Supporting Information

For

Synthesis of 3,4,5-trisubstituted phenols via Rh(III)-catalyzed C-H activation assisted by phosphoniums

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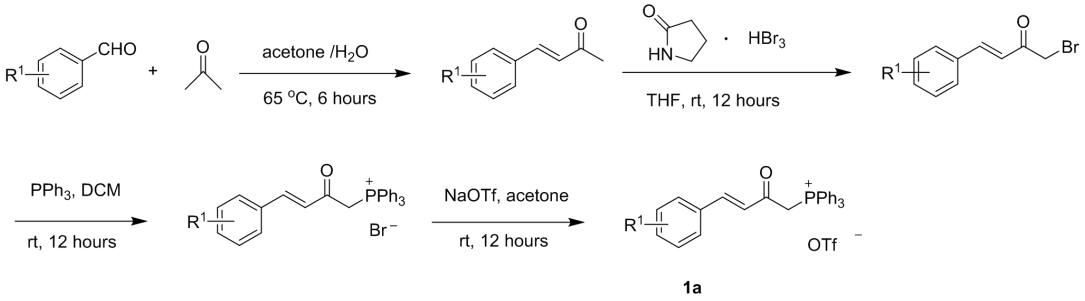
1. General information

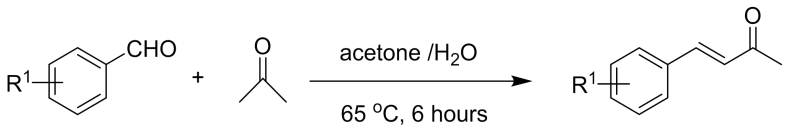
All reagents and solvents used in this work were obtained from commercial sources and were used without further purification. Thin-layer chromatography (TLC) was performed on silica gel GF254 (0.25 mm thickness) plates and visualized under UV light. Organic solutions were concentrated under reduced pressure at 40 °C (water bath temperature) using a Büchi rotary evaporator, unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance spectrometers operating for ^1H NMR at 400 MHz or 600 MHz, for ^{13}C NMR at 100 MHz or 150 MHz. Chemical shifts are expressed in ppm and *J* values are given in Hz. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument GCT Premier, which is produced by WATERS company, and the collision energy is 70eV. Infrared spectra were recorded with a Bruker ATRFTIR spectrometer. The single crystal was formed in n-hexane/dichloromethane and the data were recorded on Bruker smart apex II.

2. General Procedure for the synthesis of Polysubstituted phenol derivatives

2.1 General Procedure for the synthesis of ((trifluoromethyl) sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt.[1-3]



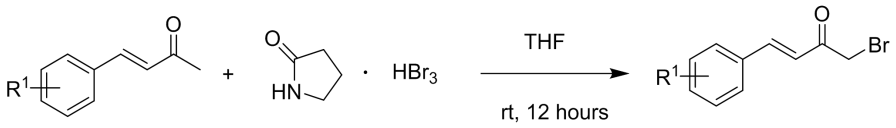
（I）



Suspend benzaldehyde (36 mmol) in a mixture of acetone/water (5 mL/5 mL). Add a 1% aqueous solution of sodium hydroxide (10 mL) slowly to the reaction mixture. Heat the reaction mixture to 65 °C. Stir the reaction mixture until no benzaldehyde is detected by TLC. Cool the

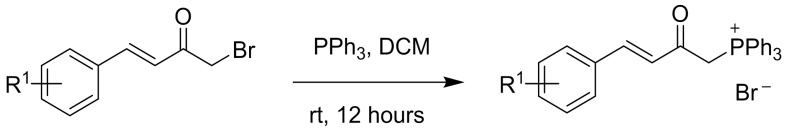
reaction mixture to ambient temperature. Add water (20 mL) and toluene (20 mL) to the flask. Separate the organic phase. Wash the organic phase with brine. Dry the combined organic layer with $MgSO_4$. Concentrate the combined organic layer to dryness. Purify the residue by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:5, v/v) to obtain the pure 4-phenylbut-3-en-2-one.

(II)



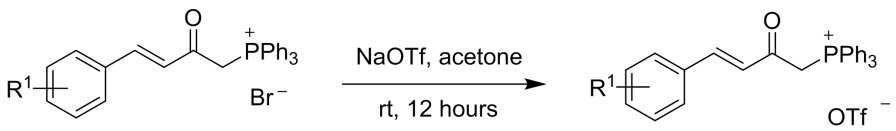
To a solution of the pure -4-phenylbut-3-en-2-one (4.4 g, 30 mmol) in dry THF (80 mL) at room temperature under nitrogen was slowly added a solution of the pyrrolidone hydrotribromide (10.75 g, 33 mmol) in dry THF (120 mL) in 1 hour. The mixture was stirred at room temperature for 12 hours. After completion of the reaction, excess pyrrolidone hydrotribromide was removed by filtration. The filtrate was concentrated to dryness. The resulting residue was dissolved in Et_2O, washed with brine, and dried (Na_2SO_4). Removal of the solvents afforded crude product, which was purified (silica gel, ethyl acetate/ petroleum ether = 1:30, v/v) to give the pure 1-bromo-4-phenylbut-3-en-2-one.

(III)



A solution of bromomethyl ketone derivative (3.61 g, 16 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 20 min to a solution of the triphenylphosphine (8.39 g, 32 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 12 hours. the mixture was concentrated under reduced pressure. The resulting precipitate was washed with Et_2O to obtain [2-oxo-4-phenyl-3-butenyl] triphenylphosphonium bromide.

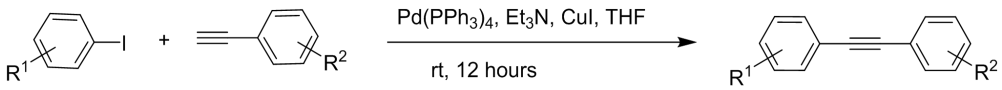
(IV)



1

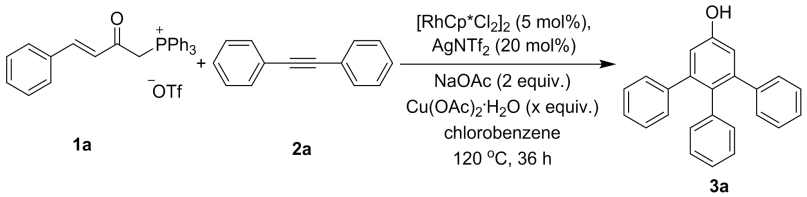
To a solution of the pure [2-oxo-4-phenyl-3-butenyl] triphenylphosphonium bromide. in acetone (30 mL) at room temperature under nitrogen was added a solution of sodium trifluoromethanesulfonate (11.01 g, 64 mmol) in acetone (20 mL) The mixture was stirred at room temperature for 12 hours. After completion of the reaction, the mixture was filtered and the filtrate was concentrated at reduced pressure. The residue was purified by flash column chromatography (silica gel, ethyl acetate/dichloromethane = 1:3, v/v) to obtain the pure ((trifluoromethyl) sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt.

2.2 General Procedure for the Synthesis of 1,2-diphenylethyne:[4]



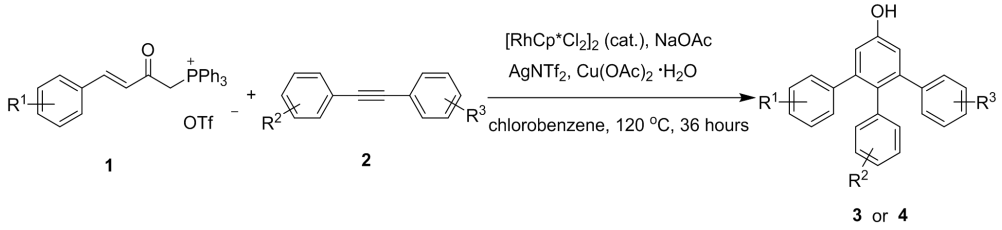
Add iodobenzene (6.0 mmol), ethynylbenzene (6.6 mmol), and Et_3N (8.0 mL, 60 mmol) to a vigorously stirred mixture of CuI (23 mg, 0.12 mmol) and Pd (PPh_3)$_4$ (70 mg, 0.060 mmol) in THF (1.5 mL). Keep for 12 hours and filter the reaction mixture through celite. Rinse with EtOAc (40 mL) and concentrate under reduced pressure. Dissolve the residue in EtOAc (40 mL) and wash with saturated aqueous NH_4Cl (40 mL×3). Dry the organic layer over $MgSO_4$. Filter through a glass frit and concentrate under reduced pressure. Purify the residue by column chromatography (ethyl acetate/petroleum ether = 1:20, v/v) to obtain the pure 1,2-diphenylethyne.

2.3 Optimize the amount of $Cu(OAc)_2{\cdot}H_2O$



The amount of $Cu(OAc)_2{\cdot}H_2O$ (equiv.)	0	0.25	0.5	1.0	2.0
Yield (%)	71	72	77	77	78

2.4 General procedure for the synthesis of compound 3 and 4:



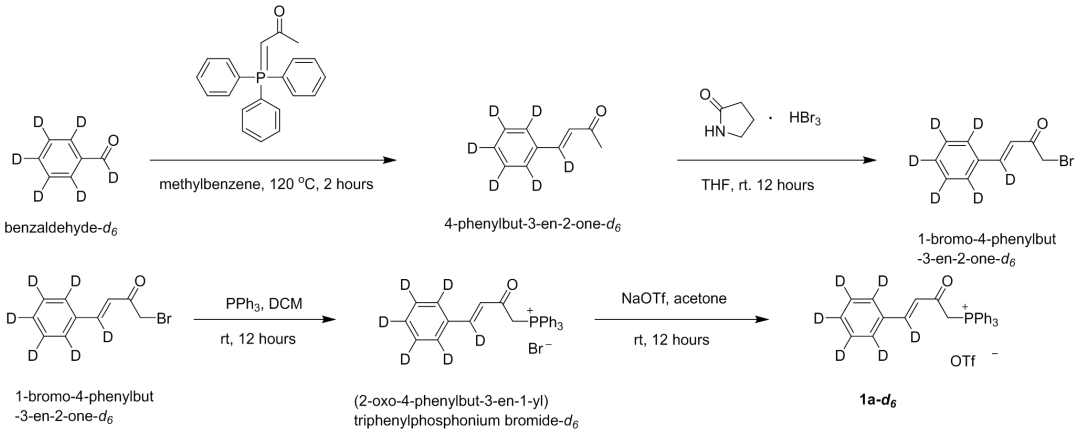
To a 25 mL sealed tube containing a magnetic stir bar, were added compound **1** (0.2 mmol), compound **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%), NaOAc (32.8 mg, 0.4 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol), $Cu(OAc)_2•H_2O$ (20.0 mg, 0.1 mmol), chlorobenzene (2.0 mL). The tube was sealed under nitrogen and heated to 120 °C with stirring for 36 hours. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of Celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to afford the corresponding products **3** or **4**.

3.Mechanistic studies

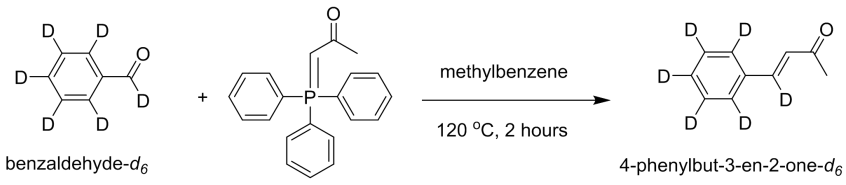
3.1 Intermolecular isotope kinetic experiment:

3.1.1 Intermolecular isotope kinetic experiment of 1a and 1a-d_6

Procedure for synthesis of ((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt -d_6 (1a-d_6):[6]



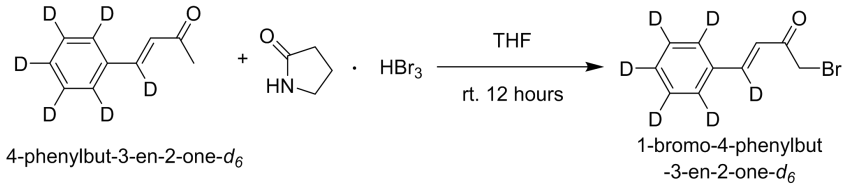
(I)



Equip the 100 mL round bottom flask with a stir bar. Dry the condenser by flame under vacuum and backfill with argon three times. Add benzaldehyde-d_6 (2.2 g, 20 mmol) follow by the addition of 1- (triphenylphosphoranylidene) -2-propanone (7.6 g, 24mmol) and toluene (20 ml). Heat the

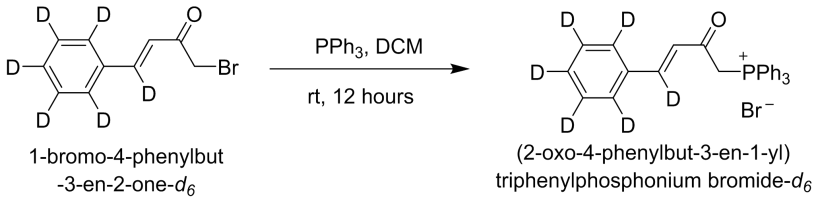
reaction mixture at reflux for two hours. Purify the Product using silica gel column chromatography with proper eluent [5].

(II)



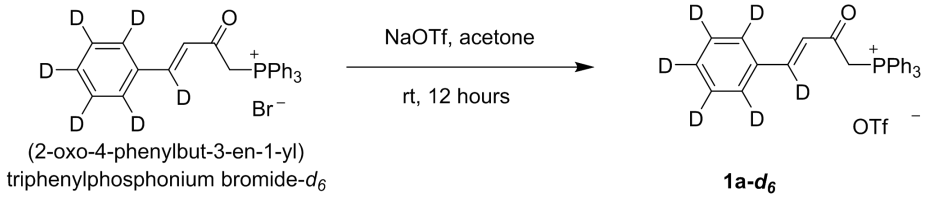
To a solution of the pure 4-phenylbut-3-en-2-one- d_6 (457 mg, 3 mmol) in dry THF (20 mL) at room temperature under nitrogen was slowly added a solution of the pyrrolidone hydrotribromide (1.1 g, 3.3 mmol) in dry THF (20 mL) in 1 hour. The mixture was stirred at room temperature for 12 hours. After completion of the reaction, excess pyrrolidone hydrotribromide was removed by filtration. The filtrate was concentrated to dryness. The resulting residue was dissolved in Et_2O, washed with brine, and dried (Na_2SO_4). Removal of the solvents afforded crude product, which was purified (silica gel, ethyl acetate/petroleum ether = 1:30, v/v) to give the 1-bromo-4-phenylbut-3-en-2-one-d_6.

(III)



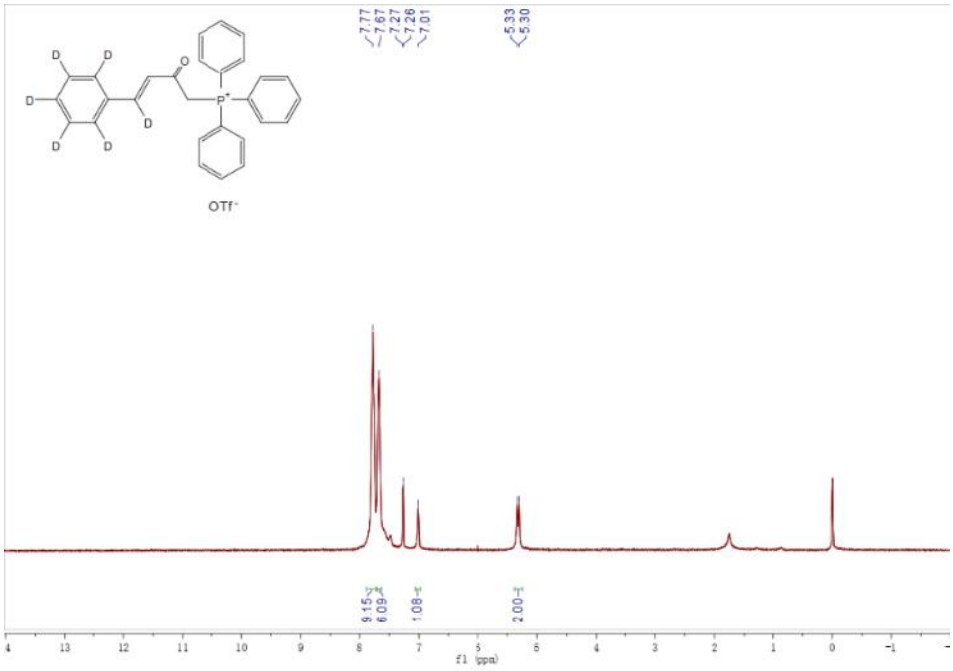
Add 1-bromo-4-phenylbut-3-en-2-one-d_6 derivative (361 mg, 1.56 mmol) to a refluxed solution of the triphenylphosphine (818 mg, 3.12 mmol) in DCM (20 mL) under nitrogen slowly. Reflux the reaction mixture for 12 hours. Cool the mixture to room temperature. Concentrate the mixture at reduced pressure and wash with Et_2O to obtain [2-oxo-4-phenyl-3-butenyl] triphenylphosphonium bromide-d_6.

(IV)



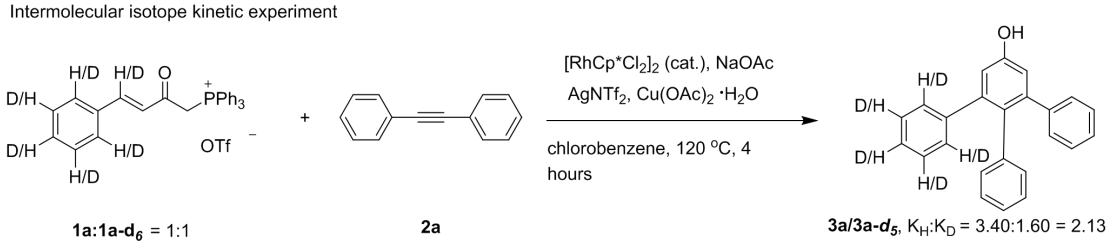
To a solution of the pure [2-oxo-4-phenyl-butenyl] triphenylphosphonium bromide- d_6 in acetone (20 mL) at room temperature under nitrogen was added a solution of sodium

trifluoromethanesulfonate (1.07 g, 6.24 mmol) in acetone (20 mL) The mixture was stirred at room temperature for 12 hours. After completion of the reaction, the mixture was filtered and the filtrate was concentrated at reduced pressure. The crude material was purified by flash column chromatography to obtain the pure compound **1a-*d*$_6$**.



3.1.2 The investigation of ((trifluoromethyl) sulfonyl)-l1-oxidane, (*E*)-(2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt (1a) and ((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt-*d*$_6$ (1a-*d*$_6$) with 2a:

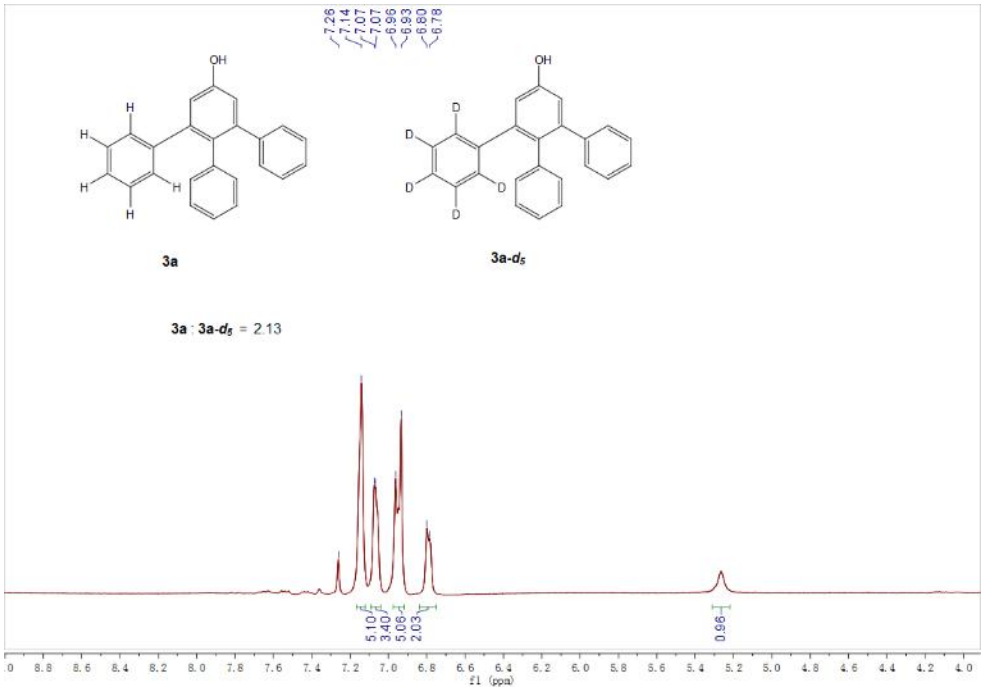
Intermolecular isotope kinetic experiment



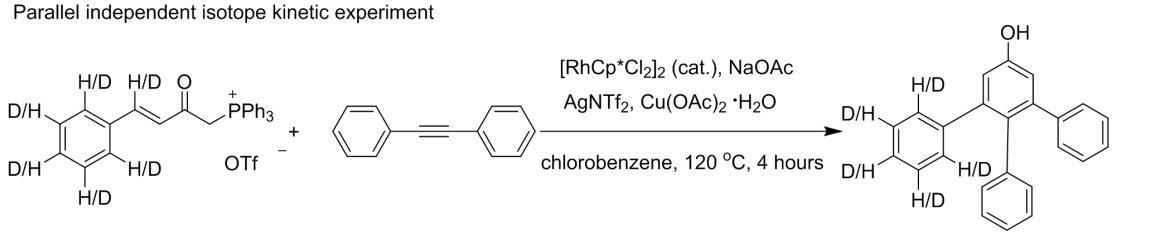
1a:1a-d$_6$ = 1:1 **2a** **3a/3a-*d*$_5$**, K_H:K_D = 3.40:1.60 = 2.13

To a 25 mL sealed tube containing a magnetic stir bar, were added **1a** (0.1 mmol) and **1a-*d*$_6$** (0.1 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%), NaOAc (32.8 mg, 0.4 mmol), $AgNTf_2$ (15.5 mg, 0.04 mmol), $Cu(OAc)_2$•H_2O (20 mg), chlorobenzene (2.0 mL). The tube was sealed under nitrogen and heated to 120 °C with stirring for 4 hours. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of Celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined

organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to afford the desired mixture of **3a** and **3a-*d*$_5$** products. The ratio was determined to be **3a**/**3a-*d*$_5$** = 3.40:1.60 = 2.13 on the basis of ^{1}H NMR analysis.



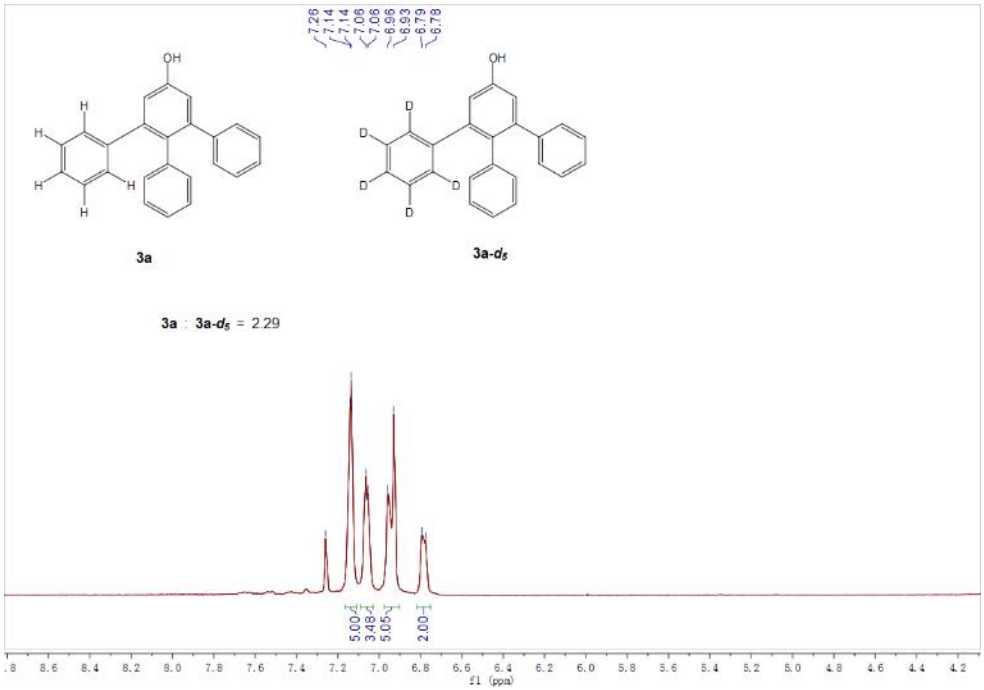
Parallel independent isotope kinetic experiment



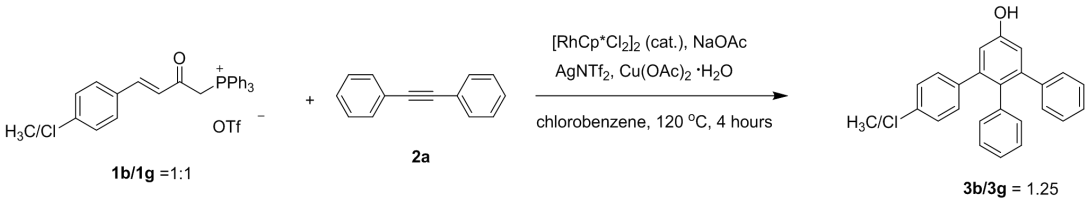
1a:1a-d$_6$ = 1:1 **2a** **3a/3a-*d*$_5$**, K_H:K_D = 3.48:1.52 = 2.29

Two pressure tubes were separately charged with ((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt **1a** (0.1 mmol) and **1a-*d*$_6$** (0.1 mmol), and to each tube was added **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg), NaOAc (16.4 mg, 0.2 mmol), $AgNTf_2$ (7.75 mg, 0.02 mmol), $Cu(OAc)_2•H_2O$ (10 mg), chlorobenzene (2.0 mL). The two reaction mixtures were sealed under nitrogen and heated to 120 °C with stirring for 4 hours. Then the reaction mixture was cooled to room temperature and the two mixtures were combined, diluted with ethyl acetate. The reaction mixture was filtered through a plug of Celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum

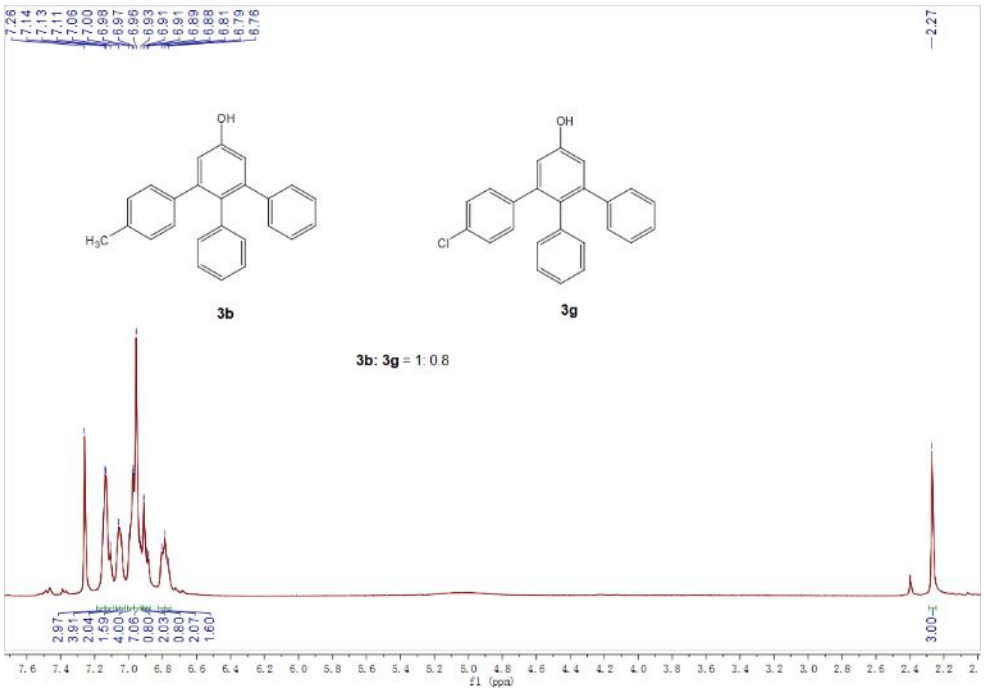
and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to afford the desired mixture of **3a** and **3a-*d*$_5$** products. The ratio was determined to be **3a**/**3a-*d*$_5$** = 3.48:1.52 = 2.29 on the basis of ^{1}H NMR analysis.

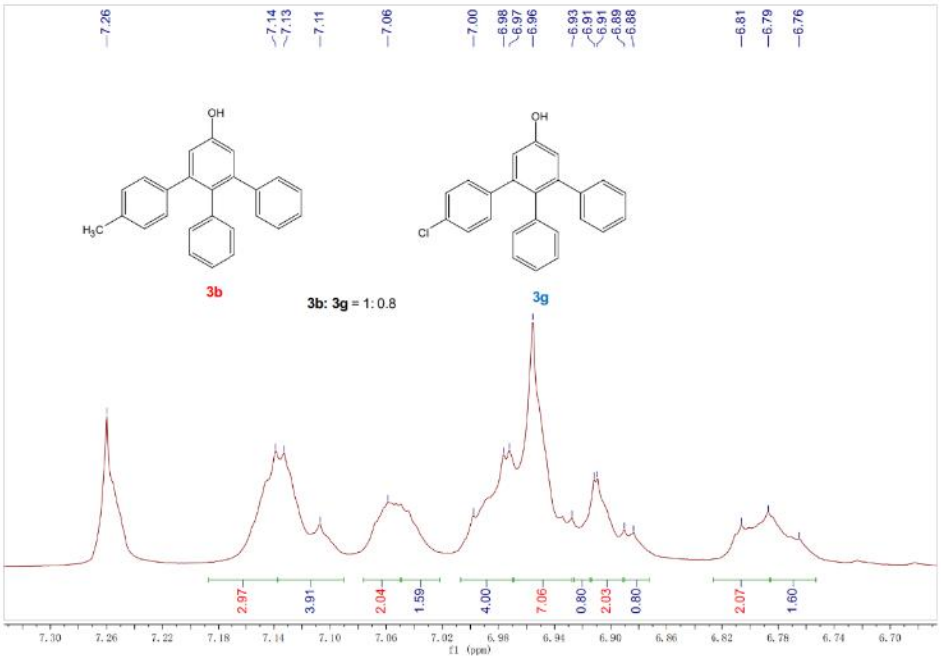


3.2 Competition reactions:



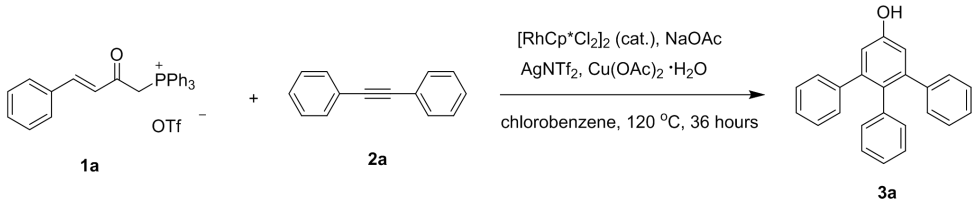
To a 25 mL sealed tube containing a magnetic stir bar, were added **1b** (42.1 mg, 0.1 mmol) and **1g** (44.2 mg, 0.1 mmol), **2a** (71.3 mg, 0. 4mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%), $AgNTf_2$ (15.5 mg,0.04 mol), $Cu(OAc)_2•H_2O$ (20 mg, 0.1mmol), NaOAc (32.8 mg, 0.4 mmol), chlorobenzene (2.0 mL). The tube was sealed under nitrogen and heated to 120 °C with stirring for 4 hours. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:15, v/v) to afford the corresponding products to afford the desired mixture of **3b** and **3g** products. The ratio was determined to be **3b**/**3g** = 1.25 on the basis of ^{1}H NMR analysis.





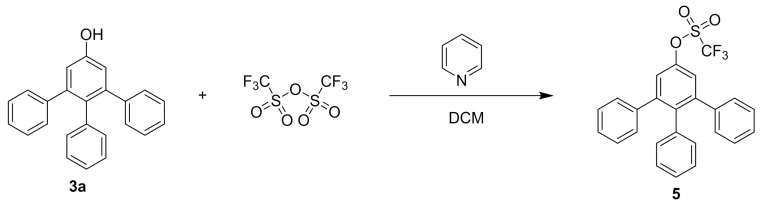
4. Procedure for the synthesis of the product of derivatization reactions of the trisubstituted phenol. [6]

(1) Gram-scale synthesis:



To a 250 mL sealed tube containing a magnetic stir bar, were added ((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt **1a** (1.11g, 2 mmol), 1,2-diphenylethyne **2a** (713 mg, 4 mmol), $[Cp^*RhCl_2]_2$ (62 mg, 5 mol%), NaOAc (328 mg, 4 mmol), $AgNTf_2$ (155 mg, 0.4 mmol), $Cu(OAc)_2•H_2O$ (200 mg, 1 mmol), chlorobenzene (20 mL). The tube was sealed under nitrogen and heated to 120 °C with stirring for 36 hours. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of Celite and the residue was washed with ethyl acetate. The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to afford the corresponding products **3a** (458 mg, 71%).

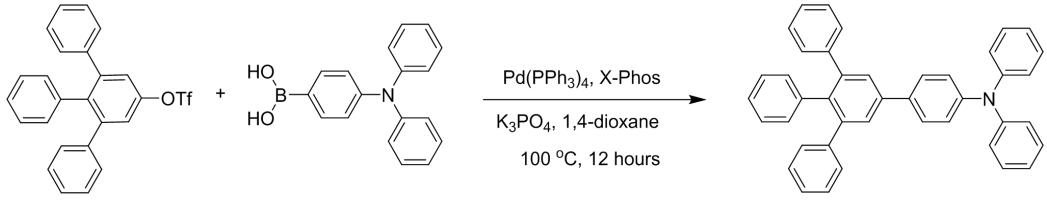
（II）



3a 5

Charge a flame-dried flask with **3a** (160 mg, 0.5 mmol), CH_2Cl_2 (10 mL) and pyridine (158.2mg, 2 mmol) successively at 0°C.Add a solution of triflic anhydride (423.2 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) dropwise to the mixture. Stir the reaction mixture at room temperature for 12 hours. Quench the reaction mixture with the addition of ethyl acetate (15 mL) and aqueous HCl (10%, 5 mL). Wash the reaction mixture successively with aqueous saturated $NaHCO_3$(10 mL) and brine (10 mL). Dry the reaction mixture over $MgSO_4$. The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to afford the desired product **5** (202 mg, 89% yield).

(III)

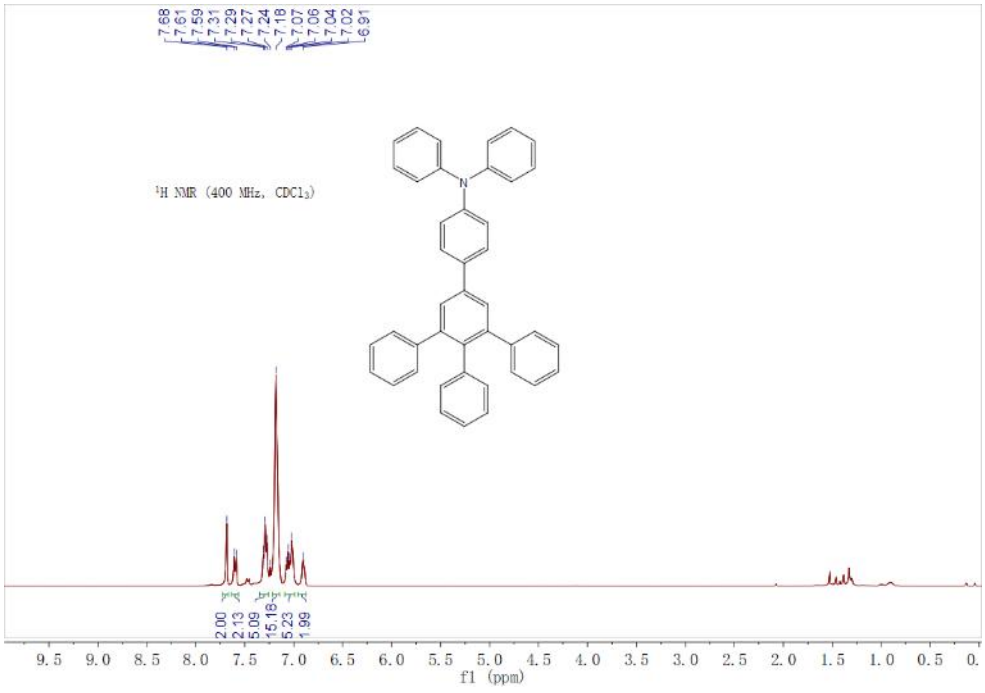


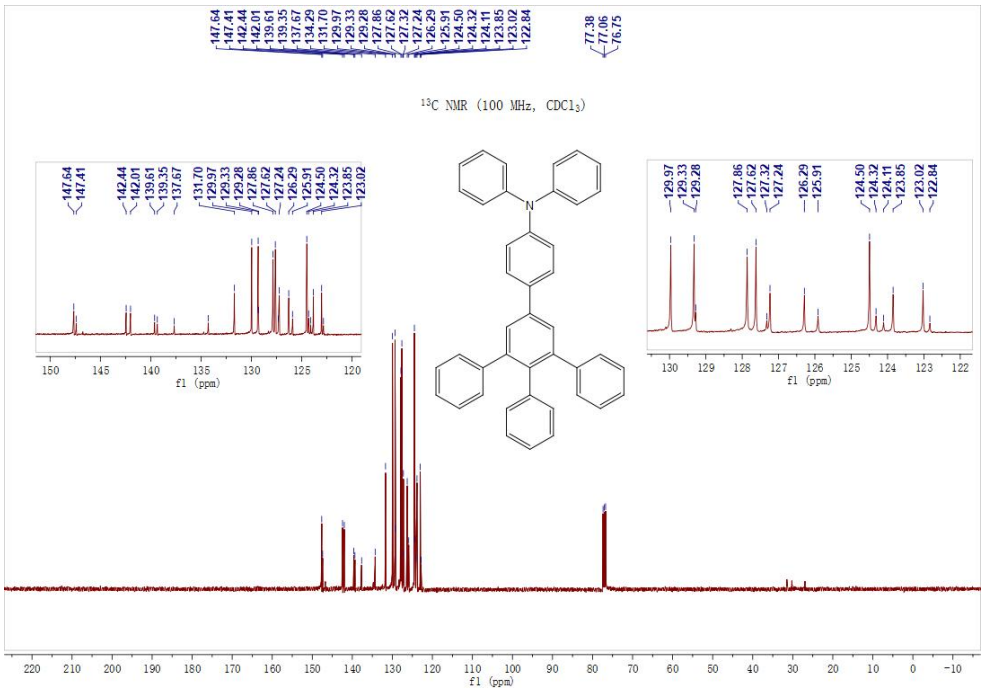
5 6

To a 25 mL sealed tube containing a magnetic stir bar, were added compound **5** (45.4 mg, 0.1 mmol, 1 equiv.), 4-(Diphenylamino) phenylboronic acid (34.7 mg, 0.12 mmol, 1.2 equiv.),

$Pd(PPh_3)_4$ (5.8 mg, 5 mol%), X-Phos (4.8 mg, 10 mol%), K_3PO_4(42.5 mg, 0.2 mmol), 1,4-dioxane (2 mL). The tube was sealed under nitrogen and heated to 100°C with stirring for 12 hours. Then the reaction mixture was cooled to room temperature and washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate petroleum ether = 1:10, v/v) to afford the corresponding product **6** (53.9 mg, 98% yield).

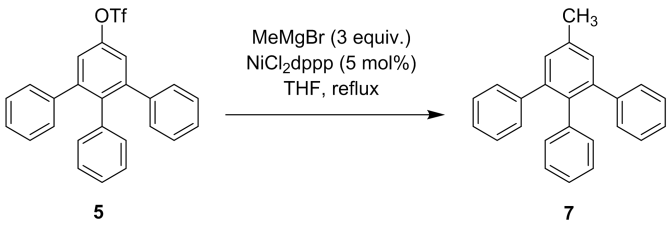
The ^{1}H and ^{13}C NMR spectra of compound 6





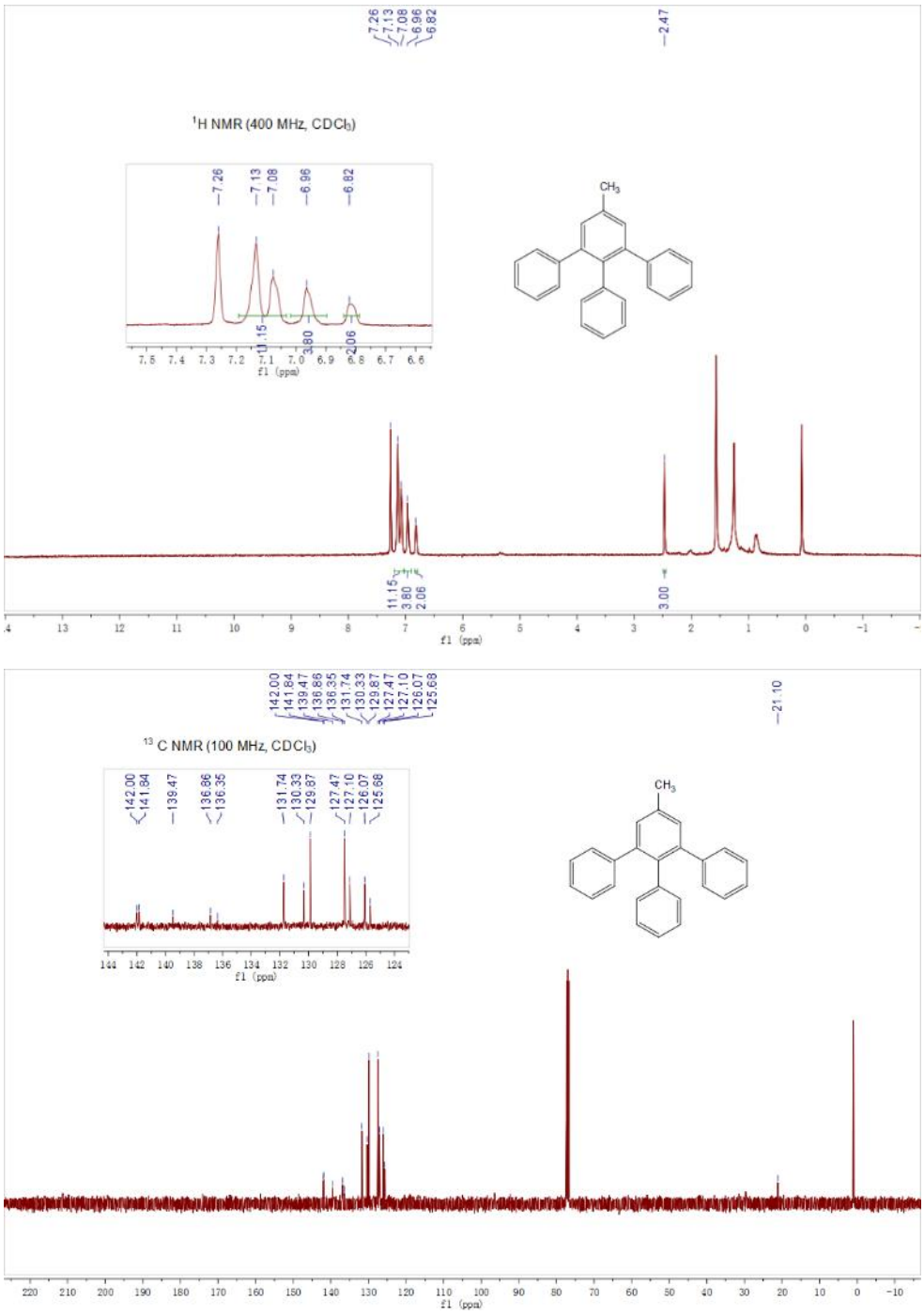
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 7.6 Hz, 5H), 7.18 (s, 15H), 7.05 (dd, J = 14.4, 7.2 Hz, 5H), 6.91 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.64, 147.41, 142.44, 142.01, 139.61, 139.35, 137.67, 134.29, 131.70, 129.97, 129.33, 129.28, 127.86, 127.62, 127.32, 127.24, 126.29, 125.91, 124.50, 124.32, 124.11, 123.85, 123.02, 122.84. calcd for $[M+H]^+$ $C_{42}H_{32}N^+$ 550.2529, found 550.2532.

(IV)



An oven-dried two-neck flask equipped with a magnetic stir bar was charged with compound **5** (45.5 mg, 0.1 mmol) and $NiCl_2$dppp (2.7 mg, 5 mol%), then purged with argon three times. Anhydrous THF (1mL) was followed by MeMgBr (0.3 mL, 1 mol/L in THF, 0.6 mmol). The reaction was heated to reflux for 2 hours. Water was added and the mixture was extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and the filtrated was concentrated under vacuum to obtain the residue, which was purified by silicac gel column chromatography eluting with PE:EA = 10:1 to give the product **7** (16 mg, 50% yield).

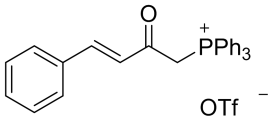
The ^{1}H and ^{13}C NMR spectra of compound 7



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 22.6 Hz, 11H), 6.96 (s, 4H), 6.82 (s, 2H), 2.47 (s, 3H).

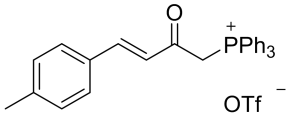
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.00, 141.84, 139.47, 136.86, 136.35, 131.74, 130.33, 129.87, 127.47, 127.10, 126.07, 125.68, 21.10. calcd for $[M+Na]^+$ $C_{25}H_{20}Na^+$ 343.1457, found 343.1473.

