Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Photoinduced Radical Cascade Domino Heck Coupling of N-Aryl Acrylamide with Vinyl Arenes Enabled by Palladium Catalysis

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General Information

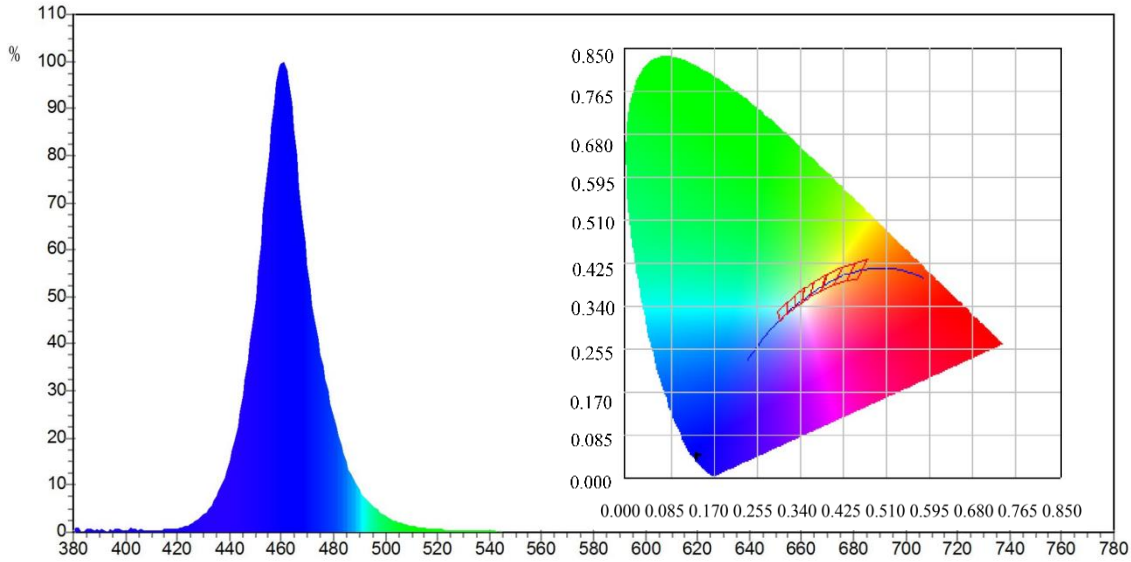
Unless noted otherwise, all the solvents and commercially available reagents were purchased and used directly. Benzene, 1,4-dioxaneand tetrahydrofuranwere distilled freshly over sodium, benzotrifluoride was distilled freshly over P_2O_5, DCM was distilled freshly over CaH_2andcarefullyfreeze-pump-thawed. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Reactions were monitored with thin layer chromatography (TLC) using silica gel 60 F-254 plates. TLC plates were normally visualized by UV irradiation (254 nm or 365 nm), stained with basic $KMnO_4$. Flash chromatography was performed using silica gel 60 (200−300 mesh). Vials (15 x 45 mm 1 dram (4 mL) / 17 x 60 mm 3 dram (7.5 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight and cooled in a desiccator. Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). UV-visible spectroscopy analysis was conducted using METASH X-8S. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with Bruker AVANCE Ⅲ–400 (400 MHz, ^{1}H at 400 MHz, ^{13}C at 101 MHz).^{19}F NMR spectra were recorded on Bruker AVANCE Ⅲ–400.Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C). Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Energy Chemical and were used as received.

The Parameters of the Blue LEDs

Test Report of LED Photoelectric Test System

Test project:	LED spectral analysis	
Test equipment:	Photochromic-electric integrated test system	
The test identification	Product model: 3 W Blue LED	
	Ambient temperature: 27 ℃	Ambient humidity: 65%
	Test organization: spectrotest department	

Spectral relative energy distribution curve



Wavelength/nm

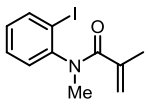
Spectrum parameter		Photoelectric parameter	
peak wavelength:	453.6 nm	lighting current:	3.0 mA
main wavelength:	460.2 nm	preheating time:	500 ms
centroid wavelength:	445.7 nm	test current:	700.0 mA
central wavelength:	446.0 nm	direct voltage:	3.52 V
half-wave width:	22.0 nm	light flow:	40547.6 mlm
colour temperature:	K	light efficiency:	16.456 lm/w
chromaticity coordinate (x, y):	0.1467, 0.0349	optical power:	896.0946 mv
chromaticity coordinate (u, v):	0.1877, 0.0670	backward voltage:	5.00 V
CRI (color rendering index):	0	leakage current:	0.0 μA
colour purity:	0.984		

Note:Guanghong 45, 460

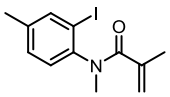
-462

Syntheses of *N*-Aryl Acrylamide

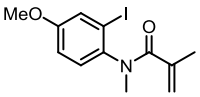
The amides were prepared according to the previously reported literature. The **1a~f**[1], **1j**[1], **5-7**[1], are known compounds, **1m, 1n** are unknown compounds.



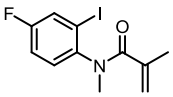
1a



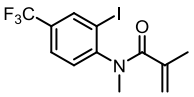
1b



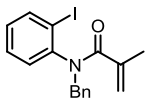
1c



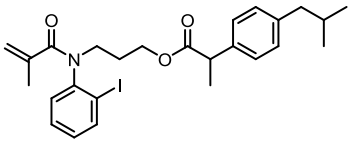
1d



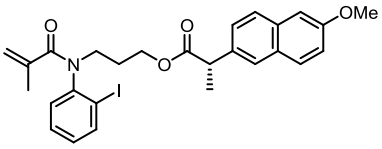
1e



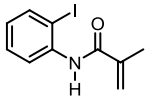
1f



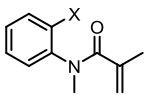
1g



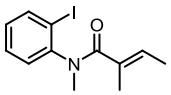
1h



1j



X = Br, 1a-Br
X = Cl, 1a-Cl



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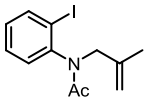

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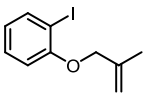
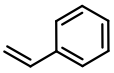
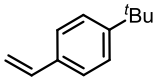


7

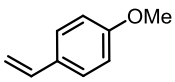
The styrene **2f**[2], **2g**[3], **2h**[4], **2i**[5], **2n**[6], and **2t**[7], were prepared according to the previously reported literature. The others are commercially available and were used as received.



2a



2b



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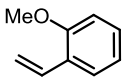
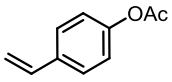


2d



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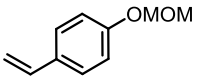
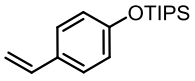
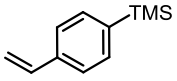


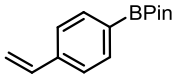
2f



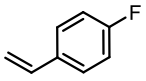
2g



2h



2i



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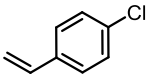
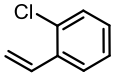
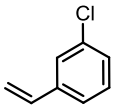


2k



2l



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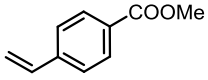
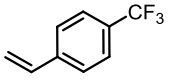
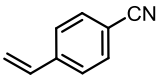


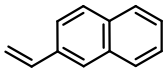
2n



2o



2p



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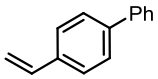

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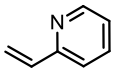
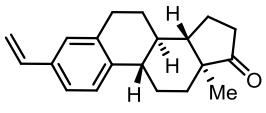
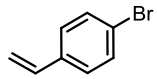


2s



2t



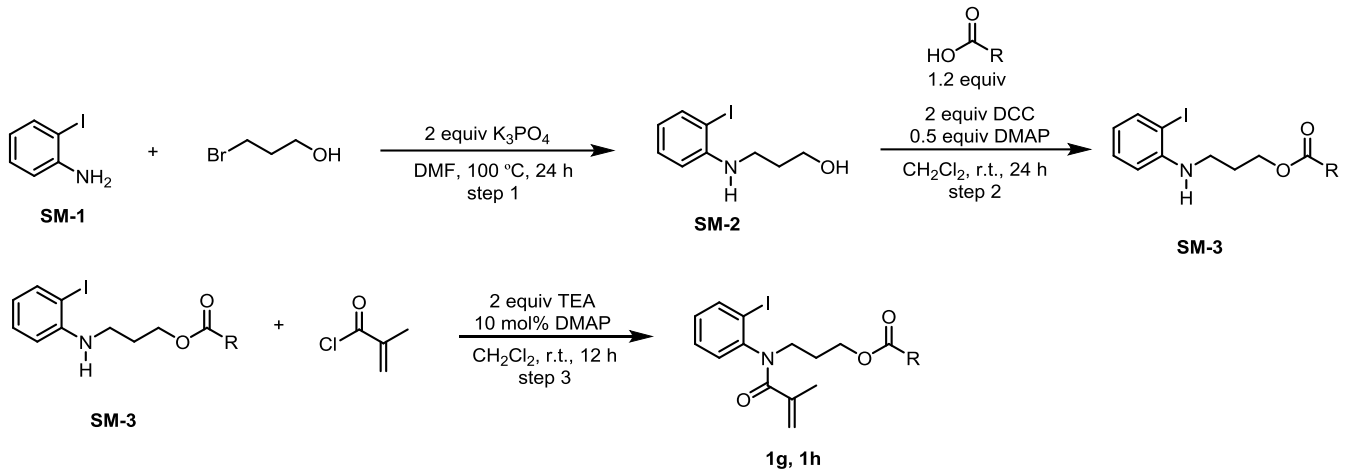
2u

2v

2w

Experimental Section

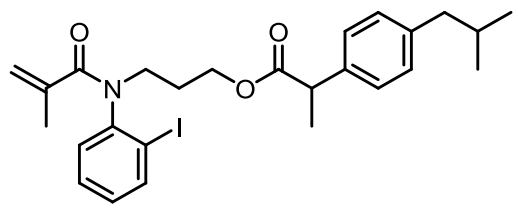
Procedure for the Preparation of *N*-Aryl Acrylamide 1g and 1h



Step 1: To a solution of the **SM-1** (1.1 g, 5.0 mmol, 1.0 equiv.) in DMF (1.67 M) under atmosphere was added K_3PO_4 (2.1 g, 10 mmol, 2 equiv), 3-bromopropan-1-ol (1.4 g, 10 mmol, 2 equiv). After stirring for 24 h at 100 °C in a sealed tube, after removal of the solvent, the resulting residue was added saturated H_2O and EtOAc stirred for 30 minutes. Then, the layers were separated. Purification by column chromatography on silica geleluting with petroleum ether: ethyl acetate = 10:1 gave **SM-2** in 45% isolated yield (602 mg).

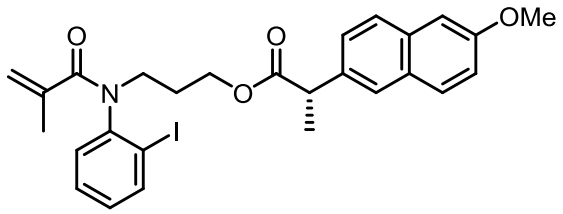
Step 2: To a solution of **SM-2** in anhydrous CH_2Cl_2 (0.2 M) at room temperature, under air was added Ibuprofen (743 mg, 3.6 mmol, 1.2 equiv). After stirring for 24 h at room temperature in a sealed tube, after removal of the solvent. Then the resulting **SM-3** used directly for the next step without further purification.

Step 3: To a solution of **SM-3** in anhydrous CH_2Cl_2 (0.3 M) and TEA (607 mg, 6 mmol, 2 equiv) at room temperature, methacryloyl chloride (376 mg, 3.6 mmol, 1.2 equiv.) was added dropwise over 30 minutes. The reaction was vigorously stirred at room temperature for 20 hours. The solvent was removed in vacuum. The resulting residue was added saturated H_2O and CH_2Cl_2 stirred for 30 minutes. Then, the layers were separated. Purification by column chromatography on silica geleluting with petroleum ether: ethyl acetate = 5:1 gave **1g** in 74% isolated yield (1.2 g).



1g

3-(*N*-(2-iodophenyl)methacrylamido)propyl 2-(4-isobutylphenyl)propanoate (1g). Isolated yield = 74% on 3 mmol scale; colourless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.35– 7.31 (m, 3H), 7.07 – 6.99 (m, 3H), 4.99 (d, *J* = 18.4 Hz, 2H), 4.21 – 4.06 (m, 3H), 3.65 (p, *J* = 7.2 Hz, 1H), 3.23 (m, 1H), 2.43 (d, 2H), 2.04 – 1.78 (m, 6H), 1.45 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.6, 171.5, 145.0, 140.4, 140.2, 137.6, 130.6, 129.3, 129.3, 129.1, 127.2, 127.1, 118.9, 100.0, 62.5, 62.4, 46.2, 46.1, 45.1, 30.2, 26.6, 22.5, 20.6, 18.5. **HRMS (ESI)** calcd for $C_{26}H_{33}INO_3$ $[M+H]^+$: 534.1500, found 534.1498.



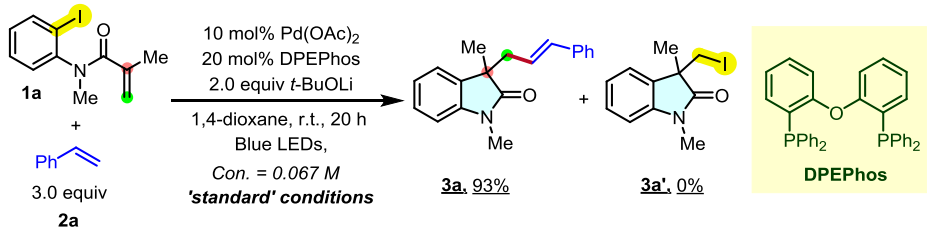
1h

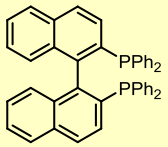
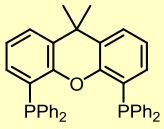
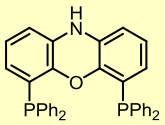
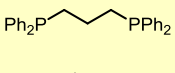
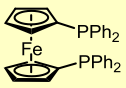
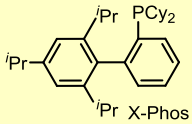
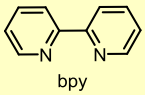
3-(*N*-(2-iodophenyl)methacrylamido)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (1h). Isolated yield = 89% on 1.1 mmol scale; colourless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 – 7.79 (m, 1H), 7.69 – 7.62 (m, 3H), 7.35 (ddd, *J* = 8.4, 3.2, 2.0 Hz, 1H), 7.26 (s, 2H), 7.14 – 7.09 (m, 2H), 7.04 (td, *J* = 8.0, 1.6 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 2H), 4.13 (p, *J* = 7.6, 6.8 Hz, 3H), 3.91 (d, *J* = 0.8 Hz, 3H), 3.81 (t, *J* = 7.2 Hz, 1H), 3.19 – 3.17 (m, 1H), 1.96– 1.80 (m, 5H), 1.54 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.6, 171.5, 157.6, 145.0, 140.3, 140.2, 135.6, 133.7, 130.5, 129.4, 129.3, 129.0, 128.9, 127.2, 127.2, 126.2, 125.9, 118.9, 105.6, 99.9, 62.5, 55.4, 46.2, 45.4, 26.6, 20.6, 18.5. **HRMS (ESI)** calcd for $C_{27}H_{32}IN_2O_4$ $[M+NH_4]^+$: 575.1401. found 575.1404.

Reaction Optimization

Table S1. Optimization for the Radical Cascade Domino Heck Coupling Reaction

.



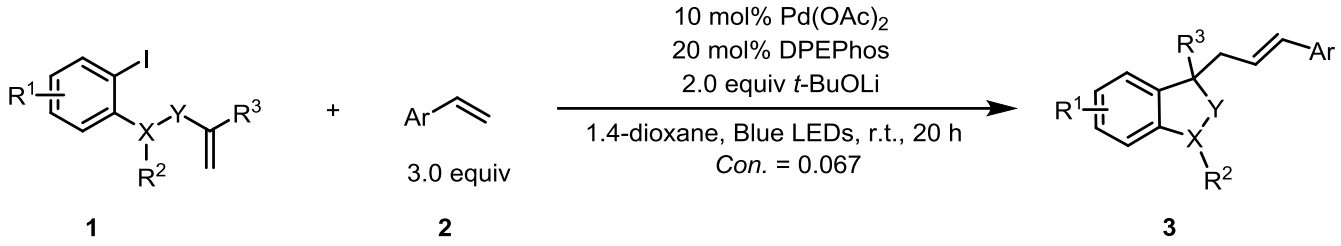
Entry	Variations from the 'standard' conditions	Yield (%) of **3a/3a'**[a]
1	Without **$Pd(OAc)_2$ (C1)**	0/0
2	Without **Blue LEDs**	0/0
3	Without ***t*-BuOLi (B1)**	19/33
4	Without **DPEPhos (L1)**	0/31
5	**C2-5** instead of **$Pd(OAc)_2$**	Listed below
6	**L2-8** instead of **DPEPhos**	Listed below
7	**B2-9** instead of ***t*-BuOLi**	Listed below
8	carried out in air	30/65
9	Without **Blue LEDs,** carried out in 80 °C	0/0
10	solvent = THF	74/0
11	solvent = PhH	59/34
12	solvent = Ph-F	60/27
13	solvent = DMSO	0/0
$Pd(PPh_3)_4$ **C2,** 75/0	$Pd_2(dba)_3$ **C3**, 89/0	$Pd(TFA)_2$ **C4,** 91/0	$(PPh_3)_2PdCl_2$ **C5,** 92/0
 *rac*-BINAP **L2**, 16/62	 XantPhos **L3**, 89/0	 *N*-XantPhos **L4**, 28/31	 dppp **L5**, 0/0
 dppf **L6**, 0/0	 **L7**, 6/32	 **L8**, 0/0	 bpy **L9**, 0/0
K_2CO_3 **B2**, 31/64	K_3PO_4 **B3**, 62/30	$NaHCO_3$ **B4**, 23/50	Cs_2CO_3 **B5**, 63/0
NaOAc **B6**, 25/45	*t*-BuONa **B7**, 58/0	*t*-BuOK **B8**, 0/0	Cy_2NMe **B9**, 71/26

[a]Each reaction was run on a 0.1 mmol scale in a sealed 4 mL vial for 20 h; [b]Yields of **3a** and **3a'** were determined by ^1H NMR using CH_2Br_2 as the internal standard. Cy = cyclohexane, dba = dibenzylideneacetone, TFA = trifluoroacetate.

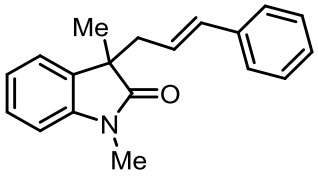
Our investigations began with the reaction of *N*-(2-iodophenyl)-acrylamide **1a** and styrene **2a** as the model substrates. Through extensive optimization, the desired domino Heck product **3a** was successfully obtained in a yield of 93% with complete (*E*)-selectivity. Notably, no carboiodination byproduct **3a'** was observed. The reaction conditions involved the use of $Pd(OAc)_2$, DPEPhos as the metal/ligand combination, and ^{t}BuOLi as the base in 1,4-dioxane under blue LED irradiation. The necessity of each reactant was investigated through control experiments. It was evident that both the palladium catalyst and blue light were essential for the desired transformation (entries 1-2). Without the base, the reaction yielded **3a** in 19% yield, accompanied by a 33% yield of the carboiodination side product **3a'** (entry 3). In the absence of DPEPhos, carboiodination of the olefin became the dominant pathway, resulting in a 31% yield of **3a'** (entry 4). Additionally, various other Pd(0) and Pd(II) complexes also showed high efficiencies (entry 5). Subsequently, a series of ligands were examined (entry 6). Xantphos (**L3**) yielding comparable results, the use of *rac*-BINAP and *N*-XantPhos (**L2** and **L4**) exhibited lower efficiency. Other mono- or bidentate P/N ligands (**L5-L9**) gave sluggish results. Investigation of different bases (entry 7) revealed the crucial role of ^{t}BuOLi in controlling chemoselectivity. Cs_2CO_3 and ^{t}BuONa provided moderate yields of a single domino Heck product **3a**, while other inorganic bases such as K_2CO_3, K_3PO_4, $NaHCO_3$, NaOAc, and organic base Cy_2NMe resulted in significant formation of undesired carboiodination byproducts **3a'**. KO^{t}Bu completely inhibited the reaction. When the reaction was conducted in ambient air, the desired product **3a** was obtained in low yield, accompanied by the formation of **3a'** with a 65% yield. This indicates that the presence of oxygen reduces the efficiency of the radical domino Heck coupling (entry 8). Notably, under the heating conditions, the reaction was shut down (entry 9). A survey of various solvents revealed that 1,4-dioxane was the optimal choice. Polar solvents such as THF also yielded the desired product in good yield. However, nonpolar solvents like PhH and PhF gave moderate yields with a significant amount of carboiodination byproduct. DMSO did not show any reactivity in this reaction (entries 10-13).

General Procedure of the Radical cascade Domino Heck Reaction

Typical procedure for the synthesis of product 3

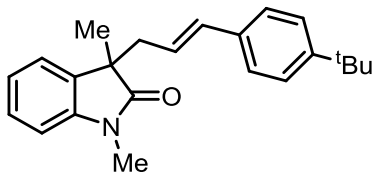


An oven-dried 4.0 mL vial was charged with amide **1** (0.2 mmol，1.0 equiv.), alkene **2** (0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 3 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LEDs lamps for 20 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3**.



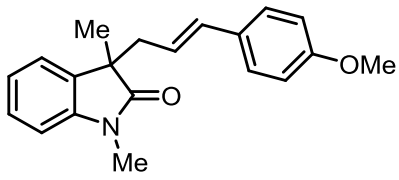
3a

3-Cinnamyl-1,3-dimethylindolin-2-one (3a). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), styrene (62.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 93% isolated yield (48.7 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.17 (m, 7H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.88 (ddd, *J* = 15.6, 8.0, 7.2 Hz, 1H), 3.18 (s, 3H), 2.70 – 2.60 (m, 2H), 1.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 143.1, 137.2, 133.6, 133.5, 128.4, 127.8, 127.1, 126.1, 124.2, 122.9, 122.4, 108.0, 48.6, 41.6, 26.1, 22.5. The spectroscopic data match the reported literature[8].



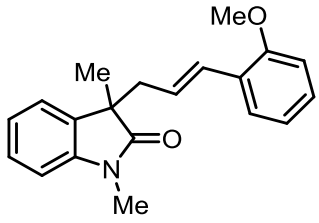
3b

(*E*)-3-(3-(4-(*tert*-butyl)phenyl)allyl)-1,3-dimethylindolin-2-one (3b). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-(tert-butyl)-4-vinylbenzene (96.2 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 94% isolated yield (59.4 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 5.85 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.18 (s, 3H), 2.64 (ddd, *J* = 8.0, 4.0, 1.2 Hz, 2H), 1.28 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 150.2, 143.1, 134.5, 133.6, 133.4, 127.8, 125.9, 125.3, 123.3, 122.9, 122.3, 108.0, 48.6, 41.6, 34.5, 31.2, 26.2, 22.6. The spectroscopic data match the reported literature[9].



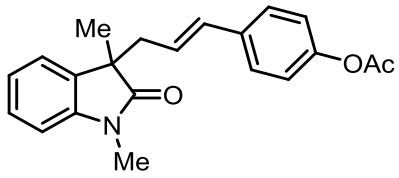
3c

(*E*)-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (3c). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-methyl-4-vinylbenzene (98.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 94% isolated yield (57.8 mg) and *E*/*Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 2H), 7.14 – 7.12 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 – 6.72 (m, 3H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 3.76 (s, 3H), 3.17 (s, 3H), 2.67 – 2.57 (m, 2H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 158.8, 143.1, 133.6, 133.0, 130.0, 127.7, 127.2, 122.9, 122.3, 121.9, 113.7, 107.9, 55.2, 48.6, 41.6, 26.1, 22.4. The spectroscopic data match the reported literature[9].



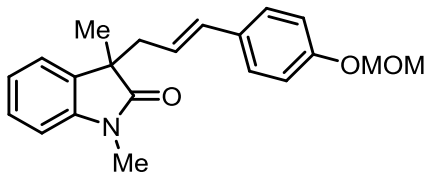
3d

(*E*)-3-(3-(2-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (3d). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-2-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 95% isolated yield (58.0 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 2H), 7.19 – 7.15 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (dddd, *J* = 10.0, 9.2, 7.6, 1.2 Hz, 3H), 6.67 – 6.63 (m, 1H), 5.90 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 3.77 (s, 3H), 3.19 (s, 3H), 2.71 – 2.60 (m, 2H), 1.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.3, 156.4, 143.1, 133.7, 128.5, 128.2, 127.7, 126.7, 126.5, 124.9, 123.1, 122.3, 120.5, 110.8, 107.9, 55.4, 48.6, 42.0, 26.1, 22.3. The spectroscopic data match the reported literature[9].



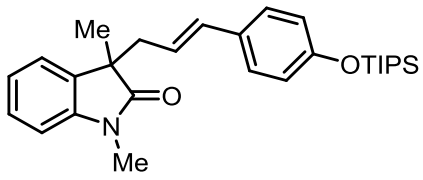
3e

(*E*)-4-(3-(1,3-dimethyl-2-oxoindolin-3-yl)prop-1-en-1-yl)phenyl acetate (3e). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 4-vinylphenyl acetate (97.4 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 62% isolated yield (41.6 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.18 (m, 4H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 – 6.94 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.82 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.19 (s, 3H), 2.65 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.28 (s, 3H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.1, 169.5, 149.7, 143.1, 135.0, 133.4, 132.6, 127.9, 127.1, 124.5, 122.9, 122.4, 121.5, 108.0, 48.6, 41.5, 26.1, 22.6, 21.1. **HRMS (ESI)** calcd for $C_{21}H_{21}NO_3Na$ $[M+Na]^+$: 358.1414, found 358.1407.



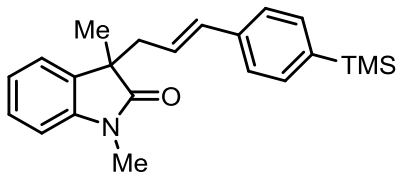
3f

(*E*)-3-(3-(4-(methoxymethoxy)phenyl)allyl)-1,3-dimethylindolin-2-one (3f). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-(methoxymethoxy)-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:8) afforded the title product in 98% isolated yield (64.2 mg) and *E/Z* = 18:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 8:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.21 (m, 2H), 7.13 – 7.04 (m, 3H), 6.92 – 6.90 (m, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.75 (ddd, *J* = 15.6, 8.0, 7.2 Hz, 1H), 5.13 (s, 2H), 3.45 (s, 3H), 3.18 (s, 3H), 2.62 (ddd, *J* = 8.0, 3.6, 1.2 Hz, 2H), 1.41 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 156.4, 143.1, 133.6, 132.9, 131.2, 127.8, 127.2, 122.9, 122.4, 122.3, 116.1, 107.9, 94.3, 55.9, 48.6, 41.6, 26.1, 22.5. **HRMS (ESI)** calcd for $C_{21}H_{27}N_2O_3$ $[M+NH_4]^+$: 355.2016, found 355.2014.



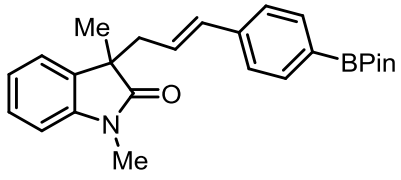
3g

(*E*)-1,3-dimethyl-3-(3-(4-((triisopropylsilyl)oxy)phenyl)allyl)indolin-2-one (3g). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), triisopropyl(4-vinylphenoxy)silane (165.8 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:8) afforded the title product in 63% isolated yield (56.6 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.22 (m, 2H), 7.07 (dd, *J* = 8.0, 6.4 Hz, 3H), 6.84 – 6.74 (m, 3H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (ddd, *J* = 15.6, 8.0, 7.2 Hz, 1H), 3.18 (s, 3H), 2.65 – 2.56 (m, 2H), 1.41 (s, 3H), 1.27 – 1.19 (m, 3H), 1.08 (d, *J* = 7.2 Hz, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.3, 155.4, 143.1, 133.7, 133.2, 130.2, 127.7, 127.2, 123.0, 122.3, 121.8, 119.7, 107.9, 48.6, 41.6, 26.1, 22.4, 17.9, 12.6. **HRMS (ESI)** calcd for $C_{28}H_{40}NO_2Si$ $[M+H]^+$: 450.2823, found 450.2815.



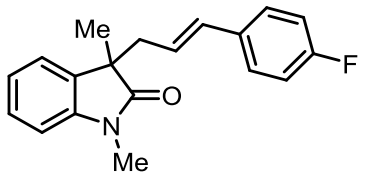
3h

(*E*)-1,3-dimethyl-3-(3-(4-(trimethylsilyl)phenyl)allyl)indolin-2-one (3h). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), trimethyl(4-vinylphenyl)silane (105.8 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 68% isolated yield (47.2 mg) and *E/Z* =15:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.39 (m, 2H), 7.28 – 7.17 (m, 4H), 7.05 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.91 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.18 (s, 3H), 2.65 (dt, *J* = 7.6, 1.2 Hz, 2H), 1.41 (s, 3H), 0.23 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 181.4, 144.3, 140.5, 138.8, 134.8, 134.7, 134.6, 129.0, 126.7, 125.7, 124.1, 123.5, 109.2, 49.8, 42.8, 27.3, 23.8, 0.0. **HRMS (ESI)** calcd for $C_{22}H_{31}N_2OSi$ $[M+NH_4]^+$: 367.2200, found 367.2196.



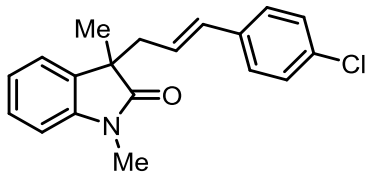
3i

(*E*)-1,3-dimethyl-3-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl)indolin-2-one (3i). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (138.2 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 95% isolated yield (59.0 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.67 (m, 2H), 7.28 – 7.18 (m, 5H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.95 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 3.17 (s, 3H), 2.68 – 2.60 (m, 2H), 1.42 (s, 3H), 1.32 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 143.1, 139.9, 134.9, 133.7, 133.4, 127.8, 125.4, 125.3, 122.9, 122.4, 108.0, 83.7, 48.6, 41.7, 26.1, 24.8, 24.8, 22.5. **HRMS (ESI)** calcd for $C_{25}H_{34}BN_2O_3$ $[M+NH_4]^+$: 421.2657, found 421.2651.



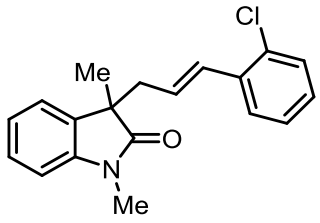
3j

(*E*)-3-(3-(4-fluorophenyl)allyl)-1,3-dimethylindolin-2-one (3j). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-fluoro-4-vinylbenzene (73.1 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.2 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 77% isolated yield (43.5 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.21 (m, 2H), 7.16 – 7.12 (m, 2H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.83 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.32 – 6.28 (m, 1H), 5.78 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.18 (s, 3H), 2.64 (dd, *J* = 8.0, 1.2 Hz, 2H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.1, 160.2 (d, $^1J_{C-F}$ = 247.2 Hz), 143.1, 133.5, 133.3 (d, $^3J_{C-F}$ = 3.3 Hz), 132.4, 127.8, 127.5(d, $^3J_{C-F}$ = 8.0 Hz), 123.9 (d, $^4J_{C-F}$ = 2.3 Hz), 123.9, 122.6 (d, $^2J_{C-F}$ = 46.3 Hz), 115.2 (d, $^2J_{C-F}$ = 21.7 Hz), 108.0, 48.6, 41.5, 26.1, 22.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.0. **HRMS (ESI)** calcd for $C_{19}H_{19}FNO$ $[M+H]^+$: 296.1445, found 296.1441.



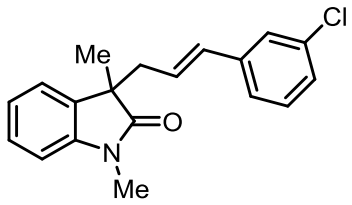
3k

(*E*)-3-(3-(4-chlorophenyl)allyl)-1,3-dimethylindolin-2-one (3k). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-chloro-4-vinylbenzene (83.1 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 83% isolated yield (48.9 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.18 (m, 4H), 7.11 – 7.06 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 5.91 – 5.79 (m, 1H), 3.18 (d, *J* = 1.6 Hz, 3H), 2.64 (d, *J* = 7.6 Hz, 2H), 1.42 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 143.1, 135.6, 133.4, 132.7, 132.4, 128.5, 127.9, 127.3, 124.9, 122.8, 122.4, 108.0, 48.6, 41.6, 26.1, 22.5. The spectroscopic data match the reported literature[9].



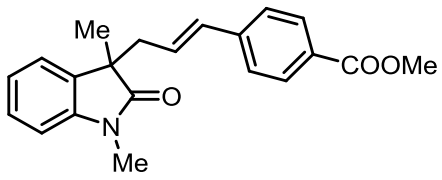
3l

(*E*)-3-(3-(2-chlorophenyl)allyl)-1,3-dimethylindolin-2-one (3l). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-chloro-2-vinylbenzene (83.1 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5. mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 80% isolated yield (49.7 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.23 (m, 4H), 7.15 – 7.06 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 5.88 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.20 (s, 3H), 2.69 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 143.0, 135.5, 133.4, 132.7, 160.2, 129.5, 128.2, 127.9, 127.3, 126.9, 126.6, 122.9, 122.5, 108.0, 48.5, 41.6, 26.2, 22.5. **HRMS (ESI)** calcd for $C_{19}H_{19}ClNO$ $[M+H]^+$: 312.1150, found 312.1147.



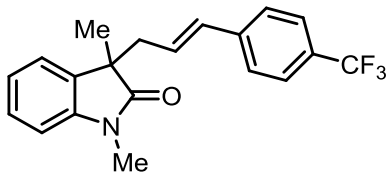
3m

(*E*)-3-(3-(3-chlorophenyl)allyl)-1,3-dimethylindolin-2-one (3m). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-chloro-3-vinylbenzene (83.1 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 78% isolated yield (48.5 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 2H), 7.17 – 7.10 (m, 3H), 7.10 – 7.04 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.89 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.19 (s, 3H), 2.65 (dd, *J* = 7.7, 1.2 Hz, 2H), 1.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 143.1, 139.0, 134.3, 133.4, 132.4, 129.6, 127.9, 127.1, 126.0, 125.8, 124.4, 122.9, 122.5, 108.1, 48.5, 41.5, 26.2, 22.6. **HRMS (ESI)** calcd for $C_{19}H_{22}ClN_2O$ $[M+NH_4]^+$: 329.1415, found 329.1410.



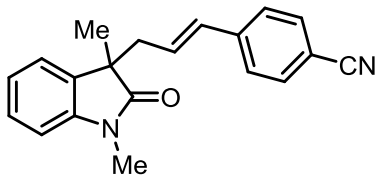
3n

Methyl (*E*)-4-(3-(1,3-dimethyl-2-oxoindolin-3-yl)prop-1-en-1-yl)benzoate (3n). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), methyl 4-vinylbenzoate (97.4 mg, 0.4 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5 afforded the title product in 89% isolated yield (60.2 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.00 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.88 (s, 3H), 3.18 (s, 3H), 2.68 (dd, *J* = 7.5, 1.3 Hz, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 166.8, 143.0, 141.6, 133.3, 132.8, 129.8, 128.6, 128.0, 127.2, 126.0, 122.8, 122.5, 108.0, 52.0, 48.5, 41.6, 26.1, 22.6. **HRMS (ESI)** calcd for $C_{21}H_{25}N_2O_3$ $[M+NH_4]^+$: 353.1860, found 353.1858.



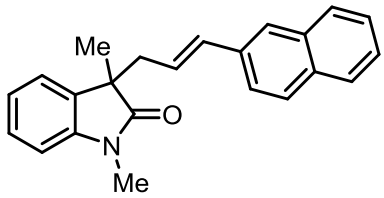
3o

(*E*)-1,3-dimethyl-3-(3-(4-(trifluoromethyl)phenyl)allyl)indolin-2-one (3o). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-(trifluoromethyl)-4-vinylbenzene (103.2 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 81% isolated yield (55.2 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 4H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.97 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.18 (s, 3H), 2.75 – 2.63 (m, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 143.1, 140.6, 133.3, 132.4, 129.0(q, $^2J_{C-F}$ = 32.5 Hz), 128.0, 127.1, 126.2, 125.3(q, $^3J_{C-F}$ = 3.8Hz), 124.2(q, $^1J_{C-F}$ = 272.9 Hz), 122.8, 122.5, 108.1, 48.6, 41.6, 26.1, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. **HRMS (ESI)** calcd for $C_{20}H_{19}F_3NO$ $[M+H]^+$: 346.1413, found 346.1409.



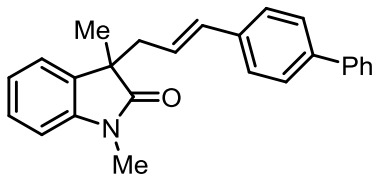
3p

(*E*)-4-(3-(1,3-dimethyl-2-oxoindolin-3-yl)prop-1-en-1-yl)benzonitrile (3p). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 4-vinylbenzonitrile (77.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 82% isolated yield (49.5 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.50 (m, 2H), 7.31 – 7.21 (m, 4H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.38 – 6.33 (m, 1H), 6.01 (ddd, *J* = 15.8, 7.9, 7.1 Hz, 1H), 3.18 (s, 3H), 2.74 – 2.66 (m, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.9, 143.1, 141.6, 133.2, 132.3, 132.1, 128.6, 128.1, 126.6, 122.8, 122.6, 119.0, 110.4, 108.2, 48.6, 41.6, 26.2, 22.7. **HRMS (ESI)** calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$: 303.1492, found 303.1484.



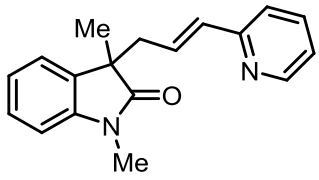
3q

(*E*)-1,3-dimethyl-3-(3-(naphthalen-2-yl)allyl)indolin-2-one (3q). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 2-vinylnaphthalene (92.4 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 77% isolated yield (50.6 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.53 (m, 2H), 7.49 – 7.47 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 5.93 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.19 (s, 3H), 2.69 – 2.66 (m, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 143.1, 140.6, 139.9, 136.2, 133.5, 133.2, 128.7, 127.8, 127.2, 127.1, 126.8, 126.5, 124.3, 122.9, 122.4, 108.0, 48.6, 41.6, 26.1, 22.5. The spectroscopic data match the reported literature[9].



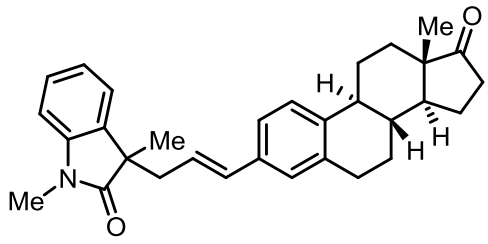
3r

(*E*)-3-(3-([1,1'-biphenyl]-4-yl)allyl)-1,3-dimethylindolin-2-one (3r). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 4-vinyl-1,1'-biphenyl (100.2 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 72% isolated yield (50.6 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.54 (m, 2H), 7.49 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 – 7.23 (m, 5H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.38 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.93 (ddd, *J* = 15.6, 8.0, 7.2 Hz, 1H), 3.19 (s, 3H), 2.69 – 2.66 (m, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 143.2, 140.7, 140.0, 136.3, 133.6, 133.3, 128.8, 127.9, 127.3, 127.2, 126.9, 126.6, 124.4, 123.0, 122.5, 108.1, 48.7, 41.7, 26.2, 22.6. **HRMS (ESI)** calcd for $C_{25}H_{27}N_2O$ $[M+NH_4]^+$: 371.2118, found 371.2113.



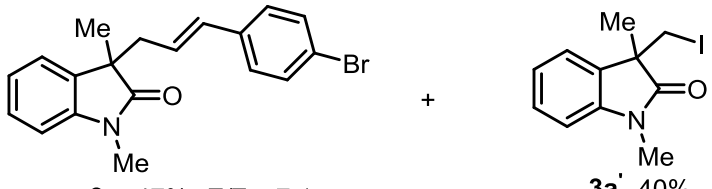
3s

(*E*)-1,3-dimethyl-3-(3-(pyridin-2-yl)allyl)indolin-2-one (3s). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 2-vinylpyridine (62.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 84% isolated yield (46.4 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (ddd, *J* = 4.8, 2.0, 0.8 Hz, 1H), 7.56 (td, *J* = 7.6, 2.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.15 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.46 (q, *J* = 2.0 Hz, 2H), 3.20 (s, 3H), 2.70 (qdd, *J* = 13.6, 4.4, 2.0 Hz, 2H), 1.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.1, 155.3, 149.3, 143.0, 136.3, 133.7, 133.4, 129.0, 127.8, 123.1, 122.5, 121.9, 121.2, 108.0, 48.3, 41.3, 26.2, 22.6. **HRMS (ESI)** calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279.1492, found 279.1495.



3t

1,3-dimethyl-3-((*E*)-3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)allyl)indolin-2-one (3t). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (168.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 67% isolated yield (60.1 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.21 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.82 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 5.87 (dddd, *J* = 15.6, 8.0, 7.2, 2.8 Hz, 1H), 3.18 (s, 3H), 2.86 (dd, *J* = 9.2, 4.0 Hz, 2H), 2.65 – 2.61 (m, 2H), 2.53 – 2.46 (m, 1H), 2.38 (dq, *J* = 9.2, 2.4 Hz, 1H), 2.28 – 2.23 (m, 1H), 2.18 – 1.92 (m, 5H), 1.67 – 1.46 (m, 5H), 1.41 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.3, 143.1, 138.9, 136.5, 134.9, 133.7, 133.4, 127.8, 126.9, 125.5, 125.4, 123.6, 123.0, 122.4, 108.0, 50.5, 48.7, 48.0, 44.4, 41.6, 38.2, 35.9, 31.6, 29.4, 26.5, 26.2, 25.7, 22.6, 21.6, 13.8. **HRMS (ESI)** calcd for $C_{31}H_{36}NO_2$ $[M+H]^+$: 454.2741, found 454.2733.

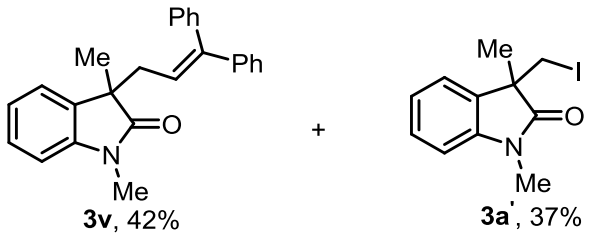


3u, 47%, *E*/*Z* = 7:1 + **3a'**, 40%

(*E*)-3-(3-(4-bromophenyl)allyl)-1,3-dimethylindolin-2-one (3u). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), 1-bromo-4-vinylbenzene (109.9 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the desired product **3u** (*E*/*Z* = 13:1) in 47% yield and byproduct **3a'** in 40% yield as a mixture colorless oil (52.1 mg); R_f = 0.5 (Hexane: Ethyl acetate = 10:1).

(*E*)-3-(3-(4-bromophenyl)allyl)-1,3-dimethylindolin-2-one (3u). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.29 – 7.20 (m, 3H), 7.13 – 7.03 (m, 3H), 6.82 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.29 – 6.25 (d, *J* = 15.6, 1H), 5.86 (dt, *J* = 15.6, 7. 6Hz, 1H), 3.17 (s, 3H), 2.64 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.0, 143.0, 136.1, 133.4, 132.4, 131.4, 127.9, 127.6, 125.1, 122.6, 122.4, 120.9, 108.0, 48.5, 41.6, 26.1, 22.5. The spectroscopic data match the reported literature[10].

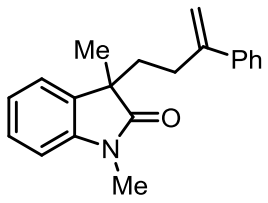
3-(Iodomethyl)-1,3-dimethylindolin-2-one (3a'). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 7.10 (td, J = 7.6, 1.2 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 3.51 (d, J = 9.6 Hz, 1H), 3.42 (d, J = 9.6 Hz, 1H), 3.25 (s, 3H), 1.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.9, 143.1, 132.6, 128.6, 122.8, 122.7, 108.3, 48.6, 26.3, 22.9, 10.8. The spectroscopic data match the reported literature[1].



3v, 42% **3a'**, 37%

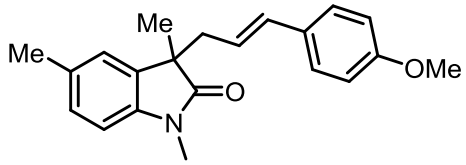
3-(3,3-Diphenylallyl)-1,3-dimethylindolin-2-one (3v). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), ethene-1,1-diyldibenzene (108.2 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the desired product **3v** in 42% and byproduct **3a'** in 37% as a mixture colorless oil (51.2 mg); R_f = 0.5 (Hexane: Ethyl acetate = 10:1).
3-(3,3-Diphenylallyl)-1,3-dimethylindolin-2-one (3v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.28 – 7.24 (m, 1H), 7.19 – 7.15 (m, 3H), 7.14 – 7.06 (m, 1H), 7.02 – 6.96 (m, 5H), 6.91 – 6.84 (m, 1H), 5.74 (dd, *J* = 7.6, 7.2 Hz, 1H), 3.24 (s, 3H), 2.63 (m, 2H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.3, 144.4, 143.2, 142.5, 139.6, 133.7, 130.0, 128.5, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.2, 127.1, 123.4, 123.1, 122.5, 107.9, 48.5, 38.1, 26.3, 22.8. **HRMS (ESI)** calcd for $C_{25}H_{24}NO$ $[M+H]^+$: 354.1852, found 354.1850.

3-(Iodomethyl)-1,3-dimethylindolin-2-one (3a'). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 1H), 7.28 – 7.16 (m, 1H), 7.11 (td, J = 7.6, 0.8 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 3.52 (d, J = 9.6 Hz, 1H), 3.42 (d, J = 9.6 Hz, 1H), 3.24 (s, 3H), 1.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.0, 143.2, 132.7, 128.7, 122.8, 122.7, 108.3, 48.7, 26.4, 23.0, 10.8. The spectroscopic data match the reported literature[1].



