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Photoinitiated Carbonyl-Metathesis: Deoxygenative Reductive Olefination of Aromatic Aldehydes via Photoredox Catalysis

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Supplementary Information

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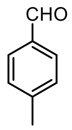
1. Generation information

All NMR spectra were recorded on a Bruker Avance Bruker Avance 300 or 400 spectrometer. Chemical shifts (δ scale) are reported in parts per million and carlibrated using the solvent residue peak as the internal standard.[1] Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, University of Regensburg. GC/MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation were done with MSD ChemStation E.02.02.1431. Photocatalytic reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 455 nm (± 15 nm), 3.5 V, 700 mA). Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). Flash column chromatography for photocatalytic reactions was performed with silica gel (particle size:40 - 63 µm or 25 µm) on a Biotage® Isolera ™ Spektra system. Solvents were dried over activated (at 250 °C for 2 hours) 3 Å molecular sieves.

2. Supplemental Experimental Data

Starting materials

The following starting materials were commercially available and purified by distilling (if liquid) prior to use; aldehydes (if solid) were purified by washing with saturated Na_2CO_3 solution and then the purity was checked by ^1H NMR spectroscopy analysis.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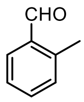
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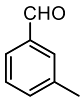
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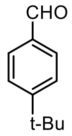
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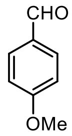
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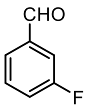
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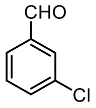
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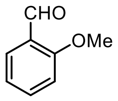
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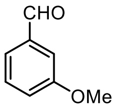
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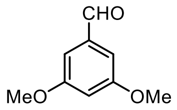
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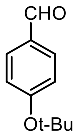
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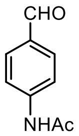
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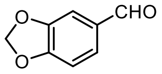
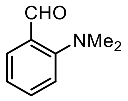
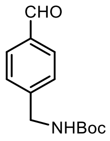
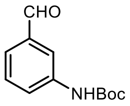
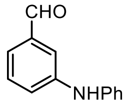

benzo[*d*][1,3]dioxole-5-carbaldehyde


2-(dimethylamino)benzaldehyde

The following starting materials were synthesized according to literature reports[2-11]


tert-butyl (4-formylbenzyl)carbamate[2]


tert-butyl (3-formylphenyl)carbamate[3]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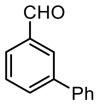
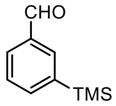

[1,1'-biphenyl]-3-carbaldehyde[5]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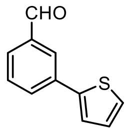
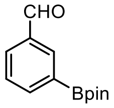
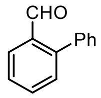
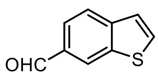
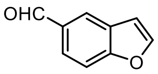
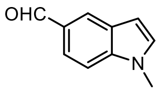

3-(thiophen-2-yl)benzaldehyde[7]


3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzaldehyde[8]

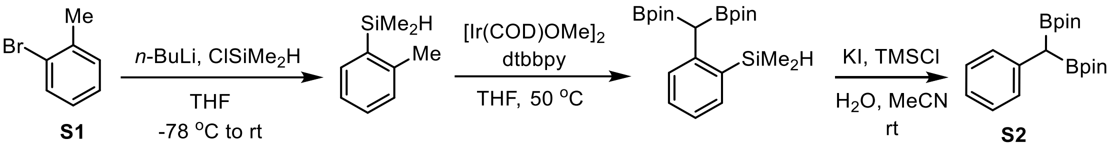

[1,1'-biphenyl]-2-carbaldehyde[5]


benzo[*b*]thiophene-6-carbaldehyde[9]


benzofuran-5-carbaldehyde[10]


1-methyl-1*H*-indole-5-carbaldehyde[11]

Synthesis of 1,1-benzyldiboronate ester.[12]

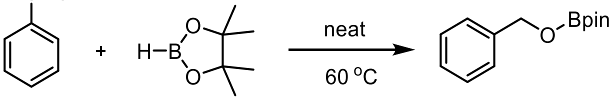


Step 1: To a 50 mL round bottom flask containing a stir bar was added the 2-bromomethylbenzene **S1** (10.00 mmol). The flask was sealed with a septum, and dry THF (30 mL) was added under N_2. The reaction mixture was cooled to –78 °C, then a solution of *n*-BuLi (7.4mL, 15 mmol, 1.60 M in hexane) was added dropwise to the reaction mixture. The reaction was stirred for 30 minutes, and chlorodimethylsilane (1.42 g, 15 mmol) was added in one portion at the same temperature. The reaction mixture was then warmed to room temperature and stirred for overnight. The reaction was quenched with a saturated NH_4Cl solution (15.0 mL) and extracted with Et_2O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vaccum. The crude product was purified by flash column chromatography on silica gel (hexane as eluent) to give 2-methylphenyl dimethylsilane derivative as colorless liquid (1.15 g, 85%).

Step 2: To a 50 mL round bottom flask containing a stir bar was added B_2pin_2 (2.0 eq, 10 mmol, 2.54 g). The flask was sealed with a septum, evacuated with pump and refilled with N_2 for three cycles, then (2-methylphenyl)dimethylsilane (5 mmol, 750 mg), freshly prepared stock solutions of $[Ir(COD)OMe]_2$ (0.025 mmol, 0.5 mol %) in THF (5.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (0.05 mmol, 1.00 mol %) were added in sequence by syringes. The flask was stirred at 50 °C overnight, the resulting reaction mixture filtered through a pad of Celite and concentrated under reduced pressure. The obtained yellowish solid was directly used for the next step.

Step 3: To a 20 mL snap vial containing a stir bar was added 1,1-benzyldiboronate ester, KI (1.20 equiv.), TMSCl (1.20 equiv.), H_2O (1.20 equiv.), and CH_3CN (0.100 M). The reaction was sealed and stirred for 2 h at room temperature. The mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The crude mixture was purified by flash column chromategraphy (PE:EA = 100:0 to 90:10) to give the 1,1-benzyldiboronate ester **S2** as a white solid (1.2 g, 70% yield over 2 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 4H), 7.12 – 7.03 (m, 1H), 2.30 (s, 1H), 1.22 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.47 , 129.12 , 127.90 , 124.14 , 83.33 , 24.66 , 24.58.

Synthesis of 2-(Benzyloxy)pinacolborane[13]



S3

To a 10 mL snap vial containing a stir bar was added benzaldehyde (5.0 mmol, 530 mg) and pinacolborane (7.0 mmol, 1.4 eq., 1.0 mL). The reaction mixture was stirred at 60 °C for 30 minutes. The reaction mixture was concentrated under reduced pressure. Next, the potassium carbonate (0.75 mmol, 0.15 eq., 103.5 mg.) and 5 mL of DCM were added and stirred with the crude product for 25 minutes. After that, the solution was filtrated through a pad of Celite and concentrated under reduced pressure to give the product **S3** as a colorless oil (1.11g, 95%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 4.93 (s, 2H), 1.27 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.14 , 128.22 , 127.30 , 126.65 , 82.93 , 66.61 , 24.56 .

Experimental procedures

General procedure A for the homo-coupling olefination of aldehydes

To a 5 mL snap vial with a stirring bar, B_2pin_2 (0.24 mmol, 1.2 equiv.), [Ir($FCF_3ppy)_2$dtbbpy] (1 mol%) and Cs_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The vial was evacuated and back filled with nitrogen for three times. A solution of 4-Me-BnSH (20 mol%) and aldehyde (0.2 mmol) in dry DMF (0.6 mL) was added by syringe. After degassed with two freeze-pump-thaw cycles via a syringe needle, the reaction mixture was irradiated with a 455 nm LED (~3W) for 24 hours at 25 ^oC. The reaction mixture was then diluted with water and extracted with ethyl acetate (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum and subjected to flash column chromatography.

General procedure B for the homo-coupling olefination of aldehydes

To a 5 mL snap vial with a stirring bar, B_2pin_2 (0.24 mmol, 1.2 equiv.), [Ir($FCF_3ppy)_2$dtbbpy] (1 mol%) and Cs_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The vial was evacuated and back filled with nitrogen for three times. A solution of 4-Me-BnSH (20 mol%) and aldehyde (0.2 mmol) in dry DMF (0.6 mL) was added by syringe. After degassed with two freeze-pump-thaw cycles via a syringe needle, the reaction mixture was irradiated with a 455 nm LED (~3W) for 24 hours at 25 ^oC. The reaction mixture was diluted with water and ethyl acetate. $NaBO_3$ (2.0 equiv.) was then added into the mixture and stirred for 30 minutes. The solution was extracted with ethyl acetate (10 mL *3). The combined organic phase was then washed by H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum and subjected to flash column chromatography.

General procedure C for the cross-coupling olefination of two aldehydes

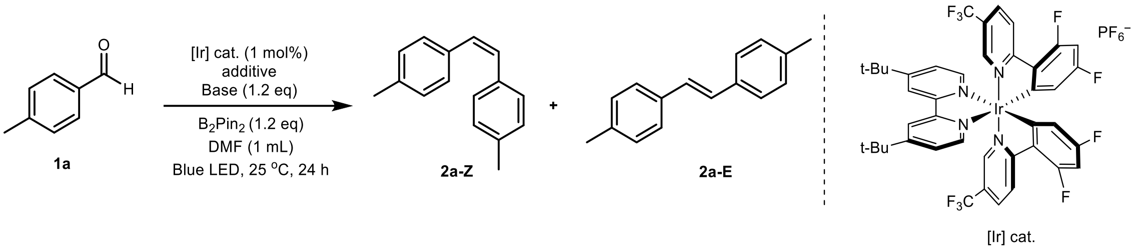
To a 5 mL snap vial with stirring bar, B_2pin_2 (0.24 mmol, 2.4 equiv.), [Ir($FCF_3ppy)_2$dtbbpy] (4 mol%) and Cs_2CO_3 (0.24 mmol, 2.4 equiv.) were added. The vial was evacuated and back filled with nitrogen three times. A solution of 4-Me-BnSH (40 mol%) and aldehyde **1a** (0.1 mmol) and aldehyde **2a** (0.15 mmol) in dry DMF (1.0 mL) was added by syringe. After degassed with two freeze-pump-thaw cycles via a syringe needle, the reaction mixture was irradiated with a 455 nm LED (~3W) for 24 hours at 25 ^oC. The reaction mixture was diluted with water and extracted with ethyl acetate (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum and subjected to flash column chromatography.

General procedure D for the cross-coupling olefination of two aldehydes

To a 5 mL snap vial with stirring bar, B_2pin_2 (0.24 mmol, 2.4 equiv.), [Ir($FCF_3ppy)_2$dtbbpy] (4 mol%) and Cs_2CO_3 (0.24 mmol, 2.4 equiv.) were added. The vial was evacuated and back filled with nitrogen three times. A solution of 4-Me-BnSH (40 mol%) and aldehyde **1a** (0.1 mmol) and aldehyde **2a** (0.15 mmol) in dry DMF (1.0 mL) was added by syringe. After degassed with two freeze-pump-thaw cycles via a syringe needle, the reaction mixture was irradiated with a 455 nm LED (~3W) for 24 hours at 25 °C. The reaction mixture was diluted with water and ethyl acetate. $NaBO_3$ (2.0 equiv.) was then added into the mixture and stirred for 30 minutes. The solution was extracted with ethyl acetate (10 mL *3). The combined organic phase was then washed by H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum and subjected to flash column chromatography.

Optimization of the reaction conditions

Table S1. Screening of bases and additives

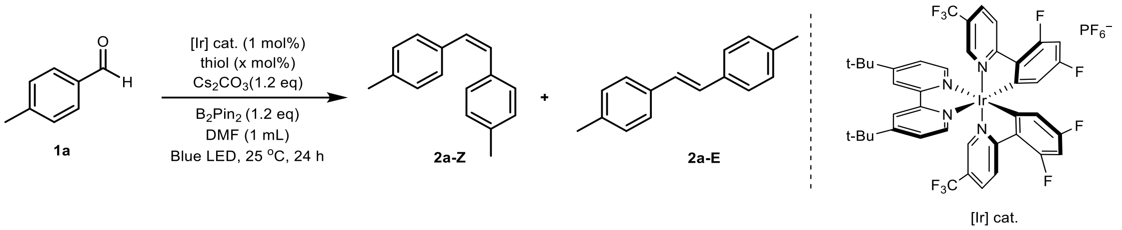


Entry[a]	Base	Additive	Yield [%]	Z:E[b]
1	**Cs_2CO_3**	**DIPEA (3.0 eq)**	trace	-
2	**Cs_2CO_3**	-	**6**	-
3	-	-	**0**	-
4[c]	**Cs_2CO_3**	-	**0**	-
5	**Cs_2CO_3**	quinuclidine (10 mol%)	**trace**	-
6	**Cs_2CO_3**	BnSH (10 mol%)	**39**	**1/2.6**
7	K_3PO_4	BnSH (10 mol%)	8	1.3/1
8	K_2CO_3	BnSH (10 mol%)	15	1.2/1
9	Na_2CO_3	BnSH (10 mol%)	trace	-
10	NaOAc	BnSH (10 mol%)	trace	-
11	Na_2HPO_4	BnSH (10 mol%)	n.r	-
12	t-BuOK	BnSH (10 mol%)	9	1/1.6
13	pyridine	BnSH (10 mol%)	trace	-

14	DMAP	BnSH (10 mol%)	trace	-
15	DBU	BnSH (10 mol%)	trace	-

[a] Reaction condition: *p*-tolualdehyde **1a** (0.2 mmol), B$_2$pin$_2$ (0.24 mmol), base (0.24 mmol), BnSH (10 mol%) and photocatalyst (1 mol%) in 1 mL DMF, irridiation with blue LED at 25 ^{o}C. Yields were determined by ^{1}H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b] Determined by ^{1}H NMR. [c] without B$_2$pin$_2$.

Table S2. Screening of thiols

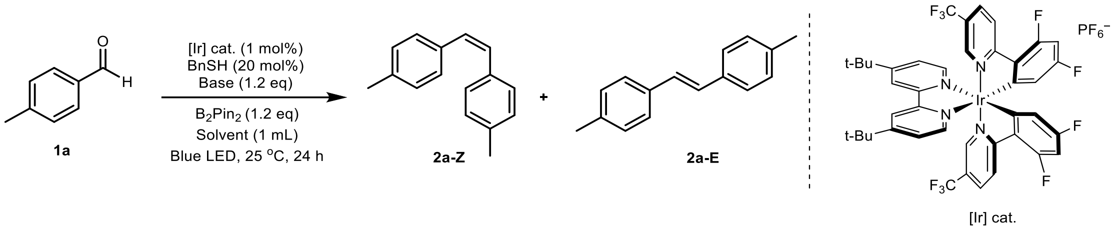


Entry[a]	Thiol (x mol%)	Yield [%]	Z:E[b]
1	BnSH (10 mol%)	39	1/2.6
2	PhSH (10 mol%)	11	1/1.5
3	^{i}Pr$_3$SiSH (10 mol%)	20	1.1/1
4	AcCH(Me)SH (10 mol%)	29	1.7/1
5	BnCH$_2$SH (10 mol%)	trace	-
6	**BnSH (20%)**	**66**	**1/1.8**
7	BnSH (5%)	8	1.4/1
8	BnSH (30%)	63	1.9/1
9	BnSH (50%)	36	1.5/1
10	BnSSBn (20%)	30	1/1.6
11	4-CF$_3$-BnSH (20%)	39	1/1.8
12	PhCH(Me)SH (20%)	53	1/1.4
13	4-^{t}Bu-BnSH (20%)	39	1/2.2
14	**4-Me-BnSH (20%)**	**63**	**1/1**
15	2,4,6-trimethyl-BnSH (20%)	52	1/2.2
16	-	7	1.5/1

[a] Reaction condition: *p*-tolualdehyde **1a** (0.2 mmol), B$_2$pin$_2$ (0.24 mmol), Cs$_2$CO$_3$ (0.24 mmol),

thiol and photocatalyst (1 mol%) in 1 mL DMF, irridiation with blue LED at 25 ^{o}C. Yields were determined by ^{1}H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b] Determined by ^{1}H NMR.

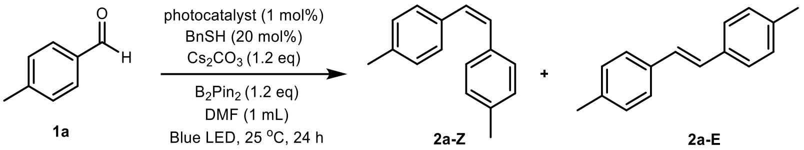
Table S3. Screening of solvents



Entry[a]	Solvent	Yield [%]	Z/E[b]
1	**DMF**	**66**	**1/1.8**
2	DMA	56	1/1.1
3	DMSO	9	1/5.4
4	acetone	trace	-
5	$MeNO_2$	0	-
6	DCE	trace	-
7	EtOH	10	3.2/1
8	NMP	4	only Z
10	DMPU	17	1.1/1
11	DMF/MeCN=4/1	36	2.2/1
12	DMF/DMA=4/1	19	2.4/1
13	DMF/DMSO=4/1	61	1.3/1
14	DMF/EtOAc=4/1	58	1.6/1
15	DMF/NMP=4/1	23	1.8/1
16	DMF+10 eq H_2O	trace	-

[a] Reaction condition: *p*-tolualdehyde **1a** (0.2 mmol), B_2pin_2 (0.24 mmol), base (0.24 mmol), BnSH (20 mol%) and photocatalyst (1 mol%) in 1 mL solvent, irridiation with blue LED at 25 ^oC. Yields were determined by ^1H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b] Determined by ^1H NMR.

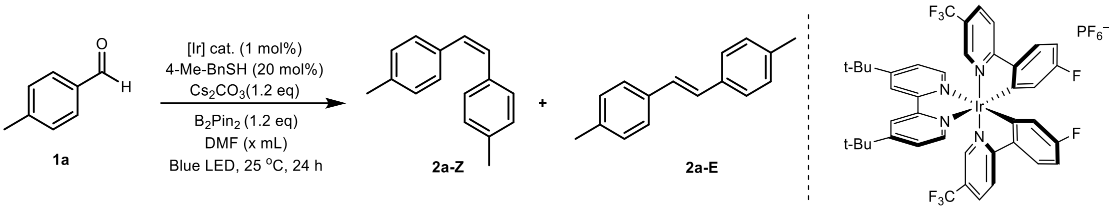
Table S4. Screening of photocatalysts



Entry[a]	Photocatalyst (x mol%)	Yield [%]	Z:E[b]
1	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	66	1/1.8
2	**$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)**	**74**	**2.2/1**
3[c]	**$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)**	**77**	**2.5/1**
4	$[Ir(dFCF_3ppy)_2(5,5'\text{-}dCF_3bpy)]PF_6$ (1 mol%)	41	1/1.3
5	4CzIPN (5 mol%)	trace	-
6	EoSin Y (5 mol%)	trace	-
7	$[Ir(ppy)_2dtbbpy]PF_6$ (1 mol%)	14	2.4/1
8	$[Ir(ppy)_2bpy]PF_6$ (1 mol%)	9	1.4/1
9	$Ru(bpy)_3Cl_2$ (1 mol%)	11	1/4.8
10	$[Ru(bpz)_3][PF_6]_2$ (1 mol%)	11	1/5.3

[a] Reaction condition: *p*-tolualdehyde **1a** (0.2 mmol), B_2pin_2 (0.24 mmol), Cs_2CO_3(0.24 mmol), BnSH (20 mol%) and photocatalyst (x mol%) in 1 mL DMF, irridiation with blue LED at 25 °C. Yields were determined by ^1H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b] Determined by ^1H NMR. [c] 4-Methyl benzyl thiol (20 mol%) was used.

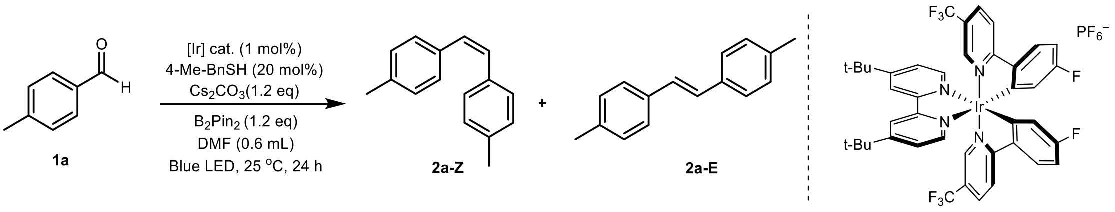
Table S5. Screening of reaction concentration



Entry[a]	PC	Thiol	Concentration	Yield[%]	Z/E[b]
1	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	4-MeBnSH (20 mol%)	0.1 M	25	1/1
2	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	4-MeBnSH (20 mol%)	0.13 M	71	1.8/1
3	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	4-MeBnSH (20 mol%)	0.33 M	**87(83)**[c]	**2.6/1**
4	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	4-MeBnSH (20 mol%)	0.5 M	68	2.4/1

[a] Reaction condition: *p*-tolualdehyde 1a (0.2 mmol), B_2pin_2 (0.24 mmol), Cs_2CO_3 (0.24 mmol), BnSH (20 mol%) and $[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%) in DMF, irridiation with blue LED at 25 °C. Yields were determined by ^{1}H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b] Determined by ^{1}H NMR. [c] Isolated yield.

Table S6. Control experiments



Entry[a]	Photocatalyst	Light	Thiol	Yield [%]	Z/E[b]
1[c]	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	OFF	4-MeBnSH (20 mol%)	0	-
2[d]	-	ON	4-MeBnSH (20 mol%)	17	3.5/1
3[e]	$[Ir(FCF_3ppy)_2dtbbpy]PF_6$ (1 mol%)	ON	4-MeBnSH (20 mol%)	8	1.8/1

[a]: Reaction condition: *p*-tolualdehyde **1a** (0.2 mmol), B_2pin_2 (0.24 mmol), Cs_2CO_3 (0.24 mmol), 4-MeBnSH (20 mol%) and catalyst (1 mol%) in 0.6 mL solvent, irridiation with blue LED at 25 ^oC. Yields were determined by ^1H NMR analysis of crude reaction mixture; 1,3,5-trimethoxybenzene was used as internal standard. [b]: Determined by ^1H NMR [c]: In the dark. [d]: Without photocatalyst. [e] Adding TEMPO (1.0 eq.)

Mechanistic studies

Cyclic Voltammetry

CV measurements were taken on a three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab by using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode. The voltammograms were taken at room temperature in a degassed DMF or MeCN solution ([n-Bu_4NBF_4] = 0.1 M, [substrate] = 1 mM, ferrocene as the internal standard) under Argon atmosphere. The scan rate was 0.1 V/s. Potentials vs. SCE were reported according to $E_{SCE} = E_{Fc/Fc+} + 0.38$ V.

Index	Peak position
1	-1.1783
2	-1.6013
3	-1.2991
4	-1.1078
5	0.65964
6	0.58411

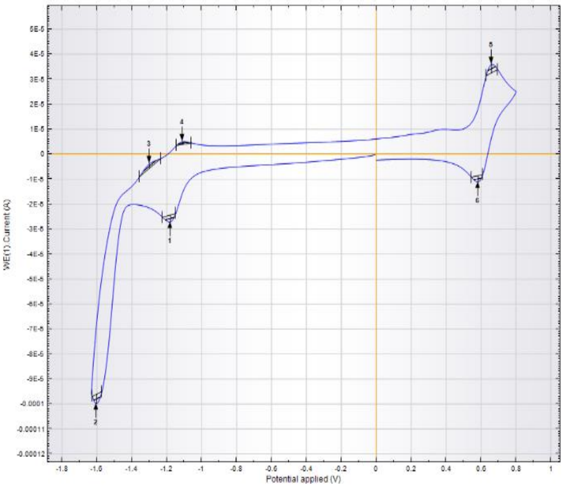


Figure S1. Cyclic voltammogram of [Ir(FCF$_3$ppy)$_2$dtbbpy]PF$_6$ in MeCN (with Ferrocene)

E_{red} [Ir(III)/Ir(II)] = -1.38V *vs*. SCE

Index	Peak position
1	1.5056
2	1.0725
3	0.9718

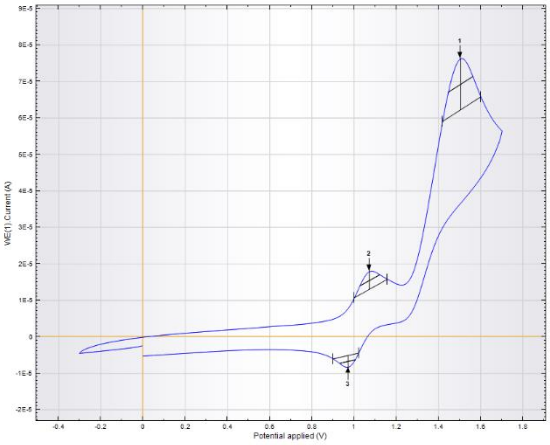


Figure S2. Cyclic voltammogram of 4-Me-BnSH in DMF (with Ferrocene)

E_{ox}(4-Me-BnSH) = 0.86 V *vs*. SCE

Index	Peak position
1	-1.5056
2	0.99701
3	0.8963

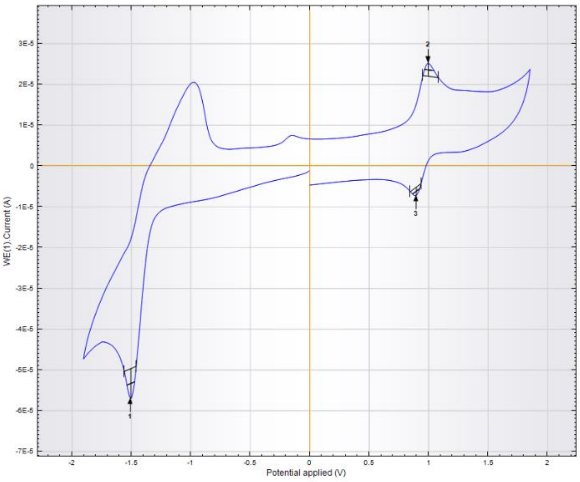


Figure S3. Cyclic voltammogram of benzaldehyde **1a** in DMF (with Ferrocene)

E_{red} (**1a**) = -2.07 V *vs.* SCE

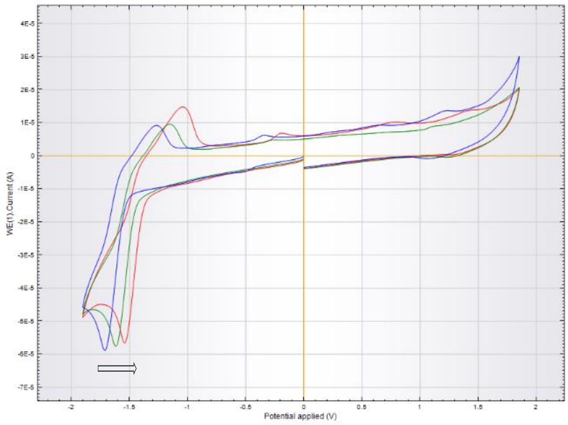


Figure S4. Cyclic voltammogram of benzaldehyde **1a** in DMF (blue curve) and a mixture of **1a** with B_2pin_2 (2.0 eq.) in DMF after stirring for 3 minutes (green curve). The reduction potential of **1a** after adding more B_2pin_2 (red curve). The corresponding reduction peak of **1a** shifted towards lower potential after adding B_2pin_2.

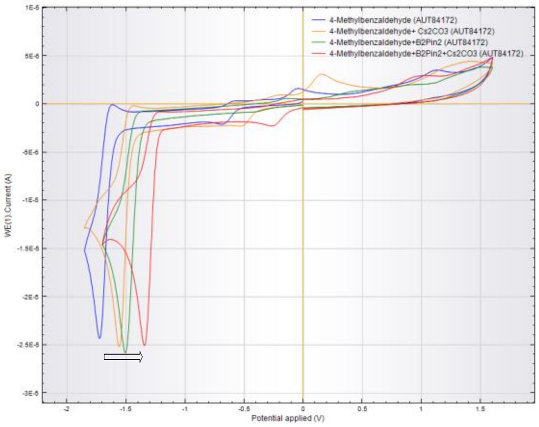


Figure S5. Cyclic voltammogram of benzaldehyde **1a** (blue curve) in DMF in the presence of different additives. Adding Cs_2CO_3 (4.0 eq) (orange curve). Adding B_2pin_2 (4.0 eq) (green curve). Adding Cs_2CO_3 (4.0 eq) and B_2pin_2 (4.0 eq) (red curve).

Fluoresence quenching study

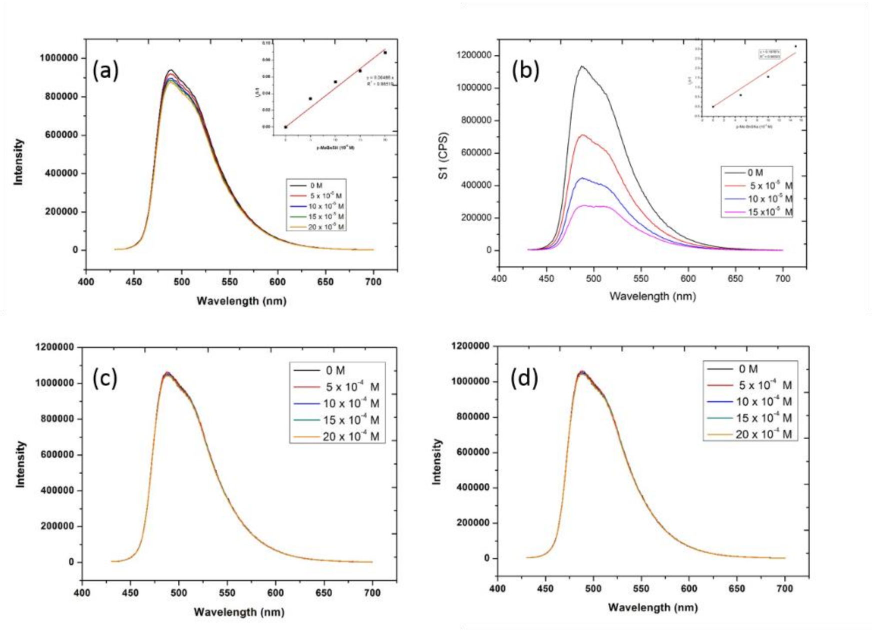


Figure S6. Luminescence spectra of [Ir(FCF$_3$ppy)$_2$dtbbpy]PF$_6$ (1.0 × 10^{-5}M) was collected as a function of different quenchers in degassed DMF with excitation at 420 nm. Inset is the Stern-Volmer plot of [Ir(FCF$_3$ppy)$_2$dtbbpy]PF$_6$ by different quenchers. a) A solution of p-Me-BnSH in DMF was added and its concentration was changed from 0 to 20 × 10^{-5} M. b) A solution of *p*-Me-BnSNa in DMF was added and its concentration was changed from 0 to 15 × 10^{-5} M. c) A solution of B$_2$pin$_2$ in DMF was added and its concentration was changed from 0 to 20 × 10^{-4} M. d) A solution of *p*-Me-PhCHO in DMF was added and its concentration was changed from 0 to 20 × 10^{-4} M.

Detection of by-products

GC-MS analysis of reaction mixtures

To a 5 mL snap vial with stirring bar, B_2pin_2 (0.24 mmol, 1.2 equiv.), [Ir(FCF$_3$ppy)$_2$dtbbpy] (1 mol%) and Cs_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The vial was evacuated and back filled with nitrogen three times. A solution of 4-Me-BnSH (20 mol%) and aldehyde **1a** (0.2 mmol) in dry DMF (0.6 mL) was added by syringe. After degassing by the freeze-pump-thaw via a syringe needle for two circles, the reaction mixture was irritated with a 455 nm LED for 6 hours at 25 ^{o}C. Then the resulting reaction mixture was filtered and subjected for GC-MS measurement. Boronic ester **S4** and borate ester **S5** were detected along with the generation of products.

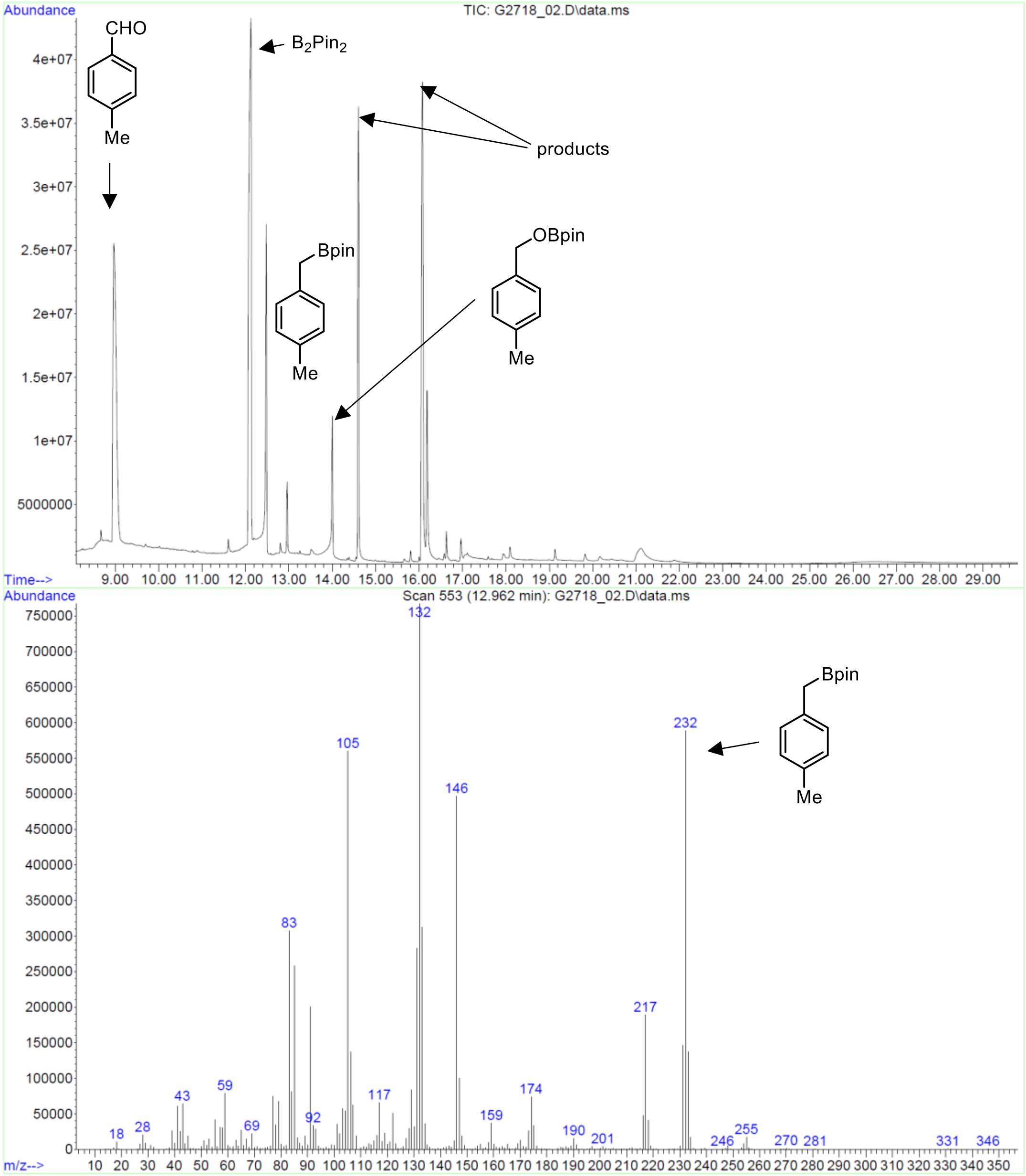


Figure S7-1. GC-MS report of the reaction mixtures after 6 hours

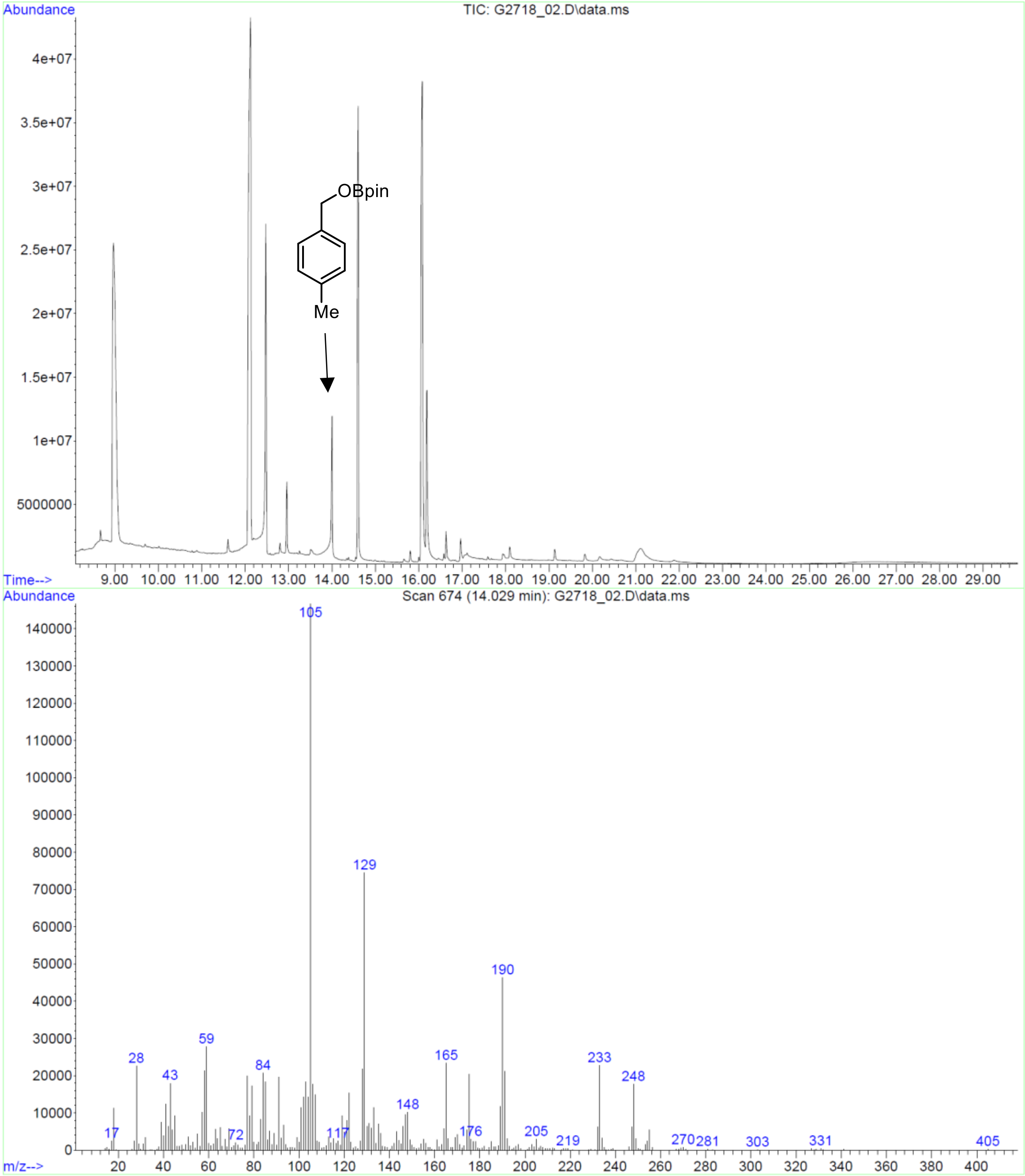
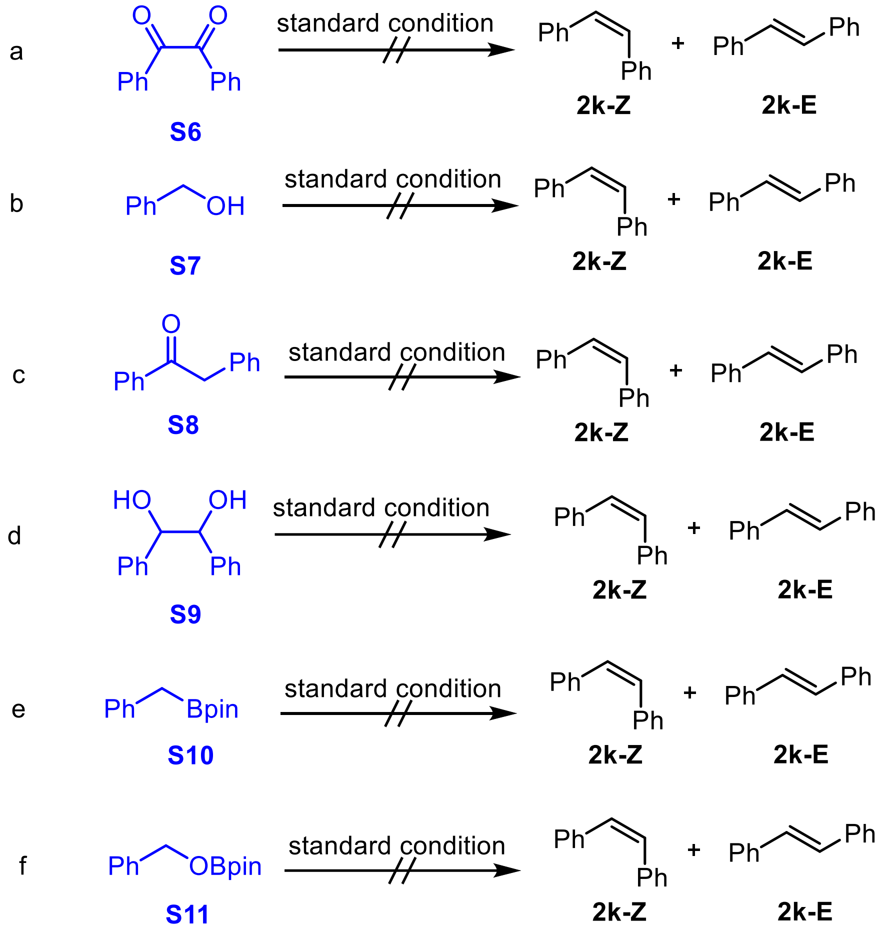


Figure S7-2. GC-MS report of the reaction mixtures after 6 hours

Control experiments

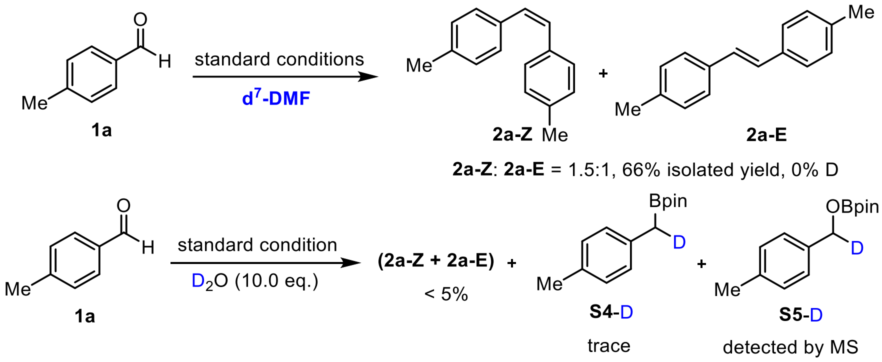


Scheme S1. Control experiments with potential intermediates

In order to detect the possible intermediates involved in the reaction processes, several control experiments employing the possible intermediates **S4-S7** in the place of benzaldehyde were carried out (Scheme S1a-1d). However, none of them gave detectable yields of alkenes as the products.

Moreover, considering that the boronic ester **S4** and borate ester **S5** were detected in the reaction mixtures after irradiation, we also tested the possible intermediacy of boronic esters during the reaction process. When non-substituted boronates **S10** and **S11** were used as the starting material in place of banzaldehyde, the generation of product **2k** was not observed. So the direct intermediacy of boronic ester **S4** and borate ester **S5** in the product generation process was excluded. In addition, this result inspired us to investigate the possible intermediates involved for the generation of boronic ester **S4** and borate ester **S5**.

Deuteration experiments



Scheme S2. Deuteration experiments with deuterated solvent

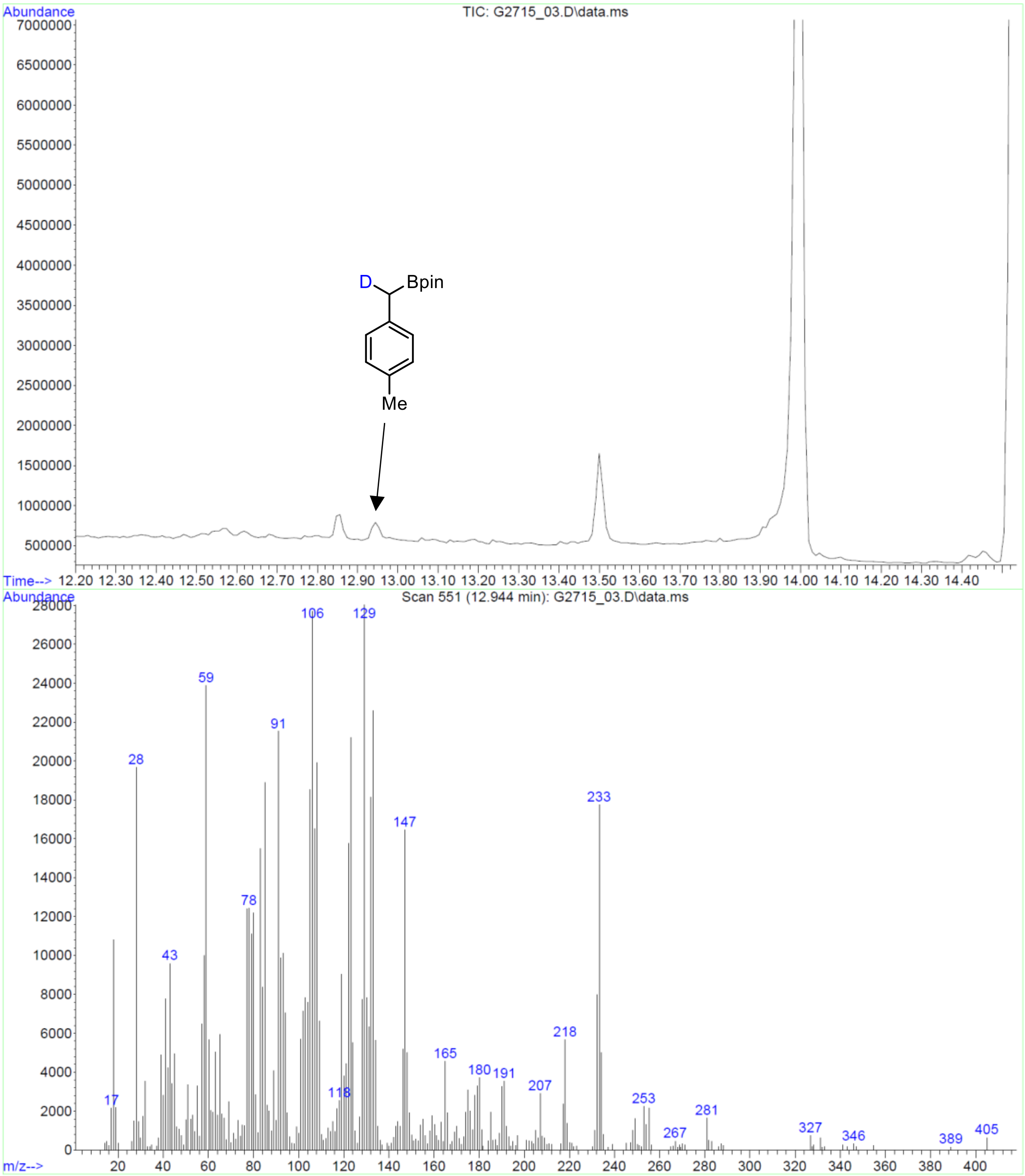


Figure S8-1. GC-MS report of the deuterated boronic ester S4-D

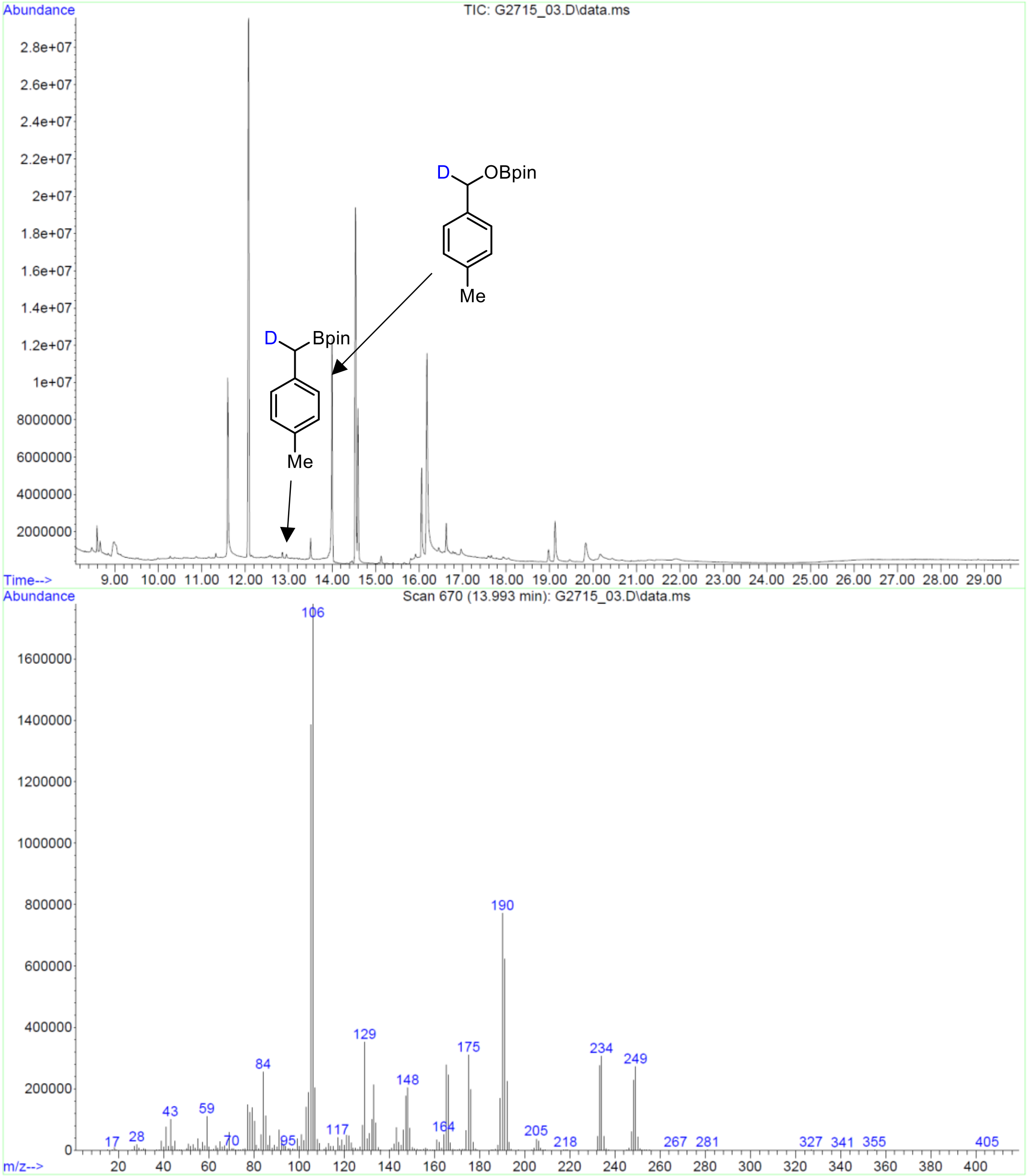


Figure S8-2. GC-MS report of the deuterated borate ester S5-D

NMR Mechanistic Study

For mechanistic studies, specifically ^{13}C-labelled benzaldehyde (labelled at carbonyl position) substrate is used, while keeping the other reaction conditions identical as mentioned above. Both *in situ* NMR sample and batch reaction sample studies were carried out. In case of batch reaction, prior to the NMR measurements the reaction mixture was irradiated for 3 hours (*ex situ*). For *in situ* NMR sample, the samples were prepared in argon atmosphere directly inside NMR tube. To minimize light expose to the sample, the NMR tube was covered with aluminum foil during the sample preparation.

The NMR experiments were measured on a Bruker Avance III HD 600 MHz spectrometer with a 5 mm TBI-F probe and a Bruker Avance III 600 MHz with Prodigy BBO-probe, equipped with BCU II temperature control unit. The ^{13}C of C=O group in solvent DMF was used as the reference in ^{13}C NMR spectra. NMR experiments are modified to minimize NOE enhancement from ^{1}H nuclei and predominantly observe the labelled ^{13}C peaks.

For the *in situ* illumination, the LED-based optical fiber connected device was used .[14] The sample was prepared in 5 mm amberized NMR tubes of spintec which were used together with an insert for the optical fiber and a transistor circuit operated by the spectrometer to switch the LED automatically. The temperature was controlled by the BCU II unit of the spectrometer. For light source a Lumitronix Cree XT-E (royalblue) with a peak wavelength of 450 nm and 500 mW optical output was used.

CEST NMR

CEST NMR experiment is analogous to EXSY method for study of chemical exchange. CEST is more sensitive than EXSY.[15] The higher sensitivity of the method can be exploited to detect low-populated reaction intermediates.[16] CEST involves selective saturation of peaks or spectra, and observing intensity modulations in the peak of corresponding exchanged peaks. In the present study, following 1D ^{13}C CEST pulse sequence is used

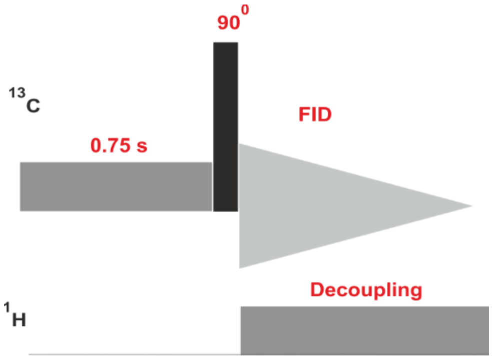


Figure S9. 1D ^{13}C CEST pulse sequence. Saturation pulse is applied for 0.75 s duration with 200 Hz RF field strength. To maximize the intensity and enhance the effect, ^{1}H decoupling is applied during the acquisition.

Identification and characterization of intermediates

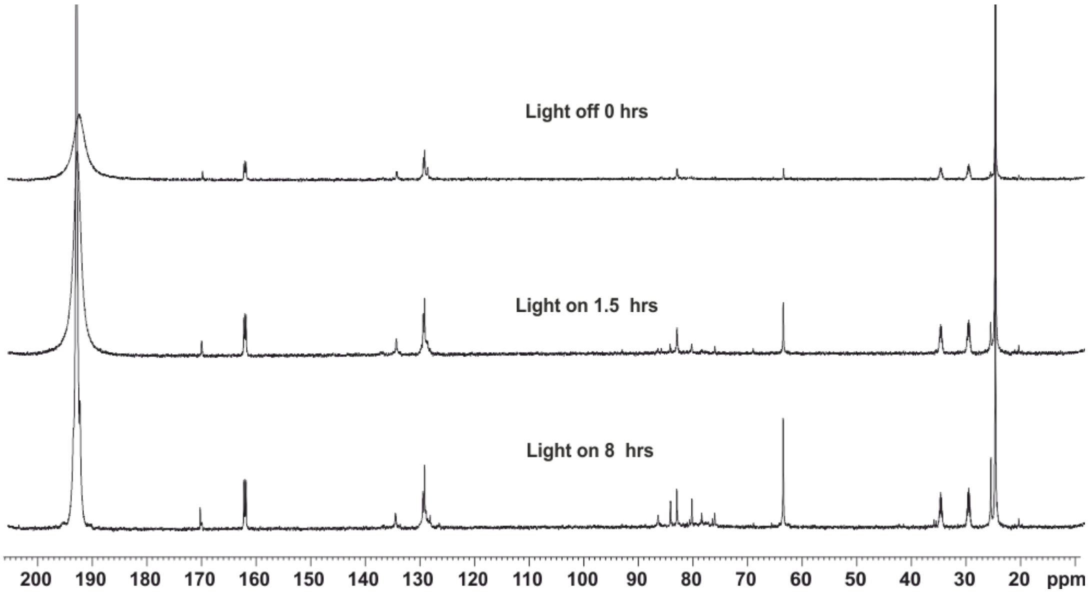


Figure S10. *In situ* ^{1}H decoupled ^{13}C spectra of reaction mixture at different time. The ^{13}C resonance of aldehyde shows relatively broader peak, possibly indicating a radical formation at carbonyl position. Upon irradiation, the spectra show development of new set of signals with time, corresponding to intermediates, by-products and products

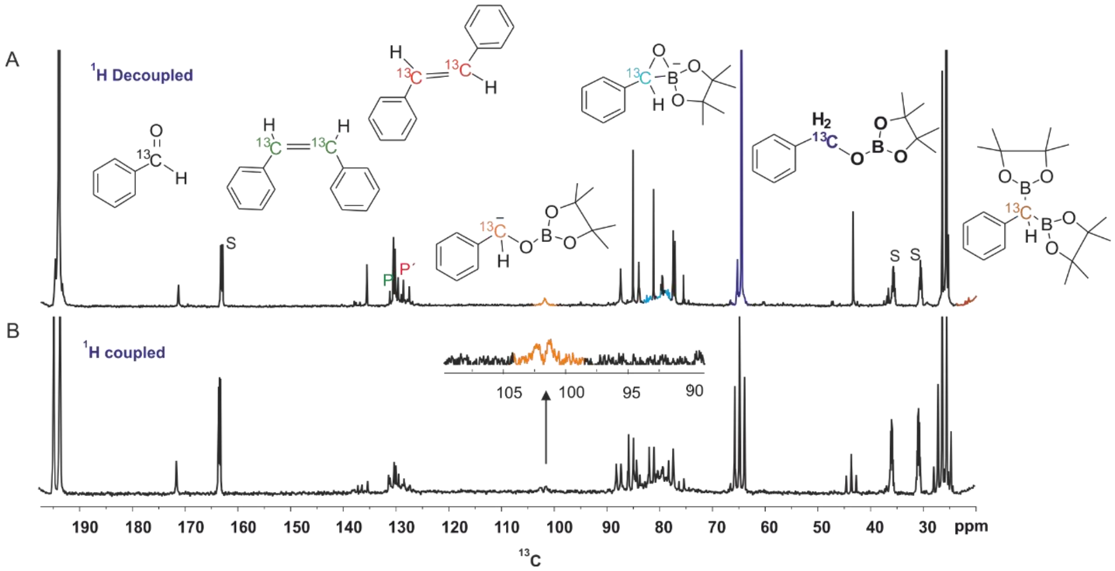


Figure S11. Complete *in situ* ^{1}H decoupled (A) and coupled (B) ^{13}C spectra of reaction mixture after 18 hours.

