Supporting Information

Nickel/ligand Loading-controlled Divergent and Selective Coupling between Redox-Active Methylenecyclopropanes and ArBr

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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 shifts were reported in ppm and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.00 ppm for ^{13}C NMR). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, EI, DART and HRMS was measured on a HP-5989 instrument. 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.

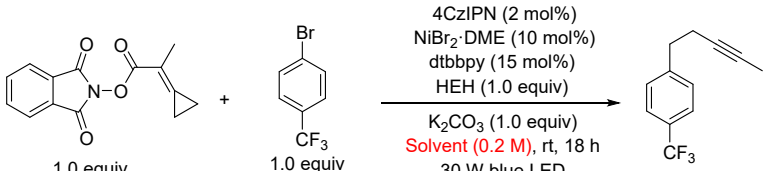
The photoreaction setup is reassembled as following picture with a blue-LED, a fan and a magnetic stirrer. The reaction tube was about 5 cm far from the light source. The 30 W Blue LED (Wavelength: 455 – 460 nm) was directly purchased online from Taobao.com.

Figure S1. The photoreaction setup

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, photocatalyst, electron donor, ligand, nickel source, base and degassed solvent were added. The tube was degassed by alternating vacuum evacuation (5 min) and argon backfill for three times. The mixture was stirred for 10 min before being placed 5 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, 1,3,5-trimethoxybenzene (1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was analyzed by ^1H NMR.

2.1 Table S1. Solvent Optimization

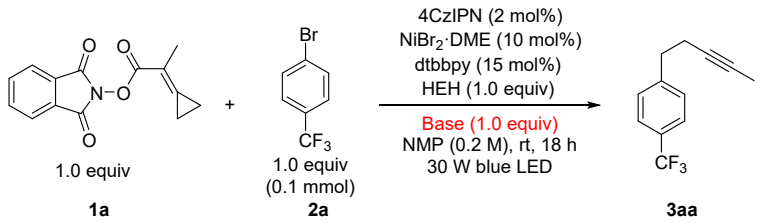


1.0 equiv **1a** + 1.0 equiv (0.1 mmol) **2a** → **3a**

Entry	Solvent	**3aa**, Yield (%)[a]
1	NMP	20
2	DMF	13
3	CH_3CN	15
4	DMAc	18
5	1,4-Dioxane	—
6	MTBE	—

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

2.2 Table S2. Base Optimization



1.0 equiv
1a

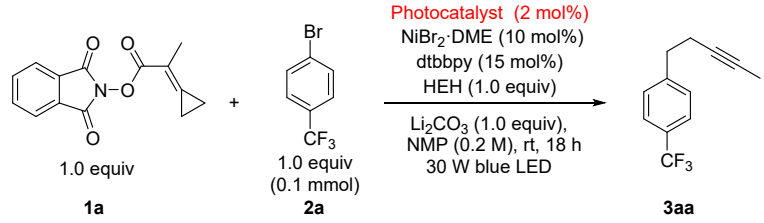
1.0 equiv
(0.1 mmol)
2a

3aa

Entry	Base	**3aa**, Yield (%)[a]
1	K_2CO_3	20
2	Li_2CO_3	39
3	Na_2CO_3	18
4	K_2HPO_4	17
5	$^iPr_2NEt$	35
6	Et_3N	34
7	w/o	21

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

2.3 Table S3. Photocatalyst Optimization



1.0 equiv
1a

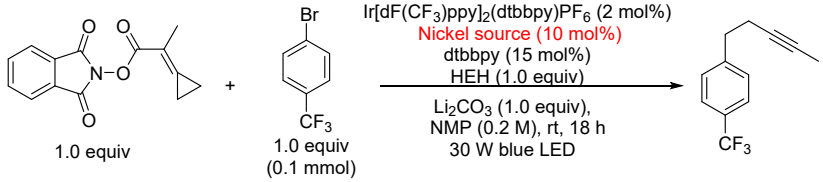
1.0 equiv
(0.1 mmol)
2a

3aa

Entry	Photocatalyst	**3aa**, Yield (%)[a]
1	4CzIPN	39
2	$Ir[dF(Me)ppy]_2(dtbbpy)PF_6$	33
3	$Ir(dtbbpy)(ppy)_2PF_6$	34
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	45

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

2.4 Table S4. Nickel source Optimization



1.0 equiv
1a

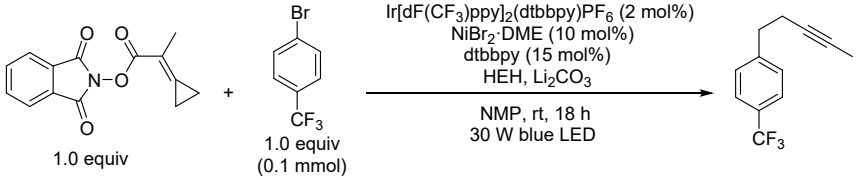
1.0 equiv
(0.1 mmol)
2a

3aa

Entry	Nickel source	**3aa**, Yield (%)[a]
1	$NiBr_2$·DME	45
2	$NiBr_2$·diglyme	33
3	$NiCl_2$·DME	42
4	$Ni(TMHD)_2$	—

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

2.5 Table S5. HEH loading, Base loading, and Concentration Optimization



1.0 equiv
1a

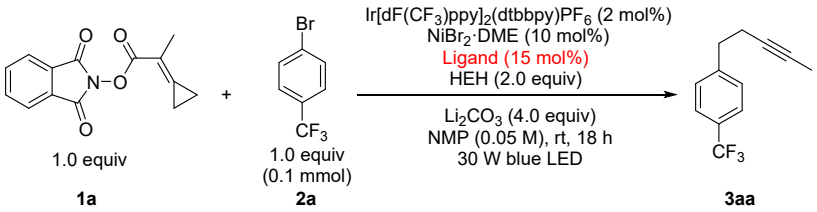
1.0 equiv
(0.1 mmol)
2a

3aa

Entry	HEH (equiv)	Li_2CO_3 (equiv)	Conc. (M)	**3aa**, Yield (%)[a]
1	1.0	1.0	0.2	45
2	1.5	1.0	0.2	50
3	2.0	1.0	0.2	53
4	2.0	3.0	0.33	15
5	2.0	3.0	0.1	57
6	2.0	4.0	0.05	83

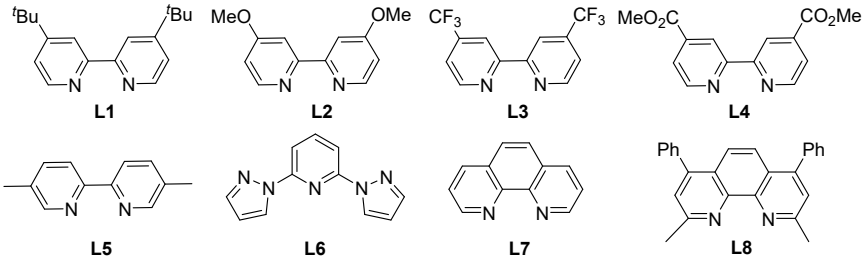
[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

2.6 Table S6. Ligand Optimization

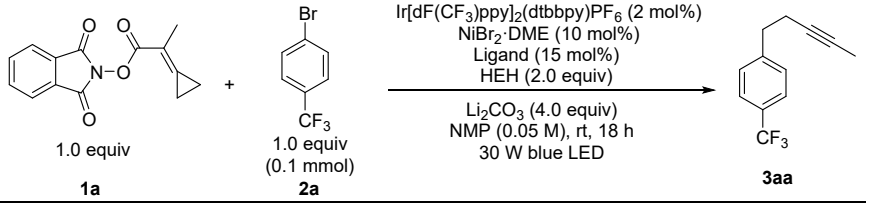


Entry	Ligand	**3aa**, Yield (%)[a]
1	**L1**	83
2	**L2**	50
3	**L3**	—
4	**L4**	—
5	**L5**	57
6	**L6**	—
7	**L7**	43
8	**L8**	—

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



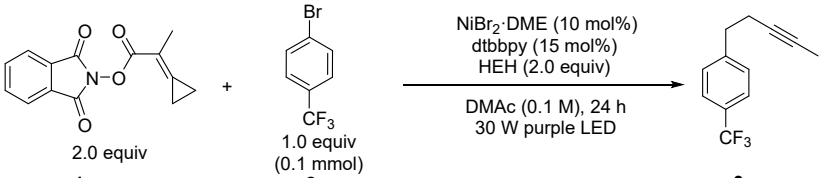
2.7 Table S7. Control experiments



Entry	Deviation	**3aa**, Yield (%)[a]
1	none	83 (75)[b]
2	w/o irradiation	—
3	w/o Nickel catalyst	—
4	w/o HEH	—
5	w/o Photocatalyst	—
6	w/o ligand	—

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; [b]Isolated yield on 0.2 mmol scale.

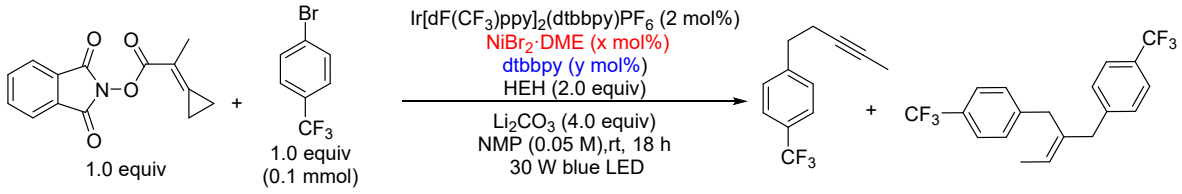
2.8 Table S8. Slight optimization of the EDA complex strategy according to the previous report[1]



Entry	Deviation	**3aa**, Yield (%)[a]
1	None	71 (65)[b]
2	LiCl (2.0 equiv) as an additive	12
3	4.0 equiv HEH	32
4	1.5 equiv **1a**, 1.5 equiv HEH	50
5	DMAc (0.2 M)	40

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; [b]Isolated yield on 0.2 mmol scale.

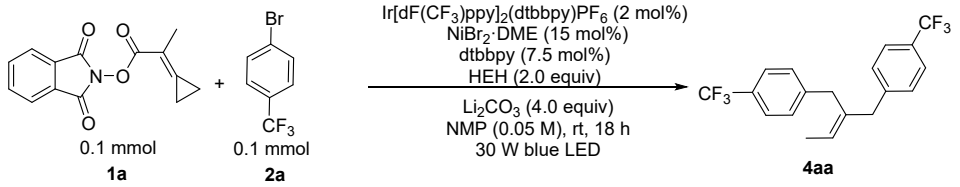
2.9 Table S9. Nickel catalyst and ligand loading Optimization



Entry	$NiBr_2$·DME (x mol%)	dtbbpy (y mol%)	**3aa**, Yield (%)[a]	**4aa**, Yield (%)[b]
1	5	5	67	10
2	5	10	73	—
3	10	5	—	50
4	20	10	—	78
5	15	7.5	—	81
6	10	15	83	—

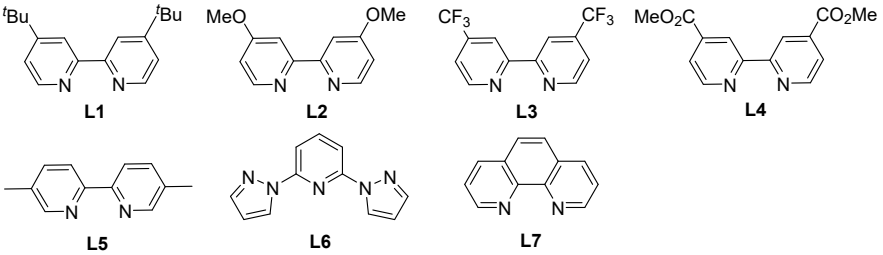
[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard and were calculated on 0.05 mmol scale;

2.10 Table S10. Further Optimization of Product 4aa



Entry	Deviation	**4aa**, Yield (%)[a]
1	None	81 (72)[b]
2	4CzIPN as photocatalyst	51
3	$Ir(dtbbpy)(ppy)_2PF_6$ as photocatalyst	69
4	$Ir[dF(Me)ppy]_2(dtbbpy)PF_6$ as photocatalyst	58
5	$NiBr_2$·DME (10 mol%), dtbbpy (5 mol%)	50
6	$NiBr_2$·DME (20 mol%), dtbbpy (10 mol%)	78
7	$NiBr_2$·dtbbpy (10 mol%)	24
8	$NiCl_2$·DME instead of $NiBr_2$·DME	68
9	$Ni(acac)_2$ instead of $NiBr_2$·DME	—
10	**L3**, **L4** or **L6** instead of **L1**	—
11	**L2** instead of **L1**	75
12	**L5** instead of **L1**	58
13	**L7** instead of **L1**	35
14	1.0 equiv HEH	56
15	DMAc instead of NMP	32
16	NMP (0.1 M)	33
17	w/o HEH, irradiation, nickel source, ligand or photocatalyst	—

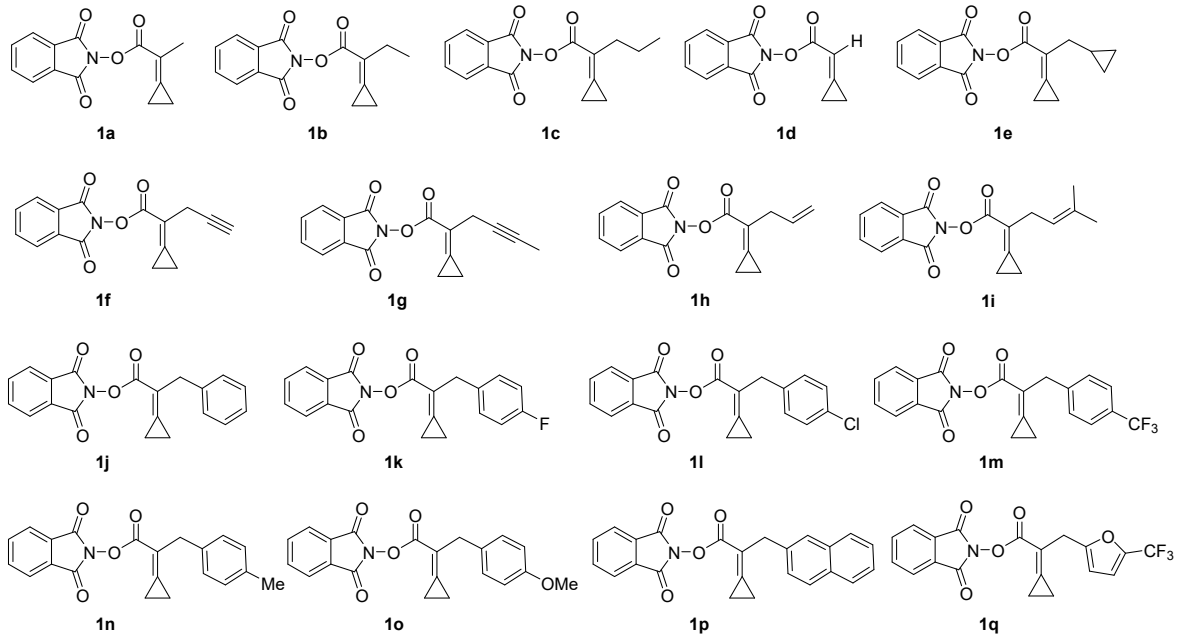
[a]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard and were calculated on 0.05 mmol scale; [b]Isolated yield on 0.3 mmol scale.



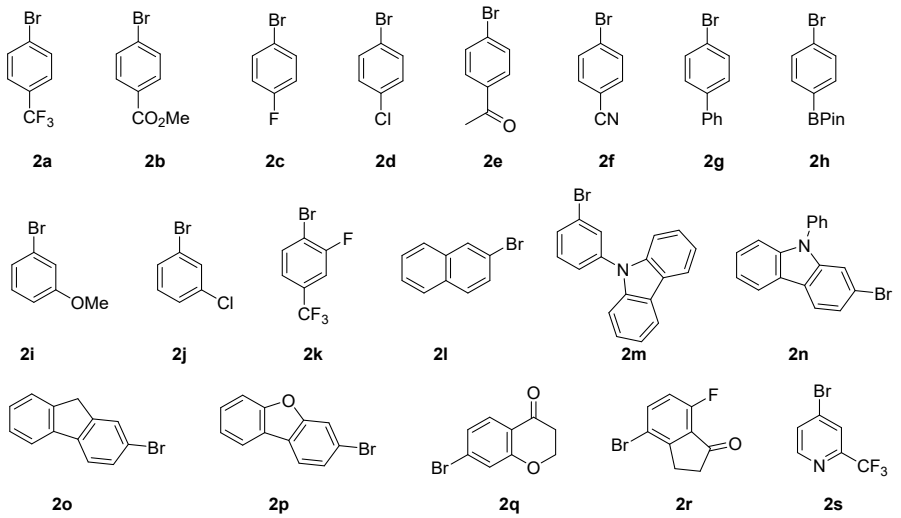
3. Preparation of Substrates

The *N*-Hydroxyphthalimide Esters (NHPI esters, Substrates **1**) were synthesized according to the previous report of our group and the procedures were slightly modified. Compounds **1a – 1d**, **1g** – **1h**, **1j**, **1l**, **1o**, and **1q** are known products reported in our group's previous report.[2] The substrates of ArBr **2** were all commercially available.

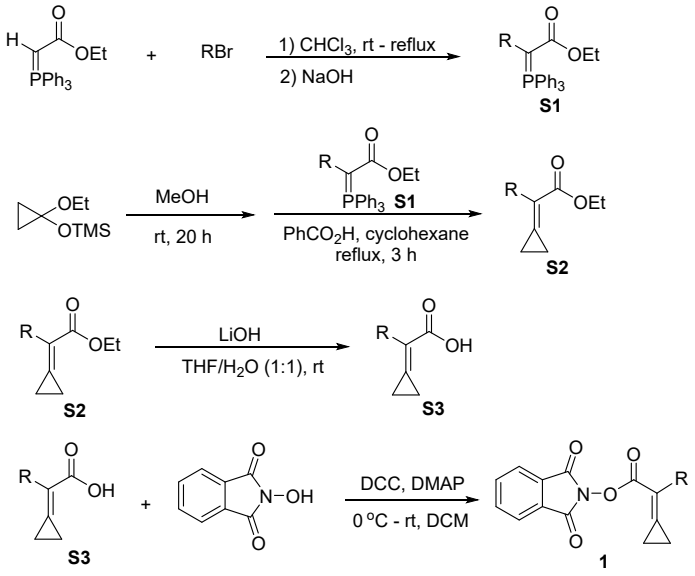
Substrates of NHPI esters



Substrates of ArBr



General Procedure for the Synthesis of Substrates 1



Step 1: A solution of ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (20 mmol, 1.0 equiv) and the corresponding RBr (20 mmol, 1.0 equiv) in $CHCl_3$ (60.0 mL) was stirred at room temperature for 30 min. Afterwards the mixture was refluxed for 12 h in an oil bath. The solvent was removed under reduced pressure and the residue was dissolved in water (75 mL) and CH_2Cl_2 (75 mL). Then 2 M NaOH was added and the mixture was allowed to stirred vigorously for 20 min. The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue could be directly used in the next step without further purification.[3]

Step 2: A round bottom flask equipped with a magnetic stir bar was added (1-ethoxycyclopropoxy)trimethylsilane (1.74 g, 10 mmol, 1.0 equiv) and methanol (5.0 mL). The solution was stirred at room temperature for 20 h. Then the methanol was removed in vacuo and the residue was dissolved in cyclohexane (50 mL). Benzoic acid (122 mg, 1.0 mmol, 0.1 mmol) was also added and the mixture was heated to reflux in an oil bath. The corresponding ylide **S1** (12 mmol, 1.2 equiv) was slowly added in 30 min. The mixture was allowed to reflux for another 2.5 h. After cooling down to room temperature, the solution was collected and the residue was washed with petroleum ether. The solution and the washings were combined and concentrated under reduced pressure. The residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1) to afford the compound **S2** as a colorless oil in moderate yields (ranging

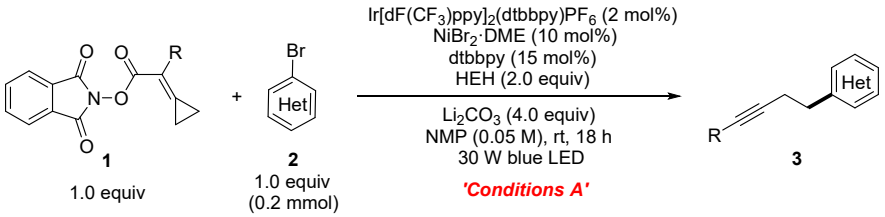
from 50% to 70%).

Step 3: A solution of compound **S2** in THF (20 mL) and water (20 mL) was stirred at 0 °C in an ice bath for 10 min, Lithium hydroxide (5.0 equiv) was slowly added to the solution. The resulting mixture was stirred at room temperature and monitored by TLC analysis. Upon completion, the mixture was acidified by adding HCl (1.0 M). The aqueous solution was extracted with ether and the combined organics was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 2/1) to give the compound **S3** as a colorless oil.

Step 4: A solution of compound **S3** (3.0 mmol, 1.0 equiv), *N*-hydroxyphthalimide (3.6 mmol, 1.2 equiv) and 4-dimethylaminopyridine (37 mg, 0.3 mmol) in DCM (20 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (742 mg, 3.6 mmol, 1.2 equiv) in DCM (10.0 mL) was added dropwise for 25 min. The reaction system 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 = 6/1) to afford the compound **1** in moderate to good yields.

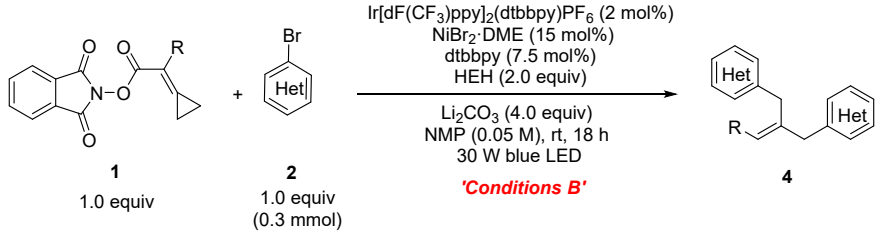
4. General Procedure for the Synthesis of Products

General Procedure B for the Synthesis of Products 3



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1** (0.2 mmol), ArBr **2** (0.2 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.5 mg, 2 mol%), HEH (101.3 mg, 2.0 equiv), dtbbpy (8.1 mg, 15 mol%), Li_2CO_3 (59.1 mg, 4.0 equiv), $NiBr_2$·DME (6.2 mg, 10 mol%) and 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (30 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by a column chromatography on silica gel to afford the purified product **3**.

General Procedure C for the Synthesis of Products 4

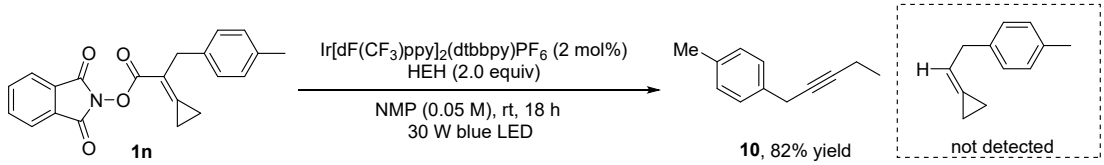


In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1** (0.3 mmol), ArBr **2** (0.3 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (6.7 mg, 2 mol%), HEH (152.0 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), $NiBr_2$·DME (13.9 mg, 15 mol%) and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain

temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by a column chromatography on silica gel to afford the purified product **4**.

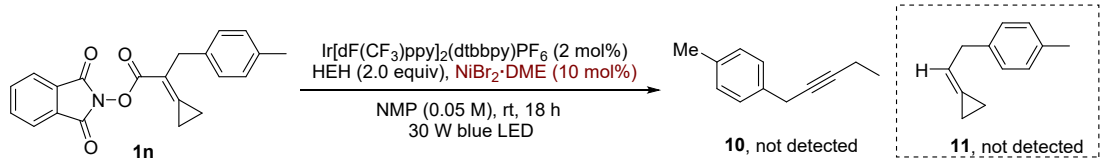
5. Mechanistic Studies

5.1 Transformations of substrate 1n under the photocatalytic conditions



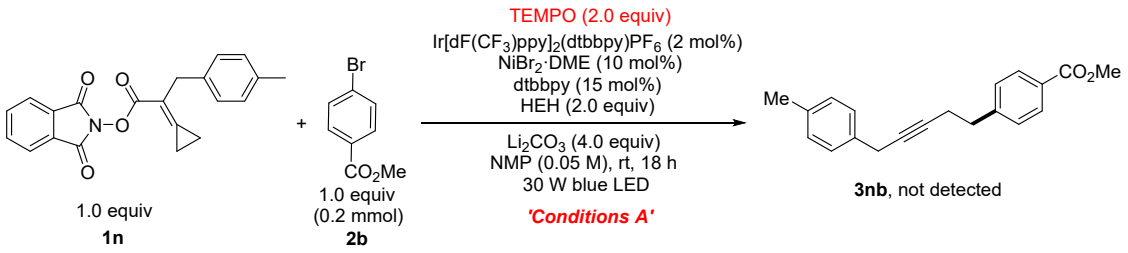
In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1n** (69.4 mg, 0.2 mmol), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.5 mg, 2 mol%), HEH (101.3 mg, 2.0 equiv) and degassed NMP (4.0 mL, 0.05 M) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. The mixture was placed 5 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (30 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by PTLC to afford the rearrangement product **10** (25.9 mg, 82% yield) as a colorless oil in 82% yield, while the 1-(2-cyclopropylideneethyl)-4-methylbenzene product was not detected in this reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 3.53 (t, *J* = 2.6 Hz, 2H), 2.32 (s, 3H), 2.22 (qt, *J* = 7.5, 2.4 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.9, 134.5, 129.1, 127.7, 83.7, 77.2, 24.7, 21.0, 14.2, 12.5; **IR (neat)**: ν 2956, 2924, 2855, 1733, 1514, 1494, 1459, 1362, 1186, 1080, 967, 806 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}$ 159.1168; found 159.1168.

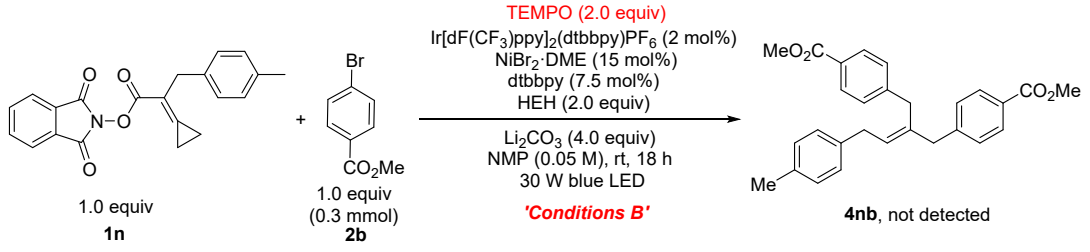


Based on the above reaction conditions, when we added extra $NiBr_2$·DME (10 mol%), neither product **10** nor the cyclopropane-maintained product **11** was detected. Other complexes from the reaction were isolated. These resulting ring-opening products from the MCP fragment were mixed together owing to their similar polarity and molecular weight, and we failed to figure out their structures. These results indicate that the free nickel species could destroy the MCP moiety.

5.2 Radical Trapping Experiments



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1n** (69.4 mg, 0.2 mmol), **2b** (42.8 mg, 0.2 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (4.5 mg, 2 mol%), HEH (101.3 mg, 2.0 equiv), dtbbpy (8.1 mg, 15 mol%), Li_2CO_3 (59.1 mg, 4.0 equiv), $NiBr_2$·DME (6.2 mg, 10 mol%), TEMPO (62.5 mg, 2.0 equiv) and 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (30 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was analyzed by ^{1}H NMR, where the desired product **3nb** was not observed.



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1n** (104.1 mg, 0.3 mmol), **2b** (64.2 mg, 0.3 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (6.7 mg, 2 mol%), HEH (152.0 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), $NiBr_2$·DME (13.9 mg, 15 mol%), TEMPO (93.8 mg, 2.0 equiv) and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was analyzed by ^{1}H NMR, where the desired product **4nb** was not observed.

The above results indicated that a radical process was involved in the generation of product **3** and product **4**.

5.3 UV/vis absorption Studies

All the UV-Vis absorption spectra were recorded on the SHIMADZU UV-2600 UV-visible spectrophotometer. As shown in Figure S2, substrate **1a** in DMAc (0.01 M) have an absorbtion tail that extends to 400 nm. Figure S3 shows the UV-Vis absorption spectra of DMAc solutions of HEH (0.1 M), **1a** (0.1 M), and a mixture of HEH (0.1 M) with **1a** (0.1 M). Consistent with the previous reports, a bathochromic shift (Figure S3, rea band) is observed for a mixture of NHPI ester **1a** and Hantzsch-ester, which indicates the formation of an electron donor-acceptor (EDA) complex. Hence, EDA-complex could probably provide another pathway for radical production.

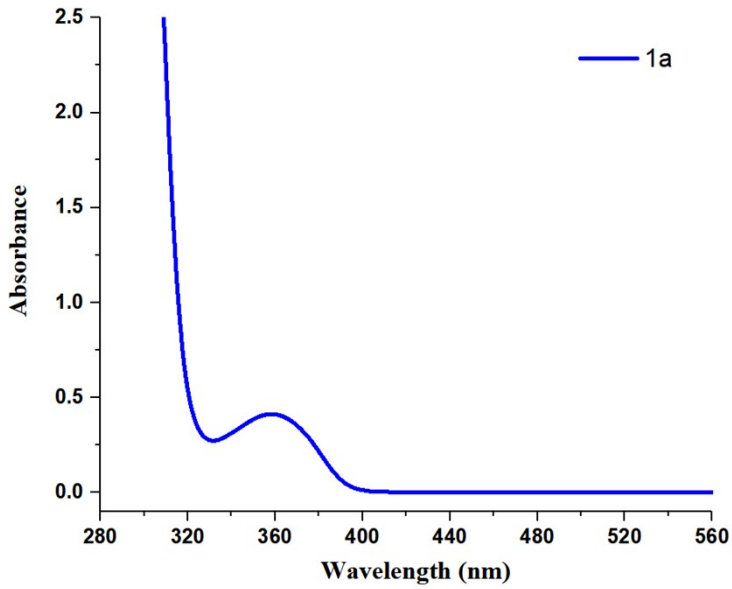


Figure S2. UV-Vis absorption spectra of **1a**

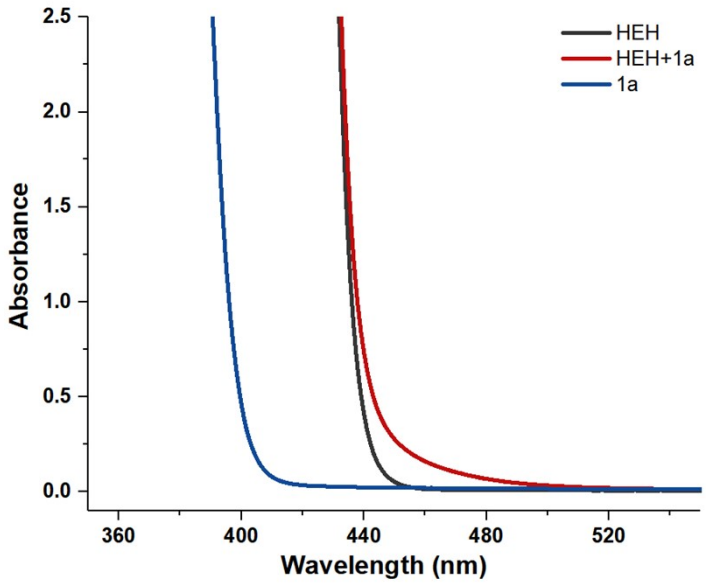


Figure S3. UV-Vis absorption spectra of HEH, **1a**, and their mixture

5.4 Emission Quenching Studies

All the emission intensities were recorded by Hitachi F-4600 FL spectrometer. Solutions of $Ir[dF(CF_3)ppy]_2(dtbbpy)\ PF_6$ (2×10^{-5} M) in dry NMP were excited at 380 nm and the emission intensity was collected at the maximum wavelength 480 – 481 nm. Solutions of different concentration of HEH, $NiBr_2$·diglyme and substrate **1a** were prepared respectively and introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum.

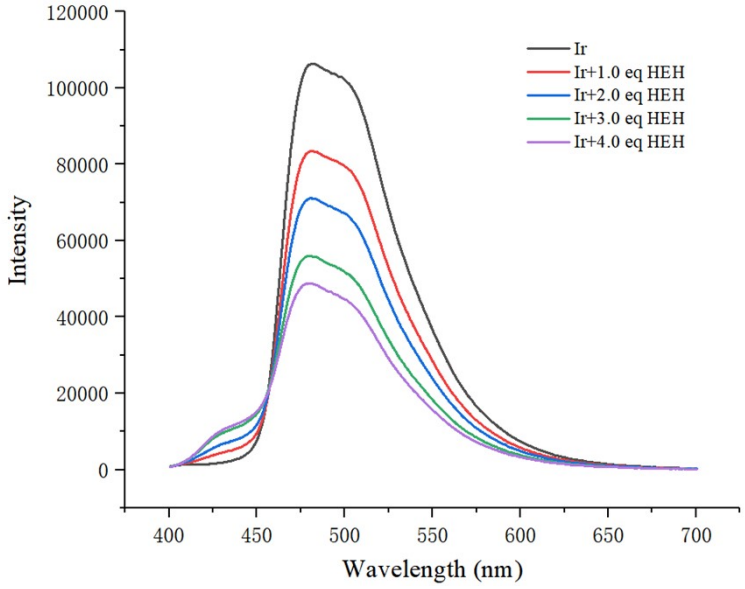


Figure S4. Stern-Volmer Quenching of Photocatalyst with HEH

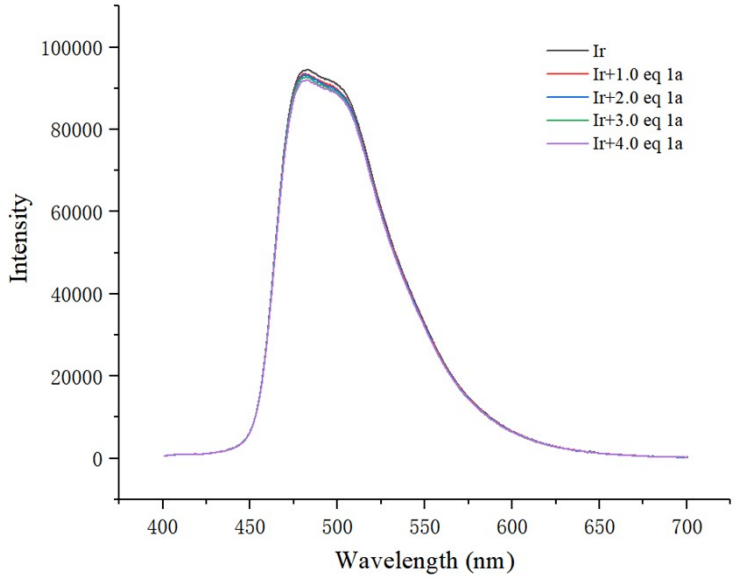


Figure S5. Stern-Volmer Quenching of Photocatalyst with Substrate **1a**

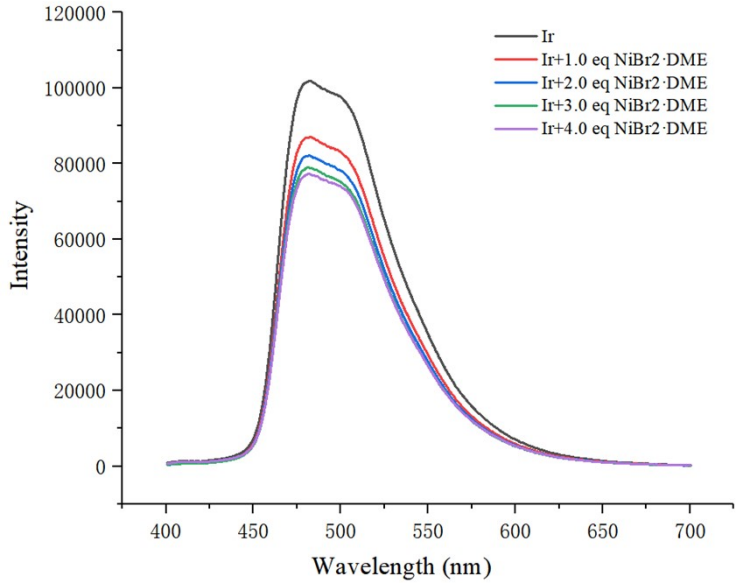


Figure S6. Stern-Volmer Quenching of Photocatalyst with $NiBr_2$·DME

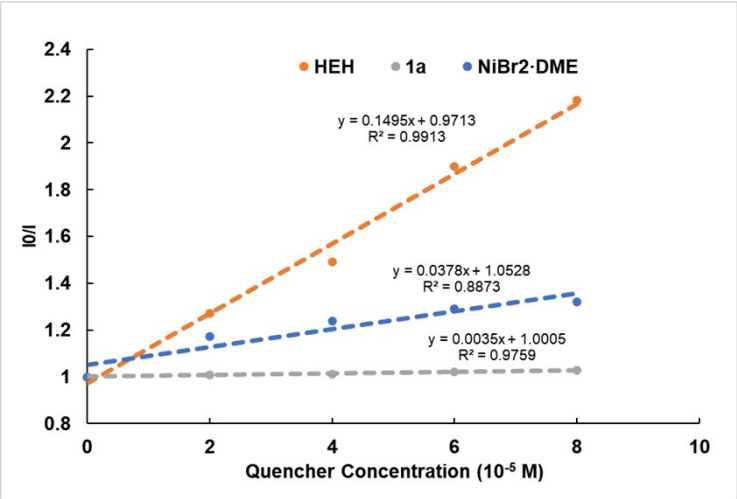
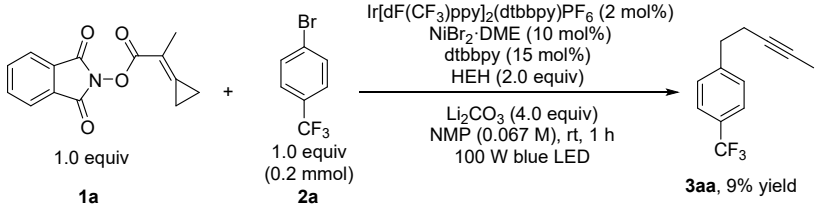


Figure S7. Stern-Volmer Quenching of Photocatalyst with HEH, **1a**, and $NiBr_2$·diglyme

5.5 Quantum Yield Determination[4]

To further investigate the mechanism of the reactions, we employed the two model reactions of **1a** to **3aa** and **4aa** to measure their quantum yields, respectively. 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.



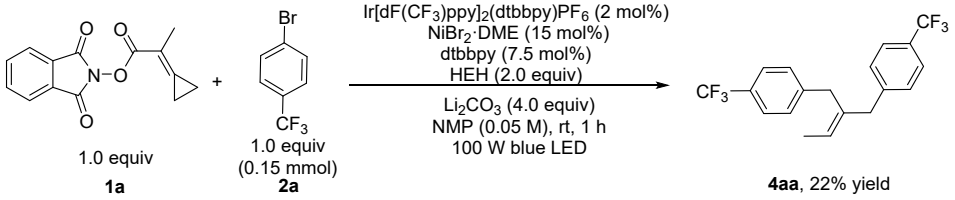
A cuvette equipped with a magnetic stir bar was added substrate **1a** (51.4 mg, 0.2 mmol), **2a** (28 μL, 0.2 mmol, 1.0 equiv), $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (4.5 mg, 2 mol%), HEH (101.3 mg, 2.0 equiv), dtbbpy (8.1 mg, 15 mol%), Li_2CO_3 (59.1 mg, 4.0 equiv), $NiBr_2$·DME (6.2 mg, 10 mol%) and degassed NMP (3.0 mL, 0.067 M) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the tube was placed 5 cm away from the blue LED (100 W) and stirred for 1 h at room temperature. Upon completion, 1,3,5-trimethoxybenzene (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 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. The quantum yield is calculated to be

0.15.

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

$$\frac{0.09 \times 0.2 \times 10^{-3} mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m \cdot s^{-1}}{(3 \times 10^{-3} W \cdot cm^{-2} \times 3 cm^{2}) \times 3600 s \times 455 \times 10^{-9} m} = 0.15$$

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 ^{1}H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.



A cuvette equipped with a magnetic stir bar was added substrate **1a** (38.6 mg, 0.15 mmol), **2a** (21 μL, 0.15 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (3.4 mg, 2 mol%), HEH (76.0 mg, 2.0 equiv), dtbbpy (3.0 mg, 7.5 mol%), Li_2CO_3 (44.4 mg, 4.0 equiv), $NiBr_2$·DME (7.0 mg,10 mol%) and degassed NMP (0.05 M, 3.0 mL) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the tube was placed 5 cm away from the blue LED (100 W) and stirred for 1 h at room temperature. Upon completion, 1,3,5-trimethoxybenzene (25.2 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 Na_2SO_4, filtered, and concentrated to dryness. The crude was analyzed by ^{1}H NMR. The quantum yield is calculated to be 0.04.

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

$$\frac{0.11 \times 0.15 \times 10^{-3} mol \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m \cdot s^{-1}}{(10.0 \times 10^{-3} W \cdot cm^{-2} \times 3 cm^{2}) \times 3600 s \times 455 \times 10^{-9} m} = 0.04$$

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 ^{1}H NMR, ΔE was measured by ILT1400 Portable Radiometer/Photometer.

5.6 Cyclic Voltammetry Experiment

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model Chi660e. The substrate **1a** in DMAc (0.001 M) was tested with Bu_4NPF_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. Ar 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.

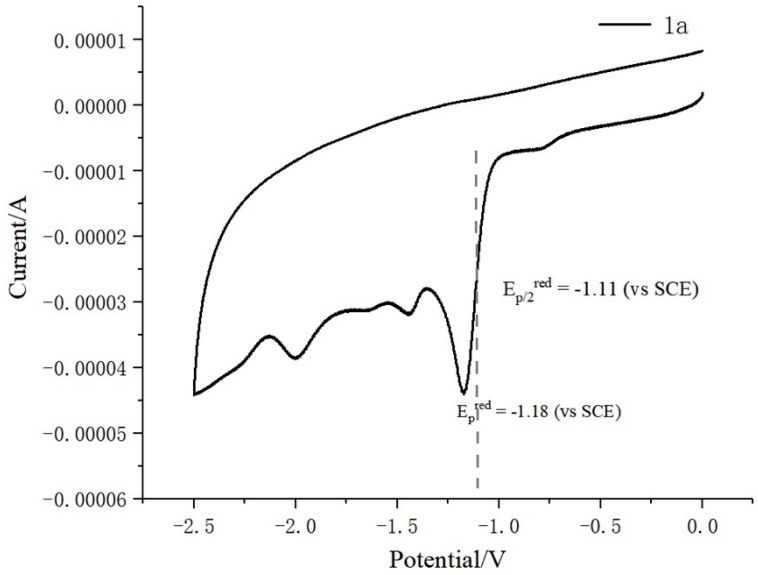
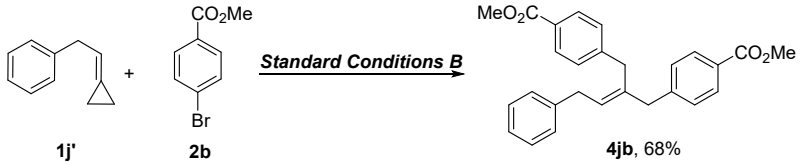


Figure S8. Cyclic Voltammogram of **1a**

5.7 Using classical MCP substrate instead under conditions B

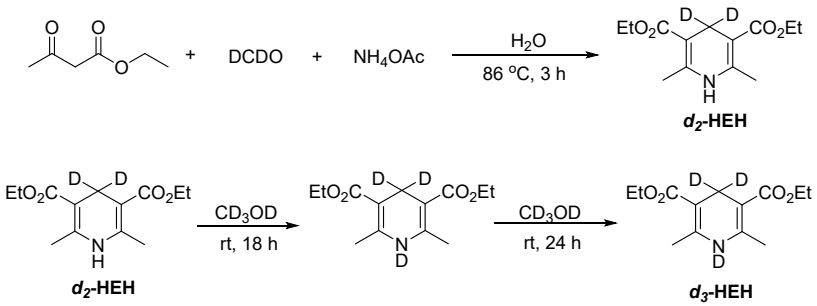


1j' **2b** **4jb**, 68%

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1j'**[5] (43.3 mg, 0.3 mmol), **2b** (64.2 mg, 0.3 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (6.7 mg, 2 mol%), HEH (152.0 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), $NiBr_2$·DME (13.9 mg, 15 mol%), and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The product **4jb** was isolated in 68% yield (43.7 mg).

5.8 Deuterium studies

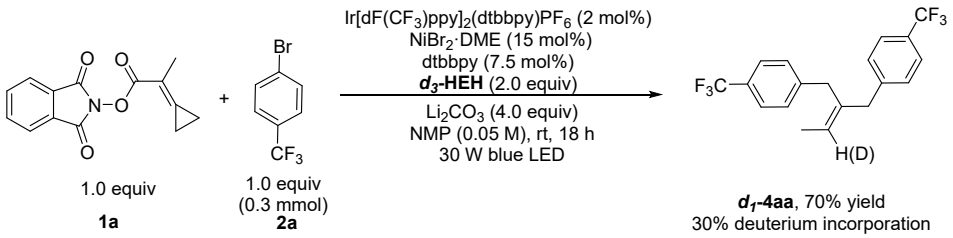
Synthesis of Deuterated Hantzsch Esters



The deuterated Hantzsch esters was prepared according to the previous reported procedure.[2] 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 mixture was filtered and the obtained precipitate was dried to afford compound ***d*$_2$-HEH** (542.0 mg, 71% yield) as a yellow solid.

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 18 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 (501.0 mg, 98% yield). The spectral data of deuterated Hantzsch Esters is consisted with the previous reports.[2] **^{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



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (77.1 mg, 0.3 mmol), **2a** (42 μL, 0.3 mmol, 1.0 equiv), $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (6.7 mg, 2 mol%), ***d*$_3$-HEH** (153.7 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), $NiBr_2$·DME (13.9

mg, 15 mol%) and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by a column chromatography on silica gel to afford the final product in 70% yield with 30% deuterium incorporation.

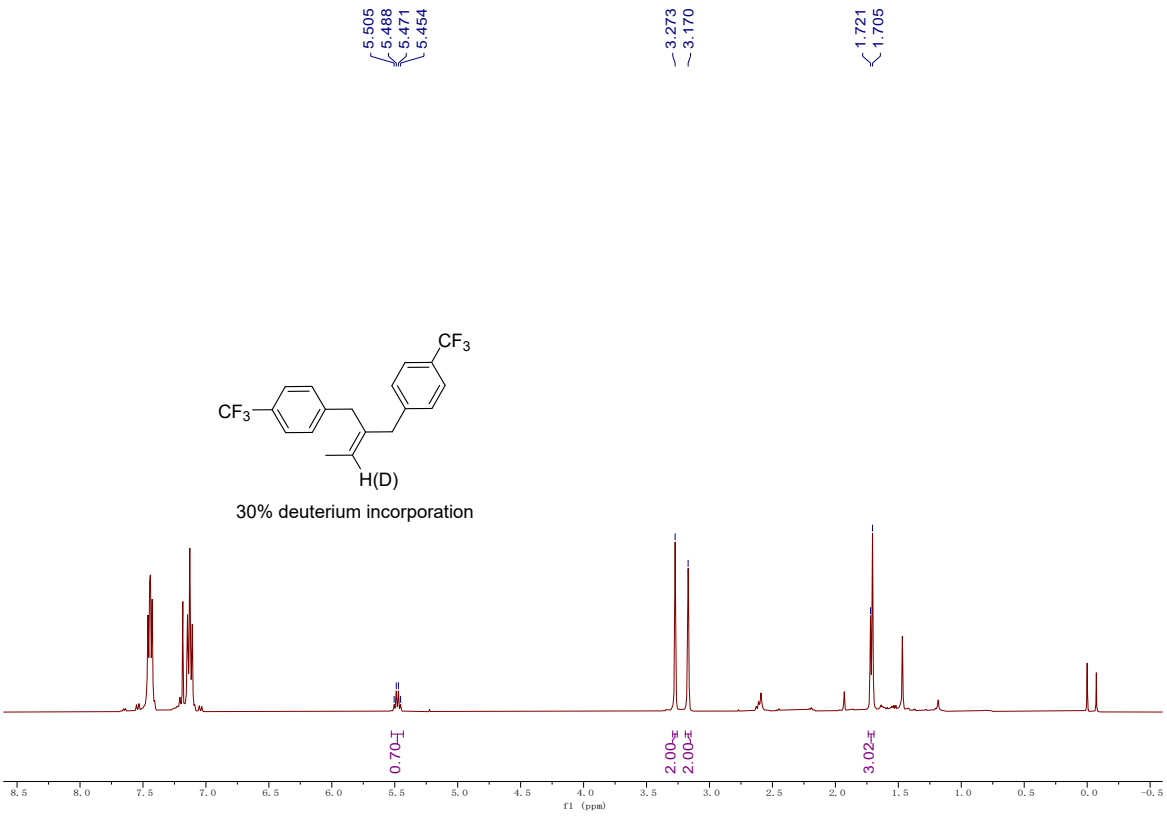
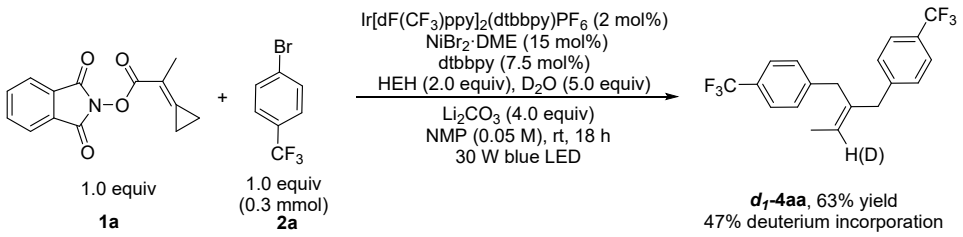


Figure S9. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of deuterium studies with ***d_3*-HEH**

D_2O was added under the standard conditions



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (77.1 mg, 0.3

mmol), **2a** (42 μL, 0.3 mmol, 1.0 equiv), $Ir[dF(CF_3)ppy)_2(dtbbpy)PF_6$ (6.7 mg, 2 mol%), HEH (152.0 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), D_2O (27 μL, 5.0 equiv), $NiBr_2$·DME (13.9 mg, 15 mol%) and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by a column chromatography on silica gel to afford the final product (containing a trace amount of impurities that failed to be separated) in 63% yield with 47% deuterium incorporation.

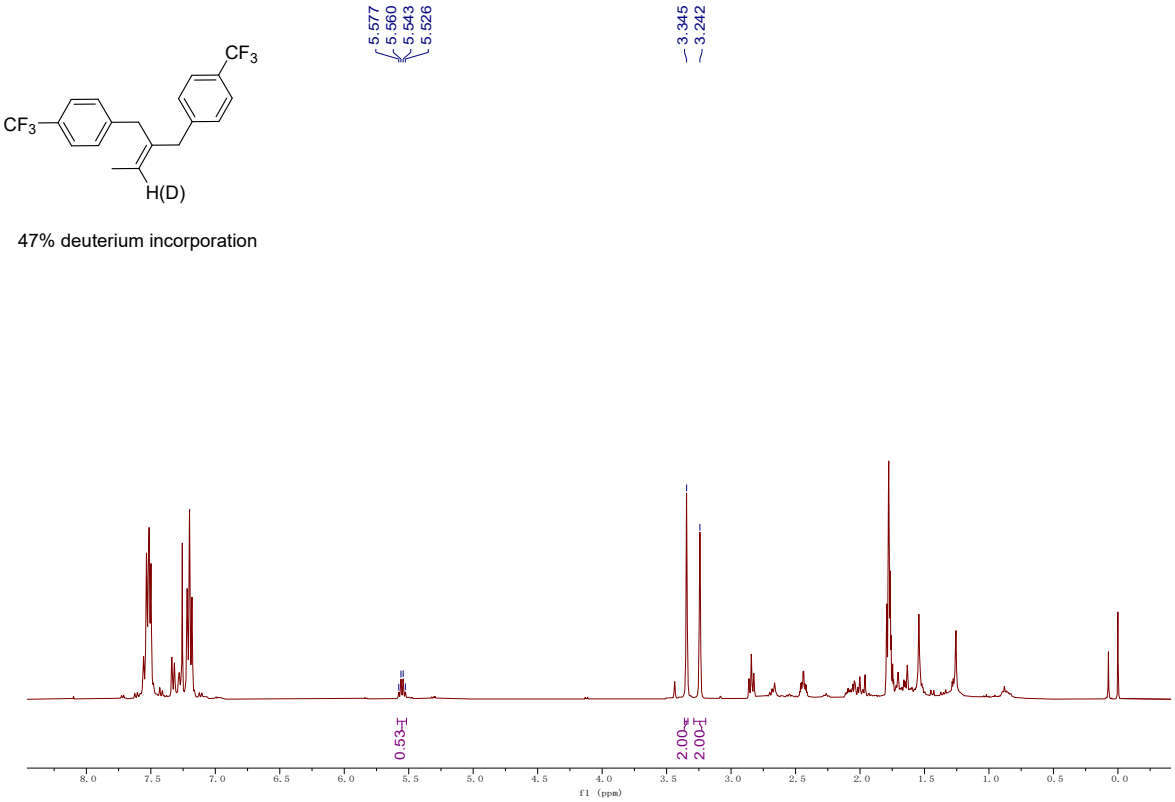
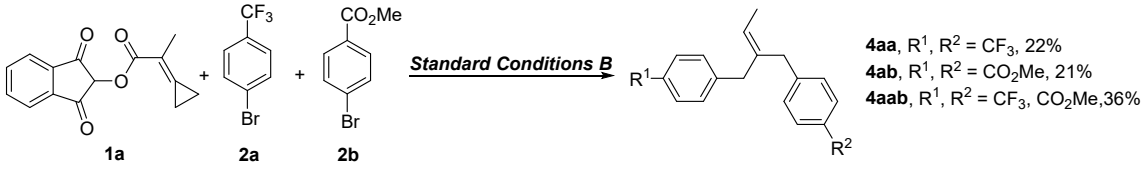


Figure S10. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum of deuterium studies with D_2O

5.9 Crossover experiment

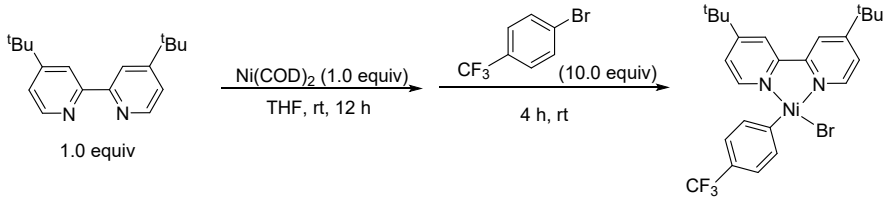


1a **2a** **2b**

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (77.1 mg, 0.3 mmol), **2a** (21 μL, 0.15 mmol), **2b** (32.2 mg, 0.15 mmol), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (6.7 mg, 2 mol%), HEH (152.0 mg, 2.0 equiv), dtbbpy (6.0 mg, 7.5 mol%), Li_2CO_3 (88.7 mg, 4.0 equiv), $NiBr_2$·DME (13.9 mg, 15 mol%) and degassed NMP (6.0 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 cm away from the blue LED (30 W) and stirred for 18 h with a fan to maintain temperature. Upon completion, EtOAc (40 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 10 mL), the organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude was purified by a column chromatography on silica gel to afford product **4aa** in 22% yield and product **4ab** in 21% yield (yields were calculated on 0.15 mmol scale). Mixed coupling product **4aab** was also isolated as a colorless oil (19.0 mg, 36% yield, Z/E mixture). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.55 – 7.50 (m, 2H), 7.23 – 7.14 (m, 4H), 5.58 – 5.50 (m, 1H), 3.91 (s, 3H, Z/E mixture), 3.34 (s, 2H), 3.23 (s, 2H), 1.78 (d, *J* = 5.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ (167.08, 167.05, Z/E mixture), (145.3, 145.2, Z/E mixture), (144.0, 143.9, Z/E mixture), (136.6, 136.5, Z/E mixture), (129.8, 129.6, Z/E mixture), (129.3, 129.0, Z/E mixture), (128.8, 128.58, Z/E mixture), 128.63 (q, *J* = 31.9 Hz), [125.3 (q, *J* = 4.0 Hz), 125.2 (q, *J* = 4.0 Hz), Z/E mixture], 124.3 (q, *J* = 272.1 Hz), (124.0, 123.9, Z/E mixture), (52.009, 51.996, Z/E mixture), (43.1, 42.8, Z/E mixture), (35.1, 34.9, Z/E mixture), 13.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2972, 2894, 1722, 1416, 1325, 1088, 1046, 880 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}F_3O_2$ 349.1410; found 349.1408.

5.10 Control Experiments with *(dtbbpy)Ni(p-CF_3Ar)Br*

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

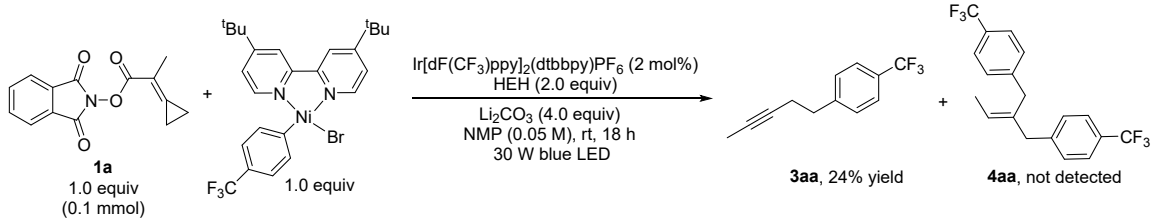


The *(dtbbpy)Ni(p-CF_3Ar)Br* was prepared according to the previous literature.[6] In an Ar-filled glove-box, a solution of $Ni(COD)_2$ (275.1 mg, 1.0 mmol, 1.0 equiv) and 4,4'-di-tert-butyl-2,2'-bipyridine (268.4 mg, 1.0 mmol, 1.0 equiv) was stirred in dry THF (5.0 mL) for 12 h at room temperature, then 1-bromo-4-(trifluoromethyl)benzene (1.4 mL, 10.0 mmol, 10.0 equiv) 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 × 10 mL) and dried to afford *(dtbpy)Ni(p-CF_3Ar)Br* (363.0 mg, 66% yield) as a brown solid. The product was directly used without further purification.

The ^{1}HNMR data of *(dtbbpy)Ni(p-CF_3Ar)Br* were consistent with previously reported;[6]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.14 (s, 1H), 7.77 – 7.62 (m, 4H), 7.44 (br, 1H), 7.10 (br, 4H), 1.34 (s, 18H).

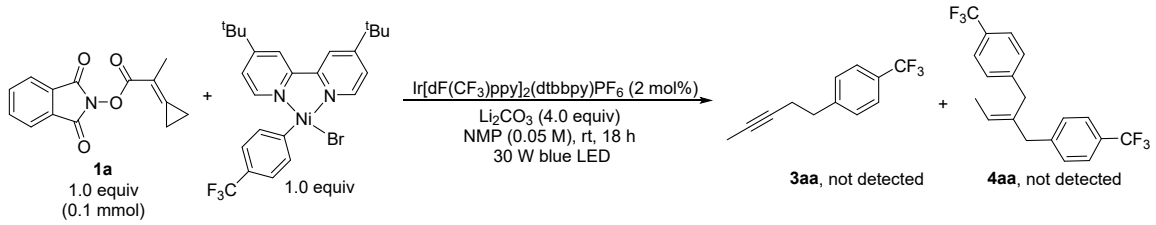
Stoichiometric Experiments using *(dtbbpy)Ni(p-CF_3Ar)Br* as catalyst



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (25.7 mg, 0.1 mmol), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (2.2 mg, 2 mol%) HEH (50.6 mg, 2.0 equiv), and Li_2CO_3 (29.5 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where *(dtbbpy)Ni(p-CF_3Ar)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

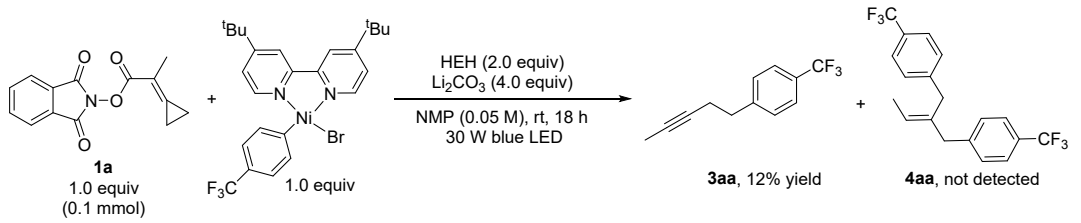
tube was placed 5.0 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, 1,3,5-trimethoxybenzene (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR.

Stoichiometric Experiments using *(dtbbpy)Ni(p-CF$_3$Ar)Br* as catalyst in the absence of HEH



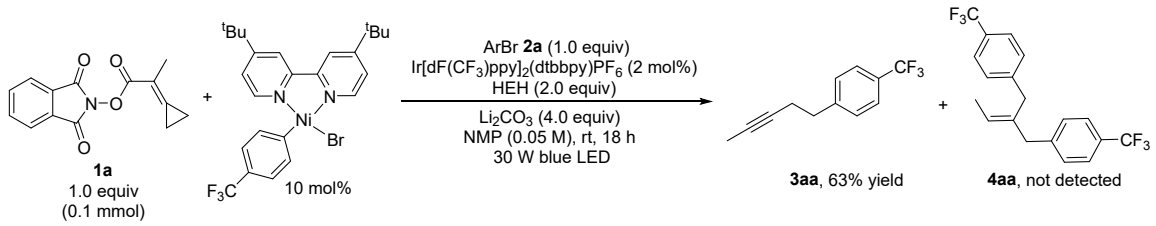
In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (25.7 mg, 0.1 mmol), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (2.2 mg, 2 mol%), and Li_2CO_3 (29.5 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where *(dtbbpy)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-trimethoxybenzene (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR. The product **3aa** and product **4aa** were not detected under this condition.

Stoichiometric Experiments using *(dtbbpy)Ni(p-CF$_3$Ar)Br* as catalyst in the absence of photocatalyst



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (25.7 mg, 0.1 mmol), HEH (50.6 mg, 2.0 equiv), and Li_2CO_3 (29.5 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where *(dtbbpy)Ni(p-CF_3Ar)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-trimethoxybenzene (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 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.

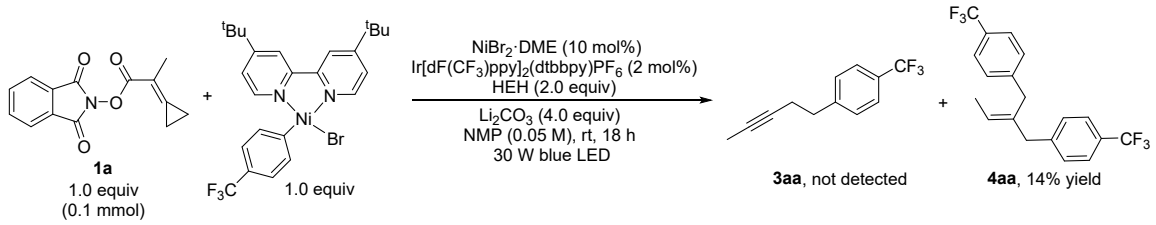
Substoichiometric experiments using *(dtbbpy)Ni(p-CF_3Ar)Br* as catalyst



In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (25.7 mg, 0.1 mmol), **2a** (14 μL，0.1 mmol, 1.0 equiv), Ir[dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (2.2 mg, 2 mol%) HEH (50.6 mg, 2.0 equiv), and Li_2CO_3 (29.5 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where *(dtbbpy)Ni(p-CF_3Ar)Br* (5.5 mg, 0.1 mmol, 10mol%) 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-trimethoxybenzene

(16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR.

Substoichiometric experiments using *(dtbbpy)Ni(p-CF$_3$Ar)Br* as catalyst with external NiBr$_2$·DME



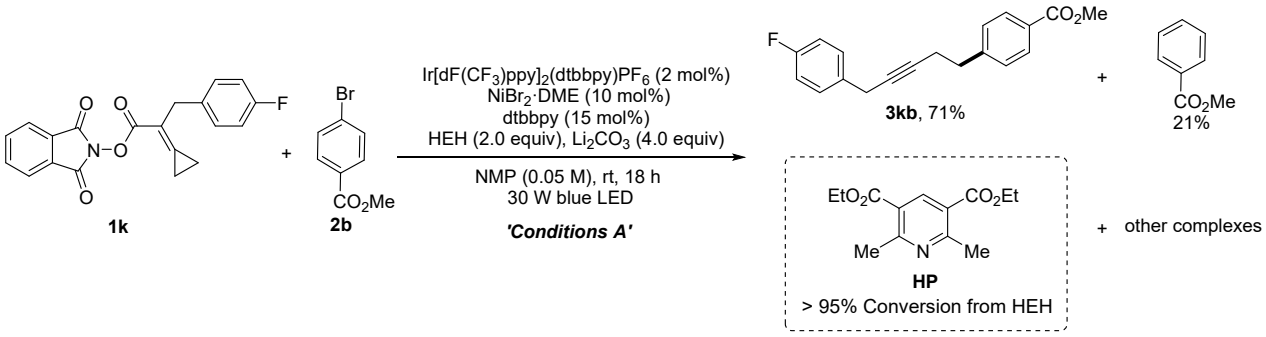
In an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (25.7 mg, 0.1 mmol), Ir[dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$ (2.2 mg, 2 mol%) HEH (50.6 mg, 2.0 equiv), and Li_2CO_3 (29.5 mg, 4.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the reaction tube was brought into the Ar-filled glove-box, where NiBr$_2$·DME (3.1 mg, 10 mol%), *(dtbbpy)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-trimethoxybenzene (16.8 mg, 1.0 equiv) used as an internal standard was added after removal of the tube from the light source. EtOAc (15 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 5 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude product was analyzed by ^1H NMR spectroscopic data.

6. Analysis of internal mixtures and some unsuccessful examples

6.1 Analysis of internal mixtures.

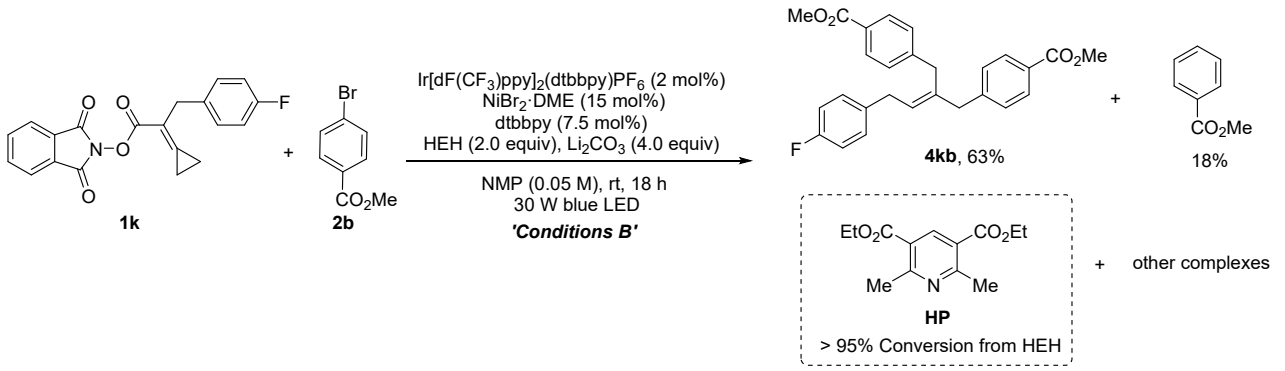
Under conditions A, the internal reaction mixture includes the alkyne product **3**, the dehalogenation product from ArBr, and the corresponding pyridine compound (HP) conversed from HEH. In addition, some other complexes also existed in the reaction mixture that failed to figure out their structures.

Herein we take the substrate **1k** as an example, we isolated the alkyne product **3kb** in 71% yield and the dehalogenation product in 21% yield. The corresponding pyridine compound (HP) was also isolated (> 95% conversion). We also isolated other complexes and analyzed them through ^{1}H NMR, the structures of these complexes were difficult to figure out.



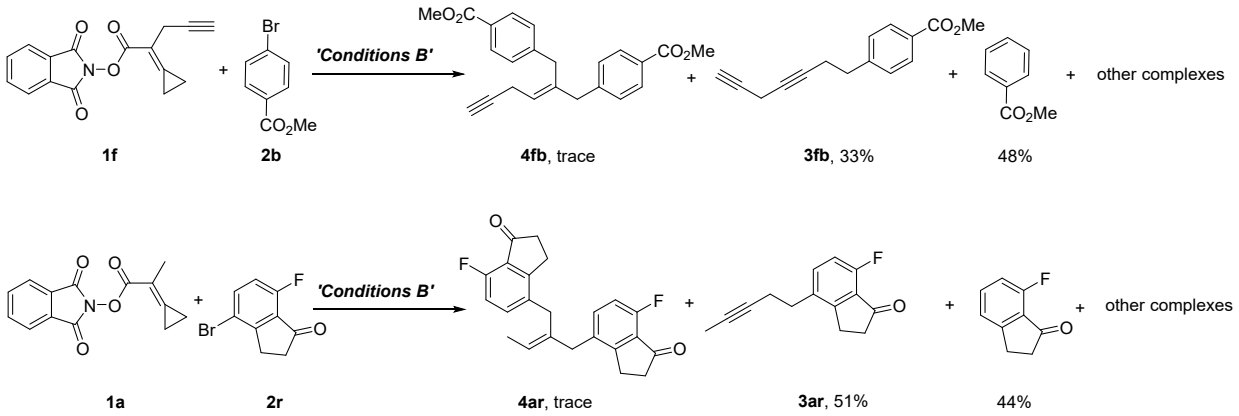
Under conditions B, the internal reaction mixture includes the dibenzylethylene product **4**, the dehalogenation product from ArBr, and the corresponding pyridine compound (HP), In addition, some other complexes also existed under such conditions.

Herein we still take the substrate **1k** as an example, we isolated the alkyne product **4kb** in 63% yield and the dehalogenation product in 18% yield. The corresponding pyridine compound (HP) was also isolated (> 95% conversion). Other complexes were also isolated and analyzed through ^{1}H NMR, but the structures of these complexes failed to be figured out.



6.2 Analysis of some unsuccessful examples.

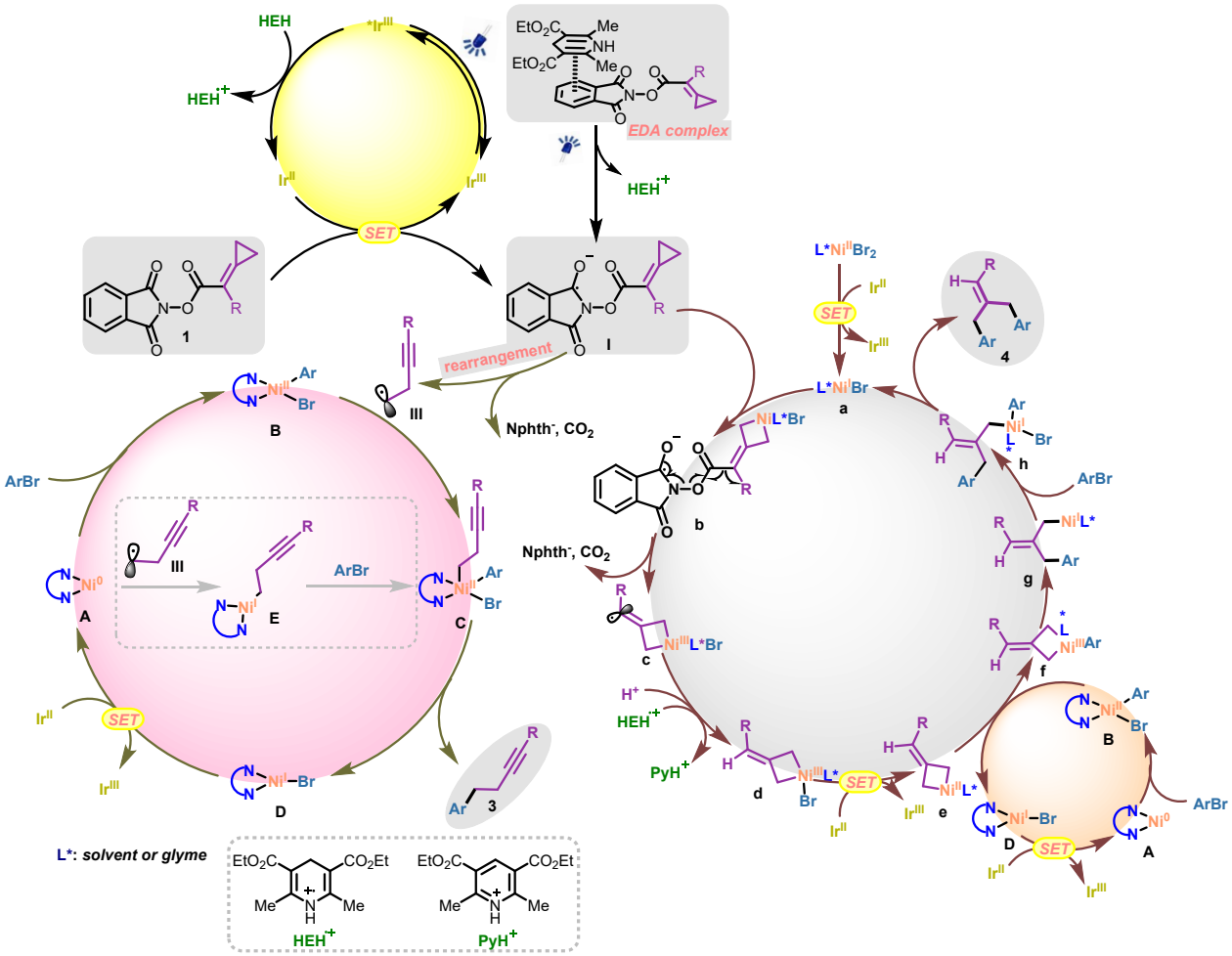
In the process of exploring the substrate scope, we found some unsuccessful examples. Herein we take the product **4fb** and **4ar** as an example to analyze the internal transformations.



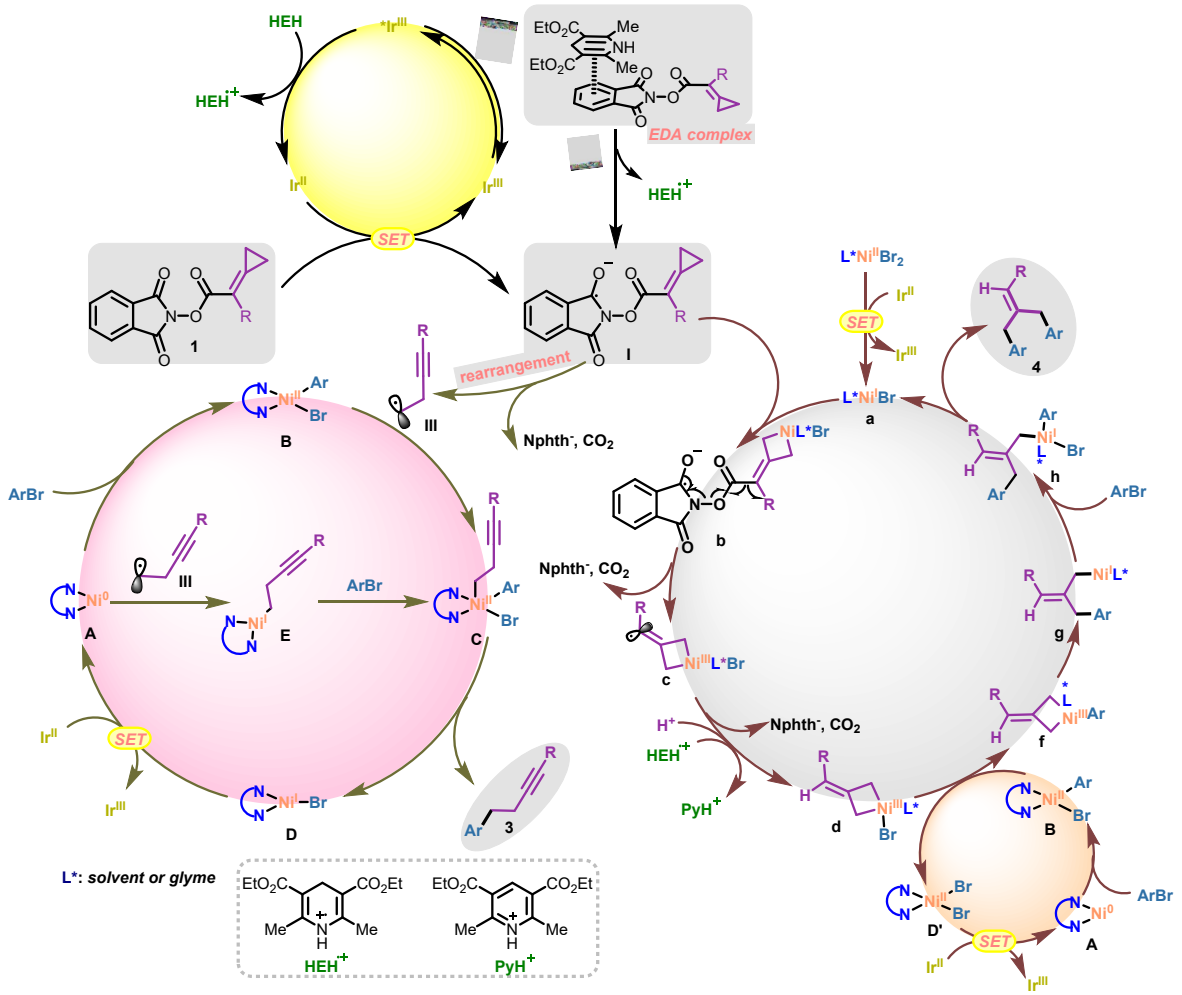
When we tried to obtain products **4fb** and **4ra** using conditions B, the double aryl groups coupling products were observed only in trace amounts. However, the corresponding alkyne products (**3fb** and **3ar**) were isolated in 33% and 51% yield, respectively. We speculated that coordination between the free nickel species with the substrates (coordination with the alkynyl group in substrate **1f** and coordination with oxygen atom and fluorine atom in substate **2r**) may restrict its catalytic ability to undergo cyclopropane insertion. Therefore, the radical rearrangement process would proceed smoothly to deliver the alkyne products. In addition, dehalogenation products were also isolated under conditions B. Notably, the structure of a small number of other complexes still could not be determined.

7. Proposed Reaction Mechanisms

Scheme S1. Proposed Mechanism

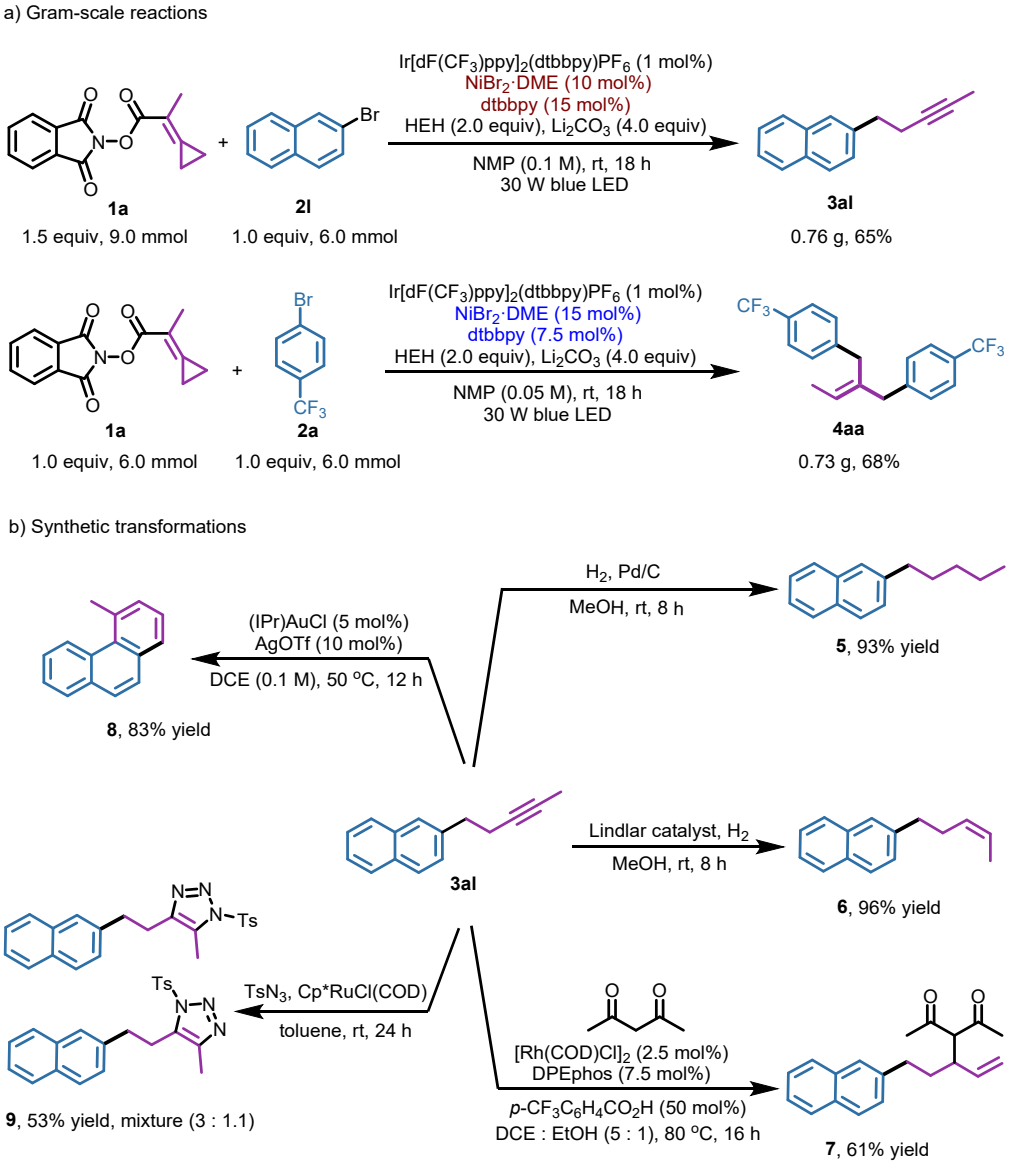


Scheme S2. Another possible mechanism involving the aryl transfer event occurring between $L_nNi^{II}ArBr$ (B) and nickel(III)acyclobutane species (d).



