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Supporting Information

Rapid Construction of Polysubstituted "Caged" Oxa-Bishomocubane Framework from Vinylidenecyclopropanes through a Sequential Dual Catalysis of Copper(I) and Visible-Light-Induced Photosensitization

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CONTENTS

(A) General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra fluorous nuclear magnetic resonance (^{19}F NMR) were recorded at 400 MHz, 100 MHz and 367 MHz, respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz) and integration. Mass and High-resolution mass spectra (HRMS) spectra were recorded by ESI method and DART (Direct analysis in real time mass spectrometry) method. Fluorescence spectra for emission and excitation were obtained on a Hitachi F-4600 FL Spectrophotometer. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. Petroleum ether refers to the fraction with boiling point in the range 60-90 ^{o}C. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

The preparation of 3-cyclopropylideneprop-2-en-1-ones **1**[1] followed the previous literature procedure.

1. Miao, M.; Cao, J.; Zhang, J.; Huang, X.; Wu, L. *Org. Lett.* **2012**, *14*, 2718-2721.

Reaction setup

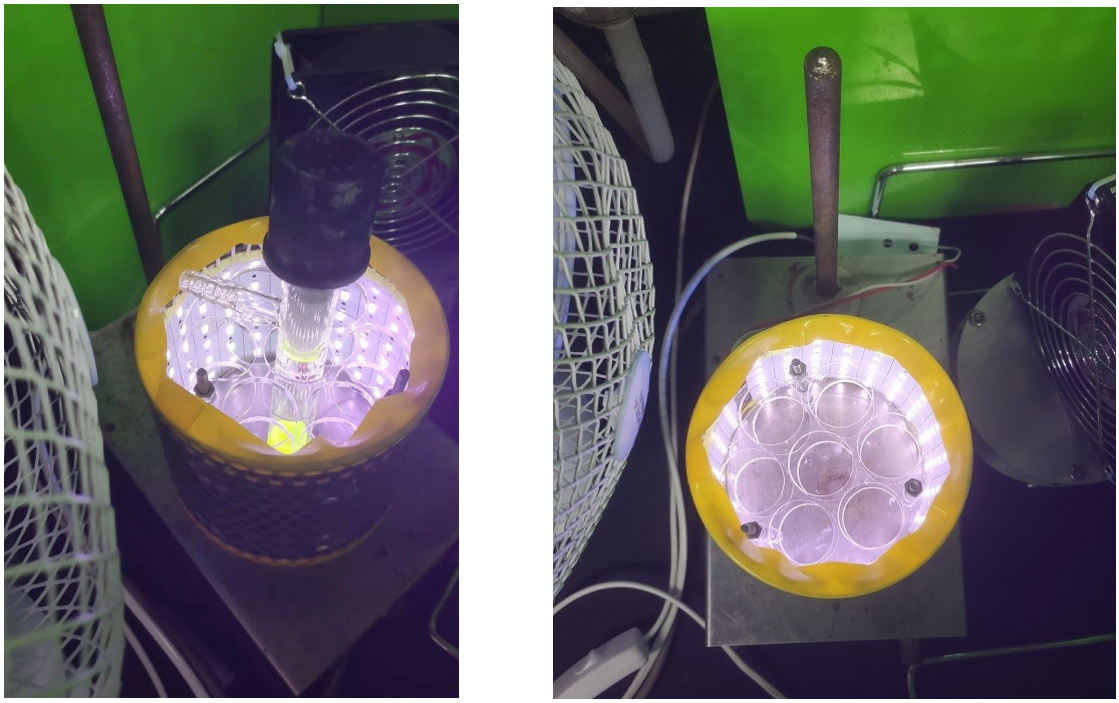
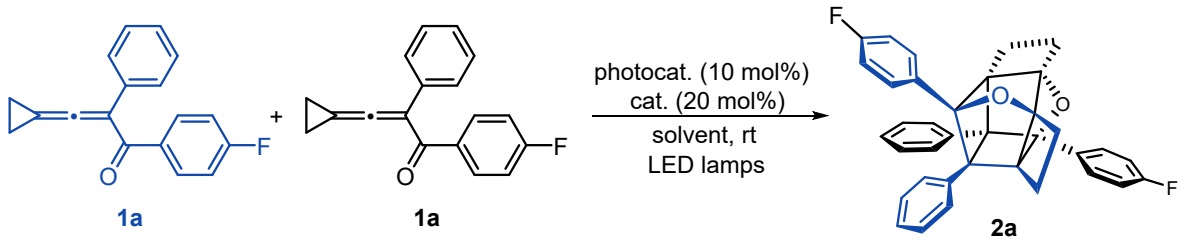


Figure S1. 380 nm LED lamps bond and reaction setup

As depicted in the picture, reactions were carried out in oven-dried sealed tubes. The reaction temperature was maintained at approximately room temperature by a desk fan.

(B) Optimization of Reaction Conditions



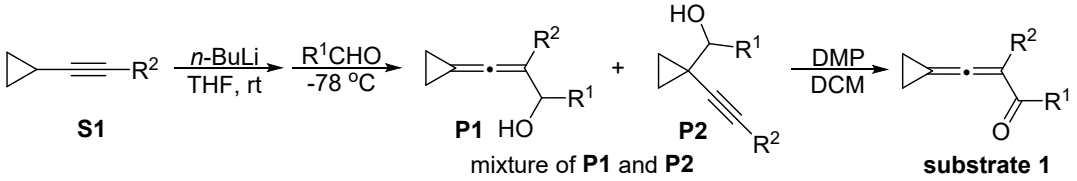
entry[a]	Photocatalyst	E_T (kacl/mol)	cat.	solvent	yield (%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	61.0	CuCl	MeCN	45
2	Mes-Acr$^+ClO_4^-$	-	CuCl	MeCN	trace
3	$Ru(bpy)_3Cl_2$	46.5	CuCl	MeCN	28
4	$Ir(ppy)_3$	57.8	CuCl	MeCN	67
5	$Ir(ppy)_2(dtbbpy)PF_6$	49.2	CuCl	MeCN	66
6	Rose bengal	40.9	CuCl	MeCN	trace
7	Eosin Y	-	CuCl	MeCN	trace
8	4CzIPN	-	CuCl	MeCN	trace
9[b]	$Ir(ppy)_3$	57.8	CuCl	MeCN	70
10	$Ir(ppy)_3$	57.8	$PdCl_2$	MeCN	17
11	$Ir(ppy)_3$	57.8	$AgNTf_2$	MeCN	9
12	$Ir(ppy)_3$	57.8	CuBr	MeCN	45
13	$Ir(ppy)_3$	57.8	CuI	MeCN	34
14	$Ir(ppy)_3$	57.8	CuCl	THF	15
15	$Ir(ppy)_3$	57.8	CuCl	Et_2O	70
16	$Ir(ppy)_3$	57.8	CuCl	DCM	20
17	$Ir(ppy)_3$	57.8	CuCl	toluene	41
18	$Ir(ppy)_3$	57.8	CuCl	DMF	17
19	$Ir(ppy)_3$	57.8	CuCl	DMSO	43
20	$Ir(ppy)_3$	57.8	CuCl	1,4-dioxane	42
21	$Ir(ppy)_3$	57.8	CuCl	MTBE	46
22[c]	$Ir(ppy)_3$	57.8	CuCl	MeCN	70

23[d]	$Ir(ppy)_3$	57.8	CuCl	MeCN	70
24[d,e]	$Ir(ppy)_3$	57.8	CuCl	MeCN	73 (70[f])
25[d,g]	$Ir(ppy)_3$	57.8	CuCl	MeCN	70
26[d,h]	$Ir(ppy)_3$	57.8	CuCl	MeCN	48
27[d,e]	VB_2	50.0	CuCl	MeCN	7
28[d,e]	$Ir(bpy)(ppy)_2BF_4$	50.0	CuCl	MeCN	6
29[d,e]	$Ir(ppy)_3$	57.8	CuCl	tBuCN	59
30[d,e]	$Ir(ppy)_3$	57.8	$AgNO_3$	MeCN	53
31[d,e]	$Ir(ppy)_3$	57.8	$Cu(OTf)_2$	MeCN	n.d.
32[d,e]	$Ir(ppy)_3$	57.8	$CuCl_2$	MeCN	n.d.
33[d,e,i]	$Ir(ppy)_3$	57.8	CuCl	MeCN	34
34[e]	-	-	CuCl	MeCN	trace
35[d]	$Ir(ppy)_3$	57.8	-	MeCN	n.r.
36[d,e,j]	$Ir(ppy)_3$	57.8	CuCl	MeCN	n.d.

[a]Reactions were conducted using 0.20 mmol of substrate **1a**, 0.02 mmol of cat. (20 mol%) and 0.01 mmol photocatalyst (10 mol%) and 2.0 mL of anhydrous and degassed solvent and irradiated with a 100 W LED lamp (435 nm) for 12 h unless otherwise noted. Yields were determined by ^{19}F NMR analysis using 1-fluoronaphthalene as an internal standard. [b]Reaction mixtures were irradiated with a 12 W LED lamps bond (380 nm). [c]Reaction was conducted using 5.0 mol% of photocatalyst. [d]Reaction was conducted using 2.5 mol% of photocatalyst. [e]Reaction was conducted using 40 mol% of cat.. [f]Isolated yield. [g]Reaction was conducted using 30 mol% of cat.. [h]Reaction was conducted using 10 mol% of cat.. [i]Reaction was conducted by adding 1.0 eq of water. [j]Reaction was conducted in the dark.

DCM is dichloromethane; DMF is *N,N*-dimethylformaide; DMSO is dimethyl sulfoxide; MTBE is tert-butyl methyl ether; VB2 is riboflavin; n.d. is not detected; n.r. is no reaction.

(C) General Procedures for the Synthesis of Substrates 1



To a stirred solution of alkyne **S1** (1.0 eq, 10 mmol) in anhydrous THF (20 mL, 0.5 M) was added *n*-BuLi (1.2 eq, 12 mmol, 2.4 M in hexane) at room temperature; the resulting mixture was stirred for 1 h and cooled to -78 °C. Then, the aldehyde was added with a syringe to this mixture at -78 °C. After being stirred for 1 h, the reaction mixture was allowed to warm up to room temperature, quenched with water, extracted with ethyl acetate, dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was purified by a flash silica gel chromatography (Petroleum Ether:Ethyl Acetate = 20:1, v/v) to afford the mixture of **P1** and **P2** as a yellow oil.

To a solution of the mixture of **P1** and **P2** (1.0 eq) in anhydrous DCM (0.5 M) was added Dess-Martin periodinane (DMP, 1.5 eq) at 0 °C. After being stirred for 10 min, silica gel (100-200 mesh) was added and the solvent was evaporated. The solid residue was purified by a column chromatography (Petroleum Ether:Ethyl Acetate = 50:1, v/v) to afford the **substrate 1**.

The substrates **1a** to **1j**, **1k, 1r to 1t**, **1u** to **1y** and **1aa** are known compounds and their spectroscopic data are in agreement with those in the previous literature (*Org. Lett.* **2012**, *14*, 2718-2721).

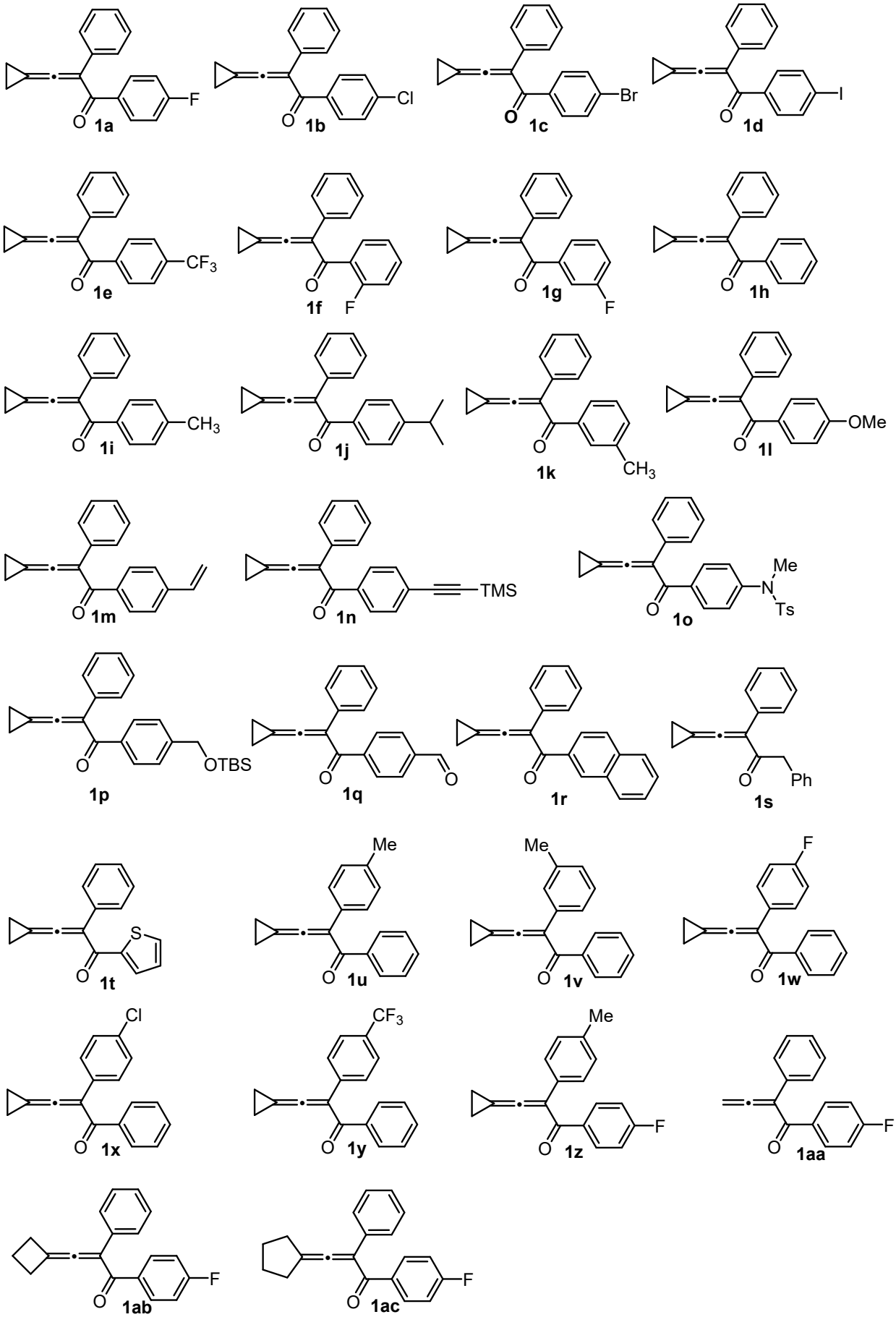
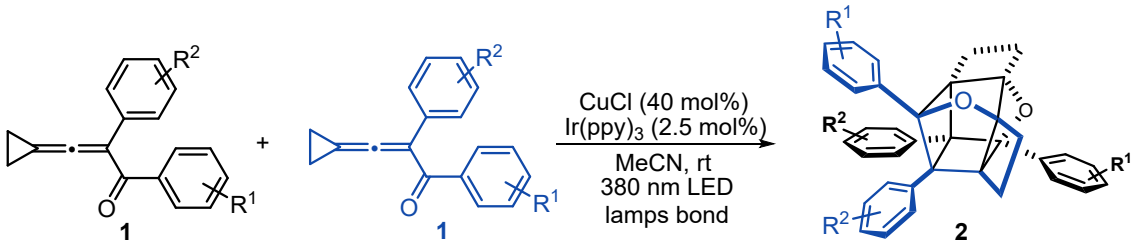


Table S1. Substrate Scope of **1**

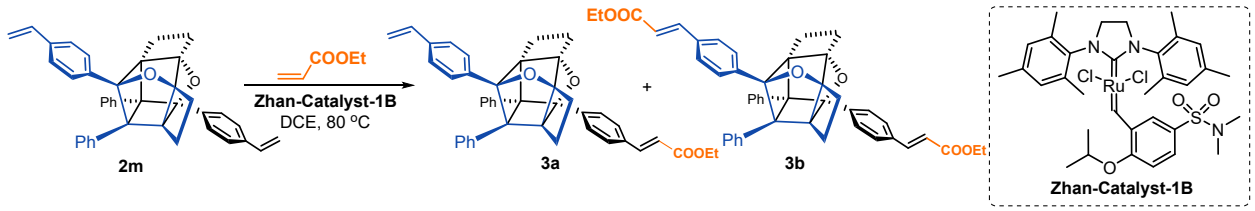
(D) General Procedure for the Preparation of Products 2 and 3

(1) Synthesis of Products **2**



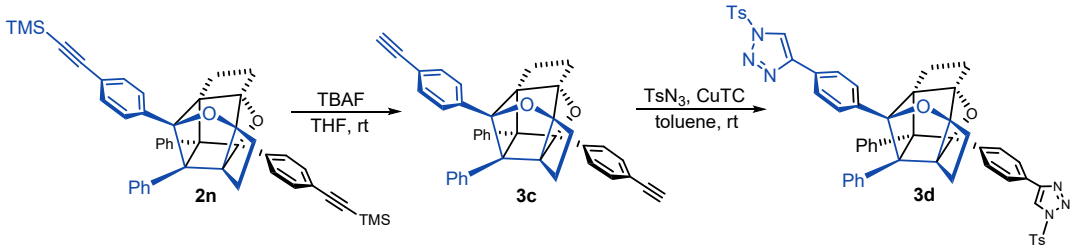
A dried 10 mL Schlenk tube was charged with CuCl (4.0 mg, 0.04 mmol, 40 mol%), $Ir(ppy)_3$ (1.7 mg, 0.0025 mmol, 2.5 mol%) and 3-cyclopropylideneprop-2-en-1-one **1** (0.20 mmol, 2.0 equiv) (if solid), then the tube was evacuated and backfilled with argon for 3 times. 3-cyclopropylideneprop-2-en-1-one **1** (0.20 mmol, 2.0 equiv) (if liquid) and anhydrous degassed MeCN (2.0 mL) were added under argon protected atmosphere. The reaction mixture was stirred under irradiation with 380 nm LEDs, maintained at approximately room temperature by a desk fan. After 12 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by a flash silica gel chromatography (Petroleum Ether:Ethyl Acetate = 20:1, v/v) to afford product **2**.

(2) Synthesis of Products **3a** and **3b**



In an oven-dried 10 mL Schlenk tube was equipped with a magnetic stir bar, compound **2m** (55 mg, 0.1 mmol, 1.0 eq), ethyl acrylate (22.8 μL, 0.21 mmol, 2.1 eq) and Zhan-Catalyst-1B (3.7 mg, 0.005 mmol, 5 mol%) were added. Then the tube was evacuated and backfilled with argon for 3 times. After that, anhydrous DCE (10 mL) were added under argon protected atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After completion, the reaction mixture was concentrated under reduced pressure and the residue was purified by a flash silica gel chromatography (Petroleum Ether:Ethyl Acetate = 10:1 to 4:1, v/v) to afford product **3a** (22 mg, 36% yield) and **3b** (21 mg, 31% yield).

(3) Synthesis of Products **3c** and **3d**

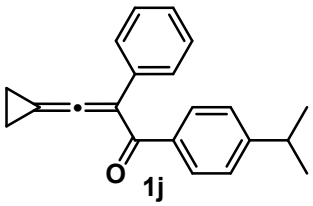


To a solution of **2n** (35 mg, 0.05 mmol, 1.0 eq) in reagent grade THF (1.5 mL) at room temperature was added TBAF (70 μL, 0.075 mmol, 1.0 M in THF). After being stirred for 10 min, silica gel (100-200 mesh) was added and the solvent was evaporated. The solid residue was purified by a column chromatography (Petroleum Ether:Ethyl Acetate = 20:1, v/v) to afford the product **3c** (26 mg, 95% yield).

In an oven-dried 10 mL Schlenk tube was equipped with a magnetic stir bar, compound **3c** (34 mg, 0.05 mmol, 1.0 eq), CuTC (2.0 mg, 0.01 mmol, 10 mol%) and toluene (1.0 mL) were added. After 10 min, TsN_3 was added in one portion. The resulting mixture was stirred vigorously at room temperature for 8 h. After that, the mixture was concentrated under reduced pressure. The residue was purified by a flash column chromatography (Petroleum Ether:Ethyl Acetate = 4:1, v/v) to afford product **3d** (37 mg, 80% yield).

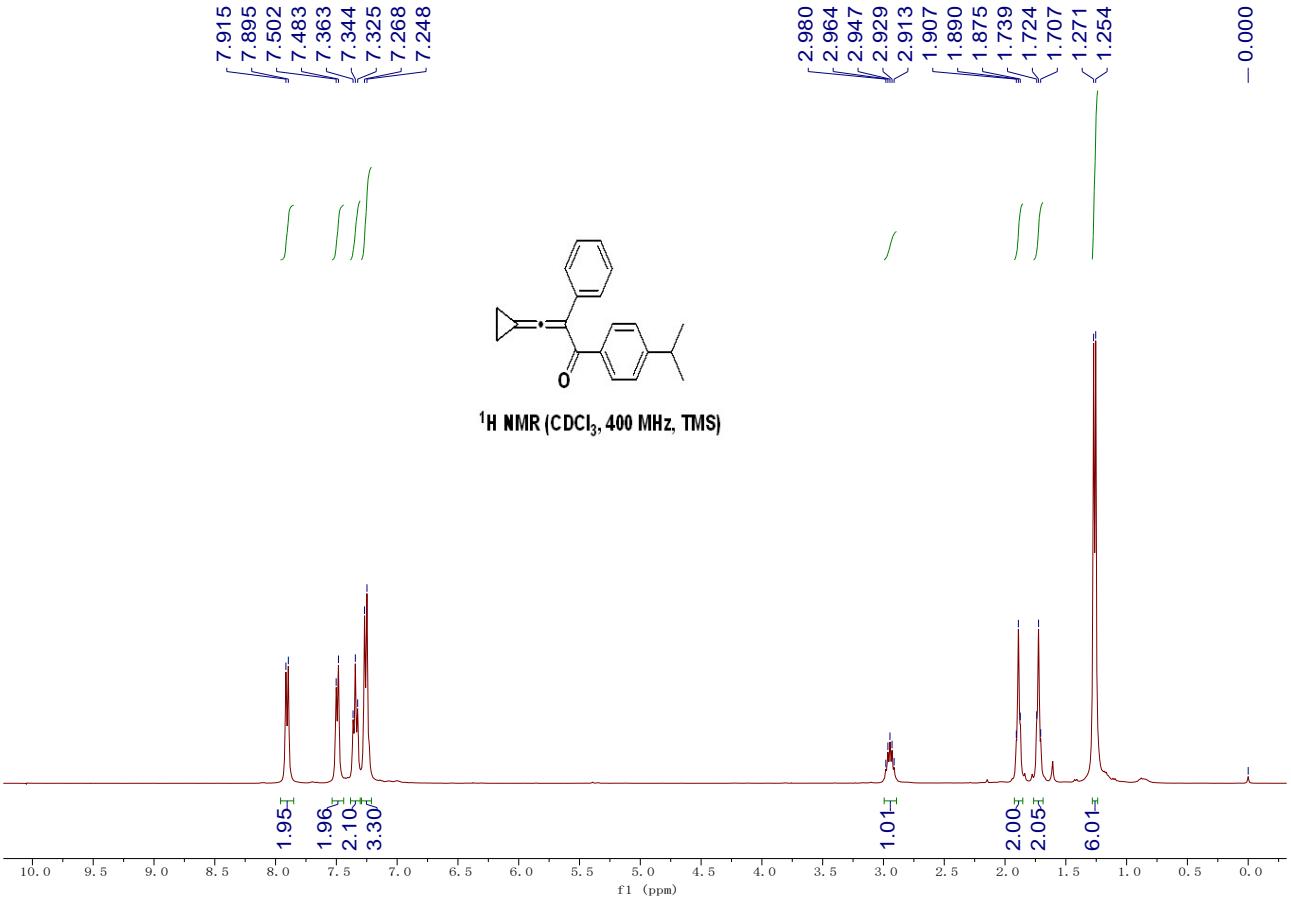
(E) Spectroscopic Data

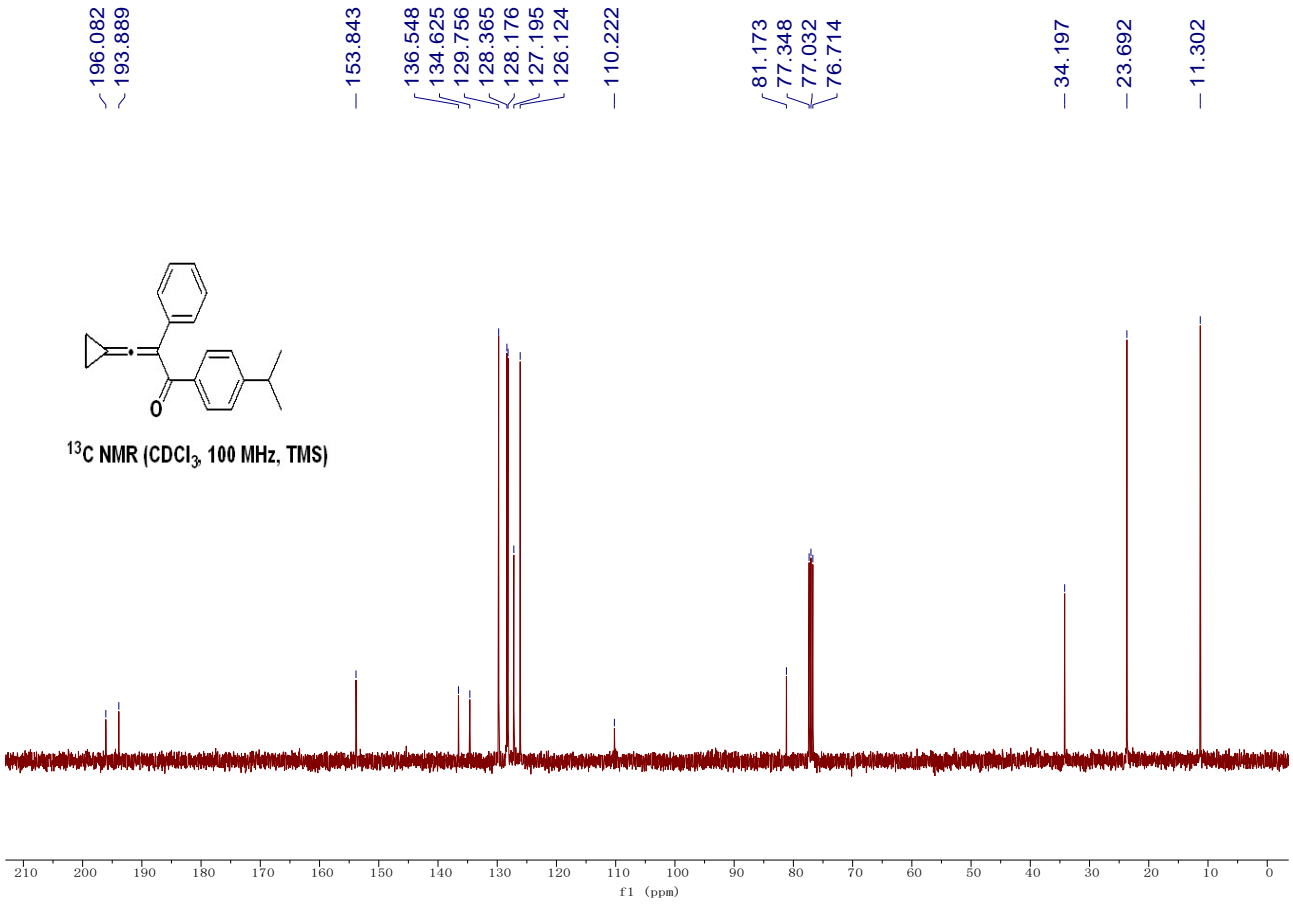
(1) Spectroscopic Data of Substrates **1j**, **1m**, **1n**, **1o**, **1p**, **1q, 1z**, **1ab** and **1ac**

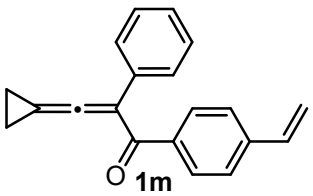


1j

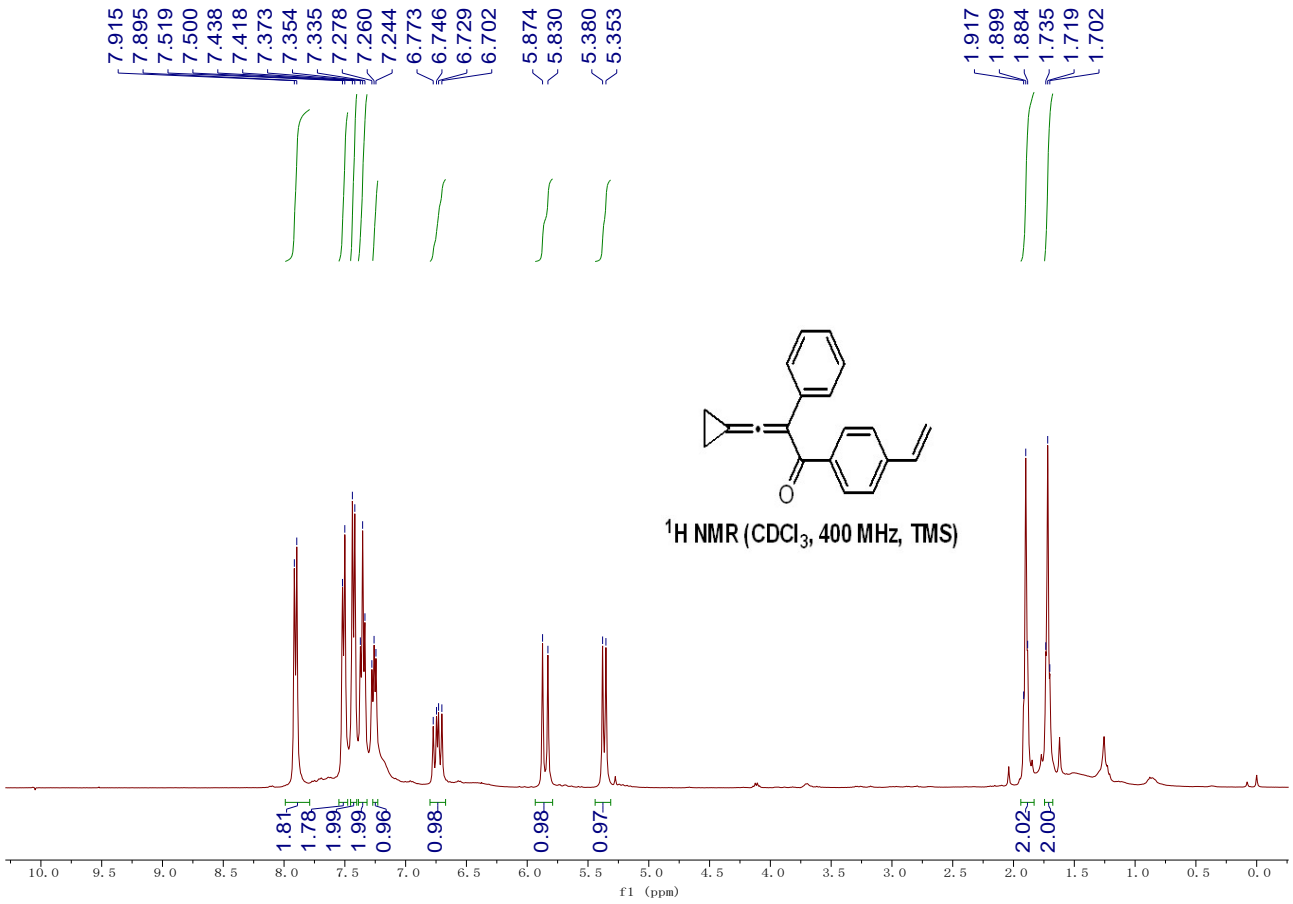
3-cyclopropylidene-1-(4-isopropylphenyl)-2-phenylprop-2-en-1-one (1j), the title compound was achieved as a white solid, MP = 48-50 °C, 1.44 g, 25% yield (20 mmol scale). R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 2.95 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.88 (dd, *J* = 6.8, 6.0 Hz, 2H), 1.73 (dd, *J* = 6.8, 6.0 Hz, 2H), 1.27 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 193.9, 153.9, 136.6, 134.6, 129.8, 128.4, 128.2, 127.2, 126.1, 110.3, 81.2, 34.2, 23.7, 11.3. IR (acetone) ν 3675, 2987, 2901, 1998, 1646, 1604, 1411, 1280, 1066, 1052, 858, 794, 693 cm^{-1}. HRMS (ESI) calcd for $[C_{21}H_{20}ONa]^+$: 311.1406, found: 311.1409.







3-cyclopropylidene-2-phenyl-1-(4-vinylphenyl)prop-2-en-1-one (1m), the title compound was achieved as a yellow solid, MP = 55-56 °C, 1.74 g, 32% yield (20 mmol scale). R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 1H), 6.74 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 1.89 (dd, *J* = 7.2, 6.4 Hz, 2H), 1.72 (dd, *J* = 7.2, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 193.8, 141.3, 138.2, 136.1, 134.4, 129.8, 128.4, 128.2, 127.3, 125.7, 116.3, 110.4, 81.2, 11.5. IR (acetone) ν 2988, 2923, 1998, 1724, 1646, 1601, 1404, 1278, 1176, 1066, 1045, 991, 845, 797, 731, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{16}ONa]^+$: 295.1093, found: 295.1096.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1.917
1.899
1.884
1.735
1.719
1.702
O
1H NMR (CDCl3, 400 MHz, TMS)
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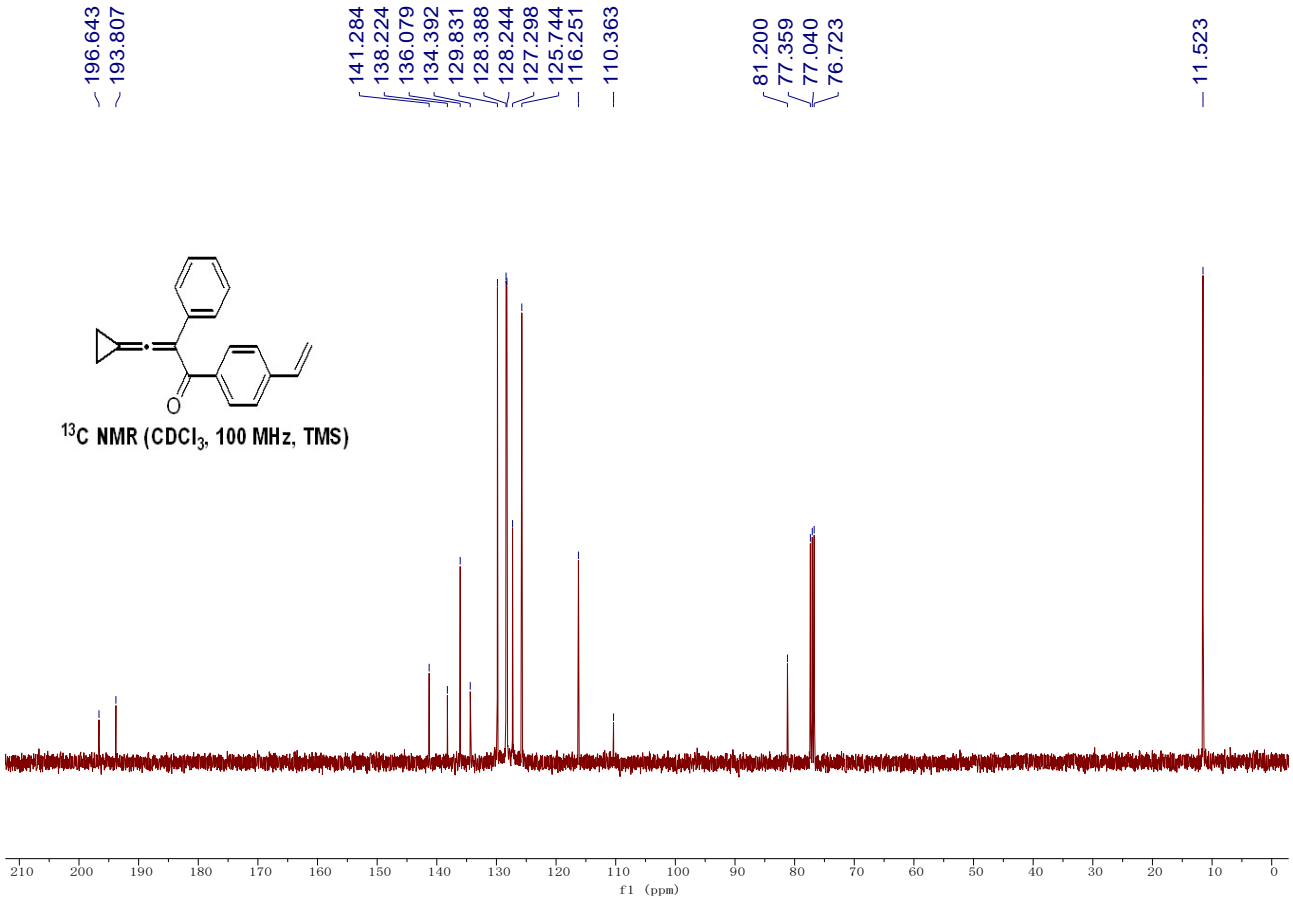
1.78
1.99
1.99
0.96
0.98
0.98
0.97
2.02
2.00
f1 (ppm)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77.359
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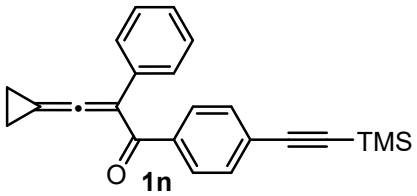
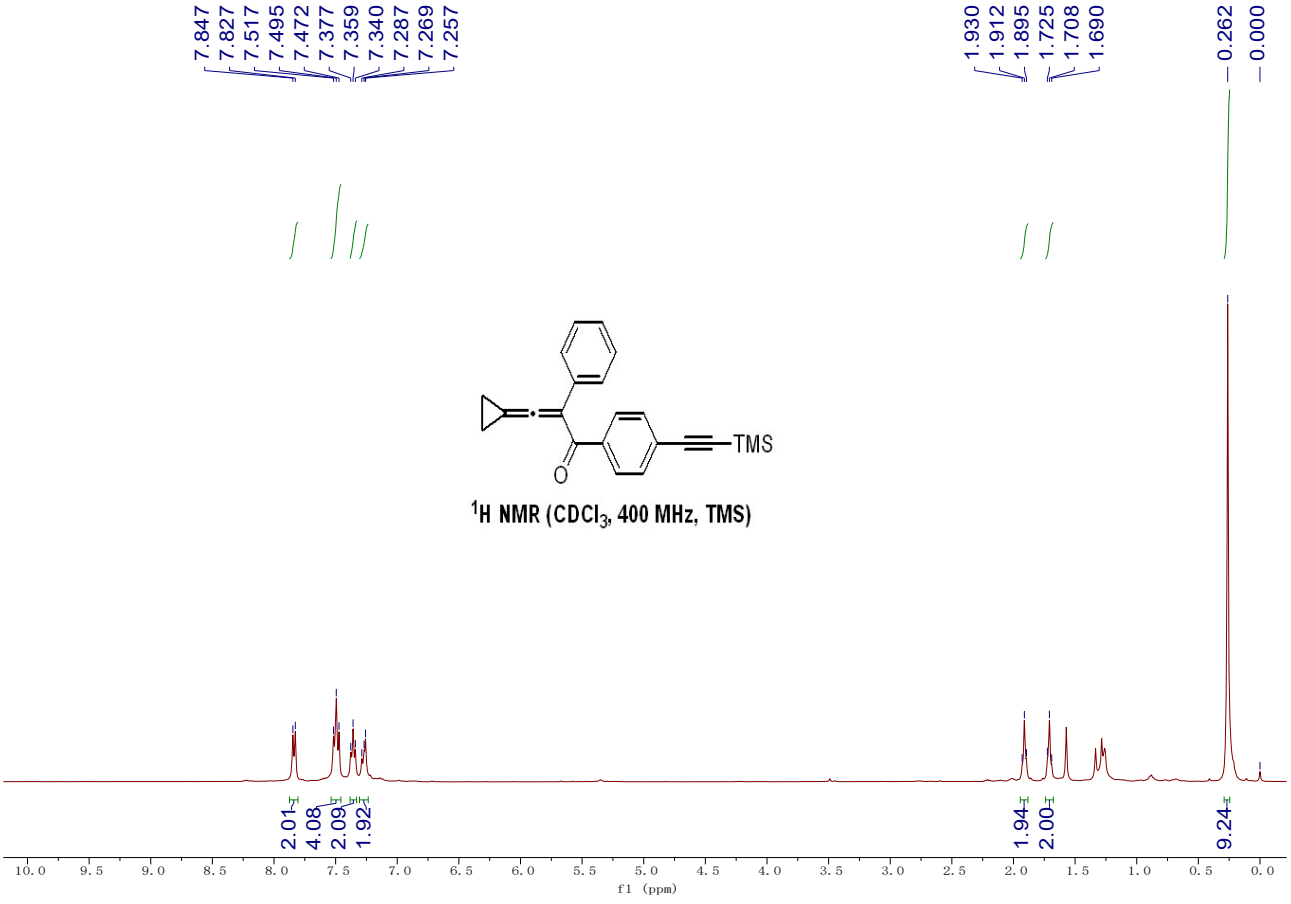
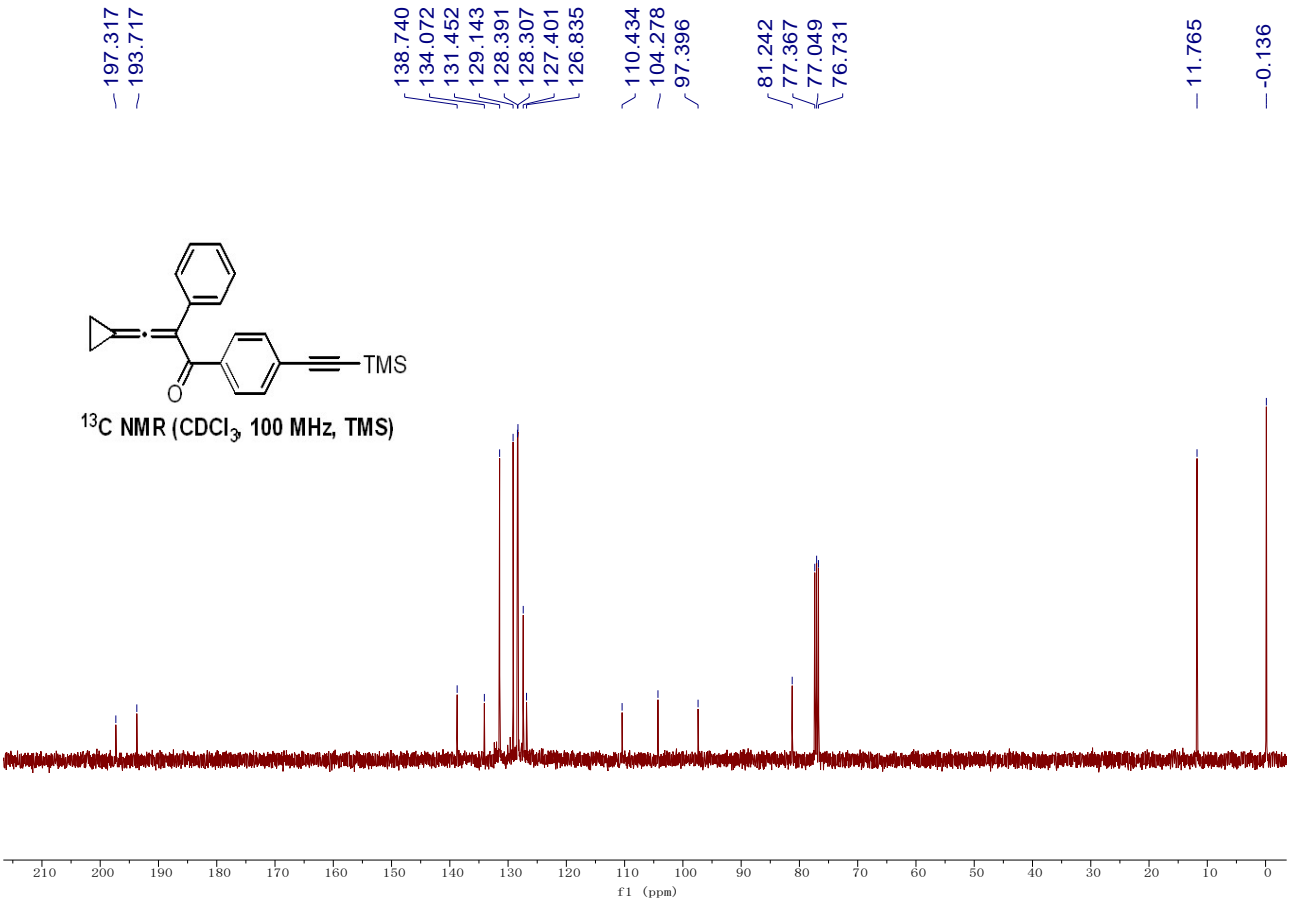
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

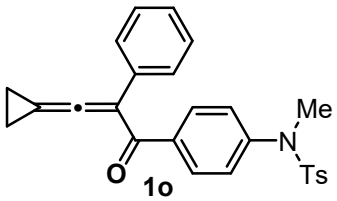


3-cyclopropylidene-2-phenyl-1-(4-((trimethylsilyl)ethynyl)phenyl)prop-2-en-1-one (1n), the title compound was achieved as a white solid, MP = 66-68 °C, 1.44 g, 21% yield (20 mmol scale). R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.8 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 1.90 (dd, *J* = 7.2, 6.8 Hz, 2H), 1.71 (dd, *J* = 7.2, 6.8 Hz, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 193.7, 138.7, 134.1, 131.5, 129.1, 128.4, 128.3, 127.4, 126.8, 110.4, 104.3, 97.4, 81.2, 11.8, -0.1. IR (acetone) ν 2988, 2901, 1998, 1703, 1627, 1509, 1265, 1072, 1014, 989, 904, 846, 734, 702 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{22}ONaSi]^+$: 365.1332, found: 365.1331.

