Supplementary Information

Aryl-to-Alkyl Radical Relay Heck Reaction of Amides with Vinyl Arenes

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General Information

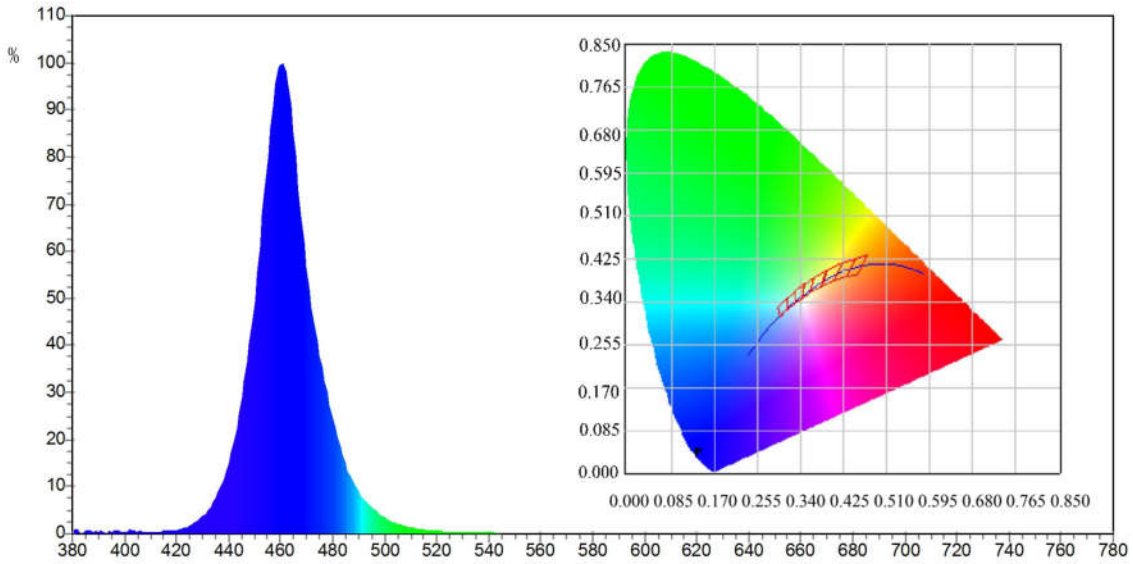
Unless noted otherwise, all the solvents and commercially available reagents were purchased and used directly. Benzene, 1,4-dioxane and tetrahydrofuran were distilled freshly over sodium, benzotrifluoride was distilled freshly over P_2O_5, DCM was distilled freshly over CaH_2 and carefully freeze-pump-thawed. 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). Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with Bruker AVANCE Ⅲ–300 (300 MHz, ^{1}H at 300 MHz, ^{13}C at 75 MHz) or 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 °C	Ambient humidity: 65%
	Test organization: spectrotest department	

Spectral relative energy distribution curve



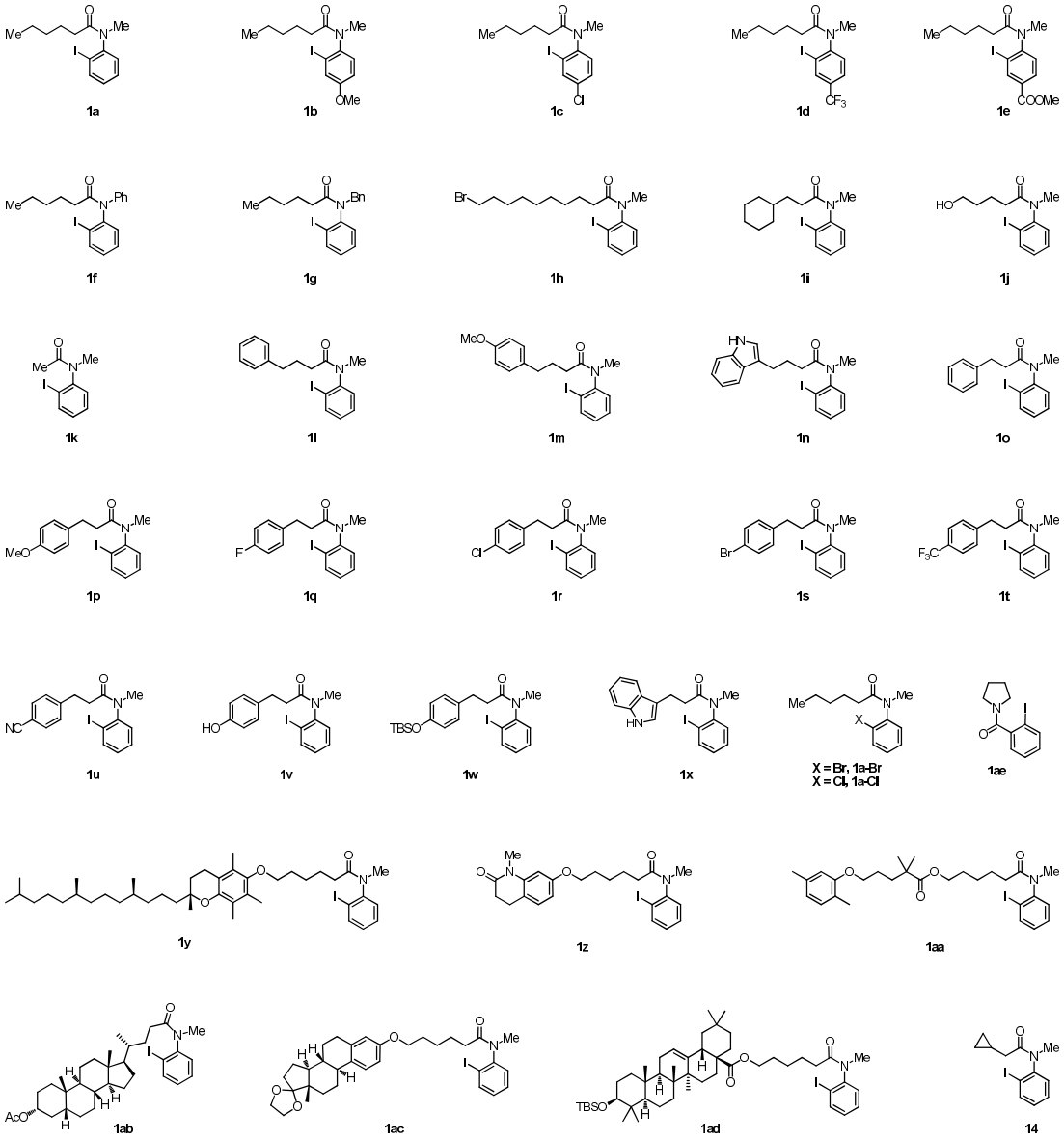
Wavelength/nm

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		

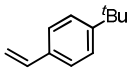
Note: Guanghong 45, 460-462

Syntheses of Amides

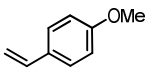
The amide **1k**[1] was prepared according to the previously reported literature. The others are known compounds.[2]



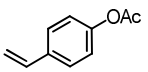
The styrene **3d**,[3] **3e**,[4] **3h**,[5] **3i**,[6] **3n**,[7] **3o**,[8] **3q**,[9] **3s**[10] and **17**[11] were prepared according to the previously reported literature. The others are commercially available and were used as recieved.



3a



3b



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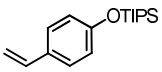
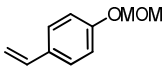
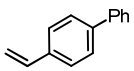


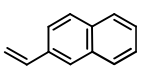
3d



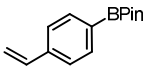
3e



3f



3g



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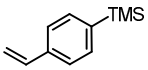
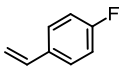


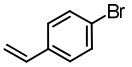
3i



3j

3k

3l



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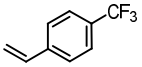
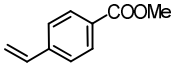


3n



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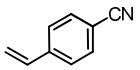
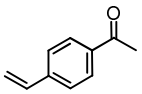
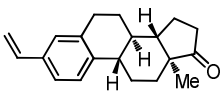


3p



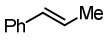
3q

3r



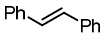
3s

3t

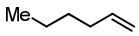


3u

3v



3w



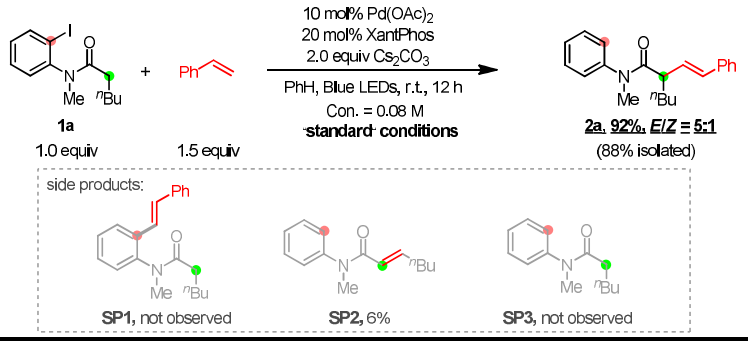
3x

3y

17

Selected Optimization Studies

Optimization for the Radical Relay Heck Reaction[a,b]

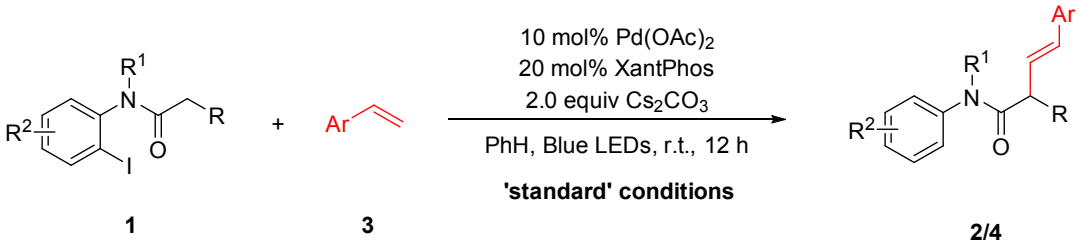


Entry	Variations from the 'standard' conditions	Yield (%) of **2a**[a]
1	Without **Pd(OAc)$_2$ (C1)**	0
2	Without **XantPhos (L1)**	0
3	Without **Cs$_2$CO$_3$ (B1)**	16, *E*/*Z* = 4:1
4	Without **Blue LEDs**	0
5	**C2-8** instead of **Pd(OAc)$_2$**	Listed below
6	**L2-10** instead of **XantPhos**	Listed below
7	**B2-9** instead of **Cs$_2$CO$_3$**	Listed below
8	carried out in air	trace
9	5 mol% Pd(OAc)$_2$/10 mol% **L1**, 24 h	33, *E*/*Z* = 4:1
10	solvent = THF	73, *E*/*Z* = 3:1
11	solvent = dioxane	90, *E*/*Z* = 4:1
12	solvent = DCM	60, *E*/*Z* = 5:1
13	solvent = PhCF$_3$	41, *E*/*Z* = 4:1
14	1.0 equiv **Cs$_2$CO$_3$**	88, *E*/*Z* = 5:1
15	3.0 equiv **Cs$_2$CO$_3$**	90, *E*/*Z* = 5:1
16	1.0 equiv **styrene**	80, *E*/*Z* = 5:1
17	2.0 equiv **styrene**	84, *E*/*Z* = 4:1
	Pd(PPh$_3$)$_4$ **C2**, 33%, *E*/*Z* = 4:1	
	Pd$_2$(dba)$_3$ **C3**, 65%, *E*/*Z* = 4:1	
	Pd(TFA)$_2$ **C4**, 79%, *E*/*Z* = 6:1	
	(PPh$_3$)$_2$PdCl$_2$ **C5**, 14%, *E*/*Z* = 5:1	
	(DPEPhos)PdCl$_2$ **C6**, 50%, *E*/*Z* = 4:1	
	(dppf)PdCl$_2$ **C7**, 15%, *E*/*Z* = 5:1	
	(COD)Pt(TFA)$_2$ **C8**, 31%, *E*/*Z* = 4:1	
	rac-BINAP **L2**, 13%, *E*/*Z* = 4:1	
	DPEPhos **L3**, 55%, *E*/*Z* = 5:1	
	N-XantPhos **L4**, 30%, E/Z = 3:1	
	dppp **L5**, trace	
	dppe **L6**, trace	
	dppf **L7**, trace	
	dtbpf **L8**, 0%	
	dcypf **L9**, trace	
	bpy **L10**, 0%	
	K$_2$CO$_3$ **B2**, 45%, *E*/*Z* = 5:1	
	K$_3$PO$_4$ **B3**, 81%, *E*/*Z* = 4:1	
	K$_2$HPO$_4$ **B4**, 43%, *E*/*Z* = 4:1	
	Na$_2$CO$_3$ **B5**, 55%, *E*/*Z* = 4:1	
	NaOAc **B6**, 45%, *E*/*Z* = 5:1	
	Ag$_2$O **B7**, 0	
	2,4,6-tri-Me-Py **B8**, 58%, *E*/*Z* = 3:1	
	2,6-di-^{t}Bu-Py **B9**, 15%, *E*/*Z* = 3:1	

[a] Each reaction was run on a 0.1 mmol scale in a sealed 4 mL vial for 12 h; [b] yields of **2a** and trans/cis (*E*/*Z*) ratios were determined by ^{1}H NMR analysis using dibromomethane as the internal standard. TFA = trifluoroacetate, COD = 1,5-cyclooctadiene, dba = dibenzylideneacetone, Py = pyridine.

General Procedure of the Radical Relay Heck Reaction

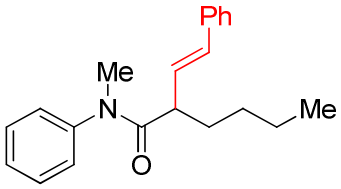
Typical procedure for the synthesis of product 2



1 **3** **2/4**

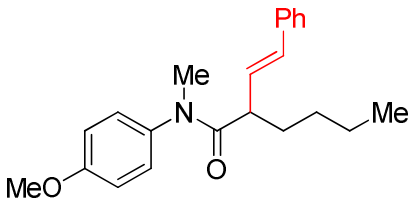
The Device of Photo-induced Reaction

An oven-dried 4.0 mL vial was charged with amide **1** (0.2 mmol), alkene **3** (0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Xantphos (23.1 mg, 0.04 mmol) and Cs_2CO_3 (130.3 mg, 0.4 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2.5 mL of degassed benzene (PhH) 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 12 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 2:3) to afford **2/4**.



2a

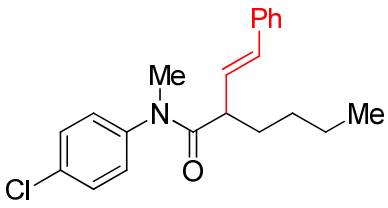
(*E*)-*N*-methyl-*N*-phenyl-2-styrylhexanamide (2a). Following the typical procedure described above, the reaction was carried out by the mixture of **1a** (66.2 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 88% isolated yield (54.1 mg) and *E/Z* = 5:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 3H), 7.32 – 7.25 (m, 4H), 7.22 – 7.17 (m, 3H), 6.19 (dd, *J* = 15.9, 9.0 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 3.27 (s, 3H), 3.08 (q, *J* = 7.5 Hz, 1H), 1.90 – 1.78 (m, 1H), 1.56 – 1.43 (m, 1H), 1.22 – 1.14 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.6, 143.7, 136.9, 131.0, 129.5, 129.5, 128.3, 127.8, 127.7, 127.2, 126.1, 47.0, 37.3, 33.0, 29.3, 22.4, 13.8. **HRMS (ESI)** calcd for $C_{21}H_{25}NO$ $[M+H]^+$: 308.2009, found 308.2007.



2b

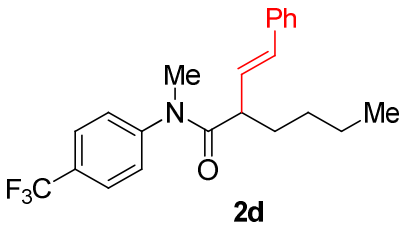
(*E*)-*N*-(4-methoxyphenyl)-*N*-methyl-2-styrylhexanamide (2b). Following the typical procedure described above, the reaction was carried out by the mixture of **1b** (72.2 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title

product in 80% isolated yield (54.0 mg) and *E*/*Z* = 4:1 as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 7.18 (m, 4H), 7.14 – 7.10 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.87 – 6.85 (m, 2H), 6.10 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.96 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 3.16 (s, 3H), 1.79 – 1.70 (m, 1H), 3.01 (q, *J* = 7.6 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.16 – 1.07 (m, 4H), 0.76 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0, 158.9, 137.1, 136.6, 131.0, 129.7, 128.8, 128.4, 127.2, 126.1, 114.6, 55.4, 46.9, 37.6, 33.1, 29.4, 22.5, 13.9. **HRMS (ESI)** calcd for $C_{22}H_{27}NO_2$ $[M+H]^+$: 338.2115, found 338.2112.



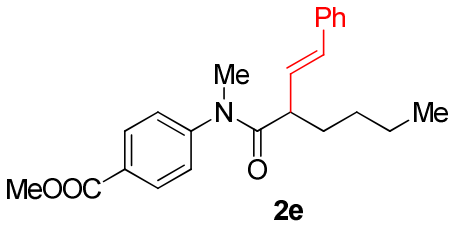
2c

(*E*)-*N*-(4-chlorophenyl)-*N*-methyl-2-styrylhexanamide (2c). Following the typical procedure described above, the reaction was carried out by the mixture of **1c** (73.1 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 55% isolated yield (37.5 mg) and *E*/*Z* = 5:1 as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.40 (m, 2H), 7.32 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 7.14 – 7.12 (m, 2H), 6.17 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.03 (d, *J* = 16.0 Hz, 1H), 3.25 (s, 3H), 3.04 (q, *J* = 8.0 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.55 – 1.46 (m, 1H), 1.24 – 1.14 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 142.4, 136.9, 133.7, 131.3, 129.8, 129.3, 129.2, 128.5, 127.4, 126.2, 47.2, 37.5, 33.2, 29.4, 22.5, 13.9. **HRMS (ESI)** calcd for $C_{21}H_{24}ClNO$ $[M+H]^+$: 342.1619, found 342.1626.



2d

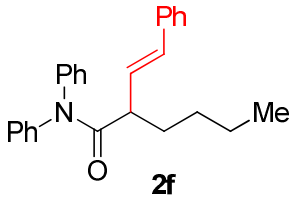
(*E*)-*N*-methyl-2-styryl-*N*-(4-(trifluoromethyl)phenyl)hexanamide (2d). Following the typical procedure described above, the reaction was carried out by the mixture of **1d** (79.8 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 63% isolated yield (47.3 mg) and *E*/*Z* = 5:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.35 (s, 1H), 7.32 – 7.29 (m, 5H), 7.25 – 7.21 (m, 1H), 6.19 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 3.30 (s, 3H), 3.05 (q, *J* = 7.8 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.56 – 1.49 (m, 1H), 1.26 – 1.16 (m, 4H), 0.85 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.3, 147.1 (q, *J* = 1.5 Hz), 136.7, 131.4, 129.1, 128.5, 128.2 (q, *J* = 0.7 Hz), 128.1, 127.5, 126.8 (q, *J* = 3.0 Hz), 126.2, 123.7 (q, *J* = 272.3 Hz), 47.4, 37.4, 33.2, 29.4, 22.5, 13.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.5. **HRMS (ESI)** calcd for $C_{22}H_{24}F_3NO$ $[M+H]^+$: 376.1883, found 376.1882.



2e

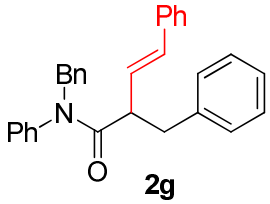
Methyl (*E*)-4-(*N*-methyl-2-styrylhexanamido)benzoate (2e). Following the typical procedure described above, the reaction was carried out by the mixture of **1e** (77.8 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere

under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 58% isolated yield (42.4 mg) and *E*/*Z* = 5:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.06 – 8.03 (m, 2H), 7.25 – 7.22 (m, 6H), 7.17 – 7.12 (m, 1H), 6.11 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.96 (d, *J* = 15.9 Hz, 1H), 3.89 (s, 3H), 3.23 (s, 3H), 3.03 – 2.96 (m, 1H), 1.82 – 1.70 (m, 1H), 1.50 – 1.38 (m, 1H), 1.15 – 1.10 (m, 4H), 0.76 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 166.2, 147.9, 136.8, 131.3, 131.0, 130.7, 129.2, 128.5, 127.6, 127.4, 126.2, 52.4, 47.3, 37.3, 33.2, 29.3, 22.5, 13.9. **HRMS (ESI)** calcd for $C_{23}H_{27}NO_3$ $[M+H]^+$: 366.2064, found 366.2061.



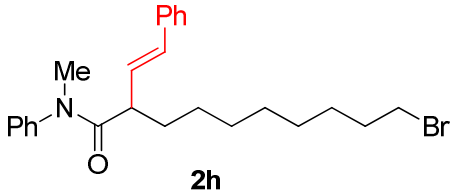
2f

(*E*)-*N*,*N*-diphenyl-2-styrylhexanamide (**2f**). Following the typical procedure described above, the reaction was carried out by the mixture of **1f** (78.7mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 61% isolated yield (45.0 mg) and *E*/*Z* = 4:1 as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.28 (m, 3H), 7.27 – 7.22 (m, 5H), 7.21 – 7.16 (m, 5H), 7.10 – 7.07 (m, 2H), 6.19 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.05 (d, *J* = 16.0 Hz, 1H), 3.18 (q, *J* = 7.6 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.53 – 1.46 (m, 1H), 1.24 – 1.15 (m, 4H), 0.79 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 142.7, 137.0, 131.5, 129.5, 129.4, 129.1, 128.8, 128.5, 128.1, 128.0, 127.4, 126.5, 126.2, 48.0, 33.5, 29.4, 22.5, 13.9. **HRMS (ESI)** calcd for $C_{26}H_{27}NO$ $[M+H]^+$: 370.2165, found 370.2162.



2g

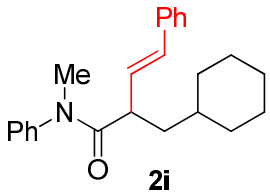
(*E*)-*N*,2-dibenzyl-*N*,4-diphenylbut-3-enamide (2g). Following the typical procedure described above, the reaction was carried out by the mixture of **1g** (81.5 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 58% isolated yield (48.5 mg) and *E*/*Z* = 13:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.34 – 7.28 (m, 4H), 7.28 – 7.21 (m, 7H), 7.19 – 7.14 (m, 5H), 7.11 – 7.07 (m, 2H), 7.02 – 6.95 (m, 2H), 6.31 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 5.01 (d, *J* = 14.4 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 3.37 – 3.23 (m, 2H), 2.77 – 2.66 (m, 1H). **^{13}C NMR (101MHz, $CDCl_3$)** δ 172.3, 141.6, 139.2, 137.1, 136.9, 131.4, 129.4, 129.1, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.9, 127.4, 127.1, 126.3, 126.2, 52.9, 49.6, 39.9. **HRMS (ESI)** calcd for $C_{30}H_{27}NO$ $[M+H]^+$: 418.2165, found 418.2163.



2h

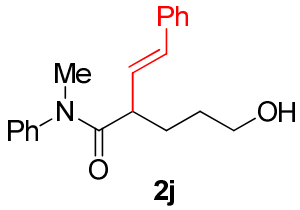
(*E*)-10-bromo-*N*-methyl-*N*-phenyl-2-styryldecanamide (2h). Following the typical procedure described above, the reaction was carried out by the mixture of **1h** (93.2 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 66% isolated yield (58.2 mg) and *E*/*Z* = 6:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 –

7.40 (m, 3H), 7.34 – 7.28 (m, 4H), 7.25 – 7.20 (m, 3H), 6.21 (dd, J = 15.9, 8.7 Hz, 1H), 6.04 (d, J = 15.9 Hz, 1H), 3.41 (t, J = 6.9 Hz, 2H), 3.30 (s, 3H), 3.10 (q, J = 7.5 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.55 – 1.36 (m, 4H), 1.31 – 1.20 (m, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 143.7, 136.9, 131.1, 129.5, 129.5, 128.4, 127.8, 127.7, 127.2, 126.1, 47.0, 37.4, 34.0, 33.3, 32.7, 29.2, 29.1, 28.6, 28.0, 27.0. **HRMS (ESI)** calcd for $C_{25}H_{32}BrNO$ $[M+H]^+$: 442.1740, found 442.1737.



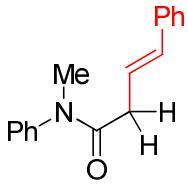
2i

(*E*)-2-(cyclohexylmethyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2i). Following the typical procedure described above, the reaction was carried out by the mixture of **1i** (74.3 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 60% isolated yield (41.7 mg) and E/Z = 2:1 as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.42 (m, 2H), 7.31 – 7.28 (m, 3H), 7.20 – 7.18 (m, 2H), 7.13 – 7.11 (m, 1H), 6.90 – 6.86 (m, 2H), 6.18 (dd, J = 16.0, 8.8 Hz, 1H), 6.02 (d, J = 16.0 Hz, 1H), 3.27 (s, 3H), 3.21 – 3.19 (m, 1H), 1.79 – 1.69 (m, 2H), 1.60 – 1.57 (m, 3H), 1.42 – 1.33 (m, 2H), 1.17 – 1.08 (m, 4H), 0.79 – 0.67 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 143.8, 137.1, 131.0, 129.8, 129.5, 128.4, 128.0, 127.7, 127.3, 126.2, 44.3, 39.3, 37.5, 34.9, 33.5, 32.9, 26.5, 26.1, 26.1. **HRMS (ESI)** calcd for $C_{24}H_{29}NO$ $[M+H]^+$: 348.2322, found 348.2319.



2j

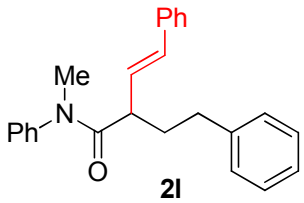
(*E*)-5-hydroxy-*N*-methyl-*N*-phenyl-2-styrylpentanamide (**2j**). Following the typical procedure described above, the reaction was carried out by the mixture of **1j** (66.6 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 65% isolated yield (39.9 mg) and *E*/*Z* = 5:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.39 – 7.30 (m, 3H), 7.22 – 7.19 (m, 4H), 7.16 – 7.10 (m, 3H), 6.08 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 3.50 – 3.45 (m, 2H), 3.20 (s, 3H), 3.07 – 2.99 (m, 1H), 1.96 (s, 1H), 1.92 – 1.76 (m, 2H), 1.46 – 1.39 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 173.5, 143.6, 136.8, 131.5, 129.6, 129.0, 128.4, 128.0, 127.7, 127.4, 126.2, 62.3, 46.8, 37.5, 30.4, 29.3. **HRMS (ESI)** calcd for $C_{20}H_{23}NO_2$ $[M+H]^+$: 310.1802, found 310.1801.



2k

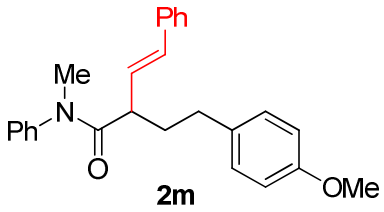
(*E*)-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2k**)**.** Following the typical procedure described above, the reaction was carried out by the mixture of **1k** (55.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:3) afforded the title product in 60% isolated

yield (30.1 mg) and *E* only as a light yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.35 (m, 3H), 7.35 – 7.26 (m, 4H), 7.25 – 7.16 (m, 3H), 6.34 – 6.15 (m, 2H), 3.29 (s, 3H), 3.05 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 170.9, 143.8, 137.0, 132.5, 129.7, 128.4, 127.9, 127.4, 127.2, 126.1, 123.5, 38.5, 37.4. **HRMS (ESI)** calcd for $C_{17}H_{17}NO$ $[M+H]^+$: 252.1383, found 252.1383.



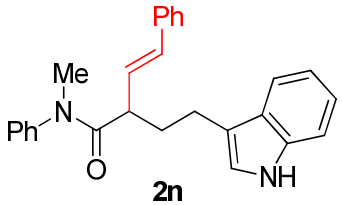
2l

(*E*)-*N*-methyl-2-phenethyl-*N*,4-diphenylbut-3-enamide (**2l**). Following the typical procedure described above, the reaction was carried out by the mixture of **1l** (75.8 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 70% isolated yield (49.7 mg) and *E*/*Z* = 7:1 as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.33 (m, 3H), 7.31 – 7.26 (m, 4H), 7.23 – 7.20 (m, 3H), 7.16 – 7.14 (m, 1H), 7.09 – 7.07 (m, 4H), 6.19 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 3.27 (s, 3H), 3.17 – 3.09 (m, 1H), 2.57 – 2.47 (m, 2H), 2.20 – 2.11 (m, 1H), 1.91 – 1.84 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.1, 143.5, 141.4, 136.9, 131.7, 129.5, 128.9, 128.4, 128.3, 128.2, 127.8, 127.6, 127.3, 126.1, 125.7, 46.3, 37.4, 34.4, 33.1. **HRMS (ESI)** calcd for $C_{25}H_{25}NO$ $[M+H]^+$: 356.2009, found 356.2010.



2m

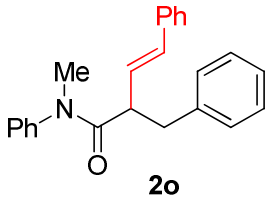
(*E*)-2-(4-methoxyphenethyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2m**). Following the typical procedure described above, the reaction was carried out by the mixture of **1m** (81.9 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 84% isolated yield (64.7 mg) and *E*/*Z* = 7:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 – 7.34 (m, 3H), 7.30 – 7.28 (m, 4H), 7.23 – 7.19 (m, 1H), 7.10 – 7.07 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.19 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 3.77 (s, 3H), 3.27 (s, 3H), 3.16 – 3.08 (m, 1H), 2.50 – 2.42 (m, 2H), 2.18 – 2.06 (m, 1H), 1.89 – 1.77 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.2, 157.6, 143.5, 136.9, 133.5, 131.6, 129.5, 129.1, 129.0, 128.4, 127.7, 127.6, 127.3, 126.1, 113.6, 55.1, 46.2, 37.4, 34.7, 32.1. **HRMS (ESI)** calcd for $C_{26}H_{27}NO_2$ $[M+H]^+$: 386.2115, found 386.2116.



2n

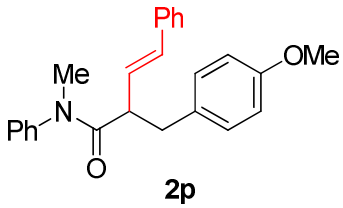
(*E*)-2-(2-(1*H*-indol-3-yl)ethyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2n**). Following the typical procedure described above, the reaction was carried out by the mixture of **1n** (83.7 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column

chromatography on silica gel (EtOAc/Petroleum ether = 1:3) afforded the title product in 75% isolated yield (59.3 mg) and *E*/*Z* = 10:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.24 (m, 8H), 7.19 – 7.07 (m, 3H), 7.02 – 6.99 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.24 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 3.26 (s, 3H), 3.23 – 3.17 (m, 1H), 2.74 – 2.59 (m, 2H), 2.34 – 2.24 (m, 1H), 2.00 – 1.95 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 143.4, 136.9, 136.3, 131.6, 129.4, 129.1, 128.4, 127.7, 127.5, 127.3, 127.3, 126.2, 121.7, 121.2, 118.9, 118.8, 115.3, 111.1, 46.5, 37.4, 33.2, 22.5. **HRMS (ESI)** calcd for $C_{27}H_{26}N_2O$ $[M+H]^+$: 395.2118, found 395.2117.



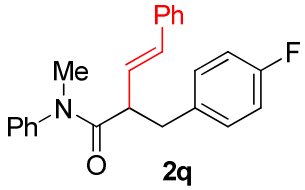
2o

(*E*)-2-benzyl-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2o**). Following the typical procedure described above, the reaction was carried out by the mixture of **1o** (73.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 80% isolated yield (54.6 mg) and *E*/*Z* = 7:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.32 – 7.27 (m, 6H), 7.26 – 7.19 (m, 5H), 7.08 – 7.05 (m, 2H), 6.66 (s, 2H), 6.30 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 3.38 – 3.30 (m, 1H), 3.25 – 3.18 (m, 1H), 3.15 (s, 3H), 2.70 (dd, *J* = 12.6, 6.0 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.5, 143.3, 139.2, 136.8, 131.3, 129.3, 129.2, 128.9, 128.4, 128.1, 127.7, 127.5, 127.3, 126.2, 126.2, 49.4, 40.0, 37.2. **HRMS (ESI)** calcd for $C_{24}H_{23}NO$ $[M+H]^+$: 342.1852, found 342.1854.



2p

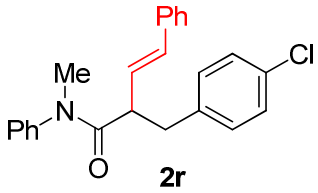
(*E*)-2-(4-methoxybenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2p). Following the typical procedure described above, the reaction was carried out by the mixture of **1p** (79.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) afforded the title product in 73% isolated yield (54.2 mg) and *E/Z* = 7:1 as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 7H), δ 7.28 – 7.24 (m, 1H), δ 7.03 – 7.02 (m, 2H), δ 6.87 – 6.78 (m, 4H), 6.34 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), δ 3.39 – 3.33 (m, 1H), δ 3.23 – 3.15 (m, 4H), δ 2.72 – 2.68 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.7, 158.1, 143.4, 136.9, 131.3, 131.3, 130.2, 129.4, 129.0, 128.4, 127.8, 127.6, 127.3, 126.2, 113.5, 55.2, 49.5, 39.1, 37.2. **HRMS (ESI)** calcd for $C_{25}H_{25}NO_2$ $[M+H]^+$: 372.1958, found 372.1959.



2q

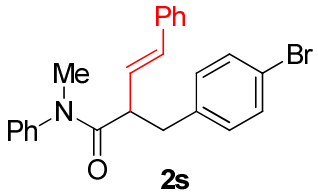
(*E*)-2-(4-fluorobenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2q**). Following the typical procedure described above, the reaction was carried out by the mixture of **1q** (76.6 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 88% isolated yield (63.2 mg) and *E/Z* = 10:1 as a colorless oil. **^{1}H NMR (300 MHz,**

$CDCl_3$) δ 7.34 – 7.28 (m, 6H), 7.25 (s, 1H), 7.24 – 7.18 (m, 1H), 7.05 – 7.00 (m, 2H), 6.96 – 6.91 (m, 2H), 6.73 – 6.71 (m, 2H), 6.27 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 3.22 – 3.10 (m, 4H), 2.69 – 2.63 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.4, 161.5 (d, *J* = 244.0 Hz), 143.4, 136.8, 135.0 (d, *J* = 3.2 Hz), 131.6, 130.6 (d, *J* = 7.9 Hz), 129.4, 128.6, 128.5, 127.9, 127.5, 127.5, 126.2, 114.9 (d, *J* = 21.0 Hz), 49.5, 39.1, 37.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ 116.8. **HRMS (ESI)** calcd for $C_{24}H_{22}FNO$ $[M+H]^+$: 360.1758, found 360.1758.



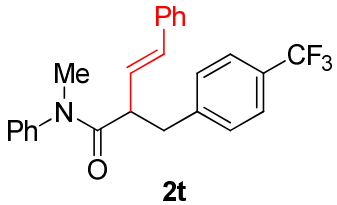
2r

(*E*)-2-(4-chlorobenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2r). Following the typical procedure described above, the reaction was carried out by the mixture of **1r** (79.9 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 80% isolated yield (60.0 mg) and *E*/*Z* = 9:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.34 – 7.28 (m, 6H), 7.25 – 7.20 (m, 4H), 7.01 – 6.98 (m, 2H), 6.75 (s, 2H), 6.26 (dd, *J* = 15.9 Hz, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 3.21 – 3.10 (m, 4H), 2.66 (dd, *J* = 12.9, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.3, 143.3, 137.7, 136.7, 132.0, 131.7, 130.6, 129.5, 128.5, 128.4, 128.2, 127.9, 127.5, 127.5, 126.2, 49.3, 39.2, 37.3. **HRMS (ESI)** calcd for $C_{24}H_{22}ClNO$ $[M+H]^+$: 376.1463, found 376.1463.



2s

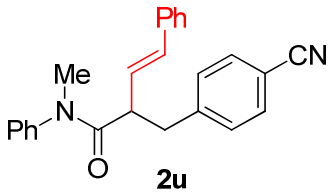
(*E*)-2-(4-bromobenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (**2s**). Following the typical procedure described above, the reaction was carried out by the mixture of **1s** (88.8 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 70% isolated yield (58.7 mg) and *E*/*Z* = 12:1 as a as a white solid. M.p. 101-102 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.39 – 7.38 (m, 1H), 7.36 – 7.35 (m, 1H), 7.34 – 7.32 (m, 3H), 7.31 – 7.29 (m, 3H), 7.27 – 7.19 (m, 2H), 6.95 – 6.93 (m, 2H), 6.75 (s, 2H), 6.26 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 3.35 – 7.27 (m, 1H), 3.20 – 3.13 (m, 4H), 2.65 (dd, *J* = 12.9, 5.4 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.3, 143.3, 138.3, 136.7, 131.7, 131.2, 131.0, 129.5, 128.5, 128.4, 127.9, 127.6, 127.5, 126.2, 120.1, 49.2, 39.2, 37.3. **HRMS (ESI)** calcd for $C_{24}H_{22}BrNO$ $[M+H]^+$: 420.0958, found 420.0958.



2t

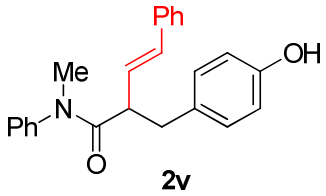
(*E*)-*N*-methyl-*N*,4-diphenyl-2-(4-(trifluoromethyl)benzyl)but-3-enamide (**2t**). Following the typical procedure described above, the reaction was carried out by the mixture of **1t** (86.6 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column

chromatography on silica gel (EtOAc/Petroleum ether = 1:8) afforded the title product in 77% isolated yield (63.0 mg) and *E*/*Z* = 12:1 as a yellow solid. M.p. 104-106 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.19 (m, 7H), 7.18 – 7.14 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 2H), 6.20 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 3.31 – 3.16 (m, 2H), 3.08 (s, 3H), 2.67 (dd, *J* = 12.3, 4.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 143.5 (q, *J* = 1.0 Hz), 143.2, 136.6, 131.8, 129.5, 129.5, 129.3 (q, *J* = 14.1 Hz), 128.5, 128.2, 128.0, 127.6, 127.5, 126.3, 125.1 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 272.7 Hz), 49.1, 39.6, 37.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ 62.3. **HRMS (ESI)** calcd for $C_{25}H_{22}F_3NO$ $[M+H]^+$: 410.1726, found 410.1724.



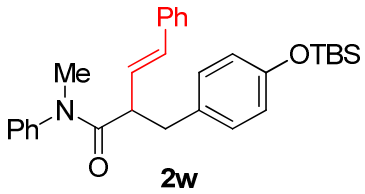
2u

(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2u). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 81% isolated yield (59.3 mg) and *E*/*Z* = 12:1 as a yellow solid. M.p. 103-105 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.24 (m, 8H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.77 (s, 2H), 6.24 (dd, *J* = 15.9, 8.1 Hz, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 3.37 – 3.26 (m, 2H), 3.17 (s, 3H), 2.76 (dd, *J* = 12.1, 4.5 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.8, 145.0, 143.1, 136.4, 132.1, 132.0, 130.0, 129.6, 128.5, 128.1, 127.8, 127.7, 127.4, 126.2, 118.9, 110.1, 48.9, 39.7, 37.3. **HRMS (ESI)** calcd for $C_{25}H_{22}N_2O$ $[M+H]^+$: 367.1805, found 367.1806.



2v

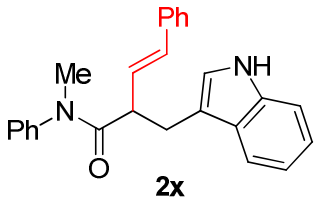
(*E*)-2-(4-hydroxybenzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2v). Following the typical procedure described above, the reaction was carried out by the mixture of **1v** (76.2 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 2:3) afforded the title product in 44% isolated yield (31.4 mg) and *E*/*Z* = 6:1 as a light yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.29 (m, 4H), 7.27 – 7.18 (m, 3H), 7.13 – 7.06 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.79 – 6.67 (m, 2H), 6.29 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 3.37 – 3.31 (m, 1H), 3.18 – 3.13 (m, 4H), 2.63 (dd, *J* = 13.2, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 155.0, 143.2, 136.8, 131.5, 130.5, 130.3, 129.5, 128.7, 128.5, 128.0, 127.6, 127.4, 126.2, 115.3, 49.7, 39.1, 37.5. **HRMS (ESI)** calcd for $C_{24}H_{23}NO_2$ $[M+H]^+$: 358.1802, found 358.1797.



2w

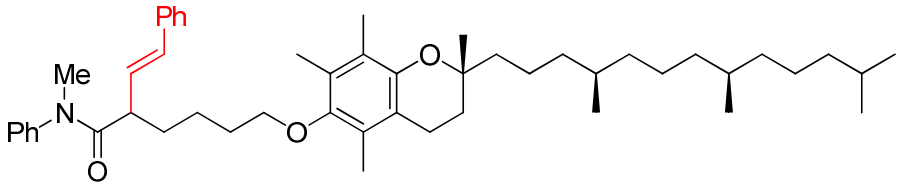
(*E*)-2-(4-((*tert*-butyldimethylsilyl)oxy)benzyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2w). Following the typical procedure described above, the reaction was carried out by the mixture of **1w** (99.1 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:7) afforded the title product in 81% isolated yield (76.3 mg) and *E*/*Z* = 7:1 as a colorless oil. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 5H), 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.80 – 6.75 (m, 4H), 6.34 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.24 – 3.18 (m, 4H), 2.69 – 2.64 (m, 1H), 1.04 (s, 9H), 0.25 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.7, 154.1, 143.5, 136.9, 132.0, 131.2, 130.2, 129.3, 129.0, 128.4, 127.7, 127.6, 127.3, 126.2, 119.8, 49.6, 39.2, 37.2, 25.7, 18.2, -4.5. **HRMS (ESI)** calcd for $C_{30}H_{37}NO_2Si$ $[M+H]^+$: 472.2666, found 472.2666.



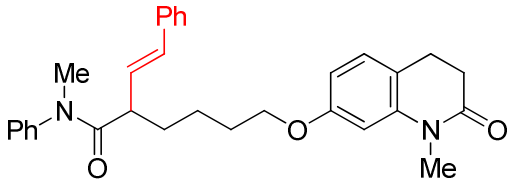
2x

(*E*)-2-((1*H*-indol-3-yl)methyl)-*N*-methyl-*N*,4-diphenylbut-3-enamide (2x). Following the typical procedure described above, the reaction was carried out by the mixture of **1x** (80.9 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:2) afforded the title product in 65% isolated yield (49.4 mg) and *E*/*Z* = 4:1 as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (s, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 7.15 – 7.06 (m, 4H), 6.96 – 6.86 (m, 3H), 6.70 – 6.64 (m, 1H), 6.53 (s, 2H), 6.27 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.31 – 3.26 (m, 1H), 3.08 (s, 3H), 2.85 – 2.80 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.5, 143.4, 137.0, 136.1, 131.3, 129.3, 129.3, 128.4, 127.6, 127.5, 127.3, 126.2, 122.7, 121.8, 119.1, 118.8, 113.2, 111.0, 48.0, 37.3, 29.6. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O$ $[M+H]^+$: 381.1961, found 381.1961.



2y

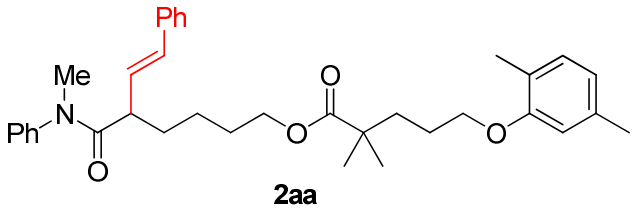
***N*-methyl-*N*-phenyl-2-((*E*)-styryl)-6-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)hexanamide (2y).** Following the typical procedure described above, the reaction was carried out by the mixture of **1y** (152.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 55% isolated yield (80.9 mg) and *E*/*Z* = 6:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 – 7.29 (m, 3H), 7.25 – 7.19 (m, 3H), 7.18 – 7.09 (m, 4H), 6.13 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.96 (d, *J* = 15.9 Hz, 1H), 3.50 (t, *J* = 6.6 Hz, 2H), 3.20 (s, 3H), 3.09 – 3.02 (m, 1H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.06 (s, 3H), 2.01 – 1.99 (m, 6H), 1.78 – 1.59 (m, 6H), 1.51 – 1.27 (m, 14H), 1.21 – 1.18 (m, 4H), 1.09 – 0.96 (m, 8H), 0.80 – 0.75 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.5, 148.2, 147.6, 143.7, 136.9, 131.2, 129.6, 129.4, 128.4, 128.4, 127.9, 127.8, 127.7, 127.3, 126.2, 126.2, 125.7, 122.7, 117.4, 74.7, 72.6, 47.1, 40.0, 39.3, 37.5, 37.4, 37.4, 37.2, 33.4, 32.7, 32.6, 31.2, 30.0, 27.9, 24.7, 24.4, 24.0, 23.8, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 12.7, 11.8, 11.7. **HRMS (ESI)** calcd for $C_{50}H_{73}NO_3$ $[M+H]^+$: 736.5663, found 736.5655.



2z

(*E*)-*N*-methyl-6-((1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-7-yl)oxy)-*N*-phenyl-2-styrylhexanamide (2z). Following the typical procedure described above, the reaction was carried out by the mixture of **1z** (101.3 mg, 0.2 mmol, 1.0 equiv), styrene

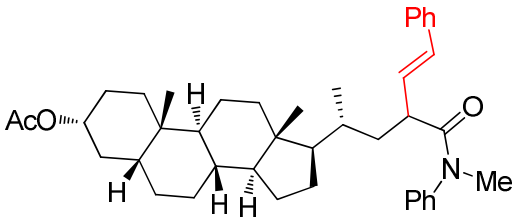
(31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 78% isolated yield (75.2 mg) and *E*/*Z* = 7:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.39 – 7.27 (m, 3H), 7.22 – 7.19 (m, 4H), 7.16 – 7.10 (m, 3H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.44 – 6.39 (m, 2H), 6.10 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.93 (d, *J* = 15.9 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 3.22 (s, 3H), 3.20 (s, 3H), 3.08 – 3.00 (m, 1H), 2.74 (dd, *J* = 8.7, 5.7 Hz, 2H), 2.54 (dd, *J* = 8.7, 6.0 Hz, 2H), 1.89 – 1.77 (m, 1H), 1.68 – 1.48 (m, 3H), 1.35 – 1.25 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.3, 170.6, 158.5, 143.6, 141.5, 136.8, 131.4, 129.6, 129.1, 128.4, 128.0, 127.9, 127.7, 127.4, 126.1, 118.2, 107.0, 102.9, 67.8, 47.0, 37.5, 32.9, 32.0, 29.5, 29.0, 24.5, 23.7. **HRMS (ESI)** calcd for $C_{31}H_{34}N_2O_3$ $[M+H]^+$: 483.2642, found 483.2641.



2aa

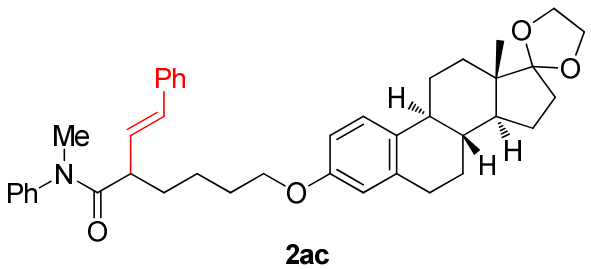
(*E*)-5-(methyl(phenyl)carbamoyl)-7-phenylhept-6-en-1-yl 5-(2,5-dimethylpheno-xy)-2,2-dimethylpenta-noate (**2aa**)**.** Following the typical procedure described above, the reaction was carried out by the mixture of **1aa** (115.9 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 65% isolated yield (72.2 mg) and *E*/*Z* = 7:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.42 – 7.30 (m, 3H), 7.25 – 7.21 (m, 4H), 7.19 – 7.12 (m, 3H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.62 – 6.55 (m, 2H), 6.14 (dd, *J* = 15.9, 9.0 Hz, 1H), 5.97 (d, *J* = 15.9 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.86 – 3.82 (m, 2H), 3.23 (s, 3H), 3.08 – 3.00 (m, 1H), 2.26 (s, 3H), 2.12 (s, 3H),

1.67 – 1.64 (m, 5H), 1.54 – 1.44 (m, 3H), 1.27 – 1.21 (m, 2H), 1.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.7, 173.3, 156.8, 143.6, 136.8, 136.3, 131.4, 130.2, 129.6, 129.1, 128.4, 127.9, 127.7, 127.3, 126.1, 123.4, 120.6, 111.8, 67.8, 64.0, 46.9, 41.9, 37.4, 37.0, 32.8, 28.4, 25.1, 25.1, 23.5, 21.3, 15.7. **HRMS (ESI)** calcd for $C_{36}H_{45}NO_4$ $[M+H]^+$: 556.3421, found 556.3419.



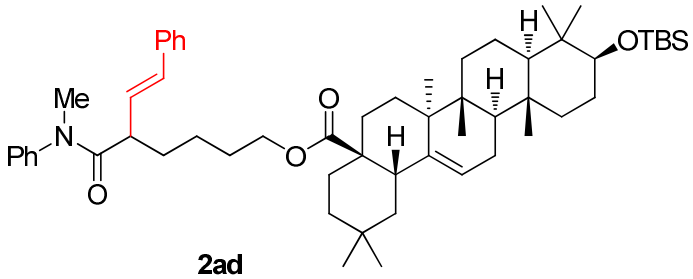
2ab

(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((2*R*,*E*)-4-(methyl(phenyl)carbamoyl)-6-phenylhex-5-en-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl acetate (2ab). Following the typical procedure described above, the reaction was carried out by the mixture of **1ab** (126.7 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in dioxane (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 60% isolated yield (73.1 mg) and *E*/*Z* = 2:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.40 – 7.31 (m, 3H), 7.23 – 7.19 (m, 3H), 7.13 – 7.10 (m, 2H), 6.94 – 6.81 (m, 2H), 6.11 (dd, *J* = 15.9, 8.4 Hz, 1H), 5.97 (d, *J* = 15.9 Hz, 1H), 4.70 – 4.59 (m, 1H), 3.21 (s, 3H), 3.13 – 3.10 (m, 1H), 2.22 – 2.10 (m, 1H), 1.95 (s, 3H), 1.89 – 1.71 (m, 8H), 1.48 – 1.44 (m, 3H), 1.36 – 1.26 (m, 8H), 1.00 – 0.94 (m, 6H), 0.86 (s, 3H), 0.59 – 0.56 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 170.7, 143.8, 137.1, 130.5, 130.4, 129.5, 128.5, 128.0, 127.9, 127.3, 126.1, 74.4, 56.8, 56.5, 44.7, 42.7, 41.9, 40.5, 40.4, 40.2, 37.6, 35.7, 35.0, 34.6, 34.3, 32.2, 28.3, 27.0, 26.6, 26.3, 24.2, 23.3, 21.5, 20.8, 19.0, 12.1. **HRMS (ESI)** calcd for $C_{41}H_{55}NO_3$ $[M+H]^+$: 610.4255, found 610.4249.



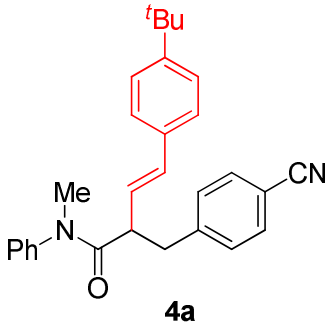
2ac

***N*-methyl-6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)-*N*-phenyl-2-((*E*)-styryl)hexanamide (2ac).** Following the typical procedure described above, the reaction was carried out by the mixture of **1ac** (128.7 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 40% isolated yield (49.5 mg) and *E*/*Z* = 5:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.38 – 7.30 (m, 3H), 7.23 – 7.21 (m, 3H), 7.18 (s, 1H), 7.13 – 7.09 (m, 3H), 7.06 – 6.94 (m, 1H), 6.62 – 6.57 (m, 1H), 6.55 – 6.51 (m, 1H), 6.10 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.94 (d, *J* = 15.9 Hz, 1H), 3.84 – 3.77 (m, 3H), 3.67 (s, 3H), 3.20 (s, 3H), 2.99 (s, 1H), 2.83 – 2.75 (m, 2H), 2.47 – 2.33 (m, 1H), 2.29 – 2.13 (m, 3H), 2.01 – 1.77 (m, 5H), 1.61 – 1.42 (m, 8H), 1.31 – 1.28 (m, 2H), 0.82 (d, *J* = 8.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.5, 157.0, 143.7, 137.6, 136.9, 131.8, 131.4, 129.6, 129.2, 128.5, 128.0, 127.8, 127.4, 126.2, 119.4, 114.4, 112.1, 67.5, 64.5, 63.7, 50.3, 48.0, 47.1, 43.9, 38.3, 37.5, 35.8, 33.0, 31.5, 29.6, 29.1, 26.5, 25.9, 23.8, 21.5, 13.8. **HRMS (ESI)** calcd for $C_{41}H_{49}NO_4$ $[M+H]^+$: 620.3734, found 620.3733.



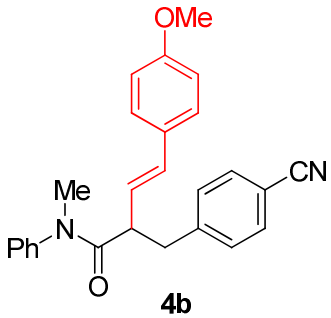
2ad

(*E*)-5-(methyl(phenyl)carbamoyl)-7-phenylhept-6-en-1-yl (4a*S*,6a*S*,6b*R*,8a*R*,10*S*, 12a*R*,12b*R*,14b*S*)-10-((*tert*-butyldimethylsilyl)oxy)-2,2,6a,6b,9,9,12a-heptamethyl -1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (2ad). Following the typical procedure described above, the reaction was carried out by the mixture of **1ad** (180.0 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 67% isolated yield (117.33 mg) and *E*/*Z* = 5:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.44 – 7.32 (m, 3H), 7.26 – 7.23 (m, 4H), 7.17 – 7.14 (m, 2H), 7.10 – 7.01 (m, 1H), 6.13 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.97 (d, *J* = 15.9 Hz, 1H), 5.24 – 5.16 (m, 1H), 3.96 – 3.86 (m, 2H), 3.24 (s, 3H), 3.17 – 3.12 (m, 1H), 3.08 – 3.00 (m, 1H), 2.82 – 2.76 (m, 1H), 1.82 – 1.74 (m, 3H), 1.62 – 1.42 (m, 15H), 1.26 – 1.07 (m, 11H), 0.86 – 0.83 (m, 23H), 0.70 (s, 3H), 0.64 (s, 3H), 0.00 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.6, 177.6, 173.3, 143.7, 136.8, 131.4, 129.6, 128.4, 127.9, 127.7, 127.3, 126.2, 122.4, 122.3, 79.4, 63.8, 55.2, 55.2, 47.6, 47.0, 46.6, 46.6, 45.8, 41.6, 41.6, 41.2, 39.2, 38.4, 37.5, 36.8, 36.8, 33.1, 30.6, 28.5, 27.5, 25.9, 25.8, 23.6, 23.5, 22.9, 18.5, 18.1, 16.9, 16.9, 16.1, 15.3, 15.3, -3.8, -5.0. **HRMS (ESI)** calcd for $C_{57}H_{85}NO_4Si$ $[M+H]^+$: 876.6321, found 876.6322.



4a

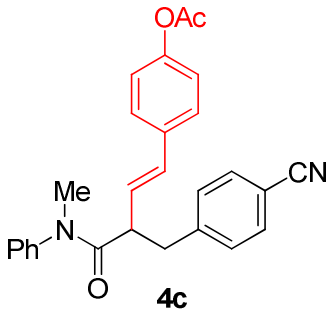
(*E*)-4-(4-(*tert*-butyl)phenyl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide (4a). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3a** (48.1 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 68% isolated yield (57.4 mg) and *E*/*Z* = 20:1 as a yellow solid. M.p. 98-100 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.24 (m, 5H), 7.18 – 7.15 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 2H), 6.11 (dd, *J* = 16.0, 8.4 Hz, 1H), 5.92 (d, *J* = 16.0 Hz, 1H), 3.28 – 3.22 (m, 1H), 3.18 (dd, *J* = 12.4, 9.2 Hz, 1H), 3.08 (s, 3H), 2.67 (dd, *J* = 12.4, 4.8 Hz, 1H), 1.23 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 150.8, 145.1, 143.2, 133.7, 132.0, 131.9, 130.0, 129.5, 128.1, 127.5, 127.0, 126.0, 125.4, 118.9, 110.1, 49.0, 39.8, 37.3, 34.5, 31.2. **HRMS (ESI)** calcd for $C_{29}H_{30}N_2O_2$ $[M+H]^+$: 423.2431, found 423.2427.



4b

(*E*)-2-(4-cyanobenzyl)-4-(4-methoxyphenyl)-*N*-methyl-*N*-phenylbut-3-enamide (4b). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3b** (40.3 mg, 0.3 mmol, 1.5 equiv),

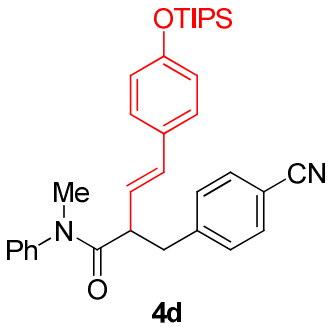
$Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:3) afforded the title product in 65% isolated yield (51.5 mg) and *E*/*Z* = 13:1 as a yellow solid. M.p. 110-112 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 3.2 Hz, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.85 – 6.82 (m, 2H), 6.78 – 6.76 (m, 2H), 6.09 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.32 – 3.29 (m, 1H), 3.25 (dd, *J* = 12.0, 9.2 Hz, 1H), 3.16 (s, 3H), 2.75 (dd, *J* = 12.0, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 159.2, 145.1, 143.1, 131.9, 131.5, 130.0, 129.5, 129.2, 128.0, 127.4, 127.4, 125.5, 118.9, 113.9, 110.0, 55.2, 48.9, 39.8, 37.3. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O_2$ $[M+H]^+$: 397.1911, found 397.1909.



4c

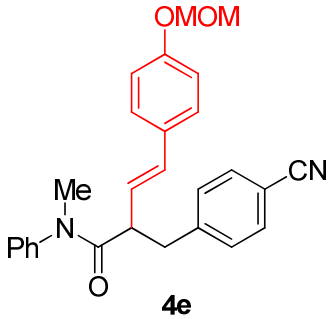
(*E*)-4-(3-(4-cyanobenzyl)-4-(methyl(phenyl)amino)-4-oxobut-1-en-1-yl)phenyl acetate (4c). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3c** (48.7 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 50% isolated yield (50.5 mg contained ca. 15% desaturation side product which could not separated from each other) and *E*/*Z* > 20:1 as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.22 – 7.20 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 2H), 6.10 (dd, *J* =

16.0, 8.0 Hz, 1H), 5.93 (d, *J* = 16.0 Hz, 1H), 3.28 – 3.15 (m, 2H), 3.09 (s, 3H), 2.67 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 169.4, 150.0, 144.8, 143.0, 134.2, 132.3, 131.9, 131.1, 130.0, 129.5, 128.1, 127.9, 127.1, 121.6, 118.8, 110.1, 48.8, 39.7, 37.3, 21.0. **HRMS (ESI)** calcd for $C_{27}H_{24}N_2O_3$ $[M+H]^+$: 425.1860, found 425.1858.



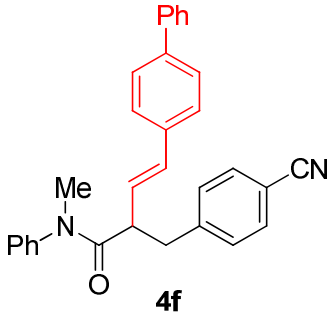
4d

(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenyl-4-(4-((triisopropylsilyl)oxy)phenyl)but-3-enamide (4d). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3d** (83.0 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 67% isolated yield (72.1 mg) and *E* only as a light yellow solid. M.p. 117-119 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.32 (m, 3H), 7.19 – 7.15 (m, 4H), 6.82 – 6.75 (m, 4H), 6.08 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 3.34 – 3.16 (m, 2H), 3.16 (s, 3H), 2.74 (dd, *J* = 12.0, 4.0 Hz, 1H), 31.28 – 1.22 (m, 3H), 1.10 (d, *J* = 8 Hz, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 155.8, 145.1, 143.1, 131.9, 131.6, 130.0, 129.5, 129.5, 128.0, 127.4, 127.3, 125.4, 119.8, 118.9, 110.0, 48.8, 39.9, 37.3, 17.8, 12.6. **HRMS (ESI)** calcd for $C_{34}H_{42}N_2O_2Si$ $[M+H]^+$: 539.3088, found 539.3082.



4e

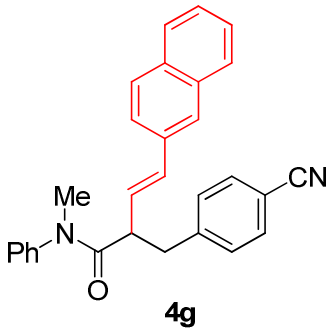
(*E*)-2-(4-cyanobenzyl)-4-(4-(methoxymethoxy)phenyl)-*N*-methyl-*N*-phenylbut-3-enamide (4e). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3e** (49.3 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 76% isolated yield (64.8 mg) and *E*/*Z* = 11:1 as a yellow solid. M.p. 88-89 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.45 (m, 2H), 7.29 – 7.25 (m, 3H), 7.16 – 7.08 (m, 4H), 6.91 – 6.88 (m, 2H), 6.70 – 6.67 (m, 2H), 6.03 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.88 (d, *J* = 15.9 Hz, 1H), 5.09 (s, 2H), 3.39 (s, 3H), 3.24 – 3.21 (m, 1H), 3.21 – 3.14 (m, 1H), 3.09 (s, 3H), 2.70 – 2.64 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 156.8, 145.1, 143.1, 132.0, 131.5, 130.4, 130.0, 129.5, 128.1, 127.5, 127.4, 126.0, 118.9, 116.2, 110.1, 94.3, 55.9, 48.9, 39.8, 37.3. **HRMS (ESI)** calcd for $C_{27}H_{26}N_2O_3$ $[M+H]^+$: 427.2016, found 427.2013.



4f

(*E*)-4-([1,1'-biphenyl]-4-yl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide (4f). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3f** (54.1 mg, 0.3 mmol, 1.5 equiv),

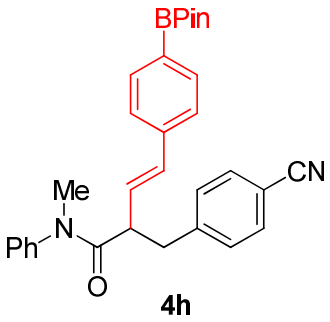
$Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 45% isolated yield (39.8 mg) and *E*/*Z* = 4:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.52 – 7.45 (m, 6H), 7.40 – 7.33 (m, 3H), 7.30 – 7.25 (m, 5H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 2H), 6.20 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 3.32 – 3.17 (m, 2H), 3.10 (s, 3H), 2.69 (dd, *J* = 12.3, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 145.0, 143.1, 140.5, 140.5, 135.5, 132.0, 131.7, 130.0, 129.6, 128.7, 128.1, 127.9, 127.5, 127.3, 127.2, 126.9, 126.7, 118.9, 110.2, 49.0, 39.8, 37.4. **HRMS (ESI)** calcd for $C_{31}H_{26}N_2O$ $[M+H]^+$: 443.2118, found 443.2114.



4g

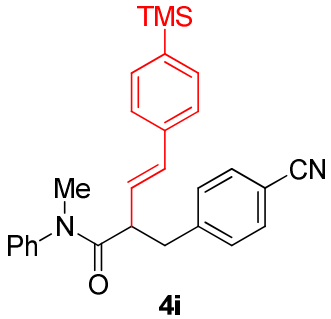
(*E*)-2-(4-cyanobenzyl)-*N*-methyl-4-(naphthalen-2-yl)-*N*-phenylbut-3-enamide (4g). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3g** (46.3 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 48% isolated yield (40.0 mg) and *E*/*Z* = 20:1 as a yellow solid. M.p. 143-144 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.80 – 7.76 (m, 3H), 7.61 (s, 1H), 7.57 – 7.51 (m, 3H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 3H), 7.21 – 7.18 (m, 2H), 6.79 (s, 2H), 6.36 (dd, *J* = 15.9, 8.4 Hz, 1H), 6.19 (d, *J* = 15.9 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.34 – 3.27 (m, 1H), 3.18 (s, 3H), 2.80 (dd, *J* = 12.3, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ

171.9, 145.0, 143.2, 134.0, 133.4, 133.0, 132.2, 132.0, 130.1, 129.6, 128.2, 128.2, 128.1, 127.9, 127.6, 127.5, 126.3, 126.2, 125.9, 123.3, 119.0, 110.2, 49.1, 39.9, 37.4. **HRMS (ESI)** calcd for $C_{29}H_{24}N_2O$ $[M+H]^+$: 417.1961, found 417.1962.



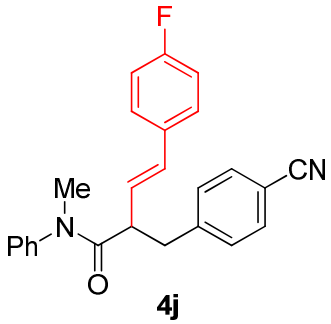
4h

(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-enamide (4h). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3h** (69.0 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 65% isolated yield (64.0 mg) and *E*/*Z* = 12:1 as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.30 – 7.27 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 2H), 6.30 (dd, *J* = 15.9, 8.4 Hz, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 3.39 – 3.31(m, 1H), 3.28 (dd, *J* = 12.3, 9.3 Hz, 1H), 3.17 (s, 3H), 2.76 (dd, *J* = 12.3, 4.8 Hz, 1H), 1.34 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 144.9, 143.1, 139.1, 135.0, 132.2, 132.0, 130.0, 129.6, 128.9, 128.1, 127.5, 125.5, 118.9, 110.2, 83.8, 49.0, 39.7, 37.4, 24.8, 24.8. **HRMS (ESI)** calcd for $C_{31}H_{33}BN_2O_3$ $[M+H]^+$: 493.2657, found 493.2663.



4i

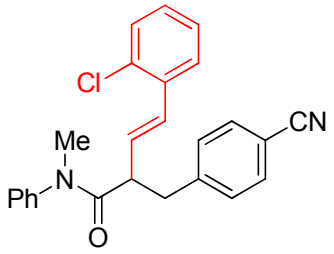
(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenyl-4-(4-(trimethylsilyl)phenyl)but-3-ena mide (4i). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3i** (52.9 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 49% isolated yield (42.9 mg) and *E* only as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.29 – 7.26 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 2H), 6.25 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 3.37 – 3.31 (m, 1H), 3.29 – 3.24 (mz, 1H), 3.17 (s, 3H), 2.76 (dd, *J* = 12.4, 5.6 Hz, 1H), 0.26 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 145.0, 143.1, 140.1, 136.8, 133.5, 132.2, 132.0, 130.0, 129.6, 128.1, 128.0, 127.5, 125.5, 118.9, 110.1, 49.0, 39.7, 37.4, -1.2. **HRMS (ESI)** calcd for $C_{28}H_{30}N_2OSi$ $[M+H]^+$: 439.2200, found 439.2200.



4j

(*E*)-2-(4-cyanobenzyl)-4-(4-fluorophenyl)-*N*-methyl-*N*-phenylbut-3-enamide (4j). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3j** (36.6 mg, 0.3 mmol, 1.5 equiv),

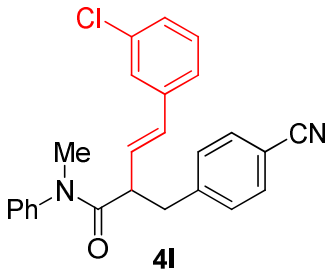
$Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 70% isolated yield (53.8 mg) and *E*/*Z* = 13:1 as a yellow solid. M.p. 121-122 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.54 (m, 2H), 7.37 – 7.34 (m, 3H), 7.28 – 7.24 (m, 2H), 7.19 – 7.17 (m, 2H), 7.01 – 6.96 (m, 2H), 6.79 – 6.74 (m, 2H), 6.15 (dd, *J* = 16.0, 8.4 Hz, 1H), 6.00 (d, *J* = 16.0 Hz, 1H), 3.36 – 3.31 (m, 1H), 3.29 – 3.24 (m, 1H), 3.17 (s, 3H), 2.78 – 2.73 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 162.2 (d, *J* = 247.4 Hz), 144.9, 143.1, 132.6 (d, *J* = 3.0 Hz), 132.0, 130.9, 130.0, 129.6, 128.1, 127.7 (d, *J* = 8.1 Hz), 127.5 (d, *J* = 3.0 Hz), 127.4, 118.9, 115.4 (d, *J* = 21.2 Hz), 110.1, 48.8, 39.7, 37.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ 114.1. **HRMS (ESI)** calcd for $C_{25}H_{21}FN_2O$ $[M+H]^+$: 385.1711, found 385.1709.



4k

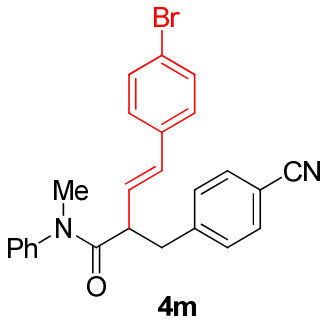
(*E*)-4-(2-chlorophenyl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide (4k). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3k** (41.6 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:3) afforded the title product in 69% isolated yield (55.2 mg) and *E*/*Z* = 3:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.30 – 7.25 (m, 3H), 7.14 – 7.09 (m, 4H), 6.71 (s, 2H), 6.37 (d, *J* = 15.0 Hz, 1H), 6.14 (dd, *J* = 15.0, 9.0 Hz, 1H), 3.37 – 3.29 (m, 1H), 3.24 – 3.16 (m, 1H), 3.09 (s, 3H), 2.70 (dd, *J* = 12.0, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 144.7, 143.0, 134.5, 132.8, 132.0, 130.8, 130.0, 129.7, 129.5, 128.7, 128.5, 128.2, 127.4, 126.8, 126.7, 118.9, 110.2, 49.1, 39.6, 37.3. **HRMS (ESI)** calcd for $C_{25}H_{21}ClN_2O$ $[M+H]^+$: 401.1415, found 401.1409.



4l

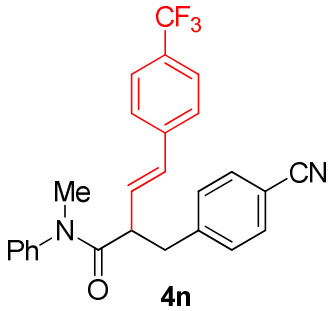
(*E*)-4-(3-chlorophenyl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide (4l). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3l** (41.6 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 70% isolated yield (56.0 mg) and *E* only as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.46 (m, 2H), 7.30 – 7.26 (m, 3H), 7.20 – 7.19 (m, 1H), 7.15 – 7.06 (m, 5H), 6.68 (s, 2H), 6.17 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.91 (d, *J* = 15.9 Hz, 1H), 3.30 – 3.23 (m, 1H), 3.22 – 3.15 (m, 1H), 3.09 (s, 3H), 2.68 (dd, *J* = 12.3, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 144.7, 143.0, 138.3, 134.4, 132.0, 130.8, 130.0, 129.7, 129.6, 129.4, 128.1, 127.6, 127.4, 126.2, 124.4, 118.9, 110.2, 48.8, 39.6, 37.3. **HRMS (ESI)** calcd for $C_{25}H_{21}ClN_2O$ $[M+H]^+$: 401.1415, found 401.1411.



4m

(*E*)-4-(4-bromophenyl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide

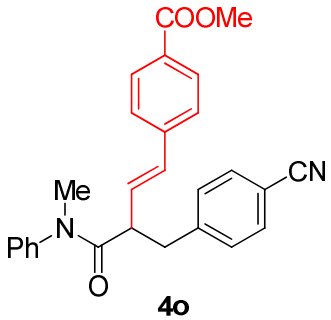
(**4m**). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3m** (54.9 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 75% isolated yield (66.6 mg) and *E*/*Z* = 20:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 – 7.46 (m, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.26 (m, 3H), 7.10 – 7.06 (m, 4H), 6.68 (s, 2H), 6.15 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.89 (d, *J* = 15.9 Hz, 1H), 3.30 – 3.24 (m, 1H), 3.21 – 3.14 (m, 1H), 3.09 (s, 3H), 2.67 (dd, *J* = 12.3, 4.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 144.8, 143.0, 135.4, 132.0, 131.6, 130.9, 130.0, 129.6, 128.6, 128.1, 127.7, 127.4, 121.4, 118.9, 110.2, 48.8, 39.6, 37.4. **HRMS (ESI)** calcd for $C_{25}H_{21}BrN_2O$ $[M+H]^+$: 445.0910, found 445.0906.



4n

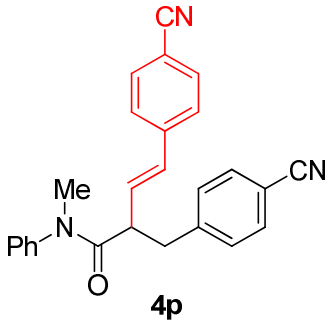
(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en amide (**4n**). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3n** (51.6 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 70% isolated yield (60.8 mg) and *E* only as a yellow solid. M.p. 161-162 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.45 (m, 4H), 7.32 – 7.26 (m, 5H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.69 (s, 2H), 6.27 (dd, *J* = 15.9, 8.4 Hz, 1H), 6.00 (d, *J* =

15.9 Hz, 1H), 3.34 – 3.26 (m, 1H), 3.24 – 3.16 (m, 1H), 3.10 (s, 3H), 2.69 (dd, *J* = 12.6, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 144.6, 143.0, 139.9 (q, *J* = 1.1 Hz), 132.0, 130.8, 130.6, 130.0, 129.7, 129.4 (q, *J* = 32.3 Hz), 128.2, 127.4, 126.4, 125.5 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 271.6 Hz), 118.8, 110.3, 48.8, 39.6, 37.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ 62.5. **HRMS (ESI)** calcd for $C_{26}H_{21}F_3N_2O$ $[M+H]^+$: 435.1679, found 435.1675.