8. Synthetic Applications

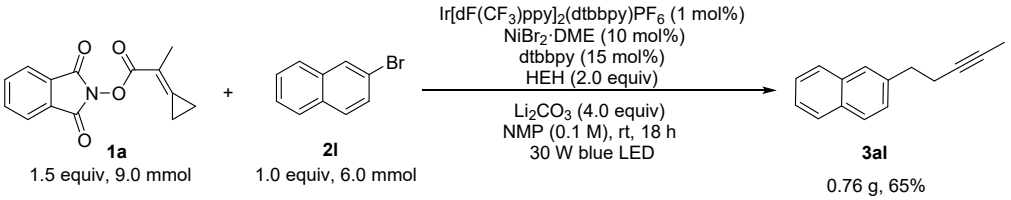
Scheme S3. Gram-scale reactions and synthetic transformations



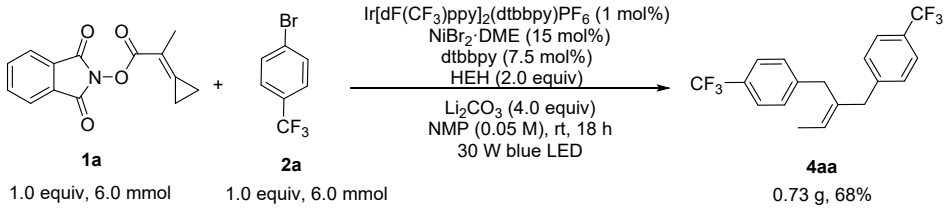
To investigate the synthetic applicability of the nickel-catalyzed protocol for the synthesis of alkynes, we conducted a gram-scale reaction (6.0 mmol) using the redox-active substrate **1a** and **2l** under the standard conditions A, where the loading of photocatalyst decreased to 1.0 mol%. The coupling product **3al** could be obtained in 65% yield. In addition, dibenzylethylene product **4aa** was also obtained in 68% yield through a gram-scale reaction (6.0 mmol) under the conditions B (Scheme S3a). Considering that alkynes are versatile building blocks for the diverse transformations in synthetic chemistry, product **3al** was selected to carry out some feasible transformations (Scheme S3b). The corresponding alkane **5** and alkene **6** could be obtained in 93% and 96% yields by

hydrogenation or partial hydrogenation of **3al**. A rhodium-catalyzed addition of 3al with 1,3-diketone was conducted to regioselectively afford the branched α-allylated 1,3-dicarbonyl product **7** in 61% yield. The intramolecular hydroarylation reaction of **3al** was realized utilizing the electrophilic (IPr)AuCl/AgOTf catalytic system, giving the 4-methylphenanthrene **8** in 83% yield. Ruthenium-catalyzed click reaction of 3al with tosyl azide afforded the [3 + 2] cycloaddition product **9** in 53% yield as a isomeric mixture (3 : 1.1).

8.1 Scale-up experiments of 1a.



An oven-dried Schlenk tube (100 mL) equipped with a magnetic stir bar was added **1a** (2.3 g, 9.0 mmol, 1.5 equiv), **2l** (1.23 g, 6.0 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (67.3 mg, 1 mol%), $NiBr_2$·DME (185.1 mg, 10 mol%), dtbbpy (241.6 mg, 15 mol%), HEH (3.04 g, 2.0 equiv), and Li_2CO_3 (1.77 g, 4.0 equiv). The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then degassed NMP (60 mL, 0.1 M) was injected into the tube under Ar. The mixture was stirred for 15 min before placed 10 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, EtOAc (120 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 40 mL). The organic layer was dried over 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 **3al** (0.76 g, 65% yield) as a colorless oil.

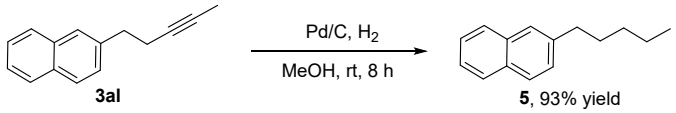


An oven-dried Schlenk tube (250 mL) equipped with a magnetic stir bar was added **1a** (1.54 g, 6.0 mmol, 1.0 equiv), **2a** (0.84 mL, 6.0 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (67.3 mg, 1

mol%), $NiBr_2$·DME (277.8 mg, 15 mol%), dtbbpy (120.8 mg, 7.5 mol%), HEH (3.04 g, 2.0 equiv), and Li_2CO_3 (1.77 g, 4.0 equiv). The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then degassed NMP (120 mL, 0.05 M) was injected into the tube under Ar. The mixture was stirred for 15 min before placed 10 cm away from the blue LED (30 W) and stirred for 18 h at room temperature. Upon completion, EtOAc (120 mL) was added into the tube and the mixture was washed with water for 3 times (3 × 60 mL). The organic layer was dried over 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 **4aa** (0.73 g, 68% yield) as a colorless oil.

8.2 Product transformations

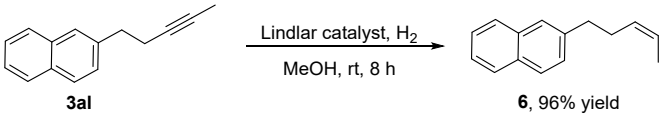
Synthesis of Compound 5



To a flask was added compound **3** (38.8 mg, 0.2 mmol), Pd/C (21.3 mg, 0.1 equiv, 10% Pd) and menthol (8.0 mL). The mixture was stirred vigorously at room temperature for 8 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 **5** (37.0 mg, 93% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 3H), 7.65 (s, 1H), 7.53 – 7.41 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.47 – 1.33 (m, 4H), 0.94 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 133.6, 131.9, 127.7, 127.6, 127.44, 127.37, 126.3, 125.8, 124.9, 36.1, 31.5, 31.1, 22.6, 14.0; **IR (neat)**: ν 3051, 2955, 2926, 2855, 1633, 1600, 1507, 1465, 1376, 1269, 1018, 958, 887, 853, 814, 743 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{15}H_{18}$ 198.1403; found 198.1400.

Synthesis of Compound 6



To a flask was added compound **3** (38.8 mg, 0.2 mmol), Lindlar catalyst (82.7 mg, 5 mol% 5% Pd) and menthol (10.0 mL). The mixture was stirred vigorously at room temperature for 8 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 **6** (37.8 mg, 96% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 3H), 7.66 (s, 1H), 7.51 – 7.41 (m, 2H), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.58 – 5.44 (m, 2H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.53 – 2.44 (m, 2H), 1.61 (d, *J* = 4.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.7, 133.6, 132.0, 129.6, 127.7, 127.6, 127.42, 127.37, 126.4, 125.8, 125.0, 124.6, 35.9, 28.6, 12.8; **IR (neat)**: ν 3052, 3013, 2922, 2855, 1632, 1600, 1507, 1438, 1366, 1270, 1018, 960, 852, 815, 744 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{15}H_{16}$ 196.1247; found 196.1244.

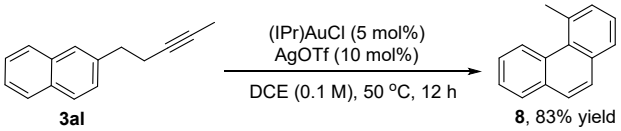
Synthesis of Compound 7[7]

An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3al** (77.7 mg, 0.4 mmol, 2.0 equiv), pentane-2,4-dione (21 μL, 0.2 mmol, 1.0 equiv), $[Rh(COD)Cl]_2$ (2.5 mg, 2.5 mol%), DPEphos (8.1 mg, 7.5 mol%), 4-(trifluoromethyl)benzoic acid (19.0 mg, 0.5 equiv). Then DCE (0.5 mL) and EtOH (0.1 mL) were injected into the tube. The mixture was allowed to stirred at 80 °C in an oil bath for 16 h. Upon completion, 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 **7** (36.0 mg, 61% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 3H), 7.58 (s, 1H), 7.50 – 7.38 (m, 2H), 7.30 – 7.26 (m, 1H), 5.59 (ddd, *J* = 17.0, 10.3, 9.4 Hz, 1H), 5.24 – 5.14 (m, 2H), 3.72 (d, *J* = 10.5 Hz, 1H), 3.02 – 2.79 (m, 2H), 2.72 – 2.60 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 1.80 – 1.68 (m, 1H), 1.63 – 1.51 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 203.5, 203.3, 138.9, 137.5, 133.6, 132.0, 128.0, 127.6, 127.4, 127.1, 126.4, 126.0, 125.2, 118.5, 74.6, 44.0, 34.1, 33.2, 30.0, 29.5; **IR (neat)**: ν 3052, 2926, 1696, 1639, 1599, 1507, 1418, 1355, 1188, 1147, 999, 922, 856, 818, 748 cm^{-1}; **HRMS** (DART) m/z:

[M+H]$^+$ Calcd. for $C_{20}H_{23}O_2$ 295.1693; found 295.1684.

Synthesis of Compound 8

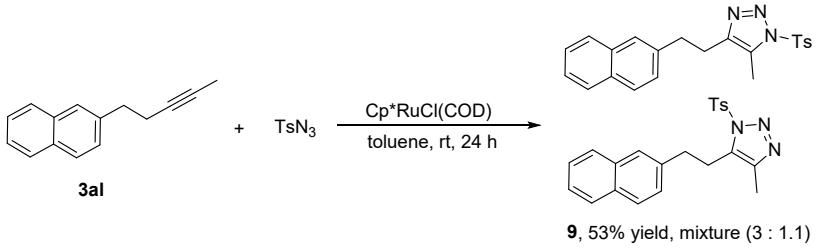


An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3al** (19.4 mg, 0.1 mmol, 1.0 equiv), (IPr)AuCl (3.5 mg, 5 mol%), and AgOTf (2.5 mg, 10 mol%). Then DCE (1.0 mL, 0.1 M) was injected into the tube. The mixture was allowed to stirred at 50 °C in an oil bath for 12 h. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (pure petroleum ether) to afford the product **8** (16.0 mg, 83% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.79 (dd, *J* = 6.3, 3.1 Hz, 1H), 7.73 (s, 2H), 7.67 – 7.57 (m, 2H), 7.52 – 7.49 (m, 2H), 3.17 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.5, 133.7, 133.5, 131.7, 131.2, 130.1, 128.7, 128.0, 127.5, 127.4, 127.1, 125.9, 125.8, 125.6, 27.4.

The spectroscopic data were consistent with those of previously reported.[8]

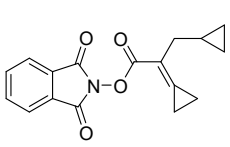
Synthesis of Compound 9[9]



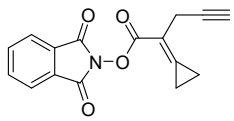
An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3al** (38.8 mg, 0.2 mmol, 1.0 equiv), Cp*RuCl(COD) (1.5 mg, 2 mol%), and toluene (2 mL, 0.1 M). Then TsN_3 (43 μL, 0.2 mmol, 1.0 equiv) was injected into the tube. The mixture was allowed to stirred at room temperature for 24 h. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (pure petroleum ether) to afford the product **9** (41.6 mg, 53% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, *mixture*) δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.89 – 7.72 (m, 5H, *mixtures of major and minor isomer*), 7.68 – 7.60 (m, 1H), 7.51 (s, 1H), 7.48 – 7.41 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 3H), 7.26 (d, *J* = 4.5 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H, *minor isomer*), 3.24 (t, *J* = 7.6 Hz, 2H), 3.13 – 3.04 (m, 3H, *mixtures of major and minor isomer*), 2.96 (t, *J* = 7.4 Hz, 1H, *minor isomer*), 2.46 (s, 1H, *minor isomer*), 2.43 (s, 3H), 2.07 (s, 1H, *minor isomer*), 1.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.8, 146.7 (*minor isomer*), 142.1, 138.2 (*minor isomer*), 137.4, 134.5, 134.12, 134.06 (*minor isomer*), 133.54, 133.49 (*minor isomer*), 132.2, 132.0 (*minor isomer*), 130.33, 130.30 (*minor isomer*), 128.5, 128.31 (*minor isomer*), 128.27, 127.9 (*minor isomer*), 127.7, 127.6 (*minor isomer*), 127.5, 127.4 (*minor isomer*), 127.1 (*minor isomer*), 127.0, 126.9, 126.7 (*minor isomer*), 126.2, 126.0 (*minor isomer*), 125.6, 125.4 (*minor isomer*), 35.7, 35.5 (*minor isomer*), 26.7 (*minor isomer*), 25.7, 21.9 (*minor isomer*), 21.8, 9.8, 8.7 (*minor isomer*); **IR (neat)**: ν 3050, 2923, 1708, 1630, 1599, 1222, 1164, 1121, 1032, 1009, 816, 749 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{22}O_6N_3S$ 392.1427; found 392.1418.

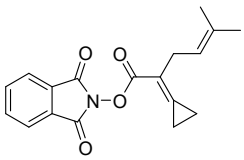
9. Characterization Data of New Substrates



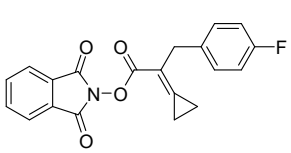
1,3-dioxoisoindolin-2-yl 3-cyclopropyl-2-cyclopropylidenepropanoate (1e): A white solid, 303.2 mg, 34% yield. M.p.: 126 – 128 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.44 (d, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.47 – 1.38 (m, 2H), 1.09 – 0.96 (m, 1H), 0.54 – 0.45 (m, 2H), 0.20 – 0.11 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9, 162.4, 144.7, 134.6, 129.1, 123.8, 118.4, 77.2, 77.0, 76.8, 36.0, 9.9, 6.2, 4.9, 4.2; **IR (neat)**: ν 3080, 2996, 2928, 1795, 1739, 1468, 1363, 1185, 877, 696 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{15}NO_4Na$ 320.0893; found 320.0900.



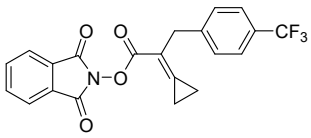
1,3-dioxoisoindolin-2-yl 2-cyclopropylidenepent-4-ynoate (1f): A white solid, 522.8 mg, 62% yield. M.p.: 188 – 190 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.48 (dt, *J* = 2.9, 1.5 Hz, 2H), 2.11 (t, *J* = 2.7 Hz, 1H), 1.69 – 1.62 (m, 2H), 1.62 – 1.55 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.2, 161.9, 147.6, 134.7, 129.0, 123.9, 113.1, 79.7, 70.6, 21.0, 5.8, 4.8. **IR (neat)**: ν 3271, 2985, 1800, 1745, 1407, 1363, 1185, 1028, 877 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{11}NO_4Na$ 304.0580; found 304.0581.



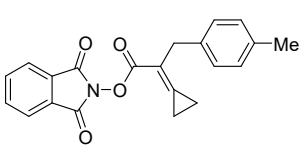
1,3-dioxoisoindolin-2-yl 2-cyclopropylidene-5-methylhex-4-enoate (1i): A white solid, 467.0 mg, 50% yield. M.p.: 88 – 90 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.32 – 5.24 (m, 1H), 3.22 (d, *J* = 7.3 Hz, 2H), 1.71 (s, 3H), 1.66 (s, 3H), 1.63 – 1.56 (m, 2H), 1.42 – 1.32 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7, 162.3, 144.6, 134.6, 133.4, 129.1, 123.8, 120.3, 117.8, 30.1, 25.7, 17.8, 6.1, 4.0; **IR (neat)**: ν 2985, 2934, 1795, 1742, 1362, 1221, 1184, 1131, 878, 698 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{17}NO_4Na$ 334.1050; found 334.1047.



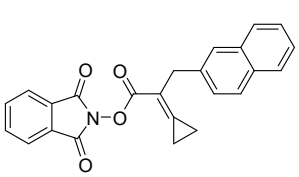
1,3-dioxoisoindolin-2-yl 2-cyclopropylidene-3-(4-fluorophenyl) propanoate (1k): A white solid, 474.0 mg, 45% yield. M.p.: 132 – 134 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.03 – 6.92 (m, 2H), 3.82 (s, 2H), 1.67 – 1.57 (m, 2H), 1.30 – 1.19 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6, , 162.2, 161.6 (d, *J* = 244.5 Hz), 146.6, 134.6, 134.3 (d, *J* = 3.5 Hz), 130.4 (d, *J* = 8.3 Hz), 129.0, 123.9, 117.8, 115.2 (d, *J* = 21.2 Hz), 36.4, 6.2, 4.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.8; **IR (neat)**: ν 2976, 2906, 1793, 1742, 1508, 1221, 1185, 878, 697 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{14}NO_4FNa$ 374.0799; found 374.0804.



1,3-dioxoisoindolin-2-yl 2-cyclopropylidene-3-(4-(trifluoromethyl)phenyl)propanoate (1m): A white solid, 541.4 mg, 45% yield. M.p.: 120 – 122 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 2H), 1.71 – 1.62 (m, 2H), 1.32 – 1.23 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.2, 147.4, 142.8, 134.7, 129.2, 129.0, 128.8 (q, *J* = 32.1 Hz), 125.3 (q, *J* = 4.2 Hz), 124.2 (q, *J* = 271.9 Hz), 123.9, 117.1, 37.0, 6.5, 4.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.4; **IR (acetone)**: ν 2987, 1795, 1742, 1361, 1323, 1120,1066, 1017, 877, 696 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{14}NO_4F_3Na$ 424.0767; found 424.0774.

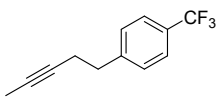


1,3-dioxoisoindolin-2-yl 2-cyclopropylidene-3-(p-tolyl) propan oate (1n): A white solid, 531.0 mg, 51% yield. M.p.: 102 – 104 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.20 – 7.04 (m, 4H), 3.82 (s, 2H), 2.32 (s, 3H), 1.67 – 1.58 (m, 2H), 1.30 – 1.20 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7, 162.3, 146.4, 135.9, 135.7, 134.8, 134.6, 129.4, 129.1, 128.9, 128.2, 124.0, 123.9, 118.0, 36.8, 21.1, 6.3, 4.1; **IR (acetone)**: ν 2993, 2940, 1793, 1742, 1418, 1359, 1220, 1184, 878, 697 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{17}NO_4Na$ 370.1050; found 370.1057.

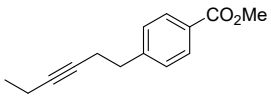


1,3-dioxoisoindolin-2-yl 2-cyclopropylidene-3-(naphthalen-2-yl) propanoate (1p): A white solid, 632.1 mg, 55% yield. M.p.: 155 – 157 °C. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.83 – 7.73 (m, 5H), 7.69 (s, 1H), 7.48 – 7.35 (m, 3H), 4.03 (s, 2H), 1.63 (t, *J* = 9.2 Hz, 2H), 1.21 (t, *J* = 9.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7, 162.3, 146.9, 136.2, 134.6, 133.5, 132.2, 129.1, 128.0, 127.6, 127.6, 127.5, 127.3, 125.9, 125.4, 123.8, 117.7, 37.3, 6.2, 4.2; **IR (neat)**: ν 3052, 2985, 1793, 1741, 1363, 1185, 877, 696 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{17}NO_4Na$ 406.1050; found 406.1055.

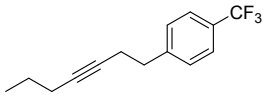
10. Characterization Data of Products



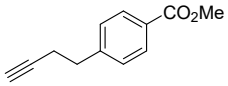
methyl 4-(hex-3-yn-1-yl)benzoate (3aa): A colorless oil, 31.8 mg, 75% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.44 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.77 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9, 128.8, 128.5 (q, *J* = 31.9 Hz), 125.2 (q, *J* = 4.4 Hz), 124.3 (q, *J* = 271.9 Hz), 77.9, 76.7, 35.2, 20.6, 3.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 2924, 2216, 1734, 1618, 1325, 1163, 1122, 1067, 1019, 825 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{11}F_3$ 212.0807; found 212.0808.



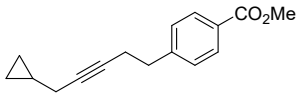
methyl 4-(hex-3-yn-1-yl)benzoate (3bb): A colorless oil, 31.6 mg, 73% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.45 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.14 (qt, *J* = 7.5, 2.4 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.4, 129.6, 128.6, 128.1, 82.9, 78.2, 52.0, 35.5, 20.6, 14.2, 12.3; **IR (neat)**: ν 2954, 2924, 2850, 1723, 1435, 1278, 1109, 804, 690 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{14}H_{16}O_2$ 216.1145; found 216.1146.



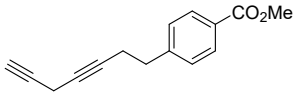
1-(hept-3-yn-1-yl)-4-(trifluoromethyl)benzene (3ca): A colorless oil, 34.0 mg, 71% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.47 (tt, *J* = 7.4, 2.4 Hz, 2H), 2.10 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.53 – 1.41 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.0, 128.8, 128.5 (q, *J* = 32.5 Hz), 125.2 (q, *J* = 4.1 Hz), 124.3 (q, *J* = 272.1 Hz), 81.5, 78.8, 35.2, 22.4, 20.7, 20.6, 13.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 2973, 2934, 1618, 1322, 1162, 1121, 1107, 1066, 1019, 824 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{14}H_{15}F_3$ 240.1120; found 240.1120.



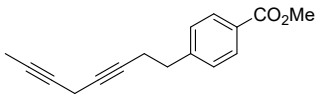
methyl 4-(but-3-yn-1-yl)benzoate (3db): A colorless oil, 26.3 mg, 70% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.51 (td, *J* = 7.4, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 145.7, 129.7, 128.5, 128.4, 83.2, 69.3, 52.0, 34.7, 20.1; **IR (neat)**: ν 3294, 2927, 2120, 1745, 1719, 1611, 1435, 1280, 1184, 1111, 1020, 878, 698 cm^{-1}; **HRMS** (EI) m/z: $[M-H]^+$ Calcd. for $C_{12}H_{11}O_2$ 187.0754; found 187.0754.



methyl 4-(5-cyclopropylpent-3-yn-1-yl)benzoate (3eb): A colorless oil, 36.8 mg, 76% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.47 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.18 (dt, *J* = 5.2, 2.4 Hz, 2H), 0.90 – 0.85 (m, 1H), 0.47 – 0.38 (m, 2H), 0.22 – 0.13 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.3, 129.6, 128.6, 128.1, 79.7, 79.2, 52.0, 35.4, 22.9, 20.6, 9.6, 3.8; **IR (EtOH)**: ν 2923, 2853, 1722, 1611, 1434, 1277, 1179, 1109, 1019, 767, 703 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{19}O_2$ 243.1380; found 243.1383.

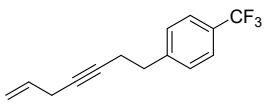


methyl 4-(hepta-3,6-diyn-1-yl)benzoate (3fb): A colorless oil, 16.3 mg, 36% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 3.13 (dt, *J* = 4.8, 2.5 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.48 (tt, *J* = 7.5, 2.4 Hz, 2H), 2.07 (t, *J* = 2.7 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.0, 129.7, 128.5, 128.3, 79.9, 78.6, 74.3, 68.6, 52.0, 34.9, 20.5, 9.5; **IR (neat)**: ν 3281, 2951, 2926, 2140, 1717, 1610, 1435, 1281, 1180, 1111, 1020, 797, 705 cm^{-1}; **HRMS** (EI) m/z: $[M-H]^+$ Calcd. for $C_{15}H_{13}O_2$ 225.0910; found 225.0908.

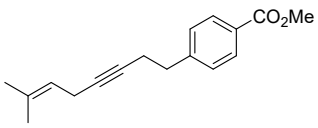


methyl 4-(octa-3,6-diyn-1-yl)benzoate (3gb): A colorless oil, 25.0 mg, 52% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.10 – 3.04 (m, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.47 (tt, *J* = 7.5, 2.4 Hz, 2H), 1.79 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151

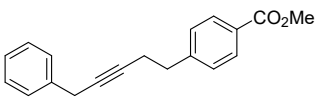
MHz, $CDCl_3$) δ 167.1, 146.1, 129.7, 128.6, 128.2, 79.2, 76.1, 75.7, 73.3, 52.0, 35.0, 20.5, 9.6, 3.5; **IR (neat)**: ν 2952, 2909, 2190, 1717, 1610, 1435, 1280, 1180, 1110, 1020, 766 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{16}O_2Na$ 263.1043; found 263.1043.



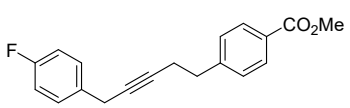
1-(hept-6-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (3ha): A colorless oil, 28.6 mg, 60% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.79 (ddt, *J* = 17.0, 10.2, 5.3 Hz, 1H), 5.23 (ddt, *J* = 17.0, 3.6, 1.8 Hz, 1H), 5.07 (ddt, *J* = 10.0, 3.6, 1.7 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.51 (tt, *J* = 7.4, 2.4 Hz, 2H); **^{13}C NMR** (151 MHz, CDCl3) δ 167.7, 144.8, 134.3, 133.0, 128.8, 128.6 (q, *J* = 31.9 Hz), 125.2 (q, *J* = 4.1 Hz), 124.3 (q, *J* = 271.9 Hz), 123.6, 81.3, 77.9, 35.1, 23.0, 20.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 2973, 2923, 2900, 2211, 1618, 1418, 1323, 1162, 1120, 1108, 1066, 1019, 825, 714 cm^{-1}; **HRMS** (EI) m/z: $[M-H]^+$ Calcd. for $C_{14}H_{12}F_3$ 237.0886; found 237.0886.



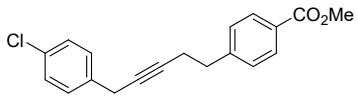
methyl 4-(7-methyloct-6-en-3-yn-1-yl)benzoate (3ib): A colorless oil, 33.3 mg, 65% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.14 (tt, *J* = 6.9, 1.5 Hz, 1H), 3.90 (s, 3H), 2.89 – 2.79 (m, 4H), 2.46 (tt, *J* = 7.5, 2.4 Hz, 2H), 1.71 (s, 3H), 1.61 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.3, 133.5, 129.6, 128.6, 128.1, 119.5, 80.1, 78.4, 52.0, 35.4, 25.5, 20.6, 17.8, 17.6; **IR (neat)**: ν 2979, 2954, 2912, 2201, 1719, 1611, 1435, 1280, 1180, 1111, 1020, 766 cm^{-1}; **HRMS** (ESI) m/z: $[M-H]^+$ Calcd. for $C_{17}H_{19}O_2$ 255.1380; found 255.1380.



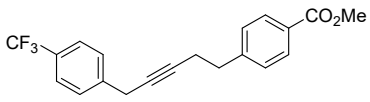
methyl 4-(5-phenylpent-3-yn-1-yl)benzoate (3jb): A colorless oil, 40.0 mg, 72% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.17 (m, 7H), 3.91 (s, 3H), 3.54 (t, *J* = 2.5 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.54 (tt, *J* = 7.4, 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.2, 137.2, 129.7, 128.6, 128.4, 128.2, 127.8, 126.4, 81.2, 78.9, 52.0, 35.2, 25.0, 20.6; **IR (neat)**: ν 3032, 2951, 2853, 1717, 1611, 1435, 1324, 1279, 1179, 1109, 1066, 1019, 764, 702 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{18}O_2$ 278.1301; found 278.1304.



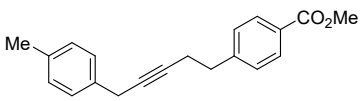
methyl 4-(5-(4-fluorophenyl)pent-3-yn-1-yl)benzoate (3kb): A colorless oil, 42.0 mg, 71% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.00 – 6.91 (m, 2H), 3.91 (s, 3H), 3.50 (t, *J* = 2.7 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.55 (tt, *J* = 7.4, 2.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 161.6 (d, *J* = 244.2 Hz), 132.8 (d, *J* = 3.5 Hz), 129.9, 129.7, 129.2 (d, *J* = 8.3 Hz), 128.6, 128.3, 128.2, 115.1 (d, *J* = 21.5 Hz), 81.4, 78.8, 52.0, 35.2, 24.3, 20.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.9; **IR (neat)**: ν 2948, 2912, 2192, 1716, 1609, 1507, 1435, 1277, 1222, 1109, 1019, 837, 765, 704 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{18}O_2F$ 297.1285; found 297.1284.



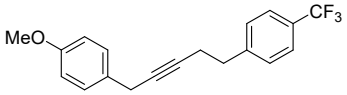
methyl 4-(5-(4-chlorophenyl)pent-3-yn-1-yl)benzoate (3lb): A colorless oil, 43.1 mg, 69% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 3.49 (t, *J* = 2.4 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.55 (tt, *J* = 7.4, 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.1, 135.7, 132.2, 129.7, 129.2, 128.6, 128.5, 128.3, 81.6, 78.4, 52.0, 35.1, 24.5, 20.5; **IR (neat)**: ν 2950, 1719, 1610, 1491, 1435, 1280, 1180, 1110, 1016, 820, 765, 705 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{17}O_2Cl$ 312.0912; found 312.0915.



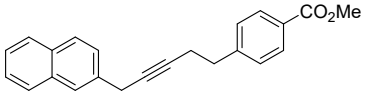
methyl 4-(5-(4-(trifluoromethyl)phenyl)pent-3-yn-1-yl) benzoate (3mb): A colorless oil, 50.5 mg, 73% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 15.0, 7.9 Hz, 4H), 3.91 (s, 3H), 3.58 (t, *J* = 2.6 Hz, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.56 (tt, *J* = 7.4, 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 146.0, 141.3, 129.7, 128.8 (q, *J* = 32.6 Hz), 128.6, 128.3, 128.1, 125.3 (q, *J* = 4.2 Hz), 124.2 (q, *J* = 272.1 Hz), 82.0, 77.8, 52.0, 35.0, 25.0, 20.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 2990, 2952, 2892, 1718, 1612, 1435, 1417, 1324, 1278, 1162, 1107, 1066, 1019, 817, 767, 704 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{18}O_2F_3$ 347.1253; found 347.1241.



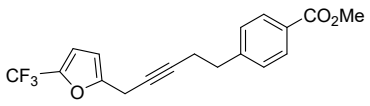
methyl 4-(5-(p-tolyl)pent-3-yn-1-yl)benzoate (3nb): A colorless oil, 38.5 mg, 66% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.06 (m, 4H), 3.93 (s, 3H), 3.51 (t, *J* = 2.7 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.55 (tt, *J* = 7.5, 2.6 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.2, 135.9, 134.2, 129.7, 129.1, 128.6, 128.2, 127.7, 80.9, 79.2, 52.0, 35.2, 24.6, 21.0, 20.6; **IR (neat)**: ν 2942, 2917, 2202, 1719, 1610, 1435, 1280, 1179, 1110, 1020, 765 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}O_2$ 293.1536; found 293.1536.



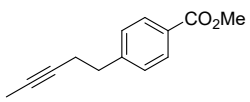
1-methoxy-4-(5-(4-(trifluoromethyl)phenyl)pent-2-yn-1-yl)benzene (3oa): A yellow oil, 36.3 mg, 57% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 – 6.80 (m, 2H), 3.79 (s, 3H), 3.47 (t, *J* = 2.5 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.54 (tt, *J* = 7.3, 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.2, 144.8, 128.9, 128.8, 128.5 (q, *J* = 32.6 Hz), 125.2 (q, *J* = 4.2 Hz), 124.3 (q, *J* = 272.1 Hz), 113.8, 80.8, 79.5, 55.3, 35.0, 24.2, 20.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2936, 2830, 2188, 1712, 1600, 1510, 1418, 1323, 1246, 1160, 1066, 1018, 827 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{17}OF_3$ 318.1226; found 318.1223.



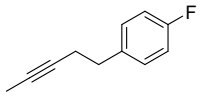
methyl 4-(5-(naphthalen-2-yl)pent-3-yn-1-yl)benzoate (3pb): A yellow oil, 44.0 mg, 67% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.85 – 7.73 (m, 3H), 7.70 (s, 1H), 7.50 – 7.40 (m, 2H), 7.35 (d, *J* = 6.5 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.70 (t, *J* = 2.7 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.58 (tt, *J* = 7.4, 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.2, 134.7, 133.5, 132.2, 129.7, 128.6, 128.2, 128.0, 127.6, 126.5, 126.0, 126.0, 125.4, 81.5, 78.8, 52.0, 35.2, 25.3, 20.6; **IR (neat)**: ν 2951, 2912, 1717, 1610, 1508, 1434, 1278, 1179, 1109, 1020, 812, 765 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{20}O_2Na$ 351.1356; found 351.1353.



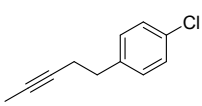
methyl 4-(5-(5-(trifluoromethyl)furan-2-yl)pent-3-yn-1-yl) benzoate (3qb): A yellow oil, 35.0 mg, 52% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 3.3 Hz, 1H), 6.15 (d, *J* = 3.4 Hz, 1H), 3.91 (s, 3H), 3.56 (t, *J* = 2.4 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.53 (tt, *J* = 7.3, 2.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 154.2, 145.9, 140.8 (q, *J* = 43.0 Hz), 129.7, 128.5, 128.3, 119.0 (q, *J* = 266.5 Hz), 112.4 (q, *J* = 3.0 Hz), 107.1, 81.5, 74.6, 52.0, 34.9, 20.4, 18.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.0; **IR (neat)**: ν 2952, 1720, 1612, 1559, 1436, 1325, 1281, 1179, 1130, 1102, 1019, 963, 801, 767 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{15}O_3F_3Na$ 359.0866; found 359.0862.



methyl 4-(pent-3-yn-1-yl)benzoate (3ab): A colorless oil, 29.9 mg, 74% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.44 (tq, *J* = 7.6, 2.5 Hz, 2H), 1.76 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.3, 129.6, 128.5, 128.1, 78.0, 76.6, 52.0, 35.4, 20.5, 3.4; **IR (neat)**: ν 2945, 2919, 2850, 1718, 1611, 1434, 1325, 1276, 1179, 1109, 1020, 767, 703 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{13}H_{14}O_2$ 202.0988; found 202.0983.

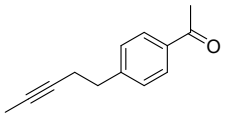


1-fluoro-4-(pent-3-yn-1-yl)benzene (3ac): A colorless oil, 20.4 mg, 63% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.02 – 6.92 (m, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.44 – 2.34 (m, 2H), 1.77 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.5 (d, *J* = 243.5 Hz), 136.6 (d, *J* = 3.5 Hz), 129.8 (d, *J* = 8.0 Hz), 115.0 (d, *J* = 21.4 Hz), 78.3, 76.4, 34.6, 21.1, 3.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.3; **IR (neat)**: ν 2920, 2855, 1601, 1508 ,1433, 1222, 1157, 1094, 1016, 857, 822, 721 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{12}F$ 163.0918; found 163.0920.

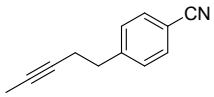


1-chloro-4-(pent-3-yn-1-yl)benzene (3ad): A colorless oil, 22.0 mg, 62% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.40 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.77 (t, *J* = 2.5 Hz, 3H); **^{13}C**

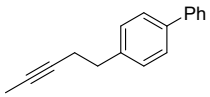
NMR (151 MHz, $CDCl_3$) δ 139.4, 131.9, 129.8, 128.4, 78.1, 76.5, 34.7, 20.8, 3.4; **IR (neat)**: ν 2919, 2855, 1492, 1437, 1091, 1015, 810, 747 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{12}Cl$ 179.0622; found 179.0639.



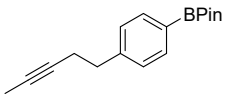
1-(4-(pent-3-yn-1-yl)phenyl)ethan-1-one (3ae): A colorless oil, 30.6 mg, 82% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.59 (s, 3H), 2.44 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.76 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.9, 146.6, 135.3, 128.7, 128.5, 77.9, 76.7, 35.3, 26.6, 20.5, 3.4; **IR (neat)**: ν 2919, 1682, 1606, 1431, 1411, 1357, 1267, 1182, 956, 820 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{15}O$ 187.1117; found 187.1104.



4-(pent-3-yn-1-yl)benzonitrile (3af): A colorless oil, 22.0 mg, 65% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.44 (tq, *J* = 7.4, 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.4, 132.1, 129.3, 119.0, 110.1, 77.5, 77.0, 35.3, 20.3, 3.4; **IR (neat)**: ν 2918, 2856, 2227, 1608, 1505, 1434, 1416, 1117, 1108, 1021, 856, 822 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{11}N$ 169.0886; found 169.0881.

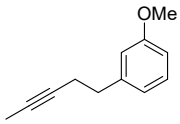


4-(pent-3-yn-1-yl)-1,1'-biphenyl (3ag): A colorless oil, 30.8 mg, 70% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.37 – 7.27 (m, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.47 (tq, *J* = 7.6, 2.6 Hz, 2H), 1.80 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.0, 140.1, 139.1, 128.8, 128.7, 127.1, 127.04, 127.00, 78.5, 76.3, 35.1, 29.7, 20.9, 3.5; **IR (neat)**: ν 2918, 2852, 1486, 1449, 1075, 1008, 824, 761 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}$ 221.1325; found 221.1226.

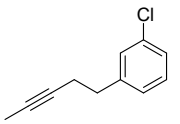


4,4,5,5-tetramethyl-2-(4-(pent-3-yn-1-yl)phenyl)-1,3,2-dioxaborolane (3ah): A colorless oil, 29.2 mg, 54% yield. Eluent: PE/EA = 10/1. Containing a trace

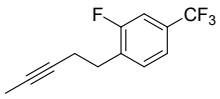
amount of impurity that failed to be separated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.41 (tq, *J* = 7.6, 2.6 Hz, 2H), 1.77 (t, *J* = 2.6 Hz, 3H), 1.34 (s, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3, 134.8, 127.9, 83.6, 78.4, 76.2, 35.7, 24.8, 20.8, 3.4; **IR (neat)**: ν 2982, 2909, 1714, 1611, 1397, 1357, 1270, 1217, 1143, 1088, 1021, 858, 822 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{24}O_2B$ 271.1864; found 271.1884.



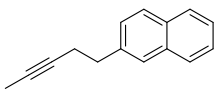
1-methoxy-3-(pent-3-yn-1-yl)benzene (3ai): A colorless oil, 19.1 mg, 55% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.7 Hz, 1H), 6.85 – 6.70 (m, 3H), 3.80 (s, 3H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.46 – 2.37 (m, 2H), 1.78 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 142.6, 129.3, 120.8, 114.2, 111.5, 78.6, 76.2, 55.1, 35.6, 20.9, 3.5; **IR (neat)**: ν 2919, 2855, 1601, 1584, 1491, 1453, 1436, 1260, 1153, 1053, 775, 694 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}O$ 175.1117; found 175.1116.



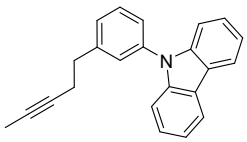
1-chloro-3-(pent-3-yn-1-yl)benzene (3aj): A colorless oil, 18.2 mg, 51% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.09 (d, *J* = 7.1 Hz, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.41 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.78 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.9, 134.0, 129.5, 128.6, 126.6, 126.3, 78.0, 76.6, 35.1, 20.7, 3.4; **IR (neat)**: ν 2918, 2856, 1715, 1599, 1573, 1478, 1429, 1093, 1078, 868, 779, 688 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{12}Cl$ 179.0622; found 179.0624.



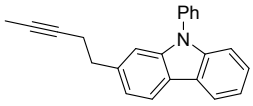
2-fluoro-1-(pent-3-yn-1-yl)-4-(trifluoromethyl)benzene (3ak): A colorless oil, 35.6 mg, 77% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 2H), 7.28 (d, *J* = 9.8 Hz, 1H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.45 (tq, *J* = 7.5, 2.6 Hz, 2H), 1.75 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.7 (d, *J* = 247.6 Hz), 131.9 (d, *J* = 16.2 Hz), 131.4 (d, *J* = 5.6 Hz), 130.3 (qd, *J* = 33.4, 8.2 Hz), 123.4 (qd, *J* = 271.9, 3.5 Hz), 120.8 (q, *J* = 4.4 Hz), 112.6 (dq, *J* = 25.9, 4.2 Hz), 77.5, 76.9, 28.6, 19.2, 3.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.6, -116.5; **IR (neat)**: ν 2914, 2856, 1585, 1507, 1427 ,1327, 1273, 1219, 1167, 1126, 1115, 1065, 912, 878, 824, 744 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{10}F_4$ 230.0713; found 230.0712.



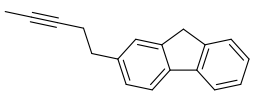
2-(pent-3-yn-1-yl)naphthalene (3al): A colorless oil, 25.6 mg, 66% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.66 (s, 1H), 7.50 – 7.39 (m, 2H), 7.36 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.51 (tq, *J* = 7.6, 2.6 Hz, 2H), 1.78 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 133.5, 132.1, 127.8, 127.6, 127.5, 127.2, 126.6, 125.9, 125.2, 78.5, 76.3, 35.7, 20.9, 3.5; **IR (neat)**: ν 2920, 2853, 1508, 1453, 1376, 1260, 1018, 852, 814, 742 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{15}$ 195.1168; found 195.1168.



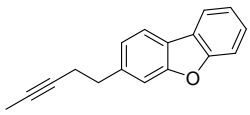
9-(3-(pent-3-yn-1-yl)phenyl)-9H-carbazole (3am): A yellow oil, 41.4 mg, 67% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.36 (m, 6H), 7.32 – 7.23 (m, 3H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.51 (tq, *J* = 7.4, 2.5 Hz, 2H), 1.78 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.0, 140.9, 137.6, 129.7, 127.5, 127.2, 125.9, 124.8, 123.3, 120.2, 119.8, 109.8, 78.2, 76.7, 35.2, 20.8, 3.5; **IR (neat)**: ν 3046, 2916, 2856, 1595, 1494, 1450, 1362, 1315, 1229, 1157, 791, 747, 724 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{20}N$ 310.1590; found 310.1593.



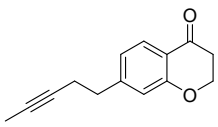
2-(pent-3-yn-1-yl)-9-phenyl-9H-carbazole (3an): A colorless oil, 32.0 mg, 52% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.59 – 7.55 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.37 (m, 2H), 7.30 – 7.24 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.46 (tq, *J* = 7.6, 2.6 Hz, 2H), 1.75 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.1, 141.0, 139.4, 137.8, 129.8, 127.4, 127.1, 125.5, 123.3, 121.7, 120.7, 120.1, 120.0, 119.8, 109.7, 109.5, 78.7, 76.2, 36.1, 21.5, 3.4; **IR (neat)**: ν 2916, 2852, 1745, 1628, 1597, 1474, 1435, 1362, 1232, 1187, 1130, 811, 744 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{20}N$ 310.1590; found 310.1595.



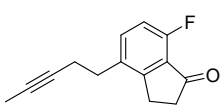
2-(pent-3-yn-1-yl)-9*H*-fluorene (3ao): A colorless oil, 30.2 mg, 65% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 (dd, *J* = 7.9, 1.6 Hz, 1H), 3.87 (s, 2H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.46 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.78 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 143.1, 141.6, 139.9, 139.7, 127.0, 126.7, 126.3, 125.1, 124.9, 119.65, 119.63, 78.6, 76.2, 36.8, 35.7, 21.2, 3.5; **IR (EtOH)**: ν 3013, 2917, 2855, 1706, 1466, 1426, 1397, 1364, 1229, 1096, 825, 768, 731 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{17}$ 233.1325; found 233.1325.



3-(pent-3-yn-1-yl)dibenzo[b,d]furan (3ap): A yellow oil, 26.8 mg, 57% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.33 (td, *J* = 7.5, 1.1 Hz, 1H), 7.21 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.51 (tq, *J* = 7.6, 2.5 Hz, 2H), 1.79 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.5, 156.3, 140.8, 126.7, 124.2, 123.3, 122.6, 122.4, 120.4, 120.3, 111.5, 111.4, 78.3, 76.5, 35.8, 21.2, 3.5; **IR (neat)**: ν 3055, 2917, 2856, 1603, 1581, 1457, 1425, 1325, 1202, 1124, 1104, 1016, 847, 765, 724 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{17}H_{14}O$ 234.1039; found 234.1032.

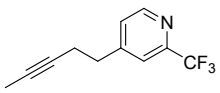


7-(pent-3-yn-1-yl)chroman-4-one (3aq): A colorless oil, 33.5 mg, 78% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.83 (s, 1H), 4.52 (t, *J* = 6.4 Hz, 2H), 2.82 – 2.74 (m, 4H), 2.43 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.77 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.5, 161.8, 150.1, 127.1, 122.0, 119.6, 117.3, 77.8, 76.7, 67.0, 37.7, 35.5, 20.1, 3.4; **IR (neat)**: ν 2951, 2920, 2861, 1686, 1615, 1432, 1326, 1254, 1152, 1039, 851, 763 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{15}O_2$ 215.1067; found 215.1066.

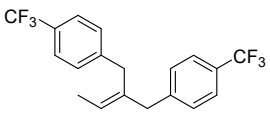


7-fluoro-4-(pent-3-yn-1-yl)-2,3-dihydro-1H-inden-1-one (3ar): A colorless oil, 22.9 mg, 53% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 1H), 6.99 – 6.91 (m, 1H), 3.14 – 3.06 (m, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.76 – 2.69 (m,

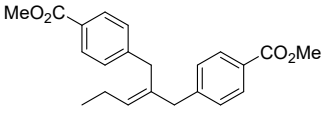
2H), 2.45 (tq, *J* = 7.4, 2.6 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 203.5, 157.8 (d, *J* = 261.5 Hz), 155.4 (d, *J* = 2.8 Hz), 136.1 (d, *J* = 8.4 Hz), 134.3 (d, *J* = 4.7 Hz), 124.5 (d, *J* = 13.1 Hz), 114.3 (d, *J* = 19.7 Hz), 77.7, 76.9, 36.7, 36.6, 30.6, 24.6, 19.5, 3.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -119.1; **IR (neat)**: ν 2922, 1717, 1609, 1489, 1443, 1245, 970, 829 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{14}OF$ 217.1023; found 217.1022.



4-(pent-3-yn-1-yl)-2-(trifluoromethyl)pyridine (3as): A colorless oil, 34.6 mg, 81% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.0 Hz, 1H), 7.58 (s, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.49 (tq, *J* = 7.2, 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.7, 149.8, 148.1 (d, *J* = 34.1 Hz), 126.5, 121.6 (q, *J* = 274.2 Hz), 120.8 (q, *J* = 3.3 Hz), 77.8 (another peak of alkyne carbon coincides with the solvent peak), 34.4, 19.6, 3.3; **^{9}F NMR** (565 MHz, $CDCl_3$) δ -68.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -119.1; **IR (neat)**: ν 2922, 1716, 1610, 1566, 1432, 1330, 1179, 1137, 1086, 996, 848, 749 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{11}H_{10}F_3N$ 213.0760; found 213.0758.

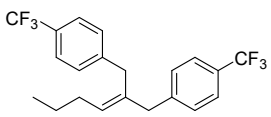


4,4'-(2-ethylidenepropane-1,3-diyl)bis((trifluoromethyl)benzene) (4aa): A colorless oil, 38.7 mg, 72% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 4H), 7.20 (t, *J* = 7.5 Hz, 4H), 5.56 (q, *J* = 6.8 Hz, 1H), 3.35 (s, 2H), 3.25 (s, 2H), 1.79 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 143.8, 136.5, 129.3, 128.8, 128.52 (q, *J* = 32.3 Hz), 128.47 (q, *J* = 32.3 Hz), 125.3 (q, *J* = 4.0 Hz), 125.2 (q, *J* = 4.1 Hz), 124.3 (q, *J* = 272.1 Hz), 124.1, 42.9, 34.9, 13.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2919, 2864, 1623, 1362, 1317, 1226, 1161, 1106, 1065, 1017, 822 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{19}F_6$ 358.1151; found 358.1166.

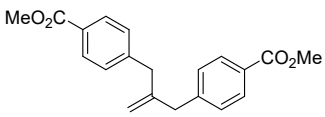


dimethyl 4,4'-(2-propylidenepropane-1,3-diyl)dibenzoate (4bb): A colorless oil, 37.0 mg, 70% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 4H), 7.19 – 7.13 (m, 4H), 5.45 (t, *J* = 7.1 Hz, 1H), 3.911 (s, 6H), 3.908 (s, 3H), 3.32 (s, 2H), 3.22 (s, 2H), 2.24 – 2.14 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.10, 167.06, 145.4, 145.3, 135.0, 131.8, 129.7, 129.6,

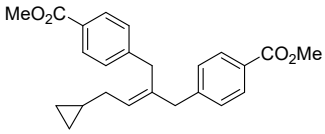
129.0, 128.6, 128.1, 128.0, 51.98, 51.97, 43.0, 35.3, 21.5, 14.4; **IR (neat)**: ν 2953, 1716, 1608, 1434, 1273, 1176, 1101, 1019, 860, 761, 709 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{25}O_4$ 353.1747; found 353.1741.



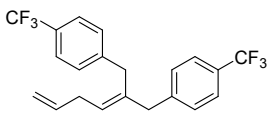
4,4'-(2-butylidenepropane-1,3-diyl)bis((trifluoromethyl)benzene) (4ca): A colorless oil, 39.4 mg, 68% yield. Eluent: PE. Containing a trace amount of impurity that failed to be separated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.23 – 7.17 (m, 4H), 5.50 (t, *J* = 7.2 Hz, 1H), 3.33 (s, 2H), 3.24 (s, 2H), 2.17 (q, *J* = 7.3 Hz, 2H), 1.53 – 1.42 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.0, 143.8, 135.5, 130.5, 129.2, 128.8, 128.51 (q, *J* = 32.6 Hz), 128.47 (q, *J* = 32.6 Hz), 125.3 (q, *J* = 4.0 Hz), 125.2 (d, *J* = 4.0 Hz), 124.3 (q, *J* = 272.1 Hz), 42.9, 35.2, 30.3, 23.0, 13.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2962, 2931, 2872, 1617, 1417, 1322, 1162, 1121, 1108, 1066, 1018, 849, 821 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{21}H_{20}F_6$ 386.1464; found 386.1465.



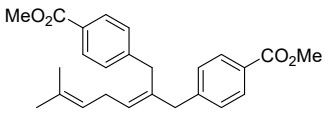
dimethyl 4,4'-(2-methylenepropane-1,3-diyl)dibenzoate (4db): A colorless oil, 31.6 mg, 65% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 4.89 (s, 2H), 3.91 (s, 6H), 3.31 (s, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 146.6, 144.6, 129.7, 129.1, 128.3, 114.7, 52.0, 42.2; **IR (neat)**: ν 2948, 2926, 1716, 1609, 1434, 1273, 1177, 1101, 1019, 901, 762, 708 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{20}O_6Na$ 347.1254; found 347.1259.



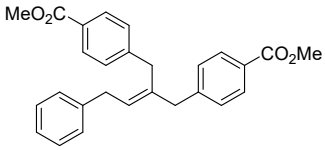
dimethyl 4,4'-(2-(2-cyclopropylethylidene)propane-1,3-diyl) dibenzoate (4eb): A colorless oil, 40.0 mg, 70% yield. Eluent: PE/EA = 10/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 7.9 Hz, 4H), 5.58 (t, *J* = 7.2 Hz, 1H), 3.91 (s, 6H), 3.31 (s, 2H), 3.24 (s, 2H), 2.11 (t, *J* = 7.0 Hz, 2H), 0.85 – 0.73 (m, 1H), 0.50 – 0.44 (m, 2H), 0.13 – 0.07 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.12, 167.06, 145.4, 145.2, 135.6, 129.7, 129.6, 129.3, 129.0, 128.6, 128.12, 128.07, 52.0, 43.1, 35.4, 32.9, 11.0, 4.2; **IR (neat)**: ν 3000, 2951, 1719, 1609, 1435, 1277, 1177, 1107, 1019, 966, 861, 762 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{27}O_4$ 379.1904; found 379.1917.



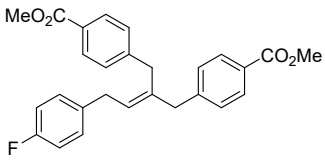
4,4'-(2-(but-3-en-1-ylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (4ha): A colorless oil, 27.1 mg, 47% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 3.1 Hz, 4H), 7.20 (dd, *J* = 8.3, 3.1 Hz, 4H), 5.87 (ddt, *J* = 16.5, 10.2, 6.1 Hz, 1H), 5.52 (t, *J* = 7.4 Hz, 1H), 5.14 – 5.01 (m, 2H), 3.35 (s, 2H), 3.27 (s, 2H), 2.99 – 2.92 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 143.4, 136.8, 136.4, 129.3, 128.9, 128.61 (q, *J* = 31.9 Hz), 128.58 (q, *J* = 31.9 Hz), 127.1, 125.4 (q, *J* = 4.0 Hz), 125.2 (q, *J* = 4.0 Hz), 115.2, 42.8, 35.2, 32.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.36, -62.37; **IR (neat)**: ν 2959, 2924, 2856, 1636, 1617, 1322, 1161, 1120, 1107, 1066, 820 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{21}H_{18}F_6$ 384.1307; found 384.1308.



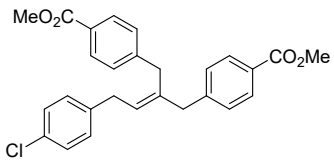
dimethyl 4,4'-(2-(4-methylpent-3-en-1-ylidene)propane -1,3-diyl)dibenzoate (4ib): A yellow oil, 40.1 mg, 68% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 4H), 7.20 – 7.14 (m, 4H), 5.44 (t, *J* = 7.3 Hz, 1H), 5.18 – 5.11 (m, 1H), 3.913 (s, 3H), 3.908 (s, 3H), 3.34 (s, 2H), 3.22 (s, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.72 (s, 3H), 1.62 (s, 3H); **C NMR** (151 MHz, $CDCl_3$) δ 167.11, 167.08, 145.3, 145.2, 135.5, 132.3, 129.8, 129.6, 129.1, 128.8, 128.6, 128.13, 128.09, 122.3, 52.01, 52.99, 43.0, 35.4, 27.3, 25.7, 17.8; **IR (neat)**: ν 2951, 2914, 2853, 1719, 1609, 1435, 1278, 1178, 1109, 1020, 763 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{28}O_4Na$ 415.1880; found 415.1874.



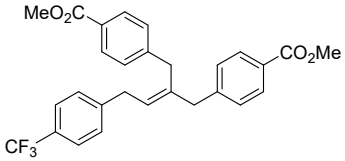
dimethyl 4,4'-(2-(2-phenylethylidene)propane-1,3-diyl) dibenzoate (4jb): A colorless oil, 40.4 mg, 65% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 4H), 7.36 – 7.28 (m, 2H), 7.24 – 7.15 (m, 7H), 5.69 (t, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.55 (d, *J* = 7.4 Hz, 2H), 3.44 (s, 2H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 167.0, 145.1, 144.8, 140.6, 136.8, 129.8, 129.7, 129.1, 128.7, 128.6, 128.4, 128.3, 128.24, 128.22, 126.1, 52.03, 52.01, 43.1, 35.5, 34.4; **IR (neat)**: ν 3024, 2951, 1719, 1608, 1434, 1277, 1177, 1103, 1019, 763, 698 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{26}O_4Na$ 437.1723; found 437.1722.



dimethyl 4,4'-(2-(2-(4-fluorophenyl)ethylidene)propane -1,3-diyl)dibenzoate (4kb): A colorless oil, 40.8 mg, 63% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 4H), 7.21 – 7.10 (m, 6H), 7.03 – 6.96 (m, 2H), 5.64 (t, *J* = 7.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.51 (d, *J* = 7.3 Hz, 2H), 3.43 (s, 2H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.04, 167.00, 161.4 (d, *J* = 244.1 Hz), 145.0, 144.7, 137.1, 136.2 (d, *J* = 3.5 Hz), 129.9, 129.7, 129.6 (d, *J* = 7.9 Hz), 129.0, 128.6, 128.3, 128.2, 115.3 (d, *J* = 21.1 Hz), 52.1, 52.0, 43.1, 35.5, 33.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.2; **IR (neat)**: ν 2985, 2952, 1716, 1608, 1507, 1435, 1278, 1221, 1108, 1020, 764, 712 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{25}O_4FNa$ 455.1629; found 455.1635.

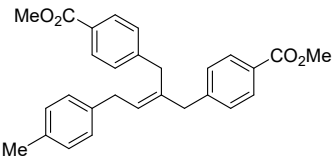


dimethyl 4,4'-(2-(2-(4-chlorophenyl)ethylidene)propane -1,3-diyl)dibenzoate (4lb): A colorless oil, 40.3 mg, 60% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 4H), 7.31 – 7.24 (m, 3H), 7.19 – 7.14 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.62 (t, *J* = 7.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.50 (d, *J* = 7.4 Hz, 2H), 3.43 (s, 2H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.03, 166.99, 144.9, 144.6, 139.0, 137.4, 131.9, 129.9, 129.7, 129.6, 129.0, 128.7, 128.6, 128.3, 127.8, 52.1, 52.0, 43.1, 35.5, 33.7; **IR (neat)**: ν 2950, 2898, 2847, 1717, 1608, 1434, 1276, 1177, 1102, 1018, 763, 710 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{25}O_4NaCl$ 471.1334; found 471.1342.

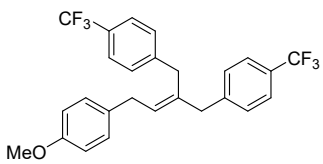


dimethyl 4,4'-(2-(2-(4-(trifluoromethyl)phenyl)ethylidene) propane-1,3-diyl)dibenzoate (4mb): A colorless oil, 40.5 mg, 56% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 4H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.14 (m, 4H), 5.64 (t, *J* = 7.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.59 (d, *J* = 7.4 Hz, 2H), 3.45 (s, 2H), 3.31 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.02, 166.97, 144.8, 144.5, 137.9, 129.9, 129.8, 129.1, 128.60, 128.59, 128.4, 128.3 (q, *J* = 32.6 Hz), 127.1, 125.5 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 271.8 Hz), 52.1, 52.0, 43.1, 35.6, 34.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.3; **IR (neat)**: ν 2945, 2912, 2850, 1718, 1609, 1435, 1323, 1276, 1177, 1106, 1018, 826, 763, 710 cm^{-1}; **HRMS** (ESI)

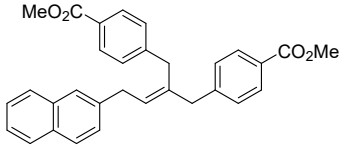
m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{25}O_4F_3Na$ 505.1597; found 505.1603.



dimethyl 4,4'-(2-(2-(p-tolyl)ethylidene)propane-1,3-diyl) dibenzoate (4nb): A colorless oil, 43.7 mg, 68% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 4H), 7.22 – 7.15 (m, 4H), 7.15 – 7.07 (m, 4H), 5.67 (t, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.51 (d, *J* = 7.4 Hz, 2H), 3.44 (s, 2H), 3.28 (s, 2H), 2.34 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 167.0, 145.2, 144.9, 137.5, 136.5, 135.6, 129.8, 129.7, 129.3, 129.1, 128.74, 128.69, 128.2, 52.03, 52.01, 43.1, 35.4, 34.0, 21.0; **IR (neat)**: ν 2951, 1719, 1609, 1435, 1278, 1178, 1278, 1020, 764, 711 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{28}O_4Na$ 451.1880; found 451.1882.

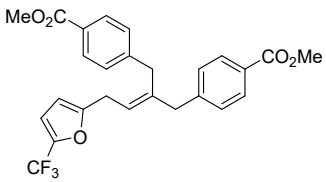


4,4'-(2-(2-(4-methoxyphenyl)ethylidene)propane-1,3-diyl)bis((trifluoromethyl)benzene) (4oa): A yellow oil, 41.1 mg, 59% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.25 – 7.17 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.70 (t, *J* = 7.4 Hz, 1H), 3.81 (s, 3H), 3.49 (d, *J* = 7.5 Hz, 2H), 3.44 (s, 2H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.1, 143.7, 143.4, 136.2, 132.5, 129.3, 129.2, 129.1, 128.9, 128.6 (q, *J* = 32.6 Hz), 124.3 (q, *J* = 271.8 Hz), 125.4 (q, *J* = 4.2 Hz), 125.3 (t, *J* = 4.2 Hz), 114.0, 55.3, 42.9, 35.2, 33.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (neat)**: ν 2920, 2830, 1615, 1510, 1321, 1245, 1160, 1118, 1106, 1065, 1018, 851, 818 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{26}H_{22}F_6O$ 464.1569; found 464.1571.

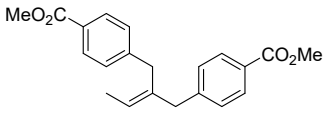


dimethyl 4,4'-(2-(2-(naphthalen-2-yl)ethylidene)propane -1,3-diyl)dibenzoate (4pb): A yellow oil, 43.2 mg, 62% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 4H), 7.85 – 7.75 (m, 3H), 7.62 (s, 1H), 7.50 – 7.42 (m, 2H), 7.38 – 7.29 (m, 1H), 7.23 – 7.17 (m, 4H), 5.77 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.70 (d, *J* = 7.4 Hz, 2H), 3.49 (s, 2H), 3.32 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 167.0, 145.1, 144.8, 138.1, 137.1, 133.6, 132.1, 129.8, 129.7, 129.1, 128.7, 128.3, 128.2, 127.6, 127.4, 127.1, 126.3, 126.1, 125.4, 52.04, 52.02, 43.1, 35.5, 34.6; **IR (neat)**: ν 2951, 2917, 1719, 1608, 1434, 1278, 1109, 1019, 762 cm^{-1}; **HRMS** (ESI) m/z:

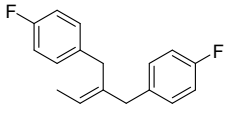
[M+Na]$^+$ Calcd. for $C_{31}H_{28}O_4Na$ 487.1880; found 487.1877.



dimethyl 4,4'-(2-(2-(5-(trifluoromethyl)furan-2-yl)ethylidene) propane-1,3-diyl)dibenzoate (4qb): A yellow oil, 28.3 mg, 40% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 4H), 7.20 – 7.14 (m, 4H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.08 (d, *J* = 3.6 Hz, 1H), 5.63 (t, *J* = 7.4 Hz, 1H), 3.920 (s, 3H), 3.915 (s, 3H), 3.57 (d, *J* = 7.4 Hz, 2H), 3.41 (s, 2H), 3.30 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.02, 166.98, 157.0, 144.5, 144.2, 140.6 (q, *J* = 43.0 Hz), 139.4, 129.9, 129.8, 129.0, 128.6, 123.2, 119.2 (q, *J* = 266.3 Hz), 112.4 (q, *J* = 3.2 Hz), 106.4, 52.1, 52.0, 42.9, 35.5, 27.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.9; **IR (neat)**: ν 2953, 1718, 1610, 1557, 1435, 1323, 1275, 1177, 1102, 1019, 798, 763, 710 cm^{-1}; **HRMS** (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{26}H_{23}O_5F_3Na$ 495.1390; found 495.1386.

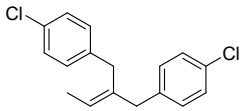


dimethyl 4,4'-(2-ethylidenepropane-1,3-diyl)dibenzoate (4ab): A colorless oil, 31.4 mg, 62% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 4H), 7.21 – 7.12 (m, 4H), 5.52 (q, *J* = 6.8 Hz, 1H), 3.913 (s, 3H), 3.908 (s, 3H), 3.34 (s, 2H), 3.23 (s, 2H), 1.78 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.10, 167.08, 145.4, 145.3, 136.7, 129.8, 129.6, 129.1, 128.6, 128.11, 128.06, 123.8, 52.00, 51.99, 43.0, 35.1, 13.8; **IR (neat)**: ν 2950, 2917, 1716, 1608, 1434, 1272, 1176, 1100, 1019, 966, 860, 836, 762 cm^{-1}; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd. for $C_{21}H_{23}O_4$ 339.1590; found 339.1595.

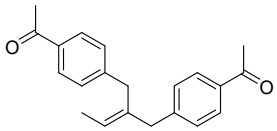


4,4'-(2-ethylidenepropane-1,3-diyl)bis(fluorobenzene) (4ac): A colorless oil, 25.4 mg, 66% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 – 7.01 (m, 4H), 7.00 – 6.90 (m, 4H), 5.46 (q, *J* = 6.6 Hz, 1H), 3.25 (s, 2H), 3.15 (s, 2H), 1.76 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.7 Hz), 161.3 (d, *J* = 243.7 Hz), 138.0, 135.56 (d, *J* = 3.5 Hz), 135.39 (d, *J* = 3.5 Hz), 130.35 (d, *J* = 7.8 Hz), 129.87 (d, *J* = 7.8 Hz), 122.6, 115.1 (d, *J* = 21.0 Hz), 114.9 (d, *J* = 21.4 Hz), 42.1, 34.1, 13.7; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.5; **IR (neat)**: ν 2923, 2855, 1601, 1506, 1437, 1220, 1155, 1093, 1016, 822,

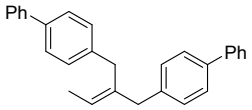
772 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{17}H_{16}F_2$ 258.1215; found 258.1214.



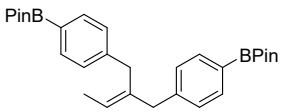
4,4'-(2-ethylidenepropane-1,3-diyl)bis(chlorobenzene) (4ad): A colorless oil, 24.4 mg, 56% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 4H), 7.07 – 6.98 (m, 4H), 5.47 (q, *J* = 6.8 Hz, 1H), 3.24 (s, 2H), 3.14 (s, 2H), 1.75 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.4, 138.2, 137.4, 131.8, 131.7, 130.4, 129.9, 128.5, 128.3, 123.2, 42.2, 34.3, 13.7; **IR (neat)**: ν 2921, 2855, 1607, 1489, 1406, 1090, 1015, 840, 802 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{17}H_{16}Cl_2$ 290.0624; found 290.0621.



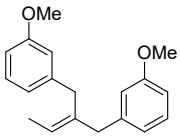
1,1'-((2-ethylidenepropane-1,3-diyl)bis(4,1-phenylene))bis(ethan-1-one) (4ae): A colorless oil, 32.2 mg, 70% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 4H), 7.22 – 7.16 (m, 4H), 5.54 (q, *J* = 6.7 Hz, 1H), 3.35 (s, 2H), 3.24 (s, 2H), 2.594 (s, 3H), 2.587 (s, 3H), 1.78 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.83, 197.79, 145.7, 145.5, 136.5, 135.32, 135.27, 129.2, 128.7, 128.6, 128.4, 124.0, 43.0, 35.1, 26.5, 13.8; **IR (neat)**: ν 2906, 2861, 1677, 1603, 1410, 1356, 1264, 1179, 1113, 1016, 956, 851, 815 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}O_2$ 307.1693; found 307.1694.



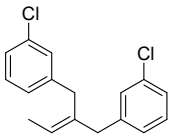
4,4''-(2-ethylidenepropane-1,3-diyl)di-1,1'-biphenyl (4ag): A yellow oil, 41.6 mg, 74% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.56 – 7.51 (m, 4H), 7.49 – 7.39 (m, 5H), 7.37 – 7.32 (m, 2H), 7.25 – 7.20 (m, 3H), 5.56 (q, *J* = 6.7 Hz, 1H), 3.40 (s, 2H), 3.31 (s, 2H), 1.83 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.09, 141.08, 139.3, 139.2, 138.91, 138.87, 138.1, 129.5, 129.1, 128.71, 128.70, 127.1, 127.02, 126.99, 126.96, 122.6, 42.7, 34.7, 13.8; **IR (neat)**: ν 2921, 2853, 1601, 1486, 1448, 1407, 1007, 847, 820, 761, 739 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{29}H_{26}$ 374.2029; found 374.2027.



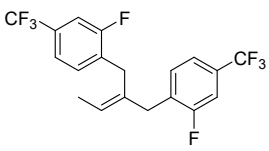
2,2'-((2-ethylidenepropane-1,3-diyl)bis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4ah): A colorless oil, 33.4 mg, 47% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.18 – 7.08 (m, 4H), 5.45 (q, *J* = 6.8 Hz, 1H), 3.29 (s, 2H), 3.18 (s, 2H), 1.75 (d, *J* = 6.7 Hz, 3H), 1.35 (s, 12H), 1.34 (s, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 143.5, 137.7, 134.9, 134.8, 134.7, 128.6, 128.1, 127.7, 122.7, 83.7, 83.6, 43.1, 35.2, 24.9, 13.7; **IR (neat)**: ν 2977, 2925, 2850, 1610, 1397, 1359, 1144, 1088, 1021, 962, 859 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{41}O_4B_2$ 475.3185; found 475.3181.



3,3'-(2-ethylidenepropane-1,3-diyl)bis(methoxybenzene) (4ai): A yellow oil, 21.1 mg, 50% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 6.76 – 6.66 (m, 6H), 5.49 (q, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.28 (s, 2H), 3.19 (s, 2H), 1.76 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 159.5, 141.9, 141.7, 137.9, 129.2, 129.1, 122.6, 121.6, 121.1, 114.8, 114.4, 111.2, 111.0, 55.1, 43.1, 34.9, 13.8; **IR (neat)**: ν 2917, 2834, 1598, 1583, 1488, 1436, 1311, 1258, 1147, 1050, 874, 782, 749 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}O_2$ 283.1693; found 283.1690.

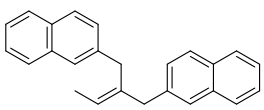


3,3'-(2-ethylidenepropane-1,3-diyl)bis(chlorobenzene) (4aj): A colorless oil, 23.0 mg, 53% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 4H), 7.09 (s, 2H), 7.03 – 6.94 (m, 2H), 5.52 (q, *J* = 6.8 Hz, 1H), 3.27 (s, 2H), 3.17 (s, 2H), 1.77 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.0, 141.8, 136.7, 134.2, 134.1, 129.6, 129.5, 129.0, 128.6, 127.3, 126.8, 126.3, 126.2, 123.8, 42.7, 34.7, 13.8; **IR (neat)**: ν 2969, 2919, 1595, 1572, 1473, 1429, 1077, 1056, 862, 781, 709 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}Cl_2$ 291.0702; found 291.0704.

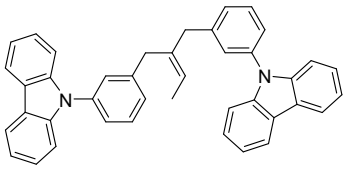


4,4'-(2-ethylidenepropane-1,3-diyl)bis(3-fluoro-1-(trifluoromethyl)benzene) (4ak): A colorless oil, 37.3 mg g, 63% yield. Eluent: PE. Containing a trace amount of impurity that failed to be separated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 3H), 7.24 – 7.19 (m, 3H), 5.52 (q, *J* = 6.8 Hz, 1H),

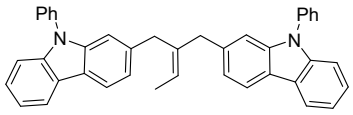
3.43 (s, 2H), 3.30 (s, 2H), 1.74 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.73 (d, *J* = 247.8 Hz), 160.67 (d, *J* = 247.6 Hz), 133.4, 131.7 (d, *J* = 4.9 Hz), 130.9 (qd, *J* = 33.4, 7.7 Hz), 130.8 (d, *J* = 16.0 Hz), 130.6 (d, *J* = 5.5 Hz), 130.4 (d, *J* = 16.0 Hz), 130.3 (qd, *J* = 33.4, 7.7 Hz), 125.2, 123.3 (q, *J* = 271.9 Hz), 120.9 (q, *J* = 4.2 Hz), 120.7 (q, *J* = 4.2 Hz), 112.7 (dq, *J* = 26.3, 4.2 Hz), 112.6 (dq, *J* = 26.3, 4.2 Hz), 35.8 (d, *J* = 3.5 Hz), 28.4 (d, *J* = 3.5 Hz), 13.7; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.62, -62.65, -115.1, -115.5; **IR (neat)**: ν 2948, 2923, 1574, 1515, 1427, 1326, 1217, 1166, 1124, 1065, 909, 878, 825, 744 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{19}H_{14}F_8$ 394.0962; found 394.0971.



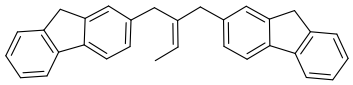
2,2'-(2-ethylidenepropane-1,3-diyl)dinaphthalene (4al): A colorless oil, 28.6 mg, 59% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 6H), 7.57 (s, 1H), 7.53 (s, 1H), 7.48 – 7.40 (m, 4H), 7.32 – 7.26 (m, 2H), 5.58 (q, *J* = 6.8 Hz, 1H), 3.49 (s, 2H), 3.39 (s, 2H), 1.84 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.0, 137.7, 137.6, 133.6, 133.5, 132.14, 132.11, 128.0, 127.8, 127.7, 127.6, 127.5, 127.41, 127.38, 126.8, 125.9, 125.8, 125.2, 122.9, 43.2, 35.2, 13.9; **IR (neat)**: ν 3051, 2922, 2853, 1631, 1599, 1507, 1438, 1364, 1269, 1016, 958, 891, 853, 815, 753 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{23}$ 323.1794; found 323.1823.



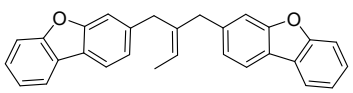
9,9'-((2-ethylidenepropane-1,3-diyl)bis(3,1-phenylene))bis(9*H*-carbazole) (4am): A yellow oil, 56.1 mg, 68% yield. Eluent: PE/EA = 20/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 4H), 7.52 – 7.43 (m, 2H), 7.41 – 7.31 (m, 13H), 7.27 – 7.21 (m, 5H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.50 (s, 2H), 3.40 (s, 2H), 1.77 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.1, 141.8, 140.82, 140.80, 137.8, 137.7, 137.1, 129.8, 129.7, 128.2, 127.7, 127.5, 127.0, 125.9, 125.8, 124.8, 124.7, 123.8, 123.3, 120.3, 119.81, 119.80, 109.8, 109.7, 43.2, 35.1, 13.8; **IR (neat)**: ν 3057, 2909, 1711, 1595, 1494, 1477, 1451, 1359, 1220, 1155, 1089, 792, 749, 724 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{41}H_{32}N_2Na$ 575.2458; found 575.2470.



2,2'-(2-ethylidenepropane-1,3-diyl)bis(9-phenyl-9H-carbazole) (4an): A colorless oil, 45.6 mg, 55% yield. Eluent: PE/EA = 20/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 8.00 (t, *J* = 7.7 Hz, 2H), 7.55 – 7.41 (m, 10H), 7.40 – 7.35 (m, 4H), 7.31 – 7.27 (m, 2H), 7.13 – 7.00 (m, 4H), 5.46 (q, *J* = 6.8 Hz, 1H), 3.48 (s, 2H), 3.37 (s, 2H), 1.76 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.2, 141.1, 140.9, 138.7, 138.6, 138.4, 137.7, 129.7, 127.23, 127.21, 127.0, 126.9, 125.44, 125.42, 123.4, 122.3, 121.49, 121.48, 121.4, 120.9, 119.98, 119.96, 119.83, 119.80, 110.2, 109.8, 109.69, 109.68, 43.7, 35.8, 13.8; **IR (neat)**: ν 3046, 2922, 2855, 1713, 1625, 1597, 1503, 1458, 1435, 1361, 1337, 1232, 811, 760, 743 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{41}H_{33}N_2$ 553.2638; found 553.2645.

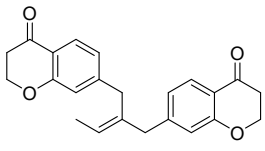


2,2'-(2-ethylidenepropane-1,3-diyl)bis(9*H*-fluorene) (4ao): A colorless oil, 30.0 mg, 50% yield. Eluent: PE. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 4H), 7.55 – 7.48 (m, 2H), 7.42 – 7.26 (m, 6H), 7.20 – 7.10 (m, 2H), 5.53 (q, *J* = 6.8 Hz, 1H), 3.86 (d, *J* = 5.7 Hz, 4H), 3.41 (s, 2H), 3.31 (s, 2H), 1.83 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 143.4, 143.18, 143.15, 141.72, 141.70, 139.7, 139.6, 139.0, 138.9, 138.8, 127.8, 127.3, 126.7, 126.6, 126.3, 125.8, 125.3, 124.97, 124.95, 122.2, 119.65, 119.59, 119.5, 43.2, 36.84, 36.80, 35.2, 13.9; **IR (acetone)**: ν 2921, 2853, 1614, 1455, 1426, 1401, 1360, 1219, 1176, 1097, 1025, 1005, 953, 823, 761, 738 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{31}H_{26}$ 398.2029; found 398.2025.



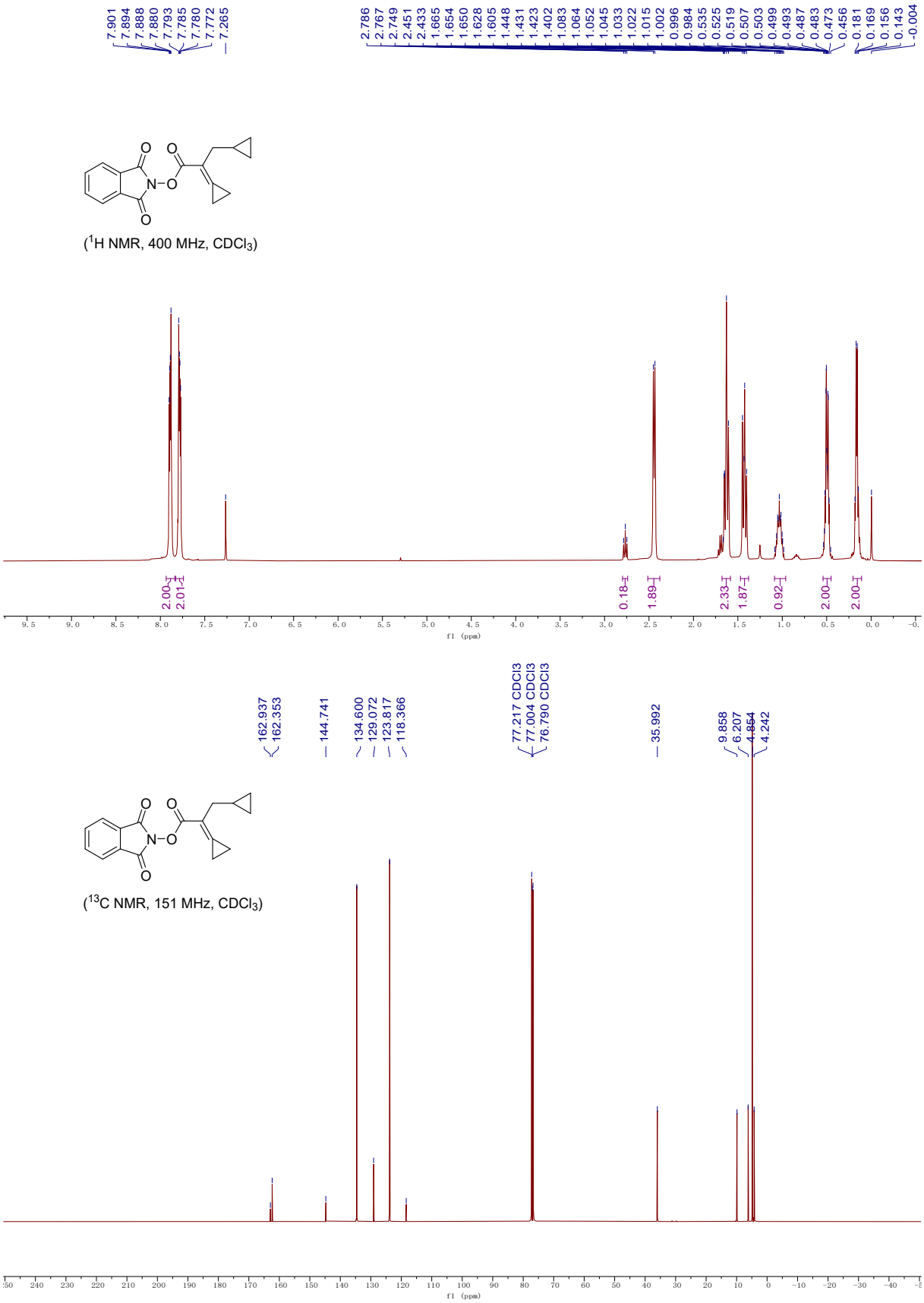
3,3'-(2-ethylidenepropane-1,3-diyl)didibenzo[b,d]furan (4ap): A yellow oil, 37.0 mg, 61% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.85 (dd, *J* = 7.8, 6.3 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.43 (tdd, *J* = 8.4, 2.9, 1.4 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.18 – 7.09 (m, 2H), 5.60 (q, *J* = 6.8 Hz, 1H), 3.49 (s, 2H), 3.40 (s, 2H), 1.85 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.7, 156.6, 156.3, 140.0, 139.9, 138.1, 126.7, 124.28, 124.26, 124.0, 123.6, 123.1, 122.62, 122.59, 122.3, 122.2, 120.4, 120.3, 120.2, 112.0, 111.6, 111.5, 43.4, 35.3, 13.8; **IR (neat)**: ν 2922, 2854, 1635, 1603, 1457, 1425, 1323, 1202, 1122, 1016, 847, 763, 724 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{22}O_2Na$

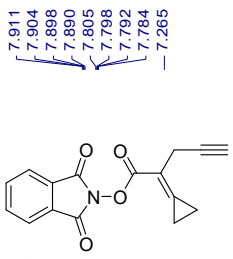
425.1512; found 425.1512.



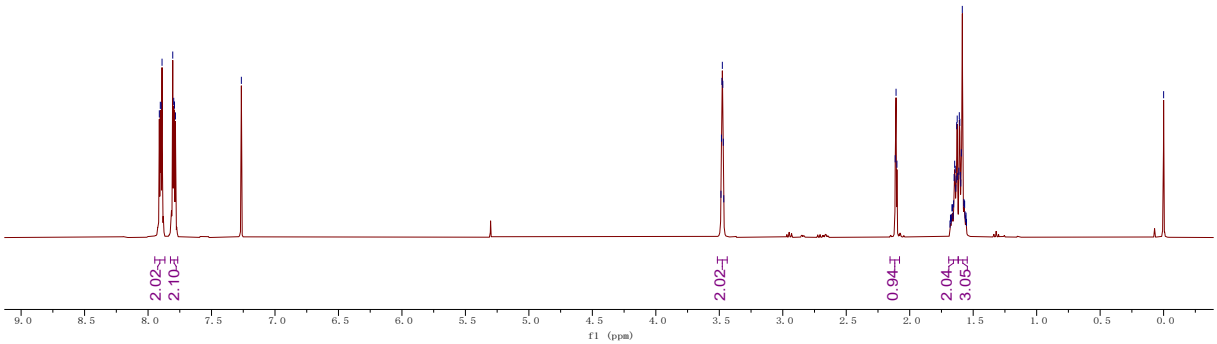
7,7'-(2-ethylidenepropane-1,3-diyl)bis(chroman-4-one) (4aq): A colorless oil, 36.0 mg, 66% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.1, 4.3 Hz, 2H), 6.77 (dd, *J* = 8.2, 4.2 Hz, 2H), 6.70 (s, 2H), 5.55 (q, *J* = 6.8 Hz, 1H), 4.51 (td, *J* = 6.5, 2.8 Hz, 4H), 3.28 (s, 2H), 3.19 (s, 2H), 2.78 (td, *J* = 6.4, 2.1 Hz, 4H), 1.76 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.53, 191.49, 162.0, 161.8, 149.3, 149.1, 135.7, 127.2, 127.0, 124.6, 122.5, 122.1, 119.60, 119.57, 117.9, 117.3, 67.04, 67.01, 43.4, 37.7, 35.4, 13.8; **IR (neat)**: ν 2965, 2898, 2864, 1683, 1609, 1566, 1430, 1380, 1324, 1296, 1253, 1223, 1146, 1037, 865, 827 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{23}O_4$ 363.1591; found 363.1593.