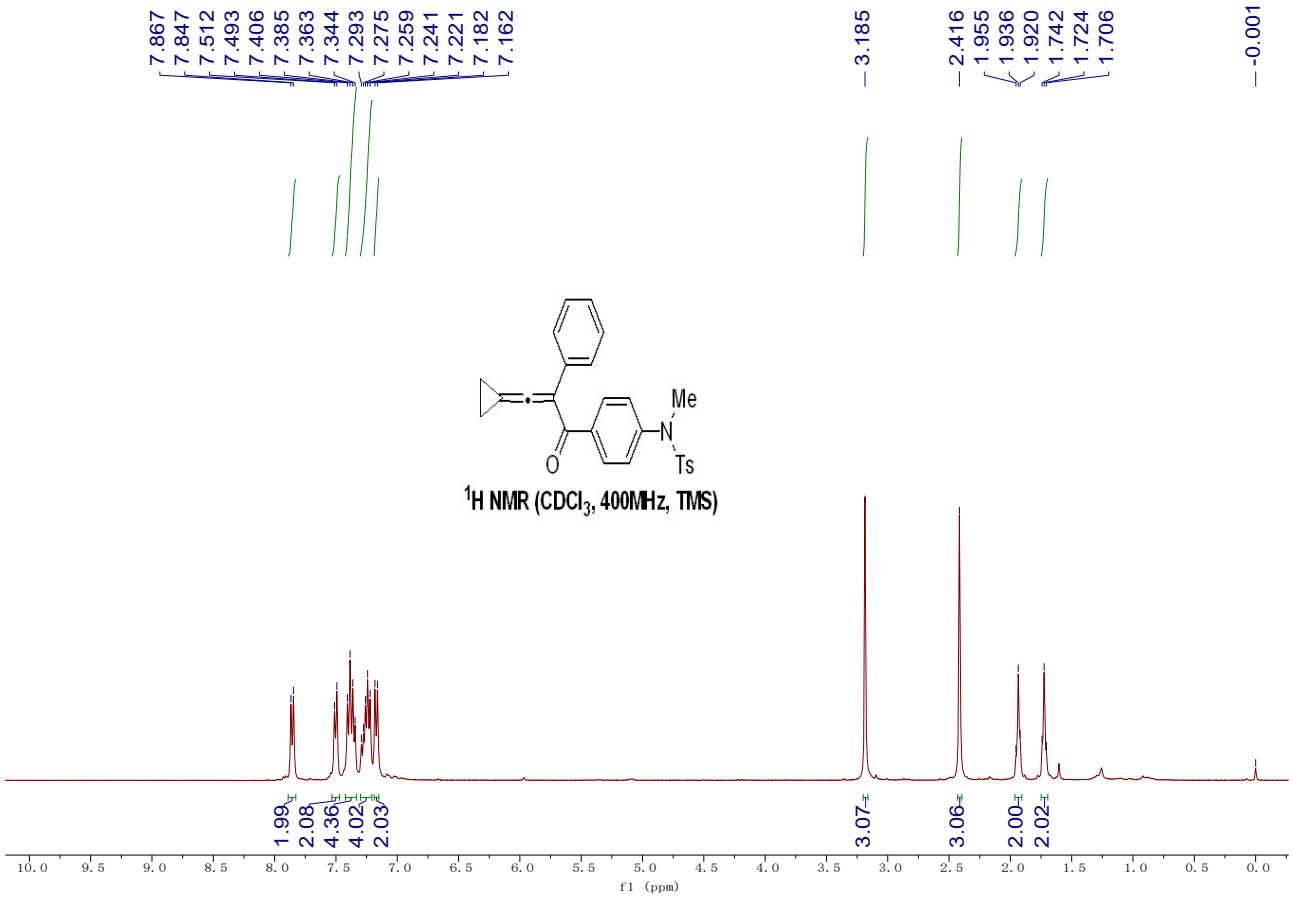


^{1}H NMR ($CDCl_3$, 400 MHz, TMS)





N-(4-(3-cyclopropylidene-2-phenylacryloyl)phenyl)-N,4-dimethylbenzenesulfonamide (1o), the title compound was achieved as a white solid, MP = 64-66 °C, 1.54 g, 18% yield (20 mmol scale). R_f = 0.35 (Petroleum Ether:Ethyl Acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.19 (s, 3H), 2.42 (s, 3H), 1.94 (dd, *J* = 7.6, 6.4 Hz, 2H), 1.72 (dd, *J* = 7.2, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 193.4, 145.0, 143.9, 137.3, 134.1, 133.3, 130.0, 129.5, 128.4, 128.3, 127.7, 127.4, 125.1, 110.4, 81.3, 37.7, 21.6, 11.7. IR (acetone) ν 2973, 2927, 1453, 1380, 1330, 1088, 1046, 880, 804, 667 cm^{-1}. HRMS (ESI) calcd for $[C_{26}H_{23}O_3NaS]^+$: 452.1291, found: 452.1301.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7.182
7.162
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2.416
1.955
1.936
1.920
1.742
1.724
1.706
-0.001
Me
N
Ts
O
1H NMR (CDCl3, 400MHz, TMS)
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4.02
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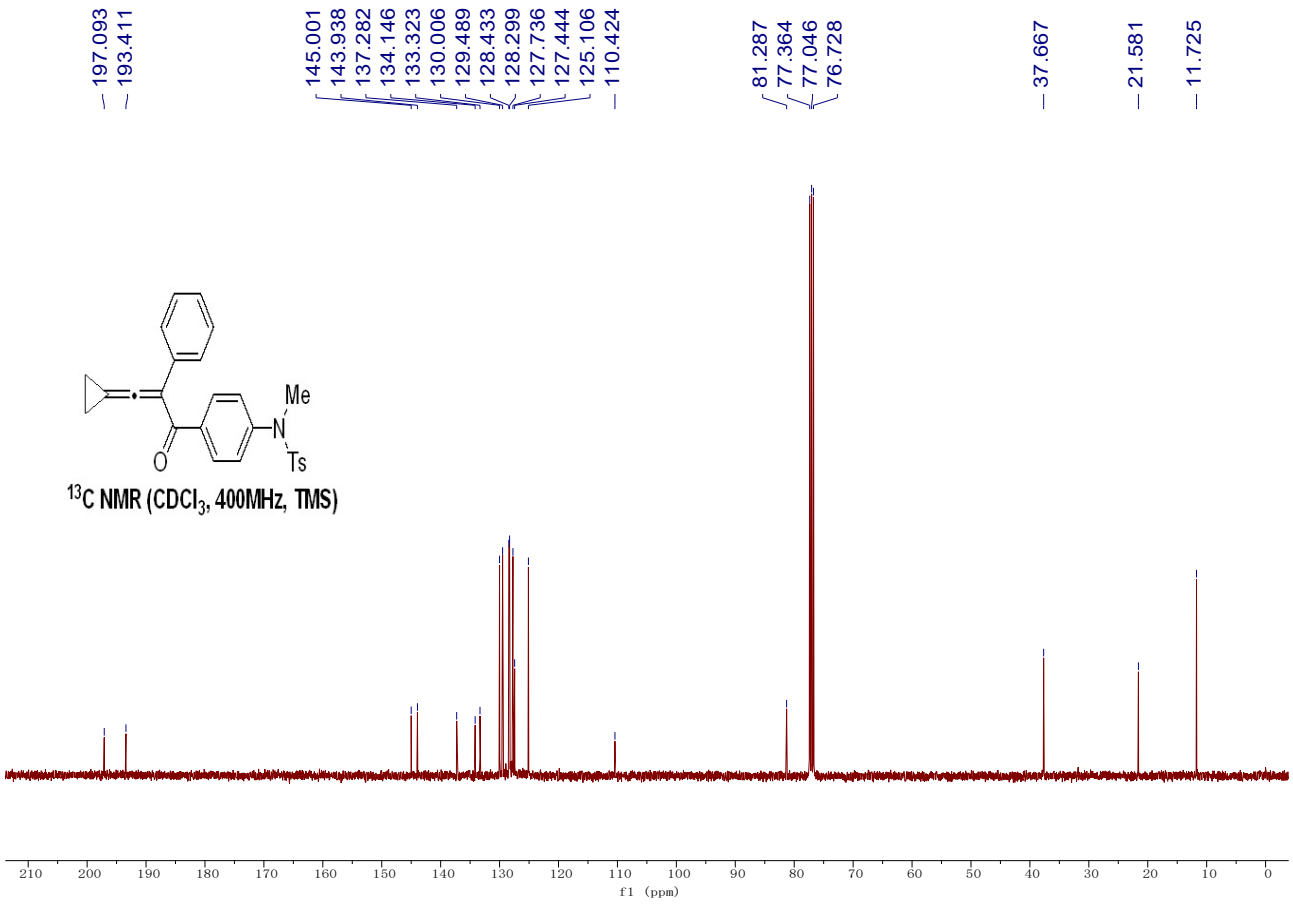
3.06
2.00
2.02
f1 (ppm)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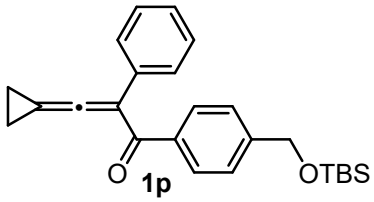
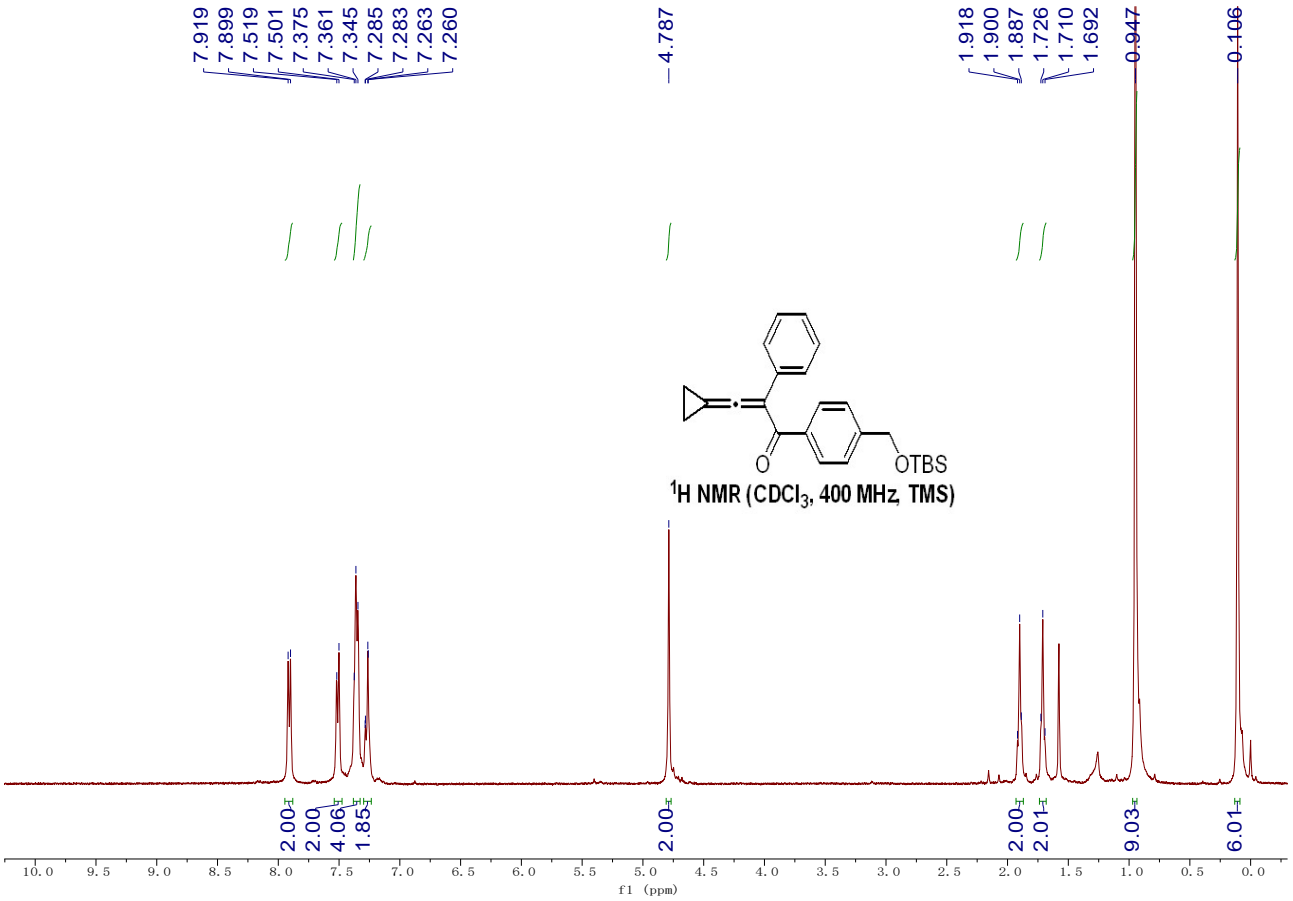
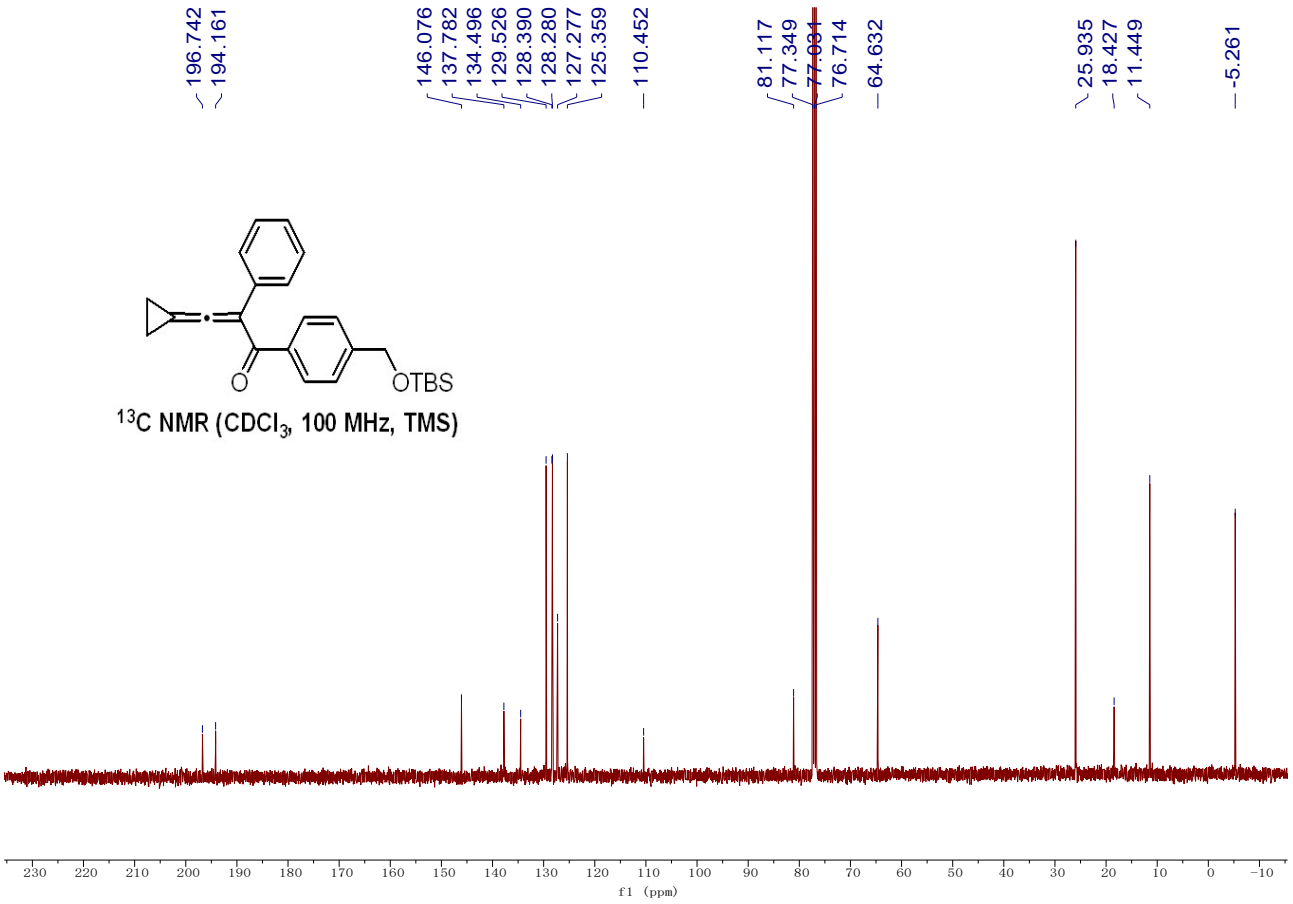
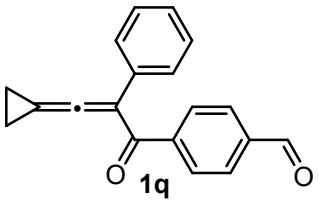
125.106
110.424
81.287
77.364
77.046
76.728
37.667
21.581
11.725
Me
N
Ts
O
13C NMR (CDCl3, 400MHz, TMS)
f1 (ppm)



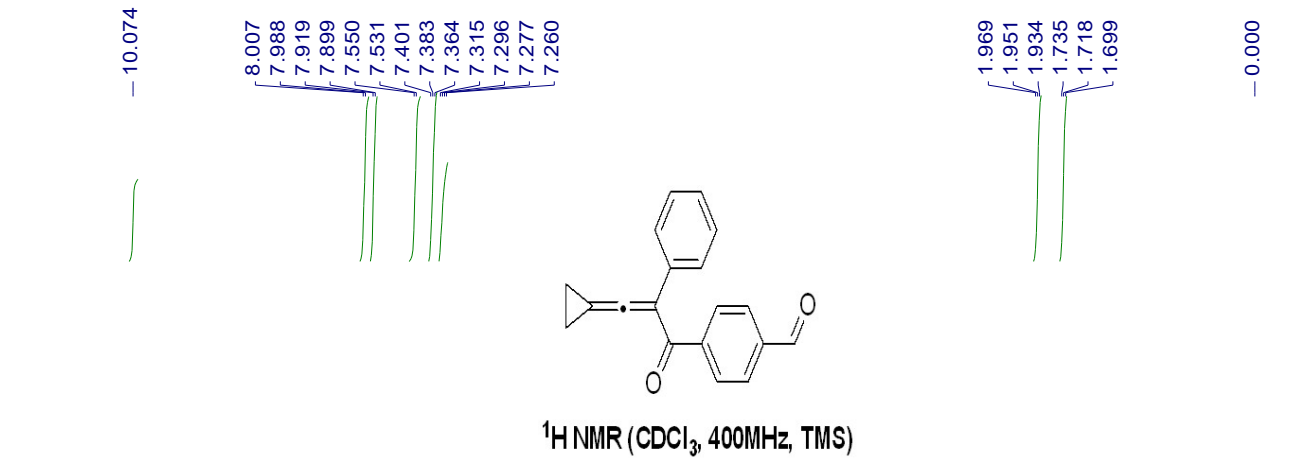
1-(4-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)-3-cyclopropylidene-2-phenylprop-2-en-1-one (**1p**), the title compound was achieved as a yellow oil, 2.66 g, 34% yield (20 mmol scale). R_f = 0.44 (Petroleum Ether:Ethyl Acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.35-7.34 (m, 4H), 7.28-7.26 (m, 1H), 4.79 (s, 2H), 1.90 (dd, *J* = 7.2, 6.4 Hz, 2H), 1.71 (dd, *J* = 7.2, 6.4 Hz, 2H), 0.95 (s, 9H), -0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 194.2, 146.1, 137.8, 134.5, 129.5, 128.4, 128.3, 127.3, 125.4, 110.5, 81.1, 64.6, 25.9, 18.4, 11.4, -5.3. IR (acetone) ν 2953, 2928, 1999, 1651, 1608, 1497, 1443, 1280, 1257, 1091, 1006, 838, 777, 693 cm^{-1}. HRMS (ESI) calcd for $[C_{25}H_{30}O_2NaSi]^+$: 413.1907, found: 413.1901.



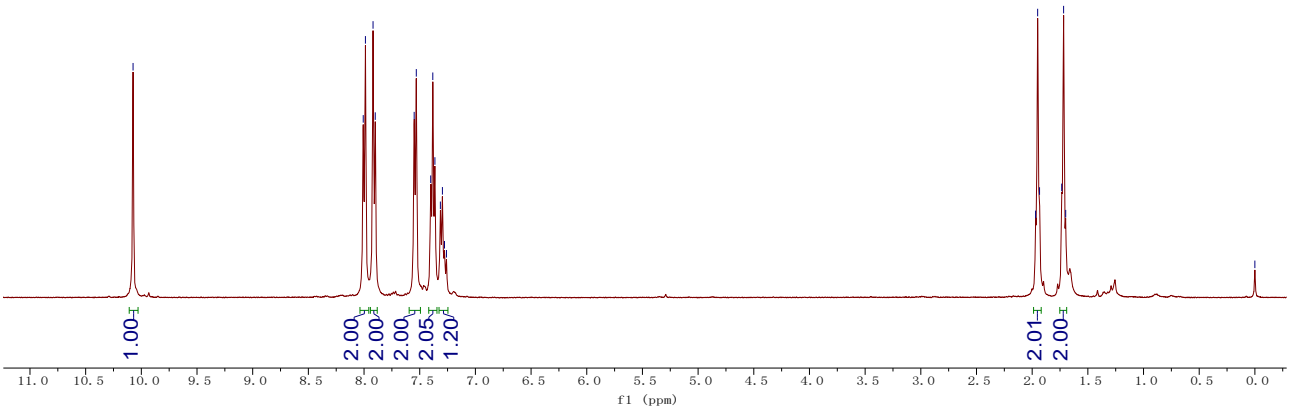


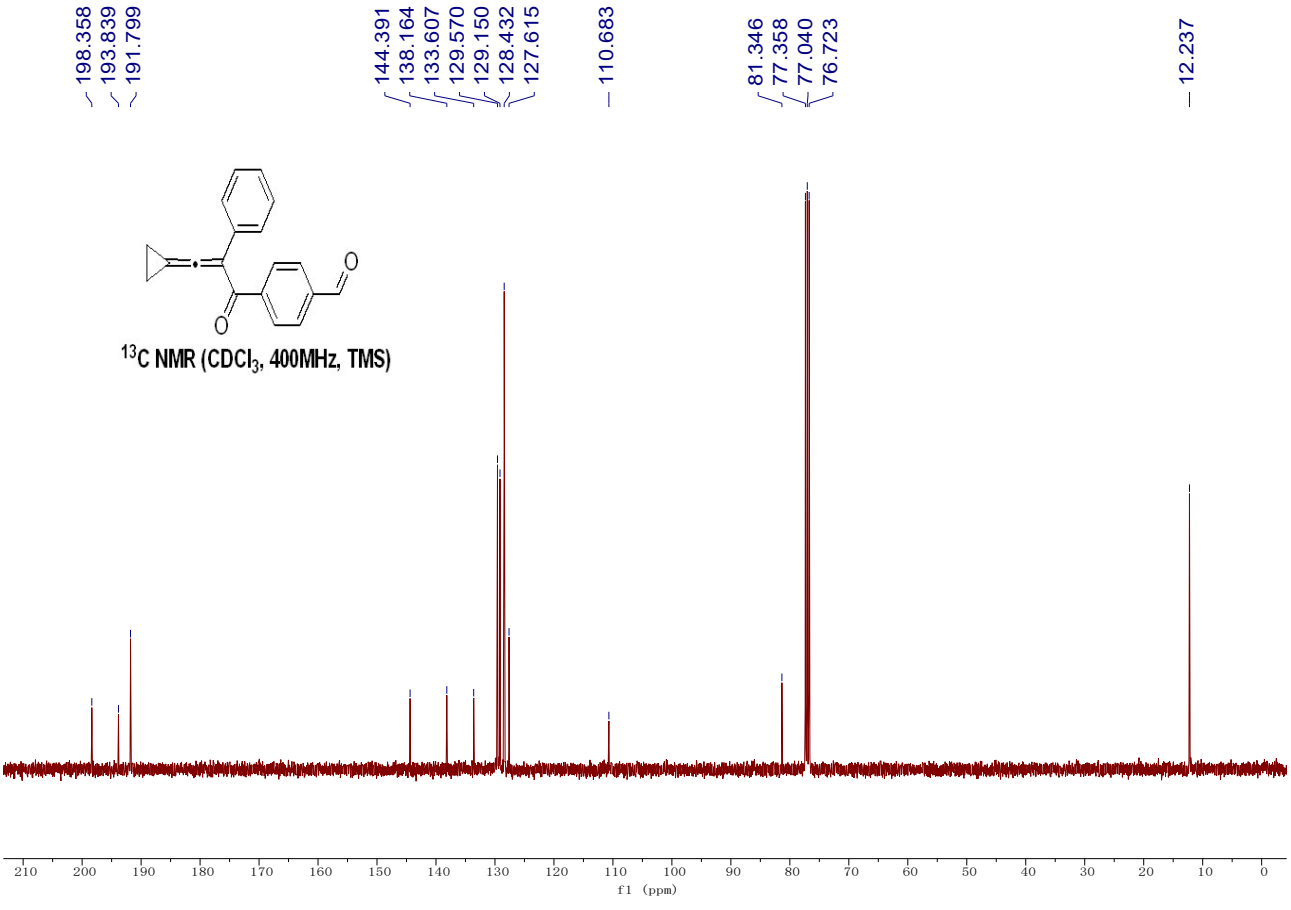


4-(3-cyclopropylidene-2-phenylacryloyl)benzaldehyde (**1q**), the title compound was achieved as a white solid, MP = 51-53 °C, 1.83 g, 33% yield (20 mmol scale). R_f = 0.57 (Petroleum Ether:Ethyl Acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 1H), 1.95 (dd, *J* = 7.6, 6.8 Hz, 2H), 1.72 (dd, *J* = 7.6, 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 193.8, 191.8, 144.4, 138.2, 133.6, 129.6, 129.2, 128.4, 127.6, 110.7, 81.3, 12.2. IR (acetone) ν 2998, 2937, 1998, 1704, 1650, 1607, 1494, 1361, 1294, 1205, 1101, 1056, 769, 700 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{14}O_2Na]^+$: 297.0886, found: 297.0884.

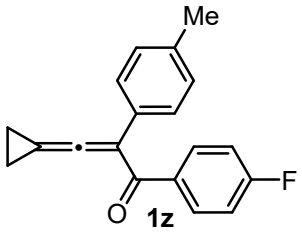


^{1}H NMR ($CDCl_3$, 400MHz, TMS)

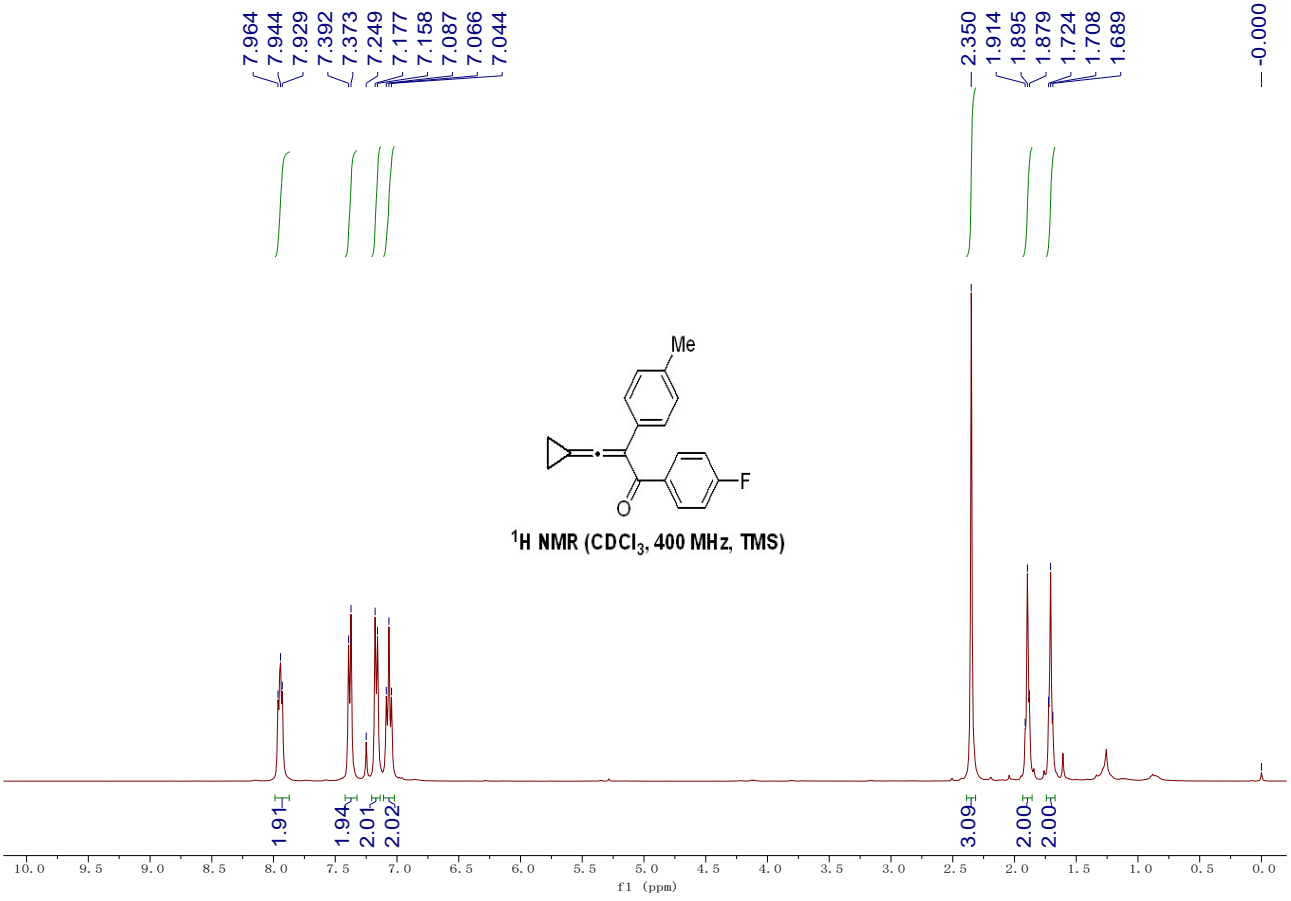


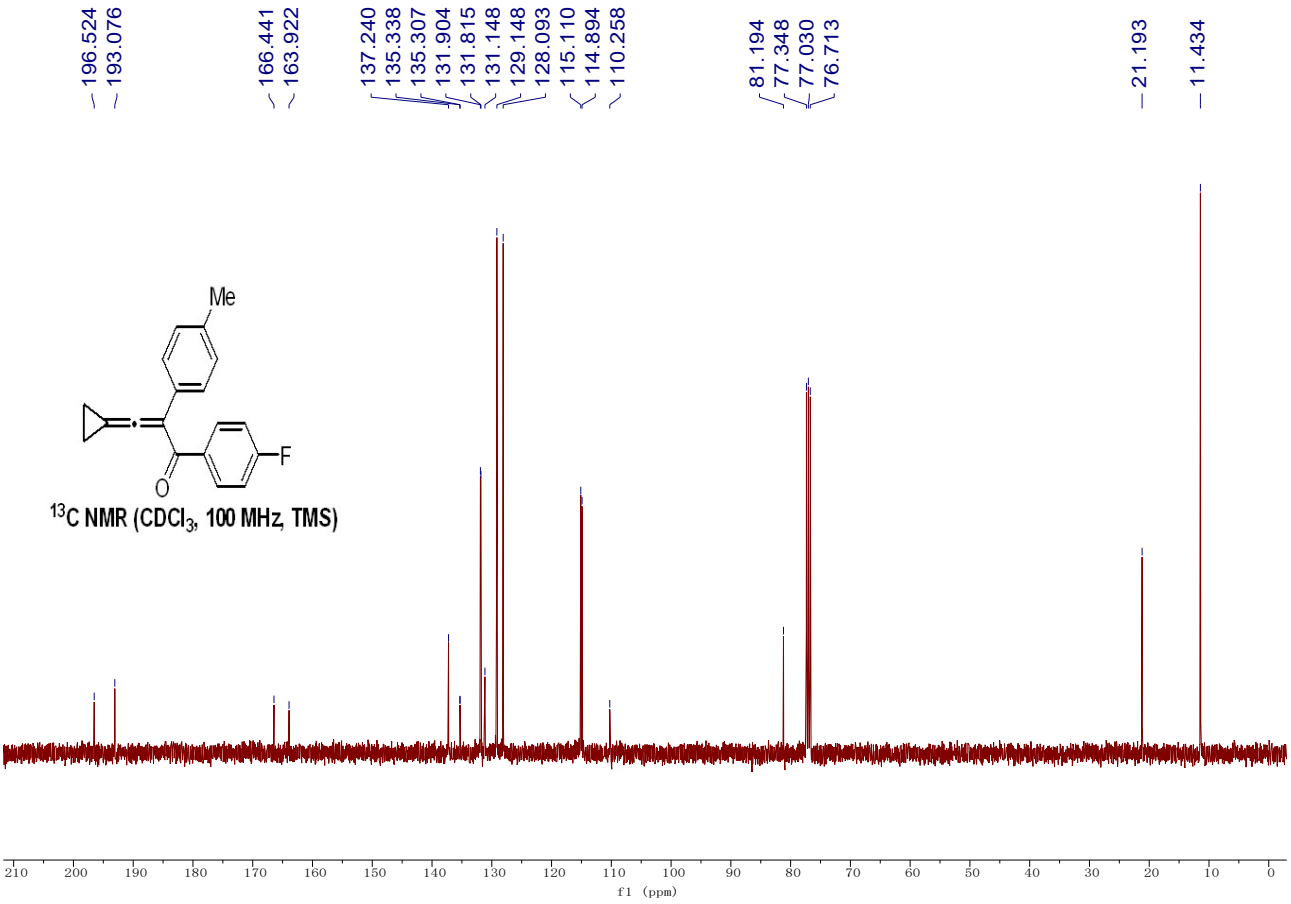


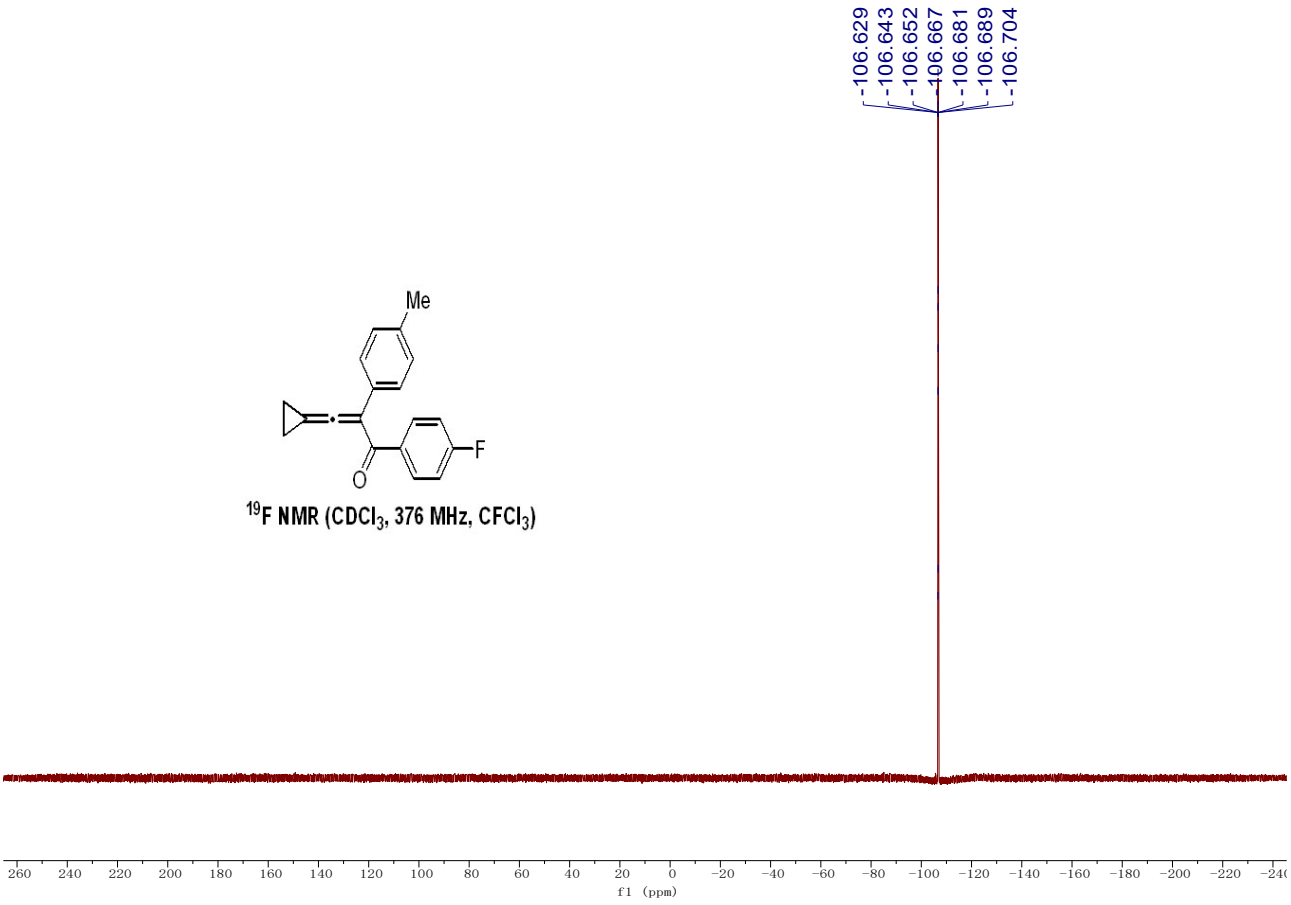
^{13}C NMR ($CDCl_3$, 400MHz, TMS)

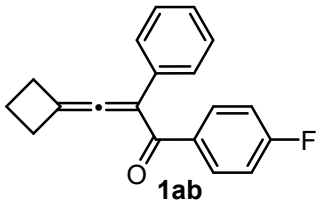


3-cyclopropylidene-1-(4-fluorophenyl)-2-(p-tolyl)prop-2-en-1-one (1z), the title compound was achieved as a yellow oil, 1.94 g, 35% yield (20 mmol scale). R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, J = 8.4, 5.2 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 8.4 Hz, 2H), 2.35 (s, 3H), 1.89 (dd, J = 7.6, 6.4 Hz, 2H), 1.73 (dd, J = 7.6, 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 193.1, 165.2 (d, J_{CF} = 251.9 Hz), 137.2, 135.3 (d, J_{CF} = 3.1 Hz), 131.9 (d, J_{CF} = 8.9 Hz), 131.1, 129.1, 128.1, 115.6 (d, J_{CF} = 21.6 Hz), 110.3, 81.2, 21.2, 11.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.7. IR (neat) ν 1997, 1649, 1597, 1504, 1465, 1280, 1230, 1154, 1005, 862, 848, 822, 781 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{15}ONa]^+$: 301.0999, found: 301.1000.



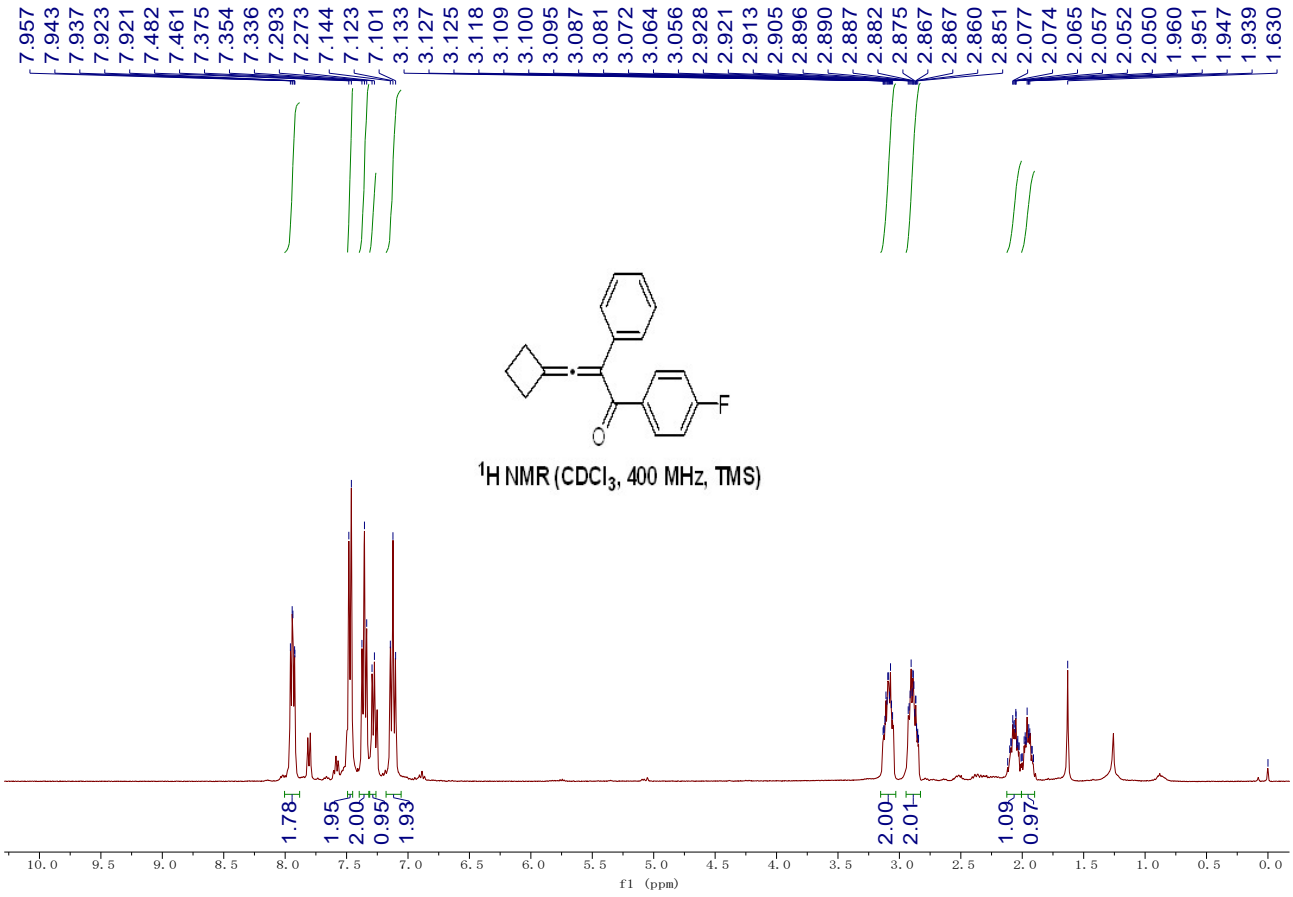

196.524
193.076
166.441
163.922
137.240
135.338
135.307
131.904
131.815
131.148
129.148
128.093
115.110
114.894
110.258
81.194
77.348
77.030
76.713
21.193
11.434
Me
F
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

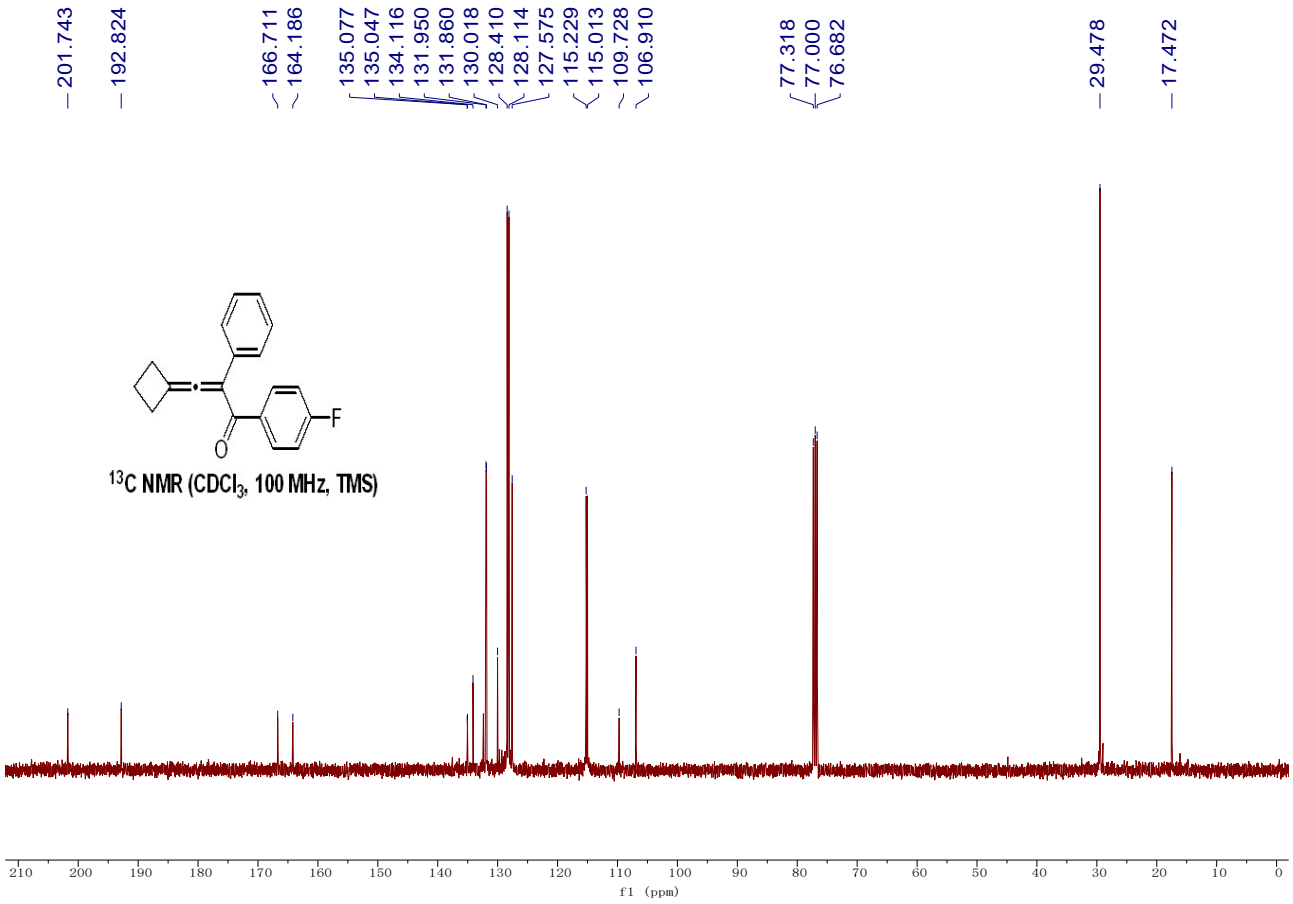

-106.629
-106.643
-106.652
-106.667
-106.681
-106.689
-106.704
Me
F
O
19F NMR (CDCl3, 376 MHz, CFCl3)
f1 (ppm)

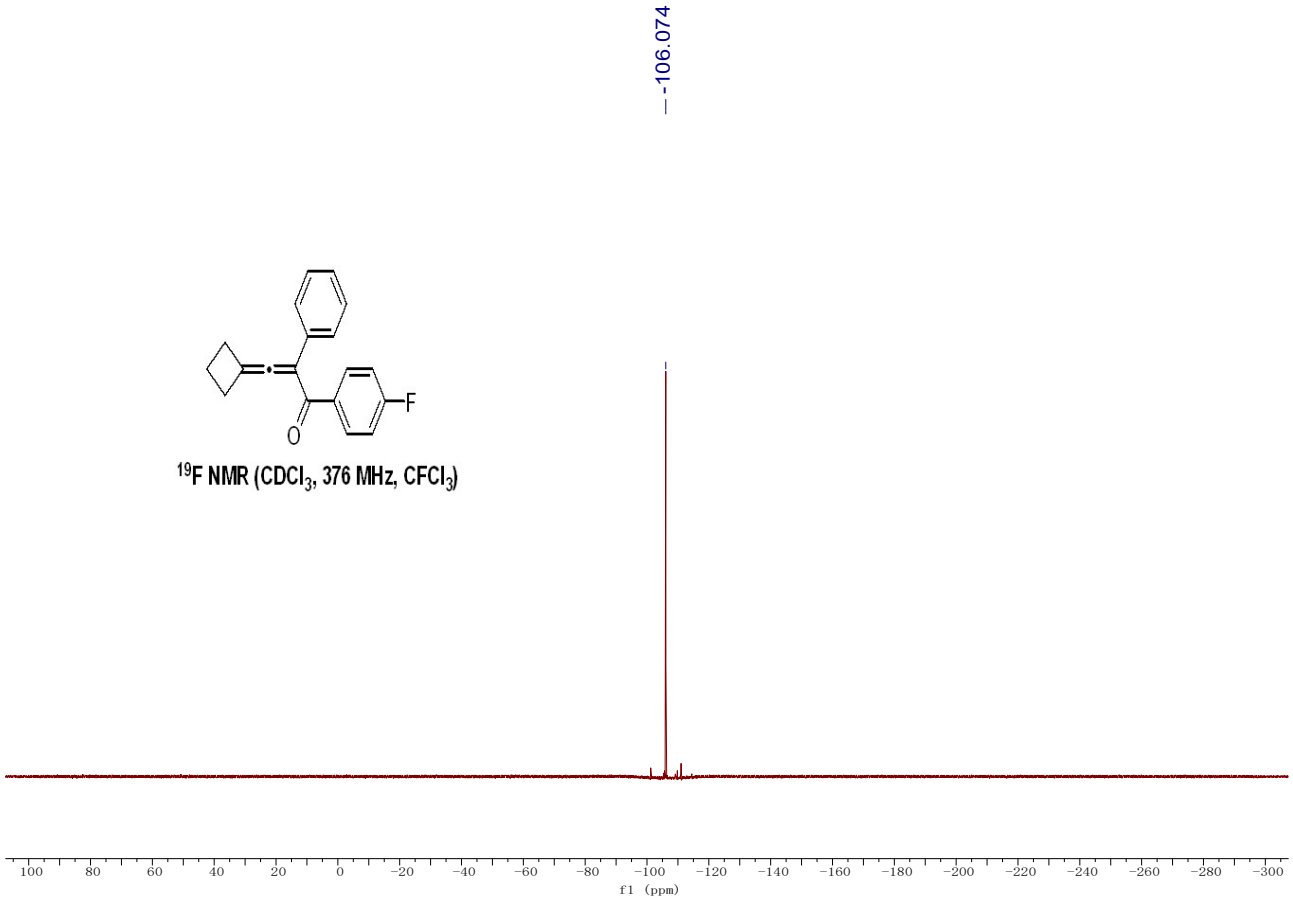


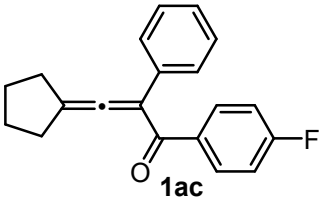
1ab

3-cyclobutylidene-1-(4-fluorophenyl)-2-phenylprop-2-en-1-one (1ab), the title compound was achieved as a white solid, MP = 48-50 °C, 0.56 g, 10% yield. R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.92 (m, 2H), 7.48-7.46 (m, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.29-7.27 (m, 1H), 7.12 (t, J = 8.0 Hz, 2H), 3.13-3.06 (m, 2H), 2.92-2.84 (m, 2H), 2.10-2.01 (m, 1H), 1.98-1.91 (m, 1H), 1.52 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 192.8, 165.4 (d, J_{CF} = 252.5 Hz), 135.1 (d, J_{CF} = 3.0 Hz), 134.1, 132.4, 131.9 (d, J_{CF} = 9.0 Hz), 128.4, 128.1, 127.6, 115.1 (d, J_{CF} = 21.6 Hz), 109.7, 106.9, 29.5, 17.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.1. IR (acetone) ν 3675, 2988, 2970, 2901, 1655, 1597, 1504, 1407, 1262, 1228, 1075, 1066, 1056, 862, 694 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{16}OF]^+$: 279.1180, found: 279.1176.