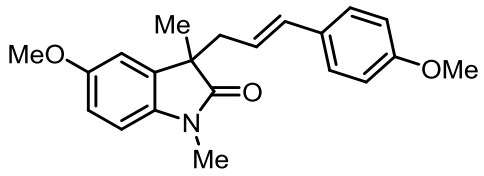
3w

1,3-Dimethyl-3-(3-phenylbut-3-en-1-yl)indolin-2-one (3w). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), prop-1-en-2-ylbenzene (70.9 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 73% isolated yield (42.4 mg) as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.21 (m, 6H), 7.15 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.18 (d, *J* = 1.2 Hz, 1H), 4.94 (d, *J* = 1.2 Hz, 1H), 3.23 (s, 3H), 2.24 – 2.17 (m, 1H), 2.13 – 1.98 (m, 2H), 1.92 – 1.83 (m, 1H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.4, 147.6, 143.4, 140.6, 133.8, 128.3, 127.9, 127.4, 126.0, 122.6, 122.5, 112.6, 108.1, 48.3, 37.2, 30.3, 26.2, 23.9. **HRMS (ESI)** calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1696, found 292.1694.



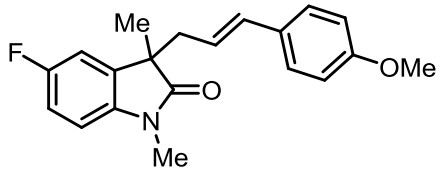
4a

(*E*)-3-(3-(4-methoxyphenyl)allyl)-1,3,5-trimethylindolin-2-one (4a). Following the typical procedure described above, the reaction was carried out by the mixture of **1b** (63.0 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 95% isolated yield (56.2 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.14 – 7.03 (m, 4H), 6.79 – 6.69 (m, 3H), 6.29 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.76 – 5.68 (m, 1H), 3.77 (s, 3H), 3.15 (s, 3H), 2.61 – 2.60 (m, 2H), 2.35 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.3, 158.9, 140.8, 133.8, 132.9, 131.8, 130.2, 128.0, 127.3, 123.8, 122.1, 113.8, 107.7, 55.3, 48.8, 41.7, 26.2, 22.6, 21.2. **HRMS (ESI)** calcd for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$: 344.1621, found 344.1621.



4b

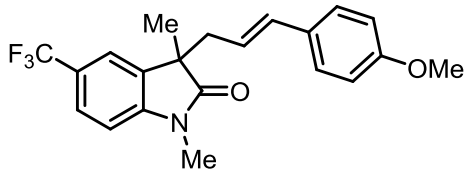
(*E*)-5-methoxy-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (4b). Following the typical procedure described above, the reaction was carried out by the mixture of **1c** (66.2 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.6 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 91% isolated yield (61.2 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 – 7.12 (m, 2H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 3.2 Hz, 3H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.73 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.15 (s, 3H), 2.62 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.9, 158.9, 155.9, 136.7, 135.1, 133.1, 160.2, 127.3, 121.9, 113.8, 111.7, 110.7, 108.2, 55.8, 55.3, 49.2, 41.7, 26.2, 22.6. **HRMS (ESI)** calcd for $C_{21}H_{24}NO_3$ $[M+H]^+$: 338.1751, found 338.1748.



4c

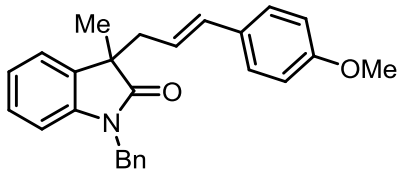
(*E*)-5-fluoro-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (4c). Following the typical procedure described above, the reaction was carried out by the mixture of **1d** (73.8 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 96% isolated yield (57.1 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 – 7.11 (m, 2H), 6.96 (ddt, *J* = 9.2, 8.4, 2.4 Hz, 2H), 6.80 – 6.70 (m, 3H), 6.29 (d, *J* = 15.6 Hz, 1H), 5.70 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.77 (s, 3H), 3.16 (s, 3H), 2.63 – 2.61 (m, 2H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.9, 159.3(d, $^1J_{C-F}$ = 241.1 Hz), 158.0, 139.1(d, $^4J_{C-F}$ = 2.0 Hz), 135.4(d, $^3J_{C-F}$ = 7.8 Hz), 133.3, 129.8, 127.3, 121.3, 114.0(d, $^2J_{C-F}$ = 23.5 Hz), 113.8, 111.2(d, $^2J_{C-F}$ = 24.6 Hz), 108.4(d, $^3J_{C-F}$ = 8.2 Hz), 55.2, 49.2, 41.5, 26.2, 22.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -

120.8. **HRMS (ESI)** calcd for $C_{20}H_{21}FNO_2$ $[M+H]^+$: 326.1551, found 326.1545.



4d

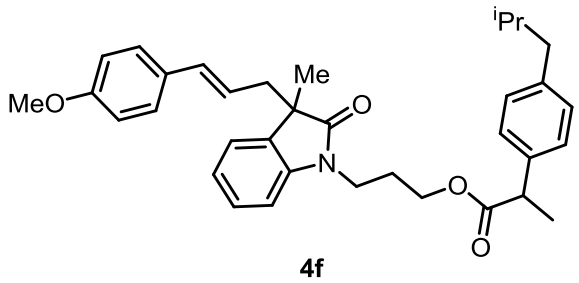
(*E*)-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (4d). Following the typical procedure described above, the reaction was carried out by the mixture of **1e** (73.8 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 93% isolated yield (70.4 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.54 (m, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.14 – 7.11 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.76 (m, 2H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.67 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.77 (s, 3H), 3.20 (s, 3H), 2.65 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 159.1, 146.2, 134.3, 133.8, 129.8, 127.3, 127.2(q, $^1J_{C\text{-}F}$ = 272.1 Hz), 125.7(q, $^3J_{C\text{-}F}$ = 4.1 Hz), 124.6(q, $^2J_{C\text{-}F}$ = 32.5 Hz), 121.0, 120.0(q, $^3J_{C\text{-}F}$ = 3.8 Hz), 113.9, 107.7, 55.2, 48.8, 41.6, 26.3, 22.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.3. **HRMS (ESI)** calcd for $C_{21}H_{21}F_3NO_2$ $[M+H]^+$: 376.1519, found 376.1513.



4e

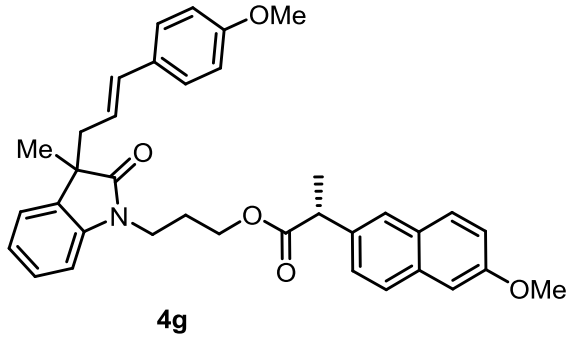
(*E*)-1-benzyl-3-(3-(4-methoxyphenyl)allyl)-3-methylindolin-2-one (4e). Following the typical procedure described above, the reaction was carried out by the mixture of **1f** (63.0 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 98% isolated yield (77.0 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 – 7.22 (m, 1H), 7.15 – 6.97 (m, 9H), 6.79 – 6.75 (m, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 5.66 (ddd, *J* = 15.6, 8.4, 6.4 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.78 (s, 3H), 2.75 (qdd, *J* = 13.2, 7.6, 1.2 Hz, 2H), 1.48 (s, 3H). **^{13}C NMR (101**

MHz, $CDCl_3$) δ 180.2, 158.9, 142.2, 135.6, 133.4, 133.1, 129.9, 128.6, 127.7, 127.3, 127.2, 126.9, 122.8, 122.4, 121.8, 113.8, 109.1, 55.2, 48.9, 43.6, 41.9, 23.3. **HRMS (ESI)** calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$: 384.1964, found 384.1956.



4f

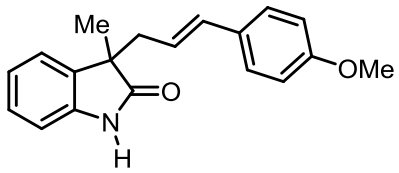
(*E*)-3-(3-(3-(4-methoxyphenyl)allyl)-3-methyl-2-oxoindolin-1-yl)propy 2-(4-isobutylphenyl)propanoate (4f). Following the typical procedure described above, the reaction was carried out by the mixture of **1g** (106.6 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 80% isolated yield (85.1 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 (dt, *J* = 10.4, 3.2 Hz, 3H), 7.16 – 7.01 (m, 6H), 6.77 – 6.74 (m, 2H), 6.52 (dd, *J* = 13.2, 7.6 Hz, 1H), 6.26 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.62 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.91 (dtd, *J* = 15.6, 11.6, 6.0 Hz, 2H), 3.75 (d, *J* = 0.8 Hz, 3H), 3.69 (ddt, *J* = 10.4, 7.2, 5.2 Hz, 2H), 3.47 (dtd, *J* = 14.4, 7.2, 3.2 Hz, 1H), 2.61 (d, *J* = 7.6 Hz, 2H), 2.43 (dd, *J* = 7.2, 2.4 Hz, 2H), 1.84 – 1.78 (m, 3H), 1.50 (dd, *J* = 7.2, 2.4 Hz, 3H), 1.38 (s, 3H), 0.86 (dd, *J* = 6.4, 3.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 174.5, 158.9, 142.4, 140.7, 137.8, 137.7, 133.6, 133.2, 129.9, 129.4, 127.8, 127.2, 123.0, 122.3, 121.7, 113.8, 107.9, 61.8, 55.3, 48.7, 45.2, 45.1, 45.0, 41.9, 36.4, 30.2, 26.9, 22.6, 22.4, 18.4. **HRMS (ESI)** calcd for $C_{35}H_{42}NO_4$ $[M+H]^+$: 540.3108, found 540.3101.



4g

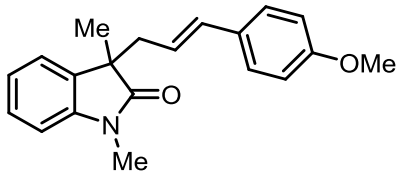
3-(3-((*E*)-3-(4-methoxyphenyl)allyl)-3-methyl-2-oxoindolin-1-yl)propyl (2R)-2-(6-methoxynaphthalen-2-yl)propanoate (4g). Following the typical procedure described above, the reaction was carried out by the mixture of **1h** (111.4 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.5 mg, 0.6 mmol,

3.0 equiv), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 74% isolated yield (83.4 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, CDCl3)** δ 7.73 – 7.69 (m, 3H), 7.43 (m, 1H), 7.23 – 7.05 (m, 6H), 7.02 – 6.871(m, 2H), 6.75 (m, 2H), 6.36 (dd, *J* = 14.4, 7.6 Hz, 1H), 6.25 (d, *J* = 15.6, 1H), 5.60 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.90 (s, 3H), 3.87 – 3.82 (m, 3.6 Hz, 1H), 3.75 (s, 3H), 3.69 (dt, *J* = 14.4, 7.0 Hz, 1H), 3.52 – 3.43 (m, *J* = 14.4, 1H), 2.60 (d, *J* = 7.6 Hz, 2H), 1.81 – 1.77 (m, 2H), 1.58 (dd, *J* = 7.2, 2.8 Hz, 3H), 1.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 174.4, 158.9, 157.7, 142.3, 135.7, 133.8, 133.5, 133.2, 129.9, 129.3, 129.0, 127.8, 127.3, 127.2, 126.2, 126.0, 123.0, 122.2, 121.7, 119.1, 113.8, 107.8, 105.6, 61.8, 55.3, 55.3, 48.7, 45.4, 41.9, 36.5, 26.9, 22.6, 18.4. **HRMS (ESI)** calcd for $C_{36}H_{38}NO_5$ $[M+H]^+$: 564.2744, found 564.2749.



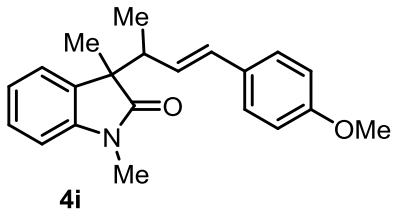
4h

(*E*)-3-(3-(4-methoxyphenyl)allyl)-3-methylindolin-2-one (4h). Following the typical procedure descrybed above, the reaction was carried out by the mixture of **1j** (57.4 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.01 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:15) afforded the title product in 53% isolated yield (30.8 mg) and *E/Z* = 7:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 15:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.11 (m, 2H), 7.06 – 7.02 (m, 1H), 6.87 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.78 – 6.74 (m, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 5.77 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.76 (s, 3H), 2.65 – 2.63 (m, 2H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 182.4, 159.0, 140.2, 134.1, 133.2, 160.2, 127.8, 127.3, 123.4, 122.4, 121.8, 113.8, 109.7, 55.3, 49.1, 41.7, 22.6. **HRMS (ESI)** calcd for $C_{19}H_{20}NO_2$ $[M+H]^+$: 294.1489, found 294.1484.



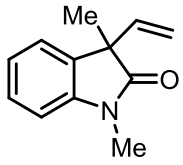
3c

(*E*)-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (3c). Following the typical procedure described above, the reaction was carried out by the mixture of **1a-Br** (50.6 mg, 0.2 mmol, 1.0 equiv), 1-methyl-4-vinylbenzene (98.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 94% isolated yield (57.8 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 2H), 7.14 – 7.12 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 – 6.72 (m, 3H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 3.76 (s, 3H), 3.17 (s, 3H), 2.67 – 2.57 (m, 2H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 158.8, 143.1, 133.6, 133.0, 130.0, 127.7, 127.2, 122.9, 122.3, 121.9, 113.7, 107.9, 55.2, 48.6, 41.6, 26.1, 22.4. The spectroscopic data match the reported literature[9].



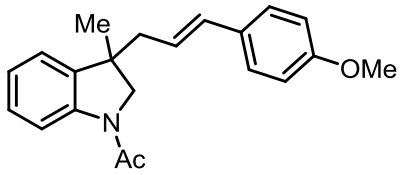
4i

(*E*)-3-(4-(4-methoxyphenyl)but-3-en-2-yl)-1,3-dimethylindolin-2-one (4i). Following the typical procedure described above, the reaction was carried out by the mixture of **5** (63.0 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product **5** in 67% isolated yield (42.4 mg) and *E/Z* = 7:1 and *d.r.* = 1.4:1 as a colorless oil; and byproduct **6** in 25% isolated yield (12.6 mg). R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.15 (m, 4H), 7.11 – 7.01 (m, 1H), 6.89 – 6.75 (m, 3H), 6.51 – 6.26 (m, 1H), 6.14 – 5.82 (m, 1H), 3.83 – 3.75 (m, 3H), 3.41 – 3.11 (m, 3H), 2.75 – 2.68 (m, 1H), 1.38 (s, 3H), 0.89 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$, major)** δ 180.2, 158.8, 143.6, 132.2, 130.2, 129.8, 128.1, 127.4, 127.3, 122.2, 114.0, 113.8, 107.8, 55.3, 51.8, 45.4, 26.0, 21.4, 15.7. **^{13}C NMR (101 MHz, $CDCl_3$, minor)** δ 180.6, 159.1, 143.47, 132.1, 131.4, 130.3, 130.2, 129.9, 127.8, 123.9, 123.1, 114.6, 107.9, 55.4, 51.8, 44.2, 26.1, 22.3, 15.5. **HRMS (ESI)** calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1802, found 322.1799.



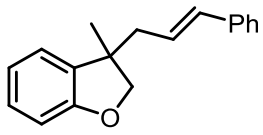
4i'

1,3-Dimethyl-3-vinylindolin-2-one (4i'). Olumn chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product **4i'** in 25% isolated yield (12.6 mg) as a colorless oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.26 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.95 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.17 – 5.11 (m, 2H), 3.22 (s, 3H), 1.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.7, 143.0, 138.1, 132.7, 128.1, 123.8, 122.5, 115.3, 108.2, 51.2, 26.3, 22.4. The spectroscopic data match the reported literature[9].



4j

(*E*)-1-(3-(3-(4-methoxyphenyl)allyl)-3-methylindolin-1-yl)ethan-1-one (4j). Following the typical procedure described above, the reaction was carried out by the mixture of **6** (63.1 mg, 0.2 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (80.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 67% isolated yield (42.5 mg) and *E* only as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 4H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.87 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.94 (d, *J* = 10.4 Hz, 1H), 3.78 (s, 3H), 3.65 (d, *J* = 10.4 Hz, 1H), 2.17 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.4, 153.8, 136.8, 133.6, 127.8, 124.6, 122.7, 122.0, 118.5, 117.8, 117.1, 111.7, 108.7, 55.5, 50.0, 39.8, 38.7, 21.0, 19.0. **HRMS (ESI)** calcd for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$: 344.1621, found 344.1622.

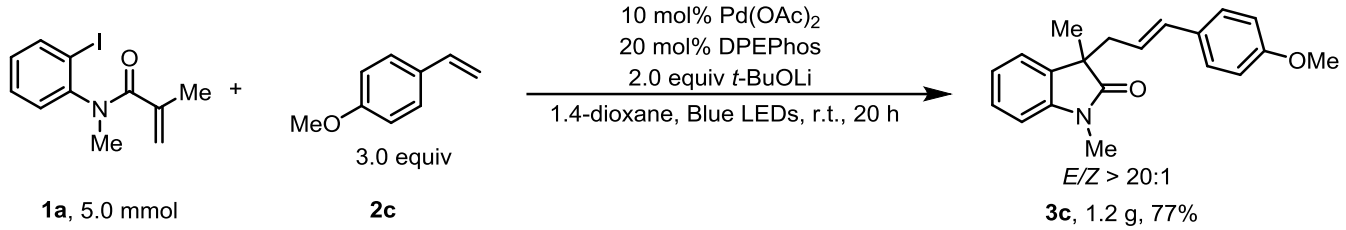


4k

3-Cinnamyl-3-methyl-2,3-dihydrobenzofuran (4k). Following the typical procedure described above, the reaction was carried out by the mixture of **7** (54.8 mg, 0.2 mmol, 1.0 equiv), styrene (62.4 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.6 mg, 0.04 mmol, 20 mol%)

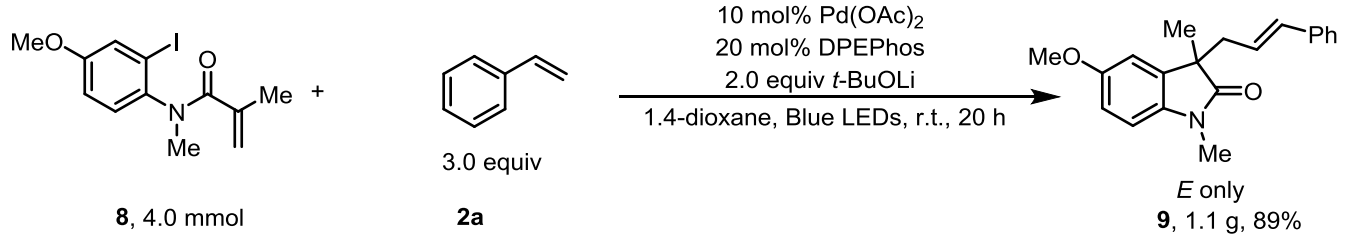
and Cs_2CO_3 (130.4 mg, 0.4 mmol, 2.0 equiv) in 1.4-dioxane (3.0 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 20 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 74% isolated yield (37.0 mg) as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.24 (m, 4H), 7.21 (dh, *J* = 8.4, 2.4, 2.0 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.41 (dt, *J* = 15.6, 1.6 Hz, 1H), 6.11 (ddd, *J* = 15.6, 8.0, 6.8 Hz, 1H), 4.44 (dd, *J* = 8.8, 1.2 Hz, 1H), 4.15 (dd, *J* = 8.8, 1.2 Hz, 1H), 2.51 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.5, 137.3, 134.9, 133.5, 128.5, 128.2, 127.3, 126.2, 125.7, 123.0, 120.5, 109.7, 82.0, 45.7, 44.3, 25.0. The spectroscopic data match the reported literature[11].

Grams Scale Synthesis



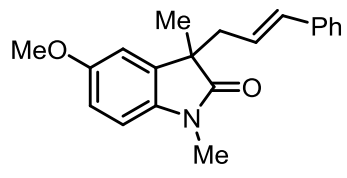
1a, 5.0 mmol **2c** **3c**, 1.2 g, 77%

An oven-dried 75 mL reaction flask was charged with amide **1a** (1.51 g, 5.0 mol, 1.0 equiv.), 1-methoxy-4-vinylbenzene **2c** (2.01 g, 15.0 mmol, 3.0 equiv.), $Pd(OAc)_2$ (112 mg, 0.5 mmol, 10 mol%), DPEPhos (538mg, 1.0 mmol, 20%) and *t*-BuOLi (800 mg, 10.0 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 75 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 20 hours. After completion of the reaction, the resulting mixture was diluted with acetone (100 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to afford **3c** in 77% isolated yield (1.2 g).



8, 4.0 mmol **2a** **9**, 1.1 g, 89%

An oven-dried 60 mL reaction flask was charged with amide **8** (1.32 g, 4.0 mol, 1.0 equiv.), styrene **2a** (1.2 g, 12.0 mmol, 3.0 equiv.), $Pd(OAc)_2$ (90 mg, 0.4 mmol, 10 mol%), DPEPhos (430mg, 0.8 mmol, 20%) and *t*-BuOLi (640 mg, 8.0 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 60 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 20 hours. After completion of the reaction, the resulting mixture was diluted with acetone (100 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to afford **9** in 89% isolated yield (1.1 g).



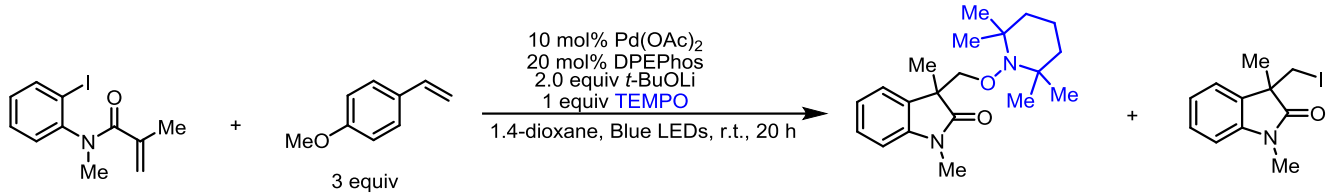
9

3-cinnamyl-5-methoxy-1,3-dimethylindolin-2-one (9). **9** was isolated in 89% yield and *E* only as a

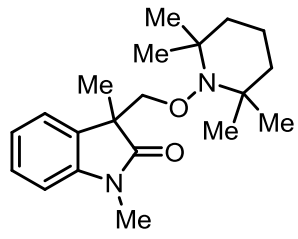
yellow oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.14 (m, 5H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.79 – 6.70 (m, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 5.87 (dt, *J* = 15.6, 7.6Hz, 1H), 3.78 (s, 3H), 3.15 (s, 3H), 2.64 (dd, *J* = 7.6, 1.2 Hz, 2H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.8, 155.9, 137.2, 136.7, 134.9, 133.6, 128.3, 127.1, 126.1, 124.1, 111.7, 110.6, 108.1, 55.8, 49.0, 41.6, 26.2, 22.6. The spectroscopic data match the reported literature[12].

Experimental Procedures for the Mechanistic Studies

The Radical Trapping Experiment with TEMPO

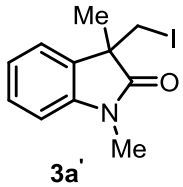


An oven-dried 4.0 mL vial was charged with amide **1a** (60.2mg, 0.2 mmol, 1.0 equiv.), 1-methoxy-4-vinylbenzene **2c** (80.5 mg, 0.6 mmol, 3.0 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.04 mmol, 20 mol%), TEMPO (31.25 mg, 0.2 mmol, 1.0 equiv.) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 3 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LEDs lamps for 20 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:7) to afford **10** in 68% and **3a'** in 40% as a mixture colorless oil (51.1 mg).



10

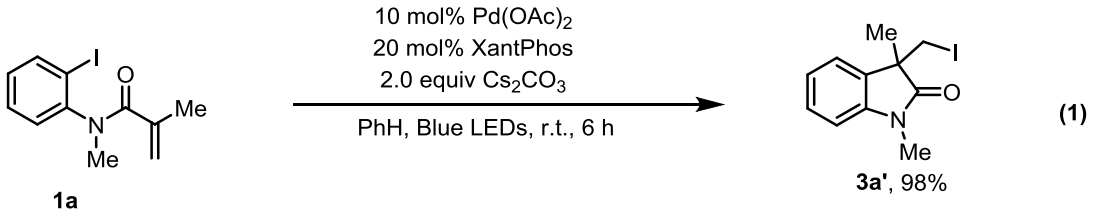
1,3-dimethyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)indolin-2-one (10). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.25 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.03 – 3.96 (m, 2H), 3.23 (s, 3H), 1.40 – 1.22 (m, 9H), 1.08 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.67 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.8, 143.6, 132.8, 127.6, 122.8, 121.9, 107.5, 79.6, 60.0, 59.9, 48.8, 39.4, 39.4, 32.6, 32.6, 26.0, 19.8, 19.5, 18.8, 16.8. **HRMS (ESI)** calcd for $C_{20}H_{31}N_2O_2$ $[M+H]^+$: 331.2380, found 331.2373.

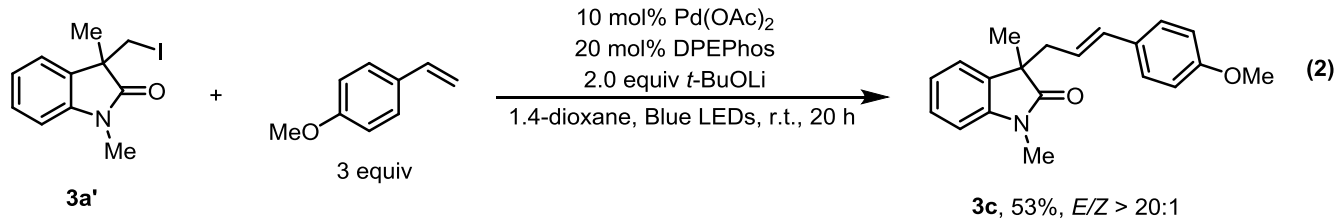


3a'

3-(iodomethyl)-1,3-dimethylindolin-2-one (3a'). Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 98% isolated yield (58.9 mg) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.34 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 9.6 Hz, 1H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.25 (s, 3H), 1.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.8, 143.0, 132.5, 128.5, 122.6, 122.5, 108.2, 48.5, 26.2, 22.8, 10.7.The spectroscopic data match the reported literature[1].

Control experiments:

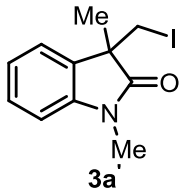




(1) An oven-dried 4.0 mL vial was charged with amide **1a** (60.2mg, 0.2 mmol, 1.0 equiv.), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), XantPhos (23.2 mg, 0.02 mmol, 20 mol%) and Cs_2CO_3 (130.4 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 3 mL of degassed benzene were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LEDs lamps for 6 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to afford **3a'** in 98% isolated yield (60.0 mg).

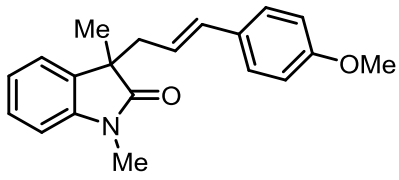
(2) An oven-dried 4.0 mL vial was charged with amide **3a'** (60.0mg, 0.2 mmol, 1.0 equiv.), 1-methoxy-4-vinylbenzene (80.6 mg, 0.6 mmol, 3.0 equiv.) $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), DPEPhos (21.5 mg, 0.02 mmol, 20 mol%) and *t*-BuOLi (32.0 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 3 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room

temperature under the irradiation of blue LEDs lamps for 20 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to afford **3c** in 53% isolated yield (32.0 mg) and *E/Z* > 20:1 as a colorless oil.



3a'

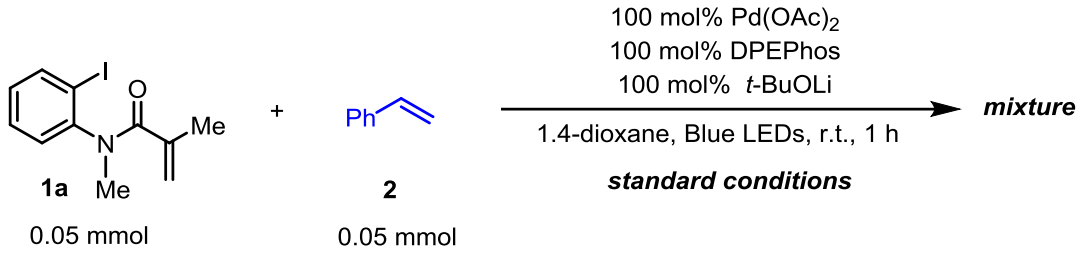
3-(Iodomethyl)-1,3-dimethylindolin-2-one (3a'). Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 98% isolated yield (58.9 mg) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 9.6 Hz, 1H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.25 (s, 3H), 1.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.9, 143.1, 132.6, 128.6, 122.7, 122.6, 108.2, 48.6, 26.3, 22.9, 10.8. The spectroscopic data match the reported literature[1].



3c

(*E*)-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (3c). Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 53% isolated yield (32.0 mg) and *E/Z* > 20:1 as a colorless oil; R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.21 (m, 2H), 7.14 – 7.12 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 – 6.72 (m, 3H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.74 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 3.76 (s, 3H), 3.17 (s, 3H), 2.67 – 2.57 (m, 2H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 180.2, 158.8, 143.1, 133.6, 133.0, 130.0, 127.7, 127.2, 122.9, 122.3, 121.9, 113.7, 107.9, 55.2, 48.6, 41.6, 26.1, 22.4. The spectroscopic data match the reported literature[9].

UV-visible spectroscopy analysis



1a: N-(2-iodophenyl)-N-methylmethacrylamide (0.05 mmol, 15.1 mg) was added to a 4 mL vial, followed by the addition of 1,4-dioxane (1.5 mL). The mixture was stirred at room temperature for 1 hour. Afterward, 5 μL of the reaction solution was diluted with 2995 μL of dioxane and analyzed using a UV-visible spectrophotometer.

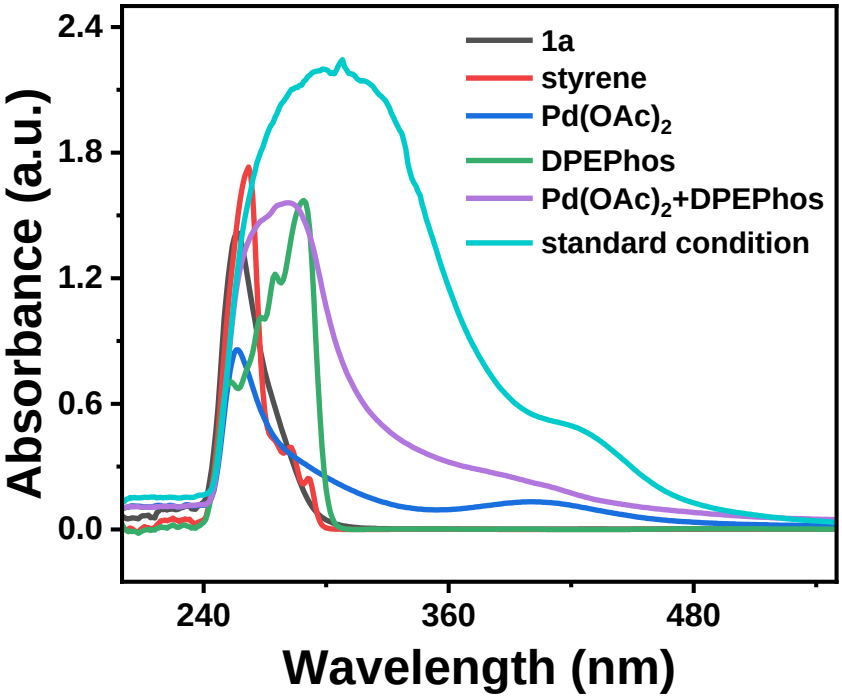
Styrene: Styrene (0.05 mmol, 5.2 mg) was added to a 4 mL vial, followed by the addition of 1,4-dioxane (1.5 mL). The mixture was stirred at room temperature for 1 hour. Subsequently, 5 μL of the reaction solution was diluted with 2995 μL of dioxane and analyzed using a UV-visible spectrophotometer.

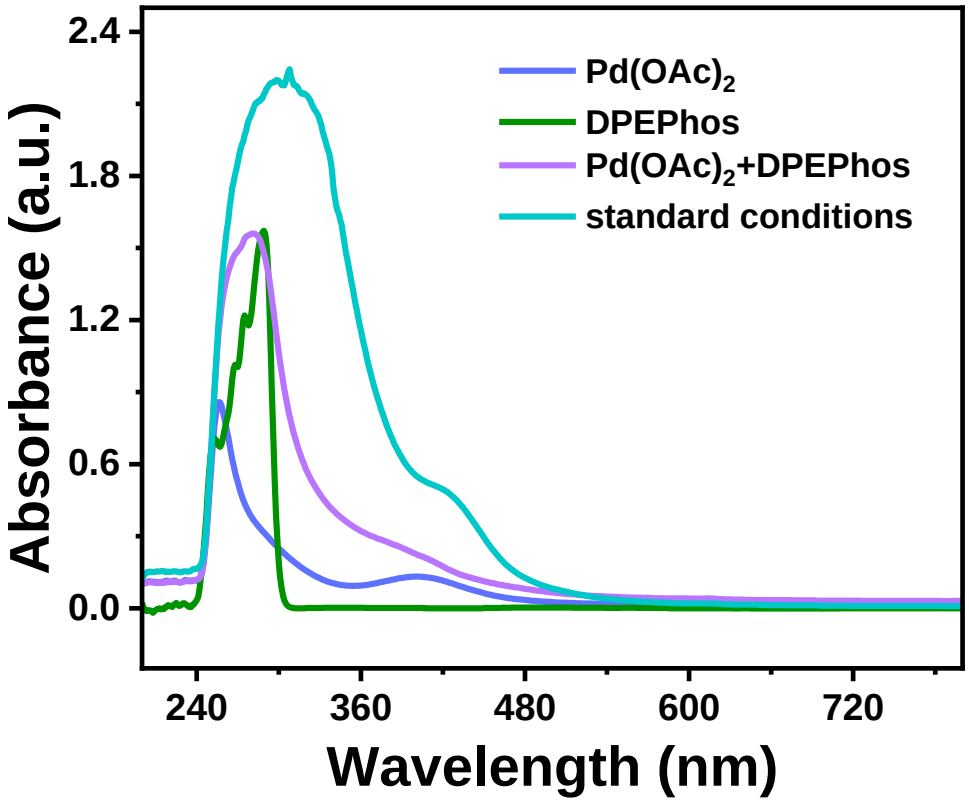
$Pd(OAc)_2$: Pd(OAc)2 (0.05 mmol, 11.2 mg) was added to a scaled 4 mL vial, followed by the addition of 1,4-dioxane (1.5 mL). The mixture was stirred at room temperature for 1 hour. Subsequently, 5 μL of the reaction solution was diluted with 2995 μL of dioxane and analyzed using a UV-visible spectrophotometer.

DPEPhos: DPEPhos (0.05 mmol, 26.9 mg) was added to a scaled 4 mL vial, and 1,4-dioxane (1.5 mL) was added to the vial. The mixture was stirred at room temperature for 1 hour. After that, 5 μL of the reaction solution was diluted with 2995 μL of dioxane and analyzed using a UV-visible spectrophotometer.

Standard conditions: Equal equivalents of N-(2-iodophenyl)-N-methyl methacrylamide (0.05 mmol, 15.1 mg), Styrene (0.05 mmol, 5.2 mg), Pd(OAc)2 (0.05 mmol, 11.2 mg), DPEPhos (0.05 mmol, 26.9 mg), and t-BuLi (0.05 mmol, 4 mg) were added to a scaled 4 mL vial, followed by the addition of 1,4-dioxane (1.5 mL). The mixture was stirred at room temperature for 1 hour. Then, 5 μL of the reaction solution was diluted with 2995 μL of dioxane and analyzed using a UV-visible spectrophotometer.

We conducted UV-Vis spectra analysis of the reaction mixture and reactants, which revealed that the complex formed by $Pd(OAc)_2$ and DPEPhos exhibits absorption in the blue light range at wavelengths of 460-465 nm, indicating its photosensitivity as a photocatalyst in the reaction. In contrast, other reactants 1a, styrene and DPEPhos showed no absorption peaks in the blue light range. While $Pd(OAc)_2$ itself exhibited weak absorption under blue light, the combination with DPEPhos significantly enhanced the absorption effect.


2.4
1.8
1.2
0.6
0.0
Absorbance (a.u.)
240
360
480
Wavelength (nm)
1a
styrene
Pd(OAc)2
DPEPhos
Pd(OAc)2+DPEPhos
standard condition


2.4
1.8
1.2
0.6
0.0
Absorbance (a.u.)
240
360
480
600
720
Wavelength (nm)
Pd(OAc)2
DPEPhos
Pd(OAc)2+DPEPhos
standard conditions

Reference

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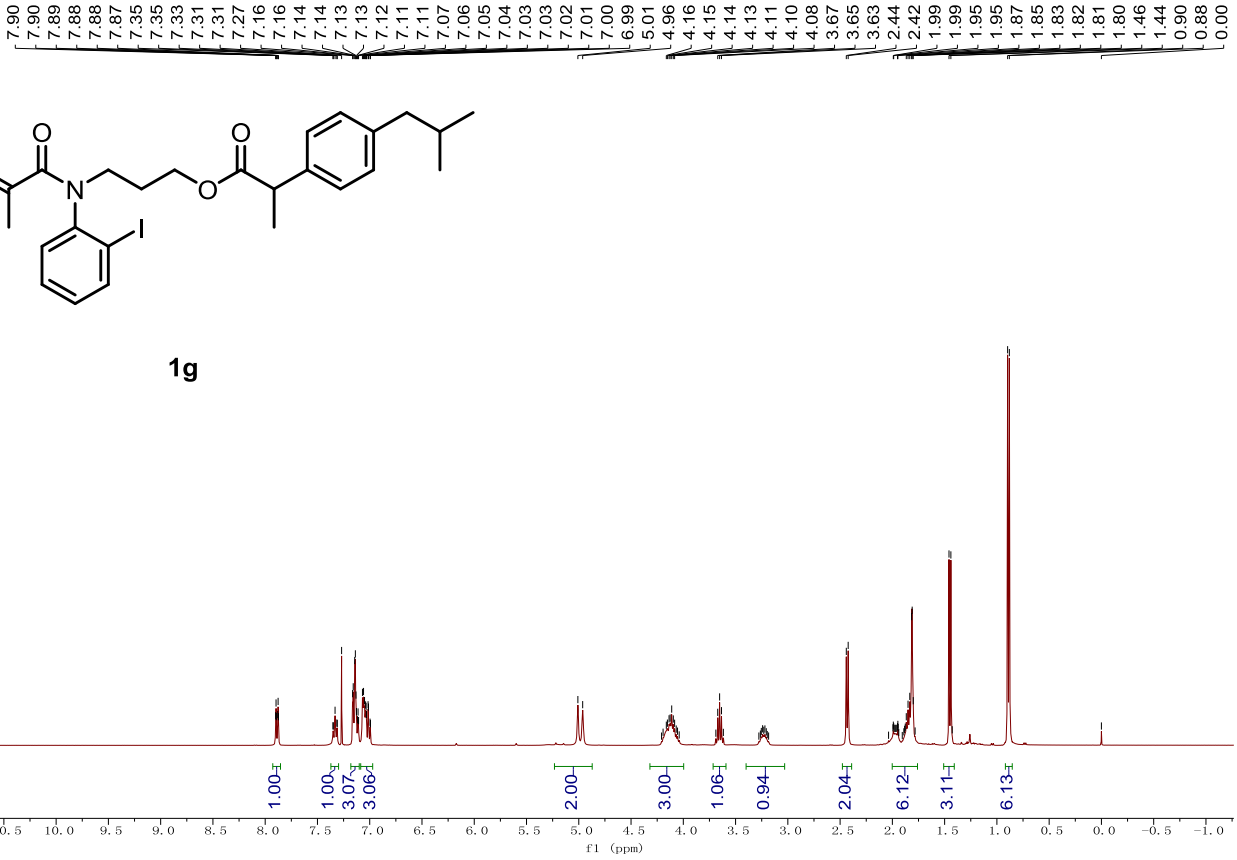
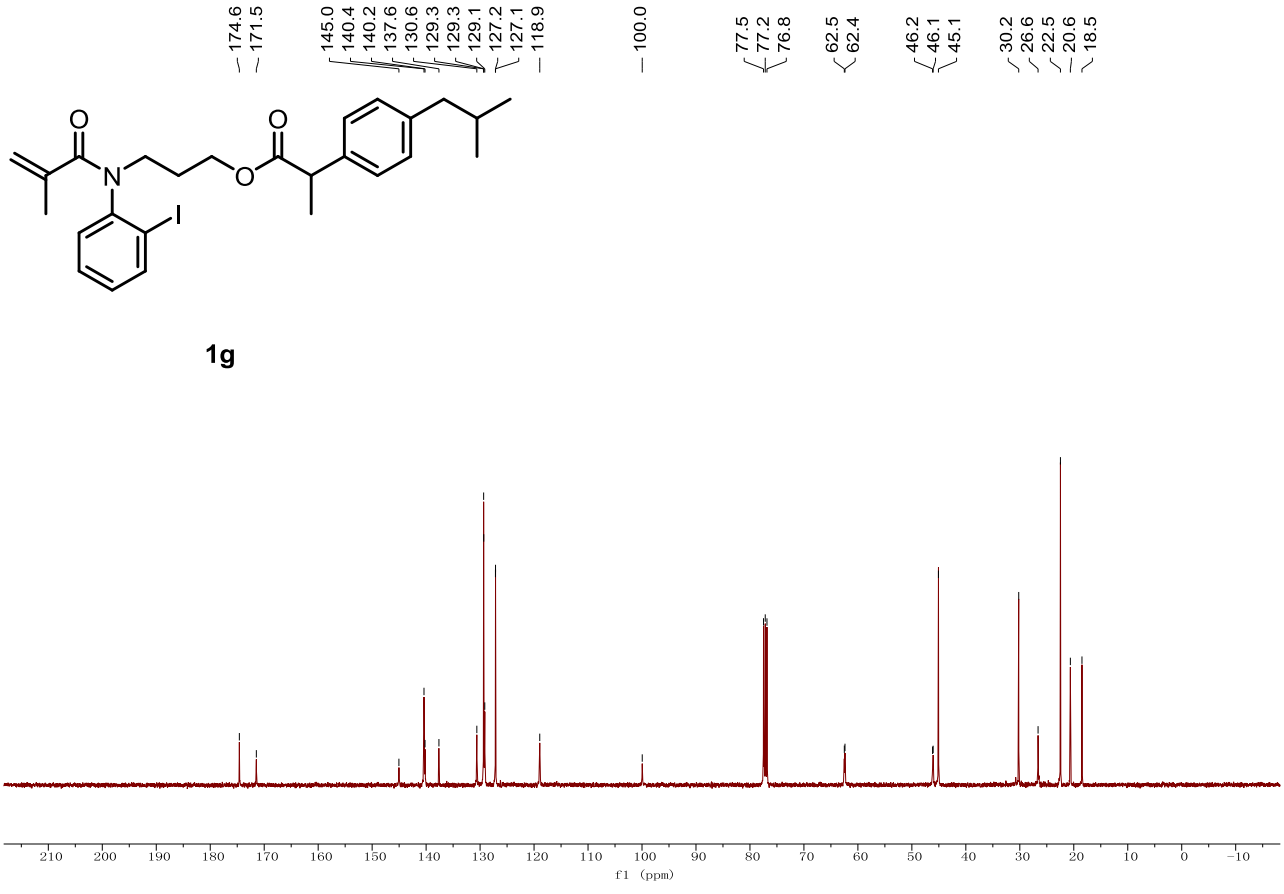
NMR Spectra

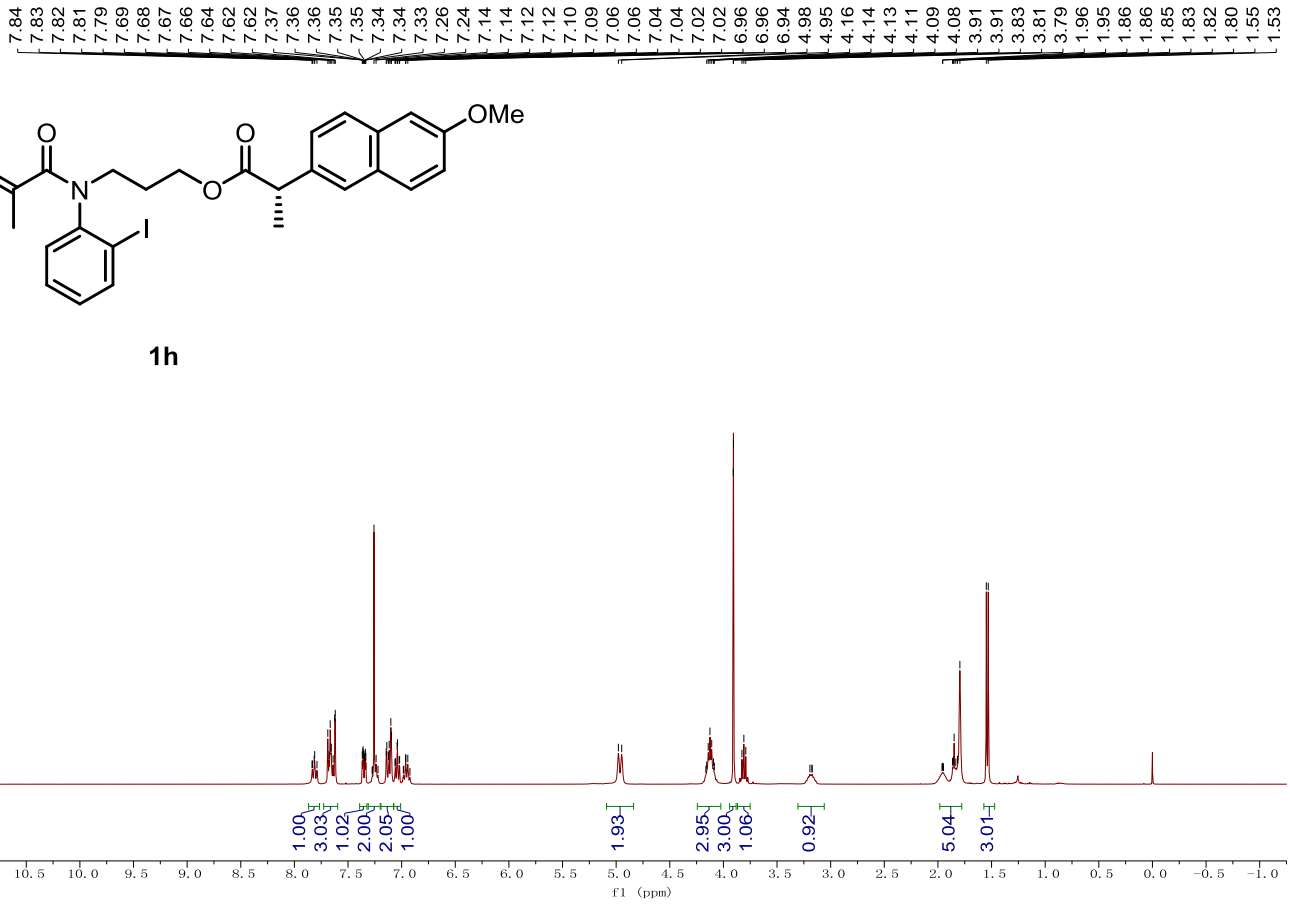
1g, ^{1}H NMR (400 MHz, $CDCl_3$)



