion 5a (0.3 mmol) and nitrosobenzene 3a (0.2 mmol) in DCM (1 mL) was added to the tube. The reaction mixture was stirred for 3 h at room temperature. Most of the material **5a** remained intact and no desired product was detected.

4. Single crystal X-ray diffraction data

Single crystal X-ray diffraction data of 4r (CCDC NO. 2456625)



Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=8.9083(7) b=10.1081(8) c=13.4088(10)
alpha=80.343(3) beta=74.758(2) gamma=85.187(2)

Temperature: 296 K

	Calculated	Reported
Volume	1147.42(15)	1147.42(15)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C26 H23 N3 O4	?
Sum formula	C26 H23 N3 O4	C26 H23 N3 O4
Mr	441.47	441.47
Dx,g cm-3	1.278	1.278
Z	2	2
Mu (mm-1)	0.088	0.088
F000	464.0	464.0
F000'	464.21	
h,k,lmax	10,12,15	10,12,15
Nref	4044	4013
Tmin,Tmax	0.975,0.983	0.975,0.984
Tmin'	0.975	

Correction method= # Reported T Limits: Tmin=0.975 Tmax=0.984
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 25.010

R(reflections)= 0.0476(2817) wR2(reflections)= 0.1365(4013)

S = 1.036 Npar= 298

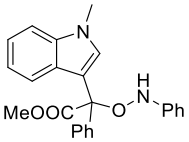
5. Reference

[1] Shu, Z. B.; Ye,Y. X.; Deng, Y. F.; Zhang, Y.; Wang, J. B., *Angew.Chem., Int. Ed.,* 2013, **52**, 10573−10576.

[2] Chan, W. W.; Yeung, S. H.; Zhou, Z. Y.; Chan, A. S. C.; Yu, W. Y. , *Org. Lett.,* 2010, **12**, 604−607.

[3] Ma M., Peng L.L., Li C.K., Zhang X. and Wang J.B., *J. Am. Chem. Soc.,* 2005, **127**, 15016.

6. Analytical data of products

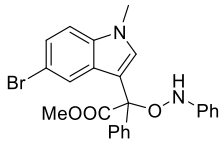


methyl 2-(1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4a: pale yellow oil, 72mg, 93% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.61 (m, 2H), 7.58 (s, 1H), 7.33 – 7.27 (m, 5H), 7.21 – 7.13 (m, 3H), 7.06 (s, 1H), 6.96 – 6.92 (m, 3H), 6.89 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.4, 148.0, 139.3, 137.1, 130.7, 128.5, 128.20 (d, *J* = 3.5 Hz), 128.0, 127.6, 126.4, 122.0, 121.8, 121.4, 119.6, 115.6, 112.2, 109.3, 87.6, 52.5, 33.0.

HRMS-ESI: calculated for $C_{24}H_{23}N_2O_3$ $[M+H]^+$: 387.1630, found 387.1632

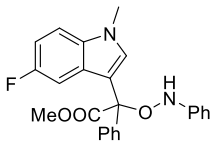


methyl 2-(5-bromo-1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4b: yellow oil, 81mg, 87% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 3H), 7.40 (s, 1H), 7.36 – 7.29 (m, 3H), 7.25 (s, 1H), 7.16 (dd, *J* = 8.4, 3.6 Hz, 3H), 7.08 (s, 1H), 6.91 (dd, *J* = 17.3, 7.9 Hz, 3H), 3.79 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 147.9, 138.8, 135.8, 131.8, 128.6, 128.4, 128.1, 128.0, 127.5, 124.8, 123.7, 122.2, 115.6, 113.2, 112.2, 110.8, 87.4, 52.6, 33.2.

HRMS-ESI: calculated for $C_{24}H_{22}BrN_2O_3$ $[M+H]^+$: 465.0736, found 465.0732



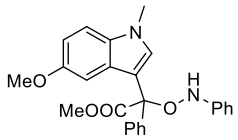
methyl 2-(5-fluoro-1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4c: pale yellow oil, 77mg, 96% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.57 (m, 3H), 7.32 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.21 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.09 (s, 1H), 6.95 – 6.86 (m, 5H), 3.81 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 157.7 (d, *J* = 234.4 Hz), 147.9, 138.9, 133.7, 132.2, 128.5, 128.3 (d, *J* = 4.4 Hz), 128.1, 127.6 (d, *J* = 9.8 Hz), 126.7 (d, *J* = 10.5 Hz), 122.1, 115.6, 112.4 (d, *J* = 4.7 Hz), 110.3 (d, *J* = 26.5 Hz), 110.0 (d, *J* = 9.8 Hz), 106.3 (d, *J* = 24.4 Hz), 87.4,

52.6, 33.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -124.1 – -124.3 (m, 1F).

HRMS-ESI: calculated for $C_{24}H_{22}FN_2O_3$ $[M+H]^+$: 405.1536, found 405.1534

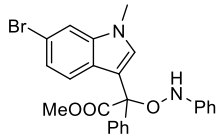


methyl 2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4d: yellow oil, 78mg, 94% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H), 7.51 (s, 1H), 7.40 – 7.28 (m, 3H), 7.23 – 7.12 (m, 3H), 7.08 (s, 1H), 6.98 – 6.92 (m, 2H), 6.92 – 6.87 (m, 1H), 6.83 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.67 (d, *J* = 2.5 Hz, 1H), 3.77 (d, *J* = 11.3 Hz, 6H), 3.57 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.4, 153.9, 148.1, 139.2, 132.5, 131.2, 128.5, 128.2, 128.0, 127.6, 126.8, 122.0, 115.7, 112.0, 111.7, 110.0, 103.1, 87.6, 55.7, 52.5, 33.2.

HRMS-ESI: calculated for $C_{25}H_{25}N_2O_4$ $[M+H]^+$: 417.1736, found 417.1733

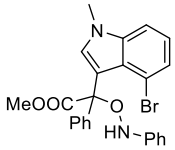


methyl 2-(6-bromo-1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4e: yellow oil, 80mg, 84% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 2H), 7.54 (s, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.18 – 7.12 (m, 2H), 7.12 – 7.06 (m, 2H), 7.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.93 – 6.87 (m, 3H), 3.78 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.1, 147.9, 139.0, 138.0, 131.3, 128.6, 128.3, 128.0, 127.5, 125.3, 122.9, 122.6, 122.2, 115.6, 115.6, 112.8, 112.4, 87.4, 52.6, 33.1.

HRMS-ESI: calculated for $C_{24}H_{22}BrN_2O_3$ $[M+H]^+$: 465.0736, found 465.0734



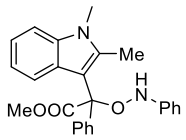
methyl 2-(4-bromo-1-methyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4f: yellow oil, 72mg, 78% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 3H), 7.36 – 7.29 (m, 3H), 7.27 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 7.08 (s, 1H), 6.96 – 6.86 (m, 3H), 3.80 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 147.9, 138.9, 135.5, 131.9, 128.6, 128.4, 128.1, 127.5, 127.3,

125.5, 122.2 , 120.7, 115.6, 112.2, 110.3, 87.4, 52.6, 33.2.

HRMS-ESI: calculated for $C_{24}H_{22}BrN_2O_3$ $[M+H]^+$: 465.0736, found 465.0733

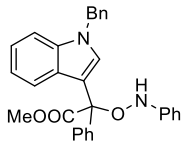


methyl 2-(1,2-dimethyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4g: yellow oil, 72mg, 90% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.42 (s, 1H), 7.34 – 7.29 (m, 3H), 7.24 – 7.20 (m, 1H), 7.12 – 7.07 (m, 1H), 7.06 – 7.01 (m, 2H), 6.96 – 6.93 (m, 1H), 6.90 – 6.85 (m, 1H), 6.82 – 6.77 (m, 1H), 6.75 – 6.70 (m, 2H), 3.76 (s, 3H), 3.63 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.9, 148.4, 139.7, 137.3, 136.4, 128.6, 128.4, 128.1, 127.8, 127.0, 121.6, 121.1, 120.6, 119.3, 115.2, 109.4, 108.6, 88.0, 52.6, 29.5, 12.6.

HRMS-ESI: calculated for $C_{25}H_{25}N_2O_3$ $[M+H]^+$: 401.1787, found 401.1782

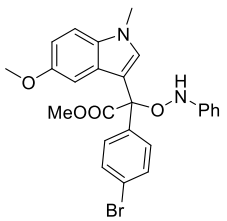


methyl 2-(1-benzyl-1H-indol-3-yl)-2-phenyl-2-((phenylamino)oxy)acetate

4h: yellow oil, 72mg, 78% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 3H), 7.35 – 7.30 (m, 3H), 7.26 – 7.23 (m, 4H), 7.23 – 7.21 (m, 1H), 7.15 – 7.09 (m, 4H), 7.09 – 7.04 (m, 2H), 6.95 – 6.90 (m, 1H), 6.90 – 6.84 (m, 3H), 5.35 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.3, 148.1, 139.2, 137.2, 136.7, 130.7, 128.8, 128.5, 128.2, 128.0, 127.6, 126.8, 126.6, 121.9, 121.5, 119.8, 115.4, 112.8, 109.9, 87.6, 52.6, 50.3.

HRMS-ESI: calculated for $C_{30}H_{27}N_2O_3$ $[M+H]^+$: 463.1943, found 463.1940



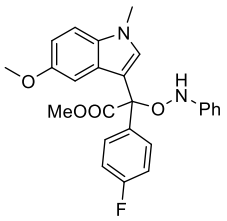
methyl 2-(4-bromophenyl)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-((phenylamino)oxy)acetate

4i: yellow oil, 79mg, 80% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.9 Hz, 3H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.14

(m, 3H), 7.10 (s, 1H), 6.95 – 6.89 (m, 3H), 6.85 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.9, 154.0, 147.9, 138.3, 132.5, 131.1, 129.6, 128.6, 126.6, 122.5, 122.2, 115.7, 112.1, 111.1, 110.1, 103.0, 87.2, 55.7, 52.6, 33.2.

HRMS-ESI: calculated for $C_{25}H_{24}BrN_2O_4$ $[M+H]^+$: 495.0841, found 495.0842

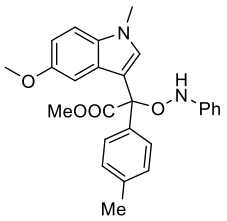


methyl 2-(4-fluorophenyl)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-((phenylamino)oxy)acetate

4j: yellow oil, 80mg, 92% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 2H), 7.50 (s, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.10 (s, 1H), 6.99 (dd, *J* = 9.7, 7.7 Hz, 2H), 6.93 – 6.89 (m, 3H), 6.85 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 162.6 (d, *J* = 247.3 Hz), 154.0, 147.96, 135.0 (d, *J* = 3.3 Hz), 132.5, 131.1, 129.8 (d, *J* = 8.1 Hz), 128.6, 126.6, 122.2, 115.6, 114.9 (d, *J* = 21.5 Hz), 112.1, 111.3, 110.1, 103.1, 87.2, 55.7, 52.6, 33.2. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.8 – -114.2 (m, 1F).

HRMS-ESI: calculated for $C_{25}H_{24}FN_2O_4$ $[M+H]^+$: 435.1642, found 435.1640

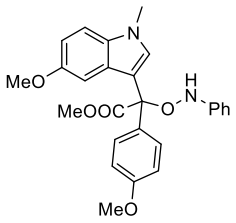


methyl 2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-((phenylamino)oxy)-2-(p-tolyl)acetate

4k: yellow oil, 80mg, 93% yield

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 3H), 7.18 – 7.12 (m, 4H), 7.09 (d, *J* = 10.6 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.90 – 6.86 (m, 1H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.59 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.5, 153.9, 148.2, 137.9, 136.3, 132.5, 131.2, 128.7, 128.5, 127.5, 126.9, 122.0, 115.7, 112.0, 111.8, 110.0, 103.2, 87.5, 55.7, 52.5, 33.2, 21.2.

HRMS-ESI: calculated for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 431.1893, found 431.1891

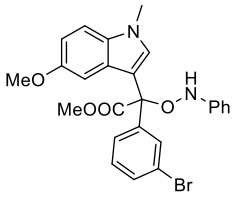


methyl 2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-(4-methoxyphenyl)-2-((phenylamino)oxy)acetate

4l: yellow oil, 78mg, 88% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.48 (s, 1H), 7.22 – 7.12 (m, 3H), 7.07 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.89 – 6.80 (m, 4H), 6.75 – 6.71 (m, 1H), 3.78 (s, 6H), 3.76 (s, 3H), 3.60 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.5, 159.4, 153.9, 148.1, 132.5, 131.1, 129.1, 128.5, 126.8, 122.0, 115.6, 113.8, 113.3, 112.0, 111.7, 110.0, 103.3, 87.3, 55.8, 55.2, 52.4, 33.2.

HRMS-ESI: calculated for $C_{26}H_{27}N_2O_5$ $[M+H]^+$: 447.1842, found 447.1844

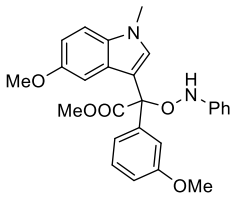


methyl 2-(3-bromophenyl)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-((phenylamino)oxy)acetate

4m: yellow oil, 72mg, 73% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (t, *J* = 1.9 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 – 7.41 (m, 1H), 7.22 – 7.14 (m, 4H), 7.08 (s, 1H), 6.97 – 6.89 (m, 3H), 6.85 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.61 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.8, 154.1, 147.8, 141.6, 132.5, 131.3, 131.2, 130.5, 129.6, 128.6, 126.5, 126.4, 122.3, 122.1, 115.7, 112.2, 111.0, 110.1, 102.9, 87.0, 55.8, 52.7, 33.2.

HRMS-ESI: calculated for $C_{25}H_{24}BrN_2O_4$ $[M+H]^+$: 495.0841, found 495.0845

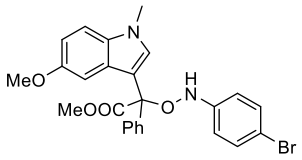


methyl 2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-(3-methoxyphenyl)-2-((phenylamino)oxy)acetate

4n: yellow oil, 79mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.25 – 7.21 (m, 3H), 7.20 – 7.13 (m, 3H), 7.08 (s, 1H), 7.00 – 6.94 (m, 2H), 6.93 – 6.80 (m, 3H), 6.75 (d, *J* = 2.5 Hz, 1H), 3.75 (t, 9H), 3.60 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.3, 159.3, 154.0, 148.1, 140.8, 132.5, 131.2, 129.0, 128.5, 126.8, 122.0, 120.0, 115.6, 113.5, 113.4, 112.0, 111.7, 110.0, 103.1, 87.4, 55.7, 55.3, 52.5, 33.2.

HRMS-ESI: calculated for $C_{26}H_{27}N_2O_5$ $[M+H]^+$: 447.1842, found 447.1839

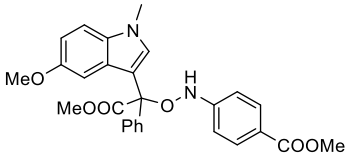


methyl 2-(((4-bromophenyl)amino)oxy)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-phenylacetate

4o: yellow oil, 81mg, 82% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 2H), 7.46 (s, 1H), 7.35 – 7.29 (m, 3H), 7.25 – 7.17 (m, 3H), 7.07 (s, 1H), 6.88 – 6.76 (m, 3H), 6.63 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.58 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 154.0, 147.2, 138.9, 132.5, 131.4, 131.2, 128.3, 128.1, 127.6, 126.7, 117.1, 114.1, 112.0, 111.4, 110.1, 103.0, 87.8, 55.7, 52.6, 33.2.

HRMS-ESI: calculated for $C_{25}H_{24}BrN_2O_4$ $[M+H]^+$: 495.0841, found 495.0842

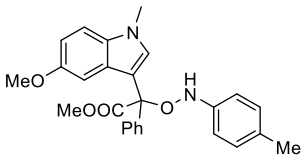


methyl 4-((2-methoxy-1-(5-methoxy-1-methyl-1H-indol-3-yl)-2-oxo-1-phenylethoxy)amino)benzoate

4p: yellow oil, 84mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.67 – 7.58 (m, 2H), 7.44 (s, 1H), 7.37 – 7.28 (m, 4H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 3.59 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.1, 167.0, 154.0, 152.2, 138.6, 132.5, 131.3, 130.6, 128.4, 128.1, 127.6, 126.7, 123.0, 113.9, 112.1, 111.2, 110.1, 103.0, 88.0, 55.7, 52.6, 51.7, 33.2.

HRMS-ESI: calculated for $C_{27}H_{27}N_2O_6$ $[M+H]^+$: 475.1791, found 475.1794

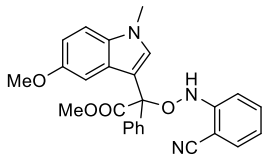


methyl 2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-phenyl-2-((p-tolylamino)oxy)acetate

4q: yellow oil, 67mg, 78% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 2H), 7.52 (s, 1H), 7.34 – 7.27 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.02 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.78 (m, 3H), 6.67 (d, *J* = 2.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.57 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.4, 153.9, 145.6, 139.3, 132.4, 131.7, 131.2, 129.1, 128.1, 128.0, 127.6, 126.8, 116.2, 112.0, 111.8, 110.0, 103.1, 87.5, 55.7, 52.5, 33.2, 20.7.

HRMS-ESI: calculated for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 431.1893, found 431.1891

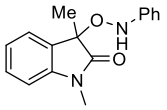


methyl 2-(((2-cyanophenyl)amino)oxy)-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2-phenylacetate

4r: yellow oil, 77mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.68 – 7.59 (m, 2H), 7.39 – 7.29 (m, 5H), 7.28 – 7.23 (m, 1H), 7.17 (dd, *J* = 8.8, 6.9 Hz, 2H), 6.86 – 6.77 (m, 2H), 6.54 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.59 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.6, 154.0, 150.7, 138.2, 133.6, 132.5, 131.8, 131.5, 128.5, 128.1, 127.8, 126.8, 121.0, 116.3, 115.9, 112.1, 110.8, 110.2, 102.9, 96.1, 88.4, 55.7, 52.8, 33.2.

HRMS-ESI: calculated for $C_{26}H_{24}N_3O_4$ $[M+H]^+$: 442.1689, found 442.1685

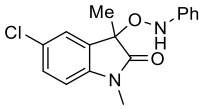


1,3-dimethyl-3-((phenylamino)oxy)indolin-2-one

7a: yellow oil, 47mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 1H), 7.14 (d, *J* = 4.3 Hz, 4H), 7.10 – 7.04 (m, 1H), 7.03 – 6.93 (m, 2H), 6.87 (s, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.07 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.8, 148.2, 143.3, 129.1, 129.0, 127.6, 125.6, 125.3, 123.5, 122.2, 108.0, 70.9, 26.1, 22.3.

HRMS-ESI: calculated for $C_{16}H_{17}N_2O_2$ $[M+H]^+$: 269.1212, found 269.1215

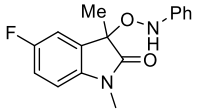


5-chloro-1,3-dimethyl-3-((phenylamino)oxy)indolin-2-one

7b: yellow oil, 57mg, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.08 (m, 6H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.38 – 6.26 (m, 1H), 3.08 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.1, 147.8, 141.9, 130.7, 128.8, 127.8, 127.7, 126.0, 125.7, 123.5, 108.9, 71.0, 26.2, 22.3.

HRMS-ESI: calculated for $C_{16}H_{16}ClN_2O_2$ $[M+H]^+$: 303.0822, found 303.0818

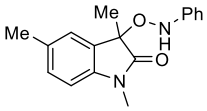


5-fluoro-1,3-dimethyl-3-((phenylamino)oxy)indolin-2-one

7c: yellow oil, 54mg, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.10 (m, 4H), 7.08 (ddd, *J* = 8.4, 5.3, 2.2 Hz, 1H), 6.95 (td, *J* = 8.8, 2.6 Hz, 1H), 6.86 – 6.74 (m, 2H), 6.63 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.06 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.4, 158.9 (d, *J* = 240.8 Hz), 147.87, 139.2, 130.7 (d, *J* = 7.8 Hz), 127.7, 125.8, 123.4, 115.1 (d, *J* = 23.5 Hz), 113.4 (d, *J* = 25.0 Hz), 108.5 (d, *J* = 8.1 Hz), 71.23, 26.24, 22.35. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -118.2 – -122.3 (m, 1F).

HRMS-ESI: calculated for $C_{16}H_{16}FN_2O_2$ $[M+H]^+$: 287.1118, found 287.1116

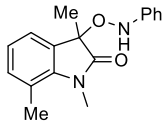


1,3,5-trimethyl-3-((phenylamino)oxy)indolin-2-one

7d: yellow oil, 53mg, 94% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 4H), 7.10 – 7.01 (m, 2H), 6.82 (d, *J* = 12.0 Hz, 2H), 6.60 (d, *J* = 7.9 Hz, 1H), 3.04 (s, 3H), 2.27 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.7, 148.3, 140.9, 131.8, 129.1, 127.5, 126.1, 125.5, 123.5, 115.9, 107.8, 71.0, 26.1, 22.3, 21.1.

HRMS-ESI: calculated for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1368, found 283.1371

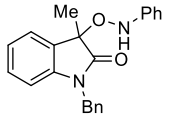


1,3,7-trimethyl-3-((phenylamino)oxy)indolin-2-one

7e: yellow oil, 53mg, 94% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.05 (m, 5H), 7.00 – 6.96 (m, 1H), 6.90 – 6.82 (m, 2H), 6.39 (s, 1H), 3.37 (s, 3H), 2.48 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 177.2, 147.9, 141.4, 133.2, 130.0, 128.1, 124.5, 122.9, 121.7, 119.9, 116.0, 76.2, 29.6, 22.1, 19.1.