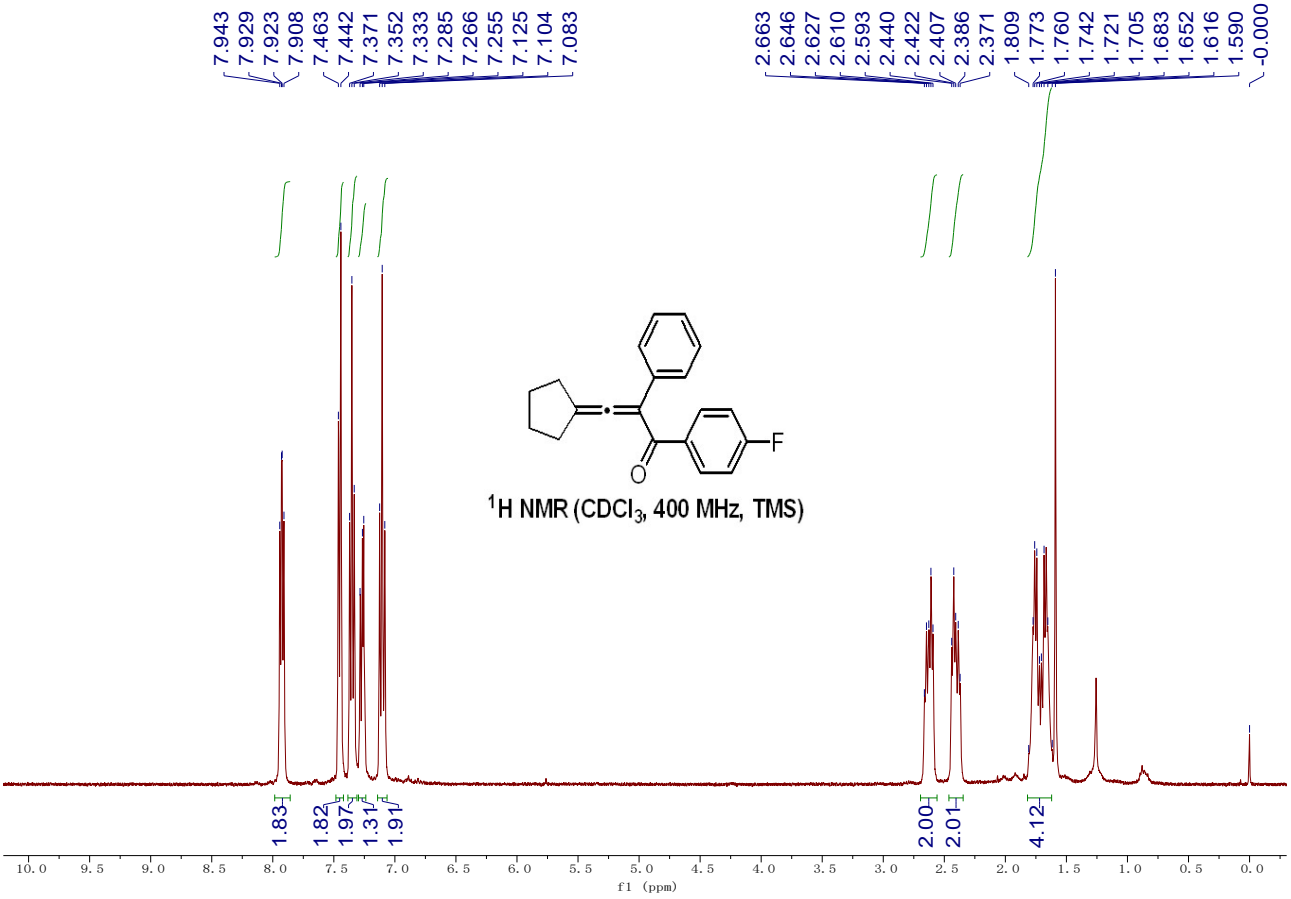


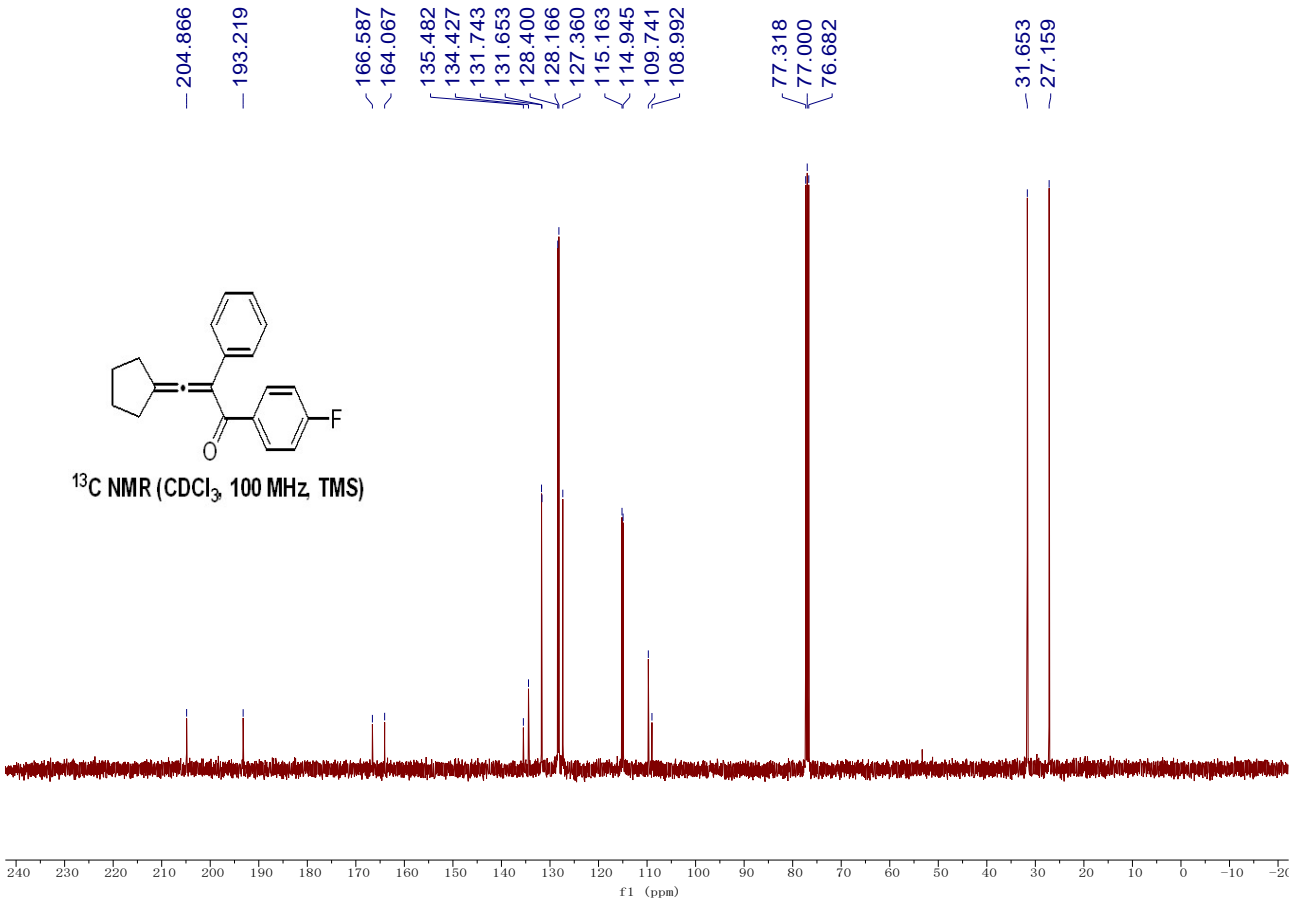

201.743
192.824
166.711
164.186
135.077
135.047
134.116
131.950
131.860
130.018
128.410
128.114
127.575
115.229
115.013
109.728
106.910
77.318
77.000
76.682
29.478
17.472
F
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

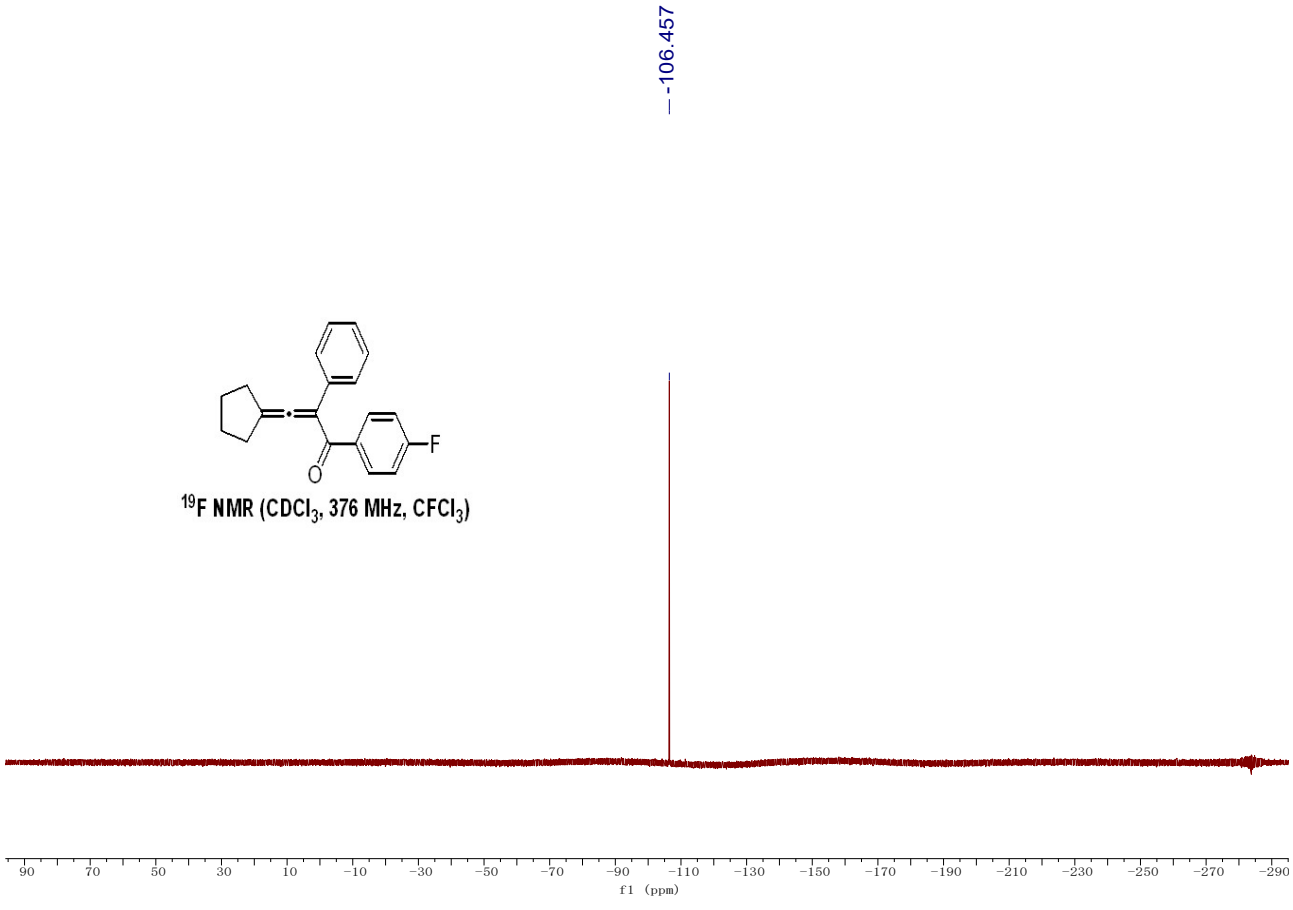

-106.074
F
O
19F NMR (CDCl3, 376 MHz, CFCl3)
f1 (ppm)



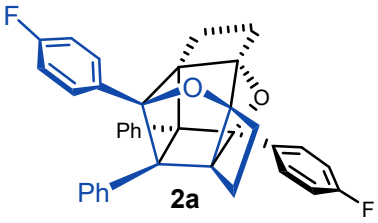
3-cyclopentylidene-1-(4-fluorophenyl)-2-phenylprop-2-en-1-one (1ac), the title compound was achieved as yellow oil, 0.88 g, 15% yield. R_f = 0.45 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, J = 8.0, 5.6 Hz, 2H), 7.46-7.44 (m, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.27-7.26 (m, 1H), 7.10 (t, J = 8.4 Hz, 2H), 2.66-2.60 (m, 2H), 2.44-2.37 (m, 2H), 1.81-1.59 (m, 4H), 1.59 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.9, 193.2, 165.3 (d, J_{CF} = 252.0 Hz), 135.5 (d, J_{CF} = 2.8 Hz), 134.4, 131.7 (d, J_{CF} = 9.0 Hz), 128.4, 128.2, 127.4, 115.1 (d, J_{CF} = 21.8 Hz), 109.7, 109.0, 31.7, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.5. IR (acetone) ν 3675, 2987, 2901, 1998, 1646, 1604, 1411, 1280, 1066, 1052, 858, 794, 693 cm^{-1}. HRMS (ESI) calcd for $[C_{20}H_{18}OF]^+$: 293.1336, found: 293.1335.



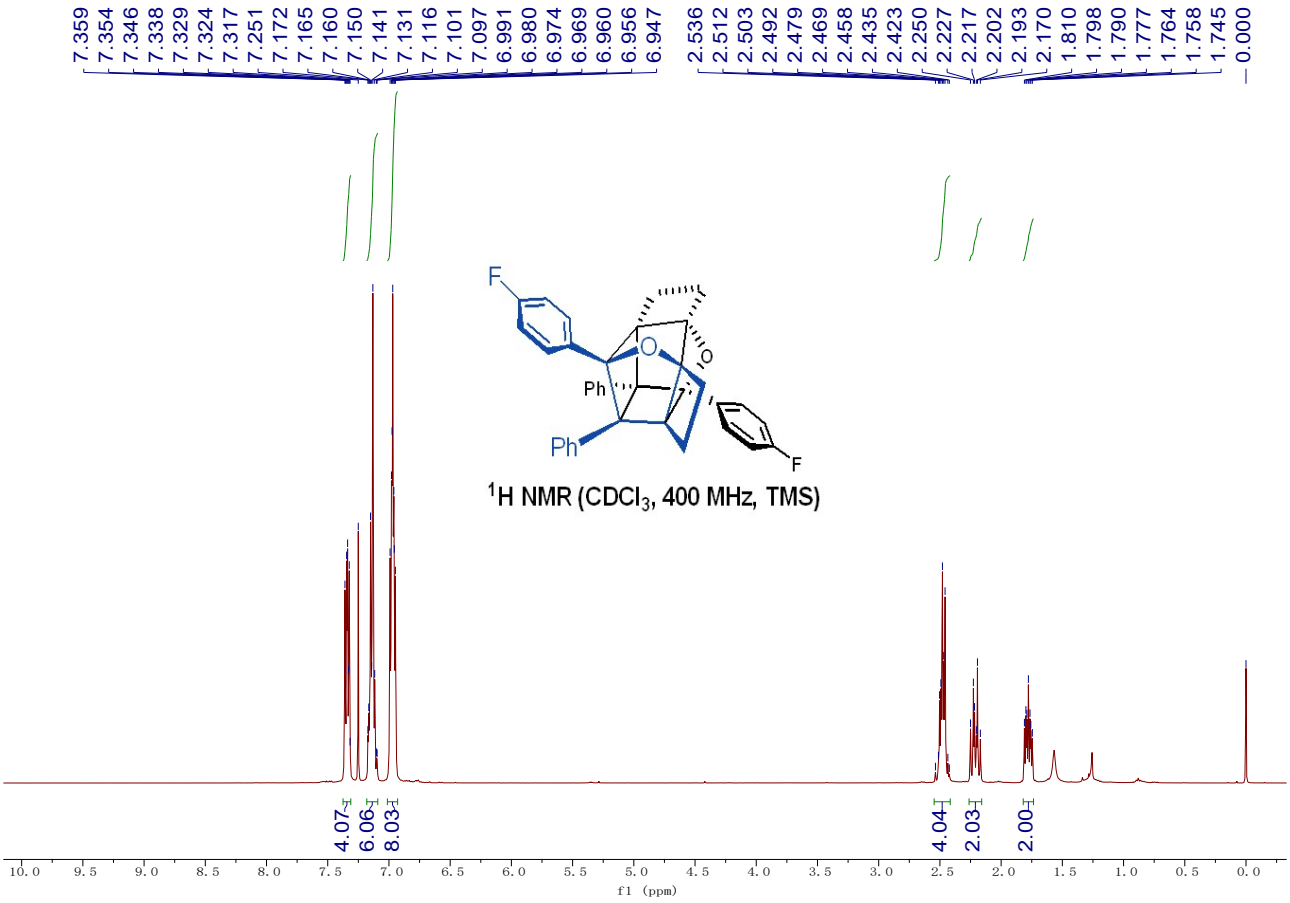

204.866
193.219
166.587
164.067
135.482
134.427
131.743
131.653
128.400
128.166
127.360
115.163
114.945
109.741
108.992
77.318
77.000
76.682
31.653
27.159
F
O
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

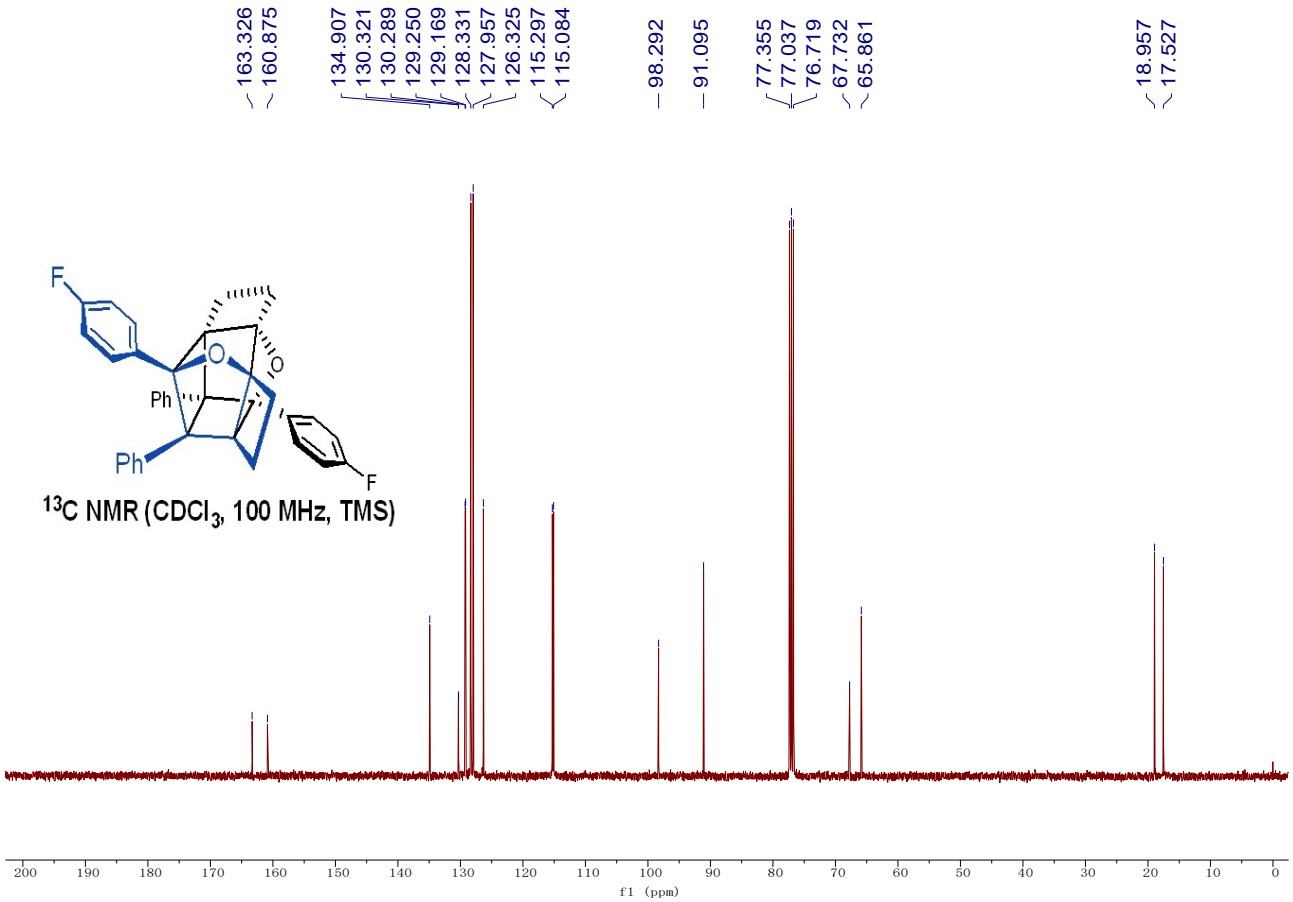

-106.457
F
O
19F NMR (CDCl3, 376 MHz, CFCl3)
f1 (ppm)

(2) Spectroscopic Data of Product

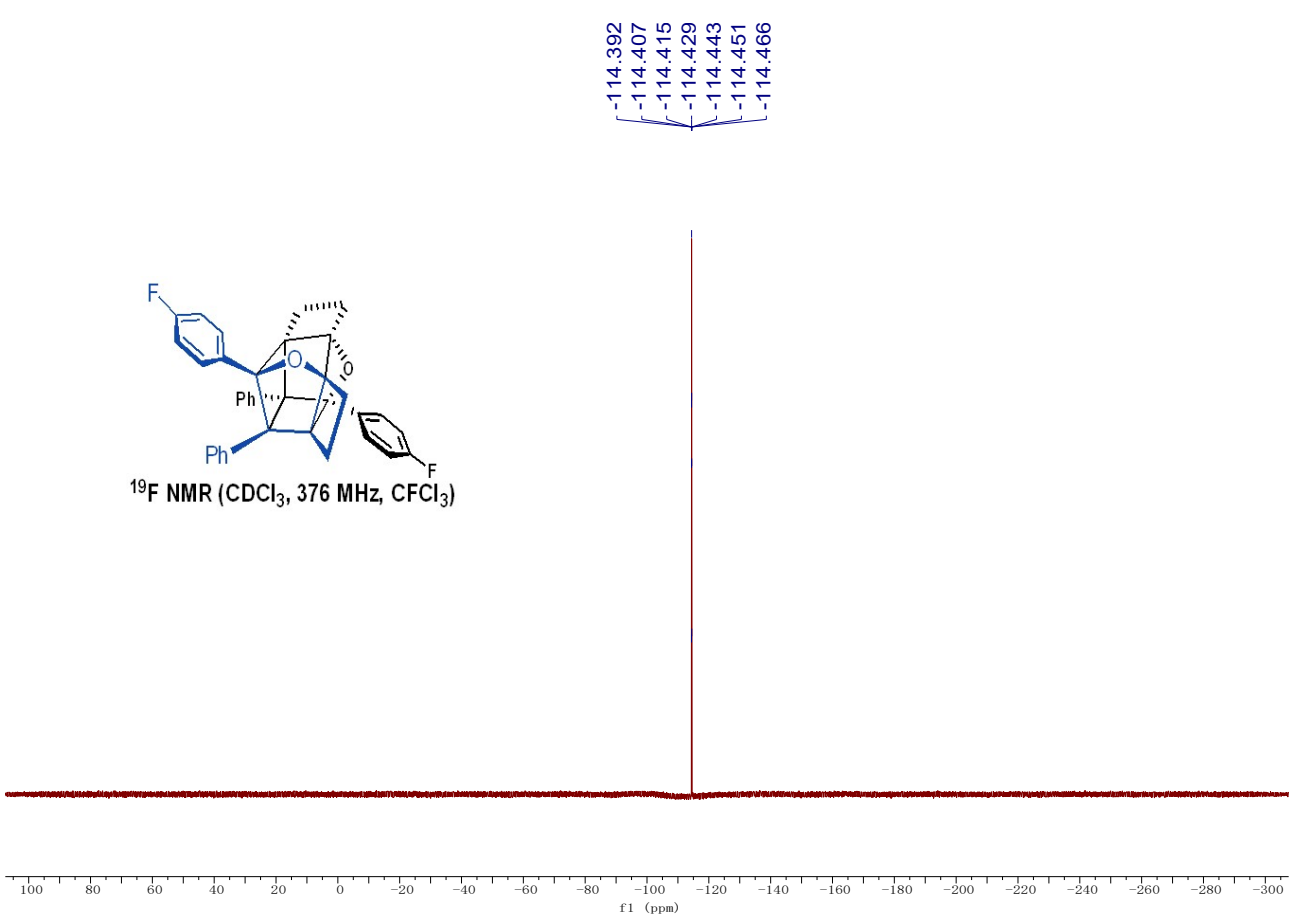


Product 2a, the title compound was achieved as a white solid, MP = 247-249 °C, 38.6 mg, 73% yield. R_f = 0.30 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 4H), 7.17-7.10 (m, 6H), 7.00-6.95 (m, 8H), 2.54-2.42 (m, 4H), 2.23 (t, J = 9.6 Hz, 1H), 2.19 (t, J = 9.6 Hz, 1H), 1.78 (dd, J = 12.8, 8.0 Hz, 1H), 1.77 (dd, J = 12.8, 8.0 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J_{CF} = 245.1 Hz), 134.9, 130.3 (d, J_{CF} = 3.2 Hz), 129.2 (d, J_{CF} = 8.1 Hz), 128.3, 128.0, 126.3, 115.2 (d, J_{CF} = 21.3 Hz), 98.3, 91.1, 67.7, 65.9, 19.0, 17.5 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.4. IR (Acetone) ν 2970, 1739, 1508, 1445, 1367, 1225, 1217, 1157, 1051, 939, 832, 732, 701 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2F_2]^+$: 529.1974, found: 529.1976.

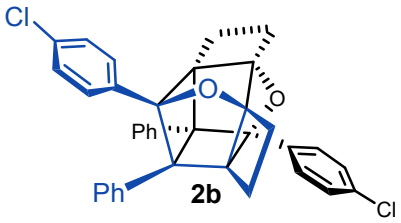




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

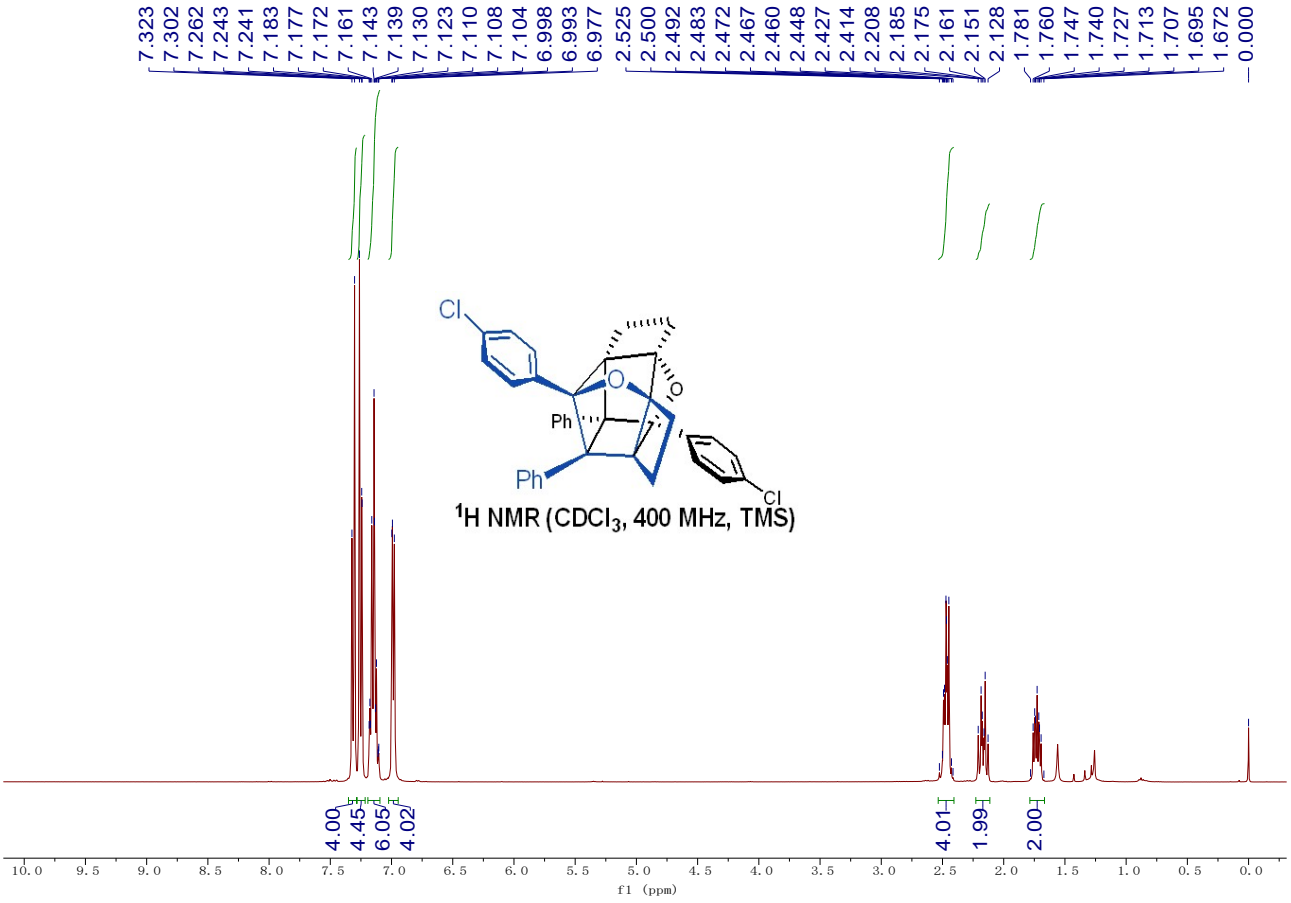


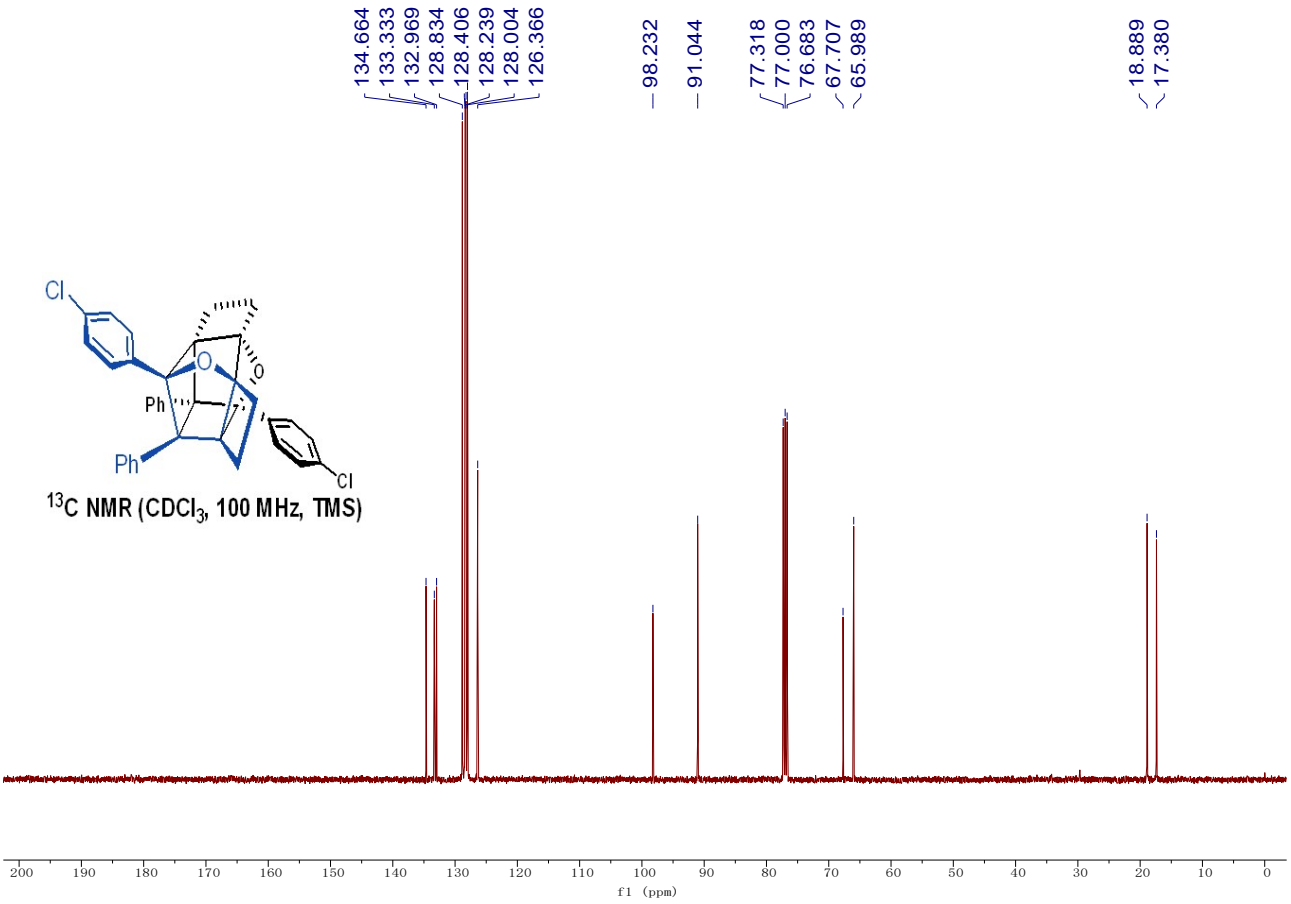
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

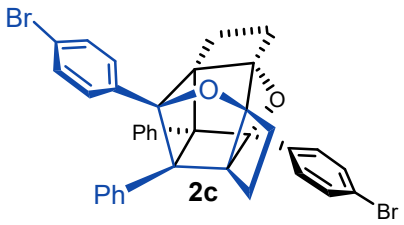


2b

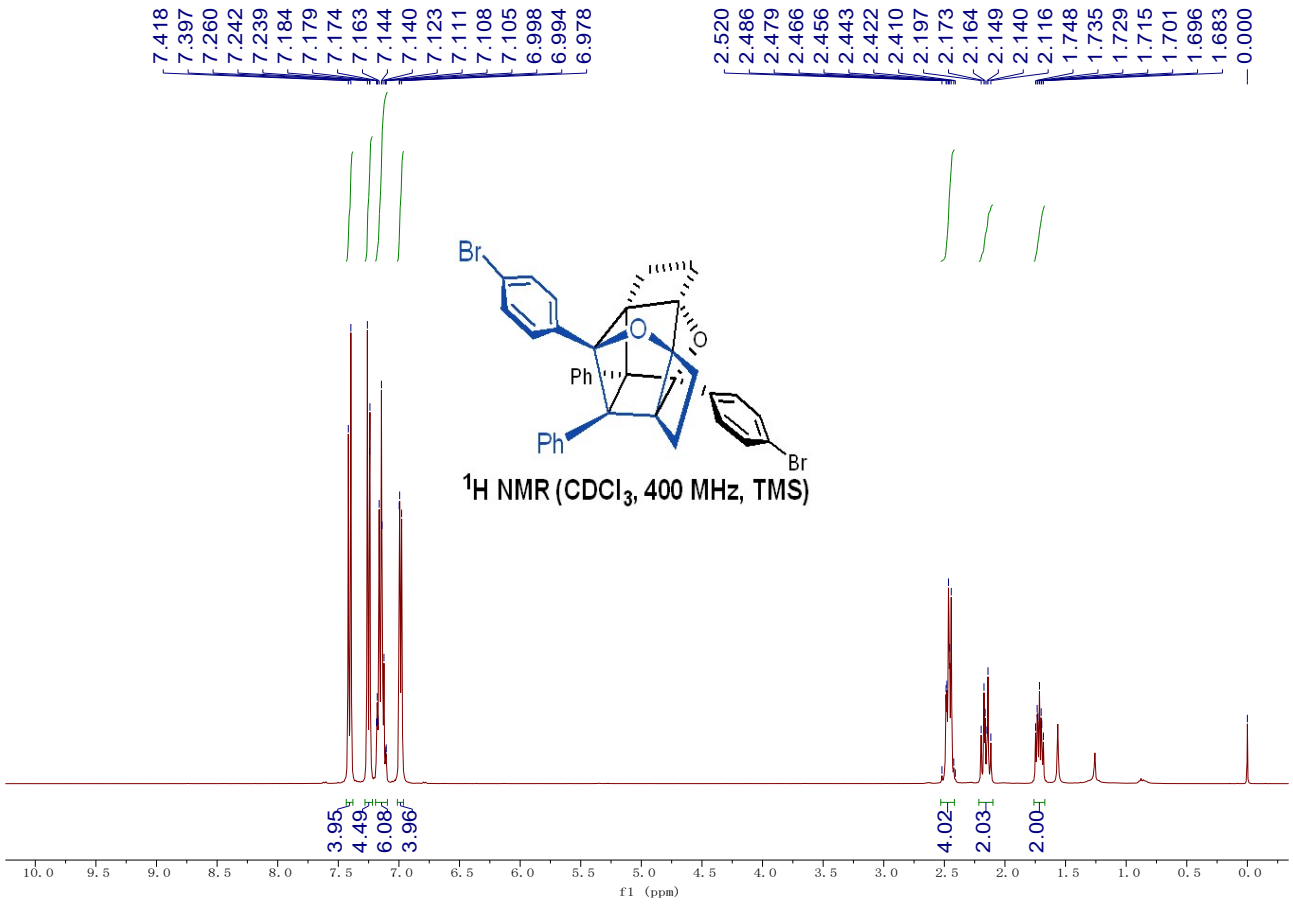
Product 2b, the title compound was achieved as a white solid, MP = 251-253 °C, 31.4 mg, 56% yield. R_f = 0.40 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 4H), 7.26-7.24 (m, 4H), 7.18-7.10 (m, 6H), 7.00-6.98 (m, 4H), 2.53-2.41 (m, 4H), 2.19 (t, *J* = 9.6 Hz, 1H), 2.15 (t, *J* = 9.6 Hz, 1H), 1.73 (dd, *J* = 13.2, 8.0 Hz, 1H), 1.72 (dd, *J* = 13.2, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.3, 133.0, 128.8, 128.4, 128.2, 128.0, 126.4, 98.2, 91.0, 67.7, 66.0, 18.9, 17.4 (each carbon signal represents two C atoms). IR (Acetone) ν 2970, 1739, 1492, 1444, 1365, 1228, 1216, 1091, 940, 824, 773, 704 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2Cl_2]^+$: 561.1383, found: 561.1387.



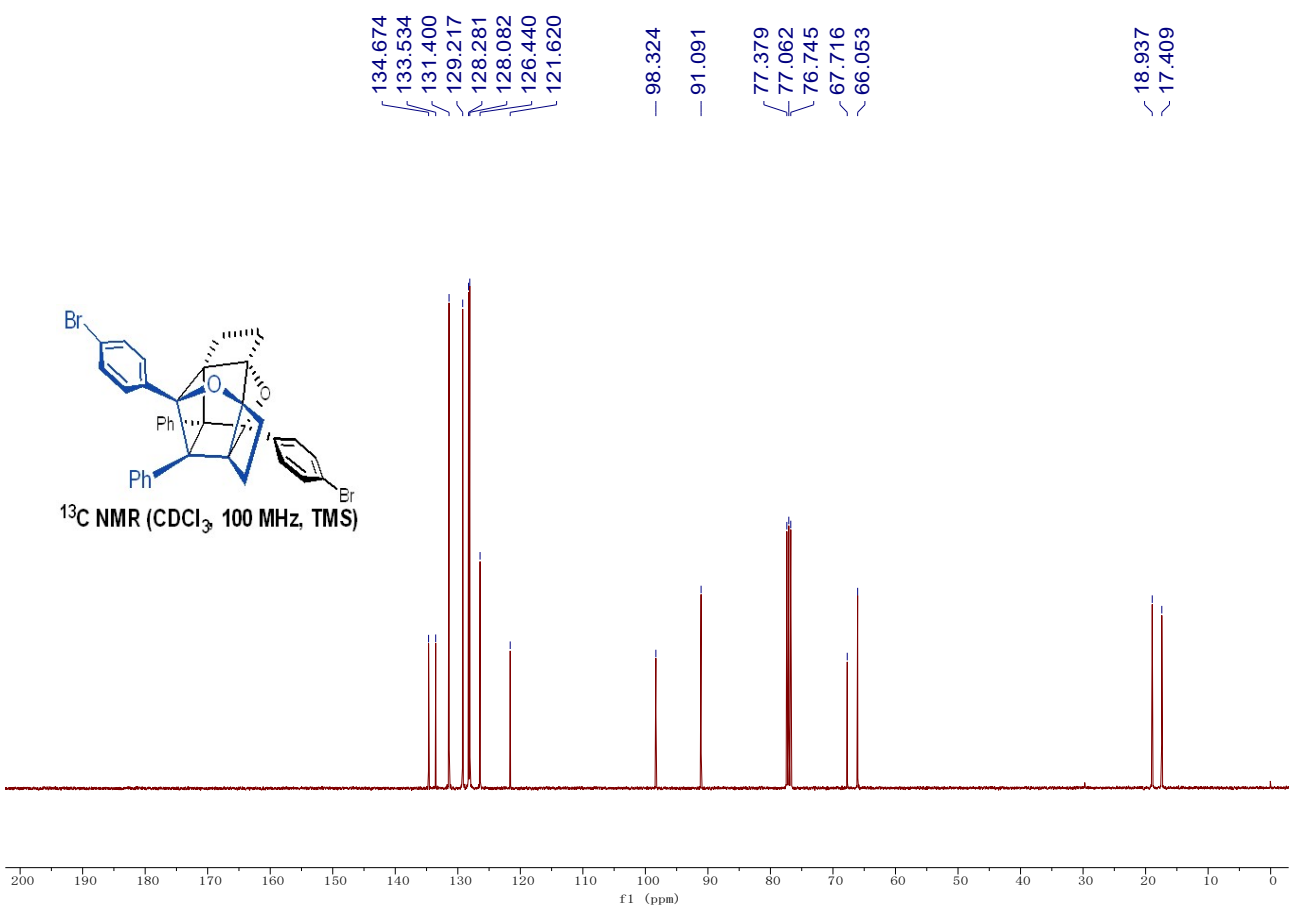




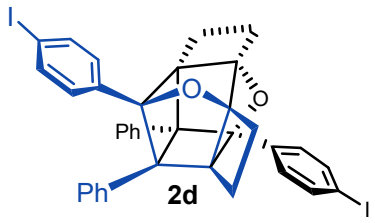
Product 2c, the title compound was achieved as a white solid, MP = 258-260 °C, 33.8 mg, 52% yield. R_f = 0.39 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 4H), 7.26-7.24 (m, 4H), 7.18-7.11 (m, 6H), 7.00-6.98 (m, 4H), 2.52-2.41 (m, 4H), 2.17 (t, *J* = 9.6 Hz, 1H), 2.14 (t, *J* = 9.6 Hz, 1H), 1.72 (dd, *J* = 13.2, 7.2 Hz, 1H), 1.71 (dd, *J* = 13.2, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.5, 131.4, 129.2, 128.3, 128.1, 126.4, 121.6, 98.3, 91.1, 67.7, 66.1, 18.9, 17.4 (each carbon signal represents two C atoms). IR (Acetone) ν 2970, 1739, 1492, 1445, 1365, 1228, 1217, 1072, 942, 822, 734, 699 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2Br_2]^+$: 649.0372, found: 649.0370.