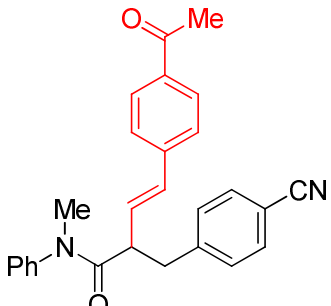
4o

Methyl(*E*)-4-(3-(4-cyanobenzyl)-4-(methyl(phenyl)amino)-4-oxobut-1-en-1-yl)benzoate (4o). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3o** (48.7 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 66% isolated yield (60.0 mg) and *E*/*Z* = 20:1 as a yellow solid. M.p. 138-139 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.88 (m, 2H), 7.49 – 7.47 (m, 2H), 7.30 – 7.26 (m, 5H), 7.11 – 7.09 (m, 2H), 6.68 (s, 2H), 6.29 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.33 – 3.27 (m, 1H), 3.20 (dd, *J* = 12.8, 9.2 Hz, 1H), 3.10 (s, 3H), 2.69 (dd, *J* = 12.8, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 166.7, 144.7, 143.0, 140.9, 132.0, 131.2, 130.6, 130.0, 129.8, 129.6, 129.1, 128.2, 127.4, 126.1, 118.8, 110.2, 52.0, 48.9, 39.6, 37.4. **HRMS (ESI)** calcd for $C_{27}H_{24}N_2O_3$ $[M+H]^+$: 425.1860, found 425.1859.



4p

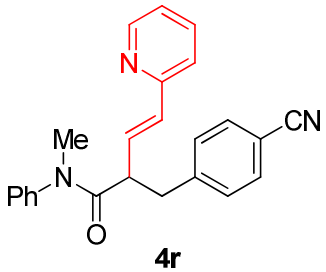
(*E*)-2-(4-cyanobenzyl)-4-(4-cyanophenyl)-*N*-methyl-*N*-phenylbut-3-enamide (4p). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3p** (38.7 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 62% isolated yield (48.5 mg) and *E*/*Z* = 20:1 as a light yellow solid. M.p. 155-157 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.52 – 7.47 (m, 4H), 7.31 – 7.27 (m, 5H), 7.10 – 7.08 (m, 2H), 6.68 (s, 2H), 6.31 (dd, *J* = 15.9, 8.4 Hz, 1H), 6.00 (d, *J* = 15.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 3.24 – 3.16 (m, 1H), 3.10 (s, 3H), 2.69 (dd, *J* = 12.8, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 144.4, 142.9, 140.9, 132.3, 132.0, 131.9, 130.5, 130.0, 129.7, 128.2, 127.3, 126.7, 118.8, 118.8, 110.9, 110.3, 48.8, 39.6, 37.4. **HRMS (ESI)** calcd for $C_{26}H_{21}N_3O$ $[M+H]^+$: 392.1757, found 392.1748.



4q

(*E*)-4-(4-acetylphenyl)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenylbut-3-enamide (4q). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3q** (43.9 mg, 0.3 mmol, 1.5 equiv),

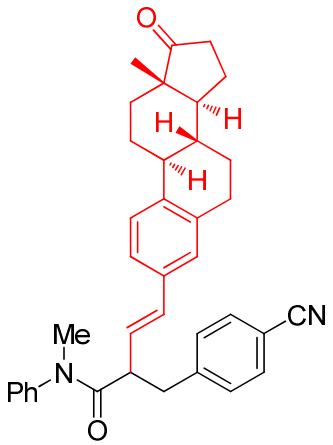
$Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 45% isolated yield (36.7 mg) and *E*/*Z* = 7:1 as a yellow solid. M.p. 144-145 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.84 – 7.81 (m, 2H), 7.50 – 7.47 (m, 2H), 7.31 – 7.27 (m, 5H), 7.10 (d, *J* = 8.1Hz, 2H), 6.68 (s, 2H), 6.30 (dd, *J* = 15.9, 8.4 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 3.34 – 3.27 (m, 1H), 3.21 (dd, *J* = 12.6, 9.3 Hz, 1H), 3.10 (s, 3H), 2.70 (dd, *J* = 12.6, 5.1 Hz, 1H), 2.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.5, 171.4, 144.7, 143.0, 141.1, 136.1, 132.0, 131.1, 130.9, 130.0, 129.7, 128.7, 128.2, 127.4, 126.3, 118.9, 110.3, 48.9, 39.7, 37.4, 26.6. **HRMS (ESI)** calcd for $C_{27}H_{24}N_2O_2$ $[M+H]^+$: 409.1911, found 409.1909.



4r

(*E*)-2-(4-cyanobenzyl)-*N*-methyl-*N*-phenyl-4-(pyridin-2-yl)but-3-enamide (4r). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3r** (31.5 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:2) afforded the title product in 70% isolated yield (51.4 mg) and *E* only as a light yellow solid. M.p. 122-123 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 – 8.44 (m, 1H), 7.58 – 7.53 (m, 1H), 7.49 – 7.46 (m, 2H), 7.28 – 7.24 (m, 3H), 7.23 – 7.20 (m, 1H), 7.12 – 7.10 (m, 2H), 7.08 – 7.05 (m, 1H), 6.66 – 6.60 (m, 3H), 6.19 (d, *J* = 16.0 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.25 – 3.18 (m, 1H), 3.09 (s, 3H), 2.72 (dd, *J* = 12.8, 5.2 Hz, 1H). **^{13}C NMR (101 MHz,**

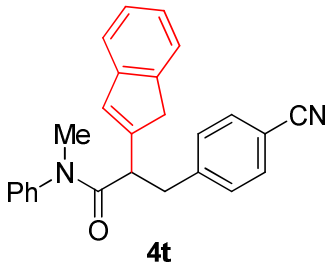
$CDCl_3$) δ 171.3, 154.8, 149.3, 144.8, 143.0, 136.5, 132.5, 132.0, 131.9, 130.0, 129.6, 128.1, 127.3, 122.2, 121.1, 118.9, 110.2, 48.4, 39.5, 37.3. **HRMS (ESI)** calcd for $C_{24}H_{21}N_3O$ $[M+H]^+$: 368.1757, found 368.1757.



4s

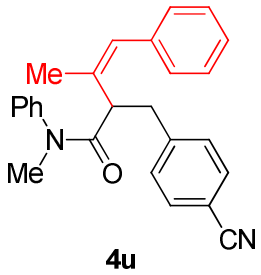
(*E*)-2-(4-cyanobenzyl)-*N*-methyl-4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-*N*-phenylbut-3-enamide (4s). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3s** (84.1 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 61% isolated yield (66.2 mg) and *E*/*Z* > 20:1 as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.19 – 7.15 (m, 1H), 7.11 – 7.08 (m, 2H), 7.03 – 6.98 (m, 2H), 6.70 (s, 2H), 6.11 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.88 (d, *J* = 15.9 Hz, 1H), 3.25 – 3.21 (m, 1H), 3.15 (d, *J* = 9.6 Hz, 1H), 3.09 (s, 3H), 2.82 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.68 (dd, *J* = 12.0, 4.8 Hz, 1H), 2.44 (dd, *J* = 18.3, 8.4 Hz, 1H), 2.25 – 2.21 (m, 1H), 2.14 – 2.04 (m, 1H), 2.03 – 1.88 (m, 3H), 1.77 (s, 1H), 1.59 – 1.33 m, 6H), 0.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 145.0, 143.2, 139.5, 136.6, 134.1, 132.0, 130.0, 129.6, 128.1, 127.5, 127.2, 126.8, 126.7, 125.6, 123.8, 123.8, 119.0, 110.1, 50.4, 49.0, 47.9, 44.4, 39.8, 38.1, 37.3, 35.8, 31.5, 29.3, 26.4,

25.7, 21.5, 13.8. **HRMS (ESI)** calcd for $C_{31}H_{33}BN_2O_3$ $[M+H]^+$: 543.3006, found 543.3001.



4t

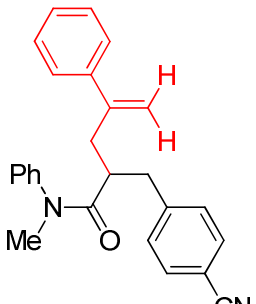
3-(4-Cyanophenyl)-2-(1H-inden-2-yl)-*N*-methyl-*N*-phenylpropanamide (4t). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3t** (34.8 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 28% isolated yield (21.2 mg) as a yellow solid. M.p. 162-163 ℃. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.51 – 7.46 (m, 2H), 7.33 – 7.30 (m, 1H), 7.26 – 7.22 (m, 3H), 7.20 – 7.13 (m, 4H), 7.10 – 7.05 (m, 1H), 6.62 (s, 2H), 6.39 (s, 1H), 3.65 (dd, J = 9.9, 5.1 Hz, 1H), 3.38 – 3.19 (m, 3H), 3.08 (s, 3H), 2.80 (dd, J = 12.9, 5.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 146.2, 145.3, 144.3, 143.2, 143.0, 132.1, 129.9, 129.6, 129.2, 128.1, 127.4, 126.4, 124.5, 123.6, 120.7, 118.9, 110.2, 47.0, 39.7, 39.5, 37.4. **HRMS (ESI)** calcd for $C_{26}H_{22}N_2O$ $[M+H]^+$: 379.1805, found 379.1811.



4u

(*Z*)-2-(4-cyanobenzyl)-*N*,3-dimethyl-*N*,4-diphenylbut-3-enamidee (4u). Following the typical procedure described above, the reaction was carried out by the mixture of **1u**

(78.0 mg, 0.2 mmol, 1.0 equiv), **3u** (35.5 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 20% isolated yield (15.2 mg) and *Z* only as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.48 (m, 2H), 7.10 – 7.02 (m, 8H), 6.56 (s, 2H), 6.48 – 6.46 (m, 2H), 6.24 (s, 1H), 4.02 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.42 (dd, *J* = 13.2, 10.0 Hz, 1H), 3.10 (s, 3H), 2.66 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.01 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.1, 145.6, 142.7, 137.0, 135.8, 131.9, 129.8, 129.5, 128.3, 127.9, 127.8, 127.6, 127.1, 126.2, 119.1, 110.0, 46.3, 38.1, 37.9, 21.1. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O$ $[M+H]^+$: 381.1961, found 381.1955.

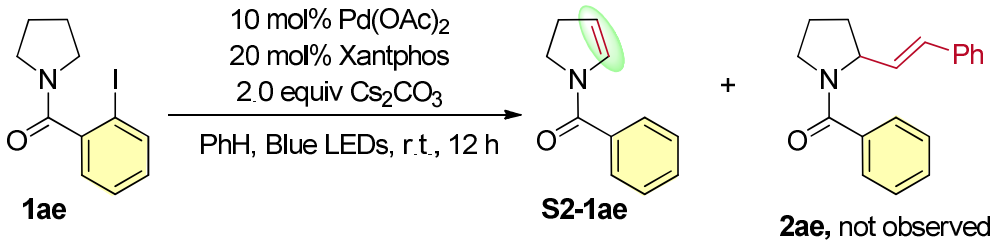


4v

2-(4-Cyanobenzyl)-*N*-methyl-*N*,4-diphenylpent-4-enamide (4v). Following the typical procedure described above, the reaction was carried out by the mixture of **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3v** (35.5 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product in 39% isolated yield (29.7 mg) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.04 (m, 6H), 6.98 – 6.96 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 2H), 5.28 (d, *J* = 1.2 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 3.04 (s, 3H), 2.88 – 2.82 (m, 2H), 2.63 – 2.56 (m, 1H), 2.53 – 2.47 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.7, 145.8, 144.9, 142.9,

139.4, 131.9, 129.8, 129.4, 128.3, 127.6, 127.5, 127.1, 125.9, 119.0, 115.5, 109.9, 43.0, 38.0, 37.8, 37.2. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O$ $[M+H]^+$: 381.1961, found 381.1957.

Reaction of Carboxamide Substrates



(2,3-Dihydro-1*H*-pyrrol-1-yl)(phenyl)methanone (S2-1ae). Following the typical procedure described above, the reaction was carried out by the mixture of **1ae** (60.2 mg, 0.2 mmol, 1.0 equiv), styrene (31.2 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 equiv) in PhH (2.5 mL) at room temperature in nitrogen atmosphere under the irradiation of blue LED lamps for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:2) afforded the title product in 70% isolated yield (24.3 mg) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.50 (m, 2H), 7.47 – 7.39 (m, 3H), 7.11 – 6.45 (m, 1H), 5.39 – 5.18 (m, 1H), 4.06 – 3.80 (m, 2H), 2.74 – 2.69 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 135.8, 130.6, 130.3, 128.4, 127.6, 111.7, 45.6, 28.3. The spectroscopic data match the reported literature.[13]

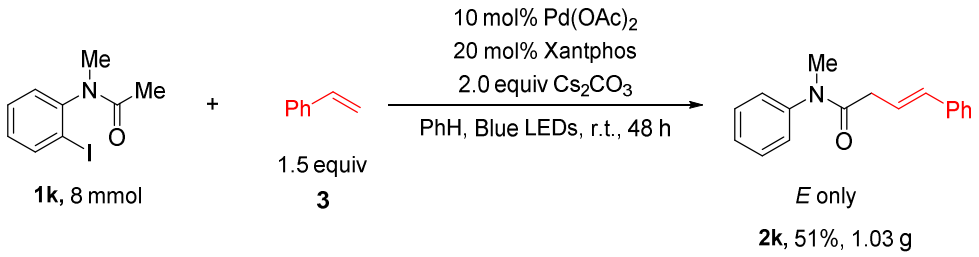
Grams Scale Synthesis

1a, 6 mmol

E/*Z* = 5:1

2a, 72%, 1.33 g

An oven-dried 100 mL reaction flask was charged with *N*-(2-iodophenyl)-*N*-methylhexanamide **1a** (2.0 g, 6. mmol), styrene **3** (937 mg, 9.0 mmol), $Pd(OAc)_2$ (135 mg, 0.6 mmol) and Xantphos (694 mg, 1.2 mmol) and Cs_2CO_3 (3.9 g, 12.0 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 50 mL of degassed benzene (PhH) were added to the flask. The flask was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 48 hours. After completion of the reaction, the resulting mixture was diluted with acetone (60 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 yield the desired product **2a** (1.33 g, 72%).



1k, 8 mmol

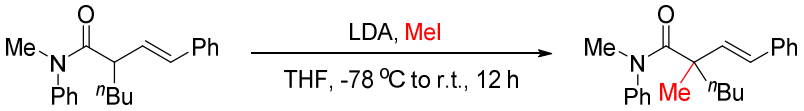
E only

2k, 51%, 1.03 g

An oven-dried 100 mL reaction flask was charged with *N*-(2-iodophenyl)-*N*-methylacetamide **1k** (2.2 g, 8.0 mmol), styrene **3** (1.25 g, 12.0 mmol), $Pd(OAc)_2$ (180 mg, 0.8 mmol) and Xantphos (926 mg, 1.6 mmol) and Cs_2CO_3 (5.21 g, 16.0 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 60 mL of degassed benzene (PhH) were added to the flask. The flask was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 48 hours. After completion of the reaction, the resulting mixture was diluted with acetone (80 mL), filtered (Celite), and concentrated under a reduced

pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) to yield the desired product **2k** (1.03 g, 51%).

Derivatizations of product 2a

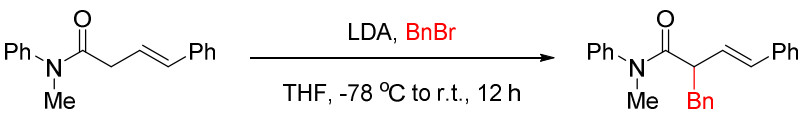


2a, *E*/*Z* = 5:1

E only
5, 72%

To a stirred soln of **2a** (61.4 mg, 0.2 mmol) in THF (1.0 mL) at -78 °C was added LDA (0.13 mL, 0.26 mmol, 1.3 equiv) dropwise, the mixture was stirred at -78 °C for 1 hour. To the resulting solution, MeI (85.2 mg, 0.6 mmol, 3.0 equiv.) in THF (1mL) was added slowly, then it was stirred at room temperature for 12 hours. The resulting solution was quenched with saturated NH_4Cl solution and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and concentration, the crude was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:5), yielding the desired compound **5** as a yellow oil (46.2 mg, 72% yield). **(*E*)-*N*,2-dimethyl-*N*-phenyl-2-styrylhexanamide (5). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 – 7.11 (m, 2H), 7.09 – 7.03 (m, 3H), 7.02 – 6.96 (m, 5H), 5.88 (d, *J* = 20.0, 1H), 5.84 (d, *J* = 20.0, 1H), 3.10 (s, 3H), 1.57 – 1.42 (m, 2H), 1.18 (s, 3H), 1.16 – 1.07 (m, 4H), 0.77 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.3, 144.2, 137.3, 135.5, 128.8, 128.8, 128.3, 127.6, 127.0, 126.8, 126.0, 49.1, 40.8, 40.0, 26.8, 24.4, 23.2, 14.1. **HRMS (ESI)** calcd for $C_{22}H_{27}NO$ $[M+H]^+$: 322.2165, found 322.2164.

Derivatizations of product 2k

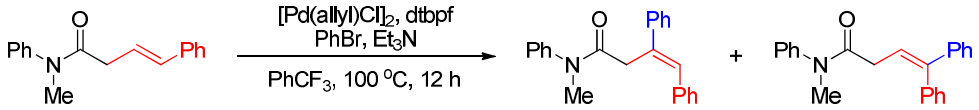


2k, *E* only

6, 64%

To a stirred soln of **2k** (50.2 mg, 0.2 mmol) in THF (1.0 mL) at -78 °C was added

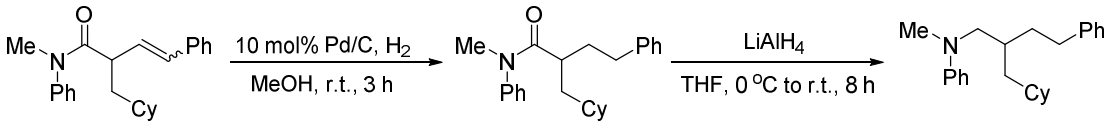
LDA (0.13 mL, 0.26 mmol, 1.3 equiv) dropwise, the mixture was stirred at -78 °C for 1 hour. To the resulting solution, BnBr (120 mg, 0.7 mmol, 3.5 equiv) in THF (1mL) was added slowly, then it was stirred at room temperature for 12 hours. The resulting solution was quenched with saturated NH_4Cl solution and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and concentration, the crude was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:5), yielding the desired compound **6** as a yellow oil (44.0 mg, 64% yield). **(*E*)-2-benzyl-*N*-methyl-*N*,4-diphenylbut-3-enamide (6). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.18 (m, 8H), 7.17 – 7.12 (m, 3H), 7.00 – 6.98 (m, 2H), 6.60 (s, 2H), 6.22 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 3.26 (td, *J* = 8.8, 5.2 Hz, 1H), 3.14 (dd, *J* = 12.8, 9.6 Hz, 1H), 3.08 (s, 3H), 2.62 (dd, *J* = 12.8, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 143.4, 139.3, 136.9, 131.4, 129.4, 129.3, 128.9, 128.5, 128.2, 127.8, 127.6, 127.4, 126.5, 126.3, 49.4, 40.0, 37.3. **HRMS (ESI)** calcd for $C_{24}H_{23}NO$ $[M+H]^+$: 342.1852, found 342.1860.



The mixture of **2k** (50.2 mg, 0.2 mmol, 1.0 equiv), PhBr (47.1 mg, 0.3 mmol, 1.5 equiv), $[Pd(allyl)Cl]_2$ (7.2 mg, 0.02 mmol, 10 mol%), dtbpf (1,1'-bis(di-*tert*-butylphosphino)ferrocene) (18.9 mg, 0.04 mmol, 20 mol%) and Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv) in $PhCF_3$ (2.0 mL) was stirred at 100 ℃ for 12 hours. Column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) afforded the title product **7** in 30% isolated yield (19.6 mg) as a colorless oil and **8** in 41% isolated yield (26.8 mg) as a colorless oil. **(*E*)-*N*-methyl-*N*,3,4-triphenylbut-3-enamide (7). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.25 (m, 10H), 7.23 – 7.18 (m, 3H), 7.03 – 7.01 (m, 2H), 6.85 (s, 1H), 3.38 (s, 2H), 3.17 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.71, 143.84, 142.30, 137.71, 136.29, 131.04, 129.79, 128.68, 128.33, 128.23, 127.82, 127.31, 127.28, 126.92, 126.34, 37.49, 36.69. **HRMS (ESI)** calcd for $C_{23}H_{21}NO$

[M+H]$^+$: 328.1696, found 328.1693. ***N*-methyl-*N*,4,4-triphenylbut-3-enamide (8)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 – 7.11 (m, 11H), 6.96 – 6.91 (m, 4H), 6.16 (t, *J* = 7.2 Hz, 1H), 3.19 (s, 3H), 2.88 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 143.8, 143.7, 142.1, 139.3, 129.6, 128.4, 128.0, 128.0, 127.6, 127.4, 127.1, 127.1, 127.0, 122.3, 37.4, 35.4. **HRMS (ESI)** calcd for $C_{23}H_{21}NO$ [M+H]$^+$: 328.1696, found 328.1695.

Derivatizations of product 2i



2i, *E*/*Z* = 2:1 **11**, 96% **12**, 89%

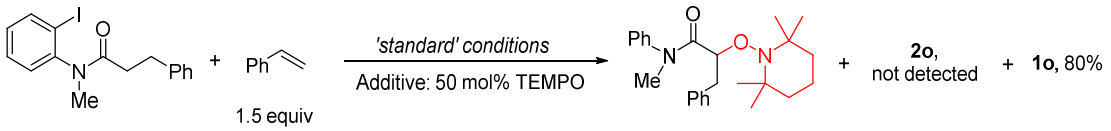
To a solution of **2i** (100 mg, 0.21 mmol, 1.0 equiv.) in MeOH (5 mL, 0.042 M) was added Palladium on carbon (20.0 mg, 5 wt. % loading). After gas exchanged using hydrogen balloon for 10 minutes, the reaction mixture was stirred under hydrogen atmosphere at room temperature for 3 h. Upon completion, the reaction was filtered through a pad of celite. The mixture was concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5) to afford the desired compound **11** as a colorless oil (96.0 mg, 96% yield). **2-(Cyclohexylmethyl) -*N*-methyl-*N*,4-diphenylbutanamide (11). ^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.29 – 7.21 (m, 3H), 7.18 – 7.12 (m, 2H), 7.10 – 7.07 (m, 1H), 7.03 – 6.97 (m, 4H), 3.20 (s, 3H), 2.47 – 2.37 (m, 3H), 1.62 – 1.77 (m, 1H), 1.64 – 1.43 (m, 5H), 1.35 – 0.98 (m, 7H), 0.65 – 0.50 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.2, 143.8, 141.9, 129.4, 128.2, 128.2, 127.5, 127.5, 125.6, 40.5, 38.7, 37.4, 35.2, 34.5, 33.6, 33.5, 33.2, 26.4, 26.1. **HRMS (ESI)** calcd for $C_{24}H_{31}NO$ [M+H]$^+$: 350.2478, found 350.2477.

To a solution of **11** (80.8 mg, 0.17 mmol, 1. equiv.) in THF (2 ml, 0.085 M) was added $LiAlH_4$ (25.8 mg, 0.68 mmol, 4.0 equiv.). The reaction mixture was stirred under hydrogen atmosphere at room temperature for 8 h. Upon completion, the reaction was poured into H_2O (5 mL) and the mixture was extracted with EtOAc (3 × 5 mL). The

organics were washed with H_2O and dried over Na_2SO_4. After solvent removal, the crude was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10), yielding the desired compound **12** as a colorless oil (69.0 mg, 89% yield). ***N*-(2-(cyclohexylmethyl)-4-phenylbutyl)-*N*-methylaniline (12). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.19 – 7.10 (m, 4H), 7.09 – 7.03 (m, 3H), 6.61 – 6.57 (m, 3H), 3.10 (d, *J* = 7.2 Hz, 2H), 2.80 (s, 3H), 2.59 – 2.47 (m, 2H), 1.92 – 1.82 (m, 1H), 1.64 – 1.45 (m, 7H), 1.21 – 1.03 (m, 6H), 0.85 – 0.70 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9, 142.7, 129.0, 128.3, 128.3, 125.6, 115.8, 112.1, 58.0, 40.3, 39.2, 35.0, 34.2, 34.1, 33.5, 33.2, 32.8, 26.6, 26.4, 26.3. **HRMS (ESI)** calcd for $C_{24}H_{33}N$ $[M+H]^+$: 336.2686, found 336.2691.

Experimental Procedures for the Mechanistic Studies

The Radical Trapping Experiment with TEMPO



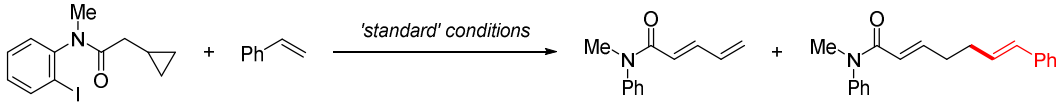
1o **3** **13**, 19%

An oven-dried 4.0 mL vial was charged with *N*-(2-iodophenyl)-*N*-methyl-3-phenylpropanamide **1o** (73.0 mg, 0.2 mmol), styrene (31.3 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Xantphos (23.1 mg, 0.04 mmol), TEMPO (15.6 mg, 0.1 mmol) and Cs_2CO_3 (65.2 mg, 0.4 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2.5 mL of degassed benzene (PhH) 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 12 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 yield the radical trapping product **13** (15.0 mg, 19%) as a colorless oil. ***N*-methyl-*N*,**

3-diphenyl-2-((2,2,6,6-tetra-methylpiperidin-1-yl)oxy) propanamide (13). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.03 (m, 10H), 4.38 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.12 – 3.06 (m, 4H), 2.90 (dd, *J* = 12.4, 4.4 Hz, 1H), 1.58 – 1.43 (m, 3H), 1.35 – 1.26 (m, 3H), 1.18 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 0.67 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 143.1, 136.6, 130.0, 128.7, 128.2, 128.2, 127.3, 126.4, 80.1, 60.7, 59.2, 40.7, 40.1, 38.1, 37.3, 32.8, 32.4, 20.3, 20.0, 17.1. **HRMS (ESI)** calcd for $C_{25}H_{34}N_2O_2$ $[M+H]^+$: 395.2693, found 395.2700.

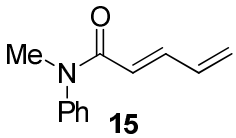
Note: No desired product **2o** was observed, and 80% of the starting material **1o** was recovered.

Radical Clock Experiment with amide 14



14 **3** **15**, 13% **16**, 10%

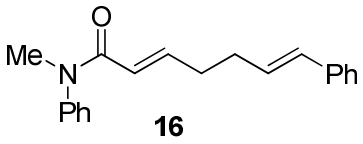
An oven-dried 4.0 mL vial was charged with 2-cyclopropyl-*N*-(2-iodophenyl)-*N*-methylacetamide **14** (63.0 mg, 0.2 mmol), styrene **3** (31.3 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Xantphos (11.6 mg, 0.04 mmol) and Cs_2CO_3 (65.2 mg, 0.4 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2.5 mL of degassed benzene (PhH) 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 12 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 yield both the ring-opened dienamide **15** and further relay alkyl heck product **16**.



15

(*E*)-*N*-methyl-*N*-phenylpenta-2,4-dienamide (15). 15 was isolated in 13% yield as a

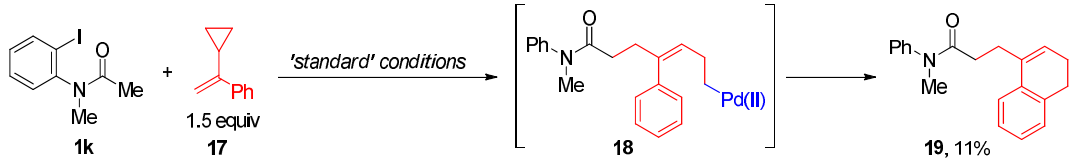
yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.40 (m, 2H), 7.37 – 7.32 (m, 1H), 7.30 – 7.24 (m, 1H), 7.20 – 7.17 (m, 2H), 6.26 (dt, *J* = 16.8, 10.4 Hz, 1H), 5.84 (d, *J* = 15.2 Hz, 1H), 5.53 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.35 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.36 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.1, 143.6, 142.0, 135.1, 129.6, 127.5, 127.3, 124.1, 122.6, 37.5. The spectroscopic data match the reported literature.[12]



16

(2*E*,6*E*)-*N*-methyl-*N*,7-diphenylhepta-2,6-dienamide (16). 16 was isolated in 10% yield as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.23 (m, 4H), 7.23 – 7.22 (m, 3H), 7.15 – 7.12 (m, 1H), 7.08 – 7.06 (m, 2H), 6.90 – 6.83 (m, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 15.6 Hz, 1H), 5.70 (d, *J* = 15.2 Hz, 1H), 3.26 (s, 3H), 2.21 – 2.16 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 144.7, 143.7, 137.5, 130.6, 129.5, 129.2, 128.5, 127.4, 127.3, 127.0, 126.0, 122.1, 37.4, 32.0, 31.6. **HRMS (ESI)** calcd for $C_{20}H_{21}NO$ $[M+H]^+$: 292.1696, found 292.1693.

Radical Clock Experiment with vinyl arene 17

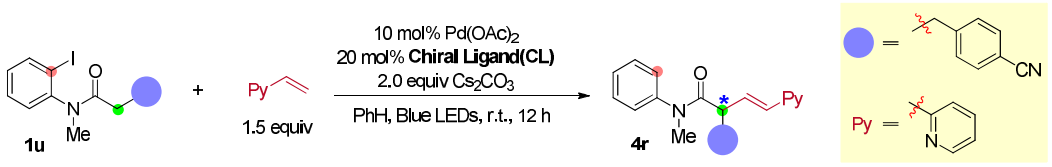


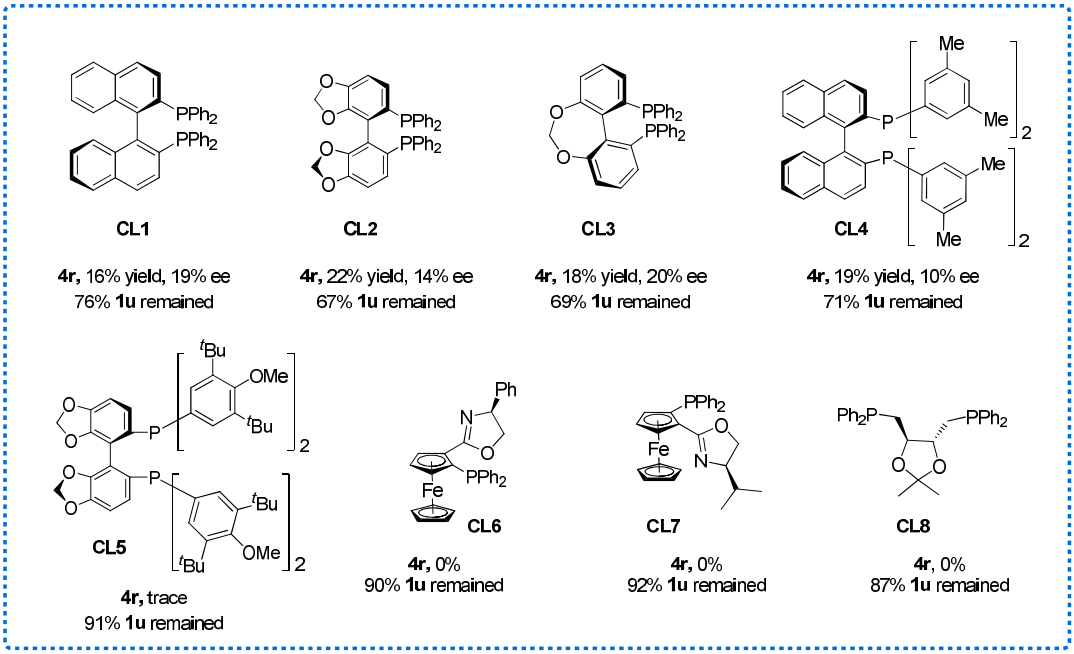
An oven-dried 4.0 mL vial was charged with amide **1k** (78.0 mg, 0.2 mmol), alkene **17** (43.2 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and Xantphos (23.1 mg, 0.04 mmol) and Cs_2CO_3 (130.3 mg, 0.4 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2.5 mL of degassed benzene (PhH) 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 12 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 (DCM) to yield the ring closing

product **19** (6.5 mg, 11%) as a colorless oil. **3-(3,4-Dihydronaphthalen-1-yl)-*N*-methyl-*N*-phenylpropanamide (19)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.29 (m, 3H), 7.15 – 7.04 (m, 5H), 6.94 (d, *J* = 6.8 Hz, 1H), 5.77 – 5.75 (m, 1H), 3.28 (s, 3H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.32 – 2.28 (m, 2H), 2.20 – 2.15 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 144.0, 136.5, 135.3, 134.3, 129.7, 127.7, 127.5, 127.3, 126.6, 126.3, 125.5, 122.4, 37.4, 33.5, 28.9, 28.2, 23.0. **HRMS (ESI)** calcd for $C_{20}H_{21}NO$ $[M+H]^+$: 292.1696, found 292.1691.

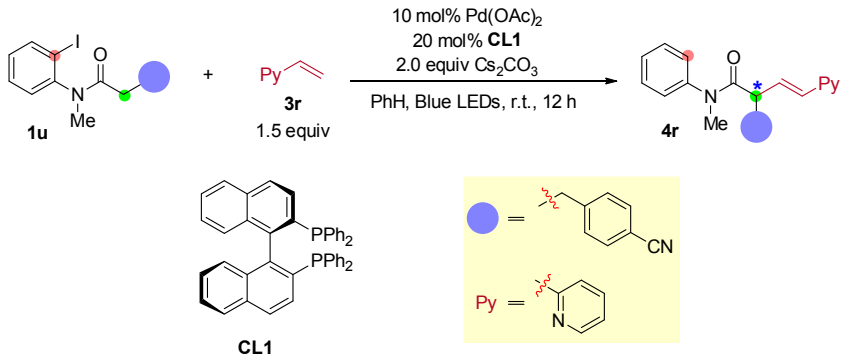
Investigation of Enantioselective Radical Relay Heck Reaction (1u to 4r)

Enantioselective aryl-to-alkyl radical relay Heck reaction was attempted using chiral ligands illustrated below. The reaction of amide 1u with 2-vinyl pyridine was employed as the model reaction due to its good yields and high trans/cis selectivity. After some chiral ligands screening, when BINAP-Type chiral ligands (**CL1-4**) were employed as the ligands (instead of Xantphos), 16-22% yield of the desired product 4r was obtained with some extent of enantio-control (from 10% to 20% ee). Other chiral ligands (**CL4-8**) all gave sluggish results.





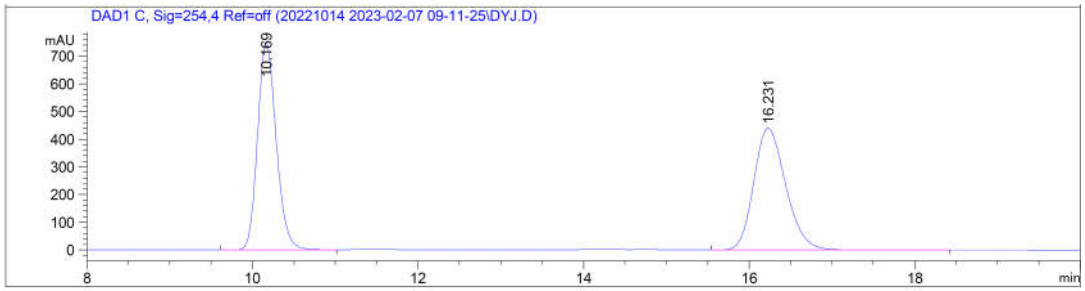
Typical procedure for the enantioselective Radical Relay Heck Reaction



An oven-dried 4.0 mL vial was charged with amide **1u** (78.0 mg, 0.2 mmol, 1.0 equiv), **3r** (31.5 mg, 0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **CL1** (24.9 mg, 0.04 mmol) and Cs_2CO_3 (130.3 mg, 0.4 mmol). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2.5 mL of degassed benzene (PhH) 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 12 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 = 1:2) to afford **4r** (11.8 mg, 16% yield with 19% ee) as a yellow solid and recover the **1u** (59.3 mg, 76%).

Chiral HPLC (Daicel CHIRALDICEL® AD-H column, 30% *i*-PrOH in *n*-hexane, flow rate = 1.0 mL/min, λ = 254 nm), t_{major} = 10.2 min, t_{minor} = 16.2 min.

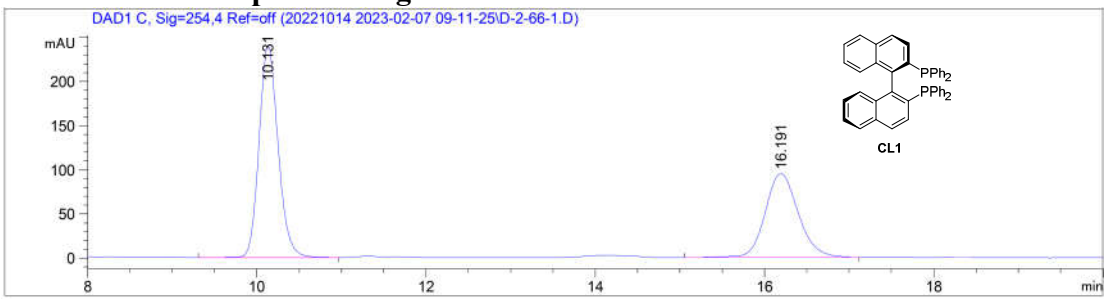
Racemic sample 4r



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.169	BB	0.2407	1.17089e4	747.88190	49.7960
2	16.231	BB	0.4155	1.18049e4	439.30399	50.2040

Peak	Rettime[min]	Type	Width[min]	Area[mAu*]	Height[mAu]	Area[%]
1	10.169	BB	0.2407	1.17089e4	747.88190	49.7960
2	16.231	BB	0.4155	1.18049e4	439.30399	50.2040

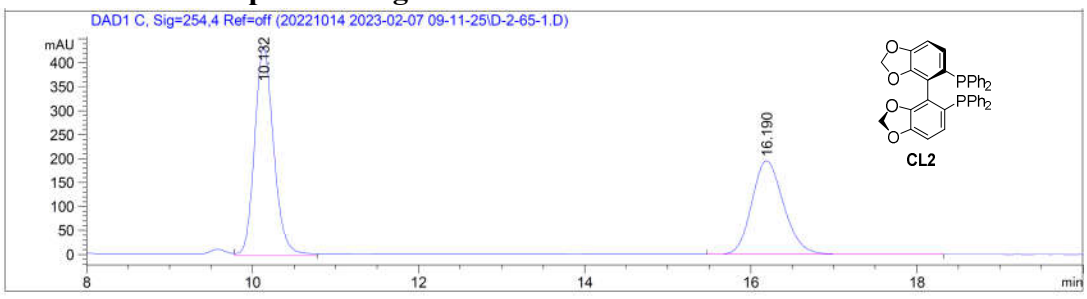
Enantiomeric sample 4r using CL1



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.131	BB	0.2405	3750.53467	239.78331	59.3002
2	16.191	BB	0.4185	2574.12671	94.89928	40.6998

Peak	Rettime[min]	Type	Width[min]	Area[mAu*]	Height[mAu]	Area[%]
1	10.131	BB	0.2405	3750.53467	239.78331	59.3002
2	16.191	BB	0.4185	2574.12671	94.89928	40.6998

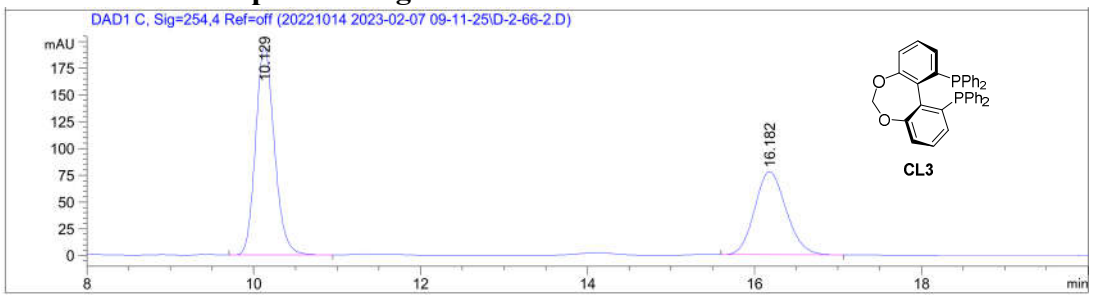
Enantiomeric sample 4r using CL2



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.132	MM	0.2675	6989.75830	435.58020	57.2619
2	16.190	BB	0.4114	5216.88086	195.45383	42.7381

Peak	Rettime[min]	Type	Width[min]	Area[mAu*]	Height[mAu]	Area[%]
1	10.132	MM	0.2675	6989.75830	435.58020	57.2619
2	16.190	BB	0.4114	5216.88086	195.45383	42.7381

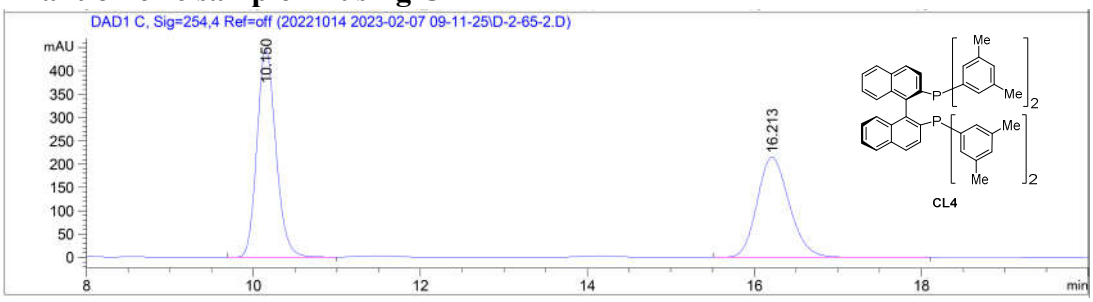
Enantiomeric sample 4r using CL3



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.129	BB	0.2408	3054.07446	194.91895	60.0274
2	16.182	BB	0.4057	2033.72693	77.60232	39.9726

Peak	Rettime[min]	Type	Width[min]	Area[mAu*]	Height[mAu]	Area[%]
1	10.129	BB	0.2408	3054.07446	194.91895	60.0274
2	16.182	BB	0.4057	2033.72693	77.60232	39.9726

Enantiomeric sample 4r using CL4



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.150	BB	0.2430	7016.37012	447.30029	54.9824
2	16.213	BB	0.4139	5744.74805	214.85043	45.0176

Peak	Rettime[min]	Type	Width[min]	Area[mAu*]	Height[mAu]	Area[%]
1	10.150	BB	0.2430	7016.37012	447.30029	54.9824
2	16.213	BB	0.4139	5744.74805	214.85043	45.0176

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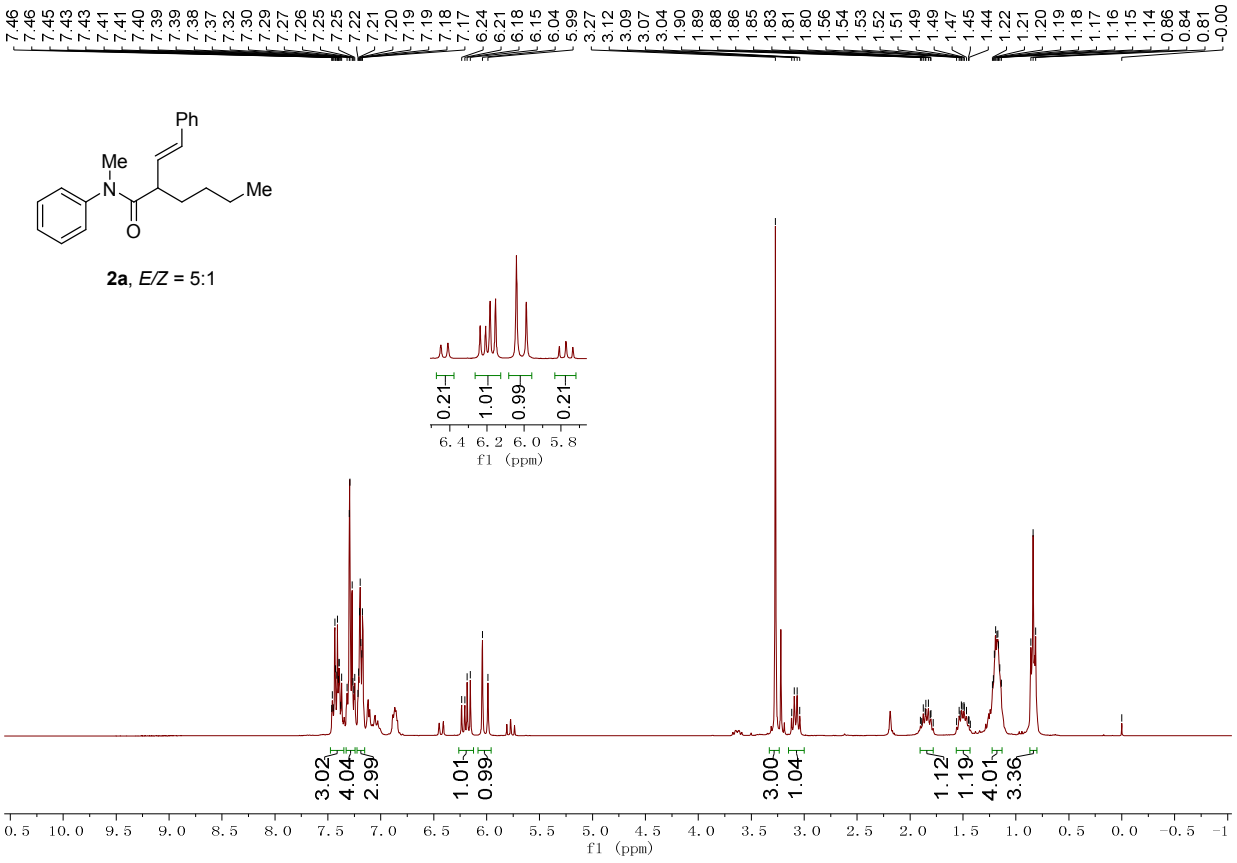
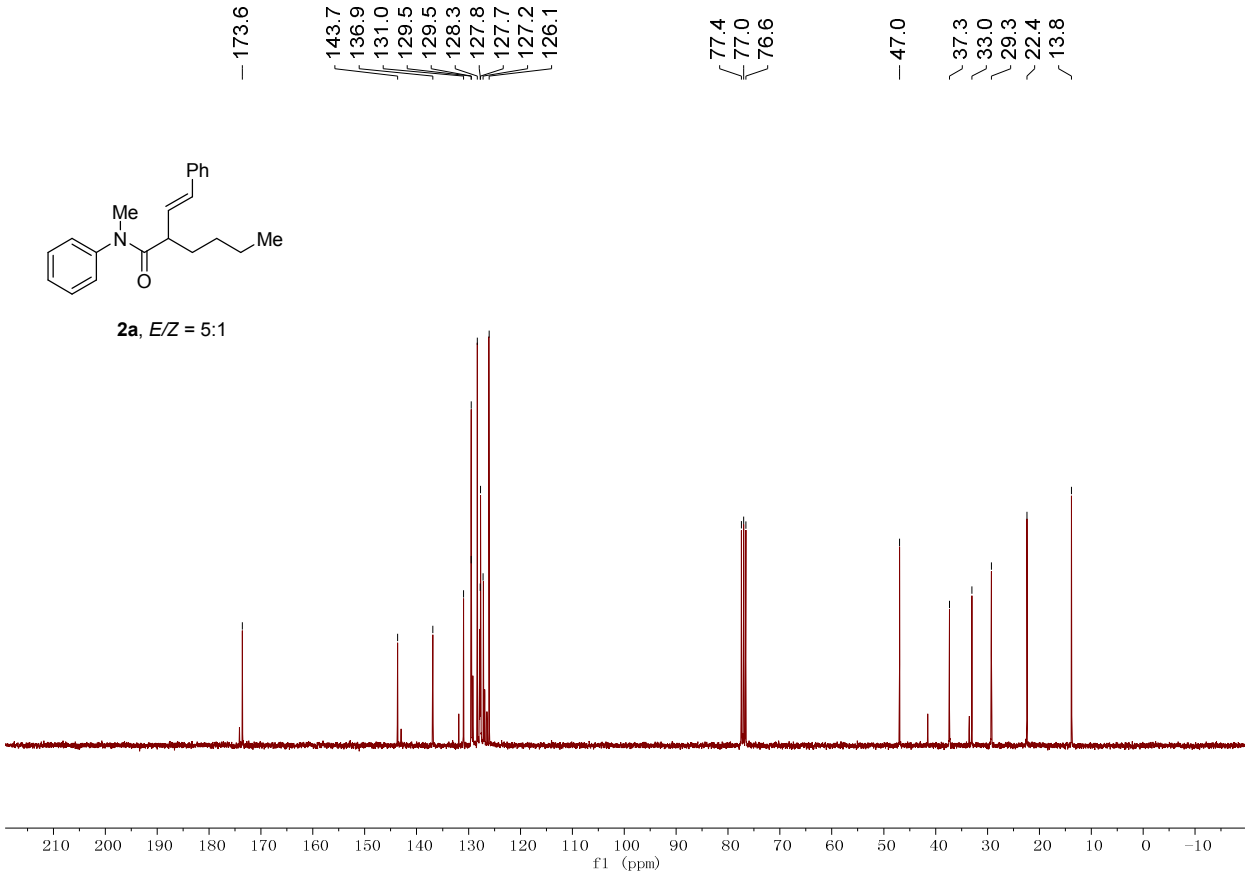
NMR Spectra

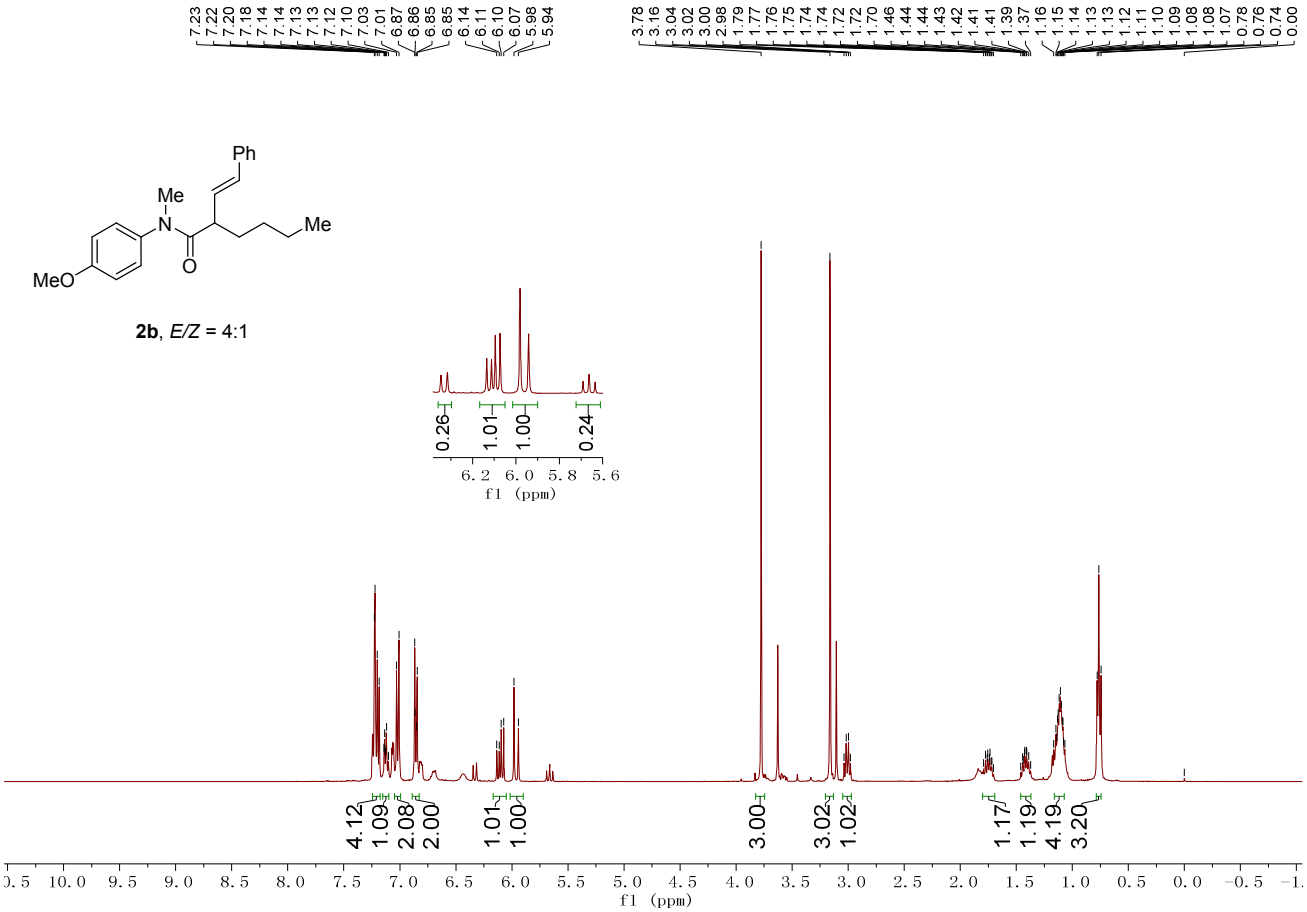
^{1}H NMR (300 MHz, $CDCl_3$)



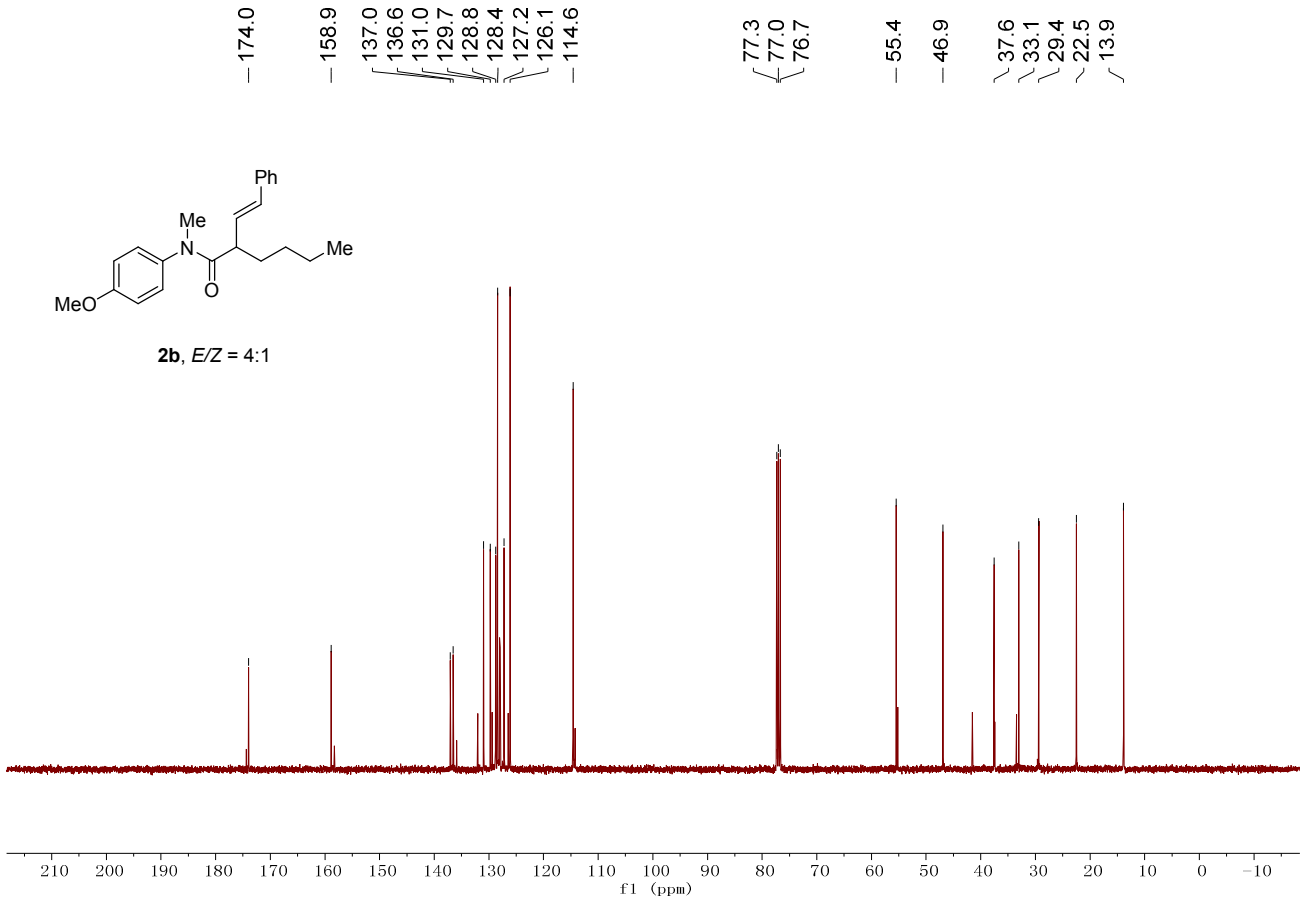
^{13}C NMR (75 MHz, $CDCl_3$)



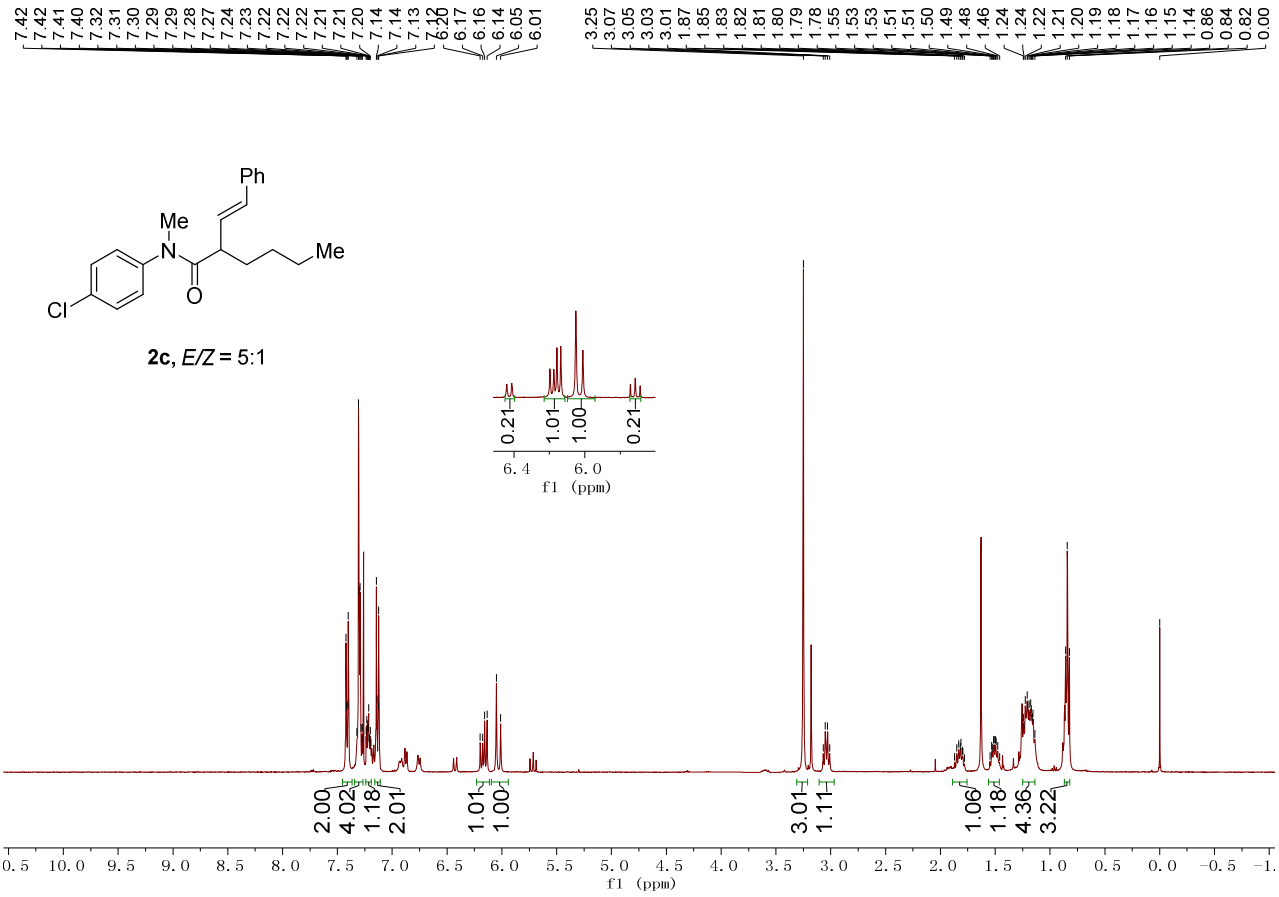
^{1}H NMR (400 MHz, $CDCl_3$)



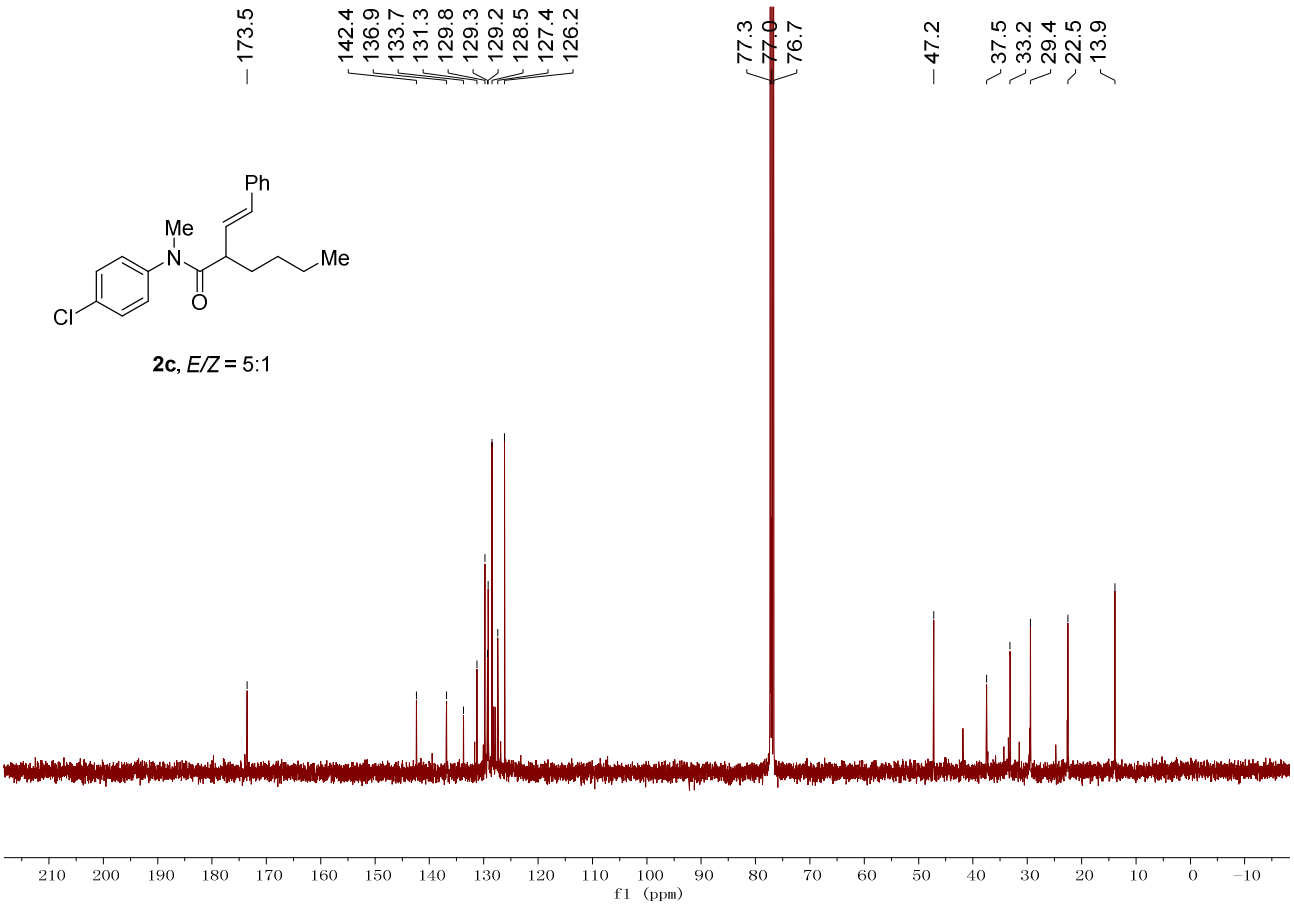
^{13}C NMR (101 MHz, $CDCl_3$)



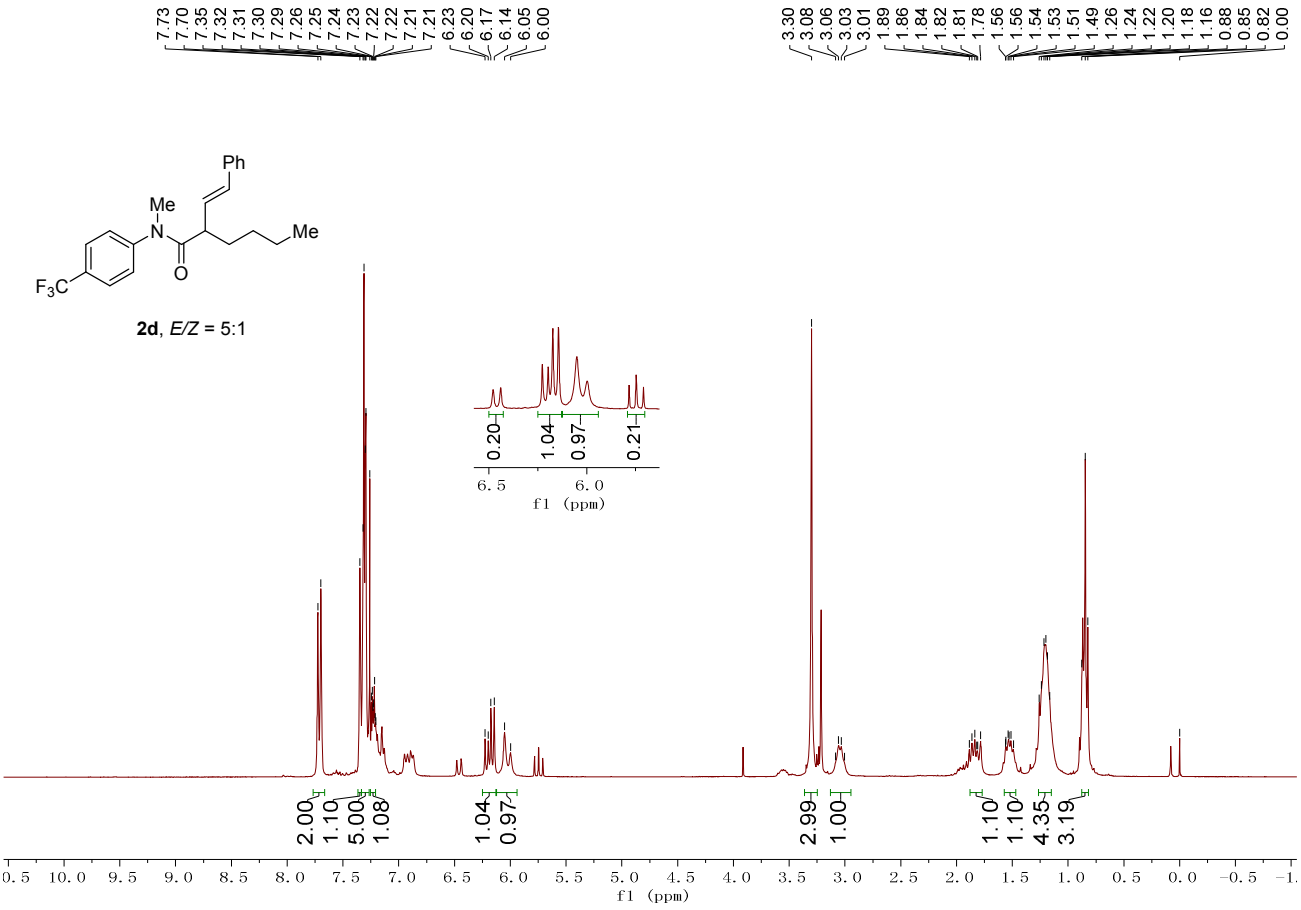
^{1}H NMR (400 MHz, $CDCl_3$)



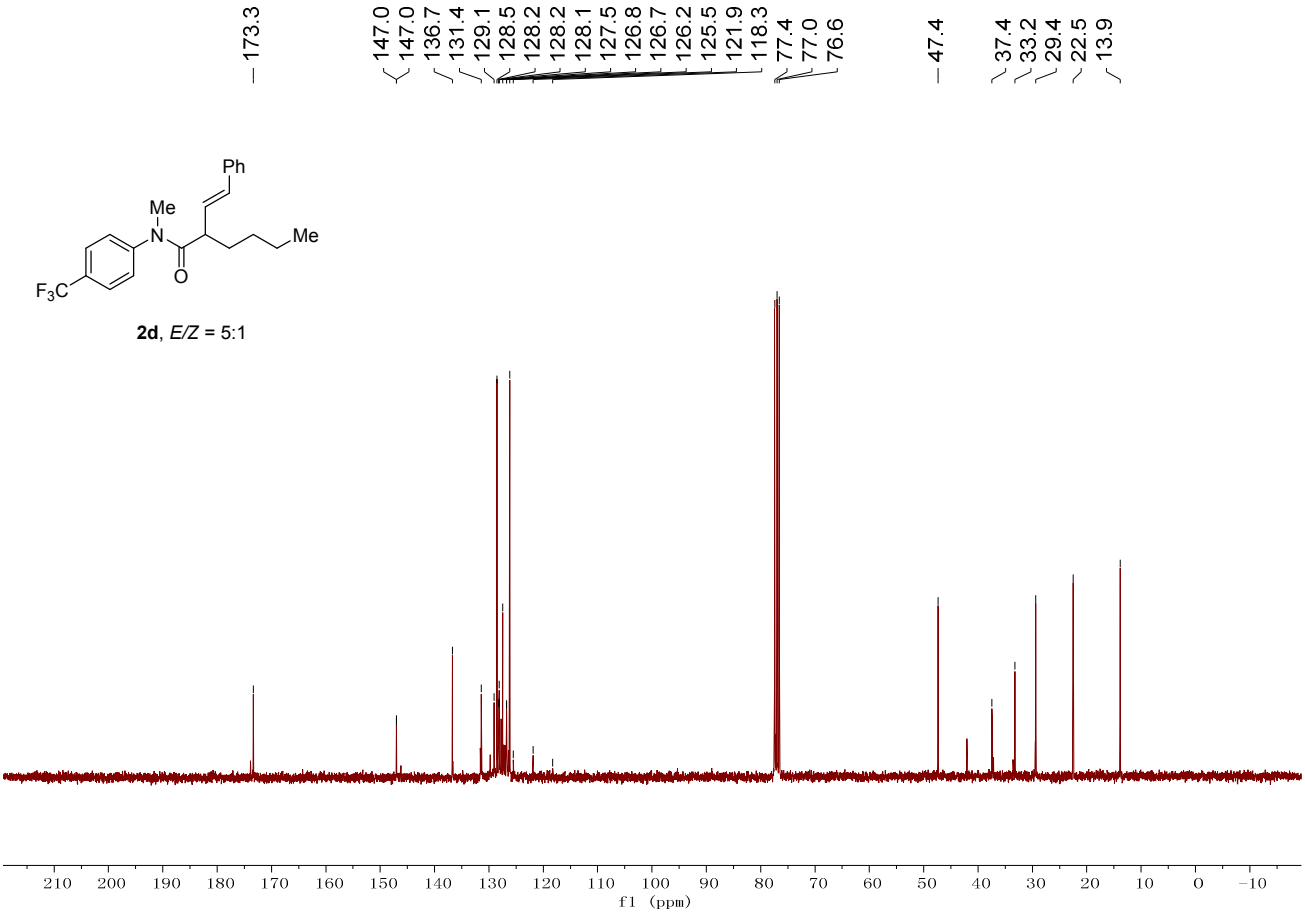
^{13}C NMR (101 MHz, $CDCl_3$)



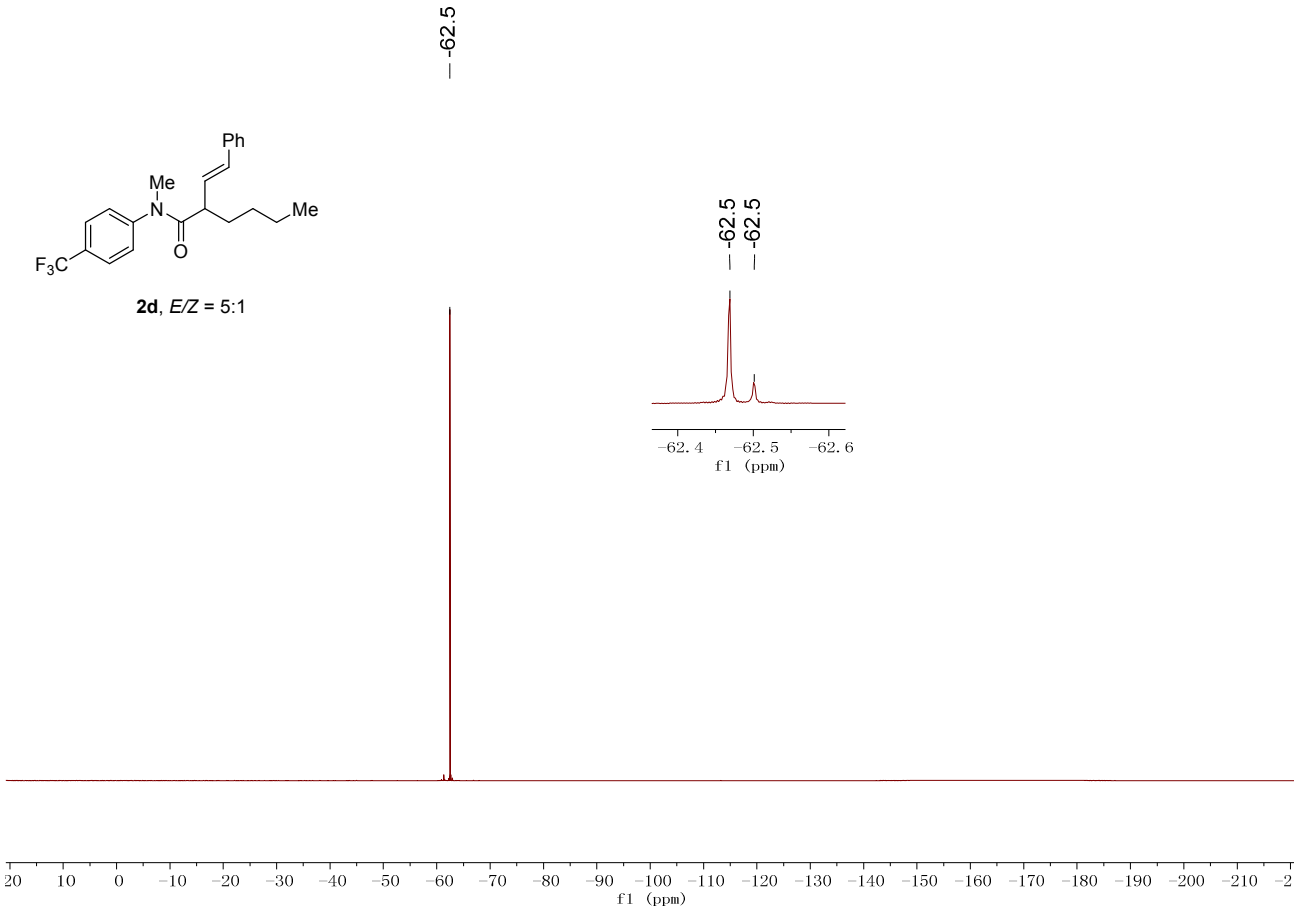
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