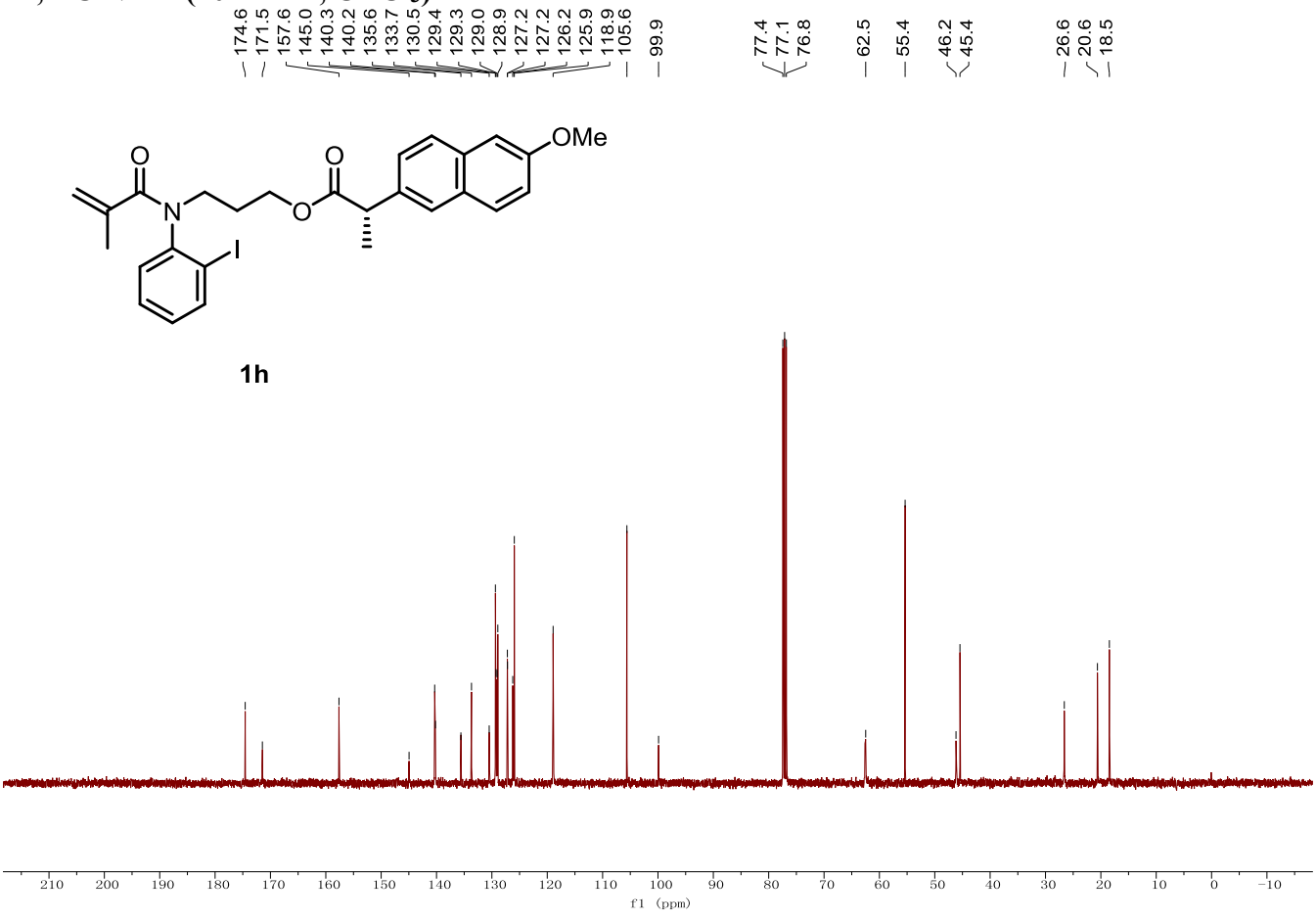
1g, ^{13}C NMR (101 MHz, $CDCl_3$)



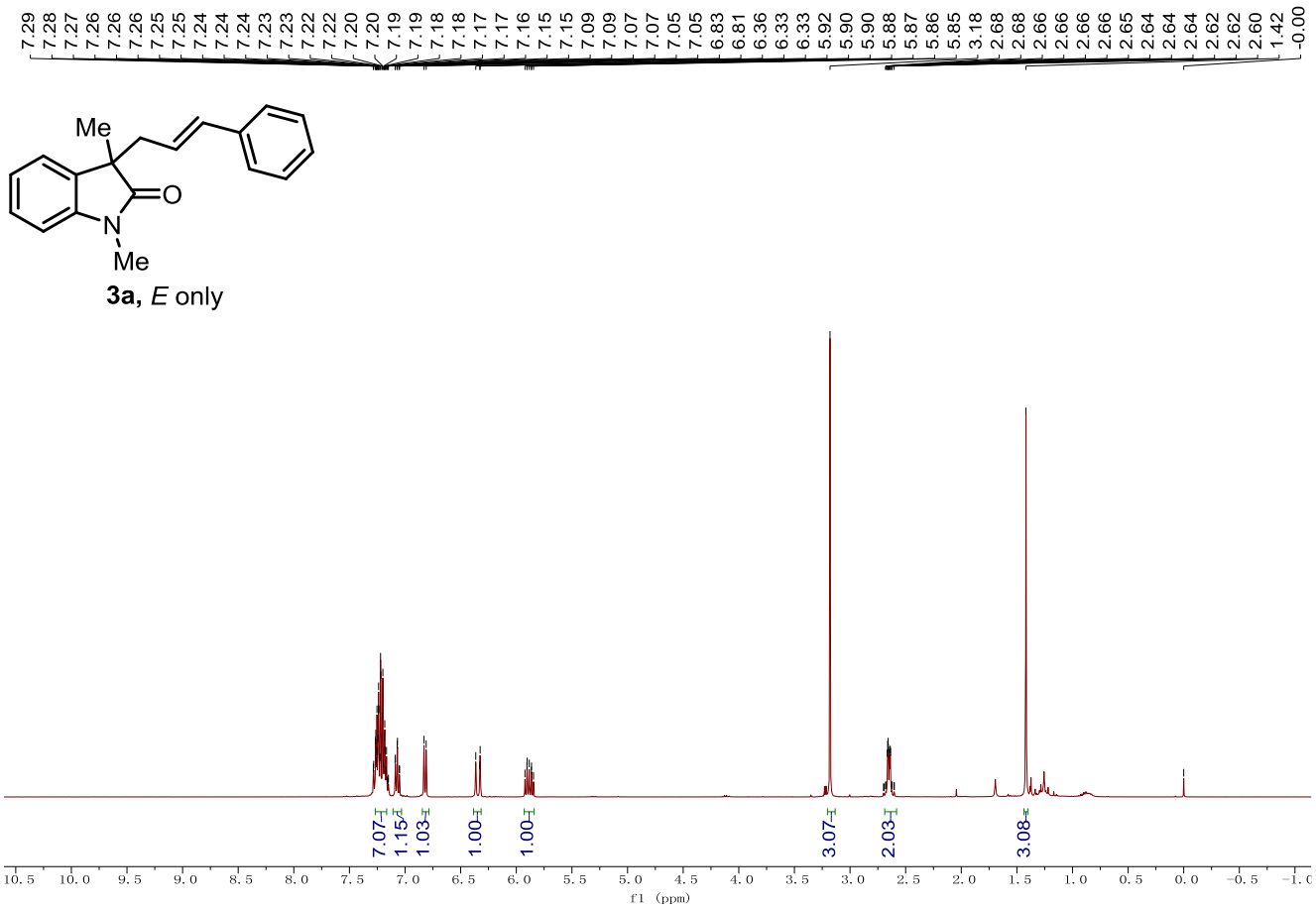
1h, ^{1}H NMR (400 MHz, $CDCl_3$)



1h, ^{13}C NMR (101 MHz, $CDCl_3$)

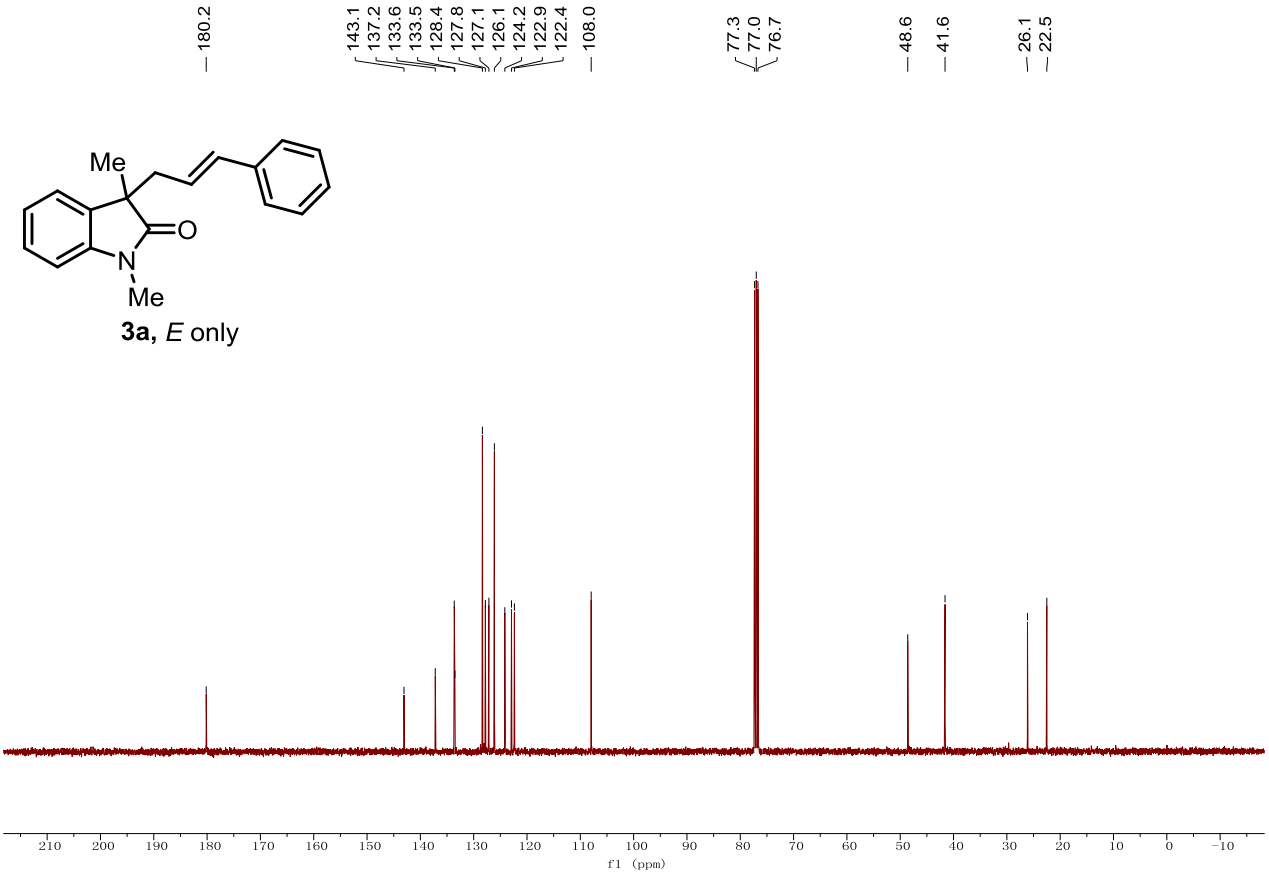


3a, ^{1}H NMR (400 MHz, $CDCl_3$)



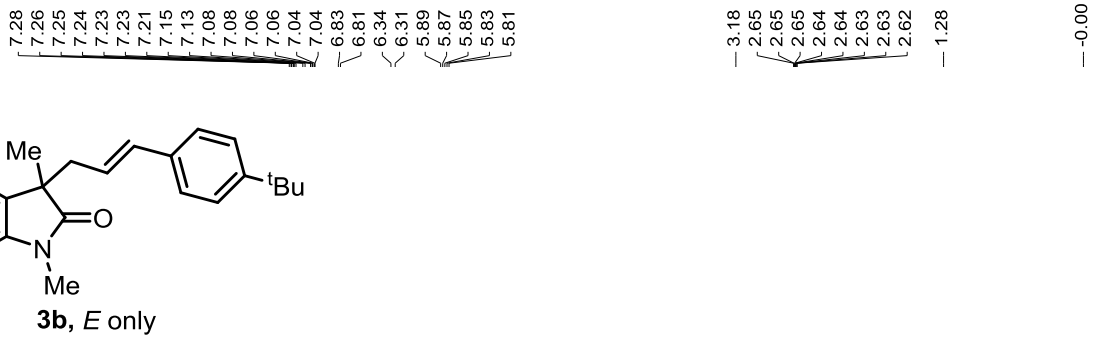
3a, *E* only

3a, ^{13}C NMR (101 MHz, $CDCl_3$)

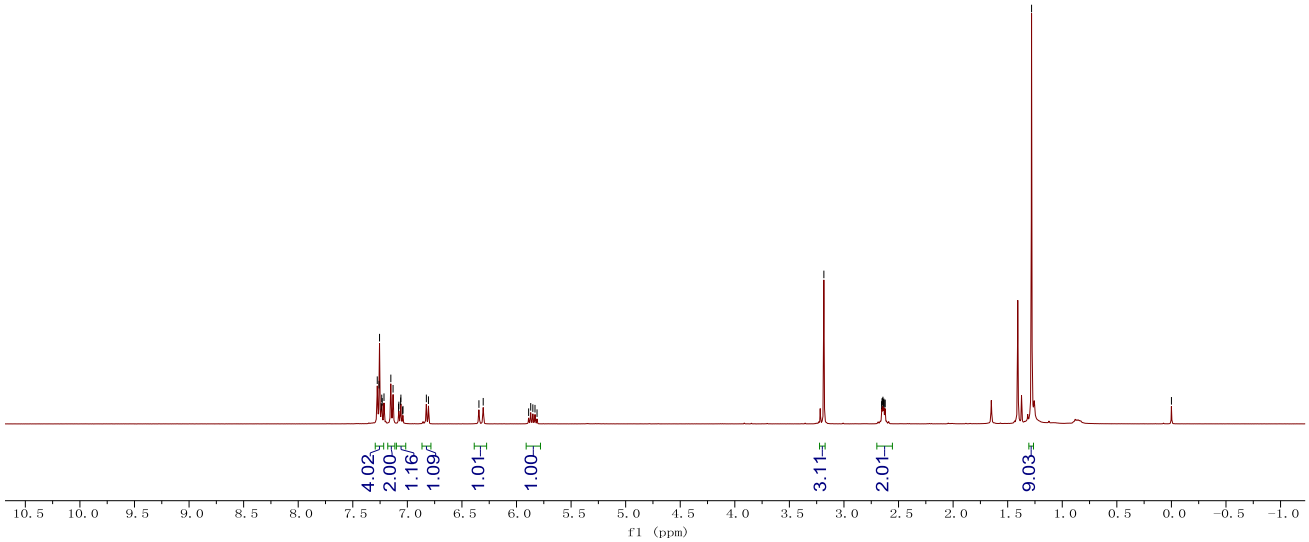


3a, *E* only

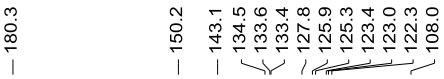
3b, ^{1}H NMR (400 MHz, $CDCl_3$)

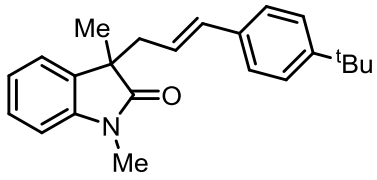


3b, *E* only



3b, ^{13}C NMR (101 MHz, $CDCl_3$)





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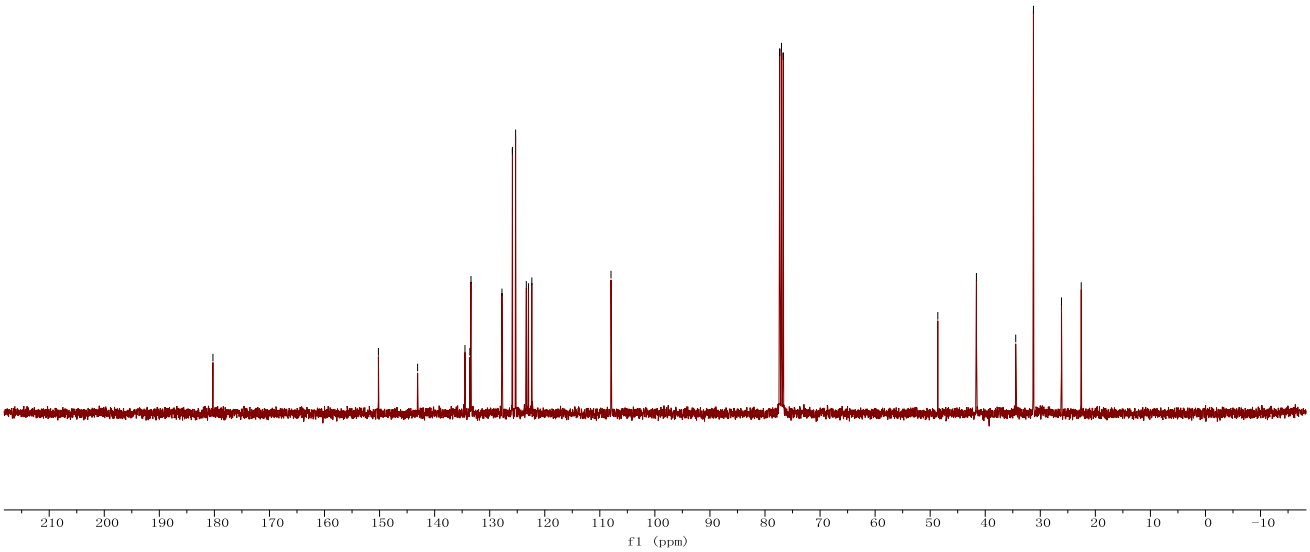
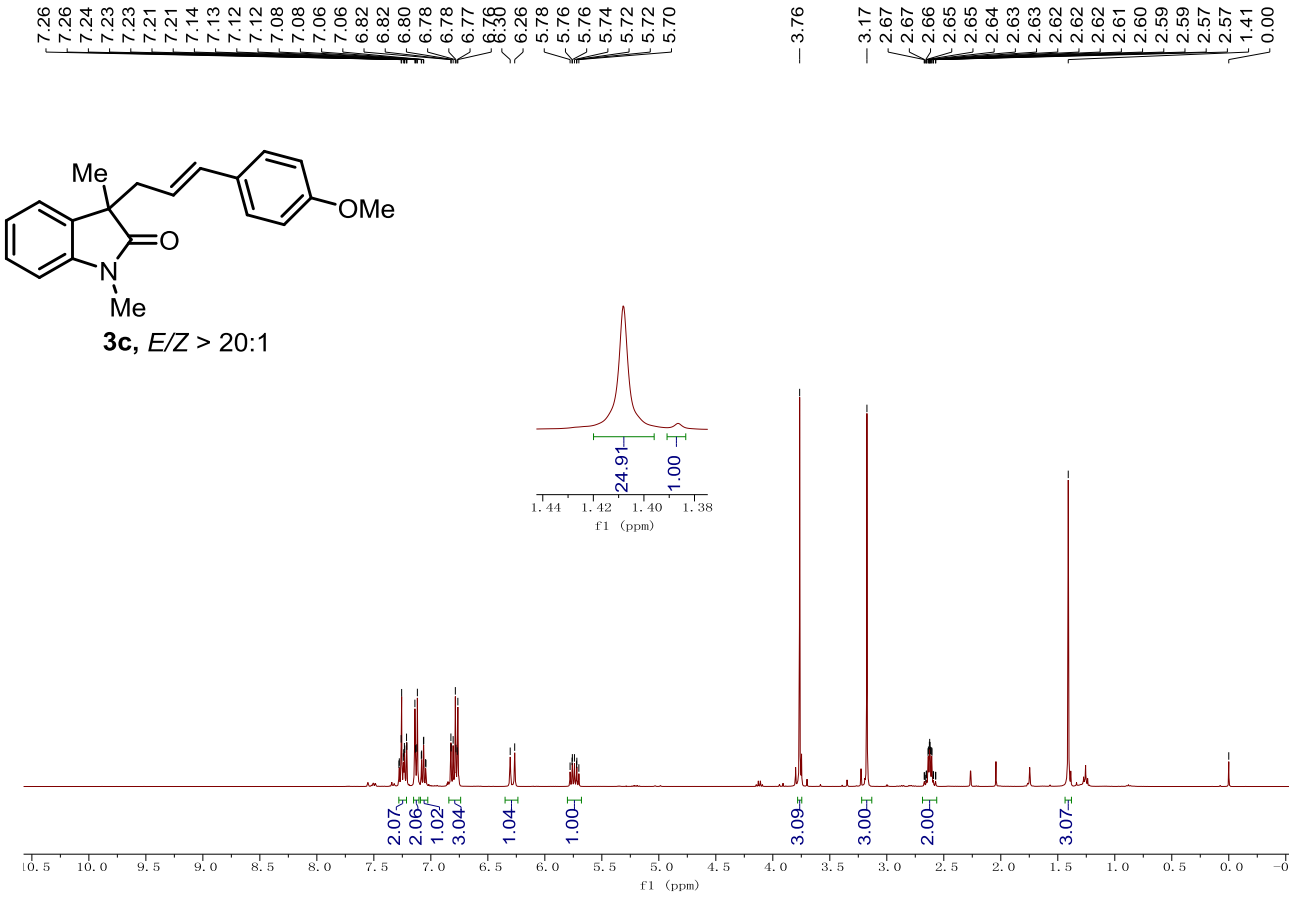
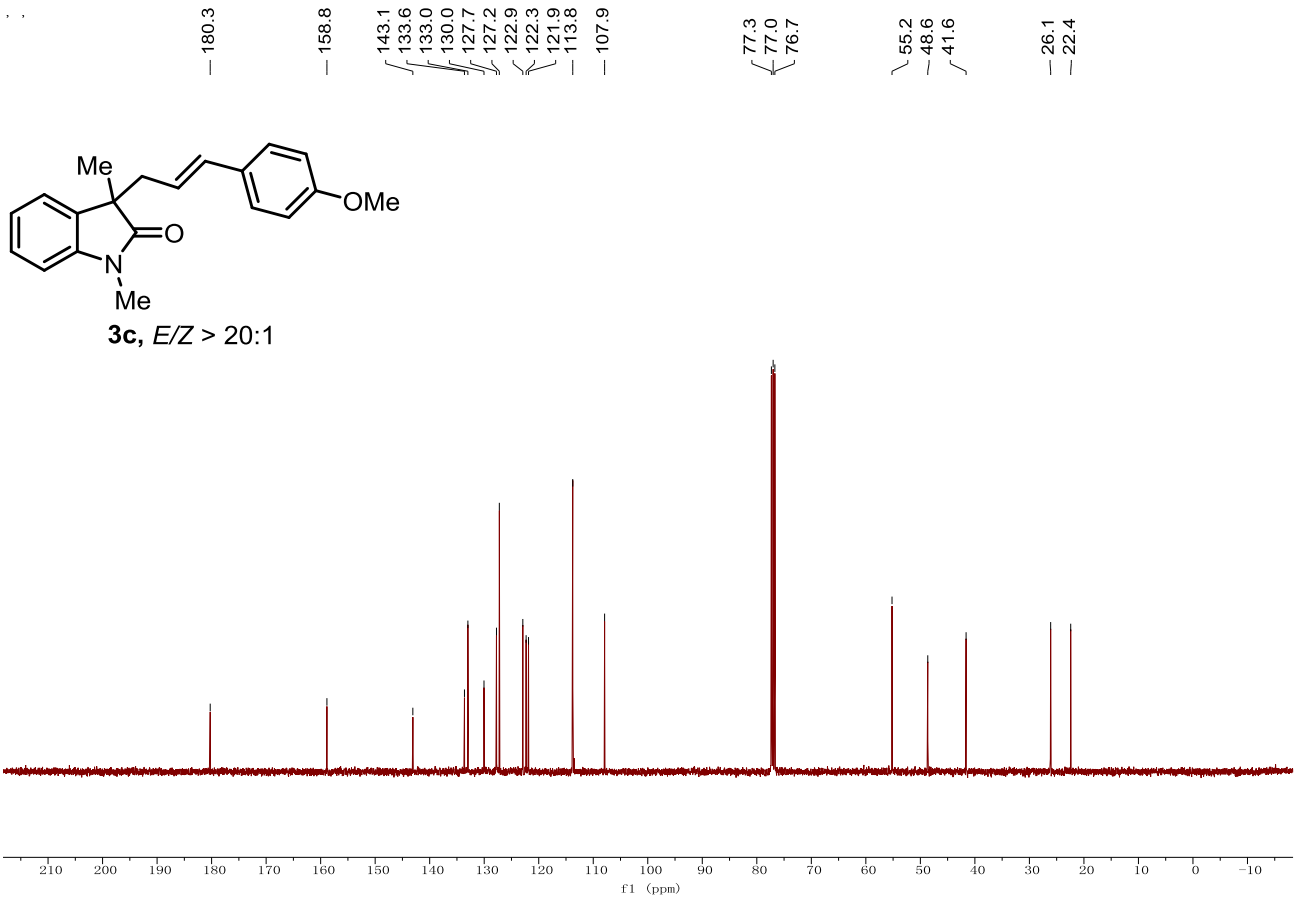


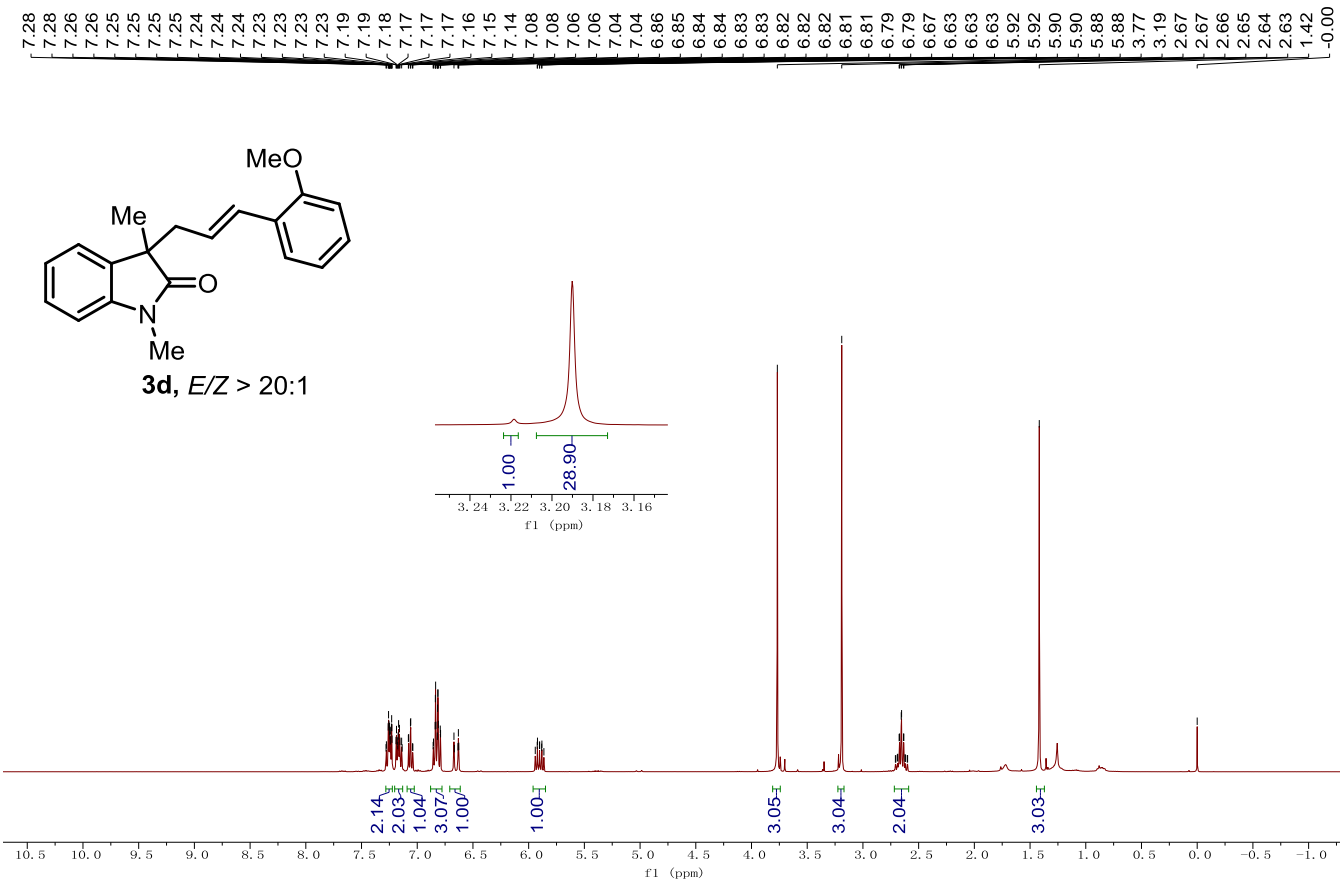
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



3c, ^{13}C NMR (101 MHz, $CDCl_3$)



3d, ^{1}H NMR (400 MHz, $CDCl_3$)



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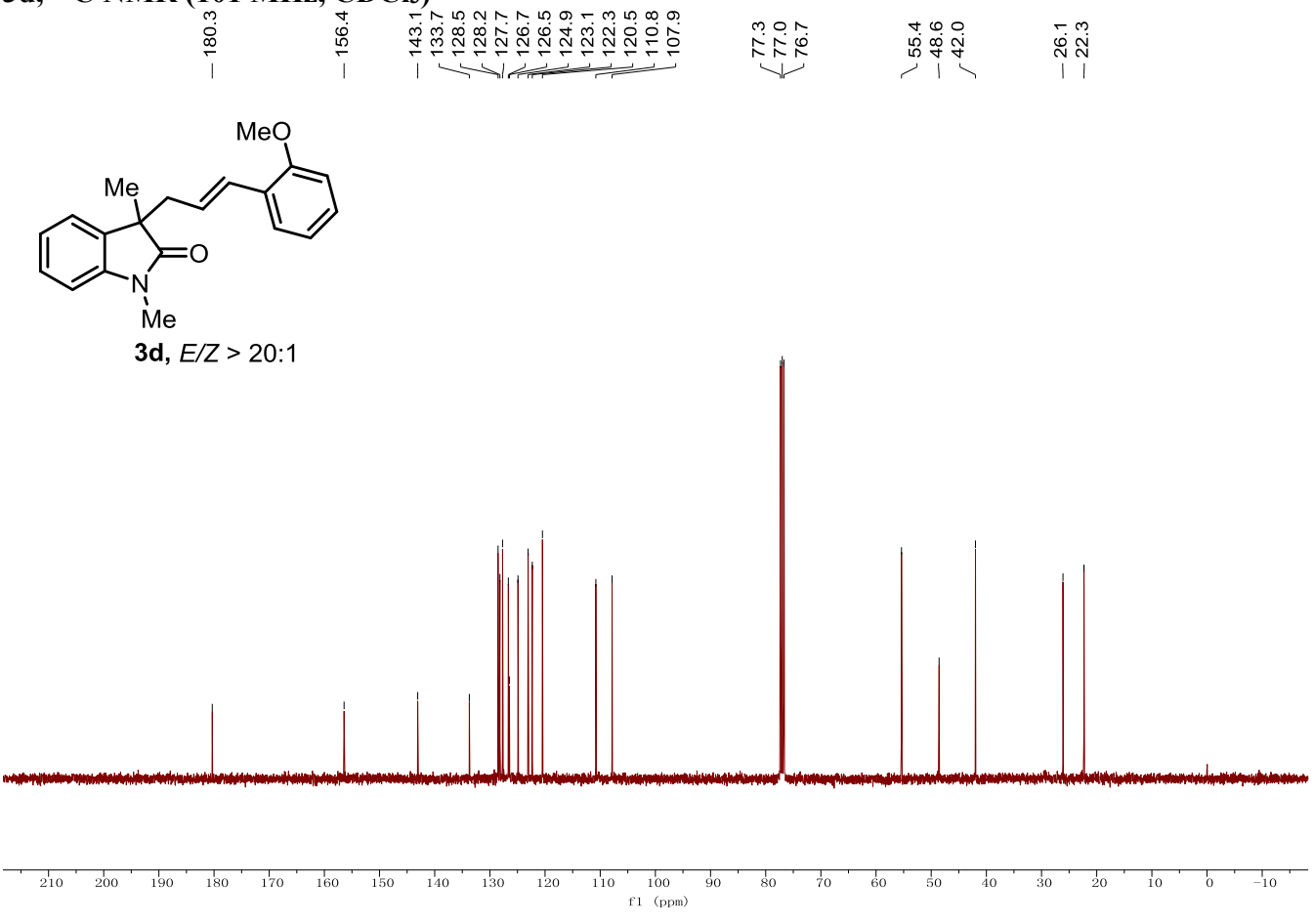
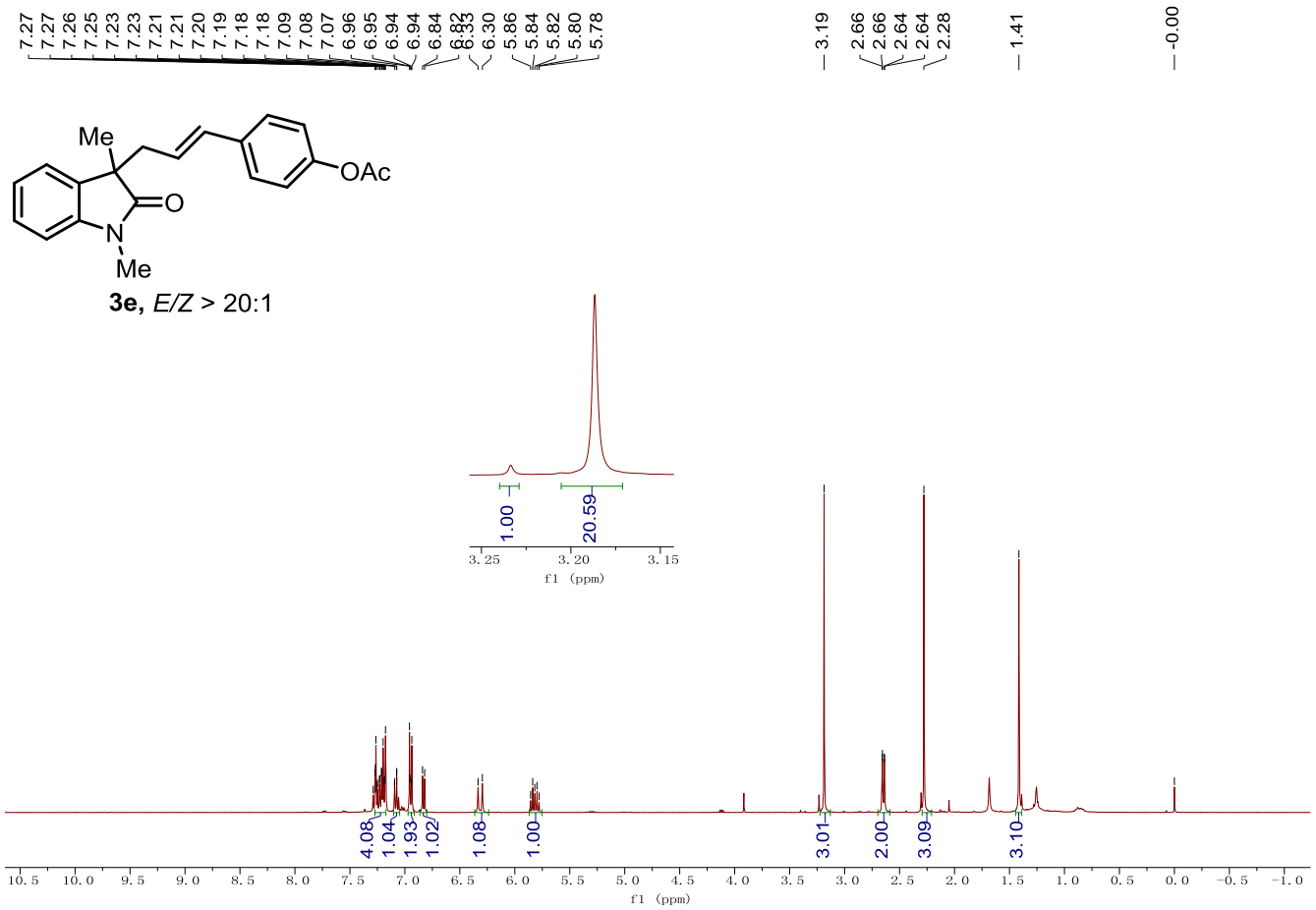
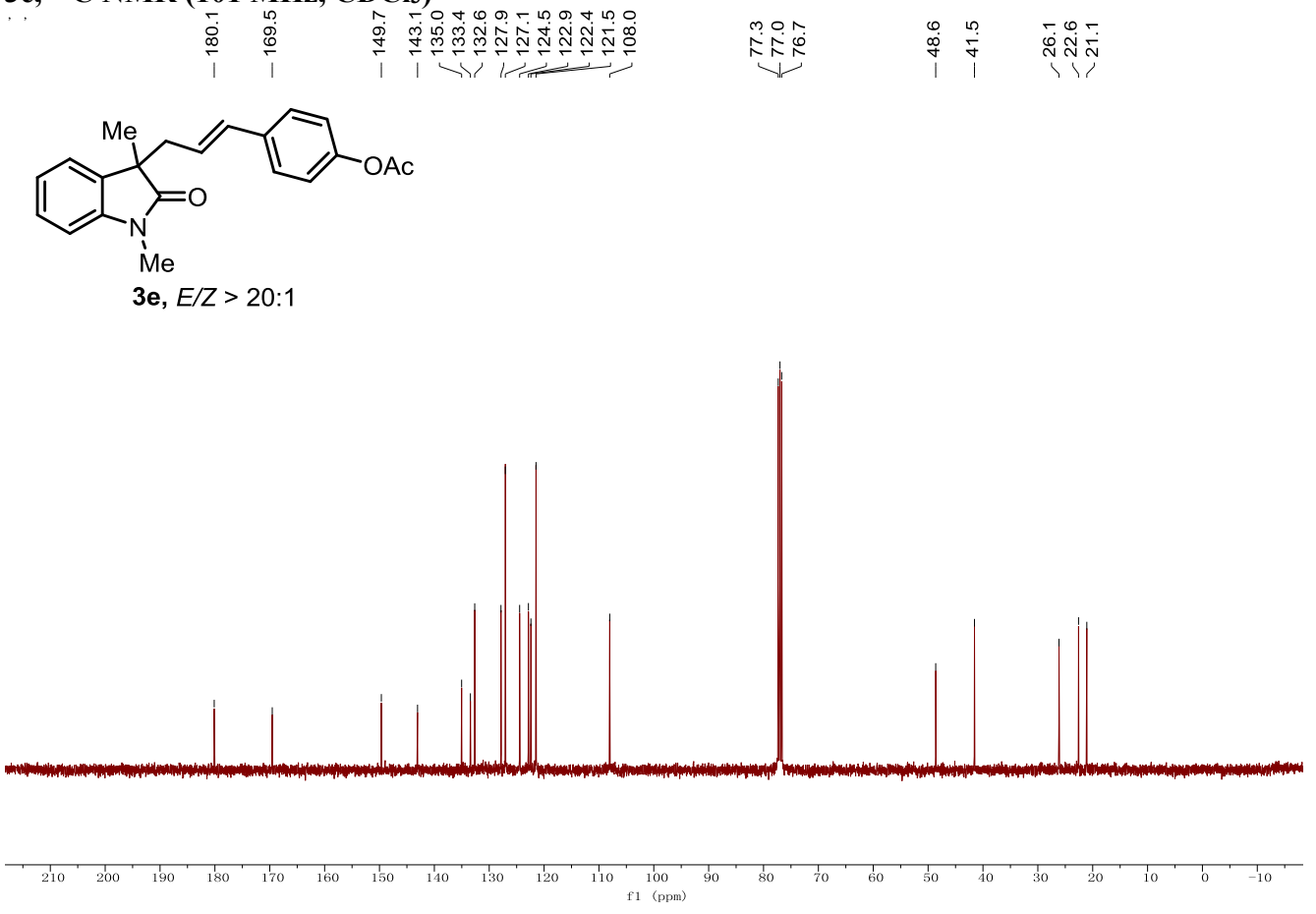


3e, ^{1}H NMR (400 MHz, $CDCl_3$)



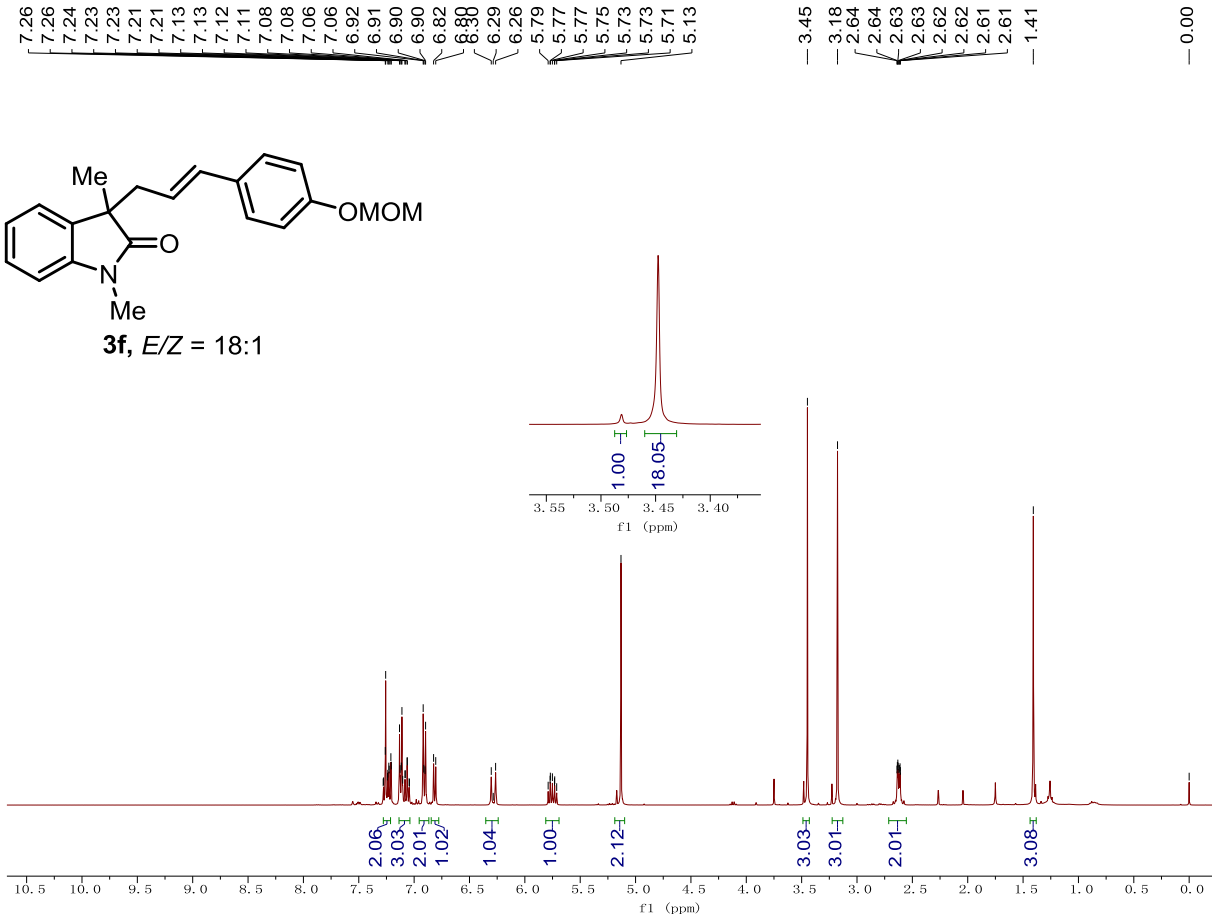
3e, *E/Z* > 20:1

3e, ^{13}C NMR (101 MHz, $CDCl_3$)