5. The ^{1}H and ^{13}C NMR spectra of raw material



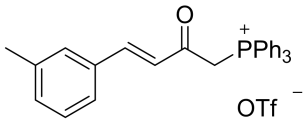
(1a)

((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-phenylbut-3-en-1-yl) triphenylphosphonium salt (1a). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (dd, J = 24.2, 11.1 Hz, 8H), 7.77 (d, J = 13.1 Hz, 10H), 7.50 (s, 3H), 6.96 (d, J = 16.4 Hz, 1H), 5.82 (d, J = 13.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.3 (d, $J_{C\text{-}P}$ = 6 Hz), 147.6, 135.3, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 132.0, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 129.7, 129.4, 126.3 (d, $J_{C\text{-}P}$ = 7 Hz), 123.8, 121.2 (d, $J_{C\text{-}F}$ = 321 Hz), 119.5 (d, $J_{C\text{-}P}$ = 88 Hz), 35.8 (d, $J_{C\text{-}P}$ = 59 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.2. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.12.



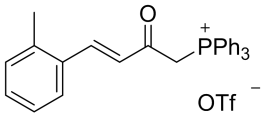
(1b)

((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-(p-tolyl) but-3-en-1-yl) triphenylphosphonium salt (1b). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 – 7.68 (m, 16H), 7.64 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 6.90 (d, J = 16.0 Hz, 1H), 5.80 (d, J = 13.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.1 (d, $J_{C\text{-}P}$ = 6 Hz), 147.7, 142.3, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 131.4, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 130.3, 129.4, 125.3 (d, $J_{C\text{-}P}$ = 6 Hz), 121.1 (d, $J_{C\text{-}F}$ = 321 Hz), 119.5 (d, $J_{C\text{-}P}$ = 88 Hz), 40.6, 40.4, 40.2, 39.9, 39.7, 39.5, 39.3, 35.7 (d, $J_{C\text{-}P}$ = 60 Hz), 21.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.13.



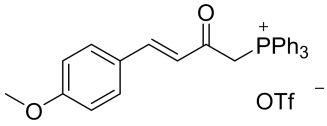
(1c)

((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-(m-tolyl) but-3-en-1-yl) triphenylphosphonium salt (1c). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (dd, J = 15.8, 12.3, 4.0 Hz, 16H), 7.56 (s, 2H), 7.35 (d, J = 16.6 Hz, 2H), 6.93 (d, J = 16.6 Hz, 1H), 5.80 (d, J = 13.5 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2 (d, $J_{C\text{-}P}$ = 6 Hz), 147.7, 138.9, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 132.7, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 129.7, 129.5, 126.7, 126.1 (d, $J_{C\text{-}P}$ = 7 Hz), 119.5 (d, $J_{C\text{-}P}$ = 89 Hz), 105.0, 35.7 (d, $J_{C\text{-}P}$ = 57 Hz), 21.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.13.



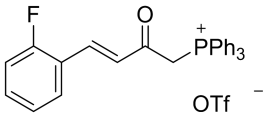
(1d)

((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-(o-tolyl) but-3-en-1-yl) triphenylphosphonium salt (1d). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 16.2 Hz, 1H), 7.91 – 7.72 (m, 16H), 7.38 (d, J = 7.2 Hz, 1H), 7.34 – 7.24 (m, 2H), 6.88 (d, J = 16.1 Hz, 1H), 5.88 (d, J = 13.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2 (d, $J_{C\text{-}P}$ = 6 Hz),144.4, 139.1, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 10 Hz),132.7, 131.7, 131.5, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 127.3, 127.0, 121.1 (d, $J_{C\text{-}F}$ = 321 Hz), 119.5 (d, $J_{C\text{-}P}$ = 88 Hz), 35.9 (d, $J_{C\text{-}P}$ = 60 Hz),19.8. ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.13.



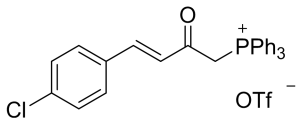
(1e)

((trifluoromethyl)sulfonyl)-l1-oxidane, (4-(4-methoxyphenyl)-2-oxobut-3-en-1-yl) triphenylphosphonium salt (1e). 1H NMR (400 MHz, DMSO-d_6) δ 7.94 – 7.63 (m, 18H), 7.04 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 16.5 Hz, 1H), 5.77 (d, J = 13.4 Hz, 2H), 3.82 (s, 3H). 13C NMR (100 MHz, DMSO-d_6) δ 191.8 (d, $J_{C\text{-}P}$ = 6 Hz),162.5, 147.6, 135.1, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 131.4, 130.4 (d, $J_{C\text{-}P}$ = 12 Hz), 126.7, 123.8 (d, $J_{C\text{-}P}$ = 6 Hz), 121.2 (d, $J_{C\text{-}F}$ = 320 Hz), 119.6 (d, $J_{C\text{-}P}$ = 89 Hz), 115.2, 55.9, 35.7 (d, $J_{C\text{-}P}$ = 60 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.26.



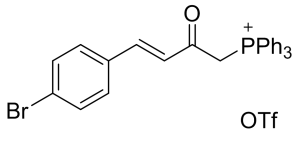
(1f)

((trifluoromethyl)sulfonyl)-l1-oxidane, (4-(2-fluorophenyl)-2-oxobut-3-en-1-yl) triphenylphosphonium salt (1f). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 – 7.74 (m, 17H), 7.57 (d, J = 6.3 Hz, 1H), 7.33 (dd, J = 15.5, 8.1 Hz, 2H), 7.02 (d, J = 16.4 Hz, 1H), 5.89 (d, J = 13.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4 (d, $J_{C\text{-}P}$ = 6 Hz), 161.4 (d, $J_{C\text{-}F}$ = 252 Hz), 139.0, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 130.2, 128.4, 125.8, 121.8 (d, $J_{C\text{-}P}$ = 10 Hz), 121.1 (d, $J_{C\text{-}F}$ = 320 Hz), 119.9 (d, $J_{C\text{-}P}$ = 11 Hz), 119.4 (d, $J_{C\text{-}F}$ = 89 Hz), 116.8 (d, $J_{C\text{-}F}$ = 22 Hz), 35.9 (d, $J_{C\text{-}P}$ = 60 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8, -114.42. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.01.



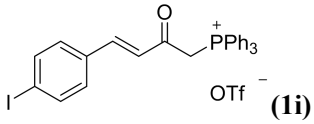
(1g)

((trifluoromethyl)sulfonyl)-l1-oxidane, (4-(4-chlorophenyl)-2-oxobut-3-en-1-yl) triphenylphosphonium salt (1g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 – 7.71 (m, 18H), 7.56 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 16.8 Hz, 1H), 5.81 (d, J = 13.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2 (d, $J_{C\text{-}P}$ = 6 Hz), 146.0, 136.5, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 133.1, 131.0, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 129.7, 126.9 (d, $J_{C\text{-}P}$ = 7 Hz), 119.4 (d, $J_{C\text{-}P}$ = 89 Hz), 35.8 (d, $J_{C\text{-}P}$ = 62 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.06.



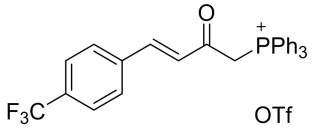
(1h)

(4-(4-bromophenyl)-2-oxobut-3-en-1-yl) triphenylphosphonium (1h). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 – 7.66 (m, 20H), 6.99 (d, J = 15.4 Hz, 1H), 5.80 (d, J = 13.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2 (d, $J_{C\text{-}P}$ = 6 Hz), 146.2, 135.2, 134.1 (d, $J_{C\text{-}P}$ = 10 Hz), 133.4, 132.7, 131.2, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 126.9 (d, $J_{C\text{-}F}$ = 6 Hz), 125.5, 121.1 (d, $J_{C\text{-}F}$ = 320 Hz), 119.4 (d, $J_{C\text{-}P}$ = 88 Hz), 35.9 (d, $J_{C\text{-}P}$ = 60 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.02.



(1i)

((trifluoromethyl)sulfonyl)-l1-oxidane, (4-(4-iodophenyl)-2-oxobut-3-en-1-yl) triphenylphosphonium salt (1i). 1H NMR (400 MHz, DMSO-d_6) δ 8.00 – 7.64 (m, 18H), 7.52 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 16.4 Hz, 1H), 5.83 – 5.75 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2 (d, $J_{C\text{-}P}$ = 6 Hz),146.5, 138.6, 135.3, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz),133.6, 131.1, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz), 126.8 (d, $J_{C\text{-}P}$ = 7 Hz), 121.1 (d, $J_{C\text{-}F}$ = 321 Hz), 119.4 (d, $J_{C\text{-}P}$ = 88 Hz), 99.6, 35.8 (d, $J_{C\text{-}P}$ = 60 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.02.

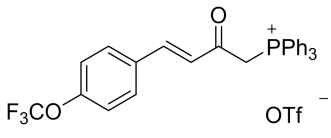


(1j)

((trifluoromethyl)sulfonyl)-l1-oxidane,

(2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)triphenylphosphonium salt (1j). ^{1}H NMR

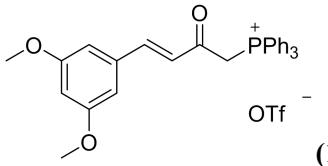
(600 MHz, DMSO-d_6) δ 7.96 (d, J = 6.6 Hz, 2H), 7.88 (d, J = 7.0 Hz, 3H), 7.83 (dd, J = 18.1, 10.3 Hz, 8H), 7.77 (s, 7H), 7.10 (d, J = 16.2 Hz, 1H), 5.84 (d, J = 13.1 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 192.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 145.4, 138.2, 135.3, 134.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.2(q, $J_{C\text{-}F}$ = 31.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 12 Hz), 130.0, 128.7, 126.5 (d, $J_{C\text{-}P}$ = 3 Hz), 124.4 (q, $J_{C\text{-}F}$ = 120 Hz), 121.2 (q, $J_{C\text{-}F}$ = 321 Hz), 119.4 (d, $J_{C\text{-}P}$ = 88.5 Hz), 36.0 (d, $J_{C\text{-}P}$ = 30 Hz). ^{19}F NMR (564 MHz, DMSO-d_6) δ -61.4, -77.8. ^{31}P NMR (181.5 MHz, DMSO-d_6) δ 20.99.



(1k)

((trifluoromethyl)sulfonyl)-l1-oxidane,

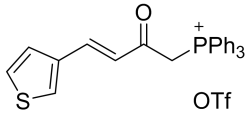
(2-oxo-4-(4-(trifluoromethoxy)phenyl)but-3-en-1-yl)triphenylphosphonium salt (1k). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.96 (d, J = 6.6 Hz, 2H), 7.88 (d, J = 7.0 Hz, 3H), 7.83 (dd, J = 18.1, 10.3 Hz, 8H), 7.77 (s, 7H), 7.10 (d, J = 16.2 Hz, 1H), 5.84 (d, J = 13.1 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 192.3 (d, $J_{C\text{-}P}$ = 6 Hz), 150.6, 145.7, 135.3, 134.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.4, 131.4, 130.5 (d, $J_{C\text{-}P}$ = 12 Hz), 127.3 (d, $J_{C\text{-}P}$ = 6 Hz), 122.0, 121.2 (q, $J_{C\text{-}F}$ = 319.5 Hz), 120.4 (q, $J_{C\text{-}F}$ = 256.5 Hz), 119.5 (d, $J_{C\text{-}P}$ = 87 Hz), 35.9 (d, $J_{C\text{-}P}$ = 60 Hz). ^{19}F NMR (564 MHz, DMSO-d_6) δ -56.7, -77.8. ^{31}P NMR (181.5 MHz, DMSO-d_6) δ 21.11.



(1l)

((trifluoromethyl)sulfonyl)-l1-oxidane,

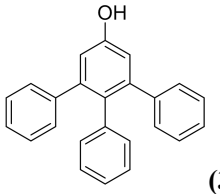
(4-(3,5-dimethoxyphenyl)-2-oxobut-3-en-1-yl)triphenylphosphonium salt (1l). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 – 7.67 (m, 16H), 7.12 – 6.79 (m, 3H), 6.64 (s, 1H), 5.80 (d, J = 13.0 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 192.3 (d, $J_{C\text{-}P}$ = 6 Hz), 161.3, 147.6, 136.1, 135.3, 134.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 127.0 (d, $J_{C\text{-}P}$ = 6 Hz), 121.2 (q, $J_{C\text{-}F}$ = 319.5 Hz), 119.5 (d, $J_{C\text{-}P}$ = 88.5 Hz), 107.1, 104.1, 55.9, 35.8(d, $J_{C\text{-}P}$ = 58.5 Hz). ^{19}F NMR (564 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (181.5 MHz, DMSO-d_6) δ 21.14.



(1m)

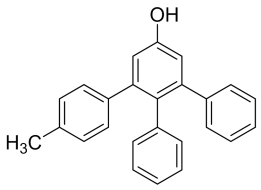
((trifluoromethyl)sulfonyl)-l1-oxidane, (2-oxo-4-(thiophen-3-yl) but-3-en-1-yl) triphenylphosphonium salt (1m). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 15.8 Hz, 1H), 7.90 – 7.72 (m, 16H), 7.65 (s, 1H), 7.23 (s, 1H), 6.63 (d, J = 15.8 Hz, 1H), 5.74 (d, J = 13.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.3 (d, $J_{C\text{-}P}$ = 6 Hz), 160.0, 139.9, 139.0, 135.2, 134.4, 134.1 (d, $J_{C\text{-}P}$ = 11 Hz), 132.6, 130.5 (d, $J_{C\text{-}P}$ = 13 Hz),129.7, 124.3 (d, $J_{C\text{-}P}$ = 8 Hz), 121.1 (d, $J_{C\text{-}F}$ = 320 Hz), 119.5 (d, $J_{C\text{-}P}$ = 88 Hz), 35.7 (d, $J_{C\text{-}P}$ = 59 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -77.8. ^{31}P NMR (121 MHz, DMSO-d_6) δ 21.06.

6. The ^{1}H and ^{13}C NMR spectra of compounds



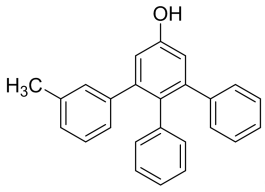
(3a)

6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3a): 49.7 mg, 77% yield. A white solid; mp:184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 6H), 7.11 – 7.02 (m, 4H), 7.02 – 6.87 (m, 5H), 6.79 (d, J = 6.4 Hz, 2H), 4.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.5, 141.6, 139.2, 132.1, 131.9, 129.8, 127.5, 127.1, 126.3, 125.6, 116.3. (CAS:1731-37-9)[7].



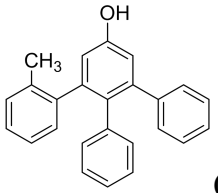
（3b）

4''-methyl-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3b): 54.5 mg, 81% yield. A white solid; mp:181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 2.0 Hz, 3H), 7.10 – 7.04 (m, 2H), 7.00 – 6.96 (m, 7H), 6.92 (s, 2H), 6.83 (s, 2H), 5.24 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.5, 143.4, 141.7, 139.4, 138.7, 135.9, 132.1, 132.0, 129.8, 129.6, 128.3, 127.5, 127.1, 126.3, 125.6, 116.4, 116.2, 21.1 HRMS (EI) calcd for $[M+H]^+$ $C_{25}H_{21}O^+$ 337.1587, found 337.1594.



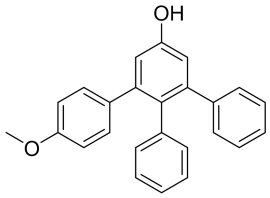
(3c)

3''-methyl-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3c): 23.6 mg, 45% yield. A yellow solid; mp:127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 3H), 7.10 – 7.04 (m, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.98 – 6.93 (m, 4H), 6.92 (d, J = 1.3 Hz, 3H), 6.81 (dd, J = 8.7, 7.0 Hz, 3H), 5.16 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.5, 143.4, 141.7, 141.5, 139.3, 137.1, 132.1, 131.9, 130.6, 129.8, 127.5, 127.3, 127.1, 127.0, 126.9, 126.3, 125.6, 116.3, 116.2, 21.3. HRMS (EI) calcd for $[M+H]^+$ $C_{25}H_{21}O^+$ 337.1587, found 337.1593.



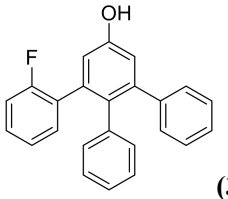
(3d)

2''-methyl-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3d): 11.4 mg, 21% yield. A white solid; mp:137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 3H), 7.11 – 7.05 (m, 3H), 7.04 – 6.98 (m, 3H), 6.94 (s, 1H), 6.89 (s, 3H), 6.77 (s, 3H), 5.12 (s, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 143.3, 143.2, 141.7, 141.2, 139.1, 135.6, 132.6, 132.6, 130.4, 129.8, 129.5, 127.6, 126.8, 126.8, 126.3, 125.5, 124.8, 116.3, 116.1, 20.2. HRMS (EI) calcd for $[M+H]^+$ $C_{25}H_{21}O^+$ 337.1587, found 337.1594.



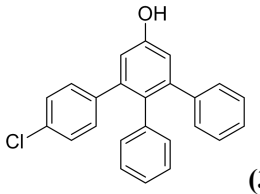
(3e)

4''-methoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3e): 61.3 mg, 87% yield. A yellow solid; mp:120-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 3H), 7.09 – 7.03 (m, 2H), 7.01 – 6.95 (m, 5H), 6.90 (d, J = 1.5 Hz, 2H), 6.80 (d, J = 3.4 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 5.13 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.04, 154.23, 143.46, 143.00, 141.72, 139.36, 134.03, 131.96, 130.81, 129.74, 127.49, 127.16, 126.24, 125.55, 116.29, 116.01, 113.00, 104.99, 55.12. (CAS:1252687-12-9)[7].



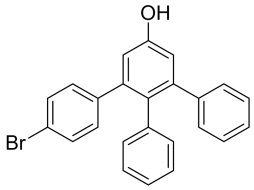
(3f)

2''-fluoro-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3f): 25.9 mg, 38% yield. A yellow solid; mp:141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 4H), 7.09 (s, 2H), 7.03 (d, J = 7.5 Hz, 1H), 6.93 (dd, J = 18.5, 7.2 Hz, 7H), 6.83 (s, 2H), 5.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $J_{C\text{-}F}$= 245), 154.1, 143.3, 141.4, 139.0, 137.3, 133.2, 132.0 (d, $J_{C\text{-}F}$= 4), 131.4, 129.8, 129.2 (d, $J_{C\text{-}F}$= 16), 128.7(d, $J_{C\text{-}F}$= 8), 127.6, 127.0, 126.4, 125.8, 122.3 (d, $J_{C\text{-}F}$= 4), 117.0, 116.5, 115.1 (d, $J_{C\text{-}F}$= 22), ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1. HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{18}FO^+$ 341.1336, found 341.1343.



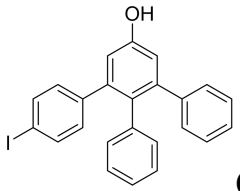
(3g)

4''-chloro-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3g):47.1 mg, 66% yield. A white solid; mp:175-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 4H), 7.11 (s, 1H), 7.09 – 7.02 (m, 2H), 6.99 (d, J = 6.7 Hz, 5H), 6.94 (d, J = 2.3 Hz, 1H), 6.90 (d, J = 2.3 Hz, 1H), 6.83 – 6.75 (m, 2H), 5.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.7, 142.1, 141.4, 140.1, 138.9, 132.4, 132.1, 131.9, 131.0, 129.7, 127.8, 127.6, 127.3, 126.4, 125.9, 116.6, 116.2. HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{18}ClO^+$ 357.1041, found 357.1052.



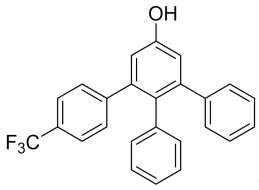
(3h)

4''-bromo-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3h): 57.0 mg, 71% yield. A white solid; mp:171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.4 Hz, 3H), 7.14 (s, 3H), 7.05 (d, J = 3.0 Hz, 2H), 6.98 (d, J = 6.4 Hz, 2H), 6.96 – 6.90 (m, 3H), 6.88 (s, 1H), 6.77 (d, J = 6.3 Hz, 2H), 5.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 143.7, 142.1, 141.4, 140.6, 138.9, 132.0, 131.9, 131.4, 130.7, 129.7, 127.6, 127.3, 126.4, 125.9, 120.6, 116.6, 116.1. HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{18}BrO^+$ 401.0536, found 401.0539.



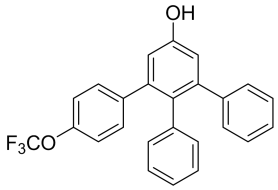
(3i)

4''-iodo-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3i): 41.2 mg, 46% yield. A white solid; mp:120-122 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 5.7 Hz, 3H), 6.99 (dd, J = 8.7, 7.2 Hz, 5H), 6.84 – 6.75 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.7, 143.3, 142.0, 141.7, 139.5, 136.8, 132.1, 131.6, 130.1, 129.8, 128.0, 127.7, 126.7, 126.2, 116.8, 116.3, 93.0, 79.6. HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{18}IO^+$ 449.0397, found 449.0403.



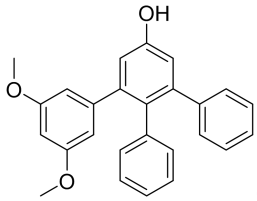
(3j)

6'-phenyl-4''-(trifluoromethyl)-[1,1':2',1''-terphenyl]-4'-ol (3j): 42.2 mg, 54% yield. A white solid; mp:116-119 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.2 Hz, 2H), 7.20 – 7.13 (m, 5H), 7.05 (dd, J = 6.6, 3.0 Hz, 2H), 7.02 – 6.94 (m, 4H), 6.90 (d, J = 2.7 Hz, 1H), 6.78 – 6.75 (m, 2H), 5.03 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 145.4, 143.8, 142.0, 141.3, 138.7, 132.1, 131.9, 130.1, 129.7, 128.4 (q, $J_{C\text{-}F}$ = 30 Hz), 127.7, 127.4, 126.5, 126.0, 124.2 (q, $J_{C\text{-}F}$ = 270 Hz), 124.5 (q, $J_{C\text{-}F}$ = 3 Hz), 117.0, 116.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.4. HRMS (EI) calcd for $[M+H]^+$ $C_{25}H_{18}F_3O^+$ 391.1305, found 391.1308.



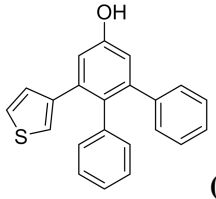
(3k)

6'-phenyl-4''-(trifluoromethoxy)-[1,1':2',1''-terphenyl]-4'-ol (3k): 43.1 mg, 53% yield. A yellow solid; mp:120-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 3H), 7.06 (m, 4H), 7.02 – 6.93 (m, 6H), 6.91 (d, J = 2.6 Hz, 1H), 6.77 (d, J = 6.7 Hz, 2H), 5.06 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 147.8, 143.7, 142.1, 141.4, 140.3, 138.8, 132.2, 131.9, 131.1, 129.8, 127.6, 127.3, 126.5, 125.9, 120.4 (q, $J_{C\text{-}F}$ = 257 Hz), 120.0, 116.7, 116.2. ^{19}F NMR (564 MHz, $CDCl_3$) δ -57.8. HRMS (EI) calcd for $[M+H]^+$ $C_{25}H_{18}F_3O_2^+$ 407.1254, found 407.1263.



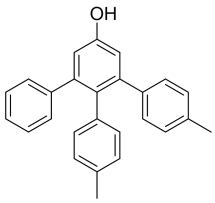
(3l)

3'',5''-dimethoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (3l): 50.5 mg, 66% yield. A white solid; mp:197-199 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (dd, J = 5.1, 1.7 Hz, 3H), 7.09 – 7.05 (m, 2H), 6.98 (dd, J = 4.9, 1.5 Hz, 3H), 6.95 (d, J = 2.7 Hz, 1H), 6.93 (d, J = 2.7 Hz, 1H), 6.83 (dd, J = 6.4, 3.0 Hz, 2H), 6.26 (d, J = 2.2 Hz, 1H), 6.22 (d, J = 2.2 Hz, 2H), 5.09 (s, 1H), 3.55 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 154.3, 143.5, 143.5, 143.2, 141.6, 139.4, 132.0, 131.8, 129.8, 127.6, 127.3, 126.4, 125.7, 116.5, 116.0, 108.0, 99.2, 55.2. HRMS (EI) calcd for $[M+H]^+$ $C_{26}H_{23}O_3^+$ 383.1642, found 383.1641.



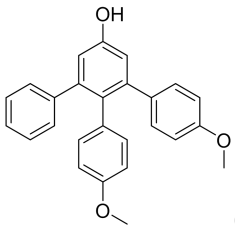
(3m)

6'-(thiophen-3-yl)-[1,1':2',1''-terphenyl]-4'-ol (3m): 46.6 mg, 71% yield. A white solid; mp:183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 4.9 Hz, 4H), 7.10 – 7.03 (m, 6H), 6.97 – 6.87 (m, 3H), 6.81 (dd, J = 5.0, 3.7 Hz, 1H), 6.61 (dd, J = 3.5, 0.9 Hz, 1H), 5.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.9, 143.1, 141.4, 139.2, 135.8, 132.3, 131.7, 129.7, 127.5, 127.4, 127.2, 126.6, 126.4, 126.3, 125.6, 116.7, 116.3. HRMS (EI) calcd for $[M+H]^+$ $C_{22}H_{17}OS^+$ 329.0995, found 329.1006.



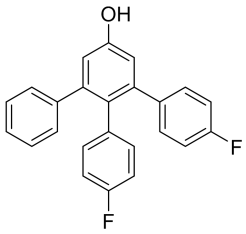
(4a)

4,4''-dimethyl-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4b): 32.2 mg, 46% yield**.** A yellow solid; mp:215-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 3H), 7.06 (dd, J = 6.6, 2.9 Hz, 2H), 6.96 (s, 4H), 6.89 (d, J = 0.9 Hz, 2H), 6.77 (d, J = 7.8 Hz, 2H), 6.67 (d, J = 8.0 Hz, 2H), 5.19 (s, 1H), 2.28 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.5, 143.4, 141.9, 138.8, 136.1, 135.8, 134.9, 132.0, 131.75, 129.8, 129.6, 128.3, 127.9, 127.5, 126.2, 116.4, 116.2, 21.1. HRMS (EI) calcd for $[M+H]^+$ $C_{26}H_{23}O^+$ 351.1743, found 351.1755.



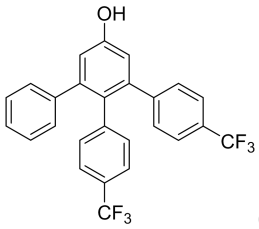
(4b)

4,4''-dimethoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4c):58.1 mg, 76% yield. A white solid; mp:100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 3H), 7.06 (dd, J = 7.2, 2.2 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.90 (s, 2H), 6.75 – 6.66 (m, 4H), 6.54 (d, J = 8.6 Hz, 2H), 5.60 (s, 1H), 3.76 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.3, 154.2, 143.6, 143.1, 141.9, 134.3, 132.9, 131.7, 131.6, 130.9, 129.8, 127.6, 126.2, 116.4, 116.1, 113.1, 112.7, 55.2, 55.0. (CAS:56430-29-6)[8].



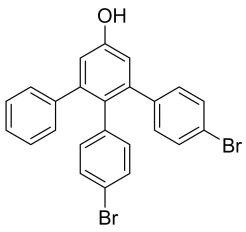
(4c)

4,4''-difluoro-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4d): 48.7 mg, 68% yield. A white solid; mp:154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 3H), 7.02 (dd, J = 16.6, 9.0, 3.3 Hz, 4H), 6.94 – 6.80 (m, 4H), 6.69 (dd, J = 11.9, 7.2 Hz, 4H), 5.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 245 Hz), 161.1 (d, $J_{C\text{-}F}$ = 245 Hz), 154.4, 143.7, 142.5, 141.3, 137.4 (d, $J_{C\text{-}F}$ = 4 Hz), 135.0 (d, $J_{C\text{-}F}$ = 4 Hz), 133.3 (d, $J_{C\text{-}F}$ = 7 Hz), 131.2 (d, $J_{C\text{-}F}$ = 8 Hz), 131.0, 129.7, 127.7, 126.5, 116.5, 116.3, 114.6 (d, $J_{C\text{-}F}$ = 21 Hz), 114.3 (d, $J_{C\text{-}F}$ = 21 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1, -116.7; HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{17}F_2O^+$ 359.1265, found 359.1242.



(4d)

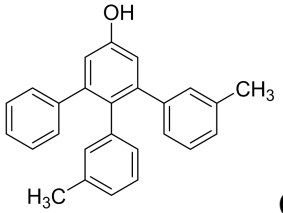
6'-phenyl-4,4''-bis(trifluoromethyl)-[1,1':2',1''-terphenyl]-4'-ol (4f): 38.5 mg, 42% yield. A white solid; mp:149-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.29 – 7.20 (m, 4H), 7.16 (dd, J = 9.2, 5.1 Hz, 4H), 7.06 – 6.94 (m, 3H), 6.90 (dd, J = 8.2, 5.4 Hz, 2H), 5.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 144.8, 143.8, 142.7, 141.9, 140.7, 132.1, 130.5, 130.0, 129.6, 128.8 (q, $J_{C\text{-}F}$ = 32 Hz), 128.1(q, $J_{C\text{-}F}$ = 32 Hz), 127.8, 126.8, 124.7 (q, $J_{C\text{-}F}$ = 3 Hz), 124.3 (q, $J_{C\text{-}F}$ = 3 Hz), 124.1 (q, $J_{C\text{-}F}$ = 271 Hz), 117.2, 116.4, ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5, -62.5. HRMS (EI) calcd for $[M+H]^+$ $C_{26}H_{17}F_6O^+$ 459.1178, found 459.1177.



(4e)

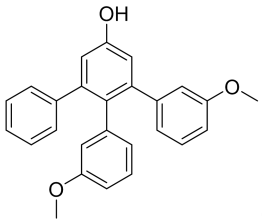
4,4''-dibromo-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4e): 53.8 mg, 56% yield. A white solid; mp:203-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.5 Hz, 2H), 7.18 (dd, J = 3.7, 2.6 Hz, 3H), 7.11 (d, J = 8.4 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.94 – 6.88 (m, 3H), 6.87 (d, J = 2.6 Hz, 1H), 6.64 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.6, 142.1, 141.1, 140.2, 137.9,

133.5, 131.3, 130.9, 130.6, 129.7, 127.8, 126.6, 120.9, 120.1, 116.8, 116.3. HRMS (EI) calcd for $[M+H]^+$ $C_{24}H_{17}Br_2O^+$ 480.9620, found 480.9616.



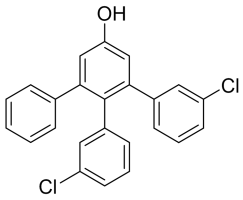
(4f)

3,3''-dimethyl-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4g):44.9 mg, 64% yield. A white solid; mp:110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 4.9, 1.5 Hz, 3H), 7.11 – 7.05 (m, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.93 (dd, J = 14.8, 6.0 Hz, 4H), 6.88 – 6.74 (m, 3H), 6.61 (s, 2H), 2.22 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.5, 143.4, 141.8, 141.6, 139.0, 137.0, 136.3, 132.8, 132.3, 130.5, 129.7, 129.0, 127.5, 127.3, 126.9, 126.9, 126.8, 126.2, 126.2, 116.2, 116.2, 21.3, 21.2. HRMS (EI) calcd for $[M+H]^+$ $C_{26}H_{23}O^+$ 351.1743, found 351.1752.



(4g)

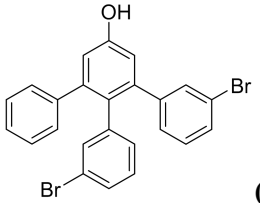
3,3''-dimethoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4h): 39.0 mg, 51% yield. A yellow solid; mp:147-148 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 5.0 Hz, 3H), 7.09 (t, J = 7.6 Hz, 3H), 6.93 (d, J = 3.8 Hz, 2H), 6.86 (d, J = 7.8 Hz, 1H), 6.72 (t, J = 9.1 Hz, 2H), 6.59 (s, 1H), 6.54 (d, J = 8.2 Hz, 1H), 6.40 (d, J = 7.5 Hz, 1H), 6.35 (s, 1H), 5.21 (s, 1H), 3.57 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.6, 154.3, 143.4, 143.2, 143.0, 141.6, 140.5, 131.8, 129.6, 128.6, 128.1, 127.6, 126.4, 124.7, 122.1, 117.0, 116.4, 116.2, 114.9, 112.8, 112.3, 55.1. (CAS:56430-32-1)[8].



(4h)

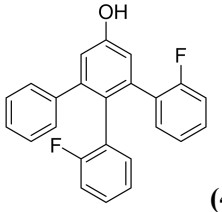
3,3''-dichloro-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4i): 43.0 mg, 55% yield. A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 5H), 7.05 (dd, J = 7.6, 4.9 Hz, 3H), 6.97 (s, 1H), 6.95 – 6.83 (m, 4H), 6.78 (s, 1H), 6.67 (d, J = 7.6 Hz, 1H), 5.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

154.6, 143.7, 143.0, 141.9, 140.9, 140.8, 133.6, 133.1, 131.8, 130.6, 130.1, 129.6, 128.9, 128.5, 128.0, 127.8, 126.8, 126.7, 126.1, 116.8, 116.2. calcd for $[M+H]^+$ $C_{24}H_{17}Cl_2O^+$ 391.0651, found 391.64.



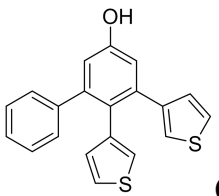
(4i)

3,3''-dibromo-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4j): 48.0 mg, 50% yield. A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.2 Hz, 2H), 7.22 – 7.11 (m, 4H), 7.08 – 6.97 (m, 3H), 6.96 – 6.81 (m, 5H), 6.71 (d, J = 7.7 Hz, 1H), 5.31 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.64, 143.2, 141.8, 141.0, 140.9, 134.7, 132.6, 130.5, 130.4, 129.6, 129.1, 129.0, 128.8, 128.4, 127.8, 126.7, 121.8, 121.3, 116.8, 116.2. calcd for $[M+H]^+$ $C_{24}H_{17}Br_2O^+$ 480.9620, found 480.9616.



(4j)

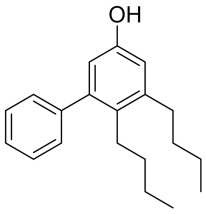
2,2''-difluoro-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4k) :29.4 mg, 41% yield. A yellow solid; mp:132-135 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 10.9 Hz, 7H), 7.04 – 6.81 (m, 6H), 6.76 (d, J = 7.4 Hz, 1H), 6.68 (s, 1H), 5.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, $J_{C\text{-}F}$ = 243 Hz), 159.4 (d, $J_{C\text{-}F}$ = 245 Hz), 154.8, 144.1, 141.1, 138.1, 133.1 (d, $J_{C\text{-}F}$ = 3 Hz), 131.6 (d, $J_{C\text{-}F}$ = 3 Hz), 129.2, 128.8 (d, $J_{C\text{-}F}$ = 37 Hz), 128.7 (d, $J_{C\text{-}F}$ = 38 Hz), 128.7 (d, $J_{C\text{-}F}$ = 15 Hz), 127.6, 126.9 (d, $J_{C\text{-}F}$ = 16 Hz), 126.8, 126.7, 123.3 (d, $J_{C\text{-}F}$ = 4 Hz), 122.9 (d, $J_{C\text{-}F}$ = 3 Hz), 116.8, 116.4, 115.1 (d, $J_{C\text{-}F}$ = 22 Hz), 114.6 (d, $J_{C\text{-}F}$ = 23 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.25, -114.96 calcd for $[M+H]^+$ $C_{24}H_{17}F_2O^+$ 359.1242, found 359.1248.



(4k)

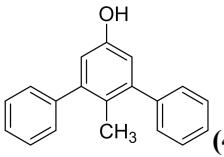
5,6-di(thiophen-3-yl)-[1,1'-biphenyl]-3-ol (4l): 52.2 mg, 78% yield. A white solid; mp:201-204 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 7.33 – 7.26 (m, 1H), 7.17 (d, J = 6.9 Hz, 5H),

7.06 (d, J = 6.1 Hz, 2H), 6.88 (s, 1H), 6.79 – 6.69 (m, 2H), 6.62 (d, J = 4.8 Hz, 1H), 6.50 (d, J = 4.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.7, 143.7, 142.4, 142.1, 139.8, 138.2, 130.9, 129.4, 128.9, 128.0, 126.8, 125.2, 125.0, 124.9, 124.8, 123.3, 116.4, 116.1. calcd for $[M+H]^+$ $C_{20}H_{15}OS_2^+$ 335.0559, found 335.0564.



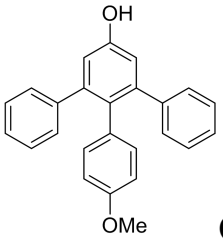
(4l)

5,6-dibutyl-[1,1'-biphenyl]-3-ol (4m): 20.3 mg, 36% yield. A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 14.5, 7.2 Hz, 3H), 7.28 (d, J = 1.4 Hz, 1H), 7.26 (s, 1H), 6.69 (d, J = 2.6 Hz, 1H), 6.51 (d, J = 2.6 Hz, 1H), 2.65 – 2.58 (m, 2H), 2.48 – 2.40 (m, 2H), 1.60 (d, J = 7.5 Hz, 2H), 1.44 (d, J = 7.4 Hz, 2H), 1.29 (d, J = 8.7 Hz, 2H), 1.14 (d, J = 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.72 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 143.8, 142.9, 142.6, 130.9, 129.1, 127.8, 126.6, 115.1, 114.6, 33.7, 33.5, 32.8, 28.3, 22.9, 22.9, 14.0, 13.6. calcd for $[M+H]^+$ $C_{20}H_{27}O^+$ 283.2056, found 283.2071.



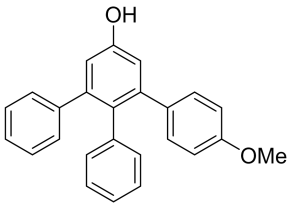
(4m)

2'-methyl-[1,1':3',1''-terphenyl]-5'-ol (4n): 37.5 mg, 72% yield. A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H), 7.36 (d, J = 6.2 Hz, 6H), 6.76 (s, 2H), 4.89 (s, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 144.1, 142.1, 129.2, 128.1, 126.9, 125.2, 115.9, 17.8. (CAS:502145-10-0)[9].



(4n)

4-methoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4o): 21.1 mg, 30% yield. A yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 6H), 7.08 (s, 4H), 6.91 (s, 2H), 6.68 (d, J = 7.5 Hz, 2H), 6.50 (d, J = 7.5 Hz, 2H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 154.1, 143.6, 141.8, 132.9, 131.7, 131.5, 129.8, 127.6, 126.2, 116.3, 112.6, 55.0. (CAS:17713-39-2)[10].



(4n')

4''-methoxy-6'-phenyl-[1,1':2',1''-terphenyl]-4'-ol (4o'): 27.5 mg, 39% yield. A yellow solid; mp:120-123 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 3H), 7.06 (s, 2H), 6.98 (d, J = 3.2 Hz, 5H), 6.90 (s, 2H), 6.80 (s, 2H), 6.69 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.2, 143.5, 143.0, 141.7, 139.3, 134.0, 132.1, 132.0, 130.8, 129.8, 127.5, 127.2, 126.3, 125.6, 116.3, 116.0, 113.0, 55.2. (CAS:1252687-12-9)[7].