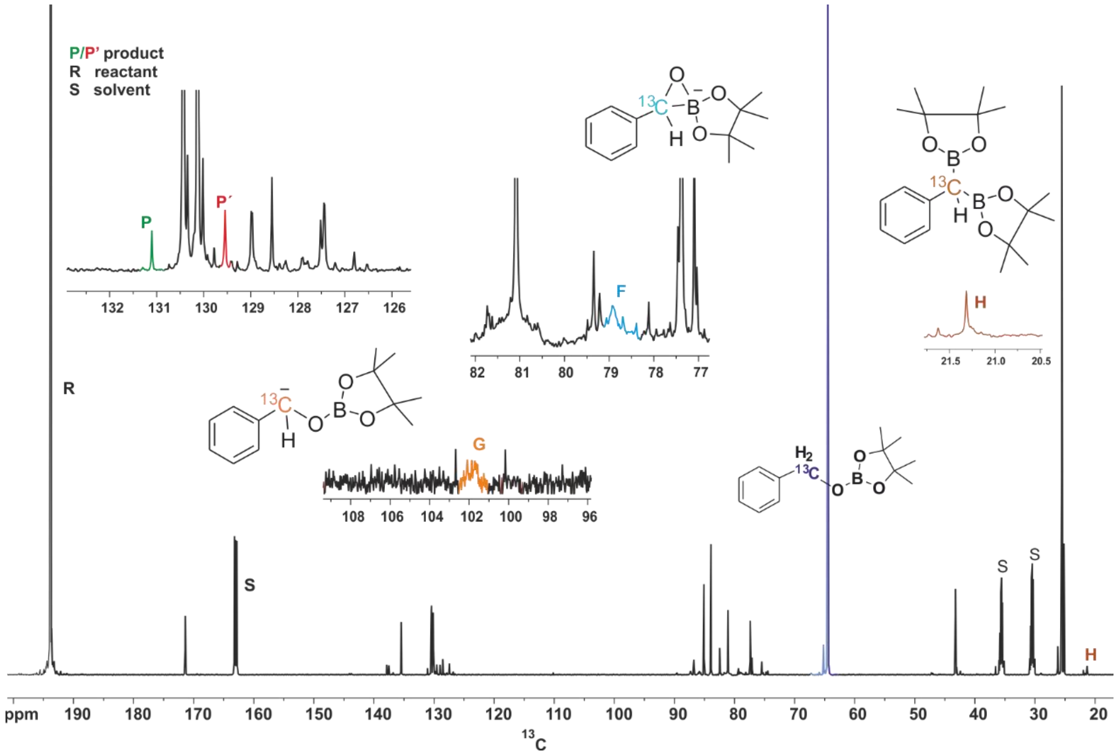


Figure S12. ^{1}H decoupled ^{13}C spectra of batch reaction mixture after 3 hours of irradiation. All identified peaks assigned to product, reactant, solvent and intermediates are distinctively marked.

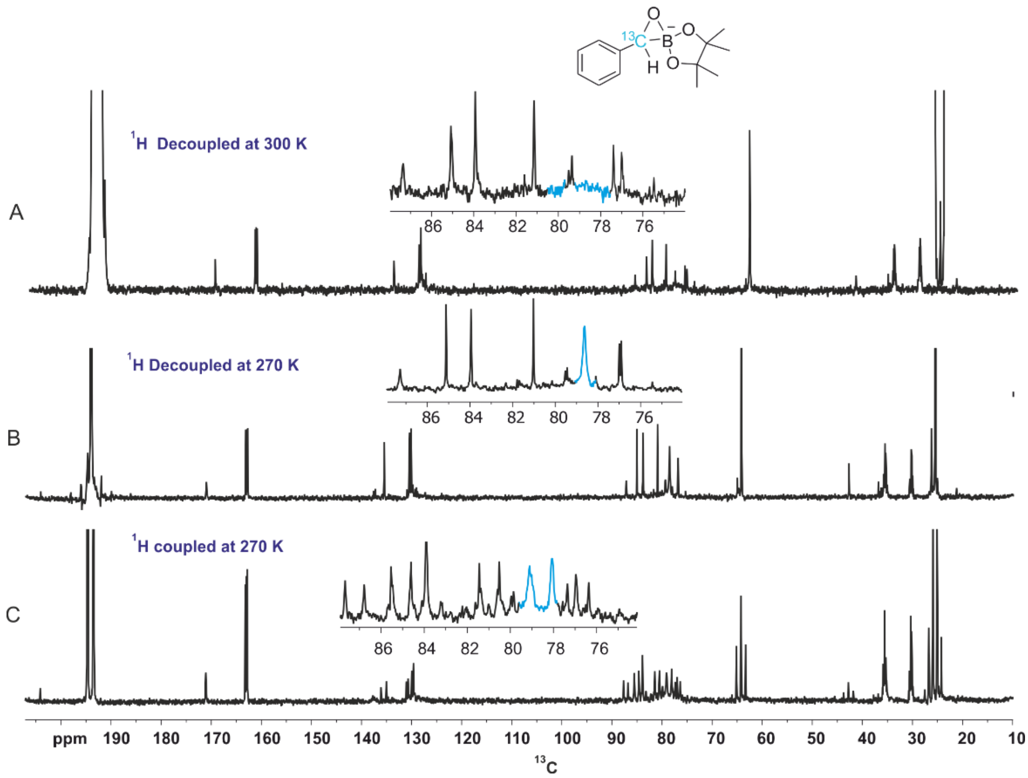


Figure S13. Stabilization and characterization of intermediate **F**, shown is the complete spectra at 300 K (A) and 270 K (B). The doublet in ^{1}H coupled spectrum (C) indicates **-**CH moiety.

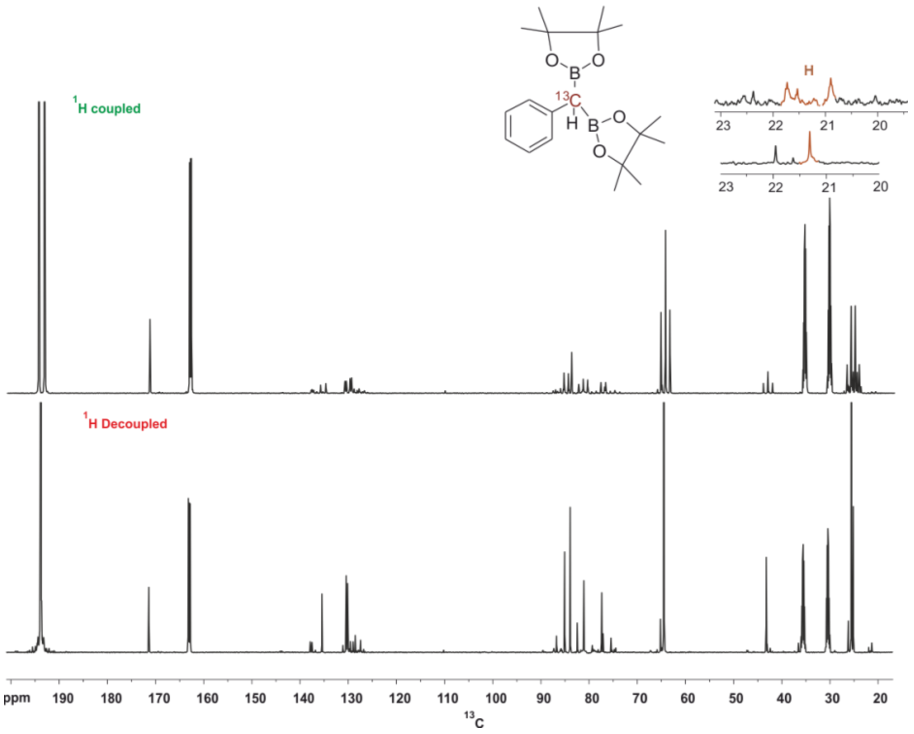


Figure S14. ^{1}H coupled (top), and decoupled (bottom) ^{13}C spectra of batch reaction mixture. Marked peaks correspond to the intermediate **H**. The ^{1}H coupled spectrum indicates C-H moiety, which corroborates the intermediate **H**.

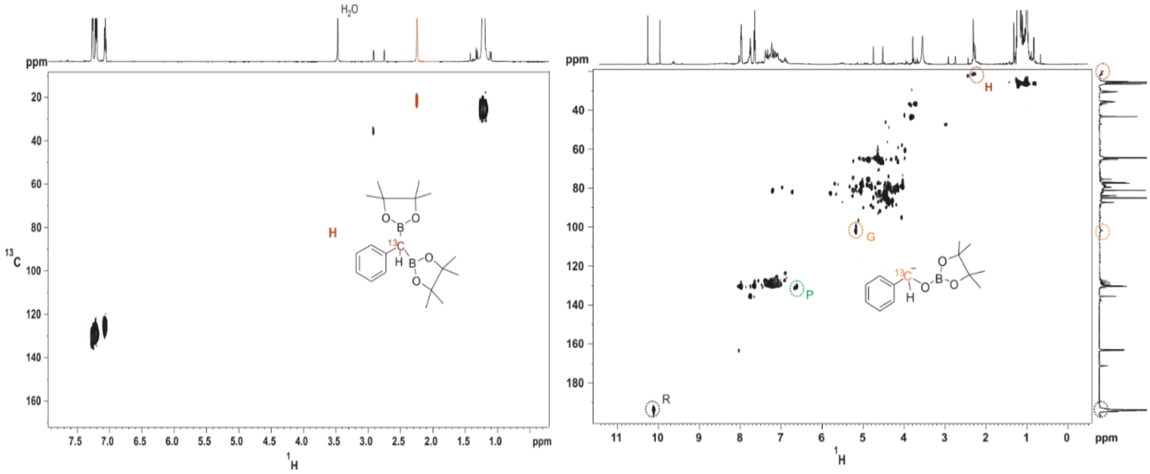


Figure S15. HSQC spectra of batch reaction mixture (right), and independently synthesized intermediates **H** (left). The marked peak H corresponds to the intermediate **H** in the reaction mixture.

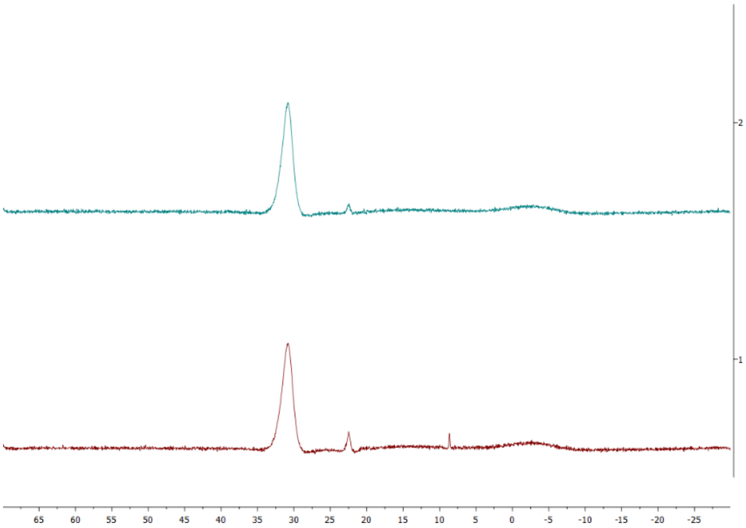
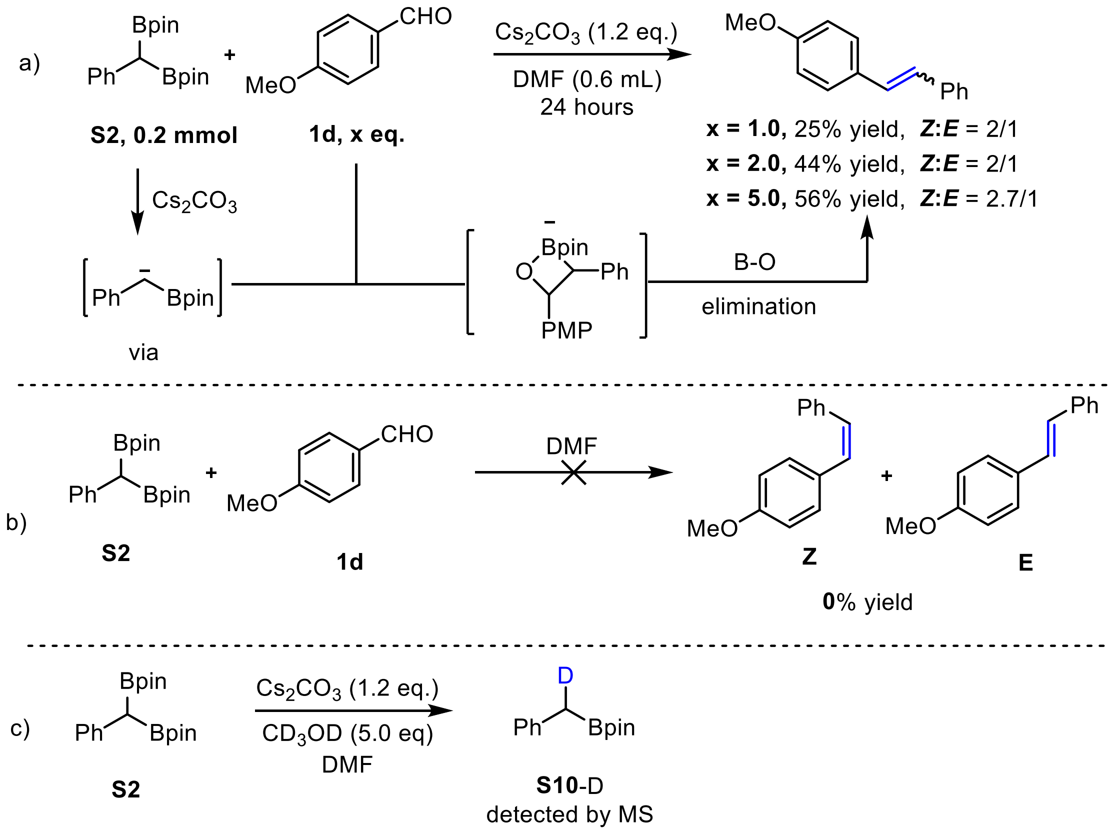


Figure S16. ^{11}B NMR spectra of B_2pin_2 (top signal) and a mixture of B_2pin_2 and Cs_2CO_3 (bottom signal) in d^7-DMF. The scale is recorded in ppm.

5.6 Further control experiments

Scheme S3. Control experiments with 1,1-benzyldiboronate ester S2



The reaction between **S2** and **1d** in the presence of Cs_2CO_3 (1.2 equiv.) afforded the corresponding unsymmetrical alkene in 25% yield (Z/E = 2/1). When increasing the amount of aldehyde **1d** used, higher reaction efficiency was observed. However, no product could be detected in the absence of Cs_2CO_3. When CD_3OD (5.0 eq) was added into the mixture containing **S2**, Cs_2CO_3 (1.2 eq) and DMF (0.6 mL), the corresponding deuterated benzyl boronic ester **S10-D** was detected as the main product which suggests that Cs_2CO_3 could promote the mono-deborylation of **S2** to give α-boryl carbanion.[17-18] **S10-D: MS** (EI) m/z: 219. **HRMS** (EI): 219.1531. Moreover, according to the literatures report we suggest the nucleophilic attack of α-boryl carbanion towards carbonyl of **1d** followed by the B-O elimination is responsible for the generation of alkene.[14]

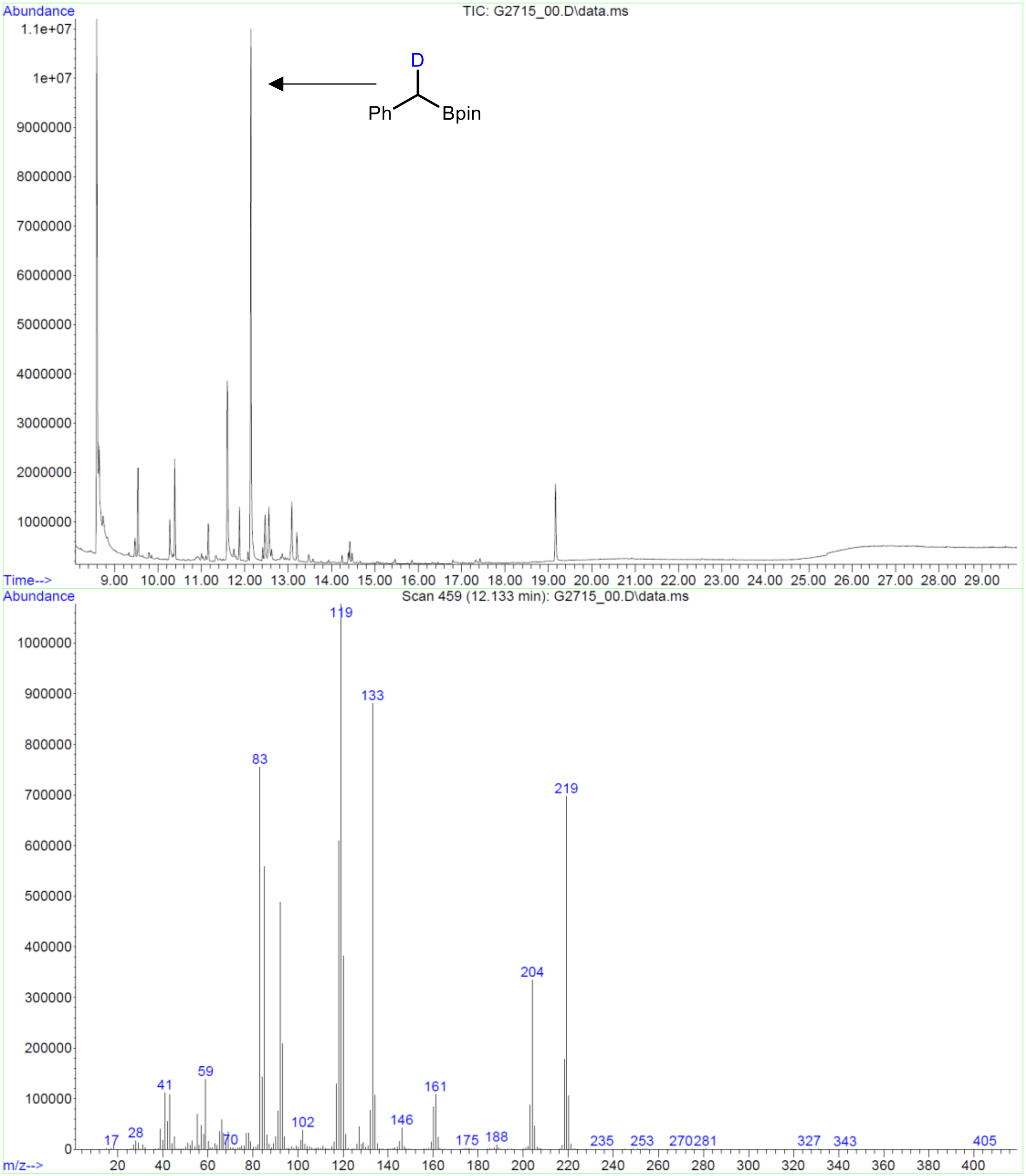
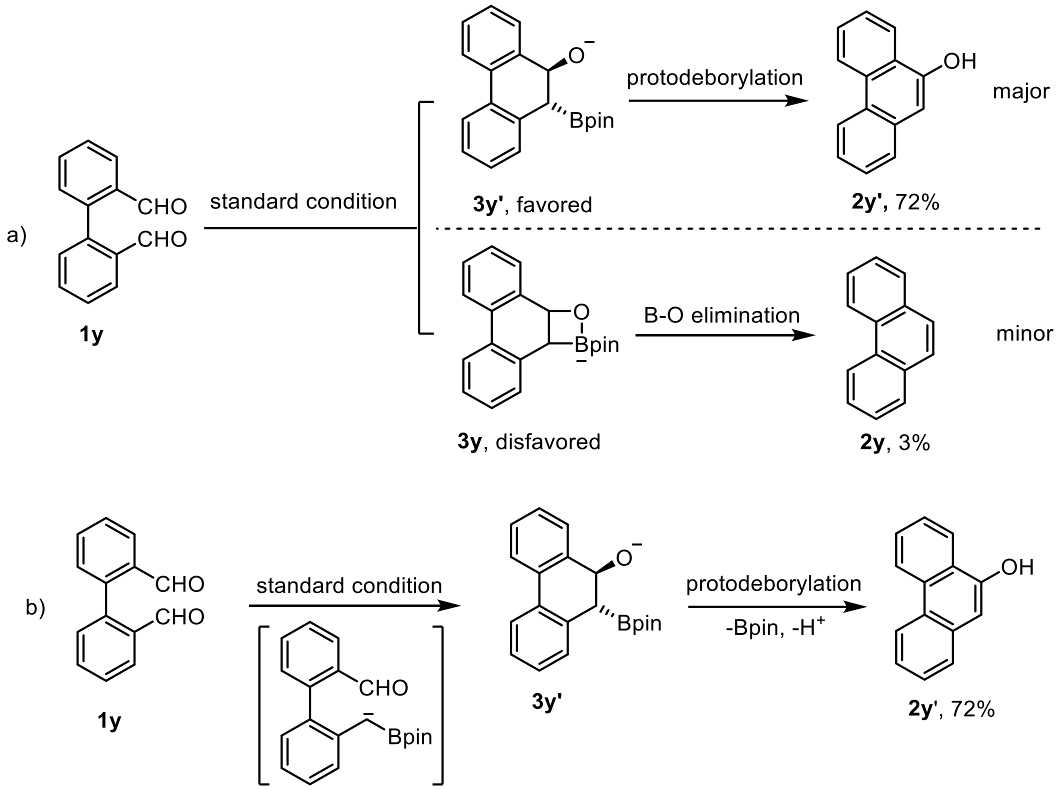


Figure S17. GC-MS report of S10-D in Scheme S3c

Scheme S4. Control reaction with 2,2'-diphenyldicarboxaldehyde 1y

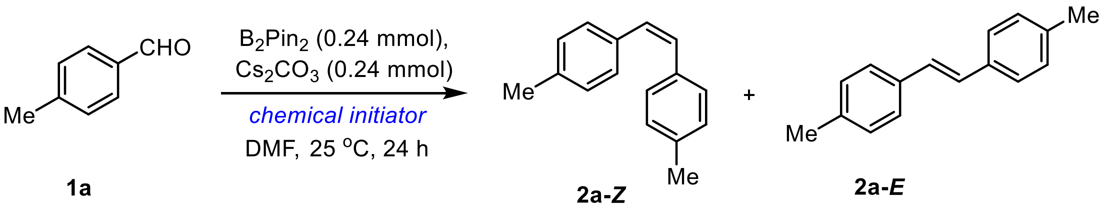


When using 2,2'-diphenyldicarboxaldehyde **1y** as the testing substrate for a potential intramolecular coupling reaction, anticipated intramolecular coupling product **2y** was obtained in only 3% yield and partially deoxygenative coupling product **2y'** was isolated as the major product (72%). We propose two possible intermediates to explain the distribution of these two products. Firstly, α-boryl stabilized carbanion was generated as the key intermediate, subsequent intramolecular attack towards vicinal carbonyl group led to four-membered ring intermediate **3y** and species **3y'**. The formation of **3y'** outcompetes the generation of highly twisted **3y**. Further deborylation[19-22] and elimination in the presence of Cs_2CO_3 to give 9-phenanthrenol **2y**' as the major product.

Evaluation of potential propagation pathway

Hypothesis: The proposed Bpin-base radical **(D)** is potentially capable of reducing another molecule of benzaldehyde to give ketyl radical anion **(C)**, leading to a radical chain propagation mechanism. In order to determine this potential propagative process, experiments using chemical initiator (SmI_2 or Na) in place of the photocatalytic system (photocatalyst, blue light and thiol) were conducted.

Scheme S5. (Sub**)**-stoichiometric experiment



To a 5 mL snap vial with stirring bar, B_2pin_2 (0.24 mmol, 2.4 equiv.), Cs_2CO_3 (0.24 mmol, 2.4 equiv.) and Sodium (when Na was used as chemical initiator) were added. The vial was evacuated and back filled with nitrogen three times. A solution of aldehyde **1a** (0.2 mmol) in dry DMF (0.6 mL) and SmI_2 in THF (when SmI_2 was used as chemical initiator) was added by syringe. After degassed with two freeze-pump-thaw cycles via a syringe needle, the reaction mixture was stirred for 24 hours at 25 °C. After this time, the reaction mixture was quenched by adding water and added ethyl acetate. 1,3,5-trimethoxybenzene was added then the reaction mixture was analyzed by ^1H NMR. Results are shown in Table S7.

Table S7. Yields obtained in the presence of chemical initiators

Initiator	**2a** (*Z*+*E*), yield (%)
SmI_2 (20 mol%)	0
SmI_2 (100 mol%)	0
Na (20 mol%)	0
Na (100 mol%)	0

5.7 Reaction Knetics and Isomerization Experiments

Reaction profile and time/isomerization experiments

To a 5 mL snap vial with a stirring bar, B_2pin_2 (0.24 mmol, 1.2 equiv.), [Ir(FCF$_3$ppy)$_2$dtbbpy] (1 mol%) and Cs_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The vial was evacuated and back filled with nitrogen three times. A solution of 4-Me-BnSH (20 mol%) and *p*-tolualdehyde (0.2 mmol, 24 mg) in dry DMF (0.6 mL) was added by syringe. After degassing by the freeze-pump-thaw via a syringe needle for two cycles, the reaction mixture was irradiated with a 455 nm LED for indicated time at 25 ^{o}C. The yield of **2a** and Z/E ratio were determined by ^{1}H NMR analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

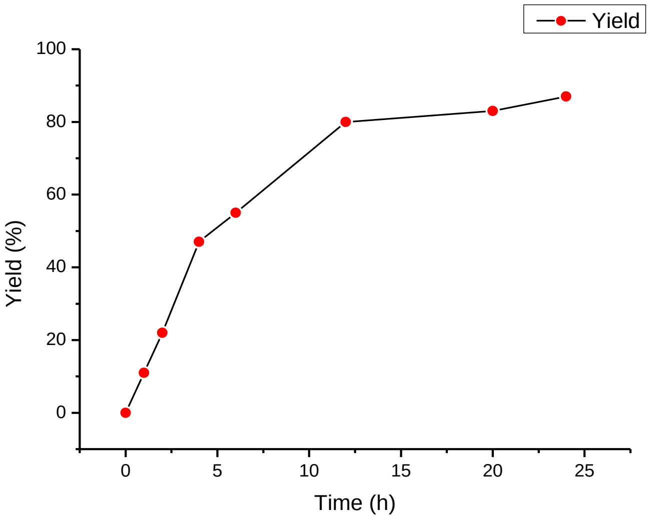
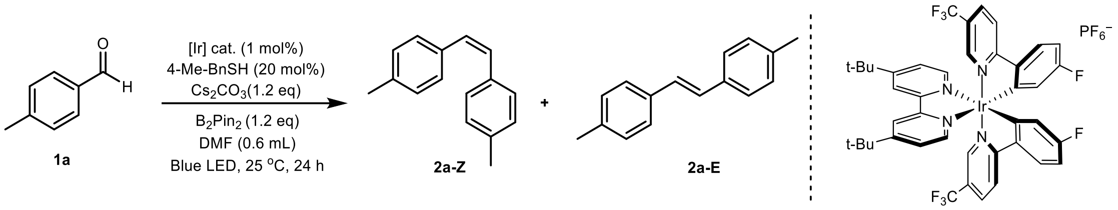
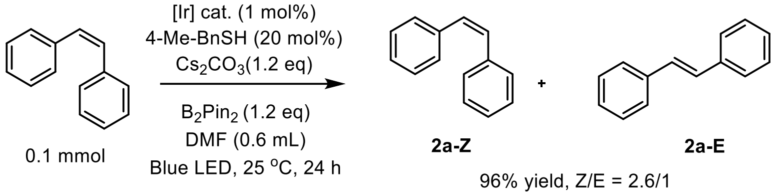


Figure S18. Reaction profile plot

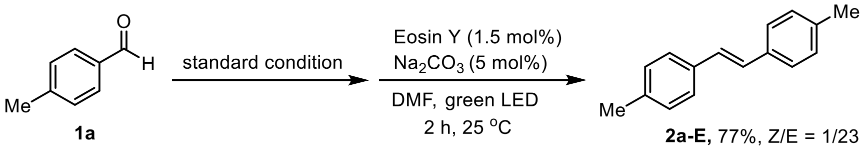
Table S8. Time/Isomerization studies



Time (h)	Yield of **2a** [%]	Z/E
1 h	11	1/**8.5**
2 h	22	1/**4.8**
4 h	47	1/**2.6**
6 h	55	1/**2.3**
12 h	80	**1.3**/1
20 h	83	**2.7**/1
24 h	**87**	**2.6**/1

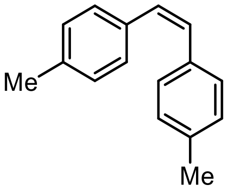


Scheme S6. *Z* to *E* isomerization of 2a

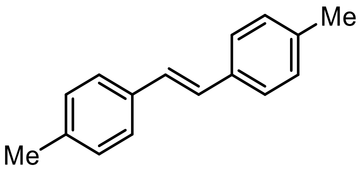


To a 5 mL snap vial with stirring bar, B_2pin_2 (0.24 mmol, 1.2 equiv.), [Ir(FCF$_3$ppy)$_2$dtbbpy] (1 mol%) and Cs_2CO_3 (0.24 mmol, 1.2 equiv.) were added. The vial was evacuated and back filled with nitrogen three times. A solution of 4-Me-BnSH (20 mol%) and **1a** (0.2 mmol, 24 mg) in dry DMF (0.6 mL) was added by syringe. After degassing by the freeze-pump-thaw via a syringe needle for two cycles, the reaction mixture was irradiated with a 455 nm LED for 24 hours at 25 °C. Reaction mixture was then diluted with DMF (2 mL) and filtered through a pad of celite. To the filtrate was added Eosin Y (3 μmol, 1.5 mol%, based on **1a**), Na_2CO_3 (5 mol%, 10 μmol, based on **1a**), the reaction was irradiated with green LED for 2 hours after degassing. The resulting solution was added 1,3,5-trimethoxybenzene as internal standard, concentrated with vacuum and subjected to ^{1}H NMR analysis.

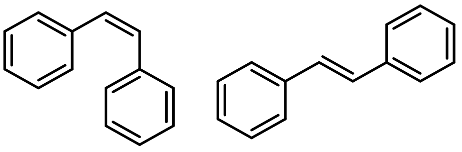
3. Characterization of products



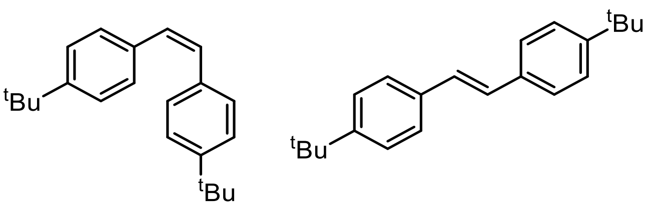
(Z)-1,2-di-p-tolylethene: Following the general procedure A, the product was obtained as the oily liquid 12.5 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.53 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.69 , 134.48 , 129.49 , 128.85 , 128.72 , 21.22. **HRMS** (EI) calculated for $C_{16}H_{16}$ $[M]^+$:208.1247, found 208.1245.



(E)-1,2-di-p-tolylethene: Following the general procedure A, the product was obtained as the white solid 4.8 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 4H), 7.04 (s, 2H), 2.36 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.25 , 134.72 , 129.34 , 127.61 , 126.28 , 21.23 . **HRMS** (EI) calculated for $C_{16}H_{16}$ $[M]^+$:208.1247, found 208.1247.

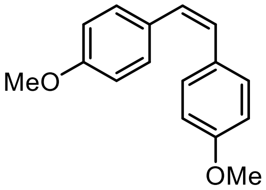


(Z)-1,2-diphenylethene and (E)-1,2-diphenylethene: Following the general procedure A, the product was obtained as the white solid 12.6 mg (70% yield, Z/E = 2/1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.26 (m, 5H), 7.26 – 7.17 (m, 6H), 7.14 (s, 1H), 6.62 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.3, 137.2, 130.21 , 128.84 , 128.65 , 128.18 , 127.60 , 127.05 , 126.48 . **HRMS** (EI) calculated for $C_{14}H_{12}$ $[M]^+$:180.0934, found 180.0926.

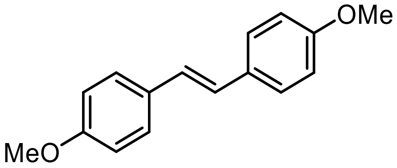


(Z)-1,2-bis(4-(tert-butyl)phenyl)ethene and (E)-1,2-bis(4-(tert-butyl)phenyl)ethene: Following the general procedure A, the product was obtained as the colorless oil 19.2 mg (60% yield, Z/E = 1/1.3). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 10H), 7.24 (s, 1H), 7.23 – 7.14 (m, 3H), 7.07 (s, 2H), 7.06 – 7.01 (m, 2H), 6.51 (s, 2H), 1.34 (s, 18H), 1.32 (s, 14H). **^{13}C NMR** (75 MHz, $CDCl_3$)

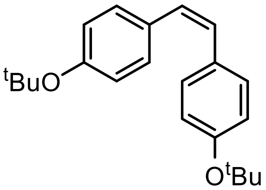
δ 150.52 , 149.98 , 134.74 , 134.47 , 129.51, 129.48, 129.37 , 129.34 , 128.85 , 128.72 , 128.69, 128.47 , 127.69 , 126.12 , 125.55 , 125.05 , 34.59 , 31.30 . **HRMS** (EI) calculated for $C_{22}H_{28}$ $[M]^+$:292.2186, found 292.2189.



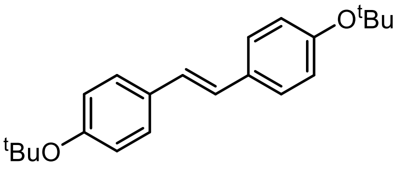
(Z)-1,2-bis(4-methoxyphenyl)ethene: Following the general procedure A, the product was obtained as the colorless oil 12.2 mg . **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 4H), 6.81 – 6.74 (m, 4H), 6.45 (s, 2H), 3.80 (s, 6H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.46 , 130.01 , 129.95 , 128.33 , 113.56 , 55.17. **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$:240.1145, found 240.1145.



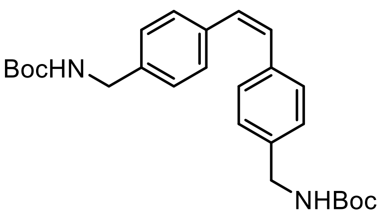
(E)-1,2-bis(4-methoxyphenyl)ethene: Following the general procedure A, the product was obtained as the white solid 3.6 mg . **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H), 6.93 (s, 2H), 6.92 – 6.86 (m, 4H), 3.83 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.96 , 130.44 , 127.38 , 126.14 , 114.07 , 55.31 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$: 240.1145, found 240.1134.



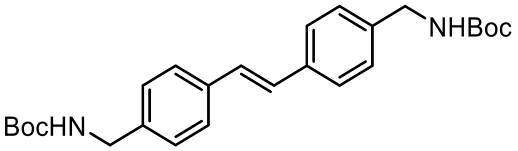
(Z)-1,2-bis(4-(tert-butoxy)phenyl)ethene: Following the general procedure A, the product was obtained as clear oil 6.2 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 4H), 6.86 – 6.81 (m, 4H), 6.49 (s, 2H), 1.34 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.33 , 132.40 , 129.40 , 128.99 , 123.71 , 78.48 , 28.84 . **HRMS** (EI) calculated for $C_{22}H_{28}O_2$ $[M]^+$: 324.2084, found 324.2090.



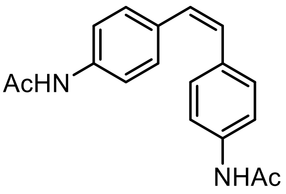
(E)-1,2-bis(4-(tert-butoxy)phenyl)ethene: Following the general procedure A, the product was obtained as clear crystal 7.8 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 6.98 (d, *J* = 2.7 Hz, 4H), 6.97 (s, 2H), 1.36 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$ δ 154.89 , 132.74 , 127.07 , 126.81 , 124.28 , 78.70 , 28.86. HRMS (EI) calculated for $C_{22}H_{28}O_2$ $[M]^+$:324.2084, found 324.2093.



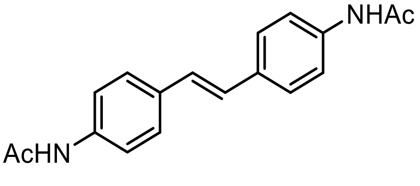
Di-tert-butyl ((ethene-1,2-diylbis(4,1-phenylene))bis(methylene))(Z)-dicarbamate: Following the general procedure A, the product was obtained as clear oil 13 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 6.55 (s, 2H), 4.85 (s, 2H), 4.28 (d, *J* = 5.9 Hz, 4H), 1.45 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.84 , 137.70 , 136.20 , 129.82 , 129.01 , 127.25 , 79.47 , 44.37 , 28.38 . **HRMS** (ESI) calculated for $C_{26}H_{35}N_2O_4$ $[M+H]^+$:439.2591, found 439.2590.



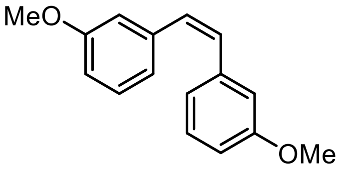
Di-tert-butyl ((ethene-1,2-diylbis(4,1-phenylene))bis(methylene))(E)-dicarbamate: Following the general procedure A, the product was obtained as white solid 7.6 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 7.5 Hz, 5H), 7.07 (s, 2H), 4.86 (s, 2H), 4.32 (d, *J* = 5.9 Hz, 4H), 1.47 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.86 , 138.32 , 136.39 , 128.14 , 127.83 , 126.67 , 79.53 , 44.43 , 28.40 . 28.38 . **HRMS** (ESI) calculated for $C_{26}H_{35}N_2O_4$ $[M+H]^+$:439.2591, found 439.2594.



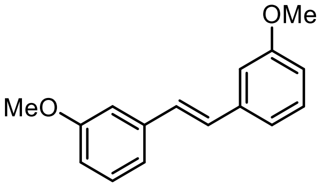
(Z)-N,N'-(ethene-1,2-diylbis(4,1-phenylene))diacetamide: Following the general procedure A, the product was obtained as white solid 12.3 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.36 – 7.29 (m, 4H), 7.20 – 7.13 (m, 4H), 6.49 (s, 2H), 2.14 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.53 , 136.75 , 133.21 , 129.47 , 129.19 , 127.78 , 119.58 , 24.55 . **HRMS** (ESI) calculated for $C_{18}H_{19}N_2O_2$ $[M+H]^+$:295.1441, found 295.1444.



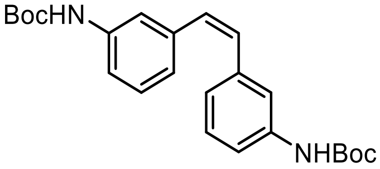
(E)-N,N'-(ethene-1,2-diylbis(4,1-phenylene))diacetamide: Following the general procedure A, the product was obtained as white solid 6.2 mg. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.00 (s, 2H), 7.60 – 7.47 (m, 8H), 7.07 (s, 2H), 3.34 (s, 2H), 2.04 (s, 6H).**^{13}C NMR** (75 MHz, DMSO-d_6) δ 168.22 , 138.63 , 132.04 , 126.67 , 126.54 , 119.04 , 24.06 . **HRMS** (ESI) calculated for $C_{18}H_{19}N_2O_2$ $[M+H]^+$:295.1441, found 295.1445.



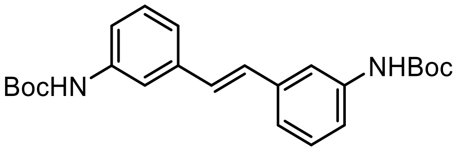
(Z)-1,2-bis(3-methoxyphenyl)ethene： Following the general procedure A, the product was obtained as clear oil 9.8 mg (total amount from two parallel reactions).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 2H), 6.88 – 6.78 (m, 4H), 6.75 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 2H), 6.58 (s, 2H). 3.67 (s, 6H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.32 , 138.50 , 130.32 , 129.17 , 128.88 , 121.48 , 113.75 , 113.27 , 55.04 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$ 240.1145, found 240.1145.



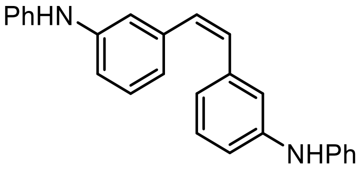
(E)-1,2-bis(3-methoxyphenyl)ethene: Following the general procedure A, the product was obtained as white solid 6.8 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.12 (dt, *J* = 7.7, 1.3 Hz, 2H), 7.08 (s, 2H), 7.05 (dd, *J* = 2.6, 1.6 Hz, 2H), 6.83 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 2H), 3.86 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.85 , 138.65 , 129.62 , 128.87 , 119.25 , 113.36 , 111.72 , 55.25. **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ 240.1145, found 240.1138 $[M]^+$.



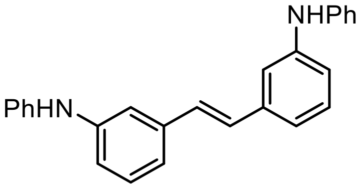
Di-tert-butyl (ethene-1,2-diylbis(3,1-phenylene))(Z)-dicarbamat: Following the general procedure B, the product was obtained as white solid 14.8 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 1.9 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.91 (dt, *J* = 7.7, 1.3 Hz, 2H), 6.53 (s, 2H), 6.52 (s, 2H), 1.50 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.92 , 138.09 , 137.66 , 130.05 , 128.83 , 124.26 , 119.33 , 118.11 , 80.42 , 28.35. **HRMS** (ESI) calculated for $C_{24}H_{34}N_3O_4$ $[M+NH_4]^+$:428.2544, found 428.2555.



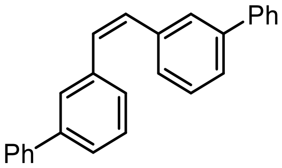
Di-tert-butyl (ethene-1,2-diylbis(3,1-phenylene))(E)-dicarbamate: Following the general procedure B, the product was obtained as white solid 9.8 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (t, *J* = 1.9 Hz, 2H), 7.28-7.19 (m, 6H), 7.06 (s, 2H), 6.52 (s, 2H), 1.54 (s, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.70 , 138.68 , 138.11 , 129.18 , 128.80 , 121.37 , 117.74 , 116.35 , 80.57 , 28.34 . **HRMS** (ESI) calculated for $C_{24}H_{34}N_3O_4$ $[M+NH_4]^+$:428.2544, found 428.2553.



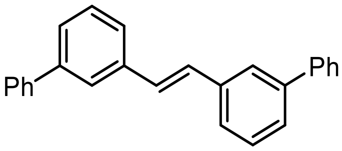
(Z)-3,3'-(ethene-1,2-diyl)bis(N-phenylaniline). Following the general procedure B, the product was obtained as yellowish solid 15.4 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 (m, 6H), 7.03 (t, *J* = 2.0 Hz, 2H), 6.95 – 6.84 (m, 10H), 6.58 (s, 2H), 5.64 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.88 , 142.70 , 138.41 , 130.55 , 129.27 , 129.23 , 121.59 , 120.83 , 117.66 , 117.63 , 116.39 . **HRMS** (ESI) calculated for $C_{26}H_{23}N_2$ [M+H]$^+$:363.1856, found 363.1854.



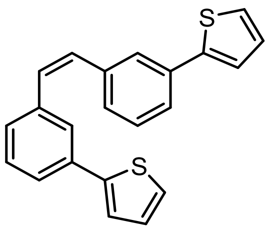
(E)-3,3'-(ethene-1,2-diyl)bis(N-phenylaniline). Following the general procedure B, the product was obtained as yellowish solid 7.4 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.26 – 7.19 (m, 4H), 7.13 – 7.06 (m, 6H), 7.02 (s, 2H), 7.00 – 6.91 (m, 4H), 5.73 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.46 , 142.98, 138.46 , 129.60 , 129.39 , 128.78 , 121.13 , 119.41 , 117.98 , 117.18 , 115.65 . **HRMS** (ESI) calculated for $C_{26}H_{23}N_2$ [M+H]$^+$:363.1856, found 363.1859



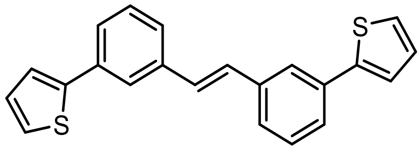
(Z)-1,2-di([1,1'-biphenyl]-3-yl)ethene. Following the general procedure A, the product was obtained as white solid 8.3 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (t, *J* = 1.8 Hz, 2H), 7.47 – 7.42 (m, 6H), 7.40 – 7.26 (m, 10H), 6.72 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.13 , 140.94 , 137.64 , 130.48 , 128.74 , 128.65 , 127.82 , 127.79 , 127.21 , 127.03 , 125.98 . **HRMS** (EI) calculated for $C_{26}H_{20}$ [M]$^+$:332.1560, found 332.1566.



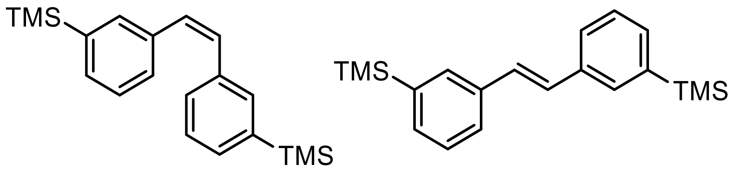
(E)-1,2-di([1,1'-biphenyl]-3-yl)ethene. Following the general procedure A, the product was obtained as white solid 11.6 mg (total amount from two parallel reactions).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 (t, *J* = 1.8 Hz, 2H), 7.67 – 7.62 (m, 4H), 7.56 – 7.44 (m, 10H), 7.42 – 7.37 (m, 2H), 7.26 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.72 , 141.05 , 137.70 , 129.11 , 128.92 , 128.77 , 127.40 , 127.19 , 126.59 , 125.45 , 125.40 . **HRMS** (EI) calculated for $C_{26}H_{20}$ [M]$^+$:332.1560, found 332.1563.



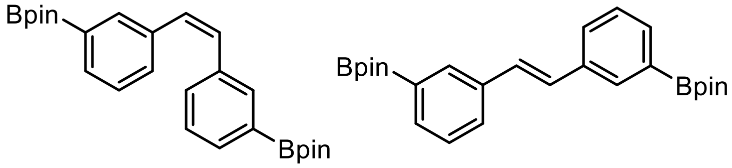
(Z)-1,2-bis(3-(thiophen-2-yl)phenyl)ethene： Following the general procedure A, the product was obtained as clear oil 15.2 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.8 Hz, 2H), 7.46 (dt, *J* = 7.4, 1.7 Hz, 2H), 7.28 (s, 1H), 7.25 – 7.16 (m, 7H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 2H), 6.67 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.63 , 134.37 , 130.35 , 128.84 , 127.98 , 127.92 , 126.39 , 124.83 , 124.81 , 123.1 . **HRMS** (EI) calculated for $C_{22}H_{16}S_2$ $[M]^+$:344.0688, found 344.0682.



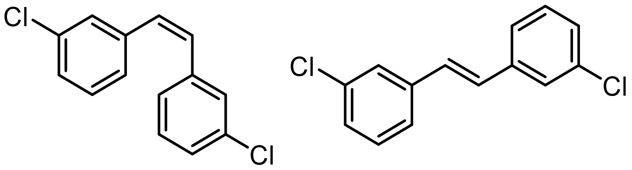
(E)-1,2-bis(3-(thiophen-2-yl)phenyl)ethene: Following the general procedure A, the product was obtained as clear oil. Following the general procedure A, the product was obtained as a white solid 8.2 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 (t, *J* = 1.8 Hz, 2H), 7.50 (ddt, *J* = 17.3, 7.8, 1.5 Hz, 4H), 7.41 (s, 1H), 7.39 – 7.35 (m, 3H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.20 (s, 2H), 7.11 (dd, *J* = 5.1, 3.6 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.15 , 137.77 , 134.83 , 129.23 , 128.86 , 128.02 , 125.52 , 125.37 , 124.96 , 124.24 , 123.31 . **HRMS** (EI) calculated for $C_{22}H_{16}S_2$ $[M]^+$:344.0688, found 344.0679.



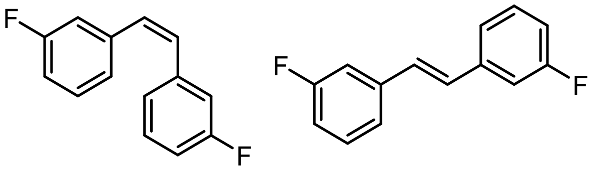
(Z)-1,2-bis(3-(trimethylsilyl)phenyl)ethene and (E)-1,2-bis(3-(trimethylsilyl)phenyl)ethene： Following the general procedure A, the product (mixture of Z and E products, Z/E = 1.6/1) was obtained as clear oil 15.2 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 1.9, 0.8 Hz, 1H), 7.52 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.34 – 7.28 (m, 5H), 7.22 – 7.16 (m, 5H), 7.12 (s, 2H), 6.61 (s, 2H), 0.29 (s, 13H), 0.13 (s, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.83 , 140.17 , 136.56 , 136.53 , 133.89 , 132.59 , 131.88 , 131.72 , 130.53 , 129.23 , 128.88 , 128.86 , 128.79 , 128.72 , 128.69 , 128.04 , 127.55 , 126.65 , 126.39 , -1.10 , -1.27 . **HRMS** (EI) calculated for $C_{20}H_{28}Si_2$ $[M]^+$:324.1724, found 324.1733.



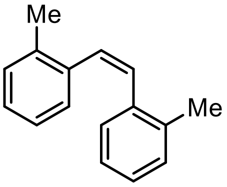
(Z)-1,2-bis(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene and (E)-1,2-bis(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene: Following the general procedure A, the product (mixture of Z and E products, Z/E = 1/1.6) was obtained as clear oil 28.6 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, CDCl$_3$). δ 8.01 – 7.95 (m, 2H), 7.70 (ddd, *J* = 5.5, 2.5, 1.2 Hz, 3H), 7.61 (m, 3H), 7.43 – 7.33 (m, 3H), 7.30 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.18 (s, 2H), 7.17 – 7.09 (m, 2H), 6.61 (s, 1H), 1.37 (s, 24H), 1.33 (s, 17H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 136.66 , 136.56 , 135.56 , 133.84 , 133.36 , 132.88 , 131.38 , 130.14 , 129.36 , 129.27 , 128.52 , 128.07 , 127.37 , 126.26 , 83.85 , 83.75 , 24.88 , 24.83 . **HRMS** (EI) calculated for $C_{26}H_{34}B_2O_4$ $[M]^+$:432.2643, found 432.2647 and 432.2645.



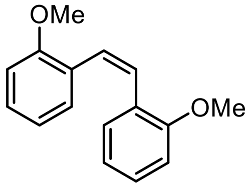
(Z)-1,2-bis(3-chlorophenyl)ethene and (E)-1,2-bis(3-chlorophenyl)ethene: Following the general procedure A, the product (mixture of Z and E products, Z/E = 1/1.2) was obtained as white solid 19.8 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.50 (t, *J* = 1.8 Hz, 2H), 7.37 (dt, *J* = 7.4, 1.7 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 7.20 – 7.12 (m, 2H), 7.08 (dt, *J* = 7.0, 1.7 Hz, 1H), 7.03 (s, 2H), 6.57 (s, 1H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 138.66 , 138.42 , 134.69 , 134.17, 129.99 , 129.93 , 129.53 , 128.80 , 128.59 , 127.88 , 127.47 , 126.90 , 126.39 , 124.88 . **HRMS** (EI) calculated for $C_{14}H_{10}Cl_2$ $[M]^+$:248.0154, found 248.0147.



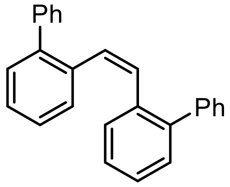
(Z)-1,2-bis(3-fluorophenyl)ethene and (E)-1,2-bis(3-fluorophenyl)ethene: Following the general procedure A, the product (mixture of Z and E products, Z/E = 1.7/1) was obtained as white solid 14 mg (total amount from two parallel reactions).**^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.37 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.22 – 7.16 (m, 2H), 7.06 (s, 1H), 7.00 (dt, *J* = 7.7, 1.3 Hz, 3H), 6.96 – 6.87 (m, 4H), 6.60 (s, 2H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 164.77, 164.29, 161.52, 161.04 , 139.20, 139.10, 138.92 , 138.81 , 130.22 , 130.10 , 130.06 , 129.85 , 129.74 , 128.78 , 128.75 , 124.61 , 124.57 , 122.61 , 122.58 , 115.63 , 115.34 , 114.91 , 114.63 , 114.43 , 114.15 , 113.03 , 112.74 . ^{19}F NMR (282 MHz, CDCl$_3$) δ -113.73, -113.77. **HRMS** (EI) calculated for $C_{14}H_{10}F_2$ $[M]^+$:216.0745, found 216.0741.



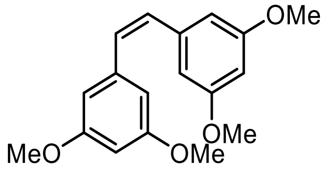
(Z)-1,2-di-o-tolylethene and (E)-1,2-di-o-tolylethene： Following the general procedure A, the products (mixture of Z and E configuration product, Z/E = 16/1) were obtained as clear oil 12.5 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 7.09 (m, 2H), 7.01 – 6.89 (m, 5H), 6.73 (s, 2H), 2.30 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.47 , 136.11 , 129.91 , 129.42 , 129.07 , 126.97 , 125.36 , 19.88 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$ 208.1247, found 208.1241.



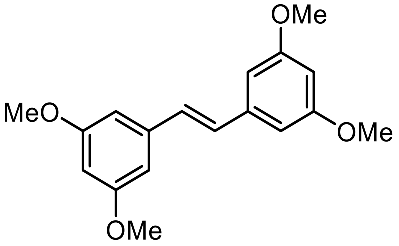
(Z)-1,2-bis(2-methoxyphenyl)ethene and (E)-1,2-bis(2-methoxyphenyl)ethene: Following the general procedure A, the products (Z/E = 8.1/1) were obtained as clear oil 13.0 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 4H), 6.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.77 (s, 2H), 6.70 (td, *J* = 7.5, 1.1 Hz, 2H), 3.89 (s, 1H), 3.83 (s, 6H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.08 , 129.97 , 128.26 , 126.30 , 125.57 , 120.03 , 110.46 , 55.42 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$ 240.1145, found 240.1151.