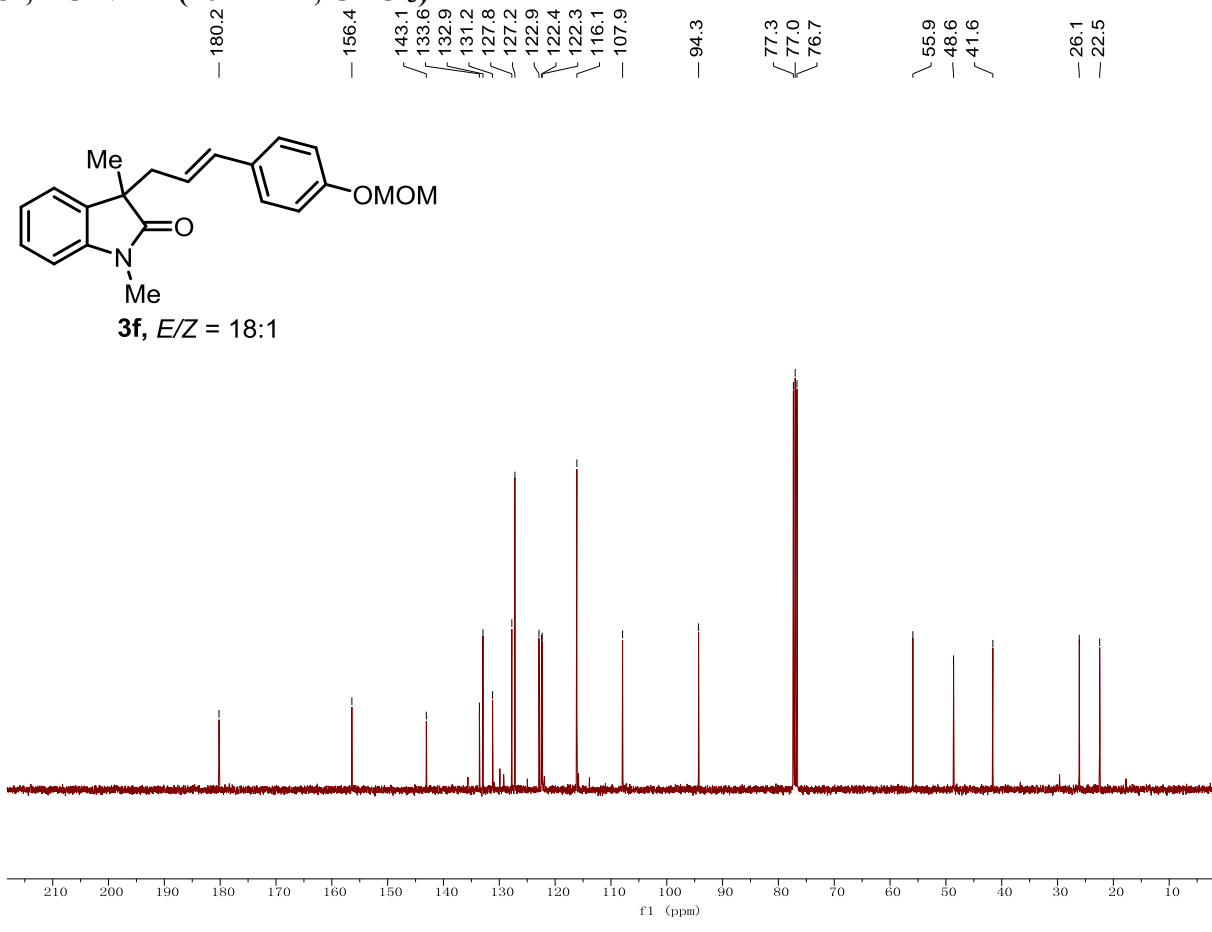


3e, *E/Z* > 20:1

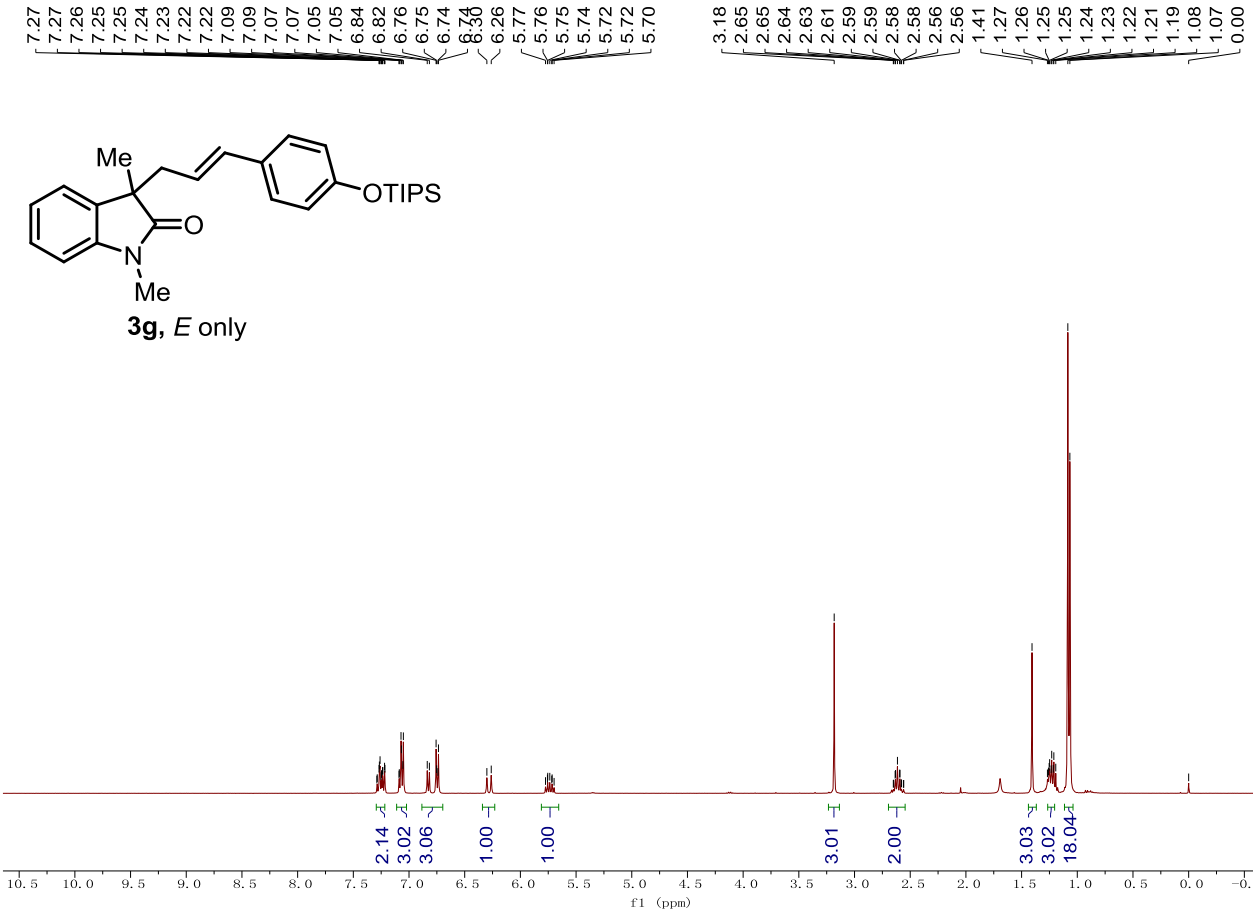
3f, ^{1}H NMR (400 MHz, $CDCl_3$)



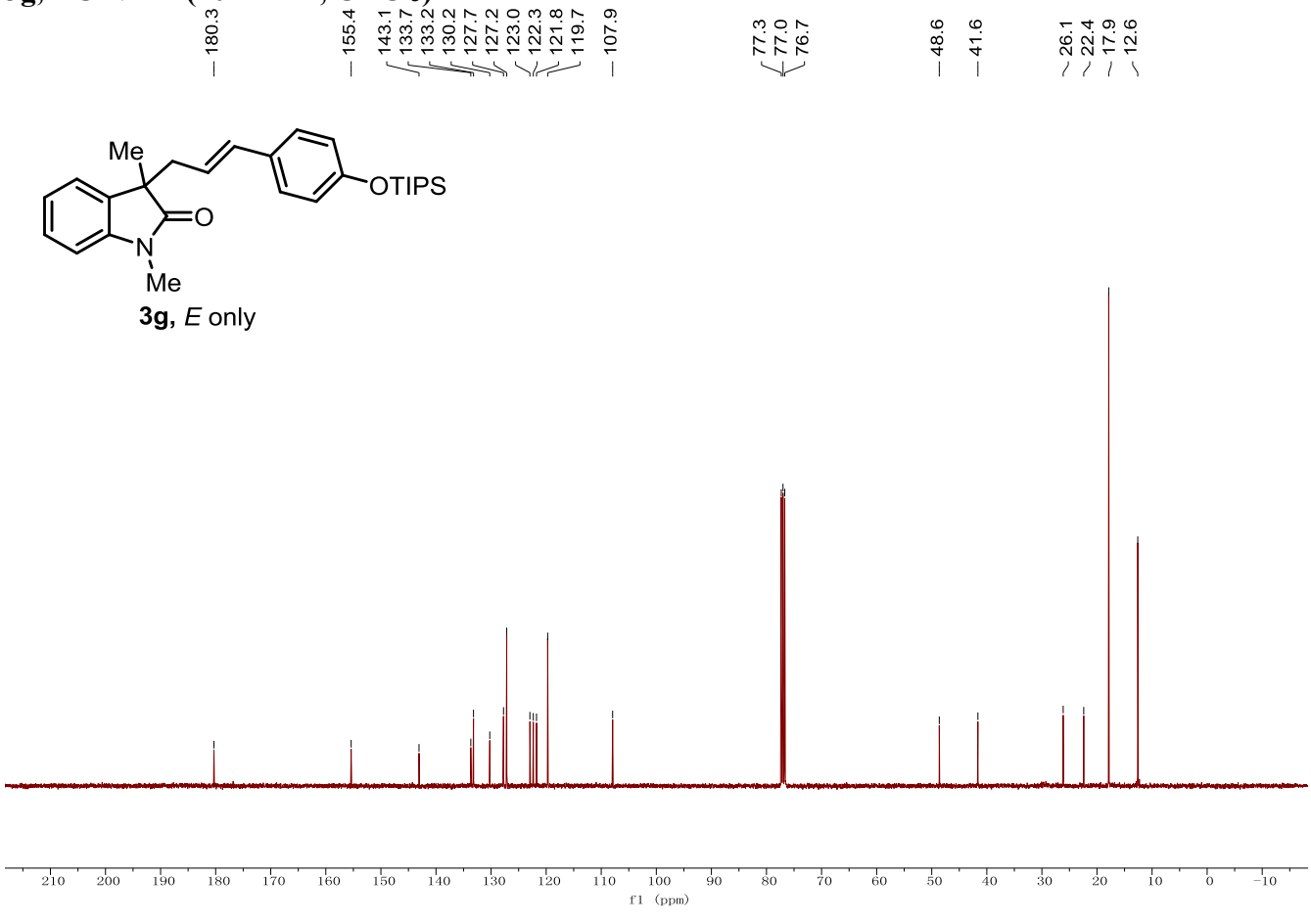
3f, ^{13}C NMR (101 MHz, $CDCl_3$)



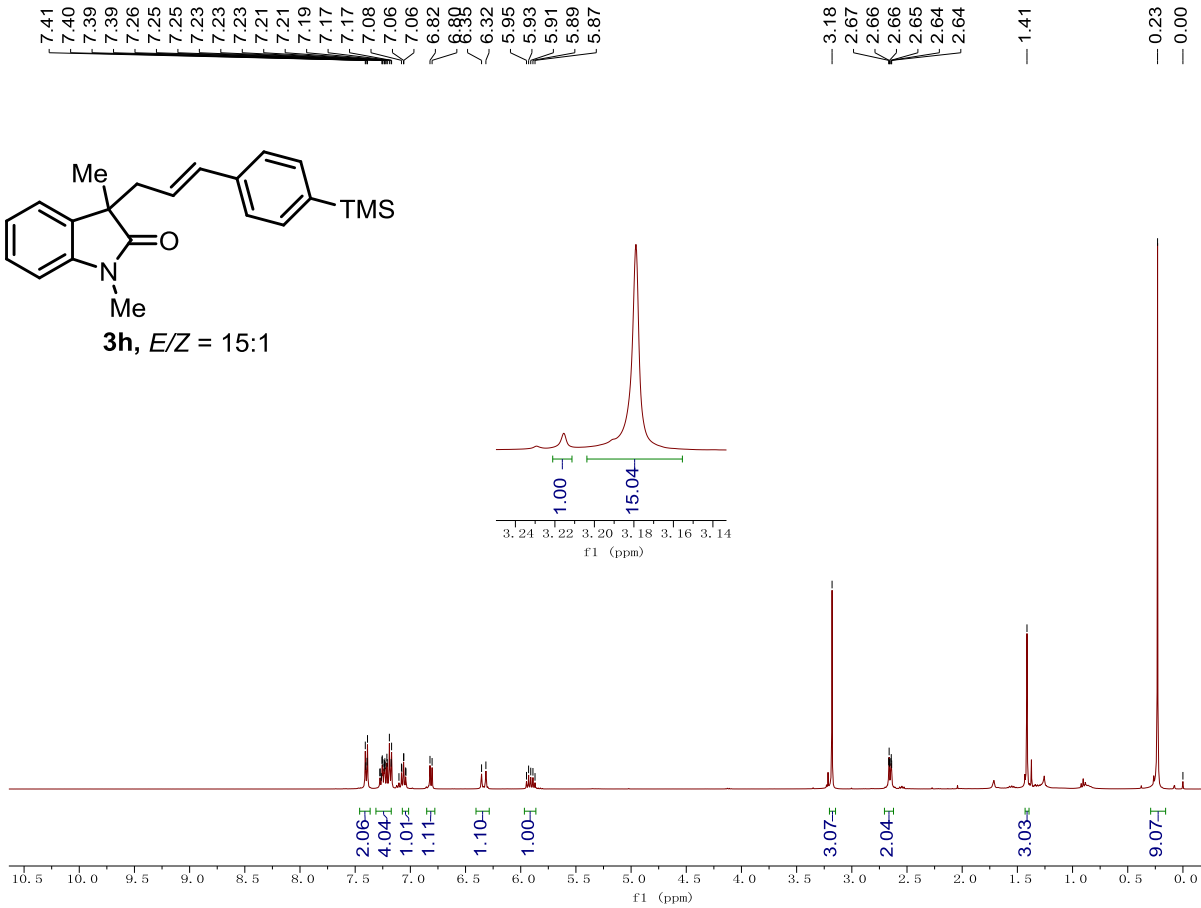
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



3g, ^{13}C NMR (101 MHz, $CDCl_3$)

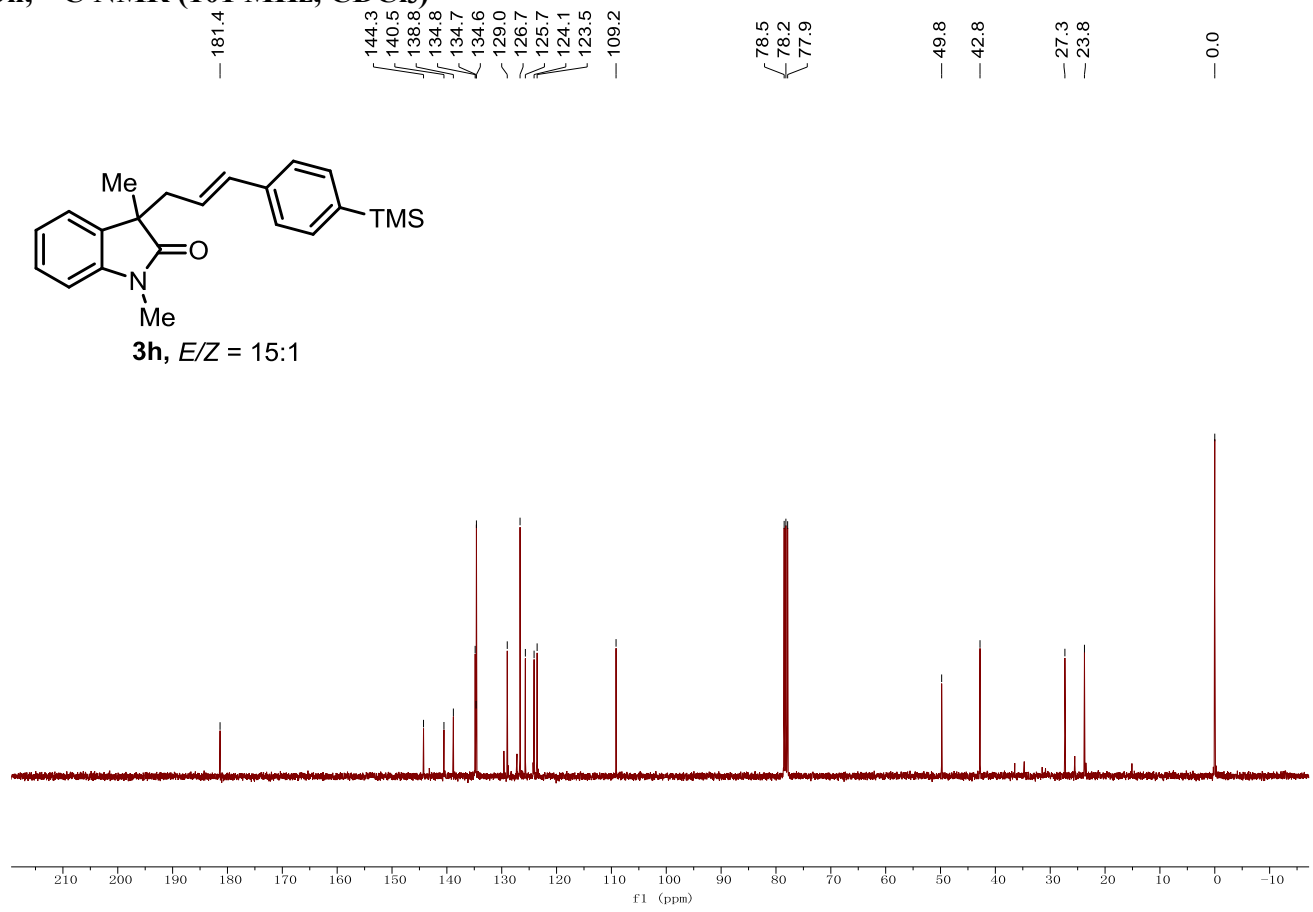


3h, ^{1}H NMR (400 MHz, $CDCl_3$)



3h, *E*/*Z* = 15:1

3h, ^{13}C NMR (101 MHz, $CDCl_3$)



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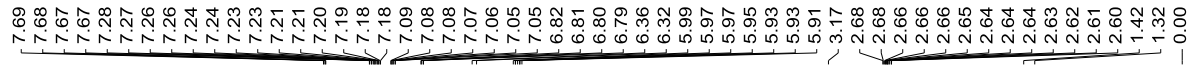
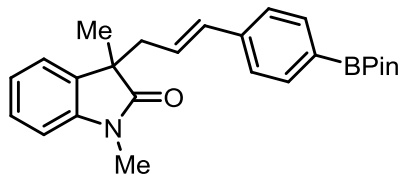
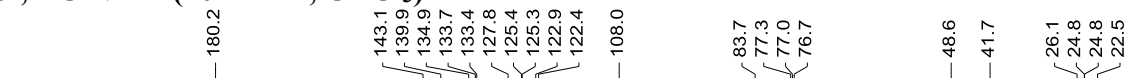
3i, ^{1}H NMR (400 MHz, $CDCl_3$)

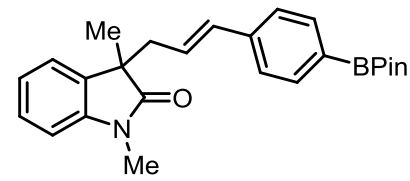




3i, *E/Z* > 20:1

3i, ^{13}C NMR (101 MHz, $CDCl_3$)





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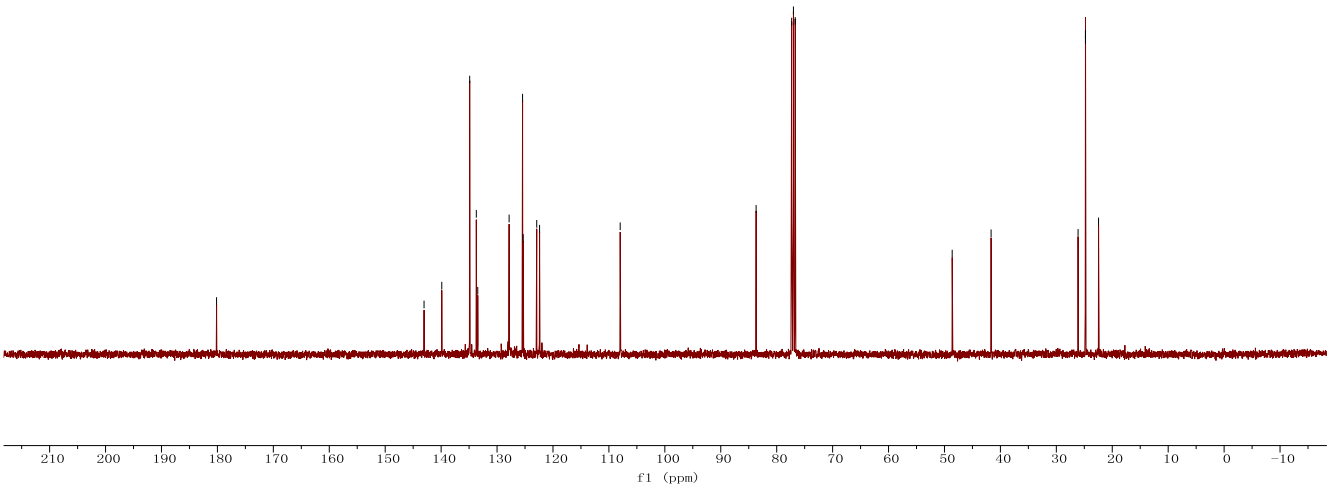
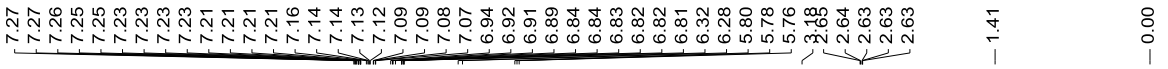
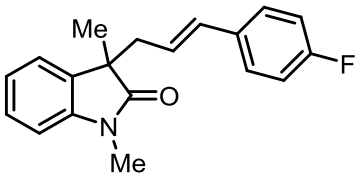
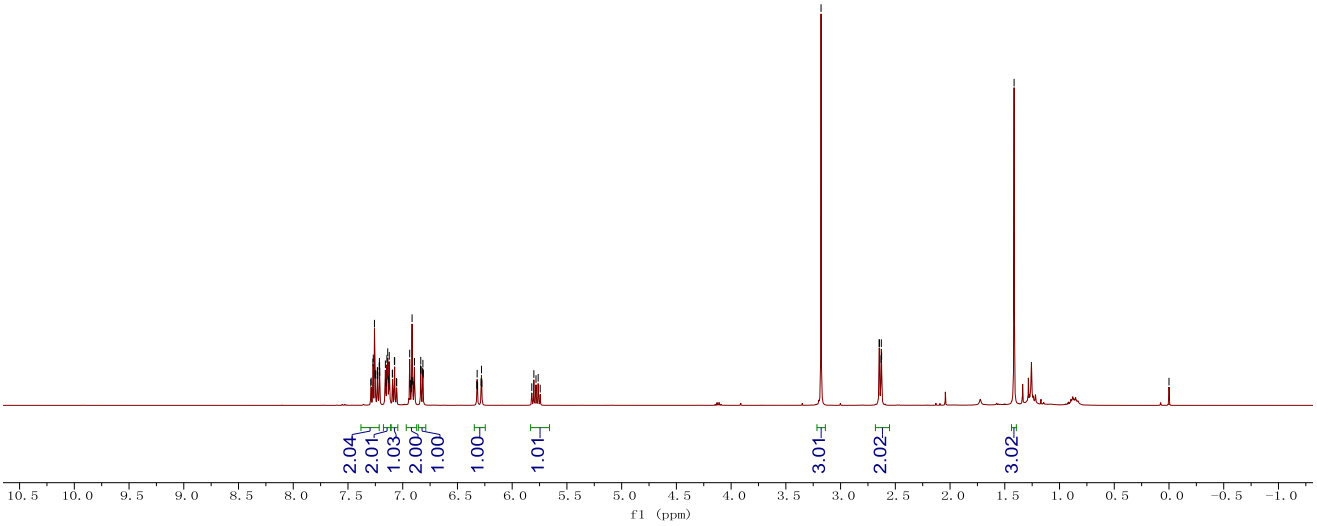


3j, ^{1}H NMR (400 MHz, $CDCl_3$)

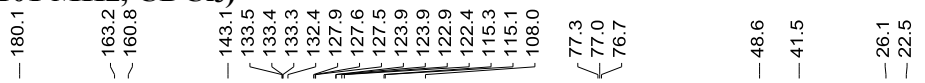


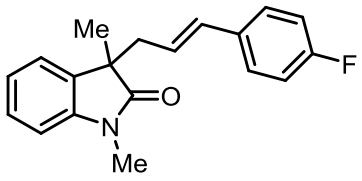


3j, *E* only

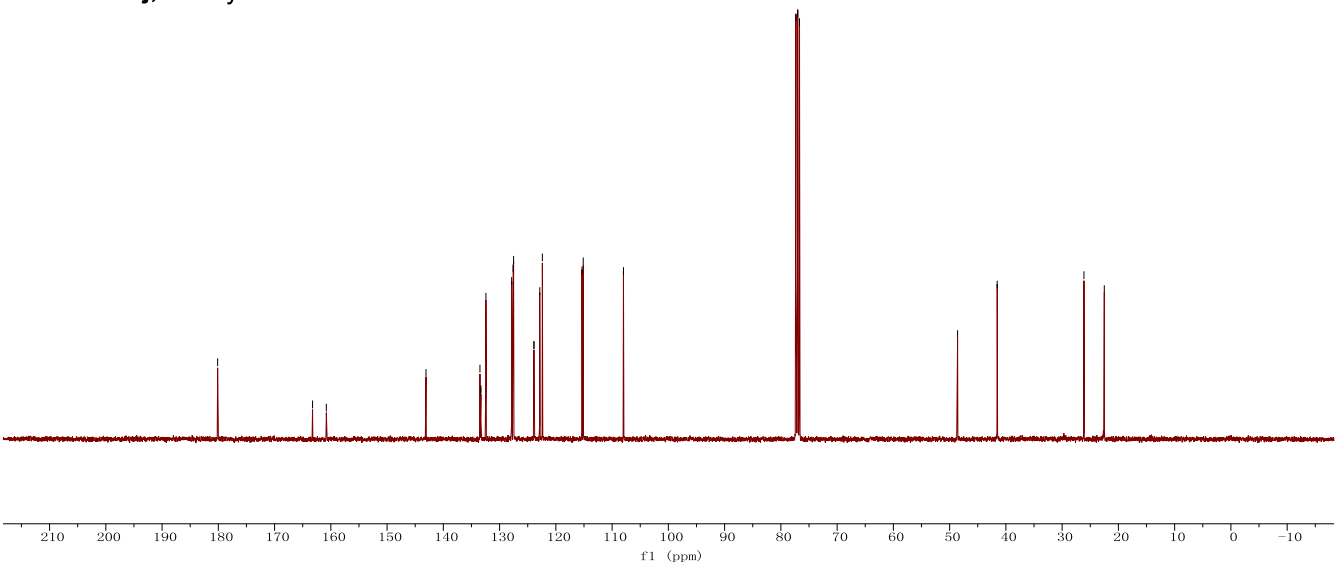


3j, ^{13}C NMR (101 MHz, $CDCl_3$)

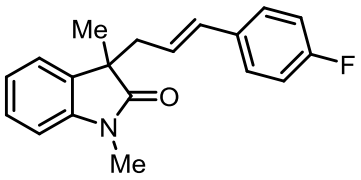




3j, *E* only

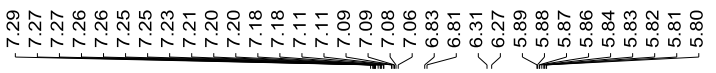


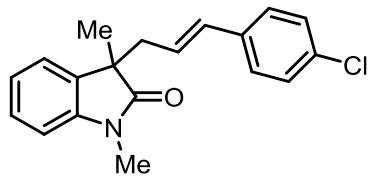
3j, ^{19}F NMR (101 MHz, $CDCl_3$)



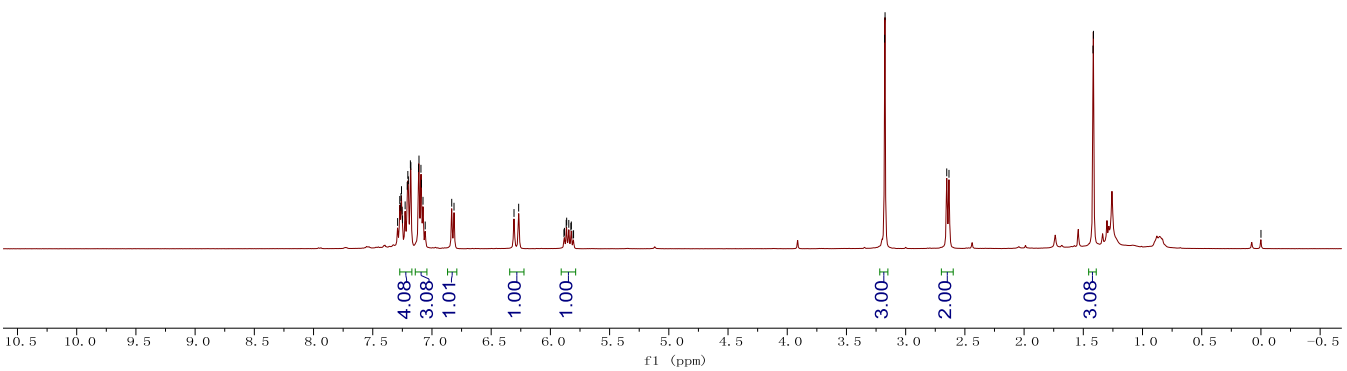
3j, *E* only

3k, ^{1}H NMR (400 MHz, $CDCl_3$)

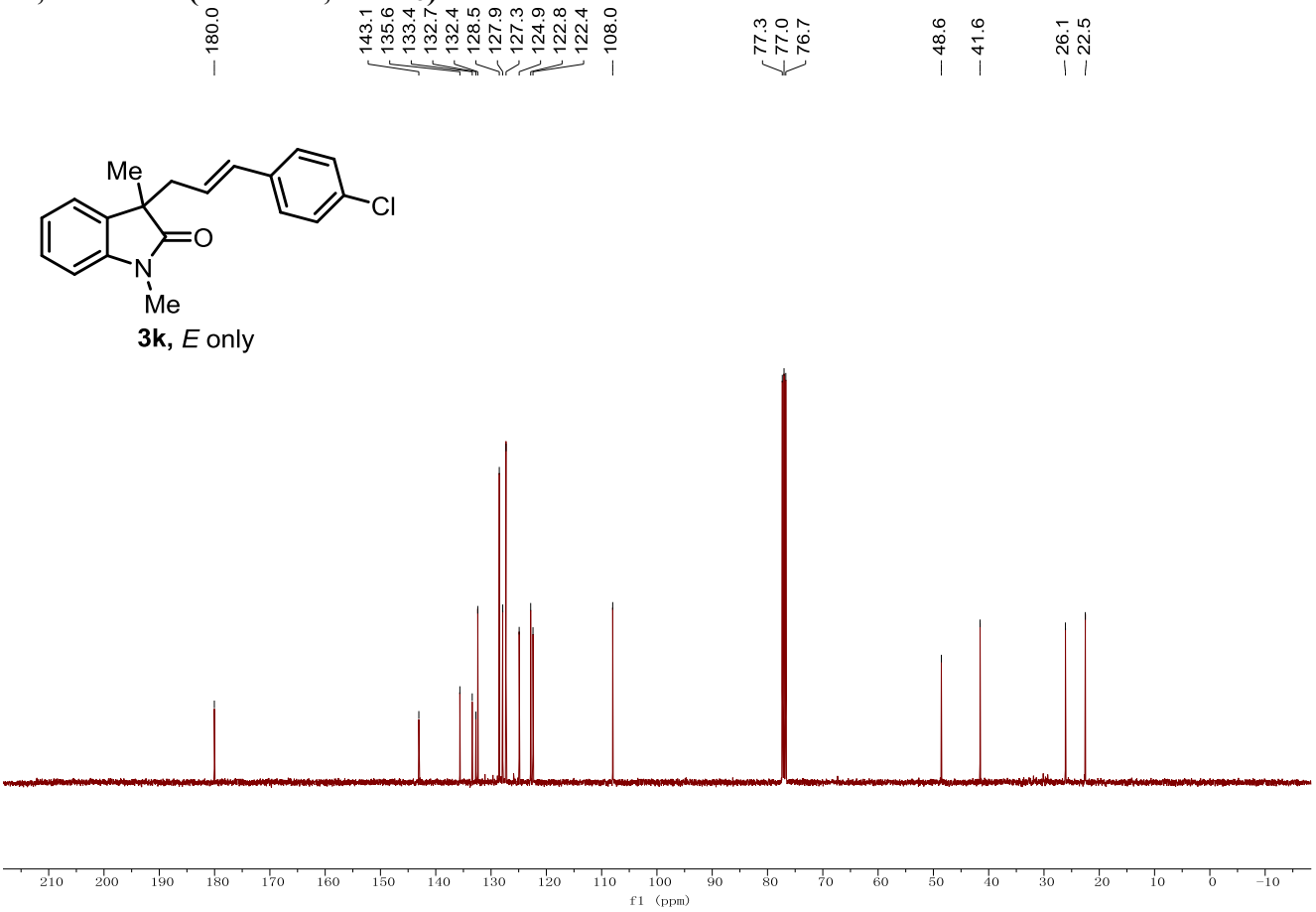




3k, *E* only

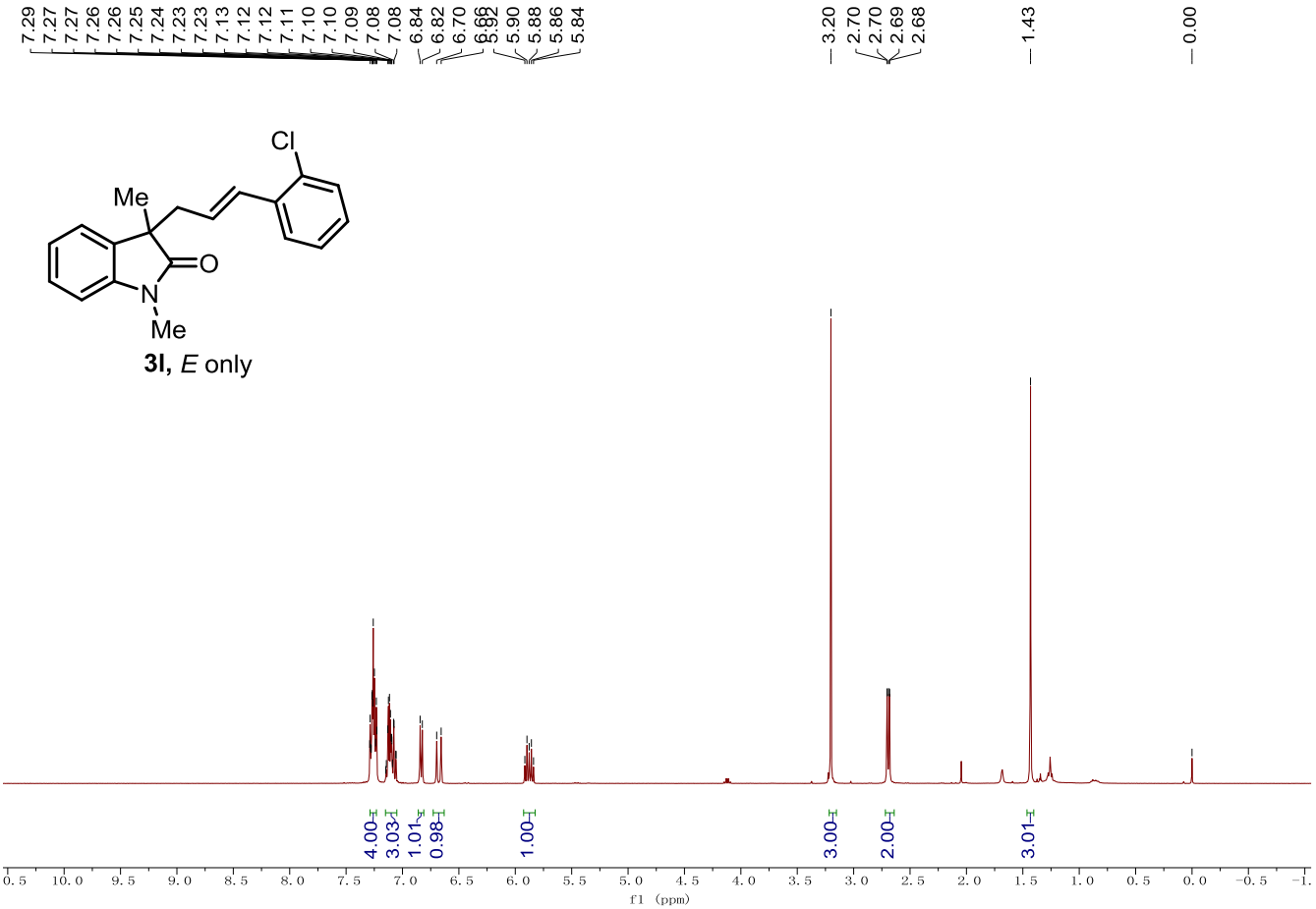


3k, ^{13}C NMR (101 MHz, $CDCl_3$)



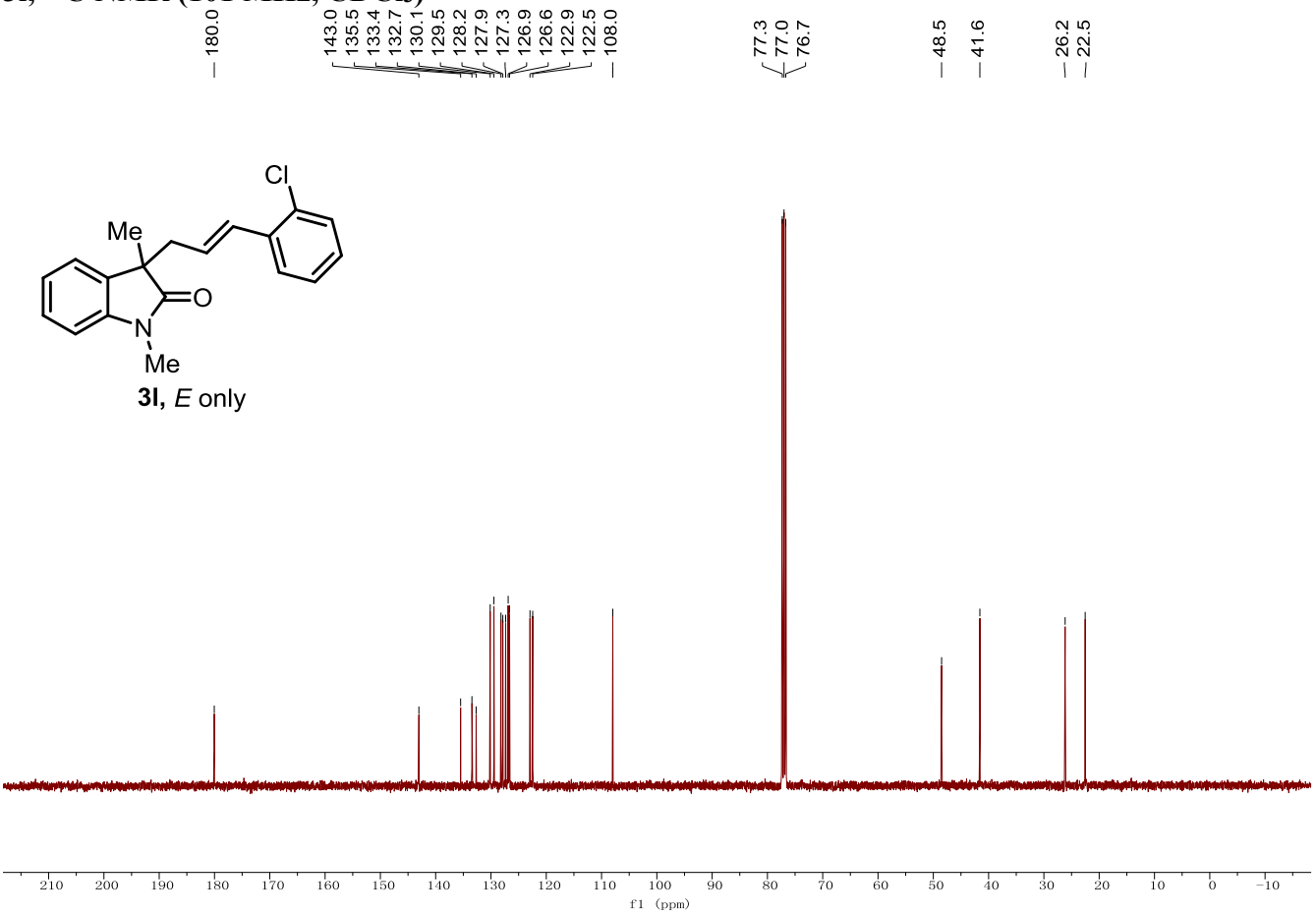
3k, *E* only

3l, ^{1}H NMR (400 MHz, $CDCl_3$)



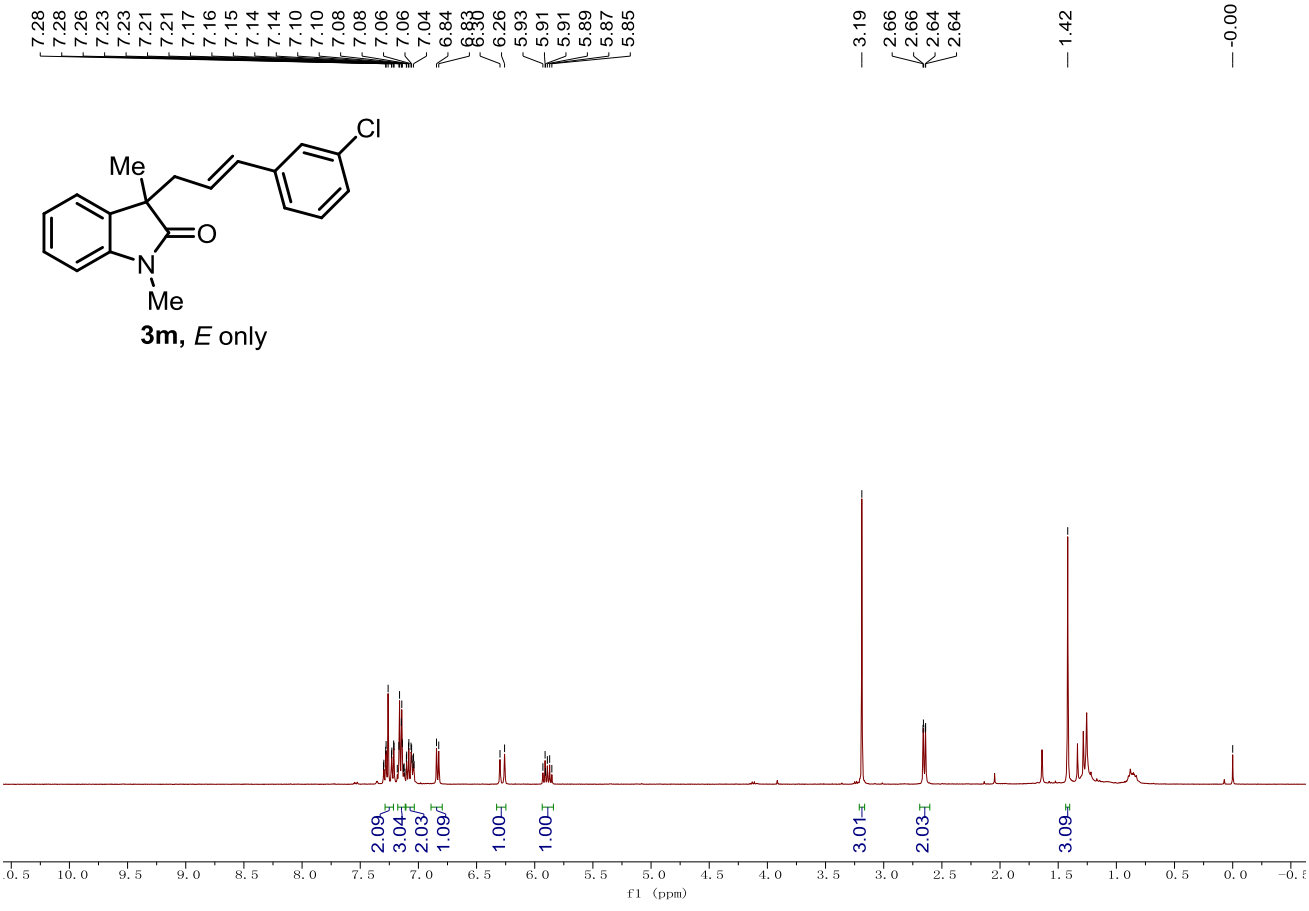
3l, *E* only

3l, ^{13}C NMR (101 MHz, $CDCl_3$)