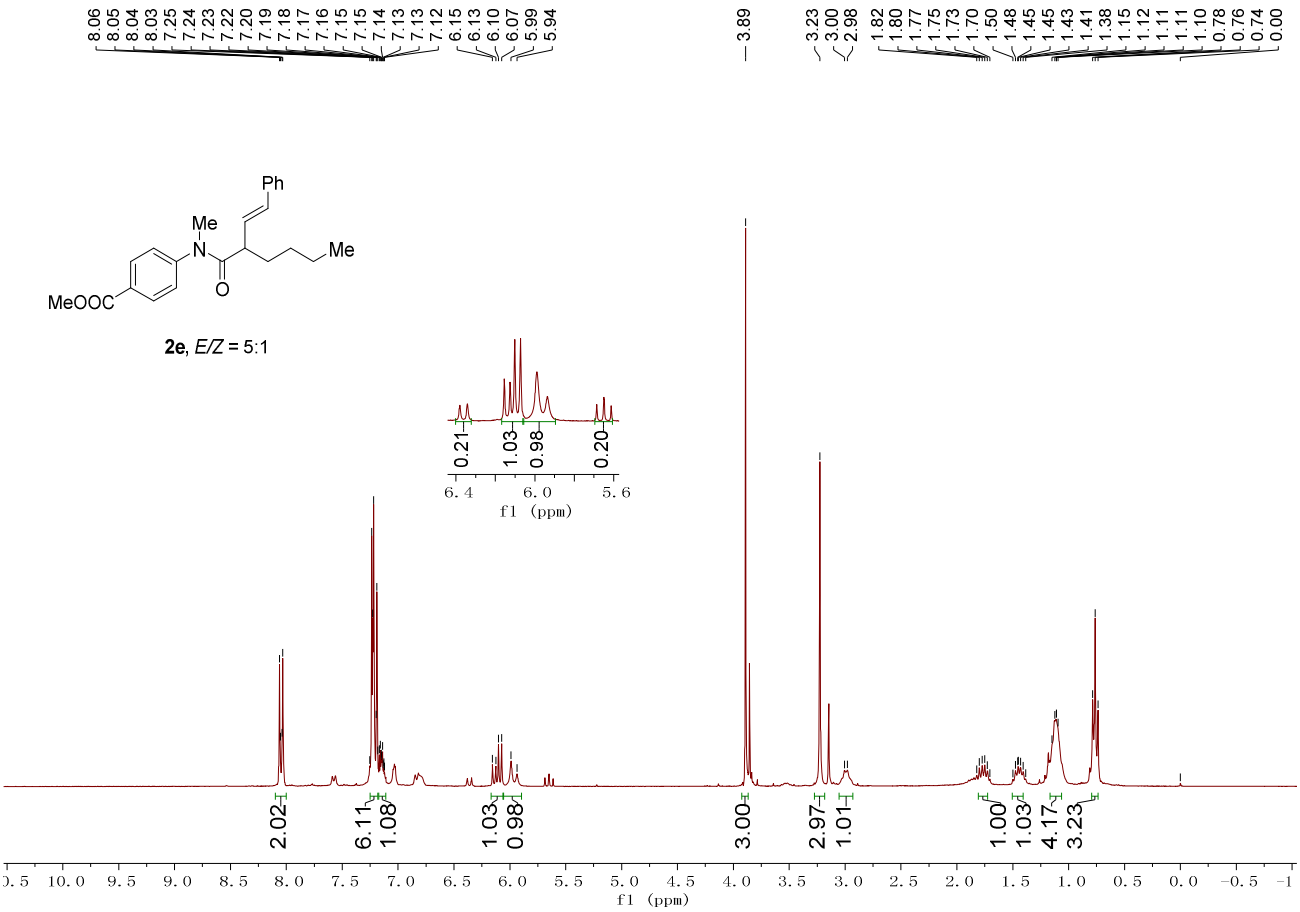


^{19}F NMR (376 MHz, $CDCl_3$)



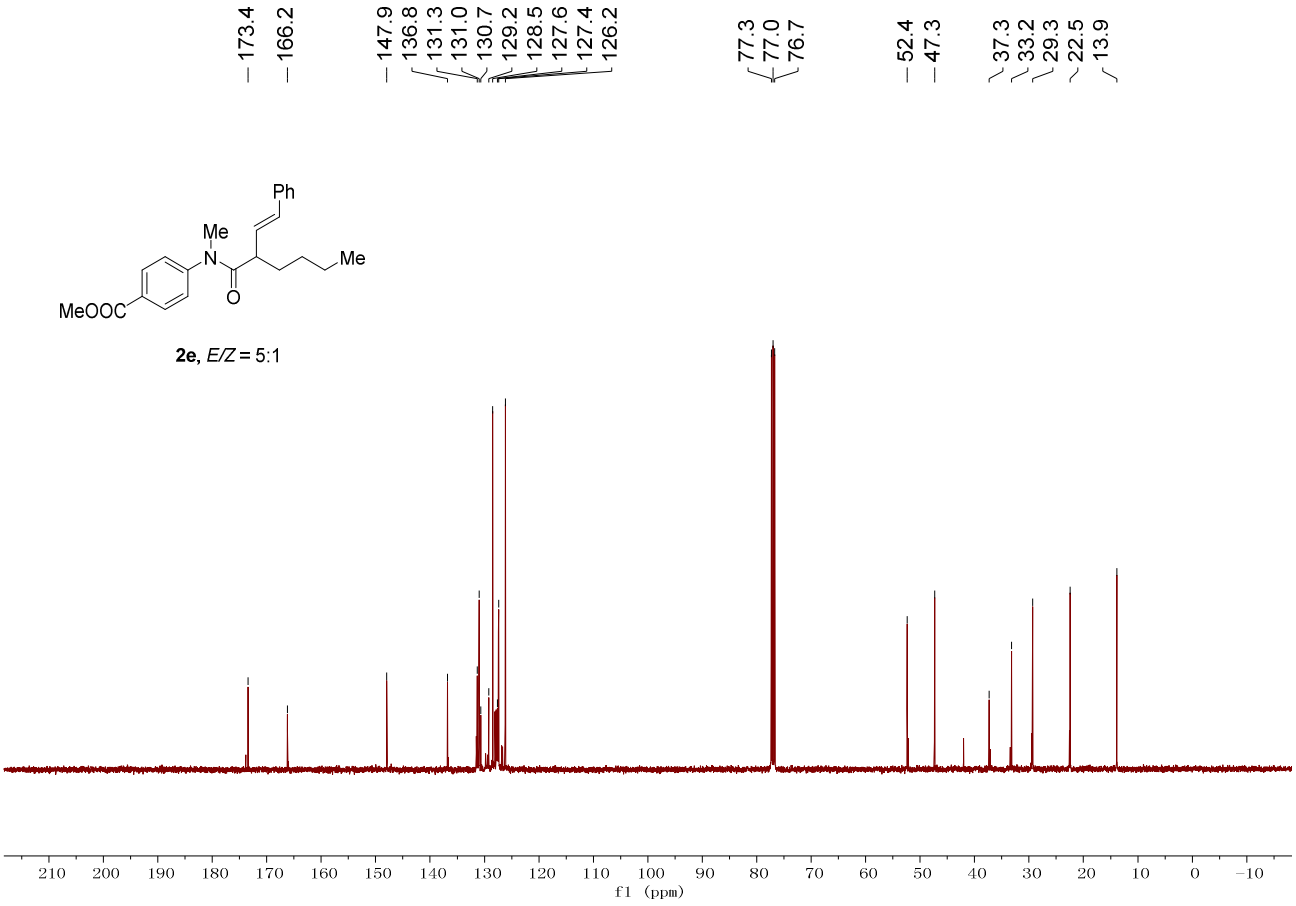
2d, *E/Z* = 5:1

^{1}H NMR (300 MHz, $CDCl_3$)



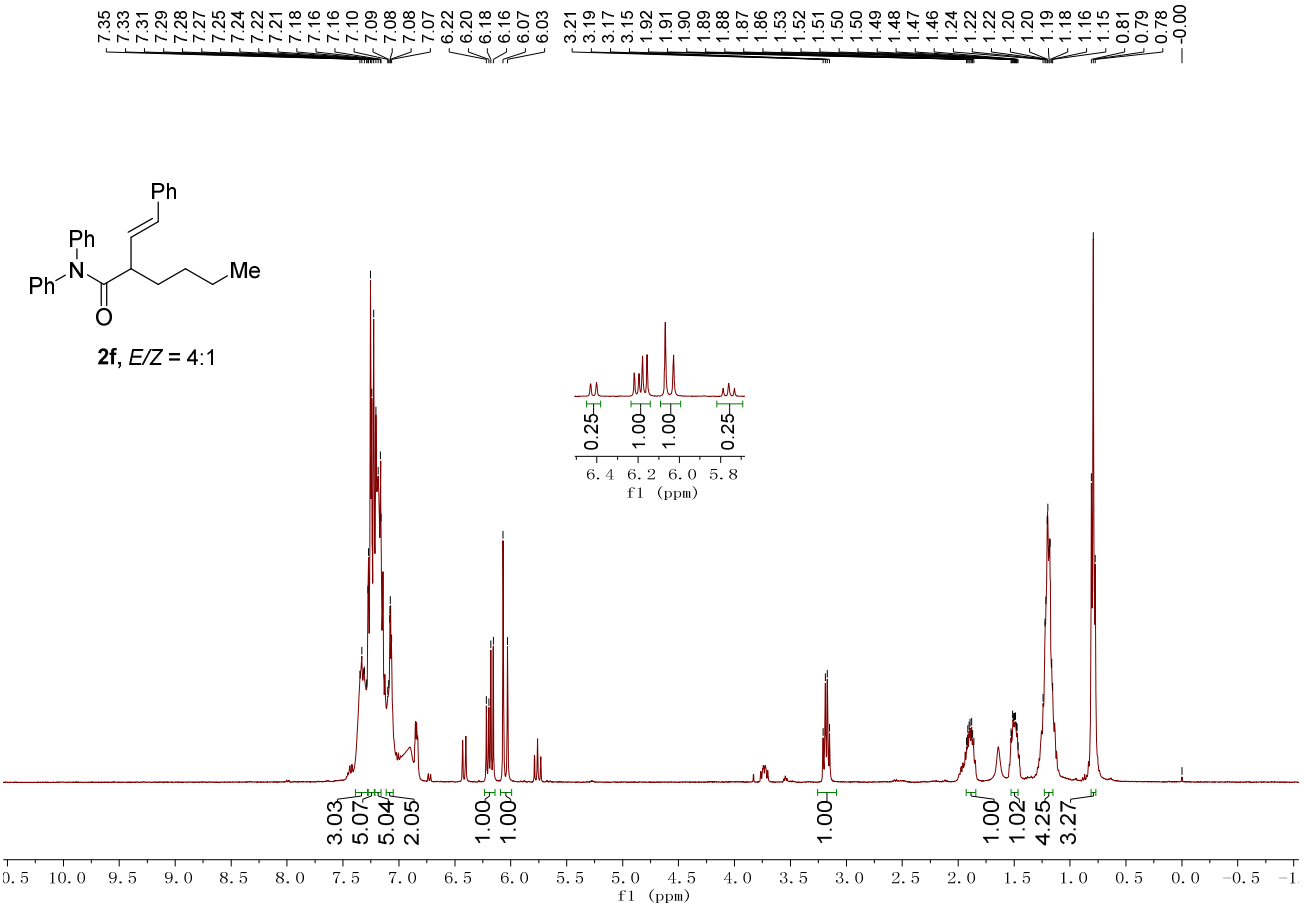
2e, *E/Z* = 5:1

^{13}C NMR (101 MHz, CDCl3)



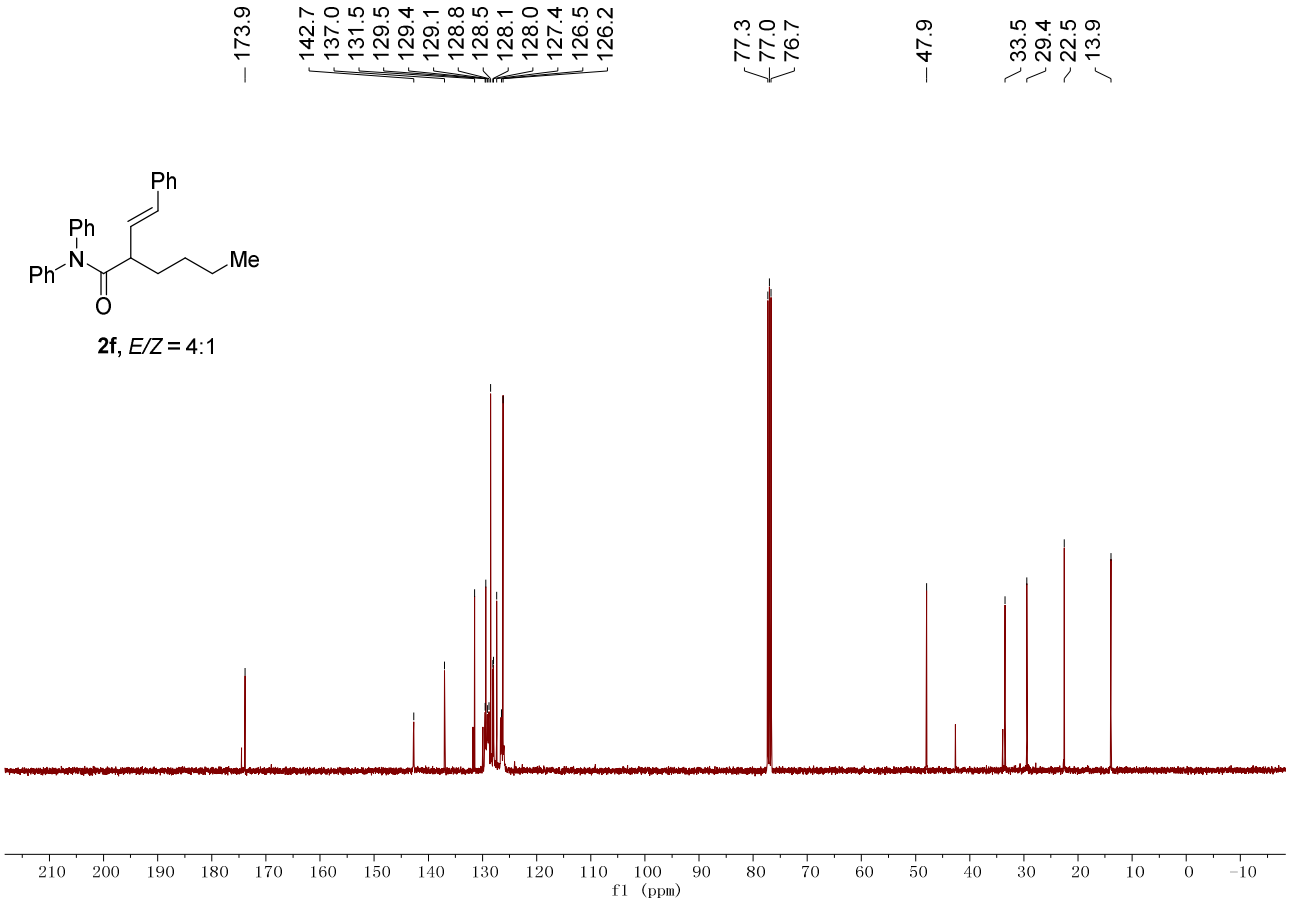
2e, *E*/*Z* = 5:1

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



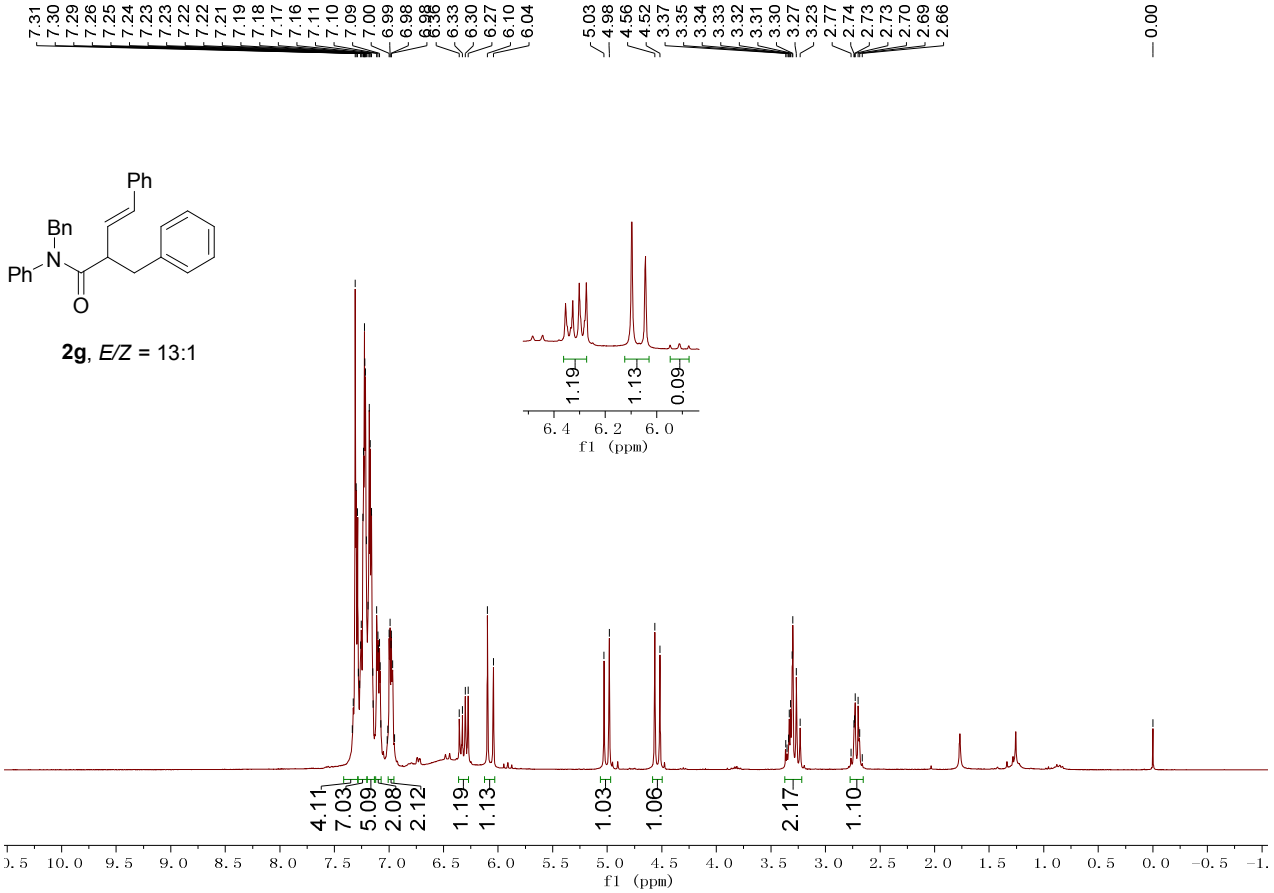
2f, *E*/*Z* = 4:1

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



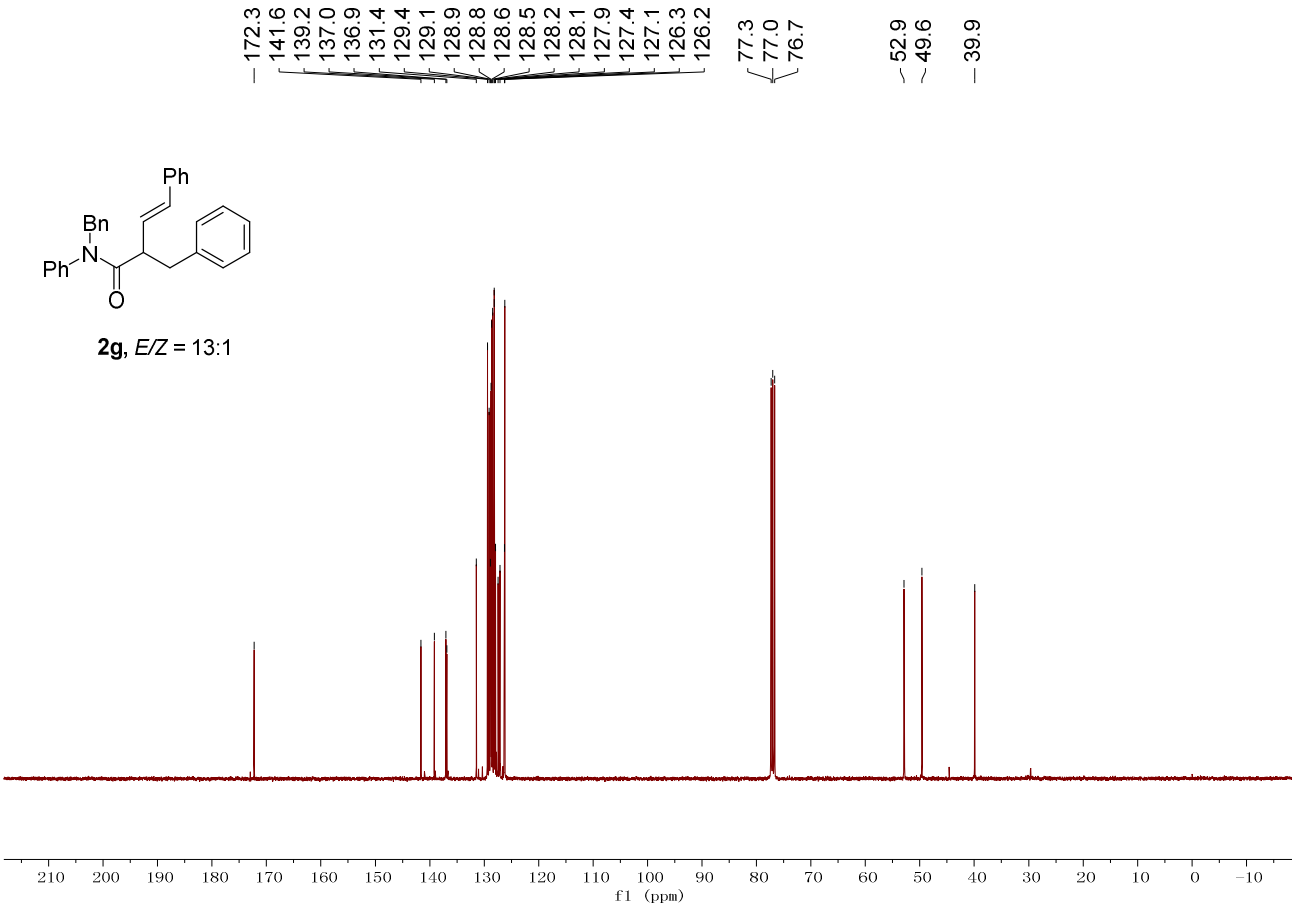
2f, *E*/*Z* = 4:1

^{1}H NMR (300 MHz, $CDCl_3$)

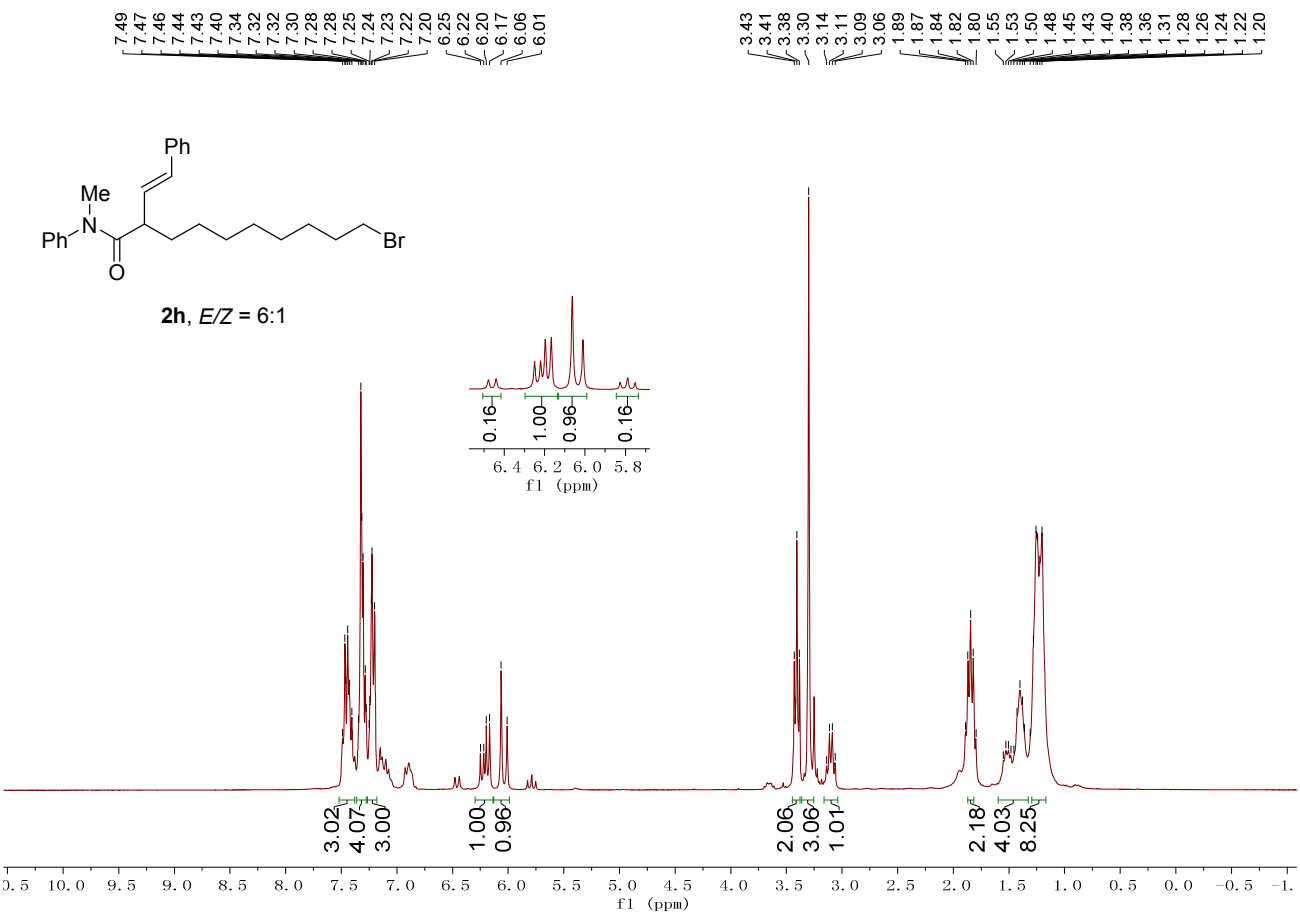


2g, *E*/*Z* = 13:1

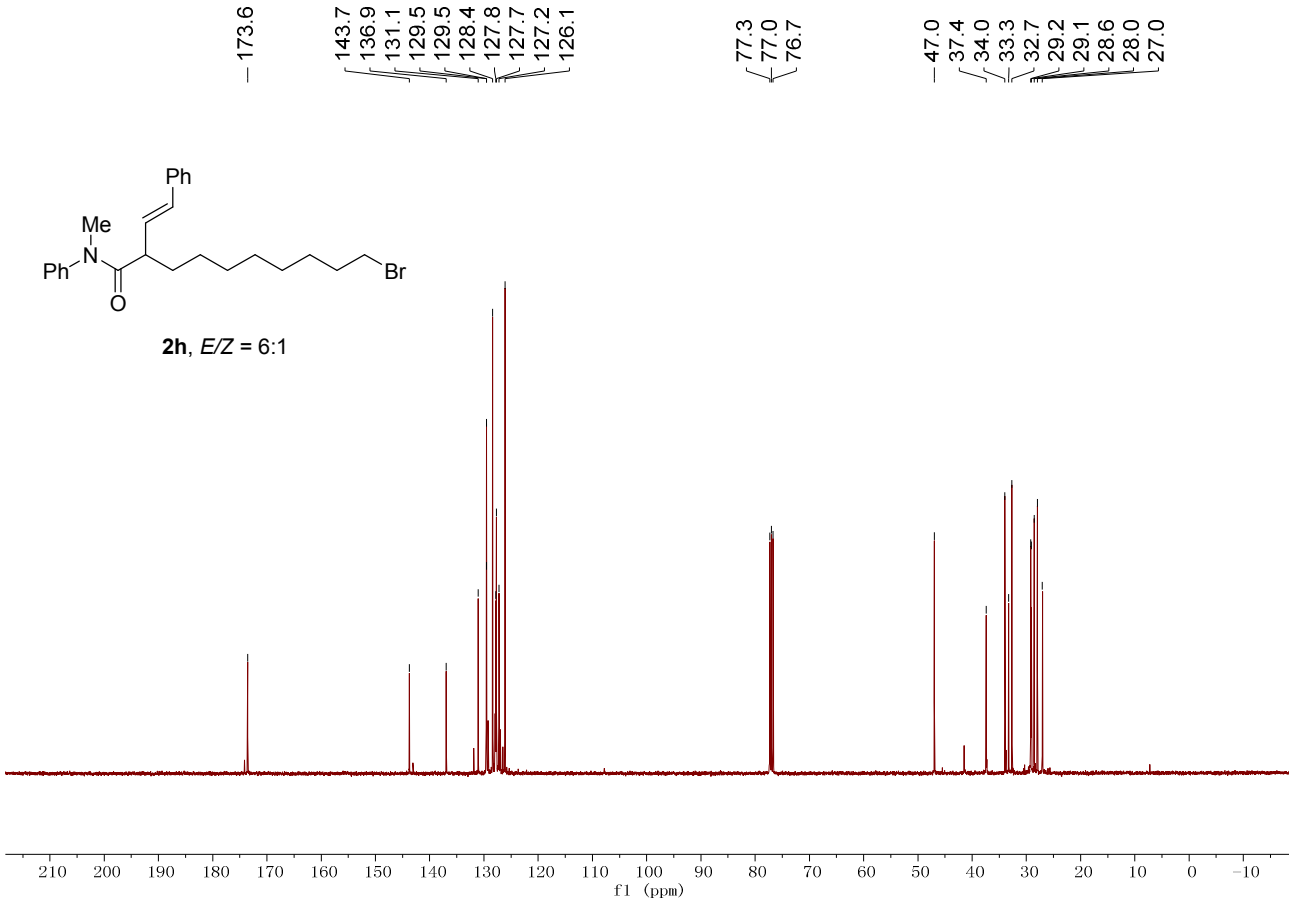
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

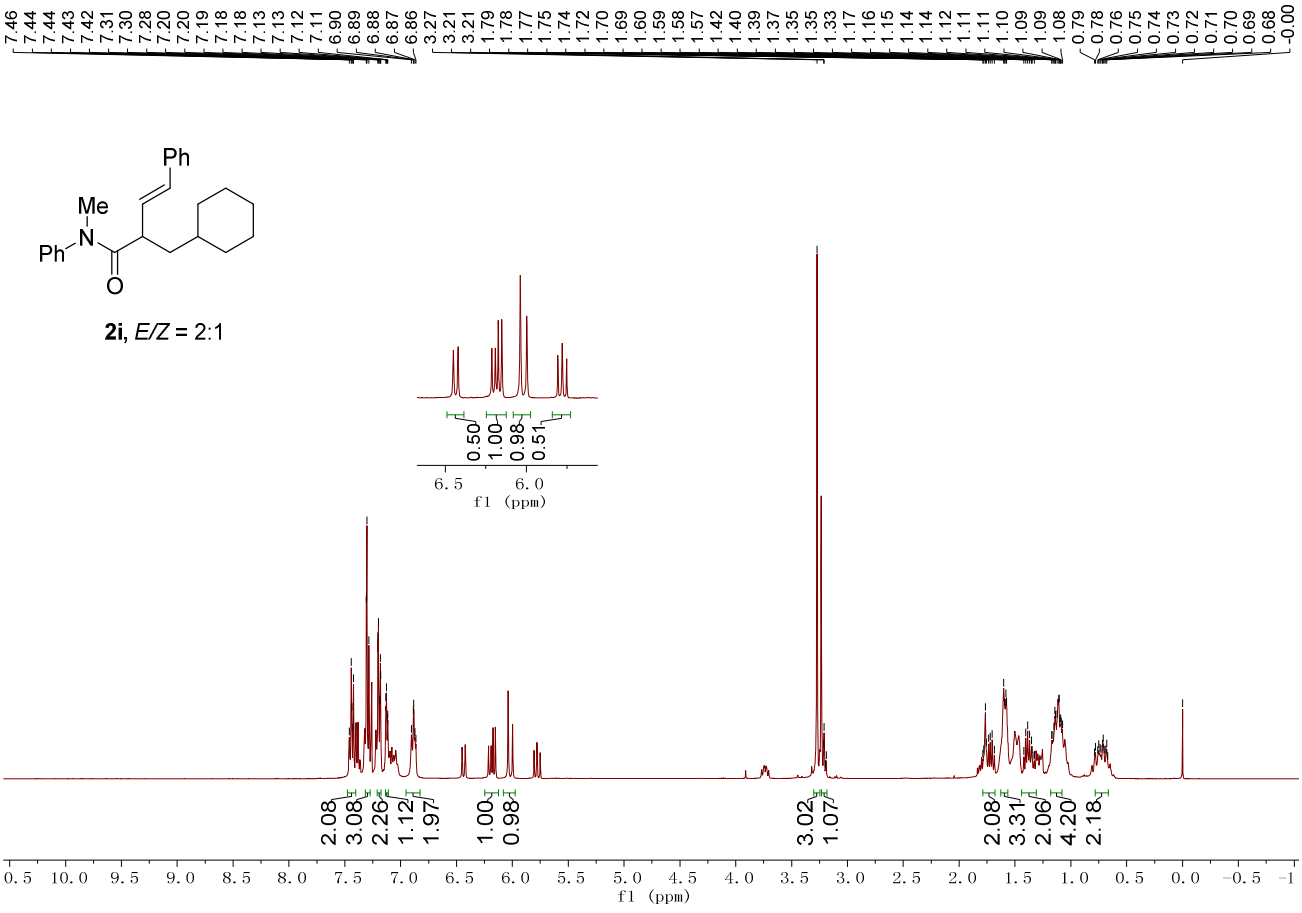


^{13}C NMR (101 MHz, CDCl3)



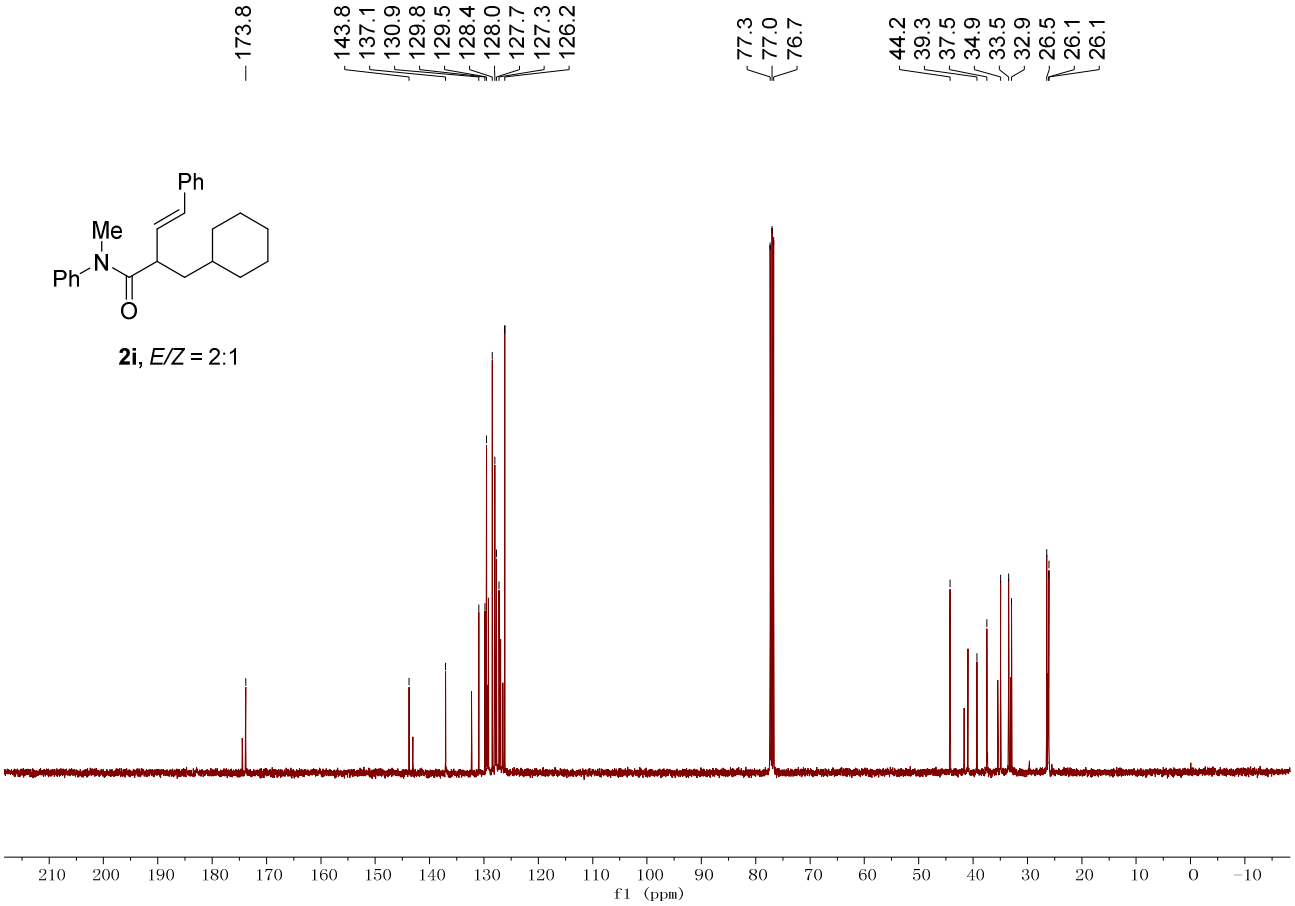
2h, *E*/*Z* = 6:1

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



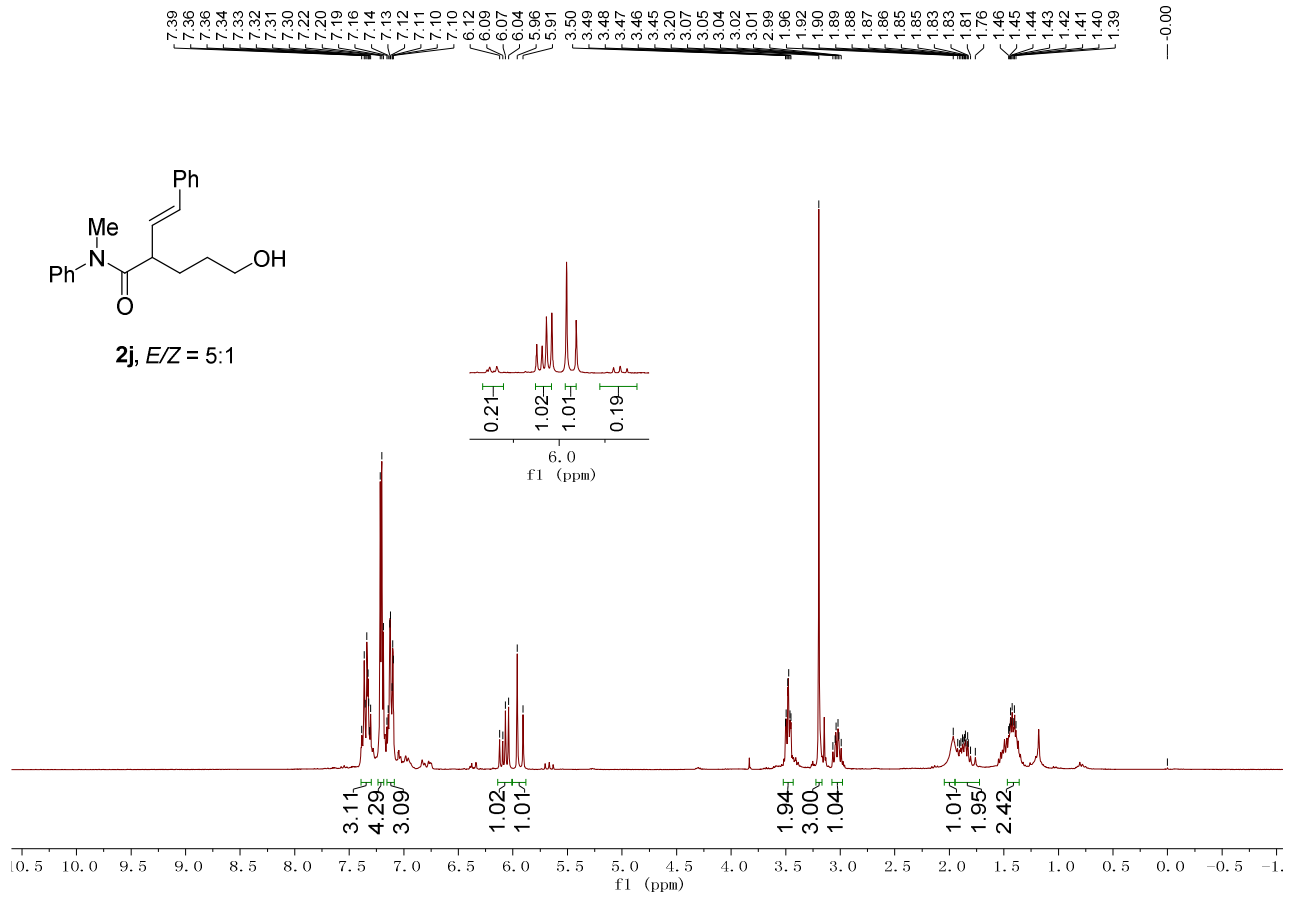
2i, *E*/*Z* = 2:1

^{13}C NMR (101 MHz, CDCl3)



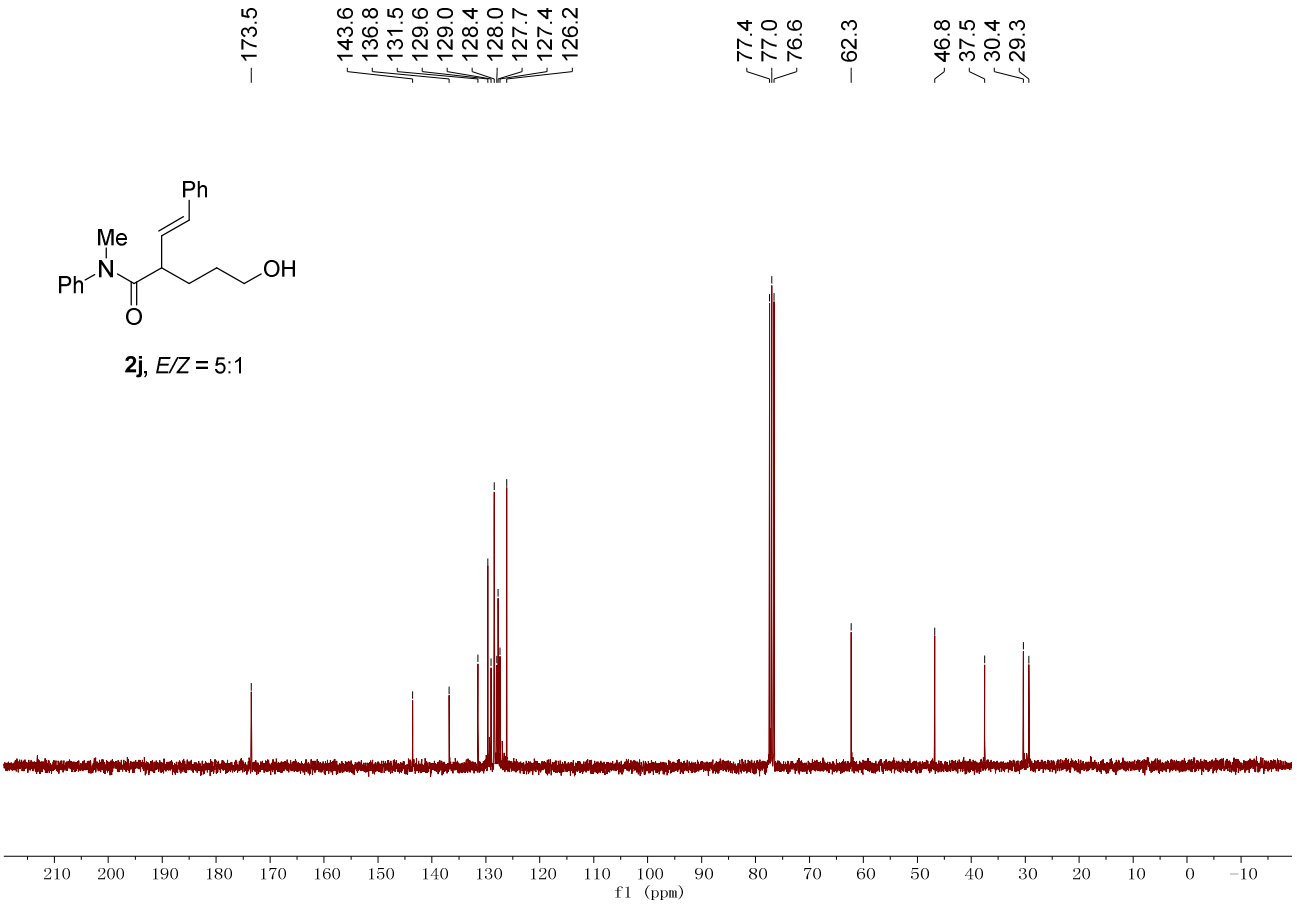
2i, *E*/*Z* = 2:1

^{1}H NMR (300 MHz, $CDCl_3$)



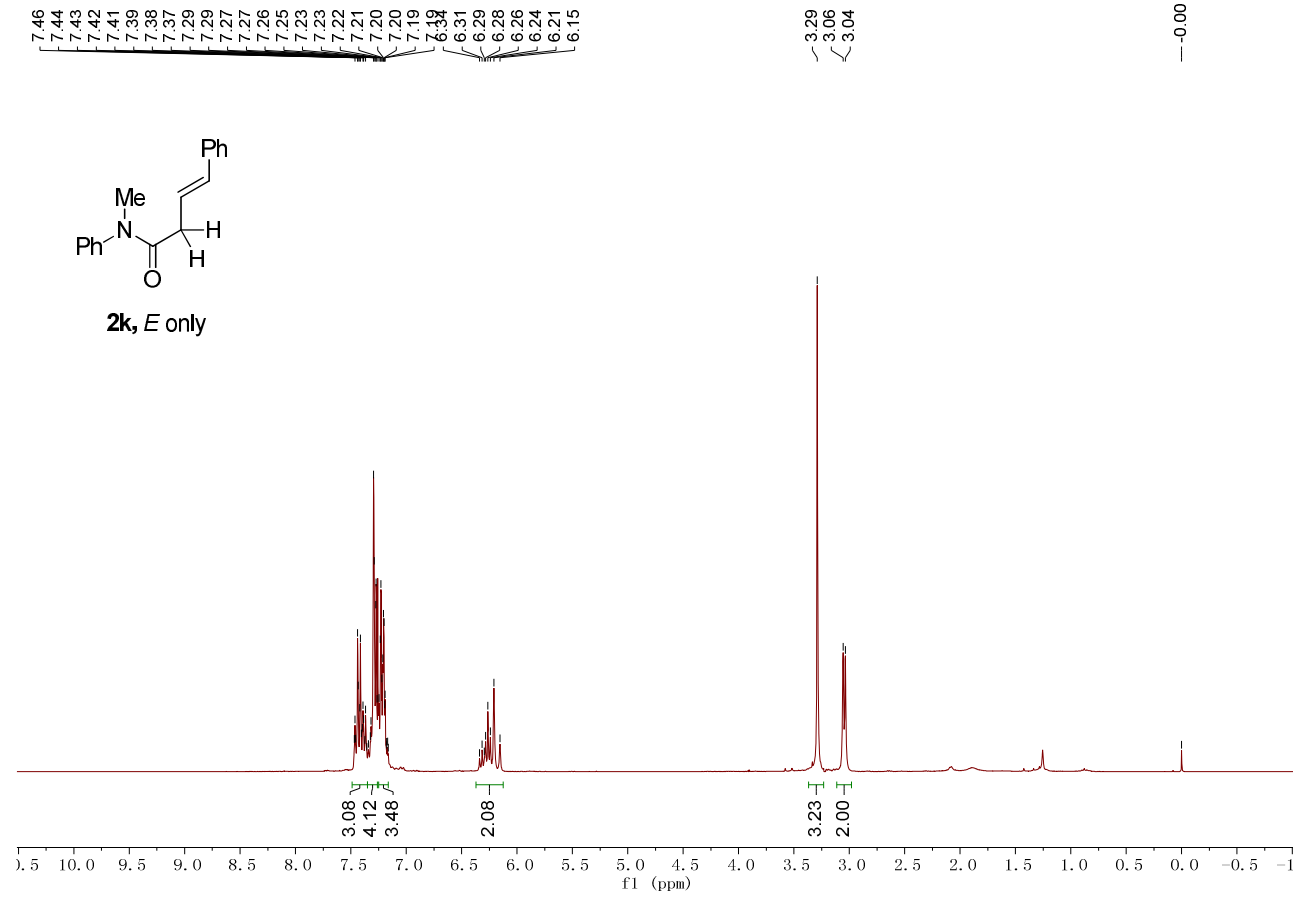
2j, *E*/*Z* = 5:1

^{13}C NMR (75 MHz, $CDCl_3$)



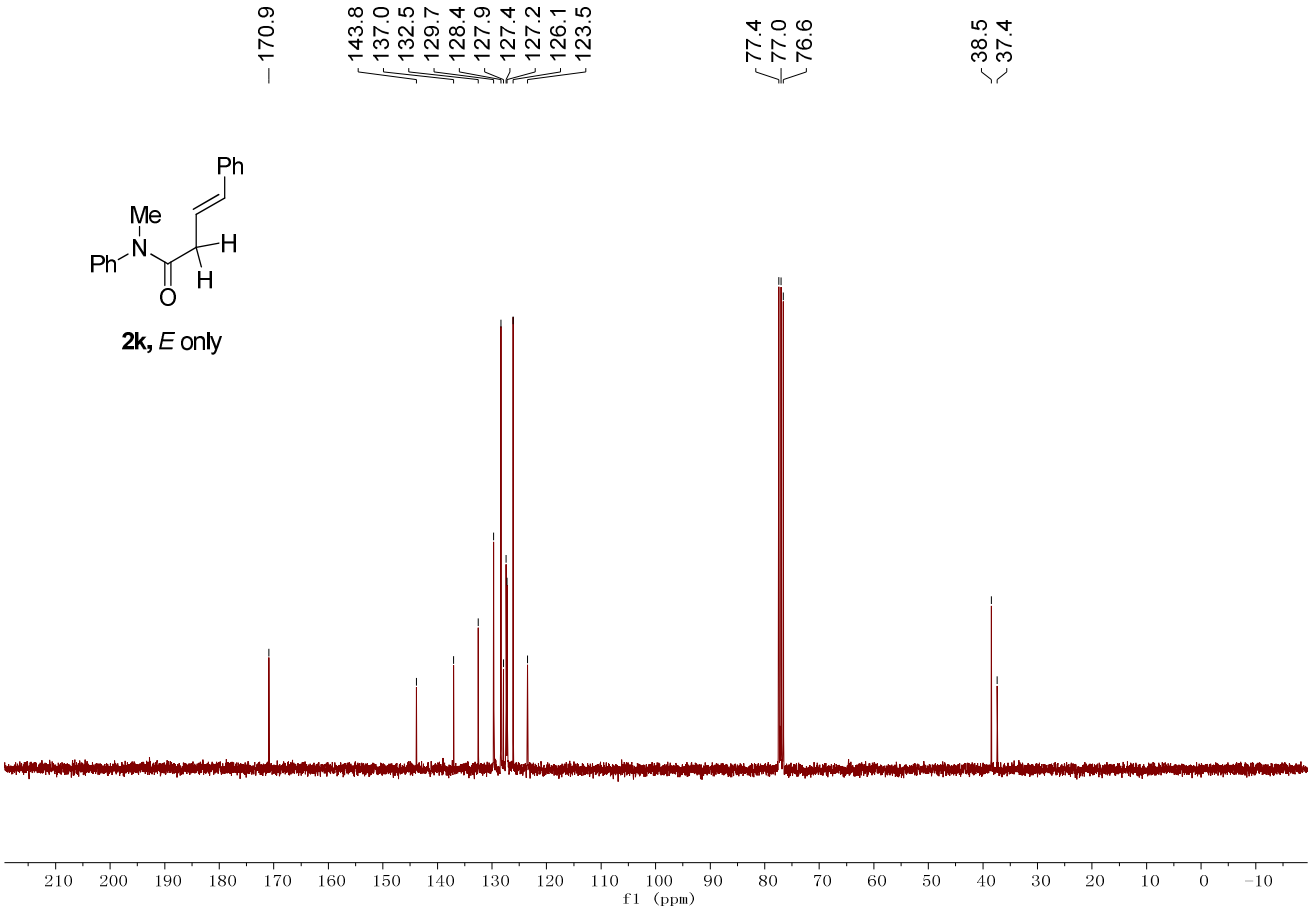
2j, *E*/*Z* = 5:1

^{1}H NMR (300 MHz, $CDCl_3$)

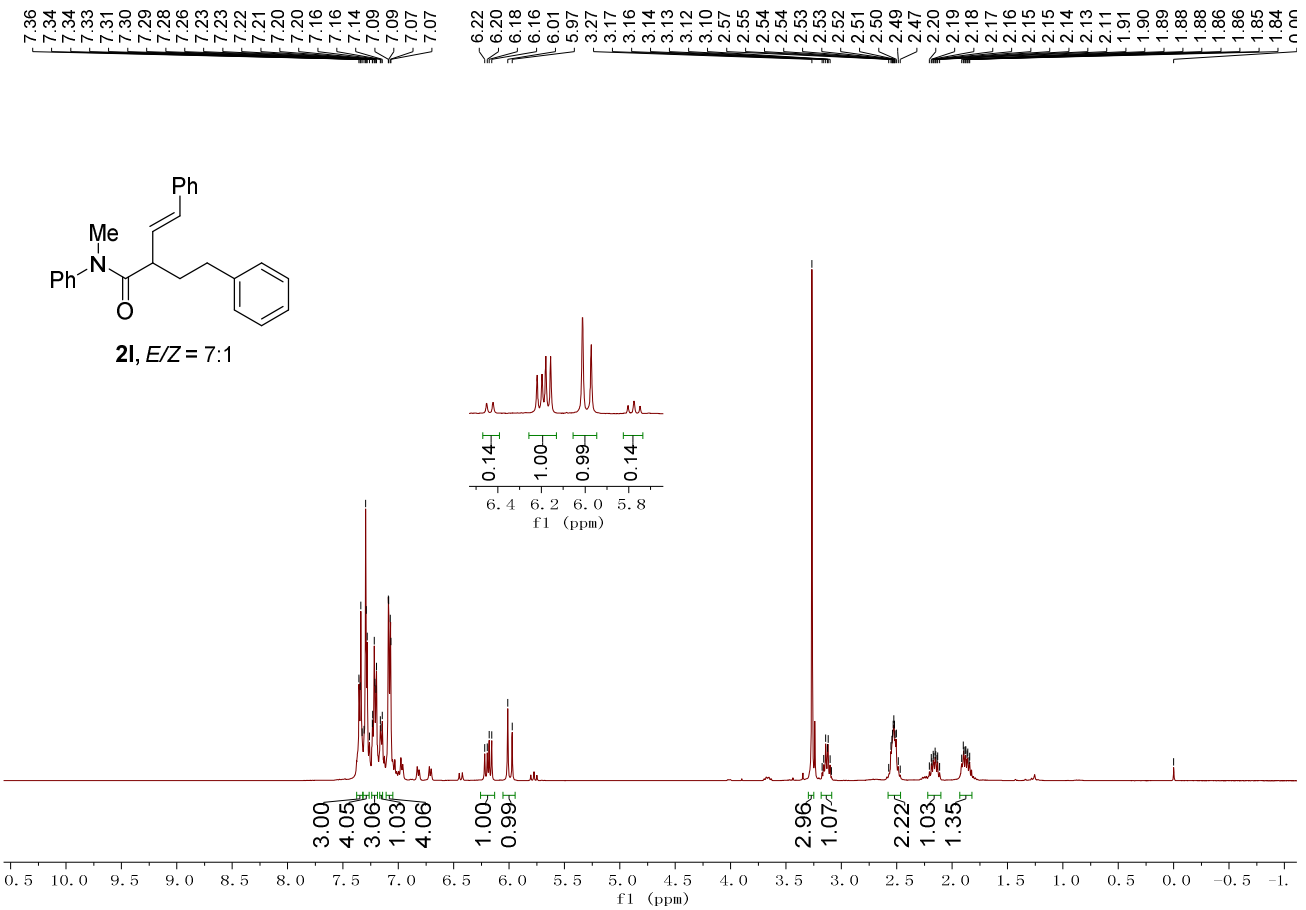


2k, *E* only

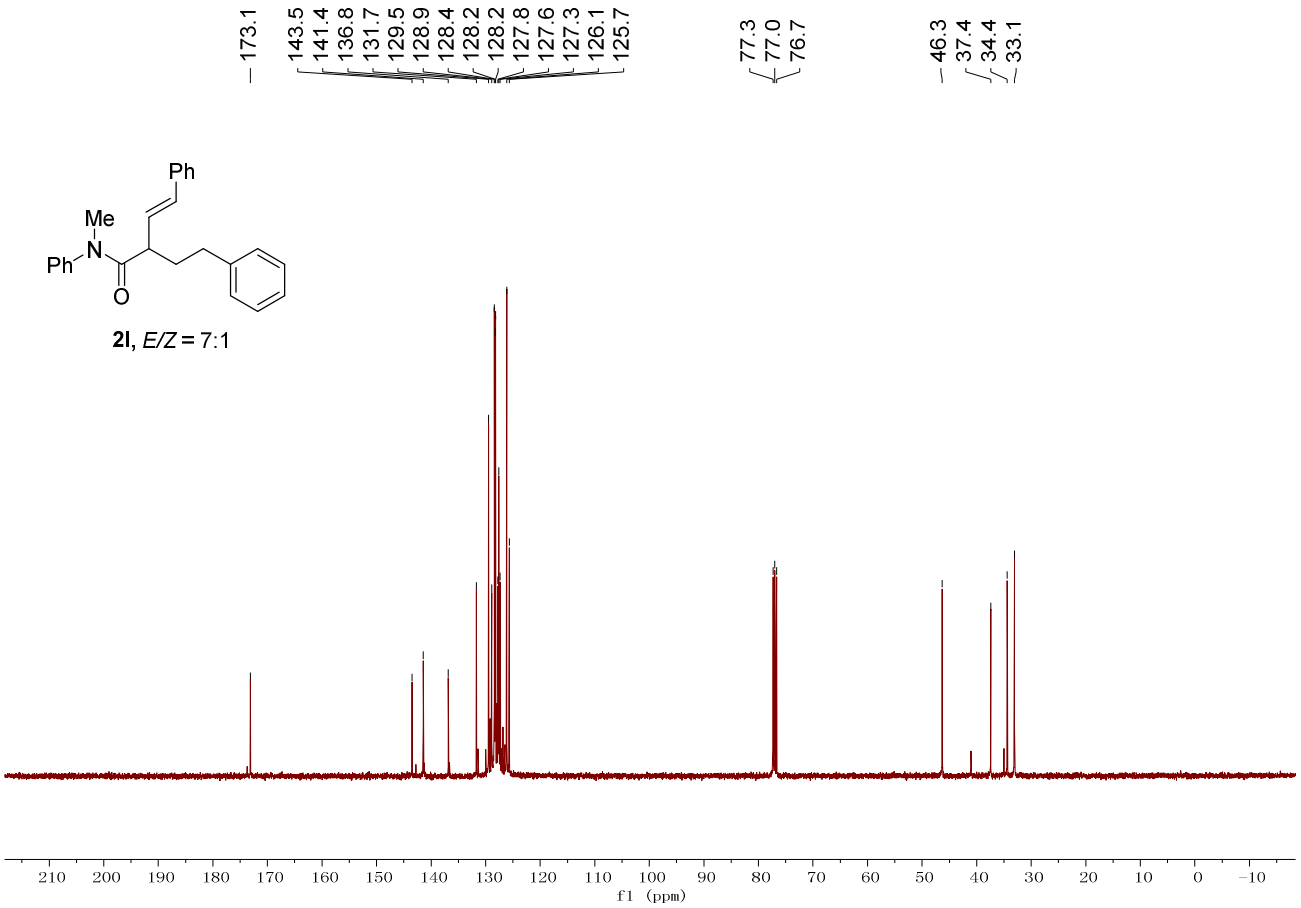
^{13}C NMR (75 MHz, $CDCl_3$)



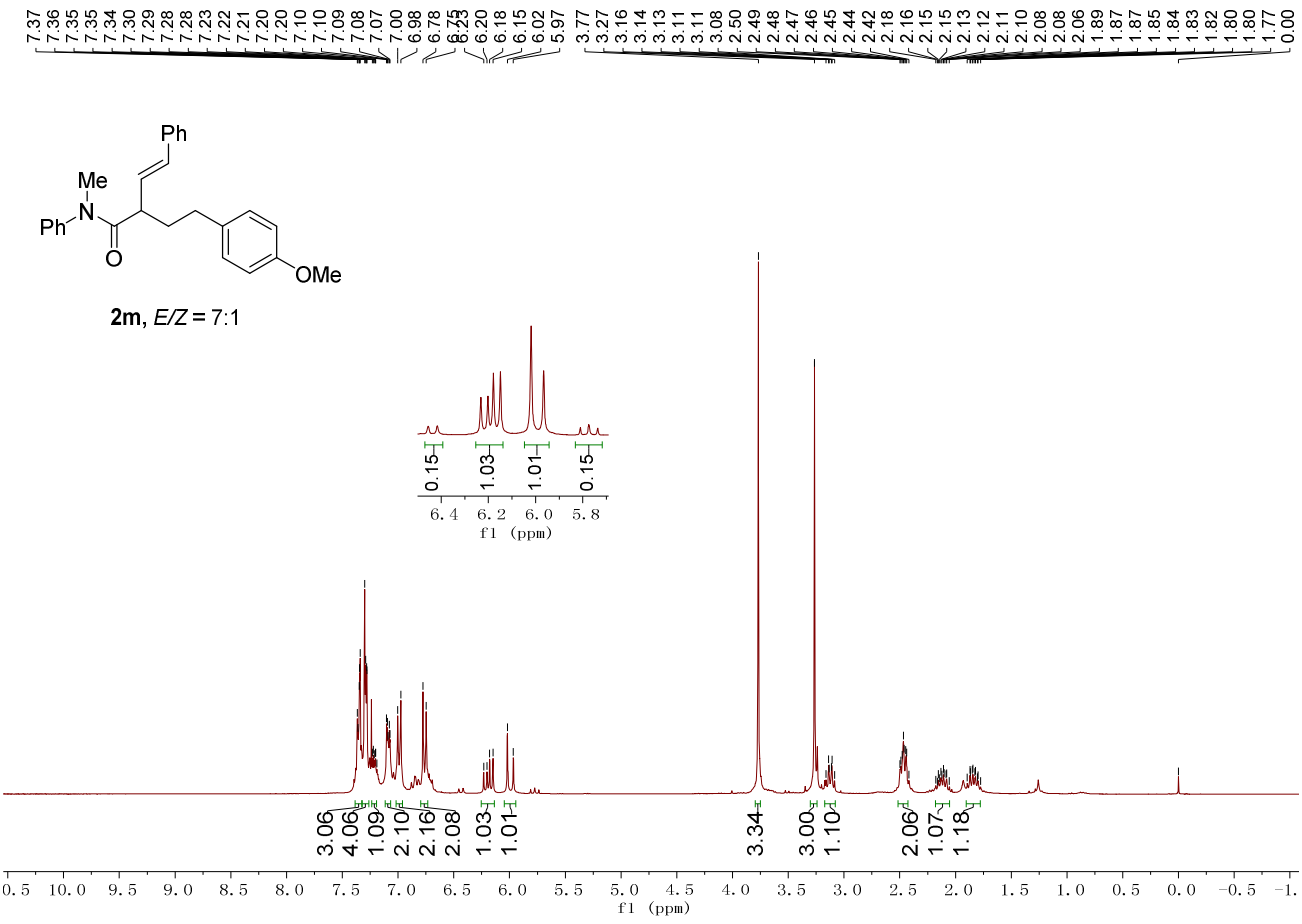
^{1}H NMR (400 MHz, $CDCl_3$)



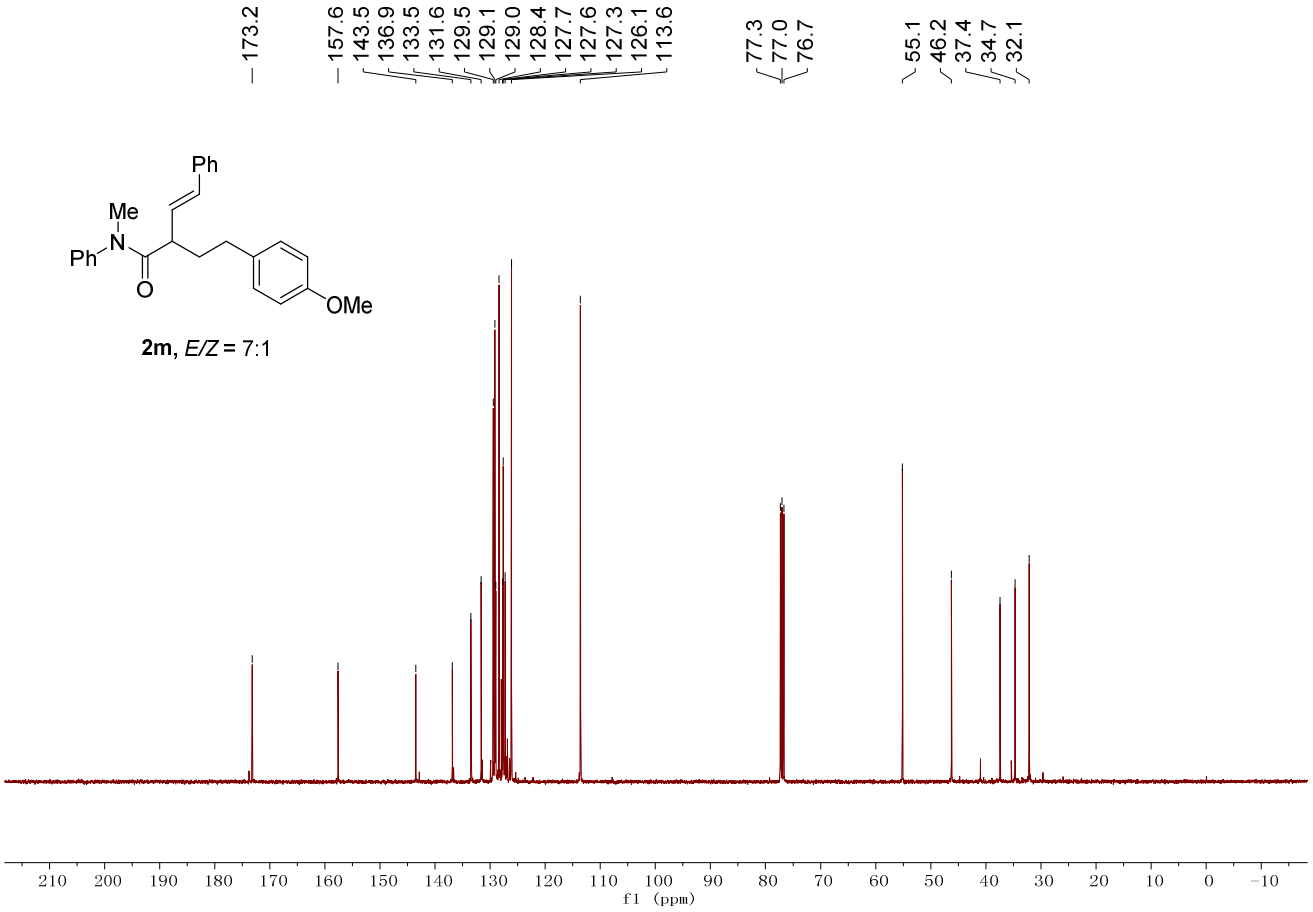
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

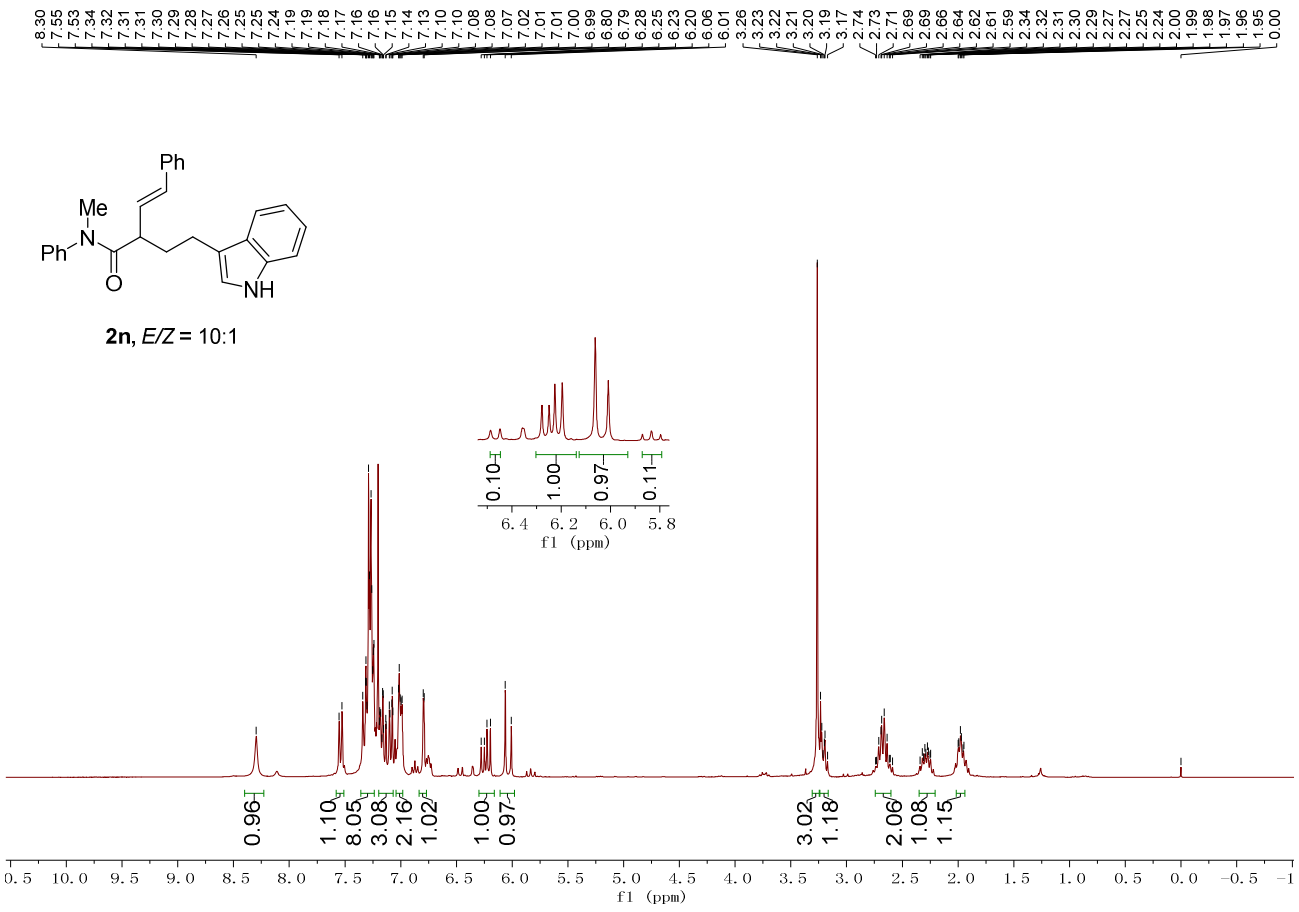


^{13}C NMR (101 MHz, $CDCl_3$)



