Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cu-Catalyzed Highly Selective Silylation and Borylation of Alkenylsulfonium Salts

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Contents of Supporting Information:

1 General Information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were distilled prior to use when necessary. NMR spectra were recorded on Bruker AMX 500 spectrophotometer (500 MHz for ^{1}H, 126 MHz for ^{13}C and 471 Hz for ^{19}F). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard (δ = 0 ppm) for ^{1}H NMR, chloroform-d (δ = 77.0 ppm) for ^{13}C NMR. The following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. HRMS (ESI-TOF) were recorded on a time-of-fligh (TOF) LC/MS instrument. Flash column chromatography was performed with Silica gel 60 (Merck) or Al_2O_3 (activated 200) (Merck).

All chemicals and solvents were purchased from commercial company and used as received. Solvents were degassed before use if necessary.

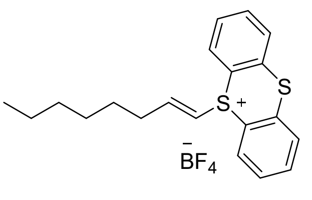
2 Experimental Details

2.1 Preparation of Substrates

Me_2PhSi-Bpin (**2**) (CAS: 185990-03-8) and B_2pin_2 (**4**) (CAS: 73183-34-3) were purchased from commercial company and used as received.

The known alkenyl thianthrenium salts (**1a**, **1c**-**1e**, **1k-1n**, **1o**, **1v**) were prepared according to the reported procedures.[1a] The new alkenyl thianthrenium salts (**1b**, **1f-1j**, **1w**) were prepared by the same method. The new alkenyl thianthrenium salts (**1p**-**1u**) were prepared by the revised procedure.[1b]

Scheme S1. Alkenyl Sulfonium Salts Substrates



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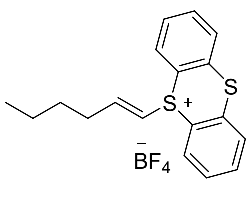
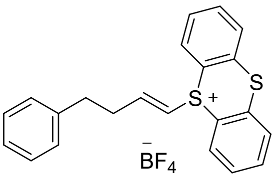


1b



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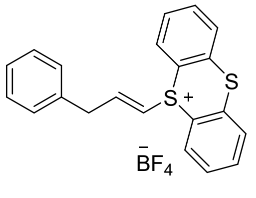

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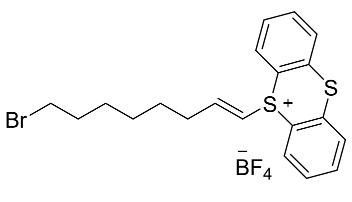

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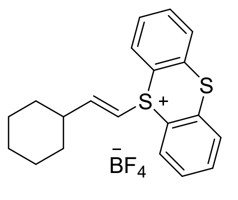

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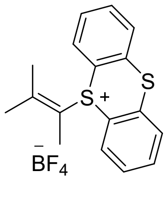

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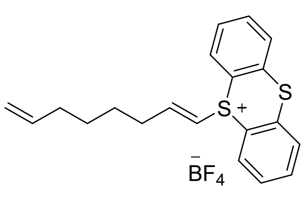

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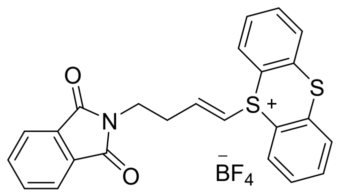

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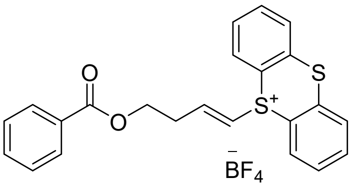

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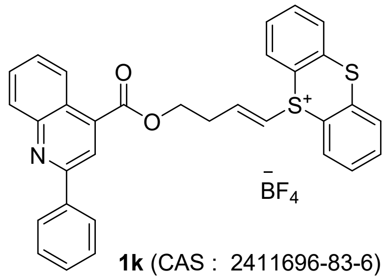