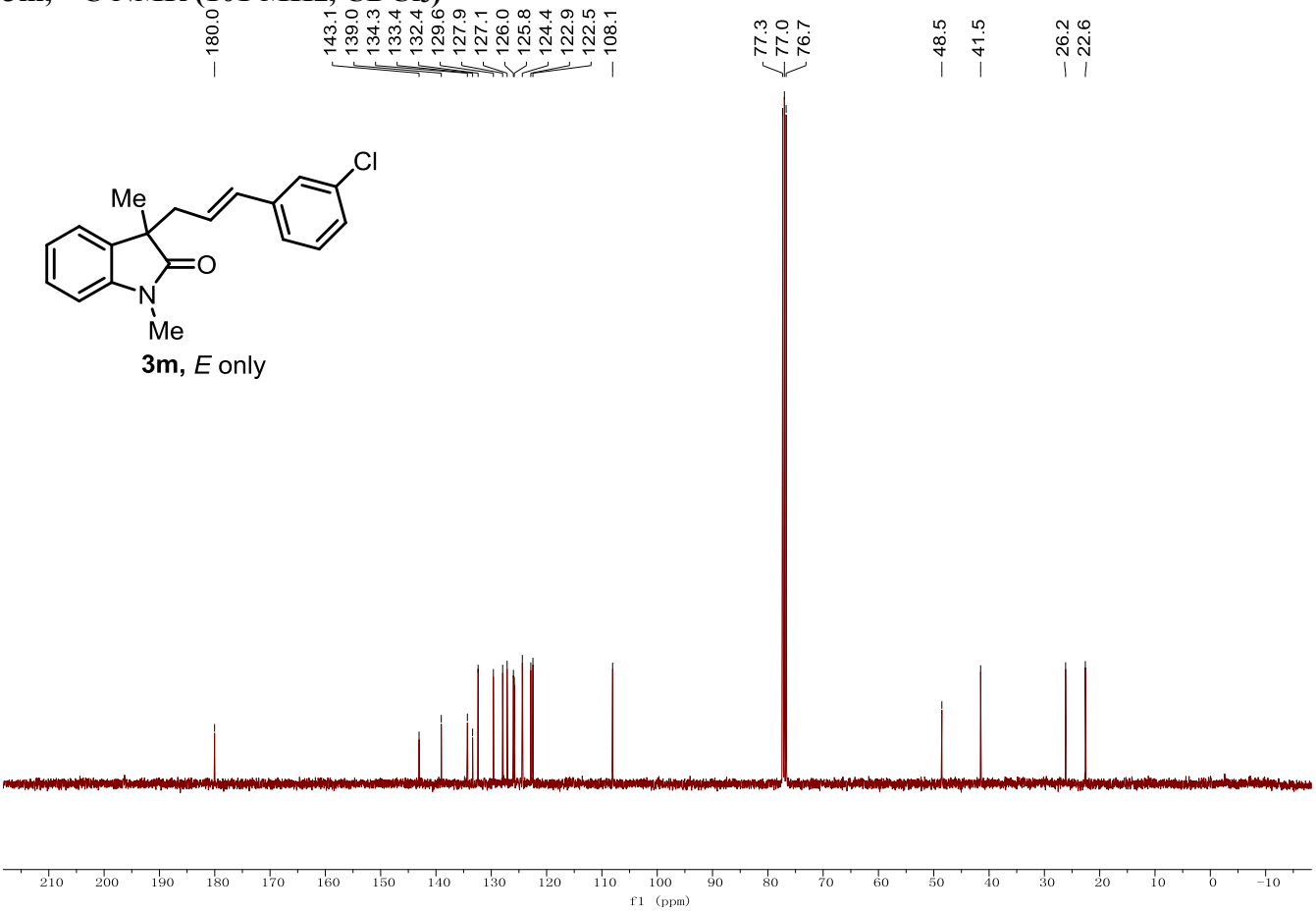
3l, *E* only

3m, ^{1}H NMR (400 MHz, $CDCl_3$)



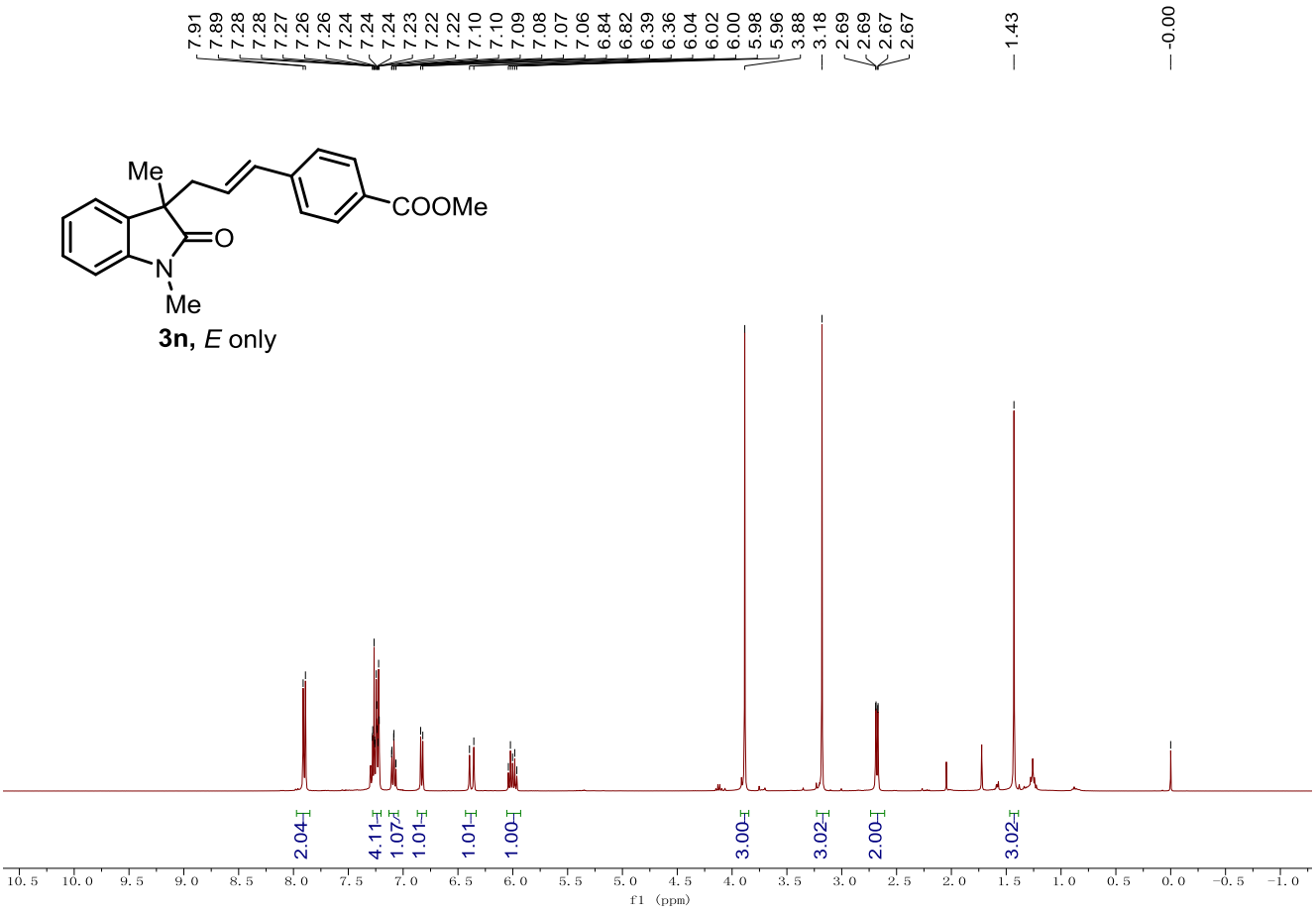
3m, *E* only

3m, ^{13}C NMR (101 MHz, $CDCl_3$)



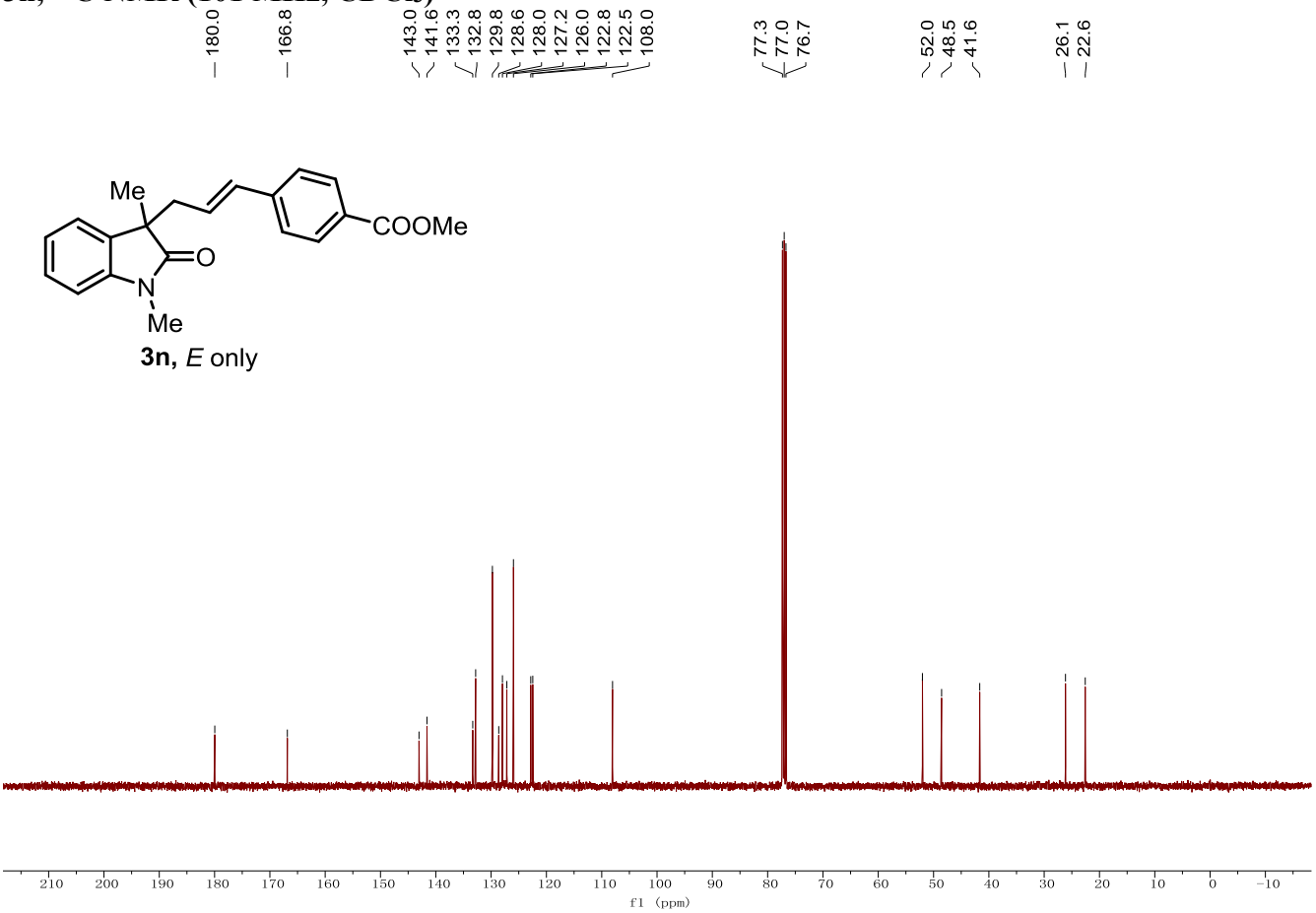
3m, *E* only

3n, ^{1}H NMR (400 MHz, $CDCl_3$)



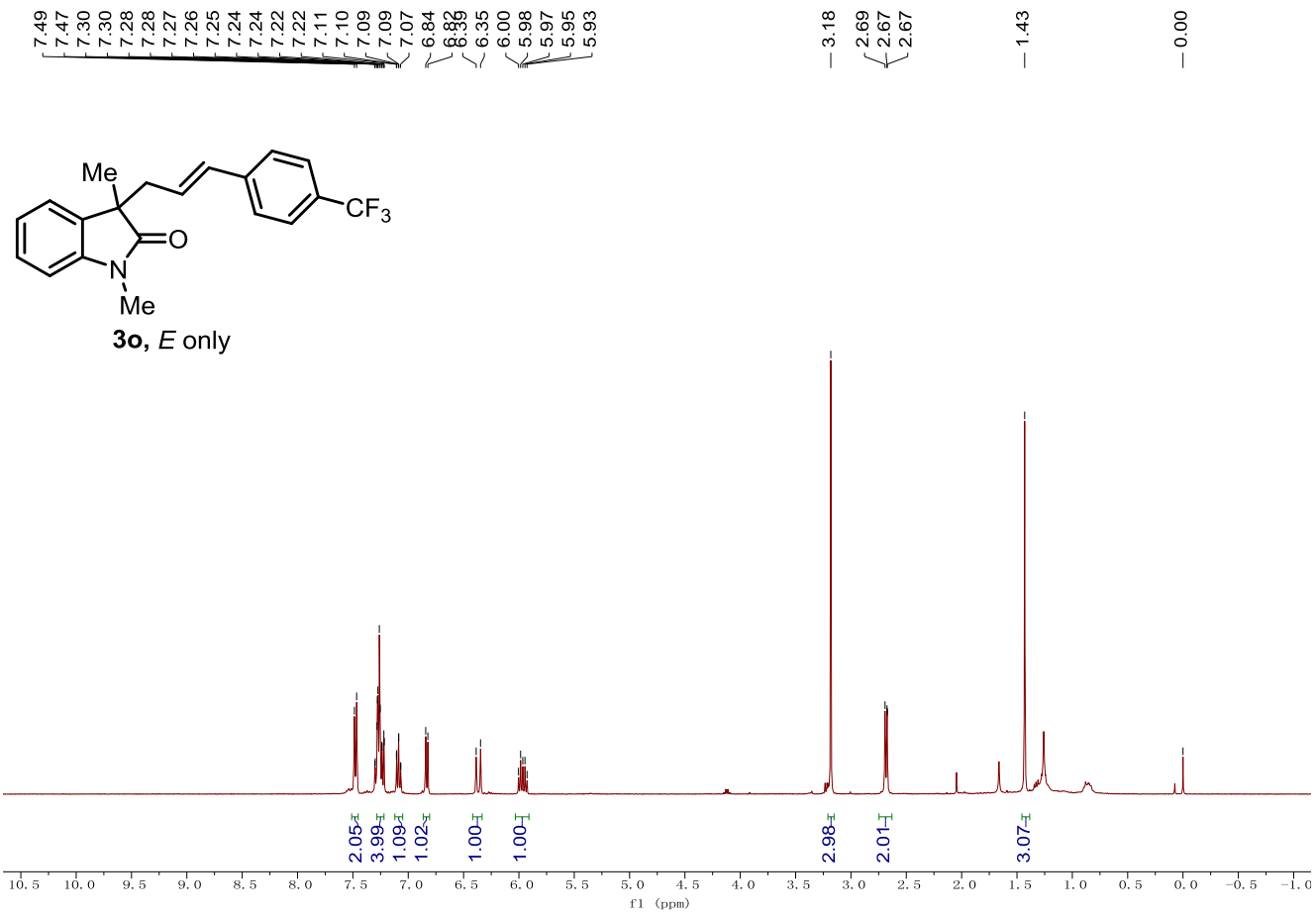
3n, *E* only

3n, ^{13}C NMR (101 MHz, $CDCl_3$)



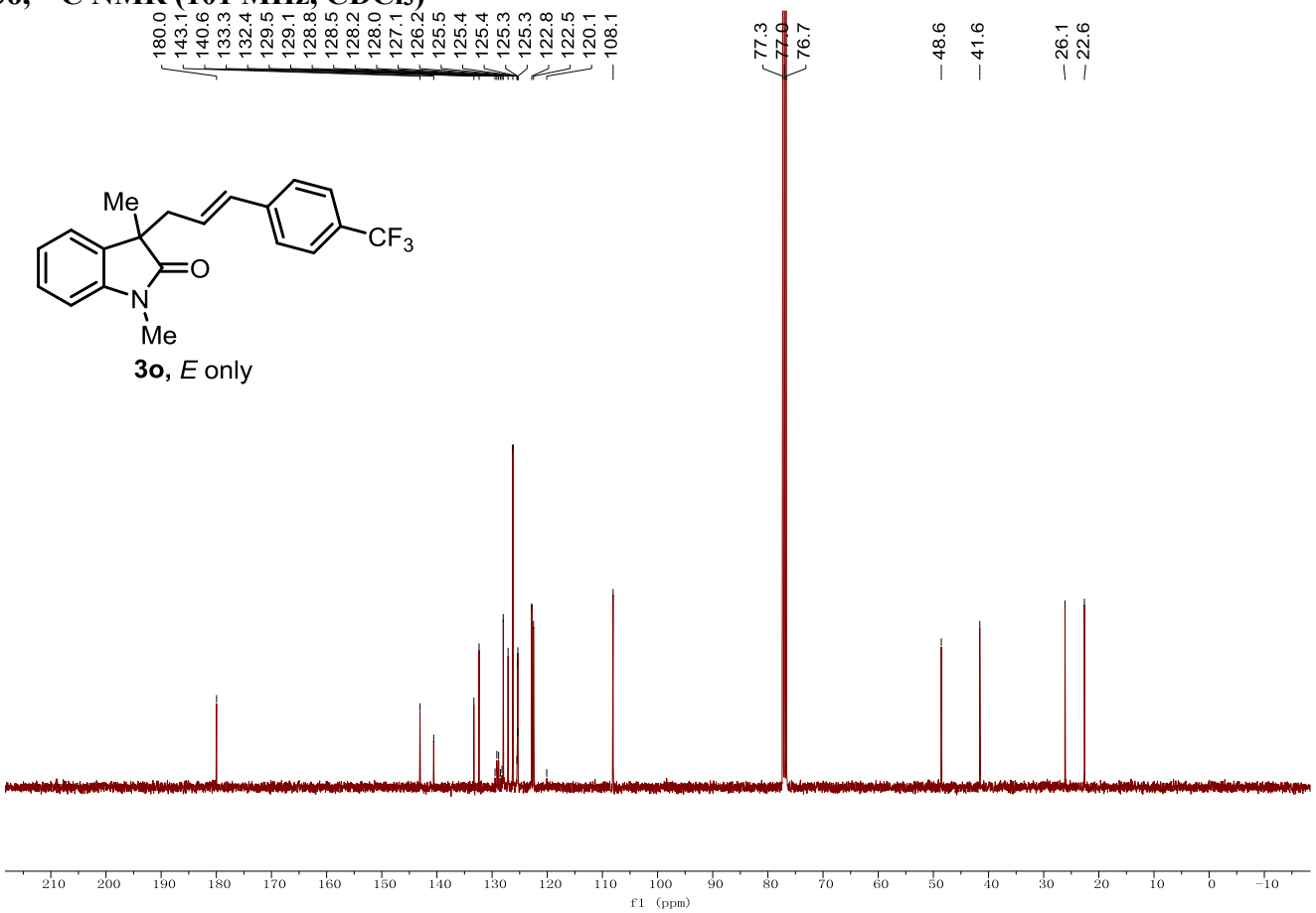
3n, *E* only

3o, ^{1}H NMR (400 MHz, $CDCl_3$)

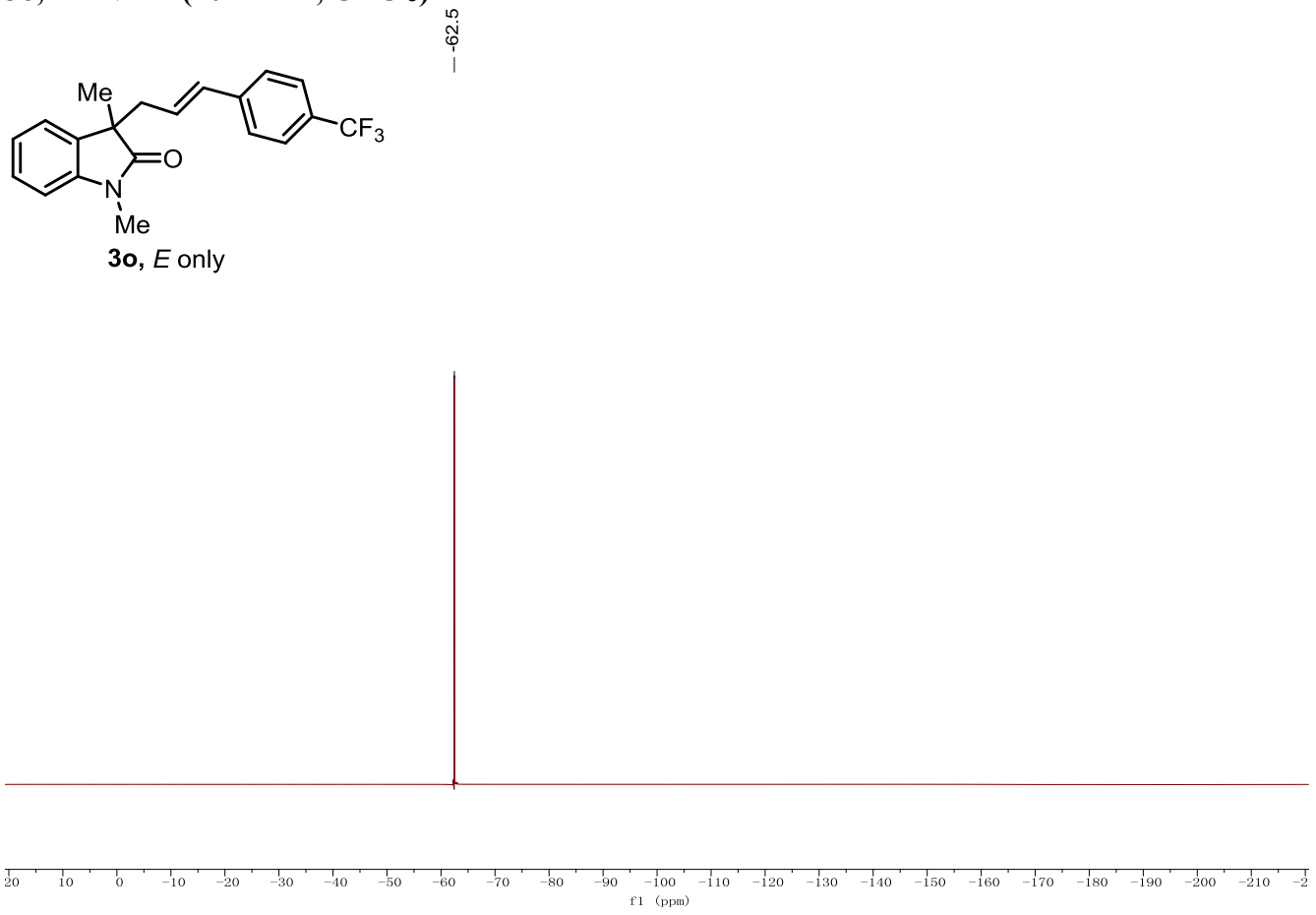


3o, *E* only

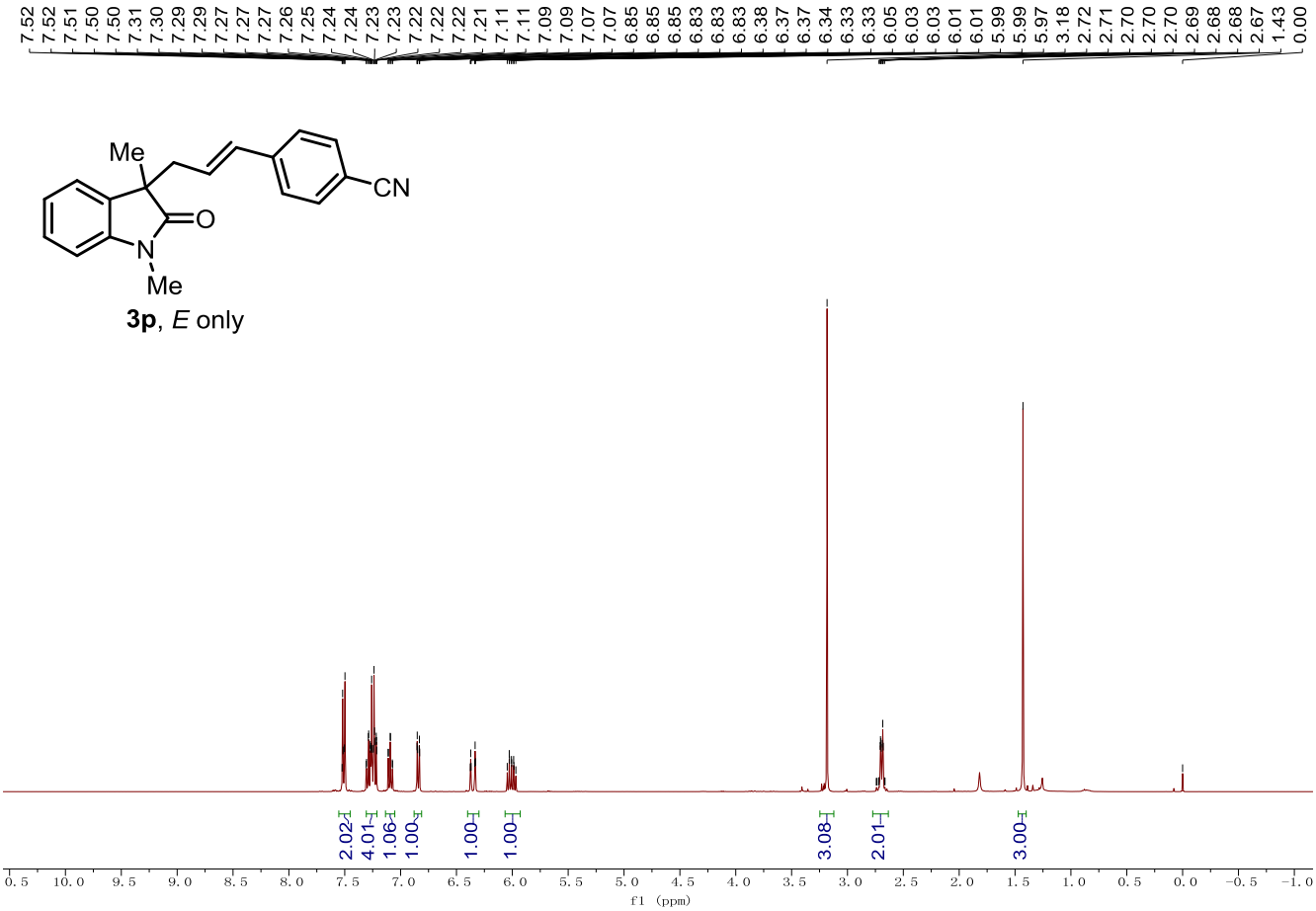
3o, ^{13}C NMR (101 MHz, $CDCl_3$)



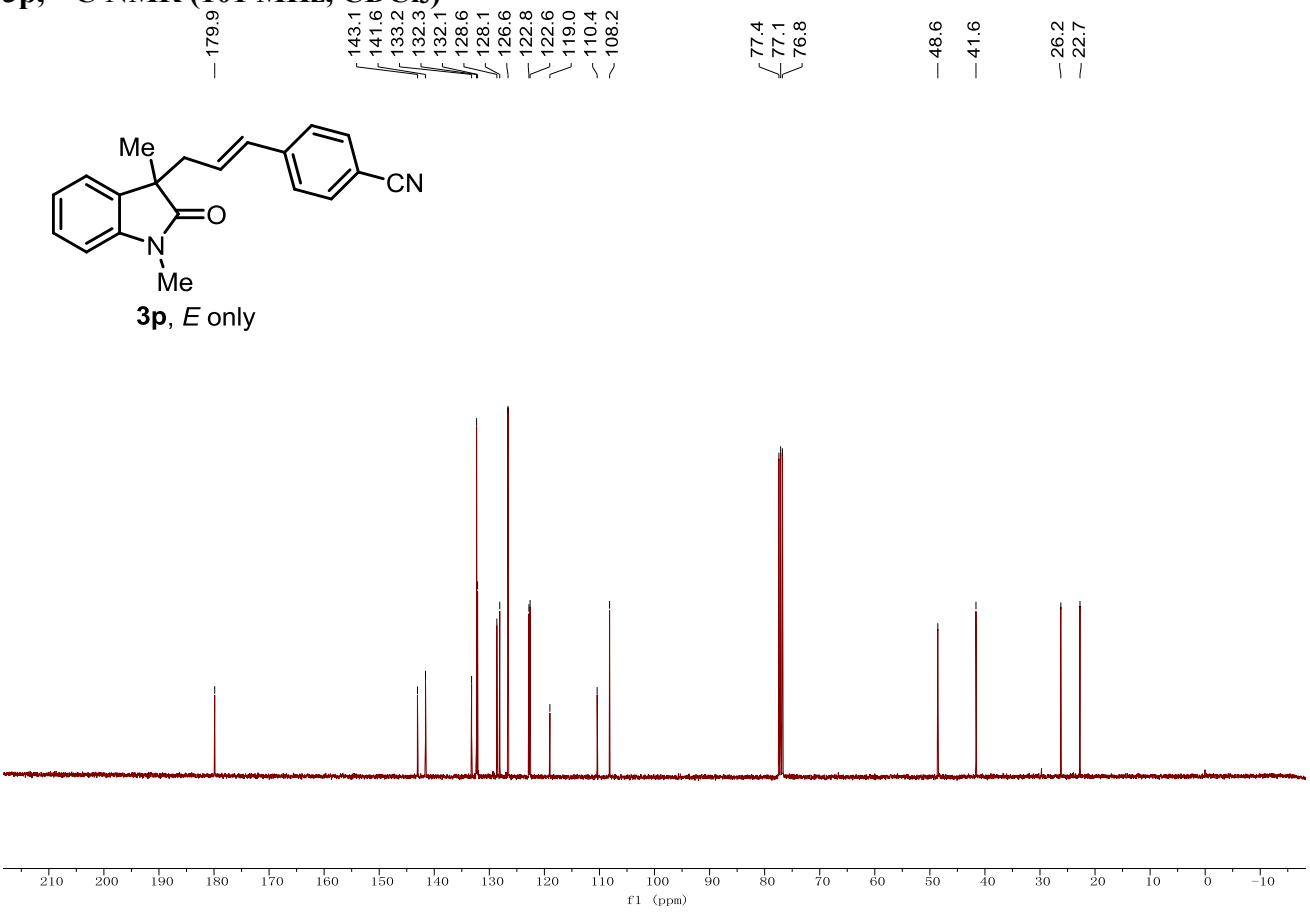
3o, ^{19}F NMR (101 MHz, $CDCl_3$)



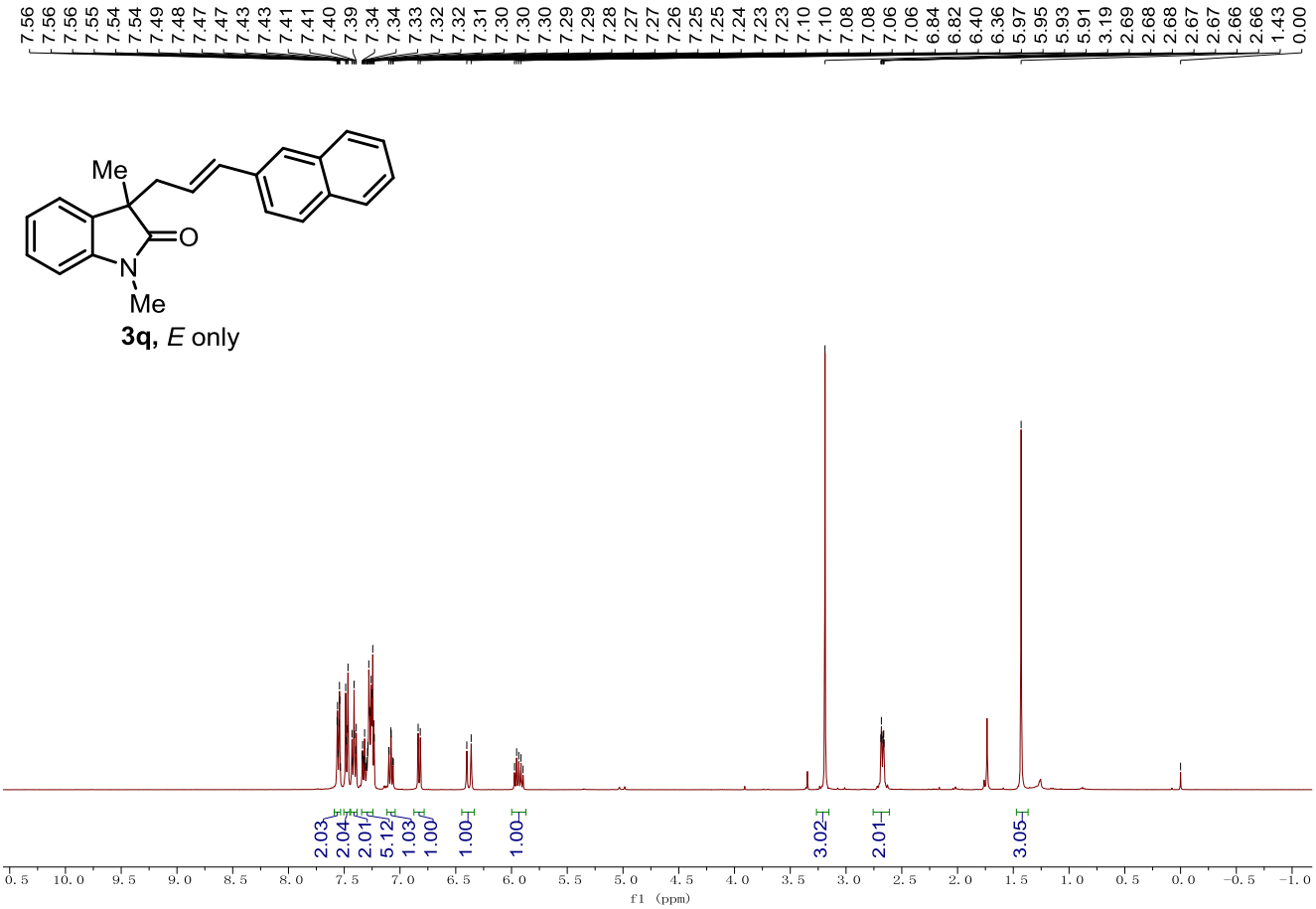
3p, ^{1}H NMR (400 MHz, $CDCl_3$)



3p, ^{13}C NMR (101 MHz, $CDCl_3$)

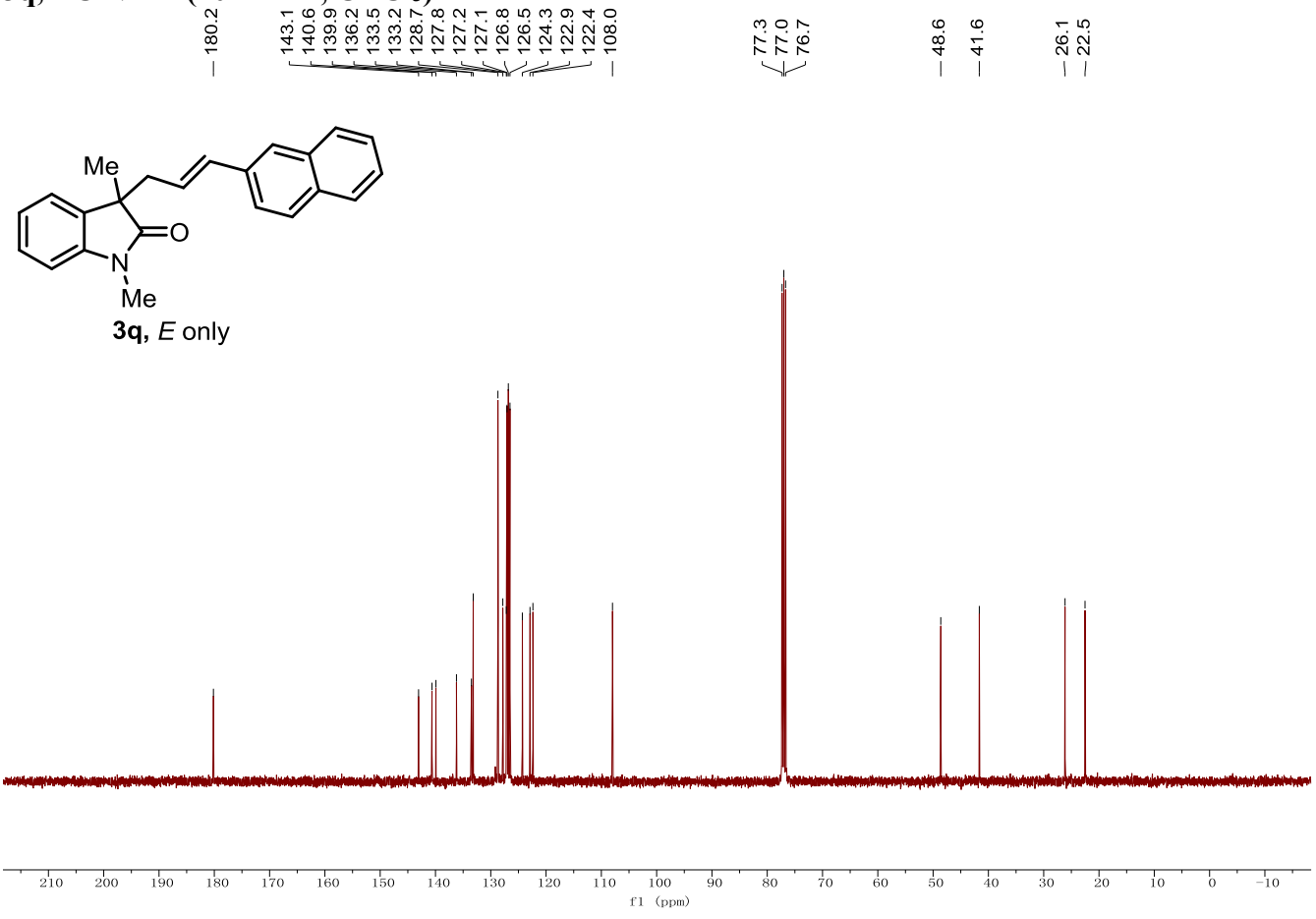


3q, ^{1}H NMR (400 MHz, $CDCl_3$)



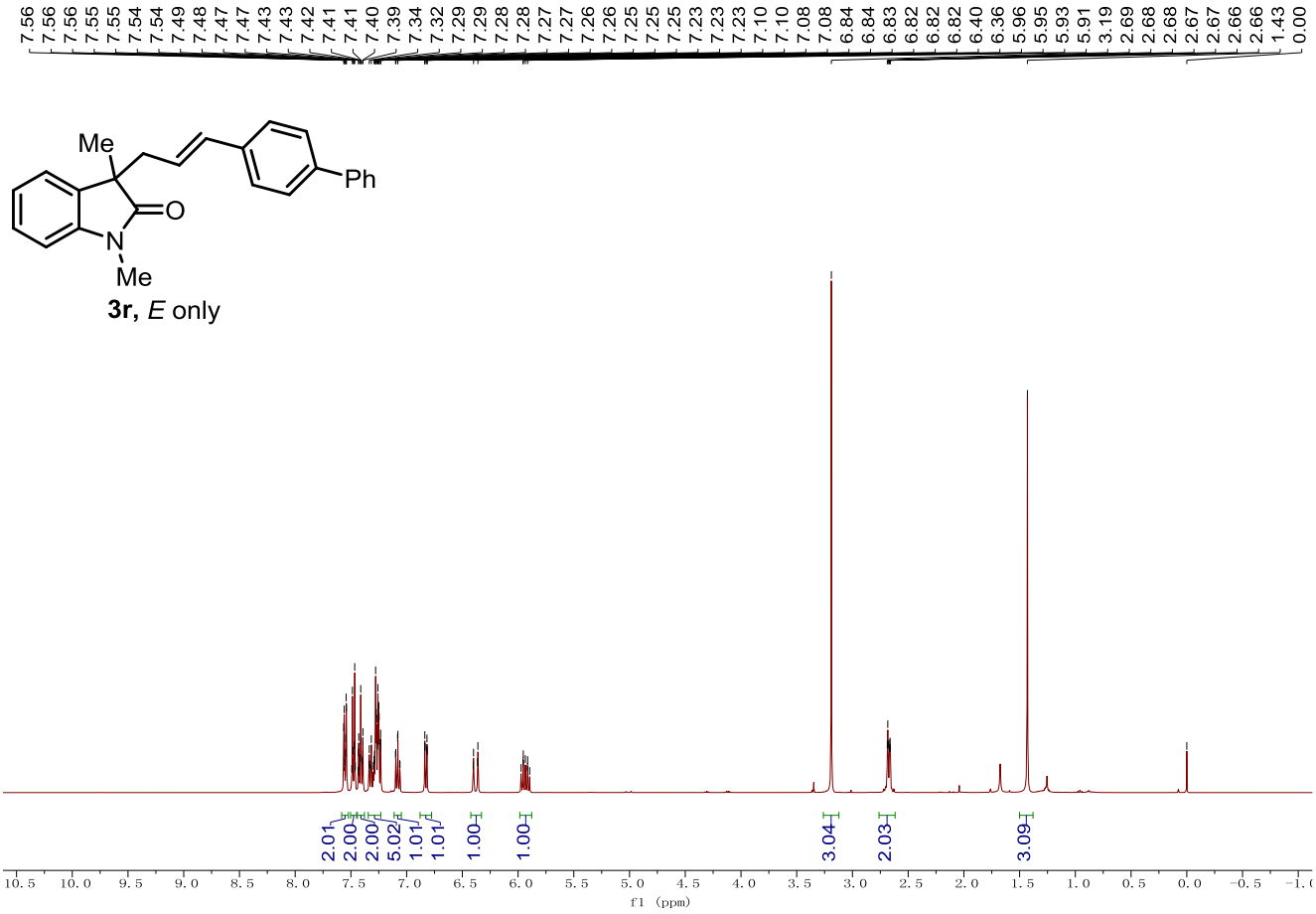
3q, *E* only

3q, ^{13}C NMR (101 MHz, $CDCl_3$)

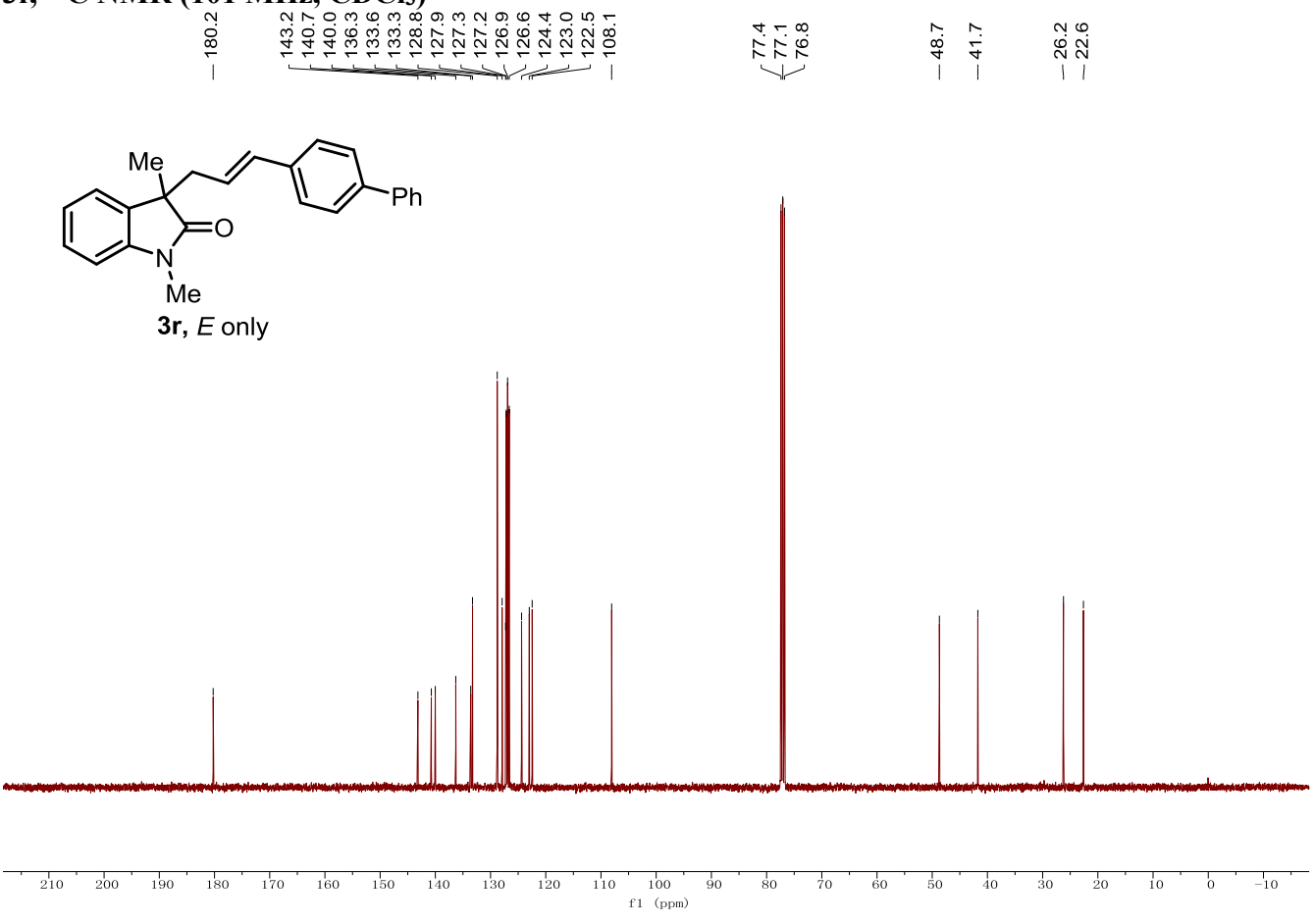


3q, *E* only

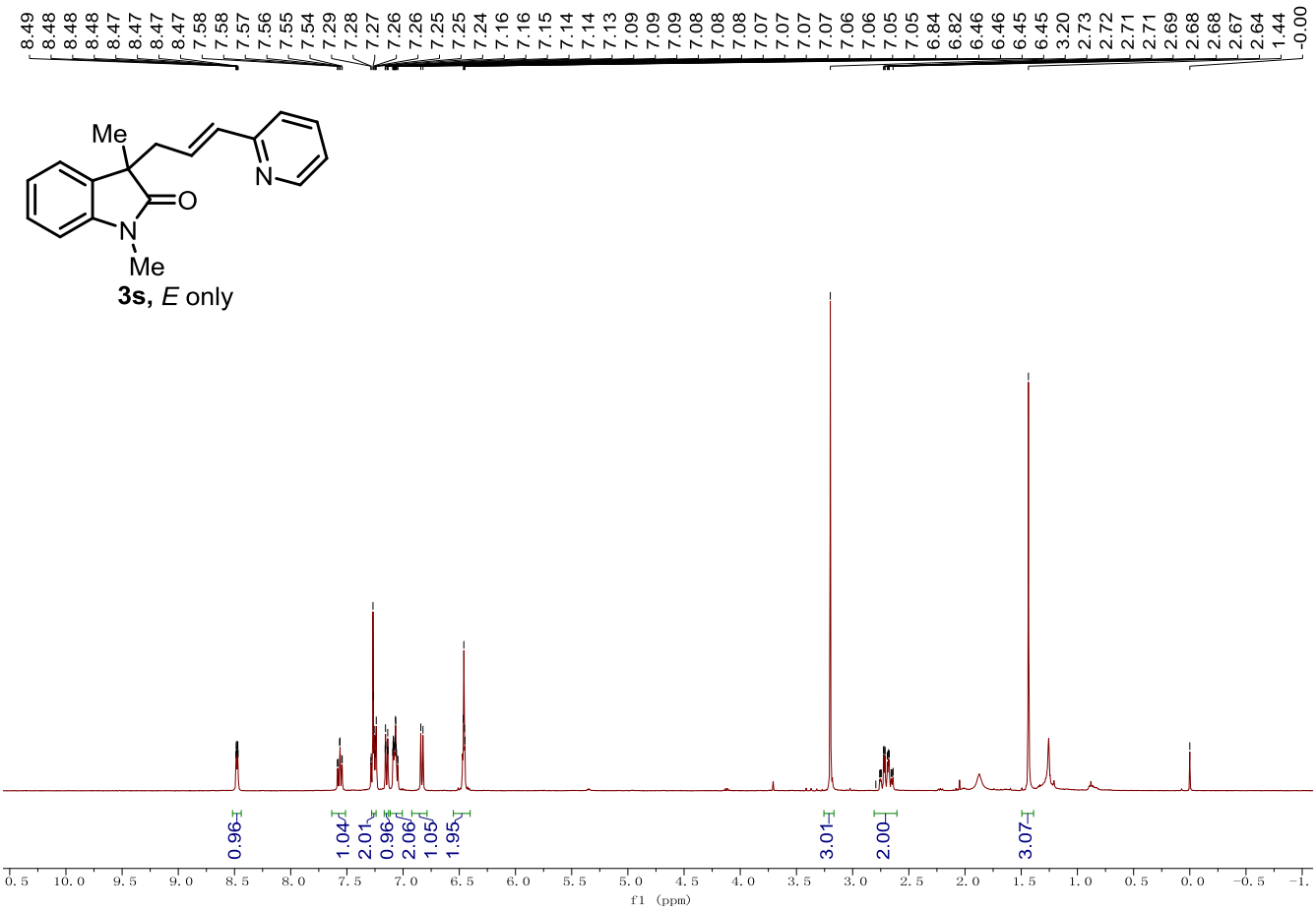
3r, ^{1}H NMR (400 MHz, $CDCl_3$)