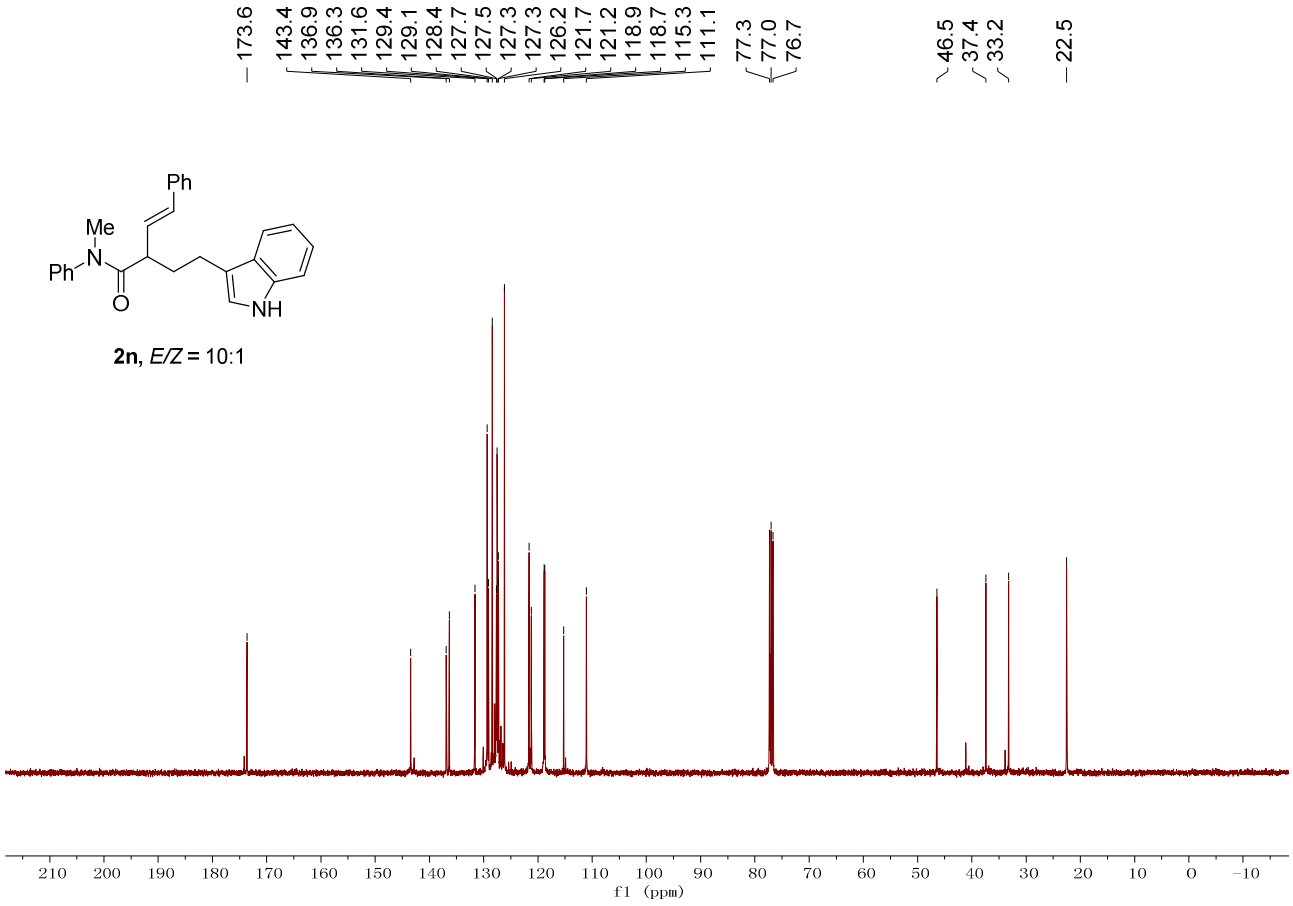
2m, *E*/*Z* = 7:1

^{1}H NMR (300 MHz, $CDCl_3$)

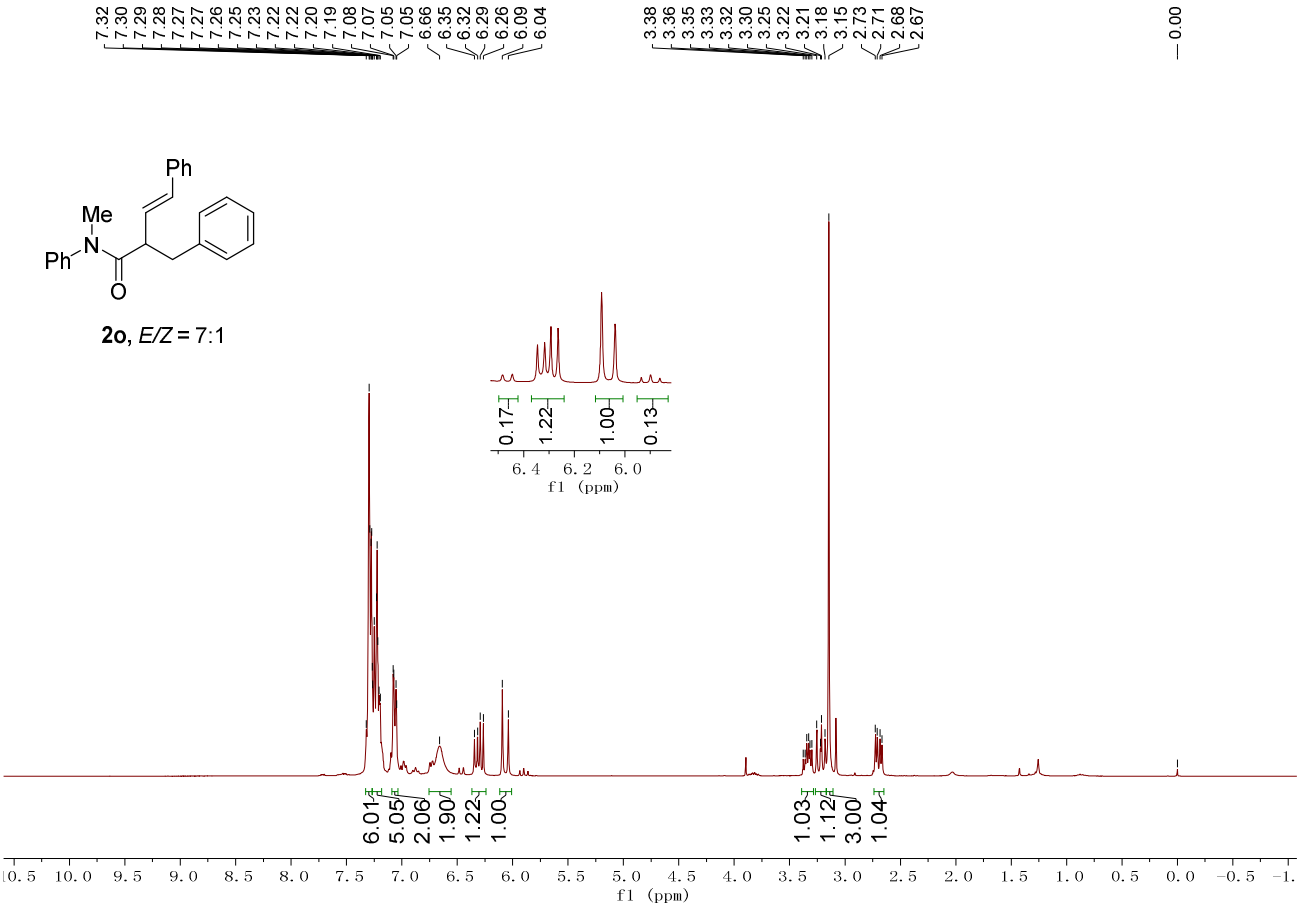


2n, *E*/*Z* = 10:1

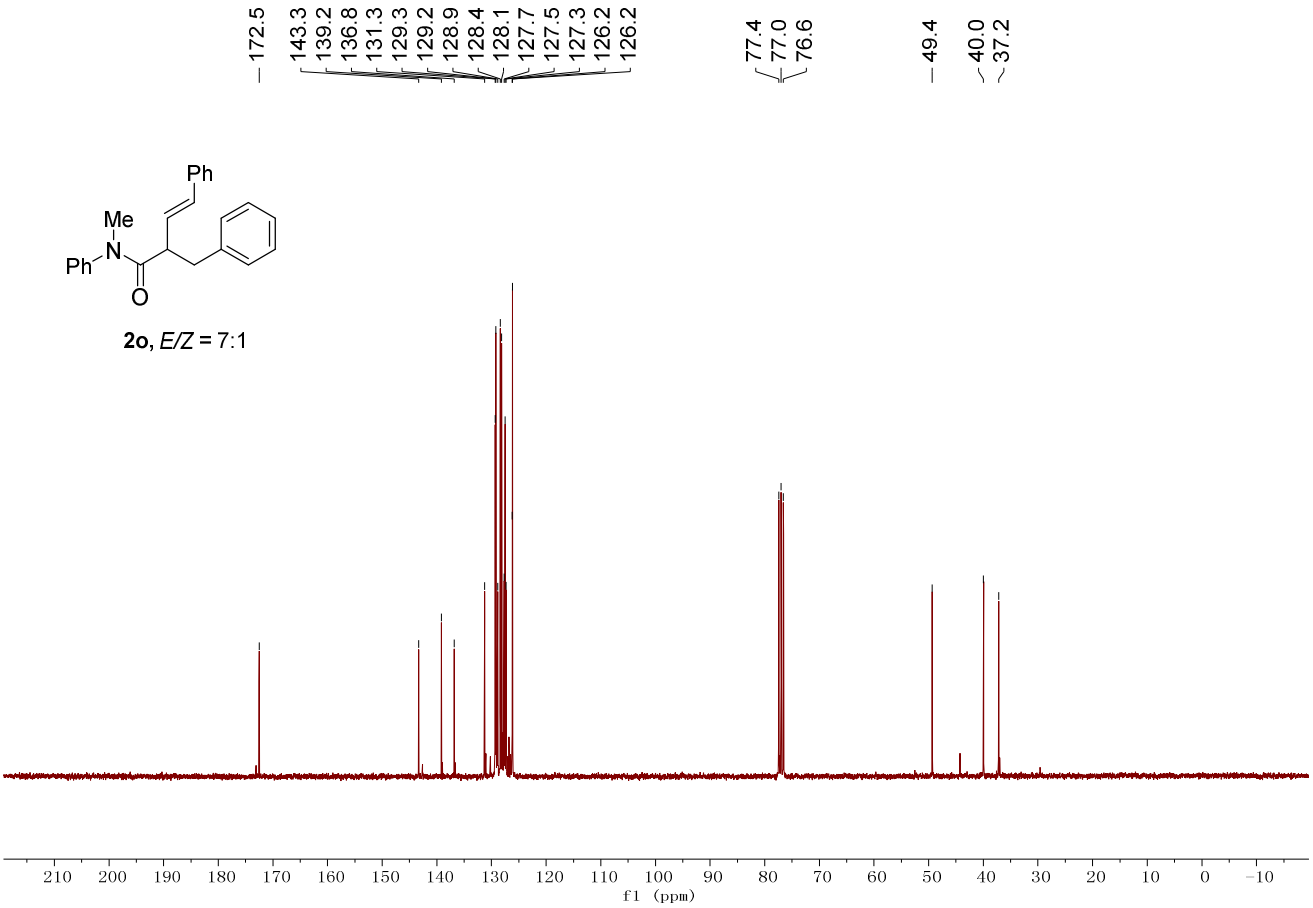
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

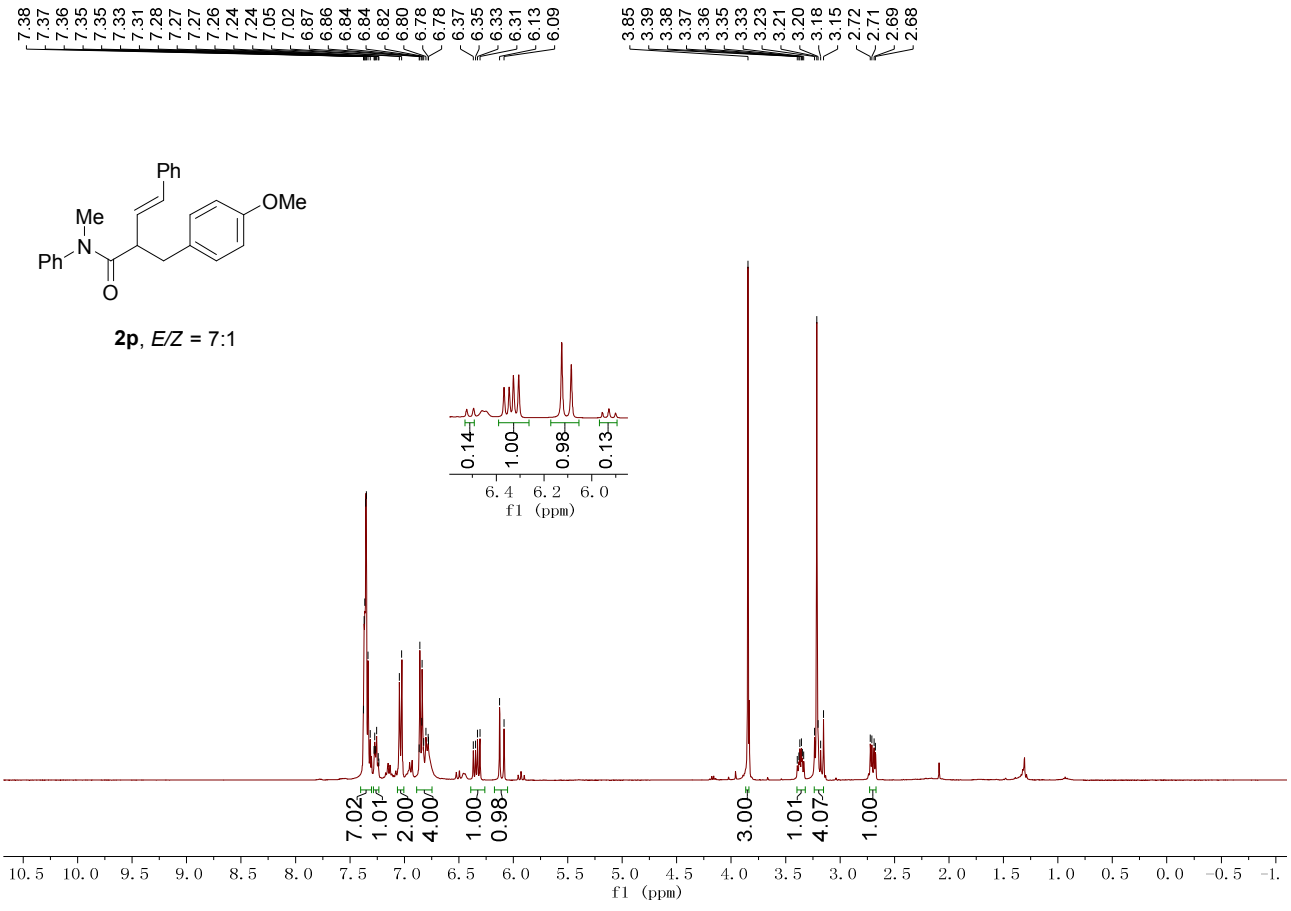


^{13}C NMR (75 MHz, $CDCl_3$)



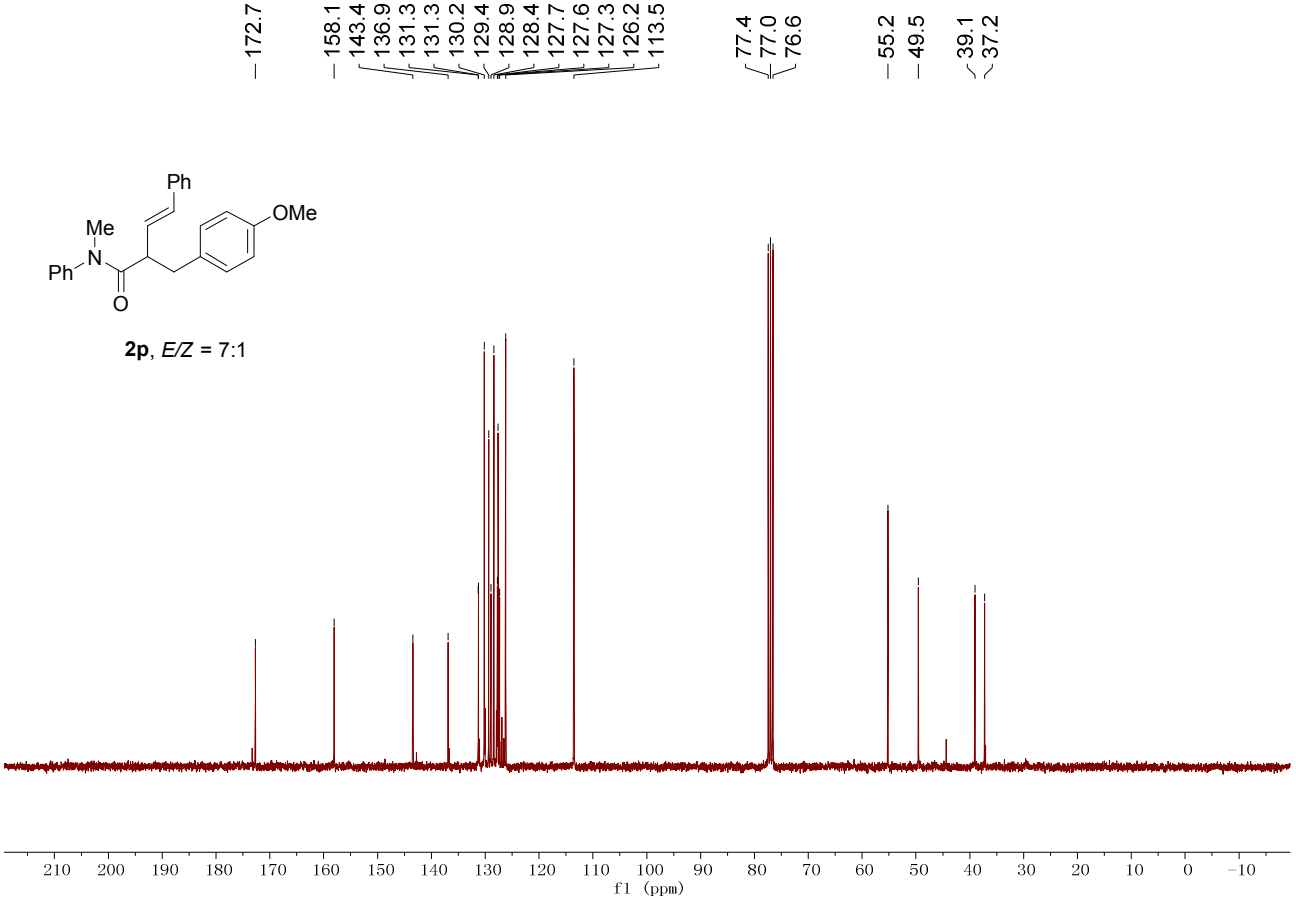
2o, *E/Z* = 7:1

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



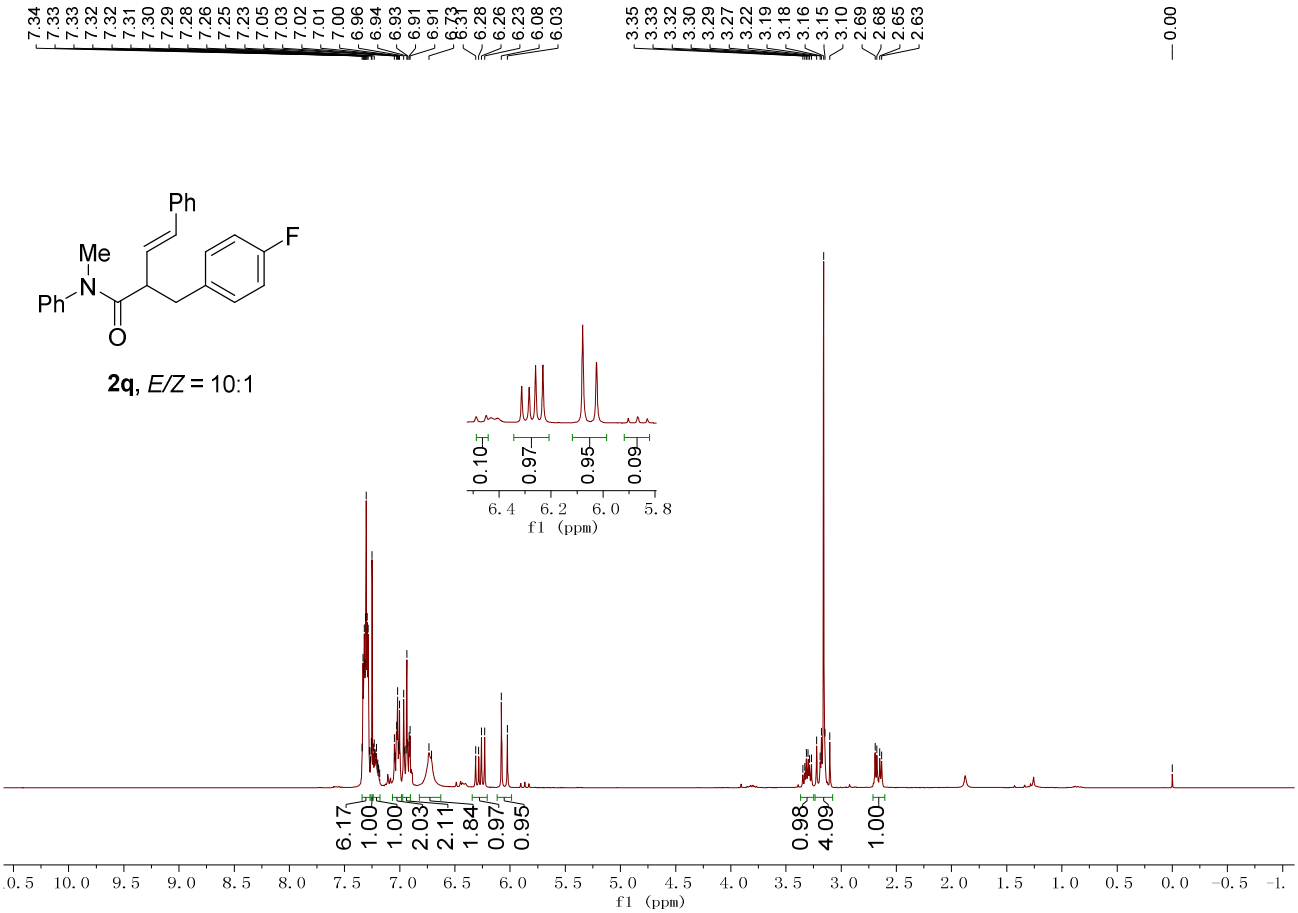
2p, *E/Z* = 7:1

^{13}C NMR (75 MHz, $CDCl_3$)



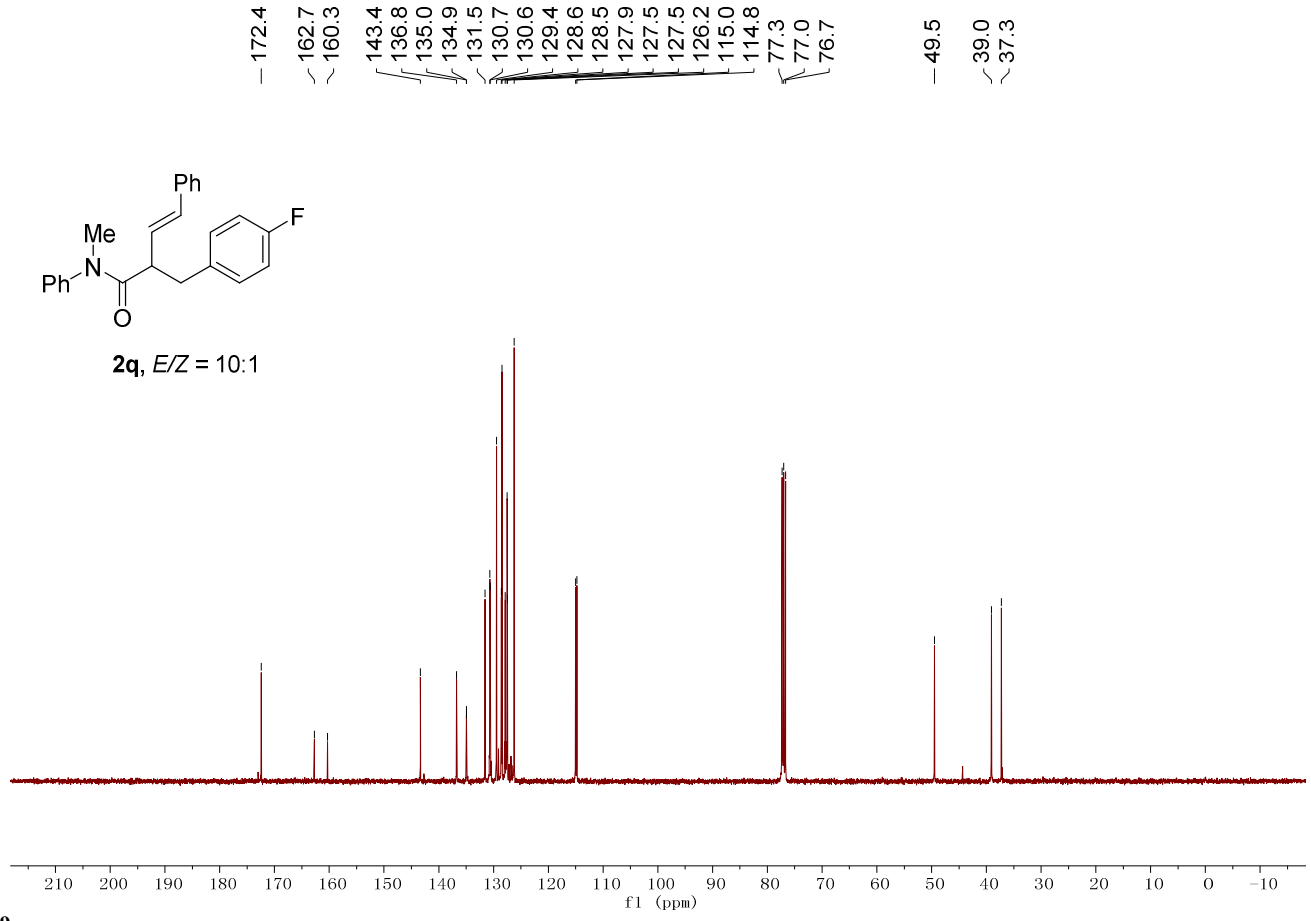
2p, *E*/*Z* = 7:1

^{1}H NMR (300 MHz, $CDCl_3$)

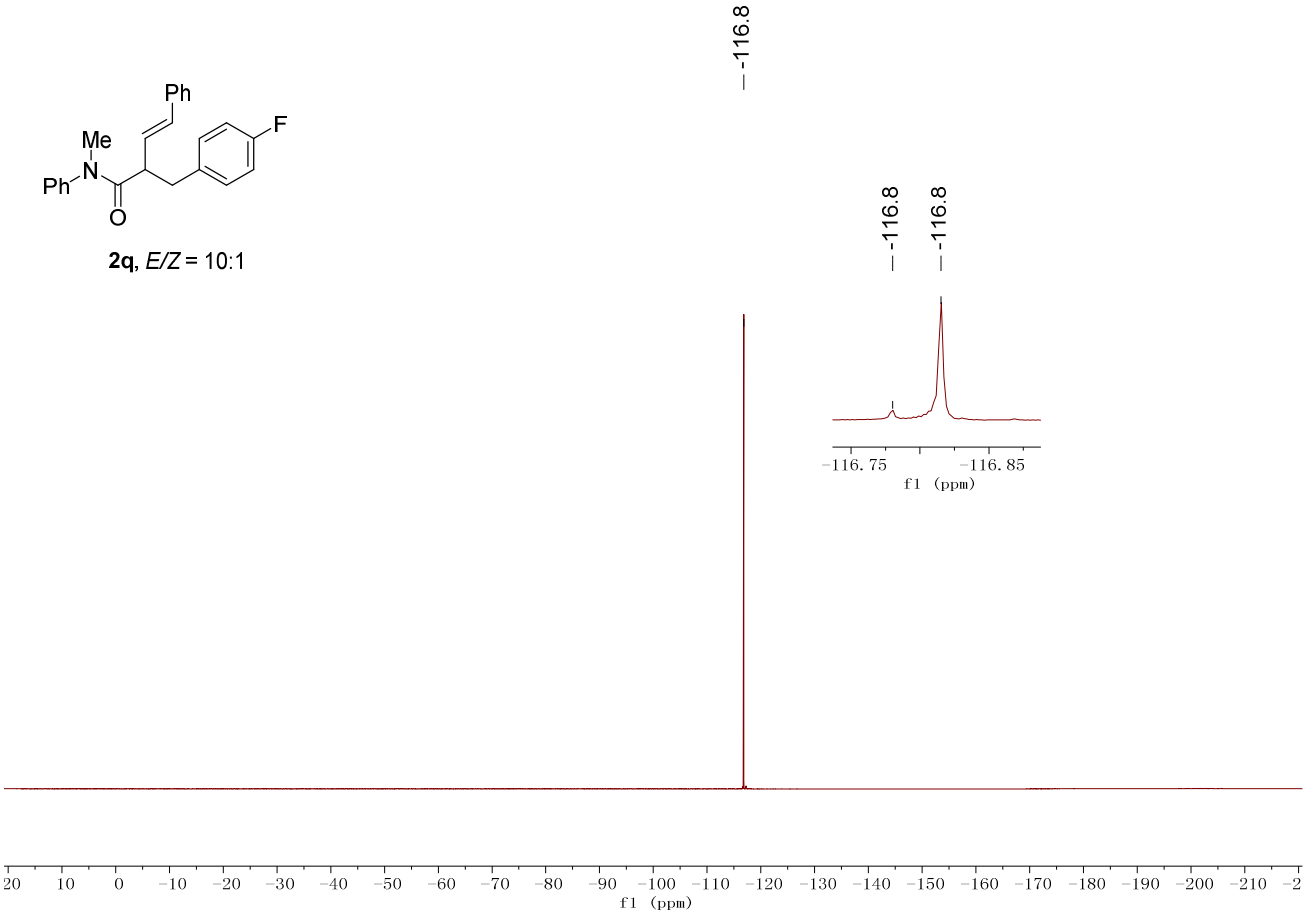


2q, *E*/*Z* = 10:1

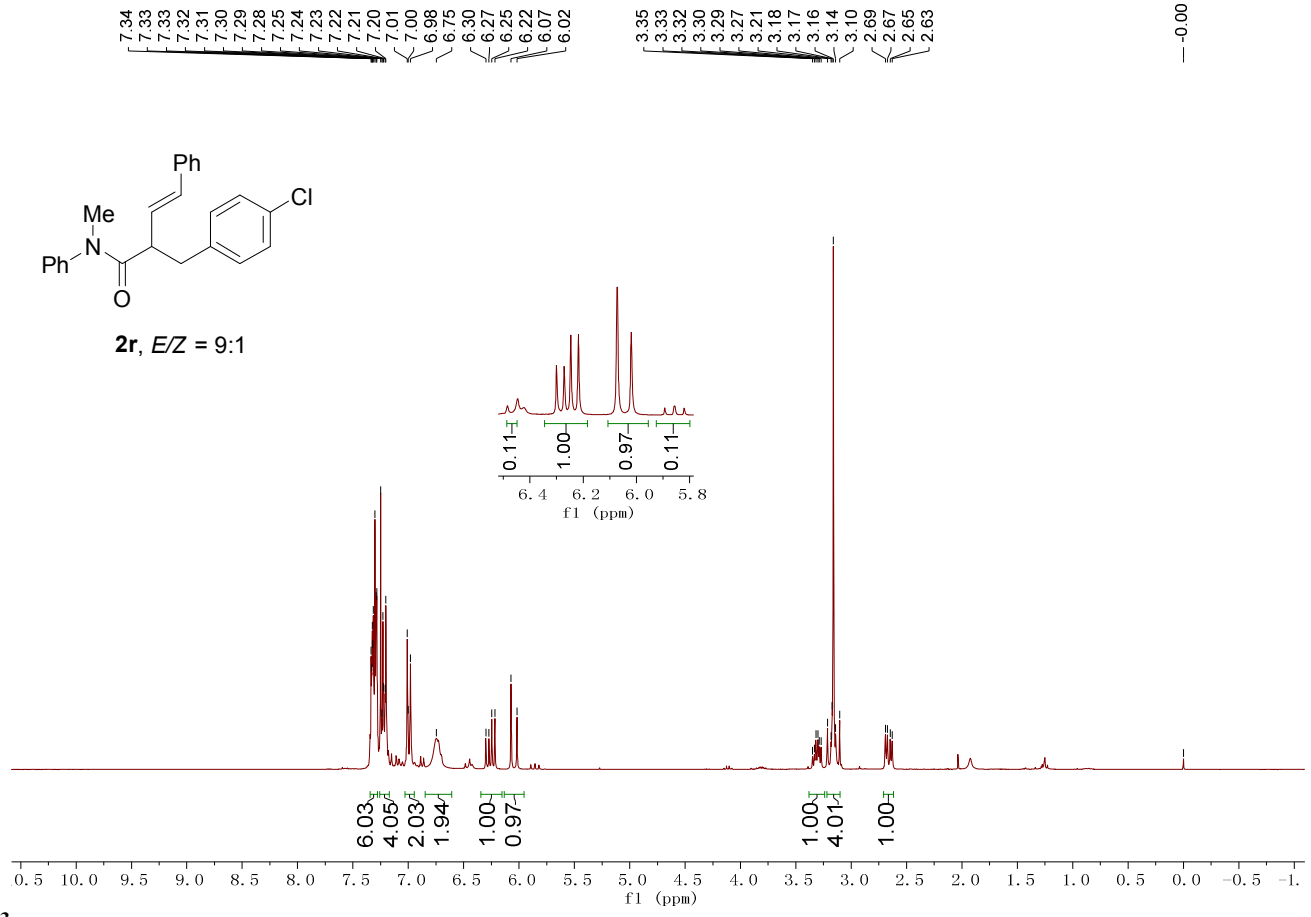
^{13}C NMR (101 MHz, $CDCl_3$)



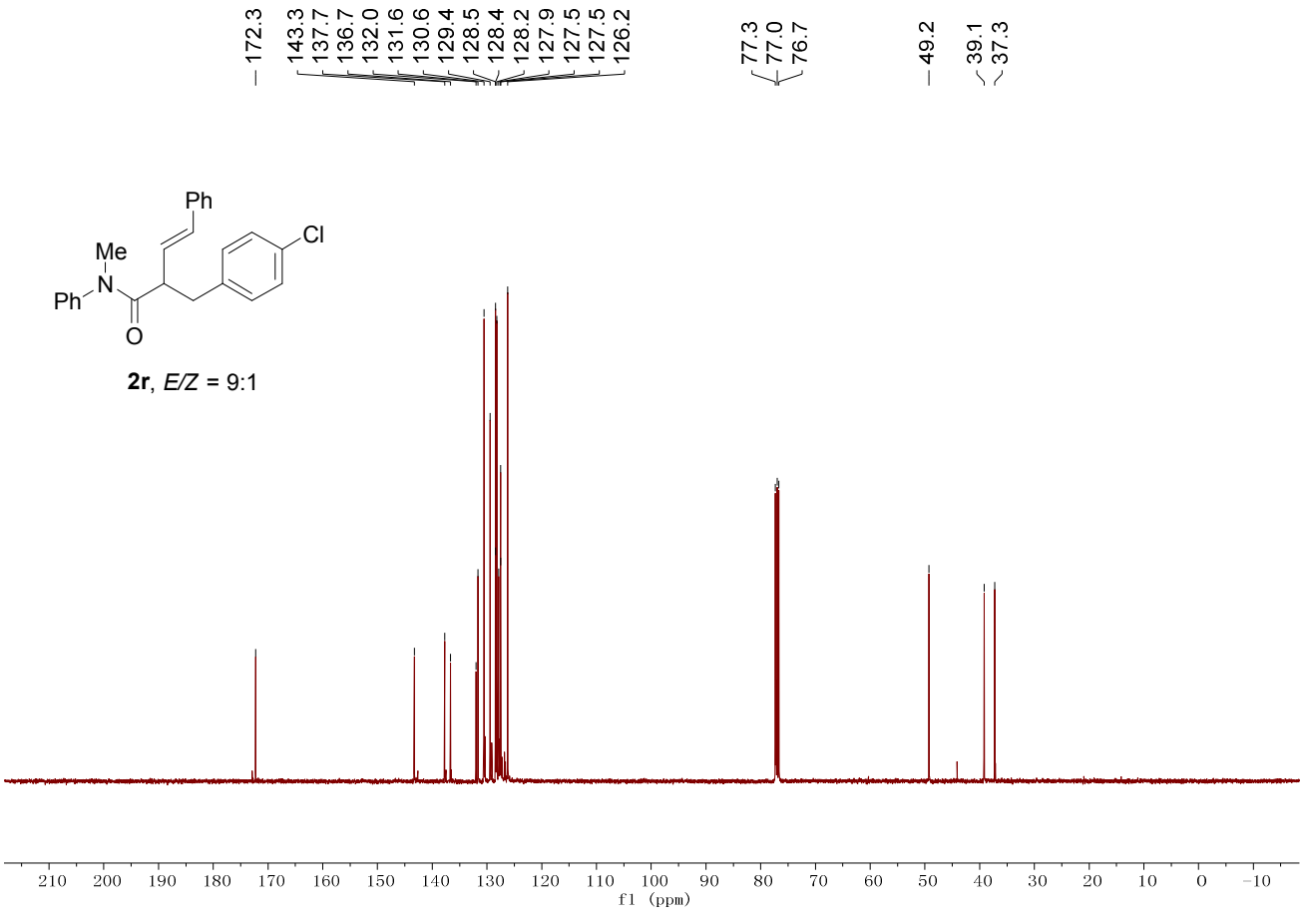
^{19}F NMR (376 MHz, $CDCl_3$)



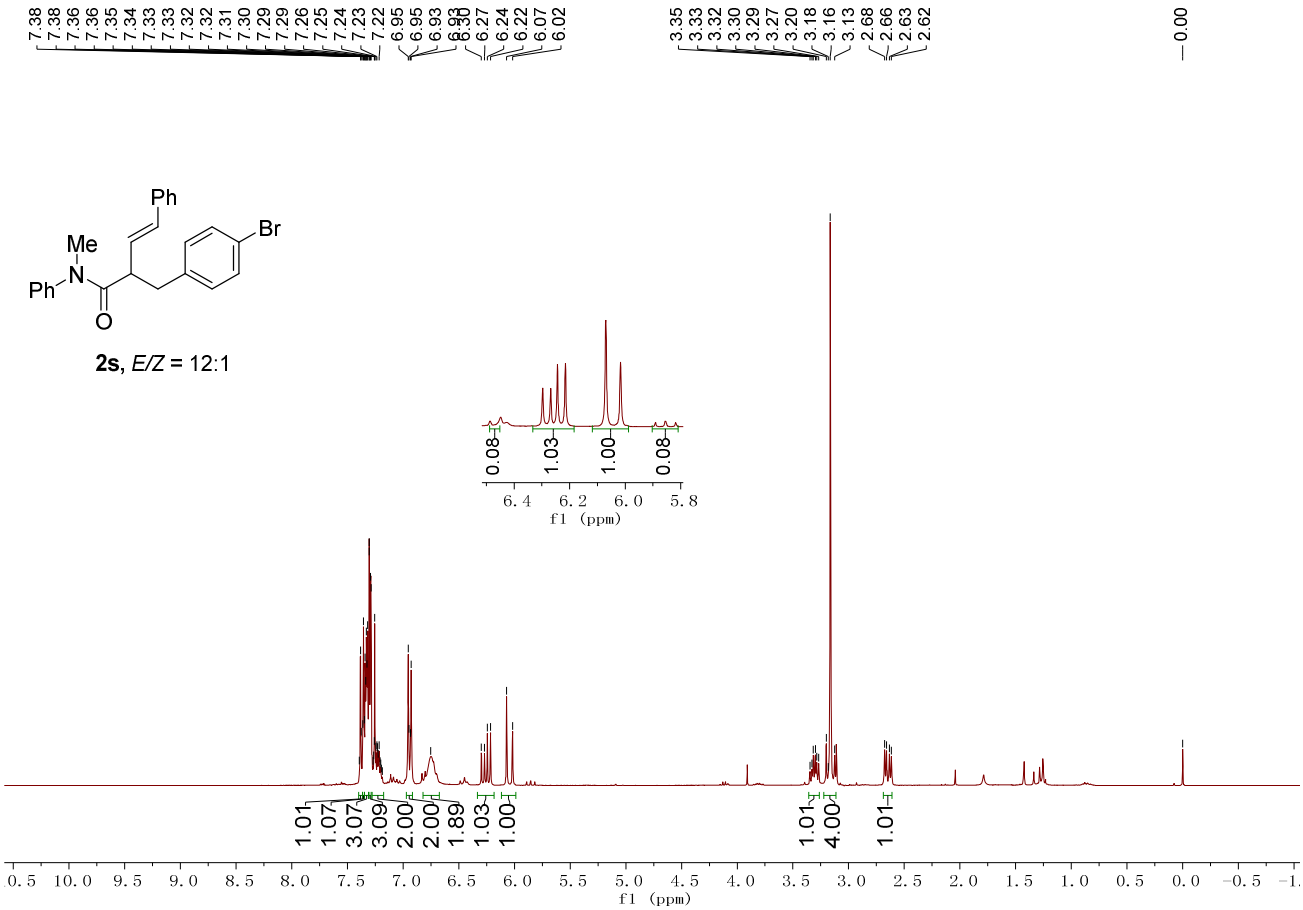
^{1}H NMR (300 MHz, $CDCl_3$)



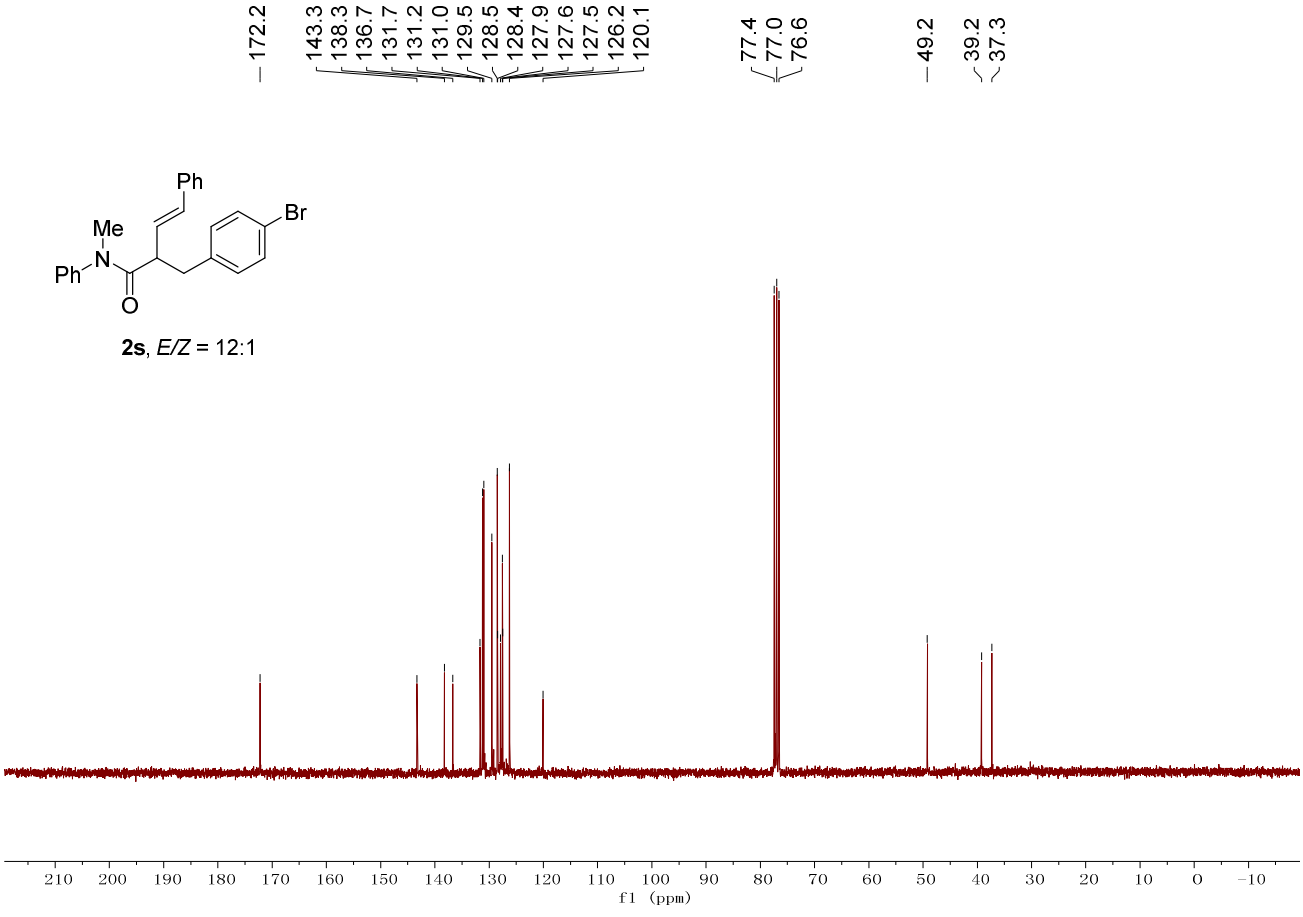
^{13}C NMR (101 MHz, $CDCl_3$)



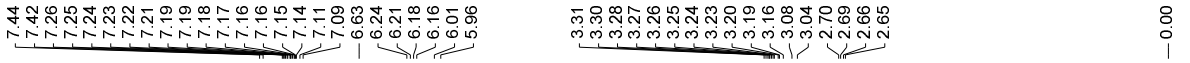
^{1}H NMR (300 MHz, $CDCl_3$)

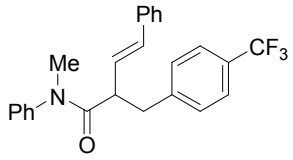


^{13}C NMR (75 MHz, $CDCl_3$)



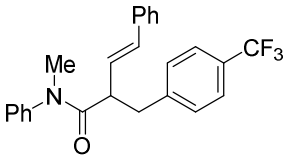
^{1}H NMR (300 MHz, $CDCl_3$)



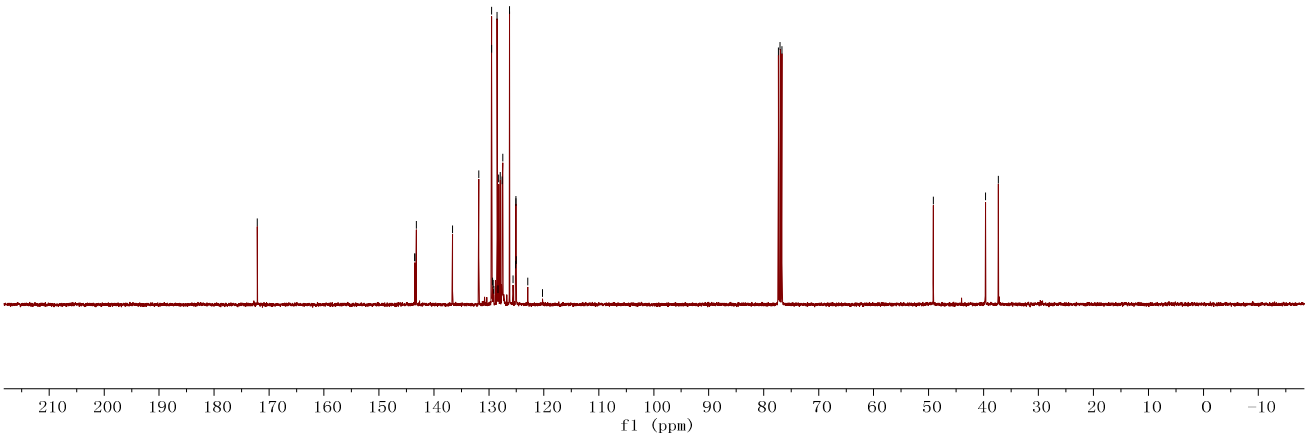


2t, *E/Z* = 12:1

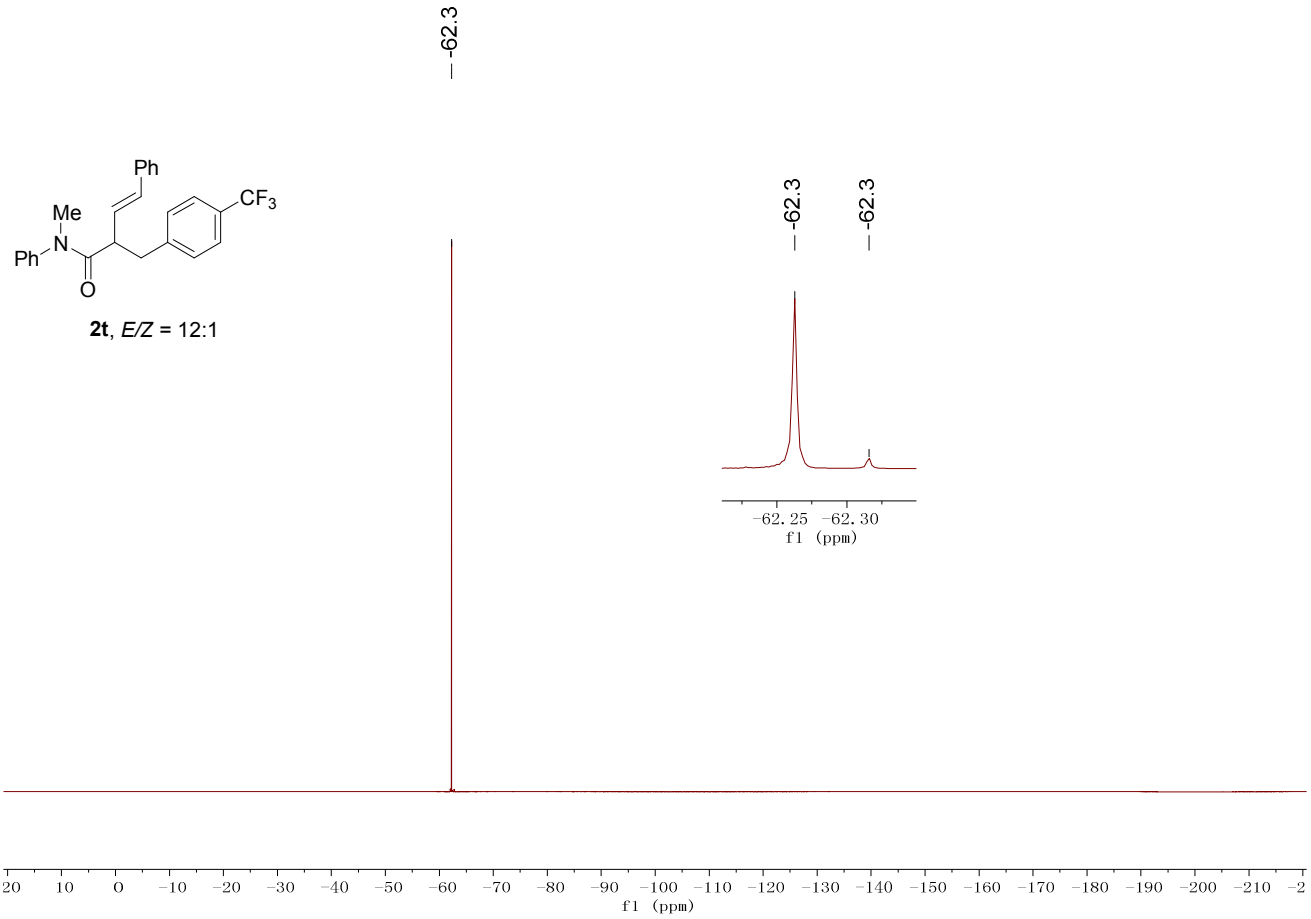
^{13}C NMR (101 MHz, $CDCl_3$)



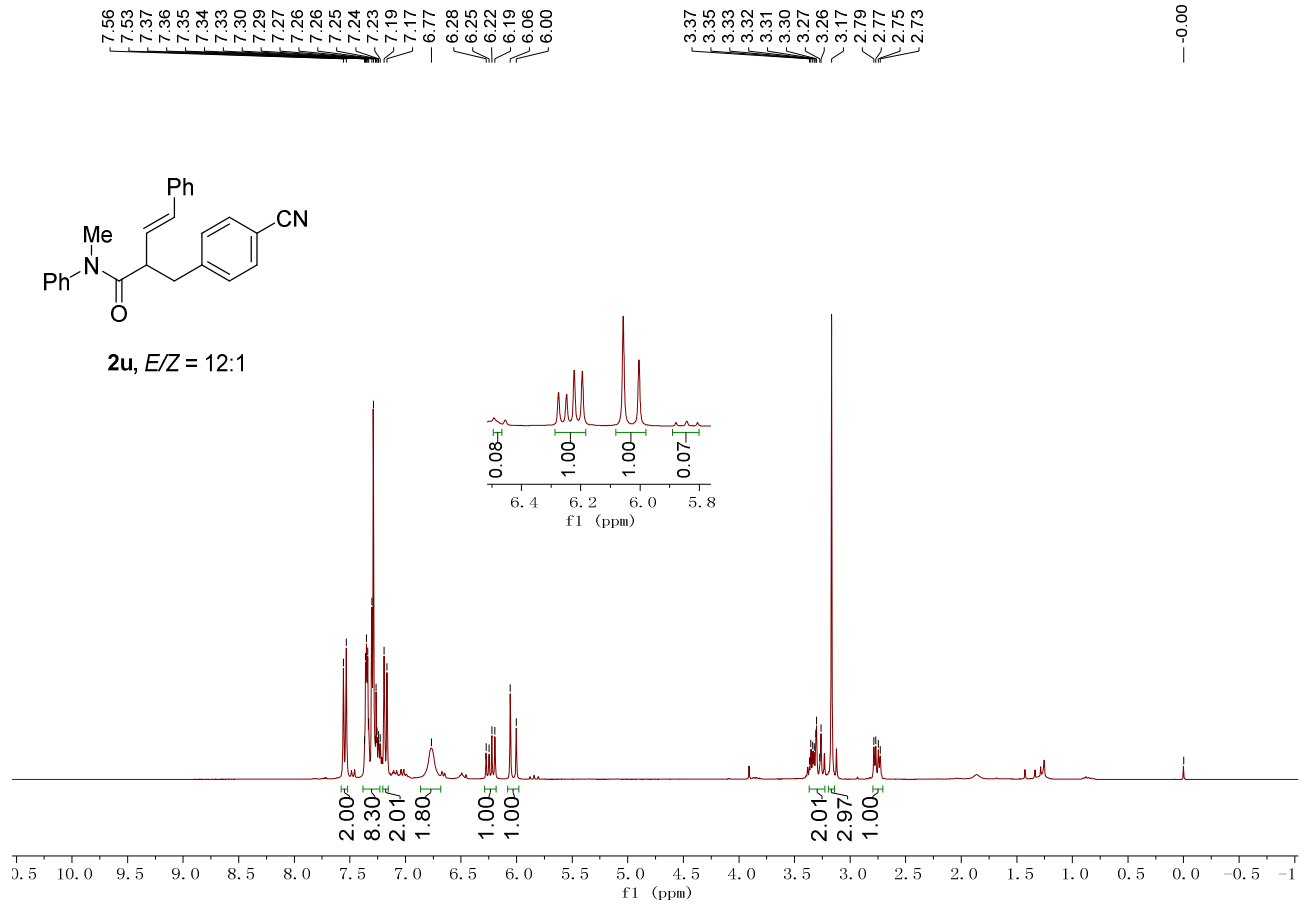
2t, *E/Z* = 12:1



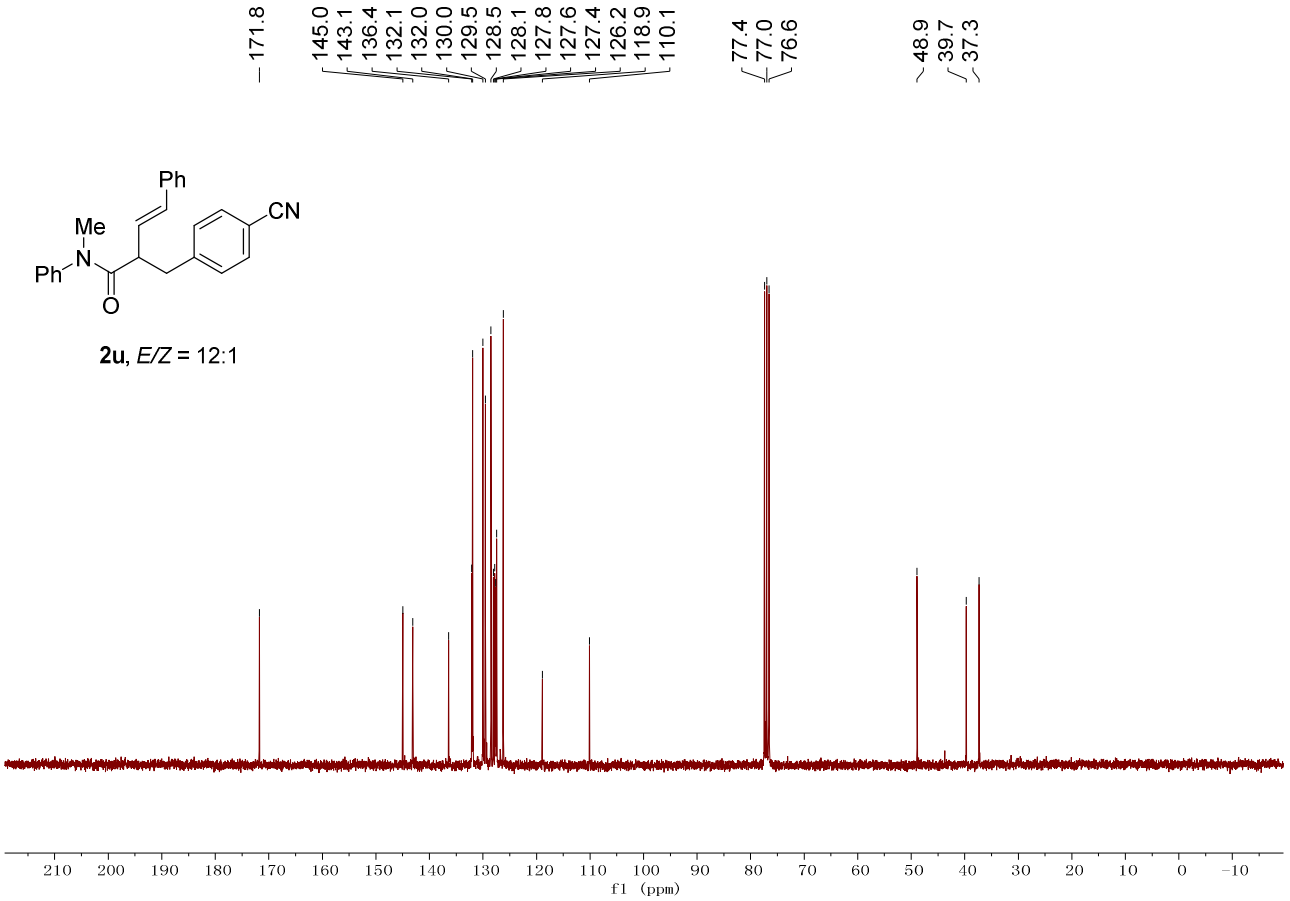
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

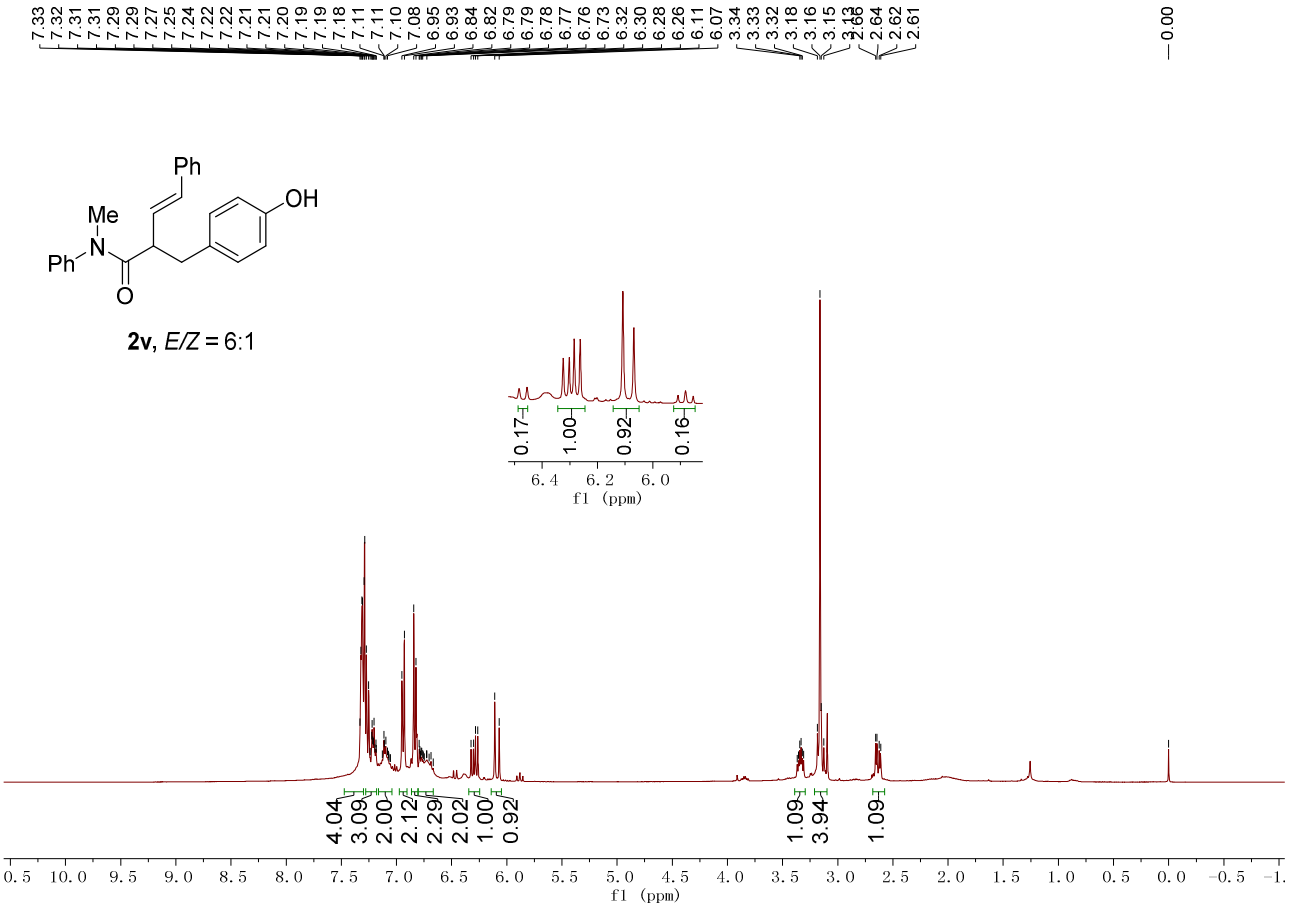


^{13}C NMR (75 MHz, $CDCl_3$)