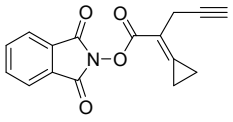
11. NMR Spectra



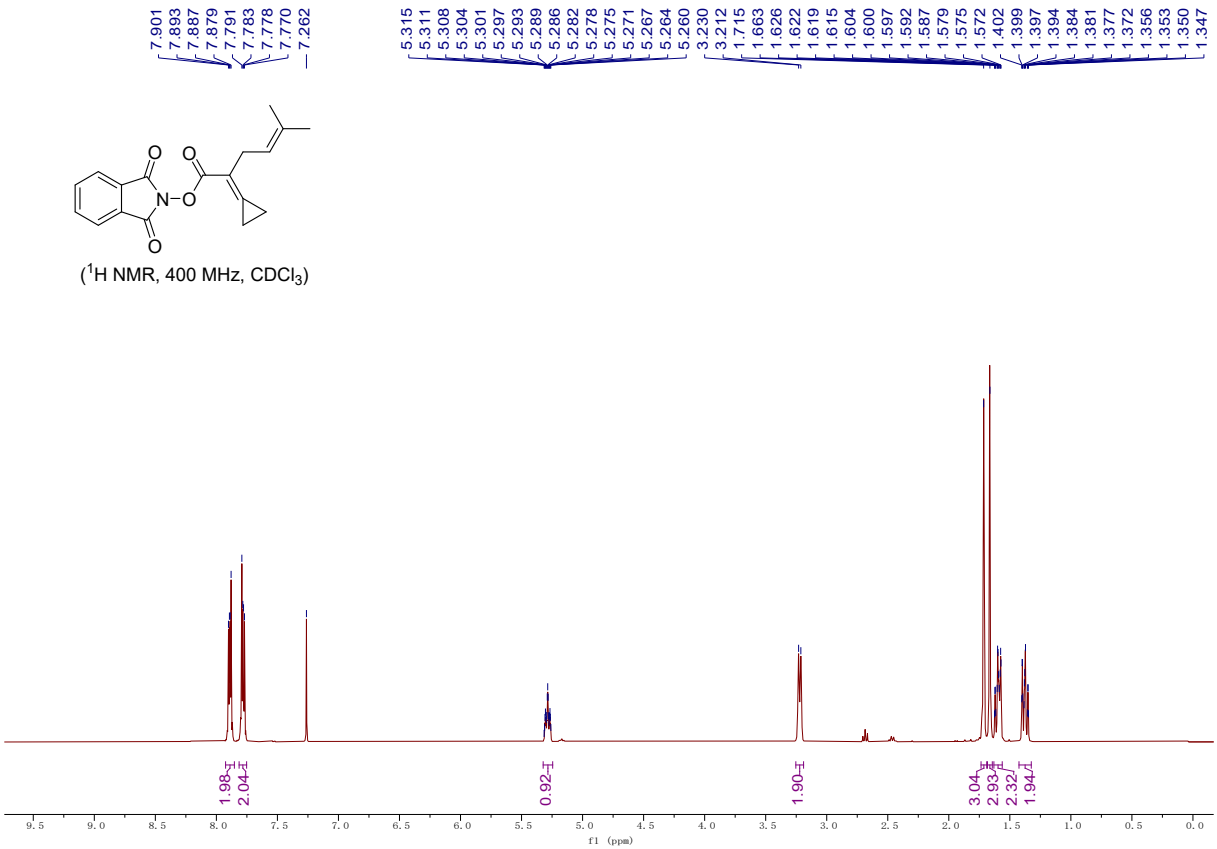


(^{1}H NMR, 400 MHz, $CDCl_3$)

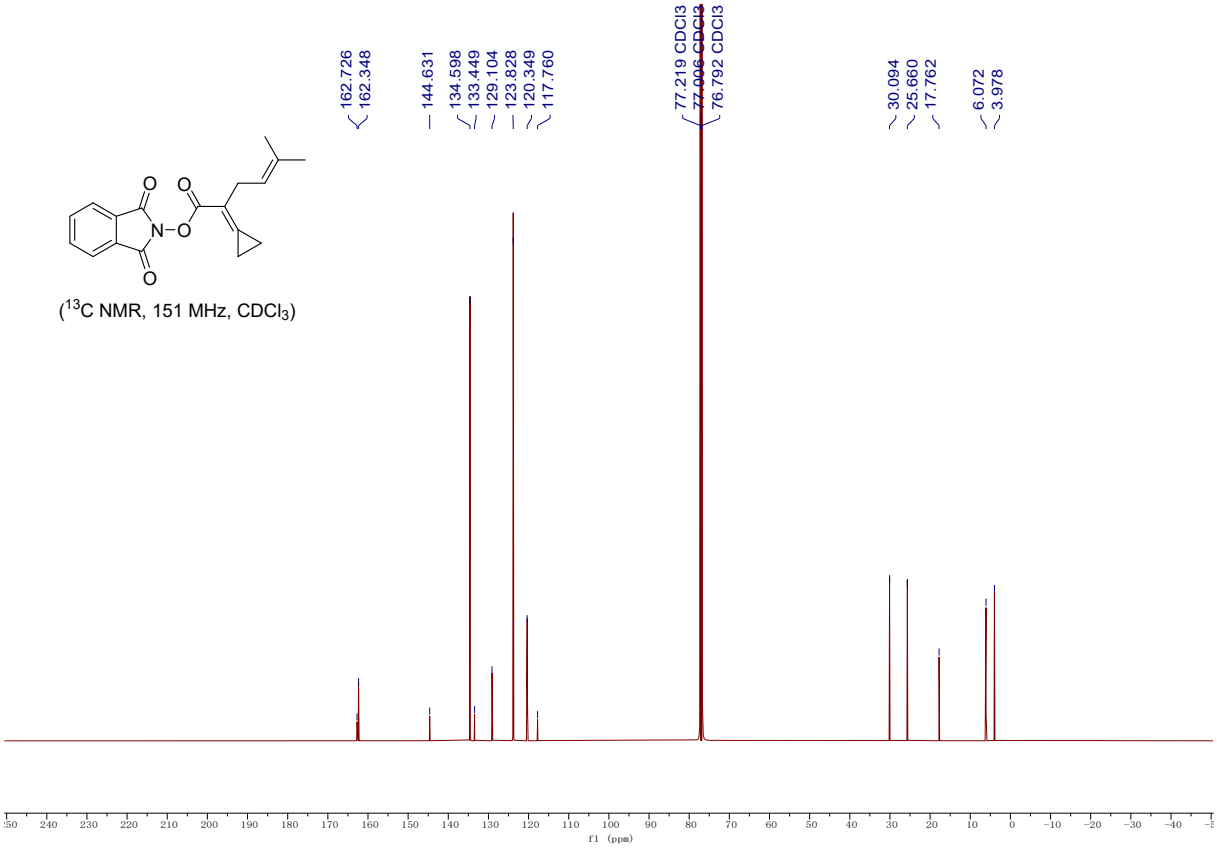




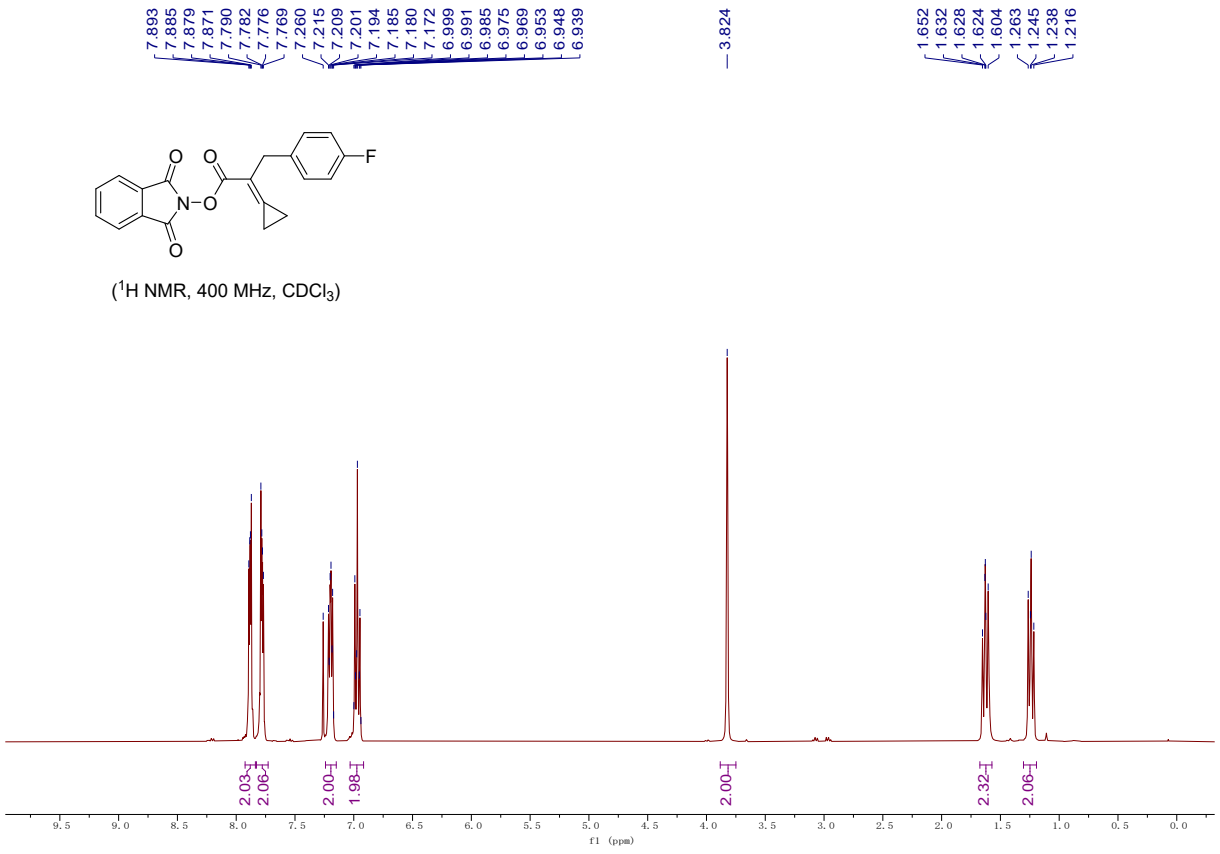
(^{13}C NMR, 151 MHz, $CDCl_3$)

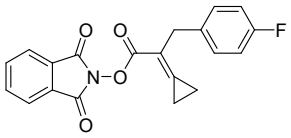


(^{1}H NMR, 400 MHz, $CDCl_3$)

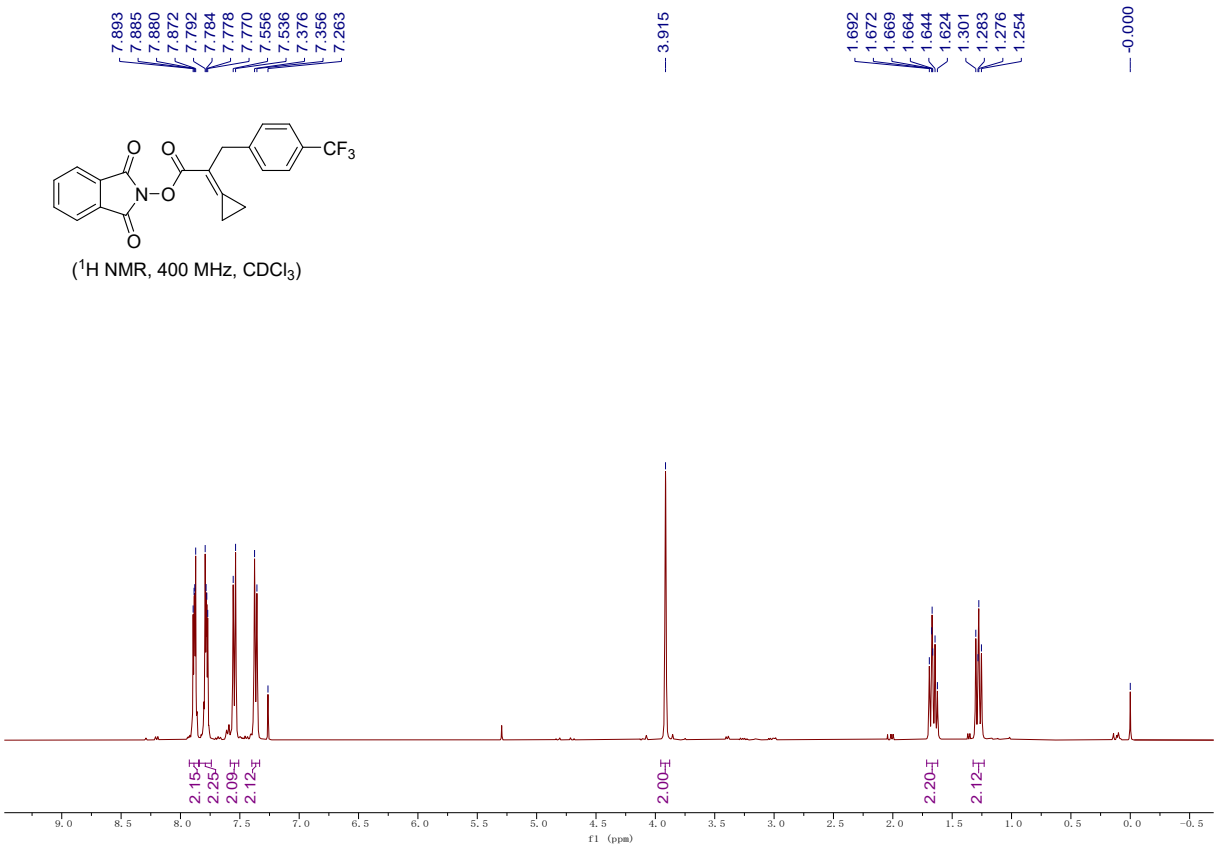


(^{13}C NMR, 151 MHz, $CDCl_3$)

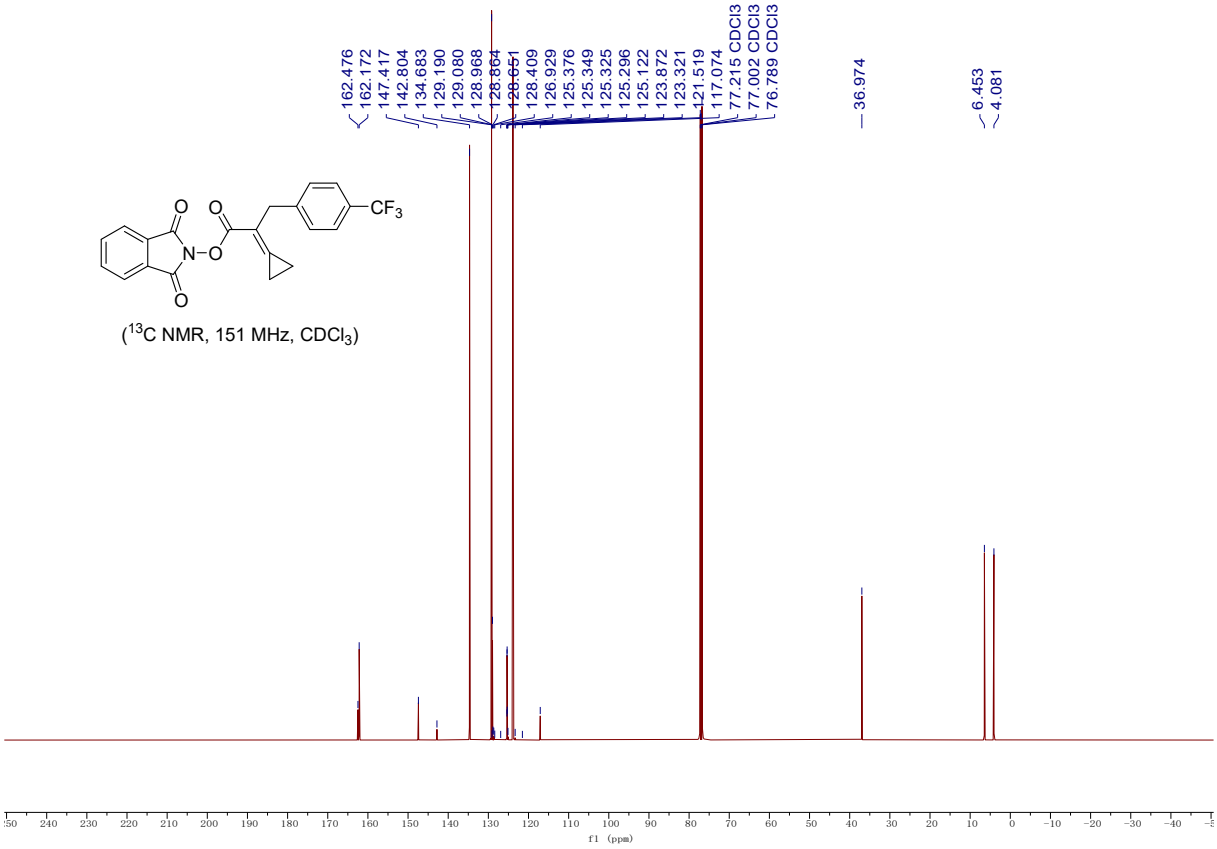

7.893
7.885
7.879
7.871
7.790
7.782
7.776
7.769
7.260
7.215
7.209
7.201
7.194
7.185
7.180
7.172
6.999
6.991
6.985
6.975
6.969
6.953
6.948
6.939
3.824
1.652
1.632
1.628
1.624
1.604
1.263
1.245
1.238
1.216
O
O
N–O
O
F
(1H NMR, 400 MHz, CDCl3)
2.03
2.06
2.00
1.98
2.00
2.32
2.06
f1 (ppm)
162.558
162.411
162.218
160.793
146.642
134.649
134.342
134.319
130.421
130.366
129.011
123.855
117.763
115.224
115.083
77.211 CDCl3
76.999 CDCl3
76.785 CDCl3
36.390
6.226
4.038
O
O
N–O
O
F
(13C NMR, 151 MHz, CDCl3)
0.06
1.00
1.00
f1 (ppm)



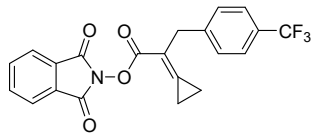
(^{19}F NMR, 565 MHz, $CDCl_3$)



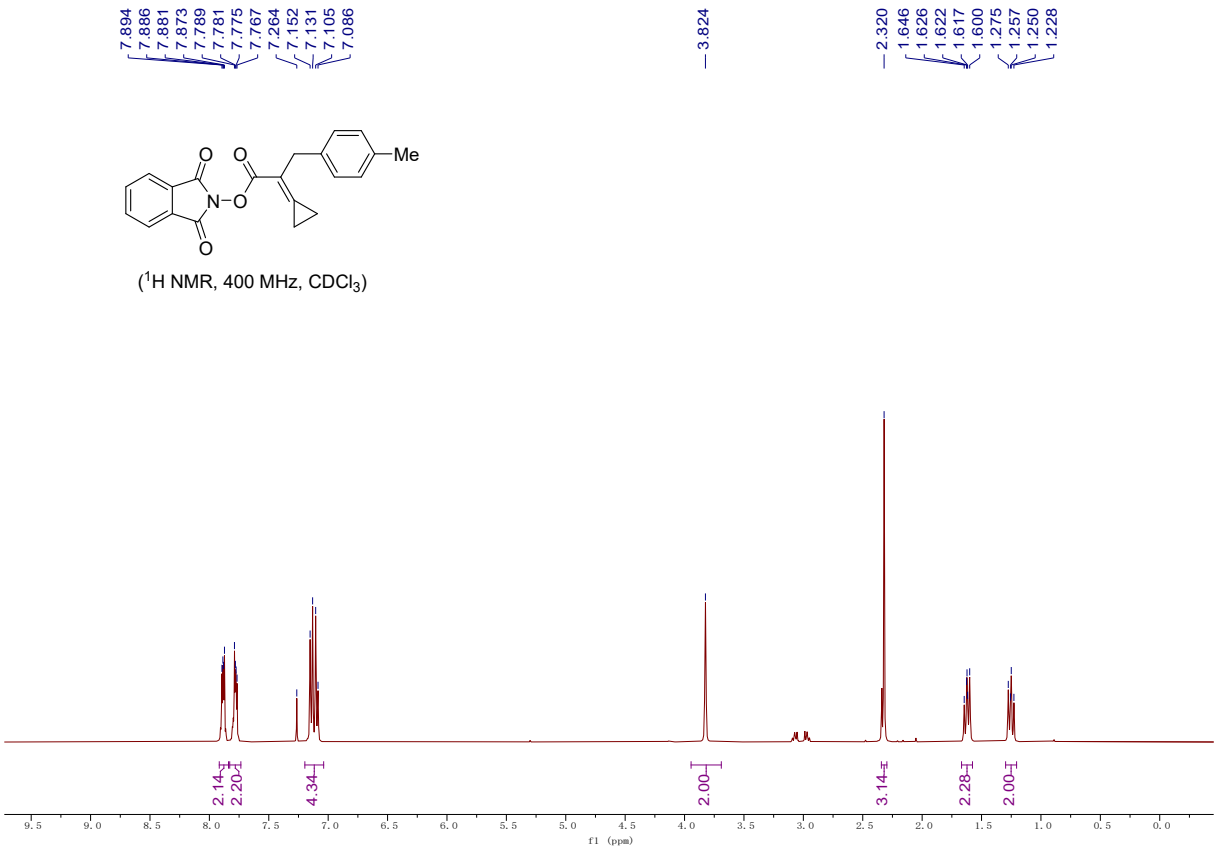
(^{1}H NMR, 400 MHz, $CDCl_3$)



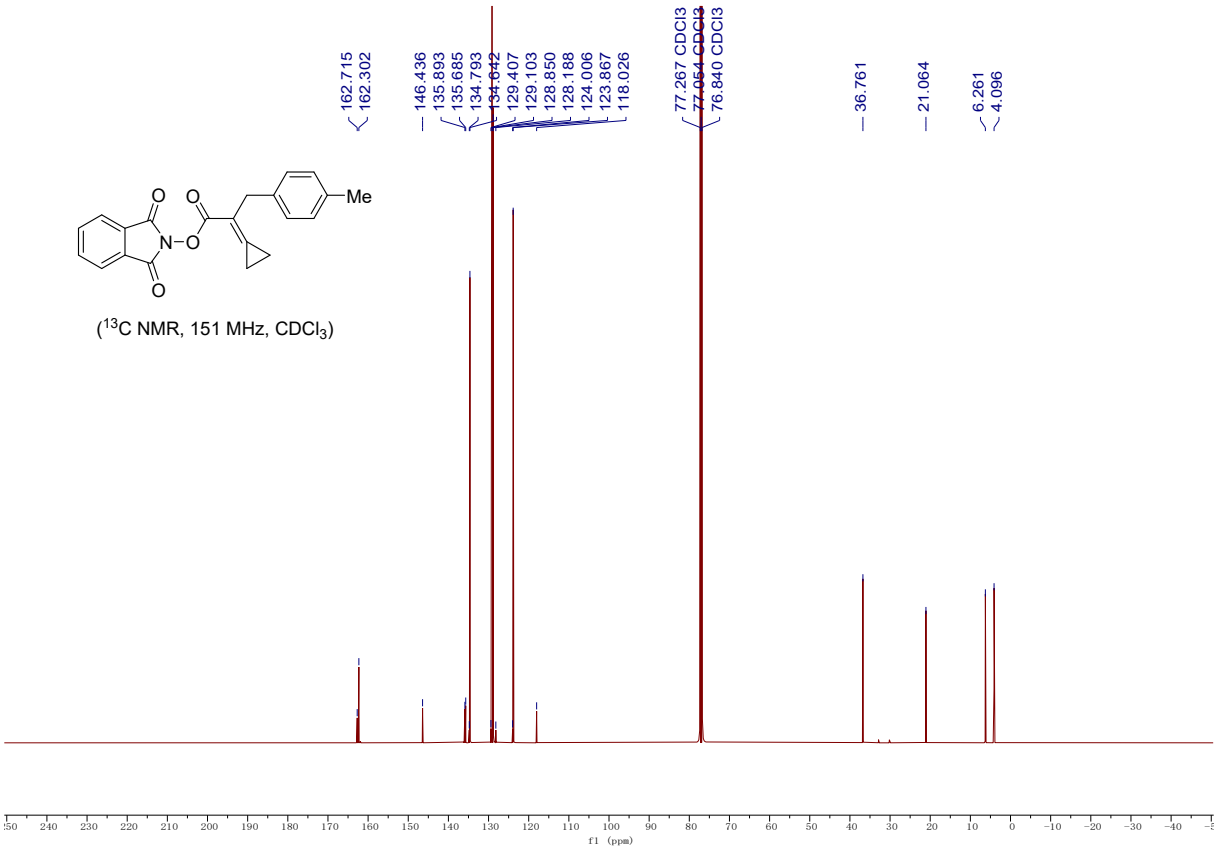
(^{13}C NMR, 151 MHz, $CDCl_3$)



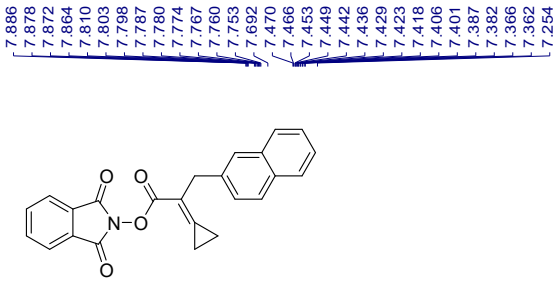
(^{19}F NMR, 565 MHz, $CDCl_3$)



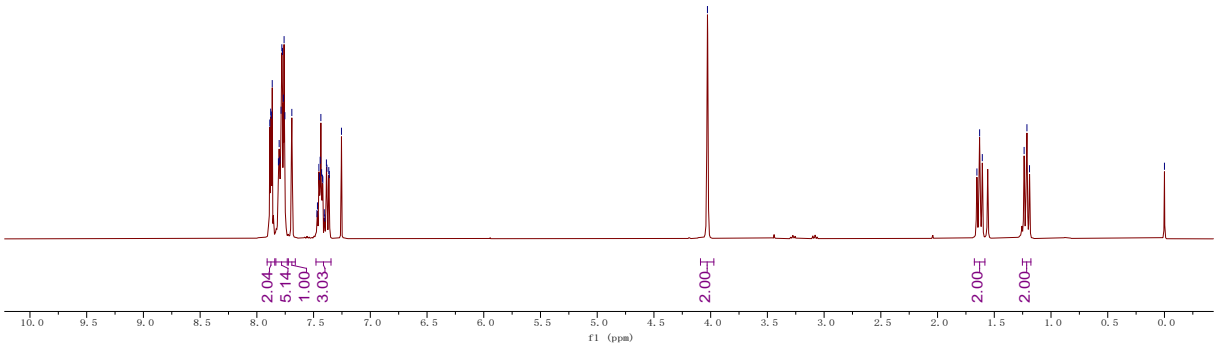
(^{1}H NMR, 400 MHz, $CDCl_3$)

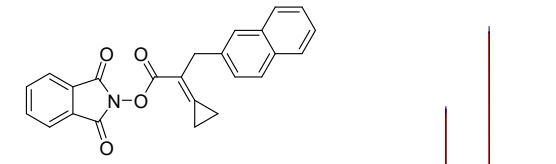


(^{13}C NMR, 151 MHz, $CDCl_3$)

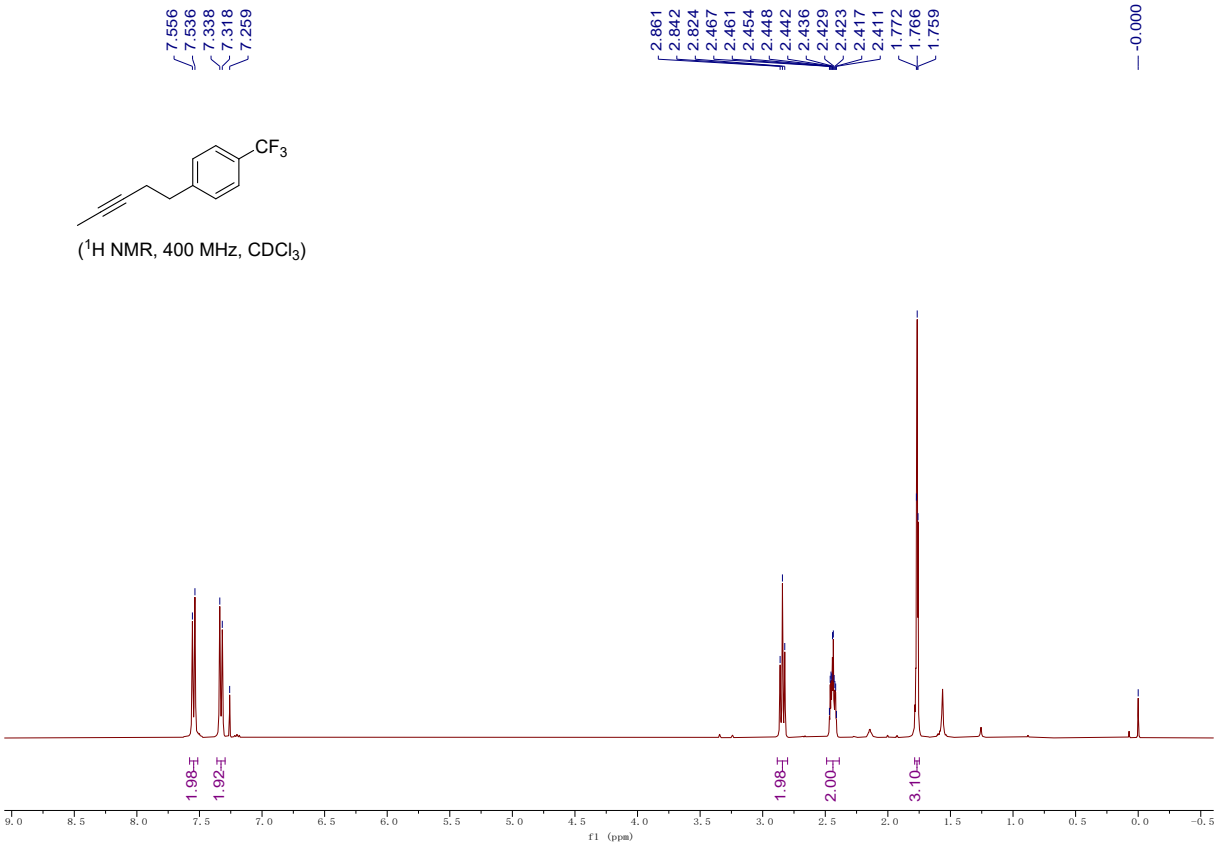


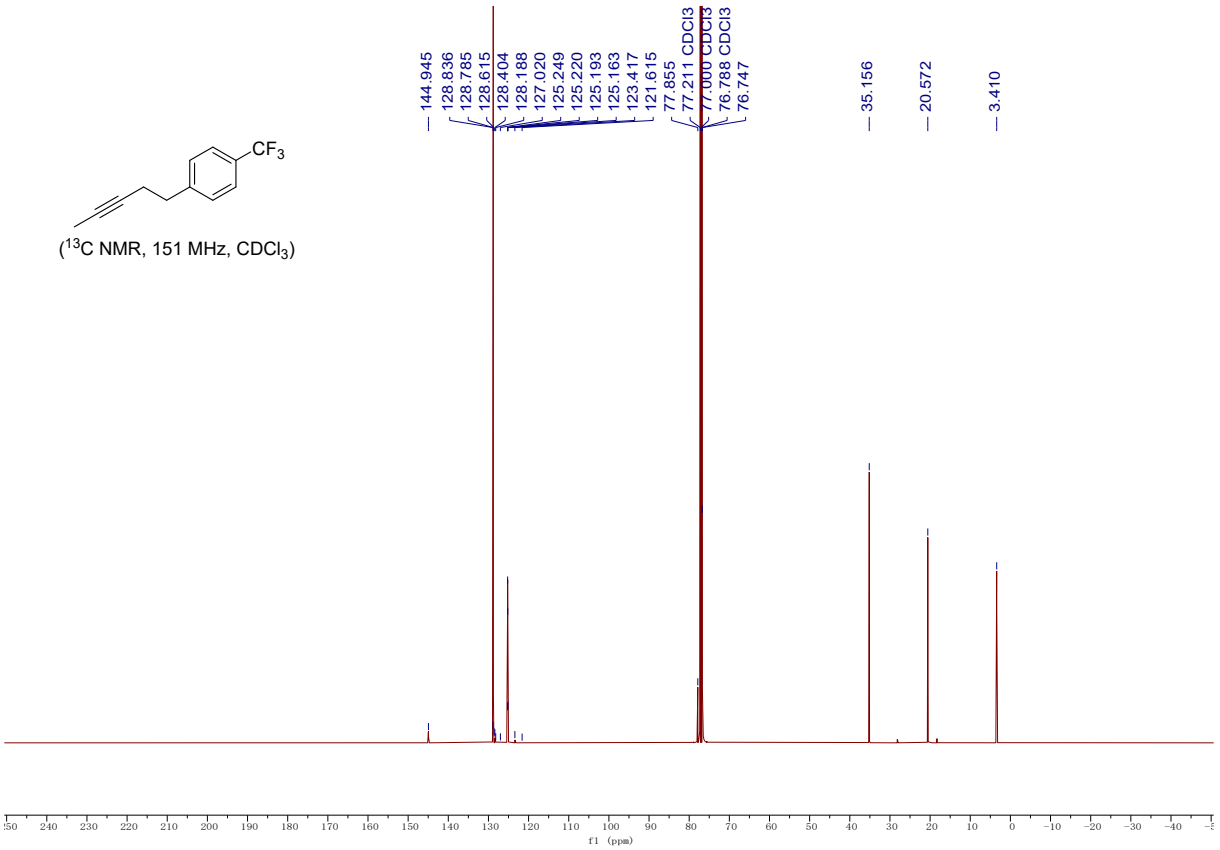
(^{1}H NMR, 400 MHz, $CDCl_3$)

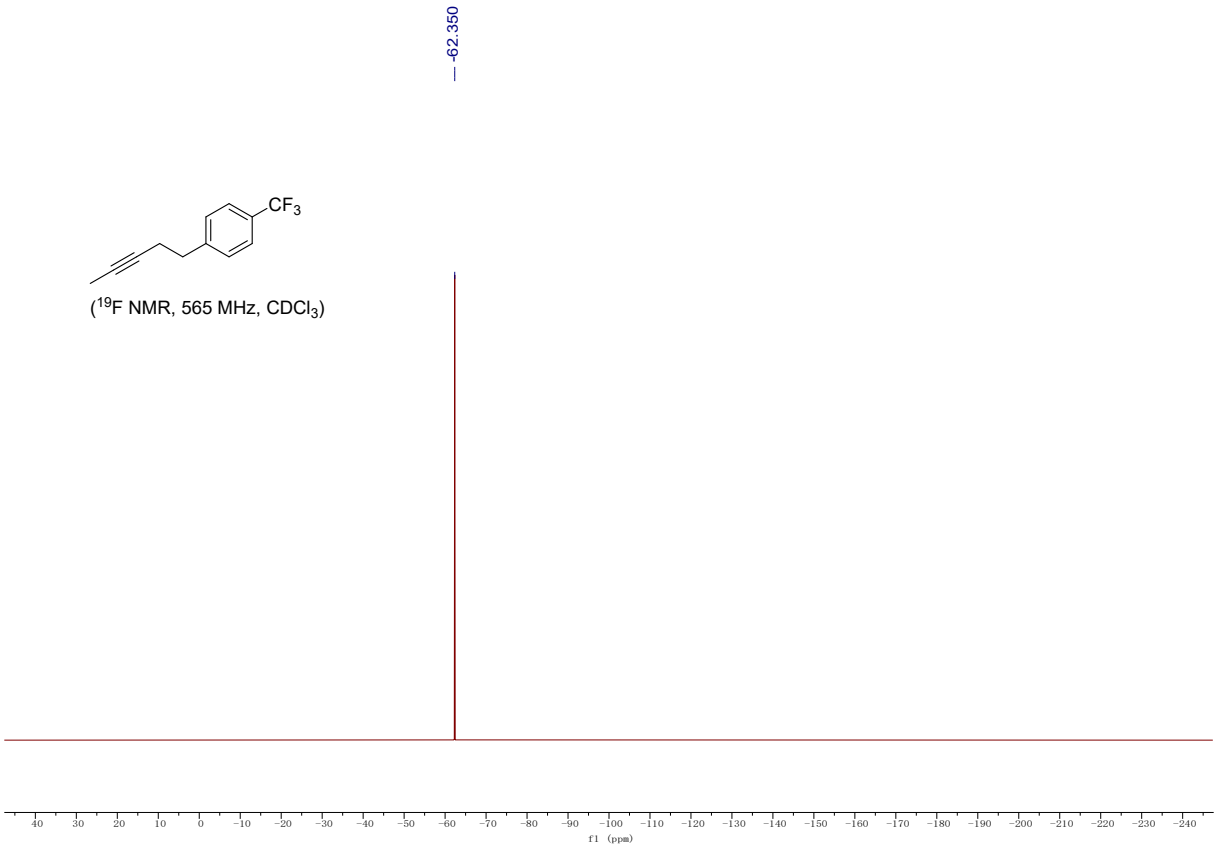




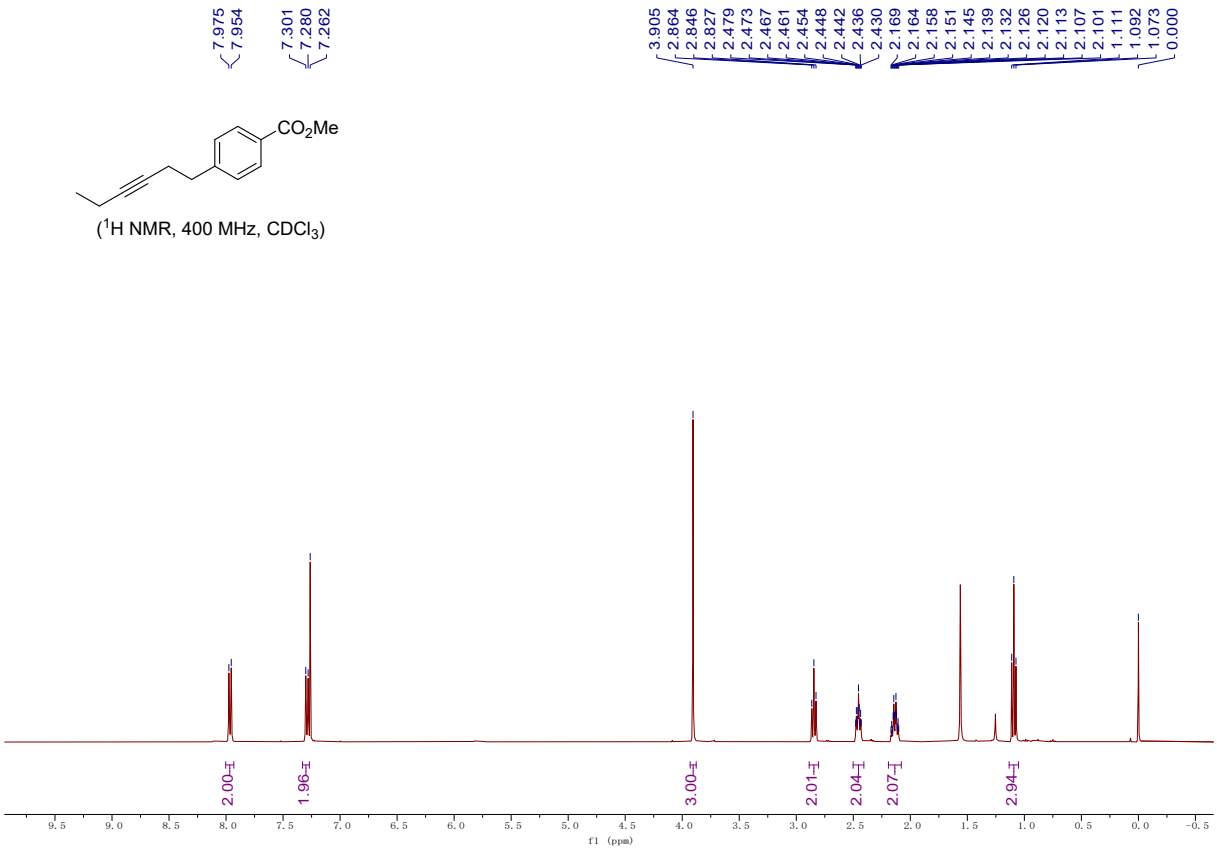
(^{13}C NMR, 151 MHz, $CDCl_3$)

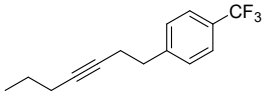

7.556
7.536
7.338
7.318
7.259
2.861
2.842
2.824
2.467
2.461
2.454
2.448
2.442
2.436
2.429
2.423
2.417
2.411
1.772
1.766
1.759
-0.000
CF3
(1H NMR, 400 MHz, CDCl3)
1.98
1.92
1.98
2.00
3.10
f1 (ppm)


144.945
128.836
128.785
128.615
128.404
128.188
127.020
125.249
125.220
125.193
125.163
123.417
121.615
77.855
77.211 CDCl3
77.000 CDCl3
76.788 CDCl3
76.747
35.156
20.572
3.410
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

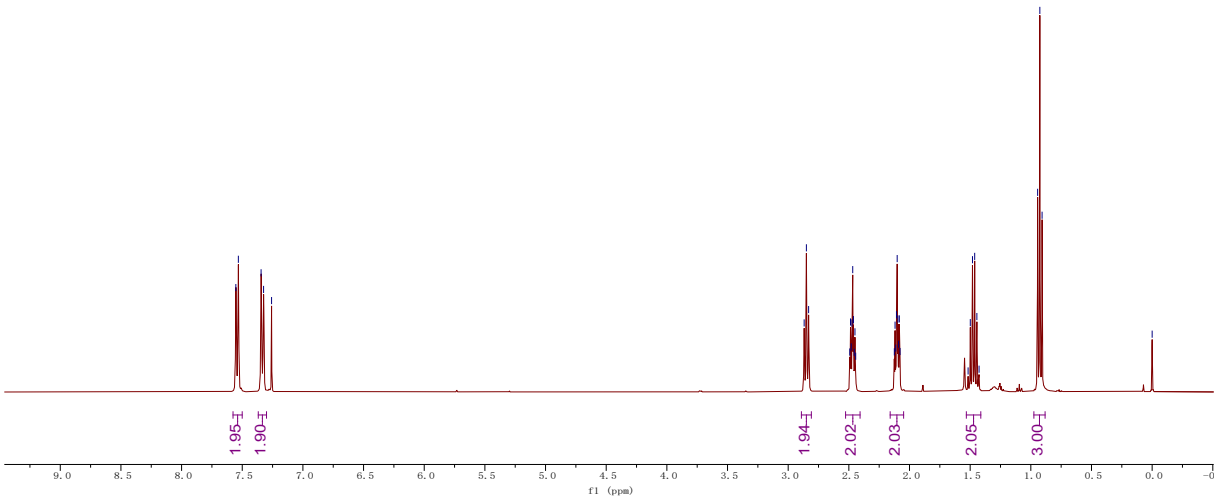


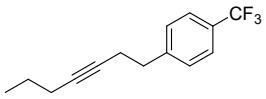
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.975
7.954
7.301
7.280
7.262
3.905
2.864
2.846
2.827
2.479
2.473
2.467
2.461
2.454
2.448
2.442
2.436
2.430
2.169
2.164
2.158
2.151
2.145
2.139
2.132
2.126
2.120
2.113
2.107
2.101
1.111
1.092
1.073
0.000
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.00
1.96
3.00
2.01
2.04
2.07
2.94
f1 (ppm)
167.129
146.363
129.611
128.571
128.130
82.885
78.183
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
51.992
35.461
20.584
14.203
12.348
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

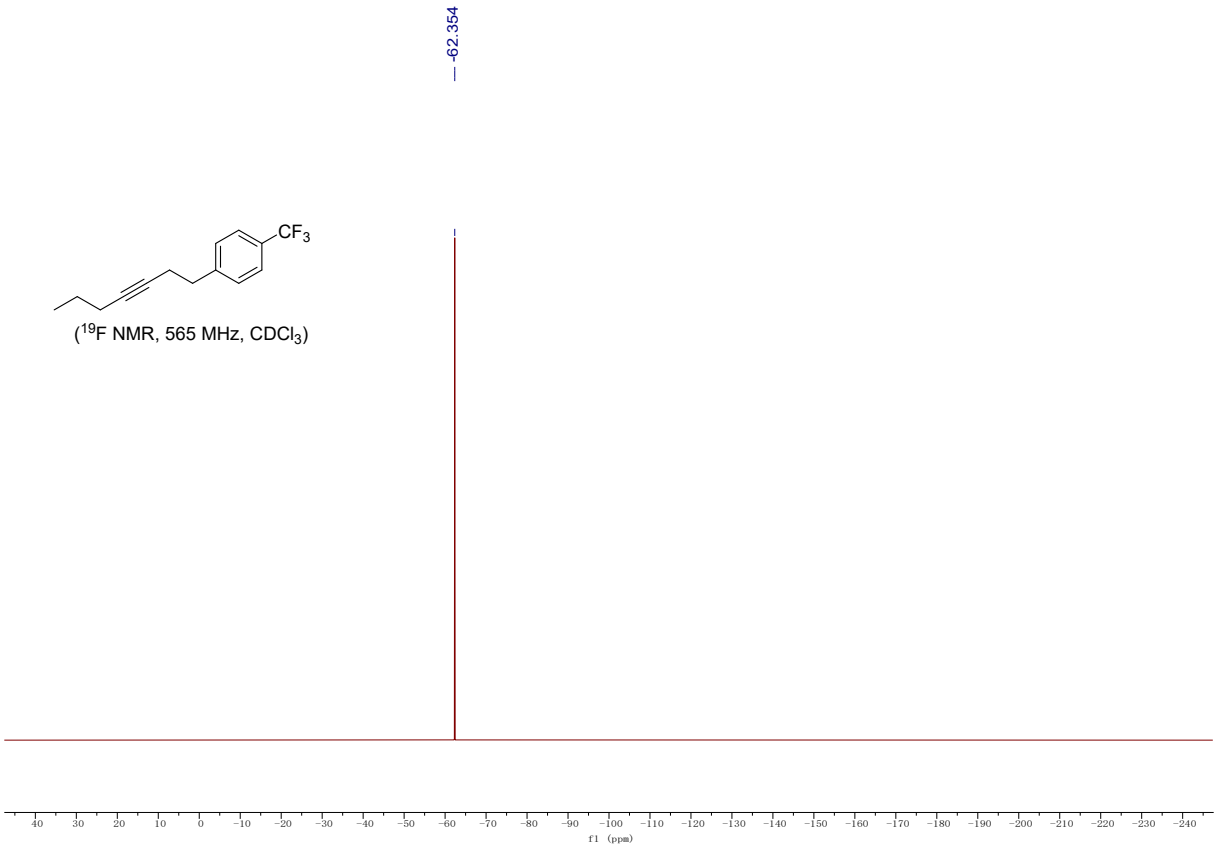


(^{1}H NMR, 400 MHz, $CDCl_3$)

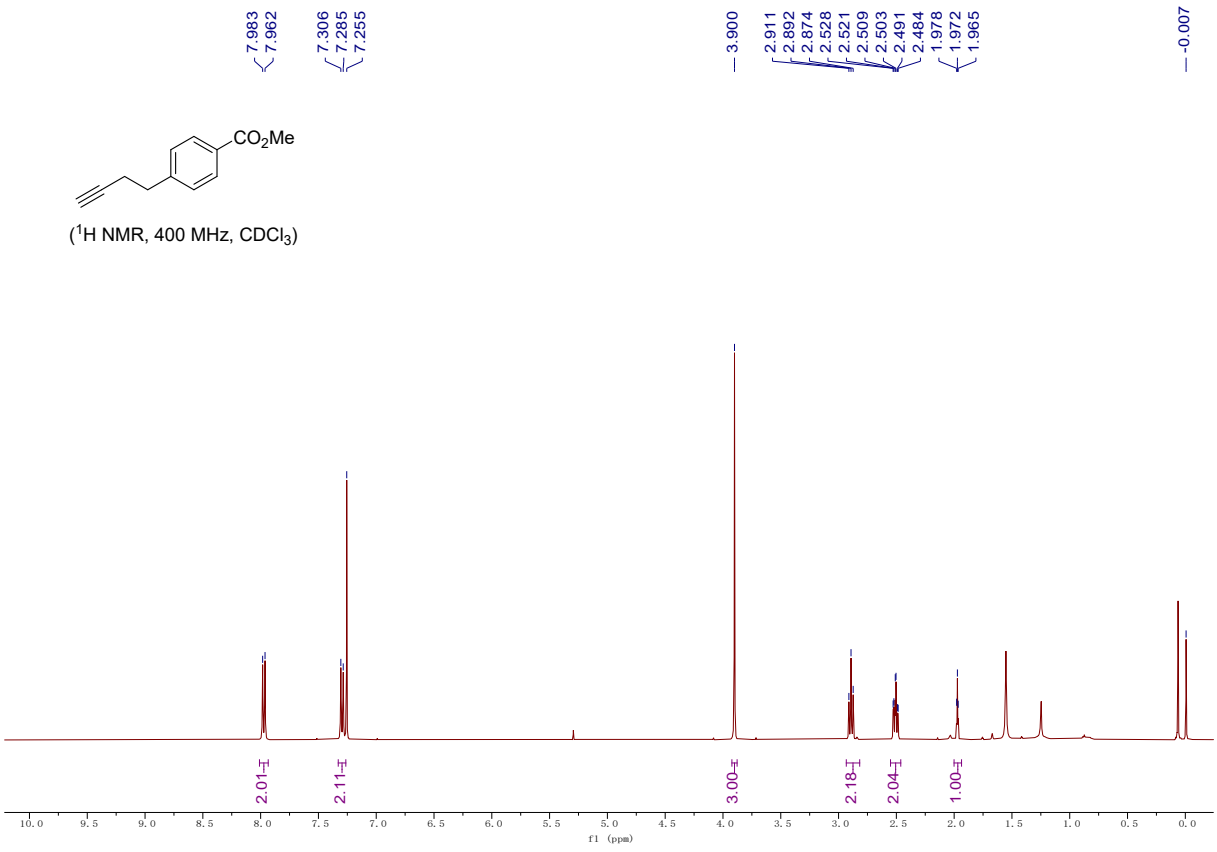




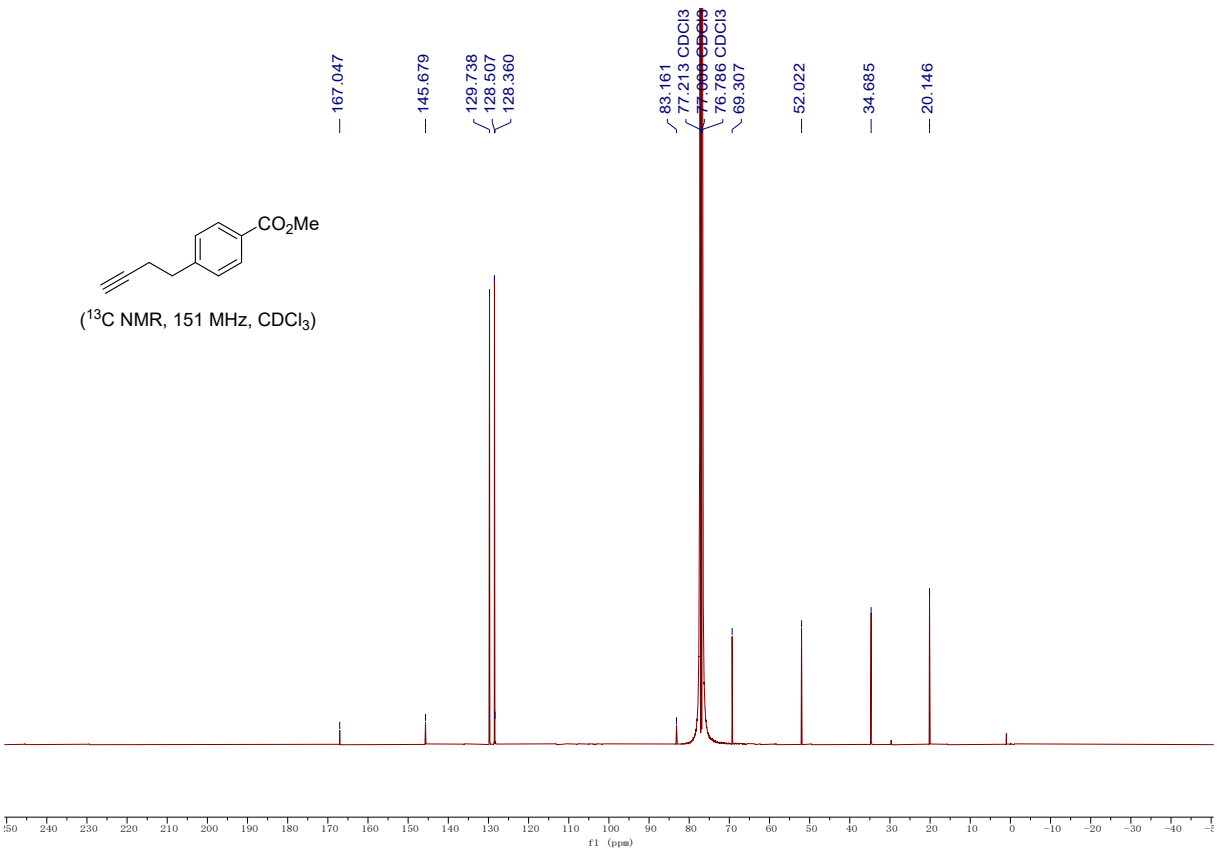
(^{13}C NMR, 151 MHz, $CDCl_3$)



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

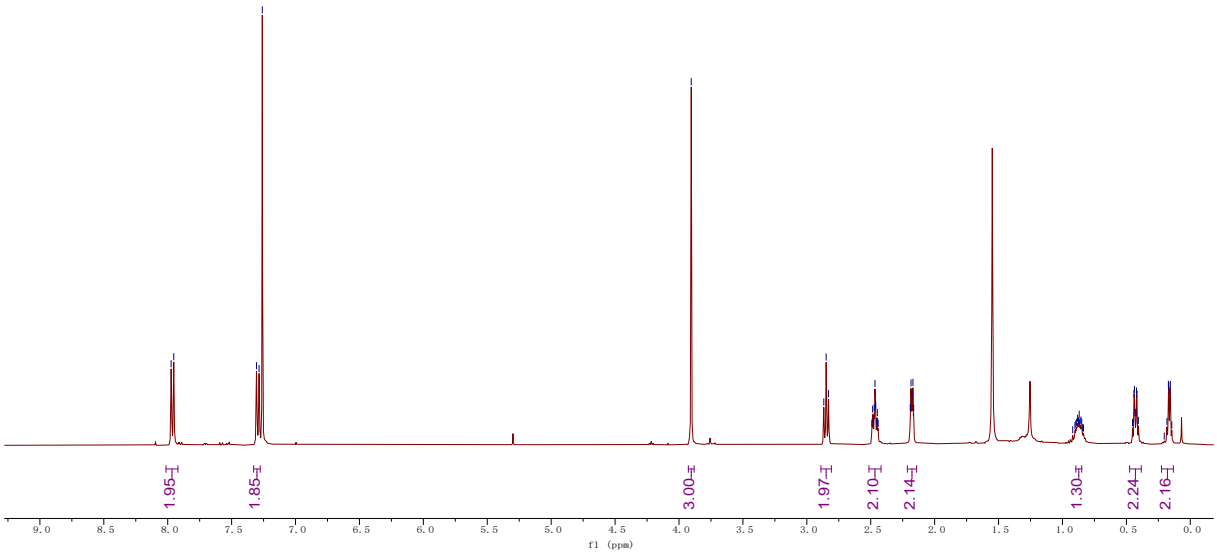


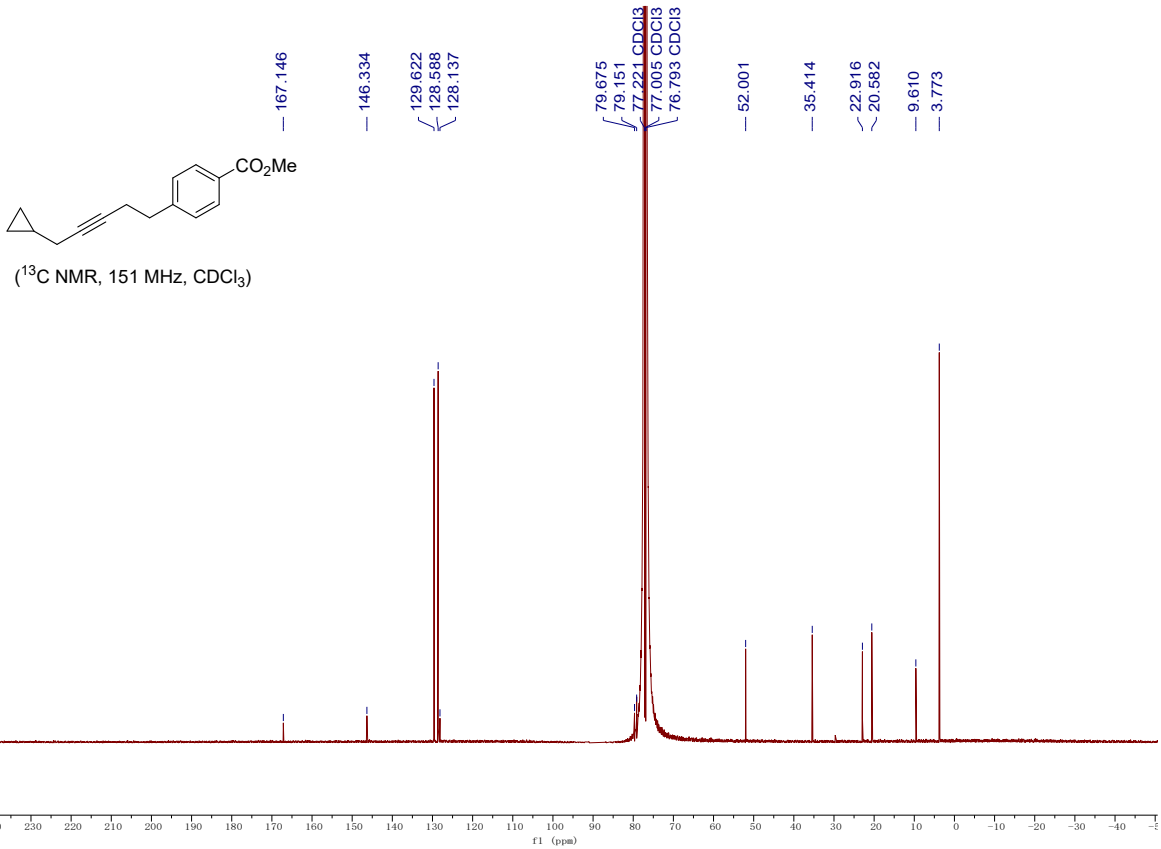
(^{1}H NMR, 400 MHz, $CDCl_3$)



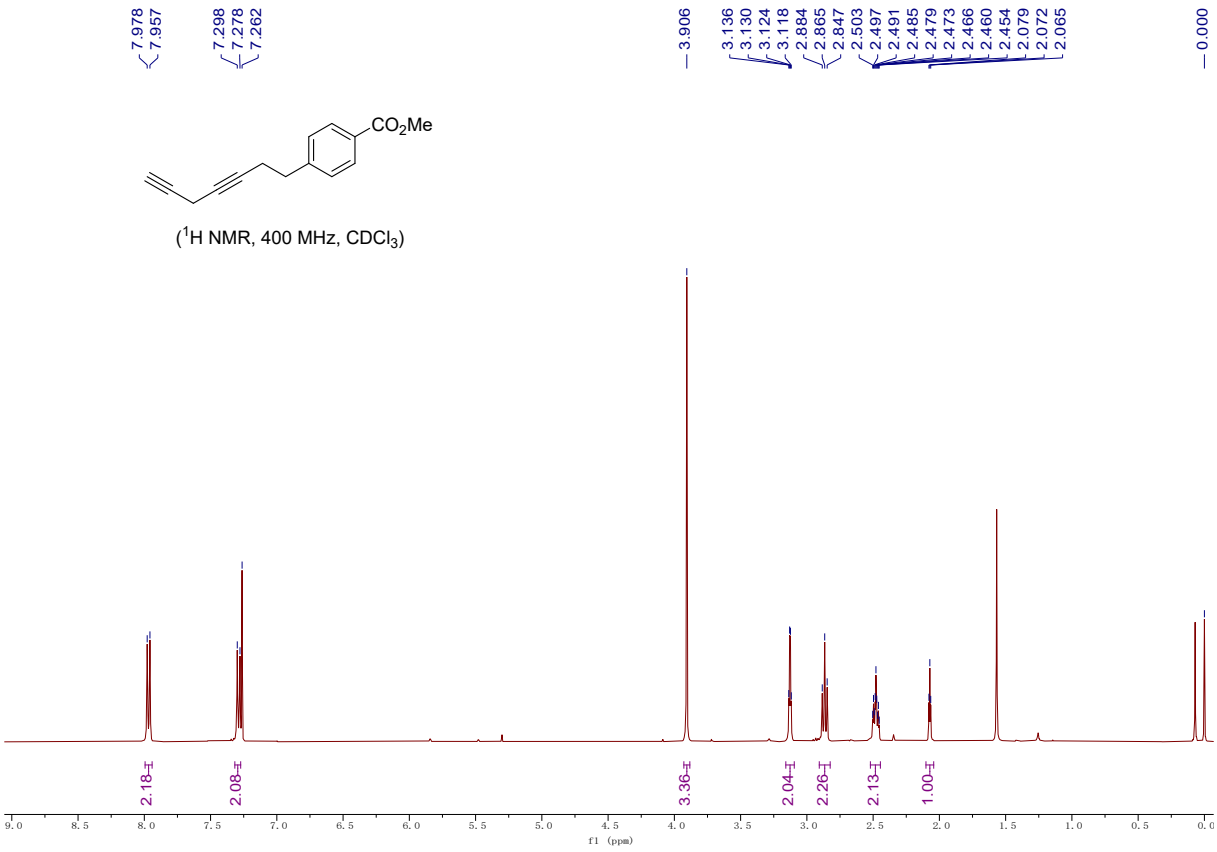
(^{13}C NMR, 151 MHz, $CDCl_3$)

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

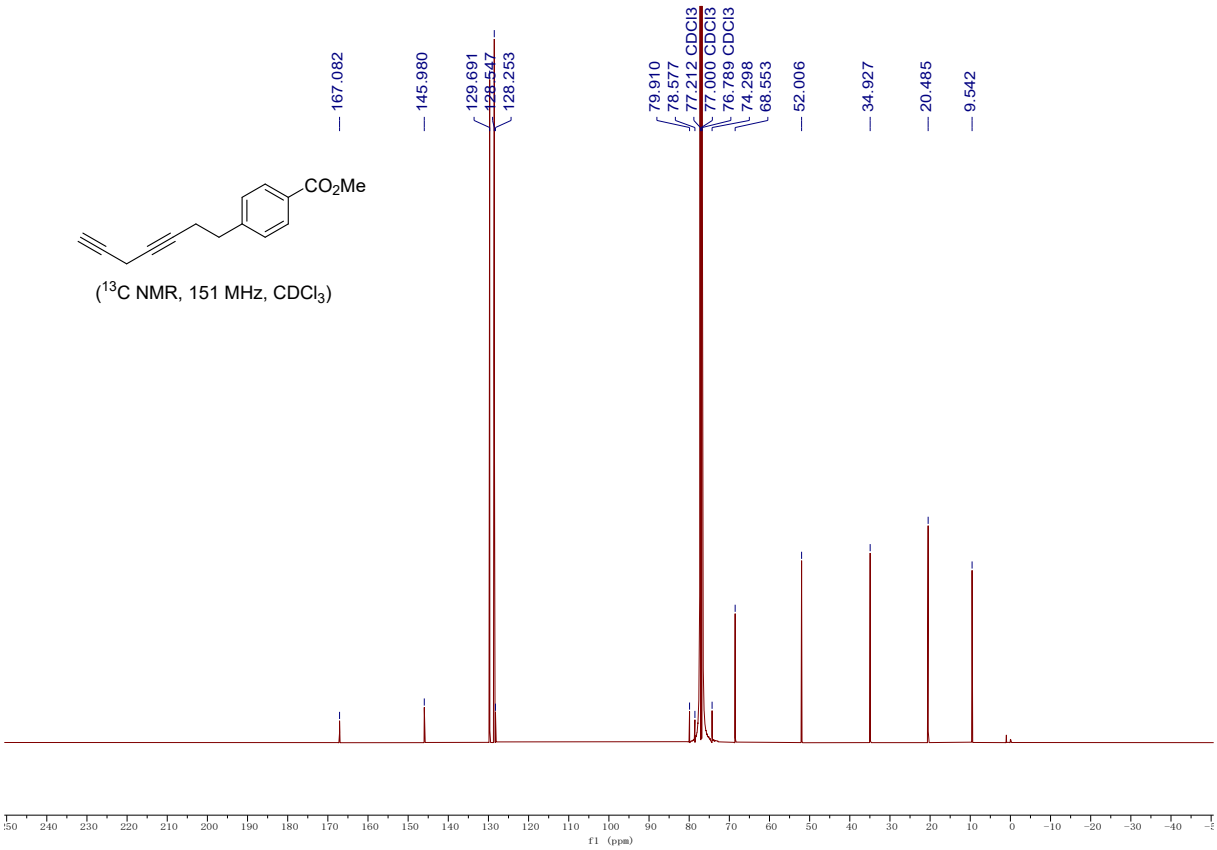




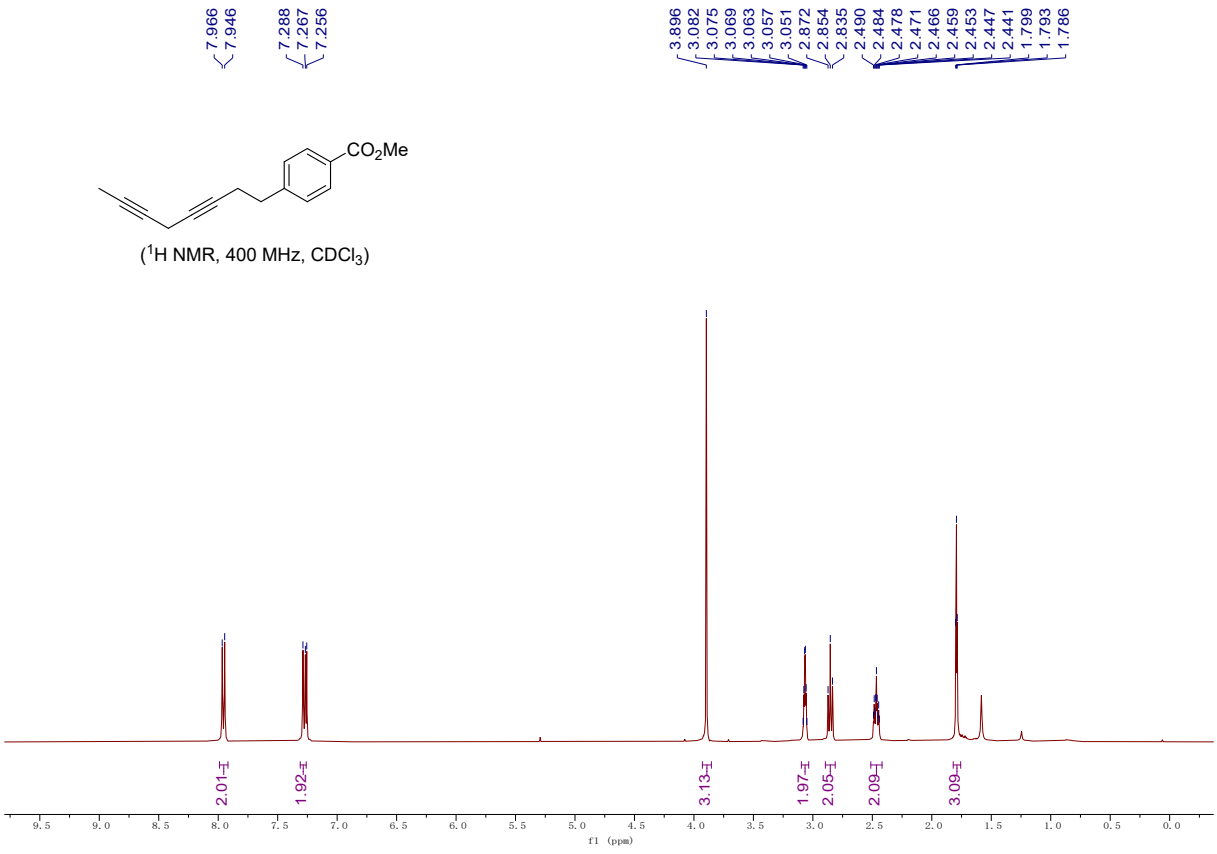
(^{13}C NMR, 151 MHz, $CDCl_3$)



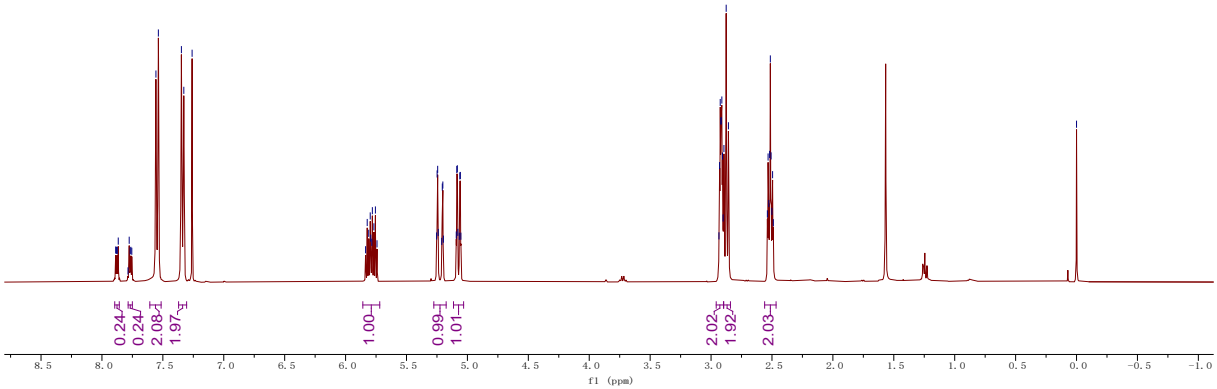
(^{1}H NMR, 400 MHz, $CDCl_3$)

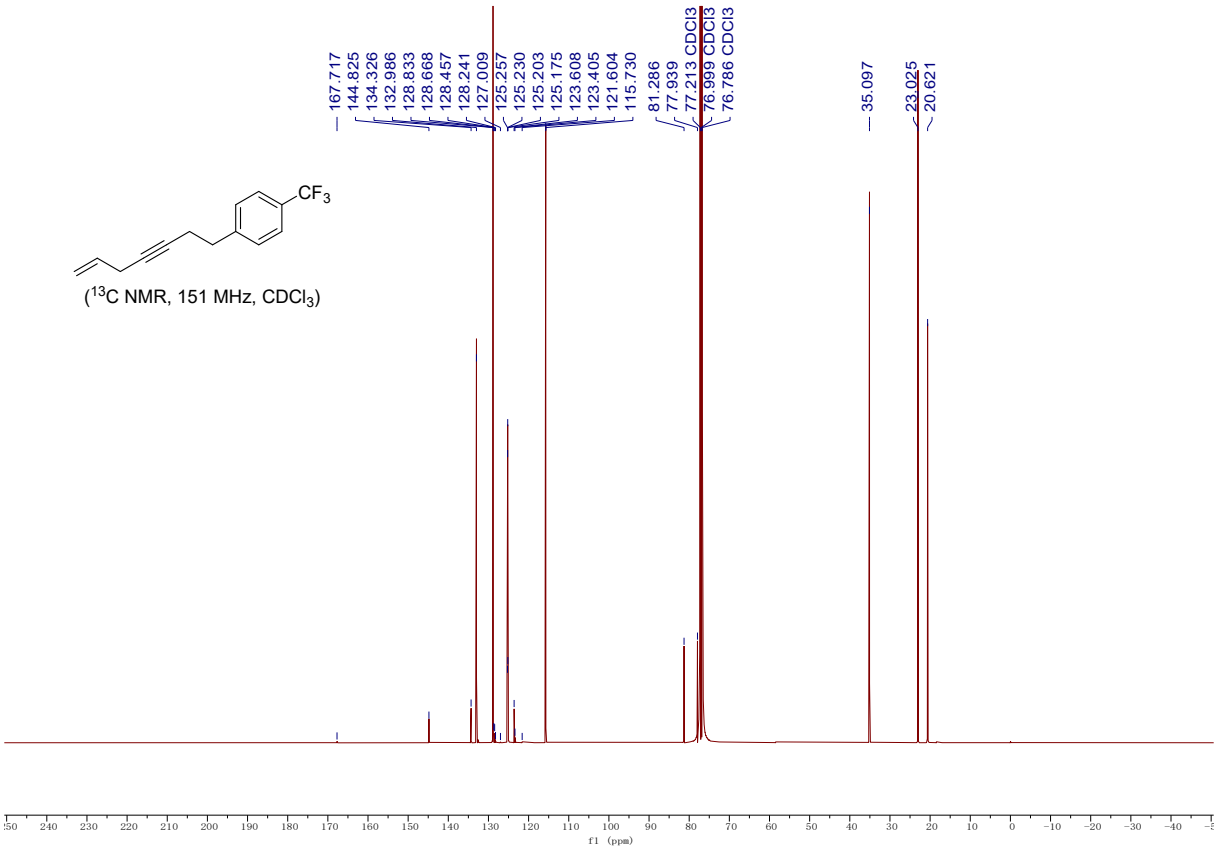


(^{13}C NMR, 151 MHz, $CDCl_3$)

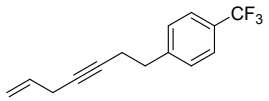

7.966
7.946
7.288
7.267
7.256
3.896
3.082
3.075
3.069
3.063
3.057
3.051
2.872
2.854
2.835
2.490
2.484
2.478
2.471
2.466
2.459
2.453
2.447
2.441
1.799
1.793
1.786
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.01
1.92
3.13
1.97
2.05
2.09
3.09
f1 (ppm)
167.084
146.092
129.661
128.551
128.203
79.185
77.213 CDCl3
77.002 CDCl3
76.791 CDCl3
76.060
75.660
73.288
51.989
35.025
20.542
9.622
3.491
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

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

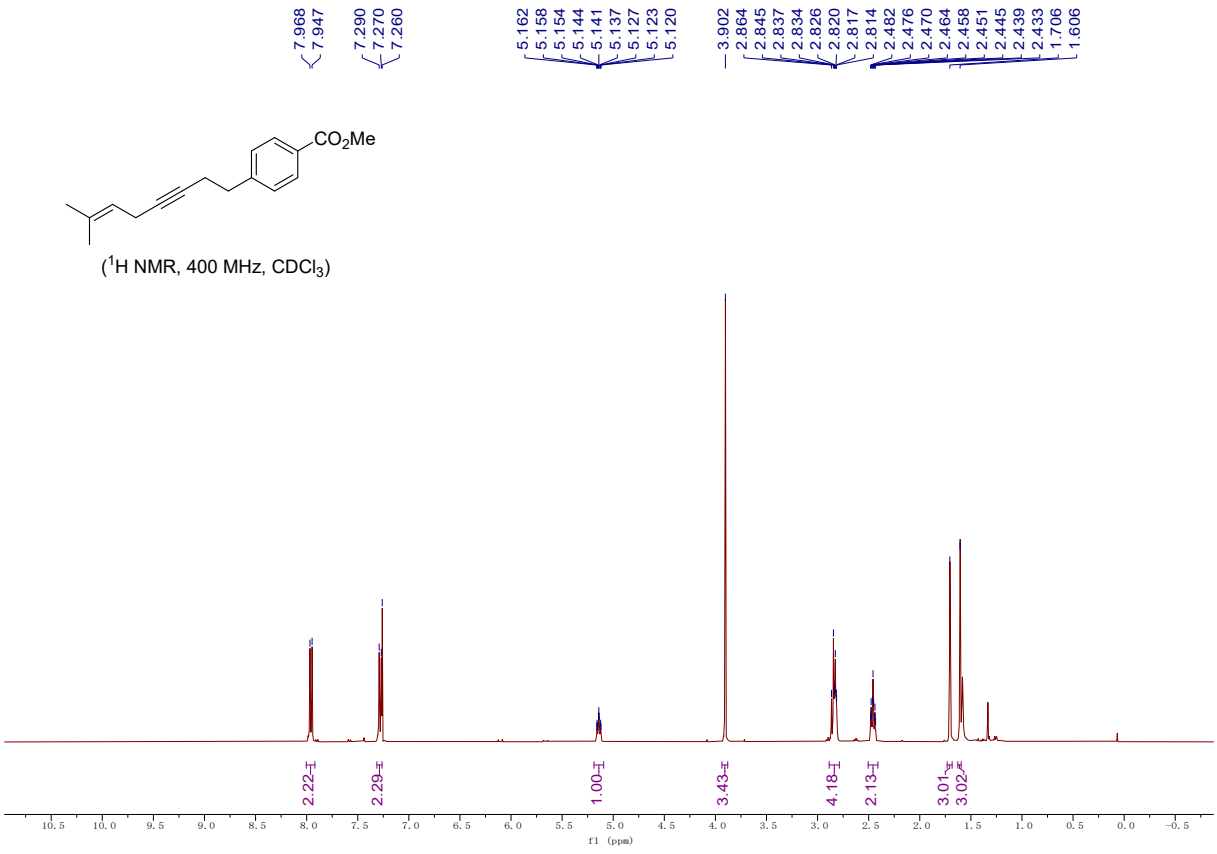


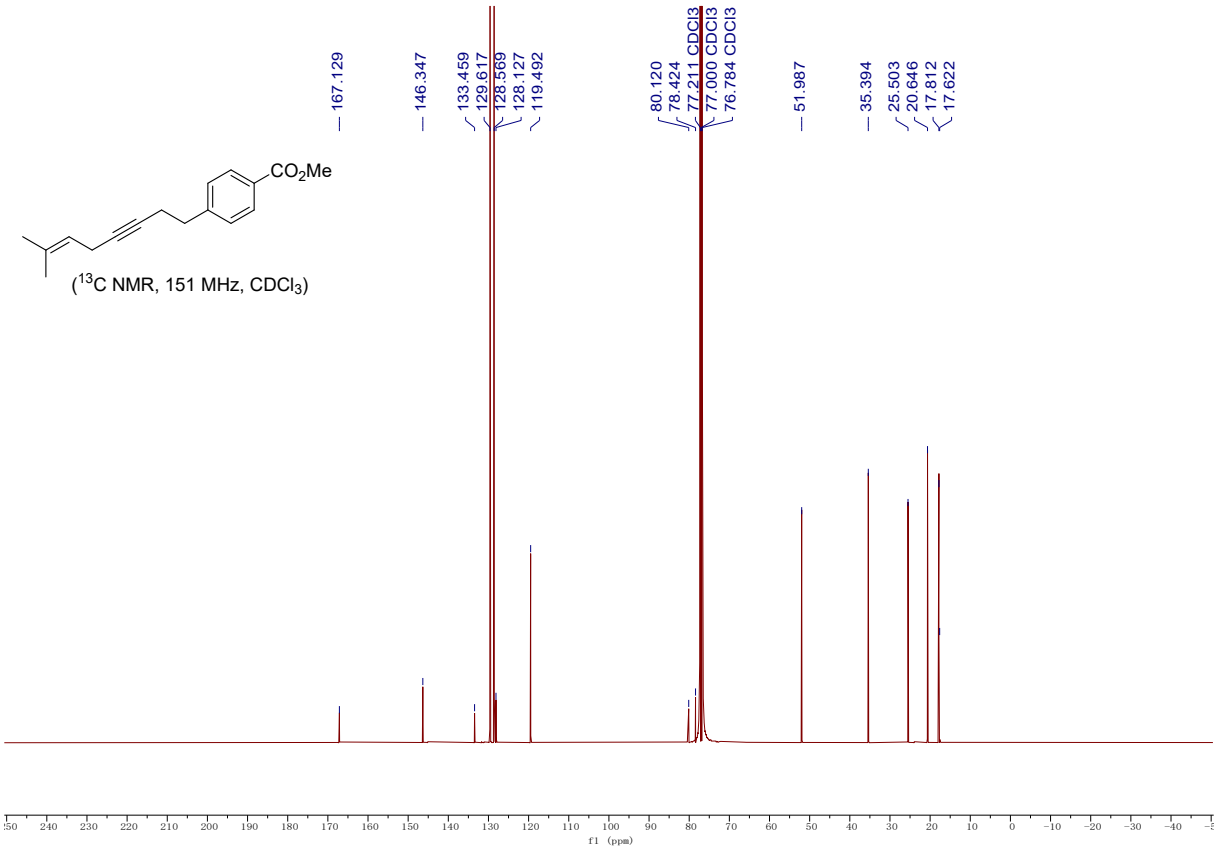


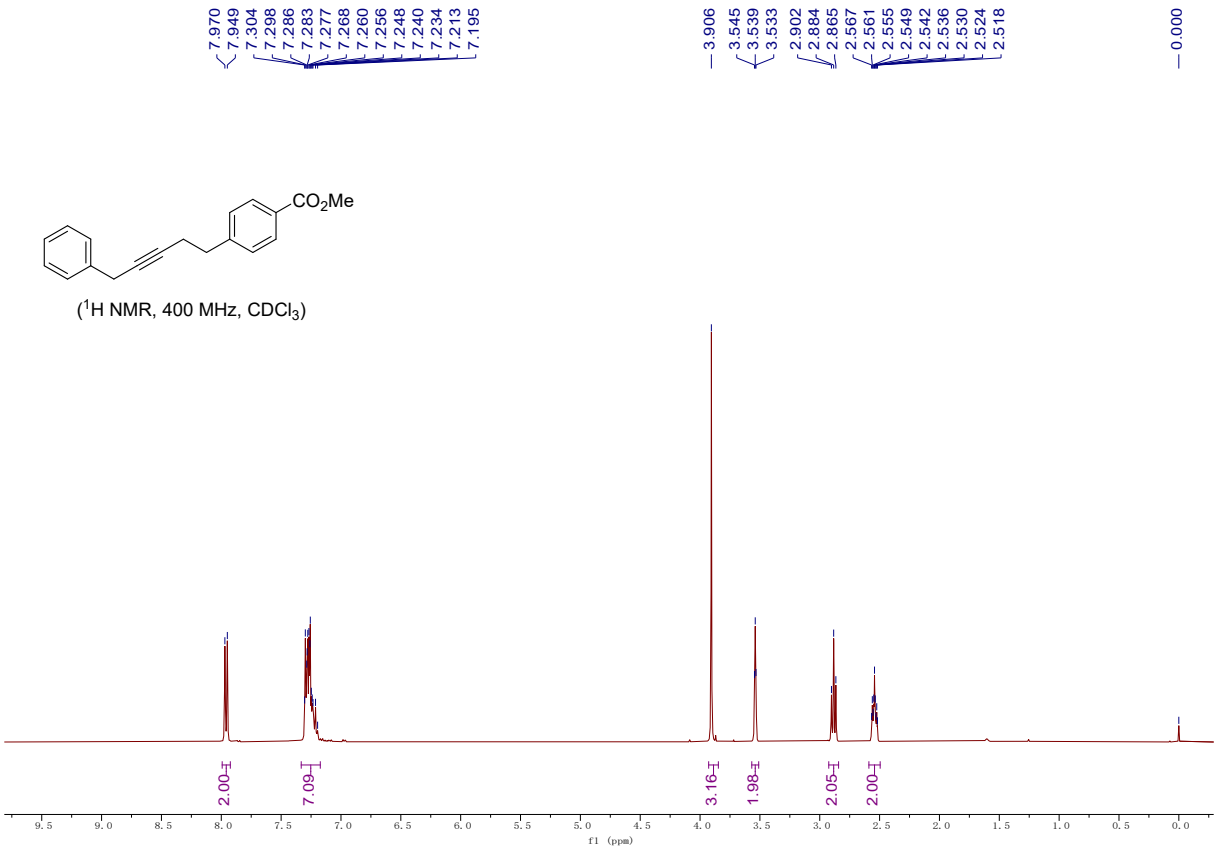
(^{13}C NMR, 151 MHz, $CDCl_3$)