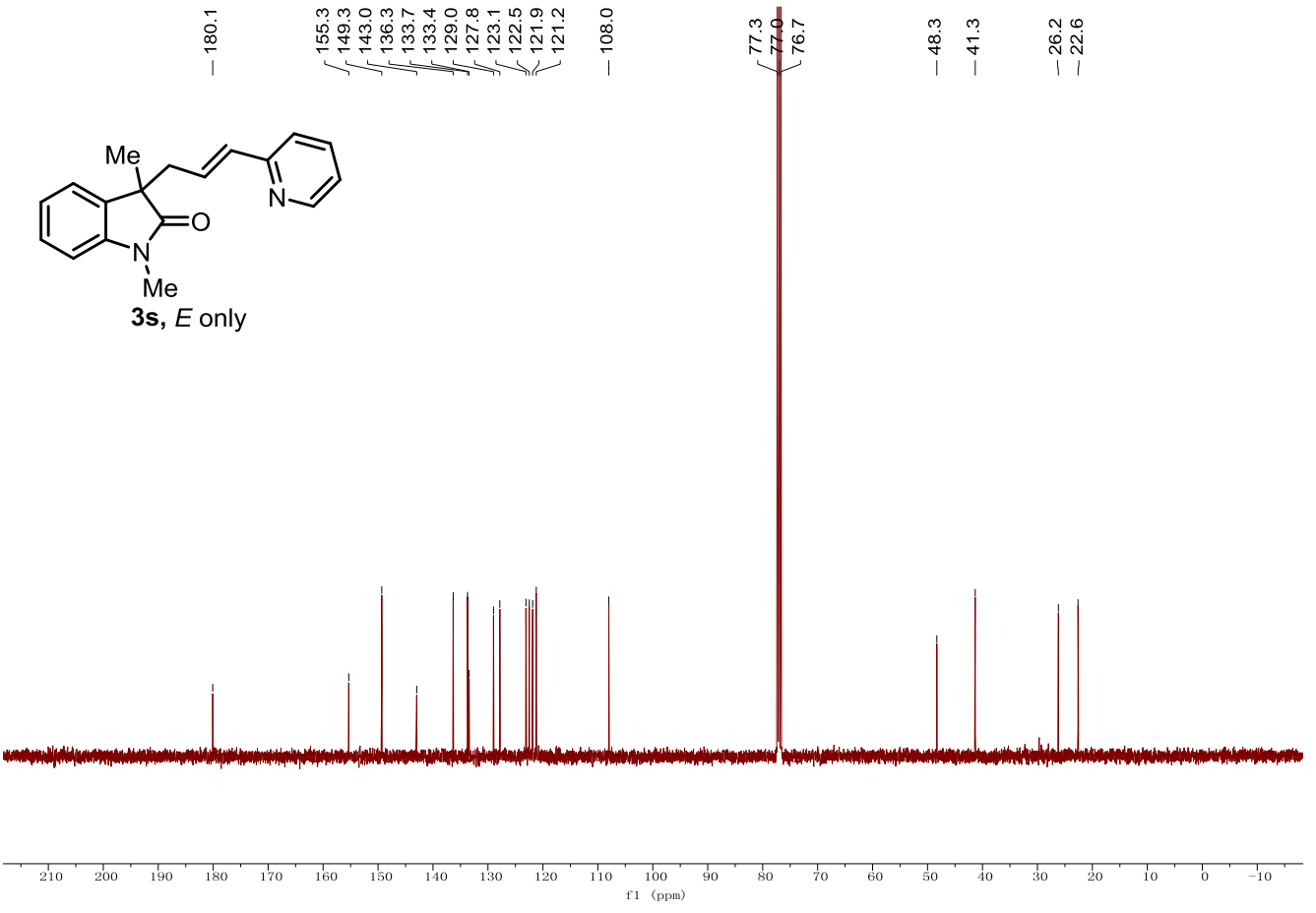
3r, ^{13}C NMR (101 MHz, $CDCl_3$)



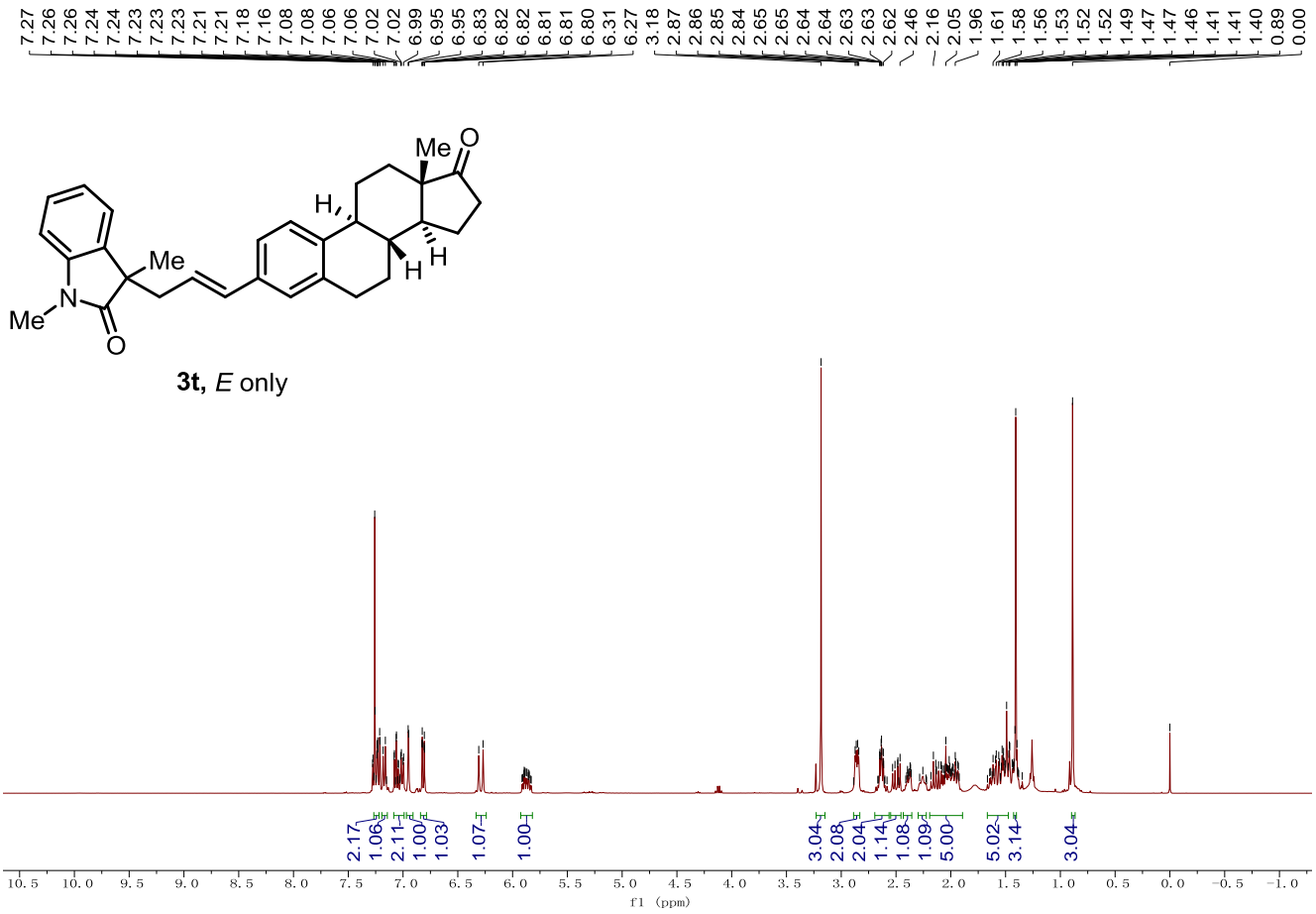
3s, ^{1}H NMR (400 MHz, $CDCl_3$)



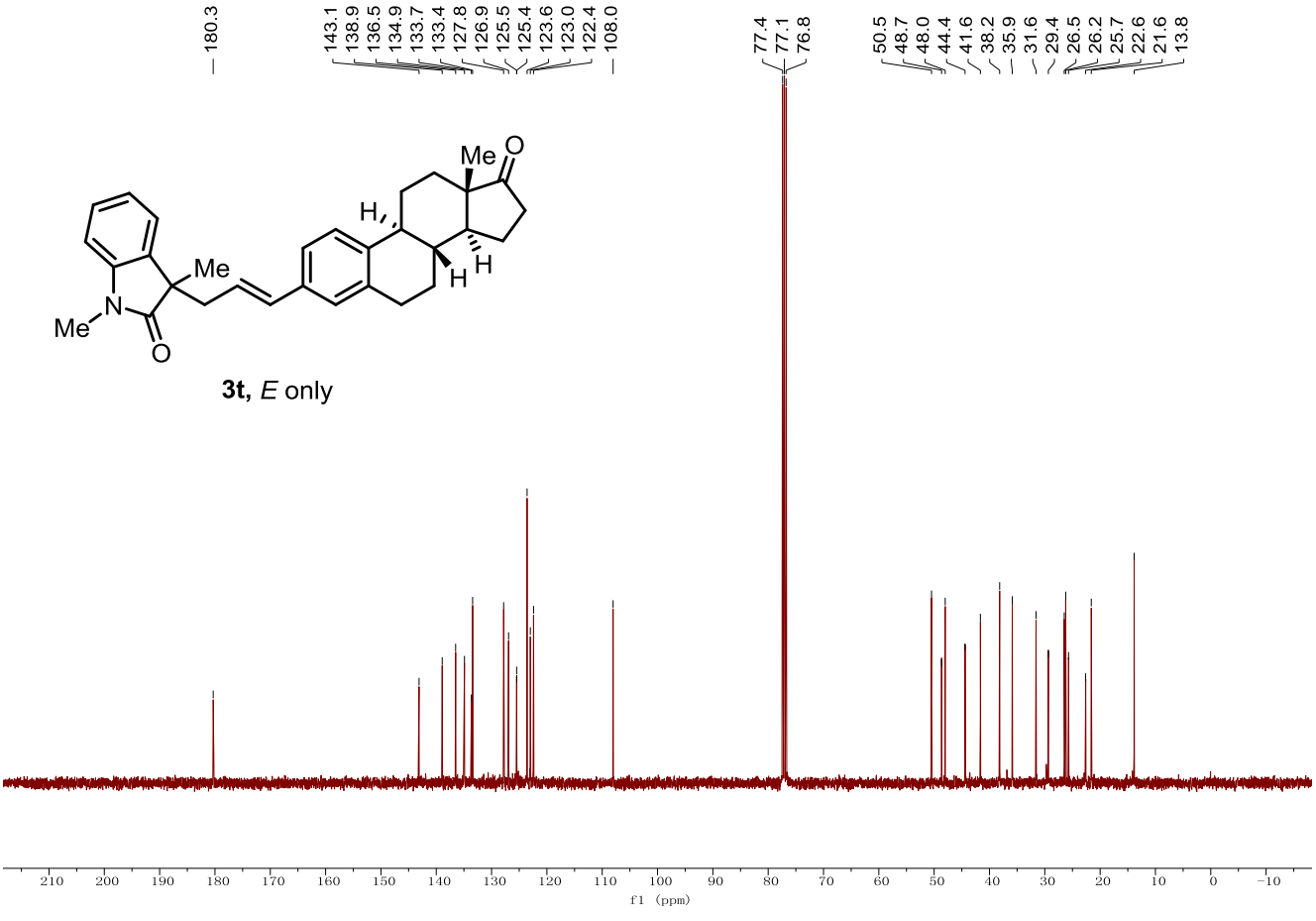
3s, ^{13}C NMR (101 MHz, $CDCl_3$)



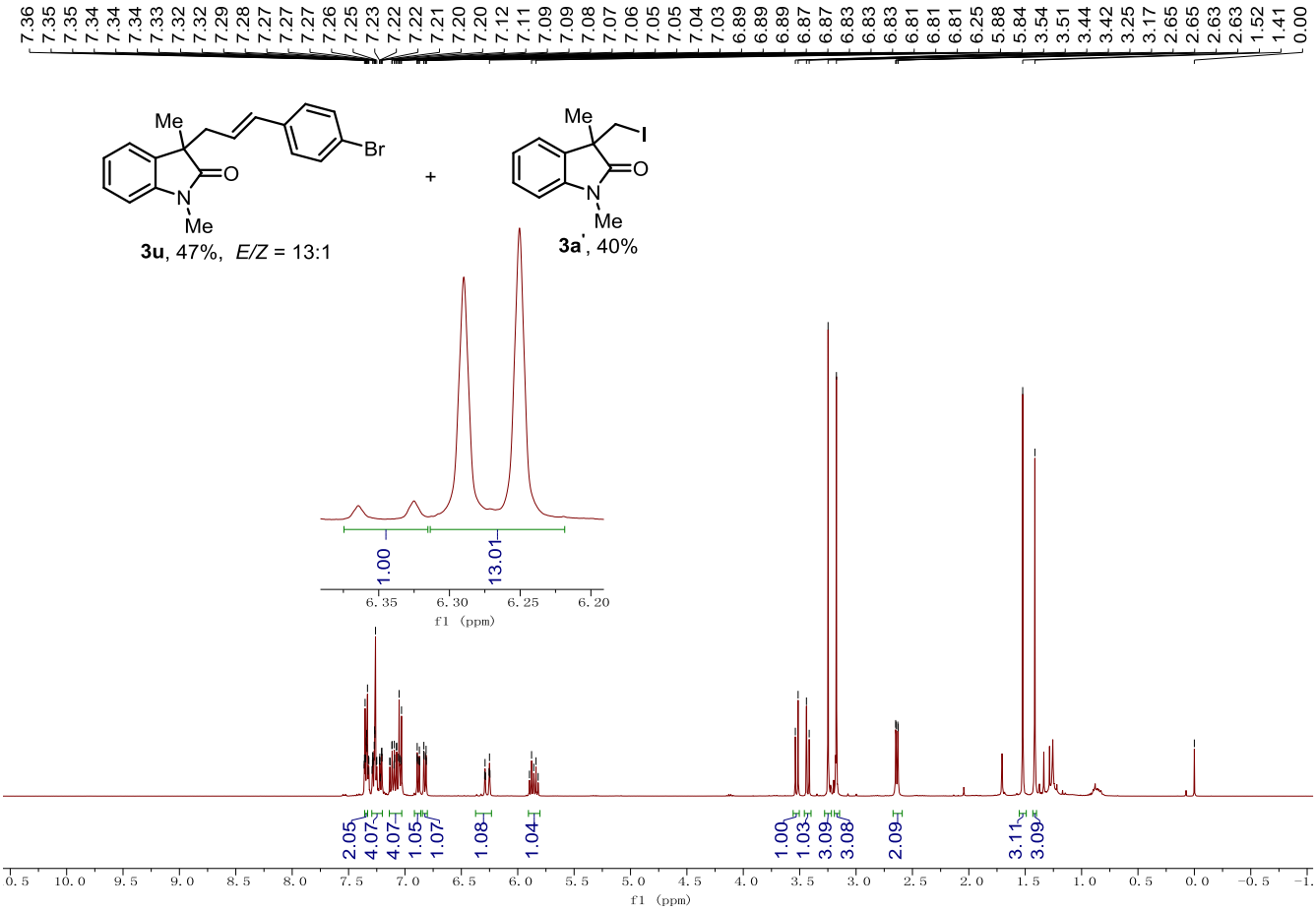
3t, ^{1}H NMR (400 MHz, $CDCl_3$)



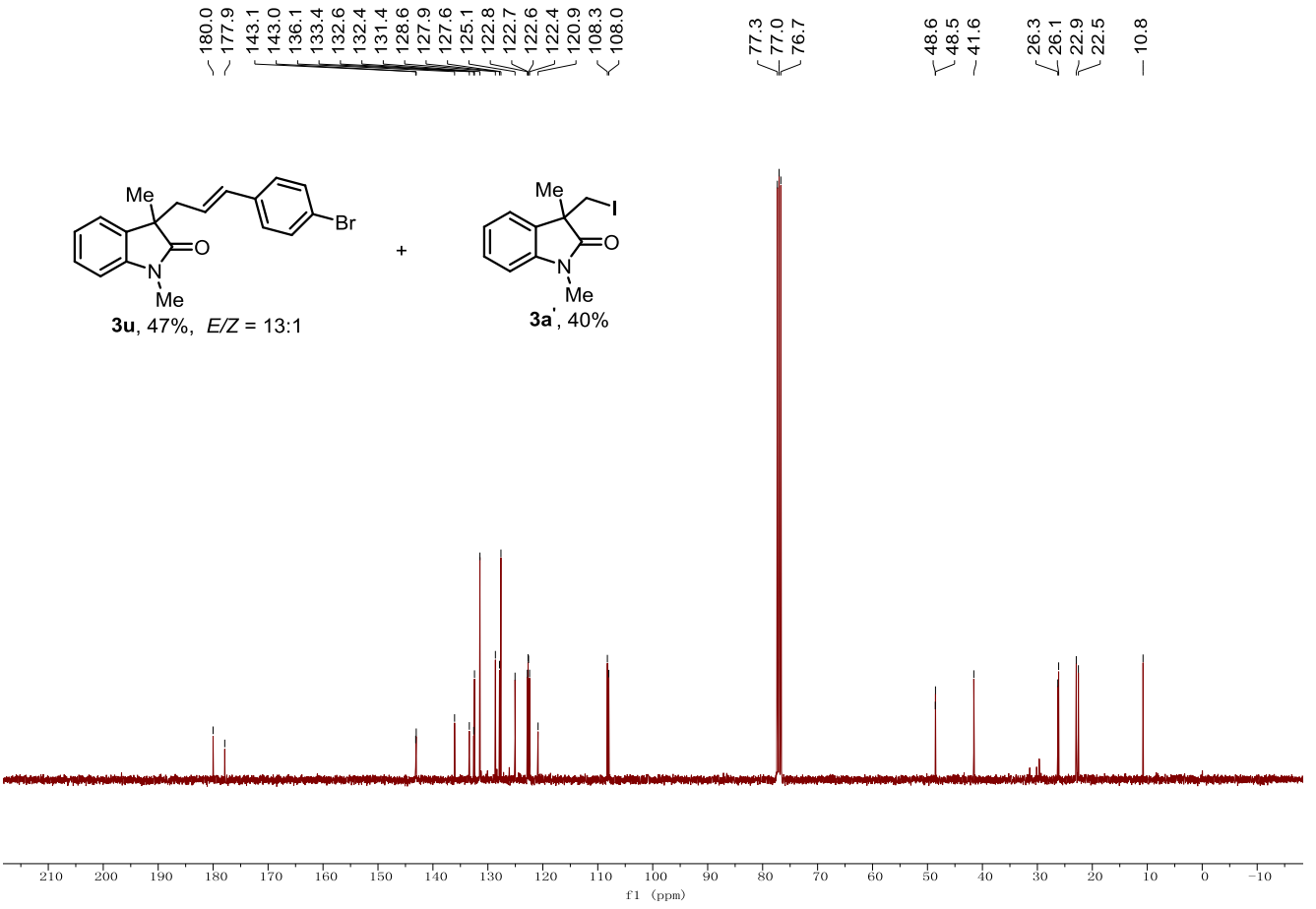
3t, ^{13}C NMR (101 MHz, $CDCl_3$)



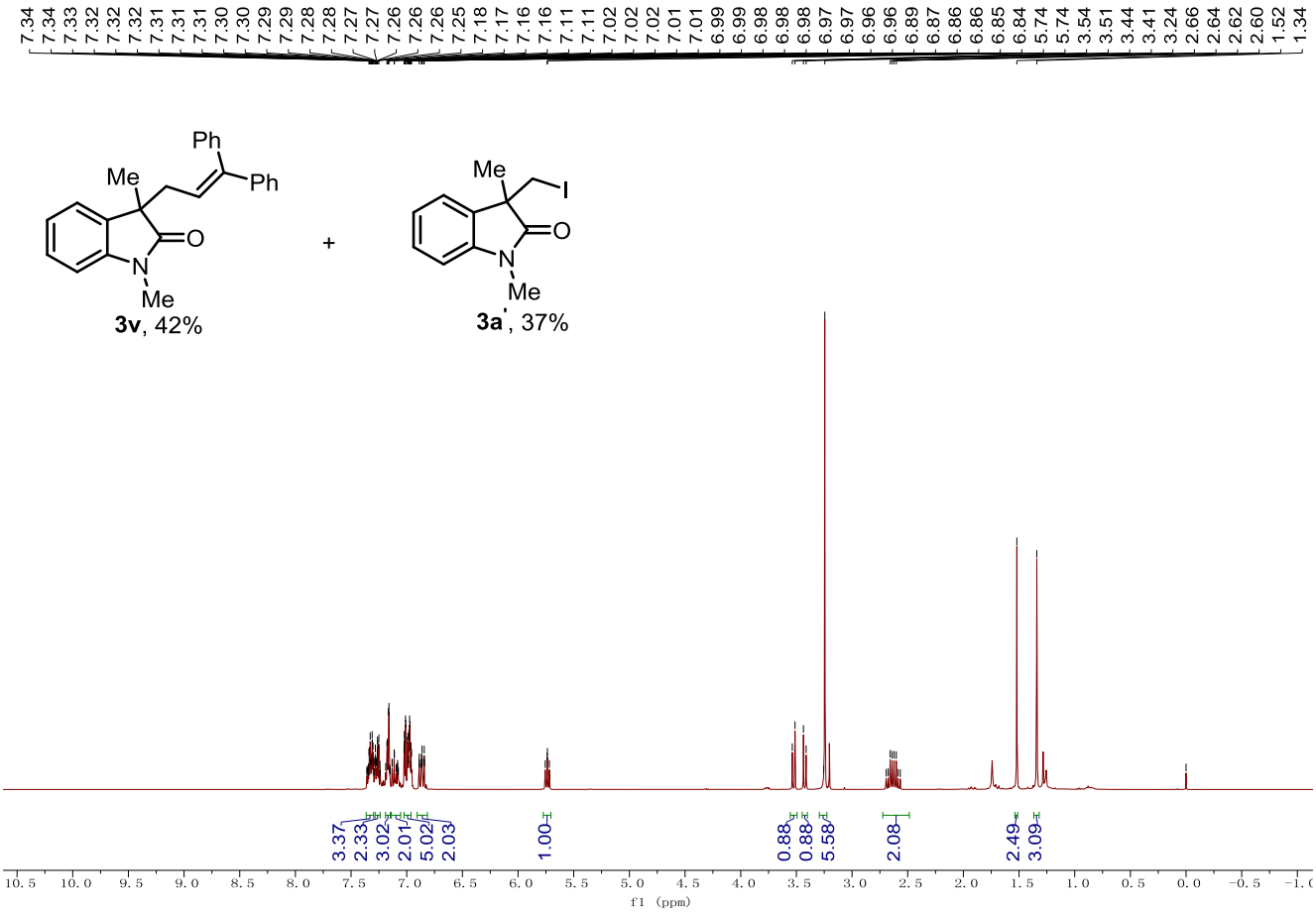
3u, ^{1}H NMR (400 MHz, CDCl$_3$)



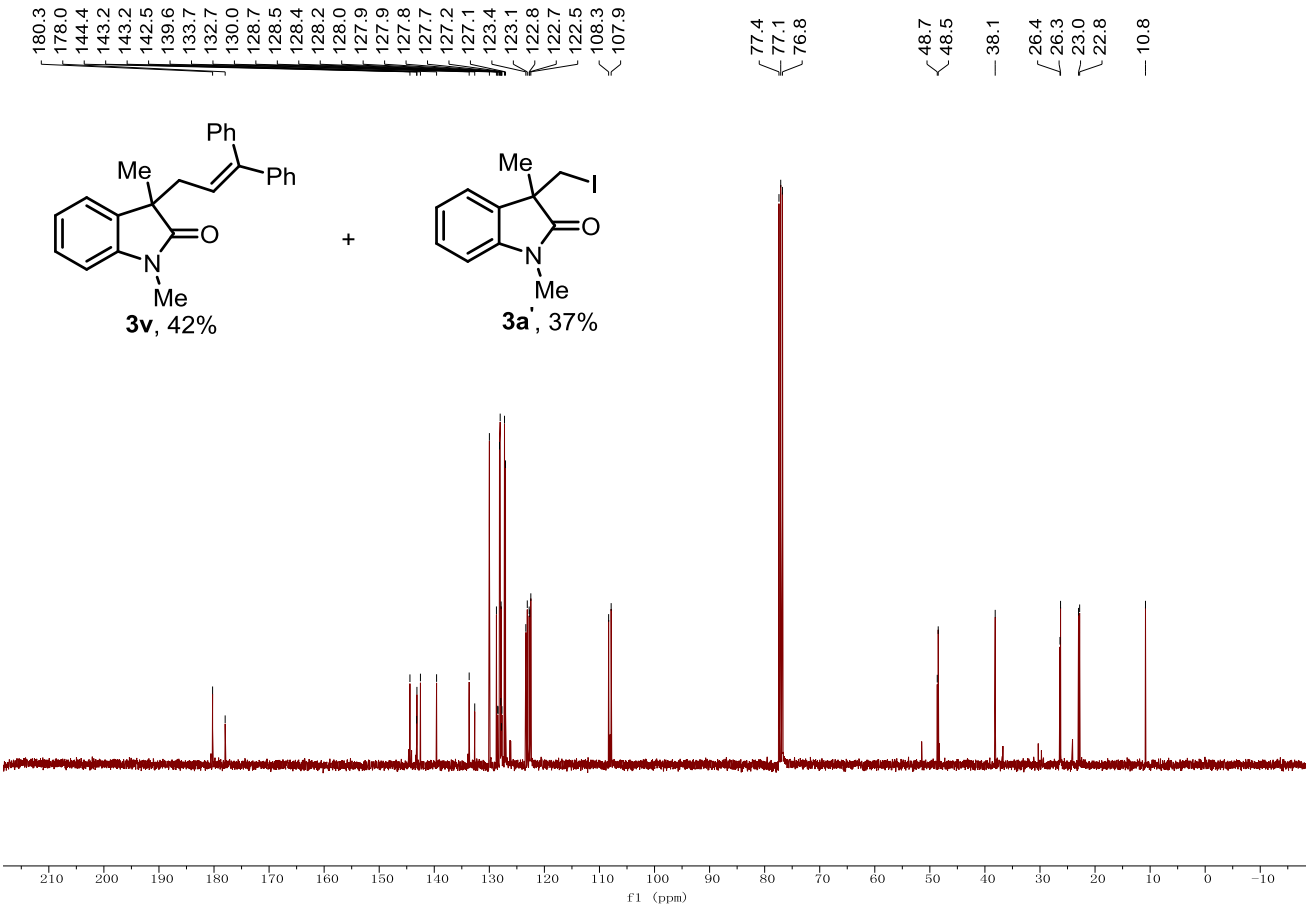
3u, ^{13}C NMR (101 MHz, CDCl$_3$)



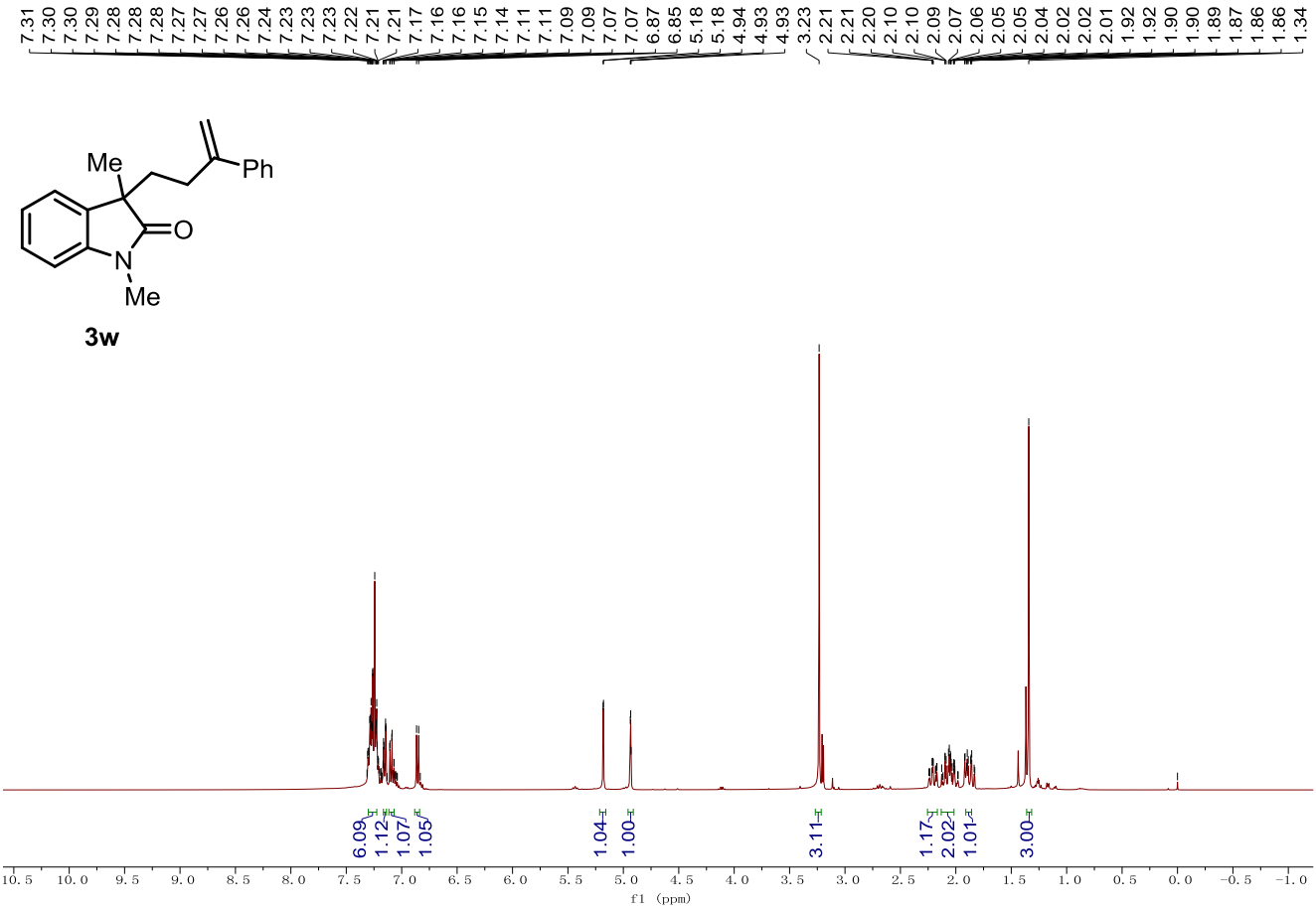
3v, ^{1}H NMR (400 MHz, $CDCl_3$)



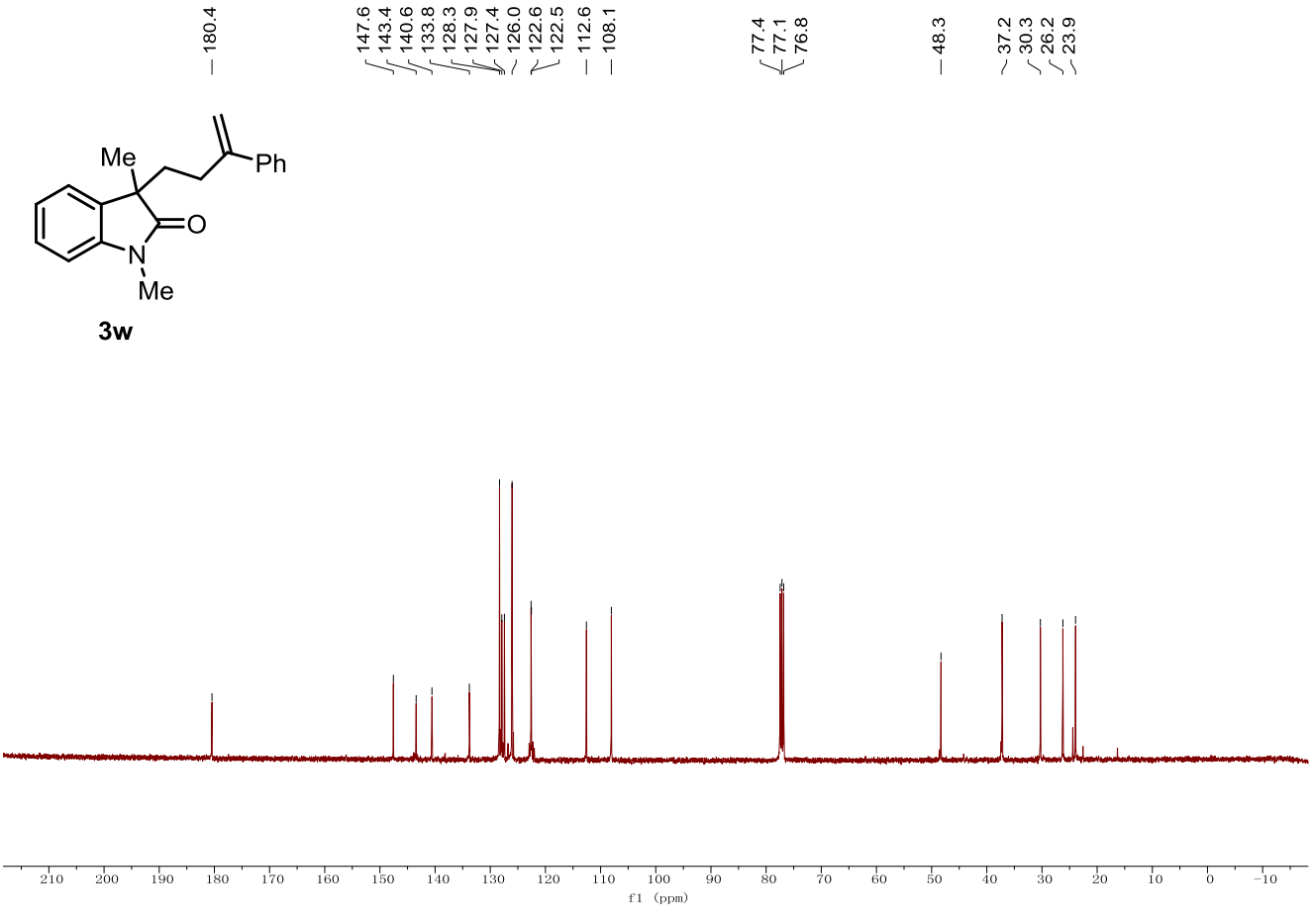
3v, ^{13}C NMR (101 MHz, $CDCl_3$)



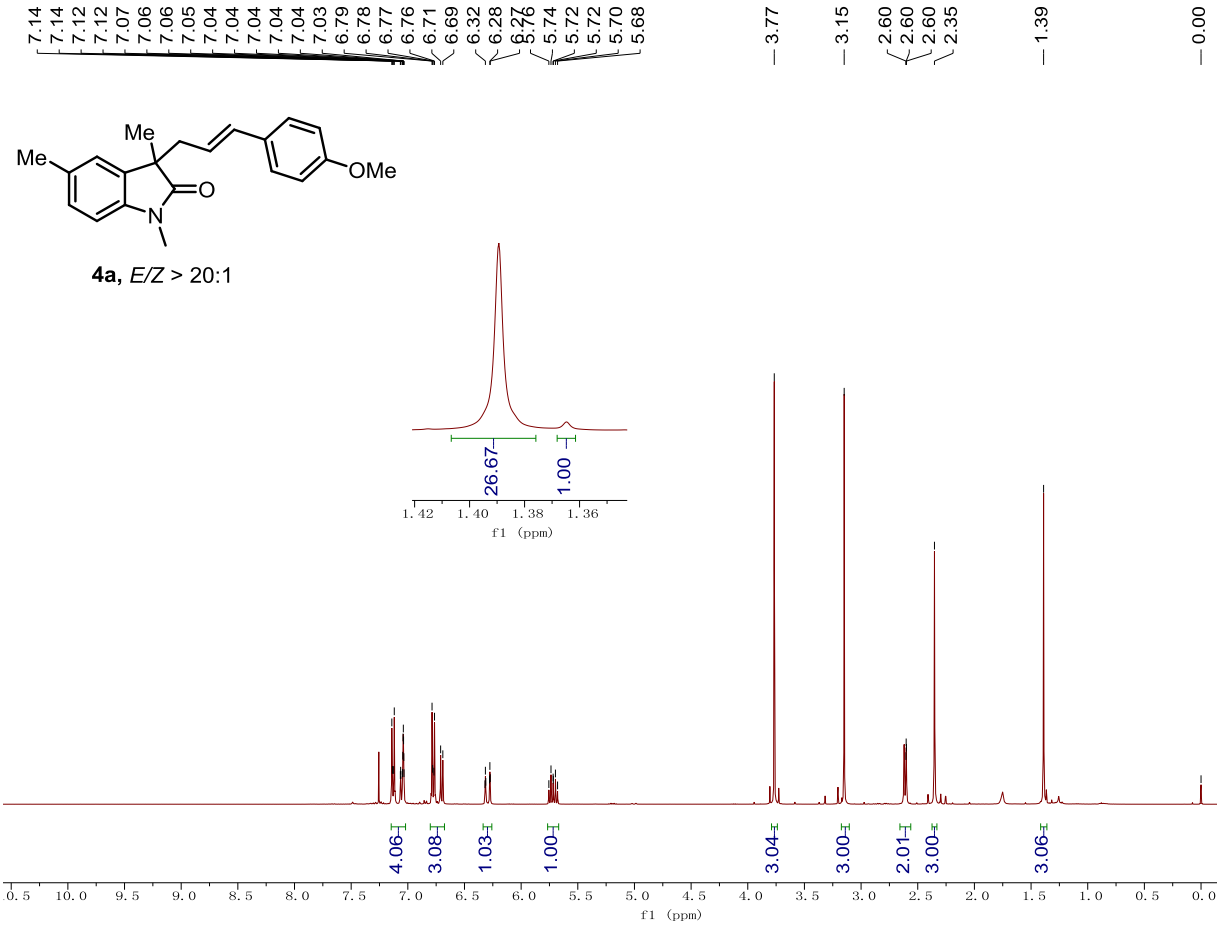
3w, ^{1}H NMR (400 MHz, $CDCl_3$)



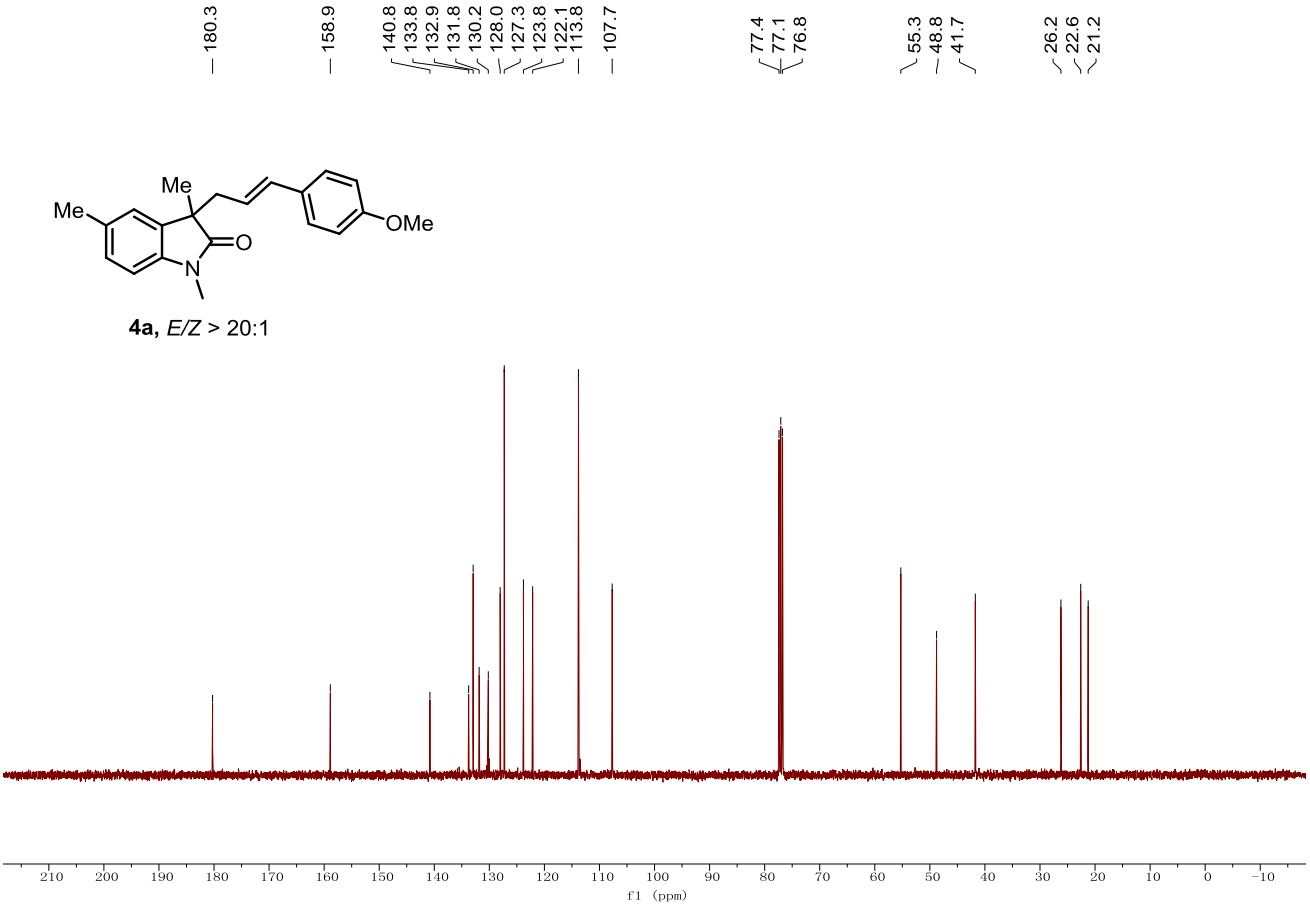
3w, ^{13}C NMR (101 MHz, $CDCl_3$)



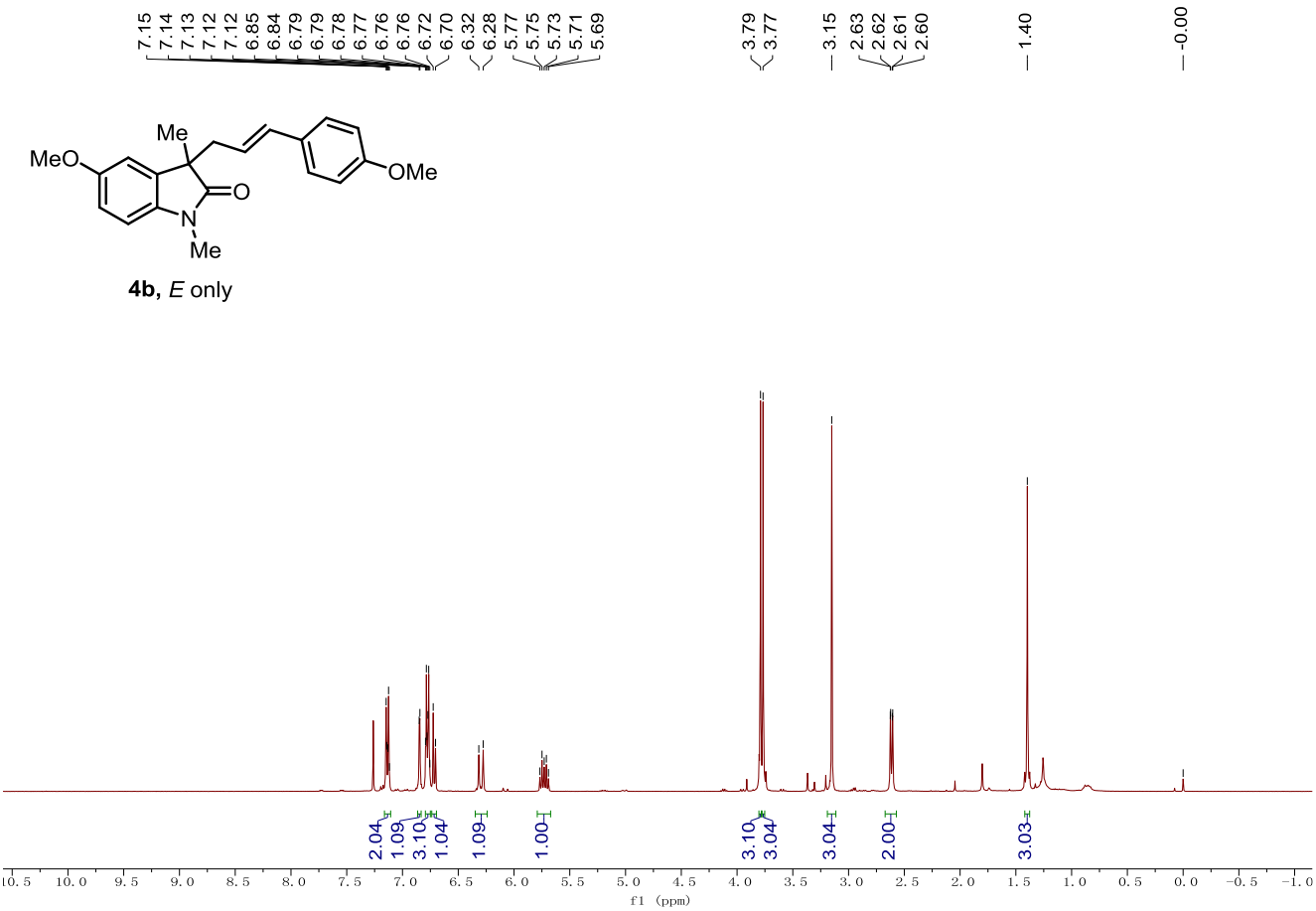
4a, ^{1}H NMR (400 MHz, CDCl$_3$)