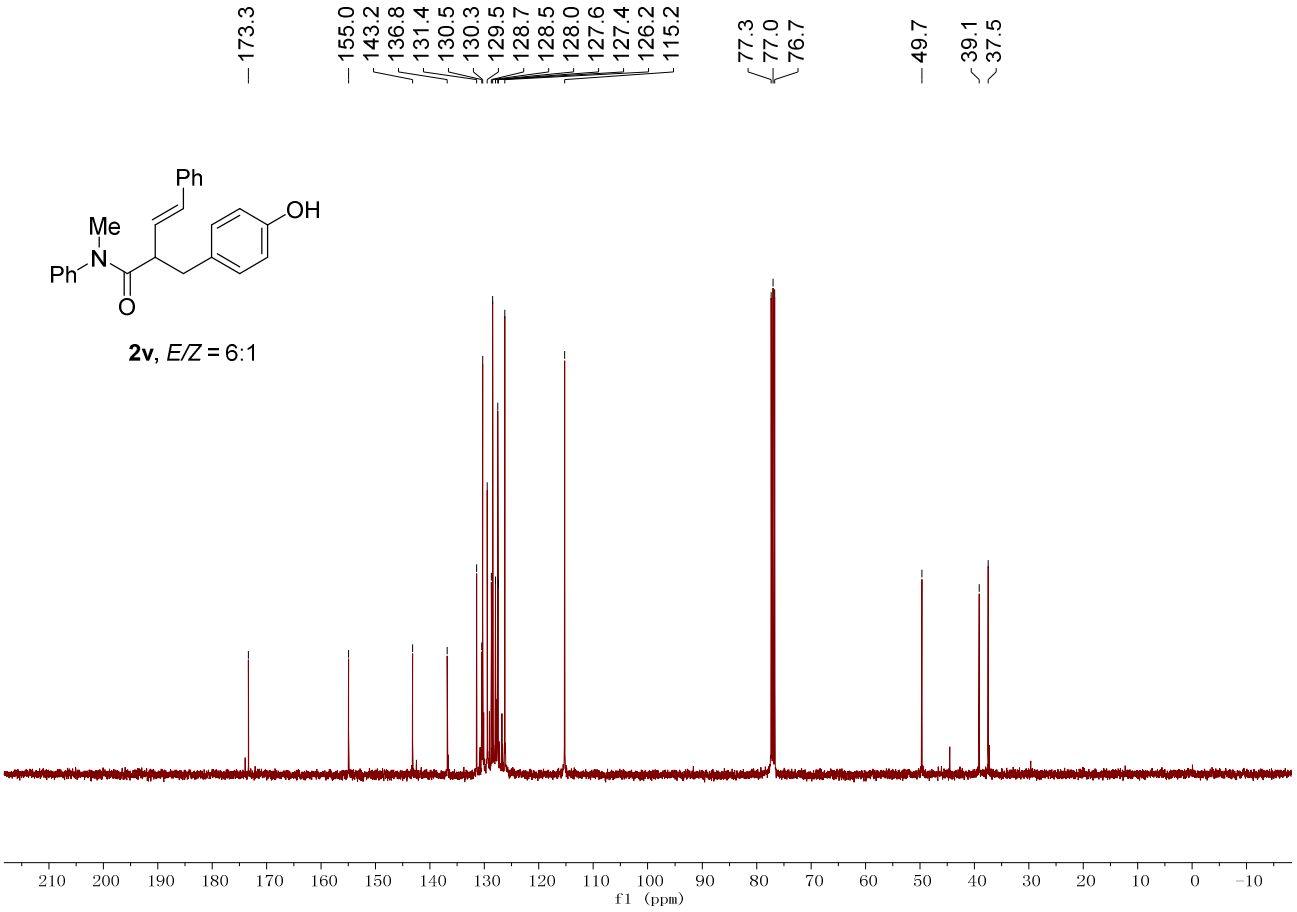
2u, *E*/*Z* = 12:1

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



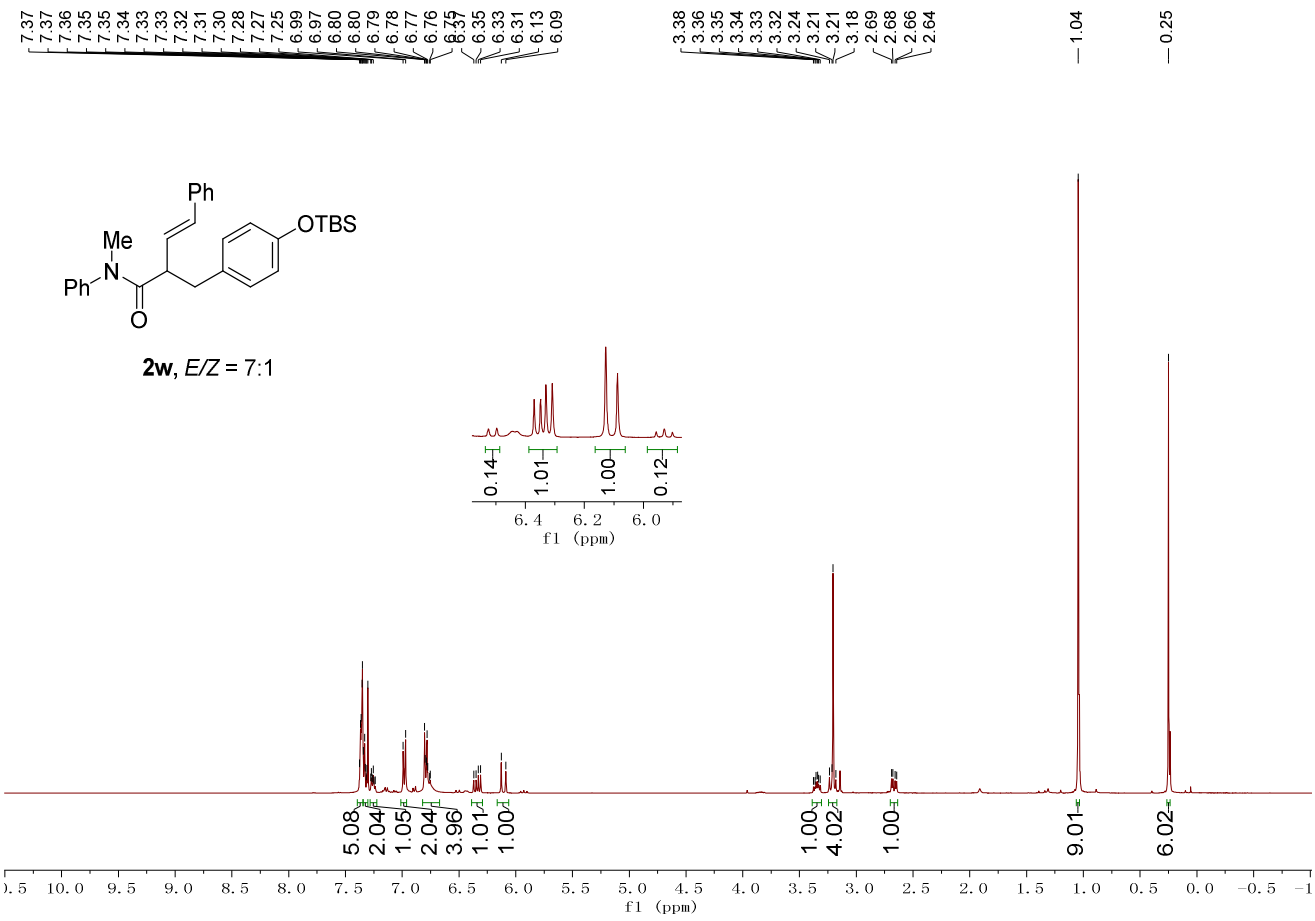
2v, *E*/*Z* = 6:1

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



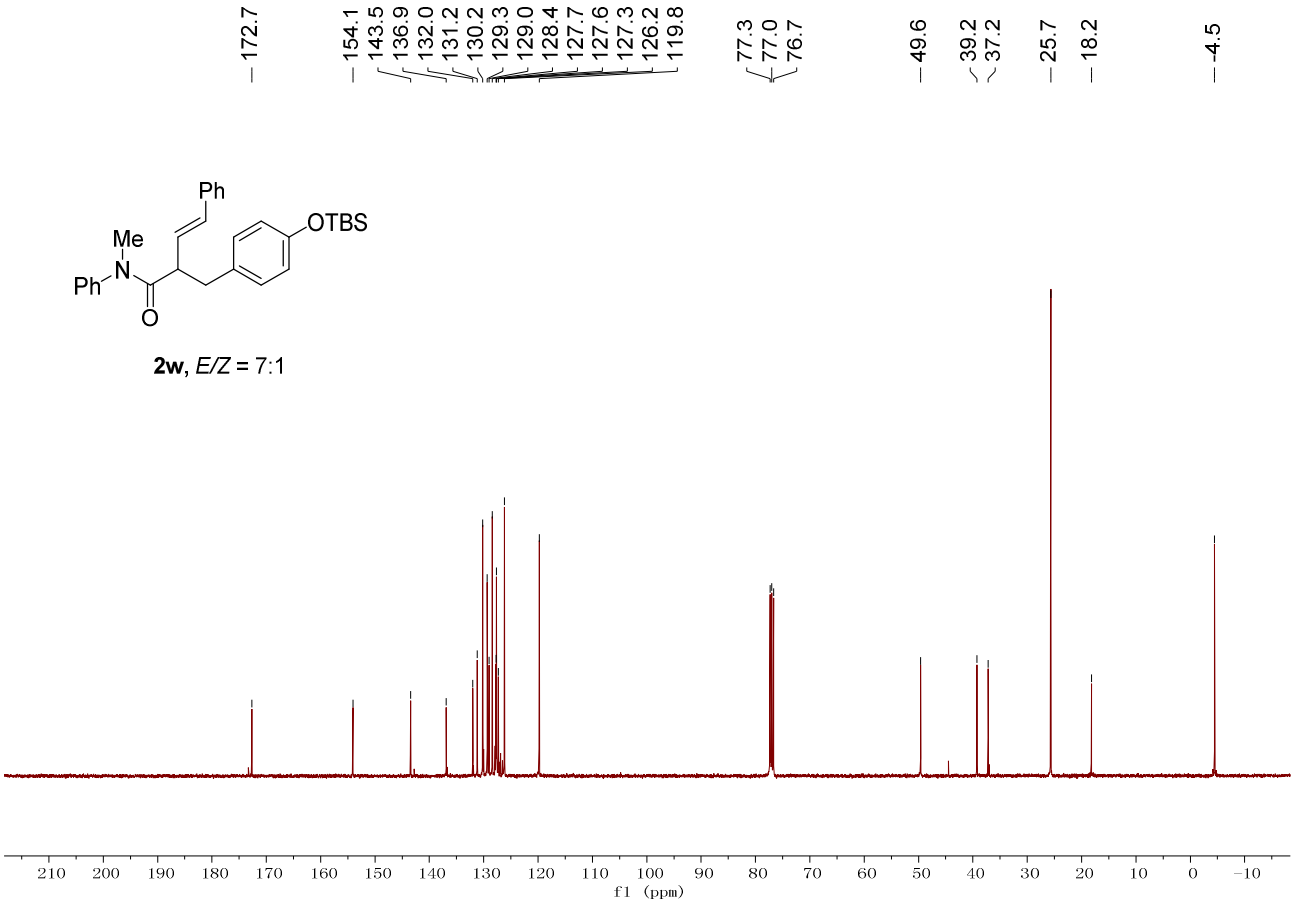
2v, *E*/*Z* = 6:1

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



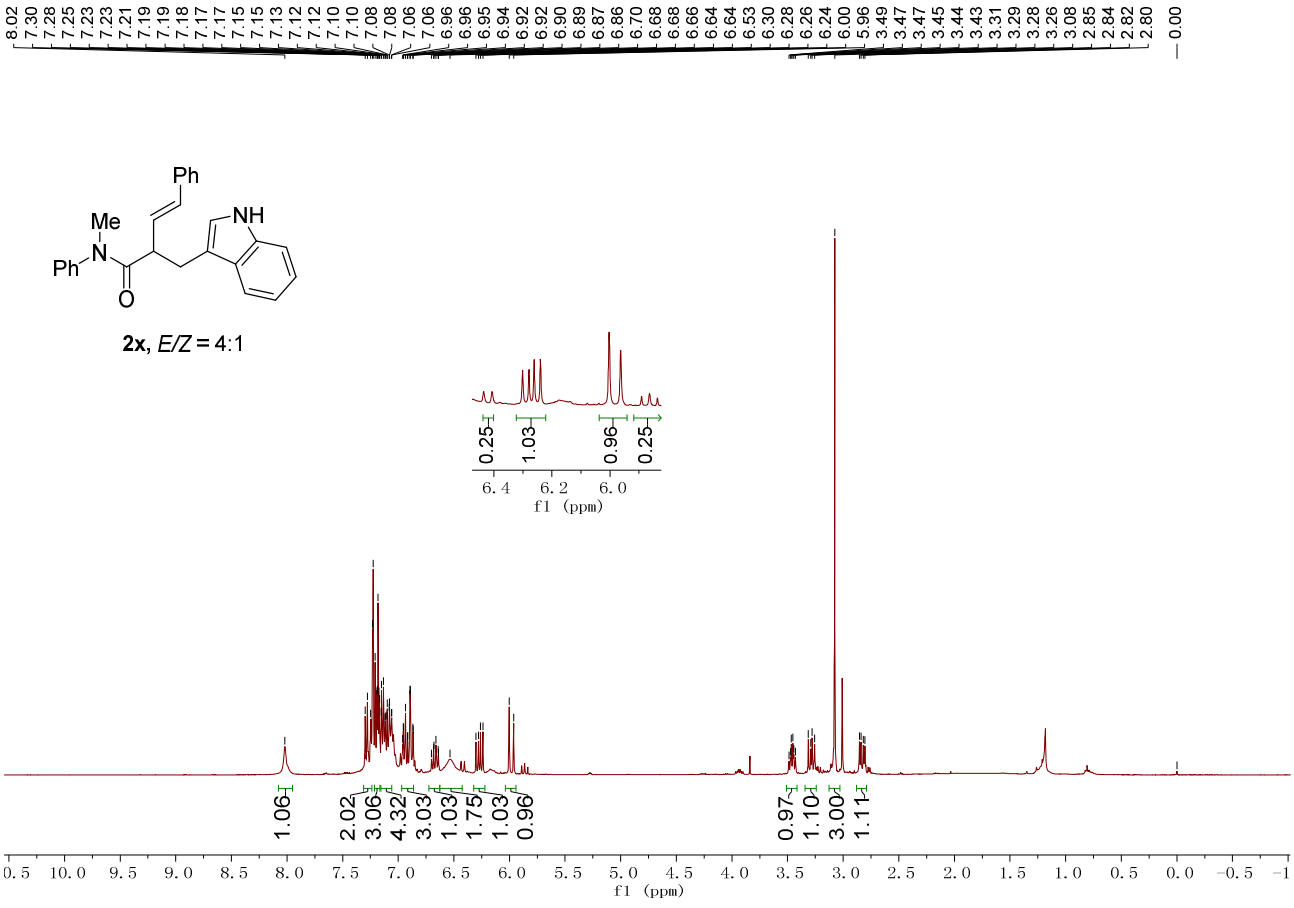
2w, *E*/*Z* = 7:1

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



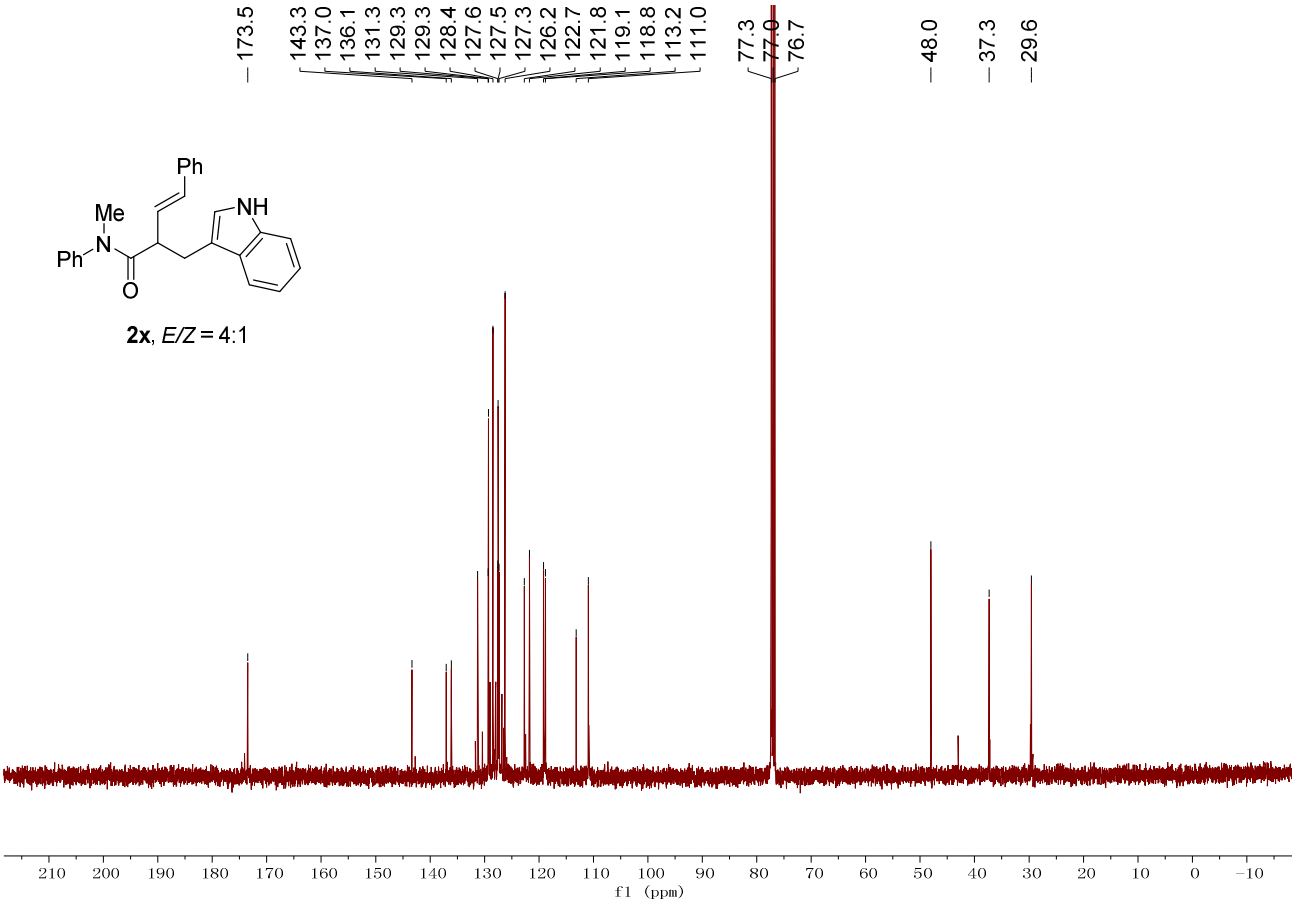
2w, *E/Z* = 7:1

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



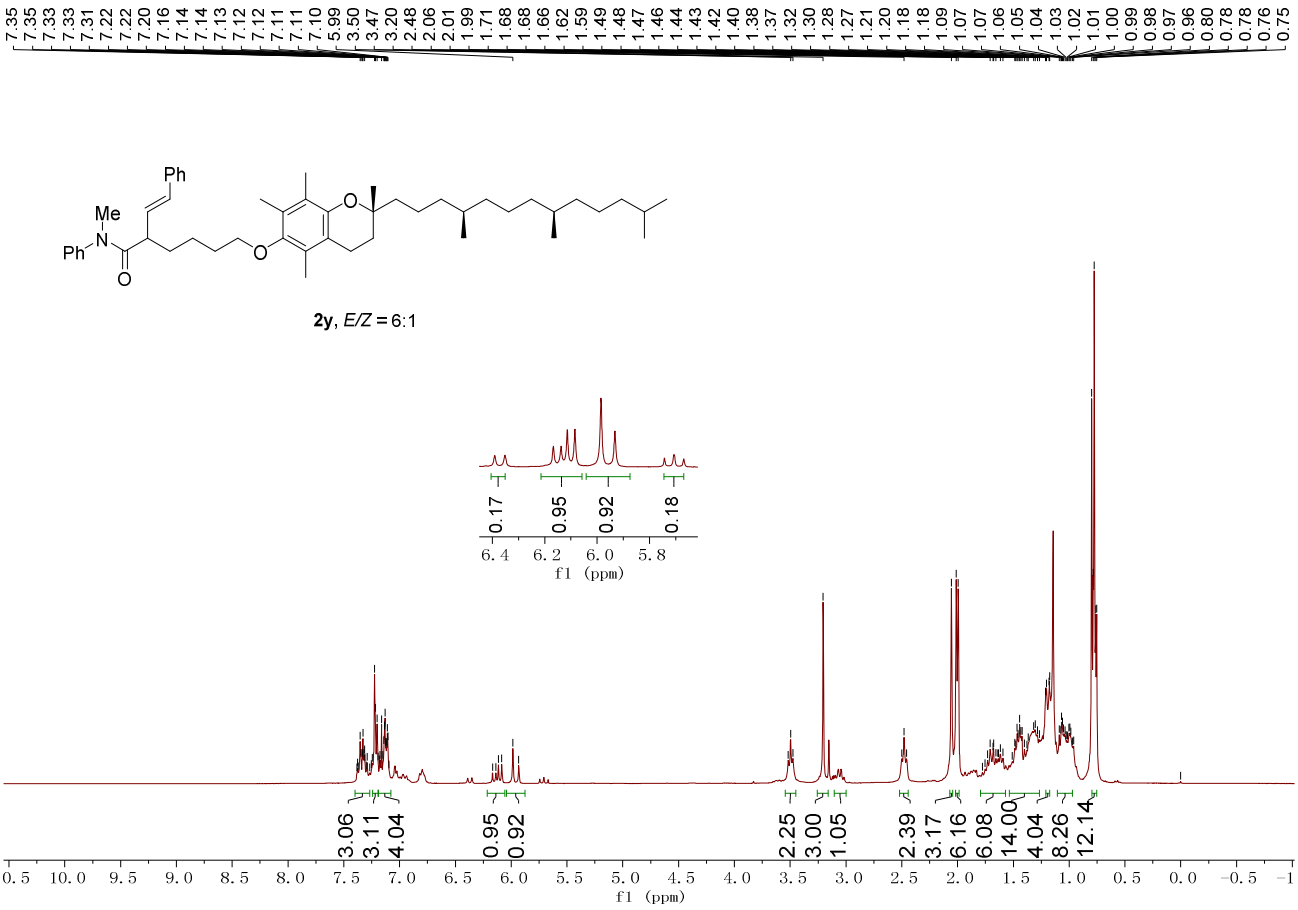
2x, *E/Z* = 4:1

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



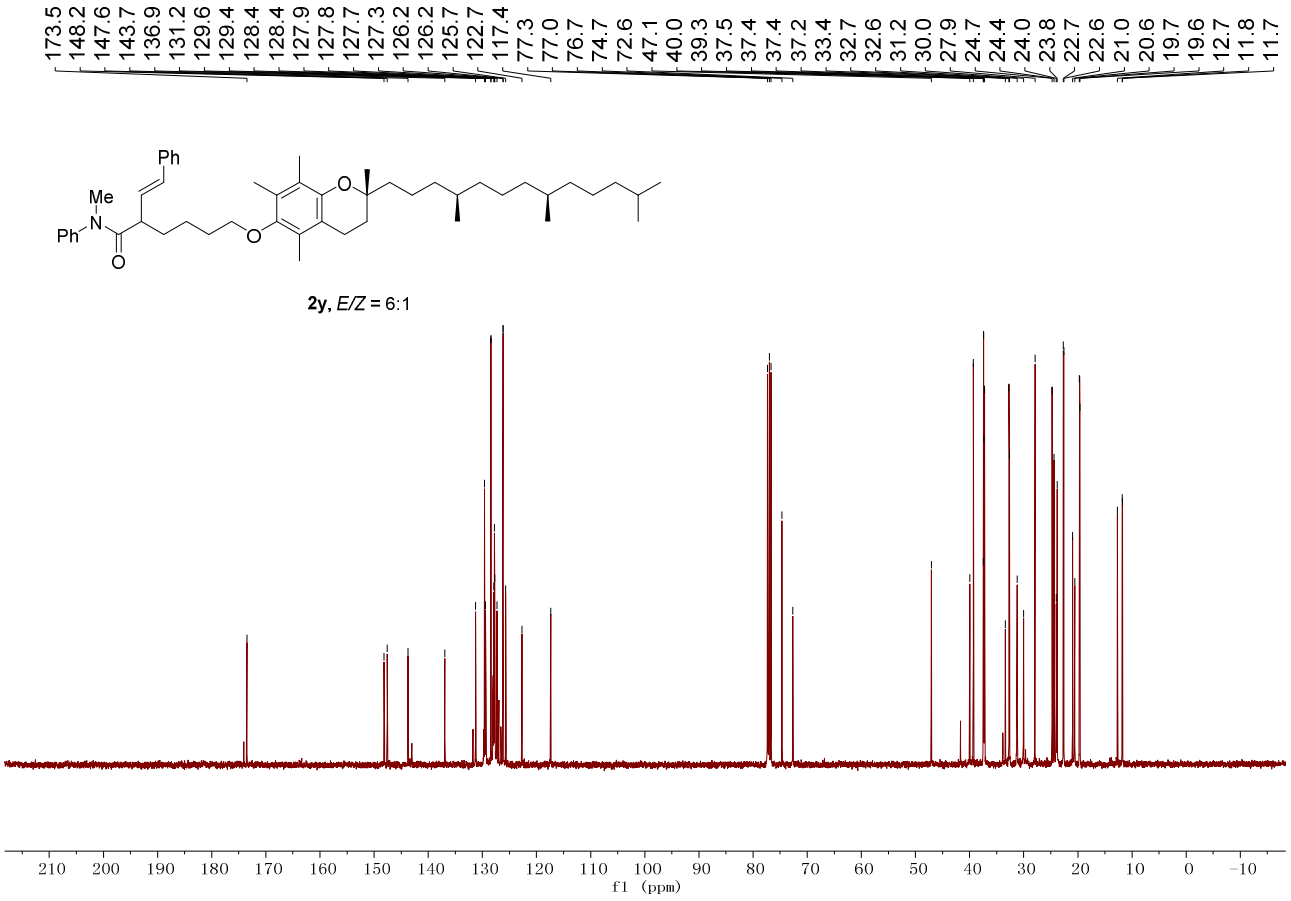
2x, *E*/*Z* = 4:1

^{1}H NMR (300 MHz, $CDCl_3$)

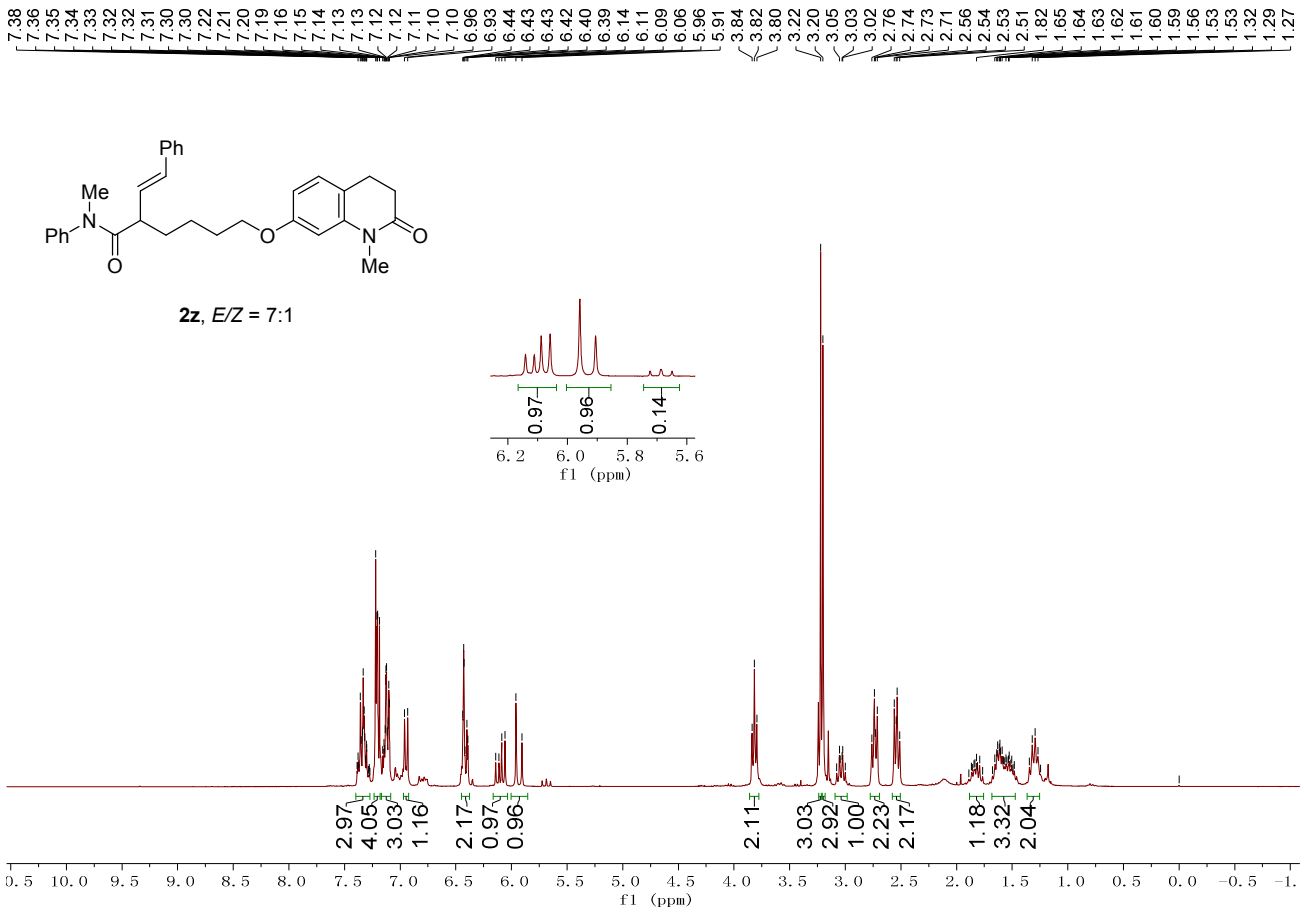


2y, *E*/*Z* = 6:1

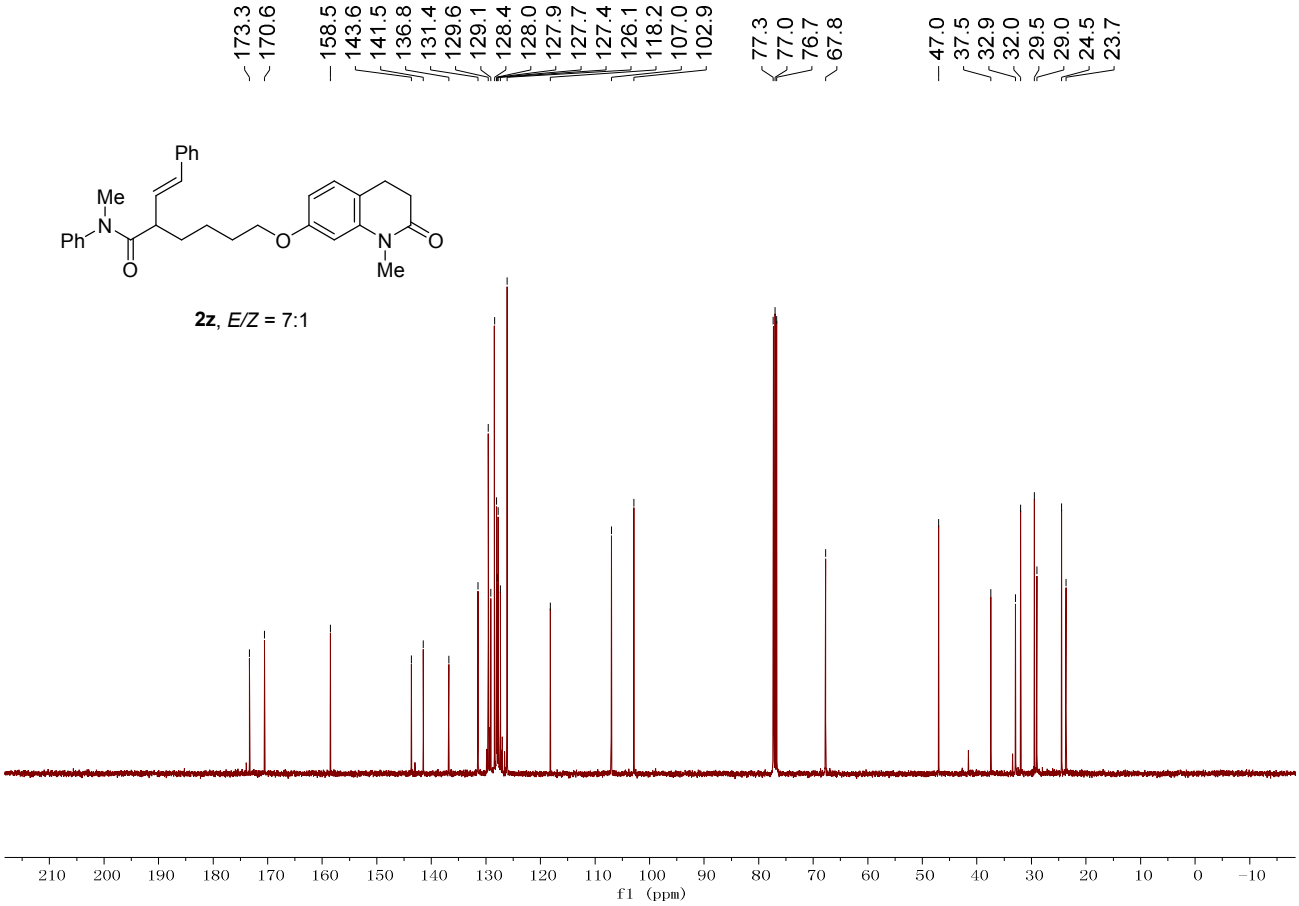
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

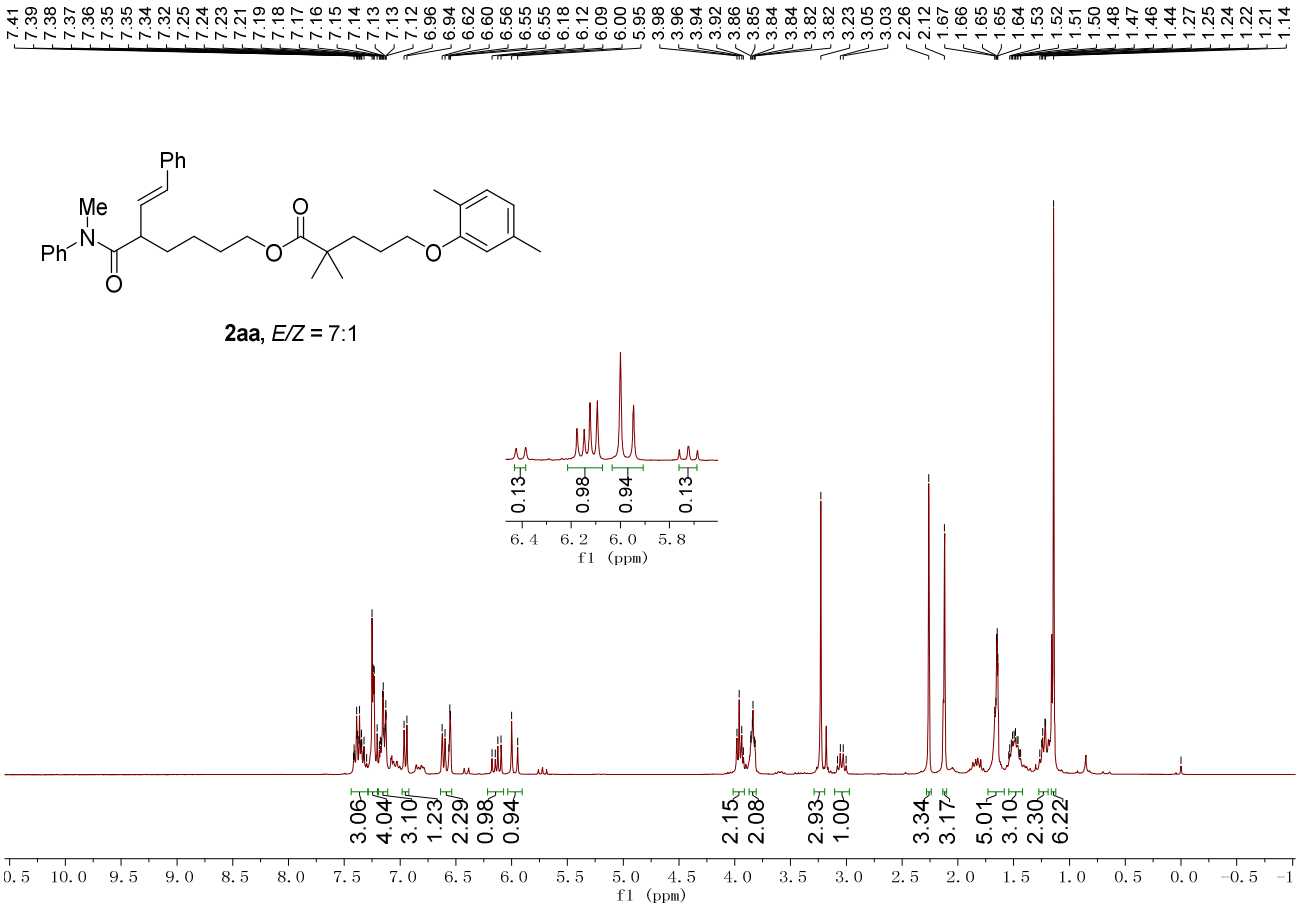


^{13}C NMR (101 MHz, $CDCl_3$)



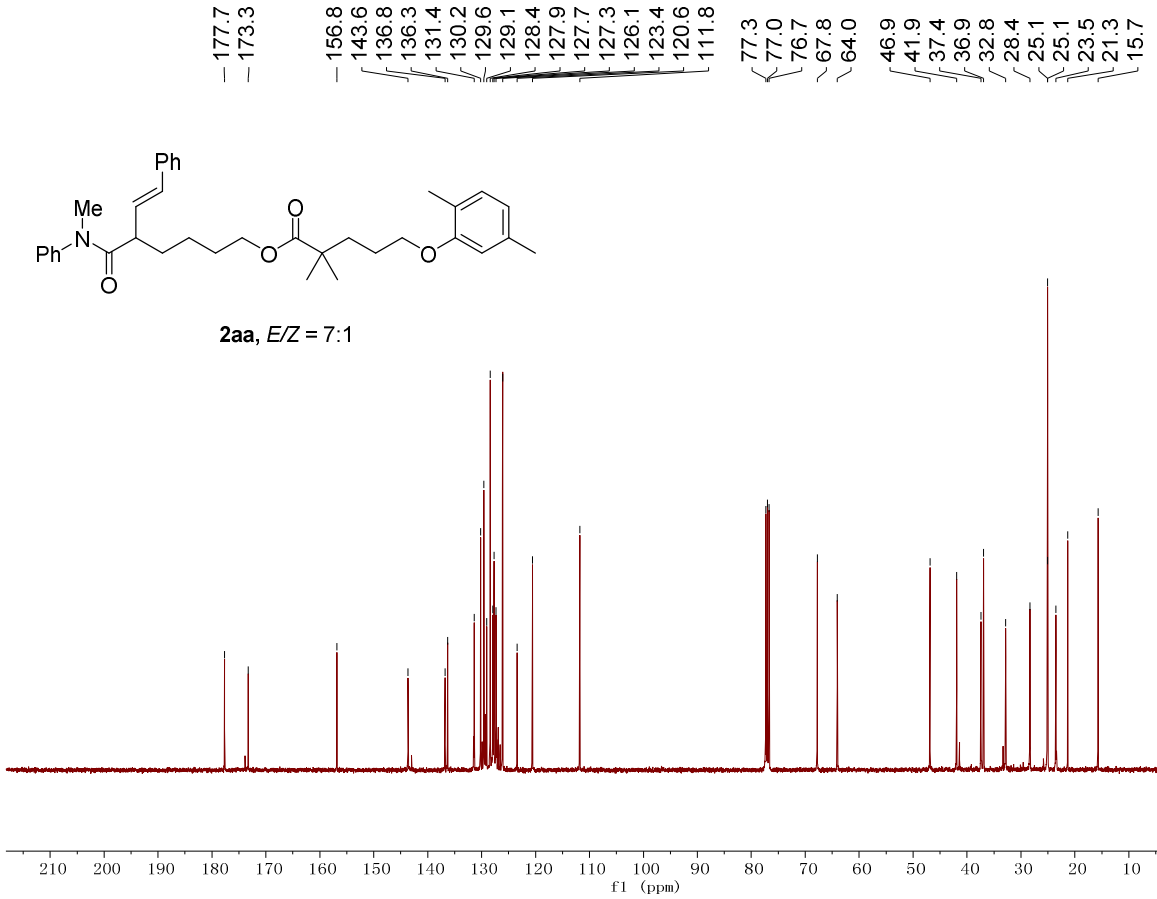
2z, *E/Z* = 7:1

^{1}H NMR (300 MHz, $CDCl_3$)



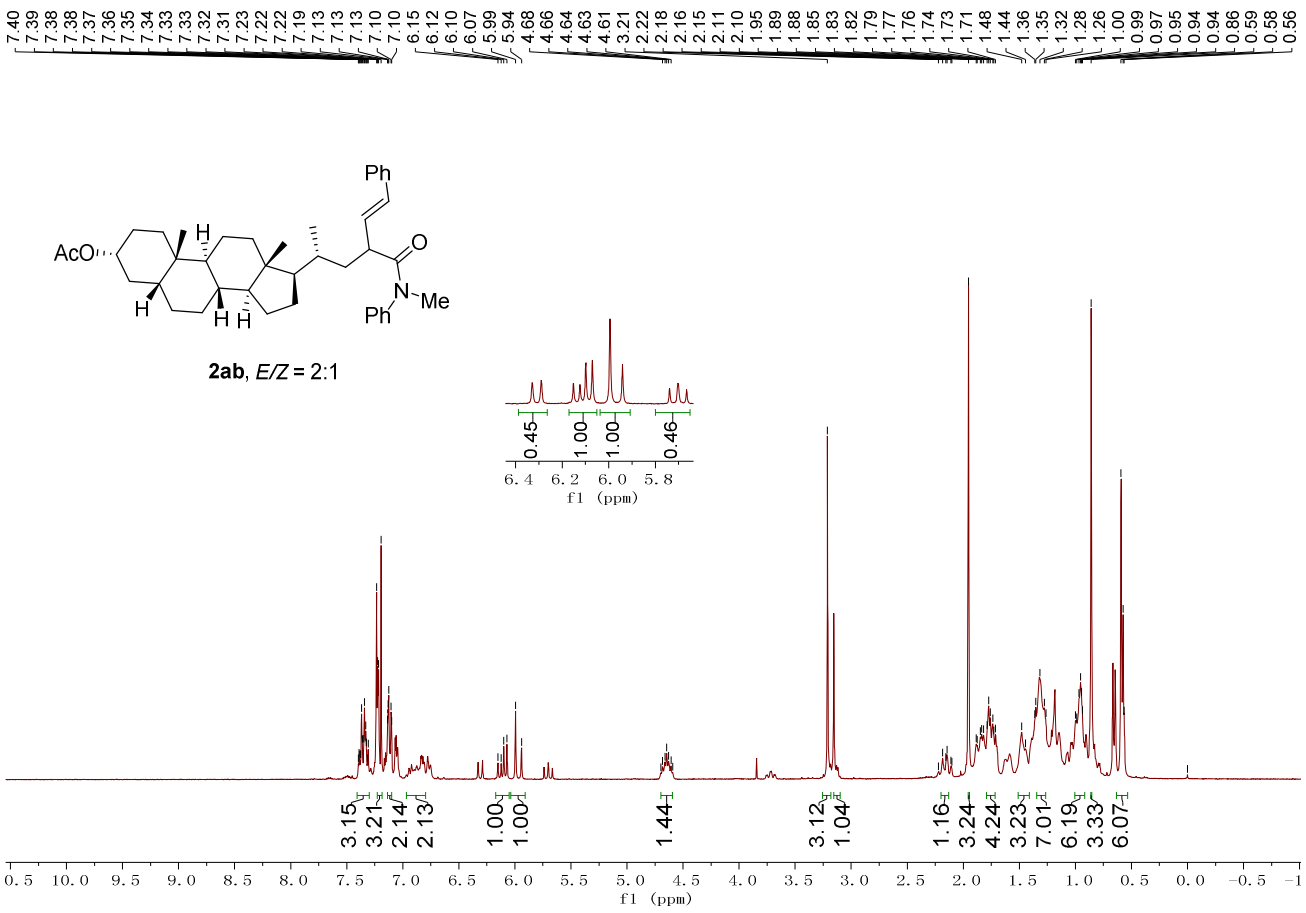
2aa, *E/Z* = 7:1

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



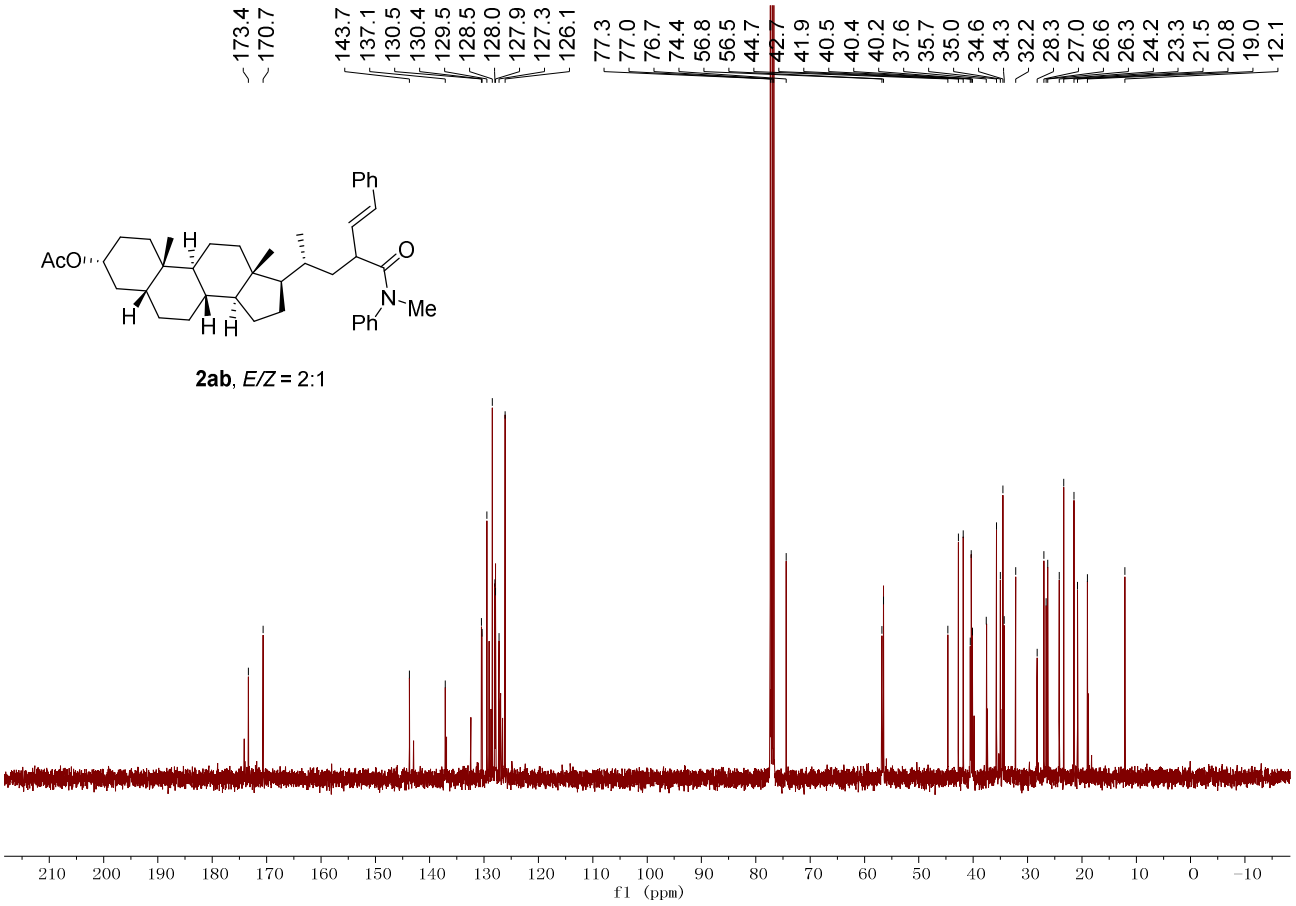
2aa, *E/Z* = 7:1

^{1}H NMR (300 MHz, $CDCl_3$)

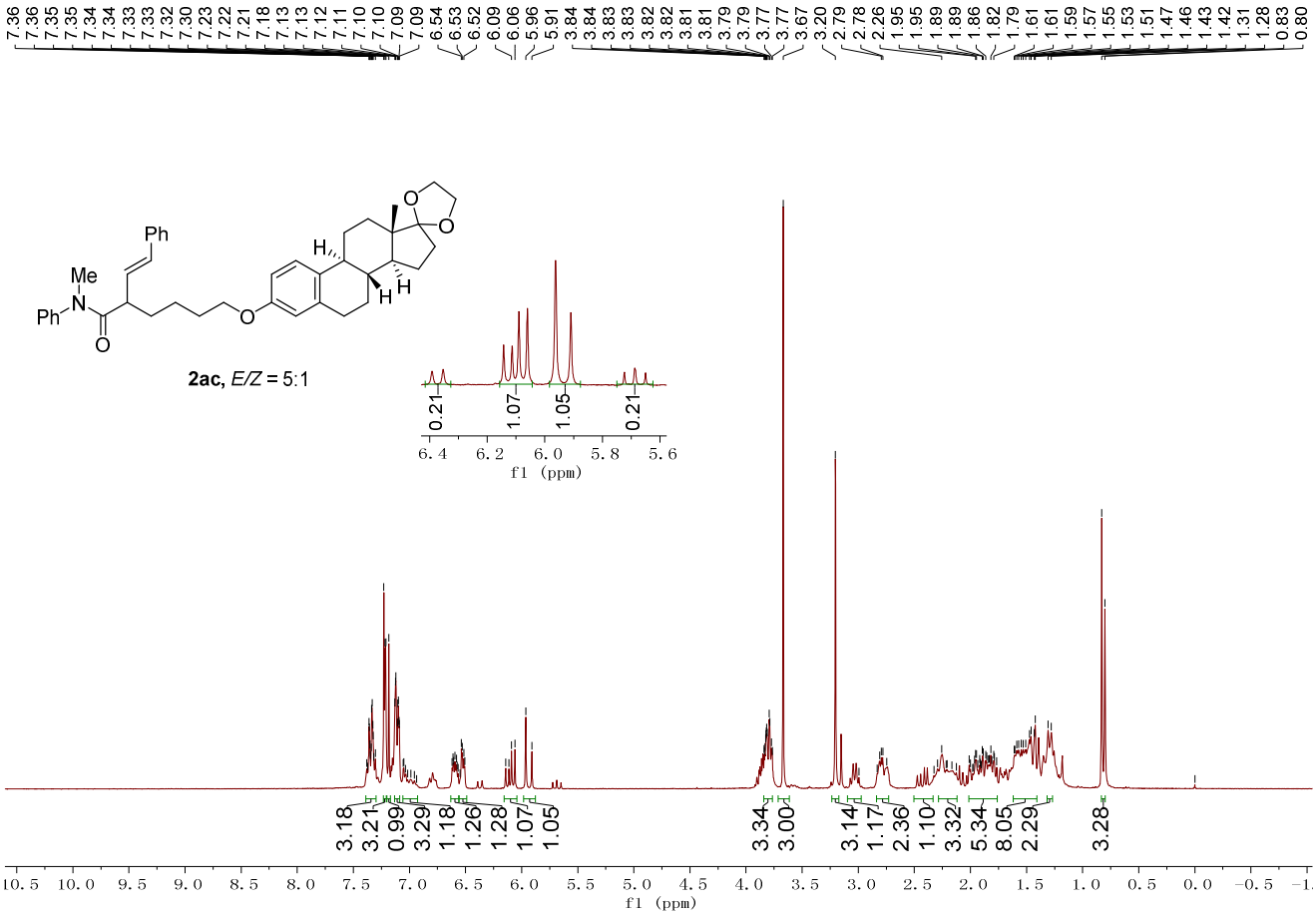


2ab, *E/Z* = 2:1

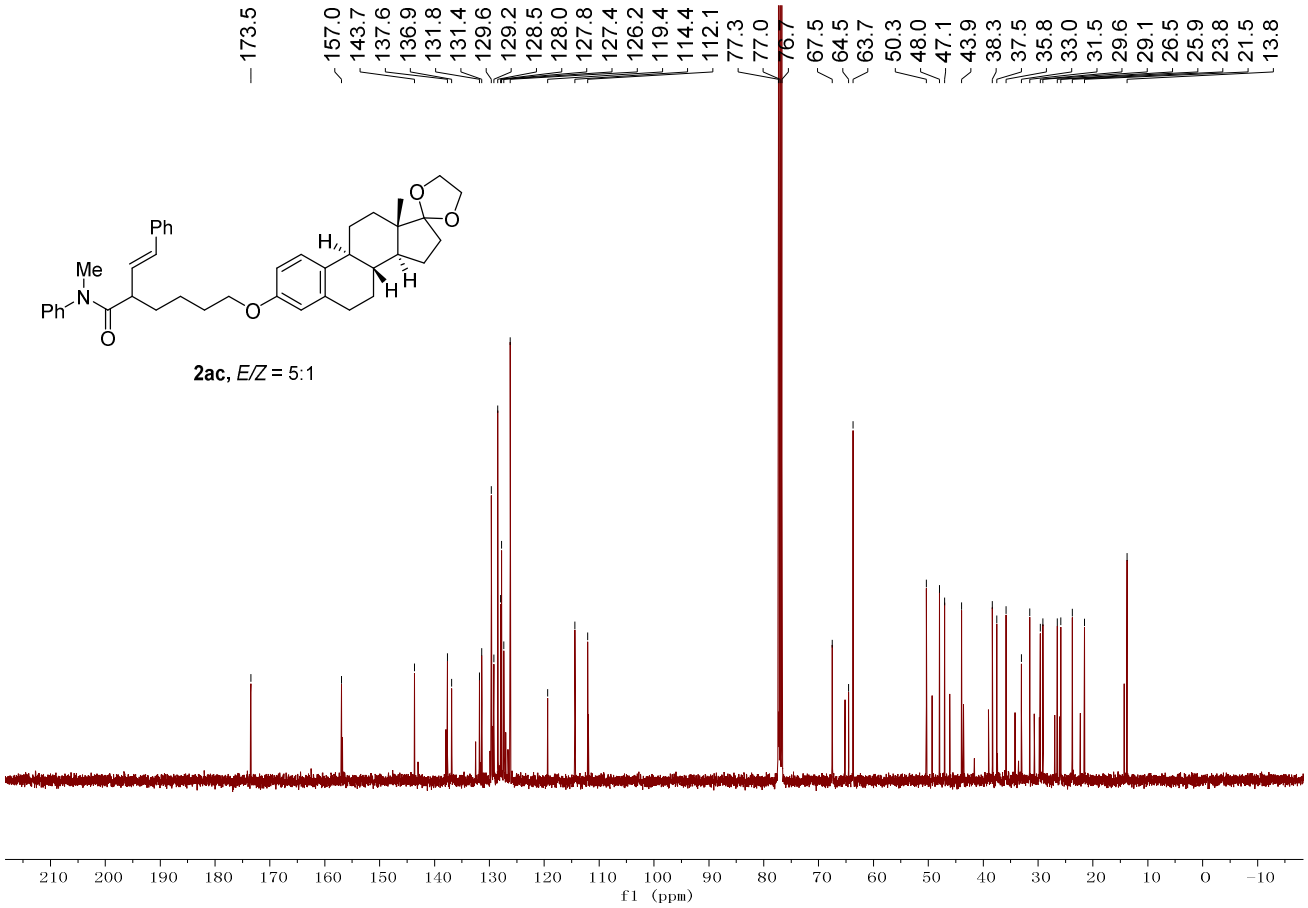
^{13}C NMR (101 MHz, $CDCl_3$)



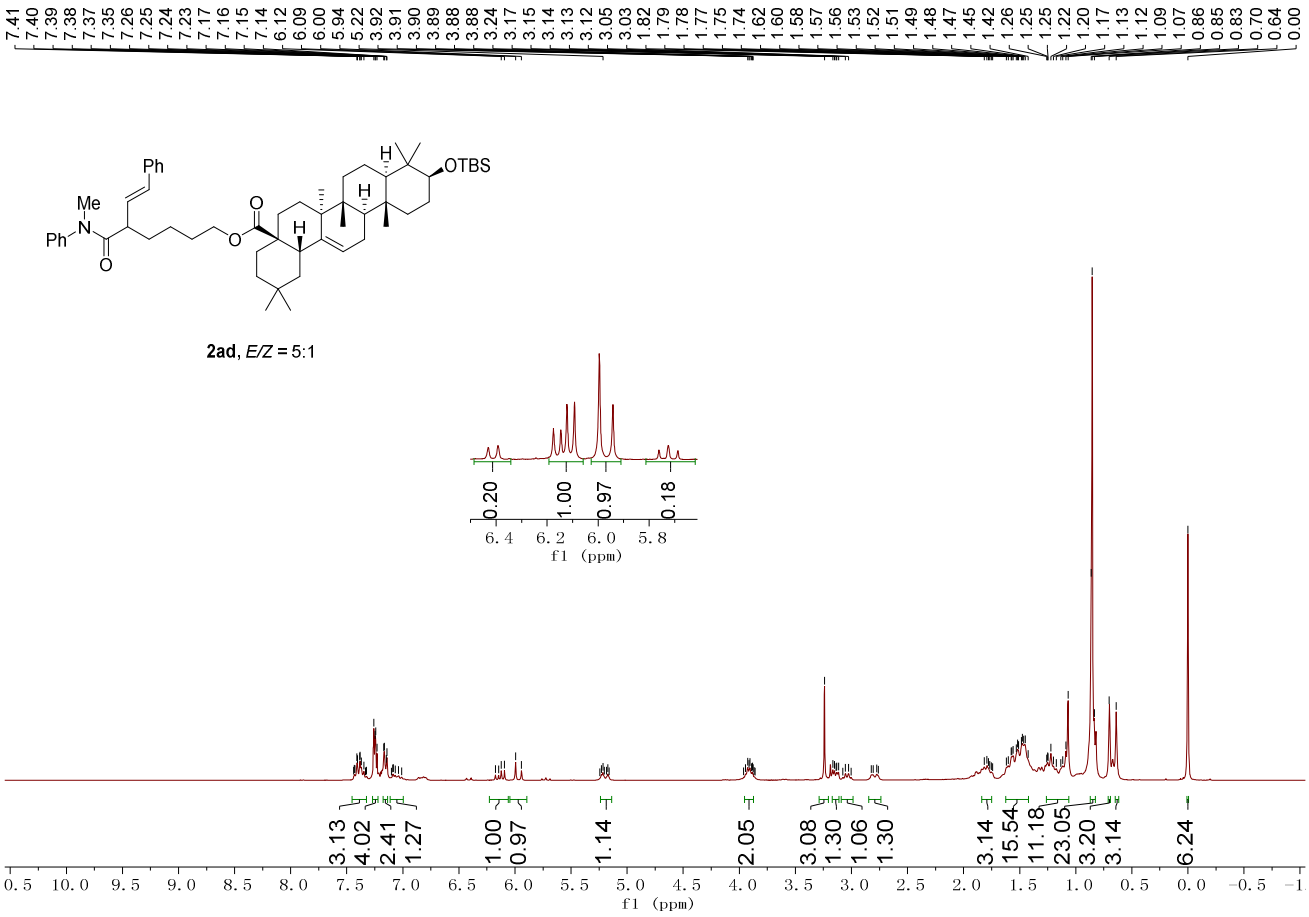
^{1}H NMR (300 MHz, $CDCl_3$)



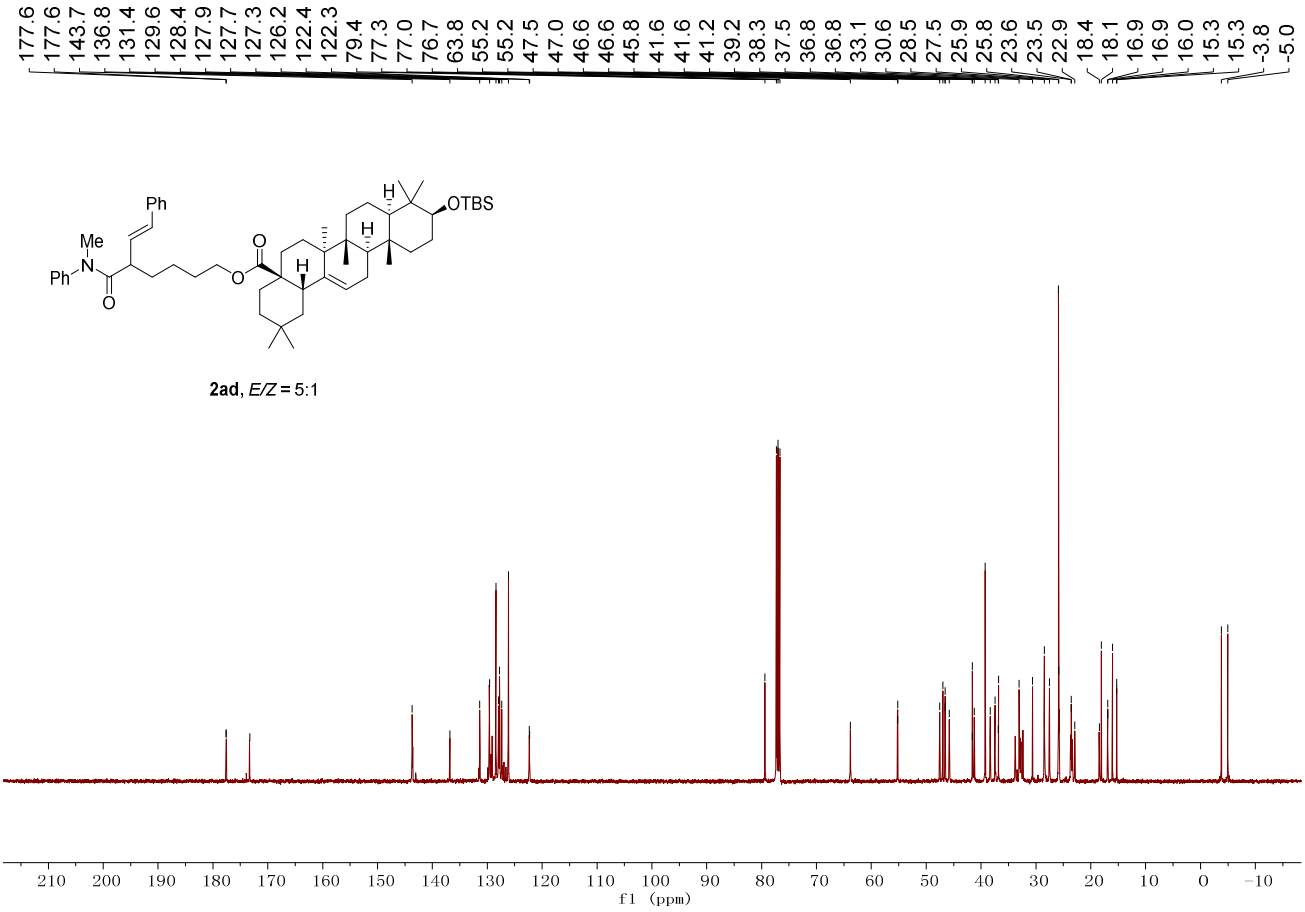
^{13}C NMR (101 MHz, $CDCl_3$)



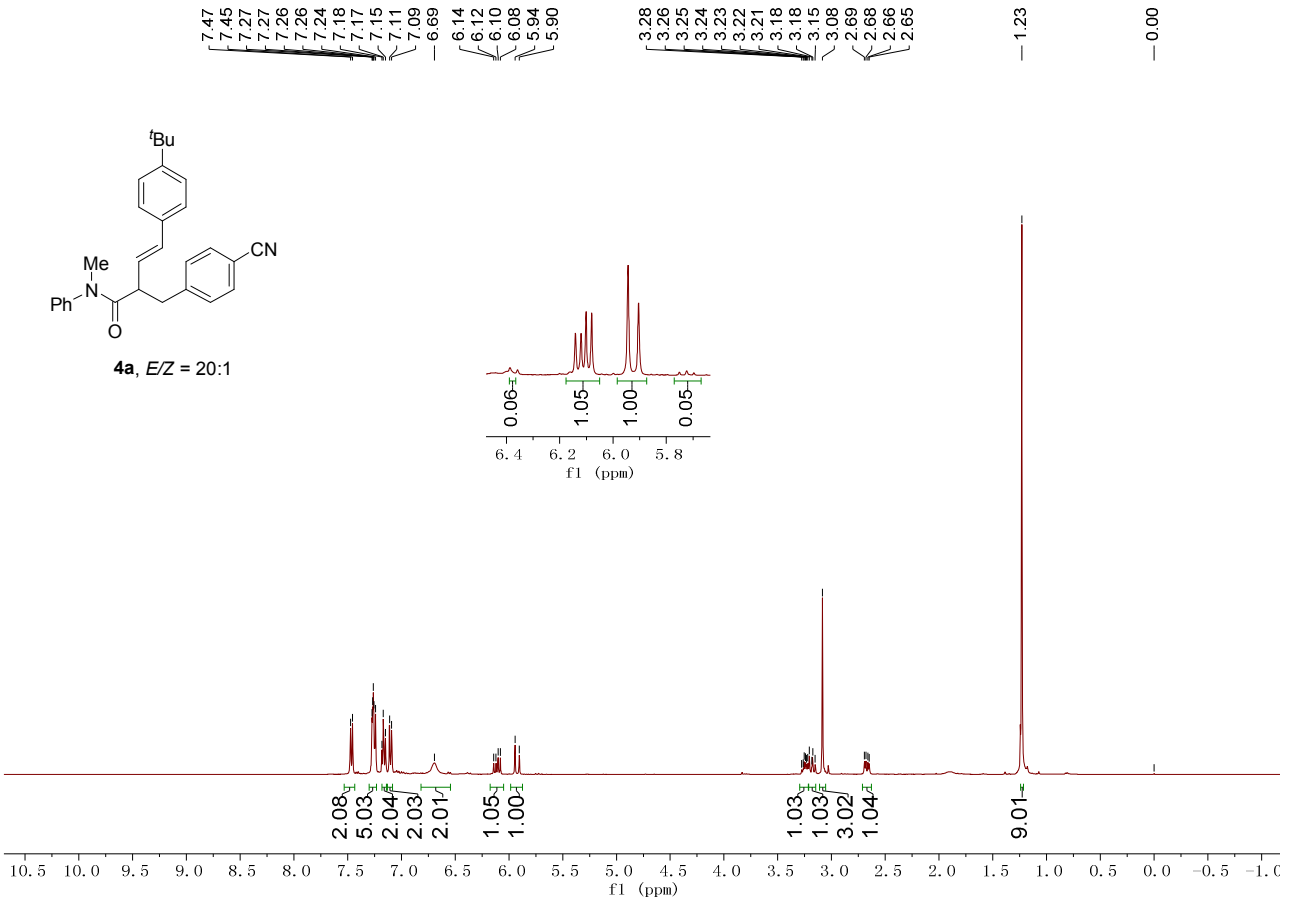
^{1}H NMR (300 MHz, $CDCl_3$)



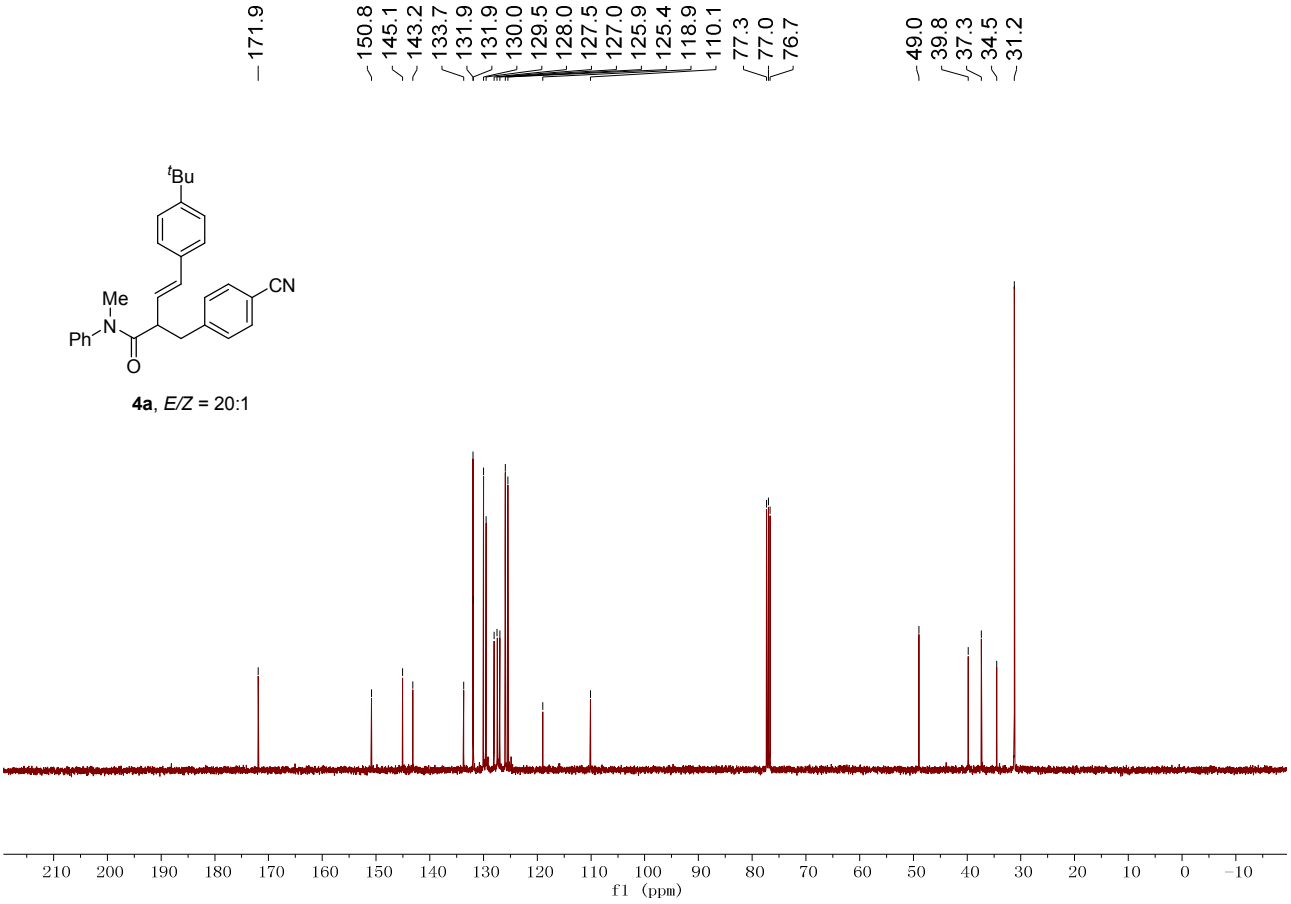
^{13}C NMR (101 MHz, $CDCl_3$)



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

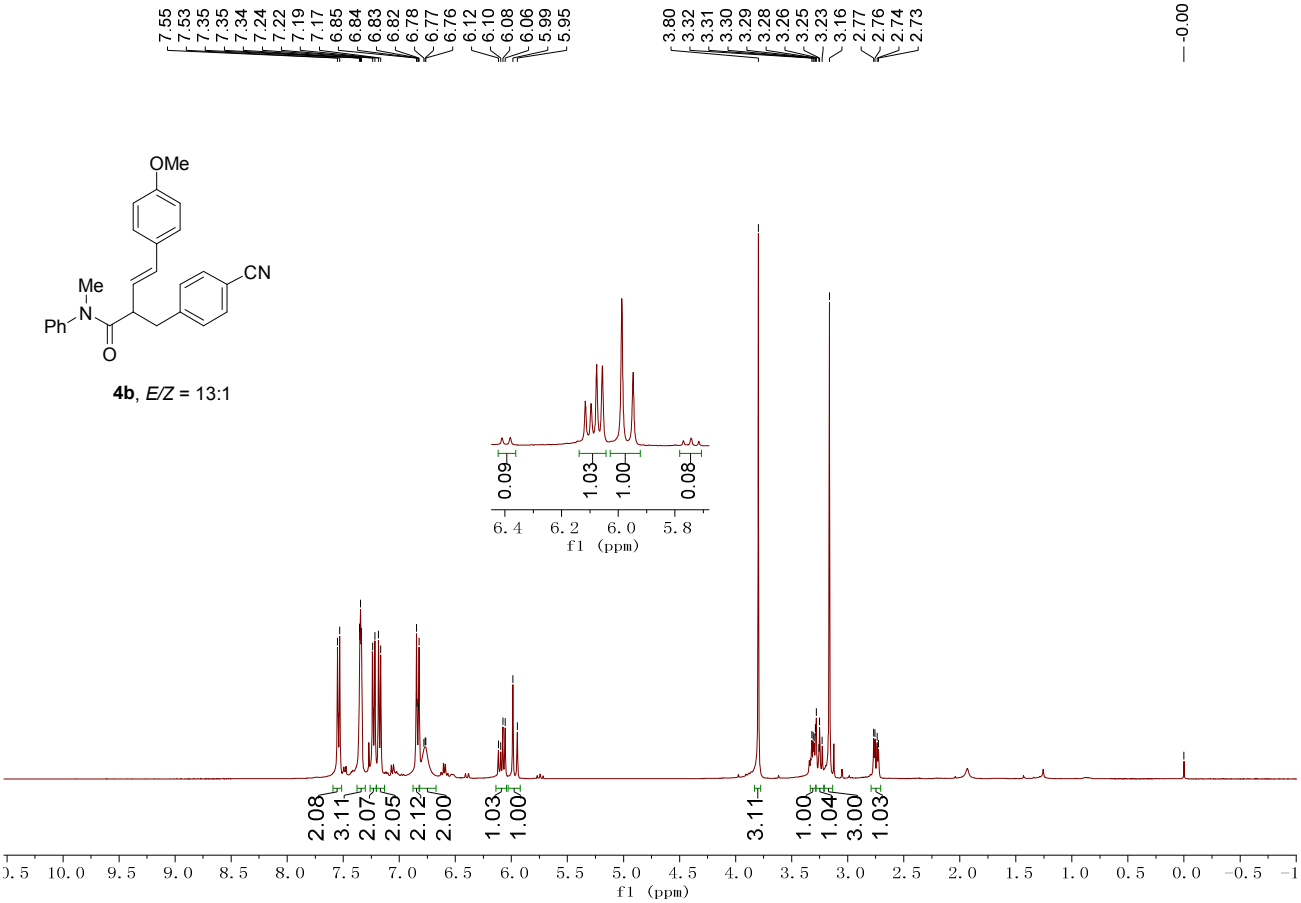


^{13}C NMR (101 MHz, $CDCl_3$)



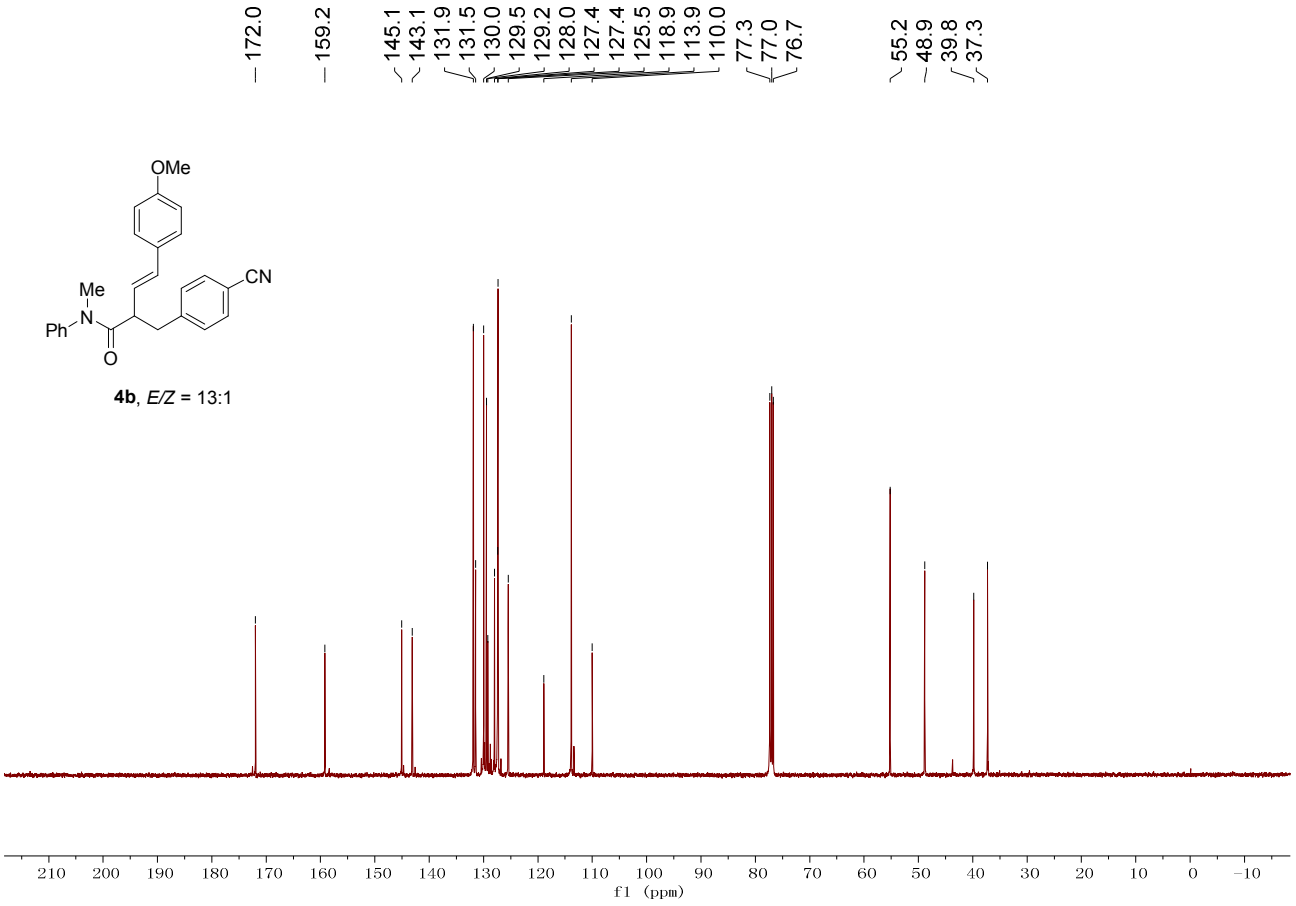
4a, *E/Z* = 20:1

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



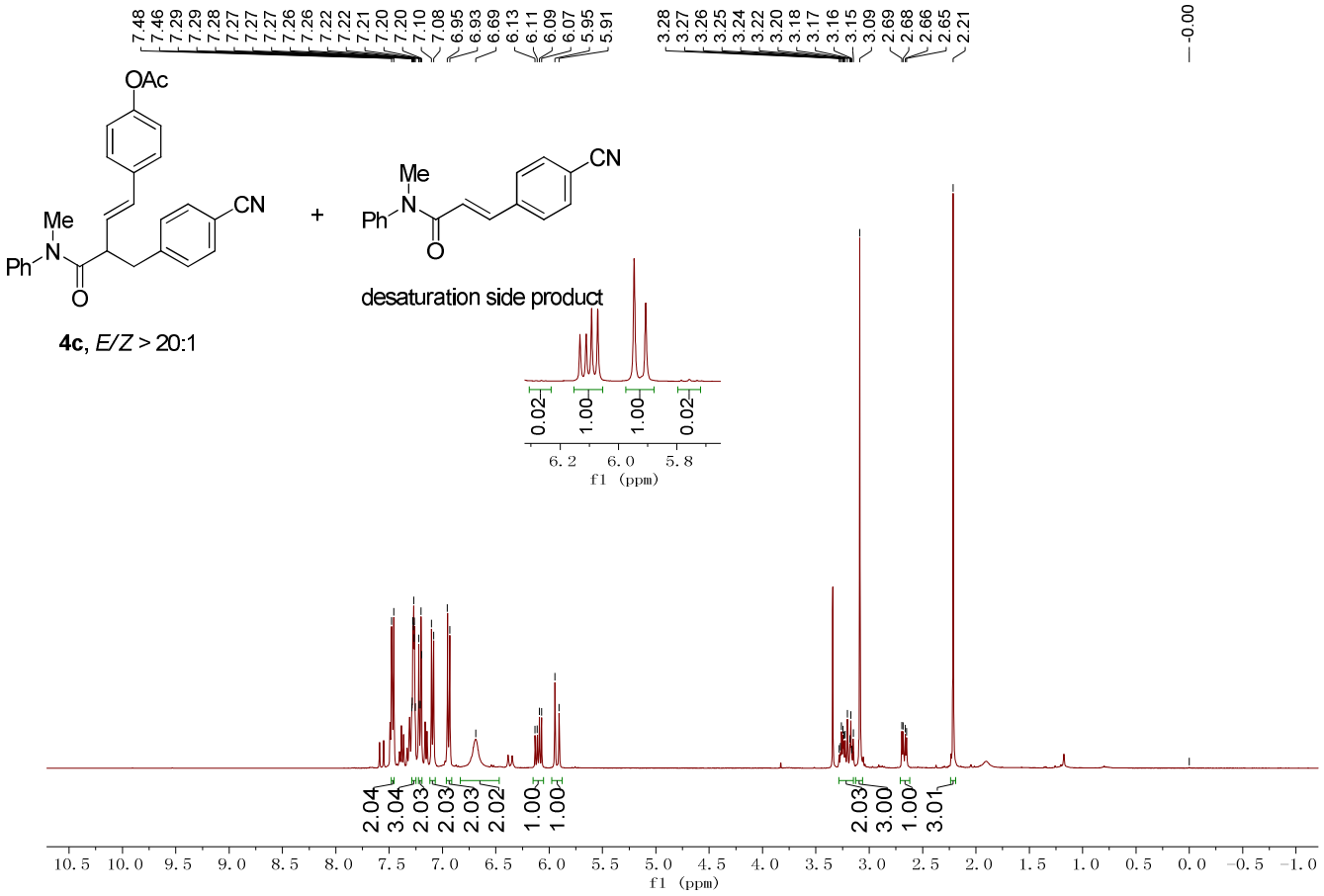
4b, *E/Z* = 13:1

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



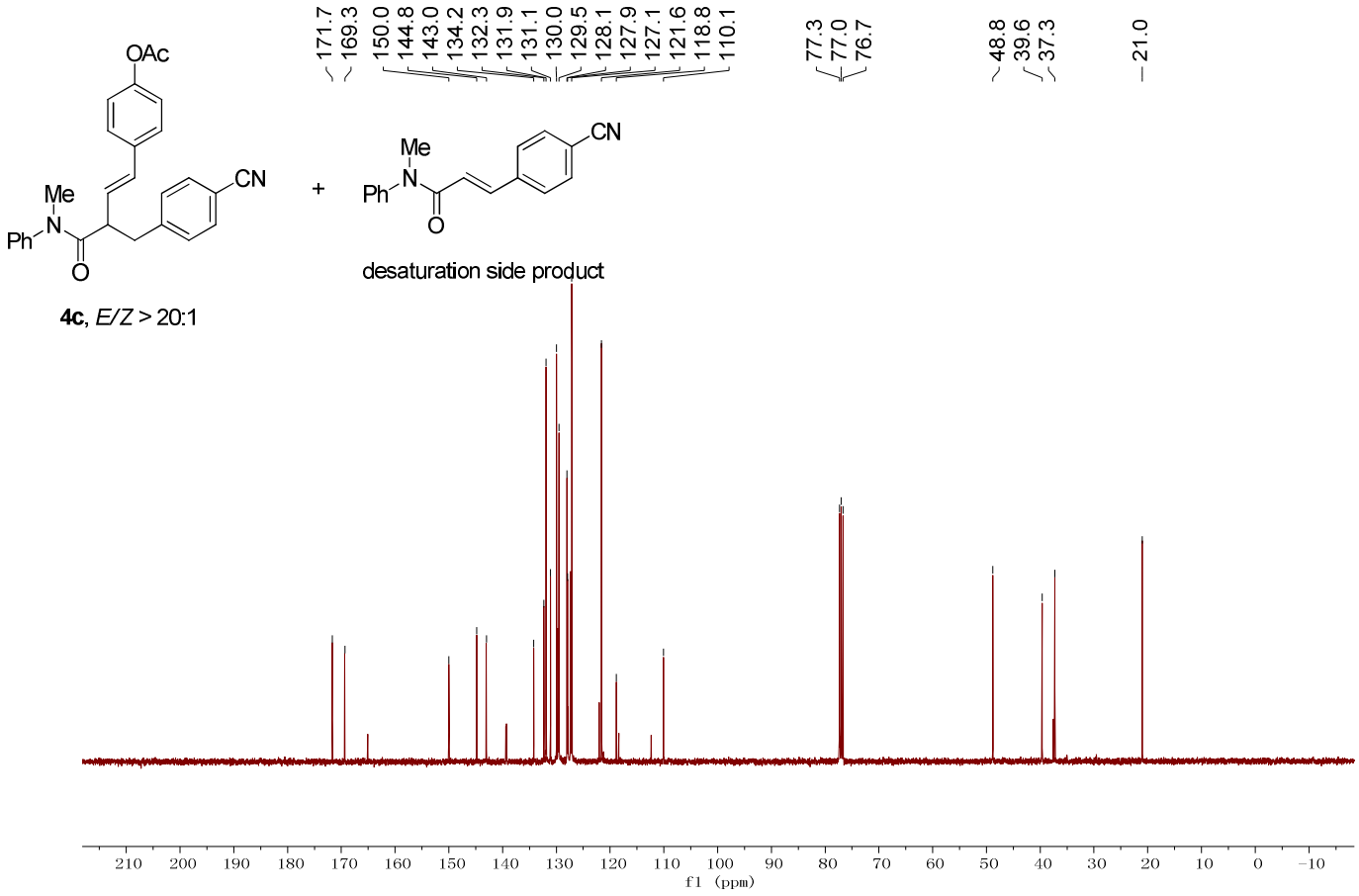
4b, *E*/*Z* = 13:1

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

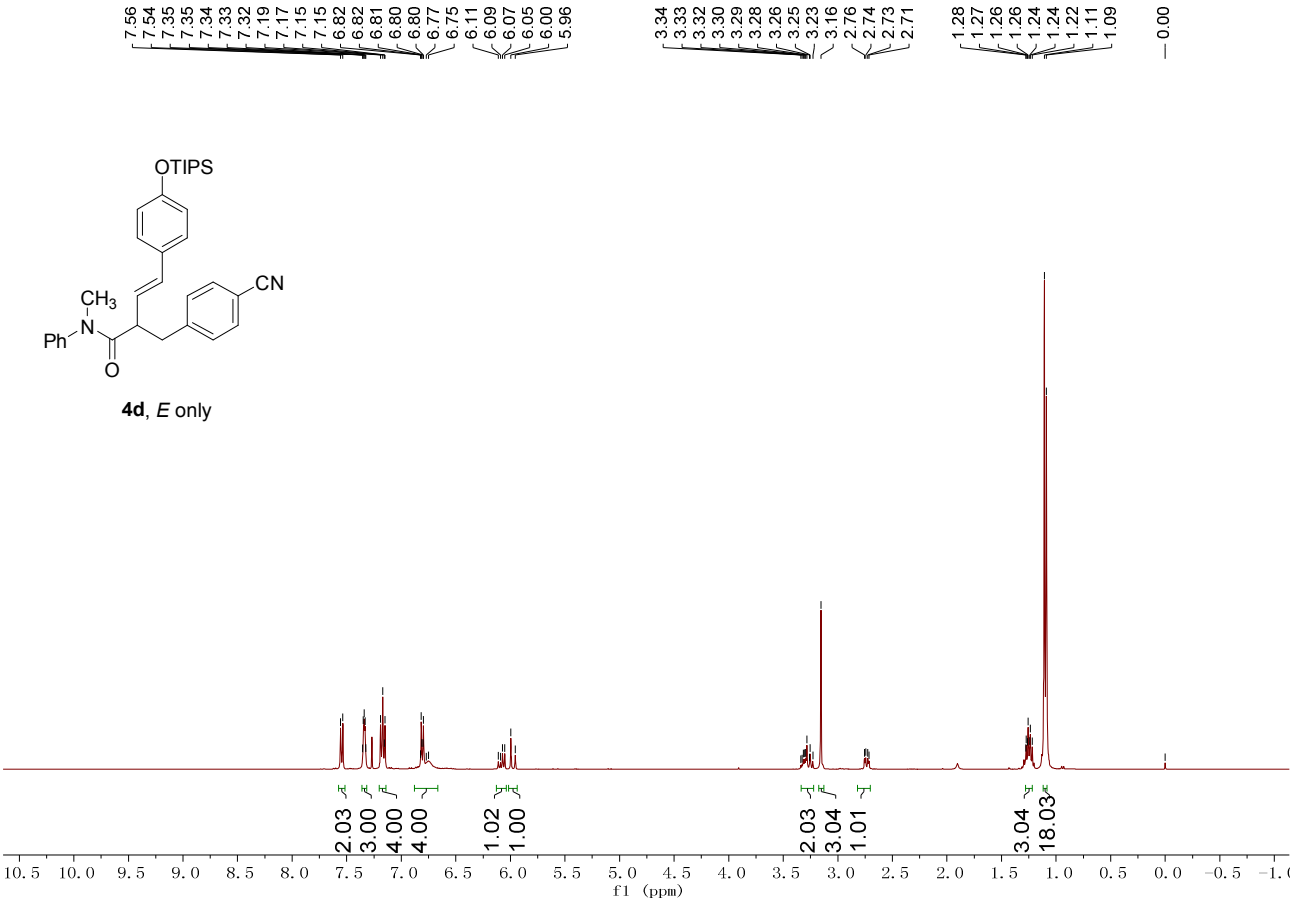


4c, *E*/*Z* > 20:1

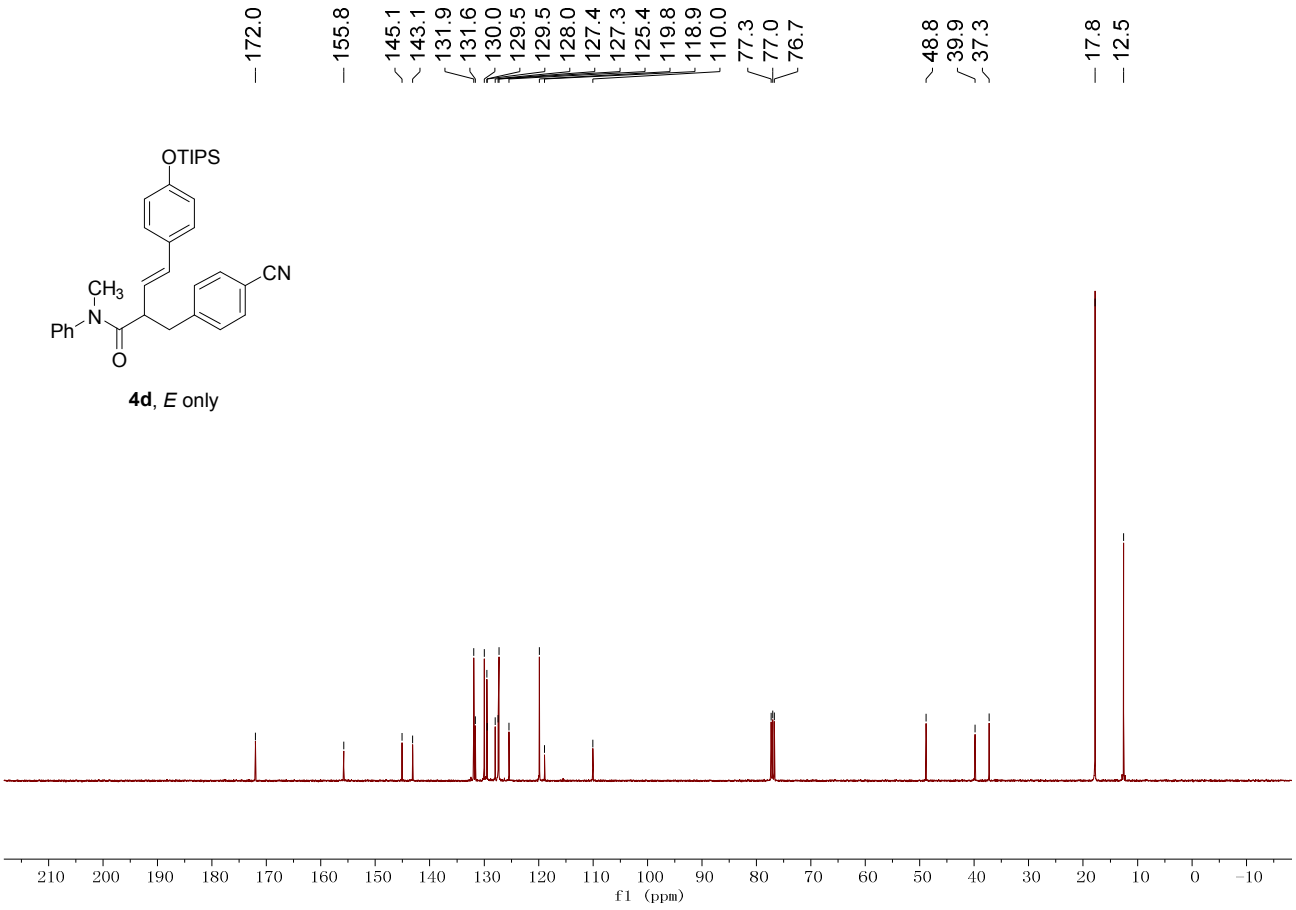
^{13}C NMR (101 MHz, $CDCl_3$)