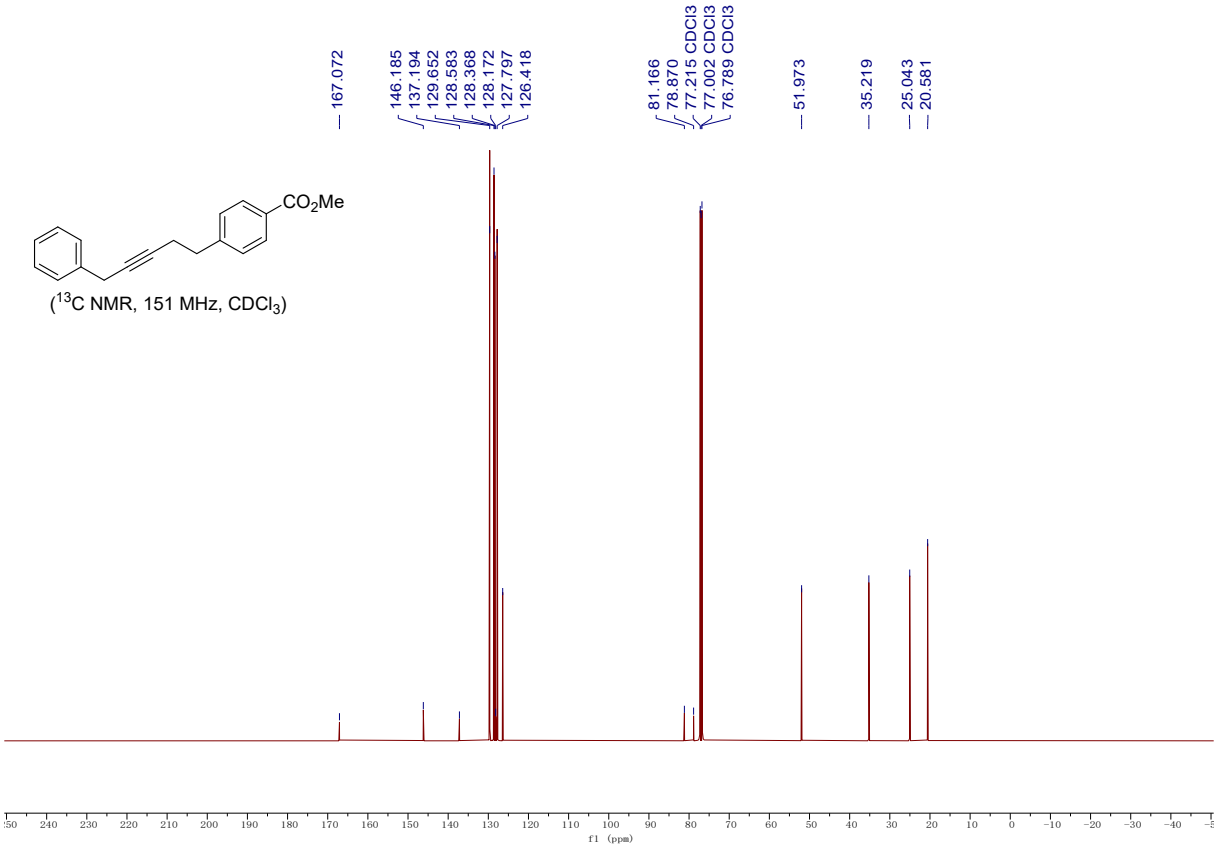


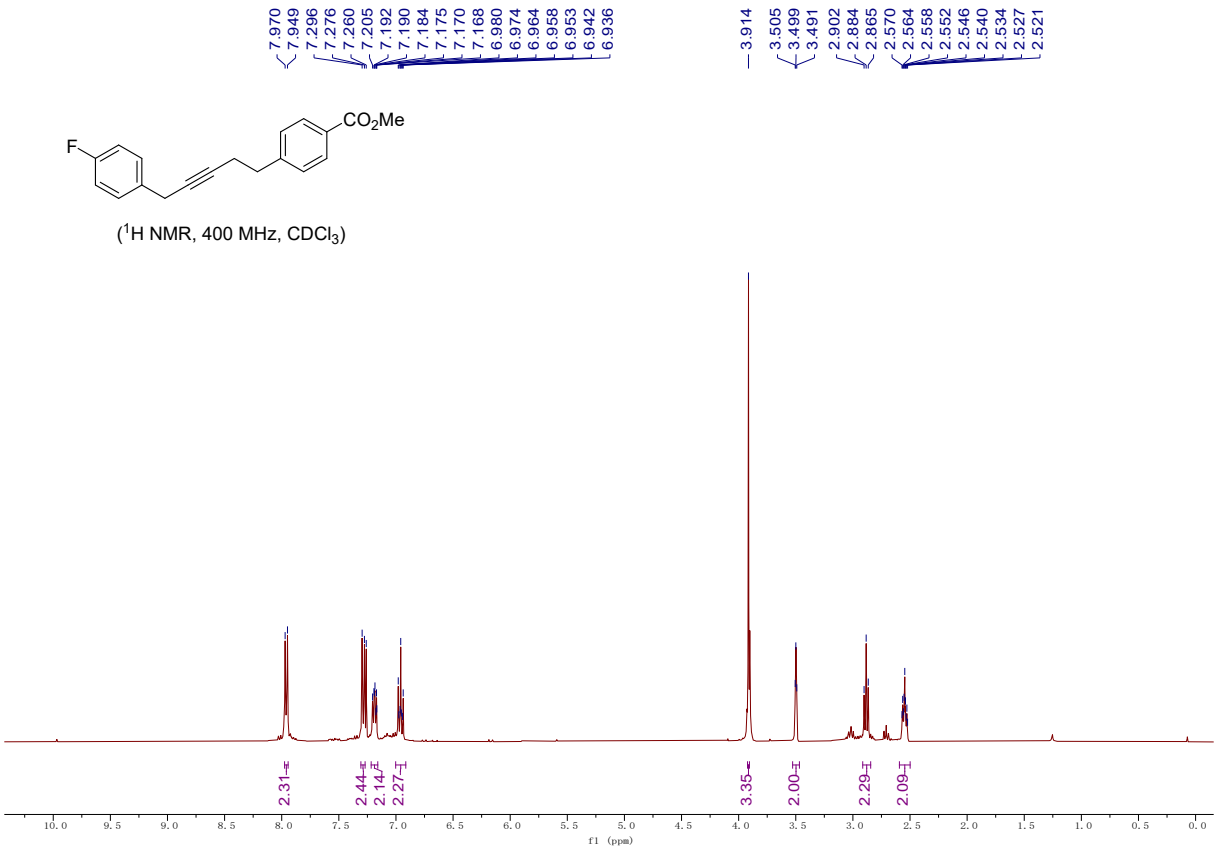
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.968
7.947
7.290
7.270
7.260
5.162
5.158
5.154
5.144
5.141
5.137
5.127
5.123
5.120
3.902
2.864
2.845
2.837
2.834
2.826
2.820
2.817
2.814
2.482
2.476
2.470
2.464
2.458
2.451
2.445
2.439
2.433
1.706
1.606
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.22
2.29
1.00
3.43
4.18
2.13
3.01
3.02
f1 (ppm)

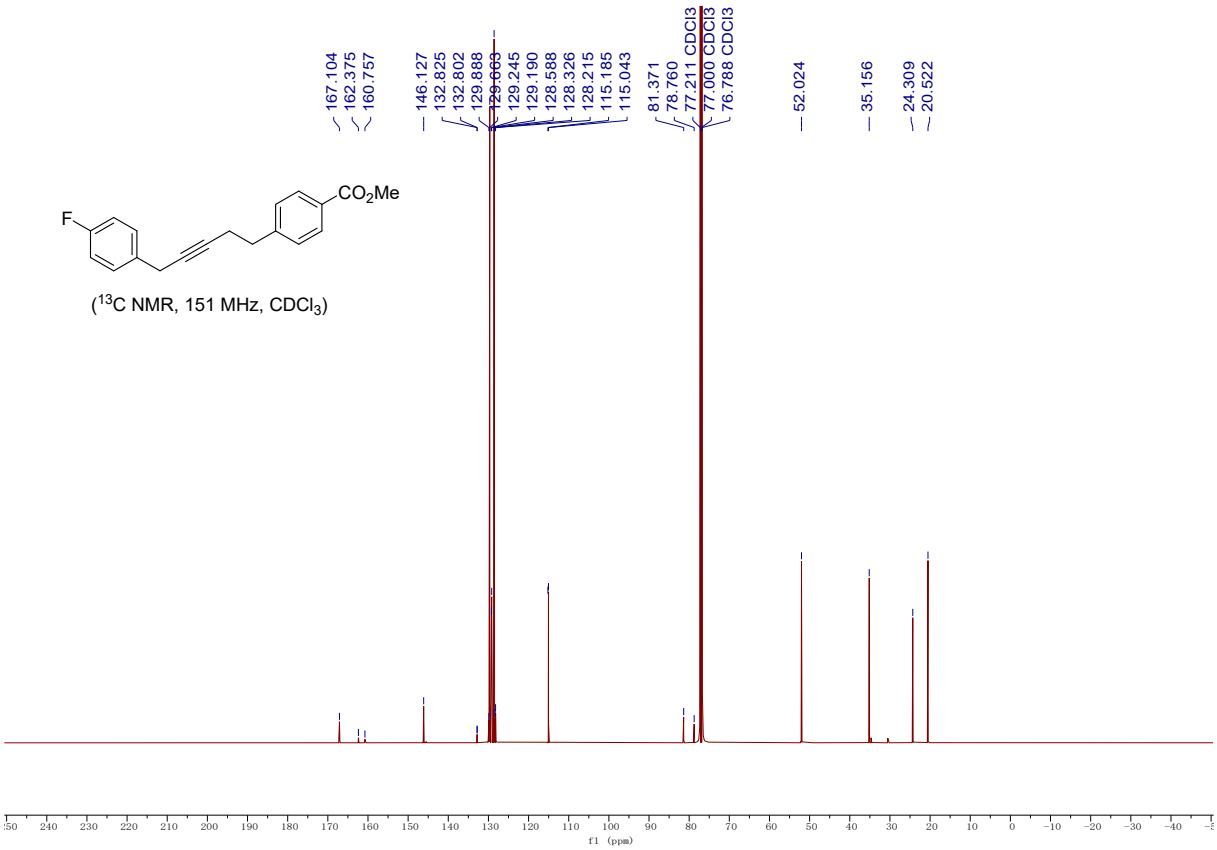

167.129
146.347
133.459
129.617
128.569
128.127
119.492
80.120
78.424
77.211 CDCl3
77.000 CDCl3
76.784 CDCl3
51.987
35.394
25.503
20.646
17.812
17.622
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)


7.970
7.949
7.304
7.298
7.286
7.283
7.277
7.268
7.260
7.256
7.248
7.240
7.234
7.213
7.195
3.906
3.545
3.539
3.533
2.902
2.884
2.865
2.567
2.561
2.555
2.549
2.542
2.536
2.530
2.524
2.518
0.000
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.00
7.09
3.16
1.98
2.05
2.00
f1 (ppm)

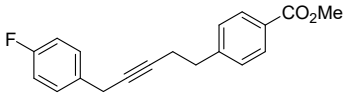

167.072
146.185
137.194
129.652
128.583
128.368
128.172
127.797
126.418
81.166
78.870
77.215 CDCl3
77.002 CDCl3
76.789 CDCl3
51.973
35.219
25.043
20.581
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



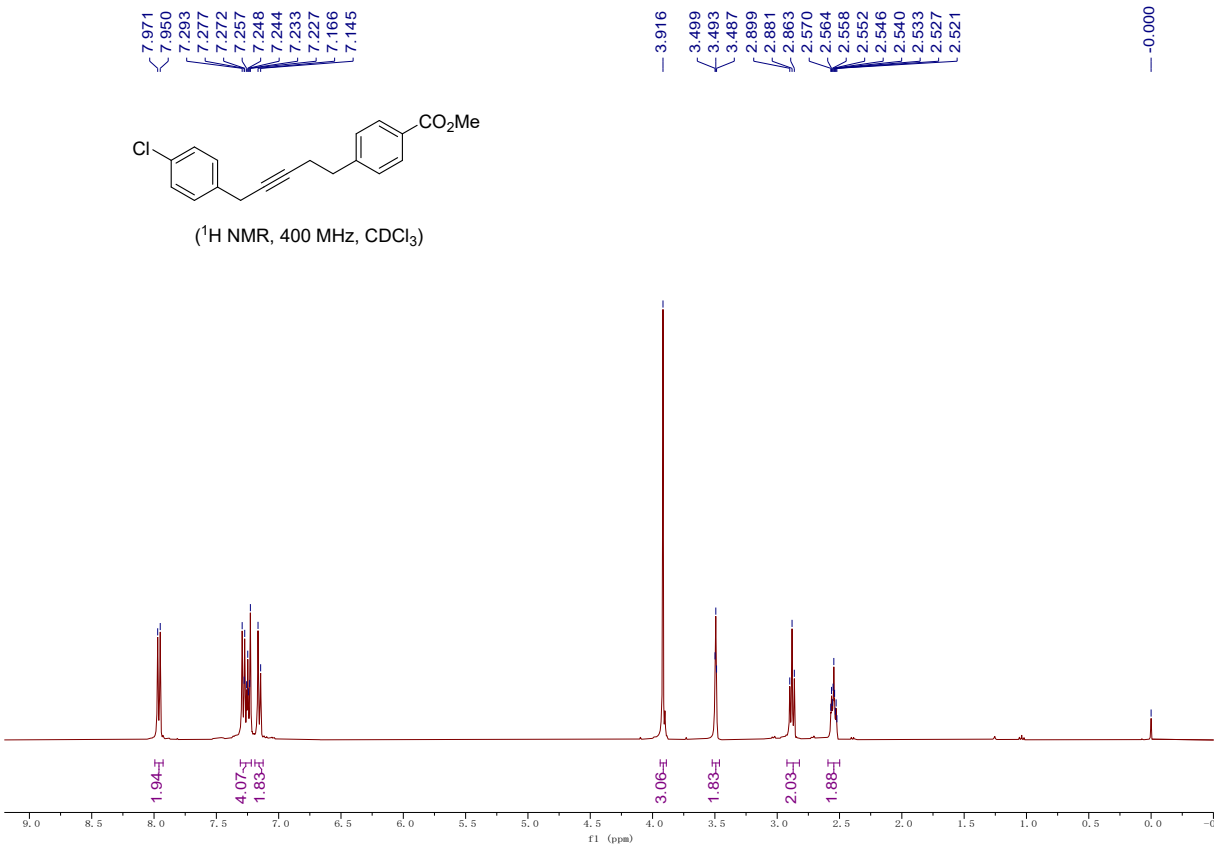
(^{1}H NMR, 400 MHz, $CDCl_3$)

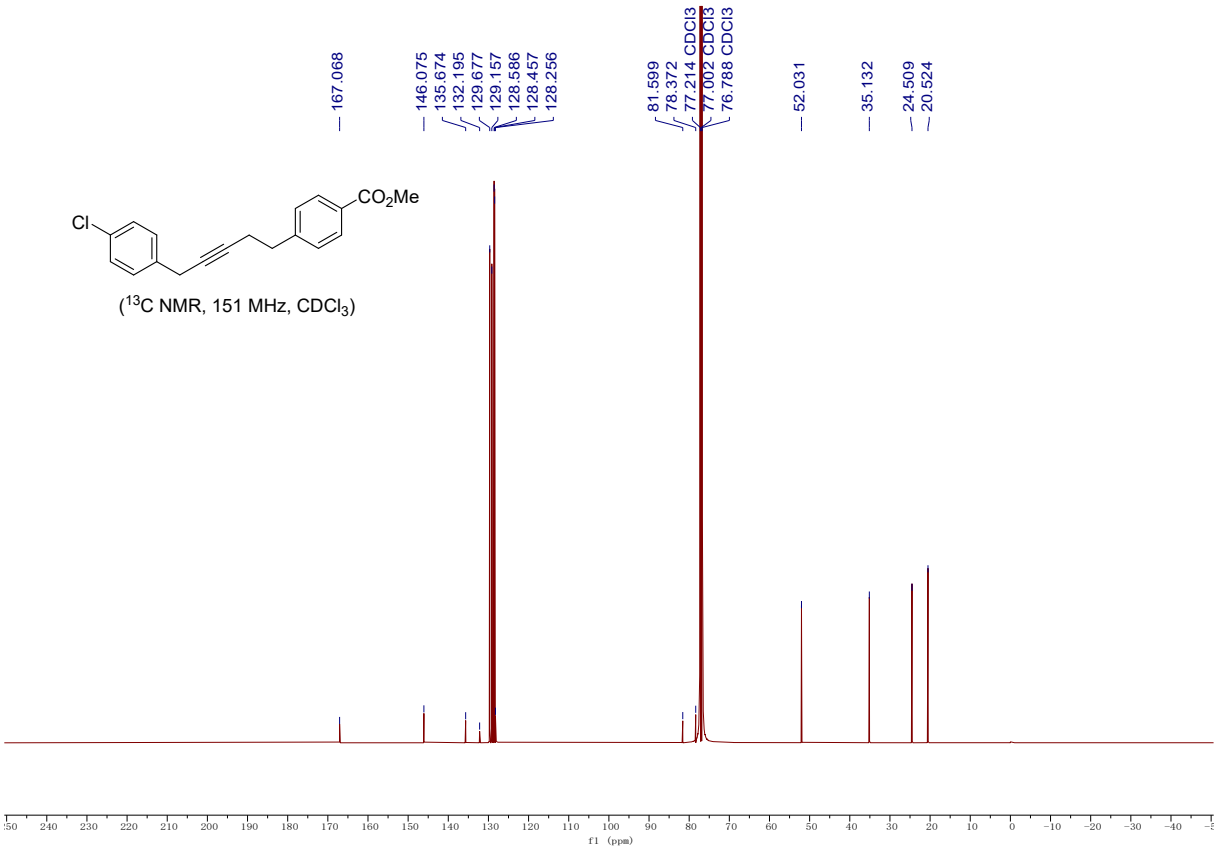


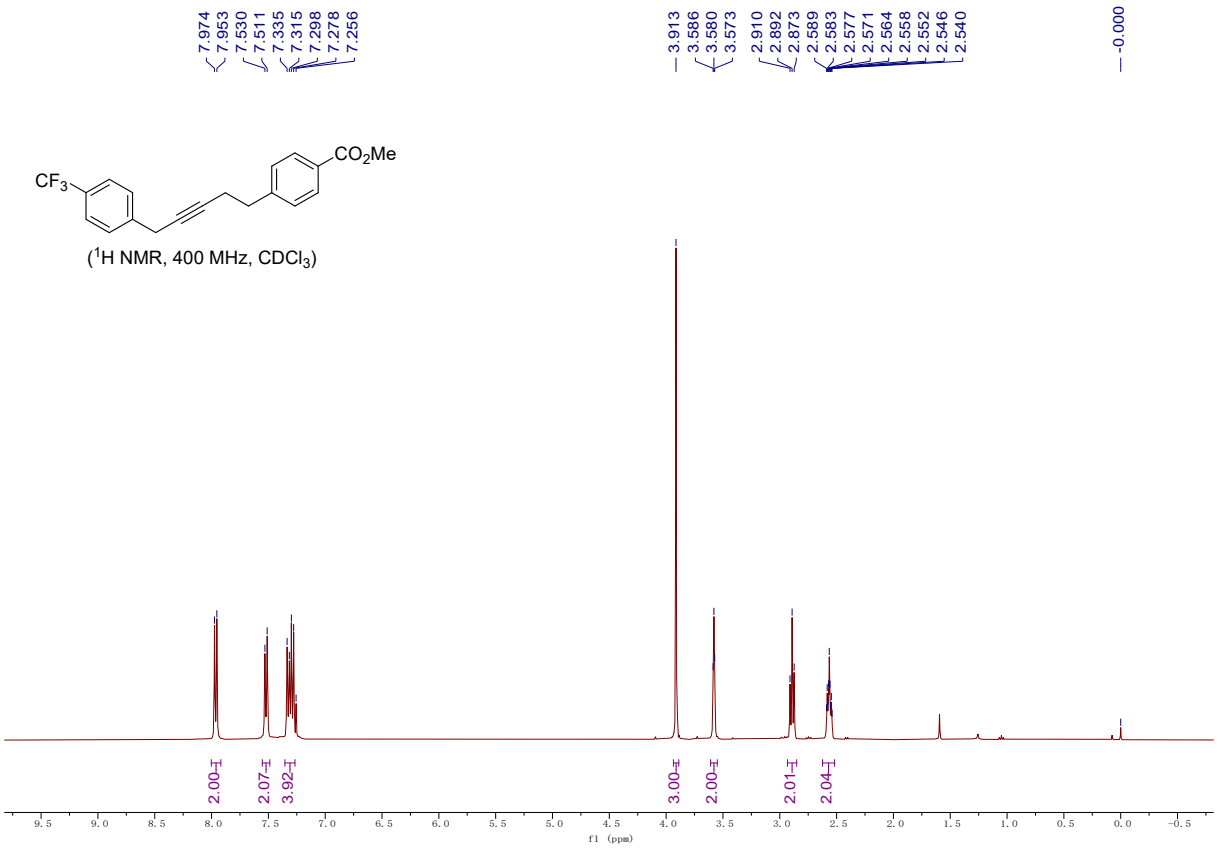
(^{13}C NMR, 151 MHz, $CDCl_3$)

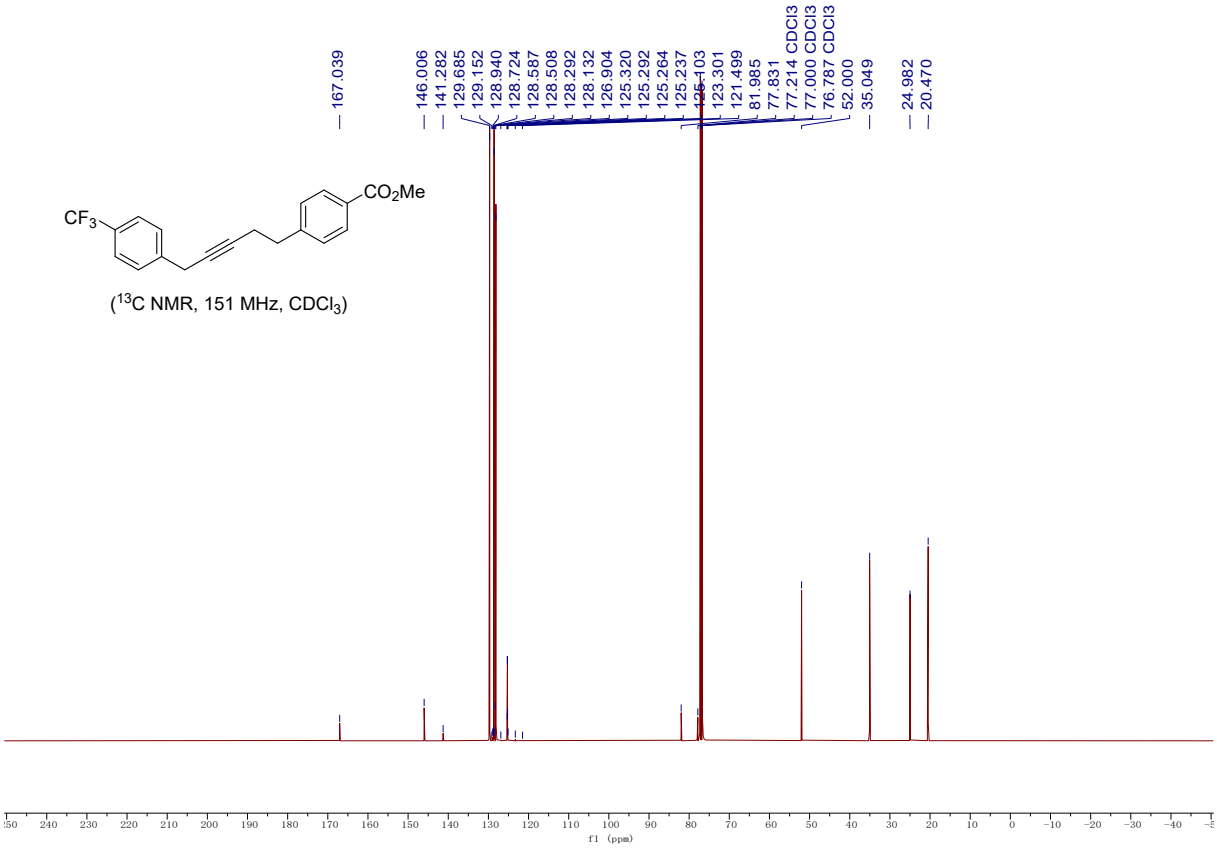


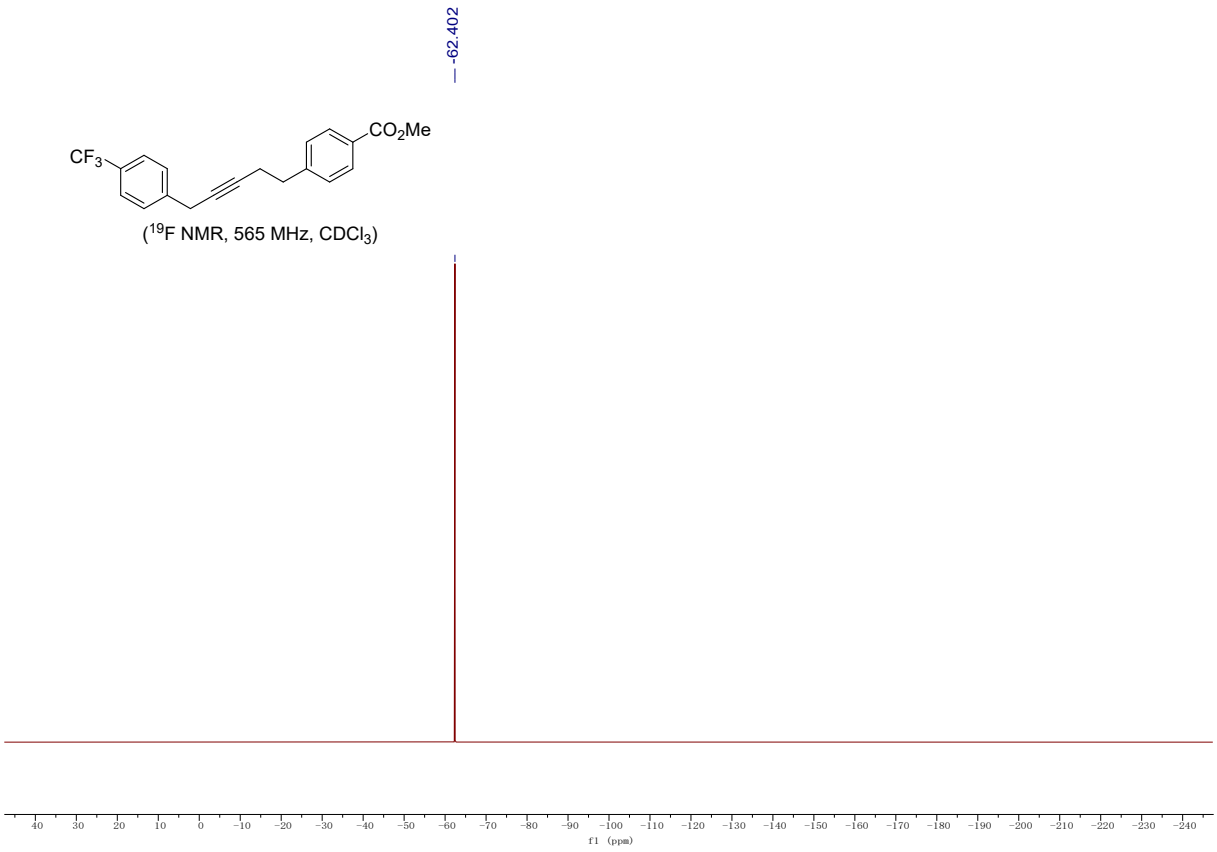
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.971
7.950
7.293
7.277
7.272
7.257
7.248
7.244
7.233
7.227
7.166
7.145
3.916
3.499
3.493
3.487
2.899
2.881
2.863
2.570
2.564
2.558
2.552
2.546
2.540
2.533
2.527
2.521
-0.000
Cl
CO2Me
(1H NMR, 400 MHz, CDCl3)
1.94
4.07
1.83
3.06
1.83
2.03
1.88
f1 (ppm)

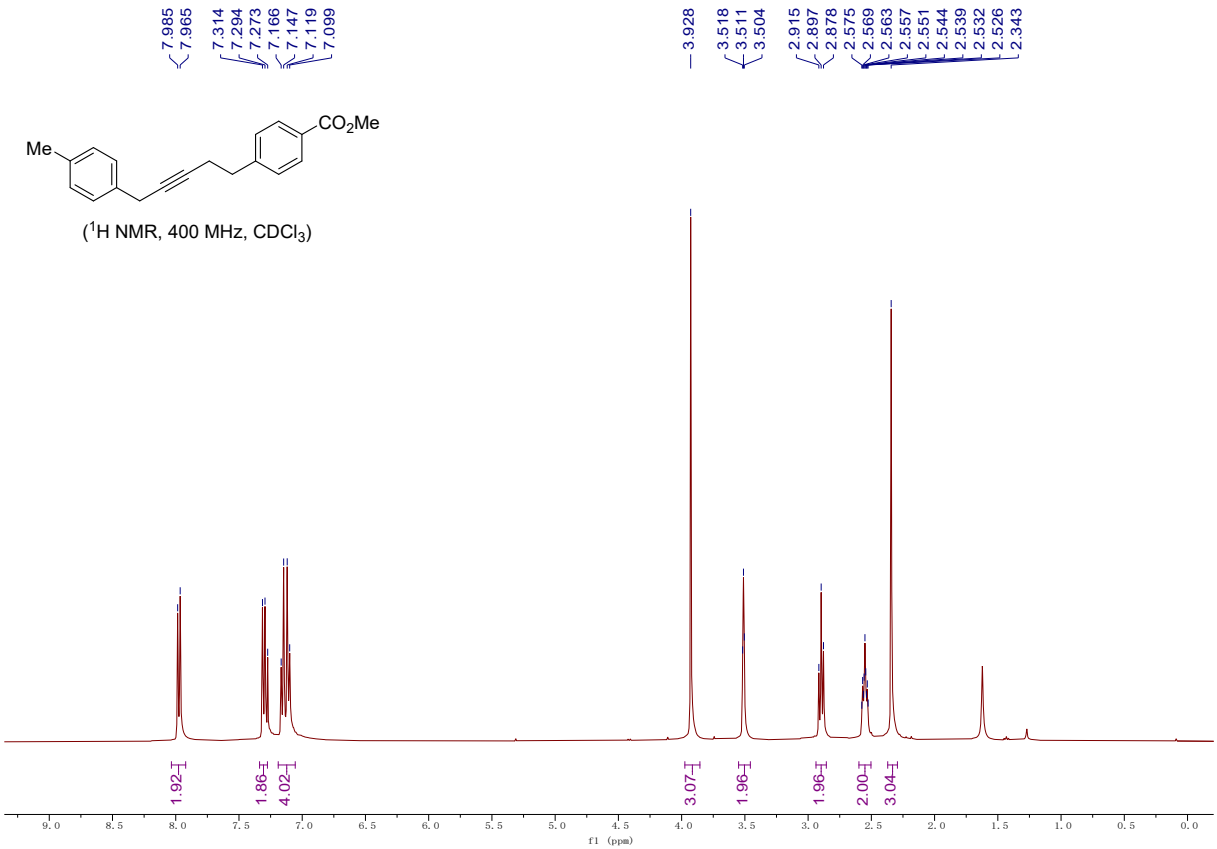

167.068
146.075
135.674
132.195
129.677
129.157
128.586
128.457
128.256
81.599
78.372
77.214 CDCl3
77.002 CDCl3
76.788 CDCl3
52.031
35.132
24.509
20.524
Cl
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

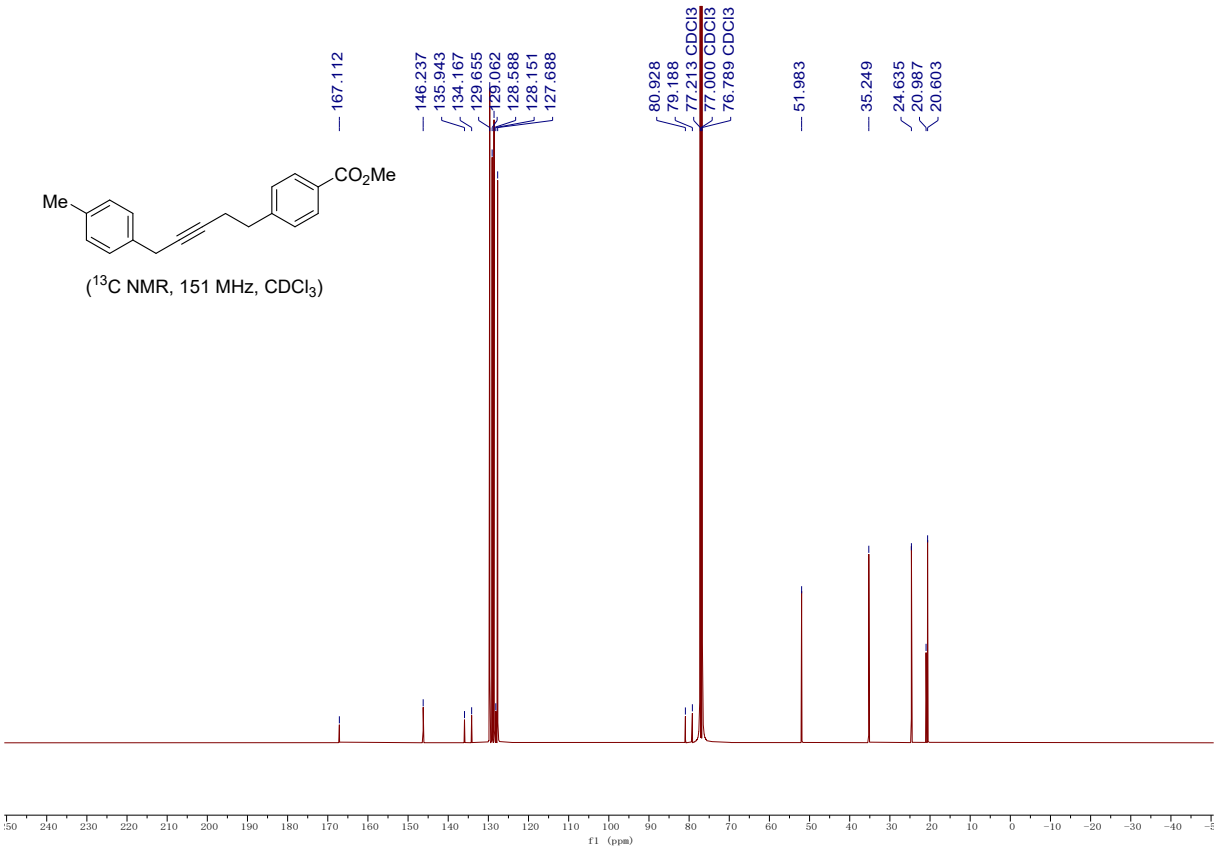

7.974
7.953
7.530
7.511
7.335
7.315
7.298
7.278
7.256
3.913
3.586
3.580
3.573
2.910
2.892
2.873
2.589
2.583
2.577
2.571
2.564
2.558
2.552
2.546
2.540
-0.000
CO2Me
CF3
(1H NMR, 400 MHz, CDCl3)
2.00
2.07
3.92
3.00
2.00
2.01
2.04
f1 (ppm)

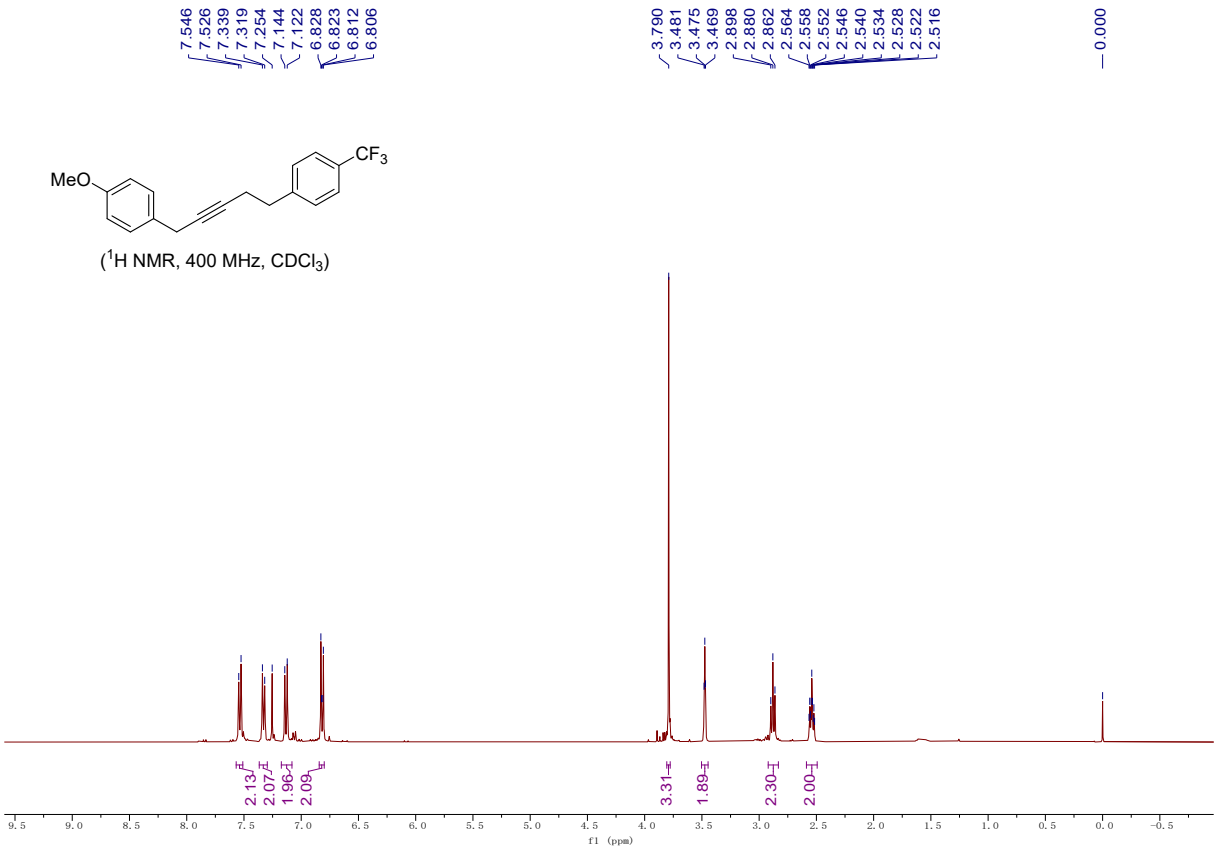

167.039
146.006
141.282
129.685
129.152
128.940
128.724
128.587
128.508
128.292
128.132
126.904
125.320
125.292
125.264
125.237
126.103
123.301
121.499
81.985
77.831
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
52.000
35.049
24.982
20.470
CO2Me
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

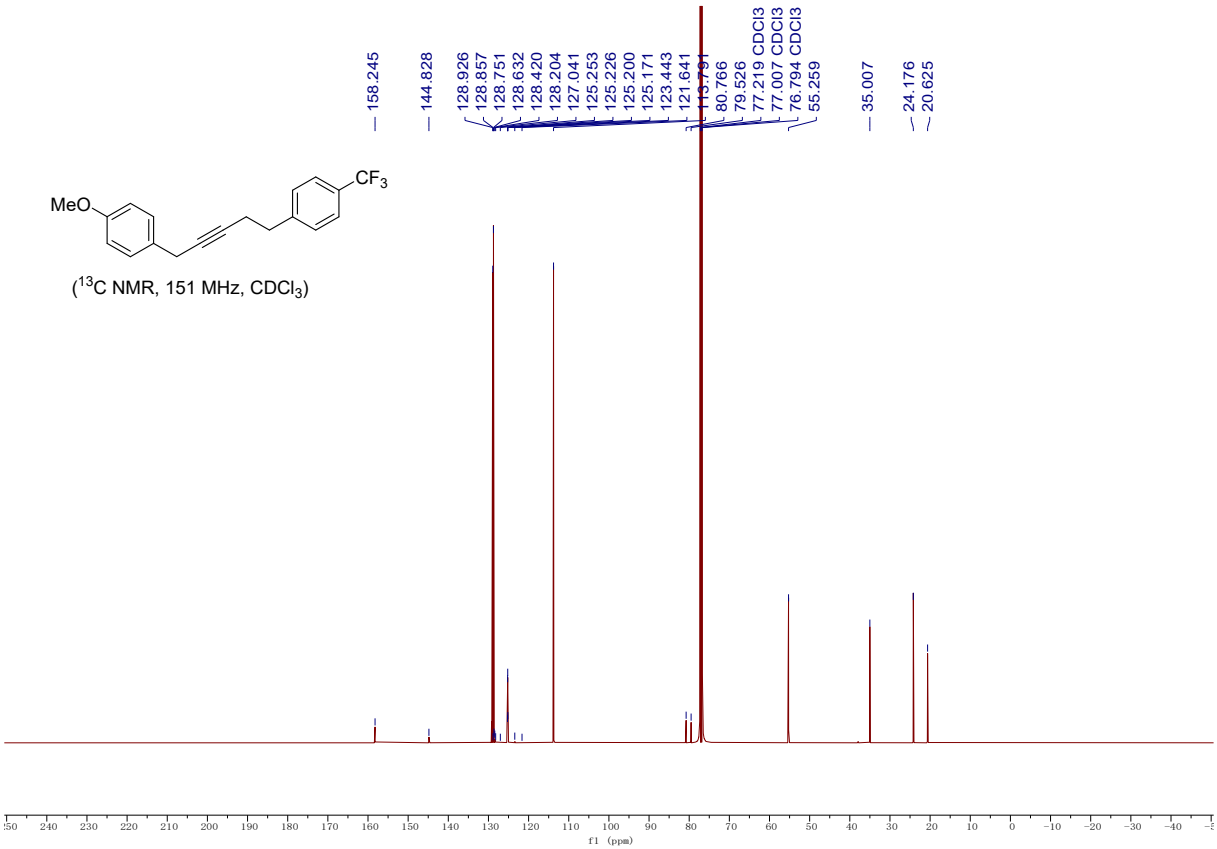


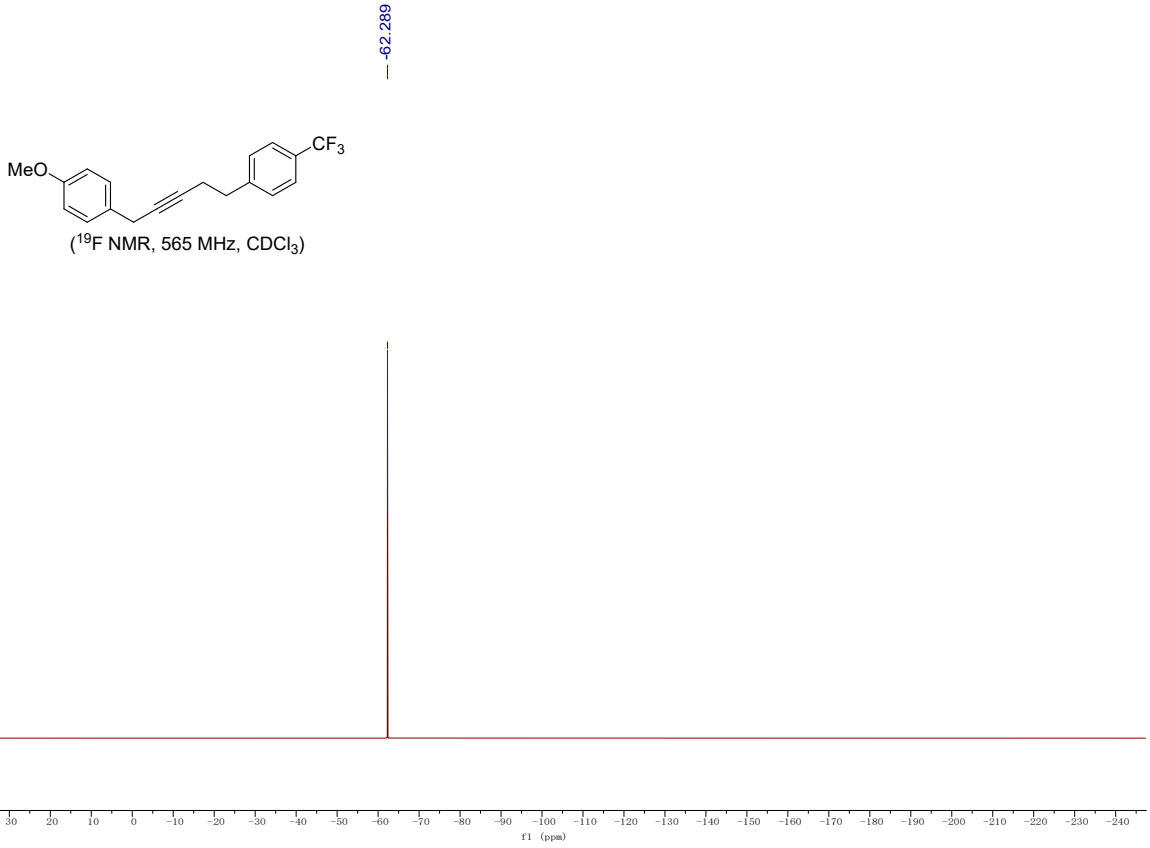
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.985
7.965
7.314
7.294
7.273
7.166
7.147
7.119
7.099
3.928
3.518
3.511
3.504
2.915
2.897
2.878
2.575
2.569
2.563
2.557
2.551
2.544
2.539
2.532
2.526
2.343
Me
CO2Me
(1H NMR, 400 MHz, CDCl3)
1.92
1.86
4.02
3.07
1.96
1.96
2.00
3.04
f1 (ppm)

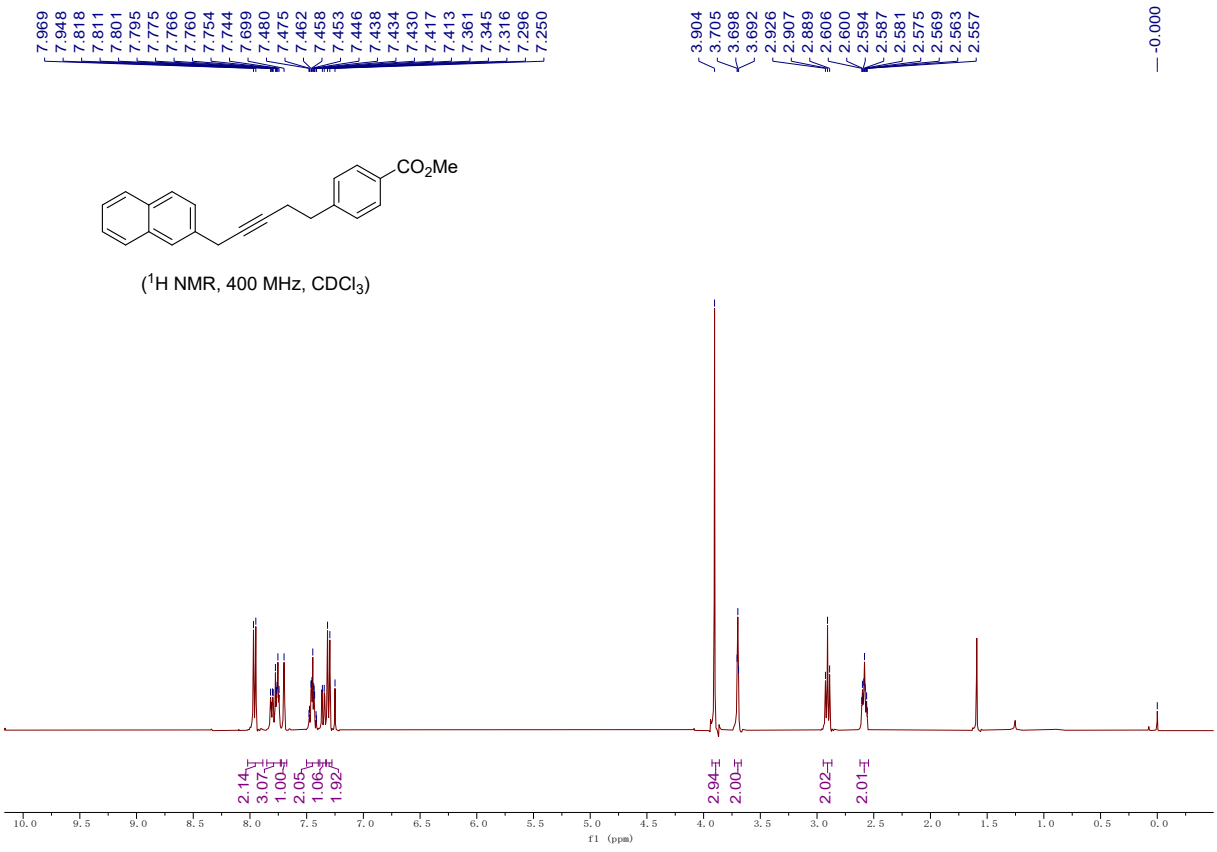

167.112
146.237
135.943
134.167
129.655
129.062
128.588
128.151
127.688
80.928
79.188
77.213 CDCl3
77.000 CDCl3
76.789 CDCl3
51.983
35.249
24.635
20.987
20.603
Me
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

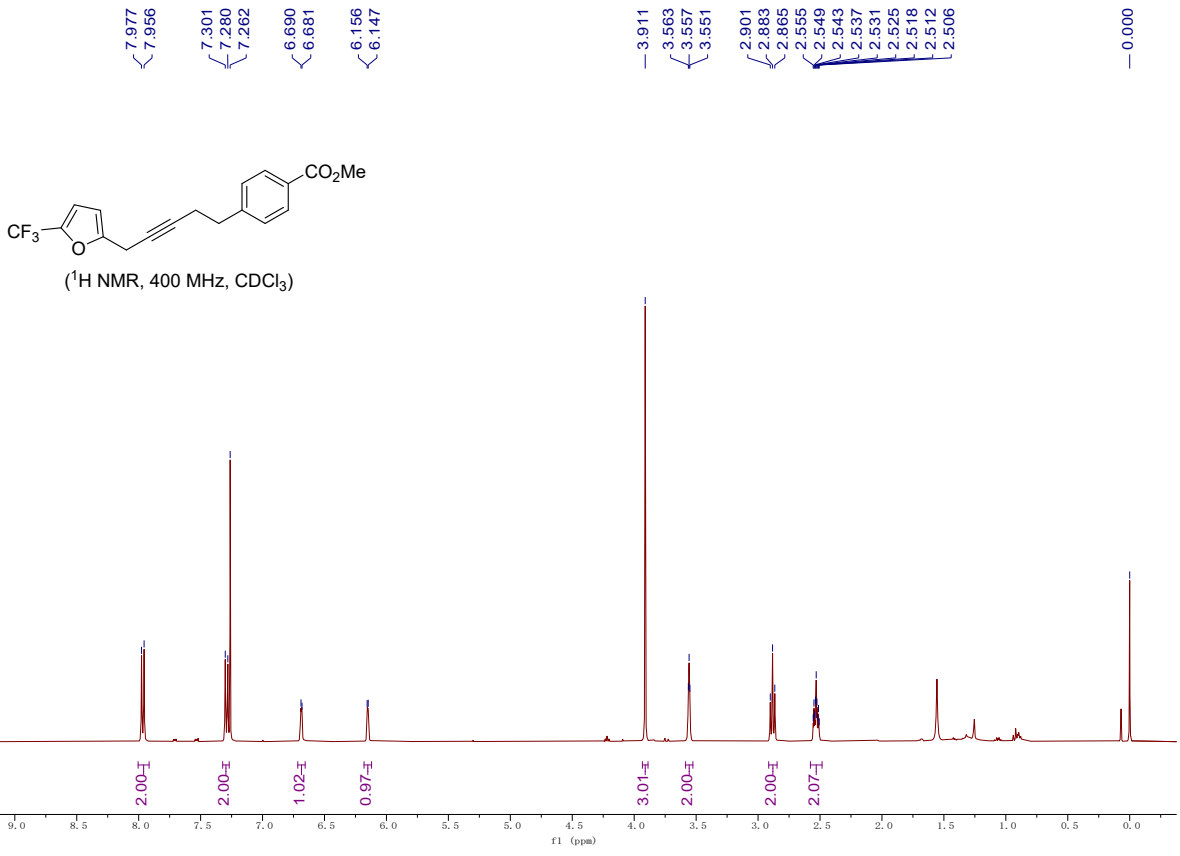

7.546
7.526
7.339
7.319
7.254
7.144
7.122
6.828
6.823
6.812
6.806
3.790
3.481
3.475
3.469
2.898
2.880
2.862
2.564
2.558
2.552
2.546
2.540
2.534
2.528
2.522
2.516
0.000
MeO
CF3
(1H NMR, 400 MHz, CDCl3)
2.13
2.07
1.96
2.09
3.31
1.89
2.30
2.00
f1 (ppm)


158.245
144.828
128.926
128.857
128.751
128.632
128.420
128.204
127.041
125.253
125.226
125.200
125.171
123.443
121.641
113.791
80.766
79.526
77.219 CDCl3
77.007 CDCl3
76.794 CDCl3
55.259
35.007
24.176
20.625
MeO
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

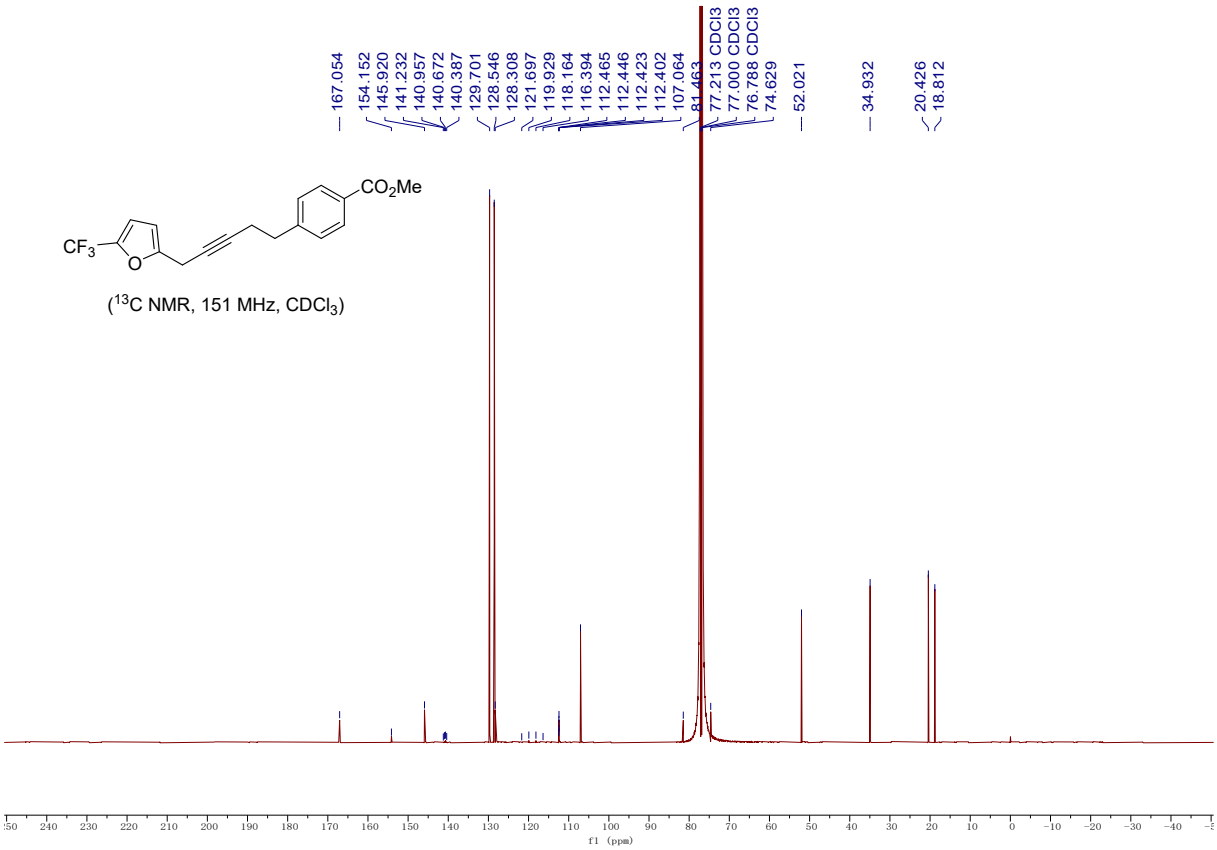


(^{19}F NMR, 565 MHz, $CDCl_3$)

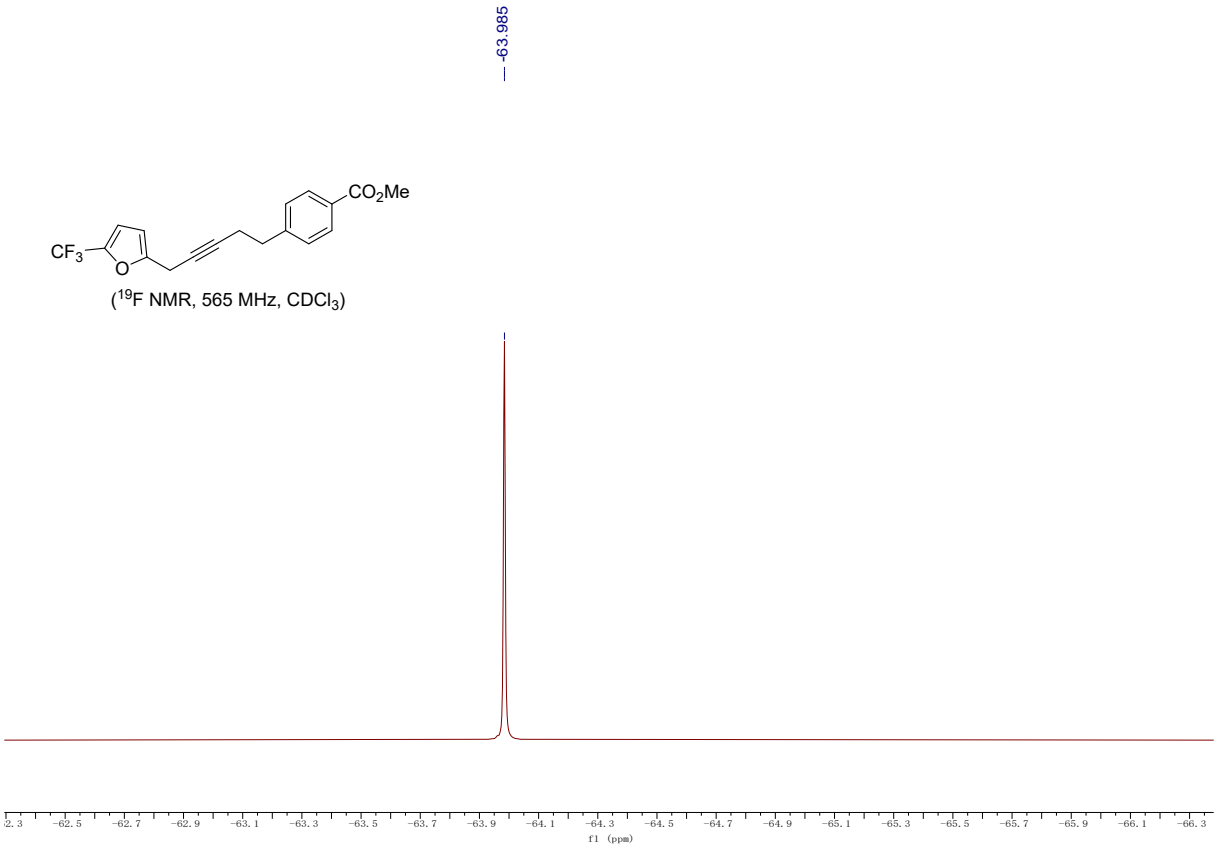

7.969
7.948
7.818
7.811
7.801
7.795
7.775
7.766
7.760
7.754
7.744
7.699
7.480
7.475
7.462
7.458
7.453
7.446
7.438
7.434
7.430
7.417
7.413
7.361
7.345
7.316
7.296
7.250
3.904
3.705
3.698
3.692
2.926
2.907
2.889
2.606
2.600
2.594
2.587
2.581
2.575
2.569
2.563
2.557
-0.000
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.14
3.07
1.00
2.05
1.06
1.92
2.94
2.00
2.02
2.01
f1 (ppm)
167.081
146.183
134.680
133.461
132.243
129.683
128.610
128.202
128.006
127.586
126.451
126.011
125.978
125.450
81.465
78.839
77.213 CDCl3
77.001 CDCl3
76.788 CDCl3
51.979
35.222
25.289
20.624
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

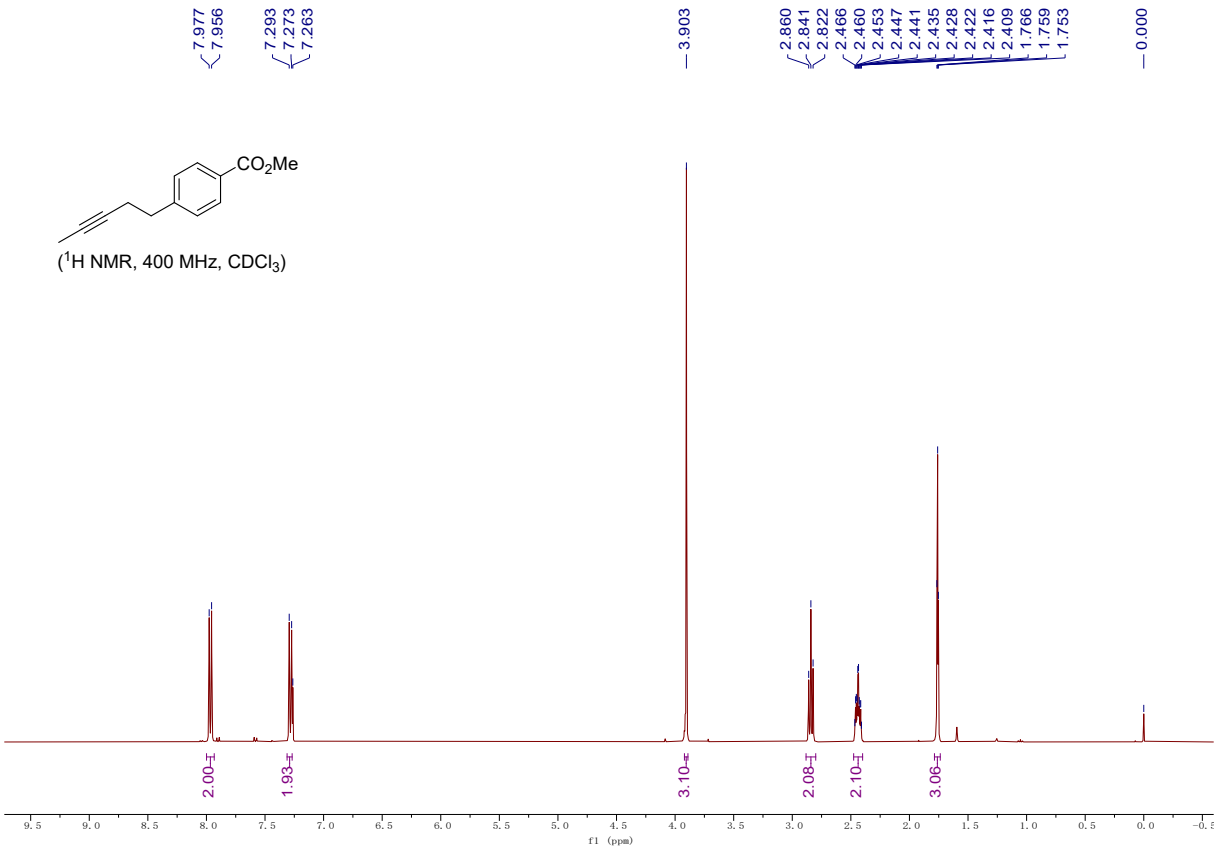


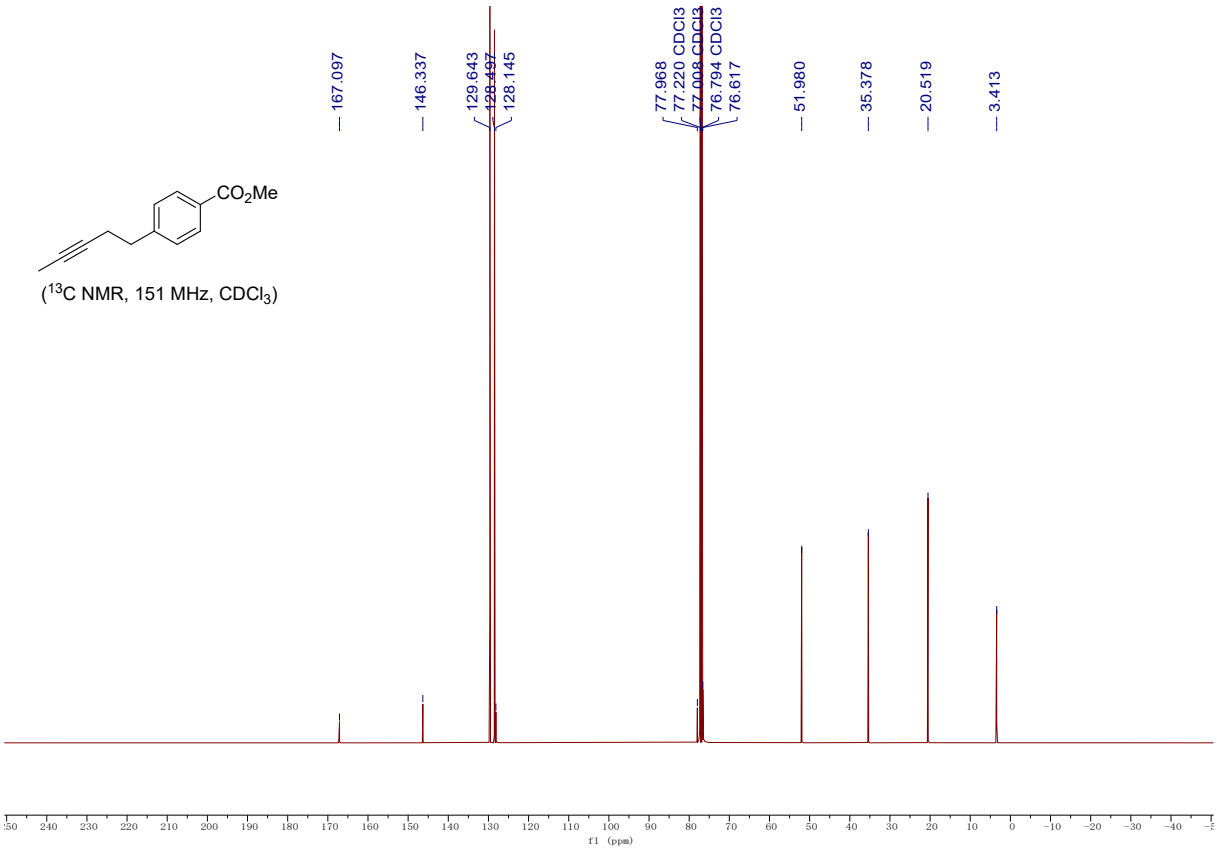
(^{1}H NMR, 400 MHz, $CDCl_3$)

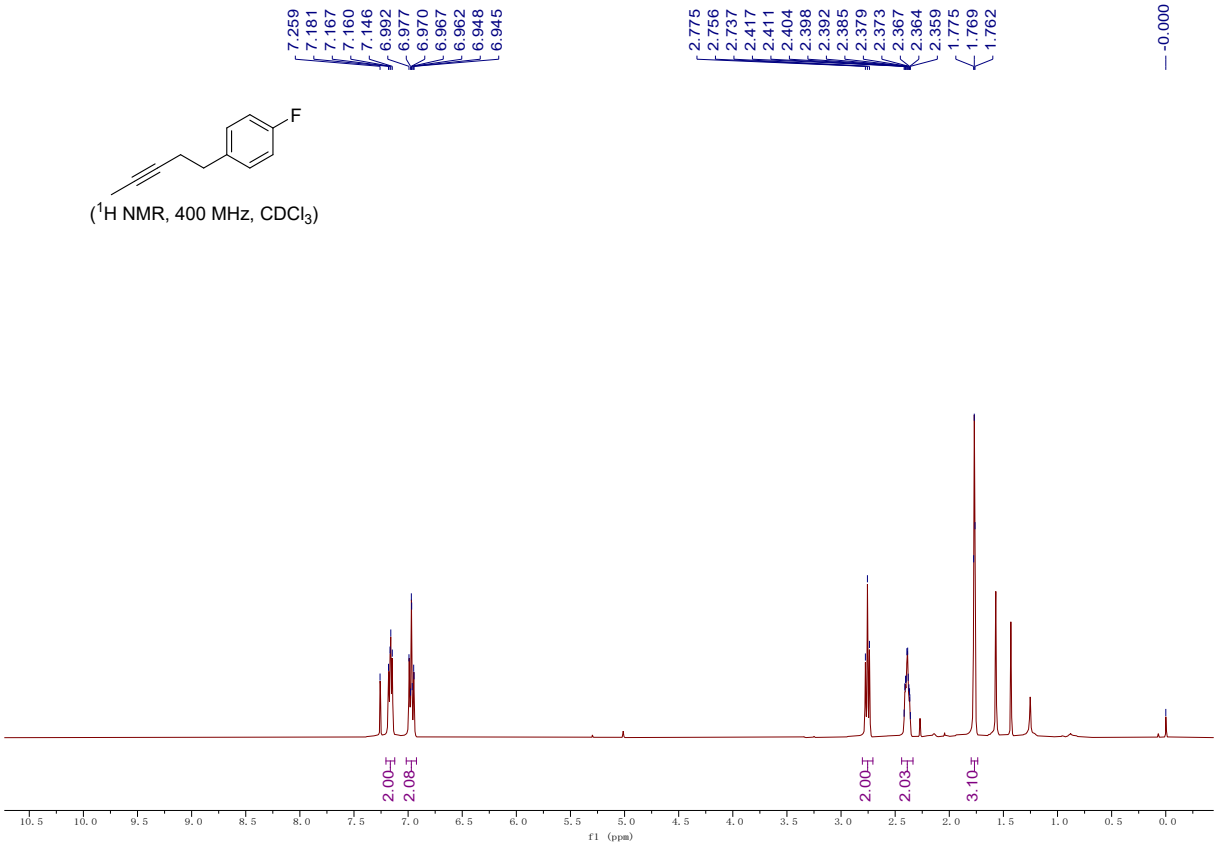


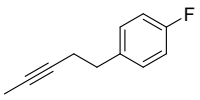
(^{13}C NMR, 151 MHz, $CDCl_3$)


-63.985
CO2Me
CF3
O
(19F NMR, 565 MHz, CDCl3)
f1 (ppm)

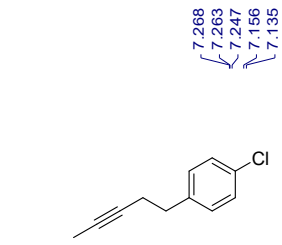

7.977
7.956
7.293
7.273
7.263
3.903
2.860
2.841
2.822
2.466
2.460
2.453
2.447
2.441
2.435
2.428
2.422
2.416
2.409
1.766
1.759
1.753
0.000
CO2Me
(1H NMR, 400 MHz, CDCl3)
2.00
1.93
3.10
2.08
2.10
3.06
f1 (ppm)


167.097
146.337
129.643
128.497
128.145
77.968
77.220 CDCl3
77.008 CDCl3
76.794 CDCl3
76.617
51.980
35.378
20.519
3.413
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

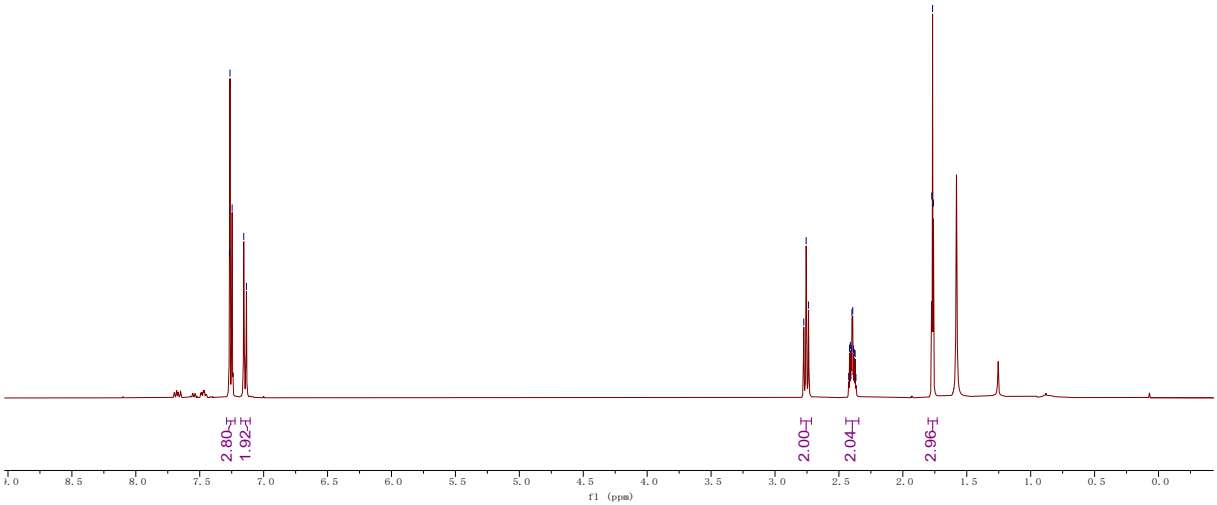

7.259
7.181
7.167
7.160
7.146
6.992
6.977
6.970
6.967
6.962
6.948
6.945
2.775
2.756
2.737
2.417
2.411
2.404
2.398
2.392
2.385
2.379
2.373
2.367
2.364
2.359
1.775
1.769
1.762
-0.000
F
(1H NMR, 400 MHz, CDCl3)
2.00
2.08
2.00
2.03
3.10
f1 (ppm)
162.270
160.656
136.604
136.581
129.834
129.781
115.094
114.952
78.281
77.217 CDCl3
77.004 CDCl3
76.790 CDCl3
76.417
34.620
21.061
3.429
F
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

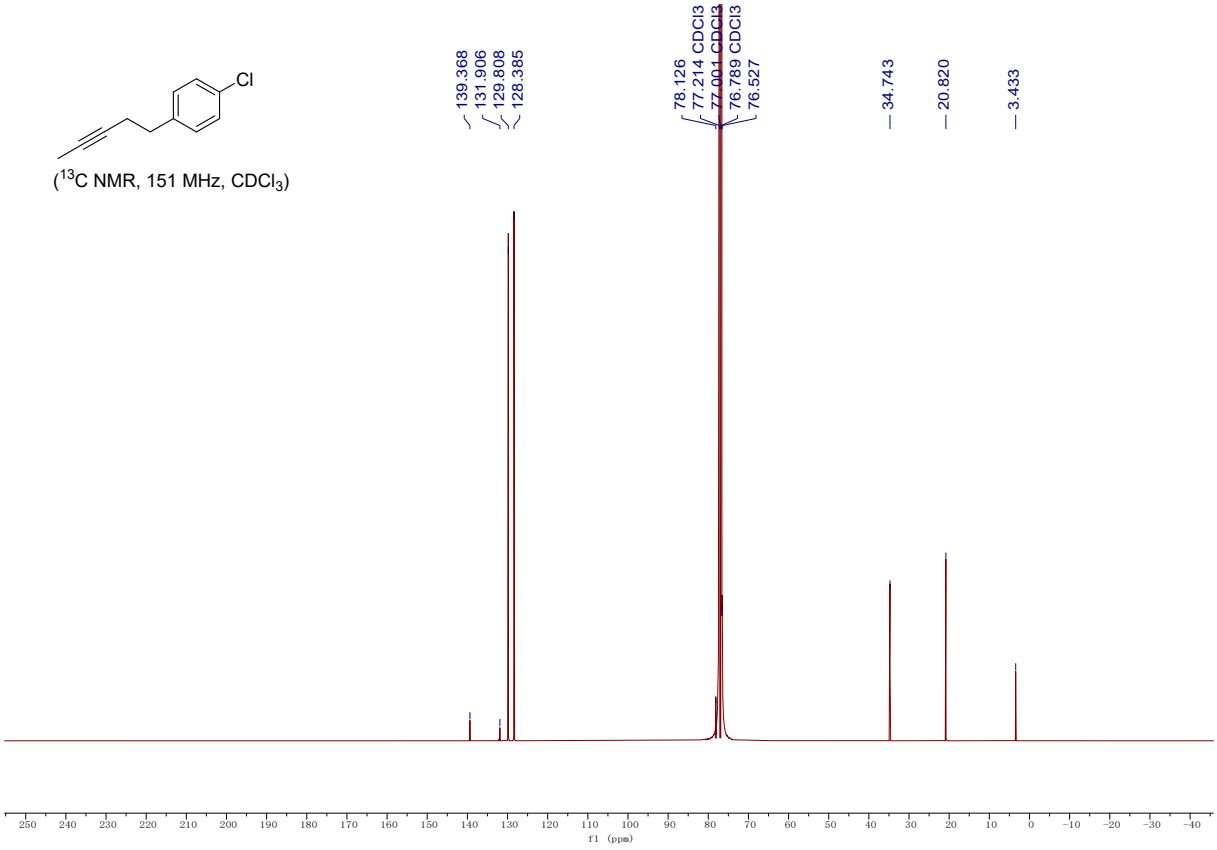


(^{19}F NMR, 565 MHz, $CDCl_3$)