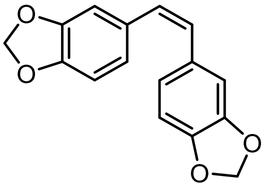
(Z)-1,2-di([1,1'-biphenyl]-2-yl)ethene: Following the general procedure A, the product was obtained as clear oil 13.0 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 3H), 7.36 (s, 7H), 7.34 (t, *J* = 1.6 Hz, 3H), 7.32 – 7.27 (m, 3H), 7.15 (td, *J* = 7.4, 1.6 Hz, 2H), 6.38 (s, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.43 , 141.03 , 135.30 , 129.96 , 129.71 , 129.48 , 127.94 , 127.23 , 127.02 , 126.85 . **HRMS** (EI) calculated for $C_{26}H_{20}$ $[M]^+$:332.1560, found 332.1566.



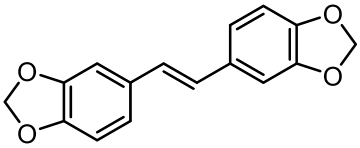
(Z)-1,2-bis(3,5-dimethoxyphenyl)ethene: Following the general procedure A, the product was obtained as white solid 16.8 mg (total amount from two parallel reactions).. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54 (s, 2H), 6.44 (d, *J* = 2.4 Hz, 4H), 6.32 (t, *J* = 2.3 Hz, 2H), 3.67 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.46 , 138.96 , 130.54 , 106.73 , 99.90 , 55.22 . **HRMS** (EI) calculated for $C_{18}H_{20}O_4$ $[M]^+$:300.1356, found 300.1360.



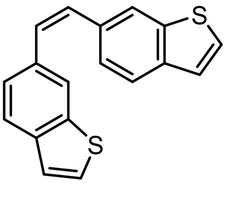
(E)-1,2-bis(3,5-dimethoxyphenyl)ethene: Following the general procedure A, the product was obtained as white solid 19.8 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.67 (d, *J* = 2.3 Hz, 4H), 6.40 (t, *J* = 2.3 Hz, 2H), 3.83 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.94 , 139.11 , 129.15 , 104.59 , 100.08 , 55.36 . **HRMS** (EI) calculated for $C_{18}H_{20}O_4$ $[M]^+$:300.1356, found 300.1355.



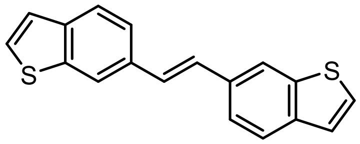
(Z)-1,2-bis(benzo[d][1,3]dioxol-5-yl)ethene. Following the general procedure A, the product was obtained as white solid 10.5 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.75 – 6.69 (m, 6H), 6.41 (s, 2H), 5.93 (s, 4H).**^{13}C NMR** (75 MHz, 300 MHz, $CDCl_3$) δ 147.36 , 146.54 , 128.84 , 122.82 , 108.87 , 108.23 , 100.89. **HRMS** (EI) calculated for $C_{16}H_{12}O_4$ $[M]^+$:268.0730, found 268.0733



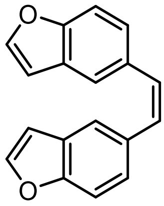
(E)-1,2-bis(benzo[d][1,3]dioxol-5-yl)ethene: Following the general procedure A, the product was obtained as white solid 5.5 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.03 (d, *J* = 1.7 Hz, 2H), 6.90 (dd, *J* = 8.1, 1.7 Hz, 2H), 6.85 (s, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.10 , 147.08 , 131.93 , 126.68 , 121.16 , 108.40 , 105.36 , 101.08 . **HRMS** (EI) calculated for $C_{16}H_{12}O_4$ $[M]^+$:268.0730, found 268.0728.



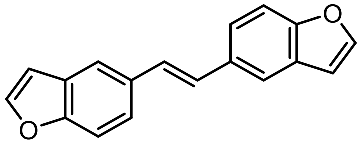
(Z)-1,2-bis(benzo[b]thiophen-5-yl)ethene: Following the general procedure A, the product was obtained as white solid 7.9 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.69 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.41 (d, *J* = 5.4 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.23 (dd, *J* = 5.5, 0.8 Hz, 2H), 6.76 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.76 , 138.45 , 133.45 , 129.99 , 126.55 , 125.32 , 123.96 , 123.90 , 122.09 . **HRMS** (EI) calculated for $C_{18}H_{12}S_2$ $[M]^+$:292.0375, found 292.0373.



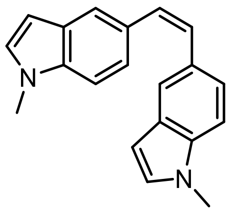
(E)-1,2-bis(benzo[b]thiophen-6-yl)ethene：Following the general procedure A, the product was obtained as white solid 7.9 mg. **Note: this compound shows poor solubility in common solvent like $CDCl_3$, DMSO-D_6, acetone-D_6 and dissolves only slight amount in TCE-D_2.** **^{1}H NMR** (400 MHz, TCE-D_2) δ 7.97 (d, *J* = 1.6 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.51 (d, *J* = 5.4 Hz, 2H), 7.39 (dd, *J* = 5.4, 0.8 Hz, 2H), 7.31 (s, 2H). **^{13}C NMR** (101 MHz, TCE-D_2) δ 139.98 , 138.69 , 133.69 , 128.35 , 127.19 , 123.93 , 122.64 , 122.45 , 121.76 , 120.18. **HRMS** (EI) calculated for $C_{18}H_{12}S_2$ $[M]^+$:292.0375, found 292.0373.



(Z)-1,2-bis(benzo[b]thiophen-5-yl)ethene：Following the general procedure A, the product was obtained as white solid 10.9 mg. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.2 Hz, 2H), 7.50 (dd, *J* = 1.9, 0.6 Hz, 2H), 7.35 (d, *J* = 0.8 Hz, 1H), 7.32 (t, *J* = 0.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 6.70 (s, 2H), 6.66 (dd, *J* = 2.2, 1.0 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.03 , 145.17 , 132.10 , 129.61 , 127.43 , 125.54 , 121.45 , 111.06 , 106.66 . HRMS (EI) calculated for $C_{18}H_{12}O_2$ $[M]^+$:260.0832, found 260.0833.

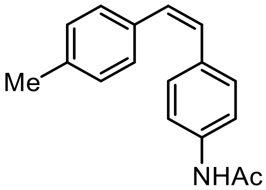


(E)-1,2-bis(benzo[b]thiophen-5-yl)ethene：Following the general procedure A, the product was obtained as white solid 6.6 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 1.2 Hz, 2H), 7.63 (d, *J* = 2.2 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.20 (s, 2H), 6.80 – 6.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.59 , 145.51 , 132.69 , 127.96 , 127.89 , 122.90 , 119.01 , 111.53 , 106.68 . **HRMS** (EI) calculated for $C_{18}H_{12}O_2$ $[M]^+$:260.0832, found 260.0828.

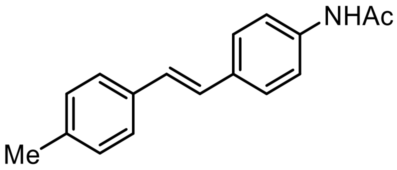


(Z)-1,2-bis(1-methyl-1H-indol-5-yl)ethene: Following the general procedure B, the products (Z/E = 5.2/1) were obtained as white solid 11.4 mg. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 0.45H), 7.61 (dd, *J* = 1.6, 0.8 Hz, 2H), 7.51 (dd, *J* = 8.6, 1.7 Hz, 0.5H), 7.31 (d, *J* = 8.5 Hz, 0.56H), 7.22

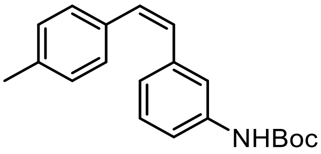
(dd, *J* = 8.6, 1.7 Hz, 3H), 7.13 (dt, *J* = 8.5, 0.8 Hz, 2H), 7.04 (d, *J* = 3.1 Hz, 0.51H), 7.00 (d, *J* = 3.1 Hz, 2H), 6.67 (s, 2H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 0.4H), 6.39 (dd, *J* = 3.1, 0.9 Hz, 2H), 3.81 (s, 1.2H), 3.76 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.21 , 135.75 , 129.20 , 129.10 , 128.86 , 128.31 , 127.28 , 123.08 , 121.35 , 120.02 , 119.07 , 109.35 , 108.70 , 101.17 , 101.15 , 32.92 , 32.83 . **HRMS** (EI) calculated for $C_{20}H_{18}N_2$ $[M]^+$:286.1465, found 286.1462.



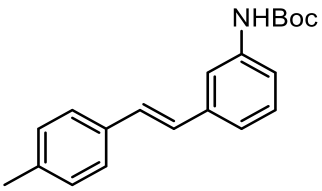
(Z)-N-(4-(4-methylstyryl)phenyl)acetamide: Following the general procedure C, the products were obtained as white solid 9.3 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.24 – 7.18 (m, 2H), 7.17 – 7.11 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.56 – 6.43 (m, 2H), 2.31 (s, 3H), 2.16 (s, 3H). H on NH was not observed. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.16 , 136.83 , 136.62 , 134.25 , 133.42 , 129.81 , 129.51 , 128.92 , 128.82 , 128.68 , 119.34 , 24.63 , 21.22 . **HRMS** (EI) calculated for $C_{17}H_{17}NO$ $[M]^+$:251.1305, found 251.1310.



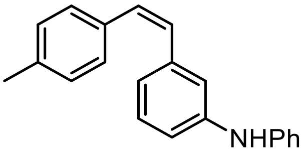
(E)-N-(4-(4-methylstyryl)phenyl)acetamide: Following the general procedure C, the products were obtained as white solid 10.1 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, DMSO-*d*$_6$) δ 10.00 (s, 1H), 7.61 – 7.48 (m, 4H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.11 (s, 2H), 2.30 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-*d*$_6$) δ 168.26 , 138.72 , 136.72 , 134.47 , 131.97 , 129.32 , 127.05 , 126.82 , 126.78 , 126.22 , 119.04 , 24.07 , 20.87 . **HRMS** (EI) calculated for $C_{17}H_{17}NO$ $[M]^+$:251.1305, found 251.1309.



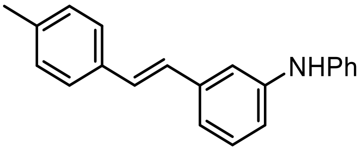
Tert-butyl (Z)-(3-(4-methylstyryl)phenyl)carbamate: Following the general procedure D, the products were obtained as clear oil 14 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.58 – 6.46 (m, 2H), 6.36 (s, 1H), 2.31 (s, 3H), 1.50 (s, 8H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.66 , 138.30 , 138.28 , 136.90 , 134.94 , 134.03 , 130.45 , 129.15 , 128.87 , 128.83 , 128.81 , 123.55 , 118.71 , 117.14 , 80.50 , 28.31 , 21.23 . **HRMS** (ESI) calculated for $C_{20}H_{23}NNaO_2$ $[M+Na]^+$:332.1621, found 332.1621.



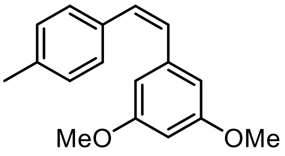
Tert-butyl (E)-(3-(4-methylstyryl)phenyl)carbamate: Following the general procedure D, the product was obtained as white solid 18.2 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.30 – 7.23 (m, 2H), 7.20 – 7.14 (m, 4H), 7.13 – 6.98 (m, 2H), 6.49 (s, 1H), 2.36 (s, 3H), 1.54 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.70 , 138.66 , 138.42 , 137.56 , 134.41 , 129.37 , 129.16 , 128.98 , 127.42 , 126.44 , 121.21 , 117.47 , 116.19 , 28.35 , 21.26 . **HRMS** (ESI) calculated for $C_{20}H_{23}NNaO_2$ $[M+Na]^+$:332.1621, found 332.1625.



(Z)-3-(4-methylstyryl)-N-phenylaniline: Following the general procedure D, the product was obtained as white solid 20.6 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 5H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 1.9 Hz, 1H), 6.93 – 6.81 (m, 5H), 6.59 – 6.49 (m, 2H), 5.59 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.77 , 142.76, 138.64 , 134.25 , 136.71 , 134.25 , 130.39 , 129.64 , 129.21 , 129.19 , 128.94 , 128.89 , 121.58 , 120.78 , 117.62 , 117.57 , 116.49 , 21.27 . **HRMS** (ESI) calculated for $C_{21}H_{20}N$ $[M+H]^+$:286.1590, found 286.1594.

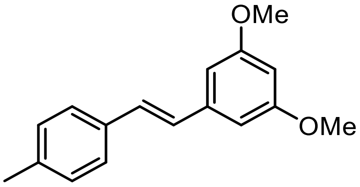


(E)-3-(4-methylstyryl)-N-phenylaniline: Following the general procedure D, the product was obtained as white solid 14.7 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.25 (m, 3H), 7.22 (t, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (m, 3H), 7.03 (d, *J* = 6.3 Hz, 2H), 6.99 – 6.93 (m, 2H), 5.76 (s, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.37 , 143.00 , 138.71 , 137.55 , 134.44, 129.57 , 129.38 , 128.76 , 127.58 , 126.42 , 121.11 , 119.34 , 117.97 , 117.02 , 115.59 , 21.26 . **HRMS** (ESI) calculated for $C_{21}H_{20}N$ $[M+H]^+$:286.1590, found 286.1592.

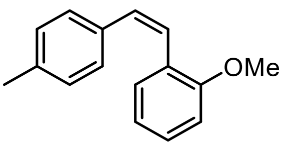


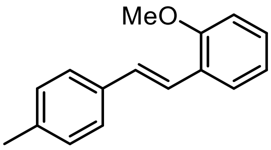
(Z)-1,3-dimethoxy-5-(4-methylstyryl)benzene: Following the general procedure C, the product was obtained as white solid 10.2 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.59 – 6.45 (m, 2H), 6.42 (d, *J* = 2.3

Hz, 2H), 6.31 (t, *J* = 2.3 Hz, 1H), 3.66 (s, 6H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 160.48 , 139.33 , 136.91 , 134.17 , 130.62 , 129.47 , 128.85 , 128.81 , 106.67 , 99.71 , 55.19 , 21.21 . **HRMS** (EI) calculated for $C_{17}H_{18}O_2$ [M]$^+$:254.1301, found 254.1303.

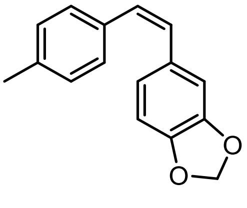


(E)-1,3-dimethoxy-5-(4-methylstyryl)benzene: Following the general procedure C, the product was obtained as white solid 19.3 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.43 – 7.38 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.03 (q, *J* = 16.3 Hz, 2H), 6.67 (d, *J* = 2.2 Hz, 2H), 6.39 (t, *J* = 2.2 Hz, 1H), 3.83 (s, 6H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 160.95 , 139.54 , 137.65 , 134.33 , 129.39 , 129.13 , 127.65 , 126.48 , 104.45 , 99.81 , 55.36 , 21.25 . **HRMS** (EI) calculated for $C_{17}H_{18}O_2$ [M]$^+$:254.1301, found 254.1306.

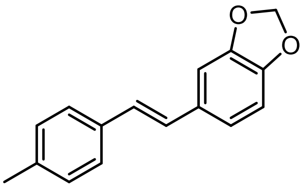




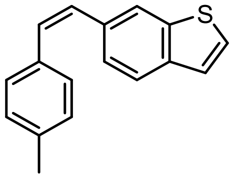
(Z)-1-methoxy-2-(4-methylstyryl)benzene and (E)-1-methoxy-2-(4-methylstyryl)benzene: Following the general procedure C, the products (mixture of Z and E configuration of products, Z/E = 1.9/1) were obtained as clear oil 11.2 mg (total amount from two parallel reactions).**^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.60 (dd, *J* = 7.7, 1.8 Hz, 0.4 H), 7.48 – 7.39 (m, 1.5H), 7.25 – 7.16 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 3H), 7.00 (dq, *J* = 6.9, 1.3, 0.8 Hz, 2H), 6.90 (dt, *J* = 8.9, 1.2 Hz, 1.5H), 6.77 (td, *J* = 7.5, 1.1 Hz, 1H), 6.67 – 6.56 (m, 2H), 3.89 (s, 1.2H), 3.84 (s, 3H), 2.36 (s, 1.55H), 2.30 (s, 3H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 157.13 , 156.78 , 137.17 , 136.63 , 134.29 , 130.14 , 130.04 , 129.27 , 129.01 , 128.74 , 128.71 , 128.44 , 128.40 , 126.45 , 126.39 , 126.25 , 124.96 , 122.39 , 120.70 , 120.17 , 110.88 , 110.60 , 55.50 , 55.46 , 21.25 , 21.21 . **HRMS** (EI) calculated for $C_{16}H_{16}O$ [M]$^+$:224.1196, found 224.1189.

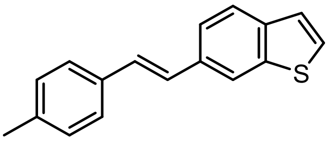


(Z)-5-(4-methylstyryl)benzo[d][1,3]dioxole: Following the general procedure C, the product was obtained as white solid 7.1 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.20 – 7.12 (m, 2H), 7.08 – 7.02 (m, 2H), 6.78 – 6.66 (m, 3H), 6.52 – 6.40 (m, 2H), 5.92 (s, 2H), 2.32 (s, 3H).**^{13}C NMR** (75 MHz, CDCl$_3$) δ 147.28 , 146.48 , 136.77 , 134.25 , 131.38 , 129.20 , 129.08 , 128.95 , 128.68 , 122.87 , 108.88 , 108.15 , 100.86 , 21.24 . **HRMS** (EI) calculated for $C_{16}H_{14}O_2$ [M]$^+$:238.0988, found 238.0982.

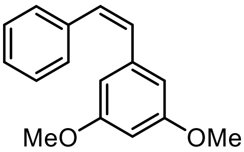


(E)-5-(4-methylstyryl)benzo[d][1,3]dioxole: Following the general procedure C, the product was obtained as white solid 14.3 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 1.7 Hz, 1H), 6.97 – 6.87 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.09 , 147.10 , 137.22 , 134.57 , 132.05 , 129.35 , 127.33 , 126.93 , 126.19 , 121.25 , 108.38 , 105.44 , 101.07 , 21.23 . **HRMS** (EI) calculated for $C_{16}H_{14}O_2$ $[M]^+$:238.0988, found 238.0988.

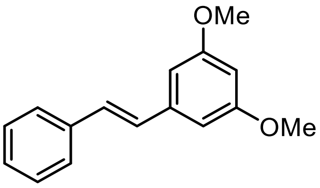




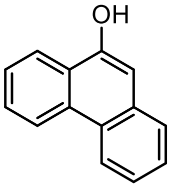
(Z)-6-(4-methylstyryl)benzo[b]thiophene and (E)-6-(4-methylstyryl)benzo[b]thiophene: Following the general procedure C, the product (mixture of mixture of Z and E configuration of products, Z/E = 1/3) was obtained as white solid 19 mg (total amount from two parallel reactions). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 5.4 Hz, 1.5H), 7.28 (d, *J* = 1.6 Hz, 0.5H), 7.24 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.20 – 7.15 (m, 3H), 7.03 (dd, *J* = 7.3, 5.0 Hz, 2.6H), 6.70 – 6.57 (m, 2H), 6.52 (s, 0.2H), 2.37 (s, 0.8H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.74 , 138.31 , 137.24 , 136.88 , 136.70 , 134.22 , 133.69 , 130.02 , 129.48 , 129.45 , 129.40 , 129.34 , 128.90 , 128.85 , 128.80 , 128.71 , 127.59 , 126.47 , 126.34 , 126.27 , 125.32 , 123.95 , 123.78 , 122.04 , 21.23 . **HRMS** (EI) calculated for $C_{17}H_{14}S$ $[M]^+$:250.0811, found 250.0808.



(Z)-1,3-dimethoxy-5-styrylbenzene: Following the general procedure C, the product was obtained as clear oil 10.7 mg (total amount from two parallel reactions). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 6.61 – 6.46 (m, 2H), 6.36 (d, *J* = 2.3 Hz, 2H), 6.27 (t, *J* = 2.3 Hz, 1H), 3.59 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.47 , 139.02 , 137.23 , 130.66 , 130.19 , 128.92 , 128.15 , 127.15 , 106.70 , 99.89 , 55.17 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$:240.1145, found 240.1144.



(E)-1,3-dimethoxy-5-styrylbenzene: Following the general procedure C, the product was obtained as white solid 37.3 mg (total amount from two parallel reactions).**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.41 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 7.15 – 6.99 (m, 2H), 6.69 (d, *J* = 2.3 Hz, 2H), 6.42 (t, *J* = 2.3 Hz, 1H), 3.84 (s, 6H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.94 , 139.31 , 137.08 , 129.17 , 128.65 , 128.63 , 127.70 , 126.54 , 104.54 , 99.95 , 55.35 . **HRMS** (EI) calculated for $C_{16}H_{16}O_2$ $[M]^+$:240.1145, found 240.1140.

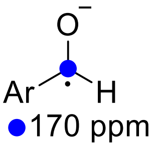


Phenanthren-9-ol[26]: Following the general procedure A, the product was obtained as white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.71 – 8.65 (m, 1H), 8.64 – 8.57 (m, 1H), 8.36 – 8.27 (m, 1H), 7.75 – 7.62 (m, 3H), 7.58 – 7.47 (m, 2H), 7.01 (s, 1H), 5.46 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.47 , 132.62 , 131.51 , 127.20 , 126.92 , 126.70 , 126.68 , 126.40 , 125.50 , 124.25 , 122.68 , 122.56 , 122.32 , 106.06 .

4 Computational details

All structures were calculated at (U)M06-2X/def2-SVP level of theory in continuum of DMF using SMD.[23-24] Subsequently all minima were confirmed by the frequency analysis at the same level as the geometry optimization. NMR calculation were performed at (U)M06-2X/IGLO-III level of theory. Software used for the calculations was Gaussian09 D.01.[25]

Intermediate C



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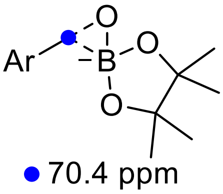

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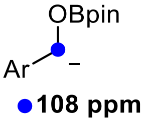
Intermediate G



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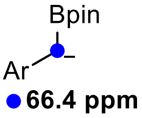
Intermediate I



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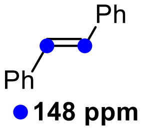
E-Stilbene



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5. Spectroscopic data

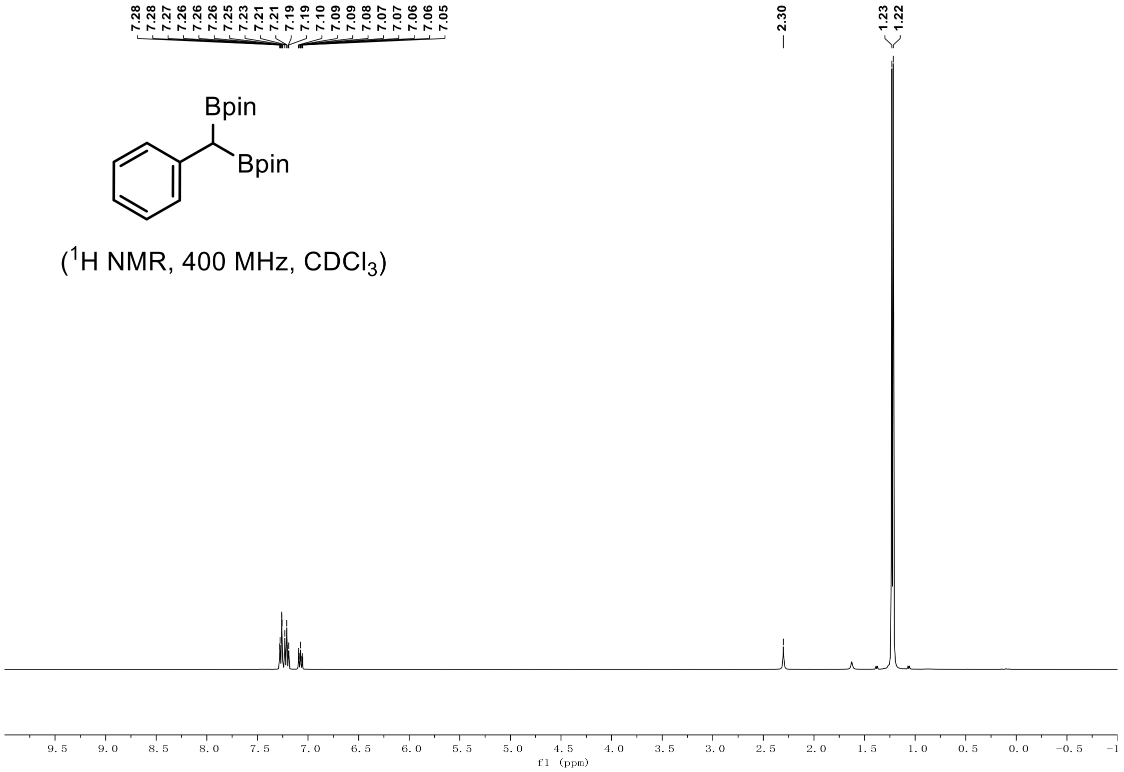


Figure S19. ^{1}H NMR of **S2**

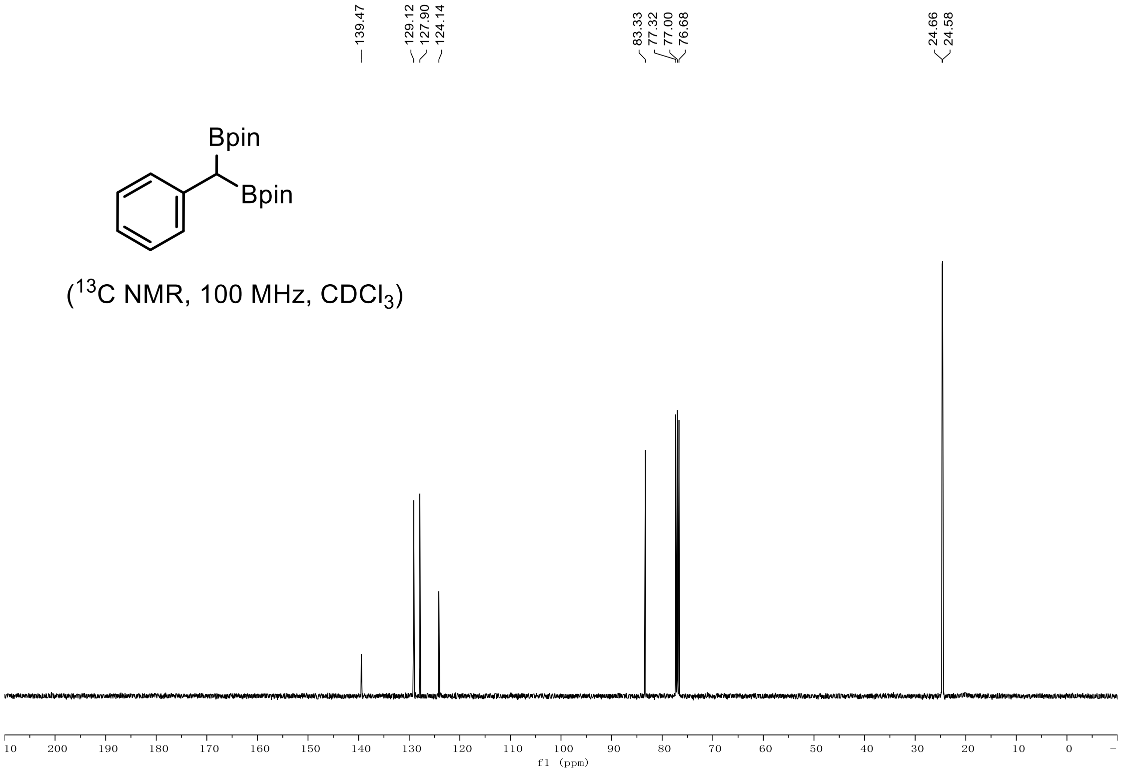


Figure S20. ^{13}C NMR of **S2**

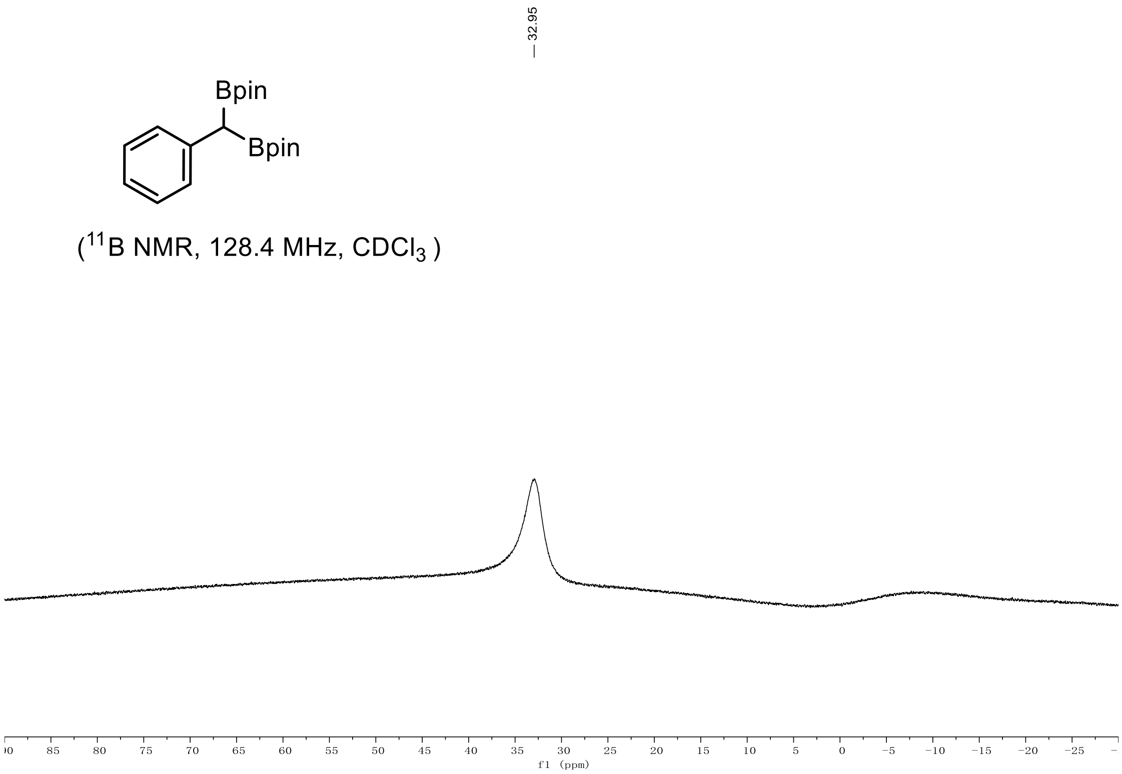
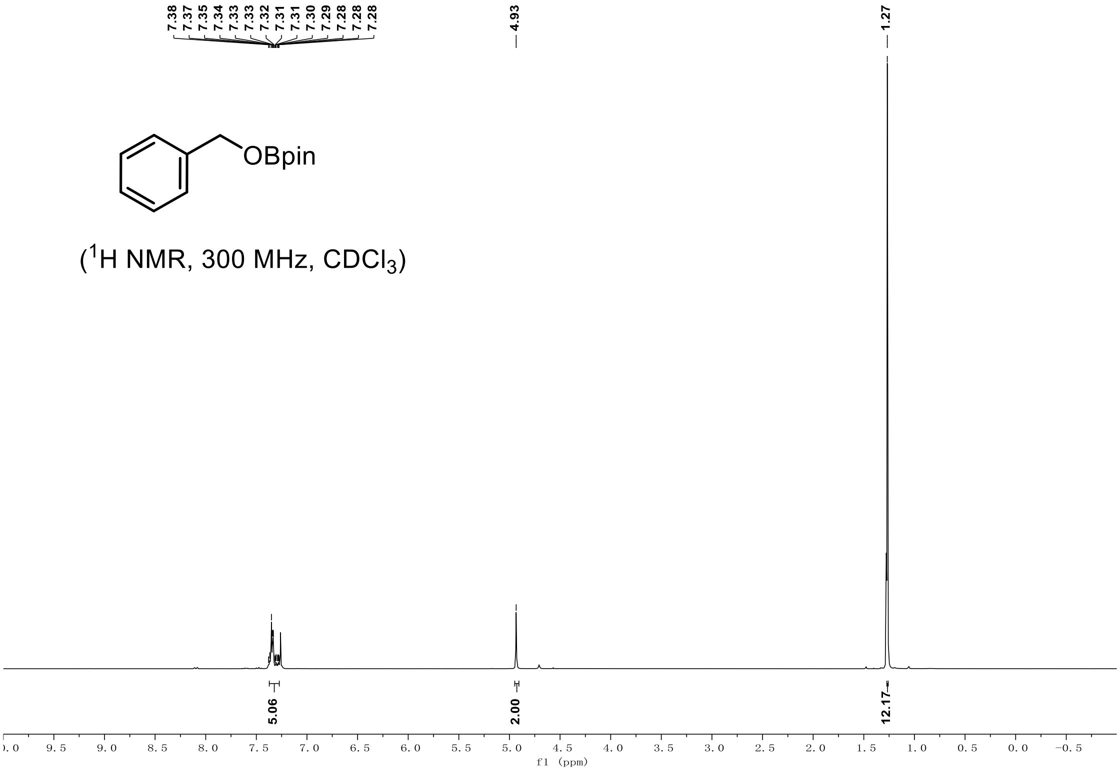


Figure S21. ^{11}B NMR of **S2**



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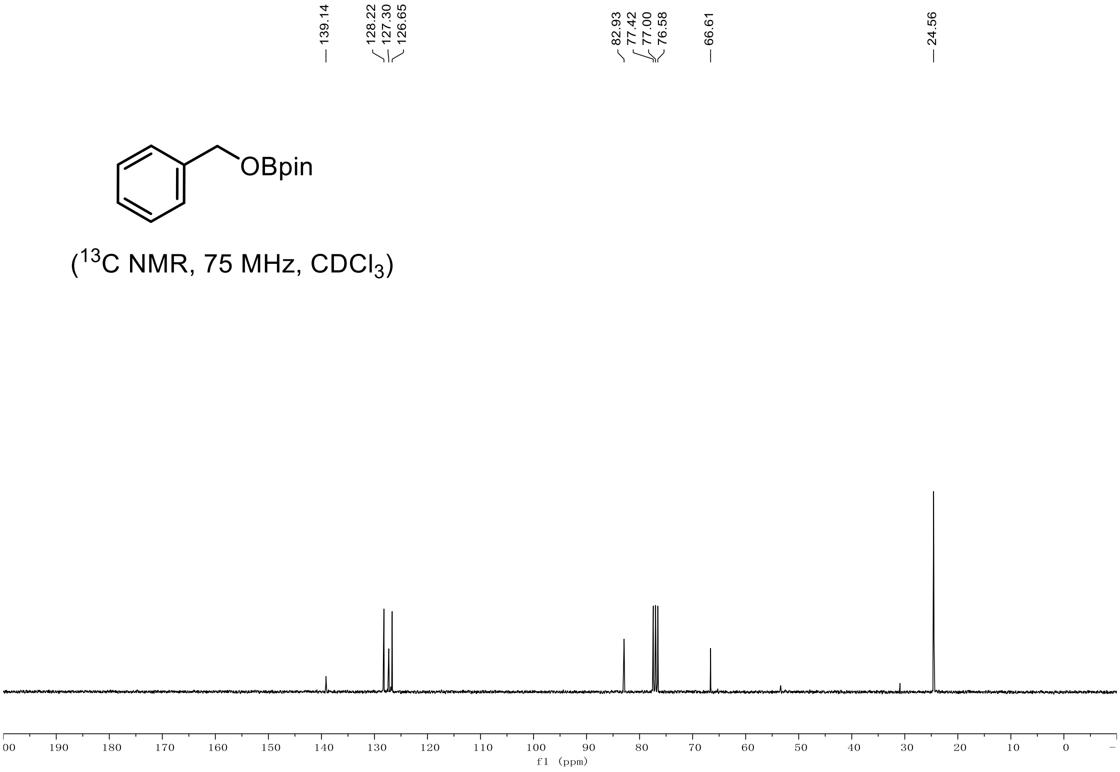

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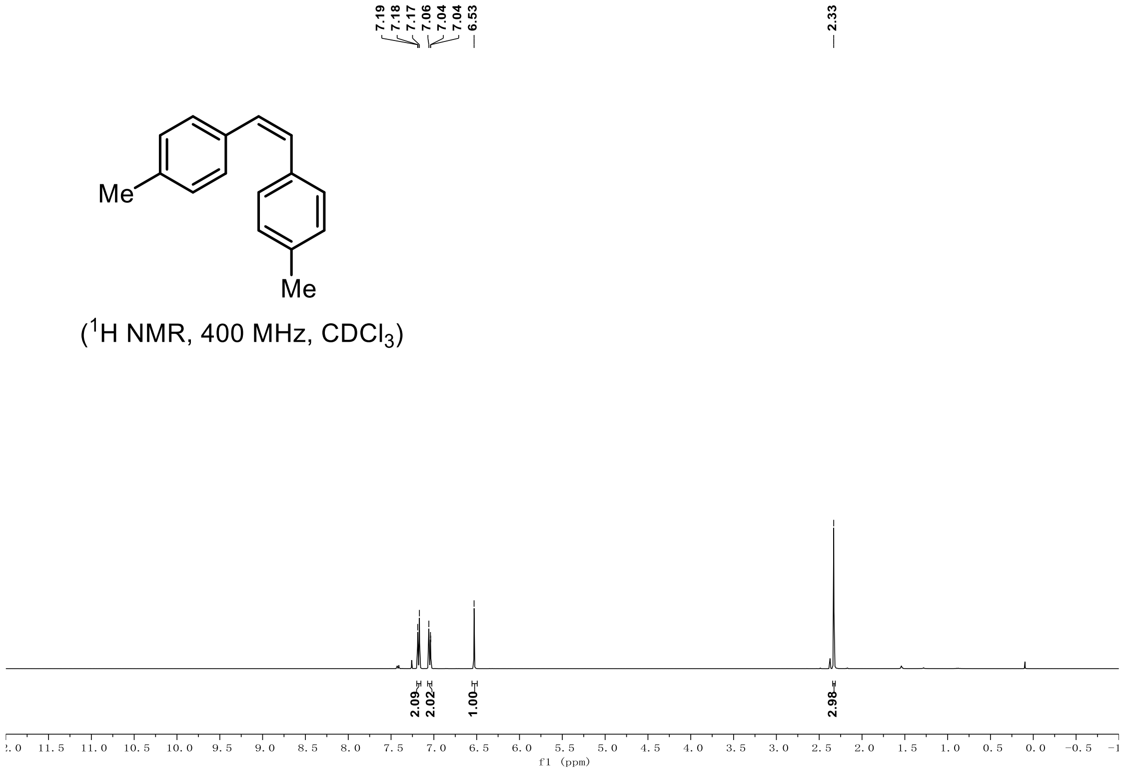