HRMS-ESI: calculated for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1368, found 283.1367

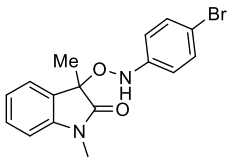


1-benzyl-3-methyl-3-((phenylamino)oxy)indolin-2-one

7f: yellow oil, 62mg, 90% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.05 (m, 10H), 7.01 – 6.93 (m, 3H), 6.83 (s, 1H), 6.56 – 6.49 (m, 1H), 4.99 (d, *J* = 15.9 Hz, 1H), 4.62 (d, *J* = 15.9 Hz, 1H), 1.69 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.7, 148.3, 142.4, 135.3, 129.3, 128.9, 128.7, 127.8, 127.4, 126.9, 125.7, 125.4, 123.7, 122.3, 109.3, 71.0, 43.6, 23.0.

HRMS-ESI: calculated for $C_{22}H_{21}N_2O_2$ $[M+H]^+$: 345.1525, found 345.1524

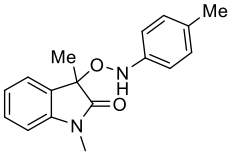


3-(((4-bromophenyl)amino)oxy)-1,3-dimethylindolin-2-one

7g: yellow oil, 62mg, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 3H), 7.07 – 6.96 (m, 4H), 6.91 (s, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.09 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.5, 147.4, 143.2, 130.6, 129.2, 128.8, 125.1, 125.1, 122.4, 118.8, 108.3, 70.9, 26.2, 22.3.

HRMS-ESI: calculated for $C_{16}H_{16}BrN_2O_2$ $[M+H]^+$: 347.0317, found 347.0319

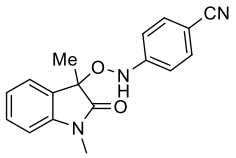


1,3-dimethyl-3-((p-tolylamino)oxy)indolin-2-one

7h: yellow oil, 49mg, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (t, 1H), 7.07 – 7.01 (m, 3H), 6.97 (t, *J* = 7.9 Hz, 3H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 3.11 (d, *J* = 1.8 Hz, 3H), 2.34 – 2.21 (m, 3H), 1.59 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 176.8, 145.5, 143.4, 135.3, 129.2, 128.9, 128.2, 125.3, 123.5, 122.2, 108.0, 70.7, 26.1, 22.3, 20.9.

HRMS-ESI: calculated for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1368, found 283.1372



4-(((1,3-dimethyl-2-oxoindolin-3-yl)oxy)amino)benzonitrile

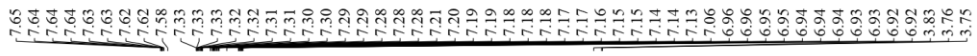
7i: yellow oil, 53mg, 91% yield.

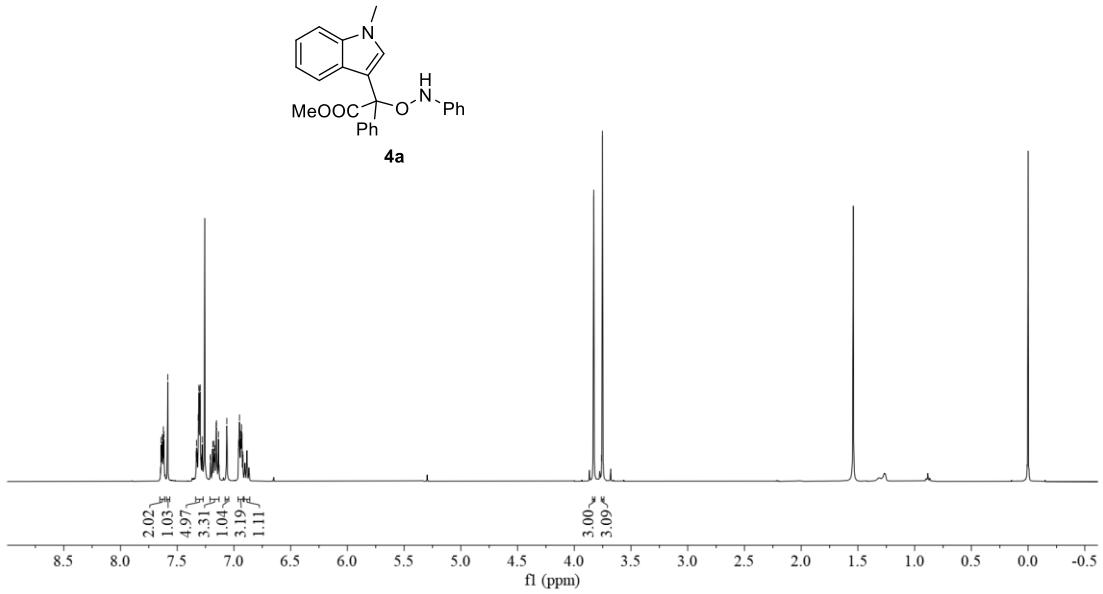
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.33 – 7.24 (m, 1H), 7.20 – 7.13 (m, 2H), 7.08 (s, 1H), 7.06 – 6.98 (m, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 3.12 (s, 3H), 1.66 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.3, 152.1, 142.9, 131.9, 129.4, 128.7, 124.6, 122.8, 122.5, 118.9, 108.5, 108.1, 71.2, 26.3, 22.7.

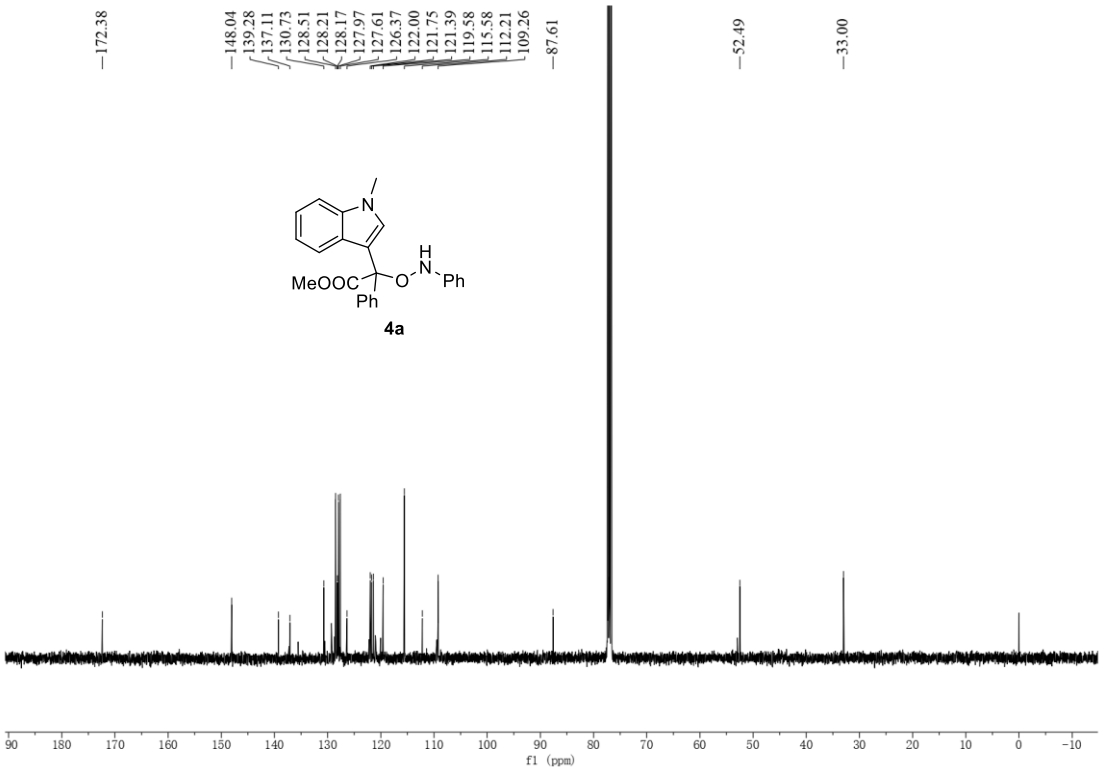
HRMS-ESI: calculated for $C_{17}H_{16}N_3O_2$ $[M+H]^+$: 294.1164, found 294.1161

7. NMR spectra of products

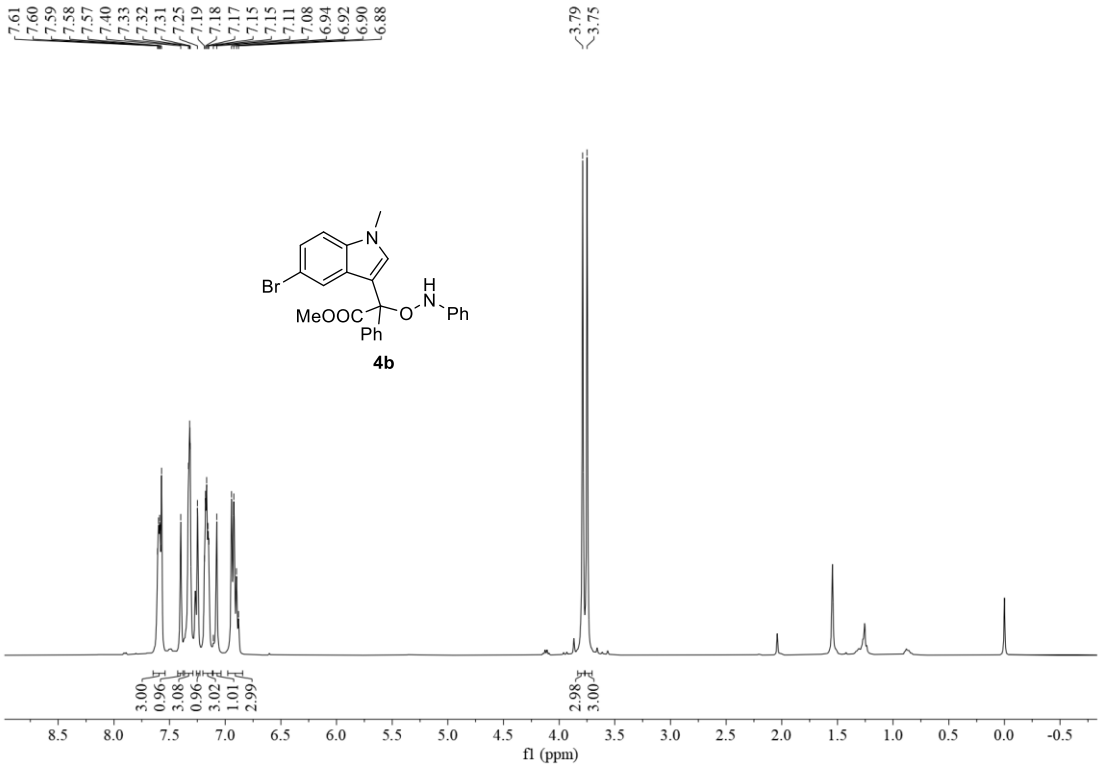
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4a

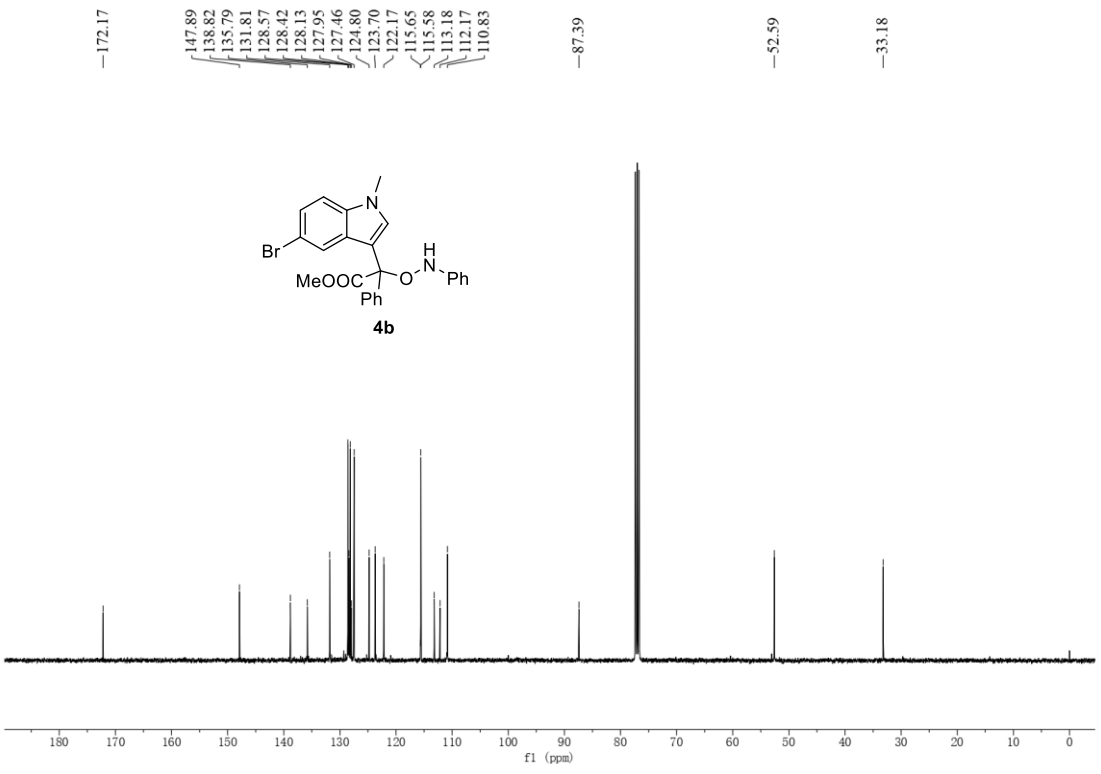




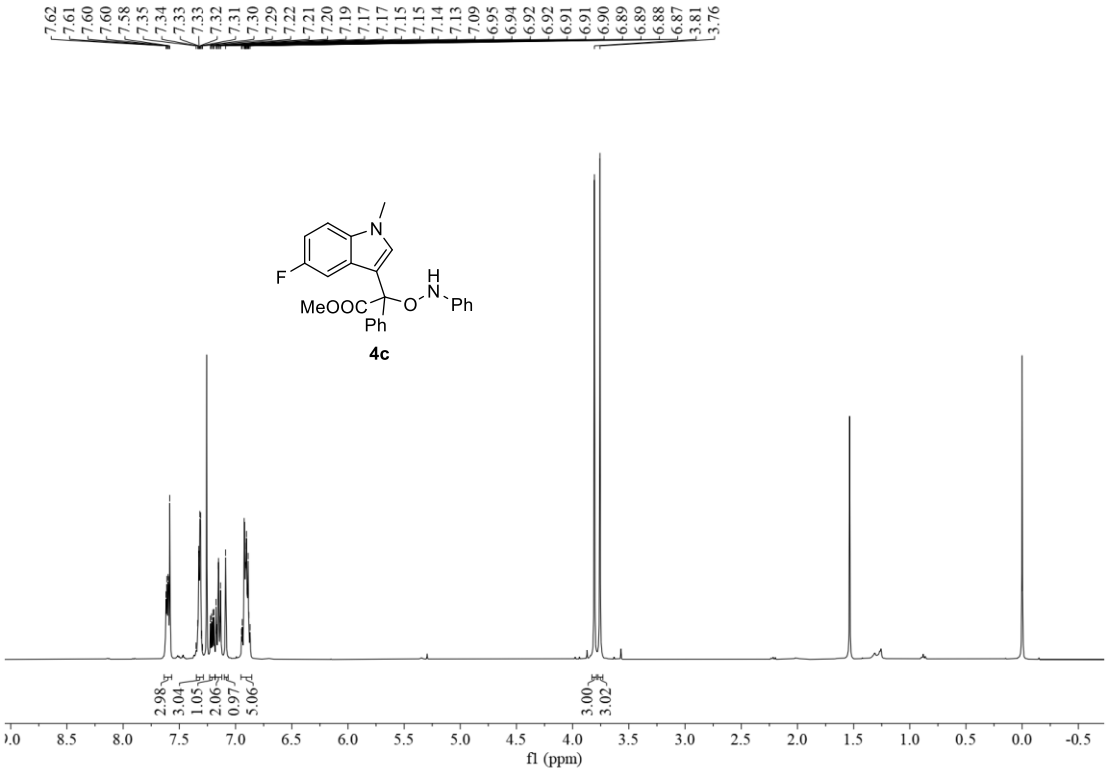


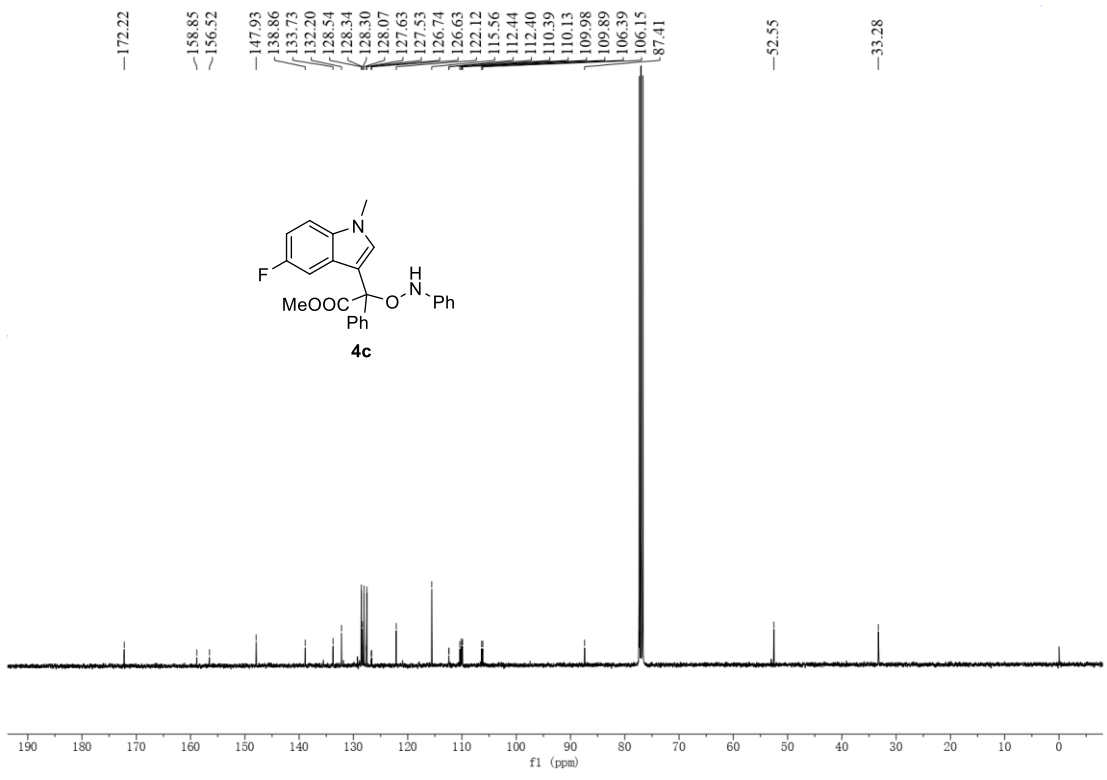
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4b

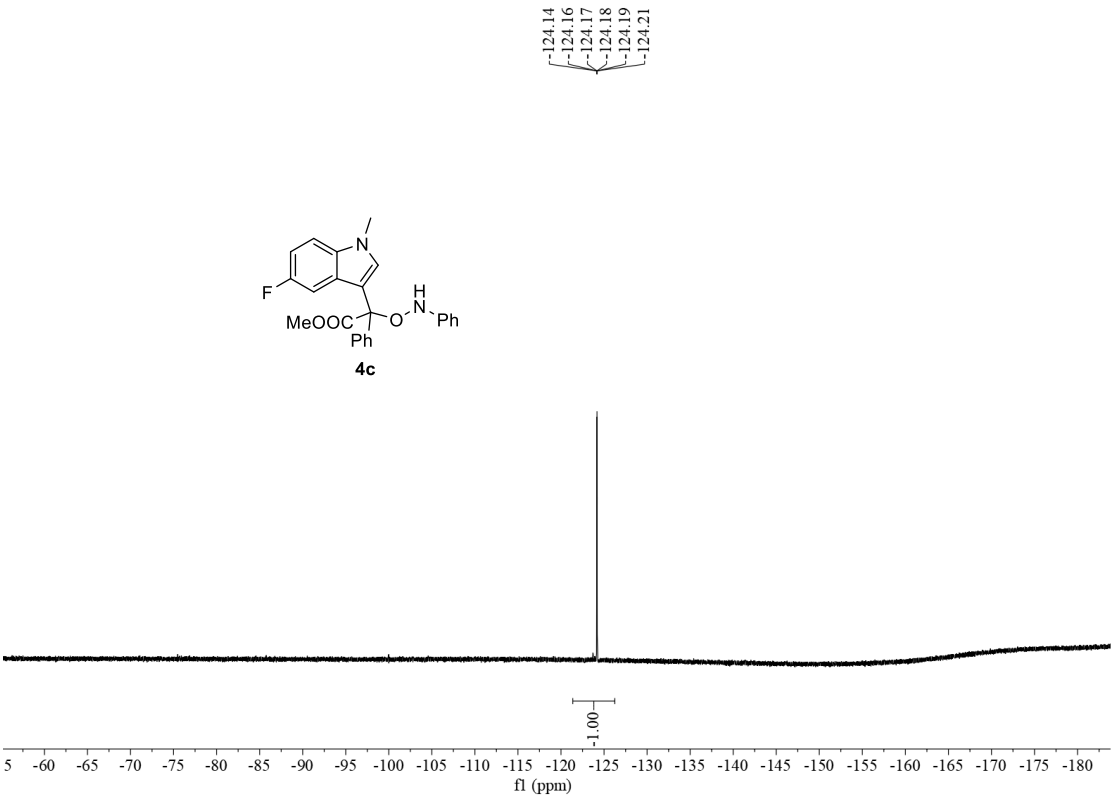




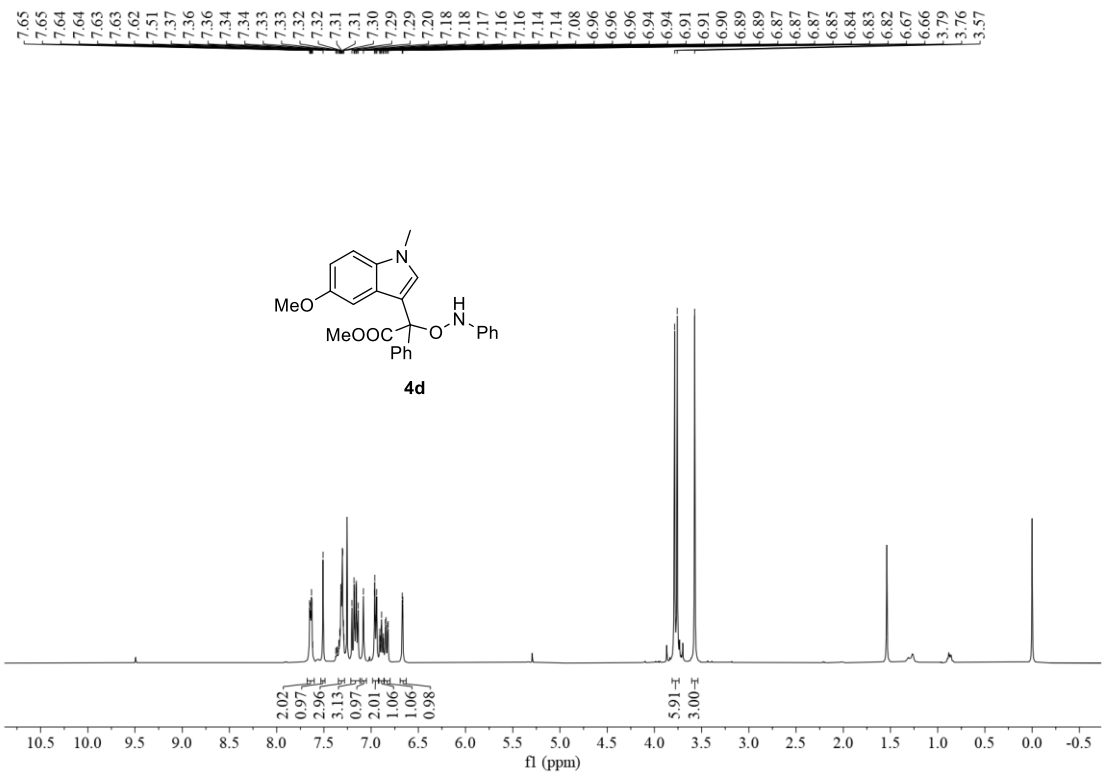
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4c