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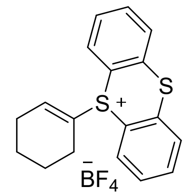

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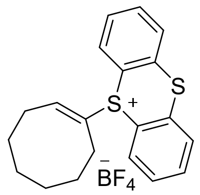

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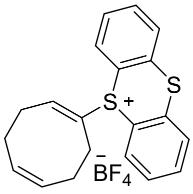

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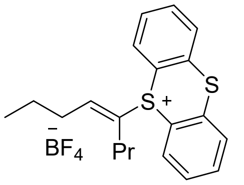

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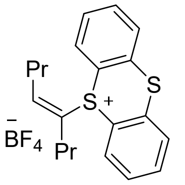

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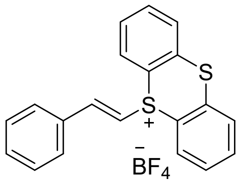

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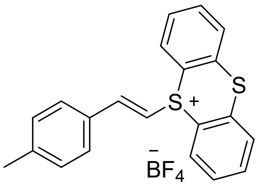

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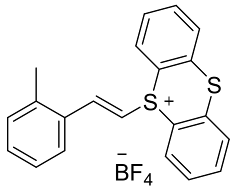
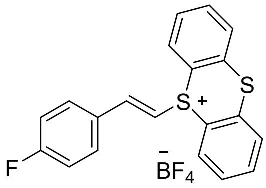


1r



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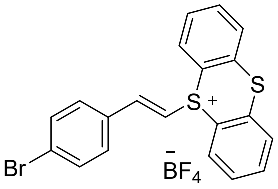

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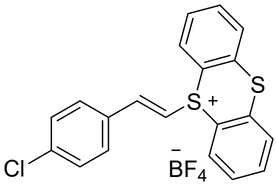
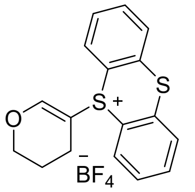


1u



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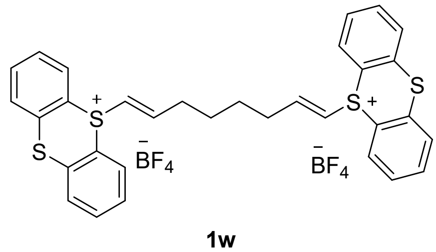
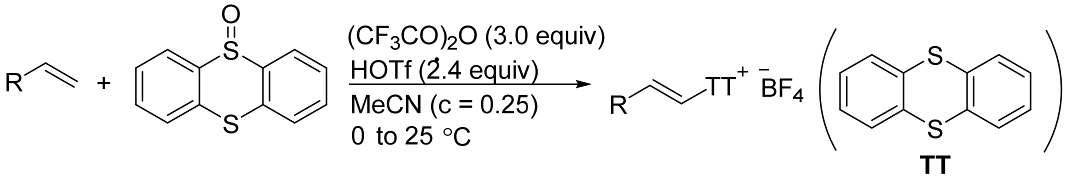


1w

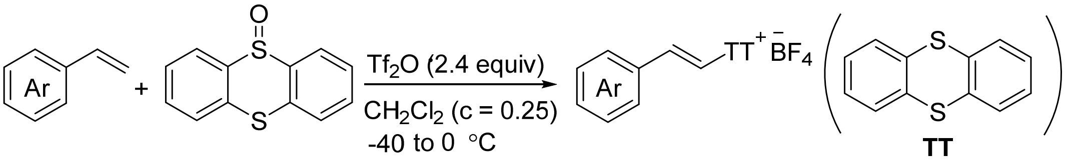
(a) General procedure for the synthesis of alkenyl thianthrenium salts (1a-1o, 1v-1w)[1a]