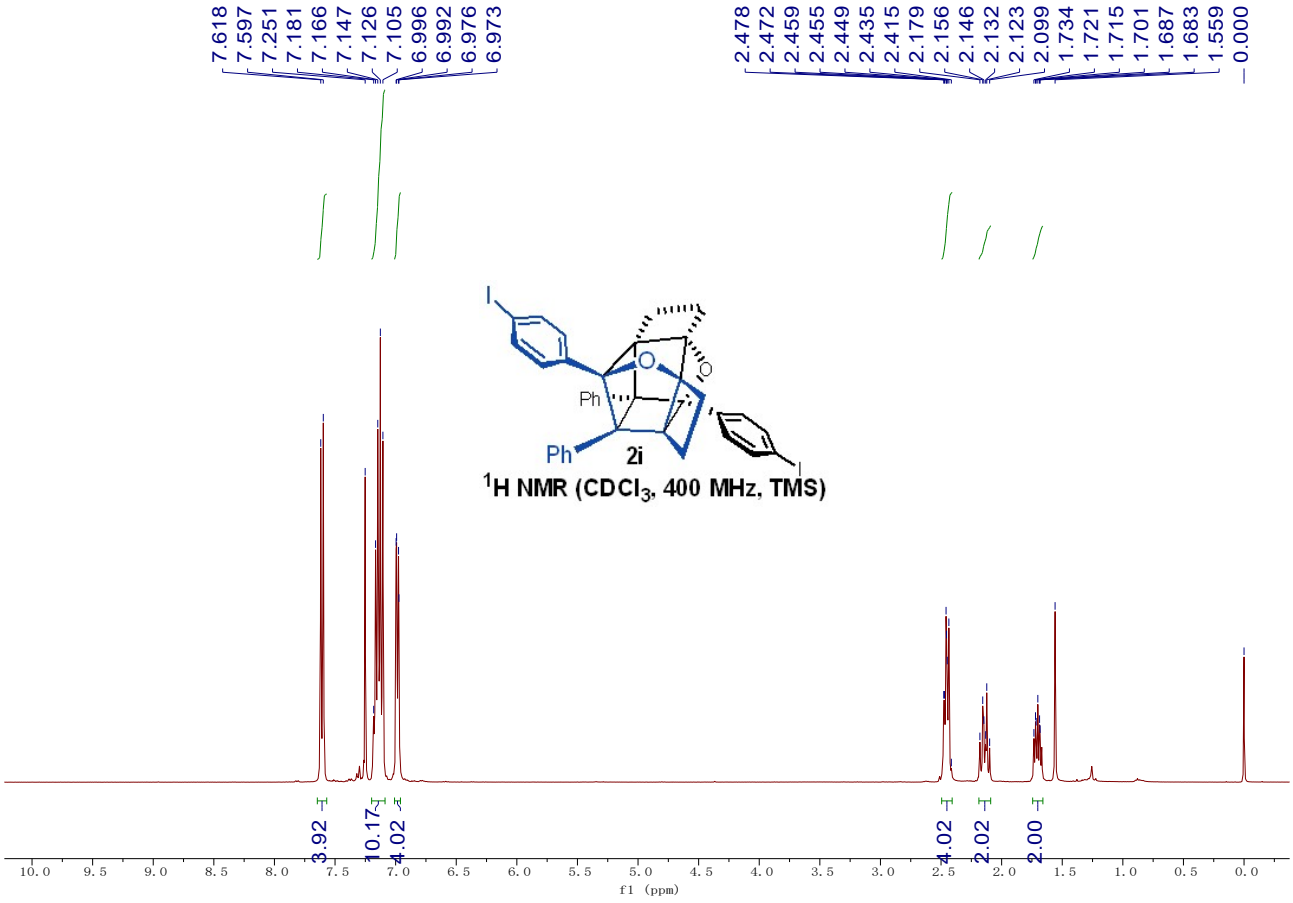
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

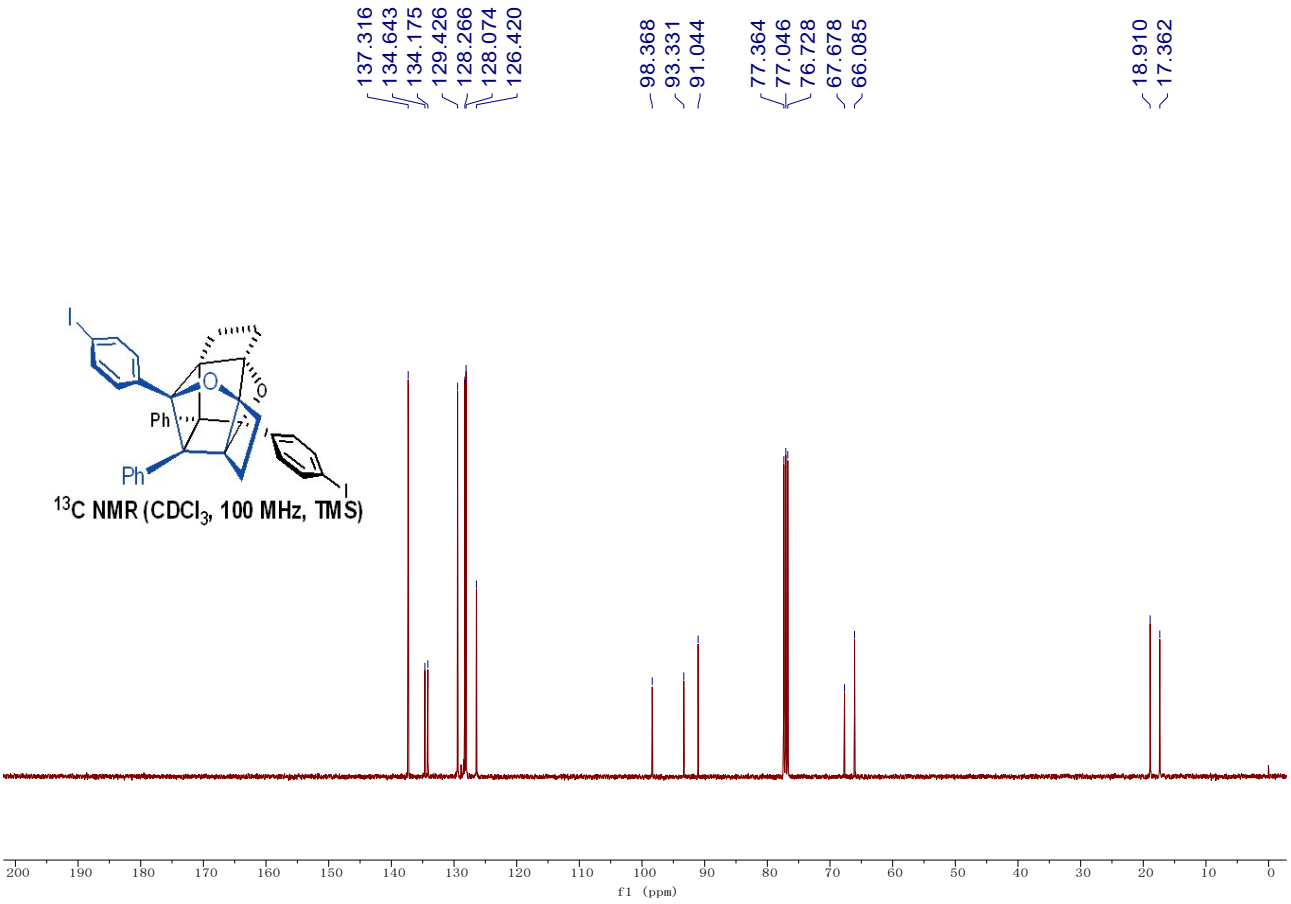


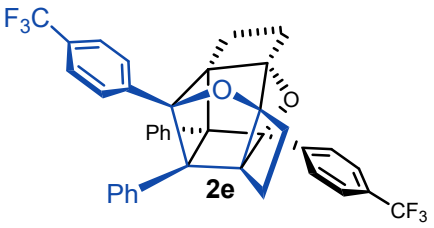
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



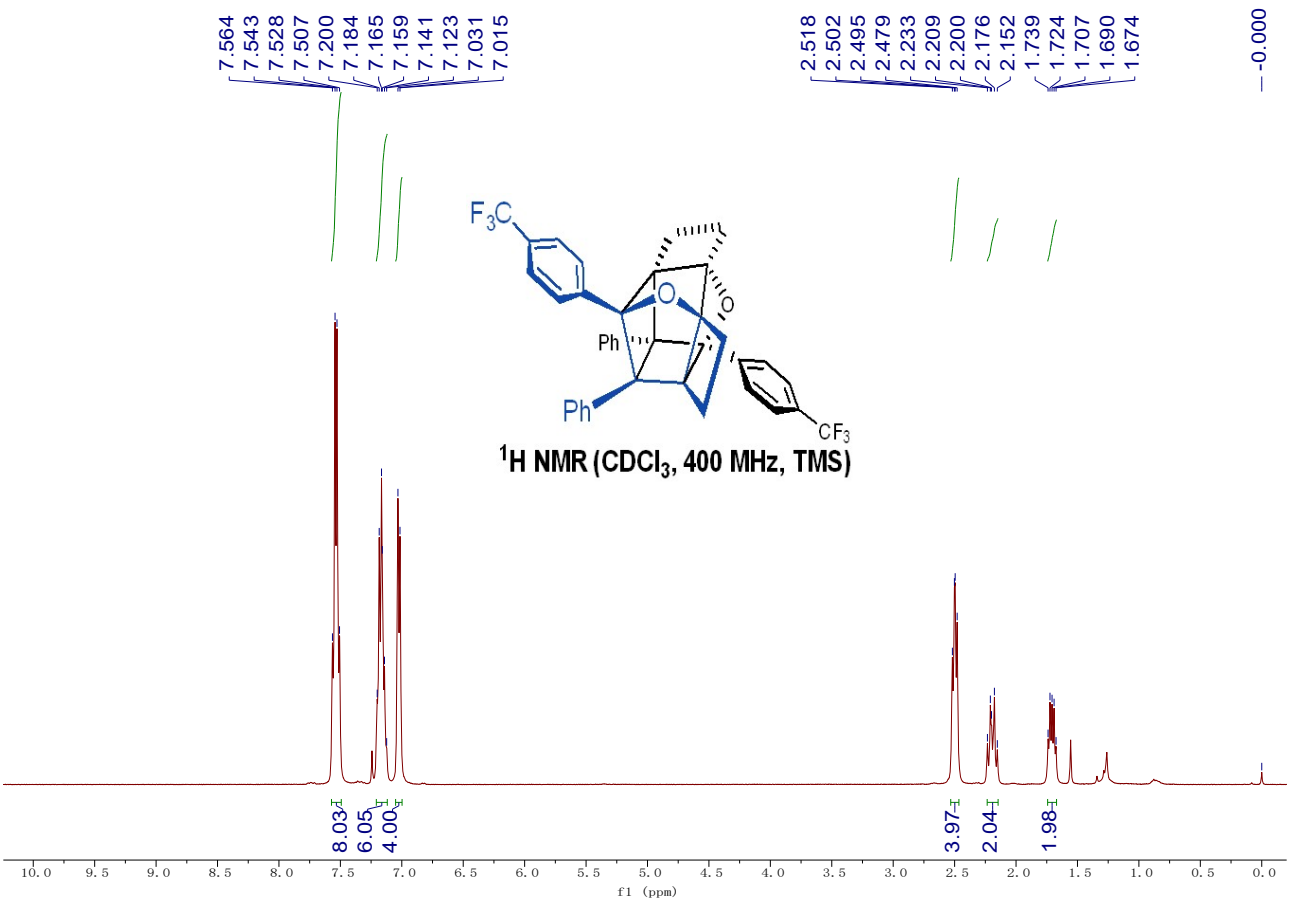
Product 2d, the title compound was achieved as a white solid, MP = 264-266 °C, 50.6 mg, 68% yield. R_f = 0.38 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 4H), 7.18-7.11 (m, 10H), 7.00-6.97 (m, 4H), 2.48-2.42 (m, 4H), 2.16 (t, *J* = 9.6 Hz, 1H), 2.12 (t, *J* = 9.6 Hz, 1H), 1.71 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.70 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.56 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 134.6, 134.2, 129.4, 128.3, 128.1, 126.4, 98.4, 93.3, 91.0, 67.7, 66.1, 18.9, 17.4 (each carbon signal represents two C atoms). IR (Acetone) ν 2970, 1738, 1496, 1445, 1365, 1228, 1217, 1007, 974, 820, 799, 698 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2I_2]^+$: 745.0095, found: 745.0097.



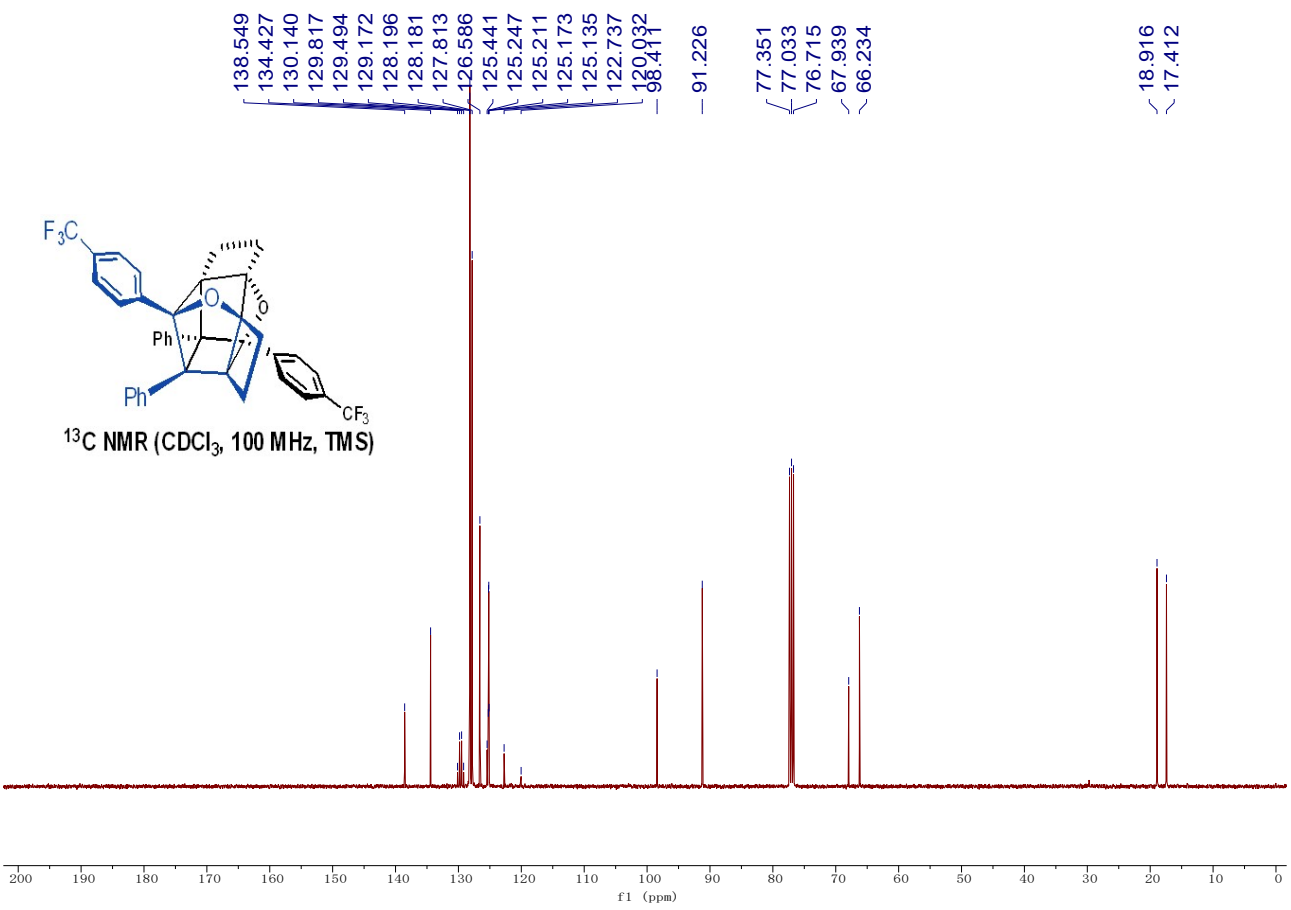




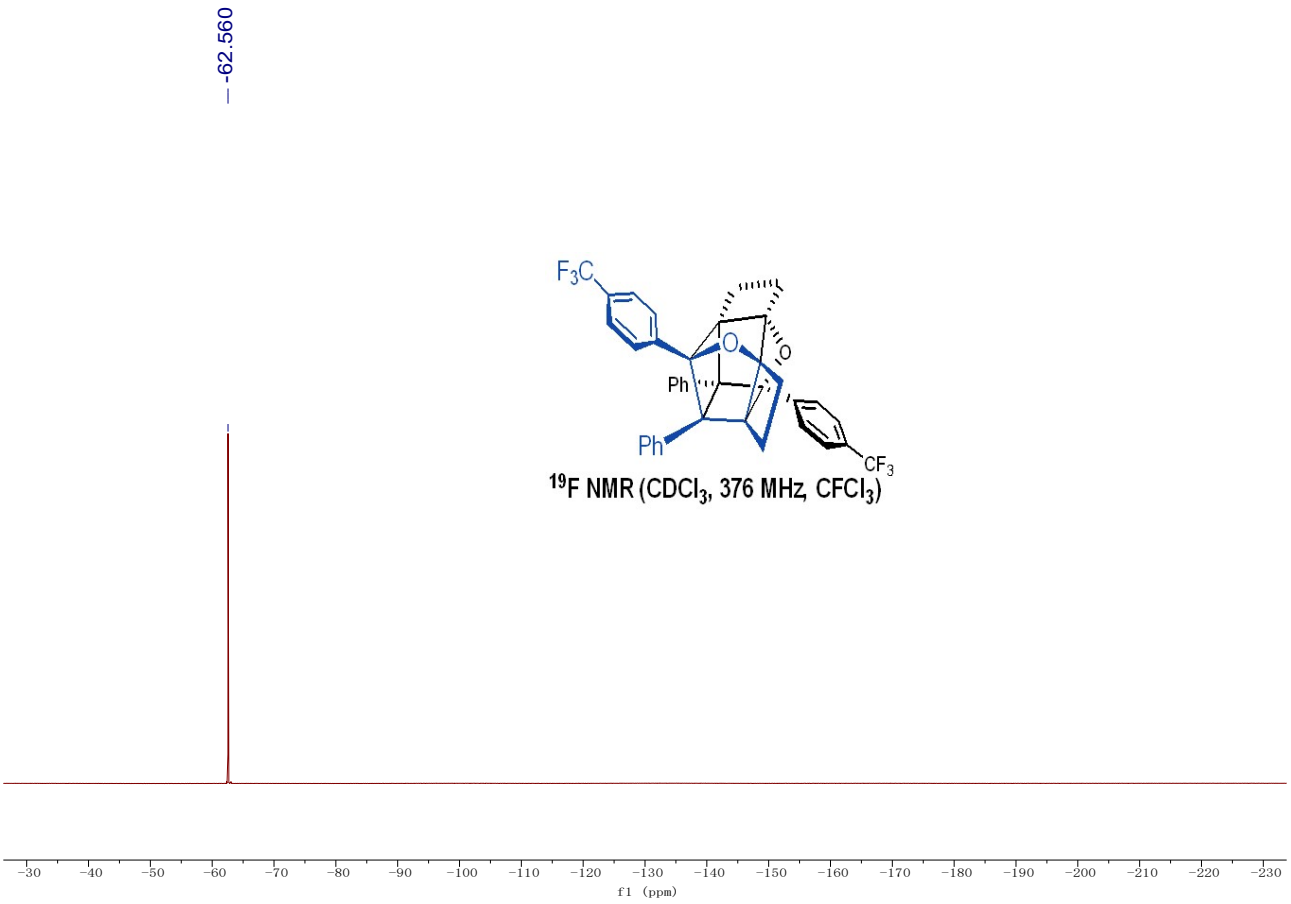
Product 2e, the title compound was achieved as a white solid, MP = 248-250 °C, 37.1 mg, 59% yield. R_f = 0.41 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (q, *J* = 8.4 Hz, 8H), 7.20-7.12 (m, 6H), 7.03-7.02 (m, 4H), 2.50 (dd, *J* = 9.2, 6.4 Hz, 4H), 2.21 (t, *J* = 9.6 Hz, 1H), 2.18 (t, *J* = 9.6 Hz, 1H), 1.72 (dd, *J* = 13.2, 6.4 Hz, 1H), 1.71 (dd, *J* = 13.2, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 134.4, 129.7 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.2, 128.1, 127.8, 126.6, 125.4, 125.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.4 Hz), 98.4, 91.2, 67.9, 66.2, 18.9, 17.4 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. IR (Acetone) ν 2970, 1777, 1410, 1322, 1168, 1113, 1072, 941, 834, 780, 699 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{27}O_2F_6]^+$: 629.1910, found: 629.1900.

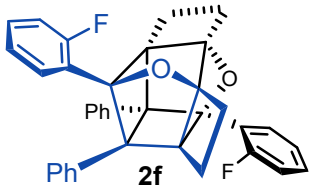


^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



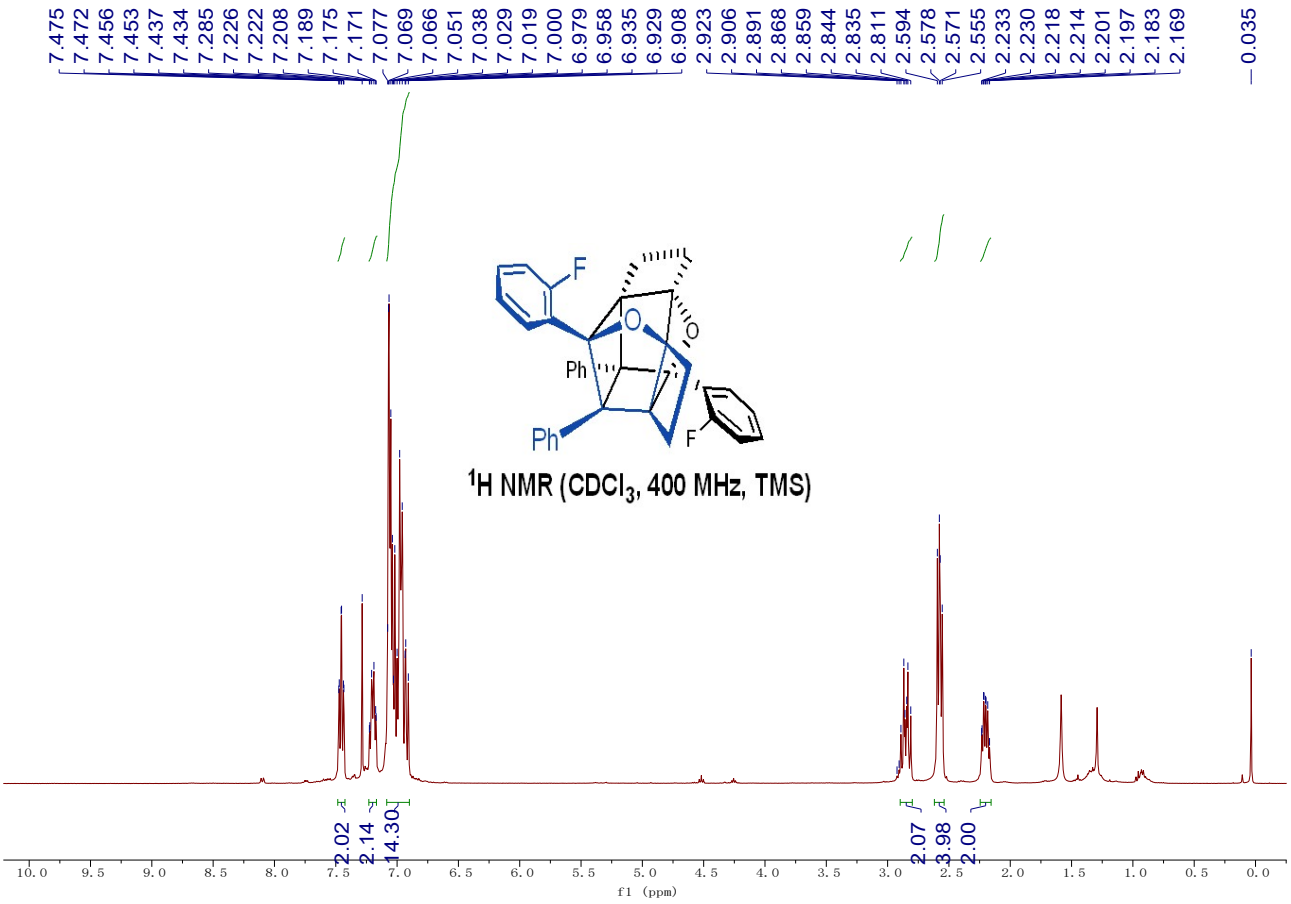
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



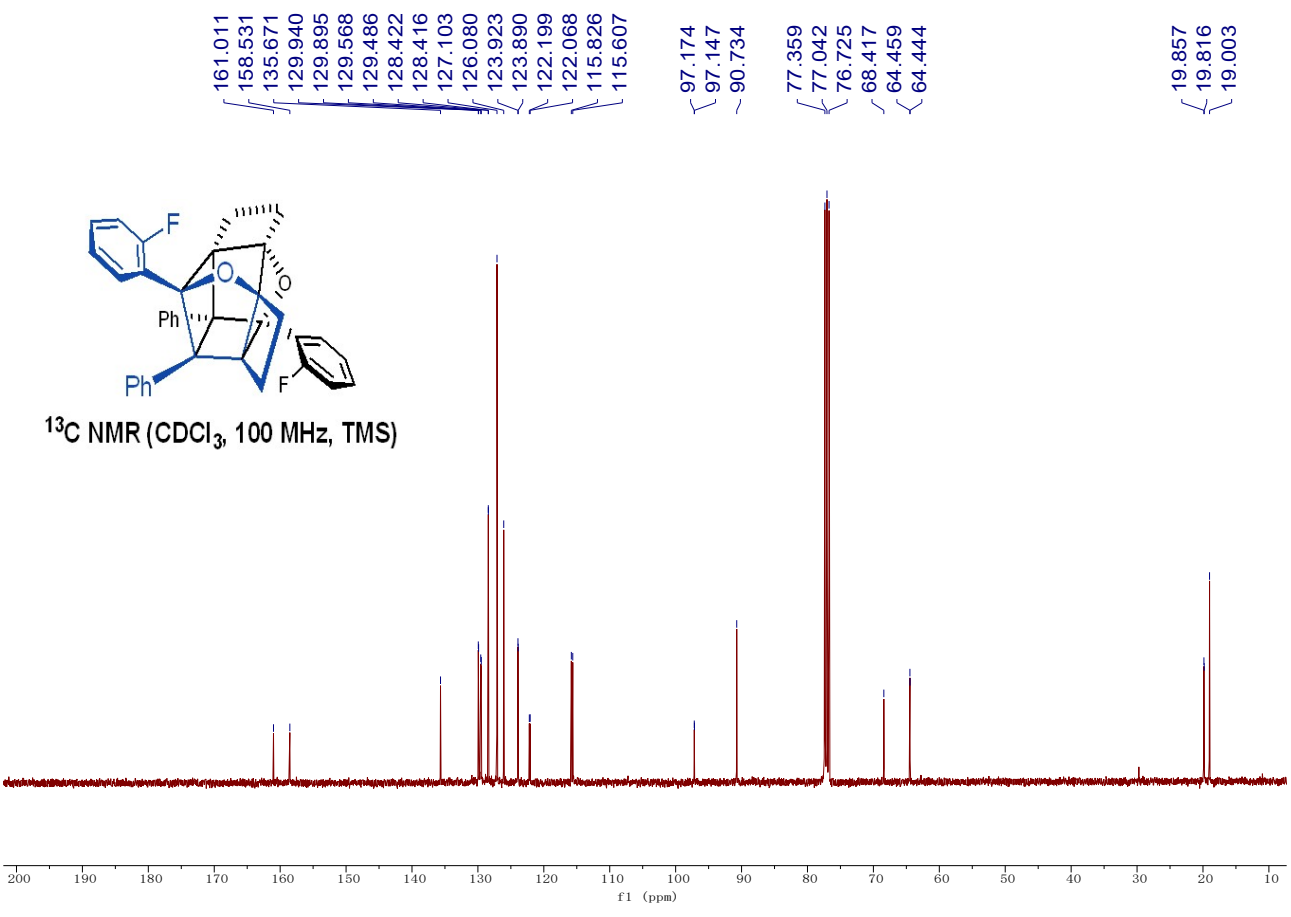


2f

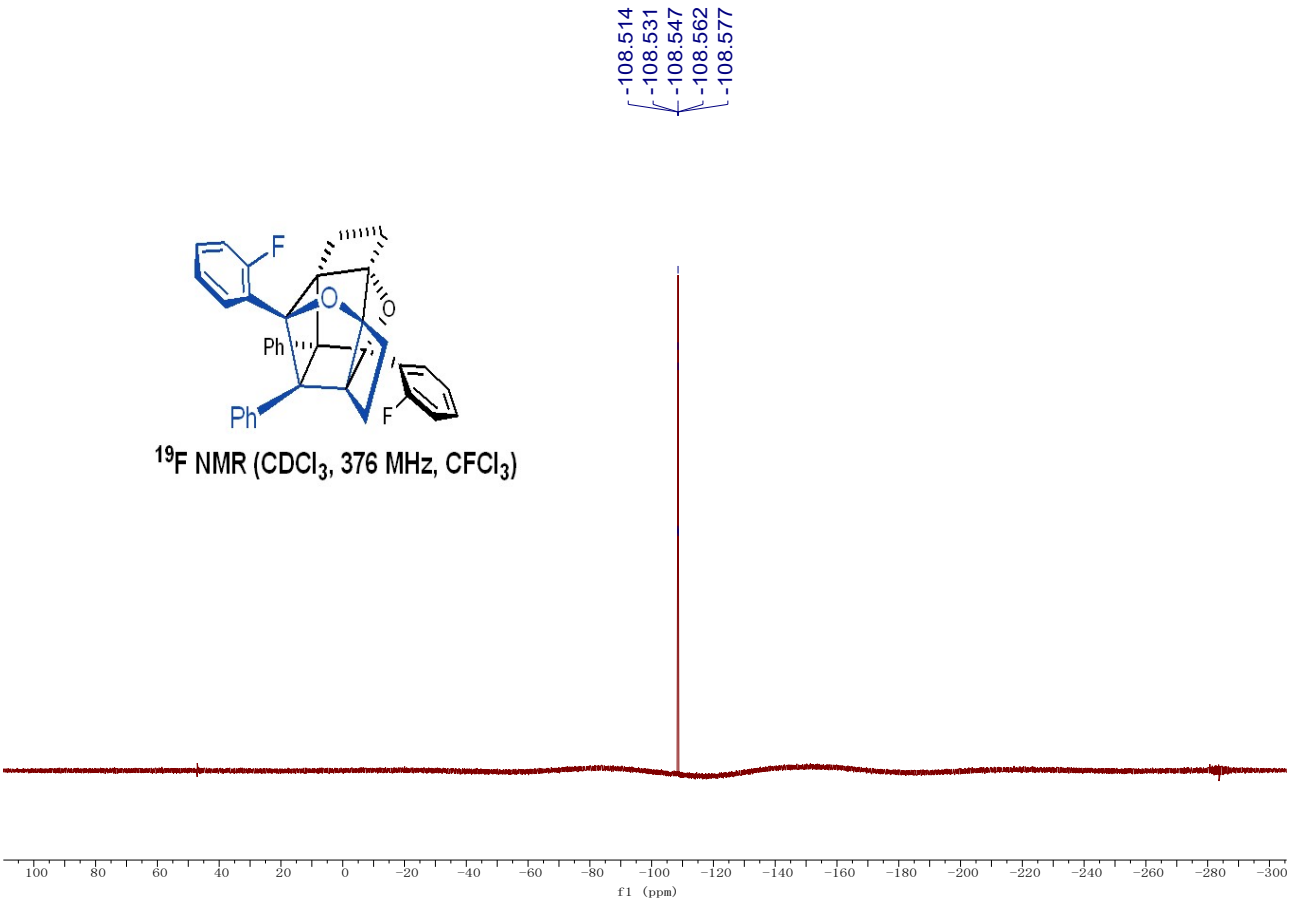
Product 2f, the title compound was achieved as a white solid, MP = 223-225 °C, 17.4 mg, 33% yield. R_f = 0.42 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.456 (t, J = 7.6 Hz, 1H), 7.453 (t, J = 7.6 Hz, 1H), 7.23-7.17 (m, 2H), 7.08-6.91 (m, 14H), 2.87 (t, J = 9.6 Hz, 1H), 2.84 (t, J = 9.6 Hz, 1H), 2.59-2.56 (m, 4H), 2.23-2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (d, J_{CF} = 248.0 Hz), 135.7, 129.9 (d, J_{CF} = 4.5 Hz), 129.5 (d, J_{CF} = 8.2 Hz), 128.4 (d, J_{CF} = 0.6 Hz), 127.1, 126.1, 123.9 (d, J_{CF} = 3.3 Hz), 122.1 (d, J_{CF} = 13.1 Hz), 115.7 (d, J_{CF} = 21.9 Hz), 97.2 (d, J_{CF} = 2.7 Hz), 90.7, 68.4, 64.4 (d, J_{CF} = 1.5 Hz), 19.8 (d, J_{CF} = 4.1 Hz), 19.0 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.5. IR (Acetone) ν 2970, 1739, 1498, 1365, 1229, 1216, 1145, 1039, 909, 760, 726, 700 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2F_2Na]^+$: 551.1793, found: 551.1797.

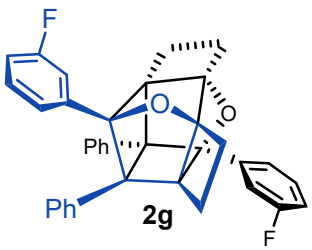


^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

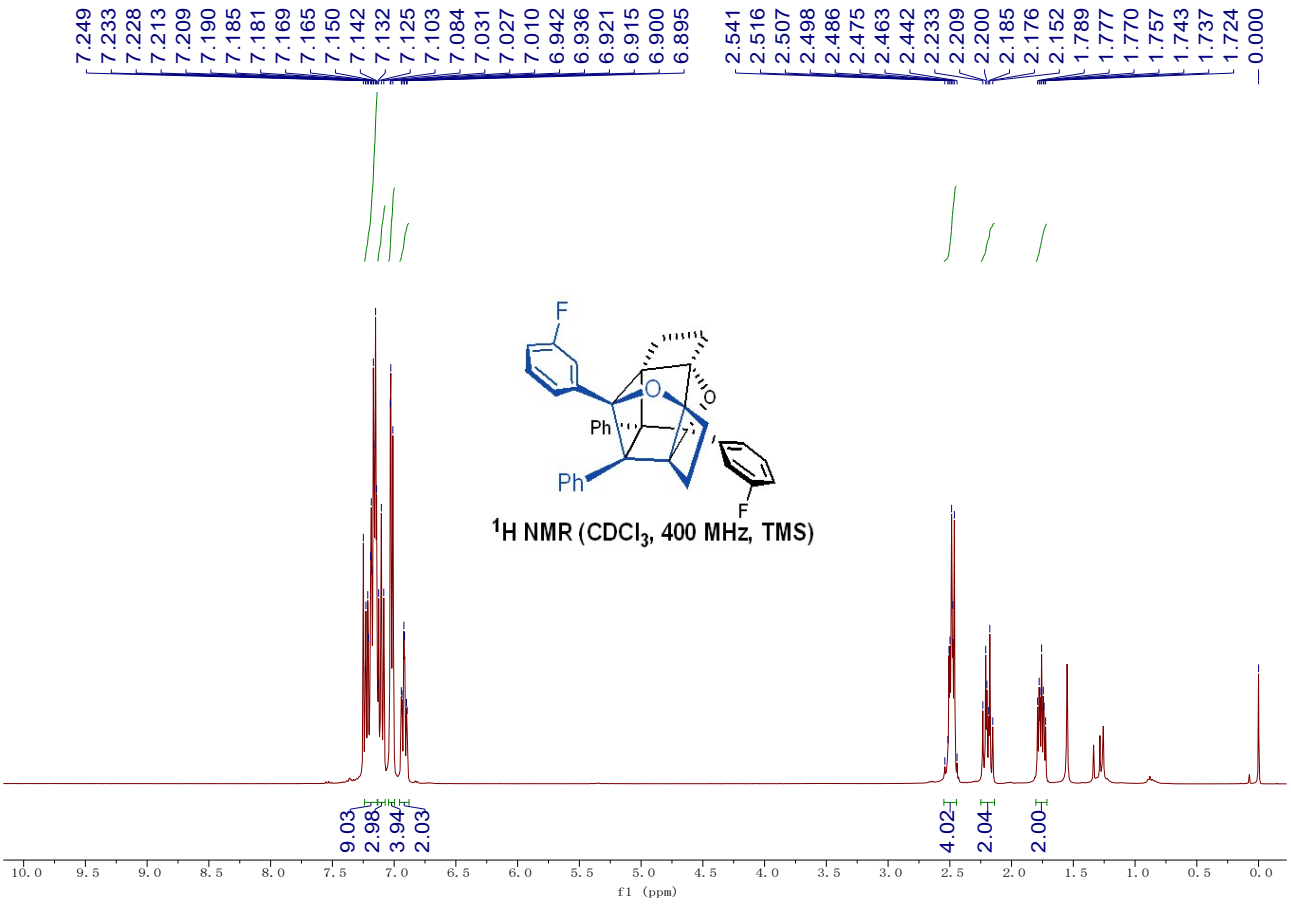


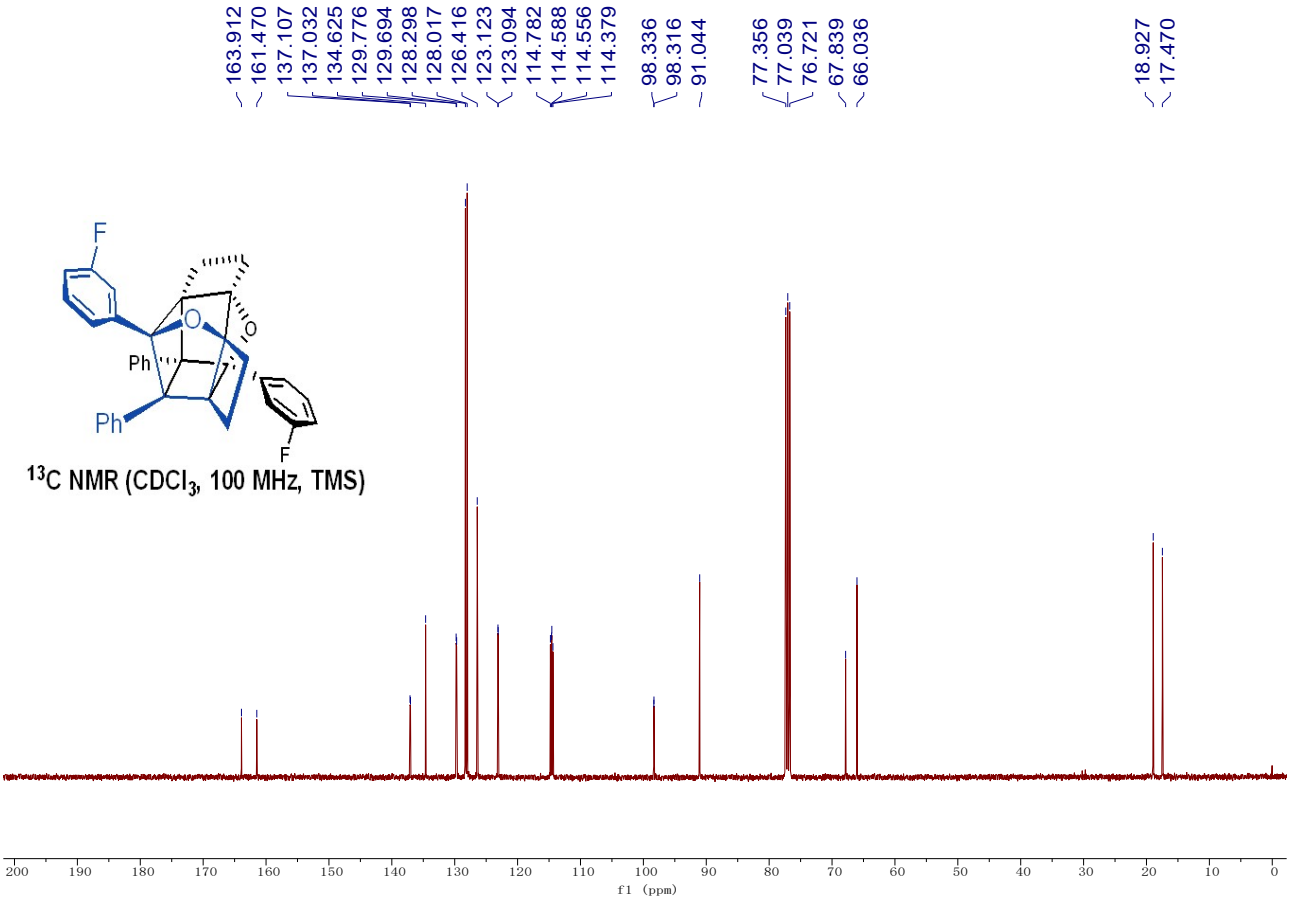
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

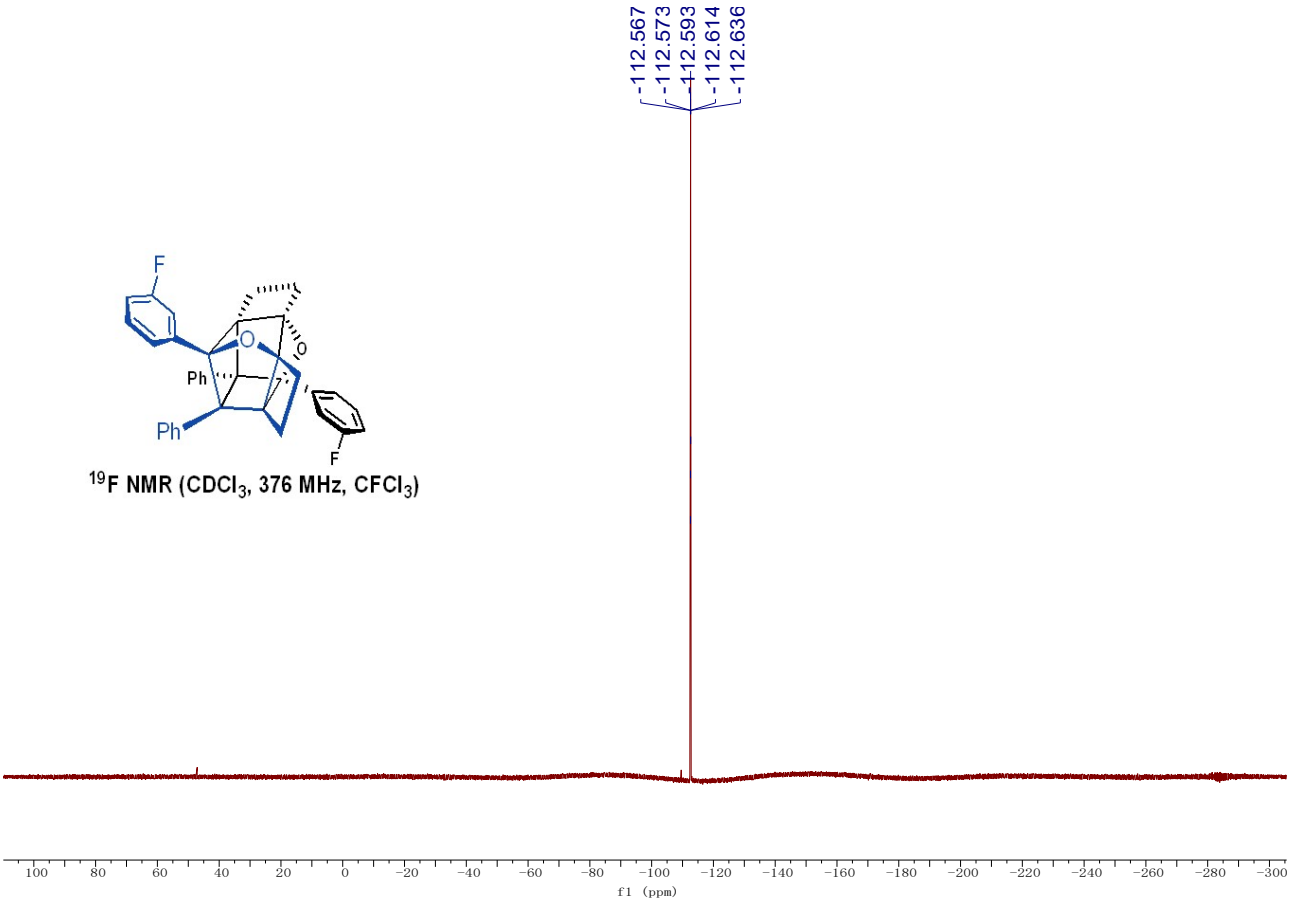




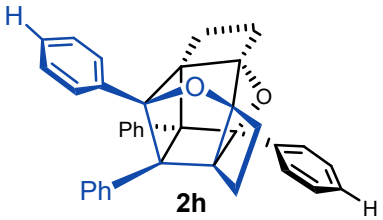
Product 2g, the title compound was achieved as a white solid, MP = 197-199 °C, 22.7 mg, 43% yield. R_f = 0.30 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.13 (m, 9H), 7.10 (t, J = 9.2 Hz, 3H), 7.03-7.01 (m, 4H), 6.92 (t, J = 8.4 Hz, 1H), 6.91 (t, J = 8.4 Hz, 1H), 2.54-2.44 (m, 4H), 2.21 (t, J = 9.6 Hz, 1H), 2.18 (t, J = 9.6 Hz, 1H), 1.76 (dd, J = 13.2, 8.0 Hz, 1H), 1.75 (dd, J = 13.2, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, J_{CF} = 244.2 Hz), 137.1 (d, J_{CF} = 7.5 Hz), 134.6, 129.7 (d, J_{CF} = 8.2 Hz), 128.3, 128.0, 126.4, 123.1 (d, J_{CF} = 2.9 Hz), 114.7 (d, J_{CF} = 22.6 Hz), 114.5 (d, J_{CF} = 20.9 Hz), 98.3 (d, J_{CF} = 2.0 Hz), 91.0, 67.8, 66.0, 18.9, 17.5 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.6. IR (Acetone) ν 2970, 1739, 1490, 1441, 1365, 1228, 1217, 1139, 1039, 861, 784, 704 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{26}O_2F_2]^+$: 529.1974, found: 529.1976.