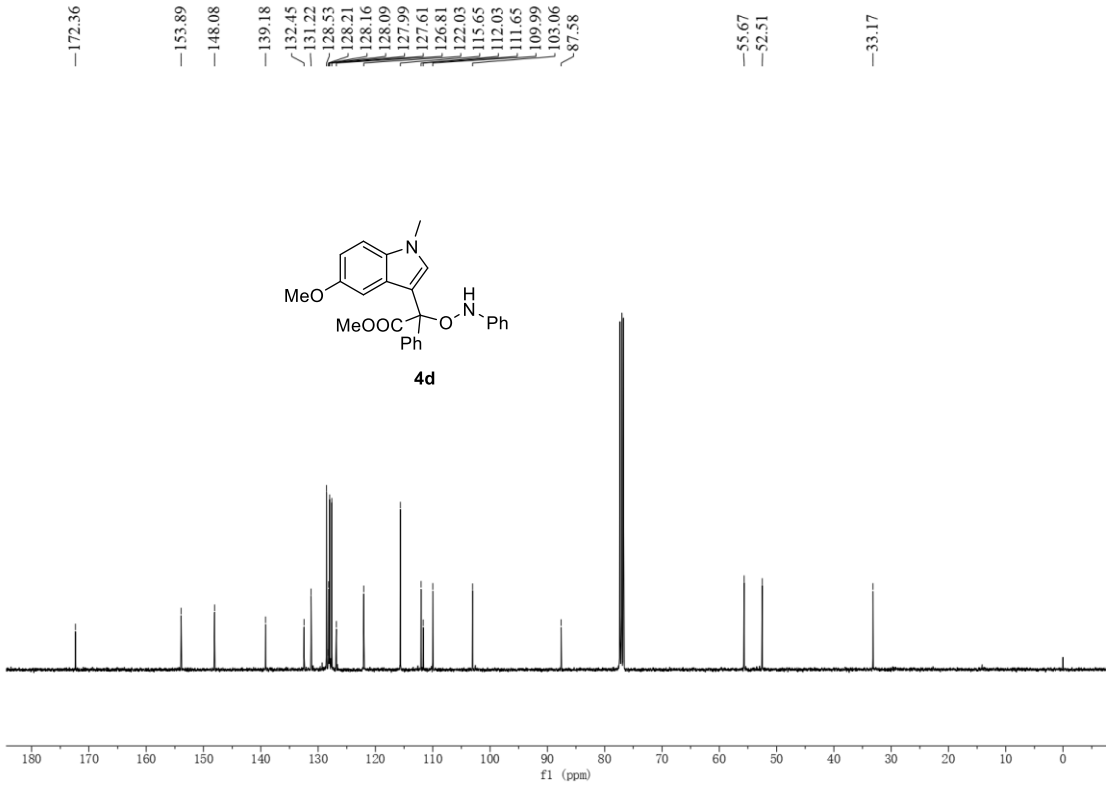




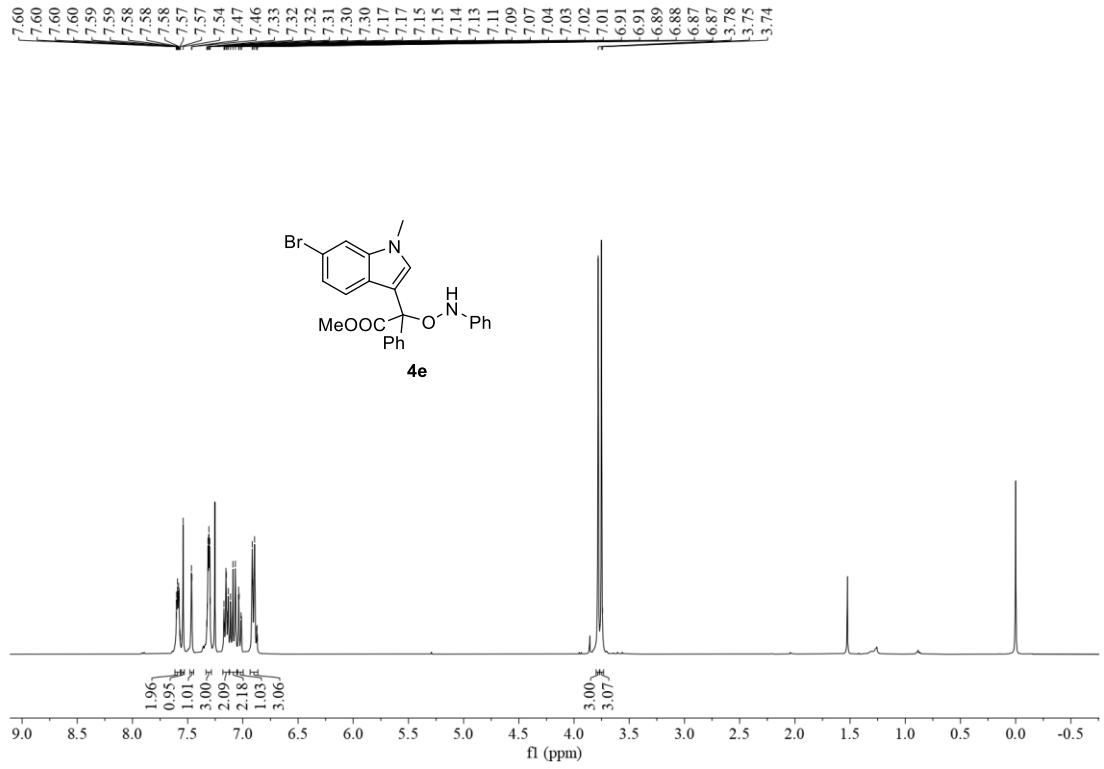


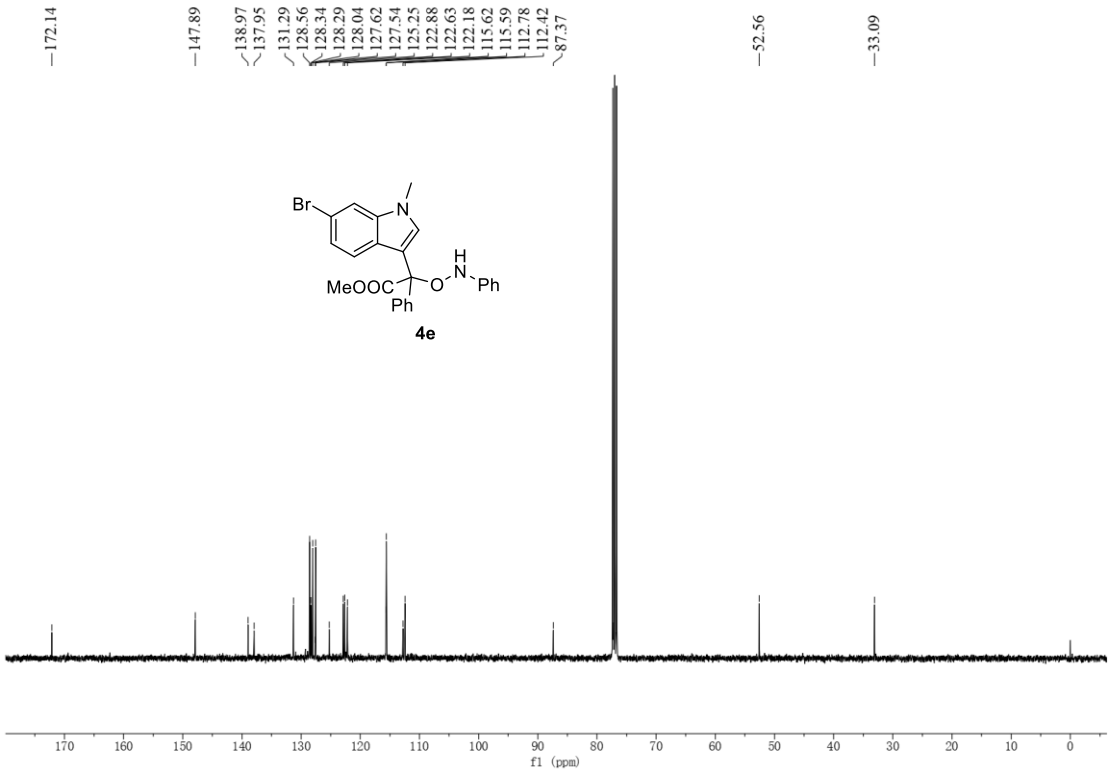
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4d



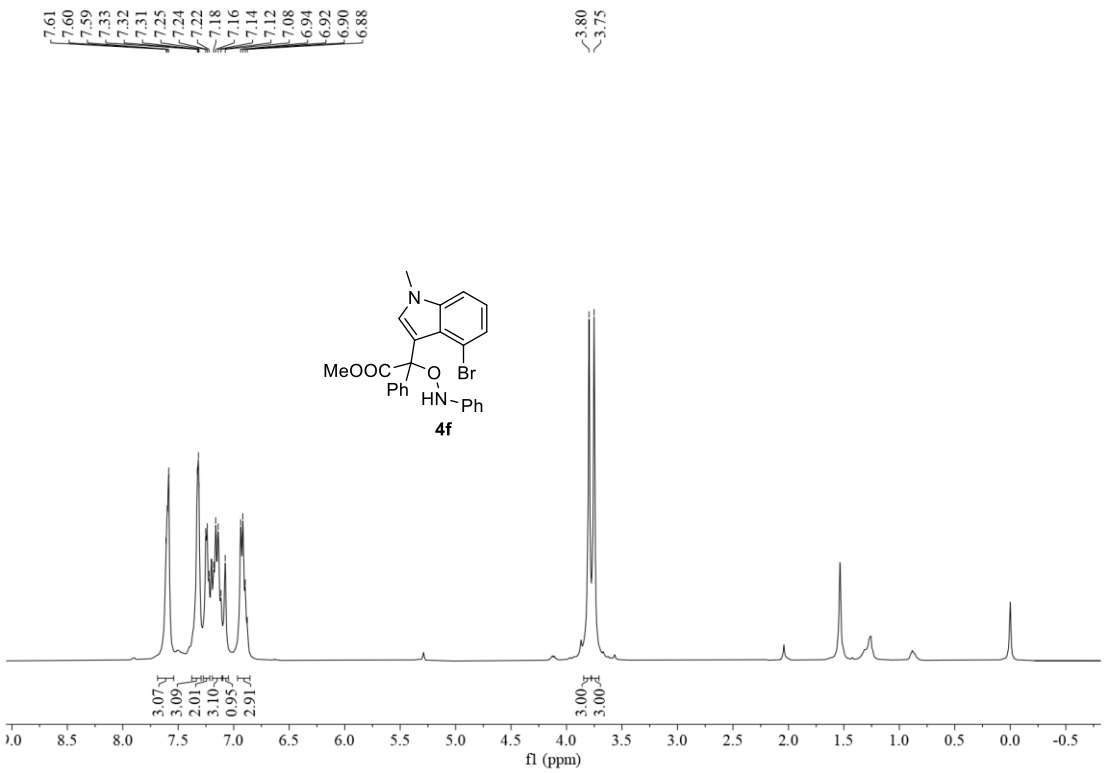


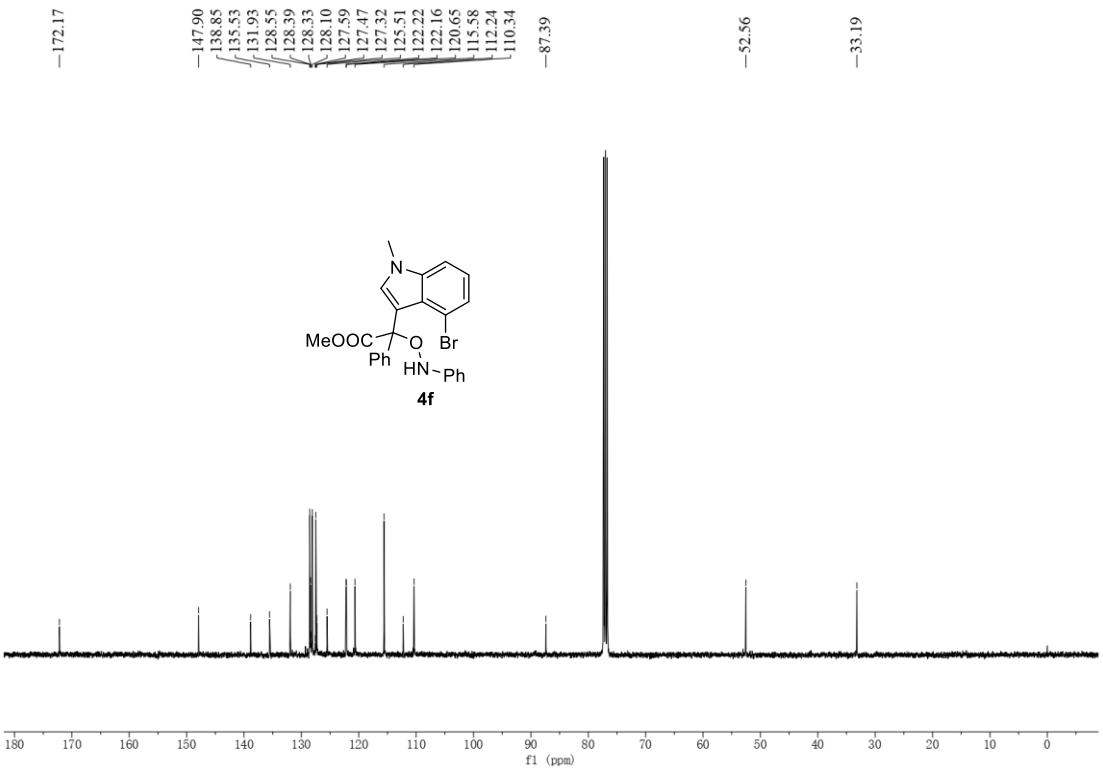
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4e



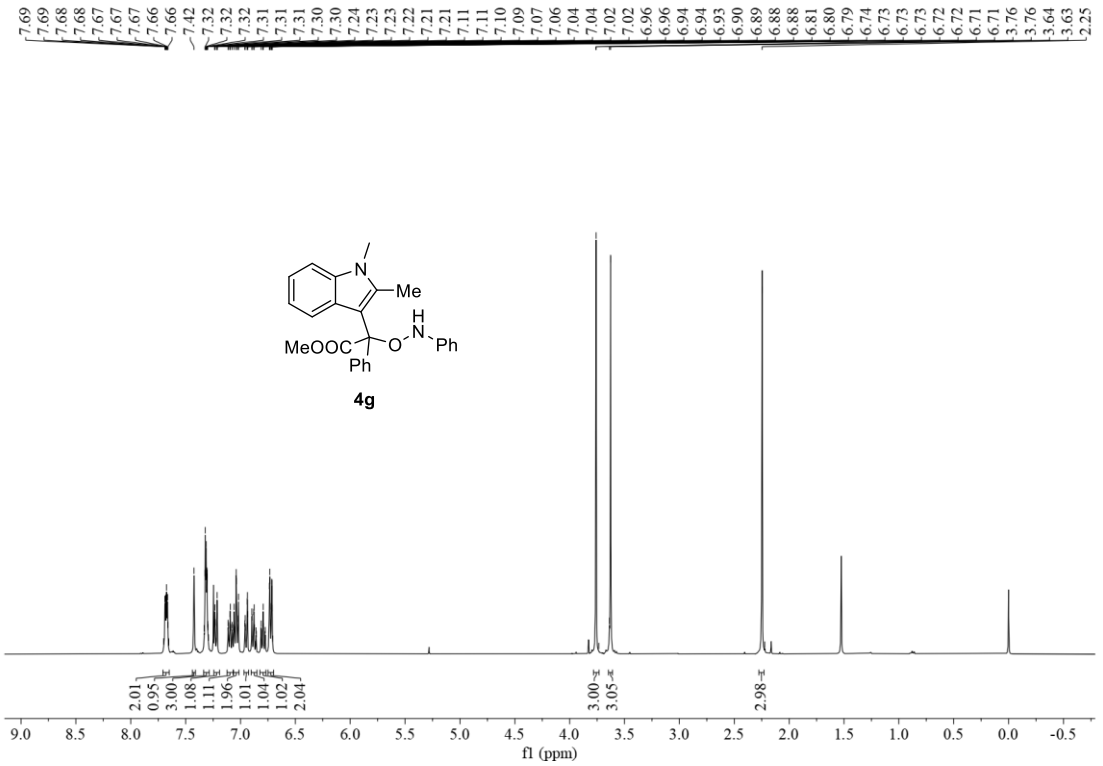


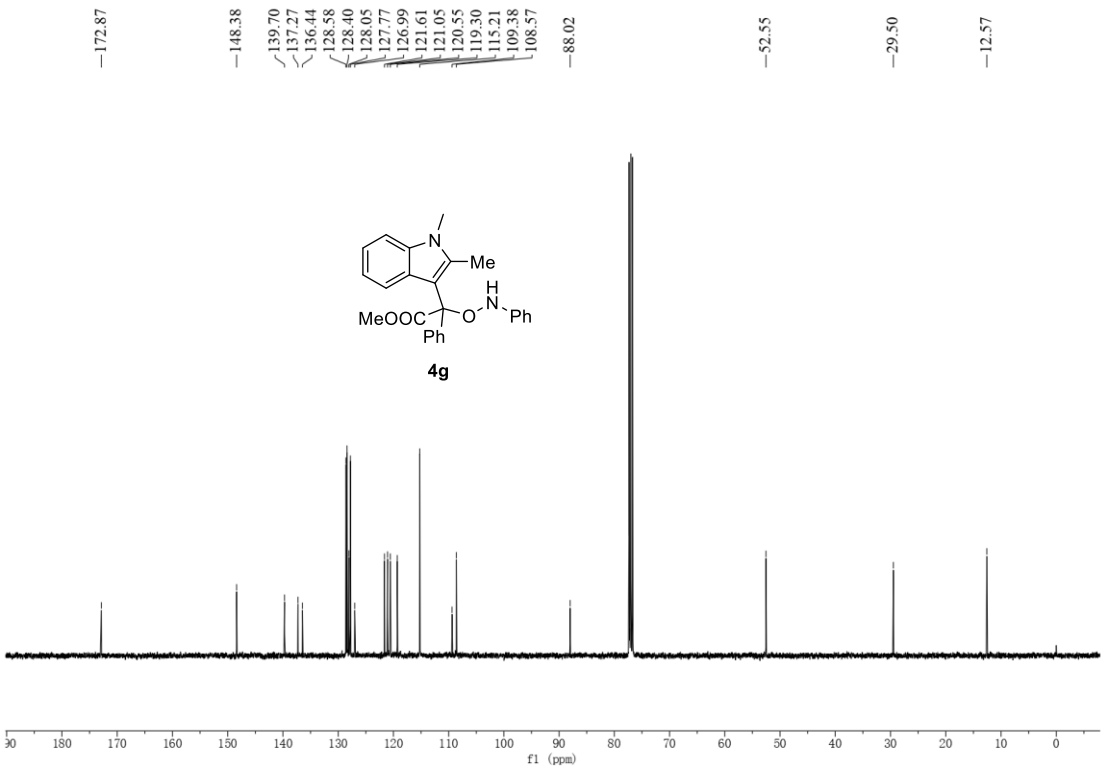
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4f