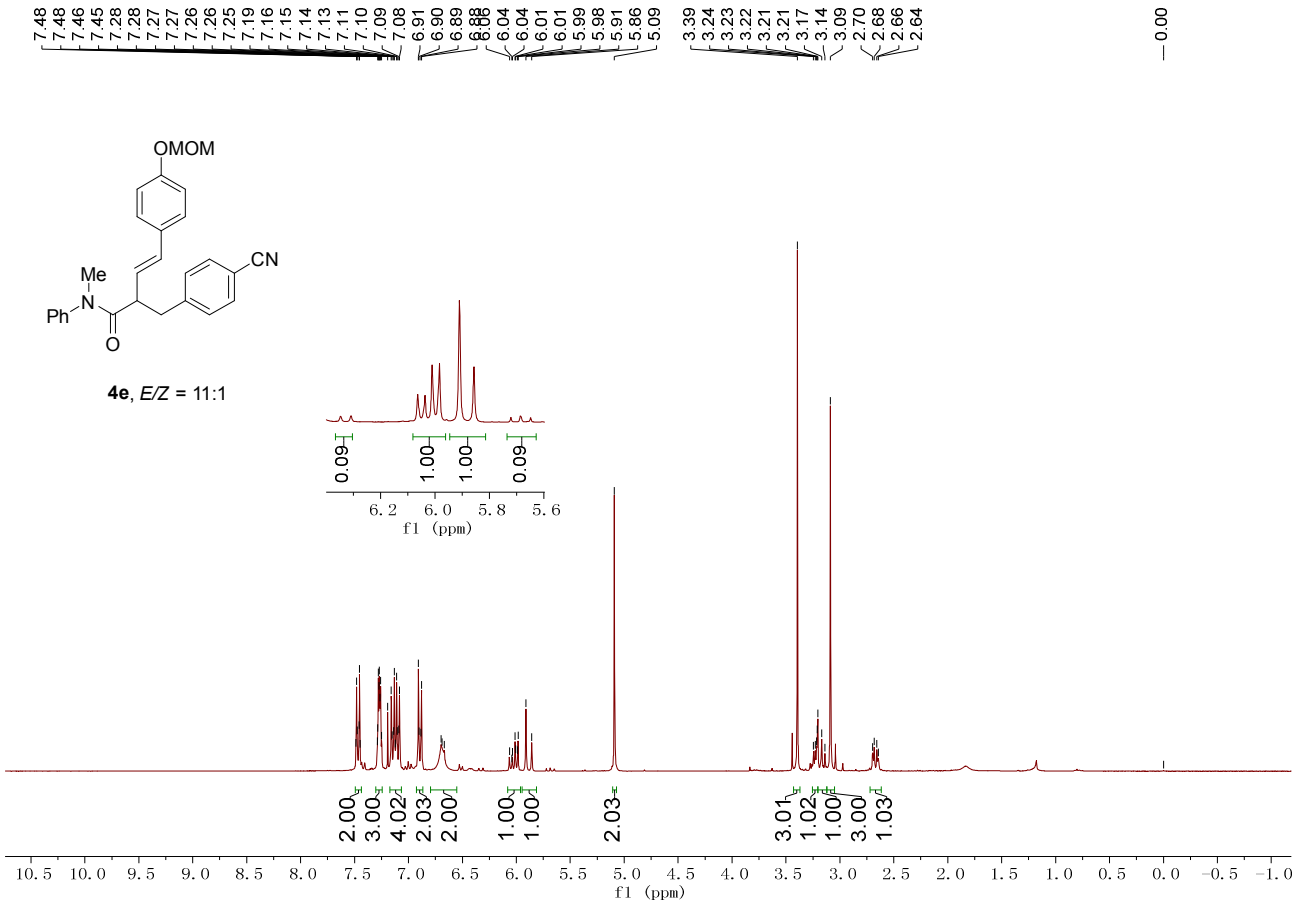
^{1}H NMR (400MHz, $CDCl_3$)



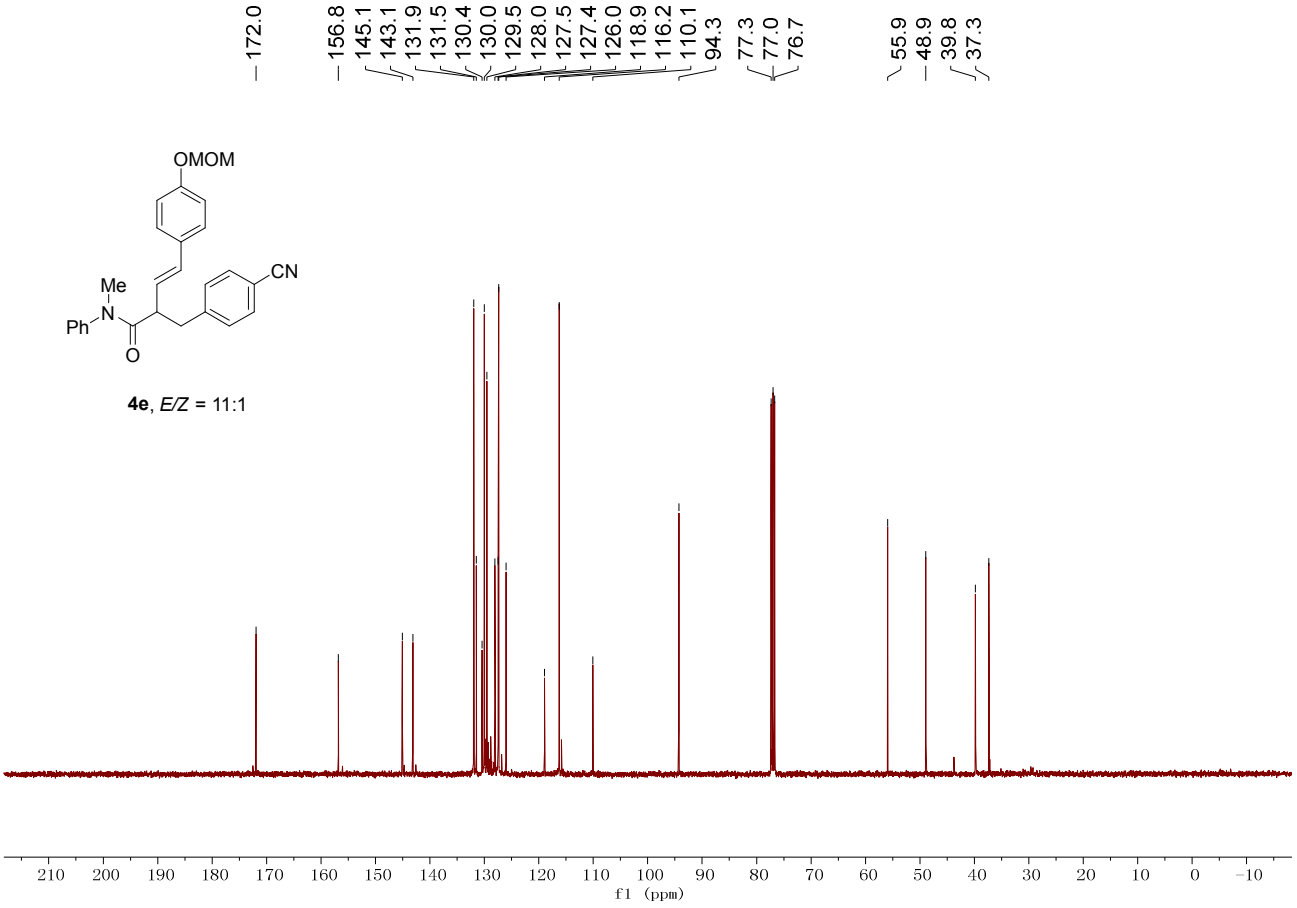
^{13}C NMR (101 MHz, $CDCl_3$)



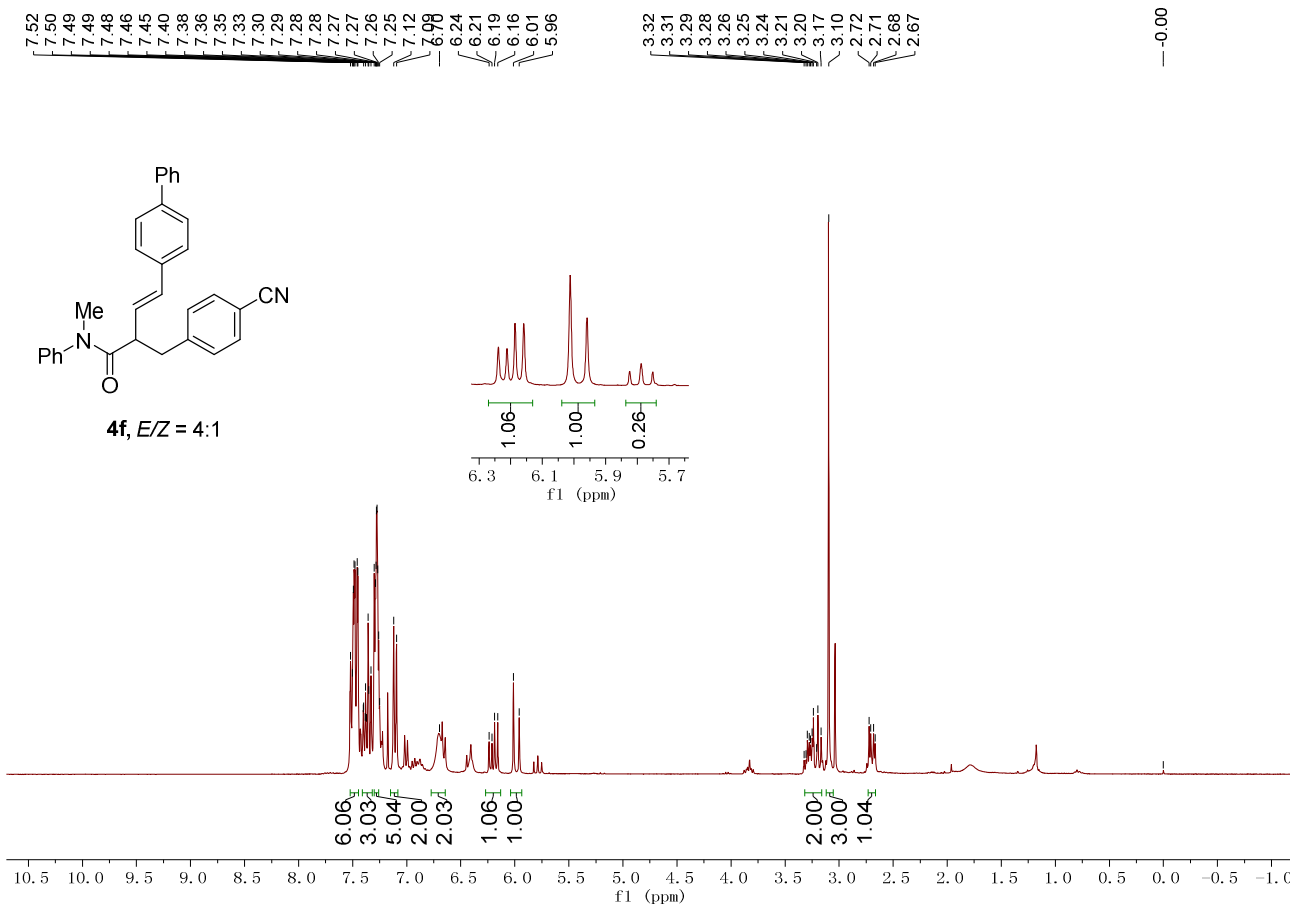
^{1}H NMR (300 MHz, $CDCl_3$)



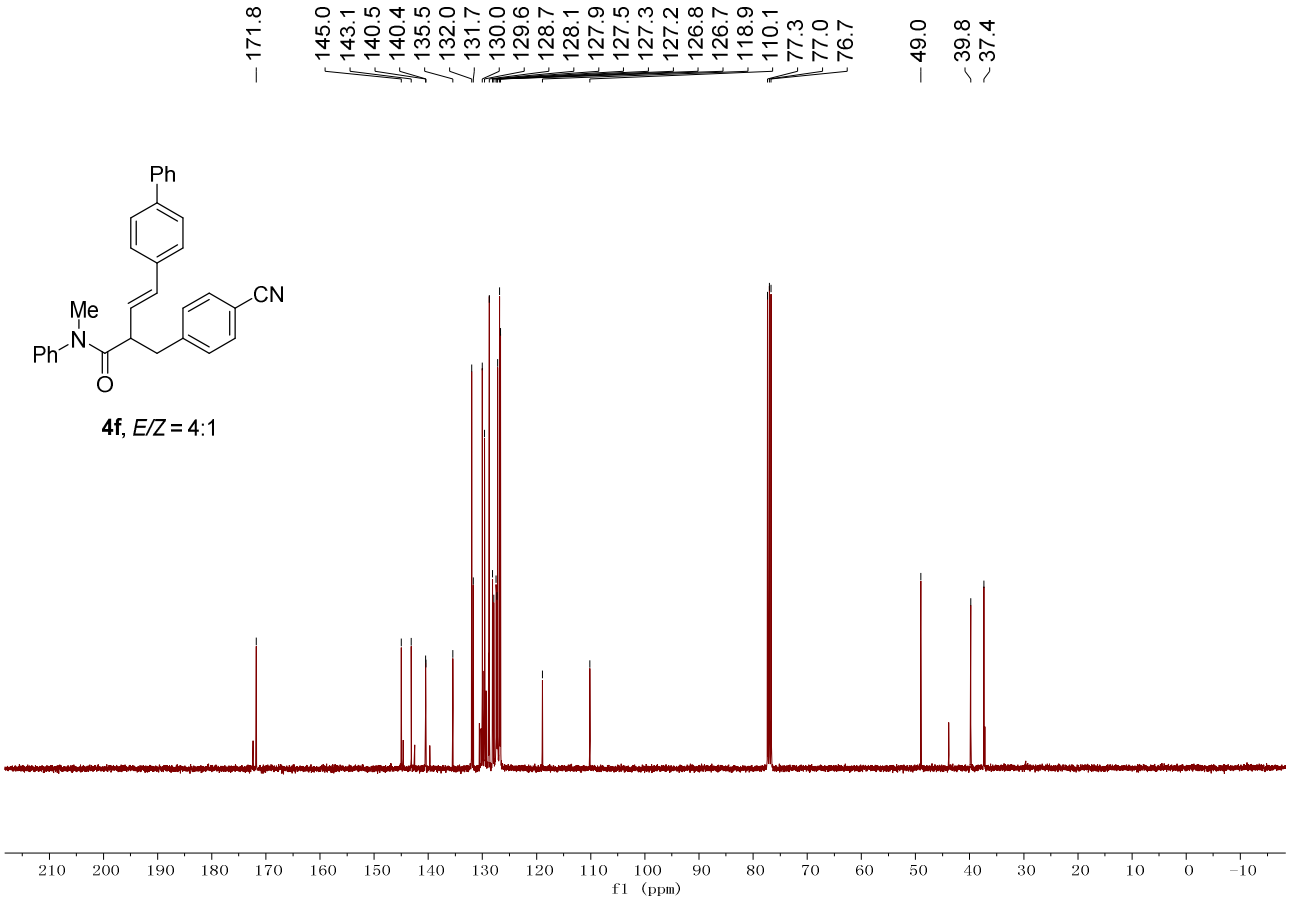
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

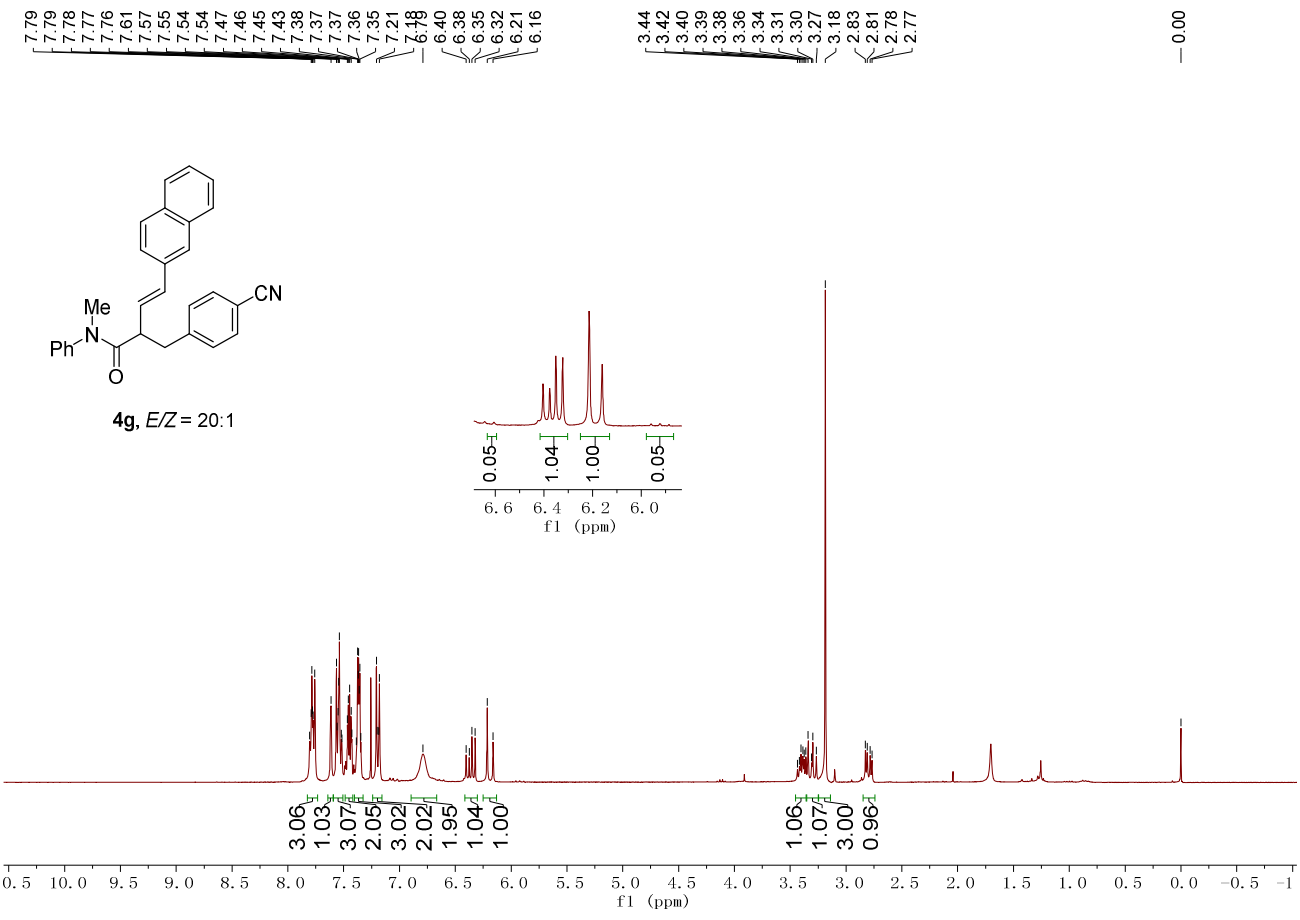


^{13}C NMR (101 MHz, $CDCl_3$)



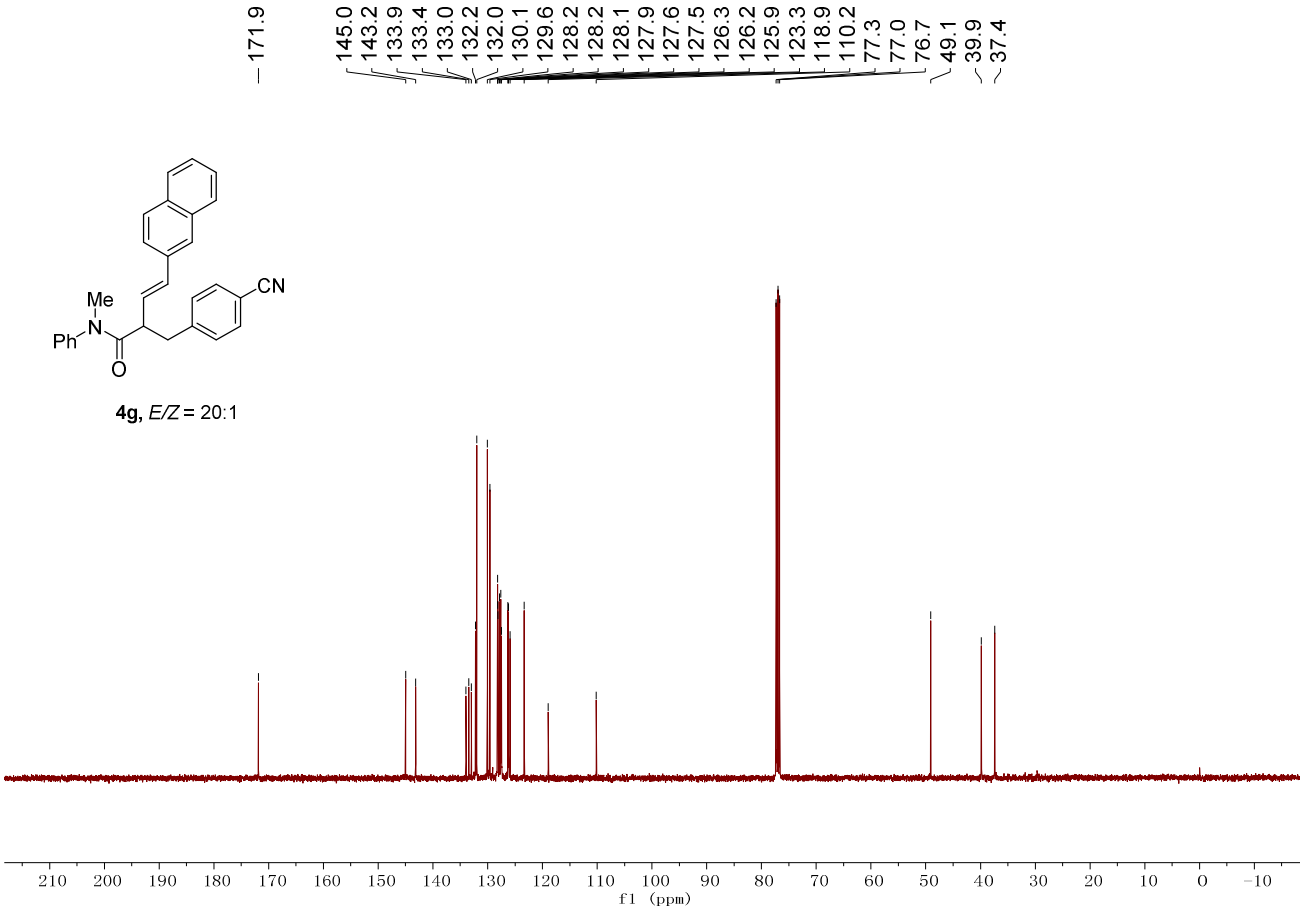
4f, *E*/*Z* = 4:1

^{1}H NMR (300 MHz, $CDCl_3$)



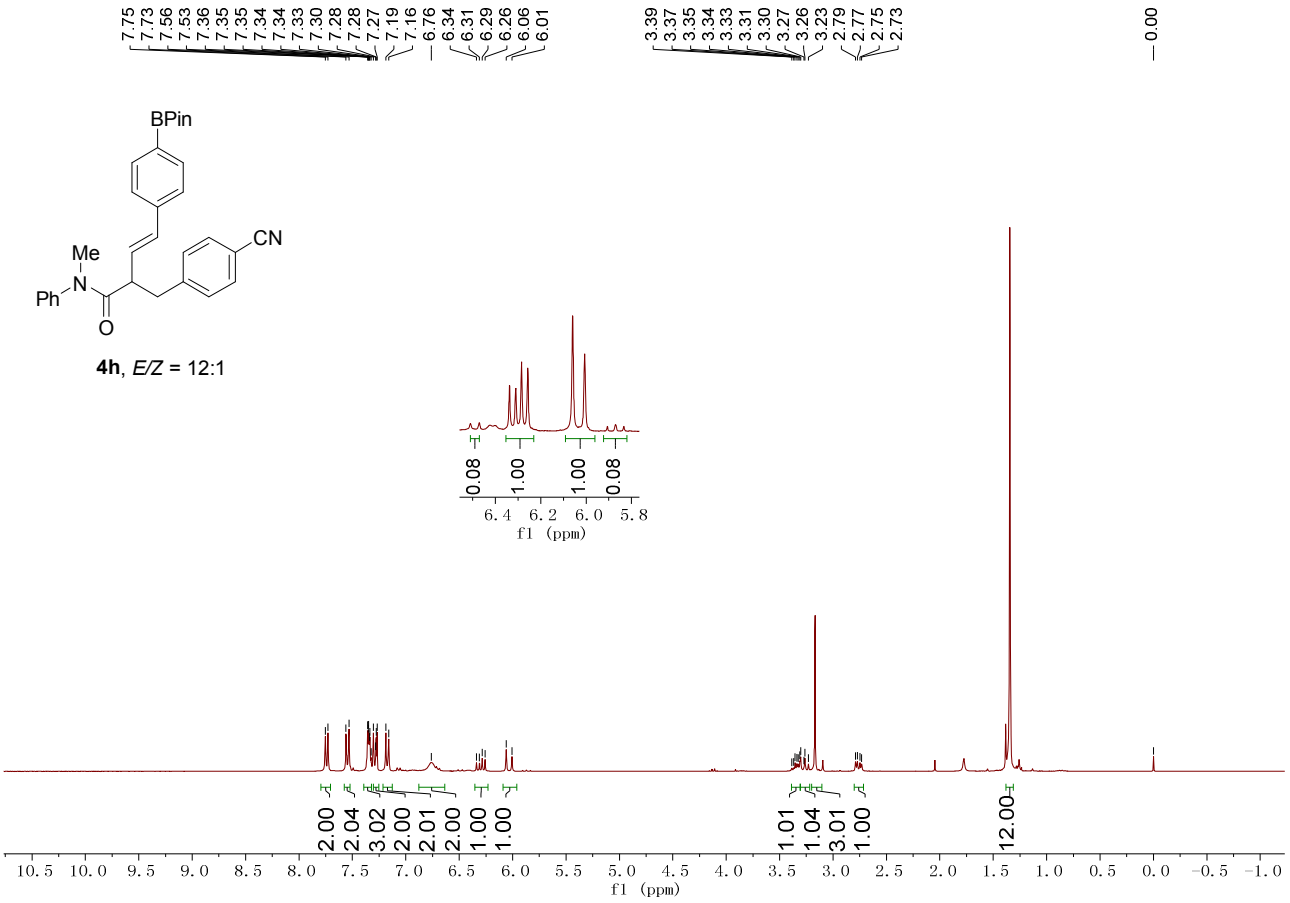
4g, *E*/*Z* = 20:1

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



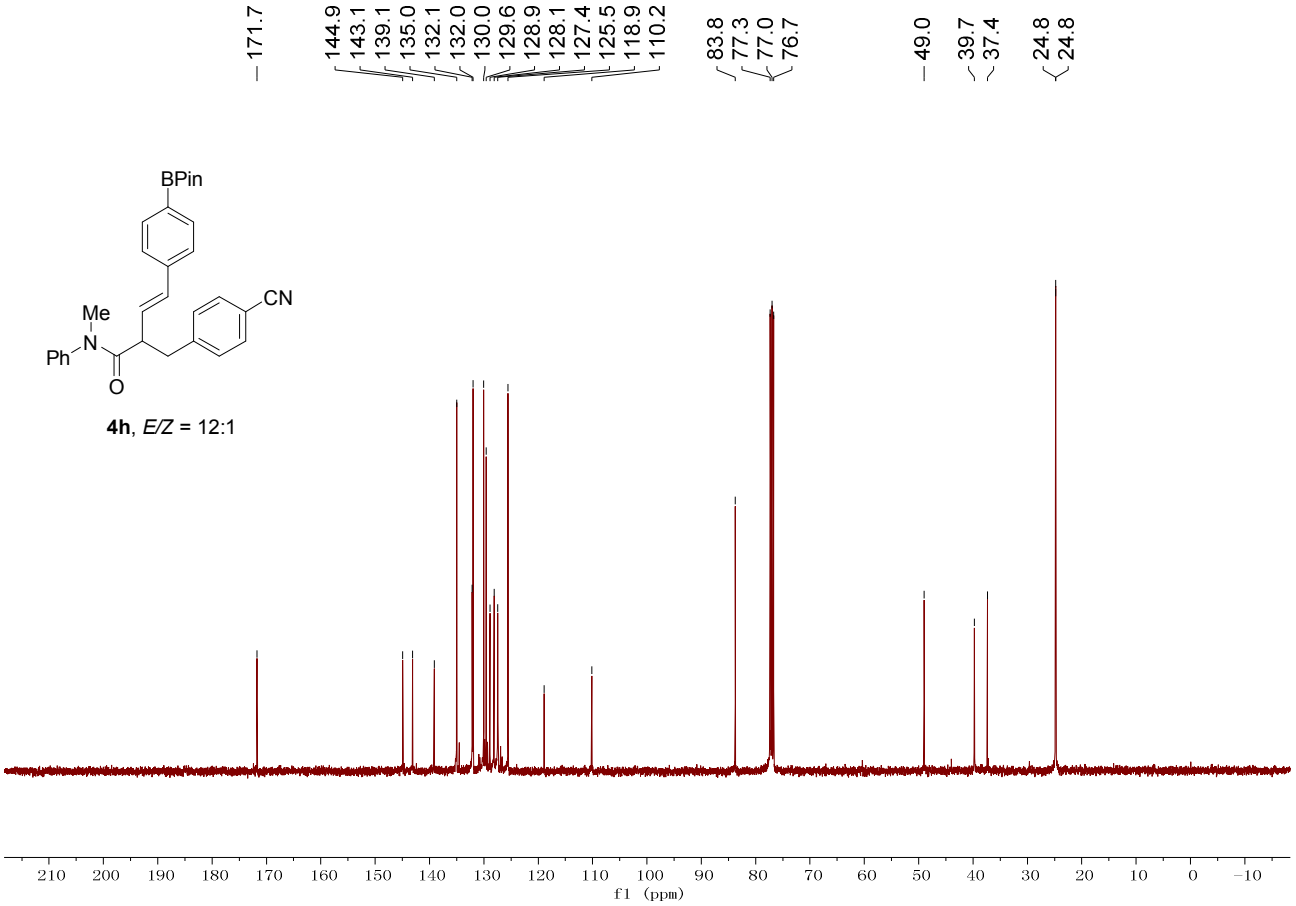
4g, *E*/*Z* = 20:1

^{1}H NMR (300 MHz, $CDCl_3$)



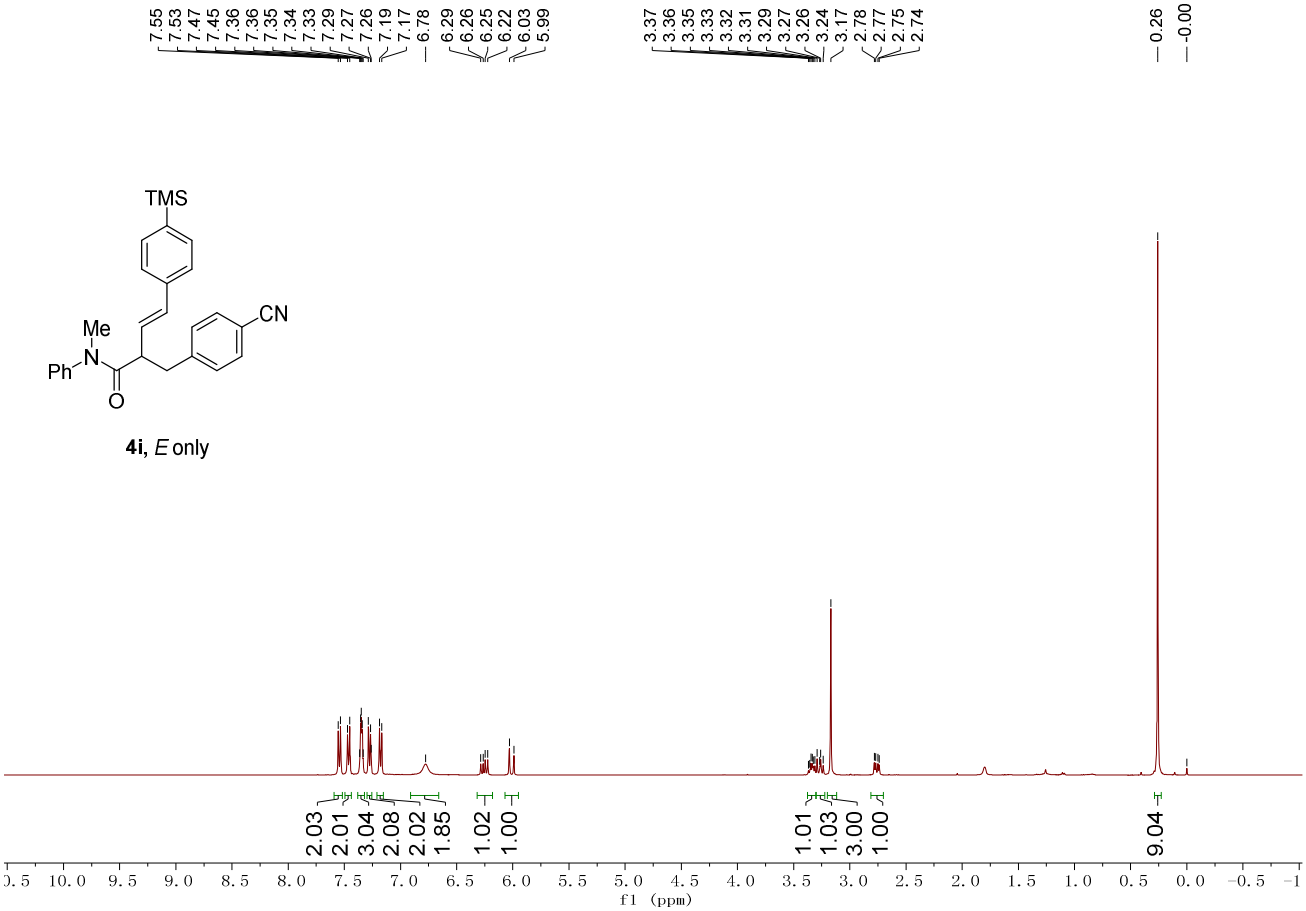
4h, *E*/*Z* = 12:1

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



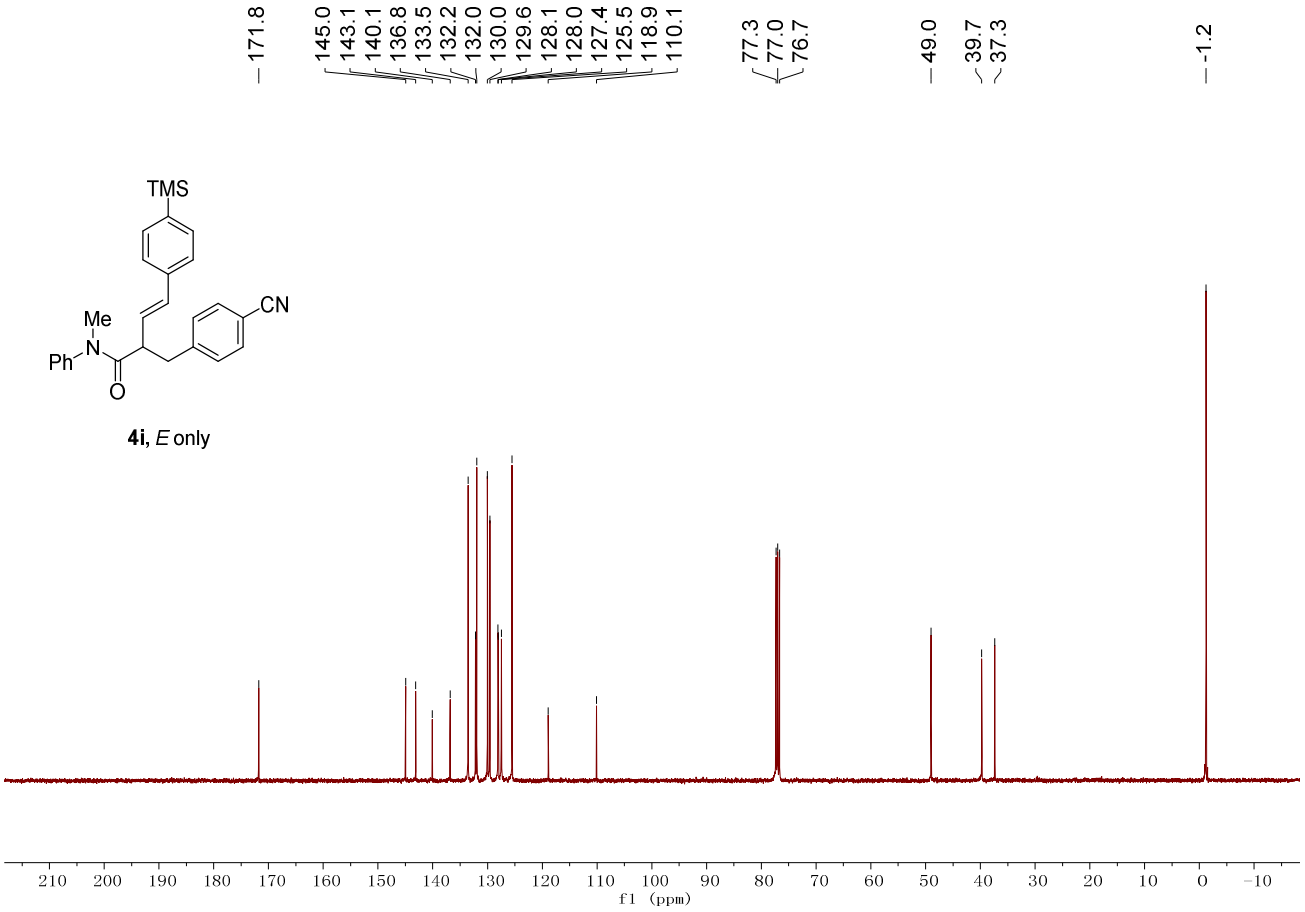
4h, *E*/*Z* = 12:1

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



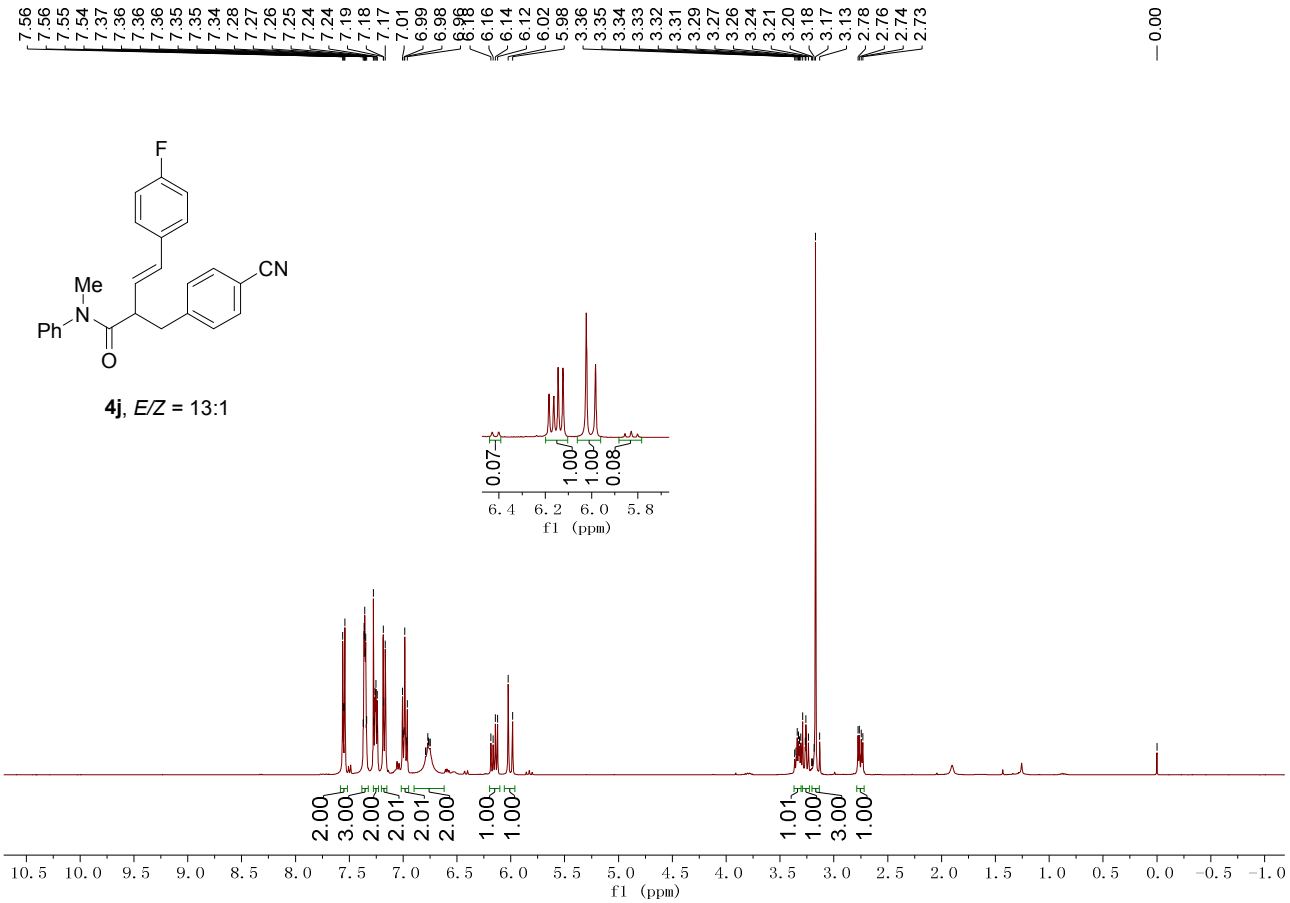
4i, *E* only

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



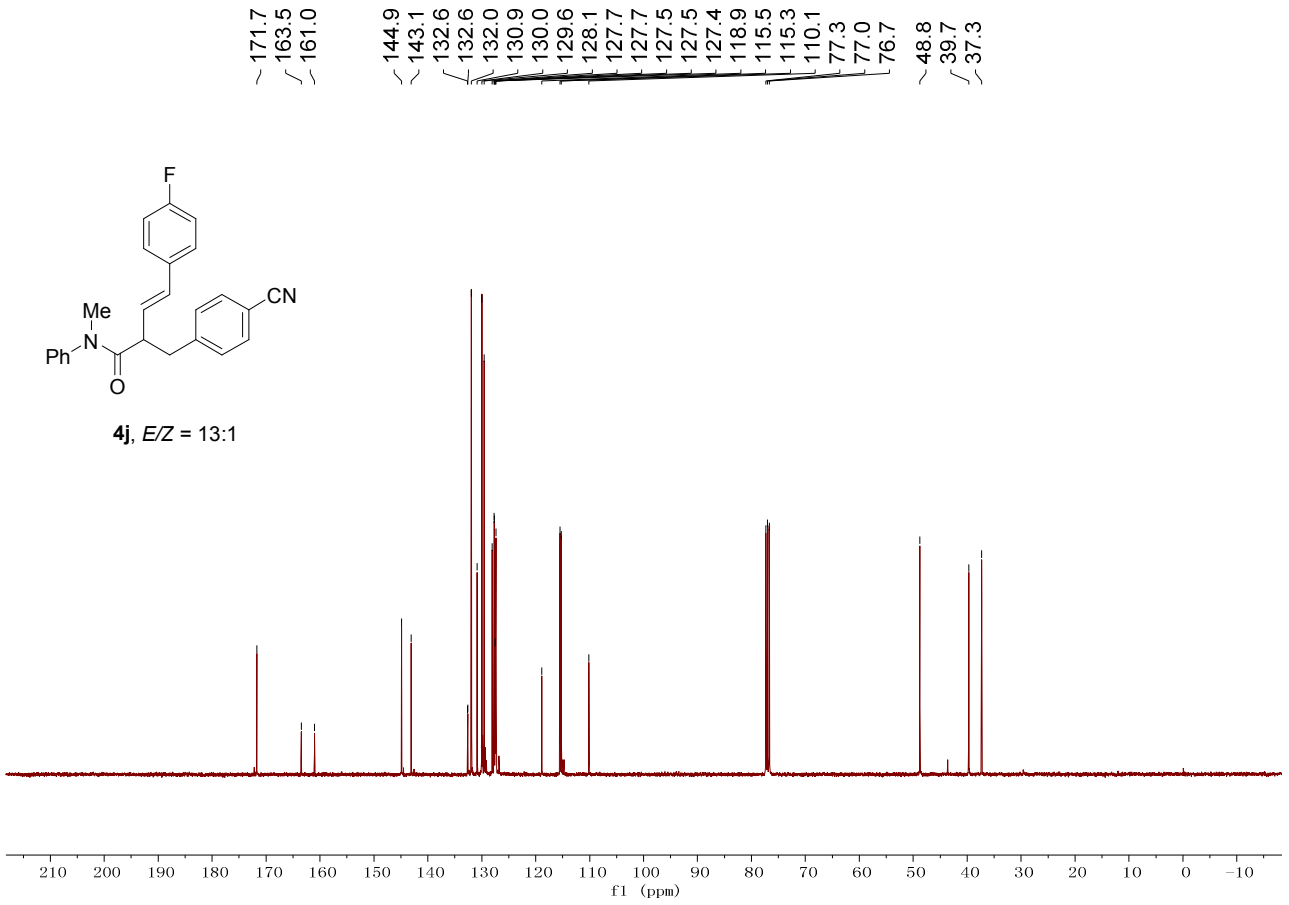
4i, *E* only

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



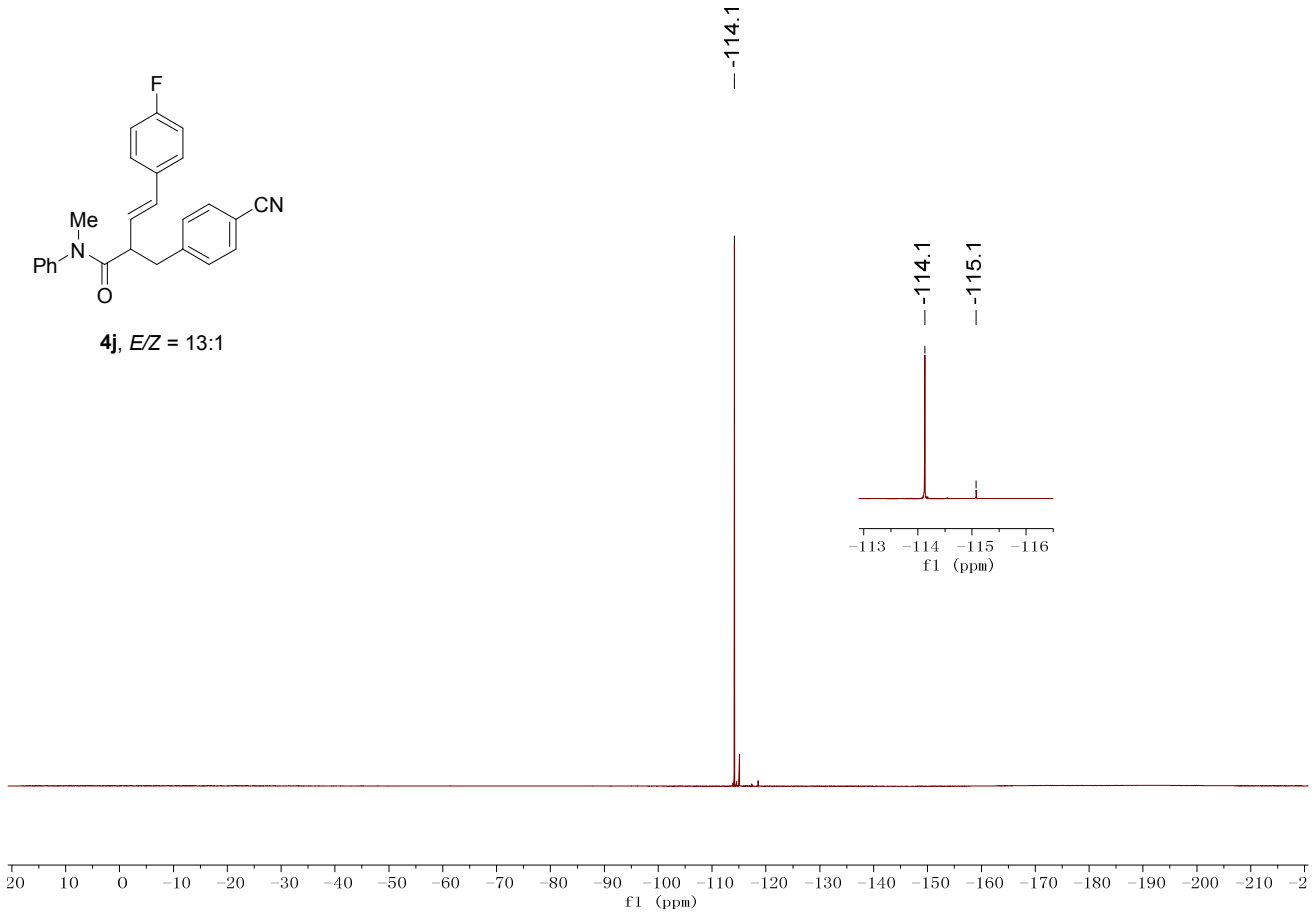
4j, *E*/*Z* = 13:1

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



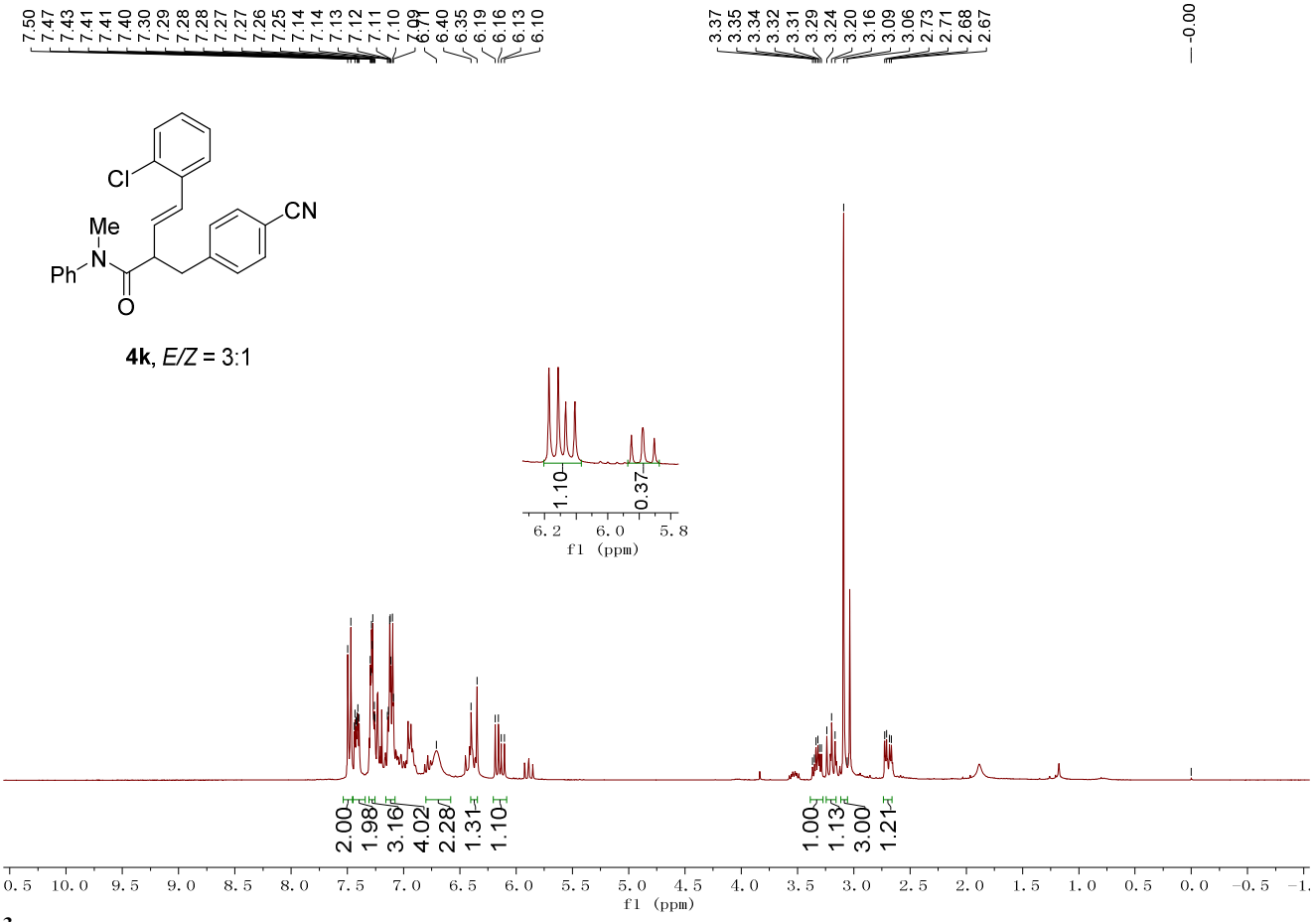
4j, *E*/*Z* = 13:1

^{19}F NMR (376 MHz, $CDCl_3$)

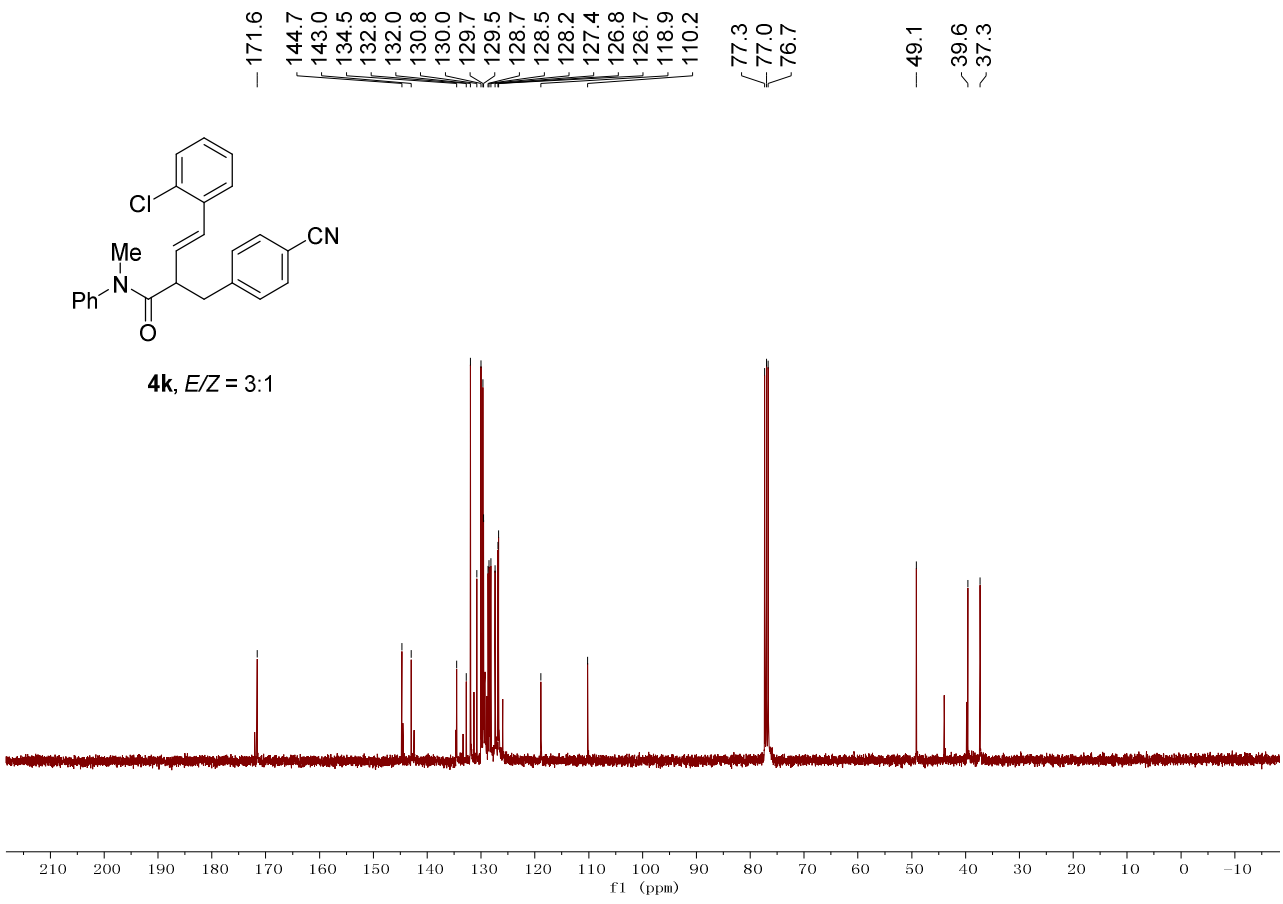


4j, *E*/*Z* = 13:1

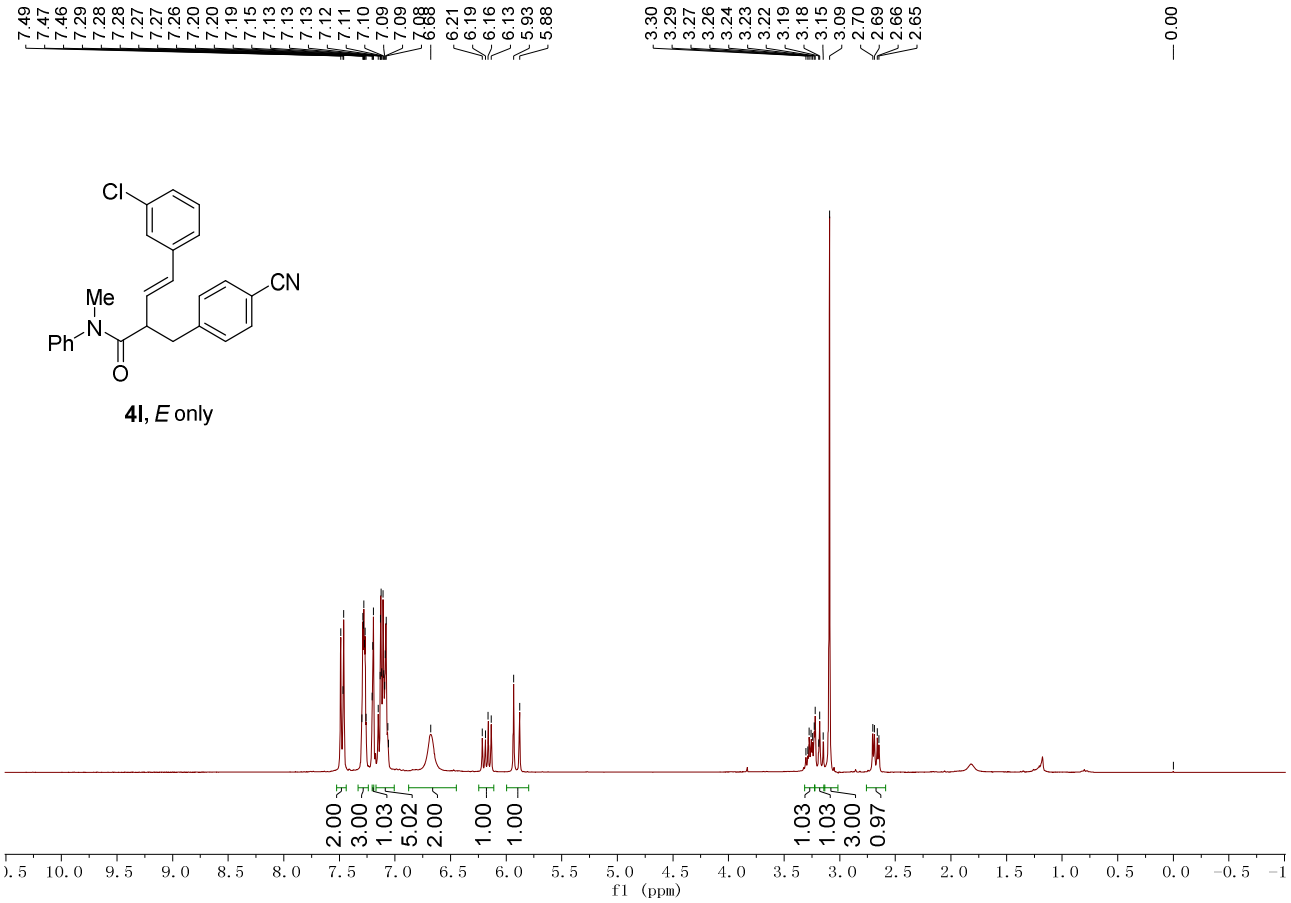
^{1}H NMR (300 MHz, $CDCl_3$)



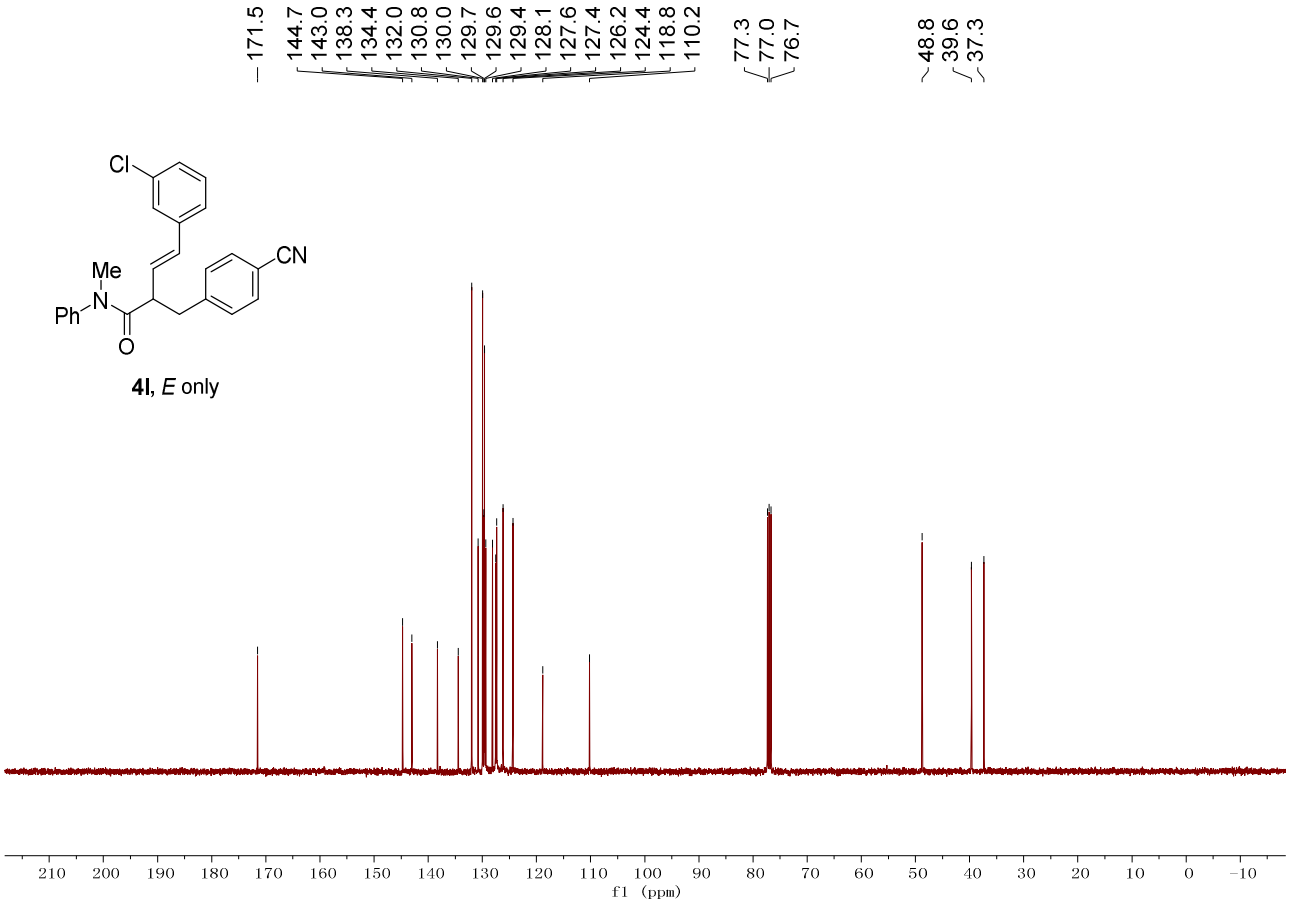
^{13}C NMR (101 MHz, $CDCl_3$)



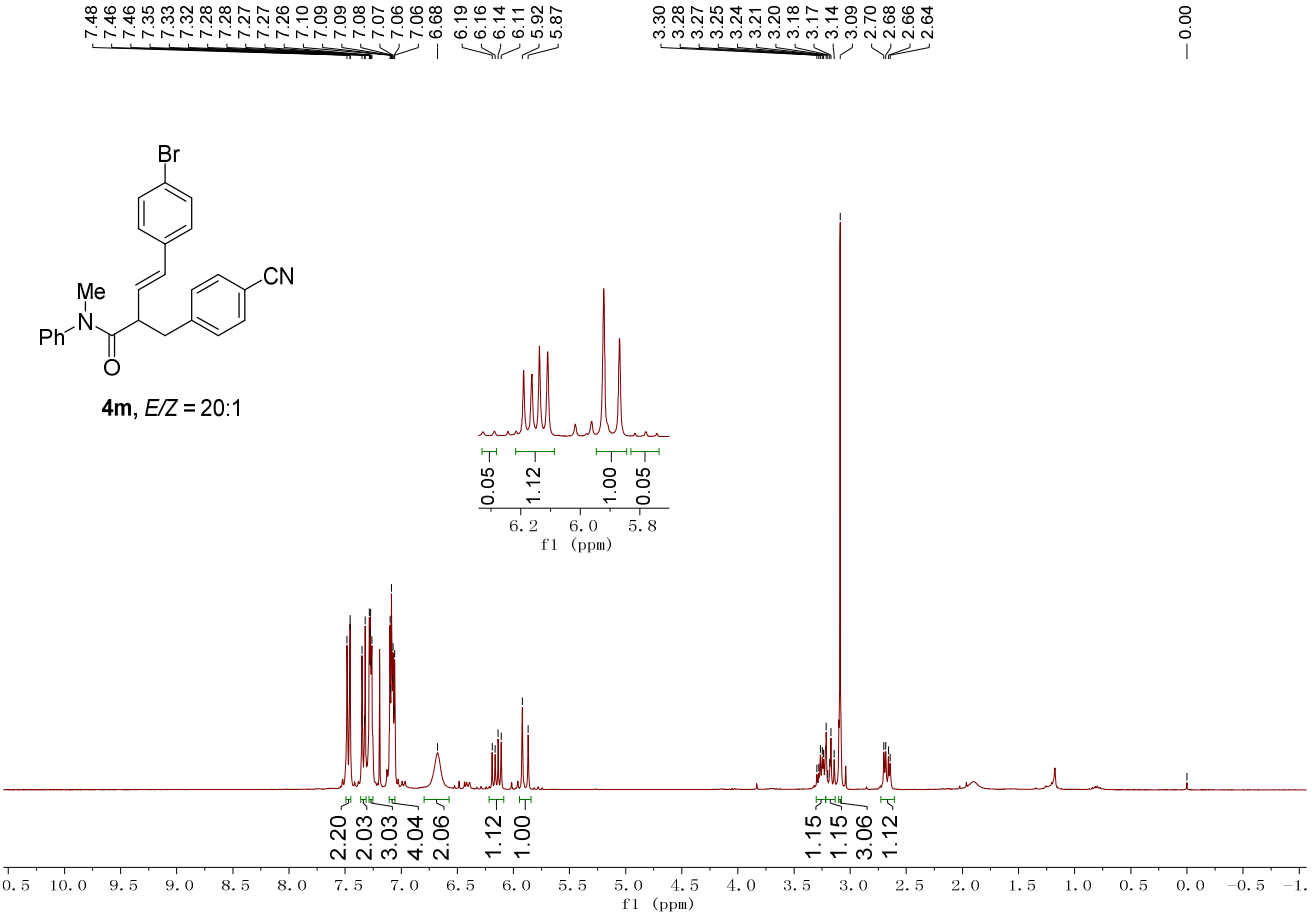
^{1}H NMR (300 MHz, $CDCl_3$)