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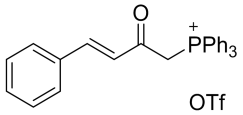
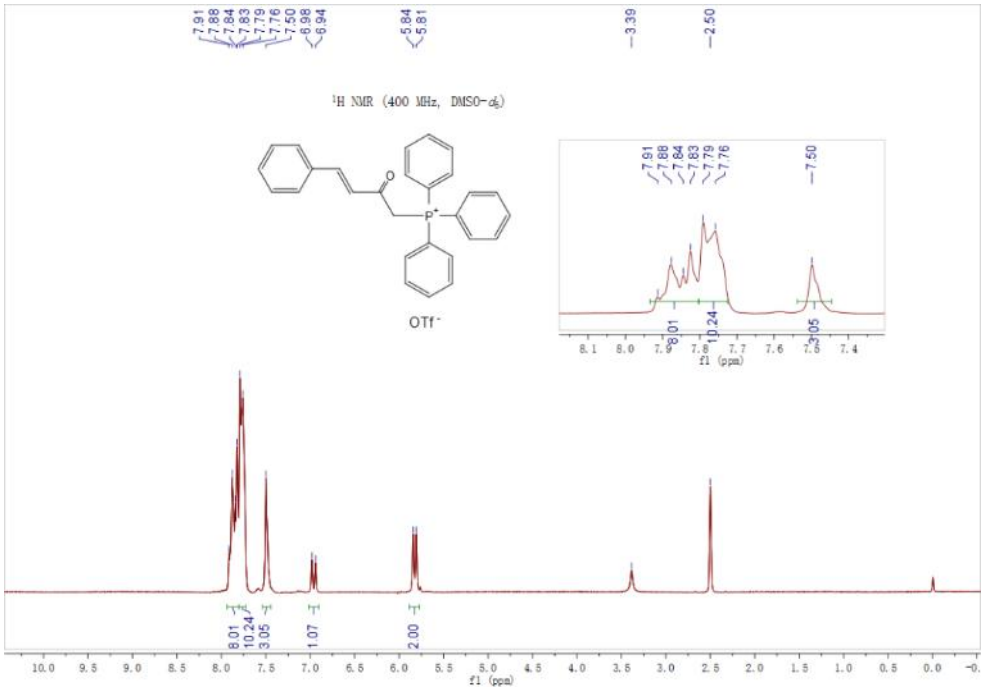
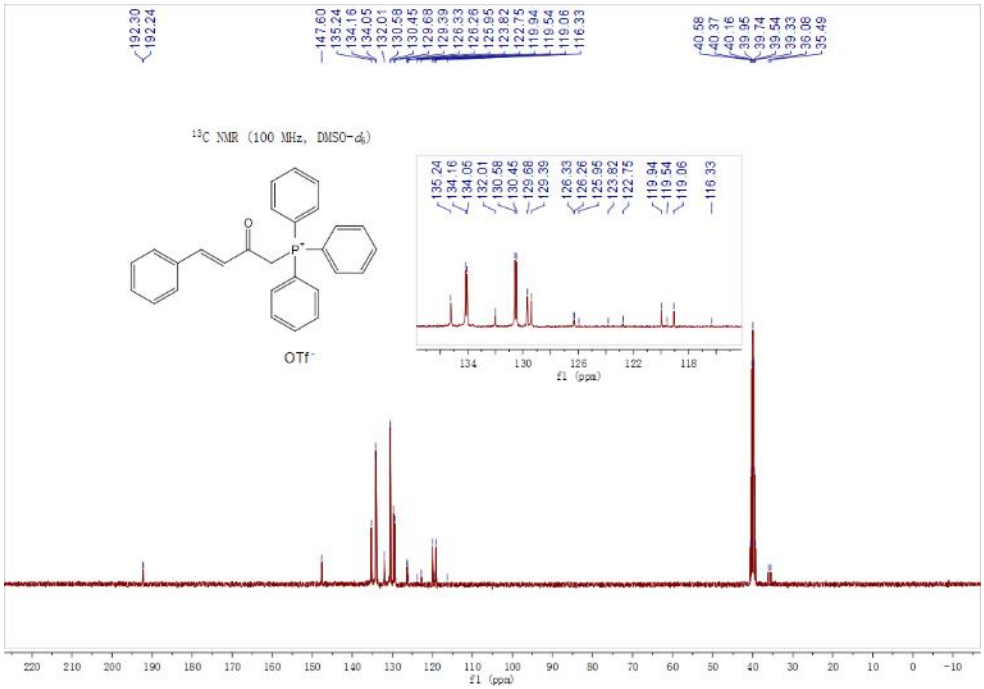
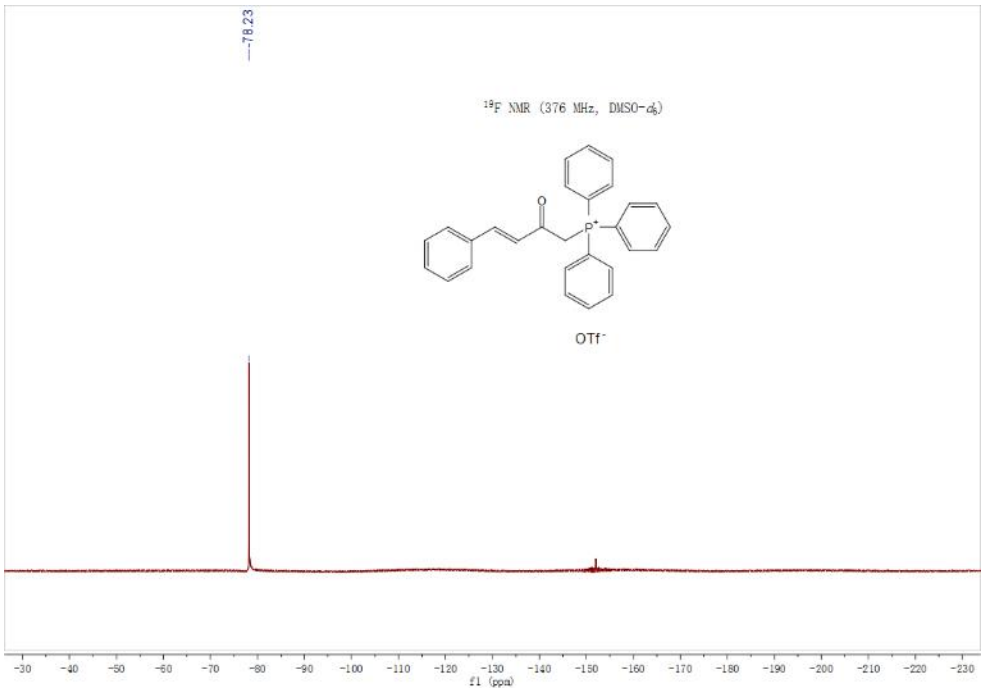
The ^{1}H and ^{13}C NMR spectra of raw material

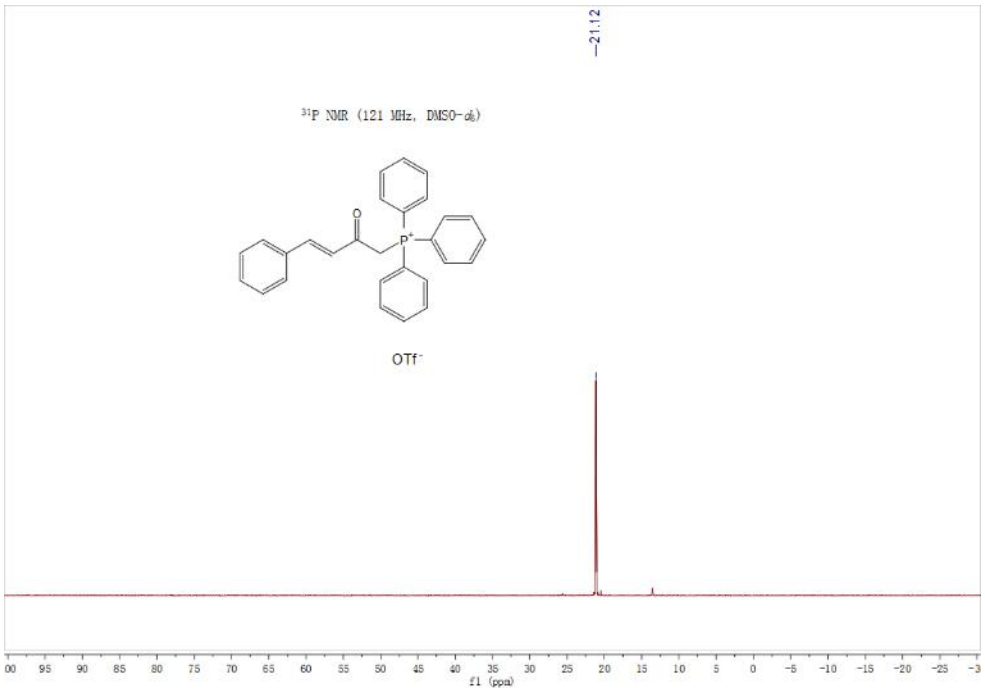


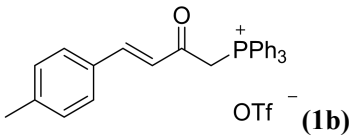
（1a）



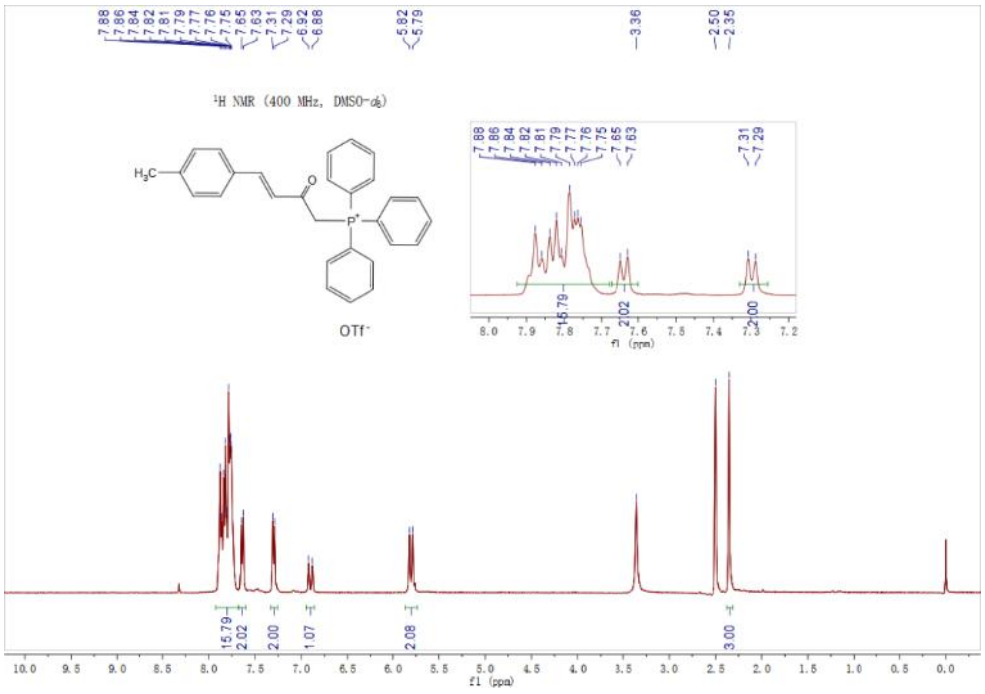


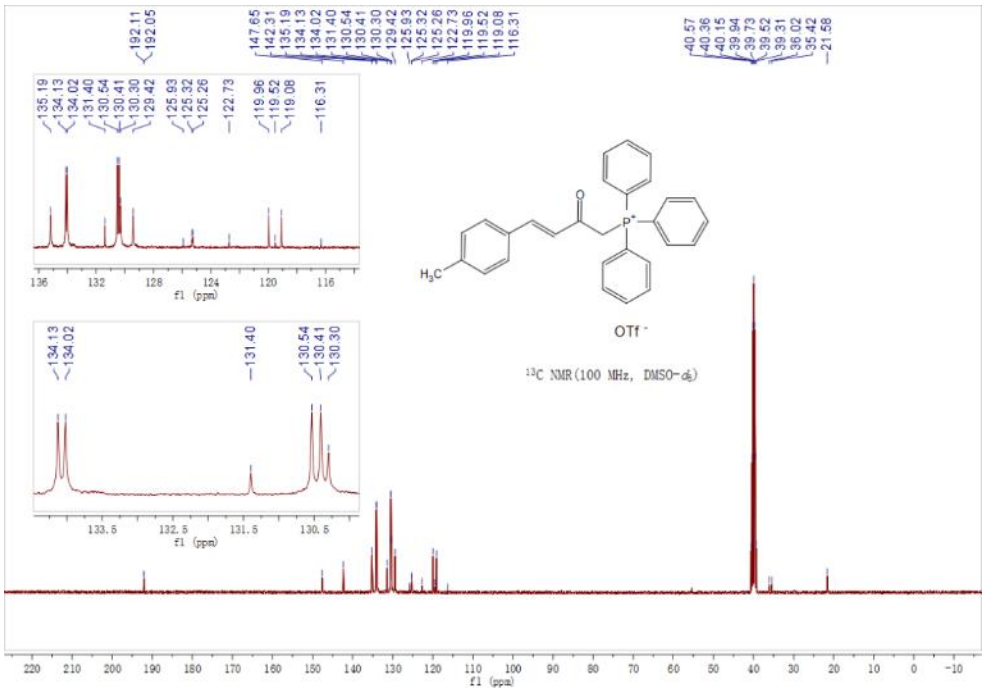

-78.23
^{19}F NMR (376 MHz, DMSO-d_6)
O
P+
OTf-
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

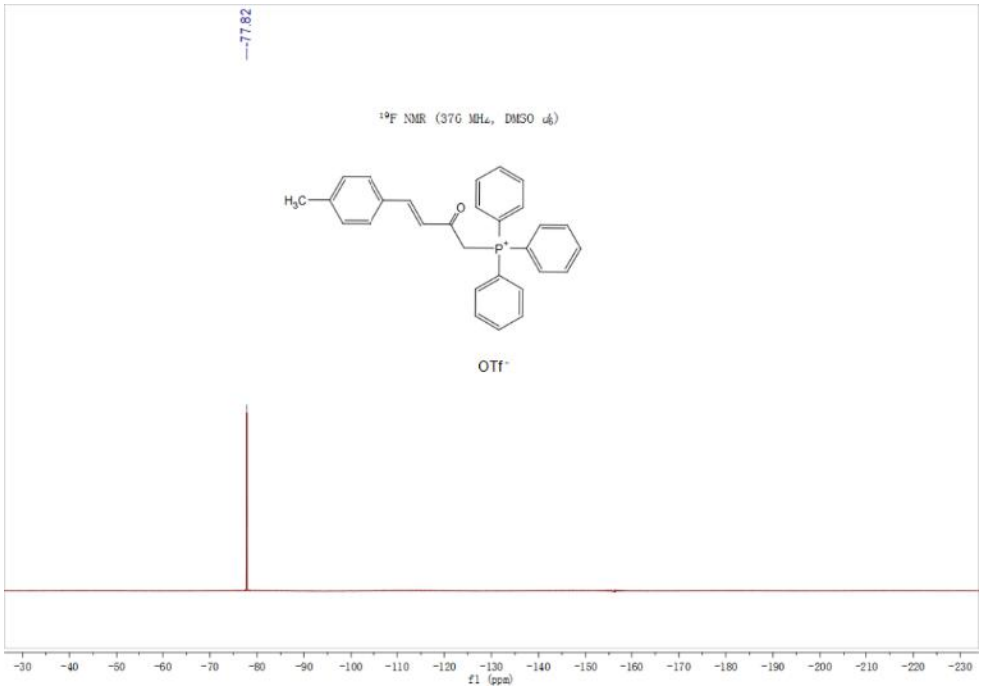

-21.12
^{31}P NMR (121 MHz, DMSO-d_6)
O
P+
OTf-
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

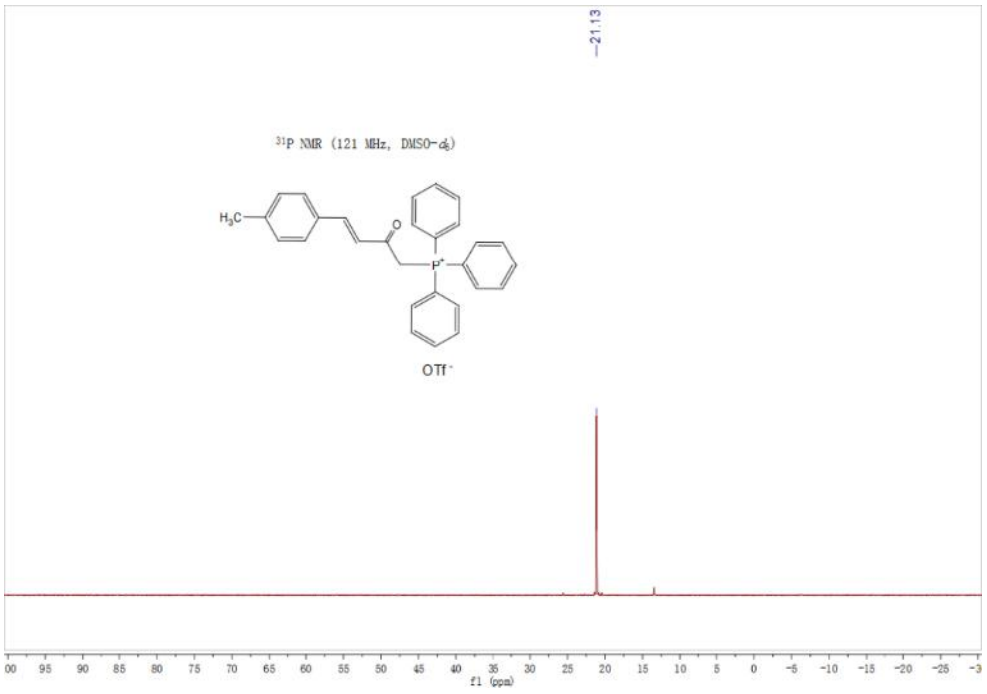

O
PPh3
OTf

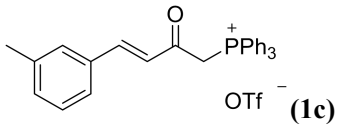
(1b)


1H NMR (400 MHz, DMSO-d6)
OTf-
f1 (ppm)

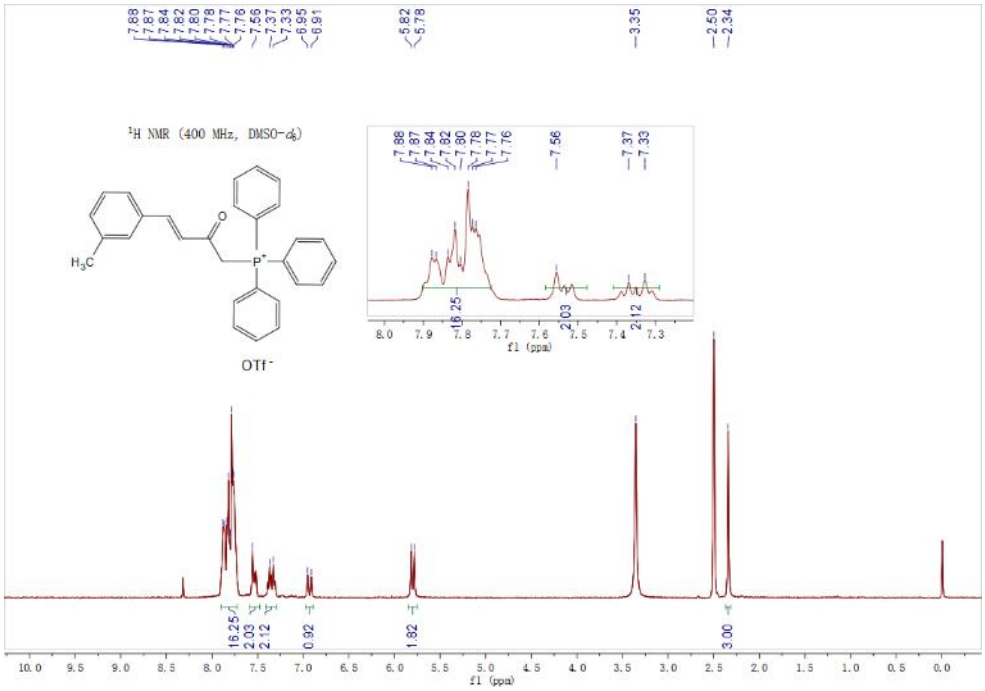

OTf-
13C NMR(100 MHz, DMSO-d6)
f1 (ppm)

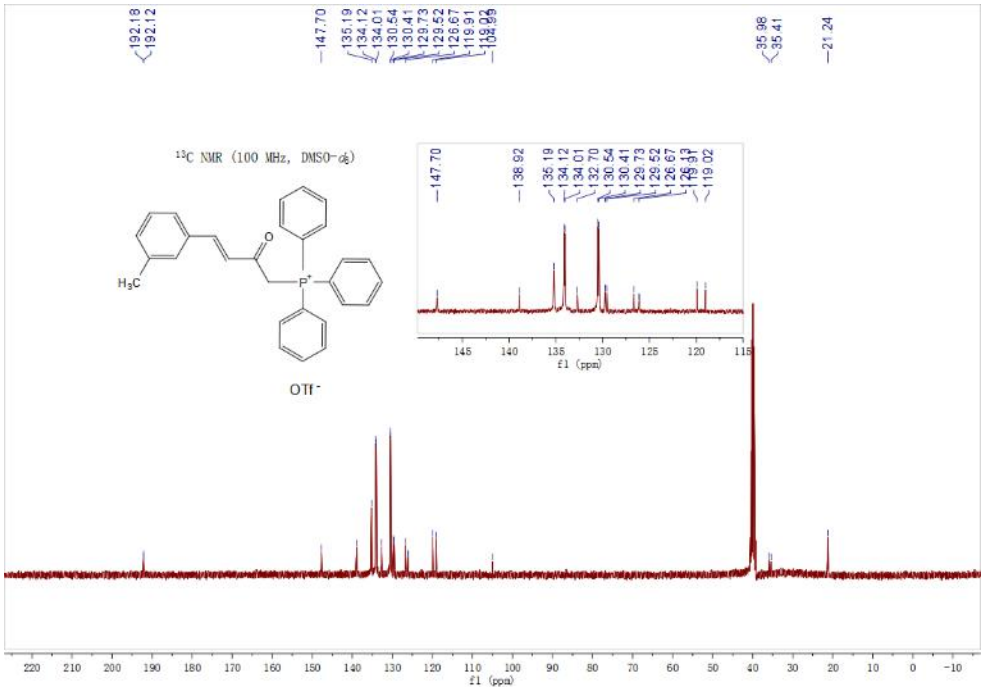

-77.82
^{19}F NMR (376 MHz, DMSO d_6)
H_3C
O
P^+
OTf^-
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

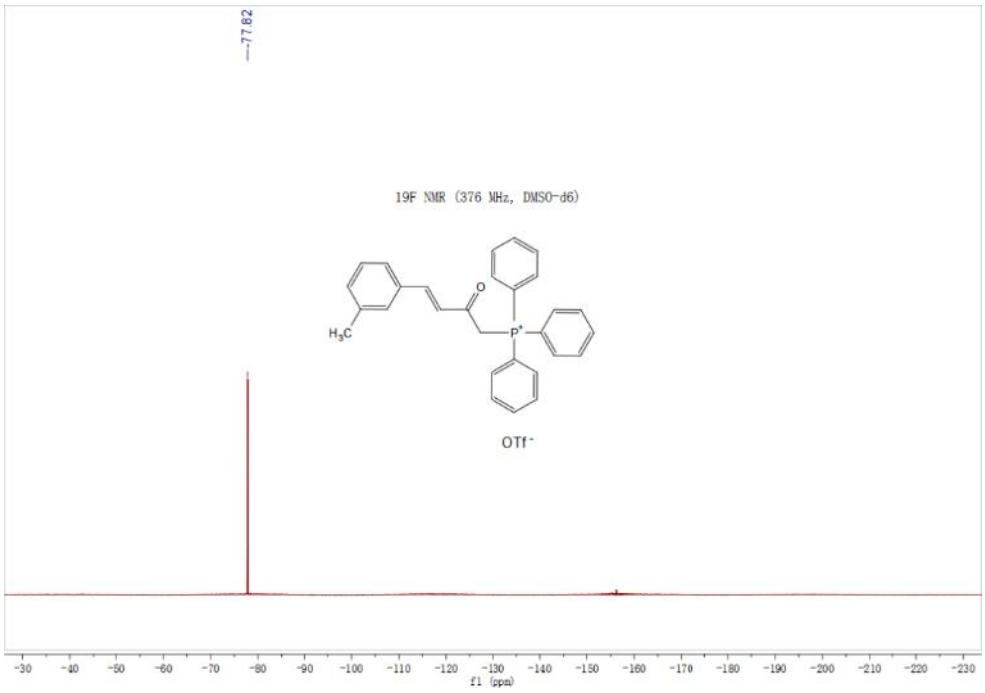

-21.13
^{31}P NMR (121 MHz, DMSO-d_6)
H_3C
O
P^+
OTf^-
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

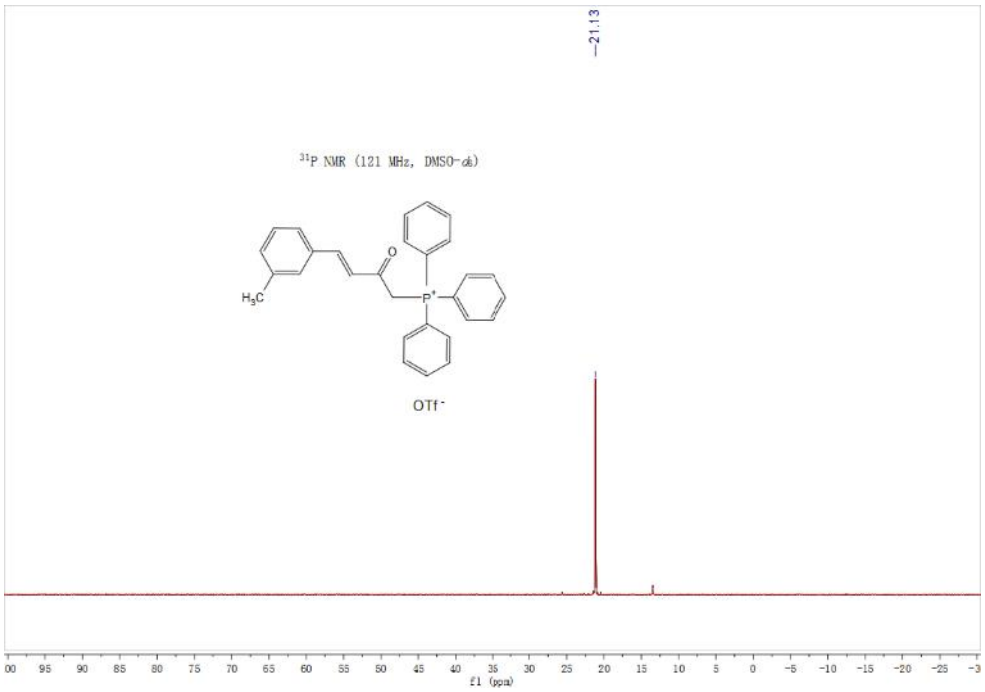

O
PPh3
OTf

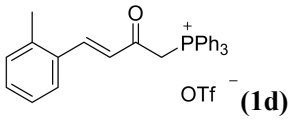
(1c)


7.88
7.87
7.84
7.82
7.80
7.78
7.77
7.76
7.56
7.37
7.33
6.95
6.91
5.82
5.78
3.35
2.50
2.34
1H NMR (400 MHz, DMSO-d6)
H3C
O
P+
OTf-
16.25
2.03
2.12
0.92
1.82
3.00
f1 (ppm)

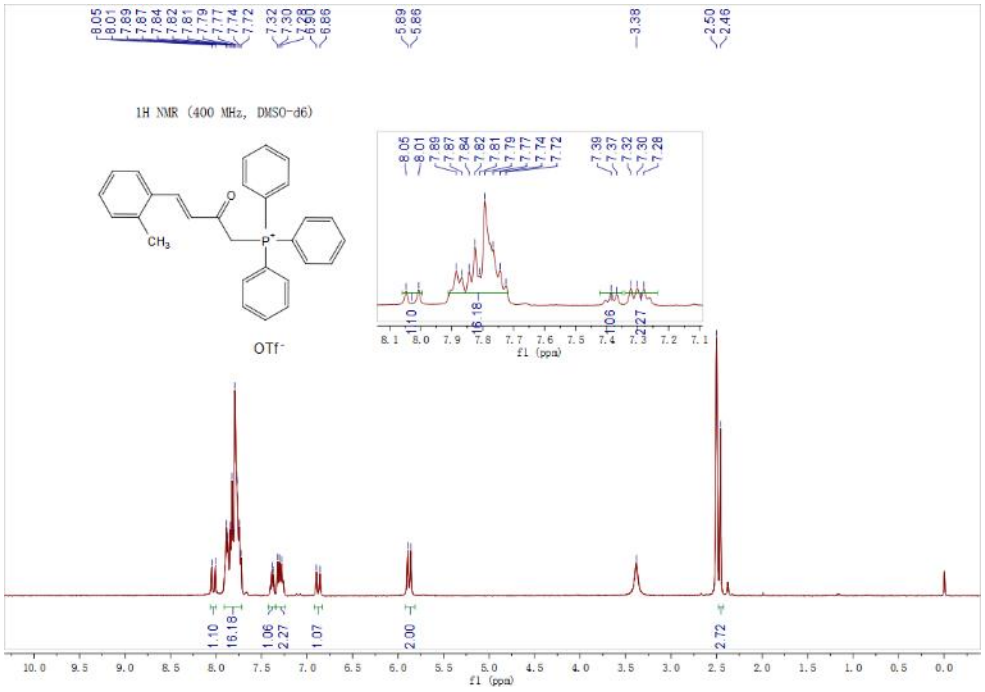

192.18
192.12
147.70
135.19
134.12
134.01
130.54
130.41
129.73
129.52
126.67
119.91
119.02
35.98
35.41
21.24
13C NMR (100 MHz, DMSO-d6)
H3C
O
P+
OTf-
f1 (ppm)

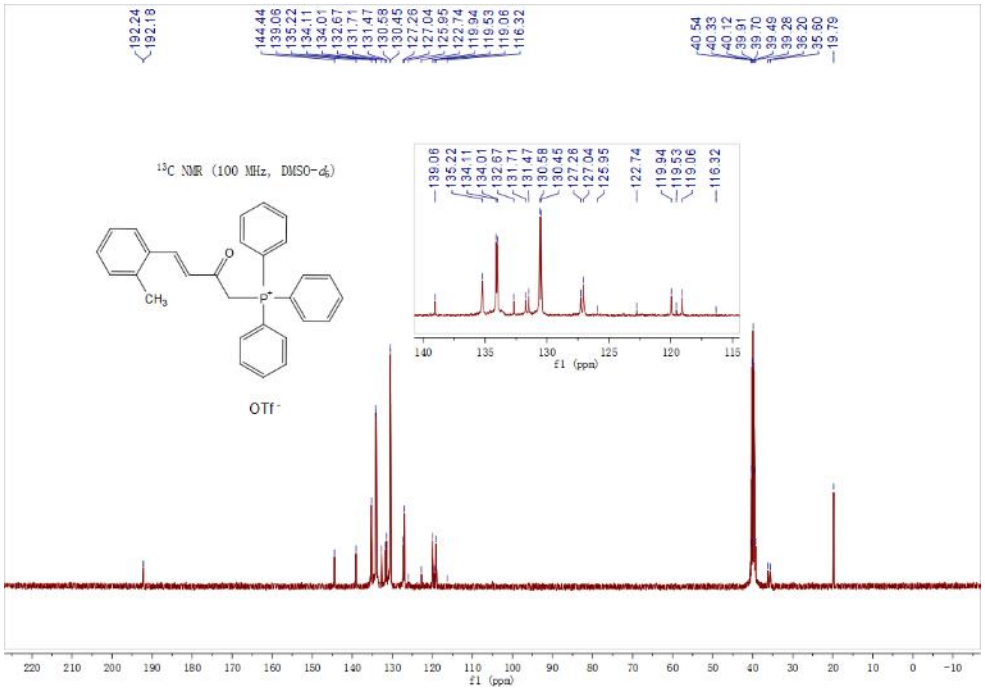

-77.62
19F NMR (376 MHz, DMSO-d6)
O
H3C
P+
OTf-
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

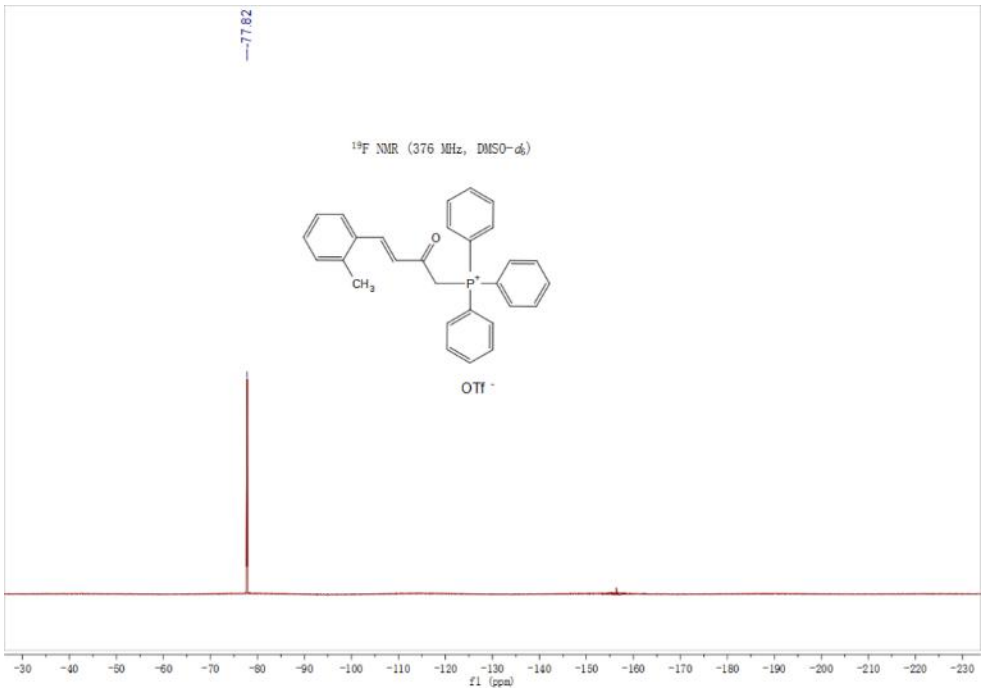

-21.13
31P NMR (121 MHz, DMSO-d6)
O
H3C
P+
OTf-
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

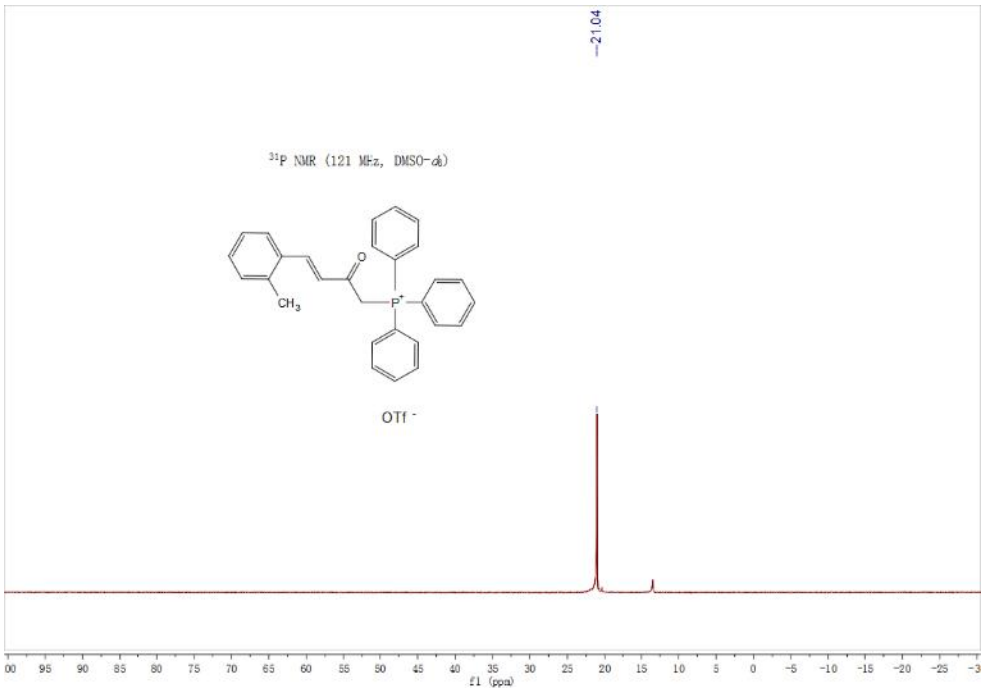

O
PPh3
+
OTf
−

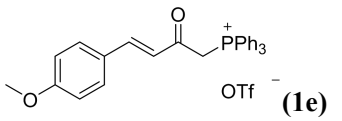
(1d)


1H NMR (400 MHz, DMSO-d6)
OTf-
f1 (ppm)

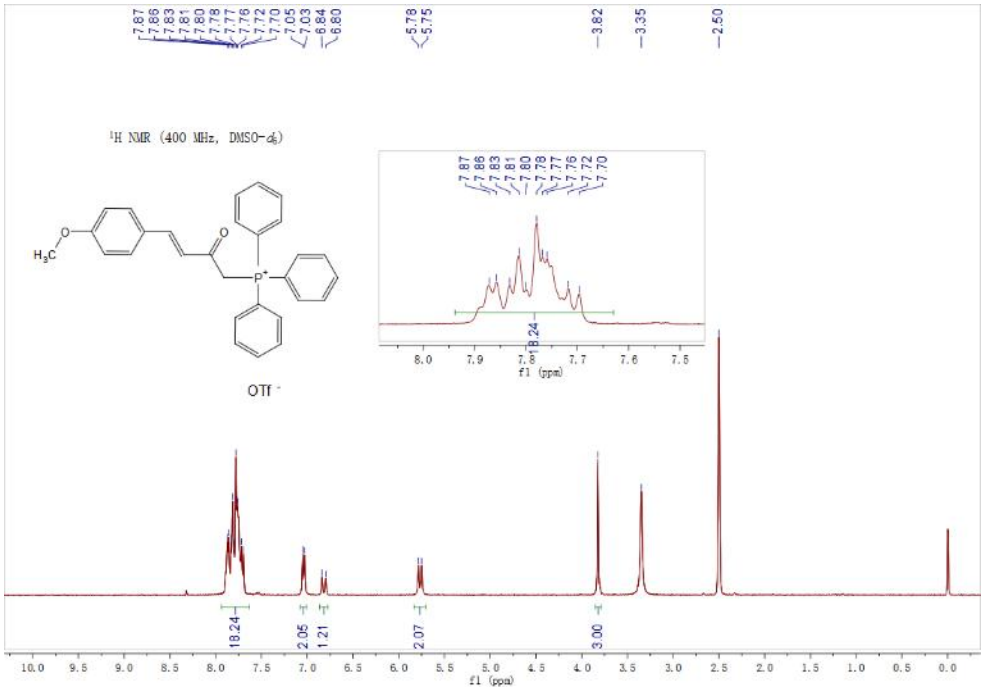

13C NMR (100 MHz, DMSO-d6)
OTf-
f1 (ppm)

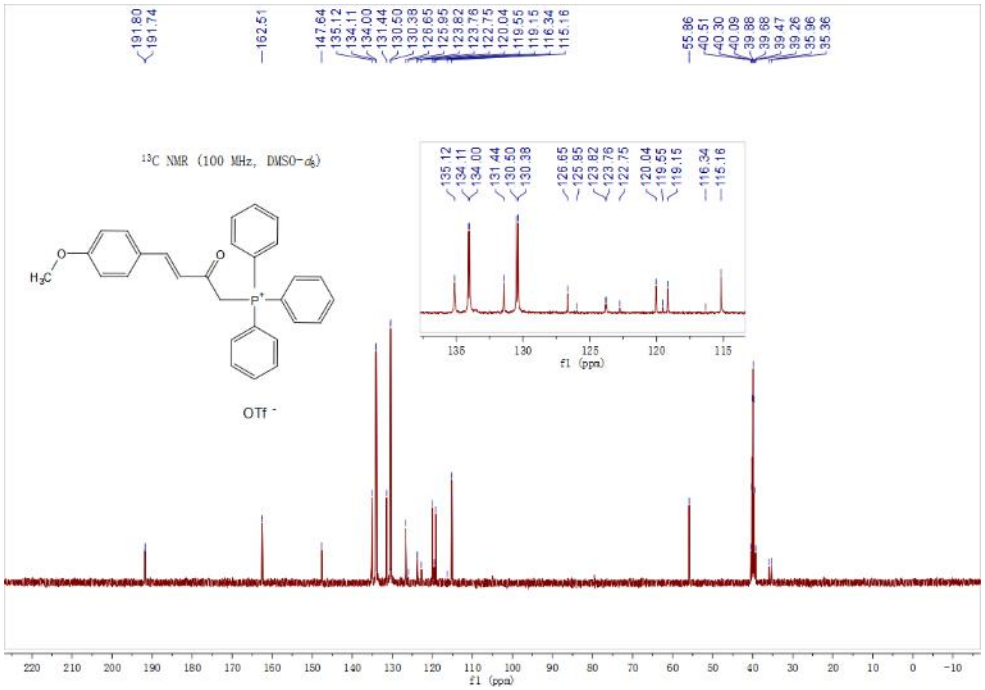

-77.62
^{19}F NMR (376 MHz, DMSO-d_6)
CH$_3$
O
P$^+$
OTf$^-$
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

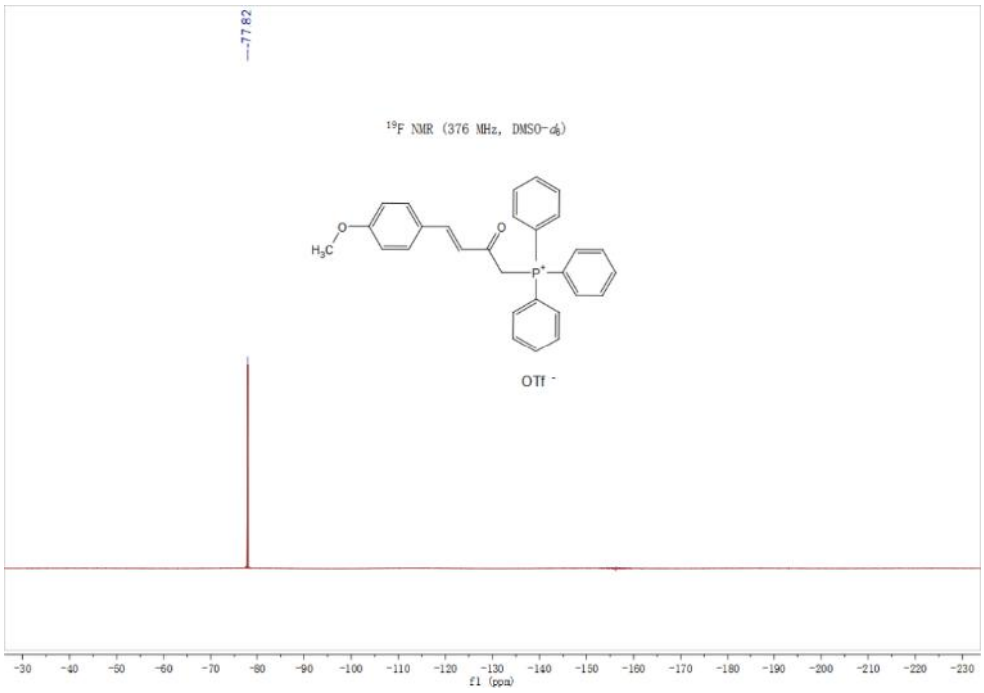

-21.04
^{31}P NMR (121 MHz, DMSO-d_6)
CH$_3$
O
P$^+$
OTf$^-$
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

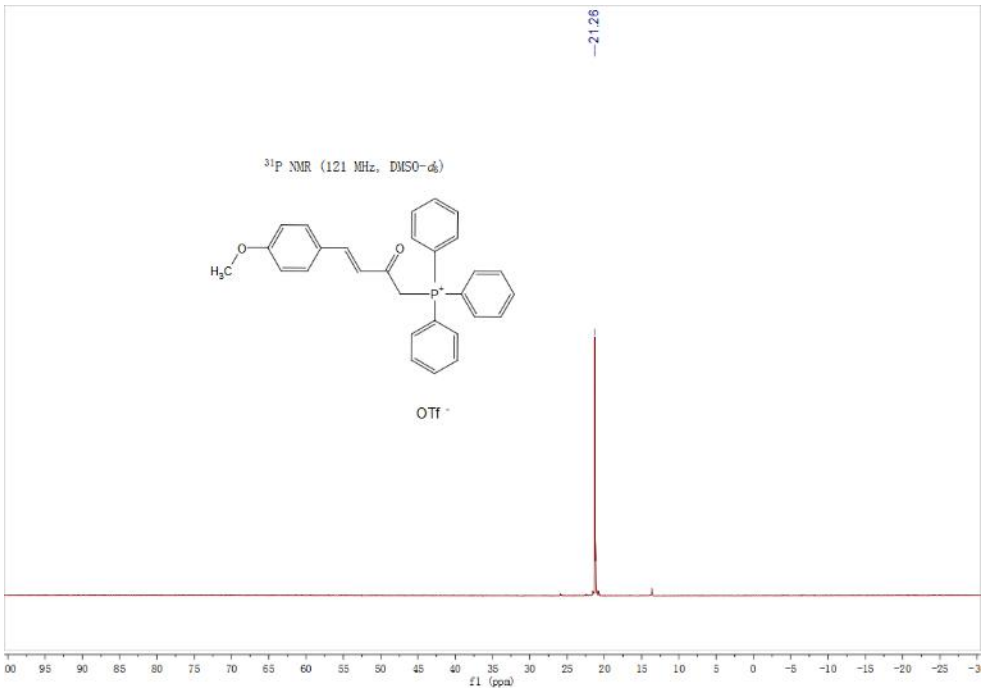

O
PPh3
OTf
O

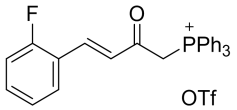
(1e)


1H NMR (400 MHz, DMSO-d6)
OTf
f1 (ppm)

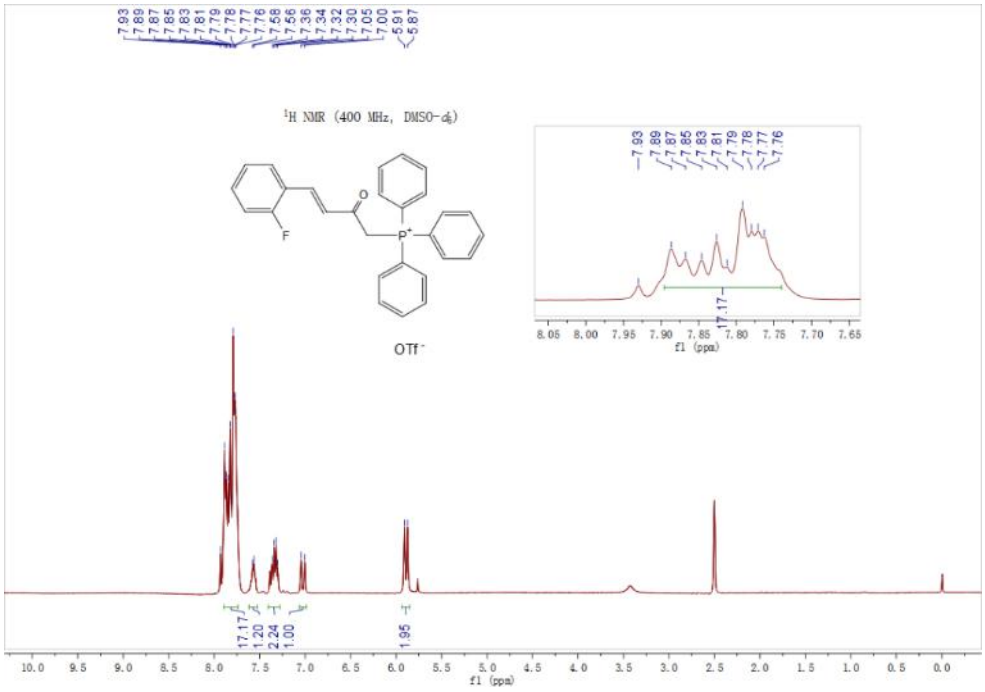

13C NMR (100 MHz, DMSO-d6)
OTf
f1 (ppm)

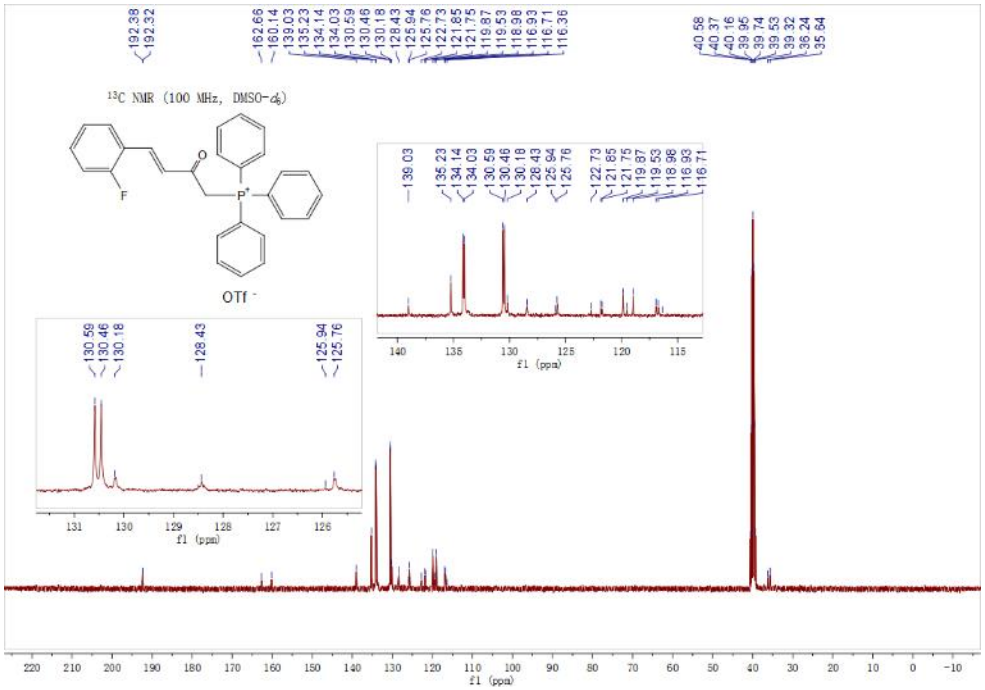

-77.62
^{19}F NMR (376 MHz, DMSO-d_6)
OTf$^-$
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