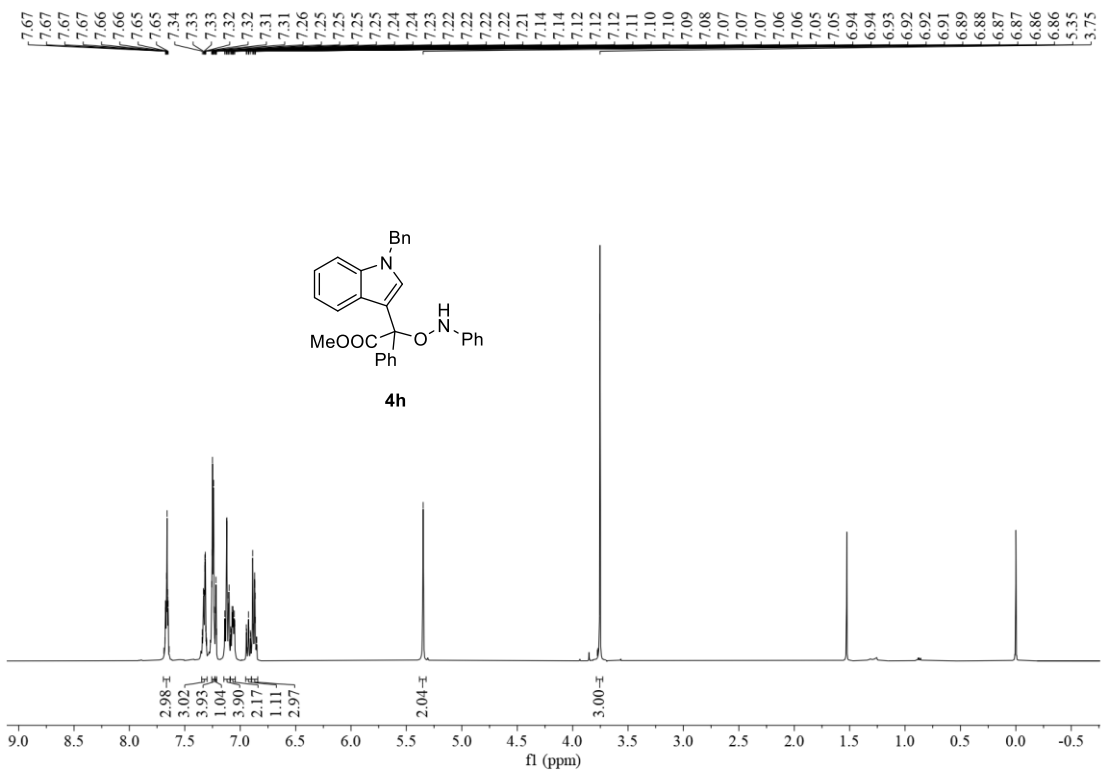


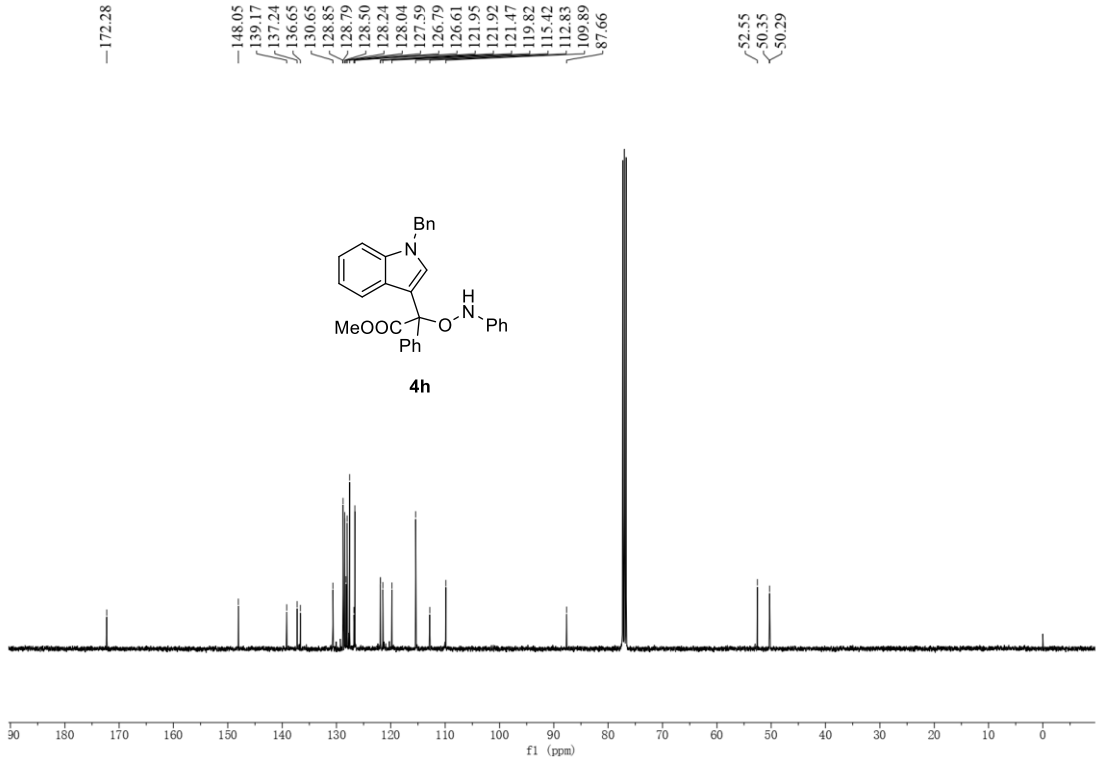
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4g



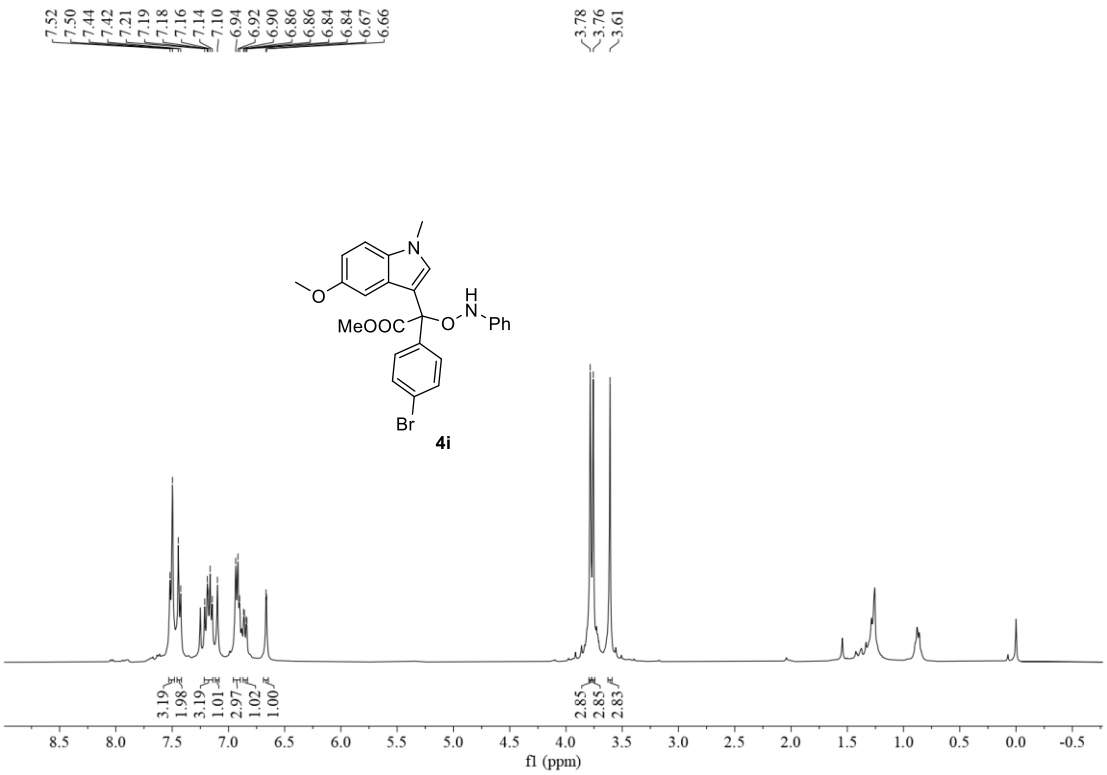


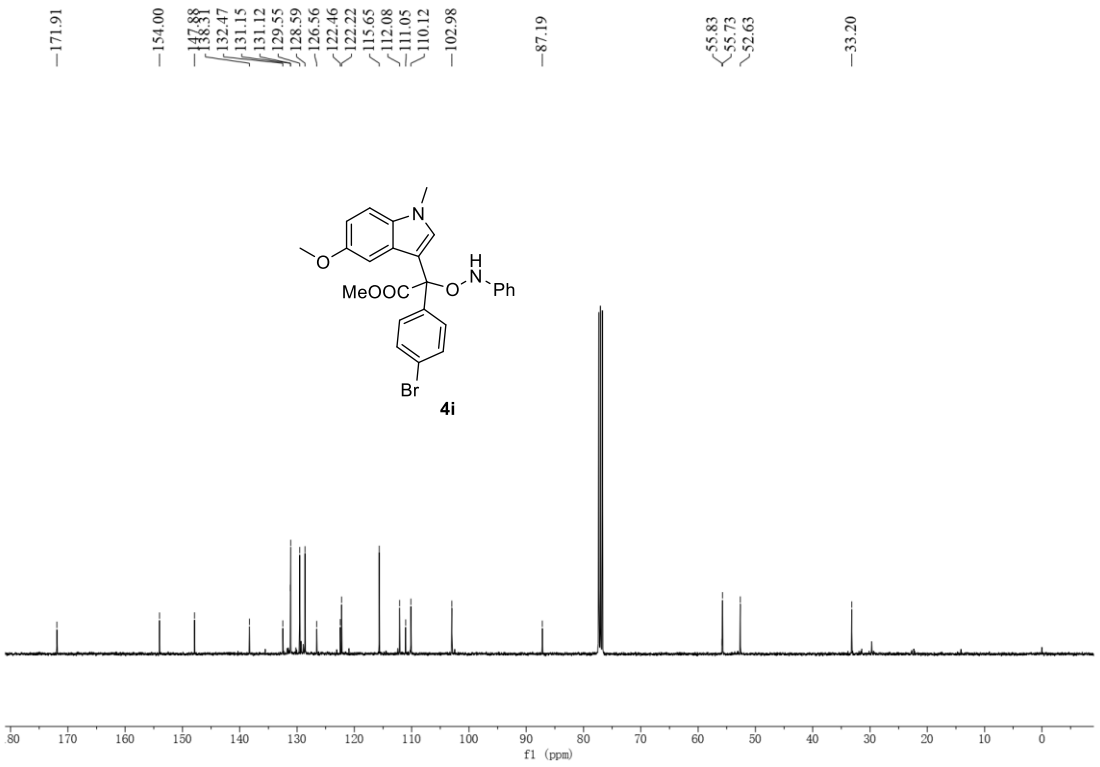
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4h



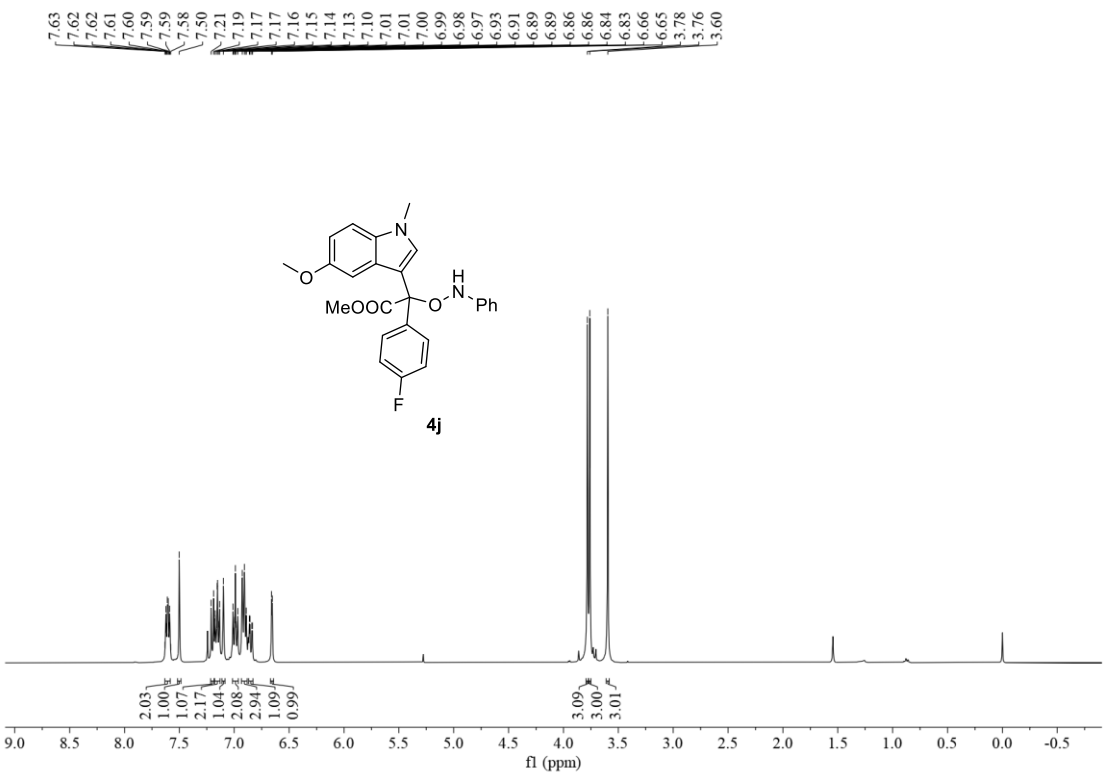


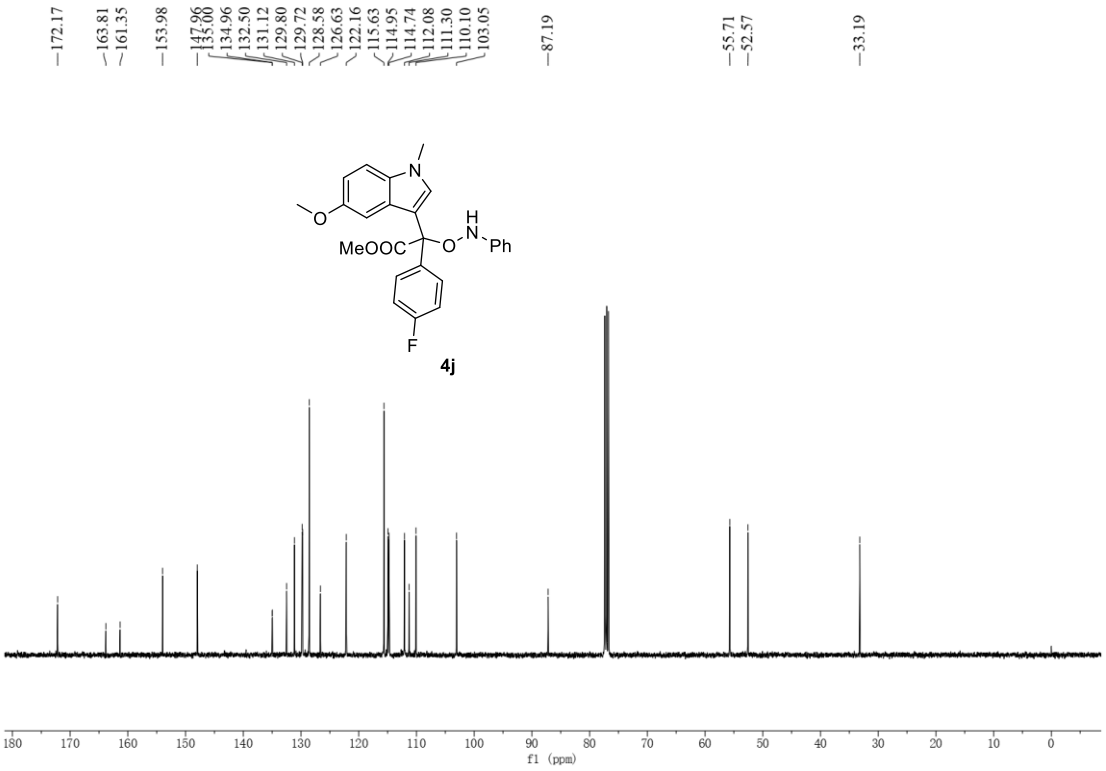
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4i





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for 4j

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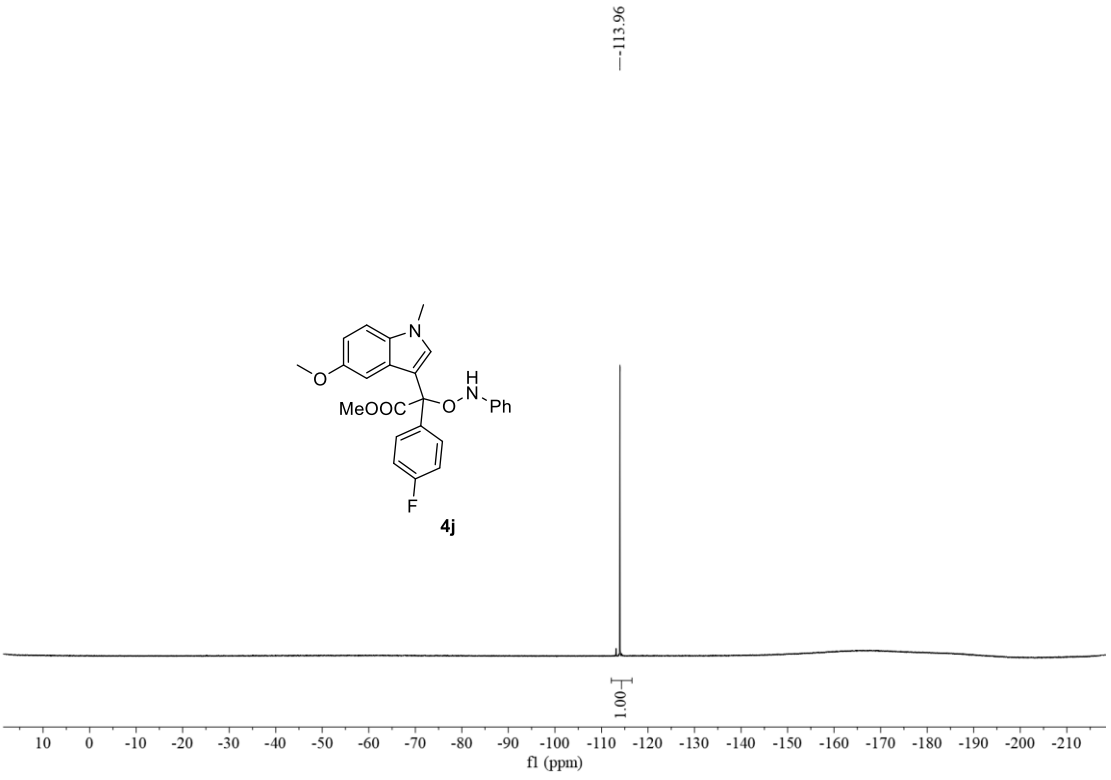
115.63
114.95
114.74
112.08
111.30
110.10
103.05
87.19
55.71
52.57
33.19
MeOOC
O
N
H
Ph
F
4j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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H
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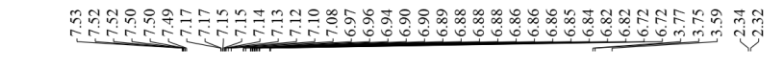
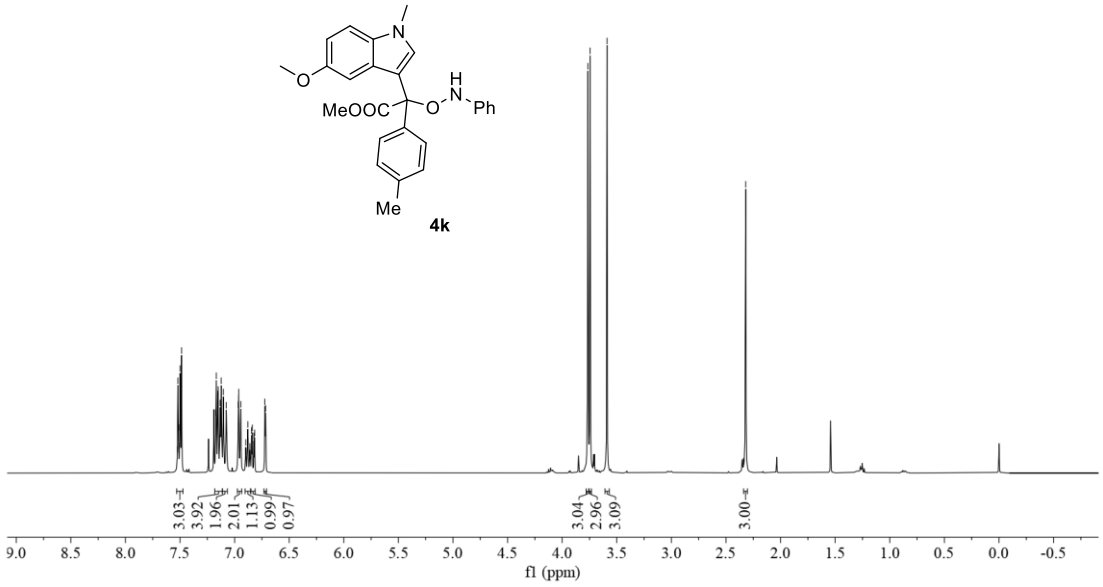
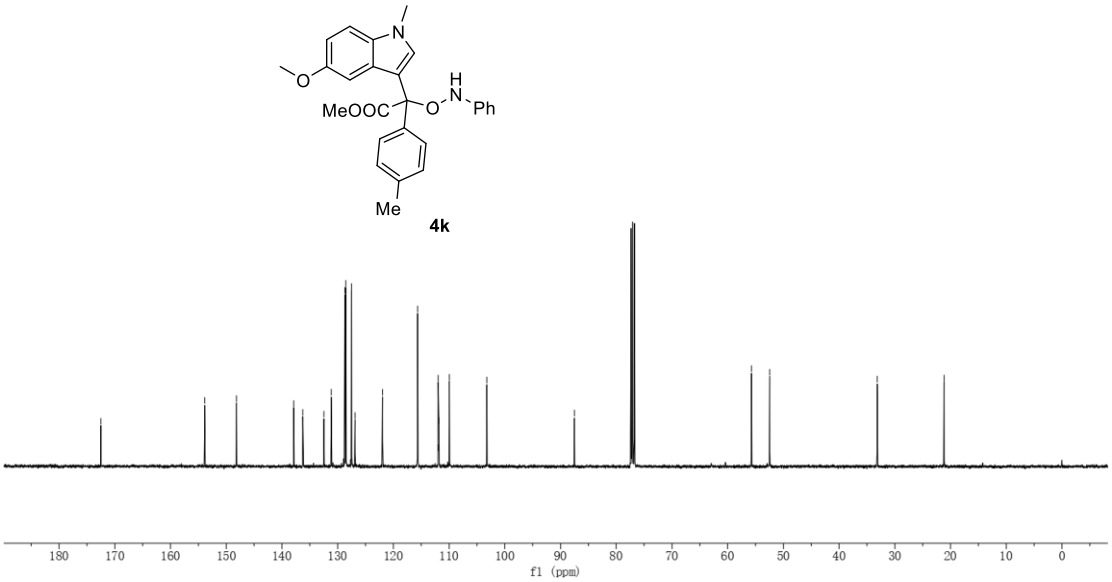
4j
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

