Supporting Information

Ni/Photoredox-catalyzed coupling of aryl bromides and methylenecyclopropanes via regioselective distal bond cleavage

Ben Mao,[a] Min Shi,[a,b*] and Yin Wei[b*]

[a]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.*

[b]*State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: mshi@mail.sioc.ac.cn*; *weiyin@sioc.ac.cn.*

CONTENTS

1. General Remarks.

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), 600 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 151 MHz (^{13}C NMR) and 565 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift was reported in ppm down field from internal TMS. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, EI and HRMS was measured on a HP-5989 instrument. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. Commercially available reagents were used without further purification. Organic solvents used were dried by standard methods when necessary. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl and petroleum at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

The photoreaction setup is reassembled as following picture with a blue-LED, a fan and a magnetic stirrer. The reaction tube was about 5 cm far from the light source. The 30 W Blue LED (Wavelength: 455 – 460 nm) was directly purchased online from Taobao.com.

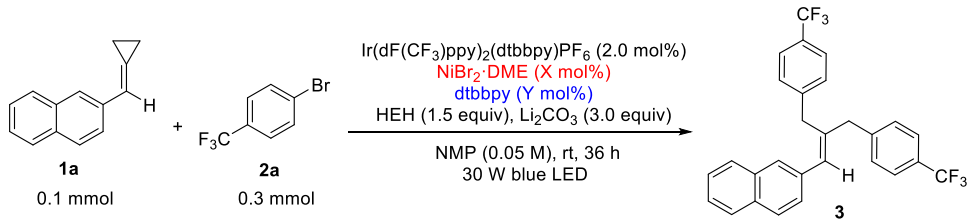
Figure S1. The photoreaction setup without an oil bath and the photoreaction setup in an oil bath

2. Optimization of Reaction Conditions

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a**, 1-bromo-4-(trifluoromethyl)benzene (3.0 equiv), Photocatalyst (2.0 mol%), Electron donor, and Base, Nickel source, and Ligand were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the Solvent was injected under Ar. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (20 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was analyzed by ^1H NMR.

Note: although the side product **67** was also detected in the reactions, its analysis was omitted in the following conditions optimization process for the trace amount (< 10% in most reactions) of this side product. The analysis of other side products in the reaction will be discussed at length in the section on mechanistic studies.

2.1 **Table S1**. Nickel and Ligand Loading Optimization

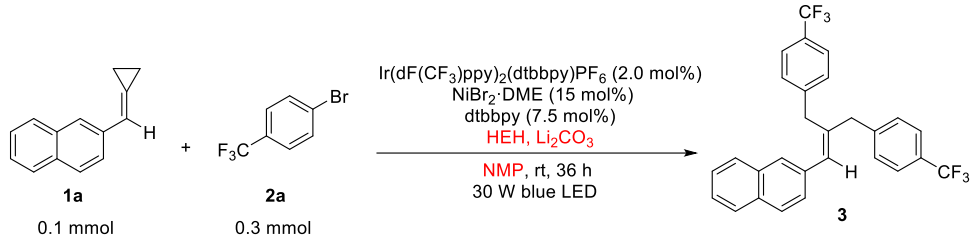


1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	X	Y	**3**, Yield (%)[a]
1	10	10	6
2	10	15	—
3	15	10	30
4	15	7.5	50

[a] Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzen as an internal standard.

2.2 **Table S2**. HEH loading, Base loading, and concentration Optimization

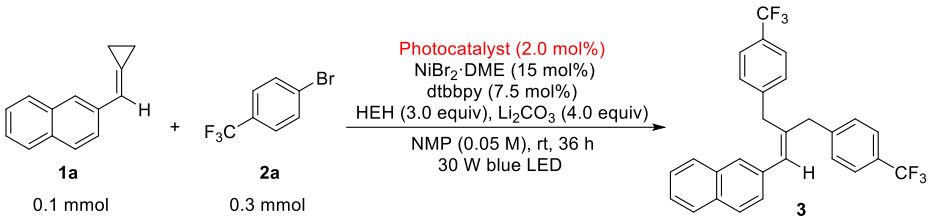


1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	HEH (equiv)	Li_2CO_3 (equiv)	Conc. (M)	**3**, Yield (%)[a]
1	1.0	2.0	0.05	39
2	1.5	—	0.05	25
3	1.5	3.0	0.05	50
4	1.5	4.0	0.05	52
5	1.5	4.0	0.1	42
6	3.0	4.0	0.05	57
7	4.0	6.0	0.05	58
8	3.0	4.0	0.033	56
9	3.0	4.0	0.025	50

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

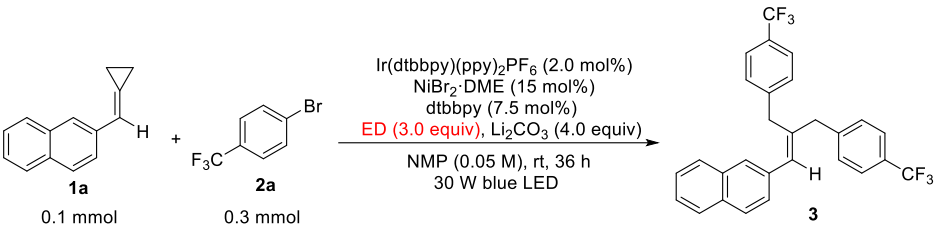
2.3 **Table S3**. Photocatalyst Optimization



Entry	Photocatalyst	**3**, Yield (%)[a]
1	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	57
2	4CzIPN	56
3	$Ir(dF(Me)ppy)_2(dtbbpy)PF_6$	60
4	$Ir(dtbbpy)(ppy)_2PF_6$	62

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

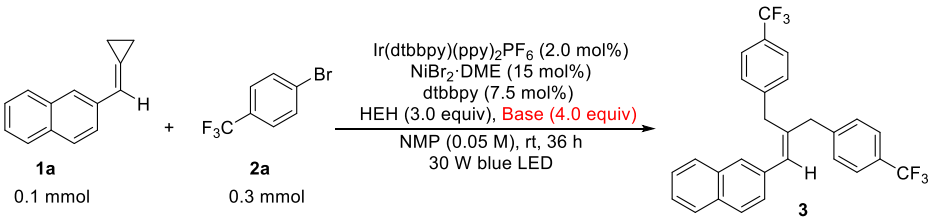
2.4 **Table S4**. Electron donor (ED) Optimization



Entry	Electron donor	**3**, Yield (%)[a]
1	HEH	62
2	TEOA	—
3	^{i}Pr$_2$NEt	7
4	w/o	—

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

2.5 **Table S5**. Base Optimization

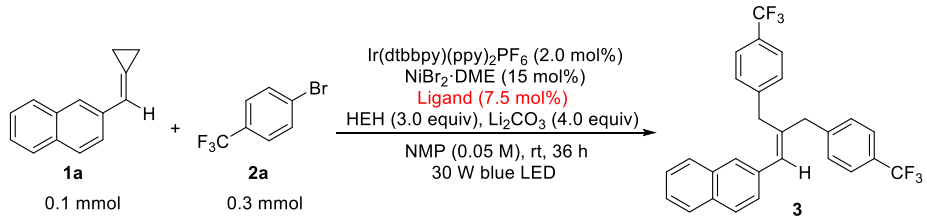


1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	Base	**3**, Yield (%)[a]
1	Li_2CO_3	62
2	Na_2CO_3	32
3	K_2CO_3	30
4	Cs_2CO_3	55
5	K_2HPO_4	41
6	Et_3N	—
7	$^{i}Pr_2NEt$	20
8	w/o	35
9	Li_2CO_3 (3.0 equiv)	56

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

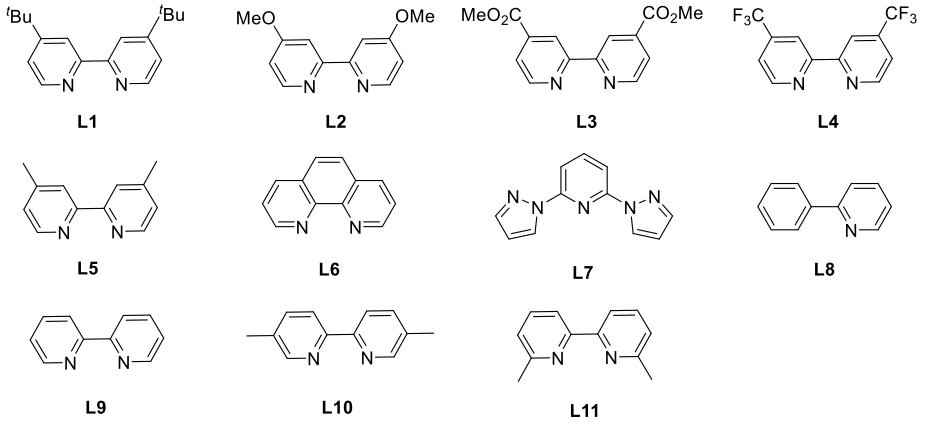
2.6 **Table S6**. Ligand Optimization



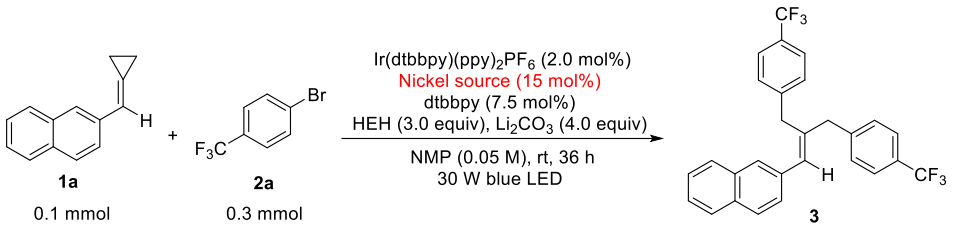
1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	Ligand	**3**, Yield (%)[a]
1	**L1**	62
2	**L2**	50
3	**L3**	6
4	**L4**	8
5	**L5**	62
6	**L6**	50
7	**L7**	4
8[b]	**L8**	< 10
9	**L9**	33
10	**L10**	37
11	**L11**	—
12[b]	**Pyridine**	< 5
13[b]	**PPh_3**	< 5
14	—	8

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard. [b]Ligand loading was 7.5 mol% or 15 mol%.



2.7 **Table S7**. Nickel Source Optimization

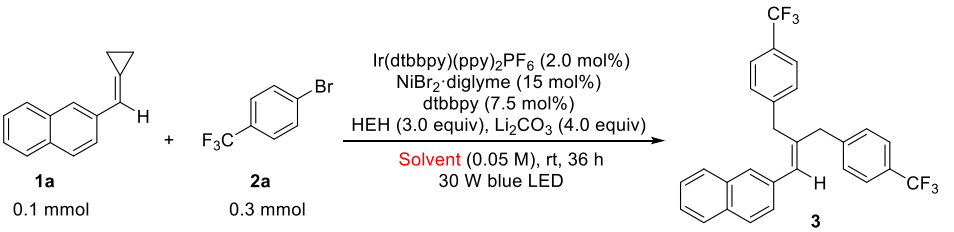


1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	Nickel source	**3**, Yield (%)[a]
1	$NiBr_2$·DME	62
2	$NiBr_2$	55
3	$Ni(acac)_2$	8
4	$NiCl_2$·DME	59
5	$NiBr_2$·diglyme	68
6	$Ni(COD)_2$	56
7	w/o	—

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

2.8 **Table S8**. Solvent Optimization

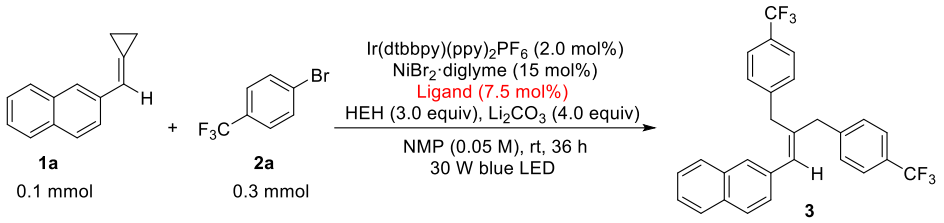


1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	Solvent	**3**, Yield (%)[a]
1	NMP	68
2	THF	37
3	DMF	7
4	CH_3CN	—
5	DMAc	58
6	DMSO	—
7[b]	NMP	63

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard. [b]The mixture was stirred at 50 °C.

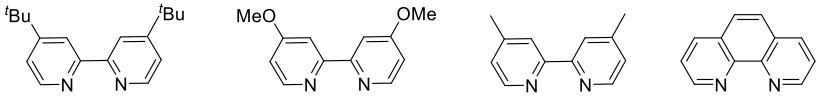
2.9 **Table S9**. Further Ligand Optimization



1a 0.1 mmol + **2a** 0.3 mmol → **3**

Entry	Ligand	**3**, Yield (%)[a]
1	**L1**	68
2	**L2**	59
3	**L5**	74 (70)[b]
4[c]	**L5**	61
5[d]	**L5**	73
6	**L6**	53

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard. [b]Isolated yield on 0.2 mmol scale. [c]$NiBr_2$·diglyme (10 mol%), **L5** (5 mol%). [d]$NiBr_2$·diglyme (20 mol%), **L5** (10 mol%).



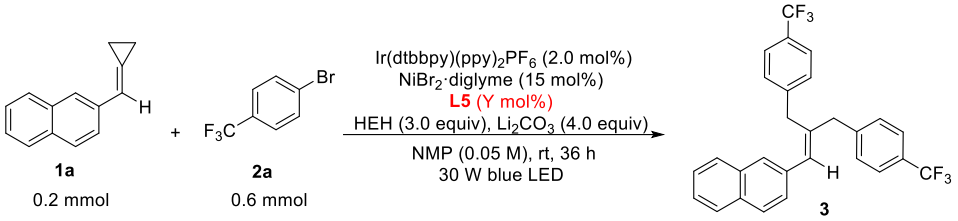
L1

L2

L5

L6

2.10 Table S10. Ligand Loading Optimization



1a 0.2 mmol + **2a** 0.6 mmol → **3**

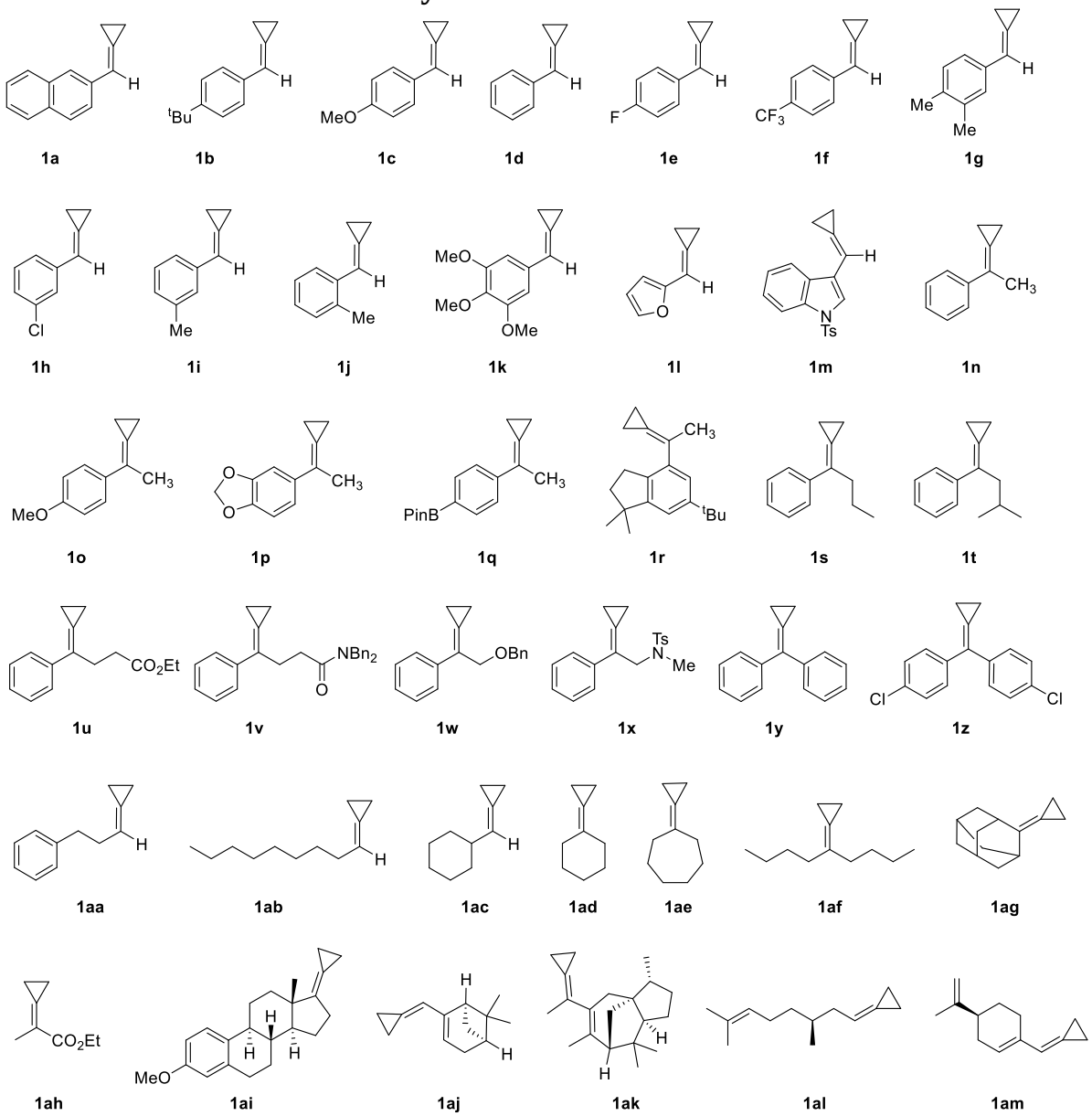
Entry	Y	**3**, Yield (%)[a]
1	0	11
2	2.5	49
3	5	53
4	7.5	72
5	10	55
6	12.5	41
7	15	5
8	17.5	—
9	20	—

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

3. Preparation of Substrates

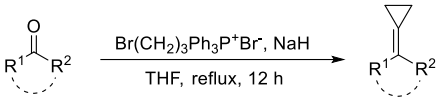
The substrates of methylenecyclopropanes **1** were prepared according to the previous reports and the substrates of ArBr **2** were all commercially available.

3.1 General Procedure for the Synthesis of Substrates 1.



Substrates **1a** – **1t**, **1y – 1ag**, and **1aj – 1am** were synthesized according to the general procedure A,[1] the corresponding ketones or aldehydes are commercially available and directly used without further purification.

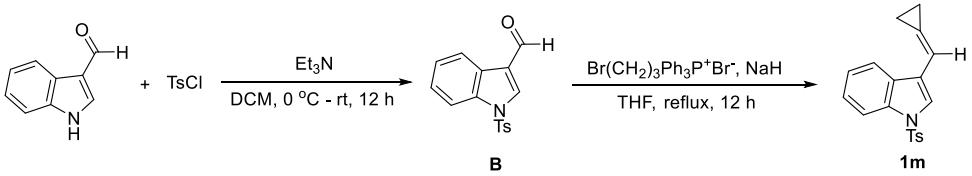
General procedure A



A solution of 3-bromopropyltriphenylphosphonium bromide (2.8 g, 6.0 mmol, 1.2 equiv) and NaH (60% in oil, 0.48 g, 12.0 mmol, 2.4 equiv) in THF (20.0 mL) was stirred at 65 °C in an oil bath under Ar for 4 h. Afterwards the corresponding ketone or aldehyde (5.0 mmol, 1.0 equiv) in THF (5.0 mL) was added and the solution was stirred at 65 °C for another 8 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1) to afford the products in moderate to good yields.

Compounds **1a** – **1f**, **1h** – **1l**, **1n**, **1o**, **1s**, **1y** – **1ah**, and **1aj** – **1am** are known products that have been reported in the previous literature.[2, 3]

Synthesis of substrate 1m (*procedure b*)

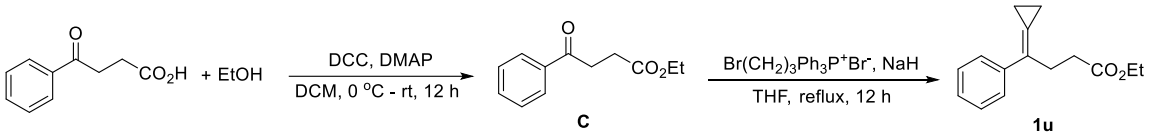


Step 1: A solution of 1*H*-indole-3-carbaldehyde (1.16 g, 8.0 mmol) and 4-methylbenzenesulfonyl chloride (2.29 g, 12.0 mmol) in DCM (20 mL, 0.4 M) was stirred at 0 °C in an ice bath under Ar for 5 mins, then Et_3N (2.2 mL, 16.0 mmol) was injected in one portion. The temperature of the reaction system gradually was warmed to room temperature for 1.0 h later and the mixture was reacted for another 11 h. Upon completion, the reaction was quenched by sat. NH_4Cl solution (20.0 mL) and extracted with $CHCl_2$ for 3 times (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the compound **B** (2.15 g, 90% yield) as a yellow solid.

Step 2: A solution of 3-bromopropyltriphenylphosphonium bromide (2.79 g, 6.0 mmol) and NaH

(60% in oil, 0.48 g, 12 mmol) in THF (20.0 mL) was stirred at 65 °C in an oil bath under Ar for 4.0 h. Afterwards the compound **B** (1.50 g, 5.0 mmol) in THF (5.0 mL) was added and the solution was stirred at 65 °C for another 8 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the substrate **1m** (0.70 g, 43% yield) as a yellow solid.

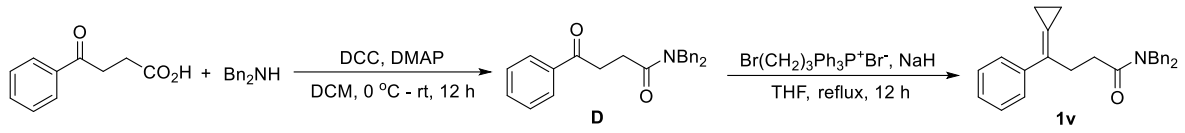
Synthesis of substrate 1u (*procedure c*)



Step 1: A solution of 4-oxo-4-phenylbutanoic acid (1.78 g, 10.0 mmol), EtOH (0.58 mL, 10.0 mmol) and 4-dimethylaminopyridine (122.2 mg, 1.0 mmol) in DCM (30.0 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.27 g, 11.0 mmol) in DCM (10.0 mL) was added dropwise for 25 min. The mixture was warmed to room temperature and stirred for 12 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the compound **C** (2.00 g, 97% yield) as a colorless oil.

Step 2: A solution of 3-bromopropyltriphenylphosphonium bromide (4.18 g, 9.0 mmol) and NaH (60% in oil, 720.0 mg, 18.0 mmol) in THF (25.0 mL) was stirred at 65 °C in an oil bath under Ar for 4.0 h. Afterwards the compound **C** (1.54 g, 7.5 mmol) in THF (5.0 mL) was added and the solution was stirred at 65 °C for another 8.0 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the substrate **1u** (0.83 g, 48% yield) as a yellow oil.

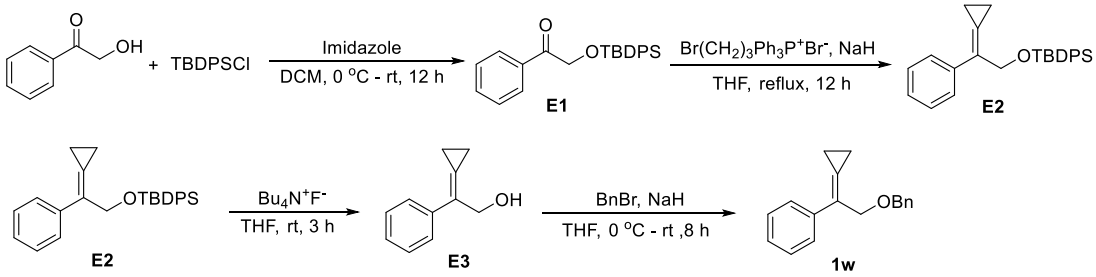
Synthesis of substrate 1v (*procedure d*)



Step 1: A solution of 4-oxo-4-phenylbutanoic acid (1.78 g, 10.0 mmol), dibenzylamine (1.97 g, 10 mmol) and 4-dimethylaminopyridine (122.0 mg, 1.0 mmol) in DCM (30.0 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.2 g, 11.0 mmol) in DCM (10.0 mL) was added dropwise for 25 min. The reaction system was warmed to room temperature and stirred overnight. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the compound **D** (2.68 g, 75% yield) as a yellow solid.

Step 2: A solution of 3-bromopropyltriphenylphosphonium bromide (4.18 g, 9.0 mmol) and NaH (60% in oil, 720.0 mg, 18.0 mmol) in THF (20.0 mL) was stirred at 65 °C in an oil bath under Ar for 4.0 h. Afterwards the compound **D** (2.68 g, 7.5 mmol) in THF (5.0 mL) was added and the solution was stirred at 65 °C for another 8.0 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the substrate **1u** (2.10 g, 73% yield) as a white solid.

Synthesis of substrate 1w and 1x (*procedure e*)[4]



Step 1: A solution of 2-hydroxy-1-phenylethan-1-one (4.08 g, 30.0 mmol) and imidazole (3.06 g, 45 mmol) in CH_2Cl_2 (45.0 mL) under Ar was stirred at 0 °C in an ice bath for 5.0 min, then *tert*-butylchlorodiphenylsilane (11.7 mL, 45.0 mmol) was added dropwise into the mixture. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, the

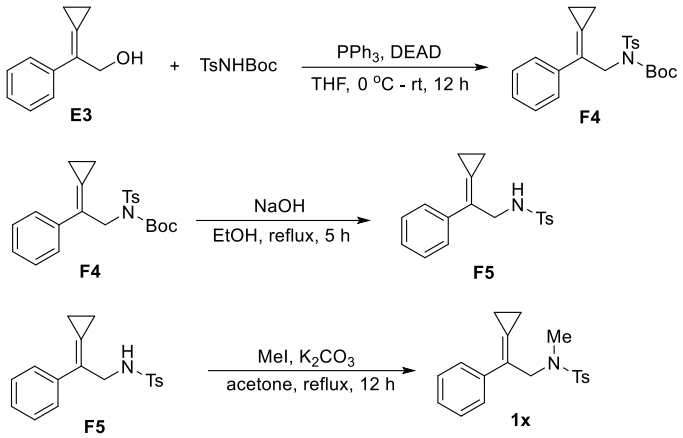
resulting mixture was treated with water (20.0 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the compound **E1** (5.98 g, 53% yield) as a white solid.

Step 2: A solution of 3-bromopropyltriphenylphosphonium bromide (8.36 g, 18.0 mmol) and NaH (60% in oil, 1.44 g, 36.0 mmol) in THF (50.0 mL) was stirred at 65 ^oC in an oil bath under Ar for 4.0 h. Afterwards the compound **E1** (5.61 g, 15.0 mmol) in THF (10.0 mL) was added and the solution was stirred at 65 ^oC for another 8.0 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the compound **E2** (5.08 g, 85% yield) as a white solid.

Step 3: Tetrabutylammonium fluoride (25.4 mL, 25.4 mmol, 1.0 M) was added to a solution of compound **S2** (5.08 g, 12.7 mmol) in THF (25.0 mL). The mixture was stirred under Ar at room temperature for 3 h. the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford compound **E3** (1.85 g, 91% yield) as a pale green solid.

Step 4: A solution of **E3** (0.80 g, 5.0 mmol) and NaH (60% in oil, 0.26 g, 6.5 mmol) in THF (15.0 mL) was stirred at 0 ^oC in an ice bath for 30 min, then benzyl bromide (0.65 mL, 5.5 mmol) was added in one portion. The mixture was warmed to room temperature and stirred for 8.0 h. Upon completion, the mixture was filtered through a celite and concentrated under reduced pressure. The residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 30/1) to afford the substrate **1w** (0.60 g, 48% yield) as a white solid.

Synthesis of substrate 1x (*procedure f*)[4]

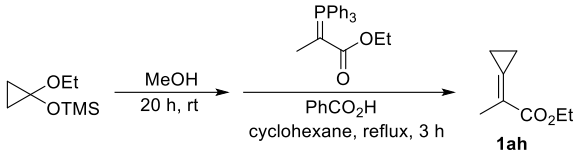


Step 1: A solution of **E3** (0.80 g, 5.0 mmol), *N*-Boc p-toluenesulfonamide (1.62 g, 6.0 mmol), triphenylphosphine (1.96 g, 7.5 mmol) in THF (15.0 mL) was stirred at 0 °C in an ice bath under Ar, then diethyl azodicarboxylate (1.2 mL, 7.5 mmol) was added dropwise into the solution. The mixture was warmed to room temperature and stirred for 12 h. Then, the mixture was filtered through a celite and concentrated under reduced pressure. The residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the compound **F4** (0.80 g, 39% yield) as a yellow solid.

Step 2: A solution of **F4** (620.3 mg, 1.5 mmol) and NaOH (180.0 mg, 4.5 mmol) in EtOH (8.0 mL) was stirred under reflux for 5.0 h. The resulting mixture was treated with water (10.0 mL) and extracted with CH_2Cl_2 (3 × 8 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to afford the compound **F5** (438.8 mg, 93% yield) as a white solid.

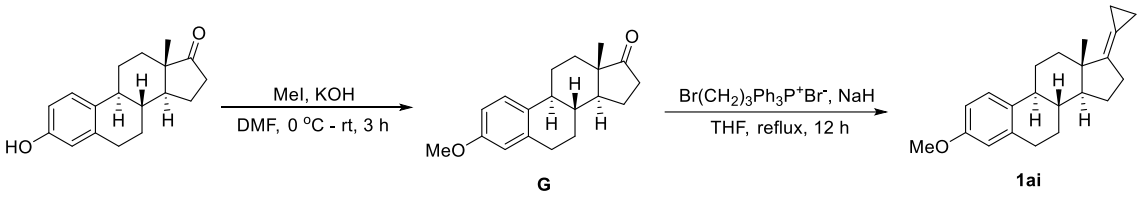
Step 3: A solution of **F5** (313.4 mg, 1.0 mmol), K_2CO_3 (690.0 mg, 5.0 mmol) and iodomethane (0.31 mL, 5.0 mmol) in acetone (5.0 mL) was stirred under reflux for 12 h. The mixture was filtered through a celite and concentrated under reduced pressure. The residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the substrate **1x** (0.31 g, 95% yield) as a yellow solid.

Synthesis of substrate 1ah (*procedure g*)[3]



A solution of (1-ethoxycyclopropoxy)trimethylsilane (1.74 g, 10.0 mmol) in methanol (4.9 mL) was stirred at room temperature for 20 h. Then the solvent was removed under reduced pressure. The resulting residue and benzoic acid (0.24 g, 2.0 mmol) were dissolved in cyclohexane (50.0 mL). The mixture was stirred at 80 °C in an oil bath and ethyl 2-(triphenyl-λ5-phosphaneylidene)propanoate (4.35 g, 12.0 mmol) was added gradually. The solution was allowed to reflux for 3.0 h. Upon completion, the solution was cooled to room temperature. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the substrate **1ah** (0.74 g, 53%) as a colorless oil.

Synthesis of substrate 1ai (*procedure h*)

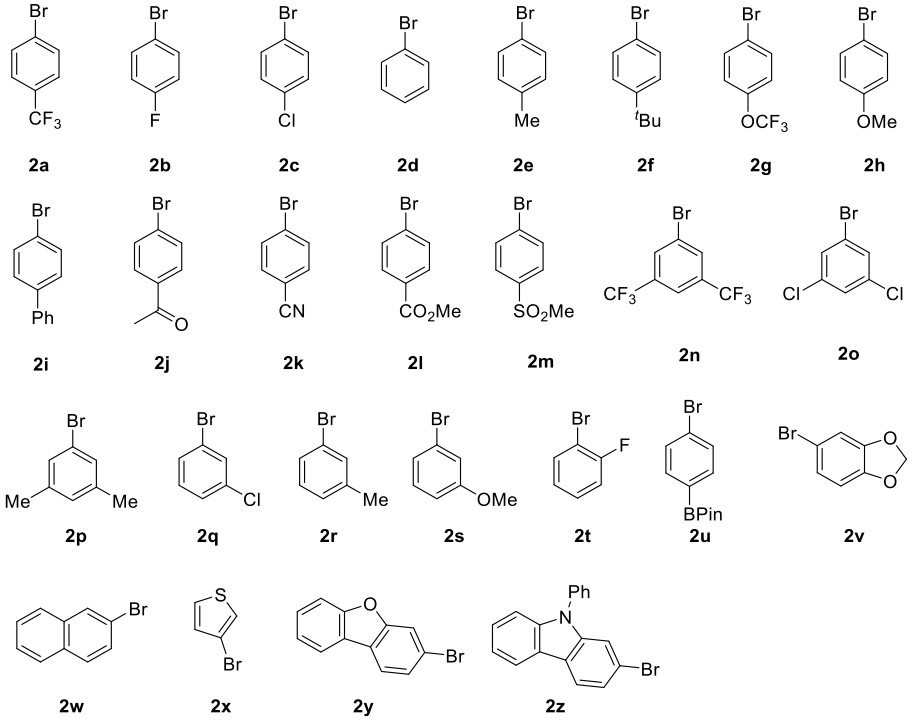


Step 1: A solution of Estrone (1.35 g, 5.0 mmol), KOH (561.1 mg, 10.0 mmol) and iodomethane (0.63 mL, 10.0 mmol) in DMF (25.0 mL) was stirred at 0 °C in an ice bath. The reaction mixture was warmed to room temperature and stirred for 3.0 h. The solution was poured onto ice/water and extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield **G** (1.29 g, 91% yield) as a white solid.[5]

Step 2: A solution of 3-bromopropyltriphenylphosphonium bromide (2.23 g, 4.8 mmol) and NaH (60% in oil, 0.38 g, 9.6 mmol) in THF (15.0 mL) was stirred at 65 °C in an oil bath under Ar for 4.0 h. Afterwards the compound **G** (1.14 g, 4.0 mmol) in THF (5.0 mL) was added and the solution was stirred at 65 °C for another 8.0 h. Upon completion, the solution was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate =

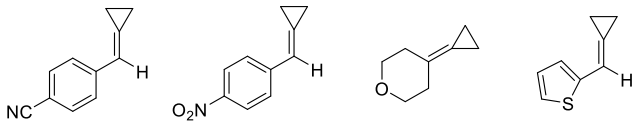
50/1) to afford the substrate **1ai** (0.63 g, 51% yield) as a white solid.

Substrates of ArBr

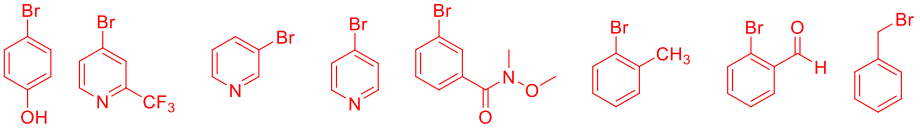


3.2 Unsuccessful examples

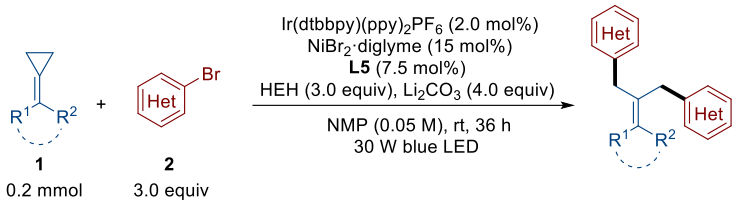
For the substrates of methylenecyclopropanes



For the substrates of ArBr



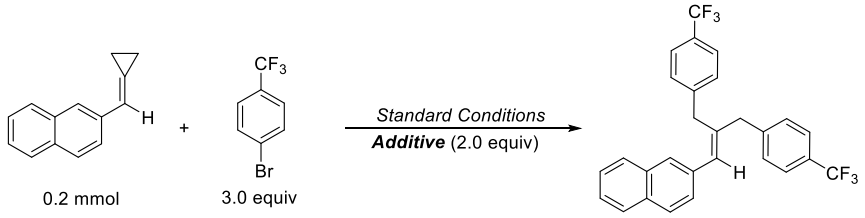
4. General Procedure B for the Synthesis of Products



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1** (0.2 mmol), ArBr **2** (0.6 mmol, 3.0 equiv), $Ir(dtbbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv), ligand **L5** (2.8 mg, 7.5 mol%), $NiBr_2$·diglyme (10.6 mg, 15 mol%) degassed NMP (4.0 mL, 0.05 M) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. Upon completion, EtOAc (20 mL) was added into the reaction tube and the reaction mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was purified by using PTLC.

5. Mechanistic Studies

5.1 Radical Trapping Experiments



Additive	TEMPO	BHT	DPE
Yield (%)	69%	66%	59%

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (36.0 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (84 μL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv), $NiBr_2$·diglyme (10.6 mg, 15 mol%), ligand **L5** (2.8 mg, 7.5 mol%), radical scavenger (0.4 mmol, 2.0 equiv), and degassed NMP (4.0 mL, 0.05 M) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (33.6 mg, 1.0 equiv) used as an internal standard was added after removal of the reaction tube from the light source. EtOAc (20 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 8.0 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR spectroscopy.

The reaction can proceed well in the presence of these radical scavengers, which may imply that the free radical pathway was not involved in the process of generating products.

5.2 Emission Quenching Studies

All the emission intensities were recorded by Varian Cary Eclipse spectrometer. Solutions of $Ir(dtbpy)(ppy)_2PF_6$ (2×10^{-5} M) in dry NMP were excited at 380 nm and the emission intensity was collected at the maximum wavelength 571 – 572 nm. Solutions of different concentration of HEH, $NiBr_2$·diglyme and substrate **1a** were prepared respectively and introduced to a 1.0 cm path length quartz cuvette equipped with a Teflon® septum.

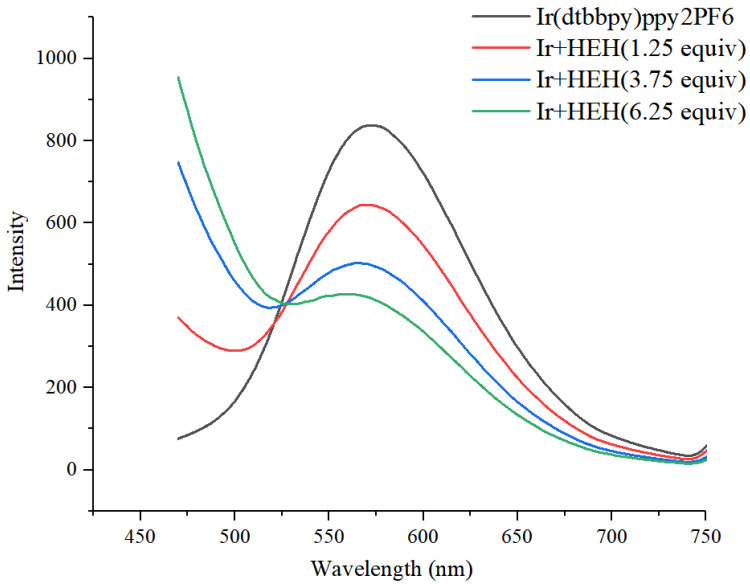


Figure S2. Stern-Volmer Quenching of Photocatalyst with HEH

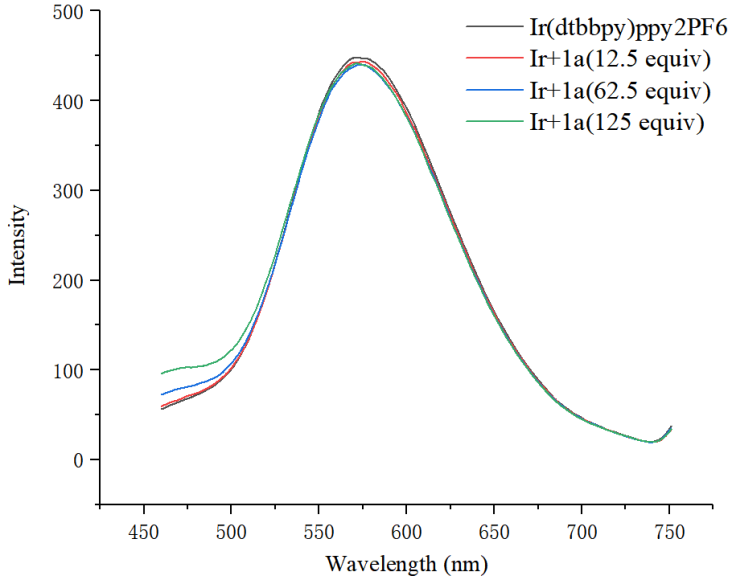


Figure S3. Stern-Volmer Quenching of Photocatalyst with Substrate **1a**

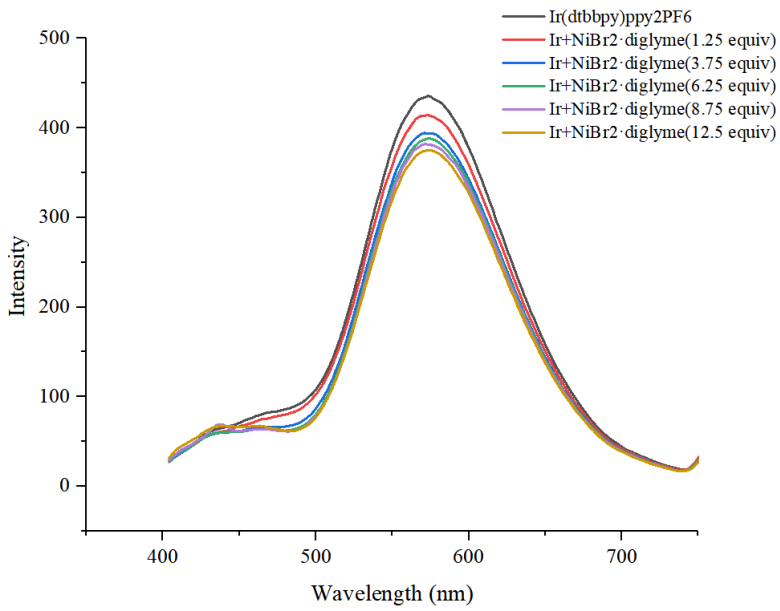


Figure S4. Stern-Volmer Quenching of Photocatalyst with $NiBr_2$·diglyme

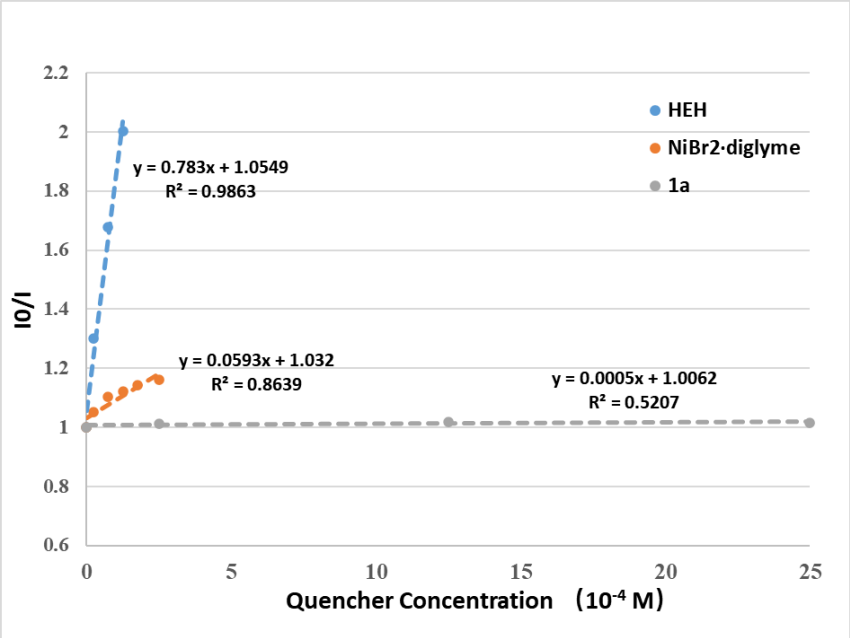
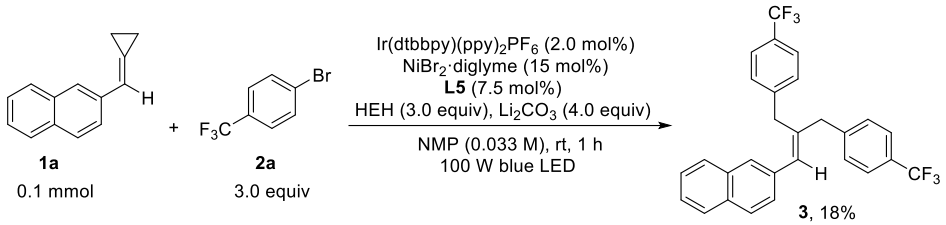


Figure S5. Stern-Volmer Quenching of Photocatalyst with HEH, **1a**, and $NiBr_2$·diglyme

5.3 Quantum Yield Determination[6]

To further investigate the mechanism of the reactions, we employed the model reaction of **1a** to **3** to measure the quantum yield. The photo flux was determined by ILT1400 Portable Radiometer/Photometer. ΔE was calculated by deduction of the recorded data directly read from the apparatus. ΔE and n_x both were measured three times and their average values were taken respectively.



A cuvette equipped with a magnetic stir bar was added substrate **1a** (18.0 mg, 0.1 mmol), 1-bromo-4-(trifluoromethyl)benzene (42 μL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 mol%), HEH (76.0 mg, 3.0 equiv), and Li_2CO_3 (29.4 mg, 4.0 equiv), $NiBr_2$·diglyme (5.3 mg, 15 mol%), ligand **L5** (1.4 mg, 7.5 mol%), and degassed NMP (3.0 mL, 0.033 M) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (100 W) and stirred for 1.0 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the reaction tube from the light source. EtOAc (20 mL) was added into the reaction tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR. The quantum yield is calculated to be 0.0365.

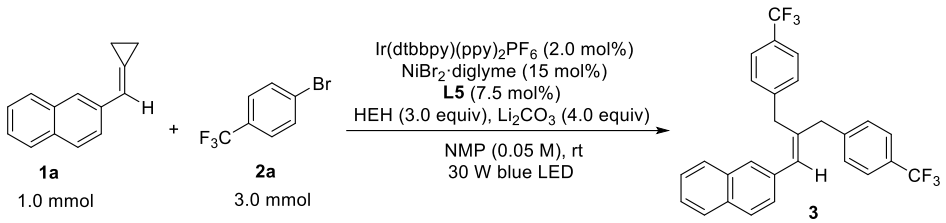
$$\phi = \frac{n_x}{n_p} = \frac{n_x}{\frac{\Delta E \times S \times t}{N_A h v}} = \frac{n_x \times N_A \times h \times c}{\Delta E \times S \times t \times \lambda}$$

$$= \frac{0.018 \times 10^{-3} mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m \cdot s^{-1}}{(12.0 \times 10^{-3} W \cdot cm^{-2} \times 3 cm^2) \times 3600 s \times 455 \times 10^{-9} m} = 0.0365$$

n_x is the amount of photochemical or photophysical events x occurred during irradiation, n_p is the number of photons absorbed by the reactant. E is the radiant power. S is the irradiated area: 3 cm^2; t is the irradiated time: 3600 s; N_A is the Avogadro constant: 6.022×10^{23}/mol; h is the Planck constant: 6.626×10^{-34} J·s; v is the frequency of incident light; c is velocity of light 2.998×10^8 m/s). λ is the wavelength: 455 nm; n_x was analyzed by ^1H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

5.4 Dark-light Experiment[1]

In the process of conditions optimization, we realized the reaction could not be initiated in the absence of light source. To further have a better insight on the effect of light source in this reaction, we conduct dark-light experiment employed the model reaction of **1a** to **3**.



In a flame dried Schlenk tube (80 mL) equipped with a magnetic stir bar, substrate **1a** (180.1 mg, 1.0 mmol), 1-bromo-4-(trifluoromethyl)benzene (0.42 mL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (18.3 mg, 2.0 mol%), HEH (759.9 mg, 3.0 equiv) and Li_2CO_3 (294.3 mg, 4.0 equiv), $NiBr_2$·diglyme (52.8 mg, 15 mol%), and ligand **L5** (13.8 mg, 7.5 mol%)were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then degassed NMP (20.0 mL, 0.05 M) was added. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred vigorously. The lights were turned on and off per one hour, and samples taken from the solution (0.5 mL per time) were analyzed by ^1H NMR with 1,3,5-trimethoxybenzen as an internal standard.

Time (h)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Yield (%)	0	12	12	31	31	47	47	57	57	64	64

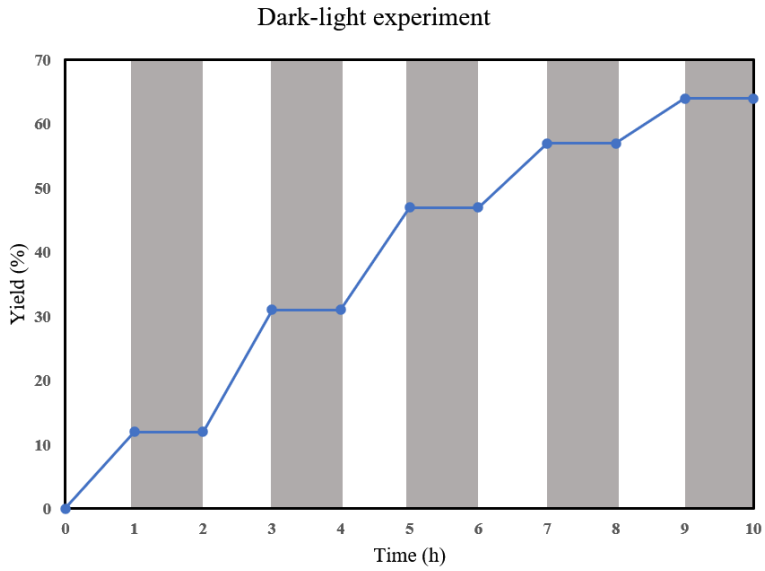


Figure S6. Light/dark cycle experiments

5.5 Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model Chi660e. Except for the substrate **1a** in MeCN (0.001 M) was tested with Bu_4NPF_6 (0.1 M) as the supporting electrolyte, other samples were all tested in DMAc (0.01 M) with Bu_4NBF_6 (0.1 M) as the supporting electrolyte using a glassy carbon as the working electrode, a Pt as the counter electrode, and a saturated calomel electrode reference electrode. Argon was bubbled into the system for 20 min to degas the solution. Scan rate = 0.1 V/s, 2 sweep segments, a sample interval of 0.001 V.

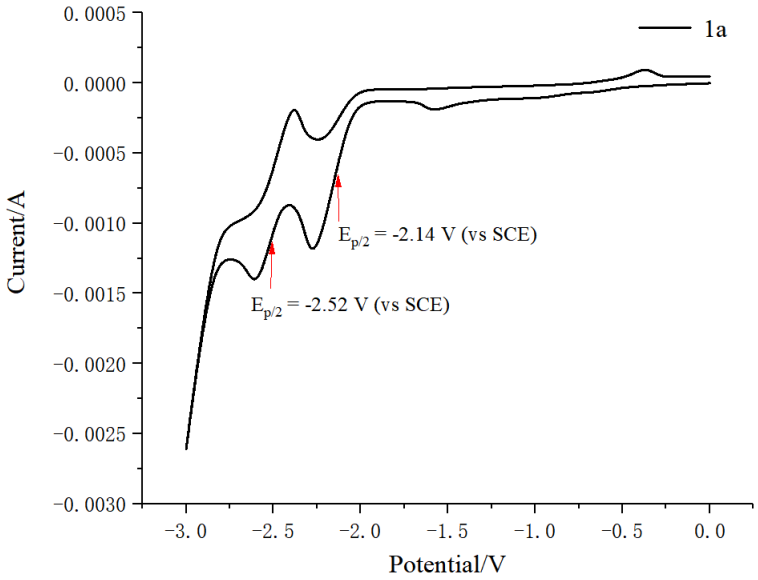


Figure S7. Cyclic Voltammogram of **1a**

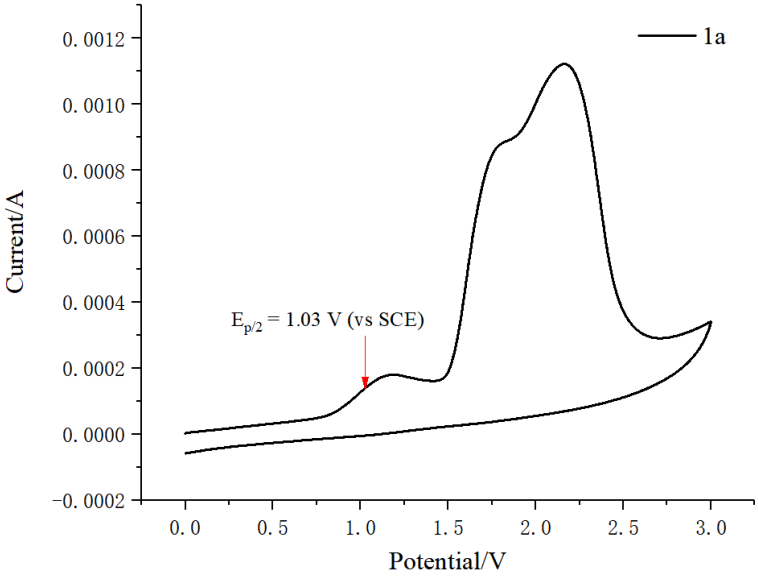


Figure S8. Cyclic Voltammogram of **1a**

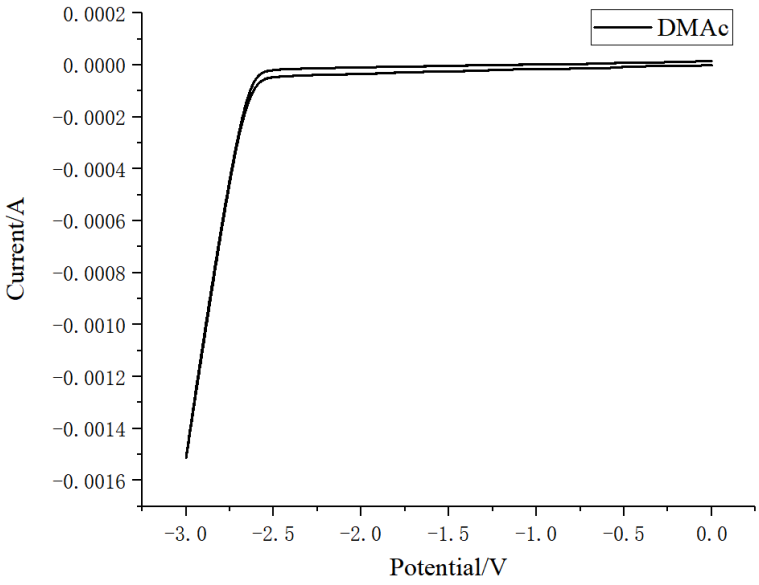


Figure S9. Cyclic Voltammogram of the Solvent DMAc

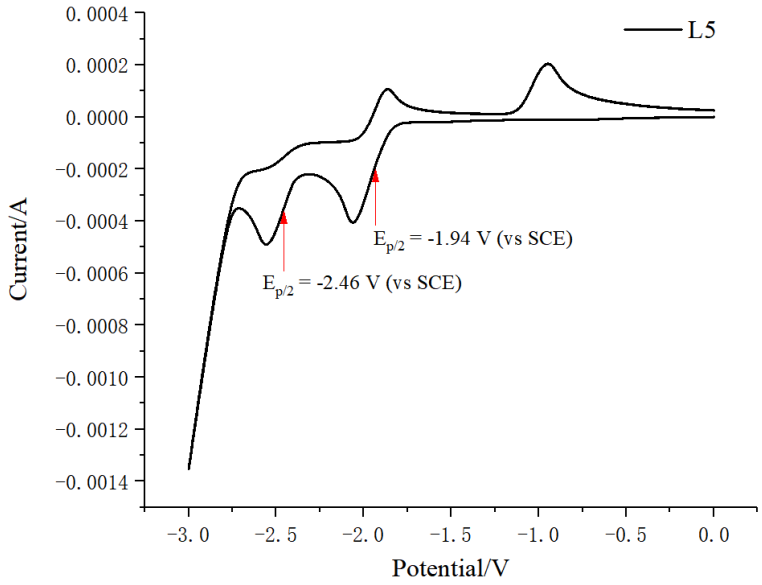


Figure S10. Cyclic Voltammogram of the Ligand **L5**

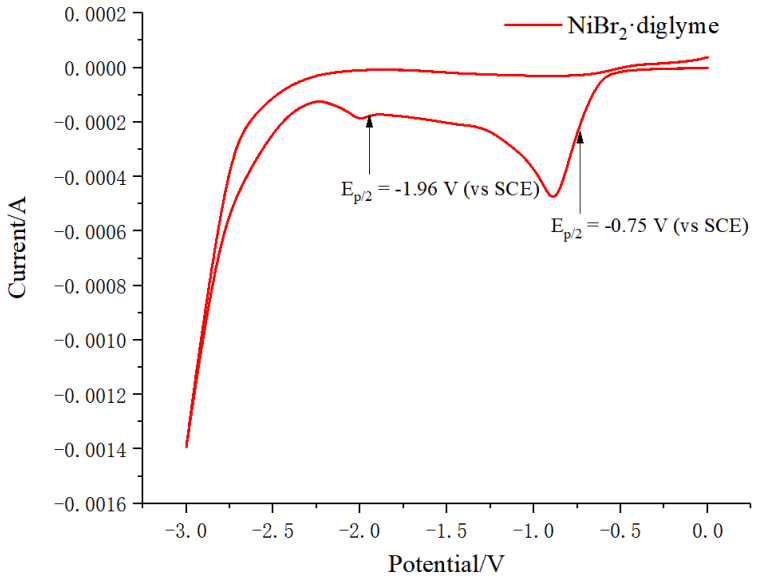


Figure S11. Cyclic Voltammogram of the $NiBr_2$·diglyme; The first irreversible reduction at $E_{p/2}$ = - 0.75 V vs. SCE should correspond to Ni^{II}/Ni^{I} redox couple, and irreversible second reduction at $E_{p/2}$ = - 1.96 V vs. SCE should correspond to second reduction of Ni^{I}/Ni^{0} redox couple.

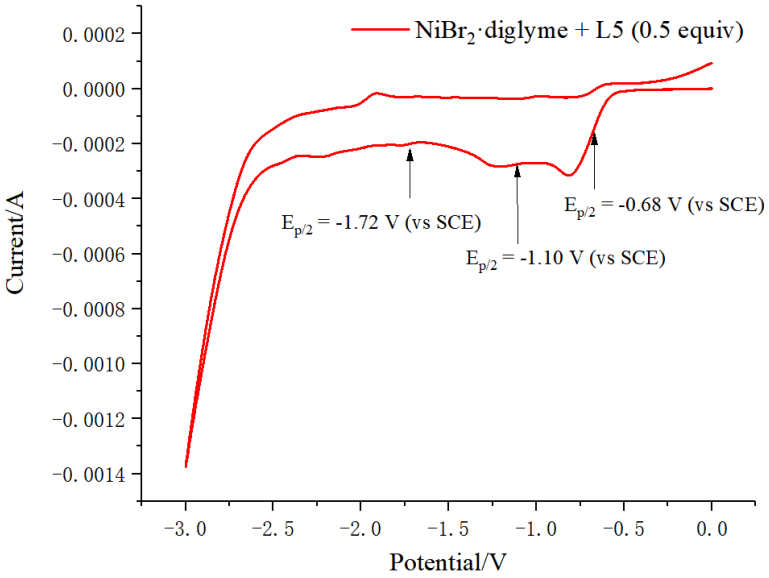


Figure S12. Cyclic Voltammogram of the $NiBr_2$·diglyme with **L5** (0.5 equiv); The first irreversible reduction at $E_{p/2}$ = - 0.68 V vs. SCE should correspond to Ni^{II}/Ni^{I} redox couple; The second irreversible reduction at $E_{p/2}$ = - 1.10 V vs. SCE should correspond to second reduction of Ni^{I}(L5)/Ni^{0}(L5) redox couple; The third irreversible reduction at $E_{p/2}$ = - 1.72 V vs. SCE possibly correspond to second reduction of Ni^{I}/Ni^{0} redox couple.

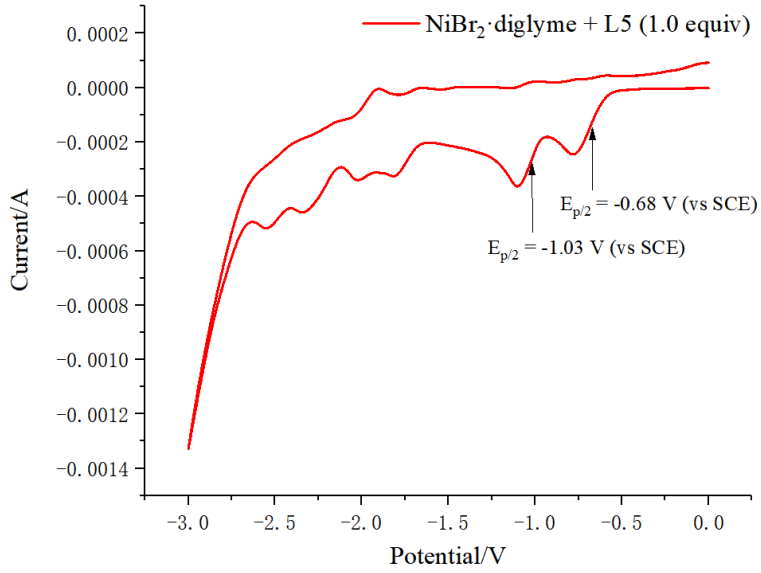


Figure S13. Cyclic Voltammogram of the $NiBr_2$·diglyme with **L5** (1.0 equiv); The first irreversible reduction at $E_{p/2}$ = - 0.68 V vs. SCE should correspond to Ni^{II}(L5)/Ni^{I}(L5) redox couple; The second irreversible reduction at $E_{p/2}$ = - 1.03 V vs. SCE should correspond to second reduction of Ni^{I}(L5)/Ni^{0}(L5) redox couple;

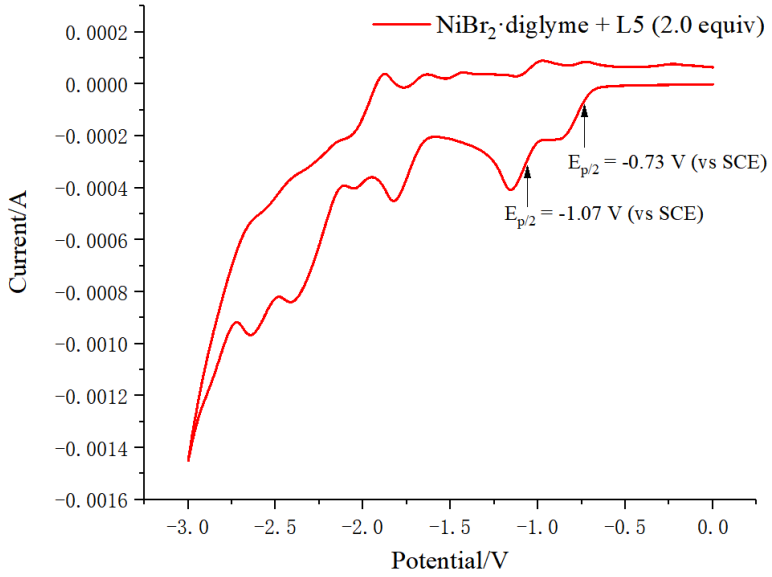


Figure S14. Cyclic Voltammogram of the $NiBr_2$·diglyme with **L5** (2.0 equiv); The first irreversible reduction at $E_{p/2}$ = - 0.73 V vs. SCE should correspond to Ni^{II}(L5)/Ni^{I}(L5) redox couple; The second irreversible reduction at $E_{p/2}$ = - 1.07 V vs. SCE should correspond to second reduction of Ni^{I}(L5)/Ni^{0}(L5) redox couple;

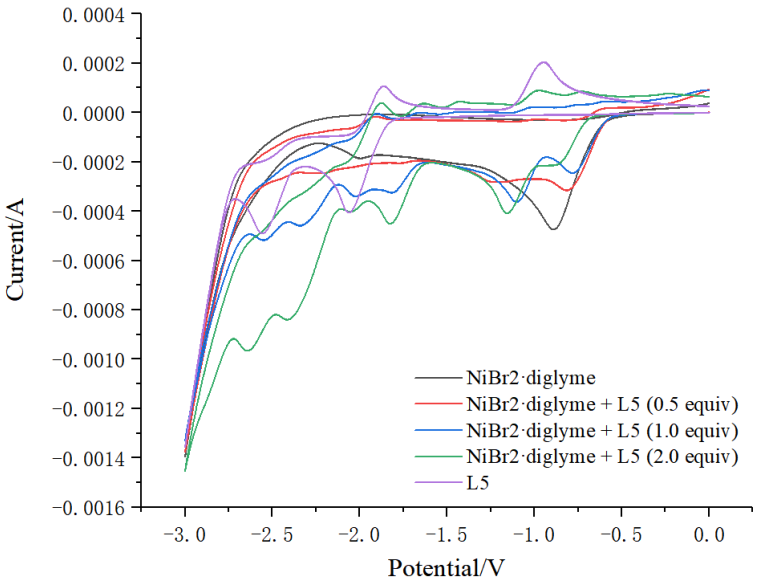
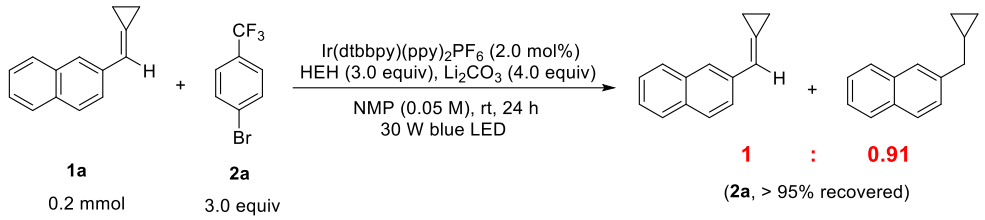


Figure S15. Stacked Cyclic Voltammograms of **Figures S10-S14**

5.6 Control experiments

5.6.1 Investigation on transformations of substrate 1a in the absence of nickel catalyst and ligand



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (36.0 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (84 μL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (2.0 min) and argon backfill for three times. Then degassed NMP (4.0 mL, 0.05 M) were added under Ar. The reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 24 h at room temperature. Upon completion, EtOAc (20 mL) was added into the reaction tube and the reaction mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude product was purified by using PTLC (Pure Hexanes).

Apart from the recovered **1a** was detected, the reduced product of **1a** was also monitored[7] in the **^{1}H NMR** spectrum. Other side products transformed from **1a** were not observed. Notably, owing to the similar polarity and molecular weight, it was hard to separate these two compounds. In addition, the substrate **2a** was kept unchanged under such conditions.

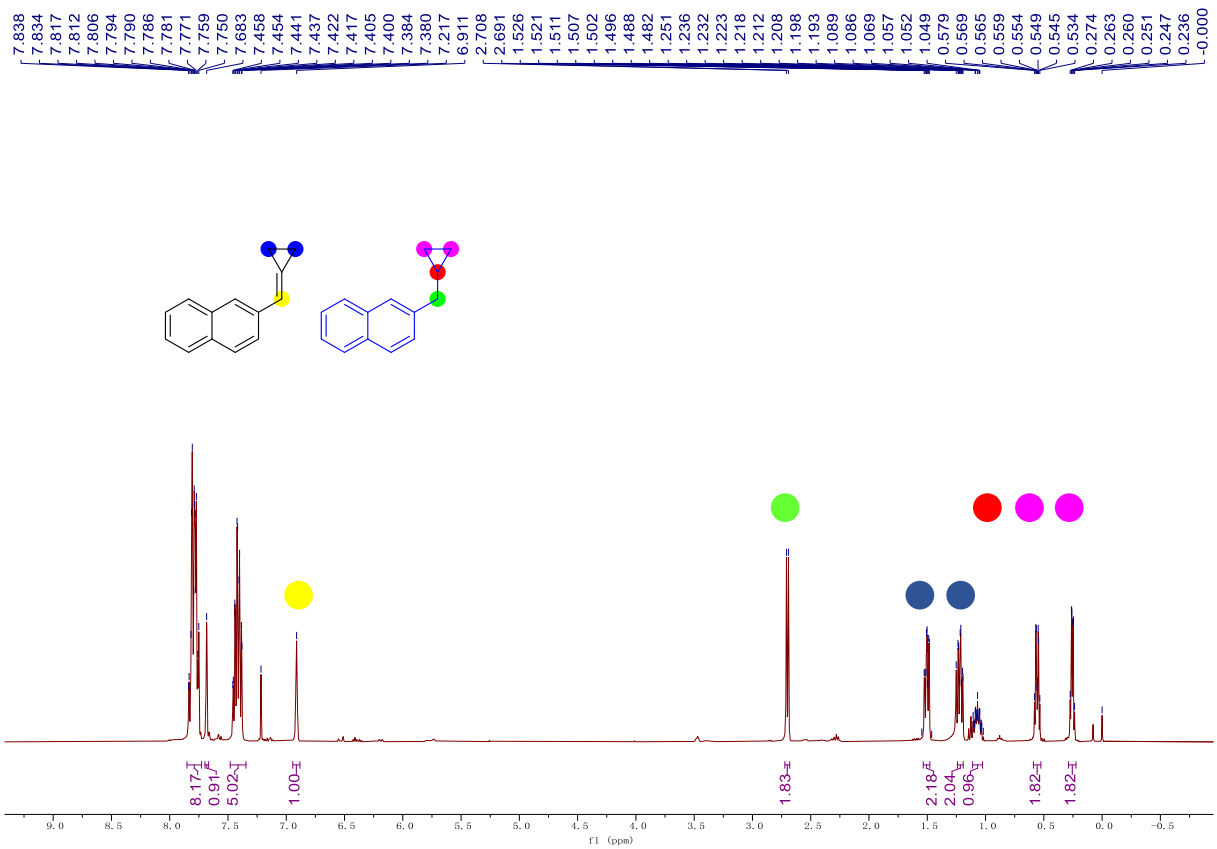
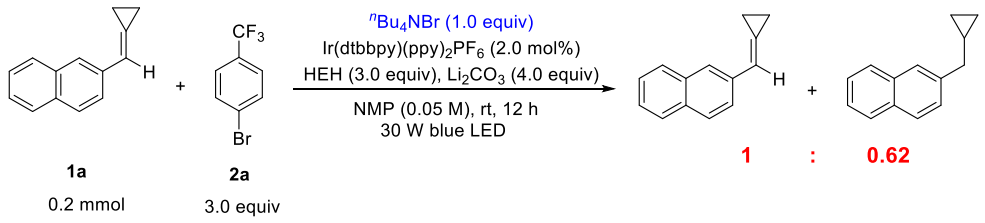


Figure S16. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of a mixture (**1a** & a reduced product, 1 : 0.91)

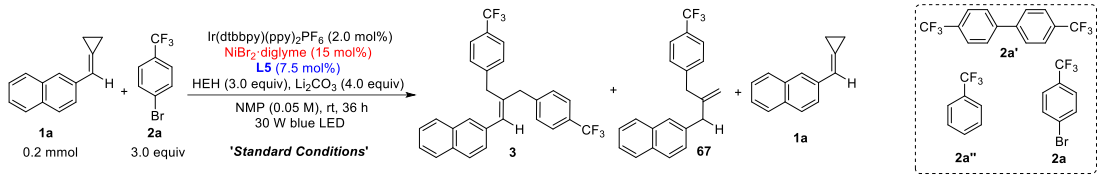


According to the above procedure, when ^{n}BuNBr (1.0 equiv) used as a bromide source was added into the reaction, the reduced product was still the only product obtained after 12 h photoirradiation. No ring-opening product was observed under this condition excluding the possibility that MCPs activation with bromide.

5.6.2 Investigation of Ni/L loading influence

In the process of conditions optimization, yields of product **3** in the presence of different ligand loading were provided in the section **2.10**. In terms of the results, ligand loading has a significant impact on the yield of desired product **3**. To gain more insights into the details of the reaction,

herein we analyzed the transformations of the substrates under diverse Ni/L loading conditions. For Entry 4 and Entry 5 in the following table, most substrate **1a** was transformed into other complexes that failed to be figured out.

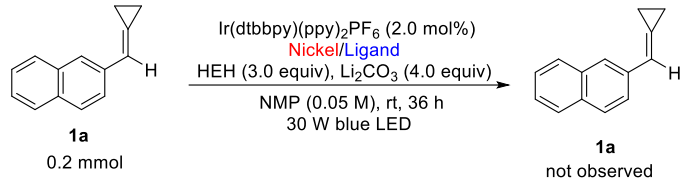


Entry	Deviation from Standard Conditions	**3**, Yield (%)[a]	**67**, Yield (%)[a]	**1a**, Recovery (%)[a]	**2a'**, Yield (%)[b]	**2a''**, Yield (%)[b]	**2a**, Recovery (%)[b]
1	None	72	8	0	21	trace	n.d.
2	$NiBr_2$·diglyme (10 mol%), **L5** (12 mol%)	0	0	96	45	trace	n.d.
3	$NiBr_2$(dtbpy) (10 mol%)	7	0	92	41	trace	n.d.
4	$NiBr_2$·diglyme (15 mol%), w/o Ligand	11	7	13	10	37	13
5	$NiBr_2$ (15 mol%), w/o Ligand	8	30	5	8	43	15
6	$NiBr_2$(dtbpy) (7.5 mol%), $NiBr_2$·diglyme (7.5 mol%)	62	4	0	17	trace	n.d.

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard. [b]Isolated yields calculated on 0.6 mmol scale. n.d. = not detected.

Noticing that the substrate **1a** was almost kept unchanged in entry 2 and entry 3, we wondered whether the complex NiL_n (Nickel/L_n < 1) was able to react with the methylenecyclopropanes substrate. Hence, we conducted experiments in the absence of ArBr.

In the absence of ArBr



Condition A: $NiBr_2$·diglyme (15 mol%), **L5** (7.5 mol%)

Condition B: $NiBr_2$·diglyme (10 mol%), **L5** (12 mol%)

Condition C: $NiBr_2$·diglyme (10 mol%), **w/o** Ligand

Condition D: $NiBr_2$(dtbpy)

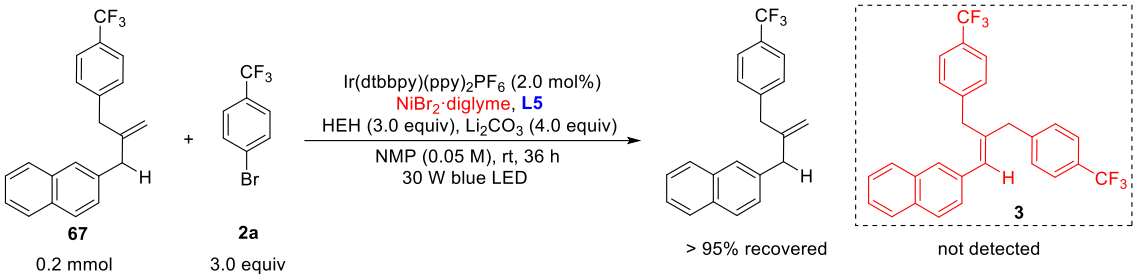
The substrate **1a** was completely decomposed under the above conditions A, B, C, and D. However, except the compounds **3b** and **3c** (will be discussed in section **5.6.4**) were observed, other resulting ring-opening products were mixed together owing to their similar polarity and molecular weight and we failed to figure out their structures.

The title compound **67** was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H), 7.57 – 7.52 (m, 3H), 7.49 – 7.43 (m, 2H), 7.31

– 7.24 (m, 4H), 4.96 (d, J = 1.9 Hz, 1H), 4.89 (d, J = 1.9 Hz, 1H), 3.43 (s, 2H), 3.34 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.3, 143.6, 136.6, 133.5, 132.2, 129.4, 129.2, 128.6 (q, J = 32.6 Hz), 128.0, 127.6, 127.47, 127.46, 127.4, 126.0, 125.4, 125.2 (q, J = 4.0 Hz), 124.3 (q, J = 271.8 Hz), 114.4, 42.5, 41.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (acetone)**: ν 2911, 1616, 1507, 1417, 1322, 1162, 1120, 1066, 1018, 901, 817, 755 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{21}H_{17}F_3$ 326.1277; found 326.1270.

5.6.3 Investigation of the potential transformations of 67



Condition A: $NiBr_2$·diglyme (10 mol%), **L5** (12 mol%)

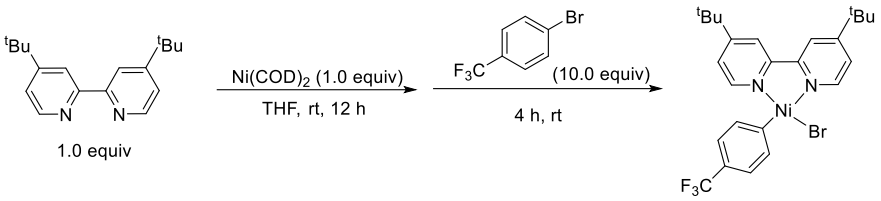
Condition B: $NiBr_2$·diglyme (15 mol%), **L5** (7.5 mol%)

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, compound **67** (65.2 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (84 μL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv), **L5** (Condition A: 12 mol% or Condition B: 7.5 mol%), $NiBr_2$·diglyme (Condition A: 10 mol% or Condition B: 15 mol%), and degassed NMP (4.0 mL, 0.05 M) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. The crude was analyzed by ^{1}H NMR relative to 1,3,5-trimethoxybenzen as an external standard.

Whether under the Condition A or Condition B, the compound **3** was not observed and compound **67** was kept unchanged.

5.6.4 Control Experiments with *(dtbpy)Ni(p-CF_3Ar)Br*

Synthesis of *(dtbpy)Ni(p-CF_3Ar)Br*

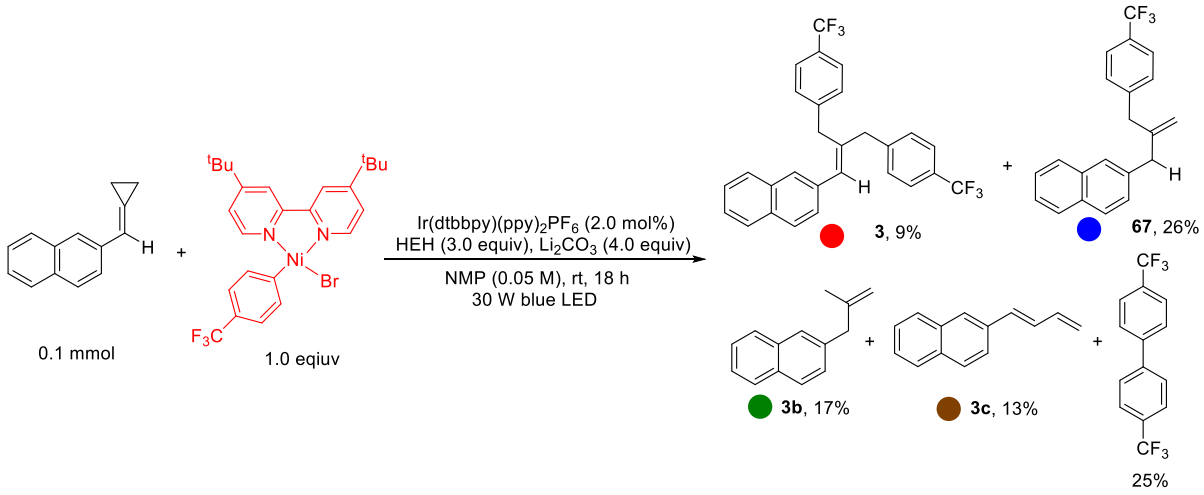


The *(dtbpy)Ni(p-CF₃Ar)Br* was prepared according to the literature procedure.[8] In an Ar-filled glove-box, a solution of $Ni(COD)_2$ (275.1 mg, 1.0 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (268.4 mg, 1.0 mmol) was stirred in dry THF (5.0 mL) for 12 h at room temperature, then 1-bromo-4-(trifluoromethyl)benzene (1.4 mL, 10.0 mmol) into the dark purple solution. The mixture was stirred for another 4.0 h and the color turned into deep red. Dry pentane (30 mL) was added into the flask and the resulting mixture was filtered. The precipitate was washed with dry pentane (3 × 15 mL) and dried to afford *(dtbpy)Ni(p-CF₃Ar)Br* (336.8 mg, 61% yield) as a brown solid. The product was directly used without further purification.

The ^{1}HNMR data of *(dtbpy)Ni(p-CF₃Ar)Br* are consistent with those in the previous report.[8]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.14 (s, 1H), 7.77 – 7.63 (m, 4H), 7.44 (br, 1H), 7.10 (br, 4H), 1.34 (s, 18H).

Stoichiometric Experiments using *(dtbpy)Ni(p-CF₃Ar)Br* as catalyst



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (18.0 mg, 0.1 mmol), $Ir(dtbpy)(ppy)_2PF_6$ (1.8 mg, 2.0 mol%), HEH (76.0 mg, 3.0 equiv), and Li_2CO_3 (29.4 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (2.0 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box,

where *(dtbpy)Ni(p-CF$_3$Ar)Br* (55.2 mg, 1.0 equiv) and degassed NMP (2.0 mL, 0.05 M) were added. The mixture was stirred for 10 min before removed from the glove-box. Then the reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (20 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^{1}H NMR relative to 1,3,5-trimethoxybenzen [δ 6.08 (s, 3H)] as an external standard. Also, 4,4'-bis(trifluoromethyl)-1,1'-biphenyl was isolated in 25% yield.

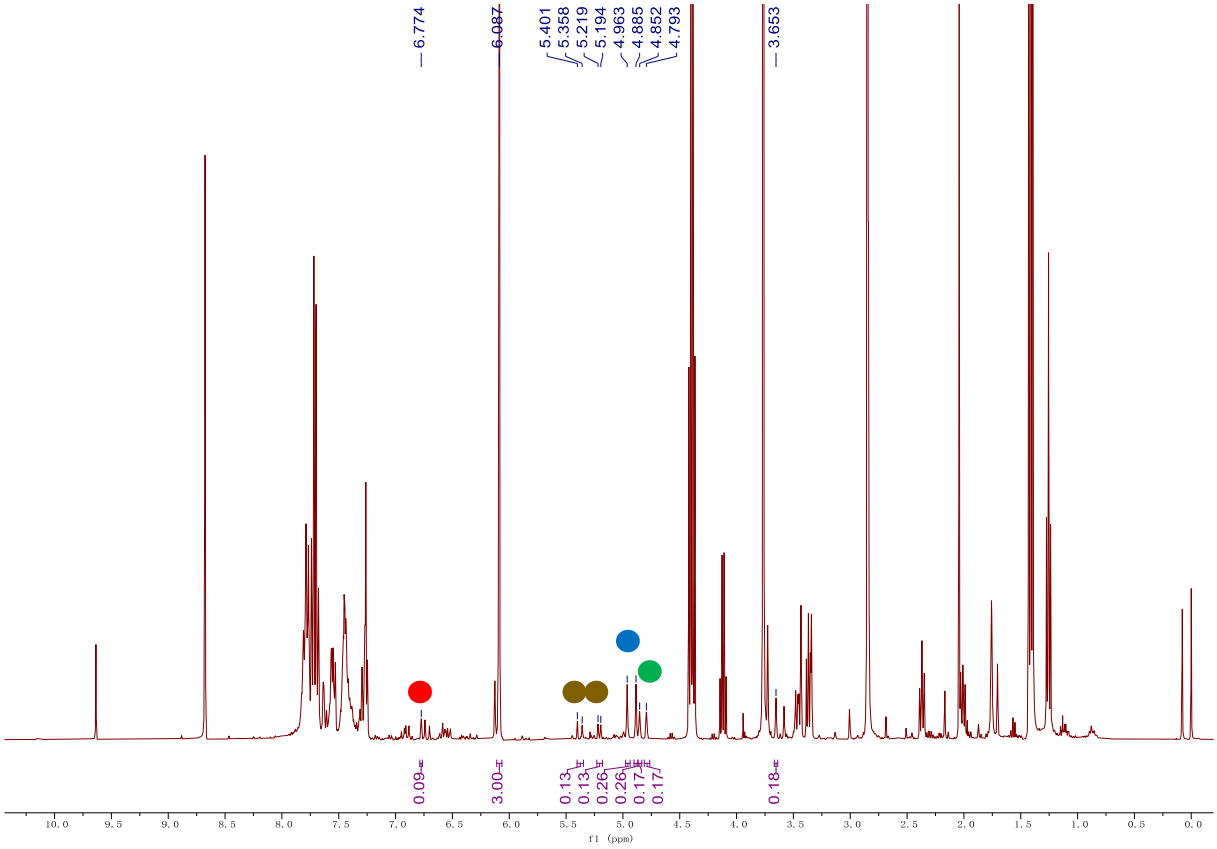
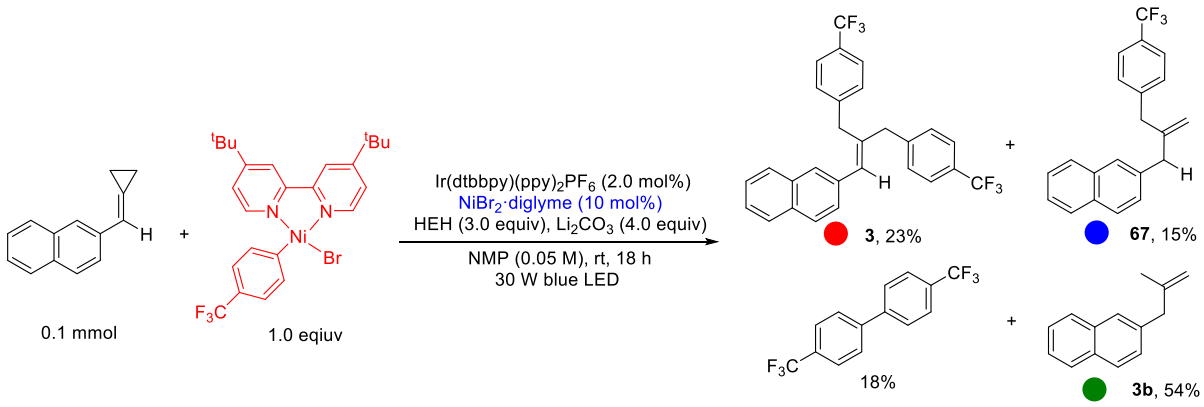


Figure S17. **^{1}H NMR** analysis of the crude product

Stoichiometric experiments using *(dtbpy)Ni(p-CF$_3$Ar)Br* as catalyst with external NiBr$_2$·diglyme



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (18.0 mg, 0.1 mmol), Ir(dtbpy)(ppy)$_2$PF$_6$ (1.8 mg, 2.0 mol%), HEH (76.0 mg, 3.0 equiv), and Li_2CO_3 (29.4 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (2.0 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where NiBr$_2$·diglyme (3.5 mg, 10 mol%), *(dtbpy)Ni(p-CF$_3$Ar)Br* (55.2 mg, 1.0 equiv) and degassed NMP (2.0 mL, 0.05 M) were added. The mixture was stirred for 10 min before removed from the glove-box. Then the reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the reaction tube from the light source. EtOAc (20 mL) was added into the reaction tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^{1}H NMR relative to 1,3,5-trimethoxybenzen [δ 6.08 (s, 3H)] as an external standard. Also, 4,4'-bis(trifluoromethyl)-1,1'-biphenyl was isolated in 18% yield.

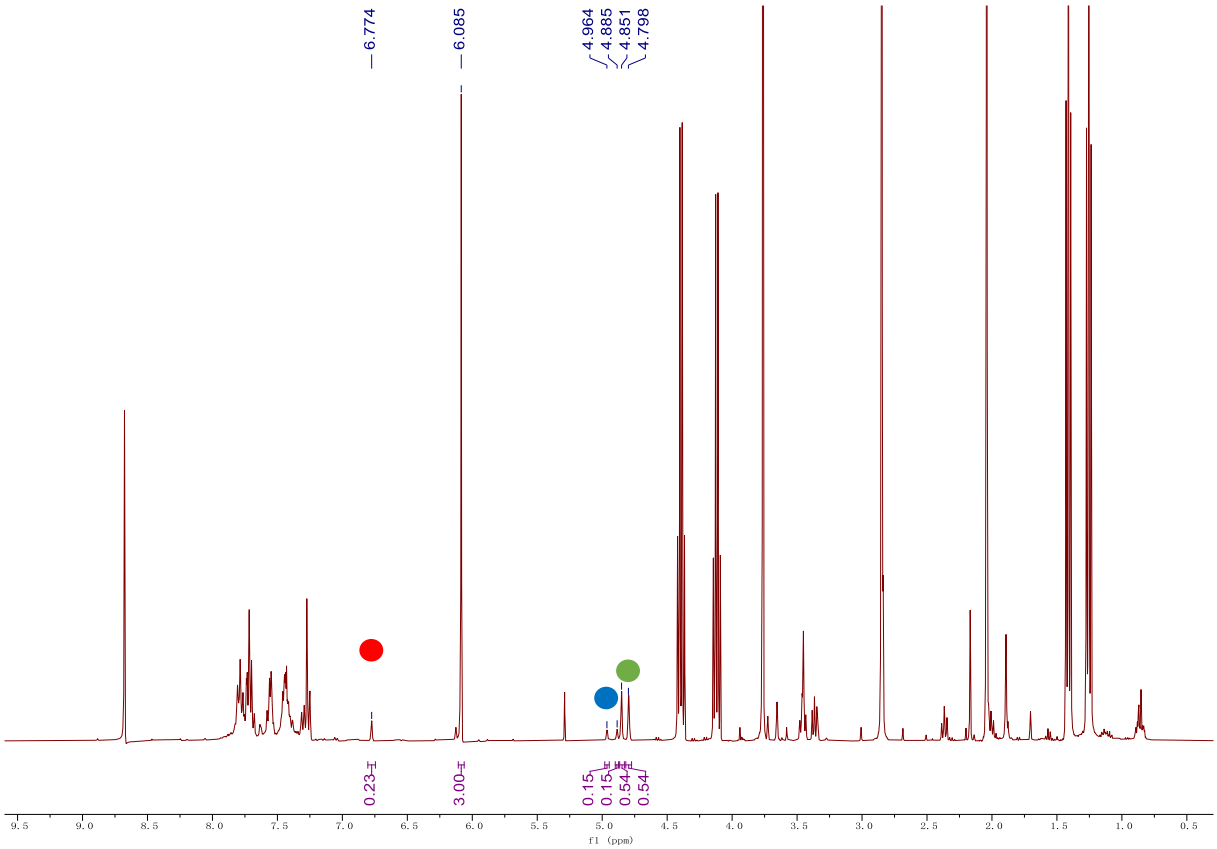
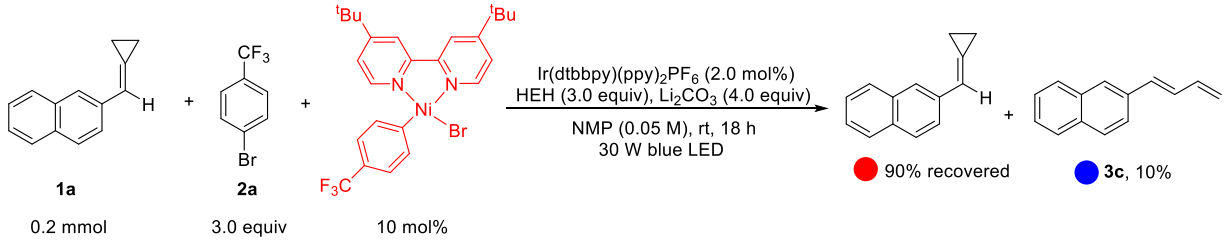


Figure S18. **^{1}H NMR** analysis of the crude product

Substoichiometric experiments using *(dtbpy)Ni(p-CF$_3$Ar)Br* as catalyst



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (36.0 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (84 μL, 3.0 equiv), Ir(dtbpy)(ppy)$_2$PF$_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (2 min) and argon backfill for three times. Then the tube was brought into the Ar-filled glove-box, where *(dtbpy)Ni(p-CF$_3$Ar)Br* (11.0 mg, 10 mol%) and degassed NMP (4.0 mL, 0.05 M) were added. The mixture was stirred for 10 min before removed from the glove-box. Then the reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzen (16.8

mg, 0.5 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (20 mL) was added into the reaction tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR relative to 1,3,5-trimethoxybenzen [δ 6.08 (s, 3H)] as an external standard.

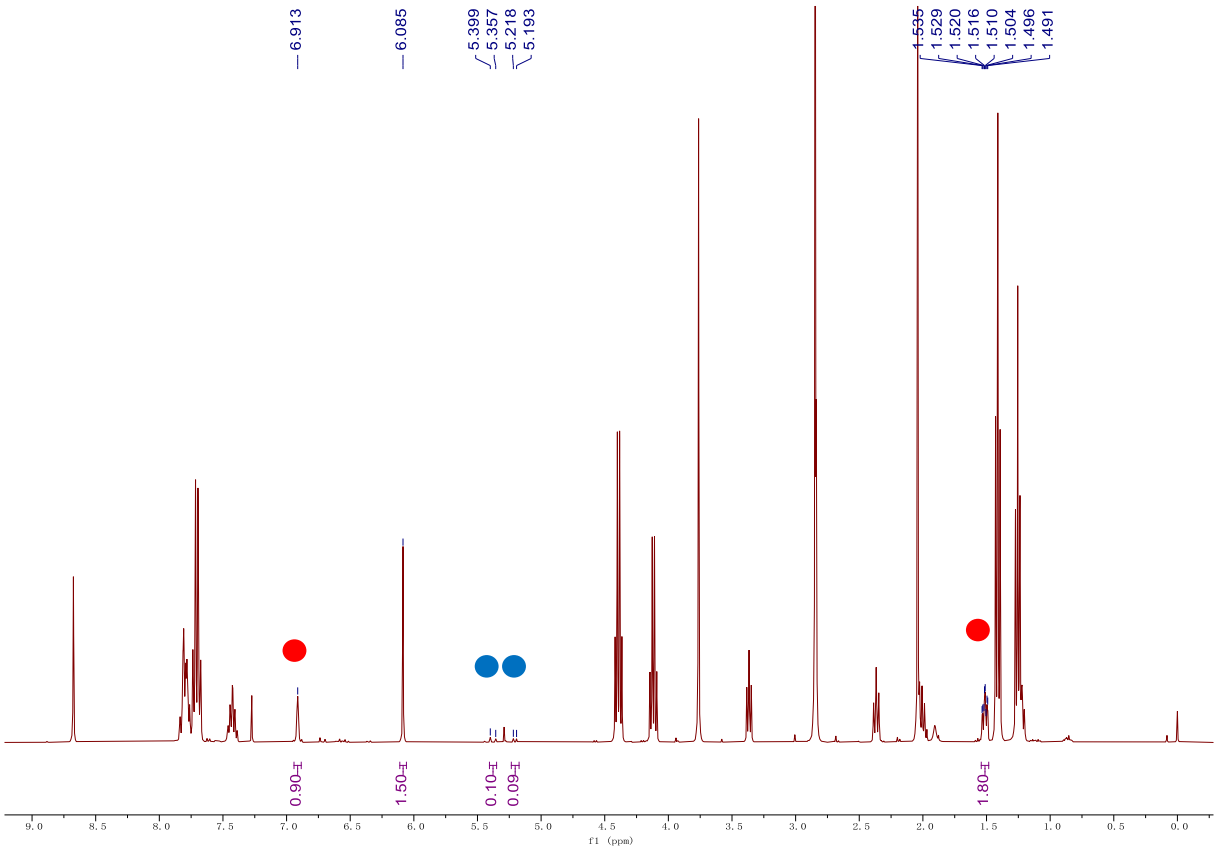
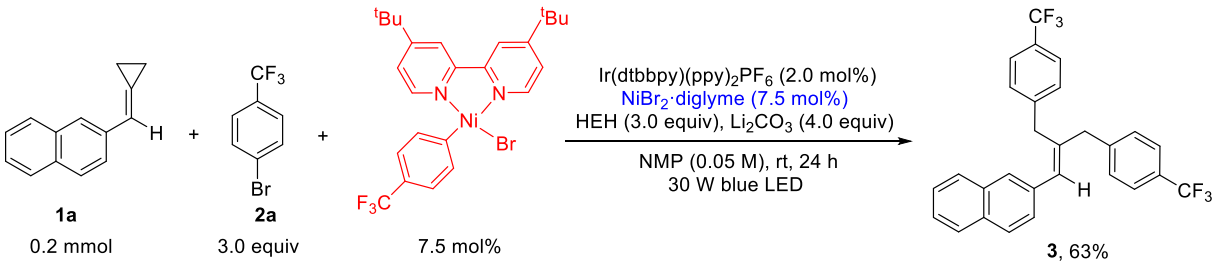


Figure S19. **^1H NMR** analysis of the crude product

Substoichiometric experiments using *(dtbpy)Ni(p-CF_3Ar)Br* as catalyst with external $NiBr_2$·diglyme



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (36.0 mg, 0.2

mmol), 1-bromo-4-(trifluoromethyl)benzene (84 μL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (2.0 min) and argon backfill for three times. Then the tube was brought into the Ar-filled glove-box, where $NiBr_2$·diglyme (5.3 mg, 7.5 mol%), *(dtbpy)Ni(p-CF_3Ar)Br* (8.3 mg, 7.5 mol%) and degassed NMP (4.0 mL, 0.05 M) were added. The mixture was stirred for 10 min before removed from the glove-box. Then the reaction tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, EtOAc (20 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 8 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The product **3** was isolated in 63% yield.

The spectroscopic data of compound **3b** were in good agreement with those in the previously reported literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 3H), 7.64 (s, 1H), 7.48-7.40 (m, 2H), 7.34 (dd, 1H, *J* = 7.6, 1.6 Hz), 4.86 (s, 1H), 4.79 (s, 1H), 3.48 (s, 2H), 1.71 (s, 3H).

The spectroscopic data of compound **3c** were in good agreement with those in the previously reported literature.[10]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.62 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 – 7.39 (m, 2H), 6.92 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.57 (dt, *J* = 16.9, 10.2 Hz, 1H), 5.38 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.21 (dd, *J* = 10.0, 1.4 Hz, 1H);

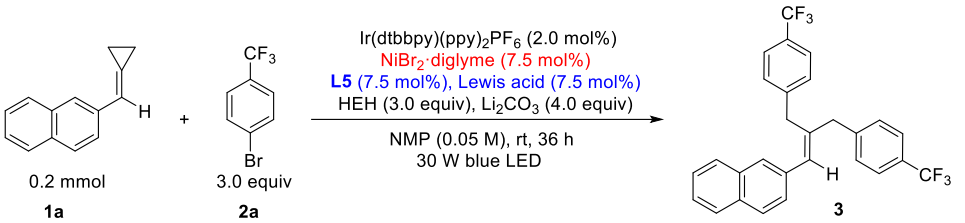
The spectroscopic data of compound homo-coupling product from 1-bromo-4-(trifluoromethyl)benzene were in good agreement with those in the previously reported literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 8H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.6.

5.6.5 Replacement of additional Nickel(II) bromide with other Lewis acids

To investigate whether the additional Nickel(II) bromide plays the role of Lewis acid in the catalytic

process, other Lewis acids were introduced to the reaction system for comparison.

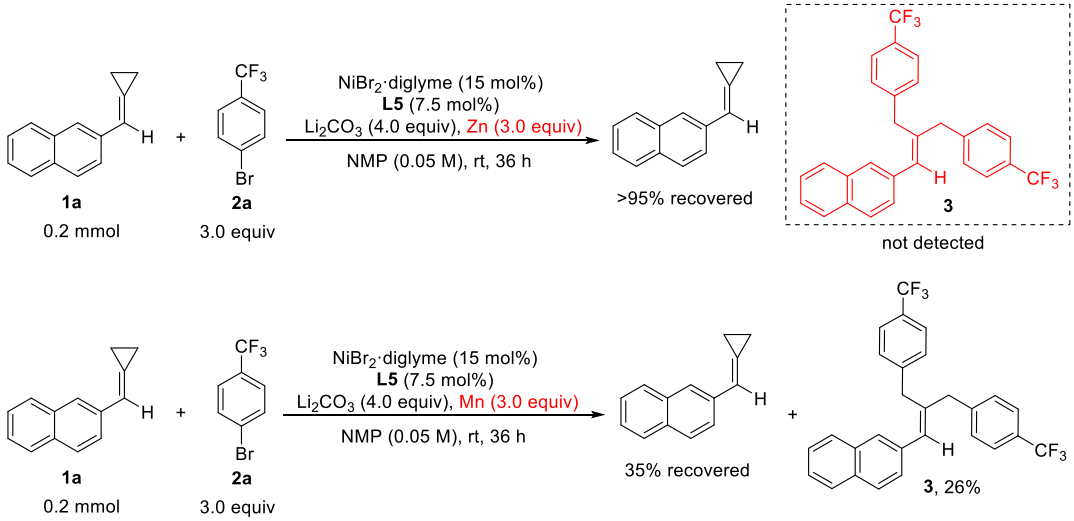


Entry	Lewis acid	**3**, Yield (%)[a]
1	$Yb(OTf)_3$	—
2	$Sc(OTf)_3$	—
3	$Sn(OTf)_2$	< 5
4	$Cu(OTf)_2$	—
5	$Zn(OTf)_2$	—
6	$FeBr_3$	—
7	None	< 5

[a] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzen as an internal standard.

In terms of results, the introduction of other Lewis acids did not promote the progress of the reaction, and the additional Ni(II) salts seemed to play an indispensable role in the catalytic process rather than the role of Lewis acid.

5.6.6 Catalytic reactions with Ni/Mn & Ni/Zn strategies



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (36.0 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (84 µL, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv), $NiBr_2$·diglyme (10.6 mg, 15 mol%), **L5** (7.5 mol%, 2.8 mg), Zn or Mn (3.0 equiv), and degassed

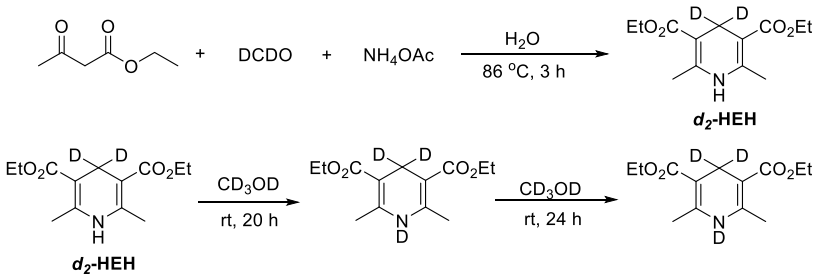
NMP (4.0 mL, 0.05 M) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The reaction mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. The crude product was analyzed by ^{1}H NMR relative to 1,3,5-trimethoxybenzen as an external standard.

Compared to the photoreduction protocol, metallic reductant Mn could also afford the product **3** with relatively lower efficiency at room temperature.

5.6.7 Deuterium labeling studies

To exclude the possibility of the involvement of Ni-H species in the process of product generation,[12] we used deuterated Hantzsch Esters to investigate the results of the reaction.

Synthesis of deuterated Hantzsch esters



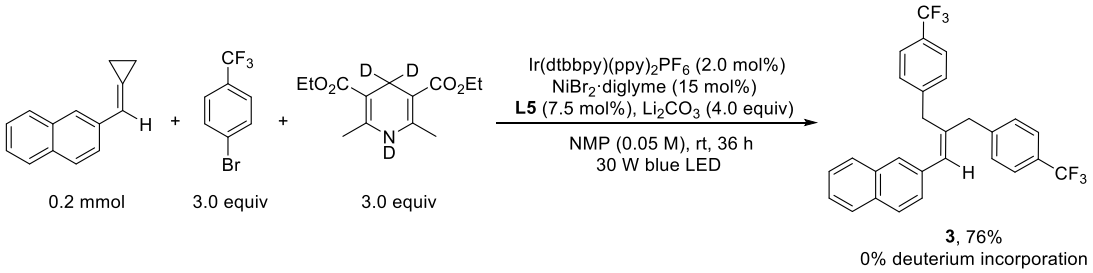
The deuterated Hantzsch Esters was prepared according to the previously reported procedure.[3]

Step 1: In an oven-dried round bottom flask equipped with a magnetic stir bar, ethyl acetoacetate (1.5 mL, 12.0 mmol, 4.0 equiv), *d*2-paraformaldehyde (96.1 mg, 3.0 mmol, 1.0 equiv), ammonium acetate (0.46 g, 6.0 mmol, 2.0 equiv) and water (6.0 mL) was added. The mixture was stirred vigorously at 86 °C in an oil bath for 3 hours. After cooling down to room temperature, the reaction mixture was filtered and the obtained precipitate was dried to afford compound ***d*2-HEH** (0.52 g, 68% yield) as a yellow solid.

Step 2: A solution of compound ***d*2-HEH** (0.51 g, 2.0 mmol) in CD_3OD (4.0 mL) was stirred under Ar at room temperature for 20 h. The solvent was evaporated and another CD_3OD (2.0 mL) was added. The mixture was allowed to stir for another 24 h. The deuterated Hantzsch Esters was obtained after removing the solvent as a pale green solid (505.2 mg, 99% yield). The spectral data of deuterated Hantzsch Esters are consistent with those in the previous reports.[3] **^{1}H NMR** (400

MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.1 Hz, 4H), 2.19 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 6H).

Deuterated Hantzsch esters used as the electron donor instead

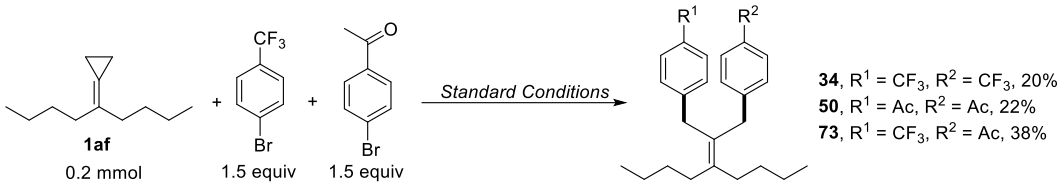


0.2 mmol | 3.0 equiv | 3.0 equiv

3, 76%
0% deuterium incorporation

According to general procedure B, when deuterated Hantzsch esters was used as the electron donor instead, product **3** was obtained in 76% yield with no D incorporation. The yield of **3** was slightly increased presumably due to the side reactions involving Ni-H species being suppressed.