Figure S24. ^{1}H NMR of ***Z*-2a**

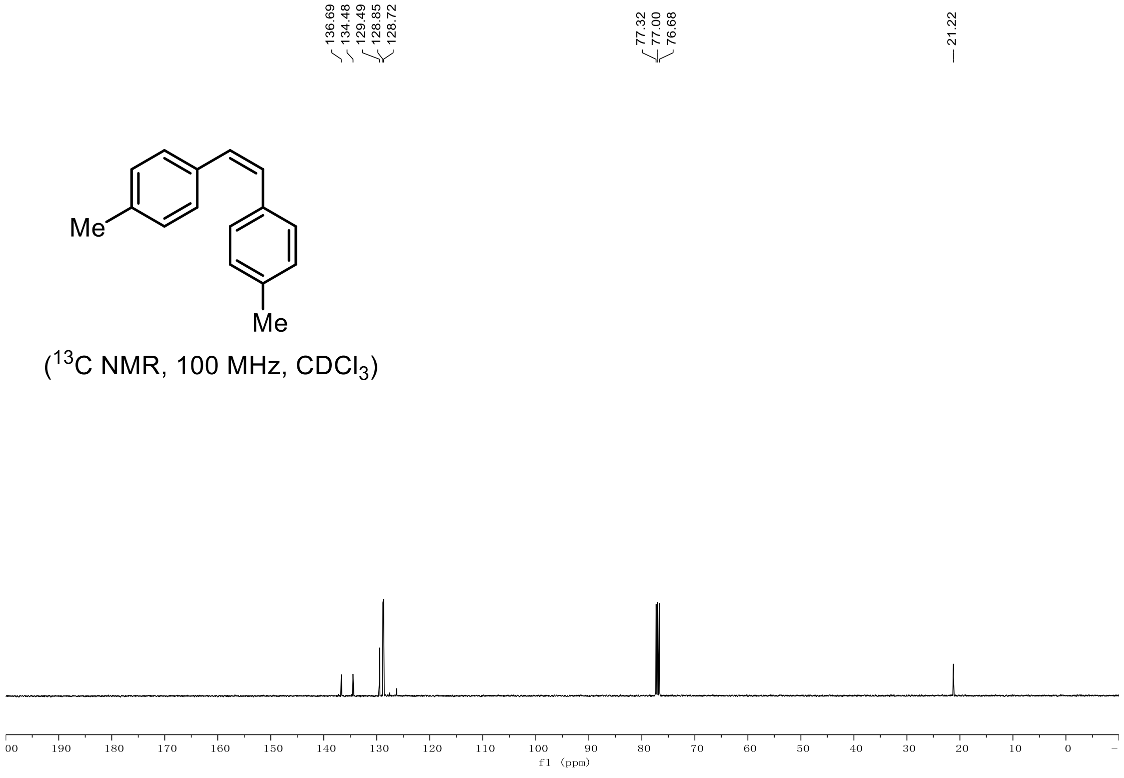

Figure S25. ^{13}C NMR of ***Z*-2a**

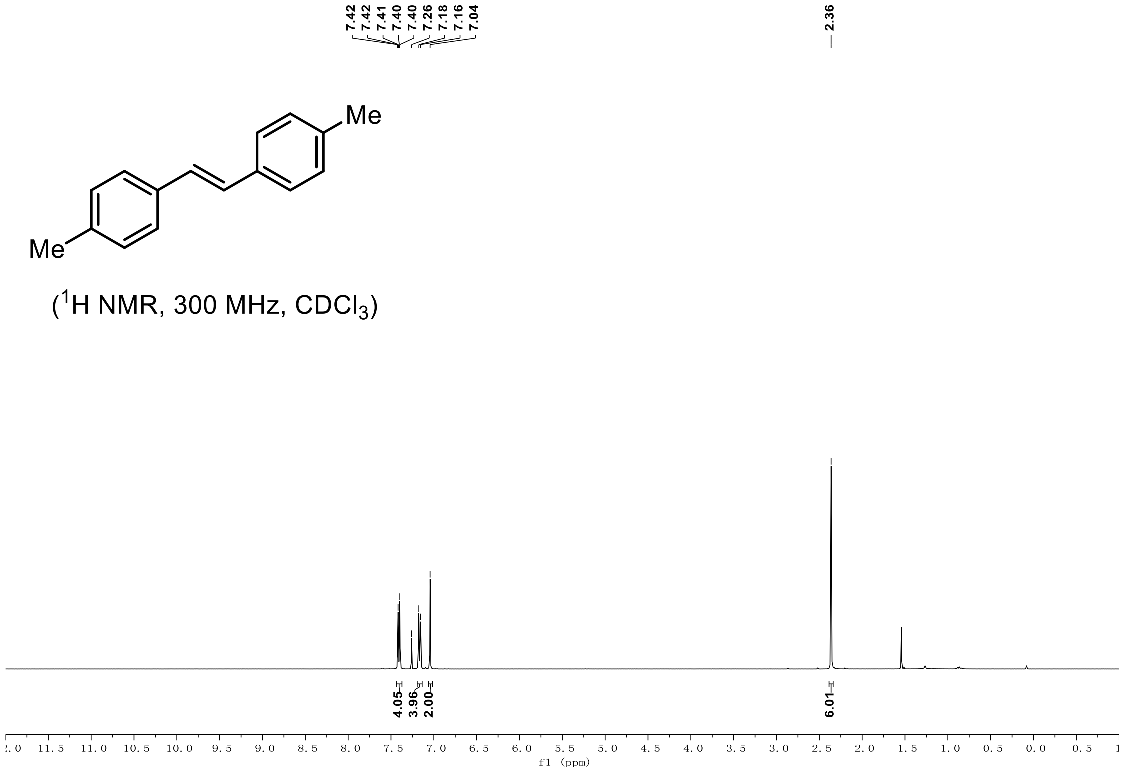

Figure S26. ^{1}H NMR of ***E*-2a**

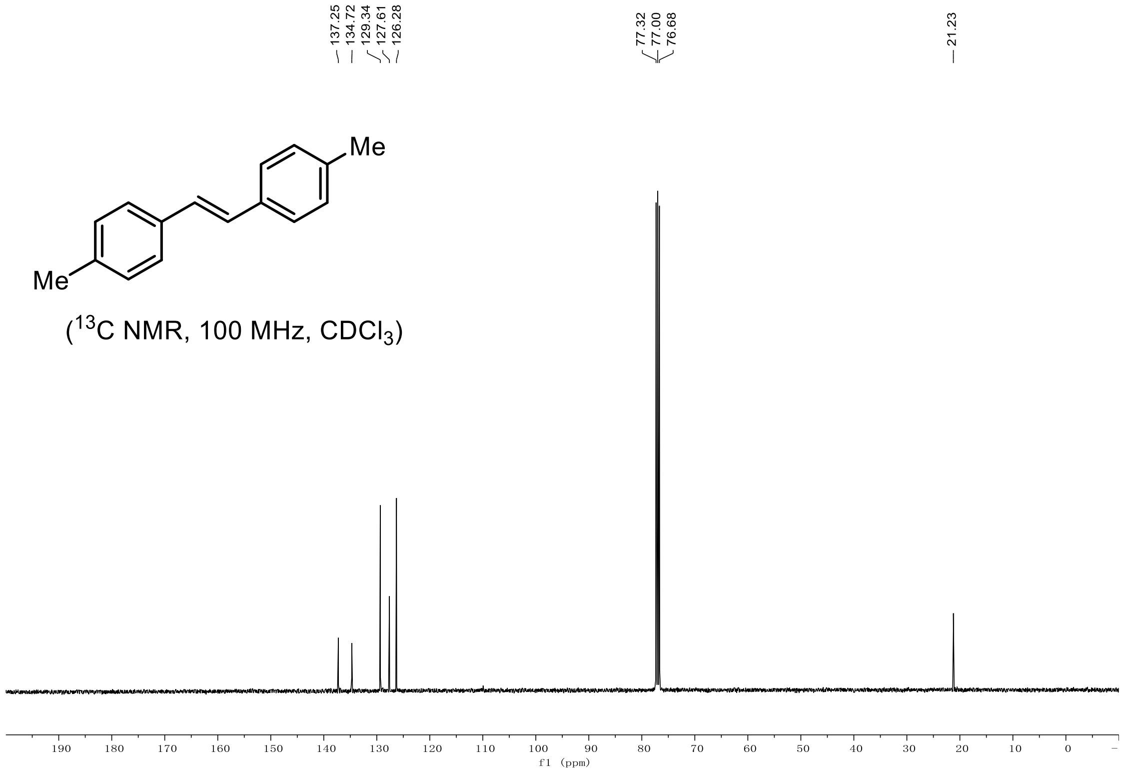

Figure S27. ^{13}C NMR of ***E*-2a**

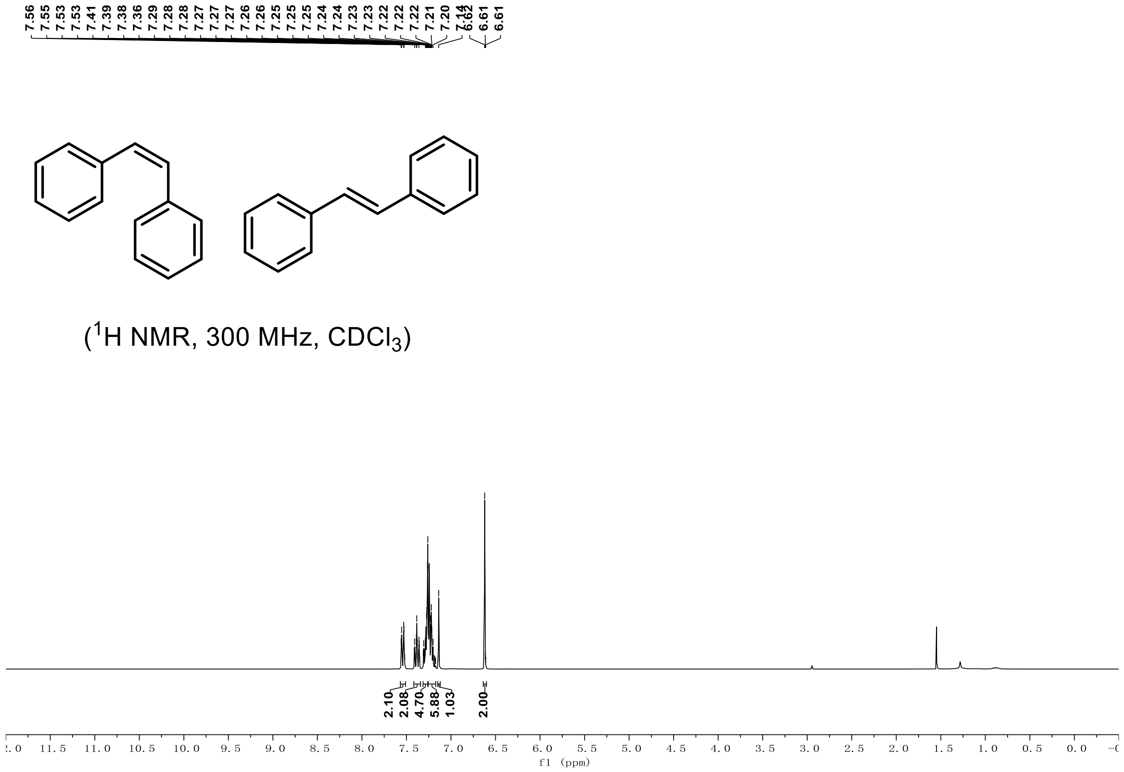

Figure S28. ^{1}H NMR of ***Z*-2b** and ***E*-2b**

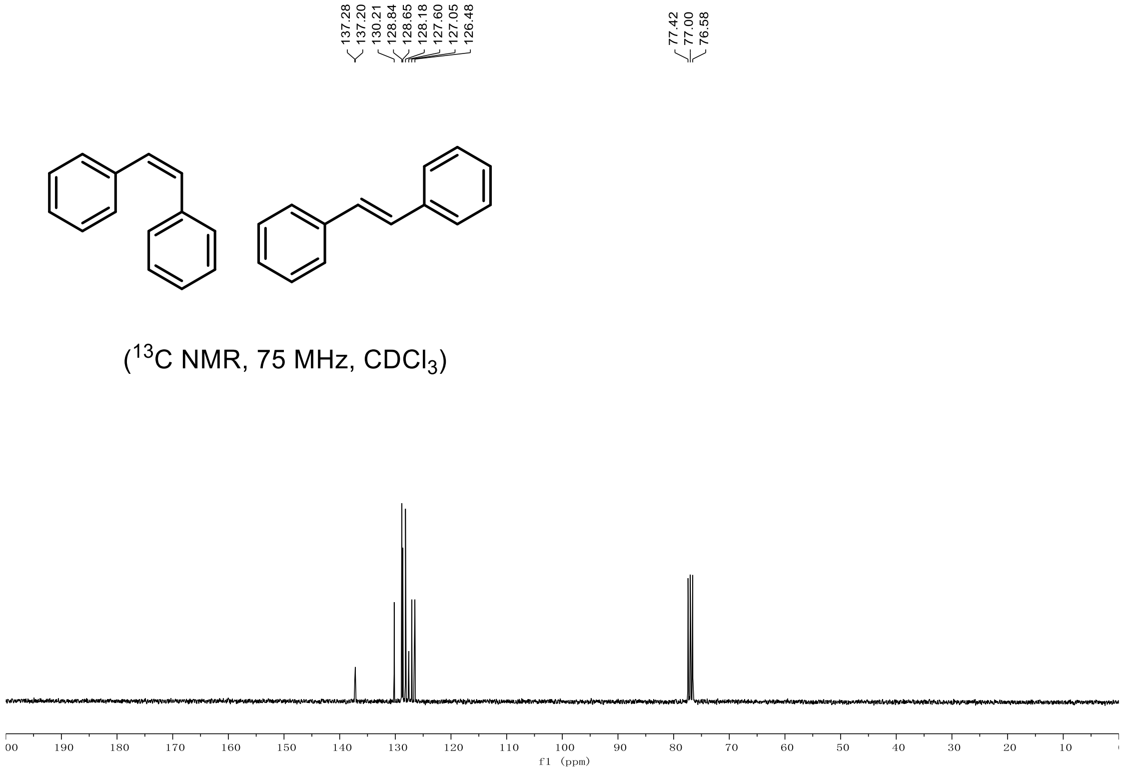

Figure S29. ^{13}C NMR of ***Z*-2b** and ***E*-2b**

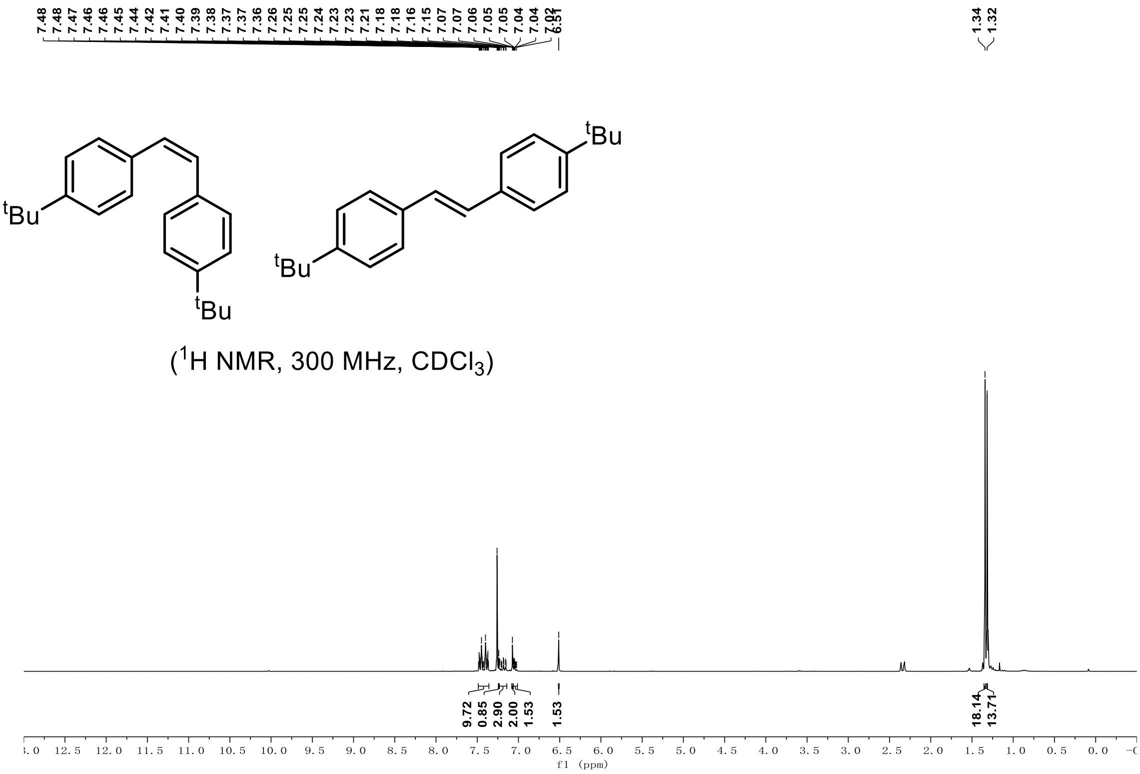

Figure S30. ^{1}H NMR of ***Z*-2c** and ***E*-2c**

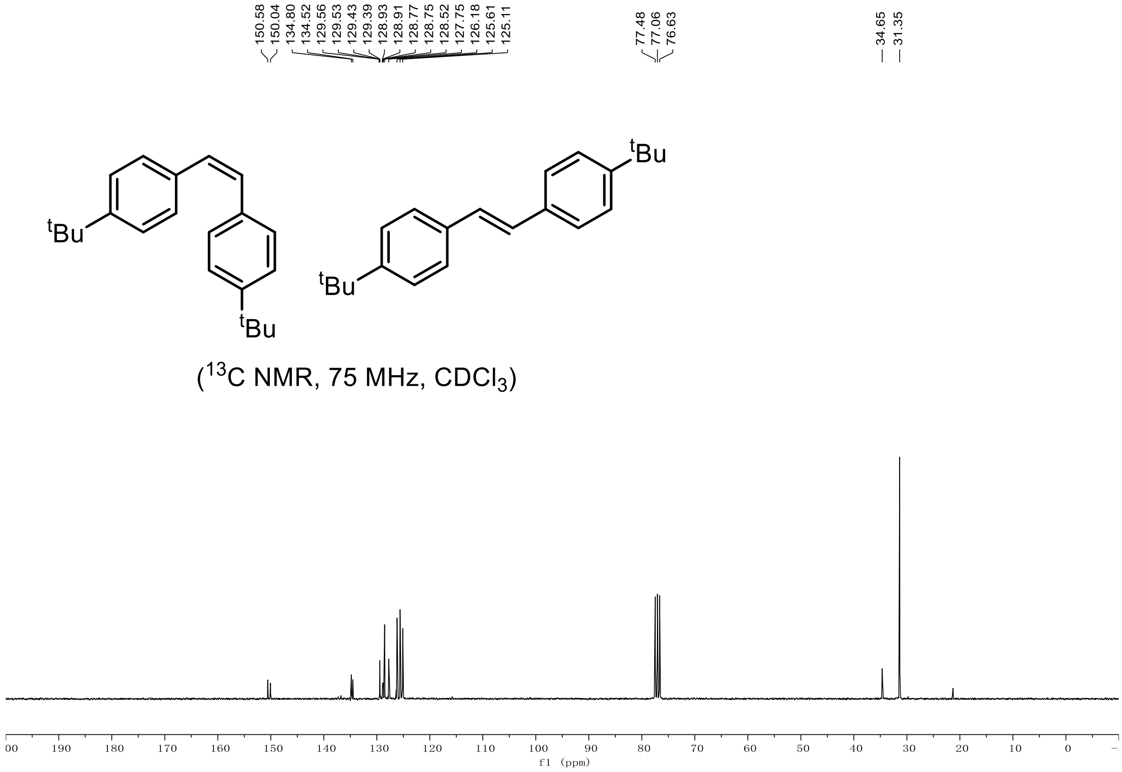

Figure S31. ^{13}C NMR of ***Z*-2c** and ***E*-2c**

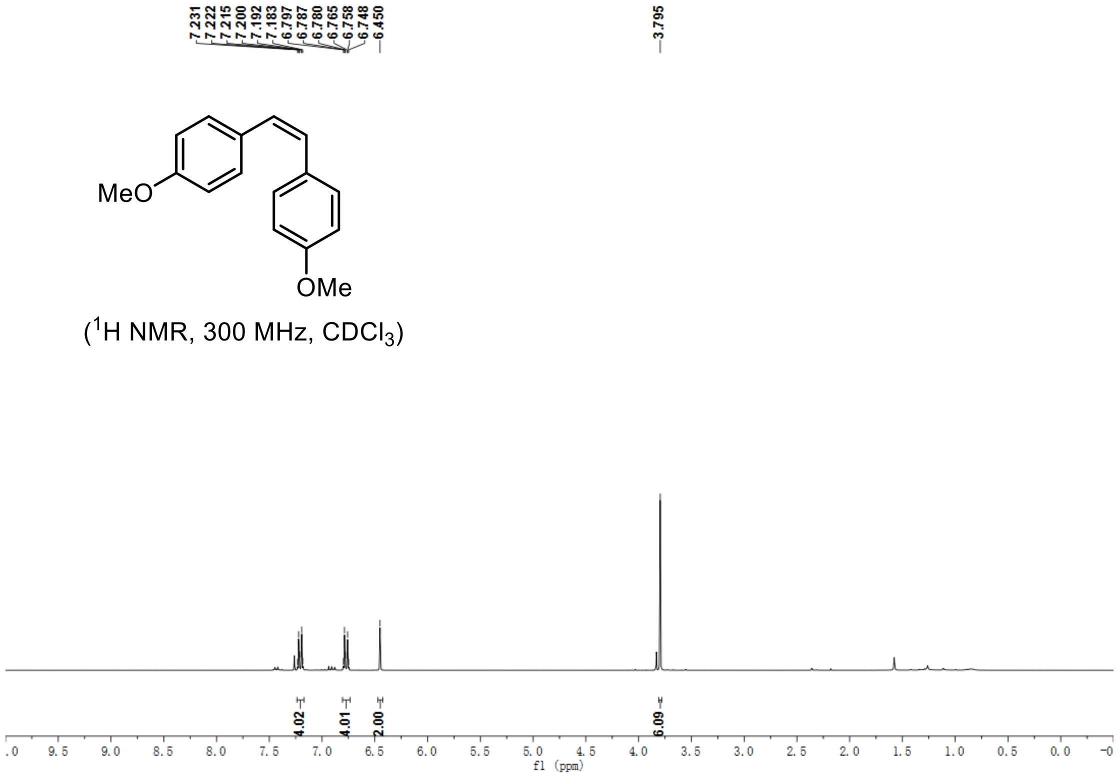

Figure S32. ^{1}H NMR of ***Z*-2d**

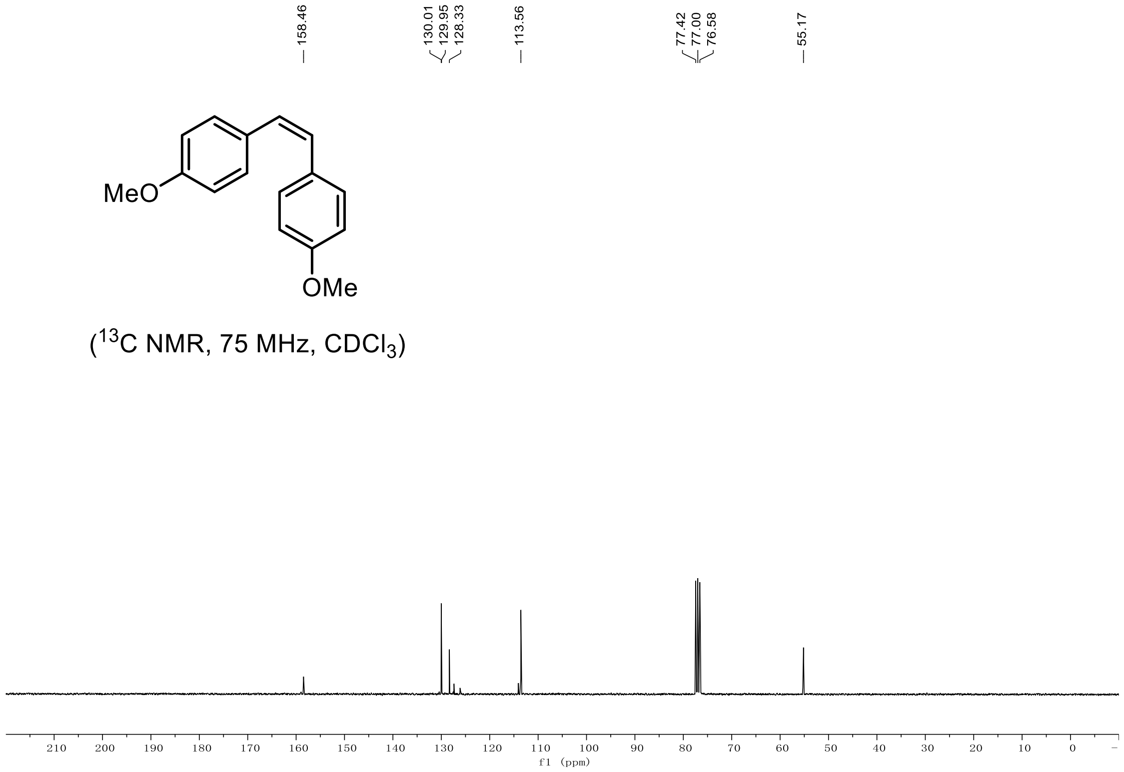

Figure S33. ^{13}C NMR of ***Z*-2d**

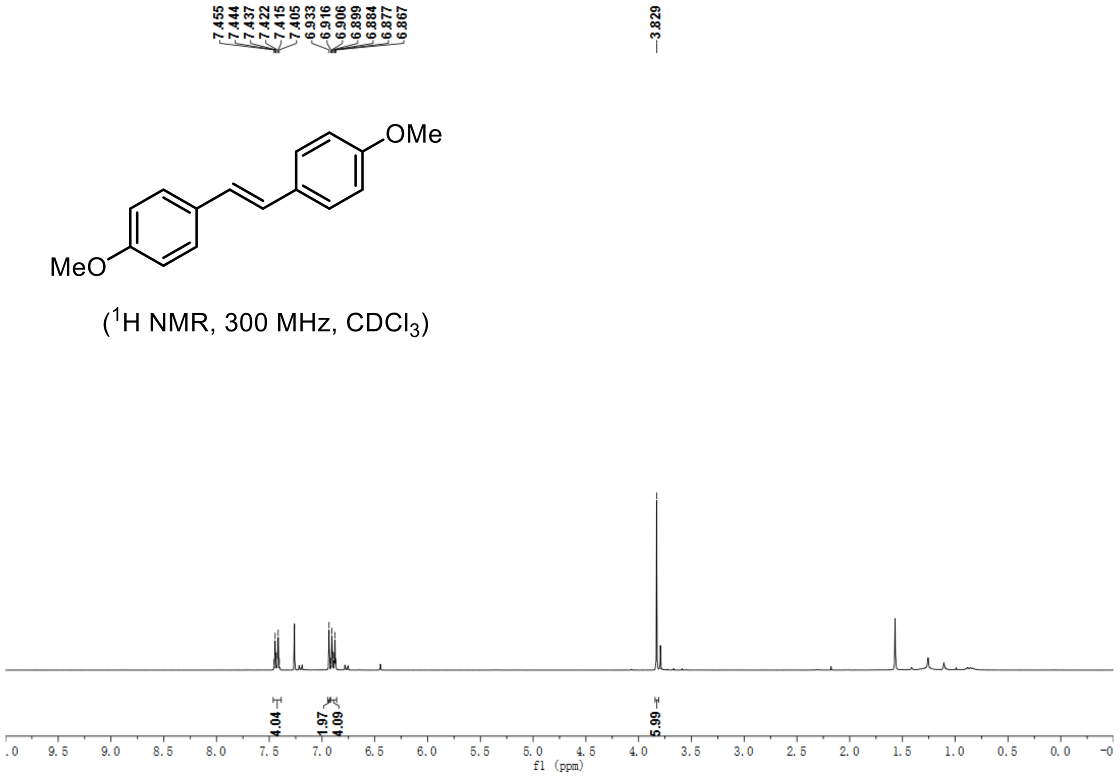

Figure S34. ^{1}H NMR of ***E*-2d**

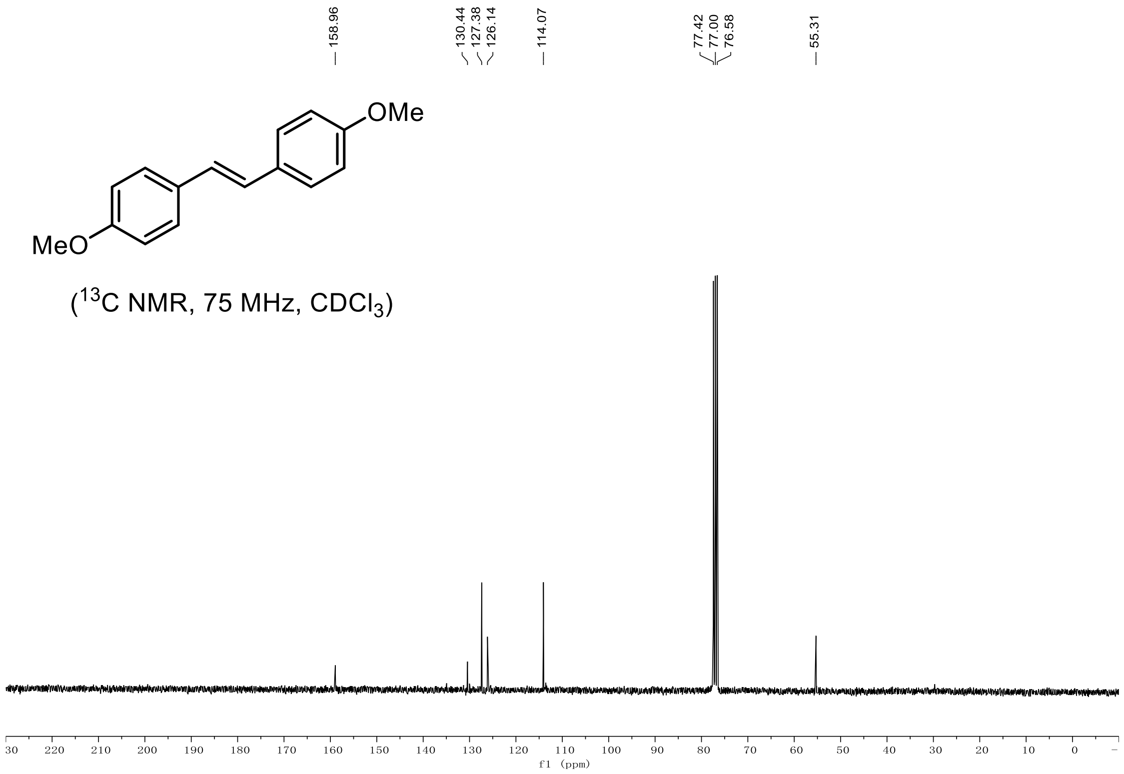

Figure S35. ^{13}C NMR of ***E*-2d**

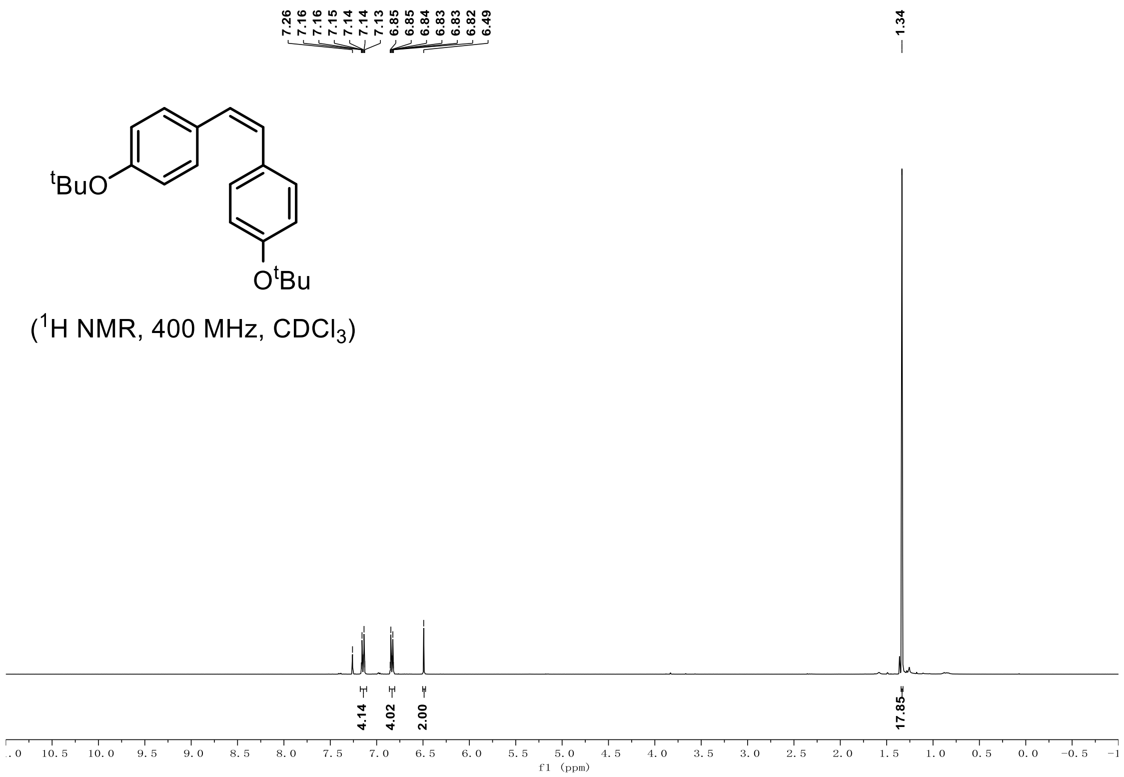

Figure S36. ^{1}H NMR of ***Z*-2e**

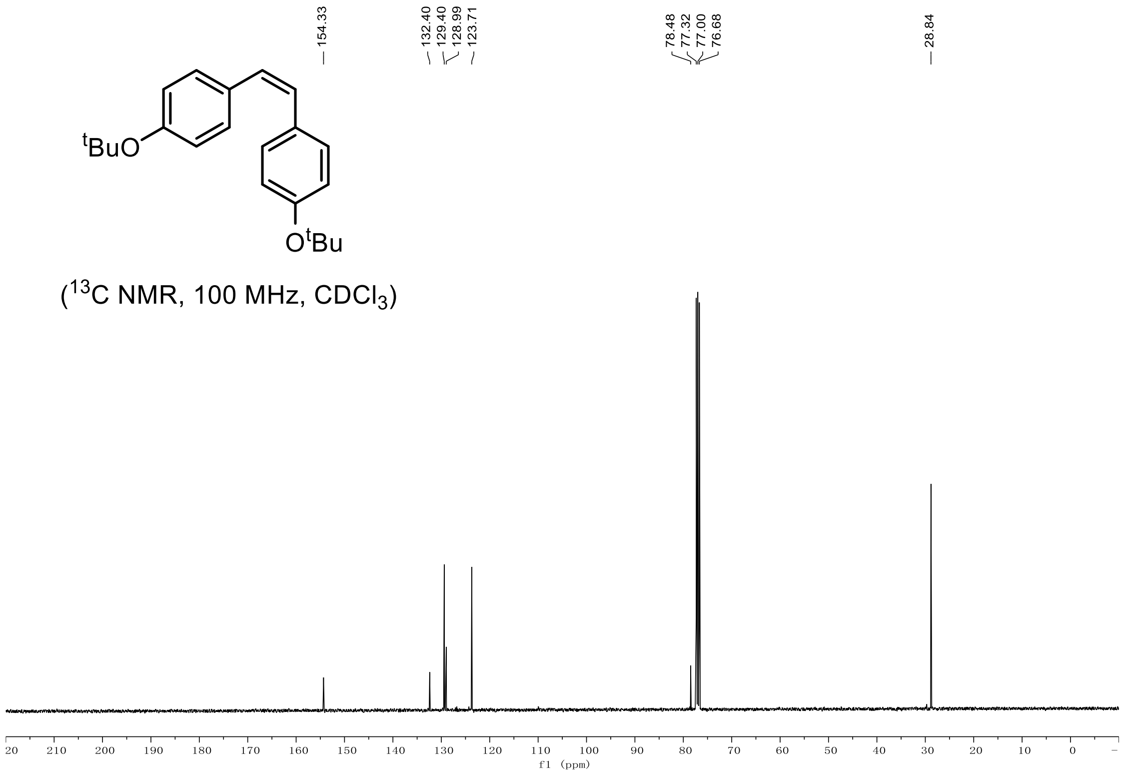

Figure S37. ^{13}C NMR of ***Z*-2e**

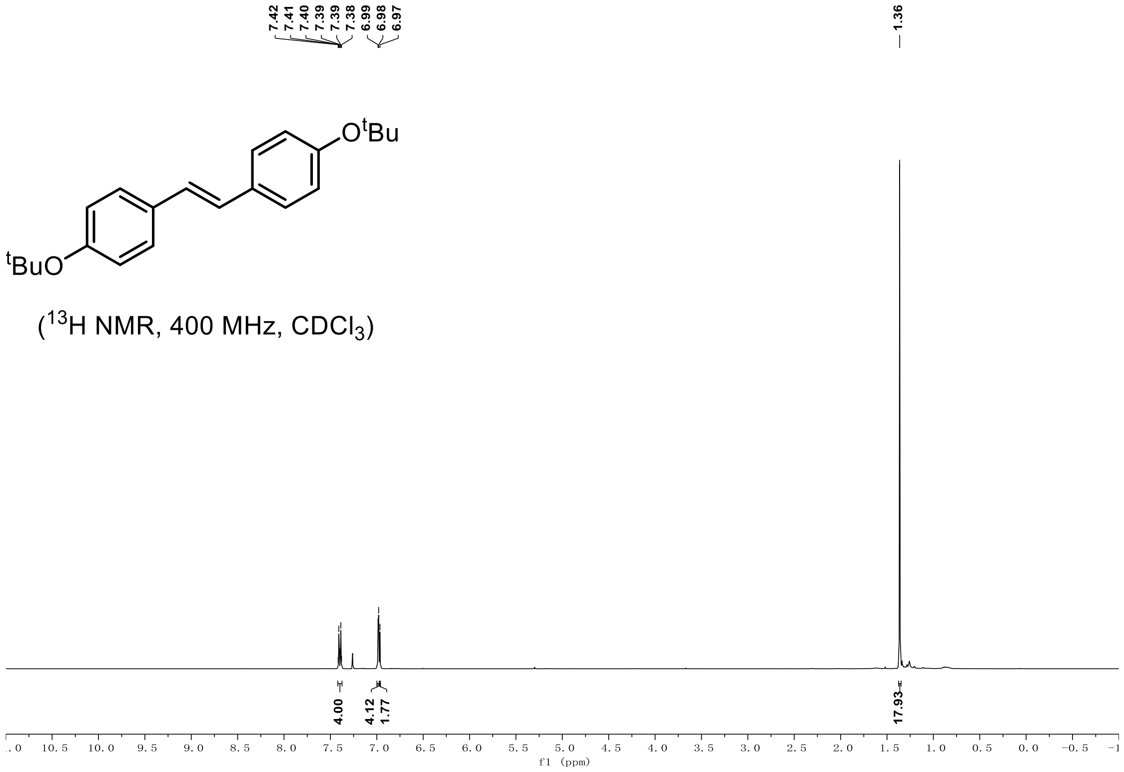

Figure S38. ^{1}H NMR of ***E*-2e**

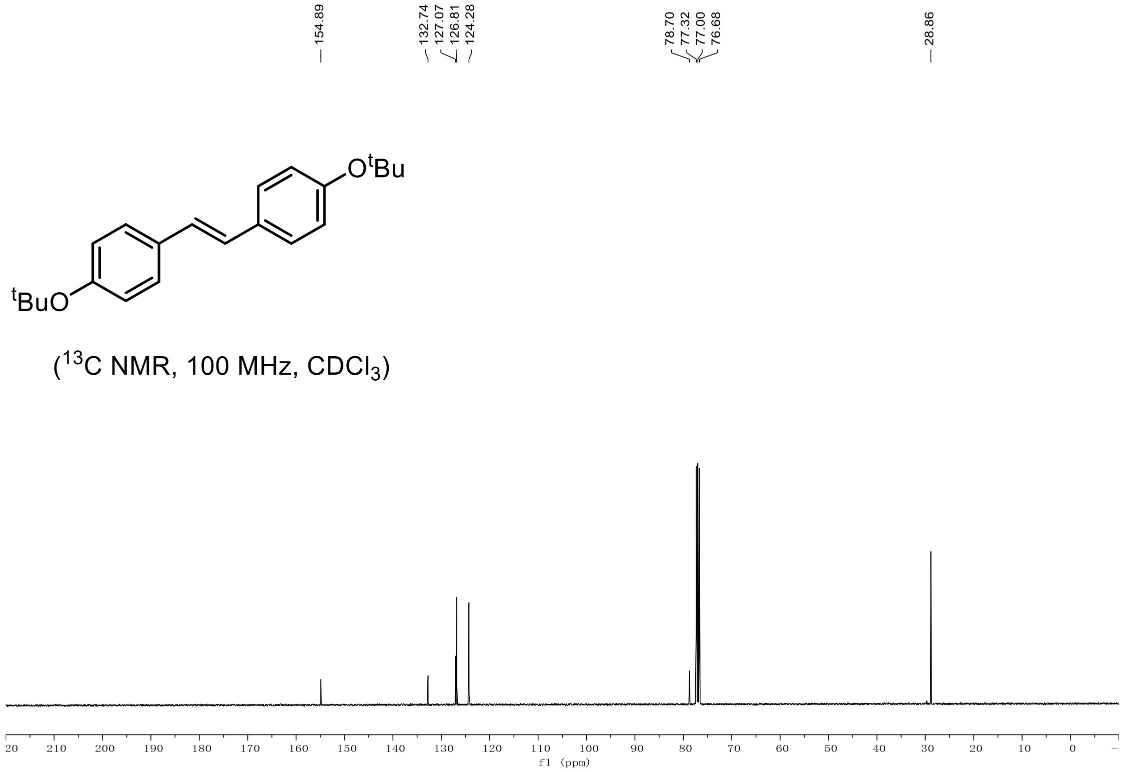

Figure S39. ^{13}C NMR of ***E*-2e**

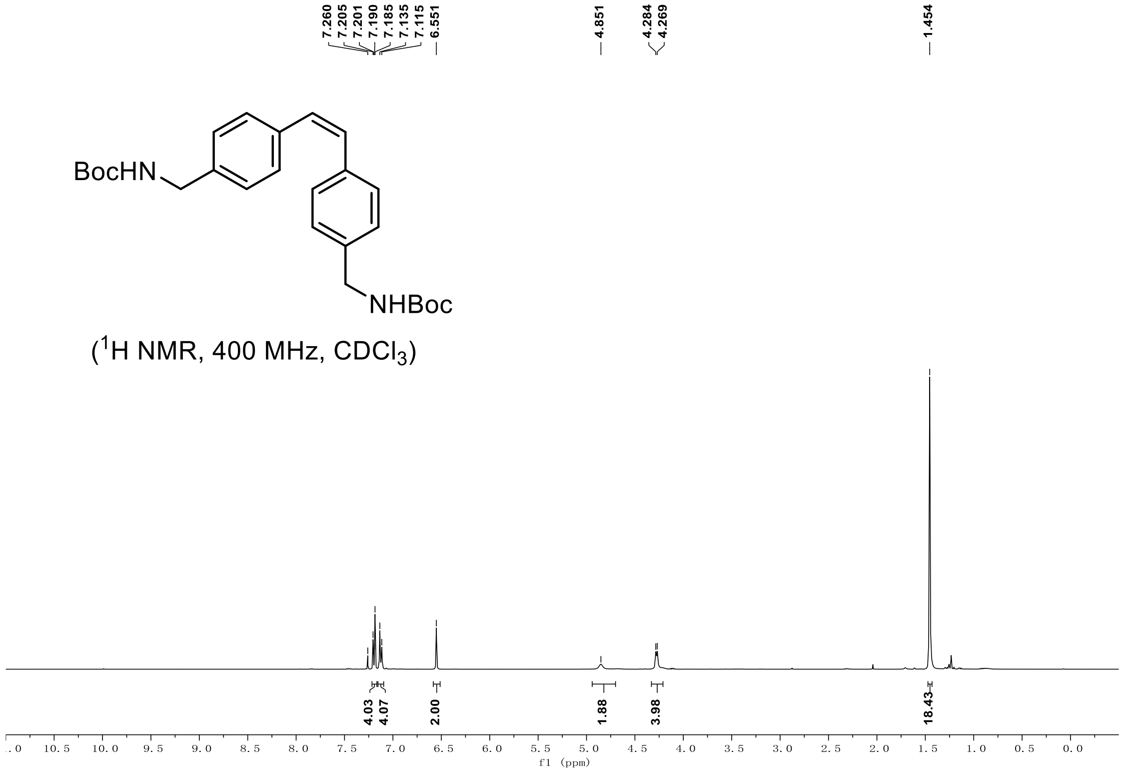

Figure S40. ^{1}H NMR of ***Z*-2f**

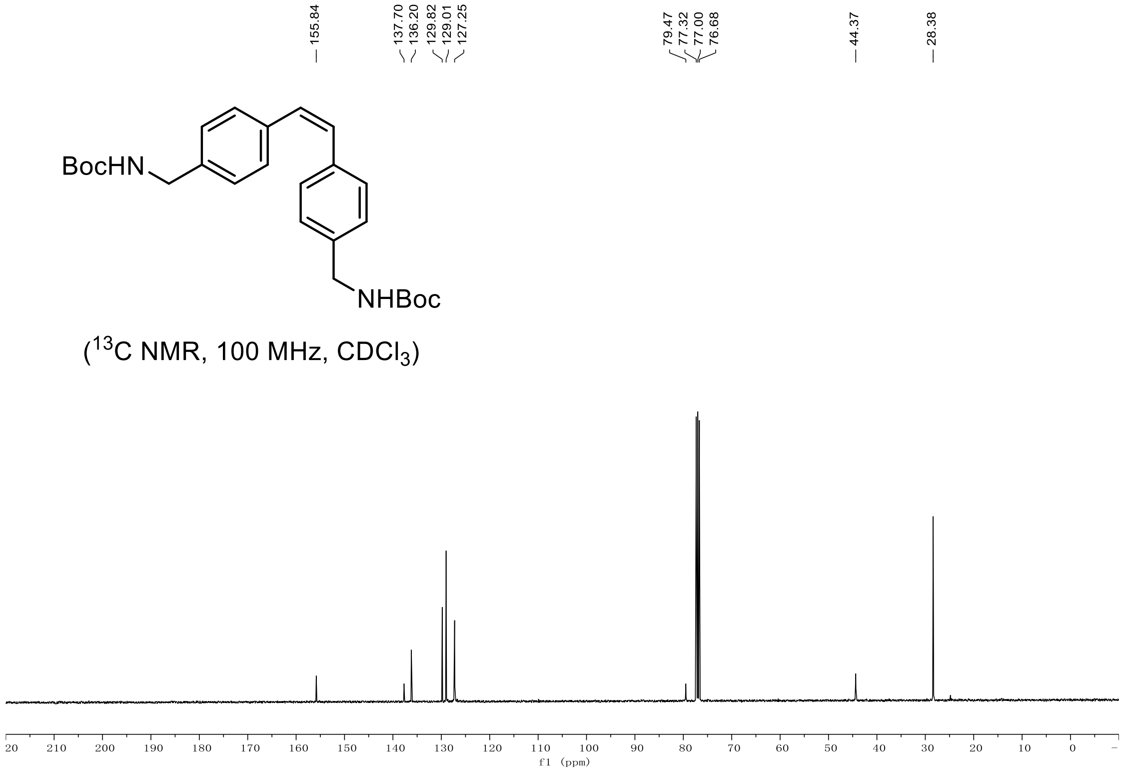

Figure S41. ^{13}C NMR of ***Z*-2f**

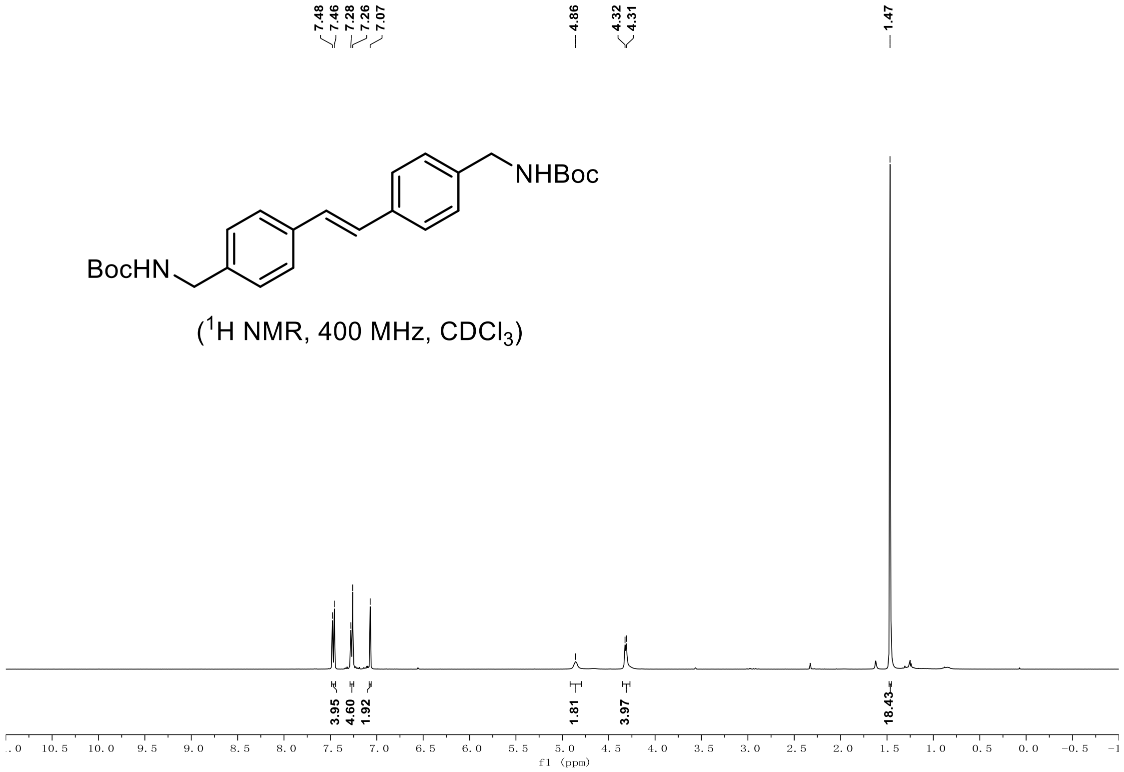

Figure S42. ^{1}H NMR of ***E*-2f**

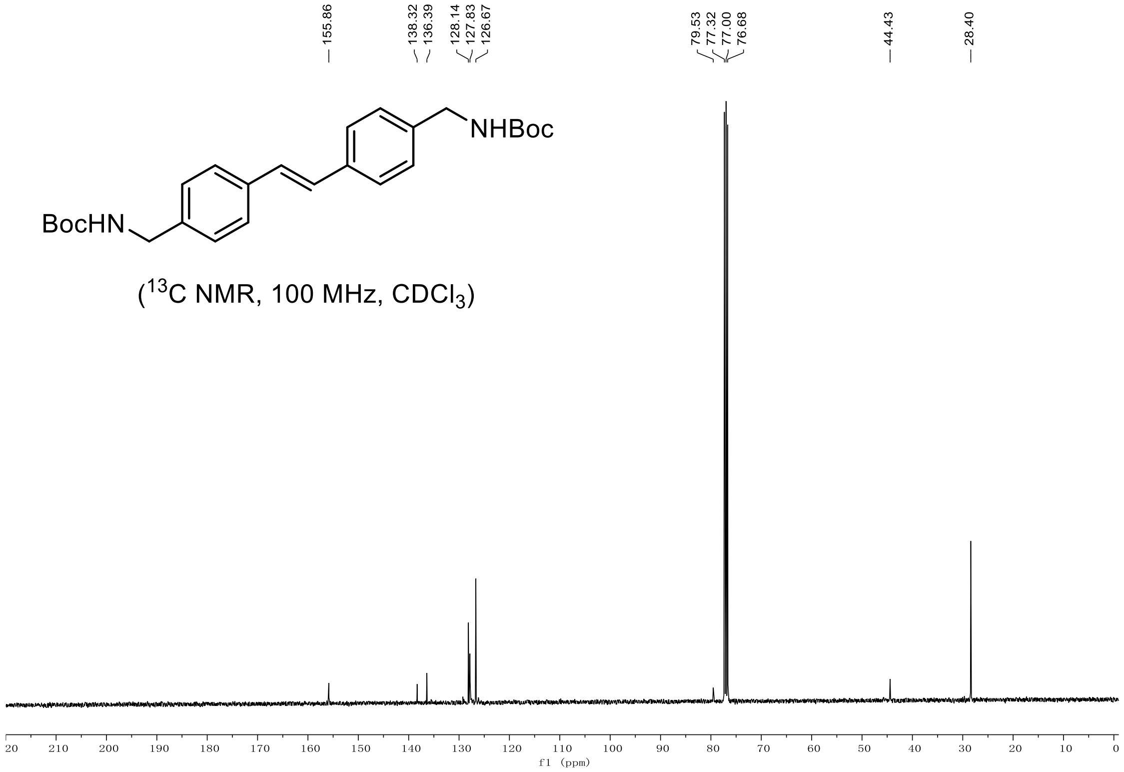

Figure S43. ^{13}C NMR of ***E*-2f**

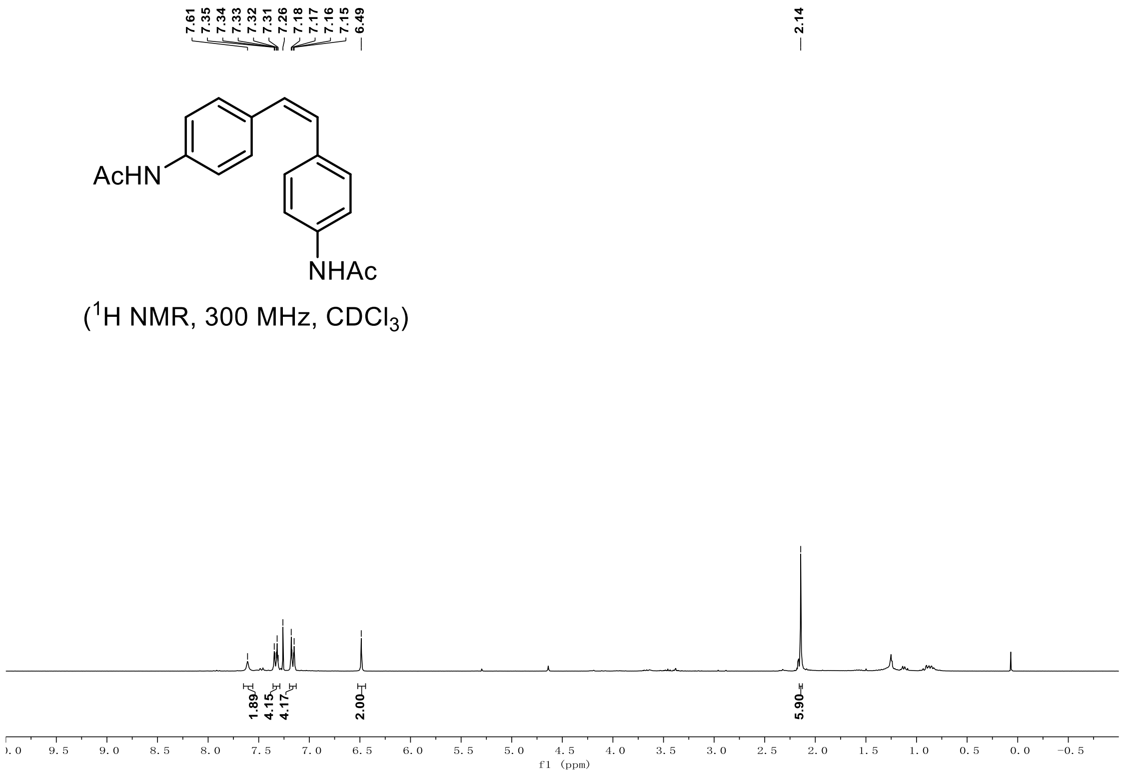

Figure S44. ^{1}H NMR of ***Z*-2g**

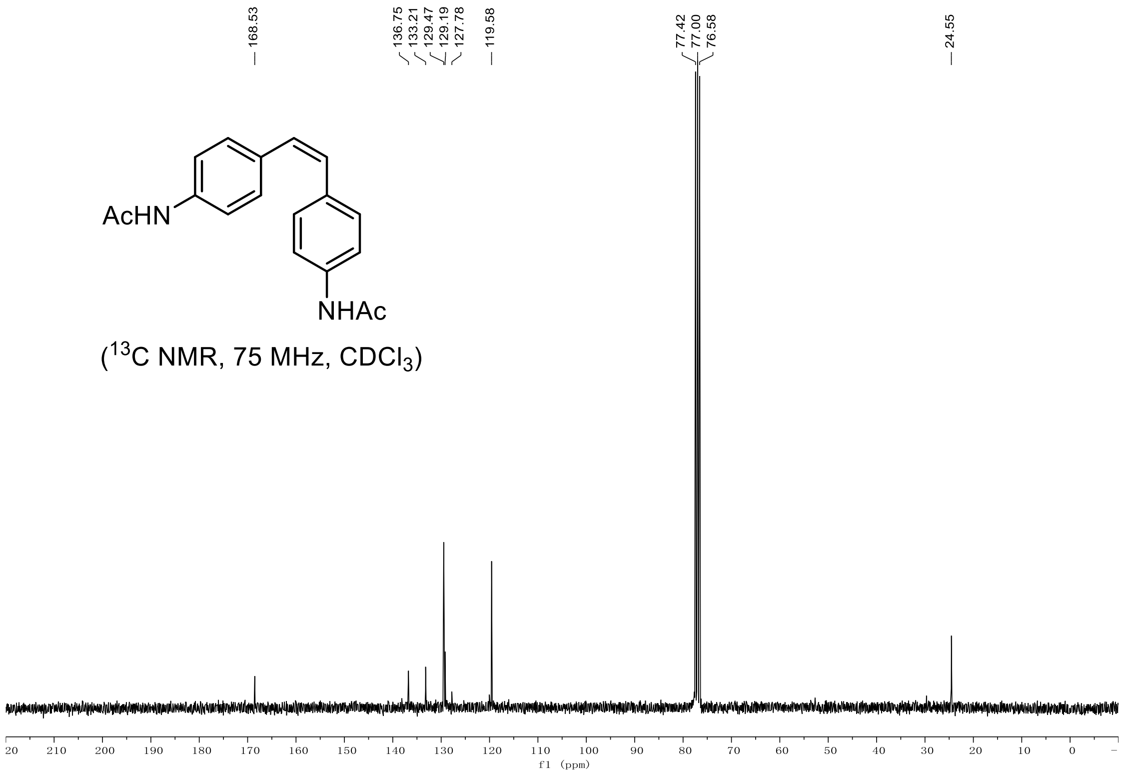

Figure S45. ^{13}C NMR of ***Z*-2g**