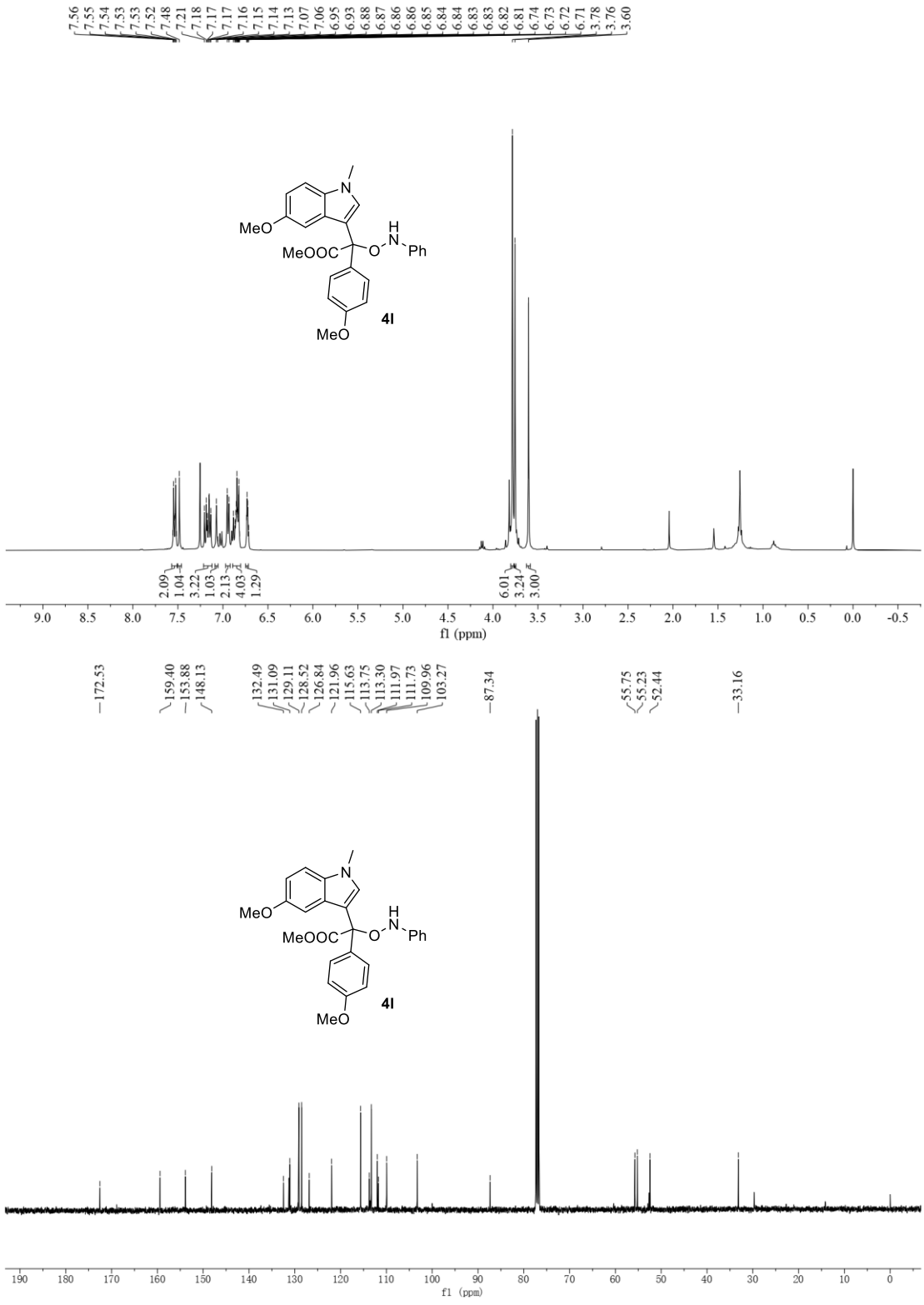
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4k



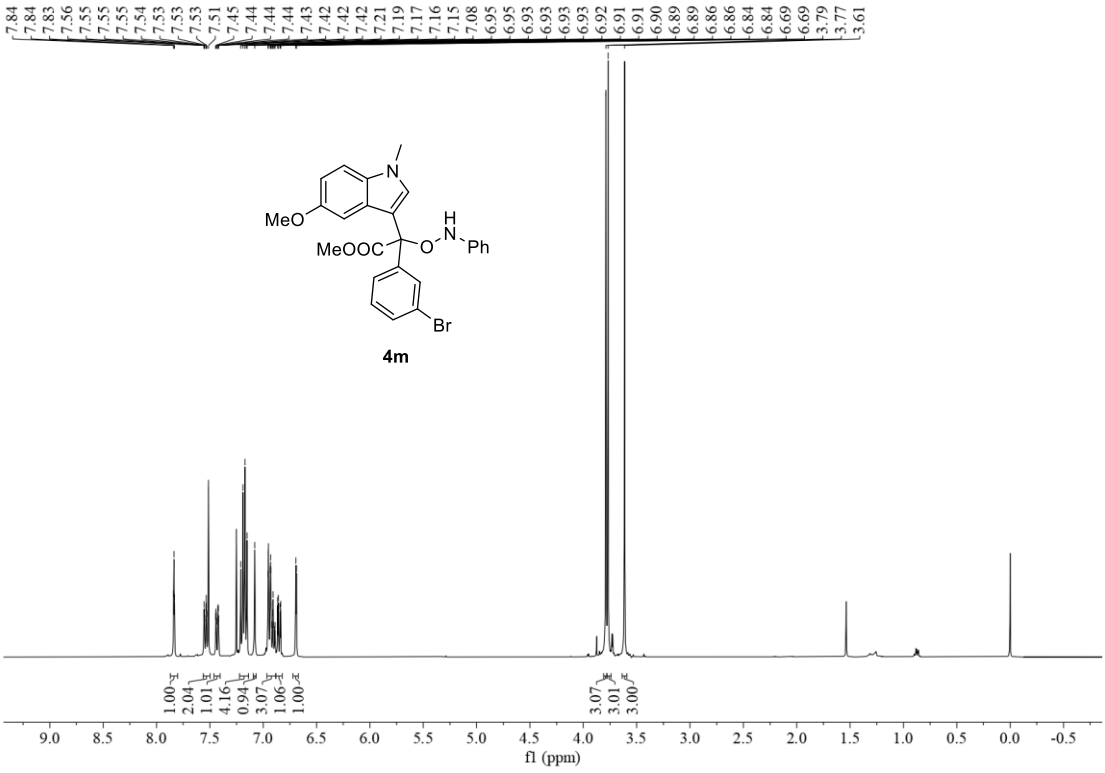


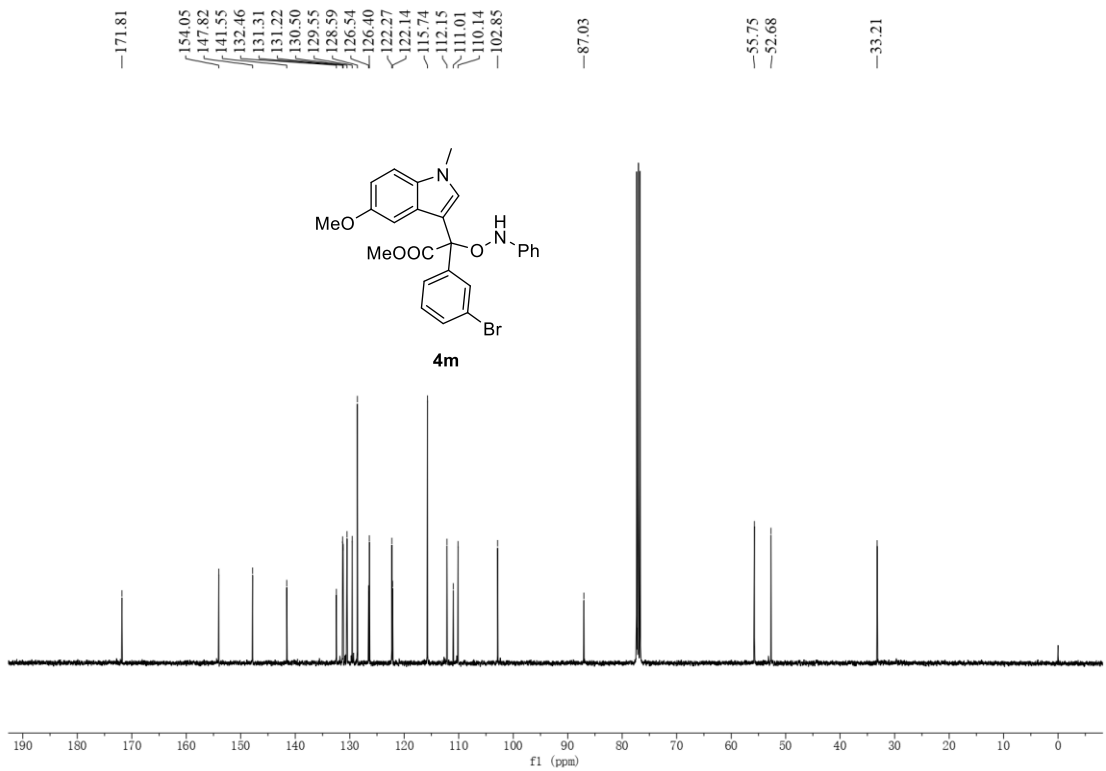


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4l

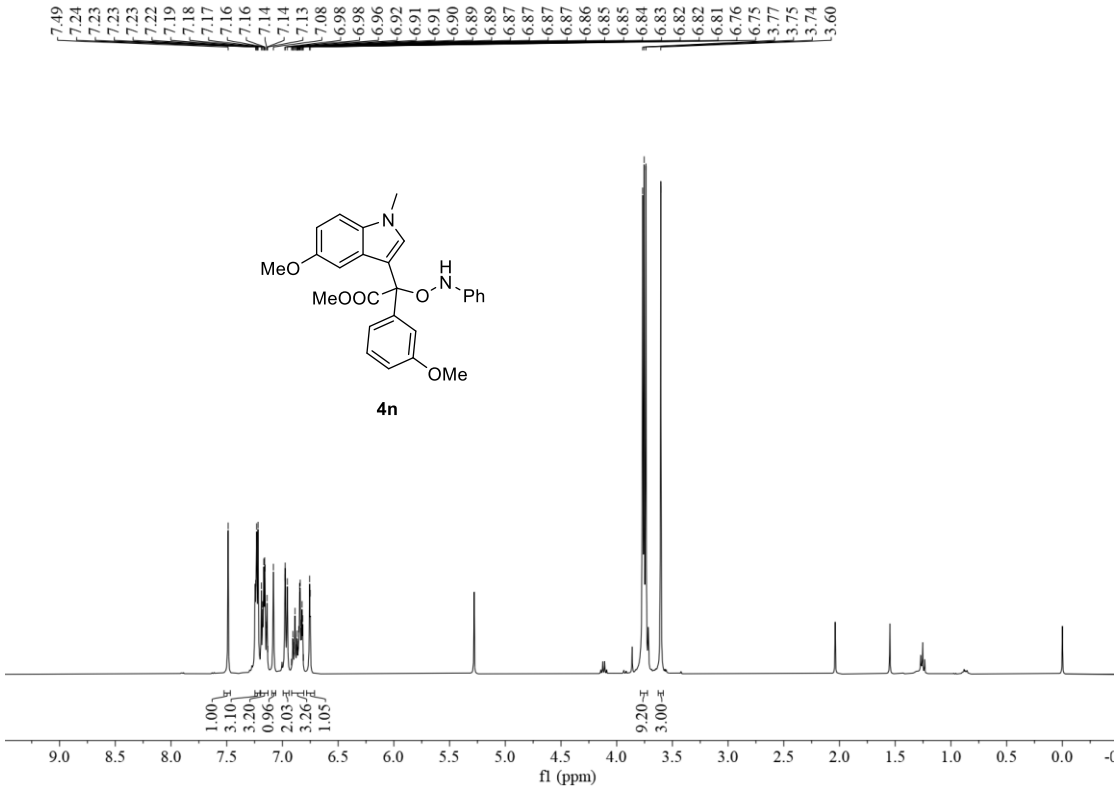


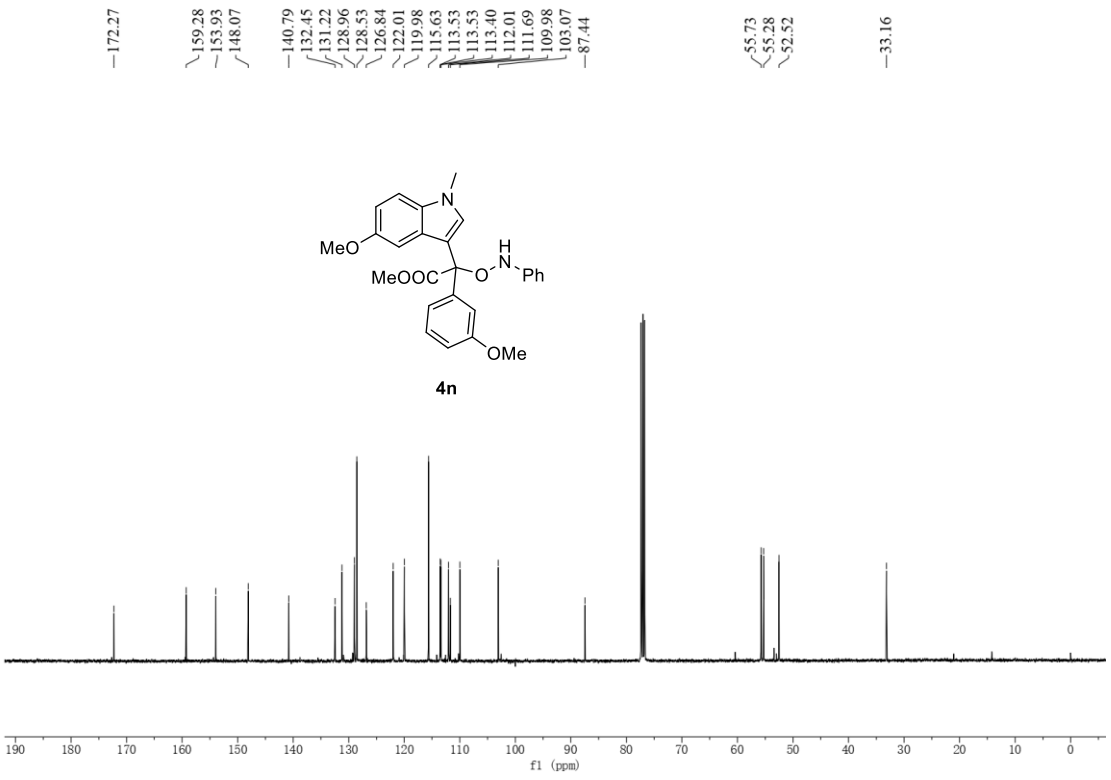
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4m



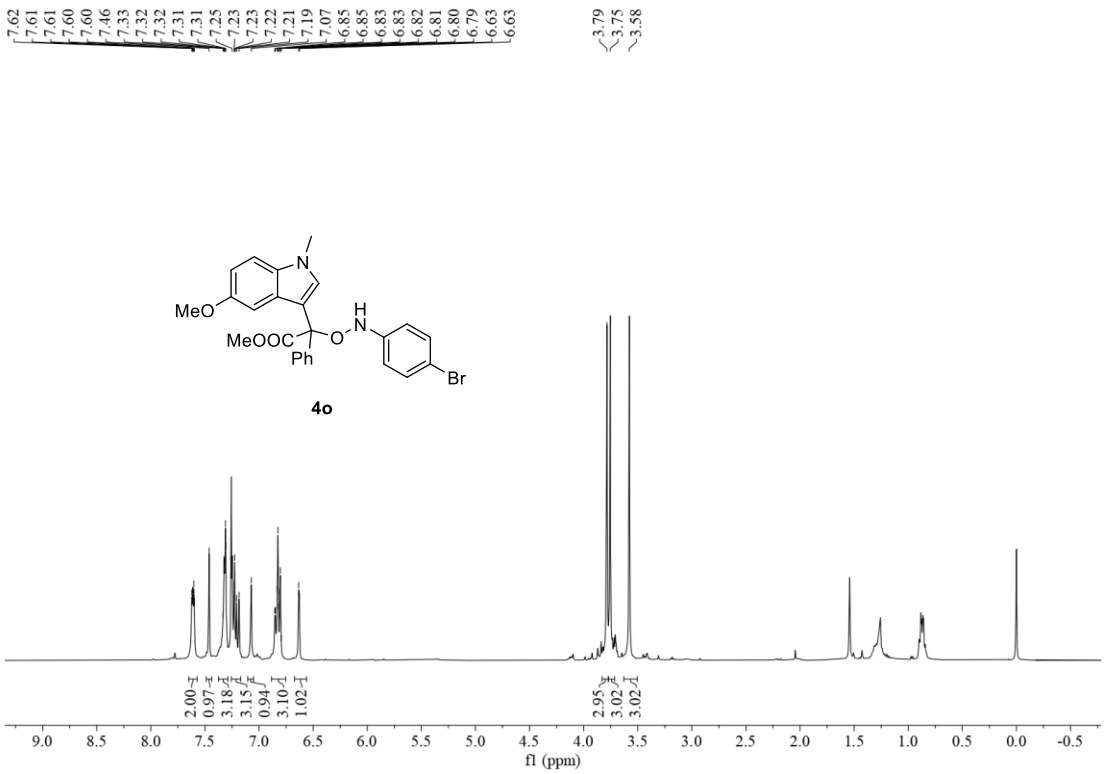


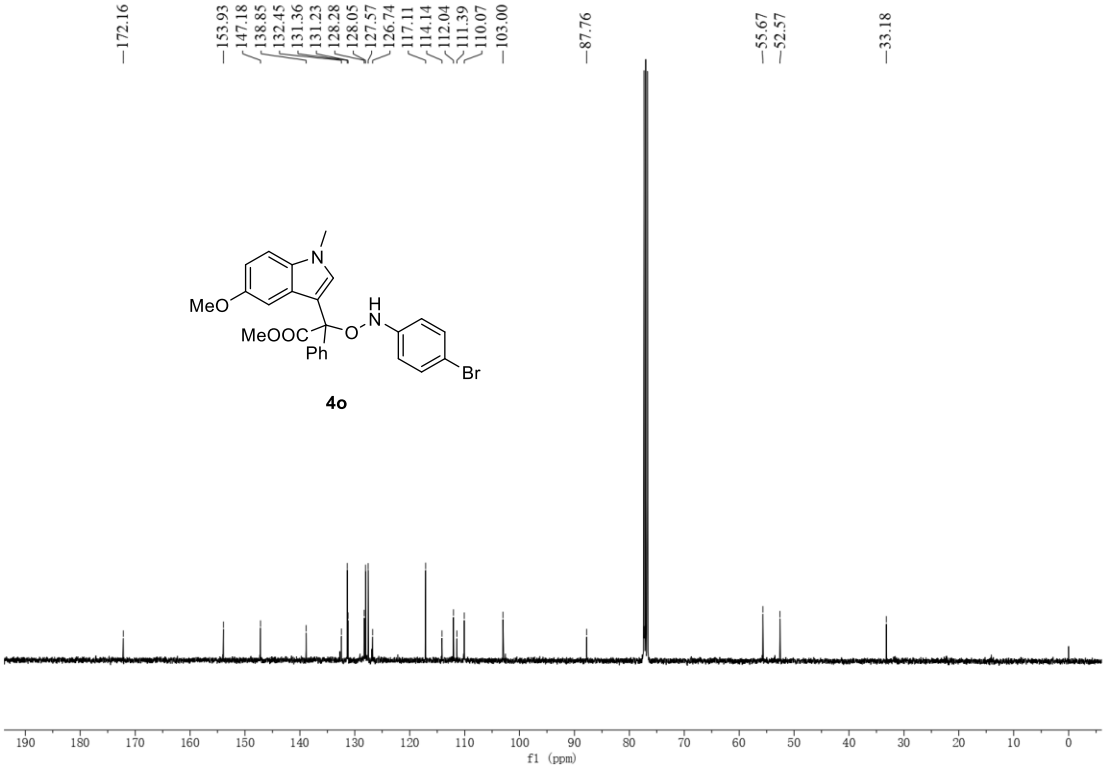
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4n