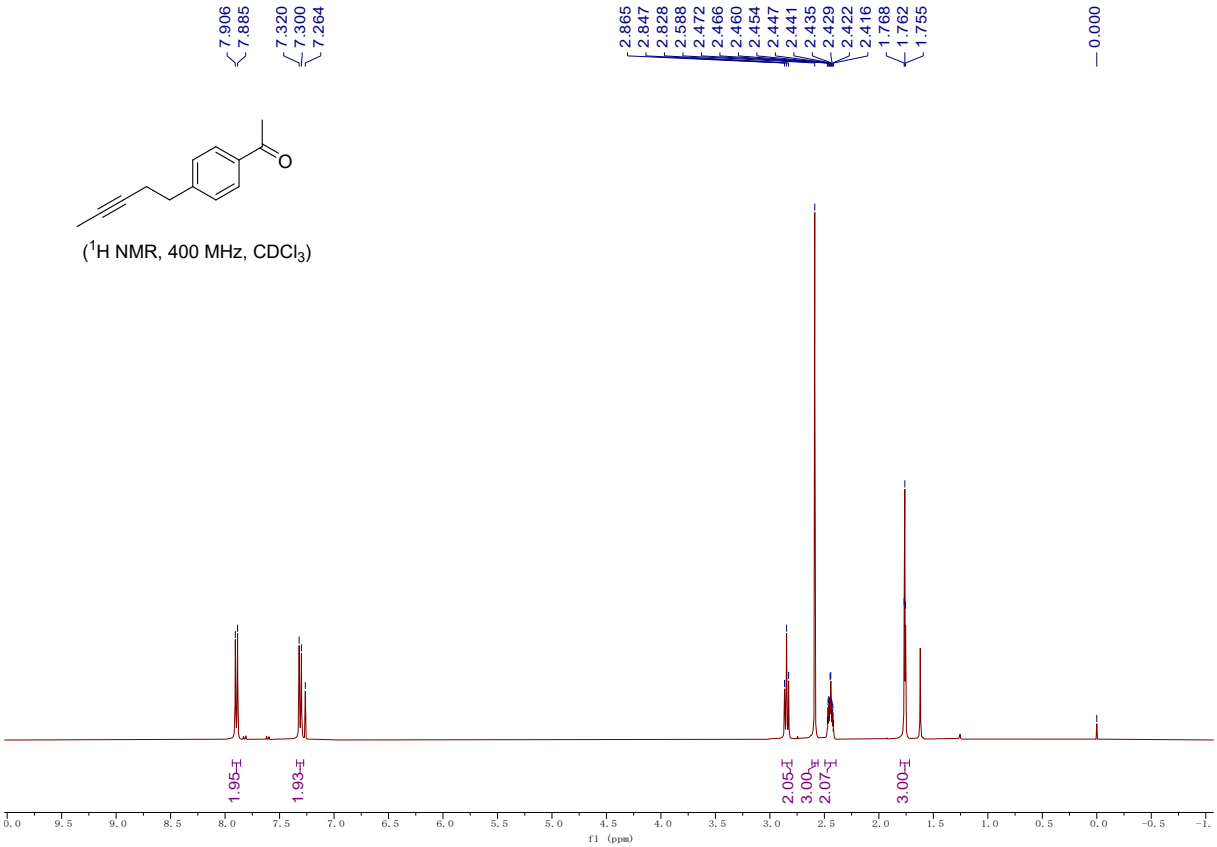


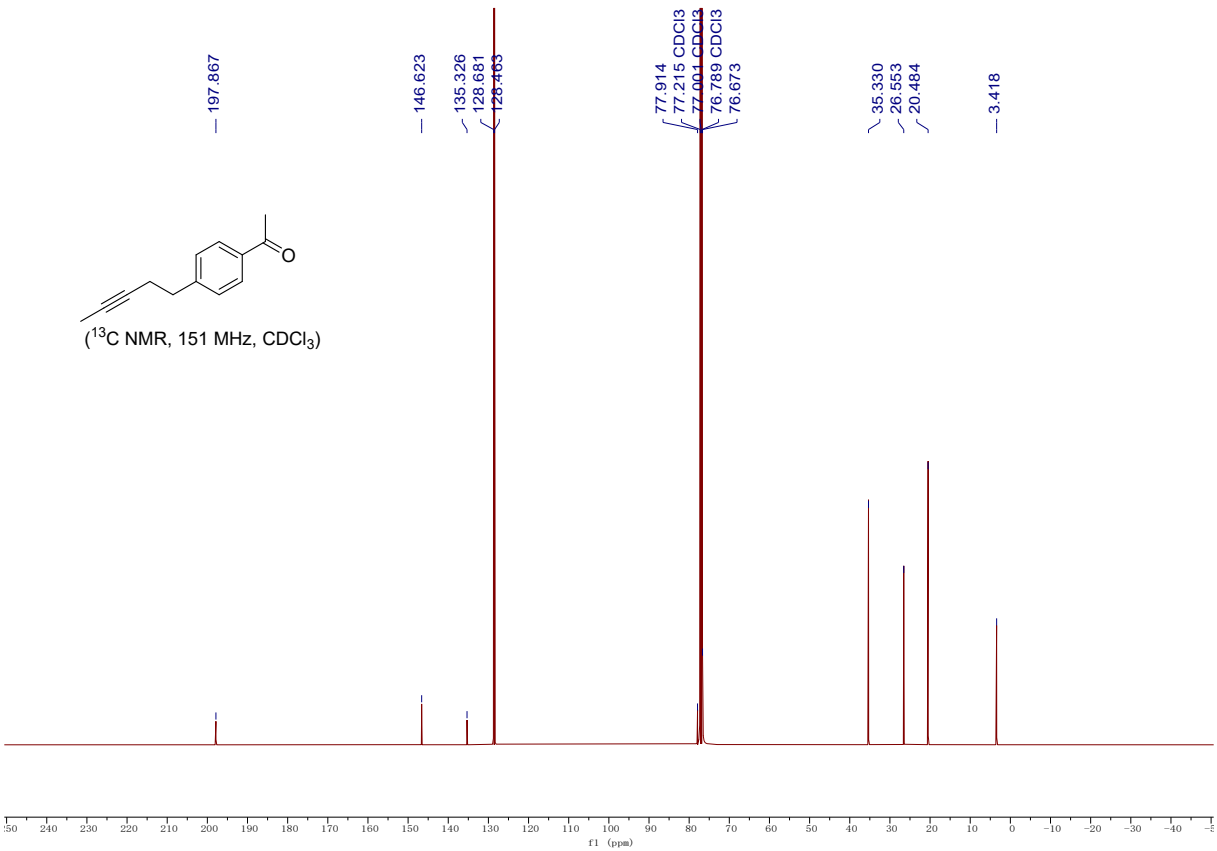
(^{1}H NMR, 400 MHz, $CDCl_3$)

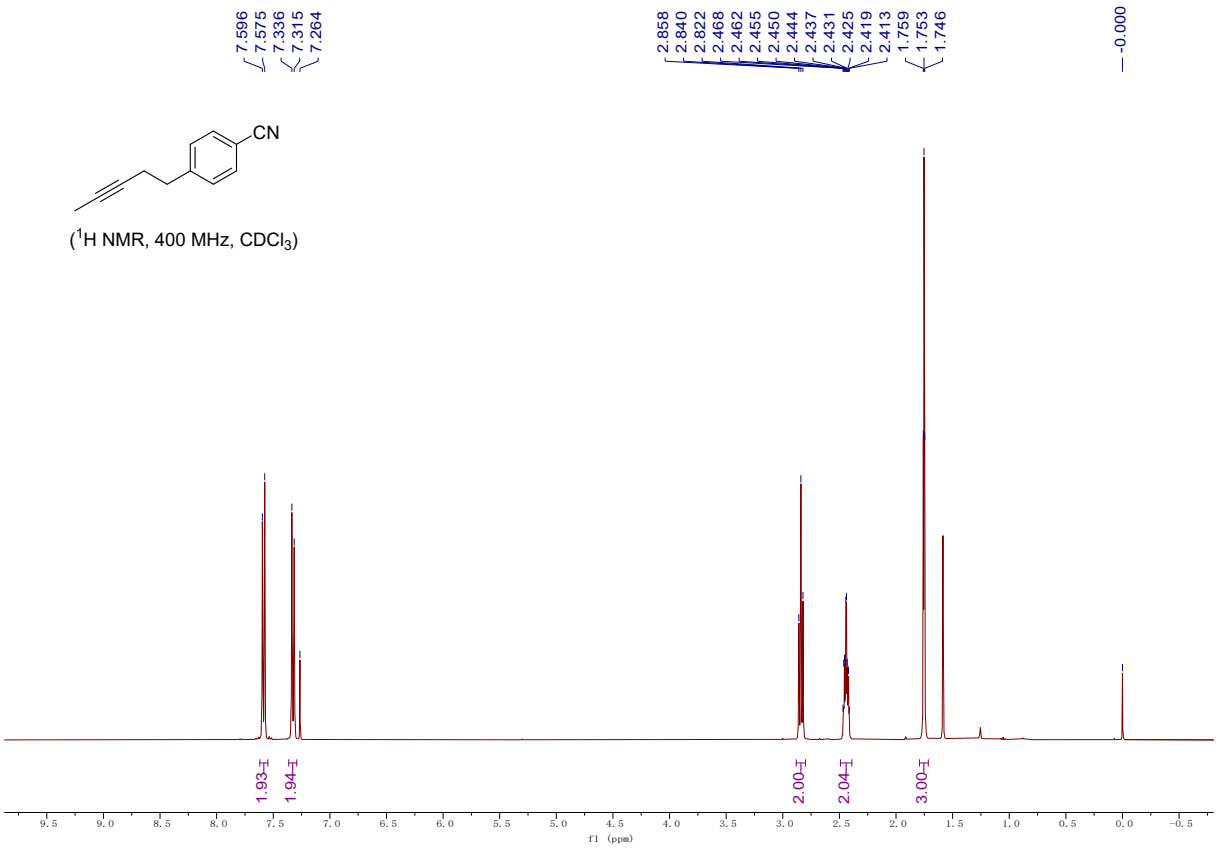




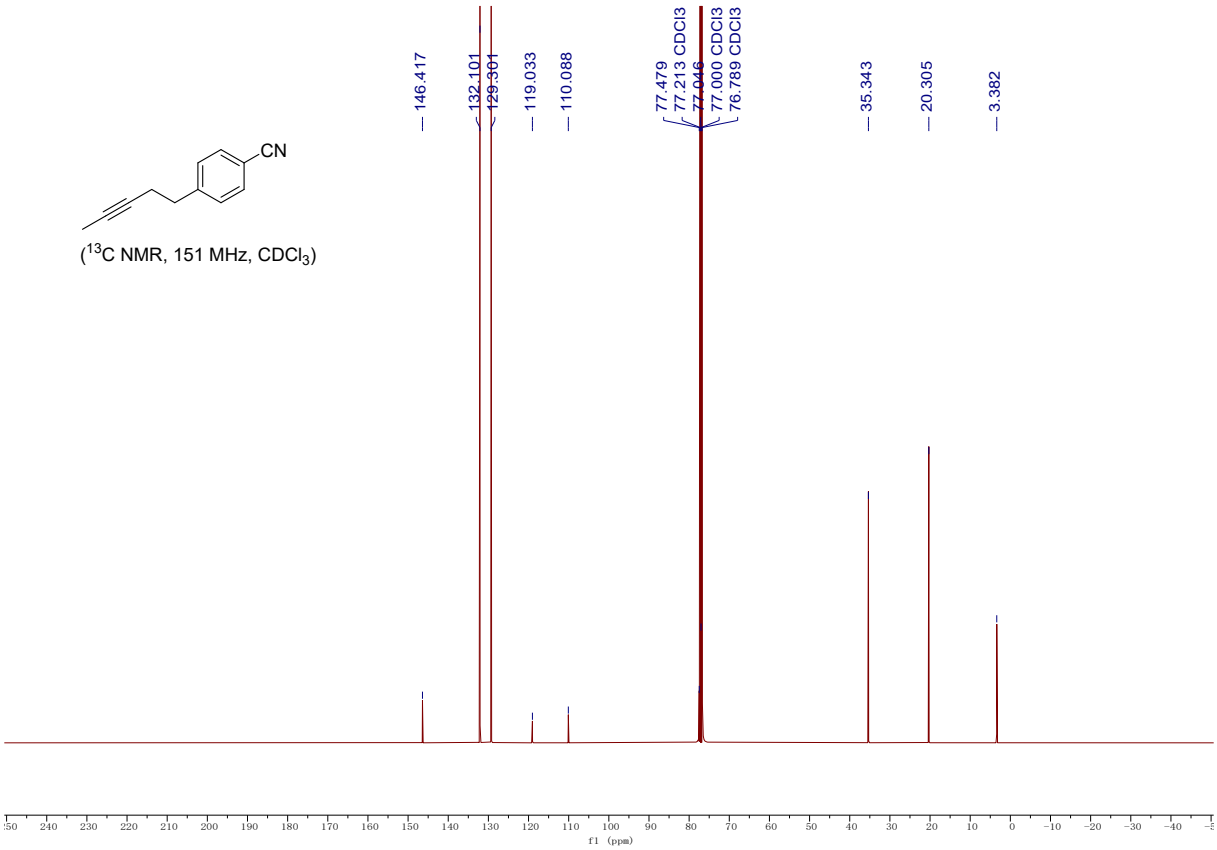
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.906
7.885
7.320
7.300
7.264
2.865
2.847
2.828
2.588
2.472
2.466
2.460
2.454
2.447
2.441
2.435
2.429
2.422
2.416
1.768
1.762
1.755
0.000
O
(1H NMR, 400 MHz, CDCl3)
1.95
1.93
2.05
3.00
2.07
3.00
f1 (ppm)

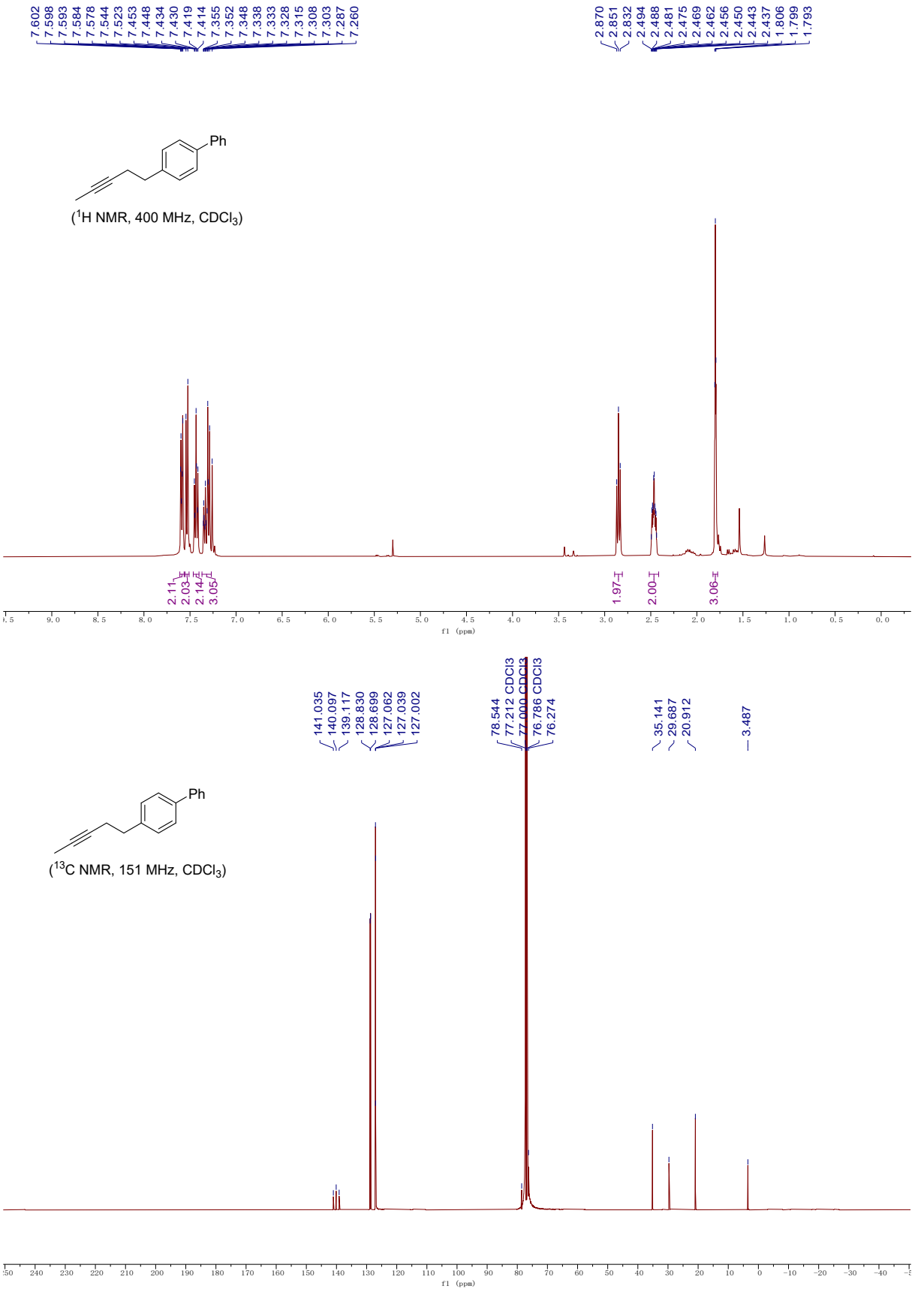

197.867
146.623
135.326
128.681
128.463
77.914
77.215 CDCl3
77.001 CDCl3
76.789 CDCl3
76.673
35.330
26.553
20.484
3.418
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



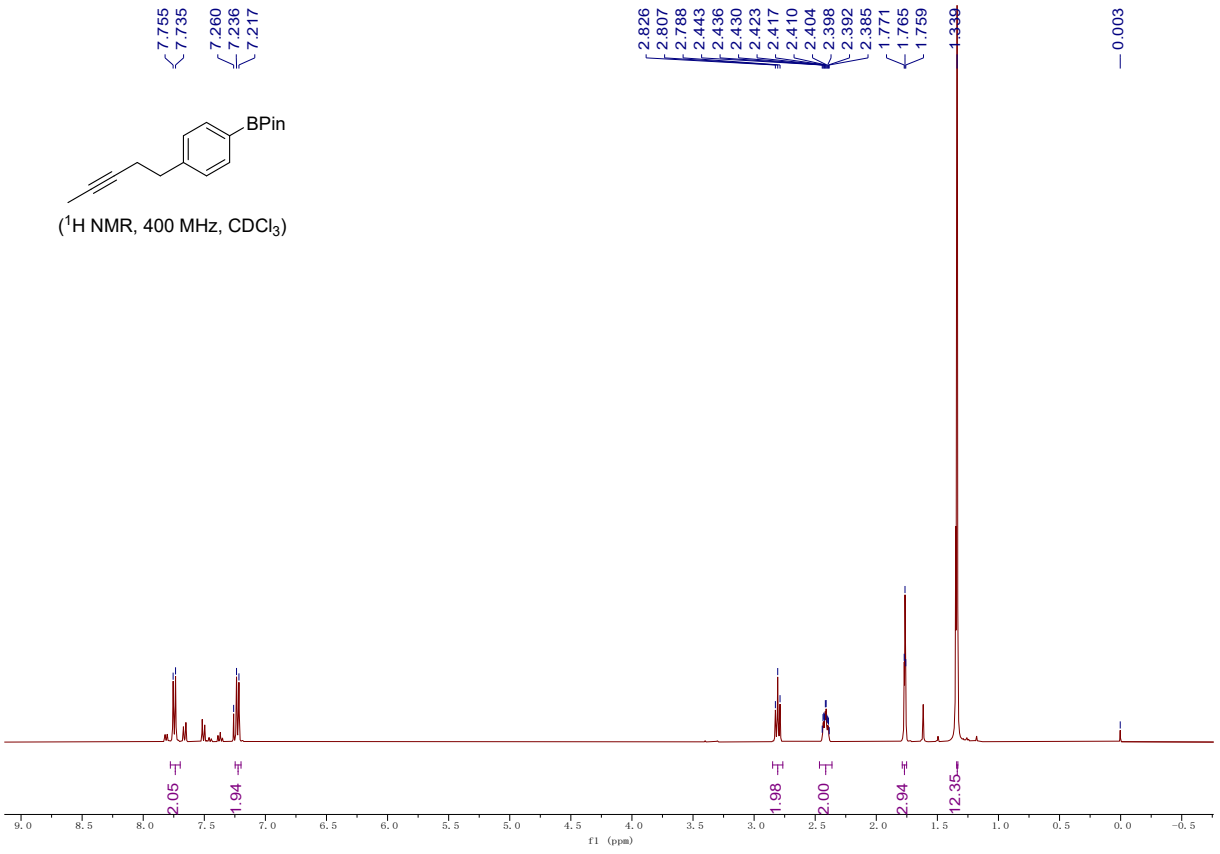
(^{1}H NMR, 400 MHz, $CDCl_3$)



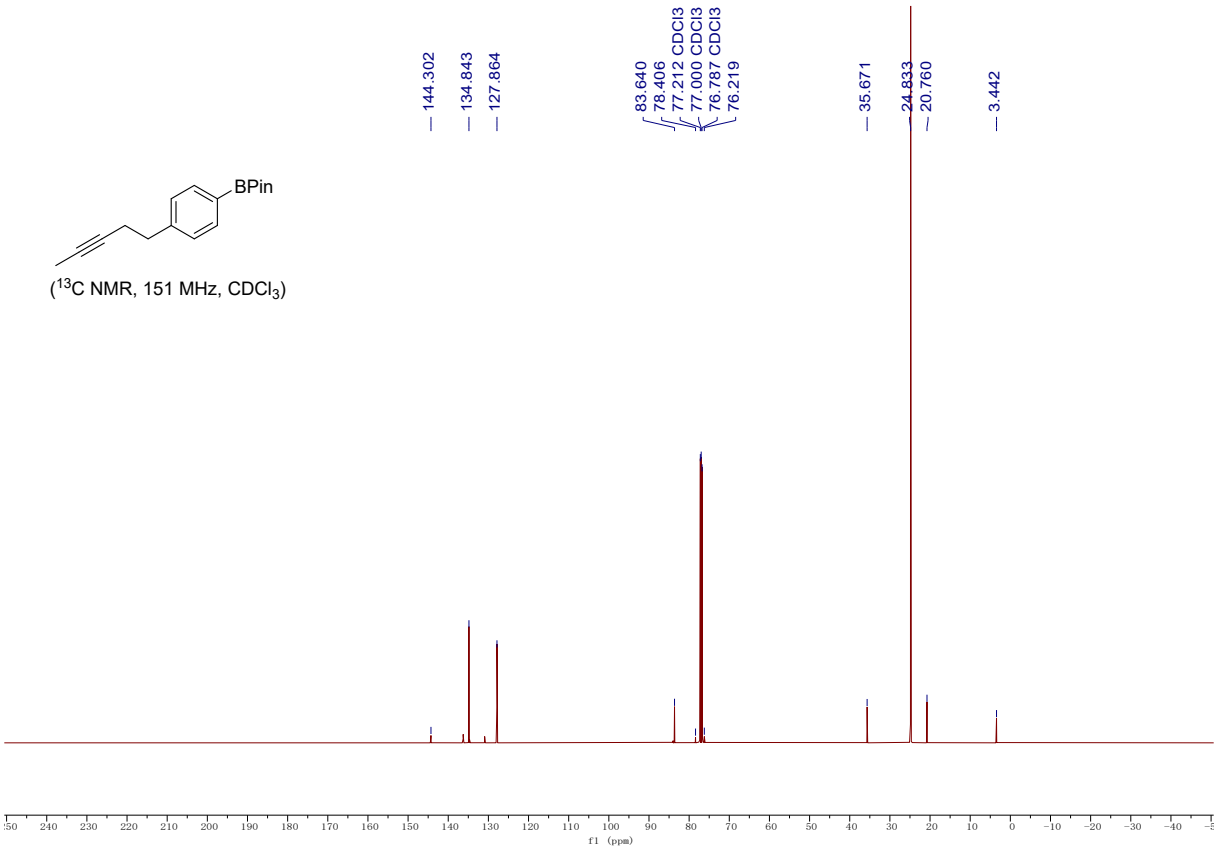
(^{13}C NMR, 151 MHz, $CDCl_3$)



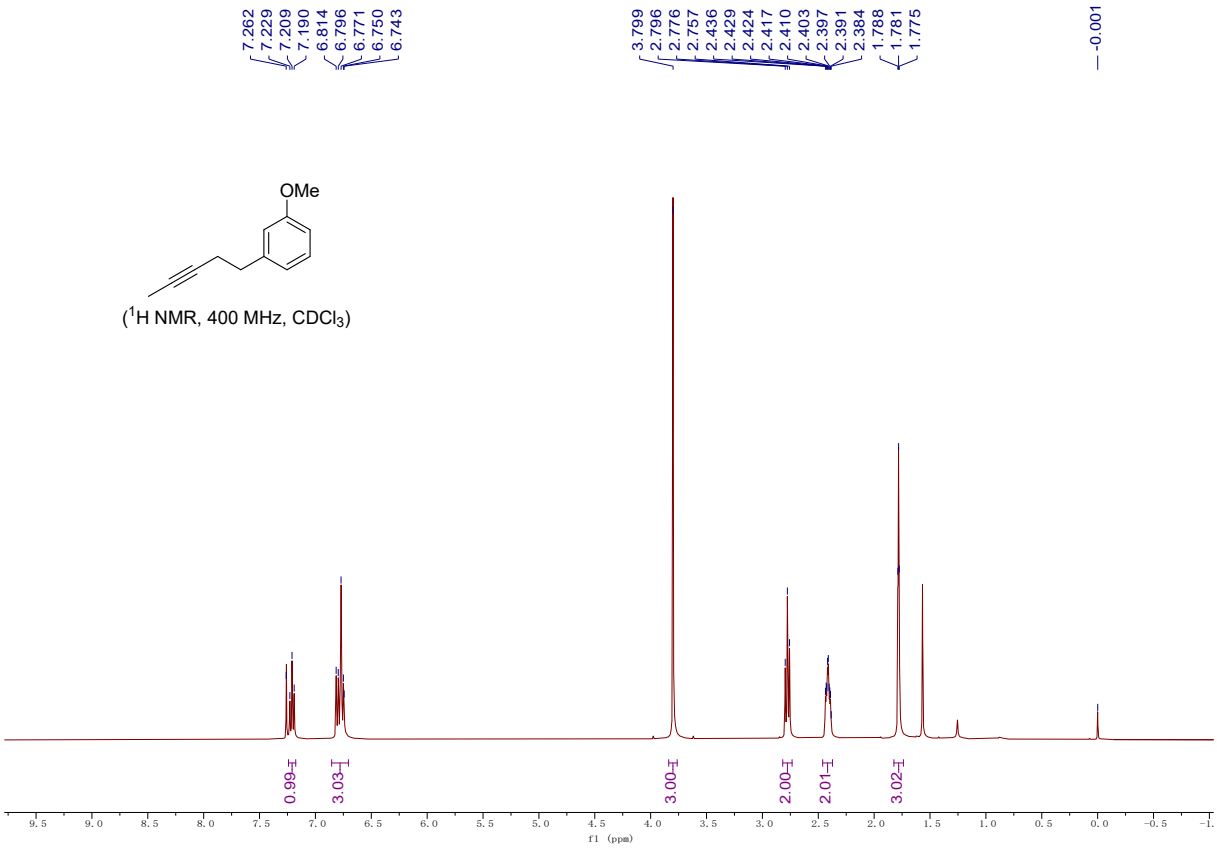
Containing a trace amount of impurity that failed to be separated.

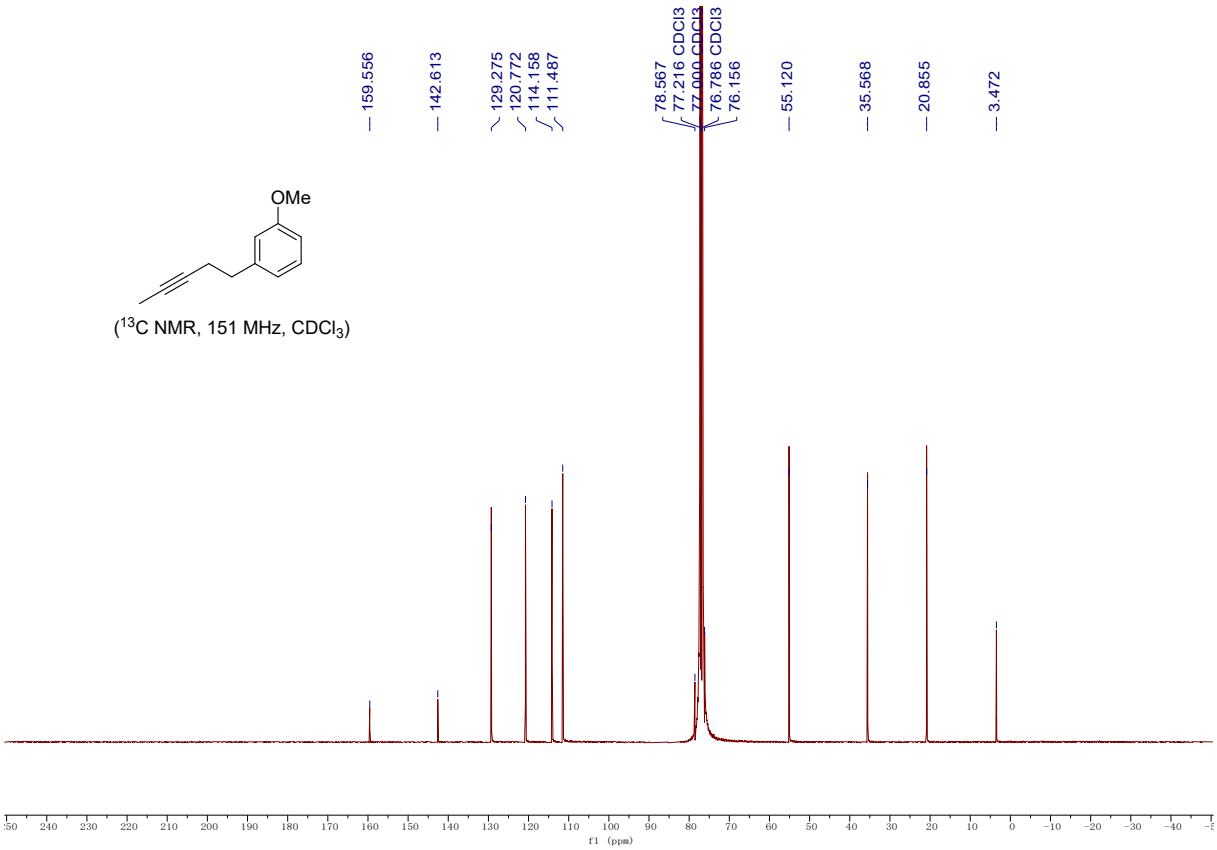


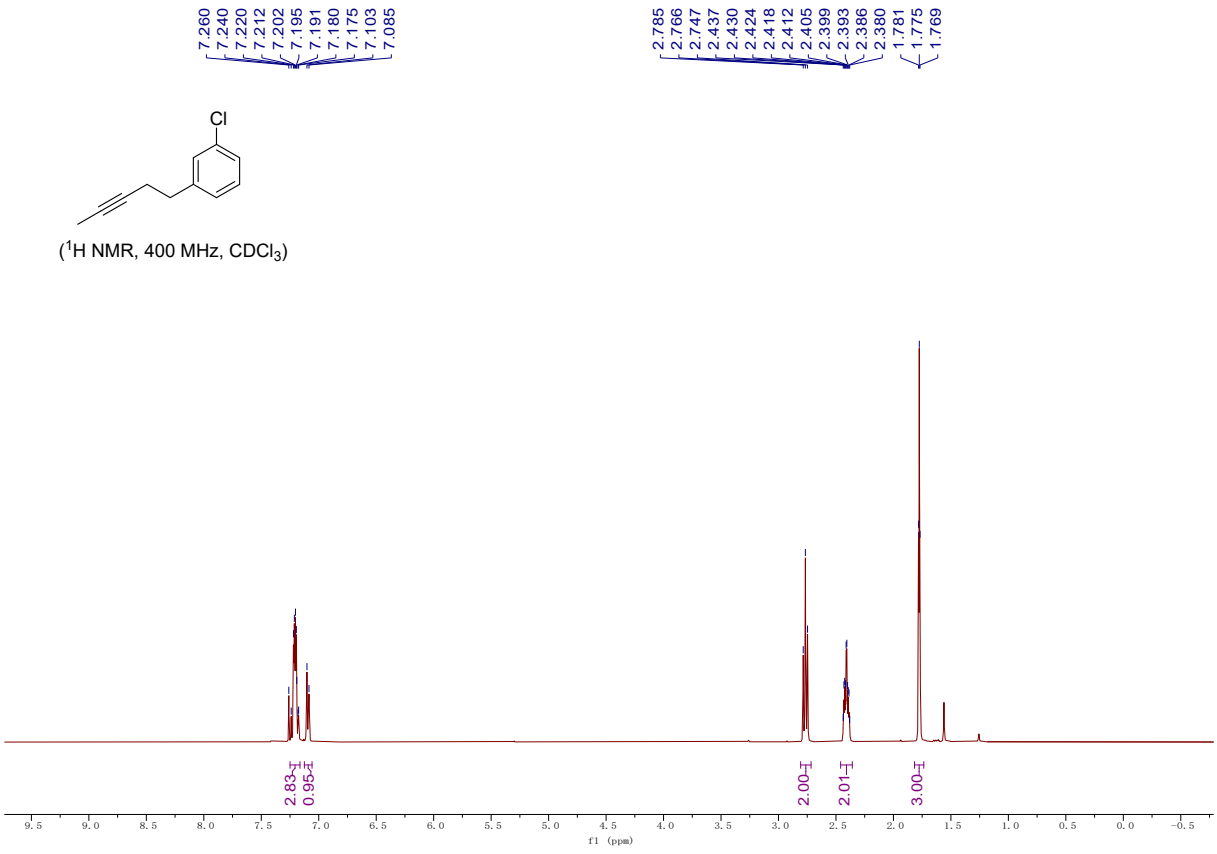
(^{1}H NMR, 400 MHz, $CDCl_3$)



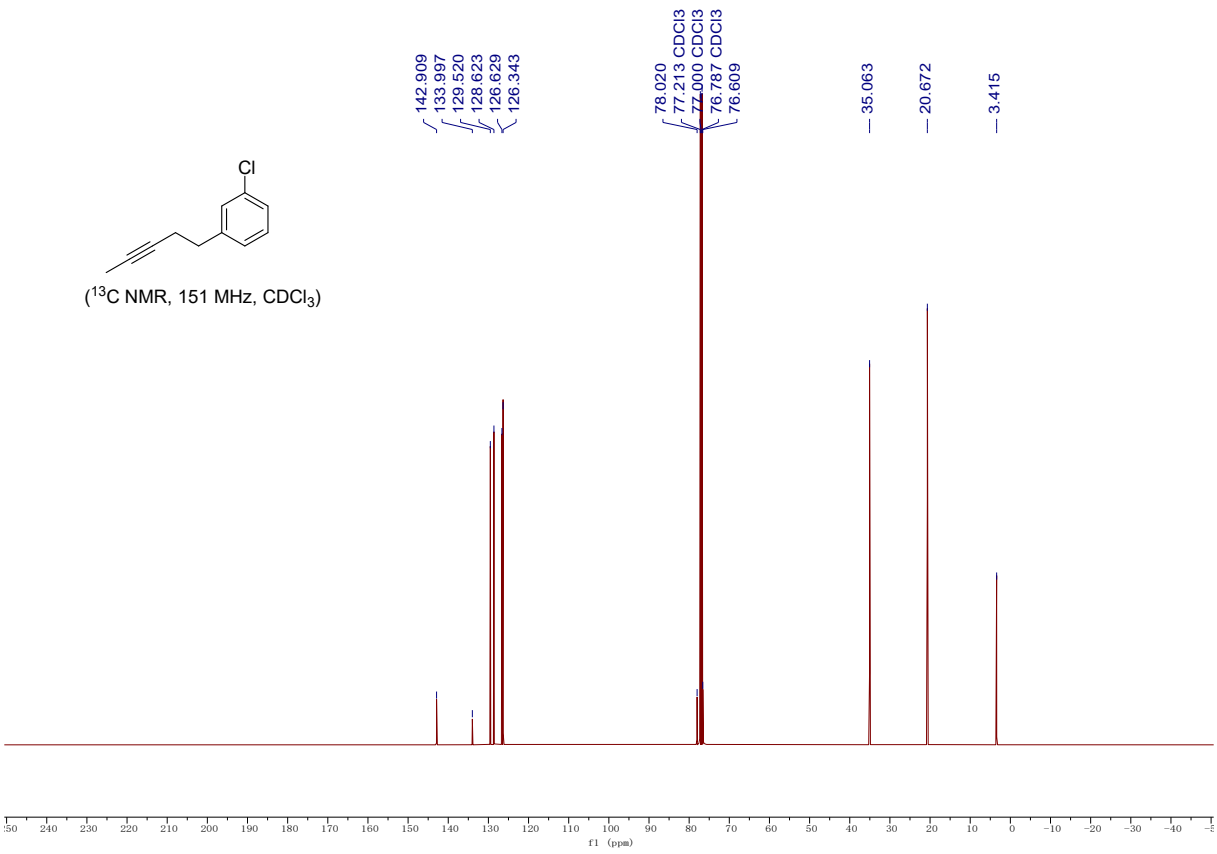
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.262
7.229
7.209
7.190
6.814
6.796
6.771
6.750
6.743
3.799
2.796
2.776
2.757
2.436
2.429
2.424
2.417
2.410
2.403
2.397
2.391
2.384
1.788
1.781
1.775
-0.001
OMe
(1H NMR, 400 MHz, CDCl3)
0.99
3.03
3.00
2.00
2.01
3.02
f1 (ppm)

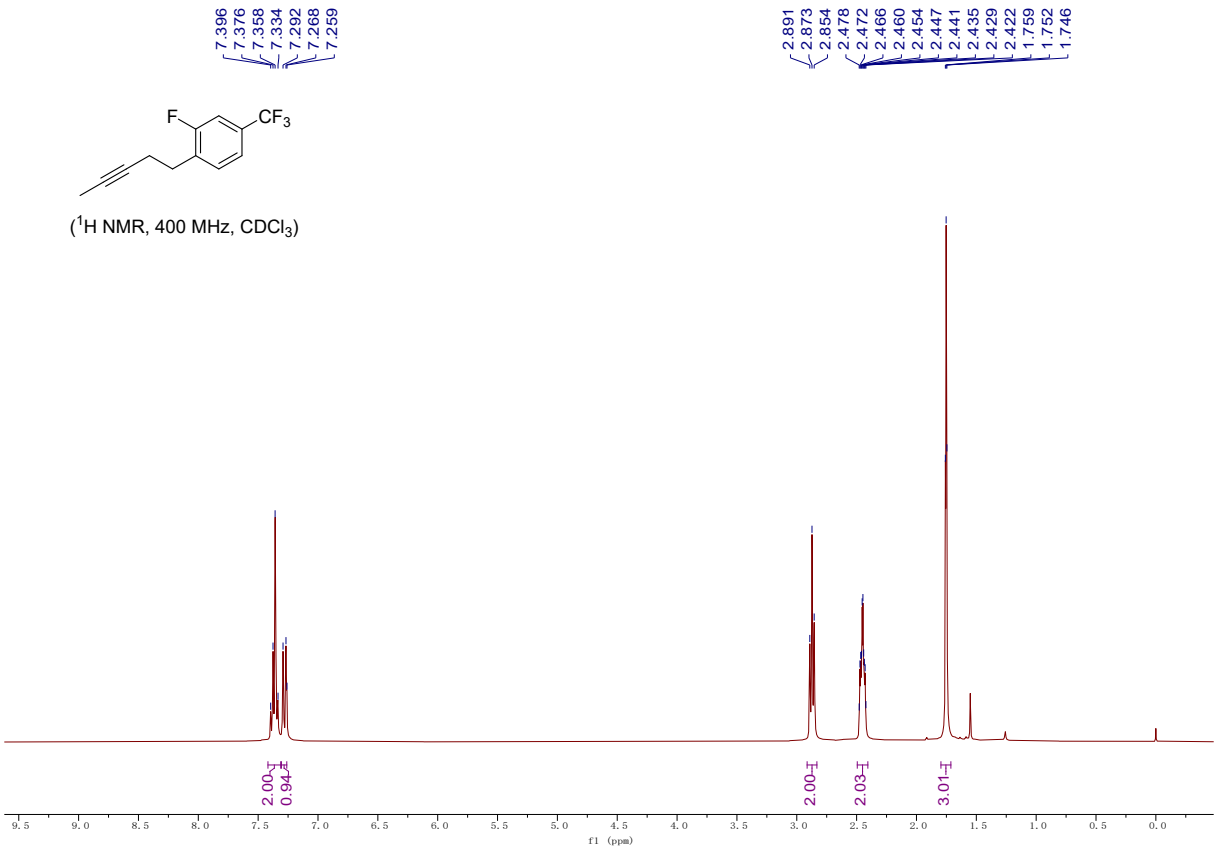

159.556
142.613
129.275
120.772
114.158
111.487
78.567
77.216 CDCl3
77.000 CDCl3
76.786 CDCl3
76.156
55.120
35.568
20.855
3.472
OMe
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



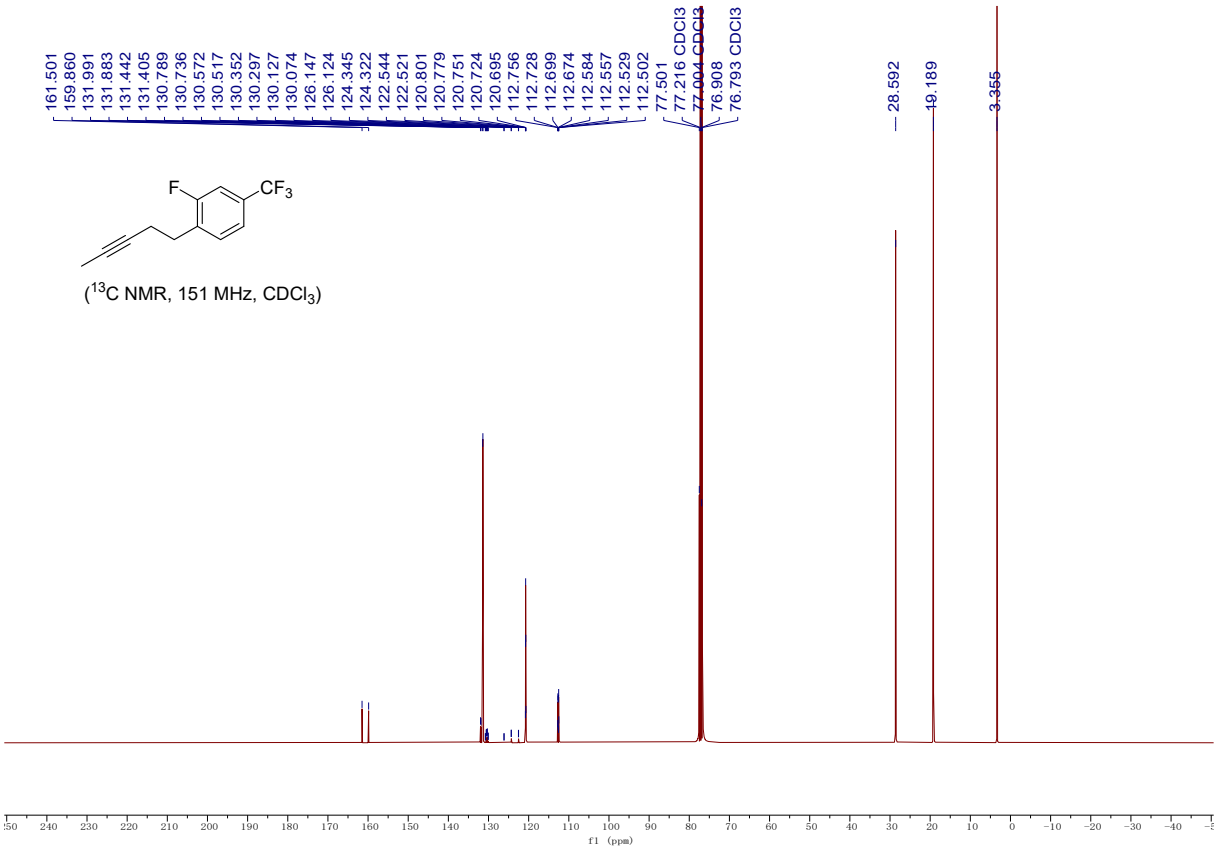
(^{1}H NMR, 400 MHz, $CDCl_3$)



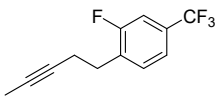
(^{13}C NMR, 151 MHz, $CDCl_3$)



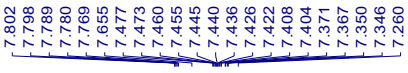
(^{1}H NMR, 400 MHz, $CDCl_3$)

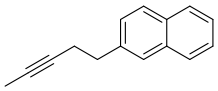


(^{13}C NMR, 151 MHz, $CDCl_3$)

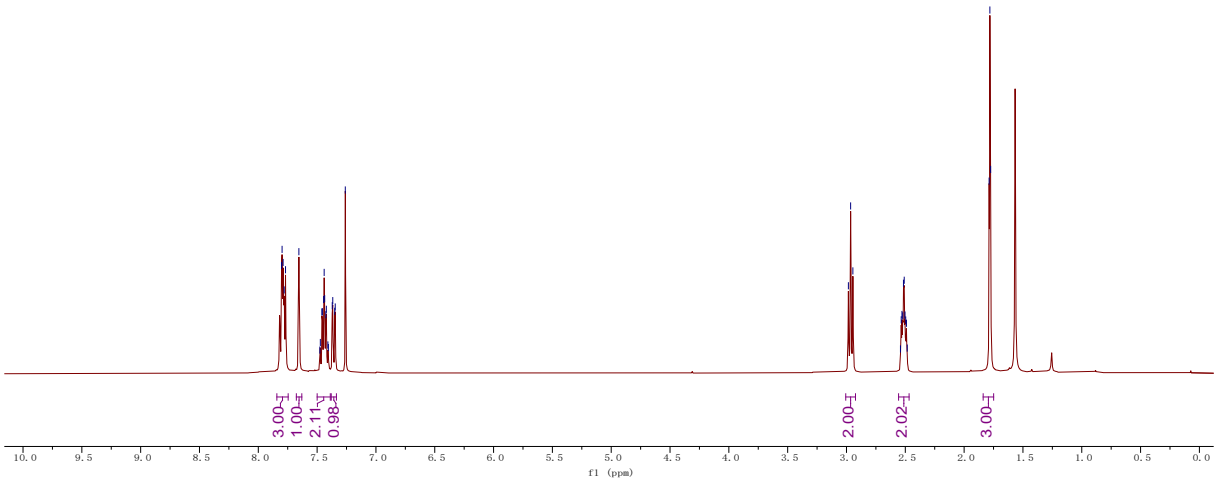


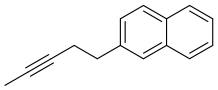
(^{19}F NMR, 565 MHz, $CDCl_3$)



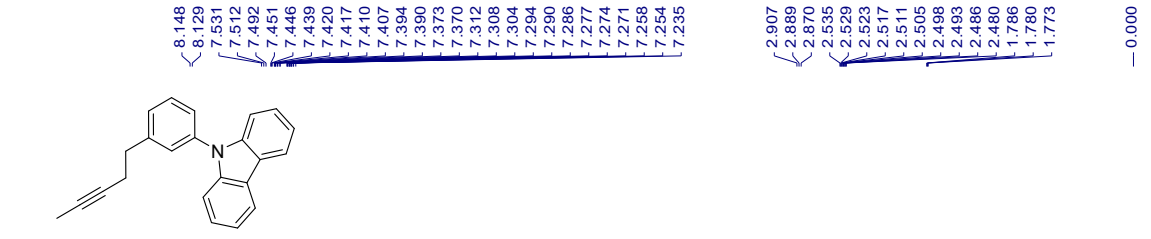


(^{1}H NMR, 400 MHz, $CDCl_3$)

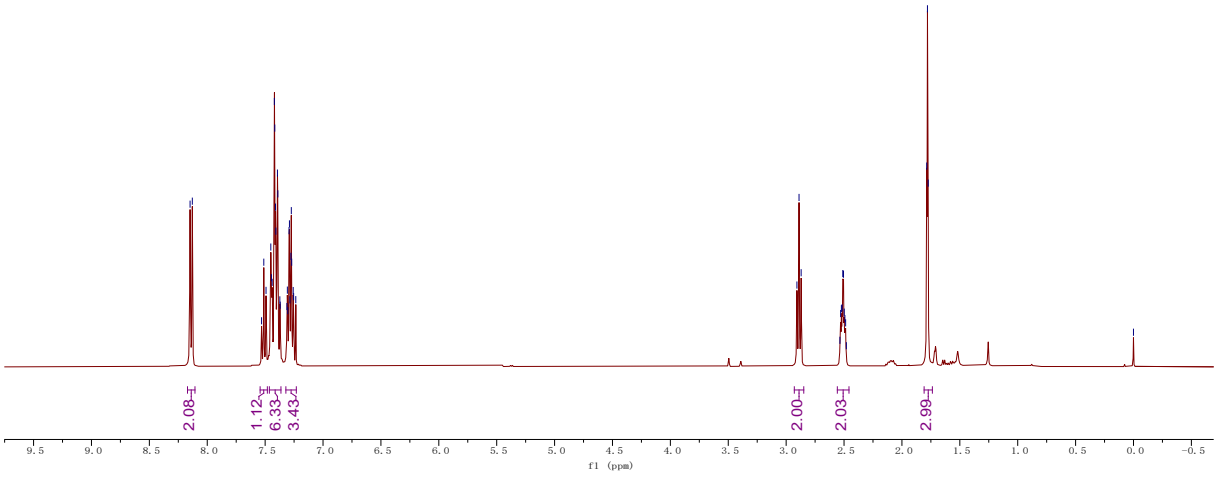


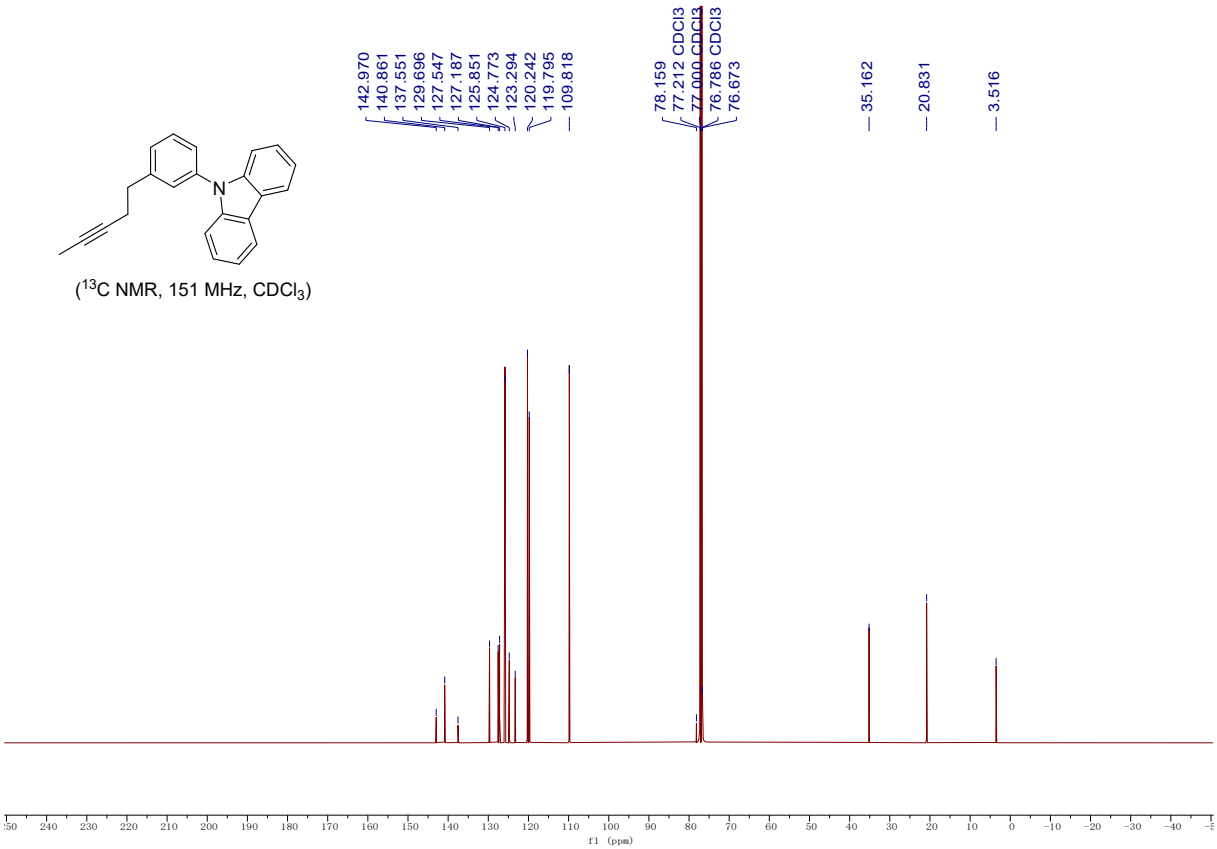


(^{13}C NMR, 151 MHz, $CDCl_3$)

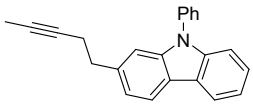


(^{1}H NMR, 400 MHz, $CDCl_3$)

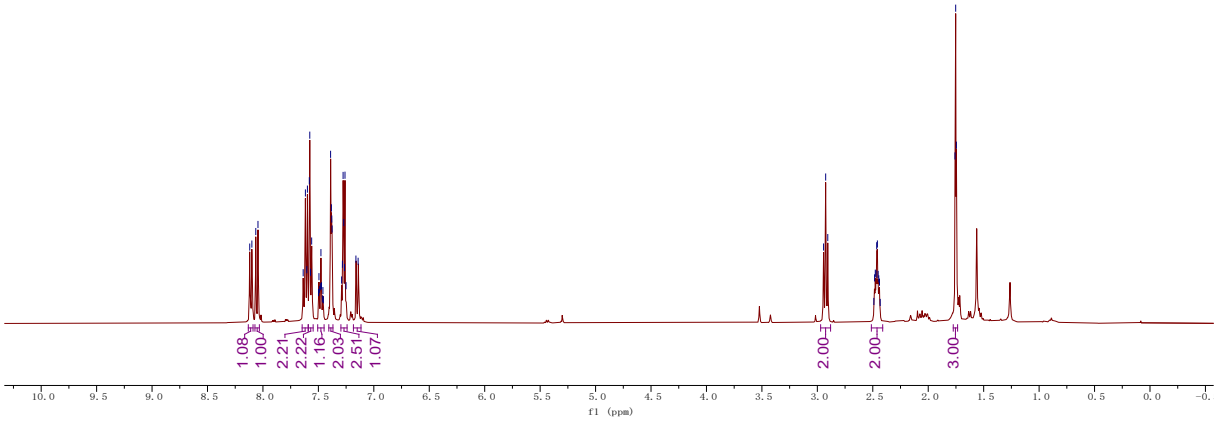


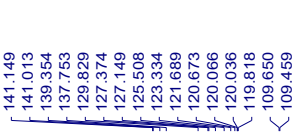


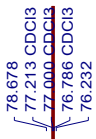
(^{13}C NMR, 151 MHz, $CDCl_3$)

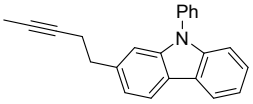


(^{1}H NMR, 400 MHz, $CDCl_3$)

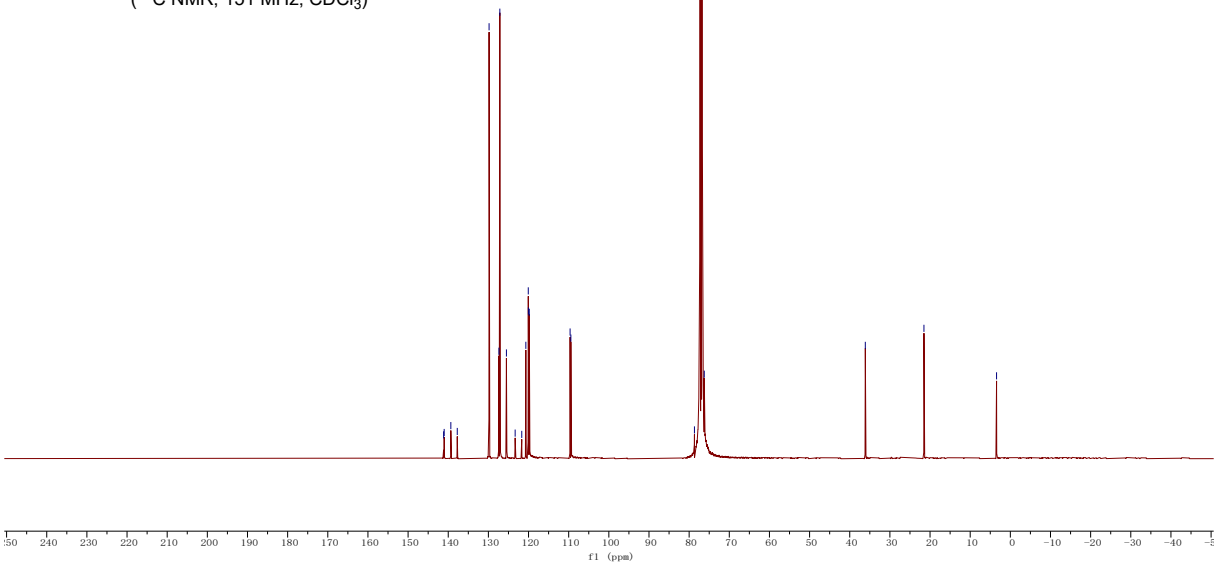


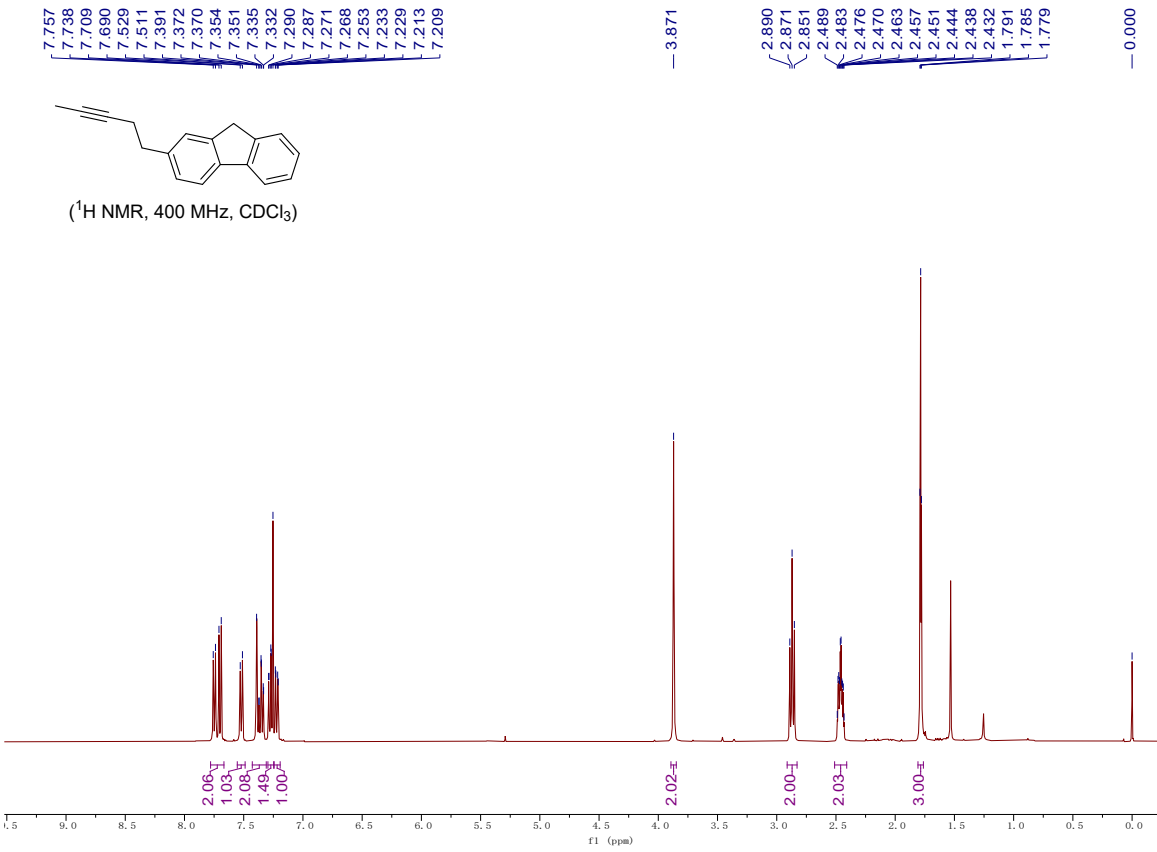




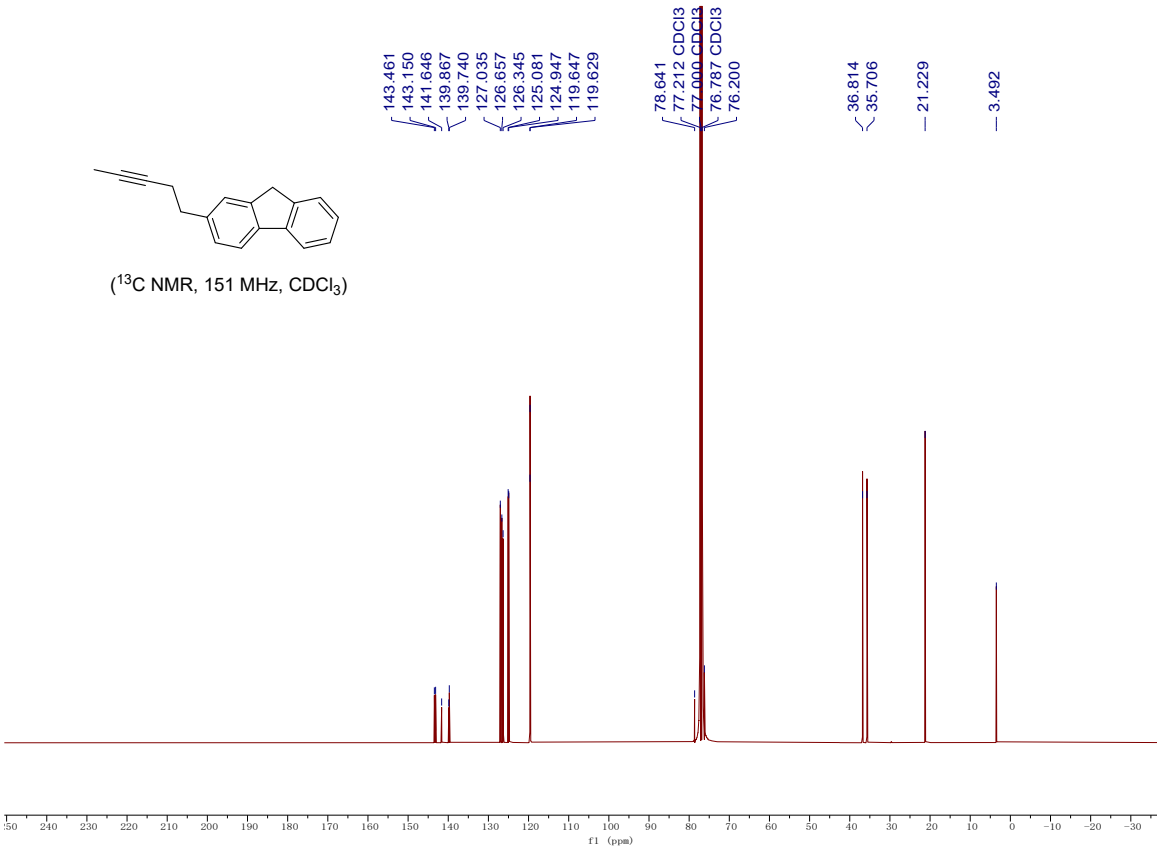


(^{13}C NMR, 151 MHz, $CDCl_3$)

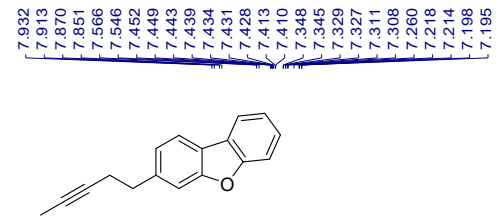




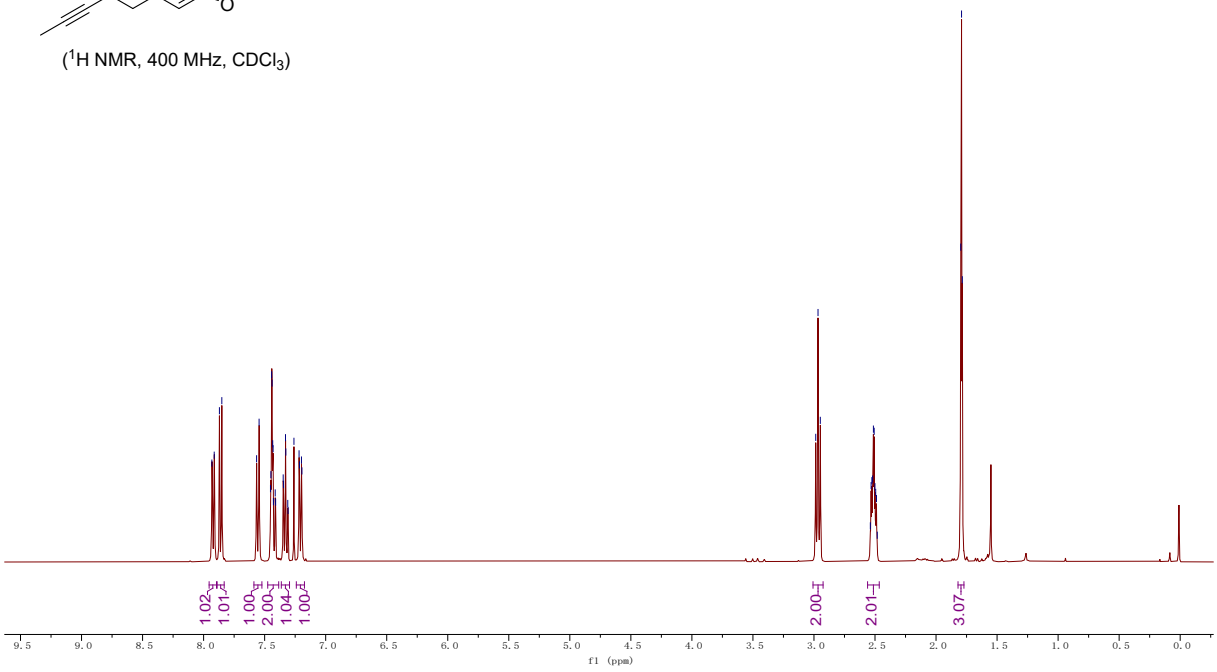
(^{1}H NMR, 400 MHz, $CDCl_3$)

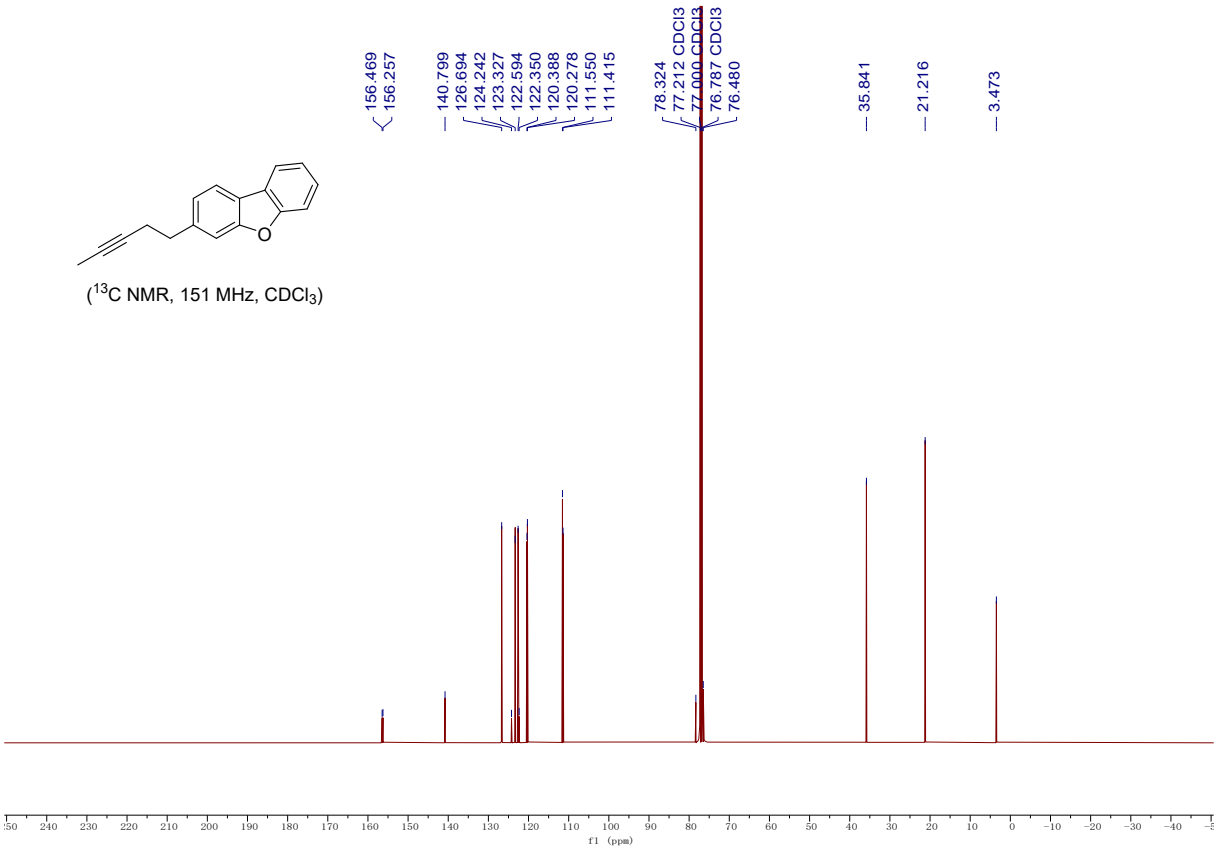


(^{13}C NMR, 151 MHz, $CDCl_3$)

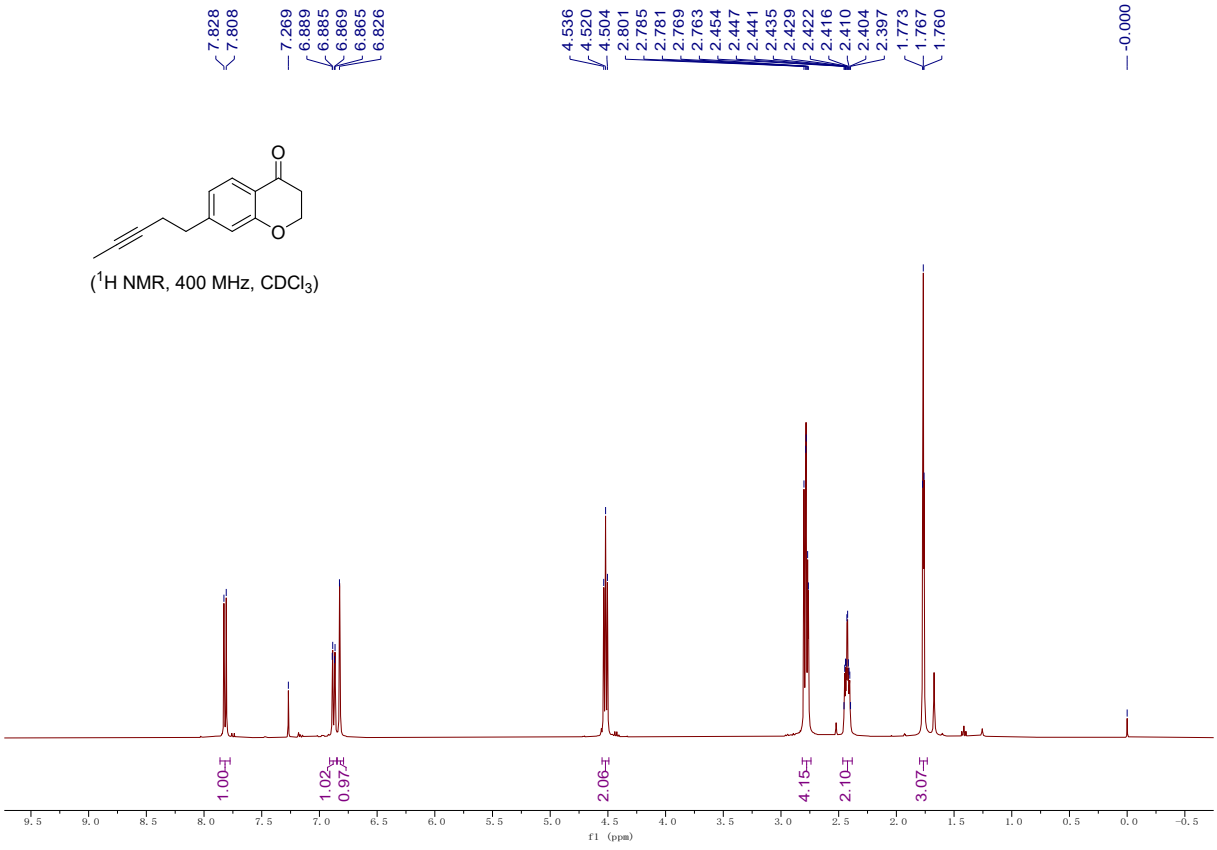


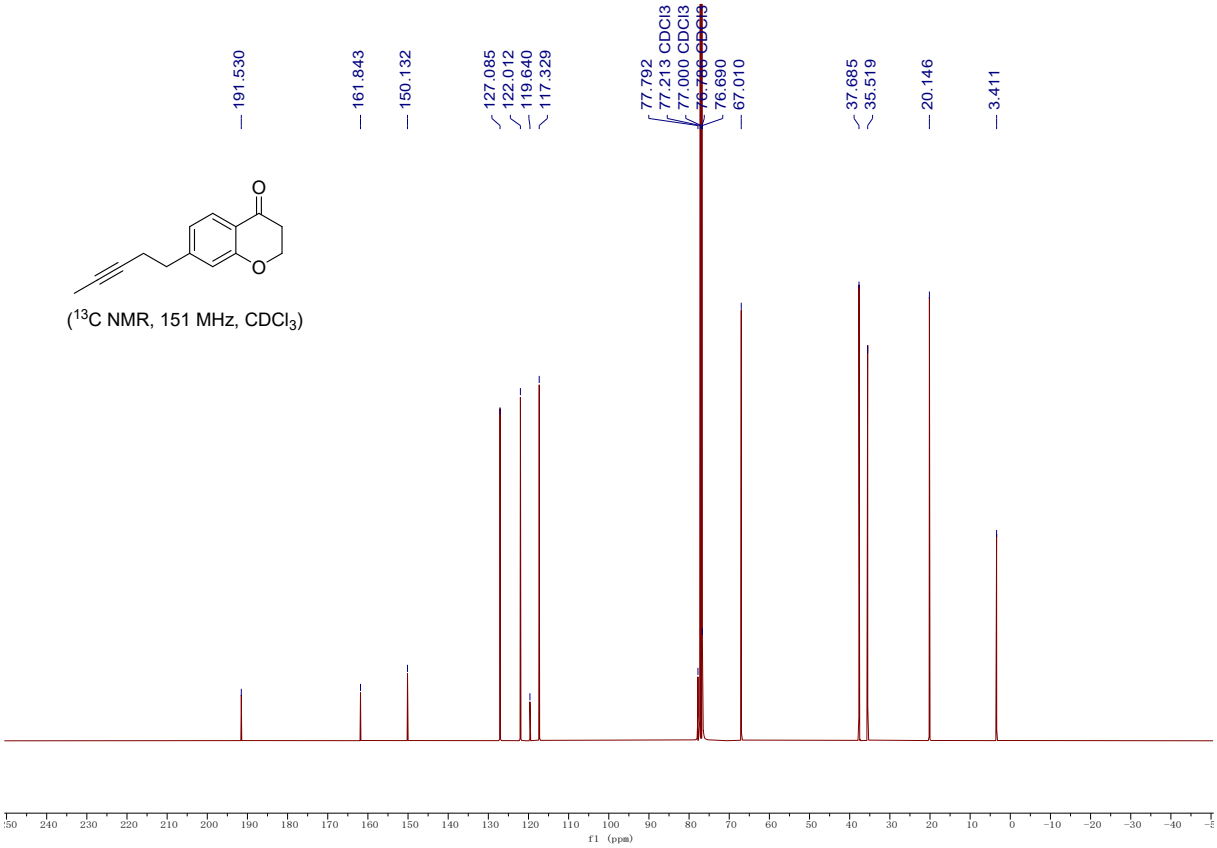
(^{1}H NMR, 400 MHz, $CDCl_3$)

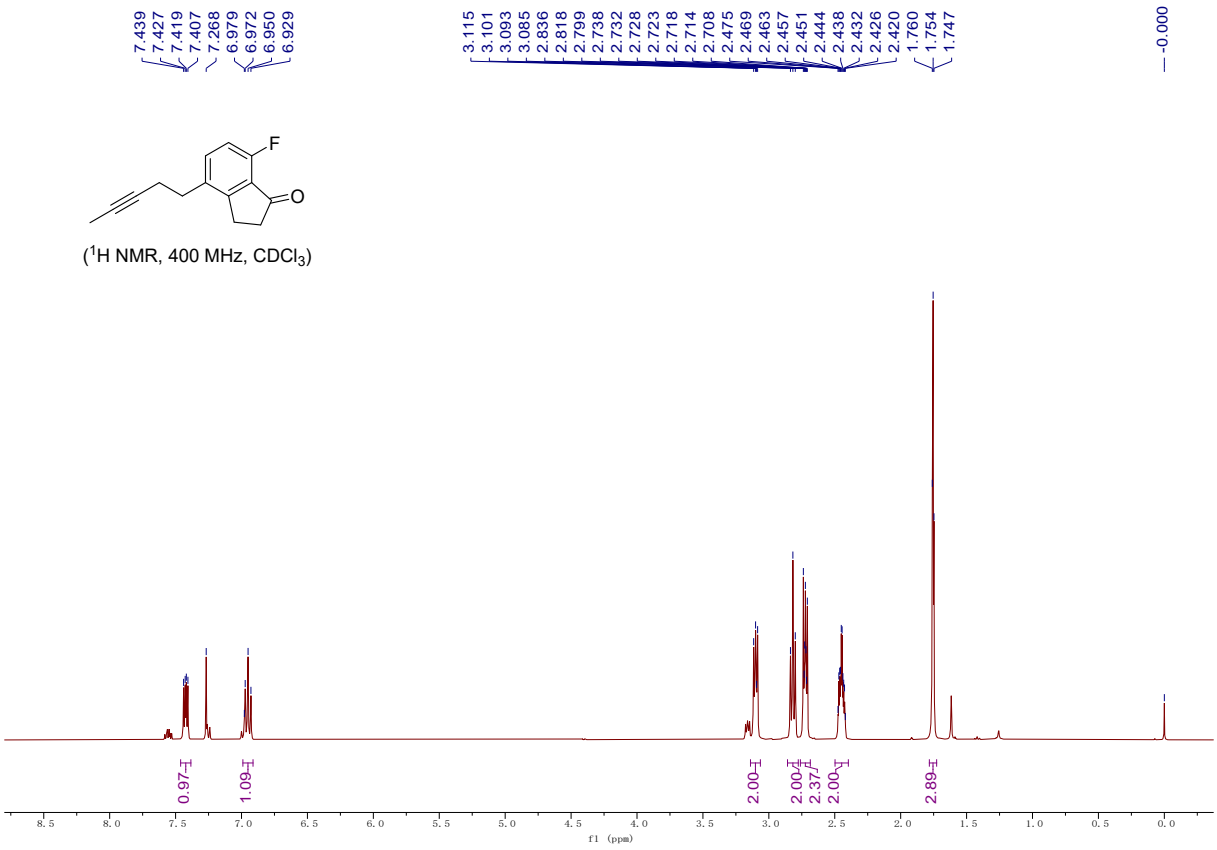




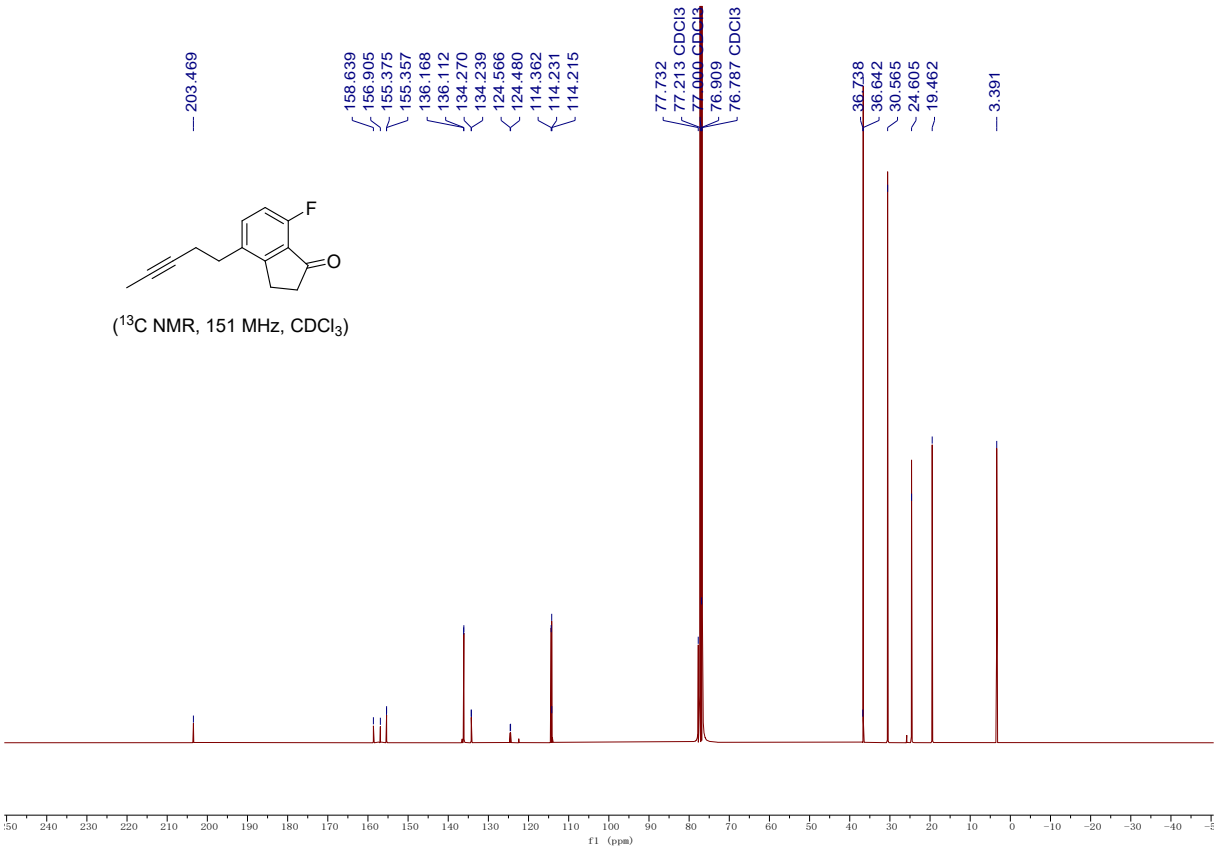
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.828
7.808
7.269
6.889
6.885
6.869
6.865
6.826
4.536
4.520
4.504
2.801
2.785
2.781
2.769
2.763
2.454
2.447
2.441
2.435
2.429
2.422
2.416
2.410
2.404
2.397
1.773
1.767
1.760
-0.000
O
O
(1H NMR, 400 MHz, CDCl3)
1.00
1.02
0.97
2.06
4.15
2.10
3.07
f1 (ppm)

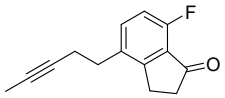

191.530
161.843
150.132
127.085
122.012
119.640
117.329
77.792
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
76.690
67.010
37.685
35.519
20.146
3.411
O
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