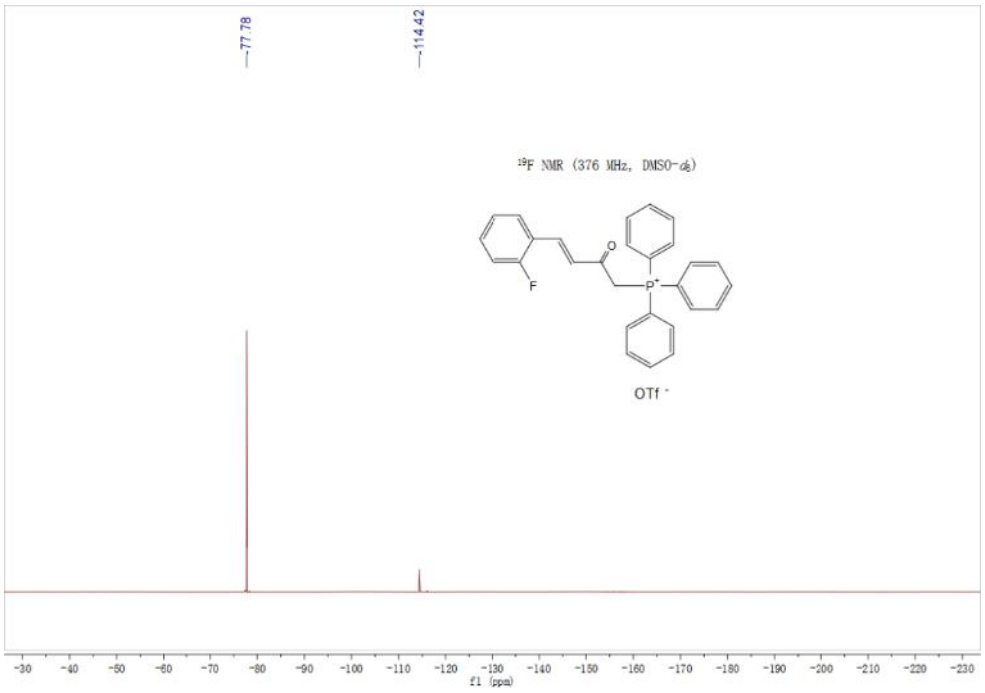

-21.26
^{31}P NMR (121 MHz, DMSO-d_6)
OTf$^-$
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

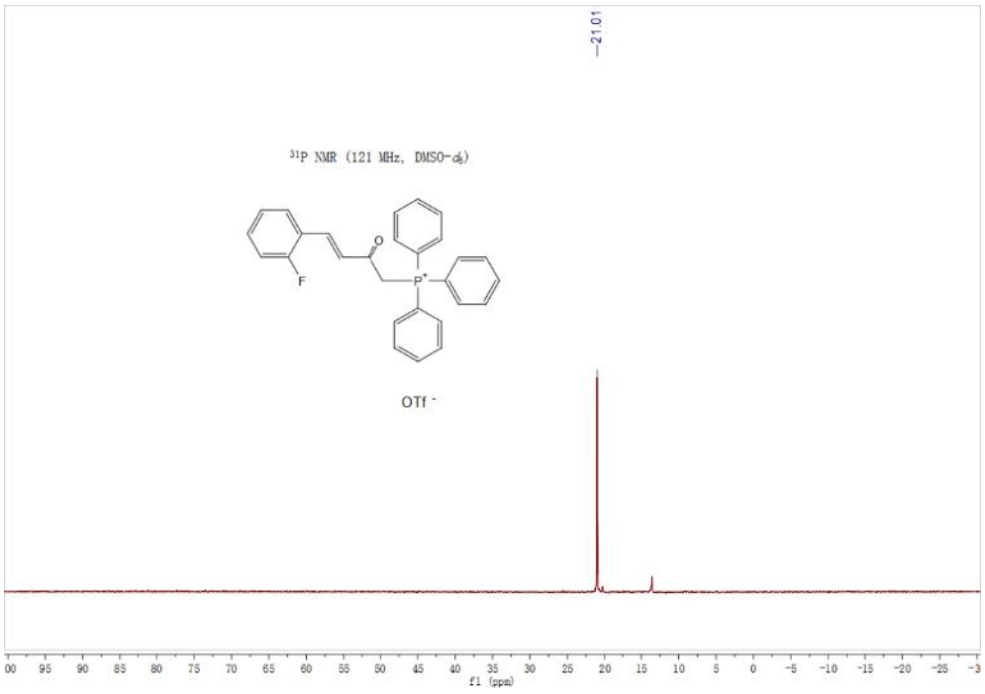

F
O
PPh3
+
OTf
−

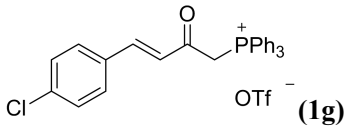
(1f)


7.93
7.89
7.87
7.85
7.83
7.81
7.79
7.78
7.77
7.76
7.58
7.56
7.36
7.34
7.32
7.30
7.05
7.00
5.91
5.87
1H NMR (400 MHz, DMSO-d6)
OTf
17.17
1.20
2.24
1.00
1.95
f1 (ppm)

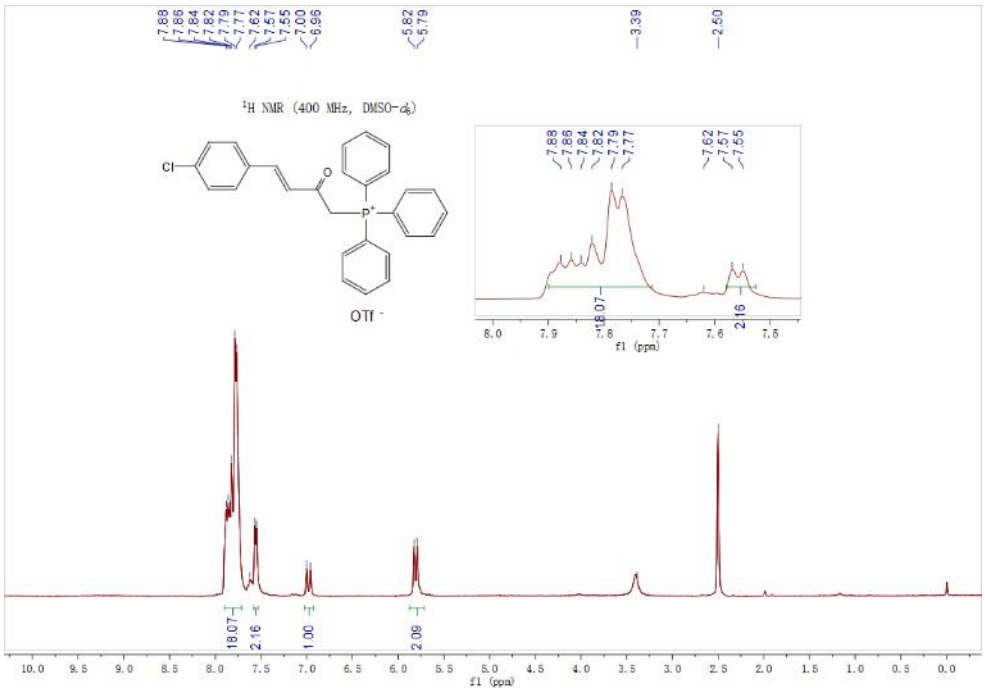

192.38
192.32
162.66
160.14
139.03
135.23
134.14
134.03
130.59
130.46
130.18
128.43
125.94
125.76
122.73
121.85
121.75
119.87
119.53
118.98
116.93
116.71
116.36
40.58
40.37
40.16
39.95
39.74
39.53
39.32
36.24
35.84
13C NMR (100 MHz, DMSO-d6)
OTf
f1 (ppm)

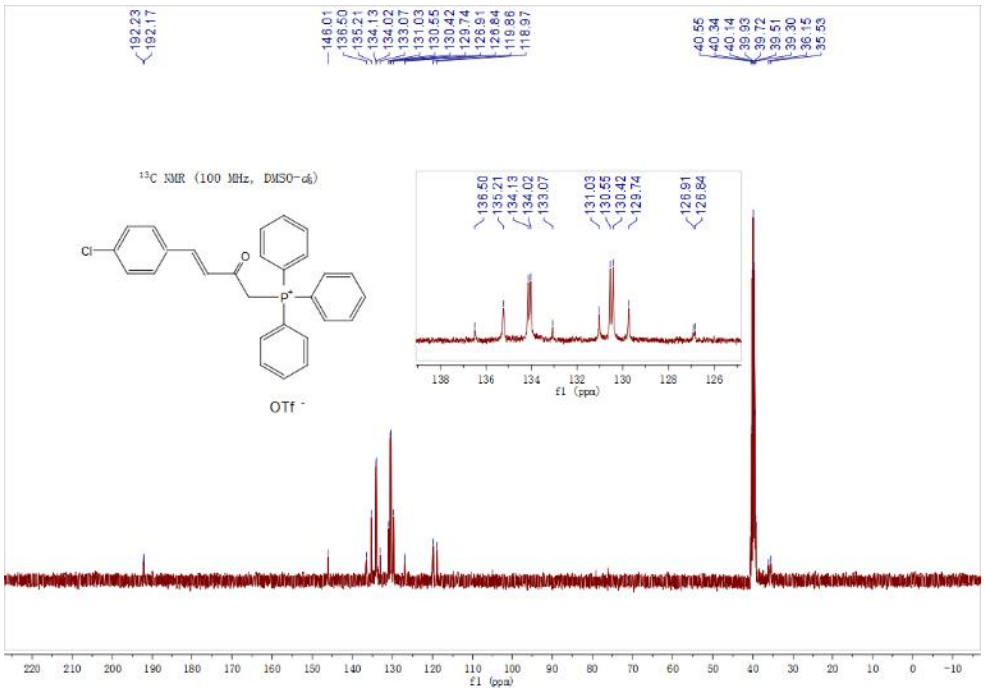

-77.78
-114.42
^{19}F NMR (376 MHz, DMSO-d_6)
O
F
P$^+$
OTf $^-$
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

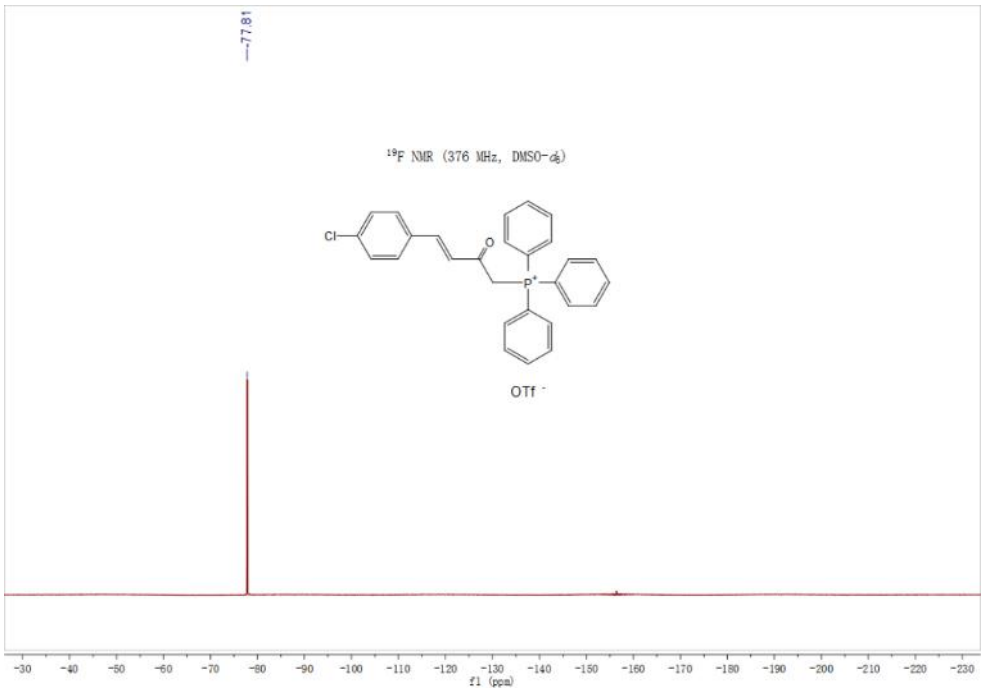

-21.01
^{31}P NMR (121 MHz, DMSO-d_6)
O
F
P$^+$
OTf $^-$
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

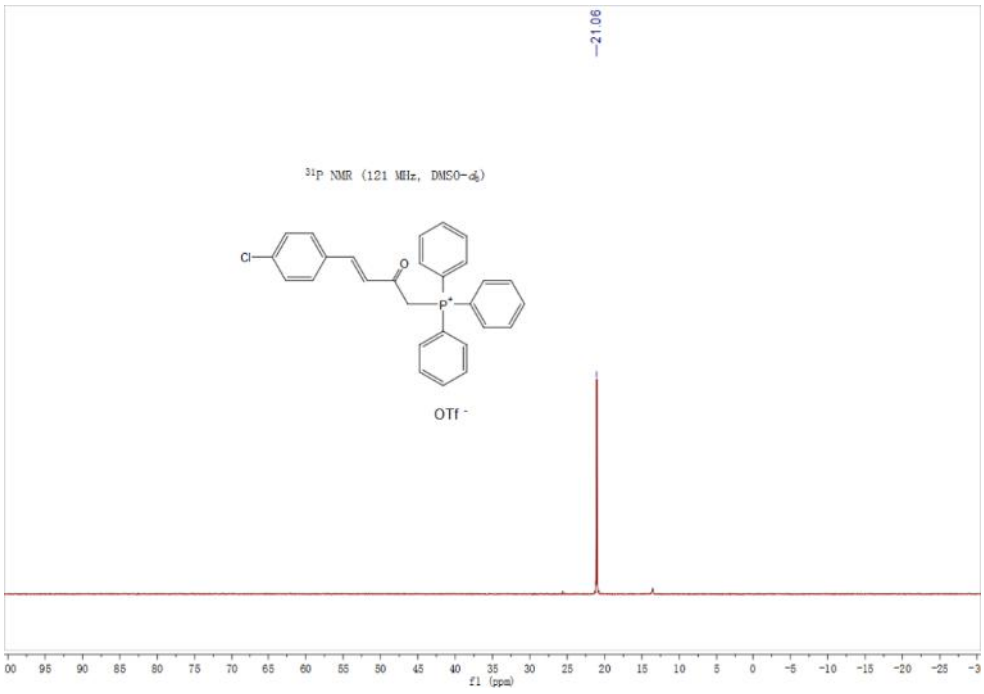

O
PPh3
Cl
OTf

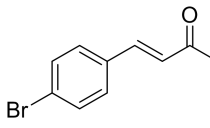
(1g)


7.88
7.86
7.84
7.82
7.79
7.77
7.62
7.57
7.55
7.00
6.96
5.82
5.79
3.39
2.50
1H NMR (400 MHz, DMSO-d6)
Cl
O
P+
OTf -
18.07
2.16
1.00
2.09
f1 (ppm)

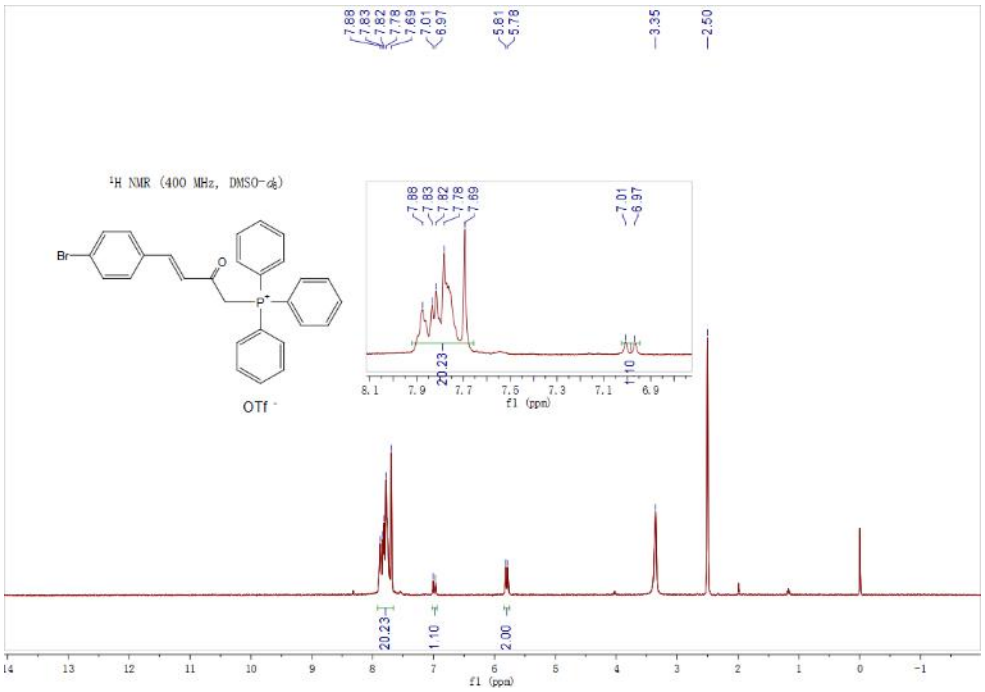

192.23
192.17
148.01
136.50
135.21
134.13
134.02
133.07
131.03
130.55
130.42
129.74
126.91
126.84
119.86
118.97
40.56
40.34
40.14
39.93
39.72
39.51
39.30
36.15
35.53
13C NMR (100 MHz, DMSO-d6)
Cl
O
P+
OTf -
f1 (ppm)

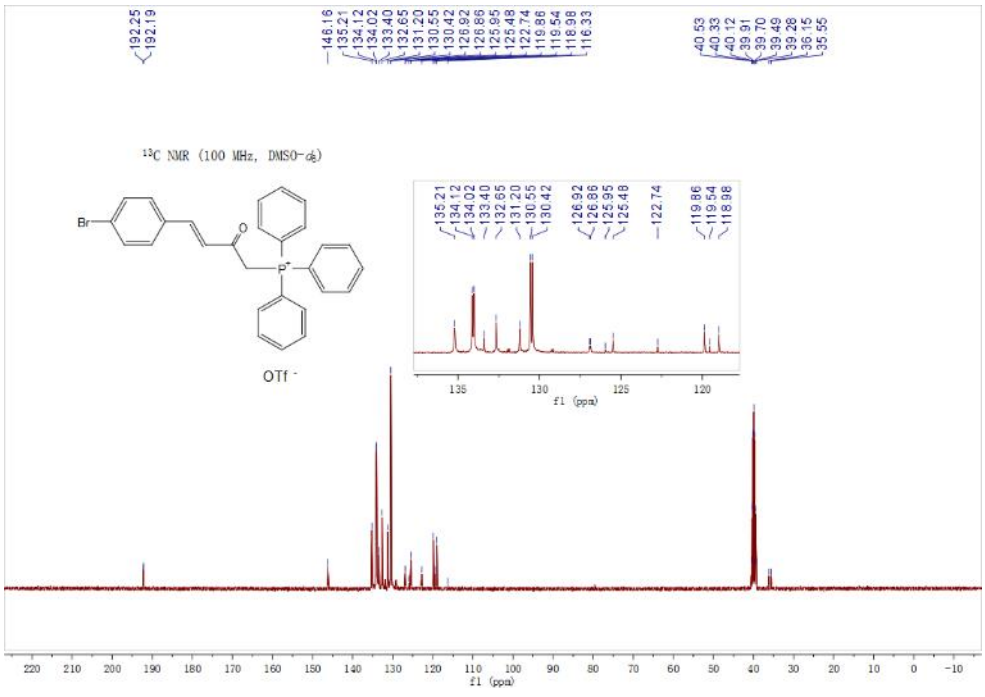

-77.81
^{19}F NMR (376 MHz, DMSO-d_6)
Cl
O
P+
OTf -
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

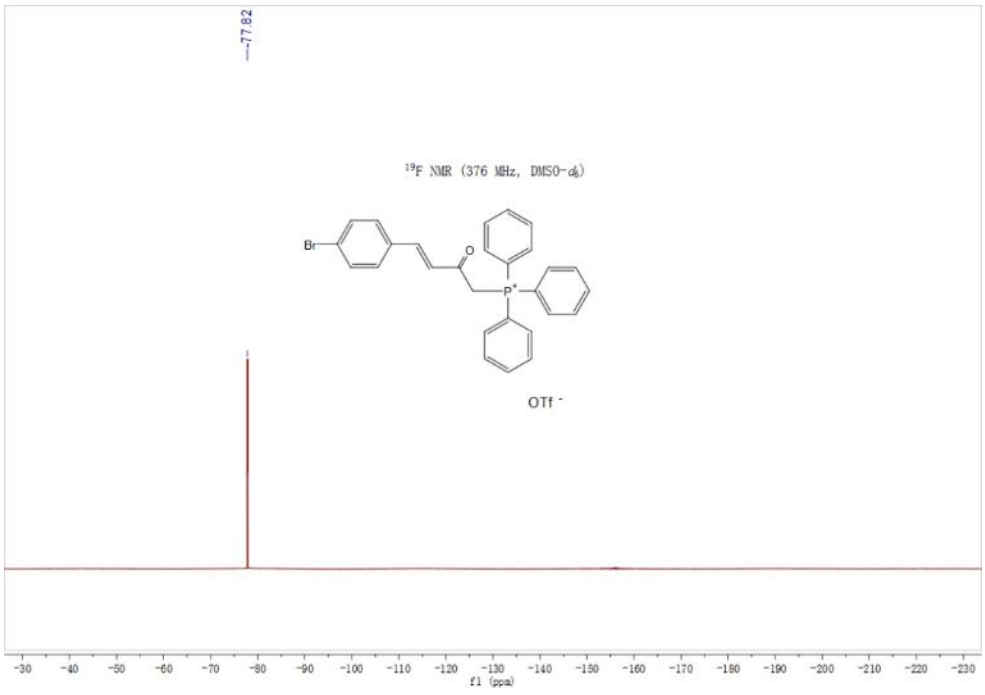

-21.06
^{31}P NMR (121 MHz, DMSO-d_6)
Cl
O
P+
OTf -
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

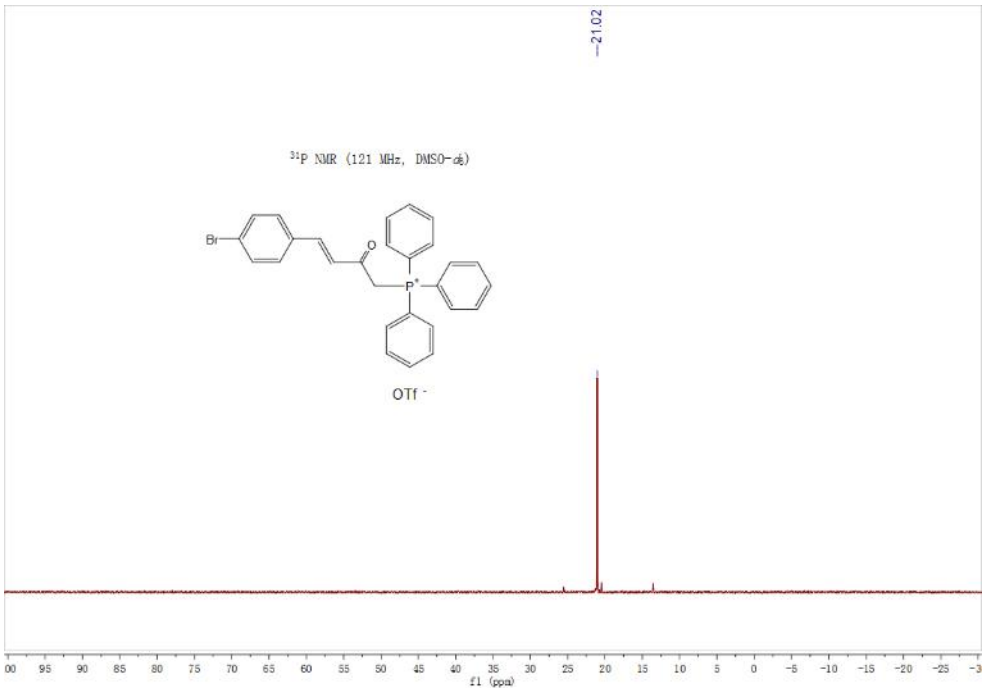

O
PPh3
Br
OTf

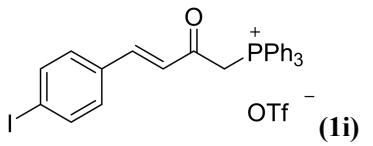
(1h)


7.88
7.83
7.82
7.78
7.69
7.01
6.97
5.81
5.78
3.35
2.50
1H NMR (400 MHz, DMSO-d6)
Br
O
P+
OTf -
20.23
1.10
2.00
f1 (ppm)

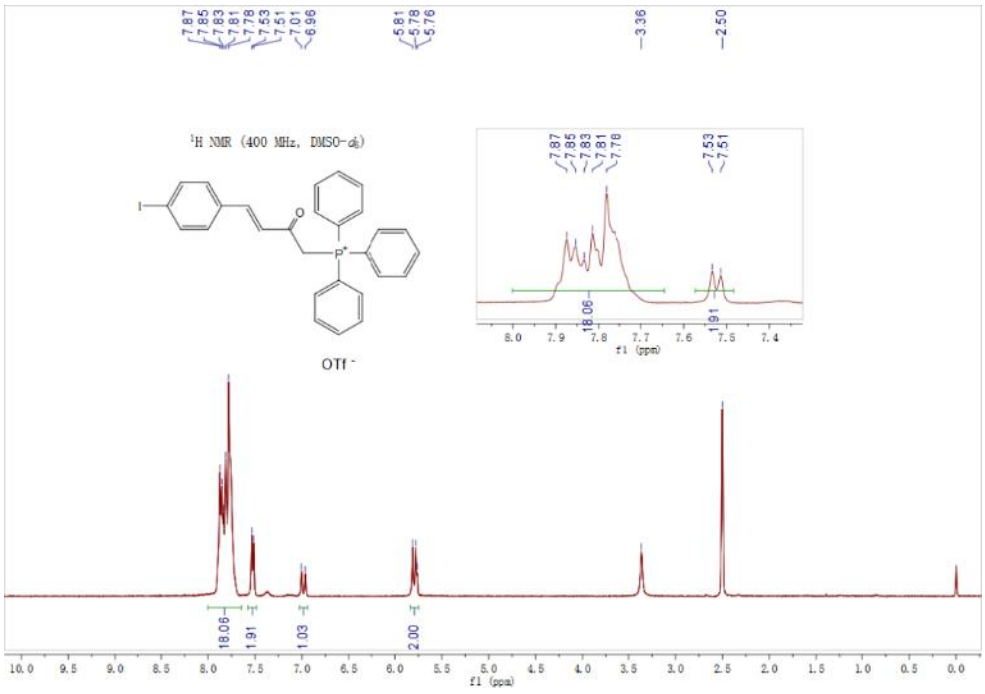

192.25
192.19
148.16
135.21
134.12
134.02
133.40
132.65
131.20
130.55
130.42
126.92
126.86
125.95
125.48
122.74
119.86
119.54
118.98
116.33
40.53
40.33
40.12
39.91
39.70
39.49
39.28
36.15
35.56
13C NMR (100 MHz, DMSO-d6)
Br
O
P+
OTf -
f1 (ppm)

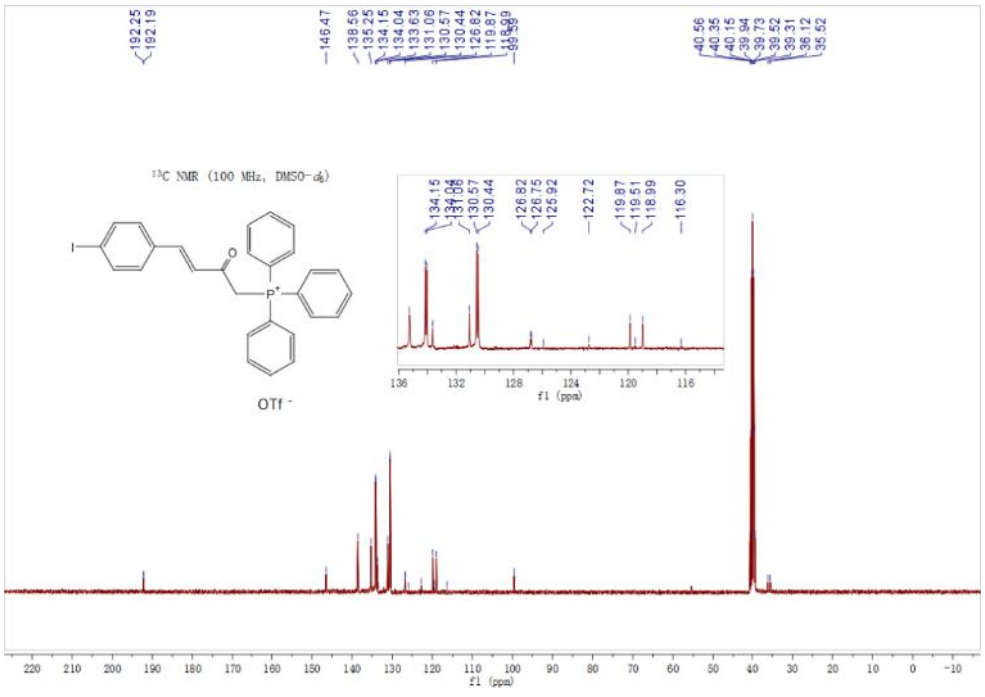

-77.62
^{19}F NMR (376 MHz, DMSO-d_6)
Br
O
P$^+$
OTf $^-$
f1 (ppm)

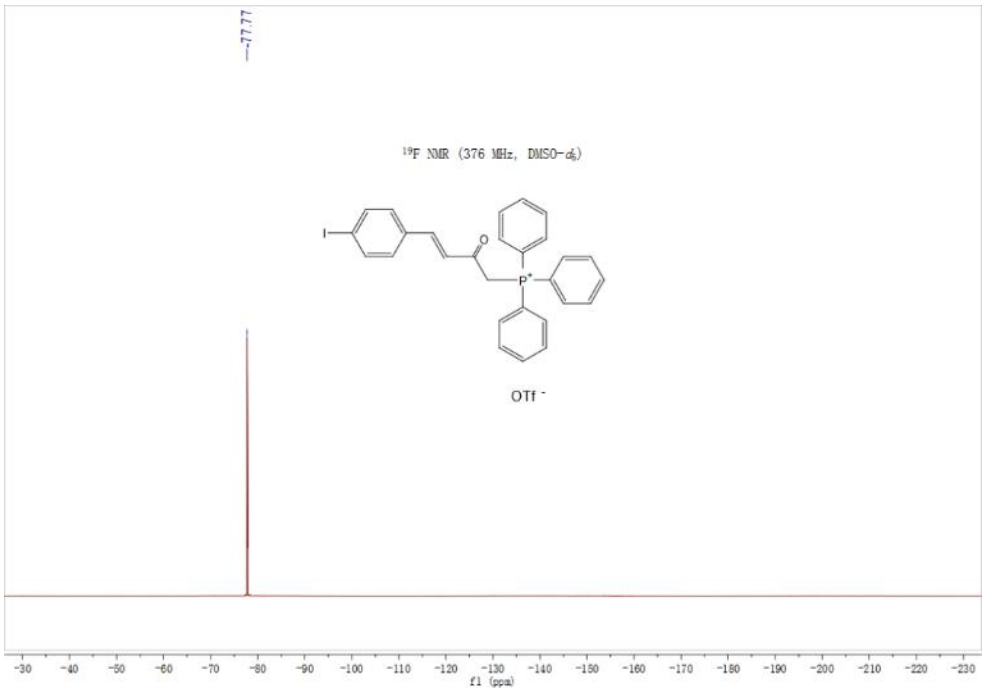

-21.02
^{31}P NMR (121 MHz, DMSO-d_6)
Br
O
P$^+$
OTf $^-$
f1 (ppm)

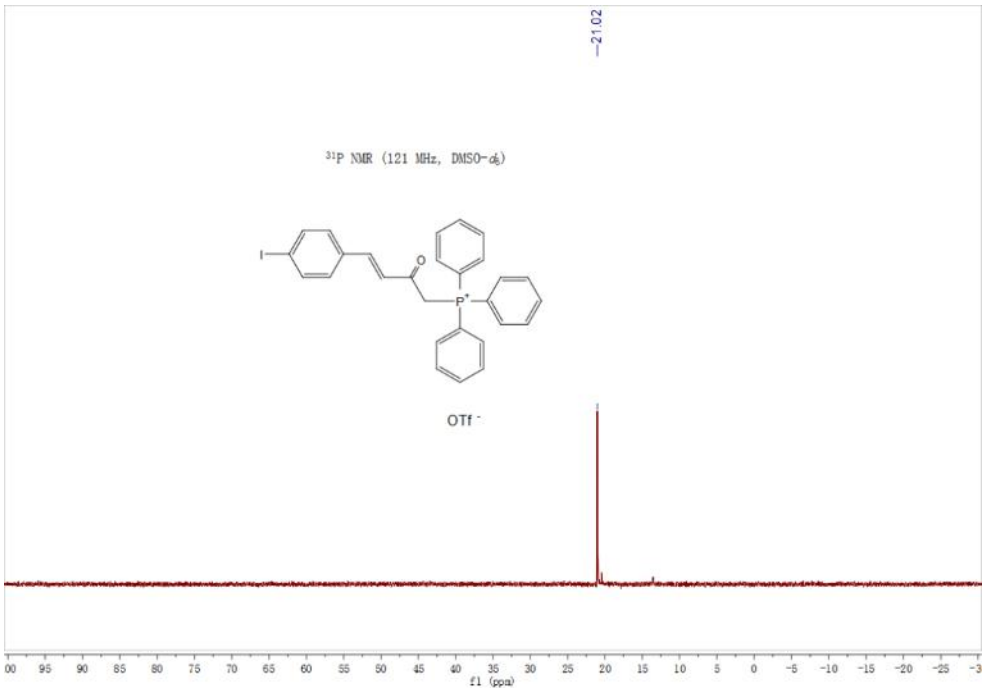

O
PPh3
+
OTf
−

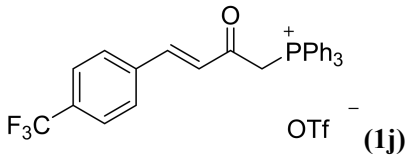
(1i)


7.87
7.85
7.83
7.81
7.78
7.53
7.51
7.01
6.96
5.81
5.78
5.76
3.36
2.50
1H NMR (400 MHz, DMSO-d6)
OTf -
18.06
1.91
1.03
2.00
f1 (ppm)

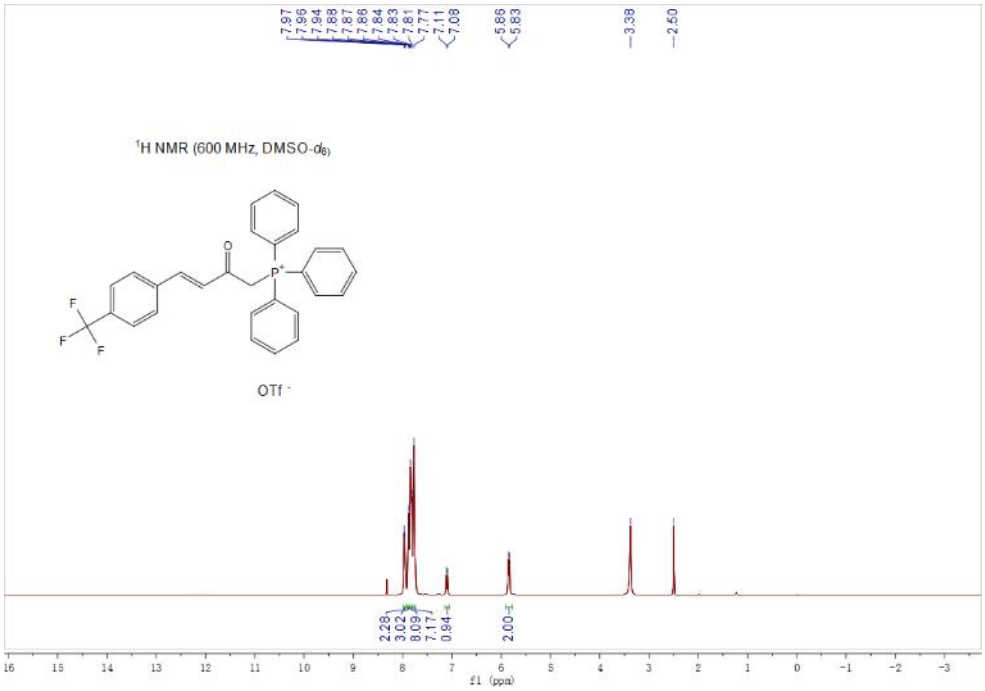

192.25
192.19
148.47
138.56
135.25
134.15
134.04
133.63
131.06
130.57
130.44
126.82
119.87
118.99
99.99
40.56
40.35
40.15
39.94
39.73
39.52
39.31
36.12
35.52
13C NMR (100 MHz, DMSO-d6)
OTf -
134.15
131.06
130.57
130.44
126.82
126.75
125.92
122.72
119.87
119.51
118.99
116.30
f1 (ppm)

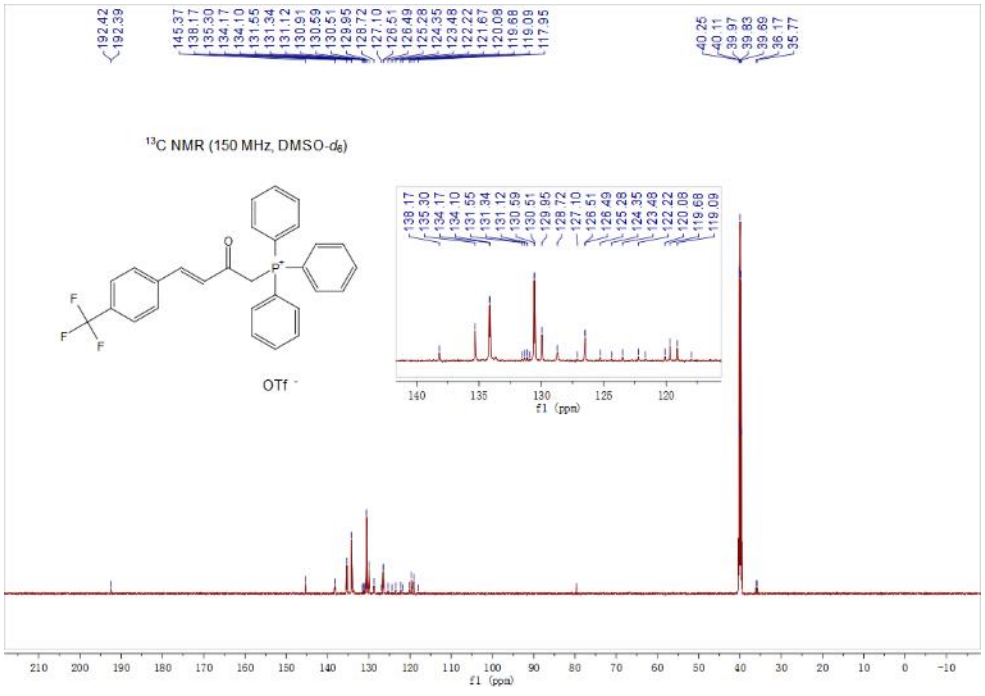

-77.77
^{19}F NMR (376 MHz, DMSO-d_6)
I
O
P$^+$
OTf $^-$
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

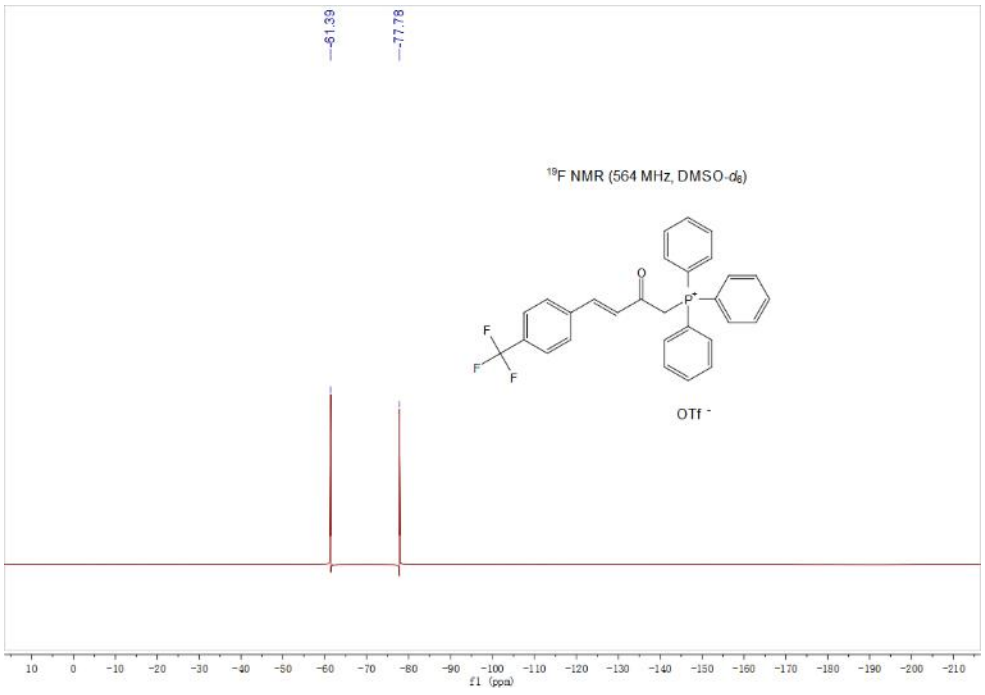

-21.02
^{31}P NMR (121 MHz, DMSO-d_6)
I
O
P$^+$
OTf $^-$
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -3
f1 (ppm)

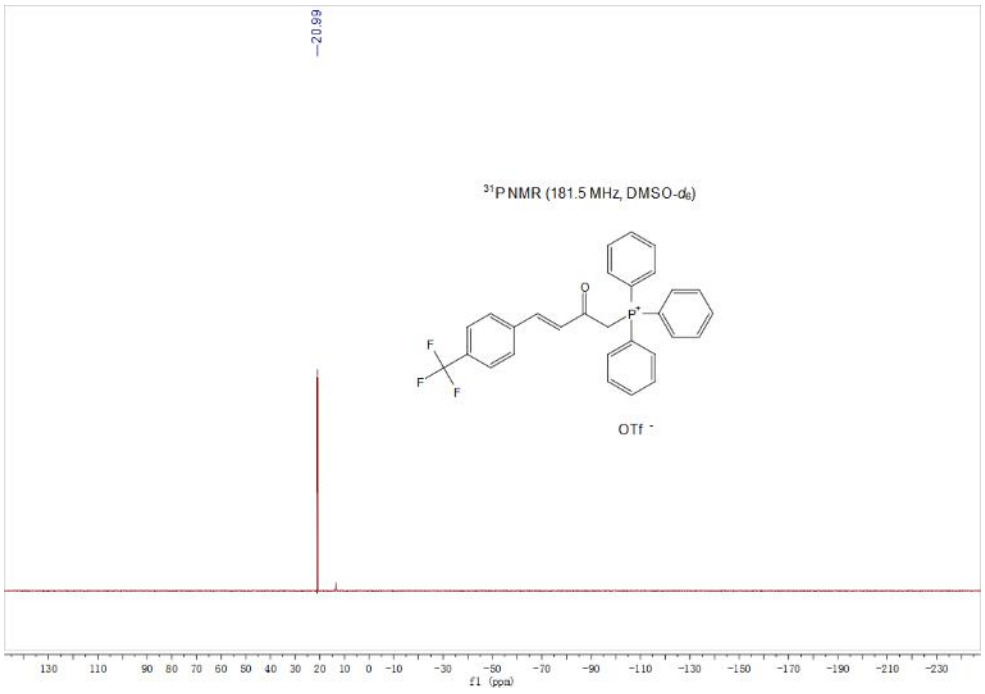

O
+
PPh3
F3C
OTf
−

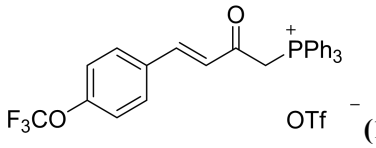
(1j)


7.97
7.96
7.94
7.88
7.87
7.86
7.84
7.83
7.81
7.77
7.11
7.08
5.86
5.83
3.38
2.50
1H NMR (600 MHz, DMSO-d6)
OTf
2.28
3.02
8.09
7.17
0.84
2.00
f1 (ppm)

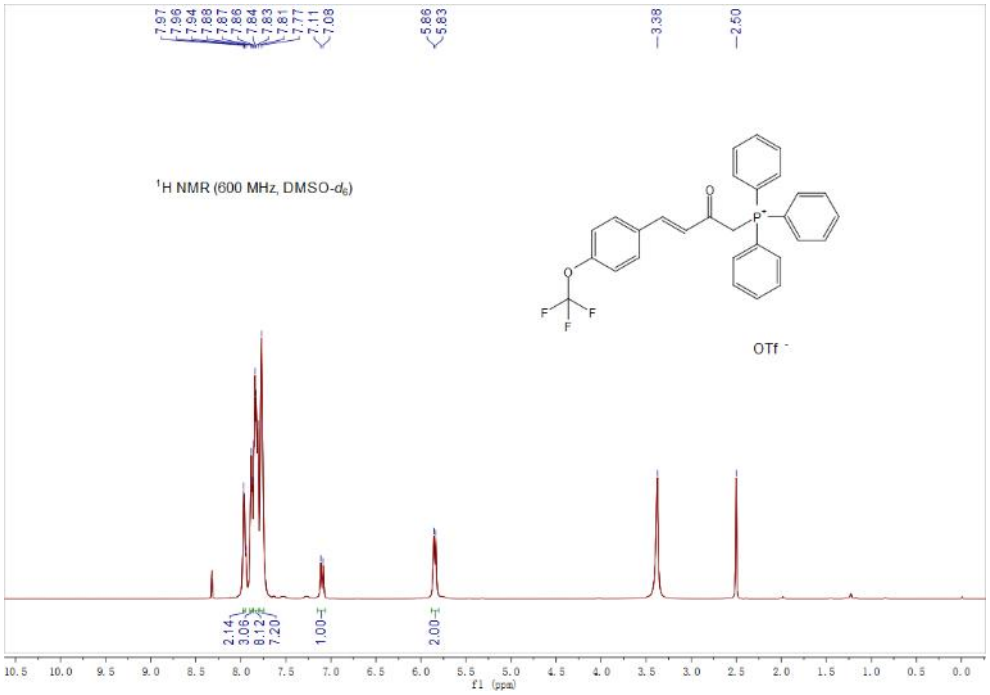

192.42
192.39
145.37
138.17
135.30
134.17
134.10
131.55
131.34
131.12
130.91
130.59
130.51
129.95
128.72
127.10
126.51
126.49
125.28
124.35
123.48
122.22
121.67
120.08
119.68
119.09
117.95
40.25
40.11
39.97
39.83
39.69
36.17
35.77
13C NMR (150 MHz, DMSO-d6)
OTf
f1 (ppm)