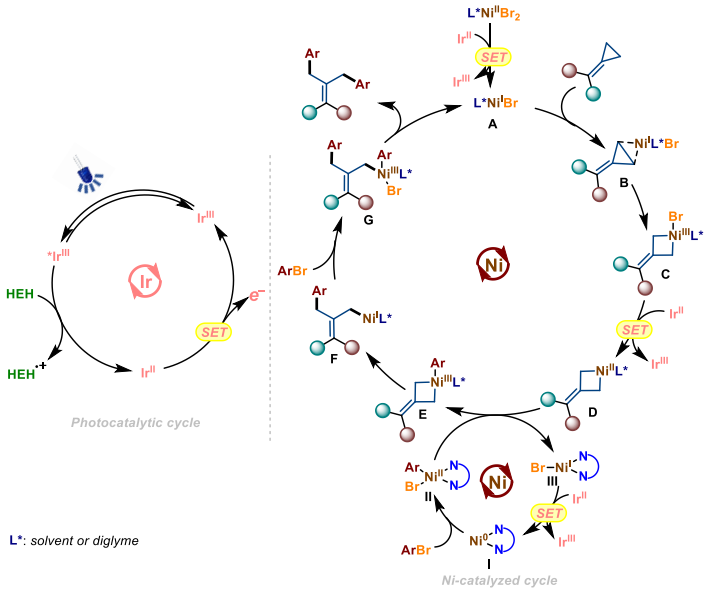
5.7 Crossover experiment



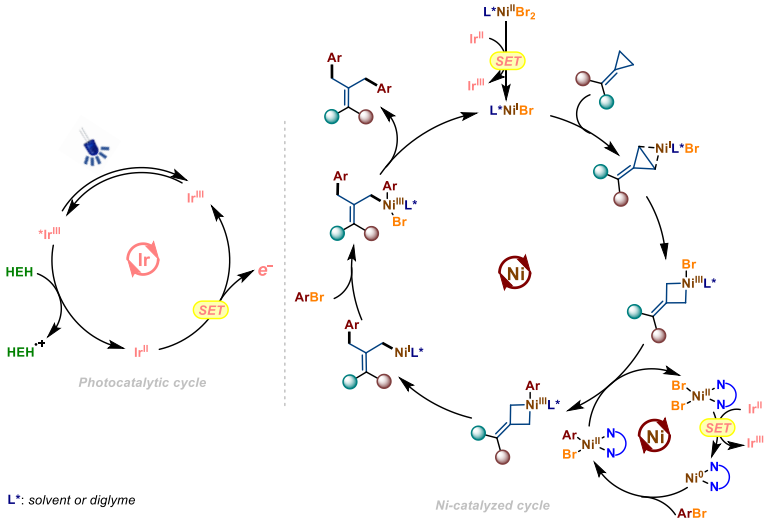
In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1af** (33.2 mg, 0.2 mmol), 1-bromo-4-(trifluoromethyl)benzene (42 μL, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (59.7 mg, 1.5 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (3.7 mg, 2.0 mol%), HEH (152.0 mg, 3.0 equiv), and Li_2CO_3 (58.9 mg, 4.0 equiv), $NiBr_2$·diglyme (10.6 mg, 15 mol%), ligand **L5** (2.8 mg, 7.5 mol%), and degassed NMP (4.0 mL, 0.05 M) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The mixture was stirred for 10 min before being placed 5.0 cm away from the blue LED (30 W) and stirred for 36 h at room temperature. Upon completion, EtOAc (20 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 8.0 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product **34** was in 20% yield and product **50** in 22% yield. In addition, compound **73** was also obtained (33.0 mg, 38% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.12 (m, 4H), 3.33 (s, 4H), 2.59 (s, 3H), 2.24 – 2.15 (m, 4H), 1.51 – 1.42 (m, 4H), 1.41 – 1.30 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8, 146.4, 144.6, 139.9, 135.2, 128.7, 128.6, 128.5, 128.3 (q, *J* = 32.0 Hz), 127.8, 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 271.9 Hz), 36.6, 36.5, 32.2, 31.5, 26.5, 23.08, 23.06, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2956, 2930, 2860, 1683, 1605, 1412, 1323, 1266, 1161, 1122, 1106, 1066, 1018, 955, 850, 818 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{33}F_3O$ 430.2478; found 430.2487.

6. Proposed Reaction Mechanisms

Scheme S1. Mechanism involving a disproportionation process (aryl transfer event) between two Ni(II) species.

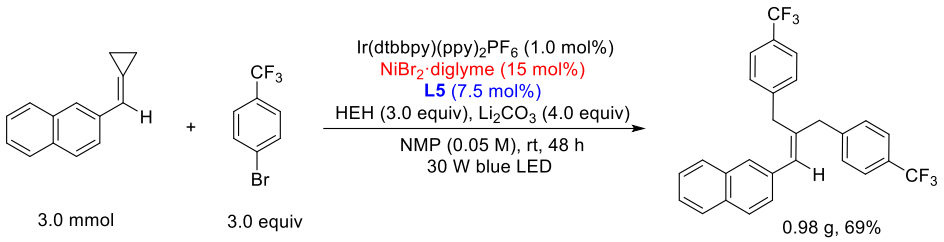


Scheme S2. Another possible mechanism involving the aryl transfer event occurring between Ni(II) species and Ni(III) species.



7. Synthetic Application of the Obtained Products

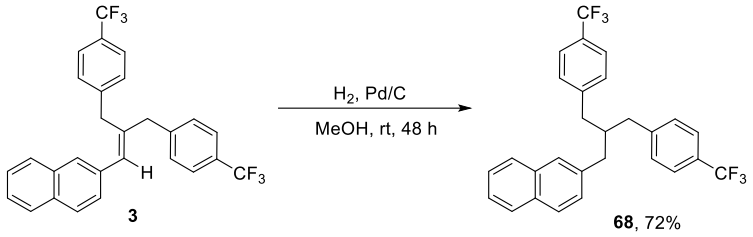
7.1 A scale-up experiment of 1a.



An oven-dried Schlenk tube (80 mL) equipped with a magnetic stir bar was added **1a** (0.54 g, 3.0 mmol), 1-bromo-4-(trifluoromethyl)benzene (1.3 mL, 3.0 equiv), $Ir(dtbpy)(ppy)_2PF_6$ (27.4 mg, 1.0 mol%), $NiBr_2$·diglyme (158.7 mg, 15 mol%), ligand **L5** (41.0 mg, 7.5 mol%), HEH (2.28 g, 3.0 equiv), and Li_2CO_3 (0.87 g, 4.0 equiv). The reaction tube was degassed by alternating vacuum evacuation (2.0 min) and argon backfill for three times. Then degassed NMP (60 mL, 0.05 M) was injected into the tube under Ar. The reaction mixture was stirred for 10 min before placed 10 cm away from the blue LED (30 W) and stirred for 48 h at room temperature. Upon completion, EtOAc (100 mL) was added into the reaction tube and the reaction mixture was washed with water for 3 times (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The residue was purified by a flash column chromatography on silica gel (pure petroleum ether) to afford the product **3** (0.98 g, 69% yield) as a white solid.

Figure S23. Setup of the scale-up experiment

7.2 Hydrogenative reductive reaction



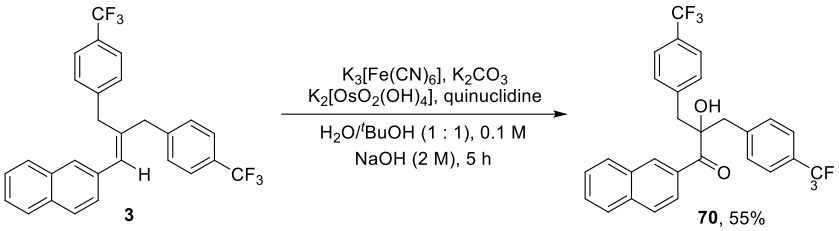
To a flask was added compound **3** (94.1 mg, 0.2 mmol), Pd/C (21.3 mg, 0.1 equiv, 10%) and menthol (8.0 mL). The reaction mixture was stirred vigorously at room temperature for 48 hours under 1 atm H_2. Upon completion, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated to dryness and the residue was purified by a flash column chromatography on silica gel (pure petroleum ether) to afford the product **68** (68.0 mg, 72% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 3H), 7.55 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 4H), 7.47 – 7.40 (m, 2H), 7.23 – 7.15 (m, 5H), 2.71 (d, *J* = 7.1 Hz, 2H), 2.69 – 2.56 (m, 4H), 2.46 – 2.36 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 137.6, 133.5, 132.1, 129.4, 128.4 (q, *J* = 32.6 Hz), 128.1, 127.6, 127.6, 127.4, 126.1, 125.4, 125.3 (q, *J* = 4.1 Hz), 124.3 (q, *J* = 271.8 Hz), 43.9, 40.2, 39.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2928, 2861, 1417, 1321, 1160, 1108, 1066, 1017, 846, 817, 749 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{22}F_6$ 472.1620; found 472.1629.

7.3 Epoxidation reaction

A solution of compound **3** (94.1 mg, 0.2 mmol), 3-chloroperoxybenzoic acid (98.6 mg, 2.0 equiv, 70%) and sodium bicarbonate (33.6 mg, 2.0 equiv) in DCM (10.0 mL)was stirred at room temperature for 48 h. Upon completion, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated to dryness and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford the product **69** (51.0 mg, 52% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.45 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.15 (s, 1H), 3.09 – 2.95 (m, 2H), 2.70 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.2, 140.5, 133.1, 133.0, 132.7, 130.1, 129.8, 129.3 (q, *J*

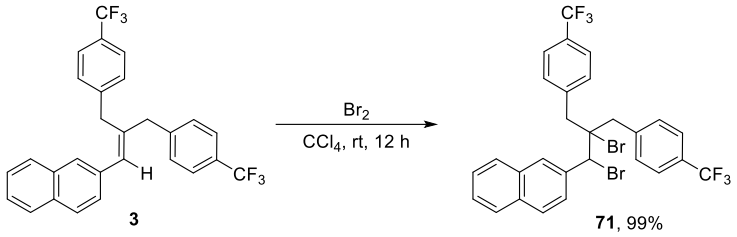
= 32.6 Hz), 129.0 (q, *J* = 32.6 Hz), 128.3, 127.9, 127.8, 126.6, 126.3, 125.5, 125.42 (q, *J* = 4.0 Hz), 125.35 (q, *J* = 4.0 Hz), 124.14 (q, *J* = 271.8 Hz), 124.11, 66.2, 62.8, 40.4, 35.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.45, -62.49; **IR (neat)**: ν 3013, 2974, 1360, 1219, 1080, 861, 668 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{20}F_6O$ 486.1413; found 486.1421.

7.4 Hydroxylation reaction[13]



An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3** (94.1 mg, 0.2 mmol), potassium ferricyanide (197.5 mg, 3.0 equiv), potassium ferricyanide (82.9 mg, 3.0 equiv), potassium osmate(VI) dihydrate (1.5 mg, 2 mol%), quinuclidine (1.1 mg, 5 mol%). Then H_2O (1.0 mL), ^{t}BuOH (1.0 mL) and NaOH (0.2 mL, 2.0 M) were injected into the reaction tube. The reaction mixture was allowed to stir at room temperature for 5.0 h. Upon completion, the reaction was quenched by HCl (0.5 mL, 2.0 M) and extracted with EtOAc for 3 times (3 × 5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product **70** (56.0 mg, 55% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.90 – 7.79 (m, 4H), 7.63 – 7.51 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 3.92 (s, 1H), 3.65 (d, *J* = 13.7 Hz, 2H), 3.32 (d, *J* = 13.7 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.1, 139.4, 135.4, 132.2, 131.6, 130.7, 129.8, 129.3 (q, *J* = 32.4 Hz), 129.2, 128.7, 127.8, 127.2, 125.0 (q, *J* = 4.0 Hz), 124.9, 124.1 (q, *J* = 272.7 Hz), 82.5, 46.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.6; **IR (neat)**: ν 3431, 1617, 1417, 1323, 1163, 1114, 1067, 1019, 853, 819 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{21}O_2F_6$ 503.1440; found 503.1430.

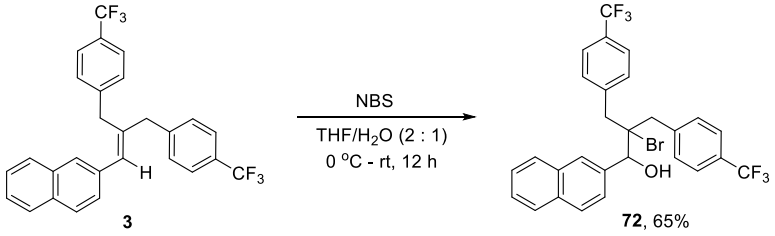
7.5 Bromination reaction



3 **71**, 99%

An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3** (47.0 mg, 0.1 mmol) and CCl_4 (2.0 mL). Then Bromine (8 μL, 1.5 equiv) was added into the tube. The mixture was allowed to stir at room temperature for 12 h. Upon completion, 10% aqueous sodium thiosulfate and aqueous saturated sodium bicarbonate were added and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether) to afford the product **71** (62.2 mg, 99% yield) as a white solid. M.p.: 196 – 198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.57 (m, 5H), 7.55 – 7.45 (m, 4H), 5.26 (s, 1H), 4.10 (d, *J* = 14.0 Hz, 1H), 3.75 – 3.63 (m, 2H), 2.98 (d, *J* = 14.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.3, 139.2, 134.6, 133.1, 132.3, 132.2, 131.8, 130.8, 129.8 (q, *J* = 32.6 Hz), 129.7 (q, *J* = 32.6 Hz), 128.3, 128.2, 127.6, 127.4, 127.0, 126.6, 125.0 (q, *J* = 4.1 Hz), 124.9 (q, *J* = 4.1 Hz), 124.23 (q, *J* = 272.1 Hz), 124.17 (q, *J* = 272.1 Hz), 73.9, 61.1, 45.0, 43.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.44, -62.45; **IR (neat)**: ν 2916, 1507, 1417, 1332, 1163, 1112, 1067, 1019, 852, 753 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{21}Br_2F_6$ 628.9909; found 628.9866.

7.6 Bromohydroxylation reaction

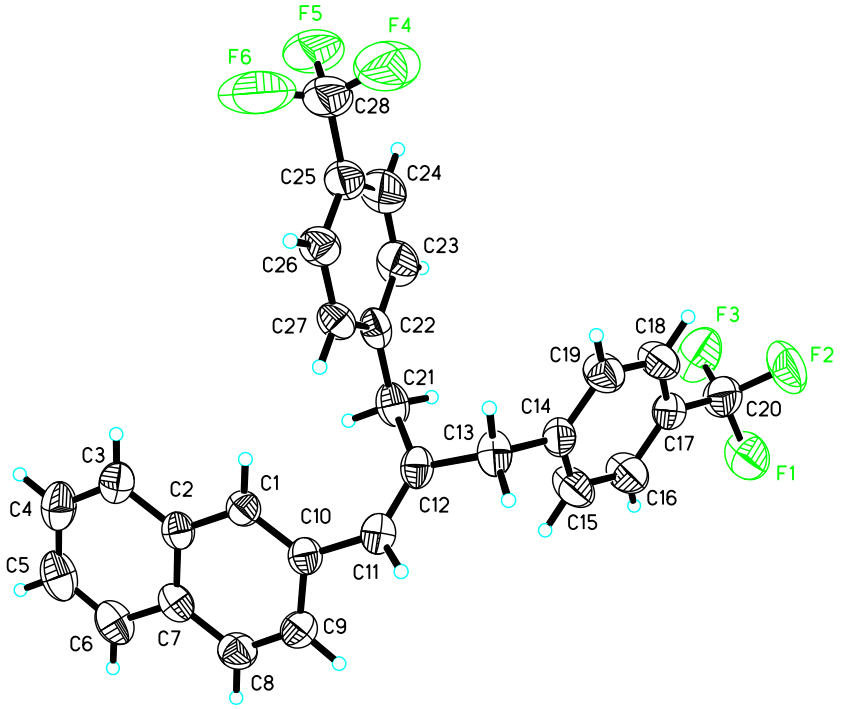


3 **72**, 65%

An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3** (47.0 mg, 0.1 mmol) and *N*-bromosuccinimide (26.7 mg, 1.5 equiv). Then THF (0.7 mL) and H_2O (0.35 mL) was added into the reaction tube. The reaction mixture was allowed to stir at room temperature for 12 h. Upon completion, 10% aqueous sodium thiosulfate were added and the

resulting mixture was extracted with EtOAc for 3 times (3 × 5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product **72** (37.0 mg, 65% yield) as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.87 – 7.77 (m, 3H), 7.63 – 7.54 (m, 7H), 7.53 – 7.41 (m, 4H), 4.92 (s, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.60 (d, *J* = 13.9 Hz, 1H), 3.25 (d, *J* = 14.0 Hz, 1H), 2.87 (d, *J* = 13.9 Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 140.1, 136.5, 133.2, 132.5, 131.9, 131.8, 129.32 (q, *J* = 32.6 Hz), 129.29 (q, *J* = 32.6 Hz), 128.7, 128.1, 127.6, 127.2, 126.9, 126.5, 126.4, 124.8 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 272.1 Hz), 124.2 (q, *J* = 272.1 Hz), 76.8, 73.7, 43.9, 42.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.34, -62.39; **IR (neat)**: ν 3435, 2927, 1617, 1417, 1332, 1162, 1111, 1067, 1019, 971, 823 cm^{-1}; **HRMS** (DART) m/z: $[M-H]^-$ Calcd. for $C_{28}H_{20}OBrF_6$ 565.0596; found 565.0555.

8. X-ray Data.



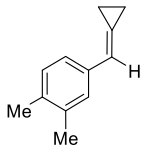
Single crystals of **3** were grown in $CHCl_3$ and hexanes. $CHCl_3$ (2.0 mL) was added to **3** (30 mg in a 4 mL vial) followed by hexanes (0.5 mL). The 4 mL vial was capped with a needle and placed at room temperature in the experimental cabinet for 48 h, whereupon the crystals were formed.

The crystal data of **3** have been deposited in CCDC with number 2216875. Empirical Formula: $C_{28}H_{20}F_6$; Formula Weight: 470.44; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.120 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.6213(5)Å, b = 11.2948(5)Å, c = 21.9100(12)Å, $\alpha = 90^o$, $\beta = 92.817(2)^o$, $\gamma = 90^o$, V = 2378.1(2)Å^3; Space group: P 21/c; Z = 4; D_{calc}= 1.314 g/cm^3; F_{000} = 968; Final R induces [I>2sigma(I)]: R1 = 0.0539; wR2 = 0.1348.

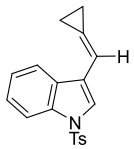
Table S11. Crystal data and structure refinement for 3.

Empirical formula	C28 H20 F6	
Formula weight	470.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.6213(5) Å	a= 90°.
	b = 11.2948(5) Å	b= 92.817(2)°.
	c = 21.9100(12) Å	g = 90°.
Volume	2378.1(2) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.108 mm^{-1}	
F(000)	968	
Crystal size	0.200 x 0.160 x 0.120 mm^3	
Theta range for data collection	2.592 to 25.999°.	
Index ranges	-11<=h<=11, -13<=k<=13, -27<=l<=27	
Reflections collected	35359	
Independent reflections	4660 [R(int) = 0.0725]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4660 / 84 / 362	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1348	
R indices (all data)	R1 = 0.0896, wR2 = 0.1647	
Extinction coefficient	0.027(3)	
Largest diff. peak and hole	0.144 and -0.141 e.$Å^{-3}$	

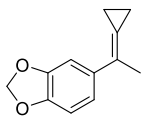
9. Characterization Data of New Substrates



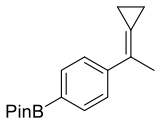
4-(cyclopropylidenemethyl)-1,2-dimethylbenzene (1g). The title compound **1g** was prepared according to General Procedure A. The product was obtained as a white solid (0.57 g, 72% yield), M.p.: 42 – 44 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.39 (td, *J* = 7.7, 2.2 Hz, 2H), 1.14 (td, *J* = 7.5, 1.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.4, 136.0, 135.1, 129.7, 127.9, 124.0, 122.8, 118.1, 19.8, 19.5, 4.1, 0.5; **IR (neat)**: ν 3084, 2969, 2922, 1610, 1499, 1403, 1020, 934, 882, 827, 764 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{14}$ 158.1090; found 158.1089.



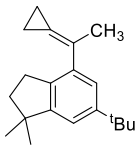
3-(cyclopropylidenemethyl)-1-tosyl-1H-indole (1m). The title compound **1m** was prepared according to *procedure b*. The product was obtained as a yellow solid (0.70 g, 43% yield), M.p.: 131 – 133 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.86 (s, 1H), 2.31 (s, 3H), 1.44 (td, *J* = 7.8, 2.2 Hz, 2H), 1.28 (td, *J* = 7.6, 1.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.8, 135.3, 135.2, 129.8, 129.5, 126.8, 124.9, 124.7, 123.2, 122.6, 121.2, 120.3, 113.6, 109.1, 21.5, 4.9, 2.7; **IR (neat)**: ν 2977, 2932, 1596, 1437, 1359, 1165, 1120, 1099, 950, 813, 754 739 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{17}NO_2S$ 323.0975; found 323.0972.



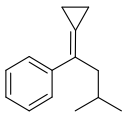
5-(1-cyclopropylideneethyl)benzo[*d*][1,3]dioxole (1p). The title compound **1p** was prepared according to General Procedure A. The product was obtained as a white solid (0.82 g, 87% yield), M.p.: 70 – 72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.07 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.94 (s, 2H), 2.19 (s, 3H), 1.42 (td, *J* = 7.1, 1.9 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.6, 146.2, 135.1, 121.9, 119.0, 118.7, 107.8, 106.0, 100.8, 20.0, 5.8, 0.5; **IR (neat)**: ν 2969, 2937, 1608, 1504, 1482, 1371, 1256, 1221, 1103, 1035, 934, 898, 806 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{13}O_2$ 189.0910; found 189.0902.



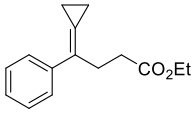
2-(4-(1-cyclopropylideneethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1q). The title compound **1q** was prepared according to General Procedure A. The product was obtained as a white solid (0.62 g, 46% yield), M.p.: 62 – 64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 2H), 2.24 (s, 3H), 1.46 (t, *J* = 7.3 Hz, 2H), 1.34 (s, 12H), 1.12 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.3, 134.6, 124.7, 122.6, 122.0, 83.6, 24.8, 19.6, 5.9, 0.5; **IR (neat)**: ν 2975, 2929, 1607, 1396, 1357, 1321, 1271, 1143, 1096, 1017, 962, 859, 828, 744 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{24}O_2B$ 271.1864; found 271.1851.



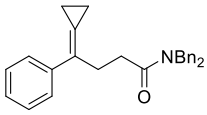
6-(tert-butyl)-4-(1-cyclopropylideneethyl)-1,1-dimethyl-2,3-dihydro-1H-indene (1r). The title compound **1r** was prepared according to General Procedure A. The product was obtained as a colorless oil (0.70 g, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.08 (s, 1H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.89 (t, *J* = 7.1 Hz, 2H), 1.33 (s, 9H), 1.28 (s, 6H), 1.26 – 1.20 (m, 2H), 1.18 – 1.09 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 149.1, 138.3, 137.3, 125.1, 122.5, 121.0, 117.3, 43.8, 41.7, 34.7, 31.7, 30.0, 28.6, 22.1, 5.4, 2.1; **IR (neat)**: ν 2956, 2924, 2858, 1683, 1596, 1458, 1360, 1249, 1234, 1143, 991, 875, 728 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{20}H_{28}$ 268.2186; found 268.2185.



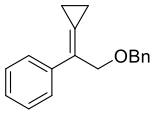
(1-cyclopropylidene-3-methylbutyl)benzene (1t). The title compound **1t** was prepared according to General Procedure A. The product was obtained as a colorless oil (0.61 g, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.35 – 7.26 (m, 2H), 7.22 – 7.15 (m, 1H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.93 – 1.82 (m, 1H), 1.45 – 1.37 (m, 2H), 1.15 – 1.07 (m, 2H), 0.89 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 128.1, 126.7, 126.3, 126.1, 121.5, 43.2, 27.2, 22.6, 5.1, 1.4; **IR (neat)**: ν 2952, 2922, 2866, 1592, 1495, 1463, 1381, 1364, 987, 903, 764, 691 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{14}H_{18}$ 186.1403; found 186.1396.



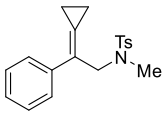
ethyl 4-cyclopropylidene-4-phenylbutanoate (1u). The title compound **1u** was prepared according to *procedure c*. The product was obtained as a yellow oil (0.83 g, 48% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.25 – 7.20 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.96 (m, 2H), 2.61 – 2.54 (m, 2H), 1.38 – 1.33 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.21 – 1.16 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.4, 139.6, 128.2, 126.6, 125.8, 125.7, 121.3, 60.3, 33.2, 29.1, 14.2, 4.4, 1.4; **IR (neat)**: ν 2976, 2961, 1730, 1495, 1444, 1371, 1160, 1034, 759 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{15}H_{18}O_2$ 230.1301; found 230.1306.



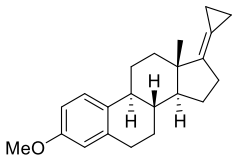
***N*,*N*-dibenzyl-4-cyclopropylidene-4-phenylbutanamide (1v).** The title compound **1v** was prepared according to *procedure d*. The product was obtained as a white solid (2.10 g, 73% yield), M.p.: 76 – 78 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.24 (m, 8H), 7.23 – 7.17 (m, 3H), 7.07 (d, *J* = 7.4 Hz, 2H), 4.61 (s, 2H), 4.34 (s, 2H), 3.10 (t, *J* = 8.7 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.37 – 1.32 (m, 2H), 1.12 – 1.05 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.3, 139.3, 137.4, 136.6, 128.8, 128.5, 128.25, 128.21, 127.5, 127.3, 126.6, 126.2, 126.0, 125.8, 121.5, 49.9, 48.3, 32.0, 29.7, 4.7, 1.1; **IR (neat)**: ν 3026, 2966, 1652, 1365, 1216, 752 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{27}NONa$ 404.1985; found 404.1985.



(2-(benzyloxy)-1-cyclopropylideneethyl)benzene (1w). The title compound **1w** was prepared according to *procedure e*. The product was obtained as a colorless oil (0.60 g, 48% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.37 – 7.29 (m, 6H), 7.28 – 7.21 (m, 2H), 4.60 (s, 2H), 4.51 (d, *J* = 1.9 Hz, 2H), 1.49 (td, *J* = 7.4, 1.5 Hz, 2H), 1.18 (td, *J* = 7.7, 1.6 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.4, 138.3, 128.3, 128.2, 127.8, 127.5, 126.8, 126.3, 126.1, 123.9, 71.8, 71.5, 5.2, 0.9; **IR (acetone)**: ν 3057, 2979, 2858, 1597, 1496, 1452, 1359, 1220, 1090, 1066, 958, 736, 694 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{18}ONa$ 273.1250; found 273.1244.

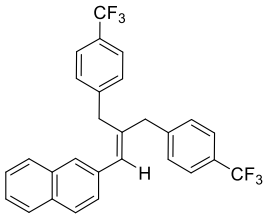


***N*-(2-cyclopropylidene-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (1x).** The title compound **1x** was prepared according to *procedure f*. The product was obtained as a white solid (0.31 g, 95% yield), M.p.: 126 – 128 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.74 – 7.66 (m, 2H), 7.40 – 7.32 (m, 4H), 7.28 – 7.23 (m, 1H), 4.16 (s, 2H), 2.50 (s, 3H), 2.45 (s, 3H), 1.51 – 1.45 (m, 2H), 1.13 – 1.08 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 137.2, 133.6, 129.7, 128.3, 127.7, 127.2, 126.8, 126.2, 121.6, 53.2, 33.7, 21.5, 5.4, 1.1; **IR (neat)**: ν 2968, 2927, 2856, 1597, 1497, 1455, 1338, 1161, 1088, 974, 919, 816, 774, 742, 711 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{21}NO_2NaS$ 350.1185; found 350.1182.

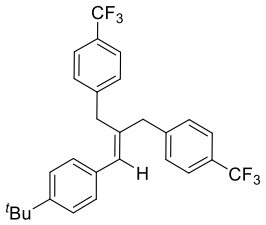


(8S,9S,13S,14S)-17-cyclopropylidene-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (1ai). The title compound **1ai** was prepared according to *procedure h*. The product was obtained as a white solid (0.63 g, 51% yield), M.p.: 93 – 95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 2.97 – 2.79 (m, 2H), 2.60 – 2.47 (m, 1H), 2.41 – 2.29 (m, 2H), 2.28 – 2.19 (m, 1H), 2.18 – 2.12 (m, 1H), 1.99 – 1.92 (m, 1H), 1.91 – 1.82 (m, 1H), 1.61 – 1.51 (m, 2H), 1.50 – 1.28 (m, 4H), 1.16 – 0.99 (m, 2H), 0.90 – 0.79 (m, 5H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.4, 139.1, 138.0, 133.0, 126.3, 113.8, 111.4, 107.1, 55.2, 54.3, 45.0, 44.2, 38.6, 36.3, 29.9, 29.0, 27.7, 26.7, 24.3, 17.8, 1.4, -0.6; **IR (neat)**: ν 3042, 2969, 2869, 1609, 1501, 1465, 1279, 1255, 1145, 1147, 882, 825 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{22}H_{28}O$ 308.2135; found 308.2137.

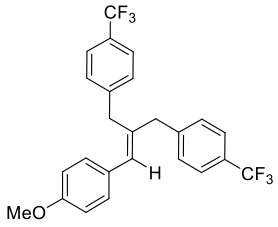
10. Characterization Data of Products



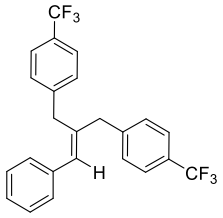
2-(2-(4-(trifluoromethyl)benzyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)naphthalene (3). The title compound **3** was prepared from **1a** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (65.8 mg, 70% yield), M.p.: 118 – 120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.39 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.32 – 7.23 (m, 4H), 6.77 (s, 1H), 3.65 (s, 2H), 3.46 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.3, 138.8, 134.7, 133.3, 132.3, 130.4, 129.4, 129.0, 128.83 (q, *J* = 32.0 Hz), 128.73 (q, *J* = 32.0 Hz), 128.0, 127.9, 127.6, 127.1, 126.8, 126.3, 125.9, 125.5 (q, *J* = 4.1 Hz), 125.4 (q, *J* = 4.1 Hz), 122.5 (q, *J* = 272.0 Hz), 122.4 (q, *J* = 272.0 Hz), 43.1, 36.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 3015, 2912, 2850, 1617, 1434, 1321, 1117, 1062, 819, 756 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{20}F_6$ 470.1464; found 470.1461.



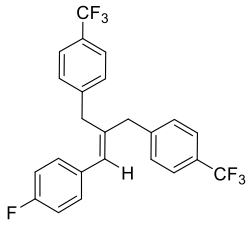
4,4'-(2-(4-(tert-butyl)benzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (4). The title compound **4** was prepared from **1b** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (70.5 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0, 2H), 7.53 (d, *J* = 8.0, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.19 (m, 6H), 6.63 (s, 1H), 3.60 (s, 2H), 3.41 (s, 2H), 1.30 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.1, 143.5, 143.4, 137.5, 134.2, 130.4, 129.3, 128.9, 128.8 (q, *J* = 32.0 Hz), 128.7 (q, *J* = 32.0 Hz), 128.1, 125.5 (q, *J* = 4.1 Hz), 125.4, 125.3 (q, *J* = 4.1 Hz), 124.3 (q, *J* = 272.1 Hz), 43.3, 36.0, 34.5, 31.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.33, -62.34; **IR (neat)**: ν 2964, 2909, 1615, 1508, 1321, 1160, 1106, 1065, 845, 822, cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{26}F_6$ 476.1933; found 476.1946.



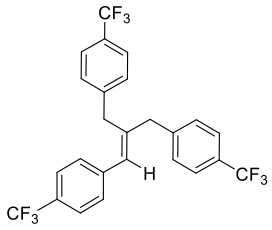
4,4'-(2-(4-methoxybenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (5). The title compound **5** was prepared from **1c** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 10 : 1). The product was obtained as a white solid (54.9 mg, 61% yield), M.p.: 97 – 99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.3, 2.5 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.58 (s, 1H), 3.79 (s, 3H), 3.57 (s, 2H), 3.40 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.6, 143.55, 143.47, 136.8, 130.1, 129.7, 129.6, 129.4, 128.9, 128.8 (q, *J* = 32.0 Hz), 128.7 (q, *J* = 32.0 Hz) 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 113.9, 55.3, 43.2, 35.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.34, -62.35; **IR (neat)**: ν 2965, 2908, 1597, 1510, 1320, 1117, 1159, 1018, 845, 817 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{20}F_6O$ 450.1413; found 450.1422.



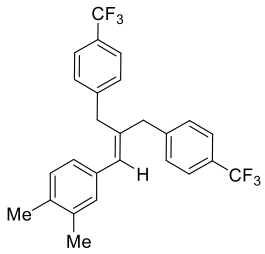
4,4'-(2-benzylidenepropane-1,3-diyl)bis((trifluoromethyl)benzene) (6). The title compound **6** was prepared from **1d** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (54.7 mg, 65% yield), M.p.:73 – 76 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 4H), 7.35 – 7.30 (m, 2H), 7.29 – 7.21 (m, 7H), 6.64 (s, 1H), 3.58 (s, 2H), 3.42 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.3, 138.2, 137.2, 130.5, 129.4, 128.9, 128.8 (q, *J* = 32.6 Hz), 128.7 (q, *J* = 32.0 Hz), 128.5, 128.4, 127.0, 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 271.3 Hz), 43.1, 35.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.35, -62.36; **IR (neat)**: ν 3076, 3047, 2911, 2851, 1616, 1487, 1406, 1312, 1103, 1064, 846, 833, 759, 746 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{18}F_6$ 420.1307; found 420.1320.



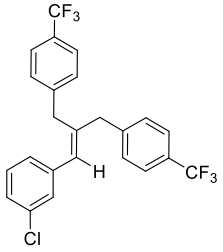
4,4'-(2-(4-fluorobenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (7). The title compound **7** was prepared from **1e** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (56.2 mg, 64% yield), M.p.: 74 – 76 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 4H), 7.29 – 7.18 (m, 7H), 7.05 – 6.97 (m, 2H), 6.58 (s, 1H), 3.55 (s, 2H), 3.41 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.8 (d, *J* = 247.0 Hz), 143.2, 143.1, 138.4, 133.1 (d, *J* = 3.5 Hz), 130.0 (d, *J* = 8.3 Hz), 129.40, 129.36, 128.897 (q, *J* = 32.6 Hz), 128.896, 128.8 (q, *J* = 32.6 Hz), 125.6 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.0 Hz), 124.2 (q, *J* = 272.0 Hz) 115.4 (d, *J* = 21.4 Hz), 43.0, 35.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4, -114.9; **IR (neat)**: ν 3041, 2912, 2850, 1616, 1506, 1434, 1322, 1228, 1103, 1064, 1061, 848, 820, 775, 659 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{17}F_7$ 438.1213; found 438.1229.



4,4'-(2-(4-(trifluoromethyl)benzyl)prop-1-ene-1,3-diyl)bis((trifluoromethyl)benzene) (8). The title compound **8** was prepared from **1f** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (62.3 mg, 64% yield), M.p.: 76 – 78 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 6H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.63 (s, 1H), 3.57 (s, 2H), 3.45 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.85, 142.76, 140.8, 140.5, 129.4, 129.15, 129.09 (q, *J* = 32.6 Hz), 129.04 (q, *J* = 32.6 Hz), 128.99 (q, *J* = 32.6 Hz), 128.9, 128.7, 125.7 (q, *J* = 4.1 Hz), 125.5 (q, *J* = 4.1 Hz) 125.4 (q, *J* = 4.1 Hz), 124.24 (q, *J* = 272.1 Hz), 124.21 (q, *J* = 272.1 Hz), 124.1 (q, *J* = 272.1 Hz), 43.1, 36.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.41, -62.42, -62.5; **IR (neat)**: ν 3021, 2927, 1615, 1427, 1411, 1411, 1320, 1103, 1064, 892, 827, 674 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{17}F_9$ 488.1181; found 488.1183.

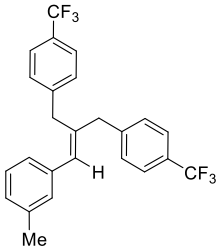


4,4'-(2-(3,4-dimethylbenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (9). The title compound **9** was prepared from **1g** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (52.4 mg, 58% yield), M.p.: 72 – 74 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 4H), 7.27 – 7.20 (m, 4H), 7.10 – 6.98 (m, 3H), 6.58 (s, 1H), 3.58 (s, 2H), 3.39 (s, 2H), 2.24 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 137.4, 136.6, 135.5, 134.7, 130.5, 129.9, 129.7, 129.4, 129.0, 128.8 (q, *J* = 32.0 Hz), 128.6 (q, *J* = 32.0 Hz), 125.7, 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 271.3 Hz), 43.1, 36.0, 19.8, 19.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.33, -62.34; **IR (neat)**: ν 3016, 2914, 2853, 1611, 1414, 1320, 1152, 1112, 1017, 843, 828, 817 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{22}F_6$ 448.1620; found 448.1636.

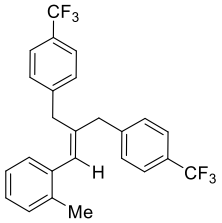


4,4'-(2-(3-chlorobenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (10). The title compound **10** was prepared from **1h** (36 mg, 0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (65.0 mg, 26% yield), containing compound **6** due to dechlorination in the reaction process that failed to be separated. **^{1}H NMR** (400 MHz, $CDCl_3$, a mixture of compound **6** & compound **10**) δ 7.55 (dd, *J* = 8.4, 3.1 Hz, 11H, *mixtures of compound **6** and compound **10***), 7.36 – 7.19 (m, 25H, *mixtures of compound **6** and compound **10***), 7.14 (dd, *J* = 6.8, 2.0 Hz, 1H), 6.64 (s, 2H, *Compound **6***), 6.54 (s, 1H), 3.58 (s, 4H, *Compound **6***), 3.55 (s, 2H), 3.45 – 3.38 (m, 6H, *mixtures of compound **6** and compound **10***); **^{13}C NMR** (151 MHz, $CDCl_3$, a mixture of compound **6** & compound **10**) δ 143.3 (*Compound **6***), 142.95, 142.91, 139.9, 139.0, 138.2 (*Compound **6***), 137.2 (*Compound **6***), 134.3, 130.5 (*Compound **6***), 129.7, 129.4 (*Compound **6***), 129.0, 128.94 (*Compound **6***), 128.91, 128.8 (q, *J* = 32.6 Hz), 128.7 (q, *J* = 32.6 Hz), 128.6, 128.5 (*Compound **6***), 128.4 (*Compound **6***), 127.1, 127.0 (*Compound **6***), 126.5, 125.6 (q, *J* = 4.2 Hz), 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 271.3 Hz), 124.2 (q, *J* = 271.3 Hz), 43.1 (*Compound **6***), 42.9, 36.0, 35.9 (*Compound **6***); **^{19}F NMR** (565 MHz, $CDCl_3$, a mixture of

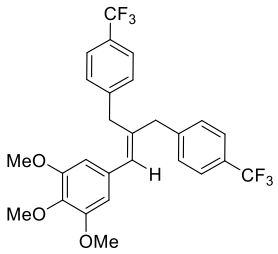
compound **6** & compound **10**) δ -62.34 (*Compound **6***), -62.36 (*Compound **6***), -62.39; **IR (neat)**: ν 3075, 2911, 2850, 1615, 1488, 1321, 1106, 833, 770, 745 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}ClF_6$ 455.0996; found 455.0943.



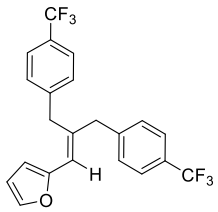
4,4'-(2-(3-methylbenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (11). The title compound **11** was prepared from **1i** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (55.9 mg, 64% yield), M.p.: 68 – 70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 4H), 7.29 – 7.17 (m, 5H), 7.10 – 7.04 (m, 3H), 6.61 (s, 1H), 3.57 (s, 2H), 3.40 (s, 2H), 2.33 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 143.4, 138.11, 138.09, 137.2, 130.6, 129.4, 129.3, 129.0, 128.9 (q, *J* = 32.6 Hz), 128.8 (q, *J* = 32.0 Hz), 128.4, 127.8, 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz) 125.3, 124.3 (q, *J* = 272.1 Hz), 43.1, 36.0, 21.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.33, -62.34; **IR (neat)**: ν 2912, 1614, 1420, 1321, 1117, 1065, 1018, 812, 691 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{20}F_6$ 434.1464; found 434.1473.



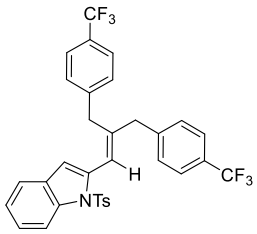
4,4'-(2-(2-methylbenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (12). The title compound **12** was prepared from **1j** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (57.2 mg, 66% yield), M.p.: 67 – 69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.13 (m, 6H), 6.57 (s, 1H), 3.42 (s, 2H), 3.40 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 143.5, 138.5, 136.53, 136.46, 130.0, 129.6, 129.3, 129.0, 128.82 (q, *J* = 32.2 Hz), 128.81 (q, *J* = 32.2 Hz), 128.7, 127.3, 125.7, 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 42.5, 35.9, 20.1;**^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2926, 1614, 1440, 1316, 1127, 1065, 1018, 847, 761, 655 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{20}F_6$ 434.1464; found 434.1479.



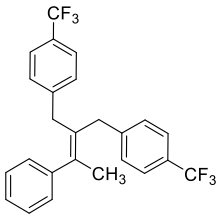
4,4'-(2-(3,4,5-trimethoxybenzylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (13). The title compound **13** was prepared from **1k** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (56.3 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.3 Hz, 4H), 7.28 (d, *J* = 5.7 Hz, 4H), 6.57 (s, 1H), 6.46 (s, 2H), 3.83 (s, 3H), 3.73 (s, 6H), 3.63 (s, 2H), 3.45 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.1, 143.4, 143.2, 137.9, 137.2, 132.7, 130.5, 129.4, 128.9 (q, *J* = 32.6 Hz), 128.80, 128.77 (q, *J* = 32.0 Hz), 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 124.2 (q, *J* = 272.1 Hz), 105.5, 60.9, 56.0, 43.3, 36.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.36, -62.39; **IR (neat)**: ν 2937, 2836, 1615, 1583, 1507, 1421, 1321, 1238, 1107, 1065, 1017, 821, 725 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{24}F_6O_3$ 510.1624; found 510.1641.



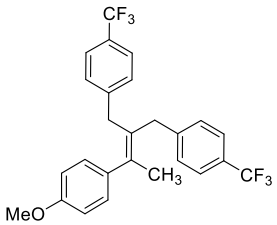
2-(2-(4-(trifluoromethyl)benzyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)furan (14). The title compound **14** was prepared from **1l** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 30 : 1). The product was obtained as a yellow oil (37.1 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 4H), 7.37 (s, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.40 (t, *J* = 2.6 Hz, 1H), 6.27 (d, *J* = 3.8 Hz, 2H), 3.83 (s, 2H), 3.41 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.3, 143.3, 143.1, 141.7, 137.1, 129.5, 129.0, 128.7 (q, *J* = 32.0 Hz), 125.44 (q, *J* = 4.2 Hz), 125.40 (q, *J* = 4.2 Hz), 124.28 (q, *J* = 272.1 Hz), 124.24 (q, *J* = 272.1 Hz), 118.3, 111.2, 109.5, 43.5, 37.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.37, -62.40; **IR (acetone)**: ν 3010, 2917, 1614, 1322, 1220, 1162, 1107, 1018, 823 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{16}F_6O$ 410.1100; found 410.1111.



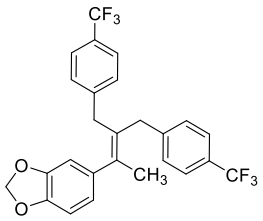
1-tosyl-2-(2-(4-(trifluoromethyl)benzyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)-1H-indole (15). The title compound **15** was prepared from **1m** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 10 : 1). The product was obtained as a colorless oil (43.5 mg, 35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.49 (m, 5H), 7.43 (s, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.51 (s, 1H), 3.60 (s, 2H), 3.50 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.1, 143.0, 142.6, 140.9, 135.0, 134.8, 130.8, 129.9, 129.4, 128.9 (q, *J* = 32.6 Hz), 128.85, 128.77 (q, *J* = 32.6 Hz), 126.7, 125.6 (q, *J* = 4.2 Hz), 125.5 (q, *J* = 4.2 Hz), 125.2, 124.2 (q, *J* = 272.1 Hz), 123.5, 122.9, 119.5, 119.1, 118.8, 113.8, 43.5, 37.2, 21.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.35,-62.38; **IR (neat)**: ν 2936, 2853, 1617, 1435, 1162, 1107, 1018, 970, 744, 678 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{33}H_{25}F_6NO_2S$ 613.1505; found 613.1502.



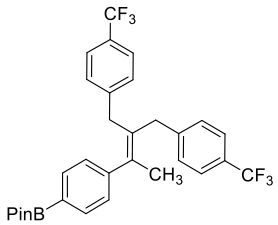
4,4'-(2-(1-phenylethylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (16). The title compound **16** was prepared from **1n** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (63.6 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.22 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.49 (s, 2H), 3.27 (s, 2H), 2.18 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.5, 144.04, 143.99, 136.8, 130.9, 128.9, 128.7, 128.53, 128.52 (q, *J* = 32.6 Hz), 128.47 (q, *J* = 32.6 Hz), 127.9, 126.7, 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 38.2, 36.1, 21.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 3003, 2922, 1620, 1419, 1323, 1220, 1119, 1066, 1017, 902, 856, 765, 701 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{20}F_6$ 434.1464; found 434.1475.



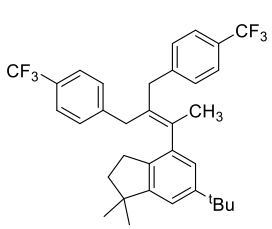
4,4'-(2-(1-(4-methoxyphenyl)ethylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (17). The title compound **17** was prepared from **1o** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (55.9 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.19 – 7.09 (m, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.48 (s, 2H), 3.29 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.3, 144.6, 144.1, 136.34, 136.30, 130.8, 128.98, 128.95, 128.7, 128.6 (q, *J* = 32.2 Hz), 128.5 (q, *J* = 32.2 Hz), 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 113.9, 55.3, 38.2, 36.3, 21.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.31, -62.32; **IR (neat)**: ν 2928, 2844, 1611, 1509, 1412, 1320, 1234, 1117, 1065, 1032, 1017, 850, 819 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{22}F_6O$ 464.1569; found 464.1579.



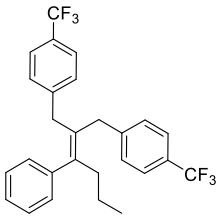
5-(3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)benzo[d][1,3]dioxole (18). The title compound **18** was prepared from **1p** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (38.2 mg, 40% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 6.68 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (s, 2H), 3.46 (s, 2H), 3.30 (s, 2H), 2.14 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.7, 146.2, 144.4, 144.0, 137.8, 136.3, 131.2, 129.0, 128.7, 128.6 (q, *J* = 32.6 Hz), 128.4 (q, *J* = 32.6 Hz), 125.4 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 121.0, 108.5, 108.4, 101.0, 38.2, 36.2, 21.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.32, -62.33; **IR (neat)**: ν 3015, 2920, 1605, 1485, 1428, 1316, 1226, 1117, 1100, 1017, 935, 814 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{20}F_6O_2$ 478.1362; found 478.1368.



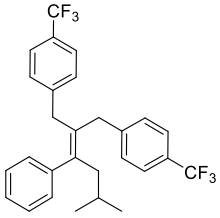
4,4,5,5-tetramethyl-2-(4-(3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)phenyl)-1,3,2-dioxaborolane (19). The title compound **19** was prepared from **1q** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (52.1 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.49 (s, 2H), 3.25 (s, 2H), 2.17 (s, 3H), 1.34 (s, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.1, 144.3, 143.9, 136.7, 135.0, 131.0, 128.9, 128.7, 128.6 (q, *J* = 32.0 Hz), 128.5 (q, *J* = 32.0 Hz), 127.3, 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 83.8, 38.2, 36.1, 24.8, 21.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2981, 2932, 1741, 1608, 1396, 1359, 1320, 1161, 1142, 1120, 1066, 1017, 962, 857, 820, 677 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{31}H_{31}BF_6O_2$ 560.2316; found 560.2333.



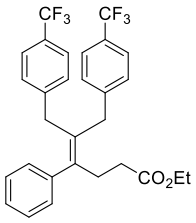
6-(tert-butyl)-1,1-dimethyl-4-(3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-2,3-dihydro-1H-indene (20). The title compound **20** was prepared from **1r** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (80.5 mg, 72% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 3H), 7.01 (s, 1H), 3.73 (d, *J* = 15.4 Hz, 1H), 3.29 (d, *J* = 15.4 Hz, 1H), 3.22 (d, *J* = 14.8 Hz, 1H), 3.02 (d, *J* = 14.8 Hz, 1H), 2.81 (dt, *J* = 15.2, 6.8 Hz, 1H), 2.65 (dt, *J* = 15.2, 6.8 Hz, 1H), 2.13 (s, 3H), 1.99 – 1.86 (m, 2H), 1.30 (s, 12H), 1.23 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 150.0, 144.7, 144.3, 139.5, 136.0, 131.0, 129.0, 128.8, 128.50 (q, *J* = 32.0 Hz), 128.48 (q, *J* = 32.0 Hz), 125.5 (q, *J* = 4.2 Hz), 125.1 (q, *J* = 4.2 Hz), 124.4 (q, *J* = 272.1 Hz), 124.3 (q, *J* = 272.1 Hz), 123.0, 117.2, 44.1, 41.5, 38.0, 36.1, 34.7, 31.6, 28.9, 28.5, 20.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.2, -62.3; **IR (neat)**: ν 2961, 2858, 1613, 1411, 1361, 1322, 1219, 1161, 1108, 1065, 1018, 843, 802 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{34}H_{36}F_6$ 558.2716; found 558.2729.



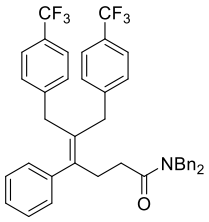
4,4'-(2-(1-phenylbutylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (21). The title compound **21** was prepared from **1s** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (57.6 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.19 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.51 (s, 2H), 3.20 (s, 2H), 2.56 – 2.48 (m, 2H), 1.48 – 1.34 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.5, 144.1, 142.7, 141.9, 130.7, 128.9, 128.8, 128.5, 128.35, 128.31 (q, *J* = 32.6 Hz), 126.7, 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 38.2, 37.0, 35.8, 21.6, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2961, 2930, 2872, 1620, 1320, 1160, 1106, 1065, 1018, 819, 701 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{24}F_6$ 462.1777; found 462.1798.



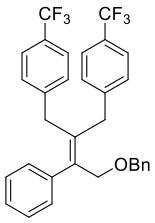
4,4'-(2-(3-methyl-1-phenylbutylidene)propane-1,3-diyl)bis((trifluoromethyl) benzene) (22). The title compound **22** was prepared from **1t** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (63.2 mg, 66% yield). M.p.: 114 – 115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.54 (s, 2H), 3.22 (s, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.67 – 1.56 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 144.0, 142.7, 141.2, 131.5, 128.9, 128.8, 128.4, 128.34, 128.32 (q, *J* = 33.3 Hz), 126.7, 125.4 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 43.8, 38.4, 36.1, 26.6, 22.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2947, 2864, 1613, 1463, 1321, 1161, 1120, 1066, 1018, 819, 702 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{26}F_6$ 476.1933; found 476.1945.



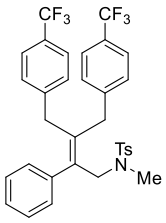
Ethyl 4-phenyl-5-(4-(trifluoromethyl)benzyl)-6-(4-(trifluoromethyl)phenyl)hex-4-enoate (23). The title compound **23** was prepared from **1u** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (66.0 mg, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 8.1 Hz, 3H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 3.21 (s, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.34 (t, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.8, 144.1, 143.8, 141.4, 139.7, 132.3, 128.9, 128.7, 128.57, 128.55, 128.4 (q, *J* = 32.0 Hz), 127.0, 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 60.5, 38.3, 35.9, 32.8, 29.9, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2989, 2919, 1731, 1613, 1416, 1321, 1159, 1065, 1017, 850, 819, 767 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{27}F_6O_2$ 521.1910; found 521.1901.



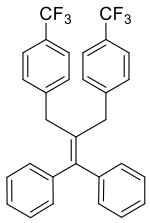
***N*,*N*-dibenzyl-4-phenyl-5-(4-(trifluoromethyl)benzyl)-6-(4-(trifluoromethyl)phenyl)hex-4-enamide (24).** The title compound **24** was prepared from **1v** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (68.2 mg, 51% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.23 (m, 9H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 4.58 (s, 2H), 4.26 (s, 2H), 3.55 (s, 2H), 3.20 (s, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.40 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.5, 144.2, 143.9, 141.5, 140.1, 137.3, 136.4, 131.9, 128.9, 128.7, 128.6, 128.5, 128.29 (q, *J* = 32.0 Hz), 128.26, 127.6, 127.4, 126.9, 126.2, 125.4 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.7 Hz) 49.9, 48.5, 38.4, 36.0, 31.5, 30.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.27, -62.30; **IR (neat)**: ν 3036, 2934, 1647, 1618, 1416, 1320, 1161, 1107, 1065, 1017, 819, 730 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{41}H_{36}NOF_6$ 672.2695; found 672.2697.



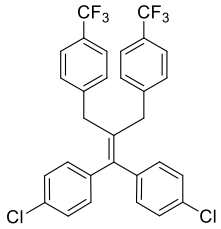
4,4'-(2-(2-(benzyloxy)-1-phenylethylidene)propane-1,3-diyl)bis((trifluoromethyl) benzene) (25). The title compound **25** was prepared from **1w** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (77.0 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.22 (m, 8H), 7.21 – 7.15 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.51 (s, 2H), 4.39 (s, 2H), 3.52 (s, 2H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 143.5, 141.5, 138.10, 138.06, 136.8, 129.01, 128.99, 128.6, 128.424, 128.417 (q, *J* = 32.6 Hz), 128.3, 127.63, 127.61, 127.0, 125.4 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 124.2 (q, *J* = 272.1 Hz), 72.8, 70.7, 38.1, 36.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.30, -62.32; **IR (neat)**: ν 3031, 2950, 2856, 1616, 1408, 1322, 1161, 1119, 1108, 1066, 1018, 851, 820, 735 cm^{-1}; **HRMS** (ESI) m/z: $[M+K]^+$ Calcd. for $C_{32}H_{26}F_6OK$ 579.1519; found 579.1512.



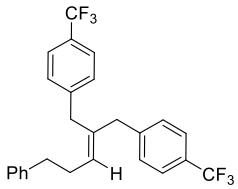
***N*,4-dimethyl-*N*-(2-phenyl-3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)benzenesulfonamide (26).** The title compound **16** was prepared from **1x** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 10 : 1). The product was obtained as a colorless oil (54.1 mg, 44% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.19 (m, 6H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.12 (s, 2H), 3.61 (s, 2H), 3.30 (s, 2H), 2.58 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 143.4, 143.2, 140.1, 137.1, 136.1, 134.2, 129.6, 128.9, 128.75, 128.71, 128.61 (q, *J* = 32.6 Hz), 128.59, 128.55 (q, *J* = 32.6 Hz), 127.44, 127.35, 125.5 (q, *J* = 4.2 Hz), 125.4 (q, *J* = 4.2 Hz), 124.2 (q, *J* = 272.1 Hz), 52.1, 38.7, 35.9, 34.8, 21.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.37, -62.38; **IR (neat)**: ν 2955, 2928, 2859, 1738, 1488, 1361, 1090, 1015, 841, 802 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{29}NO_2F_6NaS$ 640.1715; found 640.1720.



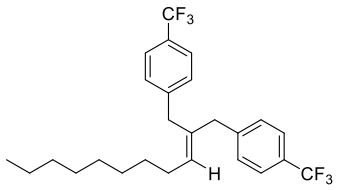
4,4'-(2-(diphenylmethylene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (27). The title compound **27** was prepared from **1y** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (54.8 mg, 55% yield), M.p.: 96 – 97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 4H), 7.36 – 7.21 (m, 10H), 7.18 (d, *J* = 8.0 Hz, 4H), 3.43 (s, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.1, 143.0, 142.1, 134.1, 129.1, 128.9, 128.53 (q, *J* = 31.9 Hz), 128.48, 127.0, 125.4 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 37.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (acetone)**: ν 3024, 2914, 2851, 1612, 1492, 1364, 1320, 1218, 1161, 1065, 1018, 842, 806, 699 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{30}H_{22}F_6$ 496.1620; found 496.1636.



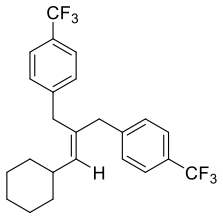
4,4'-(2-(bis(4-chlorophenyl)methylene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (28). The title compound **28** was prepared from **1z** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a white solid (51.0 mg, 45% yield), M.p.: 135 – 137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 7.21 – 7.11 (m, 8H), 3.43 (s, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 140.6, 140.0, 135.6, 133.3, 130.6, 128.9, 128.84, 128.79 (q, *J* = 32.0 Hz), 125.5 (q, *J* = 4.2 Hz), 124.2 (q, *J* =272.1 Hz), 37.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2917, 2854, 1617, 1488, 1416, 1321, 1157, 1116, 1091, 1064, 898, 829, 821 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{30}H_{20}Cl_2F_6$ 564.0841; found 564.0861



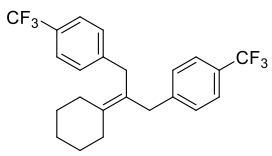
4,4'-(2-(3-phenylpropylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (29). The title compound **29** was prepared from **1aa** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (60.3 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 4H), 7.33 – 7.14 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.48 (t, *J* = 7.2 Hz, 1H), 3.23 (s, 2H), 3.19 (s, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.52 (td, *J* = 7.6, 7.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 143.6, 141.5, 136.2, 129.4, 129.2, 128.8, 128.6, 128.5 (q, *J* = 31.9 Hz), 128.4, 126.0, 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.32 (q, *J* = 272.1 Hz), 124.29 (q, *J* = 272.1 Hz), 42.8, 35.9, 35.2, 30.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.28, -62.31; **IR (neat)**: ν 2934, 2853, 1616, 1454, 1319, 1159, 1117, 1098, 1064, 1018, 842, 814, 698 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{22}F_6$ 448.1620; found 448.1632.



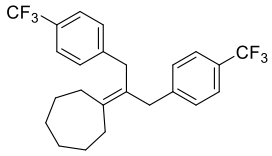
4,4'-(2-nonylidenepropane-1,3-diyl)bis((trifluoromethyl)benzene) (30). The title compound **30** was prepared from **1ab** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (56.1 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 4H), 7.23 – 7.16 (m, 4H), 5.49 (t, *J* = 7.2 Hz, 1H), 3.33 (s, 2H), 3.23 (s, 2H), 2.18 (td, *J* = 7.3, 7.2 Hz, 2H), 1.48 – 1.38 (m, 2H), 1.35 – 1.24 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.0, 143.9, 135.2, 130.8, 129.2, 128.9, 128.53 (q, *J* = 32.8 Hz), 128.48 (q, *J* = 32.8 Hz), 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.33 (q, *J* = 272.1 Hz), 124.30 (q, *J* = 272.1 Hz), 42.9, 35.2, 31.9, 29.9, 29.5, 29.4, 29.3, 28.3, 22.7, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2956, 2850, 1615, 1322, 1161, 1122, 1066, 1018, 861, 608 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{30}F_6$ 456.2246; found 456.2258.



4,4'-(2-(cyclohexylmethylene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (31). The title compound **31** was prepared from **1ac** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (57.9 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 4H), 7.23 – 7.14 (m, 4H), 5.35 (d, *J* = 9.4 Hz, 1H), 3.33 (s, 2H), 3.19 (s, 2H), 2.40 – 2.26 (m, 1H), 1.80 – 1.62 (m, 5H), 1.36 – 1.12 (m, 5H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.1, 143.8, 136.9, 133.2, 129.1, 128.9, 128.51 (q, *J* = 32.6 Hz), 128.49 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.34 (q, *J* = 272.1 Hz), 124.32 (q, *J* = 272.1 Hz), 42.7, 37.3, 35.3, 33.5, 25.95, 25.90; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.33, -62.34; **IR (neat)**: ν 2924, 2851, 1617, 1499, 1416, 1321, 1106, 1109, 1065, 1018, 848, 819 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{24}F_6$ 426.1777; found 426.1782.

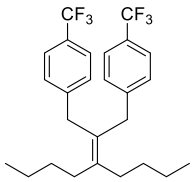


4,4'-(2-cyclohexylidenepropane-1,3-diyl)bis((trifluoromethyl)benzene) (32). The title compound **32** was prepared from **1ad** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (60.5 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 4H), 3.39 (s, 4H), 2.36 (t, *J* = 5.7 Hz, 4H), 1.68 – 1.60 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.8, 138.7, 128.7, 128.3 (q, *J* = 32.0 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 36.6, 31.1, 28.4, 26.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2920, 2850, 1619, 1414, 1332, 1159, 1117, 1065, 1017, 850, 817 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{23}H_{22}F_6$ 412.1620; found 412.1637.

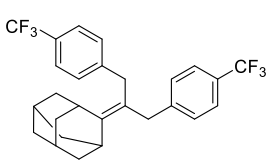


(1,3-bis(4-(trifluoromethyl)phenyl)propan-2-ylidene)cycloheptane (33). The title compound **33** was prepared from **1ae** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (69.2 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50

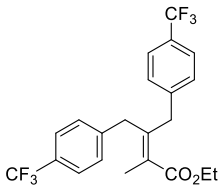
(d, *J* = 8.0 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 4H), 3.39 (s, 4H), 2.44 (t, *J* = 6.2 Hz, 4H), 1.71 – 1.54 (m, 8H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 140.1, 128.7, 128.3 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 36.7, 31.9, 28.9, 27.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2912, 2858, 1622, 1420, 1319, 1162, 1105, 1065, 1018, 851, 817 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{24}F_6$ 426.1777; found 426.1794.



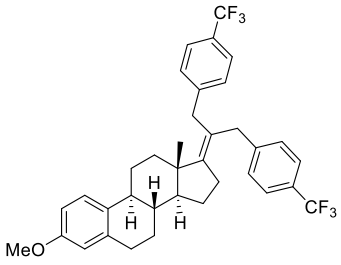
4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (34). The title compound **34** was prepared from **1af** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (68.0 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 3.33 (s, 4H), 2.24 – 2.15 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.42 (m, 4H), 1.41 – 1.31 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 140.1, 128.7, 128.3 (q, *J* = 32.0 Hz), 125.3 (q, *J* = 4.2 Hz), 124.4 (q, *J* = 272.1 Hz), 36.4, 32.2, 31.5, 23.1, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2962, 2937, 2856, 1614, 1319, 1120, 1103, 1064, 1017, 849, 817, 688 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{30}F_6$ 456.2246; found 456.2254.



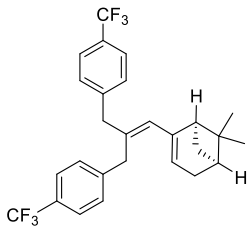
2-(1,3-bis(4-(trifluoromethyl)phenyl)propan-2-ylidene)adamantane (35). The title compound **35** was prepared from **1ag** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (53.1 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 3.38 (s, 4H), 3.03 (t, *J* = 3.2 Hz, 2H), 2.06 – 1.91 (m, 6H), 1.90 – 1.79 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.1, 144.9, 128.7, 128.2 (q, *J* = 32.6 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 39.3, 36.9, 36.2, 33.5, 27.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2908, 2849, 1615, 1450, 1320, 1160, 1122, 1106, 1017, 850, 817 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{26}F_6$ 464.1933; found 464.1934



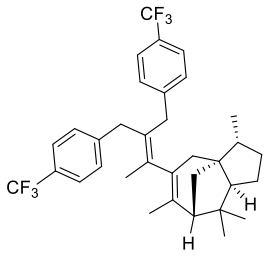
ethyl 2-methyl-3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-enoate (36). The title compound **36** was prepared from **1ah** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (60.2 mg, 70% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 3.43 (s, 2H), 2.07 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.6, 143.1, 142.2, 141.7, 129.3, 128.74, 128.70 (q, *J* = 32.6 Hz), 128.67 (q, *J* = 32.6 Hz), 128.4, 125.5 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.2 Hz), 124.24 (q, *J* = 272.1 Hz), 124.15 (q, *J* = 272.1 Hz), 60.8, 38.8, 37.2, 16.3, 14.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4, -62.5; **IR (acetone)**: ν 2961, 2940, 1737, 1615, 1324, 1229, 1122, 1066, 1018, 910, 822 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{22}H_{20}F_6O_2$ 430.1362; found 430.1370.



(8S,9S,13S,14S)-17-(1,3-bis(4-(trifluoromethyl)phenyl)propan-2-ylidene)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (37). The title compound **37** was prepared from **1ai** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (77.0 mg, 64% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 3H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 3.77 (d, *J* = 15.8 Hz, 1H), 3.76 (s, 3H), 3.36 (d, *J* = 15.8 Hz, 2H), 3.15 (d, *J* = 15.8 Hz, 1H), 2.96 – 2.83 (m, 2H), 2.58 – 2.45 (m, 2H), 2.37 – 2.24 (m, 3H), 2.02 – 1.95 (m, 1H), 1.92 – 1.78 (m, 2H), 1.60 – 1.49 (m, 3H), 1.48 – 1.36 (m, 2H), 1.06 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.5, 150.4, 144.7, 144.2, 137.9, 132.5, 129.0, 128.5, 128.3 (q, *J* = 32.6 Hz), 126.2, 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.4 (q, *J* = 272.1 Hz), 124.0, 113.8, 111.5, 55.5, 55.1, 45.2, 43.5, 38.44, 38.37, 37.9, 36.3, 30.6, 29.8, 27.6, 27.1, 24.0, 18.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.17, -62.21; **IR (acetone)**: ν 2934, 2869, 2832, 1615, 1499, 1322, 1159, 1103, 1065, 1017, 905, 850, 817, 733 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{36}H_{36}F_6O$ 598.2665; found 598.2686.

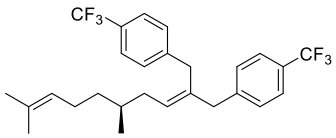


(1R,5S)-6,6-dimethyl-2-(2-(4-(trifluoromethyl)benzyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)bicyclo[3.1.1]hept-2-ene (38). The title compound **38** was prepared from **1aj** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (49.3 mg, 53% yield), containing a trace amount of impurity that failed to be separated. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 4H), 7.23 – 7.17 (m, 4H), 5.88 (s, 1H), 5.50 (s, 1H), 3.58 – 3.49 (m, 2H), 3.24 (s, 2H), 2.43 – 2.39 (m, 1H), 2.35 – 2.27 (m, 3H), 2.21 (t, *J* = 4.9 Hz, 1H), 2.12 – 2.09 (m, 1H), 1.28 (s, 3H), 0.89 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 144.0, 143.7, 135.1, 131.4, 129.3, 128.9, 128.8 (q, *J* = 32.6 Hz), 128.7 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 121.4, 46.7, 43.0, 40.4, 37.9, 36.4, 31.8, 31.6, 26.3, 21.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3, -62.4; **IR (acetone)**: ν 2987, 2917, 2858, 1617, 1417, 1321, 1161, 1120, 1065, 888, 827 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{26}F_6$ 464.1933; found 464.1946.

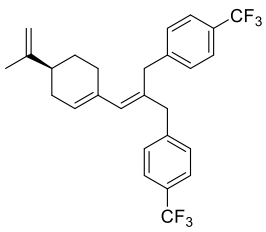


(3R,3aS,7R,8aS)-3,6,8,8-tetramethyl-5-(3-(4-(trifluoromethyl)benzyl)-4-(4-(trifluoromethyl)phenyl)but-2-en-2-yl)-2,3,4,7,8,8a-hexahydro-1H-3a,7-methanoazulene) (39). The title compound **39** was prepared from **1ak** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (61.8 mg, 55% yield), which was composed of a pair of isomers (major : minor = 3 : 2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.3, 2.7 Hz, 7H, *mixtures of major and minor isomer*), 7.15 (dd, *J* = 8.3, 3.1 Hz, 7H, *mixtures of major and minor isomer*), 3.52 – 3.40 (m, 3H, *mixtures of major and minor isomer*), 3.29 – 3.14 (m, 3H, *mixtures of major and minor isomer*), 2.45 (d, *J* = 16.4 Hz, 1H, *minor isomer*), 2.15 (d, *J* = 16.5 Hz, 1H, *major isome*r), 1.98 (d, *J* = 16.5 Hz, 1H, *major* isomer), 1.92 – 1.82 (m, 8H, *mixtures of major and minor isomer*), 1.81 – 1.59 (m, 13H, *mixtures of major and minor isomer*), 1.47 – 1.30 (m, 6H, *mixtures of major and minor isomer*), 1.06 (s, 3H, *major isomer*), 0.98 – 0.93 (m, 7H, *mixtures of major and*

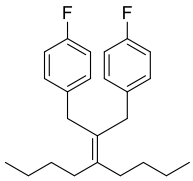
minor isomer), 0.86 (d, *J* = 7.2 Hz, 5H, *mixtures of major and minor isomer*); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9, 144.7, 144.5, 137.0, 136.3, 134.0, 133.9, 132.3, 131.7, 129.5, 129.3, 129.3, 128.8, 128.7 (there are multiple peaks of major and minor isomers between 149.9 – 128.7), 128.3 (q, *J* = 32.6 Hz), 128.2 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 59.2, 58.9 (*minor isomer*), 55.4 (*minor isomer*), 55.2, 54.2, 48.5, 48.3 (*minor isomer*), 42.9 (*minor isomer*), 42.4, 41.44, 41.35 (*minor isomer*), 40.9, 38.1 (*minor isomer*), 37.7, 36.1, 35.9 (*minor isomer*), 35.7 (*minor isomer*), 35.6, 27.9, 27.8 (*minor isomer*), 25.73 (*minor isomer*), 25.69, 24.8, 24.7 (*minor isomer*), 21.6 (*minor isomer*), 21.5, 18.4 (*minor isomer*), 18.0, 15.43, 15.38 (*minor isomer*); **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.28, -62.30; **IR (neat)**: ν 2963, 2934, 2869, 1623, 1322, 1161, 1122, 1066, 1018, 905, 862 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{34}H_{38}F_6$ 560.2872; found 560.2883.



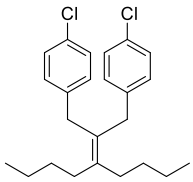
(S)-4,4'-(2-(3,7-dimethyloct-6-en-1-ylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (40). The title compound **40** was prepared from **1al** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (67.0 mg, 72% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 4H), 7.22 – 7.17 (m, 4H), 5.52 (t, *J* = 7.3 Hz, 1H), 5.10 (tt, *J* = 7.1, 1.4 Hz, 1H), 3.33 (s, 2H), 3.25 (s, 2H), 2.24 – 2.16 (m, 1H), 2.08 – 1.93 (m, 3H), 1.69 (s, 3H), 1.65 – 1.55 (m, 4H), 1.45 – 1.36 (m, 1H), 1.25 – 1.18 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.1, 143.8, 136.0, 131.4, 129.4, 129.2, 128.9, 128.54 (q, *J* = 32.6 Hz), 128.50 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.2 Hz), 125.2 (q, *J* = 4.2 Hz), 124.6, 124.3 (q, *J* = 272.1 Hz), 43.0, 36.8, 35.4, 35.2, 33.3, 25.7, 25.6, 19.7, 17.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (acetone)**: ν 2968, 2913, 2853, 1615, 1321, 1161, 1065, 850, 819 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{30}F_6$ 468.2246; found 468.2255.



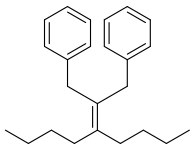
(S)-4,4'-(2-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methylene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (41). The title compound **41** was prepared from **1am** (0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (47.1 mg, 51% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.93 (s, 1H), 5.70 – 5.65 (m, 1H), 4.72 (d, *J* = 10.9 Hz, 2H), 3.56 (d, *J* = 15.4 Hz, 1H), 3.49 (d, *J* = 15.4 Hz, 1H), 3.26 (s, 2H), 2.25 – 2.11 (m, 4H), 2.07 – 1.97 (m, 1H), 1.87 – 1.81 (m, 1H), 1.73 (s, 3H), 1.55 – 1.45 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.6, 144.1, 143.8, 135.2, 134.4, 132.8, 129.3, 128.9, 128.6 (q, *J* = 32.6 Hz), 128.5 (q, *J* = 32.6 Hz), 125.9, 125.4 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 108.7, 43.2, 40.6, 36.2, 31.0, 29.6, 27.7, 20.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3, -62.4; **IR (acetone)**: ν 2963, 2937, 2827, 1615, 1417, 1361, 1321, 1219, 1161, 1119, 1065, 1018, 890, 849, 821 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{27}F_6$ 465.2011; found 465.2016.



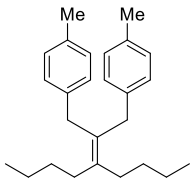
4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(fluorobenzene) (42). The title compound **42** was prepared from **1af** (0.2 mmol) and 1-bromo-4-fluorobenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (46.5 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 – 6.98 (m, 4H), 6.97 – 6.91 (m, 4H), 3.23 (s, 4H), 2.17 (t, *J* = 8.0 Hz, 4H), 1.49 – 1.40 (m, 4H), 1.38 – 1.30 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.4 Hz), 138.5, 136.1 (d, *J* = 3.5 Hz), 129.7 (d, *J* = 7.6 Hz), 129.4, 114.5 (d, *J* = 20.8 Hz), 35.5, 32.1, 31.6, 23.1, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.8; **IR (neat)**: ν 2956, 2928, 2859, 1603, 1505, 1465, 1220, 1155, 1091, 1016, 851, 822, 775 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{30}F_2$ 356.2310; found 356.2311.



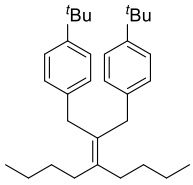
4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(chlorobenzene) (43). The title compound **43** was prepared from **1af** (0.2 mmol) and 1-bromo-4-chlorobenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (49.0 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 6.99 (d, *J* = 8.3 Hz, 4H), 3.22 (s, 4H), 2.16 (t, *J* = 8.0 Hz, 4H), 1.49 – 1.38 (m, 4H), 1.38 – 1.29 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.1, 139.0, 131.5, 129.8, 128.7, 128.4, 35.7, 32.1, 31.5, 23.1, 14.1; **IR (acetone)**: ν 2955, 2928, 2859, 1488, 1090, 1015, 841, 802 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{30}Cl_2$ 388.1719; found 388.1724.



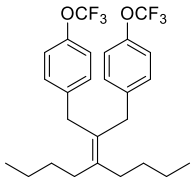
(2-(nonan-5-ylidene)propane-1,3-diyl)dibenzene (44). The title compound **44** was prepared from **1af** (0.2 mmol) and bromobenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (37.3 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 4H), 7.20 – 7.14 (m, 2H), 7.13 – 7.06 (m, 4H), 3.29 (s, 4H), 2.19 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.41 (m, 4H), 1.40 – 1.29 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.8, 138.1, 129.5, 128.5, 128.2, 125.7, 36.4, 32.1, 31.6, 23.1, 14.1; **IR (acetone)**: ν 3055, 3026, 2954, 2858, 1601, 1493, 1493, 1451, 1377, 1072, 1029, 743 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{32}$ 320.2499; found 320.2503.



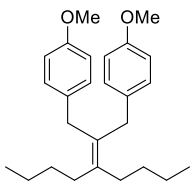
4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(methylbenzene) (45). The title compound **45** was prepared from **1af** (0.2 mmol) and 1-bromo-4-methylbenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (34.0 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.8 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 4H), 3.24 (s, 4H), 2.32 (s, 6H), 2.18 (t, *J* = 8.0 Hz, 4H), 1.49 – 1.40 (m, 4H), 1.39 – 1.29 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.75, 137.69, 135.1, 129.8, 128.9, 128.4, 35.9, 32.0, 31.6, 23.1, 21.0, 14.1; **IR (neat)**: ν 2955, 2926, 2859, 1512, 1456, 1365, 1216, 830 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{36}$ 348.2812; found 348.2815.



4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(tert-butylbenzene) (46). The title compound **46** was prepared from **1af** (0.2 mmol) and 1-bromo-4-(*tert*-butyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (36.2 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 4H), 3.27 (s, 4H), 2.18 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.41 (m, 4H), 1.38 – 1.28 (m, 22H), 0.91 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.4, 137.8, 137.7, 129.7, 128.1, 125.1, 36.0, 34.3, 32.0, 31.6, 31.5, 23.1, 14.1; **IR (neat)**: ν 2971, 2856, 1613, 1365, 1216, 1156, 858, 816, 790 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{32}H_{48}$ 432.3751; found 432.3762.

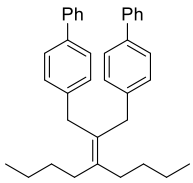


4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis((trifluoromethoxy)benzene) (47). The title compound **47** was prepared from **1af** (0.2 mmol) and 1-bromo-4-(trifluoromethoxy)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (40.3 mg, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.03 (m, 8H), 3.27 (s, 4H), 2.18 (t, *J* = 8.0 Hz, 4H), 1.50 – 1.40 (m, 4H), 1.40 – 1.30 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 139.4, 139.2, 129.6, 128.6, 120.9, 120.5 (q, *J* = 257.2 Hz), 35.8, 32.1, 31.6, 23.1, 14.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.9; **IR (neat)**: ν 2961, 2931, 2861, 1505, 1461, 1253, 1218, 1156, 1102, 1019, 920, 851, 811 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{30}F_6O_2$ 488.2145; found 488.2153.

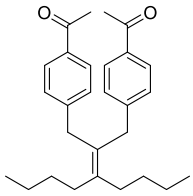


4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(methoxybenzene) (48). The title compound **48** was prepared from **1af** (0.2 mmol) and 1-bromo-4-methoxybenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (30.0 mg, 39% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 – 6.97 (m, 4H), 6.84 – 6.79 (m, 4H), 3.79 (s, 6H), 3.21 (s, 4H), 2.17 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.39 (m, 4H), 1.39 – 1.29 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.7, 137.5, 132.8, 130.2, 129.3, 113.6, 55.2, 35.3,

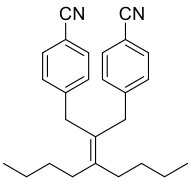
32.0, 31.6, 23.1, 14.1; **IR (neat)**: ν 2953, 2928, 2861, 2835, 1610, 1507, 1463, 1299, 1241, 1172, 1037, 818, 780 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{36}O_2$ 380.2710; found 380.2718.



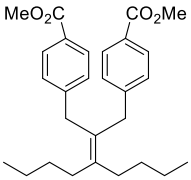
4,4''-(2-(nonan-5-ylidene)propane-1,3-diyl)di-1,1'-biphenyl (49). The title compound **49** was prepared from **1af** (0.2 mmol) and 4-bromo-1,1'-biphenyl (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (56.9 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.54 – 7.47 (m, 4H), 7.45 – 7.36 (m, 4H), 7.35 – 7.25 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 4H), 3.38 (s, 4H), 2.24 (t, *J* = 8.0 Hz, 4H), 1.55 – 1.45 (m, 4H), 1.43 – 1.32 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.1, 139.9, 138.7, 138.4, 129.3, 128.9, 128.7, 127.01, 126.96, 126.9, 36.2, 32.1, 31.6, 23.1, 14.1; **IR (neat)**: ν 3060, 3031, 2954, 2926, 2857, 1486, 1007, 848, 819, 758, 695 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{36}H_{40}$ 472.3125; found 472.3138.



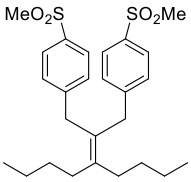
1,1'-((2-(nonan-5-ylidene)propane-1,3-diyl)bis(4,1-phenylene))bis(ethan-1-one) (50). The title compound **50** was prepared from **1af** (0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (61.0 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 3.34 (s, 4H), 2.59 (s, 6H), 2.20 (t, *J* = 8.0 Hz, 4H), 1.53 – 1.43 (m, 4H), 1.40 – 1.30 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8, 146.4, 139.8, 135.1, 128.6, 128.5, 127.9, 36.6, 32.1, 31.4, 26.5, 23.0, 14.0; **IR (neat)**: ν 2955, 2928, 2858, 1714, 1681, 1604, 1410, 1356, 1265, 1219, 1016, 956, 850, 813 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{36}O_2Na$ 427.2608; found 427.2606.



4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)dibenzonitrile (51). The title compound **51** was prepared from **1af** (0.2 mmol) and 4-bromobenzonitrile (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (23.2 mg, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 4H), 3.32 (s, 4H), 2.17 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.41 (m, 4H), 1.39 – 1.29 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.0, 141.1, 132.2, 129.1, 126.7, 119.0, 109.9, 36.8, 32.2, 31.4, 23.0, 14.0; **IR (neat)**: ν 2955, 2928, 2859, 2227, 1605, 1502, 1464, 1412, 1173, 1107, 1020, 907, 850, 818, 755 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{30}N_2$ 370.2404; found 370.2410.

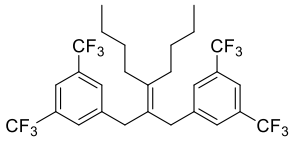


dimethyl 4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)dibenzoate (52). The title compound **52** was prepared from **1af** (0.2 mmol) and methyl 4-bromobenzoate (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (48.4 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 4H), 7.13 (d, *J* = 8.1 Hz, 4H), 3.90 (s, 6H), 3.32 (s, 4H), 2.19 (t, *J* = 8.0 Hz, 4H), 1.50 – 1.41 (m, 4H), 1.40 – 1.30 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.1, 139.6, 129.7, 128.5, 128.1, 127.9, 51.9, 36.6, 32.1, 31.4, 23.0, 14.0; **IR (neat)**: ν 2953, 2928, 2859, 1719, 1609, 1434, 1273, 1191, 1104, 1019, 860, 759, 710 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{37}O_4$ 437.2686; found 437.2686.

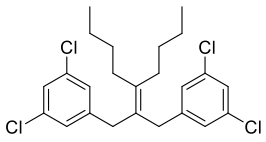


4,4'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis((methylsulfonyl)benzene) (53). The title compound **53** was prepared from **1af** (0.2 mmol) and 1-bromo-4-(methylsulfonyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 20 : 1). The product was obtained as a colorless oil (54.3 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.26 – 7.23 (m, 4H), 3.37 (s, 4H), 3.05 (s, 6H), 2.20 (t, *J* = 8.0 Hz, 4H), 1.52 – 1.43 (m, 4H), 1.42 – 1.32 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.0, 141.0, 138.3, 129.3, 127.5, 127.0, 44.5, 36.7, 32.2, 31.5, 23.1, 14.0; **IR (neat)**: ν 2955, 2928, 2858, 1595, 1398,

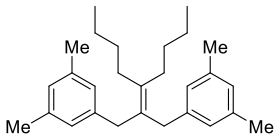
1305, 1150, 1090, 956, 761 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{37}O_4S_2$ 477.2128; found 477.2125.



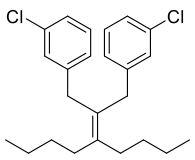
5,5'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(1,3-bis(trifluoromethyl)benzene) (54). The title compound **54** was prepared from **1af** (0.2 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (25.0 mg, 21% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.46 (s, 4H), 3.44 (s, 4H), 2.23 (t, *J* = 8.0 Hz, 4H), 1.53 – 1.43 (m, 4H), 1.42 – 1.31 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.42, 142.40, 131.6 (q, *J* = 33.3 Hz), 128.4 (q, *J* = 4.4 Hz), 125.1 (q, *J* = 272.7 Hz), 120.2 (q, *J* = 4.2 Hz), 36.8, 32.0, 31.2, 22.9, 13.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.0; **IR (neat)**: ν 2958, 2934, 2864, 1618, 1373, 1290, 1170, 1129, 891, 706 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{28}F_{12}$ 592.1994; found 592.2000.



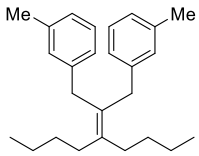
5,5'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(1,3-dichlorobenzene) (55). The title compound **55** was prepared from **1af** (0.2 mmol) and 1-bromo-3,5-dichlorobenzene (0.6 mmol) according to General Procedure, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (31.2 mg, 34% yield), containing homo-coupling product from 1-bromo-3,5-dichlorobenzene that failed to be separated.[14] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 1.9 Hz, 2H), 6.92 (d, *J* = 1.9 Hz, 4H), 3.24 (s, 4H), 2.16 (t, *J* = 8.0 Hz, 4H), 1.49 – 1.41 (m, 4H), 1.40 – 1.30 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 141.2, 134.8, 126.9, 126.7, 126.3, 36.2, 32.1, 31.3, 23.0, 14.0. **IR (neat)**: ν 2956, 2929, 2860, 1585, 1565, 1557, 1427, 1375, 1229, 1204, 1098, 852, 800, 668 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{28}Cl_4$ 456.0940; found 456.0942.



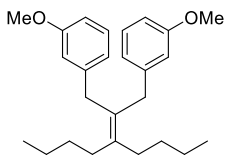
5,5'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(1,3-dimethylbenzene) (56). The title compound **56** was prepared from **1af** (0.2 mmol) and 1-bromo-3,5-dimethylbenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (37.0 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 6.72 (s, 4H), 3.23 (s, 4H), 2.27 (s, 12H), 2.18 (t, *J* = 8.0 Hz, 4H), 1.50 – 1.41 (m, 4H), 1.40 – 1.30 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.8, 137.6, 137.5, 129.8, 127.3, 126.4, 36.3, 31.9, 31.5, 23.0, 21.3, 14.1; **IR (neat)**: ν 3013, 2954, 2924, 2858, 1602, 1463, 1376, 1217, 1037, 843, 727, 685 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{28}H_{40}$ 376.3125; found 376.3132.



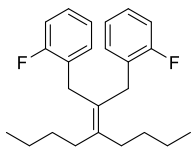
3,3'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(chlorobenzene) (57). The title compound **57** was prepared from **1af** (0.2 mmol) and 1-bromo-3-chlorobenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (49.7 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 4H), 7.05 (s, 2H), 6.95 (dt, *J* = 6.9, 1.8 Hz, 2H), 3.26 (s, 4H), 2.17 (t, *J* = 8.0 Hz, 4H), 1.50 – 1.41 (m, 4H), 1.40 – 1.29 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.6, 139.7, 134.2, 129.5, 128.5, 128.1, 126.7, 126.1, 36.2, 32.1, 31.5, 23.1, 14.1; **IR (neat)**: ν 2955, 2927, 2858, 1594, 1571, 1471, 1428, 1091, 1076, 861, 776, 720 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{30}Cl_2$ 388.1719; found 388.1725.



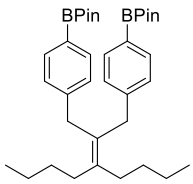
3,3'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(methylbenzene) (58). The title compound **58** was prepared from **1af** (0.2 mmol) and 1-bromo-3-methylbenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (46.1 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.93 – 6.88 (m, 4H), 3.26 (s, 4H), 2.31 (s, 6H), 2.19 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.41 (m, 4H), 1.40 – 1.29 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.8, 137.9, 137.7, 129.6, 129.4, 128.1, 126.4, 125.5, 36.4, 32.0, 31.5, 23.1, 21.4, 14.1; **IR (acetone)**: ν 3010, 2955, 2926, 2858, 1605, 1488, 1361, 1219, 1090, 788, 751, 700 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{36}$ 348.2812; found 348.2816.



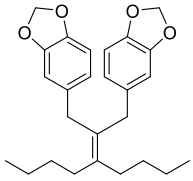
3,3'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(methoxybenzene) (59). The title compound **59** was prepared from **1af** (0.2 mmol) and 1-bromo-3-methoxybenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (57.0 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.75 – 6.64 (m, 6H), 3.76 (s, 6H), 3.28 (s, 4H), 2.19 (t, *J* = 8.0 Hz, 4H), 1.51 – 1.42 (m, 4H), 1.40 – 1.31 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 142.5, 138.4, 129.3, 129.1, 121.0, 114.0, 111.1, 55.0, 36.5, 32.0, 31.5, 23.1, 14.1; **IR (neat)**: ν 2954, 2928, 2858, 1598, 1487, 1257, 1146, 1049, 875, 781, 752 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{36}O_2$ 380.2710; found 380.2714.



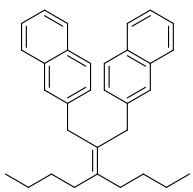
2,2'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(fluorobenzene) (60). The title compound **60** was prepared from **1af** (0.2 mmol) and 1-bromo-2-fluorobenzene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (43.1 mg, 60% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 2H), 7.09 (t, *J* = 7.2 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 3.34 (s, 4H), 2.15 (t, *J* = 8.0 Hz, 4H), 1.48 – 1.40 (m, 4H), 1.38 – 1.31 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.8 Hz), 140.4, 129.7 (d, *J* = 4.9 Hz), 127.4 (d, *J* = 8.3 Hz), 127.2 (d, *J* = 16.0 Hz), 126.1, 123.9 (d, *J* = 4.2 Hz), 114.9 (d, *J* = 22.9 Hz), 32.0, 31.4, 29.4, 23.1, 14.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.6; **IR (acetone)**: ν 2956, 2929, 2860, 1584, 1487, 1455, 1226, 1091, 972, 753 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{30}F_2$ 356.2310; found 356.2313.



2,2'-((2-(nonan-5-ylidene)propane-1,3-diyl)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (61). The title compound **61** was prepared from **1af** (0.2 mmol) and 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (68.0 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 4H), 3.28 (s, 4H), 2.18 (t, *J* = 8.0 Hz, 4H), 1.50 – 1.40 (m, 4H), 1.35 – 1.32 (m, 28H), 0.91 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 138.3, 134.8, 129.1, 128.0, 127.7, 83.6, 36.6, 32.0, 31.5, 24.8, 23.0, 14.1; **IR (acetone)**: ν 3021, 2971, 1434, 1361, 1218, 805 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{36}H_{54}B_2O_4Na$ 595.4100; found 595.4099.

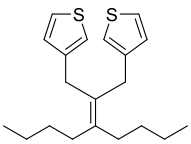


5,5'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(benzo[d][1,3]dioxole) (62). The title compound **62** was prepared from **1af** (0.2 mmol) and 5-bromobenzo[*d*][1,3]dioxole (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Hexanes : Ethyl acetate = 15 : 1). The product was obtained as a colorless oil (57.5 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 1.7 Hz, 2H), 6.53 (dd, *J* = 7.9, 1.7 Hz, 2H), 5.91 (s, 4H), 3.19 (s, 4H), 2.16 (t, 4H), 1.49 – 1.39 (m, 4H), 1.39 – 1.28 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.6, 145.5, 138.1, 134.6, 129.9, 121.3, 108.8, 108.0, 100.7, 35.8, 32.0, 31.6, 23.1, 14.1; **IR (neat)**: ν 2958, 2850, 1365, 1228, 810 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{32}O_4$ 408.2295; found 408.2306.

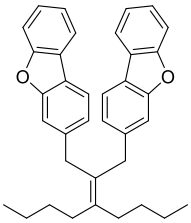


2,2'-(2-(nonan-5-ylidene)propane-1,3-diyl)dinaphthalene (63). The title compound **63** was prepared from **1af** (0.2 mmol) and 2-bromonaphthalene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (36.0 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.51 (s, 2H), 7.49 – 7.37 (m, 4H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.49 (s, 4H), 2.29 (t, *J* = 8.0 Hz, 4H), 1.59 – 1.49 (m, 4H), 1.46 – 1.33 (m, 4H), 0.95 (td, *J* = 7.3, 1.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.7, 138.3, 133.6,

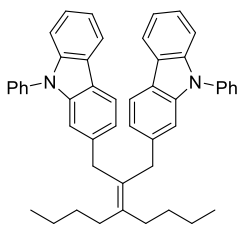
132.1, 129.3, 127.8, 127.6, 127.5, 127.4, 126.6, 125.8, 125.1, 36.6, 32.2, 31.6, 23.1, 14.1; **IR (neat)**: ν 3051, 2954, 2857, 1632, 1600, 1507, 1464, 1364, 1227, 852, 815, 754, 736 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{32}H_{36}$ 420.2812; found 420.2821.



3,3'-(2-(nonan-5-ylidene)propane-1,3-diyl)dithiophene (64). The title compound **64** was prepared from **1af** (0.2 mmol) and 3-bromothiophene (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (21.5 mg, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.86 – 6.81 (m, 4H), 3.29 (s, 4H), 2.15 (t, *J* = 8.0 Hz, 4H), 1.47 – 1.37 (m, 4H), 1.36 – 1.28 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.3, 137.2, 129.4, 128.4, 125.1, 120.5, 31.9, 31.8, 31.5, 23.1, 14.1; **IR (acetone)**: ν 2954, 2926, 2857, 1456, 1360, 1219, 835, 765 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{20}H_{28}S_2$ 332.1627; found 332.1632.



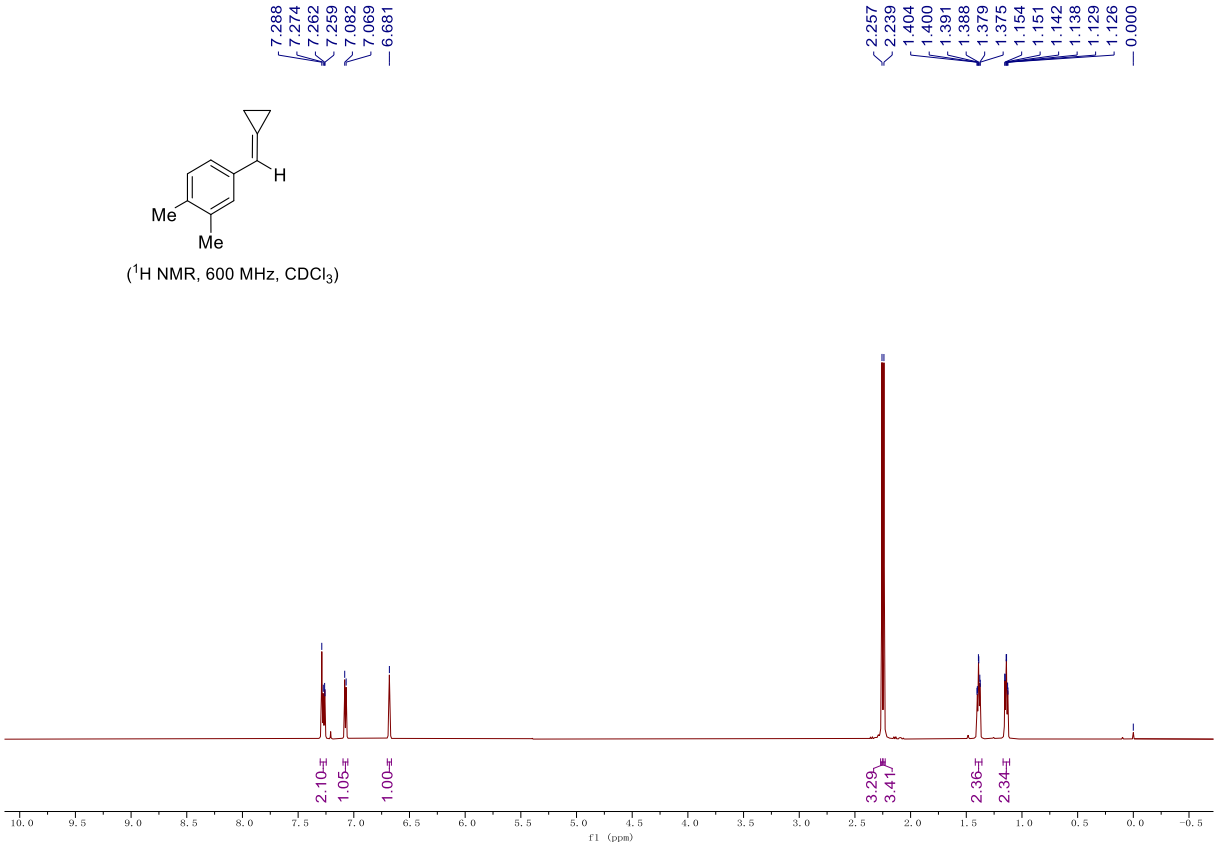
3,3'-(2-(nonan-5-ylidene)propane-1,3-diyl)didibenzo[b,d]furan (65). The title compound **65** was prepared from **1af** (0.2 mmol) and 3-bromodibenzo[*b*,*d*]furan (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained as a colorless oil (58.4 mg, 58% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 6.3 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.27 (m, 4H), 7.09 (d, *J* = 6.5 Hz, 2H), 3.49 (s, 4H), 2.28 (t, *J* = 8.1 Hz, 4H), 1.57 – 1.51 (m, 4H), 1.43 – 1.36 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.7, 156.2, 140.7, 139.0, 129.4, 126.6, 124.3, 123.6, 122.6, 122.1, 120.3, 120.2, 111.5, 111.2, 36.7, 32.2, 31.6, 23.2, 14.1; **IR (neat)**: ν 2954, 2927, 2857, 1603, 1456, 1424, 1323, 1200, 1124, 1104, 1015, 847, 745, 723 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{36}H_{36}O_2$ 500.2710; found 500.2724.



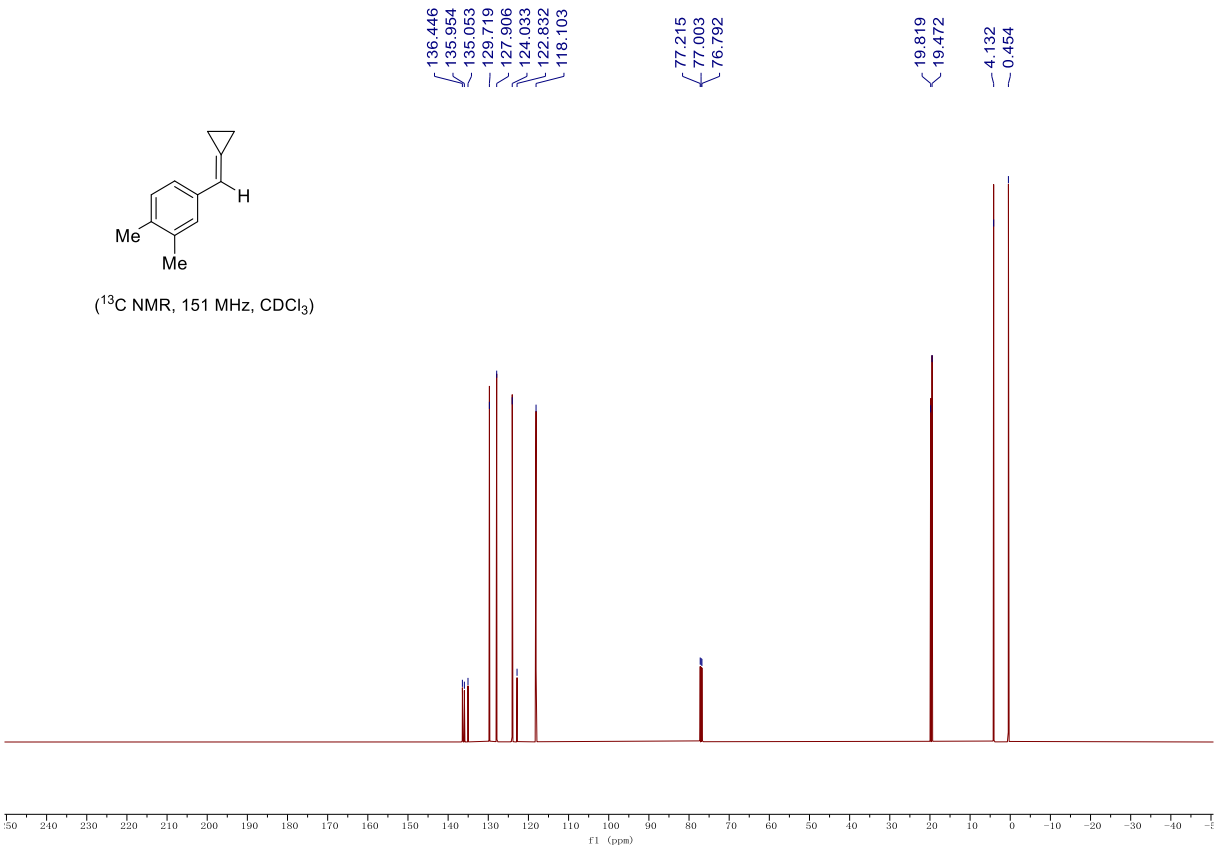
2,2'-(2-(nonan-5-ylidene)propane-1,3-diyl)bis(9-phenyl-9H-carbazole) (66). The title compound **66** was prepared from **1af** (0.2 mmol) and 2-bromo-9-phenyl-9*H*-carbazole (0.6 mmol) according to General Procedure B, and it was purified by using PTLC (Pure Hexanes). The product was obtained

as a colorless oil (59.0 mg, 45% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.50 – 7.43 (m, 8H), 7.39 – 7.32 (m, 6H), 7.26 – 7.22 (m, 2H), 7.09 (s, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.46 (s, 4H), 2.16 (t, *J* = 7.8 Hz, 4H), 1.42 – 1.35 (m, 4H), 1.34 – 1.26 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.2, 140.8, 139.1, 138.3, 137.7, 129.7, 127.1, 126.9, 125.3, 123.4, 121.4, 121.0, 120.0, 119.9, 119.8, 109.6, 109.3, 37.1, 32.0, 31.53, 31.52, 23.05, 23.03, 14.20, 14.18; **IR (acetone)**: ν 2953, 2926, 2848, 1597, 1503, 1457, 1435, 1361, 1231, 760, 743 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{48}H_{46}N_2Na$ 673.3553; found 673.3545.