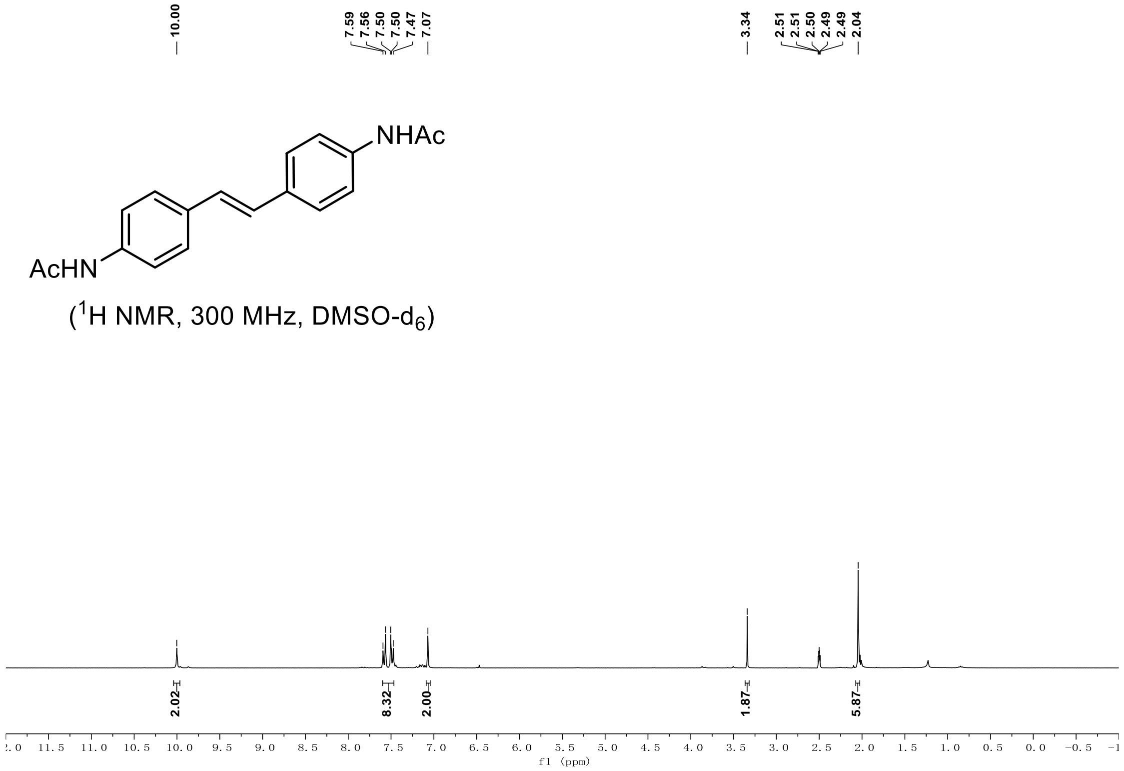

Figure S46. ^{1}H NMR of ***E*-2g**

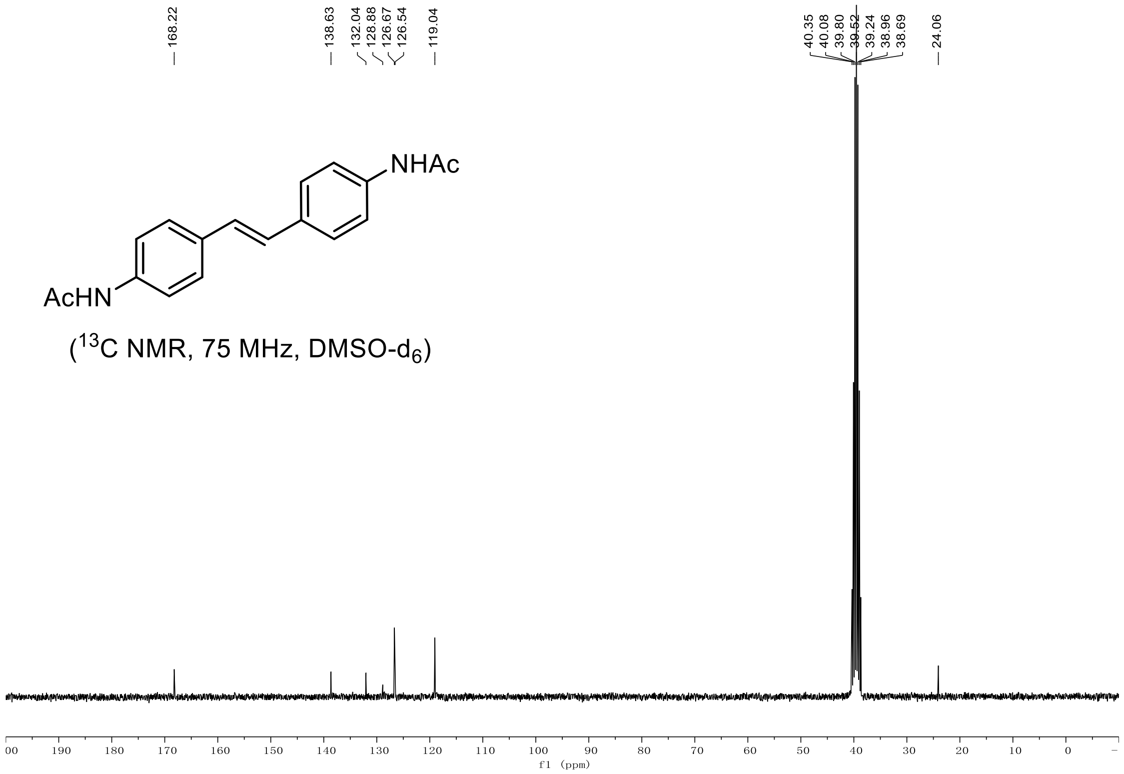

Figure S47. ^{13}C NMR of ***E*-2g**

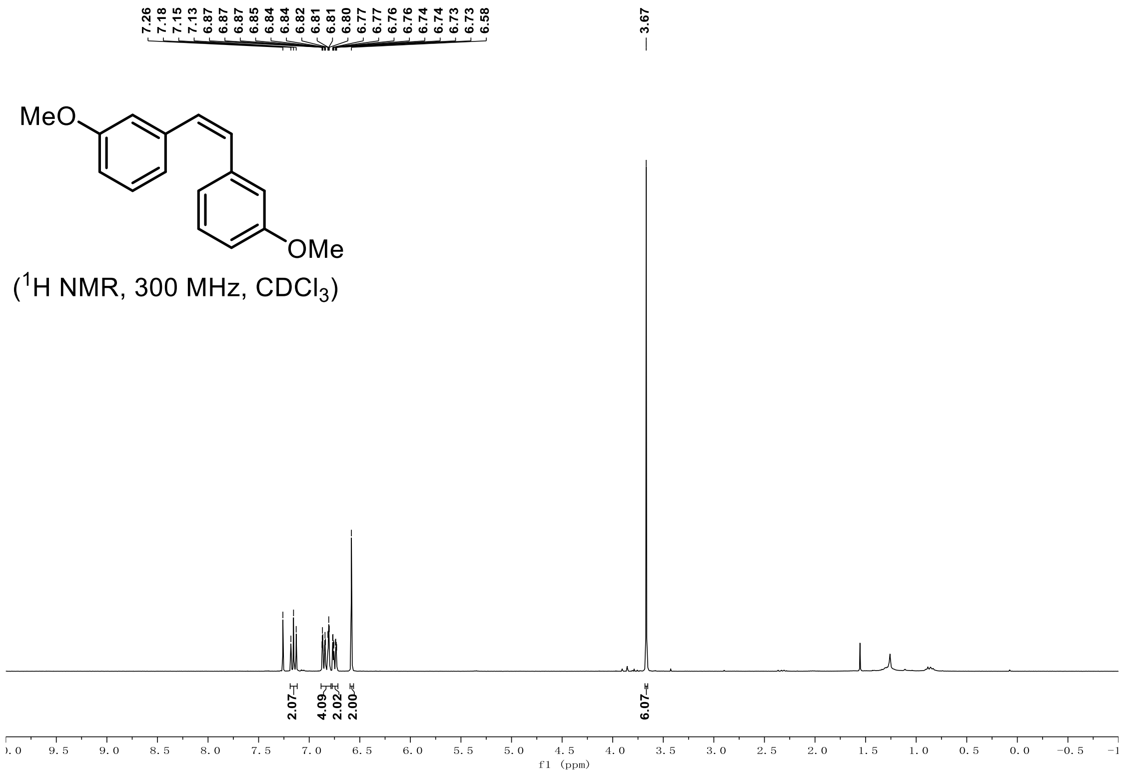

Figure S48. ^{1}H NMR of ***Z*-2h**

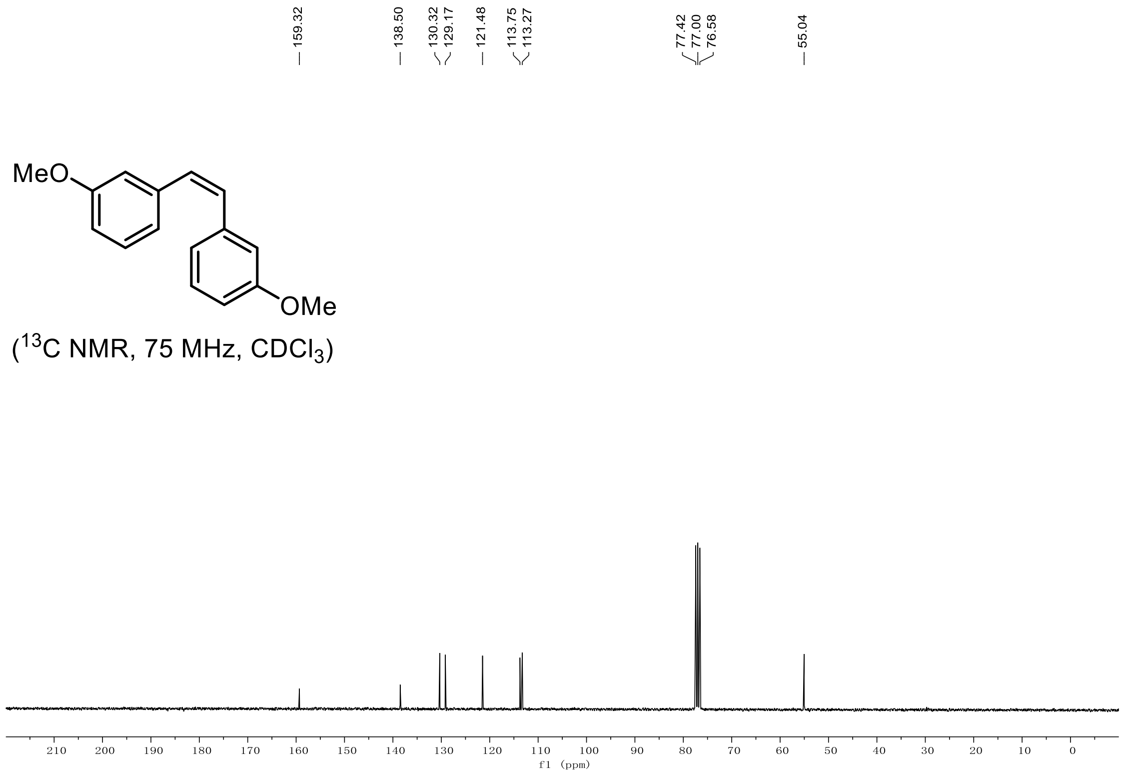

Figure S49. ^{13}C NMR of ***Z*-2h**

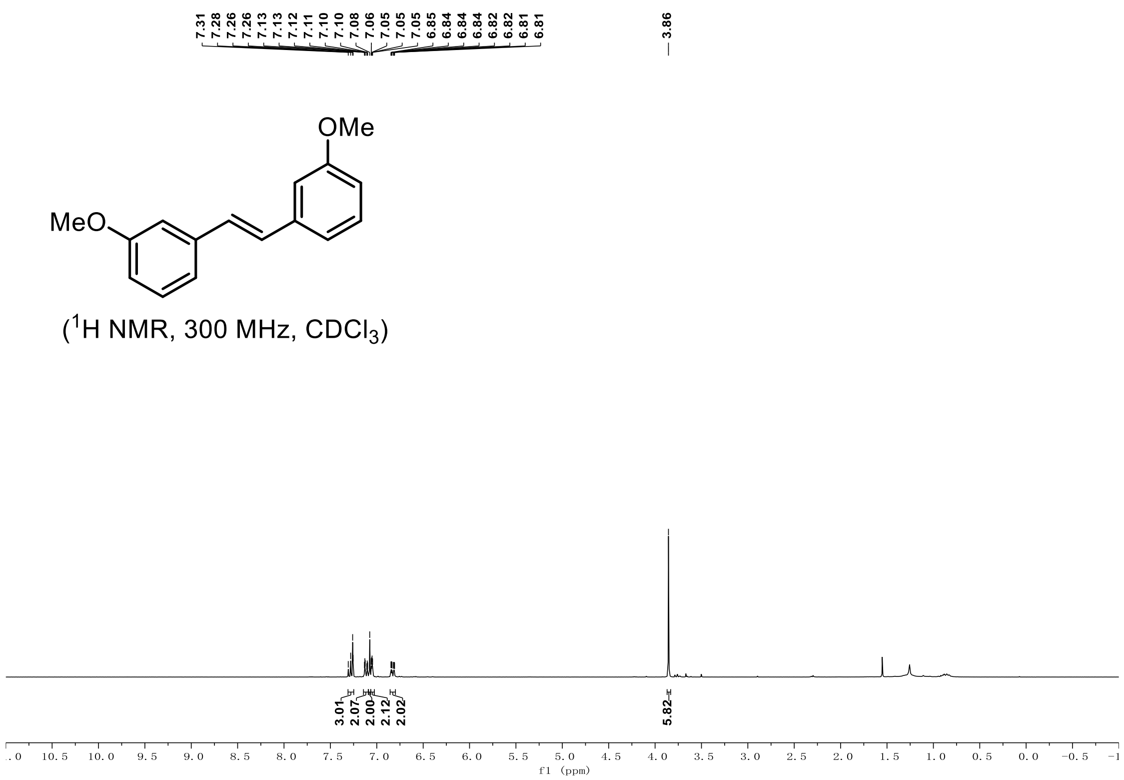

Figure S50. ^{1}H NMR of ***E*-2h**

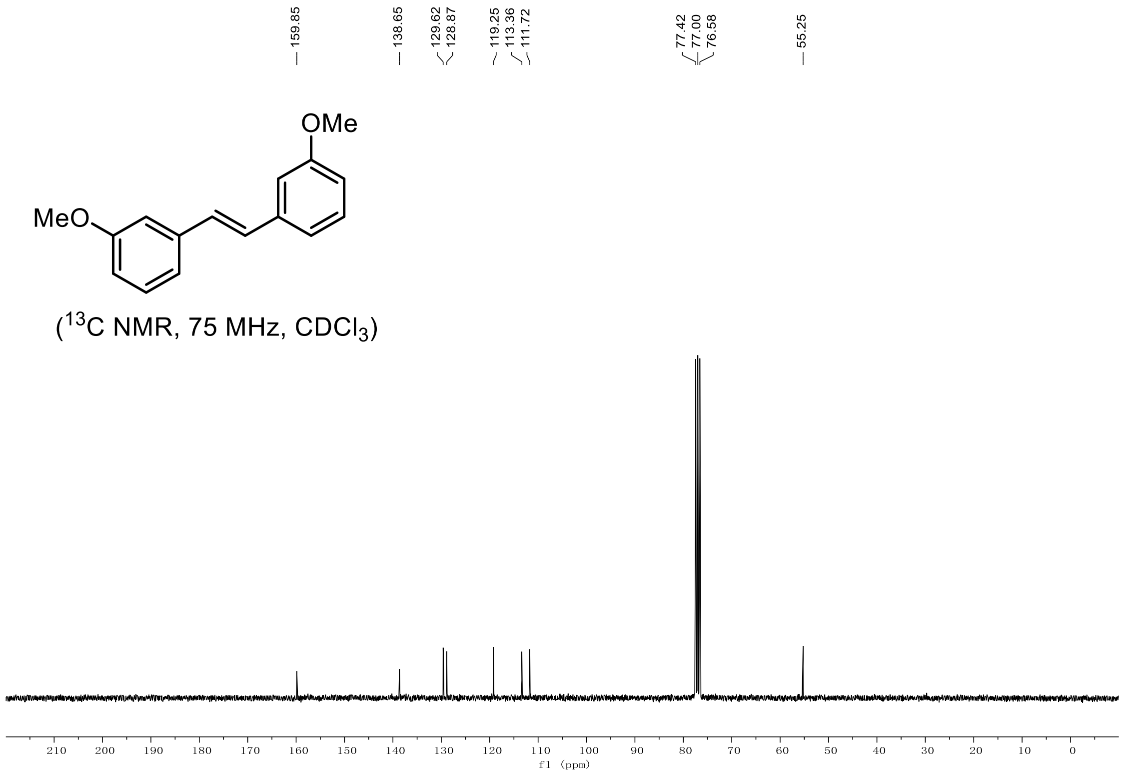

Figure S51. ^{13}C NMR of ***E*-2h**

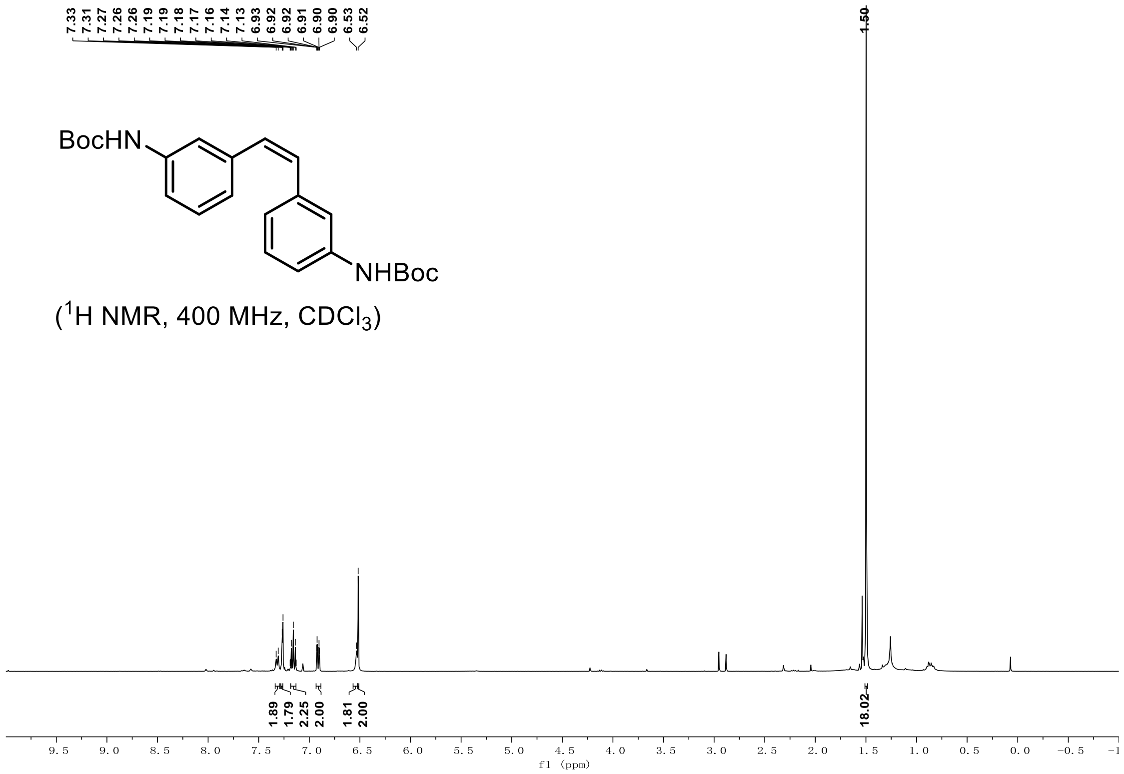

Figure S52. ^{1}H NMR of ***Z*-2i**

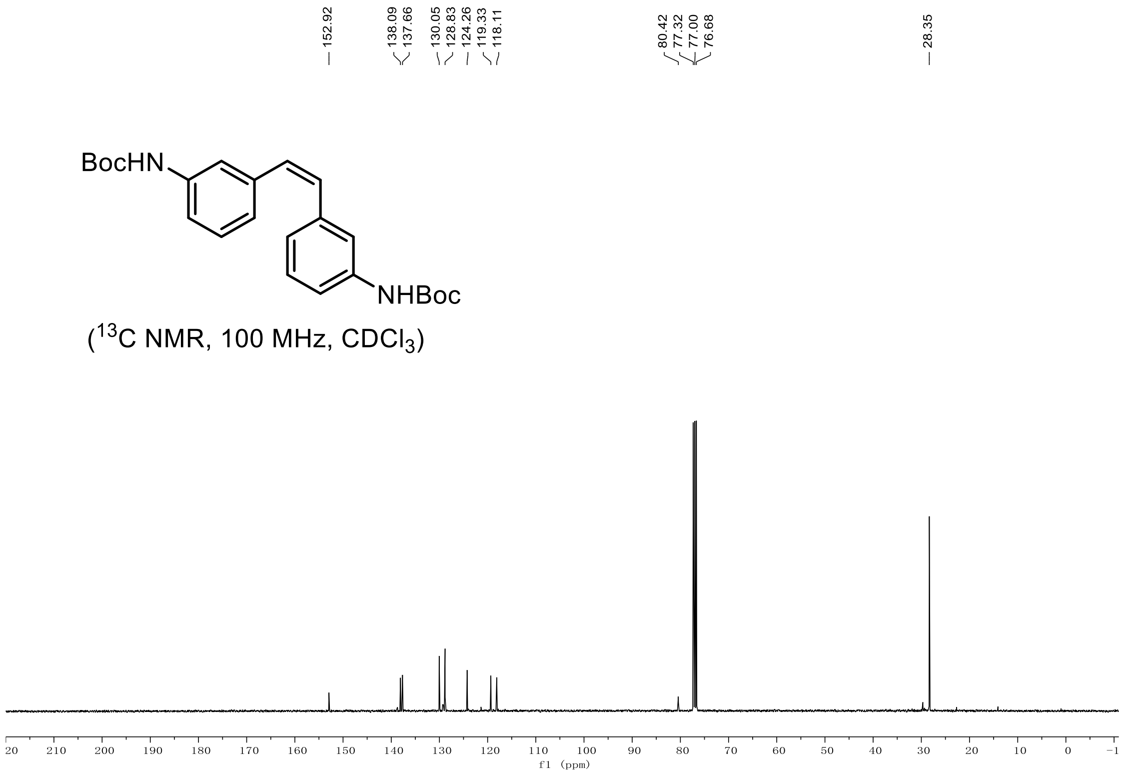

Figure S53. ^{13}C NMR of ***Z*-2i**

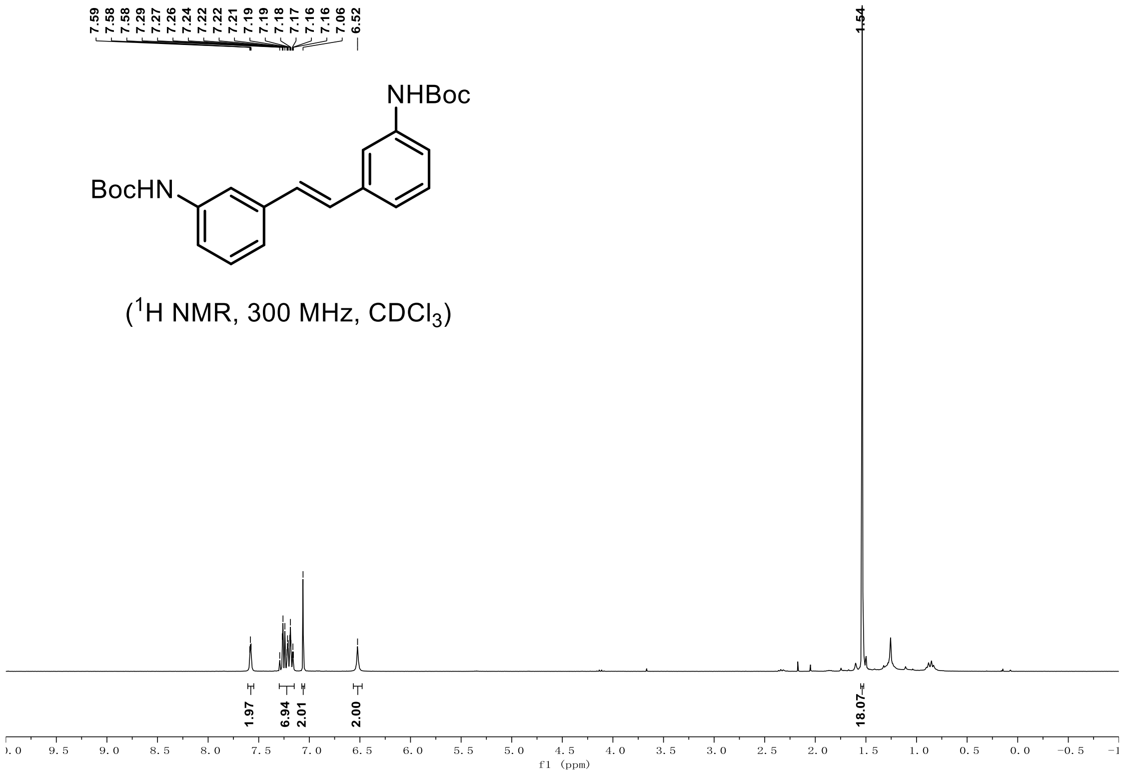

Figure S54. ^{1}H NMR of ***E*-2i**

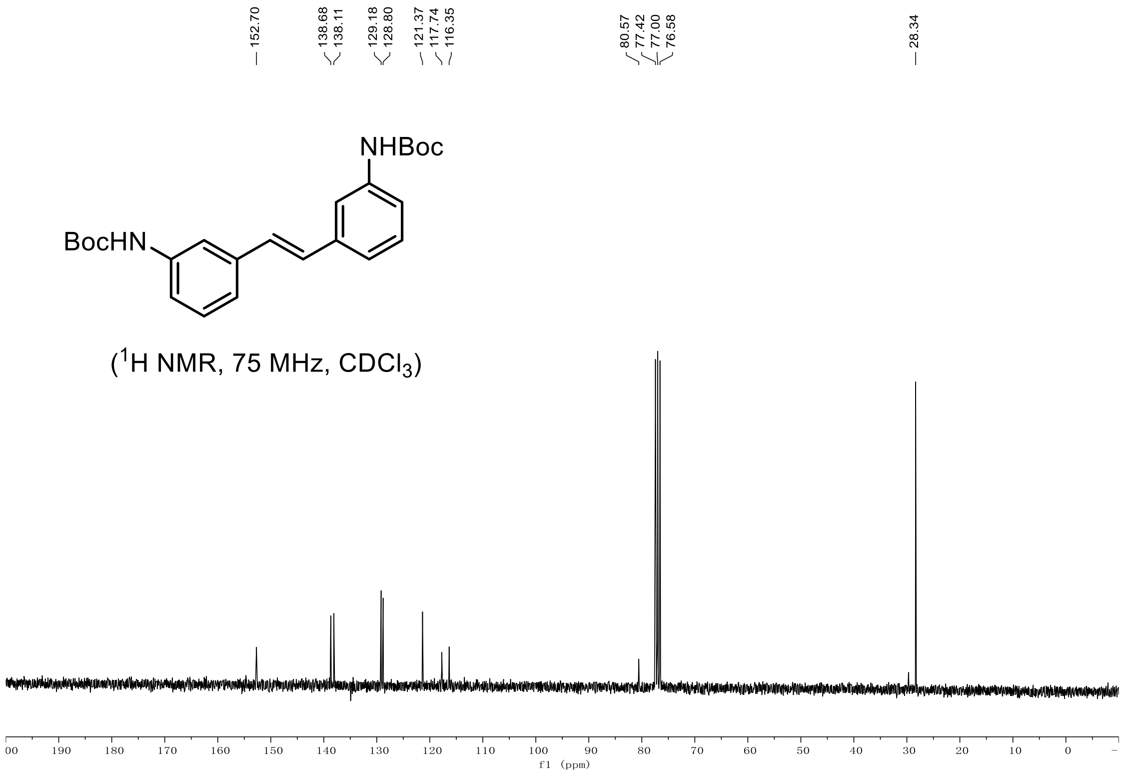

Figure S55. ^{13}C NMR of ***E*-2i**

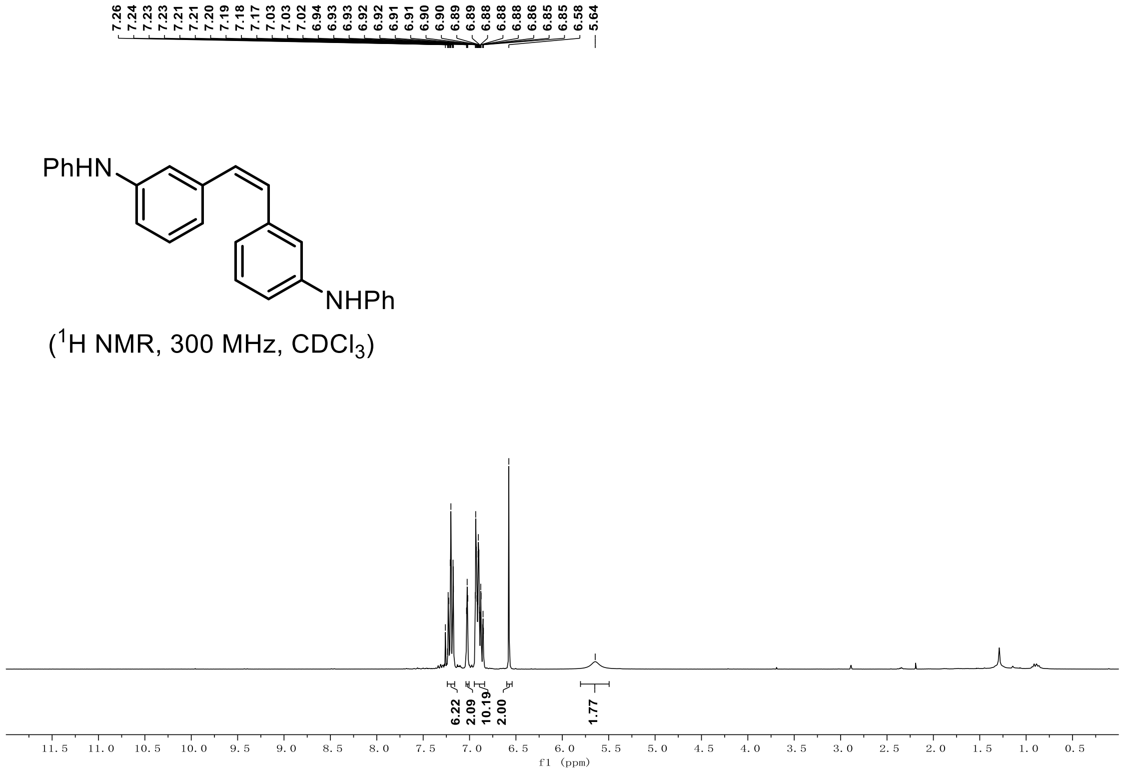

Figure S56. ^{1}H NMR of ***Z*-2j**

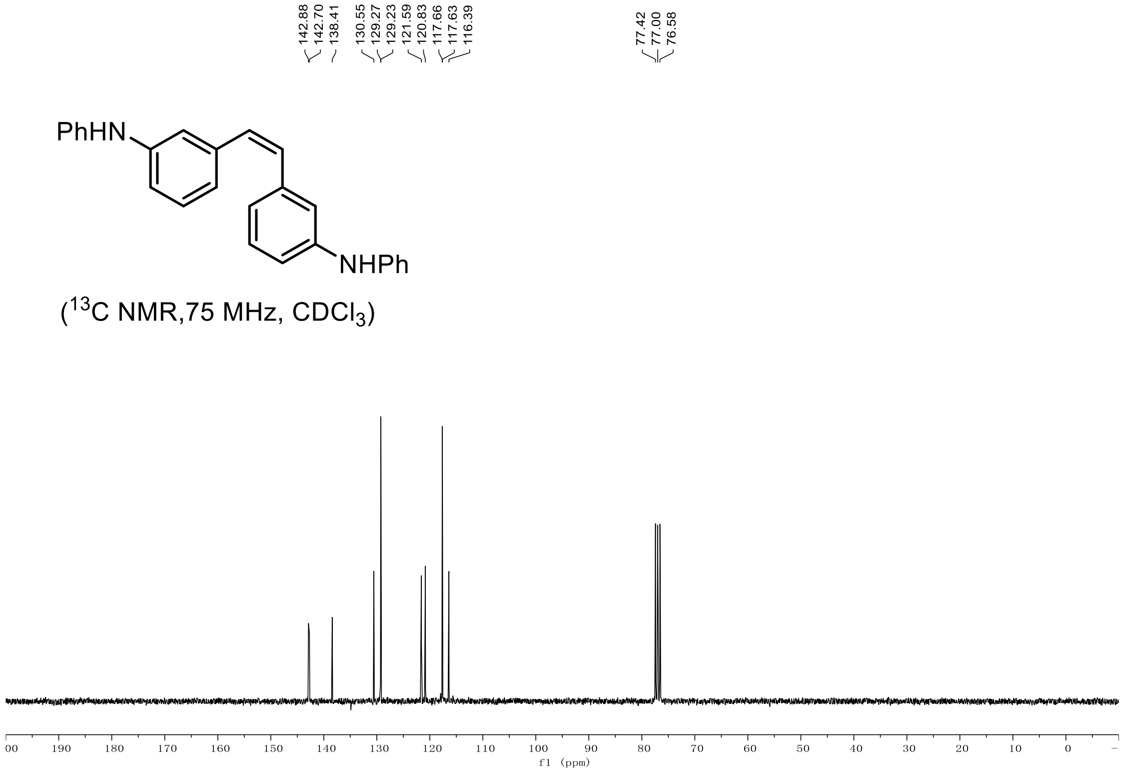

Figure S57. ^{13}C NMR of ***Z*-2j**

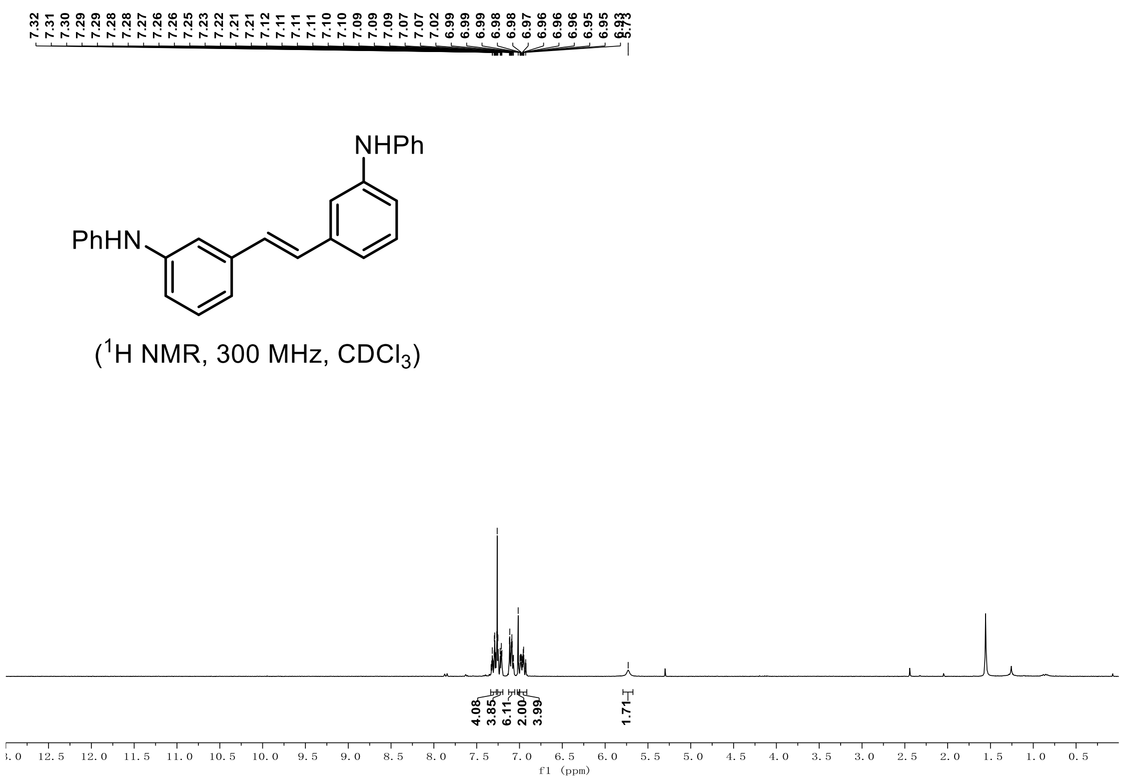

Figure S58. ^{1}H NMR of ***E*-2j**

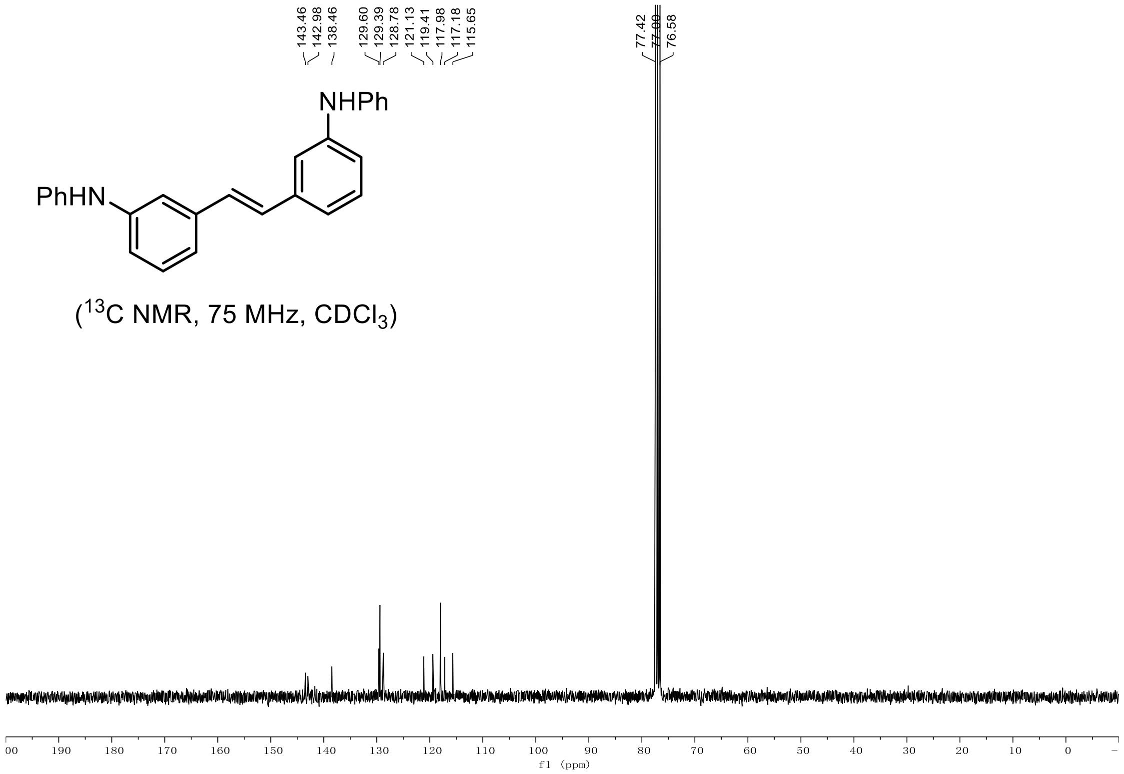

Figure S59. ^{13}C NMR of ***E*-2j**

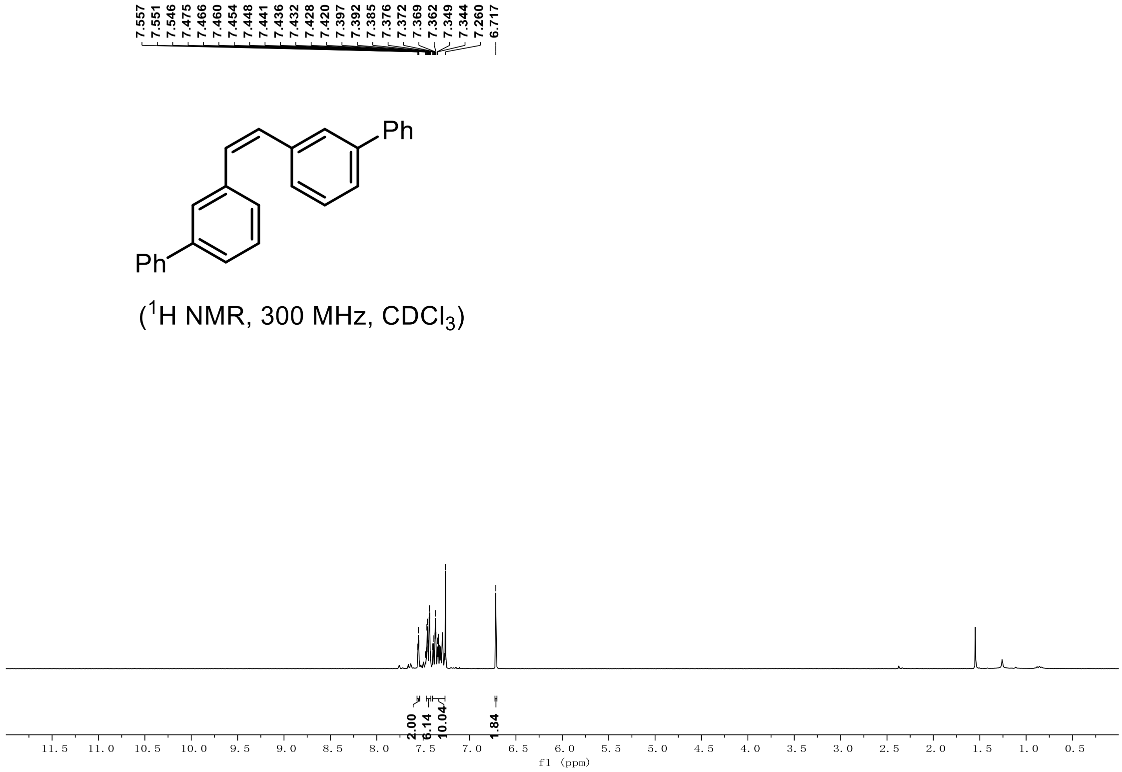

Figure S60. ^{1}H NMR of ***Z*-2k**

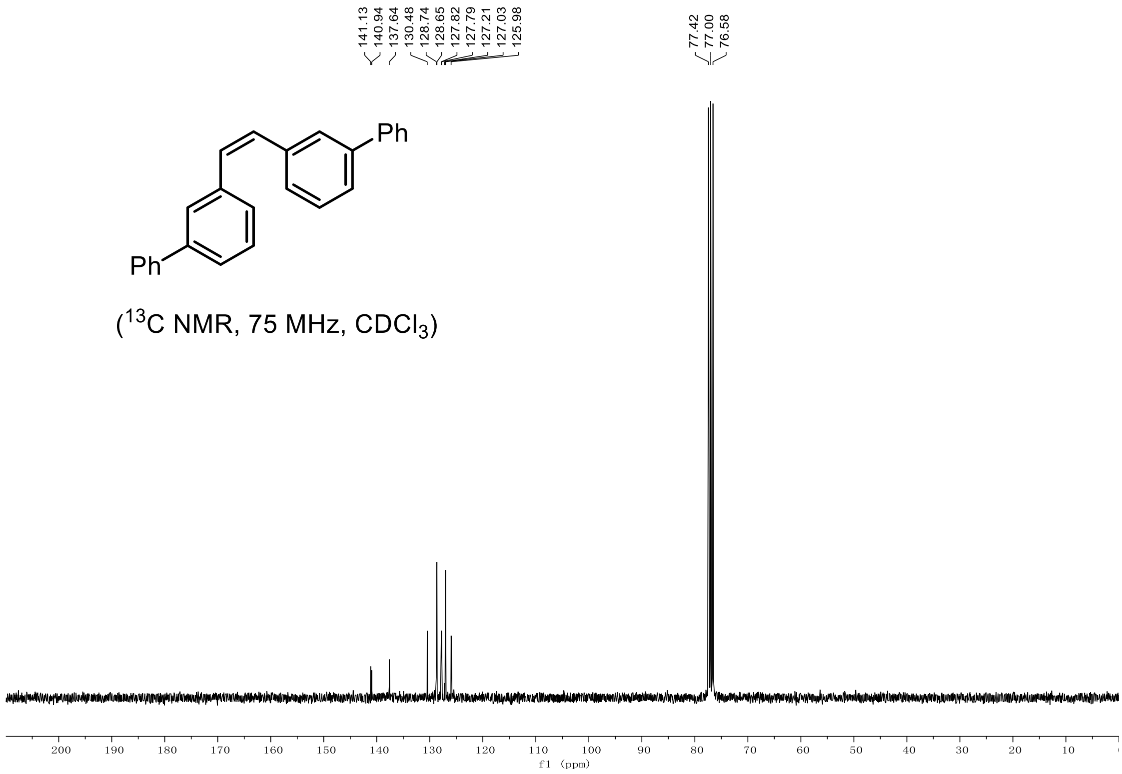

Figure S61. ^{13}C NMR of ***Z*-2k**

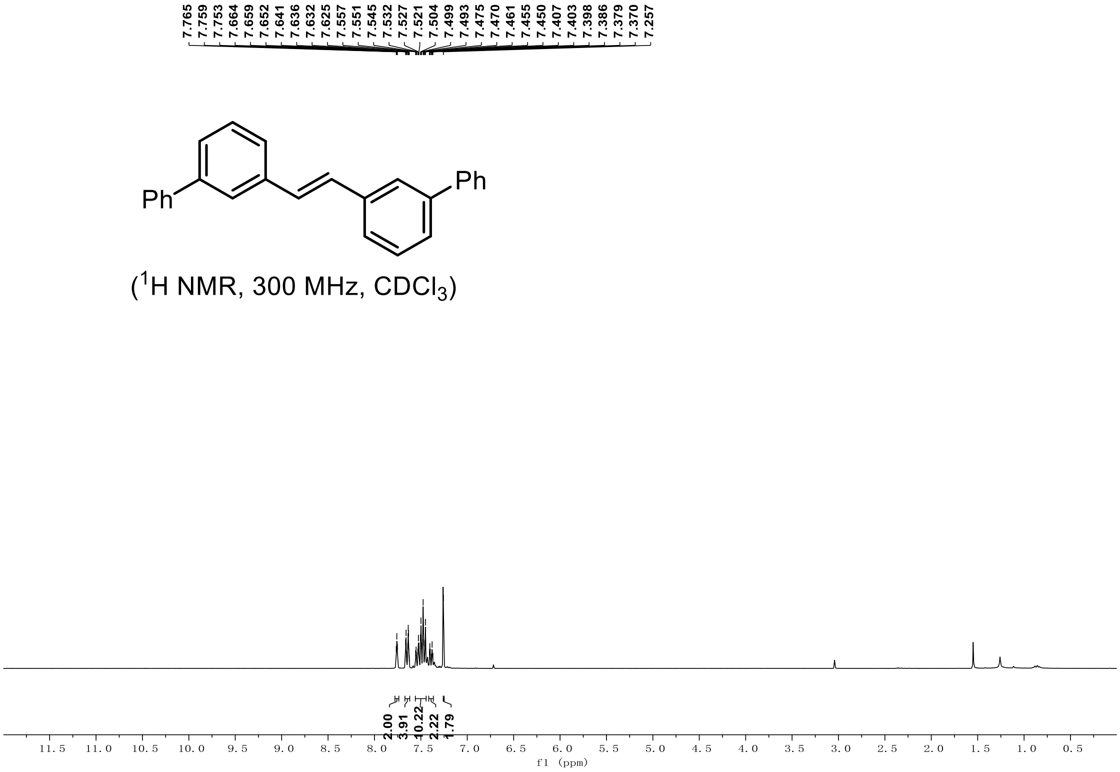

Figure S62. ^{1}H NMR of ***E*-2k**

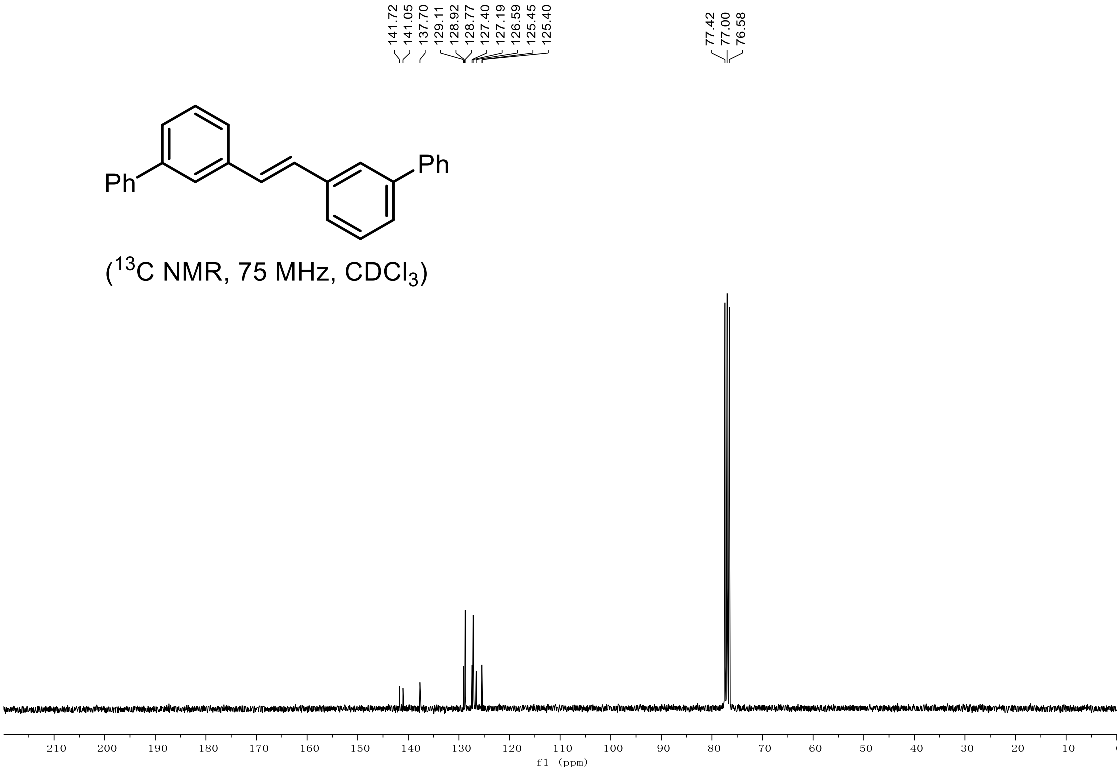

Figure S63. ^{13}C NMR of ***E*-2k**

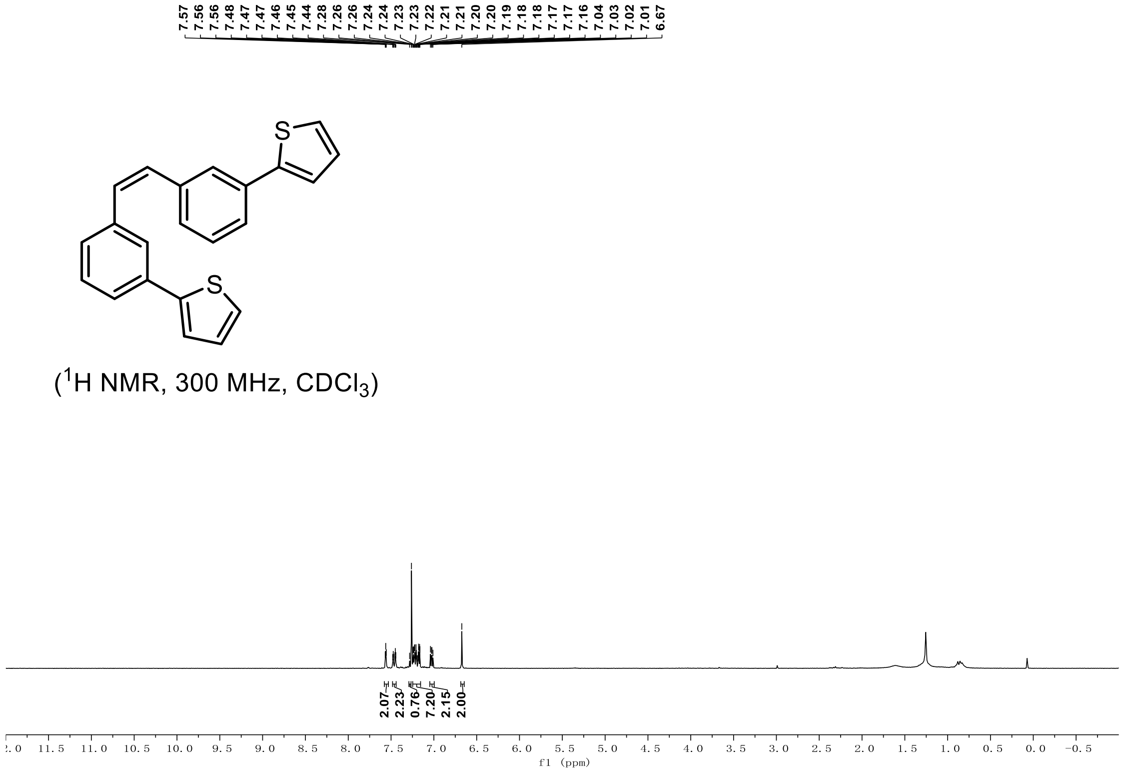

Figure S64. ^{1}H NMR of ***Z*-2l**

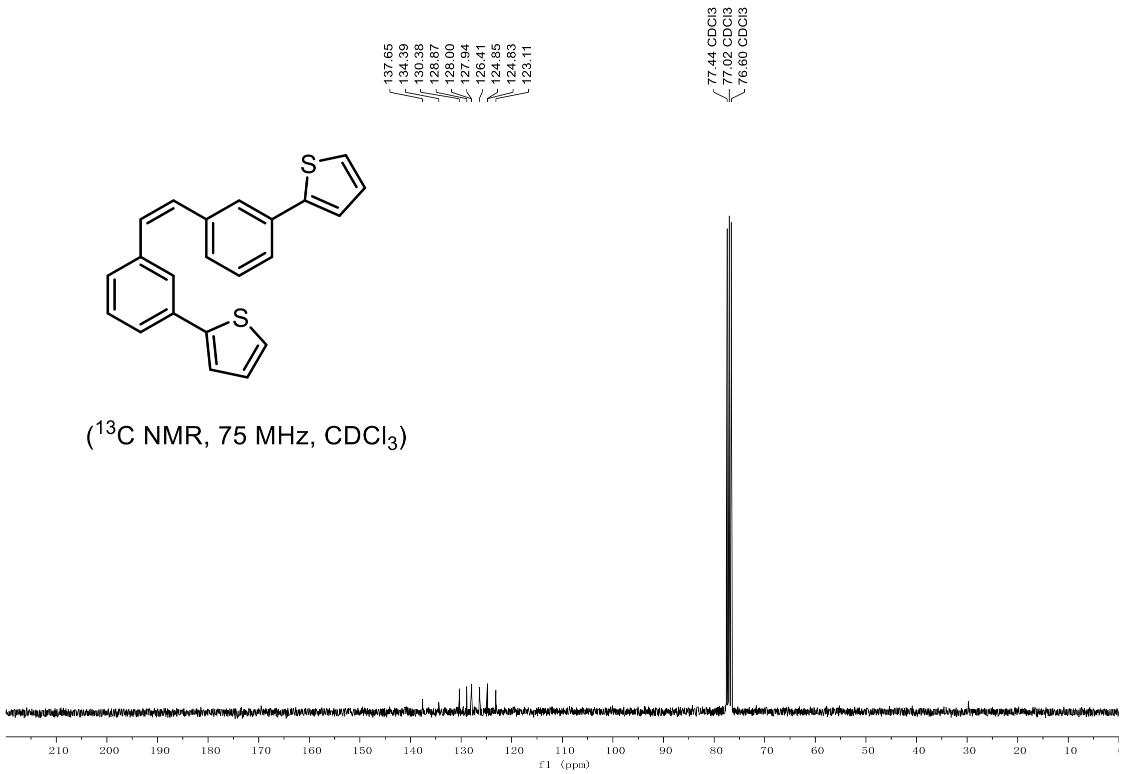

Figure S65. ^{13}C NMR of ***Z*-2l**

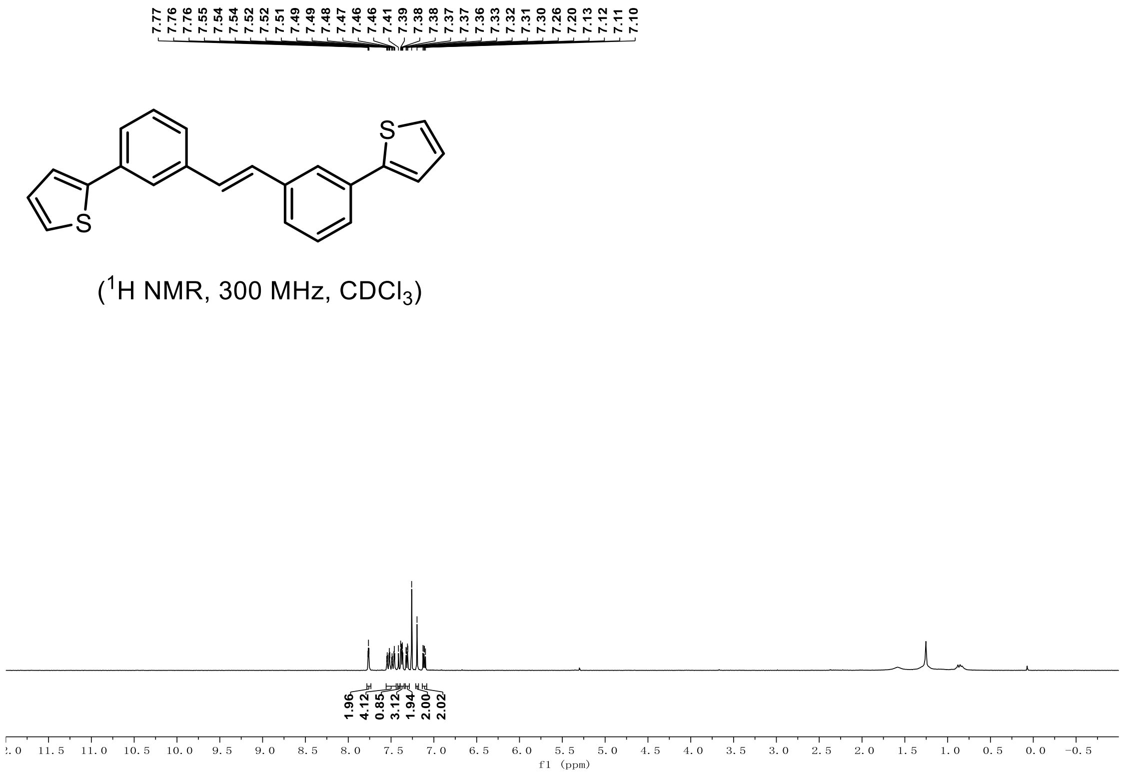

Figure S66. ^{1}H NMR of ***E*-2l**

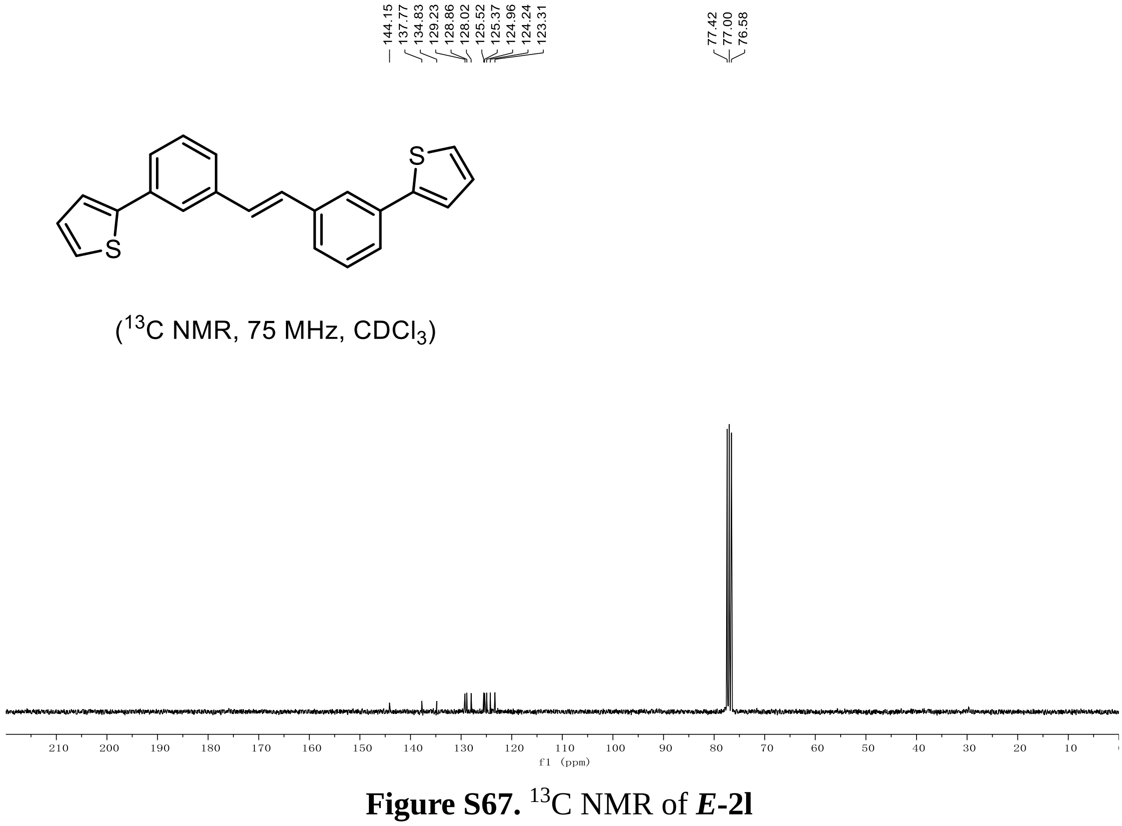

Figure S67. ^{13}C NMR of ***E*-2l**

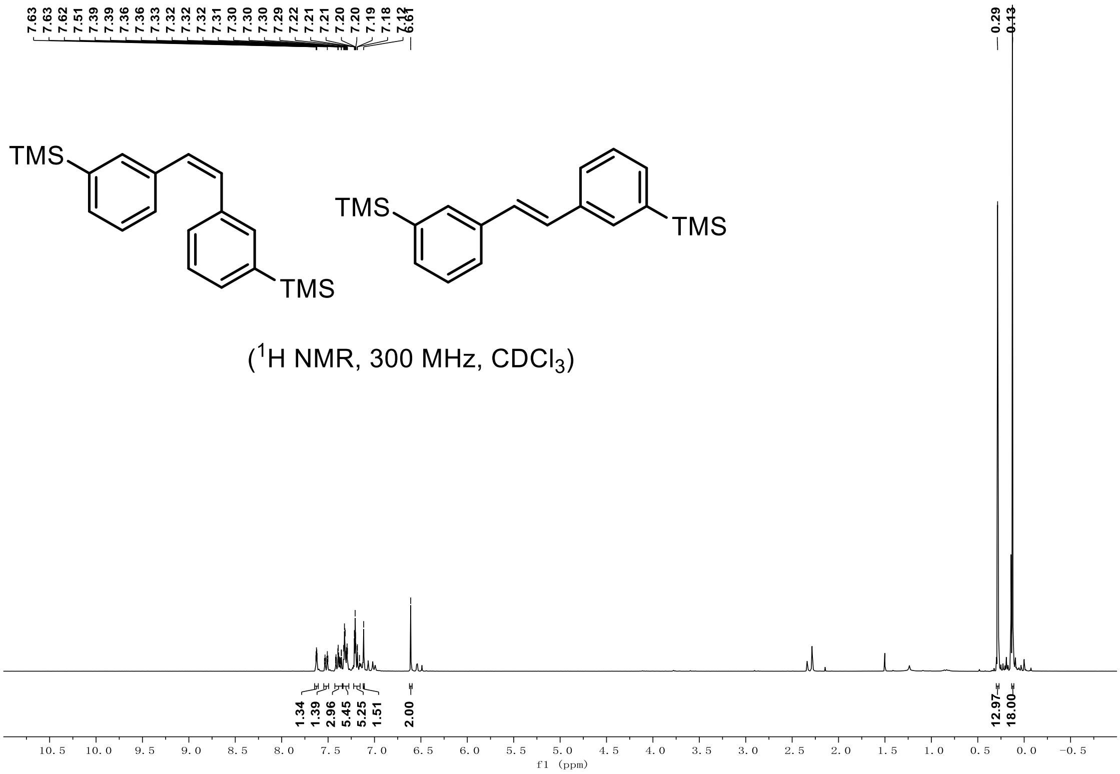