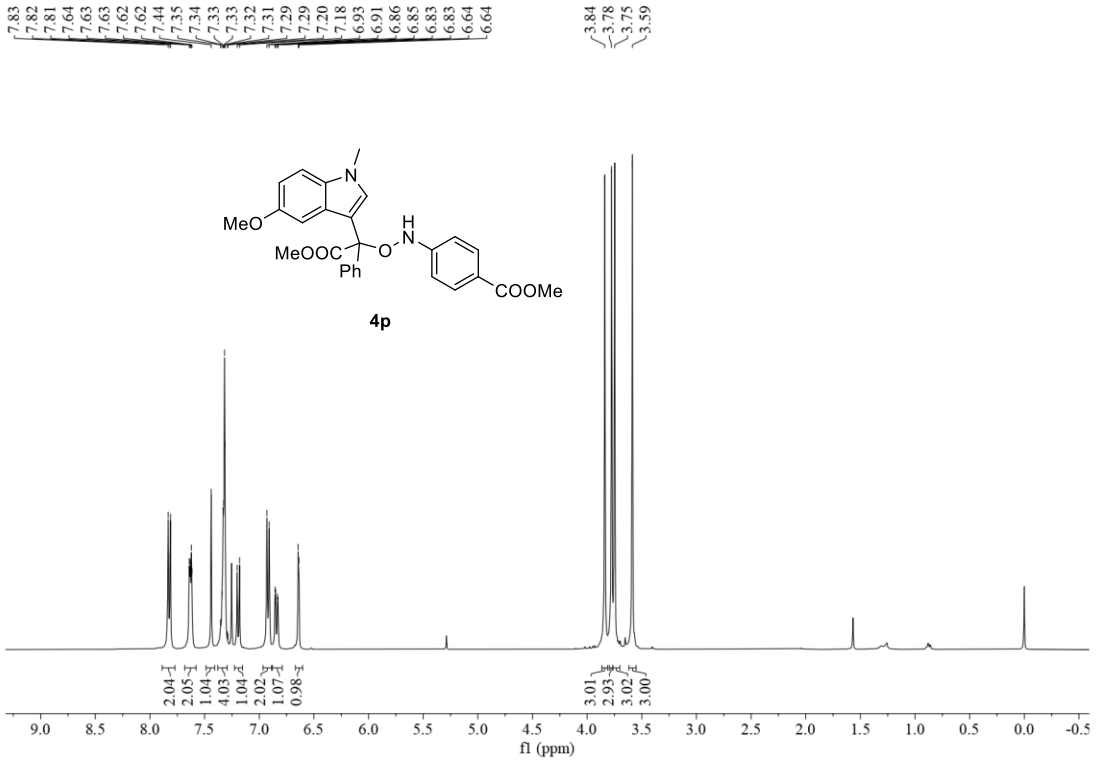


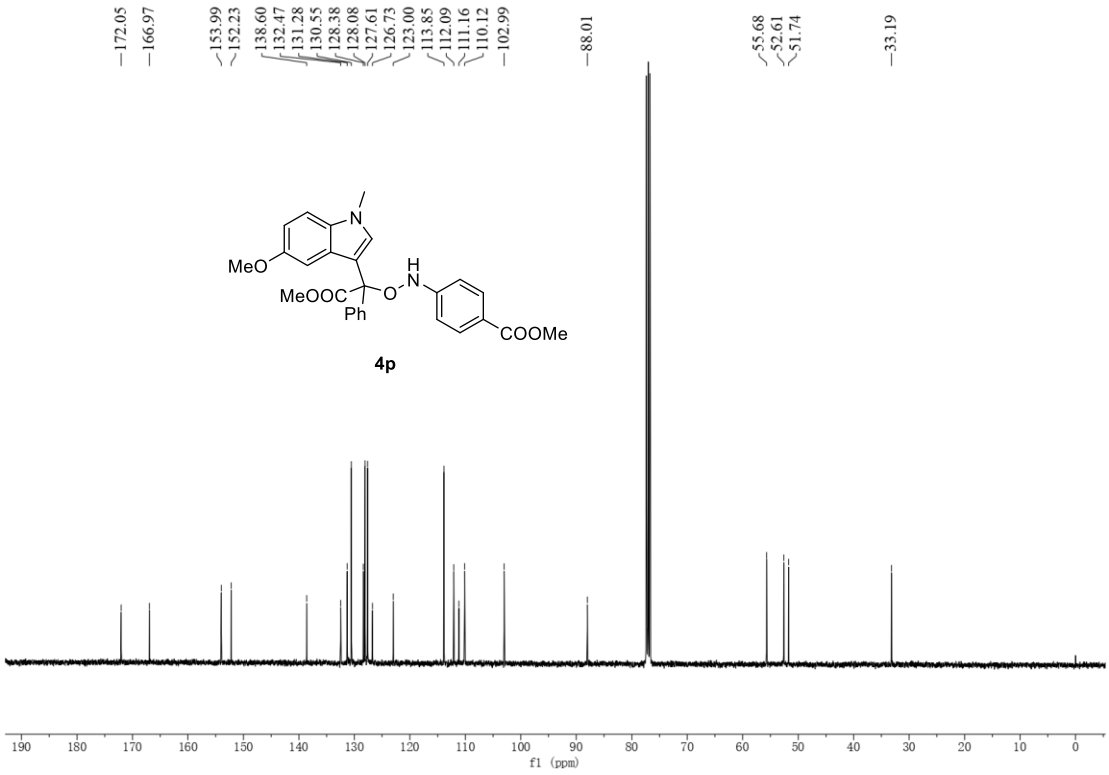
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4o



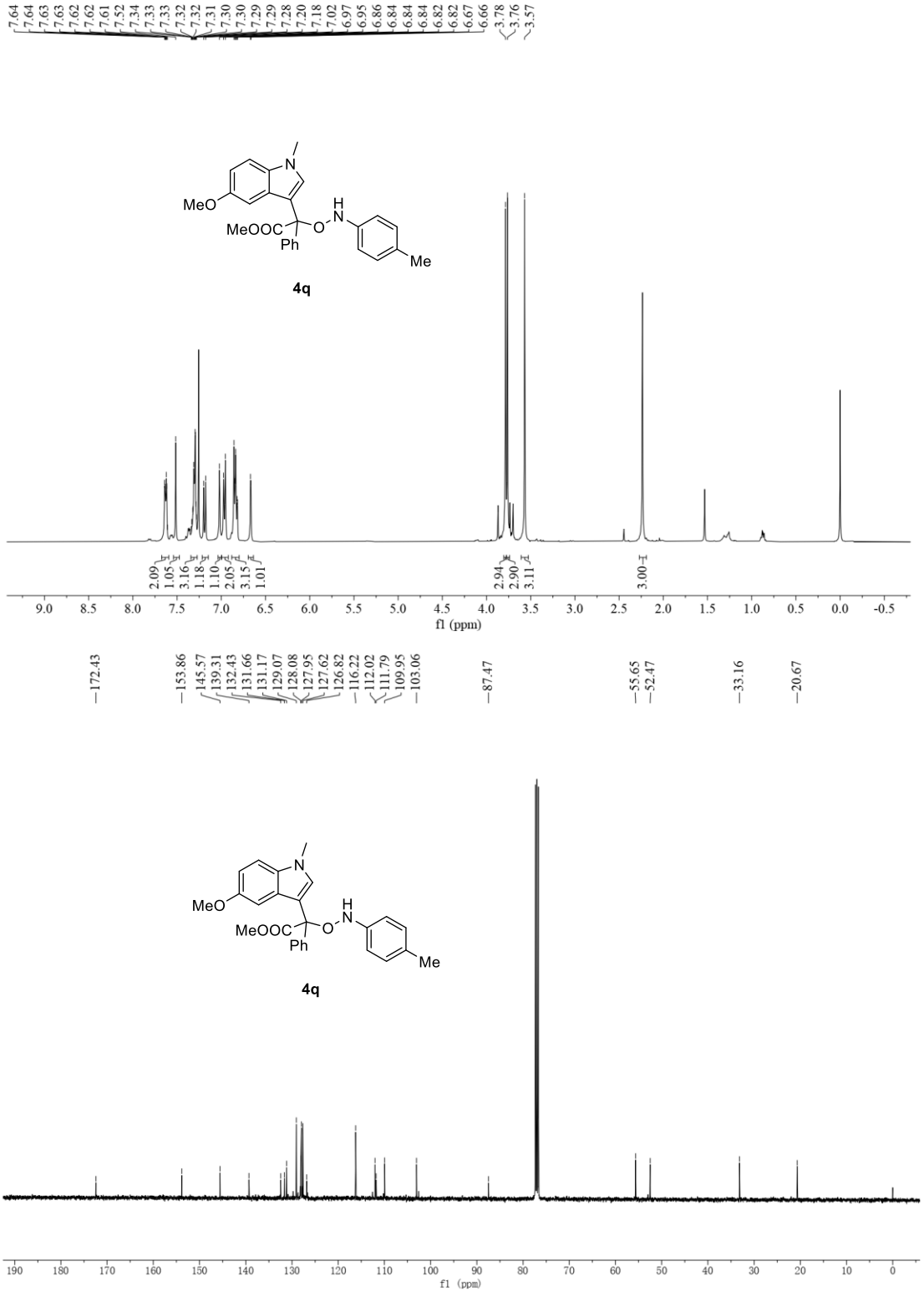


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4p

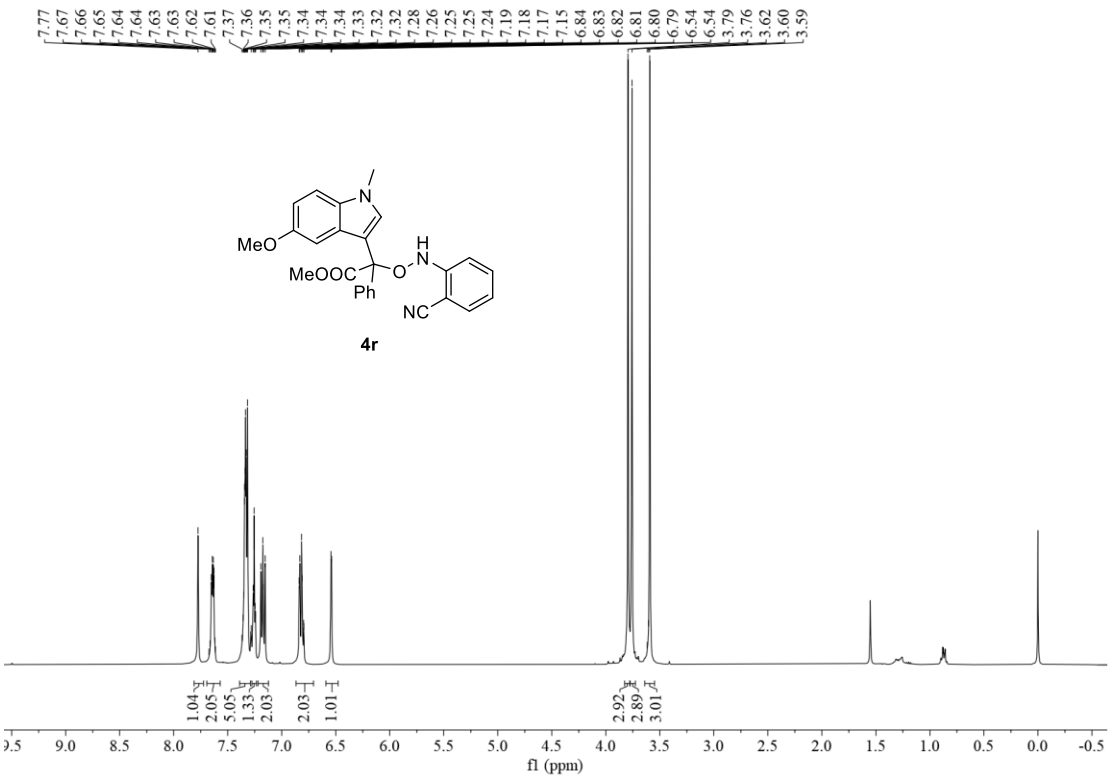


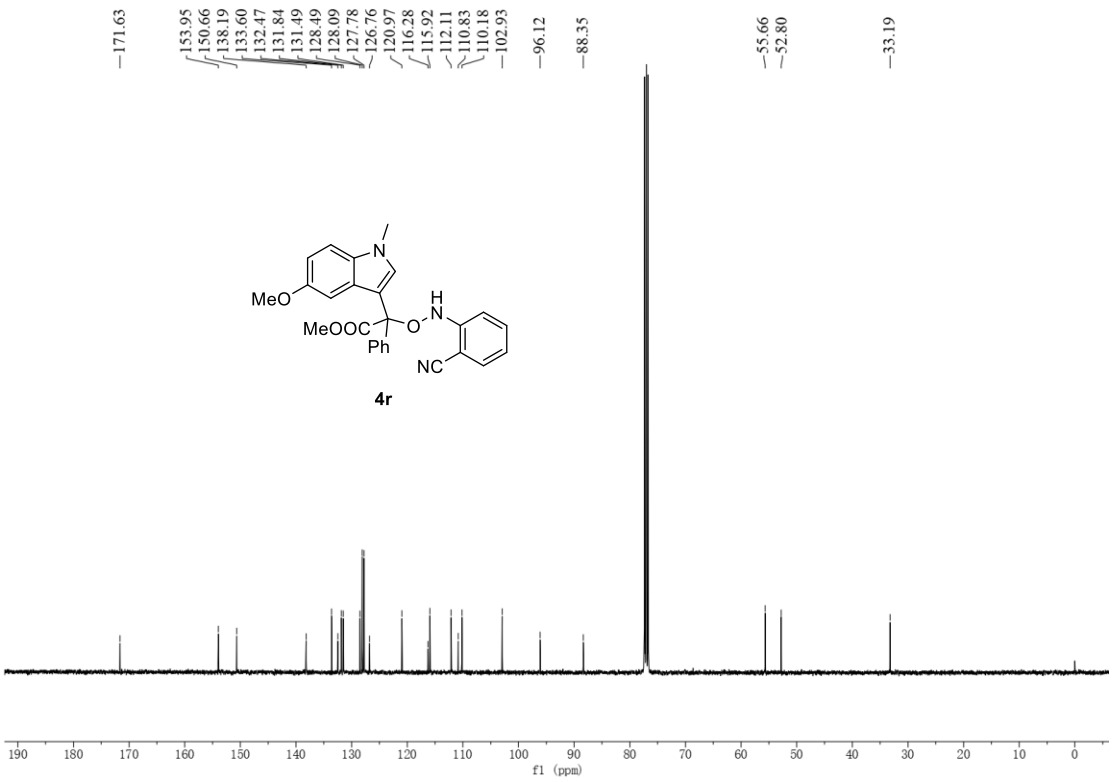


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4q

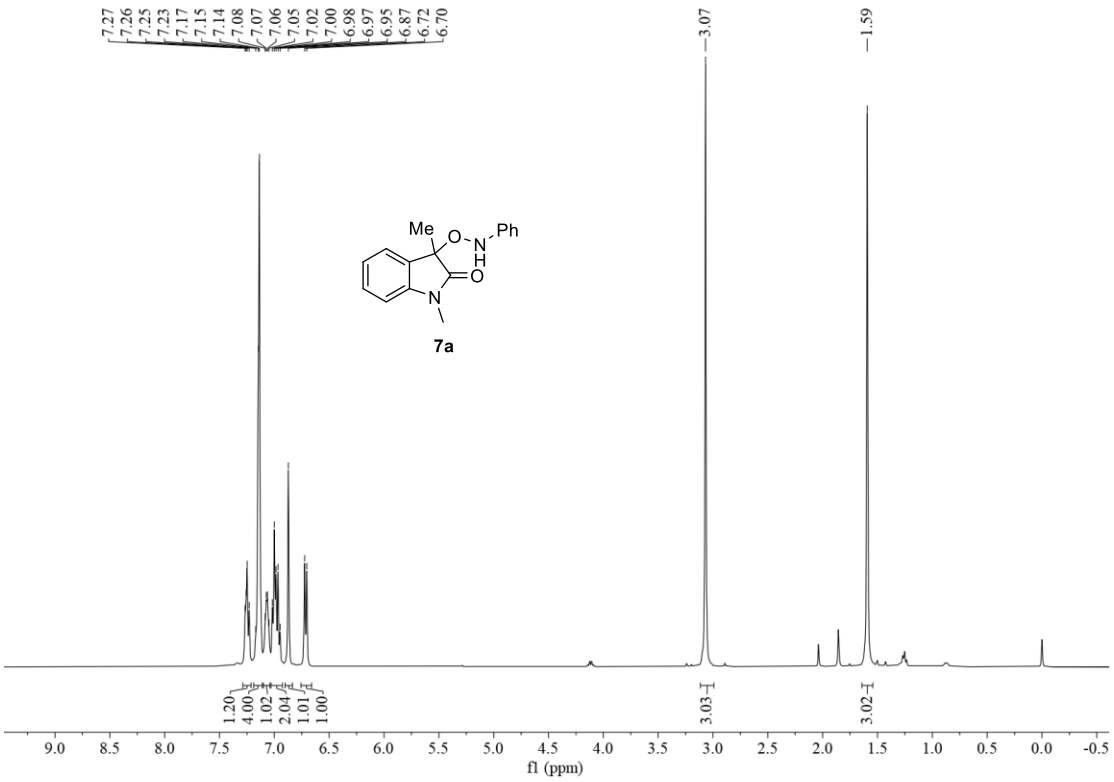


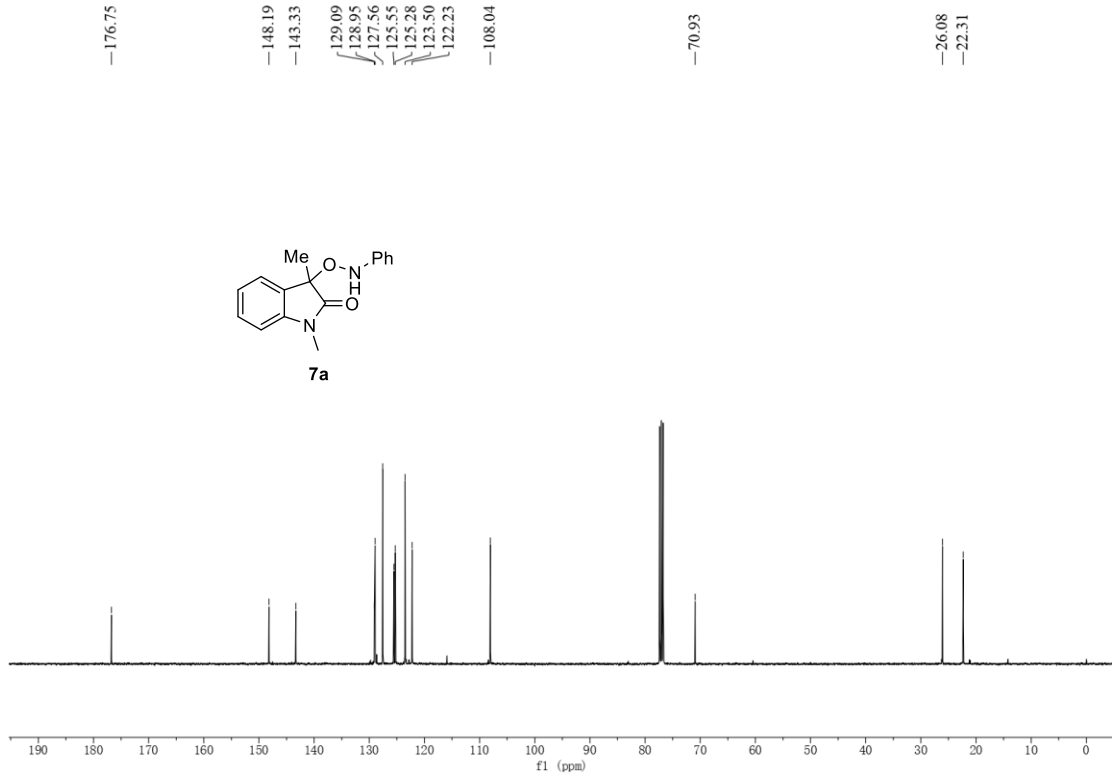
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 4r