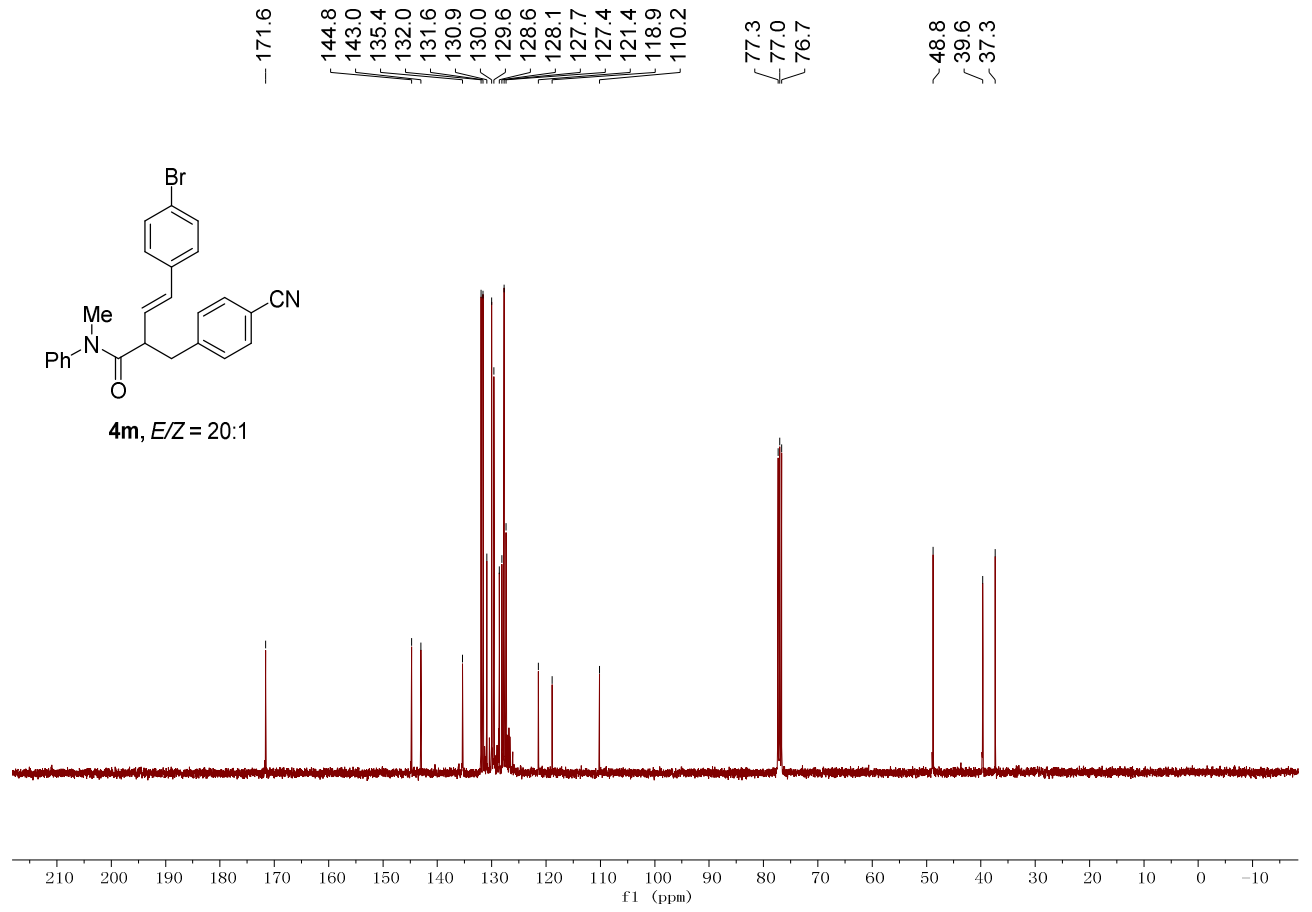
^{13}C NMR (101 MHz, $CDCl_3$)



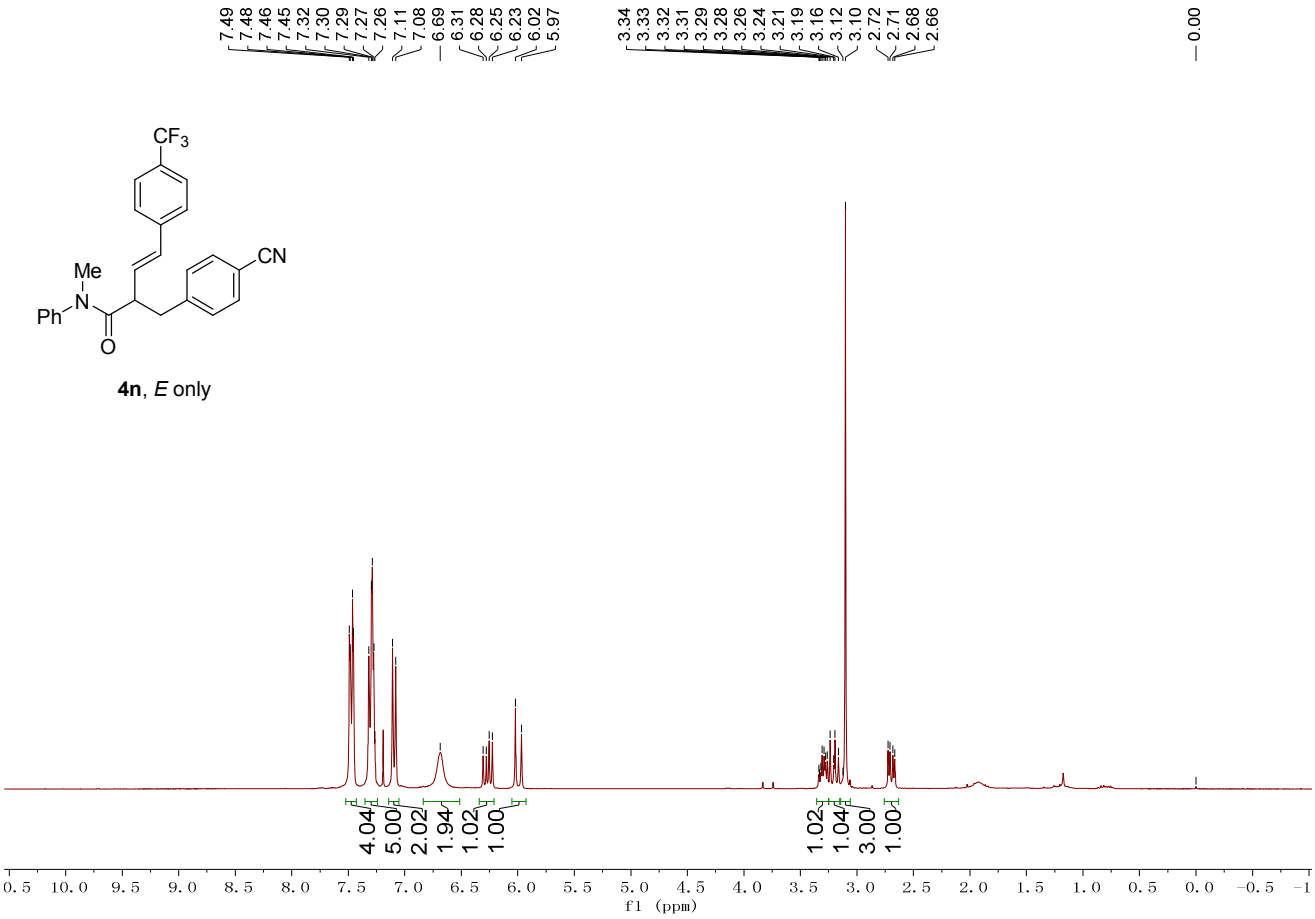
^{1}H NMR (300 MHz, $CDCl_3$)



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

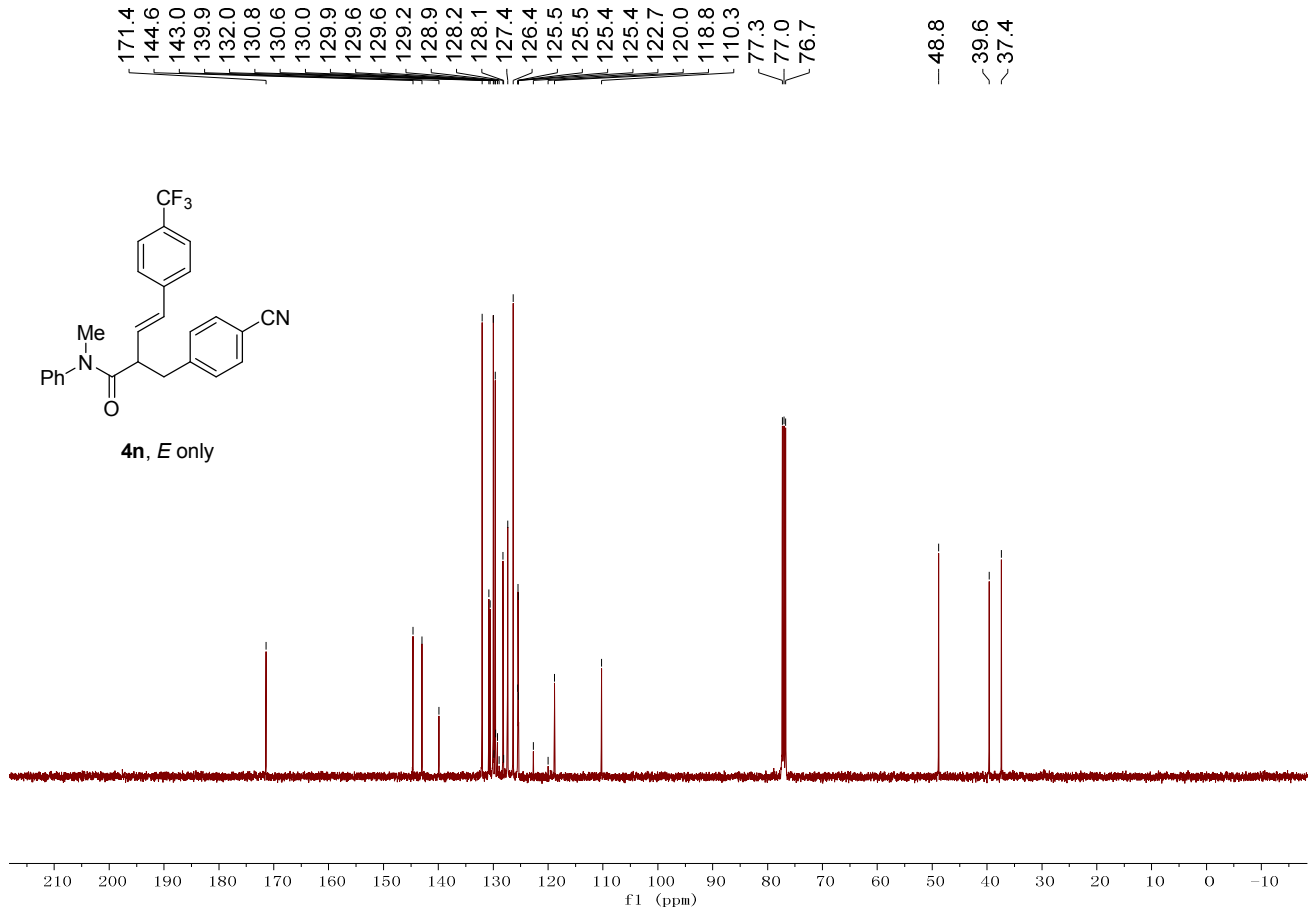


^{1}H NMR (300 MHz, $CDCl_3$)



4n, *E* only

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

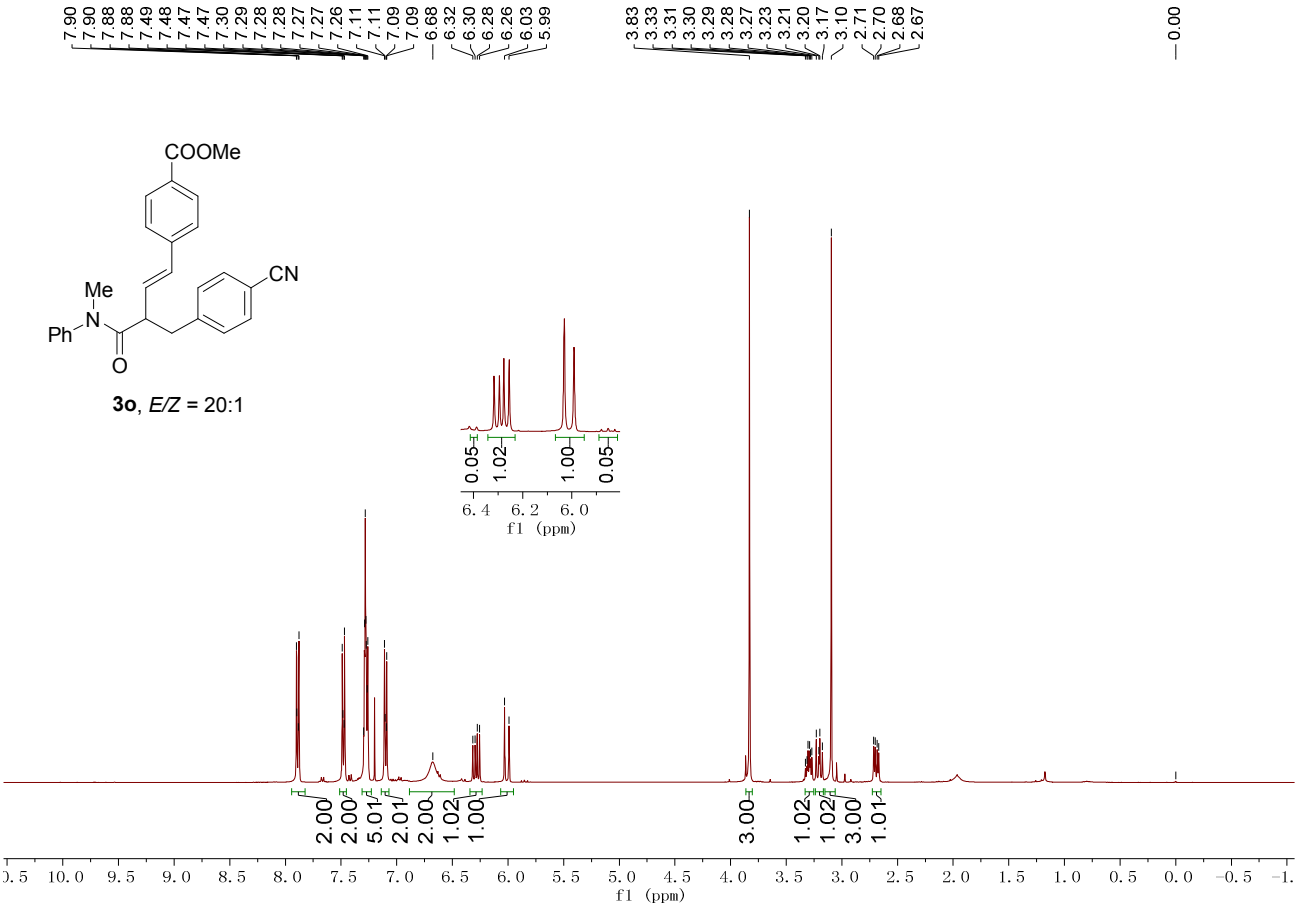


4n, *E* only

^{19}F NMR (376 MHz, $CDCl_3$)

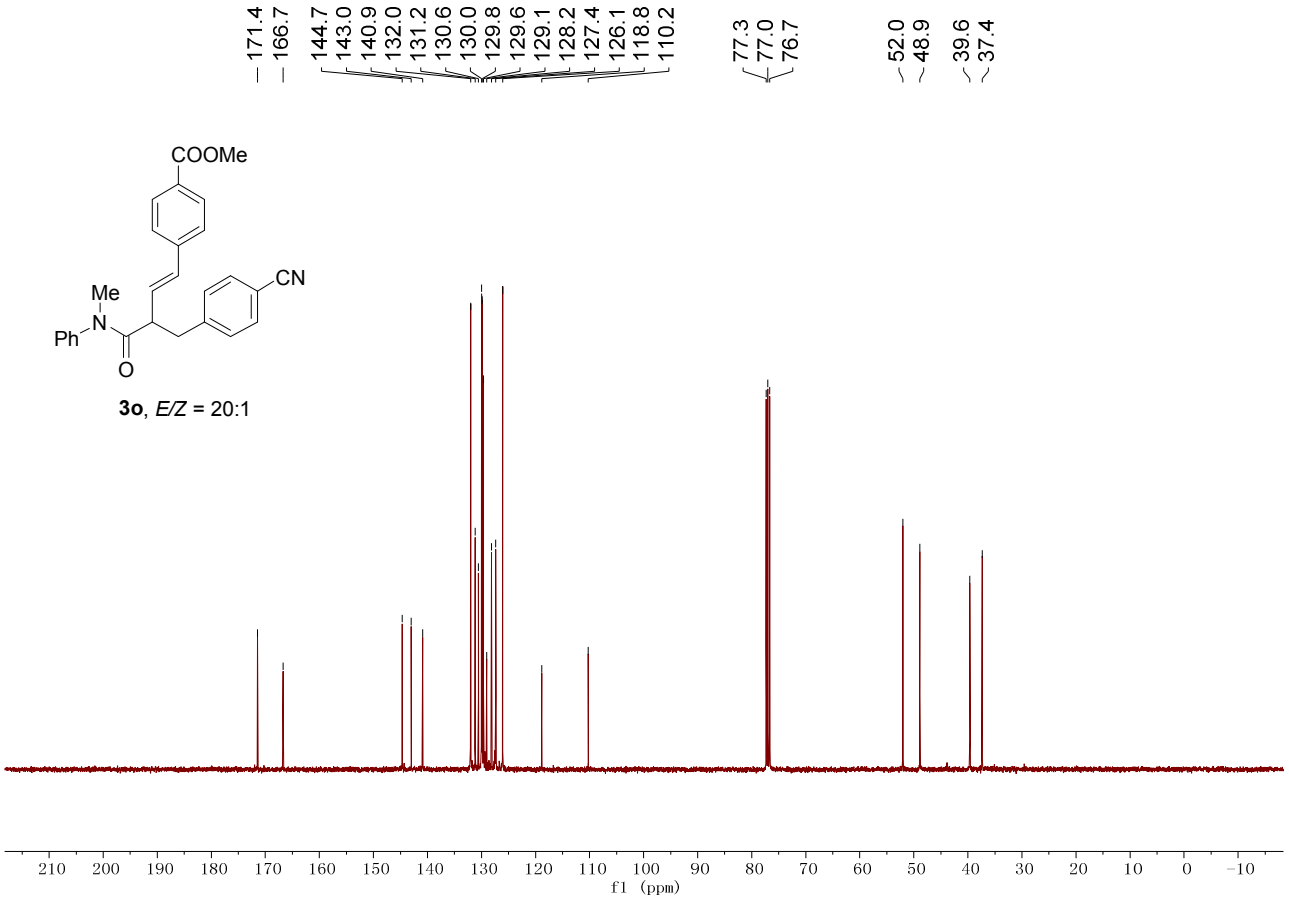
4n, *E* only

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



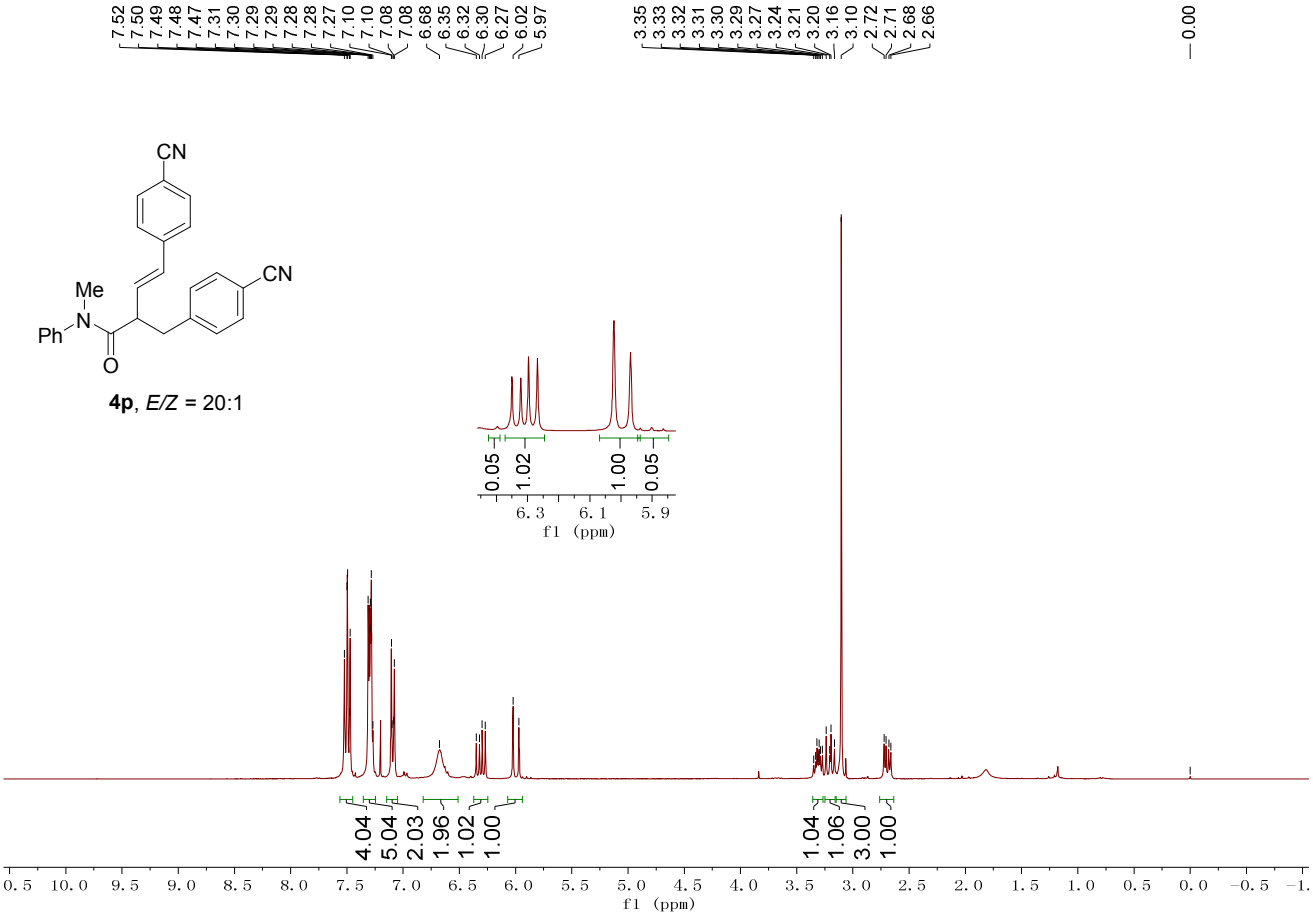
3o, *E*/*Z* = 20:1

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



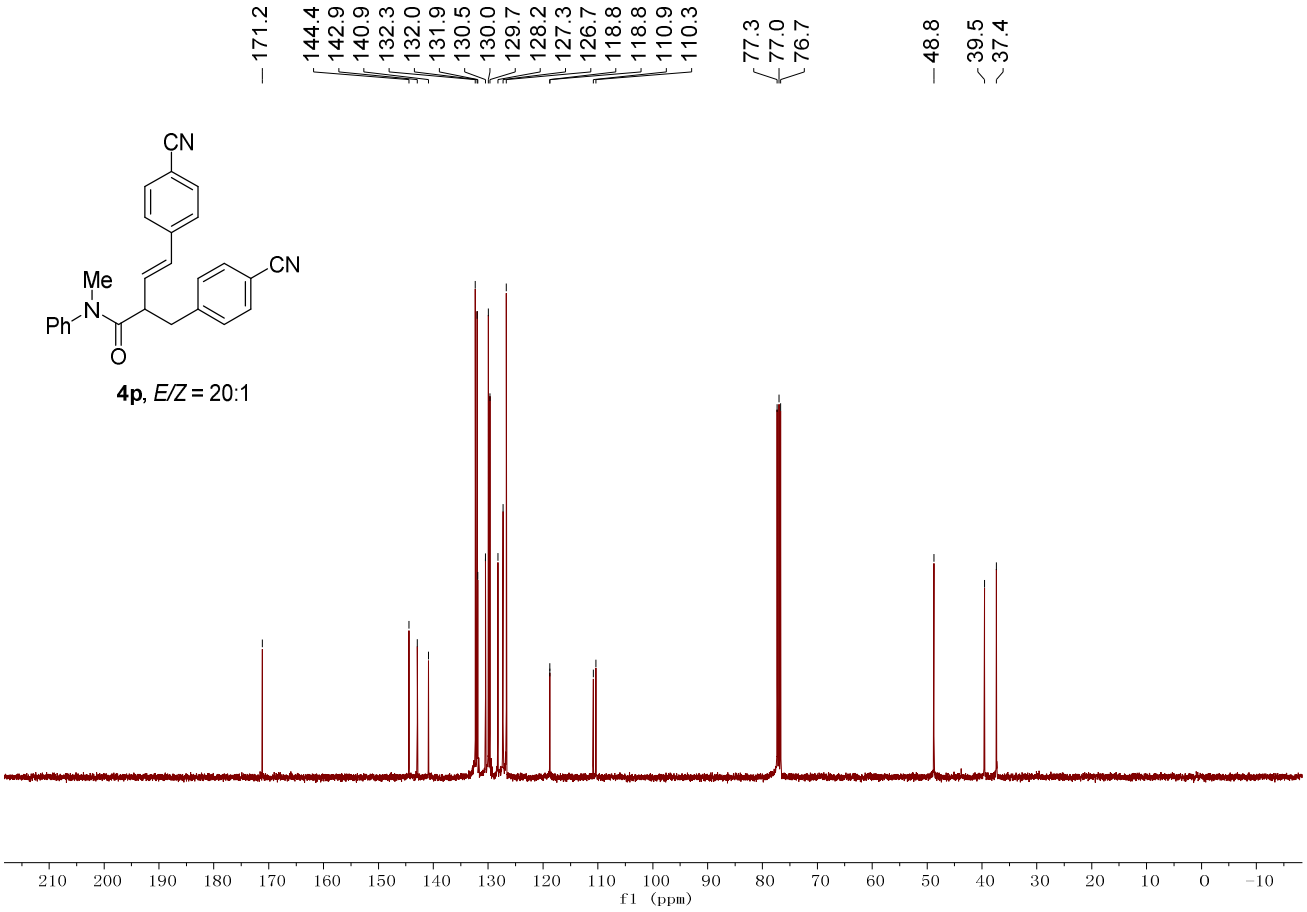
3o, *E*/*Z* = 20:1

^{1}H NMR (300 MHz, $CDCl_3$)



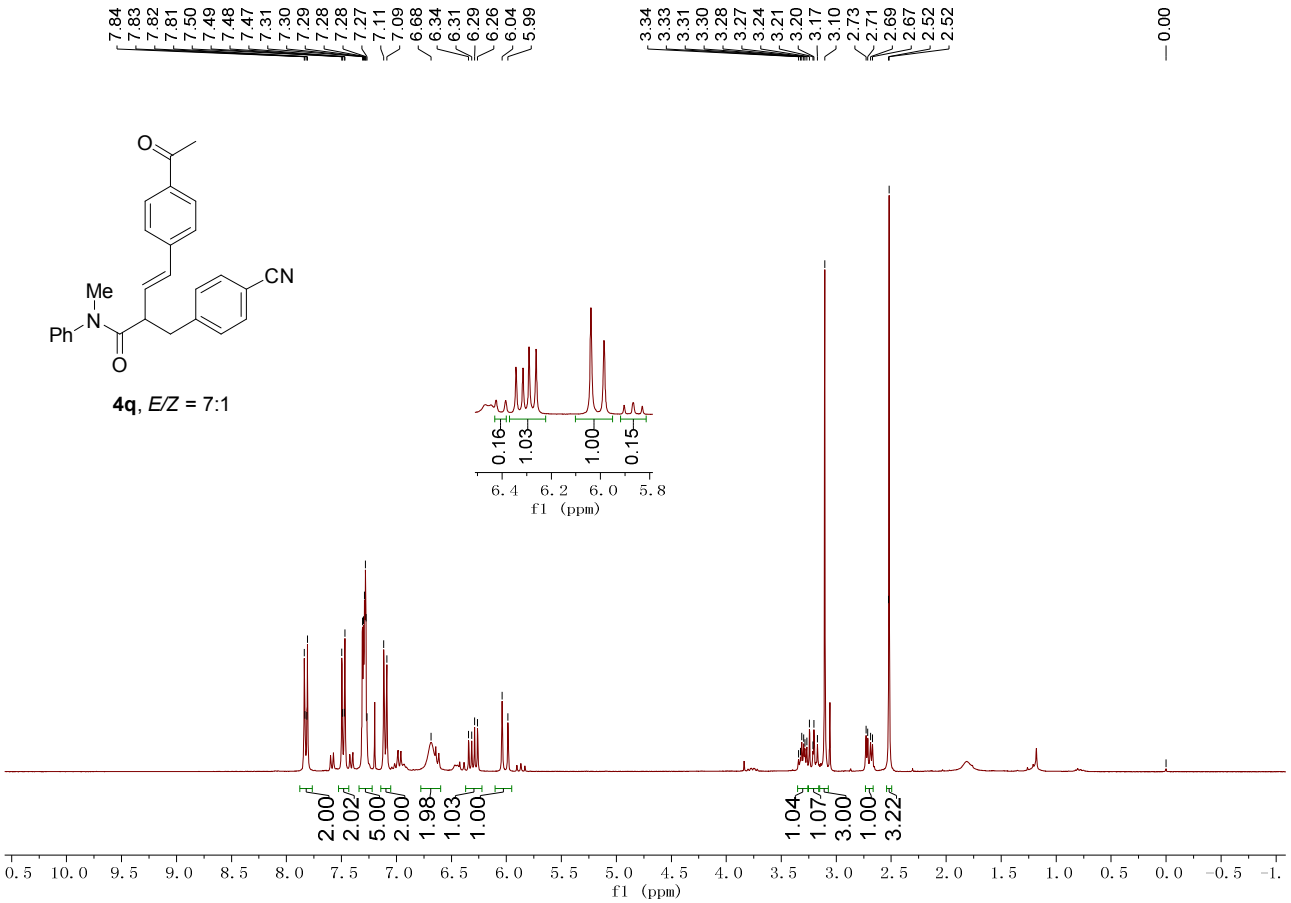
4p, *E*/*Z* = 20:1

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



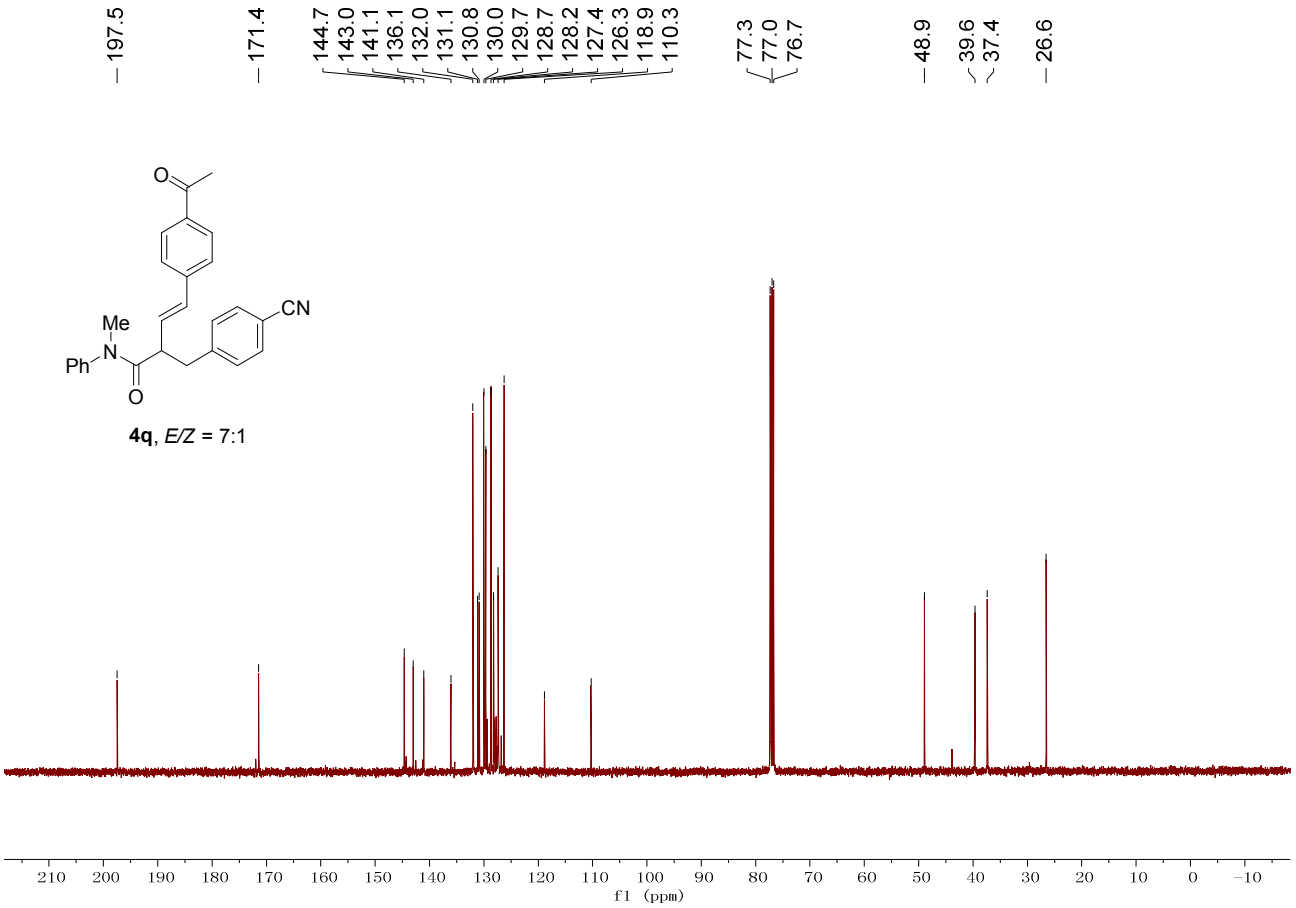
4p, *E*/*Z* = 20:1

^{1}H NMR (300 MHz, $CDCl_3$)



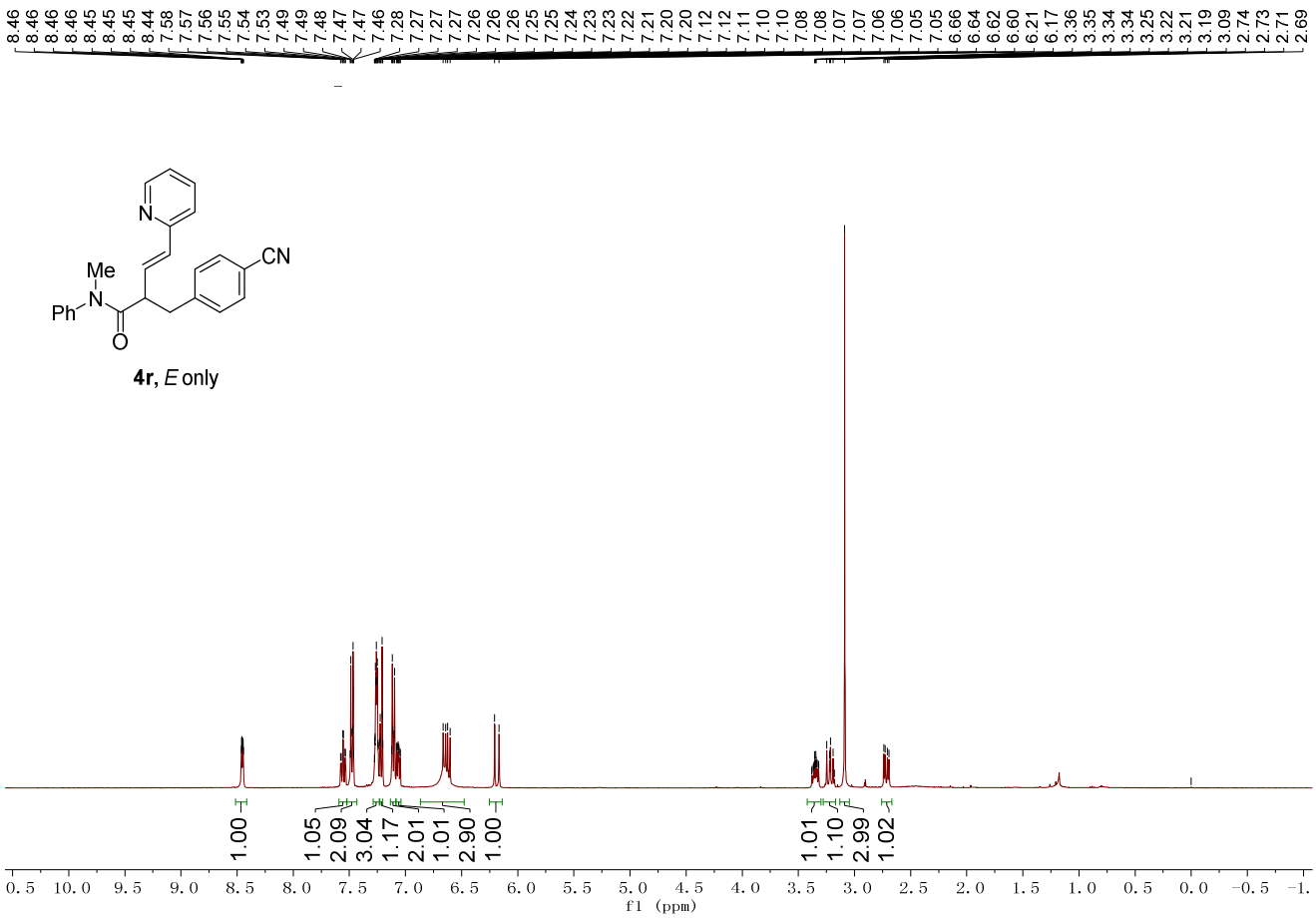
4q, *E*/*Z* = 7:1

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



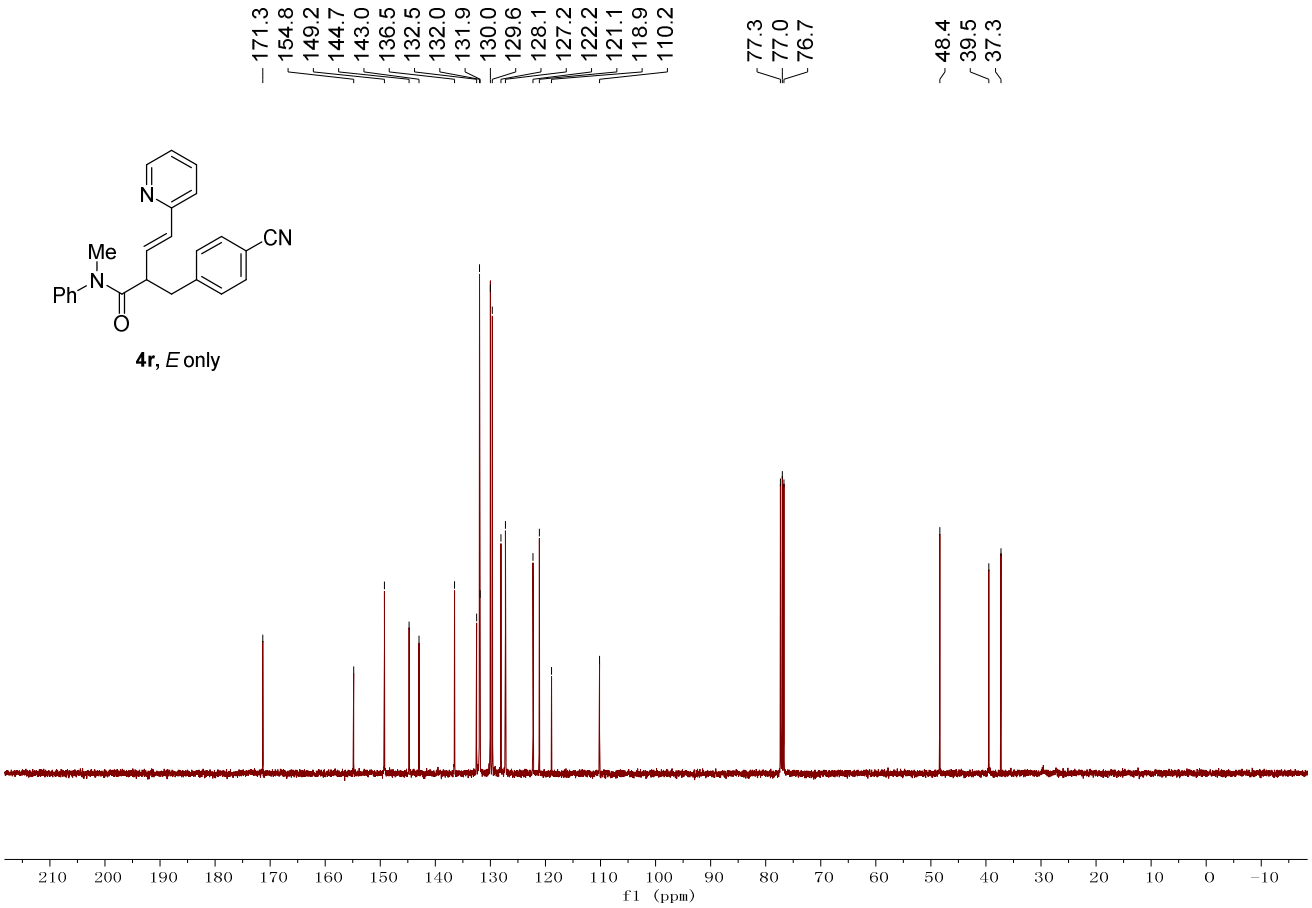
4q, *E*/*Z* = 7:1

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



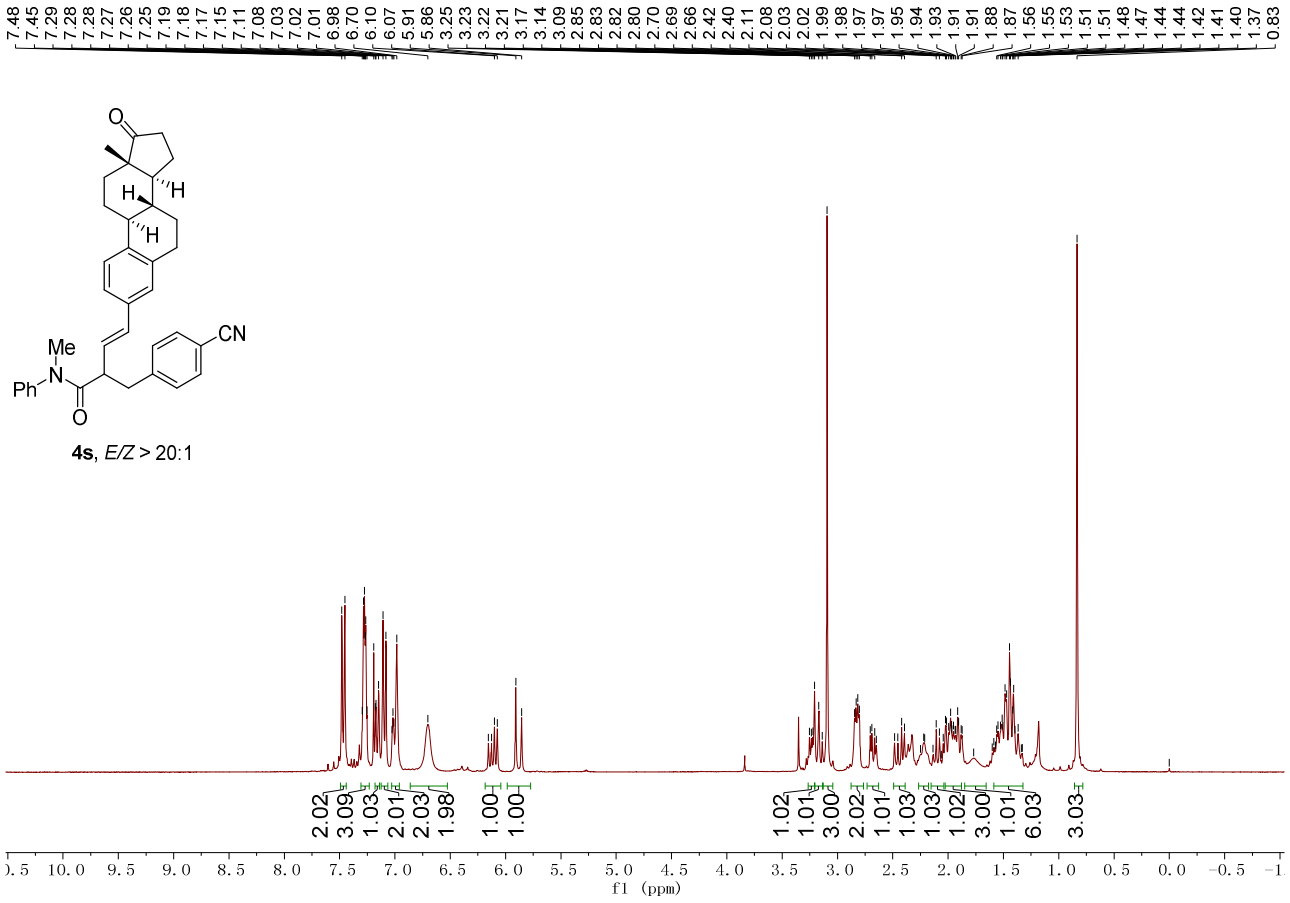
4r, *E* only

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



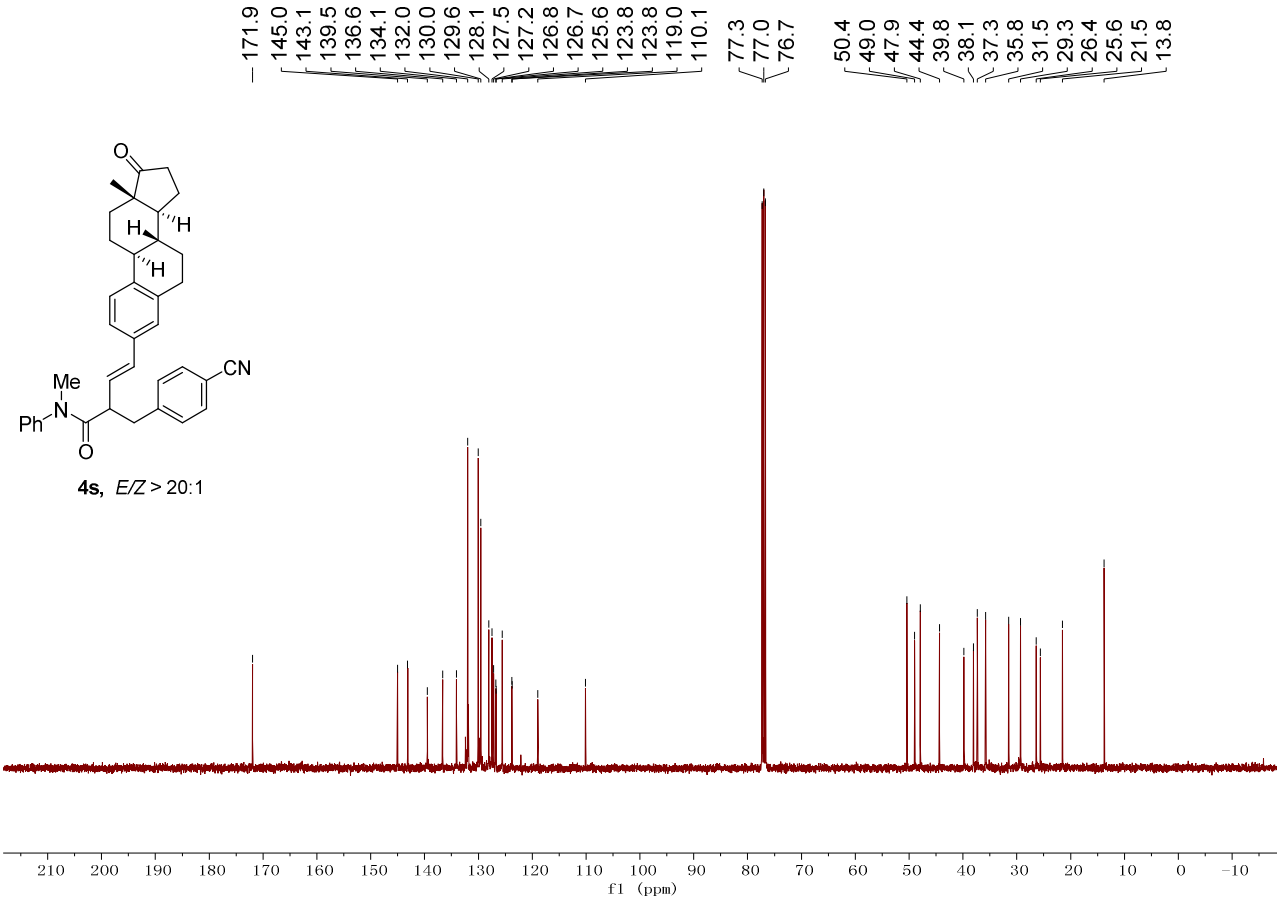
4r, *E* only

^{1}H NMR (300 MHz, $CDCl_3$)

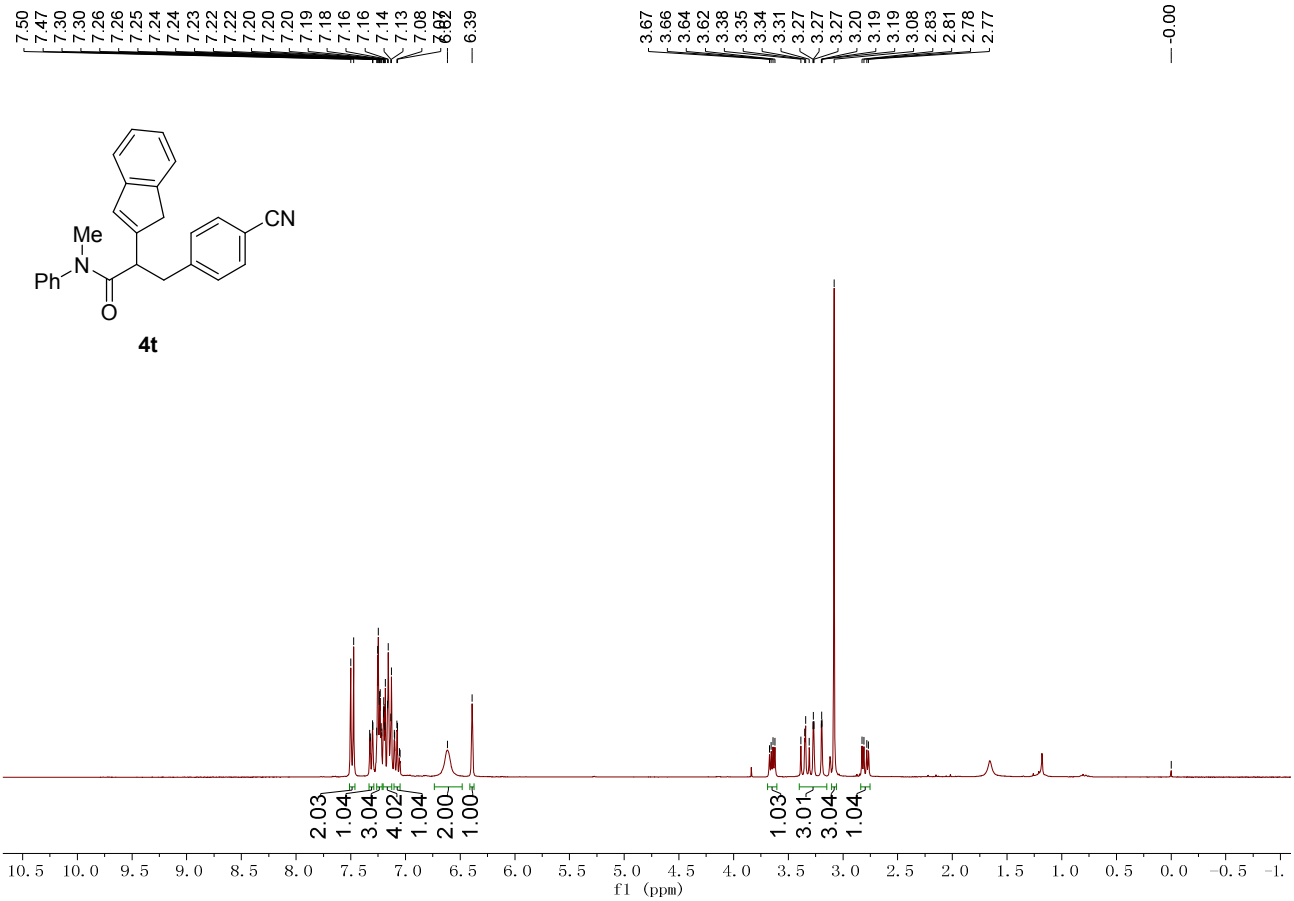


4s, *E*/*Z* > 20:1

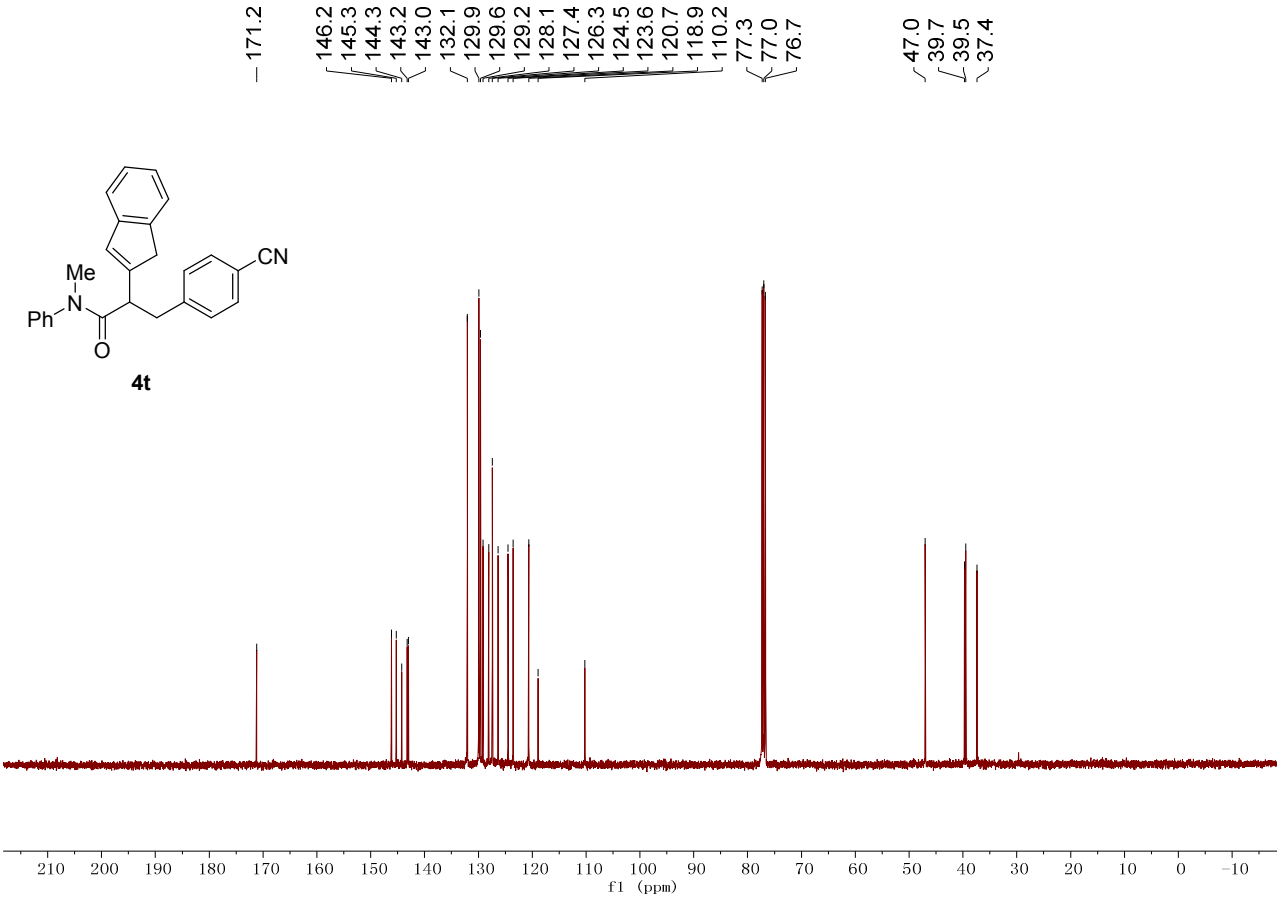
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

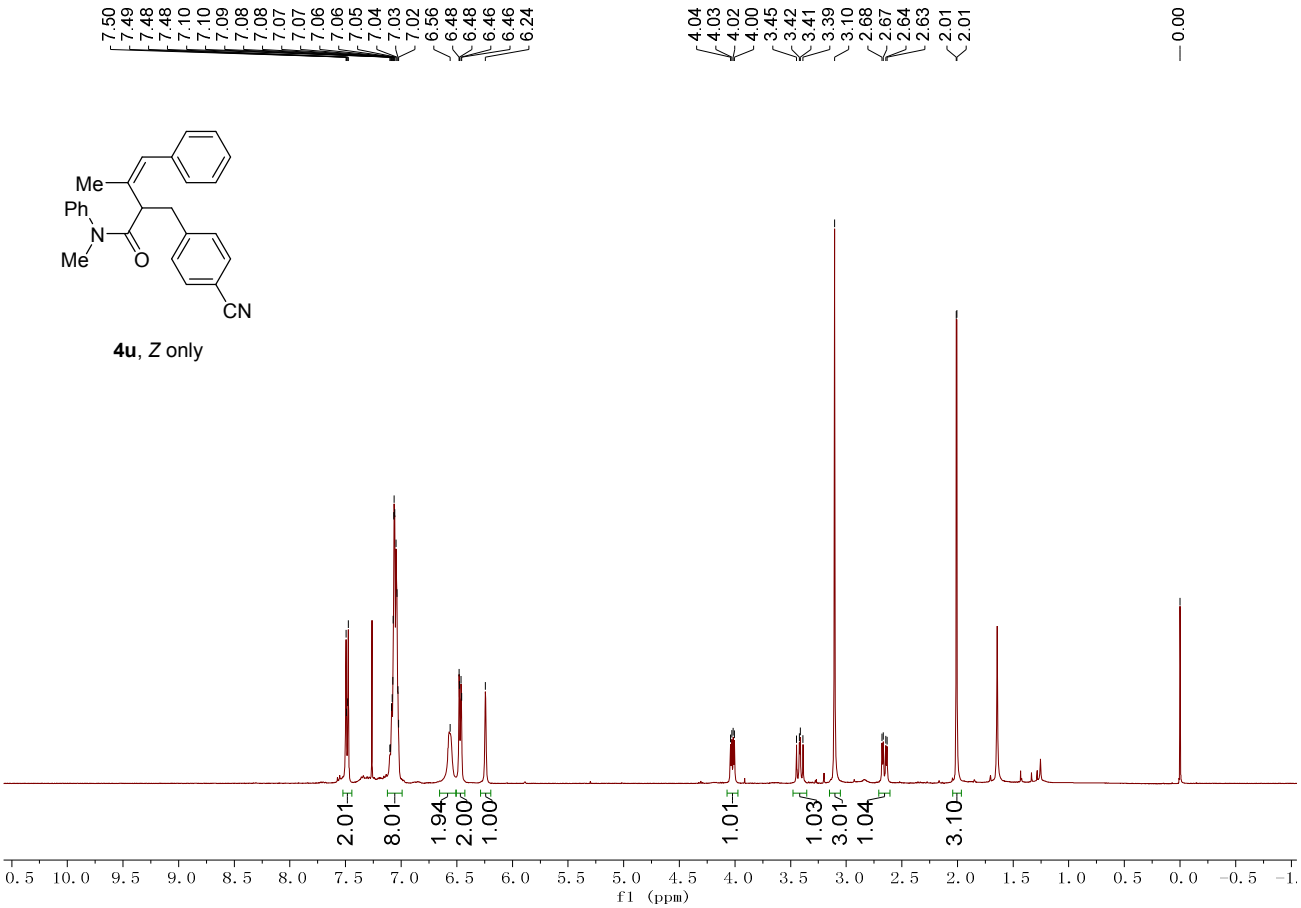


^{13}C NMR (101 MHz, $CDCl_3$)



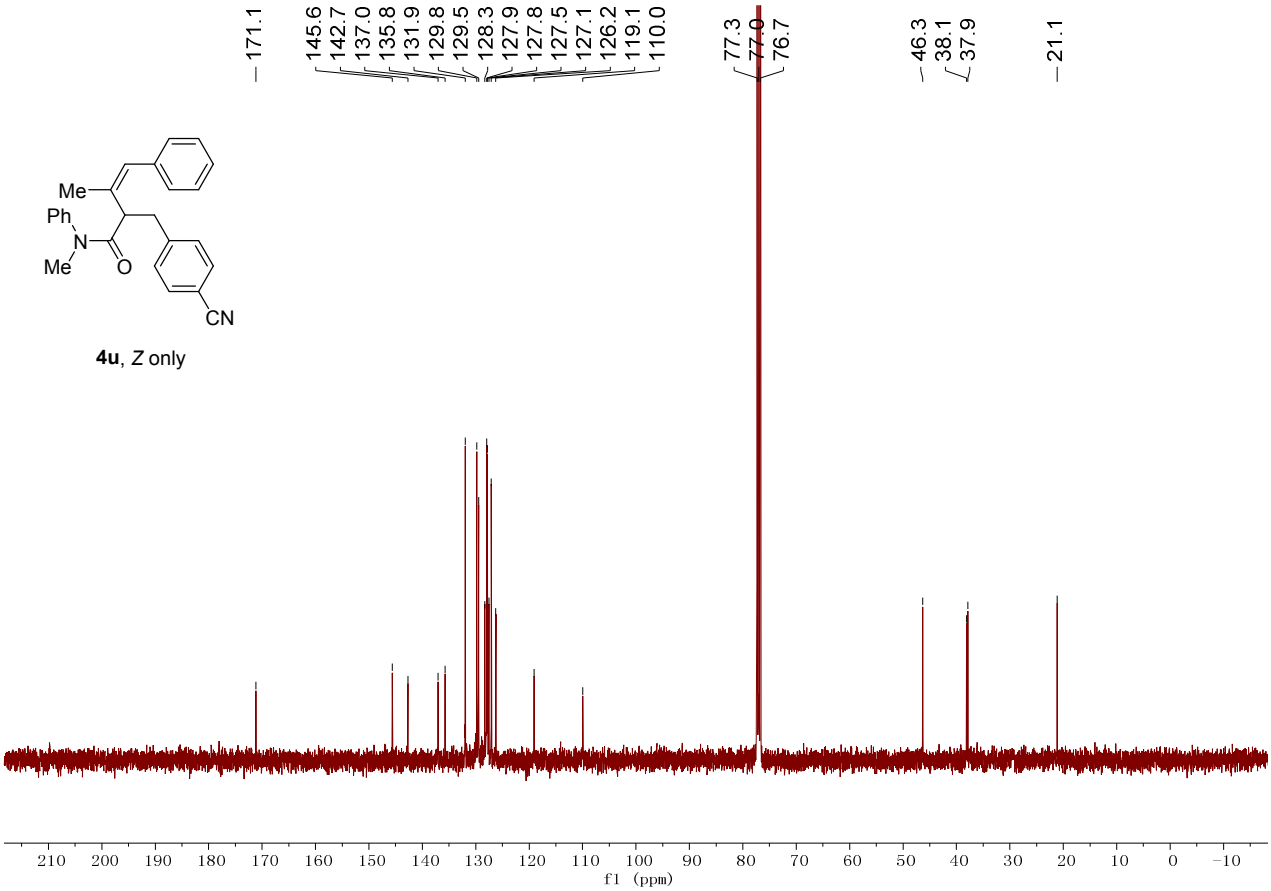
4t

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



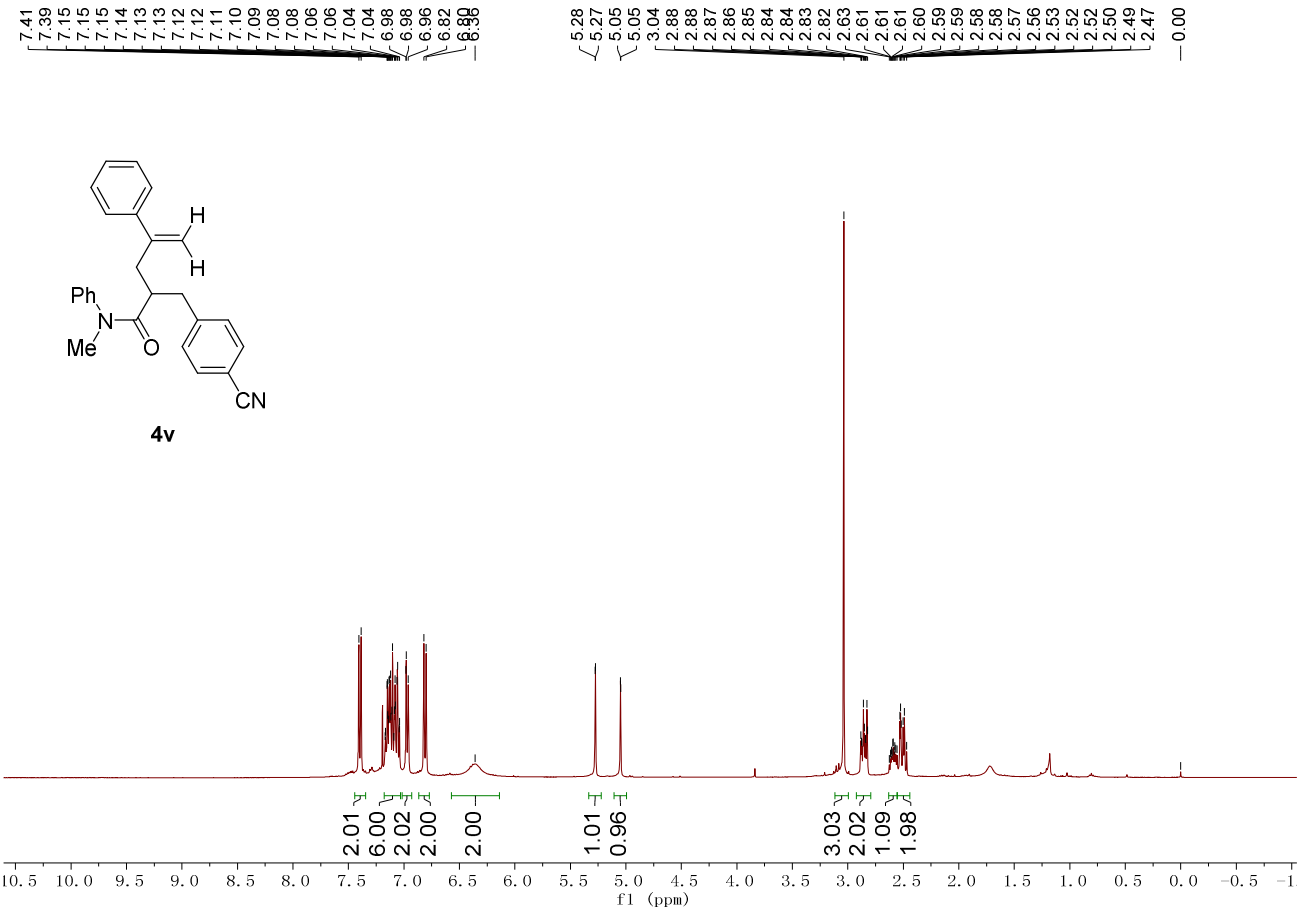
4u, *Z* only

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



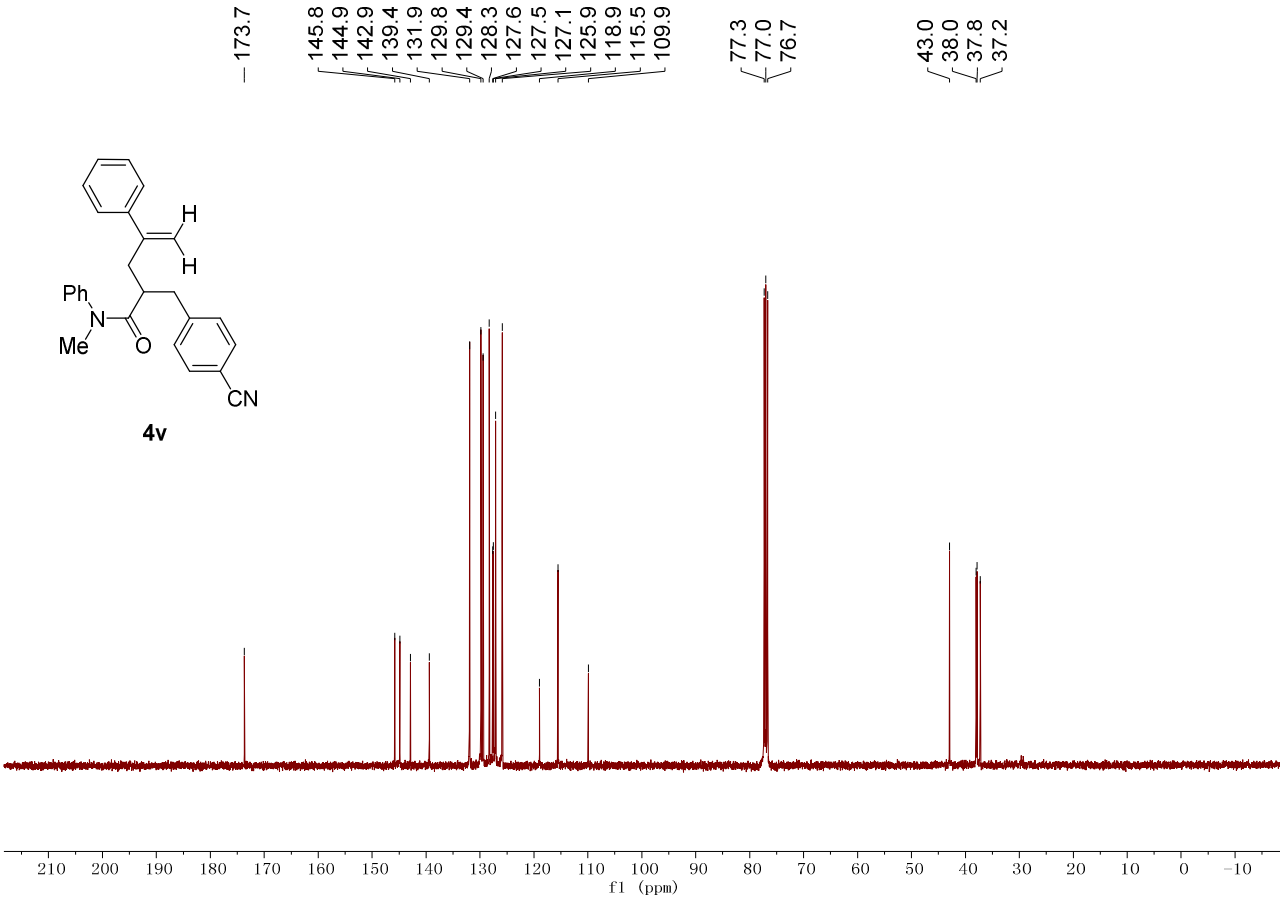
4u, *Z* only

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

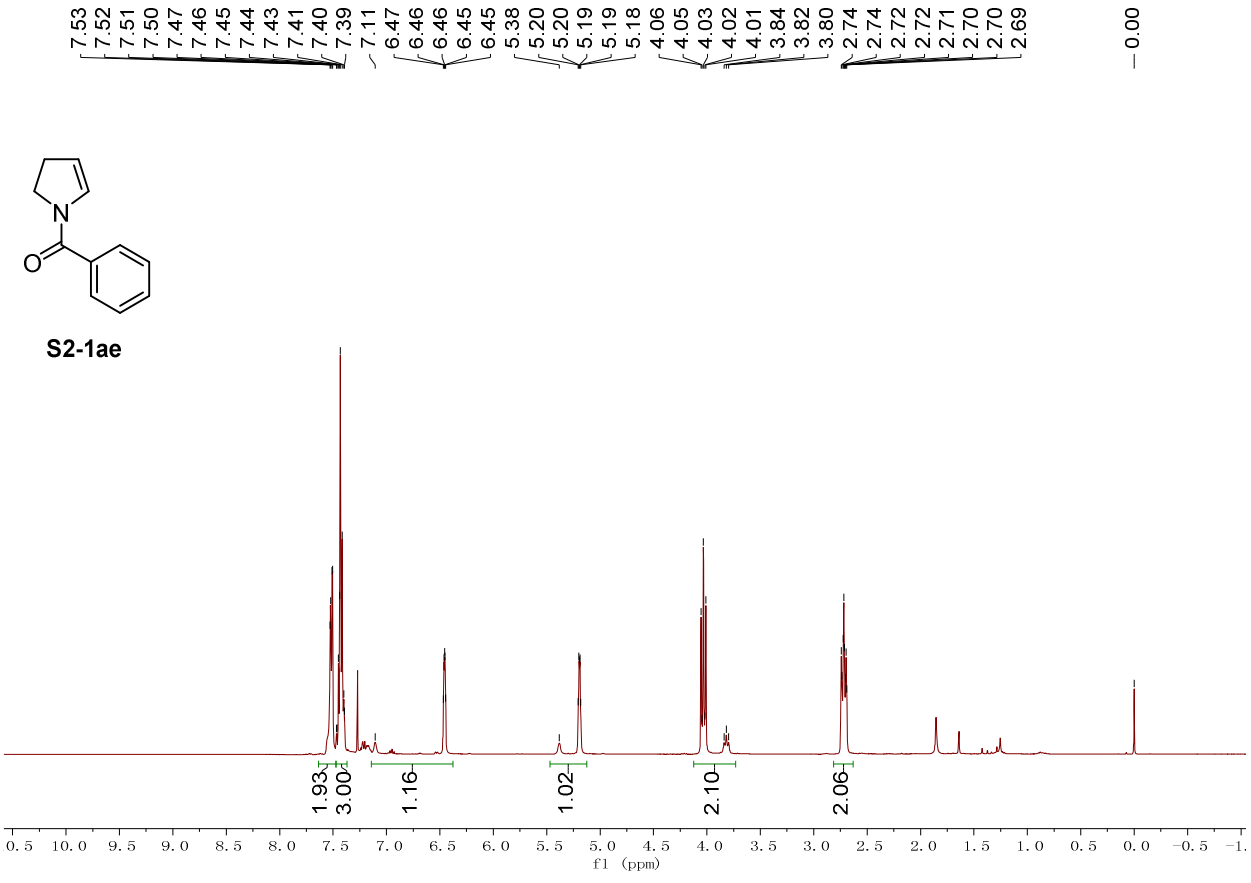


4v

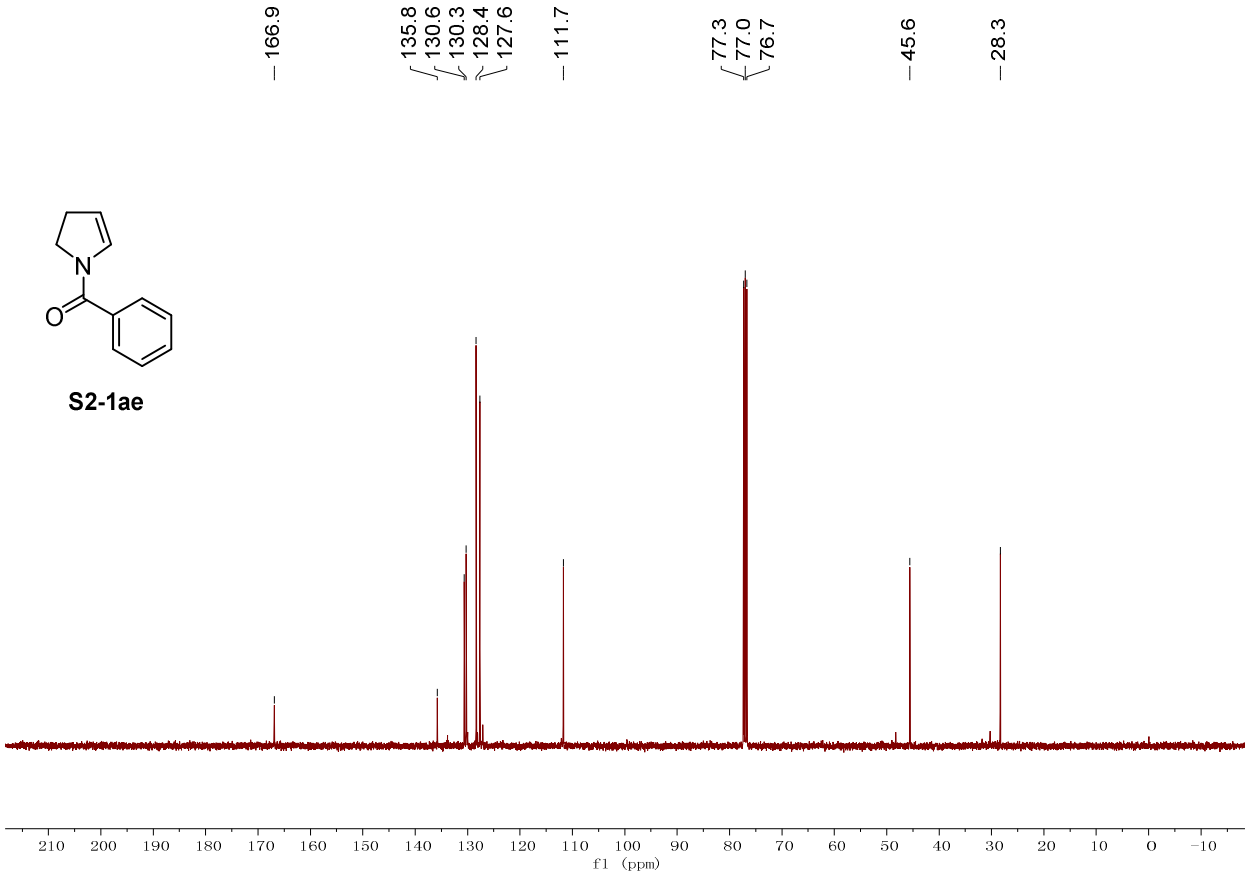
^{13}C NMR (101 MHz, $CDCl_3$)