7.249
7.233
7.228
7.213
7.209
7.190
7.185
7.181
7.169
7.165
7.150
7.142
7.132
7.125
7.103
7.084
7.031
7.027
7.010
6.942
6.936
6.921
6.915
6.900
6.895
2.541
2.516
2.507
2.498
2.486
2.475
2.463
2.442
2.233
2.209
2.200
2.185
2.176
2.152
1.789
1.777
1.770
1.757
1.743
1.737
1.724
0.000
F
O
O
Ph
Ph
F
1H NMR (CDCl3, 400 MHz, TMS)
9.03
2.98
3.94
2.03
4.02
2.04
2.00
f1 (ppm)


163.912
161.470
137.107
137.032
134.625
129.776
129.694
128.298
128.017
126.416
123.123
123.094
114.782
114.588
114.556
114.379
98.336
98.316
91.044
77.356
77.039
76.721
67.839
66.036
18.927
17.470
F
O
O
Ph
Ph
F
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

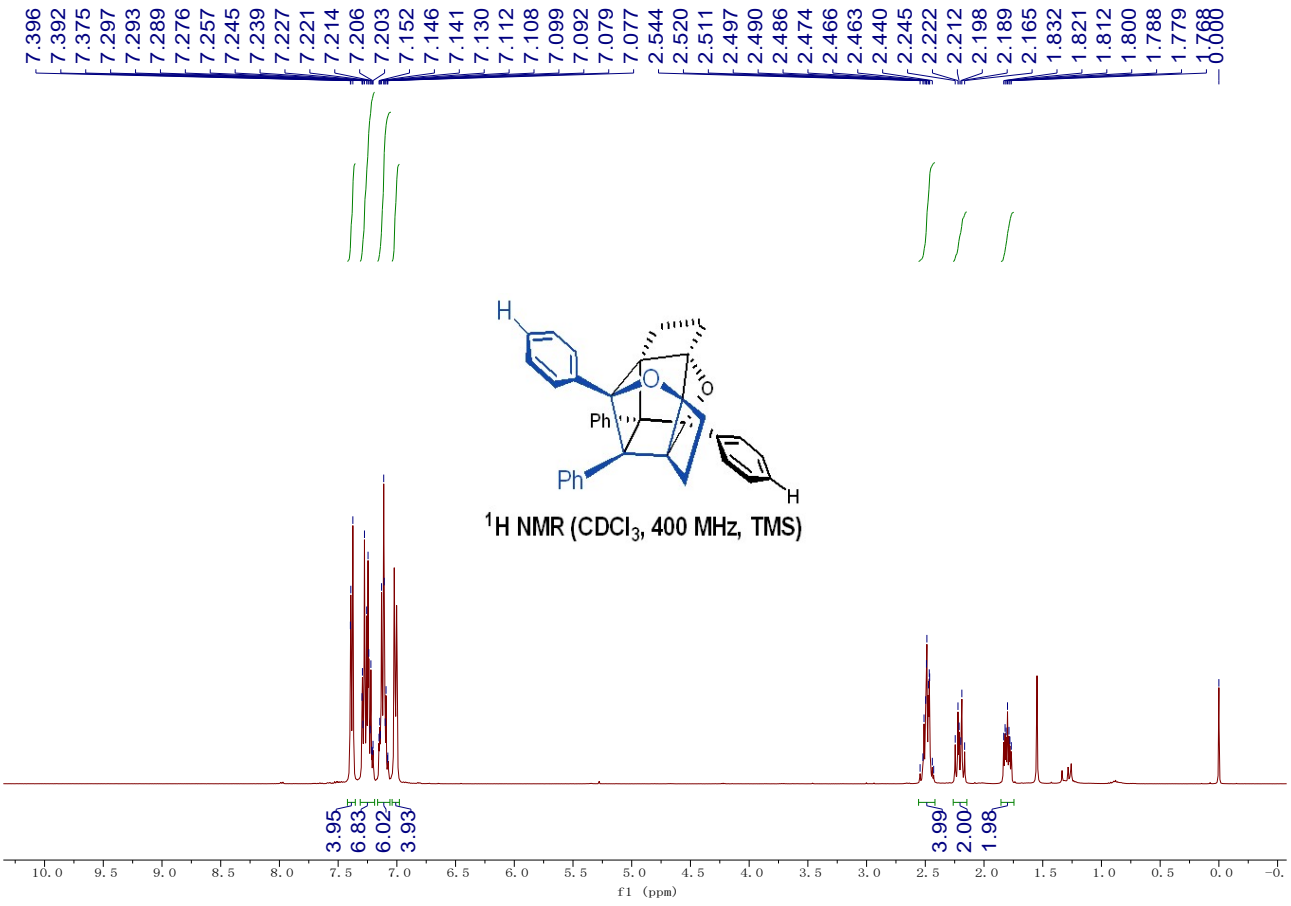


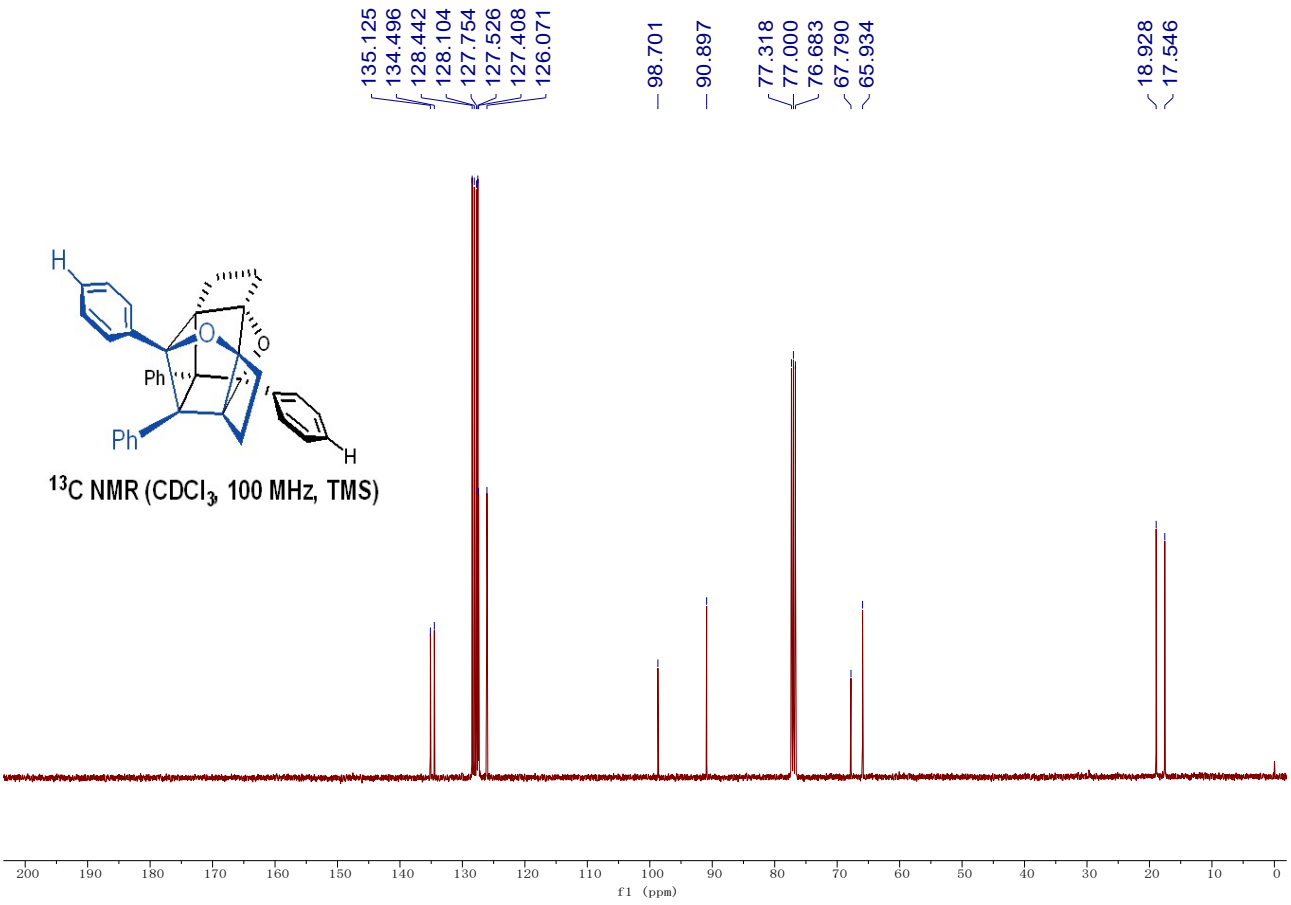
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

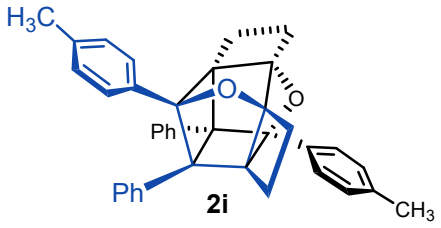


2h

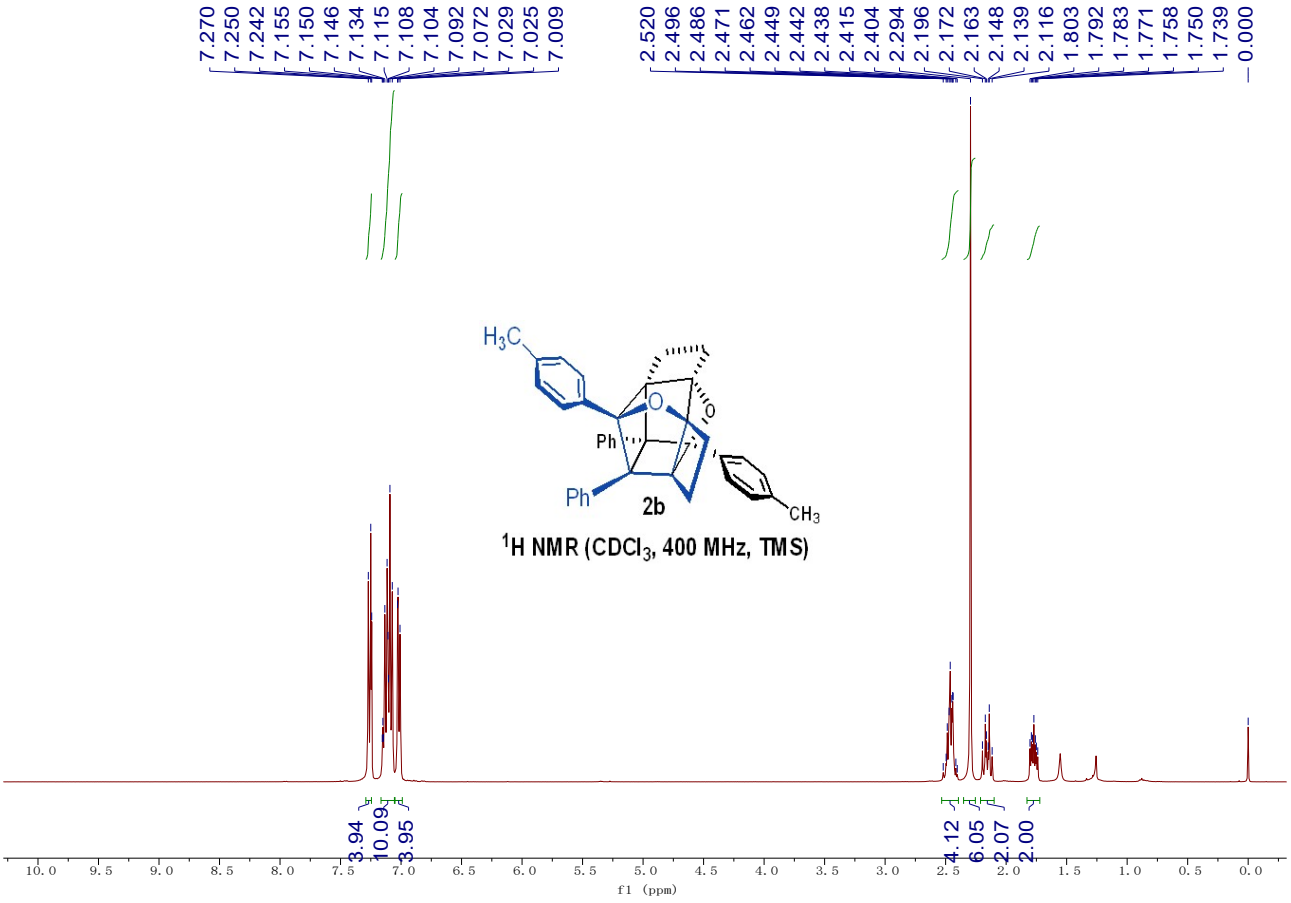
Product 2h, the title compound was achieved as a white solid, MP = 217-219 °C, 30.0 mg, 61% yield. R_f = 0.36 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.30-7.20 (m, 6H), 7.15-7.08 (m, 6H), 7.02-7.00 (m, 4H), 2.54-2.43 (m, 4H), 2.22 (t, *J* = 9.6 Hz, 1H), 2.19 (t, *J* = 9.6 Hz, 1H), 1.81 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.79 (dd, *J* = 12.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 134.5, 128.4, 128.1, 127.8, 127.5, 127.4, 126.1, 98.7, 90.9, 67.8, 65.9, 18.9, 17.5 (each carbon signal represents two C atoms). IR (Acetone) ν 3028, 2970, 1740, 1497, 1446, 1366, 1228, 1217, 1205, 1065, 976, 794, 747, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{29}O_2]^+$: 493.2162, found: 493.2161.

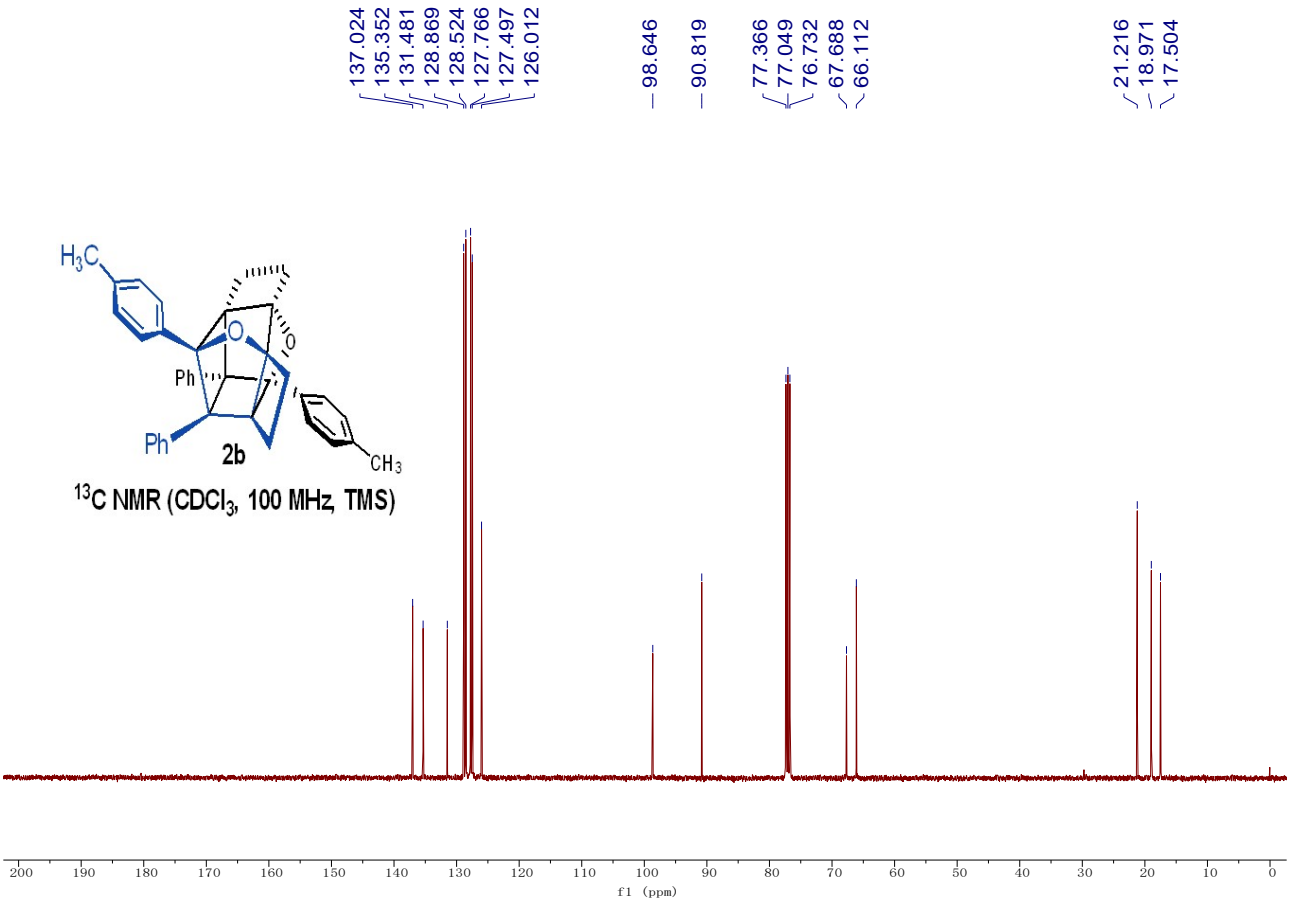

7.396
7.392
7.375
7.297
7.293
7.289
7.276
7.257
7.245
7.239
7.227
7.221
7.214
7.206
7.203
7.152
7.146
7.141
7.130
7.112
7.108
7.099
7.092
7.079
7.077
2.544
2.520
2.511
2.497
2.490
2.486
2.474
2.466
2.463
2.440
2.245
2.222
2.212
2.198
2.189
2.165
1.832
1.821
1.812
1.800
1.788
1.779
1.768
0.000
H
O
O
Ph
Ph
H
1H NMR (CDCl3, 400 MHz, TMS)
3.95
6.83
6.02
3.93
3.99
2.00
1.98
f1 (ppm)

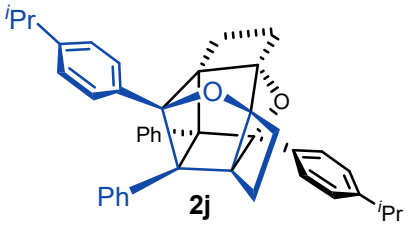

135.125
134.496
128.442
128.104
127.754
127.526
127.408
126.071
98.701
90.897
77.318
77.000
76.683
67.790
65.934
18.928
17.546
H
O
O
Ph
Ph
H
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)



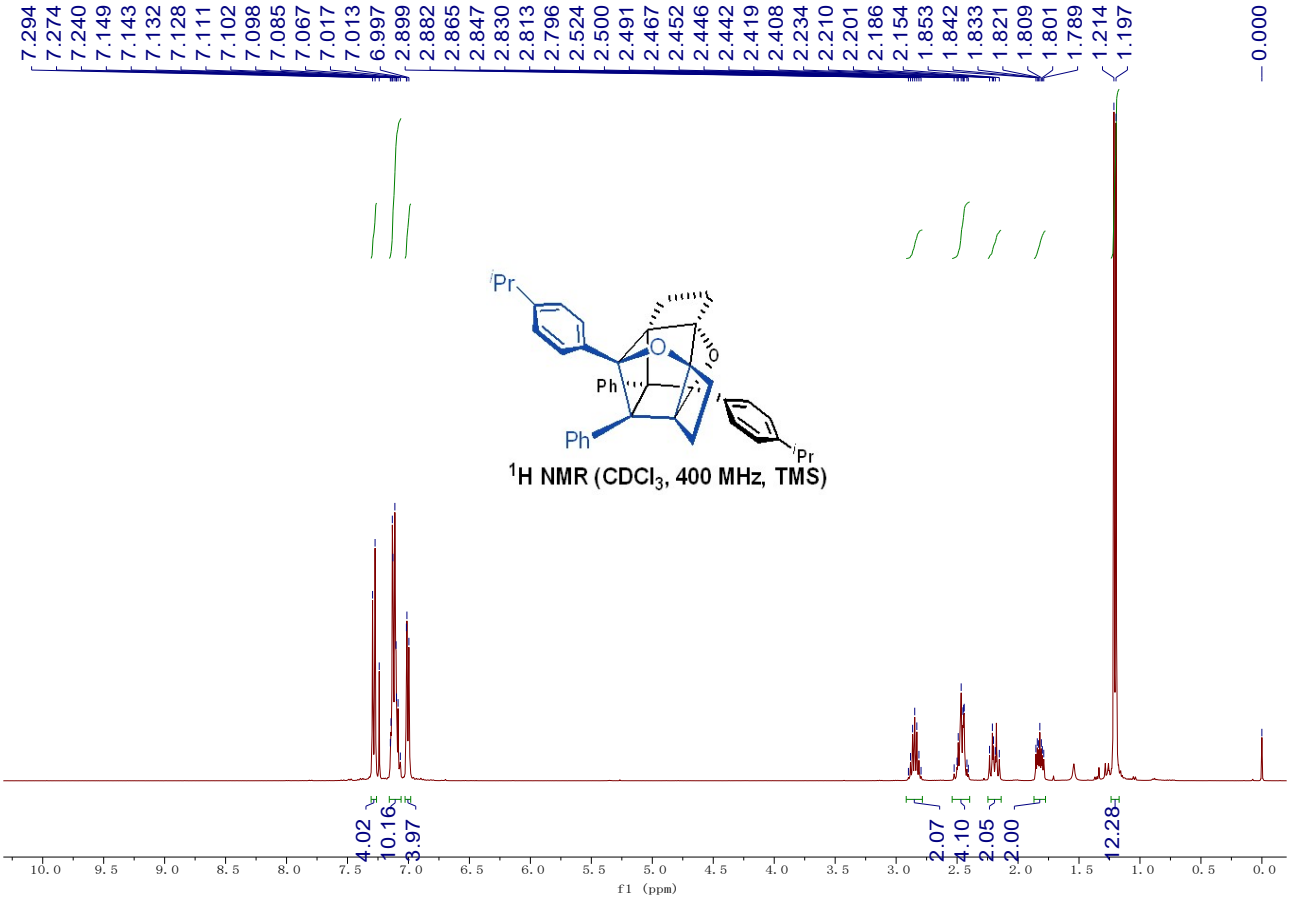
Product 2i, the title compound was achieved as a white solid, MP = 236-238 °C, 24.5 mg, 47% yield. R_f = 0.35 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.25 (m, 4H), 7.16-7.07 (m, 10H), 7.03-7.01 (m, 4H), 2.52-2.40 (m, 4H), 2.30 (s, 6H), 2.17 (t, *J* = 9.6 Hz, 1H), 2.14 (t, *J* = 9.6 Hz, 1H), 1.77 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.76 (dd, *J* = 12.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 135.4, 131.5, 128.9, 128.5, 127.8, 127.5, 126.0, 98.6, 90.8, 67.7, 66.1, 21.2, 19.0, 17.5 (each carbon signal represents two C atoms). IR (Acetone) ν 2983, 1775, 1704, 1396, 1328, 1250, 1177, 1038, 816, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{33}O_2]^+$: 521.2475, found: 521.2478.







Product 2j, the title compound was achieved as a white solid, MP = 192-194 °C, 24.8 mg, 43% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.27 (m, 4H), 7.15-7.07 (m, 10H), 7.02-7.00 (m, 4H), 2.90-2.80 (m, 2H), 2.52-2.41 (m, 4H), 2.21 (t, *J* = 9.6 Hz, 1H), 2.18 (t, *J* = 9.6 Hz, 1H), 1.83 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.81 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 135.4, 131.8, 128.6, 127.7, 127.5, 126.2, 125.9, 98.7, 90.9, 67.7, 66.0, 33.8, 23.9, 19.0, 17.6 (each carbon signal represents two C atoms, and one carbon signal was overlapped). IR (Acetone) ν 2945, 1740, 1495, 1463, 1364, 1217, 1205, 1039, 974, 832, 773, 684 cm^{-1}. HRMS (ESI) calcd for $[C_{42}H_{41}O_2]^+$: 577.3101, found: 577.3099.


7.294
7.274
7.240
7.149
7.143
7.132
7.128
7.111
7.102
7.098
7.085
7.067
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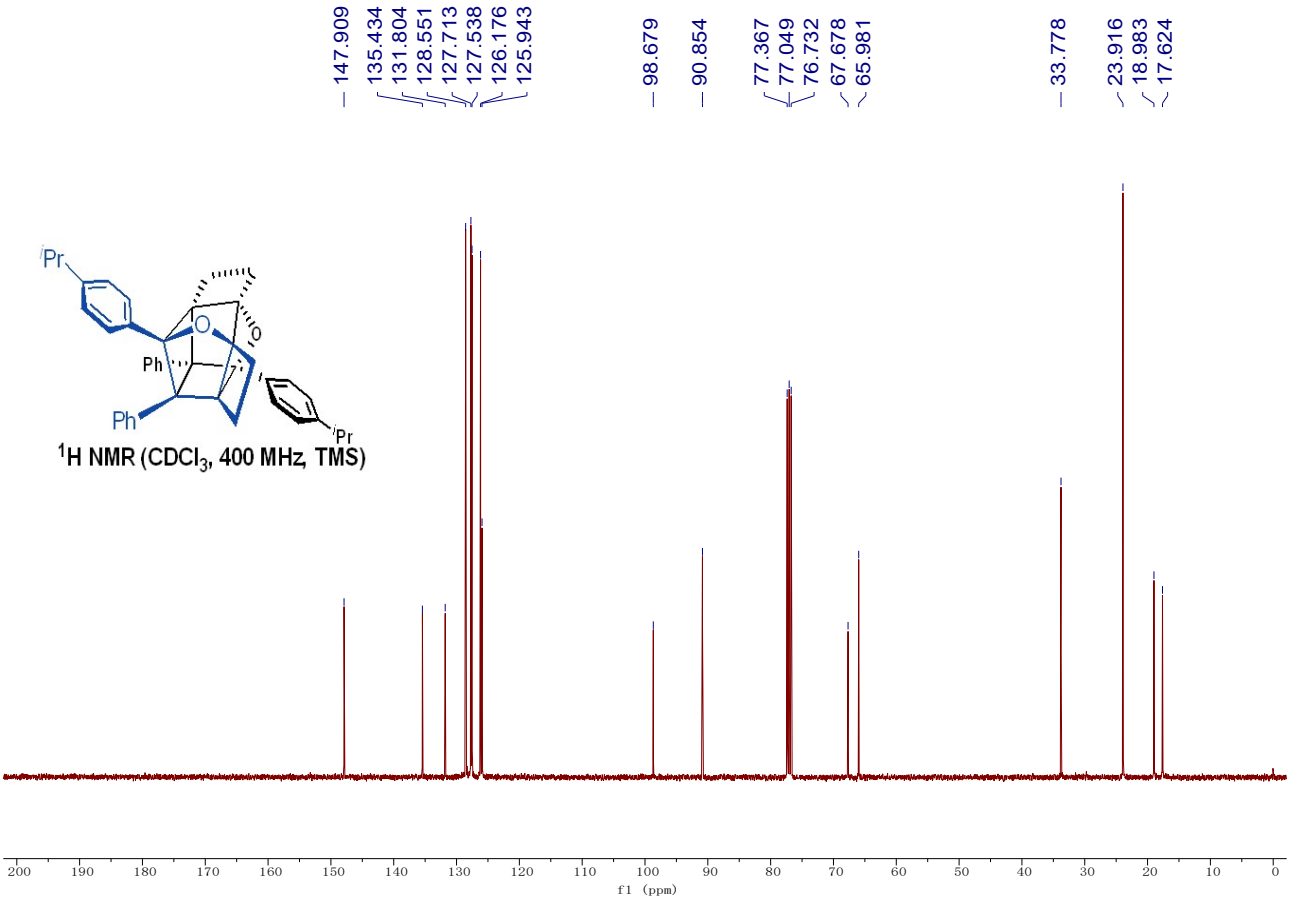
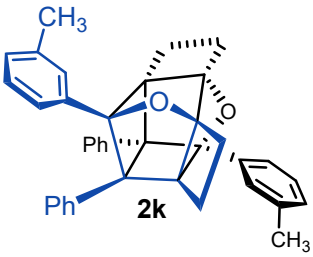
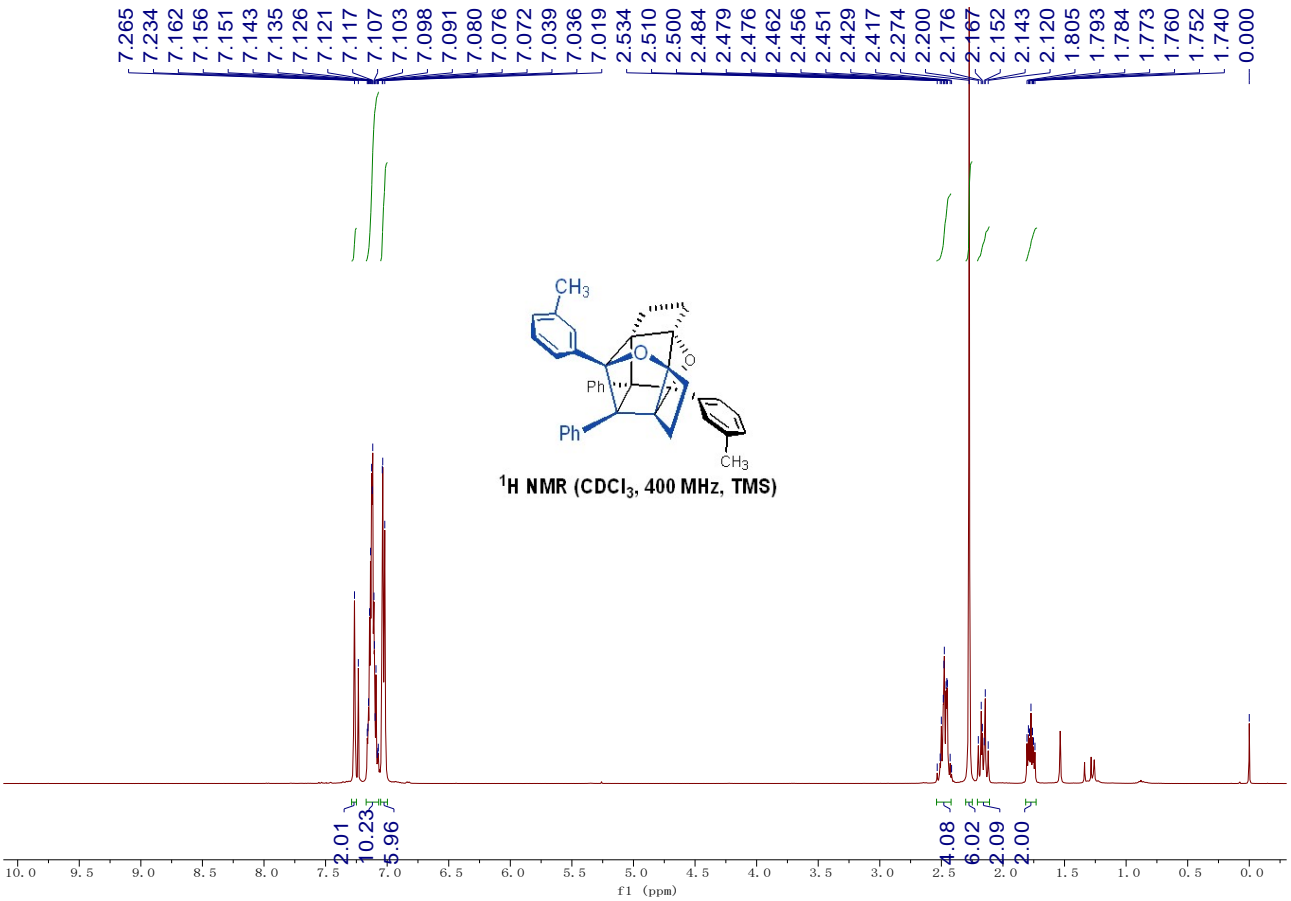
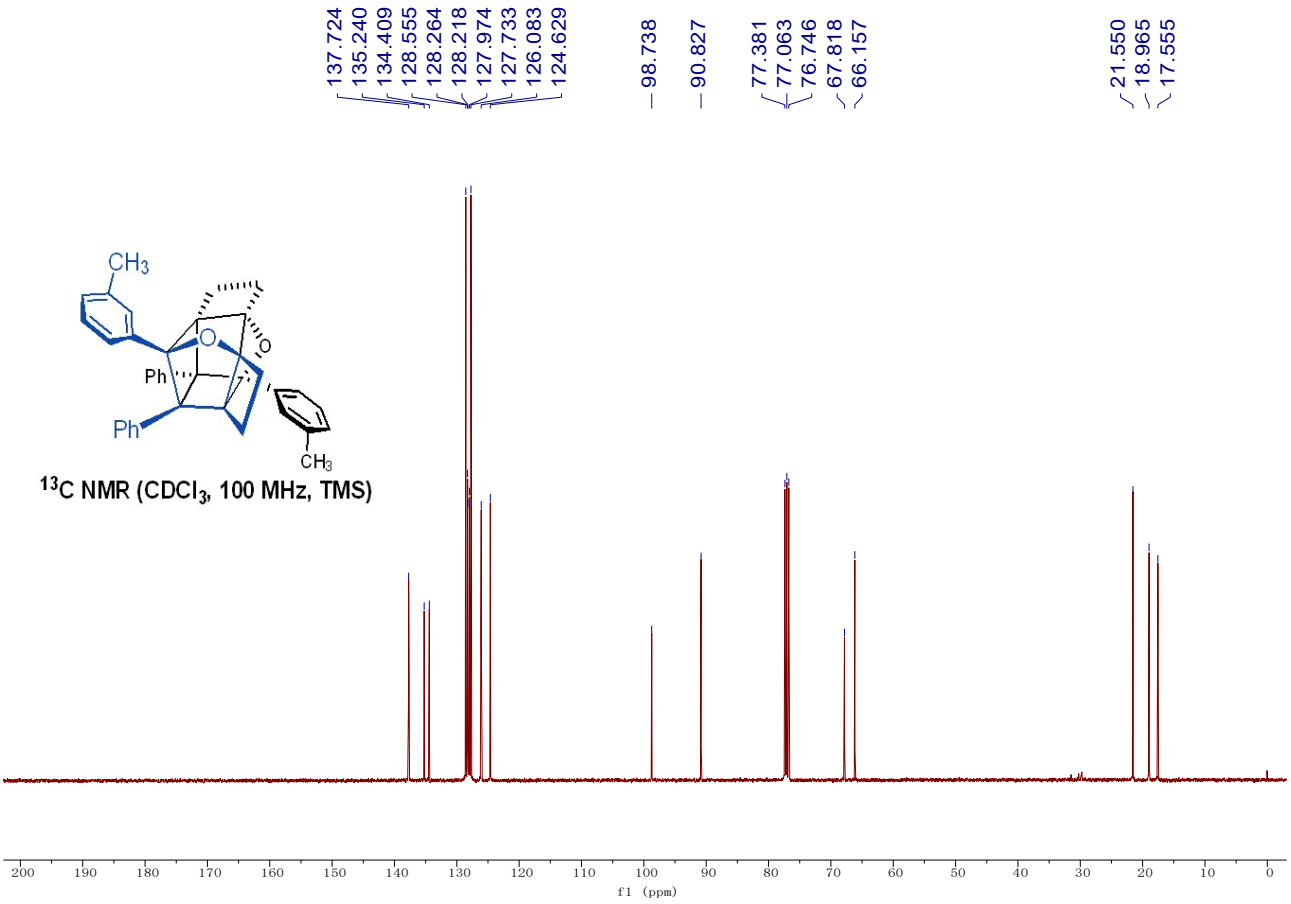
7.013
6.997
2.899
2.882
2.865
2.847
2.830
2.813
2.796
2.524
2.500
2.491
2.467
2.452
2.446
2.442
2.419
2.408
2.234
2.210
2.201
2.186
2.154
1.853
1.842
1.833
1.821
1.809
1.801
1.789
1.214
1.197
0.000
iPr
O
O
Ph
Ph
iPr
1H NMR (CDCl3, 400 MHz, TMS)
4.02
10.16
3.97
2.07
4.10
2.05
2.00
12.28
f1 (ppm)

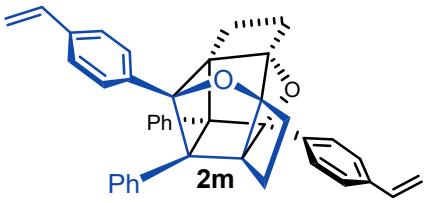

147.909
135.434
131.804
128.551
127.713
127.538
126.176
125.943
98.679
90.854
77.367
77.049
76.732
67.678
65.981
33.778
23.916
18.983
17.624
iPr
O
O
Ph
Ph
iPr
1H NMR (CDCl3, 400 MHz, TMS)
f1 (ppm)



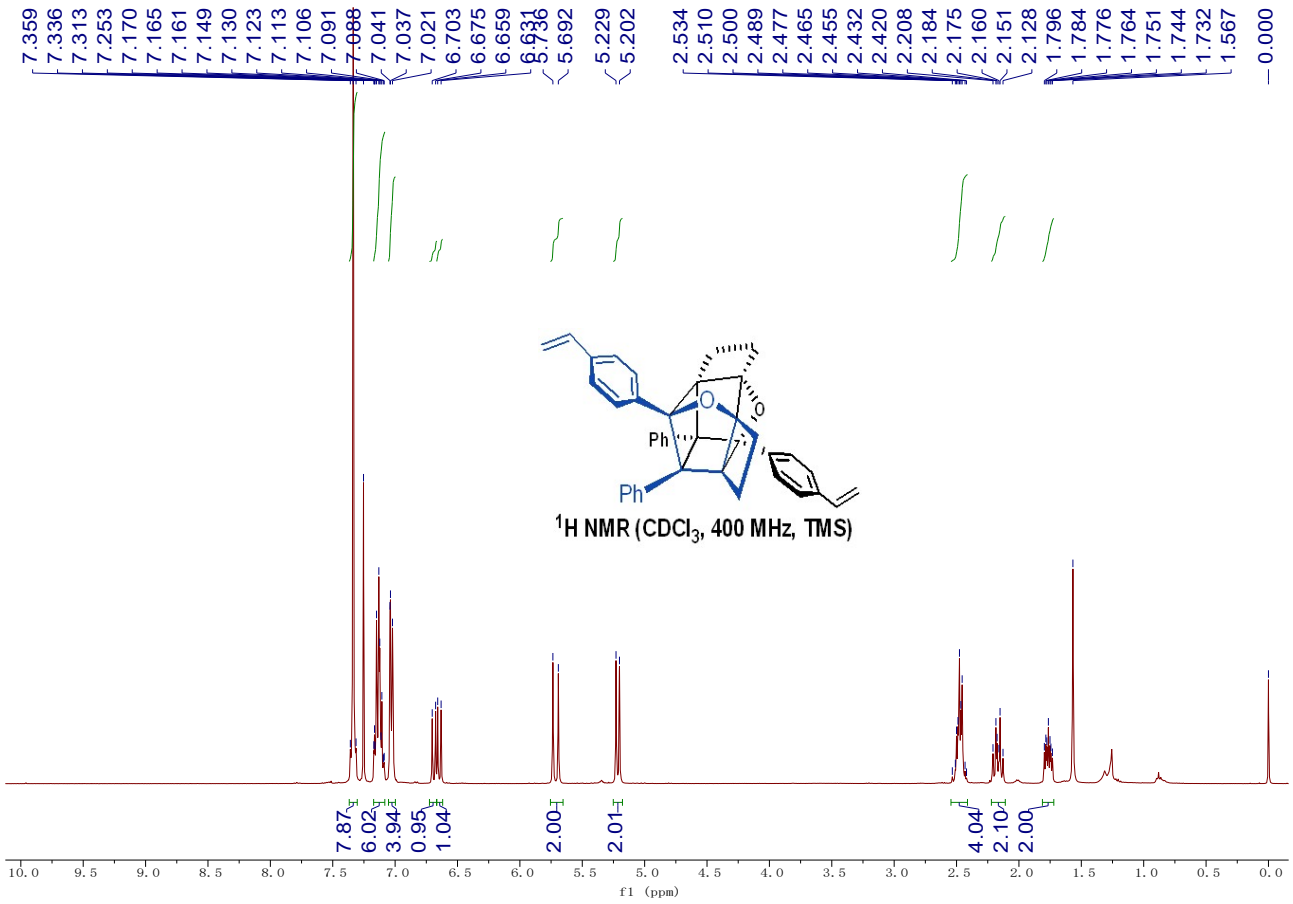
Product 2k, the title compound was achieved as a white solid, MP = 252-254 °C, 22.4 mg, 43% yield. R_f = 0.43 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 2H), 7.16-7.07 (m, 10H), 7.04-7.02 (m, 6H), 2.51-2.45 (m, 4H), 2.27 (s, 6H), 2.18 (t, *J* = 9.6 Hz, 1H), 2.14 (t, *J* = 9.6 Hz, 1H), 1.78 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.77 (dd, *J* = 12.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 135.2, 134.4, 128.6, 128.3, 128.2, 128.0, 127.7, 126.1, 124.6, 98.7, 90.8, 67.8, 66.2, 21.6, 19.0, 17.6 (each carbon signal represents two C atoms). IR (Acetone) ν 2969, 1740, 1436, 1366, 1228, 1217, 780, 704 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{33}O_2]^+$: 521.2475, found: 521.2482.



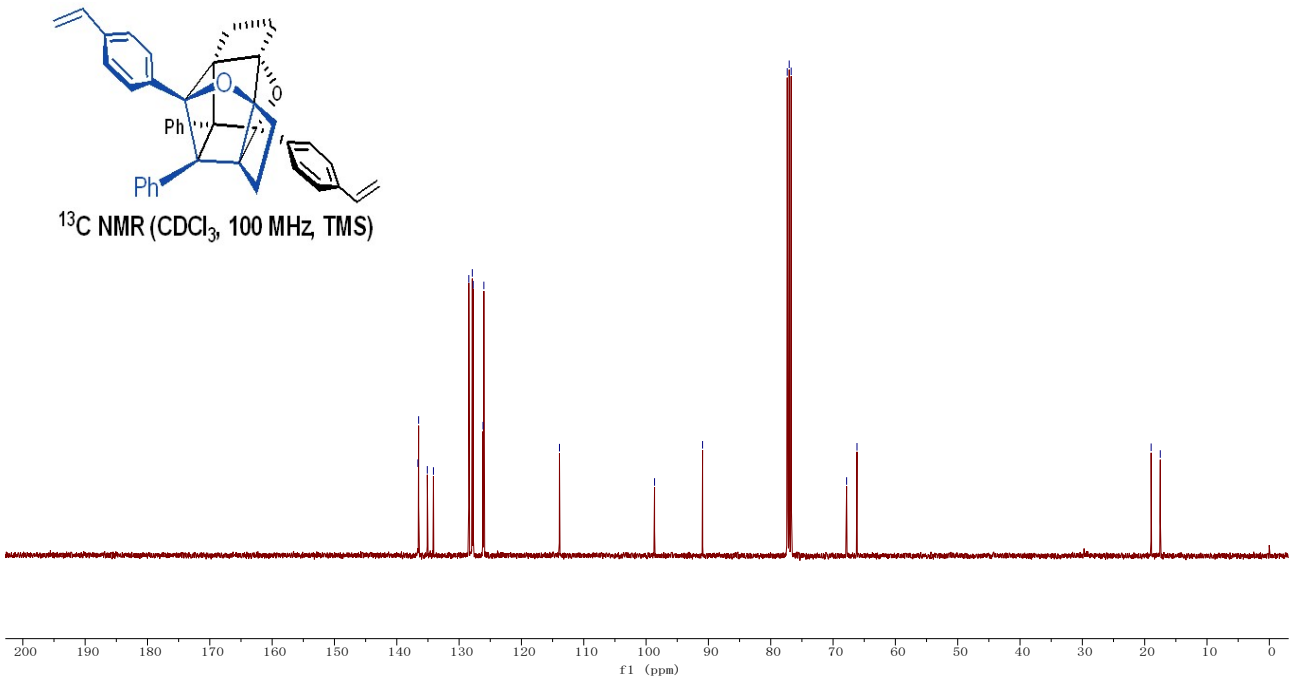




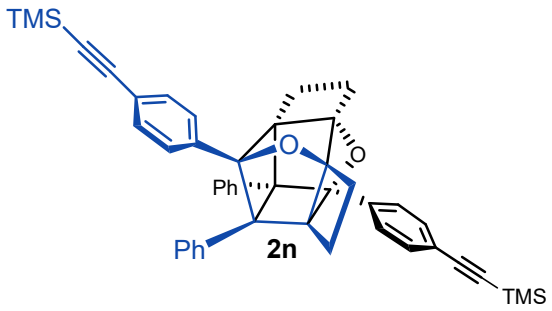
Product 2m, the title compound was achieved as a white solid, MP = 233-235 °C, 22.3 mg, 41% yield. R_f = 0.35 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 8H), 7.17-7.09 (m, 6H), 7.04-7.02 (m, 4H), 6.69 (d, *J* = 11.2 Hz, 1H), 6.65 (d, *J* = 11.2 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 2H), 5.22 (d, *J* = 10.8 Hz, 2H), 2.53-2.13 (m, 4H), 2.18 (t, *J* = 9.6 Hz, 1H), 2.15 (t, *J* = 9.6 Hz, 1H), 1.77 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.76 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.57 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 136.5, 135.1, 134.1, 128.4, 127.9, 127.7, 126.2, 126.0, 113.9, 98.6, 90.3, 67.8, 66.2, 19.0, 17.5 (each carbon signal represents two C atoms). IR (Acetone) ν 2988, 1600, 1496, 1404, 1251, 1206, 1066, 1054, 1042, 989, 908, 837, 731, 703 cm^{-1}. HRMS (ESI) calcd for $[C_{40}H_{33}O_2]^+$: 545.2475, found: 545.2476.