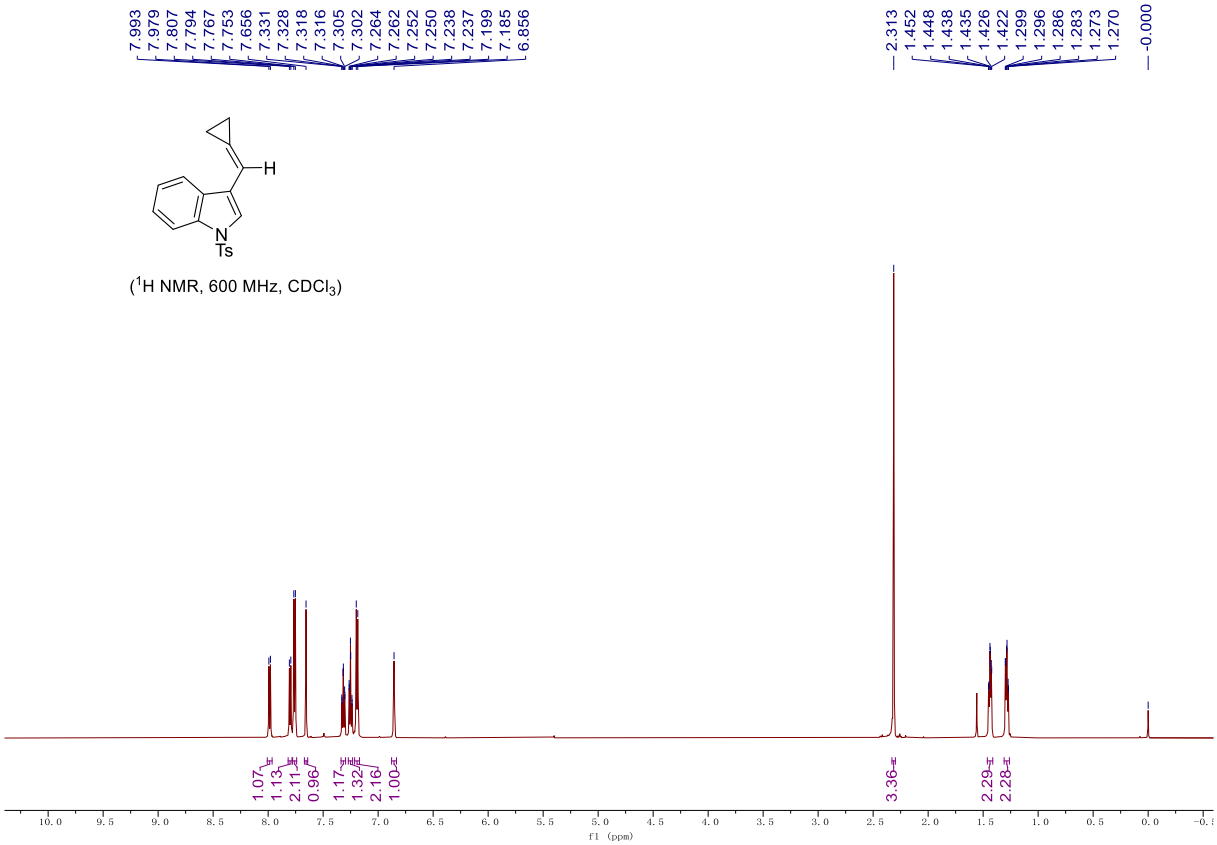
11. Spectroscopic Data of New Substrates (NMR Spectrum)



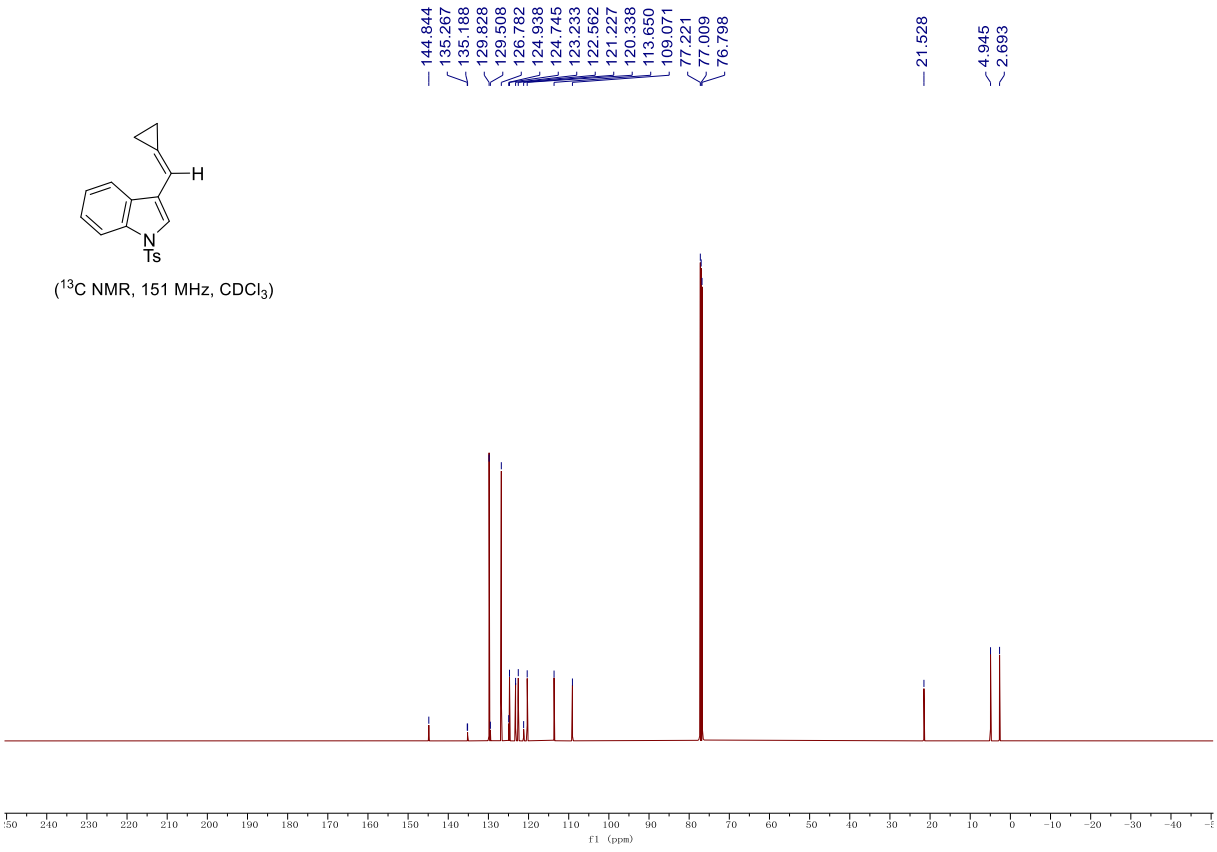
(^{1}H NMR, 600 MHz, $CDCl_3$)



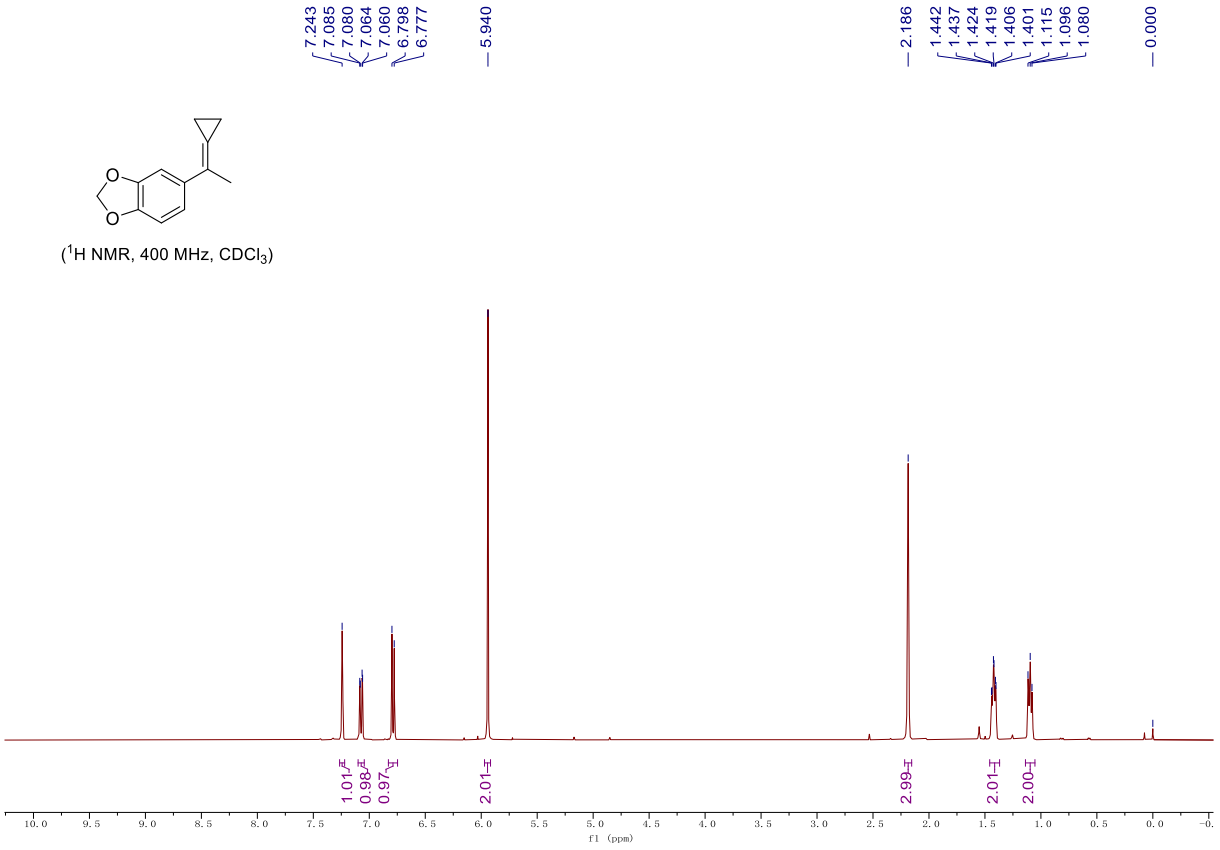
(^{13}C NMR, 151 MHz, $CDCl_3$)



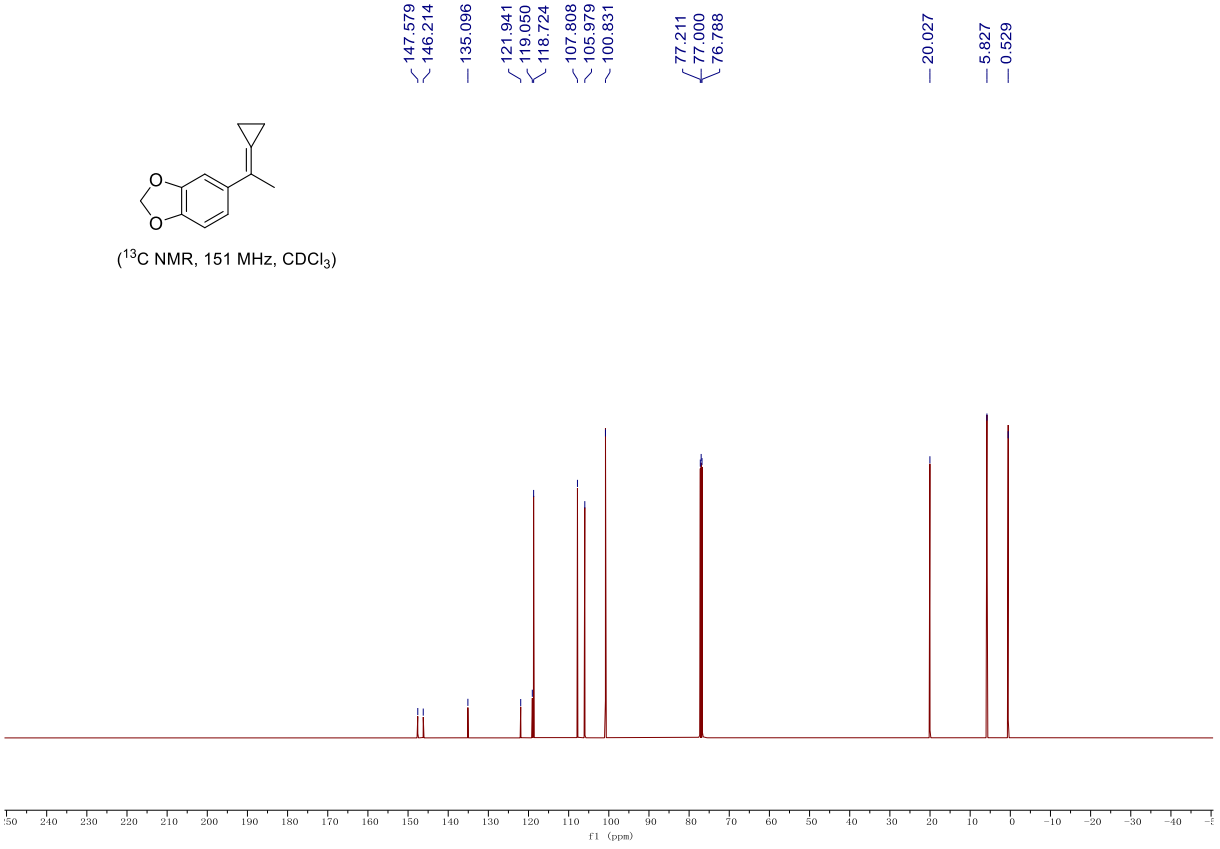
(^{1}H NMR, 600 MHz, $CDCl_3$)



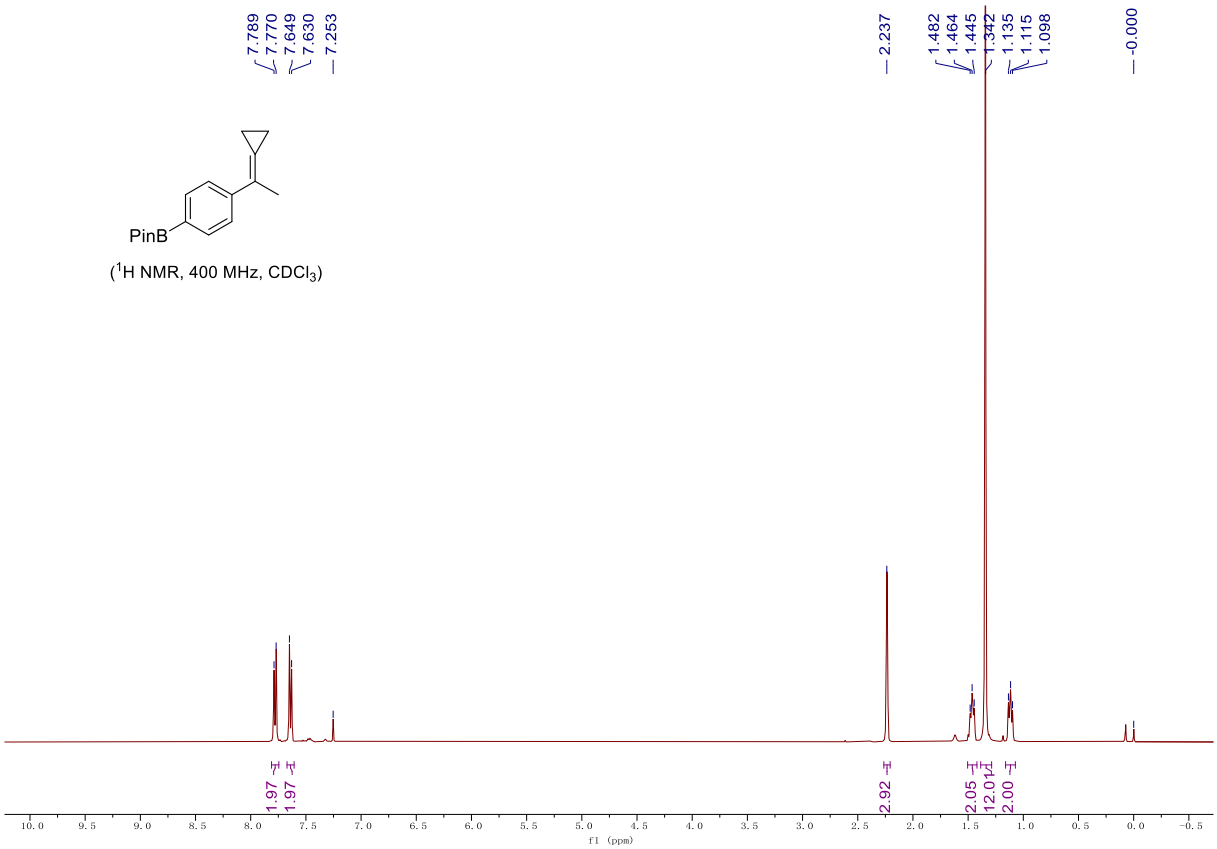
(^{13}C NMR, 151 MHz, $CDCl_3$)



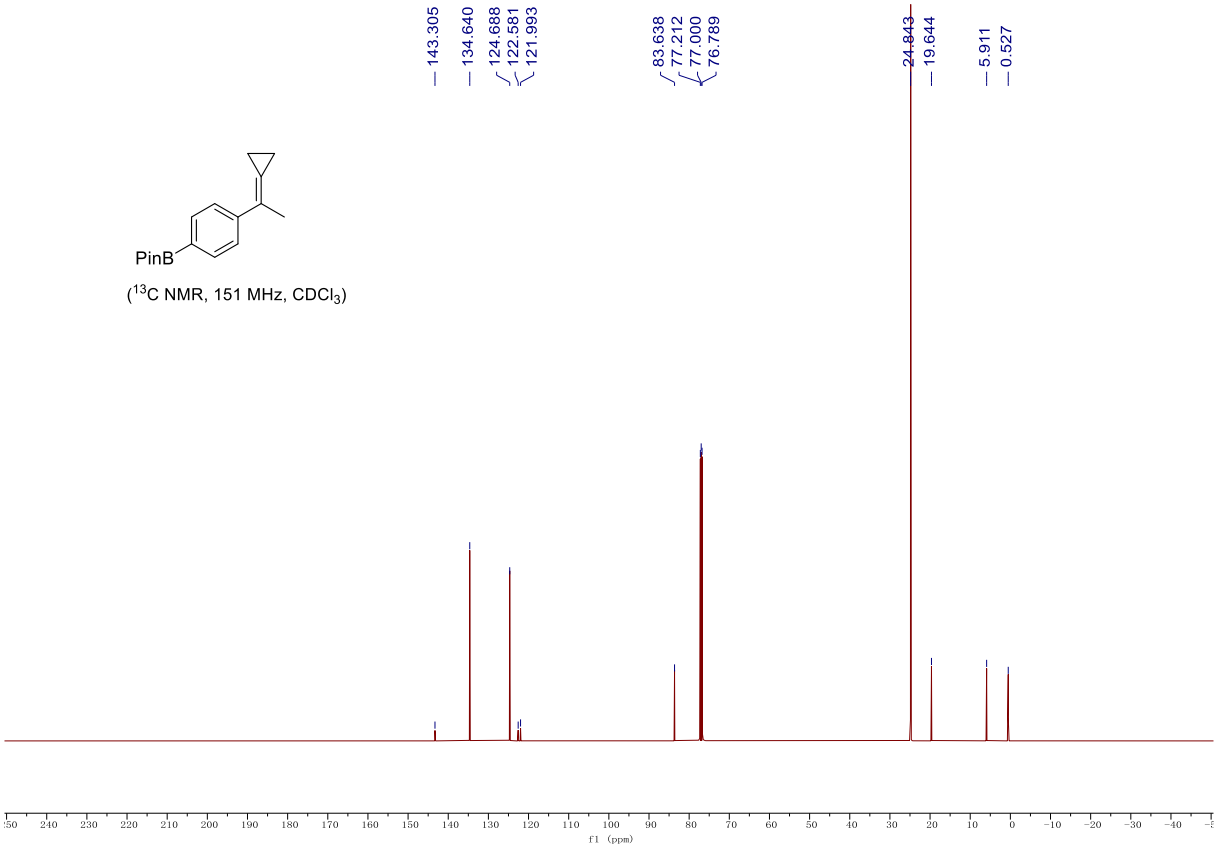
(^{1}H NMR, 400 MHz, $CDCl_3$)



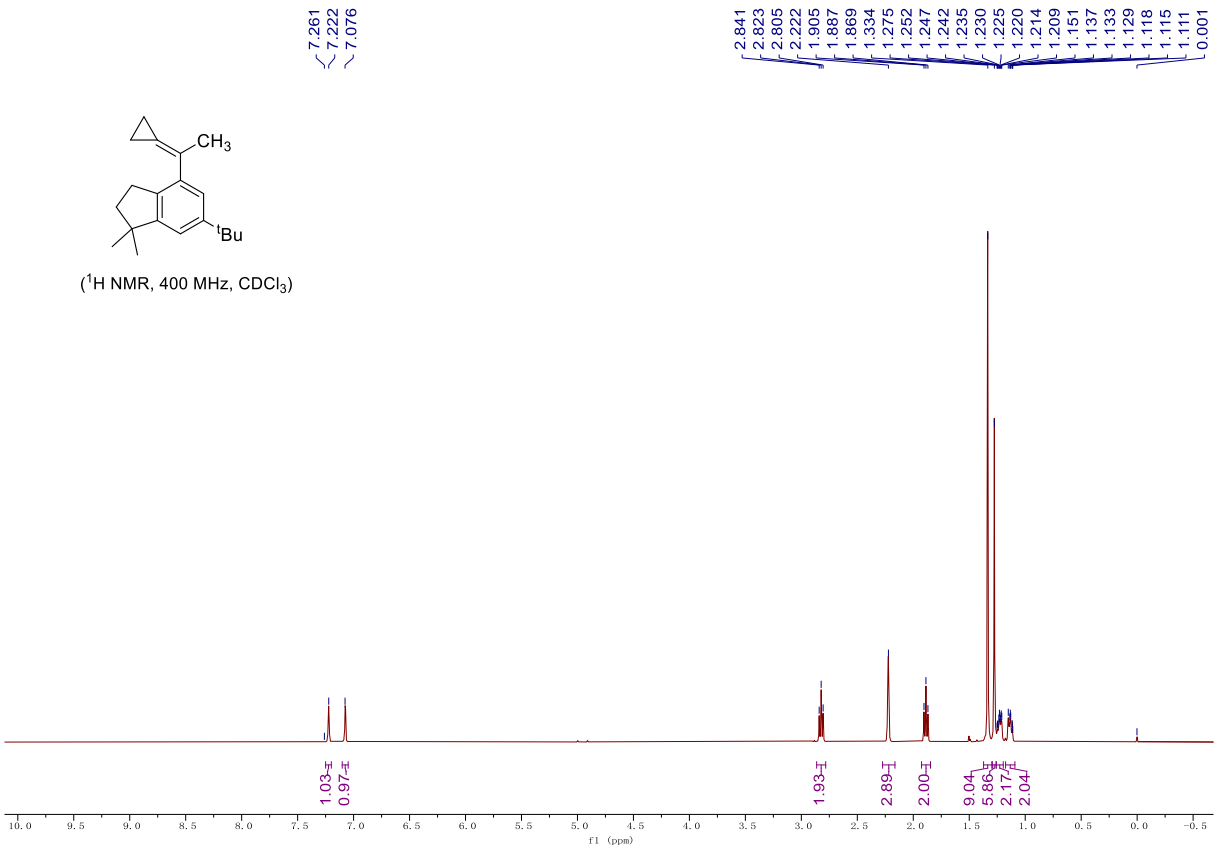
(^{13}C NMR, 151 MHz, $CDCl_3$)

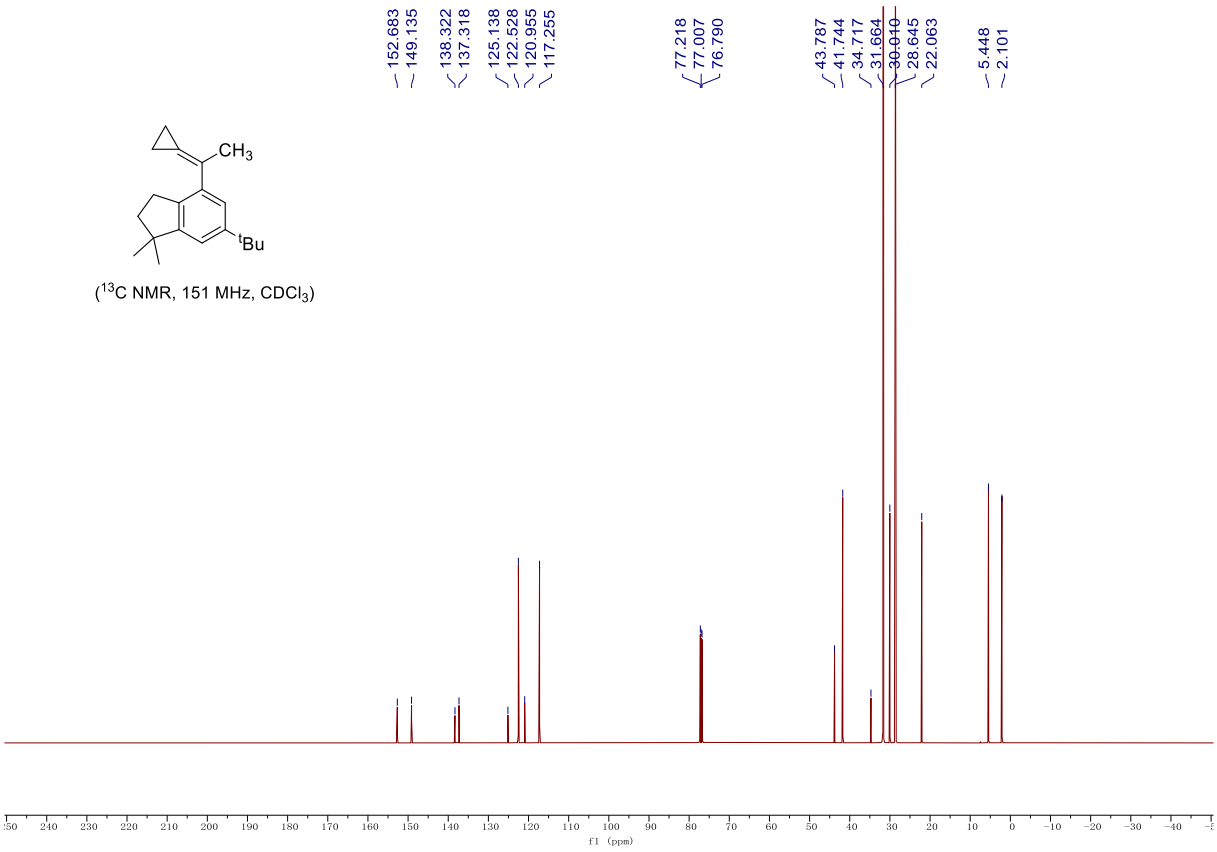


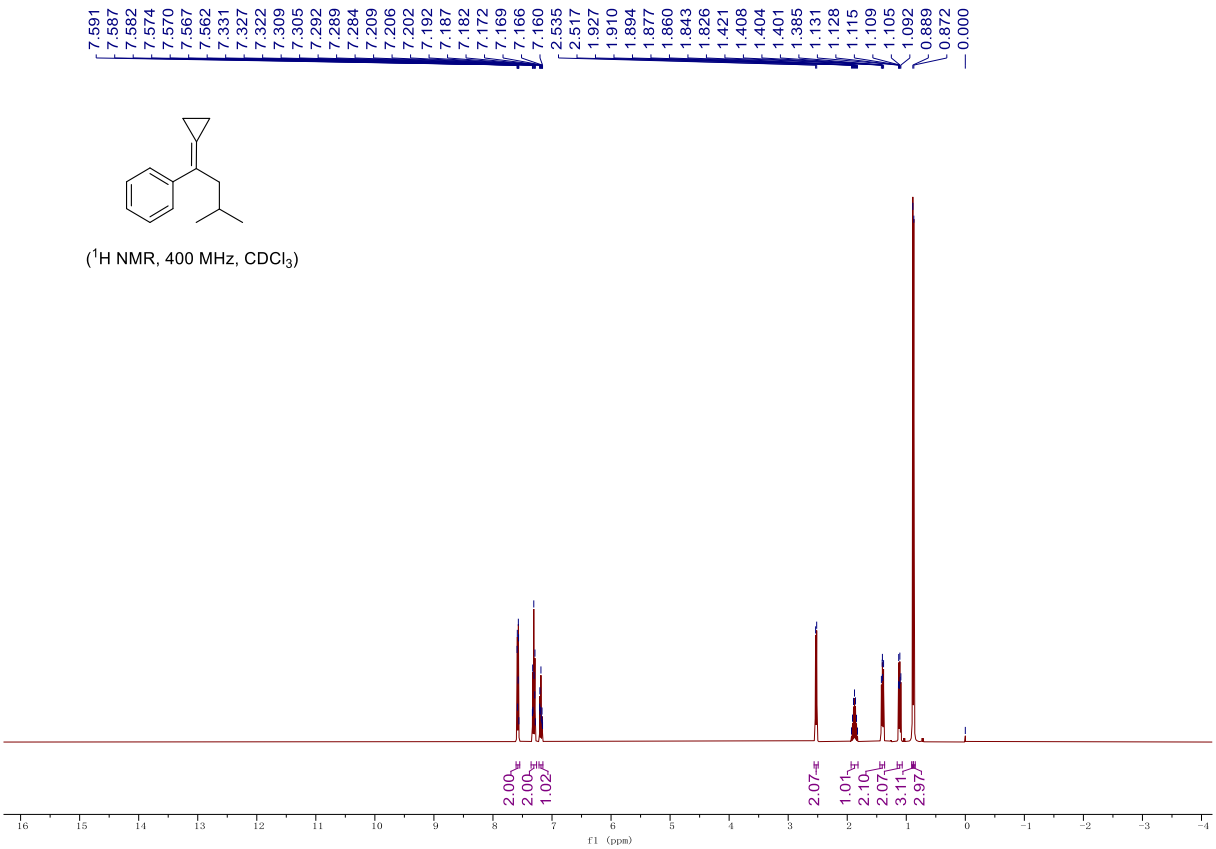
(^{1}H NMR, 400 MHz, $CDCl_3$)

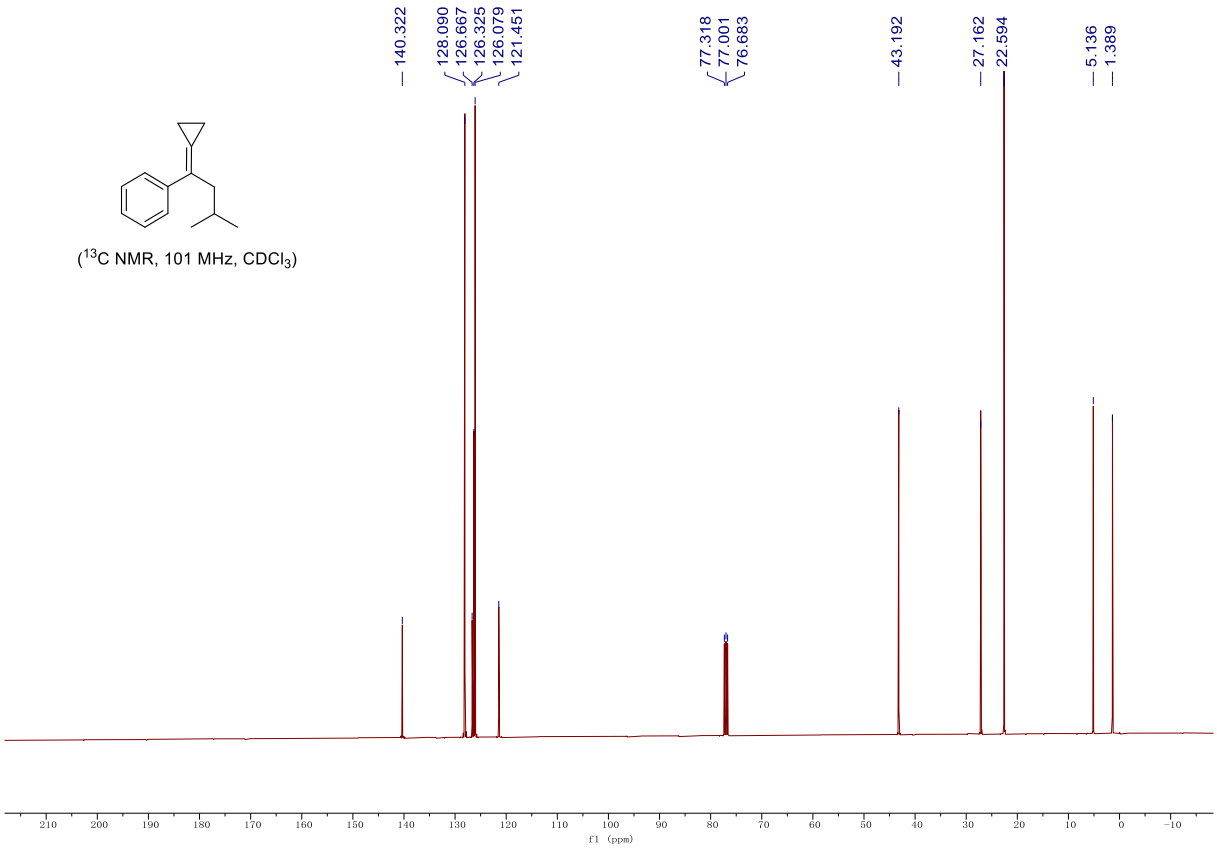


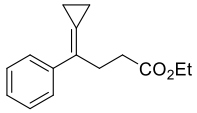
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.261
7.222
7.076
2.841
2.823
2.805
2.222
1.905
1.887
1.869
1.334
1.275
1.252
1.247
1.242
1.235
1.230
1.225
1.220
1.214
1.209
1.151
1.137
1.133
1.129
1.118
1.115
1.111
0.001
CH3
tBu
(1H NMR, 400 MHz, CDCl3)
1.03
0.97
1.93
2.89
2.00
9.04
5.86
2.17
2.04
f1 (ppm)

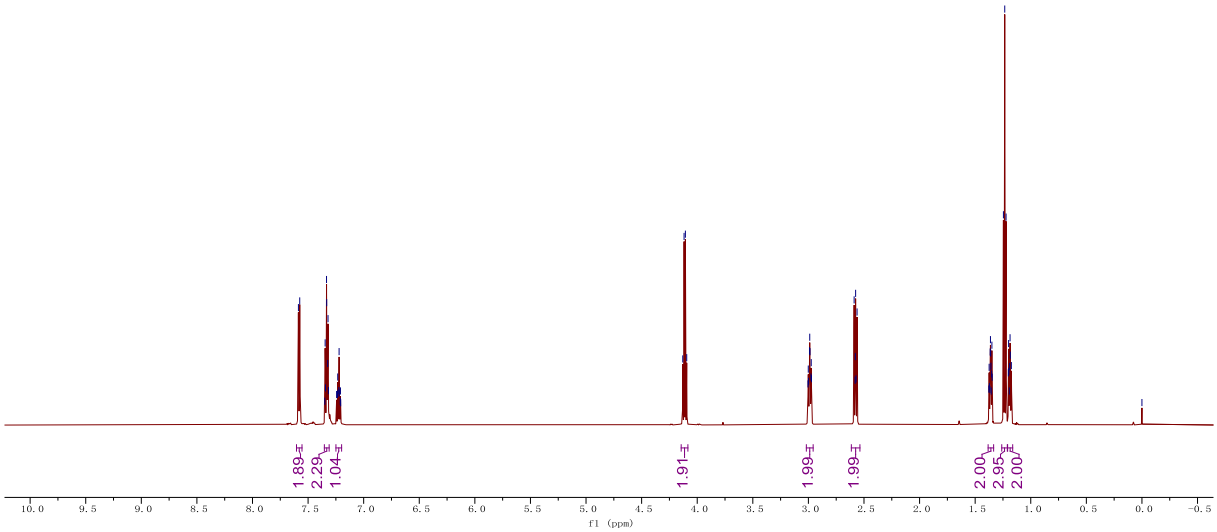

152.683
149.135
138.322
137.318
125.138
122.528
120.955
117.255
77.218
77.007
76.790
43.787
41.744
34.717
31.664
30.040
28.645
22.063
5.448
2.101
CH3
tBu
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

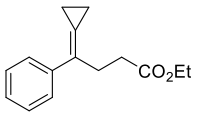

7.591
7.587
7.582
7.574
7.570
7.567
7.562
7.331
7.327
7.322
7.309
7.305
7.292
7.289
7.284
7.209
7.206
7.202
7.192
7.187
7.182
7.172
7.169
7.166
7.160
2.535
2.517
1.927
1.910
1.894
1.877
1.860
1.843
1.826
1.421
1.408
1.404
1.401
1.385
1.131
1.128
1.115
1.109
1.105
1.092
0.889
0.872
0.000
(^{1}H NMR, 400 MHz, $CDCl_3$)
2.00
2.00
1.02
2.07
1.01
2.10
2.07
3.11
2.97
f1 (ppm)


140.322
128.090
126.667
126.325
126.079
121.451
77.318
77.001
76.683
43.192
27.162
22.594
5.136
1.389
(^{13}C NMR, 101 MHz, $CDCl_3$)
f1 (ppm)

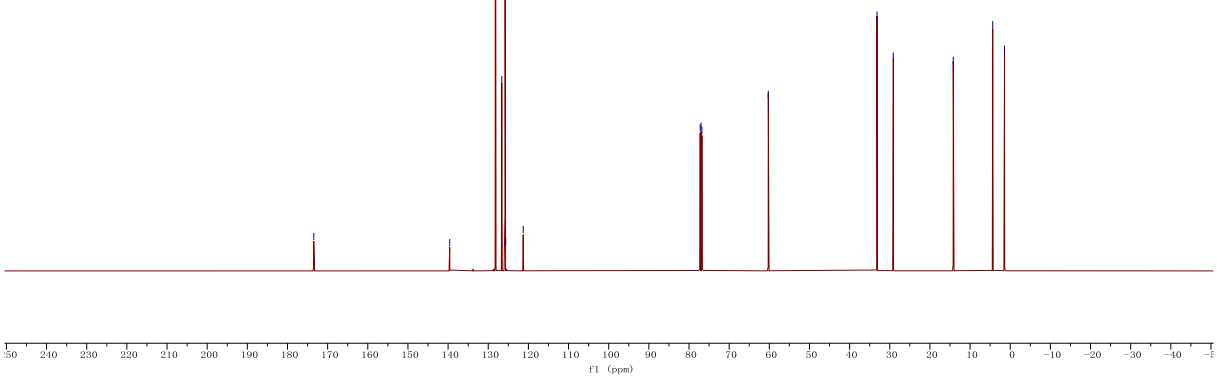


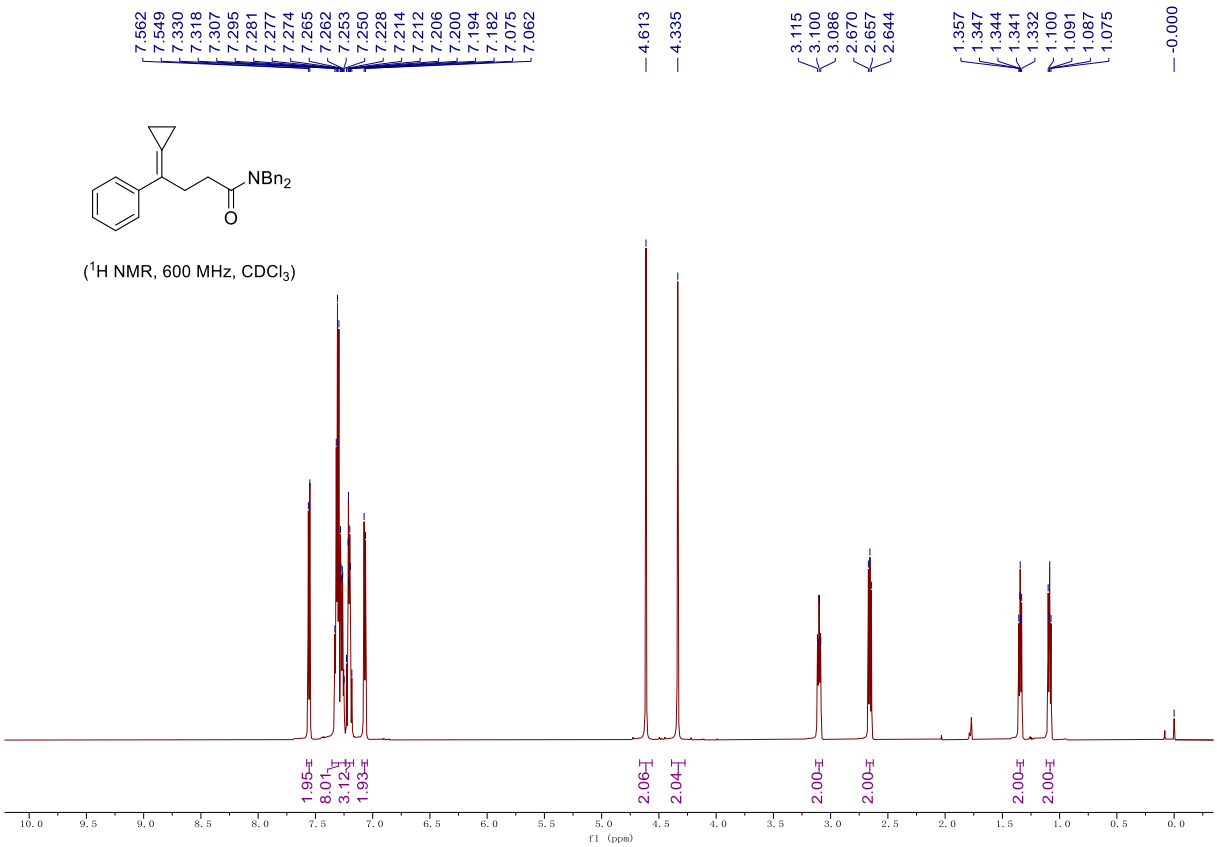
(^{1}H NMR, 600 MHz, $CDCl_3$)

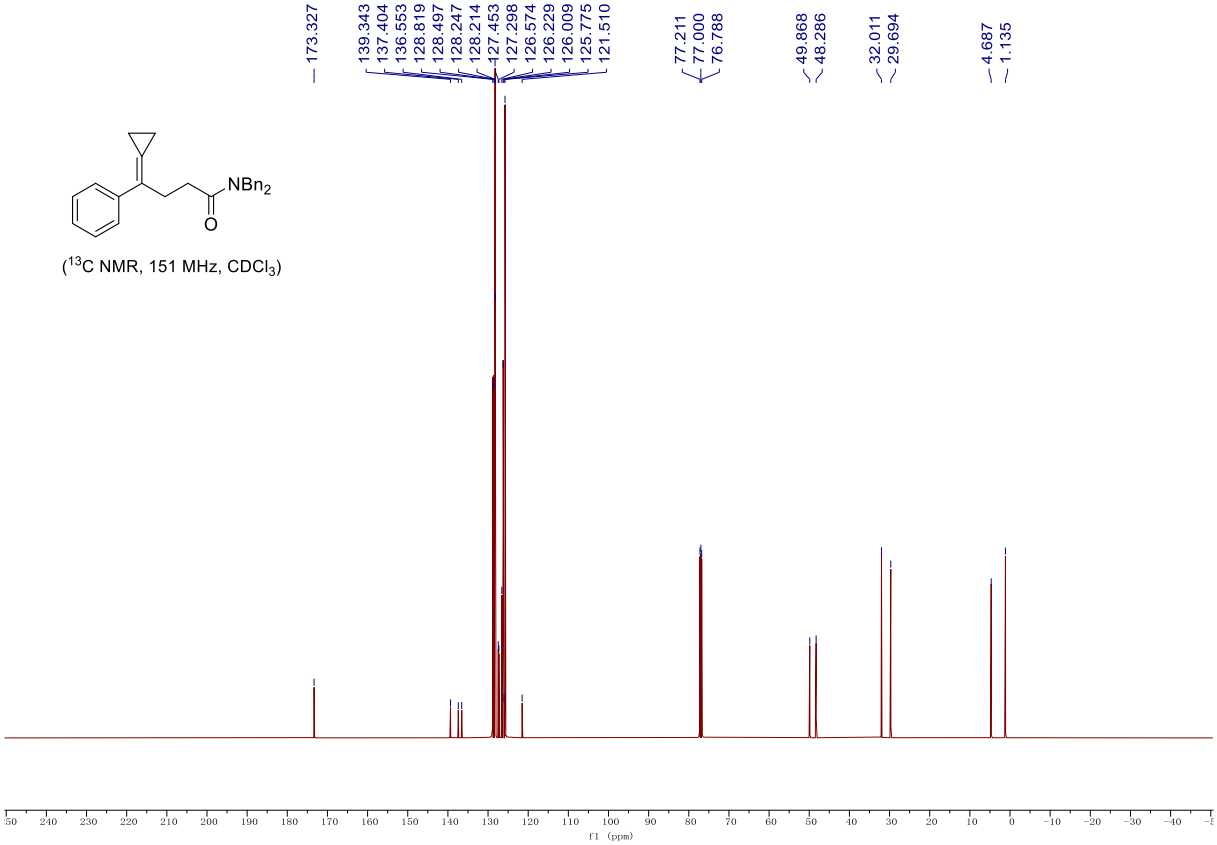


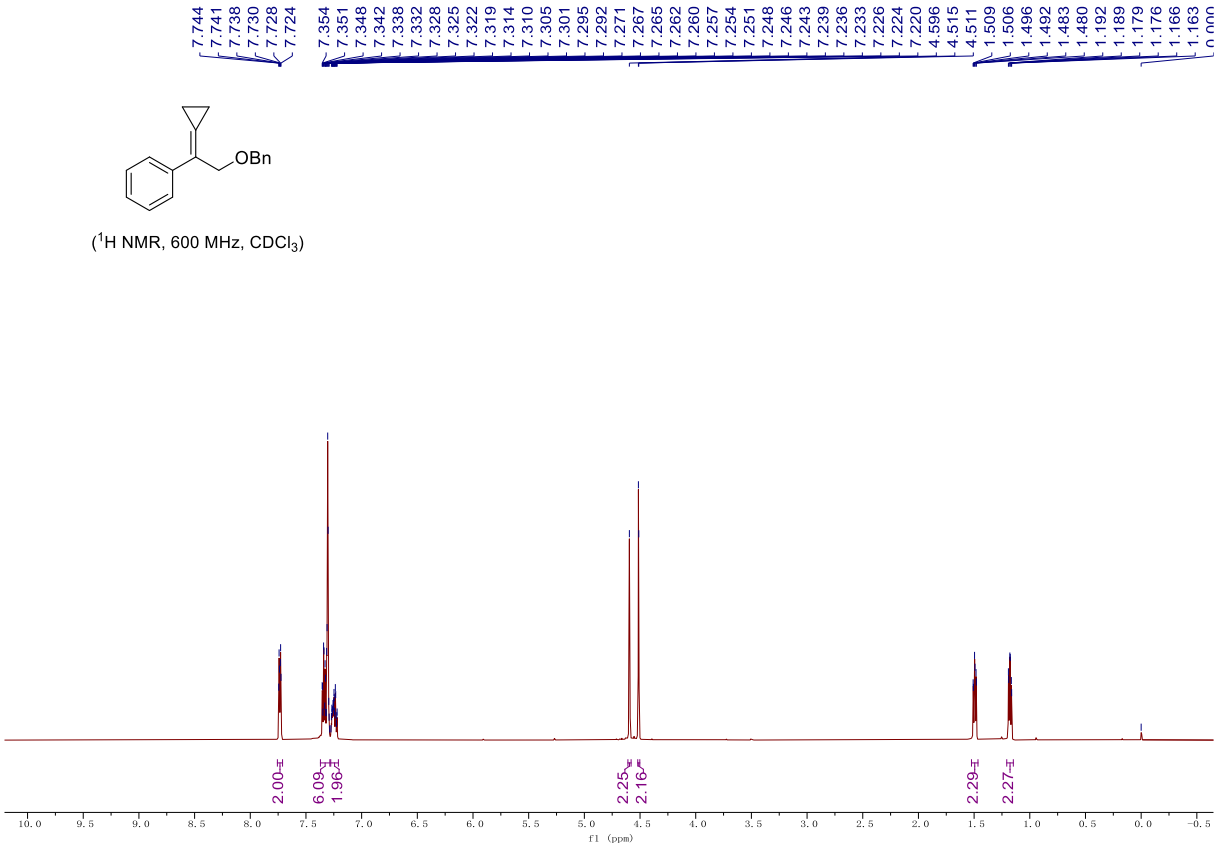


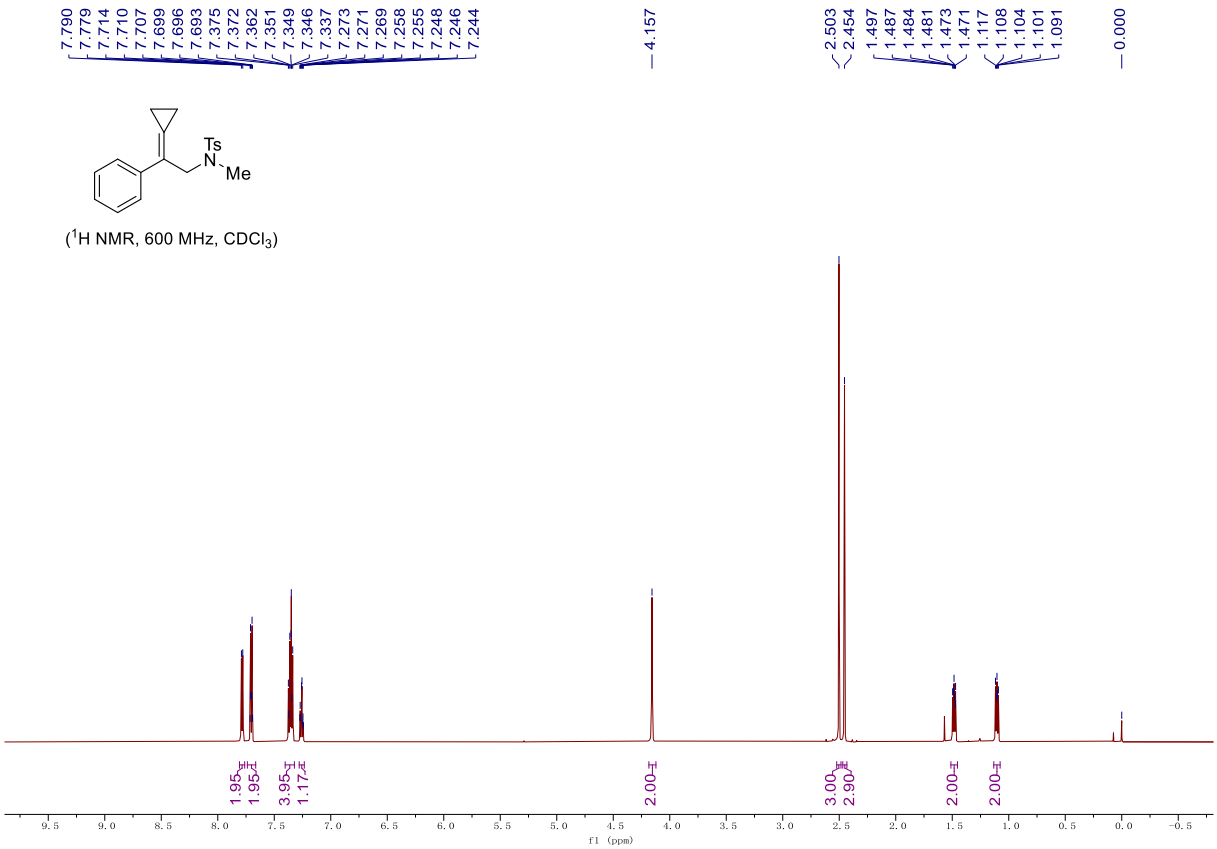
(^{13}C NMR, 151 MHz, $CDCl_3$)



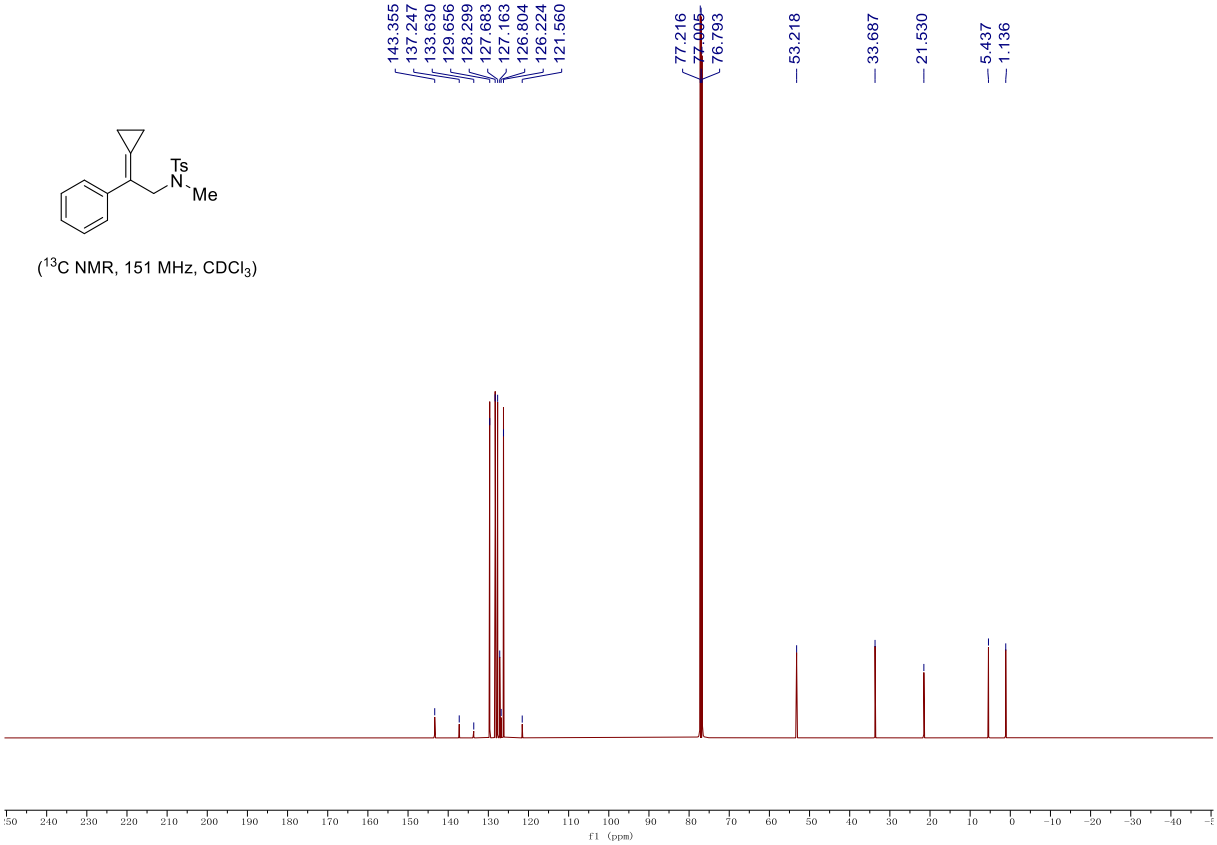

7.562
7.549
7.330
7.318
7.307
7.295
7.281
7.277
7.274
7.265
7.262
7.253
7.250
7.228
7.214
7.212
7.206
7.200
7.194
7.182
7.075
7.062
4.613
4.335
3.115
3.100
3.086
2.670
2.657
2.644
1.357
1.347
1.344
1.341
1.332
1.100
1.091
1.087
1.075
-0.000
NBn2
O
(1H NMR, 600 MHz, CDCl3)
1.95
8.01
3.12
1.93
2.06
2.04
2.00
2.00
2.00
2.00
f1 (ppm)


173.327
139.343
137.404
136.553
128.819
128.497
128.247
128.214
127.453
127.298
126.574
126.229
126.009
125.775
121.510
77.211
77.000
76.788
49.868
48.286
32.011
29.694
4.687
1.135
NBn2
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

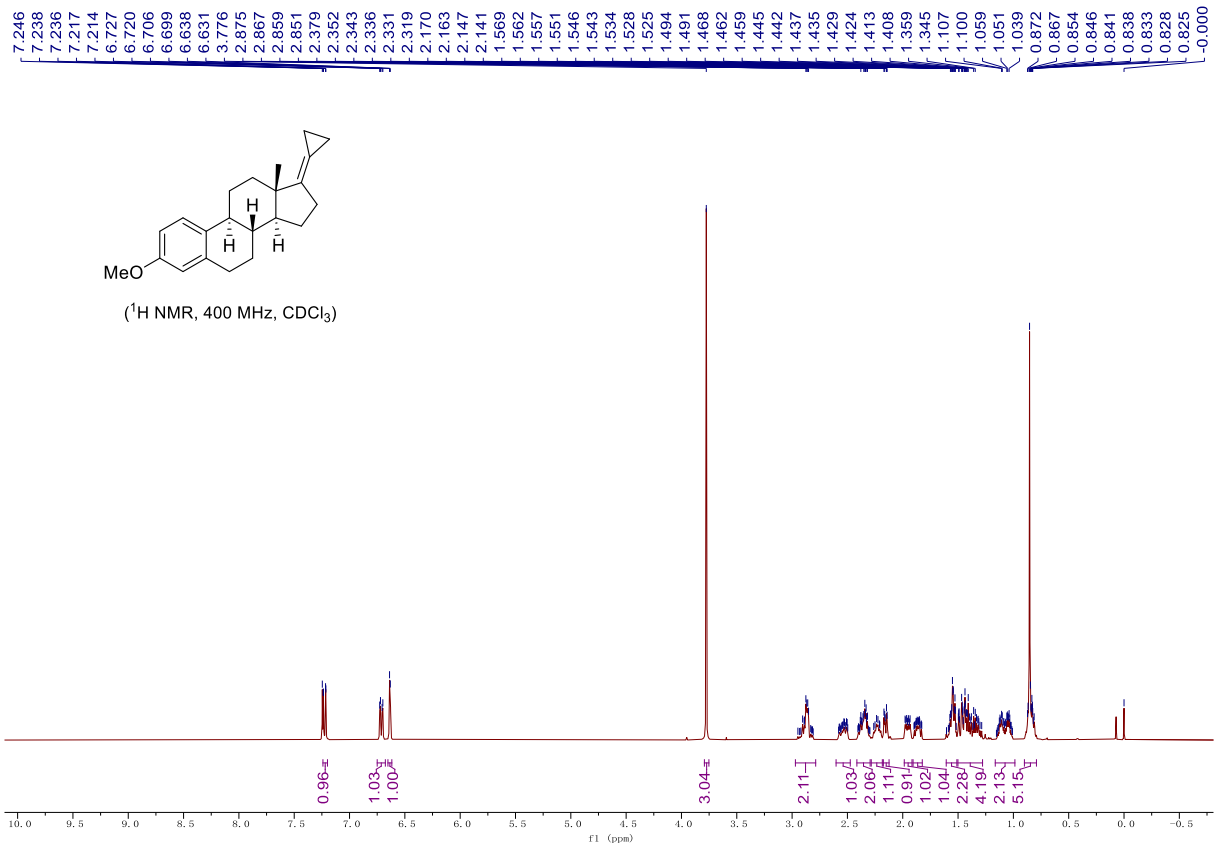

7.744
7.741
7.738
7.730
7.728
7.724
7.354
7.351
7.348
7.342
7.338
7.332
7.328
7.325
7.322
7.319
7.314
7.310
7.305
7.301
7.295
7.292
7.271
7.267
7.265
7.262
7.260
7.257
7.254
7.251
7.248
7.246
7.243
7.239
7.236
7.233
7.226
7.224
7.220
4.596
4.515
4.511
1.509
1.506
1.496
1.492
1.483
1.480
1.192
1.189
1.179
1.176
1.166
1.163
OBn
(1H NMR, 600 MHz, CDCl3)
2.00
6.09
1.96
2.25
2.16
2.29
2.27
f1 (ppm)
138.439
138.260
128.263
128.183
127.817
127.473
126.815
126.260
126.052
123.887
77.213
77.002
76.790
71.822
71.515
5.169
0.860
OBn
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

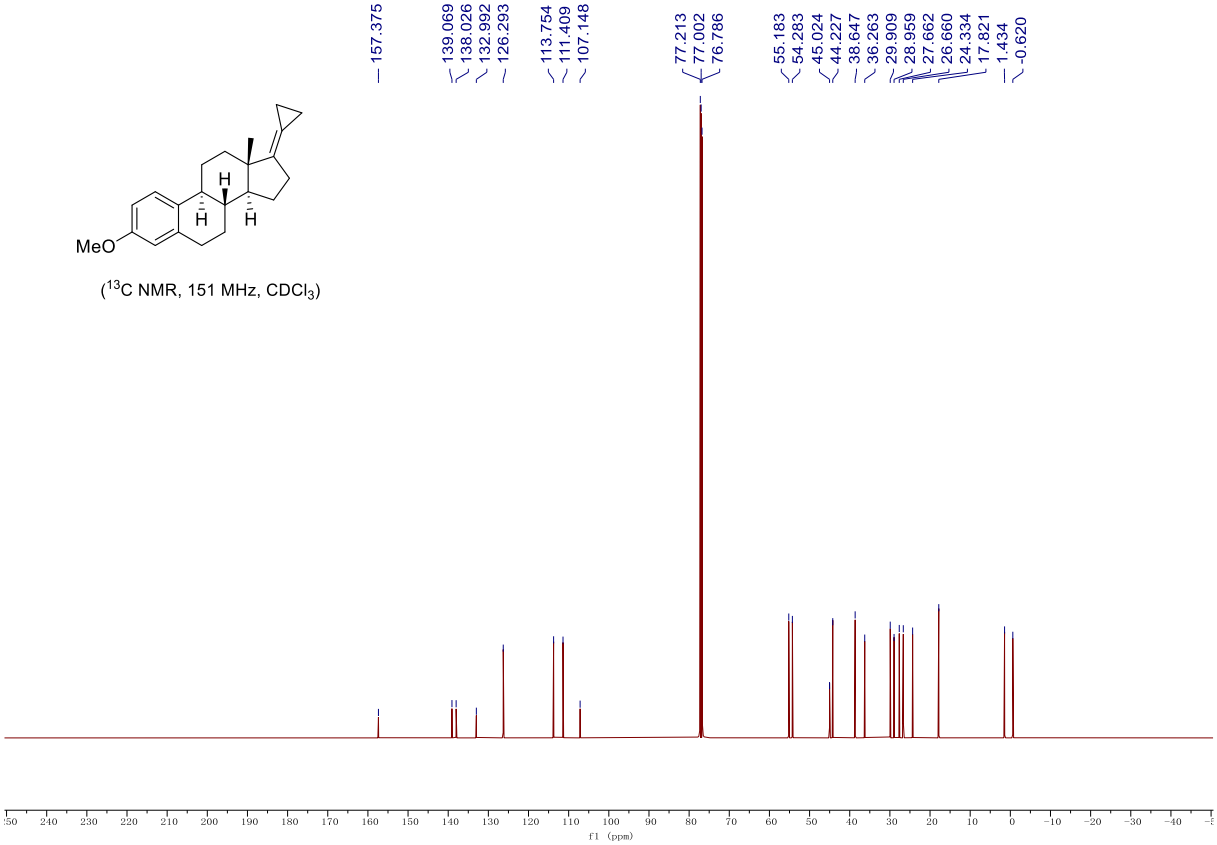


(^{1}H NMR, 600 MHz, $CDCl_3$)

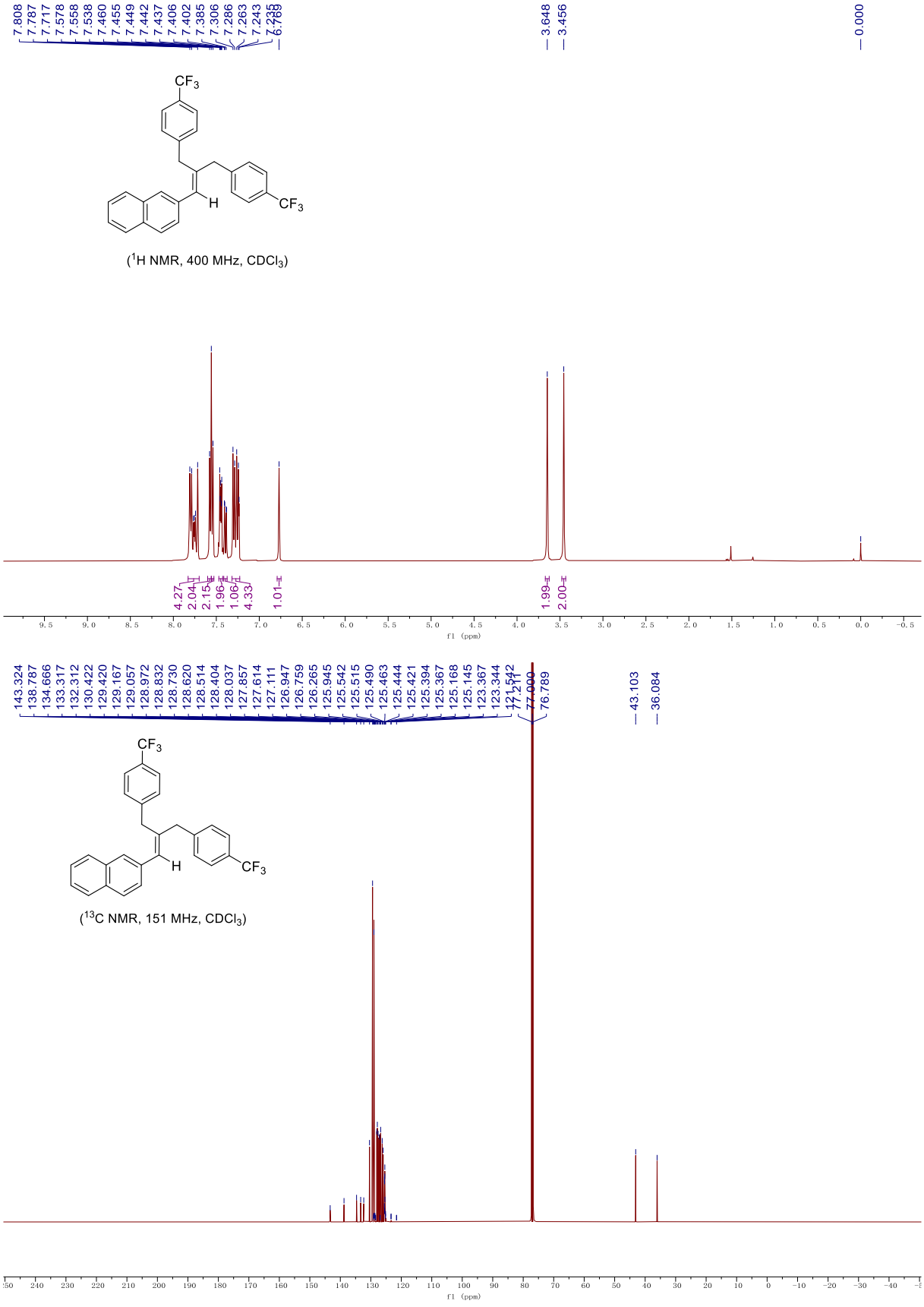


(^{13}C NMR, 151 MHz, $CDCl_3$)


7.246
7.238
7.236
7.217
7.214
6.727
6.720
6.706
6.699
6.638
6.631
3.776
2.875
2.867
2.859
2.851
2.379
2.352
2.343
2.336
2.331
2.319
2.170
2.163
2.147
2.141
1.569
1.562
1.557
1.551
1.546
1.543
1.534
1.528
1.525
1.494
1.491
1.468
1.462
1.459
1.445
1.442
1.437
1.435
1.429
1.424
1.413
1.408
1.359
1.345
1.107
1.100
1.059
1.051
1.039
0.872
0.867
0.854
0.846
0.841
0.838
0.833
0.828
0.825
-0.000
H
H
H
MeO
(1H NMR, 400 MHz, CDCl3)
0.96
1.03
1.00
3.04
2.11
1.03
2.06
1.11
0.91
1.02
1.04
2.28
4.19
2.13
5.15
f1 (ppm)

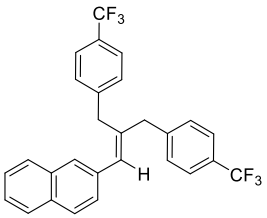

157.375
139.069
138.026
132.992
126.293
113.754
111.409
107.148
77.213
77.002
76.786
55.183
54.283
45.024
44.227
38.647
36.263
29.909
28.959
27.662
26.660
24.334
17.821
1.434
-0.620
H
H
H
MeO
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

12. Spectroscopic Data of Products (NMR Spectrum)

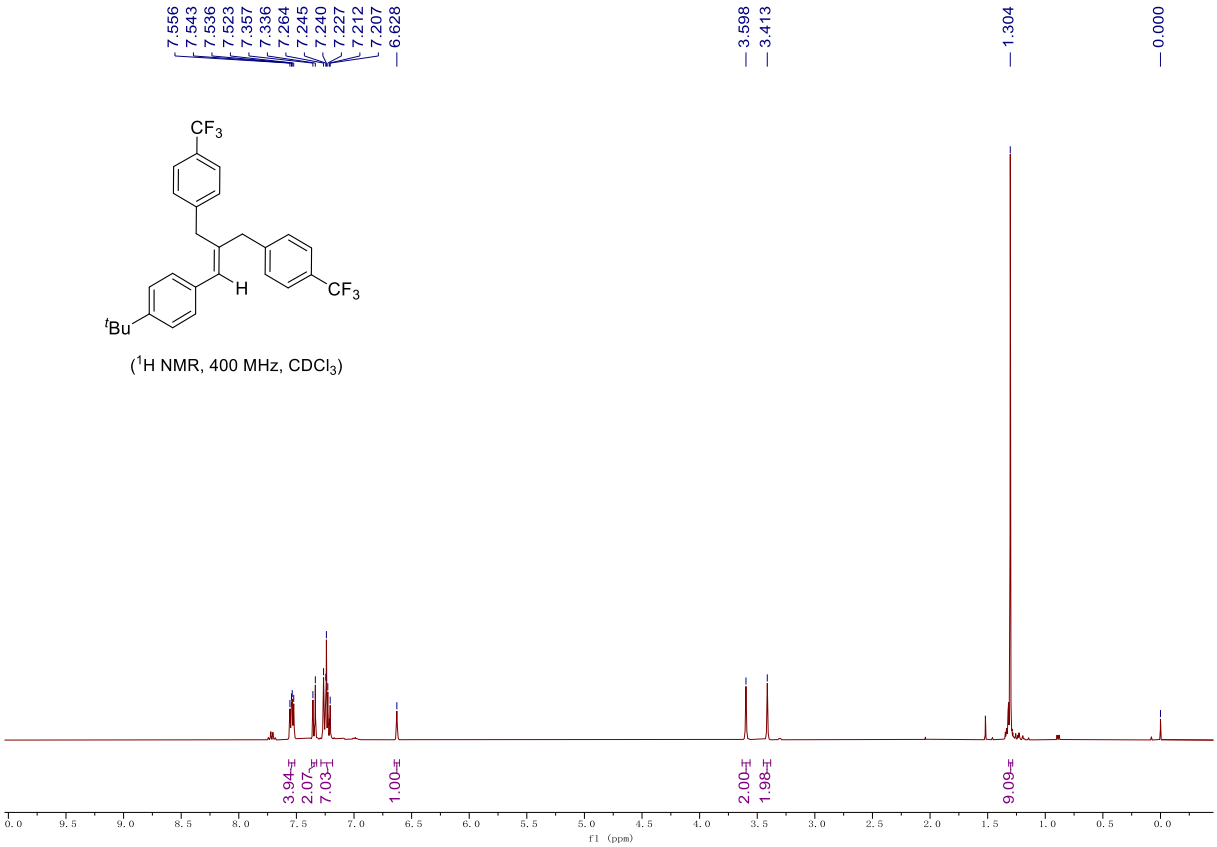


(^{1}H NMR, 400 MHz, $CDCl_3$)

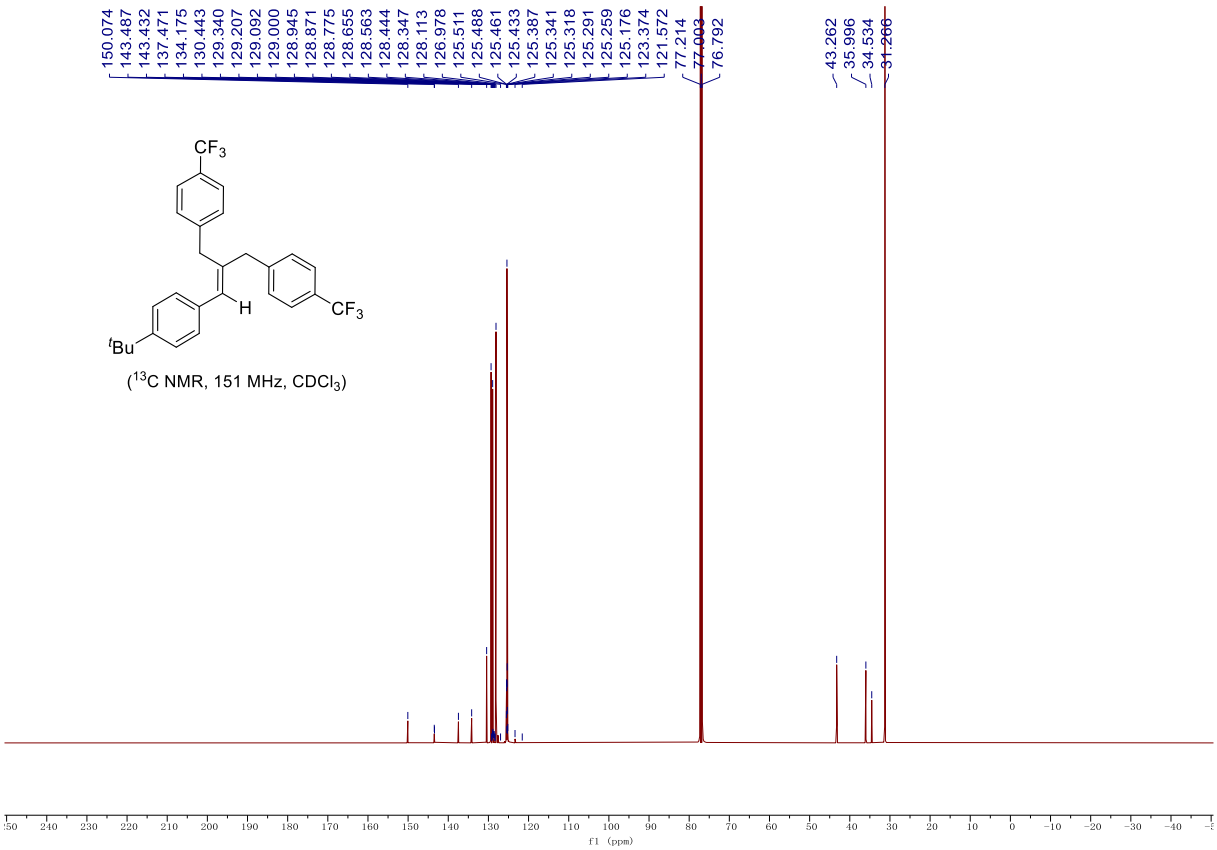
(^{13}C NMR, 151 MHz, $CDCl_3$)



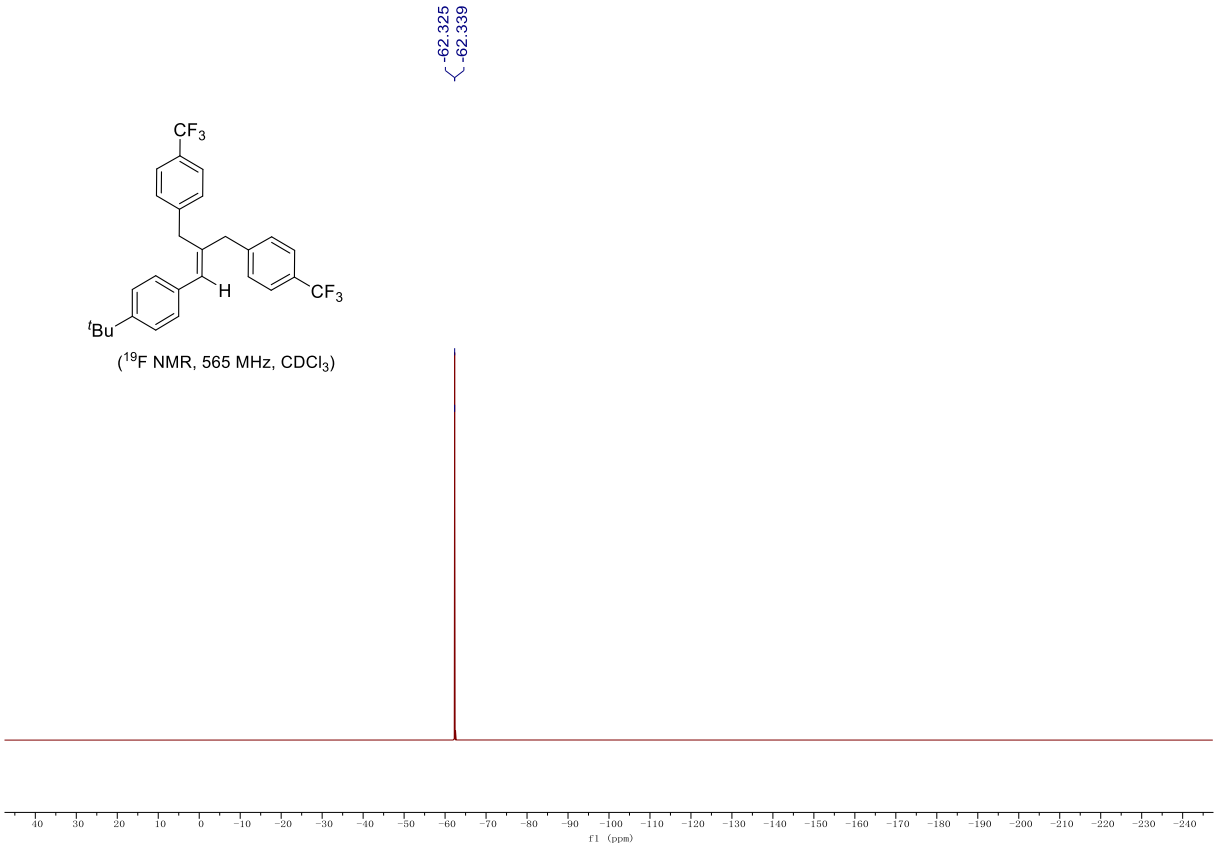
(^{19}F NMR, 565 MHz, $CDCl_3$)



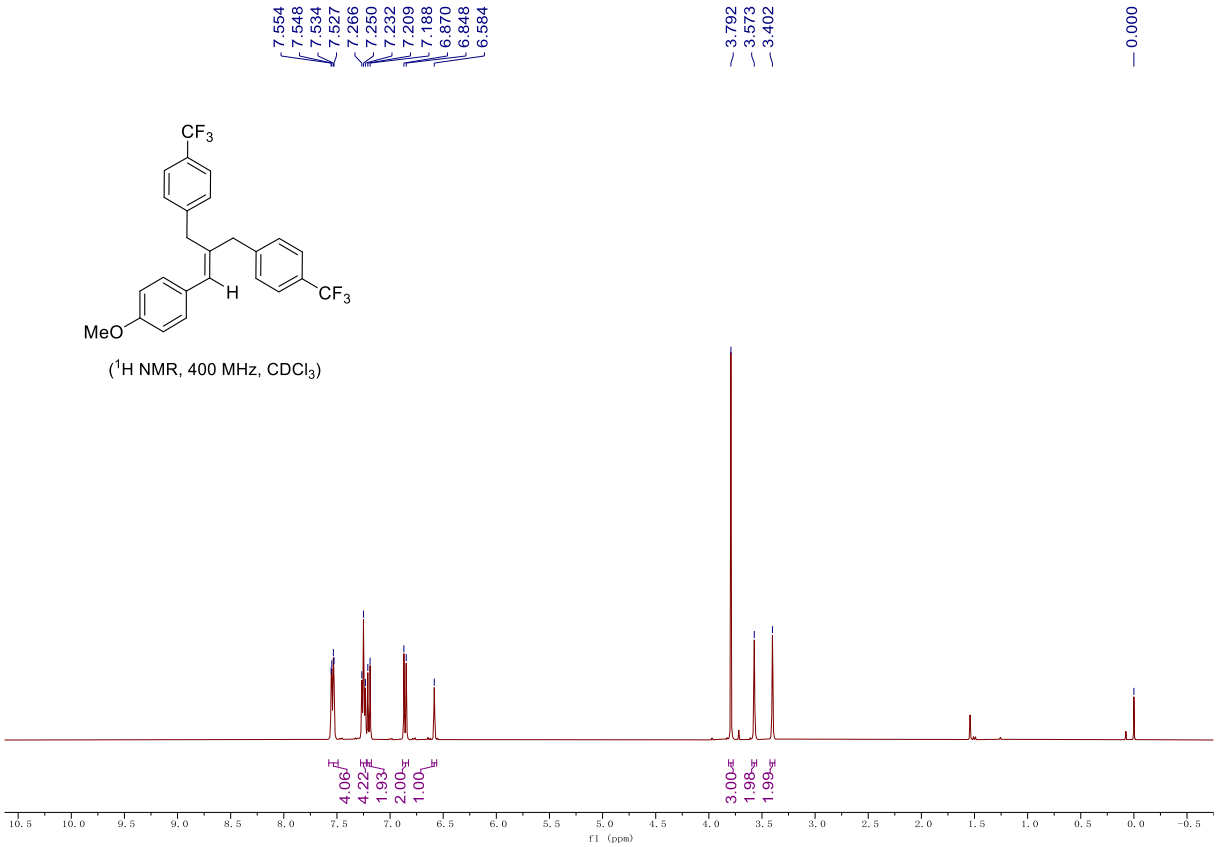
(^{1}H NMR, 400 MHz, $CDCl_3$)

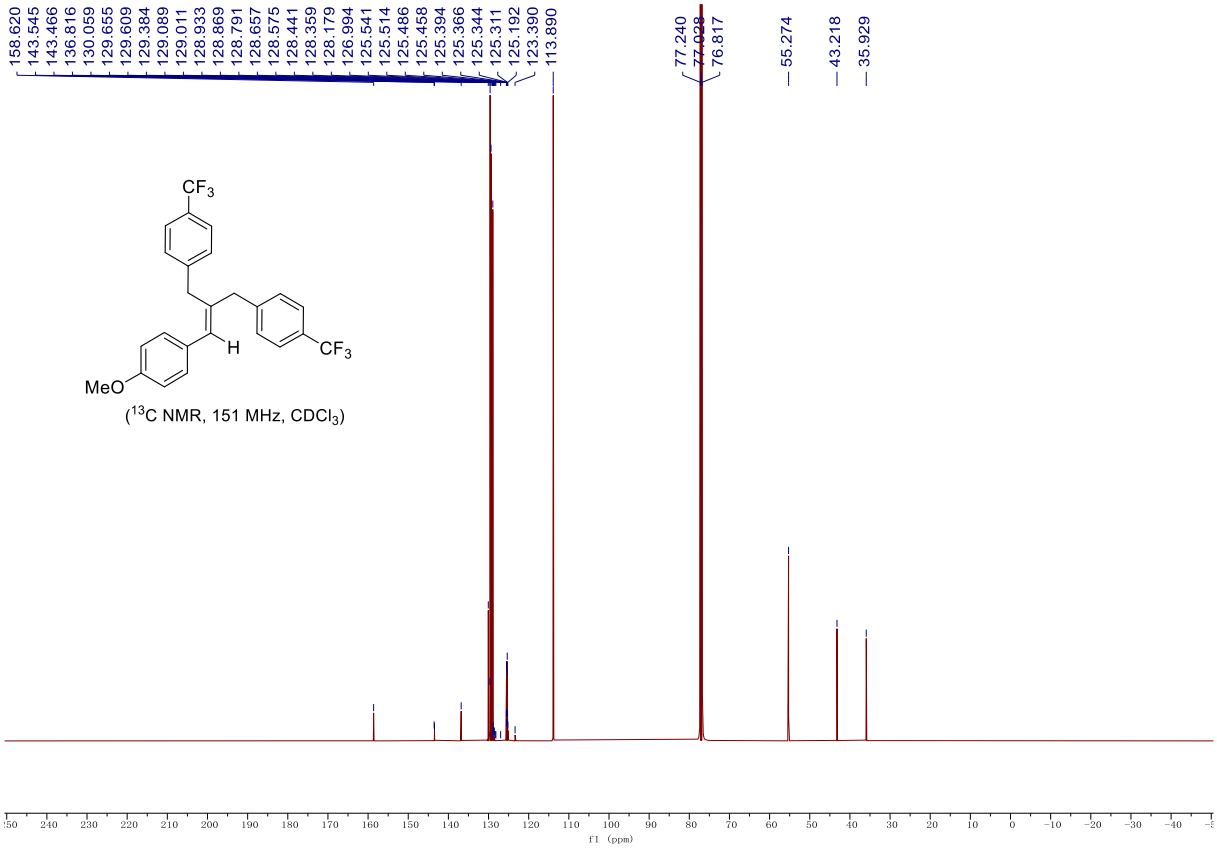


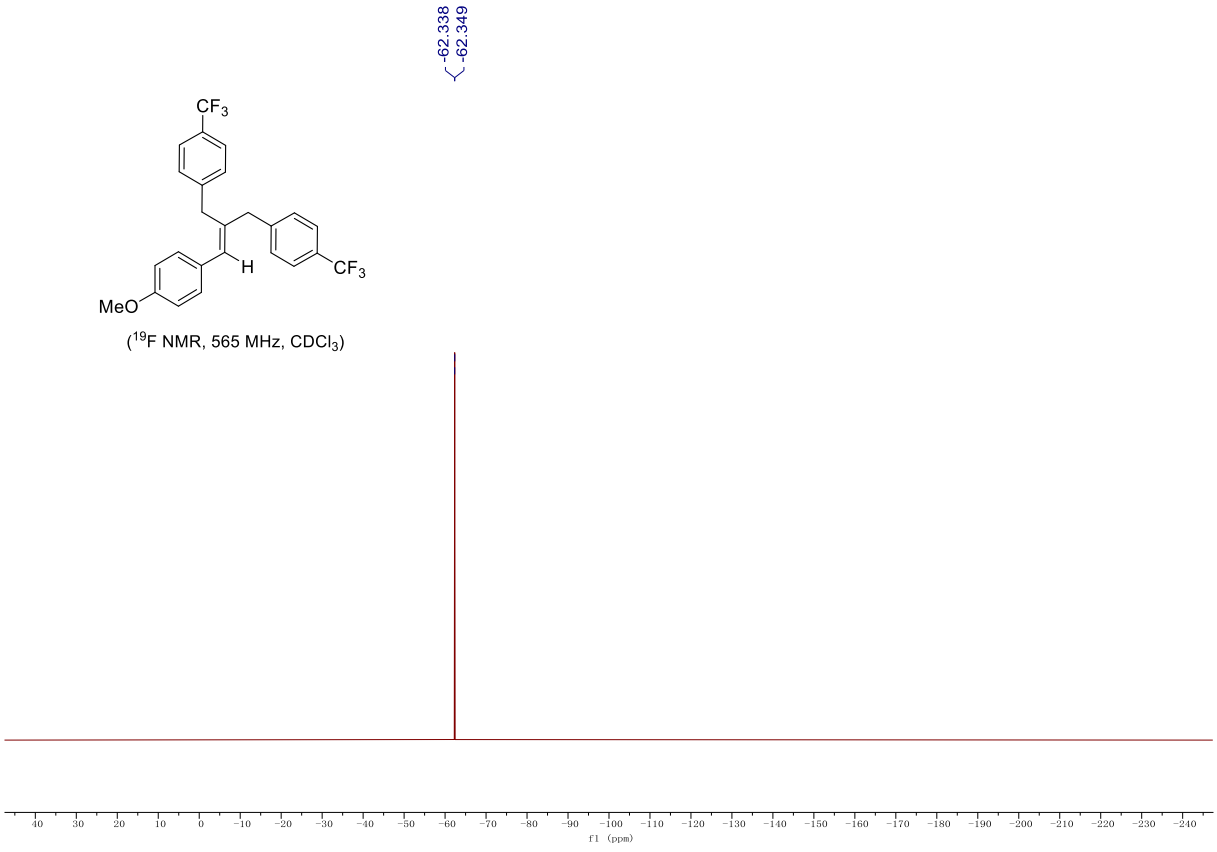
(^{13}C NMR, 151 MHz, $CDCl_3$)

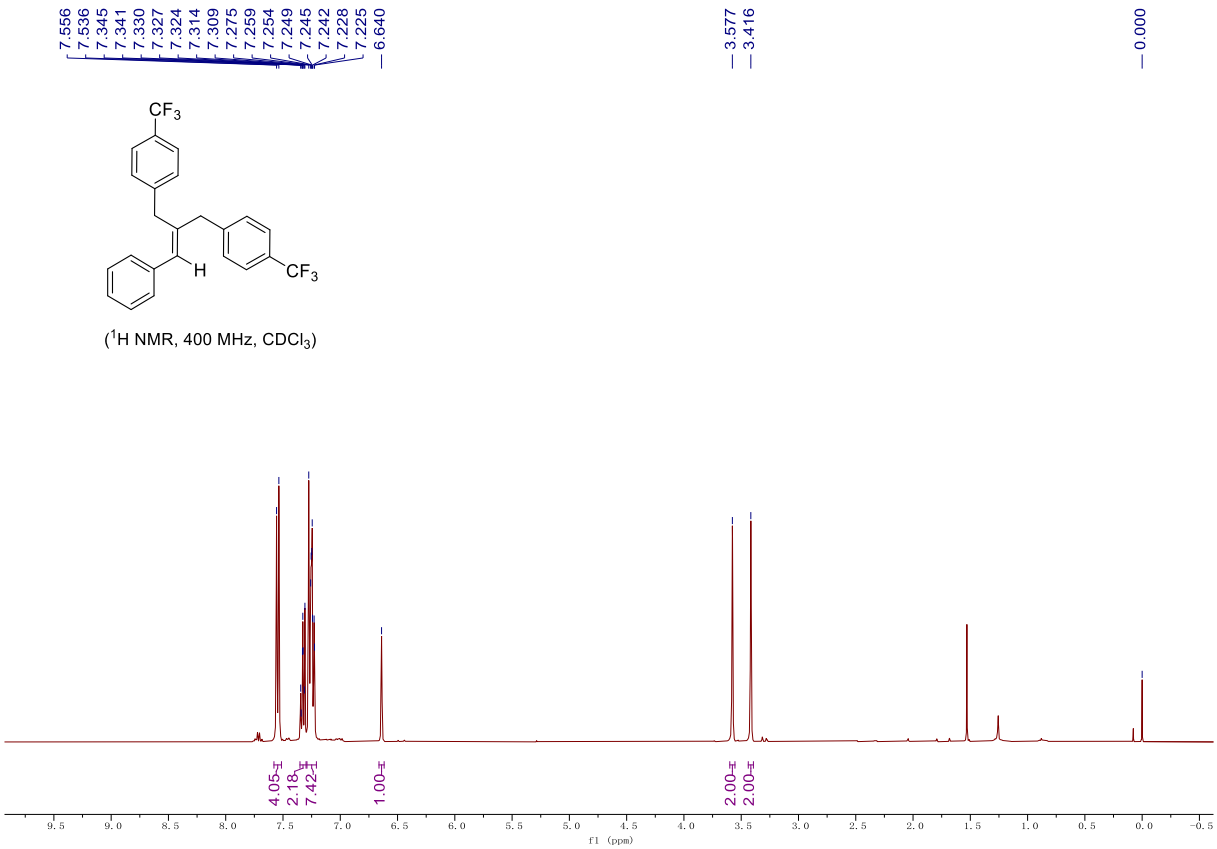


(^{19}F NMR, 565 MHz, $CDCl_3$)

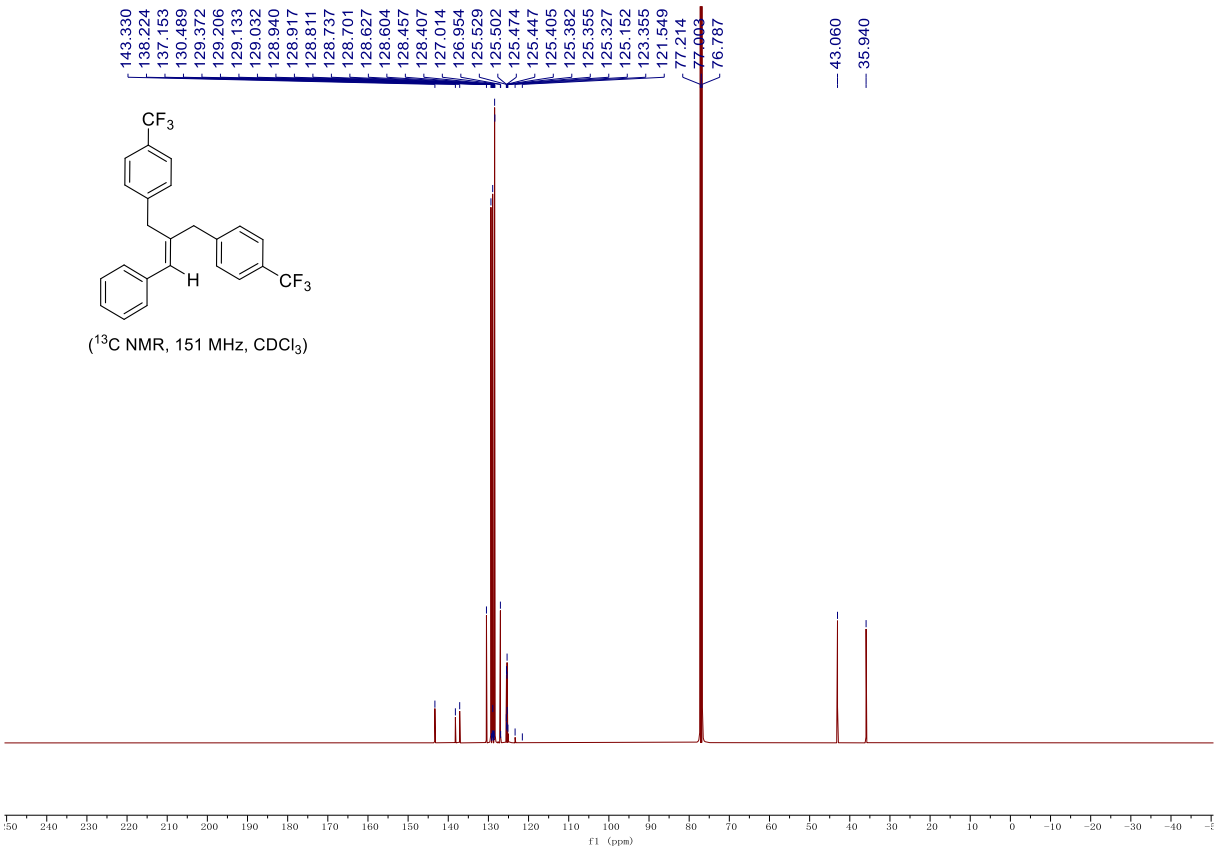

7.554
7.548
7.534
7.527
7.266
7.250
7.232
7.209
7.188
6.870
6.848
6.584
3.792
3.573
3.402
0.000
CF3
H
CF3
MeO
(1H NMR, 400 MHz, CDCl3)
4.06
4.22
1.93
2.00
1.00
3.00
1.98
1.99
f1 (ppm)


158.620
143.545
143.466
136.816
130.059
129.655
129.609
129.384
129.089
129.011
128.933
128.869
128.791
128.657
128.575
128.441
128.359
128.179
126.994
125.541
125.514
125.486
125.458
125.394
125.366
125.344
125.311
125.192
123.390
113.890
77.240
77.028
76.817
55.274
43.218
35.929
CF3
H
CF3
MeO
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

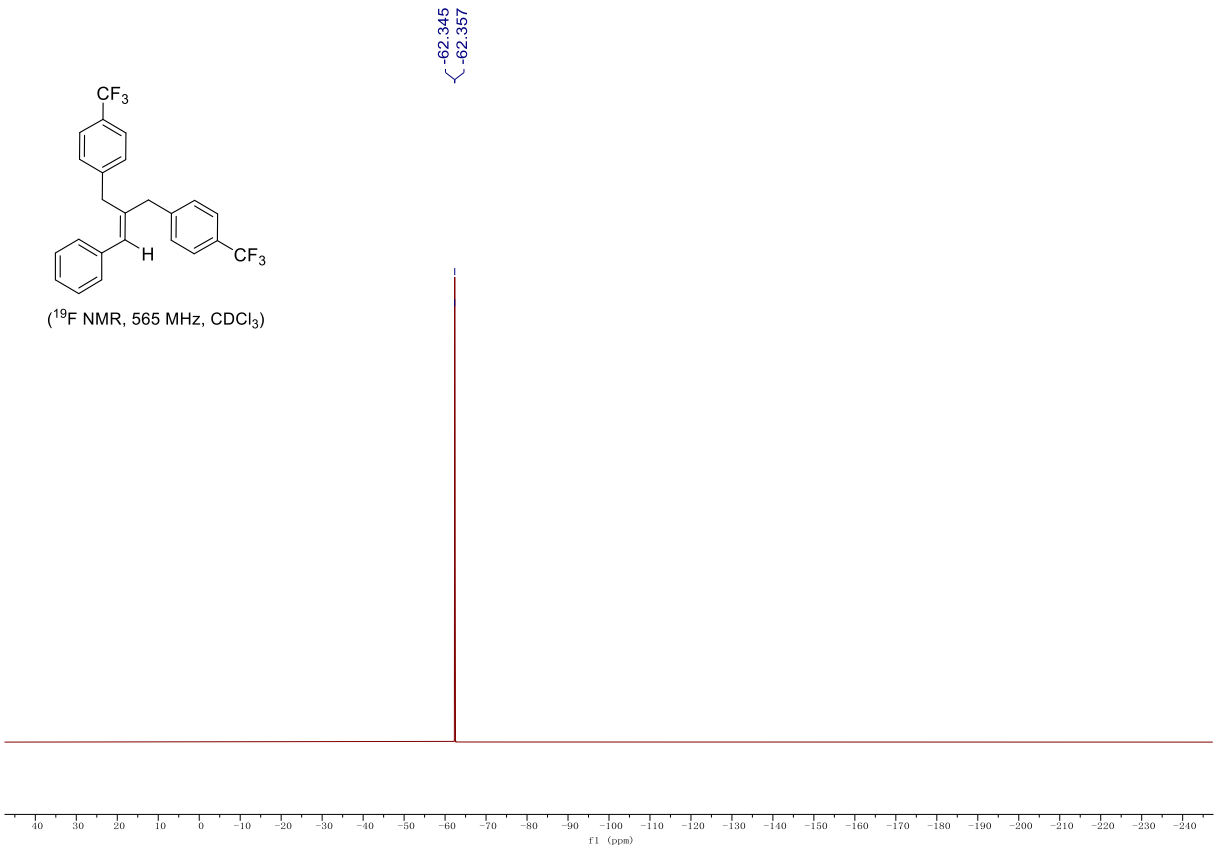

-62.338
-62.349
CF3
H
CF3
MeO
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)



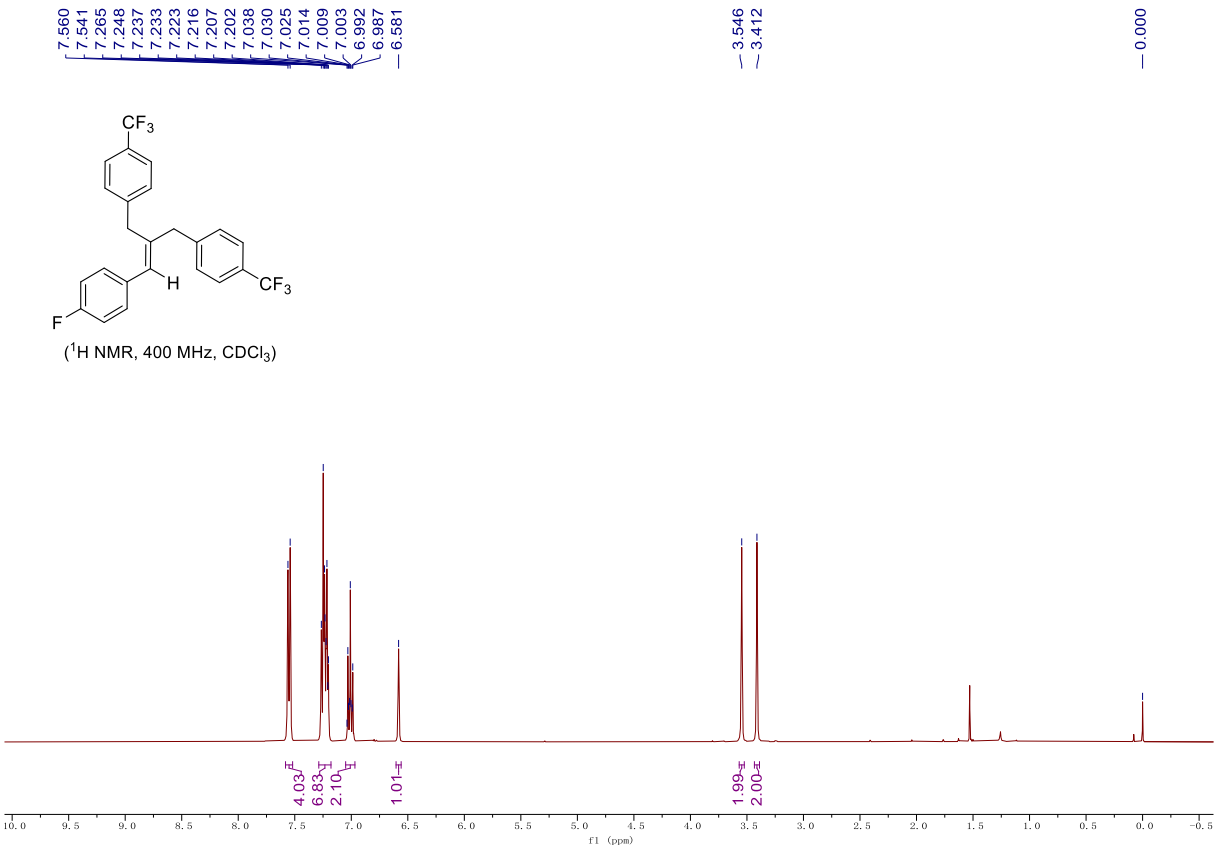
(^{1}H NMR, 400 MHz, $CDCl_3$)



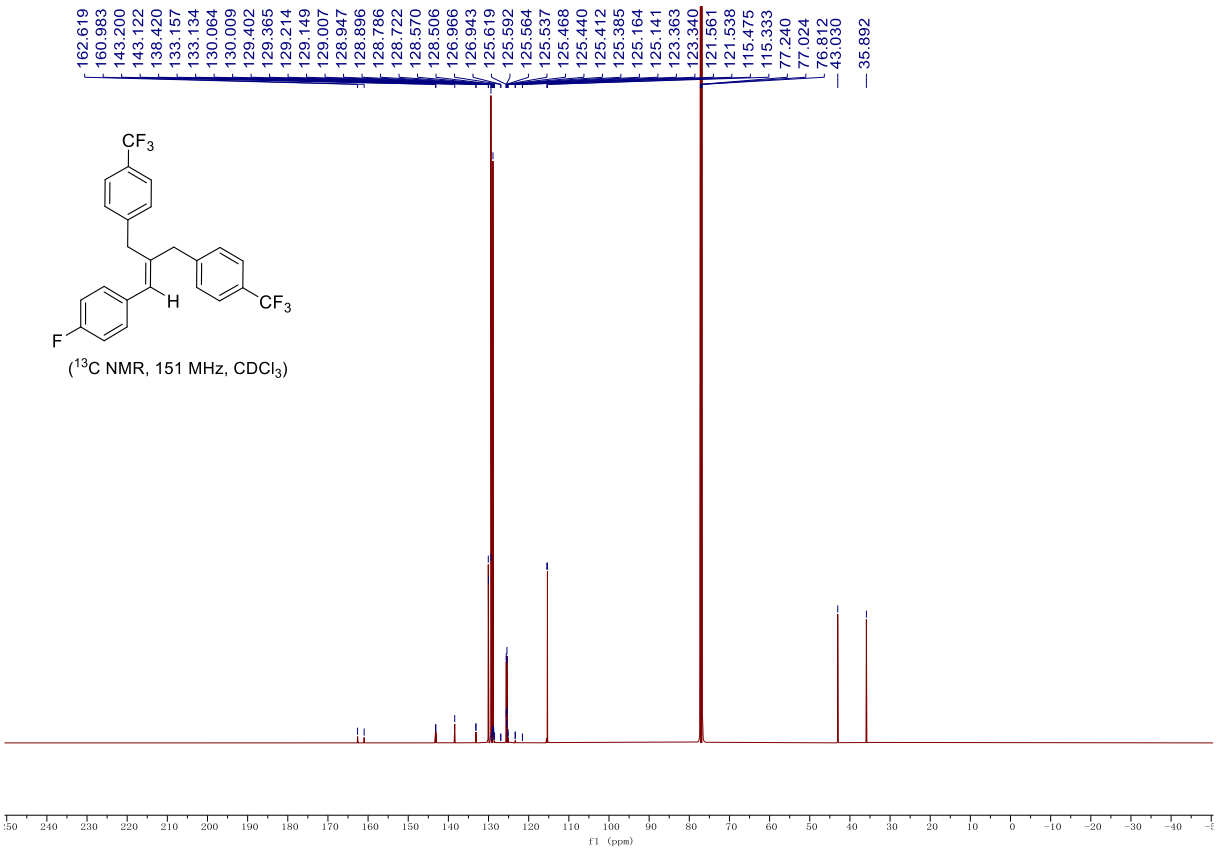
(^{13}C NMR, 151 MHz, $CDCl_3$)



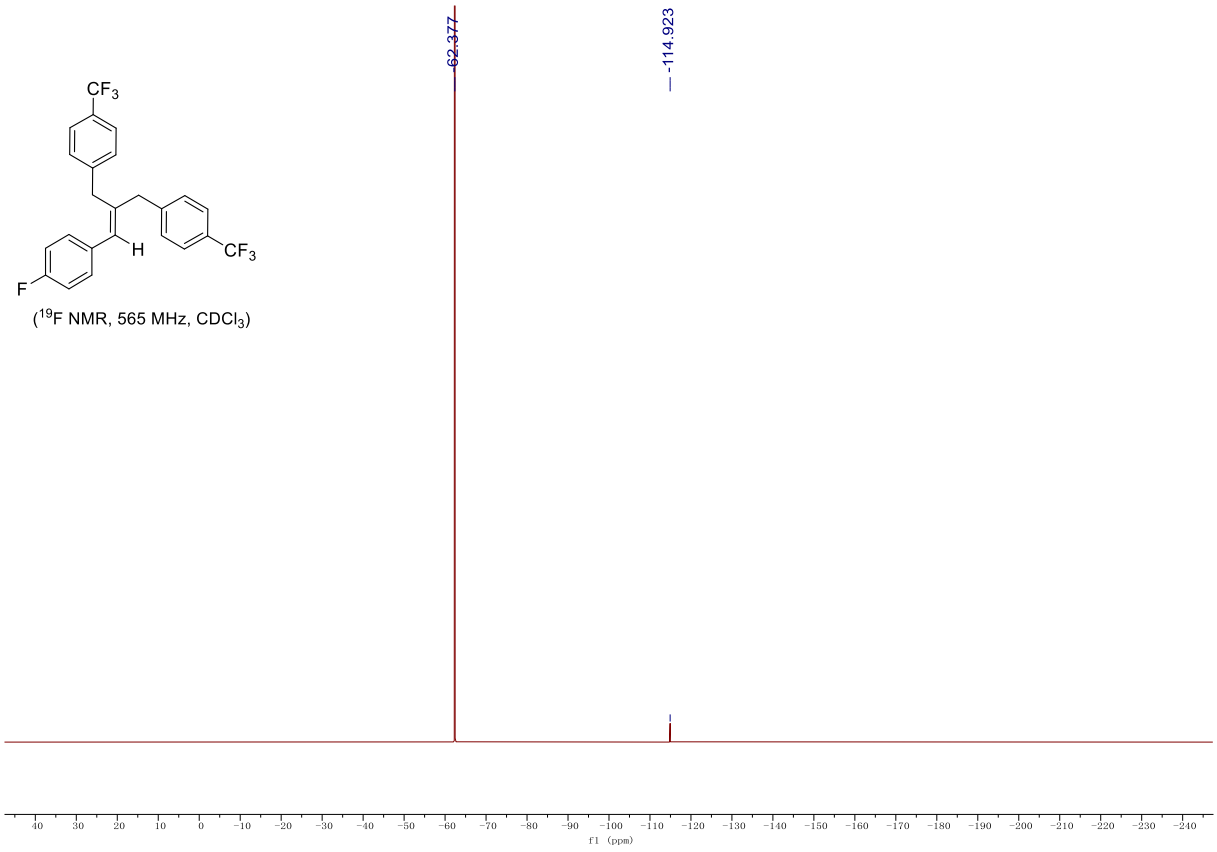
(^{19}F NMR, 565 MHz, $CDCl_3$)



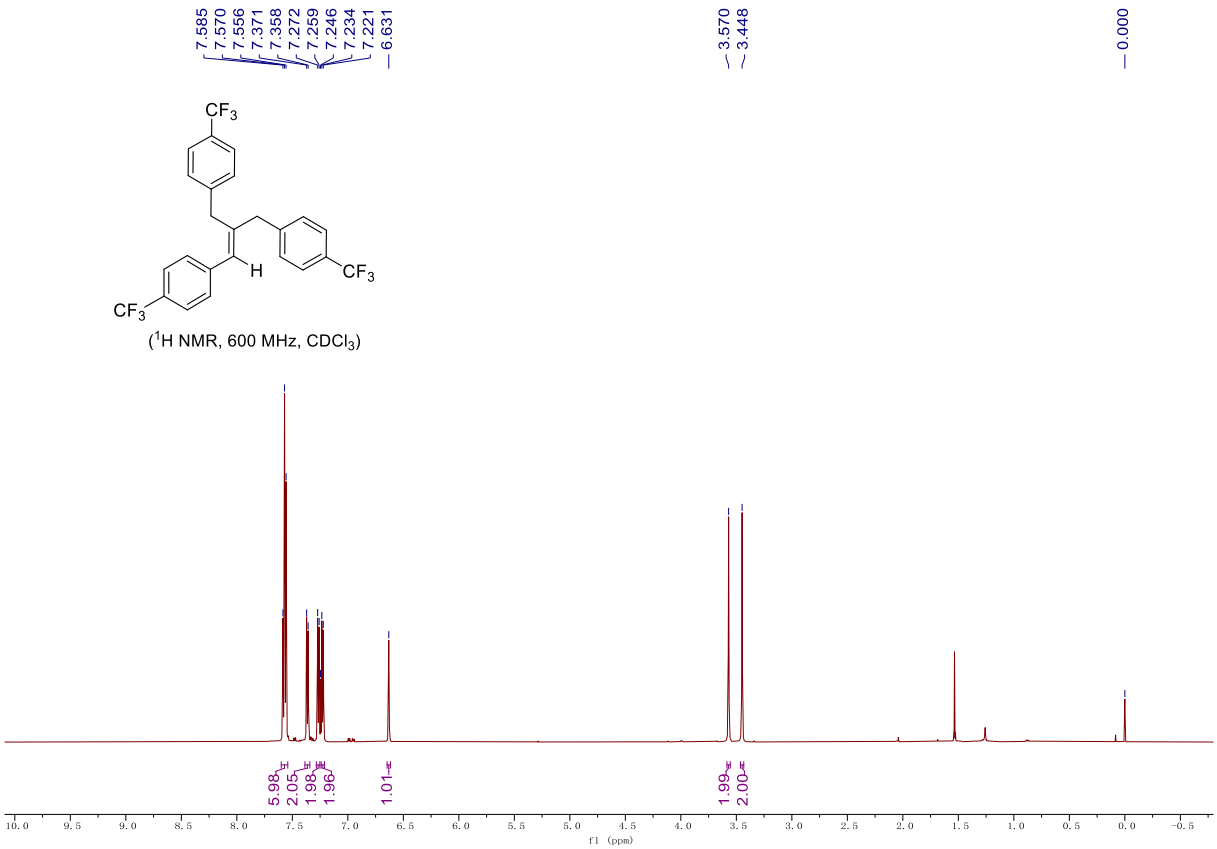
(^{1}H NMR, 400 MHz, $CDCl_3$)