General procedure A (GPA): Under ambient atmosphere, a 20 mL glass-vial equipped with a magnetic stir bar was charged with alkene compound (3.00

mmol, 1.00 equiv.), thianthrene S-oxide (718 mg, 3.09 mmol, 1.03 equiv.), and MeCN (12 mL, c = 0.25 M). After cooling to 0 °C, trifluoroacetic anhydride (1.26 mL, 1.89 g, 9.00 mmol, 3.00 equiv.) was added dropwise, followed by dropwise addition of HOTf (624 μL, 1.06 g, 7.20 mmol, 2.40 equiv.). After stirring the lilac mixture at 0 °C for 60 min followed by stirring at 25 °C for 30 min, the resulting light pink mixture was concentrated under reduced pressure and subsequently diluted with CH_2Cl_2 (10 mL). The CH_2Cl_2 solution was poured onto a saturated aqueous $NaHCO_3$ solution (ca. 20 mL). The combined mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × 10 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (2 × 20 mL, 5% w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2/MeOH (1:0 gradient to 20:1 (v/v)). The product-containing fractions were collected and concentrated under reduced pressure. The residue was further dried in vacuo to afford the corresponding alkenyl thianthrenium salt.

(b) General procedure for the synthesis of alkenyl thianthrenium salts (1p-1u).[1b]

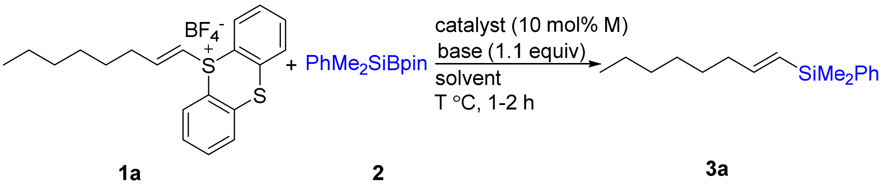


General procedure B (GPB): Under ambient atmosphere, a 20 mL glass-vial equipped with a magnetic stir bar was charged with styrene (3.00 mmol, 1.00 equiv.), thianthrene S-oxide (767 mg, 3.30 mmol, 1.1 equiv.), and CH_2Cl_2 (12 mL, c = 0.25 M). After cooling to -40 °C, triflic anhydride (0.440 mL, 846 mg, 3.00 mmol, 1.00 equiv.) was added dropwise. After stirring the lilac mixture at -40 °C for 30 min followed by stirring at 0 °C for 30 min. And the resulting dark blue mixture was stirred at 25 °C for 2 h. The solution was poured onto a saturated aqueous $NaHCO_3$ solution (ca. 20 mL). The combined mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2 × 10 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$

solution (2 × 20 mL, 5% w/w). The CH_2Cl_2 layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (1:0 gradient to 20:1 (v/v)). The product-containing fractions were collected and concentrated under reduced pressure. The residue was further dried in vacuo to afford the corresponding product.

2.1 Optimization of Conditions

Table S1. Optimization of Conditions[a]



1a **2** **3a**

entry	catalyst[b]	base	solvent	yield (%)[c] **3a**
1[d]	none	NaO^{t}Bu	dioxane	<3
2	$Pd(OAc)_2$	NaO^{t}Bu	dioxane	30
3	$Pd(PPh_3)_4$	NaO^{t}Bu	dioxane	37
4[d]	$Pd_2(dba)_3$	NaO^{t}Bu	dioxane	<3
5	CuI	NaO^{t}Bu	dioxane	20
6	$Cu(OTf)_2$	NaO^{t}Bu	dioxane	30
7	CuCl	NaO^{t}Bu	dioxane	50
8	CuCl	LiO^{t}Bu	dioxane	89
9	CuCl	KO^{t}Bu	dioxane	10
10	CuCl	K_2CO_3	dioxane	30
11[e]	CuCl	LiO^{t}Bu	dioxane	85
12[f]	CuCl	LiO^{t}Bu	dioxane	98
13	CuCl	LiO^{t}Bu	MeOH	30
14	CuCl	LiO^{t}Bu	THF	85
15[f]	**CuCl**	**LiO^{t}Bu**	**DCM**	**99(95)**