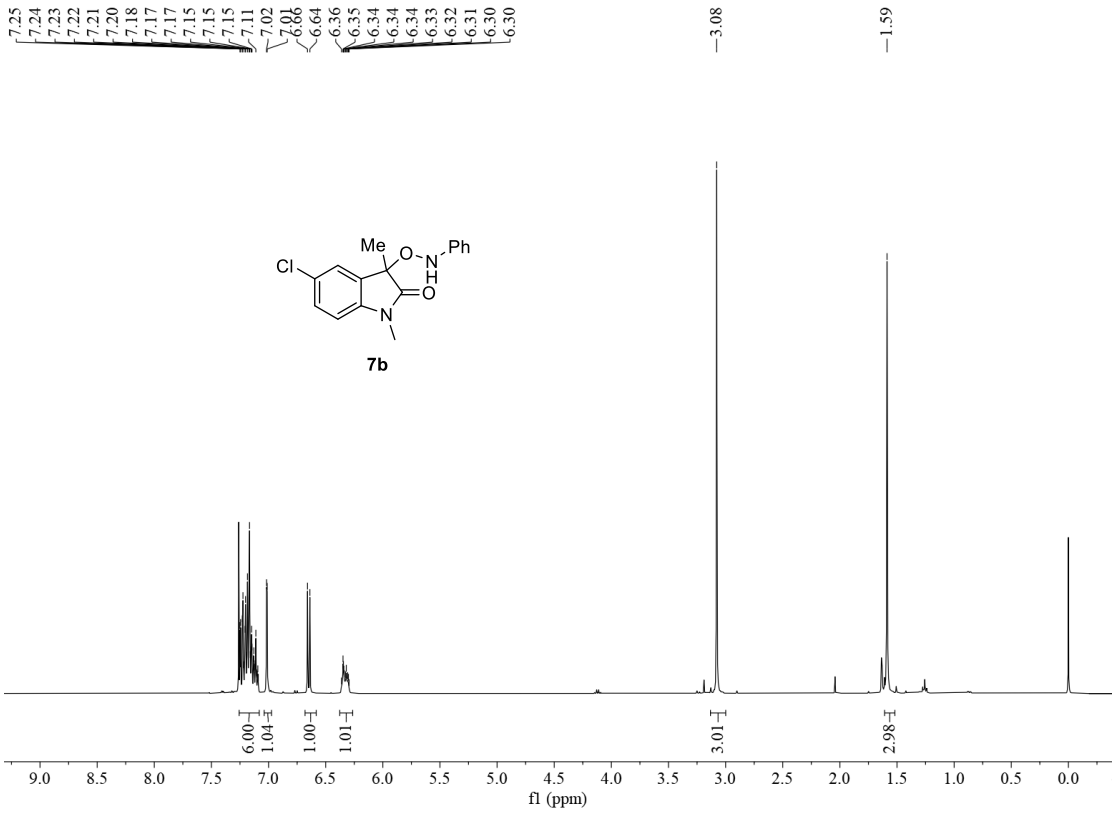


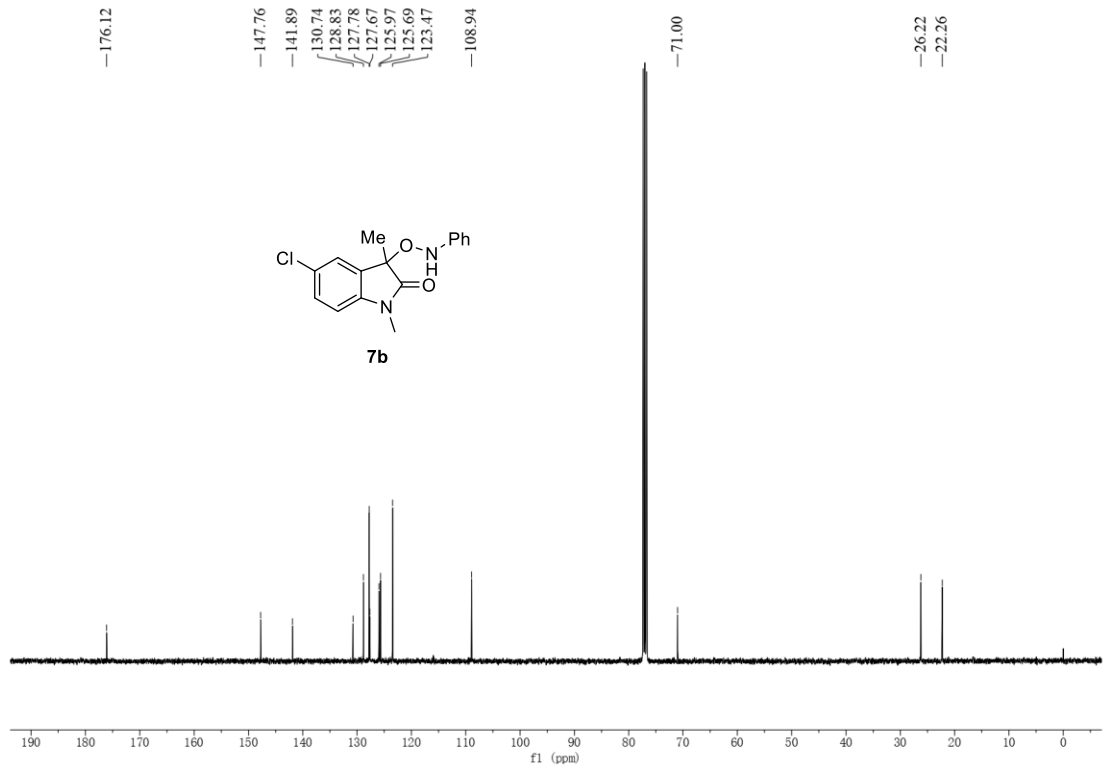
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7a



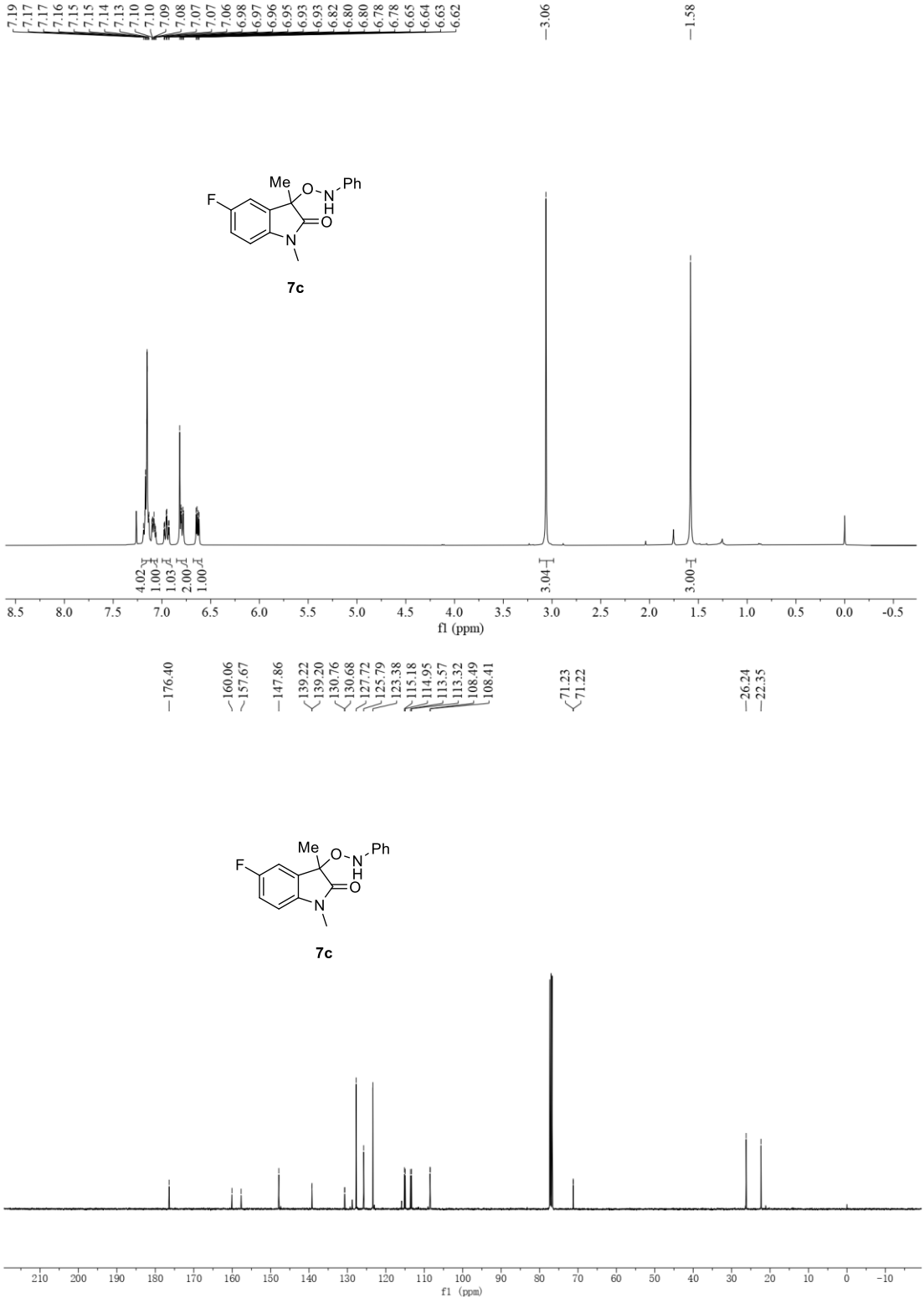


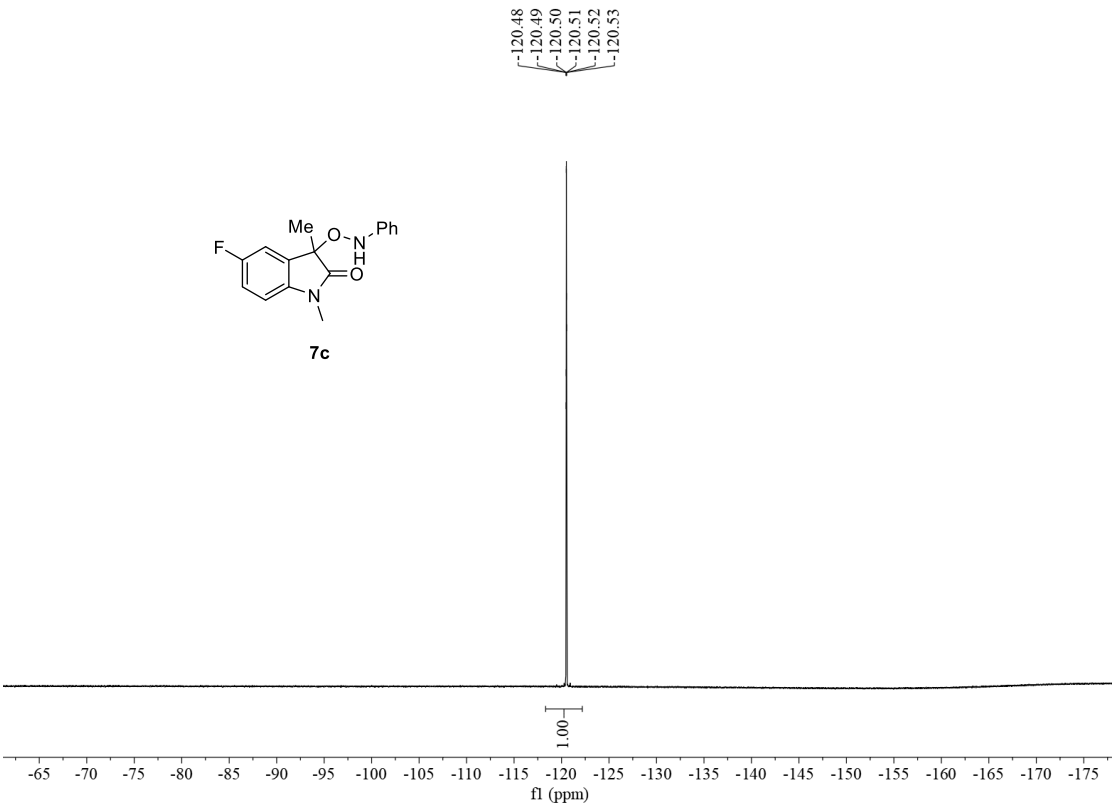
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7b



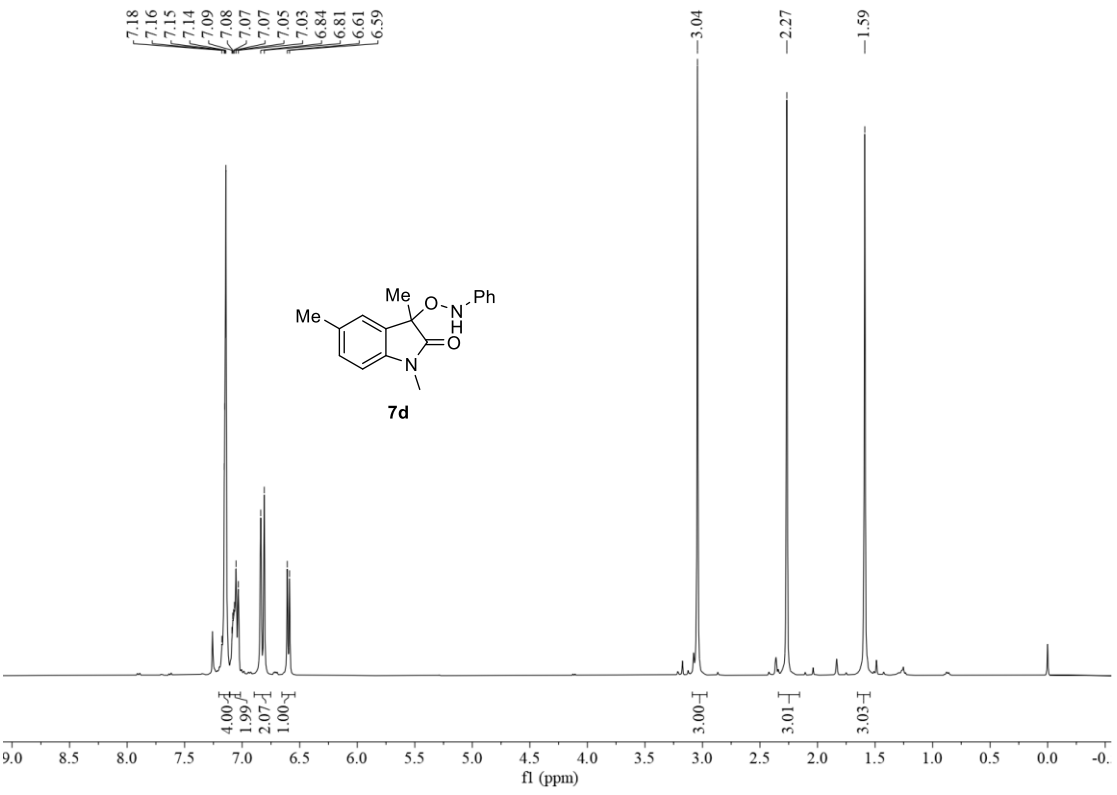


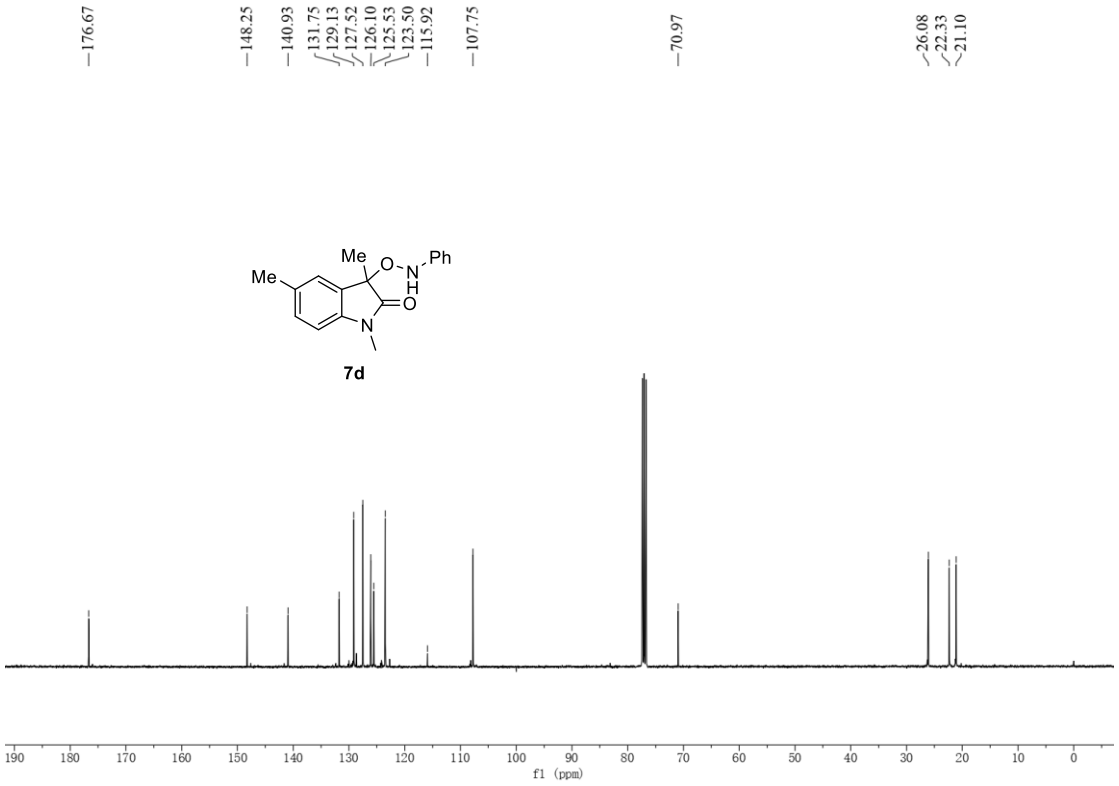
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra for 7c



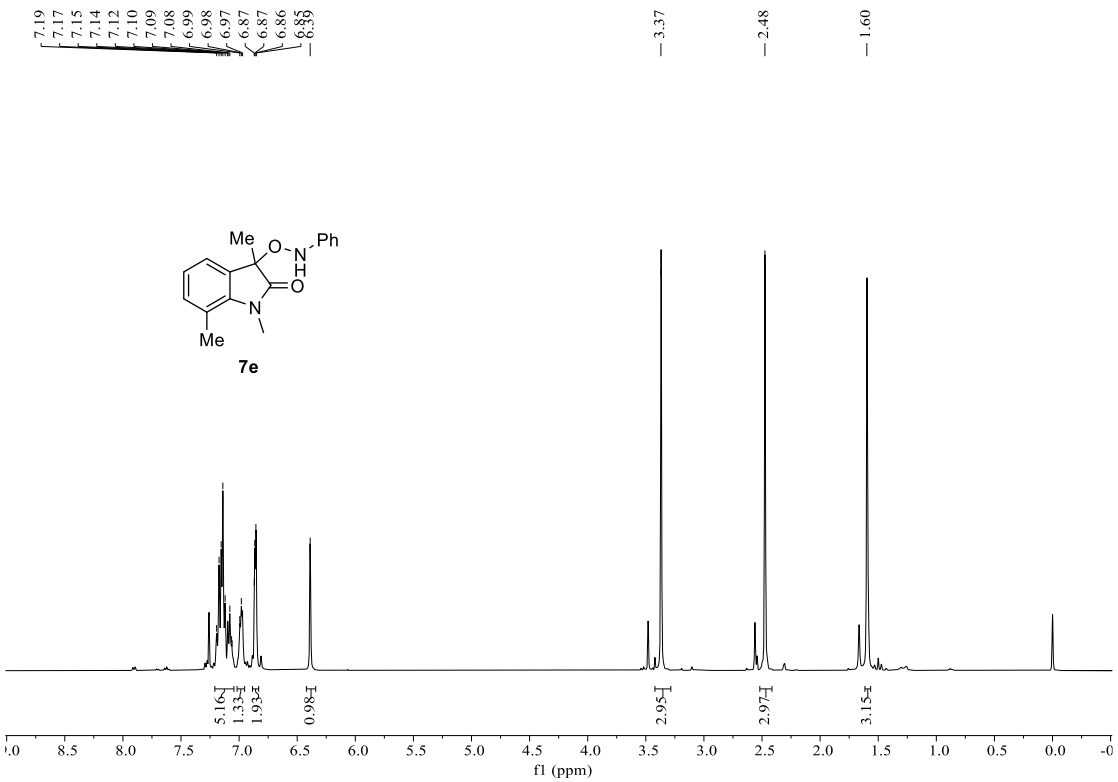


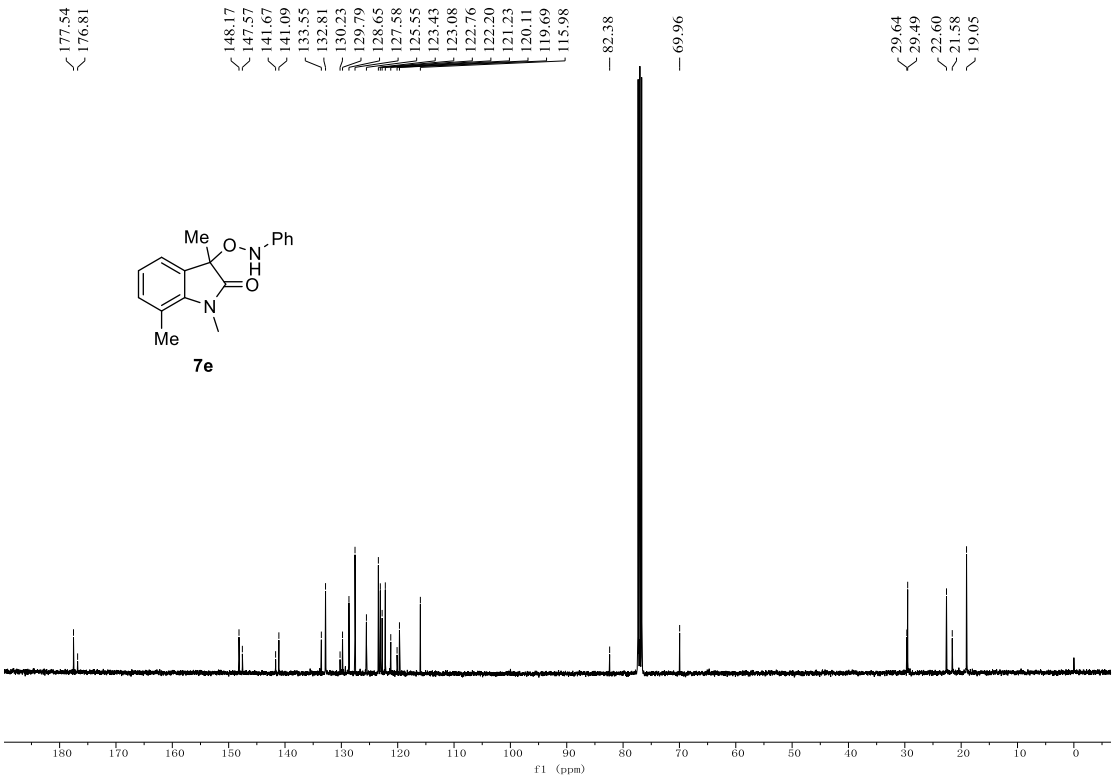
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7d