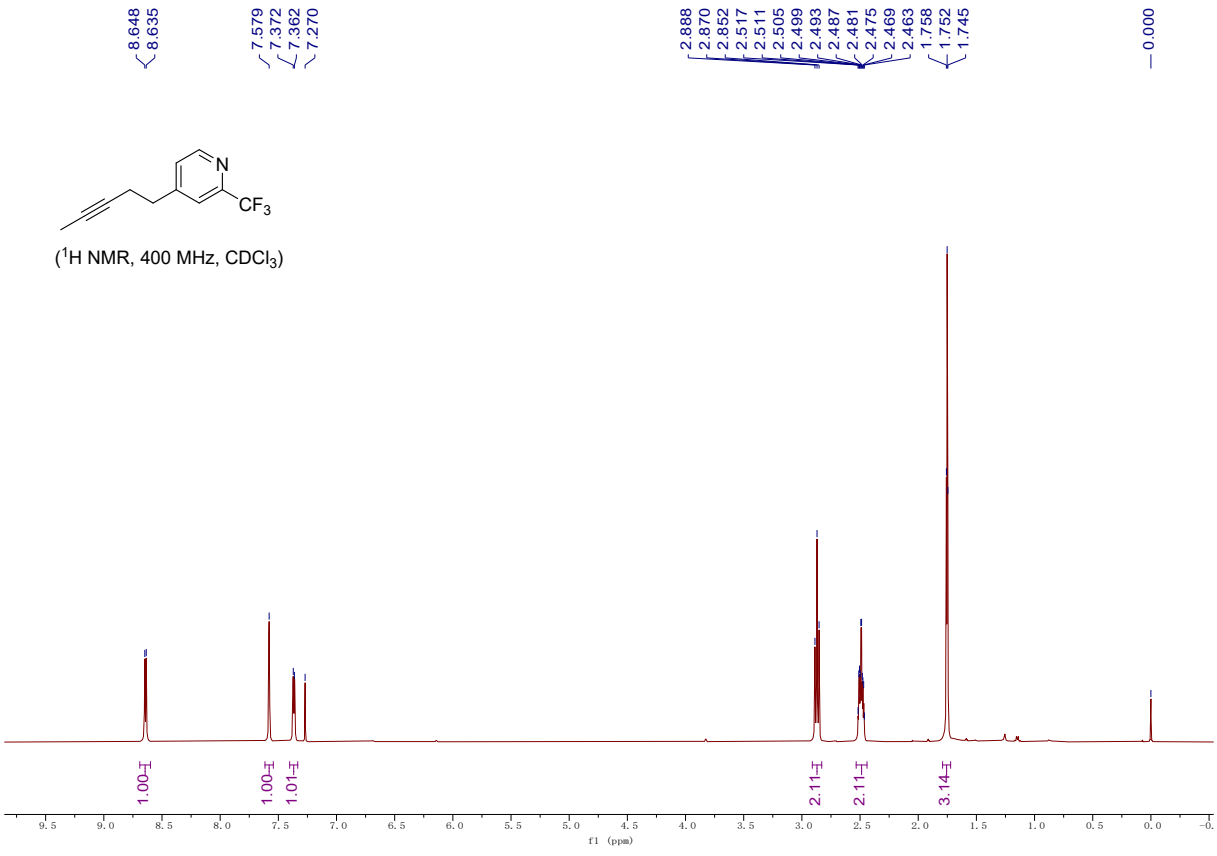
(^{1}H NMR, 400 MHz, $CDCl_3$)

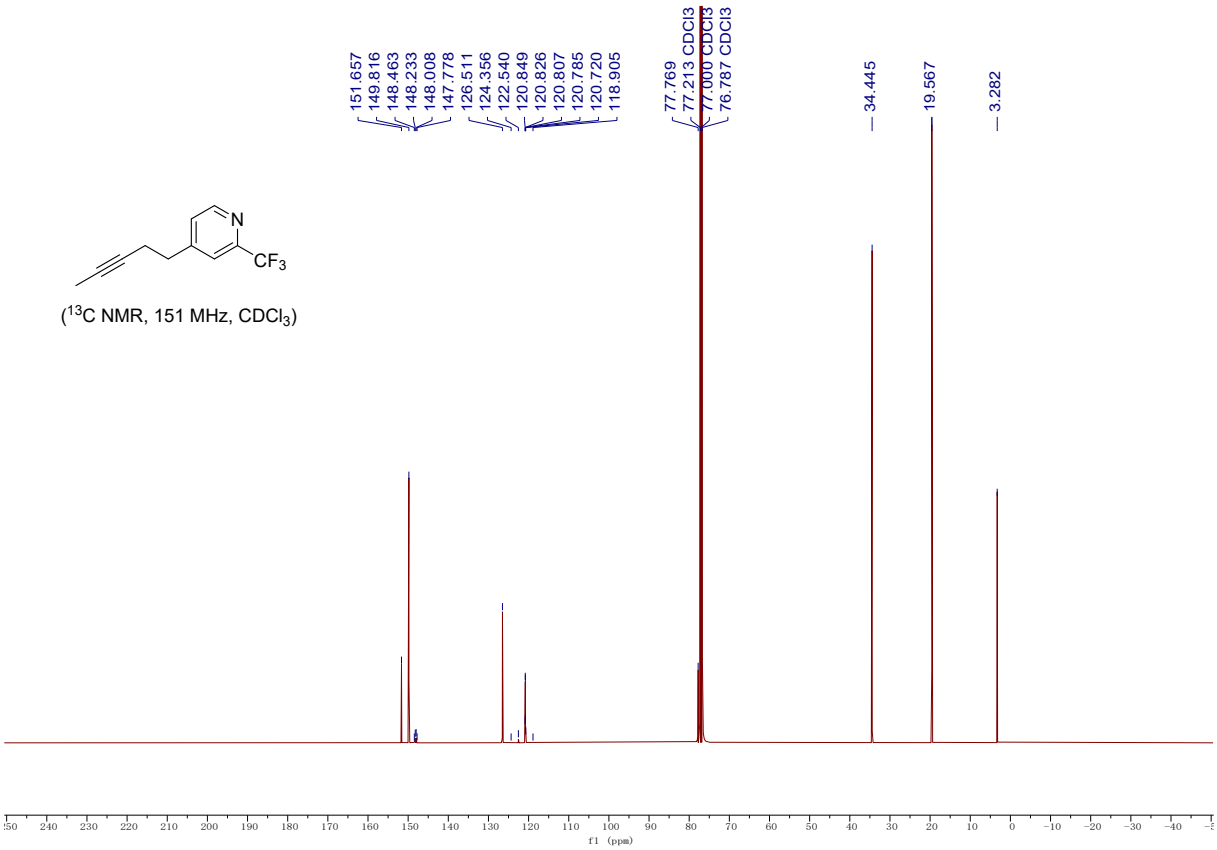


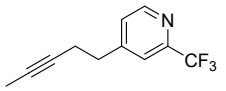
(^{13}C NMR, 151 MHz, $CDCl_3$)



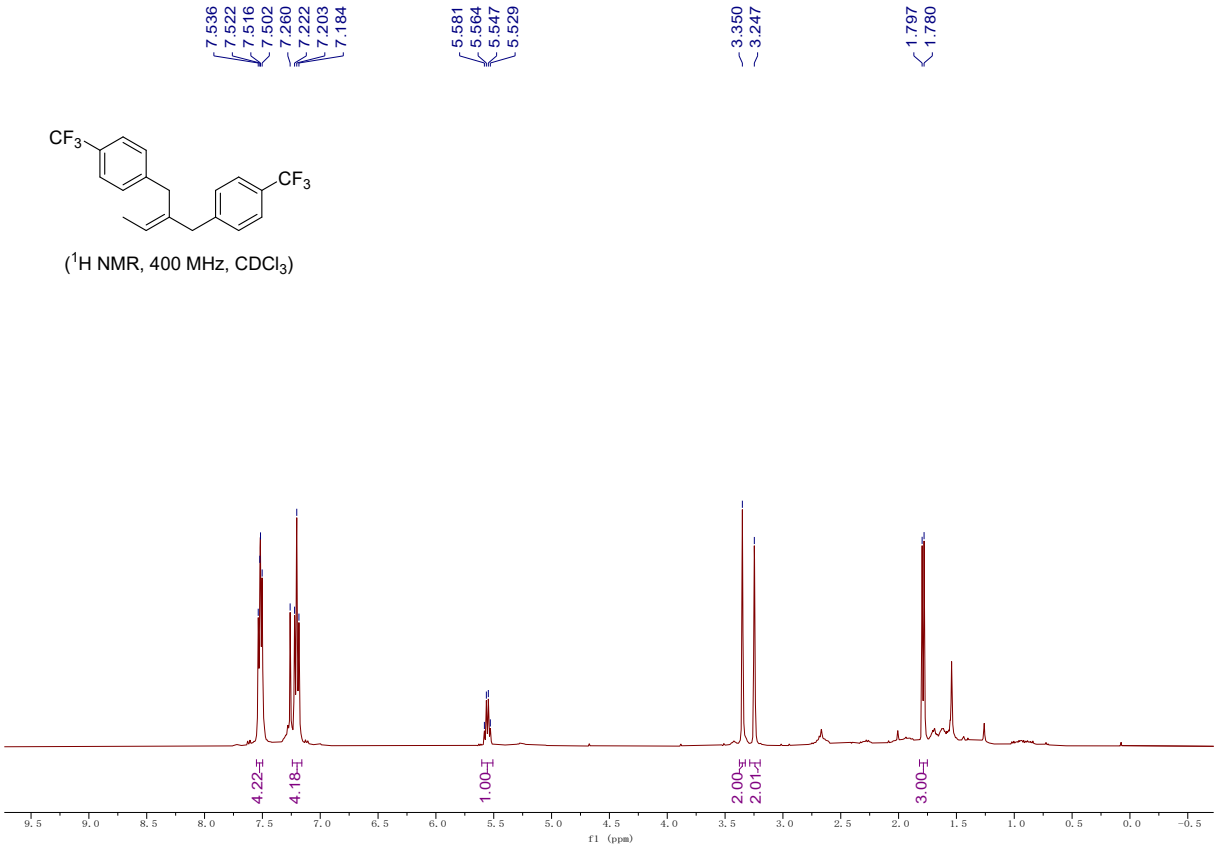
(^{19}F NMR, 565 MHz, $CDCl_3$)


8.648
8.635
7.579
7.372
7.362
7.270
2.888
2.870
2.852
2.517
2.511
2.505
2.499
2.493
2.487
2.481
2.475
2.469
2.463
1.758
1.752
1.745
0.000
N
CF3
(1H NMR, 400 MHz, CDCl3)
1.00
1.00
1.01
2.11
2.11
3.14
f1 (ppm)

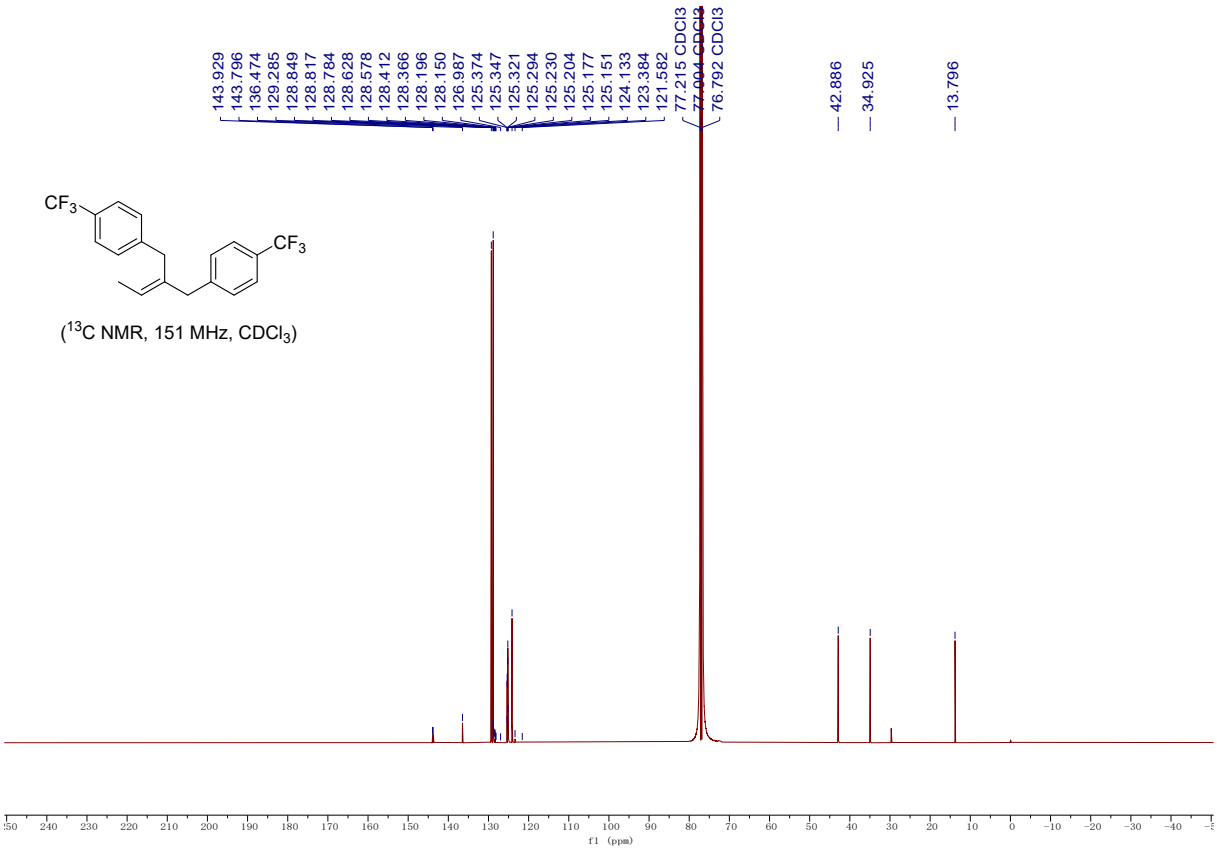

151.657
149.816
148.463
148.233
148.008
147.778
126.511
124.356
122.540
120.849
120.826
120.807
120.785
120.720
118.905
77.769
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
34.445
19.567
3.282
N
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



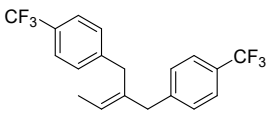
(^{19}F NMR, 565 MHz, $CDCl_3$)



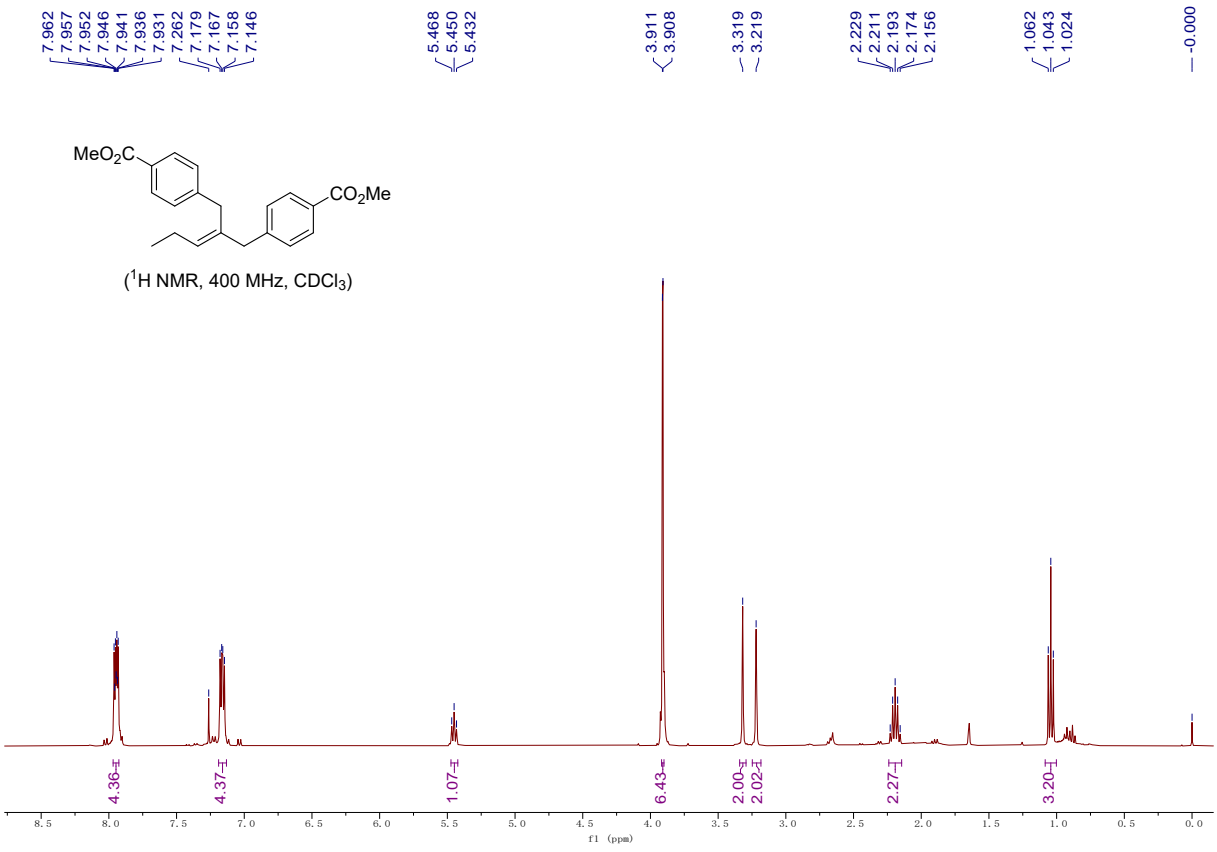
(^{1}H NMR, 400 MHz, $CDCl_3$)

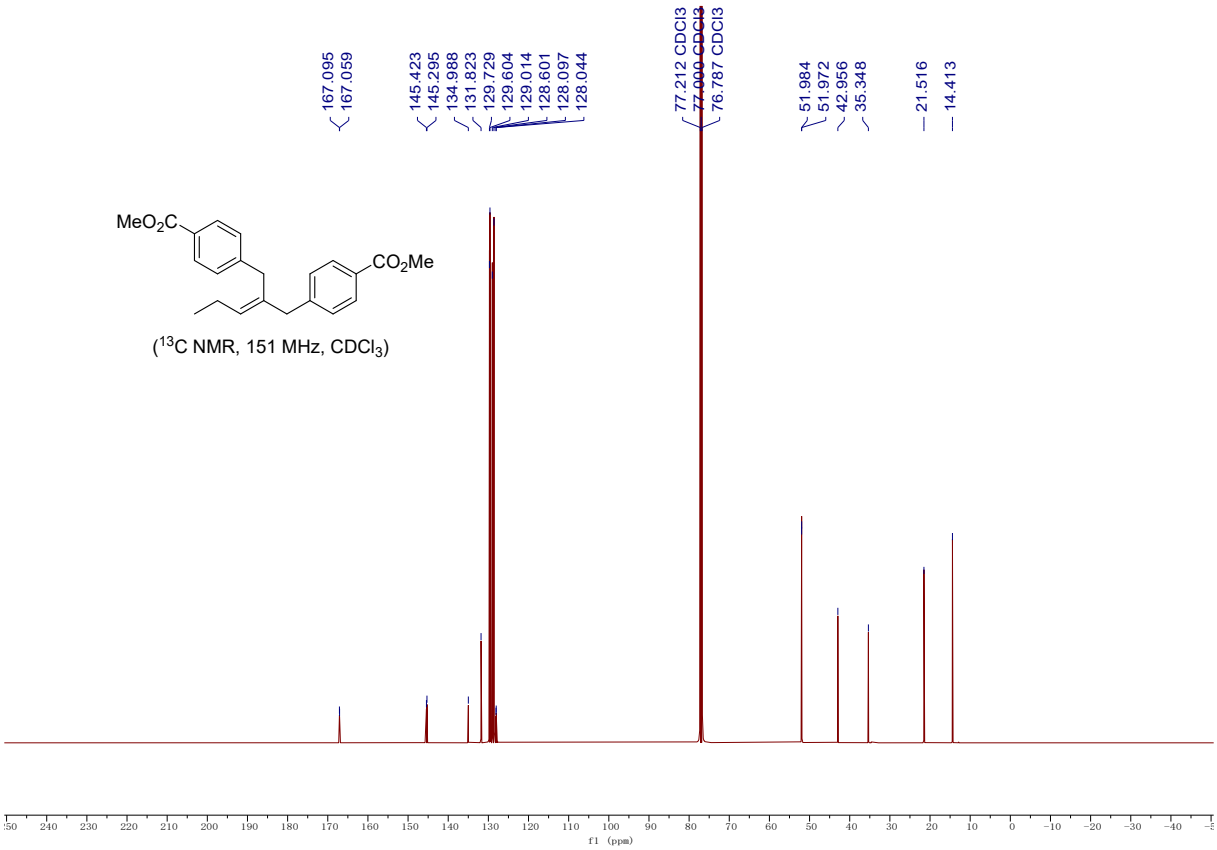


(^{13}C NMR, 151 MHz, $CDCl_3$)

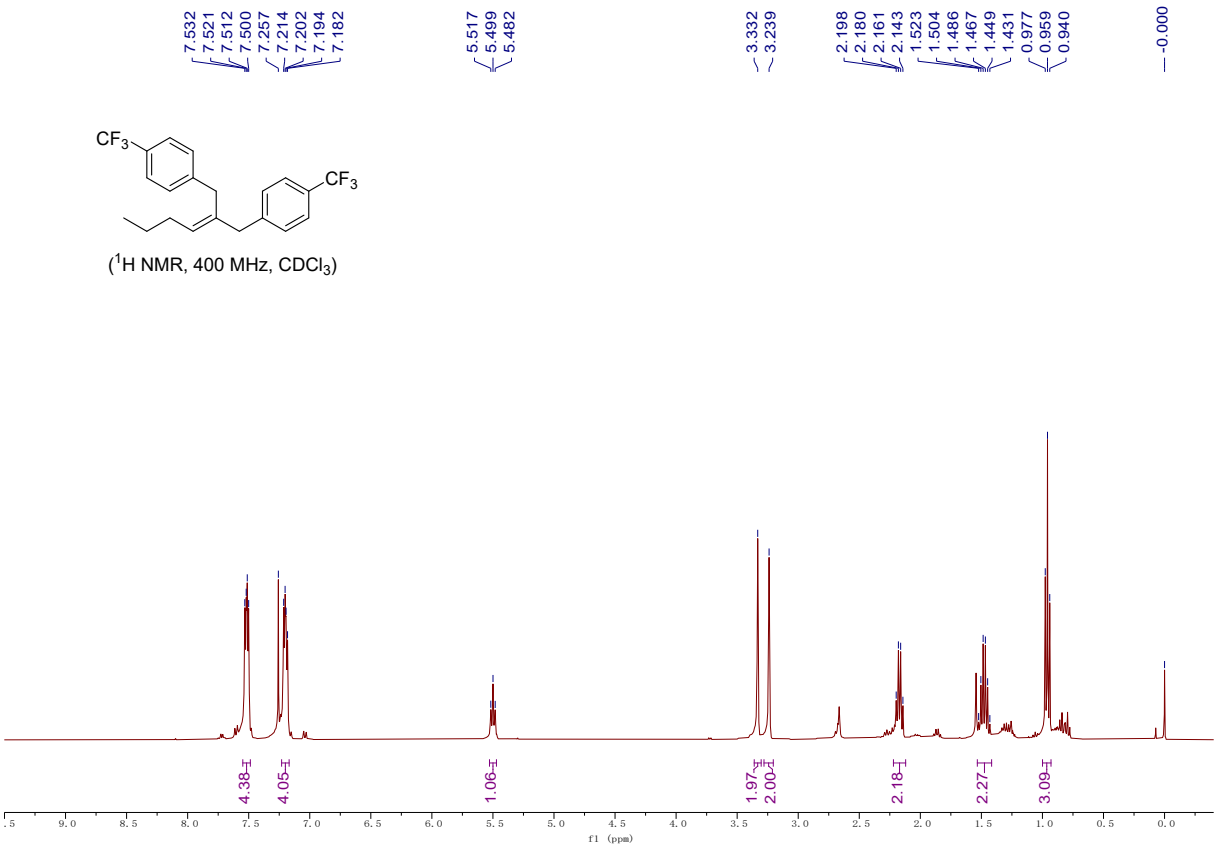


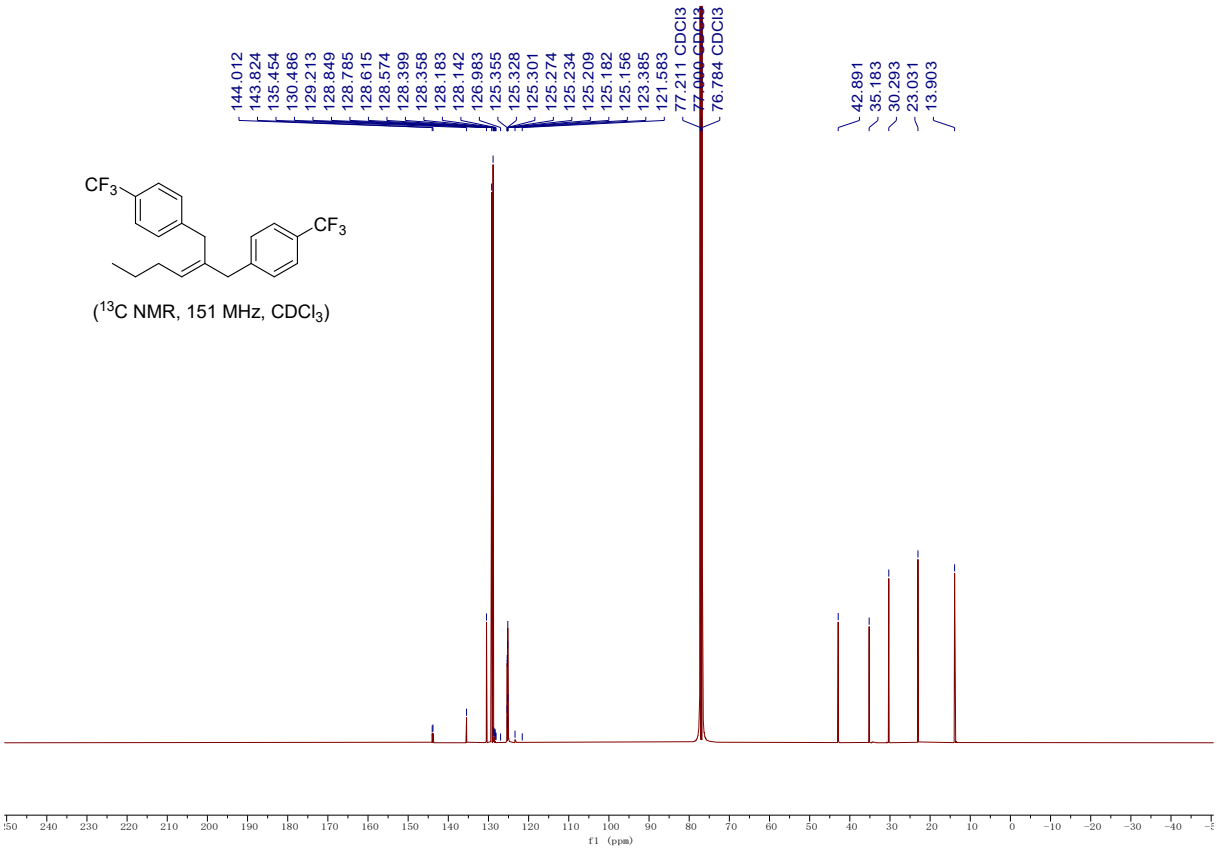
(^{19}F NMR, 565 MHz, $CDCl_3$)

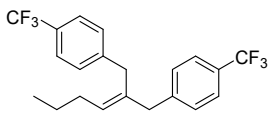




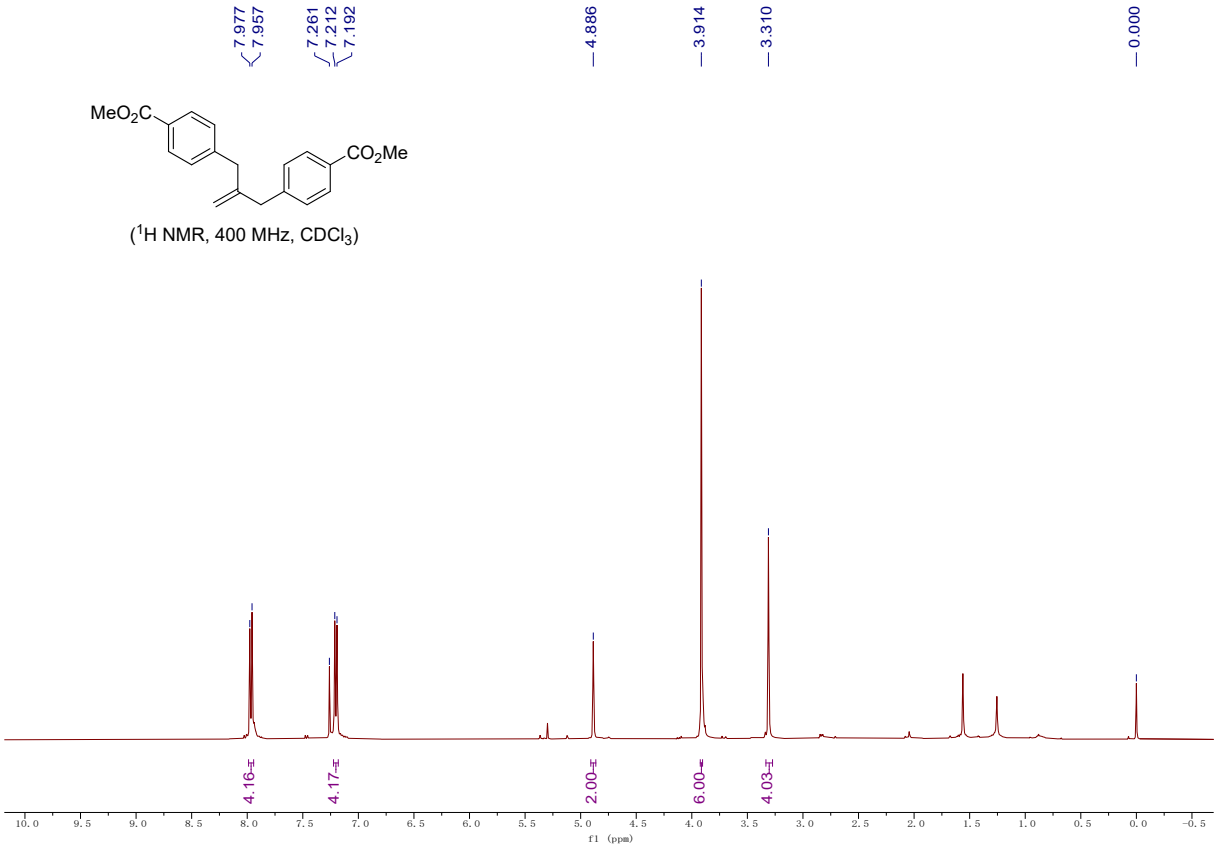
Containing a trace amount of impurity that failed to be separated.


7.532
7.521
7.512
7.500
7.257
7.214
7.202
7.194
7.182
5.517
5.499
5.482
3.332
3.239
2.198
2.180
2.161
2.143
1.523
1.504
1.486
1.467
1.449
1.431
0.977
0.959
0.940
-0.000
CF3
CF3
(1H NMR, 400 MHz, CDCl3)
4.38
4.05
1.06
1.97
2.00
2.18
2.27
3.09
f1 (ppm)

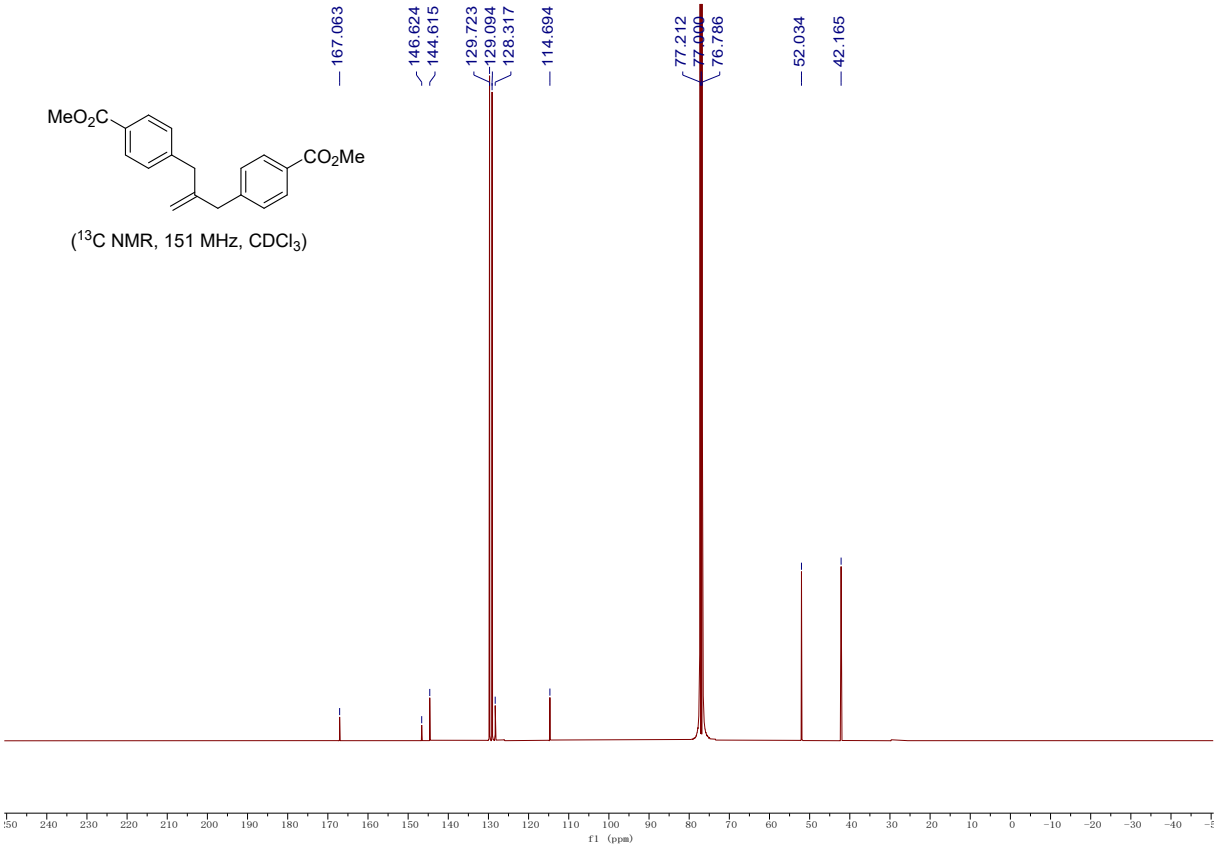

144.012
143.824
135.454
130.486
129.213
128.849
128.785
128.615
128.574
128.399
128.358
128.183
128.142
126.983
125.355
125.328
125.301
125.274
125.234
125.209
125.182
125.156
123.385
121.583
77.211 CDCl3
77.000 CDCl3
76.784 CDCl3
42.891
35.183
30.293
23.031
13.903
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



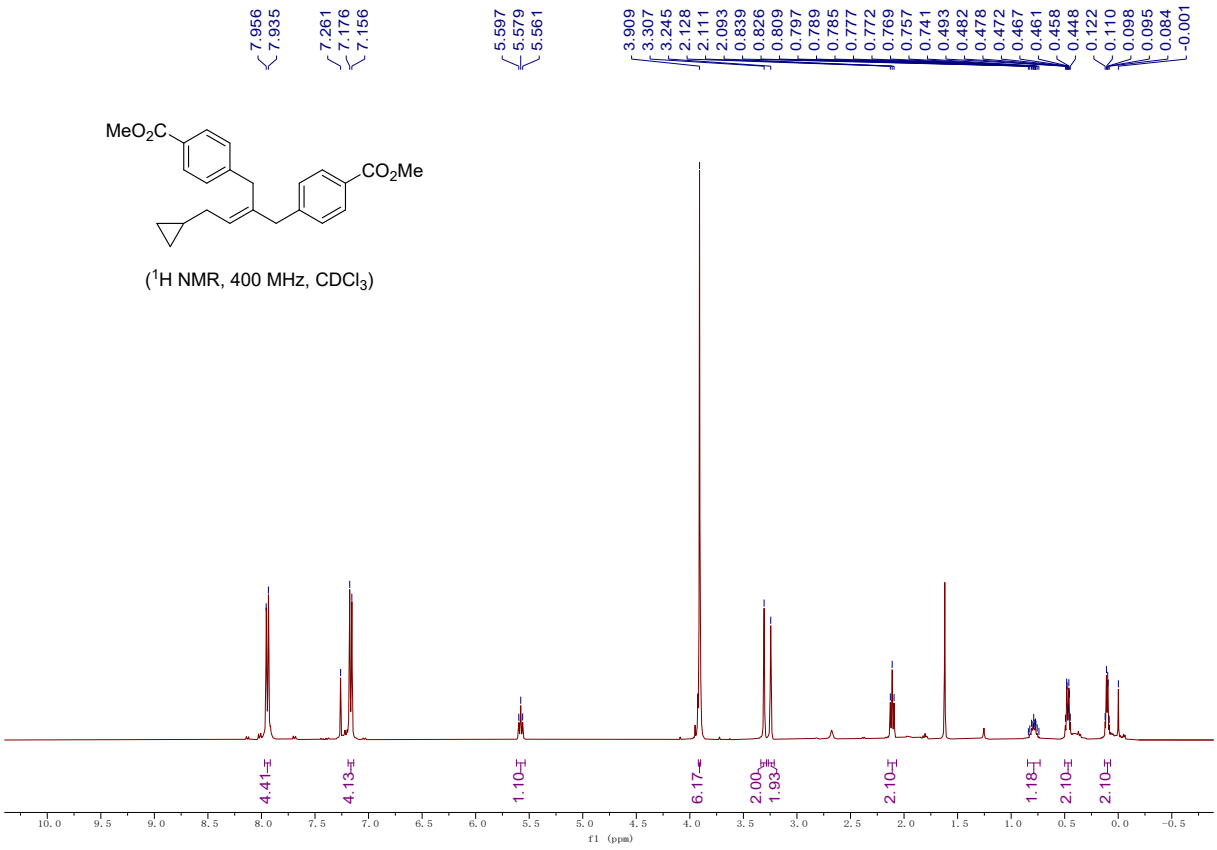
(^{19}F NMR, 565 MHz, $CDCl_3$)



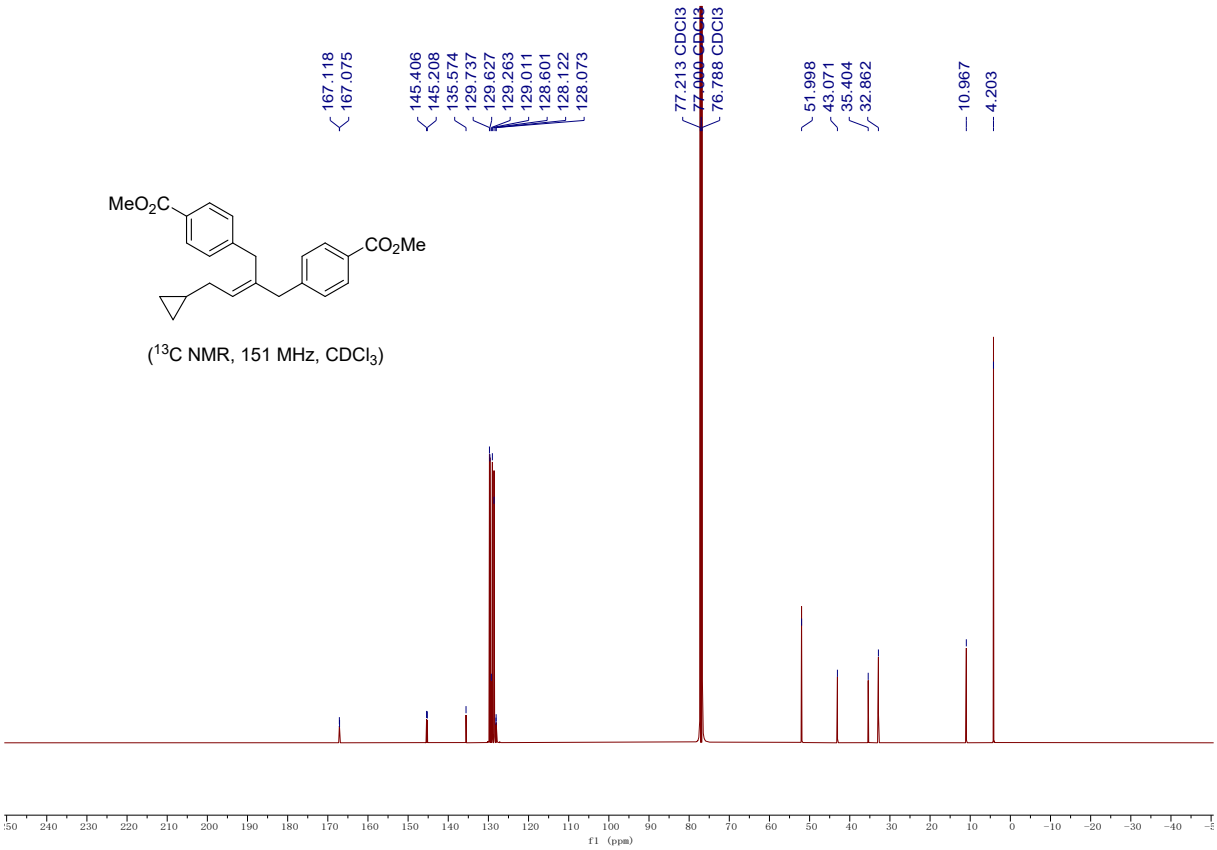
(^{1}H NMR, 400 MHz, $CDCl_3$)



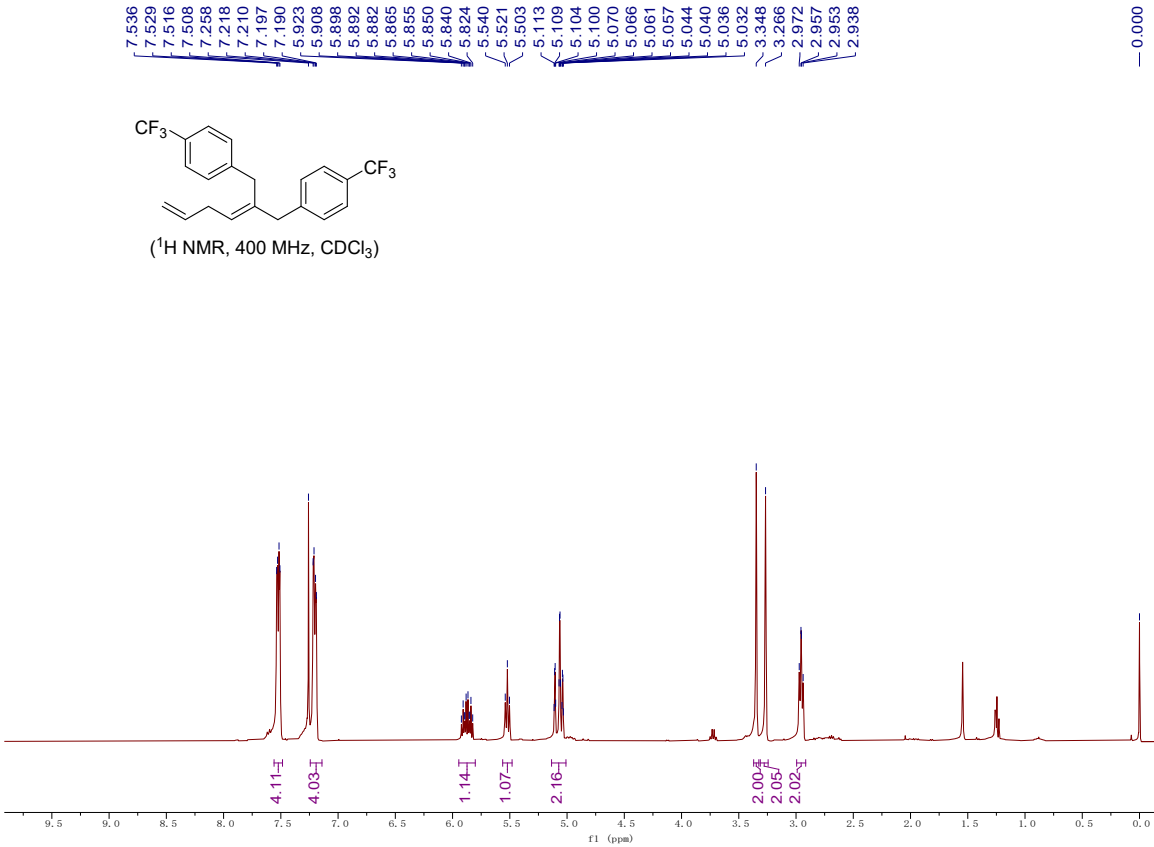
(^{13}C NMR, 151 MHz, $CDCl_3$)

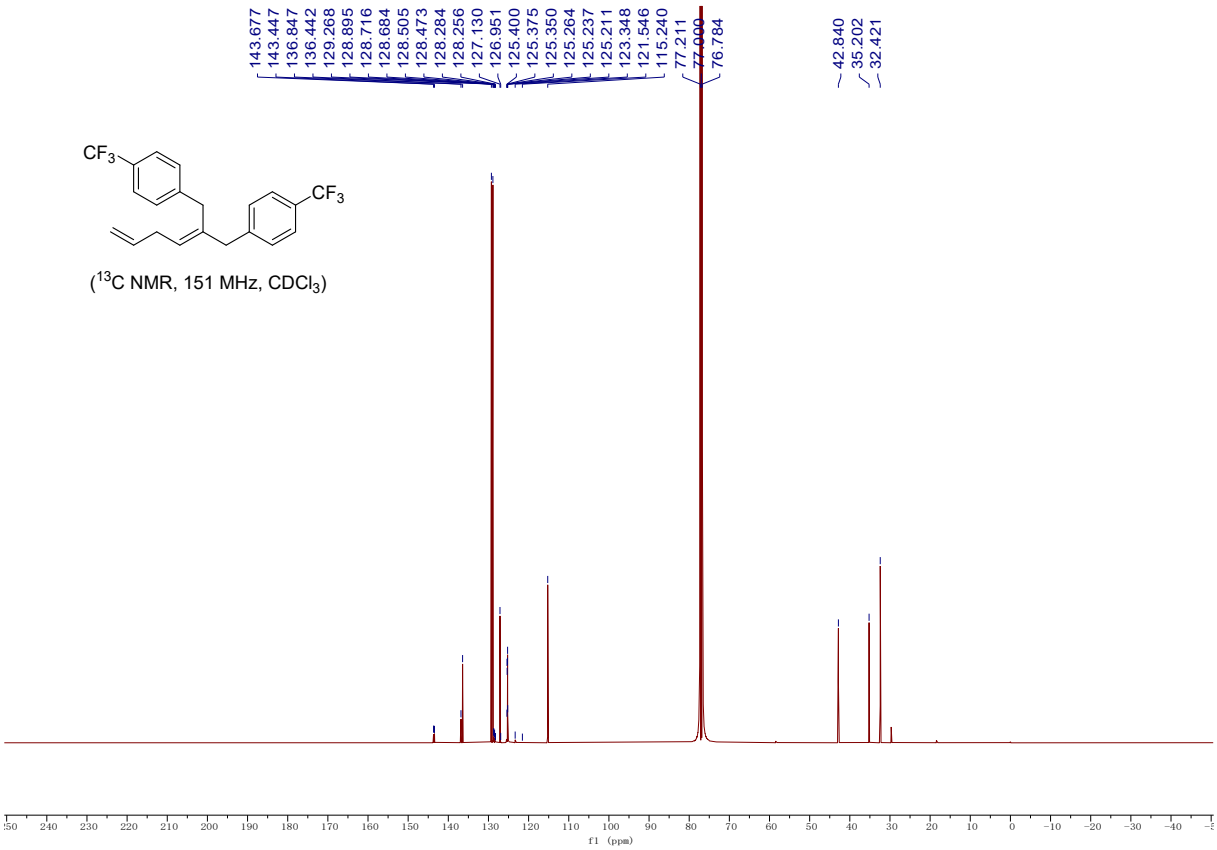


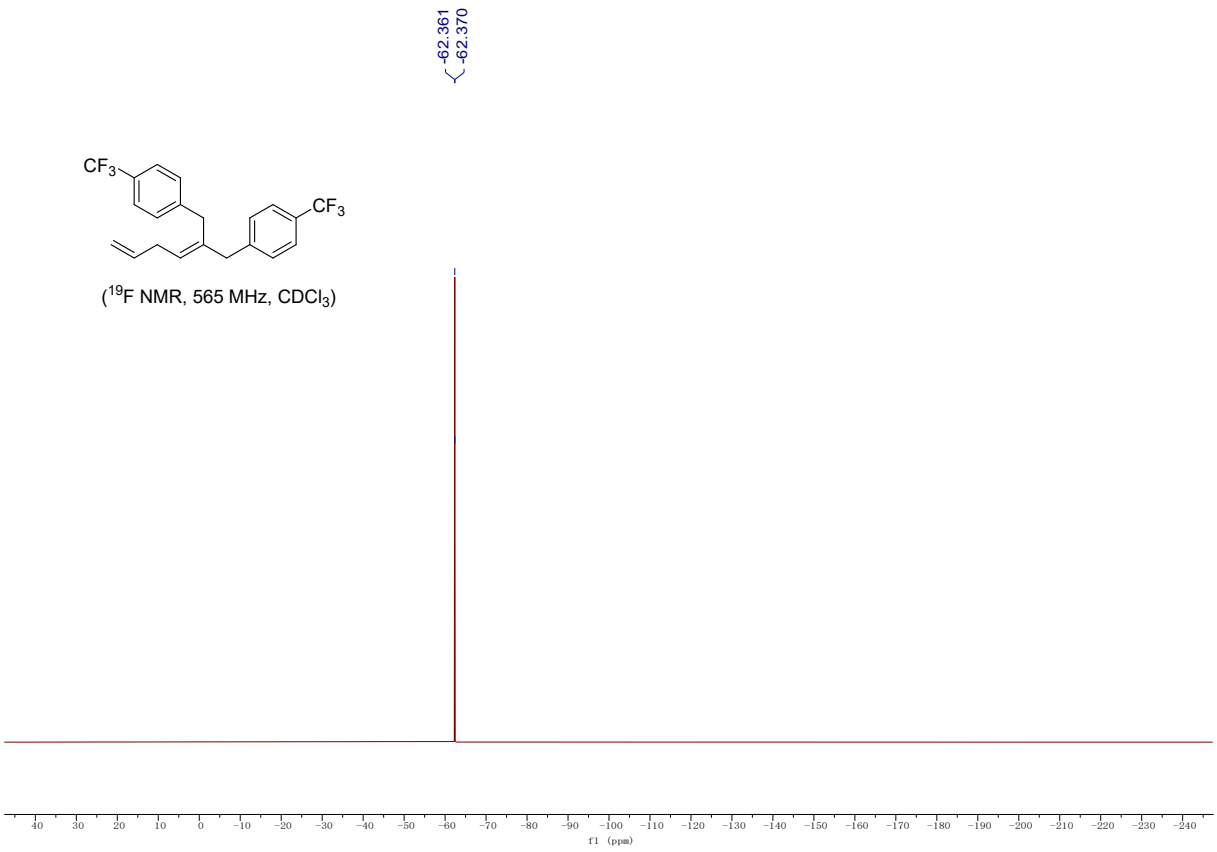
(^{1}H NMR, 400 MHz, $CDCl_3$)



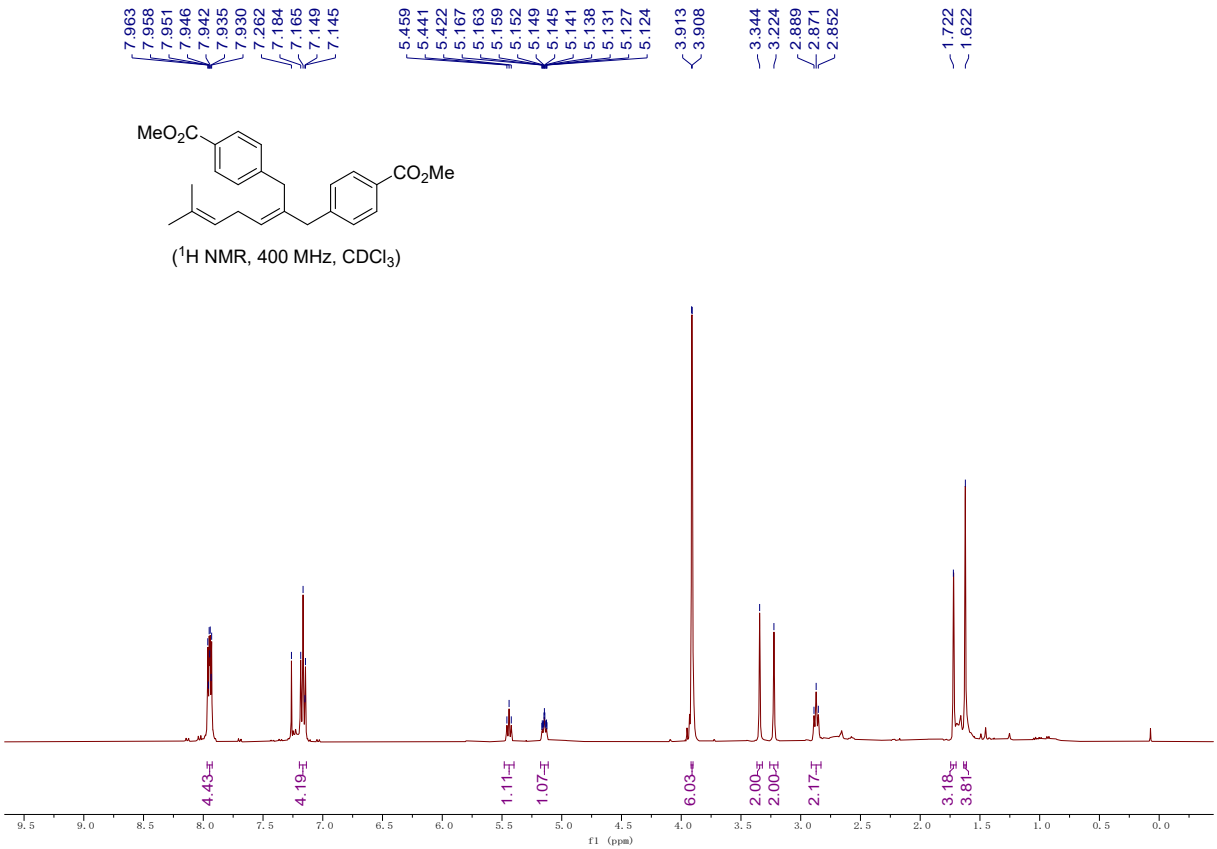
(^{13}C NMR, 151 MHz, $CDCl_3$)

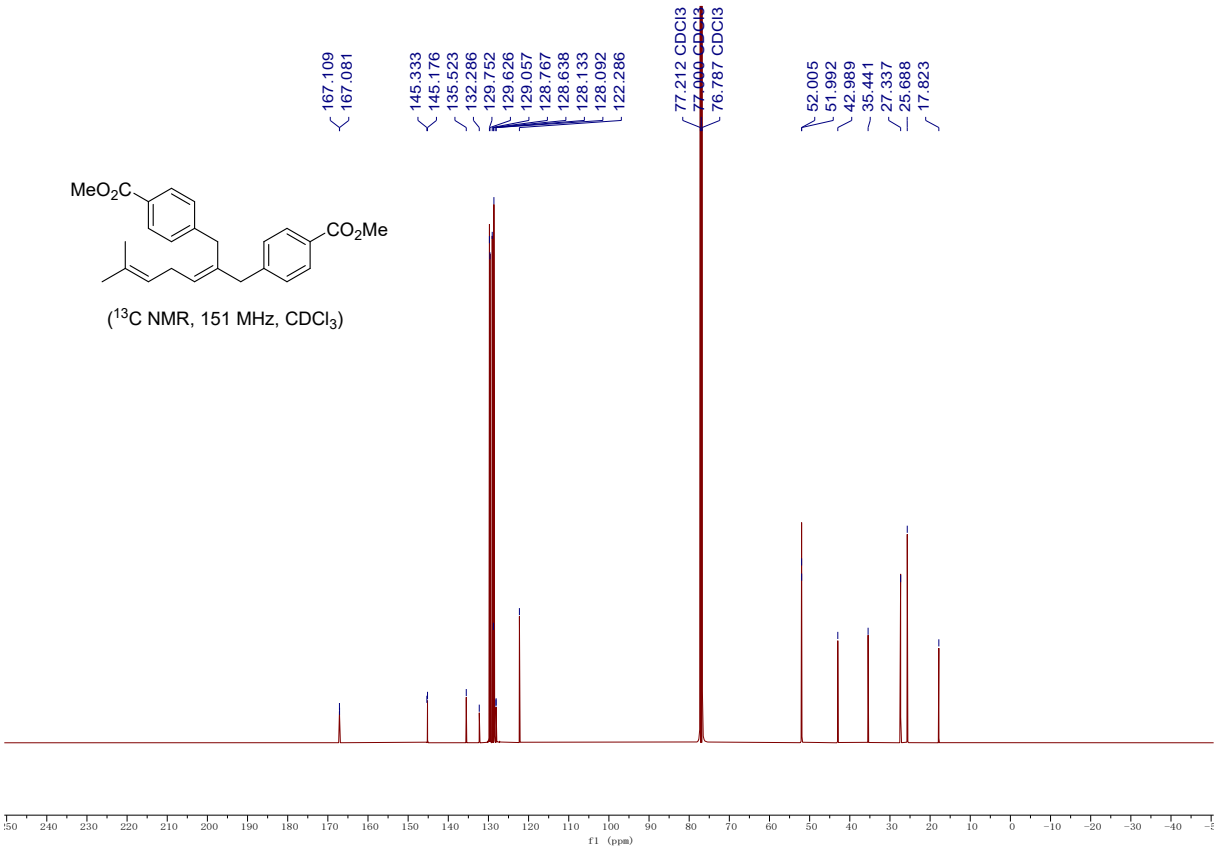

7.536
7.529
7.516
7.508
7.258
7.218
7.210
7.197
7.190
5.923
5.908
5.898
5.892
5.882
5.865
5.855
5.850
5.840
5.824
5.540
5.521
5.503
5.113
5.109
5.104
5.100
5.070
5.066
5.061
5.057
5.044
5.040
5.036
5.032
3.348
3.266
2.972
2.957
2.953
2.938
0.000
CF3
CF3
(1H NMR, 400 MHz, CDCl3)
4.11
4.03
1.14
1.07
2.16
2.00
2.05
2.02
f1 (ppm)

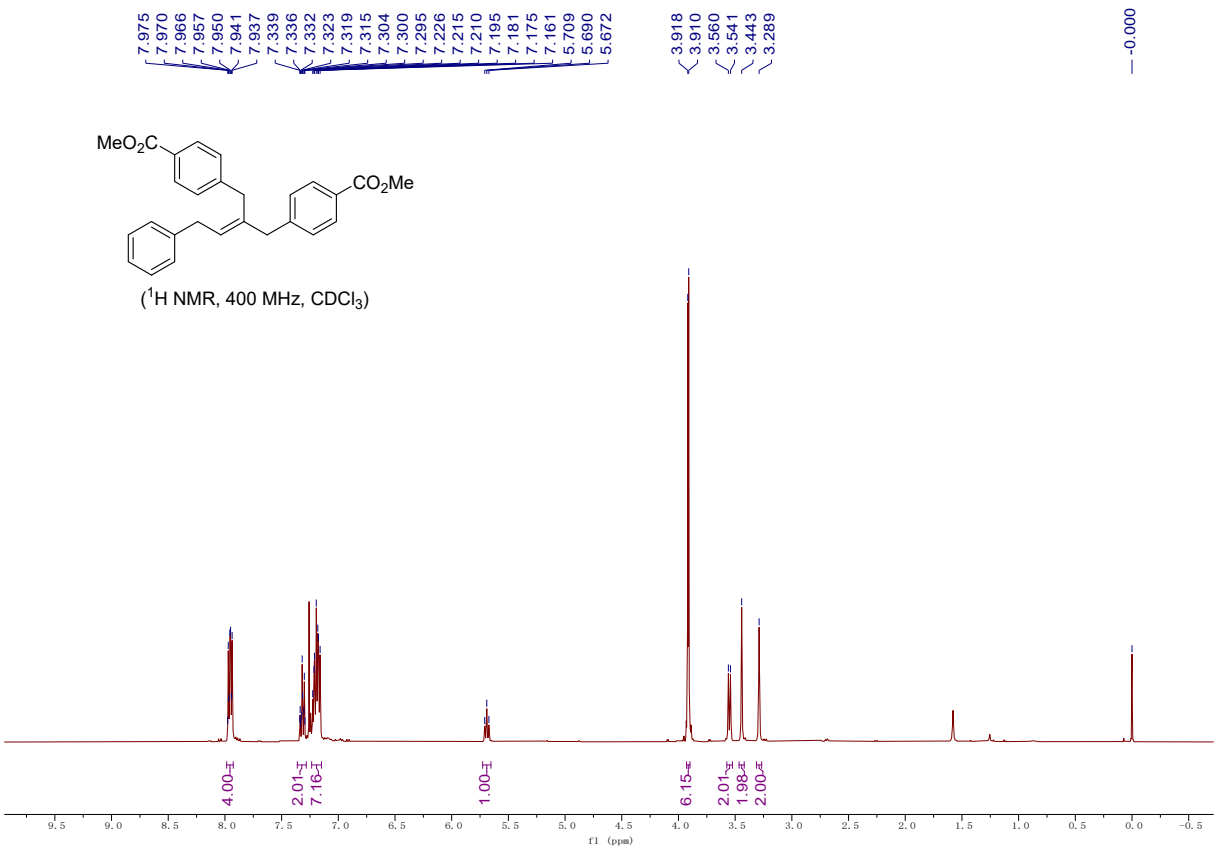

143.677
143.447
136.847
136.442
129.268
128.895
128.716
128.684
128.505
128.473
128.284
128.256
127.130
126.951
125.400
125.375
125.350
125.264
125.237
125.211
123.348
121.546
115.240
77.211
77.000
76.784
42.840
35.202
32.421
CF3
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

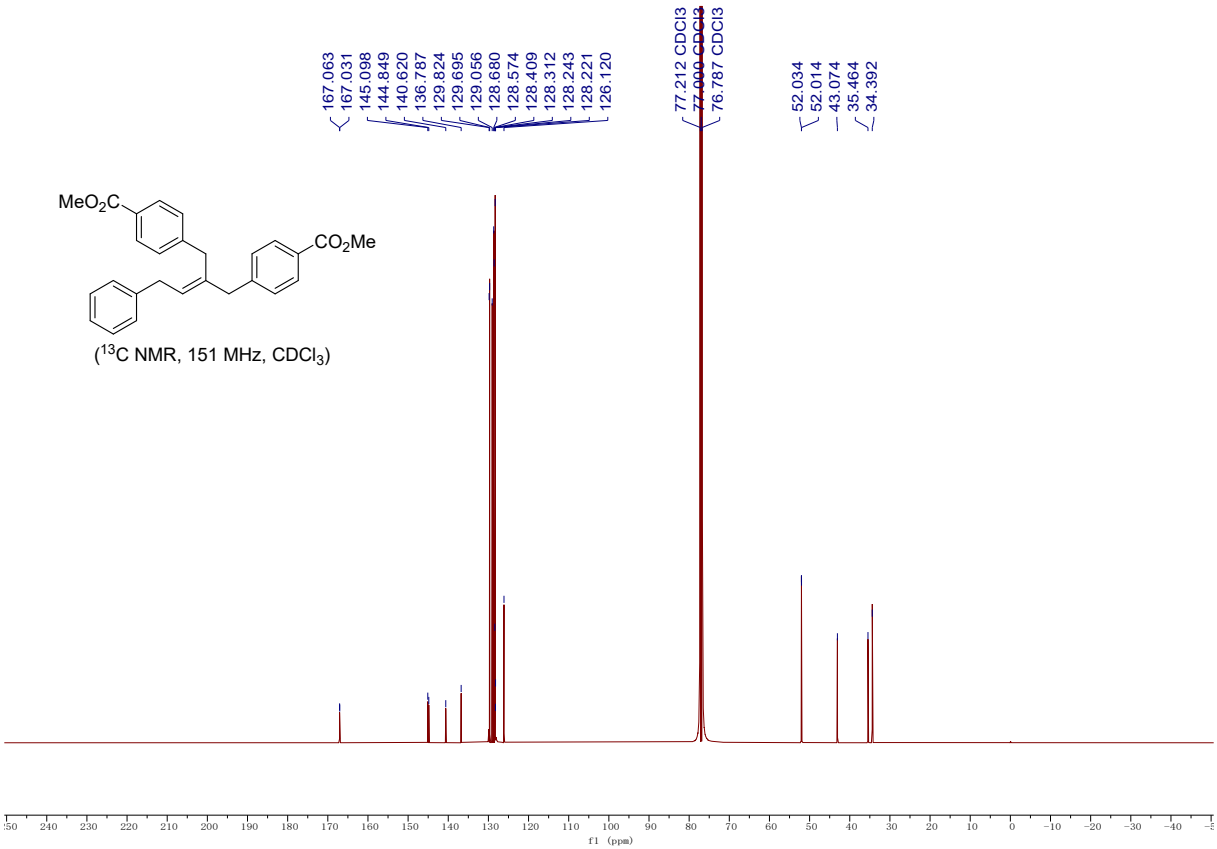


(^{19}F NMR, 565 MHz, $CDCl_3$)

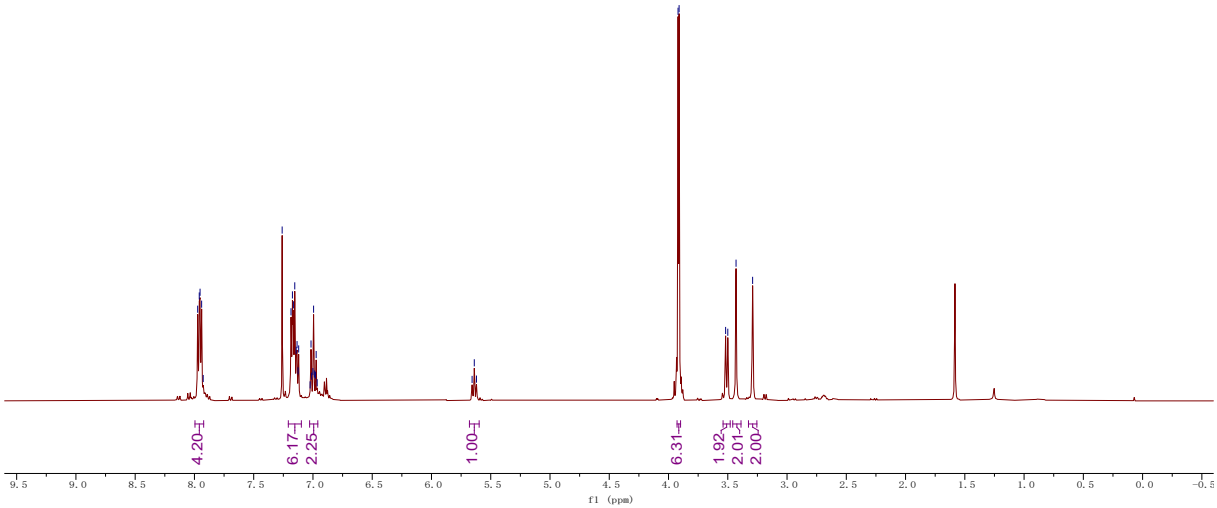

7.963
7.958
7.951
7.946
7.942
7.935
7.930
7.262
7.184
7.165
7.149
7.145
5.459
5.441
5.422
5.167
5.163
5.159
5.152
5.149
5.145
5.141
5.138
5.131
5.127
5.124
3.913
3.908
3.344
3.224
2.889
2.871
2.852
1.722
1.622
MeO2C
CO2Me
(1H NMR, 400 MHz, CDCl3)
4.43
4.19
1.11
1.07
6.03
2.00
2.00
2.17
3.18
3.81
f1 (ppm)

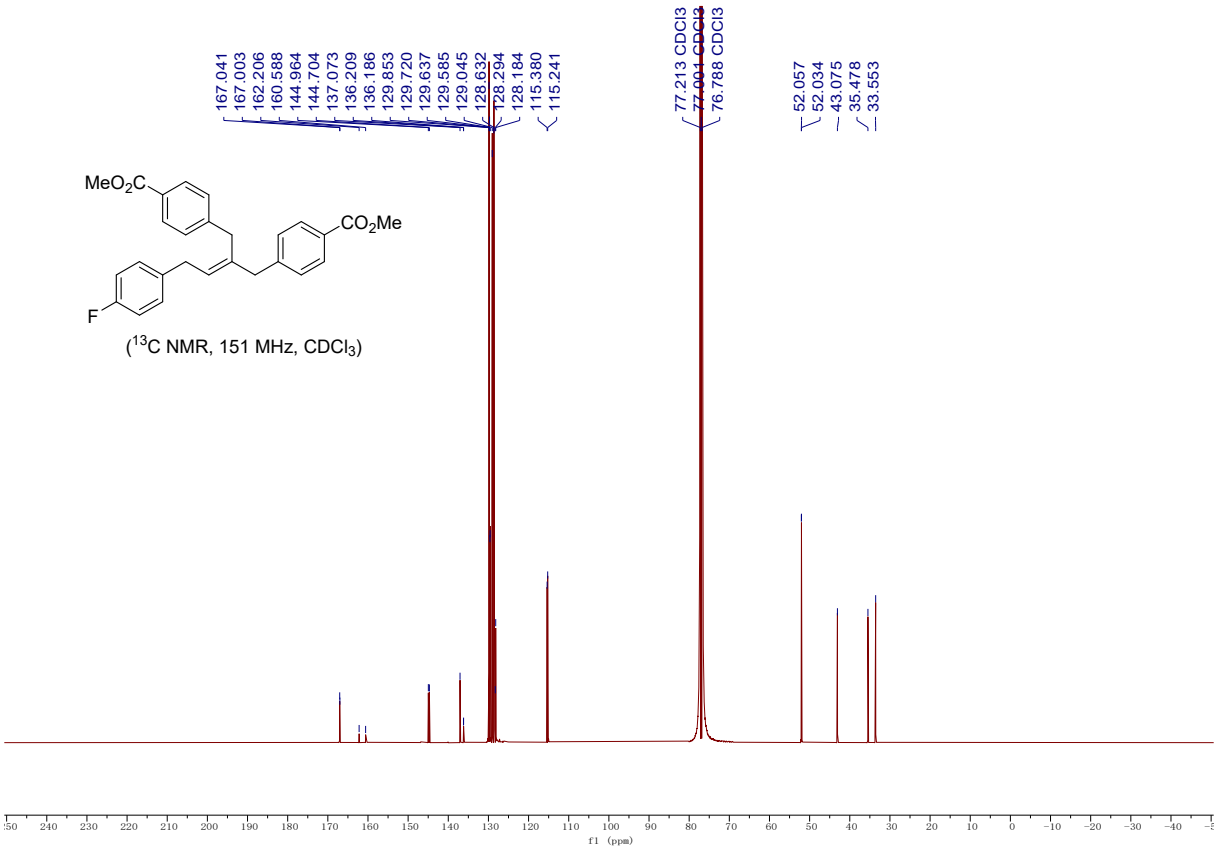

167.109
167.081
145.333
145.176
135.523
132.286
129.752
129.626
129.057
128.767
128.638
128.133
128.092
122.286
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
52.005
51.992
42.989
35.441
27.337
25.688
17.823
MeO2C
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)


7.975
7.970
7.966
7.957
7.950
7.941
7.937
7.339
7.336
7.332
7.323
7.319
7.315
7.304
7.300
7.295
7.226
7.215
7.210
7.195
7.181
7.175
7.161
5.709
5.690
5.672
3.918
3.910
3.560
3.541
3.443
3.289
-0.000
MeO2C
CO2Me
(1H NMR, 400 MHz, CDCl3)
4.00
2.01
7.16
1.00
6.15
2.01
1.98
2.00
f1 (ppm)

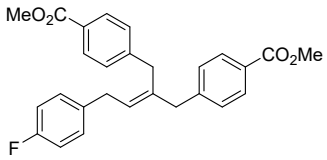

167.063
167.031
145.098
144.849
140.620
136.787
129.824
129.695
129.056
128.680
128.574
128.409
128.312
128.243
128.221
126.120
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
52.034
52.014
43.074
35.464
34.392
MeO2C
CO2Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

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

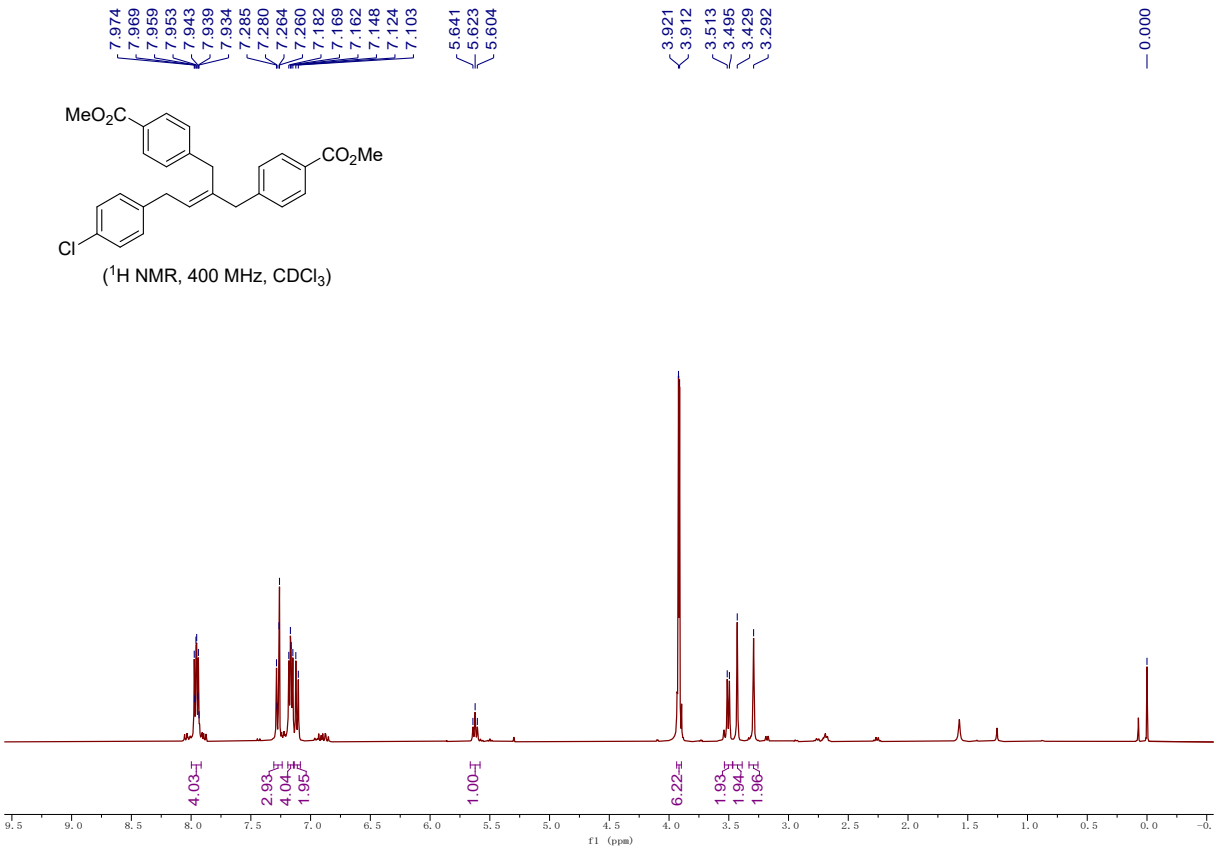


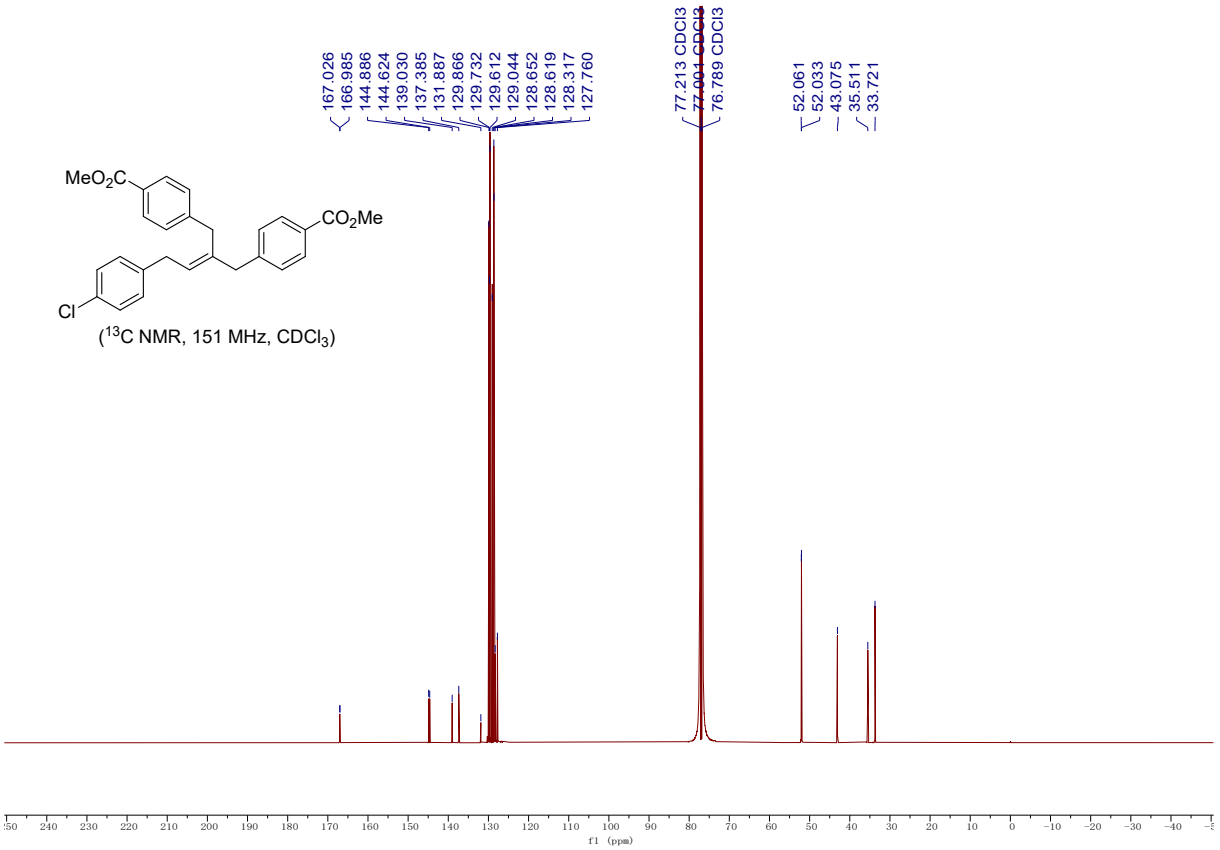


(^{13}C NMR, 151 MHz, $CDCl_3$)

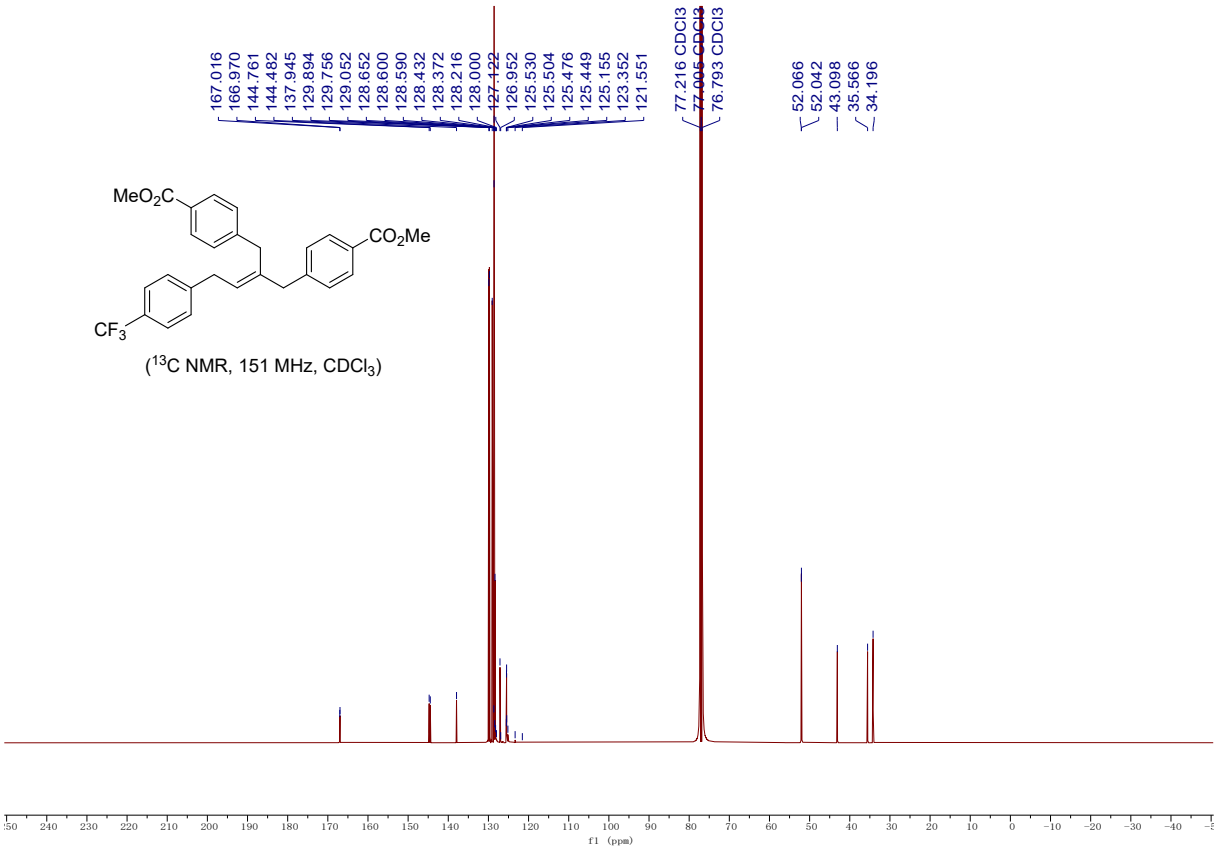


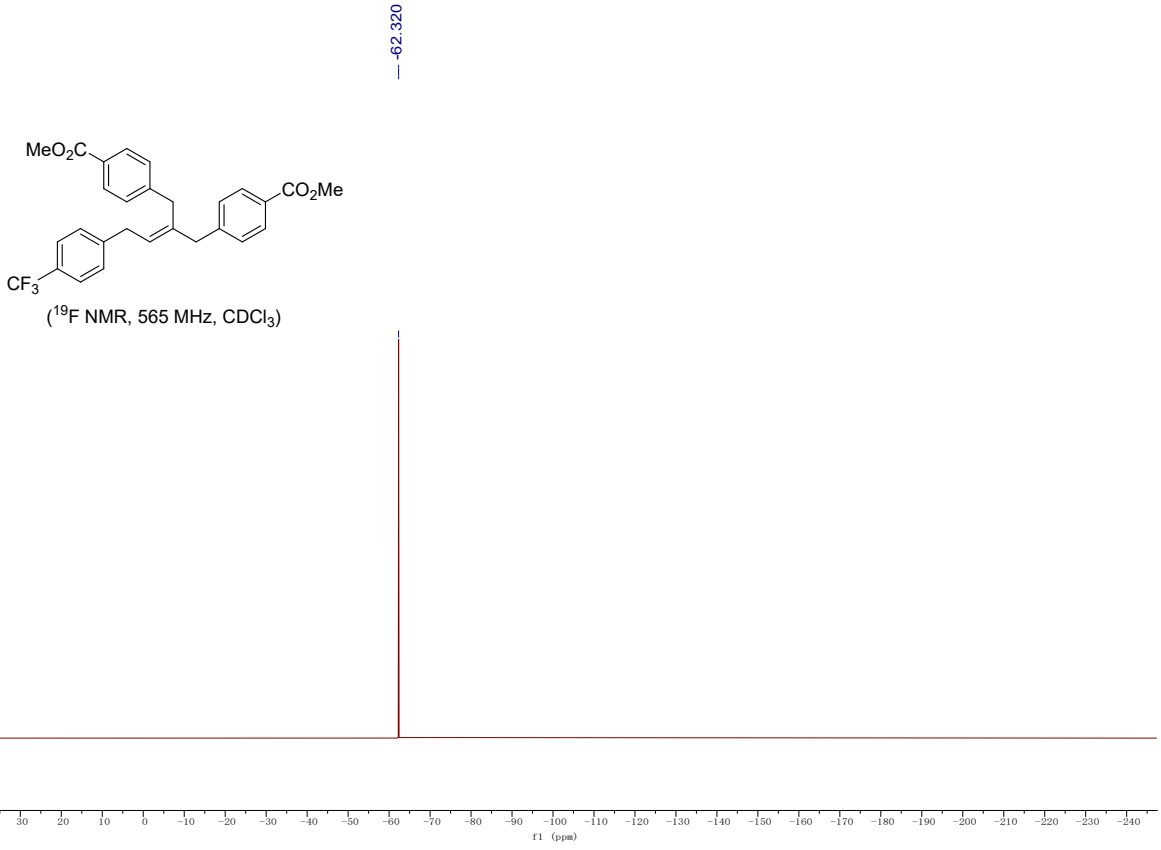
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.974
7.969
7.959
7.953
7.943
7.939
7.934
7.285
7.280
7.264
7.260
7.182
7.169
7.162
7.148
7.124
7.103
5.641
5.623
5.604
3.921
3.912
3.513
3.495
3.429
3.292
0.000
MeO2C
CO2Me
Cl
(1H NMR, 400 MHz, CDCl3)
4.03
2.93
4.04
1.95
1.00
6.22
1.93
1.94
1.96
f1 (ppm)