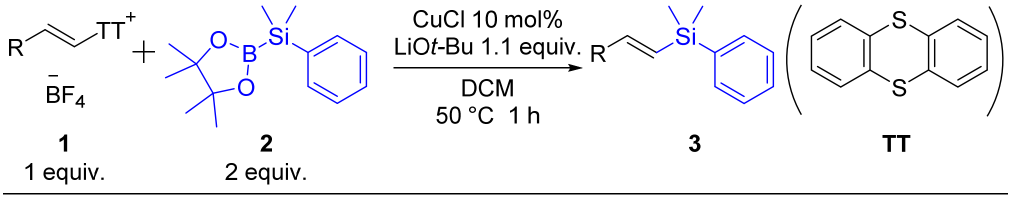
[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol), base (1.1 equiv), solvent (1 mL), at 25 °C for 2 h. [b] Catalyst (10 mol% of M) was loaded if applicable. [c] The yields were obtained by ^1H NMR analysis of the crude reaction mixture with the aid of $Cl_2CHCHCl_2$ as an internal standard. Isolated yields in parentheses. [d] The starting material **1a** decomposed seriously. [e] The reaction was open to air. [f] The reaction was stirred at 50 °C for 1 h. THF = tetrahydrofuran; DCM = dichloromethane.

A typical procedure for entry 15:

CuCl (1.0 mg, 0.010 mmol, 10 mol%), Me_2PhSi-Bpin (**2)** (52.4 mg, 0.200 mmol), alkenyl thianthrenium salt **1a** (41.4 mg, 0.100 mmol), and LiO^{t}Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 50 °C in a pre-heated oil bath for 1 h.

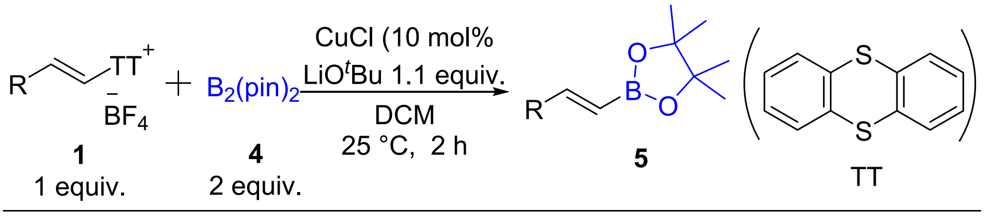
The reaction mixture was passed through a short column of silica-gel with DCM as eluent. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (petroleum ether) to give **3a** (23.3 mg, 95% yield) as a colorless oil.

2.2 General Procedure for the Reaction of Alkenyl Thianthrenium Salts with Me_2PhSi-Bpin (For Table 2)



General Procedure C (GPC): CuCl (1.0 mg, 0.01 mmol, 10 mol%), Me_2PhSi-Bpin (**2**) (52.4 mg, 0.200 mmol), alkenyl thianthrenium salt **1** (0.100 mmol), and LiO^{t}Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 50 °C in a pre-heated oil bath for 1 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (petroleum ether) to give the corresponding product **3**.

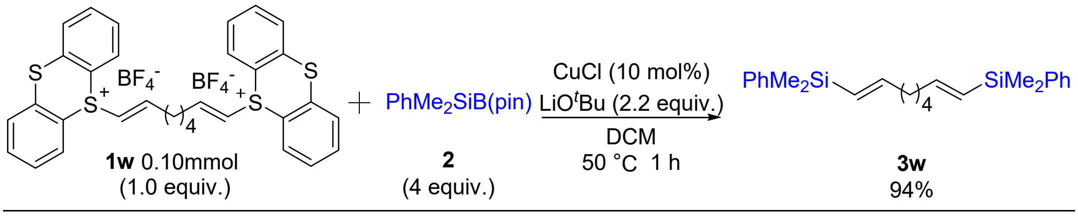
2.3 General Procedure for the Reaction of Alkenyl Thianthrenium Salts with $B_2(pin)_2$ (For Table 3)



General Procedure D (GPD): CuCl (1.0 mg, 0.010 mmol, 10 mol%), $B_2(pin)_2$ (**4**) (50.8 mg, 0.200 mmol), alkenyl thianthrenium salt **1** (0.100 mmol), and LiO*t*-Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 25 °C in for 2 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/20) to give the corresponding product **5**.