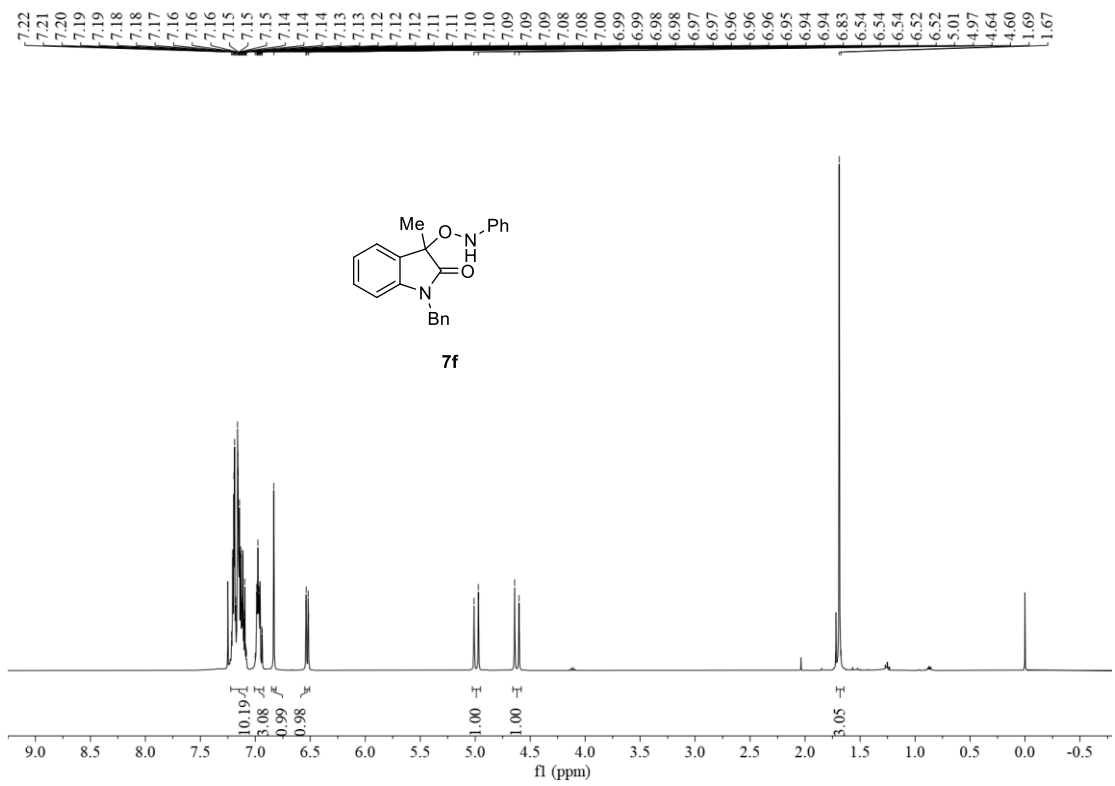
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7e



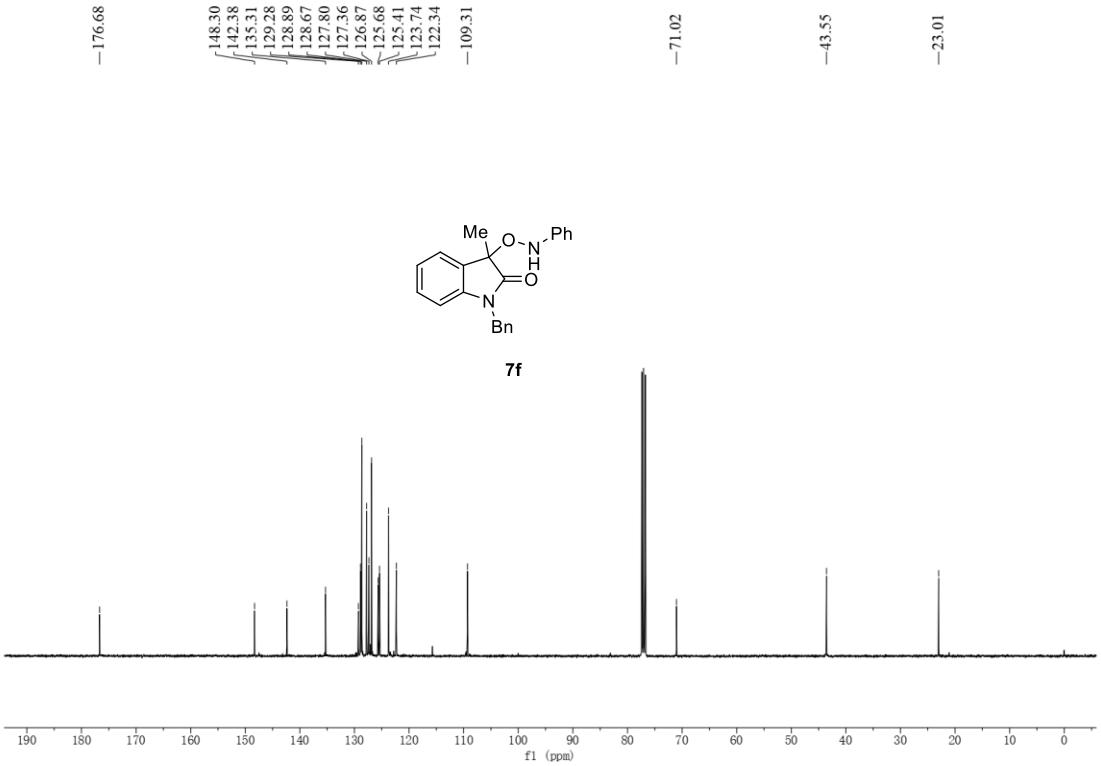


7e

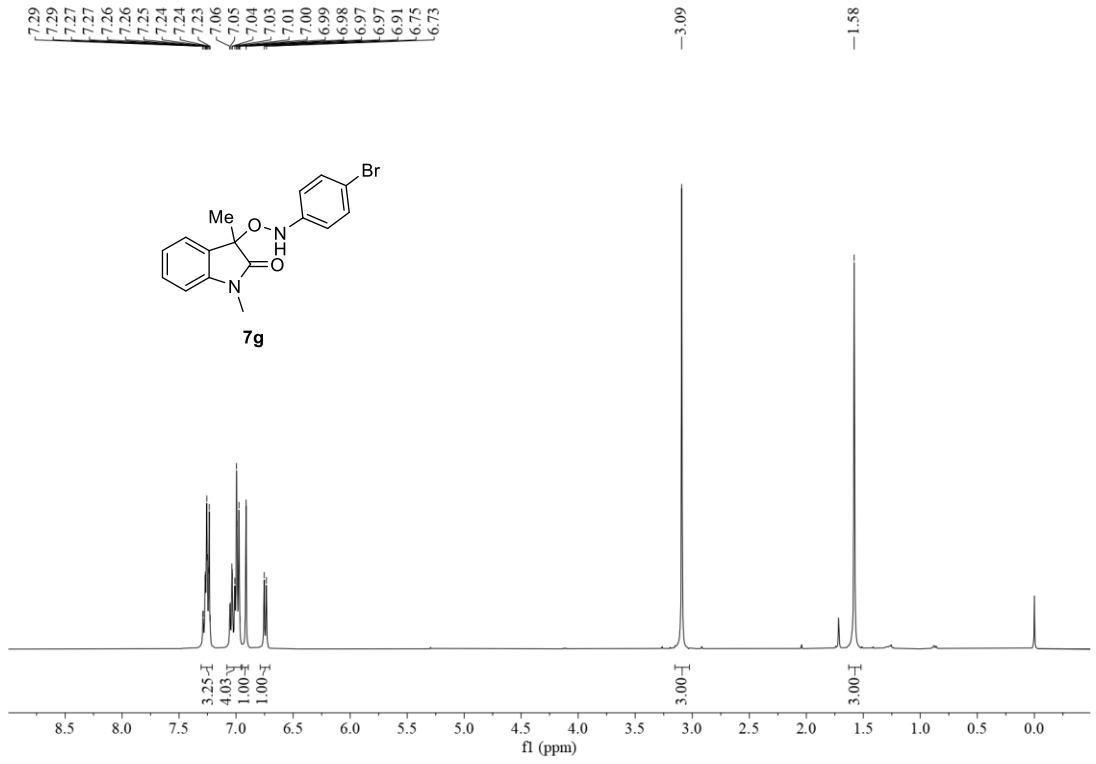
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7f

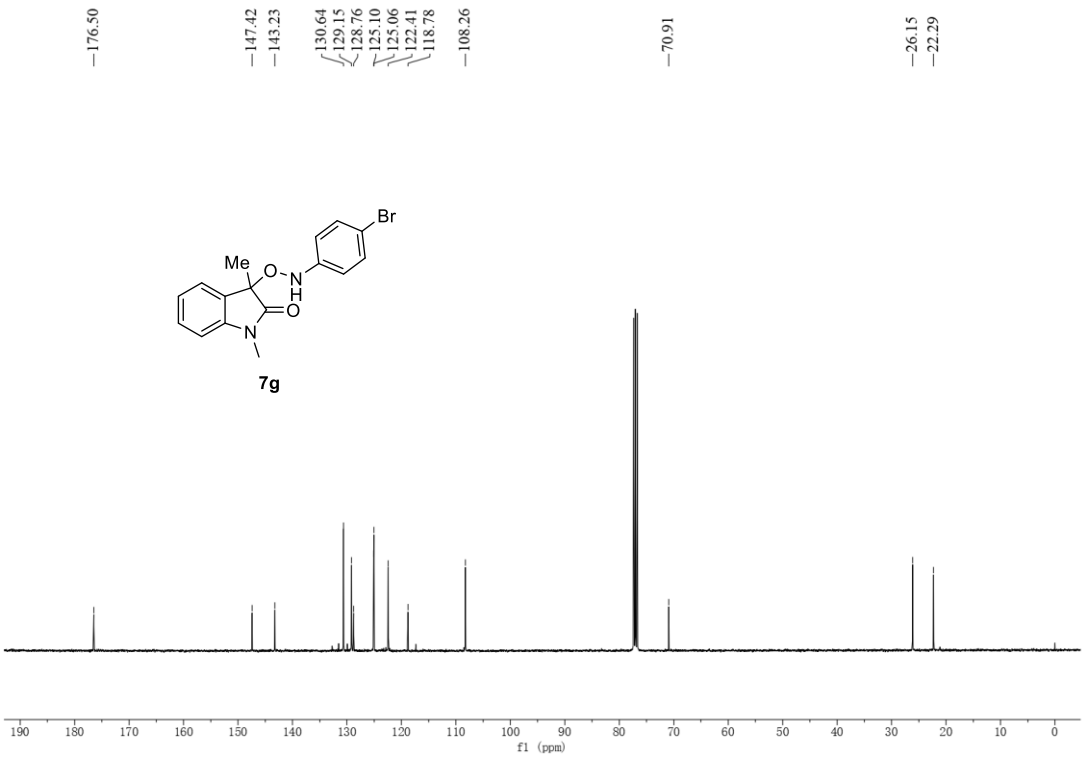


7f

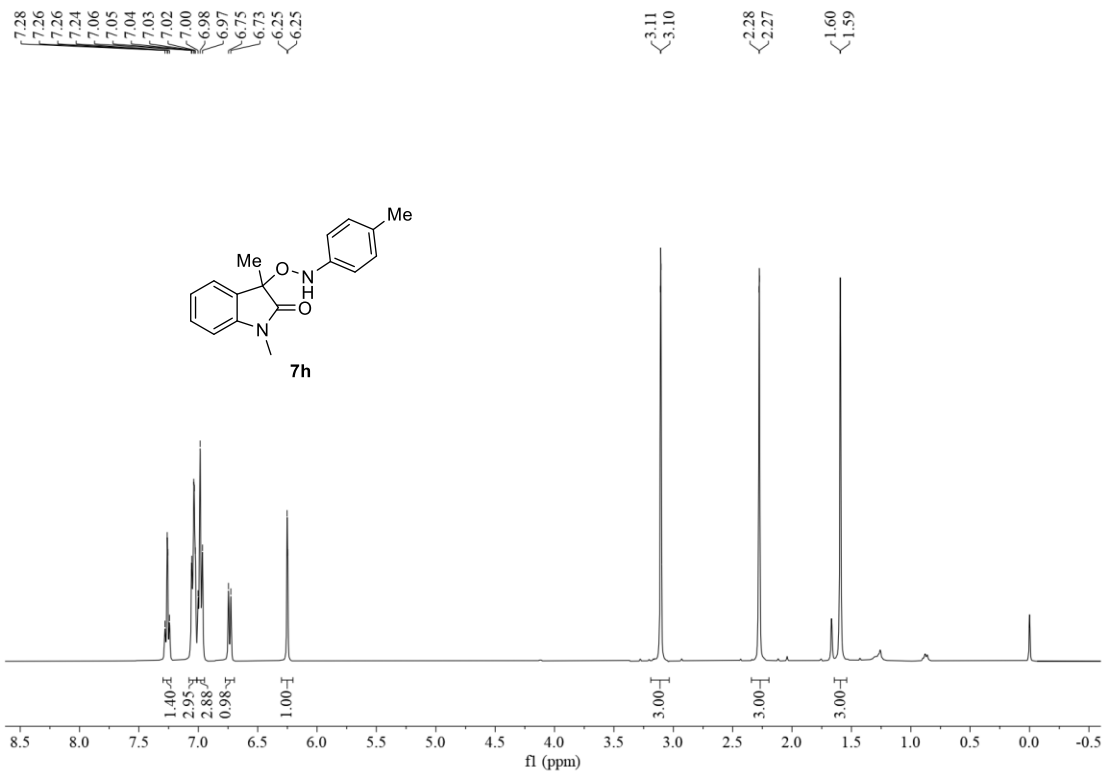


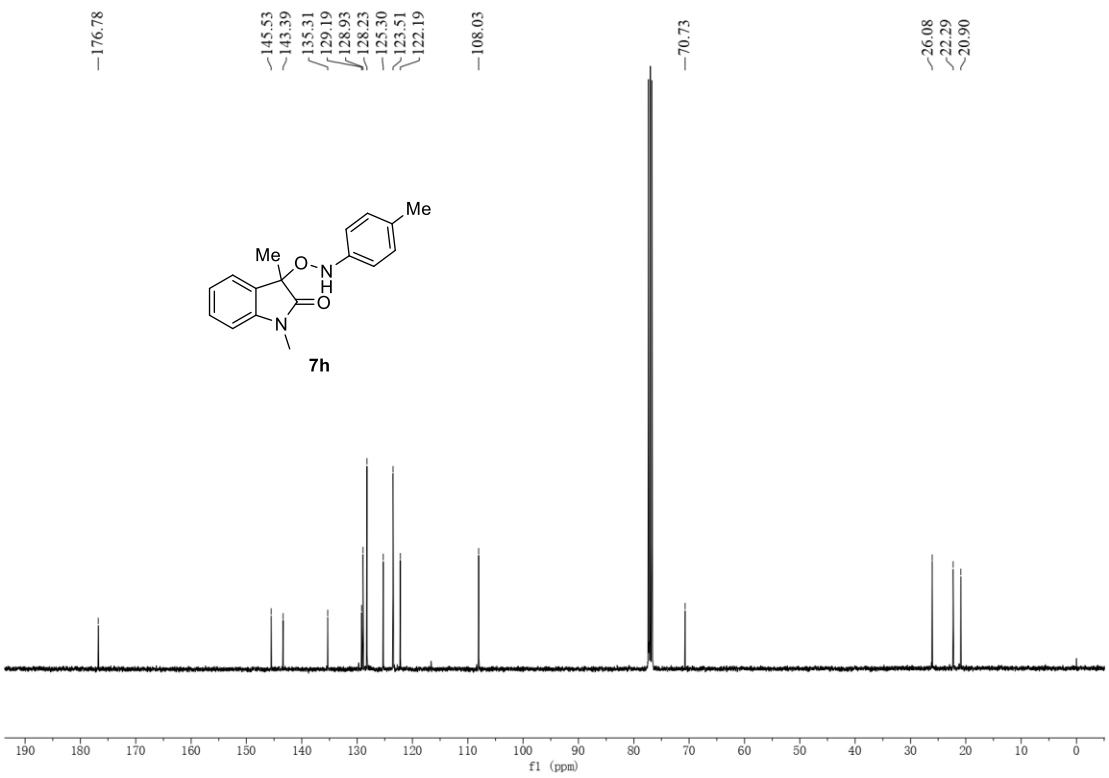
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7g



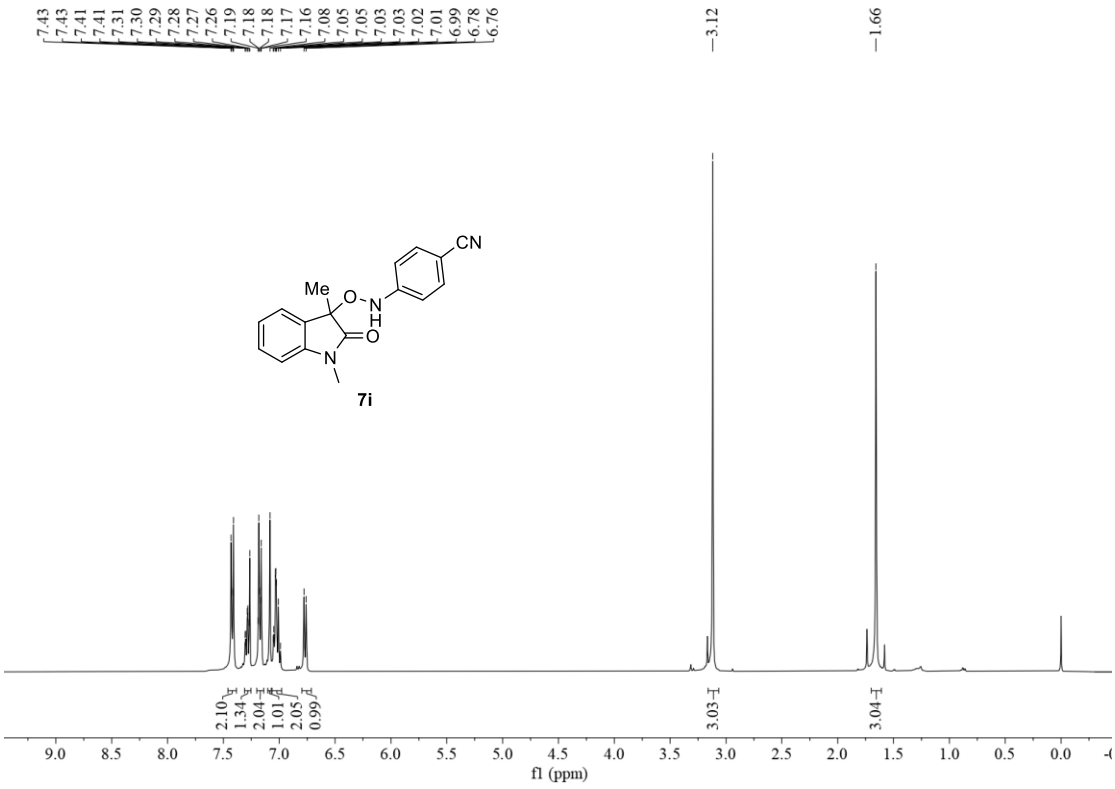


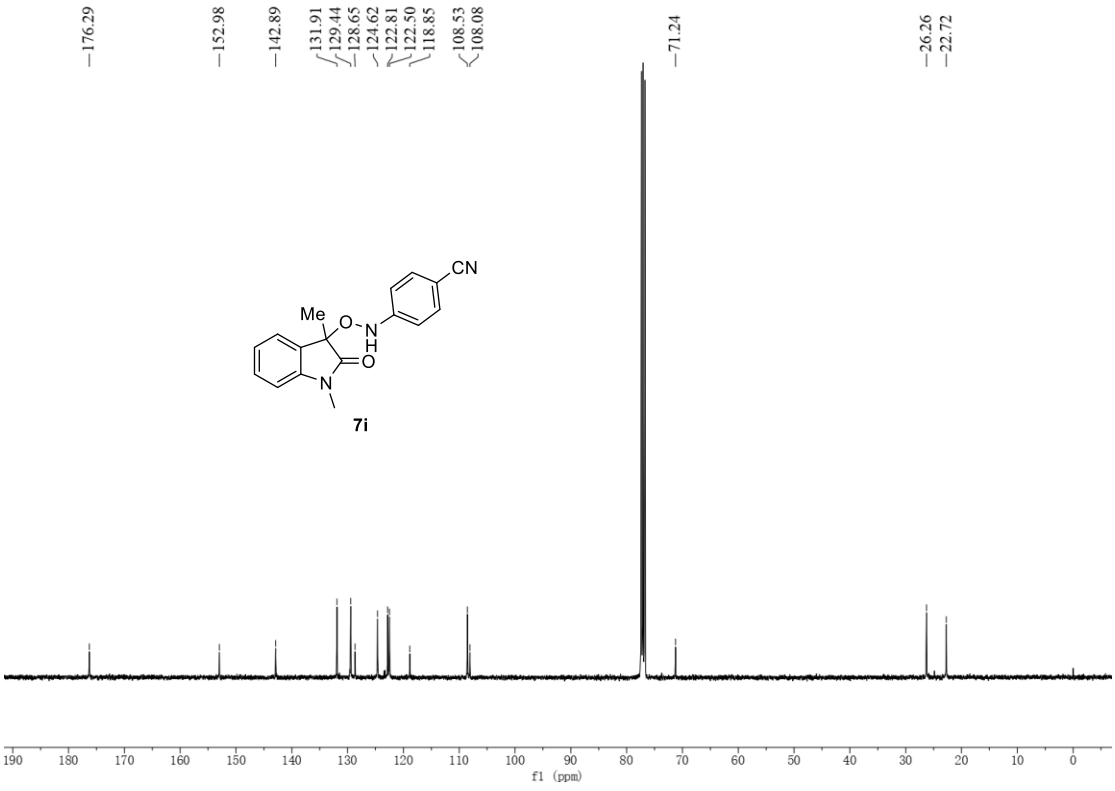
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7h





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra for 7i

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f1 (ppm)