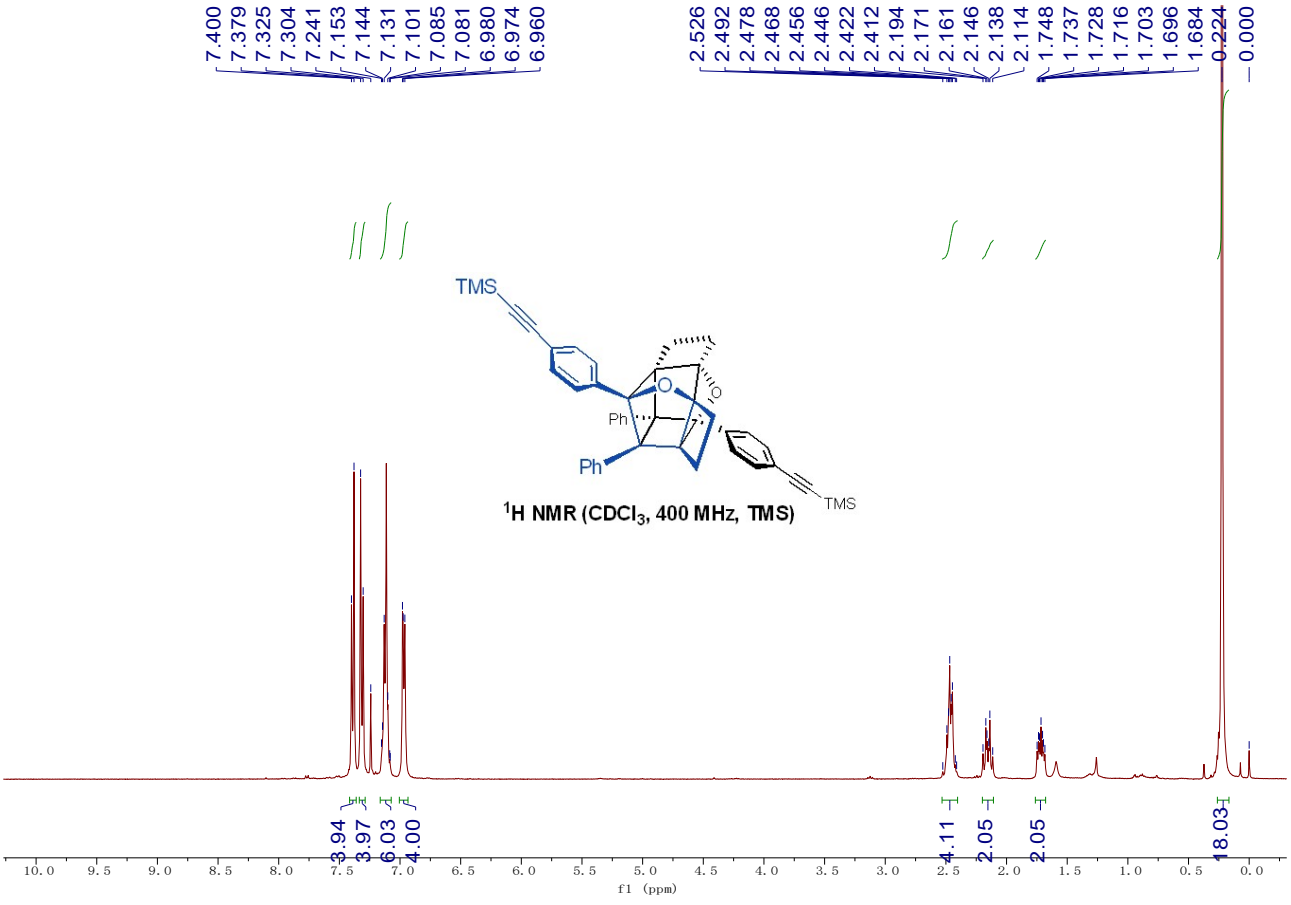
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

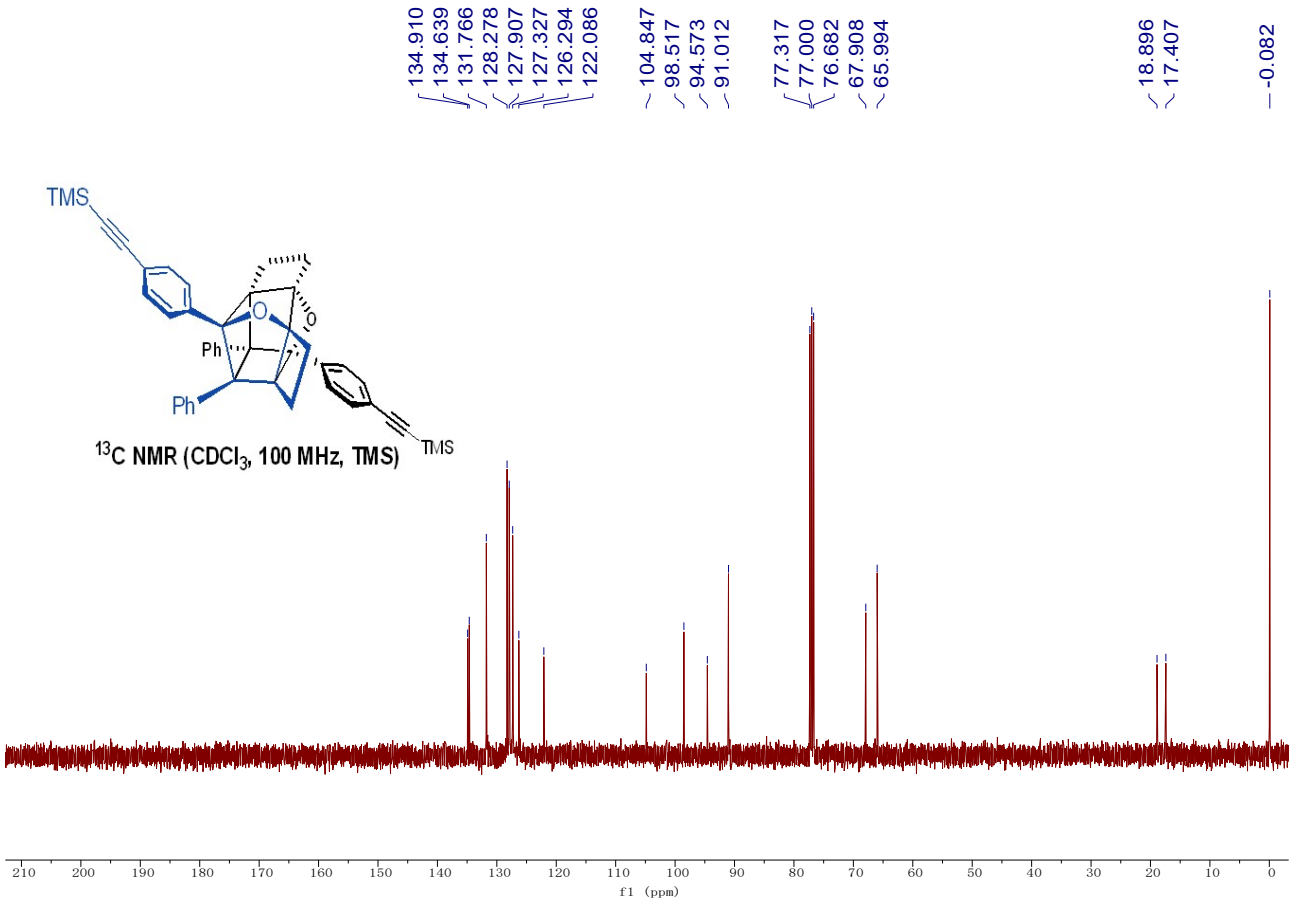


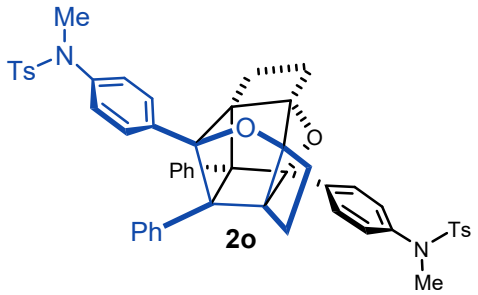
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



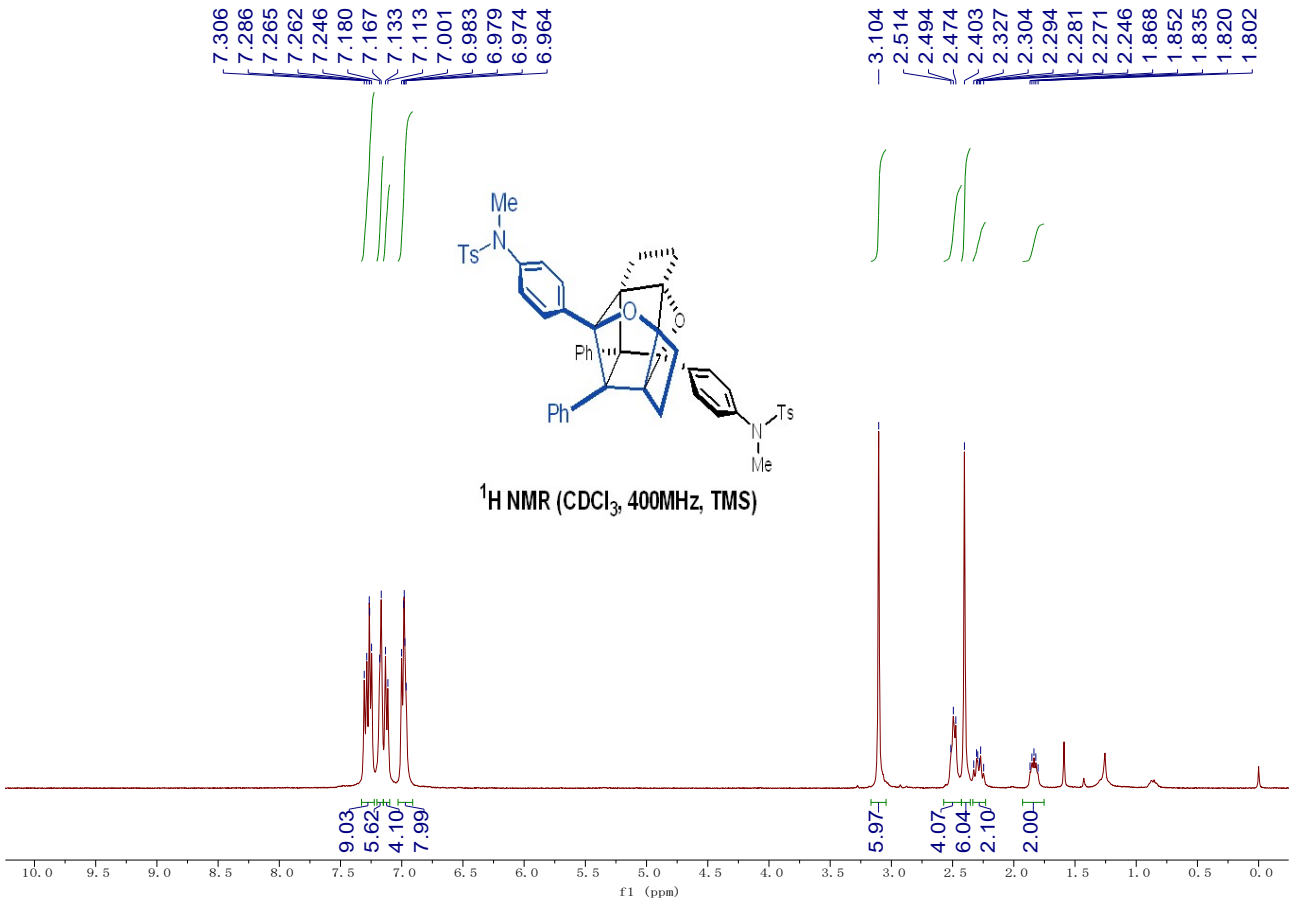
Product 2n, the title compound was achieved as a white solid, MP = 251-253 °C, 39.0 mg, 57% yield. R*f* = 0.43 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.33-7.30 (m, 4H), 7.15-7.08 (m, 6H), 6.98-6.96 (m, 4H), 2.53-2.41 (m, 4H), 2.17 (t, *J* = 9.6 Hz, 1H), 2.14 (t, *J* = 9.6 Hz, 1H), 1.72 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.71 (dd, *J* = 12.8, 8.0 Hz, 1H), 0.22 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 134.6, 131.8, 128.3, 127.9, 127.3, 126.3, 122.1, 104.8, 98.5, 94.6, 91.0, 67.9, 66.0, 18.9, 17.4, -0.1 (each carbon signal represents two C atoms, two carbon signals were overlapped). IR (Acetone) ν 2988, 2900, 2160, 1738, 1406, 1394, 1249, 1228, 1075, 1065, 1057, 865, 844, 760, 700 cm^{-1}. HRMS (ESI) calcd for $[C_{46}H_{45}O_2Si_2]^+$: 685.2953, found: 685.2952.



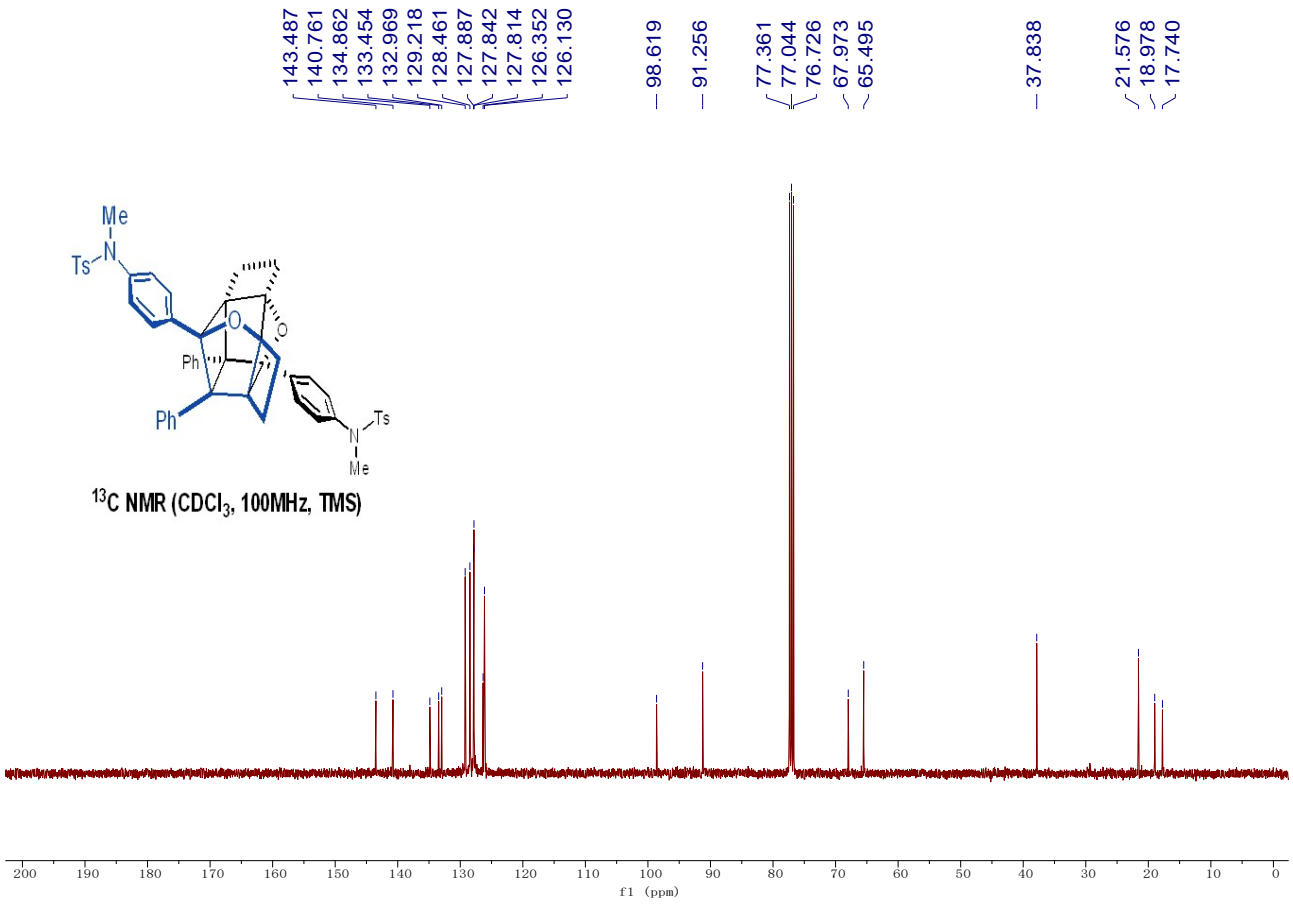




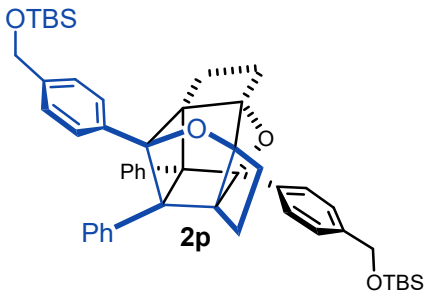
Product 2o, the title compound was achieved as a white solid, MP = 262-264 °C, 41.1 mg, 48% yield. R_f = 0.43 (Petroleum Ether:Ethyl Acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 4H), 7.27-7.24 (m, 5H), 7.18-7.17 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 4H), 7.00-6.96 (m, 8H), 3.10 (s, 6H), 2.51-2.47 (m, 4H), 2.40 (s, 6H), 2.30 (t, *J* = 9.2 Hz, 1H), 2.27 (t, *J* = 9.2 Hz, 1H), 1.84 (dd, *J* = 13.2, 6.4 Hz, 1H), 1.83 (dd, *J* = 13.2, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 140.8, 134.9, 133.5, 133.0, 129.2, 128.5, 127.9, 127.84, 127.81, 126.4, 126.1, 98.6, 91.3, 68.0, 65.5, 37.8, 21.6, 19.0, 17.7 (each carbon signal represents two C atoms). IR (acetone) ν 2922, 1710, 1420, 1357, 1220, 1171, 1067, 903, 866, 724, 659 cm^{-1}. HRMS (ESI) calcd for $[C_{52}H_{47}O_6N_2S_2]^+$: 859.2870, found: 859.2873.



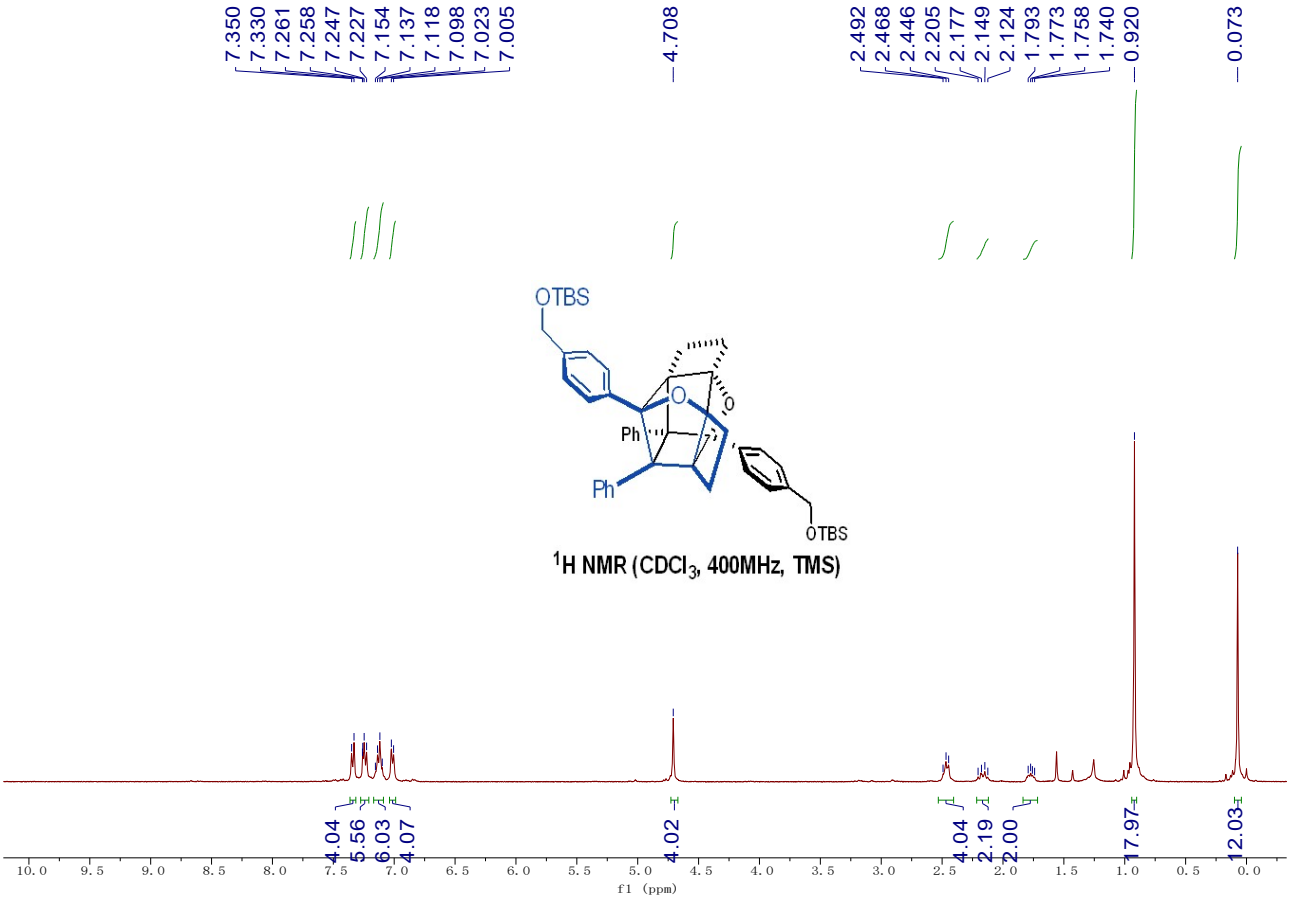
^{1}H NMR ($CDCl_3$, 400MHz, TMS)

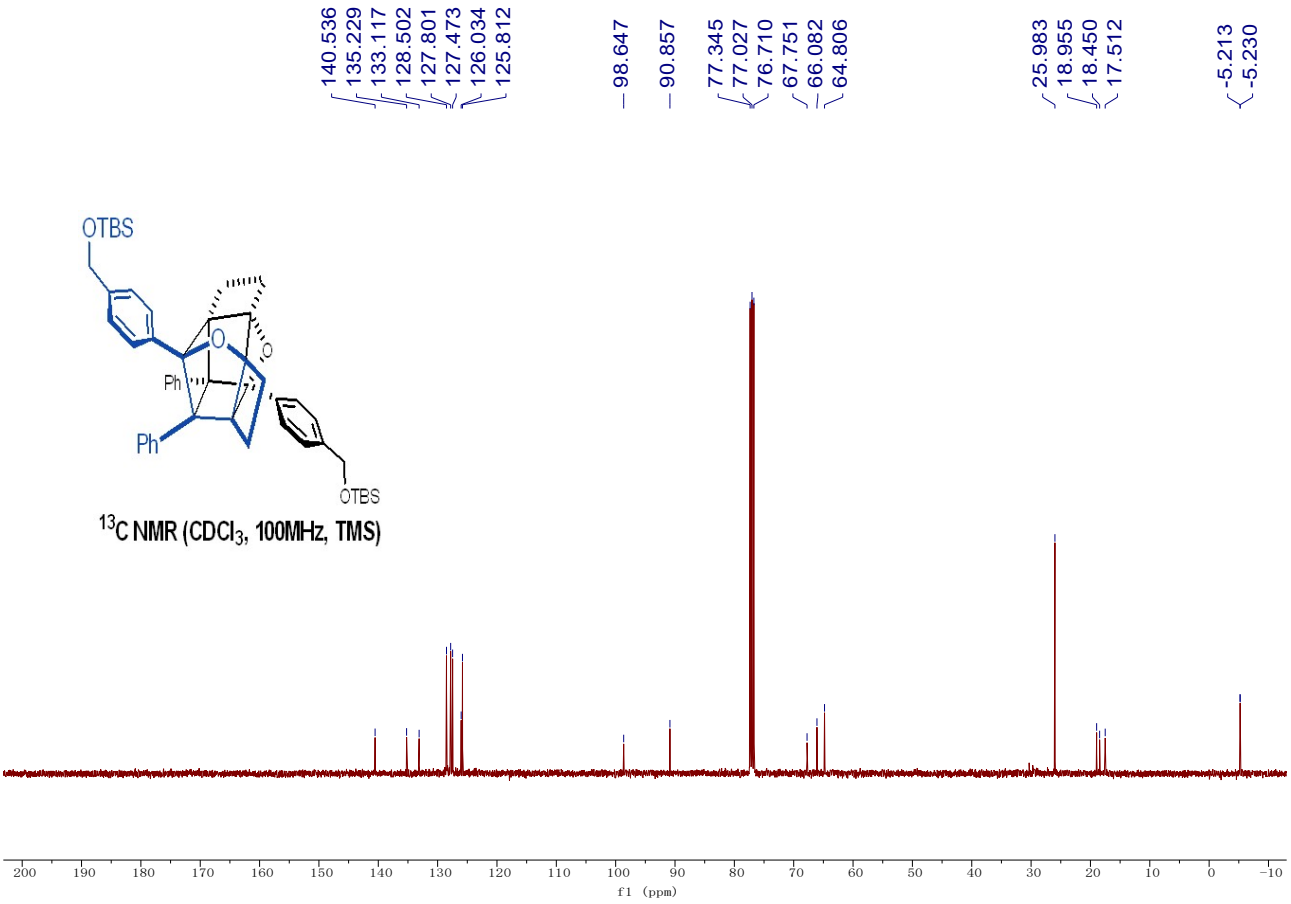


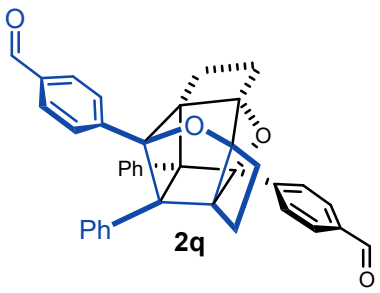
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



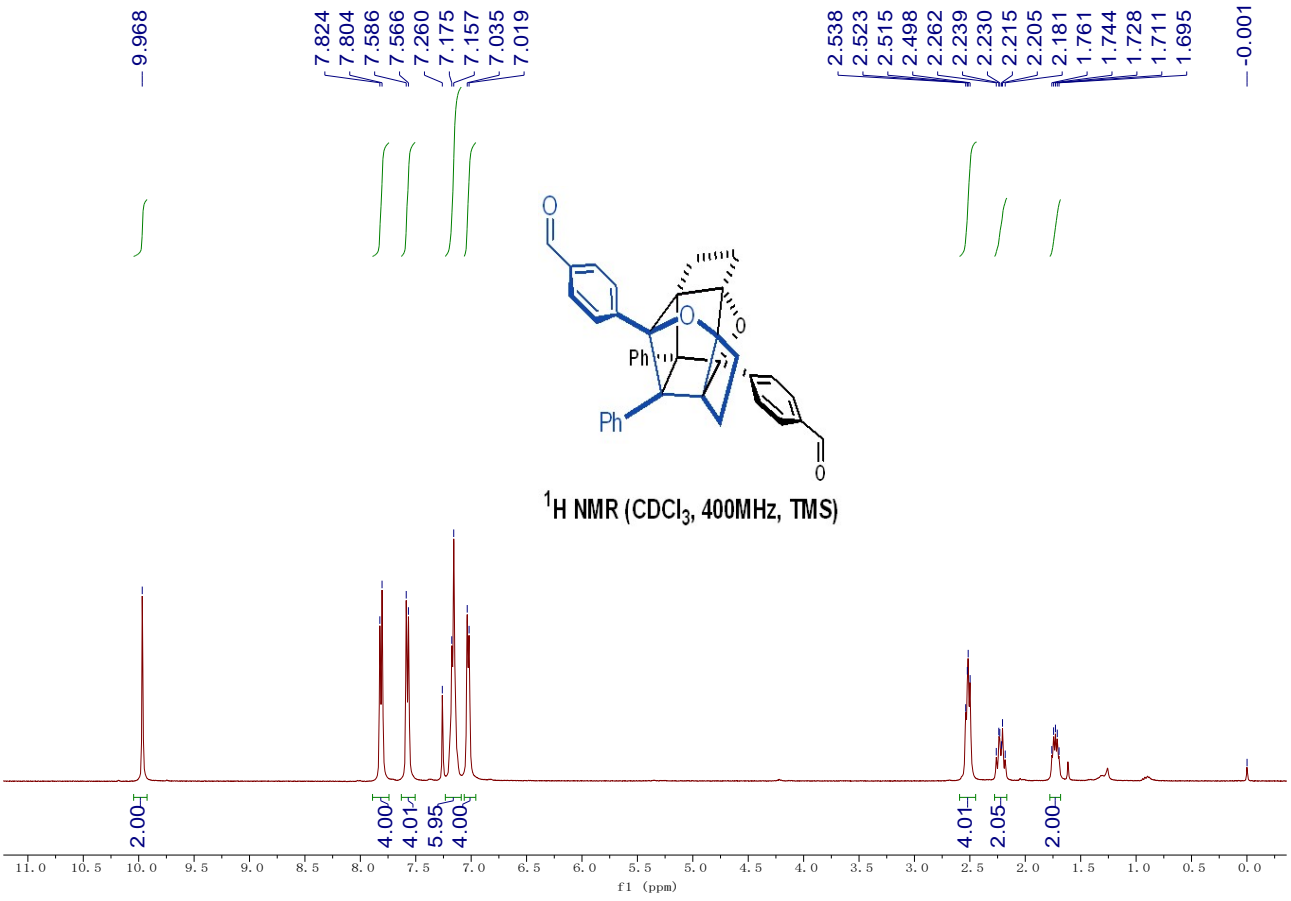
Product 2p, the title compound was achieved as colorless oil, 14.1 mg, 18% yield. R_f = 0.48 (Petroleum Ether:Ethyl Acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.0 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 7.15-7.10 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 4H), 4.71 (s, 4H), 2.49-2.45 (m, 4H), 2.18 (t, *J* = 9.2 Hz, 1H), 2.15 (t, *J* = 9.2 Hz, 1H), 1.78 (dd, *J* = 12.8, 7.6 Hz, 1H), 1.77 (dd, *J* = 12.8, 7.6 Hz, 1H), 0.92 (s, 18H), -0.07 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 135.2, 133.1, 128.5, 127.8, 127.5, 126.0, 125.8, 98.6, 90.6, 67.8, 66.1, 64.8, 25.9, 19.0, 18.5, 17.5, -5.21, -5.23 (each carbon signal represents two C atoms, four carbon signals were overlapped). IR (neat) ν 2952, 2856, 1496, 1471, 1254, 1209, 1090, 1041, 974, 941, 838, 776, 703 cm^{-1}. HRMS (ESI) calcd for $[C_{50}H_{60}O_4NaSi_2]^+$: 803.3922, found: 803.3920.



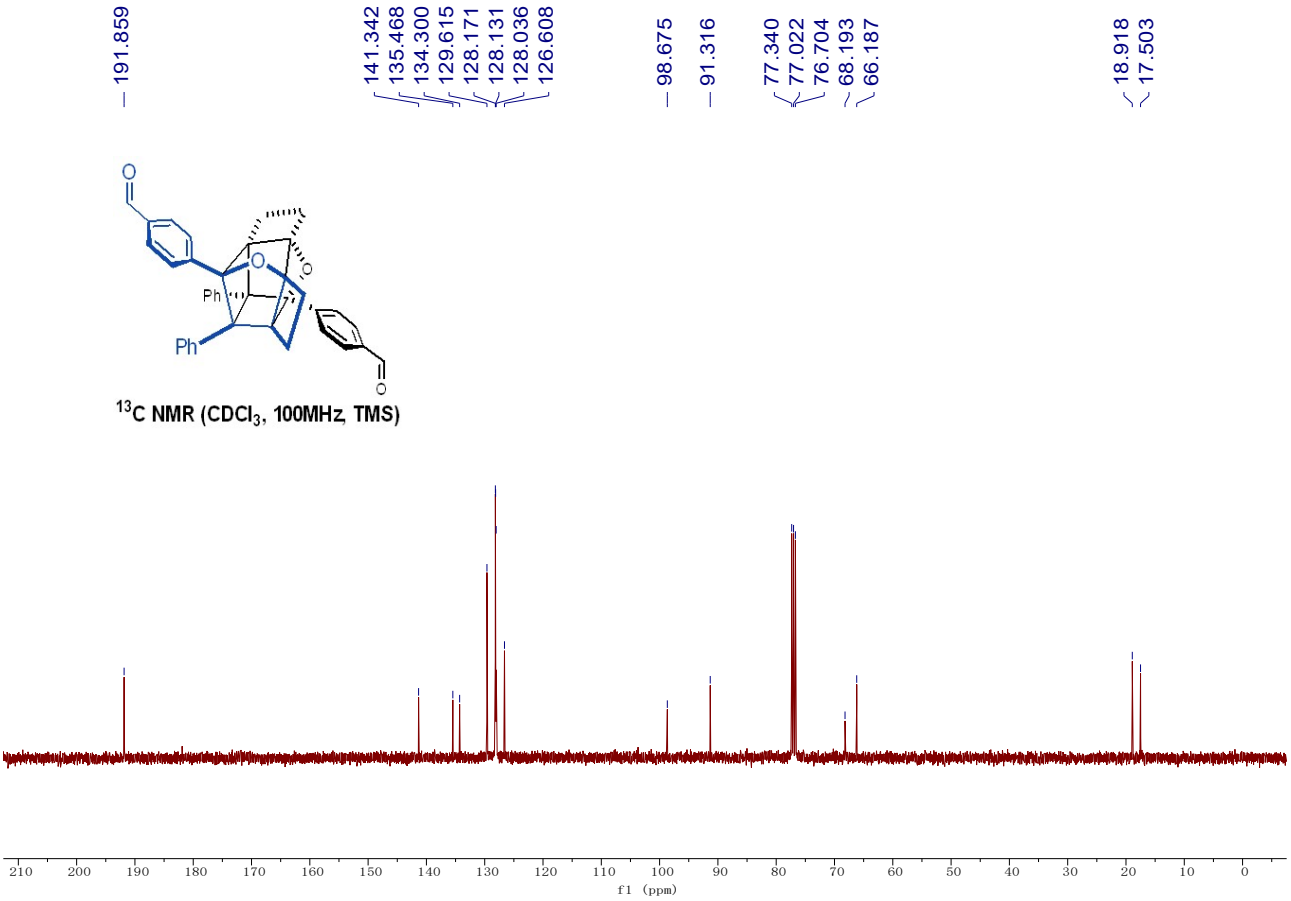




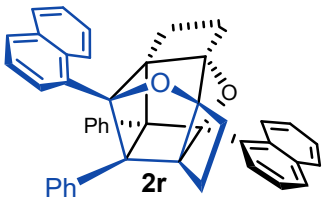
Product 2q, the title compound was achieved as a white solid, MP = 248-250 °C, 34.6 mg, 63% yield. R_f = 0.63 (Petroleum Ether:Ethyl Acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 4H), , 7.26-7.16 (m, 6H), 7.03 (d, *J* = 6.4 Hz, 4H), 2.53 (d, *J* = 7.2 Hz, 2H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.24 (t, *J* = 9.6 Hz, 1H), 2.21 (t, *J* = 9.6 Hz, 1H), 1.74 (dd, *J* = 13.2, 6.8 Hz, 1H), 1.73 (dd, *J* = 13.2, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 141.3, 135.5, 134.3, 129.6, 128.2, 128.0, 126.6, 98.7, 91.3, 68.2, 66.2, 18.9, 17.5 (each carbon signal represents two C atoms). IR (acetone) ν 2987, 2928, 1977, 1703, 1609, 1496, 1363, 1252, 1141, 1066, 1052, 979, 832, 704 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{29}O_4]^+$: 549.2060, found: 549.2066.



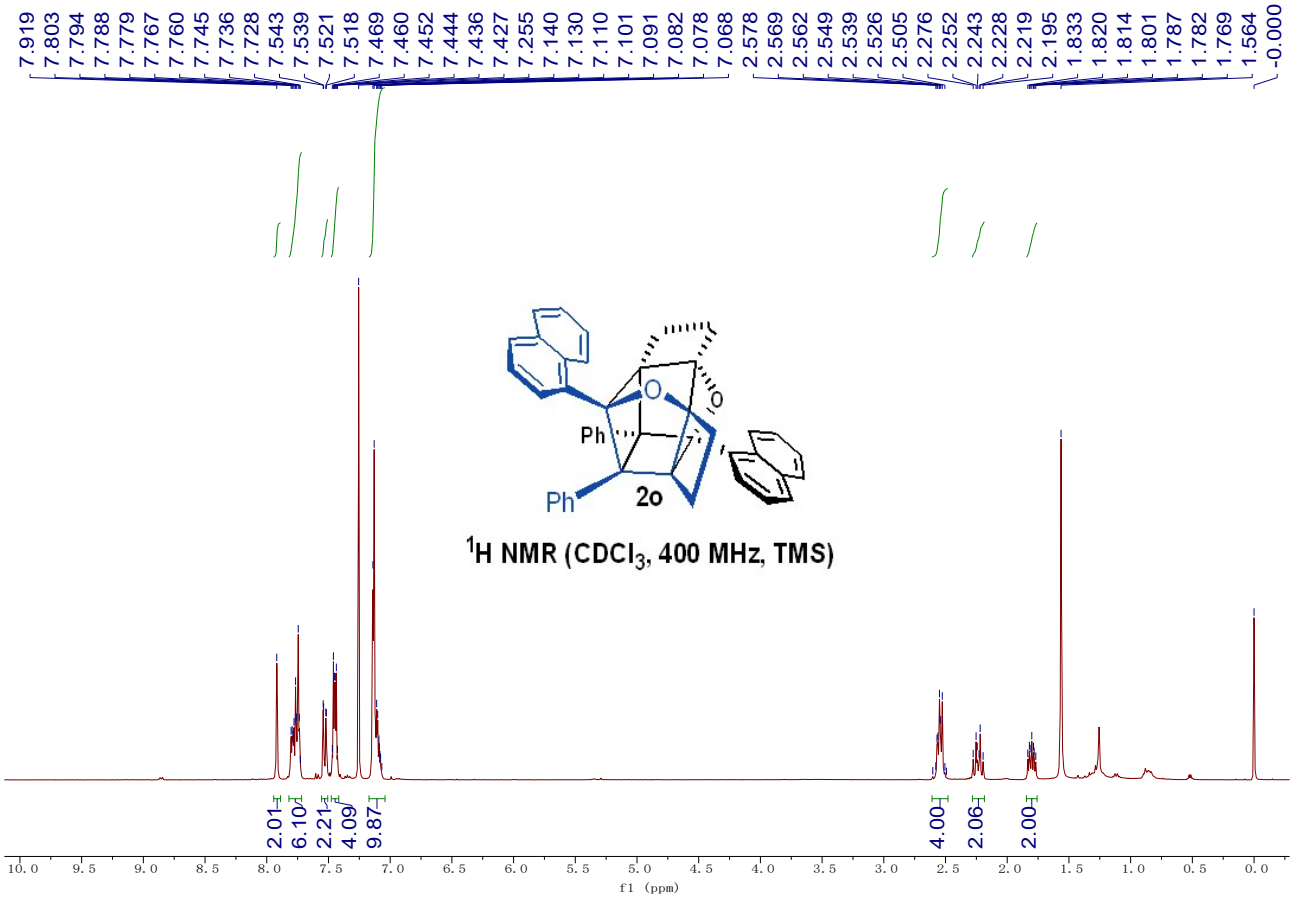
^{1}H NMR ($CDCl_3$, 400MHz, TMS)

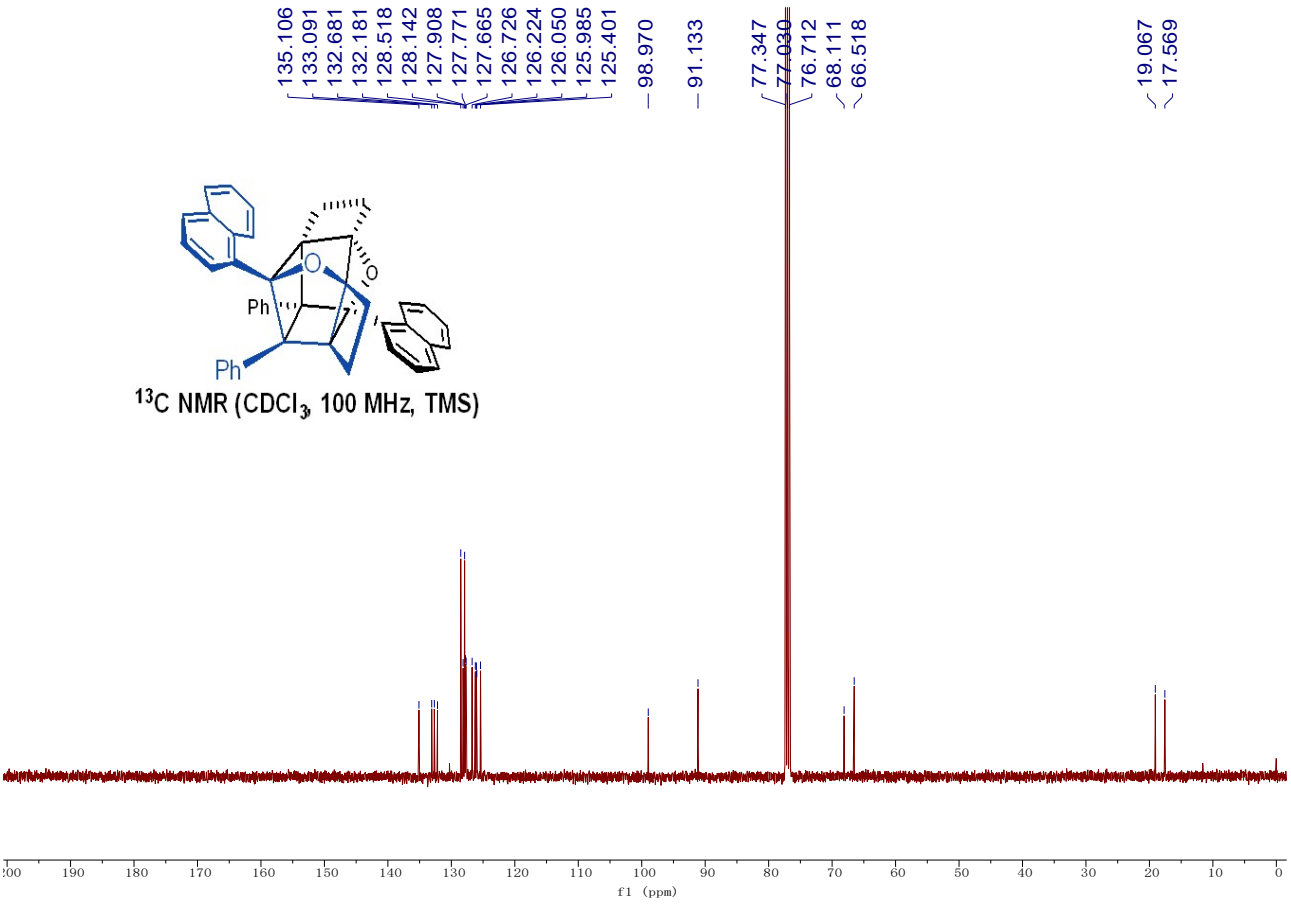


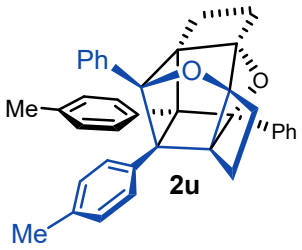
^{13}C NMR ($CDCl_3$, 100MHz, TMS)



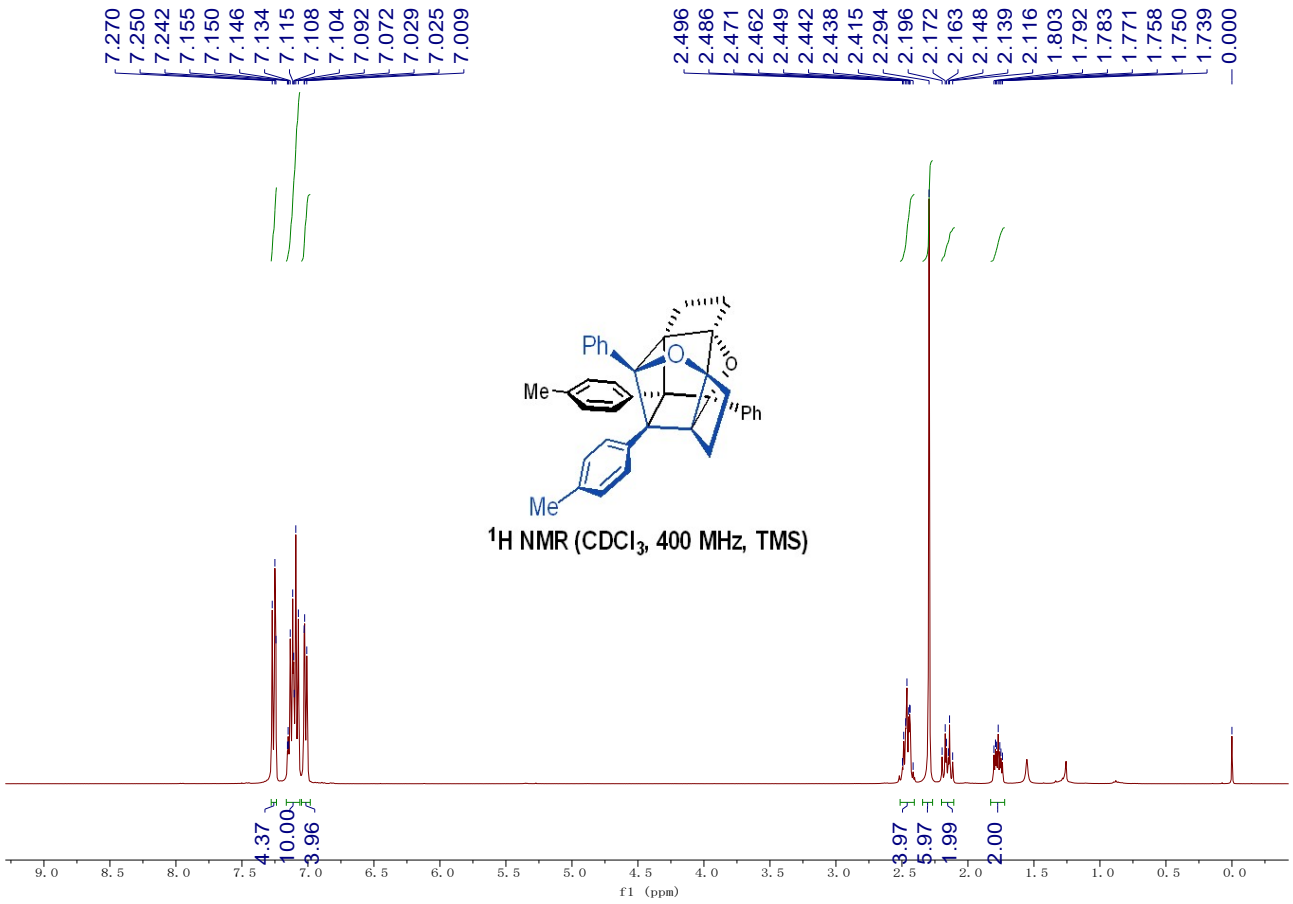
Product 2r, the title compound was achieved as a white solid, MP = 260-262 °C, 23.1 mg, 39% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.80-7.73 (m, 6H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.47-7.43 (m, 4H), 7.14-7.07 (m, 10H), 2.60-2.49 (m, 4H), 2.25 (t, *J* = 9.6 Hz, 1H), 2.22 (t, *J* = 9.6 Hz, 1H), 1.81 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.80 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.56 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 133.1, 132.7, 132.2, 128.5, 128.1, 127.9, 127.8, 127.7, 126.7, 126.2, 126.1, 126.0, 125.4, 99.0, 91.1, 68.1, 66.5, 19.1, 17.6 (each carbon signal represents two C atoms). IR (Acetone) ν 2932, 1712, 1417, 1394, 1220, 1065, 1041, 822, 808, 731, 757 cm^{-1}. HRMS (ESI) calcd for $[C_{44}H_{33}O_2]^+$: 593.2475, found: 593.2479.



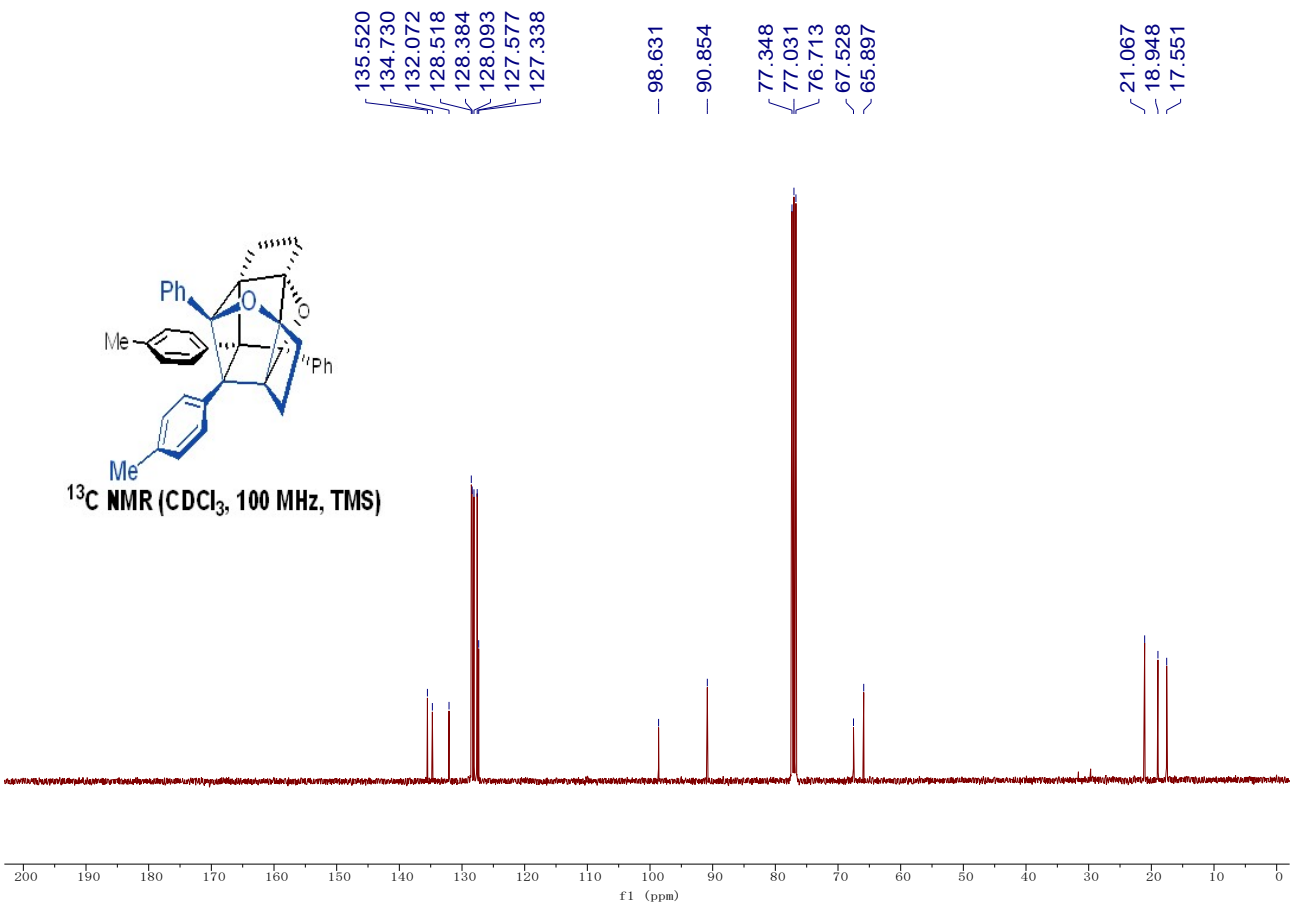




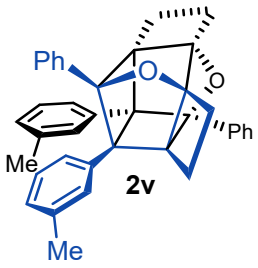
Product 2u, the title compound was achieved as a white solid, MP = 236-238 °C, 24.5 mg, 47% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.37 (m, 4H), 7.30-7.20 (m, 6H), 6.93 (d, *J* = 8.4 Hz, 4H), 6.89 (d, *J* = 8.0 Hz, 4H), 2.49-2.44 (m, 4H), 2.23 (s, 6H), 2.20 (t, *J* = 9.6 Hz, 1H), 2.16 (t, *J* = 9.6 Hz, 1H), 1.78 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.77 (dd, *J* = 12.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 134.7, 132.1, 128.5, 128.4, 128.1, 127.6, 127.3, 98.6, 90.9, 67.5, 65.9, 21.1, 18.9, 17.6 (each carbon signal represents two C atoms). IR (Acetone) ν 2983, 1775, 1704, 1249, 1177, 1137, 1038, 816, 697 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{32}O_2Na]^+$: 543.2295, found: 543.2298.