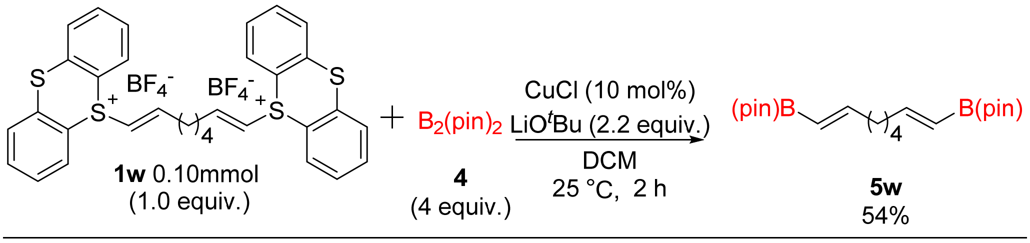
2.4 Control experiments

(1) Double silylation of 1w



CuCl (1.0 mg, 0.010 mmol, 10 mol%), Me_2PhSi-Bpin (**2**) (104 mg, 0.400 mmol), alkenyl thianthrenium salt **1w** (71.4 mg, 0.100 mmol), and LiO^{t}Bu (17.6 mg, 0.220 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 50 °C in a pre-heated oil bath for 1 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (petroleum ether) to give **3w** (35.5 mg, 94%).

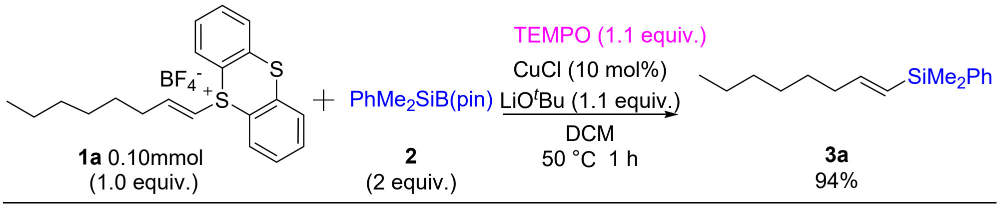
(2) Double borylation of 1w



CuCl (1.0 mg, 0.010 mmol, 10 mol%), $B_2(pin)_2$ (**4**) (102 mg, 0.400 mmol), alkenyl thianthrenium salt **1w** (71.4 mg, 0.100 mmol), and LiO^{t}Bu (17.6 mg, 0.220 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 25 °C in for 2 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/20) to give the corresponding product **5w** (19.6 mg, 54%).