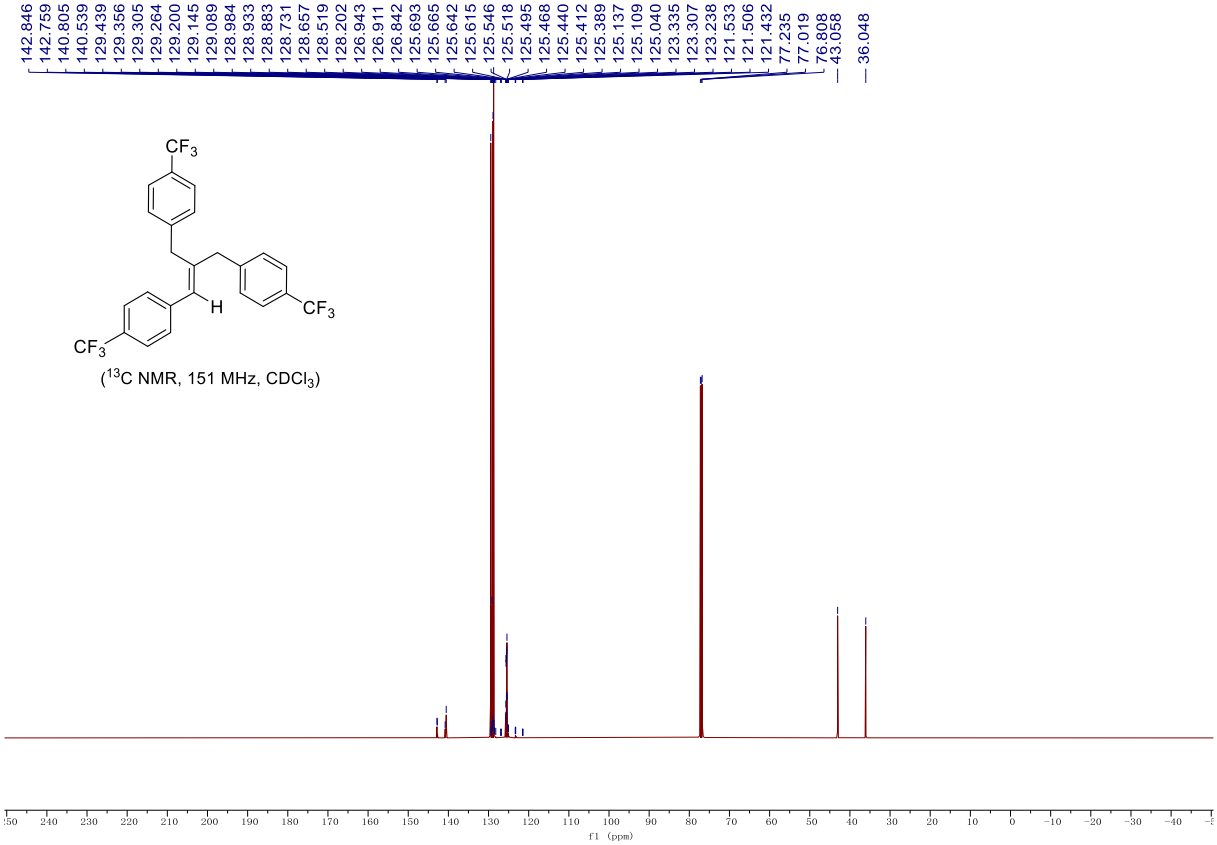


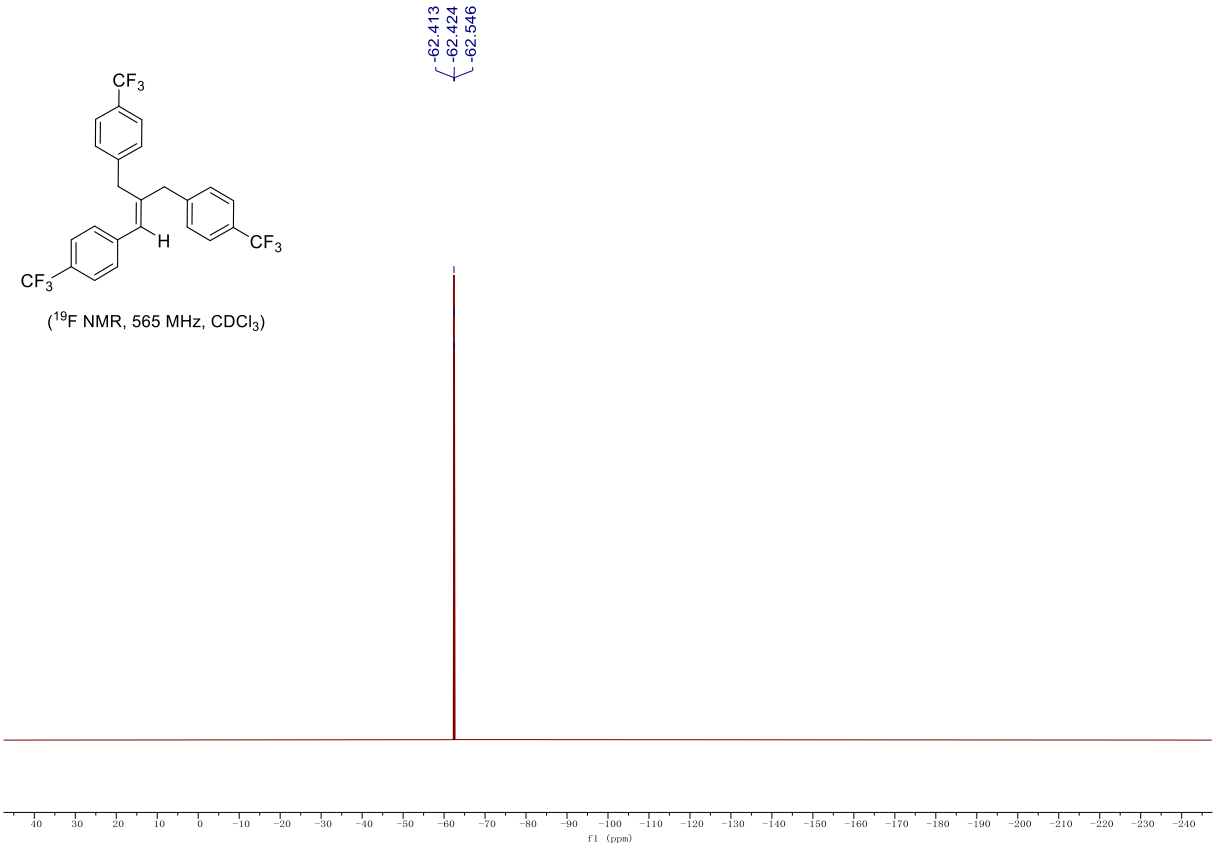
(^{13}C NMR, 151 MHz, $CDCl_3$)



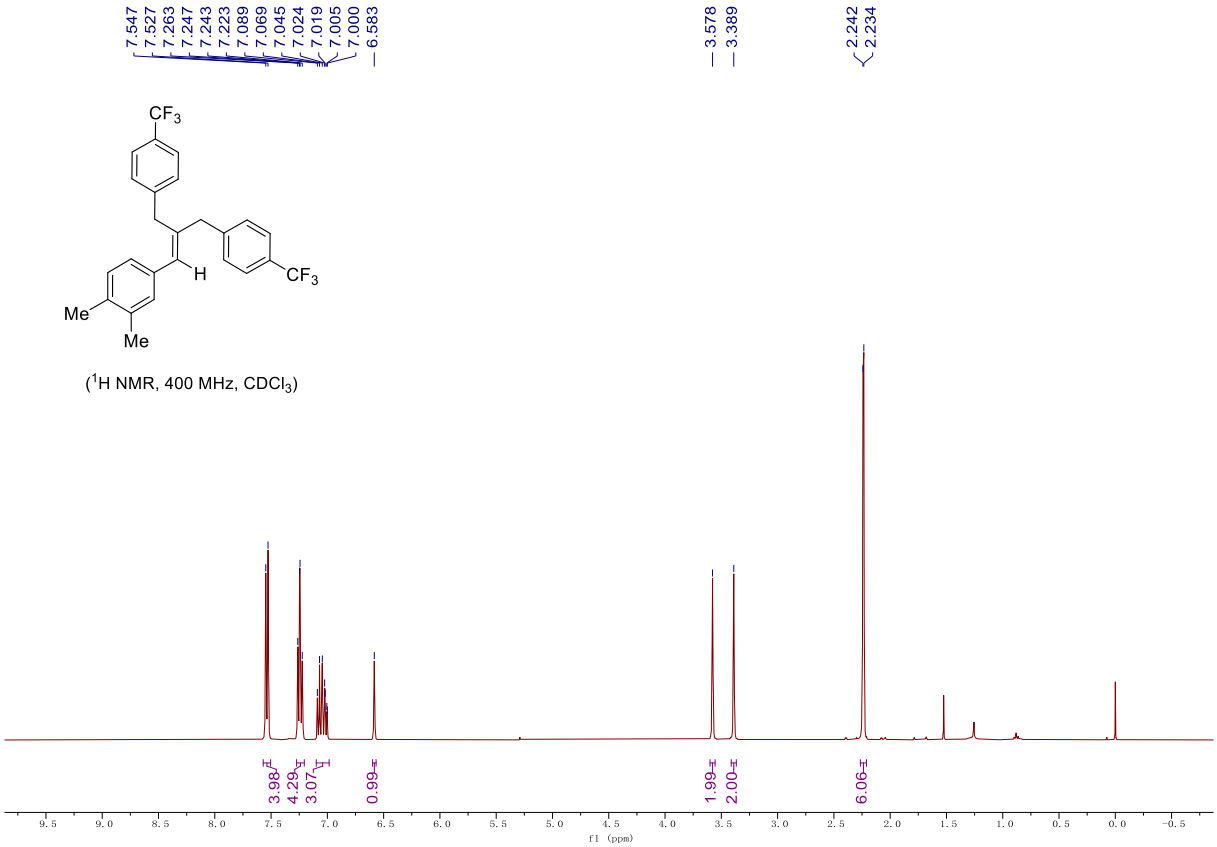
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.585
7.570
7.556
7.371
7.358
7.272
7.259
7.246
7.234
7.221
6.631
3.570
3.448
0.000
CF3
H
CF3
CF3
(1H NMR, 600 MHz, CDCl3)
5.98
2.05
1.98
1.96
1.01
1.99
2.00
f1 (ppm)

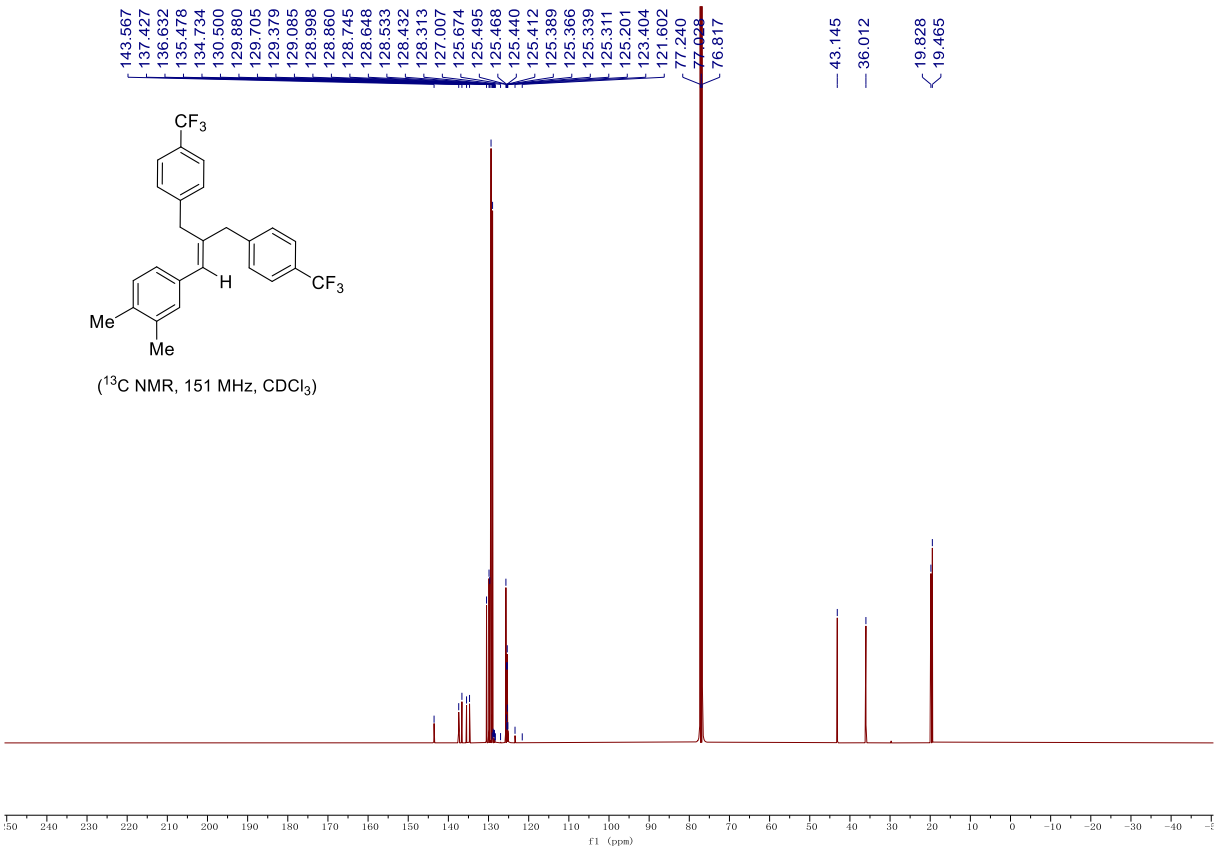

142.846
142.759
140.805
140.539
129.439
129.356
129.305
129.264
129.200
129.145
129.089
128.984
128.933
128.883
128.731
128.657
128.519
128.202
126.943
126.911
126.842
125.693
125.665
125.642
125.615
125.546
125.518
125.495
125.468
125.440
125.412
125.389
125.137
125.109
125.040
123.335
123.307
123.238
121.533
121.506
121.432
77.235
77.019
76.808
43.058
36.048
CF3
H
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



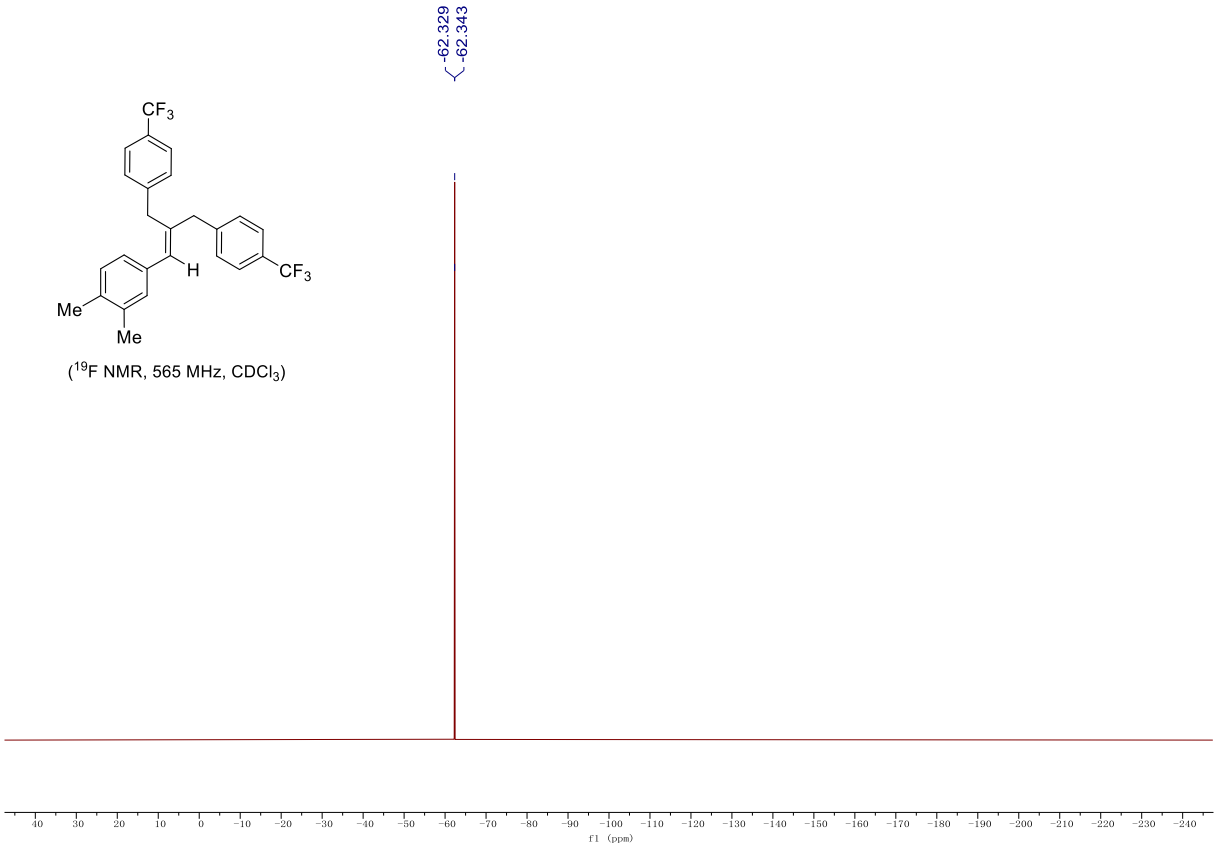
(^{19}F NMR, 565 MHz, $CDCl_3$)



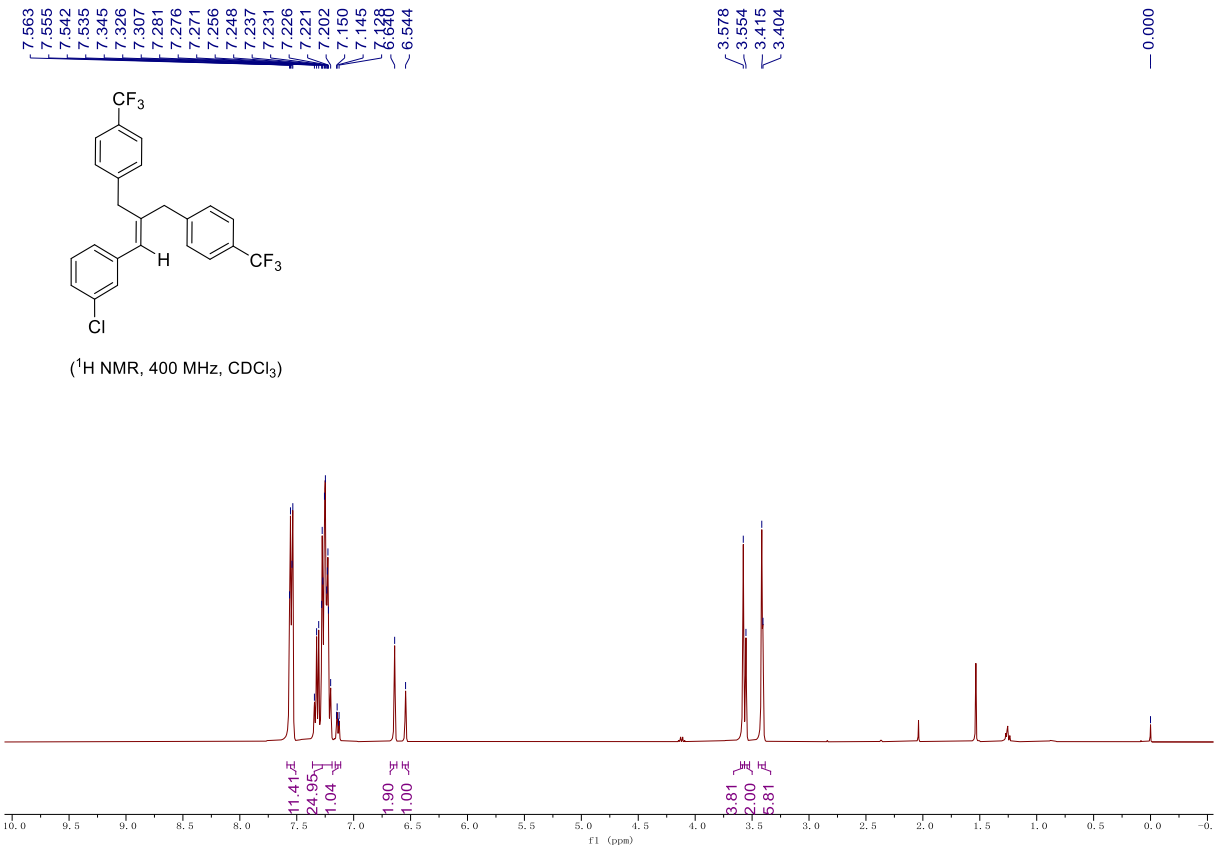
(^{1}H NMR, 400 MHz, $CDCl_3$)



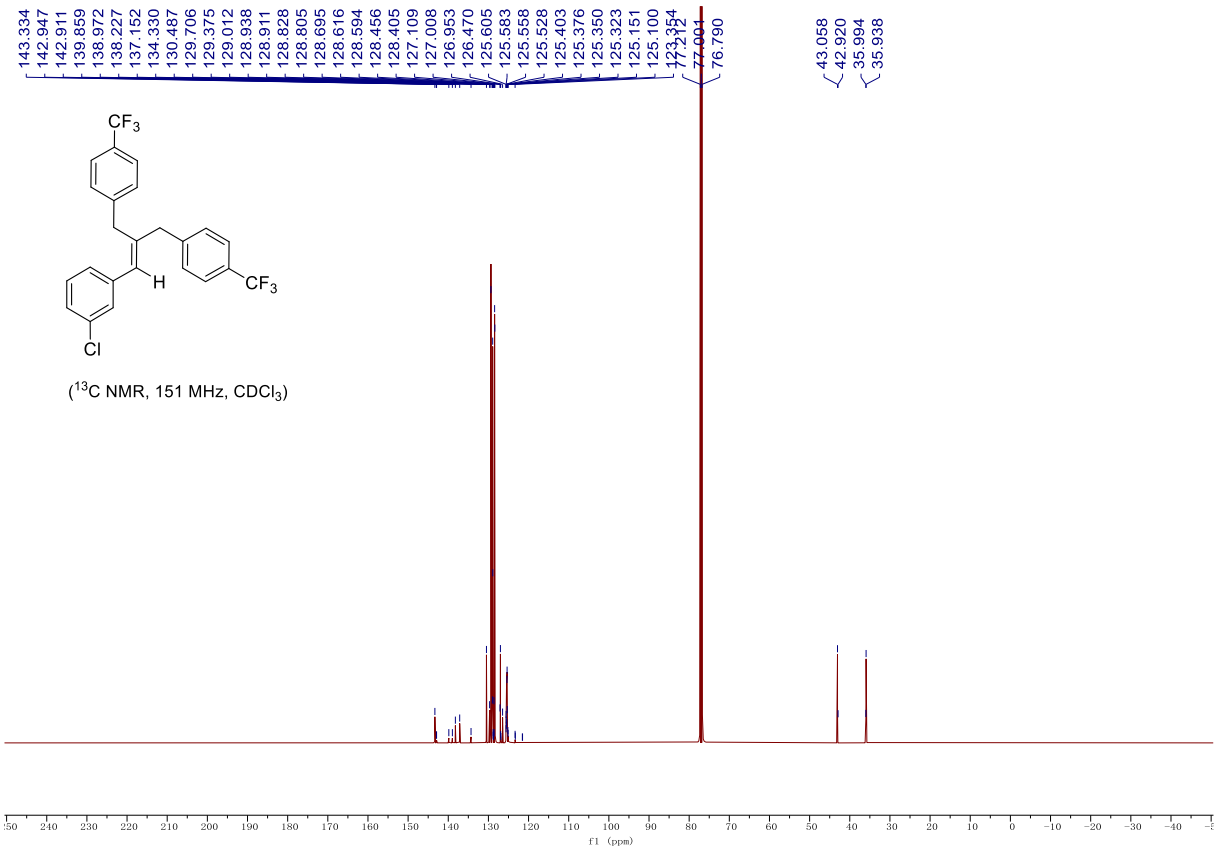
(^{13}C NMR, 151 MHz, $CDCl_3$)



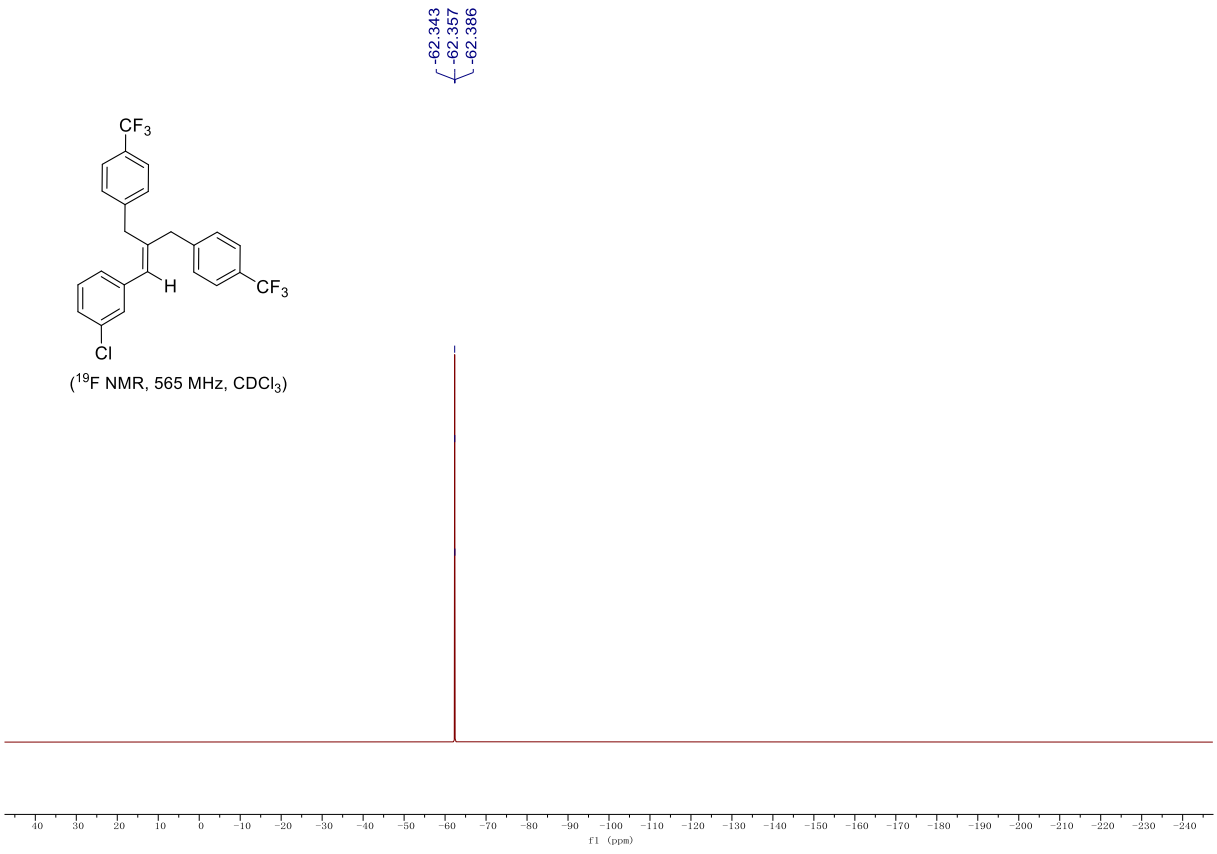
(^{19}F NMR, 565 MHz, $CDCl_3$)



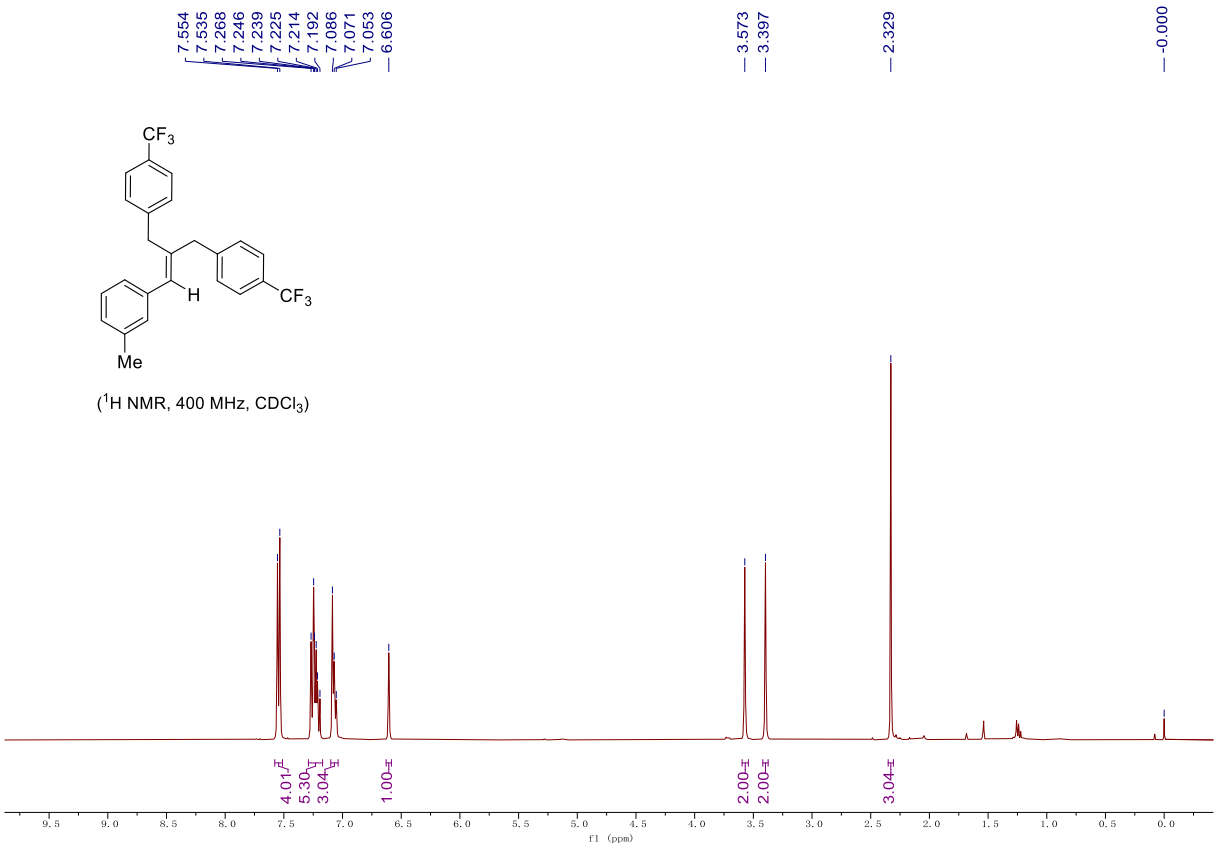
(^{1}H NMR, 400 MHz, $CDCl_3$)



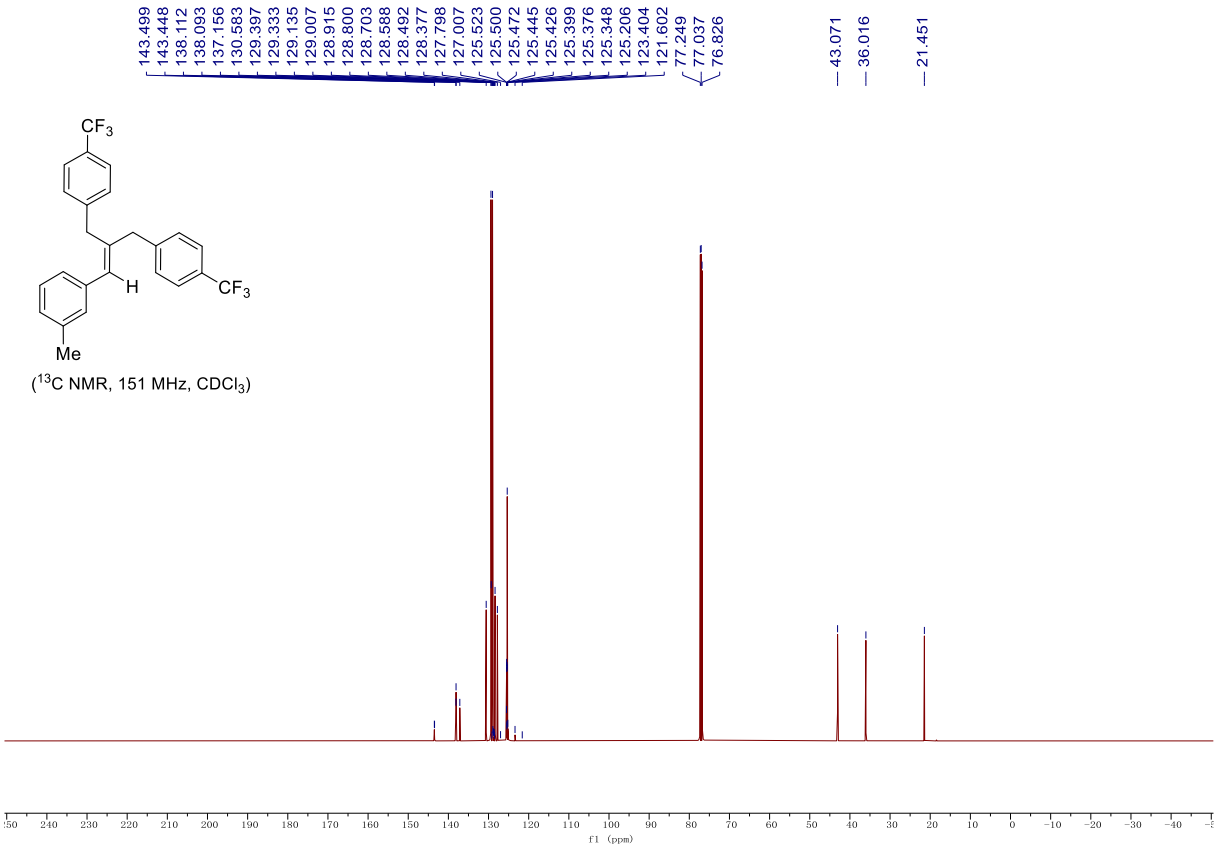
(^{13}C NMR, 151 MHz, $CDCl_3$)



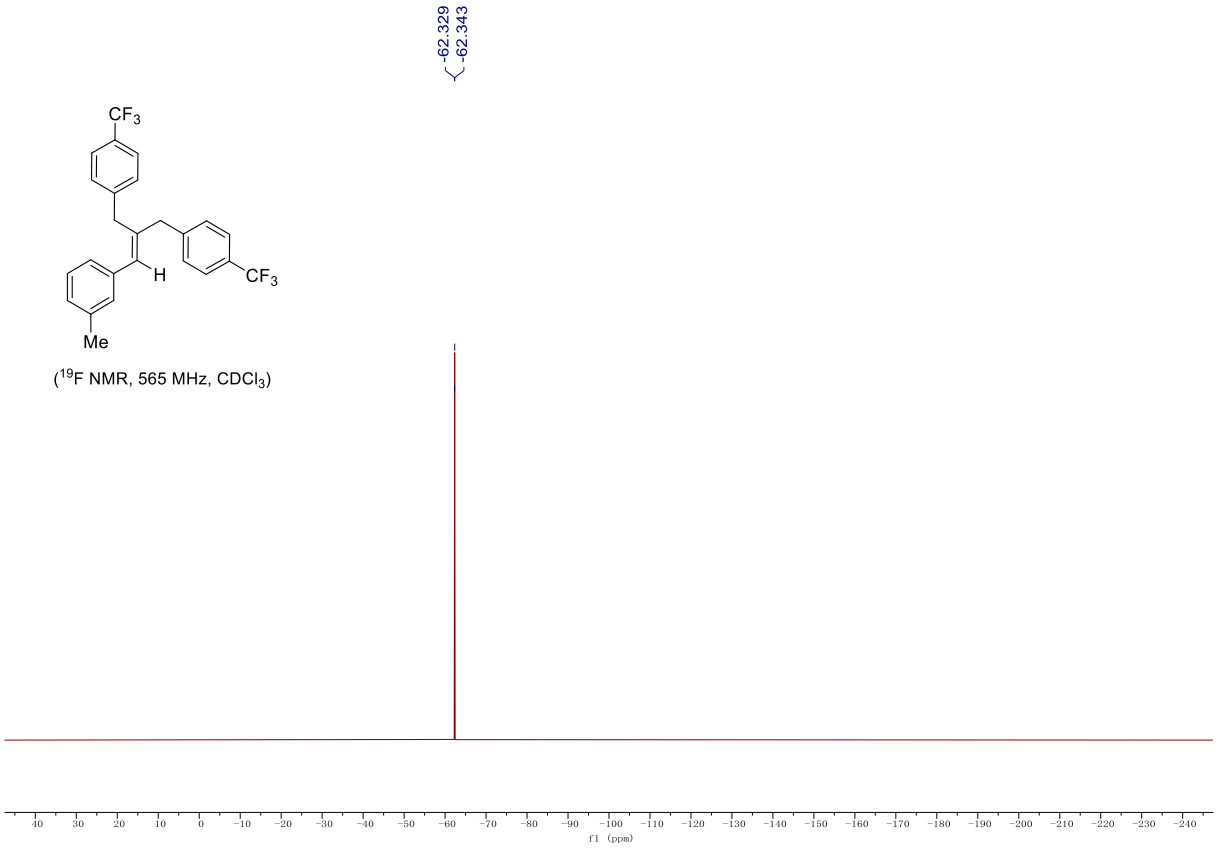
(^{19}F NMR, 565 MHz, $CDCl_3$)



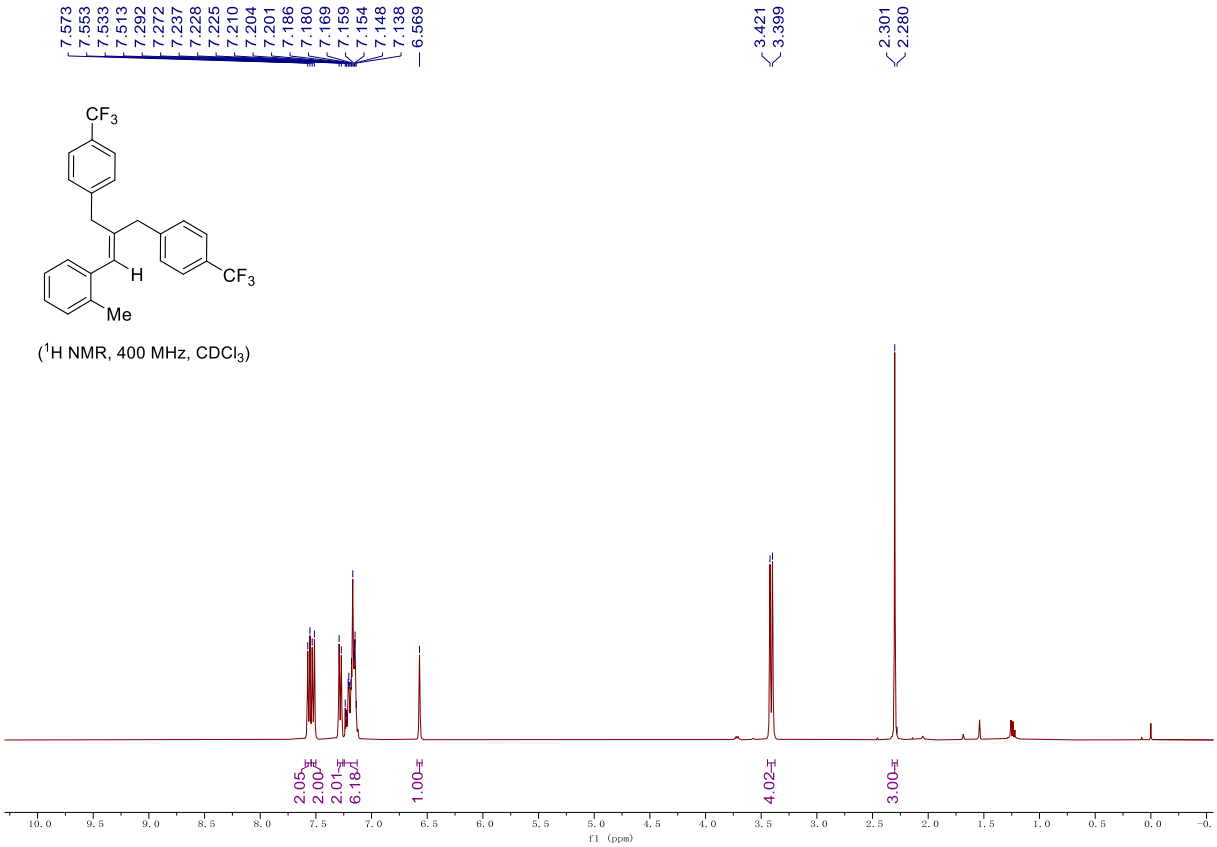
(^{1}H NMR, 400 MHz, $CDCl_3$)



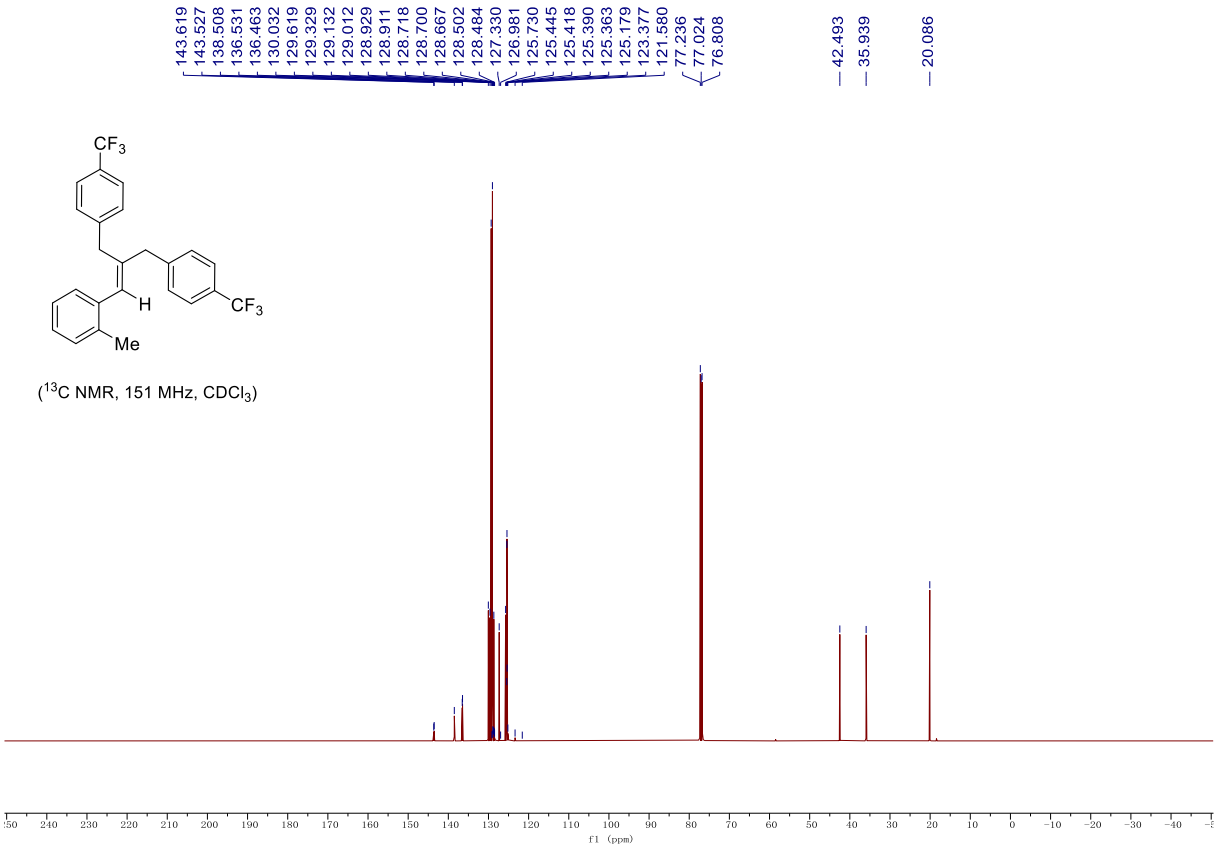
(^{13}C NMR, 151 MHz, $CDCl_3$)



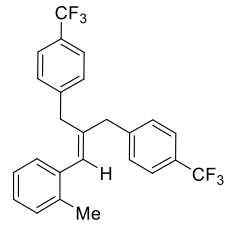
(^{19}F NMR, 565 MHz, $CDCl_3$)



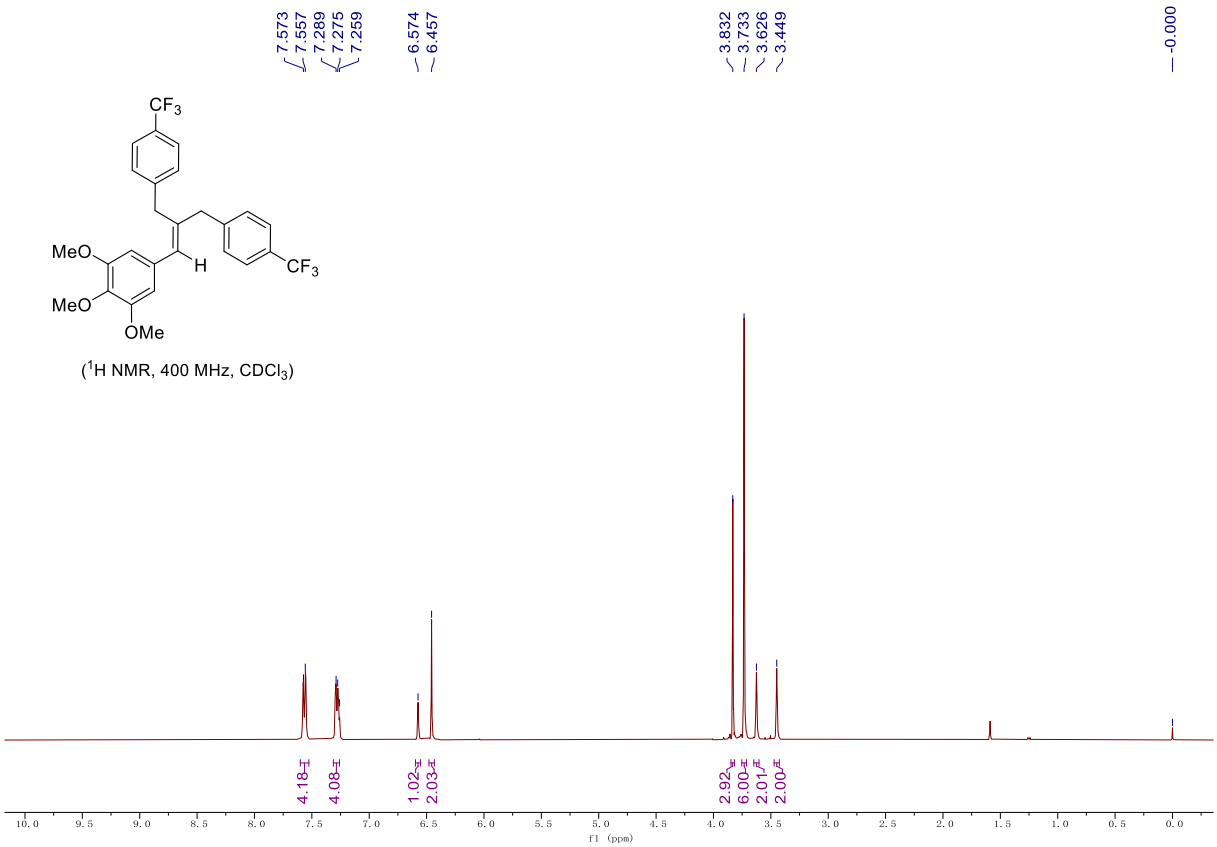
(^{1}H NMR, 400 MHz, $CDCl_3$)



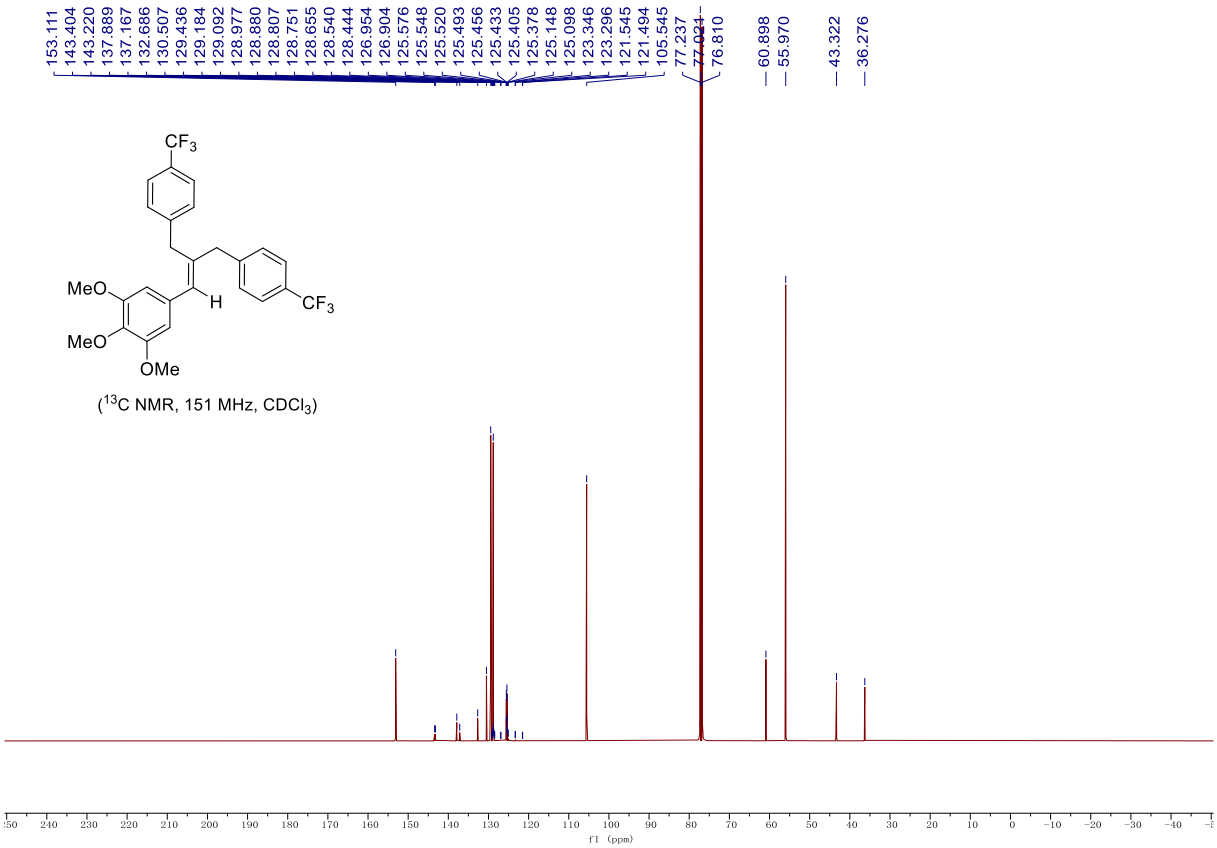
(^{13}C NMR, 151 MHz, $CDCl_3$)



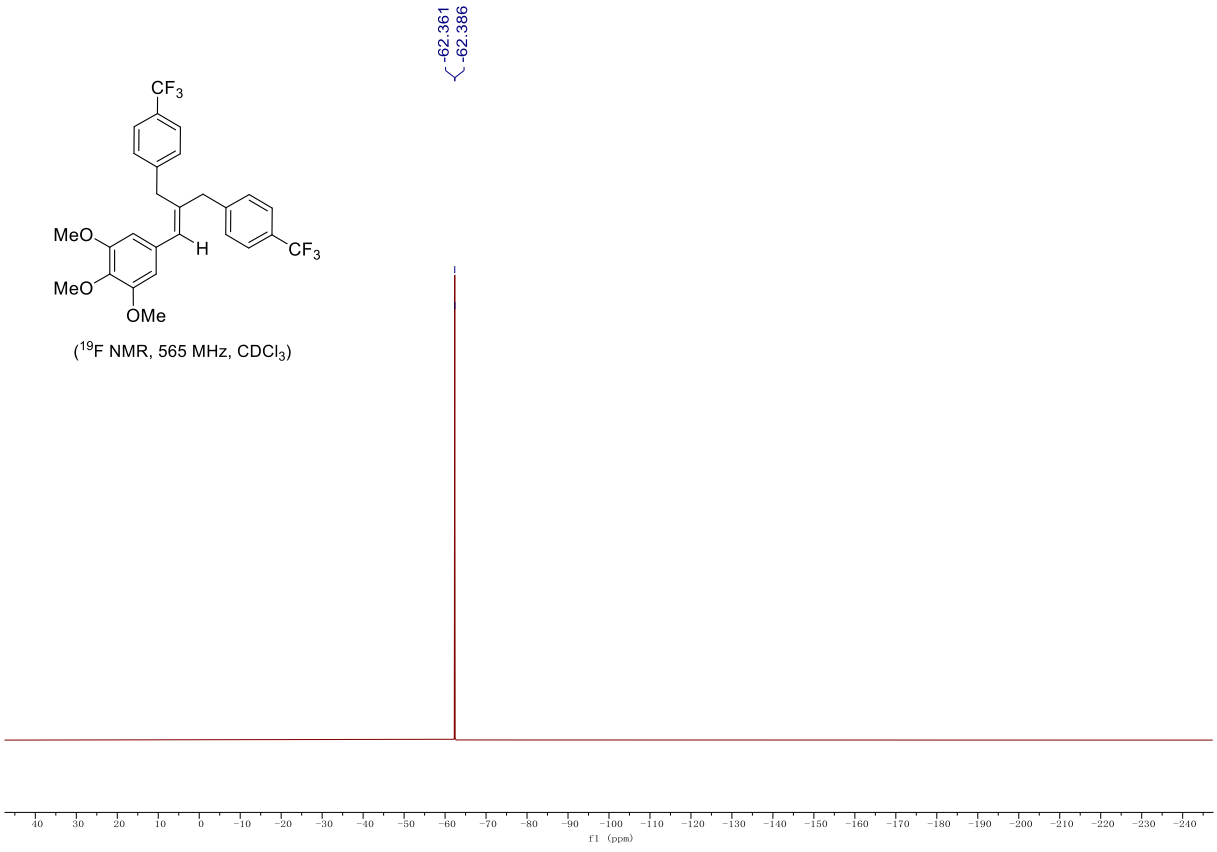
(^{19}F NMR, 565 MHz, $CDCl_3$)



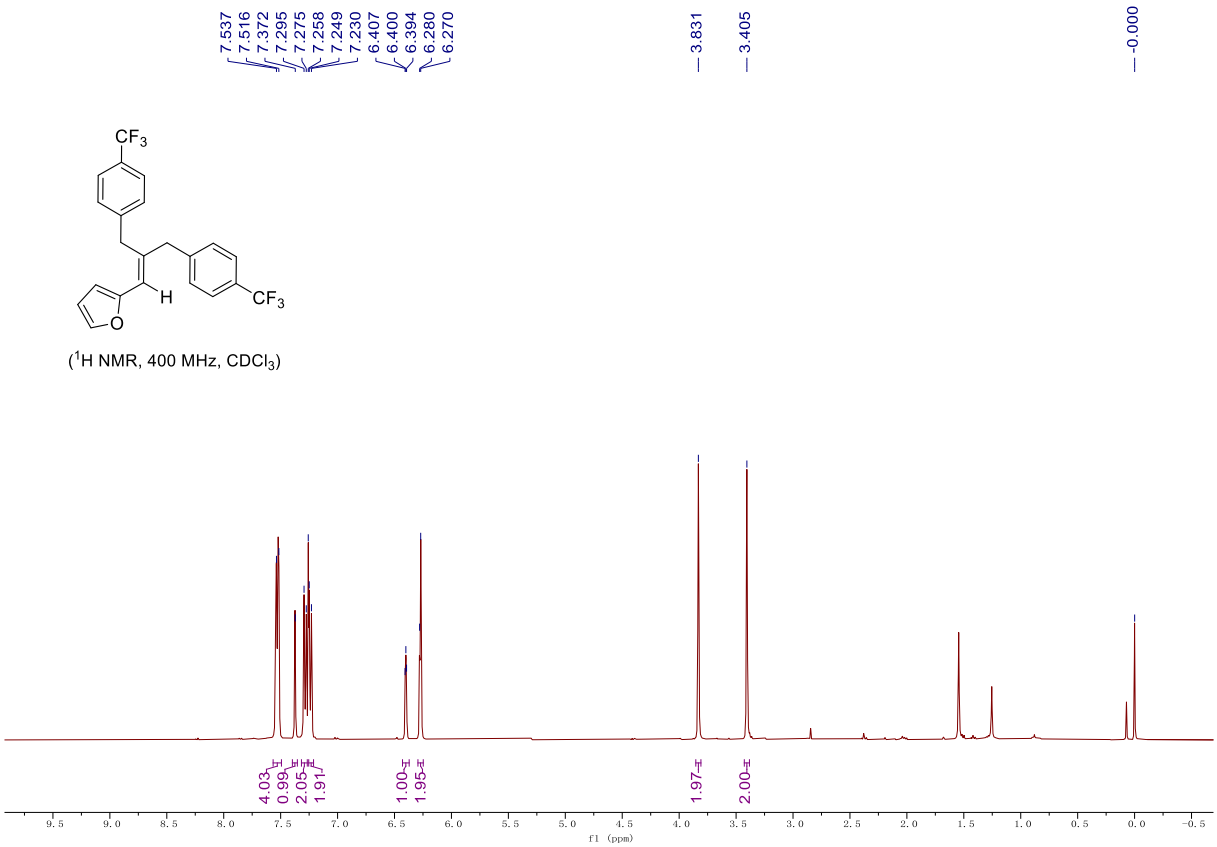
(^{1}H NMR, 400 MHz, $CDCl_3$)



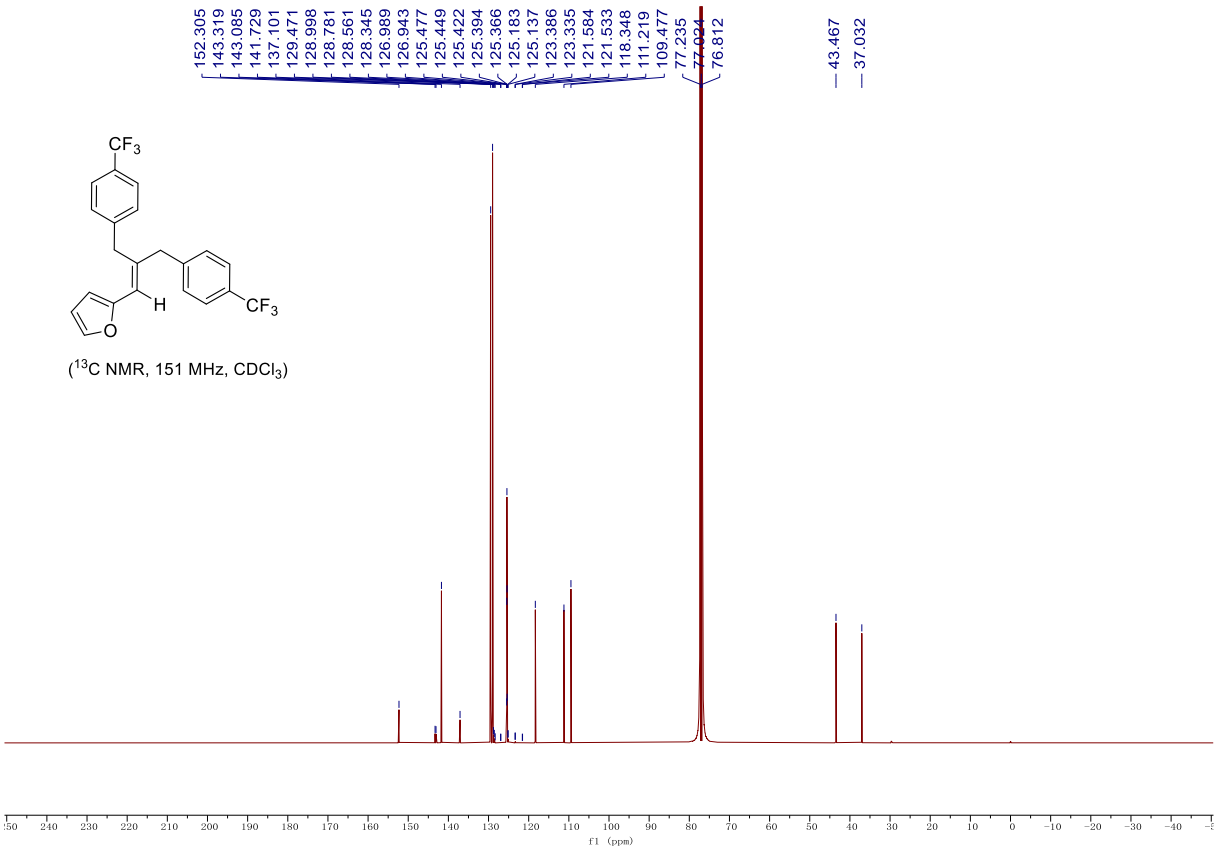
(^{13}C NMR, 151 MHz, $CDCl_3$)



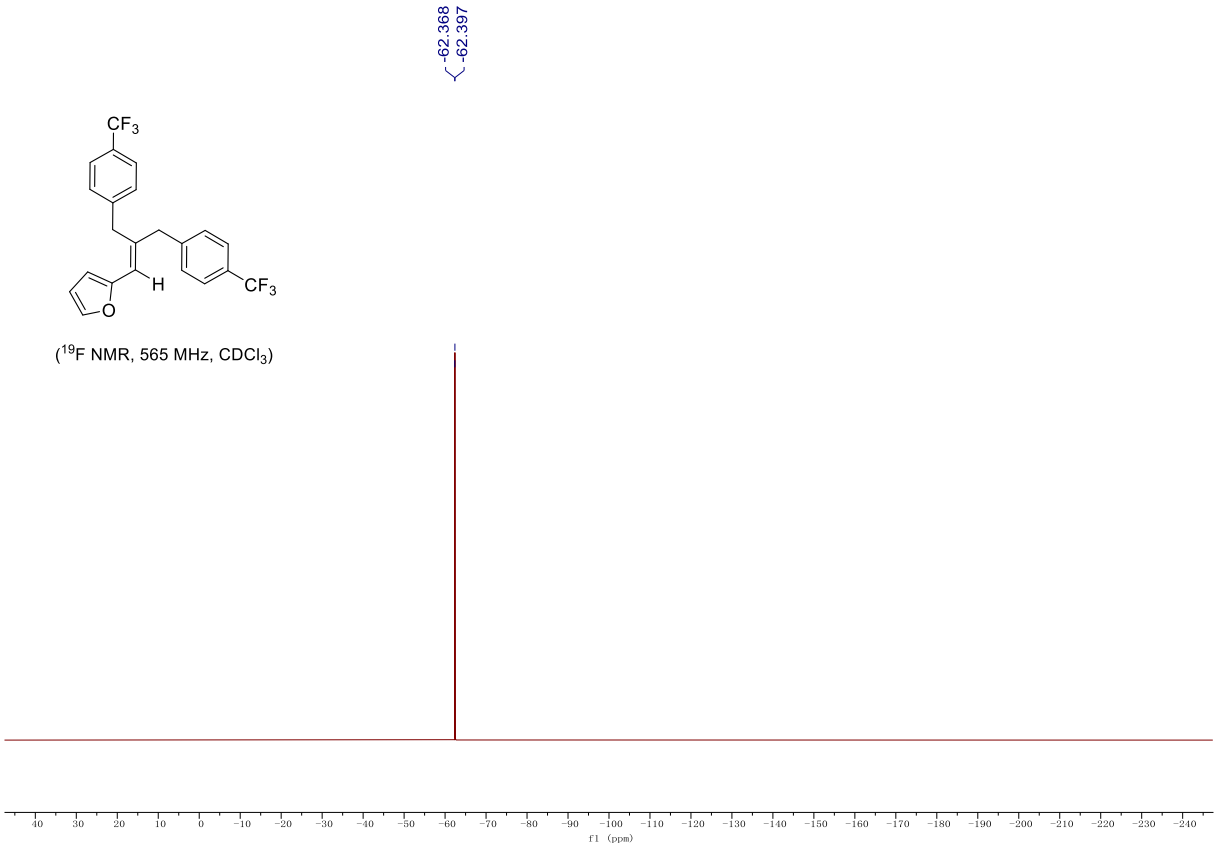
(^{19}F NMR, 565 MHz, $CDCl_3$)

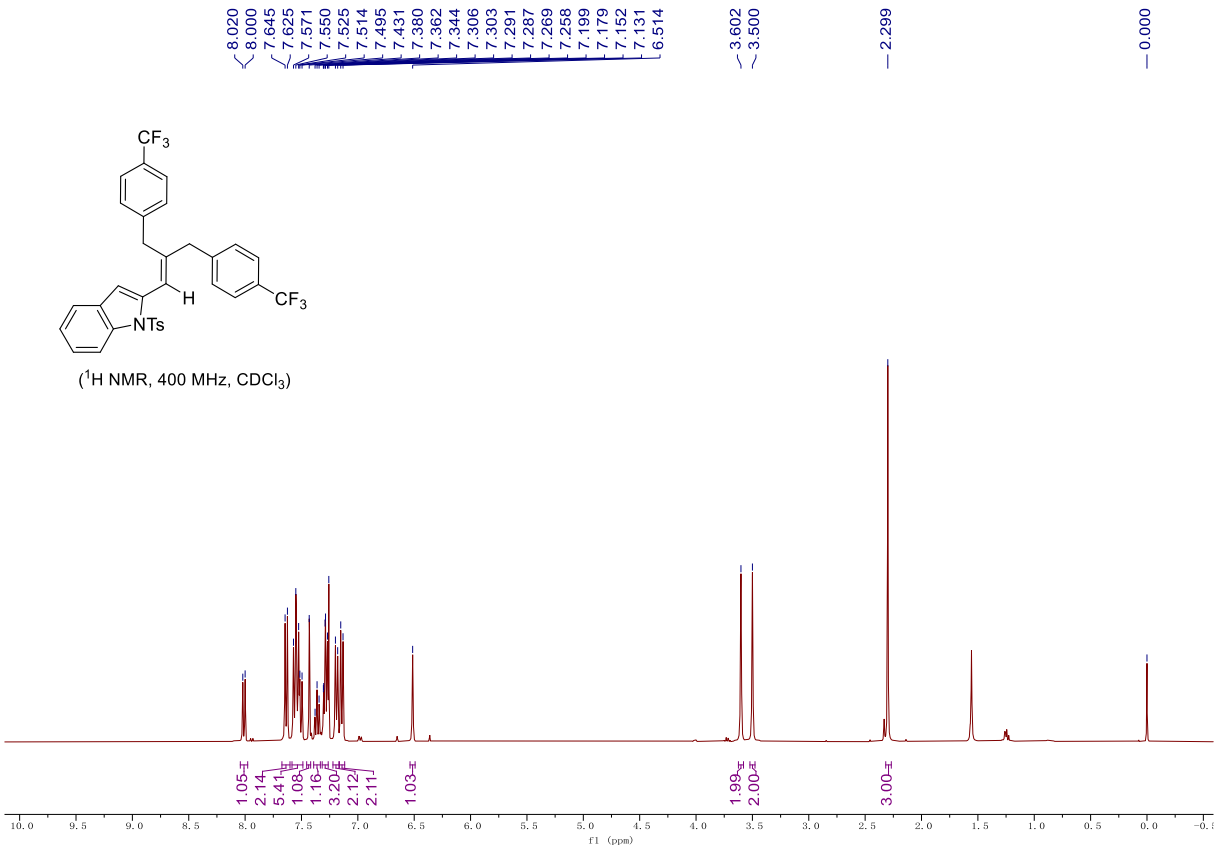


(^{1}H NMR, 400 MHz, $CDCl_3$)

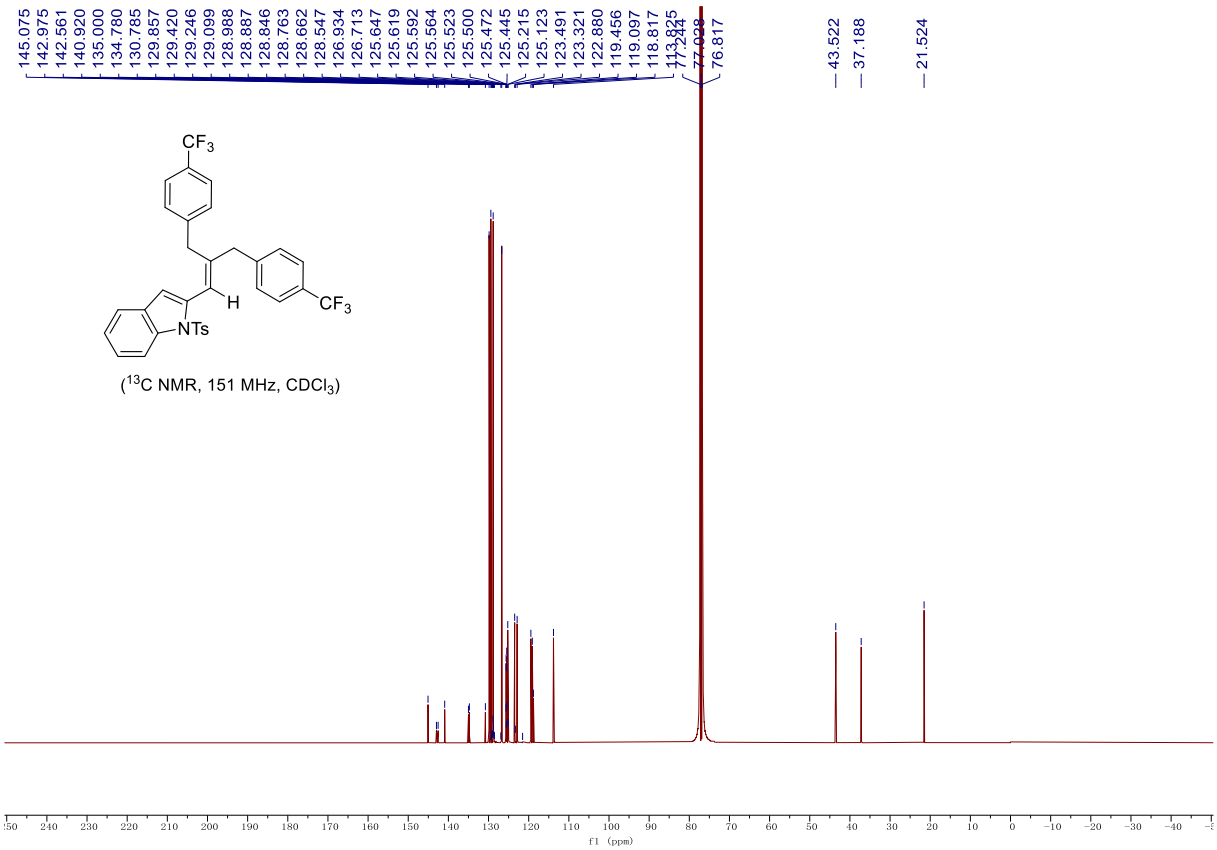


(^{13}C NMR, 151 MHz, $CDCl_3$)

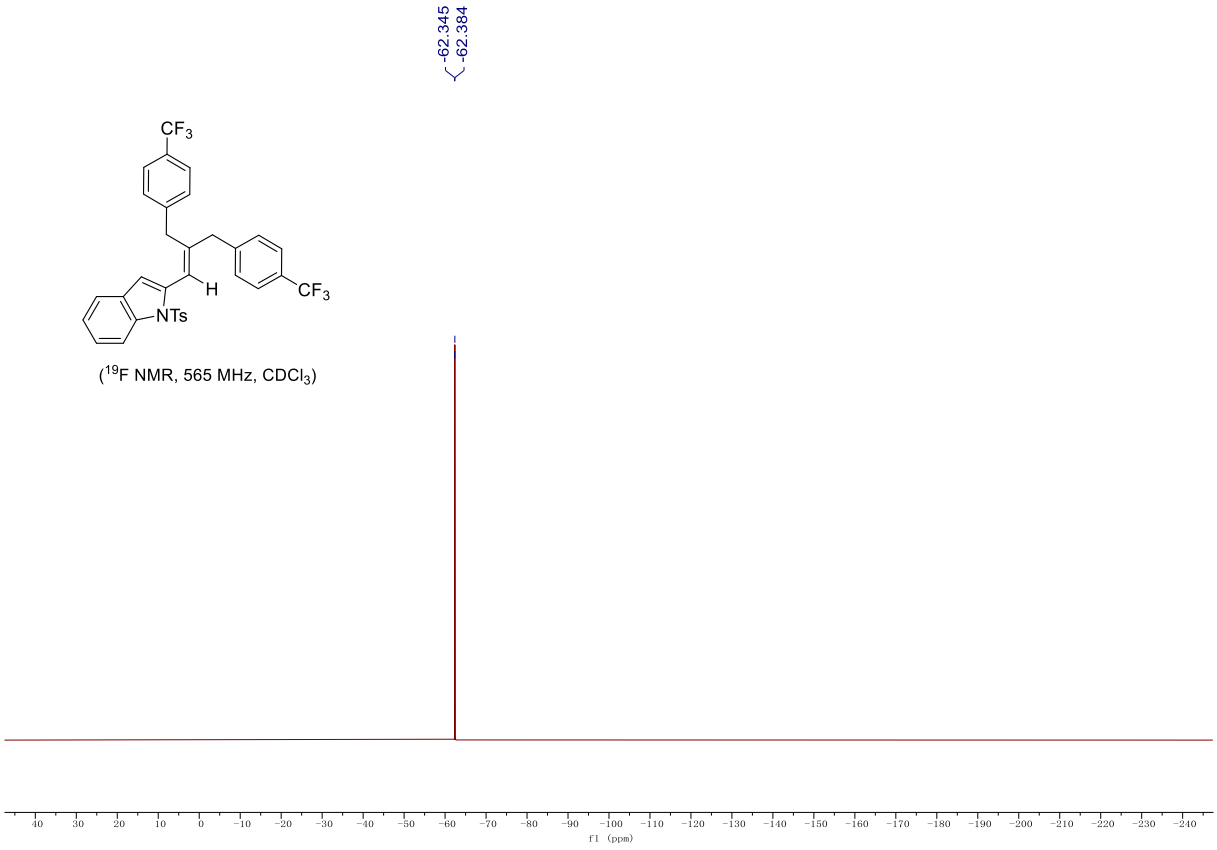

-62.368
-62.397
CF3
H
O
CF3
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)



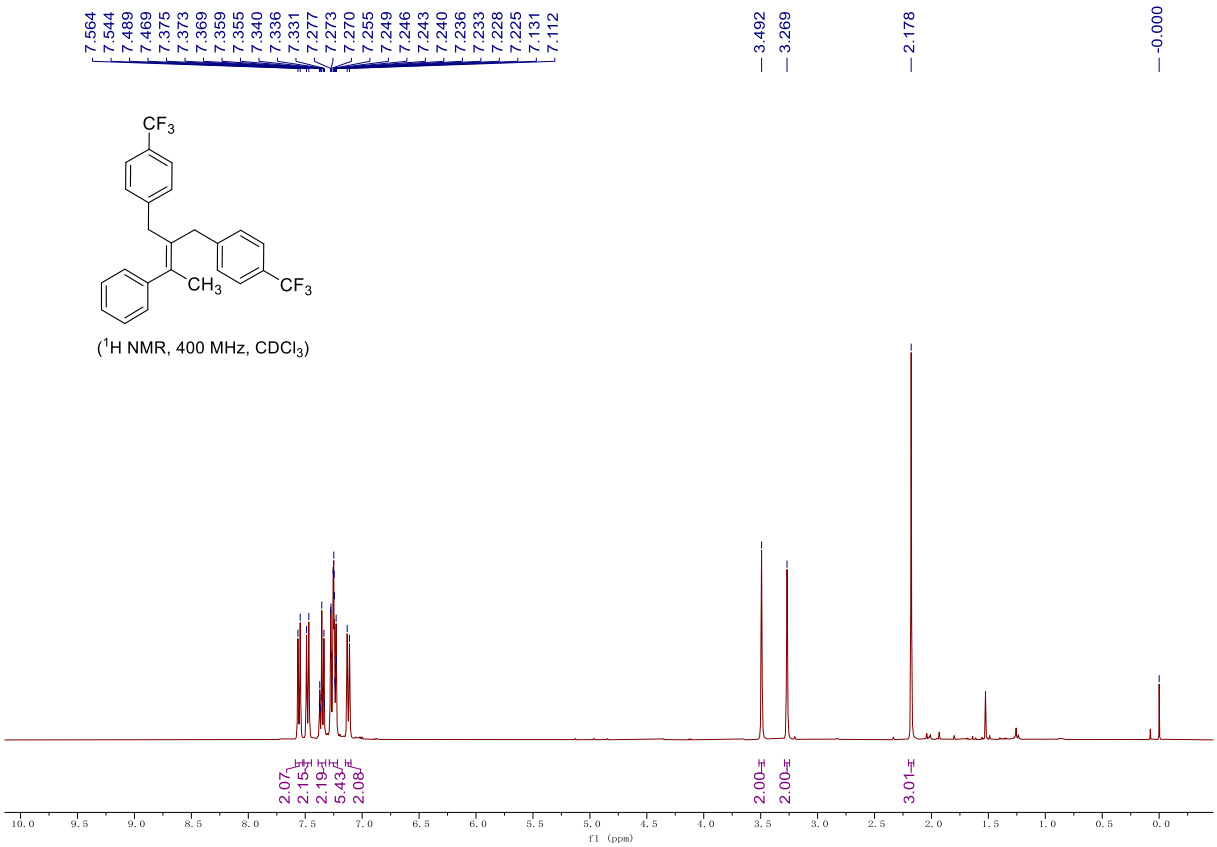
(^{1}H NMR, 400 MHz, $CDCl_3$)

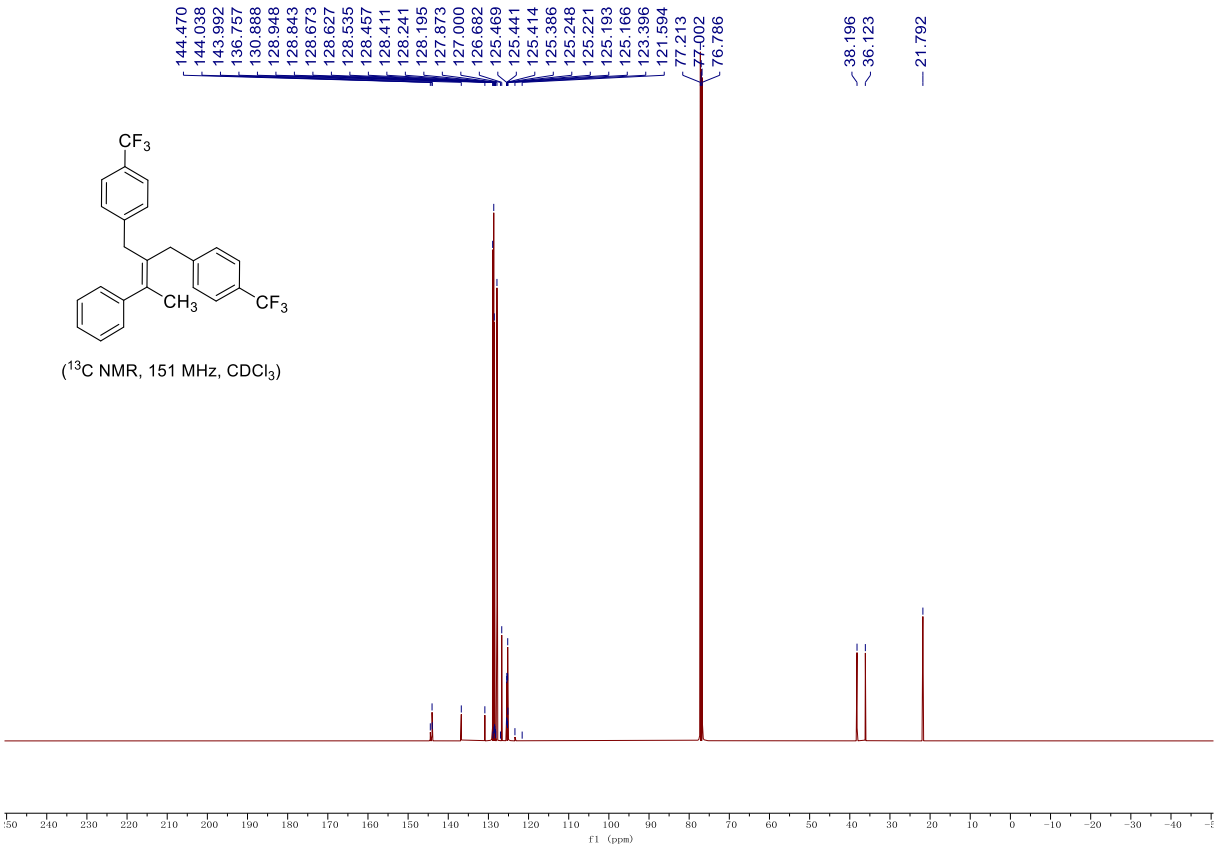


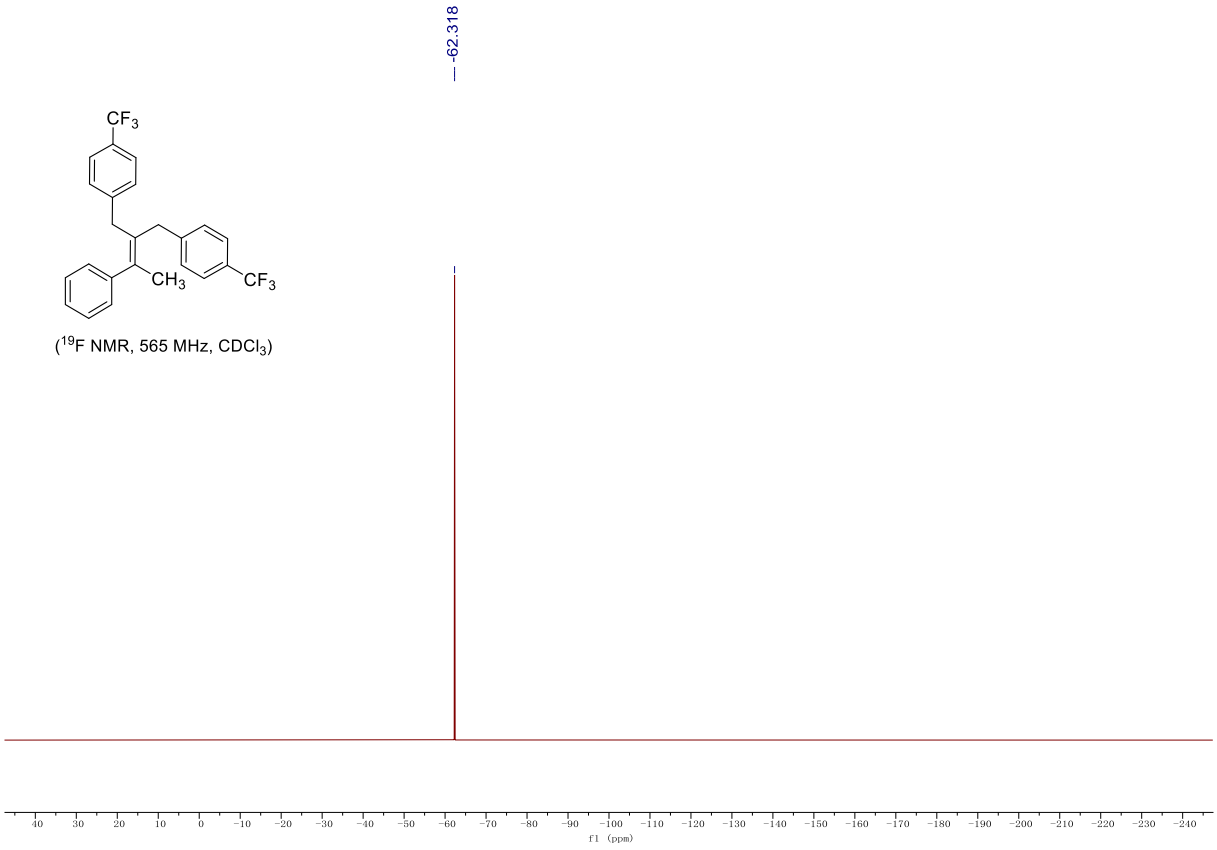
(^{13}C NMR, 151 MHz, $CDCl_3$)



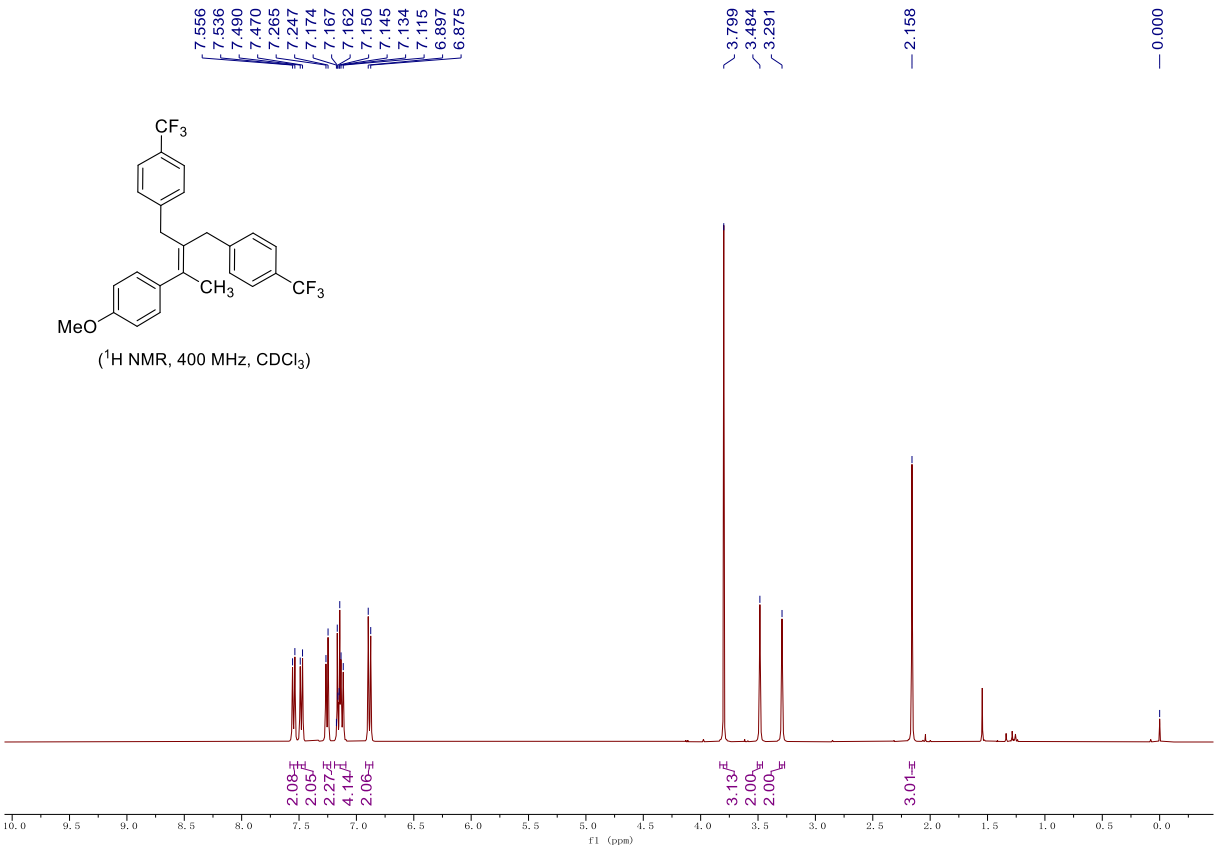
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.564
7.544
7.489
7.469
7.375
7.373
7.369
7.359
7.355
7.340
7.336
7.331
7.277
7.273
7.270
7.255
7.249
7.246
7.243
7.240
7.236
7.233
7.228
7.225
7.131
7.112
3.492
3.269
2.178
-0.000
CF3
CH3
CF3
(1H NMR, 400 MHz, CDCl3)
2.07
2.15
2.19
5.43
2.08
2.00
2.00
3.01
f1 (ppm)

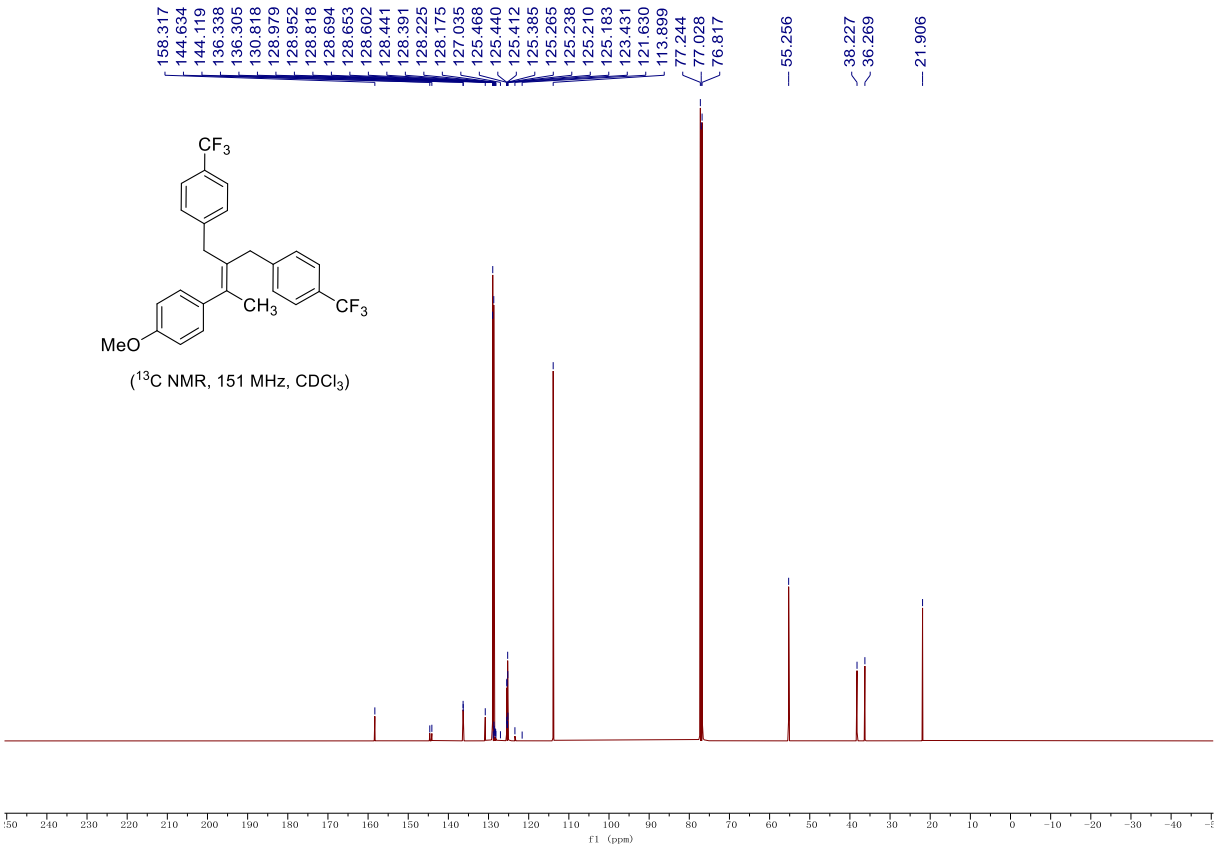

144.470
144.038
143.992
136.757
130.888
128.948
128.843
128.673
128.627
128.535
128.457
128.411
128.241
128.195
127.873
127.000
126.682
125.469
125.441
125.414
125.386
125.248
125.221
125.193
125.166
123.396
121.594
77.213
77.002
76.786
38.196
36.123
21.792
CF3
CH3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



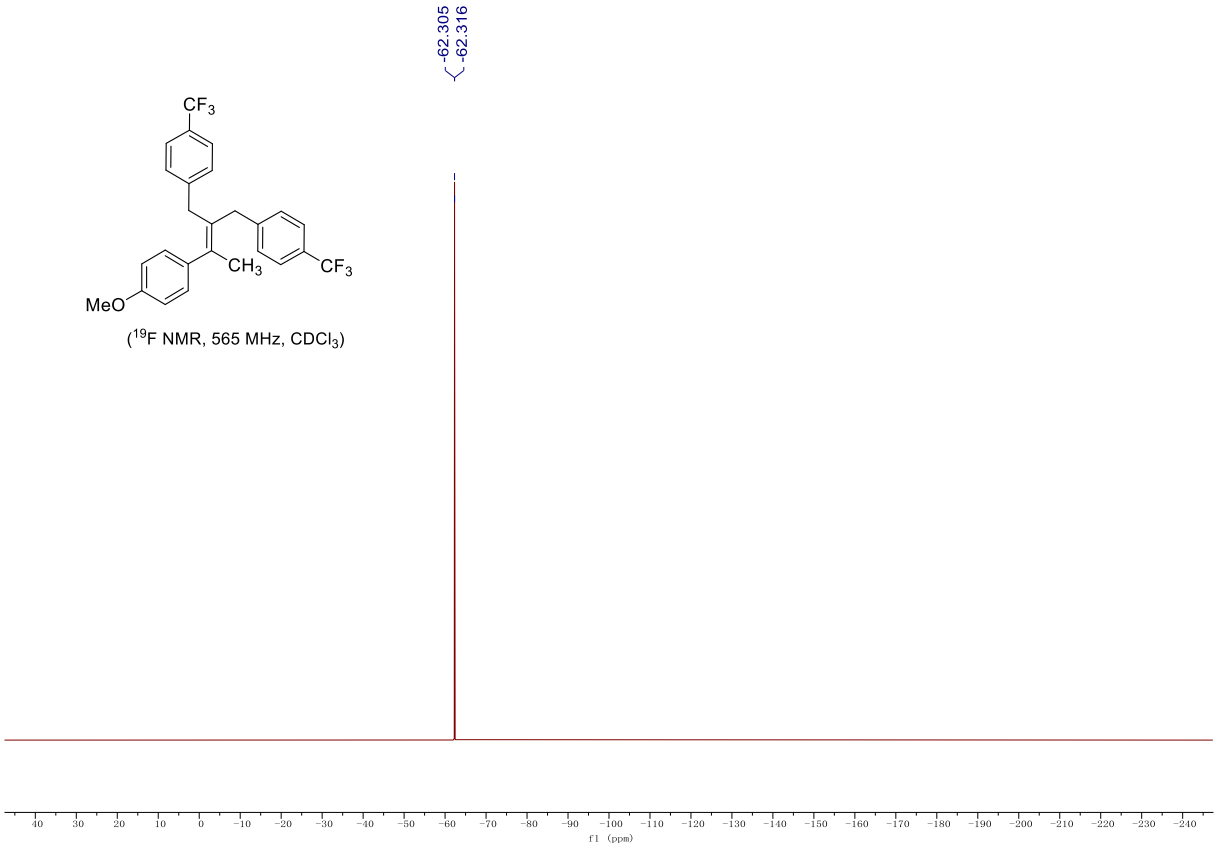
(^{19}F NMR, 565 MHz, $CDCl_3$)

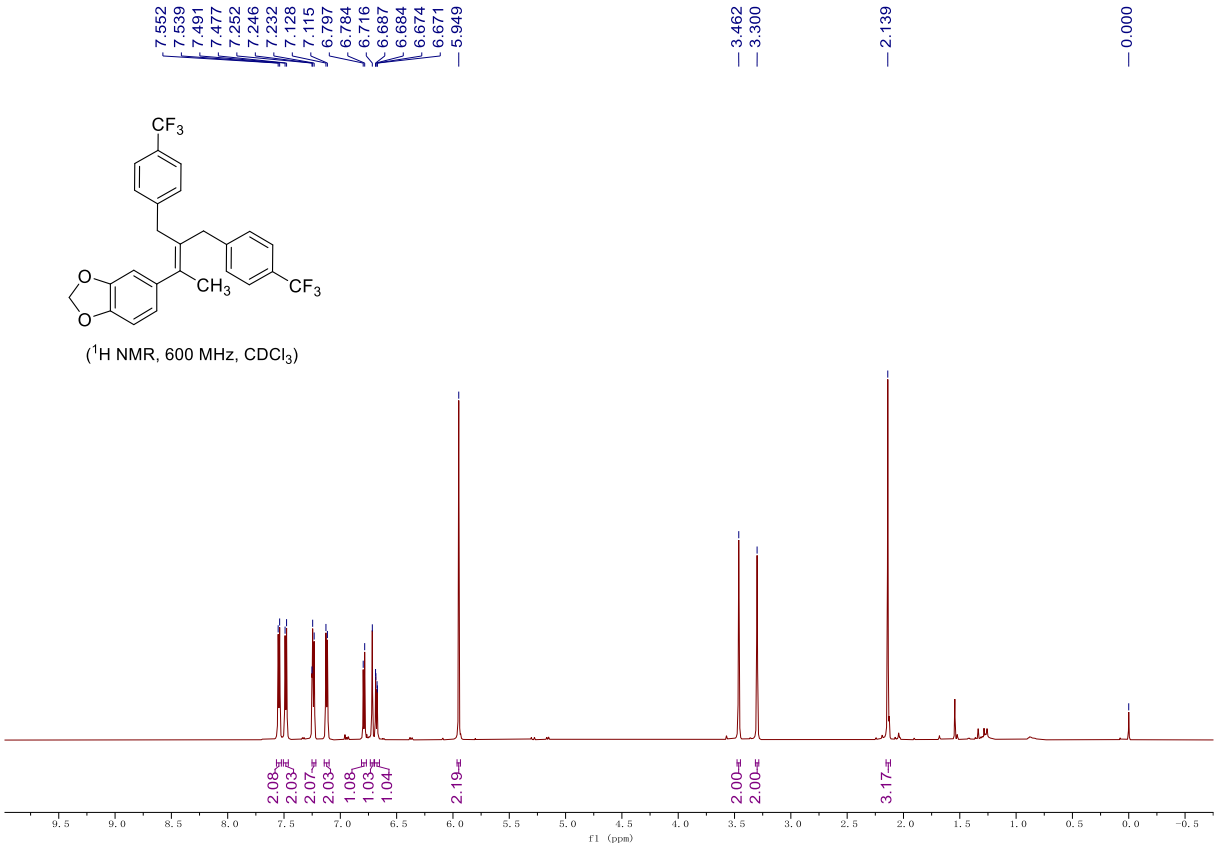


(^{1}H NMR, 400 MHz, $CDCl_3$)

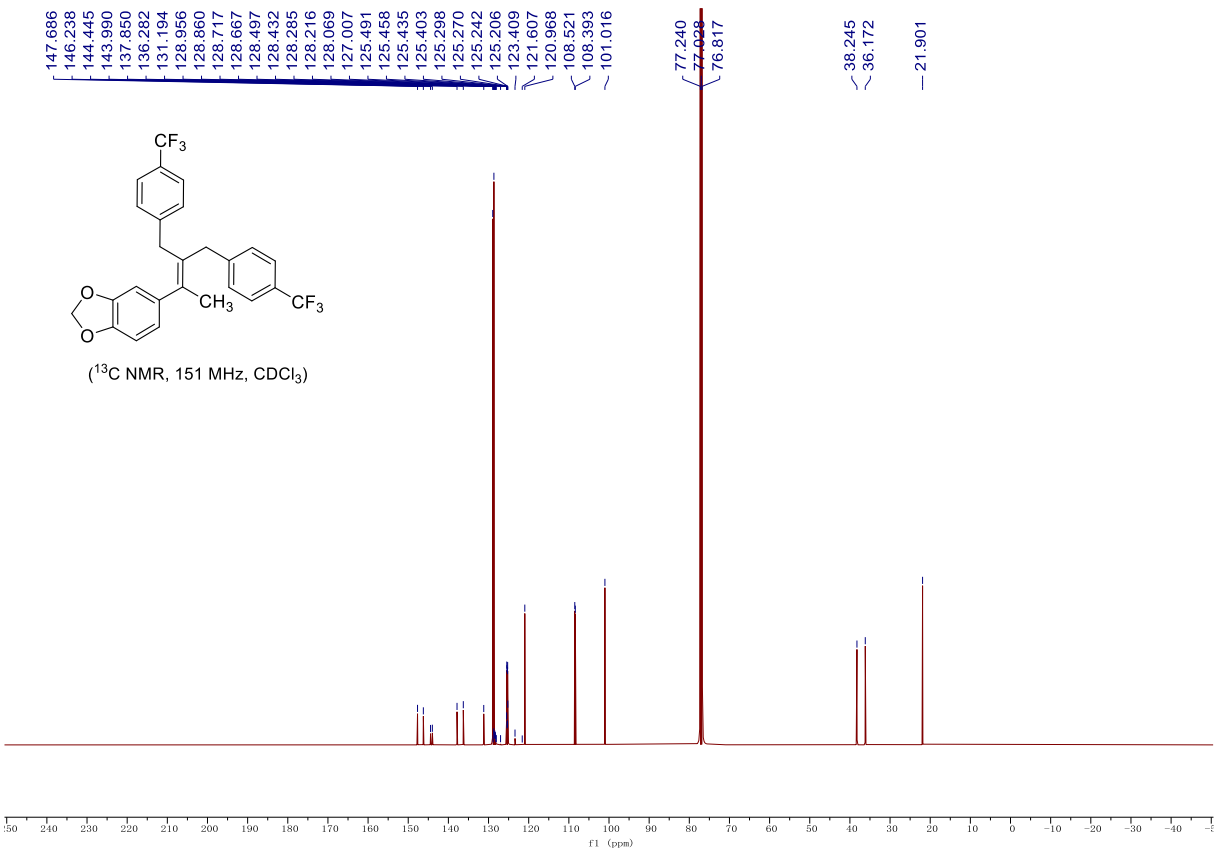


(^{13}C NMR, 151 MHz, $CDCl_3$)

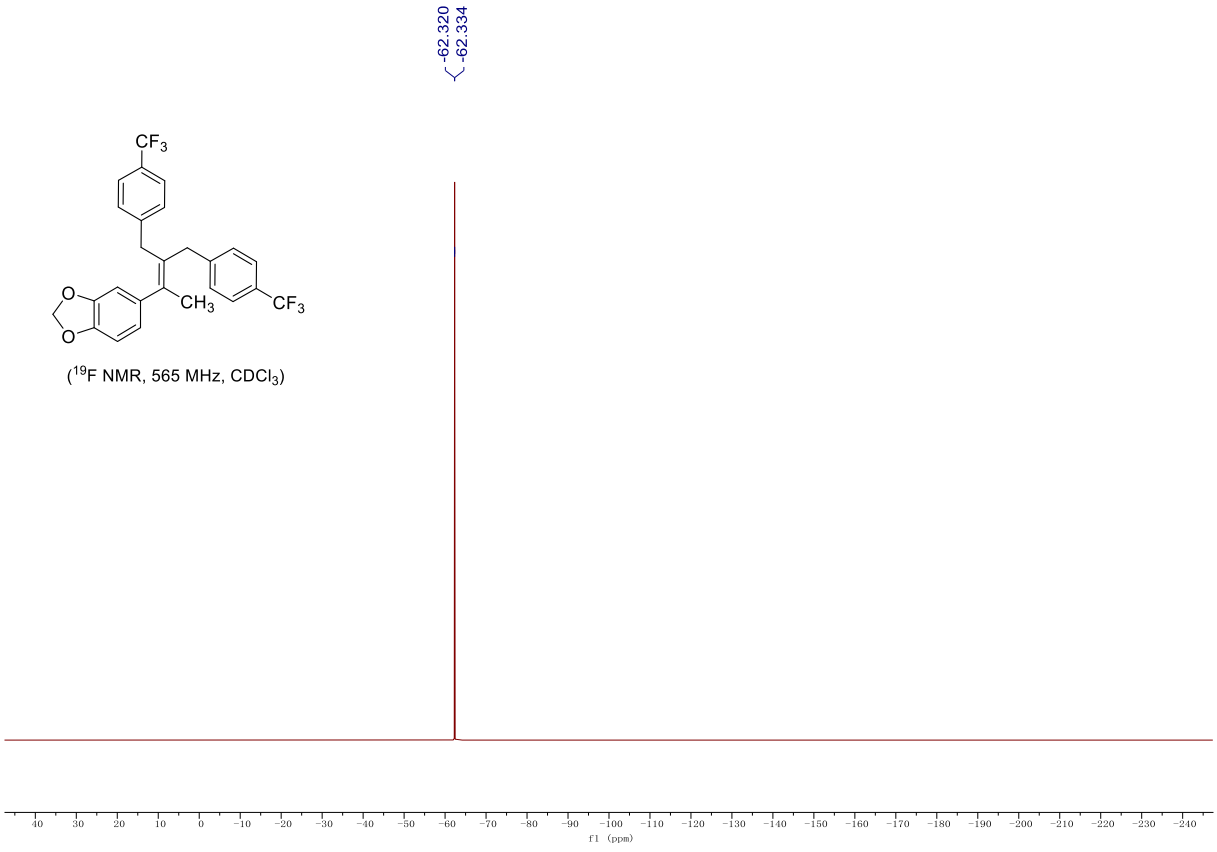

-62.305
-62.316
CF3
CH3
CF3
MeO
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)