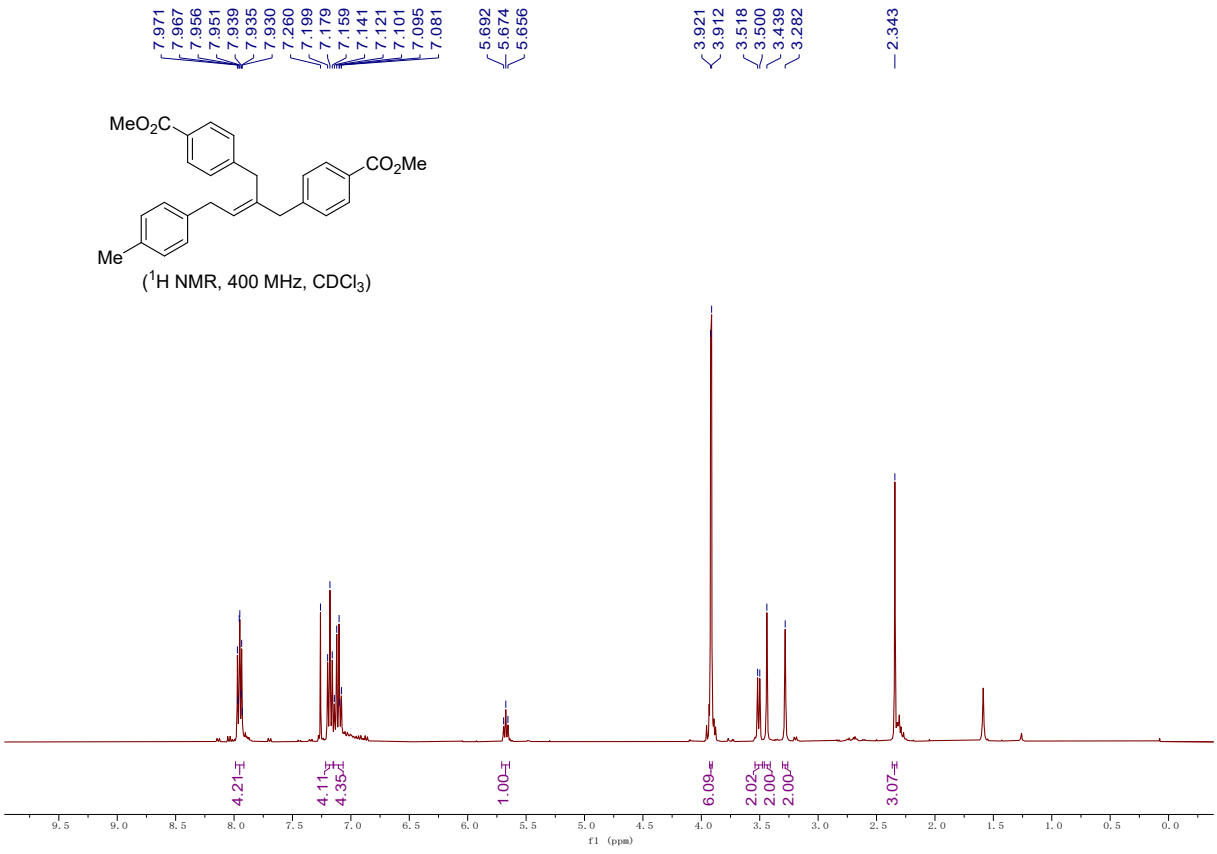

167.026
166.985
144.886
144.624
139.030
137.385
131.887
129.866
129.732
129.612
129.044
128.652
128.619
128.317
127.760
77.213 CDCl3
77.001 CDCl3
76.789 CDCl3
52.061
52.033
43.075
35.511
33.721
MeO2C
CO2Me
Cl
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

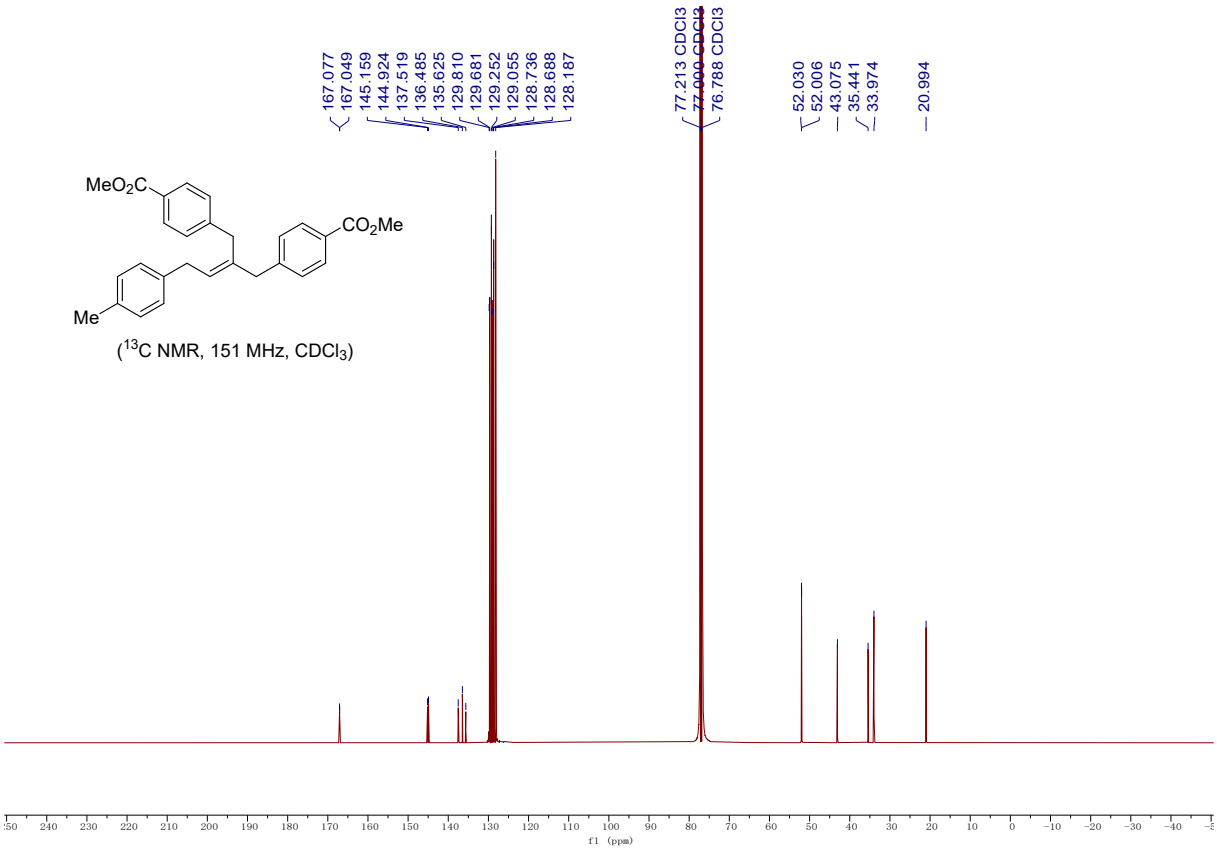

7.979
7.967
7.959
7.947
7.574
7.554
7.306
7.286
7.260
7.188
7.176
7.167
7.156
5.660
5.641
5.623
3.922
3.912
3.603
3.585
3.448
3.311
MeO2C
CO2Me
CF3
(1H NMR, 400 MHz, CDCl3)
4.23
2.09
2.13
4.27
1.04
6.22
2.00
2.02
2.03
f1 (ppm)

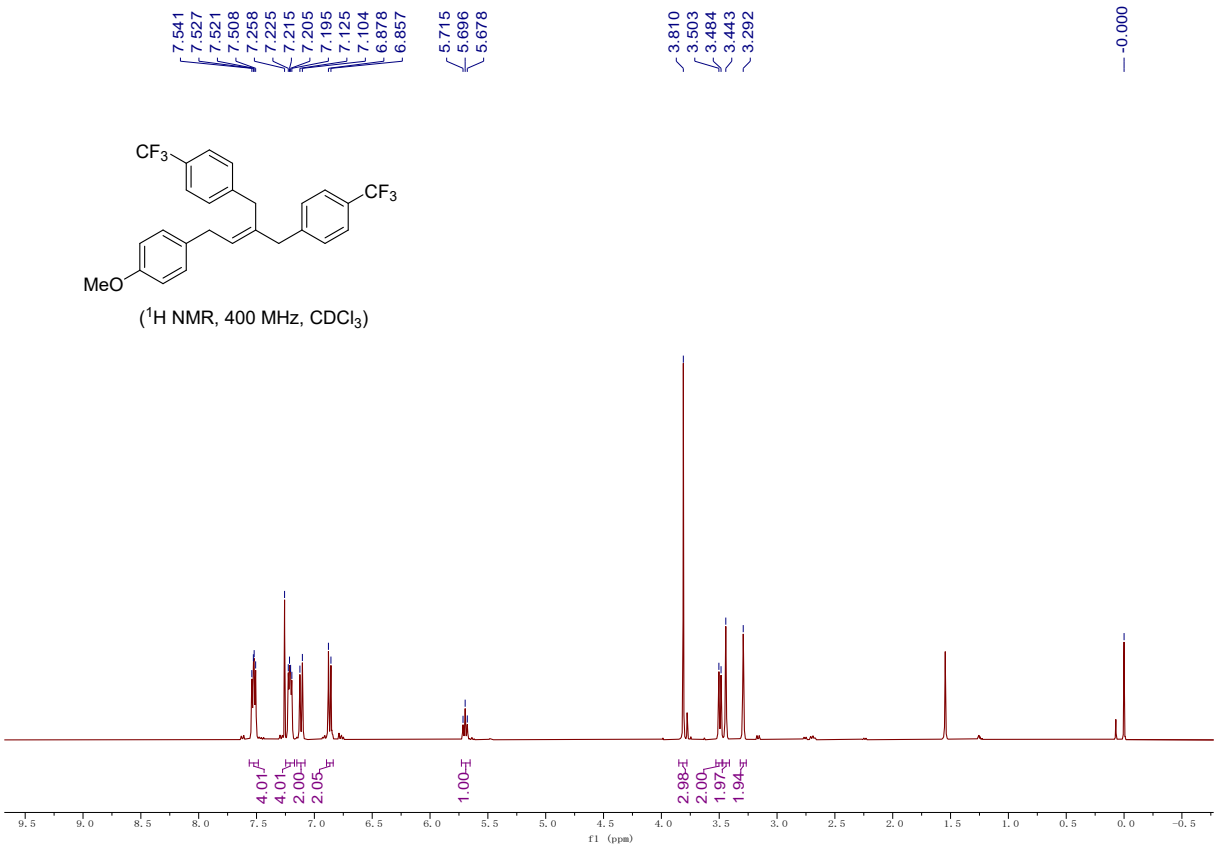

167.016
166.970
144.761
144.482
137.945
129.894
129.756
129.052
128.652
128.600
128.590
128.432
128.372
128.216
128.000
127.122
126.952
125.530
125.504
125.476
125.449
125.155
123.352
121.551
77.216 CDCl3
77.005 CDCl3
76.793 CDCl3
52.066
52.042
43.098
35.566
34.196
MeO2C
CO2Me
CF3
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



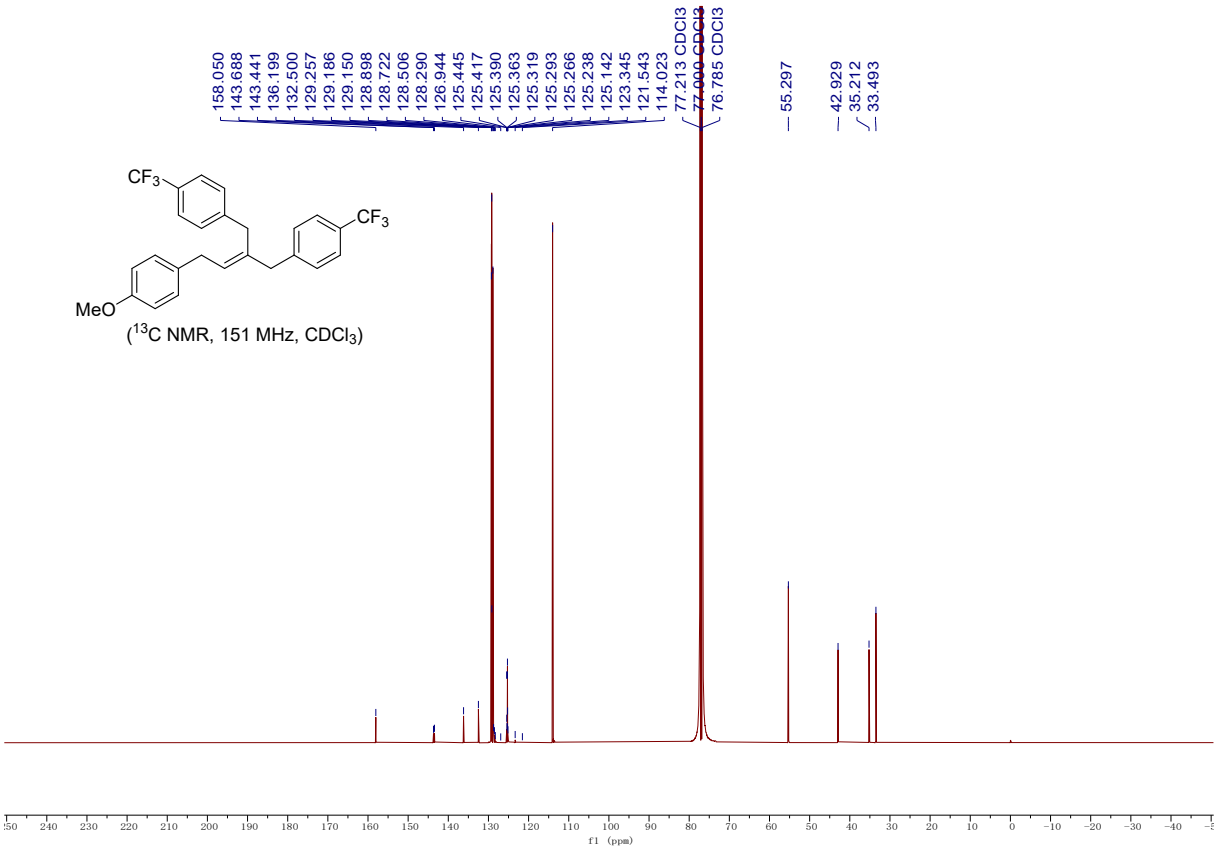
(^{19}F NMR, 565 MHz, $CDCl_3$)


7.971
7.967
7.956
7.951
7.939
7.935
7.930
7.260
7.199
7.179
7.159
7.141
7.121
7.101
7.095
7.081
5.692
5.674
5.656
3.921
3.912
3.518
3.500
3.439
3.282
2.343
MeO2C
CO2Me
Me
(1H NMR, 400 MHz, CDCl3)
4.21
4.11
4.35
1.00
6.09
2.02
2.00
2.00
3.07
f1 (ppm)

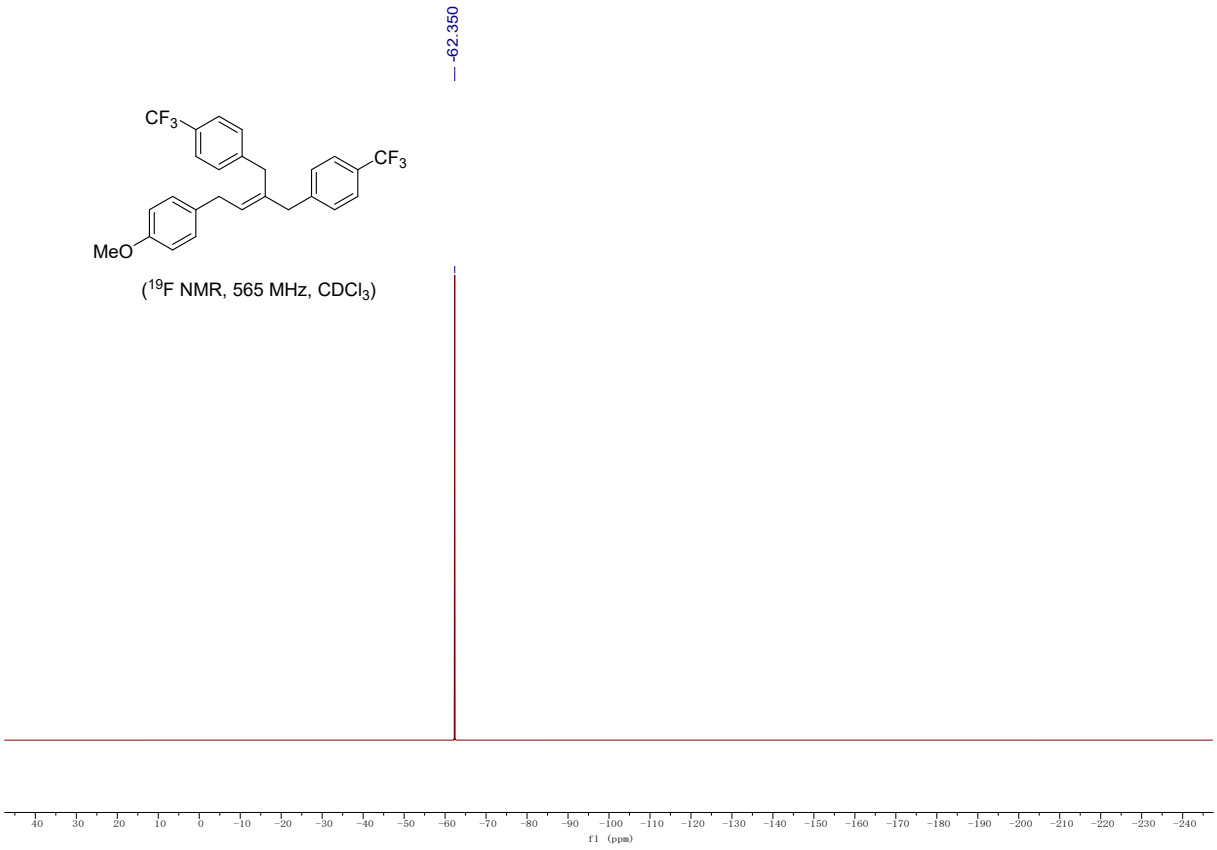

167.077
167.049
145.159
144.924
137.519
136.485
135.625
129.810
129.681
129.252
129.055
128.736
128.688
128.187
77.213 CDCl3
77.000 CDCl3
76.788 CDCl3
52.030
52.006
43.075
35.441
33.974
20.994
MeO2C
CO2Me
Me
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



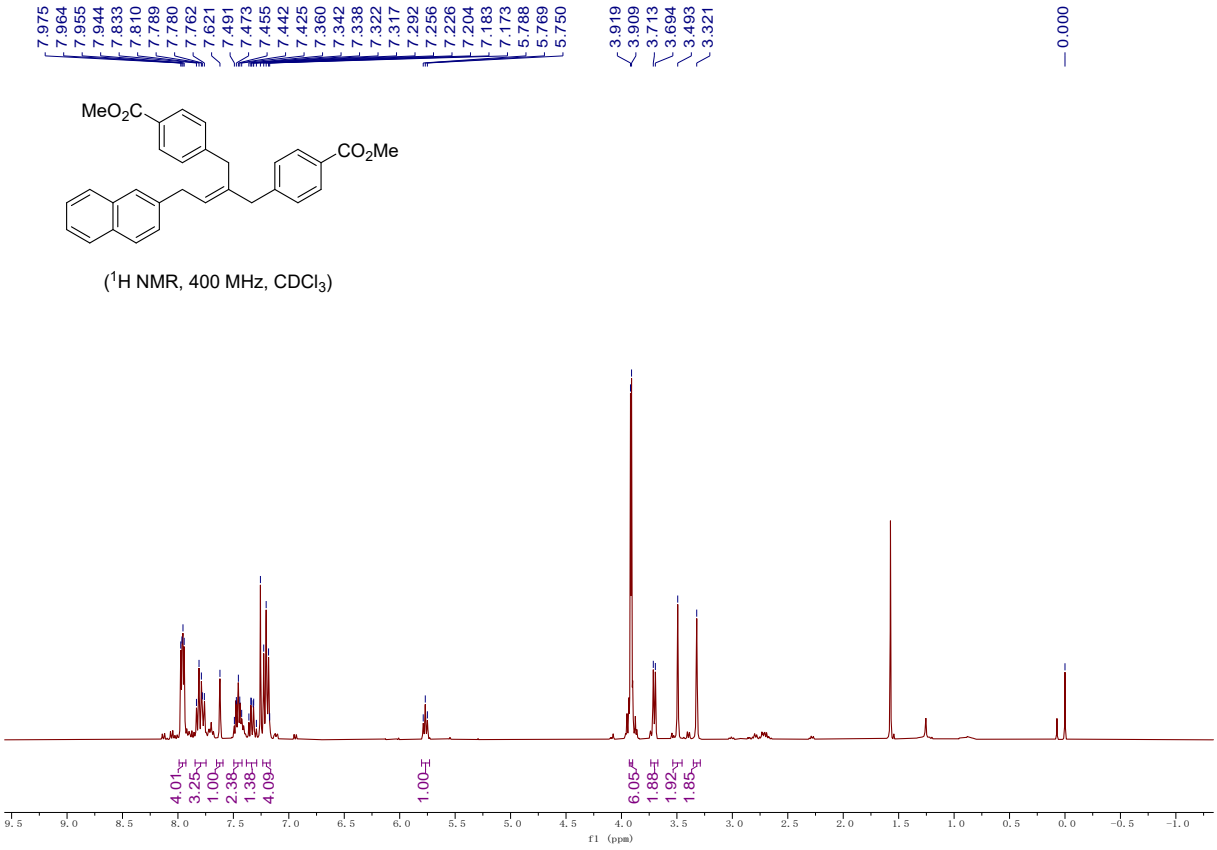
(^{1}H NMR, 400 MHz, $CDCl_3$)



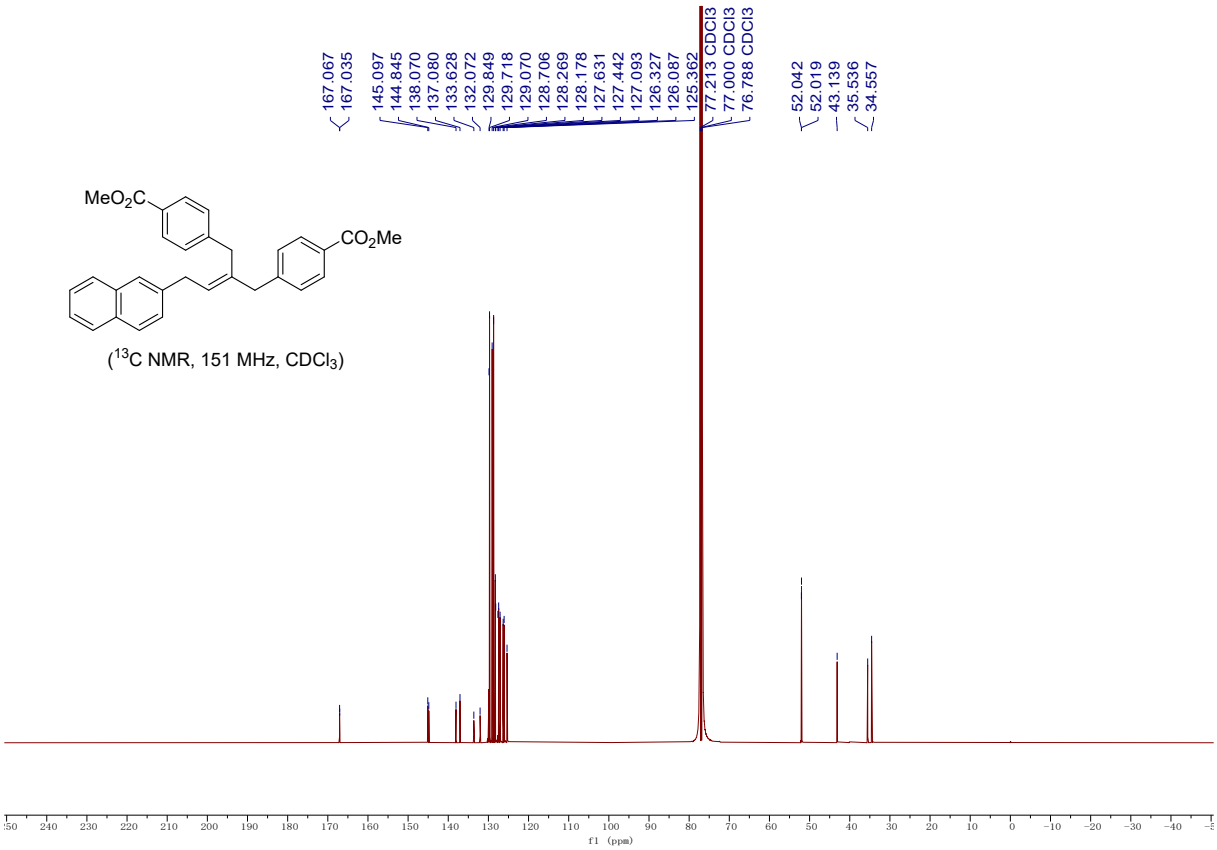
(^{13}C NMR, 151 MHz, $CDCl_3$)



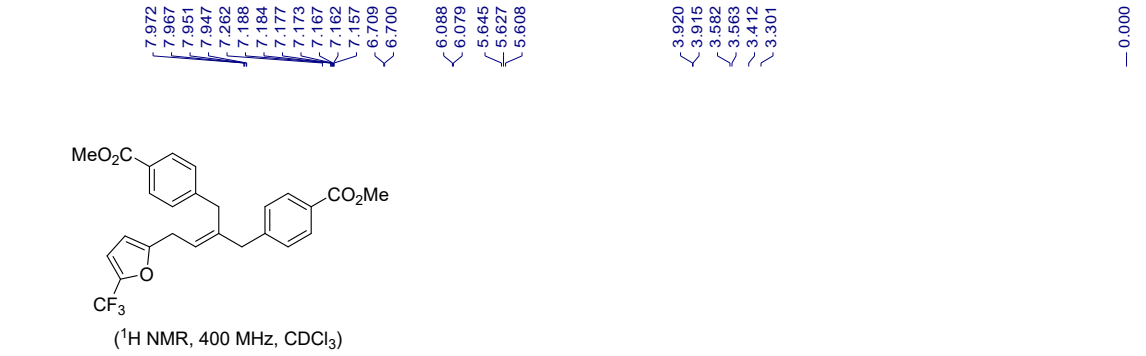
(^{19}F NMR, 565 MHz, $CDCl_3$)



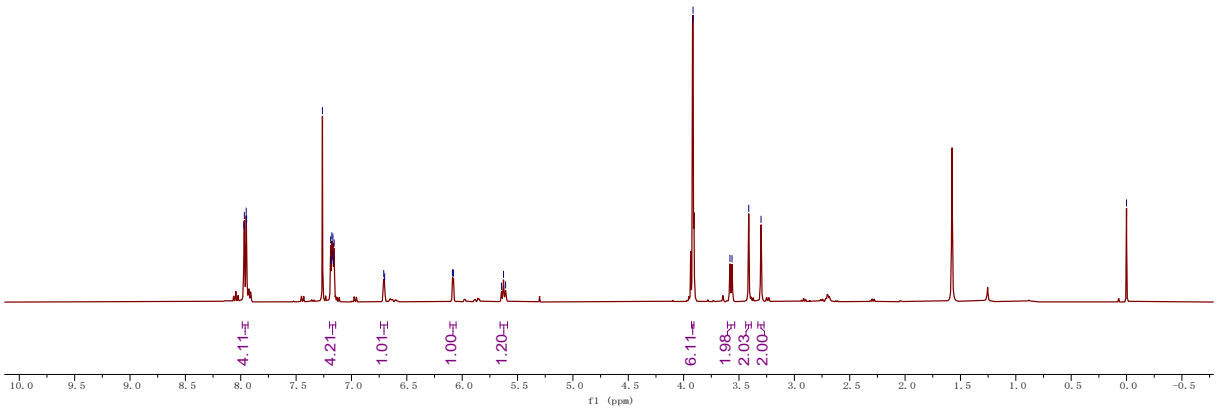
(^{1}H NMR, 400 MHz, $CDCl_3$)

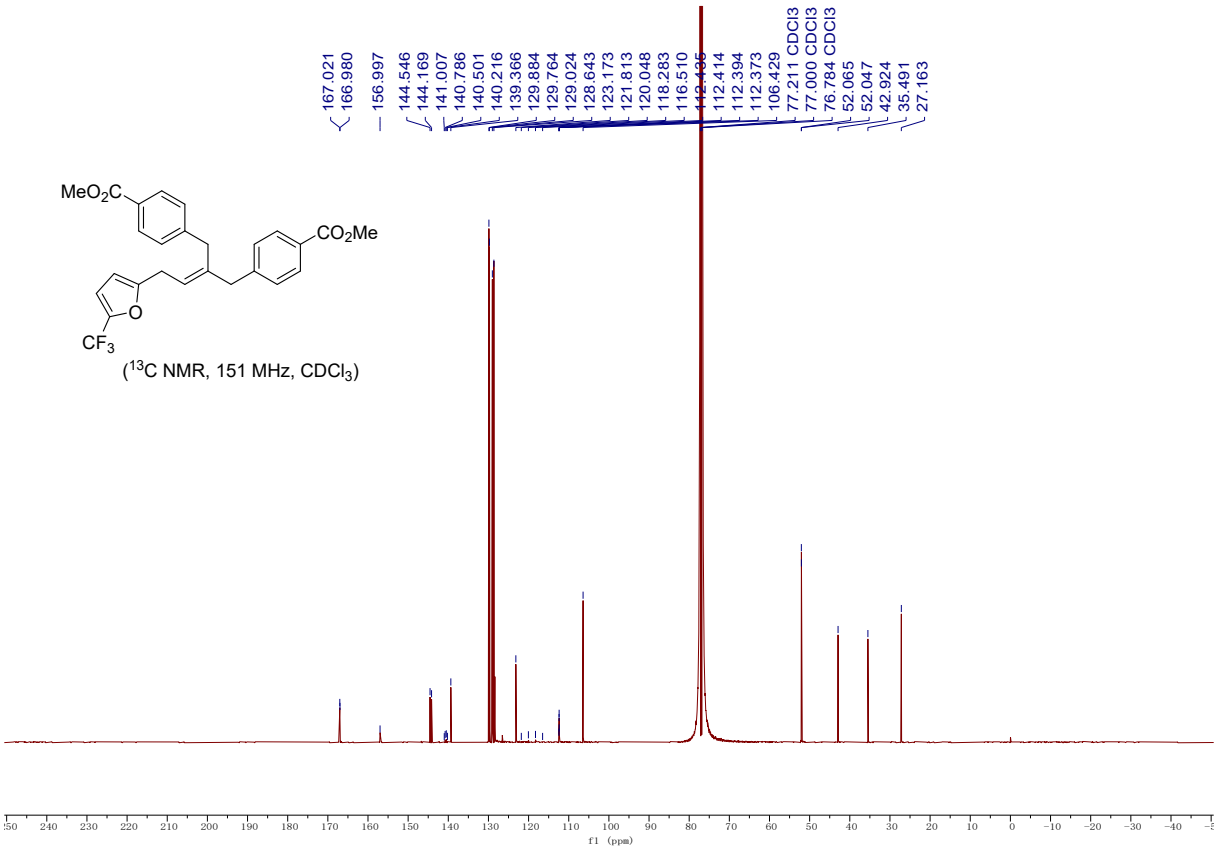


(^{13}C NMR, 151 MHz, $CDCl_3$)

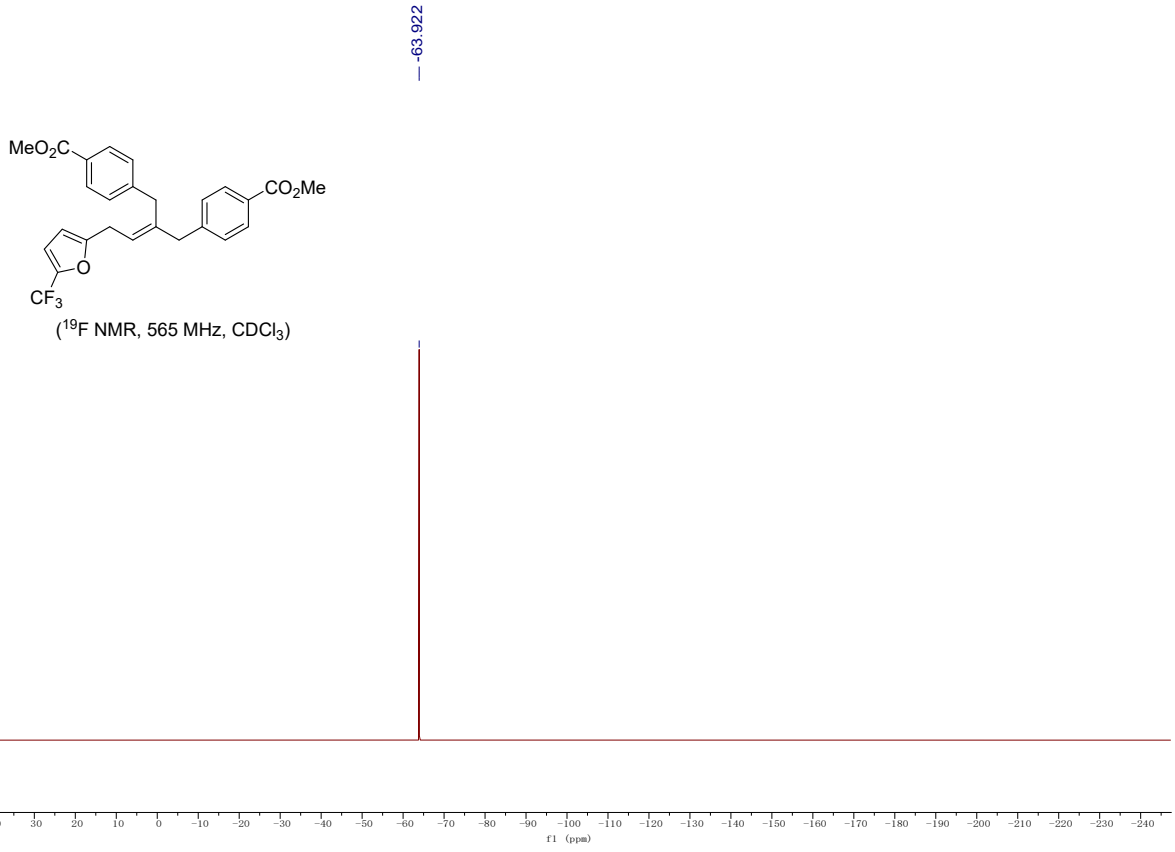


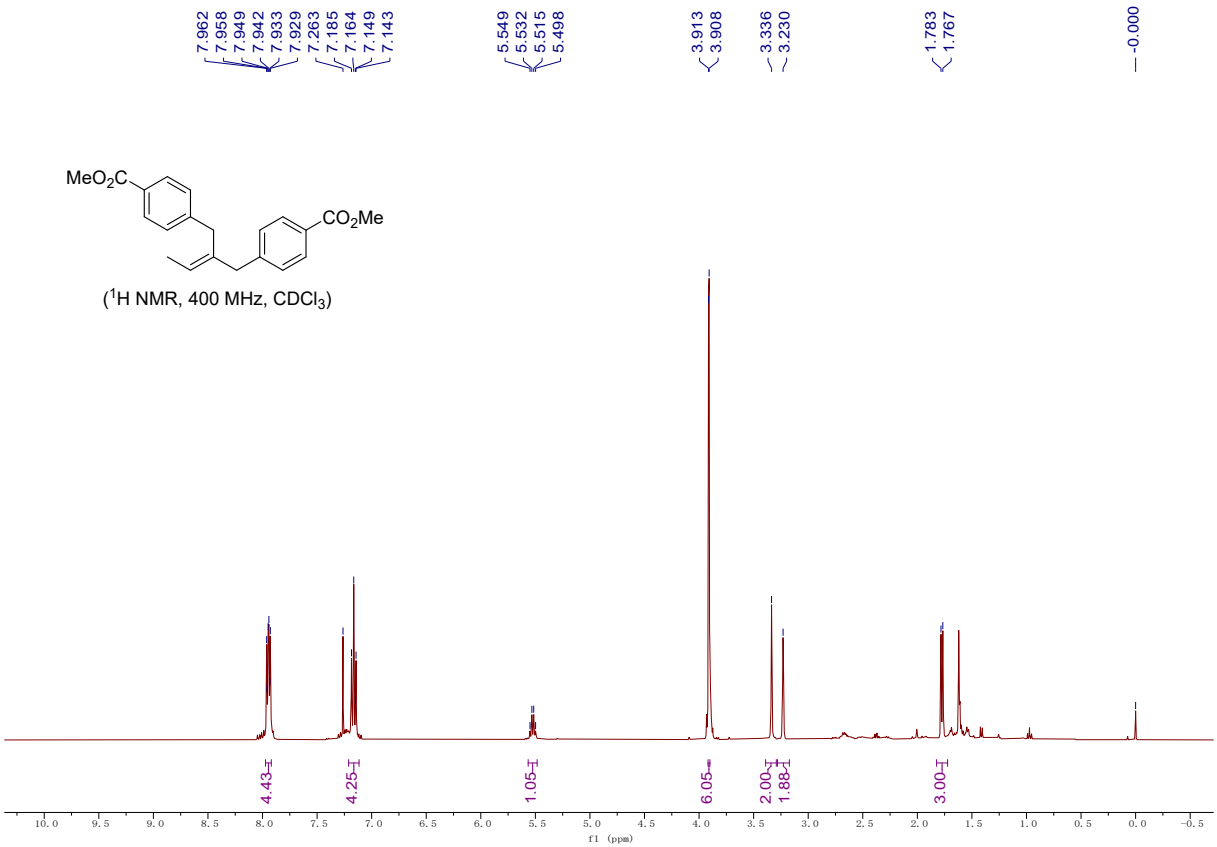
(^{1}H NMR, 400 MHz, $CDCl_3$)



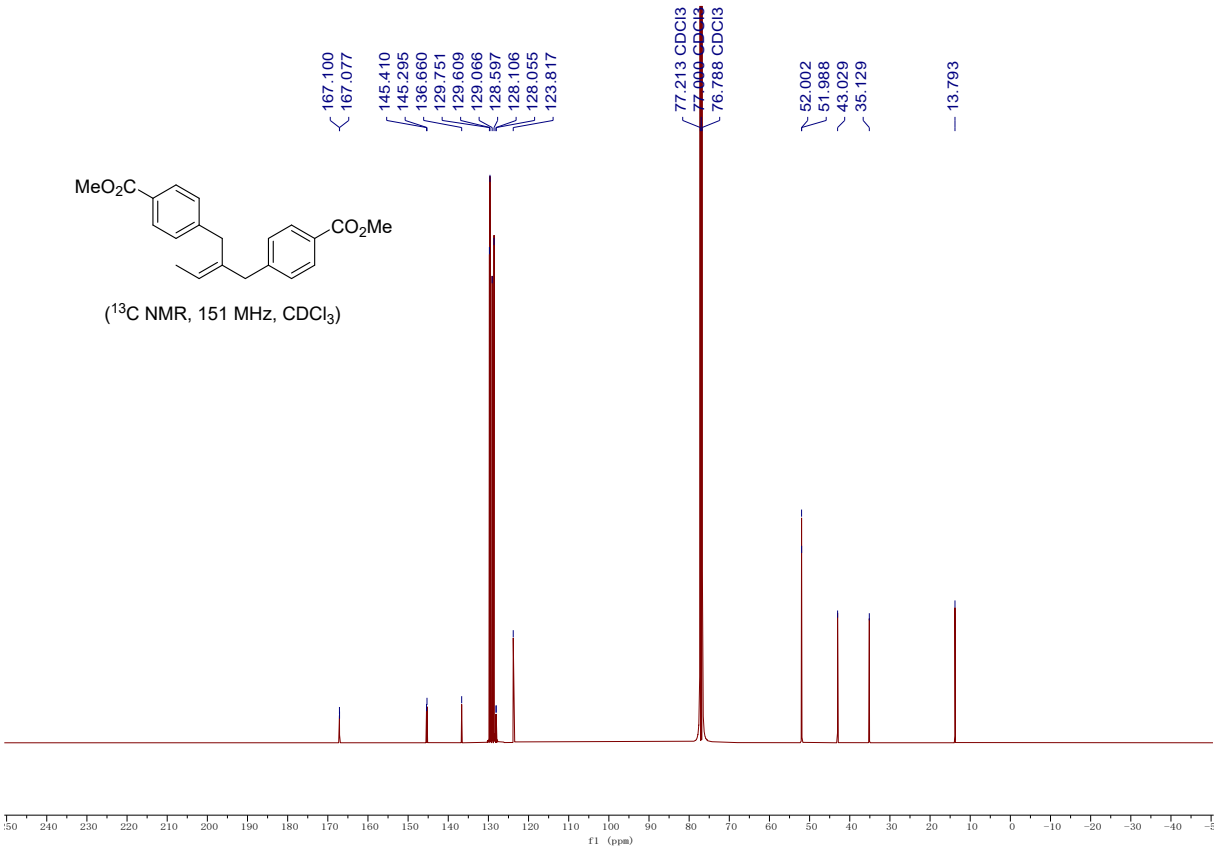


(^{13}C NMR, 151 MHz, $CDCl_3$)

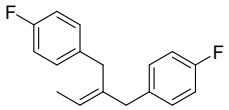

-63.922
MeO2C
CO2Me
O
CF3
(19F NMR, 565 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)



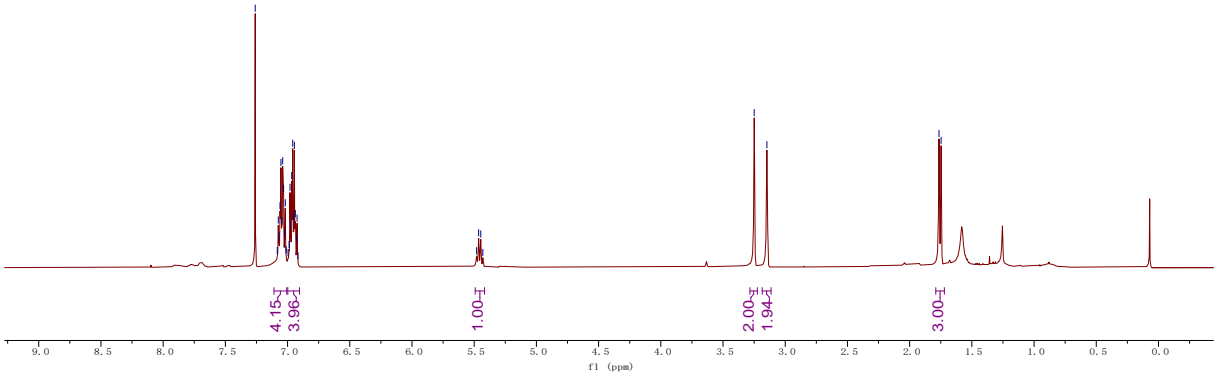
(^{1}H NMR, 400 MHz, $CDCl_3$)

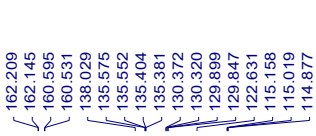


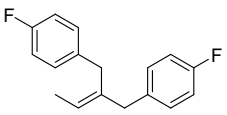
(^{13}C NMR, 151 MHz, $CDCl_3$)



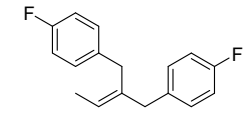
(^{1}H NMR, 400 MHz, $CDCl_3$)



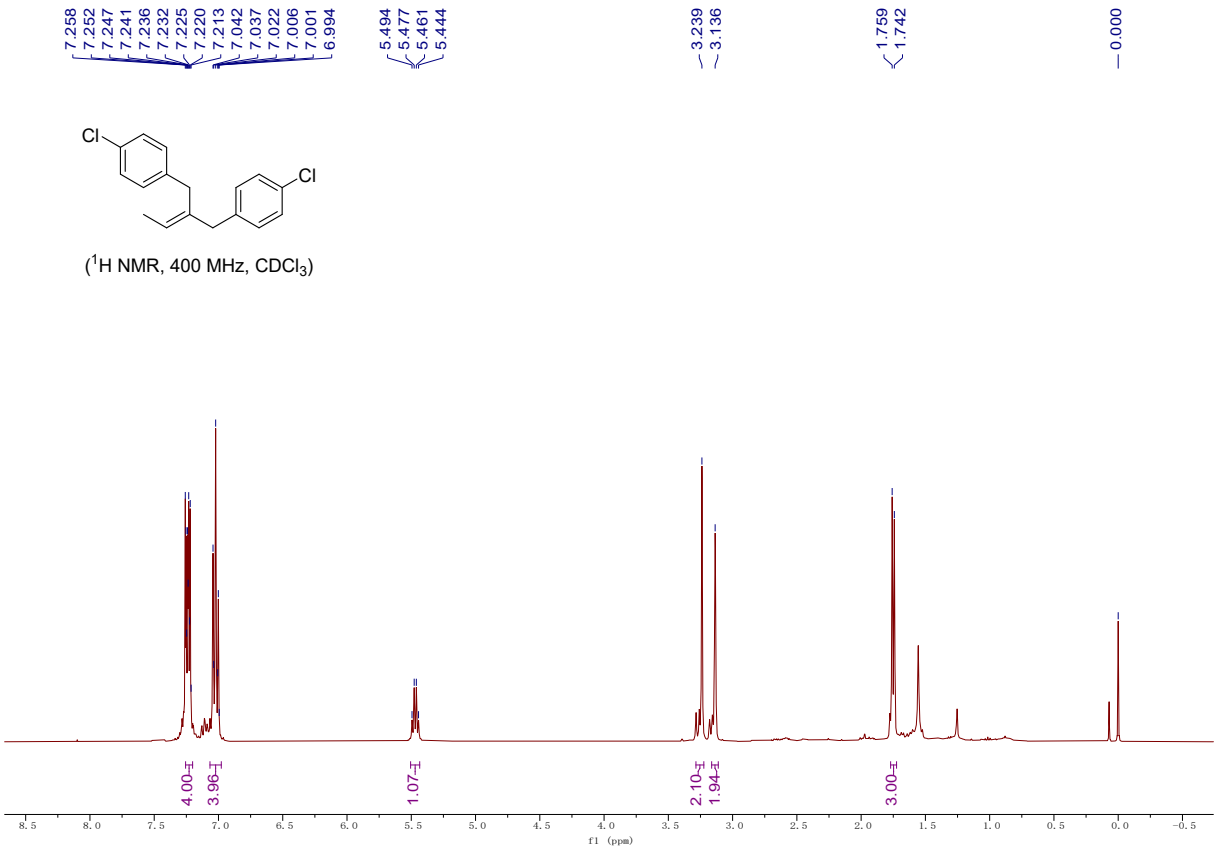




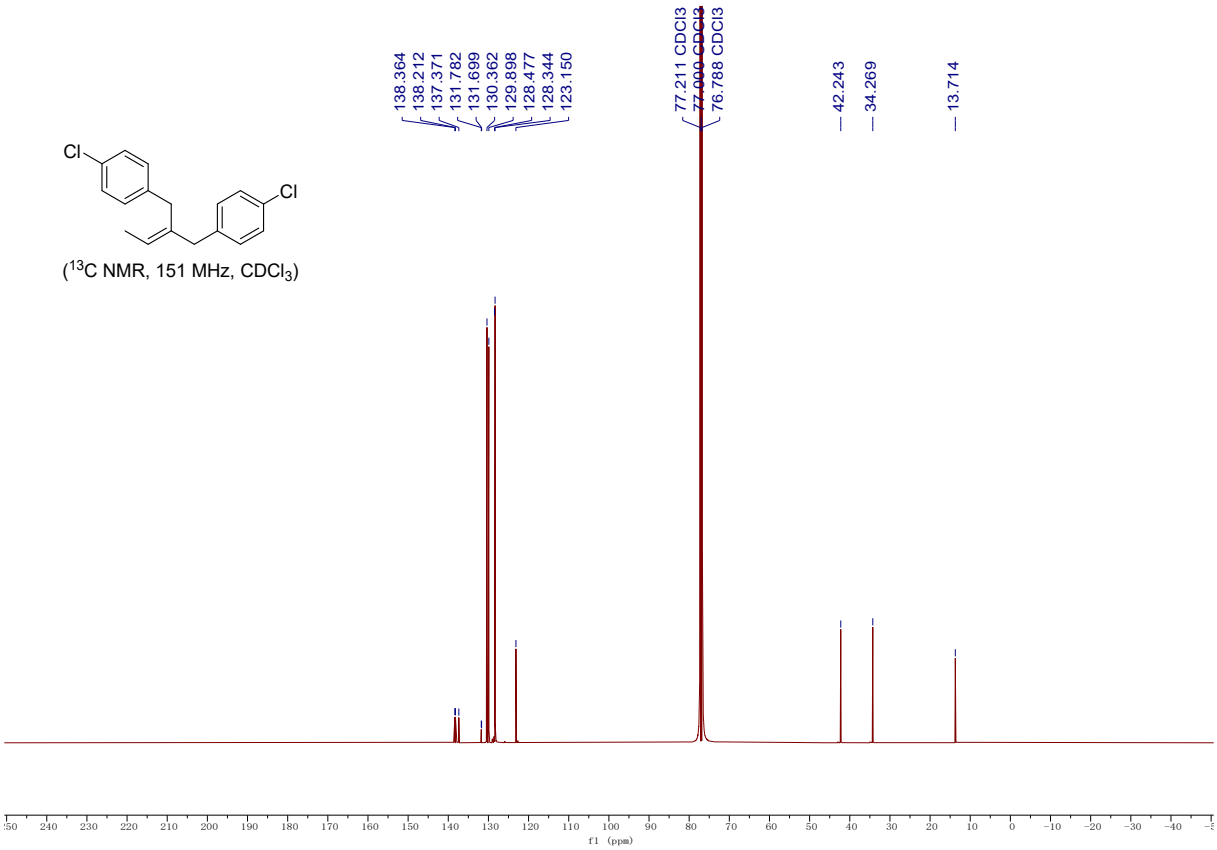
(^{13}C NMR, 151 MHz, $CDCl_3$)



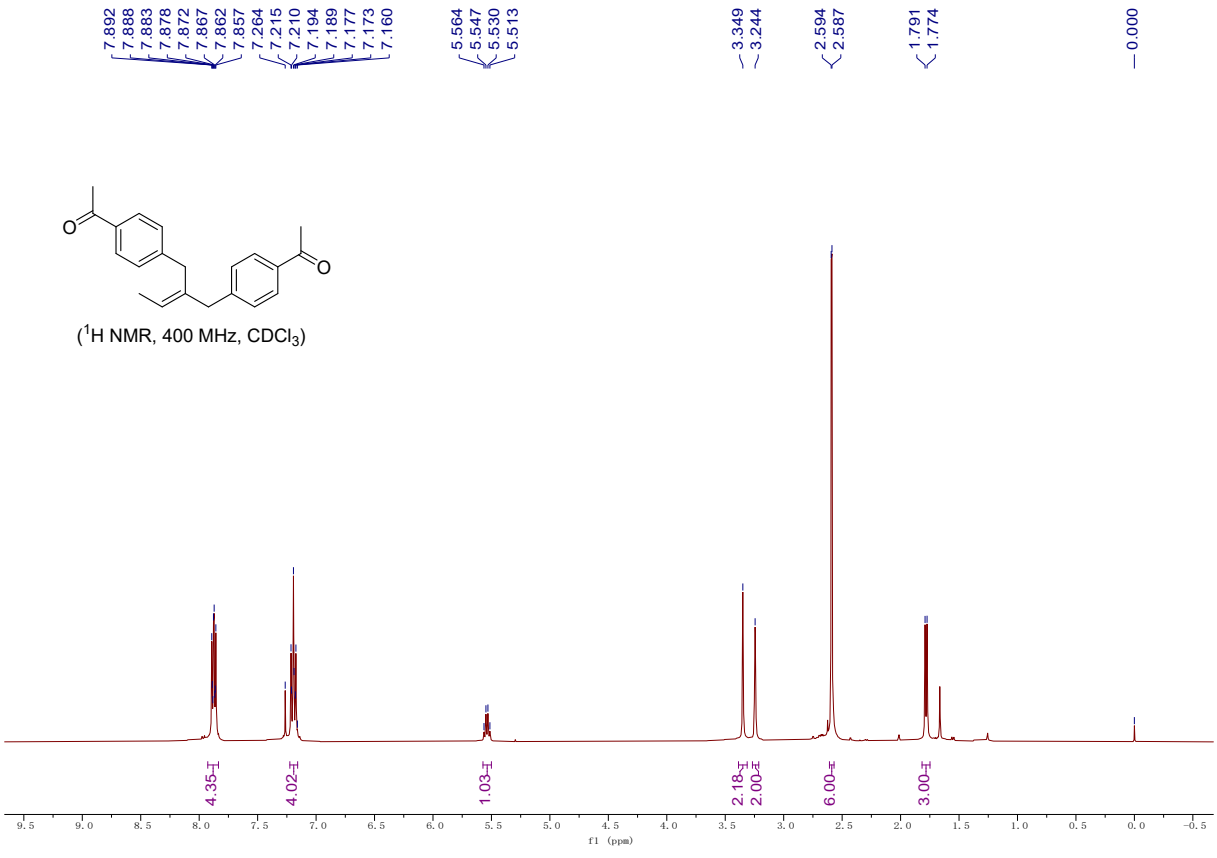
(^{19}F NMR, 565 MHz, $CDCl_3$)

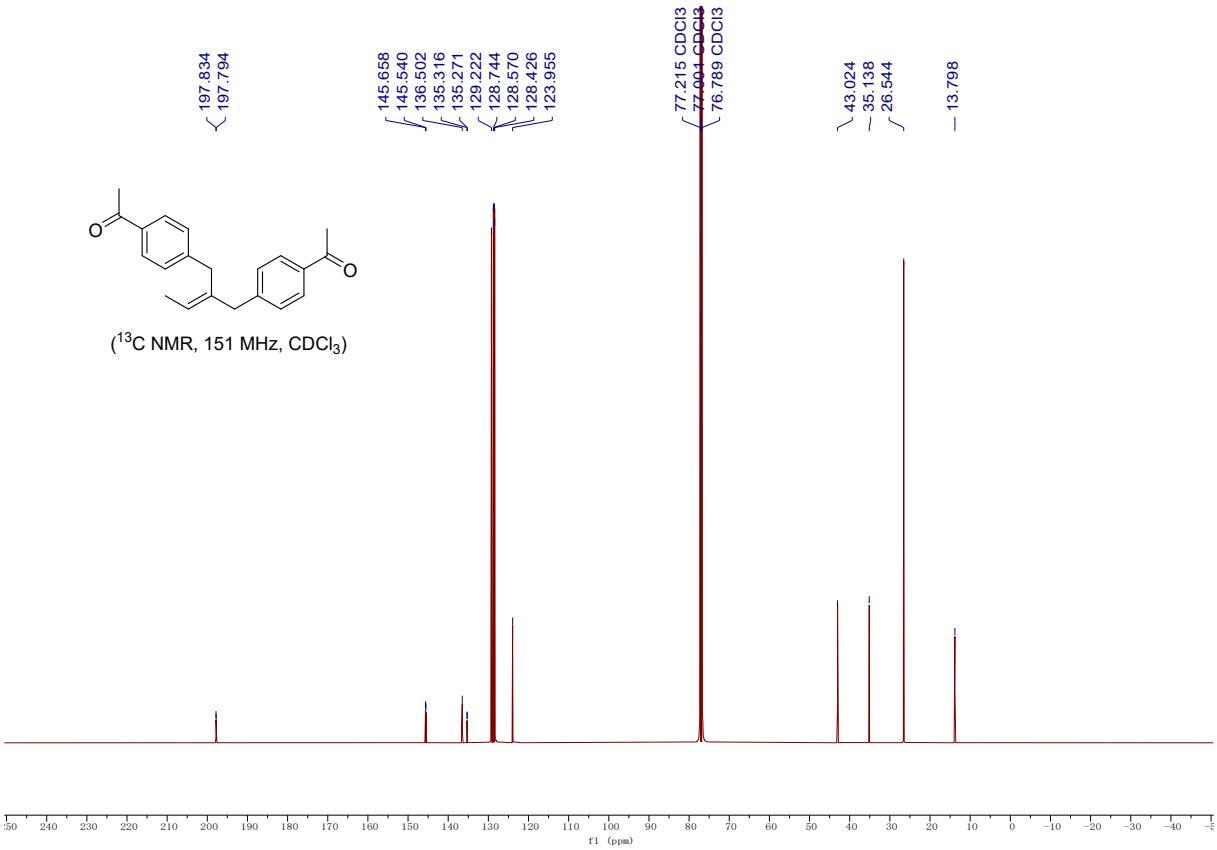


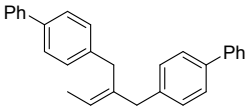
(^{1}H NMR, 400 MHz, $CDCl_3$)



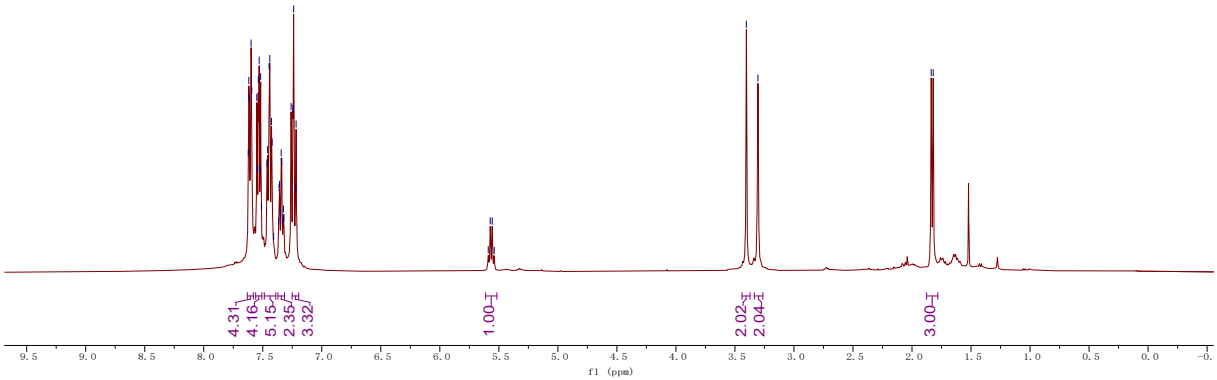
(^{13}C NMR, 151 MHz, $CDCl_3$)

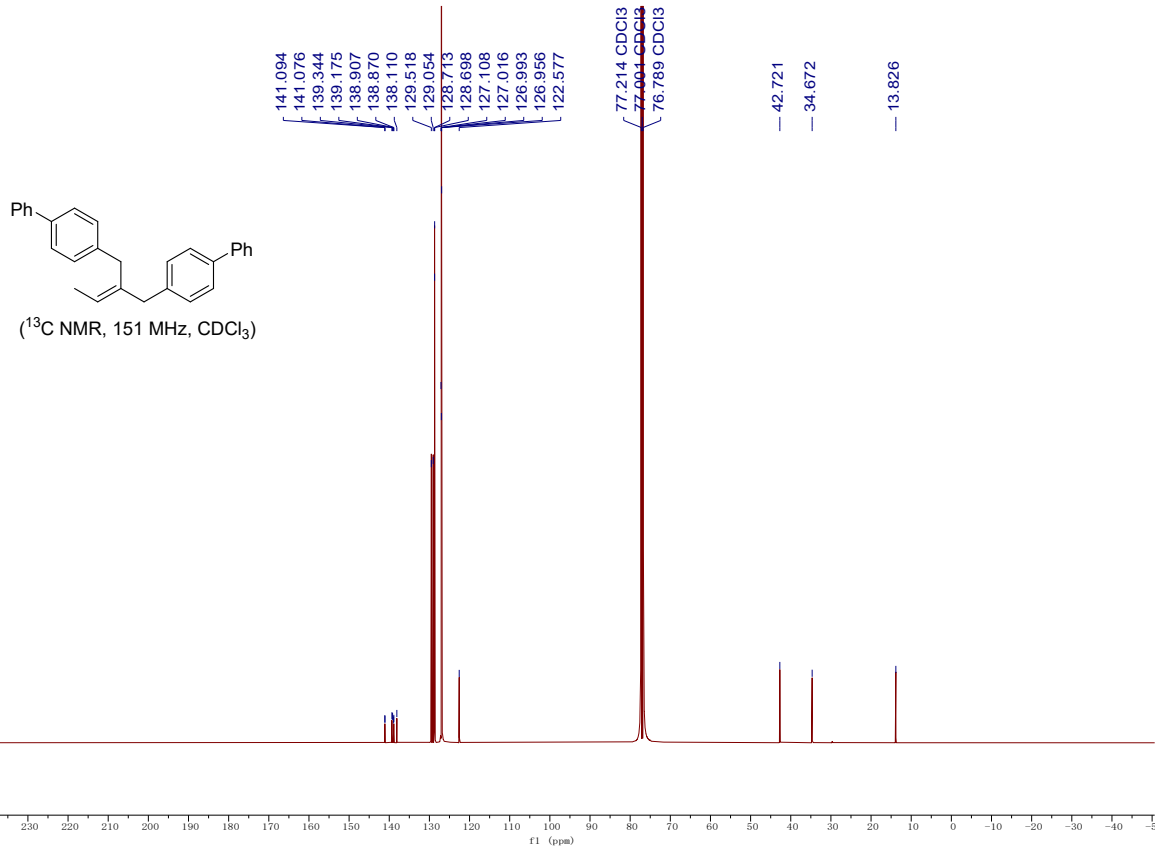

7.892
7.888
7.883
7.878
7.872
7.867
7.862
7.857
7.264
7.215
7.210
7.194
7.189
7.177
7.173
7.160
5.564
5.547
5.530
5.513
3.349
3.244
2.594
2.587
1.791
1.774
0.000
O
O
(1H NMR, 400 MHz, CDCl3)
4.35
4.02
1.03
2.18
2.00
6.00
3.00
f1 (ppm)


197.834
197.794
145.658
145.540
136.502
135.316
135.271
129.222
128.744
128.570
128.426
123.955
77.215 CDCl3
77.001 CDCl3
76.789 CDCl3
43.024
35.138
26.544
13.798
O
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

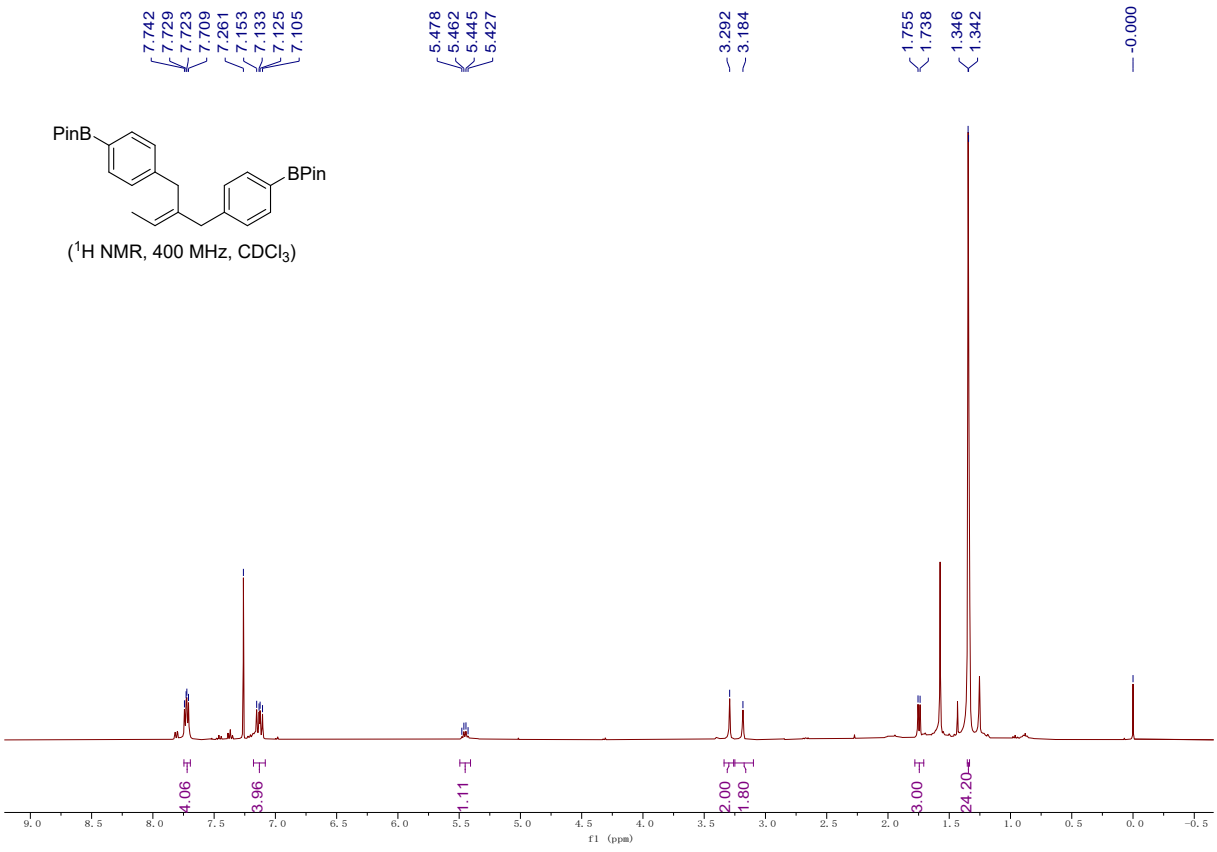


(^{1}H NMR, 400 MHz, $CDCl_3$)

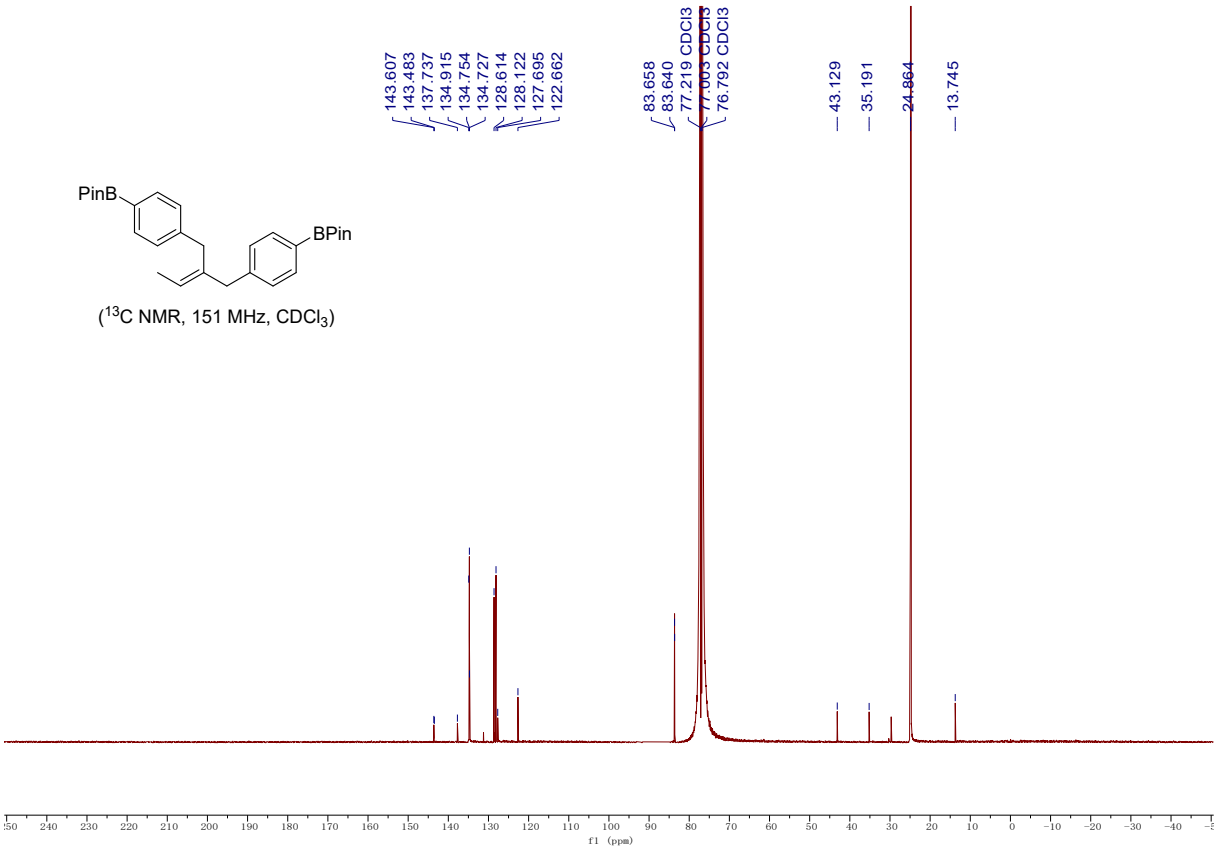




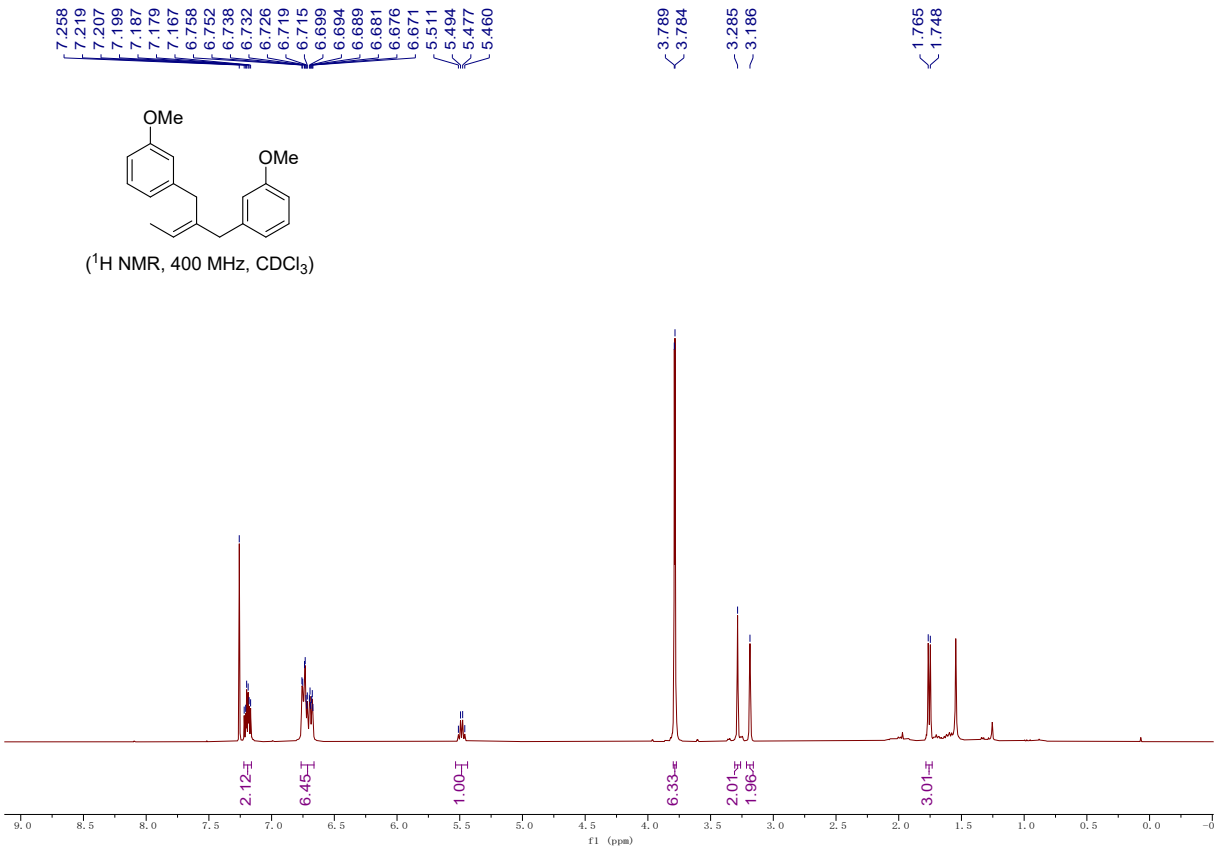
(^{13}C NMR, 151 MHz, $CDCl_3$)



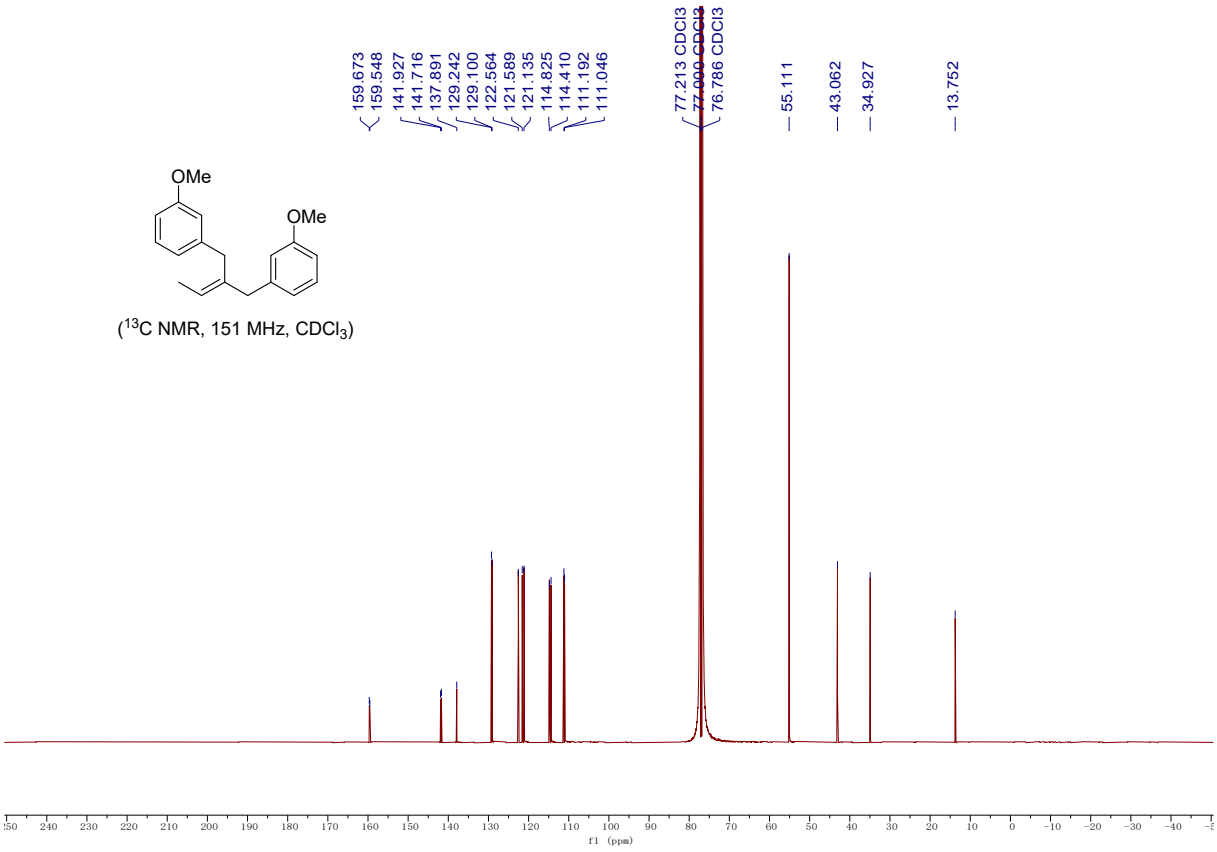
(^{1}H NMR, 400 MHz, $CDCl_3$)



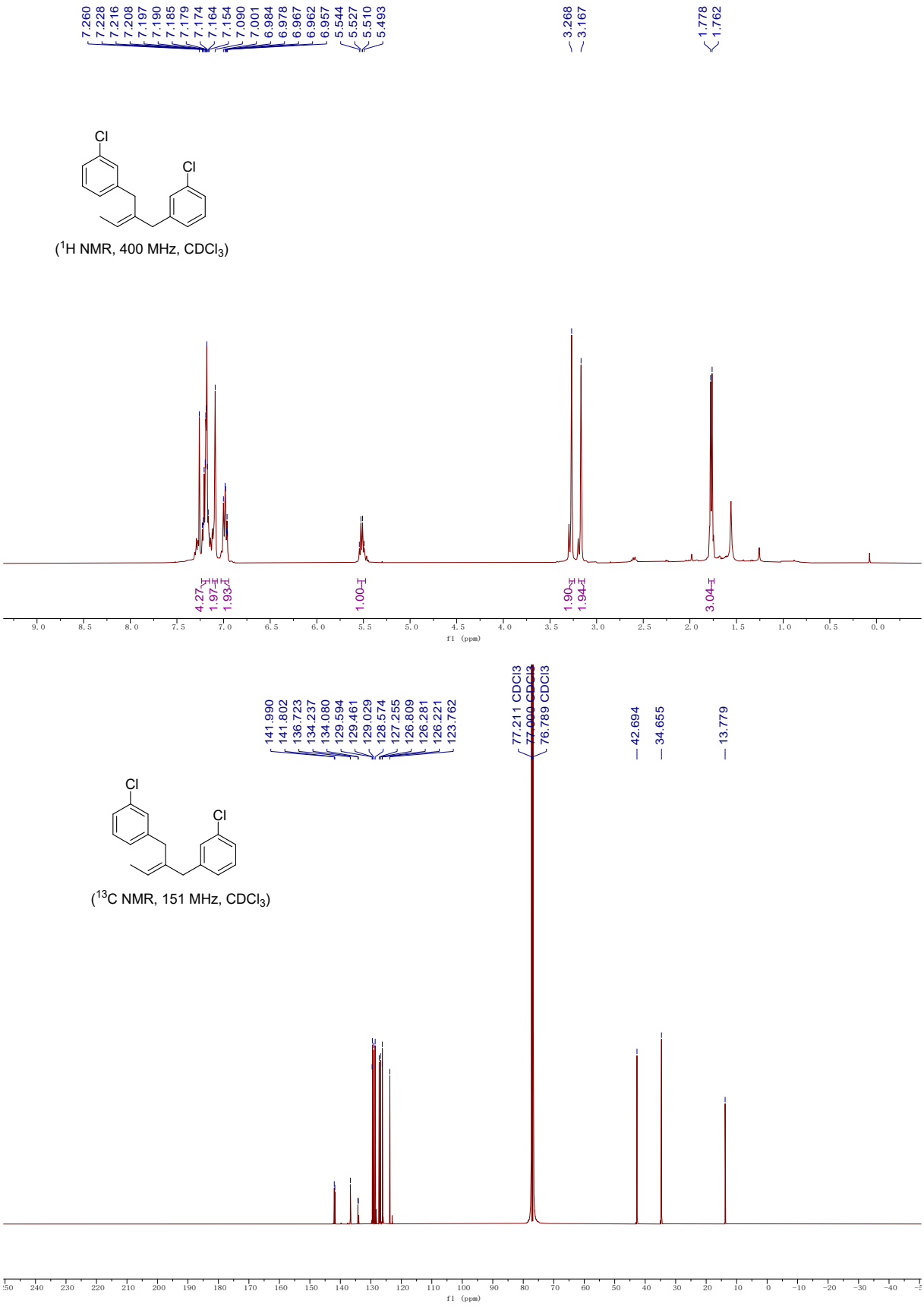
(^{13}C NMR, 151 MHz, $CDCl_3$)



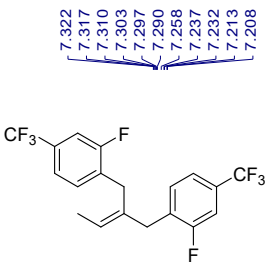
(^{1}H NMR, 400 MHz, $CDCl_3$)



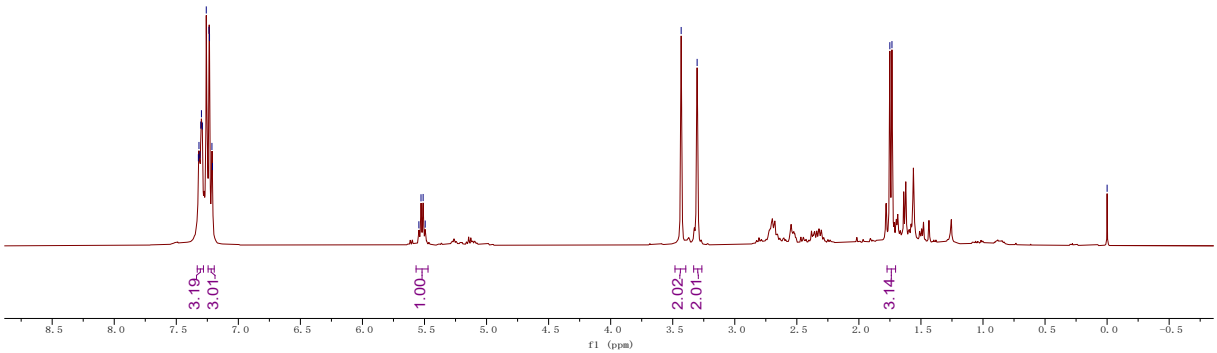
(^{13}C NMR, 151 MHz, $CDCl_3$)

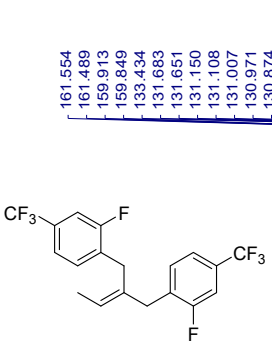


Containing a trace amount of impurity that failed to be separated.