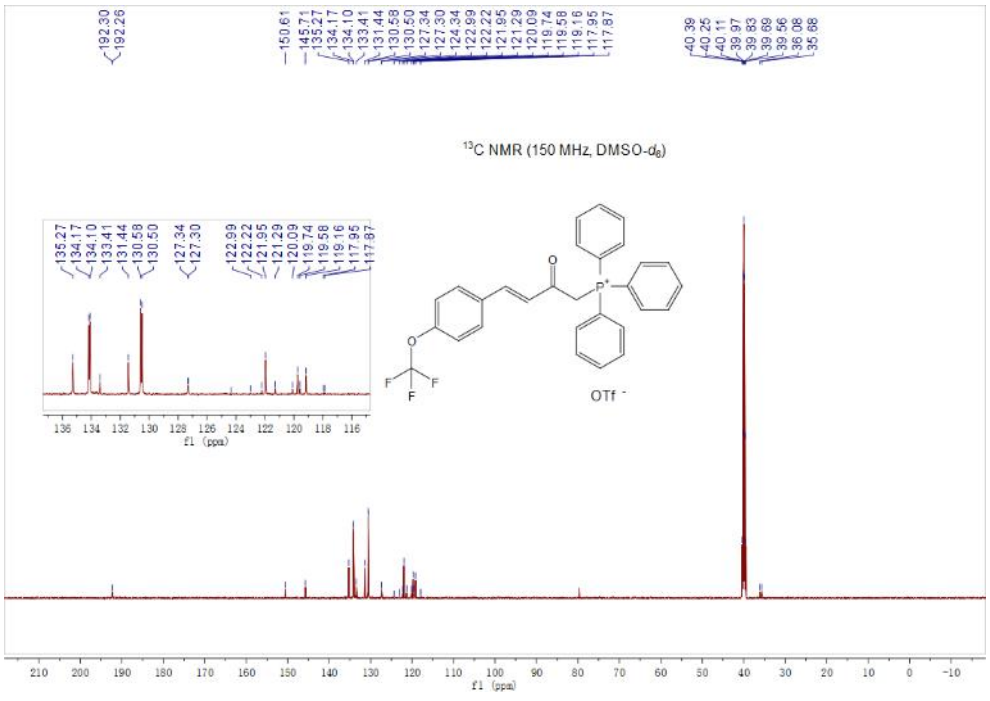

-61.39
-77.78
^{19}F NMR (564 MHz, DMSO-d_6)
O
P+
F
F
F
OTf -
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

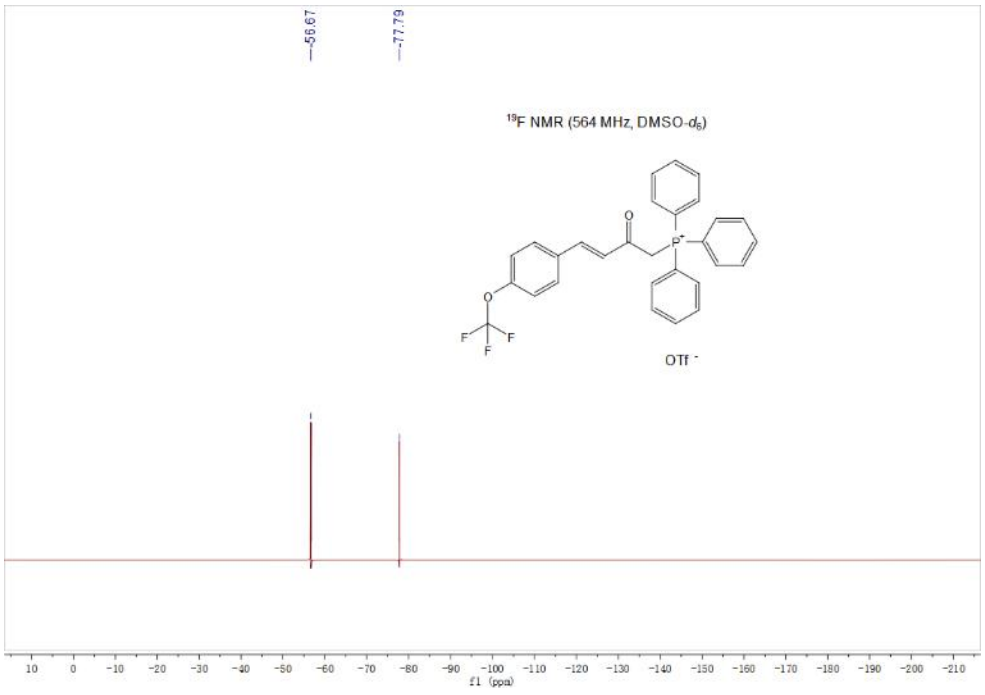

-20.99
^{31}P NMR (181.5 MHz, DMSO-d_6)
O
P+
F
F
F
OTf -
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

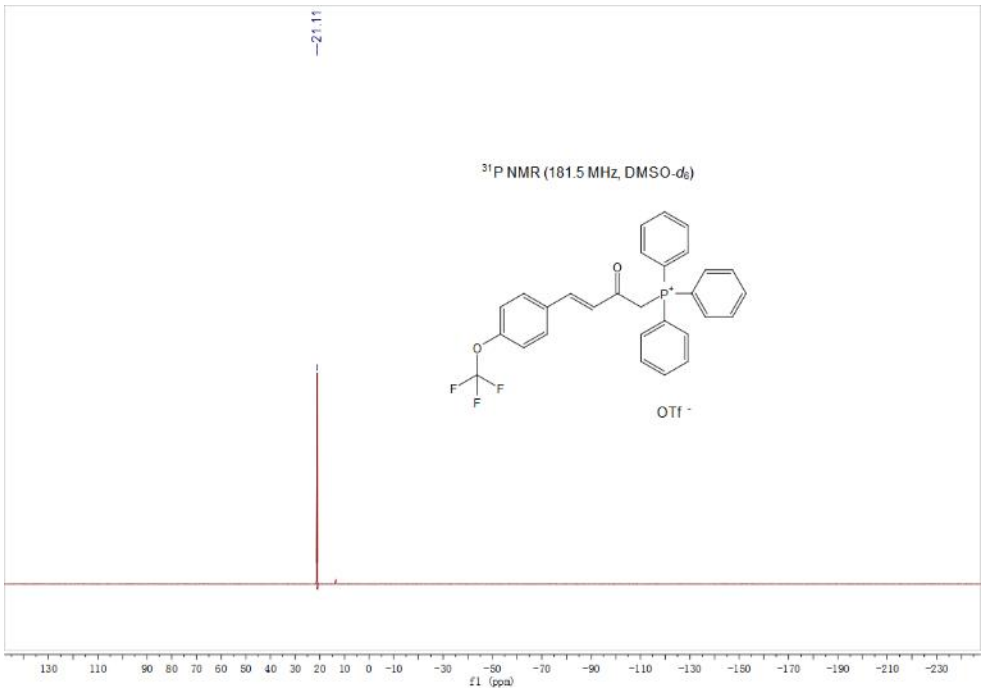

O
PPh3
F3CO
OTf

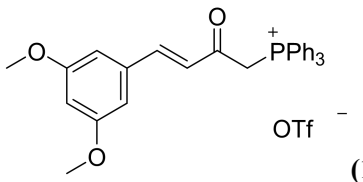
(1k)


7.97
7.96
7.94
7.88
7.87
7.86
7.84
7.83
7.81
7.77
7.11
7.08
5.86
5.83
3.38
2.50
1H NMR (600 MHz, DMSO-d6)
OTf
2.14
3.06
8.12
7.20
1.00
2.00
f1 (ppm)

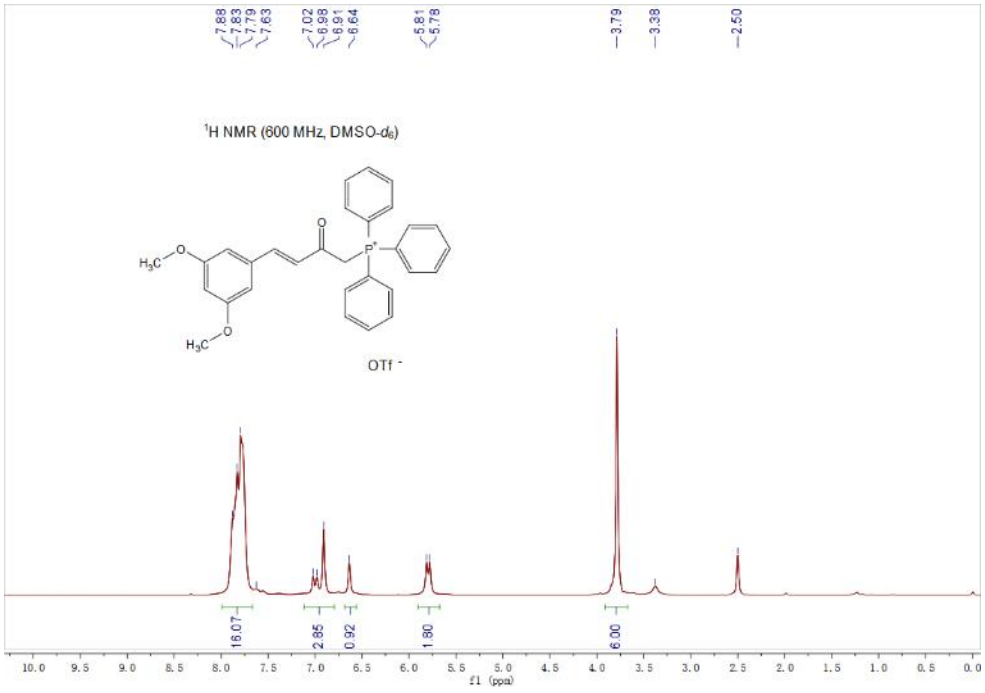

192.30
192.26
150.61
145.71
135.27
134.17
134.10
133.41
131.44
130.58
130.50
127.34
127.30
124.34
122.99
122.22
121.95
121.29
120.09
119.74
119.58
119.16
117.95
117.87
40.39
40.25
40.11
39.97
39.83
39.69
39.56
36.08
35.68
13C NMR (150 MHz, DMSO-d6)
OTf
f1 (ppm)

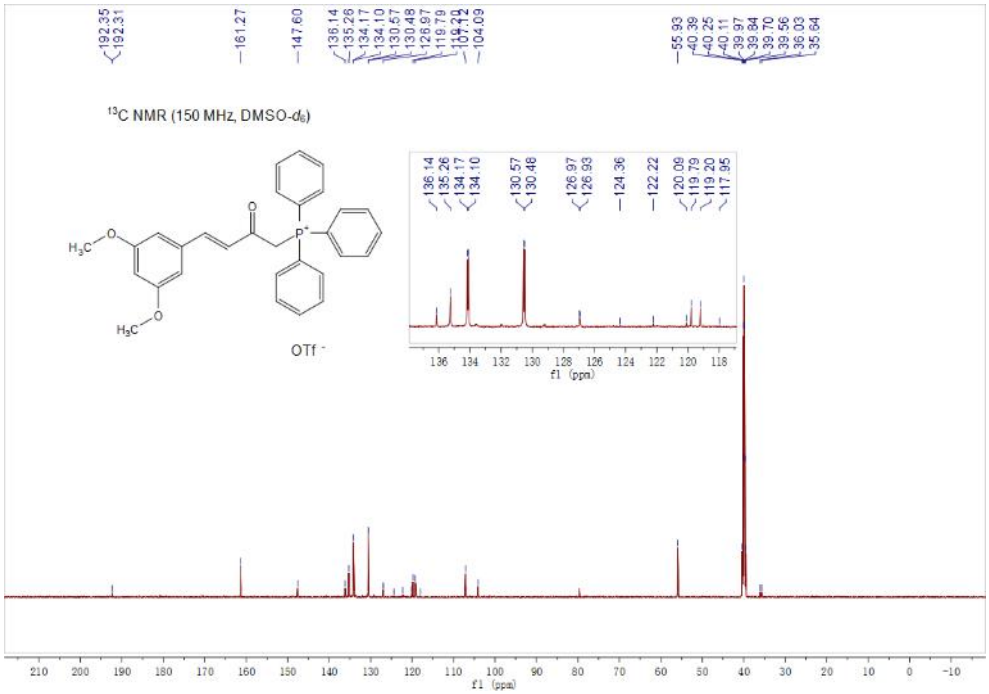

-56.67
-77.79
19F NMR (564 MHz, DMSO-d6)
O
P+
O
F
F
F
OTf -
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

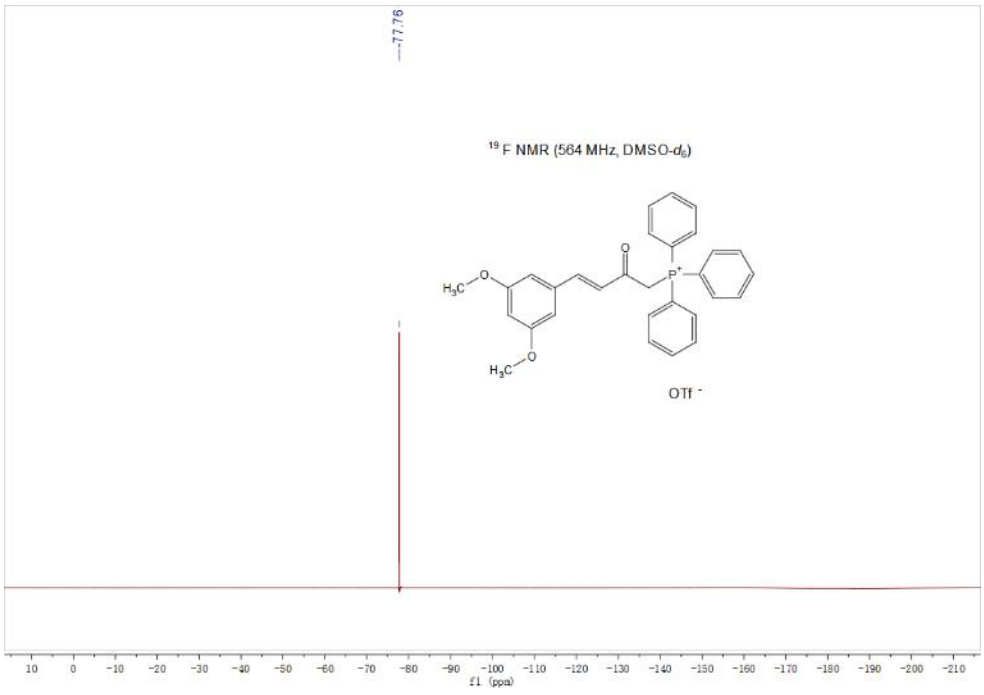

-21.11
31P NMR (181.5 MHz, DMSO-d6)
O
P+
O
F
F
F
OTf -
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

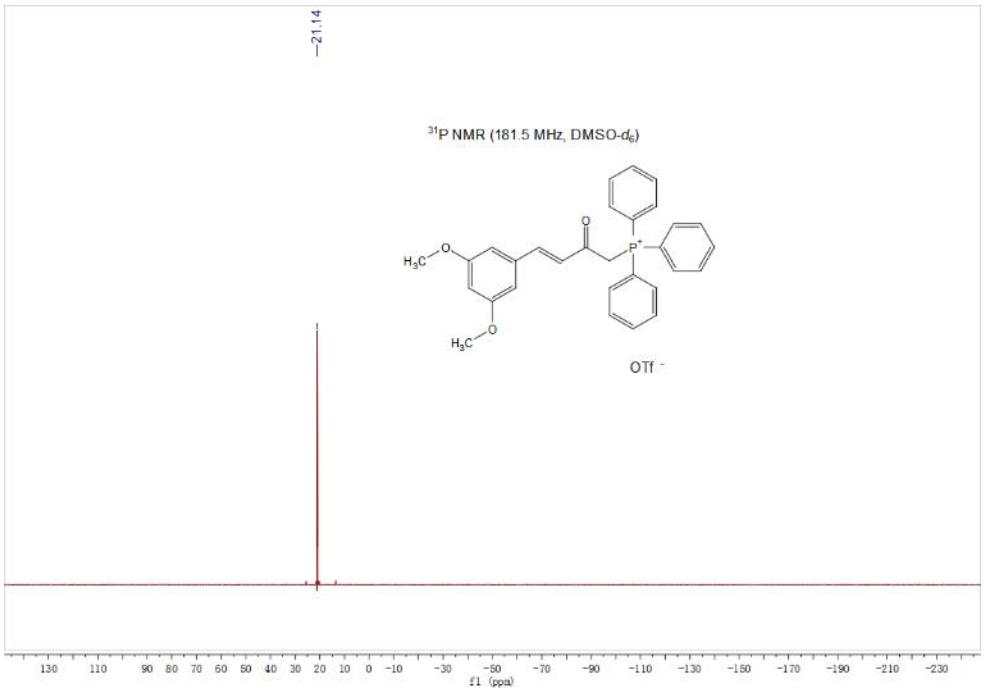

O
+
PPh3
O
OTf
−
O

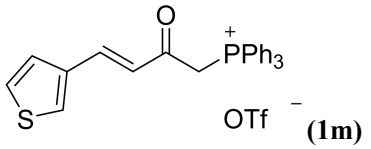
(1l)


7.88
7.83
7.79
7.63
7.02
6.98
6.91
6.64
5.81
5.78
3.79
3.38
2.50
1H NMR (600 MHz, DMSO-d6)
OTf -
16.07
2.85
0.92
1.80
6.00
f1 (ppm)

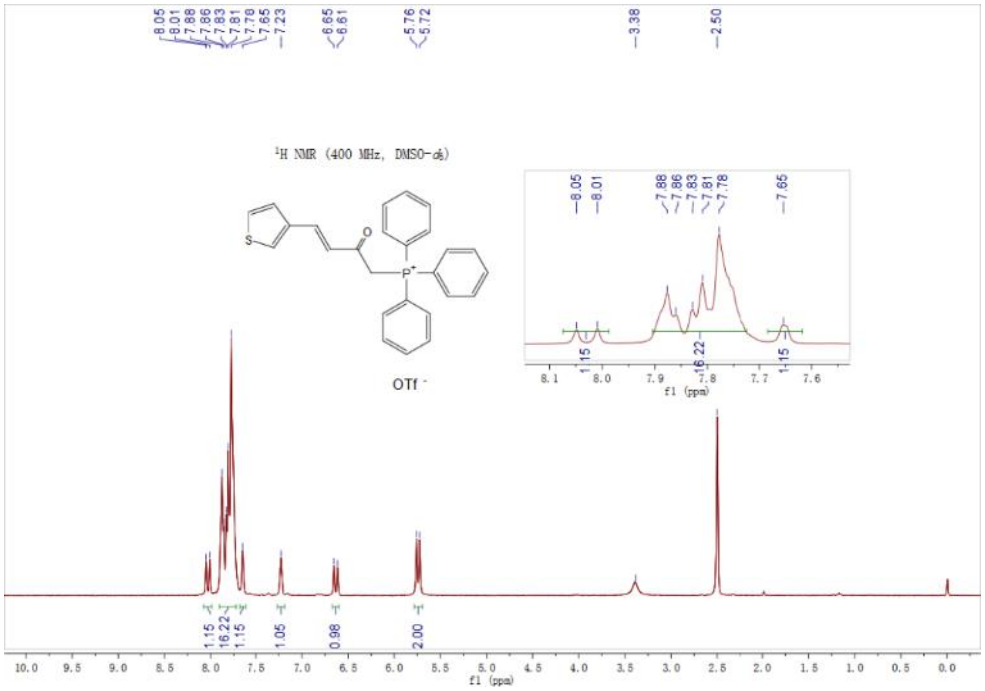

192.35
192.31
161.27
147.60
136.14
135.26
134.17
134.10
130.57
130.48
126.97
119.79
104.42
104.09
55.93
40.39
40.25
40.11
39.97
39.84
39.70
39.56
39.03
35.64
13C NMR (150 MHz, DMSO-d6)
OTf -
f1 (ppm)

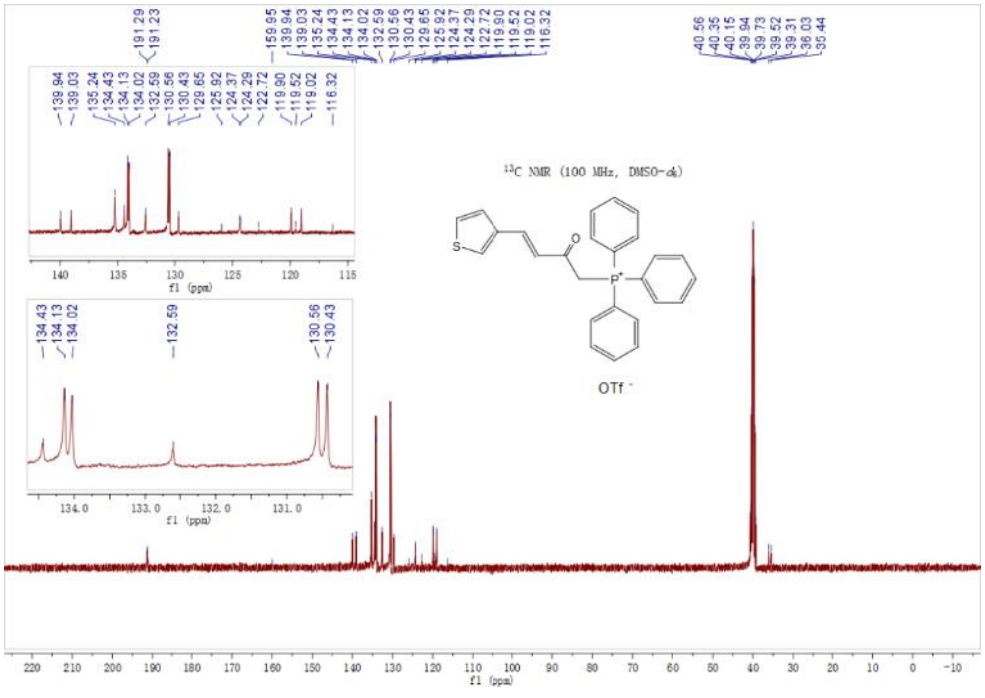

-77.76
^{19}F NMR (564 MHz, DMSO-d_6)
H_3C
O
O
H_3C
O
P^+
OTf $^-$
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

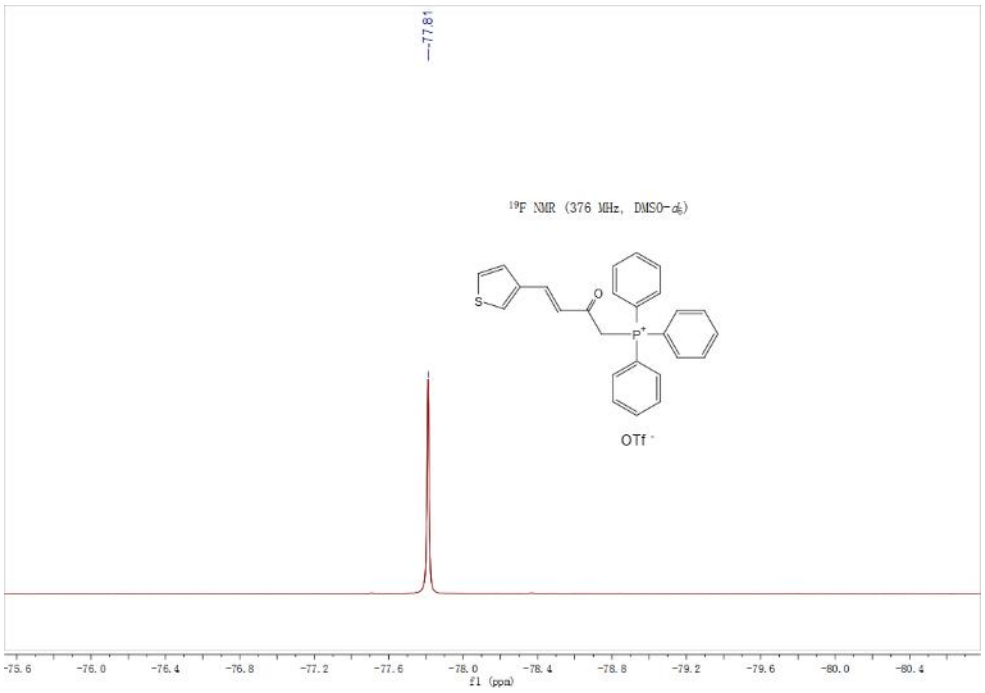

-21.14
^{31}P NMR (181.5 MHz, DMSO-d_6)
H_3C
O
O
H_3C
O
P^+
OTf $^-$
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

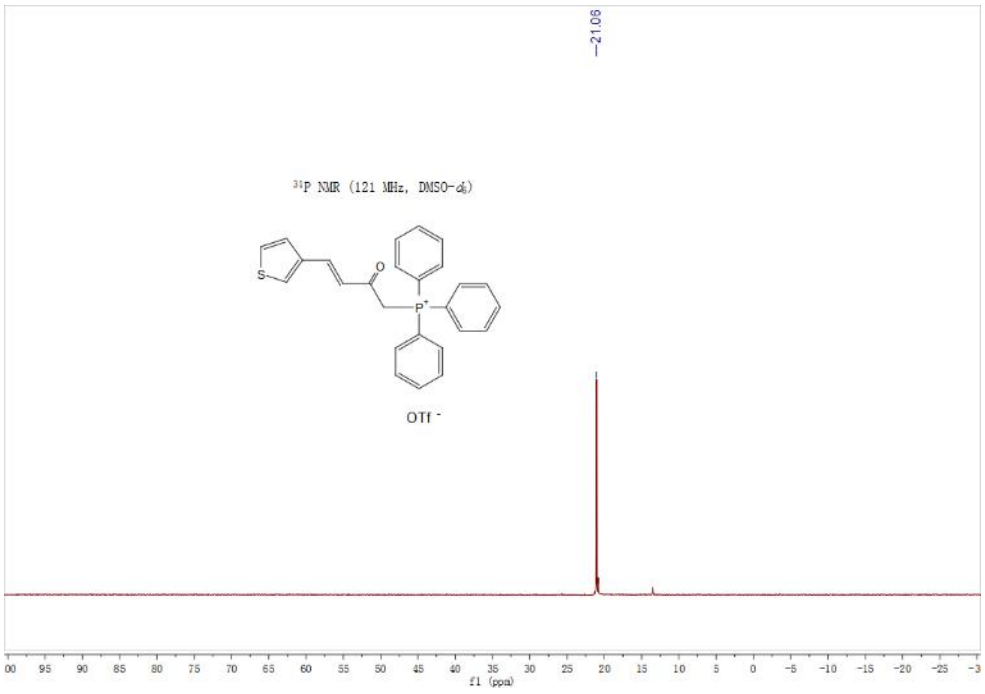

O
PPh3
+
S
OTf
−

(1m)

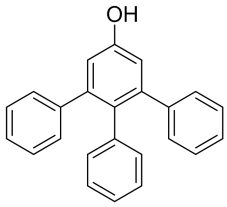

8.05
8.01
7.88
7.86
7.83
7.81
7.78
7.65
7.23
6.65
6.61
5.76
5.72
3.38
2.50
1H NMR (400 MHz, DMSO-d6)
OTf
1.15
16.22
1.15
1.05
0.98
2.00
f1 (ppm)


191.29
191.23
159.95
139.94
139.03
135.24
134.43
134.13
134.02
132.59
130.56
130.43
129.65
125.92
124.37
124.29
122.72
119.90
119.52
119.02
116.32
40.56
40.35
40.15
39.94
39.73
39.52
39.31
36.03
35.44
13C NMR (100 MHz, DMSO-d6)
OTf
f1 (ppm)

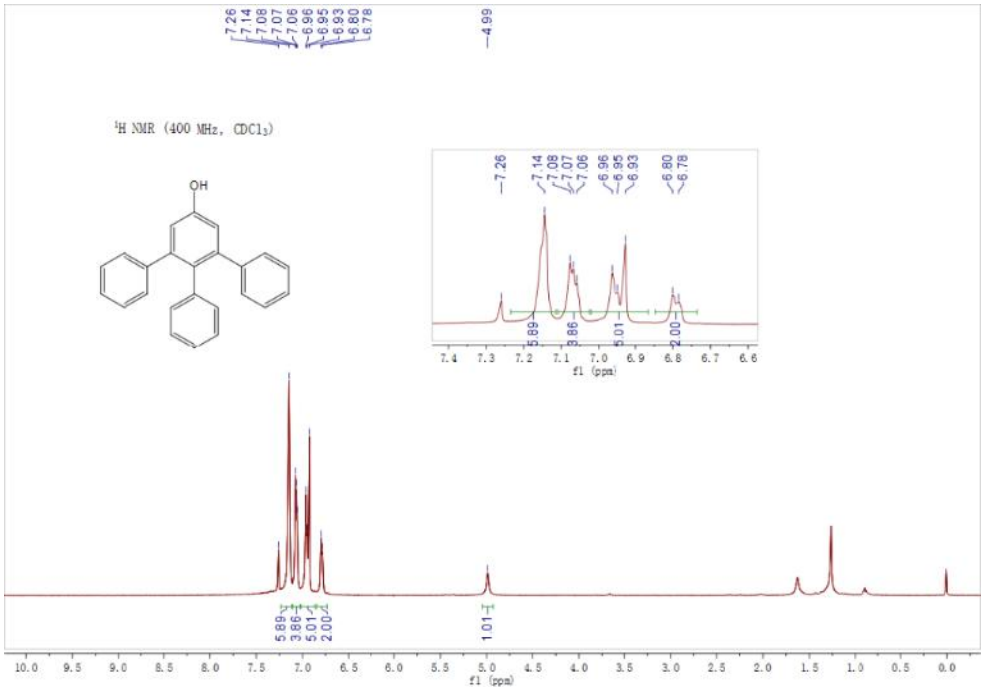

-77.81
^{19}F NMR (376 MHz, DMSO-d_6)
S
O
P$^+$
OTf$^-$
-75.6
-76.0
-76.4
-76.8
-77.2
-77.6
-78.0
-78.4
-78.8
-79.2
-79.6
-80.0
-80.4
f1 (ppm)

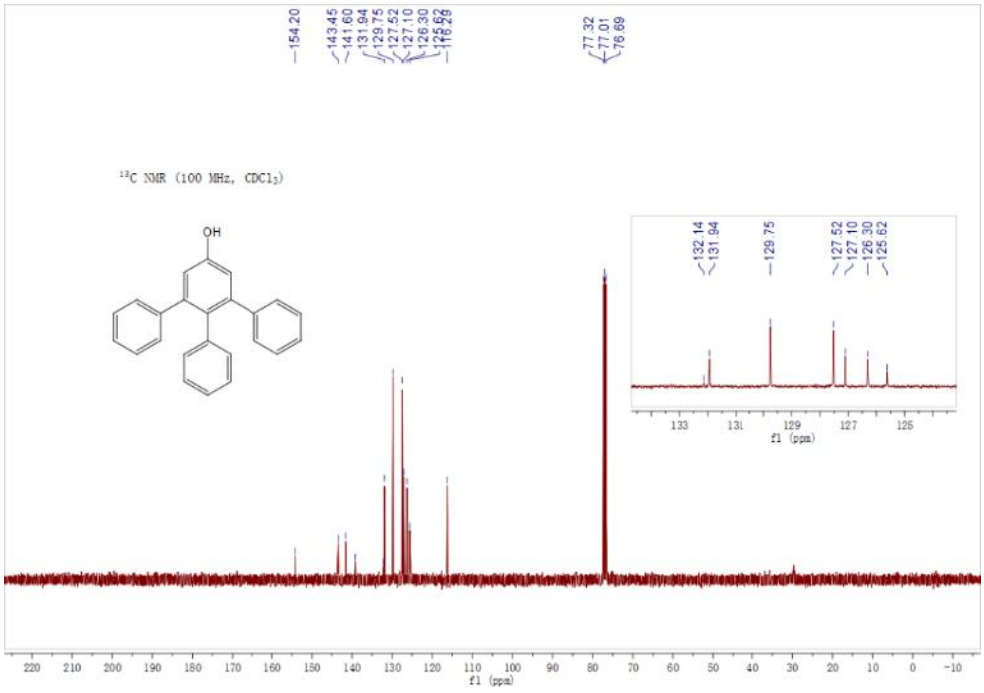

-21.06
^{31}P NMR (121 MHz, DMSO-d_6)
S
O
P$^+$
OTf$^-$
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

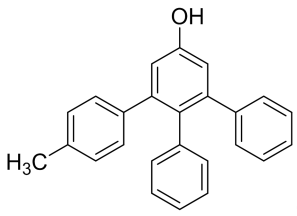
The ^{1}H and ^{13}C NMR spectra of compounds



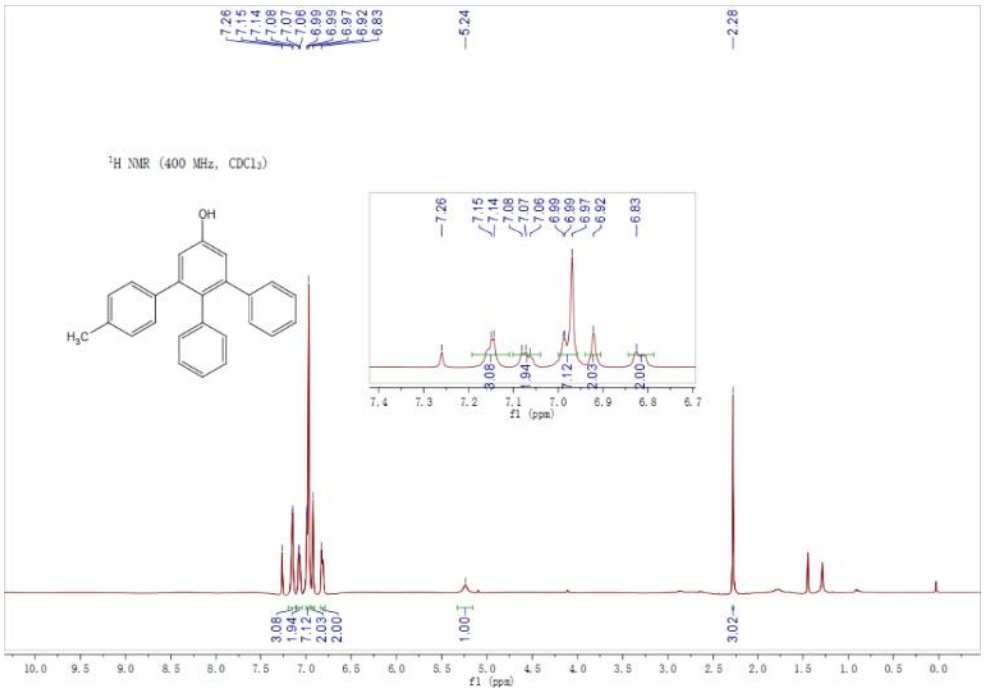
(3a)

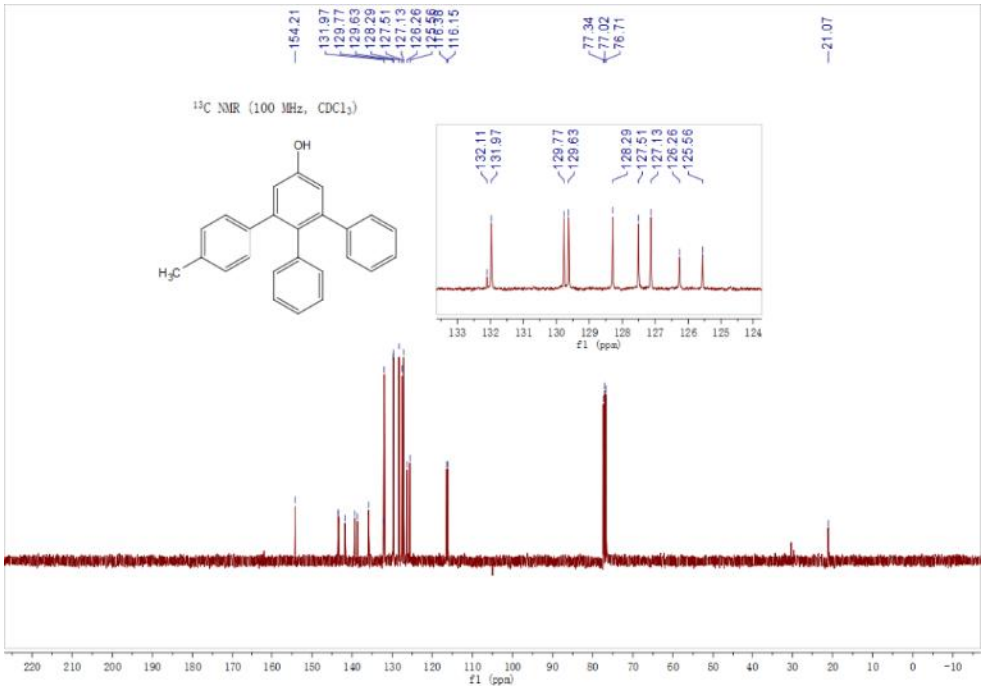


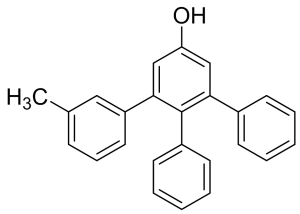



OH
H3C

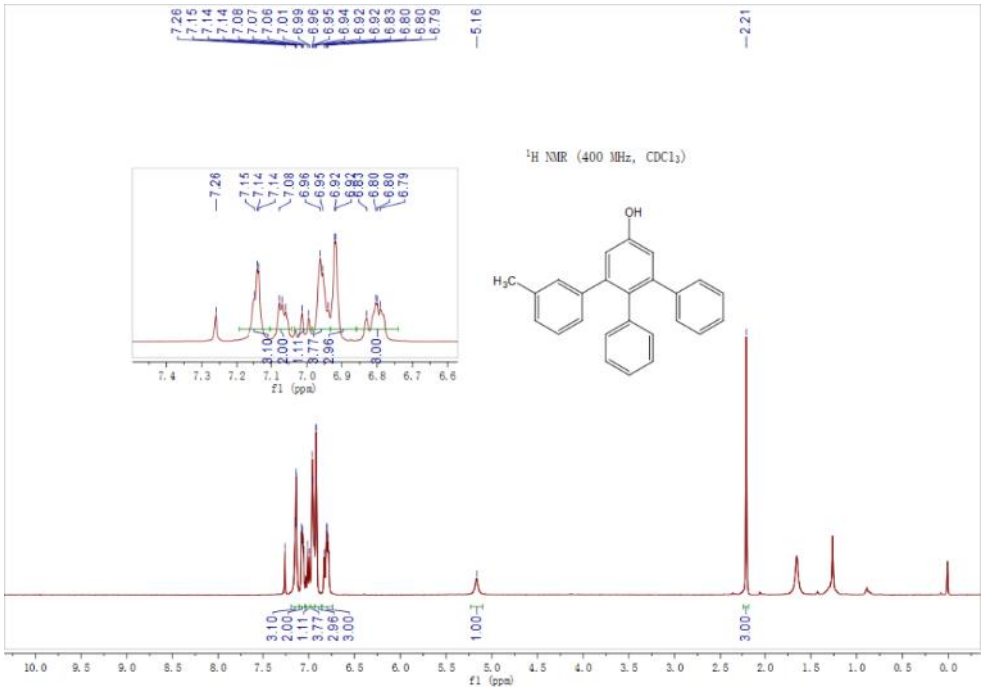
(3b)

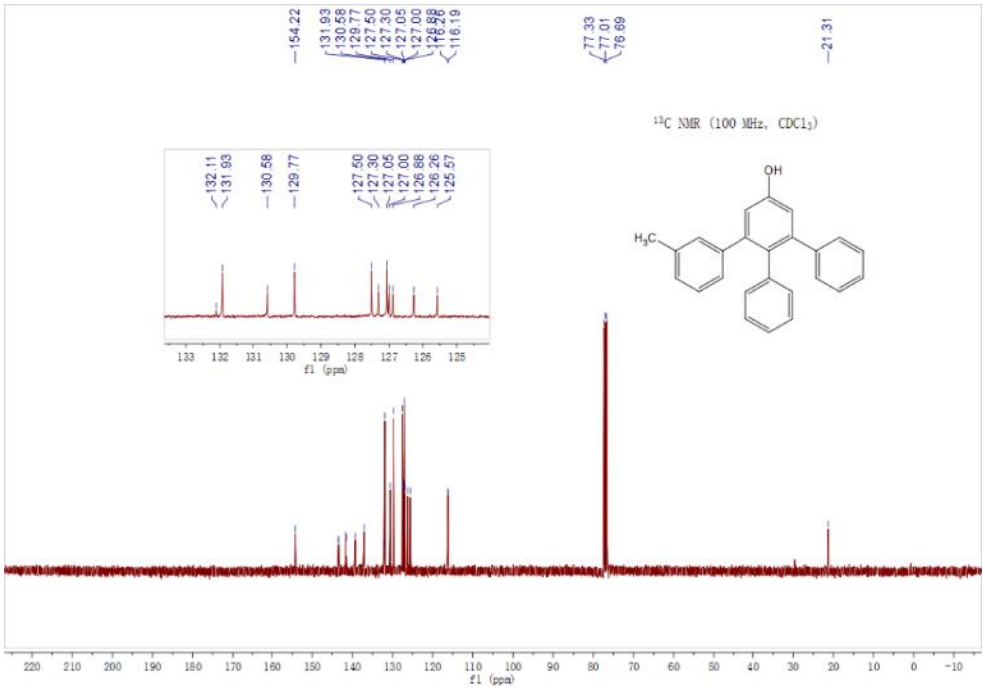

7.26
7.15
7.14
7.08
7.07
7.06
6.99
6.99
6.97
6.92
6.83
5.24
2.28
1H NMR (400 MHz, CDCl3)
OH
H3C
3.08
1.94
7.12
2.03
2.00
1.00
3.02
f1 (ppm)

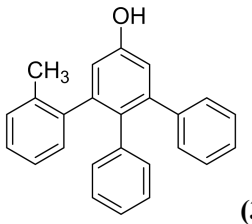

154.21
131.97
129.77
129.63
128.29
127.51
127.13
126.26
125.56
116.15
77.34
77.02
76.71
21.07
13C NMR (100 MHz, CDCl3)
OH
H3C
132.11
131.97
129.77
129.63
128.29
127.51
127.13
126.26
125.56
f1 (ppm)


OH
H3C

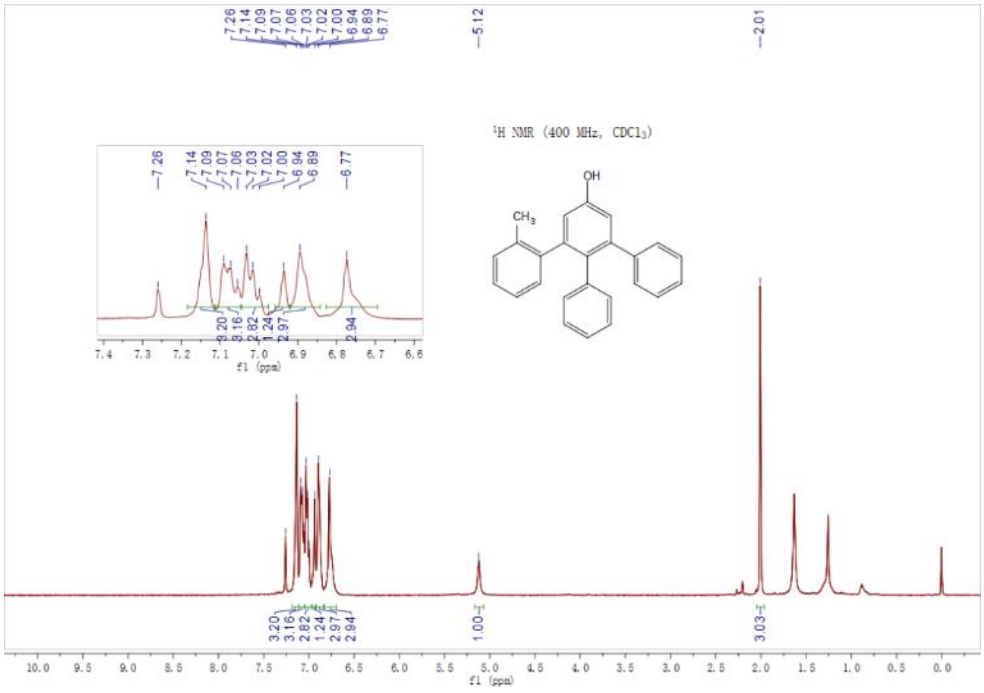
(3c)

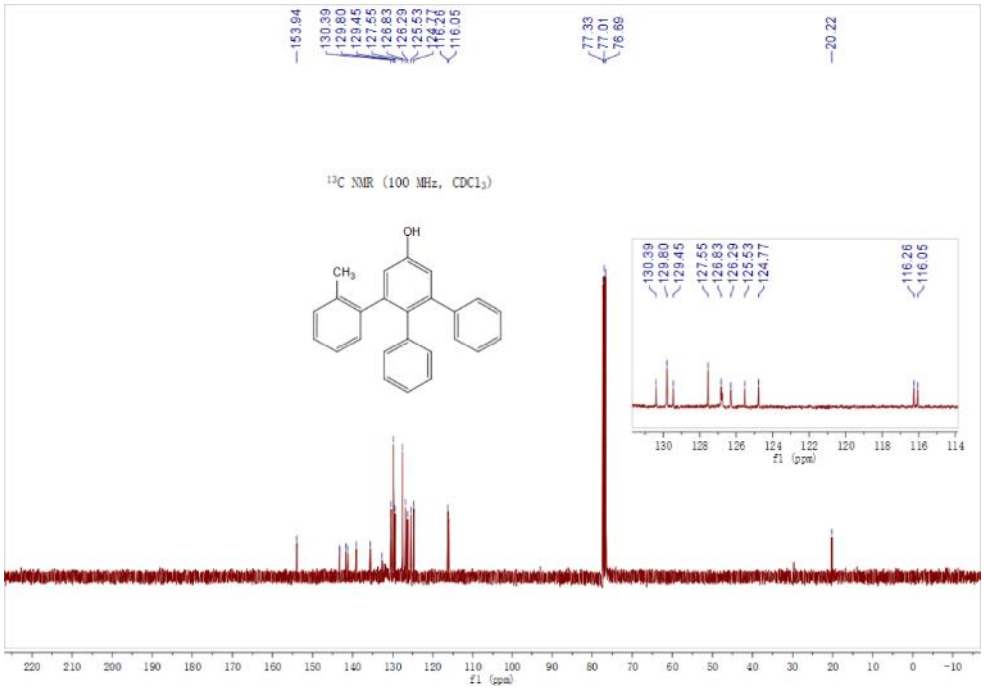

1H NMR (400 MHz, CDCl3)
OH
H3C
f1 (ppm)