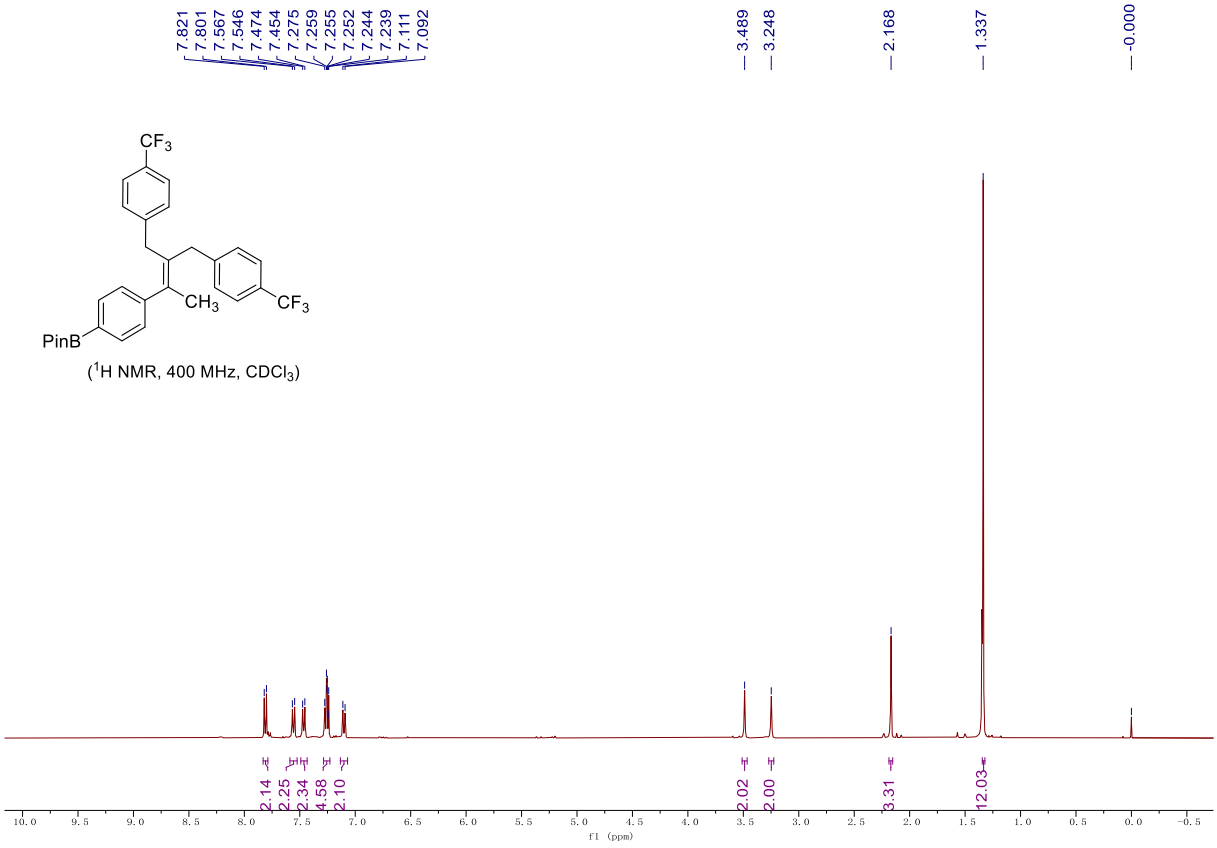
(^{1}H NMR, 600 MHz, $CDCl_3$)



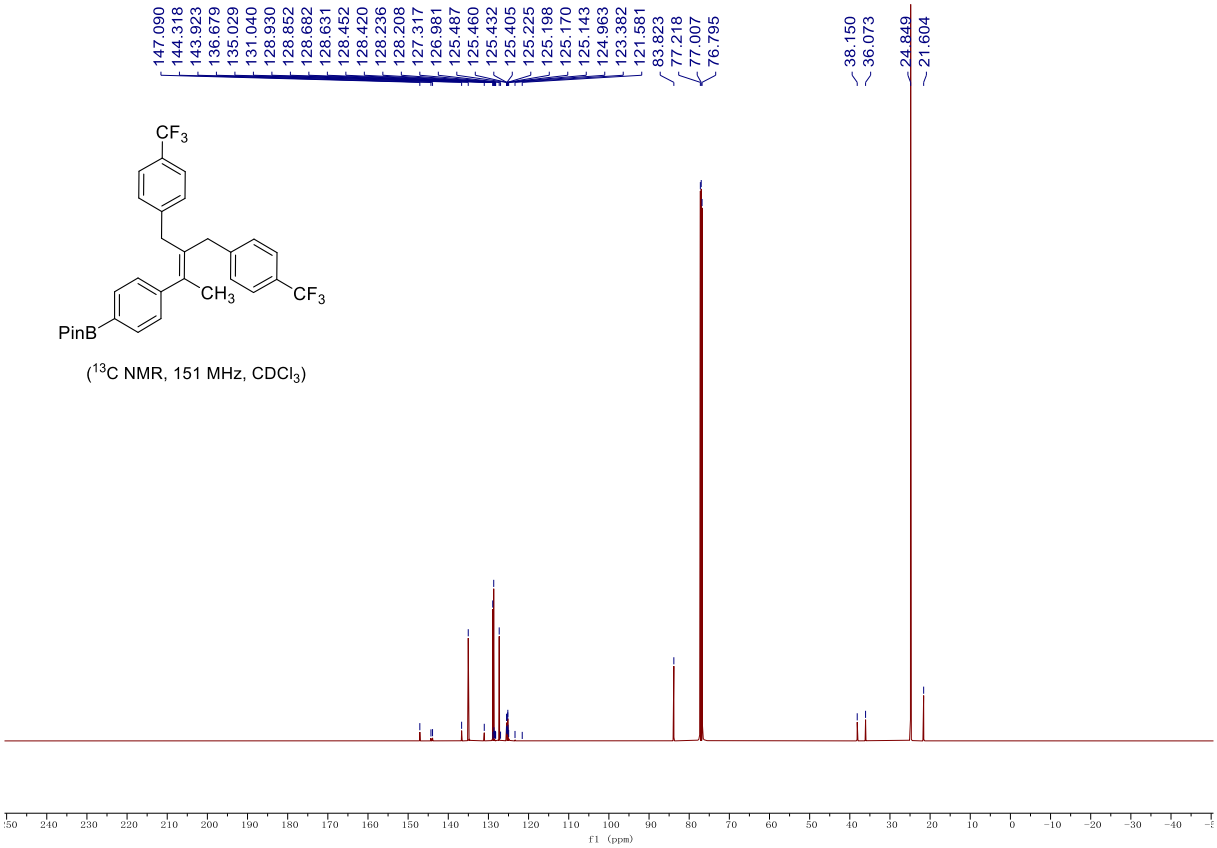
(^{13}C NMR, 151 MHz, $CDCl_3$)



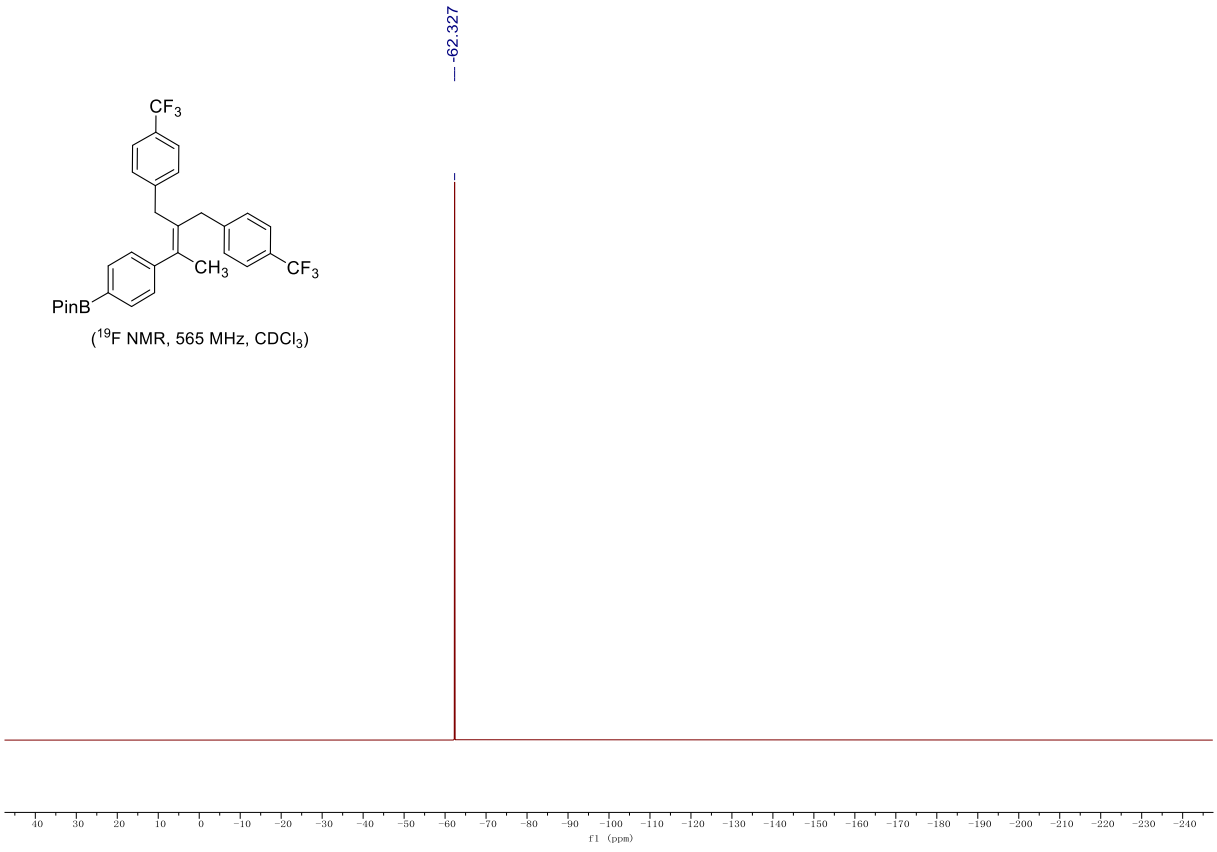
(^{19}F NMR, 565 MHz, $CDCl_3$)



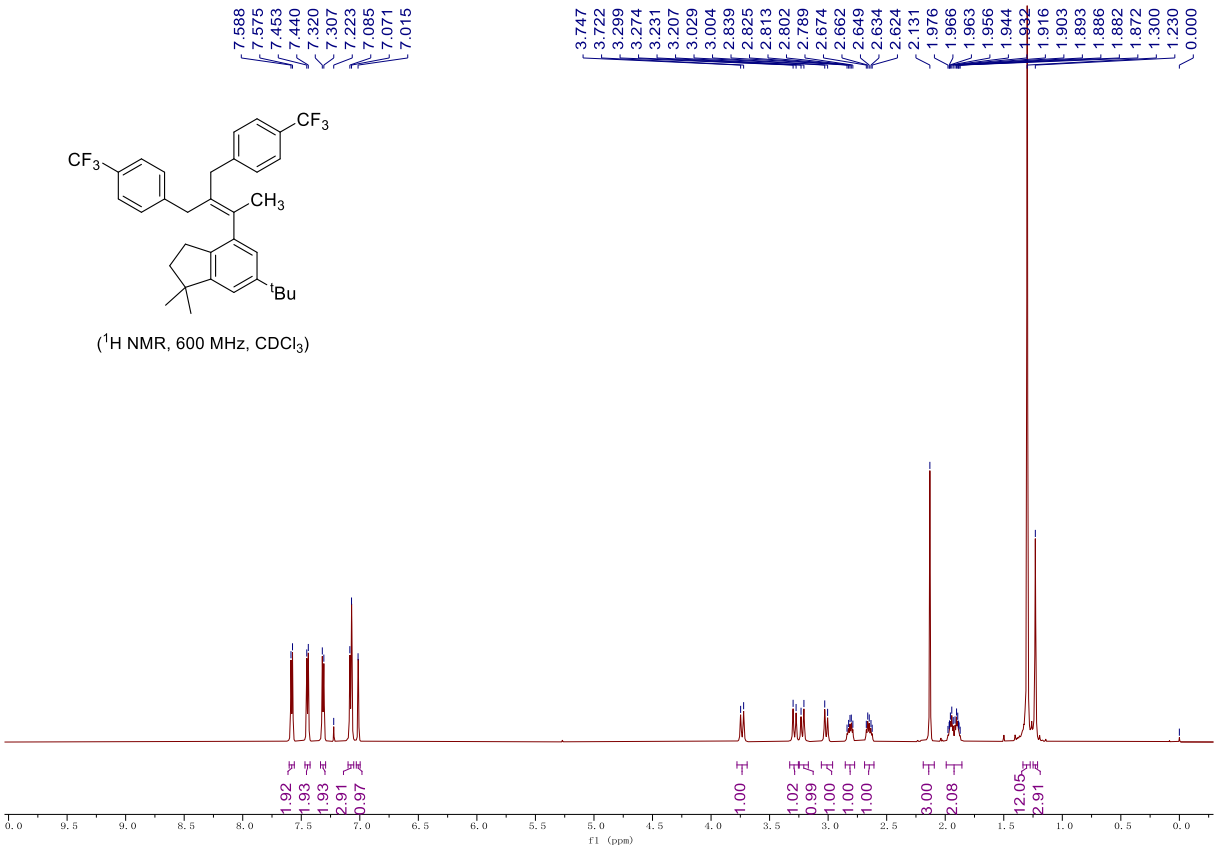
(^{1}H NMR, 400 MHz, $CDCl_3$)



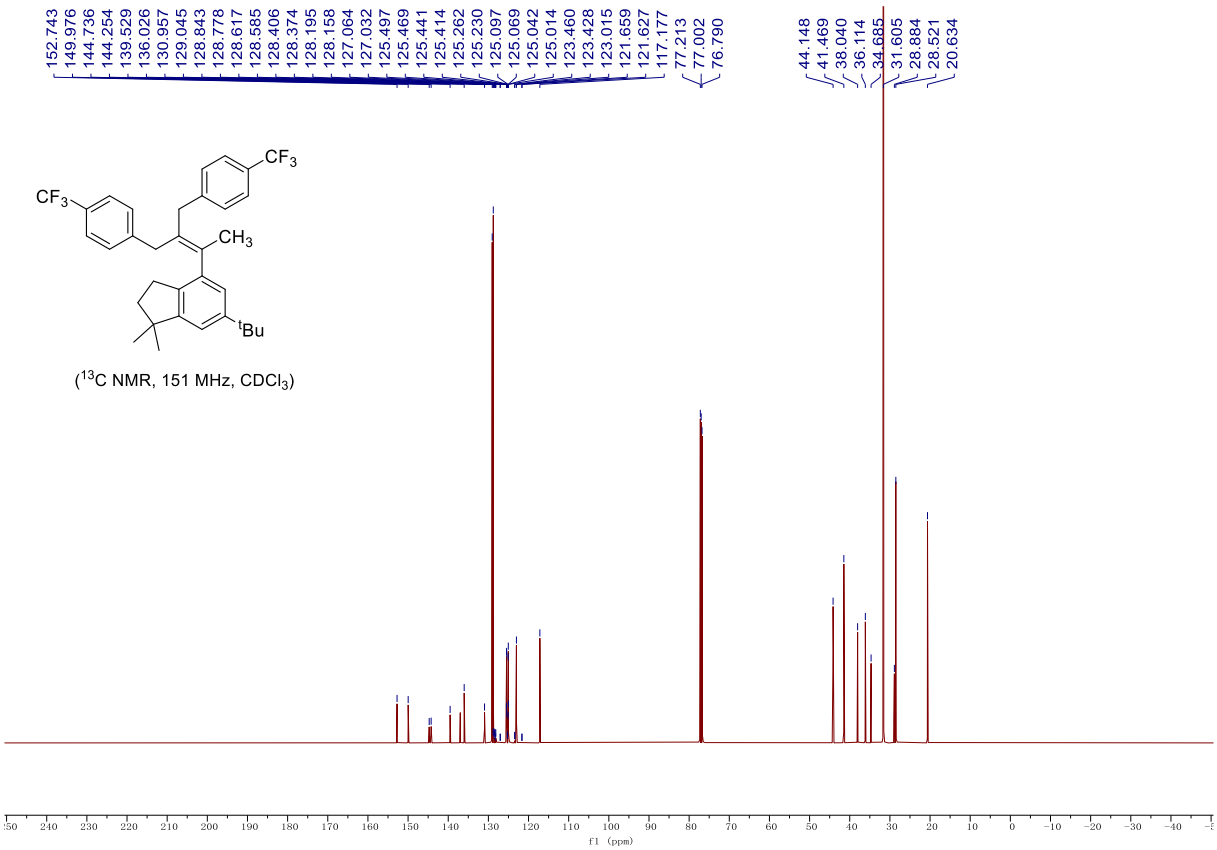
(^{13}C NMR, 151 MHz, $CDCl_3$)



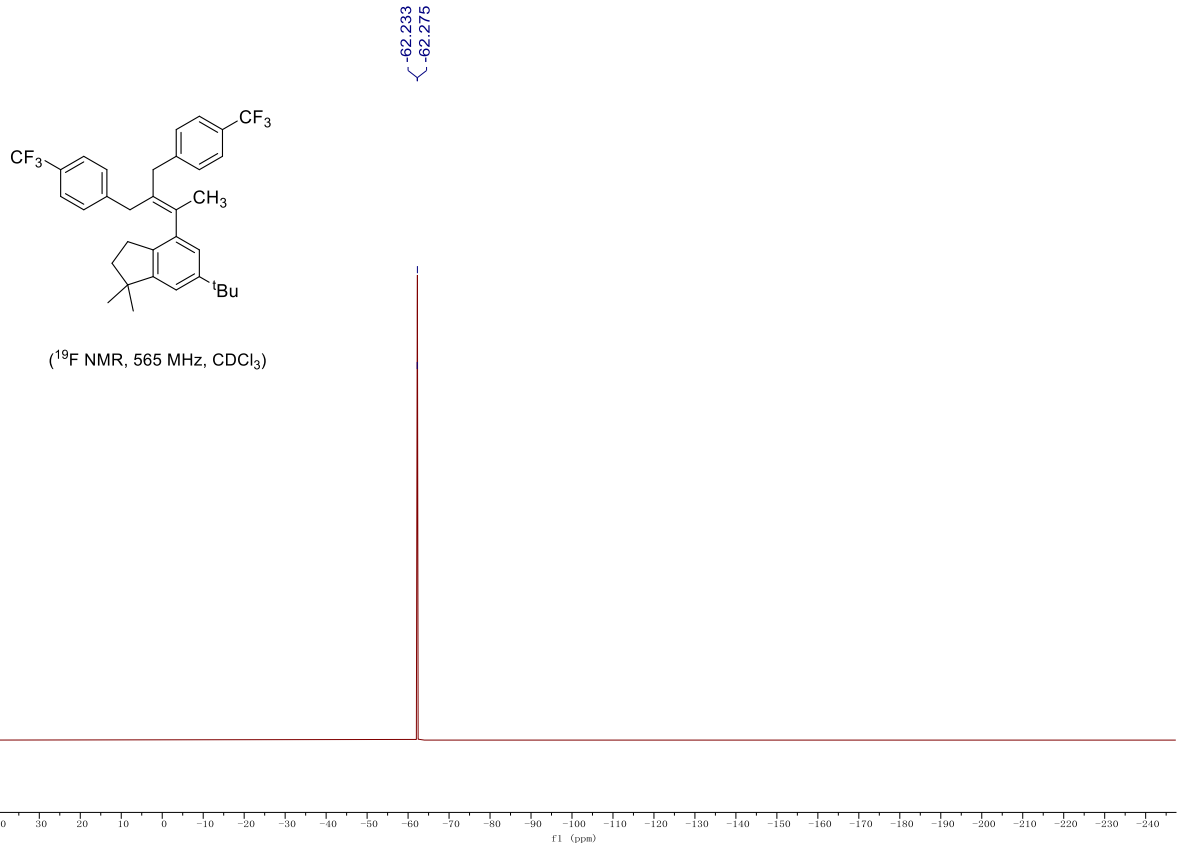
(^{19}F NMR, 565 MHz, $CDCl_3$)



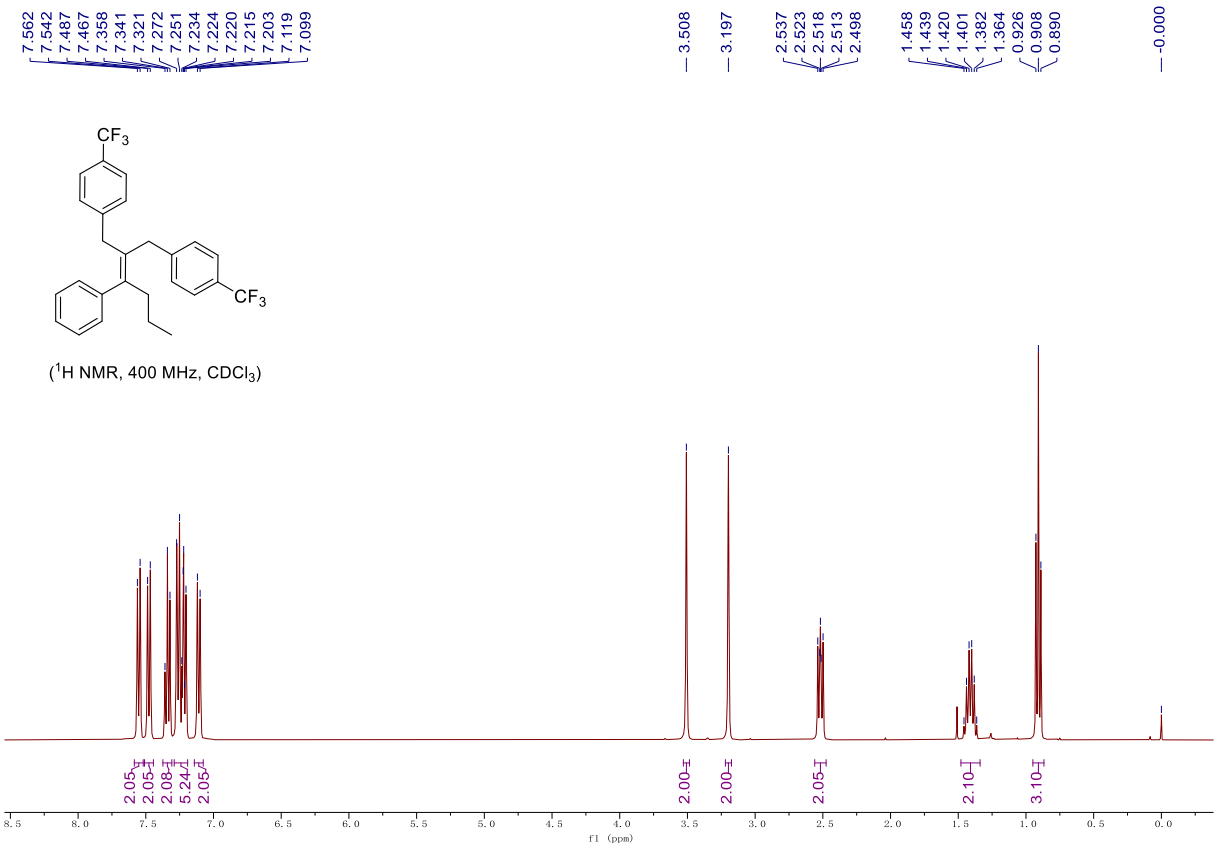
(^{1}H NMR, 600 MHz, $CDCl_3$)

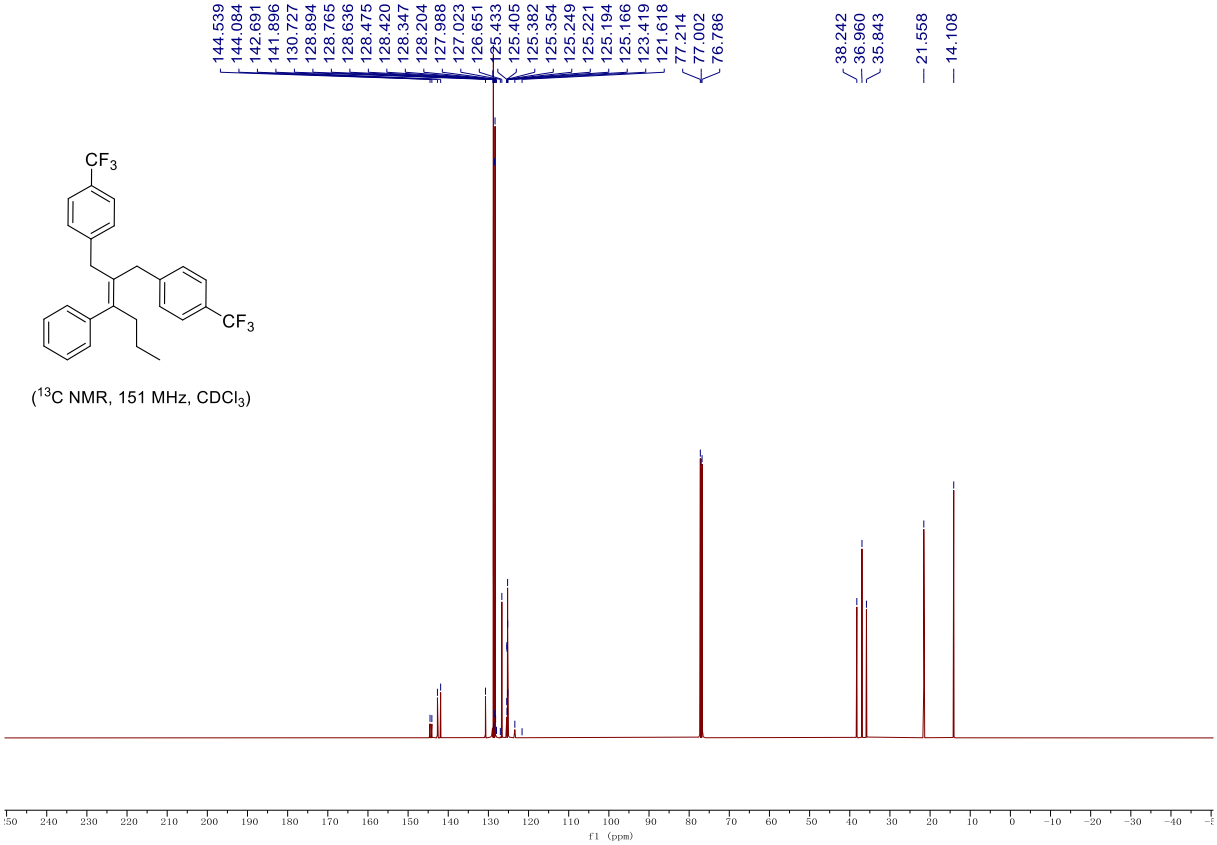


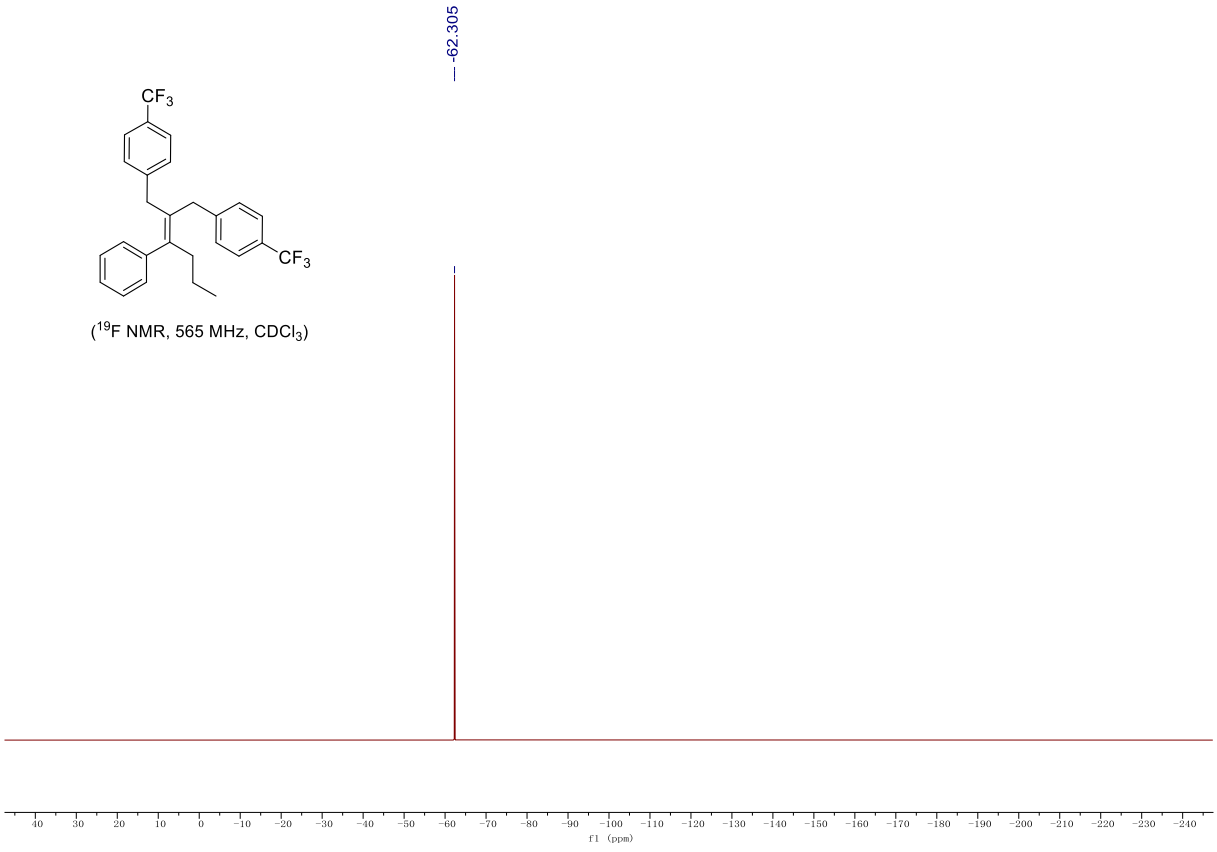
(^{13}C NMR, 151 MHz, $CDCl_3$)



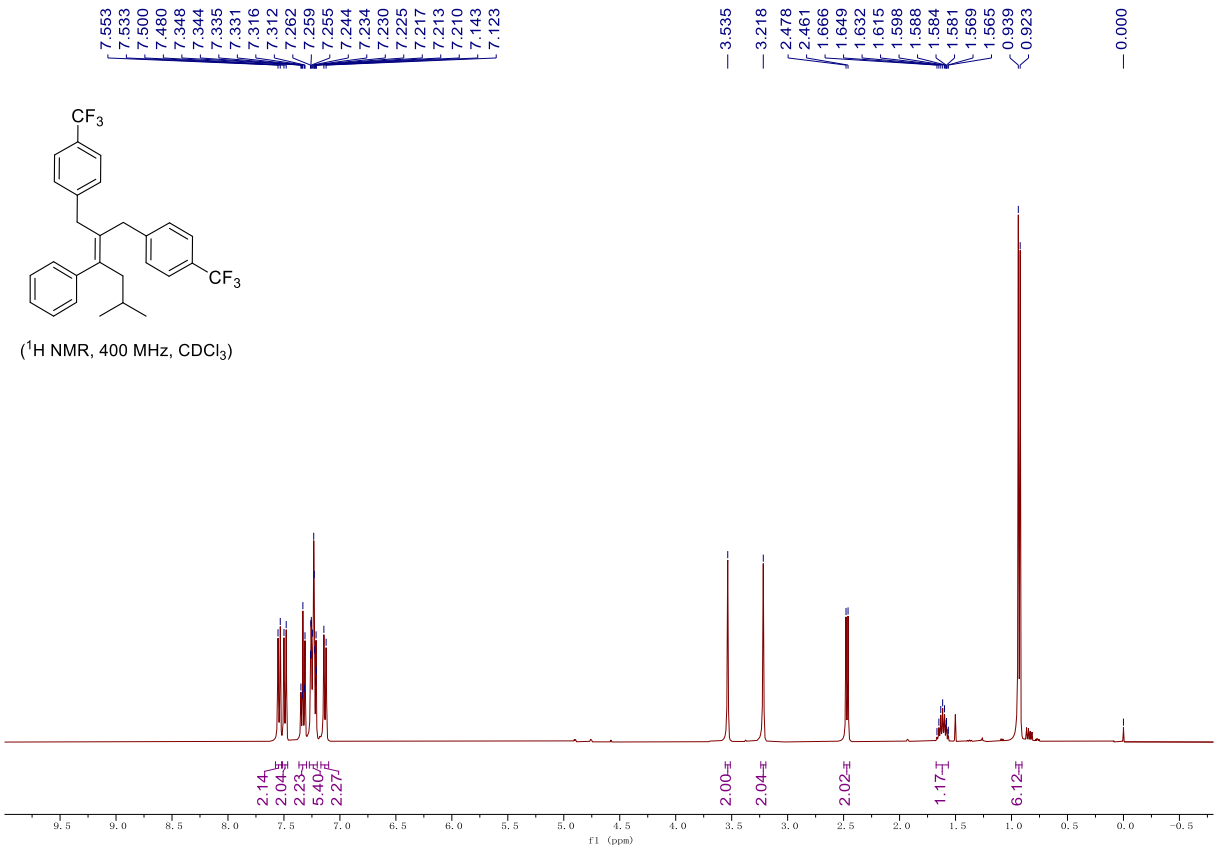
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.562
7.542
7.487
7.467
7.358
7.341
7.321
7.272
7.251
7.234
7.224
7.220
7.215
7.203
7.119
7.099
3.508
3.197
2.537
2.523
2.518
2.513
2.498
1.458
1.439
1.420
1.401
1.382
1.364
0.926
0.908
0.890
-0.000
CF3
CF3
(1H NMR, 400 MHz, CDCl3)
2.05
2.05
2.08
5.24
2.05
2.00
2.00
2.05
2.10
3.10
f1 (ppm)

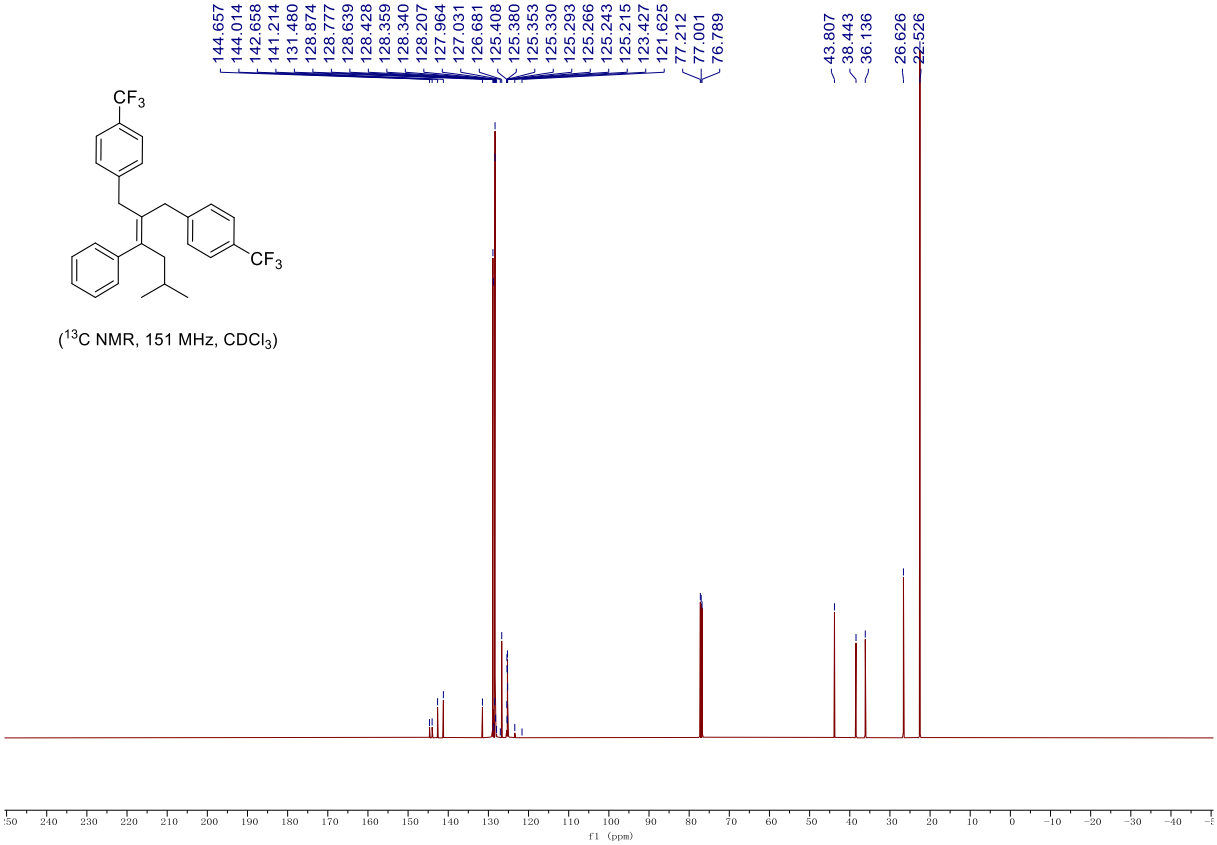

144.539
144.084
142.691
141.896
130.727
128.894
128.765
128.636
128.475
128.420
128.347
128.204
127.988
127.023
126.651
125.433
125.405
125.382
125.354
125.249
125.221
125.194
125.166
123.419
121.618
77.214
77.002
76.786
38.242
36.960
35.843
21.558
14.108
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



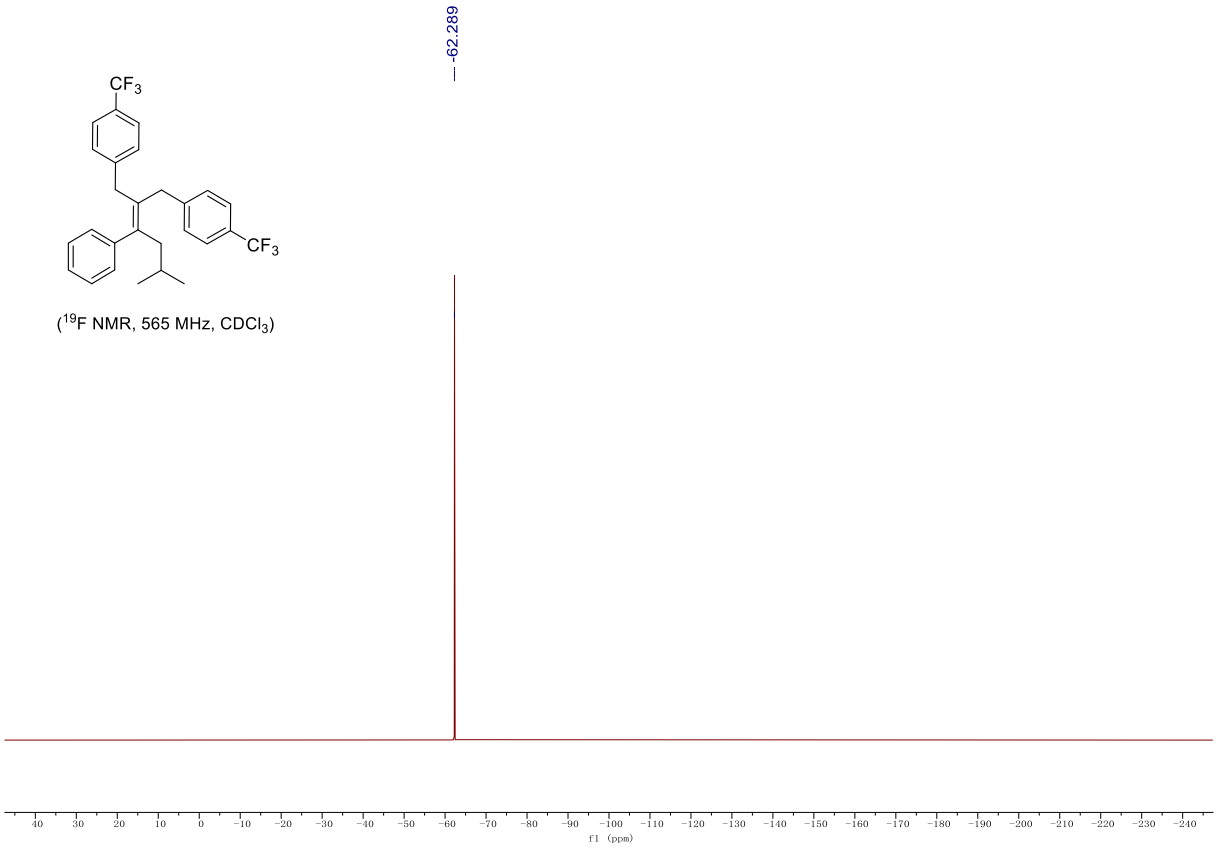
(^{19}F NMR, 565 MHz, $CDCl_3$)



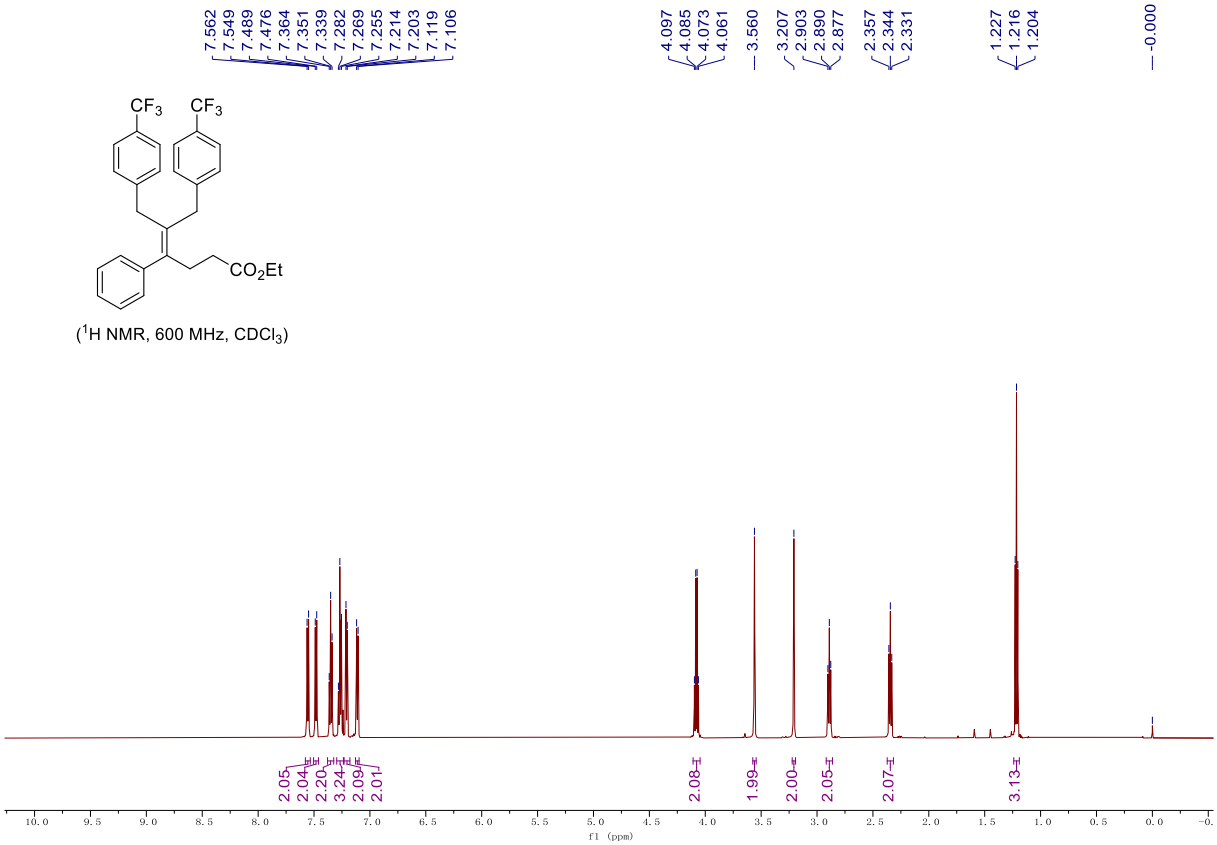
(^{1}H NMR, 400 MHz, $CDCl_3$)



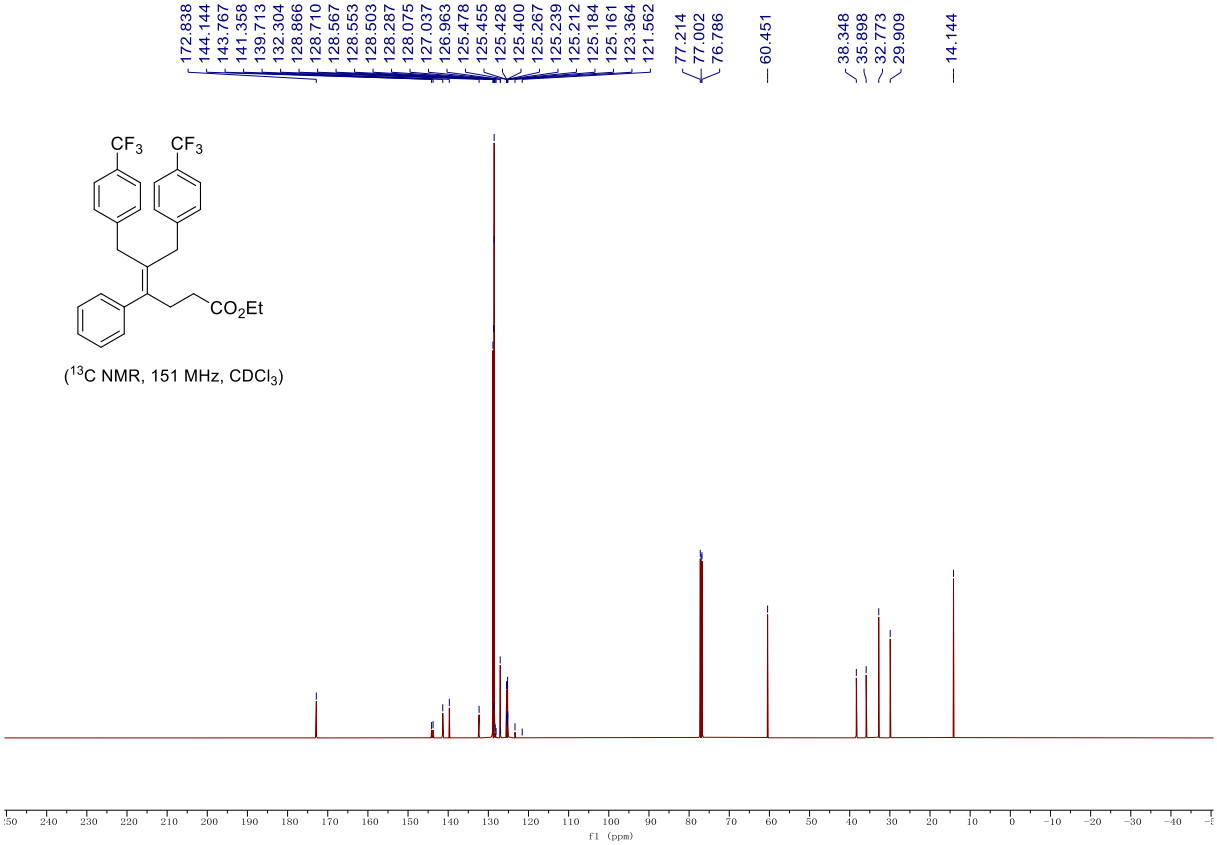
(^{13}C NMR, 151 MHz, $CDCl_3$)



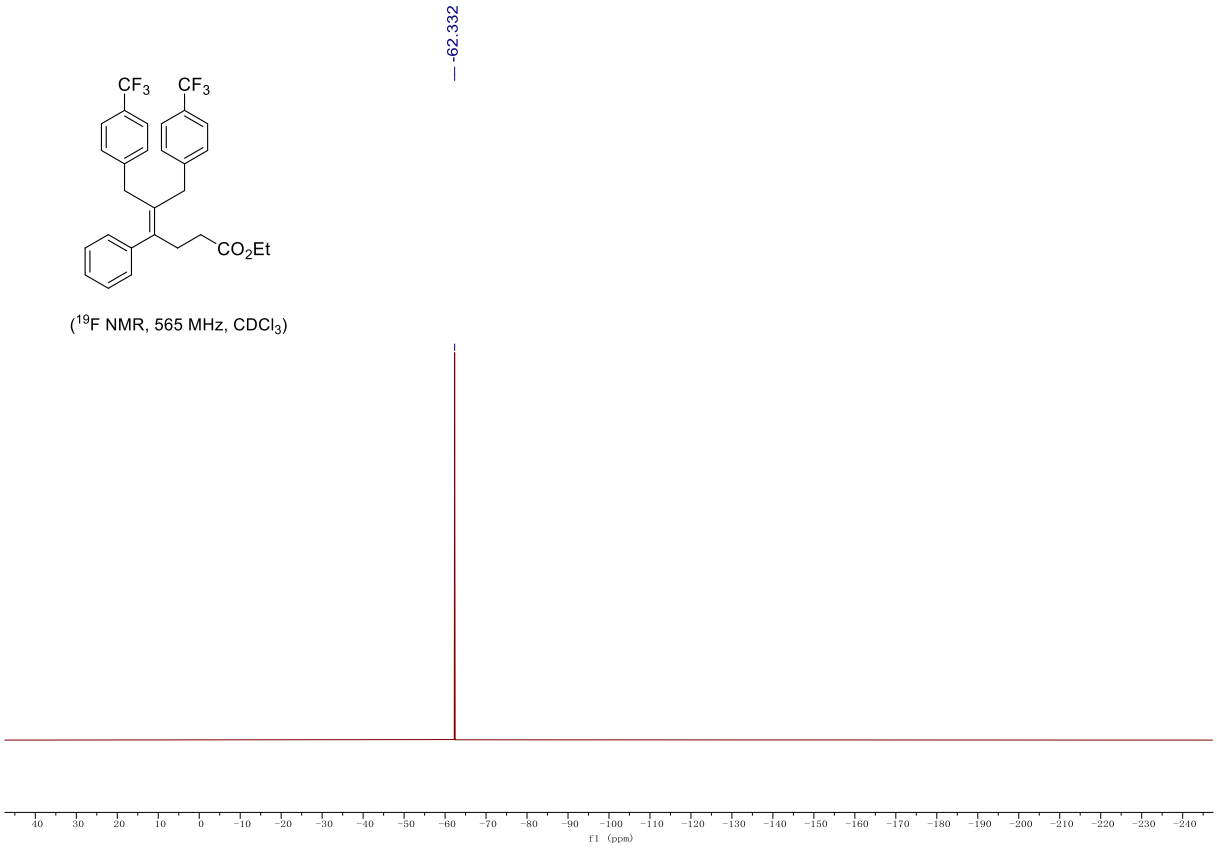
(^{19}F NMR, 565 MHz, $CDCl_3$)



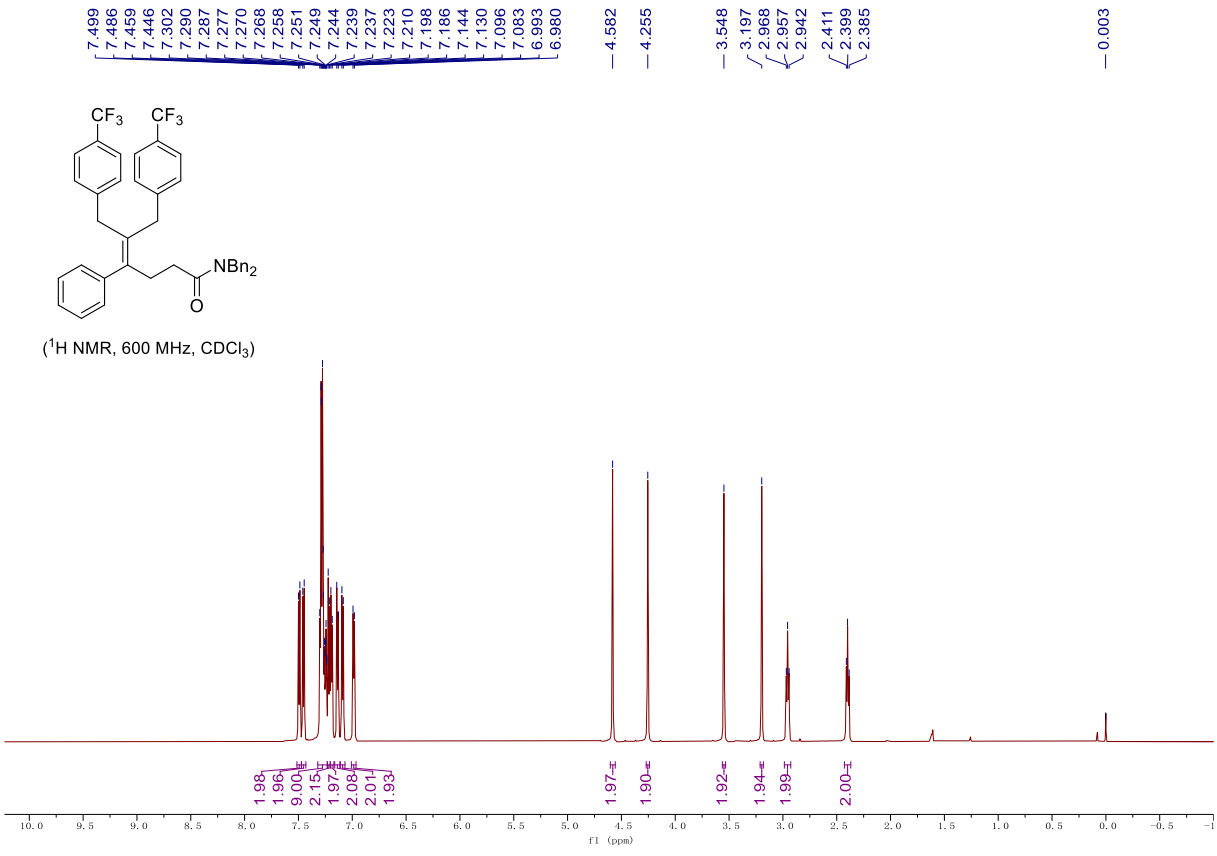
(^{1}H NMR, 600 MHz, $CDCl_3$)



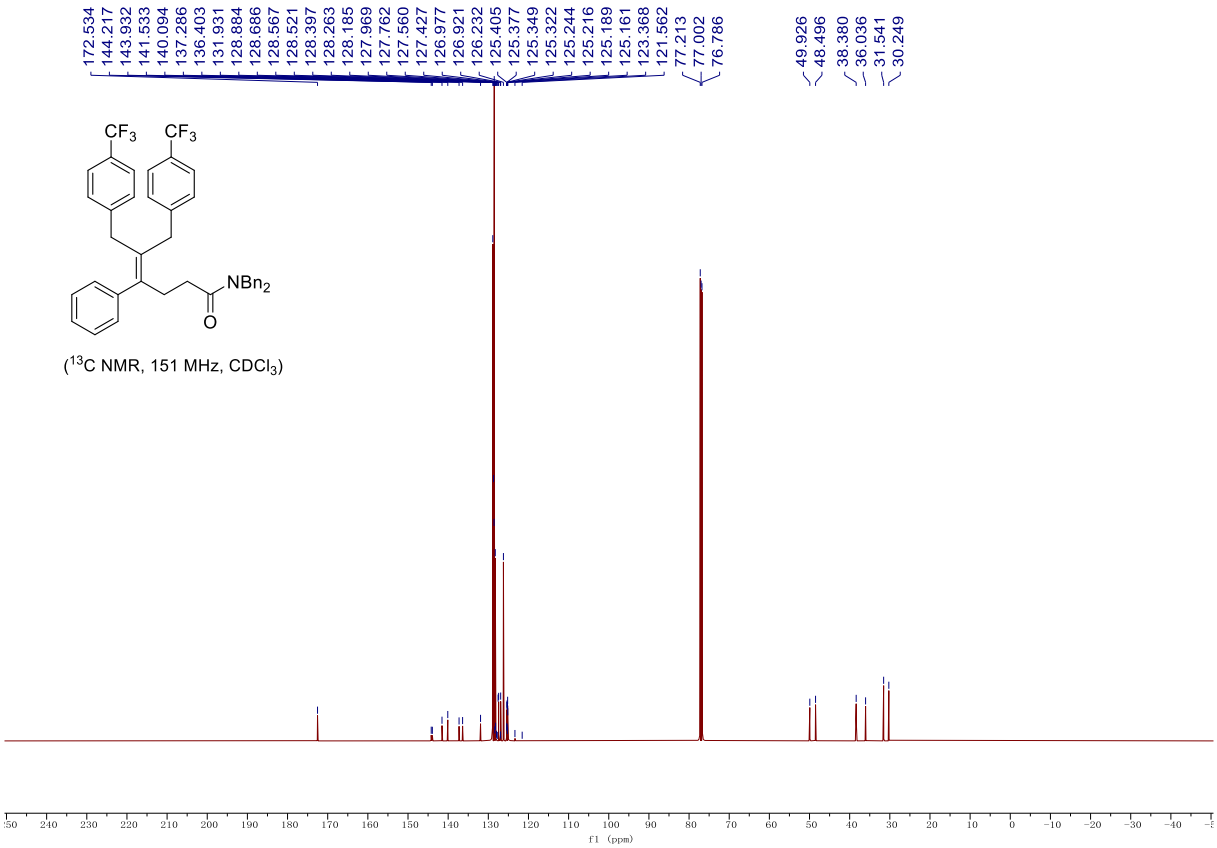
(^{13}C NMR, 151 MHz, $CDCl_3$)



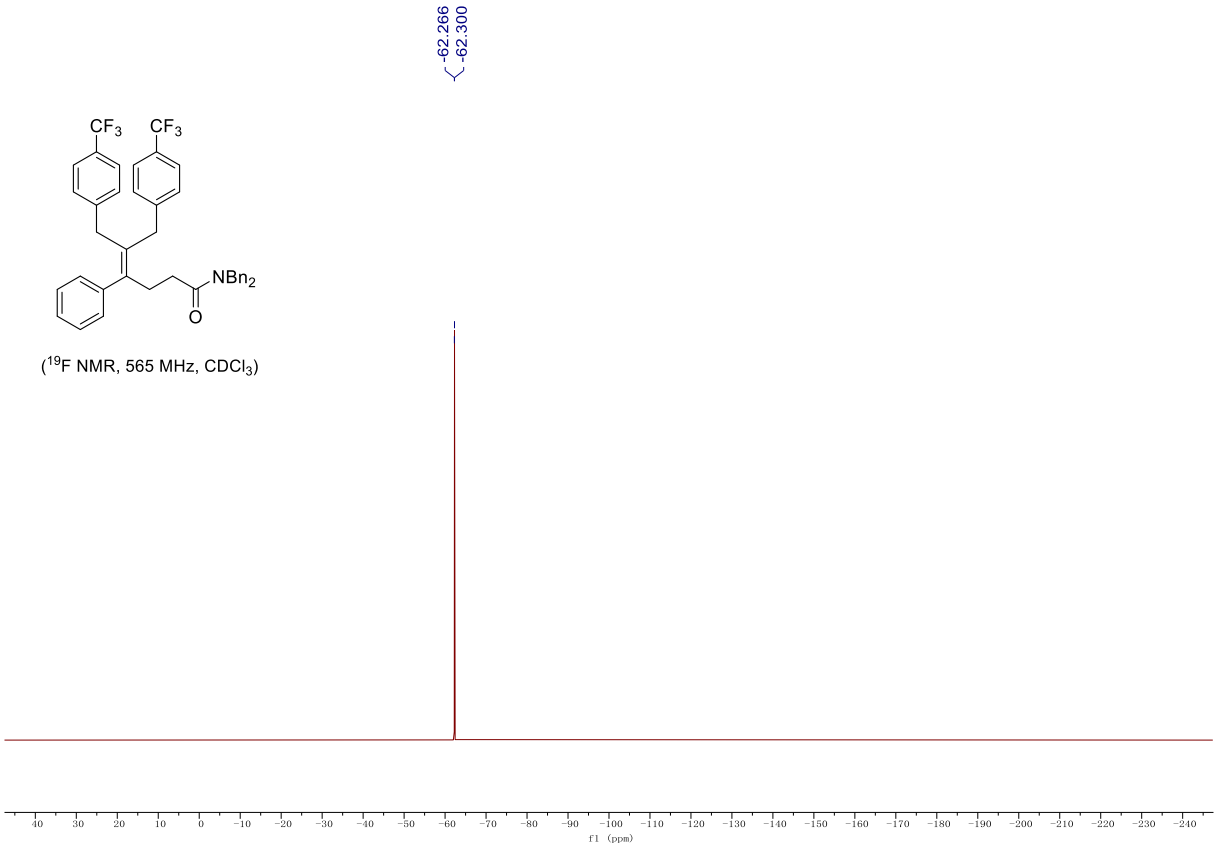
(^{19}F NMR, 565 MHz, $CDCl_3$)



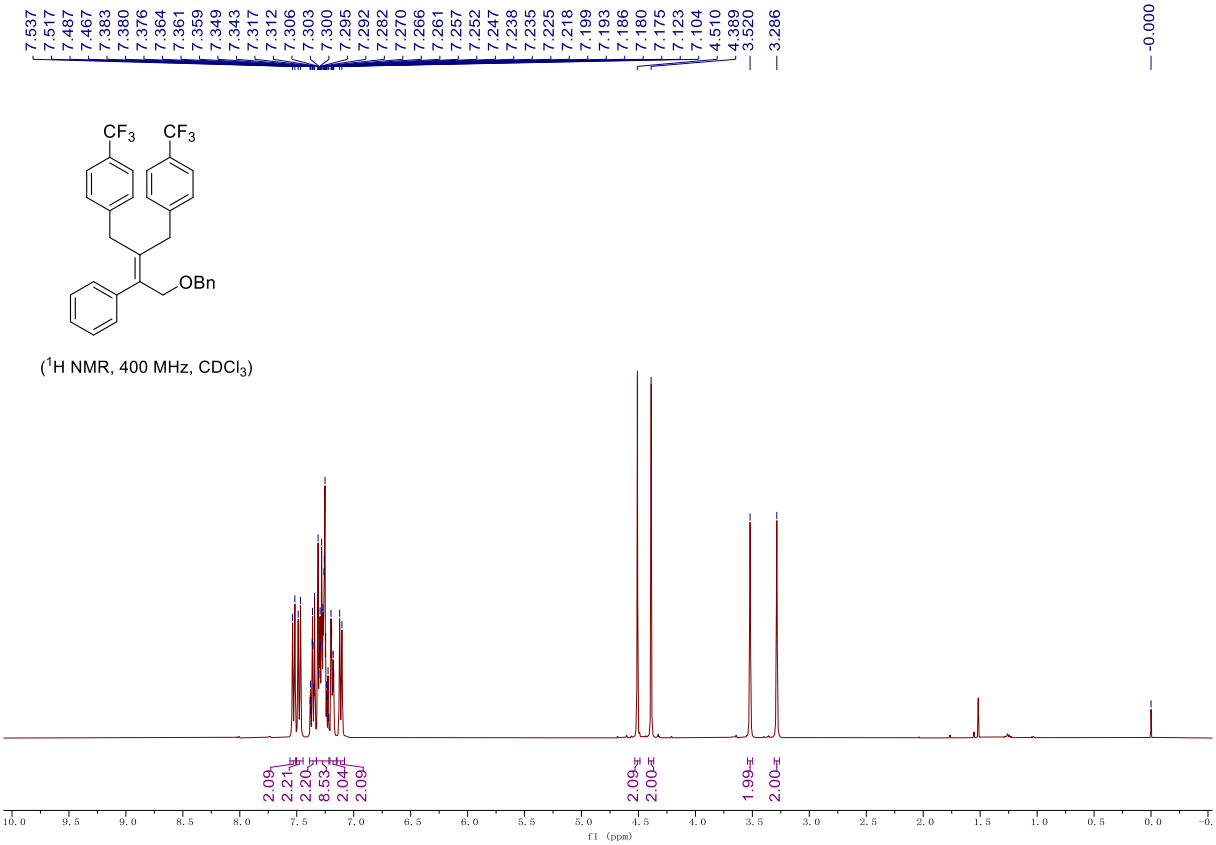
(^{1}H NMR, 600 MHz, $CDCl_3$)

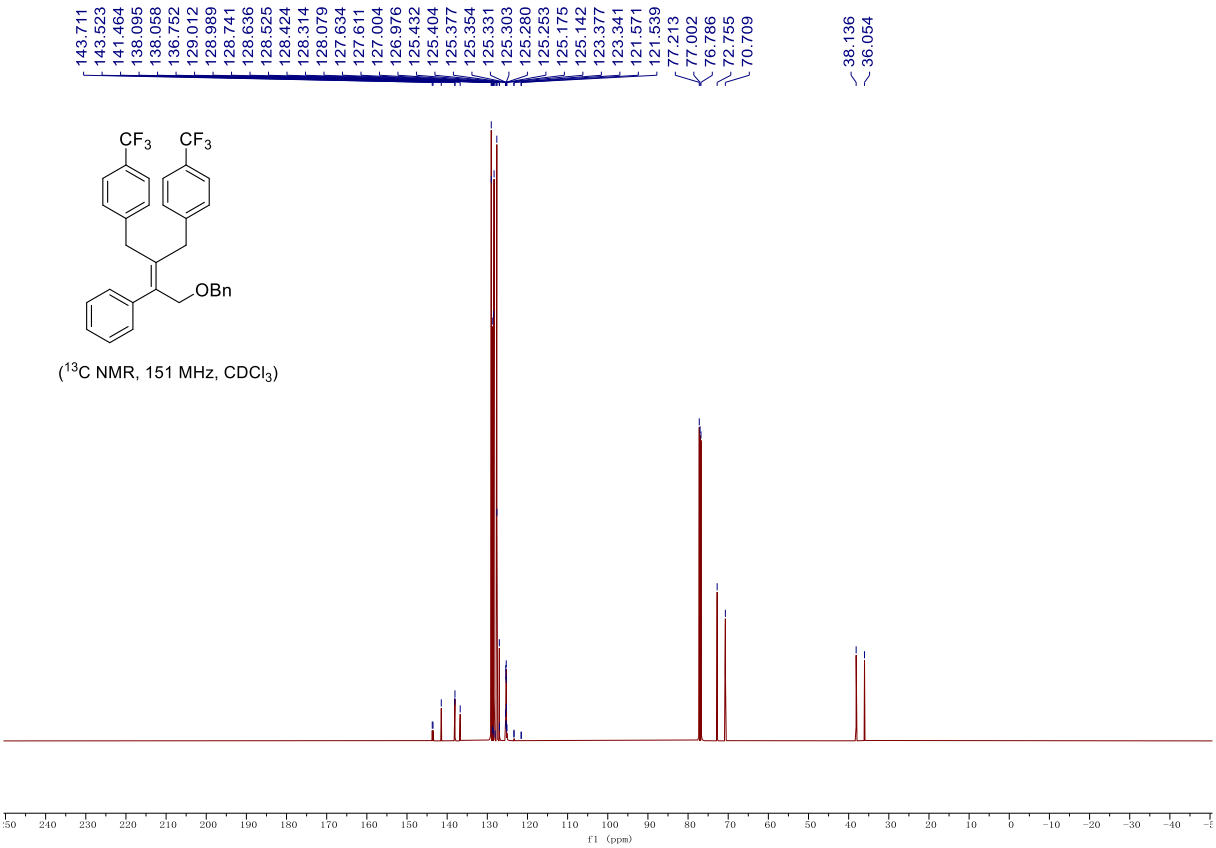


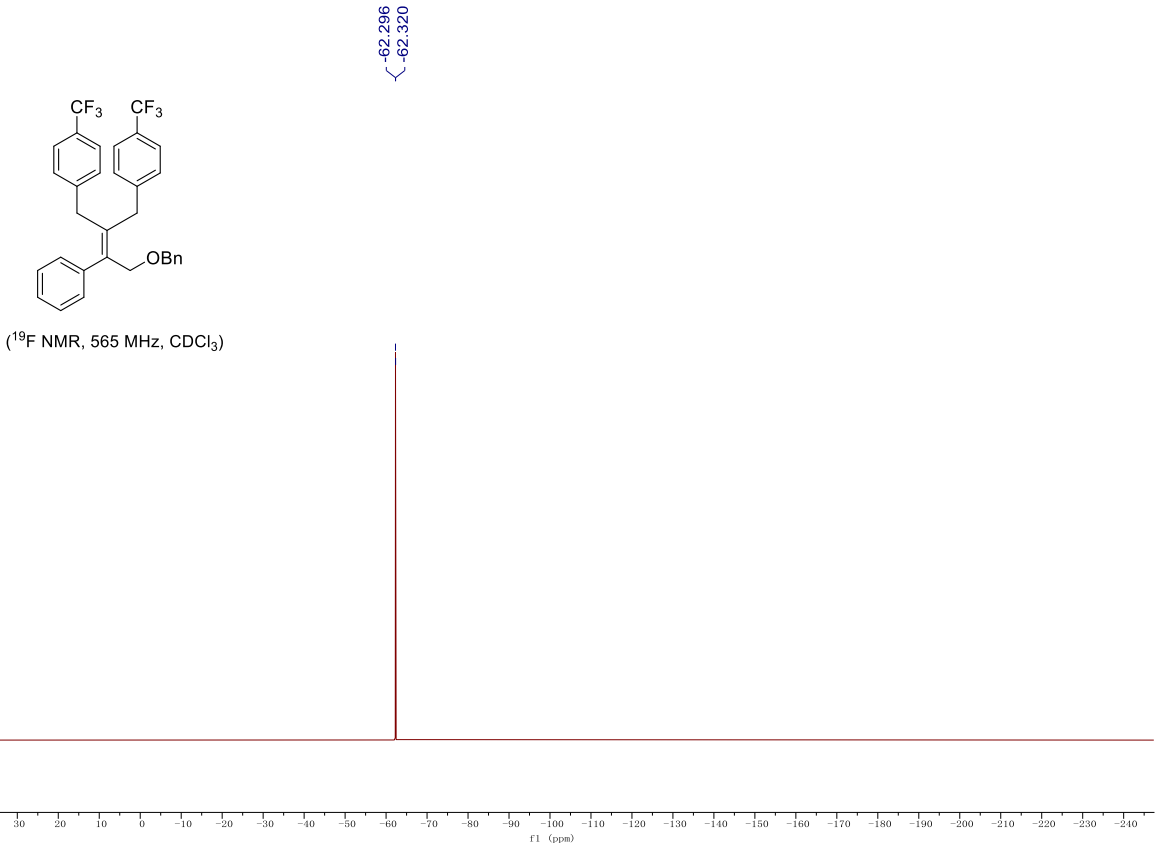
(^{13}C NMR, 151 MHz, $CDCl_3$)



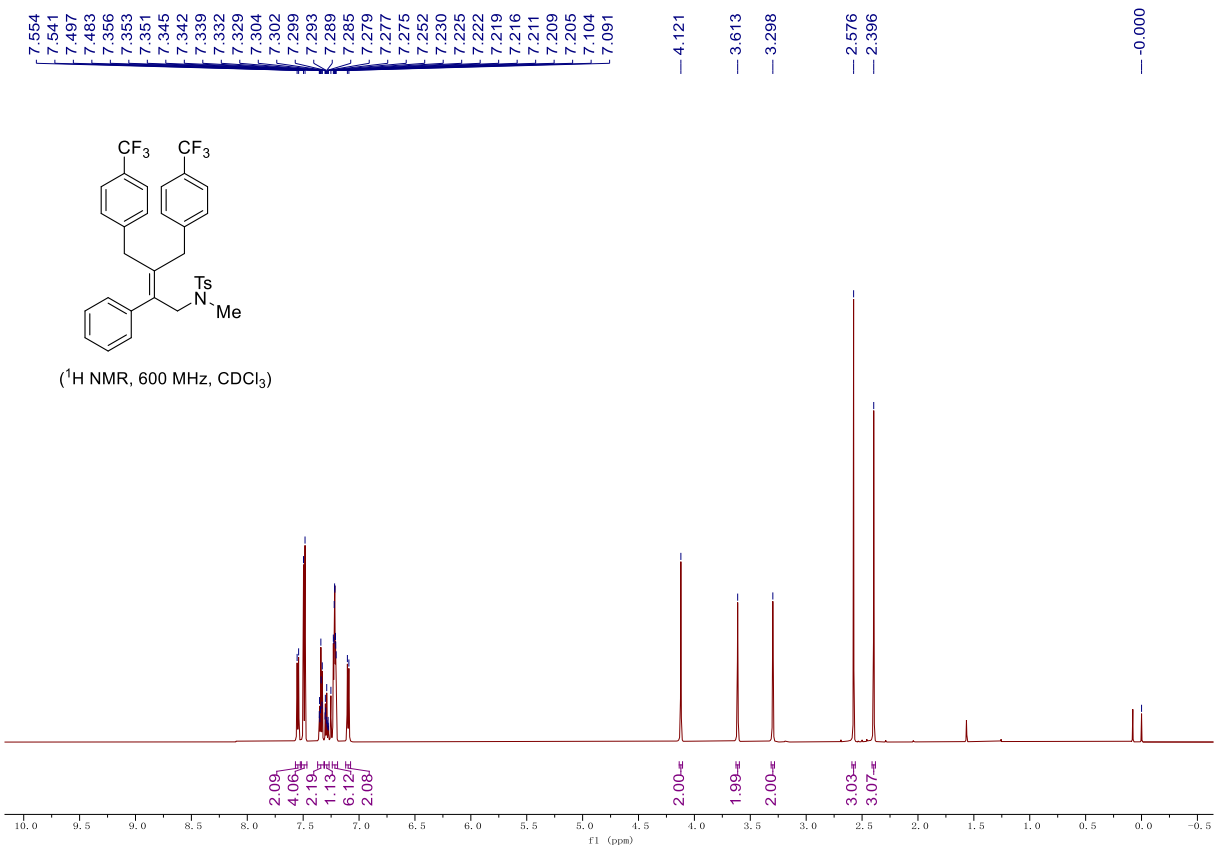
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.537
7.517
7.487
7.467
7.383
7.380
7.376
7.364
7.361
7.359
7.349
7.343
7.317
7.312
7.306
7.303
7.300
7.295
7.292
7.282
7.270
7.266
7.261
7.257
7.252
7.247
7.238
7.235
7.225
7.218
7.199
7.193
7.186
7.180
7.175
7.123
7.104
4.510
4.389
3.520
3.286
-0.000
CF3
CF3
OBn
(1H NMR, 400 MHz, CDCl3)
2.09
2.21
2.20
8.53
2.04
2.09
2.09
2.00
1.99
2.00
f1 (ppm)

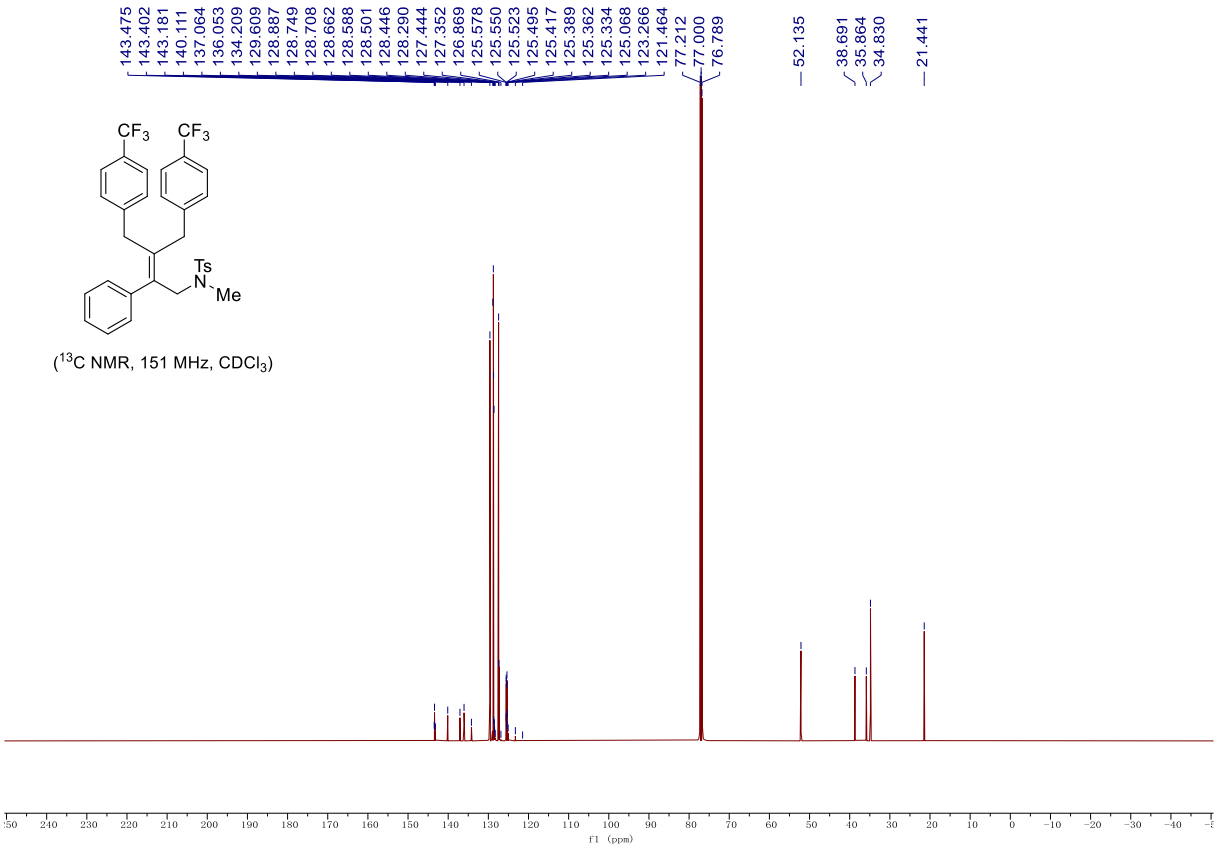

143.711
143.523
141.464
138.095
138.058
136.752
129.012
128.989
128.741
128.636
128.525
128.424
128.314
128.079
127.634
127.611
127.004
126.976
125.432
125.404
125.377
125.354
125.331
125.303
125.280
125.253
125.175
125.142
123.377
123.341
121.571
121.539
77.213
77.002
76.786
72.755
70.709
38.136
36.054
CF3
CF3
OBn
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



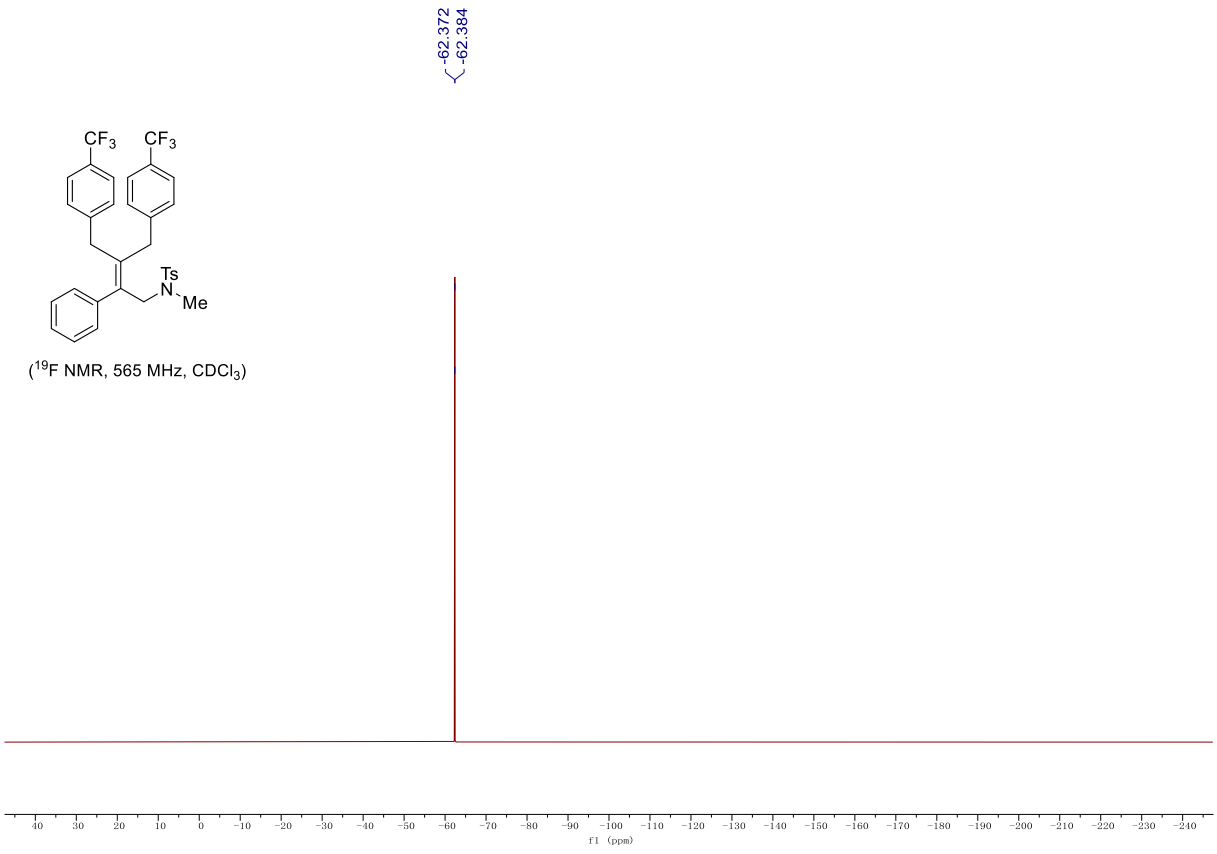
(^{19}F NMR, 565 MHz, $CDCl_3$)

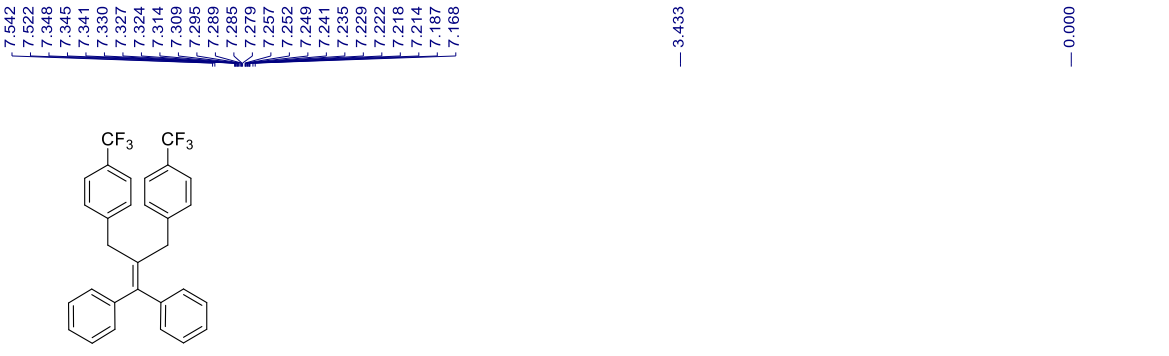


(^{1}H NMR, 600 MHz, $CDCl_3$)

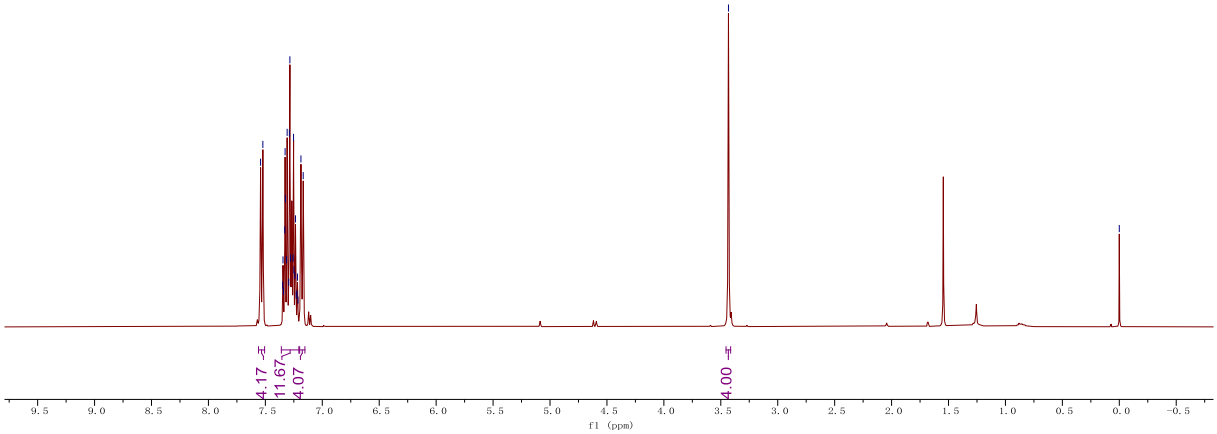


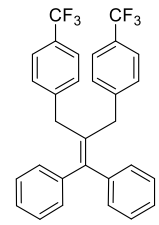
(^{13}C NMR, 151 MHz, $CDCl_3$)


-62.372
-62.384
CF3
CF3
Ts
N
Me
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

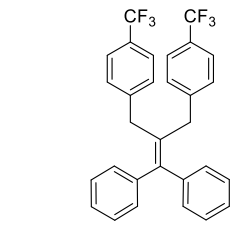


(^{1}H NMR, 400 MHz, $CDCl_3$)

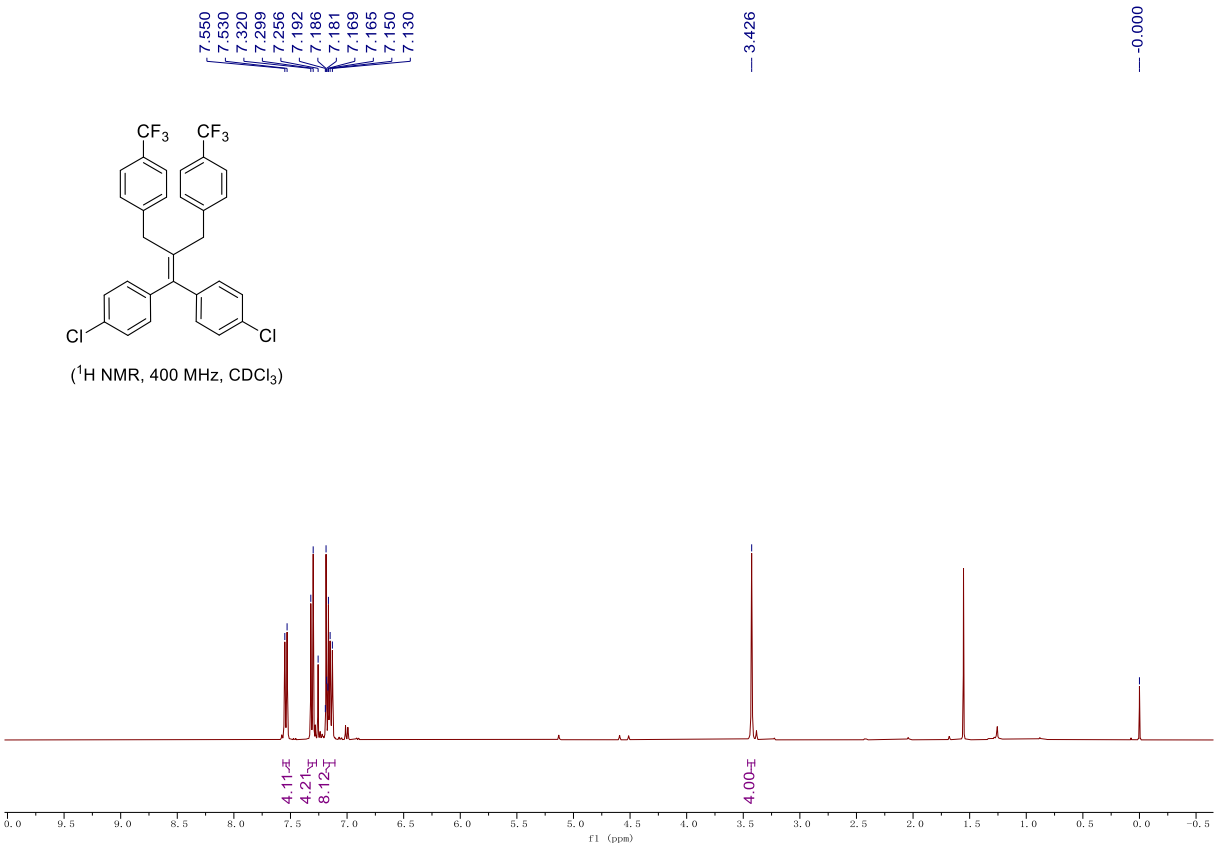




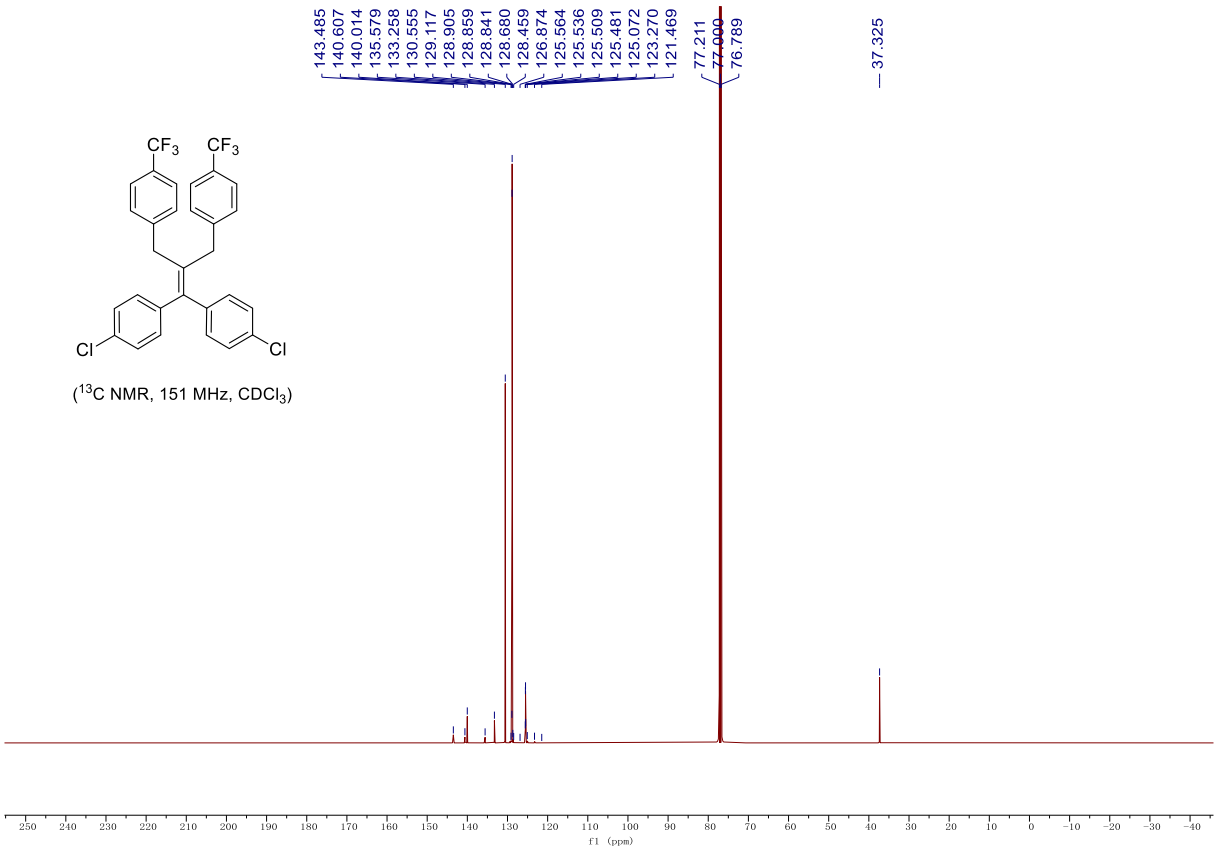
(^{13}C NMR, 151 MHz, $CDCl_3$)



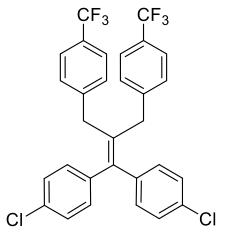
(^{19}F NMR, 565 MHz, $CDCl_3$)



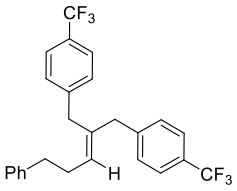
(^{1}H NMR, 400 MHz, $CDCl_3$)



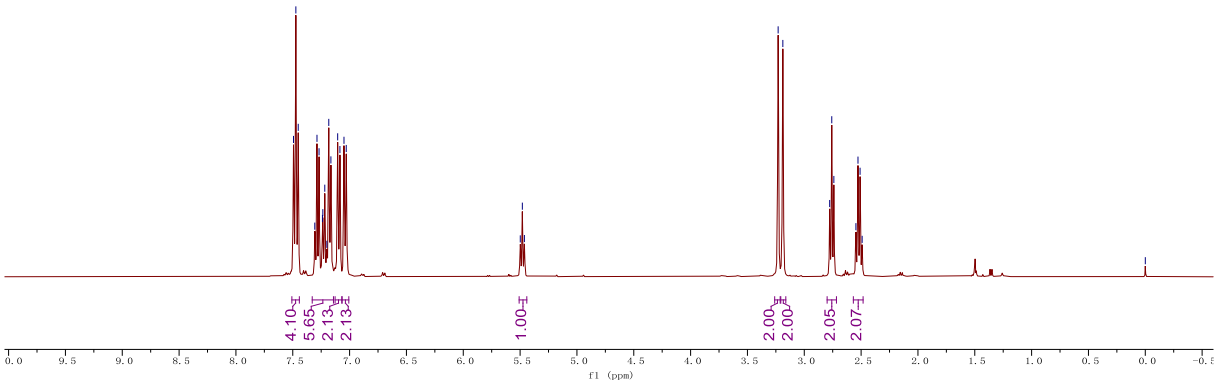
(^{13}C NMR, 151 MHz, $CDCl_3$)

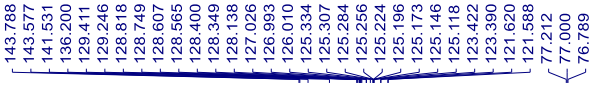


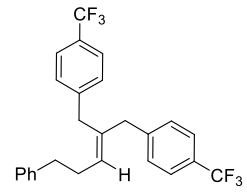
(^{19}F NMR, 565 MHz, $CDCl_3$)



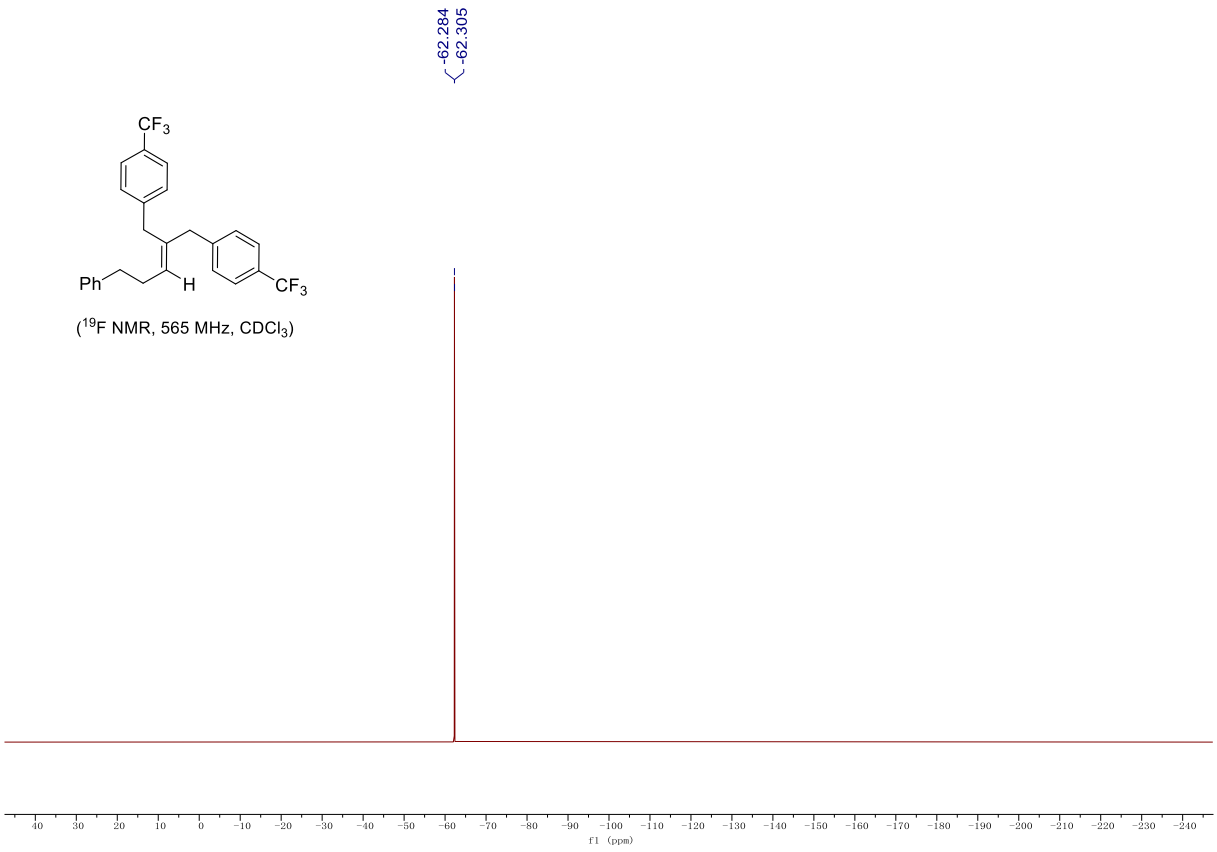
(^{1}H NMR, 400 MHz, $CDCl_3$)





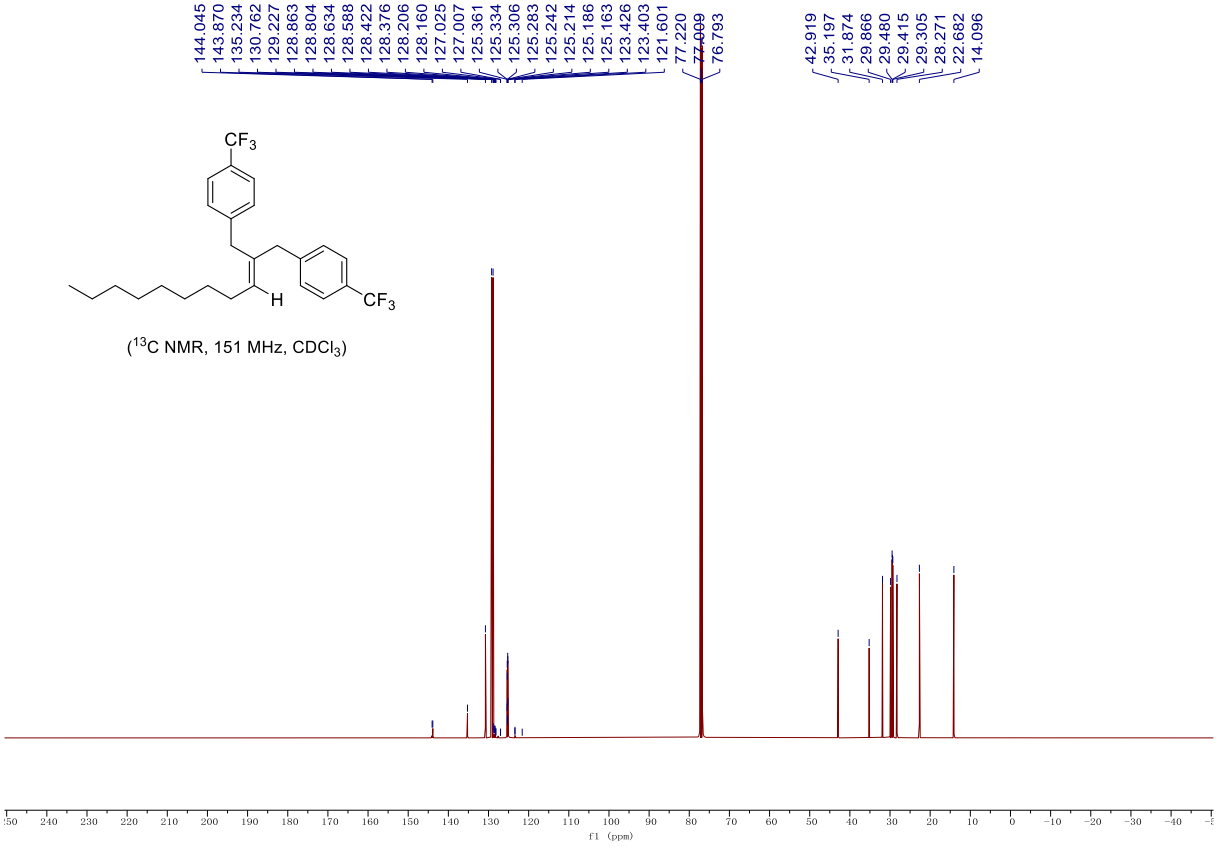


(^{13}C NMR, 151 MHz, $CDCl_3$)

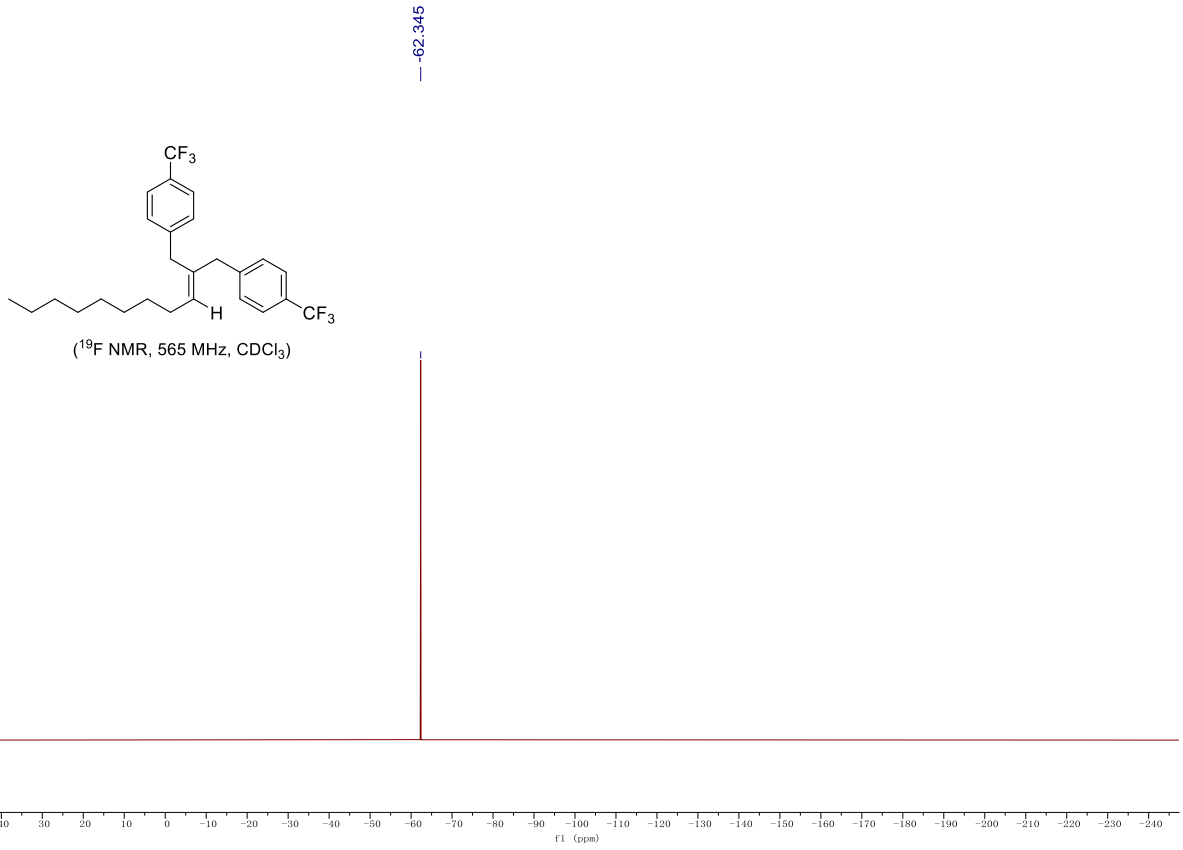


(^{19}F NMR, 565 MHz, $CDCl_3$)

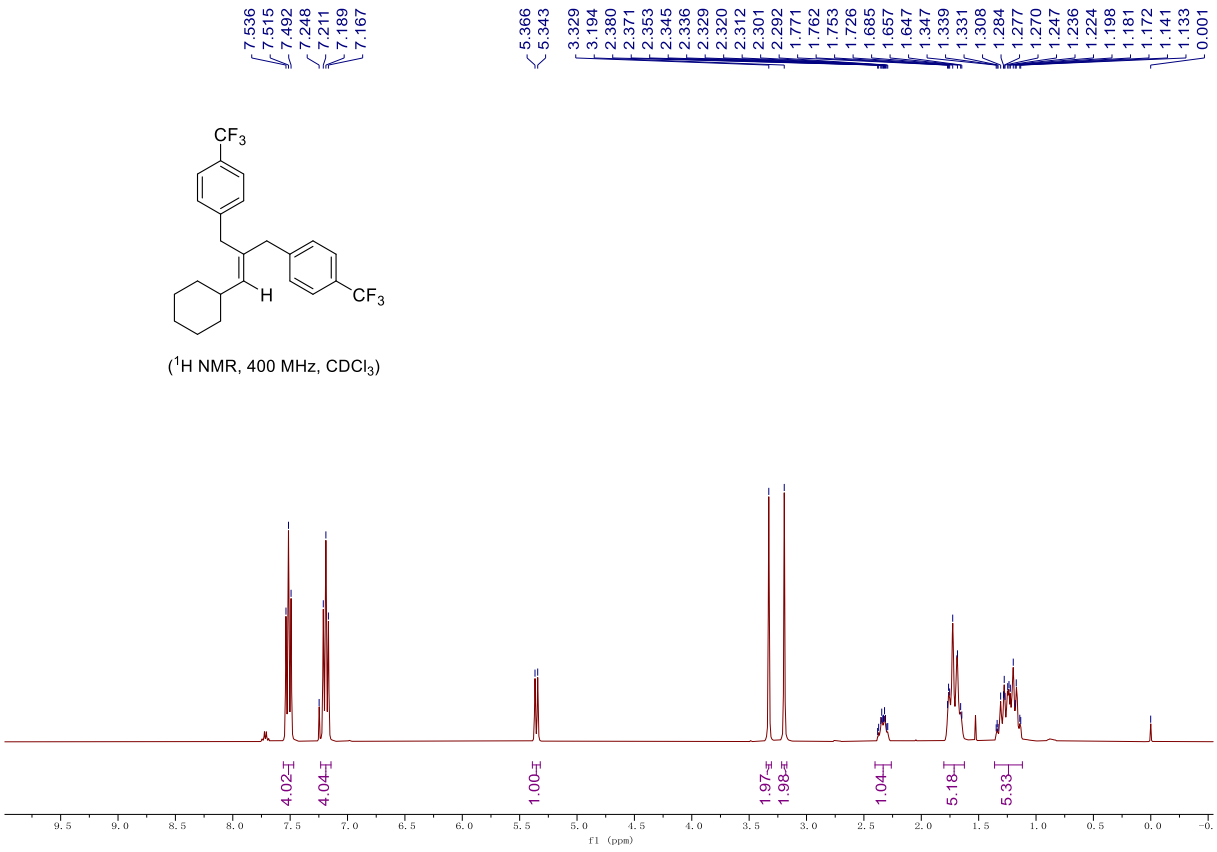
(^{1}H NMR, 400 MHz, $CDCl_3$)