4a, ^{13}C NMR (101 MHz, CDCl$_3$)

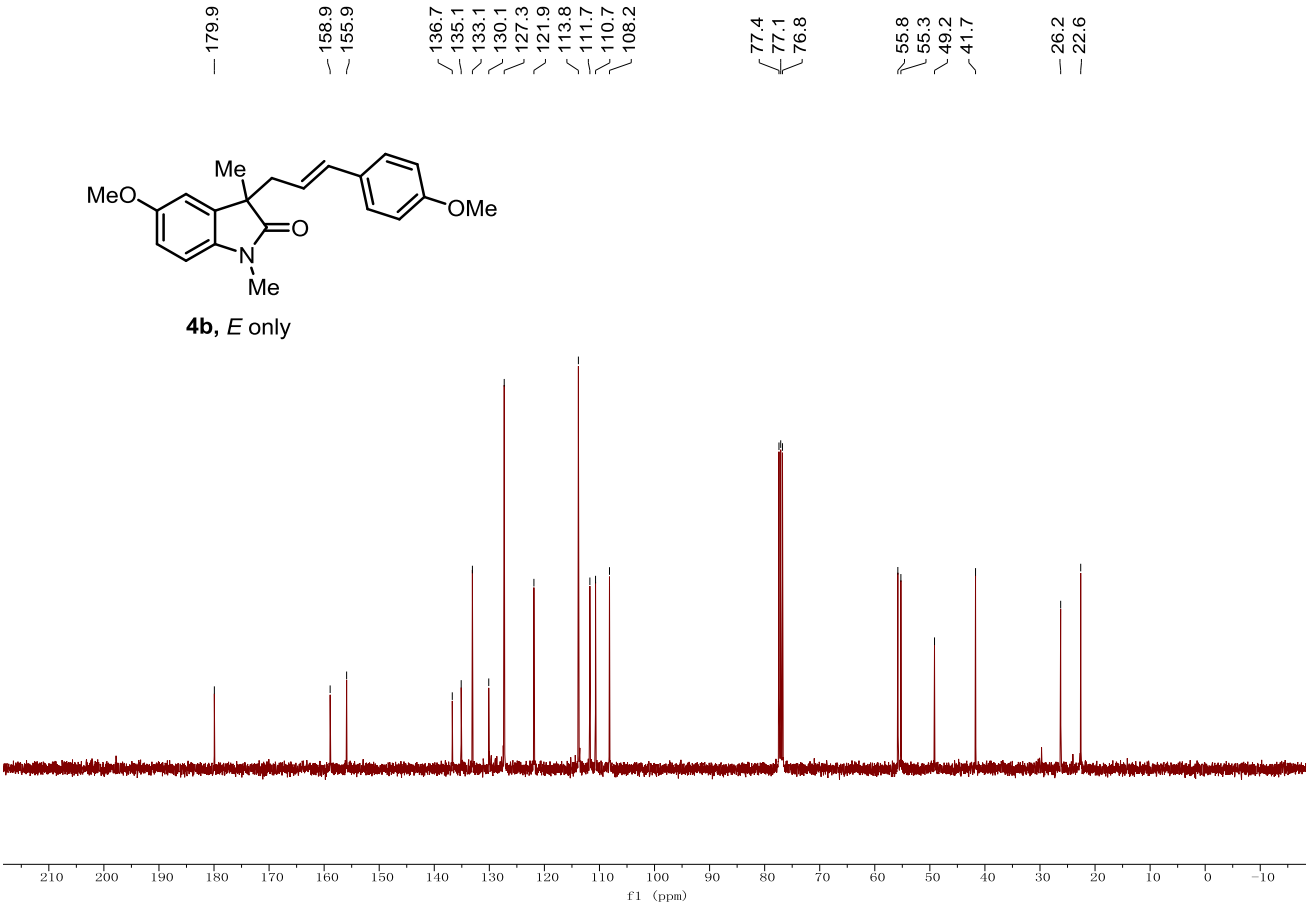


4b, ^{1}H NMR (400 MHz, $CDCl_3$)



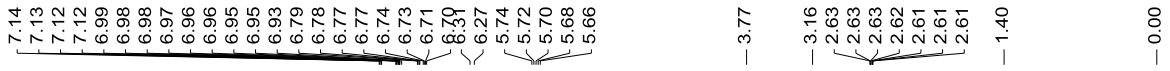
4b, *E* only

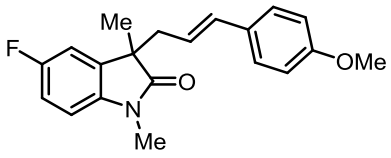
4b, ^{13}C NMR (101 MHz, $CDCl_3$)



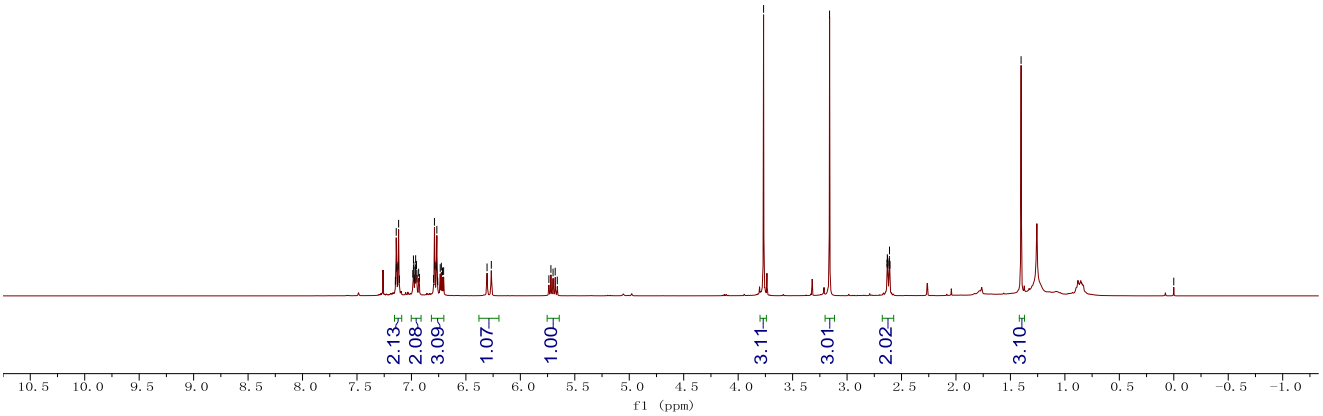
4b, *E* only

4c, ^{1}H NMR (400 MHz, $CDCl_3$)

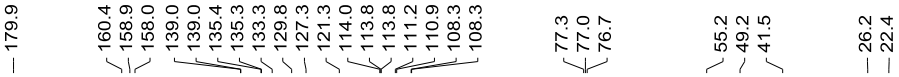


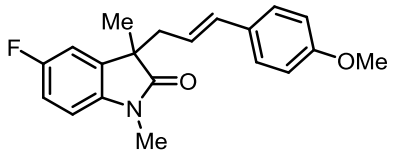


4c, *E* only

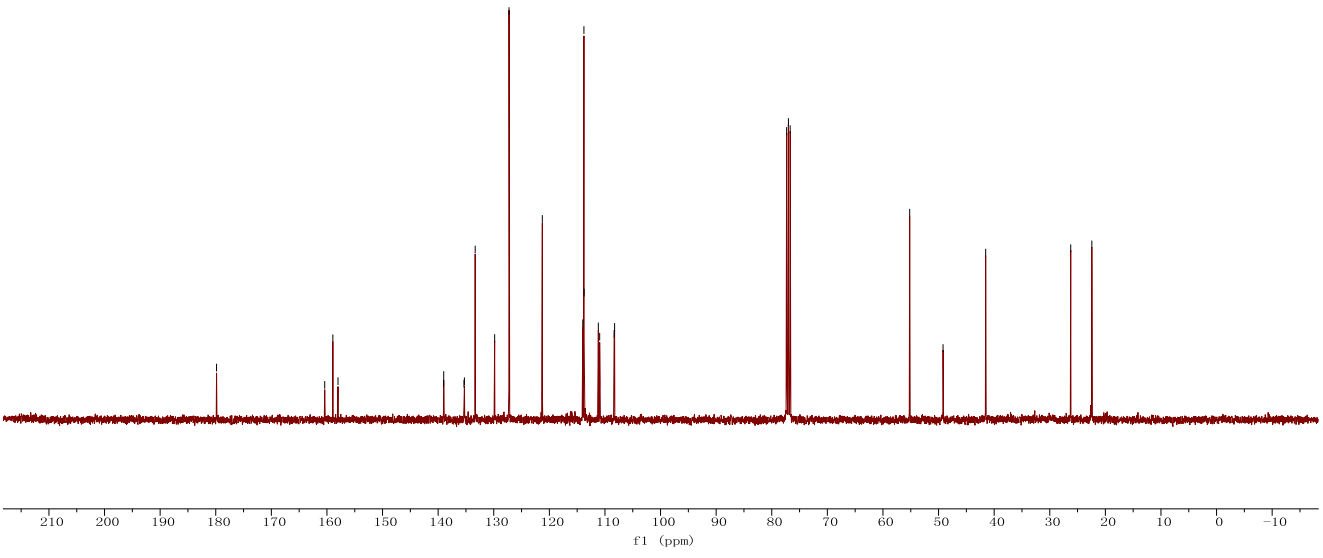


4c, ^{13}C NMR (101 MHz, $CDCl_3$)

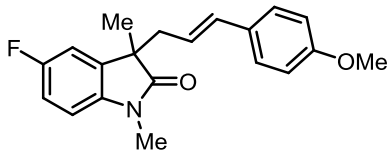




4c, *E* only

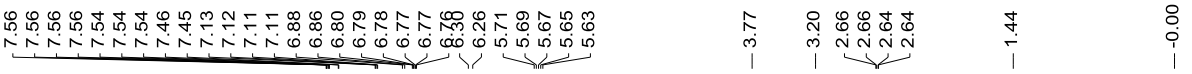


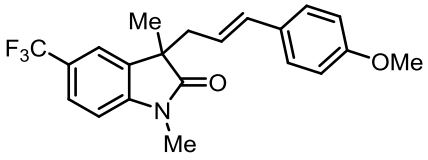
4c, ^{19}F NMR (101 MHz, $CDCl_3$)



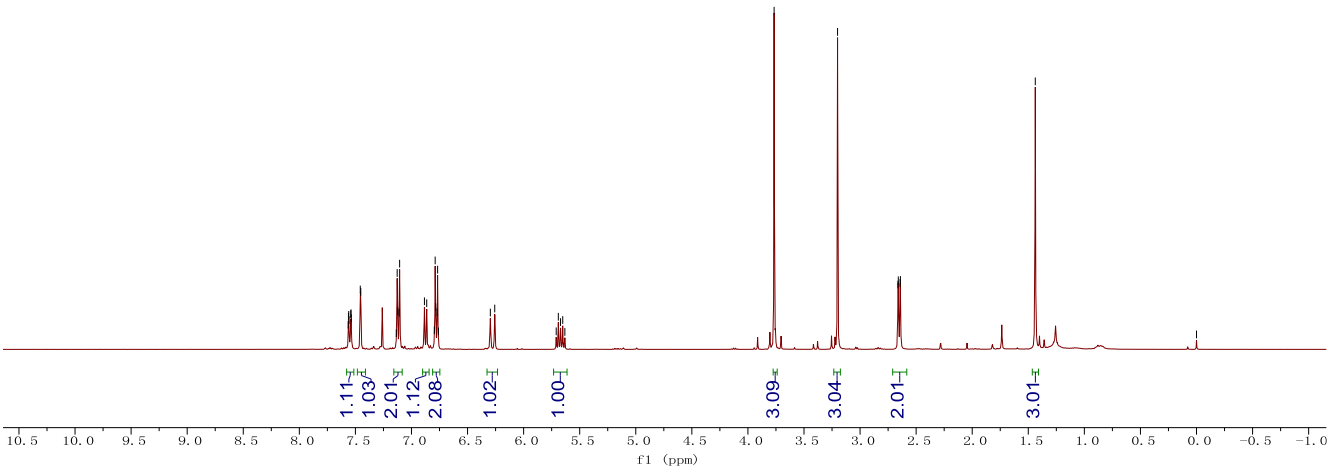
4c, *E* only

4d, ^{1}H NMR (400 MHz, $CDCl_3$)

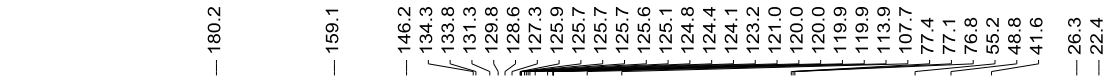


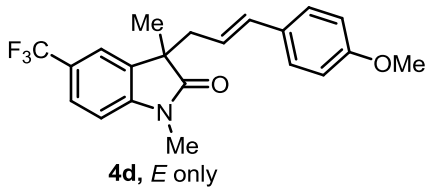


4d, *E* only

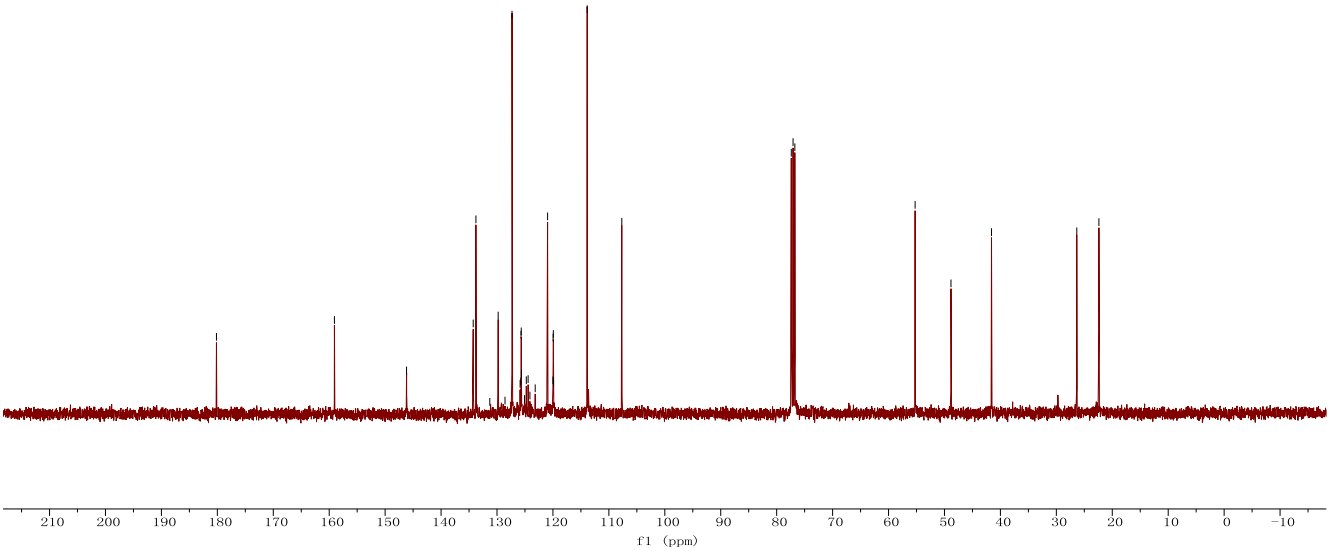


4d, ^{13}C NMR (101 MHz, $CDCl_3$)

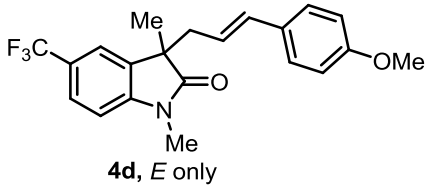




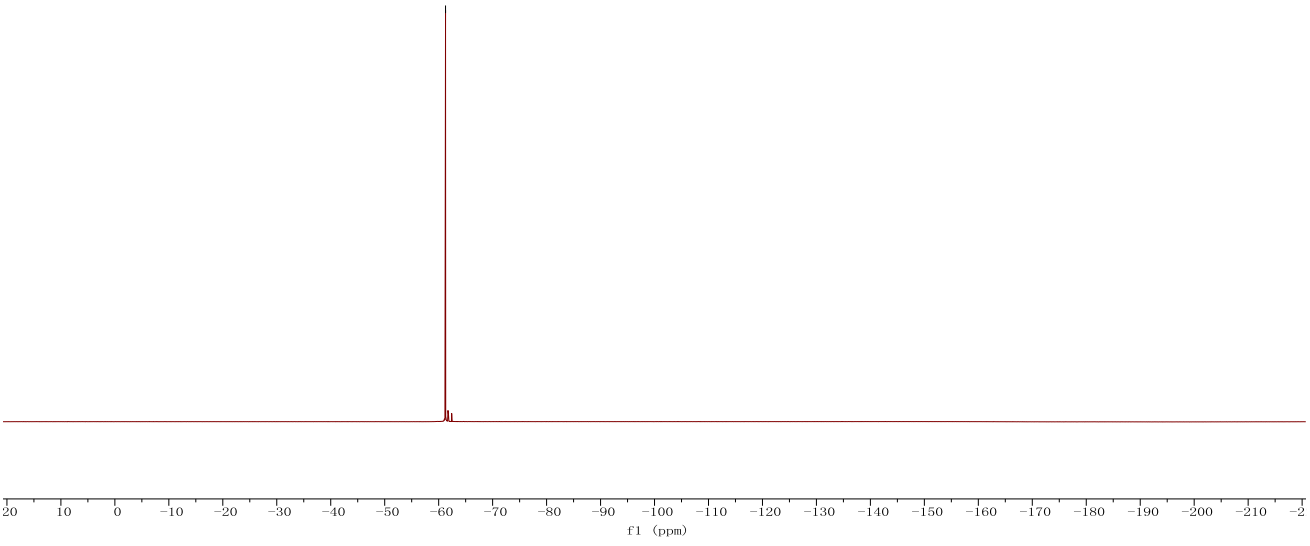
4d, *E* only



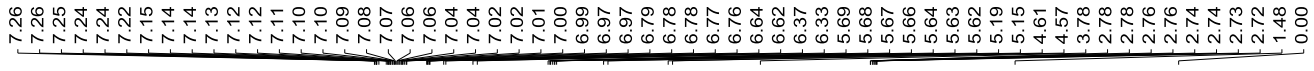
4d, ^{19}F NMR (101 MHz, $CDCl_3$)

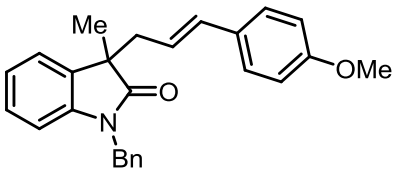


4d, *E* only

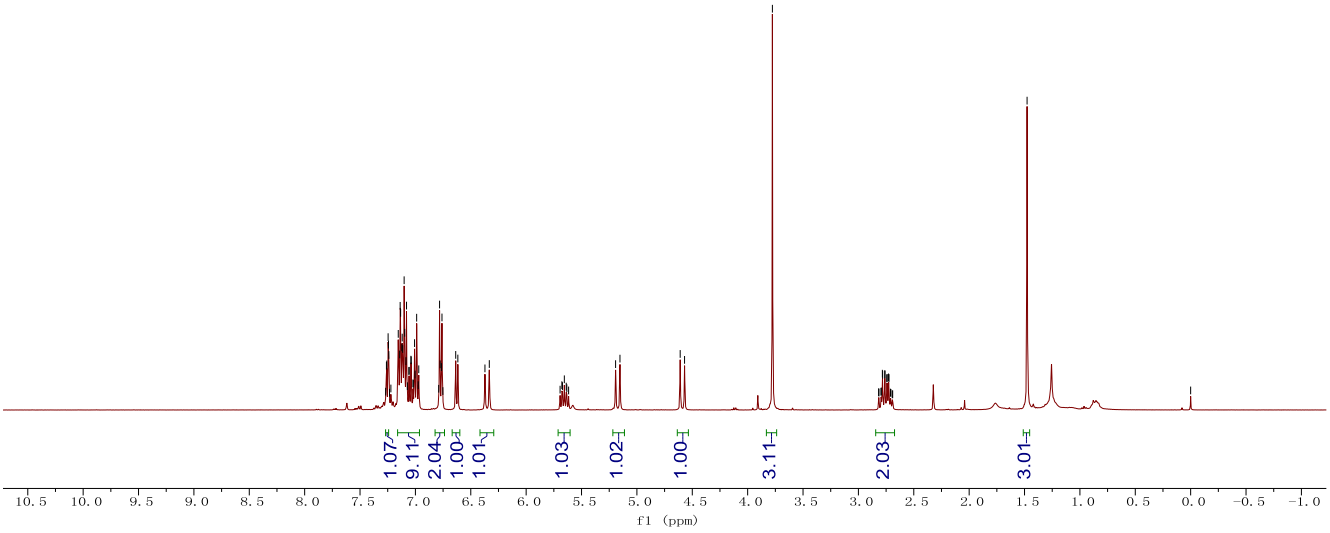


4e, ^{1}H NMR (400 MHz, $CDCl_3$)

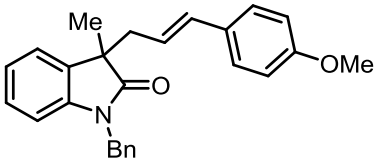




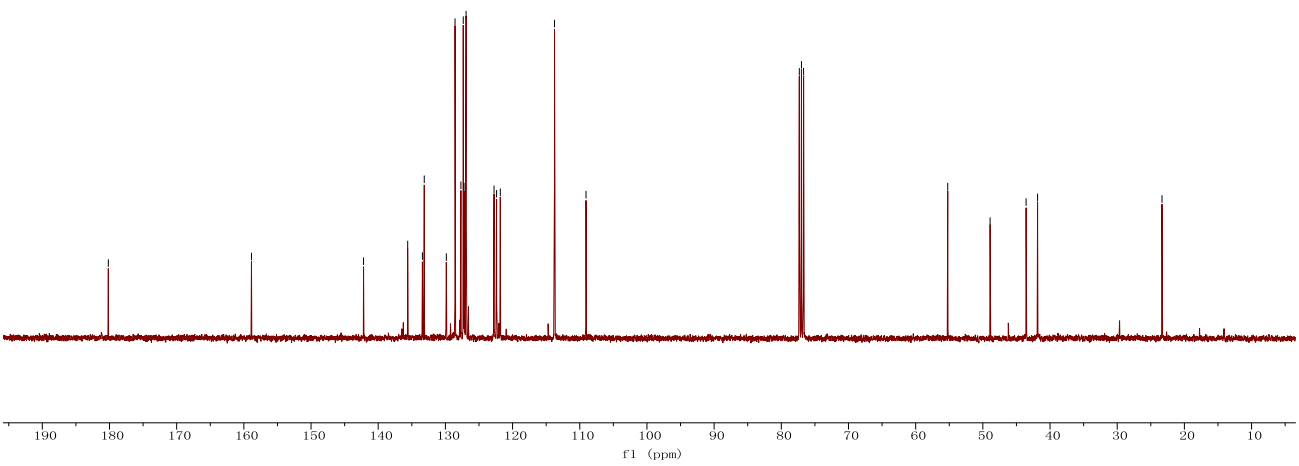
4e, *E* only



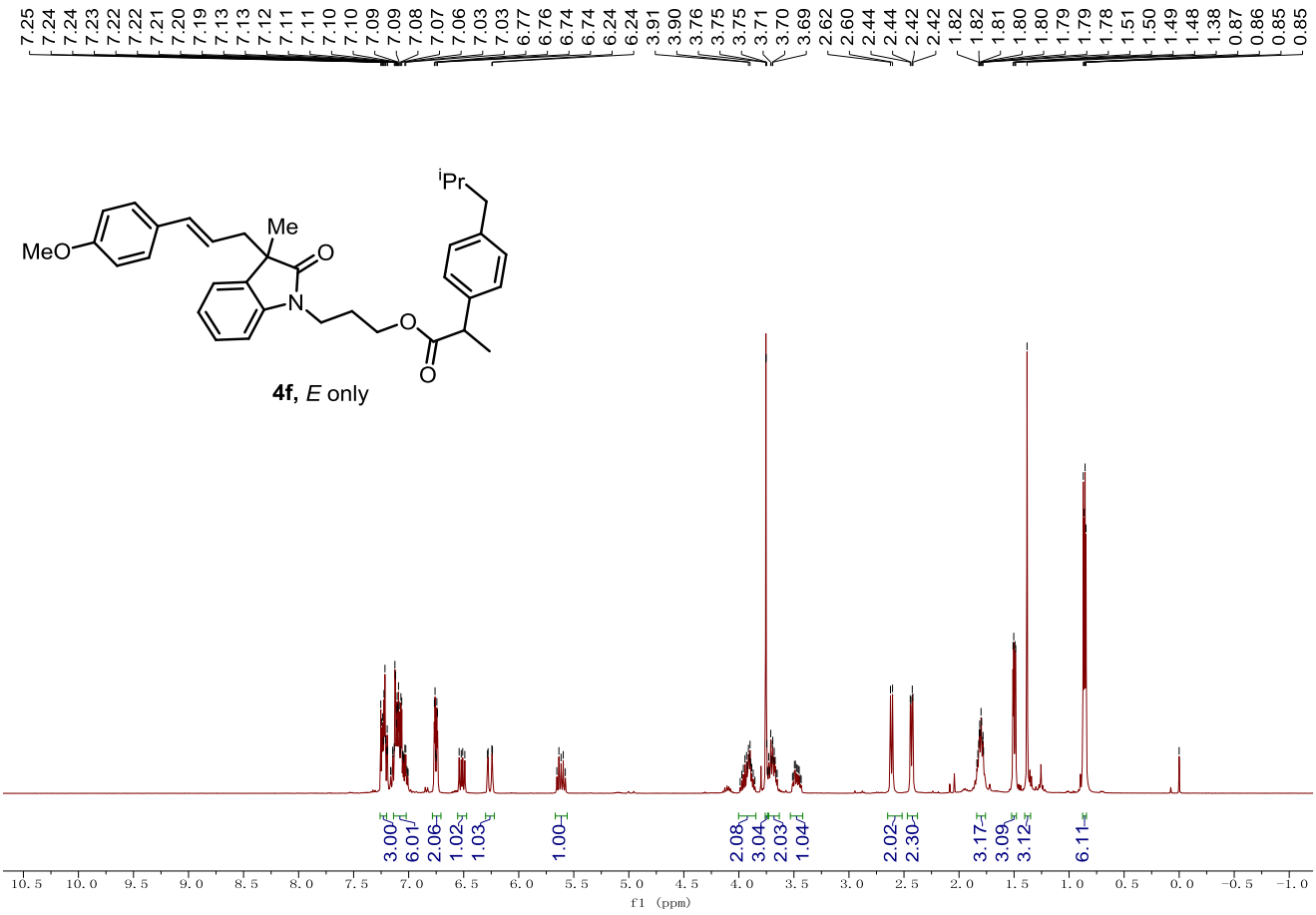
4e, ^{13}C NMR (101 MHz, $CDCl_3$)



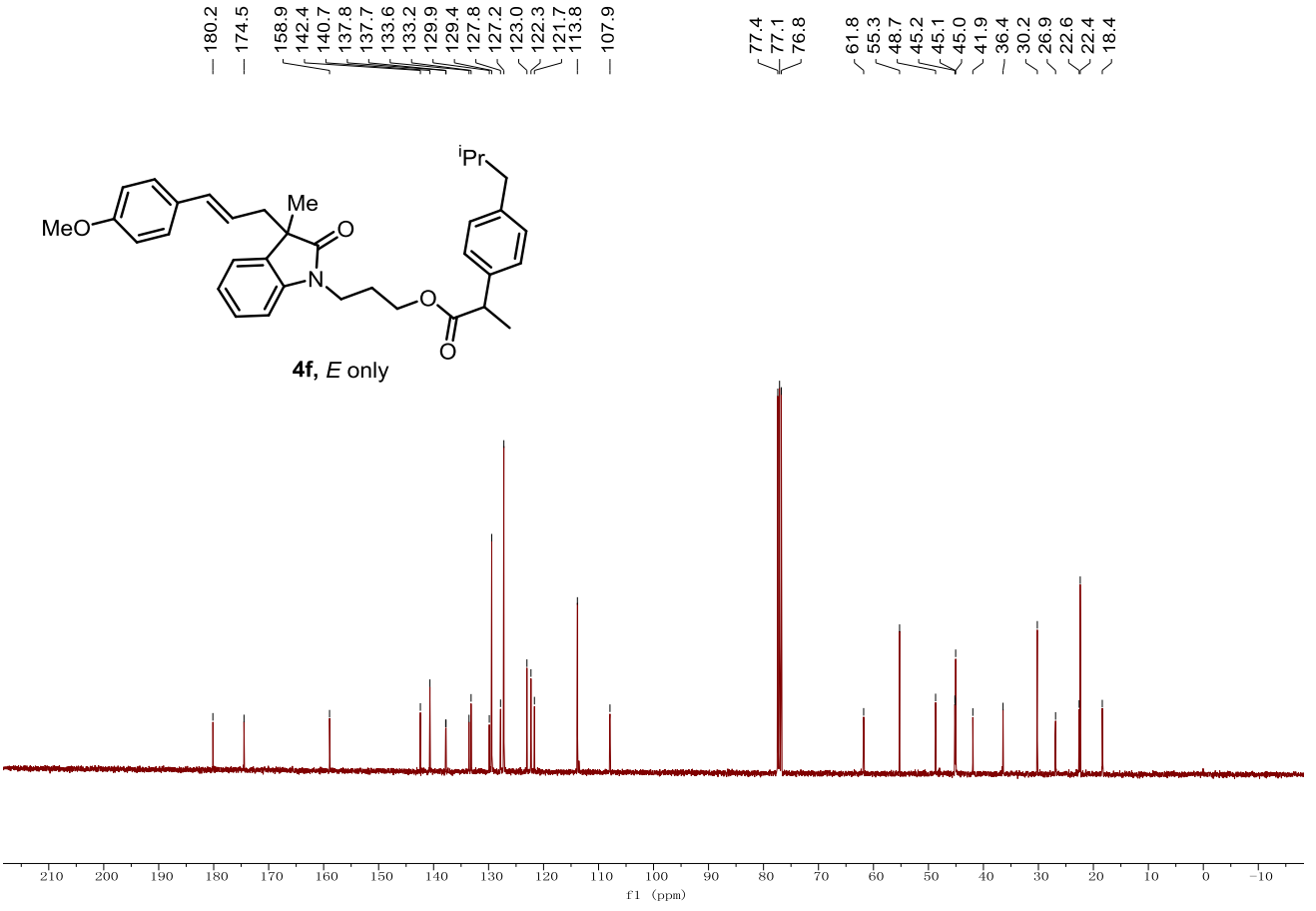
4e, *E* only



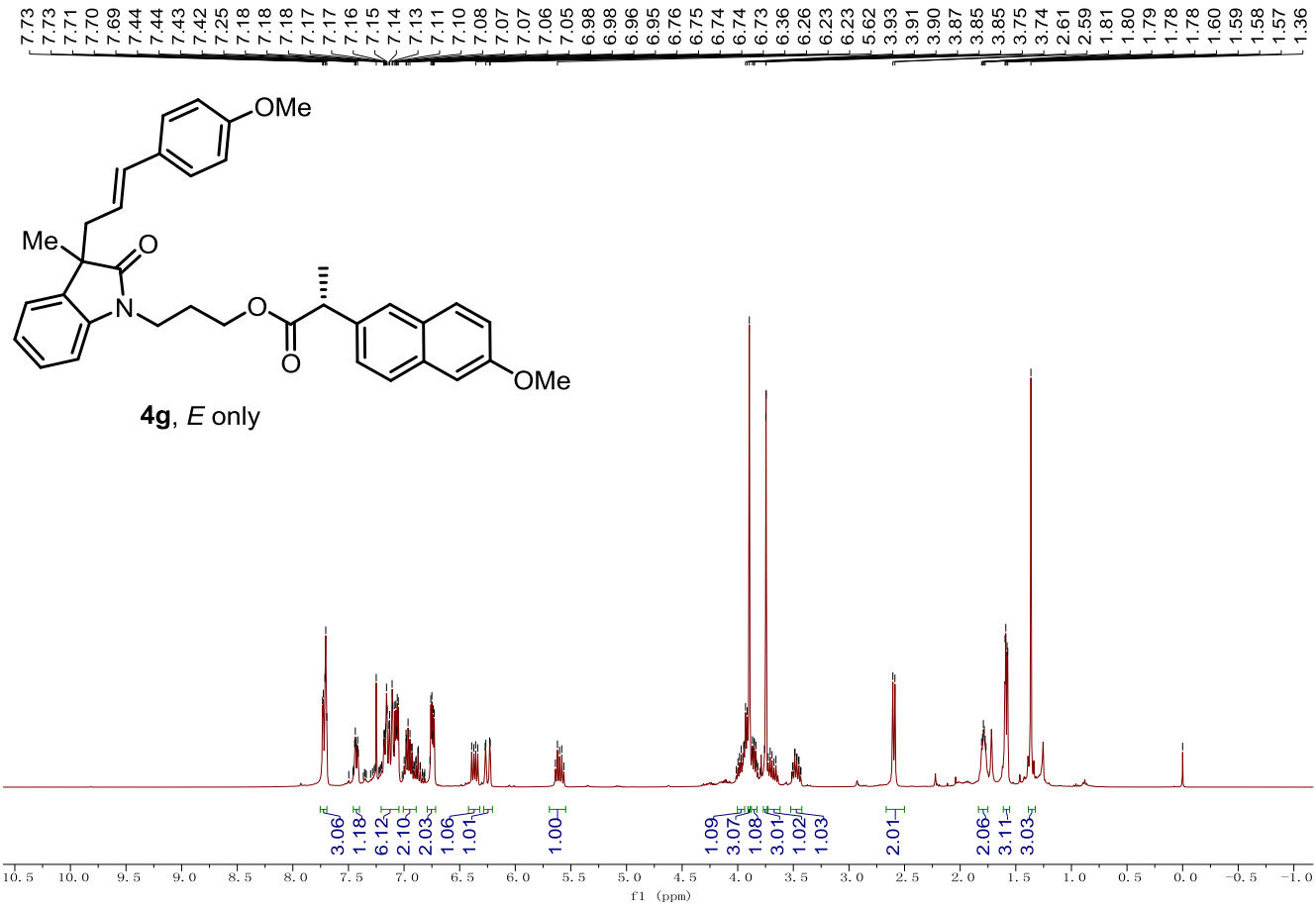
4f, ^{1}H NMR (400 MHz, $CDCl_3$)



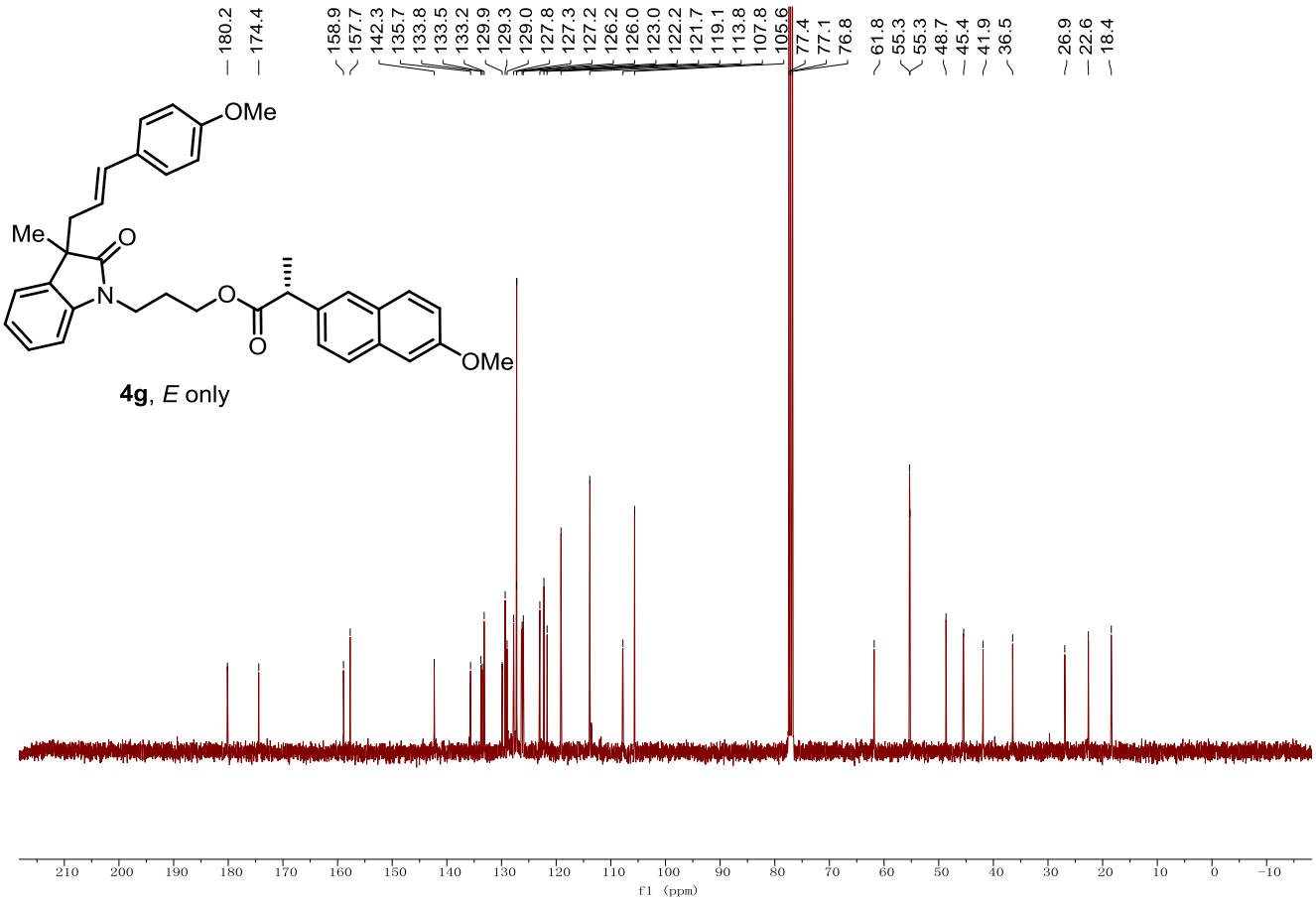
4f, ^{13}C NMR (101 MHz, $CDCl_3$)



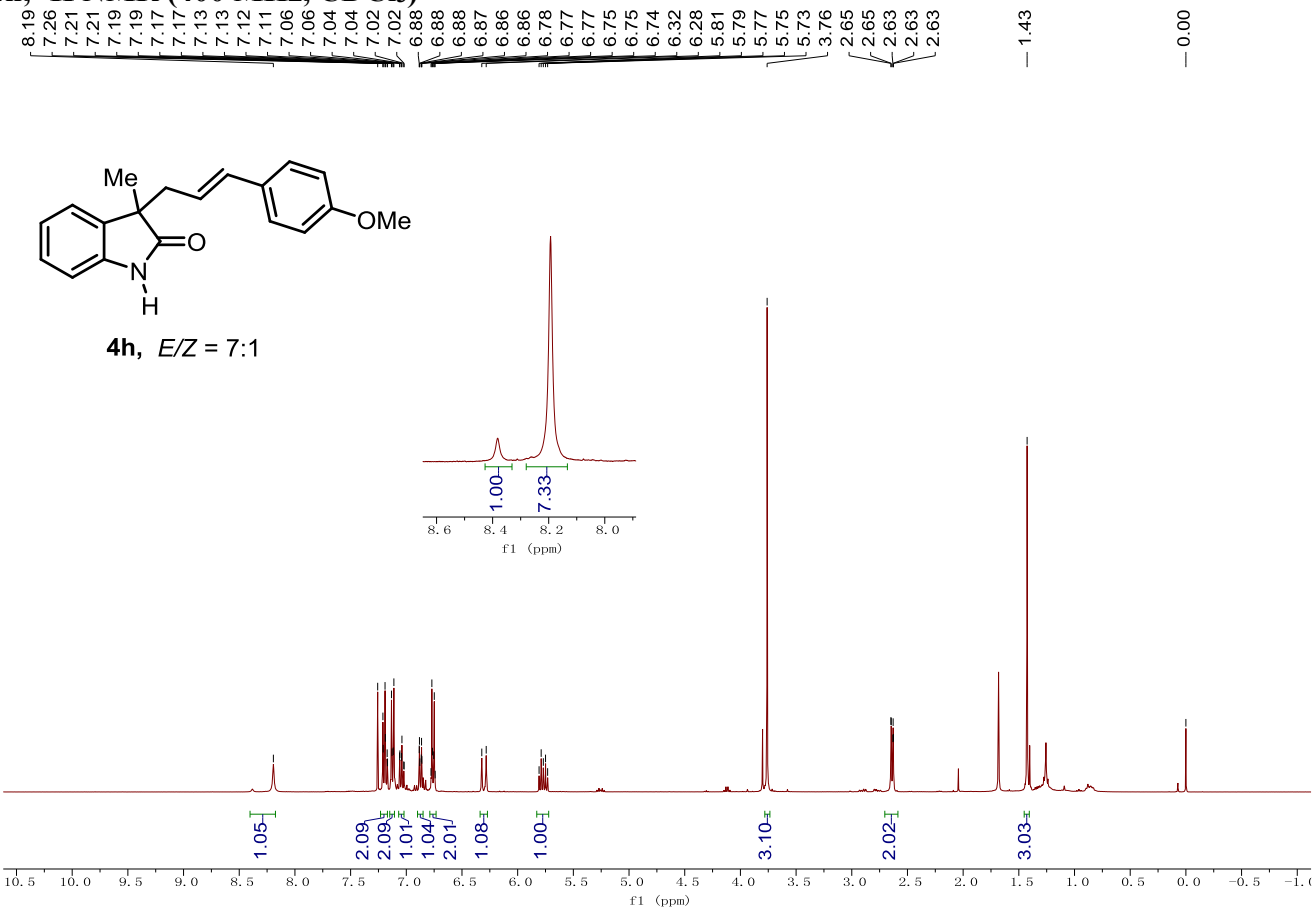
4g, ^{1}H NMR (400 MHz, $CDCl_3$)



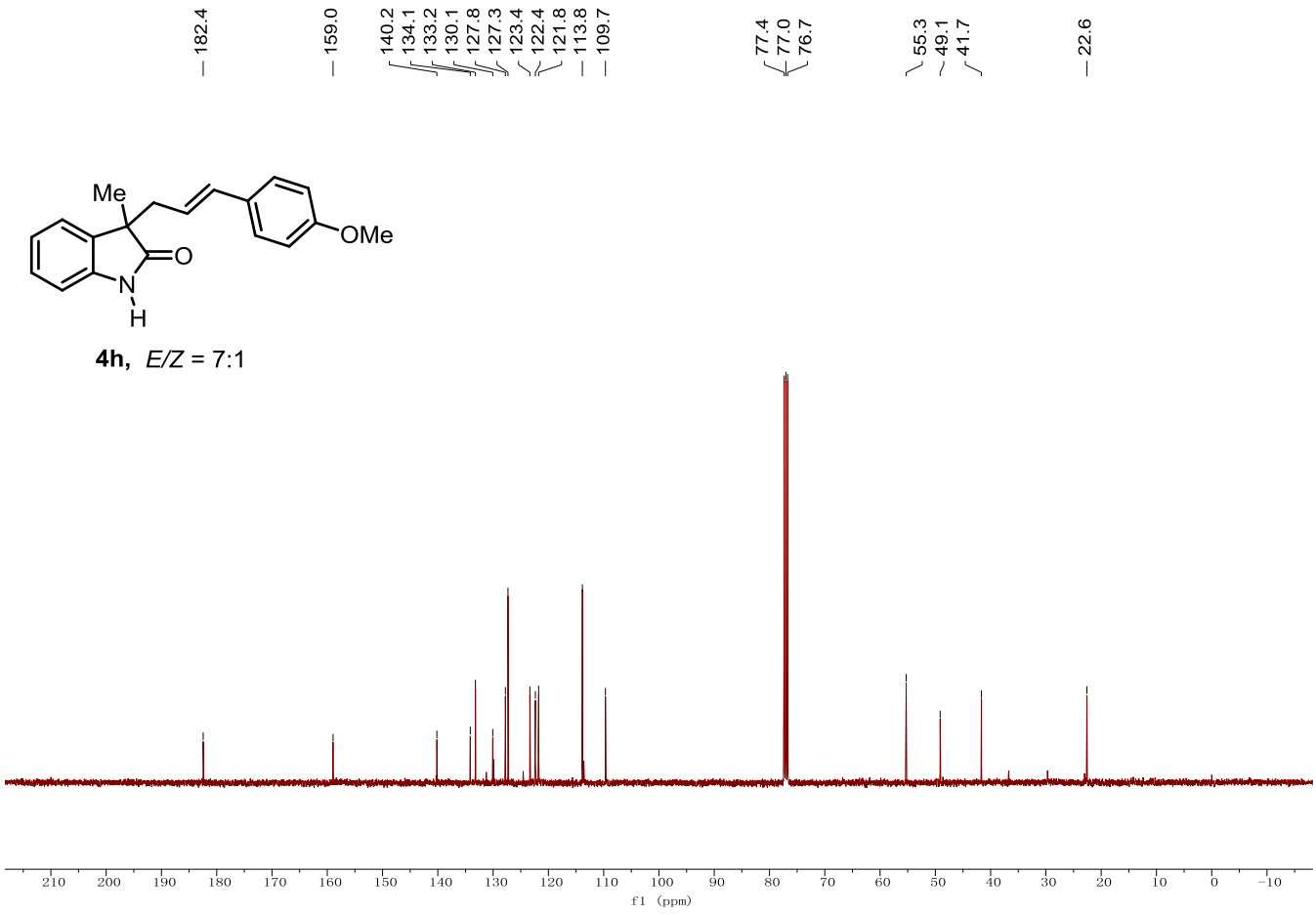
4g, ^{13}C NMR (101 MHz, $CDCl_3$)