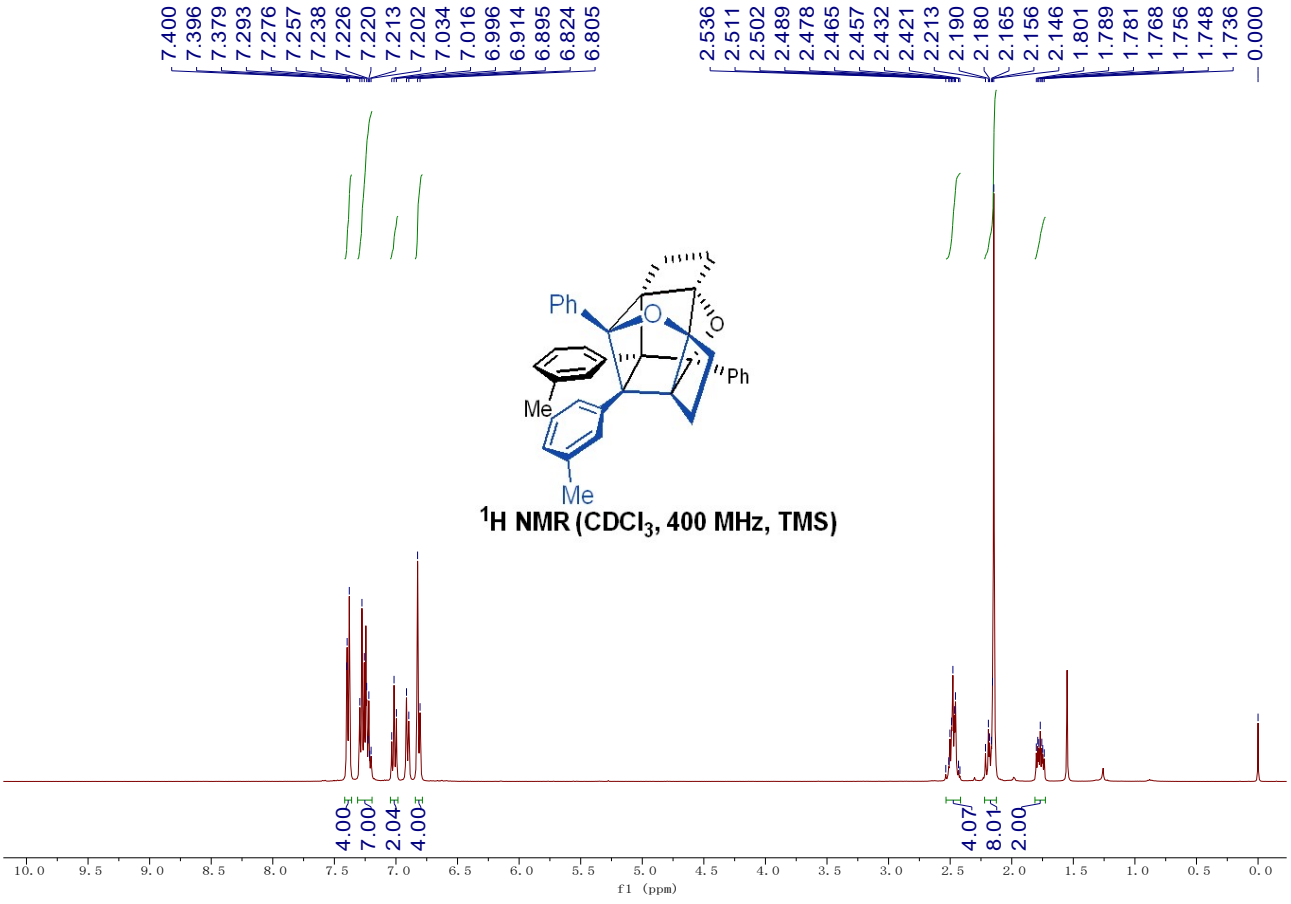
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

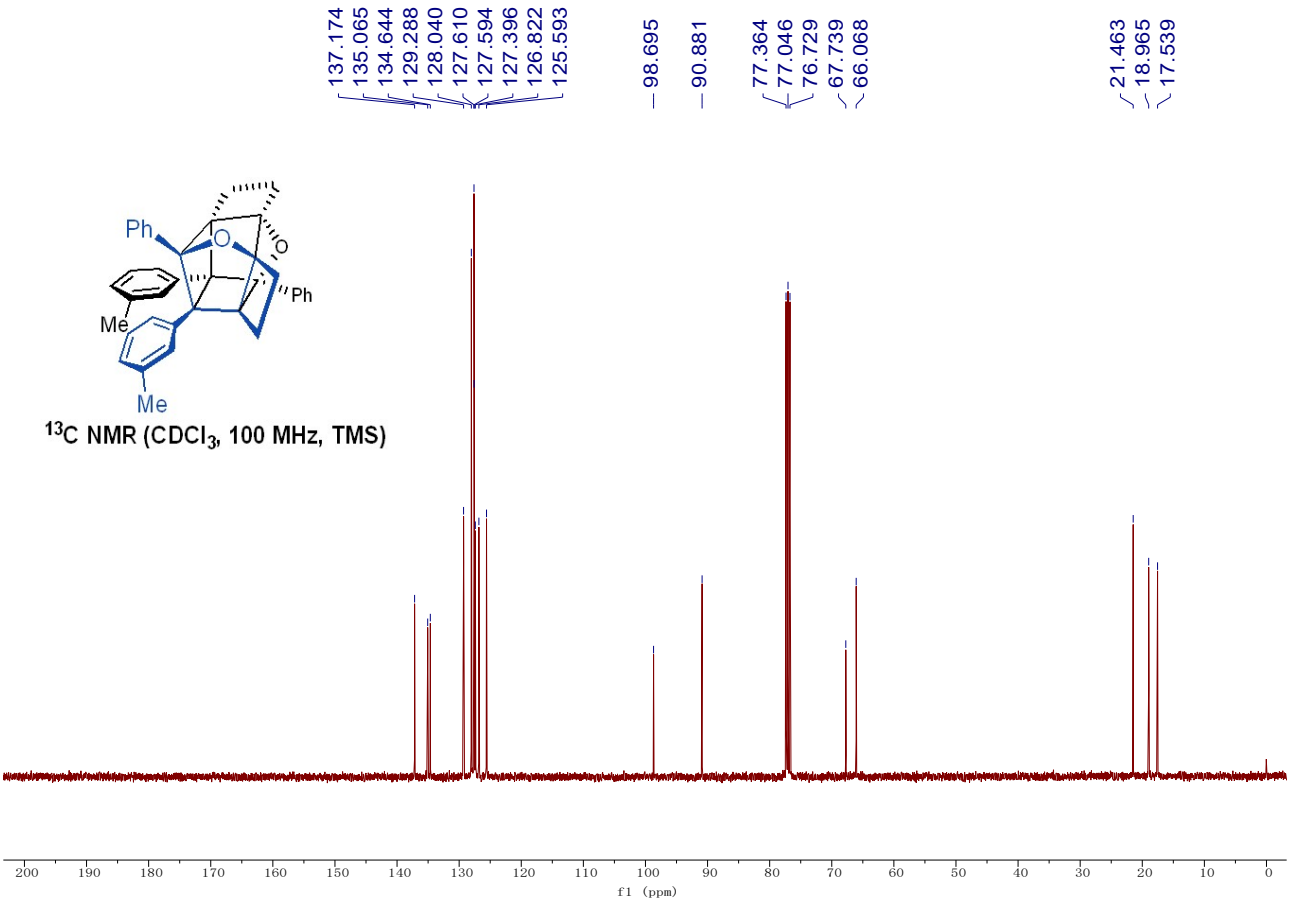


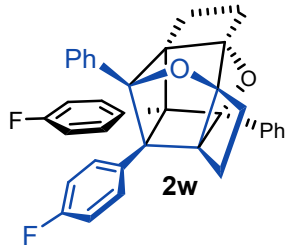
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



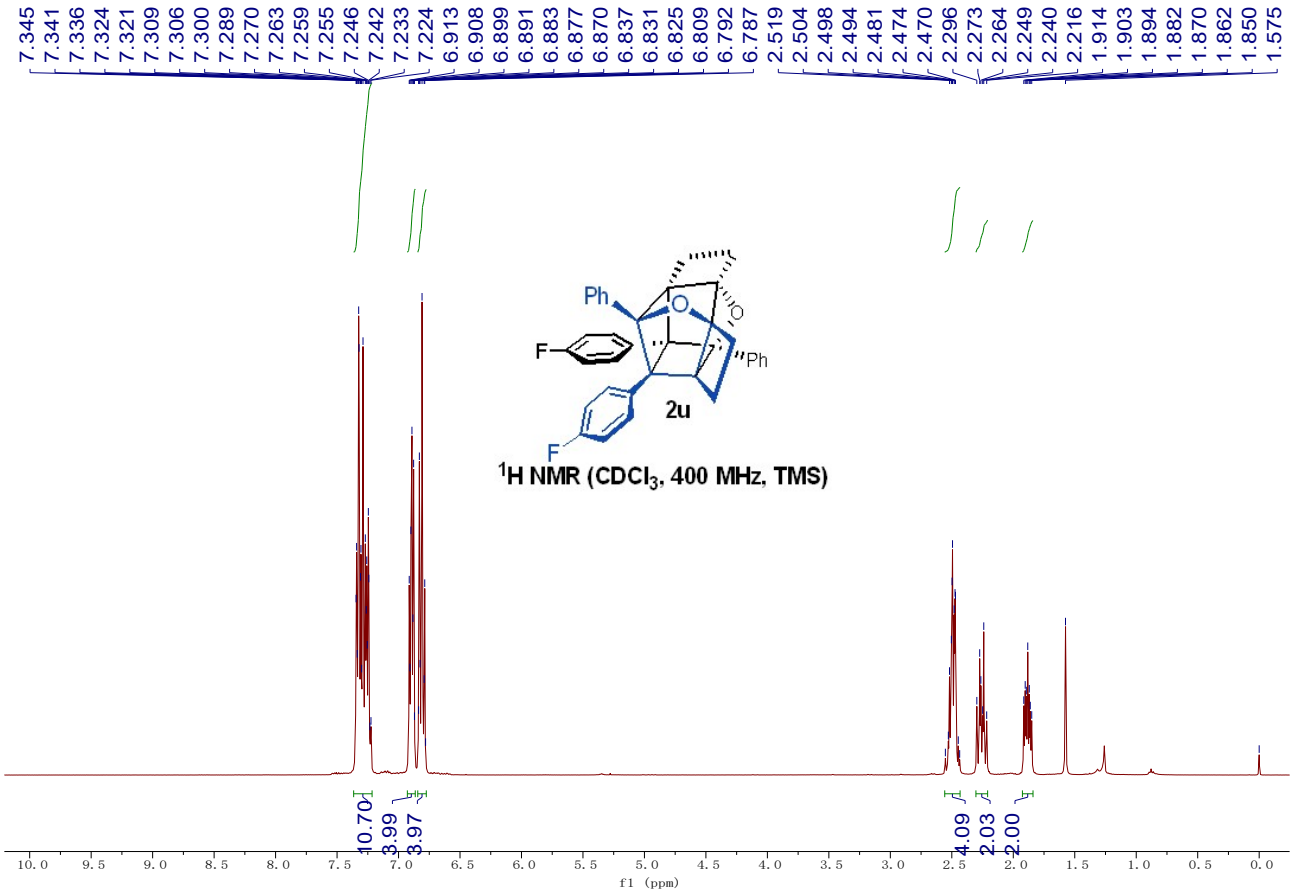
Product 2v, the title compound was achieved as a white solid, MP = 222-224 °C, 16.7 mg, 32% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.29-7.20 (m, 6H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.91-6.90 (m, 2H), 6.82-6.81 (m, 4H), 2.54-2.42 (m, 4H), 2.21-2.15 (m, 8H), 1.77 (dd, *J* = 13.2, 8.0 Hz, 1H), 1.76 (dd, *J* = 13.2, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 135.1, 134.6, 129.3, 128.0, 127.6, 127.5, 127.4, 126.8, 125.6, 98.7, 90.9, 67.7, 66.1, 21.5, 19.0, 17.5 (each carbon signal represents two C atoms). IR (Acetone) ν 2970, 2927, 1739, 1447, 1365, 1228, 1217, 1204, 1079, 1029, 977, 794, 785, 701 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{33}O_2]^+$: 521.2475, found: 521.2477.







Product 2w, the title compound was achieved as a white solid, MP = 248-250 °C, 38.6 mg, 73% yield. R_f = 0.43 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.22 (m, 10H), 6.91-6.87 (m, 4H), 6.84-6.78 (m, 4H), 2.55-2.44 (m, 4H), 2.27 (t, *J* = 9.6 Hz, 1H), 2.24 (t, *J* = 9.6 Hz, 1H), 1.89 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.88 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.58 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J_{CF} = 244.3 Hz), 134.2, 130.8 (d, J_{CF} = 3.3 Hz), 129.9 (d, J_{CF} = 7.7 Hz), 128.3, 127.7, 127.4, 114.8 (d, J_{CF} = 20.9 Hz), 98.7, 91.1, 67.3, 65.3, 19.0, 17.7 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.8. IR (Acetone) ν 2970, 1739, 1603, 1506, 1448, 1366, 1218, 1203, 1064, 1031, 972, 837, 747, 706 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2F_2]^+$: 529.1974, found: 529.1976.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7.341
7.336
7.324
7.321
7.309
7.306
7.300
7.289
7.270
7.263
7.259
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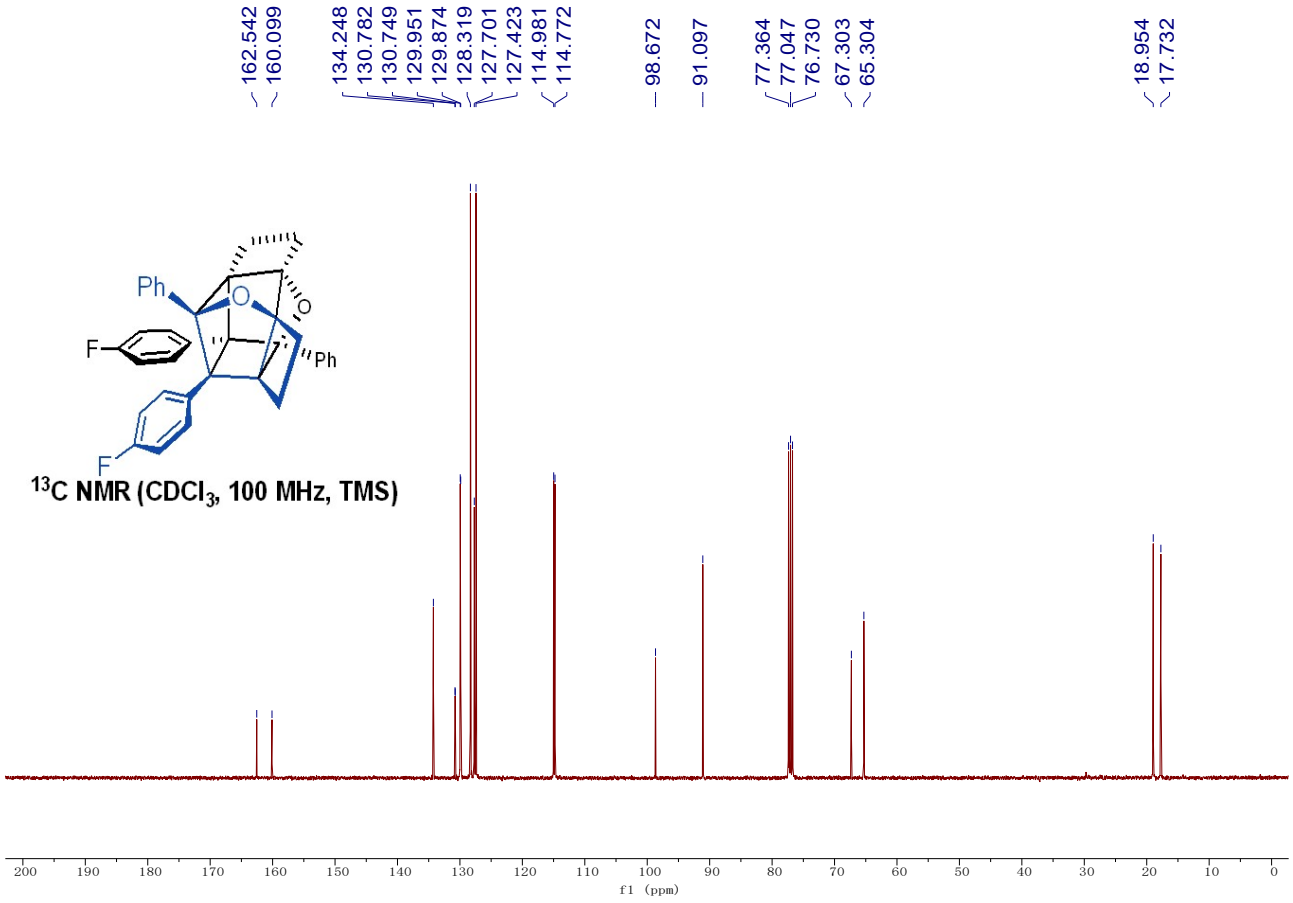
7.246
7.242
7.233
7.224
6.913
6.908
6.899
6.891
6.883
6.877
6.870
6.837
6.831
6.825
6.809
6.792
6.787
2.519
2.504
2.498
2.494
2.481
2.474
2.470
2.296
2.273
2.264
2.249
2.240
2.216
1.914
1.903
1.894
1.882
1.870
1.862
1.850
1.575
Ph
O
O
F
Ph
F
2u
1H NMR (CDCl3, 400 MHz, TMS)
10.70
3.99
3.97
4.09
2.03
2.00
f1 (ppm)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160.099
134.248
130.782
130.749
129.951
129.874
128.319
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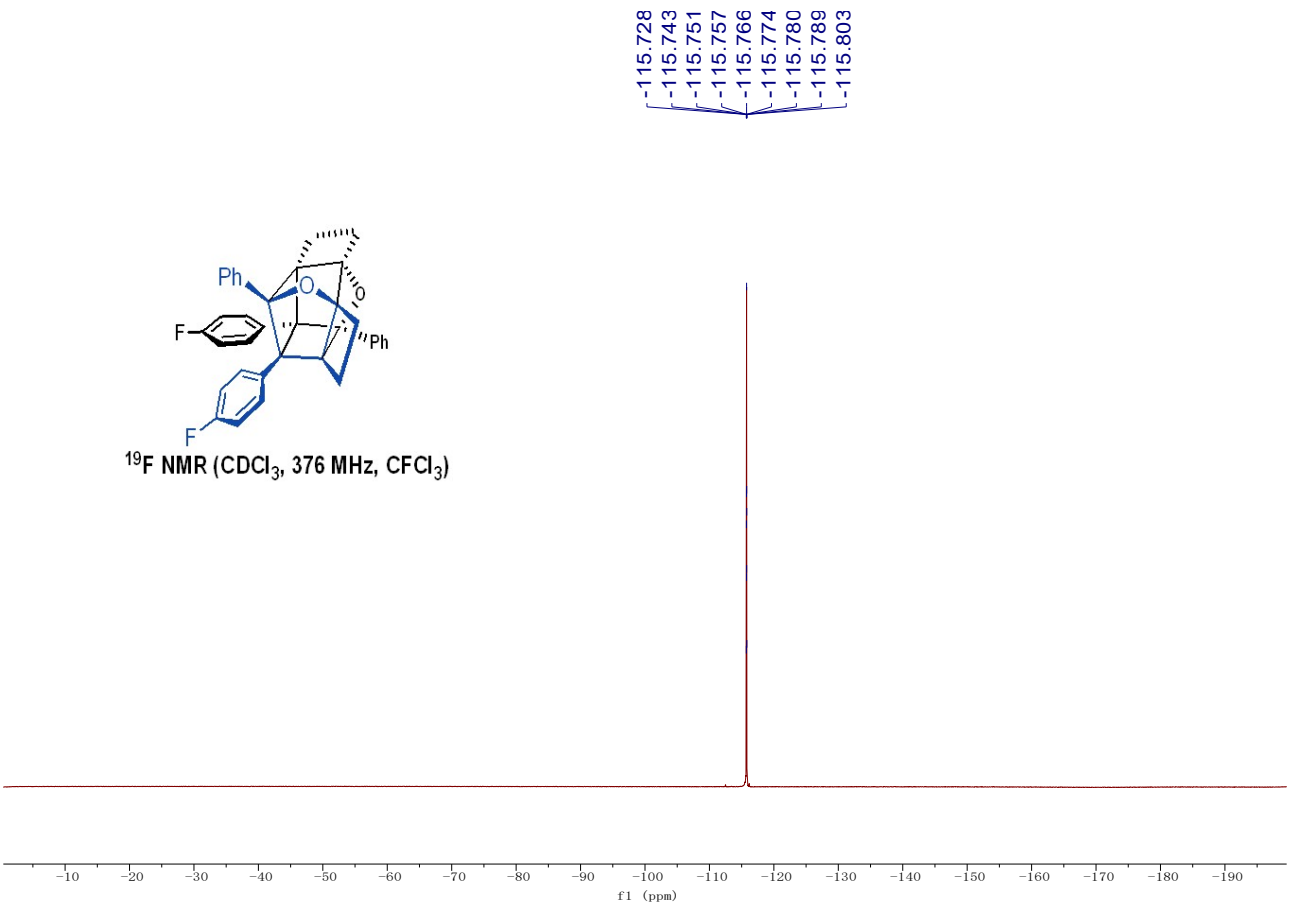
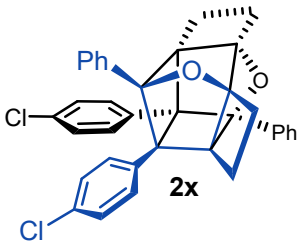
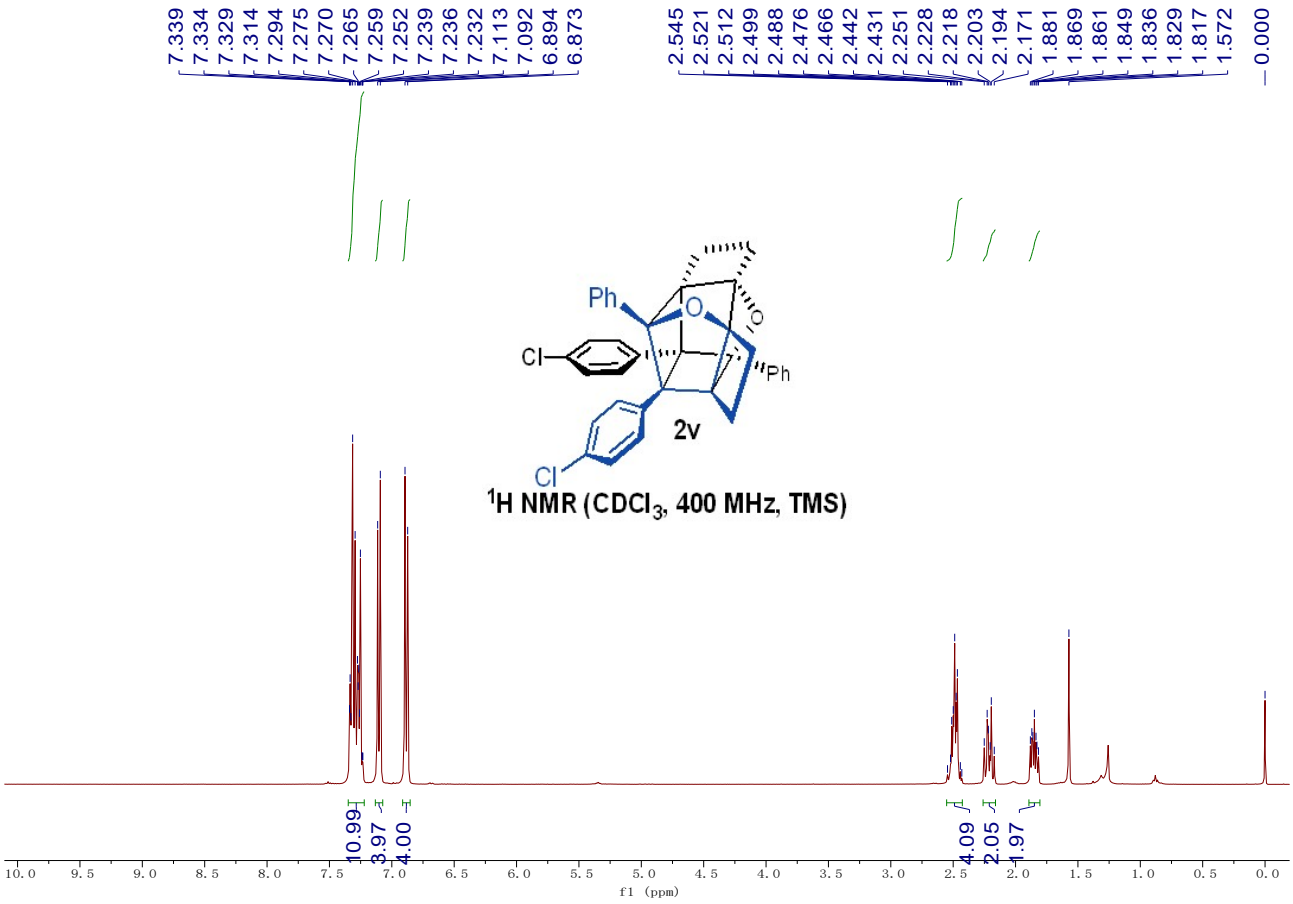
127.423
114.981
114.772
98.672
91.097
77.364
77.047
76.730
67.303
65.304
18.954
17.732
Ph
O
O
F
Ph
F
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)



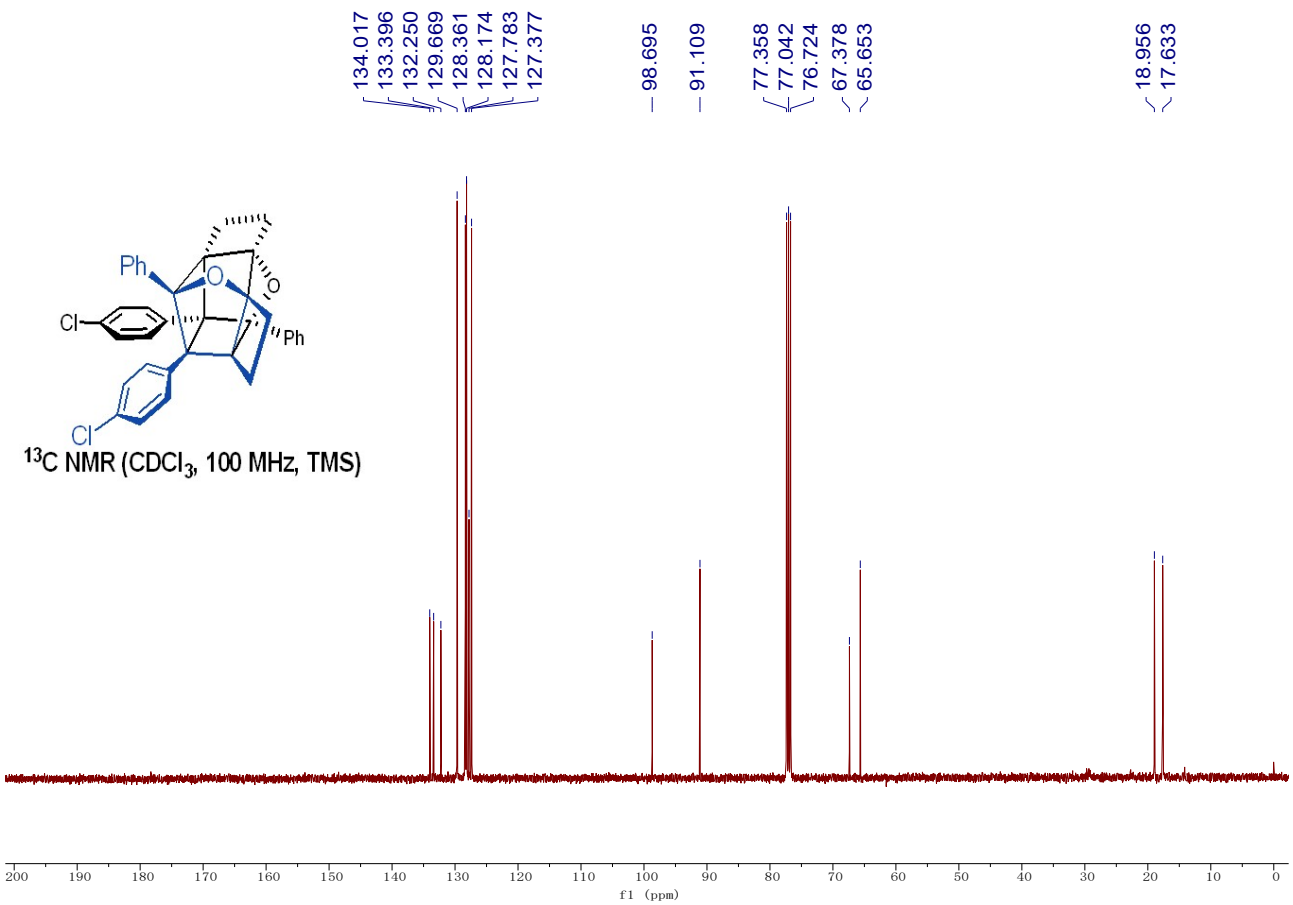


2x

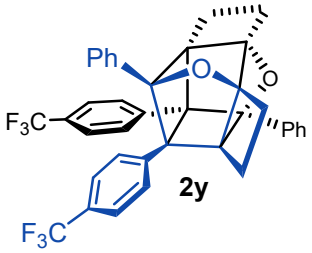
Product 2x, the title compound was achieved as a white solid, MP = 252-254 °C, 32.0 mg, 57% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.23 (m, 10H), 7.11-7.09 (m, 4H), 6.89-6.87 (m, 4H), 2.55-2.43 (m, 4H), 2.23 (t, *J* = 9.6 Hz, 1H), 2.19 (t, *J* = 9.6 Hz, 1H), 1.86 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.85 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.57 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 133.4, 132.2, 129.7, 128.4, 128.2, 127.8, 127.4, 98.7, 91.1, 67.4, 65.7, 19.0, 17.6 (each carbon signal represents two C atoms). IR (Acetone) ν 2920, 1739, 1489, 1447, 1366, 1229, 1217, 1204, 1093, 1030, 1016, 935, 830, 795, 699 cm^{-1}. HRMS (ESI) calcd for $[C_{36}H_{27}O_2Cl_2]^+$: 561.1383, found: 561.1382.



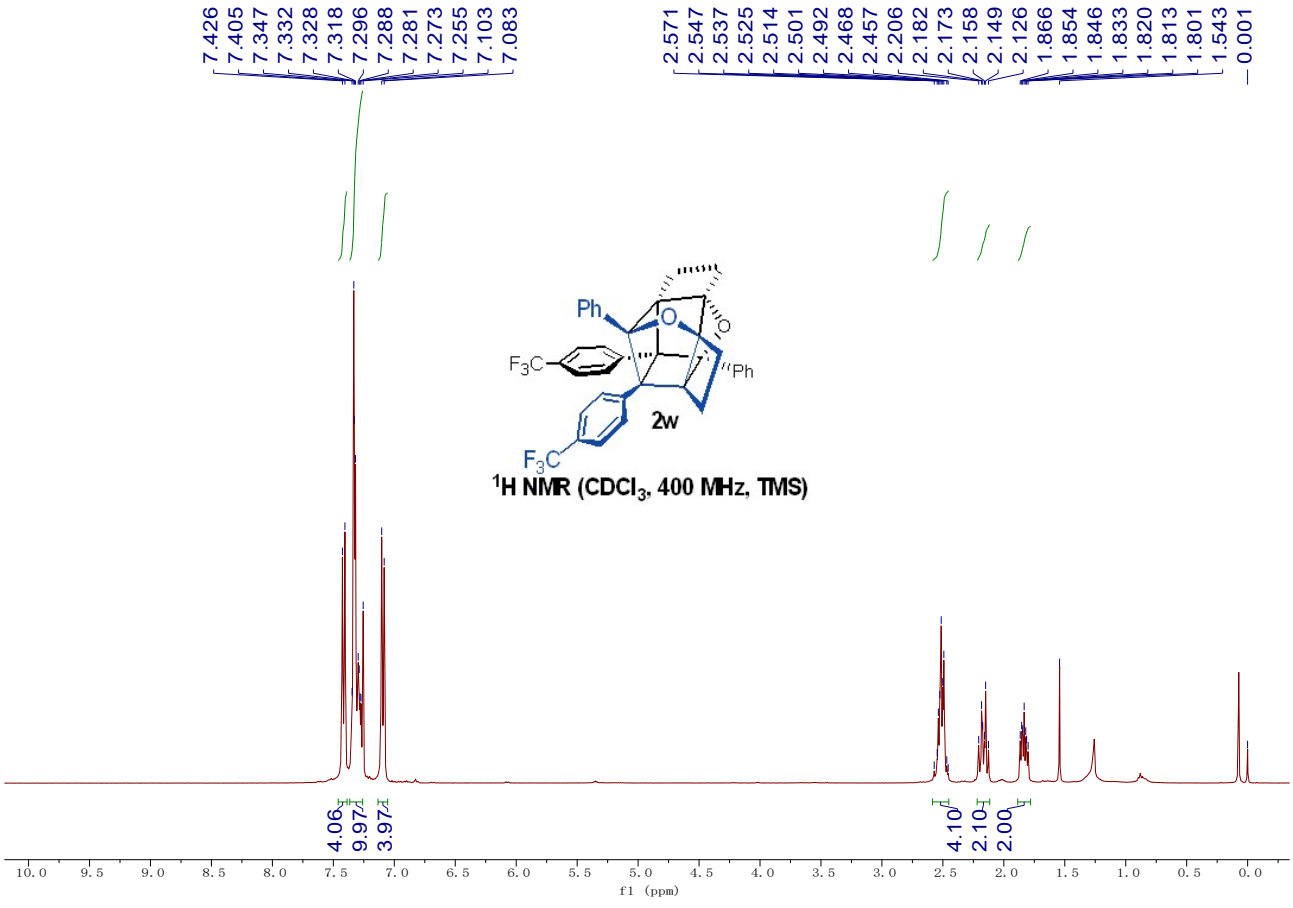
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

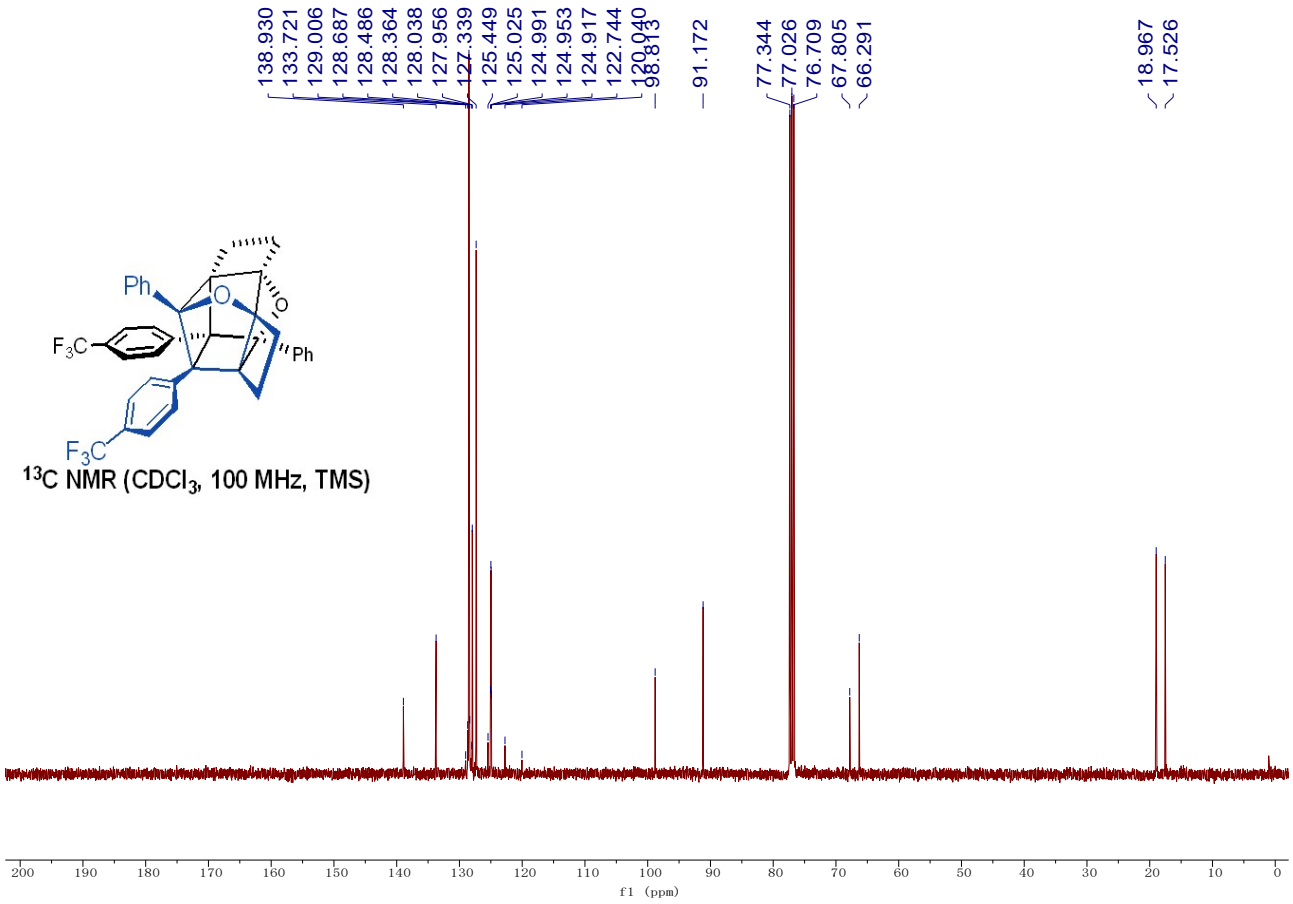


^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

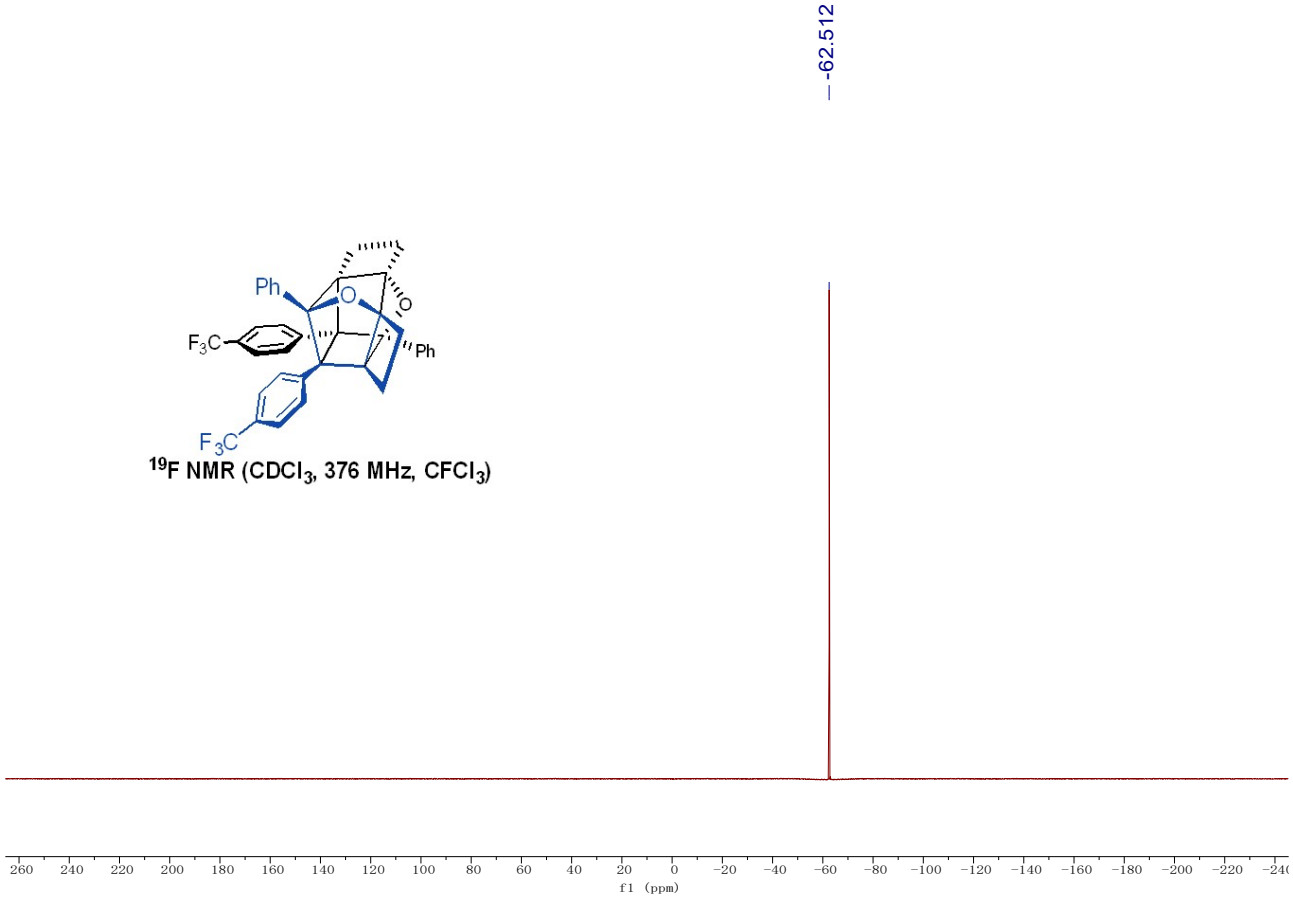


Product 2y, the title compound was achieved as a white solid, MP = 247-249 °C, 36.5 mg, 58% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 4H), 7.35-7.32 (m, 7H), 7.30-7.27 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 4H), 2.57-2.46 (m, 4H), 2.19 (t, *J* = 9.6 Hz, 1H), 2.15 (t, *J* = 9.6 Hz, 1H), 1.84 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.83 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.54 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 133.7, 128.6 (q, $J_{C\text{-}F}$ = 32.4 Hz), 128.5, 128.0, 127.9, 127.3, 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.3 Hz), 98.8, 91.2, 67.8, 66.3, 19.0, 17.5 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. IR (Acetone) ν 2970, 1773, 1705, 1616, 1320, 1120, 1110, 1070, 942, 844, 732, 695 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{27}O_2F_6]^+$: 629.1910, found: 629.1911.