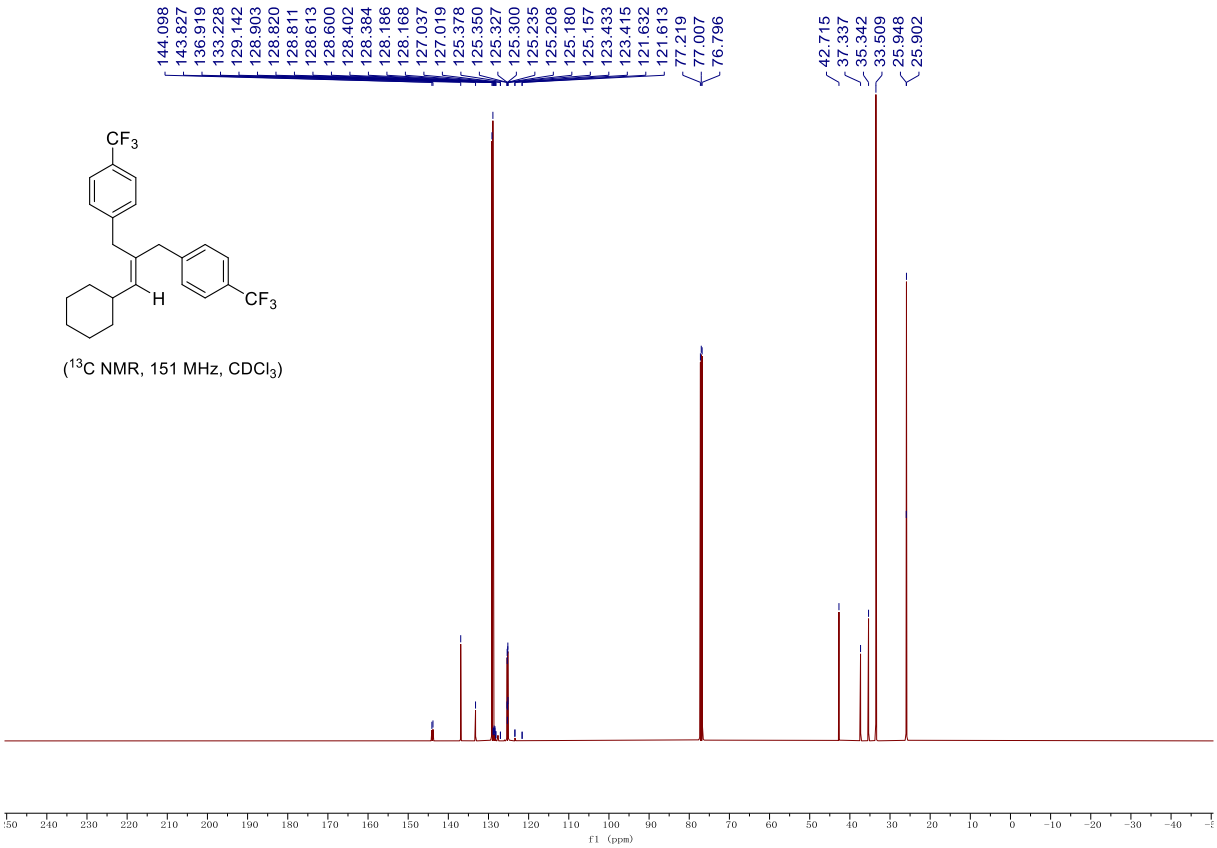


(^{13}C NMR, 151 MHz, $CDCl_3$)



(^{19}F NMR, 565 MHz, $CDCl_3$)


7.536
7.515
7.492
7.248
7.211
7.189
7.167
5.366
5.343
3.329
3.194
2.380
2.371
2.353
2.345
2.336
2.329
2.320
2.312
2.301
2.292
1.771
1.762
1.753
1.726
1.685
1.657
1.647
1.347
1.339
1.331
1.308
1.284
1.277
1.270
1.247
1.236
1.224
1.198
1.181
1.172
1.141
1.133
0.001
CF3
H
CF3
(1H NMR, 400 MHz, CDCl3)
4.02
4.04
1.00
1.97
1.98
1.04
5.18
5.33
f1 (ppm)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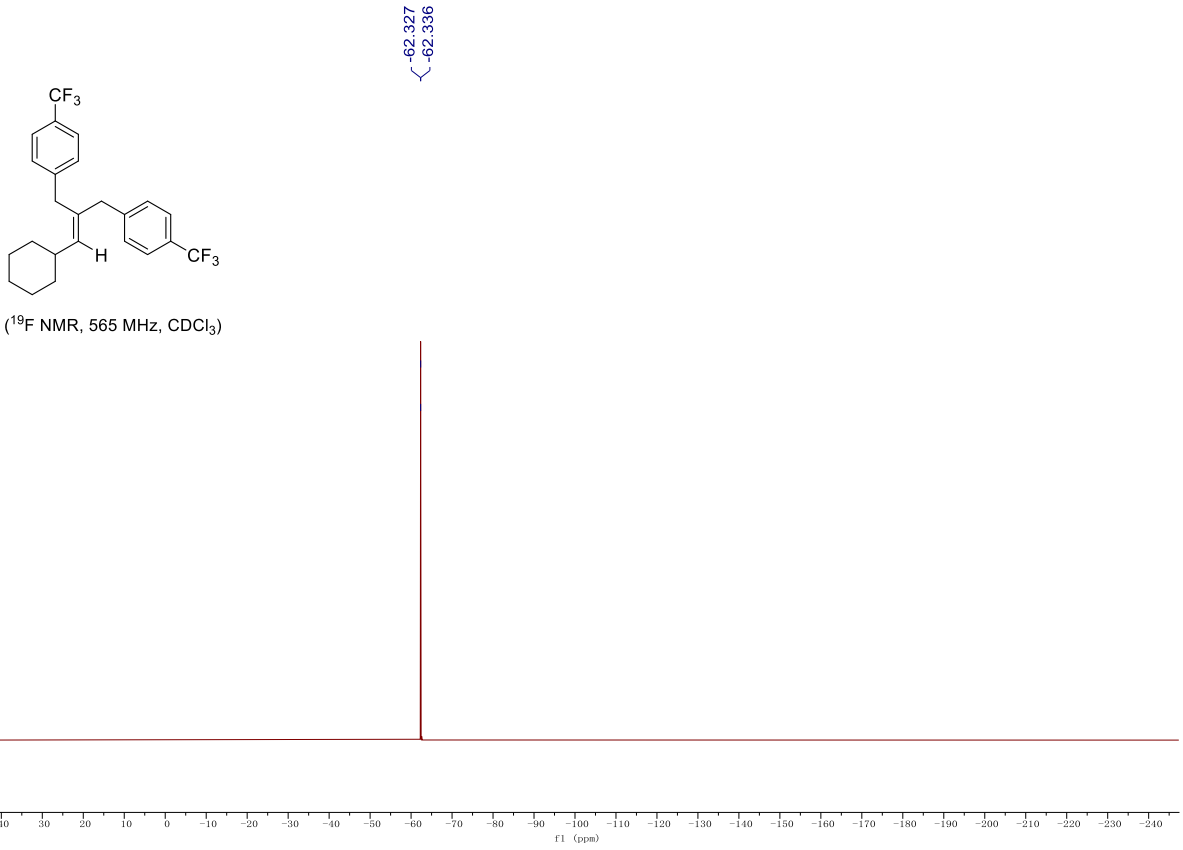
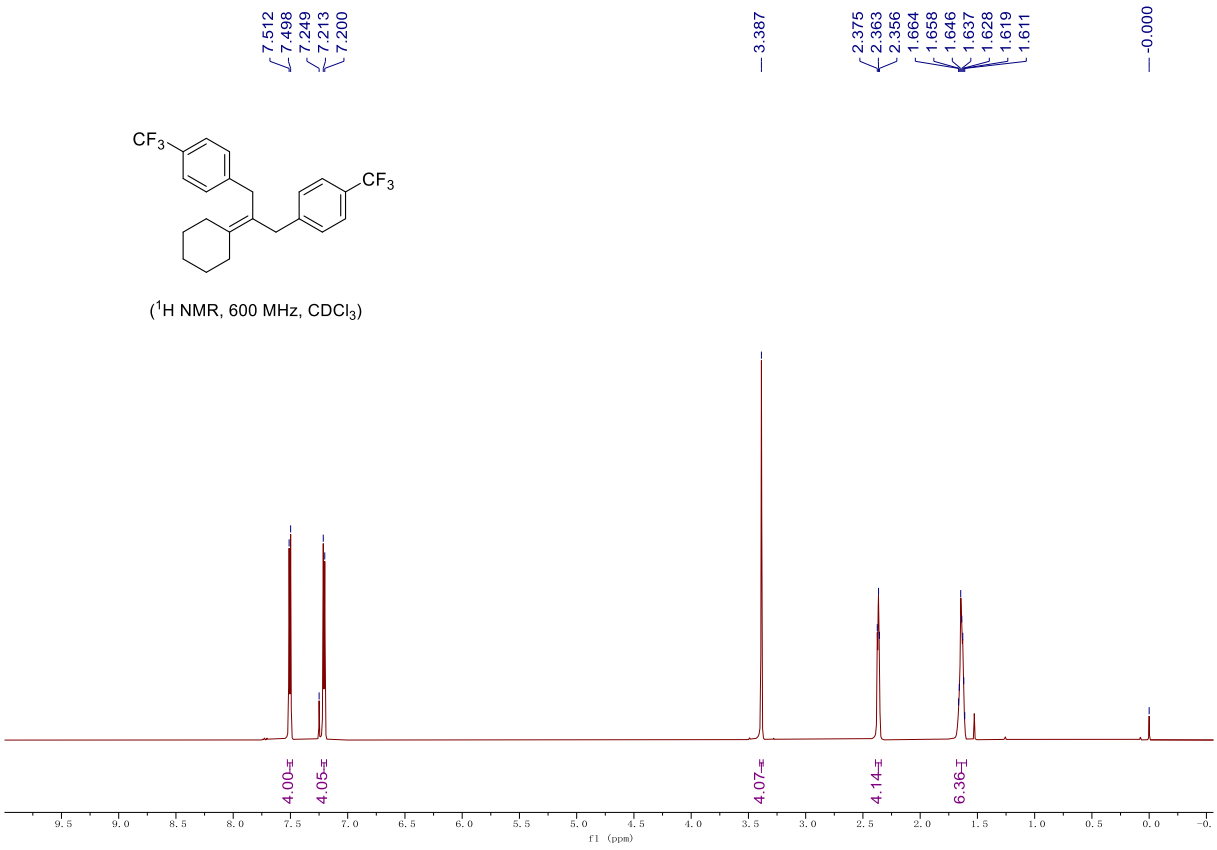
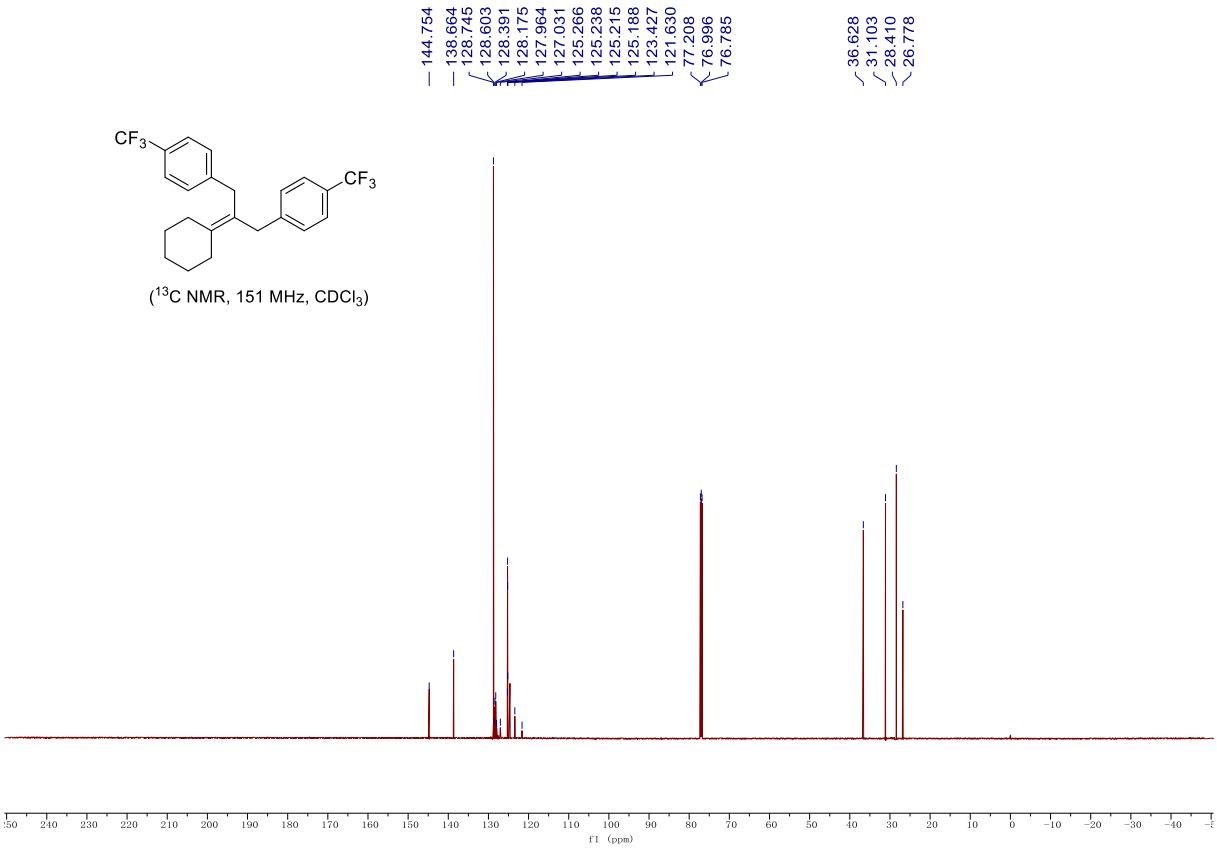
143.827
136.919
133.228
129.142
128.903
128.820
128.811
128.613
128.600
128.402
128.384
128.186
128.168
127.037
127.019
125.378
125.350
125.327
125.300
125.235
125.208
125.180
125.157
123.433
123.415
121.632
121.613
77.219
77.007
76.796
42.715
37.337
35.342
33.509
25.948
25.902
CF3
H
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



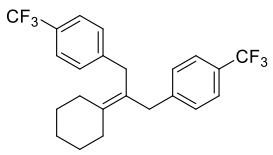
(^{19}F NMR, 565 MHz, $CDCl_3$)



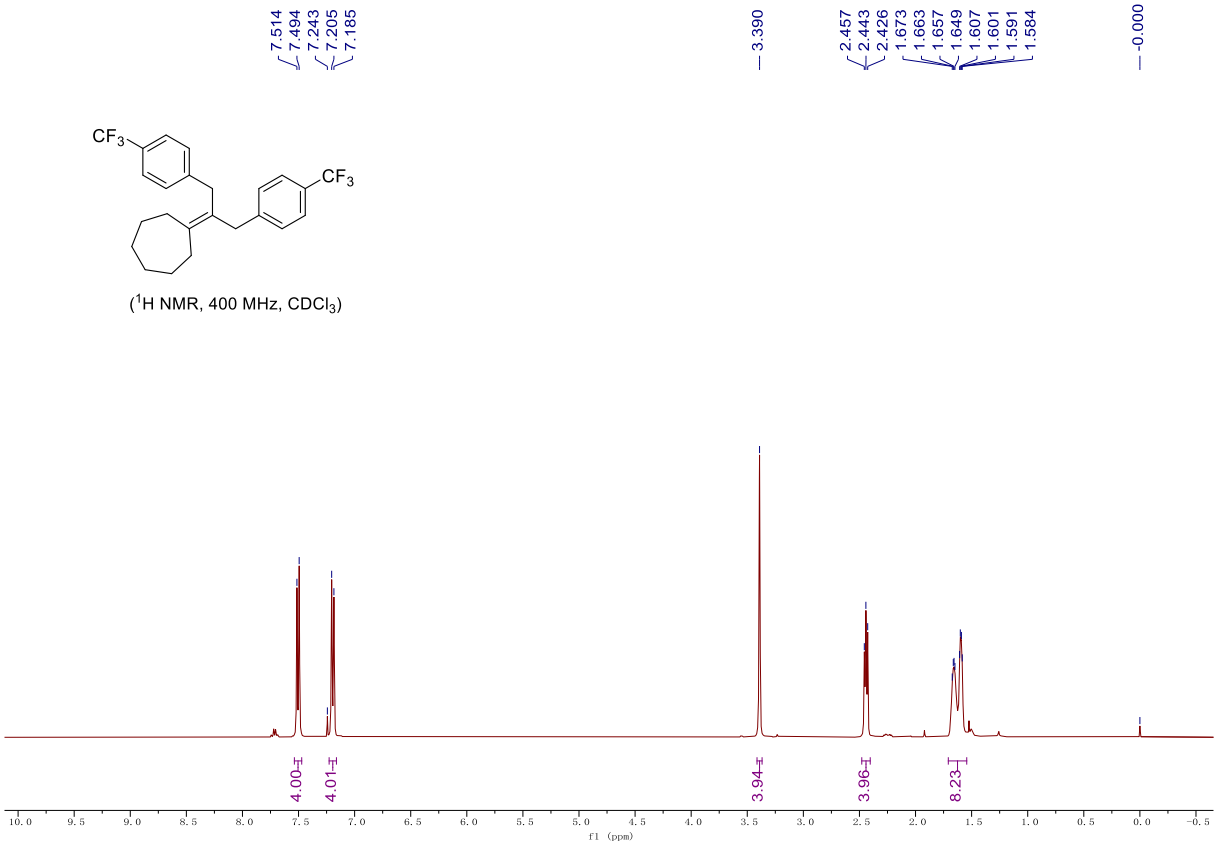
(^{1}H NMR, 600 MHz, $CDCl_3$)



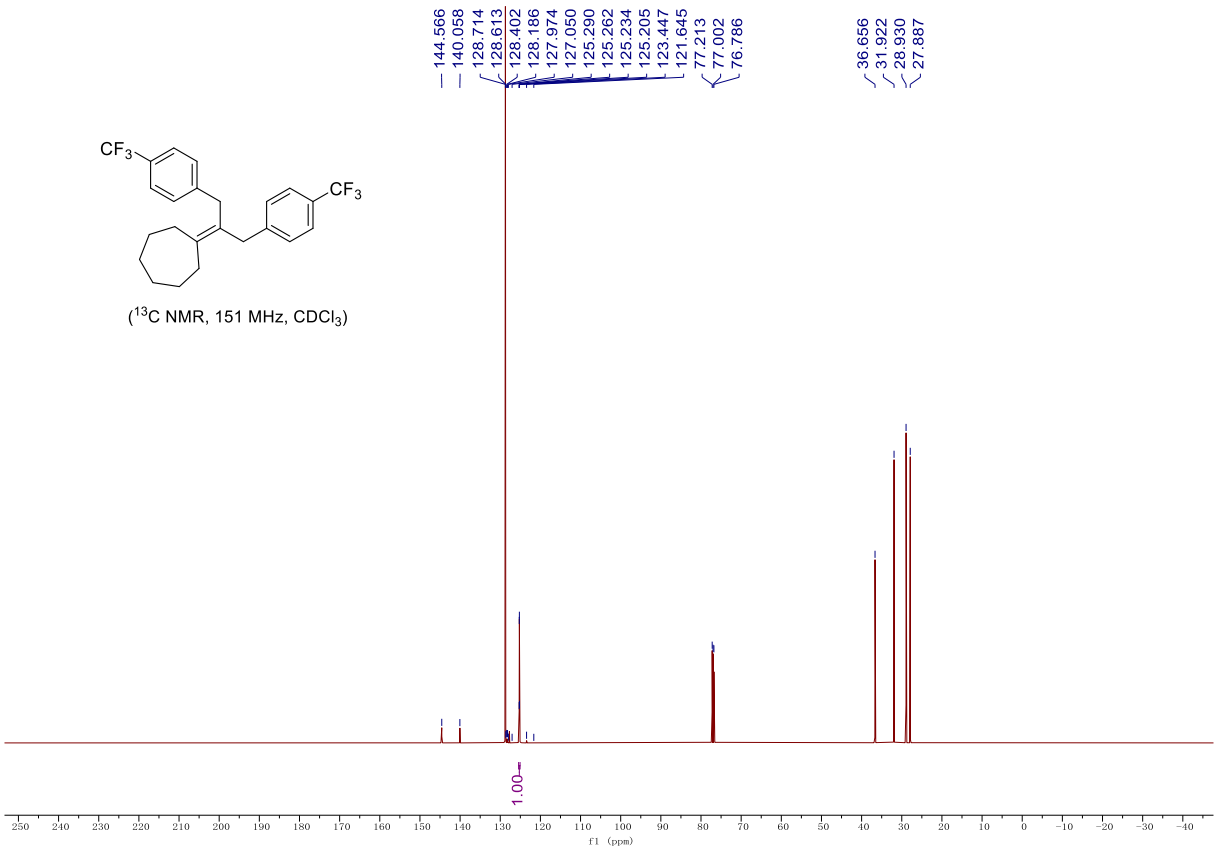
(^{13}C NMR, 151 MHz, $CDCl_3$)



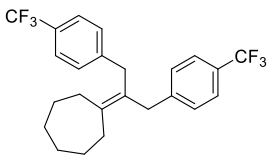
(^{19}F NMR, 565 MHz, $CDCl_3$)



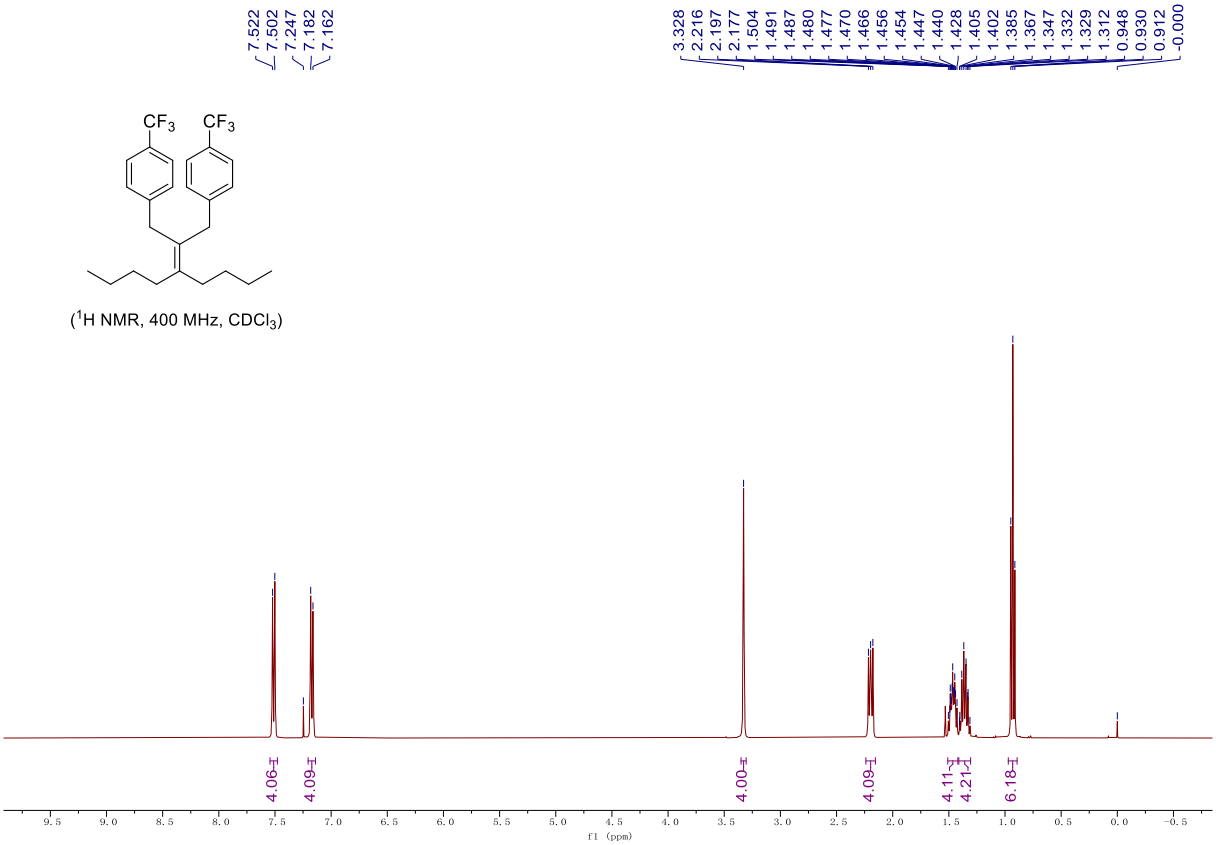
(^{1}H NMR, 400 MHz, $CDCl_3$)

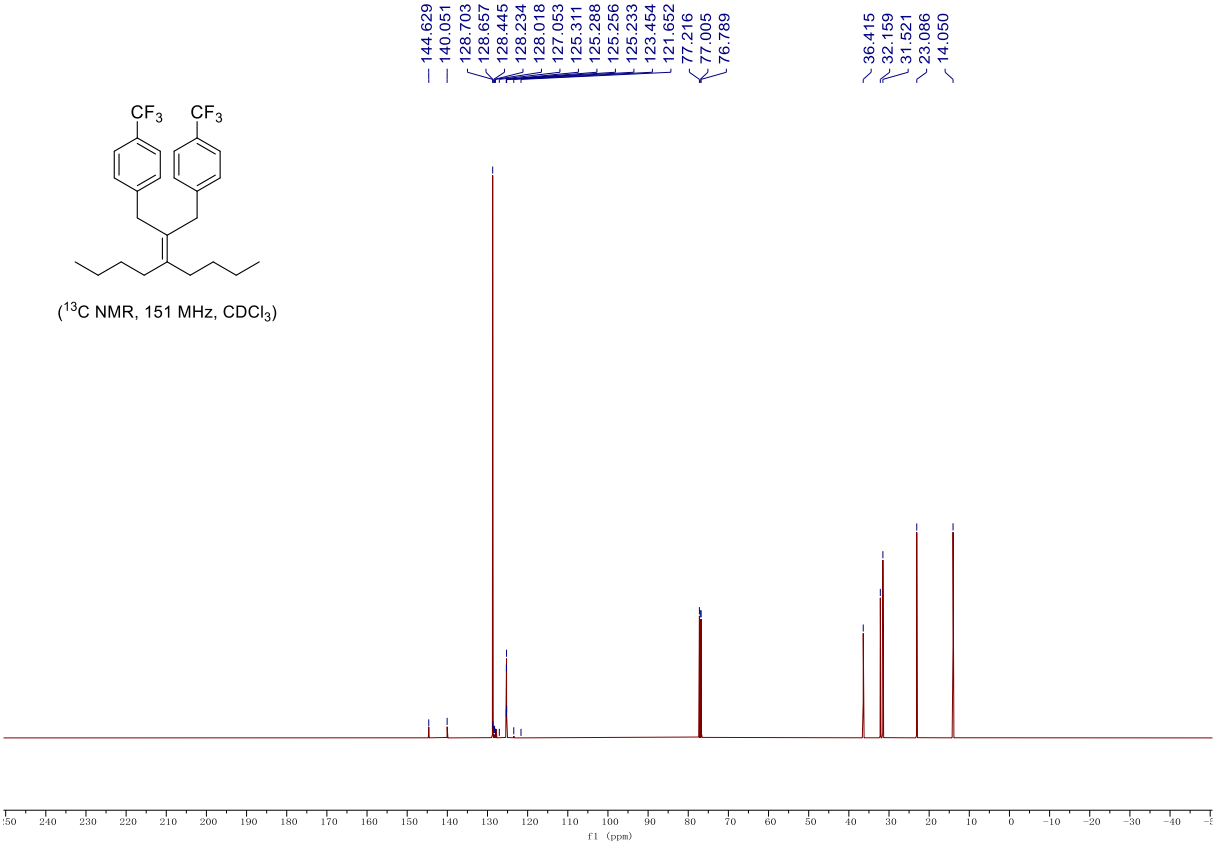


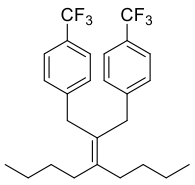
(^{13}C NMR, 151 MHz, $CDCl_3$)



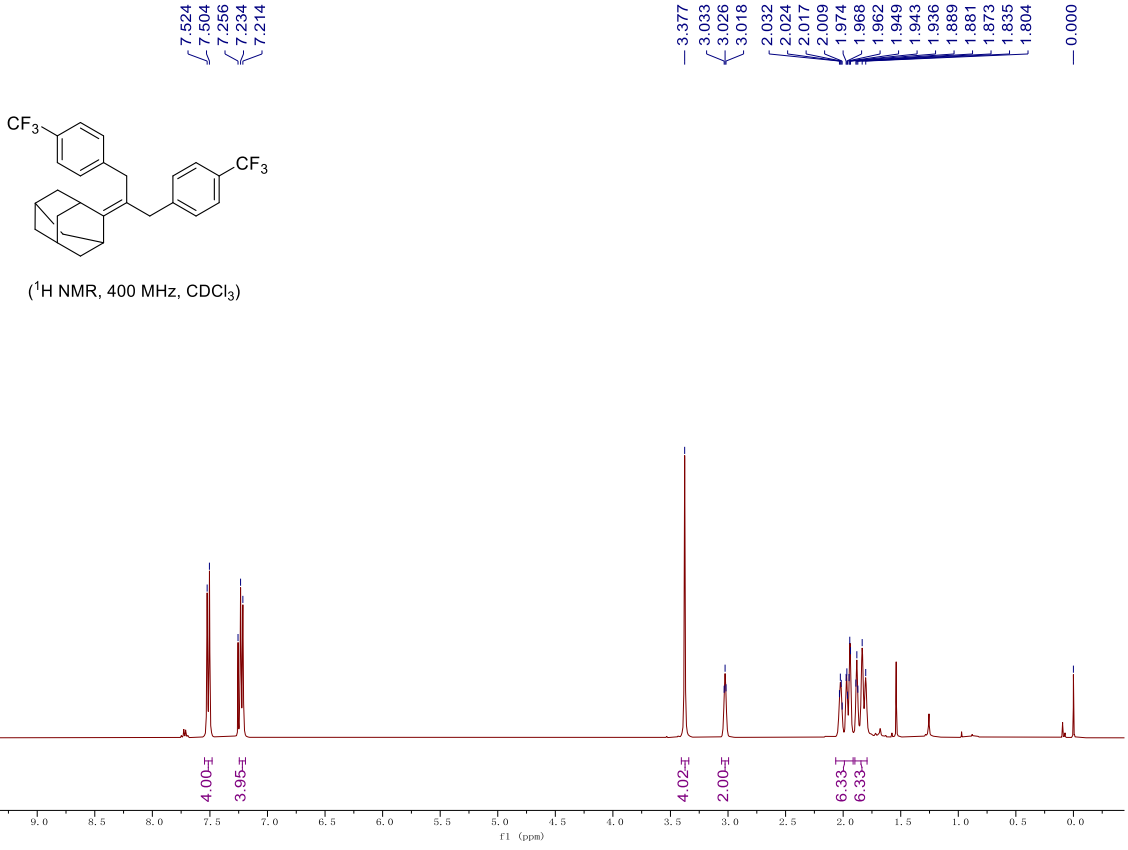
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.522
7.502
7.247
7.182
7.162
3.328
2.216
2.197
2.177
1.504
1.491
1.487
1.480
1.477
1.470
1.466
1.456
1.454
1.447
1.440
1.428
1.405
1.402
1.385
1.367
1.347
1.332
1.329
1.312
0.948
0.930
0.912
-0.000
CF3
CF3
(1H NMR, 400 MHz, CDCl3)
4.06
4.09
4.00
4.09
4.11
4.21
6.18
f1 (ppm)

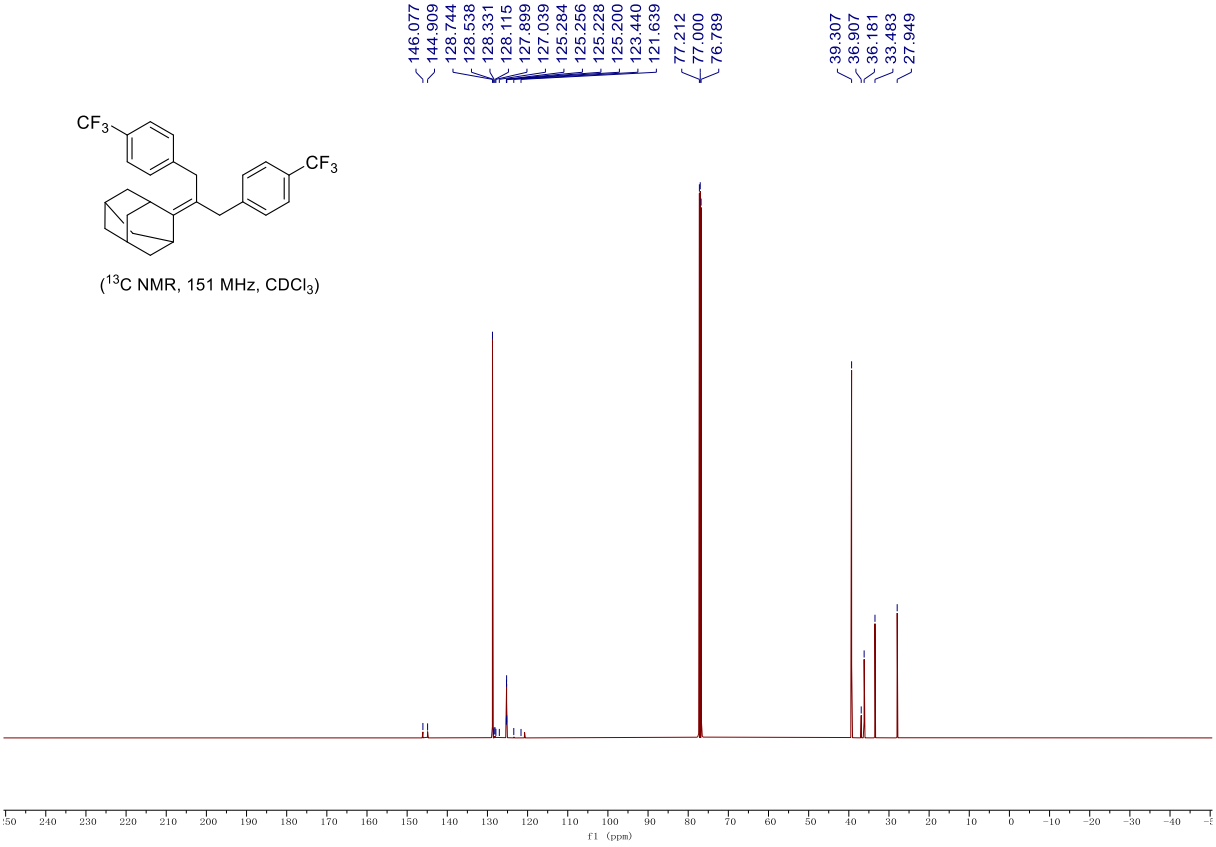

144.629
140.051
128.703
128.657
128.445
128.234
128.018
127.053
125.311
125.288
125.256
125.233
123.454
121.652
77.216
77.005
76.789
36.415
32.159
31.521
23.086
14.050
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



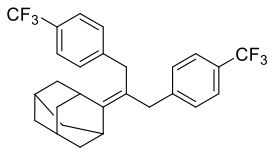
(^{19}F NMR, 565 MHz, $CDCl_3$)



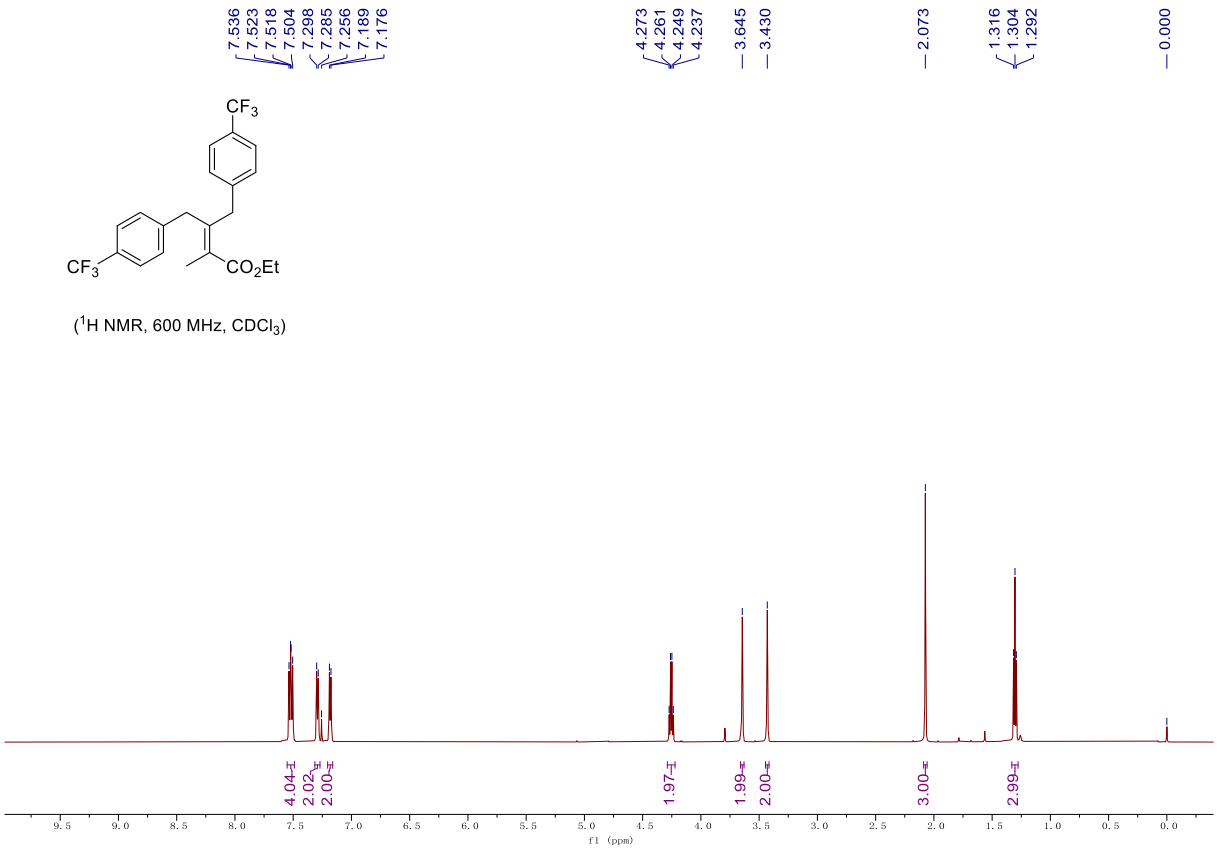
(^{1}H NMR, 400 MHz, $CDCl_3$)



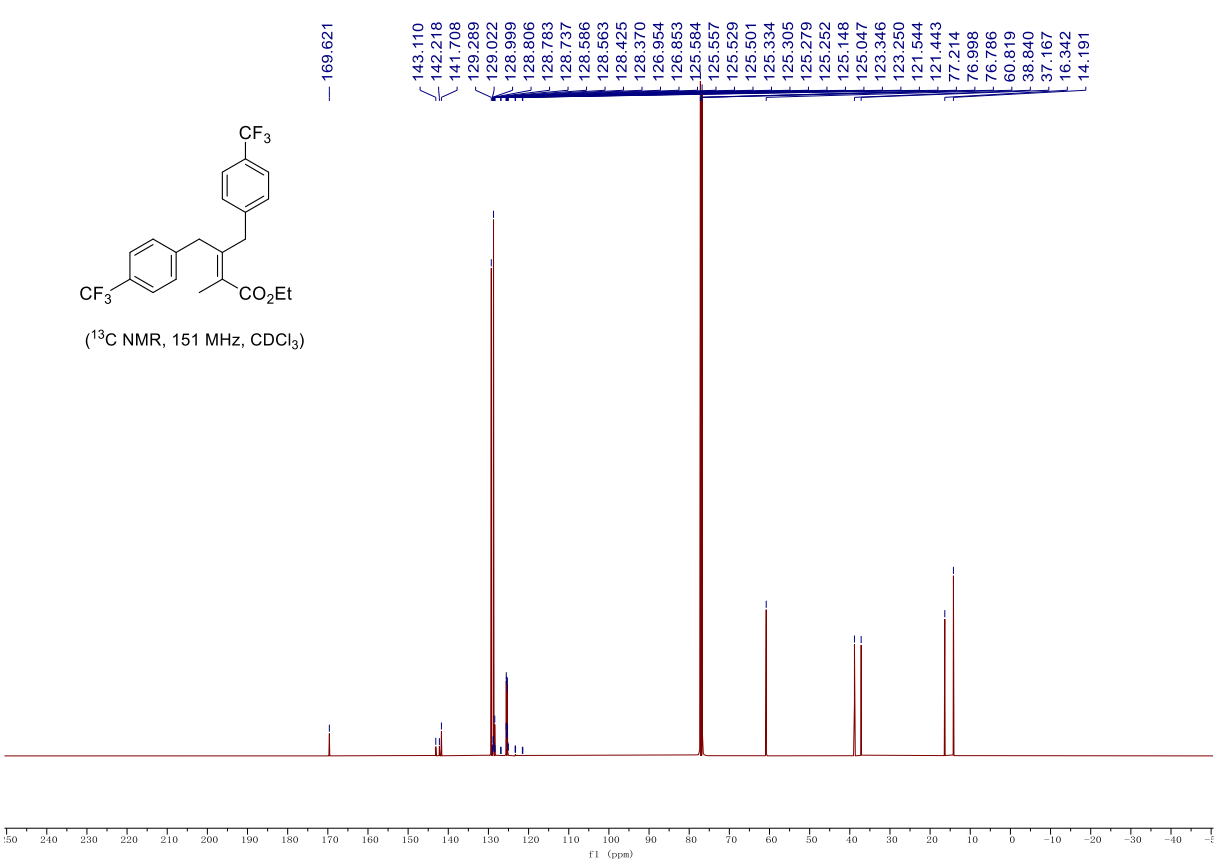
(^{13}C NMR, 151 MHz, $CDCl_3$)



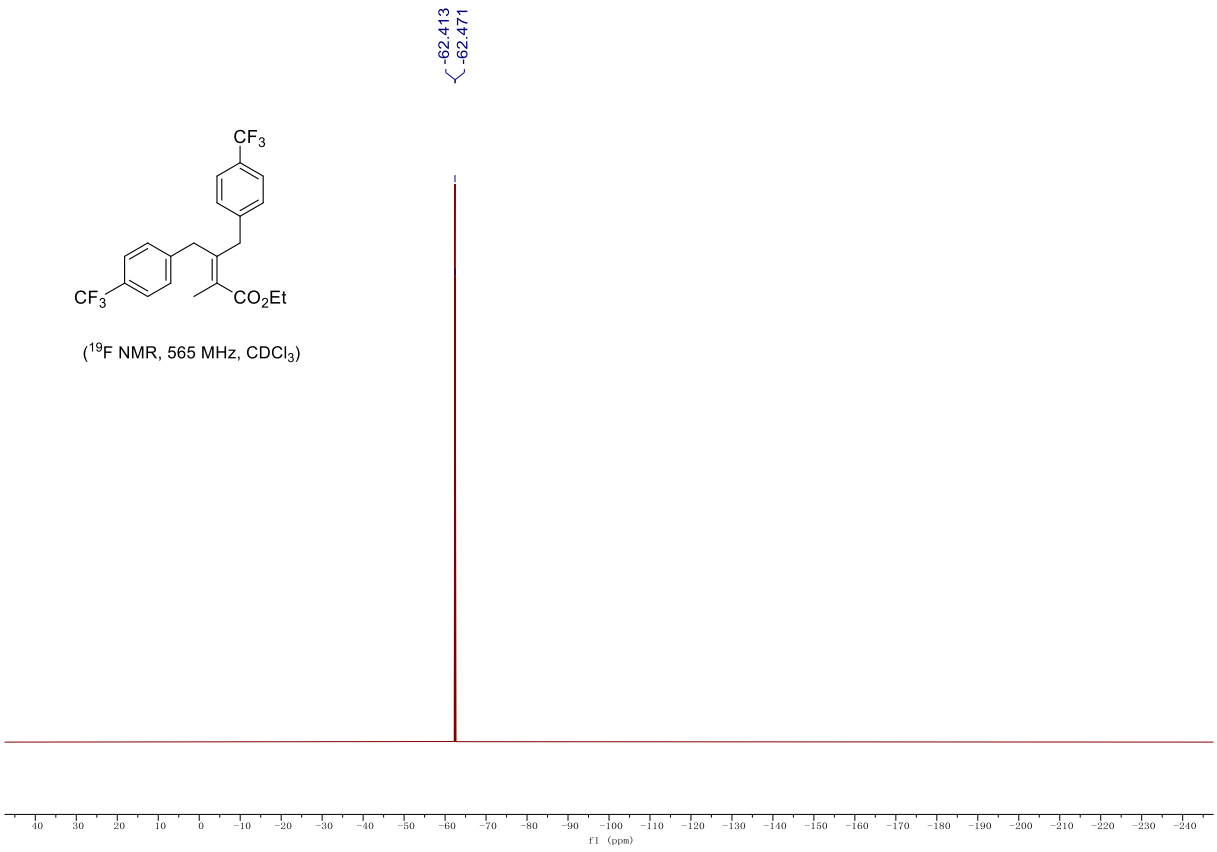
(^{19}F NMR, 565 MHz, $CDCl_3$)



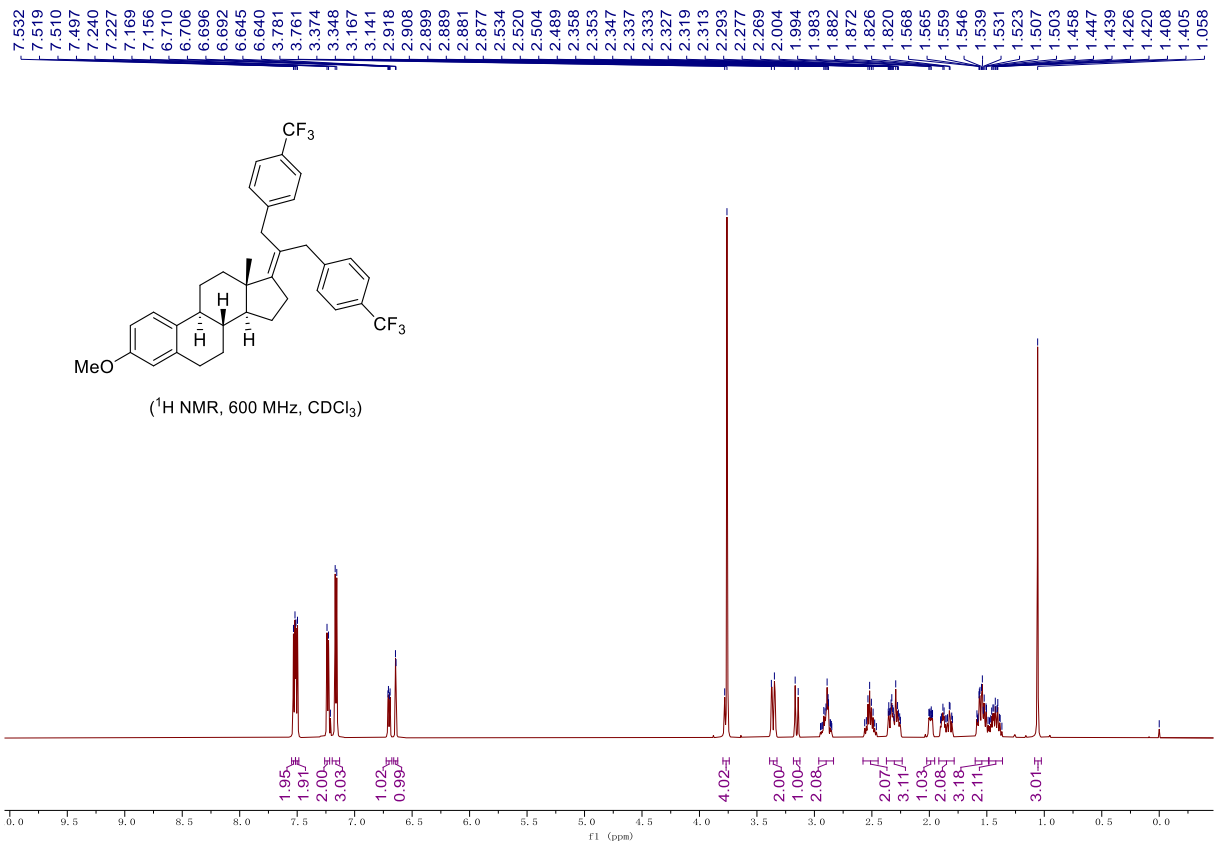
(^{1}H NMR, 600 MHz, $CDCl_3$)

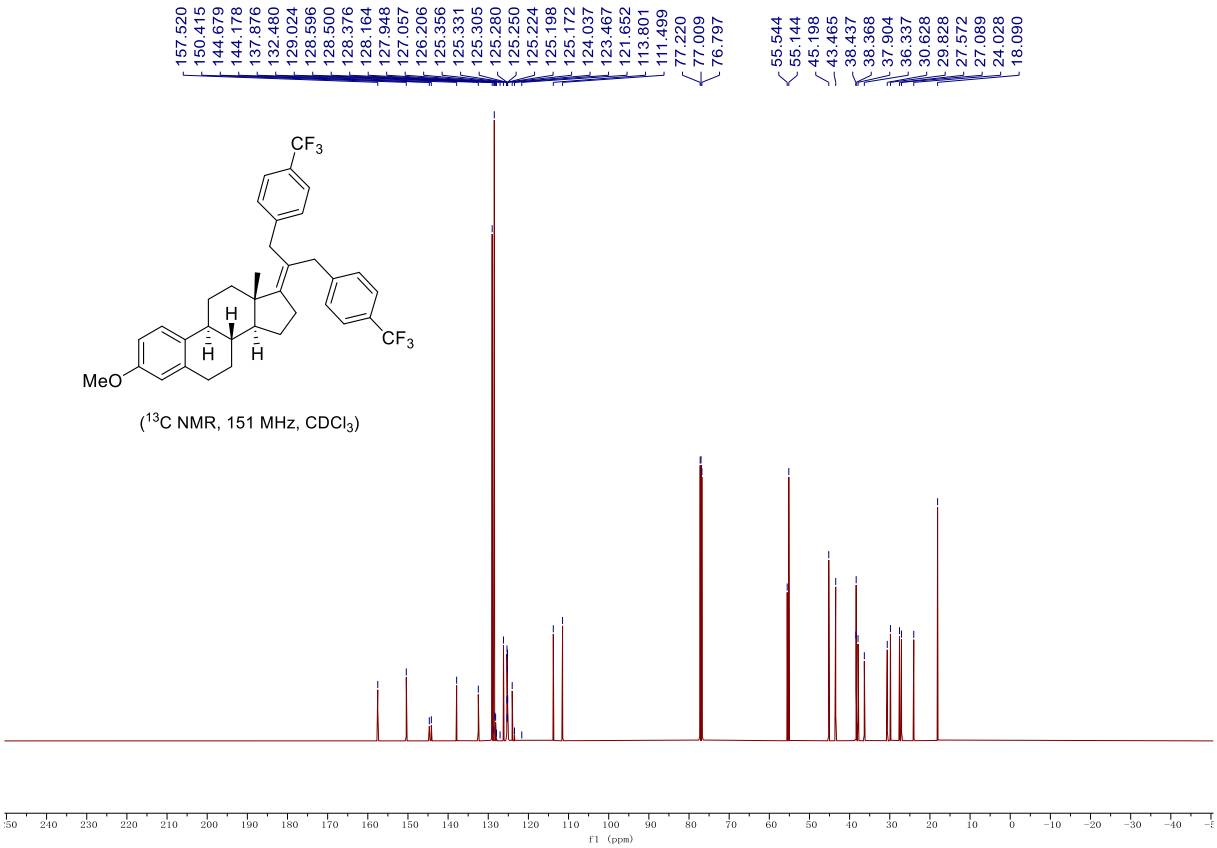


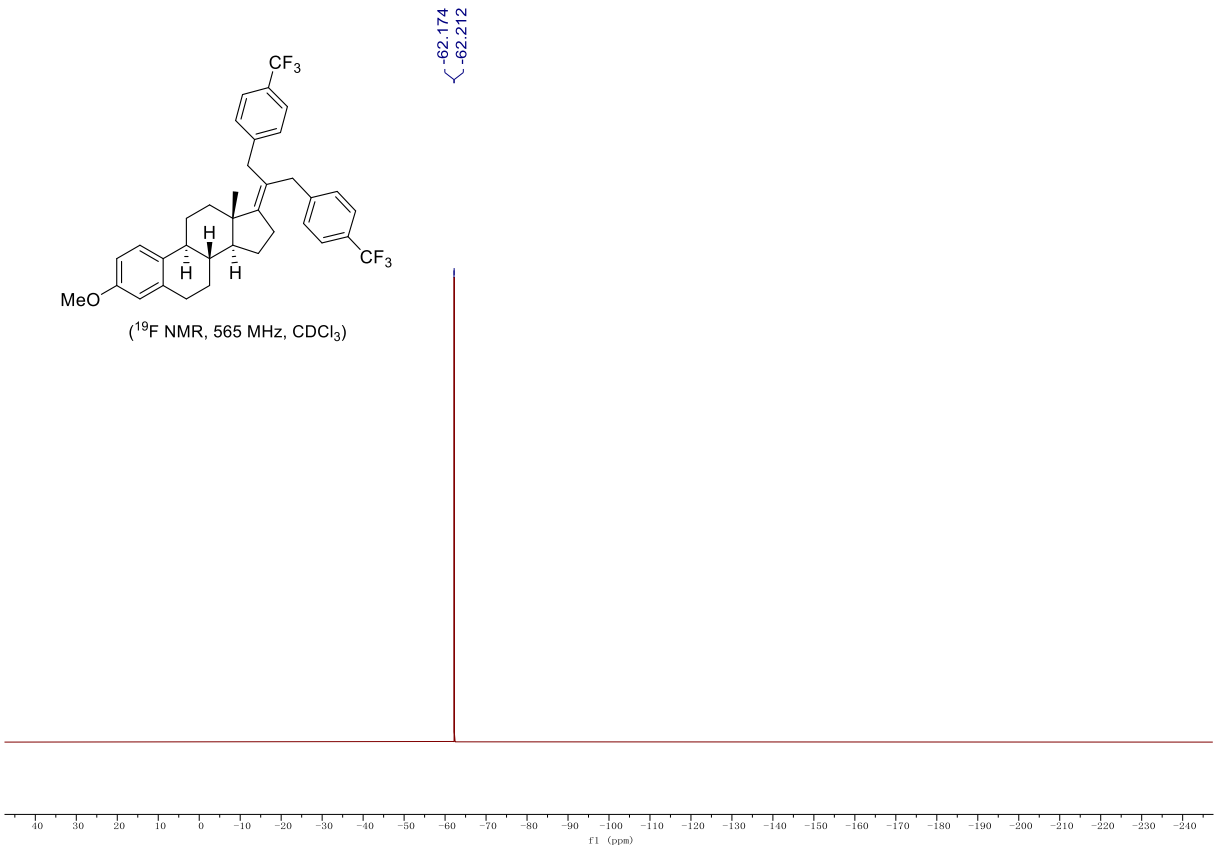
(^{13}C NMR, 151 MHz, $CDCl_3$)



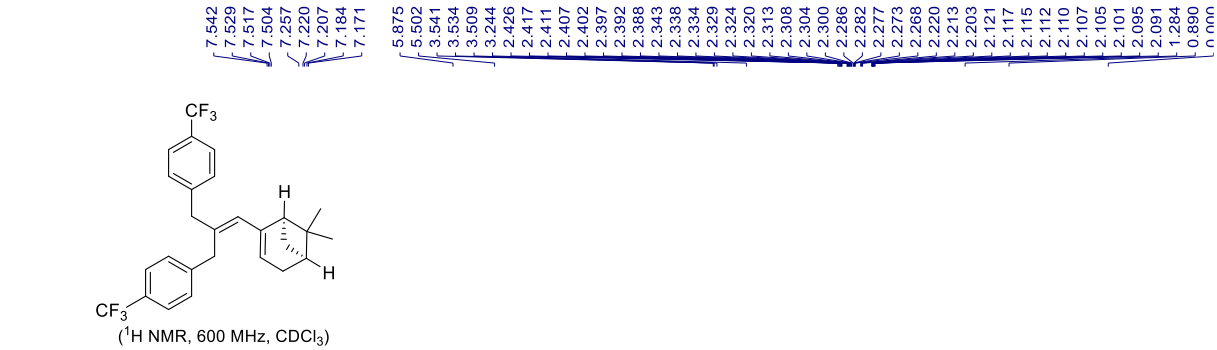
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.532 7.519 7.510 7.497 7.240 7.227 7.169 7.156 6.710 6.706 6.696 6.692 6.645 6.640 3.781 3.761 3.374 3.348 3.167 3.141 2.918 2.908 2.899 2.889 2.881 2.877 2.534 2.520 2.504 2.489 2.358 2.353 2.347 2.337 2.333 2.327 2.319 2.313 2.293 2.277 2.269 2.004 1.994 1.983 1.882 1.872 1.826 1.820 1.568 1.565 1.559 1.546 1.539 1.531 1.523 1.507 1.503 1.458 1.447 1.439 1.426 1.420 1.408 1.405 1.058
CF3
H
H
H
CF3
MeO
(1H NMR, 600 MHz, CDCl3)
1.95 1.91 2.00 3.03 1.02 0.99 4.02 2.00 1.00 2.08 2.07 3.11 1.03 2.08 3.18 2.11 3.01
f1 (ppm)

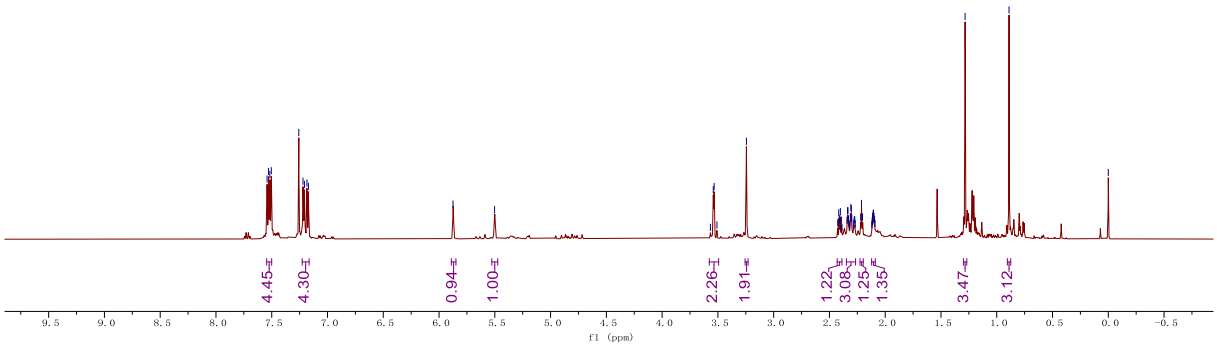

157.520 150.415 144.679 144.178 137.876 132.480 129.024 128.596 128.500 128.376 128.164 127.948 127.057 126.206 125.356 125.331 125.305 125.280 125.250 125.224 125.198 125.172 124.037 123.467 121.652 113.801 111.499 77.220 77.009 76.797 55.544 55.144 45.198 43.465 38.437 38.368 37.904 36.337 30.628 29.828 27.572 27.089 24.028 18.090
CF3
H
H
H
CF3
MeO
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

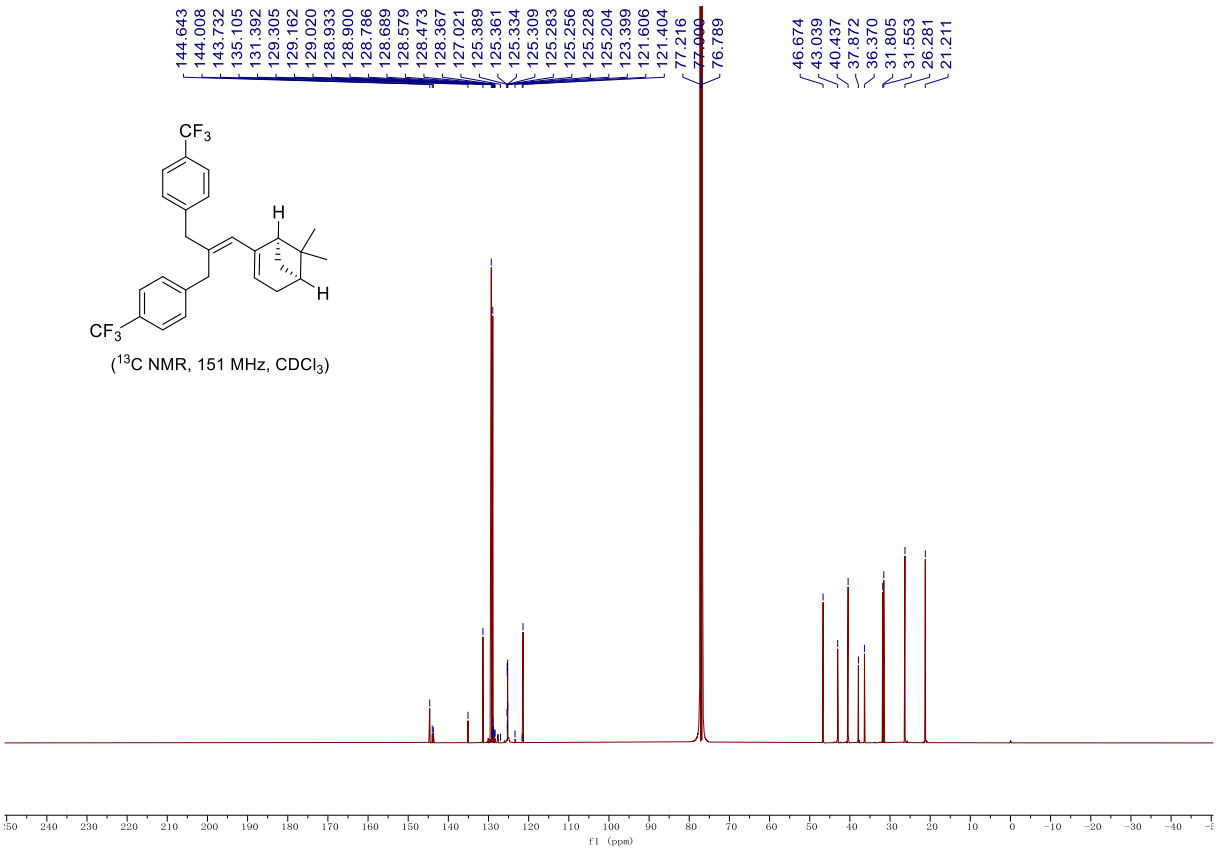


(^{19}F NMR, 565 MHz, $CDCl_3$)

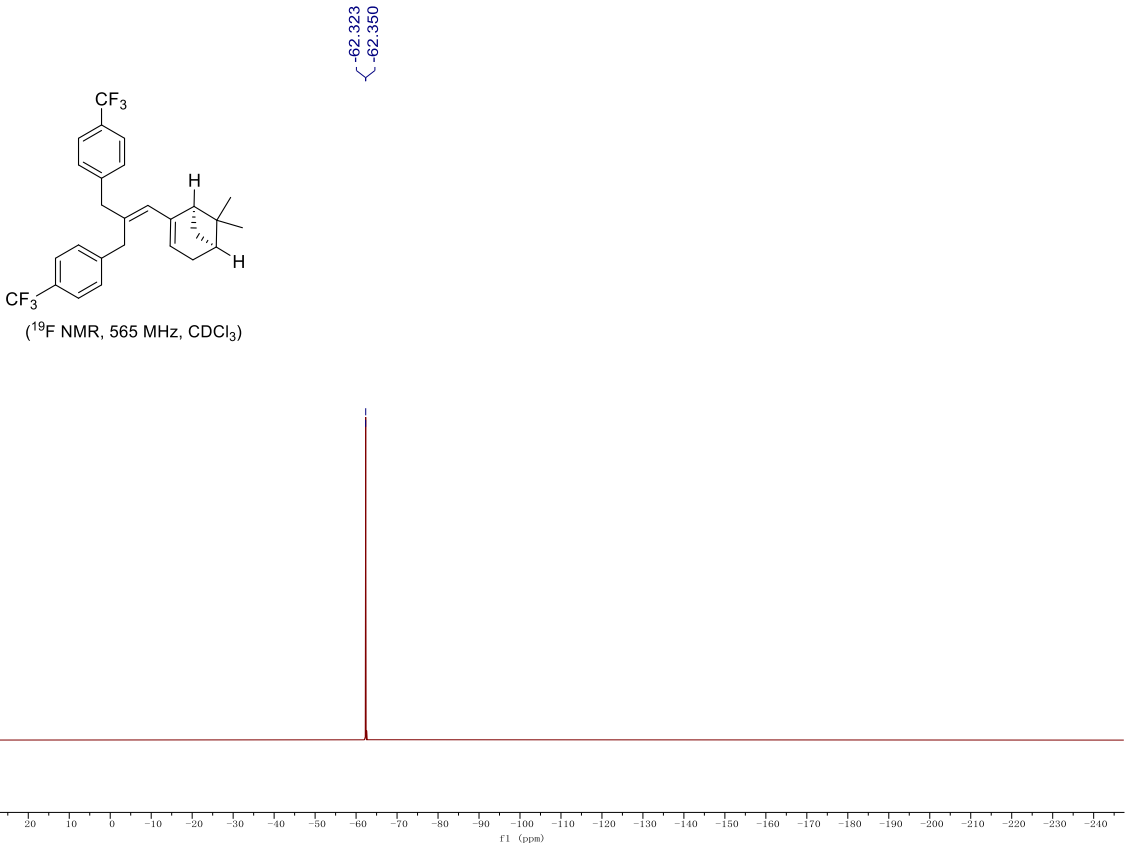


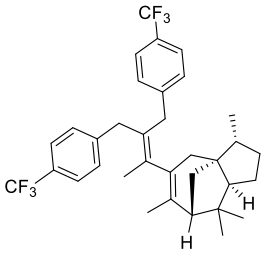
(^{1}H NMR, 600 MHz, $CDCl_3$)



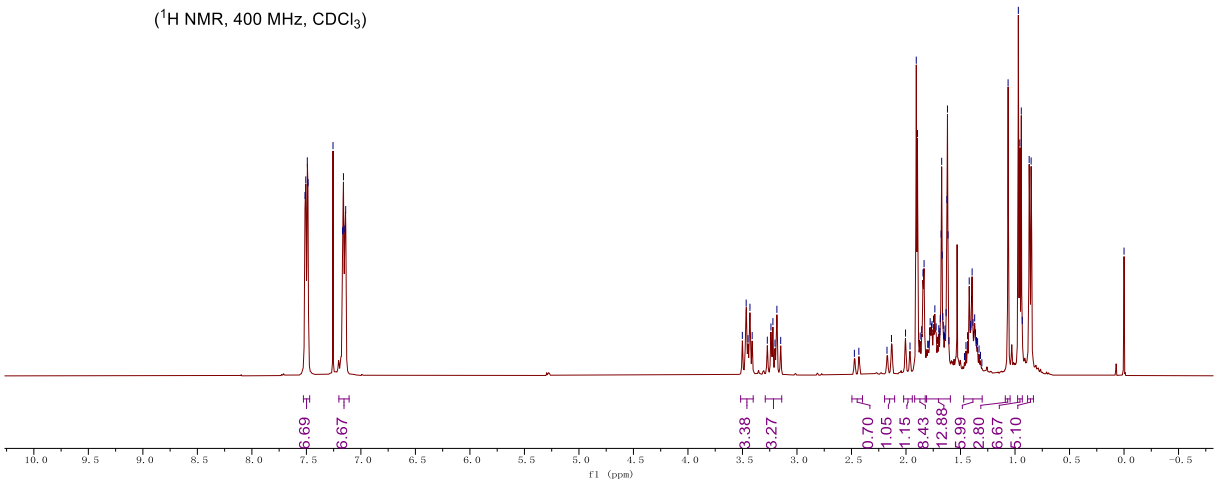


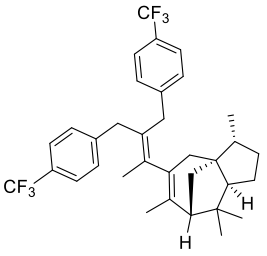
(^{13}C NMR, 151 MHz, $CDCl_3$)


-62.323
-62.350
CF3
H
H
CF3
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

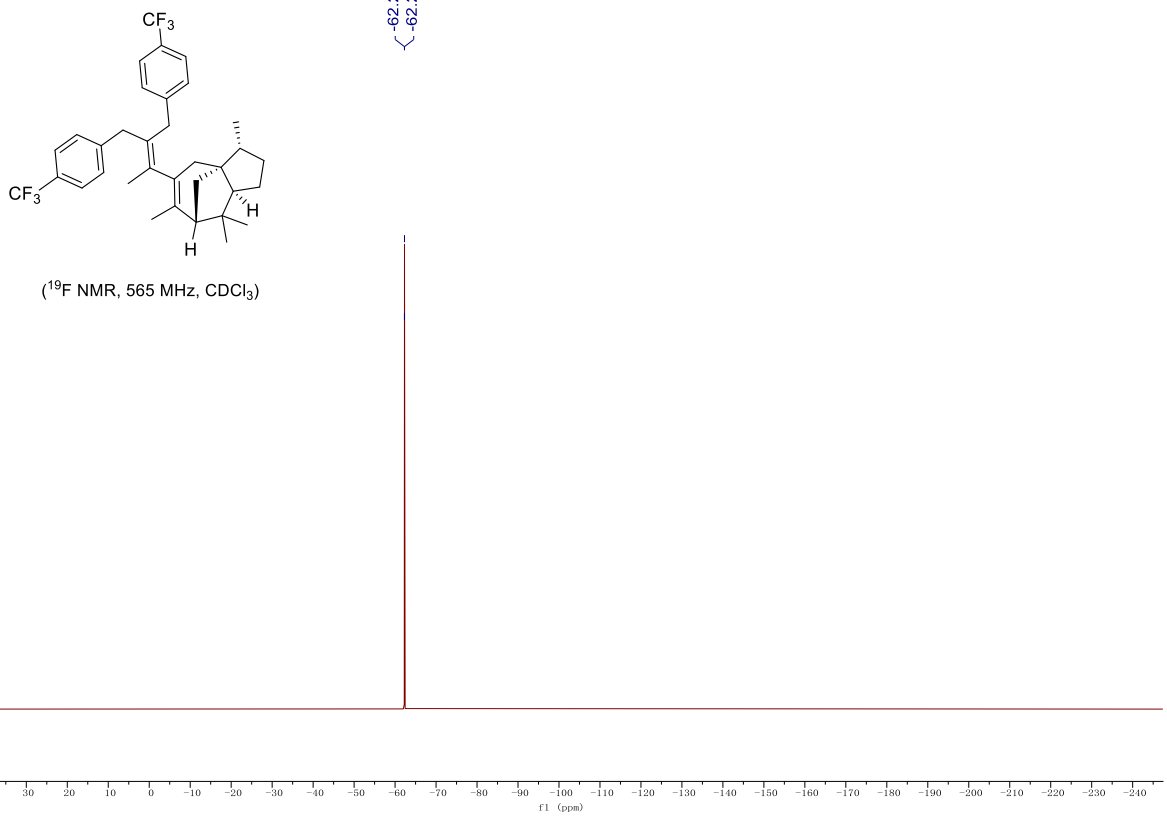


(^{1}H NMR, 400 MHz, $CDCl_3$)

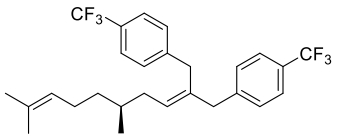




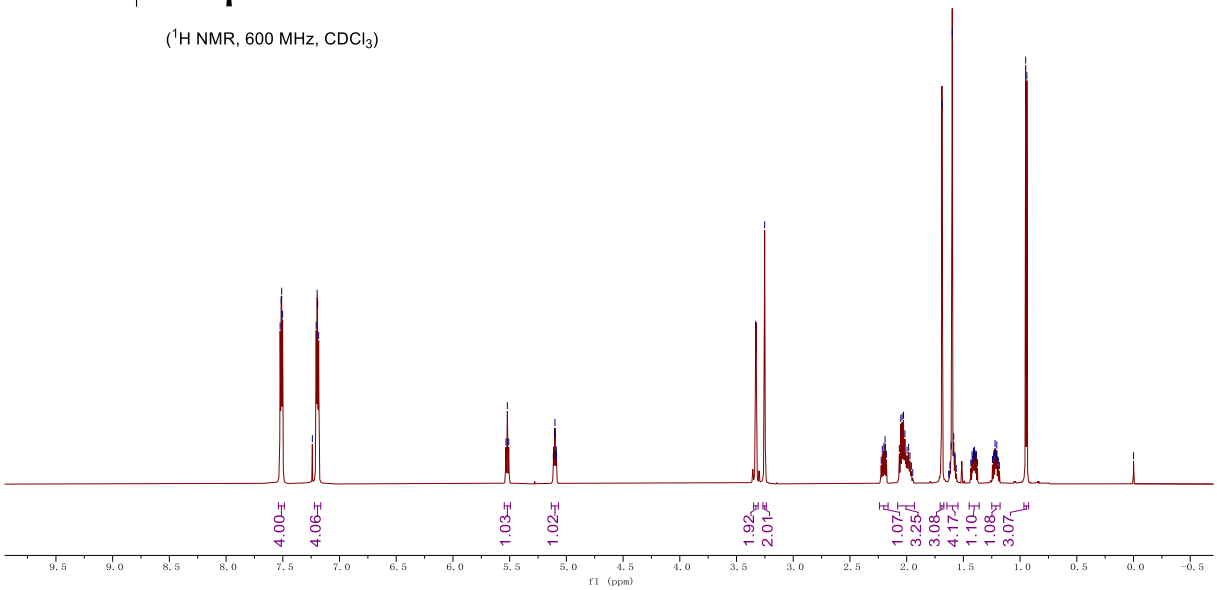
(^{13}C NMR, 151 MHz, $CDCl_3$)

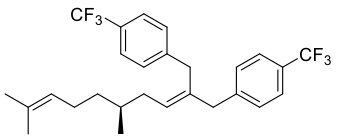


(^{19}F NMR, 565 MHz, $CDCl_3$)

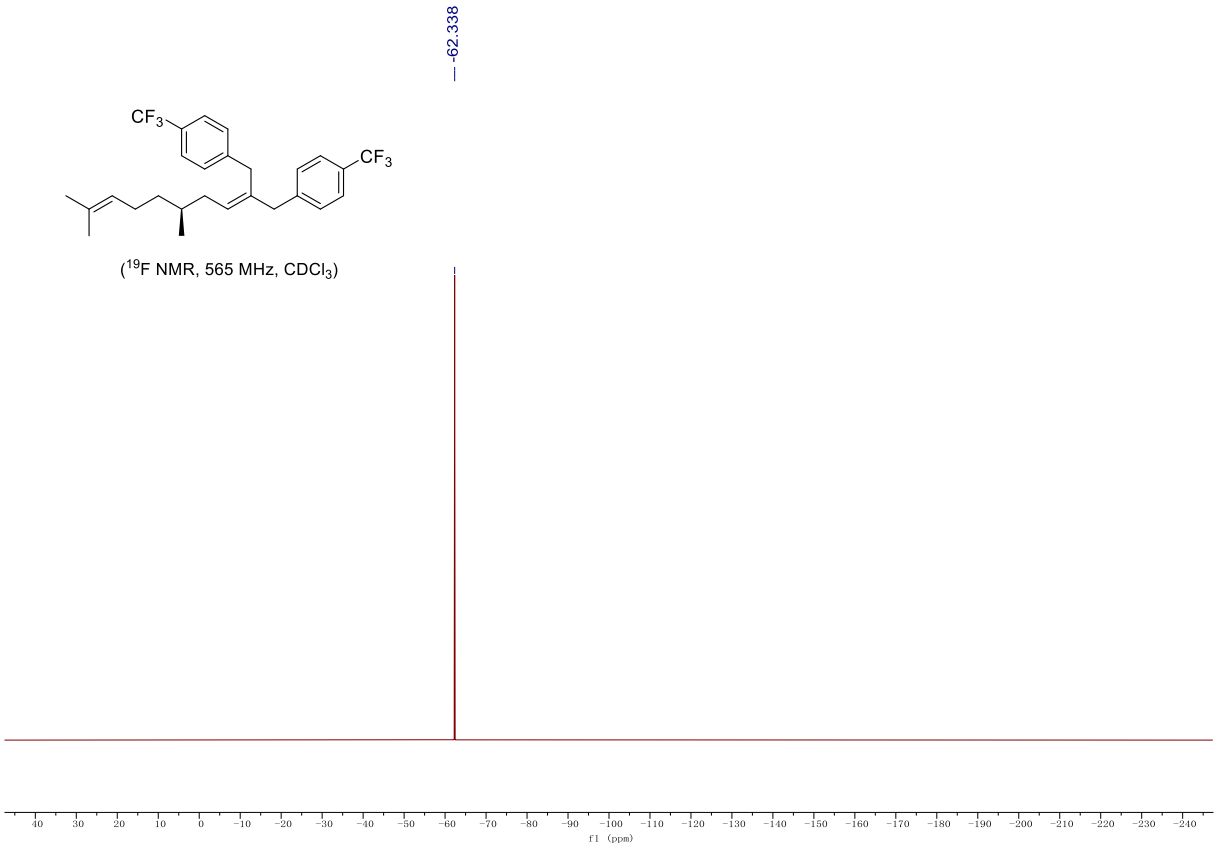


(^{1}H NMR, 600 MHz, $CDCl_3$)

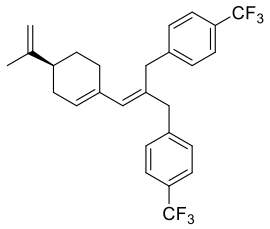




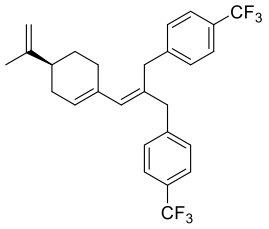
(^{13}C NMR, 151 MHz, $CDCl_3$)



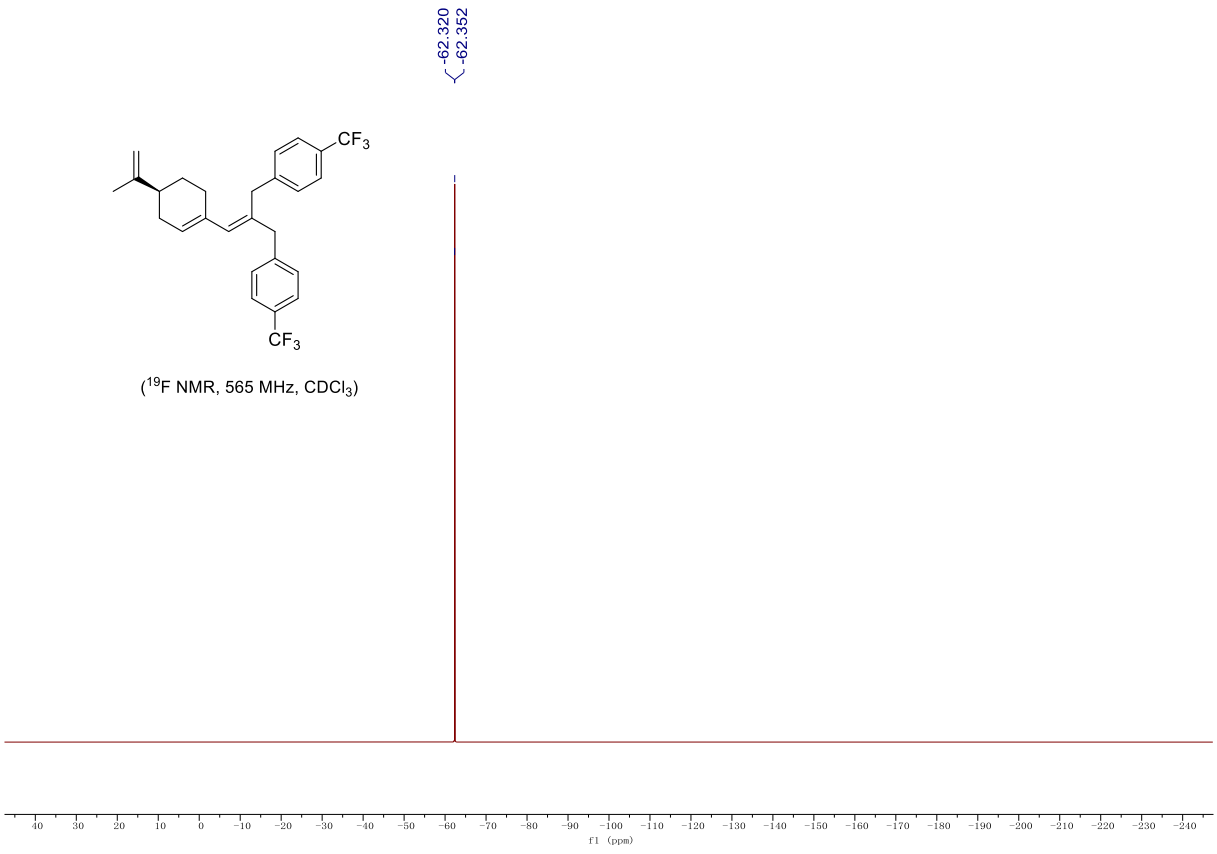
(^{19}F NMR, 565 MHz, $CDCl_3$)



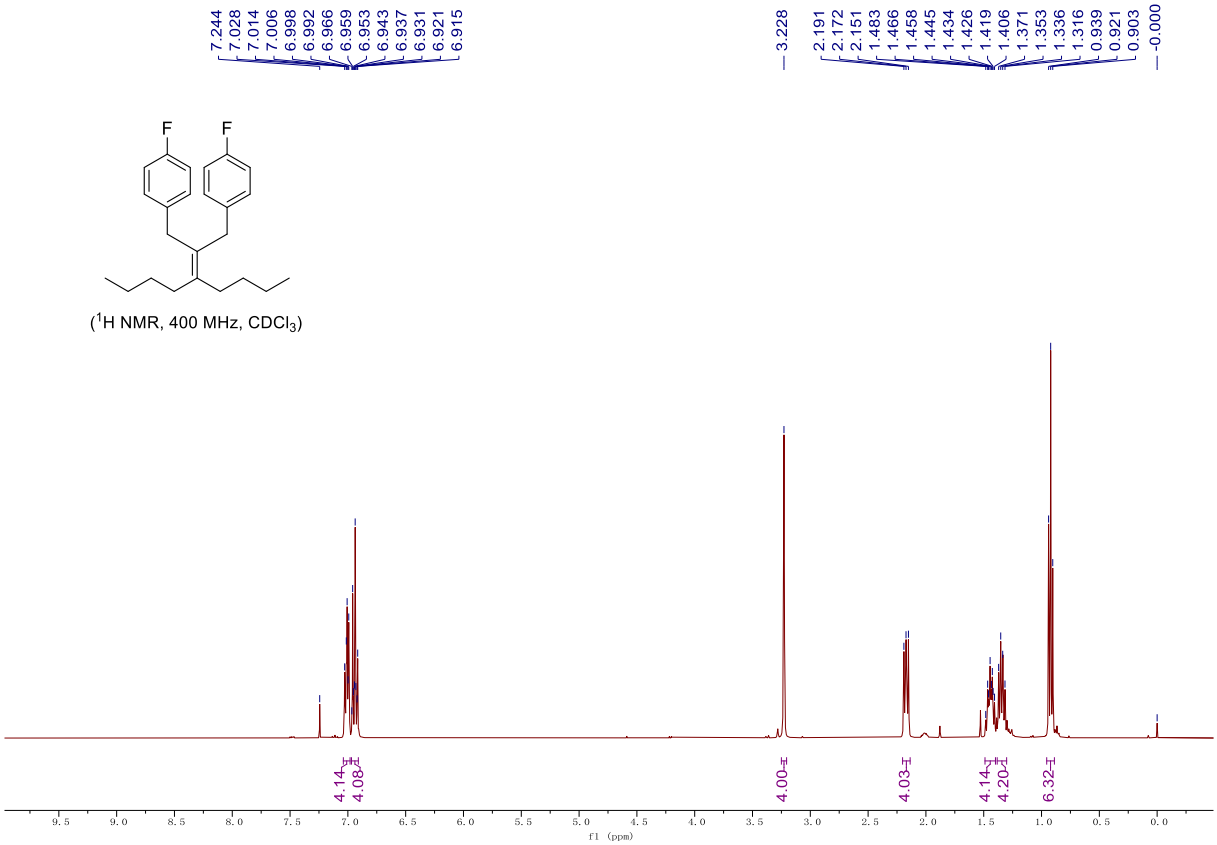
(^{1}H NMR, 600 MHz, $CDCl_3$)

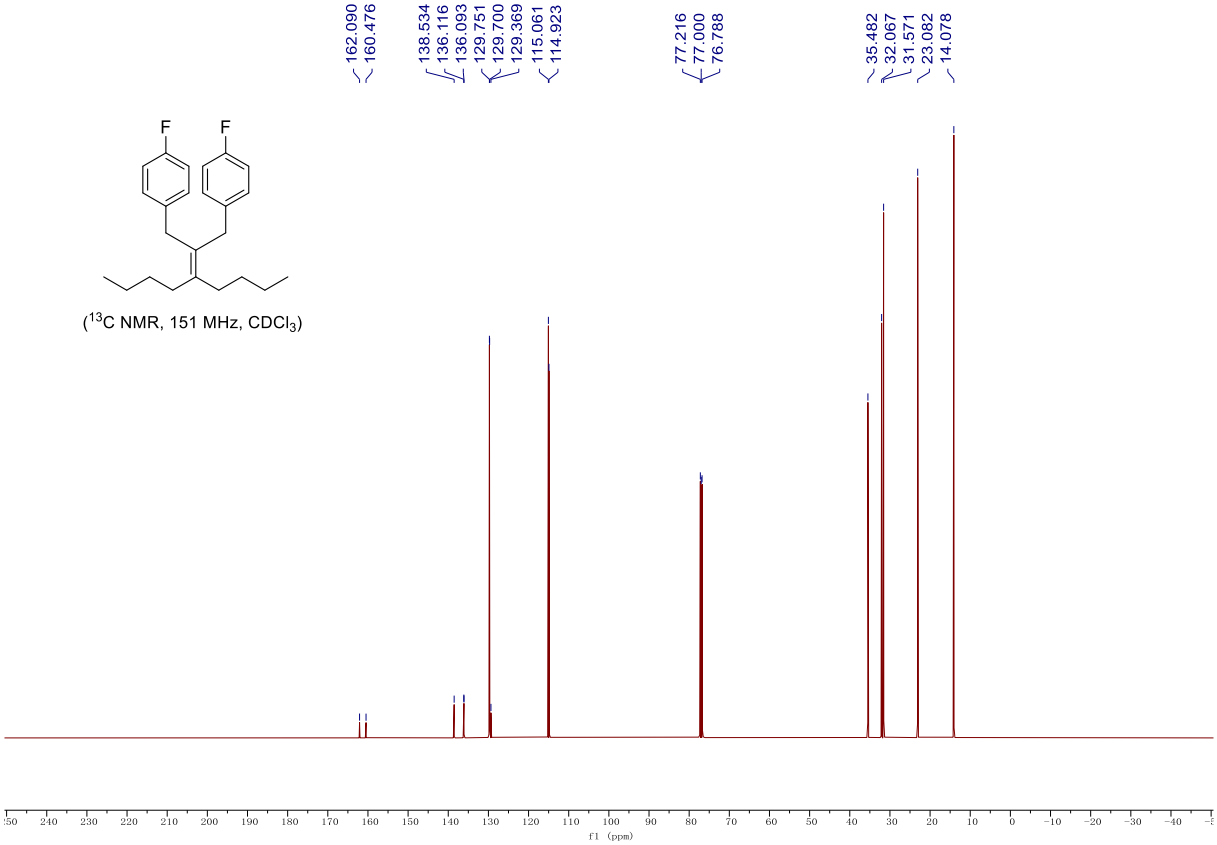


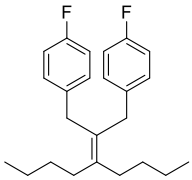
(^{13}C NMR, 151 MHz, $CDCl_3$)



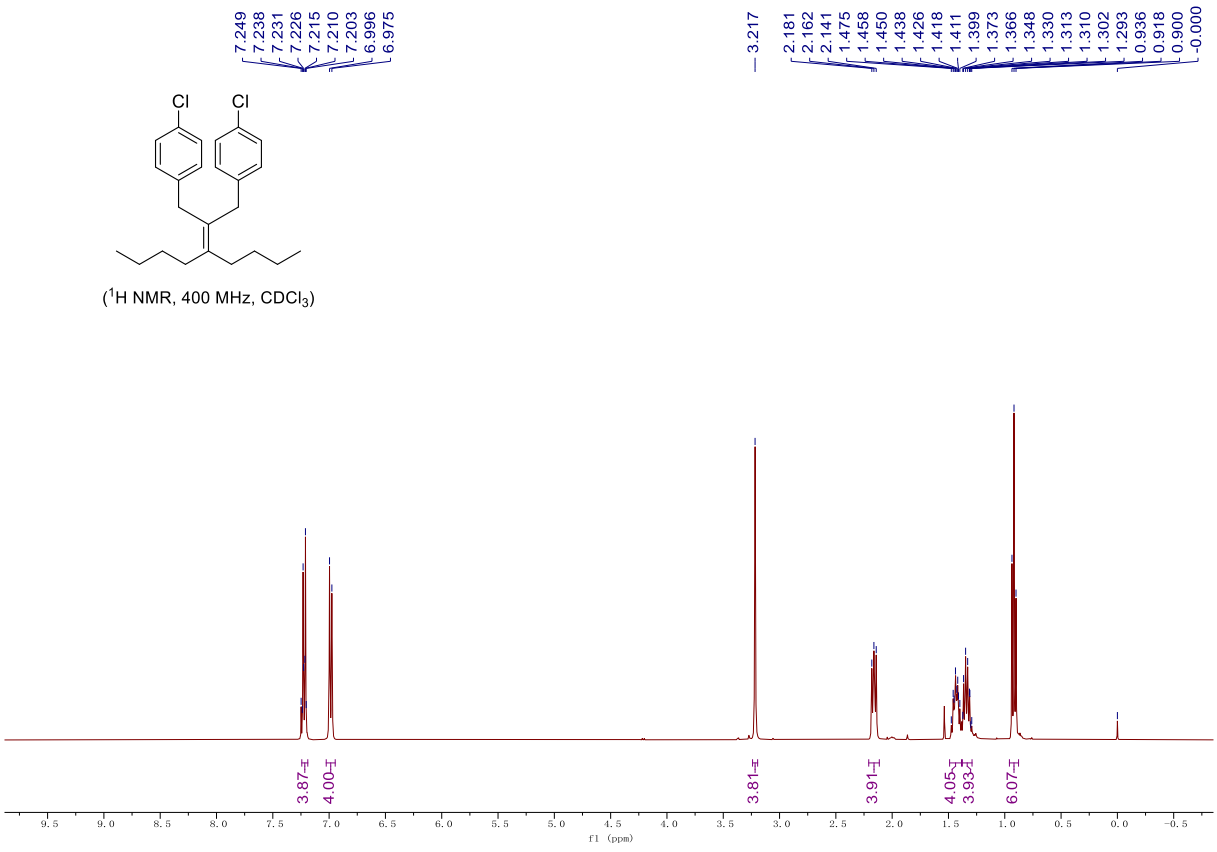
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.244
7.028
7.014
7.006
6.998
6.992
6.966
6.959
6.953
6.943
6.937
6.931
6.921
6.915
3.228
2.191
2.172
2.151
1.483
1.466
1.458
1.445
1.434
1.426
1.419
1.406
1.371
1.353
1.336
1.316
0.939
0.921
0.903
-0.000
F
F
(^{1}H NMR, 400 MHz, CDCl$_3$)
4.14
4.08
4.00
4.03
4.14
4.20
6.32
f1 (ppm)

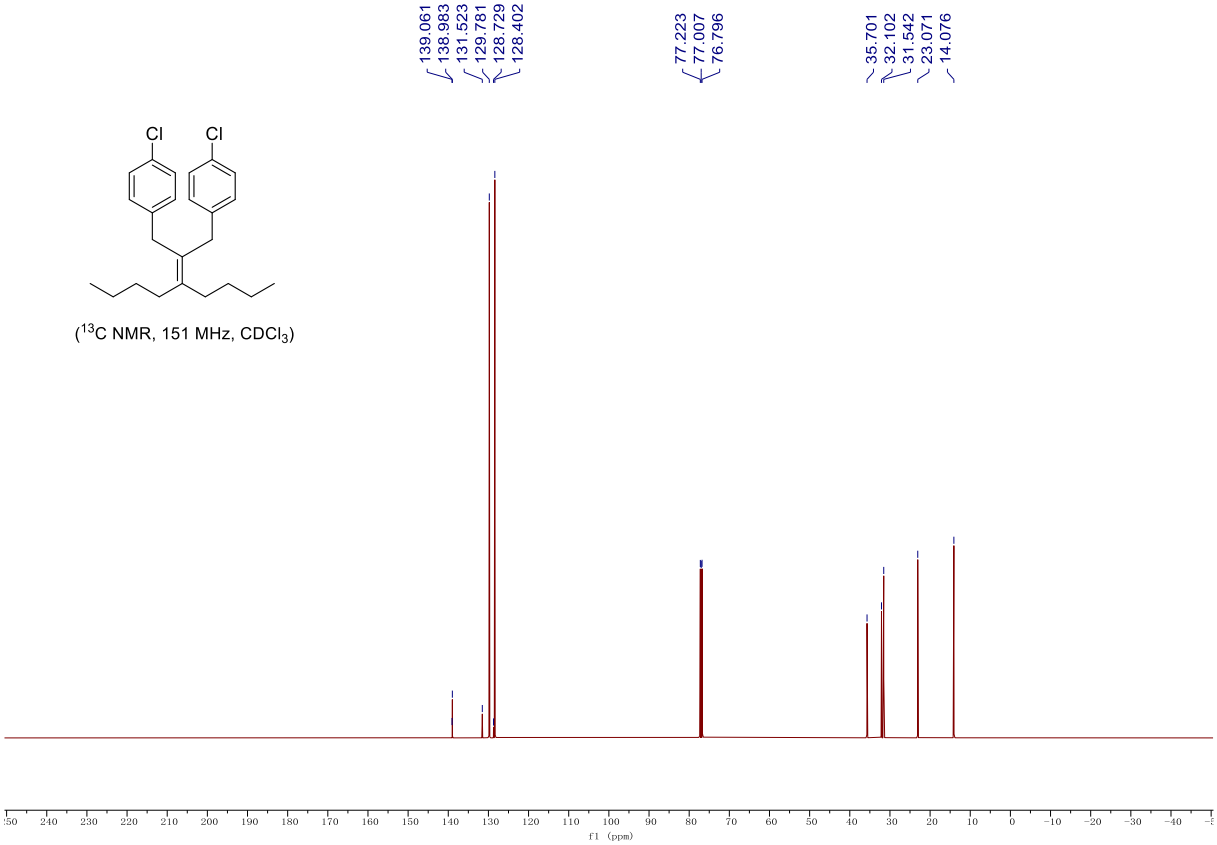

162.090
160.476
138.534
136.116
136.093
129.751
129.700
129.369
115.061
114.923
77.216
77.000
76.788
35.482
32.067
31.571
23.082
14.078
F
F
(^{13}C NMR, 151 MHz, CDCl$_3$)
f1 (ppm)



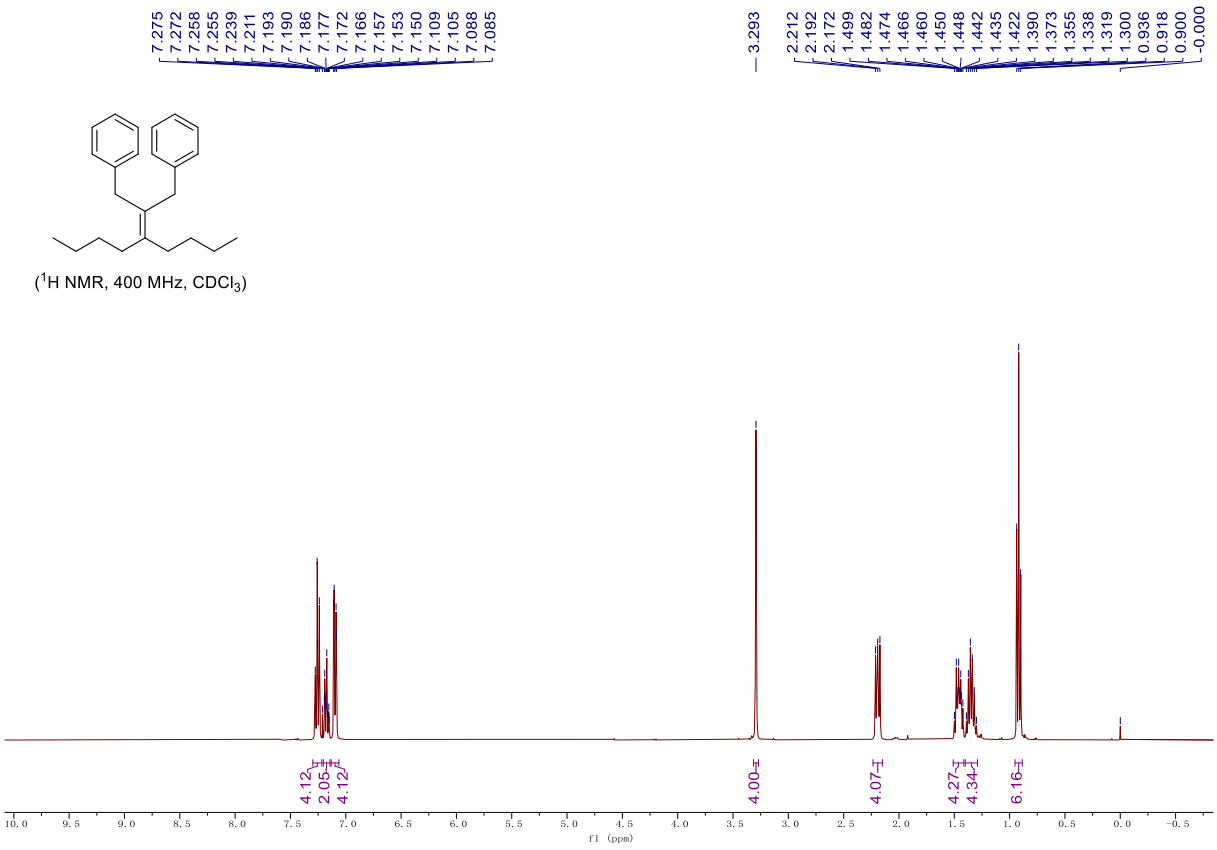
(^{19}F NMR, 565 MHz, $CDCl_3$)



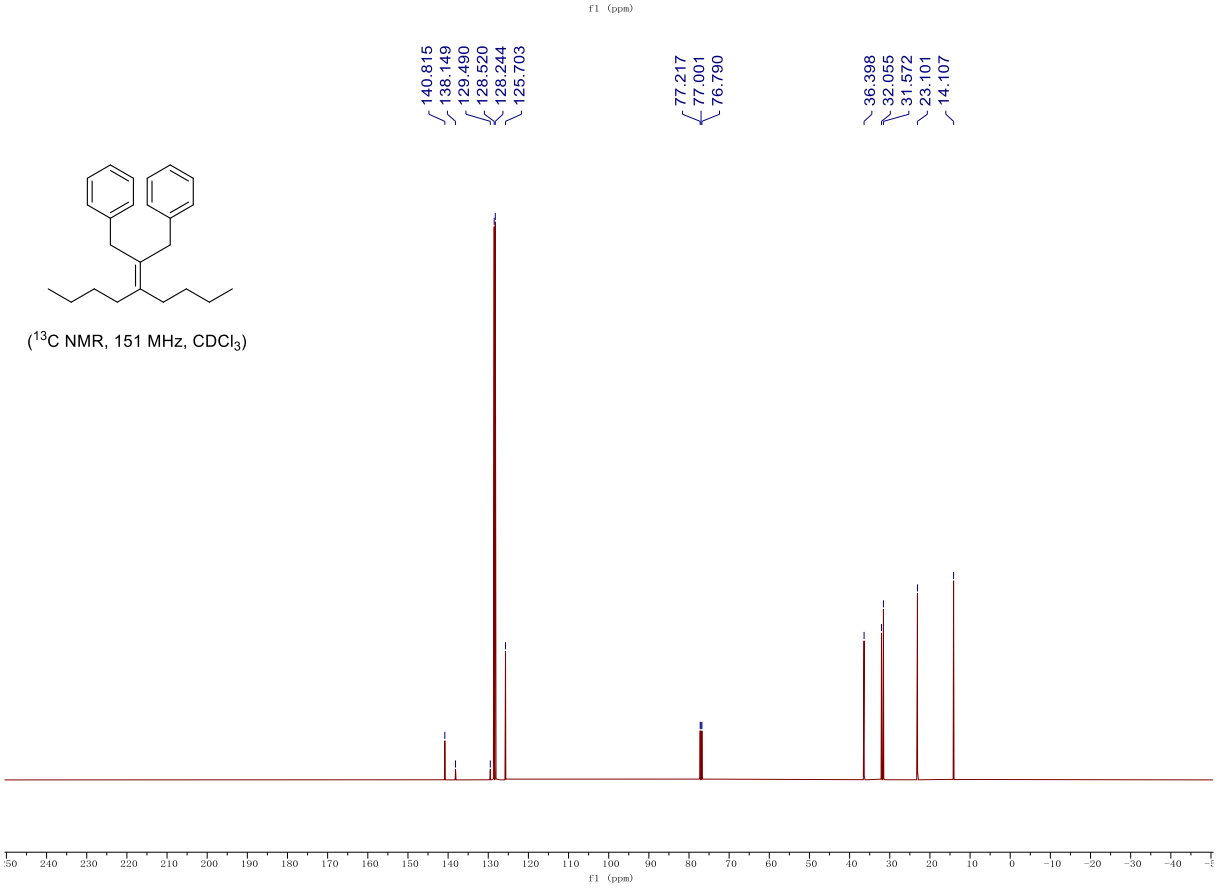
(^{1}H NMR, 400 MHz, $CDCl_3$)



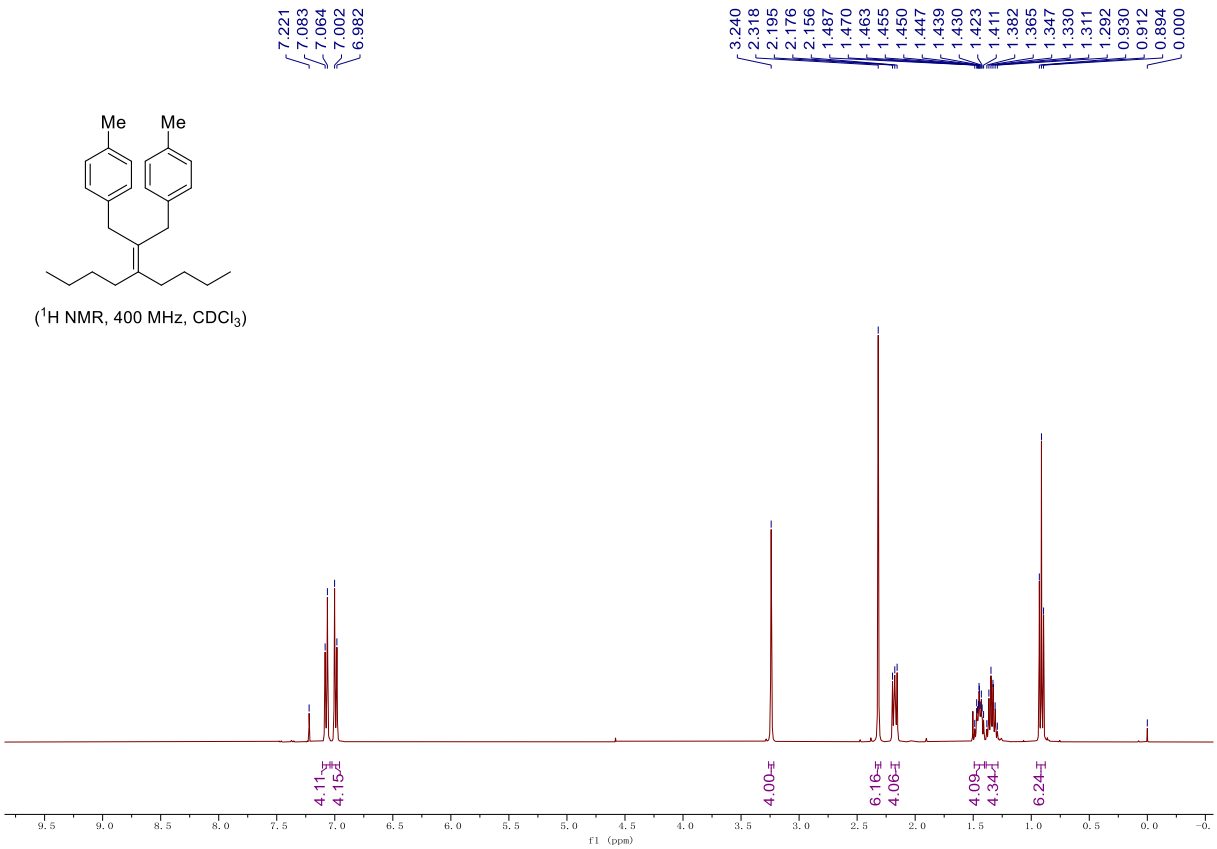
(^{13}C NMR, 151 MHz, $CDCl_3$)



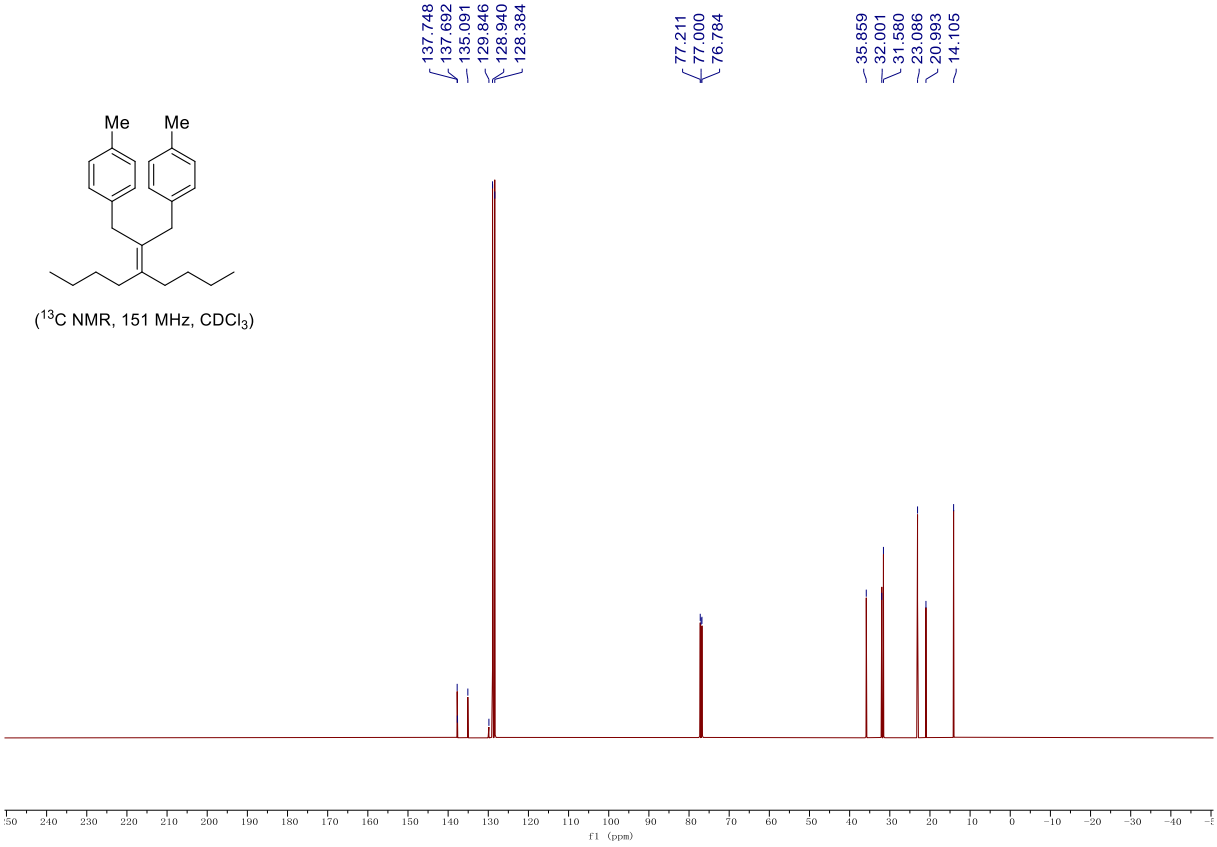
(^{1}H NMR, 400 MHz, $CDCl_3$)