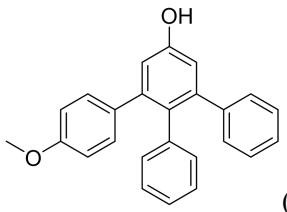

13C NMR (100 MHz, CDCl3)
OH
H3C
f1 (ppm)


OH
CH3

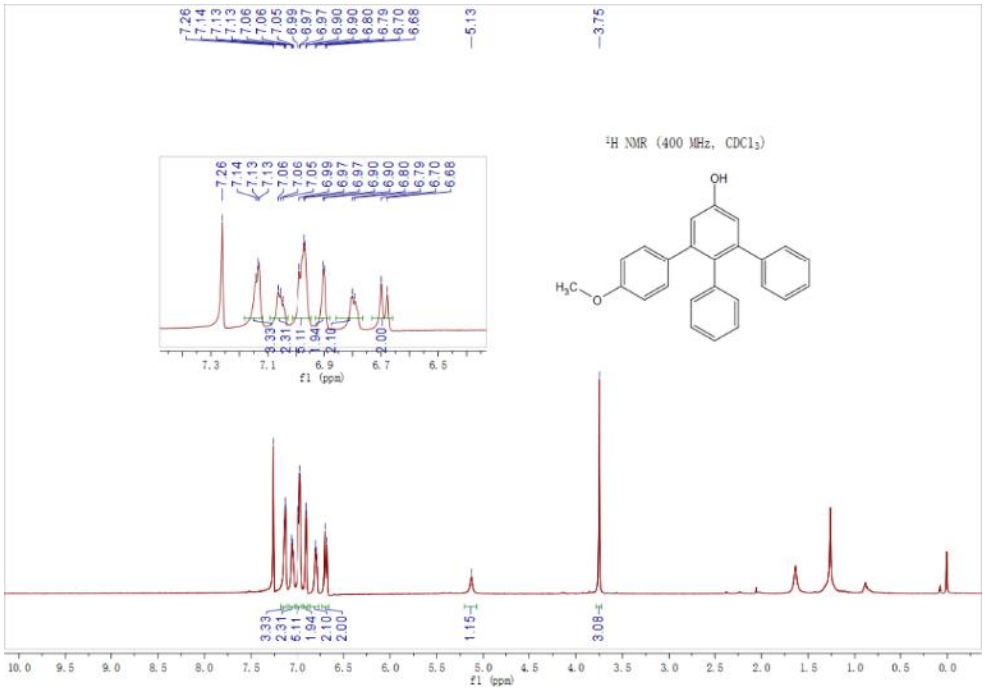
(3d)

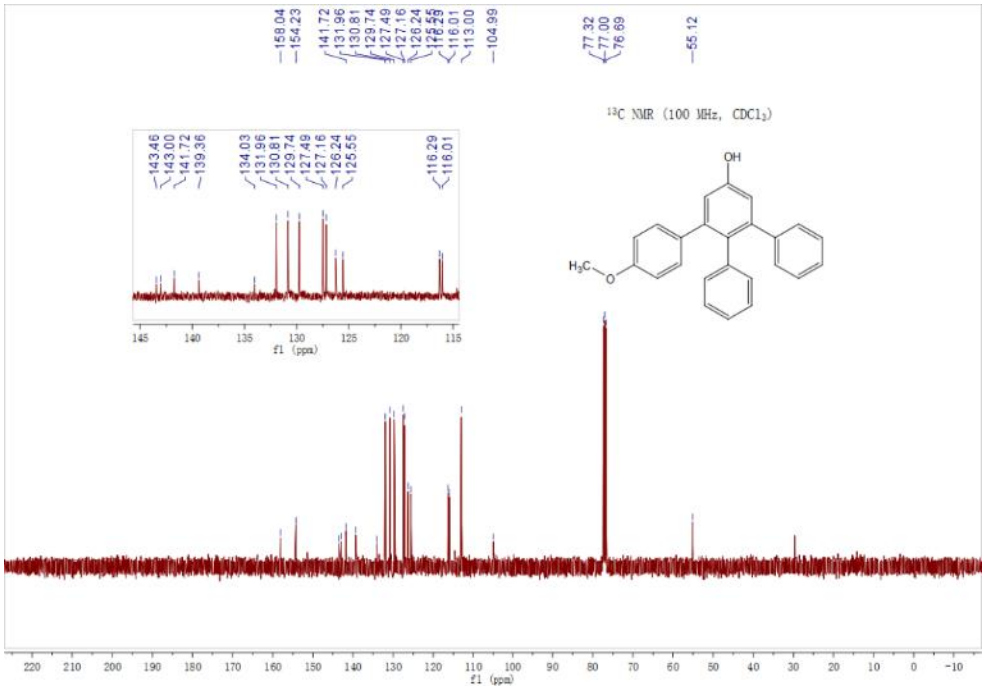

7.26
7.14
7.09
7.07
7.06
7.03
7.02
7.00
6.94
6.89
6.77
5.12
2.01
1H NMR (400 MHz, CDCl3)
OH
CH3
3.20
3.16
2.82
1.24
2.97
2.94
1.00
3.03
f1 (ppm)

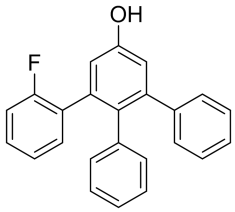

153.94
130.39
129.80
129.45
127.55
126.83
126.29
125.53
124.77
116.26
116.05
77.33
77.01
76.89
20.22
13C NMR (100 MHz, CDCl3)
OH
CH3
f1 (ppm)



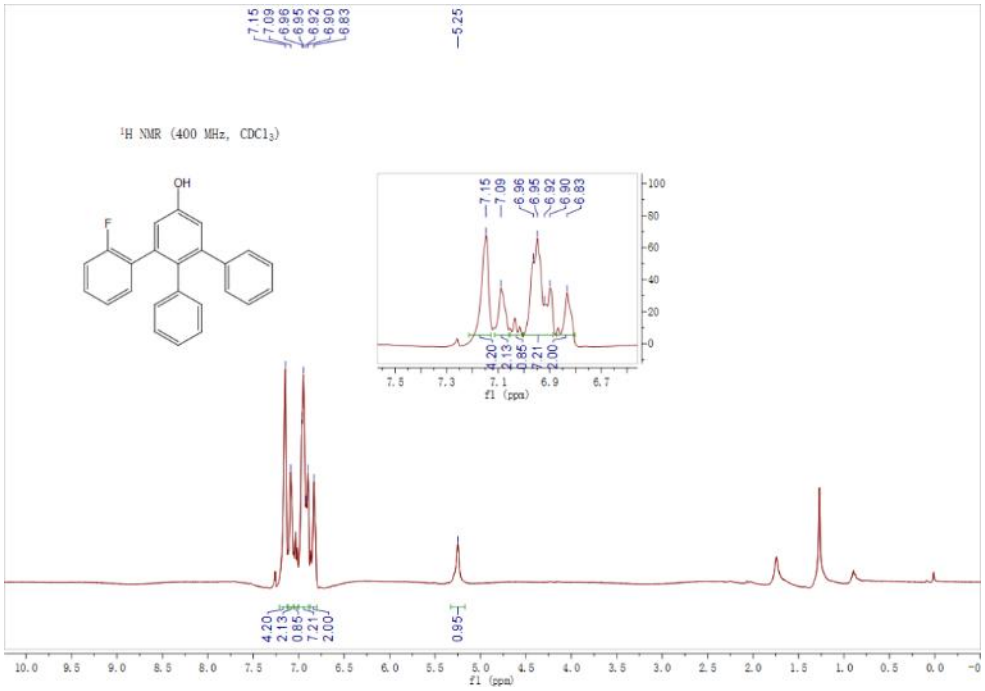
(**3e**)

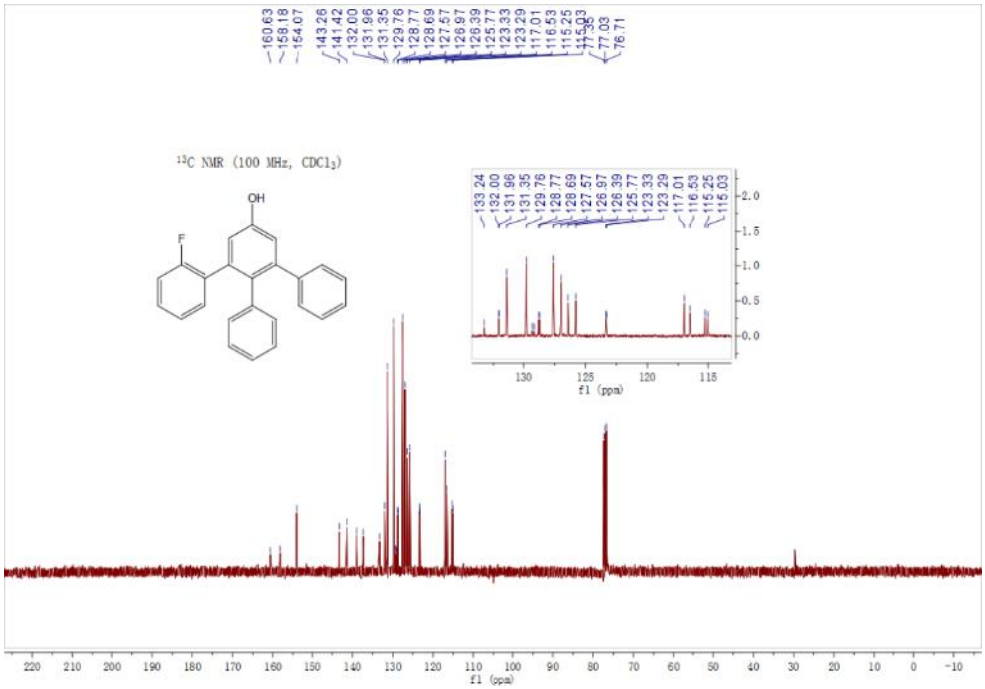


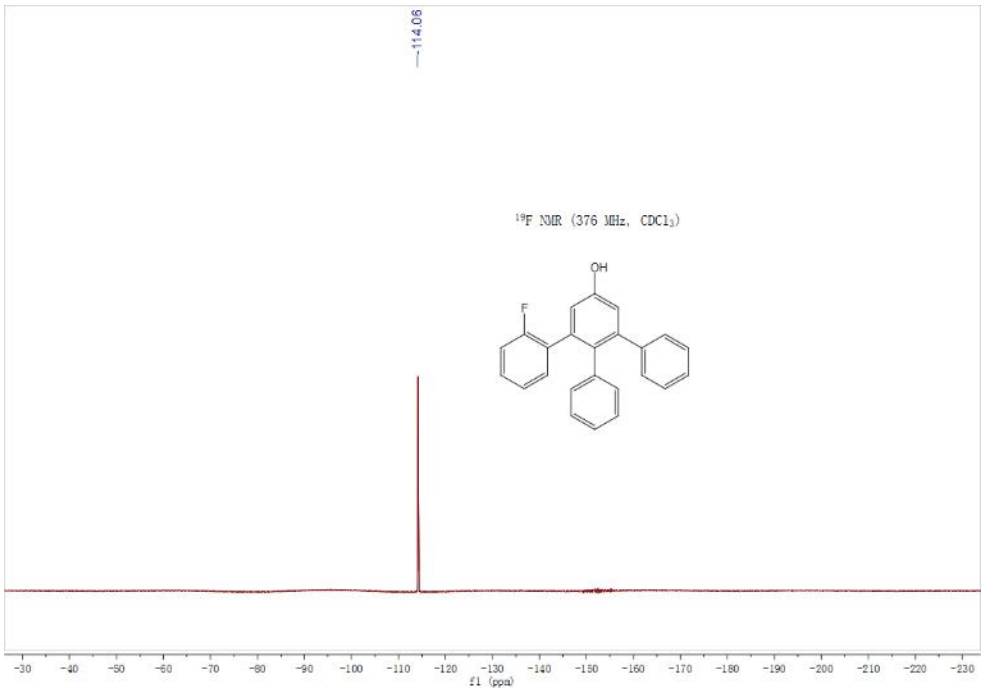


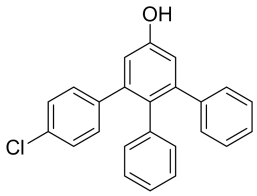

OH
F

(3f)

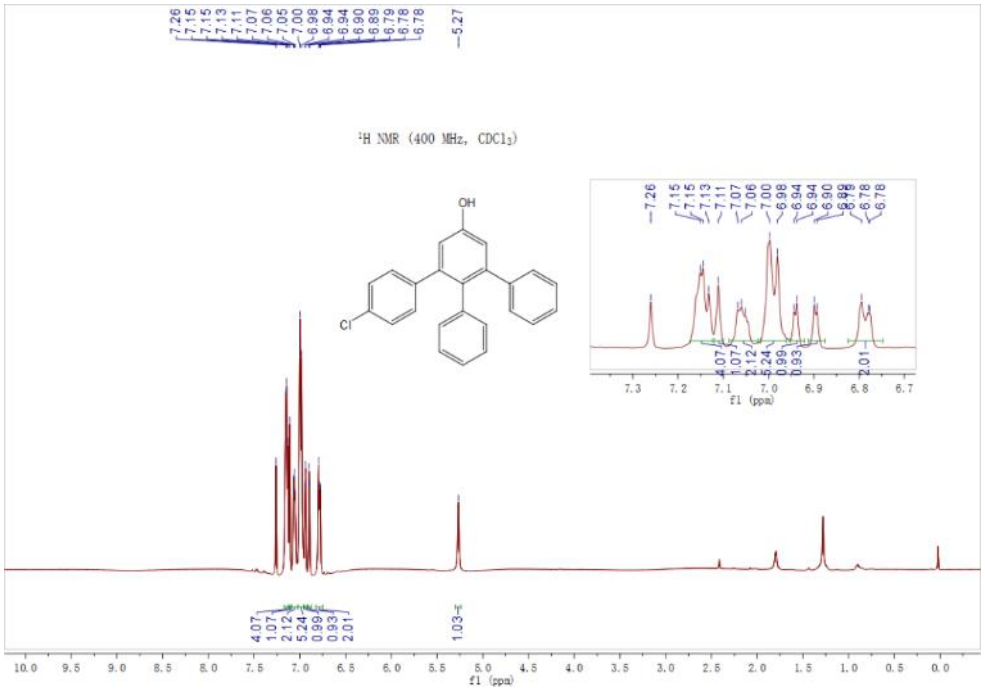

7.15
7.09
6.96
6.95
6.92
6.90
6.83
5.25
^{1}H NMR (400 MHz, CDCl$_3$)
OH
F
4.20
2.13
0.85
7.21
2.00
0.95
f1 (ppm)

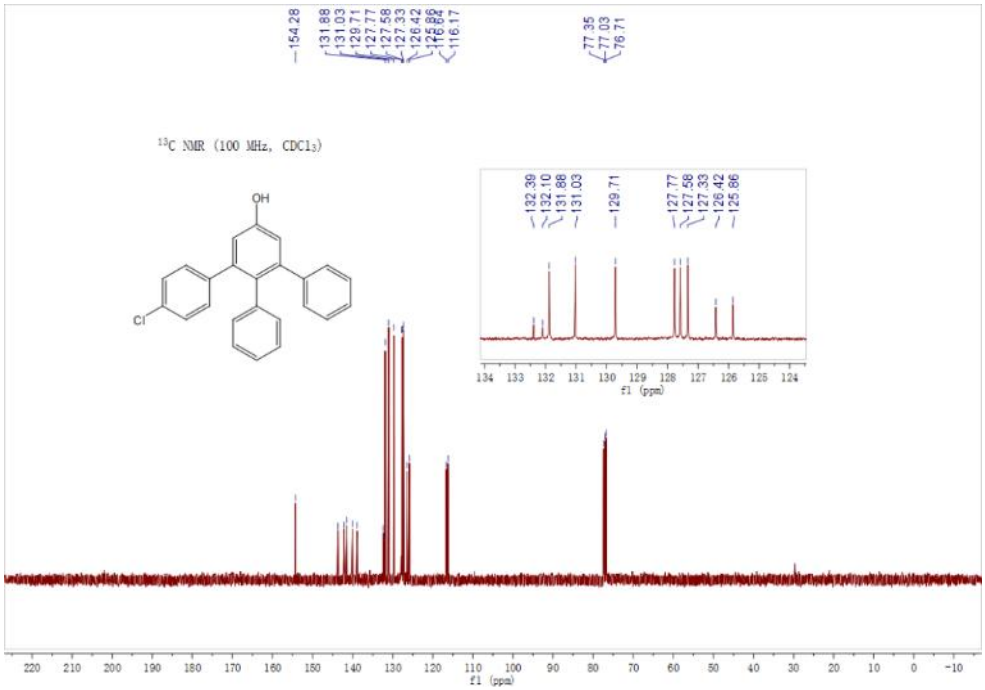

160.63
158.18
154.07
143.26
141.42
132.00
131.96
131.35
129.76
128.77
128.69
127.57
126.97
126.39
125.77
123.33
123.29
117.01
116.53
115.25
115.03
77.03
76.71
^{13}C NMR (100 MHz, CDCl$_3$)
OH
F
f1 (ppm)

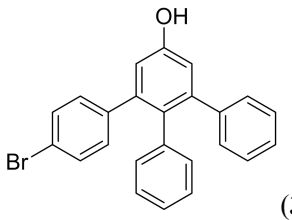

-114.06
^{19}F NMR (376 MHz, $CDCl_3$)
OH
F
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)



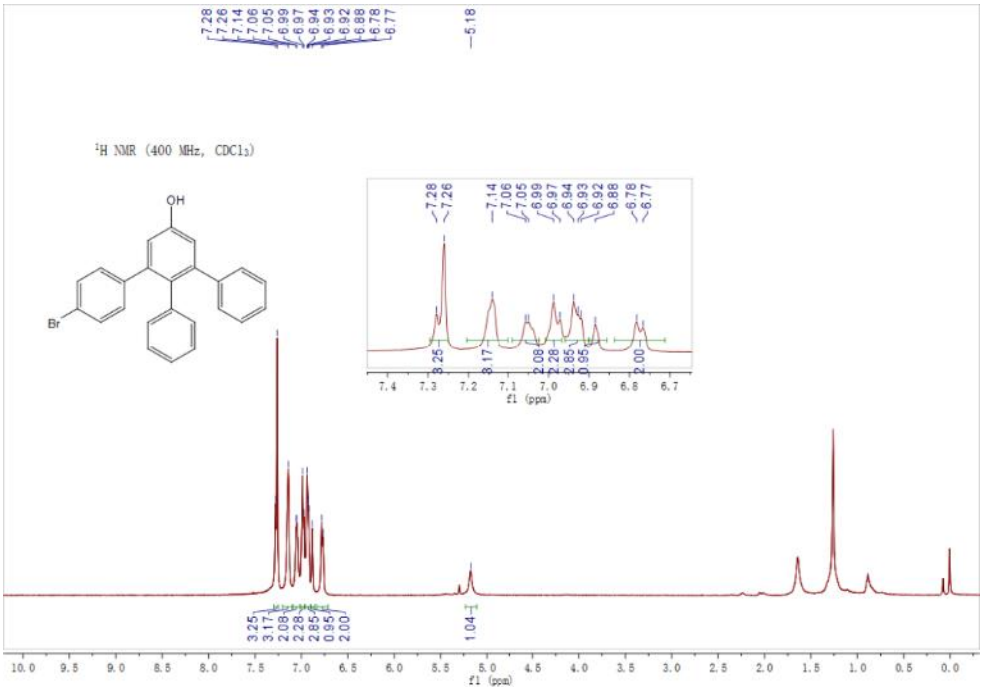
(3g)

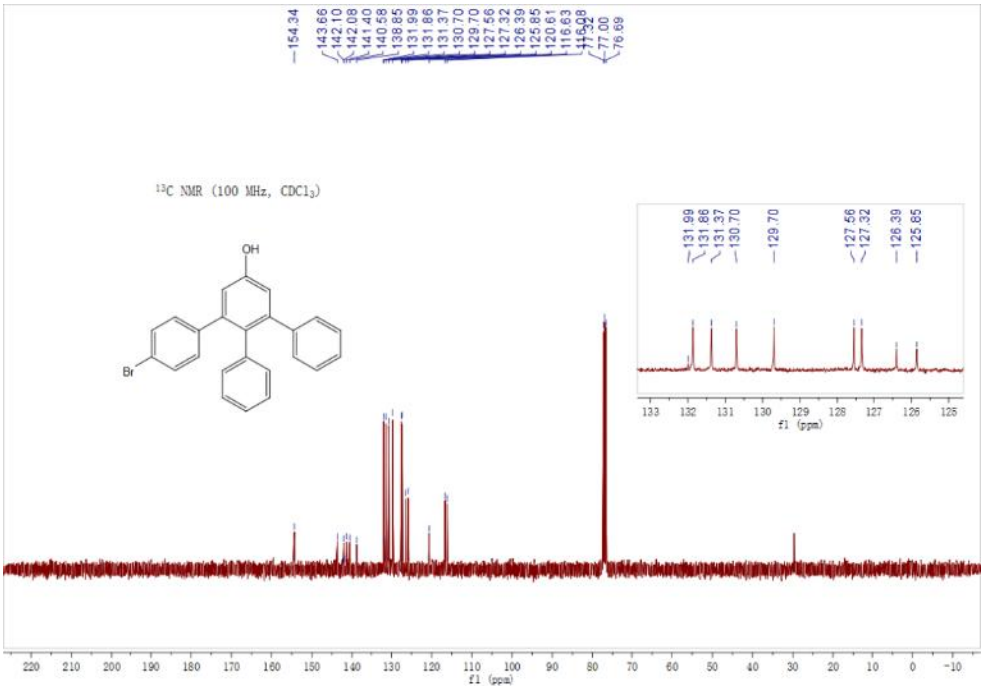


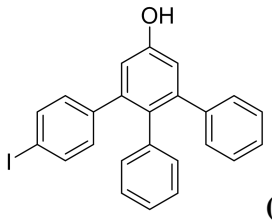



OH
Br

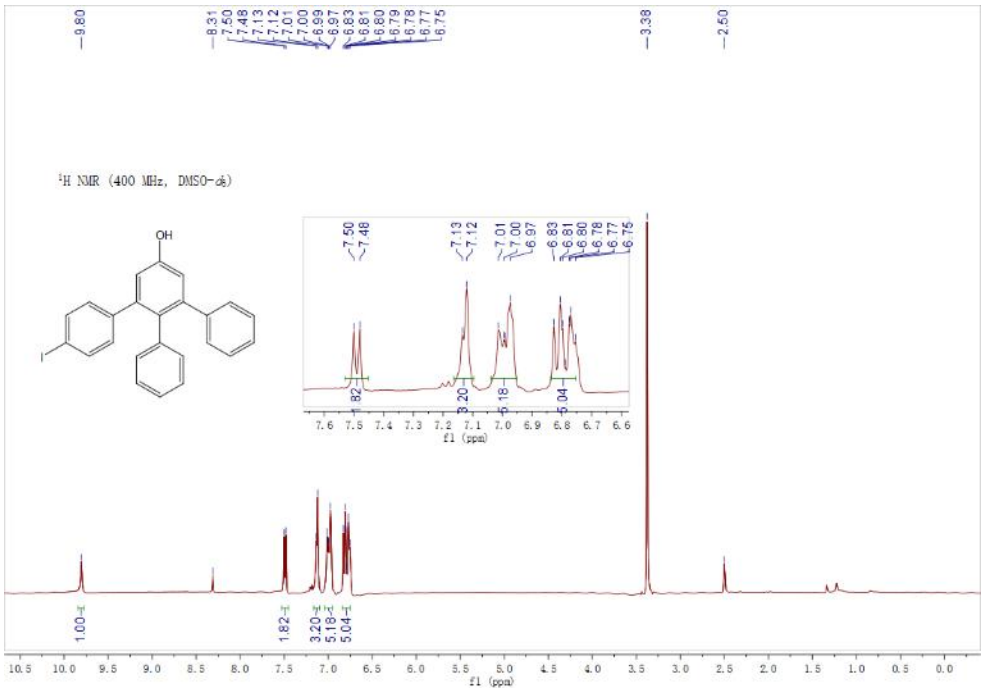
(**3h**)

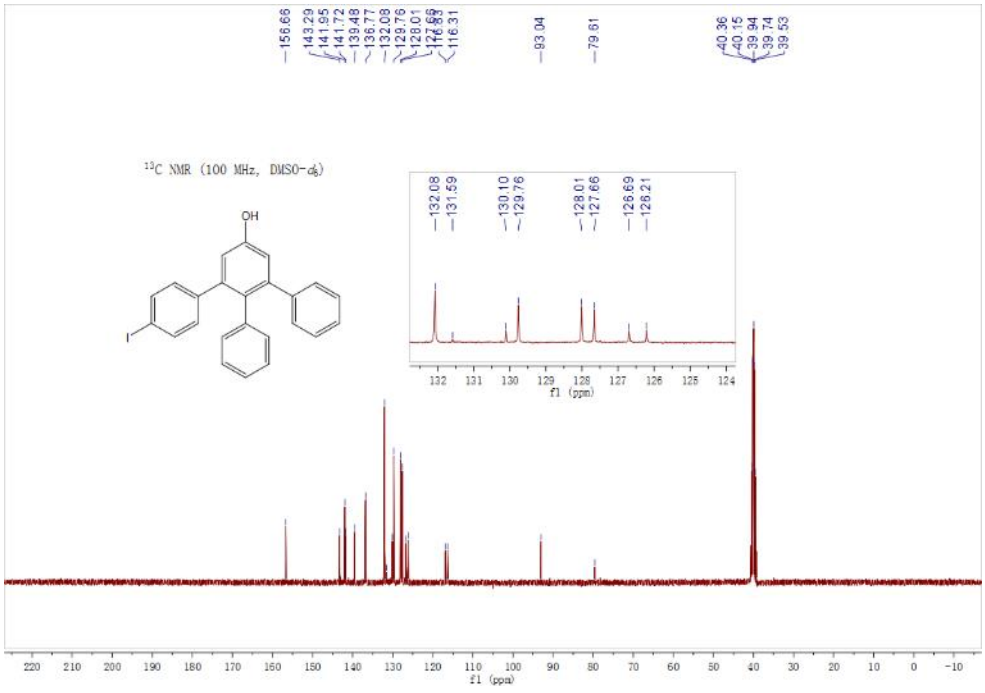

^{1}H NMR (400 MHz, CDCl$_3$)
OH
Br
f1 (ppm)

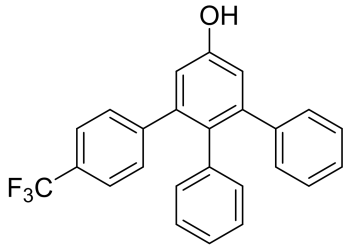

^{13}C NMR (100 MHz, CDCl$_3$)
OH
Br
f1 (ppm)


OH
I

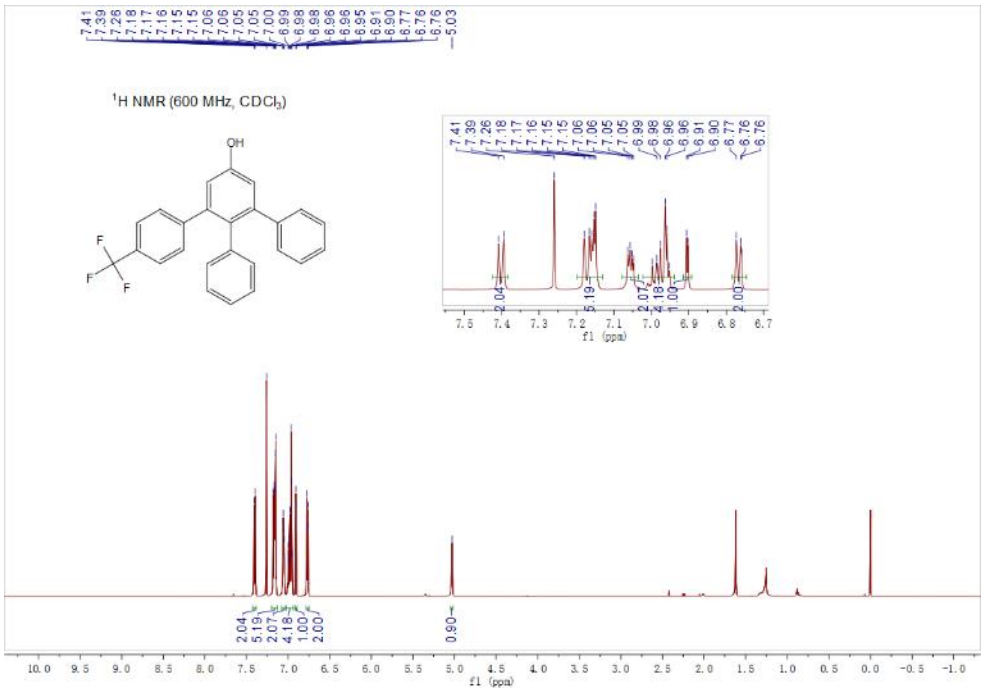
(3i)

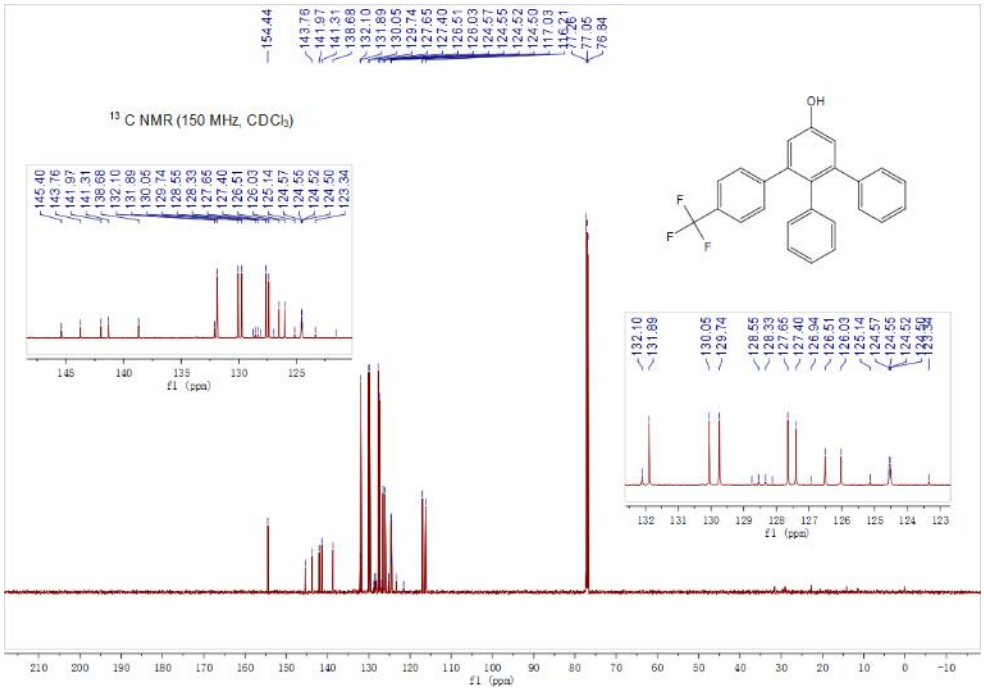

9.80
8.31
7.50
7.48
7.13
7.12
7.01
7.00
6.99
6.97
6.83
6.81
6.80
6.79
6.78
6.77
6.75
3.38
2.50
¹H NMR (400 MHz, DMSO-d6)
OH
I
1.00
1.82
3.20
5.18
5.04
f1 (ppm)

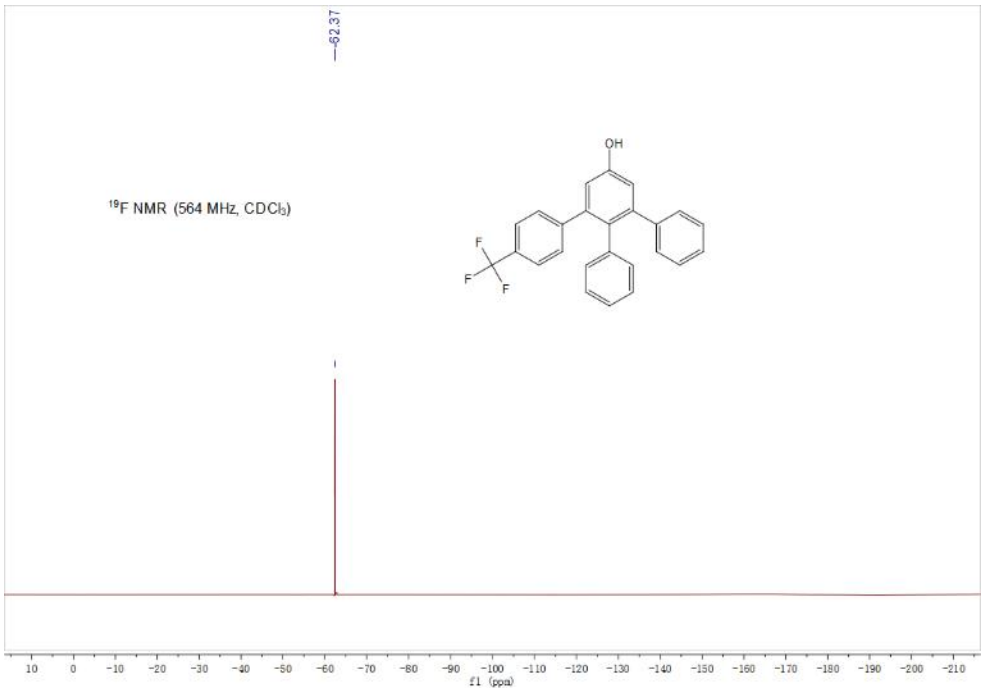

156.66
143.29
141.95
141.72
139.48
136.77
132.08
129.76
128.01
127.66
116.83
116.31
83.04
79.61
40.36
40.15
39.94
39.74
39.53
¹³C NMR (100 MHz, DMSO-d6)
OH
I
132.08
131.59
130.10
129.76
128.01
127.66
126.69
126.21
f1 (ppm)

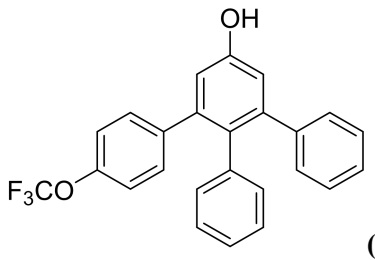

OH
F3C

(3j)

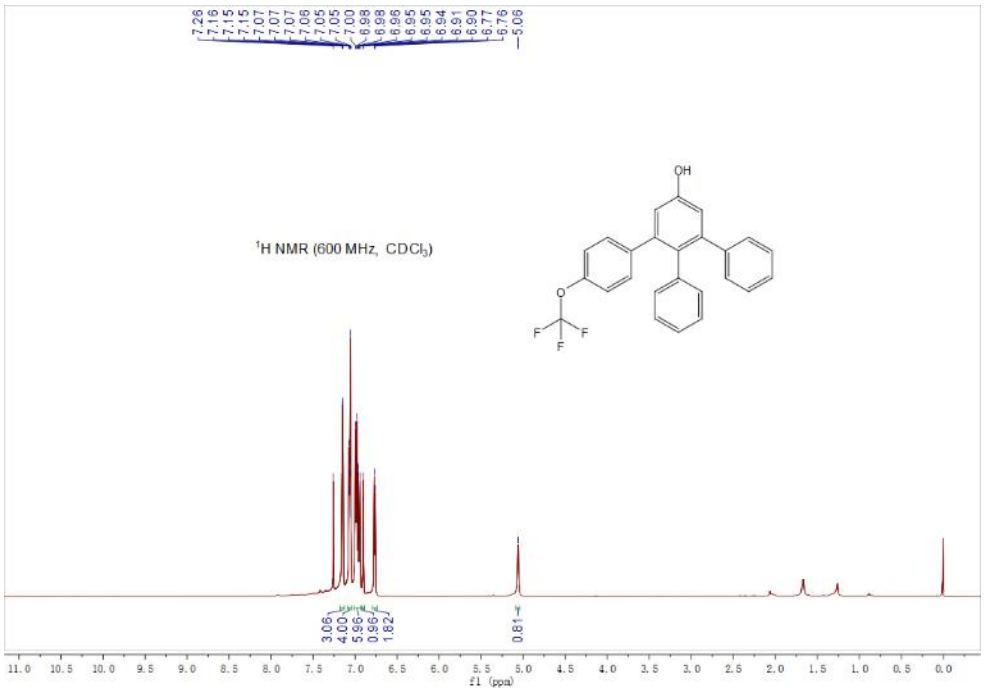

7.41
7.39
7.26
7.18
7.17
7.16
7.15
7.15
7.06
7.06
7.05
7.05
7.00
6.99
6.98
6.98
6.96
6.96
6.95
6.91
6.90
6.77
6.76
6.76
5.03
1H NMR (600 MHz, CDCl3)
OH
F
F
F
2.04
5.19
2.07
4.18
1.00
2.00
0.90
f1 (ppm)

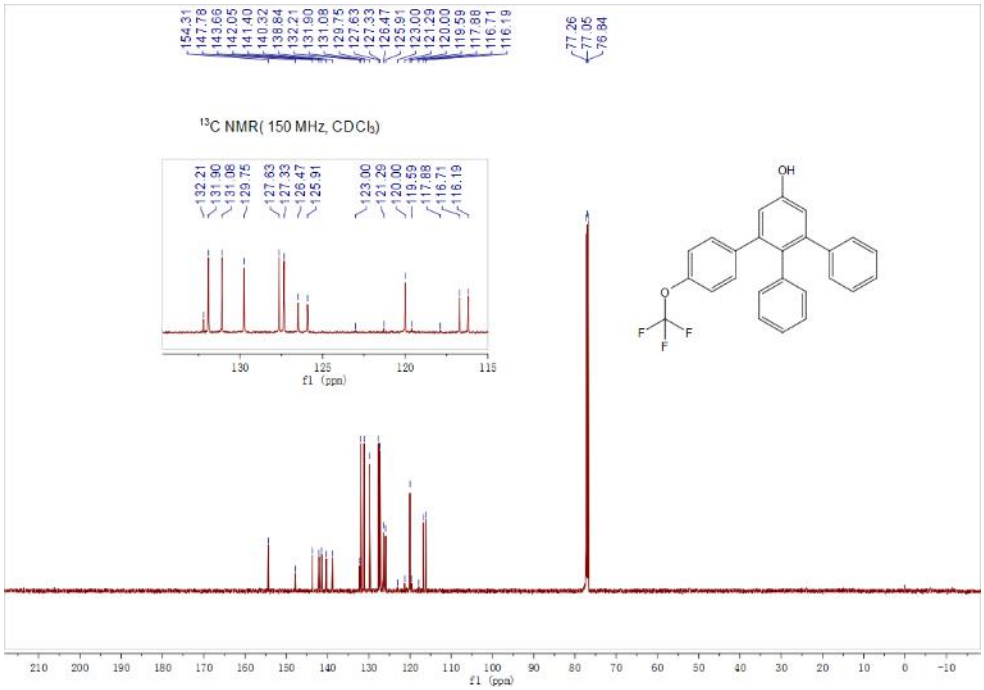

154.44
143.76
141.97
141.31
138.68
132.10
131.89
130.05
129.74
127.65
127.40
126.51
126.03
124.57
124.55
124.52
124.50
117.03
115.61
77.05
76.84
13 C NMR (150 MHz, CDCl3)
OH
F
F
F
145.40
143.76
141.97
141.31
138.68
132.10
131.89
130.05
129.74
128.55
128.33
127.65
127.40
126.51
126.03
125.14
124.57
124.55
124.52
124.50
123.34
f1 (ppm)

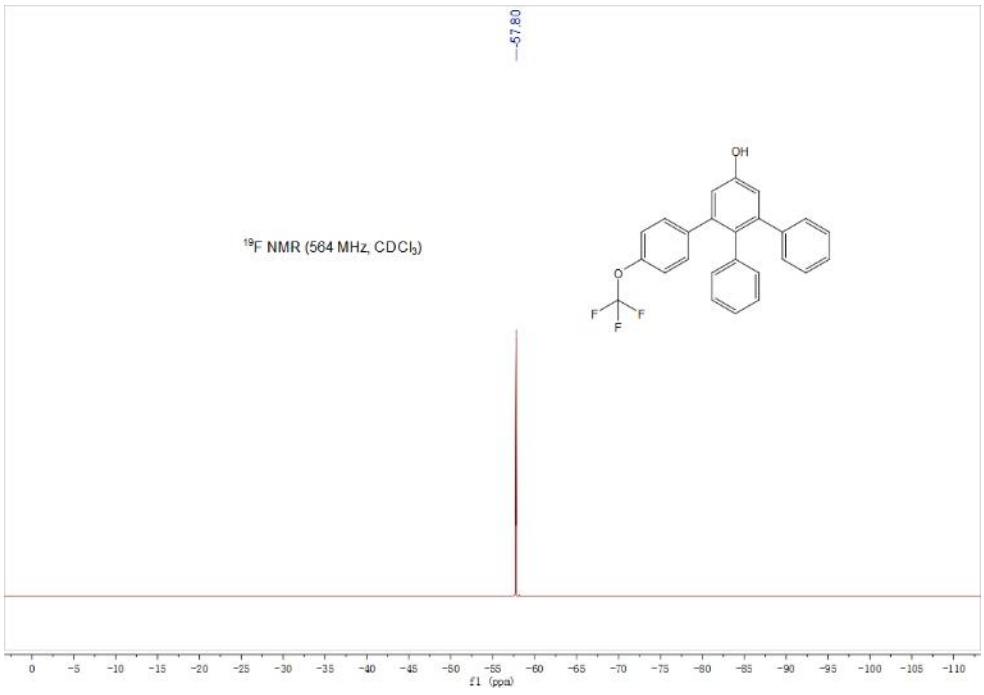

-62.37
^{19}F NMR (564 MHz, CDCl$_3$)
OH
F
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

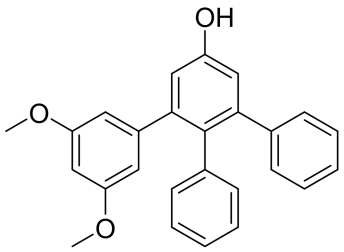

OH
F3CO

(3k)

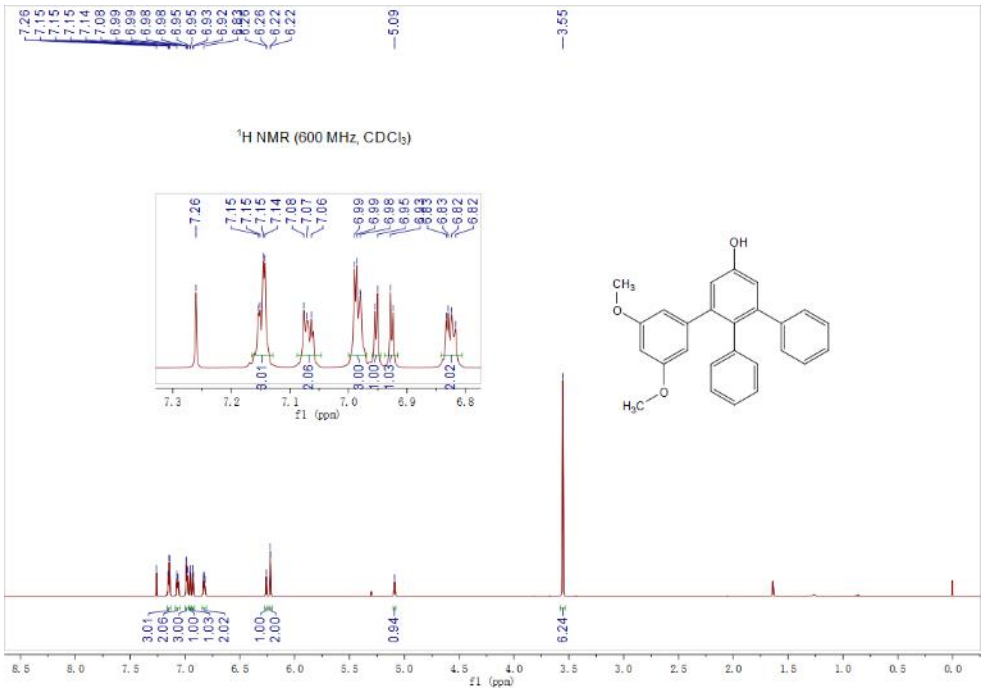

7.26
7.16
7.15
7.15
7.07
7.07
7.07
7.06
7.05
7.05
7.00
6.98
6.98
6.96
6.95
6.94
6.91
6.90
6.77
6.76
5.06
1H NMR (600 MHz, CDCl3)
OH
O
F
F
F
3.06
4.00
5.96
0.96
1.82
0.81
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