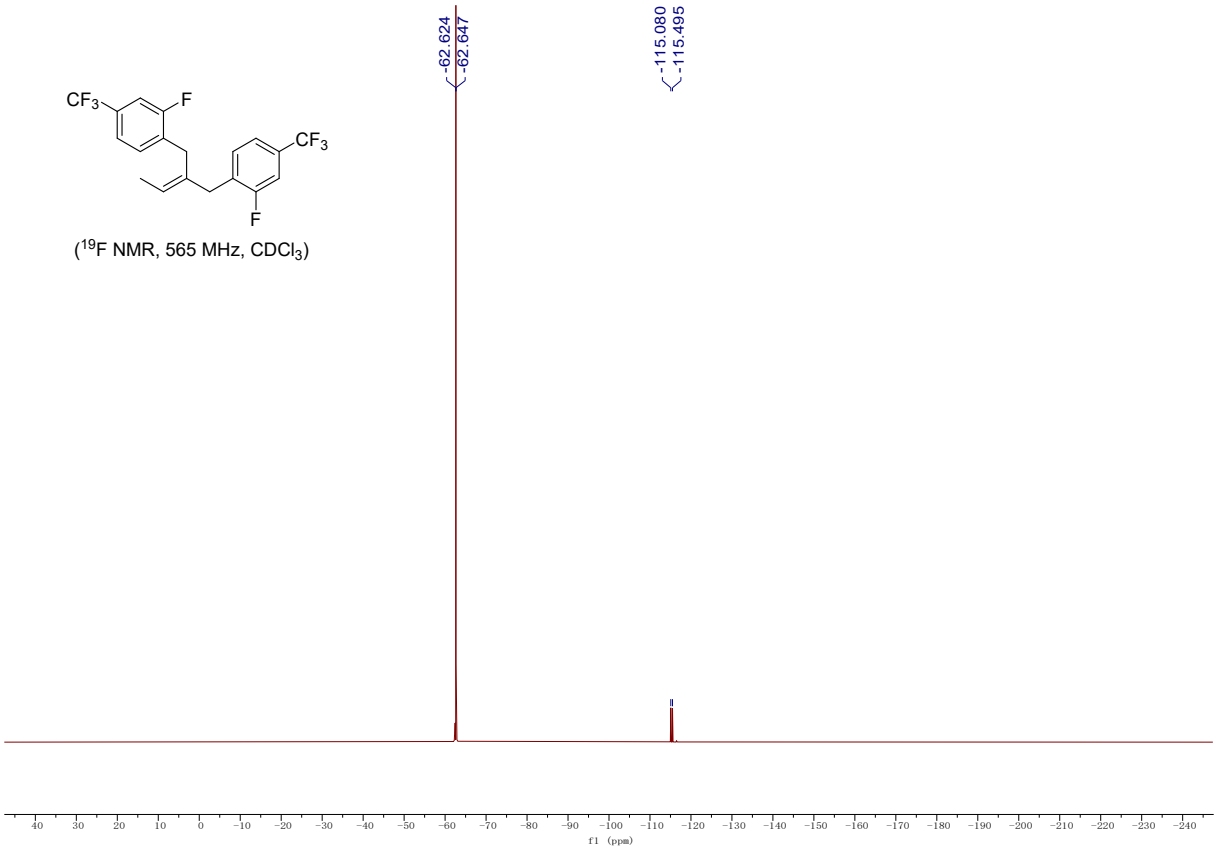


(^{1}H NMR, 400 MHz, $CDCl_3$)

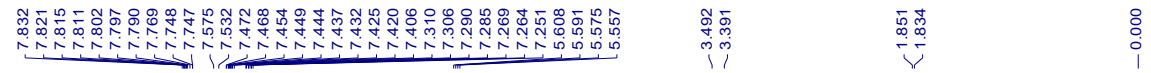


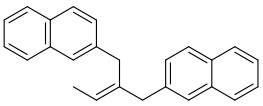


(^{13}C NMR, 151 MHz, $CDCl_3$)

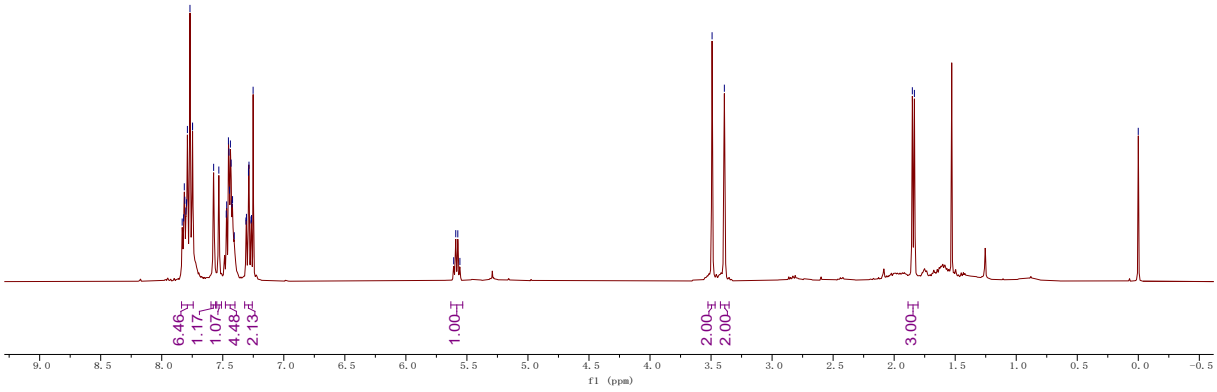


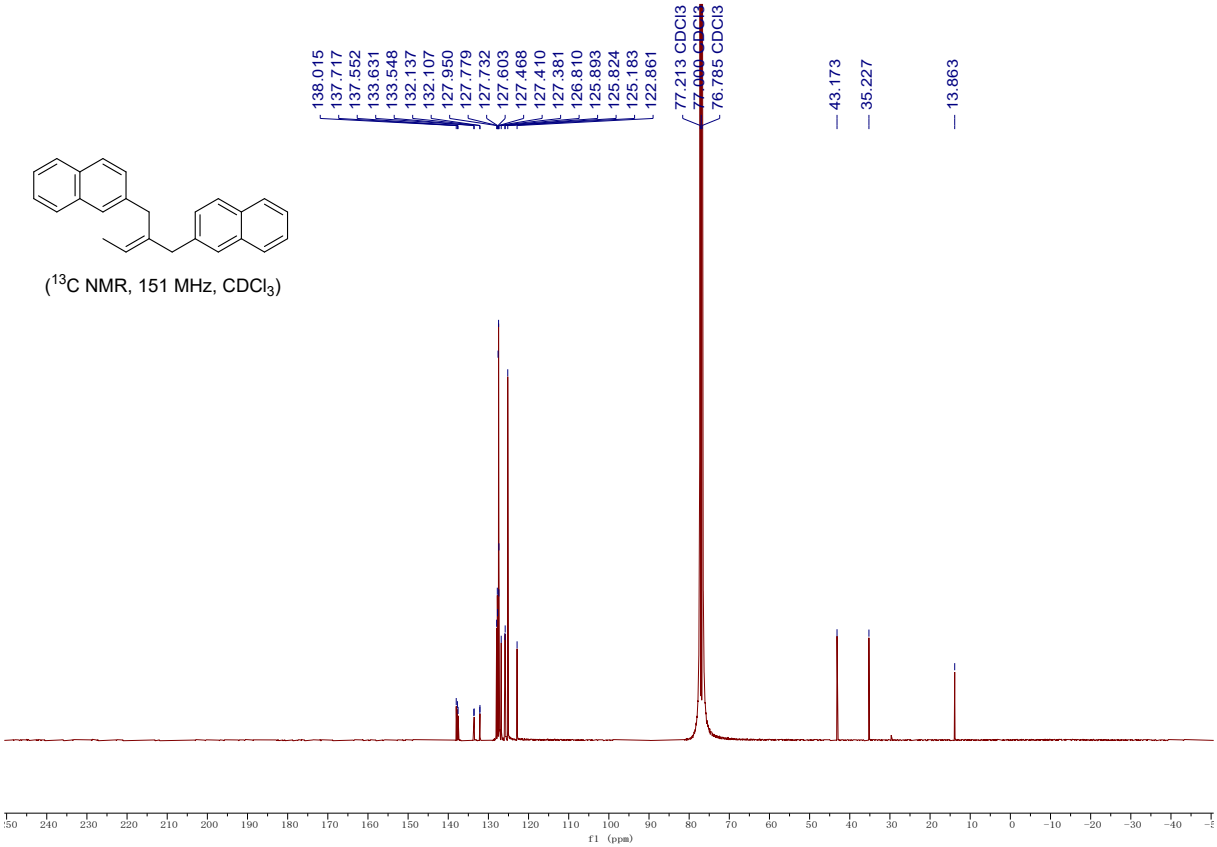
(^{19}F NMR, 565 MHz, $CDCl_3$)



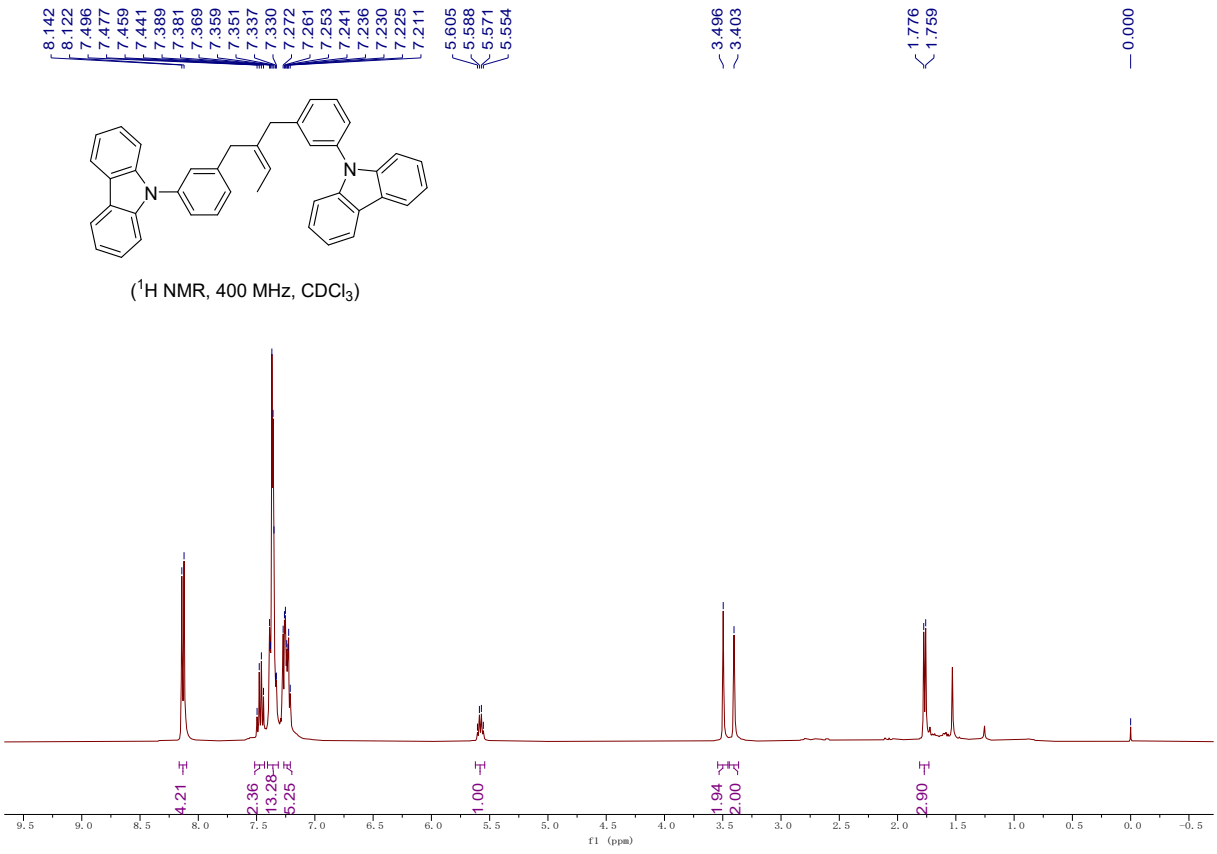


(^{1}H NMR, 400 MHz, $CDCl_3$)

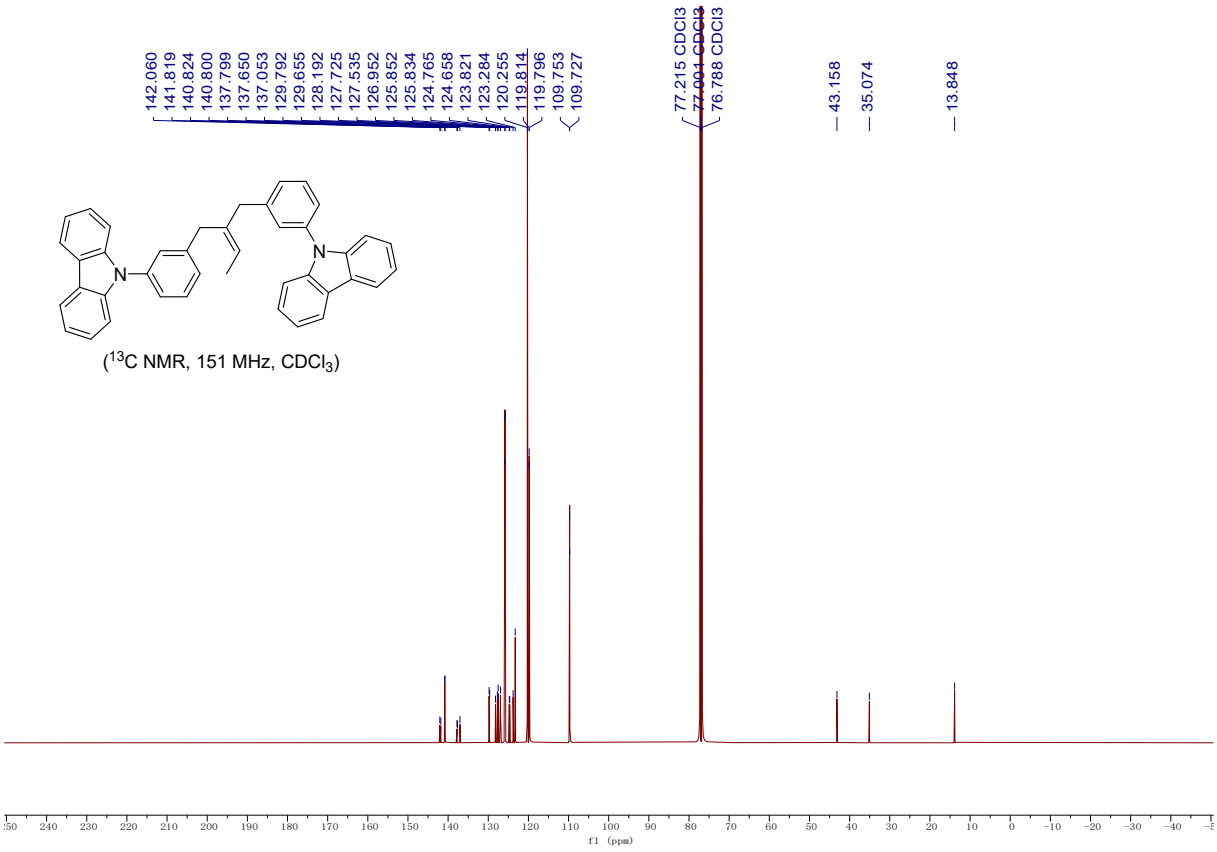




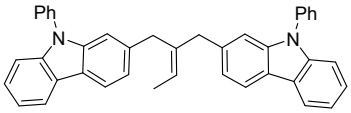
(^{13}C NMR, 151 MHz, $CDCl_3$)



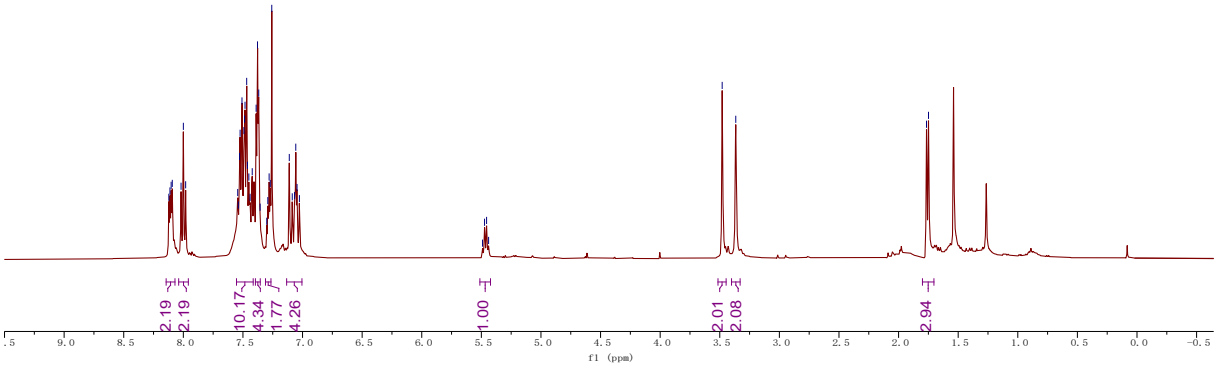
(^{1}H NMR, 400 MHz, $CDCl_3$)

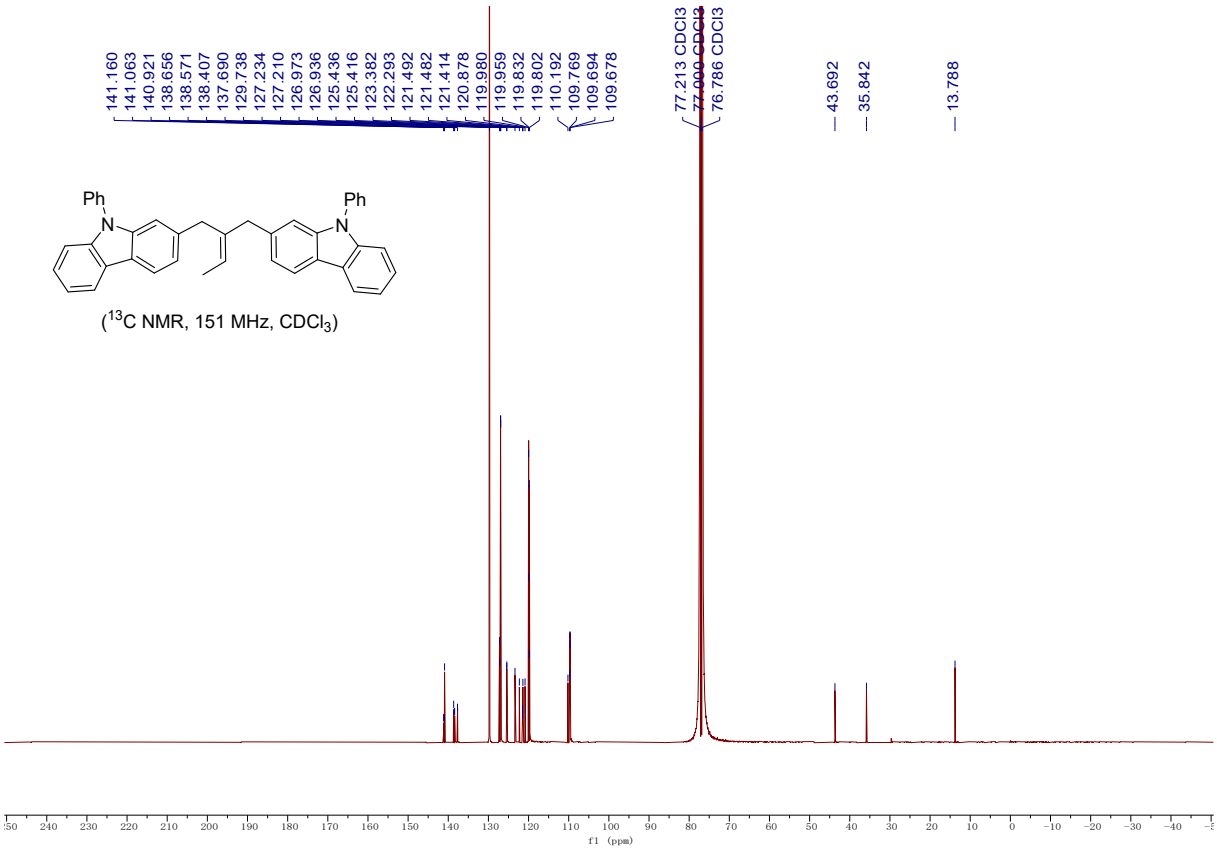


(^{13}C NMR, 151 MHz, $CDCl_3$)

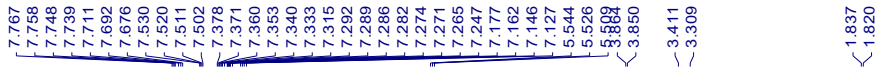


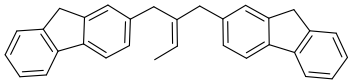
(^{1}H NMR, 400 MHz, $CDCl_3$)



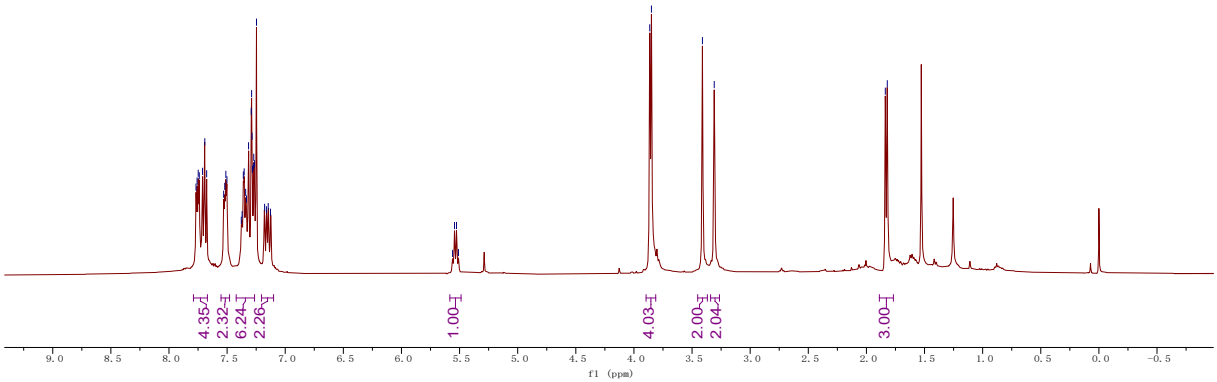


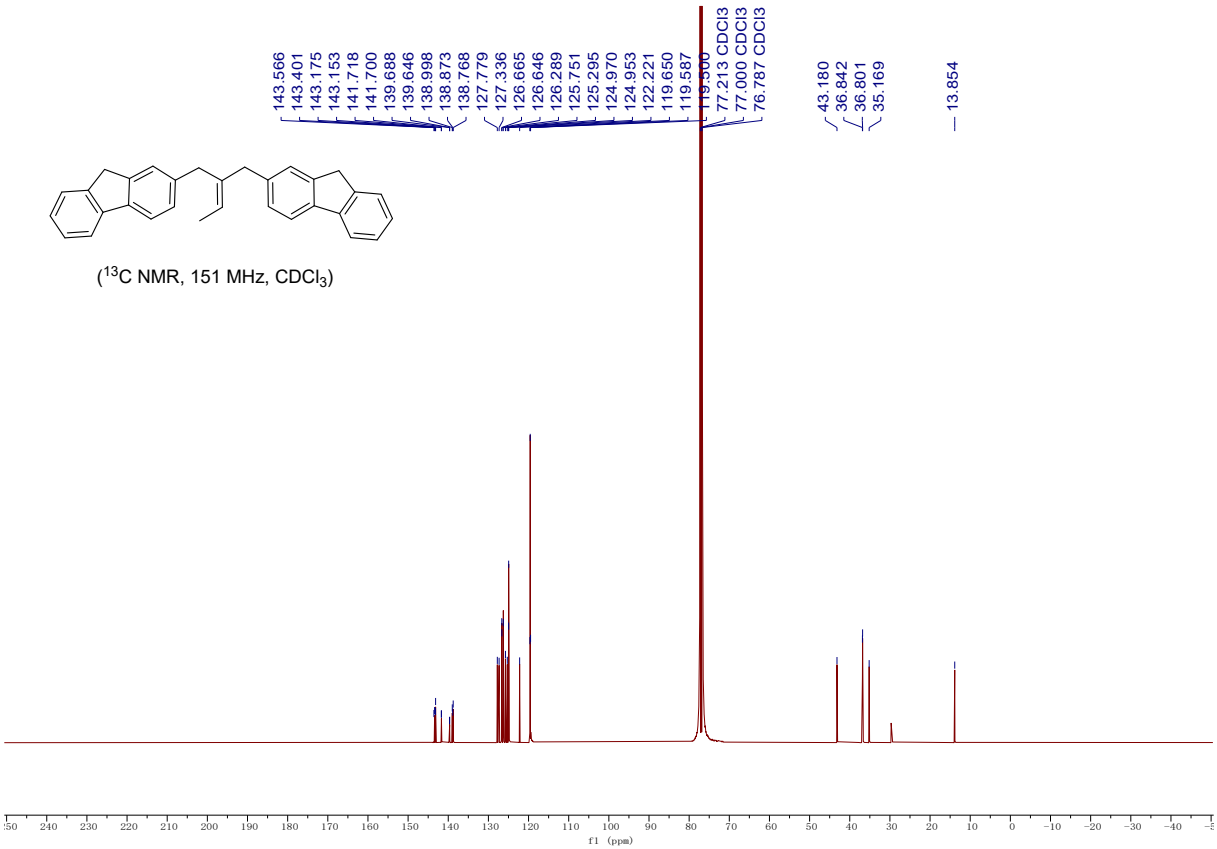
(^{13}C NMR, 151 MHz, $CDCl_3$)



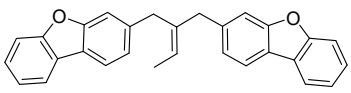


(^{1}H NMR, 400 MHz, $CDCl_3$)

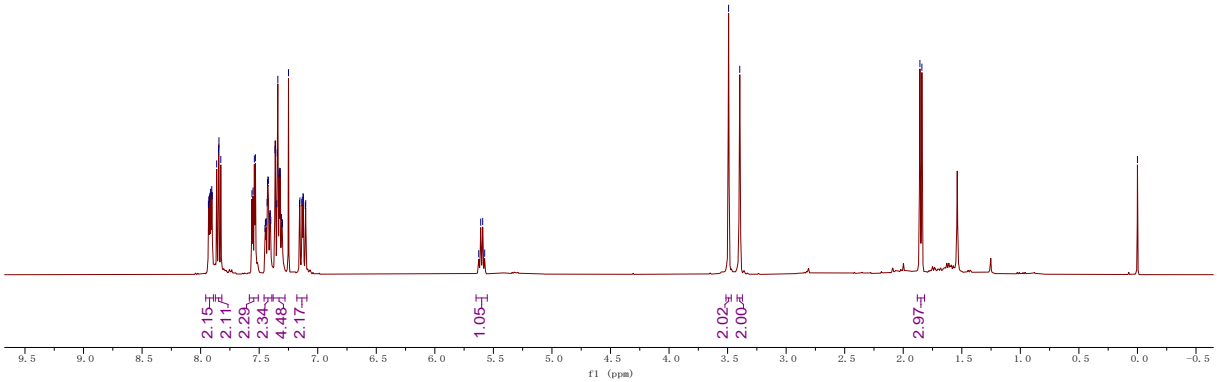


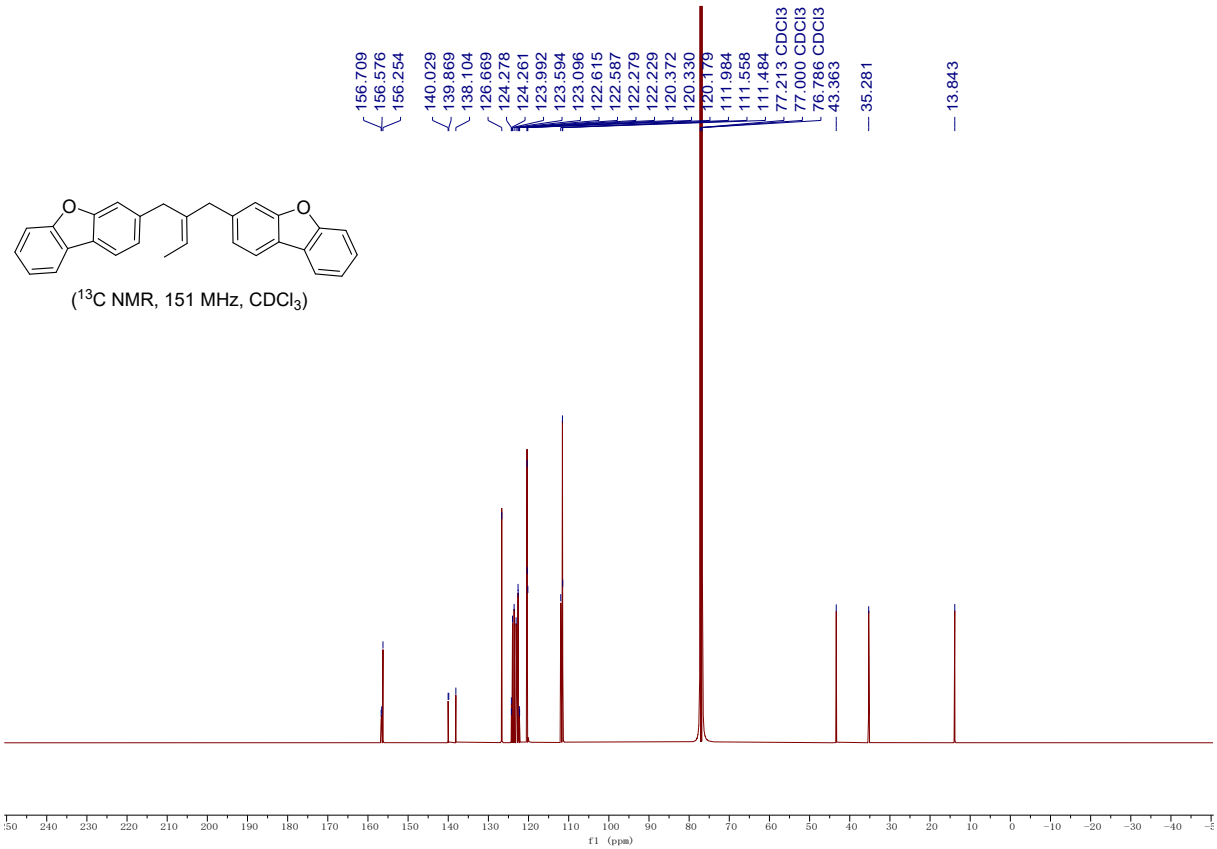


(^{13}C NMR, 151 MHz, $CDCl_3$)

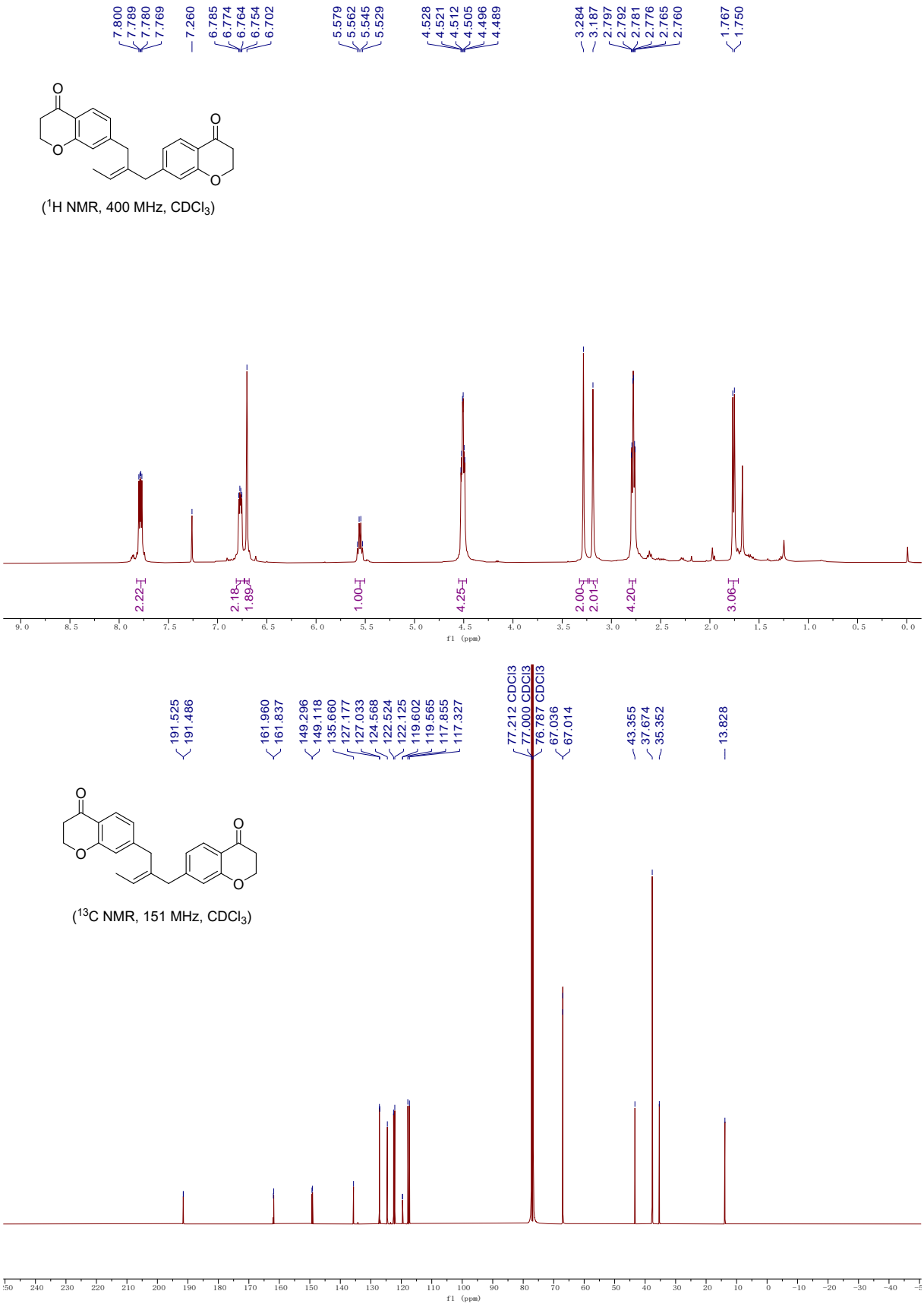


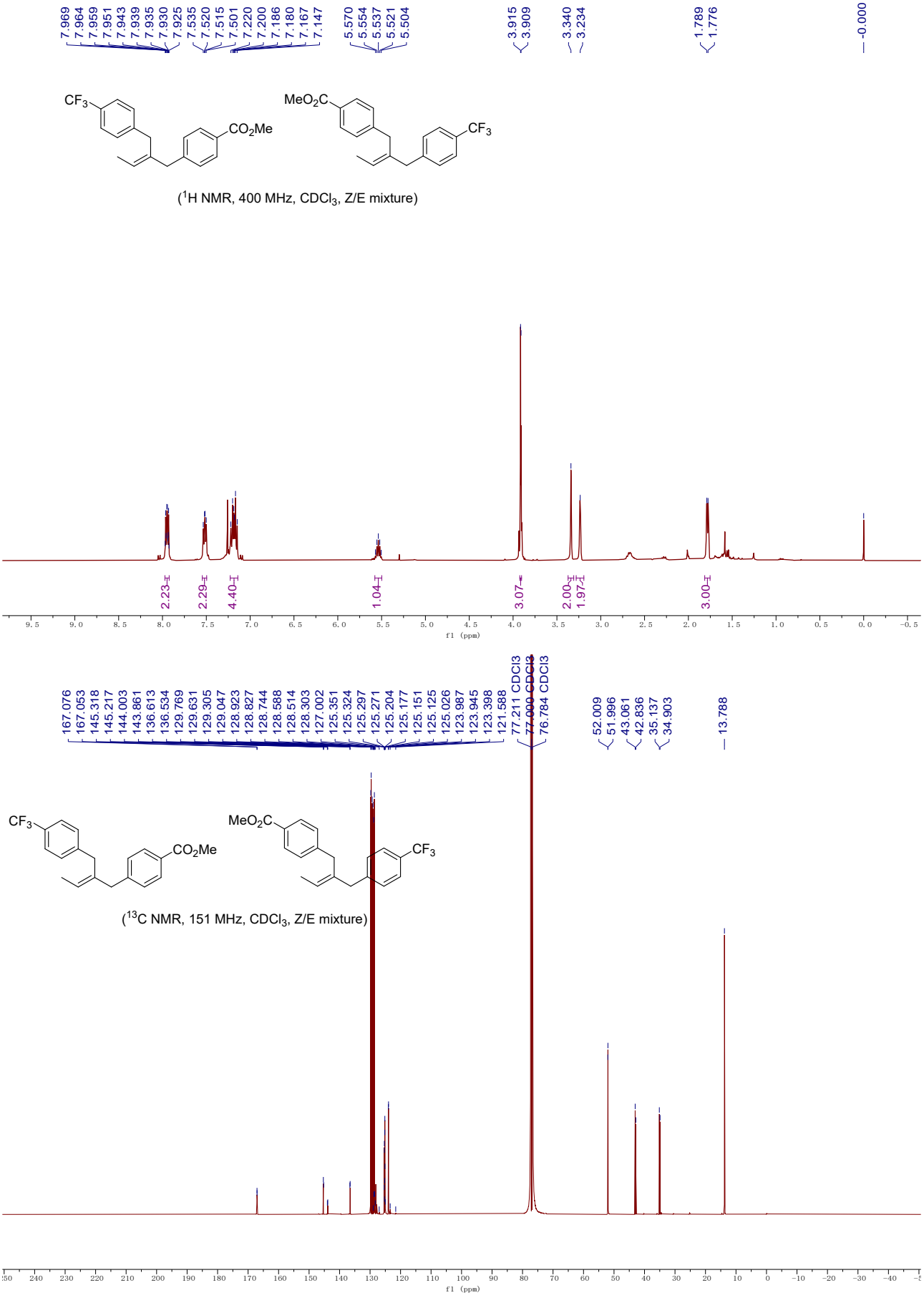
(^{1}H NMR, 400 MHz, $CDCl_3$)

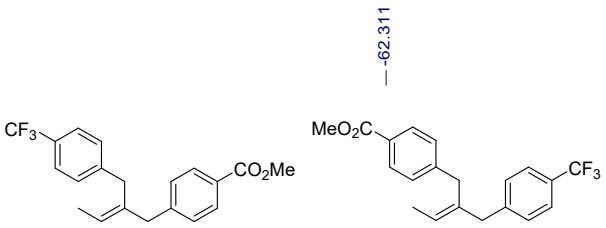




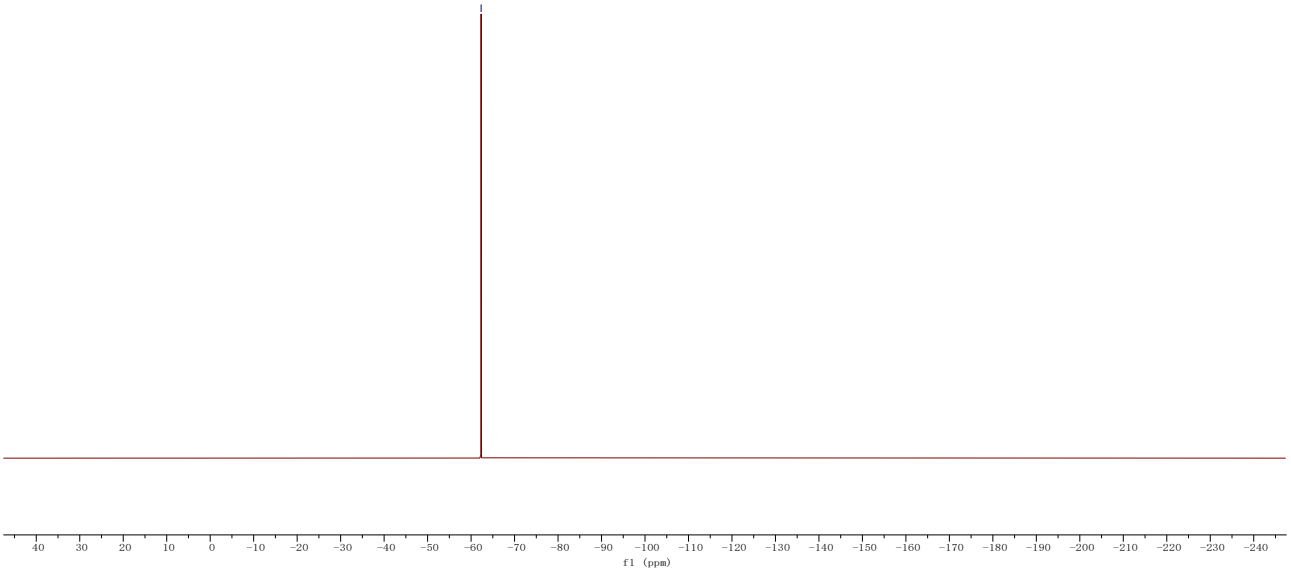
(^{13}C NMR, 151 MHz, $CDCl_3$)

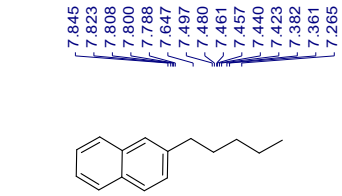

7.800
7.789
7.780
7.769
7.260
6.785
6.774
6.764
6.754
6.702
5.579
5.562
5.545
5.529
4.528
4.521
4.512
4.505
4.496
4.489
3.284
3.187
2.797
2.792
2.781
2.776
2.765
2.760
1.767
1.750
O
O
O
O
(1H NMR, 400 MHz, CDCl3)
2.22
2.18
1.89
1.00
4.25
2.00
2.01
4.20
3.06
f1 (ppm)
191.525
191.486
161.960
161.837
149.296
149.118
135.660
127.177
127.033
124.568
122.524
122.125
119.602
119.565
117.855
117.327
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
67.036
67.014
43.355
37.674
35.352
13.828
O
O
O
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)


7.969
7.964
7.959
7.951
7.943
7.939
7.935
7.930
7.925
7.535
7.520
7.515
7.501
7.220
7.200
7.186
7.180
7.167
7.147
5.570
5.554
5.537
5.521
5.504
3.915
3.909
3.340
3.234
1.789
1.776
-0.000
CF3
CO2Me
MeO2C
CF3
(1H NMR, 400 MHz, CDCl3, Z/E mixture)
2.23
2.29
4.40
1.04
3.07
2.00
1.97
3.00
f1 (ppm)
167.076
167.053
145.318
145.217
144.003
143.861
136.613
136.534
129.769
129.631
129.305
129.047
128.923
128.827
128.744
128.588
128.514
128.303
127.002
125.351
125.324
125.297
125.271
125.204
125.177
125.151
125.125
125.026
123.987
123.945
123.398
121.588
77.211 CDCl3
77.000 CDCl3
76.784 CDCl3
52.009
51.996
43.061
42.836
35.137
34.903
13.788
CF3
CO2Me
MeO2C
CF3
(13C NMR, 151 MHz, CDCl3, Z/E mixture)
f1 (ppm)

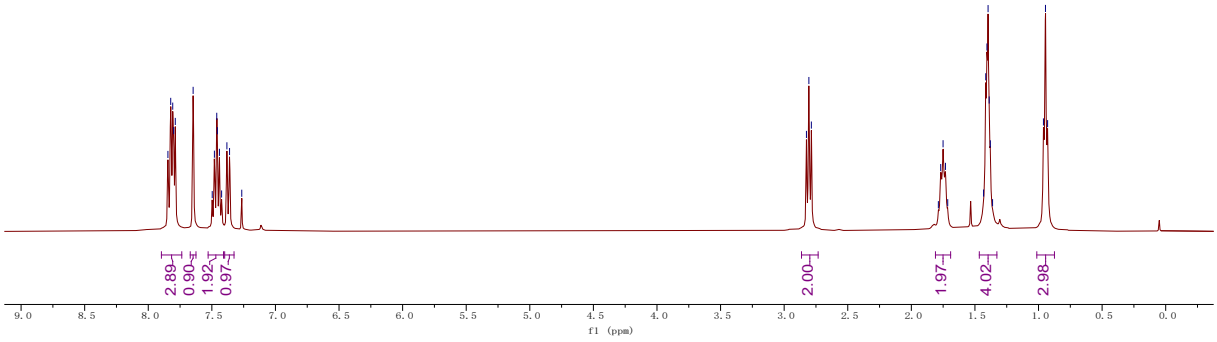


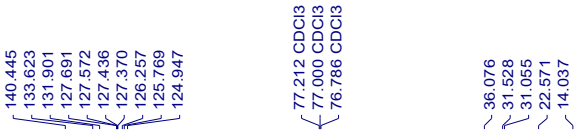
(^{19}F NMR, 565 MHz, $CDCl_3$, Z/E mixture)

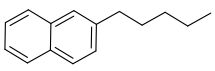




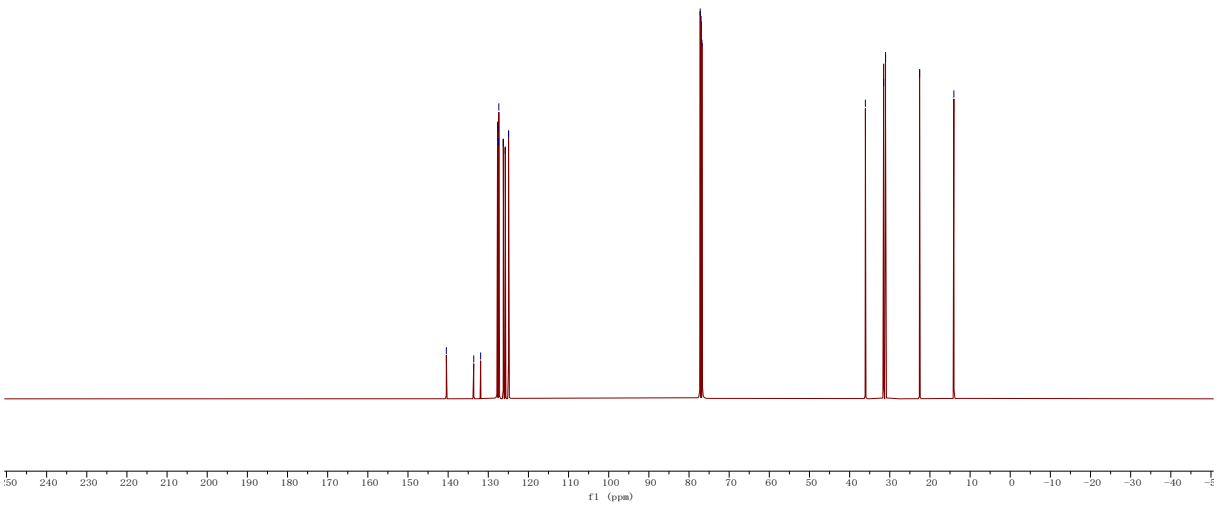
(^{1}H NMR, 400 MHz, $CDCl_3$)

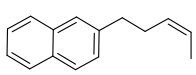




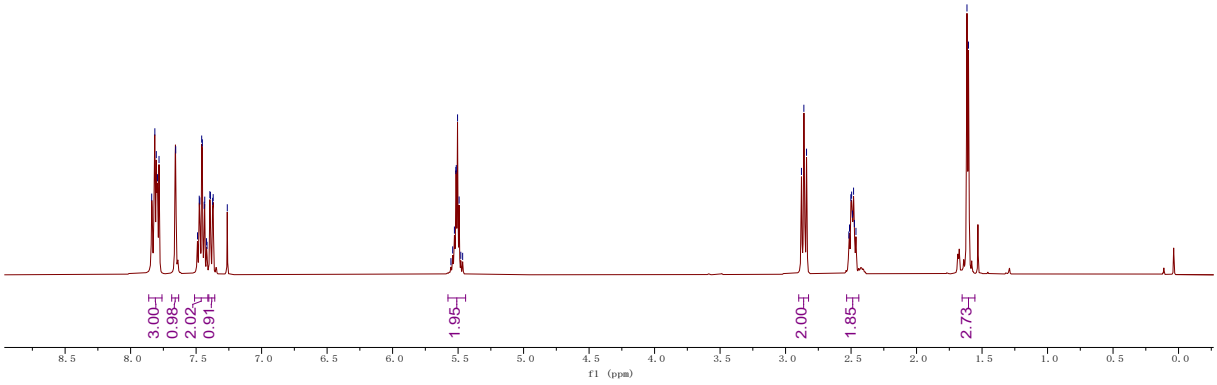


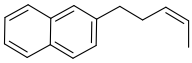
(^{13}C NMR, 151 MHz, $CDCl_3$)



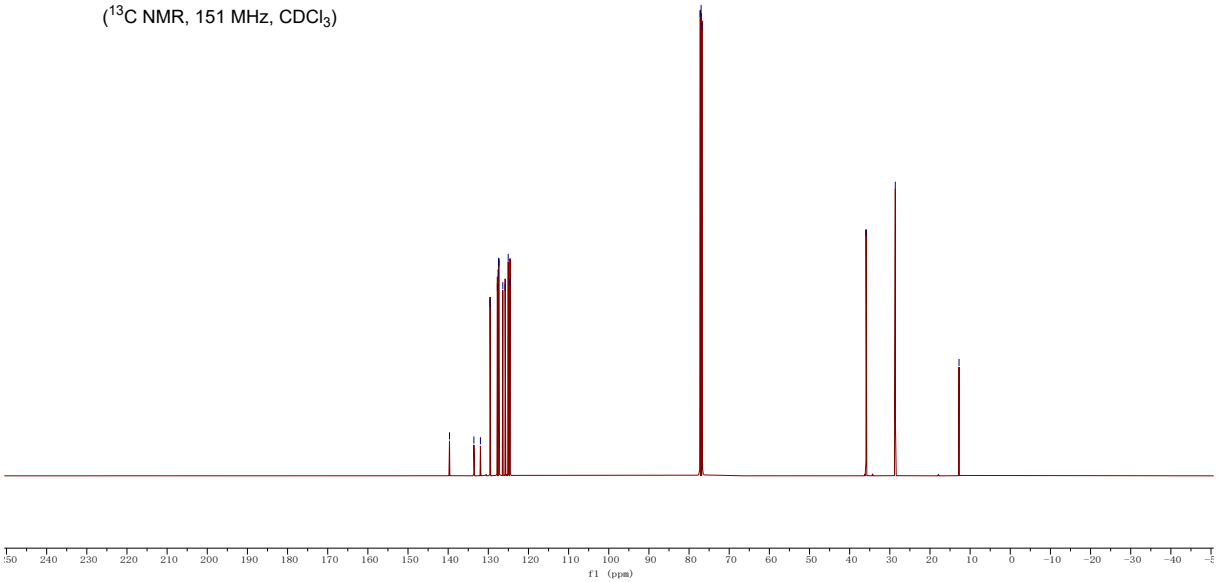


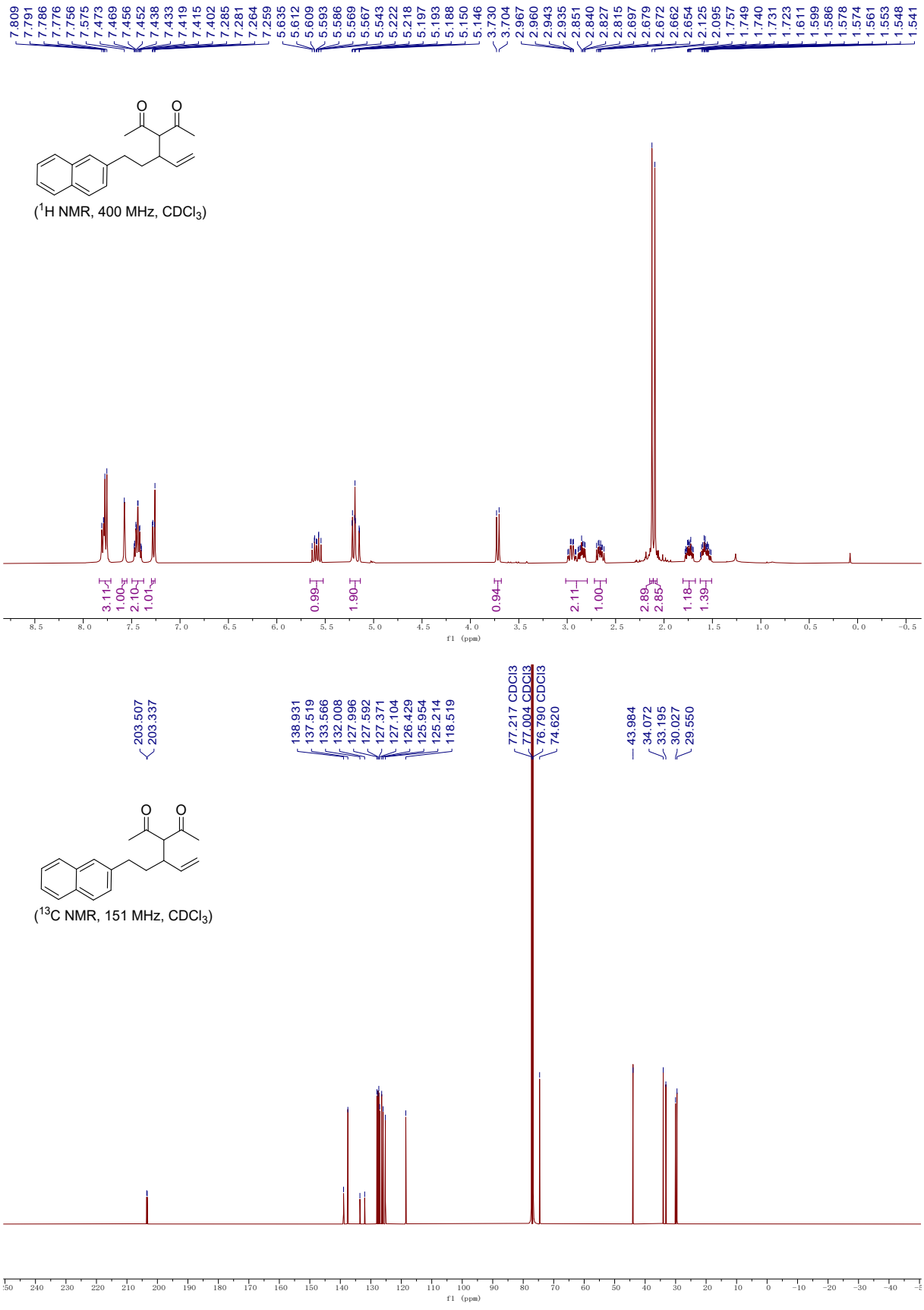
(^{1}H NMR, 400 MHz, $CDCl_3$)

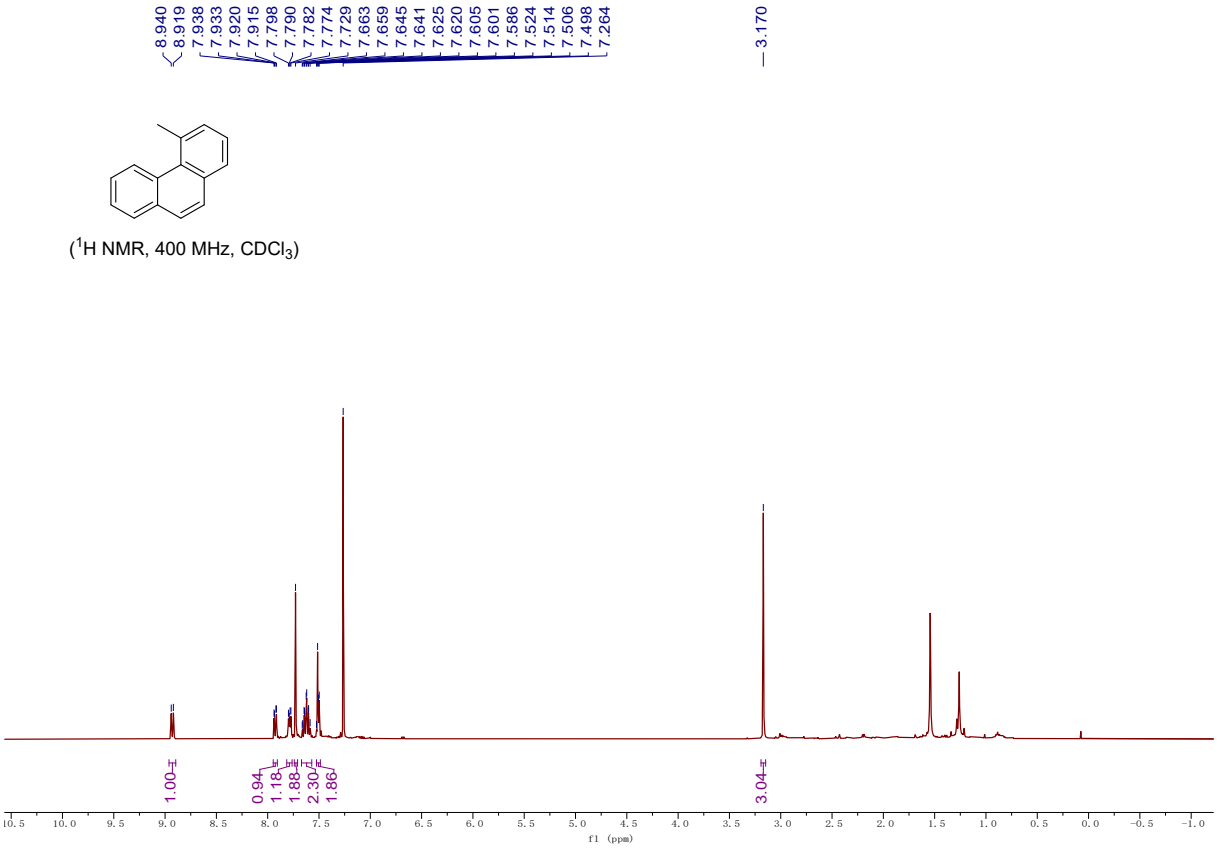




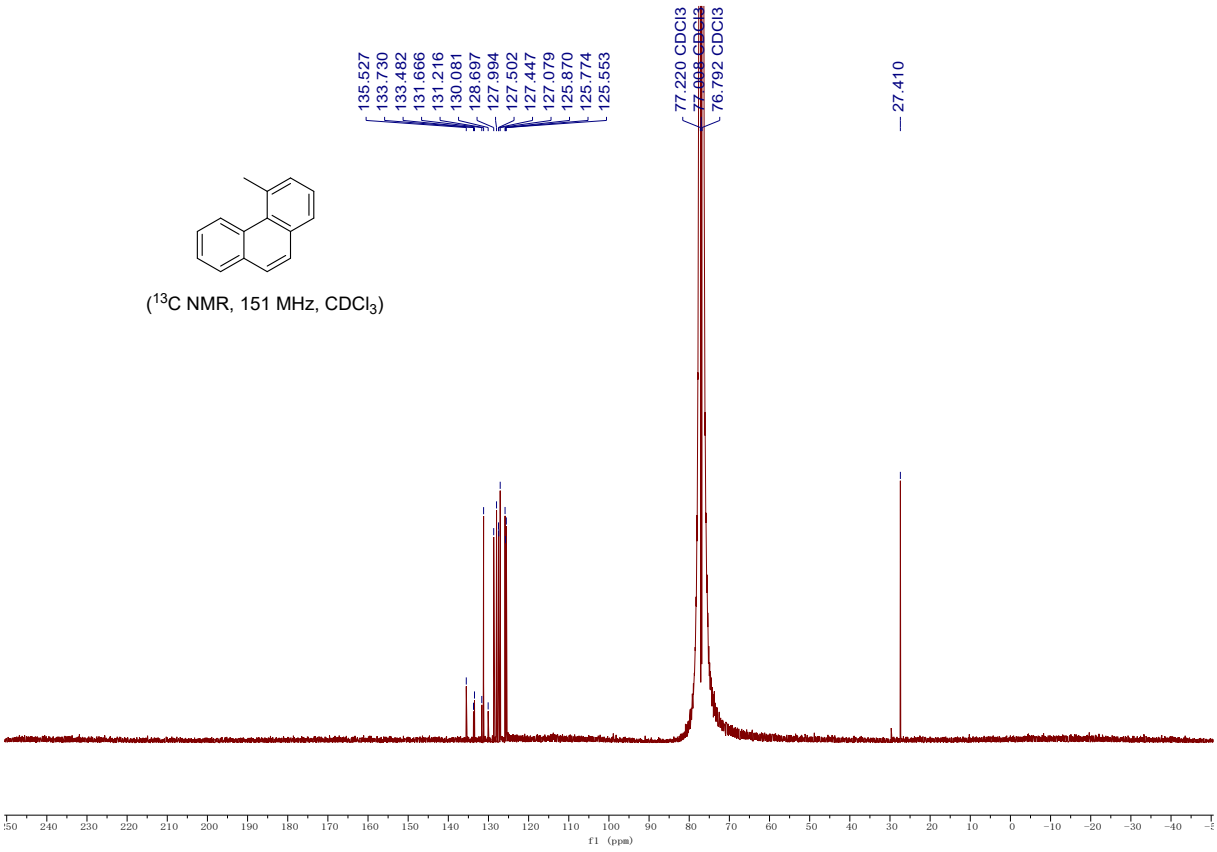
(^{13}C NMR, 151 MHz, $CDCl_3$)



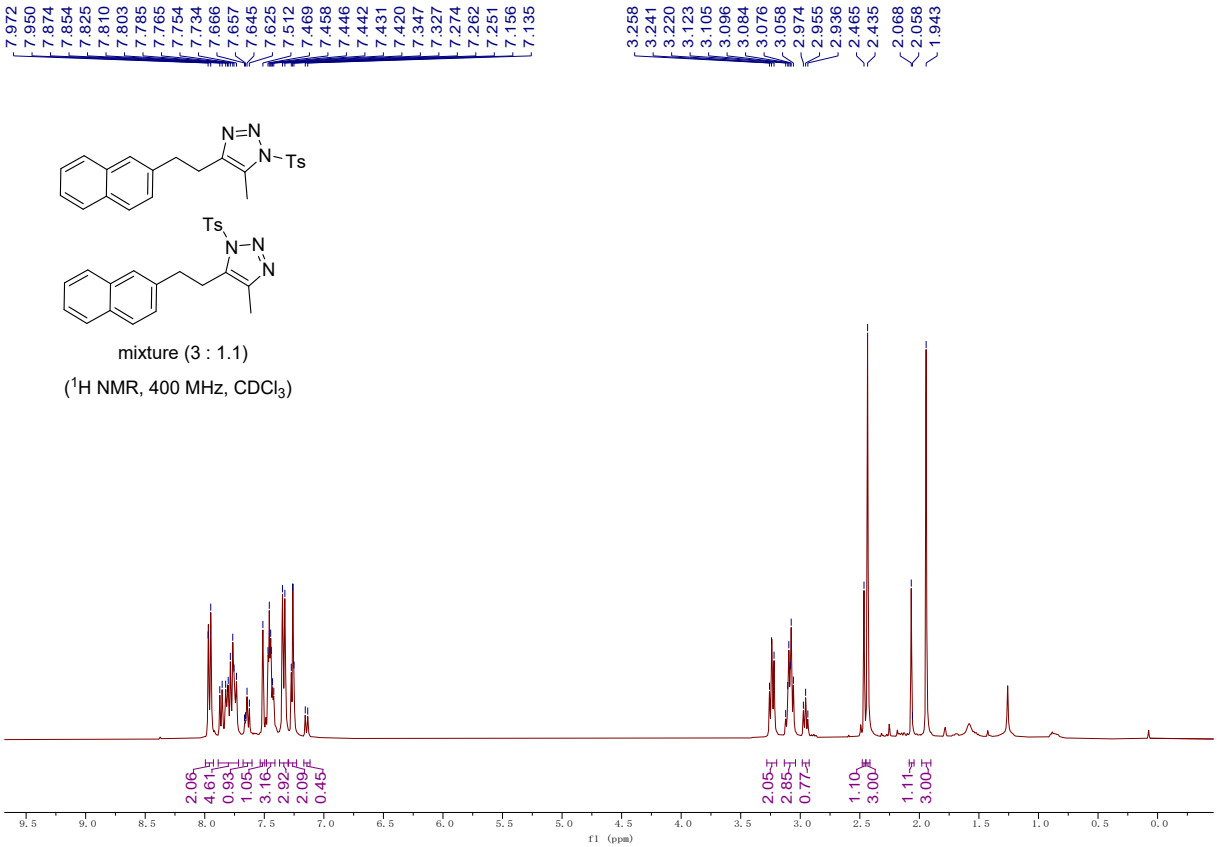

7.809
7.791
7.786
7.776
7.756
7.575
7.473
7.469
7.456
7.452
7.438
7.433
7.419
7.415
7.402
7.285
7.281
7.264
7.259
5.635
5.612
5.609
5.593
5.586
5.569
5.567
5.543
5.222
5.218
5.197
5.193
5.188
5.150
5.146
3.730
3.704
2.967
2.960
2.943
2.935
2.851
2.840
2.827
2.815
2.697
2.679
2.672
2.662
2.654
2.125
2.095
1.757
1.749
1.740
1.731
1.723
1.611
1.599
1.586
1.578
1.574
1.561
1.553
1.548
1.541
O
O
(1H NMR, 400 MHz, CDCl3)
3.11
1.00
2.10
1.01
0.99
1.90
0.94
2.11
1.00
2.89
2.85
1.18
1.39
f1 (ppm)
203.507
203.337
138.931
137.519
133.566
132.008
127.996
127.592
127.371
127.104
126.429
125.954
125.214
118.519
77.217 CDCl3
77.004 CDCl3
76.790 CDCl3
74.620
43.984
34.072
33.195
30.027
29.550
O
O
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)

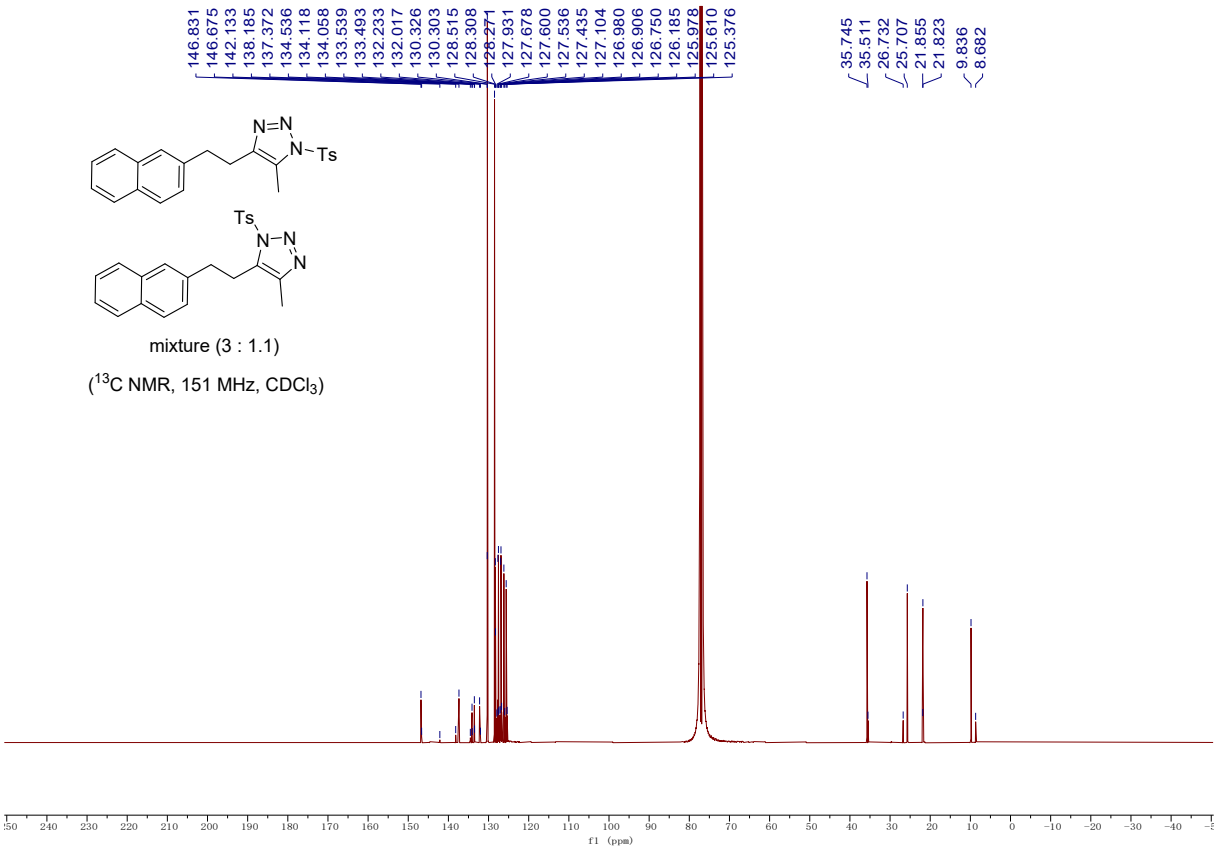


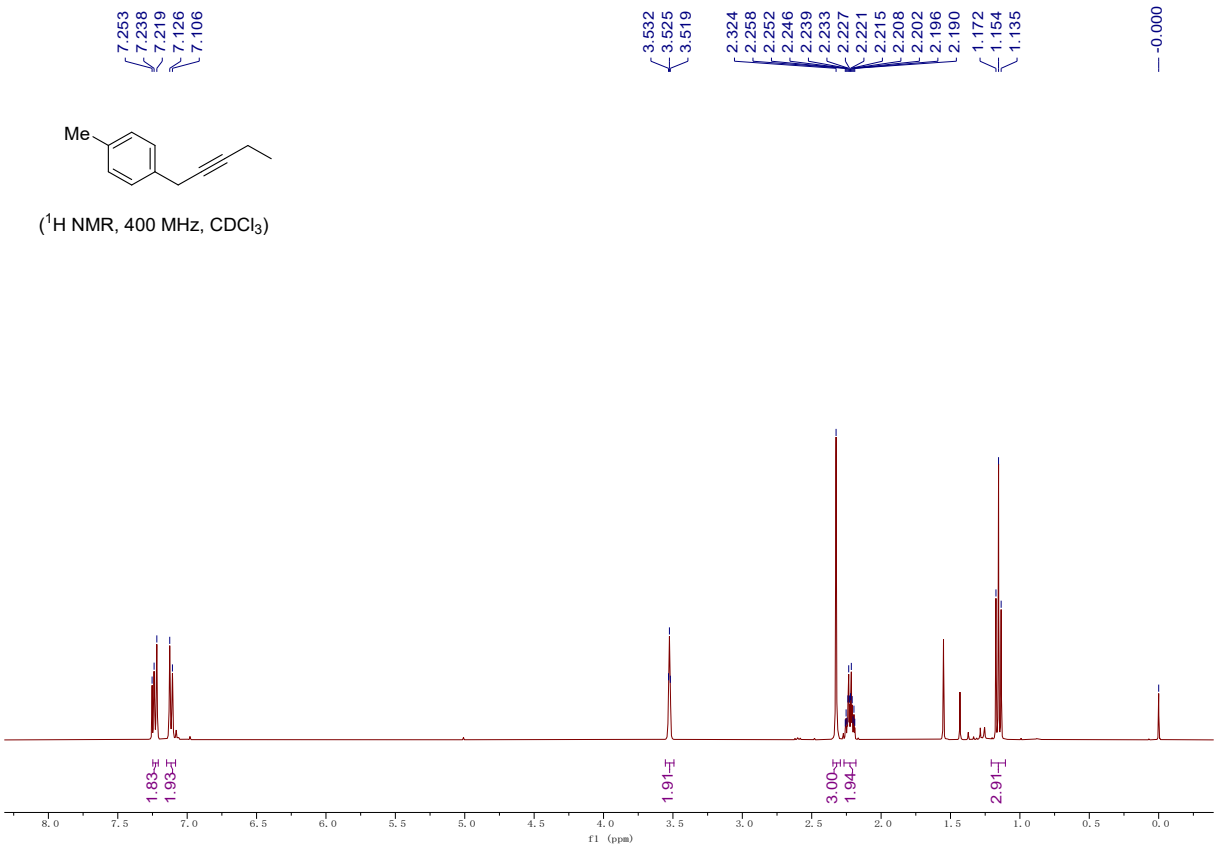
(^{1}H NMR, 400 MHz, $CDCl_3$)



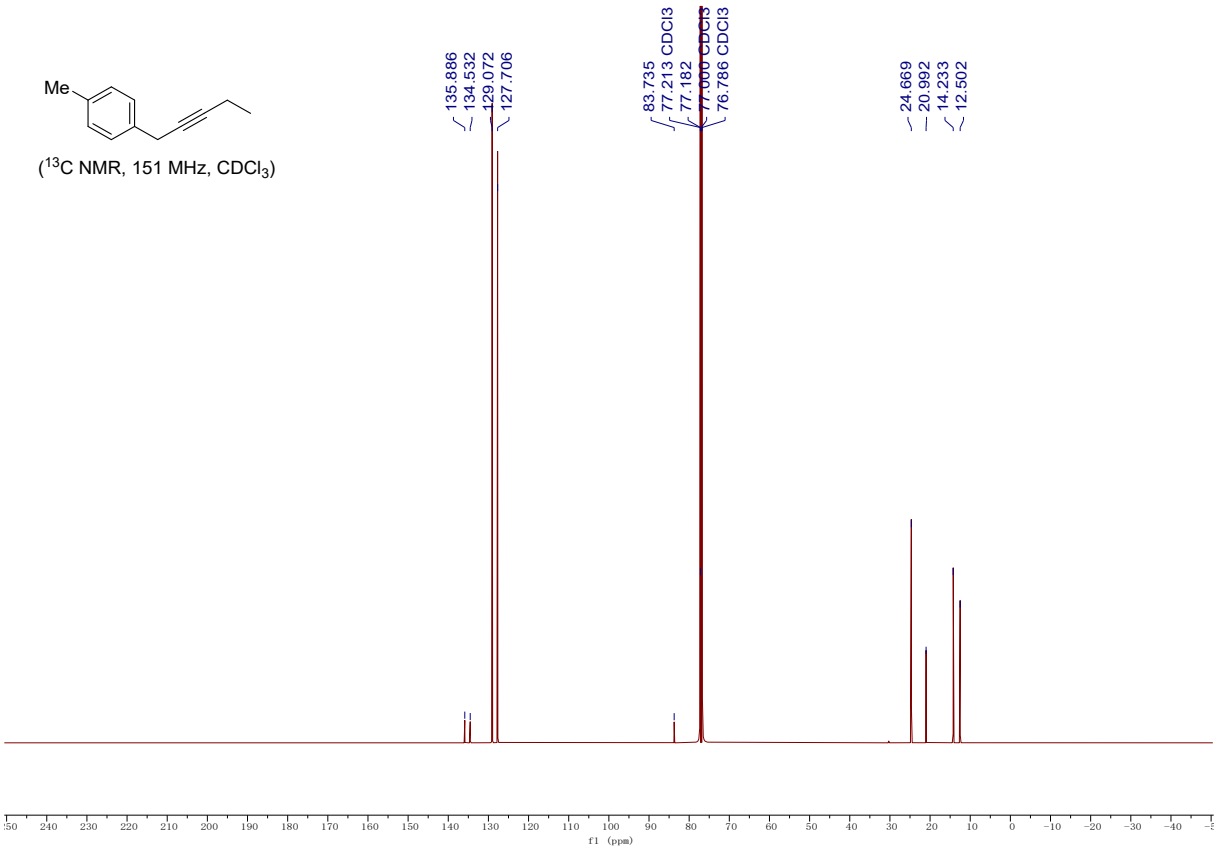
(^{13}C NMR, 151 MHz, $CDCl_3$)


7.972
7.950
7.874
7.854
7.825
7.810
7.803
7.785
7.765
7.754
7.734
7.666
7.657
7.645
7.625
7.512
7.469
7.458
7.446
7.442
7.431
7.420
7.347
7.327
7.274
7.262
7.251
7.156
7.135
3.258
3.241
3.220
3.123
3.105
3.096
3.084
3.076
3.058
2.974
2.955
2.936
2.465
2.435
2.068
2.058
1.943
N=N
N
Ts
Ts
N
N
N
mixture (3 : 1.1)
(1H NMR, 400 MHz, CDCl3)
2.06
4.61
0.93
1.05
3.16
2.92
2.09
0.45
2.05
2.85
0.77
1.10
3.00
1.11
3.00
f1 (ppm)

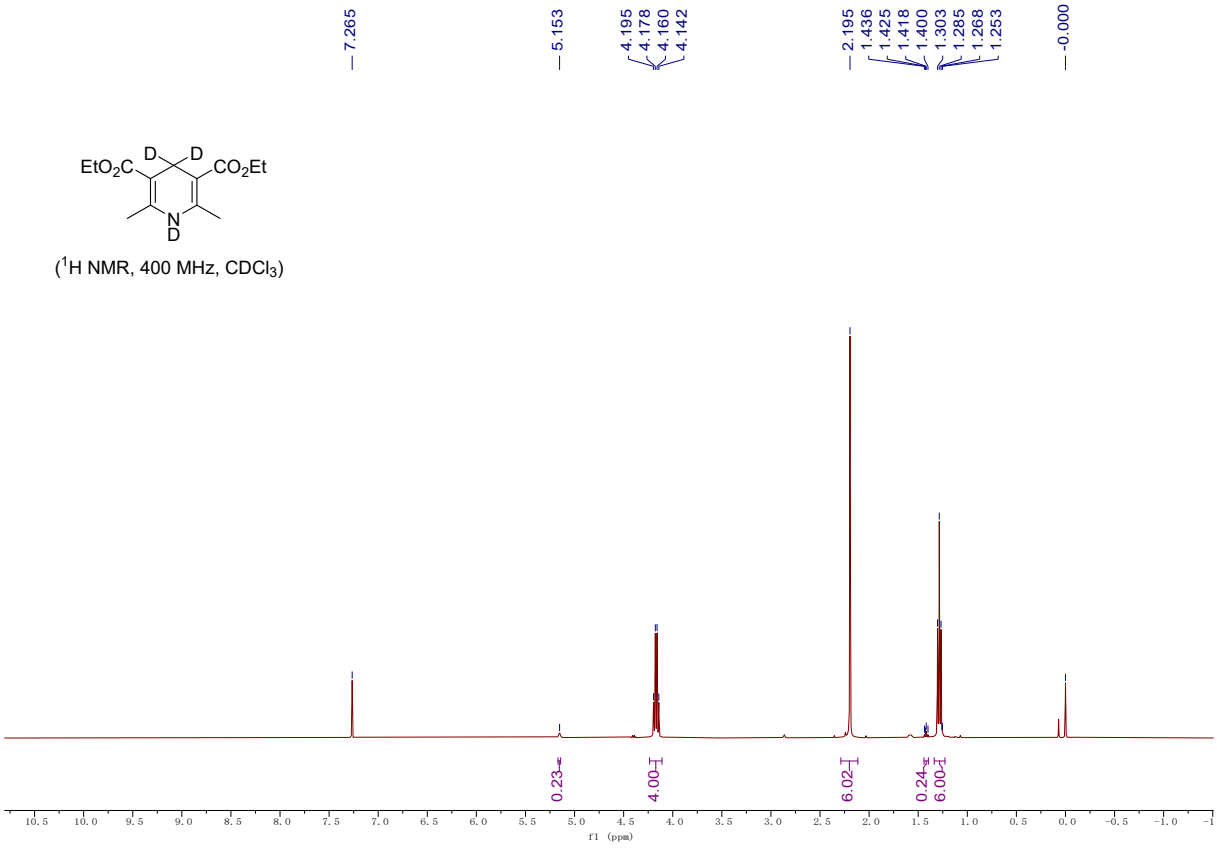

146.831
146.675
142.133
138.185
137.372
134.536
134.118
134.058
133.539
133.493
132.233
132.017
130.326
130.303
128.515
128.308
128.271
127.931
127.678
127.600
127.536
127.435
127.104
126.980
126.906
126.750
126.185
125.978
125.610
125.376
35.745
35.511
26.732
25.707
21.855
21.823
9.836
8.682
N=N
N
Ts
Ts
N
N
N
mixture (3 : 1.1)
(13C NMR, 151 MHz, CDCl3)
f1 (ppm)



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



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


7.265
5.153
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)
0.23
4.00
6.02
0.24
6.00
f1 (ppm)

12. Reference

1) L. M. Kammer, S. O. Badir, R. M. Hu and G. A. Molander, Photoactive electron donor–acceptor complex platform for Ni-mediated C(sp^3)–C(sp^2) bond formation. *Chem. Sci.*, 2021, **12**, 5450-5457.

2) X.-Y. Zhang, C. Ning, B. Mao, Y. Wei and M. Shi, A visible-light mediated ring opening reaction of alkylidenecyclopropanes for the generation of homopropargyl radicals. *Chem. Sci.*, 2021, **12**, 9088-9095.

3) C. Wang, H. Zhang, F. Xu, Y. Niu, Y. Wu, X. Wang, Y. Peng, J. Sun, L. Liang and P. Xu, Substituted 3-Benzylcoumarins as Allosteric MEK1 Inhibitors: Design, Synthesis and Biological Evaluation as Antiviral Agents. *Molecules,* **2013**, *18*, 6057-6091.

4) J. Liu, Y. Wei and M. Shi, Direct Activation of a Remote C(sp^3)–H Bond Enabled by a Visible-Light Photosensitized Allene Moiety. *Angew. Chem. Int. Ed.,* 2021, **60**, 12053-12059.

5) X. Zhao, M. Tian, L. Ji, J. Liu and K. Lu, Metal-Free sp^3 C-SCF_3 Coupling Reactions between Cycloketone Oxime Esters and S-trifluoromethyl 4-Methylbenzenesulfonothioate, *Org. Lett.*, 2020, **22**, 863-866.

6) L. Guo, H.-Y. Tu, S. Zhu and L. Chu, Selective Intermolecular Alkylarylation of Alkenes via Photoredox/Nickel Dual Catalysis. *Org. Lett.,* 2019, **21**, 4771-4776.

7) T. M. Beck and B. Breit, Regioselective Rhodium-Catalyzed Addition of β-Keto Esters, β-Keto Amides, and 1,3-Diketones to Internal Alkynes. *Eur. J. Org. Chem.*, 2016, **2016**, 5839-5844.

8) V. Akhmetov, M. Feofanov, D. I. Sharapa and K. Amsharov, Alumina-mediated π-Activation of Alkynes. *J. Am. Chem. Soc.*, 2021, **143**, 15420-15426.

9) B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia and V. V. Fokin, Ruthenium-Catalyzed Azide-Alkyne Cycloaddition: Scope and Mechanism. *J. Am. Chem. Soc.*, 2008, **130**, 8923-8930.