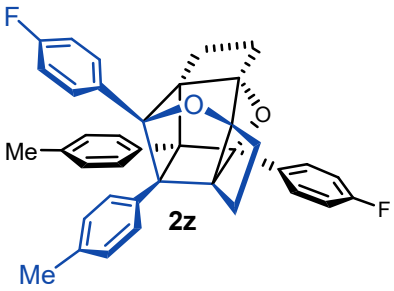




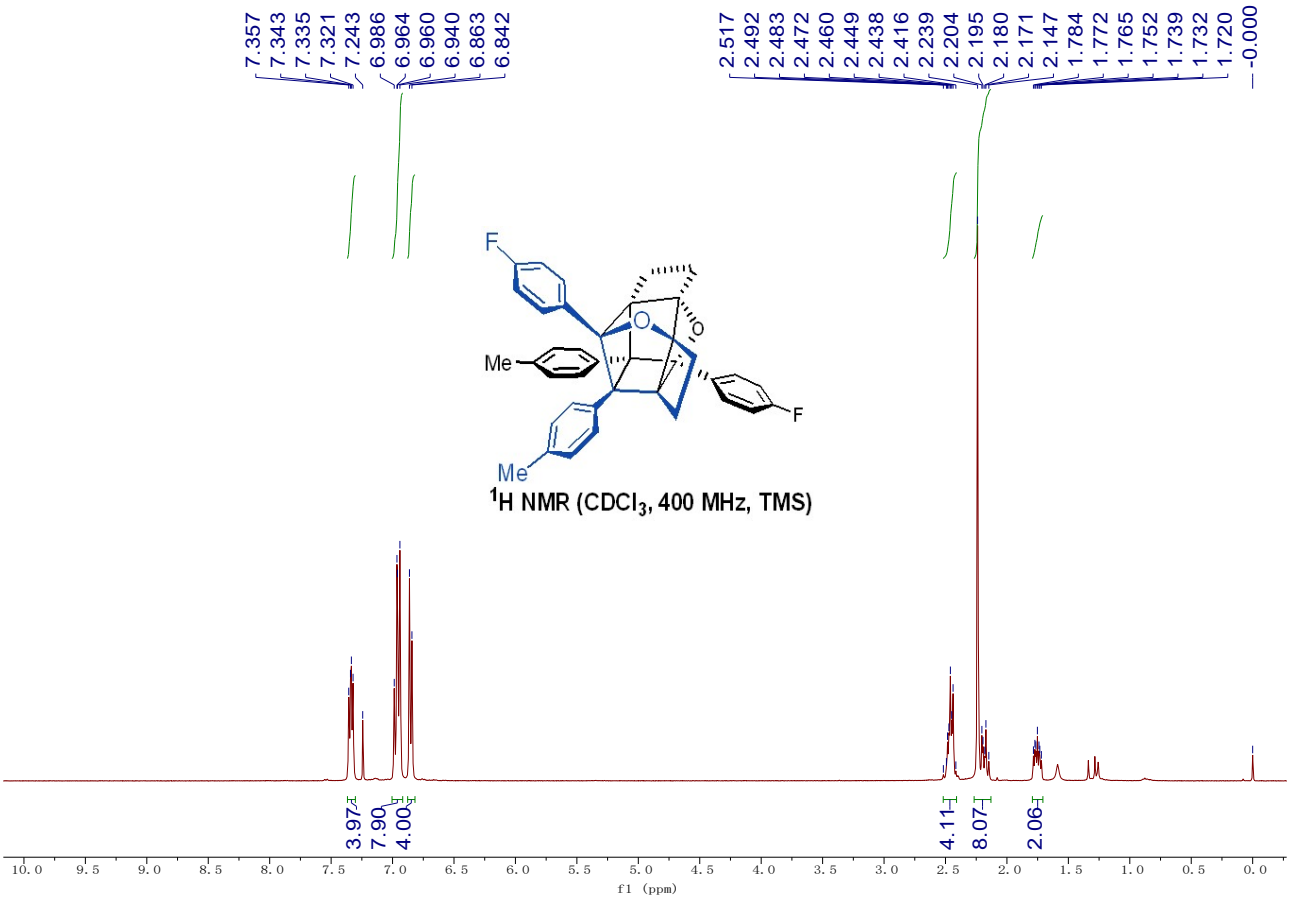
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

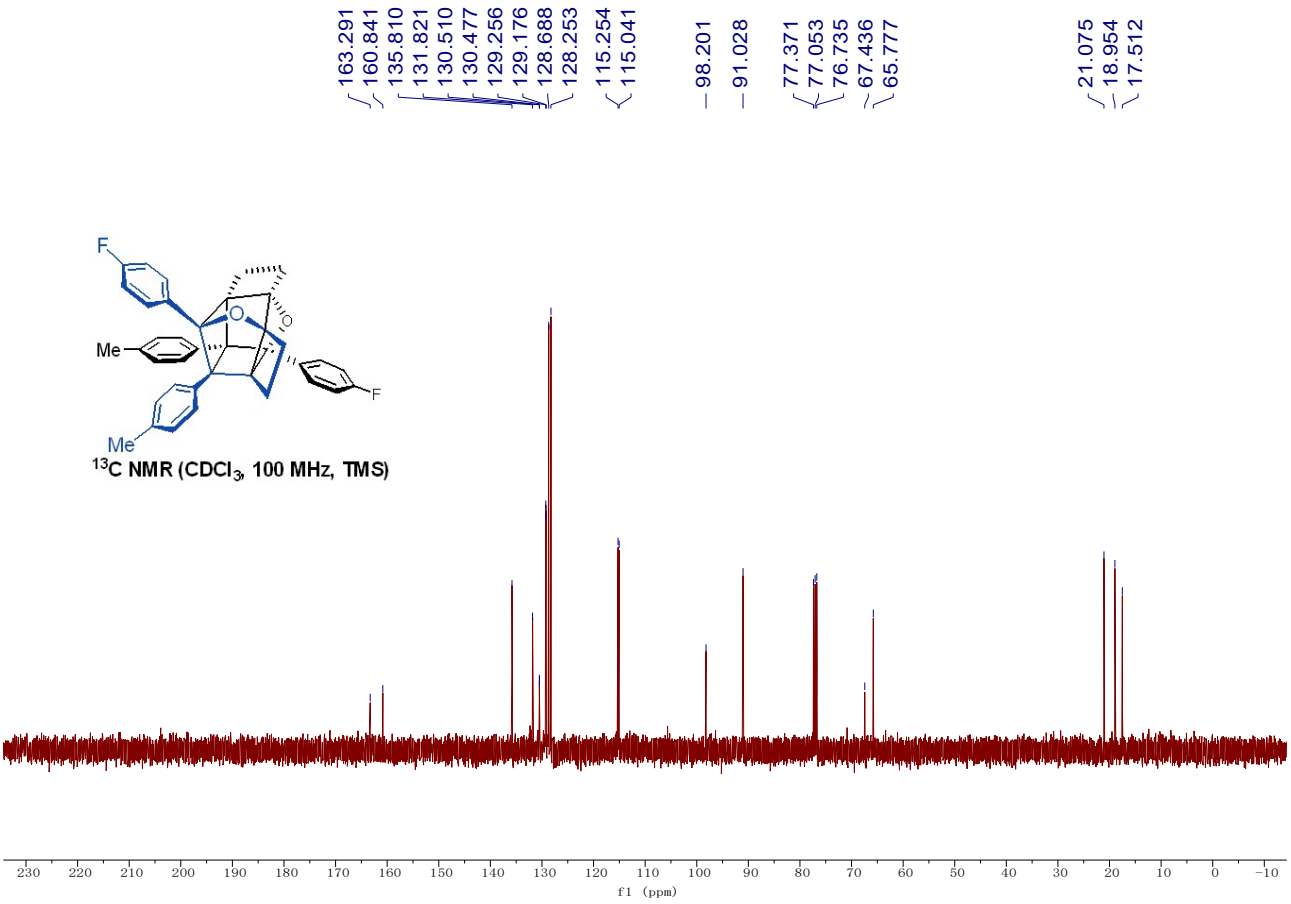


^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

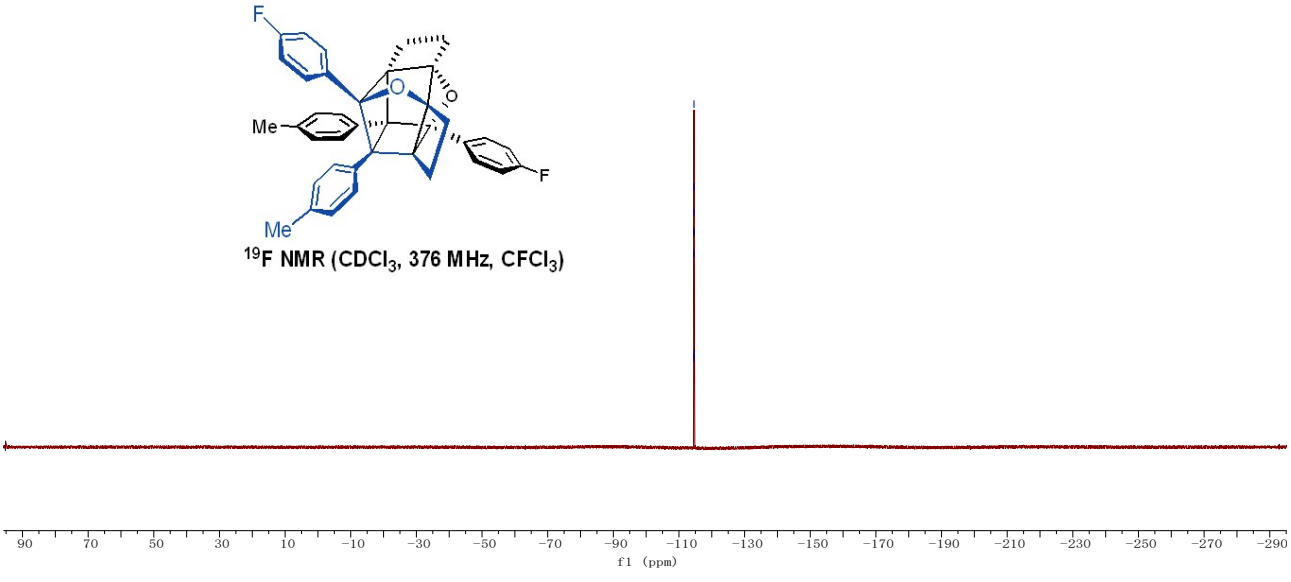


Product 2z, the title compound was achieved as a white solid, MP = 245-247 °C, 41.2 mg, 74% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 4.4, 2.0 Hz, 2H), 7.33 (dd, *J* = 4.4, 2.0 Hz, 2H), 7.00-6.94 (m, 8H), 6.87-6.84 (m, 4H), 2.52-2.40 (m, 4H), 2.42 (s, 6H), 2.21-2.15 (m, 2H), 1.79-1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J_{CF} = 245.0 Hz), 135.8, 131.8, 130.5 (d, J_{CF} = 3.3 Hz), 129.2 (d, J_{CF} = 8.0 Hz), 128.7, 128.3, 115.2 (d, J_{CF} = 21.3 Hz), 98.2, 91.0, 67.4, 65.8, 21.1, 19.0, 17.5 (each carbon signal represents two C atoms). ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.6. IR (Acetone) ν 2970, 1739, 1603, 1506, 1448, 1366, 1218, 1203, 1064, 1031, 972, 837, 747, 706 cm^{-1}. HRMS (ESI) calcd for $[C_{38}H_{31}O_2F_2]^+$: 557.2287, found: 557.2291.

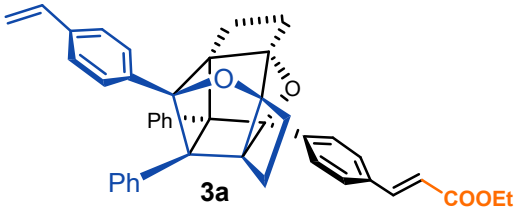




^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

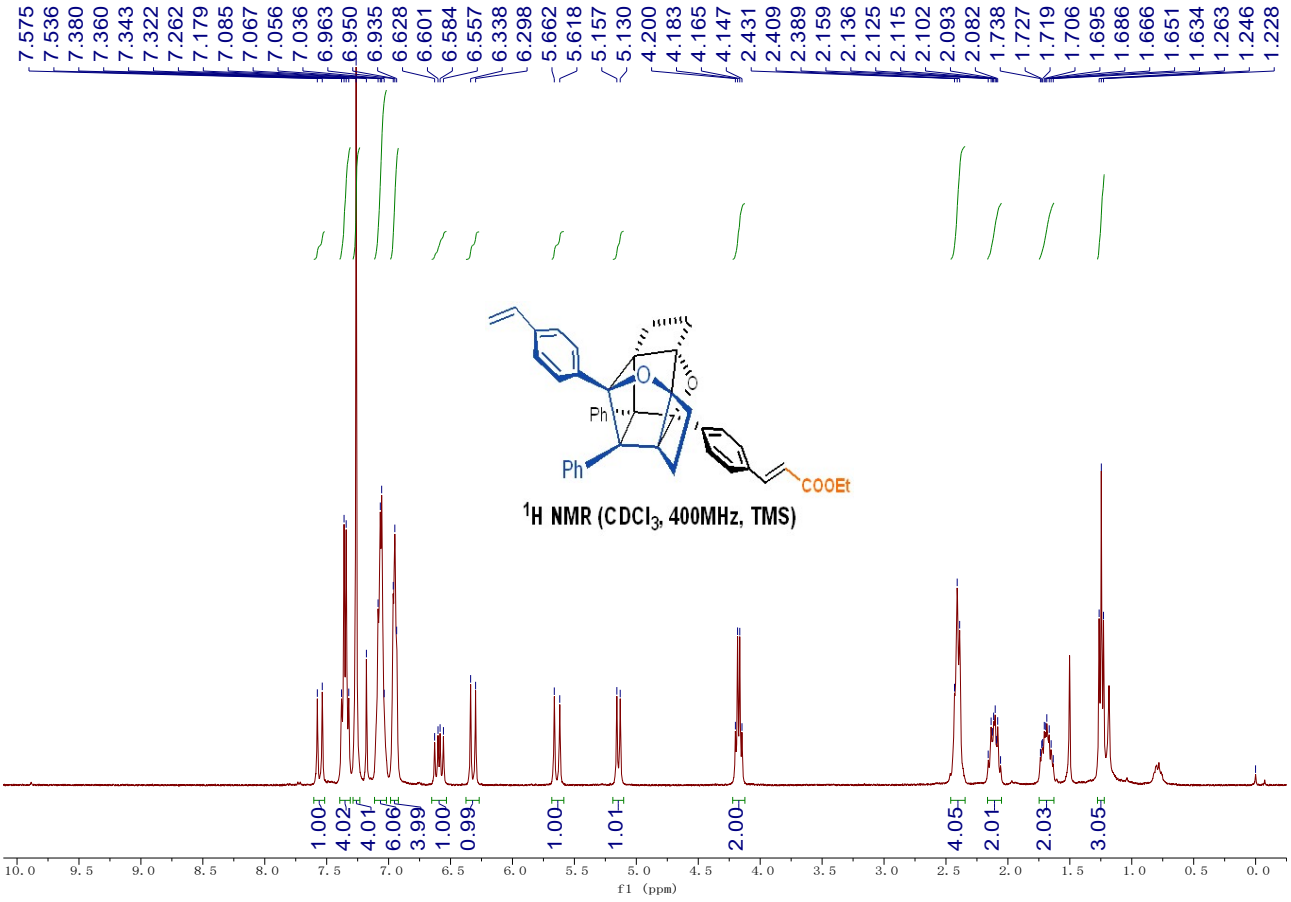


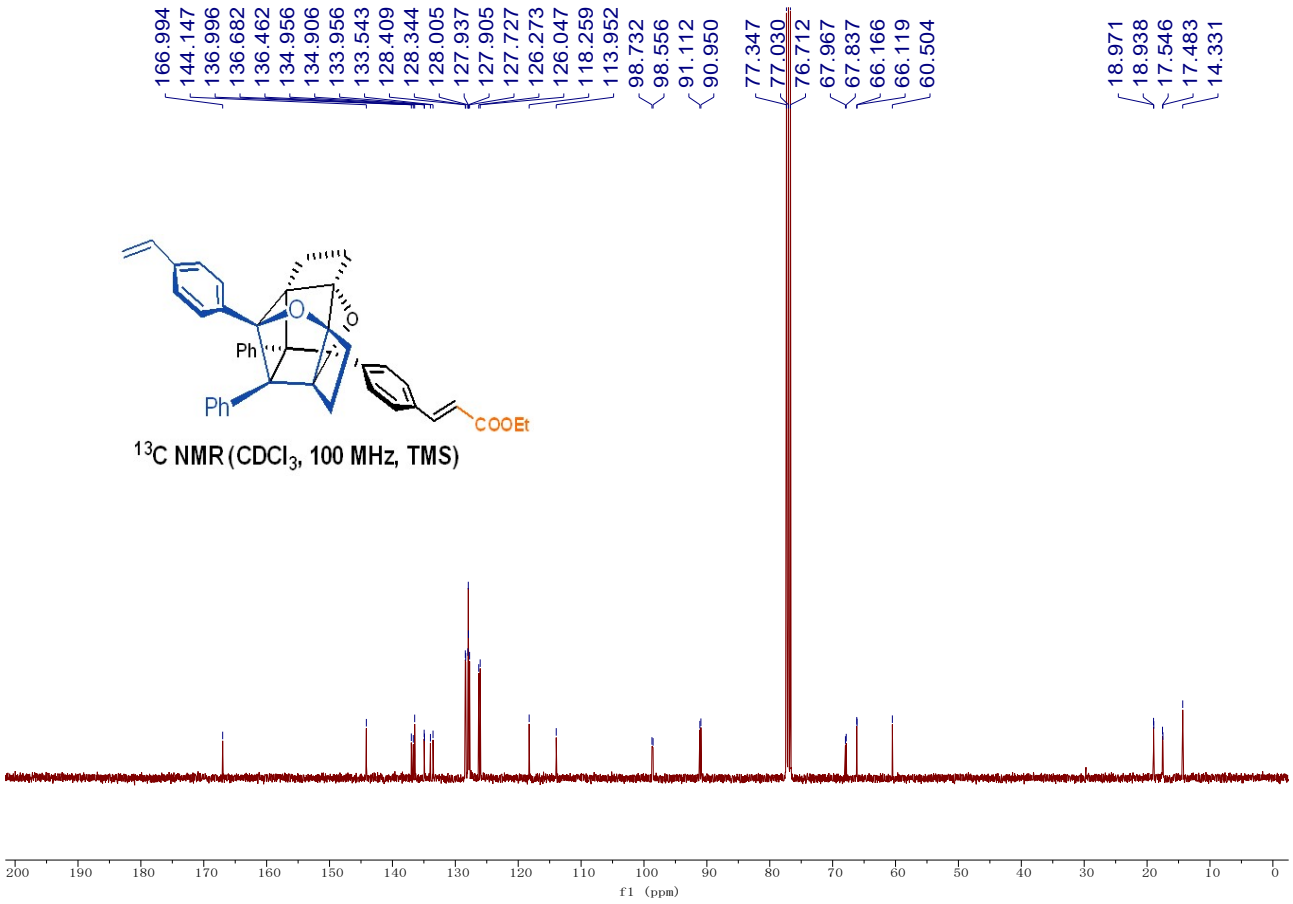
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

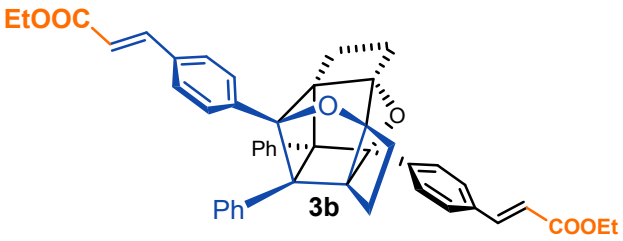


3a

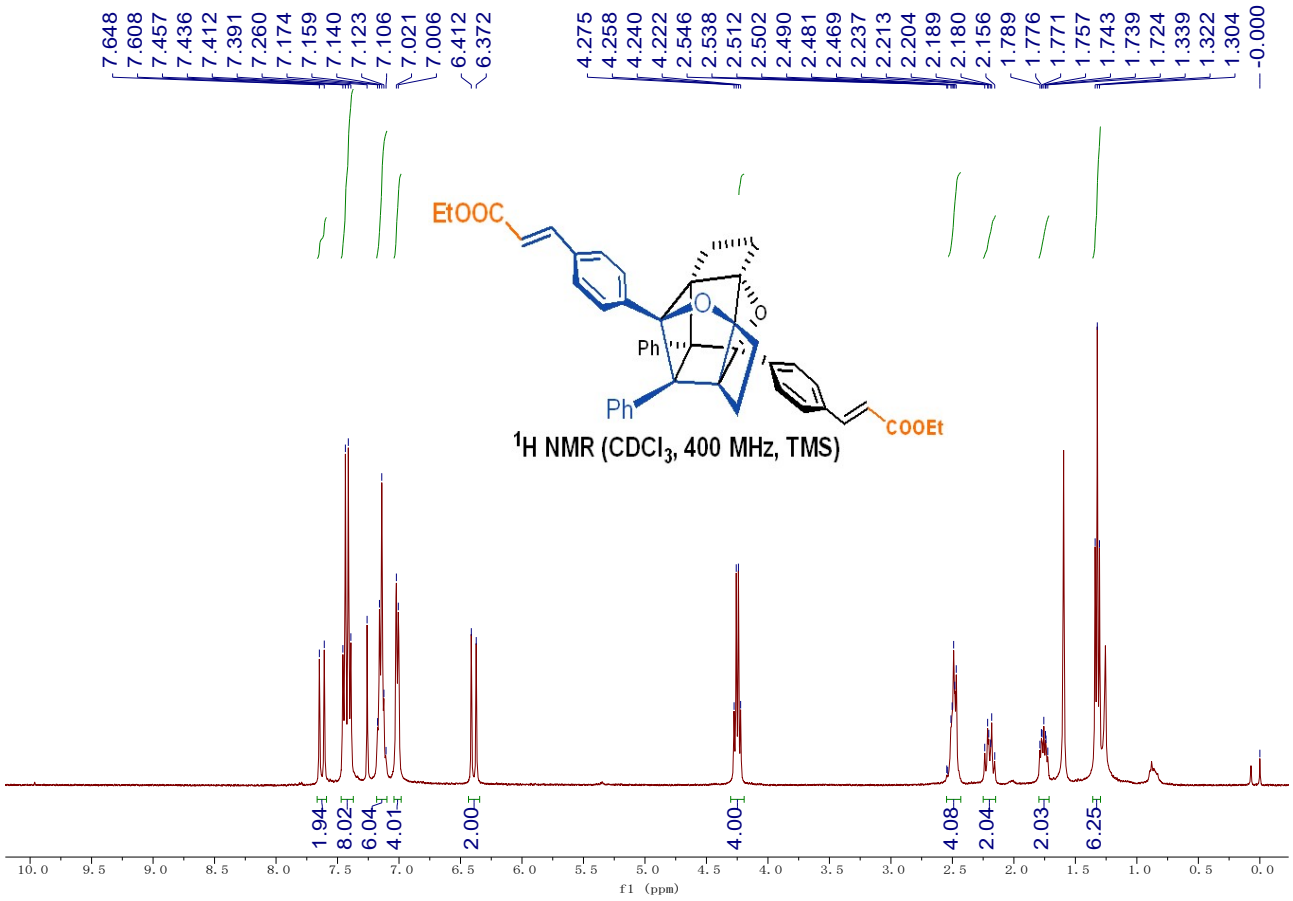
Product 3a, the title compound was achieved as a white solid, MP = 244-246 °C, 22.0 mg, 36% yield. R_f = 0.31 (Petroleum Ether:Ethyl Acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 11.2, 8.0 Hz, 4H), 7.26 (s, 4H), 7.09-7.04 (m, 6H), 6.96-6.94 (m, 4H), 6.59, (dd, *J* = 17.6, 10.8 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.43-2.39 (m, 4H), 2.13 (t, *J* = 9.2 Hz, 1H), 2.09 (t, *J* = 9.2 Hz, 1H), 1.74-1.63 (m, 2H), 1.25 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 144.1, 137.0, 136.7, 136.5, 135.0, 134.9, 134.0, 133.5, 128.4, 128.3, 128.0, 127.94, 127.91, 127.7, 126.3, 126.0, 118.3, 114.0, 98.7, 98.6, 91.1, 91.0, 68.0, 67.8, 66.2, 66.1, 60.5, 19.0, 18.9, 17.6, 17.5, 14.3 (two carbon signals were overlapped). IR (Acetone) ν 2935, 1711, 1636, 1445, 1365, 1220, 1175, 1040, 983, 829, 705 cm^{-1}. HRMS (ESI) calcd for $[C_{43}H_{37}O_4]^+$: 617.2686, found: 617.2686.







Product 3b, the title compound was achieved as a white solid, MP = 237-238 °C, 21.0 mg, 31% yield. R_f = 0.46 (Petroleum Ether:Ethyl Acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.0 Hz, 2H), 7.42 (dd, *J* = 18.0, 8.4 Hz, 8H), 7.17-7.11 (m, 6H), 7.02-7.01 (m, 4H), 6.39 (d, *J* = 16.0 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 4H), 2.55-2.24 (m, 4H), 2.20 (t, *J* = 9.2 Hz, 1H), 2.19 (t, *J* = 9.2 Hz, 1H), 1.76 (dd, *J* = 12.8, 7.2 Hz, 1H), 1.75 (dd, *J* = 12.8, 7.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 145.8, 138.5, 136.4, 135.3, 130.0, 129.7, 129.6, 128.1, 120.0, 100.3, 92.8, 69.7, 67.8, 62.2, 20.6, 19.2, 16.0 (each carbon signal represents two C atoms). IR (Acetone) ν 2988, 1713, 1637, 1407, 1385, 1253, 1229, 1175, 1066, 1056, 892, 829, 705 cm^{-1}. HRMS (ESI) calcd for $[C_{46}H_{41}O_6]^+$: 689.2925, found: 689.2912.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2.469
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2.180
2.156
1.789
1.776
1.771
1.757
1.743
1.739
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1.322
1.304
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O
Ph
Ph
COOEt
1H NMR (CDCl3, 400 MHz, TMS)
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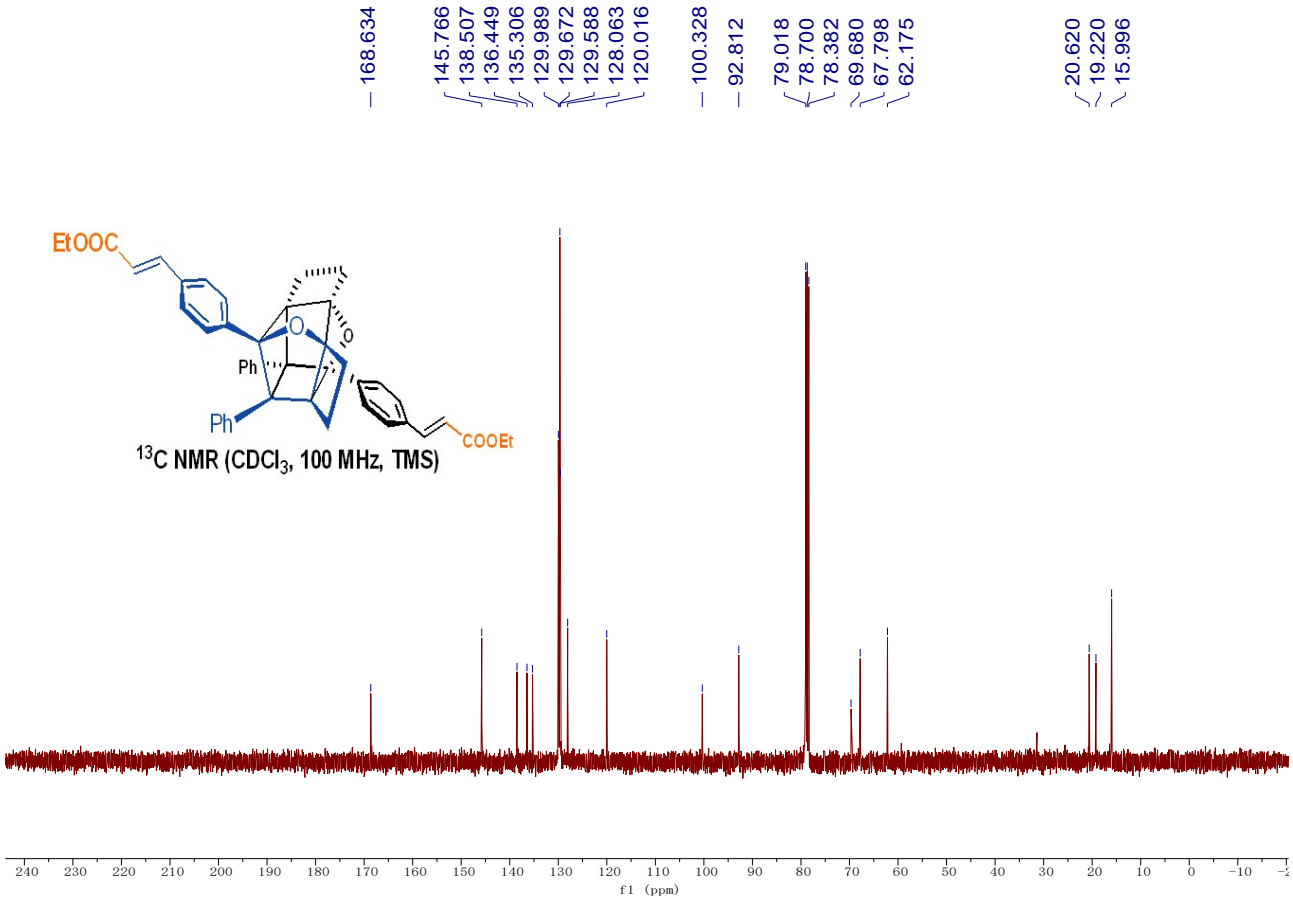
2.00
4.00
4.08
2.04
2.03
6.25
f1 (ppm)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129.989
129.672
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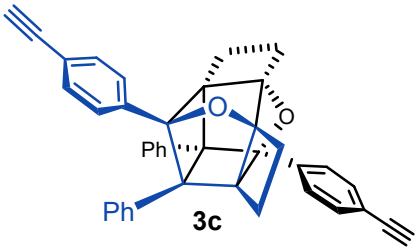
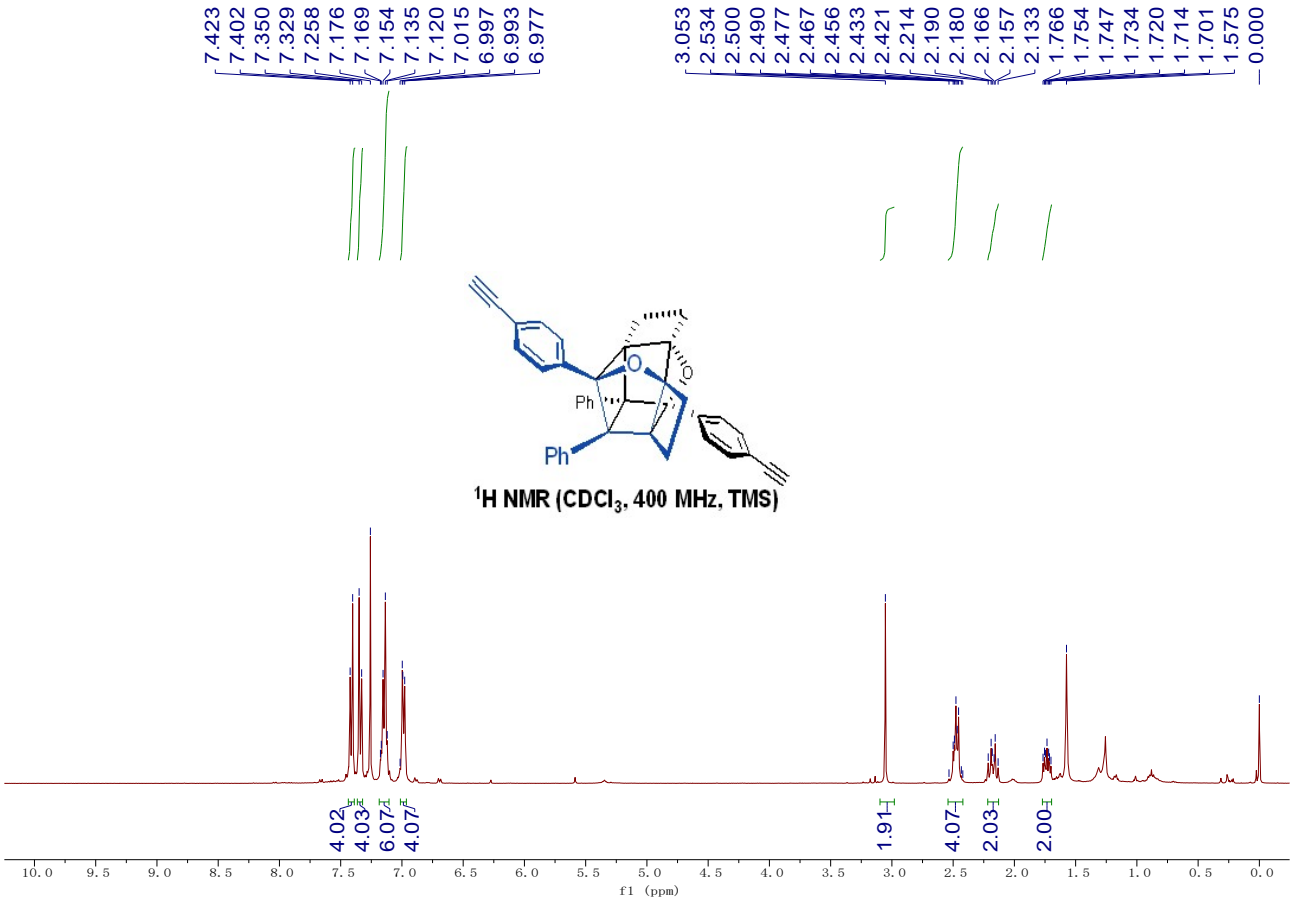
120.016
100.328
92.812
79.018
78.700
78.382
69.680
67.798
62.175
20.620
19.220
15.996
EtOOC
O
O
Ph
Ph
COOEt
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

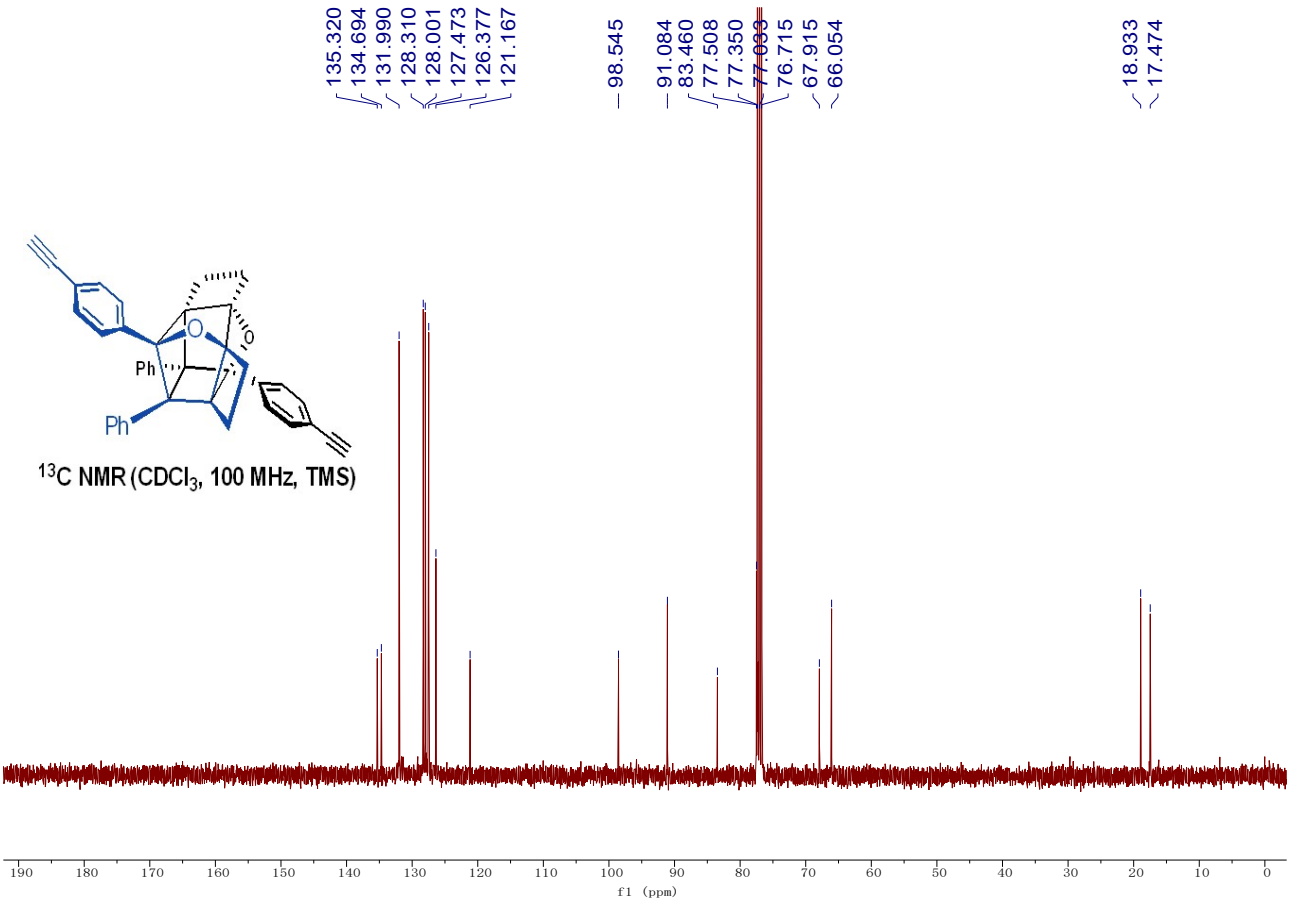


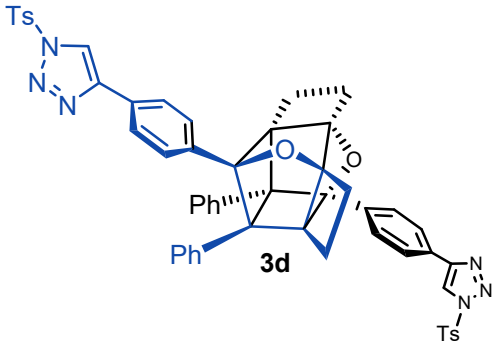
3c

Product 3c, the title compound was achieved as a white solid, MP = 217-219 °C, 30.0 mg, 61% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 4H), 7.35-7.33 (m, 4H), 7.18-7.12 (m, 6H), 7.01-6.98 (m, 4H), 3.05 (s, 2H), 2.53-2.42 (m, 4H), 2.19 (t, *J* = 9.6 Hz, 1H), 2.16 (t, *J* = 9.6 Hz, 1H), 1.74 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.73 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.58 (H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 134.7, 132.0, 128.3, 128.0, 127.5, 126.4, 121.2, 98.5, 91.1, 83.5, 77.5, 67.9, 66.1, 18.9, 17.5 (each carbon signal represents two C atoms, two carbon signals were overlapped). IR (Acetone) ν 2988, 2901, 1713, 1636, 1407, 1394, 1252, 1229, 1175, 1066, 1056, 892, 829, 705 cm^{-1}. HRMS (ESI) calcd for $[C_{40}H_{29}O_2]^+$: 541.2162, found: 541.2161.



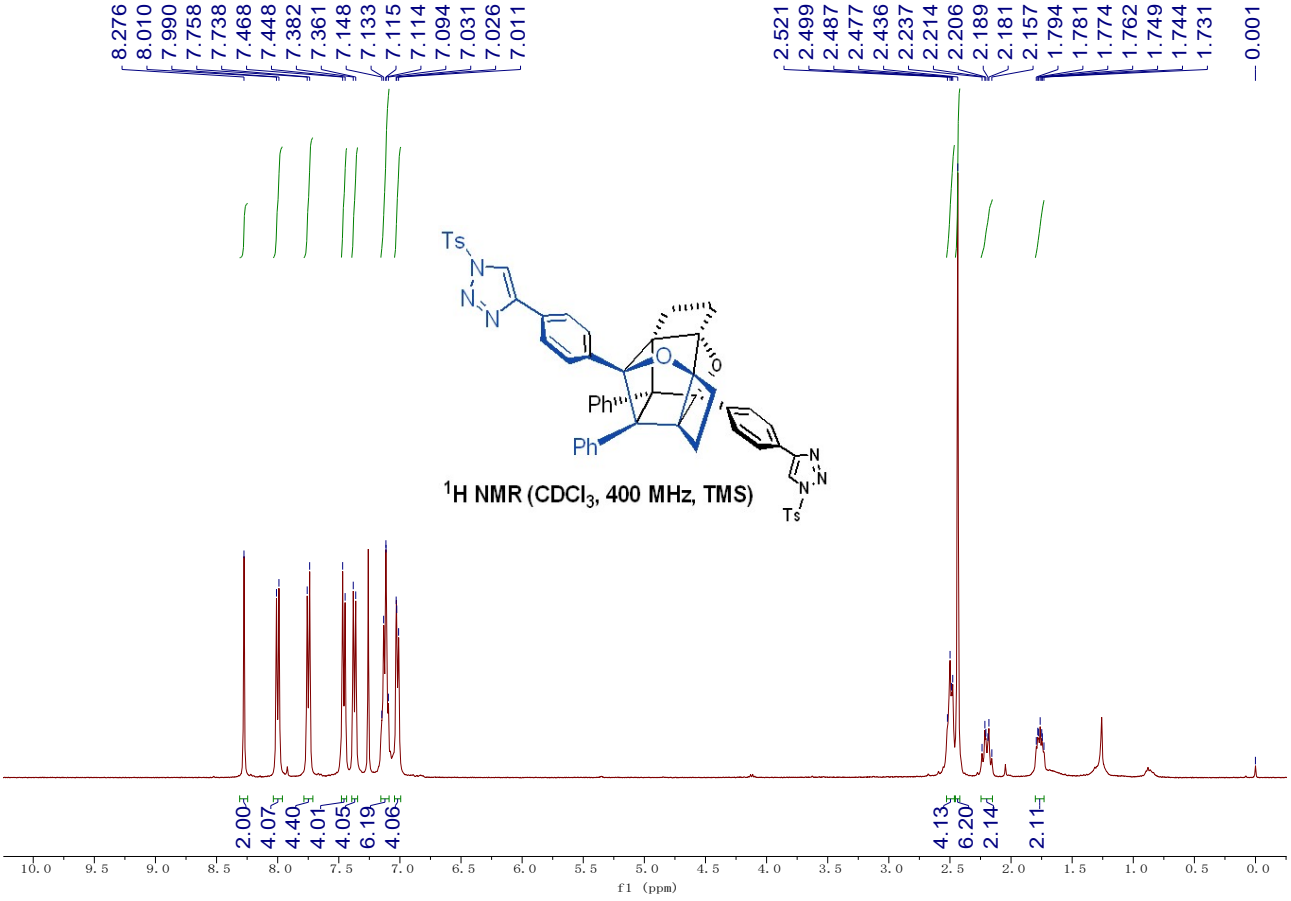
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

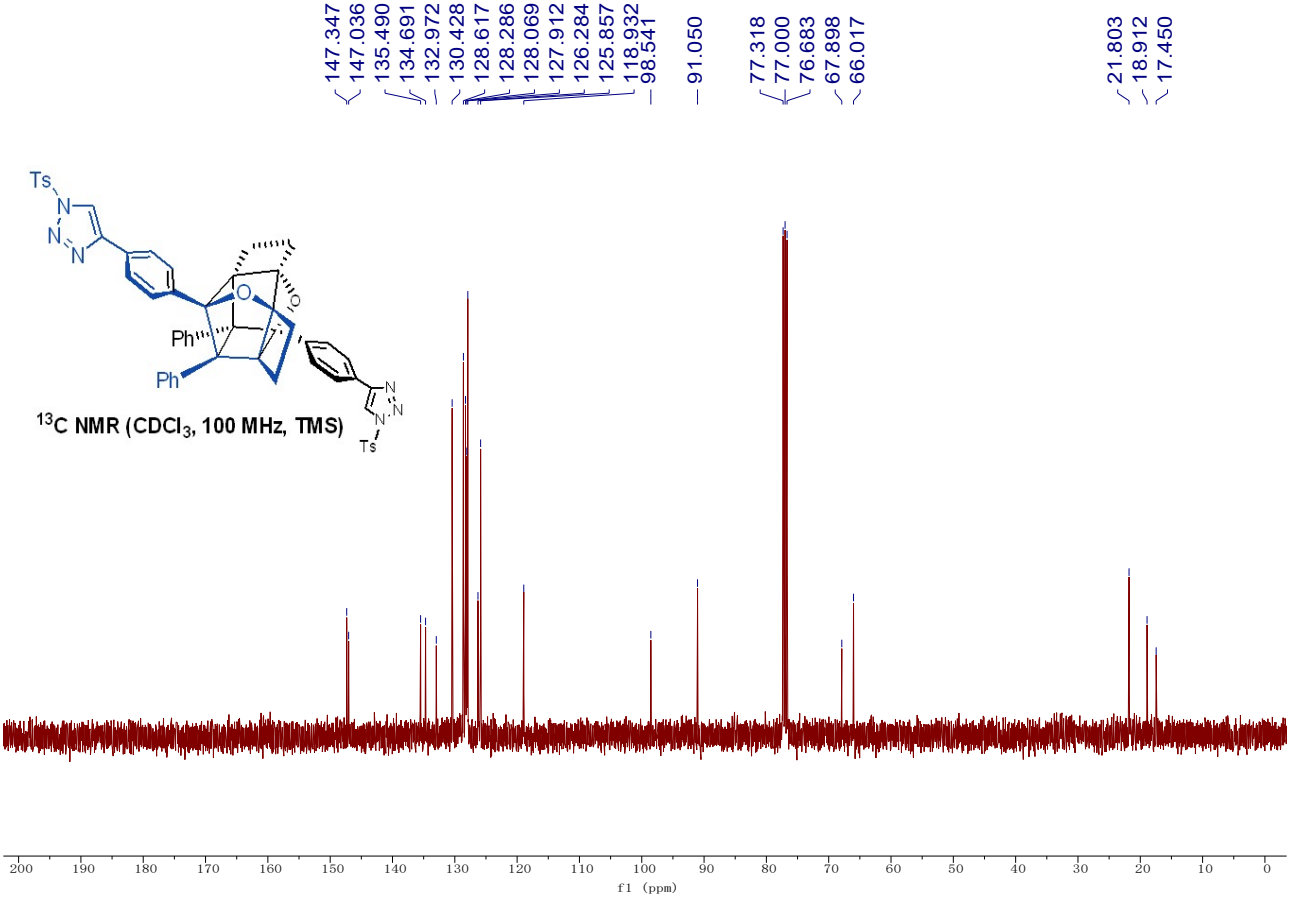




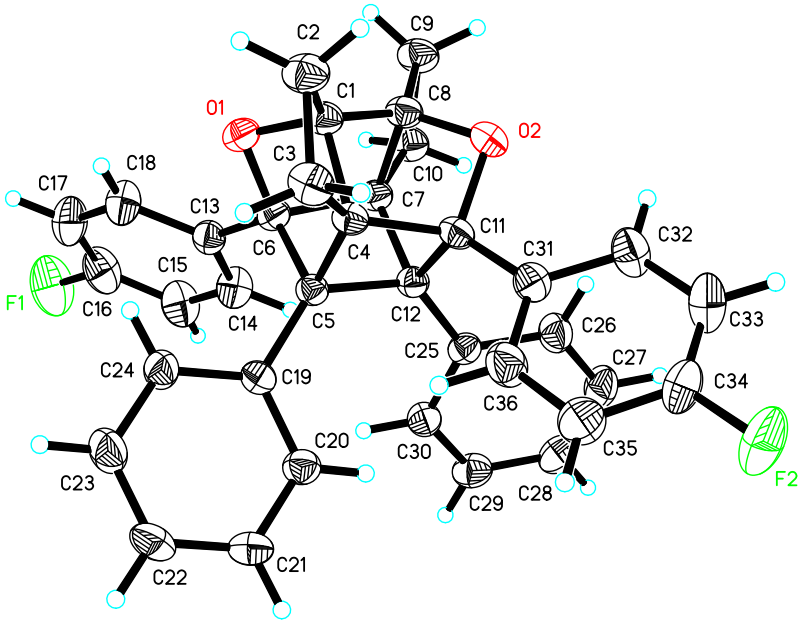
Product 3d, the title compound was achieved as a white solid, MP = 217-219 °C, 30.0 mg, 61% yield. R_f = 0.33 (Petroleum Ether:Ethyl Acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 2H), 8.00 (d, *J* = 8.0 Hz, 4H), 7.75 (d, *J* = 8.0 Hz, 4H), 7.46 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.15-7.07 (m, 6H), 7.03-7.01 (m, 4H), 2.52-2.48 (m, 4H), 2.44 (s, 6H), 2.20 (t, *J* = 9.6 Hz, 1H), 2.18 (t, *J* = 9.6 Hz, 1H), 1.77 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.76 (dd, *J* = 12.8, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 147.0, 135.5, 134.7, 133.0, 130.4, 128.6, 128.3, 128.1, 127.9, 126.3, 125.9, 118.9, 98.5, 91.1, 67.9, 66.0, 21.8, 18.9, 17.5 (each carbon signal represents two C atoms, two carbon signals were overlapped). IR (Acetone) ν 2969, 2901, 1714, 1595, 1446, 1394, 1250, 1222, 1196, 1176, 1103, 1066, 987, 892, 812 cm^{-1}. HRMS (ESI) calcd for $[C_{54}H_{43}N_6O_6S_2]^+$:

935.2680, found: 935.2690.





(F) X-ray of Product 2a



The crystal data of **2a** have been deposited in CCDC with number 2071563. Empirical Formula: $C_{36}H_{26}F_2O_2$; Formula Weight: 528.57; Crystal Color, Habit: colorless, Crystal Dimensions: 0.130 x 0.100 x 0.060 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 16.236(6) Å, b = 17.183(5) Å, c = 19.118(7) Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 5334(3) $Å^3$; Space group: P b c a; Z = 8; D_{calc} = 1.316 g/cm^3; F_{000} = 2208; Final R indices [I>2sigma(I)] R1 = 0.0559, wR2 = 0.1056.

(G) Computational Details

All quantum mechanical calculations have been performed with Gaussian 09 (**ref. 1**). The geometries of compounds have been optimized at B3LYP/6-31G(d) level. The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima on the respective potential energy surfaces. The conformational space of flexible systems has first been searched manually and checked by xtb 6.0 program (**ref.2**). Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The thermochemical corrections have been combined with single-point energies calculated at the SMD/B3LYP/6-311+G(d,p) // B3LYP/6-31G(d) level to yield free energy G_{298} at 298.15 K.

Table S2. The total energies, enthalpies and free energies of all species in gas phase.

	E_{tot}	H_{298}	G_{298}
reactant complex	-1538.995011	-1538.428268	-1538.531614
TS*exo*	-1538.956909	-1538.393042	-1538.486445
TS*endo*	-1538.962054	-1538.397832	-1538.490694
INT*exo*	-1539.004749	-1538.437726	-1538.528524
INT*endo*	-1539.011339	-1538.443958	-1538.535516

Table S2. The total energies, enthalpies and free energies of all species in MeCN.

	E_{tot}	H_{298}	G_{298}
reactant complex	-1539.407979	-1538.841236	-1538.944582
TS*exo*	-1539.369889	-1538.806022	-1538.899425
TS*endo*	-1539.371659	-1538.807437	-1538.900299
INT*exo*	-1539.418301	-1538.851278	-1538.942076
INT*endo*	-1539.420850	-1538.853469	-1538.945027

Archive Entries

Reactant complex

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[X(C36H28O2)]\\@

INT*exo*

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INT$_{endo}$

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Ref.1: Gaussian09, revision D. 01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheese-man, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, . L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. MontgomeryJr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin,V. N. Staroverov, R. Kobayashi, J. Nor-mand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J.Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,A. J. Austin,R. Cammi,C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A.Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D.Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz,J.Cioslowski,D. J. Fox, Gaussian, Inc. Wallingford, CT 2009.

Ref.2: Grimme, xtb 6.0; Mulliken Center for Theoretical Chemistry, University of Bonn, 2019; available upon request via e-mail to xtb@thch.uni-bonn.de.