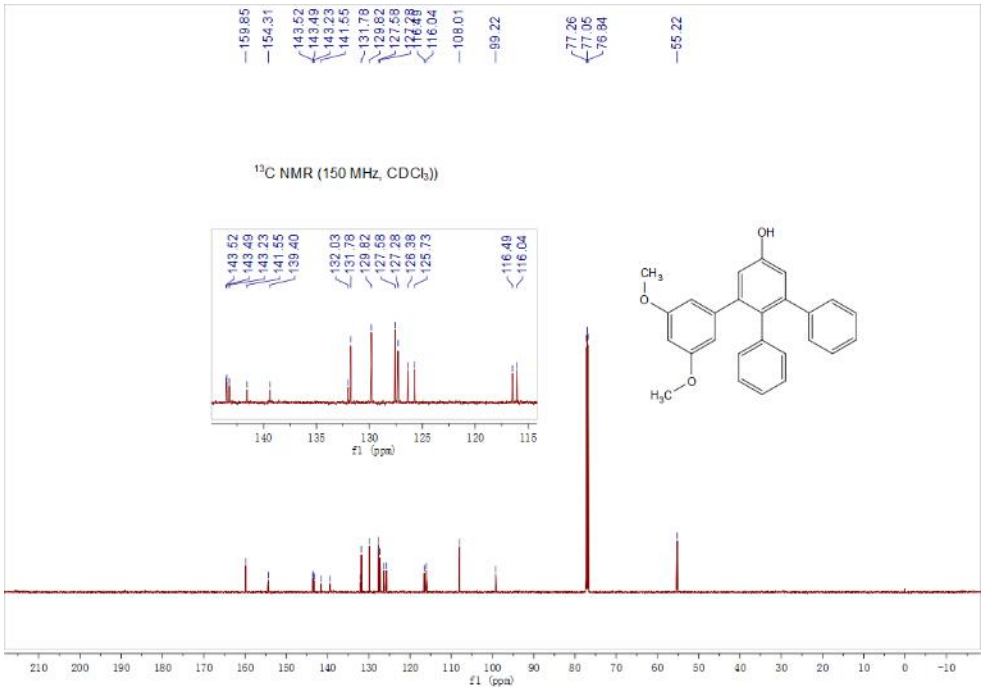

154.31
147.78
143.66
142.05
141.40
140.32
138.84
132.21
131.90
131.08
129.75
127.63
127.33
126.47
125.91
123.00
121.29
120.00
119.59
117.88
116.71
116.19
77.26
77.05
76.84
13C NMR(150 MHz, CDCl3)
132.21
131.90
131.08
129.75
127.63
127.33
126.47
125.91
123.00
121.29
120.00
119.59
117.88
116.71
116.19
130
125
120
115
f1 (ppm)
OH
O
F
F
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

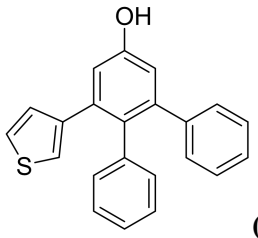

-57.80
^{19}F NMR (564 MHz, CDCl$_3$)
OH
O
F
F
F
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
f1 (ppm)


OH
O
O

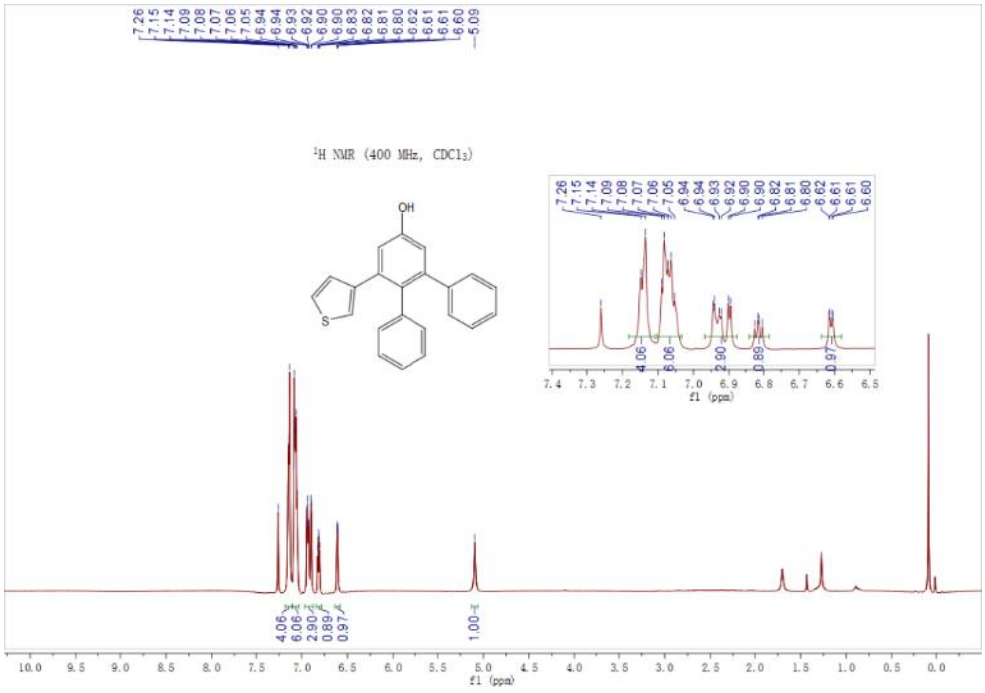
（3l）

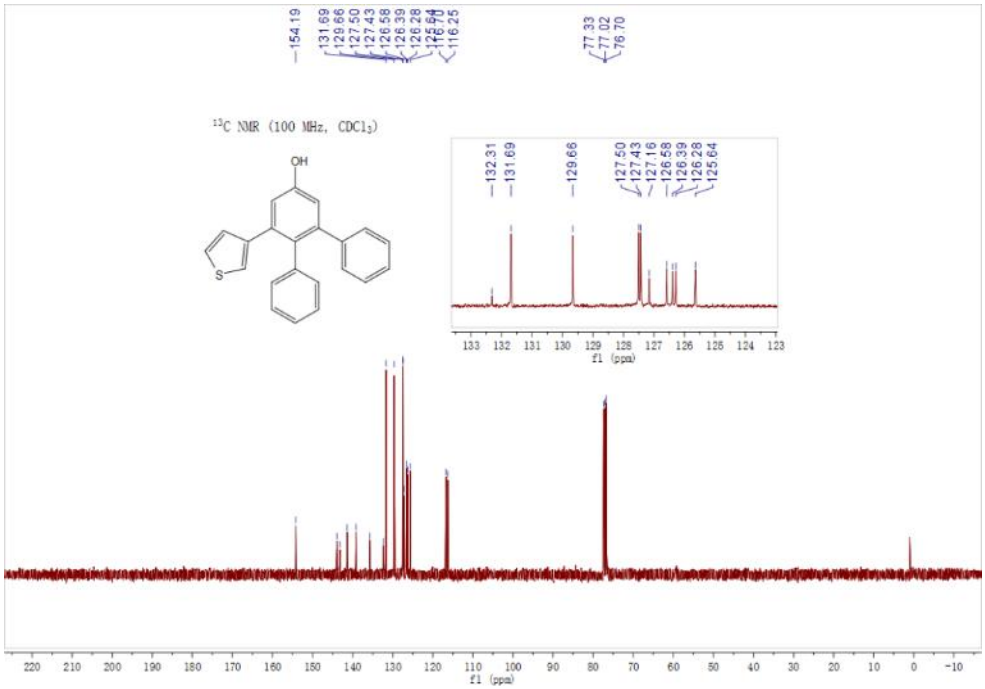

7.26
7.15
7.15
7.15
7.14
7.08
6.99
6.99
6.98
6.98
6.95
6.93
6.92
6.26
6.22
6.22
5.09
3.55
^{1}H NMR (600 MHz, CDCl$_3$)
8.01
2.06
8.00
1.00
1.03
2.02
f1 (ppm)
OH
CH$_3$
O
H$_3$C
O
3.01
2.06
3.00
1.00
1.03
2.02
1.00
2.00
0.84
6.24
f1 (ppm)

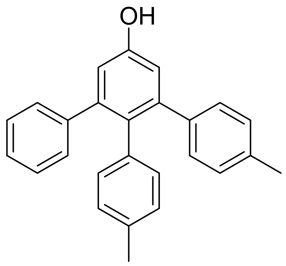

159.85
154.31
143.52
143.49
143.23
141.55
131.78
129.82
127.58
116.04
108.01
99.22
77.26
77.05
76.84
55.22
^{13}C NMR (150 MHz, CDCl$_3$))
143.52
143.49
143.23
141.55
139.40
132.03
131.78
129.82
127.58
127.28
126.38
125.73
116.49
116.04
f1 (ppm)
OH
CH$_3$
O
H$_3$C
O
f1 (ppm)


OH
S

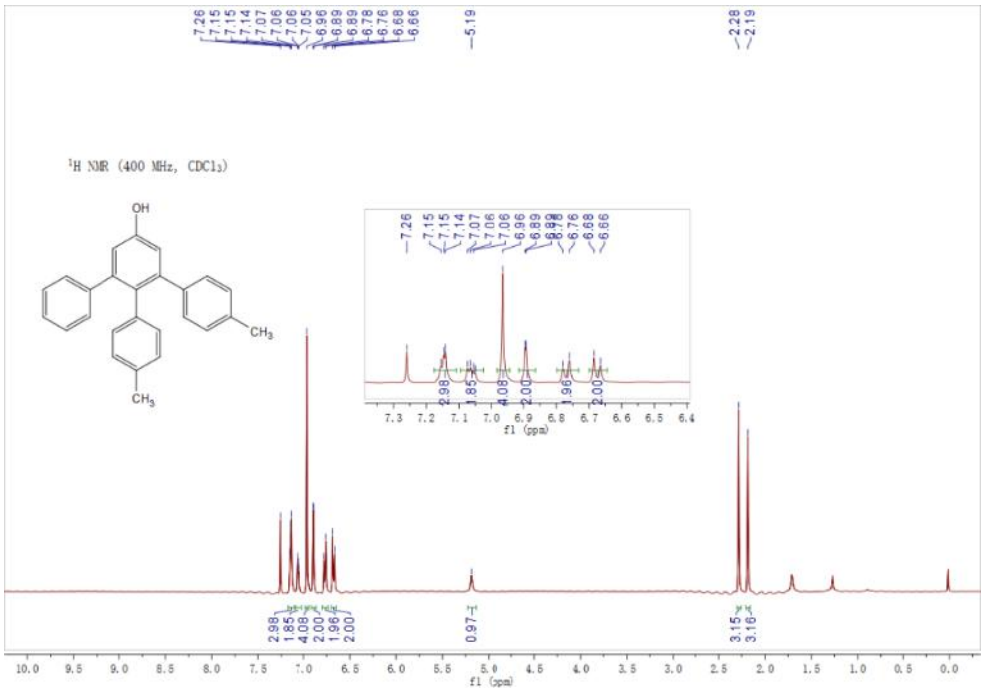
(3m)

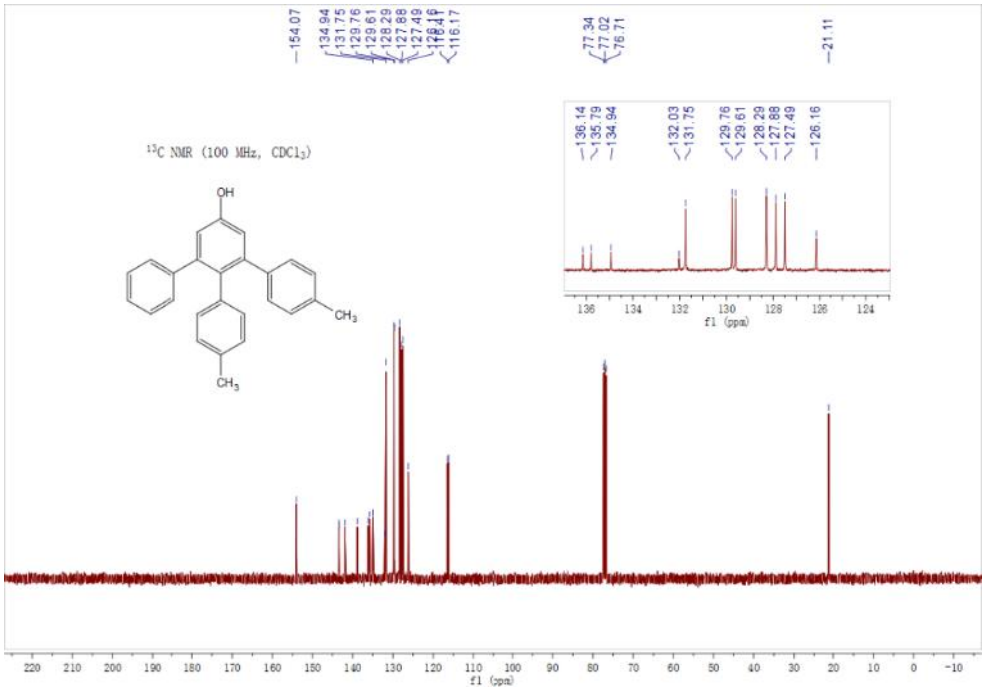

^{1}H NMR (400 MHz, CDCl$_3$)
OH
S
f1 (ppm)

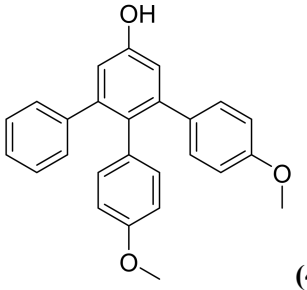

^{13}C NMR (100 MHz, CDCl$_3$)
OH
S
f1 (ppm)


OH

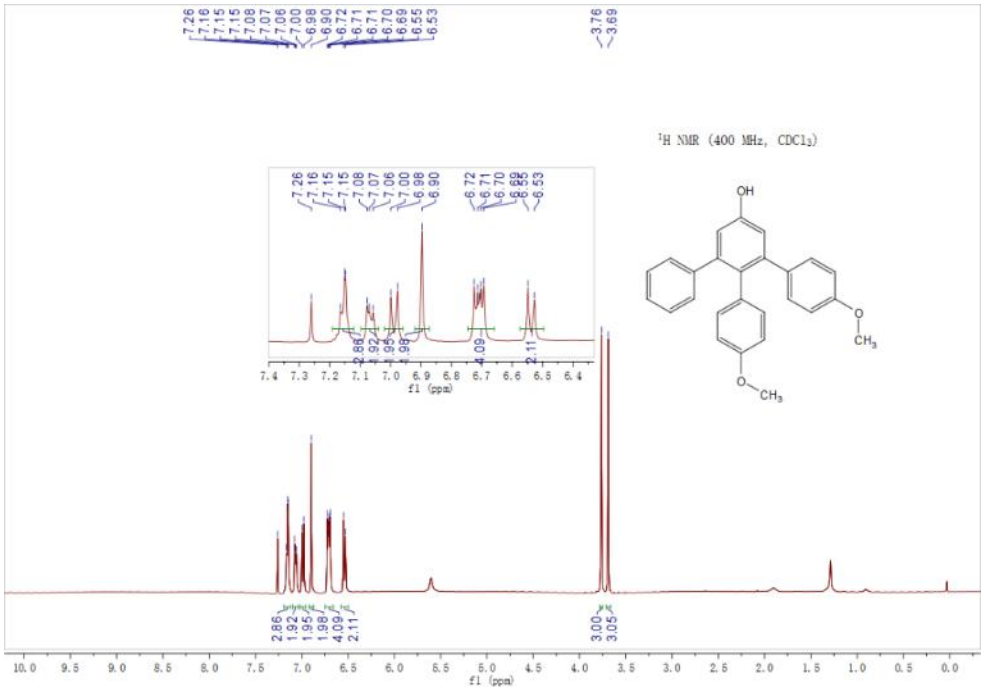
(4a)

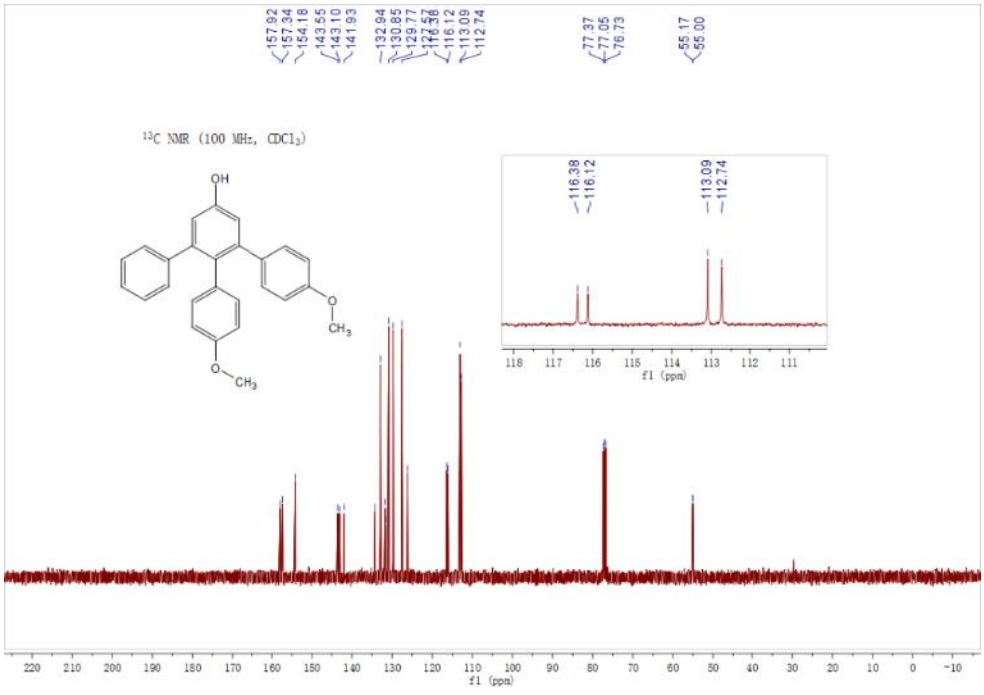

7.26
7.15
7.15
7.14
7.07
7.06
7.06
7.05
6.96
6.89
6.89
6.78
6.76
6.68
6.66
5.19
2.28
2.19
^{1}H NMR (400 MHz, CDCl$_3$)
OH
CH$_3$
CH$_3$
2.98
1.85
4.08
2.00
1.96
2.00
0.97
3.15
3.16
f1 (ppm)

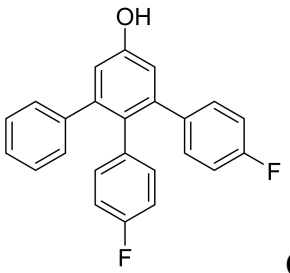

154.07
134.94
131.75
129.76
129.61
128.29
127.88
127.49
116.17
77.34
77.02
76.71
21.11
^{13}C NMR (100 MHz, CDCl$_3$)
OH
CH$_3$
CH$_3$
136.14
135.79
134.94
132.03
131.75
129.76
129.61
128.29
127.88
127.49
126.16
f1 (ppm)



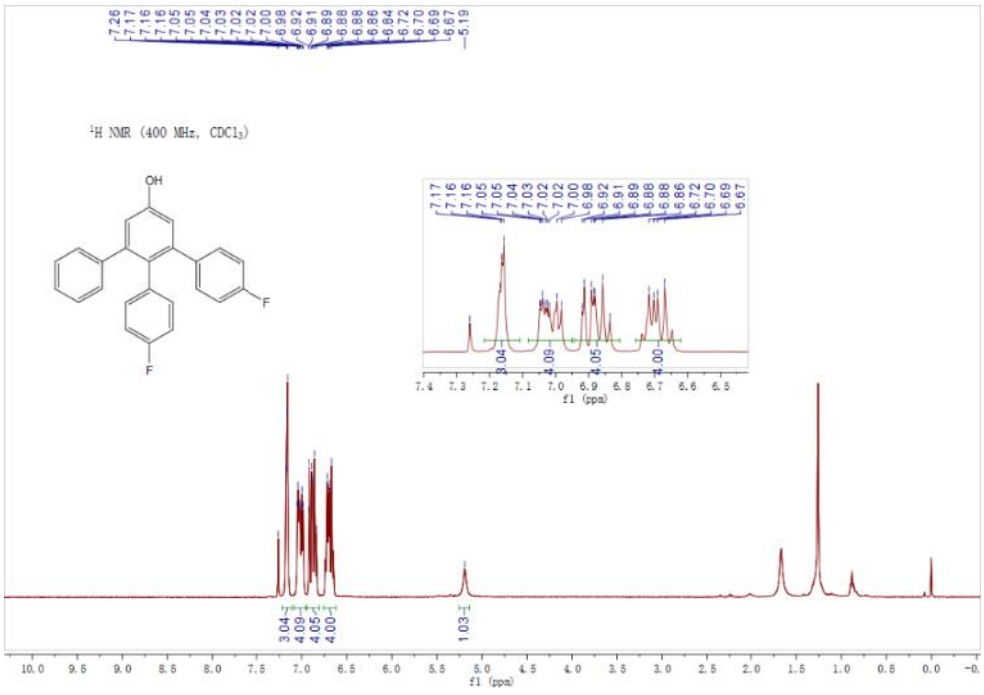
(4b)

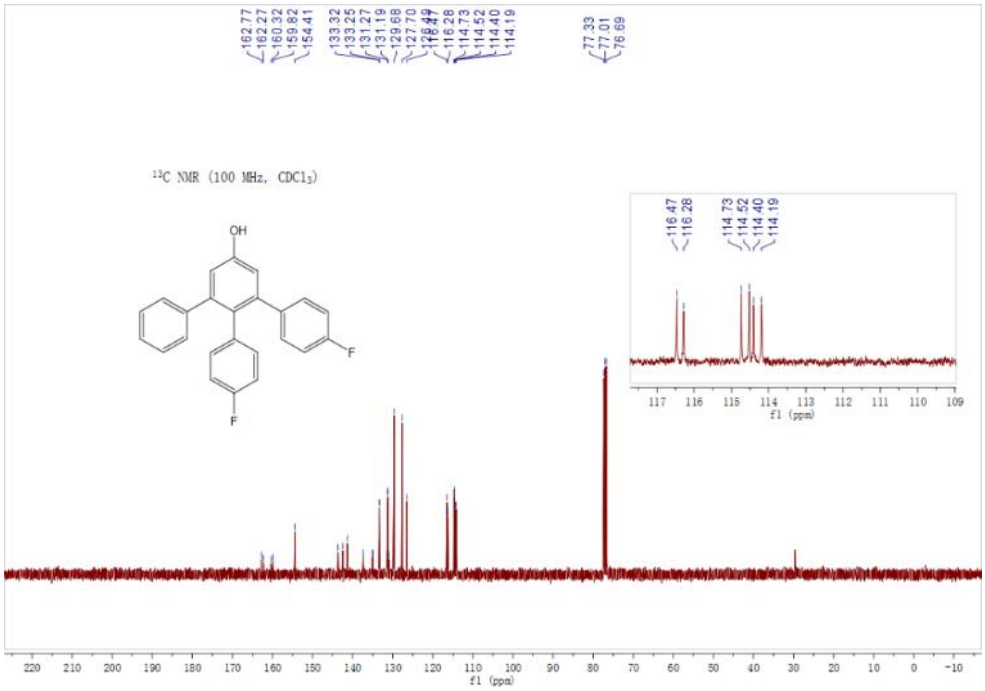


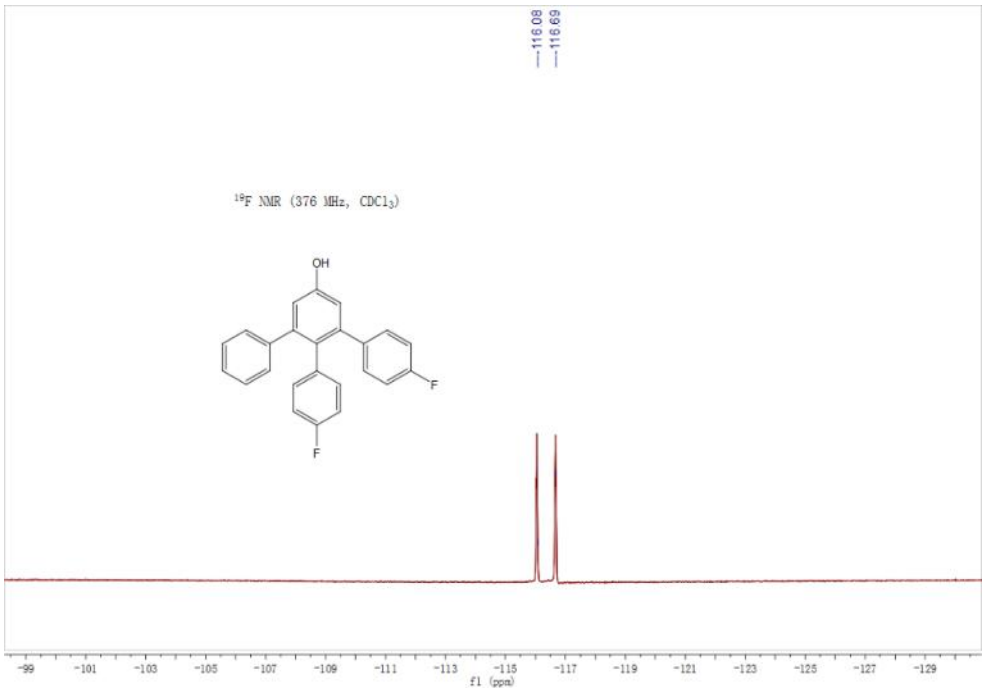


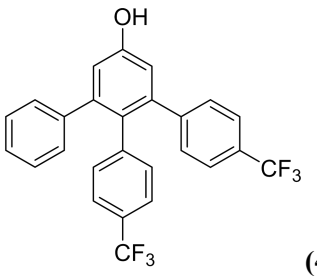


(4c)

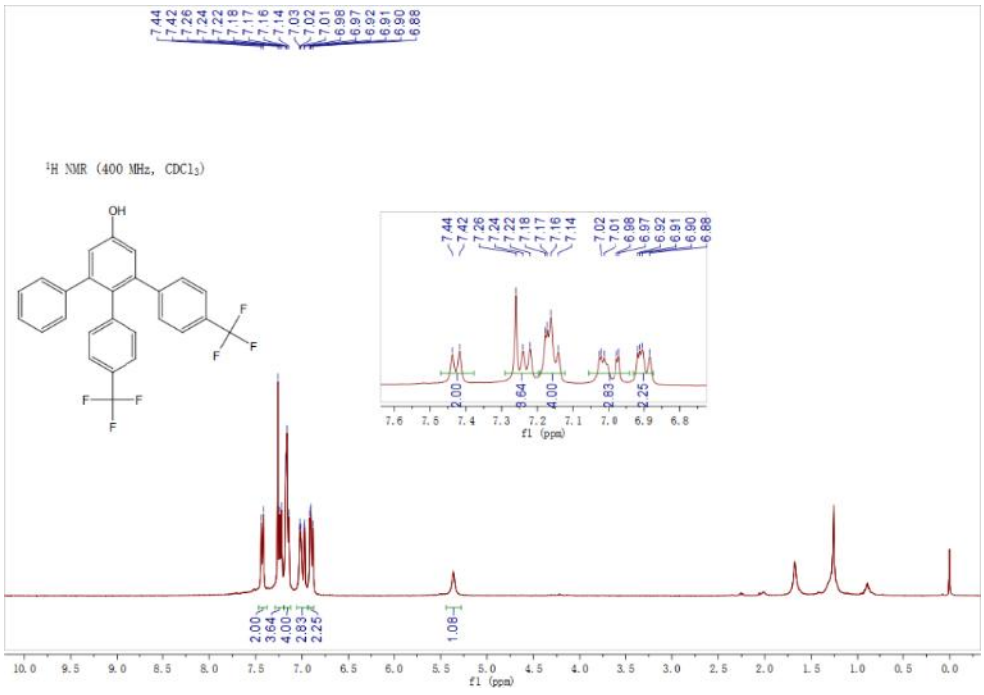


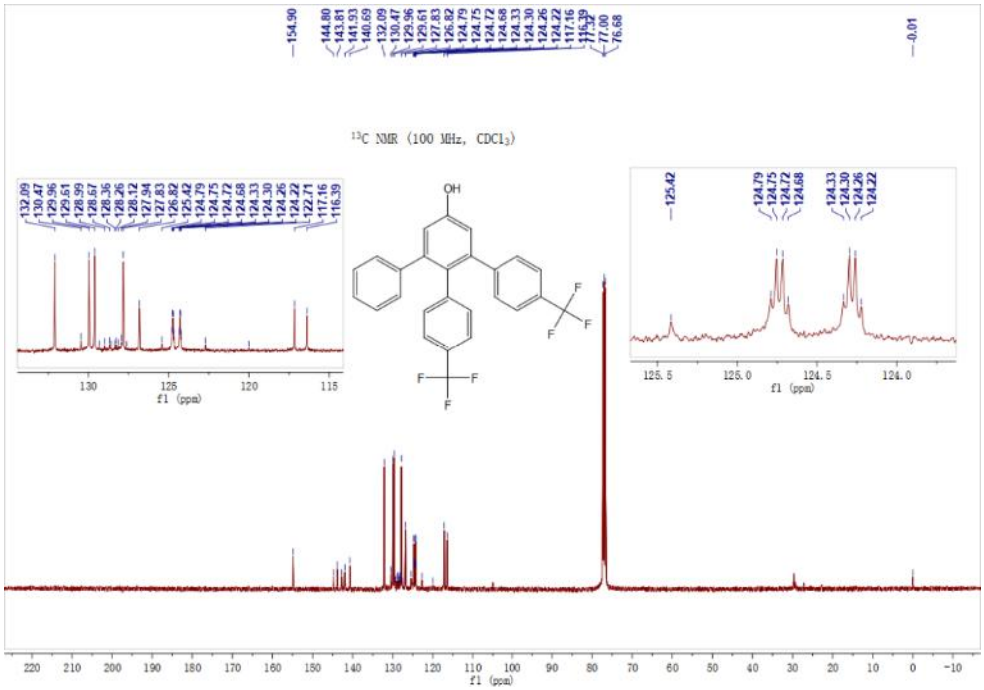


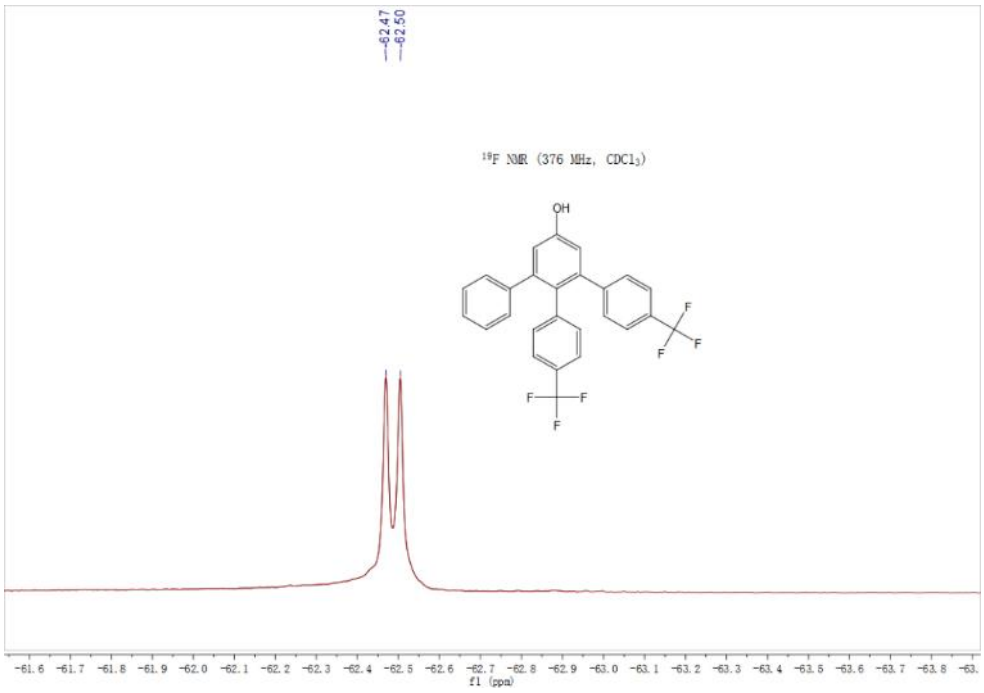

116.08
116.69
^{19}F NMR (376 MHz, $CDCl_3$)
OH
F
F
-99
-101
-103
-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
f1 (ppm)

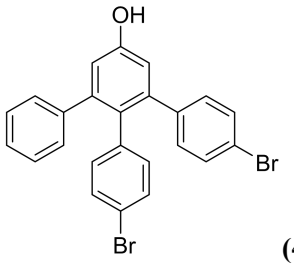

OH
CF3
CF3

(4d)

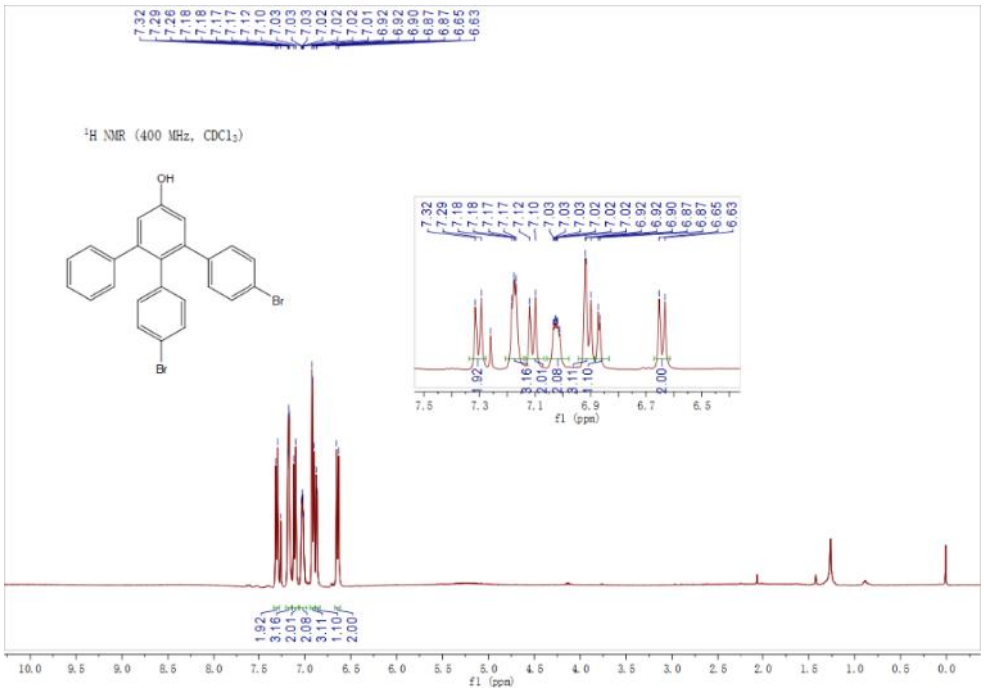

1H NMR (400 MHz, CDCl3)
OH
F
F
F
F
F
f1 (ppm)

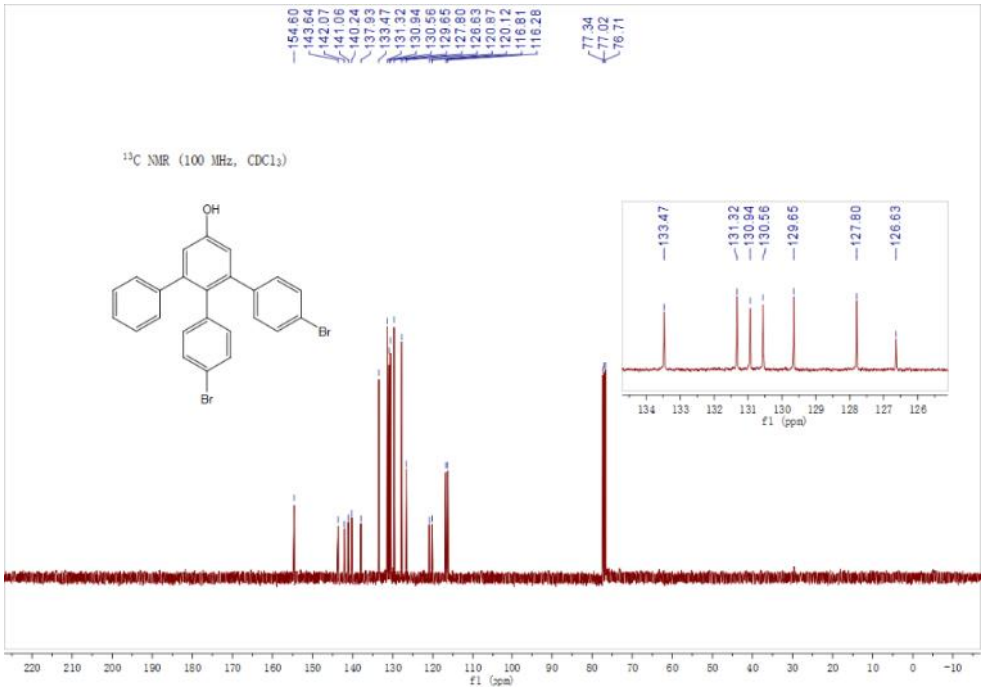

13C NMR (100 MHz, CDCl3)
OH
F
F
F
F
F
f1 (ppm)

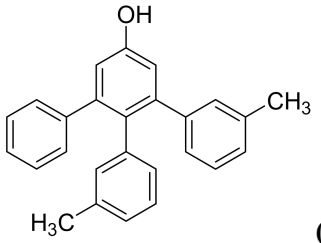

-62.47
-62.50
^{19}F NMR (376 MHz, $CDCl_3$)
OH
F
F
F
F
F
F
-61.6 -61.7 -61.8 -61.9 -62.0 -62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.
f1 (ppm)


OH
Br
Br

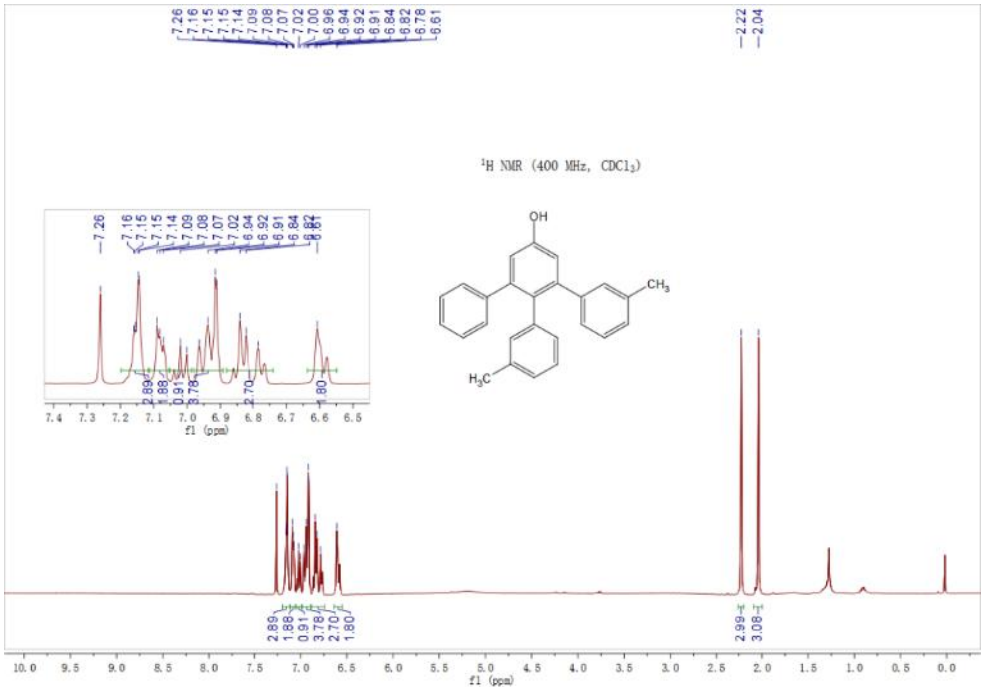
(4e)

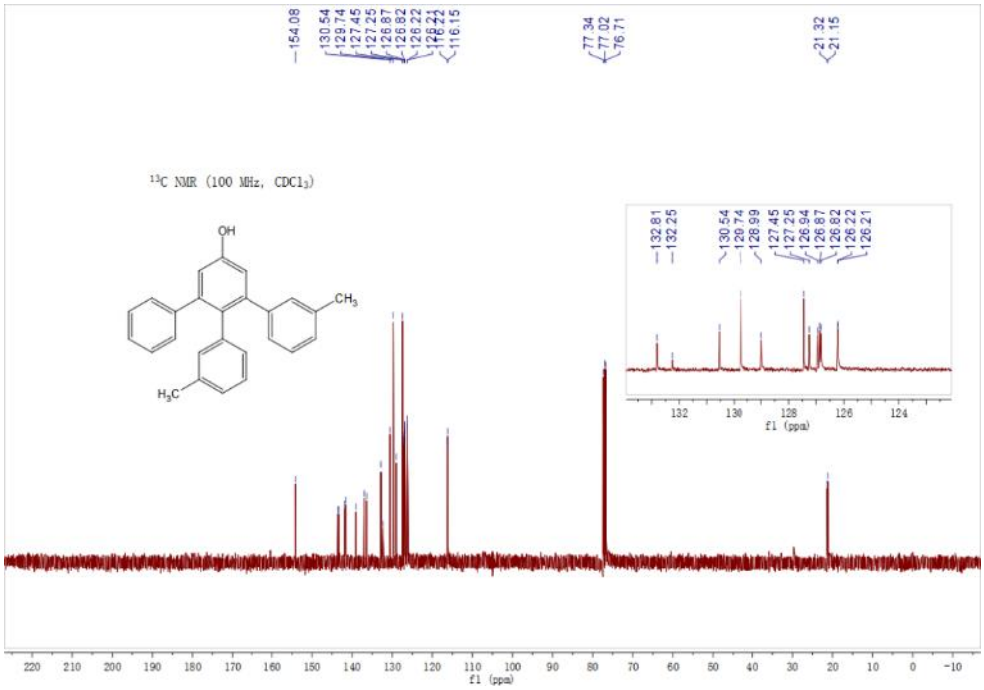

^{1}H NMR (400 MHz, CDCl$_3$)
OH
Br
Br
f1 (ppm)

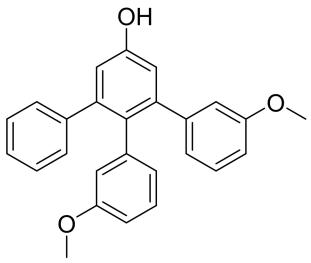

^{13}C NMR (100 MHz, CDCl$_3$)
OH
Br
Br
f1 (ppm)


OH
CH3
H3C

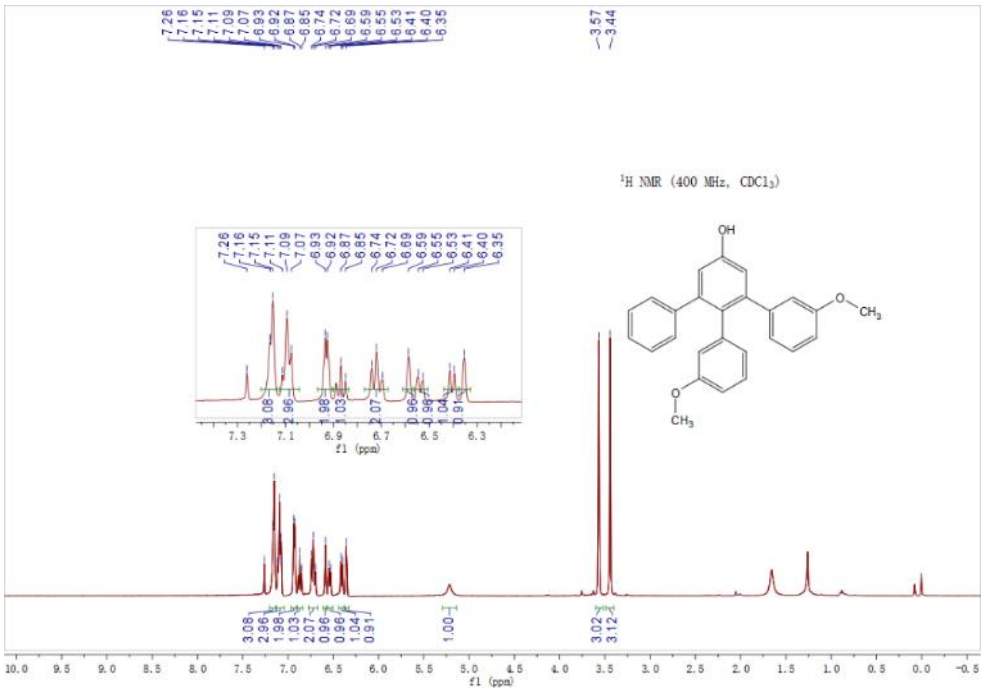
(4f)

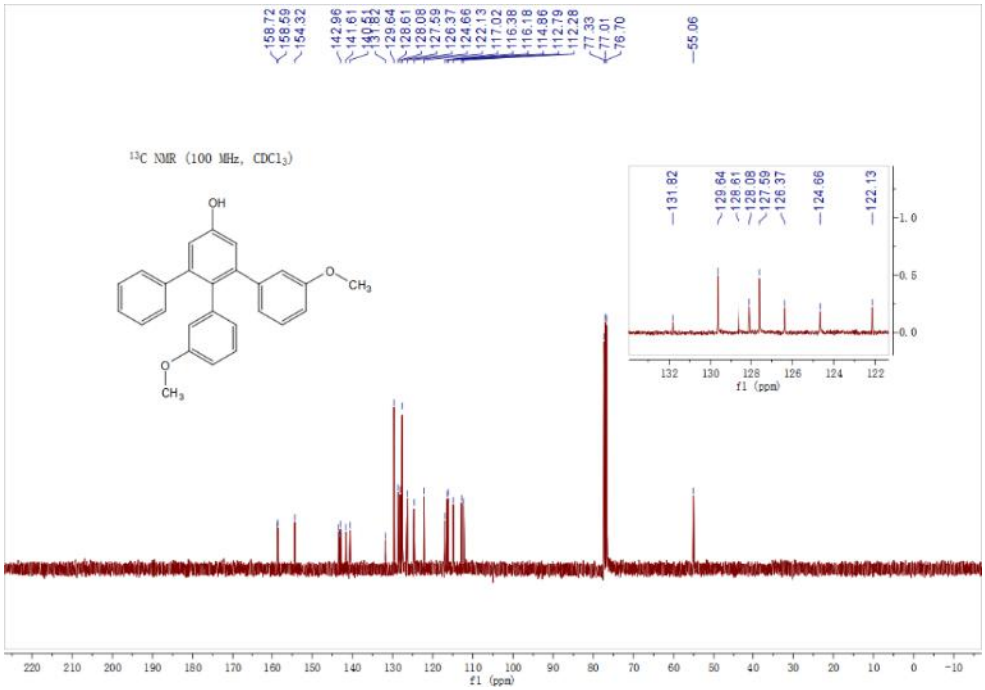

7.26
7.16
7.15
7.15
7.14
7.09
7.08
7.07
7.02
7.00
6.96
6.94
6.92
6.91
6.84
6.82
6.78
6.61
2.22
2.04
¹H NMR (400 MHz, CDCl₃)
OH
CH3
H3C
2.89
1.88
0.91
3.78
2.70
1.80
2.99
3.08
f1 (ppm)