Figure S68. ^{1}H NMR of ***Z*-2m** and ***E*-2m**

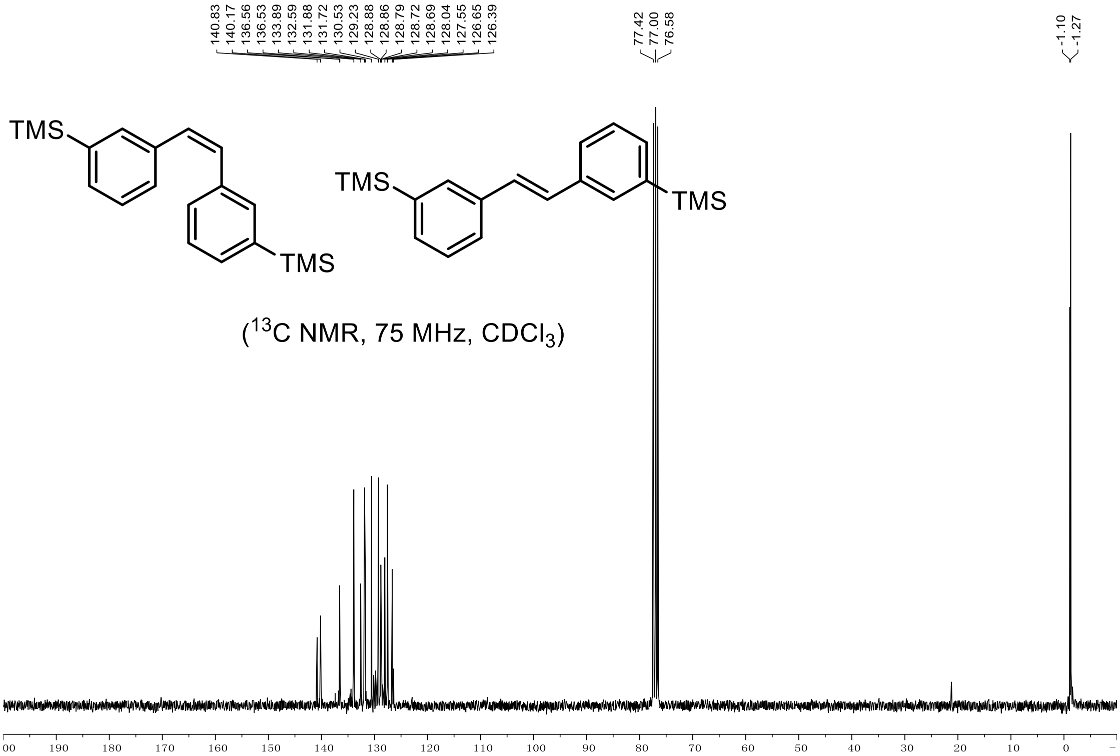

Figure S69 . ^{13}C NMR of ***Z*-2m** and ***E*-2m**

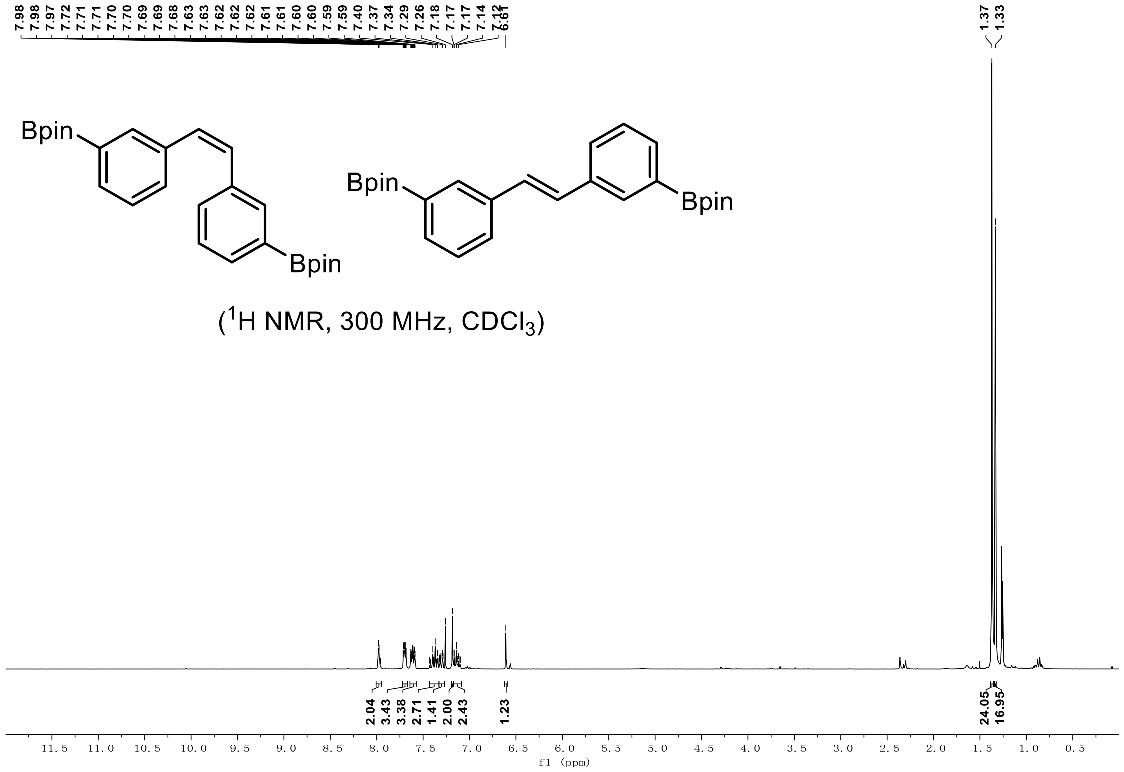

Figure S70. ^{1}H NMR of ***Z*-2n** and ***E*-2n**

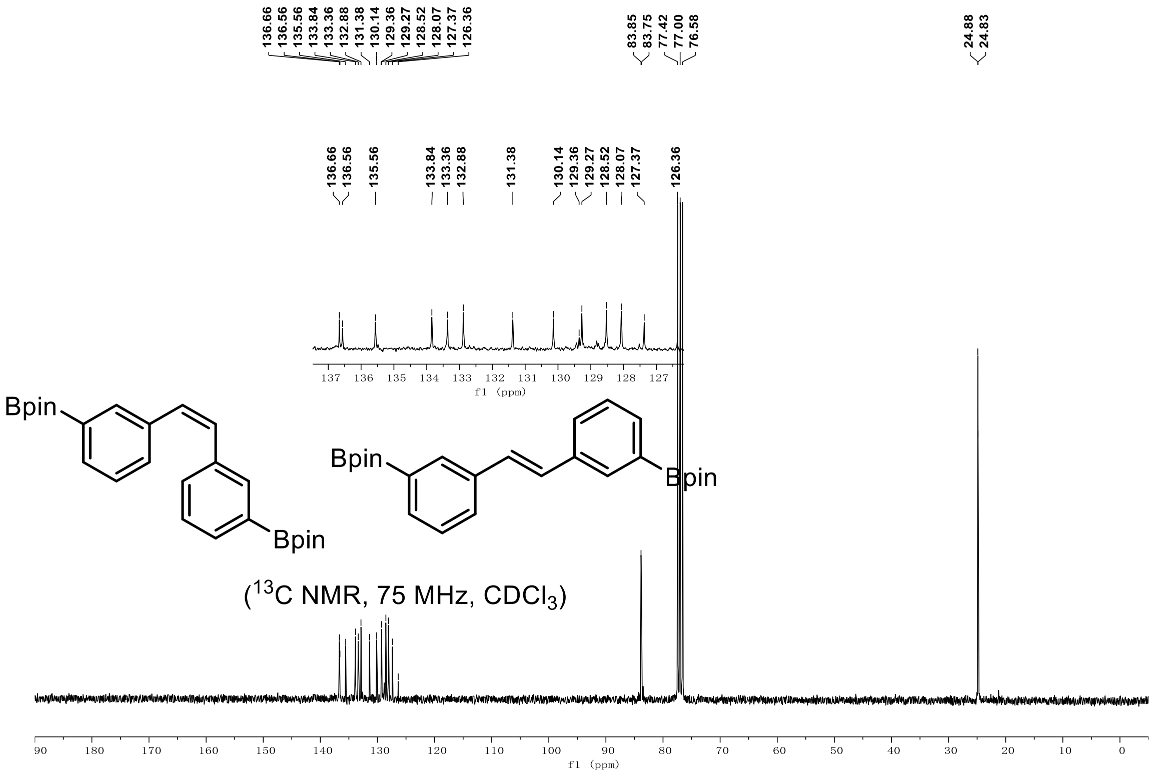

Figure S71. ^{13}C NMR of ***Z*-2n** and ***E*-2n**

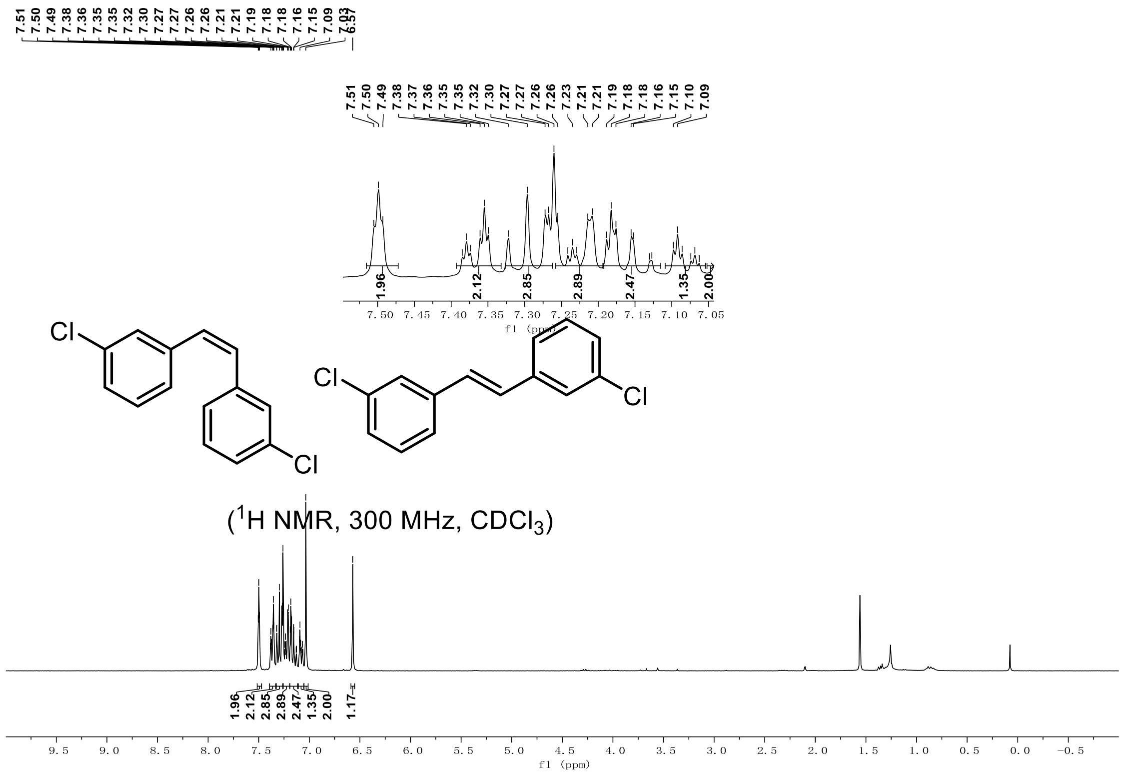

Figure S72. ^{1}H NMR of ***Z*-2o** and ***E*-2o**

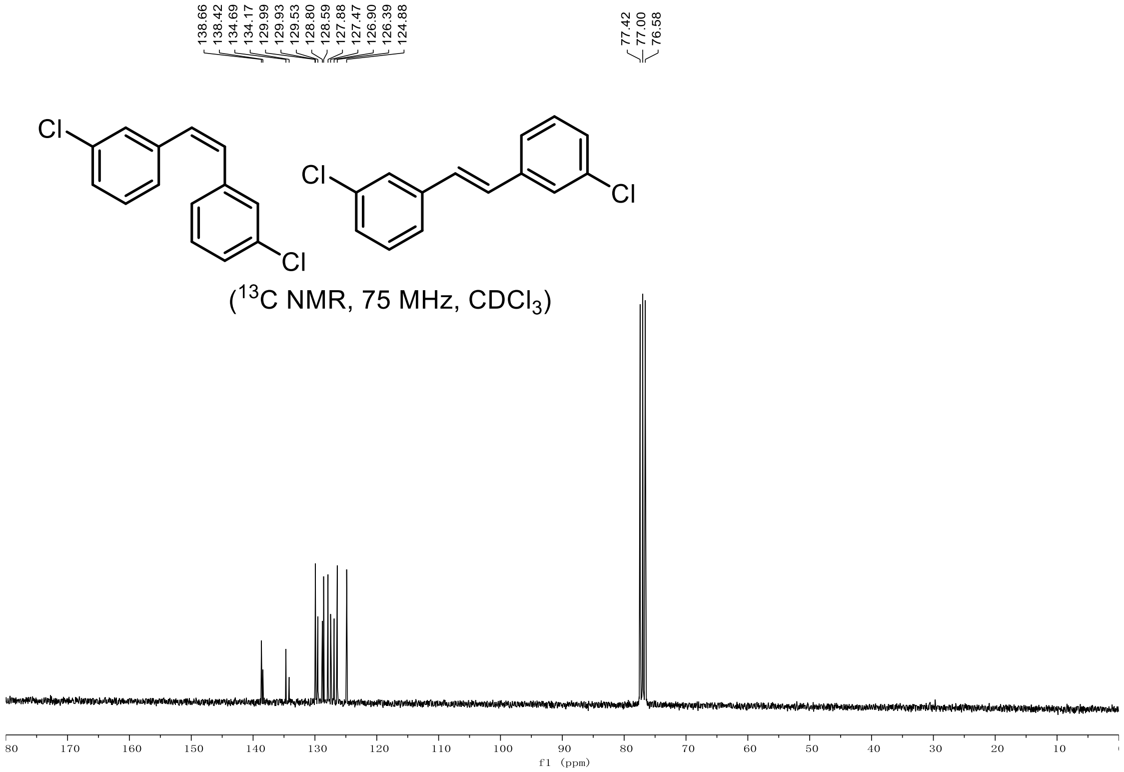

Figure S73. ^{13}C NMR of ***Z*-2o** and ***E*-2o**

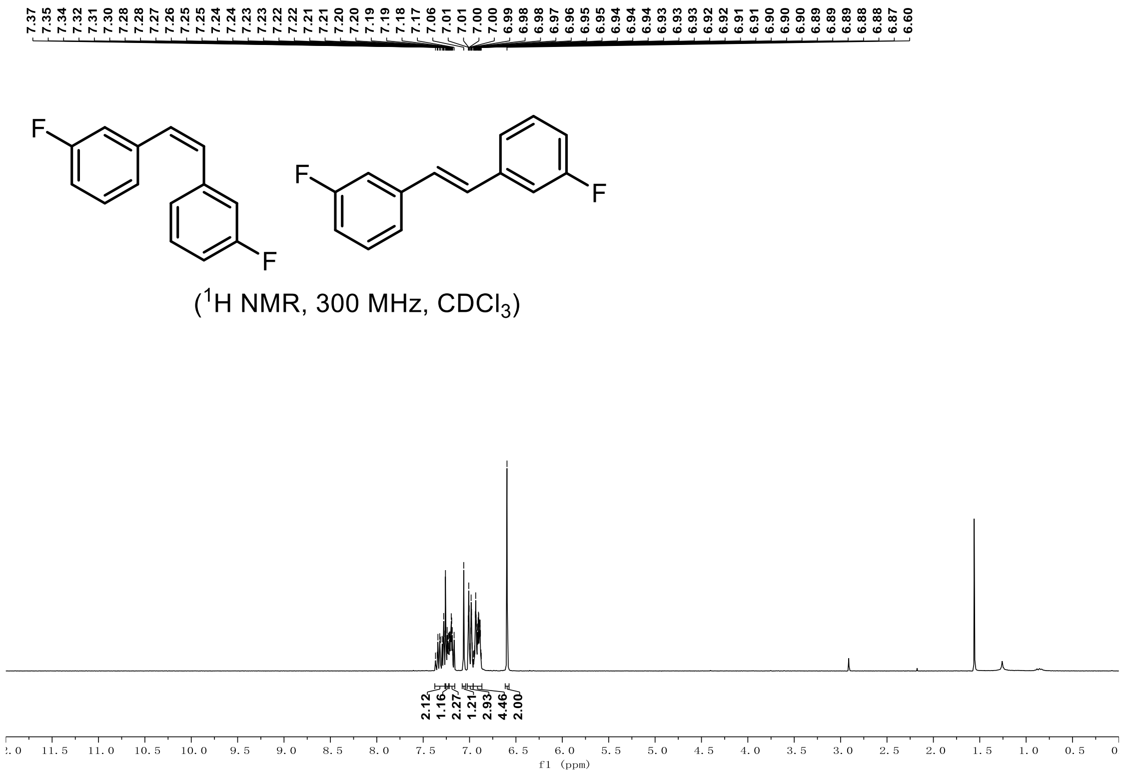

Figure S74. ^{1}H NMR of ***Z*-2p** and ***E*-2p**

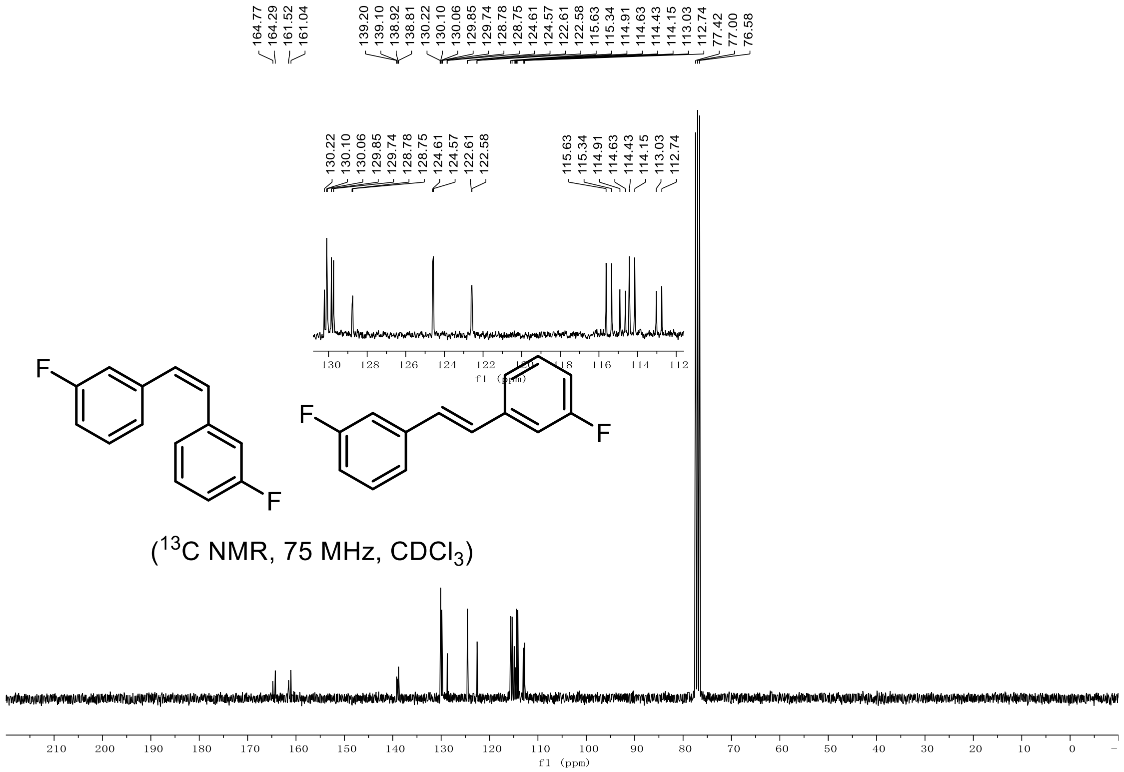

Figure S75. ^{13}C NMR of ***Z*-2p** and ***E*-2p**

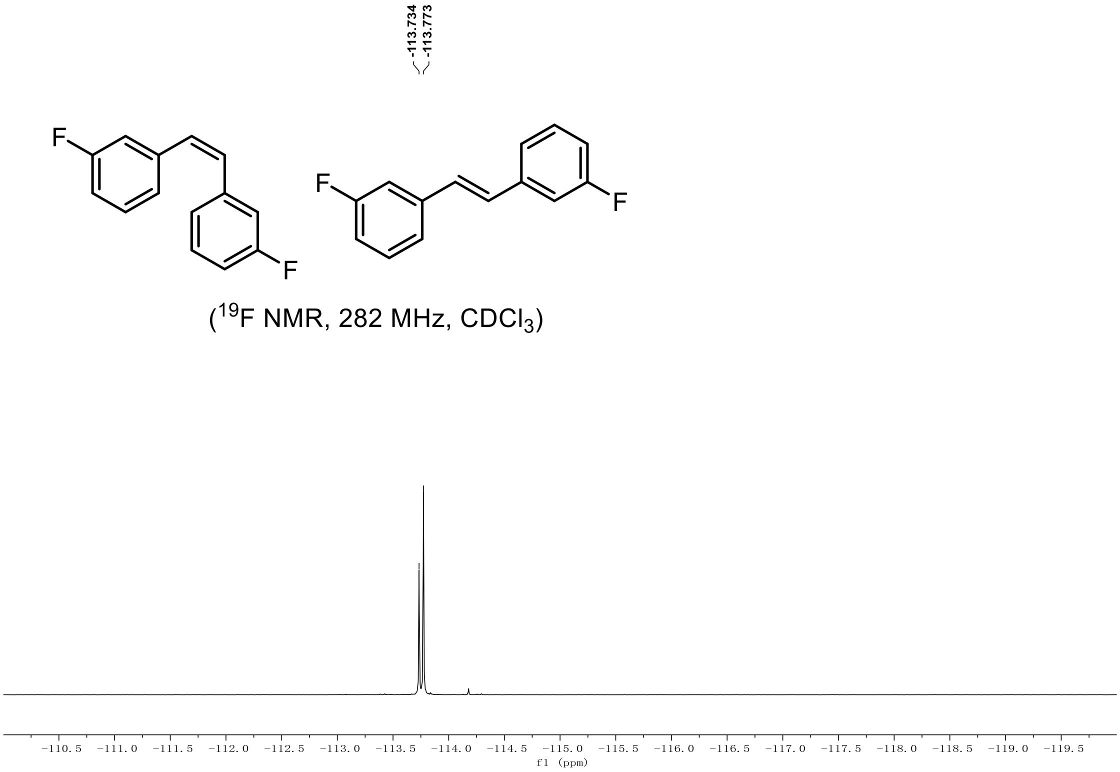

Figure S76. ^{19}F NMR of ***Z*-2p** and ***E*-2p**

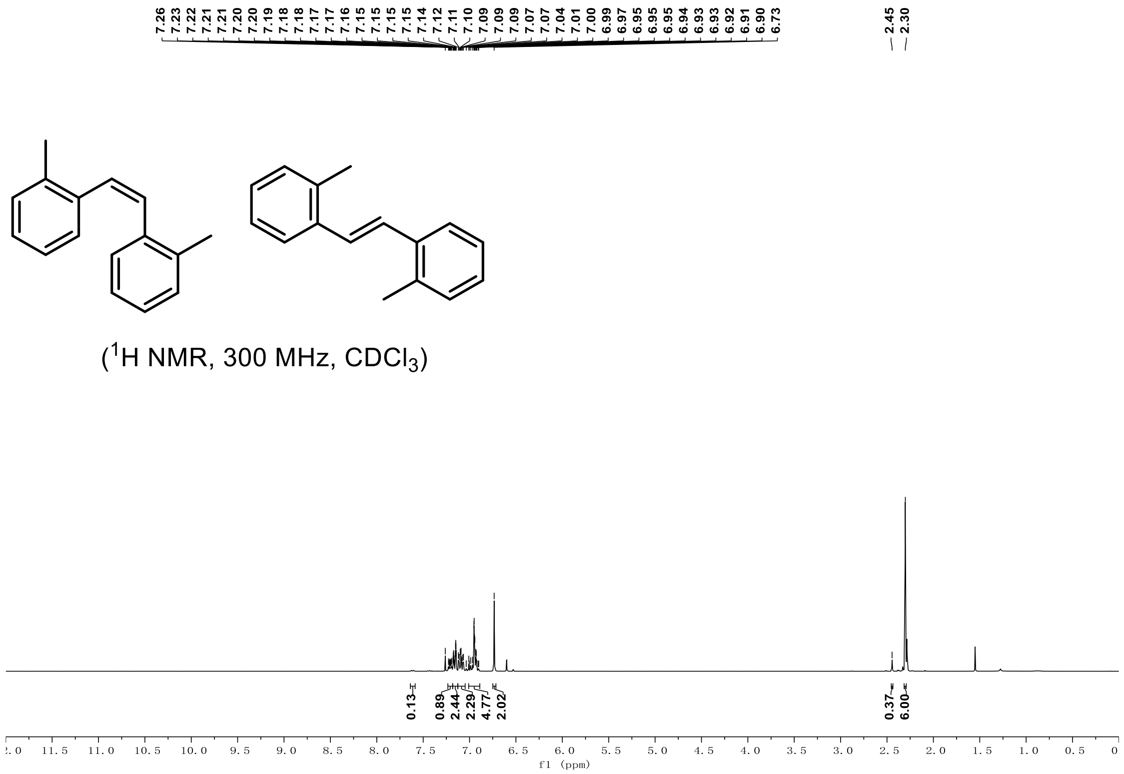

Figure S77. ^{1}H NMR of ***Z*-2q** and ***E*-2q**

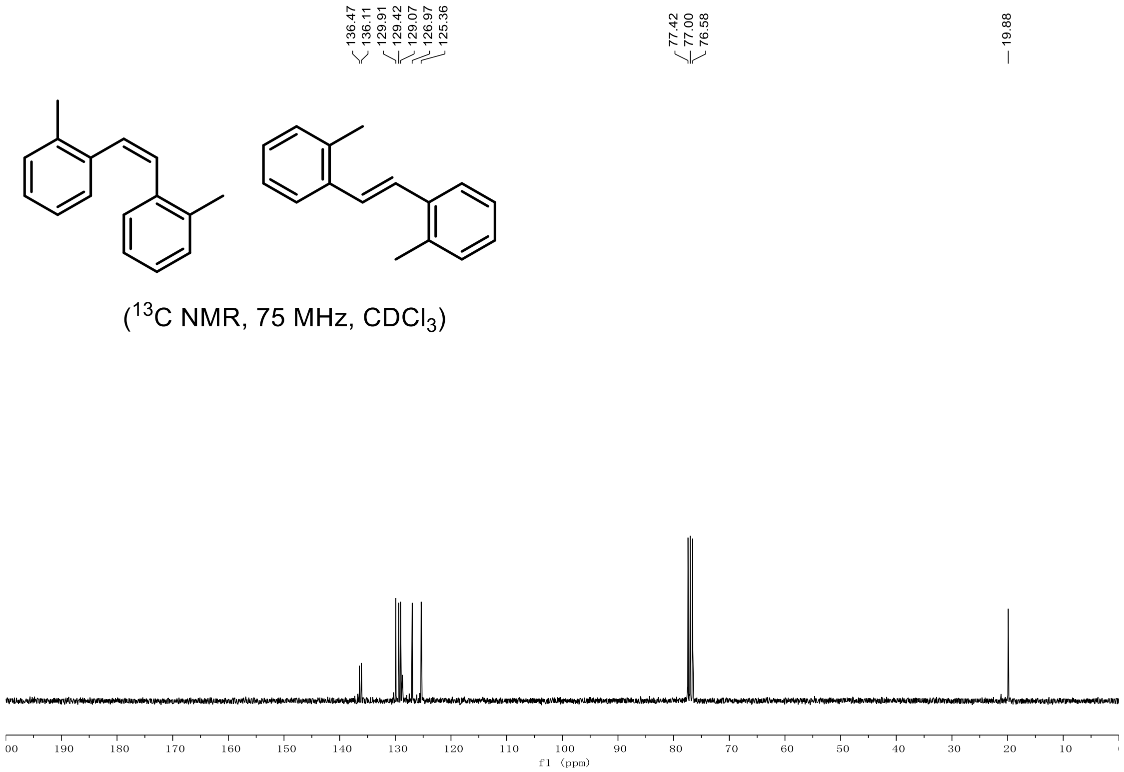

Figure S78. ^{13}C NMR of ***Z*-2q** and ***E*-2q**

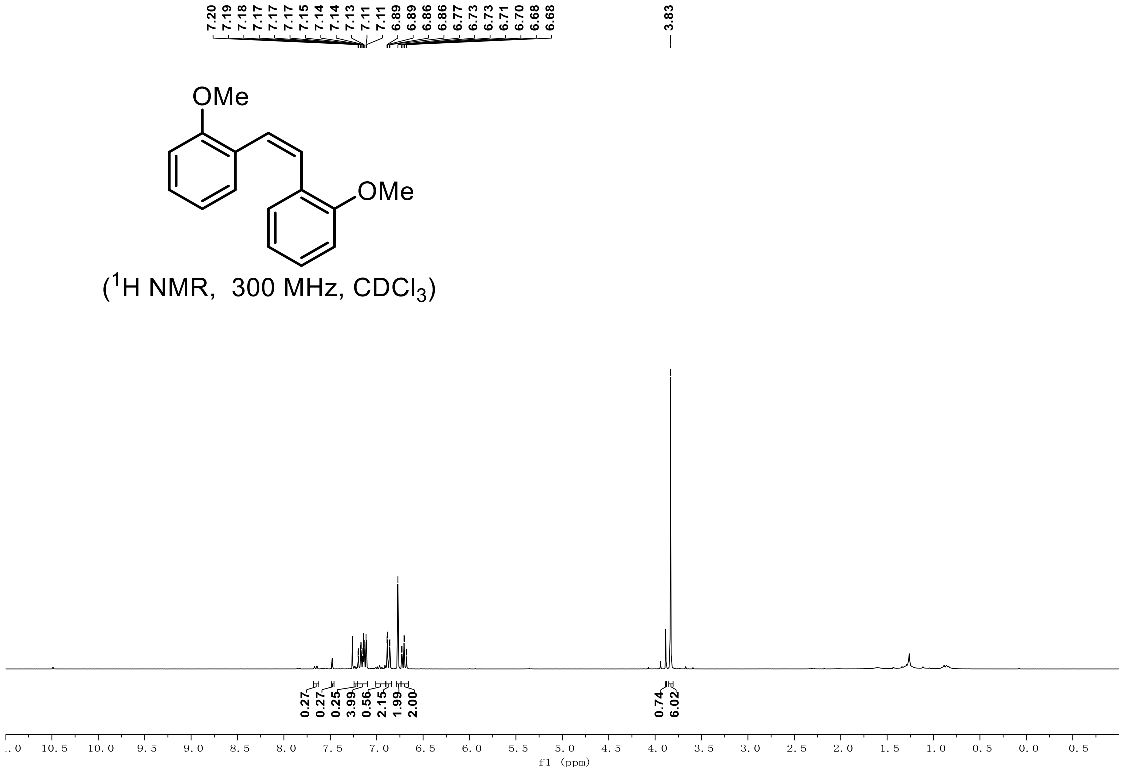

Figure S79. ^{1}H NMR of ***Z*-2r** and ***E*-2r**

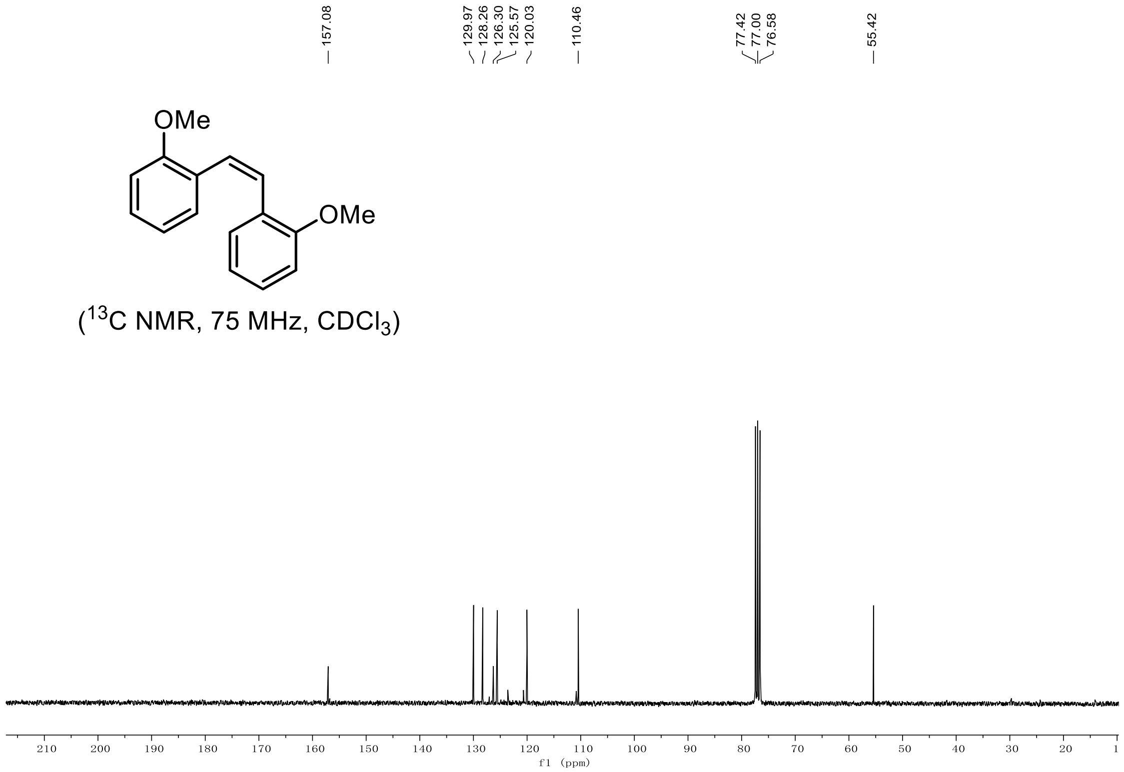

Figure S80. ^{13}C NMR of ***Z*-2r** and ***E*-2r**

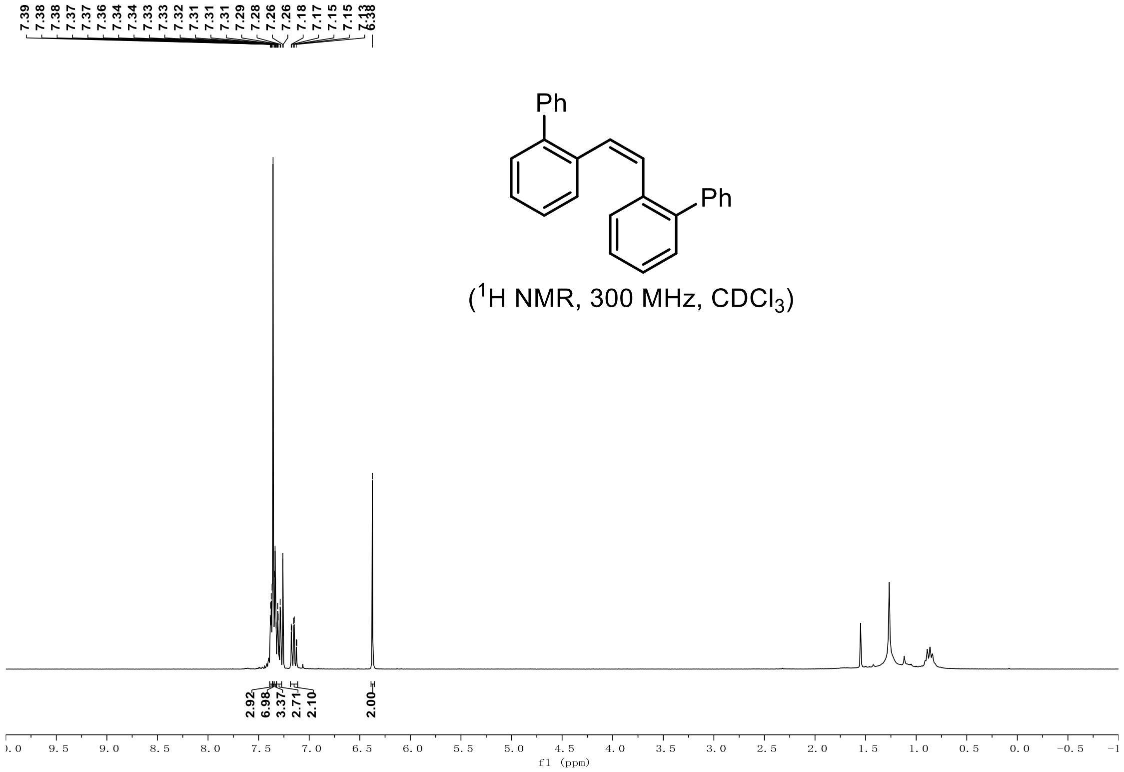

Figure S81. ^{1}H NMR of ***Z*-2s**

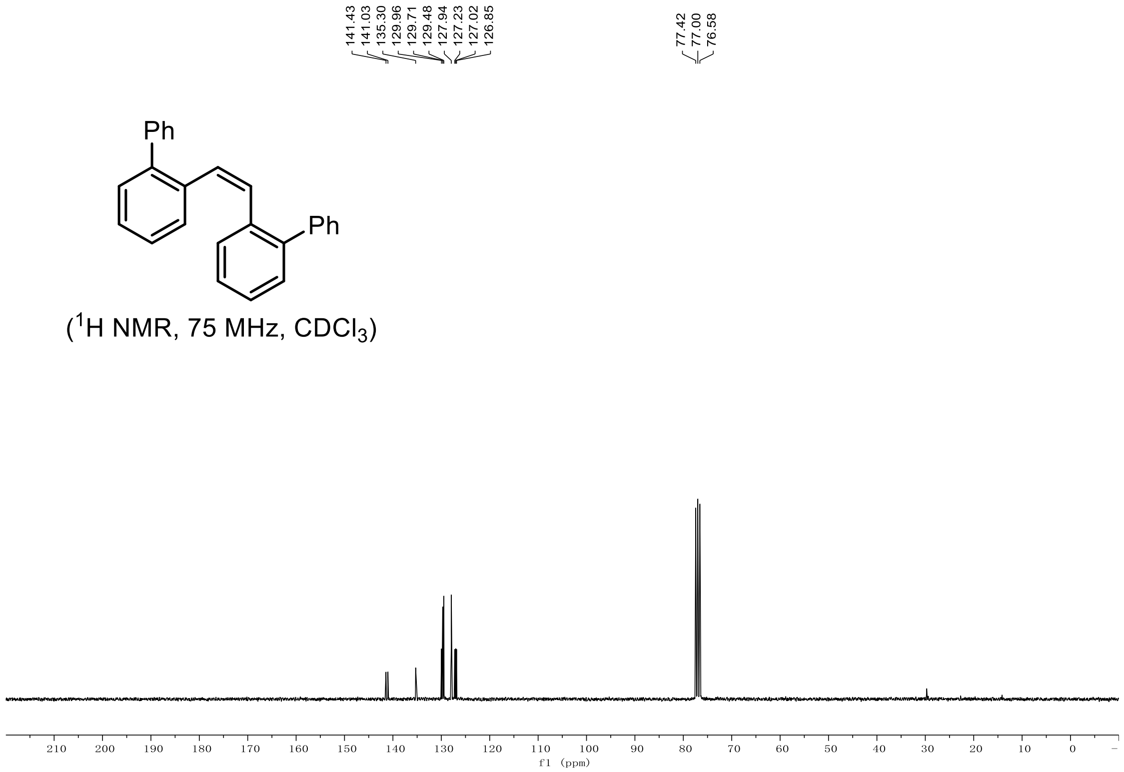

Figure S82. ^{13}C NMR of ***Z*-2s**

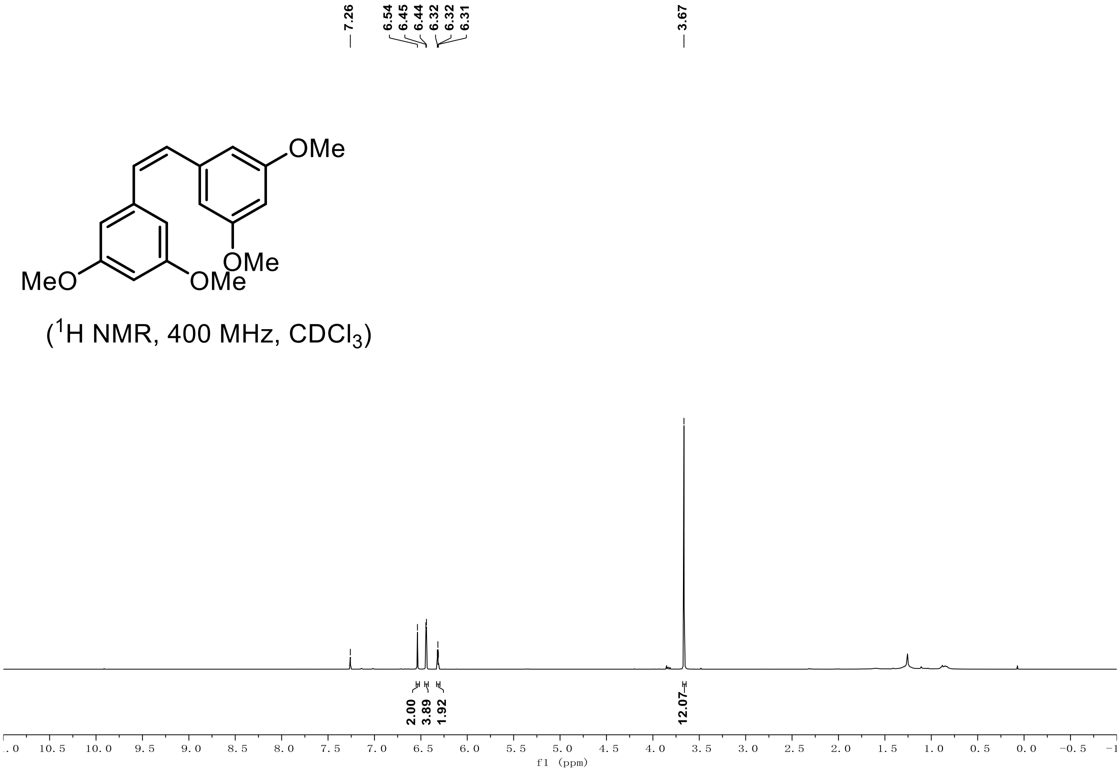

Figure S83. ^{1}H NMR of ***Z*-2t**

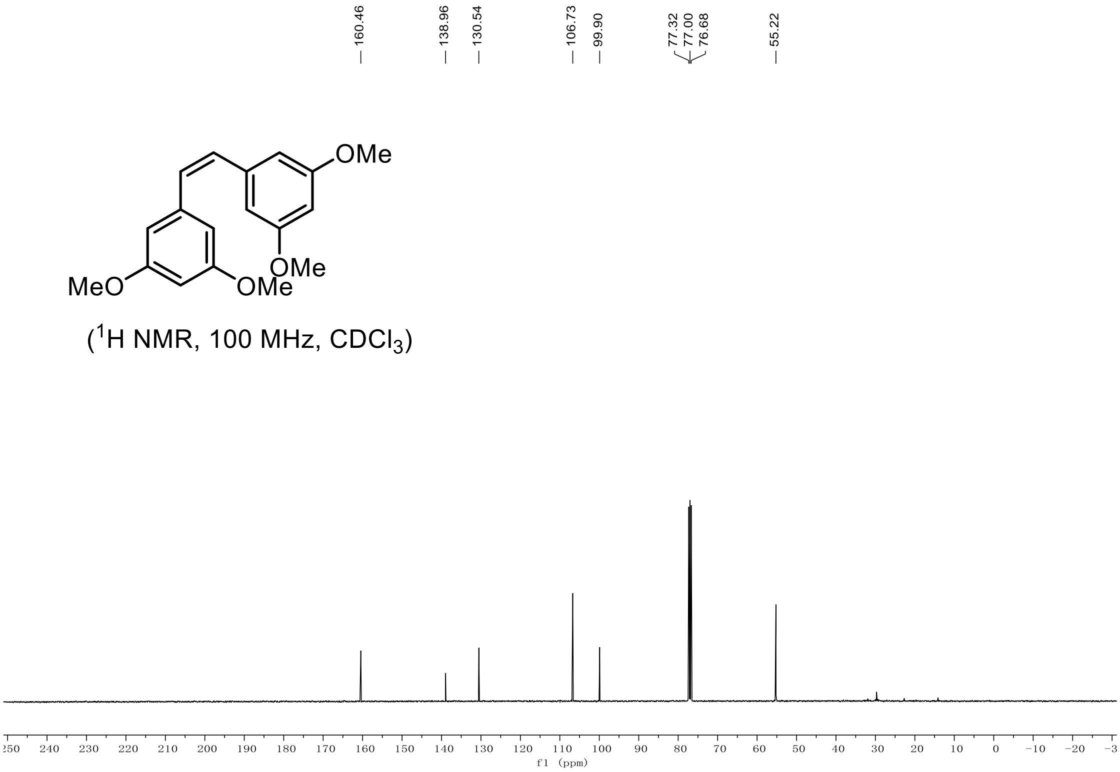

Figure S84. ^{13}C NMR of ***Z*-2t**

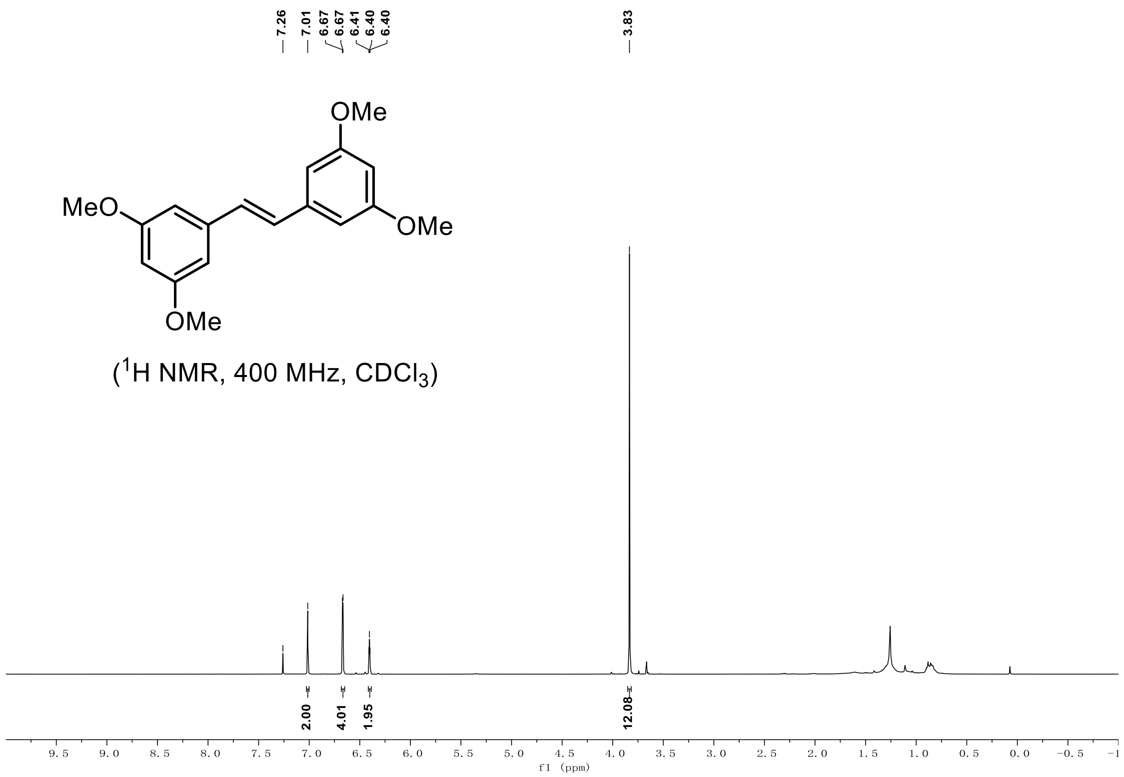

Figure S85. ^{1}H NMR of ***E*-2t**

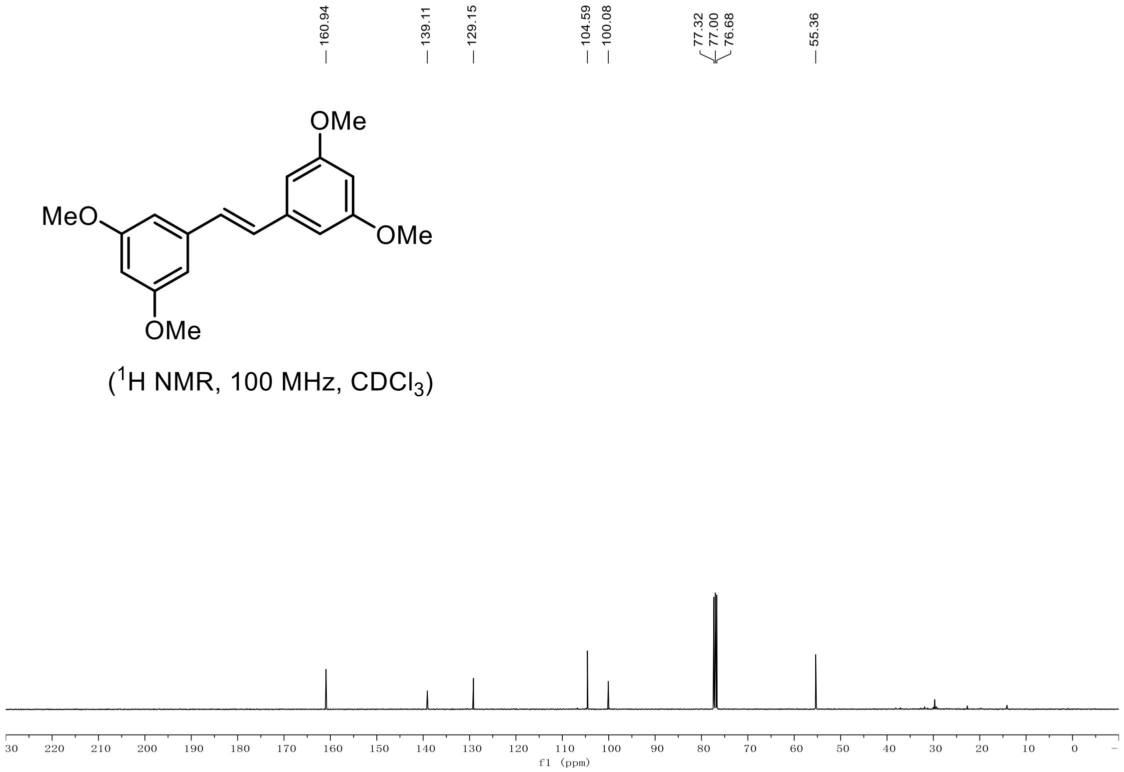

Figure S86. ^{13}C NMR of ***E*-2t**

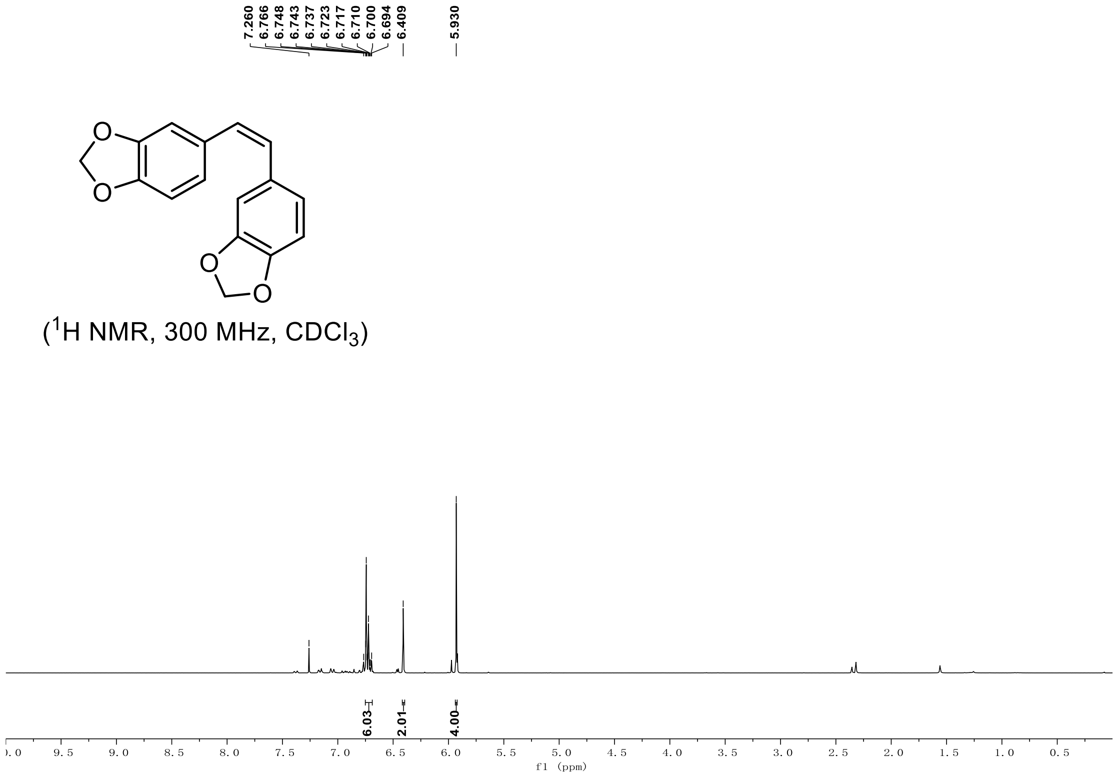

Figure S87. ^{1}H NMR of ***Z*-2u**

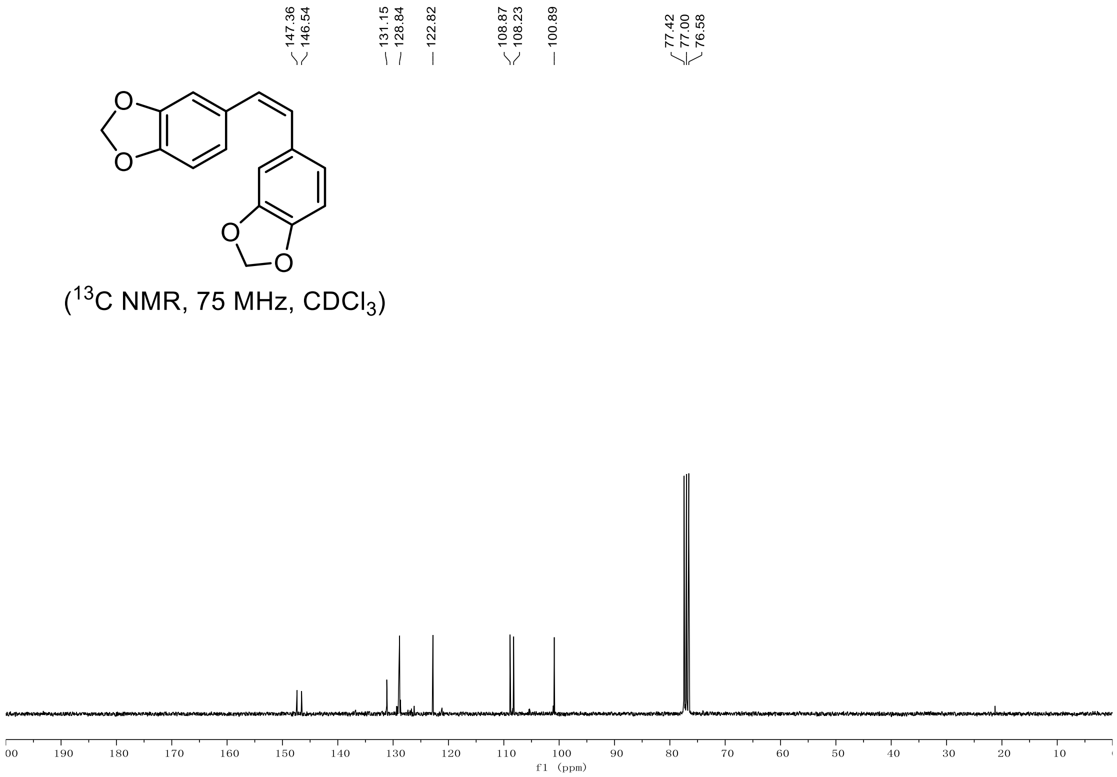