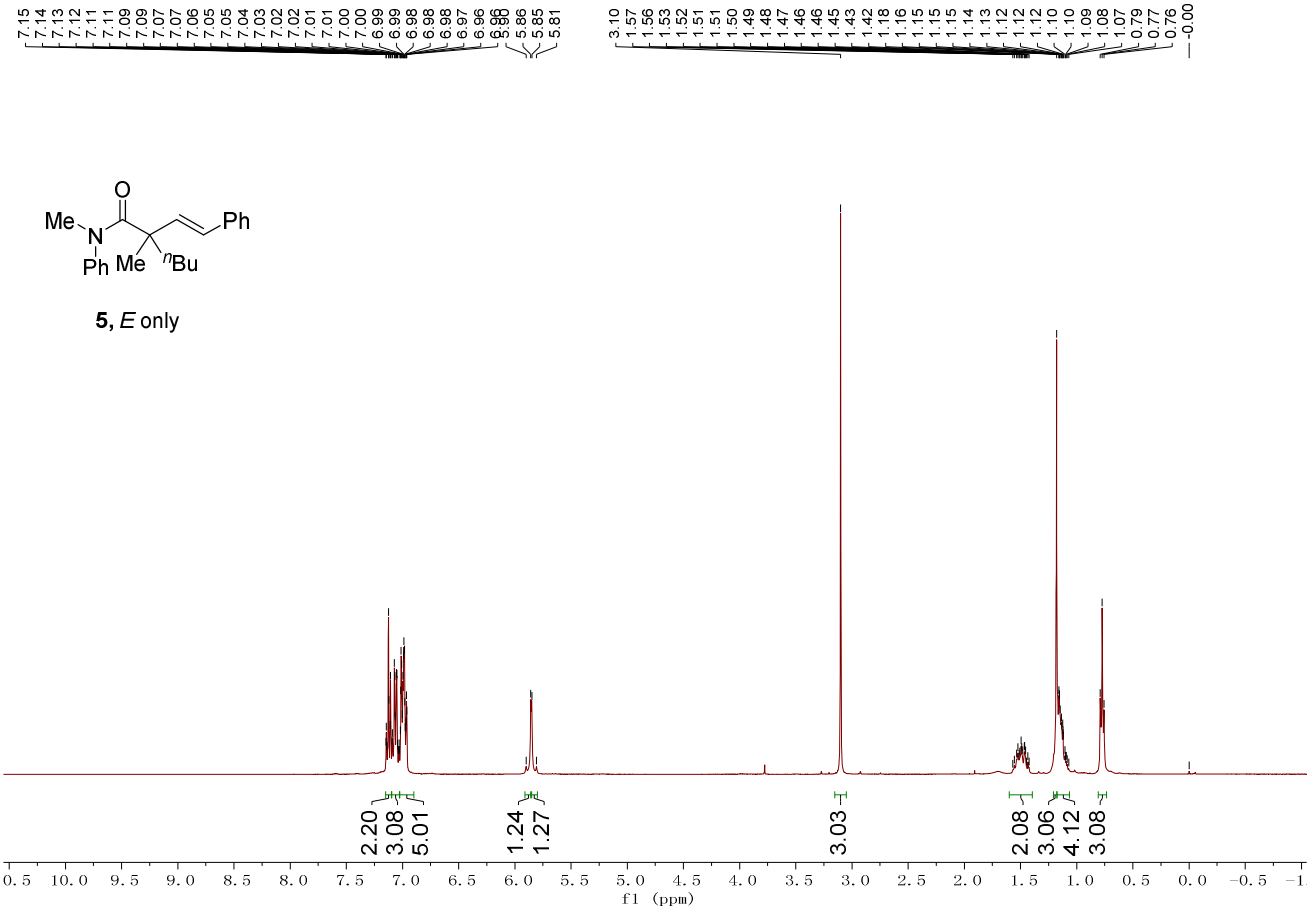
^{1}H NMR (400 MHz, $CDCl_3$)



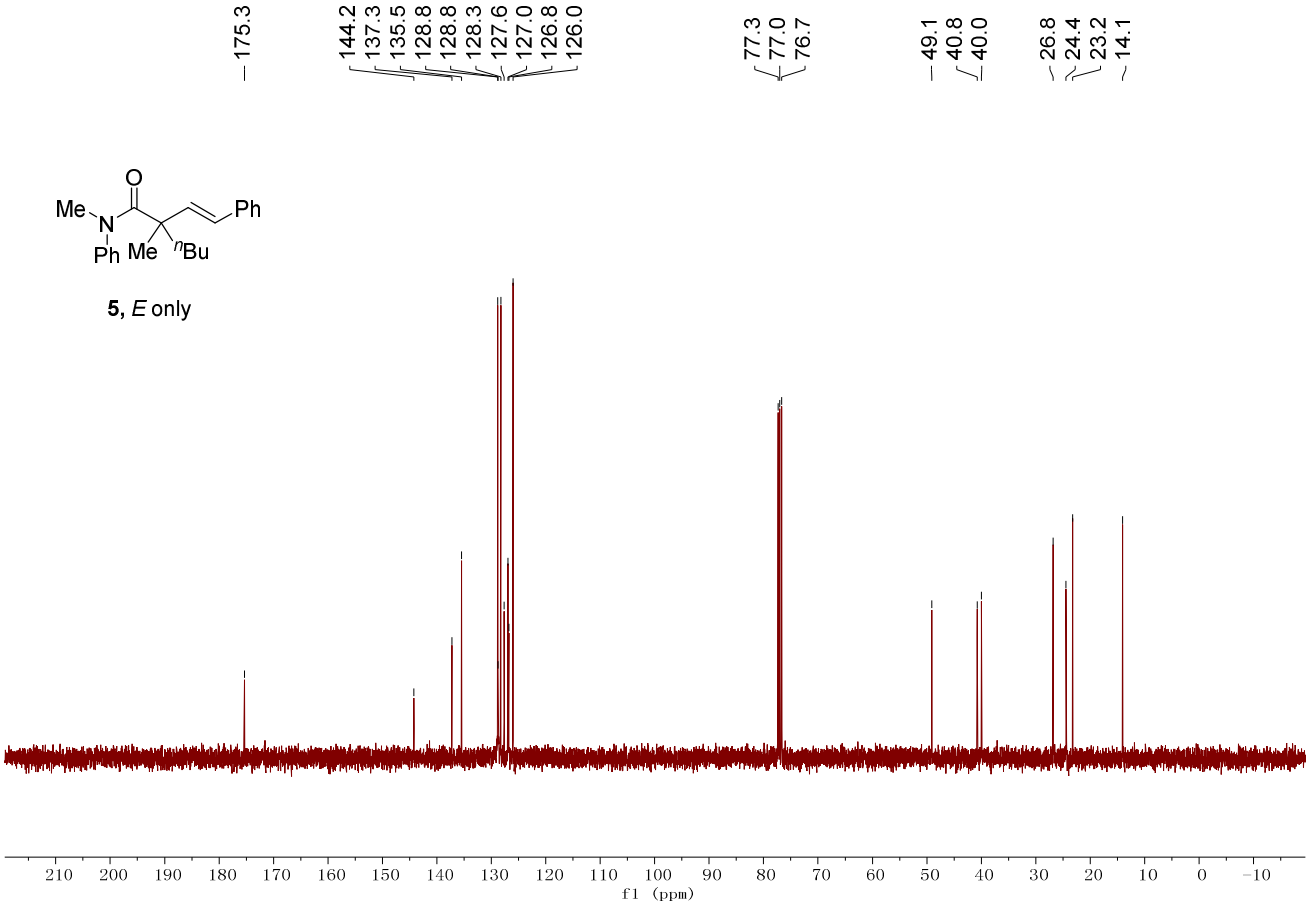
^{13}C NMR (101 MHz, $CDCl_3$)



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

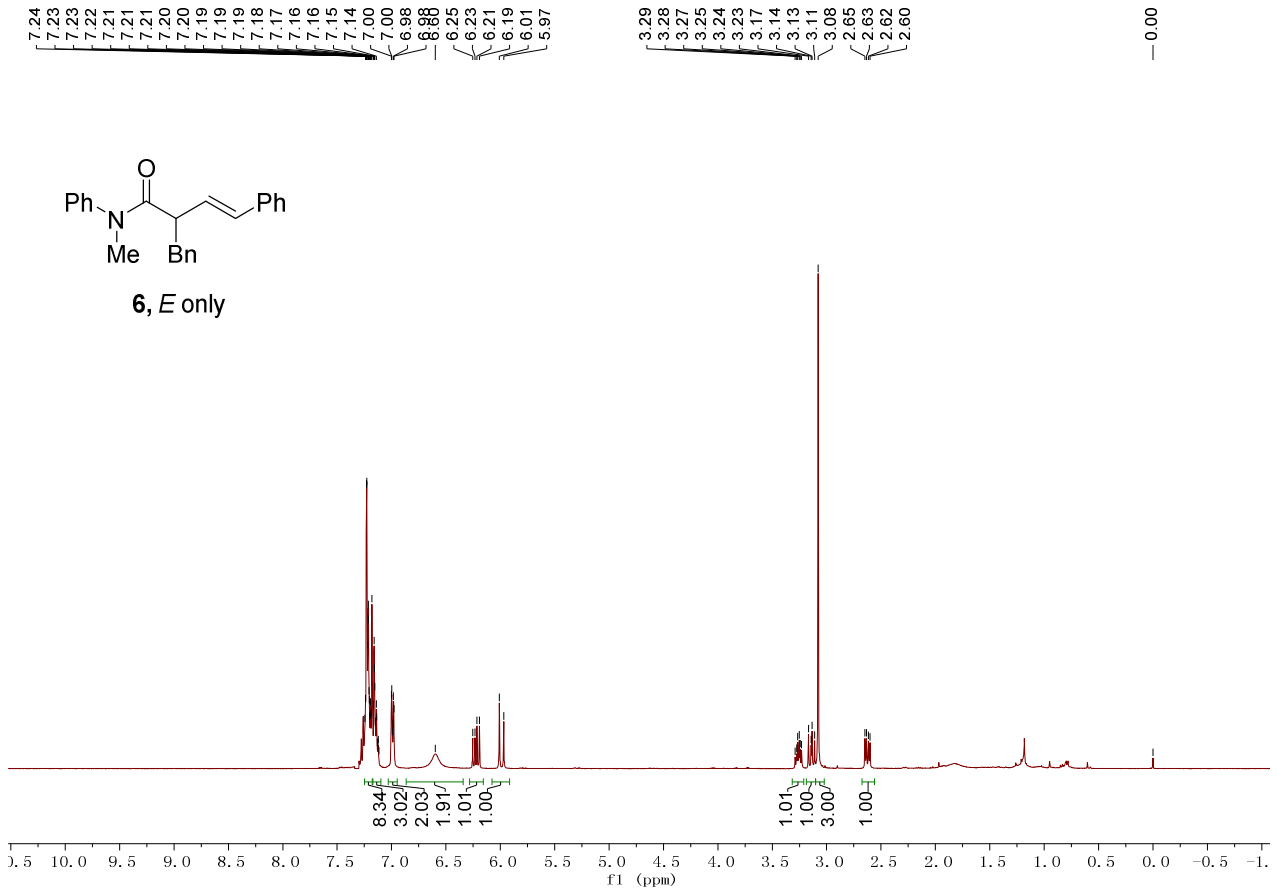


^{13}C NMR (101 MHz, $CDCl_3$)



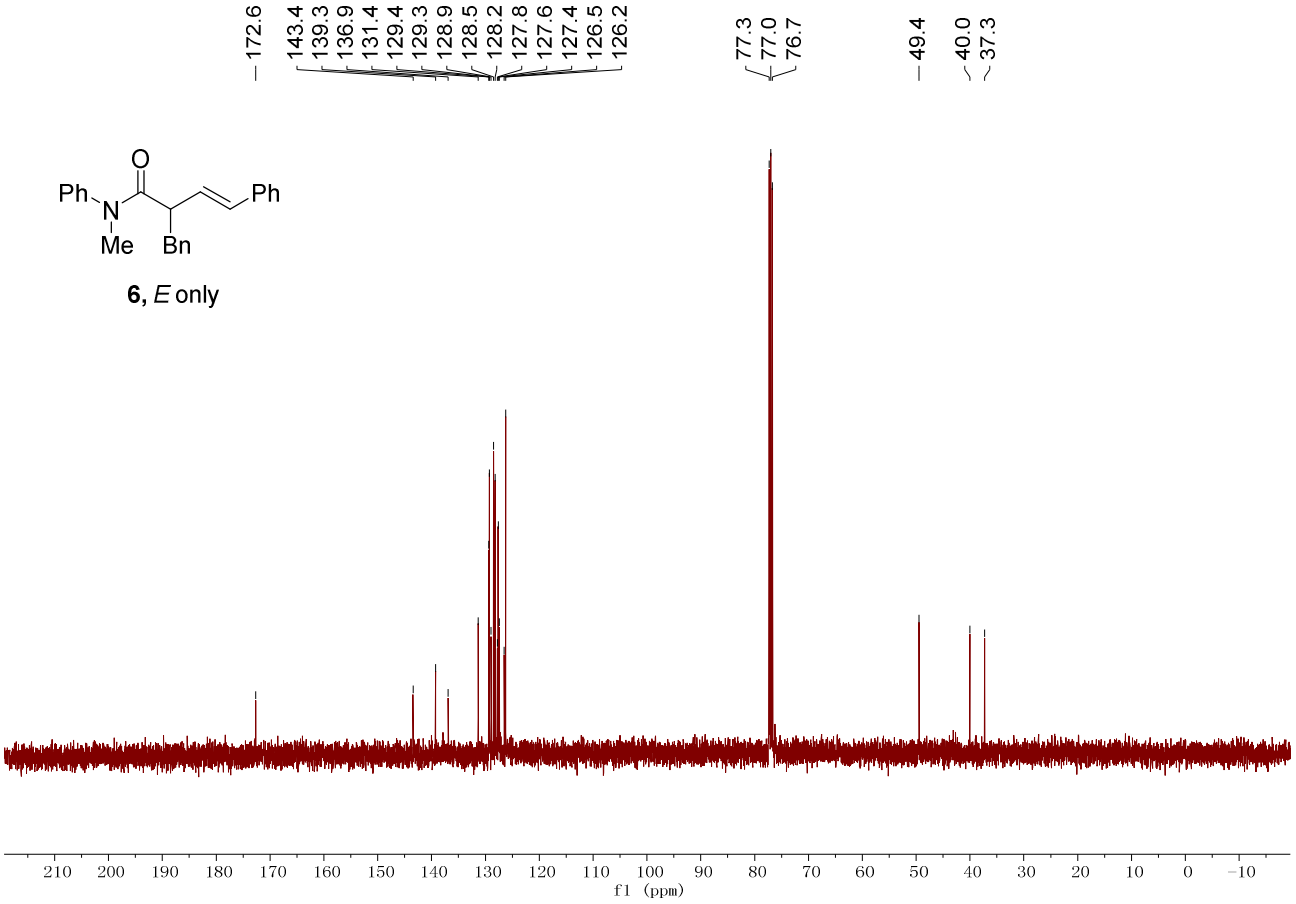
5, *E* only

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



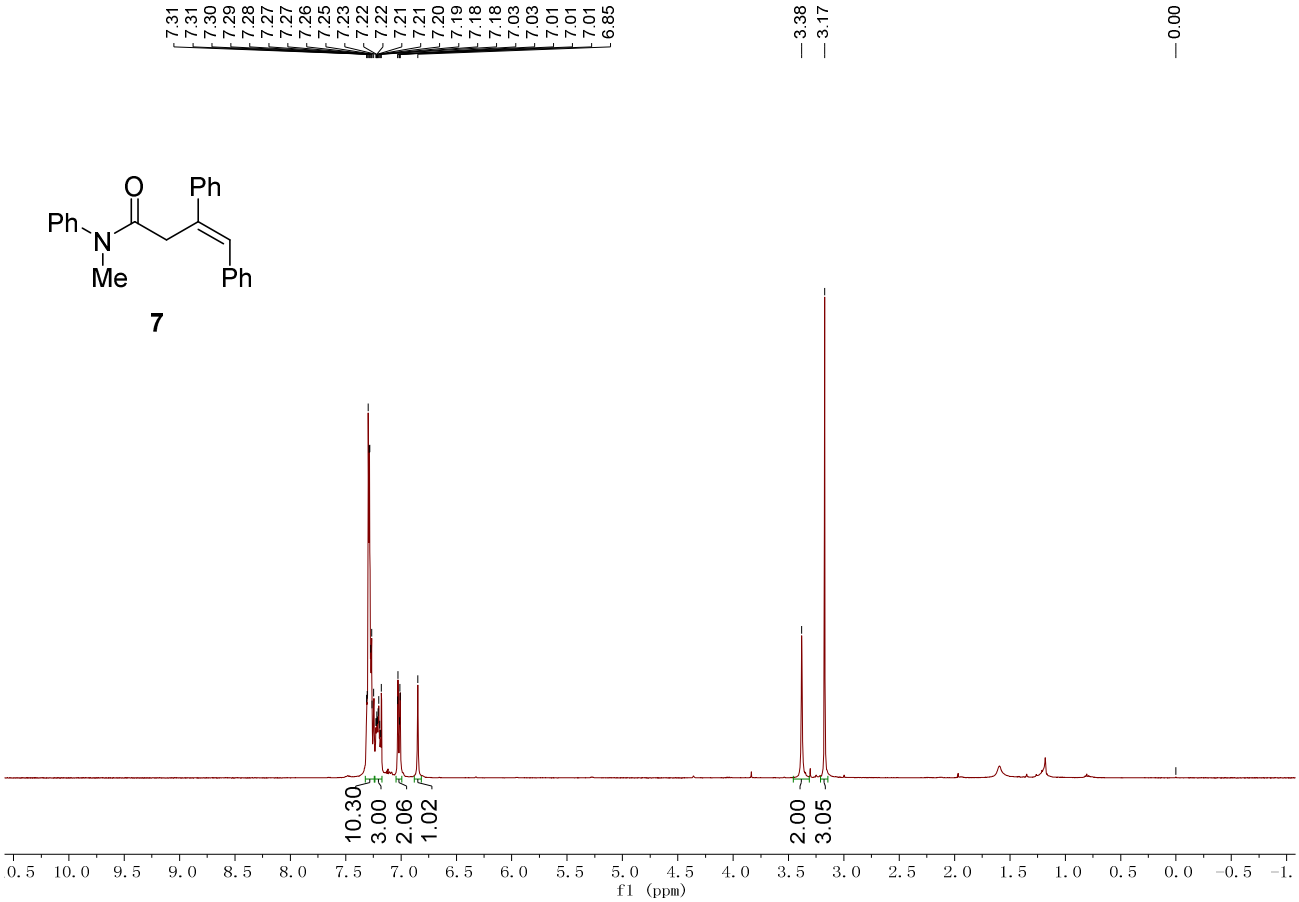
6, *E* only

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



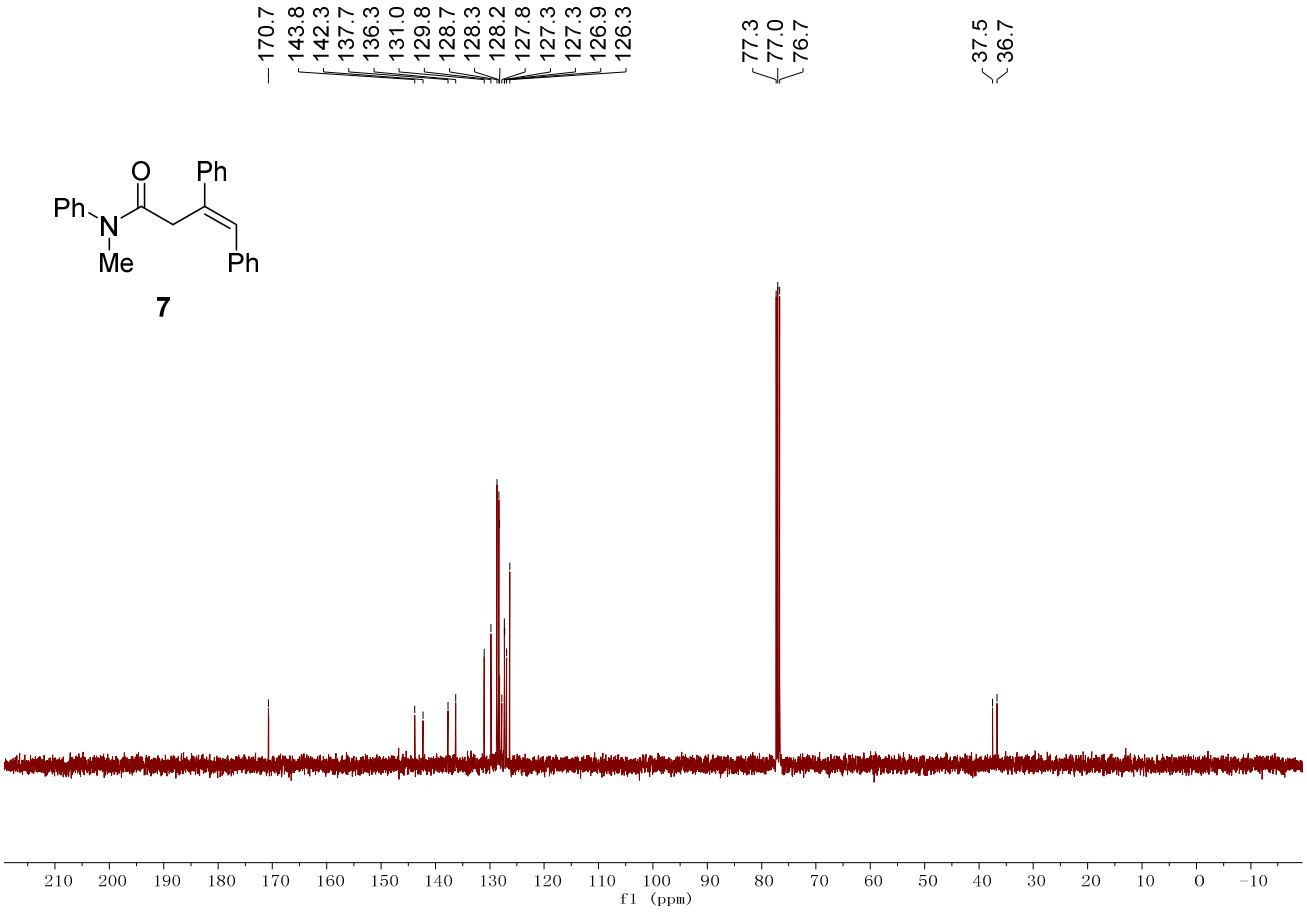
6, *E* only

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

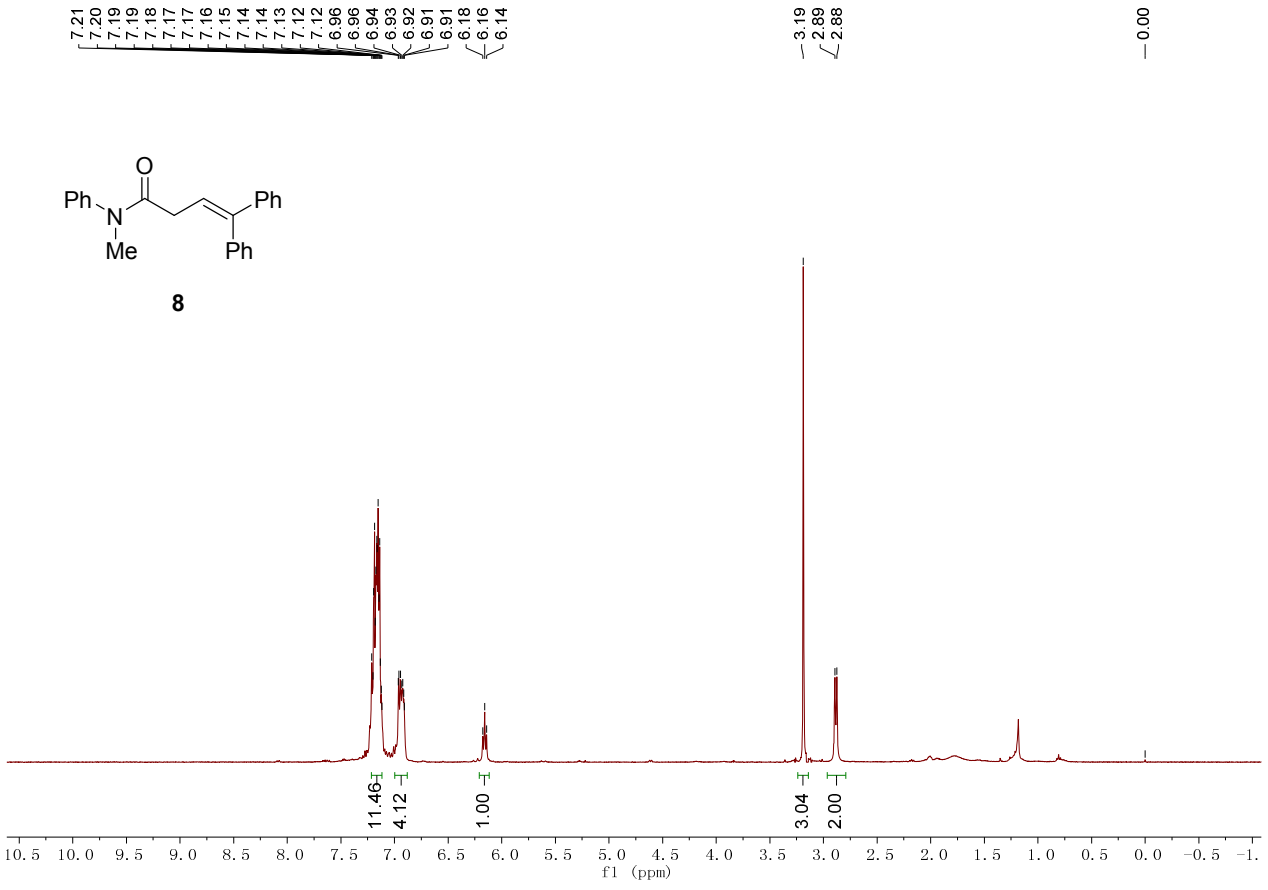


7

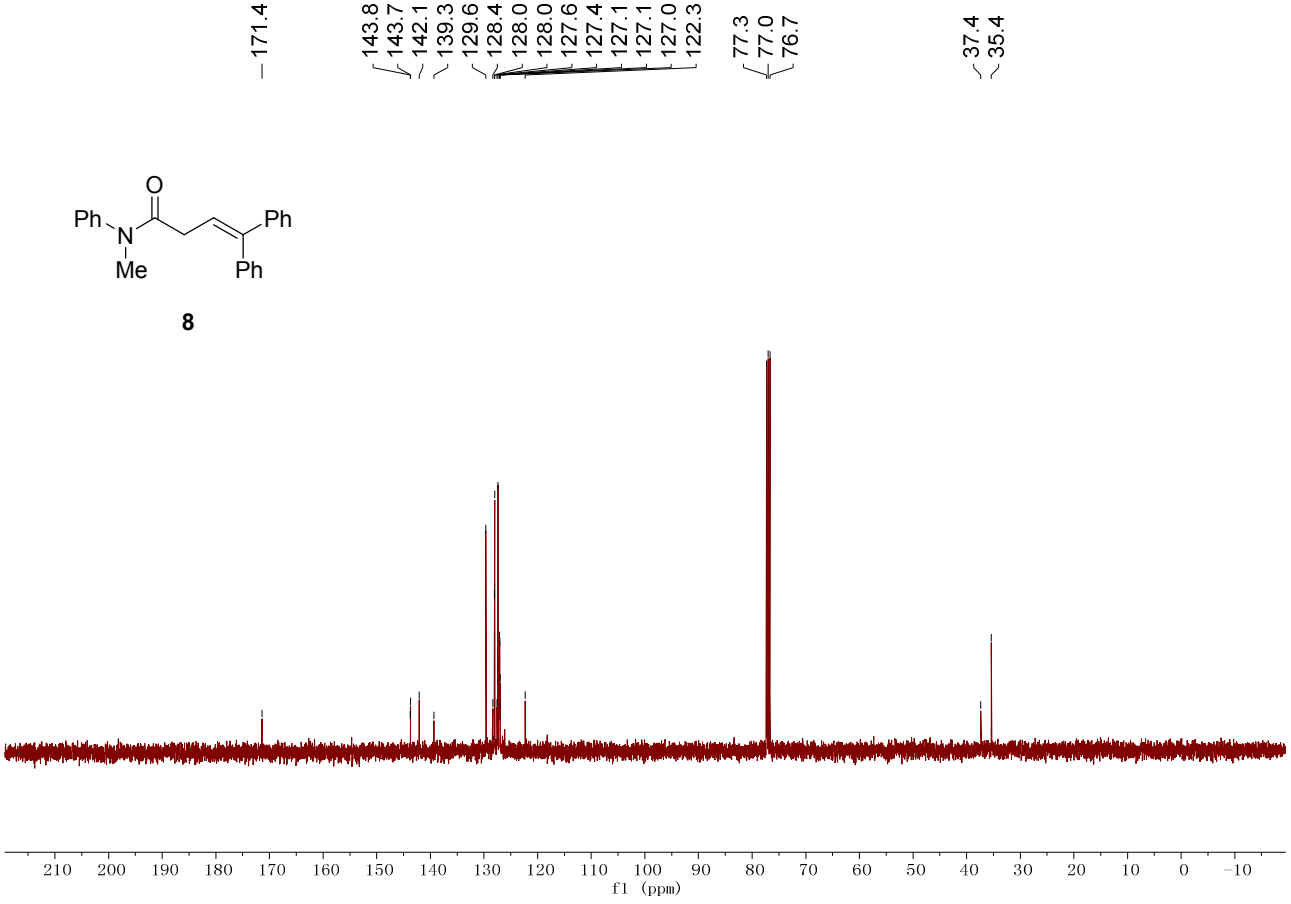
^{13}C NMR (101 MHz, $CDCl_3$)



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

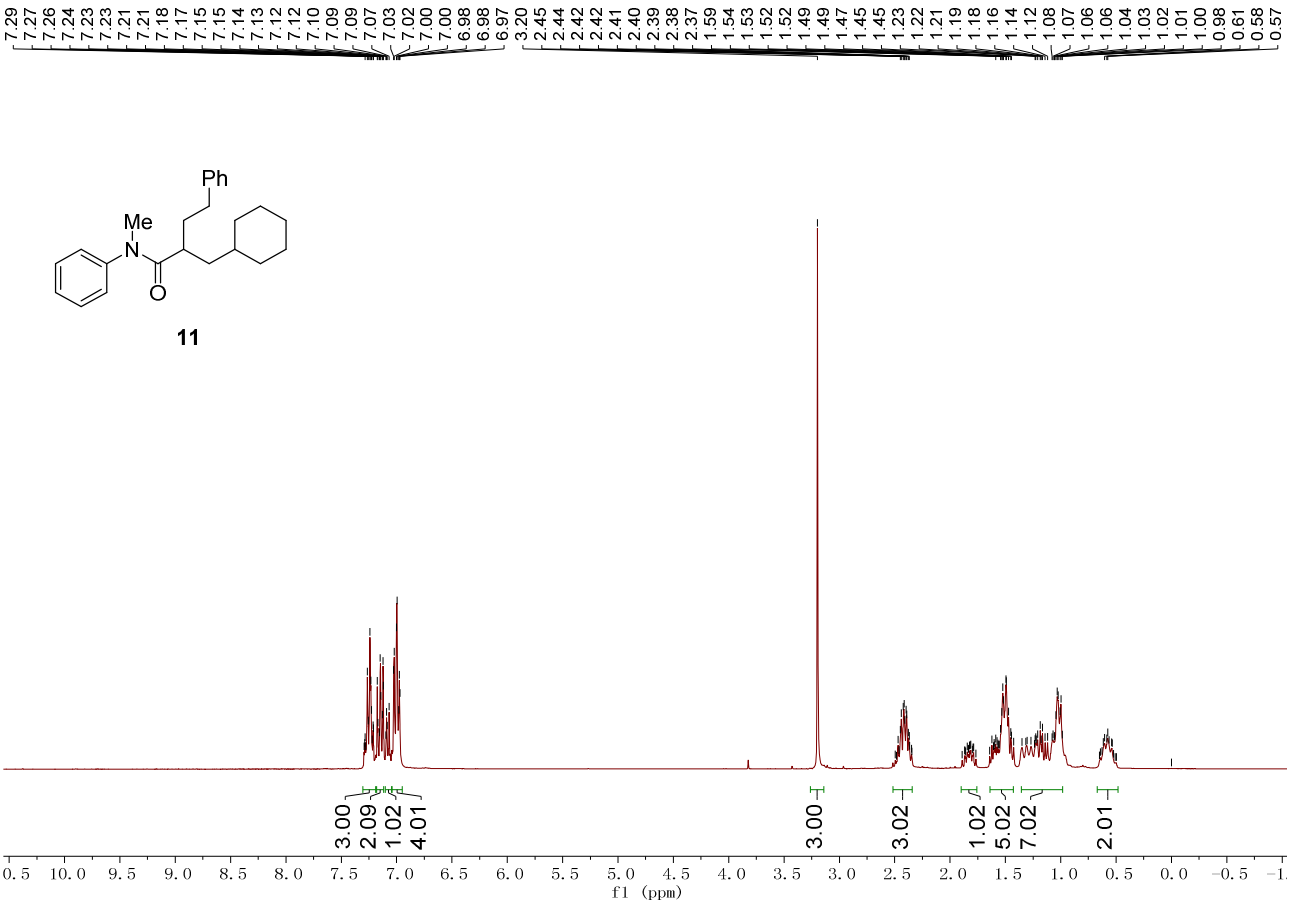


^{13}C NMR (101 MHz, $CDCl_3$)



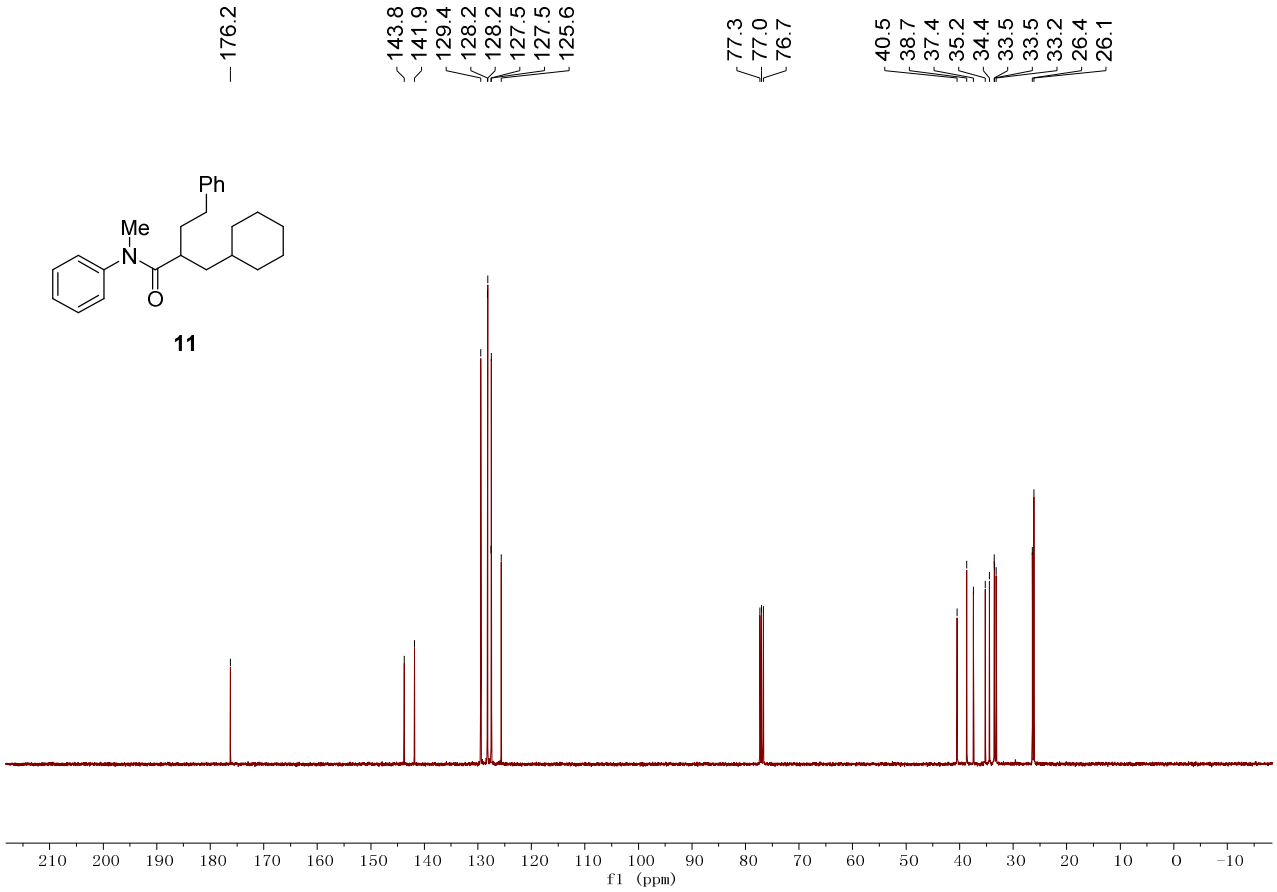
8

^{1}H NMR (300 MHz, $CDCl_3$)

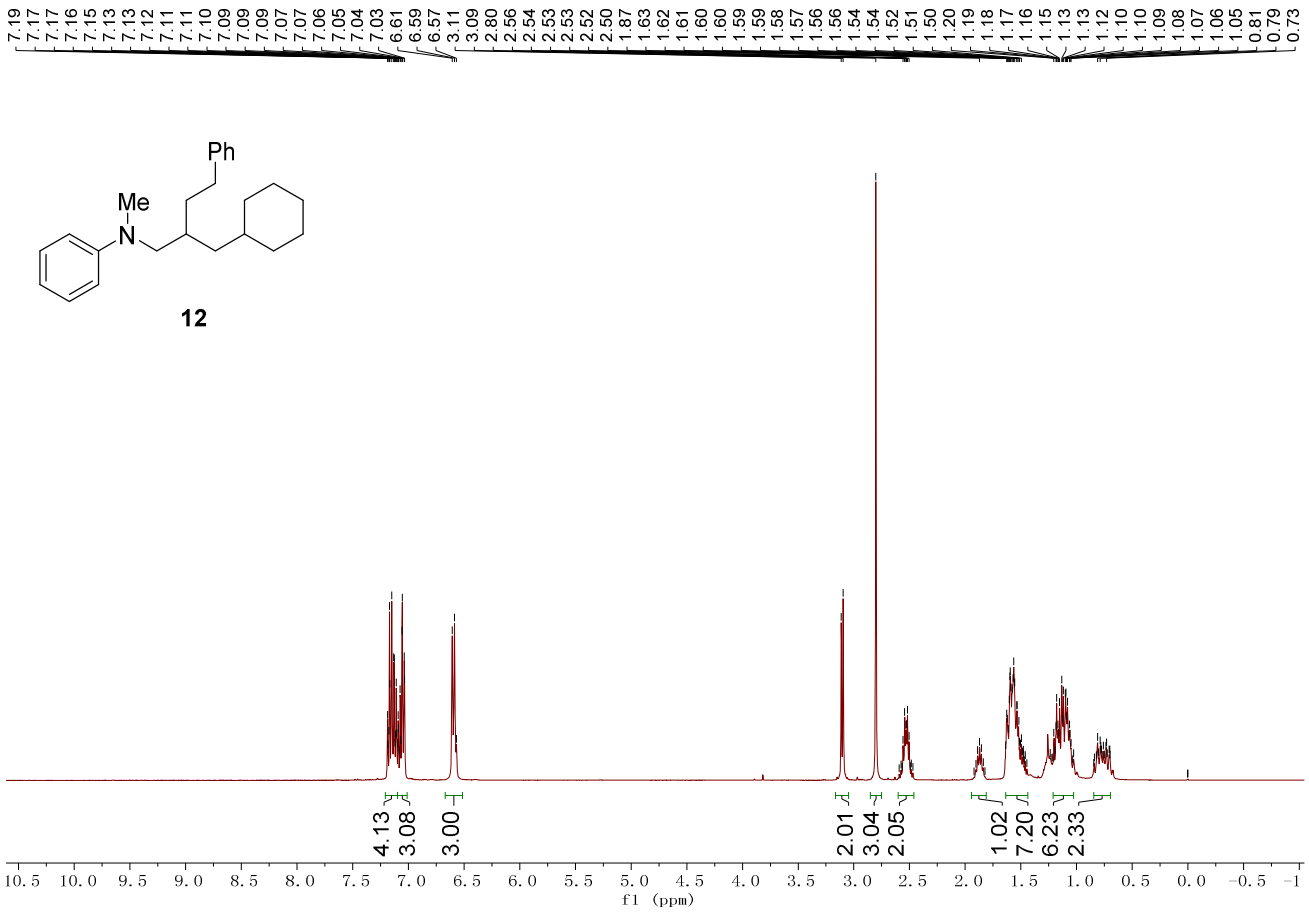


11

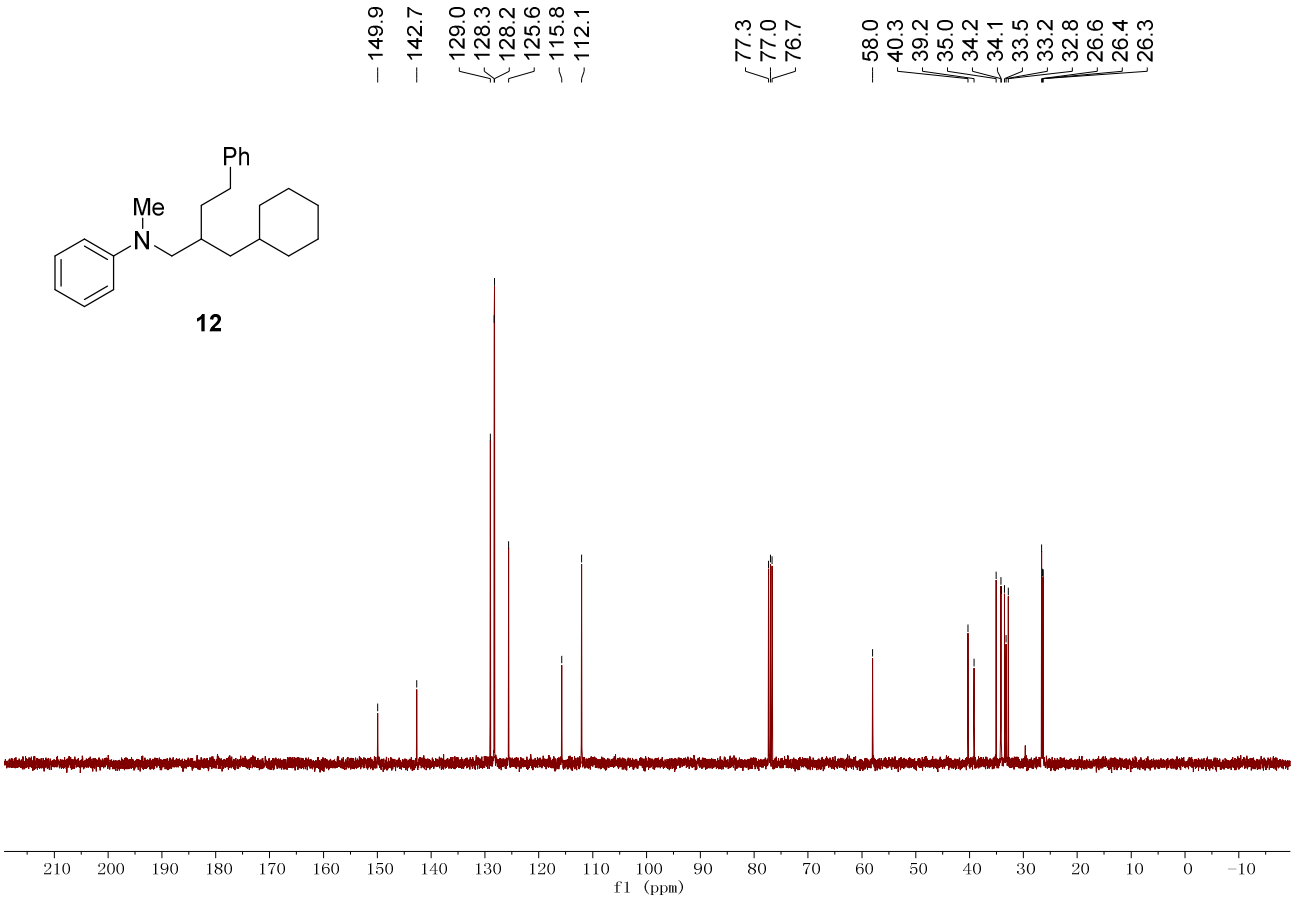
^{13}C NMR (101 MHz, $CDCl_3$)



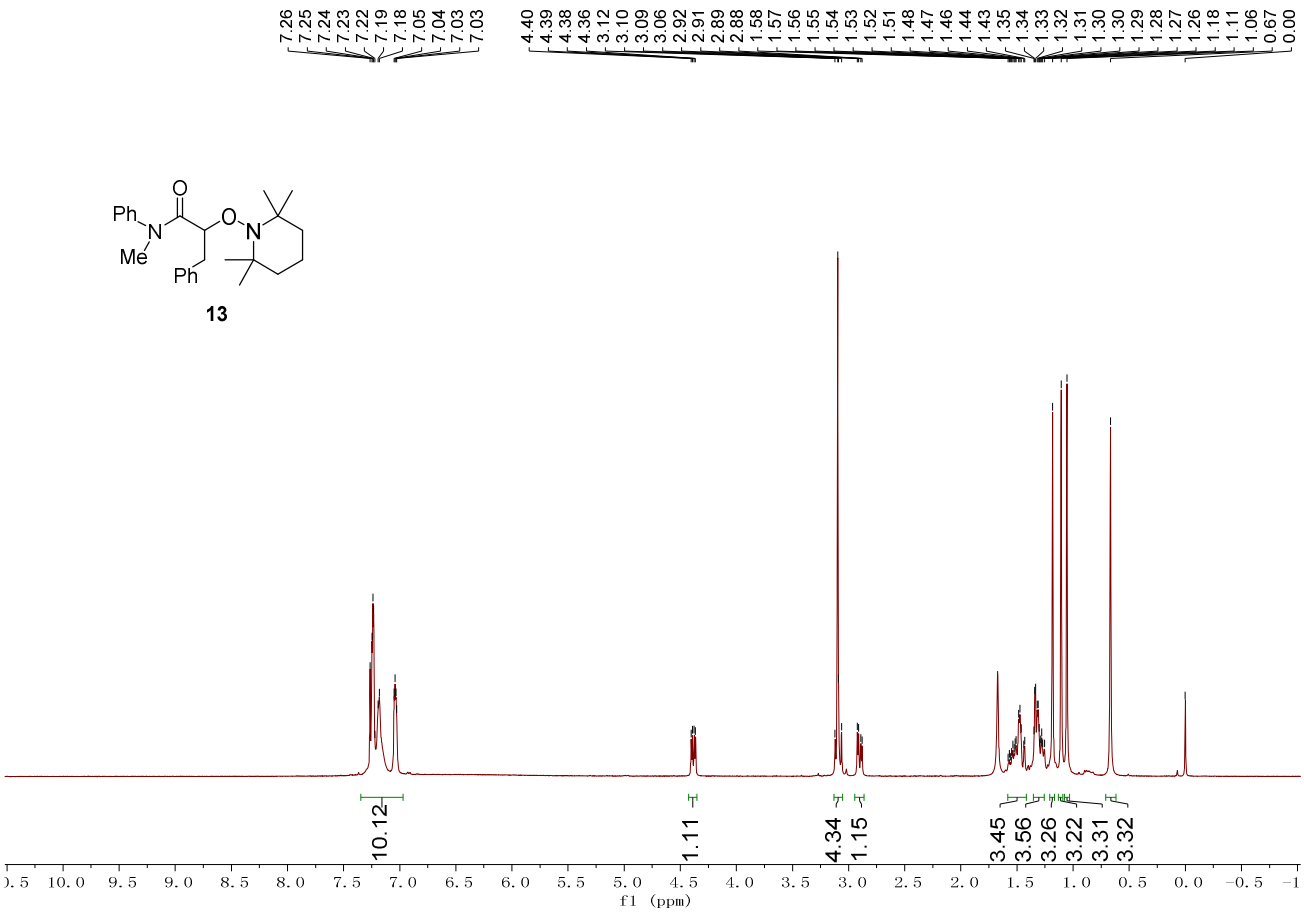
^{1}H NMR (400 MHz, $CDCl_3$)



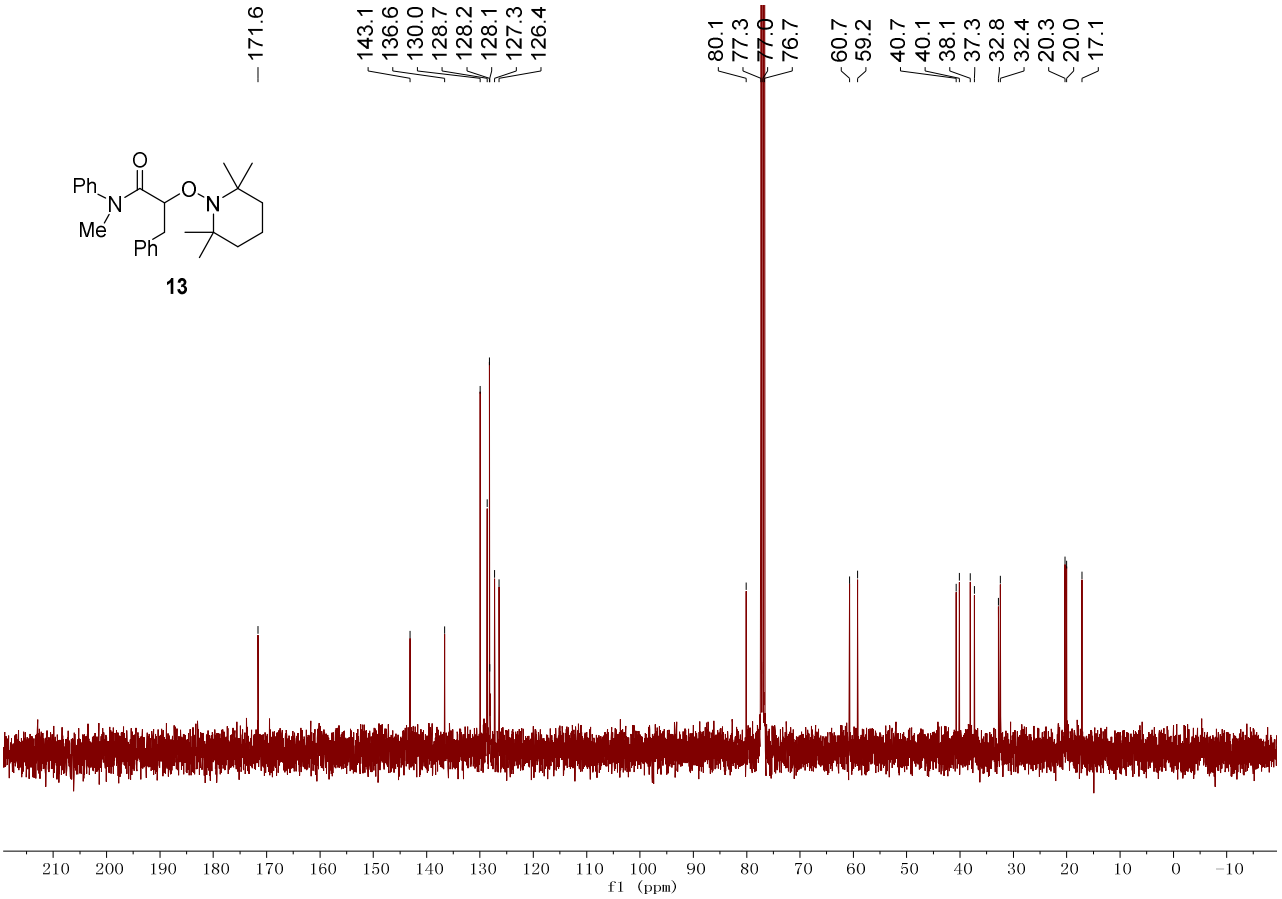
^{13}C NMR (101 MHz, $CDCl_3$)



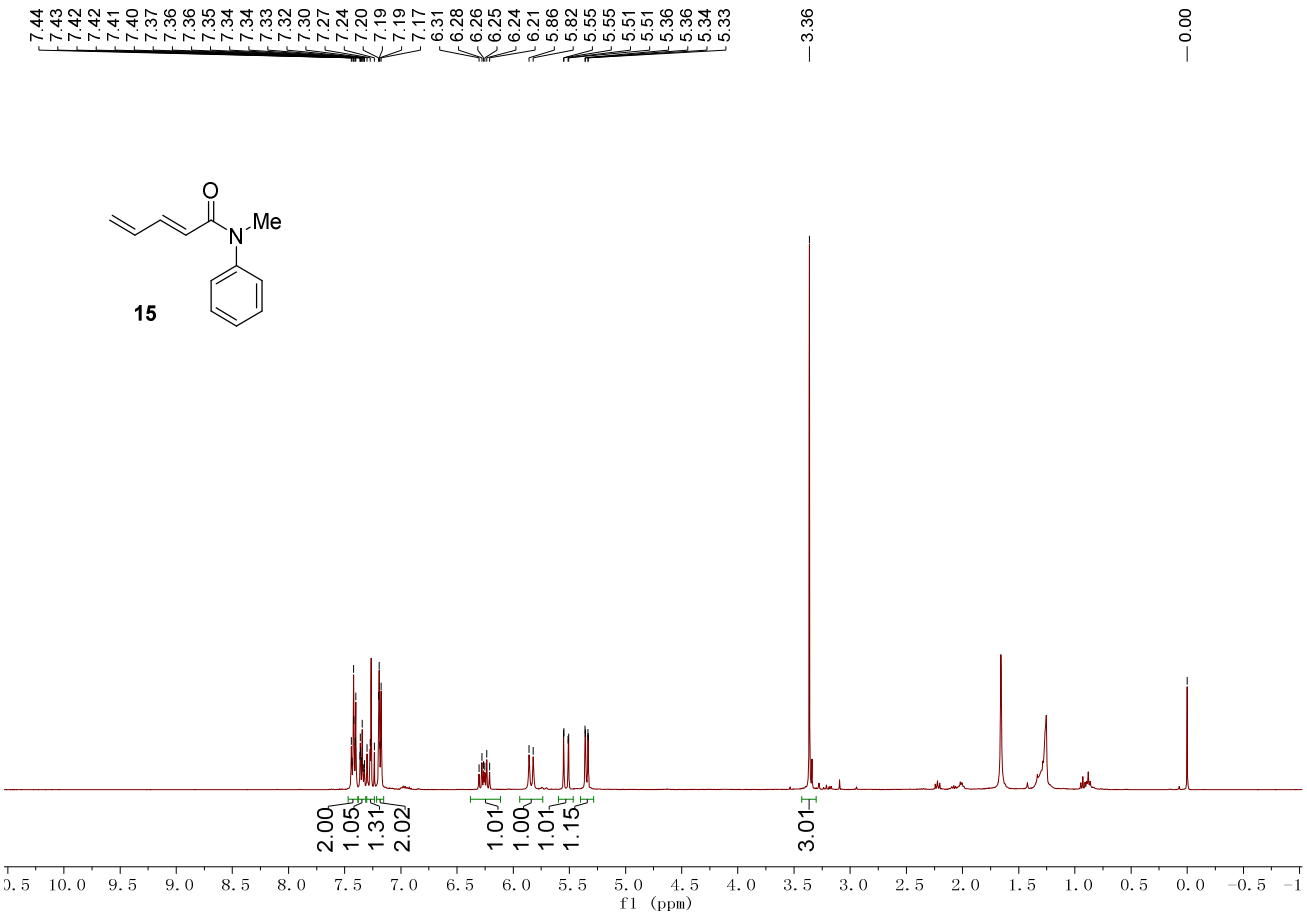
^{1}H NMR (400 MHz, $CDCl_3$)



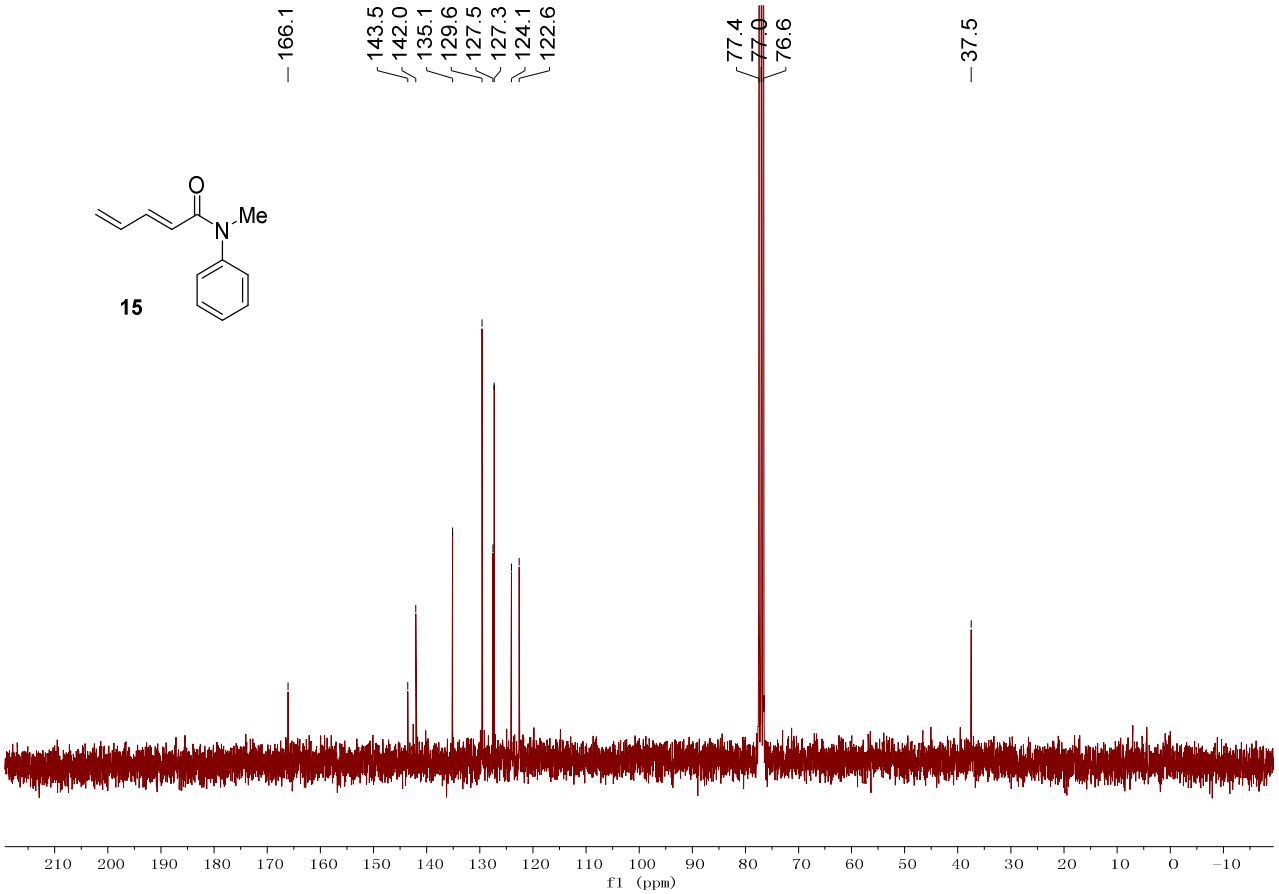
^{13}C NMR (101 MHz, $CDCl_3$)



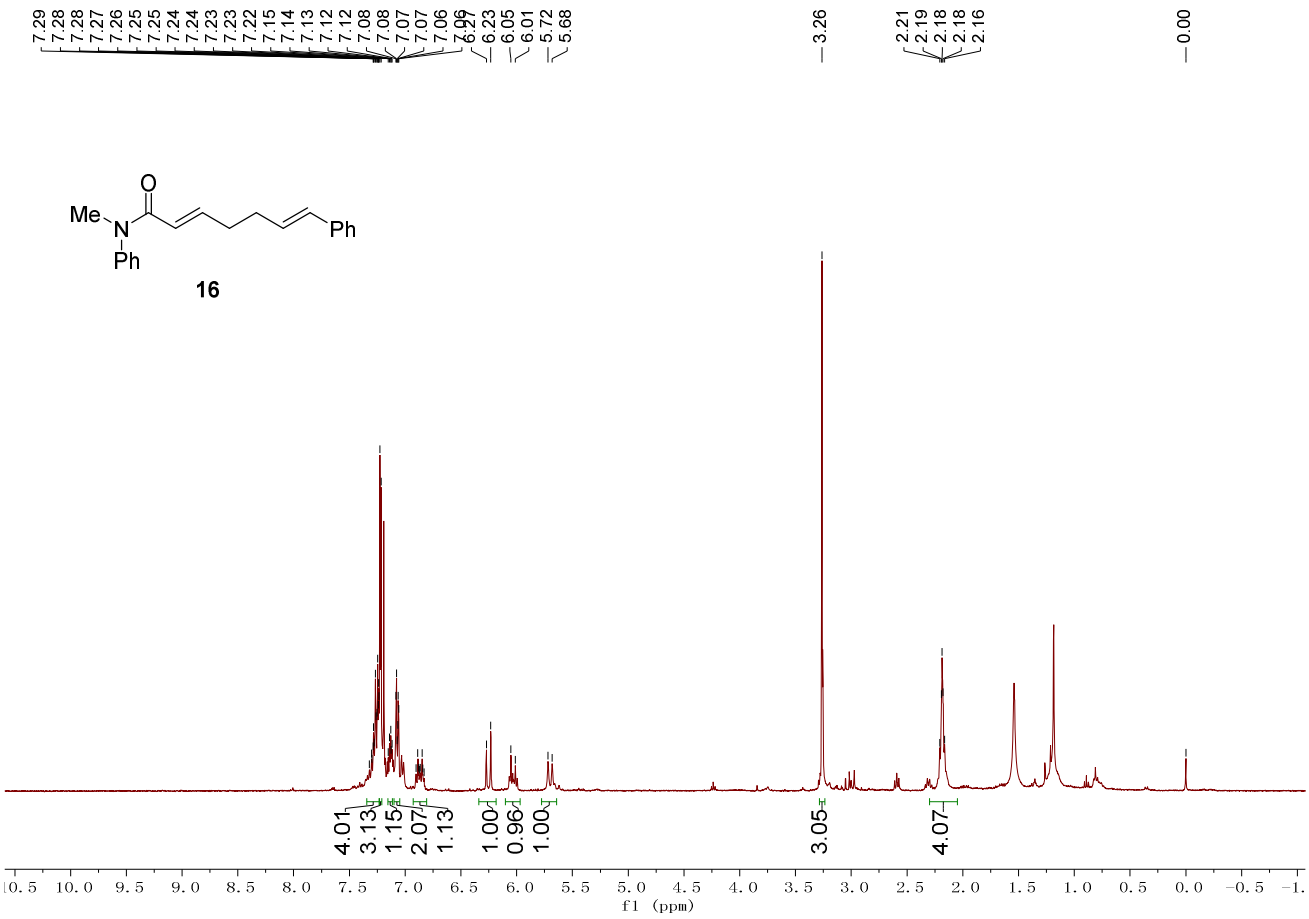
^{1}H NMR (400 MHz, $CDCl_3$)



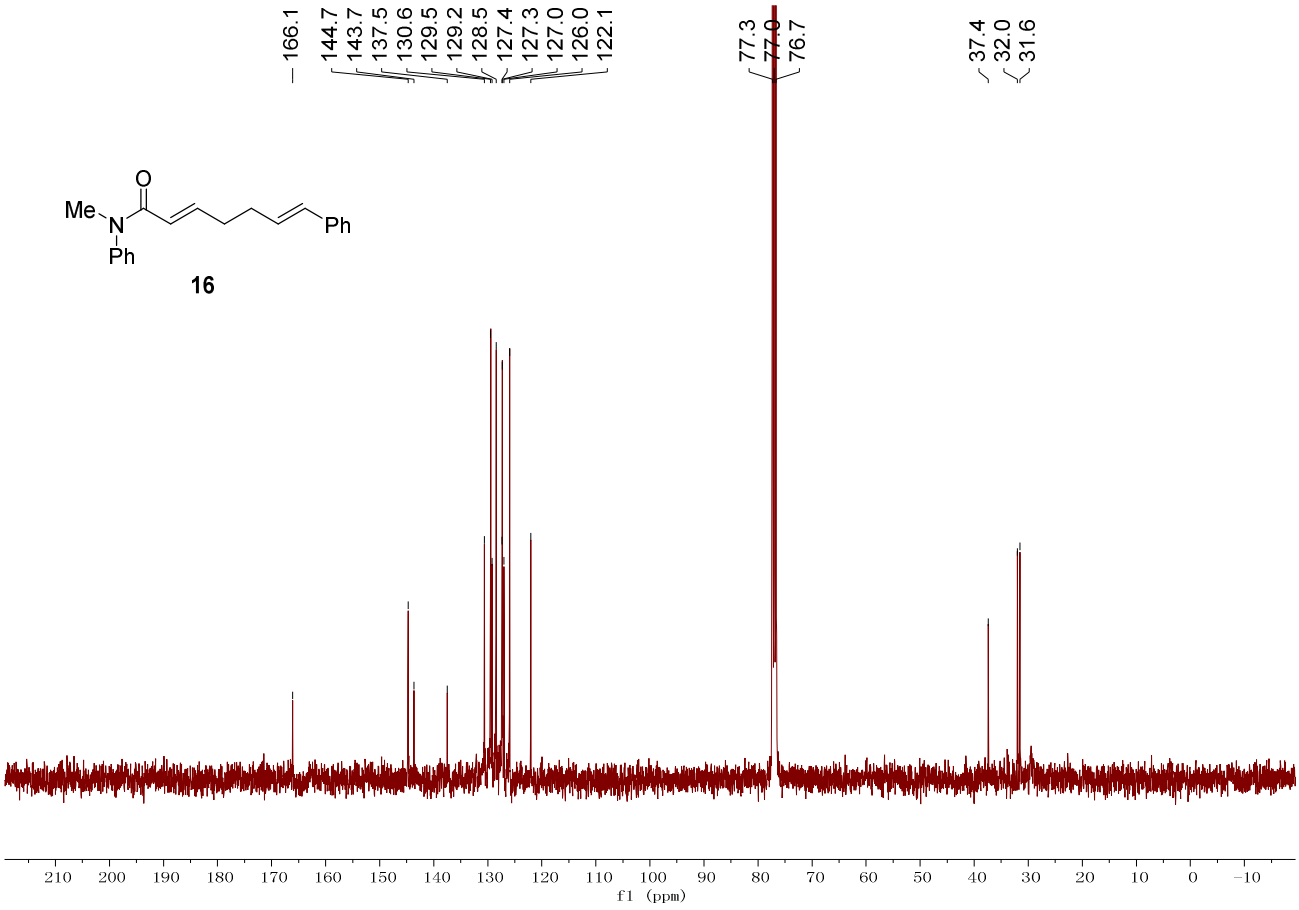
^{13}C NMR (75 MHz, $CDCl_3$)



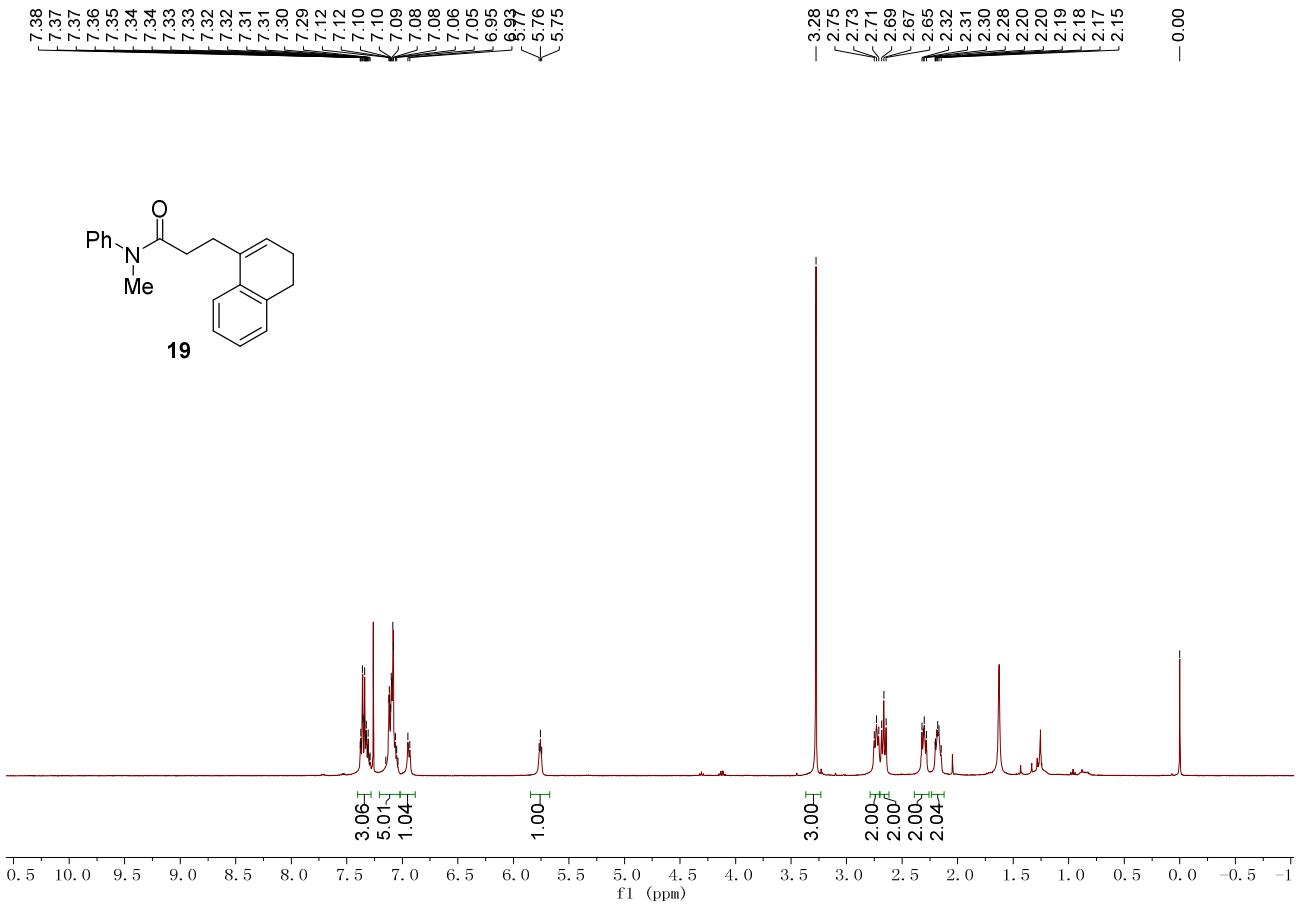
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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