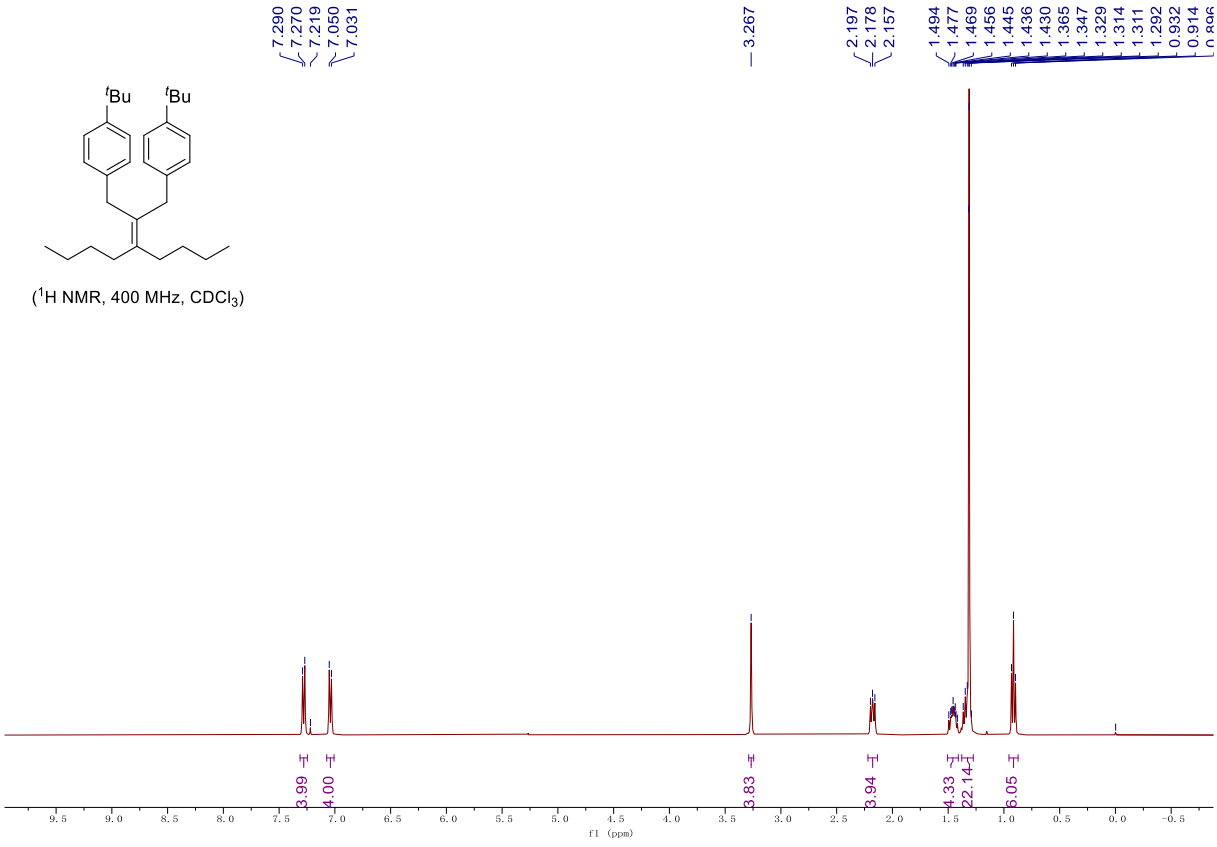
(^{13}C NMR, 151 MHz, $CDCl_3$)

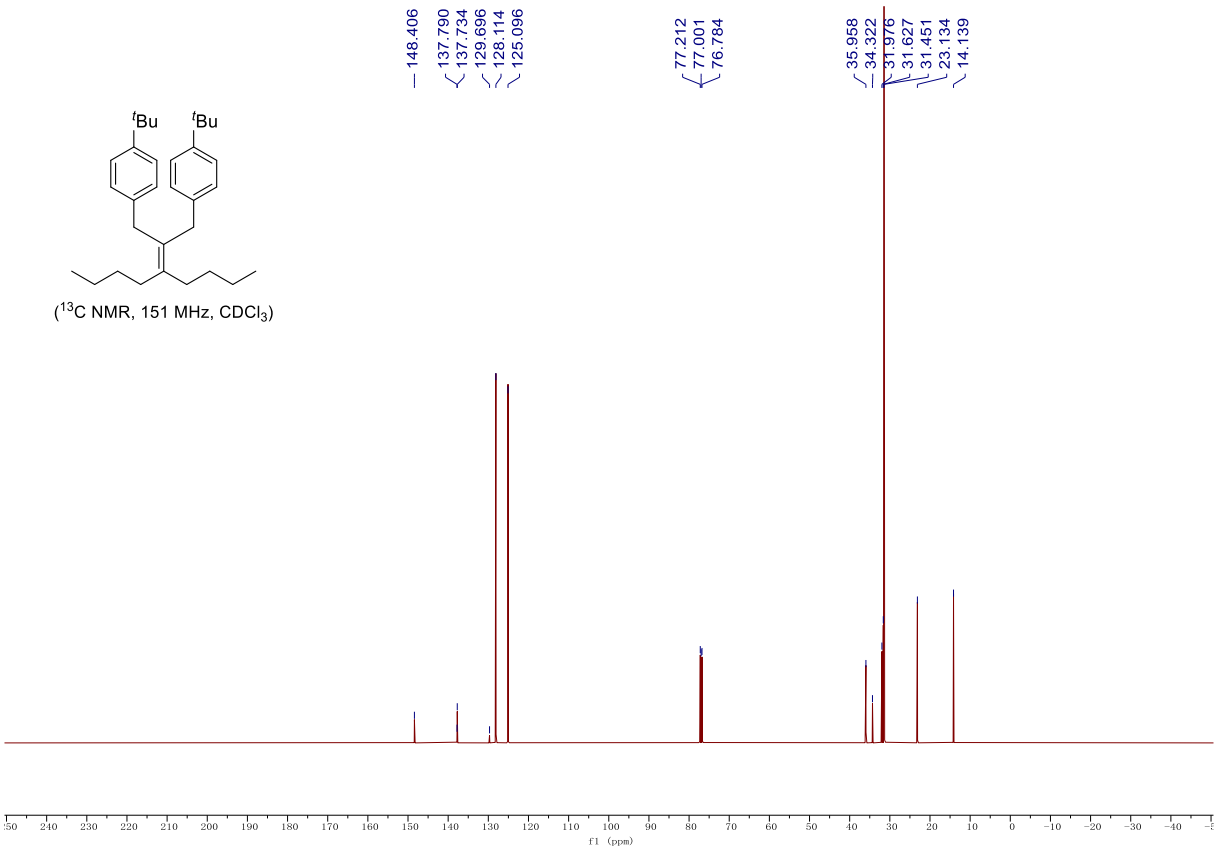


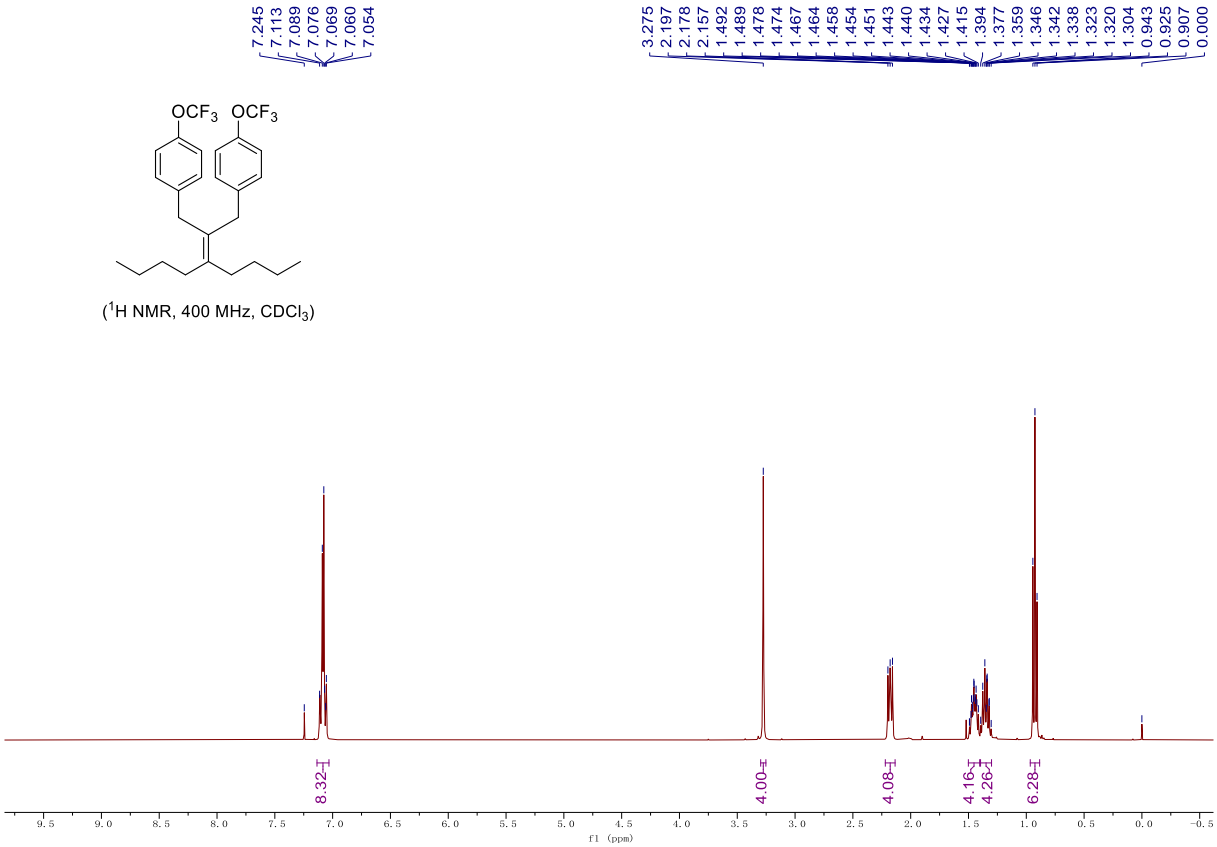
(^{1}H NMR, 400 MHz, $CDCl_3$)



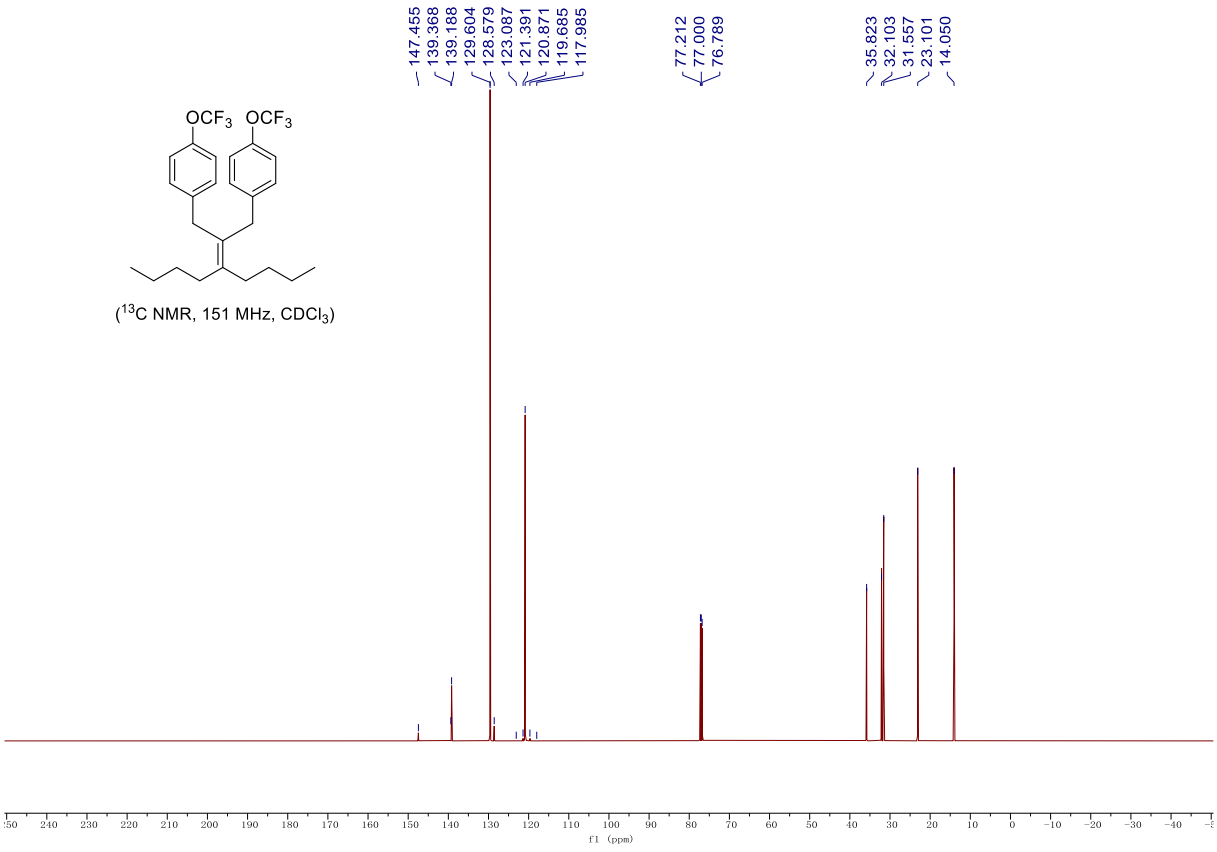
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.290
7.270
7.219
7.050
7.031
3.267
2.197
2.178
2.157
1.494
1.477
1.469
1.456
1.445
1.436
1.430
1.365
1.347
1.329
1.314
1.311
1.292
0.932
0.914
tBu
tBu
(1H NMR, 400 MHz, CDCl3)
3.99
4.00
3.83
3.94
4.33
22.14
6.05
f1 (ppm)

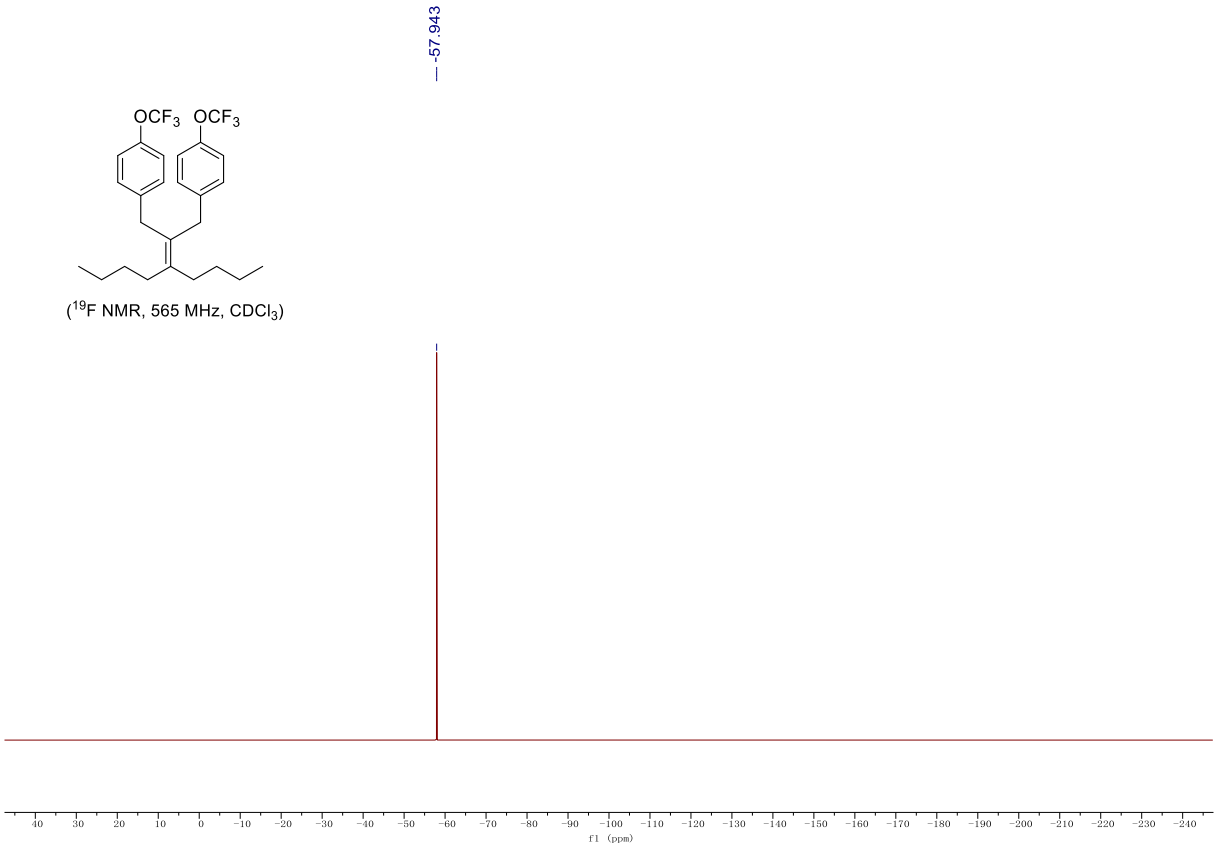

148.406
137.790
137.734
129.696
128.114
125.096
77.212
77.001
76.784
35.958
34.322
31.976
31.627
31.451
23.134
14.139
tBu
tBu
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



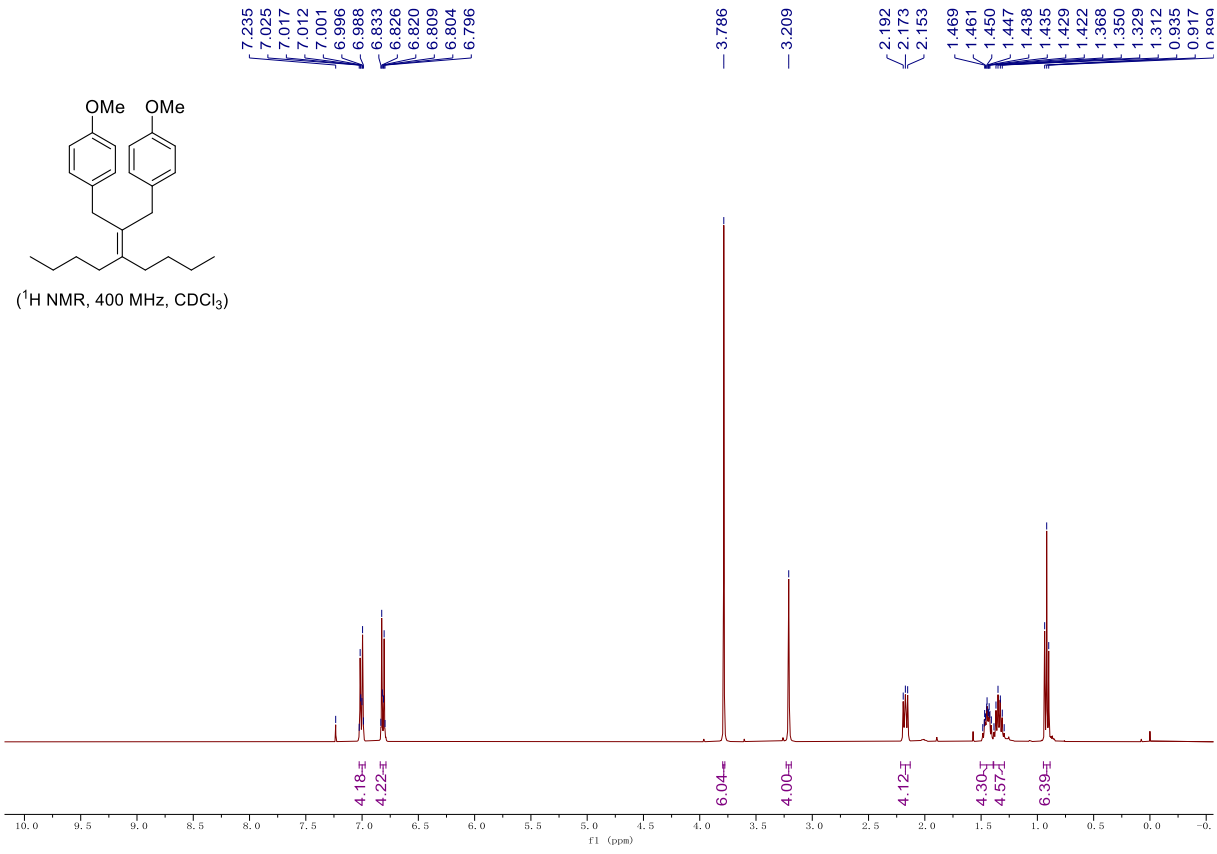
(^{1}H NMR, 400 MHz, $CDCl_3$)



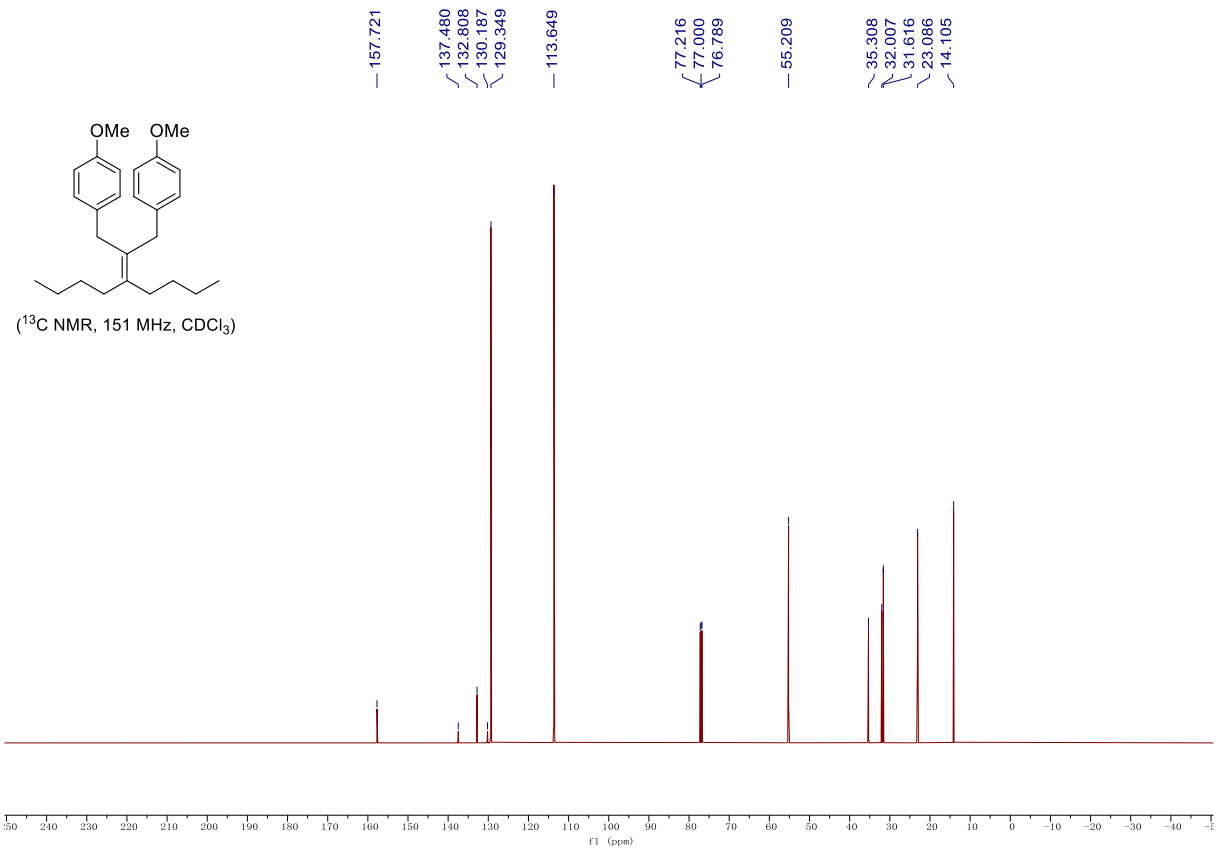
(^{13}C NMR, 151 MHz, $CDCl_3$)



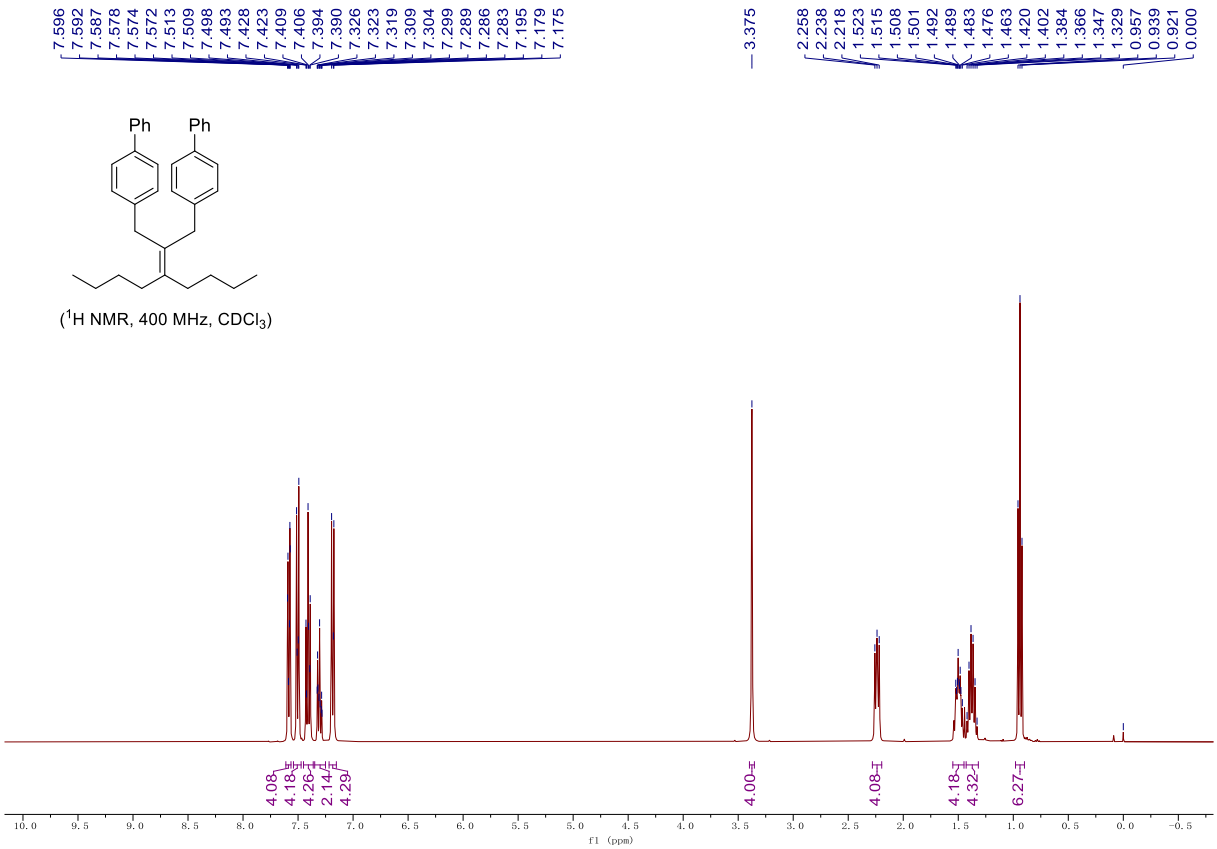
(^{19}F NMR, 565 MHz, $CDCl_3$)

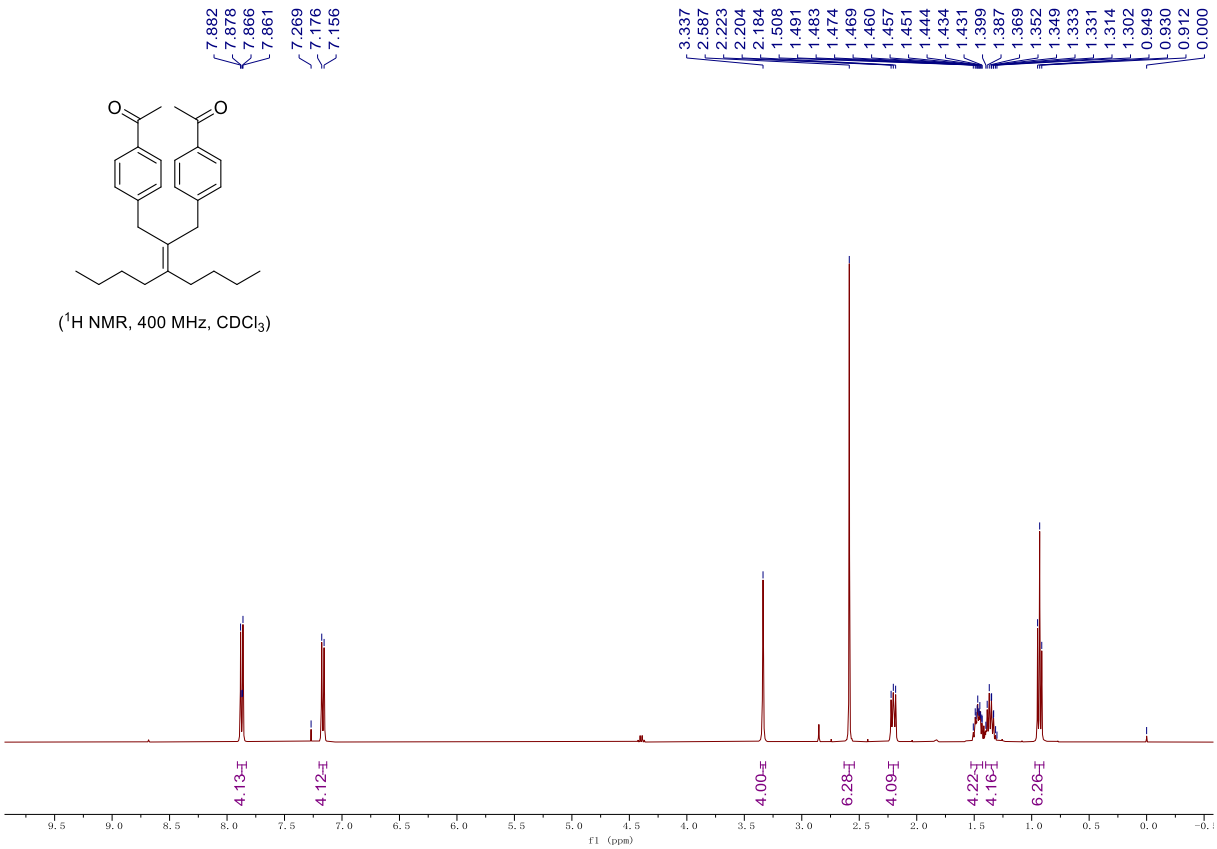


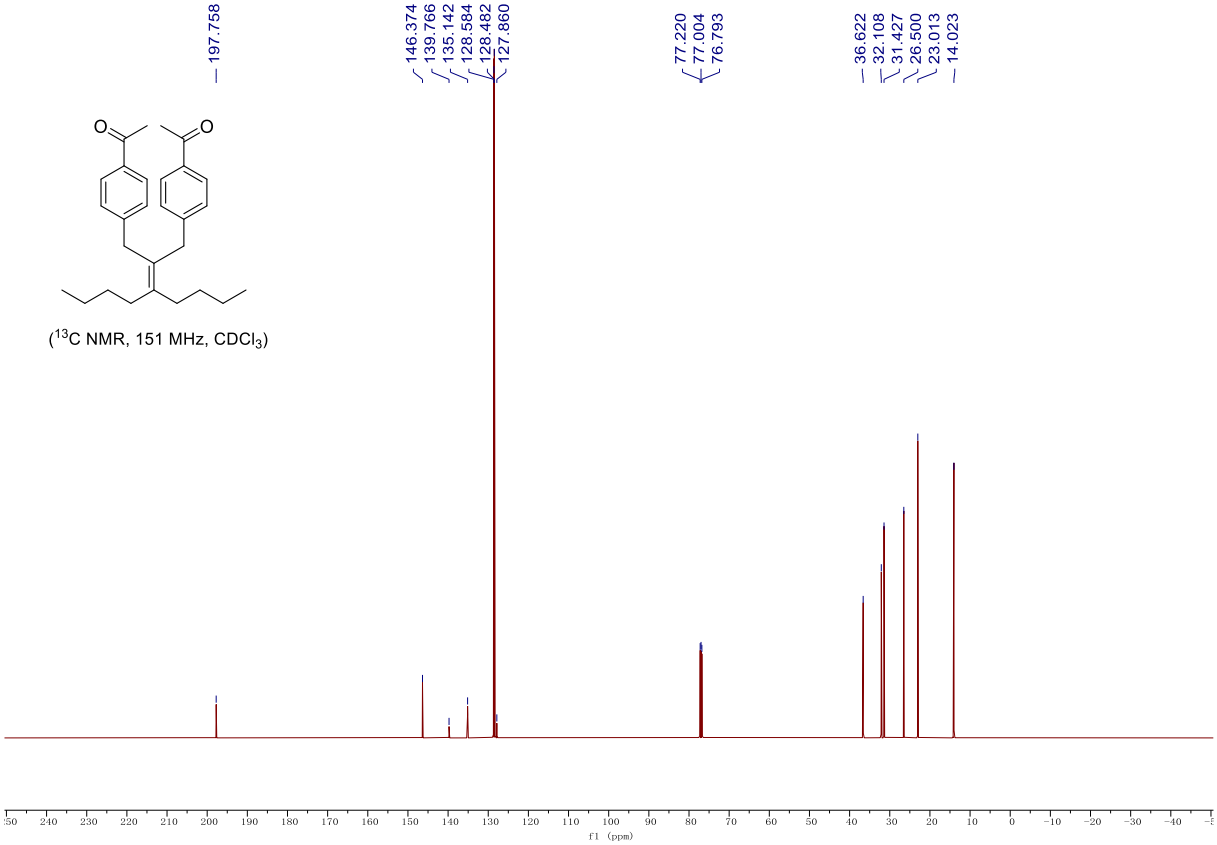
(^{1}H NMR, 400 MHz, $CDCl_3$)

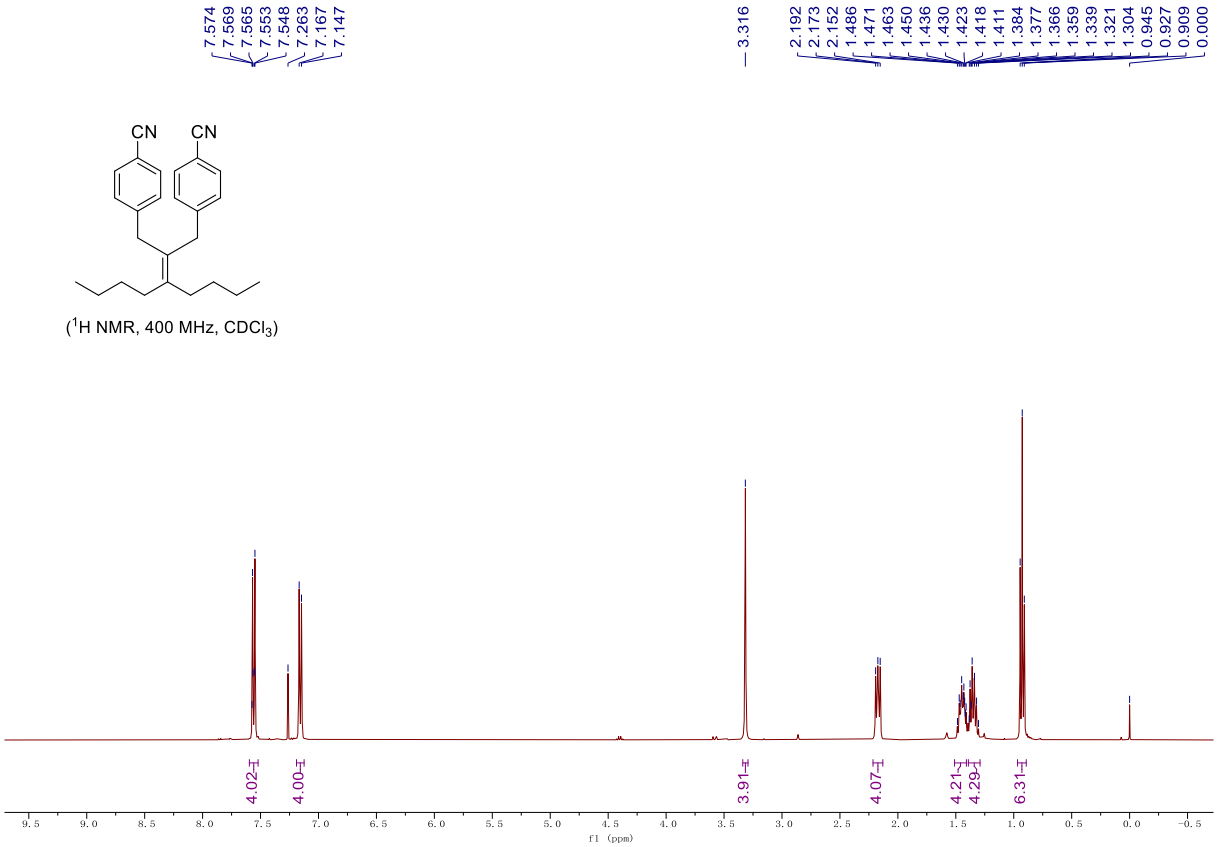


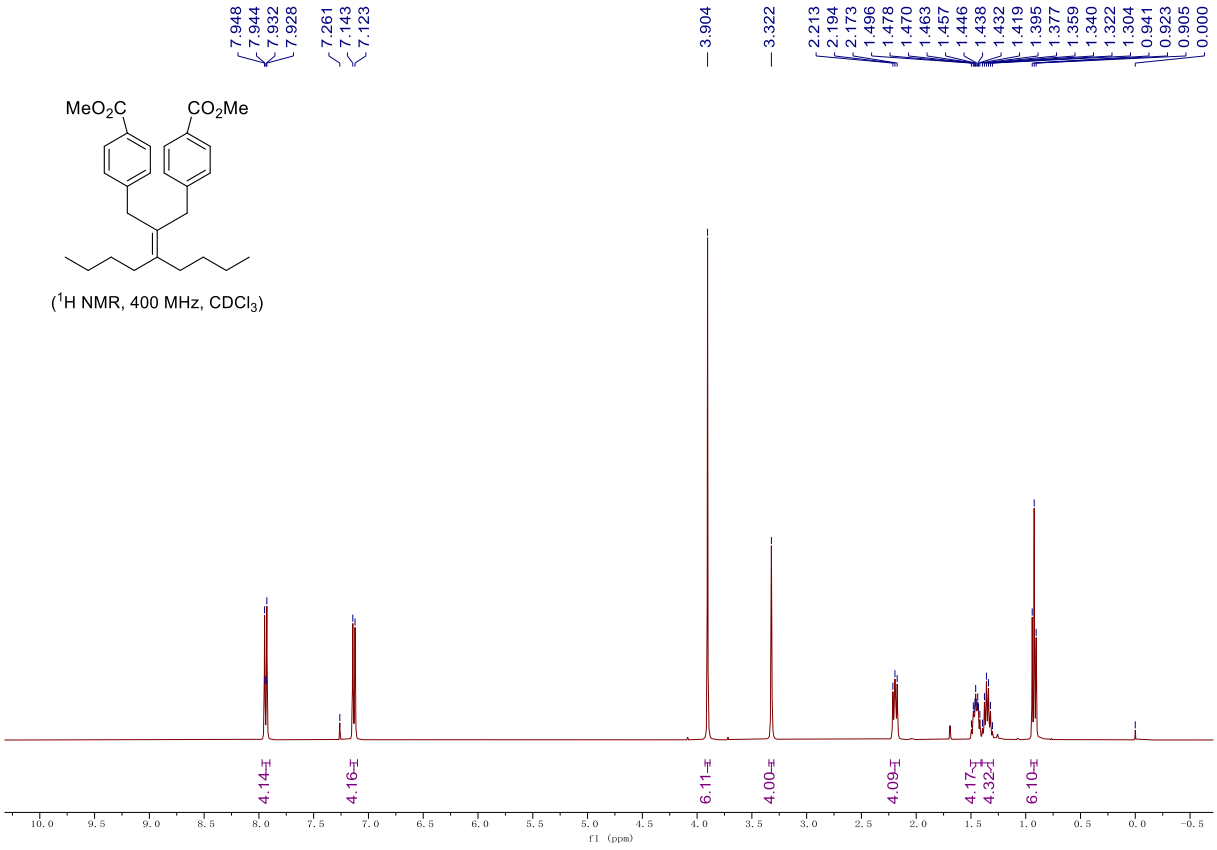
(^{13}C NMR, 151 MHz, $CDCl_3$)

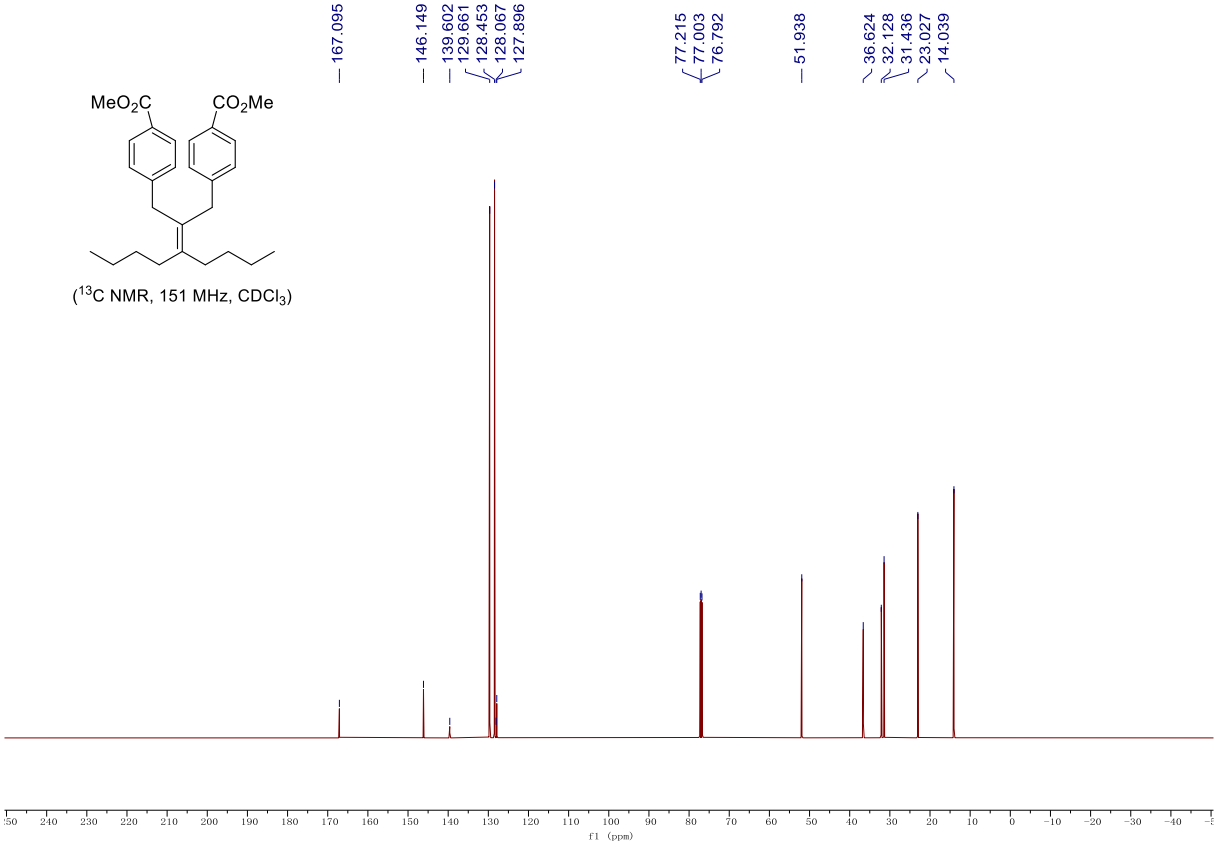

7.596
7.592
7.587
7.578
7.574
7.572
7.513
7.509
7.498
7.493
7.428
7.423
7.409
7.406
7.394
7.390
7.326
7.323
7.319
7.309
7.304
7.299
7.289
7.286
7.283
7.195
7.179
7.175
3.375
2.258
2.238
2.218
1.523
1.515
1.508
1.501
1.492
1.489
1.483
1.476
1.463
1.420
1.402
1.384
1.366
1.347
1.329
0.957
0.939
0.921
0.000
Ph
Ph
(1H NMR, 400 MHz, CDCl3)
4.08
4.18
4.26
2.14
4.29
4.00
4.08
4.18
4.32
6.27
f1 (ppm)
141.124
139.924
138.711
138.406
129.349
128.935
128.686
127.014
126.963
126.946
77.214
77.002
76.791
36.172
32.120
31.615
23.127
14.140
Ph
Ph
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

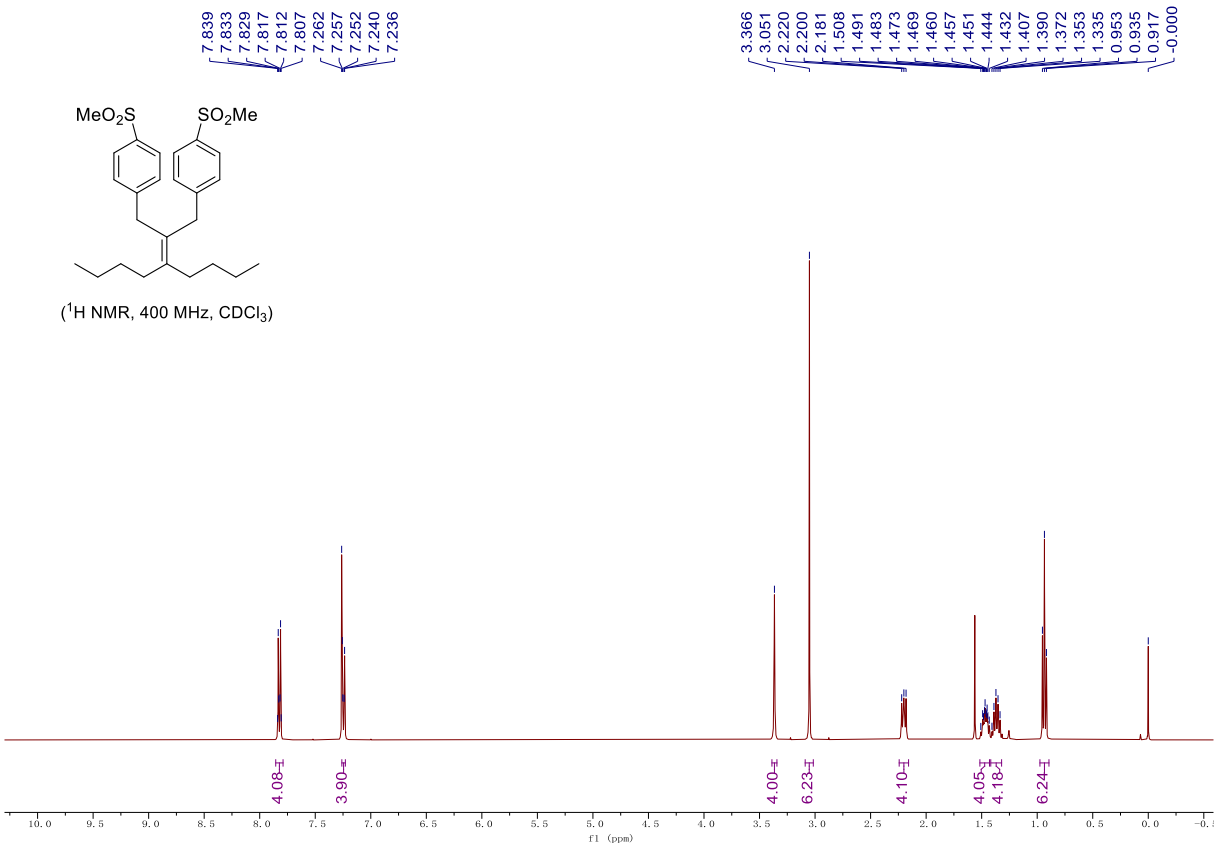

7.882
7.878
7.866
7.861
7.269
7.176
7.156
3.337
2.587
2.223
2.204
2.184
1.508
1.491
1.483
1.474
1.469
1.460
1.457
1.451
1.444
1.434
1.431
1.399
1.387
1.369
1.352
1.349
1.333
1.331
1.314
1.302
0.949
0.930
0.912
0.000
O
O
(^{1}H NMR, 400 MHz, $CDCl_3$)
4.13
4.12
4.00
6.28
4.09
4.22
4.16
6.26
f1 (ppm)

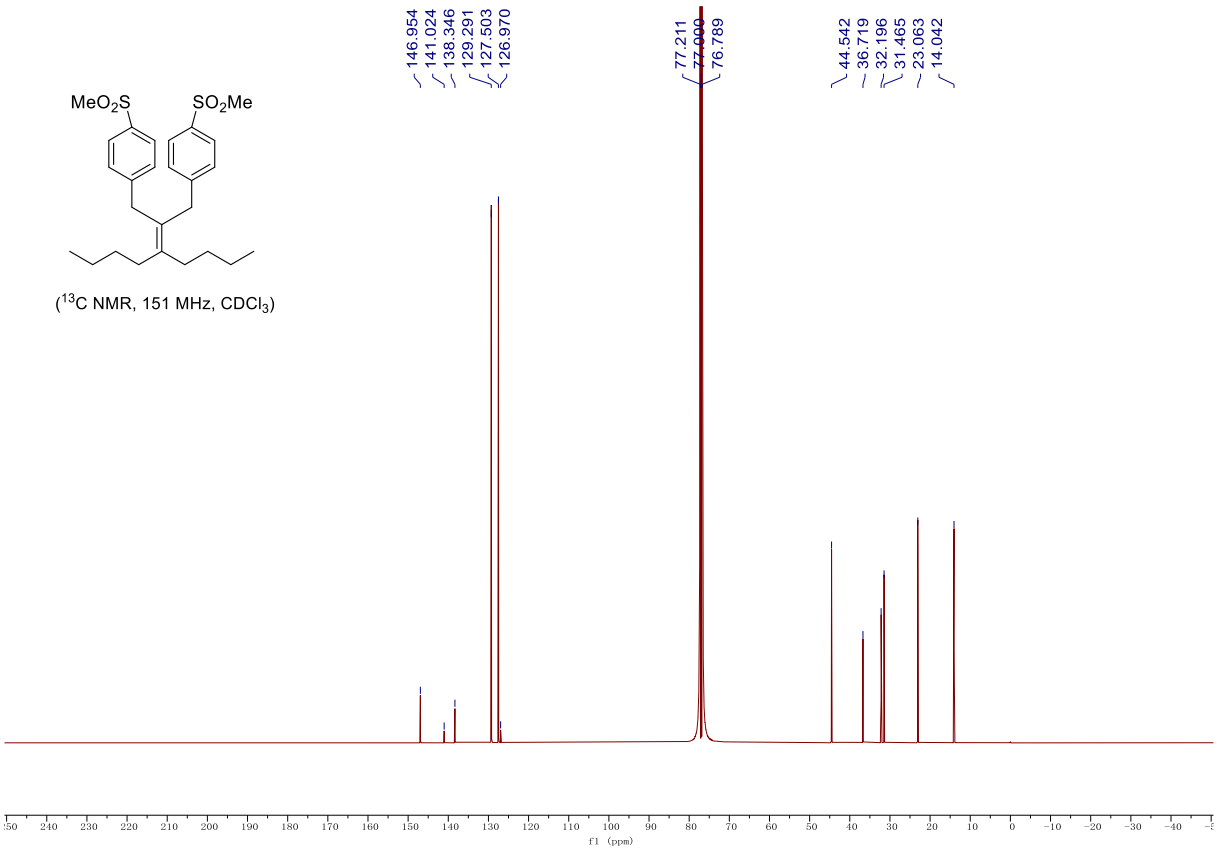

197.758
146.374
139.766
135.142
128.584
128.482
127.860
77.220
77.004
76.793
36.622
32.108
31.427
26.500
23.013
14.023
O
O
(^{13}C NMR, 151 MHz, $CDCl_3$)
f1 (ppm)

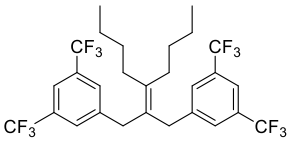

7.574
7.569
7.565
7.553
7.548
7.263
7.167
7.147
3.316
2.192
2.173
2.152
1.486
1.471
1.463
1.450
1.436
1.430
1.423
1.418
1.411
1.384
1.377
1.366
1.359
1.339
1.321
1.304
0.945
0.927
0.909
0.000
CN
CN
(1H NMR, 400 MHz, CDCl3)
4.02
4.00
3.91
4.07
4.21
4.29
6.31
f1 (ppm)
145.968
141.140
132.237
129.103
126.721
118.968
109.941
77.211
77.000
76.784
36.762
32.155
31.428
23.035
14.009
CN
CN
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)


7.948
7.944
7.932
7.928
7.261
7.143
7.123
3.904
3.322
2.213
2.194
2.173
1.496
1.478
1.470
1.463
1.457
1.446
1.438
1.432
1.419
1.395
1.377
1.359
1.340
1.322
1.304
0.941
0.923
0.905
0.000
MeO2C
CO2Me
(1H NMR, 400 MHz, CDCl3)
4.14
4.16
6.11
4.00
4.09
4.17
4.32
6.10
f1 (ppm)

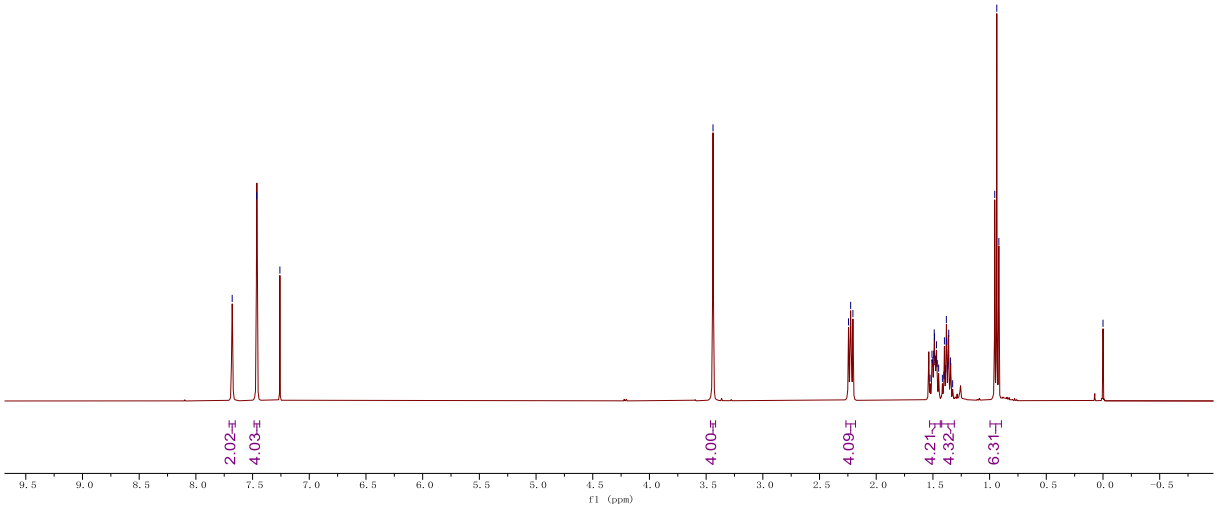

167.095
146.149
139.602
129.661
128.453
128.067
127.896
77.215
77.003
76.792
51.938
36.624
32.128
31.436
23.027
14.039
MeO2C
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

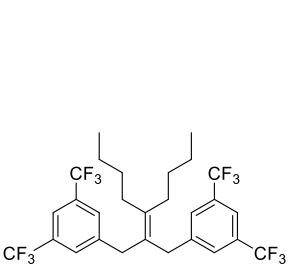

7.839
7.833
7.829
7.817
7.812
7.807
7.262
7.257
7.252
7.240
7.236
3.366
3.051
2.220
2.200
2.181
1.508
1.491
1.483
1.473
1.469
1.460
1.457
1.451
1.444
1.432
1.407
1.390
1.372
1.353
1.335
0.953
0.935
0.917
-0.000
MeO2S
SO2Me
(1H NMR, 400 MHz, CDCl3)
4.08
3.90
4.00
6.23
4.10
4.05
4.18
6.24
f1 (ppm)


146.954
141.024
138.346
129.291
127.503
126.970
77.211
77.000
76.789
44.542
36.719
32.196
31.465
23.063
14.042
MeO2S
SO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

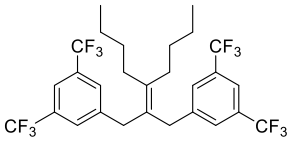


(^{1}H NMR, 400 MHz, $CDCl_3$)

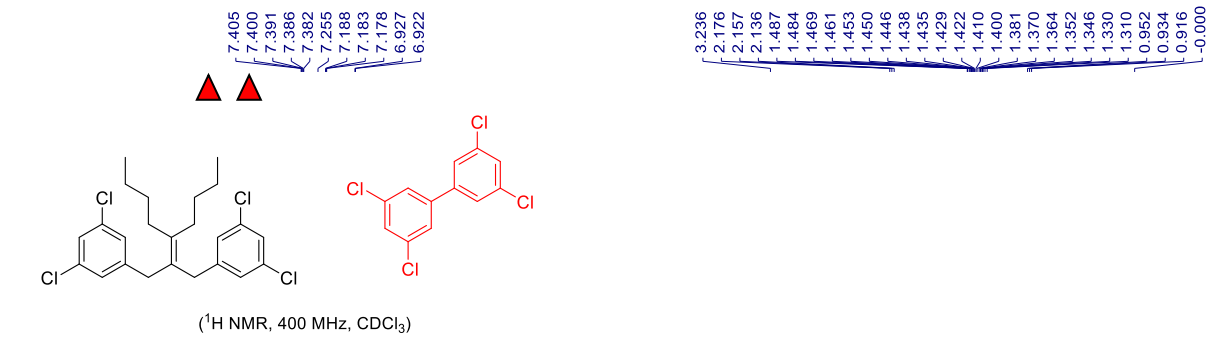




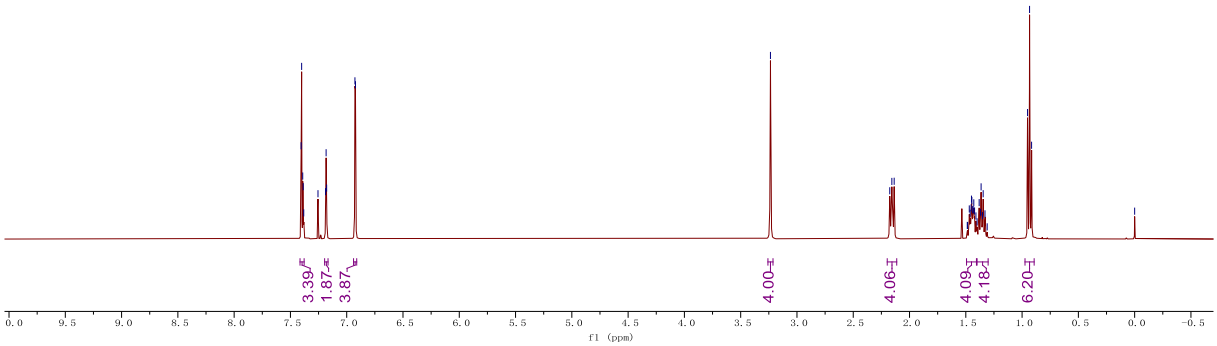
(^{13}C NMR, 151 MHz, $CDCl_3$)

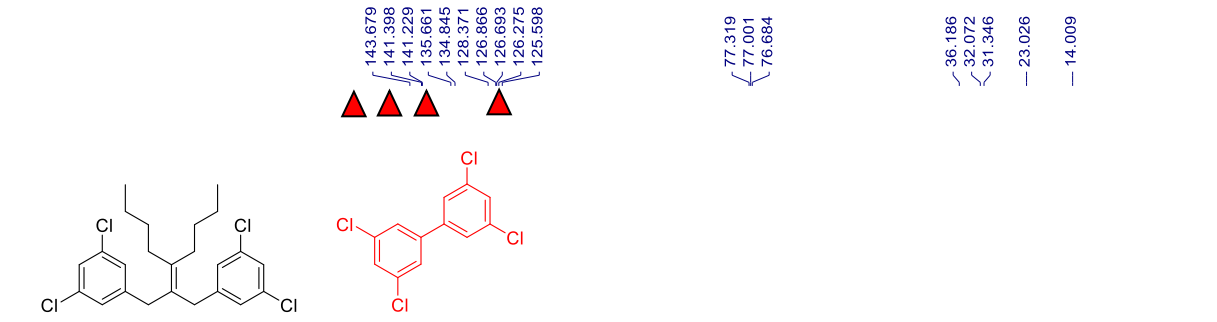


(^{19}F NMR, 565 MHz, $CDCl_3$)

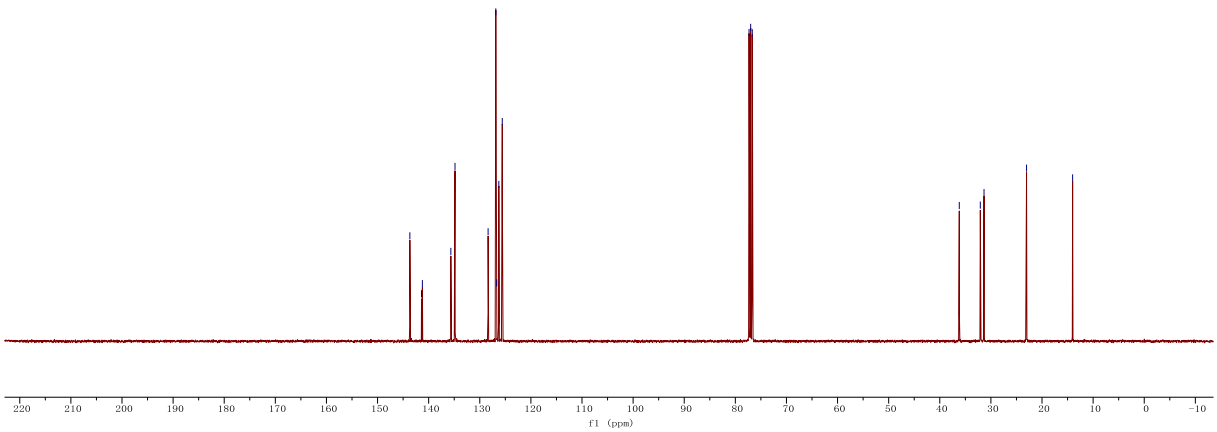


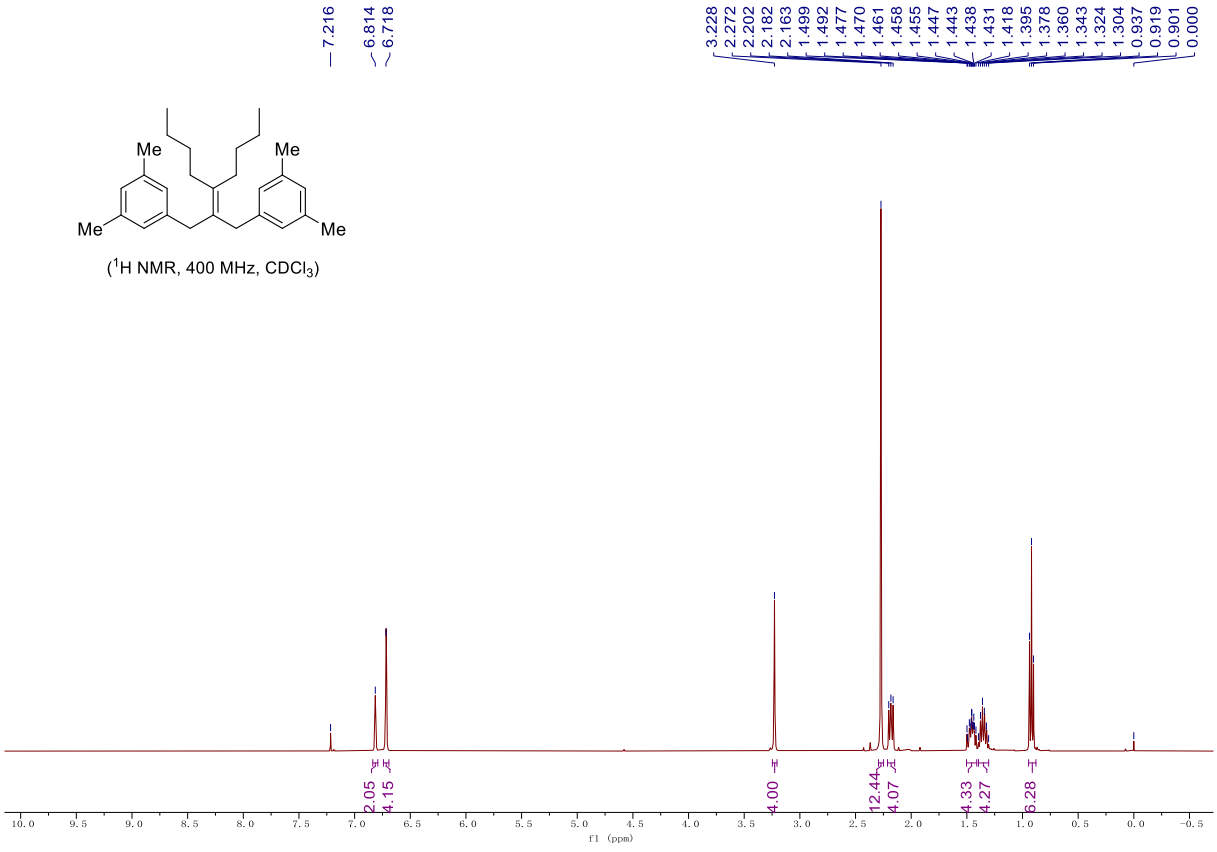
(^{1}H NMR, 400 MHz, $CDCl_3$)



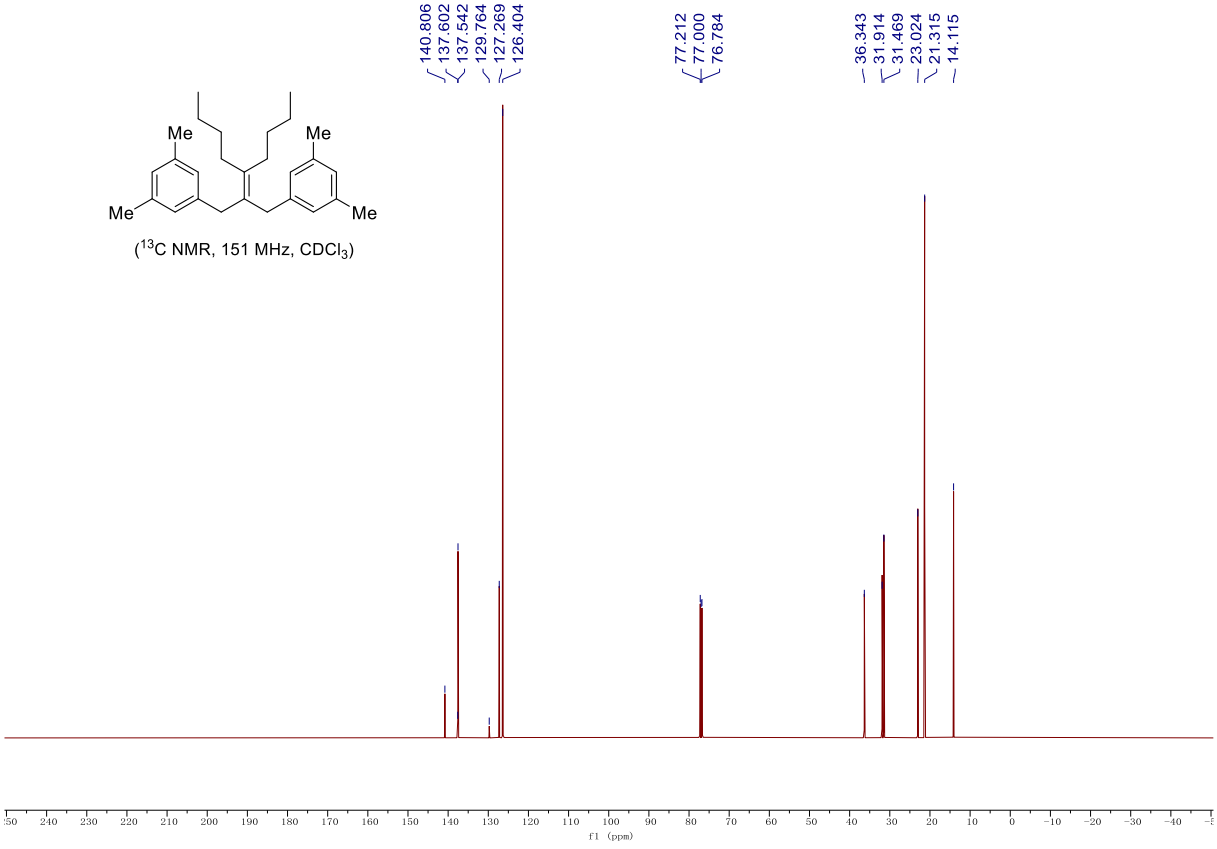


(^{13}C NMR, 151 MHz, $CDCl_3$)

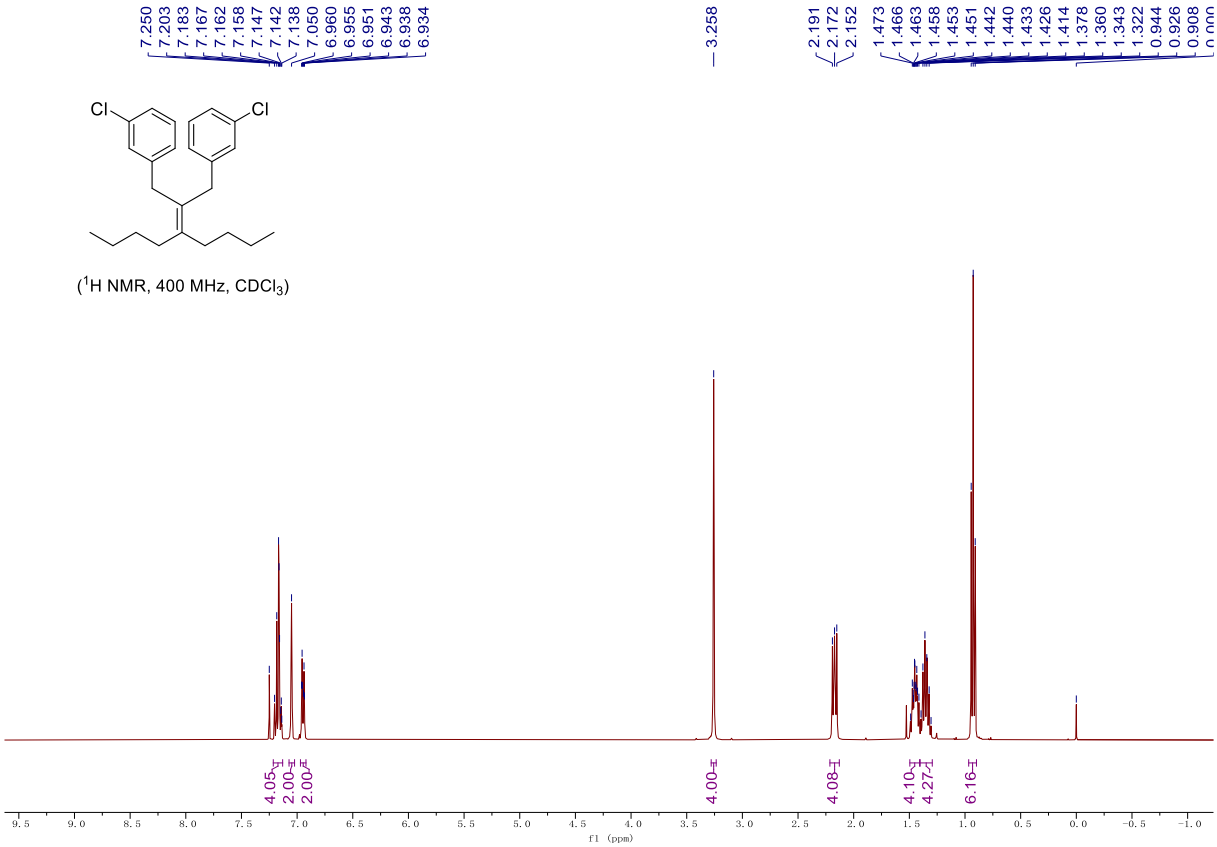


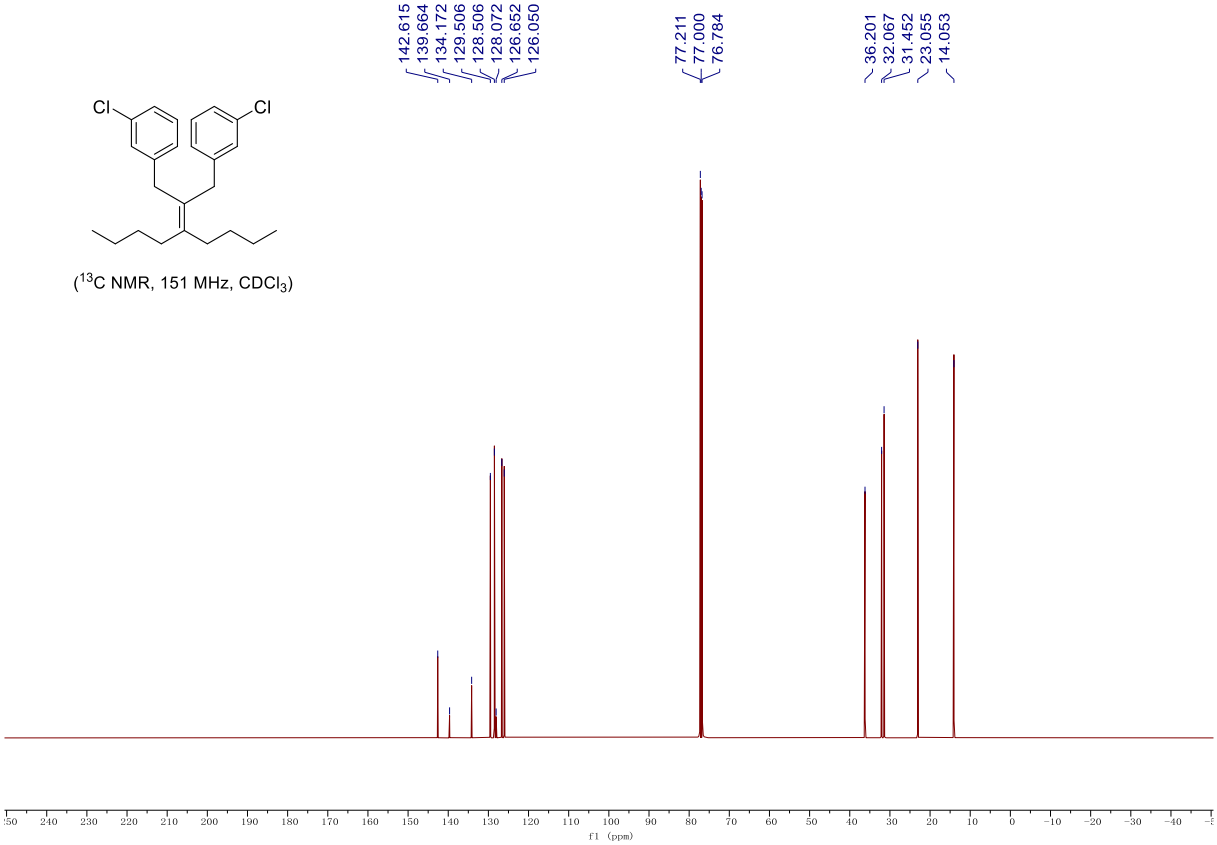


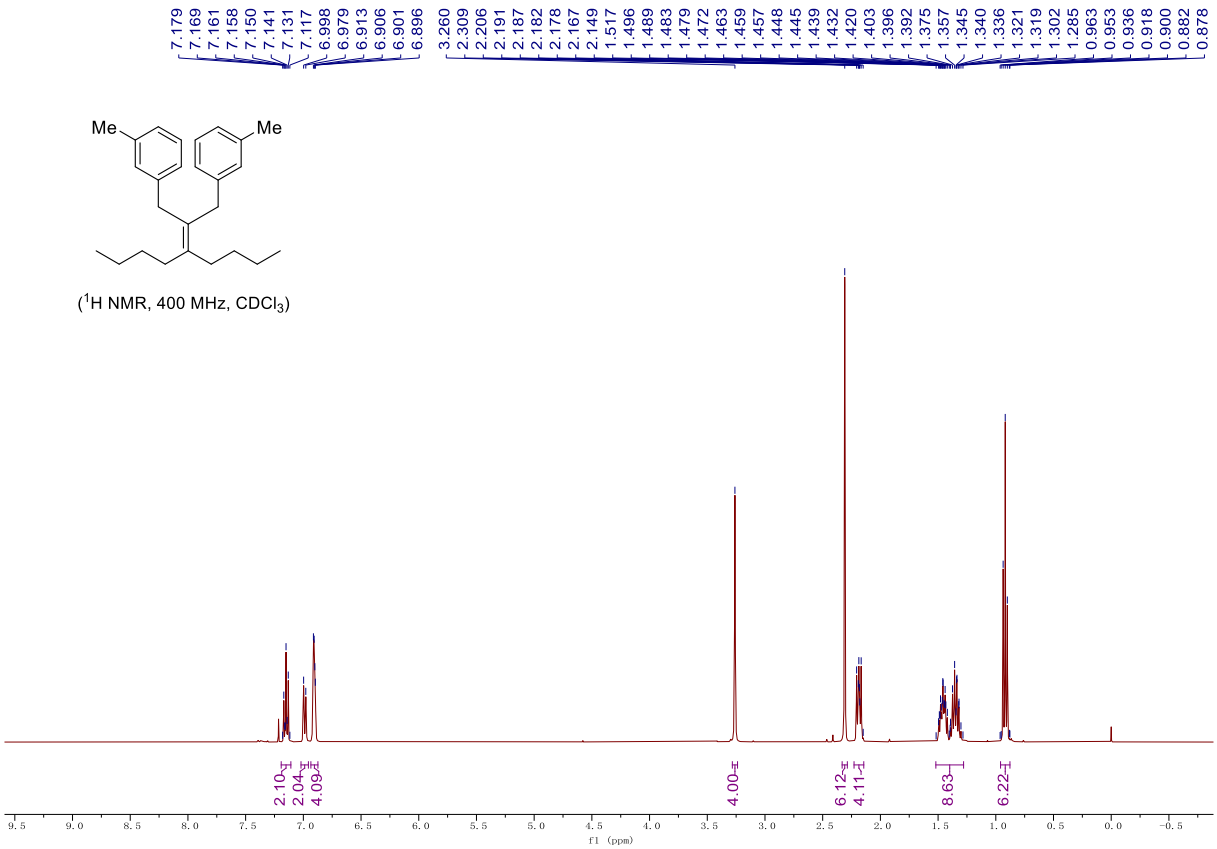
(^{1}H NMR, 400 MHz, $CDCl_3$)

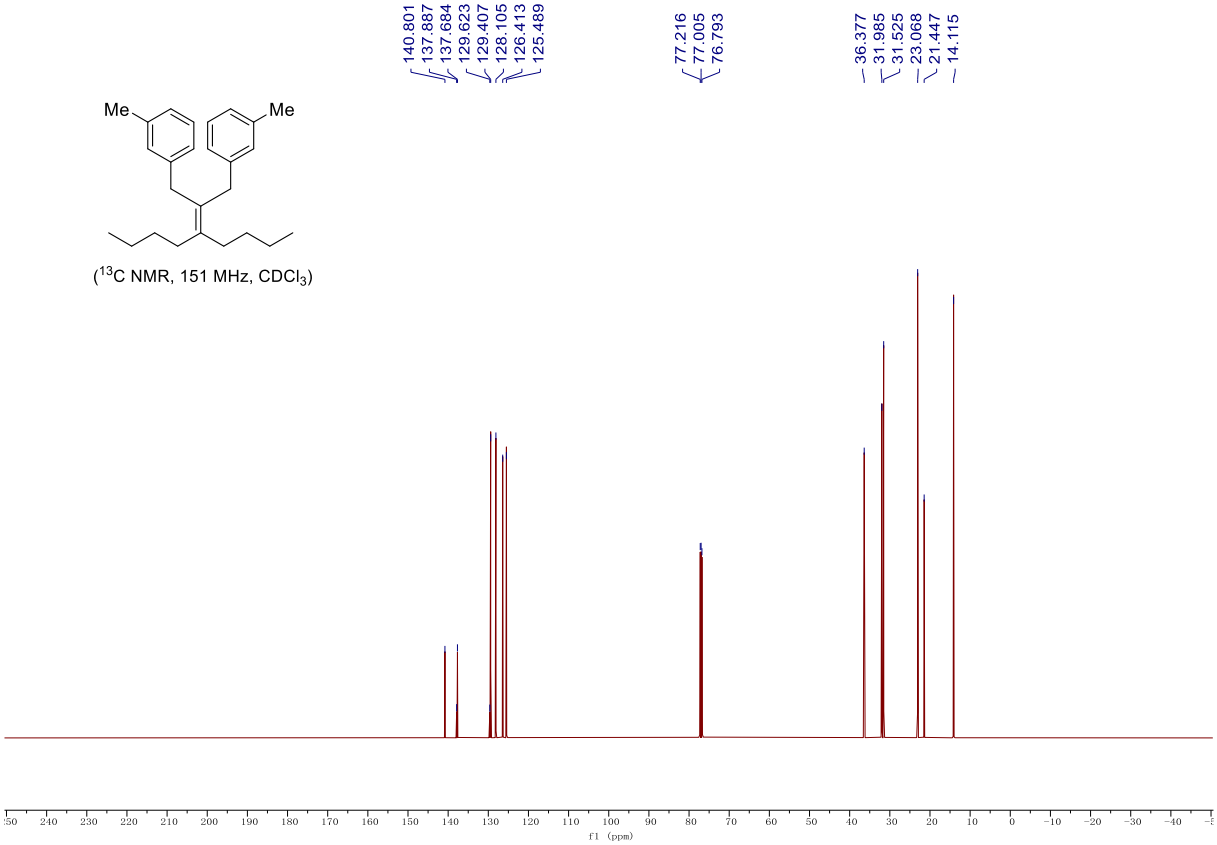


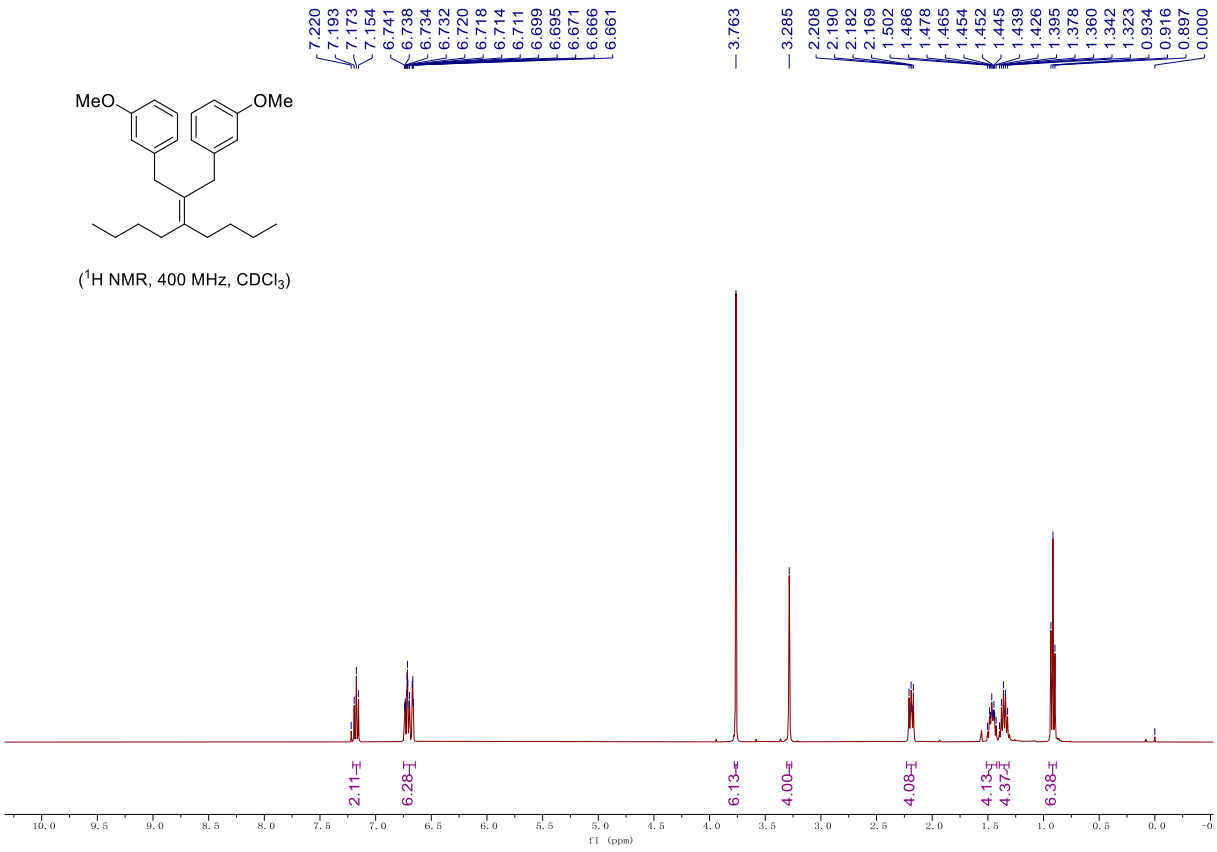
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.250
7.203
7.183
7.167
7.162
7.158
7.147
7.142
7.138
7.050
6.960
6.955
6.951
6.943
6.938
6.934
3.258
2.191
2.172
2.152
1.473
1.466
1.463
1.458
1.453
1.451
1.442
1.440
1.433
1.426
1.414
1.378
1.360
1.343
1.322
0.944
0.926
0.908
Cl
Cl
(1H NMR, 400 MHz, CDCl3)
4.05
2.00
2.00
4.00
4.08
4.10
4.27
6.16
f1 (ppm)

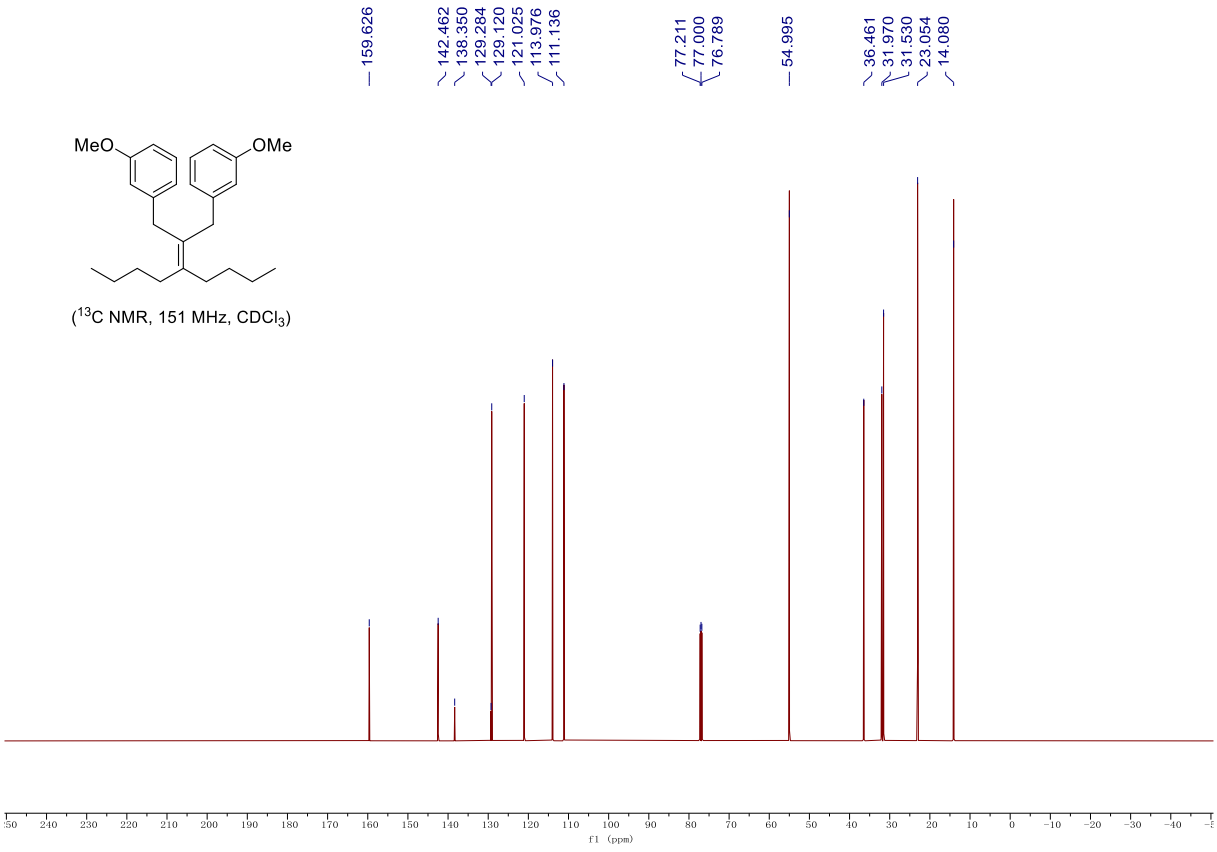

142.615
139.664
134.172
129.506
128.506
128.072
126.652
126.050
77.211
77.000
76.784
36.201
32.067
31.452
23.055
14.053
Cl
Cl
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)


7.179
7.169
7.161
7.158
7.150
7.141
7.131
7.117
6.998
6.979
6.913
6.906
6.901
6.896
3.260
2.309
2.206
2.191
2.187
2.182
2.178
2.167
2.149
1.517
1.496
1.489
1.483
1.479
1.472
1.463
1.459
1.457
1.448
1.445
1.439
1.432
1.420
1.403
1.396
1.392
1.375
1.357
1.345
1.340
1.336
1.321
1.319
1.302
1.285
0.963
0.953
0.936
0.918
0.900
0.882
0.878
Me
Me
(1H NMR, 400 MHz, CDCl3)
2.10
2.04
4.09
4.00
6.12
4.11
8.63
6.22
f1 (ppm)

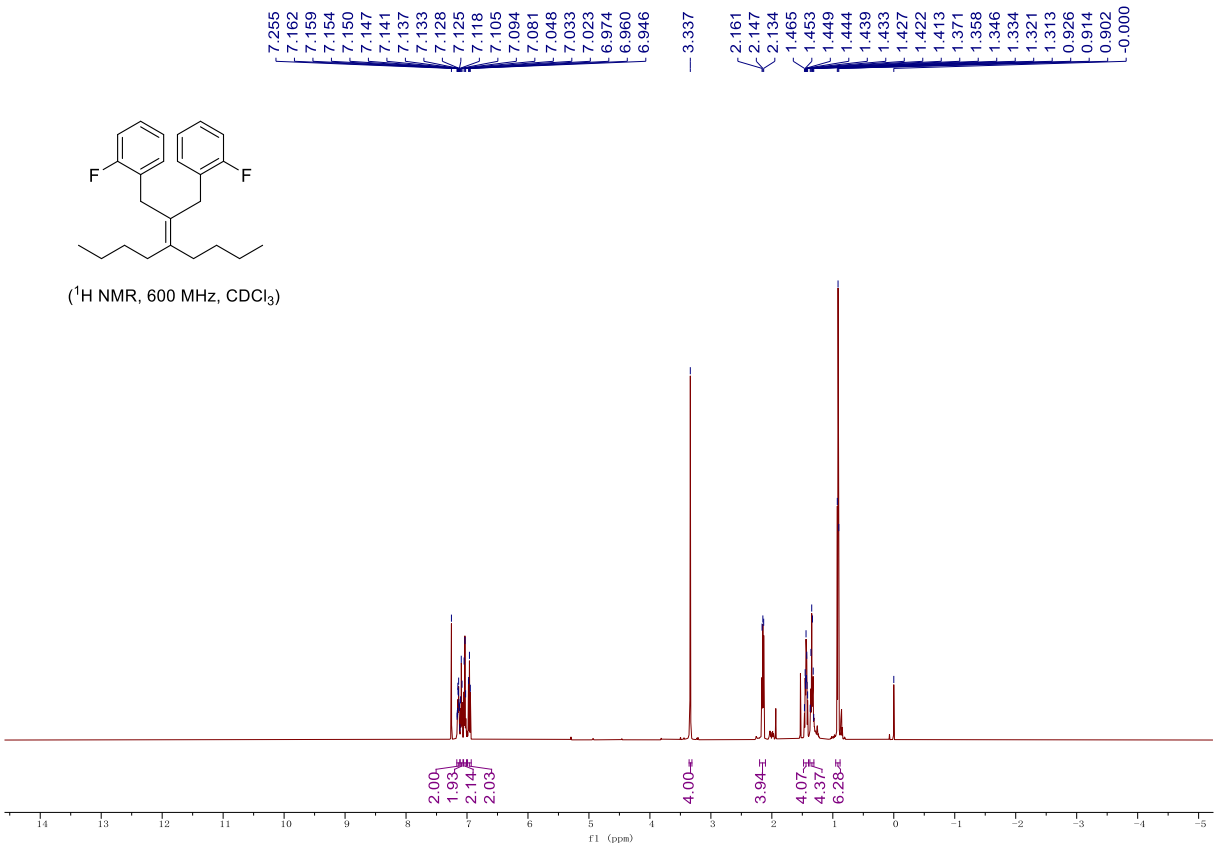

140.801
137.887
137.684
129.623
129.407
128.105
126.413
125.489
77.216
77.005
76.793
36.377
31.985
31.525
23.068
21.447
14.115
Me
Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

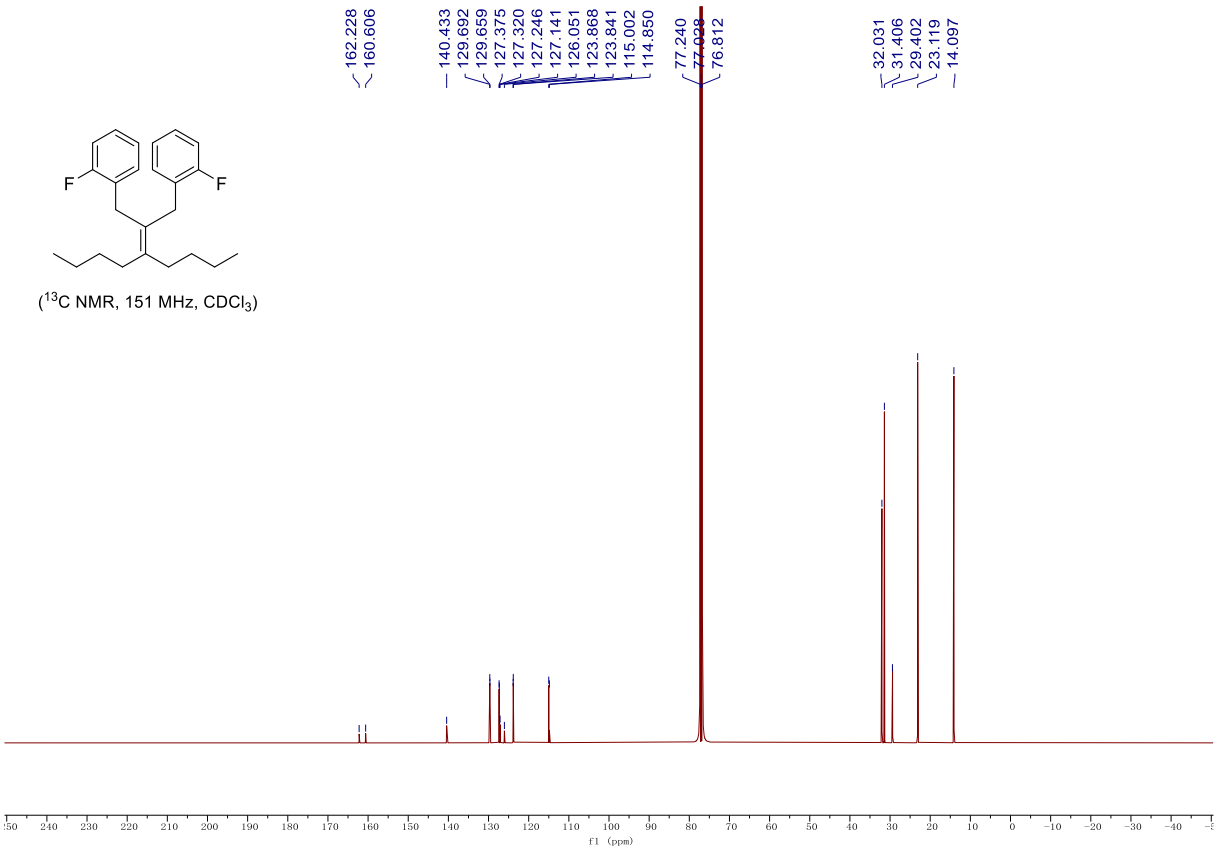


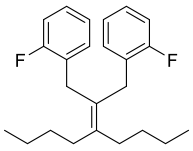
(^{1}H NMR, 400 MHz, $CDCl_3$)



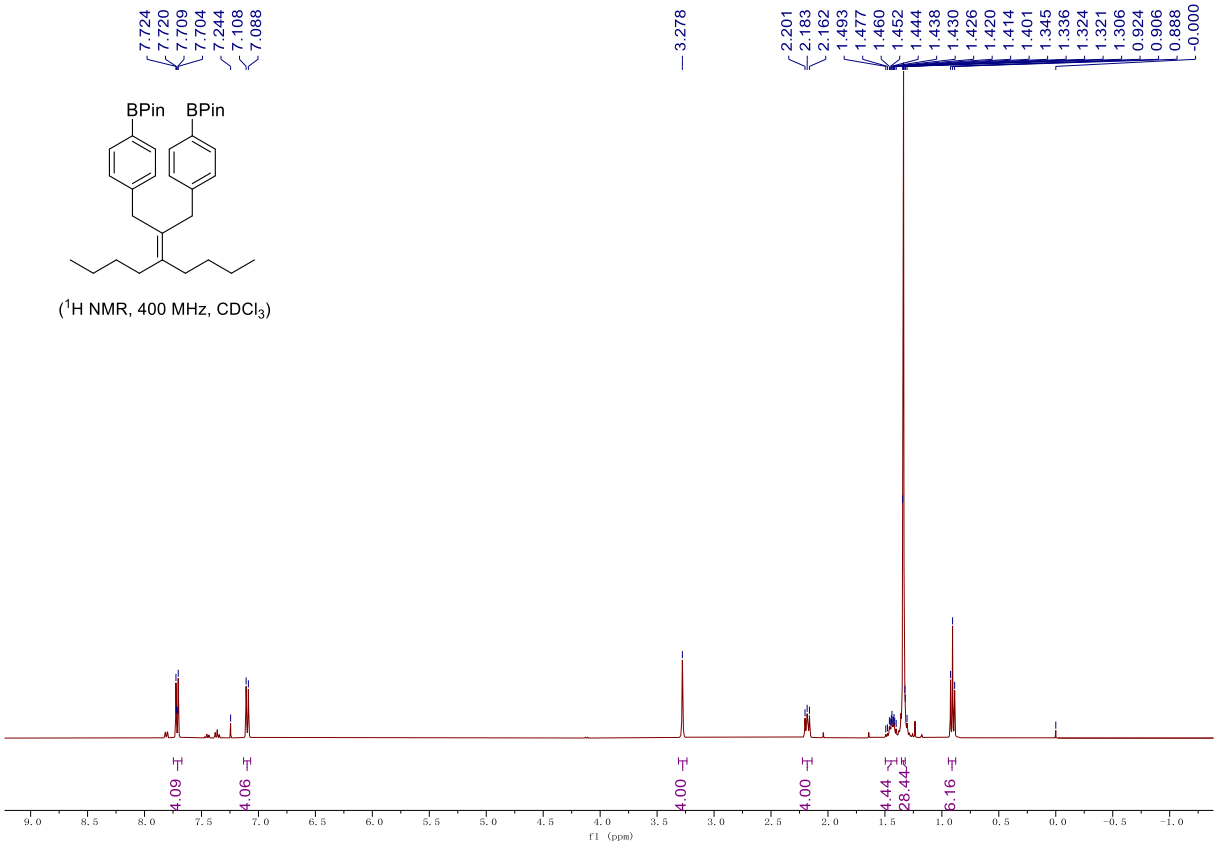
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.255
7.162
7.159
7.154
7.150
7.147
7.141
7.137
7.133
7.128
7.125
7.118
7.105
7.094
7.081
7.048
7.033
7.023
6.974
6.960
6.946
3.337
2.161
2.147
2.134
1.465
1.453
1.449
1.444
1.439
1.433
1.427
1.422
1.413
1.371
1.358
1.346
1.334
1.321
1.313
0.926
0.914
0.902
-0.000
F
F
(1H NMR, 600 MHz, CDCl3)
2.00
1.93
2.14
2.03
4.00
3.94
4.07
4.37
6.28
f1 (ppm)

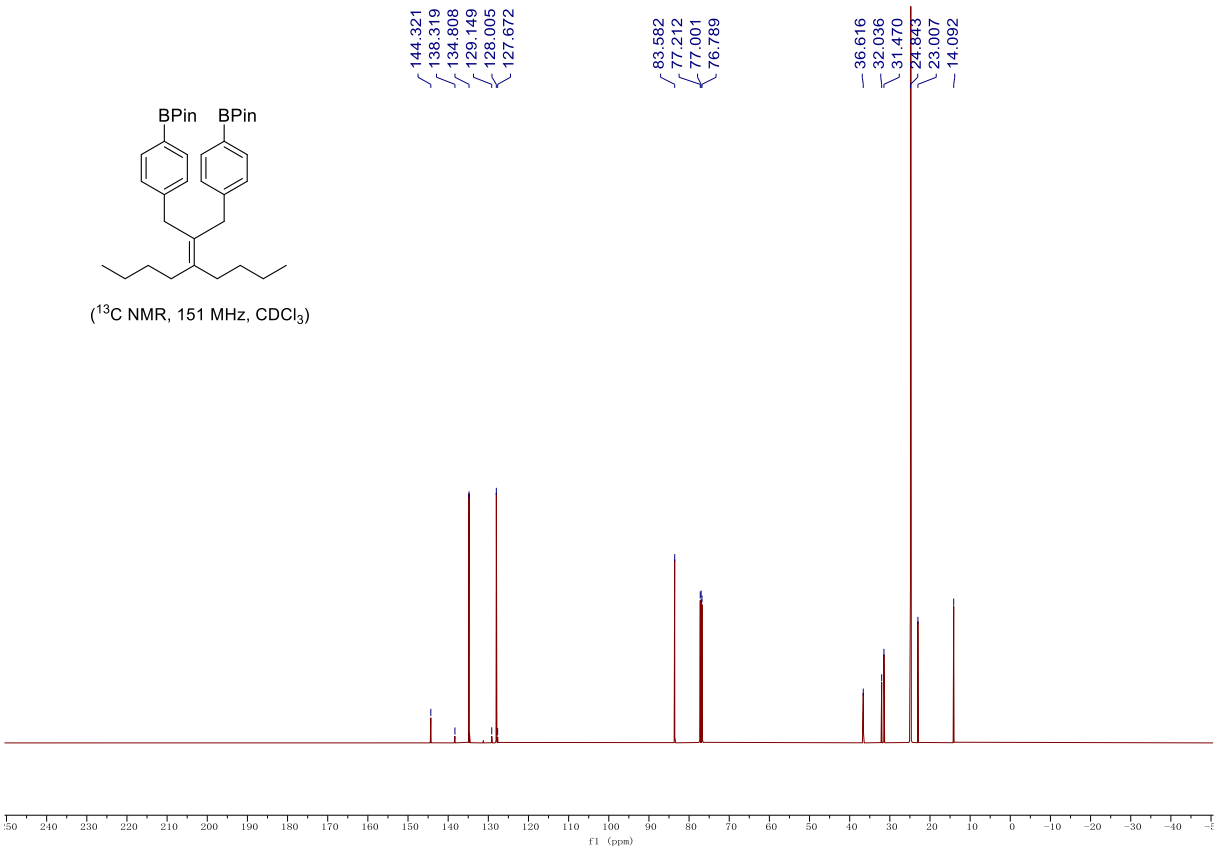

162.228
160.606
140.433
129.692
129.659
127.375
127.320
127.246
127.141
126.051
123.868
123.841
115.002
114.850
77.240
77.028
76.812
32.031
31.406
29.402
23.119
14.097
F
F
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