Figure S88. ^{13}C NMR of ***Z*-2u**

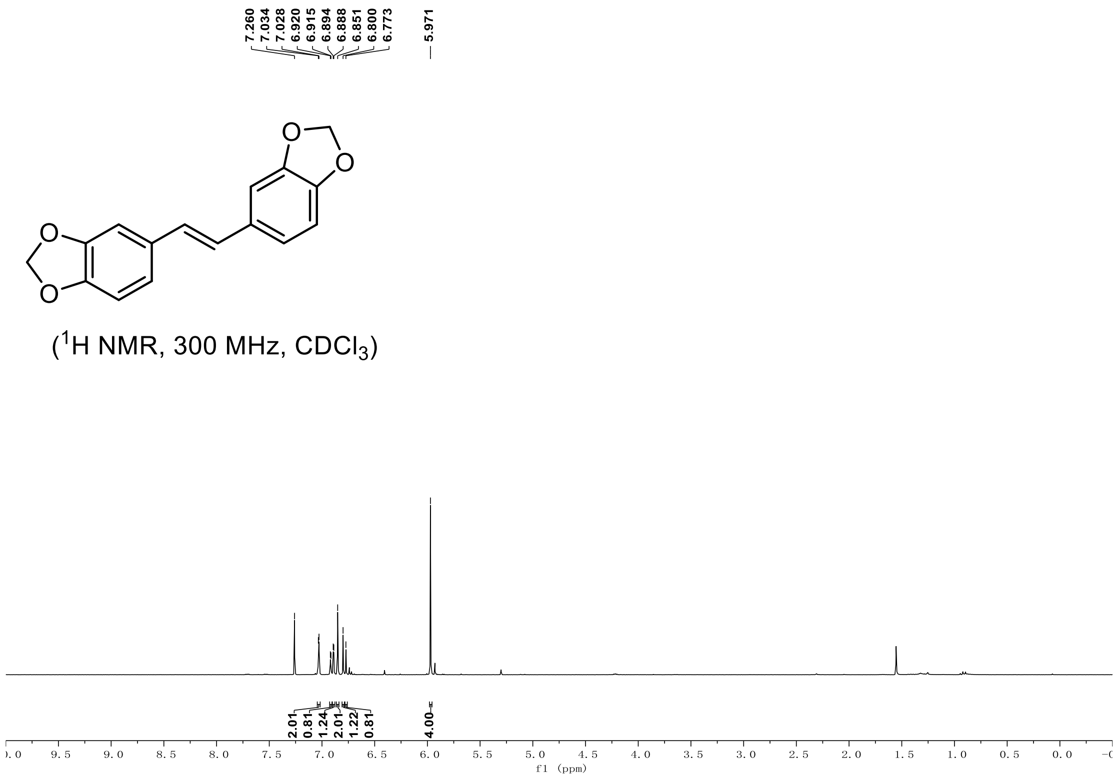

Figure S89. ^{1}H NMR of ***E*-2u**

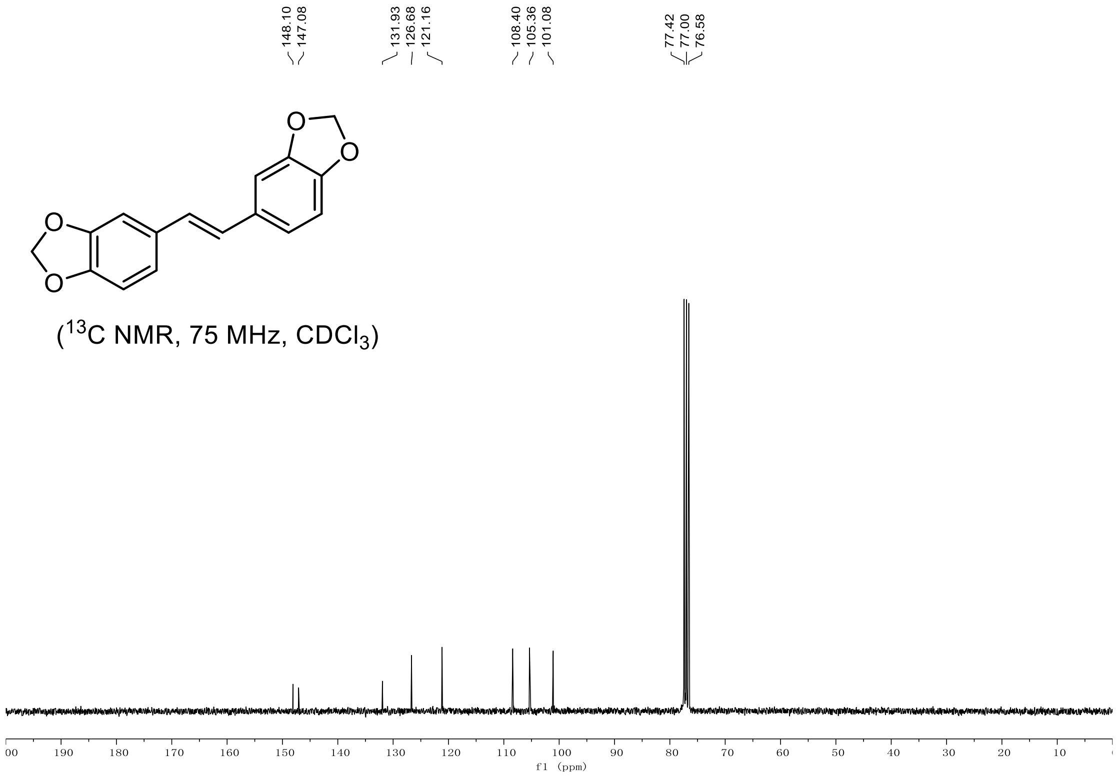

Figure S90. ^{13}C NMR of ***E*-2u**

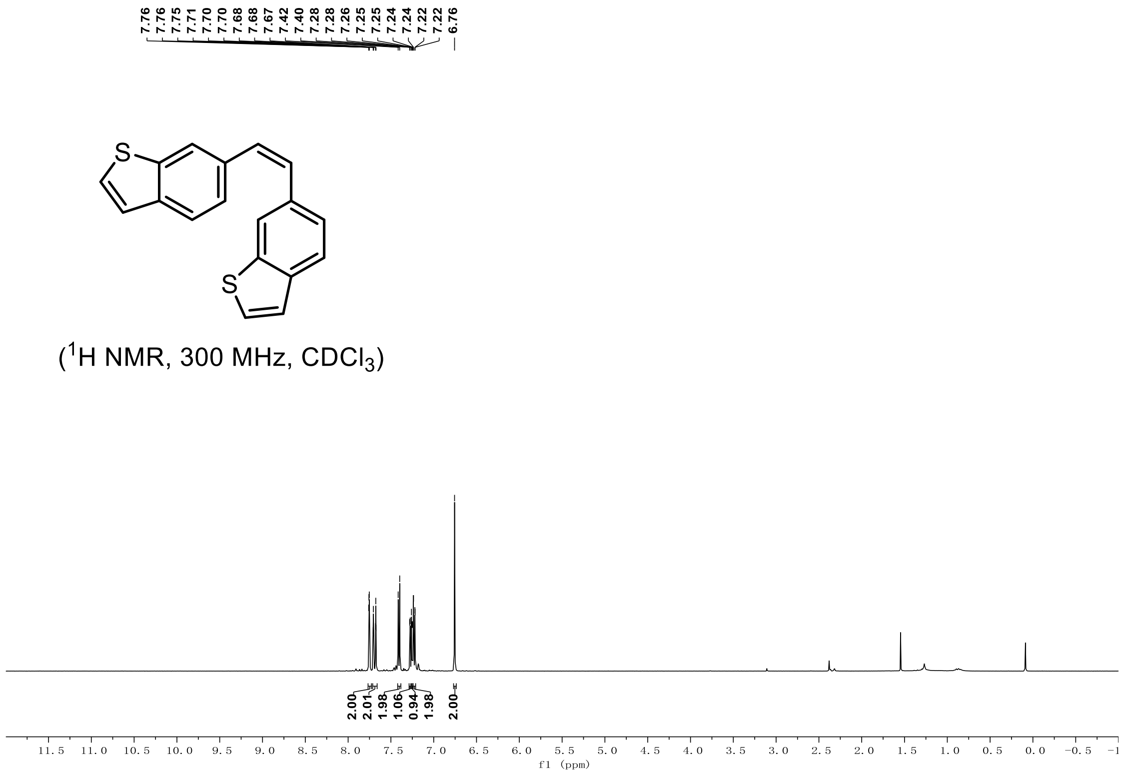

Figure S91. ^{1}H NMR of ***Z*-2v**

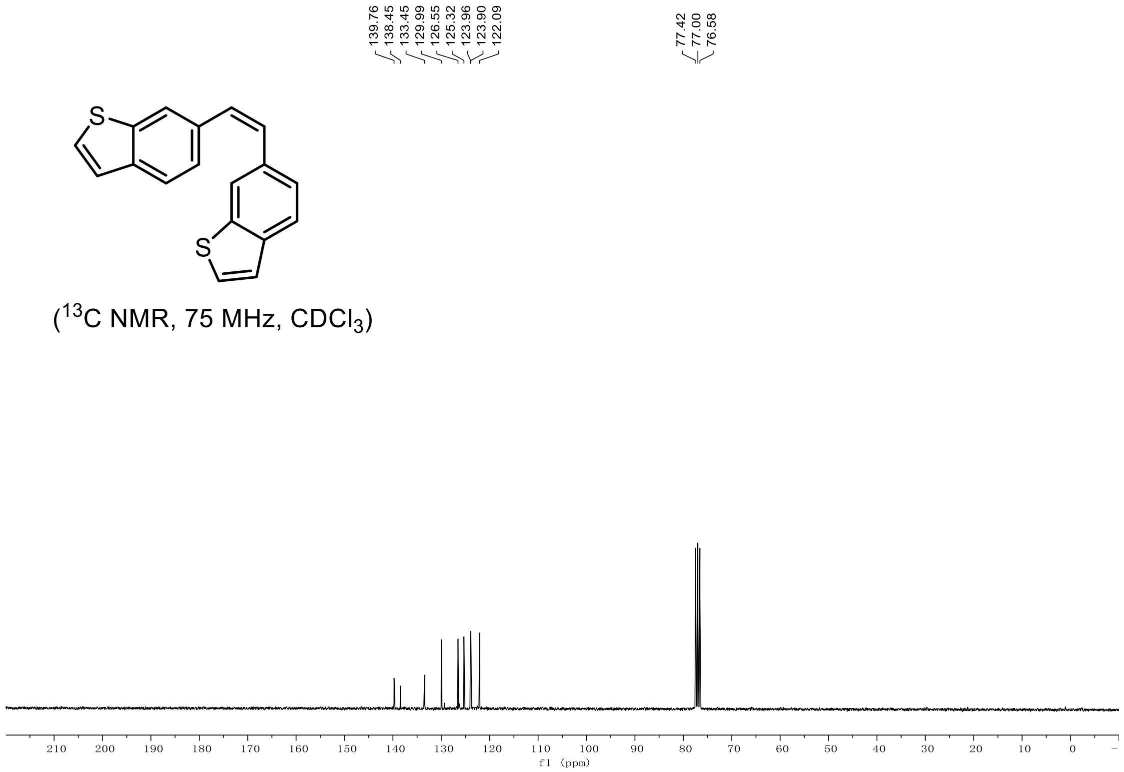

Figure S92. ^{13}C NMR of ***Z*-2v**

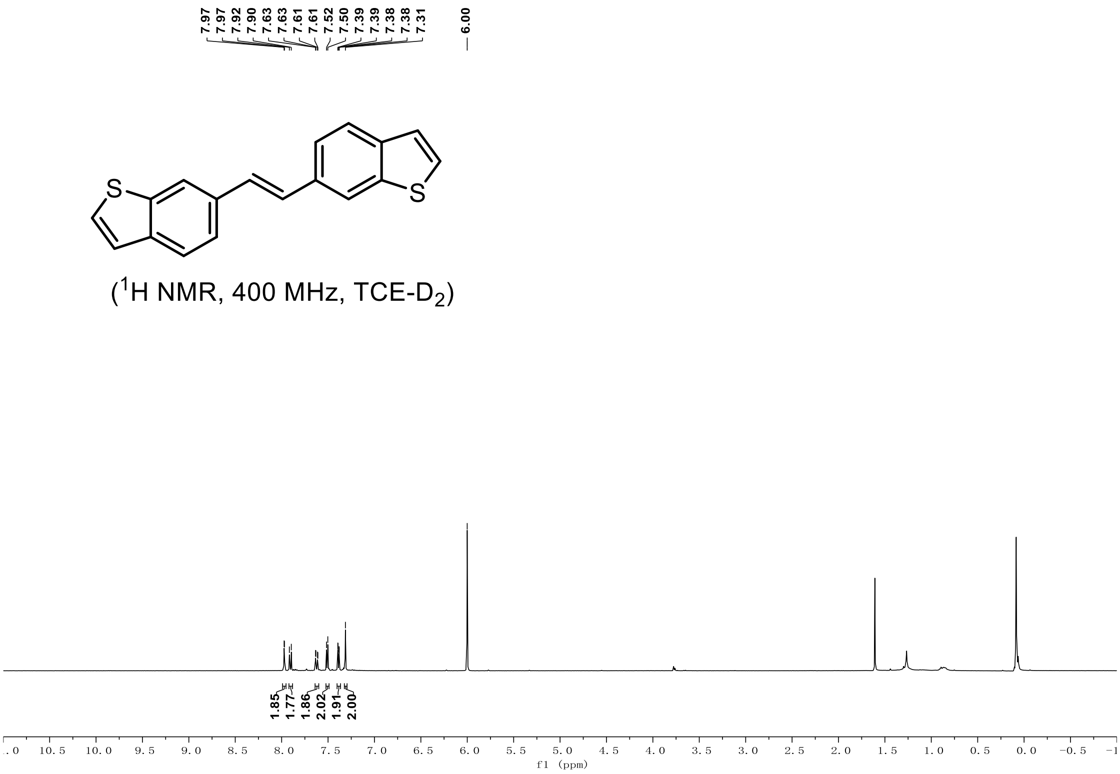

Figure S93. ^{1}H NMR of ***E*-2v**

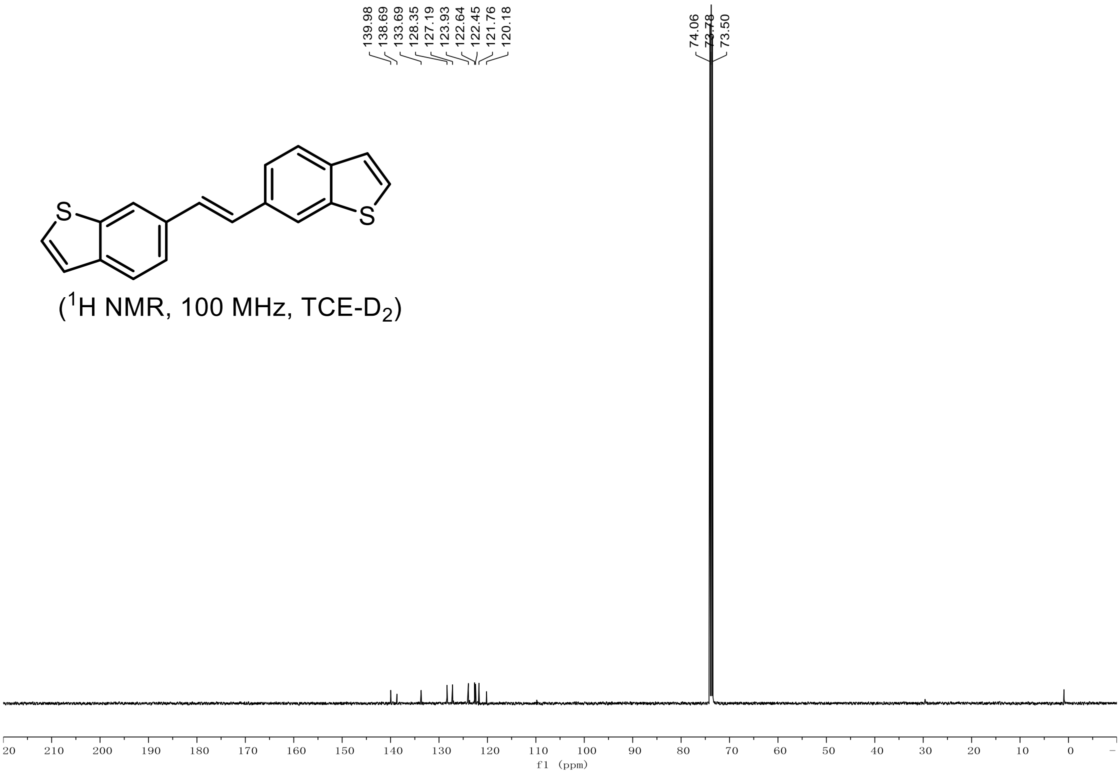

Figure S94. ^{13}C NMR of ***E*-2v**

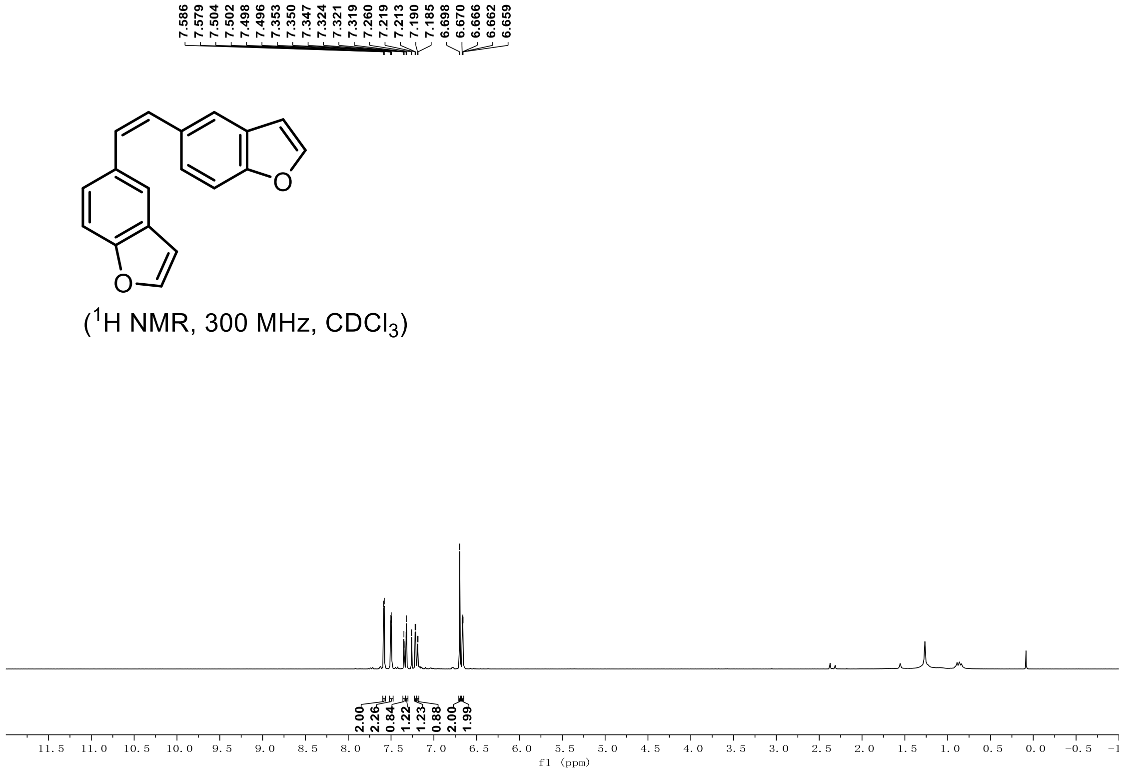

Figure S95. ^{1}H NMR of ***Z*-2w**

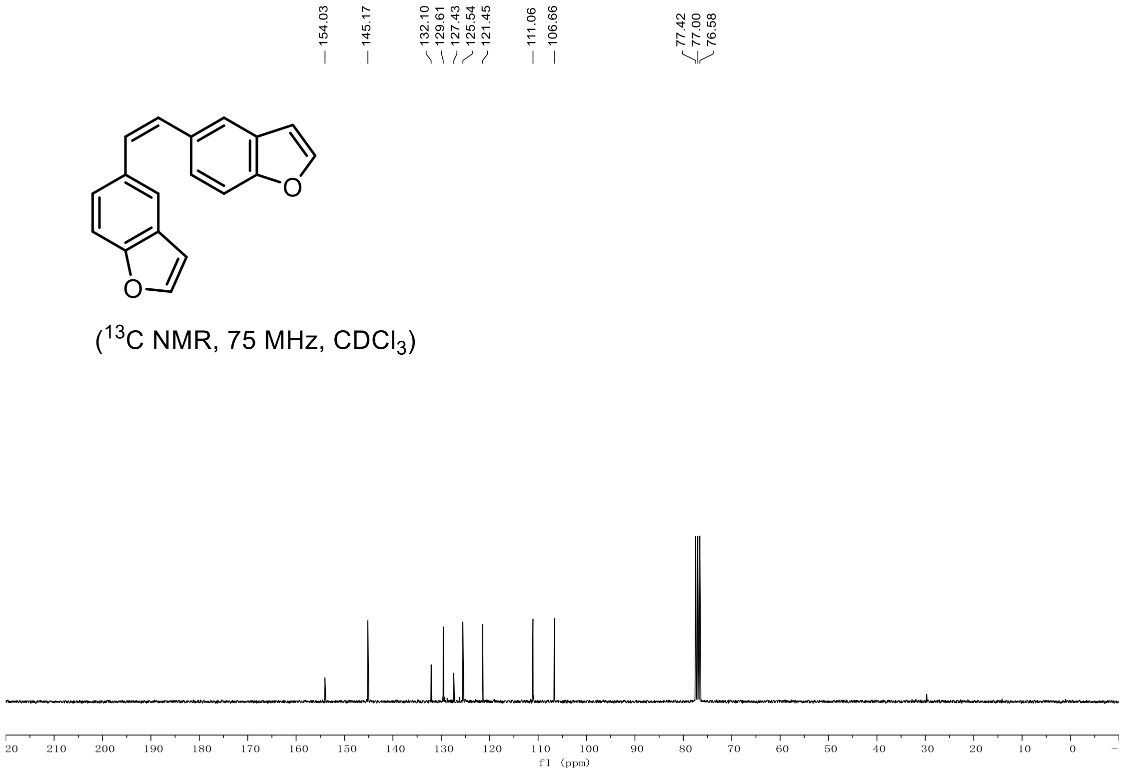

Figure S96. ^{13}C NMR of ***Z*-2w**

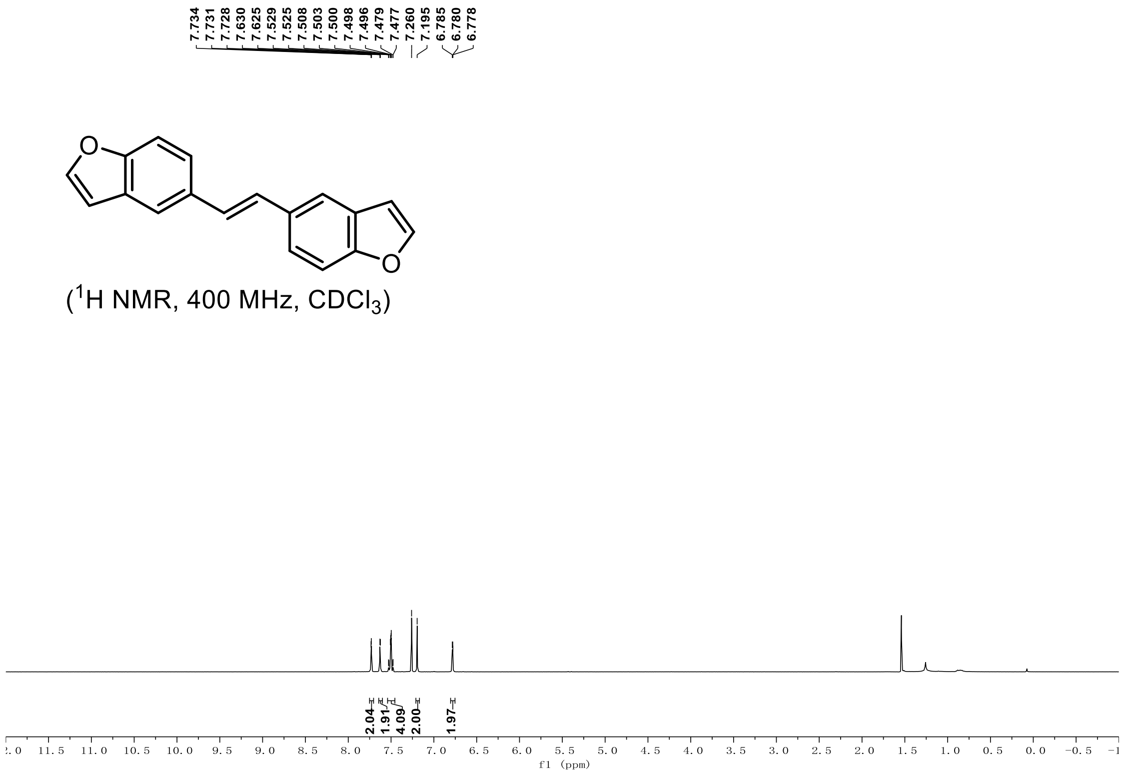

Figure S97. ^{1}H NMR of ***E*-2w**

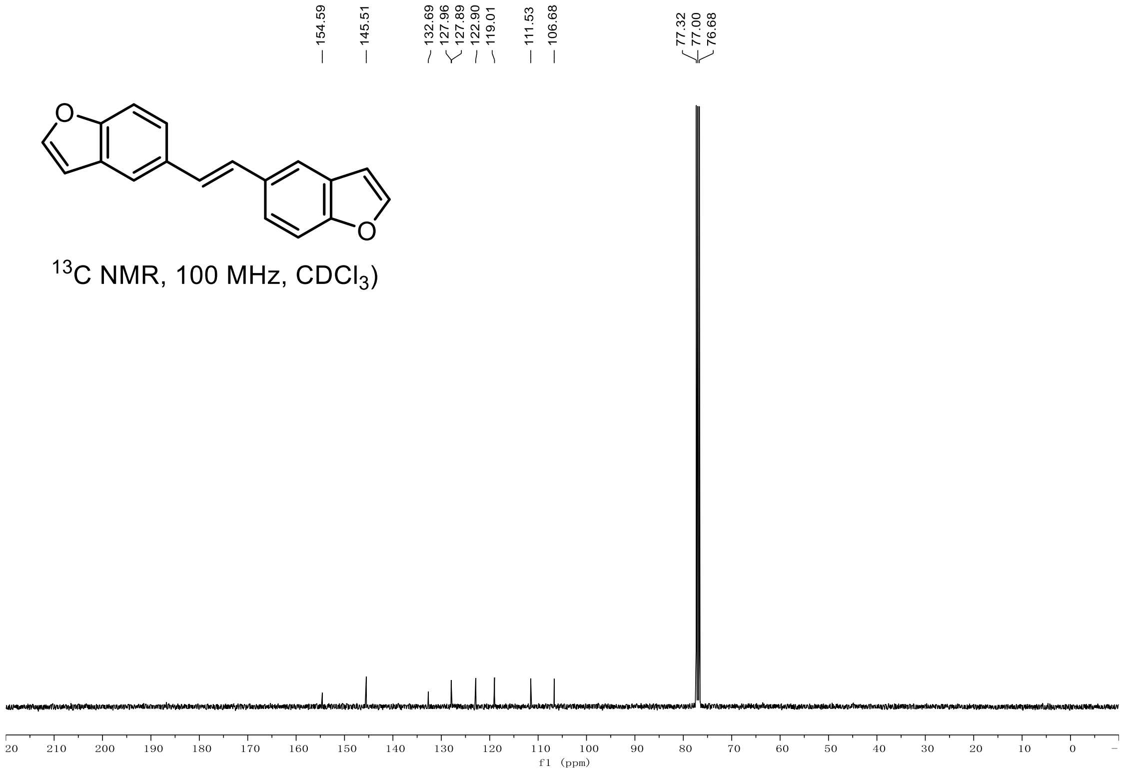

Figure S98. ^{13}C NMR of ***E*-2w**

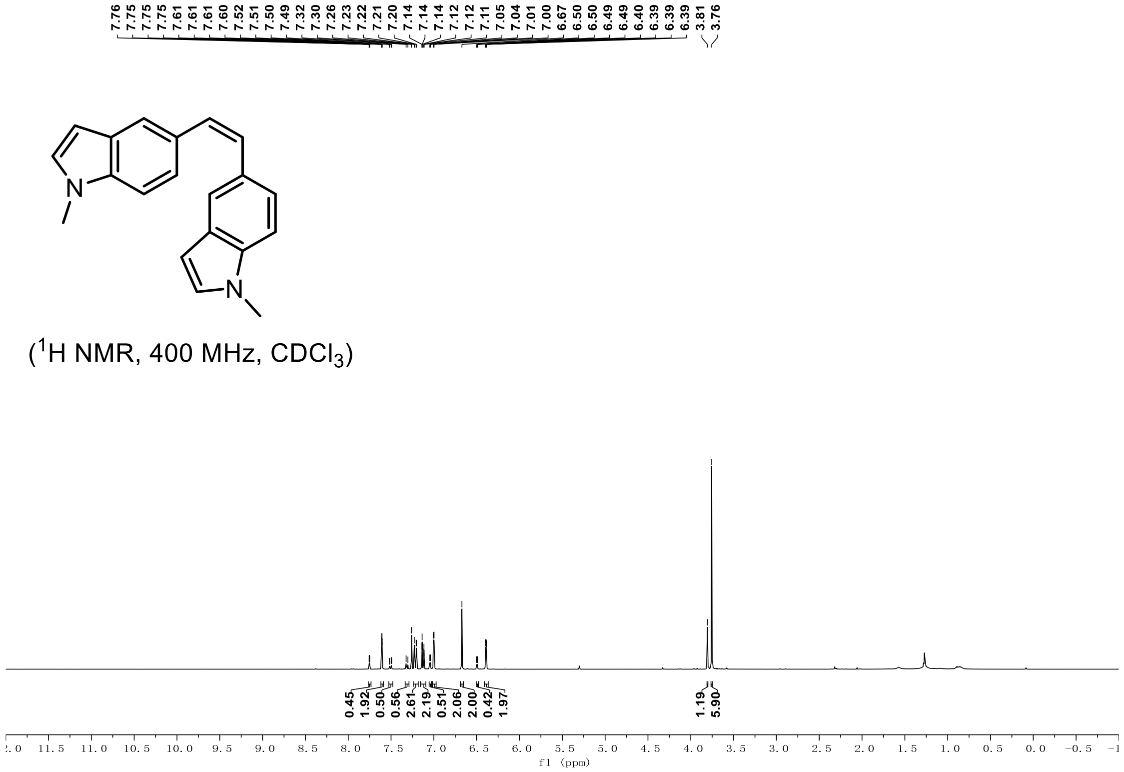

Figure S99. ^{1}H NMR of ***Z*-2x** and ***E*-2x**

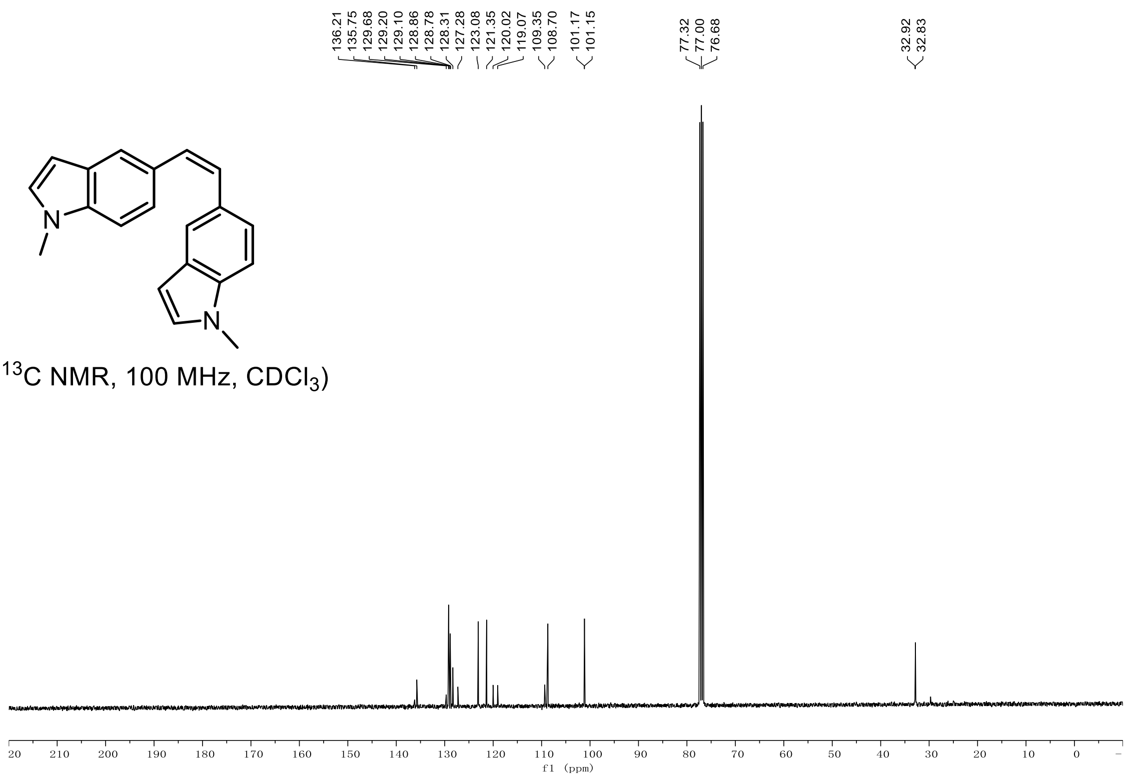

Figure S100. ^{13}C NMR of ***Z*-2x** and ***E*-2x**

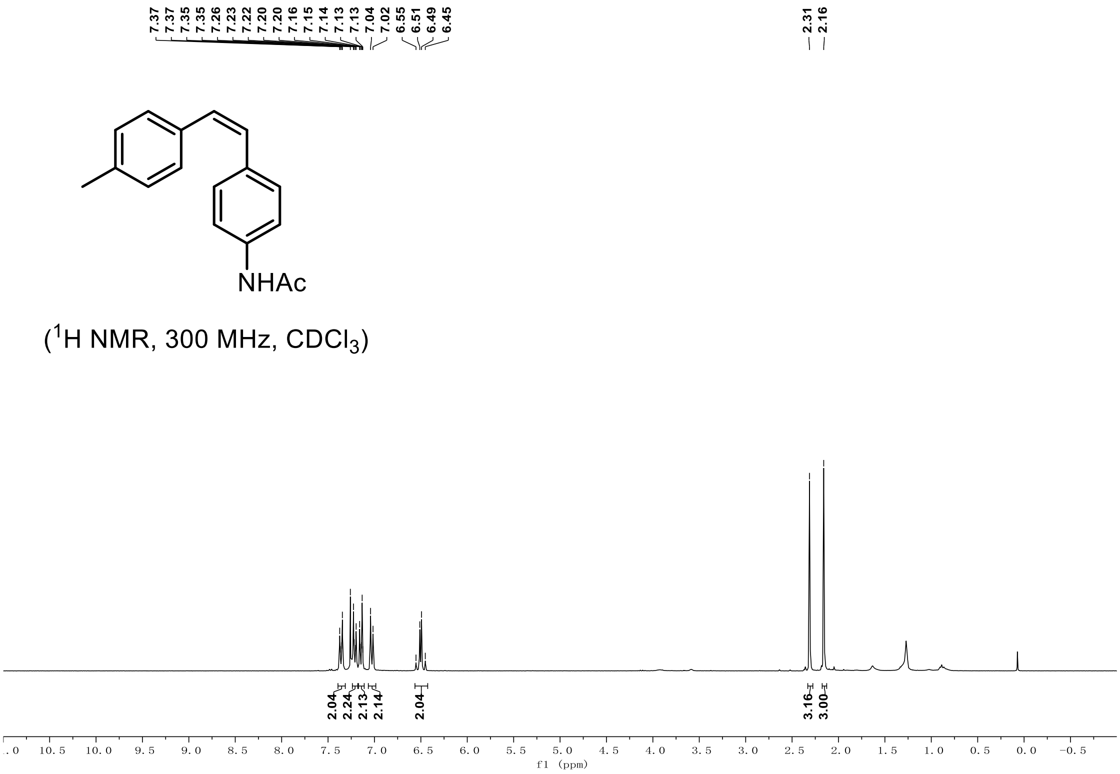

Figure S101. ^{1}H NMR of ***Z*-5a**

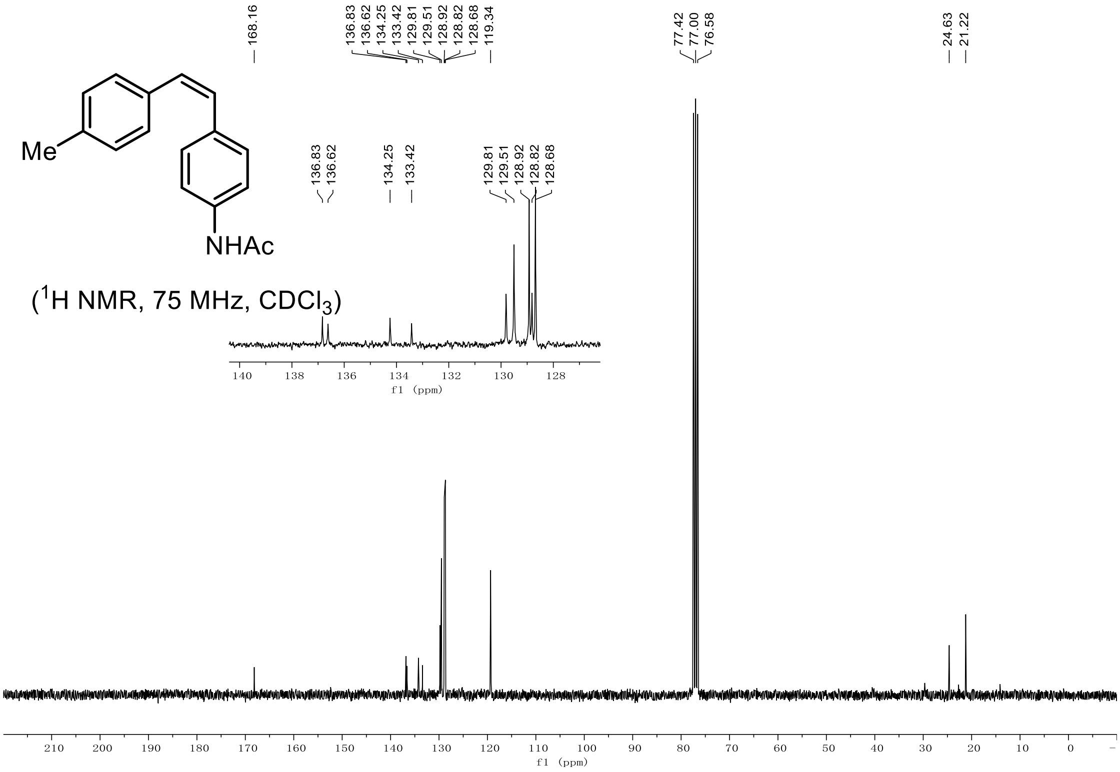

Figure S102. ^{13}C NMR of ***Z*-5a**

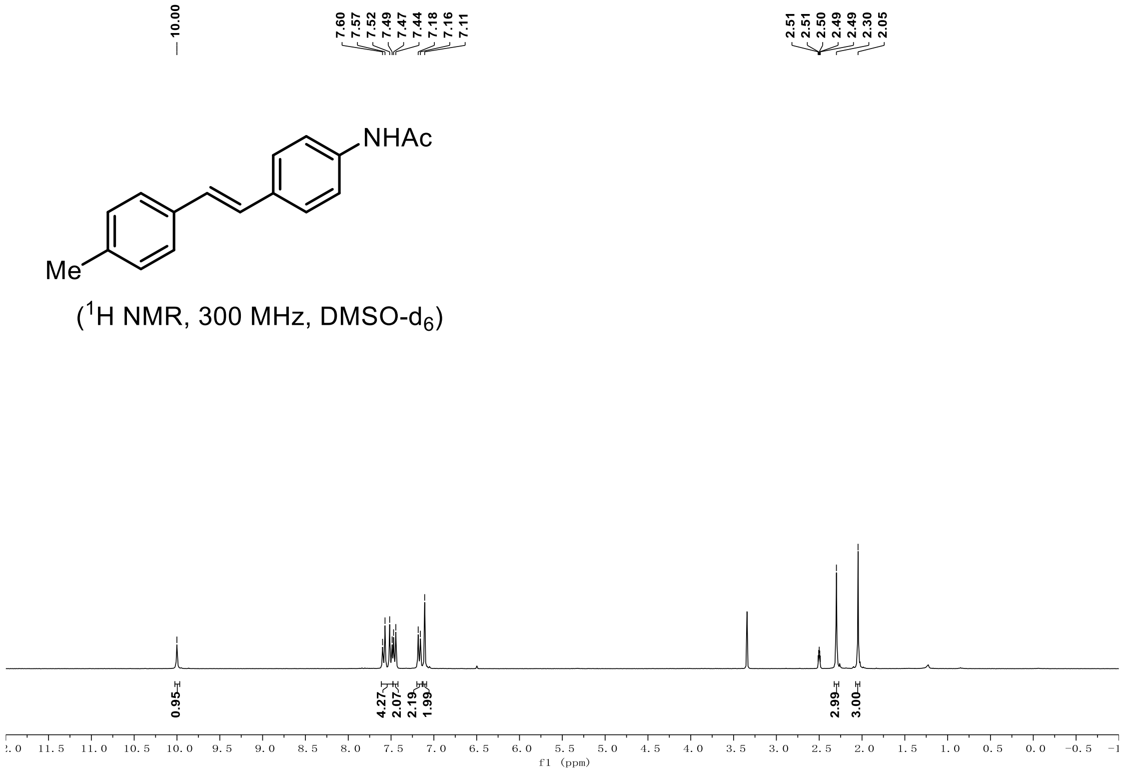

Figure S103. ^{1}H NMR of ***E*-5a**

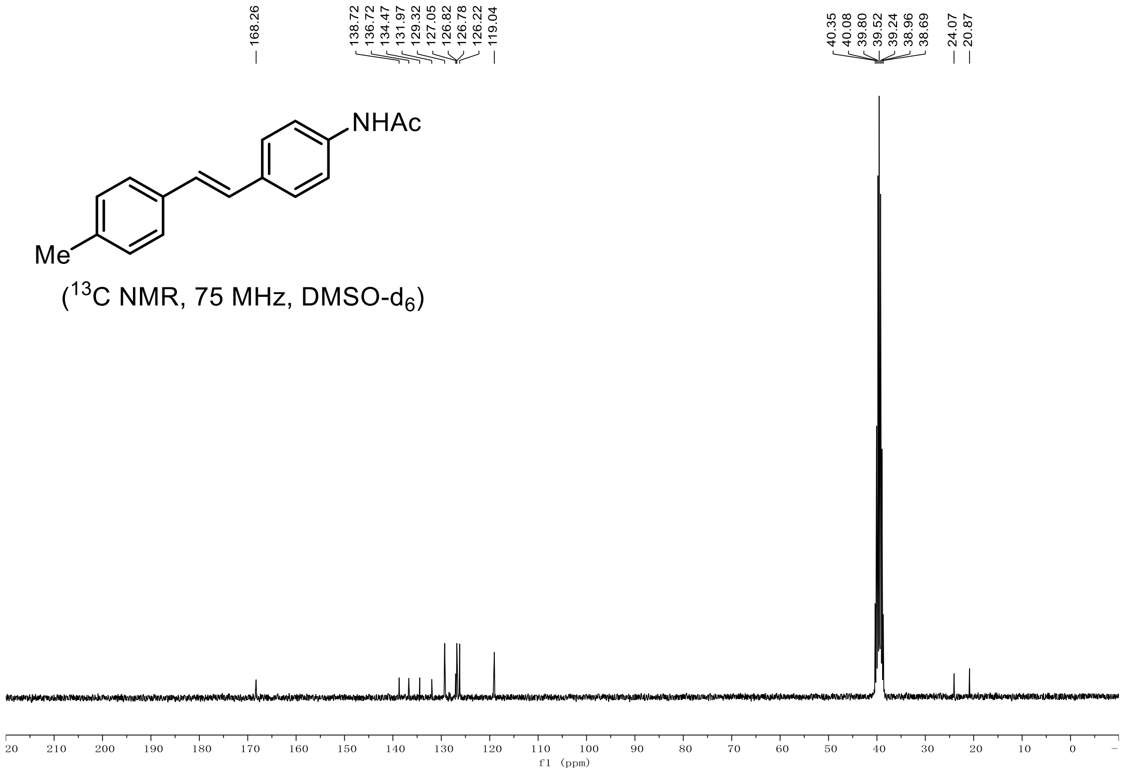

Figure S104. ^{13}C NMR of ***E*-5a**

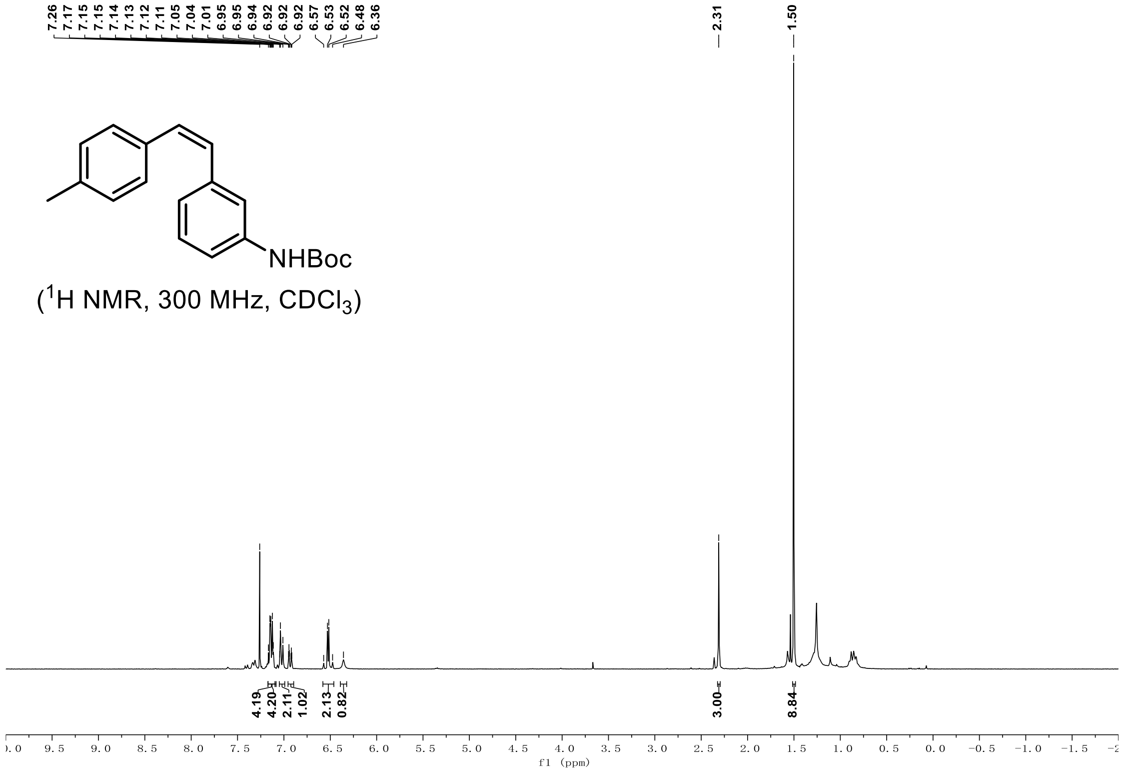

Figure S105. ^{1}H NMR of ***Z*-5b**

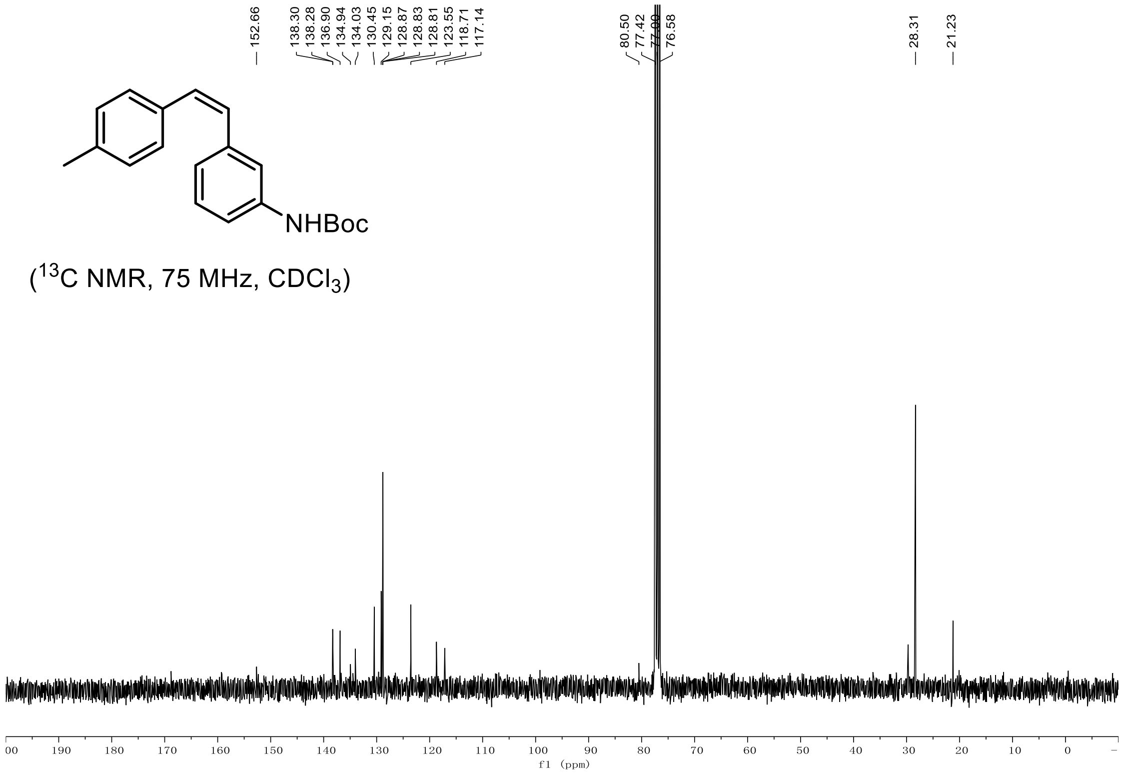

Figure S106. ^{13}C NMR of ***Z*-5b**

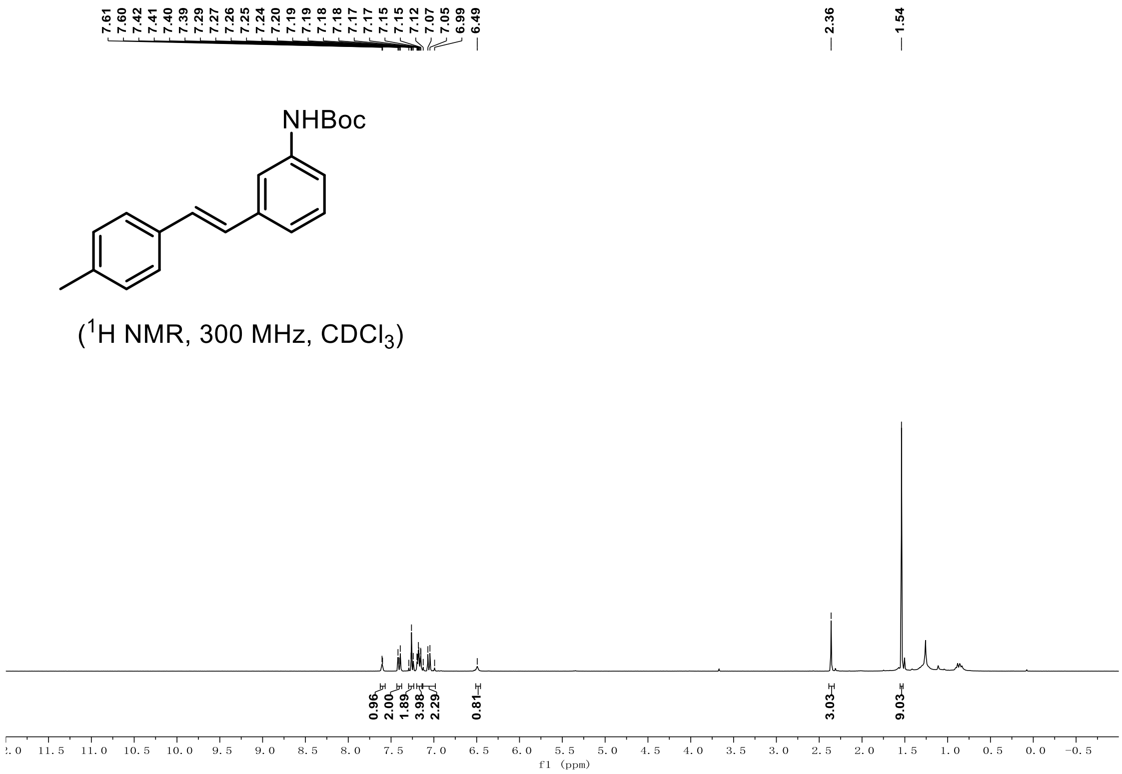

Figure S107. ^{1}H NMR of ***E*-5b**

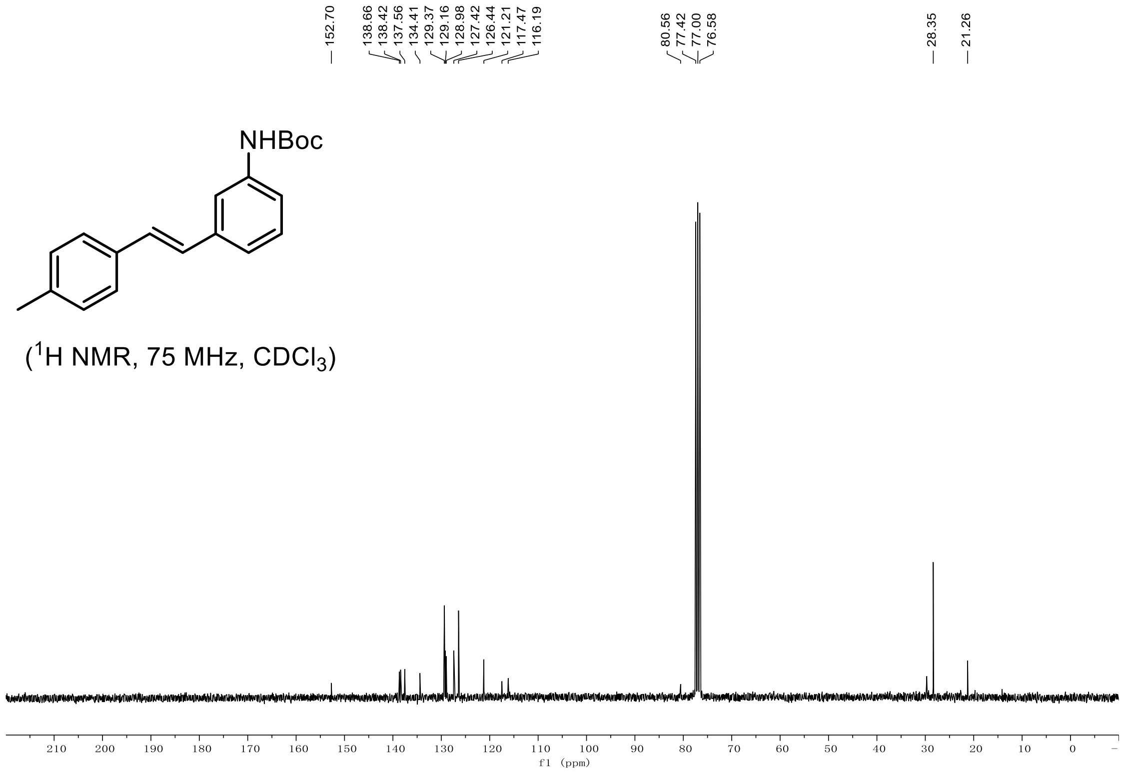

Figure S108. ^{13}C NMR of ***E*-5b**

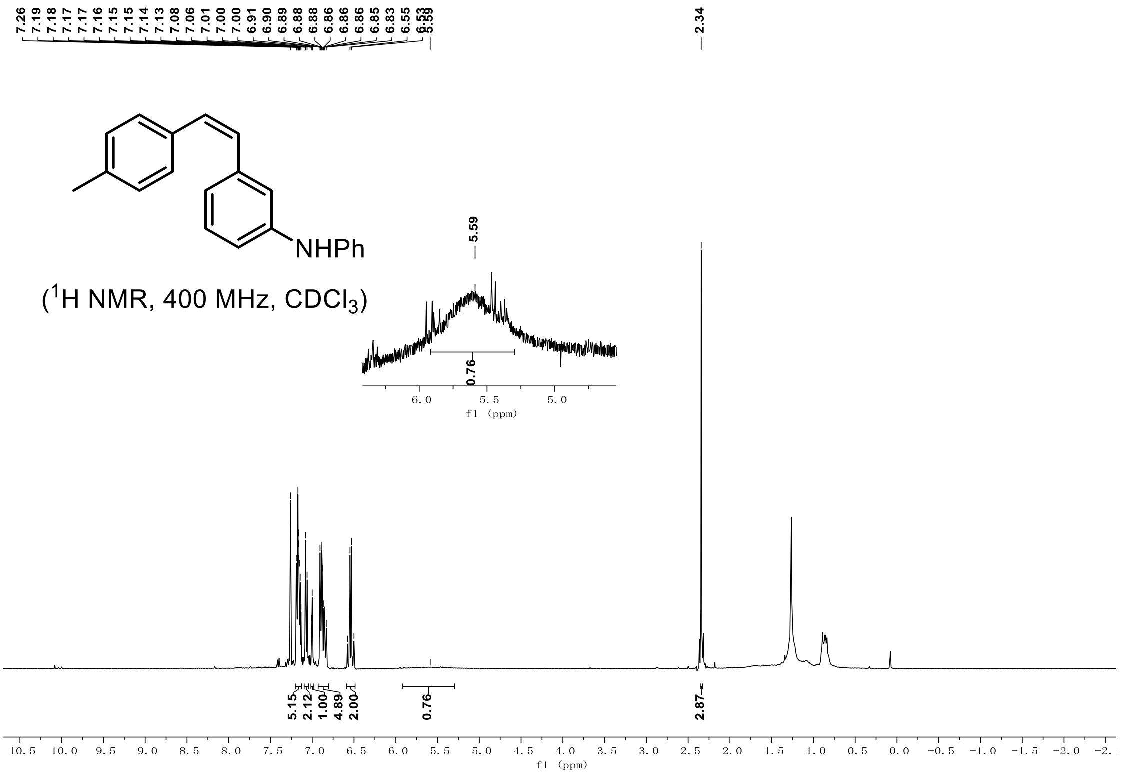

Figure S109. ^{1}H NMR of ***Z*-5c**

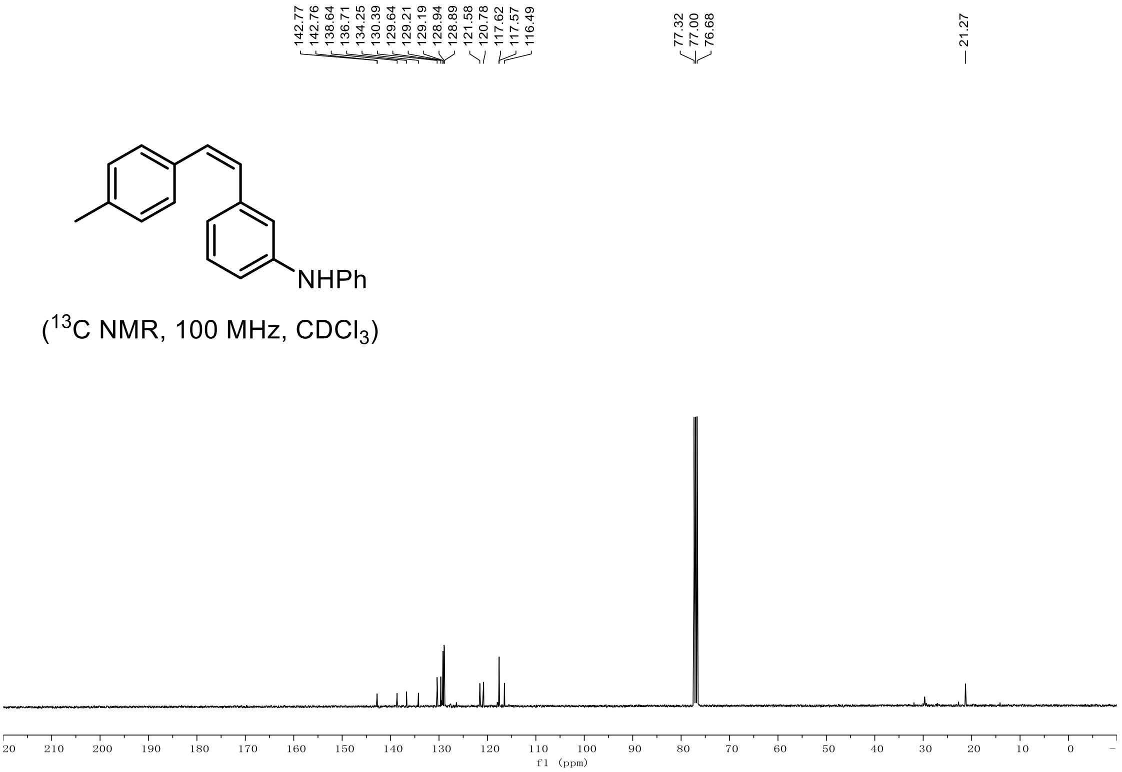