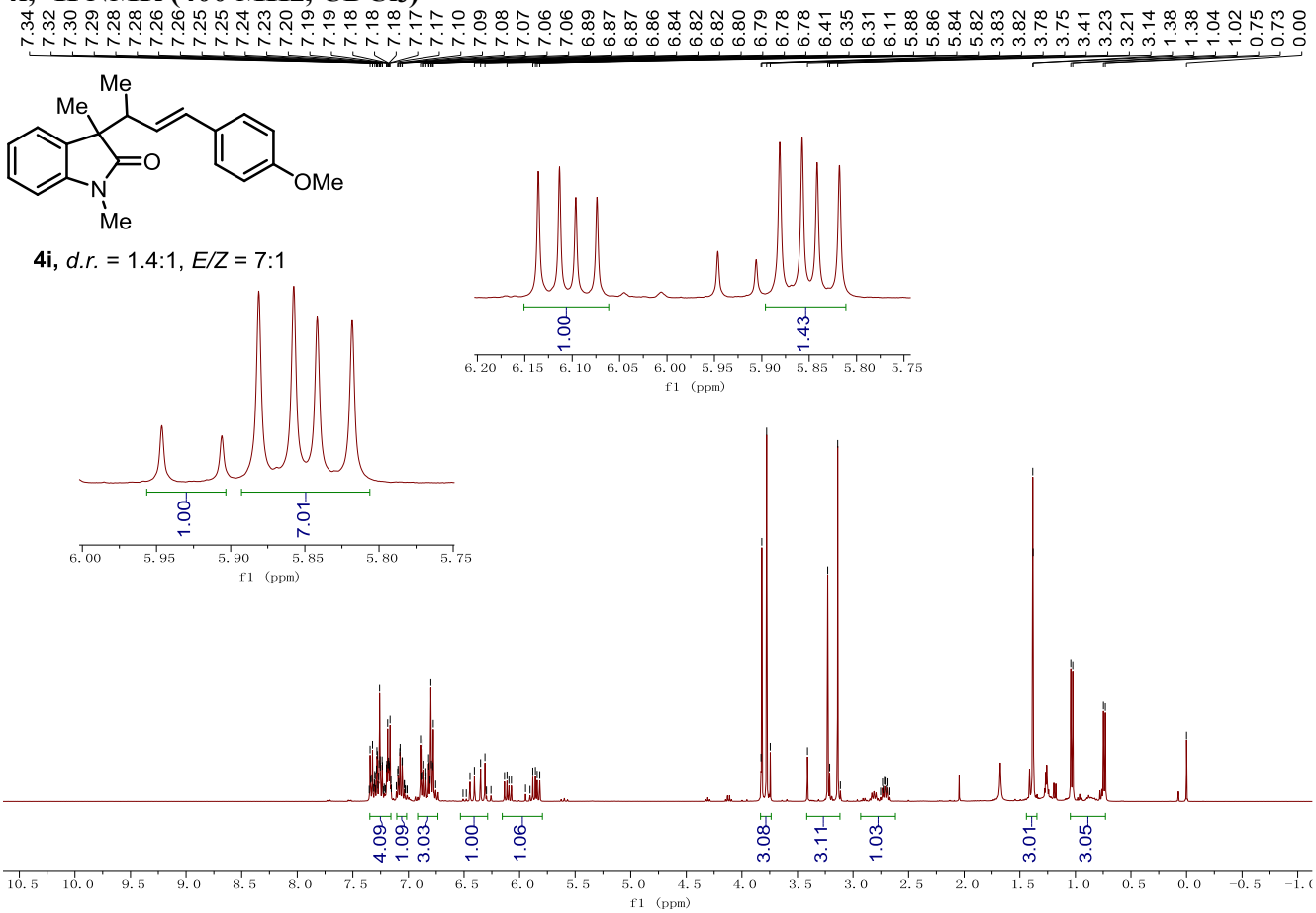
4h, ^{1}H NMR (400 MHz, $CDCl_3$)



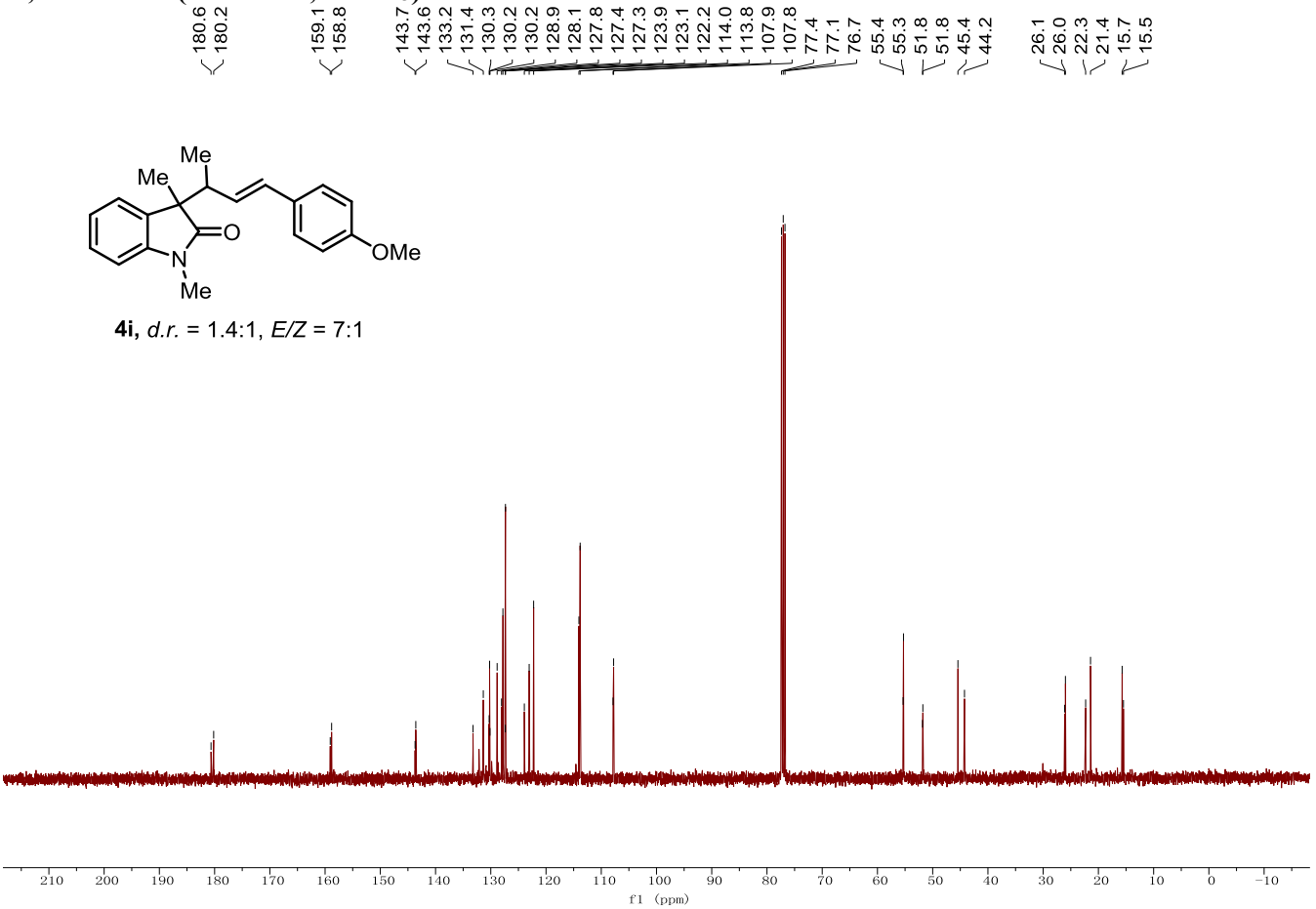
4h, ^{13}C NMR (101 MHz, $CDCl_3$)



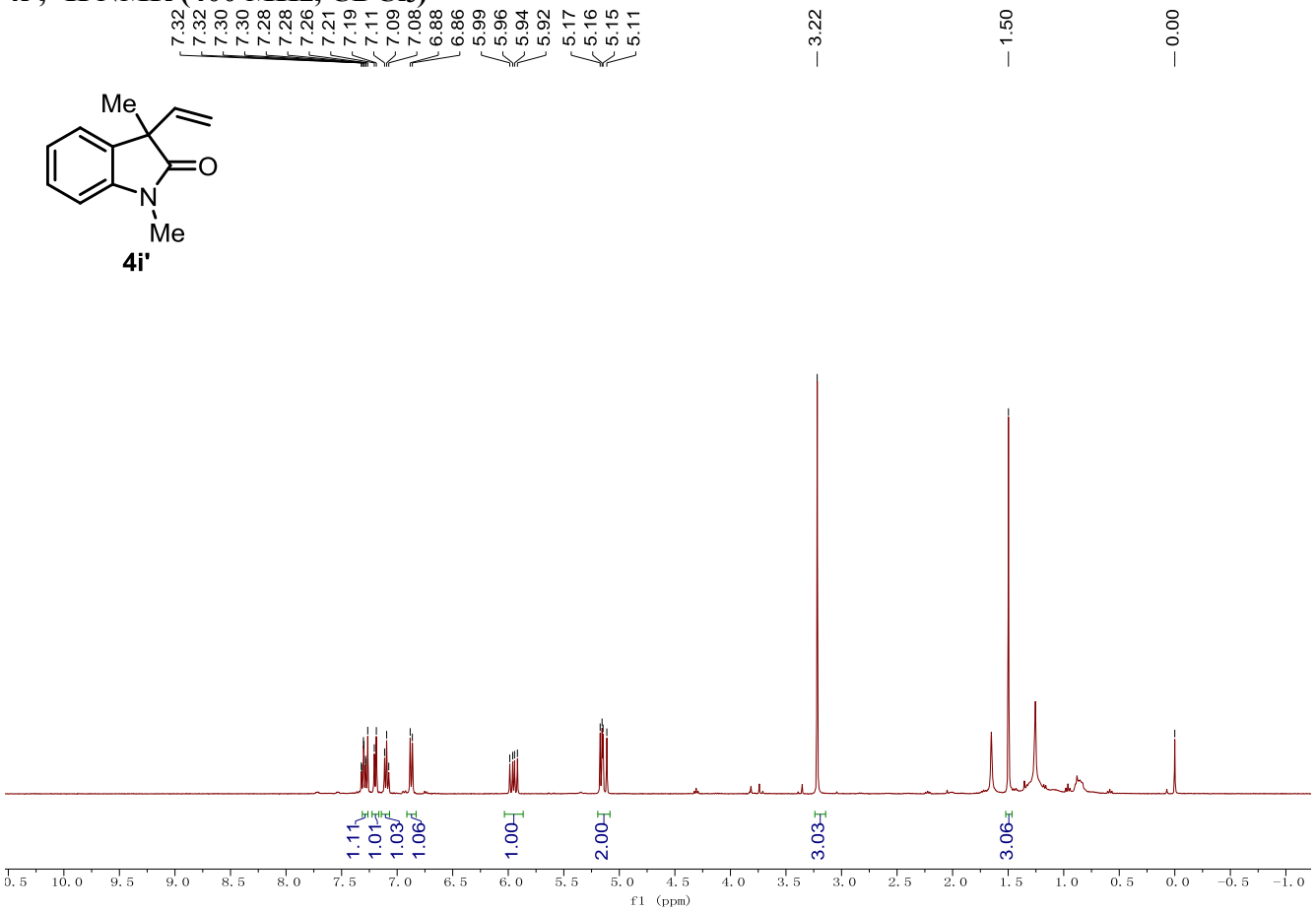
4i, ^{1}H NMR (400 MHz, $CDCl_3$)



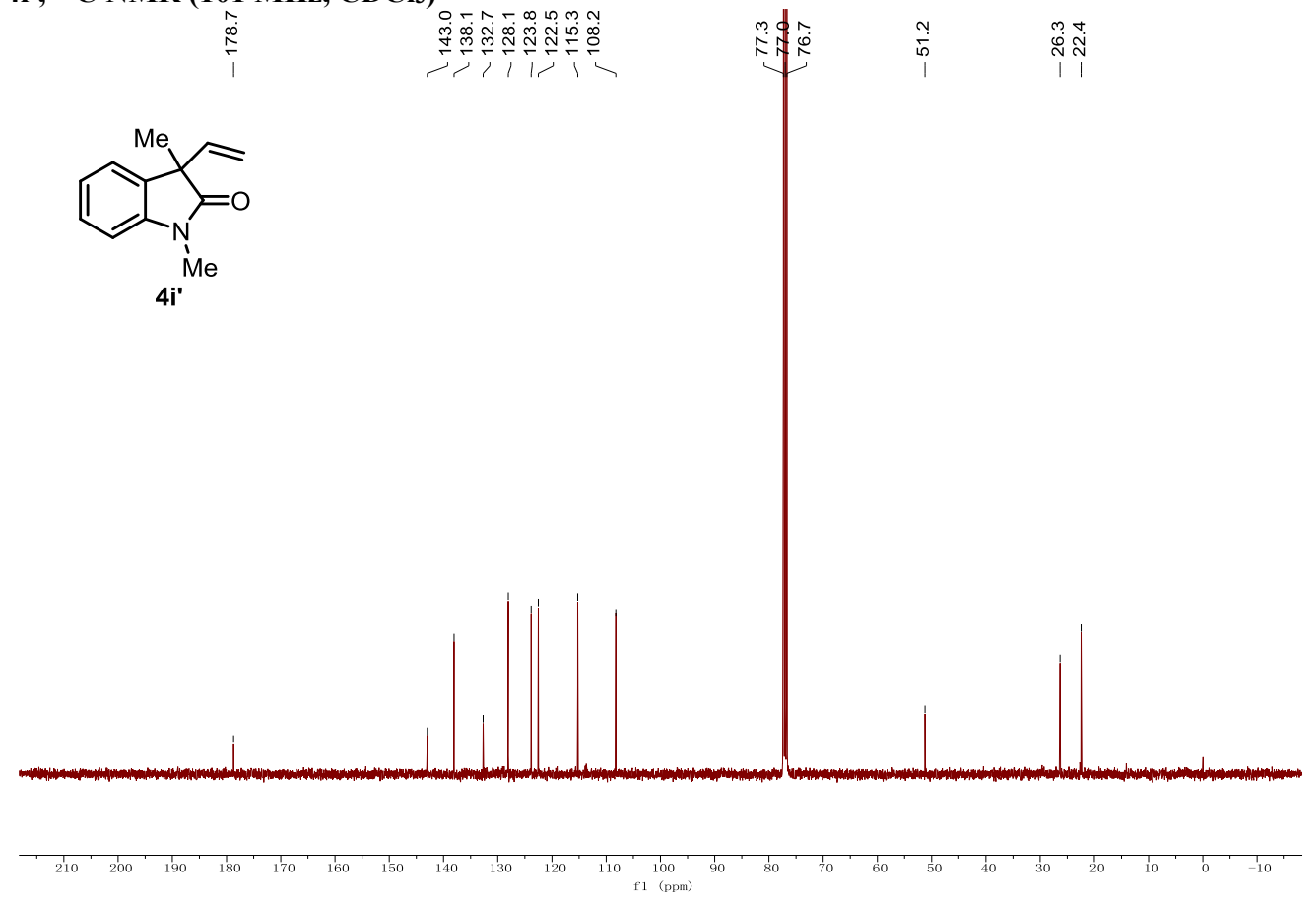
4i, ^{13}C NMR (101 MHz, $CDCl_3$)



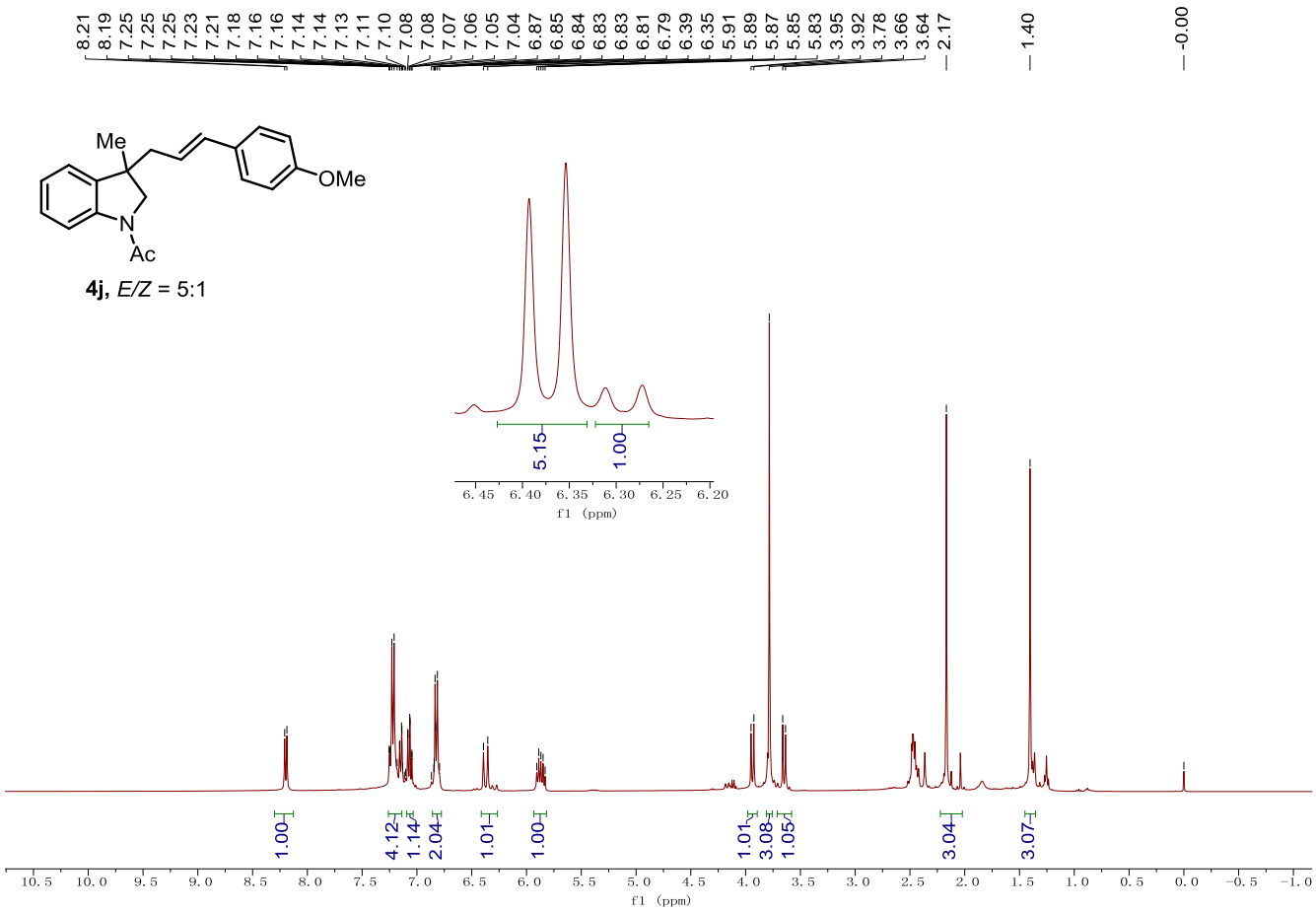
4i', ^{1}H NMR (400 MHz, $CDCl_3$)



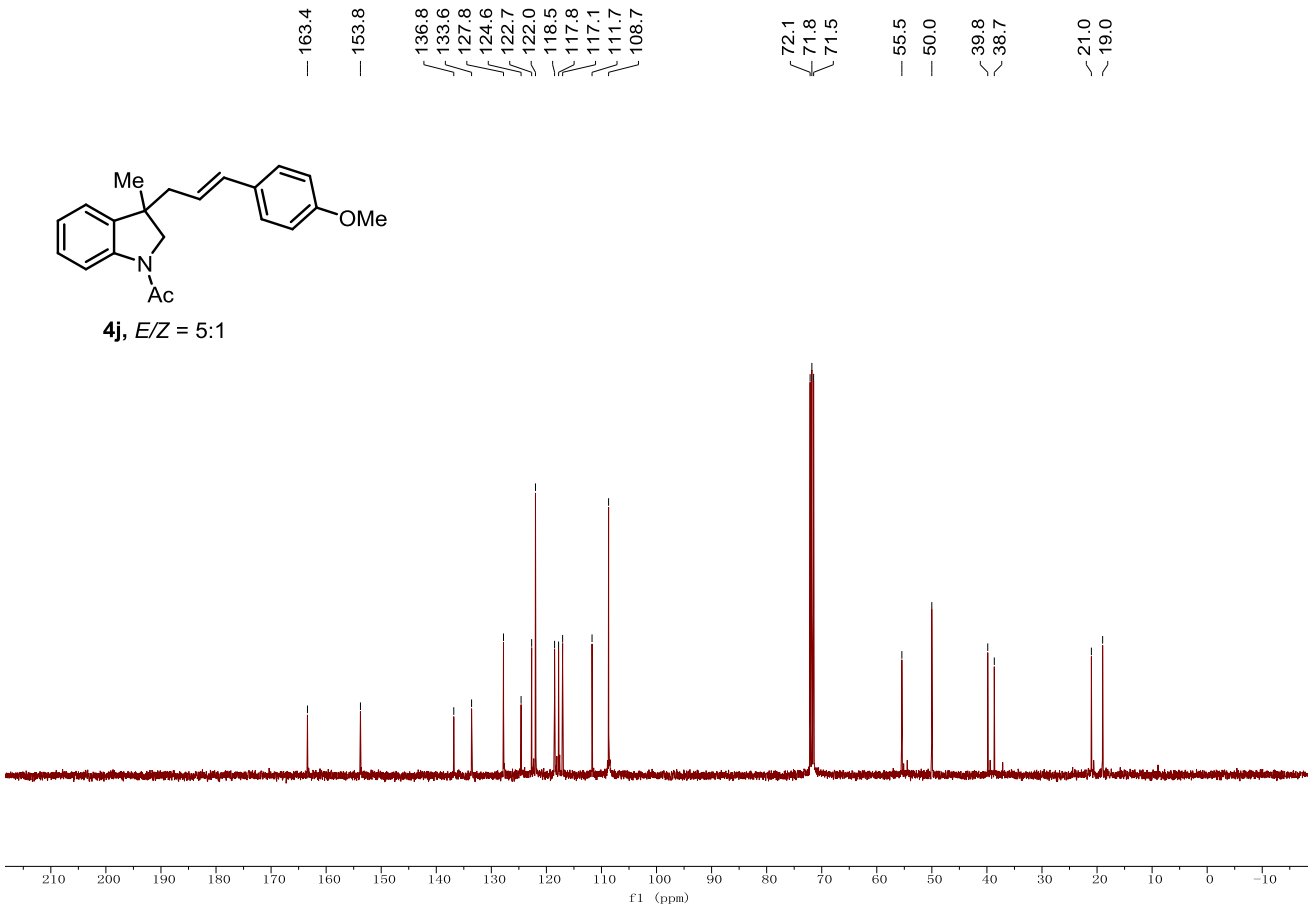
4i', ^{13}C NMR (101 MHz, $CDCl_3$)



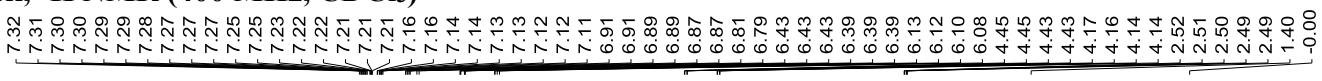
4j, ^{1}H NMR (400 MHz, $CDCl_3$)

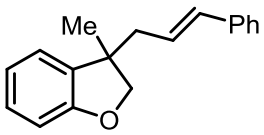


4j, ^{13}C NMR (101 MHz, $CDCl_3$)

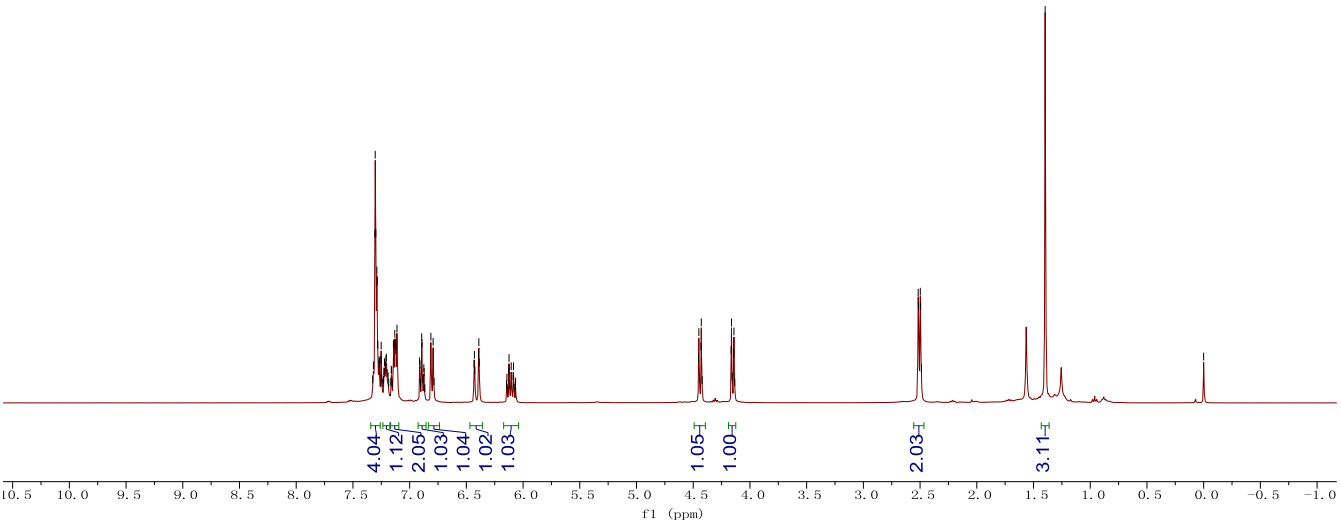


4k, ^{1}H NMR (400 MHz, $CDCl_3$)

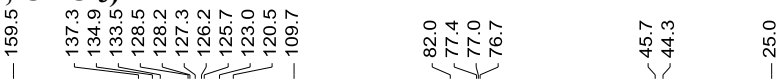


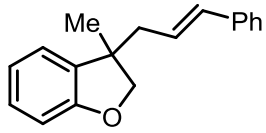


4k, *E* only

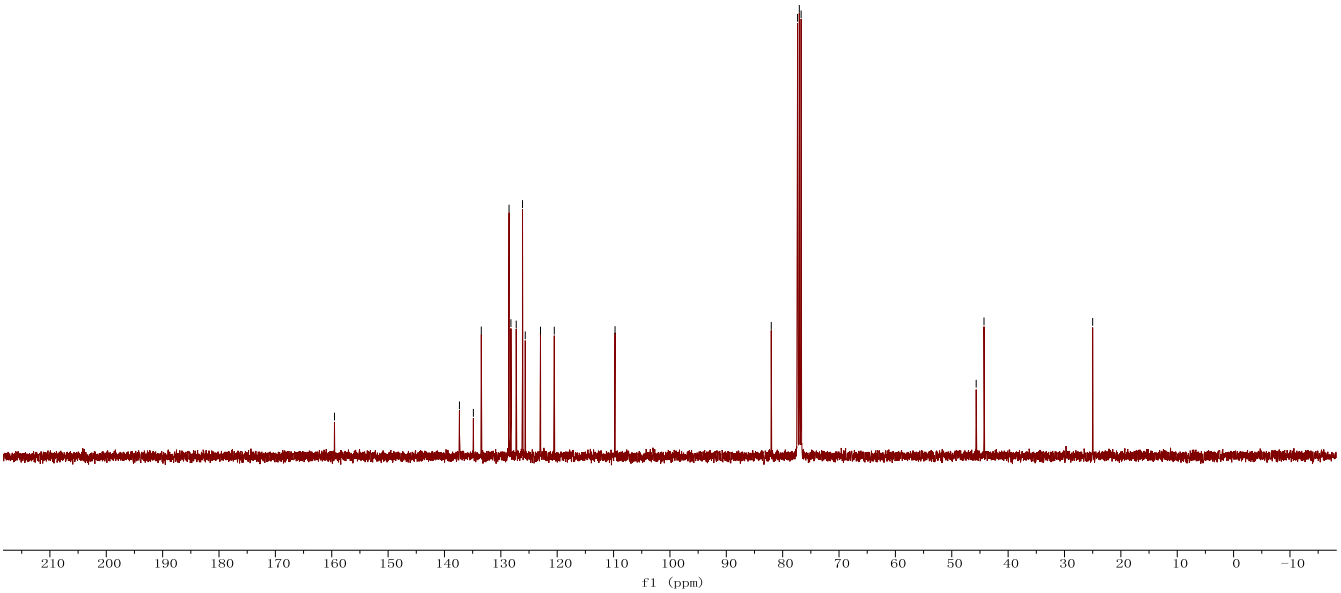


4k, ^{13}C NMR (101 MHz, $CDCl_3$)

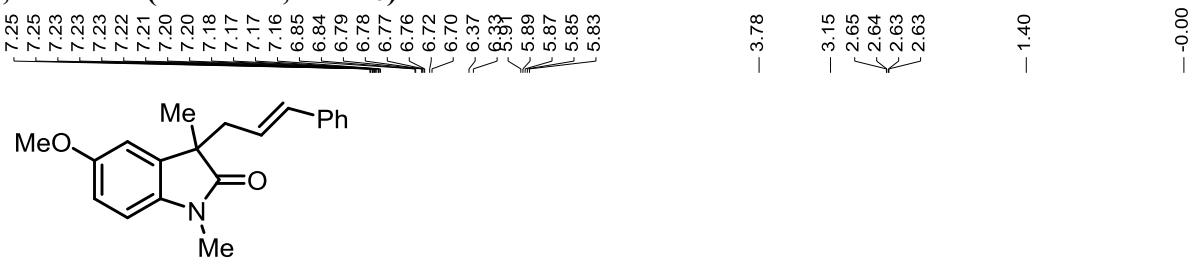




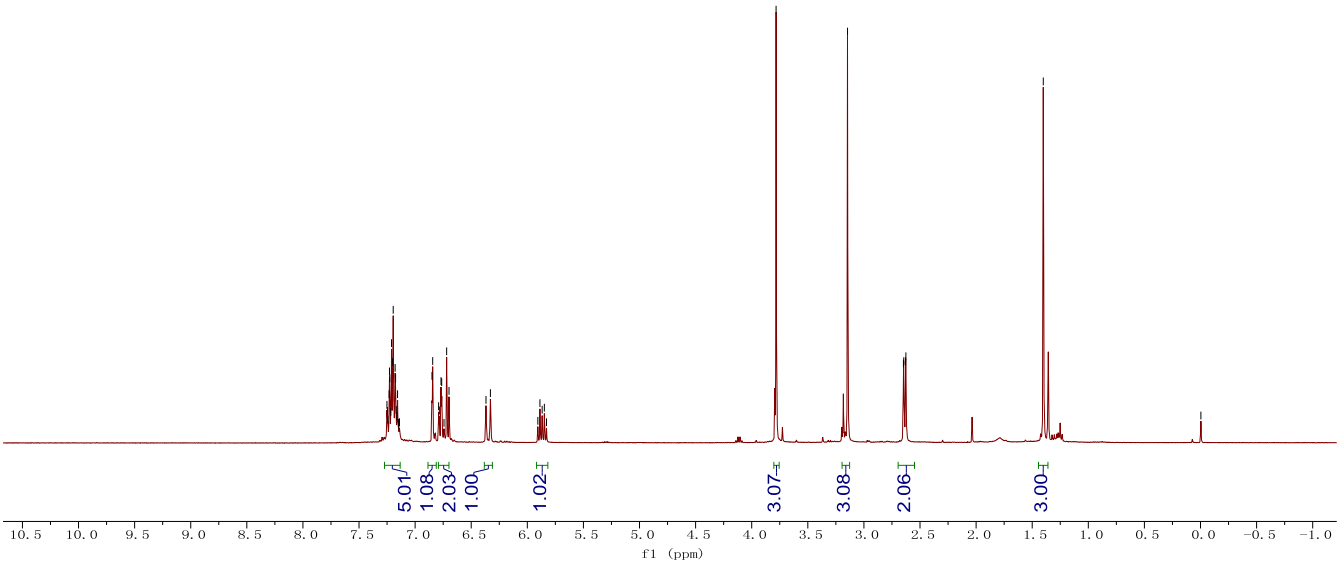
4k, *E* only



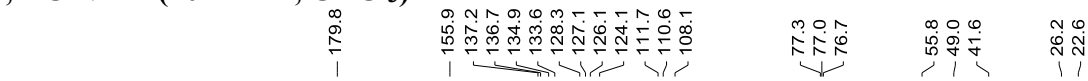
9, ^{1}H NMR (400 MHz, $CDCl_3$)

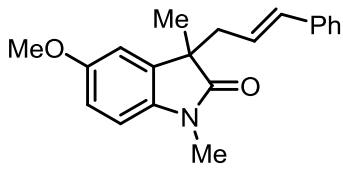


9, *E* only

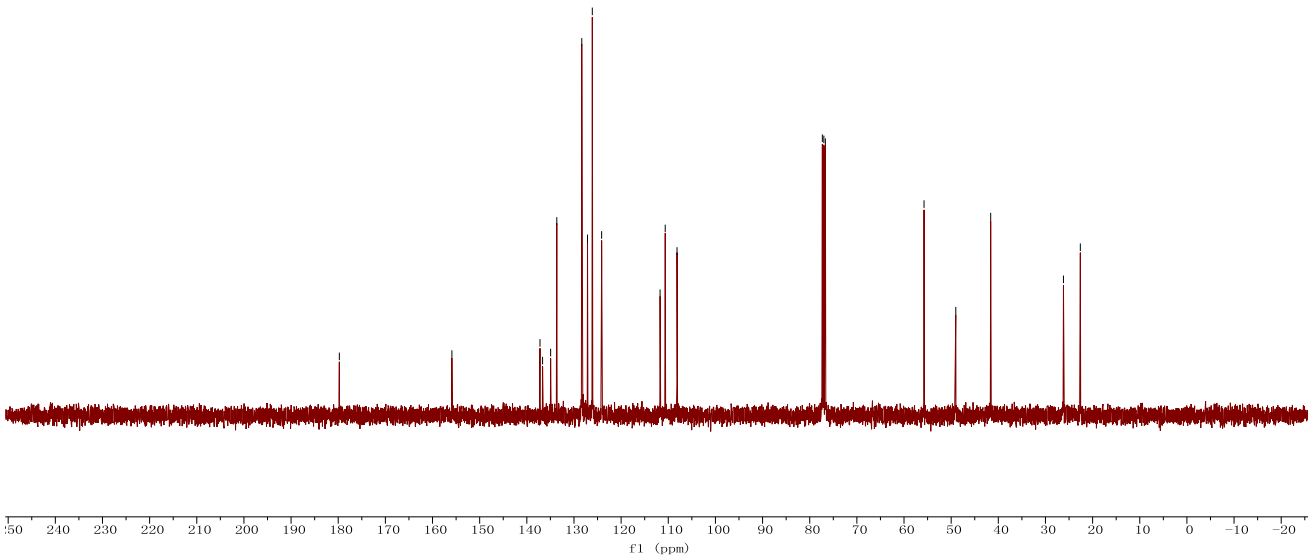


9, ^{13}C NMR (101 MHz, $CDCl_3$)

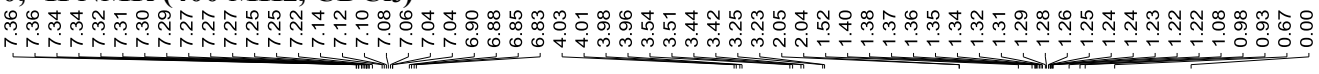


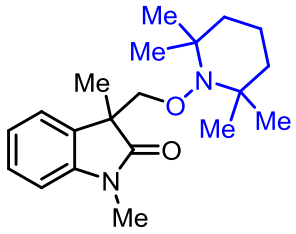


9, *E* only



10, ^{1}H NMR (400 MHz, $CDCl_3$)





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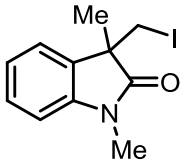
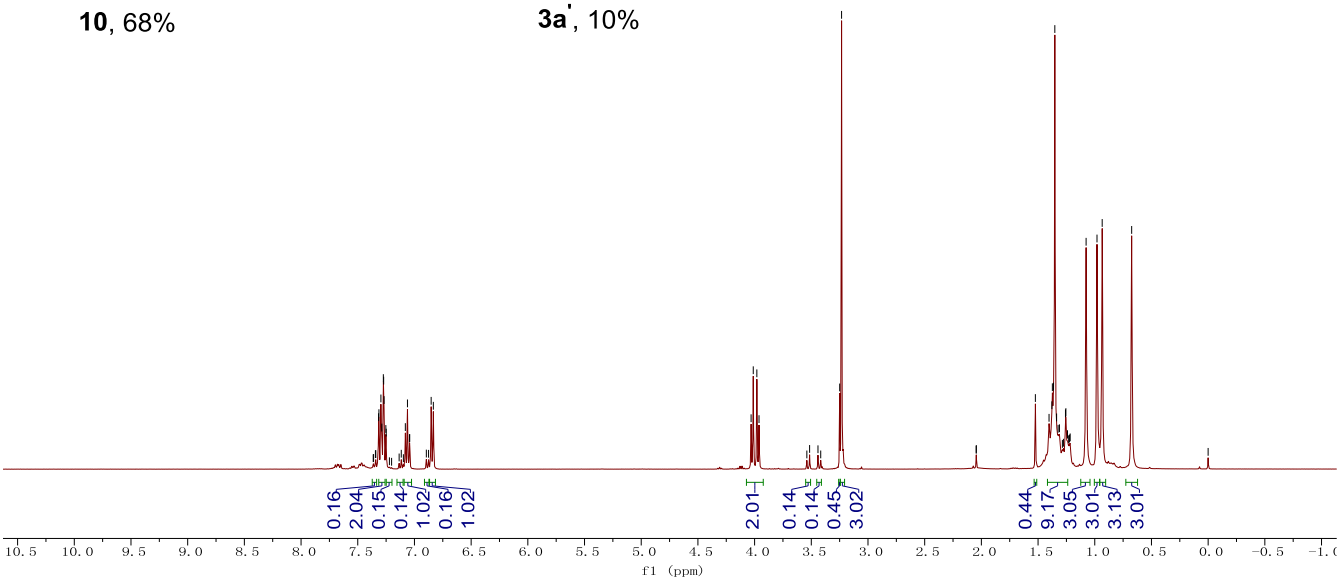
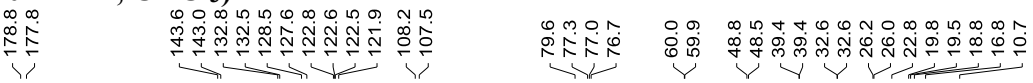


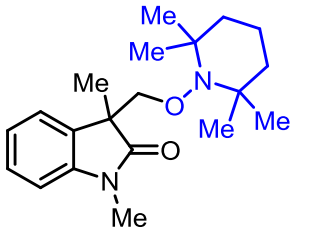
10, 68%

3a', 10%



10, ^{13}C NMR (101 MHz, $CDCl_3$)





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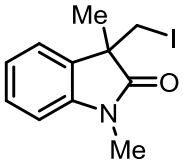
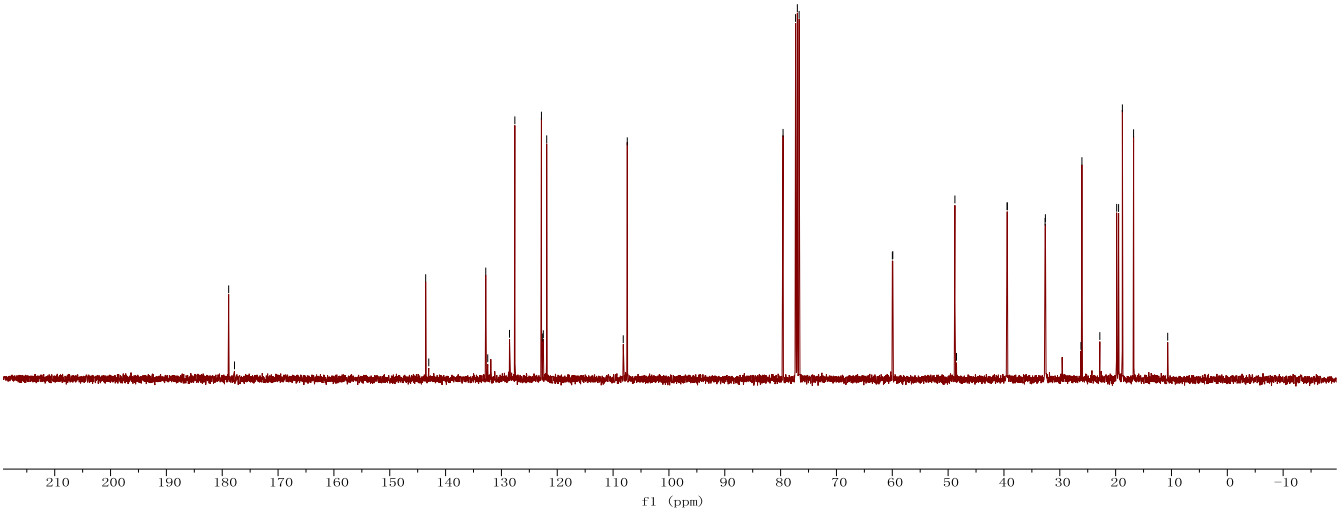
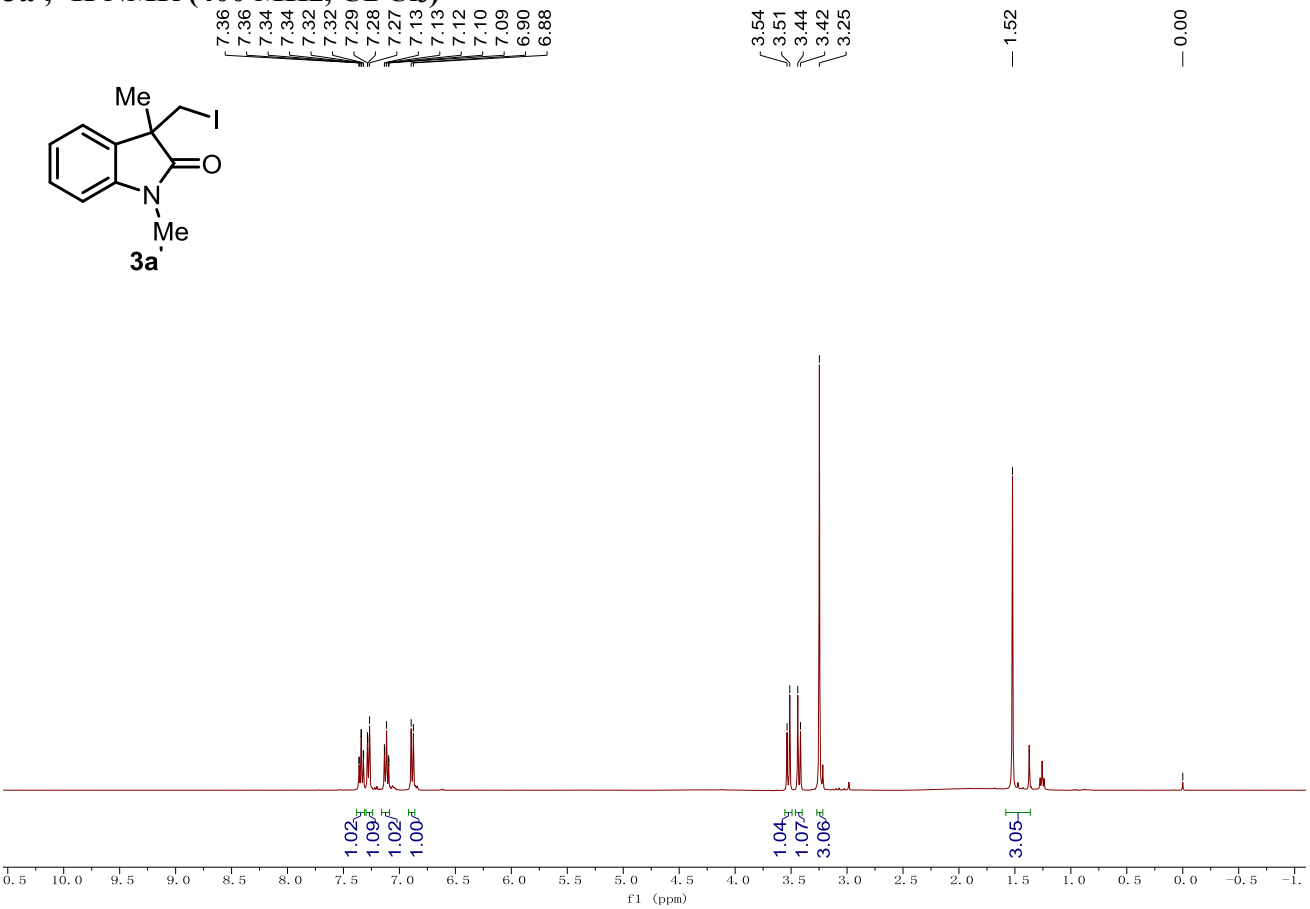


10, 68%

3a', 10%



3a', ^{1}H NMR (400 MHz, $CDCl_3$)



3a', ^{13}C NMR (101 MHz, $CDCl_3$)