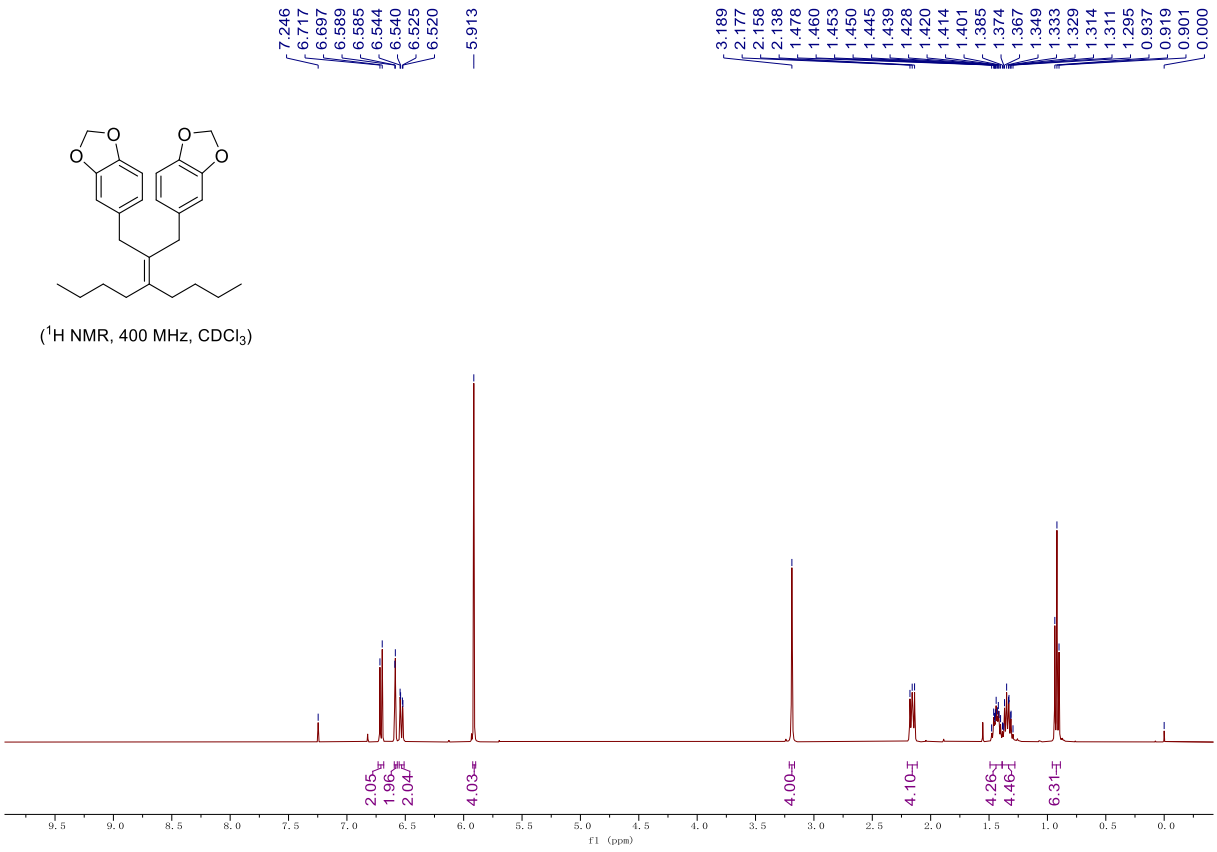
(^{19}F NMR, 565 MHz, $CDCl_3$)



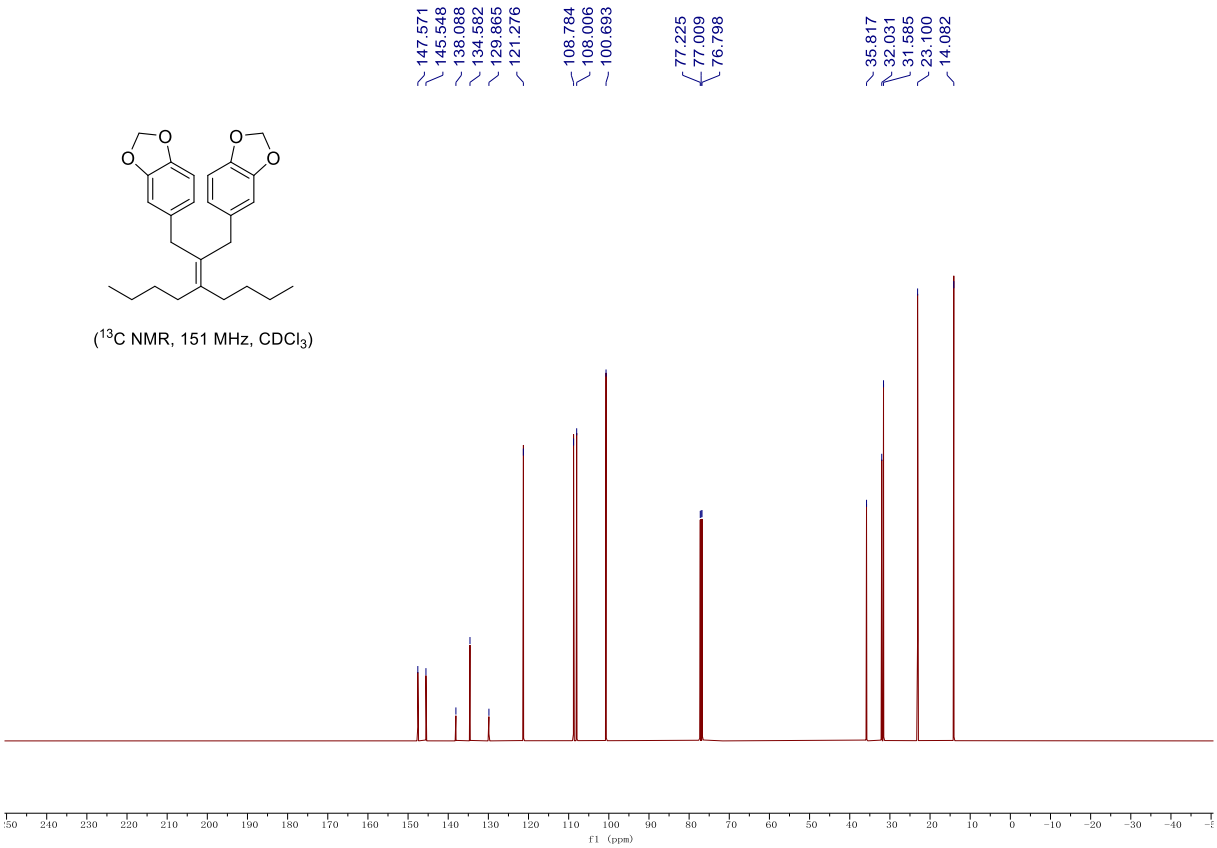
(^{1}H NMR, 400 MHz, $CDCl_3$)



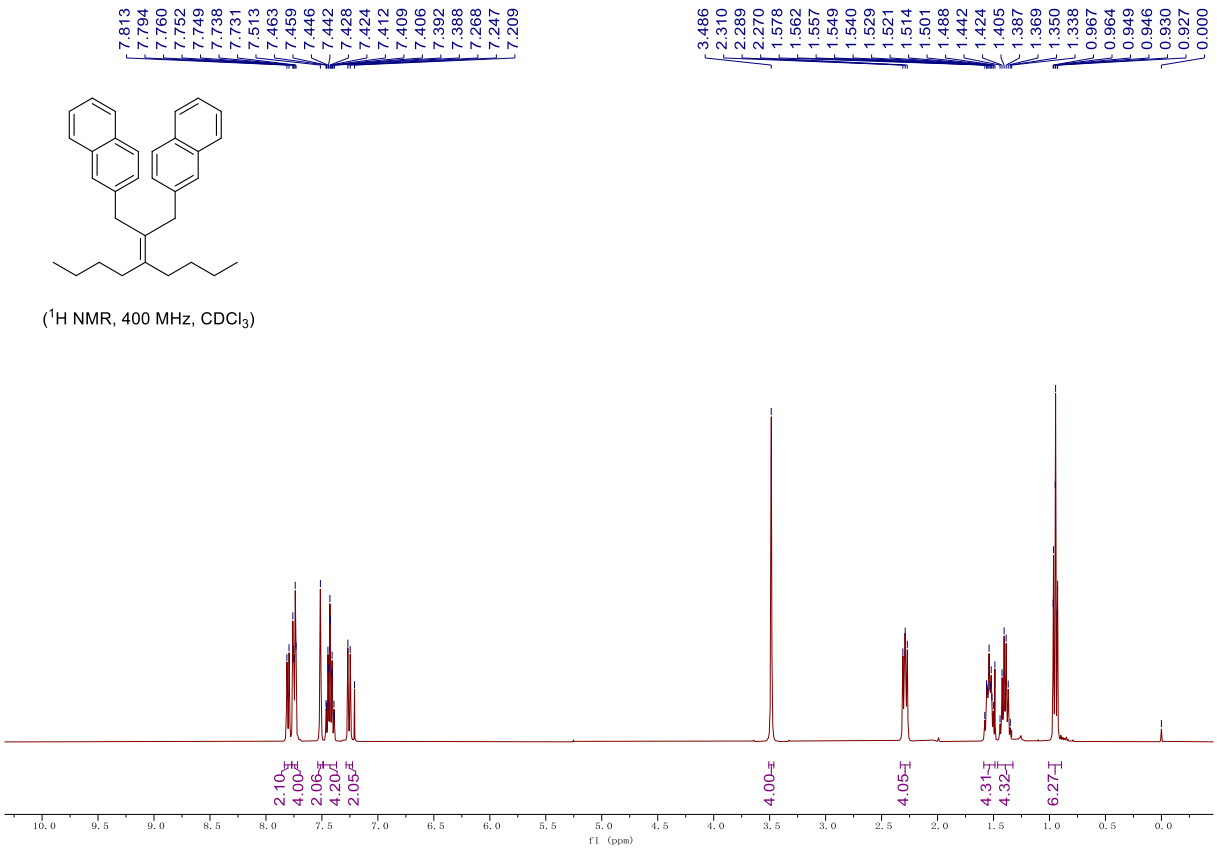
(^{13}C NMR, 151 MHz, $CDCl_3$)

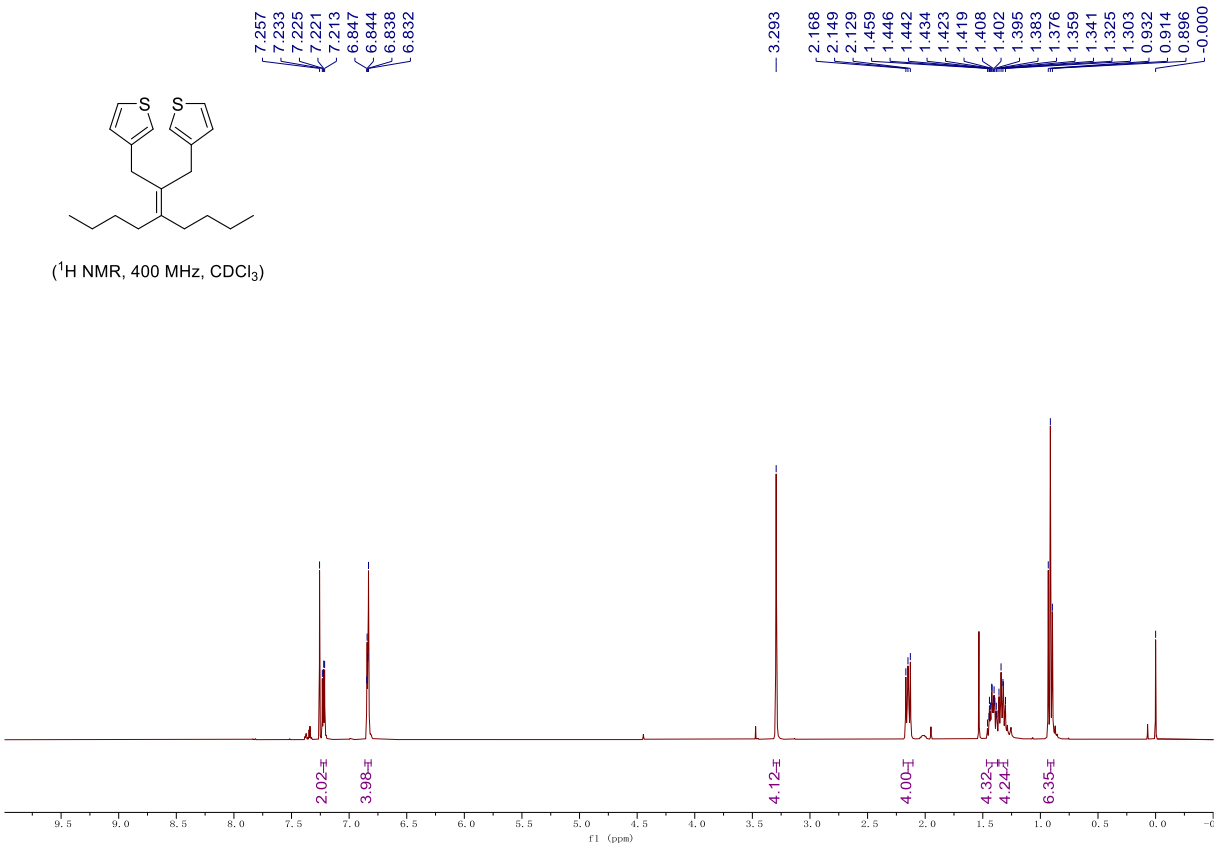


(^{1}H NMR, 400 MHz, $CDCl_3$)

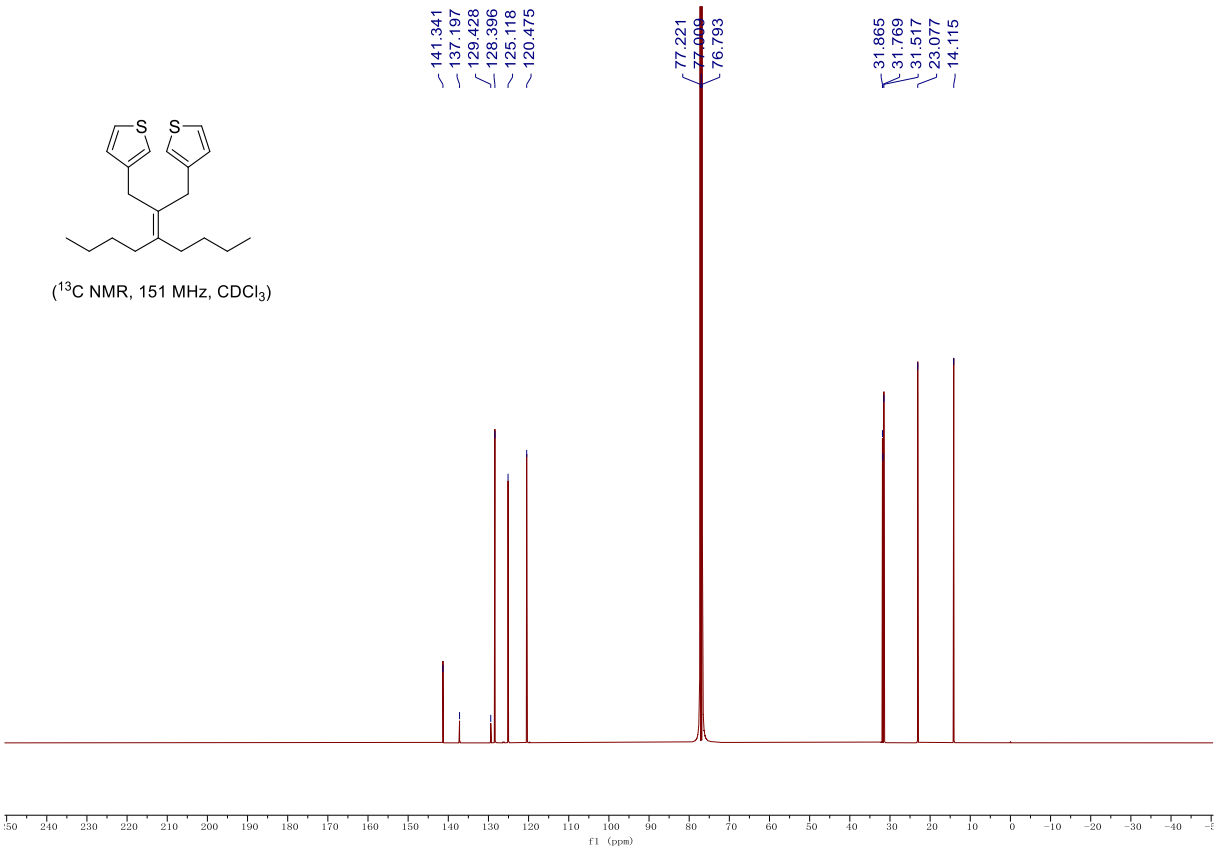


(^{13}C NMR, 151 MHz, $CDCl_3$)

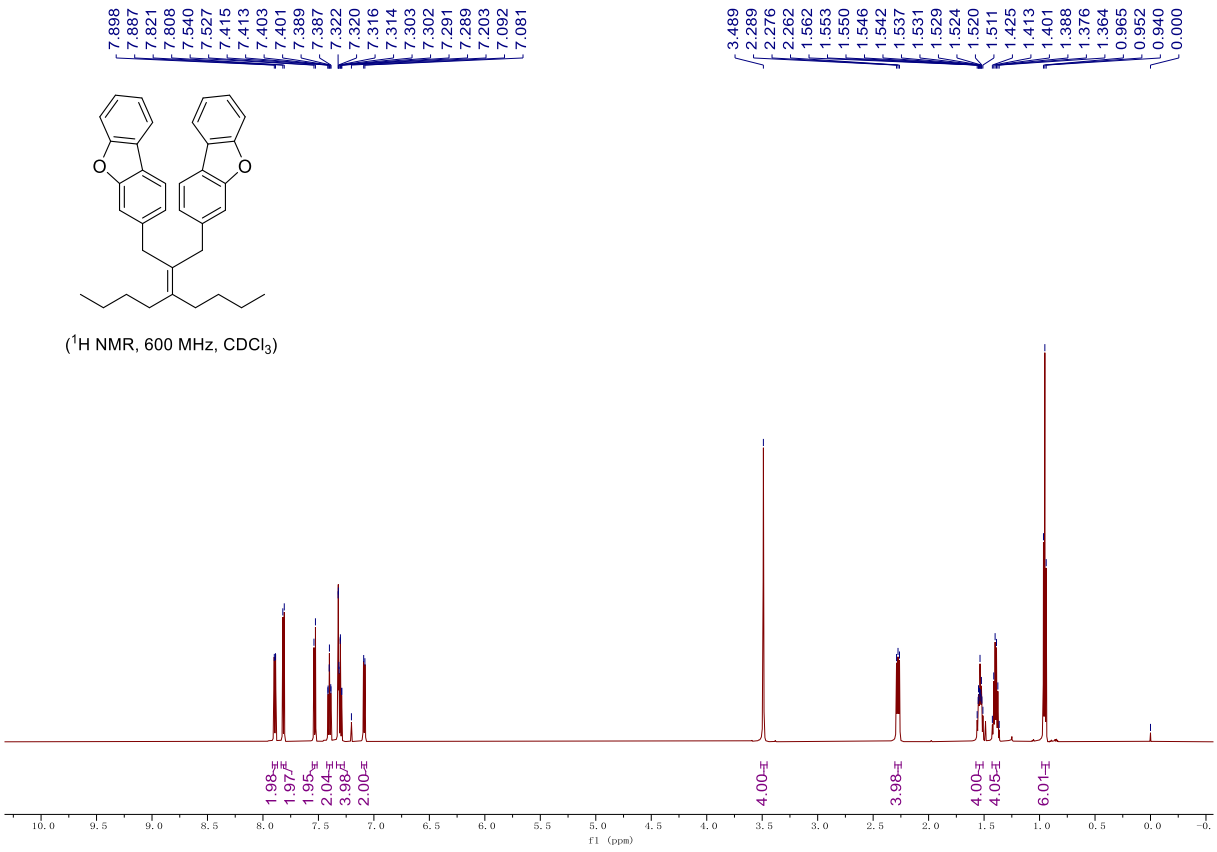

7.813
7.794
7.760
7.752
7.749
7.738
7.731
7.513
7.463
7.459
7.446
7.442
7.428
7.424
7.412
7.409
7.406
7.392
7.388
7.268
7.247
7.209
3.486
2.310
2.289
2.270
1.578
1.562
1.557
1.549
1.540
1.529
1.521
1.514
1.501
1.488
1.442
1.424
1.405
1.387
1.369
1.350
1.338
0.967
0.964
0.949
0.946
0.930
0.927
0.000
(1H NMR, 400 MHz, CDCl3)
2.10
4.00
2.06
4.20
2.05
4.00
4.05
4.31
4.32
6.27
f1 (ppm)
138.676
138.341
133.624
132.082
129.285
127.793
127.577
127.475
127.425
126.607
125.798
125.071
77.216
77.005
76.789
36.630
32.177
31.616
23.104
14.141
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



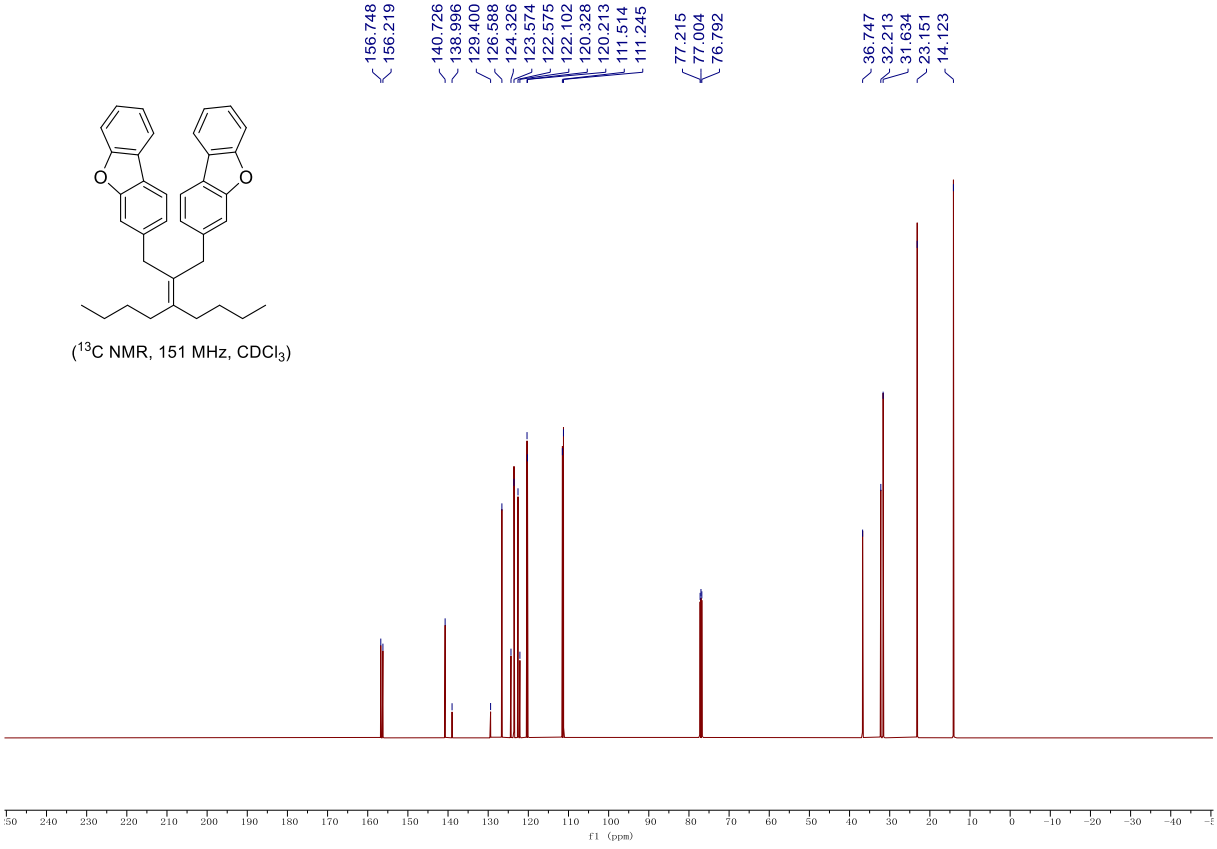
(^{1}H NMR, 400 MHz, $CDCl_3$)



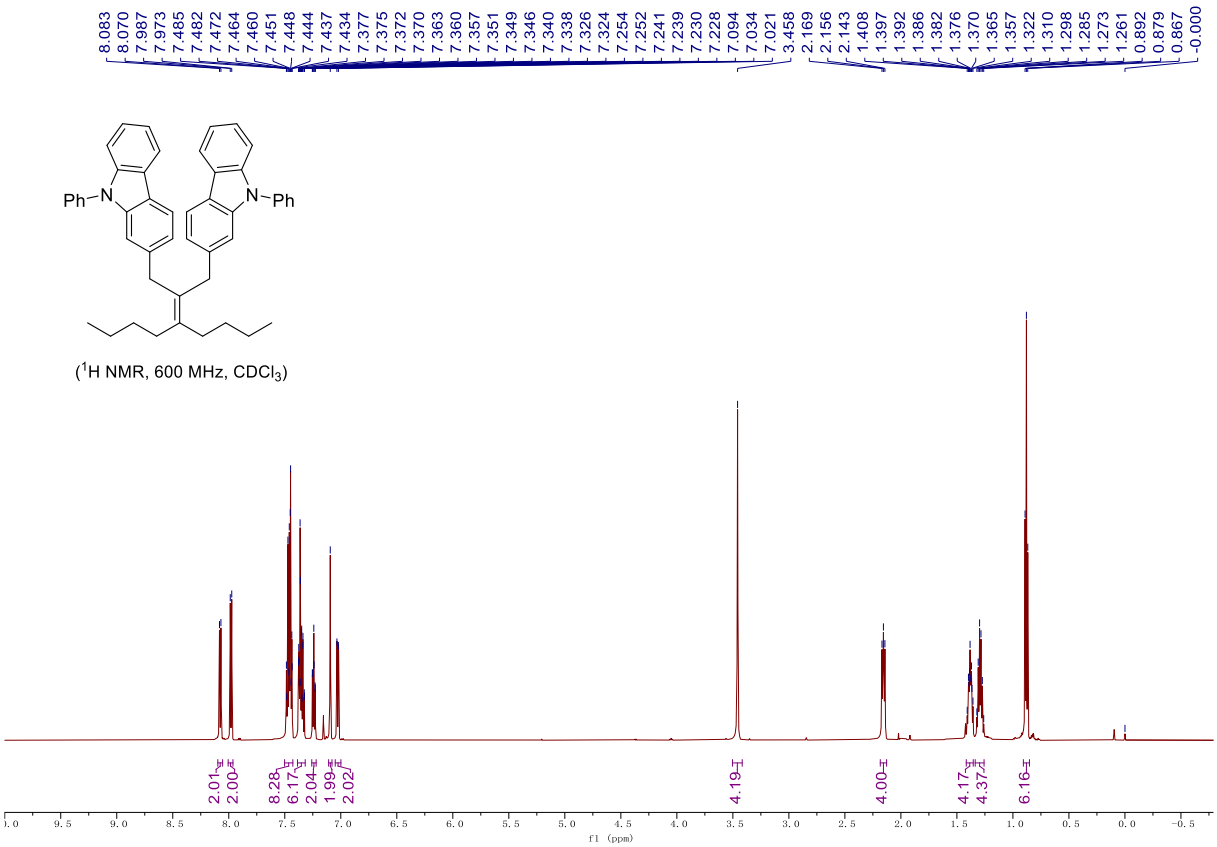
(^{13}C NMR, 151 MHz, $CDCl_3$)

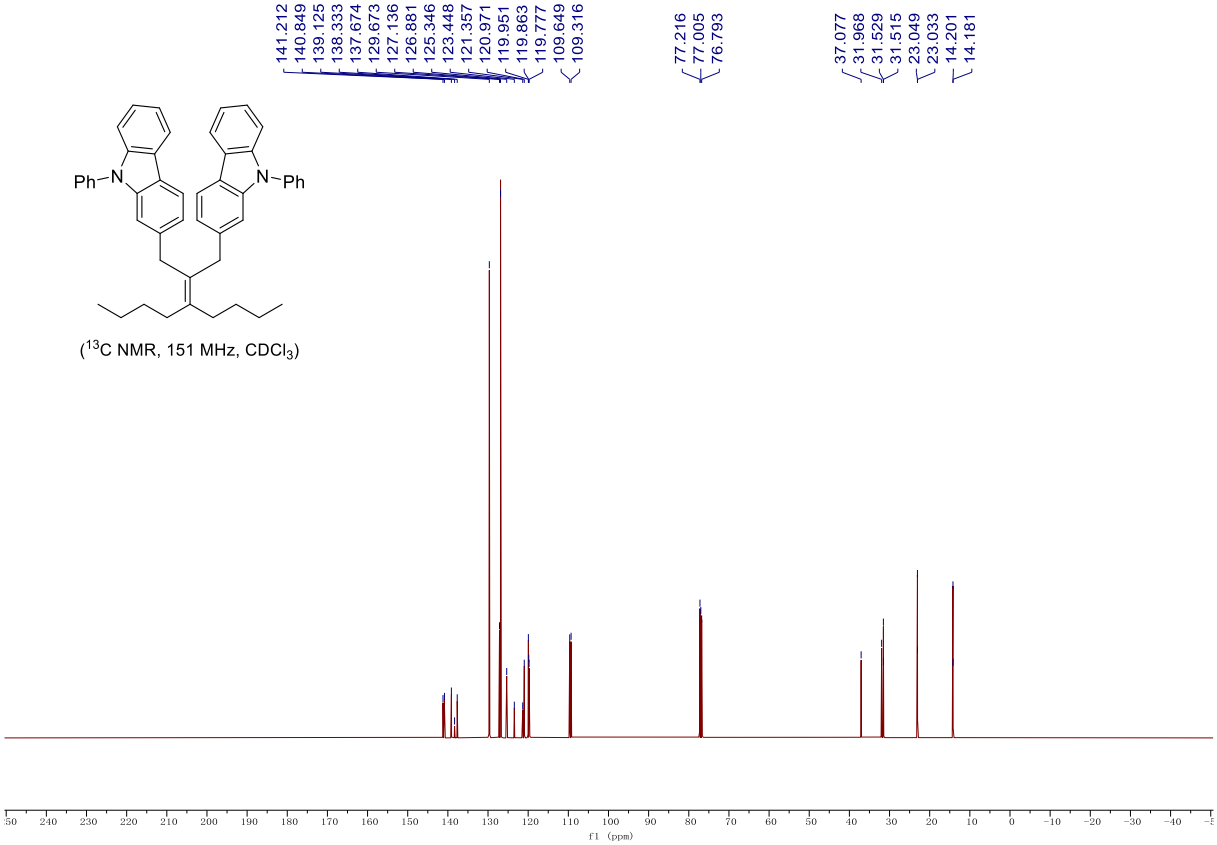


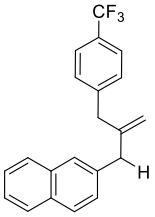
(^{1}H NMR, 600 MHz, $CDCl_3$)



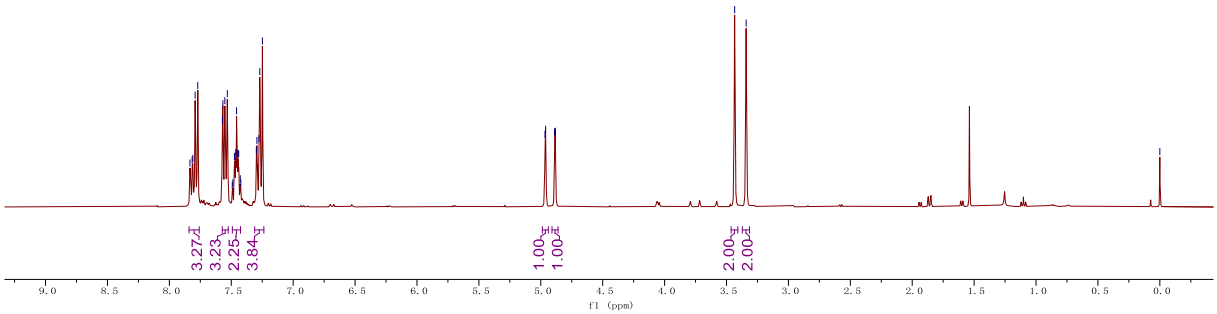
(^{13}C NMR, 151 MHz, $CDCl_3$)

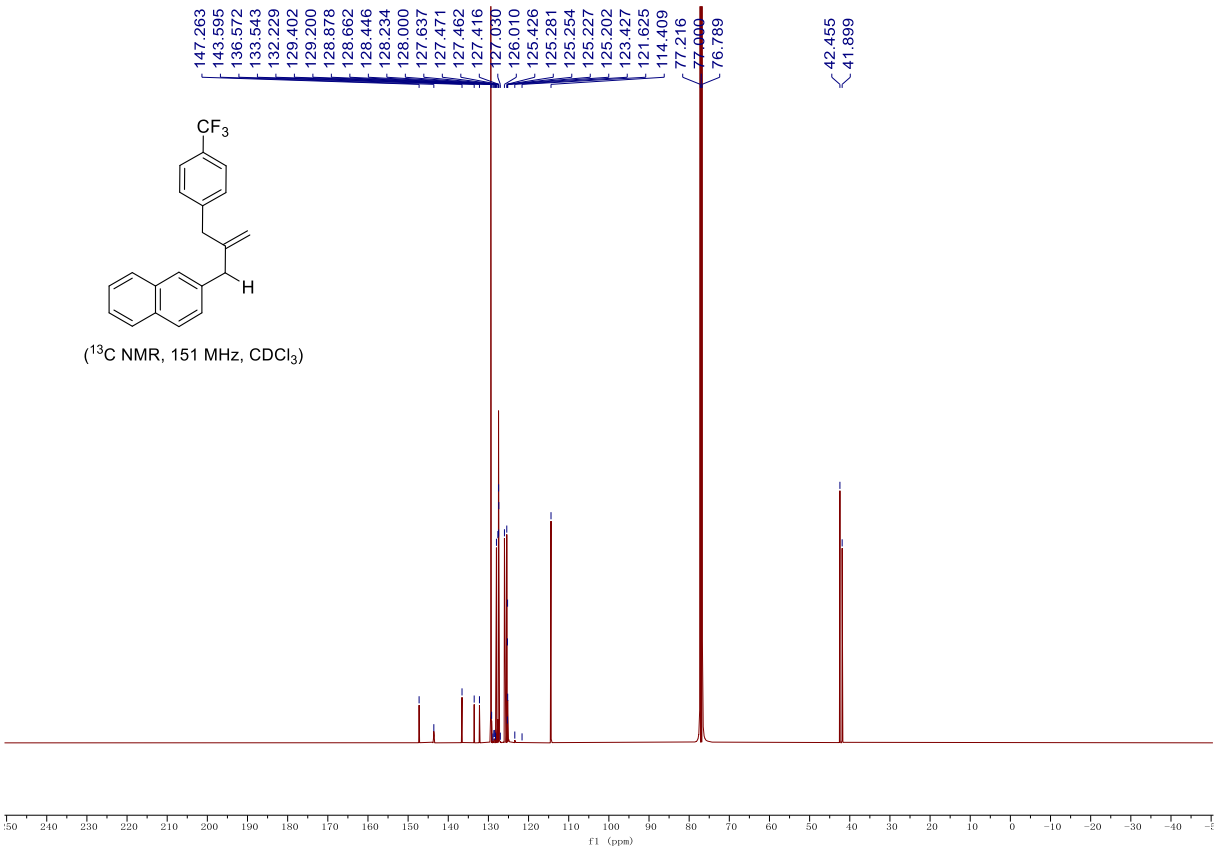

8.083
8.070
7.987
7.973
7.485
7.482
7.472
7.464
7.460
7.451
7.448
7.444
7.437
7.434
7.377
7.375
7.372
7.370
7.363
7.360
7.357
7.351
7.349
7.346
7.340
7.338
7.326
7.324
7.254
7.252
7.241
7.239
7.230
7.228
7.094
7.034
7.021
3.458
2.169
2.156
2.143
1.408
1.397
1.392
1.386
1.382
1.376
1.370
1.365
1.357
1.322
1.310
1.298
1.285
1.273
1.261
0.892
0.879
0.867
-0.000
Ph
N
N
Ph
(1H NMR, 600 MHz, CDCl3)
2.01
2.00
8.28
6.17
2.04
1.99
2.02
4.19
4.00
4.17
4.37
6.16
f1 (ppm)


141.212
140.849
139.125
138.333
137.674
129.673
127.136
126.881
125.346
123.448
121.357
120.971
119.951
119.863
119.777
109.649
109.316
77.216
77.005
76.793
37.077
31.968
31.529
31.515
23.049
23.033
14.201
14.181
Ph
N
N
Ph
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

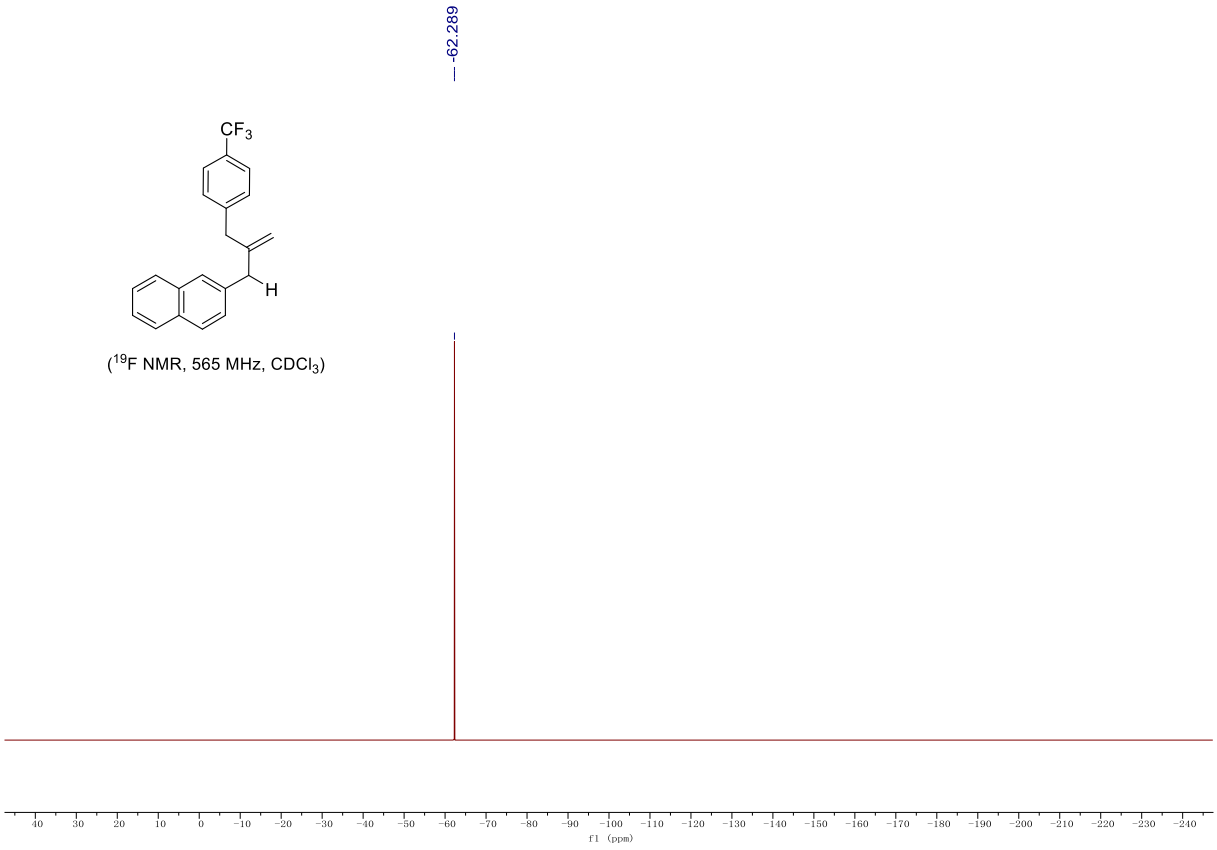


(^{1}H NMR, 400 MHz, $CDCl_3$)

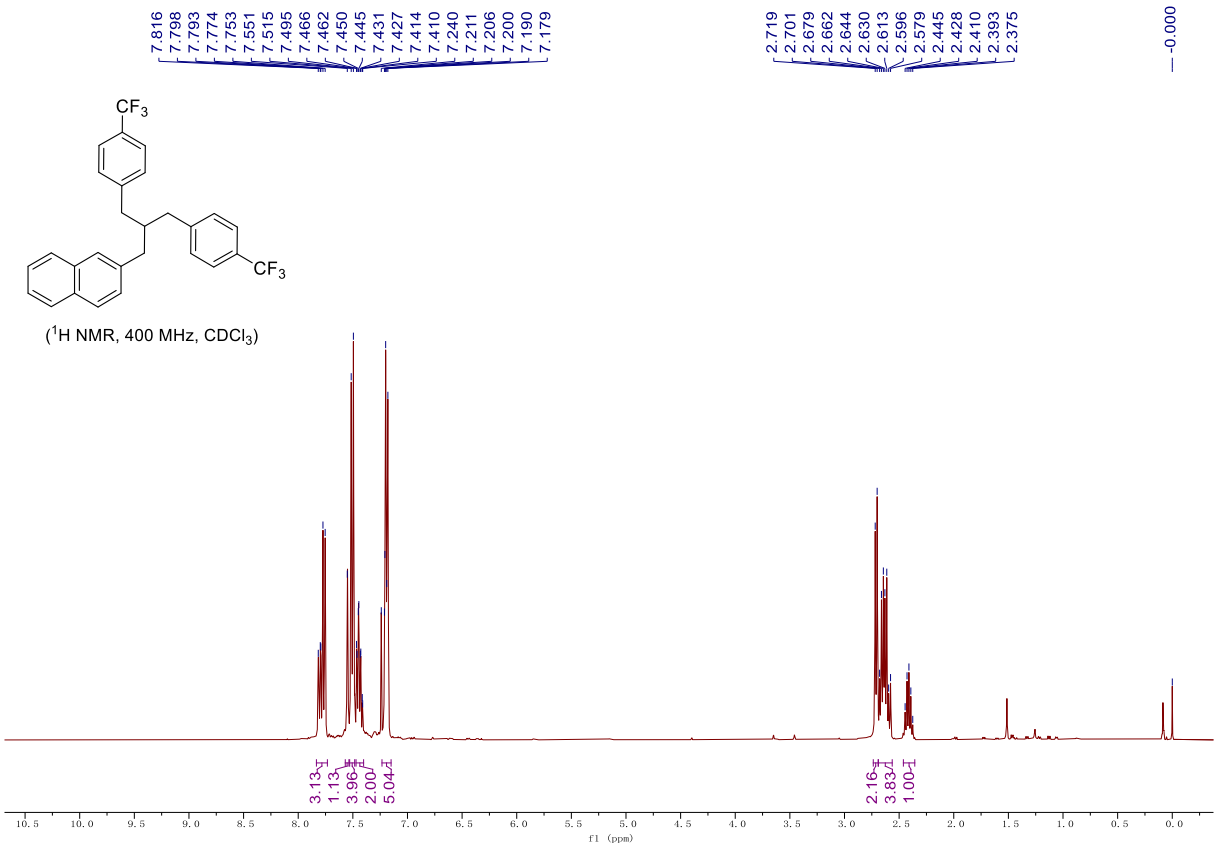


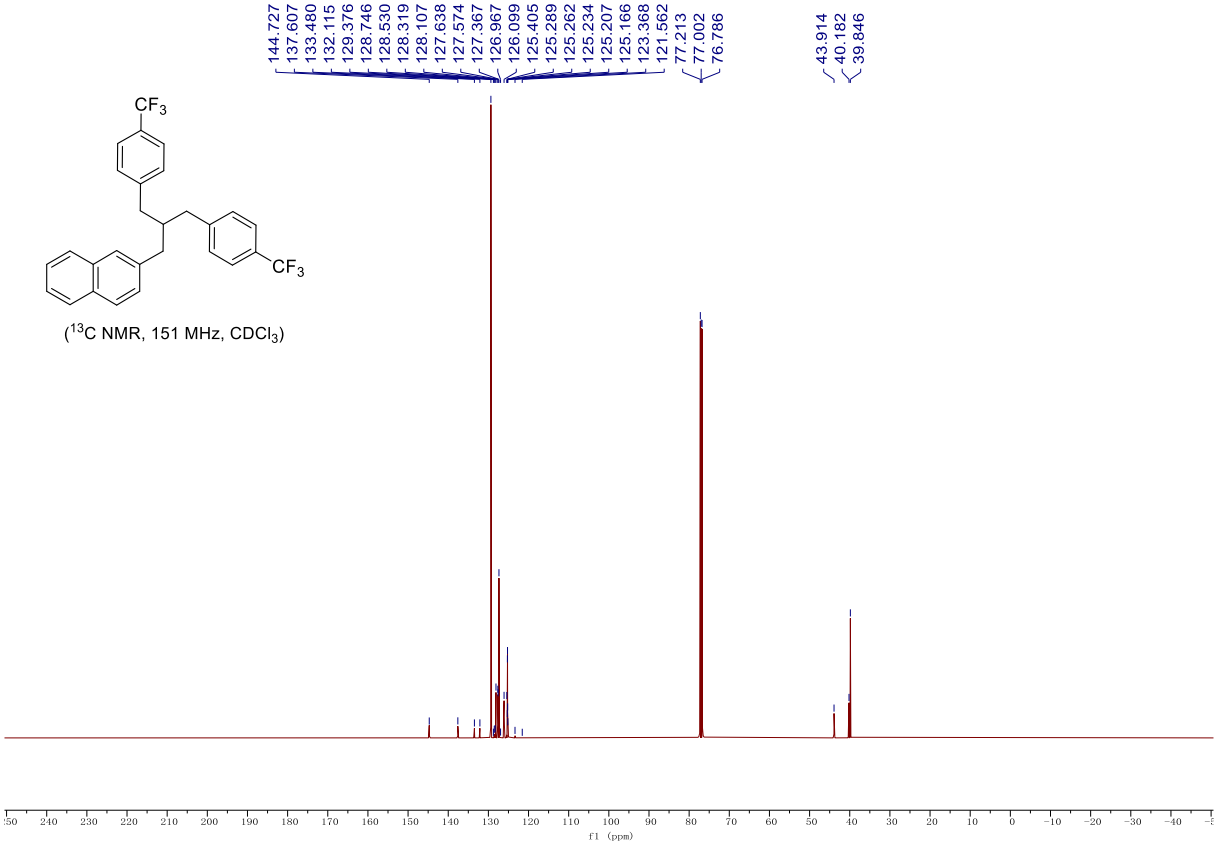


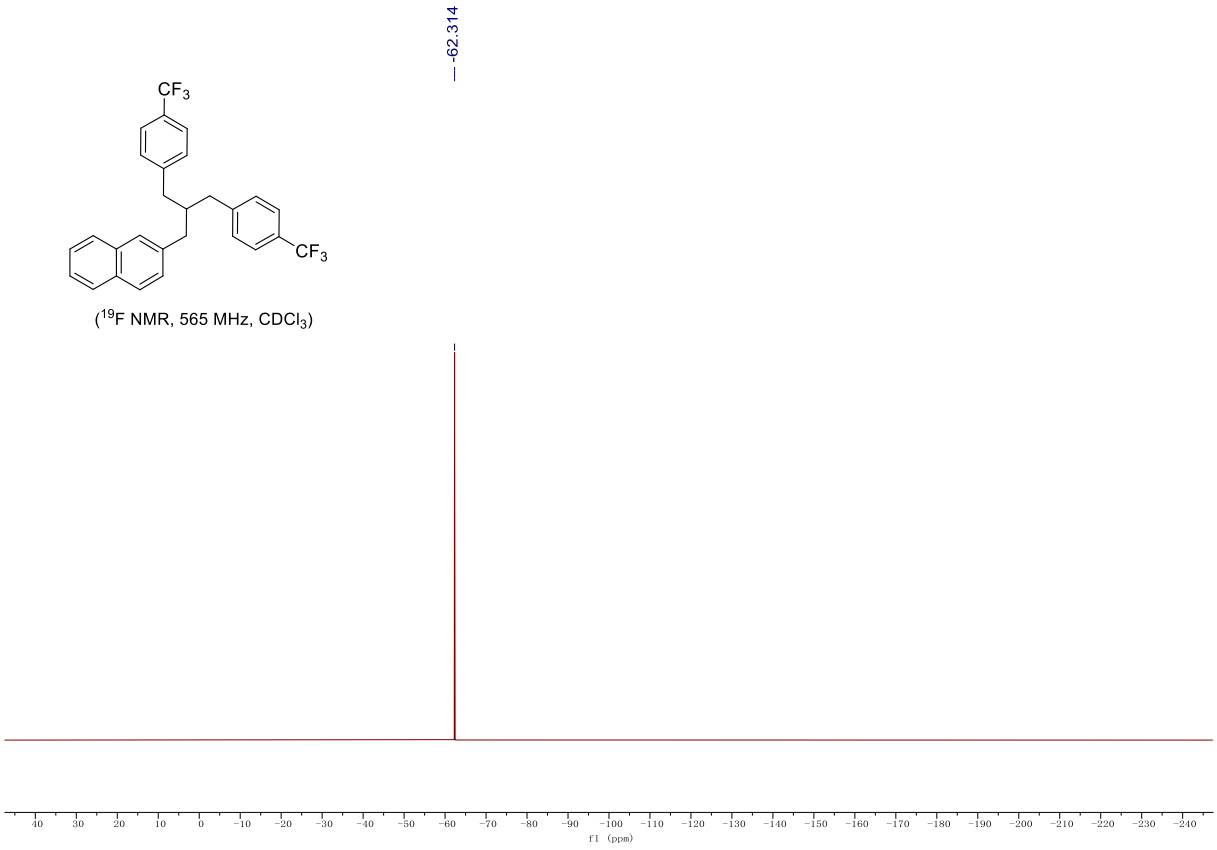
(^{13}C NMR, 151 MHz, $CDCl_3$)



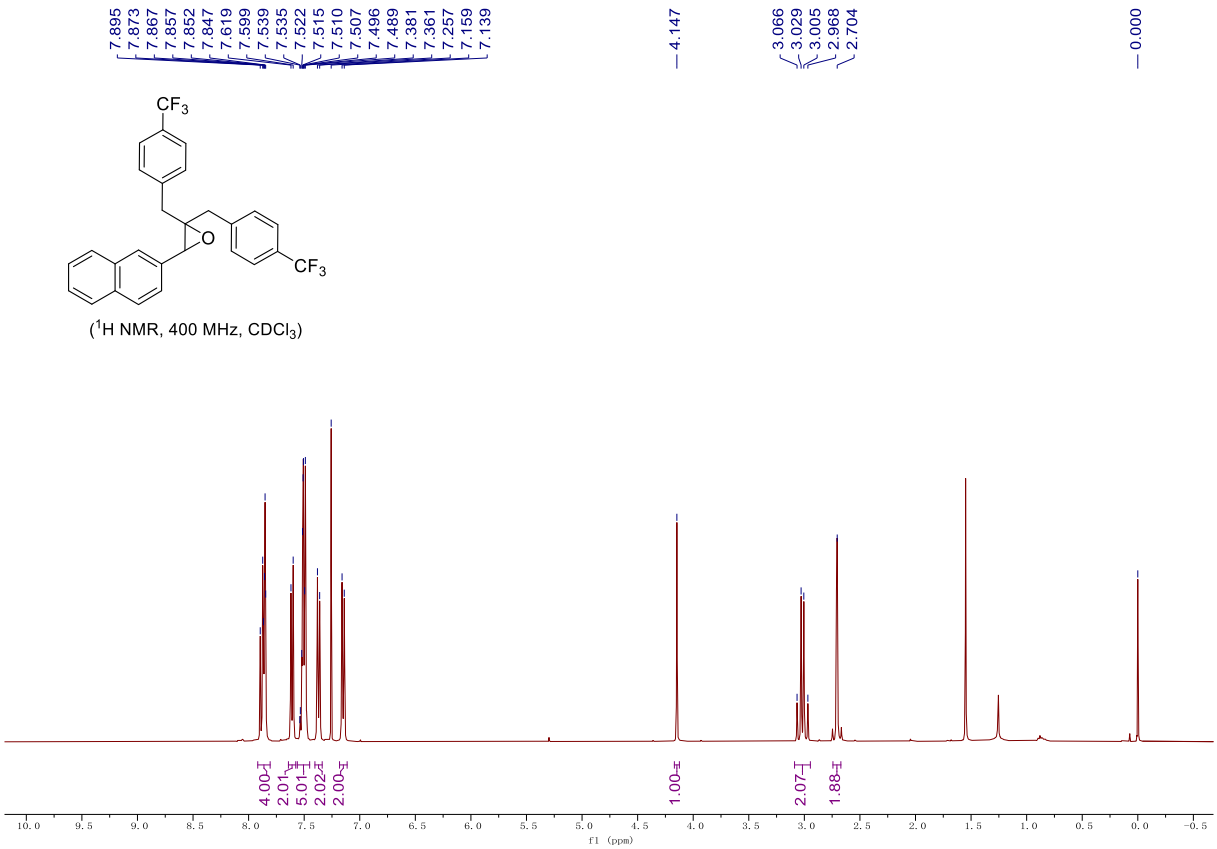
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.816
7.798
7.793
7.774
7.753
7.551
7.515
7.495
7.466
7.462
7.450
7.445
7.431
7.427
7.414
7.410
7.240
7.211
7.206
7.200
7.190
7.179
2.719
2.701
2.679
2.662
2.644
2.630
2.613
2.596
2.579
2.445
2.428
2.410
2.393
2.375
-0.000
CF3
CF3
(1H NMR, 400 MHz, CDCl3)
3.13
1.13
3.96
2.00
5.04
2.16
3.83
1.00
f1 (ppm)


144.727
137.607
133.480
132.115
129.376
128.746
128.530
128.319
128.107
127.638
127.574
127.367
126.967
126.099
125.405
125.289
125.262
125.234
125.207
125.166
123.368
121.562
77.213
77.002
76.786
43.914
40.182
39.846
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



(^{19}F NMR, 565 MHz, $CDCl_3$)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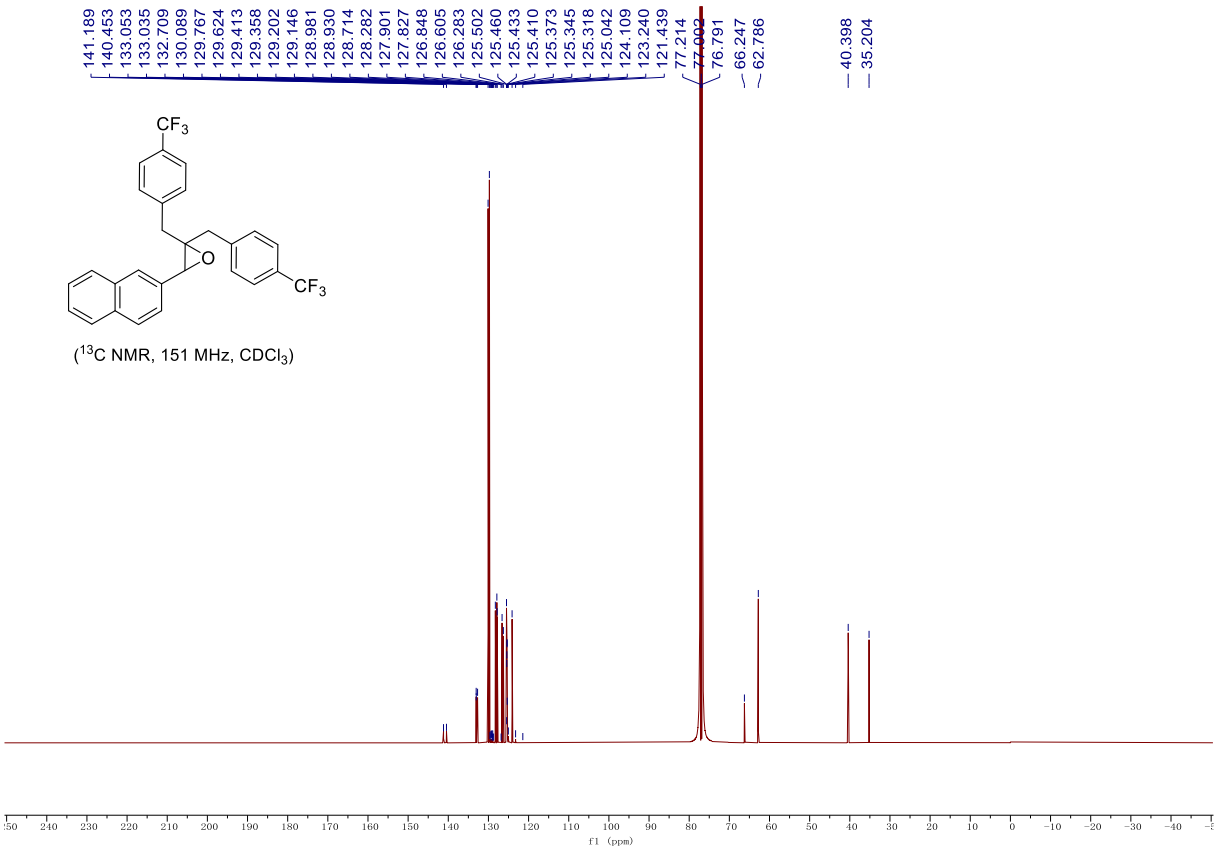
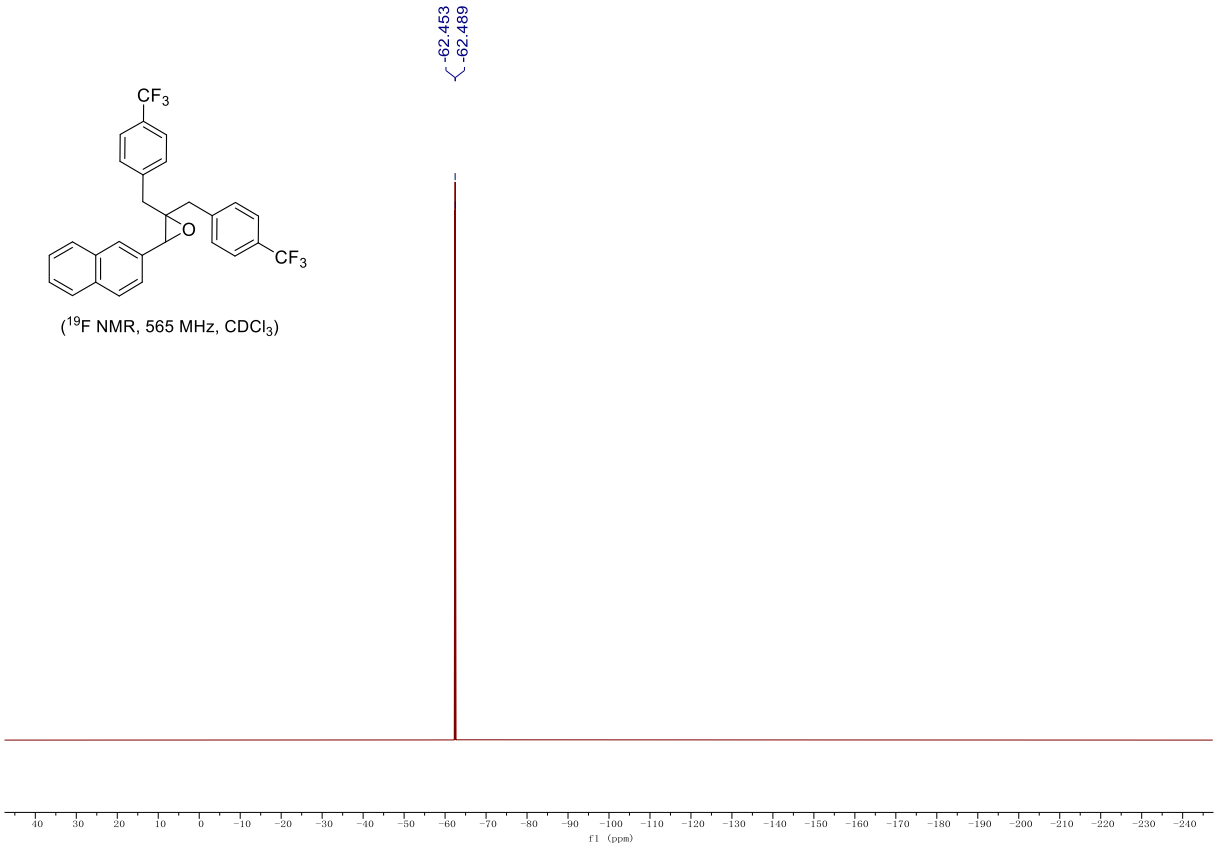
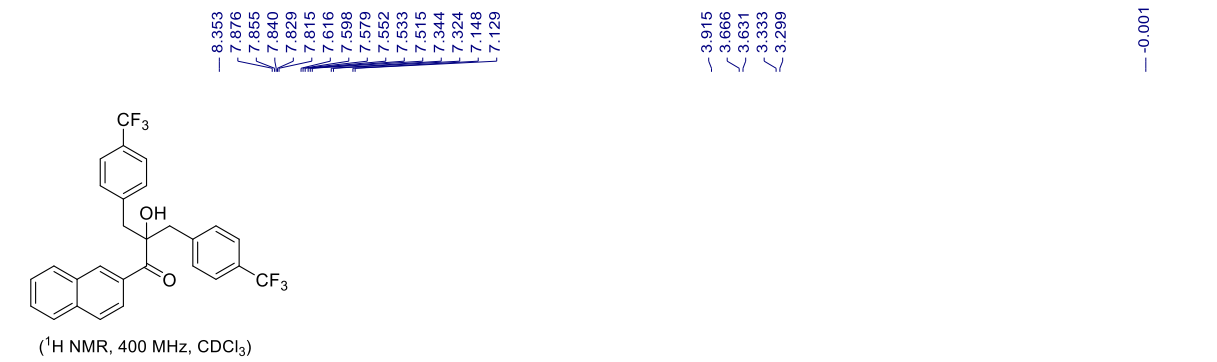
7.873
7.867
7.857
7.852
7.847
7.619
7.599
7.539
7.535
7.522
7.515
7.510
7.507
7.496
7.489
7.381
7.361
7.257
7.159
7.139
4.147
3.066
3.029
3.005
2.968
2.704
0.000
CF3
O
CF3
(1H NMR, 400 MHz, CDCl3)
4.00
2.01
5.01
2.02
2.00
1.00
2.07
1.88
f1 (ppm)

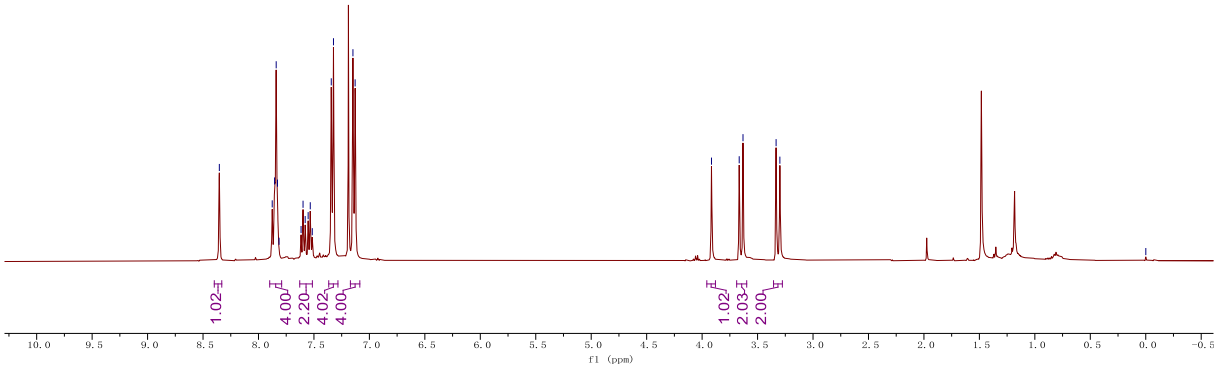

141.189
140.453
133.053
133.035
132.709
130.089
129.767
129.624
129.413
129.358
129.202
129.146
128.981
128.930
128.714
128.282
127.901
127.827
126.848
126.605
126.283
125.502
125.460
125.433
125.410
125.373
125.345
125.318
125.042
124.109
123.240
121.439
77.214
77.000
76.791
66.247
62.786
40.398
35.204
CF3
O
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

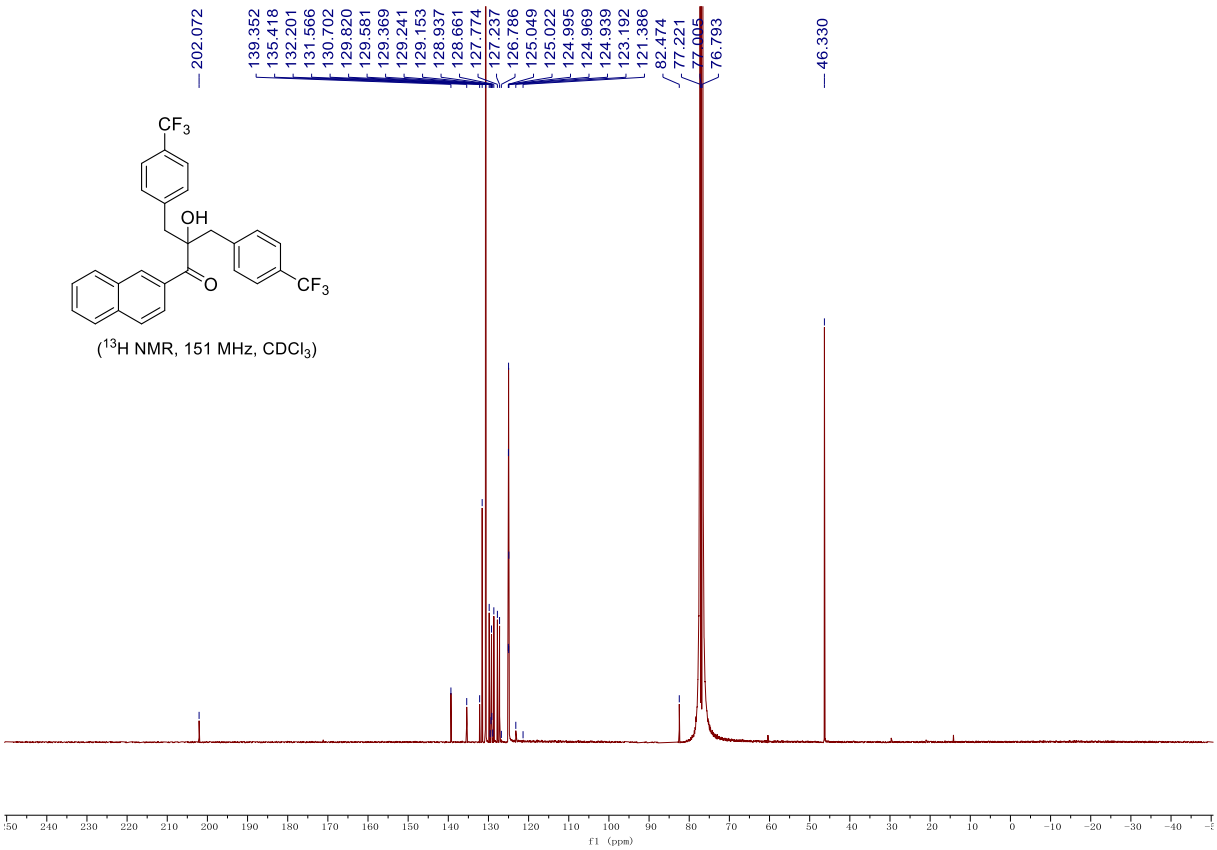


(^{19}F NMR, 565 MHz, $CDCl_3$)

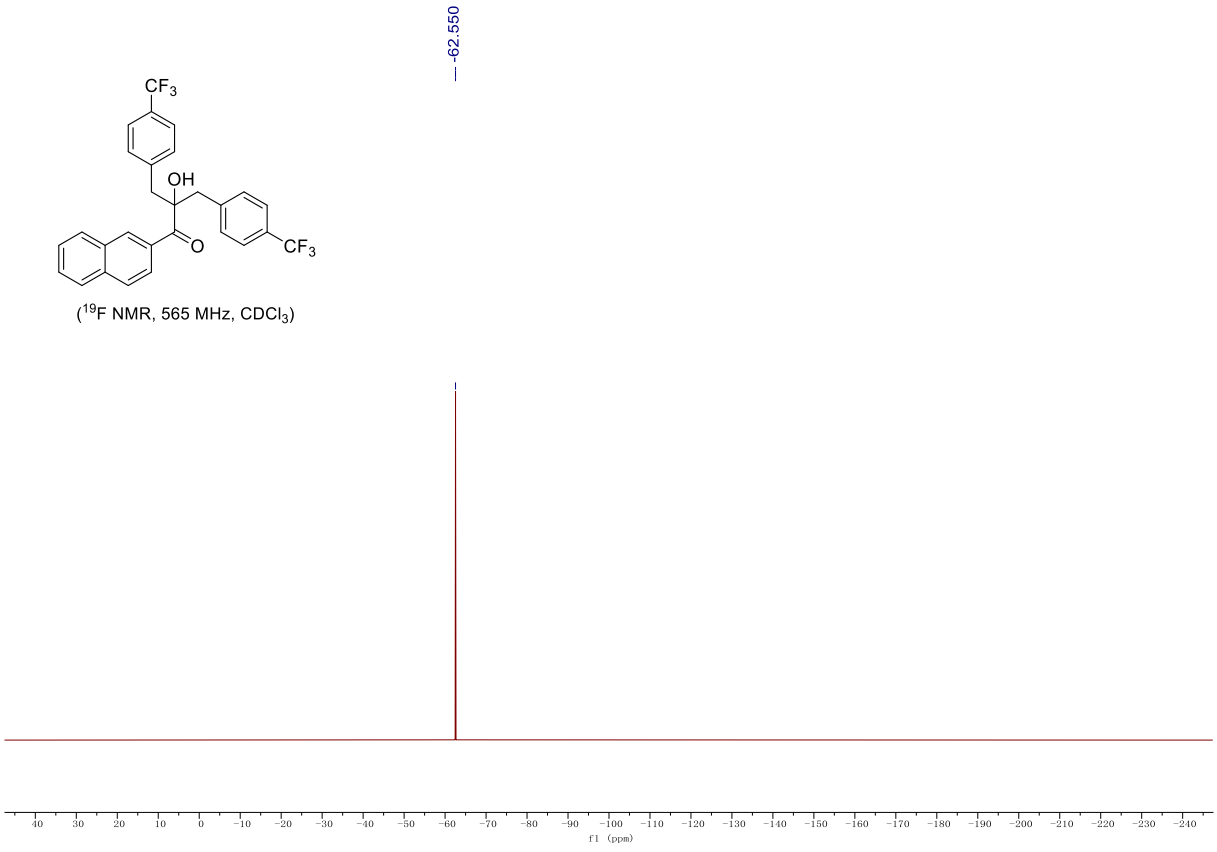


(^{1}H NMR, 400 MHz, $CDCl_3$)

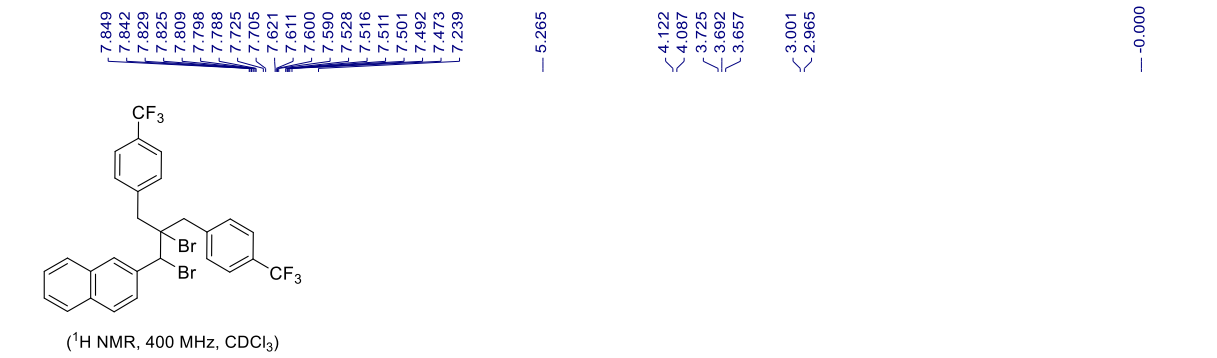




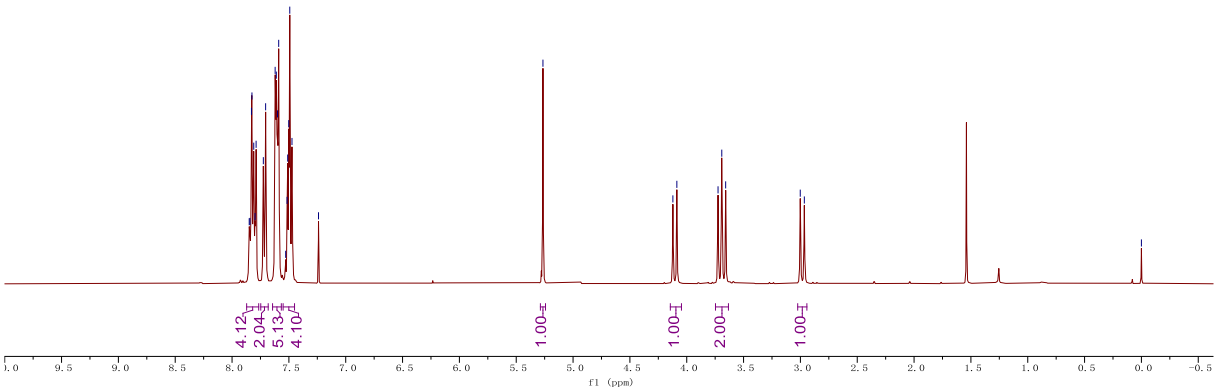
(^{13}H NMR, 151 MHz, $CDCl_3$)

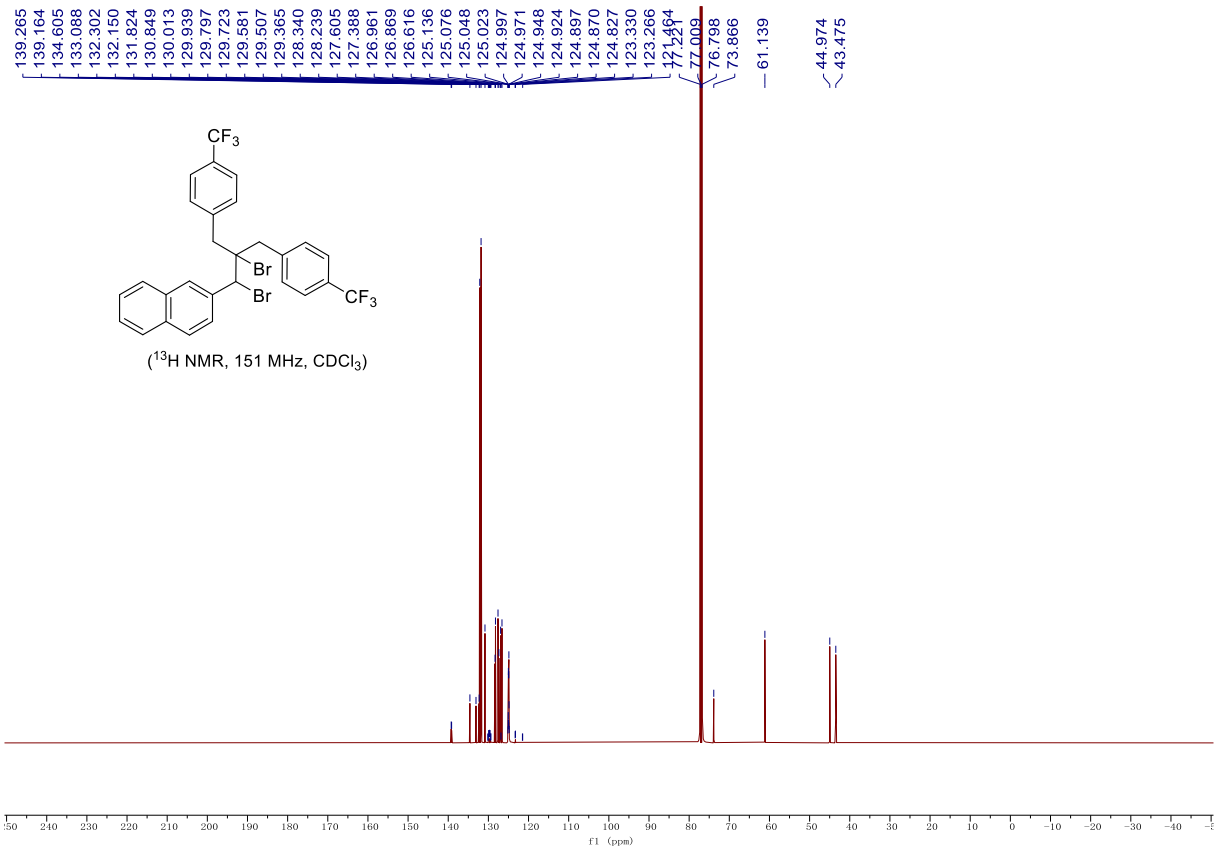


(^{19}F NMR, 565 MHz, $CDCl_3$)

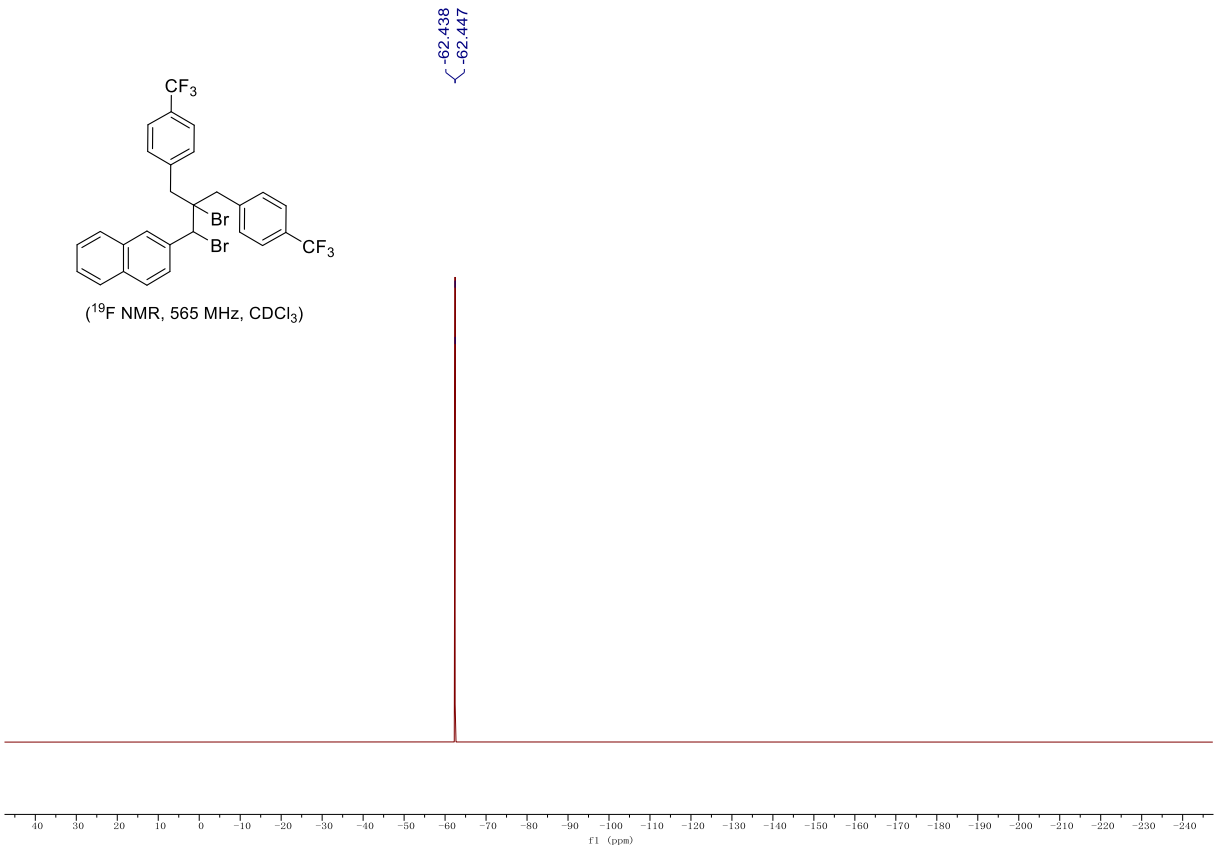


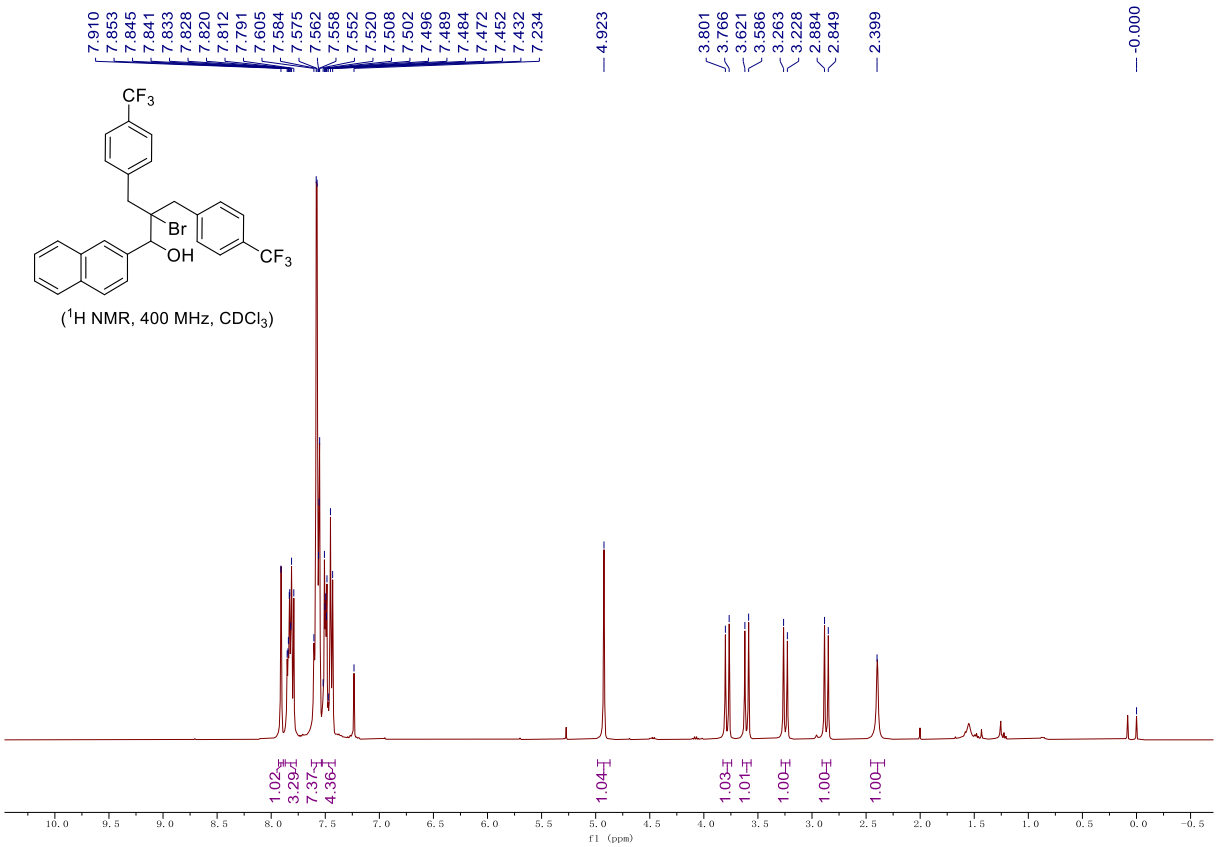
(^{1}H NMR, 400 MHz, $CDCl_3$)

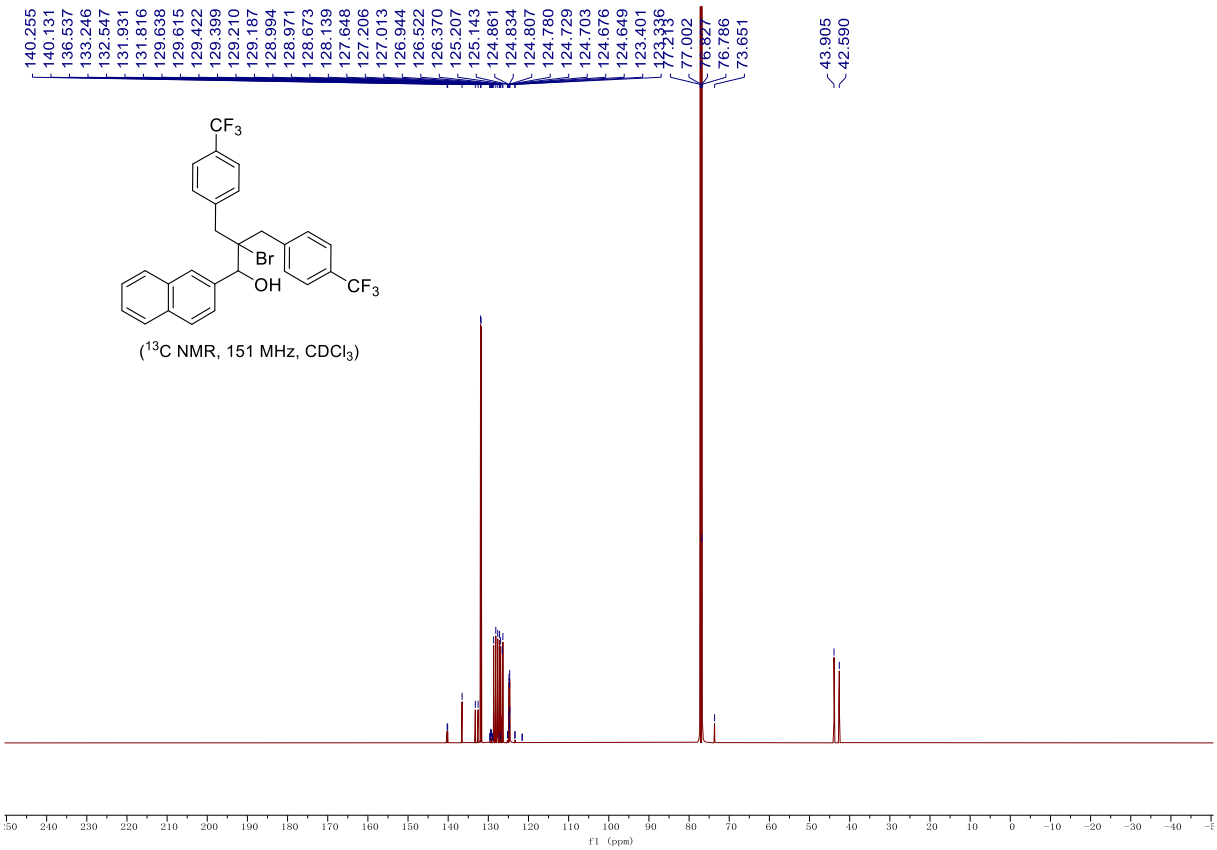


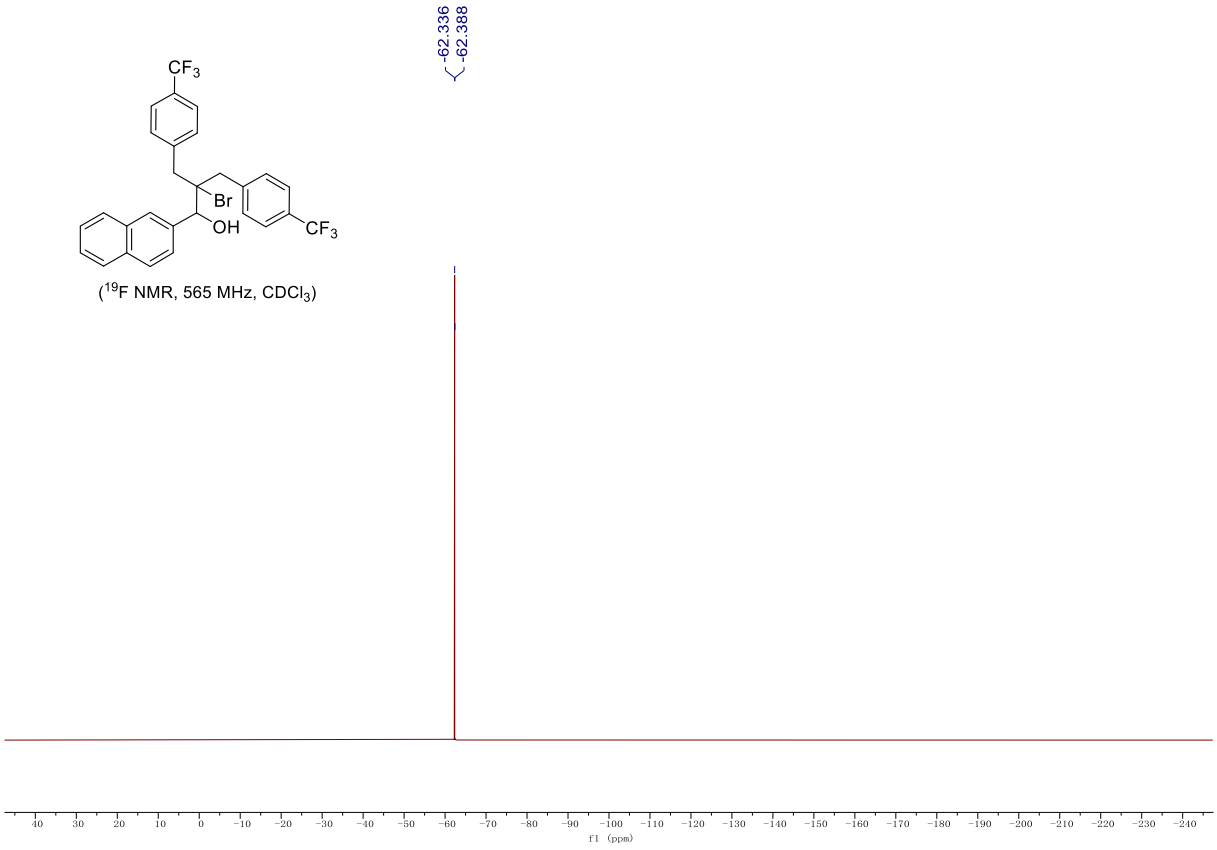


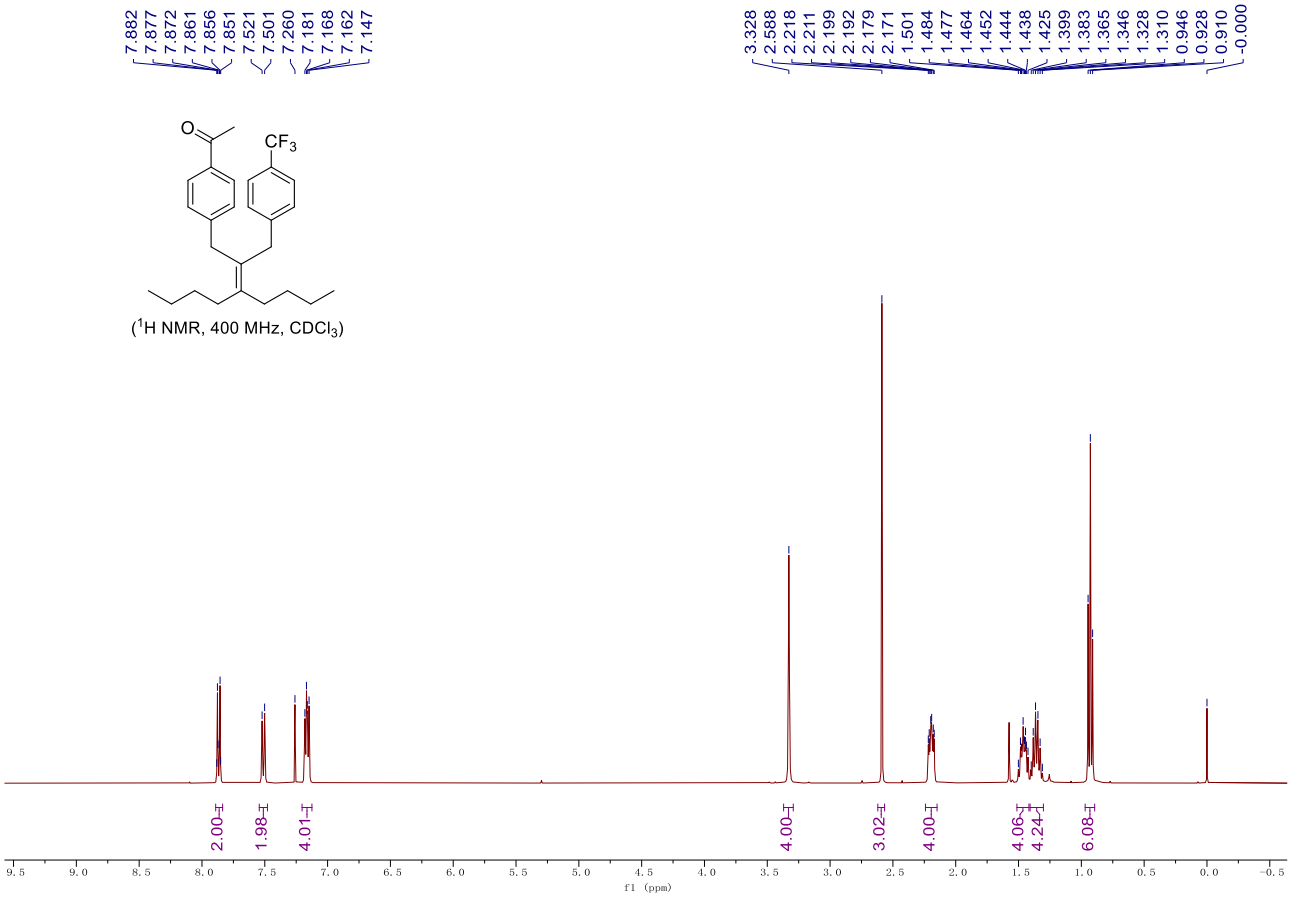
(^{13}H NMR, 151 MHz, $CDCl_3$)

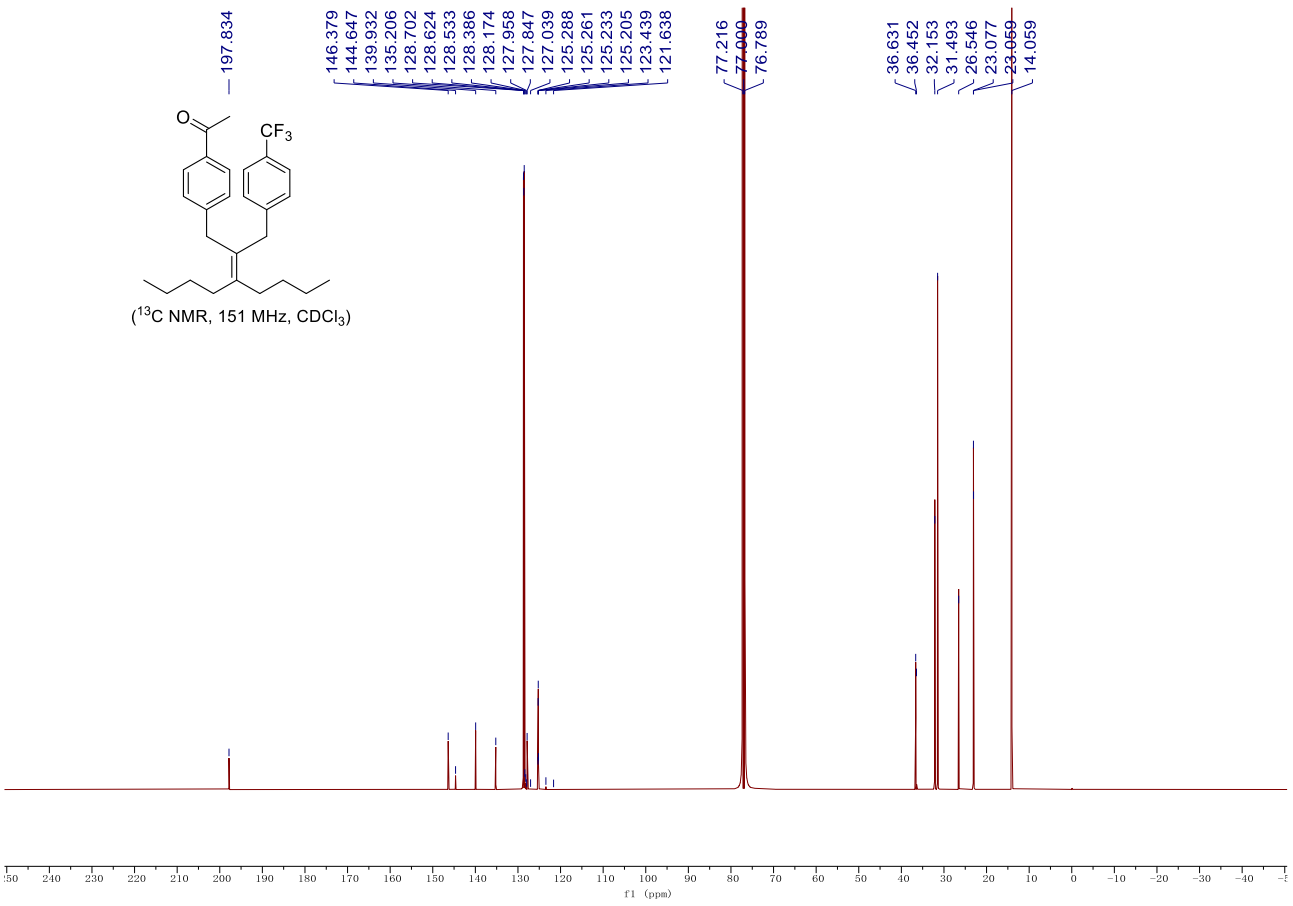

-62.438
-62.447
CF3
Br
Br
CF3
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

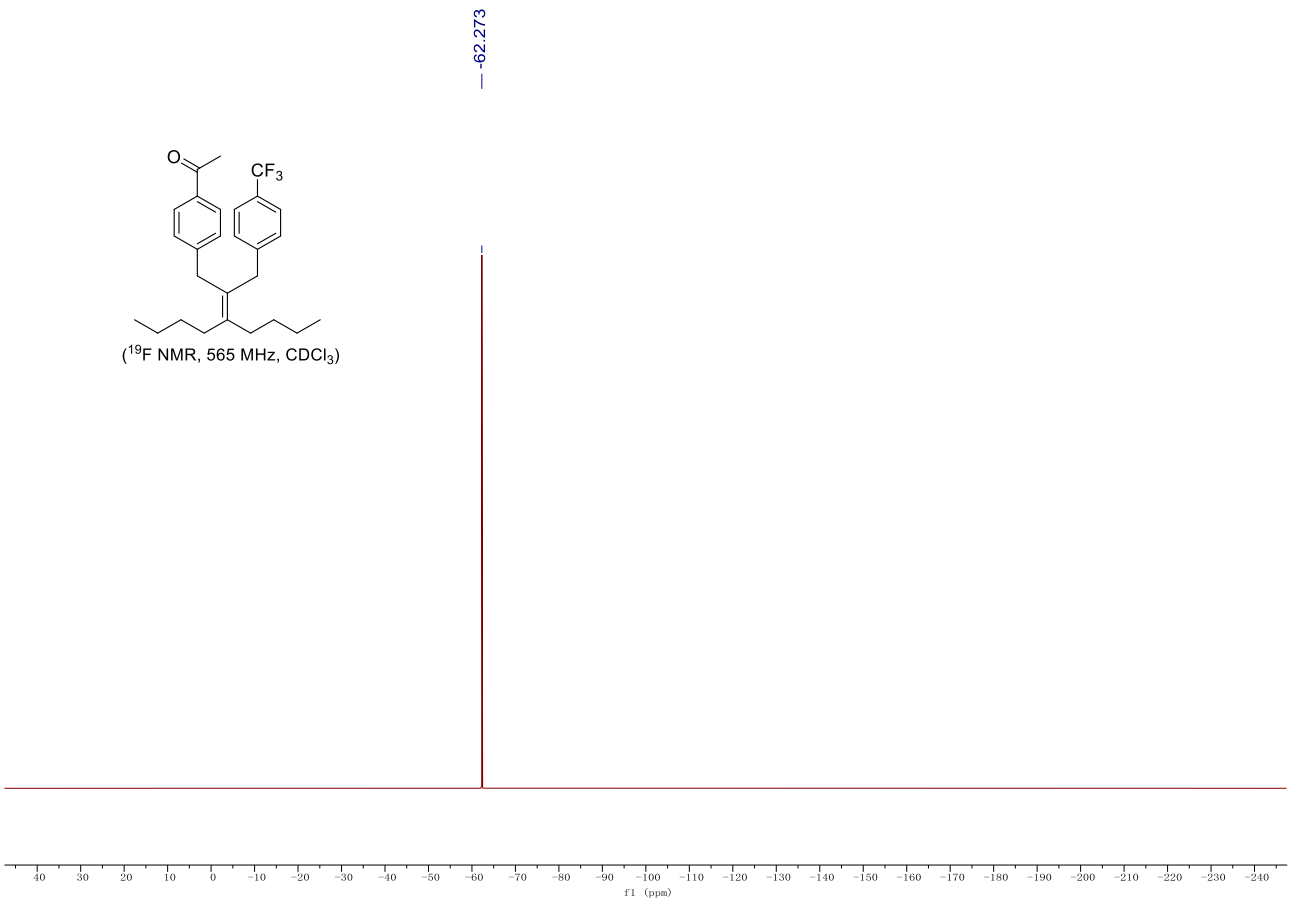

7.910
7.853
7.845
7.841
7.833
7.828
7.820
7.812
7.791
7.605
7.584
7.575
7.562
7.558
7.552
7.520
7.508
7.502
7.496
7.489
7.484
7.472
7.452
7.432
7.234
4.923
3.801
3.766
3.621
3.586
3.263
3.228
2.884
2.849
2.399
-0.000
CF3
Br
OH
CF3
(1H NMR, 400 MHz, CDCl3)
1.02
3.29
7.37
4.36
1.04
1.03
1.01
1.00
1.00
1.00
f1 (ppm)


140.255
140.131
136.537
133.246
132.547
131.931
131.816
129.638
129.615
129.422
129.399
129.210
129.187
128.994
128.971
128.673
128.139
127.648
127.206
127.013
126.944
126.522
126.370
125.207
125.143
124.861
124.834
124.807
124.780
124.729
124.703
124.676
124.649
123.401
77.213
77.002
76.827
76.786
73.651
43.905
42.590
CF3
Br
OH
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

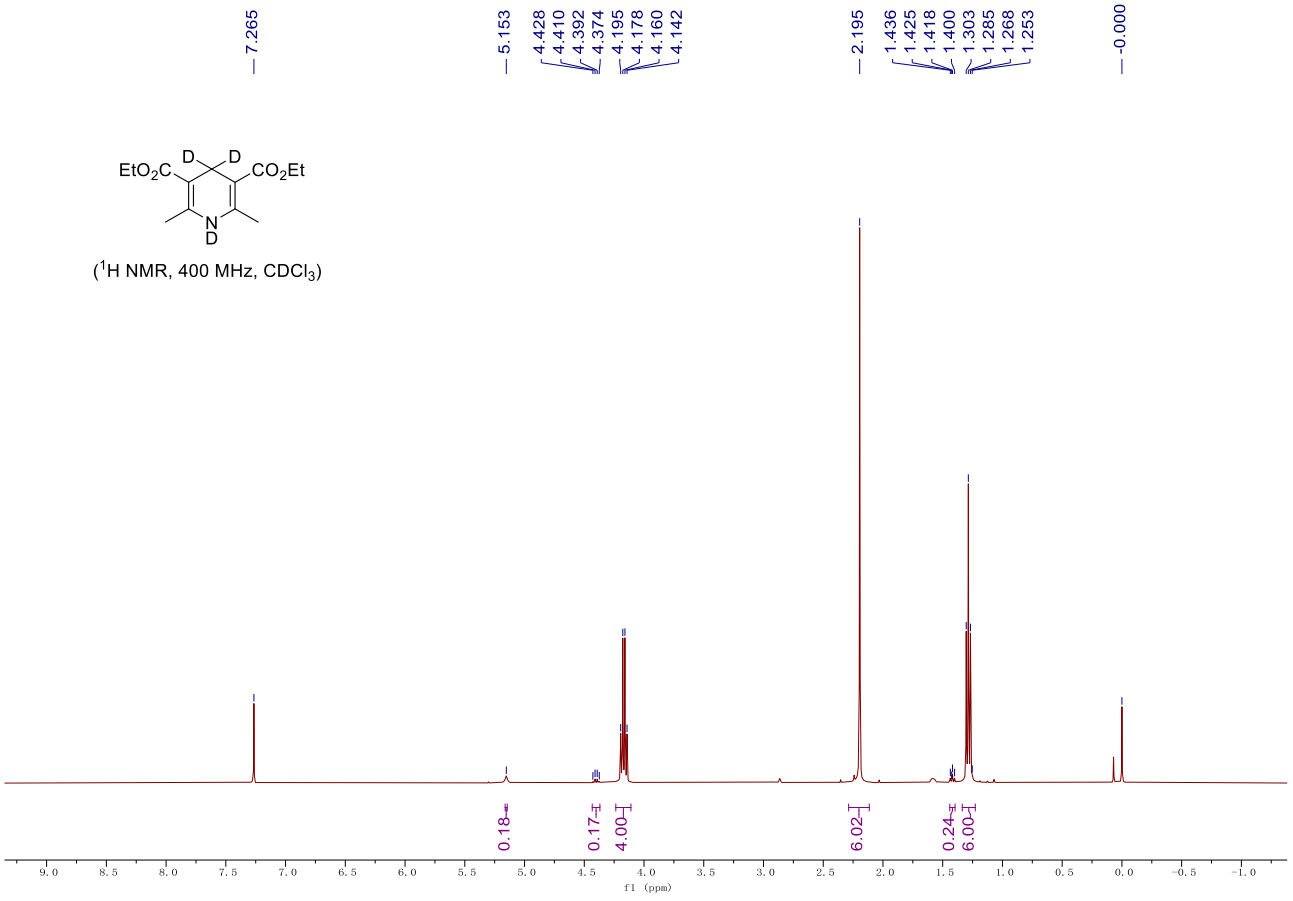

-62.336
-62.388
CF3
Br
OH
CF3
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


7.882
7.877
7.872
7.861
7.856
7.851
7.521
7.501
7.260
7.181
7.168
7.162
7.147
3.328
2.588
2.218
2.211
2.199
2.192
2.179
2.171
1.501
1.484
1.477
1.464
1.452
1.444
1.438
1.425
1.399
1.383
1.365
1.346
1.328
1.310
0.946
0.928
0.910
-0.000
O
CF3
(1H NMR, 400 MHz, CDCl3)
2.00
1.98
4.01
4.00
3.02
4.00
4.06
4.24
6.08
f1 (ppm)


197.834
146.379
144.647
139.932
135.206
128.702
128.624
128.533
128.386
128.174
127.958
127.847
127.039
125.288
125.261
125.233
125.205
123.439
121.638
77.216
77.000
76.789
36.631
36.452
32.153
31.493
26.546
23.077
23.059
14.059
O
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



(^{19}F NMR, 565 MHz, $CDCl_3$)


7.265
5.153
4.428
4.410
4.392
4.374
4.195
4.178
4.160
4.142
2.195
1.436
1.425
1.418
1.400
1.303
1.285
1.268
1.253
-0.000
EtO2C
D
D
CO2Et
N
D
(1H NMR, 400 MHz, CDCl3)
0.18
0.17
4.00
6.02
0.24
6.00
f1 (ppm)

13. Reference

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