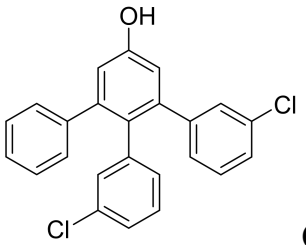

154.08
130.54
129.74
127.45
127.25
126.87
126.82
126.22
126.21
116.15
77.34
77.02
76.71
21.32
21.15
¹³C NMR (100 MHz, CDCl₃)
OH
CH3
H3C
132.81
132.25
130.54
129.74
128.99
127.45
127.25
126.94
126.87
126.82
126.22
126.21
f1 (ppm)



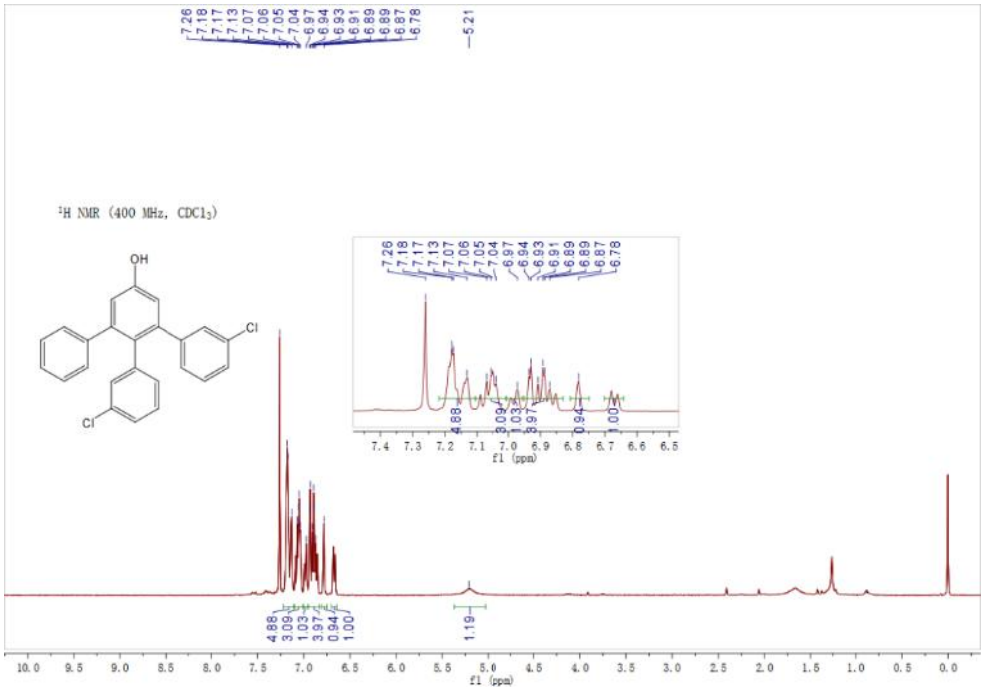
(4g)

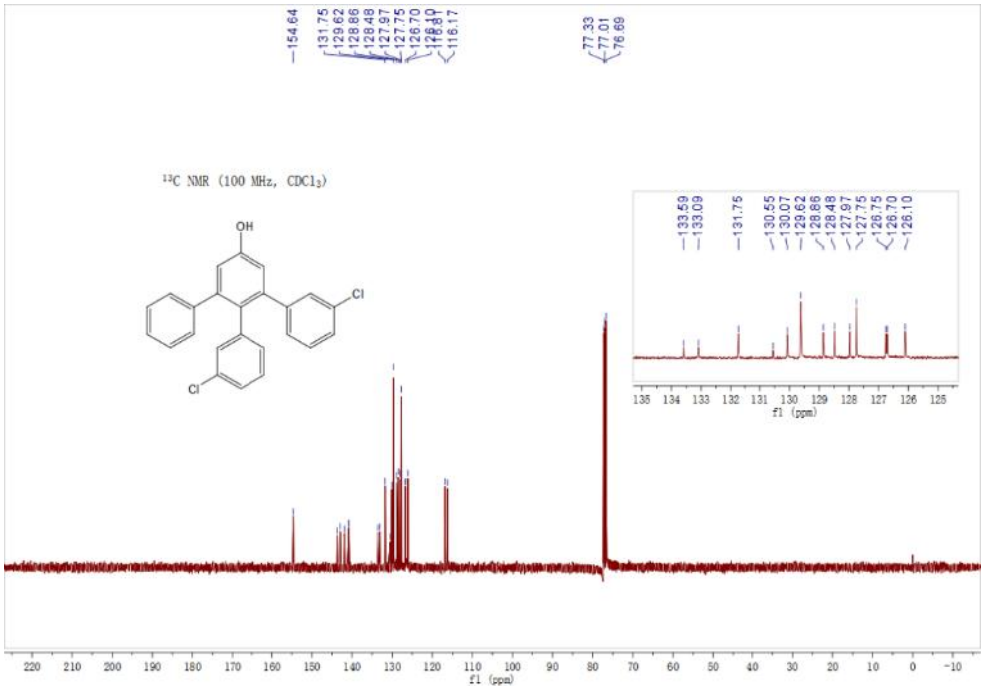


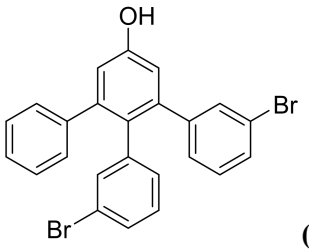



OH
Cl
Cl

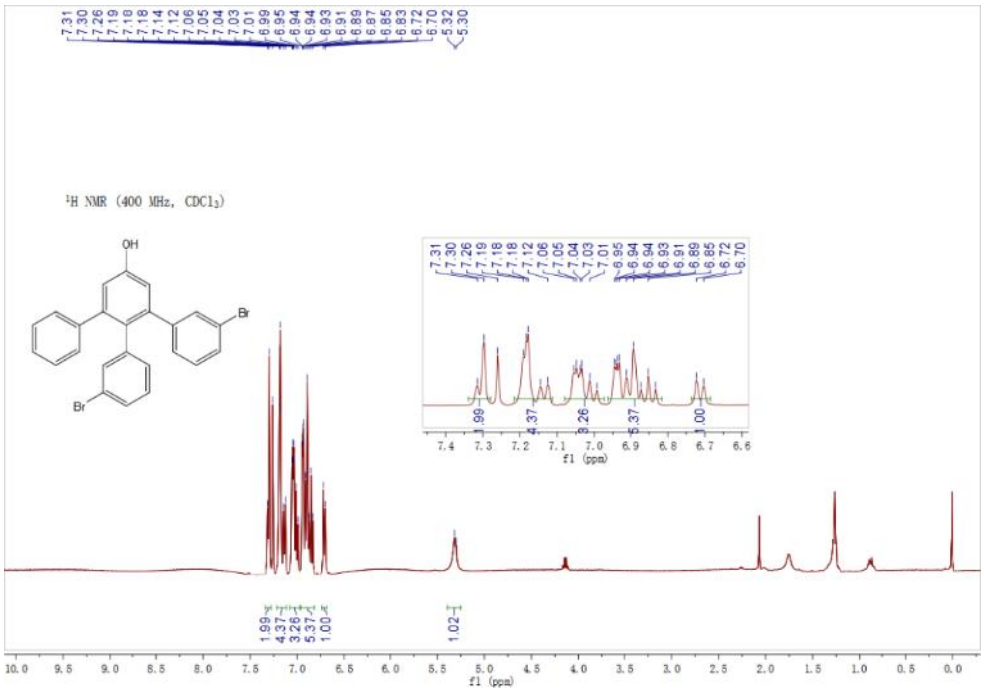
(4h)

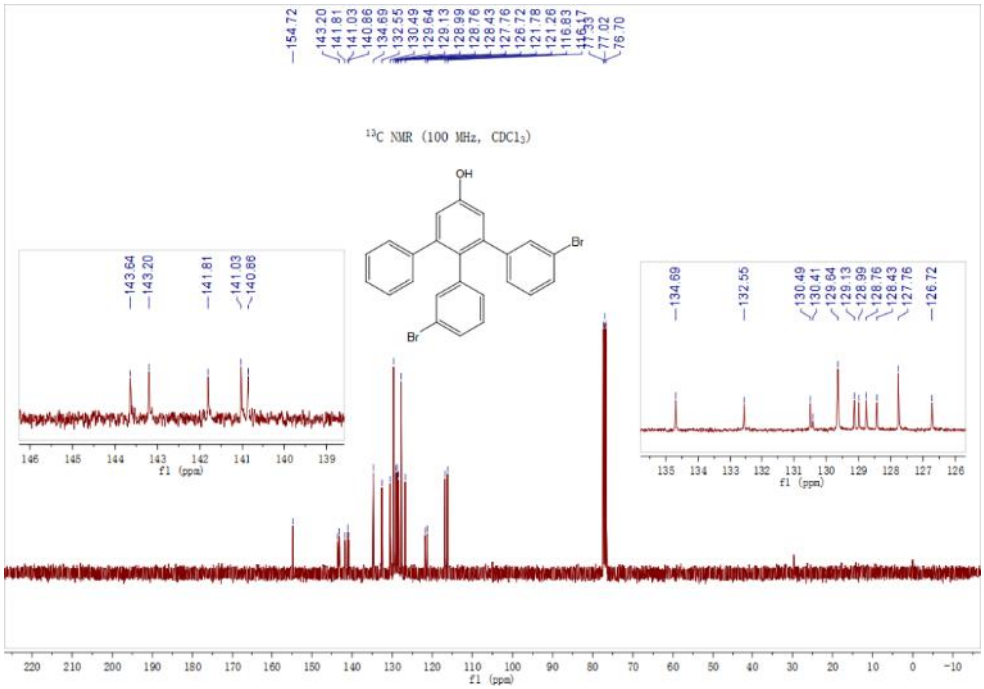

^{1}H NMR (400 MHz, CDCl$_3$)
OH
Cl
Cl
f1 (ppm)

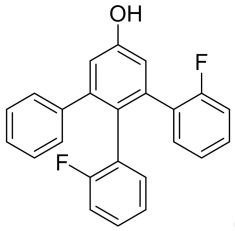

^{13}C NMR (100 MHz, CDCl$_3$)
OH
Cl
Cl
f1 (ppm)


OH
Br
Br

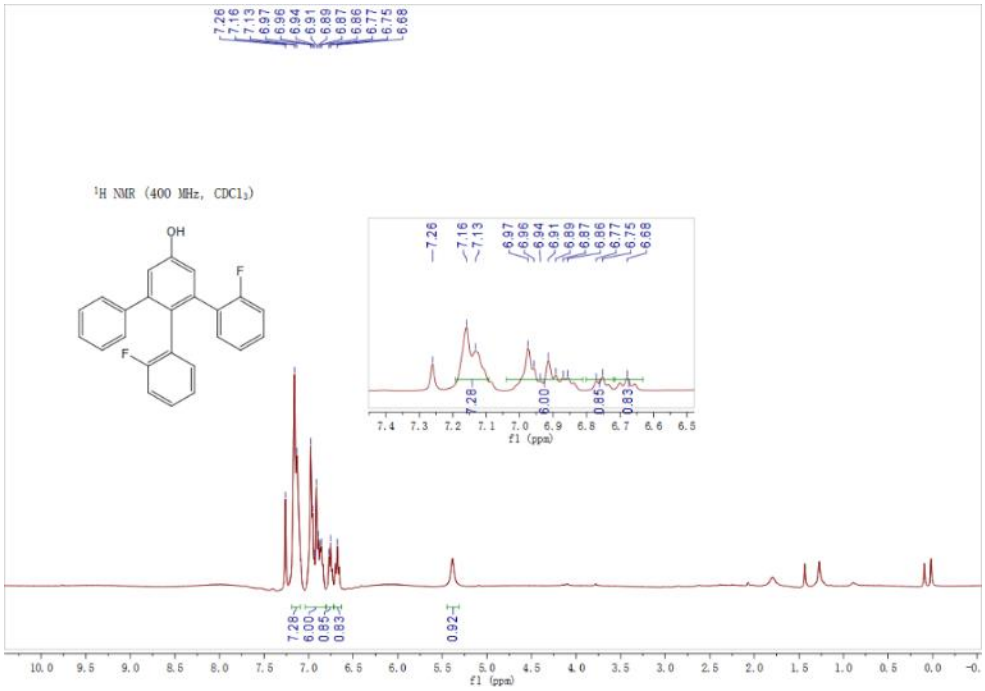
(4i)

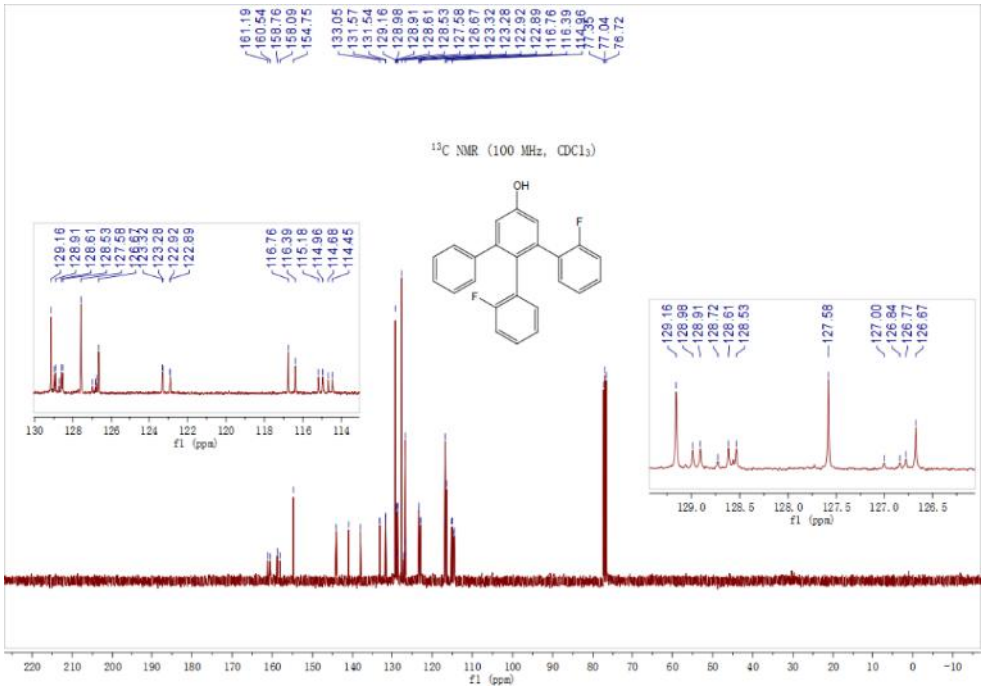

7.31
7.30
7.26
7.19
7.18
7.18
7.14
7.12
7.06
7.05
7.04
7.03
7.01
6.99
6.95
6.94
6.94
6.93
6.91
6.89
6.87
6.85
6.83
6.72
6.70
5.32
5.30
¹H NMR (400 MHz, CDCl₃)
OH
Br
Br
1.99
4.37
3.26
5.37
1.00
1.02
f1 (ppm)

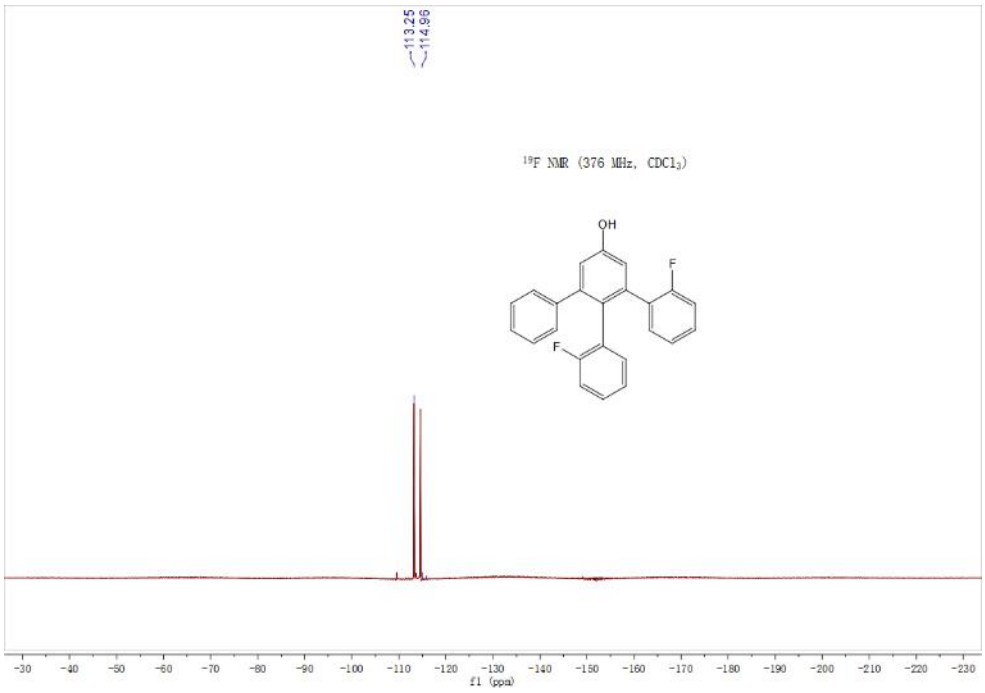

154.72
143.20
141.81
141.03
140.86
134.69
132.55
130.49
129.64
129.13
128.99
128.76
128.43
127.76
126.72
121.78
121.26
116.83
77.32
76.70
¹³C NMR (100 MHz, CDCl₃)
OH
Br
Br
143.64
143.20
141.81
141.03
140.86
134.69
132.55
130.49
130.41
129.64
129.13
128.99
128.76
128.43
127.76
126.72
f1 (ppm)

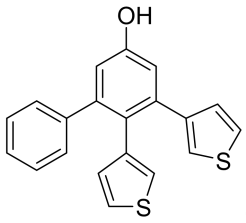

OH
F
F

(4j)

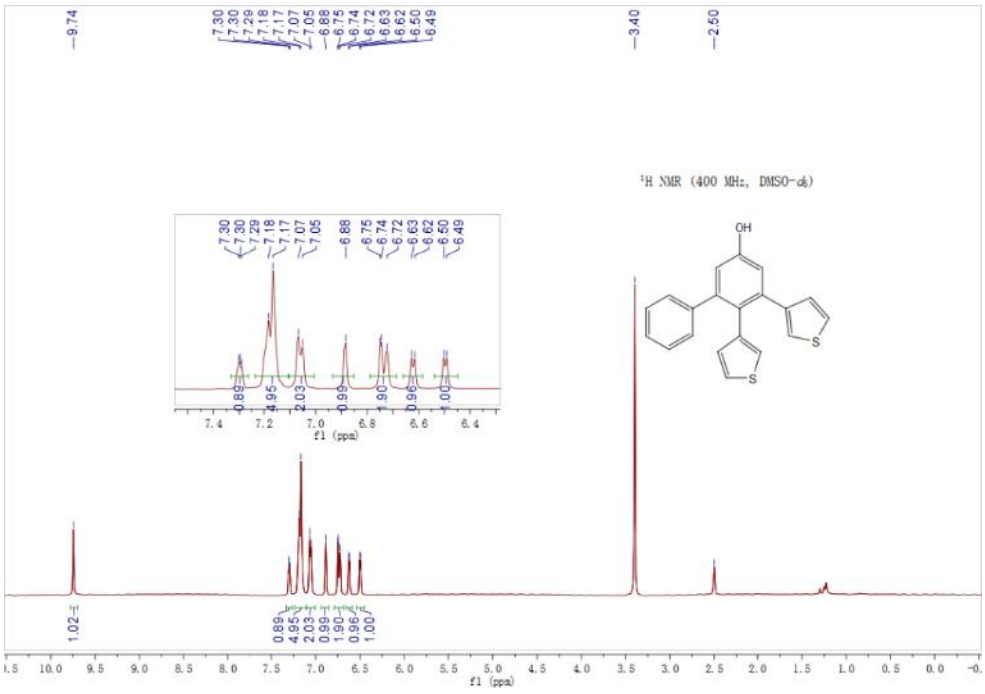

^{1}H NMR (400 MHz, CDCl$_3$)
OH
F
F
f1 (ppm)

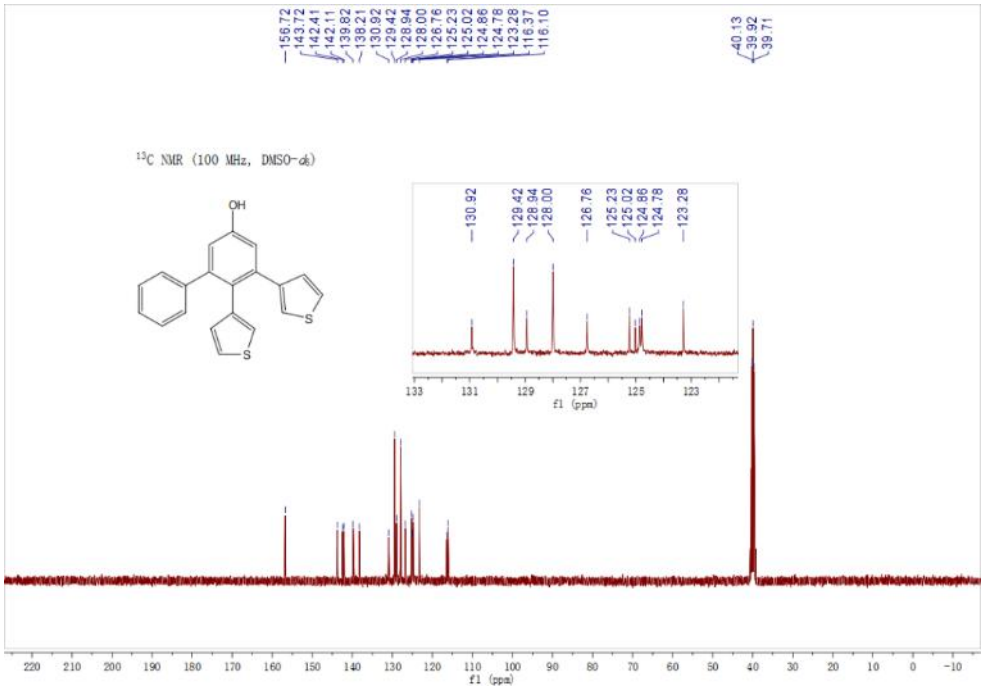

^{13}C NMR (100 MHz, CDCl$_3$)
OH
F
F
f1 (ppm)

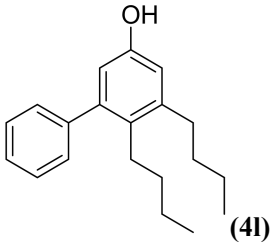

113.25
114.96
^{19}F NMR (376 MHz, $CDCl_3$)
OH
F
F
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


OH
S
S

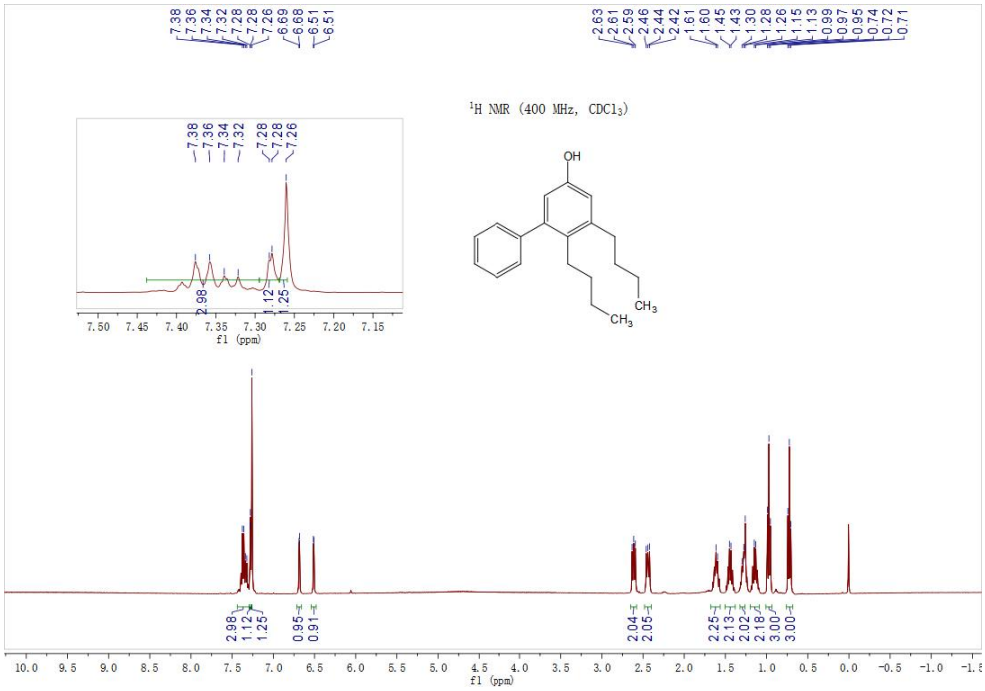
(4k)

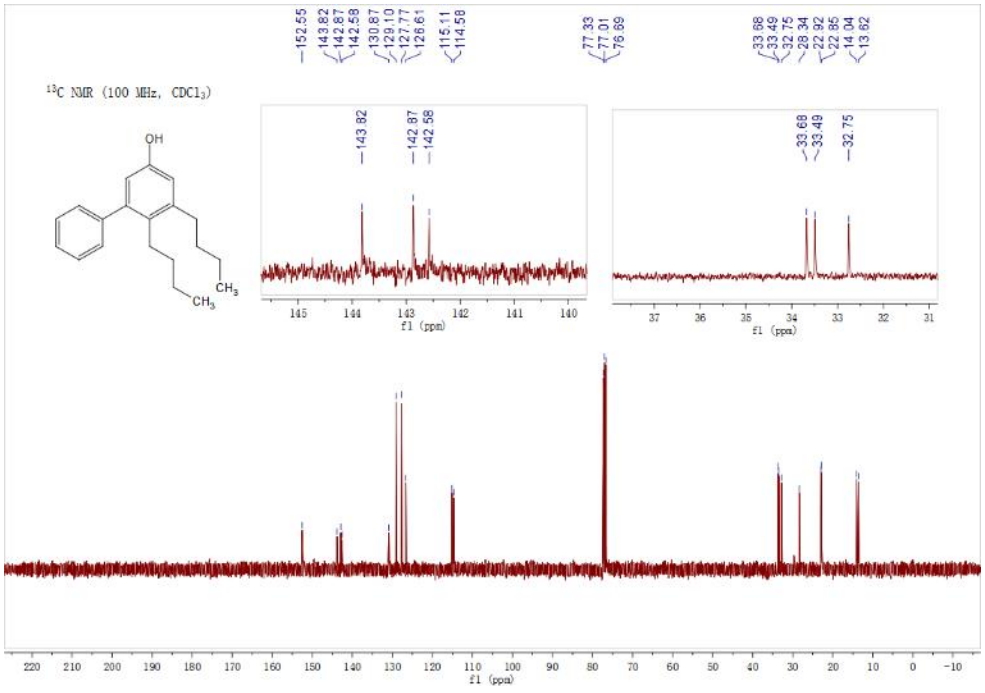

9.74
7.30
7.30
7.29
7.18
7.17
7.07
7.05
6.88
6.75
6.74
6.72
6.63
6.62
6.50
6.49
3.40
2.50
^{1}H NMR (400 MHz, DMSO-d_6)
OH
S
S
1.02
0.89
4.95
2.03
0.99
1.90
0.96
1.00
f1 (ppm)

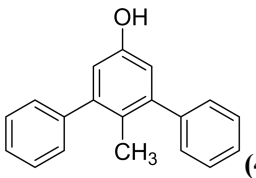

156.72
143.72
142.41
142.11
139.82
138.21
130.92
129.42
128.94
128.00
126.76
125.23
125.02
124.86
124.78
123.28
116.37
116.10
40.13
39.92
39.71
^{13}C NMR (100 MHz, DMSO-d_6)
OH
S
S
130.92
129.42
128.94
128.00
126.76
125.23
125.02
124.86
124.78
123.28
f1 (ppm)


OH

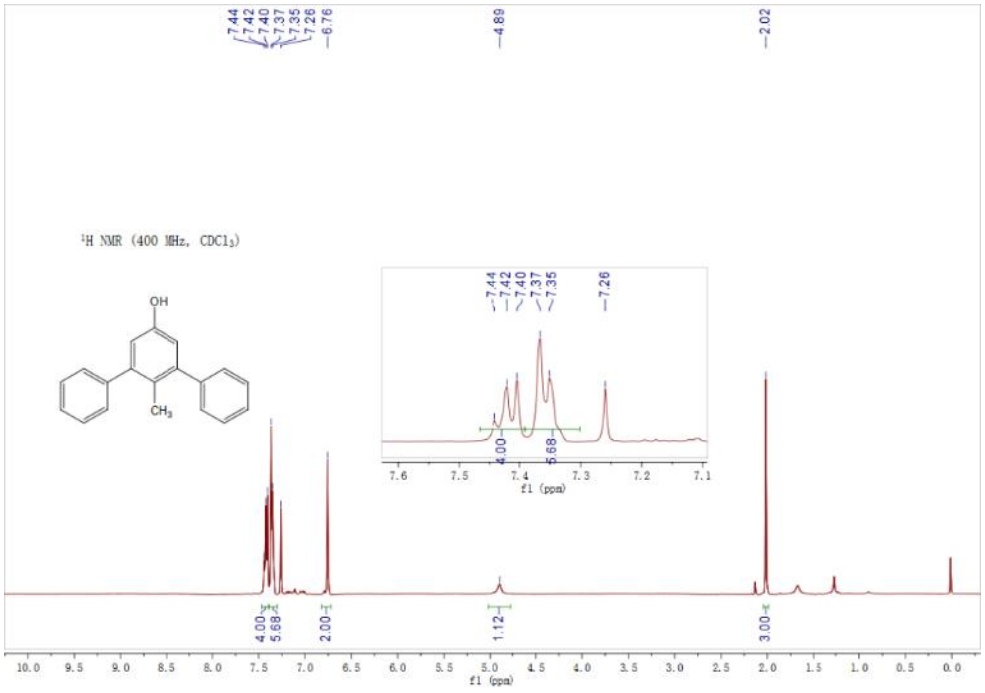
(4l)

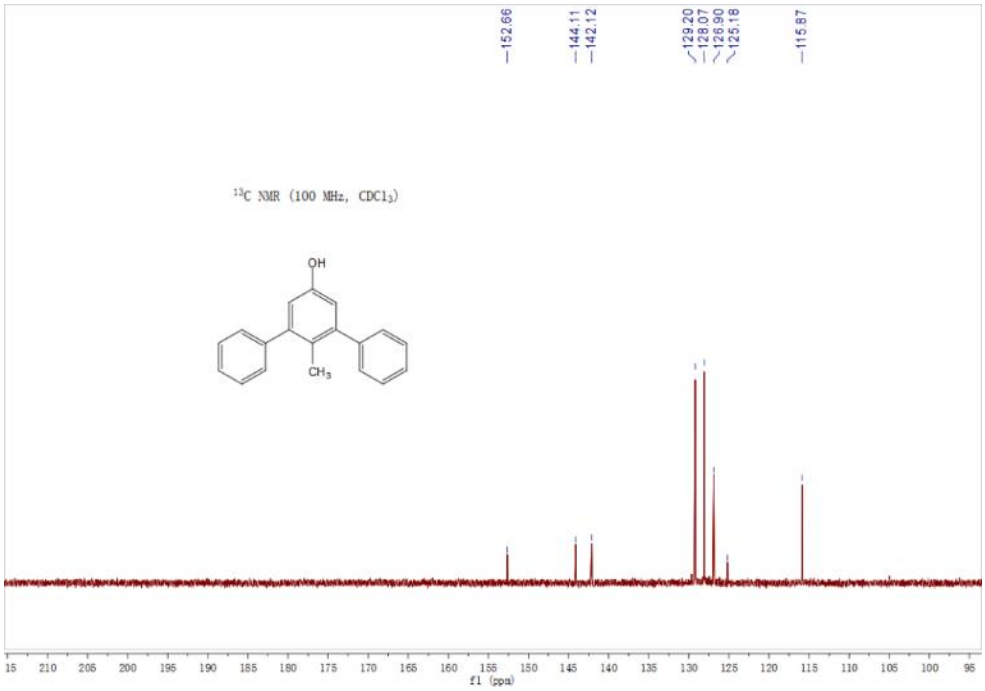

^{1}H NMR (400 MHz, CDCl$_3$)
OH
CH$_3$
CH$_3$
f1 (ppm)

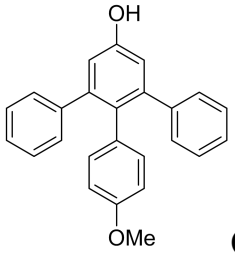

^{13}C NMR (100 MHz, CDCl$_3$)
OH
CH$_3$
CH$_3$
f1 (ppm)


OH
CH3

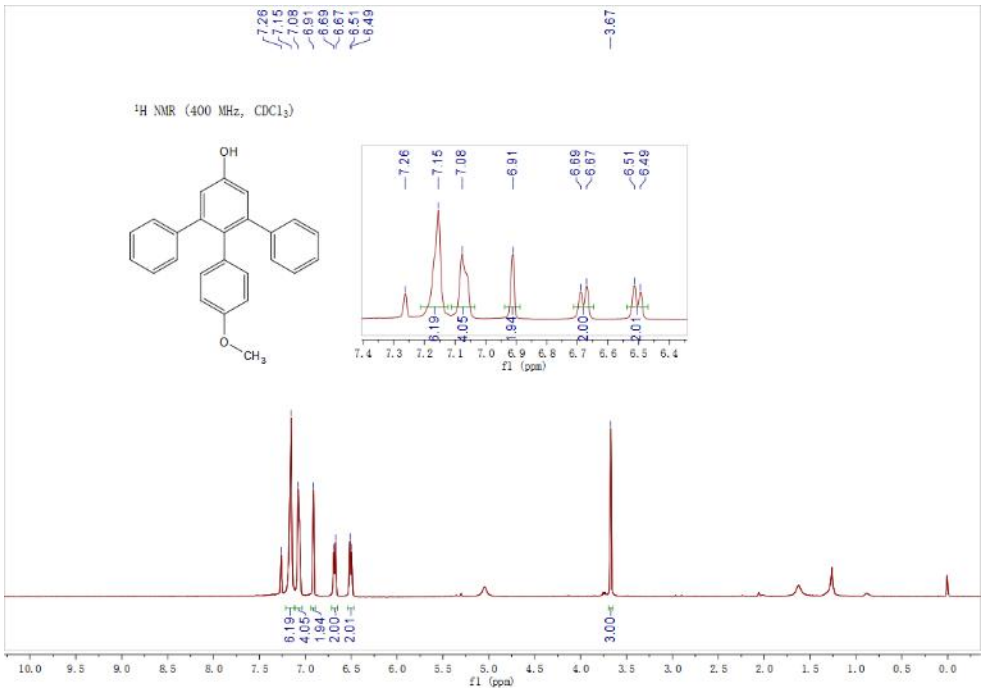
(4m)

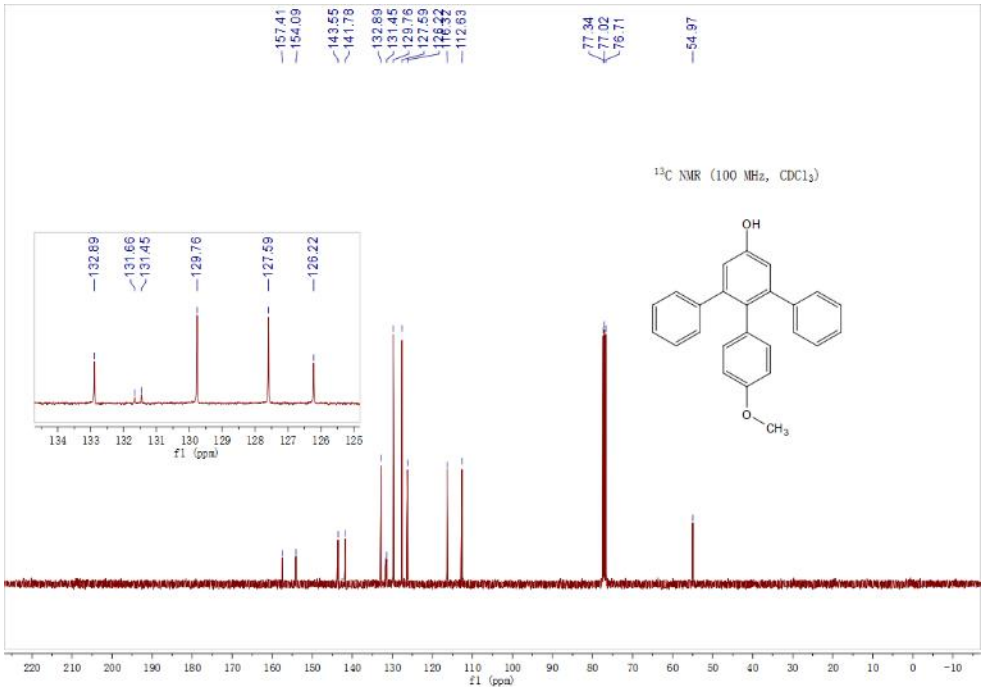

7.44
7.42
7.40
7.37
7.35
7.26
6.76
4.89
2.02
1H NMR (400 MHz, CDCl3)
OH
CH3
4.00
5.68
2.00
1.12
3.00
f1 (ppm)

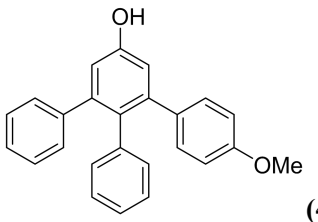

152.66
144.11
142.12
129.20
128.07
126.90
125.18
115.87
13C NMR (100 MHz, CDCl3)
OH
CH3
f1 (ppm)



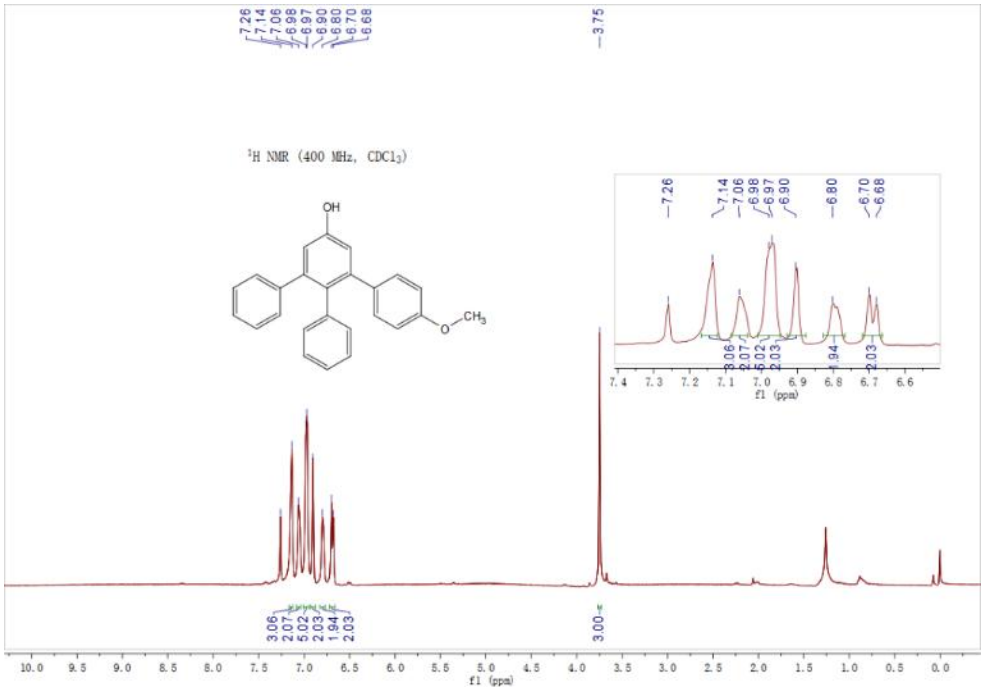
(4n)

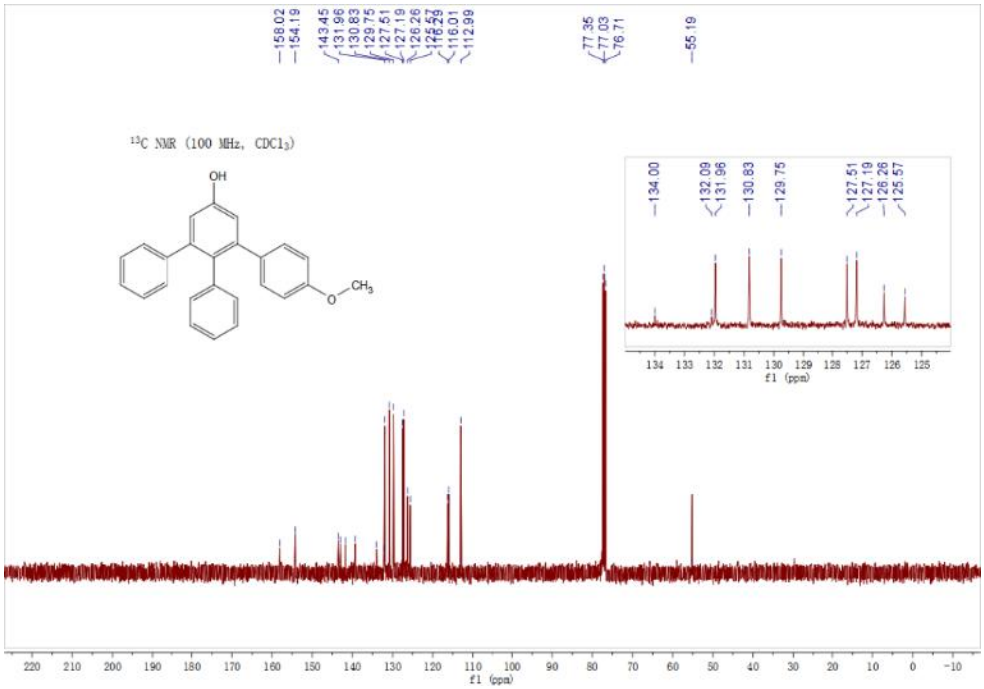





OH
OMe

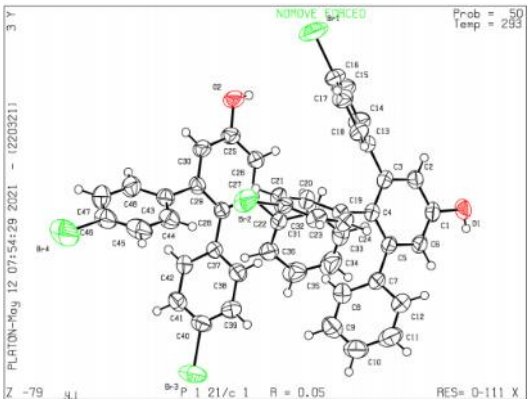
(4n')

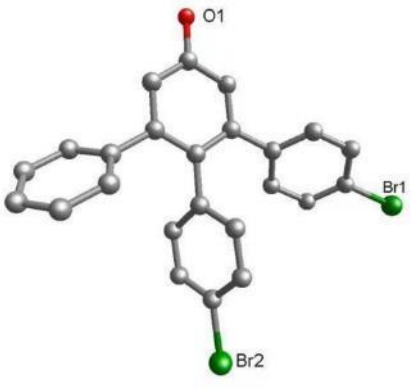

7.26
7.14
7.06
6.98
6.97
6.90
6.80
6.70
6.68
3.75
^{1}H NMR (400 MHz, CDCl$_3$)
OH
O
CH$_3$
3.06
2.07
5.02
2.03
1.94
2.03
3.00
f1 (ppm)


158.02
154.19
143.45
131.96
130.83
129.75
127.51
127.19
126.26
125.57
116.01
112.99
77.35
77.03
76.71
55.19
^{13}C NMR (100 MHz, CDCl$_3$)
OH
O
CH$_3$
134.00
132.09
131.96
130.83
129.75
127.51
127.19
126.26
125.57
f1 (ppm)

7. X-ray of 4e

Crystal data and structure refinement for **4e**





Empirical formula	$C_{24}H_{16}Br_2O$
Formula weight	480.17
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.9684(5)
b/Å	9.8282(2)
c/Å	22.2383(5)
α/°	90
β/°	112.870(3)
γ/°	90
Volume/Å^3	4021.26(18)
Z	8
ρ_{calc}g/cm^3	1.586
μ/mm^{-1}	5.187
F(000)	1904.0
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.63 to 144.562
Index ranges	-24 ≤ h ≤ 22, -11 ≤ k ≤ 7, -23 ≤ l ≤ 27

Reflections collected	15725
Independent reflections	7763 [R_{int} = 0.0260, R_{sigma} = 0.0329]
Data/restraints/parameters	7763/0/489
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1262
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1381
Largest diff. peak/hole / e $Å^{-3}$	0.97/-1.15