Figure S110. ^{13}C NMR of ***Z*-5c**

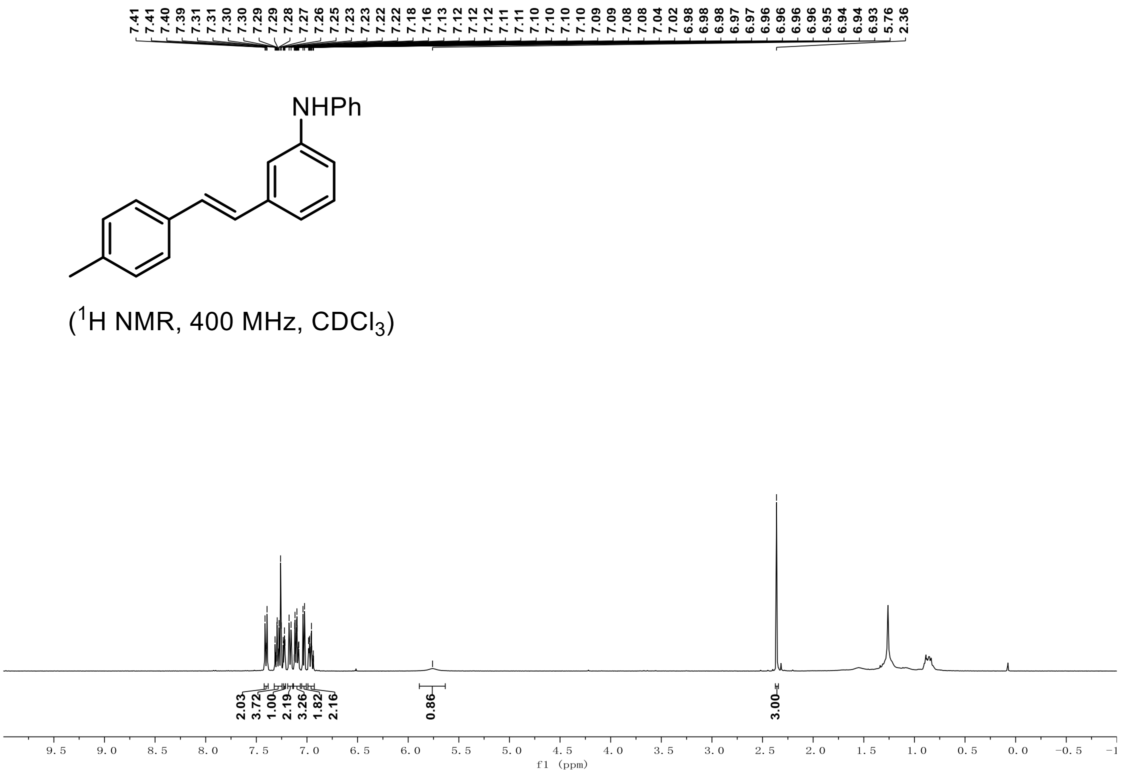

Figure S111. ^{1}H NMR of ***E*-5c**

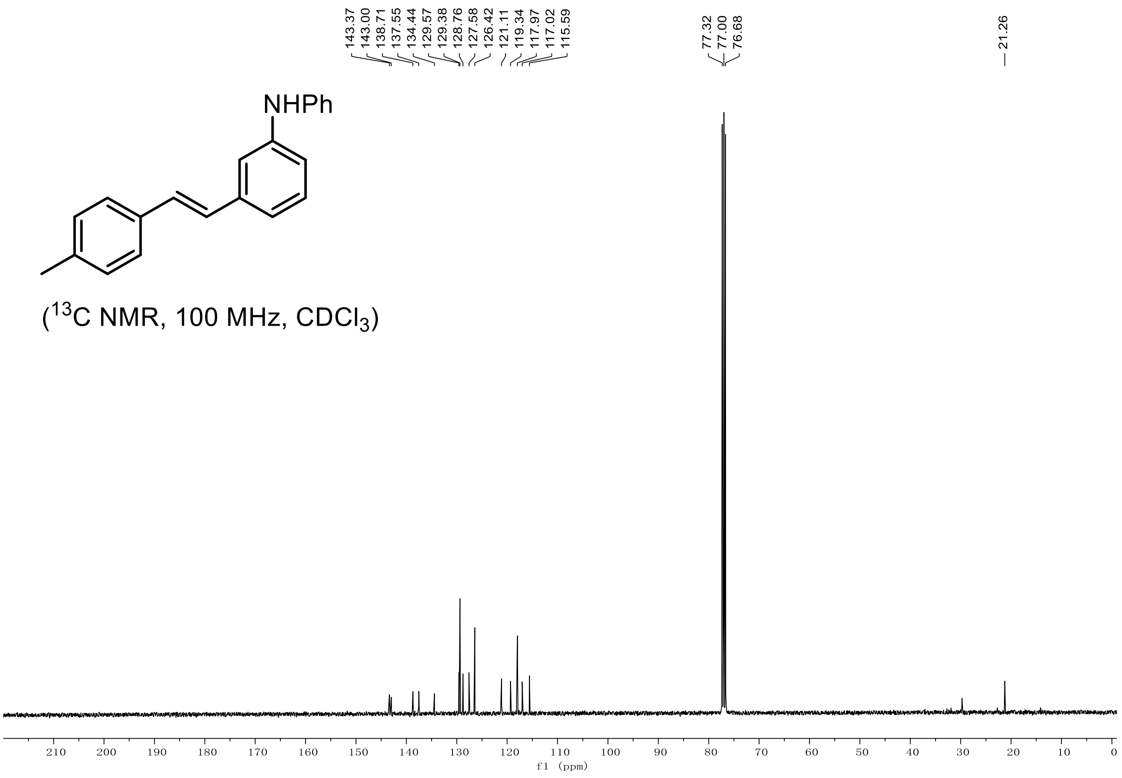

Figure S112. ^{13}C NMR of ***E*-5c**

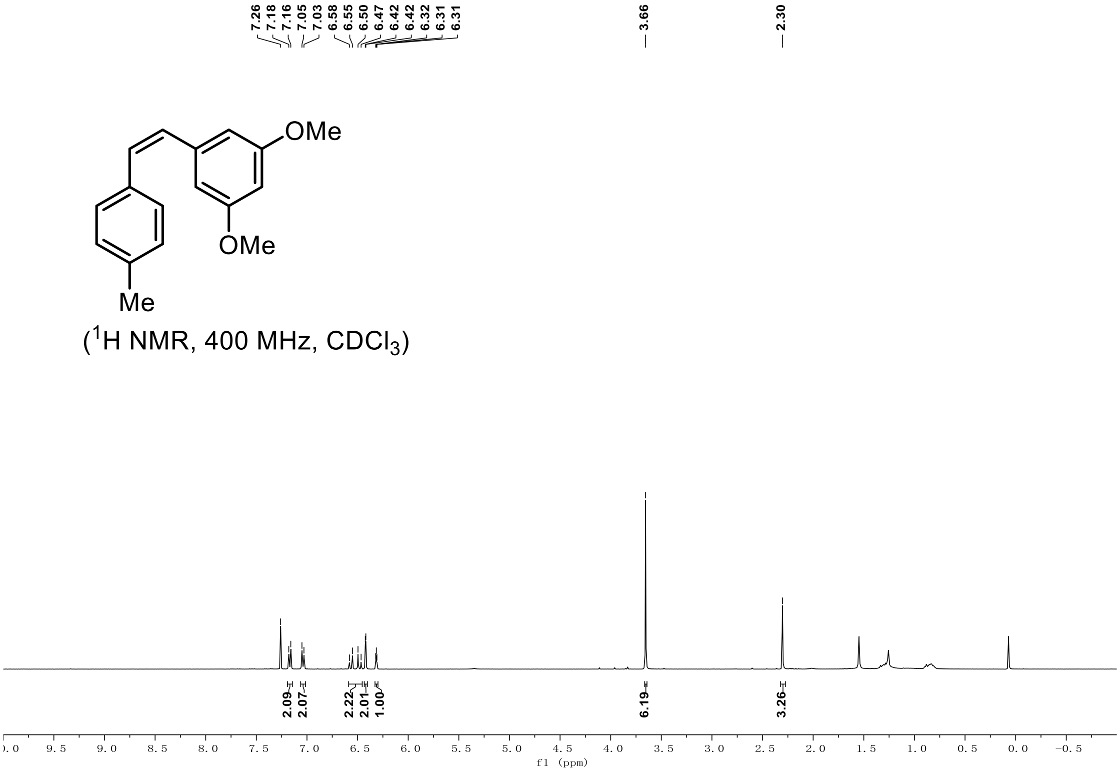

Figure S113. ^{1}H NMR of ***Z*-5d**

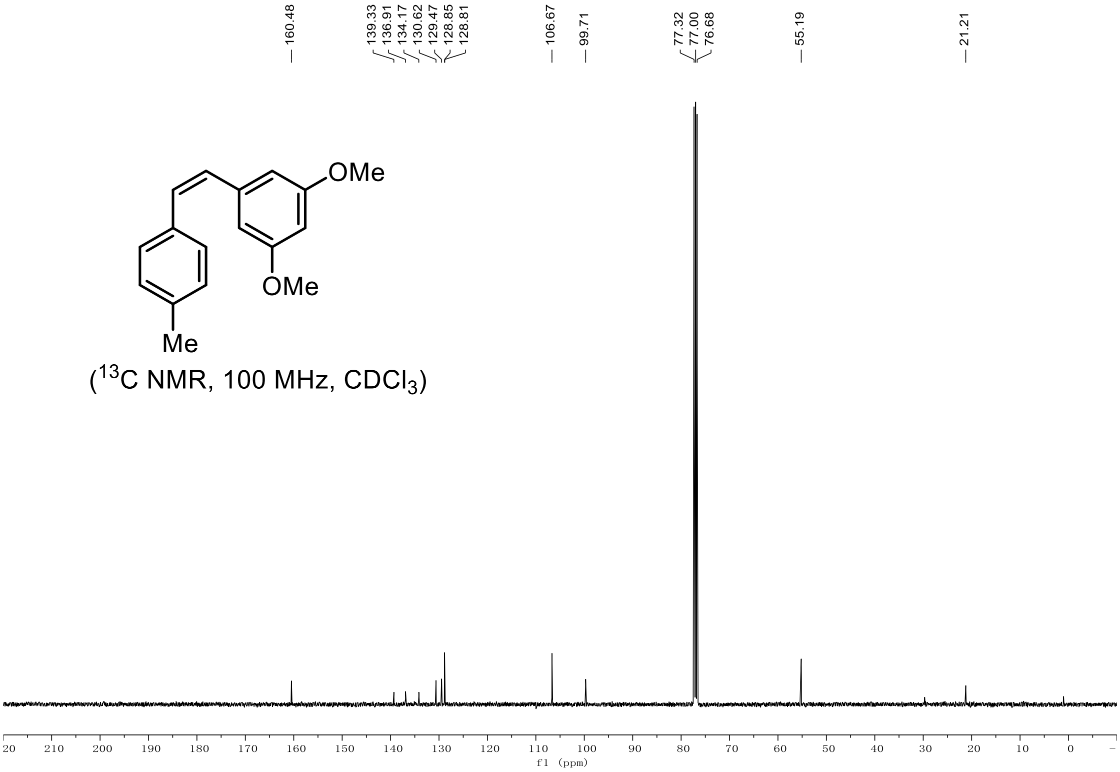

Figure S114. ^{13}C NMR of ***Z*-5d**

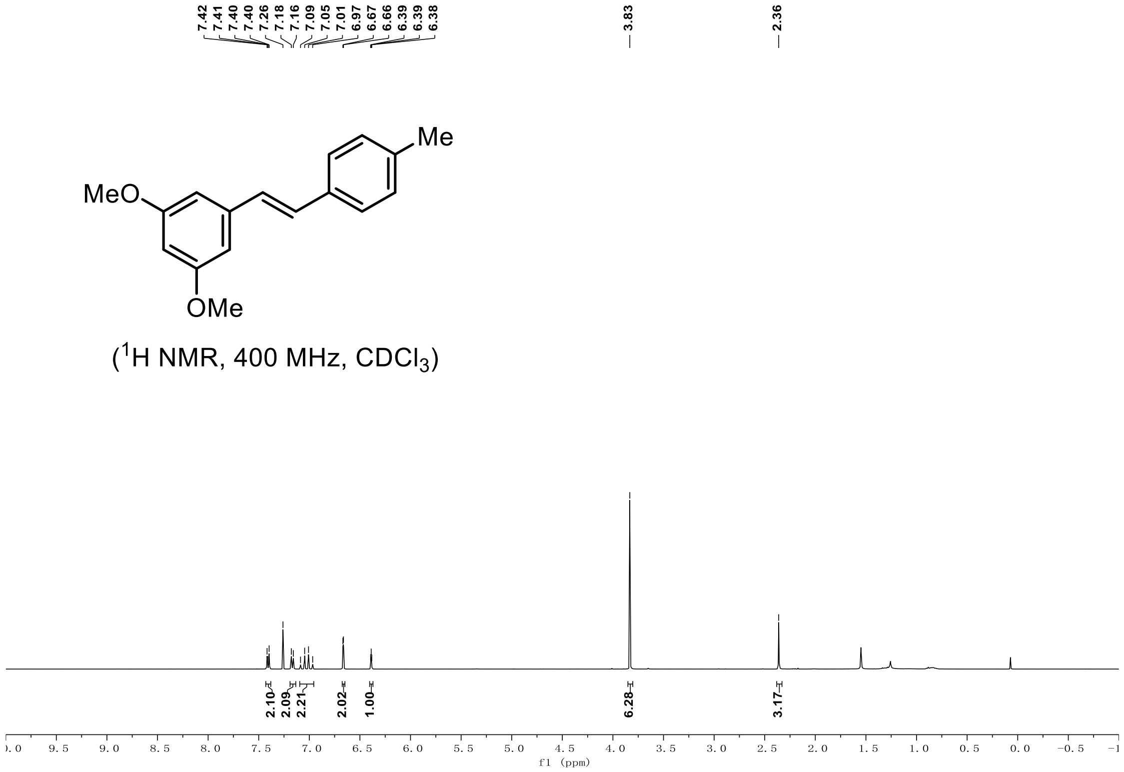

Figure S115. ^{1}H NMR of ***E*-5d**

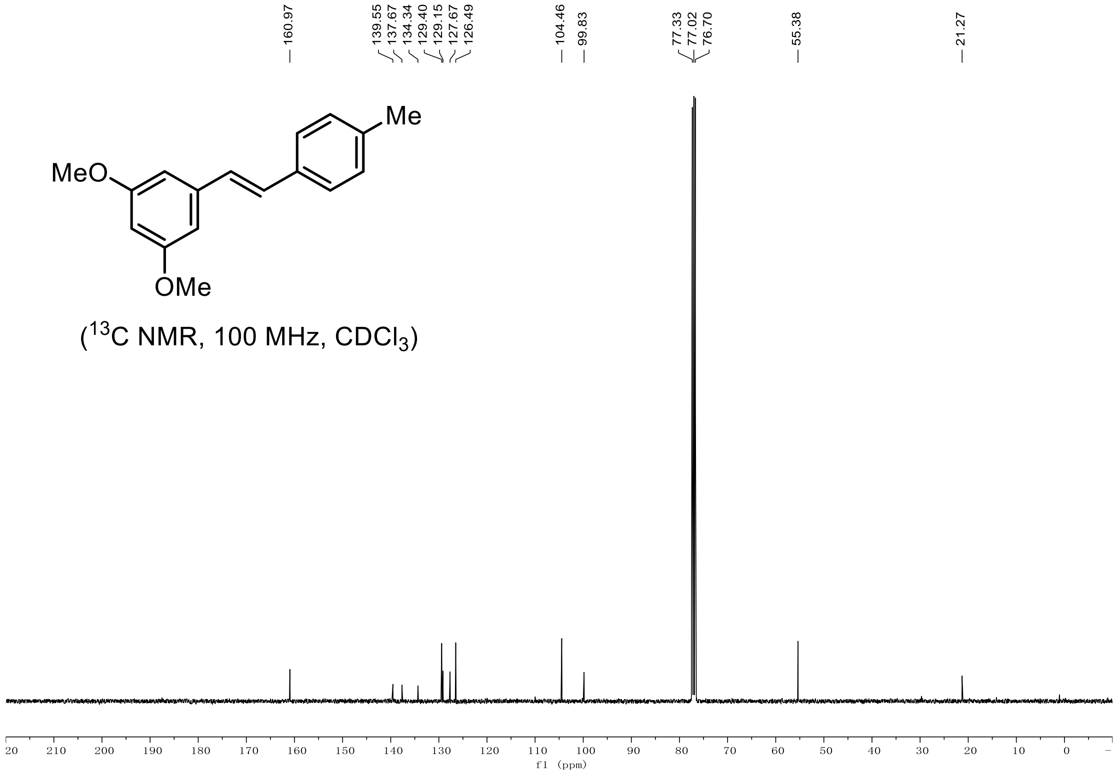

Figure S116. ^{13}C NMR of ***E*-5d**

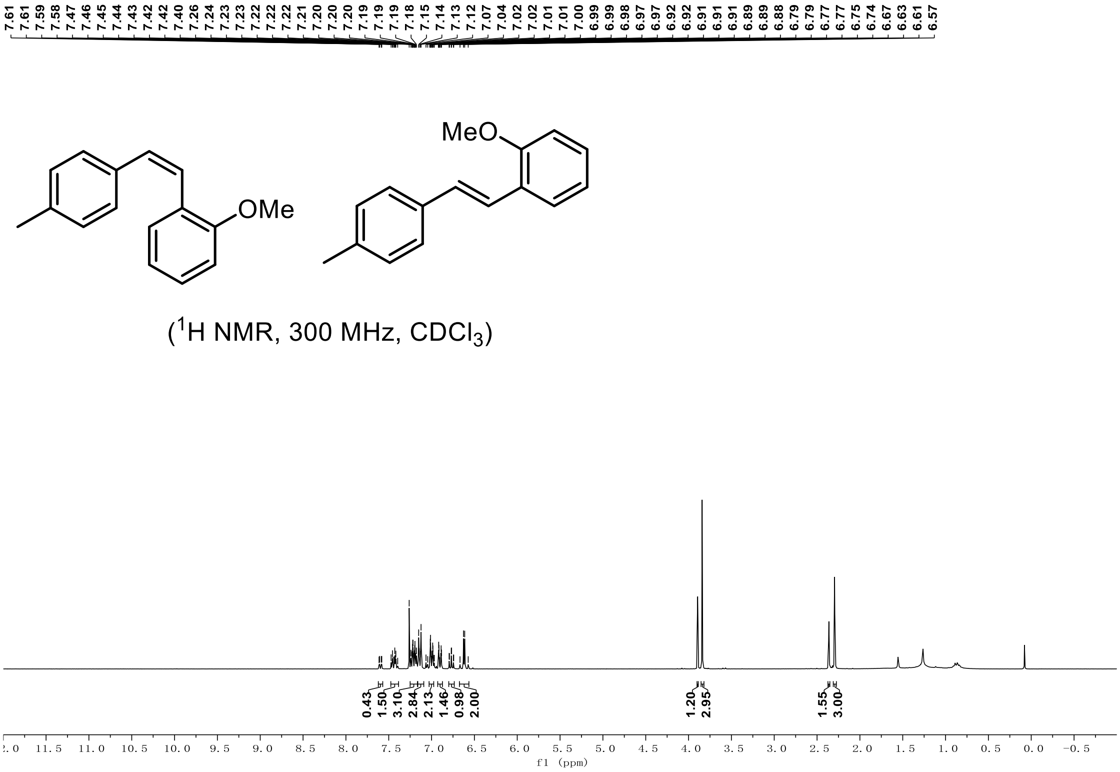

Figure S117. ^{1}H NMR of ***Z*-5e** and ***E*-5e**

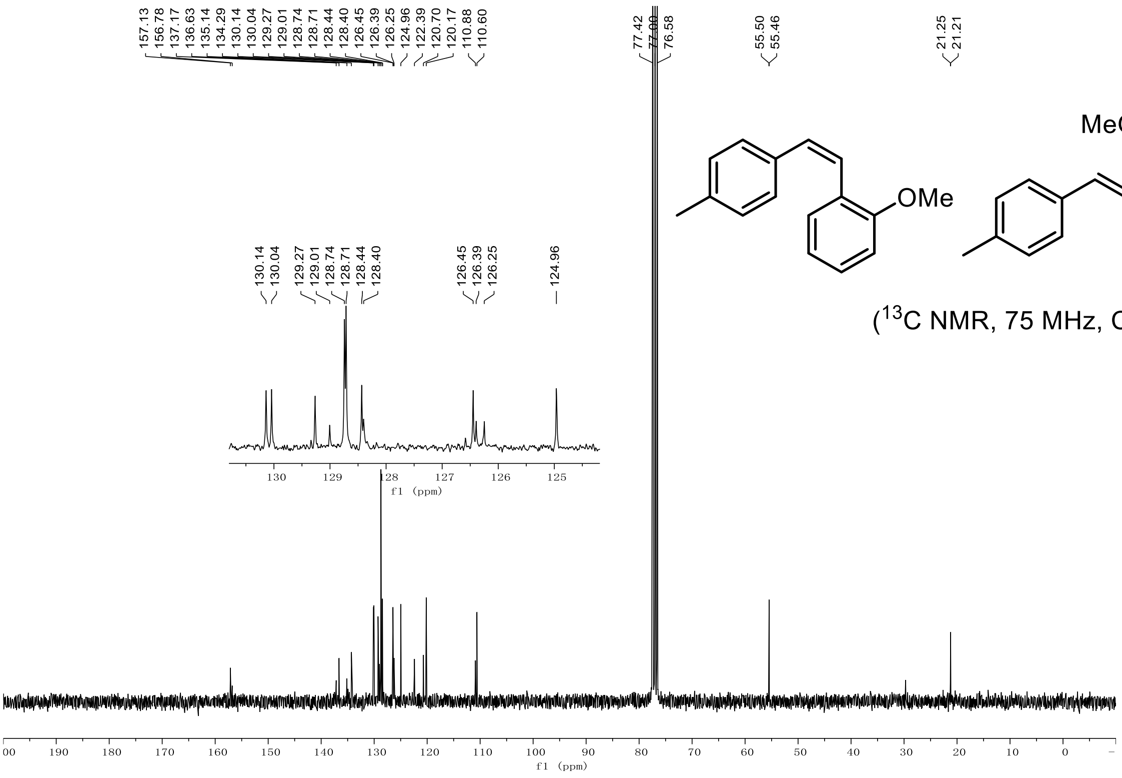

Figure S118. ^{13}C NMR of ***Z*-5e** and ***E*-5e**

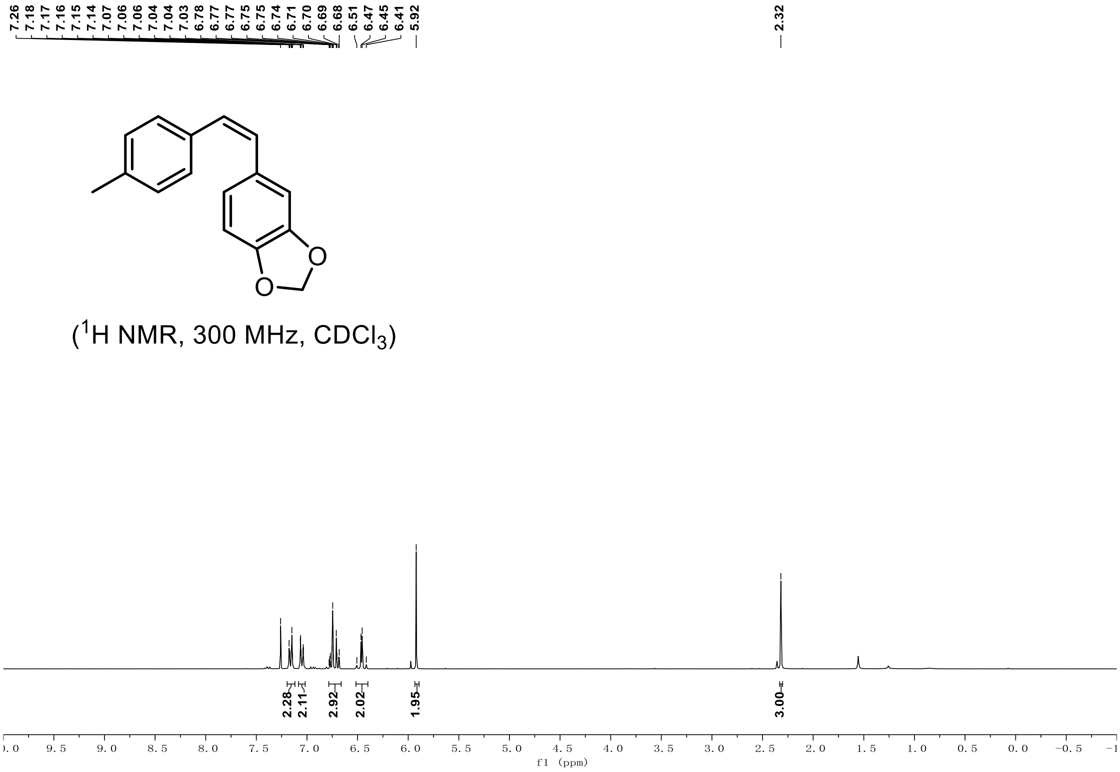

Figure S119. ^{1}H NMR of ***Z*-5f**

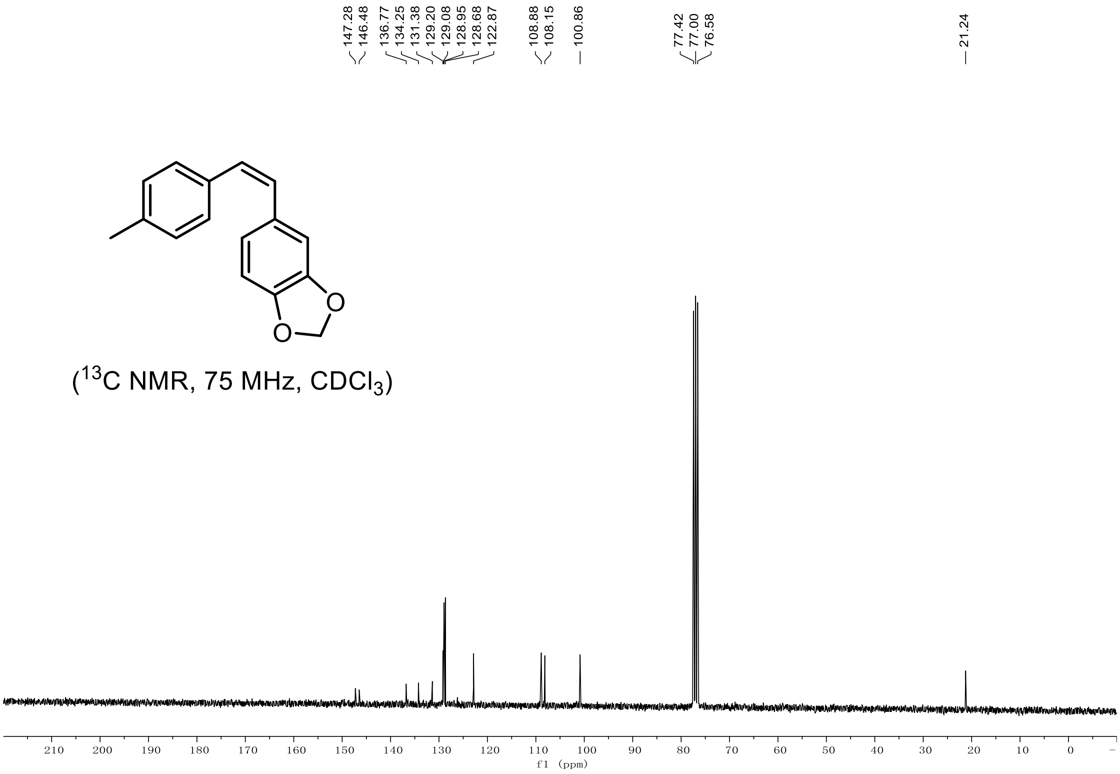

Figure S120. ^{13}C NMR of ***Z*-5f**

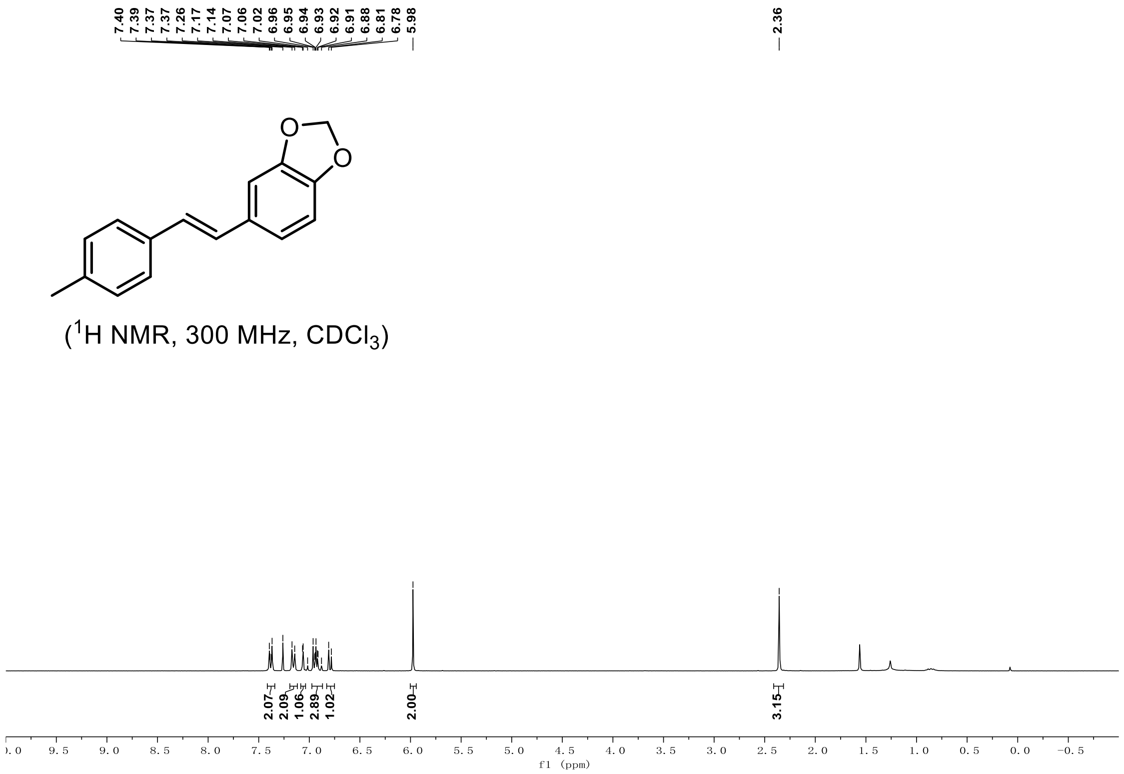

Figure S121. ^{1}H NMR of ***E*-5f**

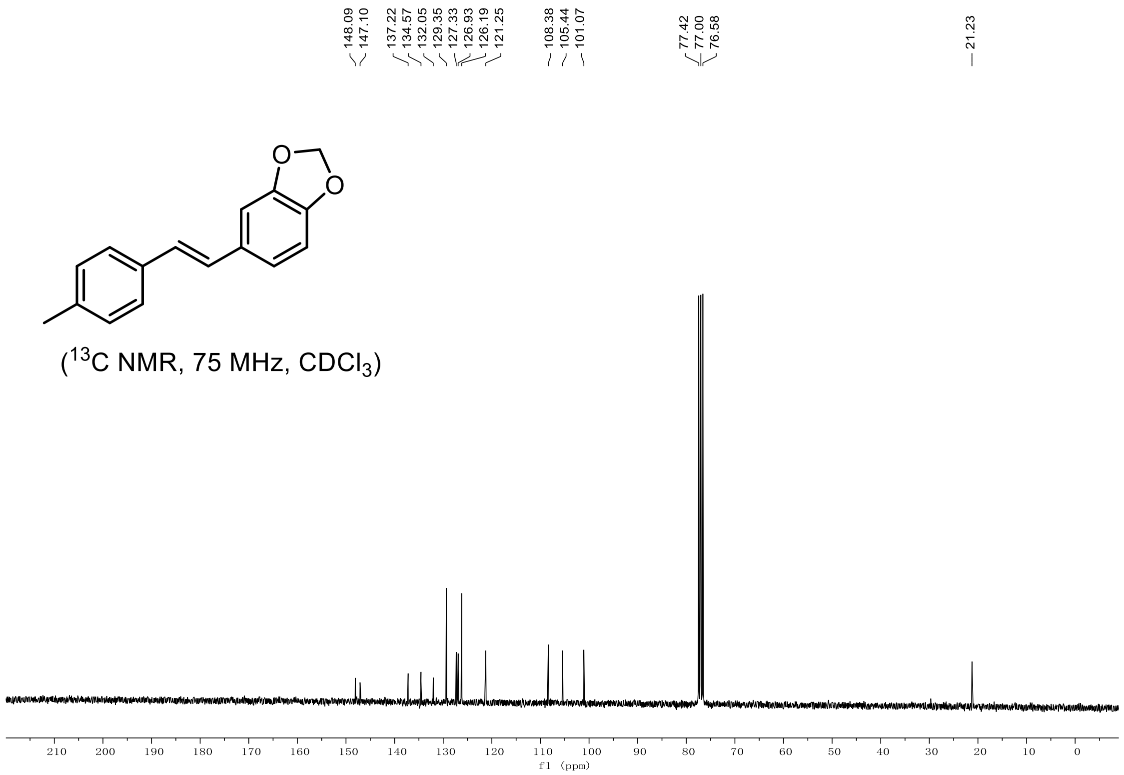

Figure S122. ^{13}C NMR of ***E*-5f**

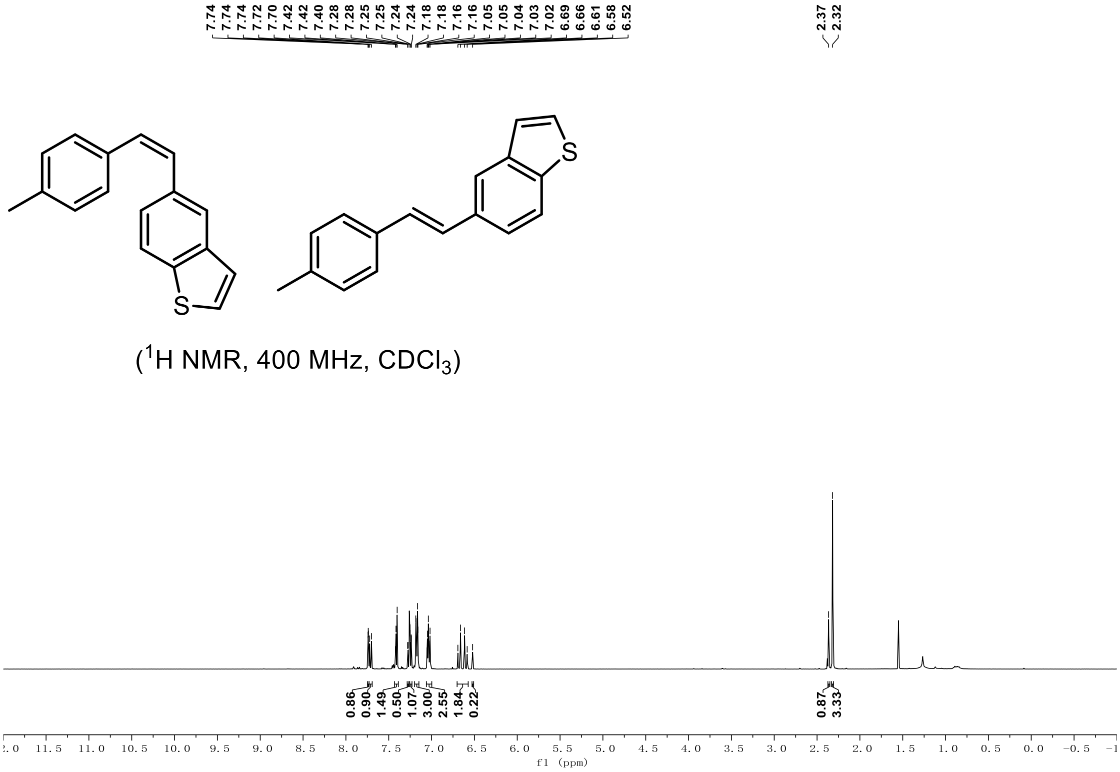

Figure S123. ^{1}H NMR of ***Z*-5g** and ***E*-5g**

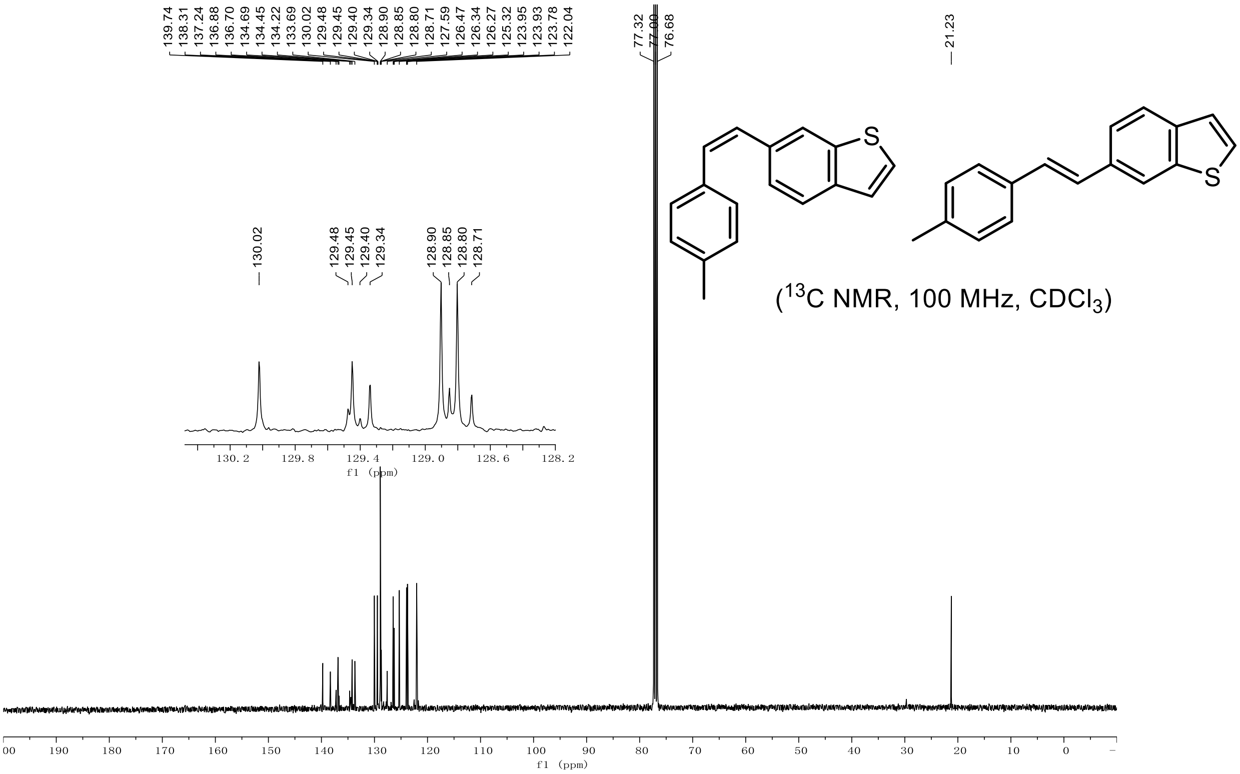

Figure S124. ^{13}C NMR of ***Z*-5g** and ***E*-5g**

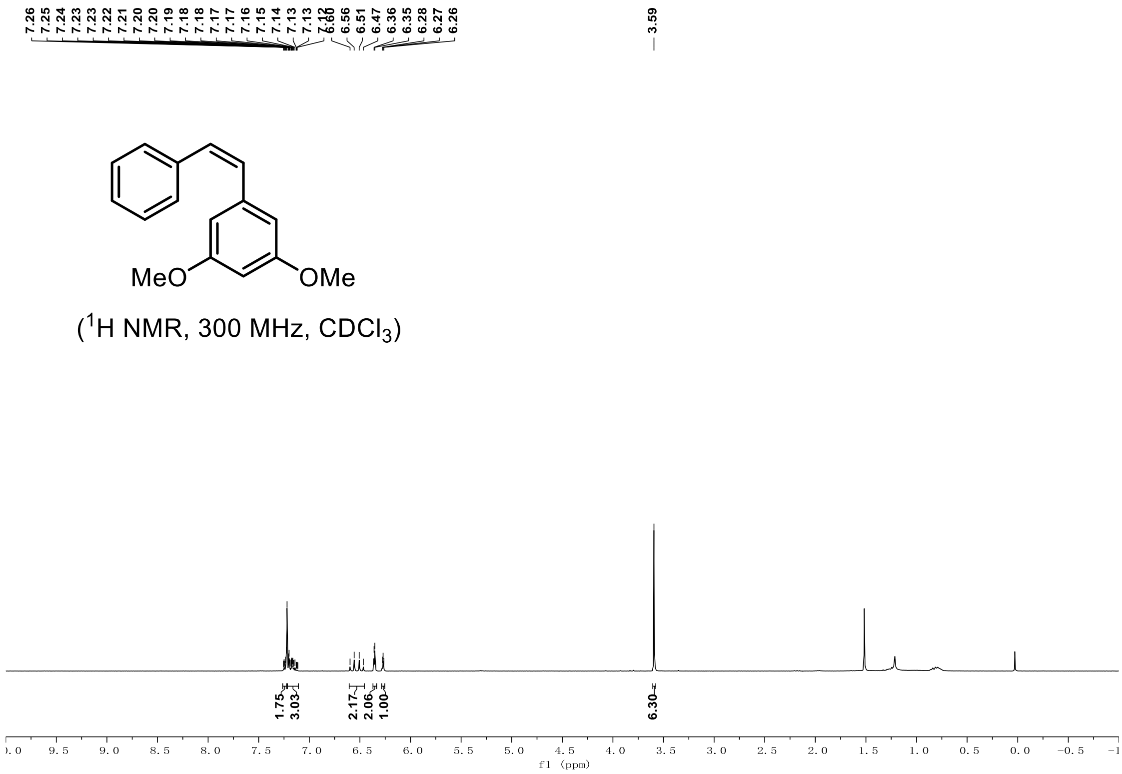

Figure S125. ^{1}H NMR of ***Z*-5h**

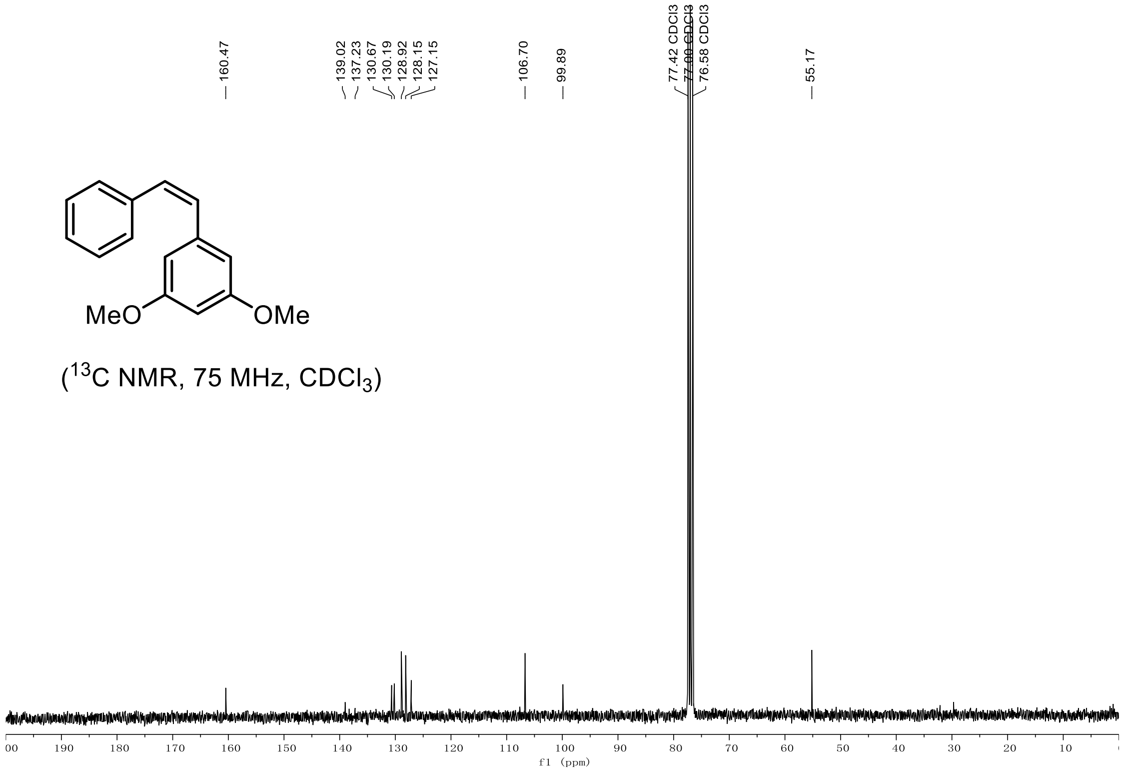

Figure S126. ^{13}C NMR of ***Z*-5h**

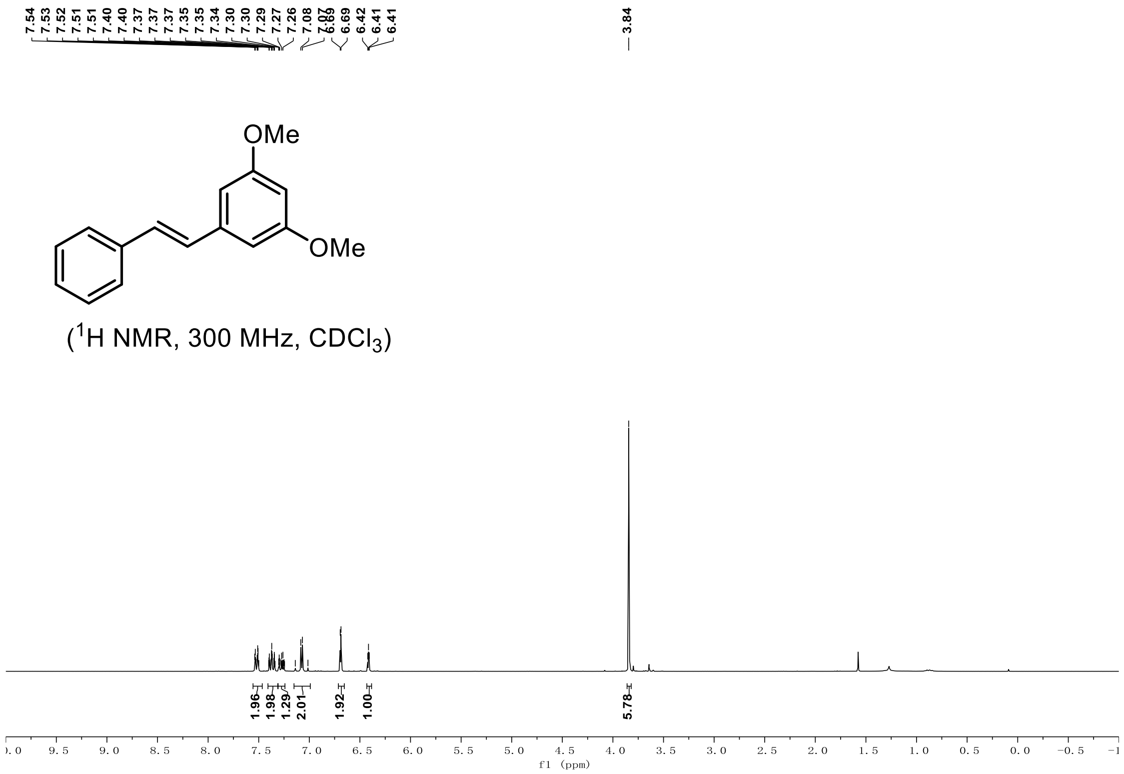

Figure S127. ^{1}H NMR of ***E*-5h**

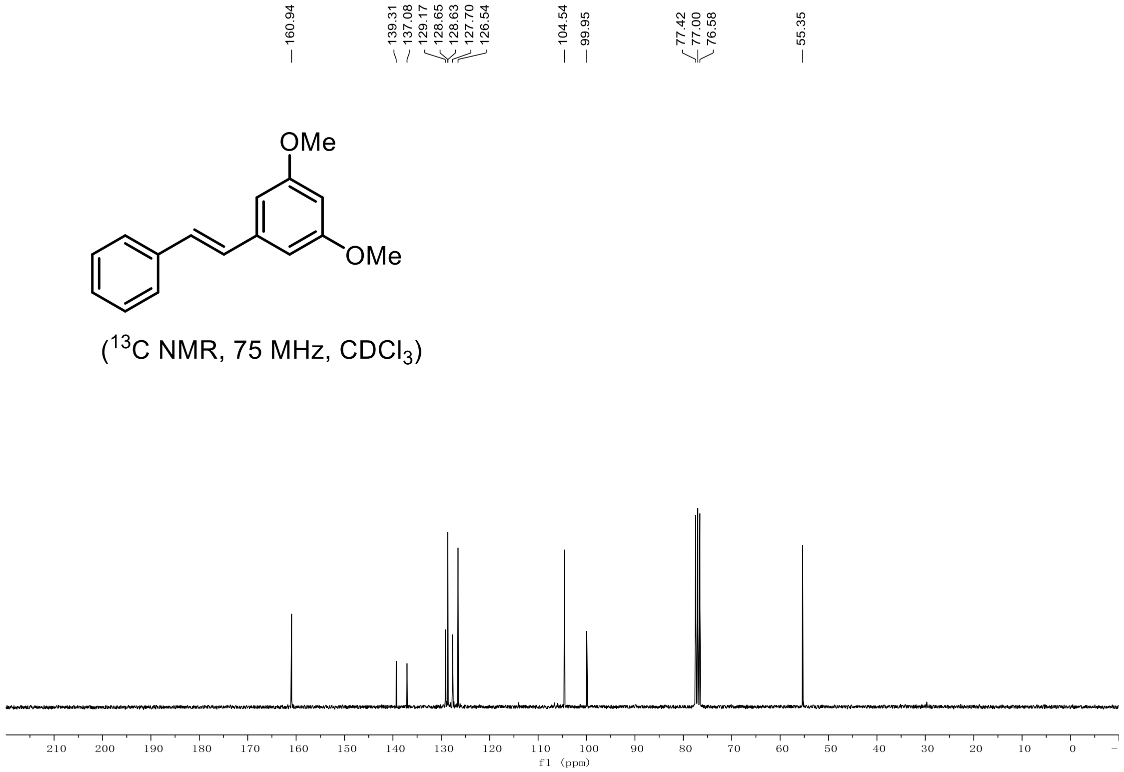

Figure S128. ^{13}C NMR of ***E*-5h**

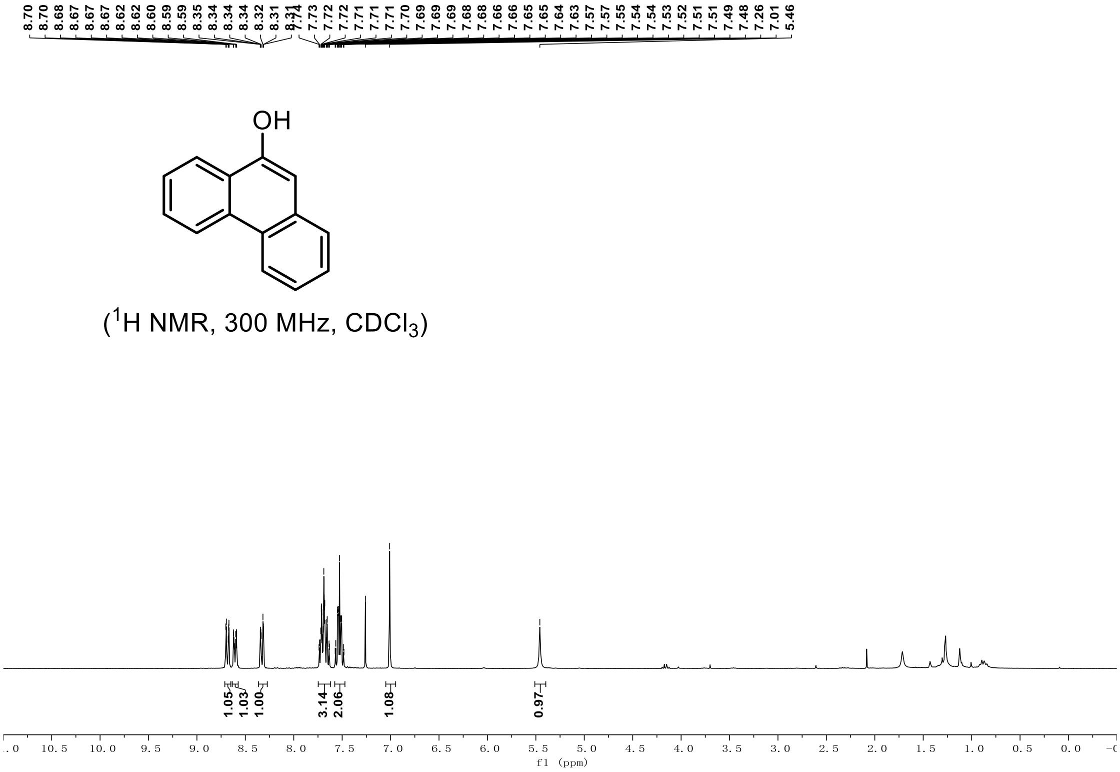

Figure S129. ^{1}H NMR of ***2y'***

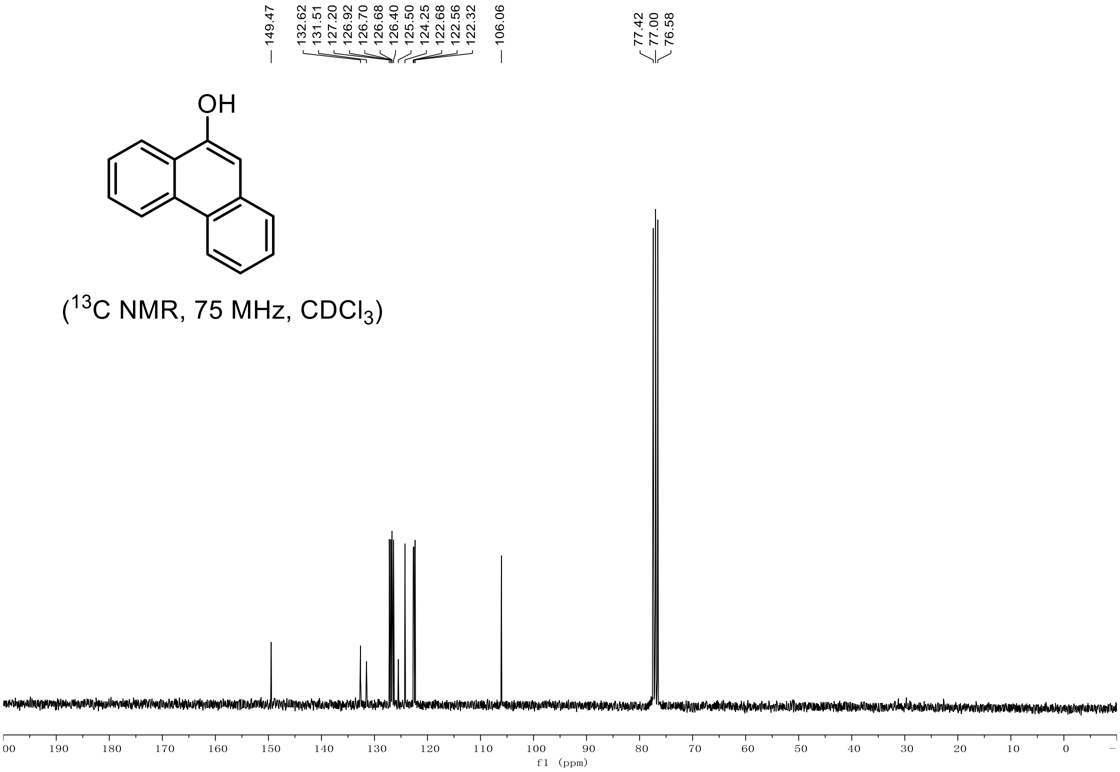

Figure S130. ^{13}C NMR of ***2y'***

6. Supplemental References

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