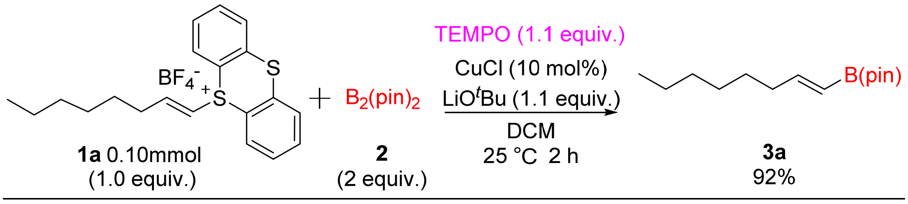
(3) Radical trapping experiments

(a) Radical trapping experiment for the silylation



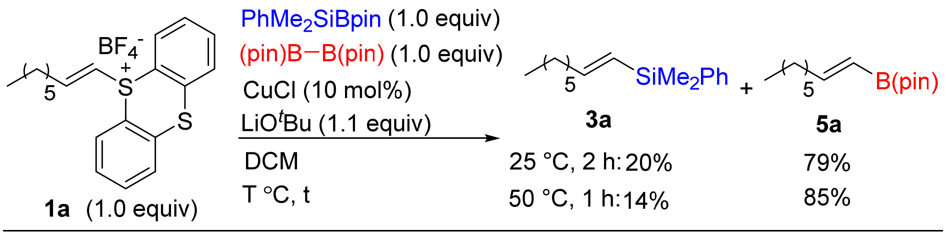
TEMPO (17.2 mg, 0.110 mmol), CuCl (1.0 mg, 0.010 mmol, 10 mol%), Me_2PhSi-Bpin (**2**) (52.4 mg, 0.200 mmol), alkenyl thianthrenium salt **1a** (41.4 mg, 0.100 mmol), and LiO^{t}Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 50 °C in a pre-heated oil bath for 1 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (petroleum ether) to give the corresponding product **3a** (23.2 mg, 94%).

(b) Radical trapping experiment for the borylation



TEMPO (17.2 mg, 0.110 mmol), CuCl (1.0 mg, 0.010 mmol, 10 mol%), $B_2(pin)_2$ (**4**) (50.8 mg, 0.200 mmol), alkenyl thianthrenium salt **1a** (41.4 mg, 0.100 mmol), and LiO*t*-Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred at 25 ˚C in for 2 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/20) to give the corresponding product **5a** (21.9 mg, 92%).

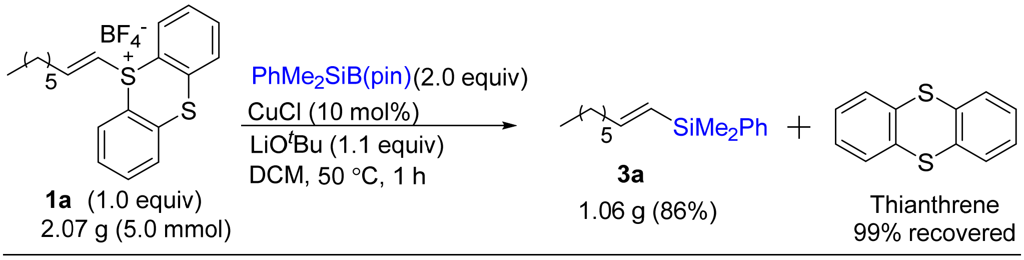
(4) Competition experiments



CuCl (1.0 mg, 0.010 mmol, 10 mol%), Me_2PhSi-Bpin (**2**) (26.2 mg, 0.100 mmol), $B_2(pin)_2$ (**4**) (25.4 mg, 0.100 mmol), alkenyl thianthrenium salt **1a** (41.4 mg, 0.100 mmol), and LiO^{t}Bu (8.8 mg, 0.11 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (1.0 mL) was added, and the mixture was stirred under the given conditions (**Conditions 1**: 25 °C, 2 h; **Conditions 2**: 50 °C, 1 h). The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The yields of **3a** and **5a** were obtained by ^{1}H NMR analysis of the crude reaction mixture with the aid of $Cl_2CHCHCl_2$ as an internal standard (Conditions 1: **3a** 20%, **5a** 79%; Conditions 2: **3a** 14%, **5a** 85%).

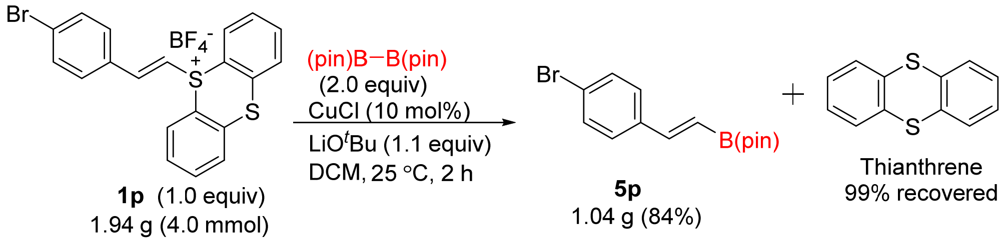
2.5 Gram Scale Experiments

a) Gram scale experiment for the silylation



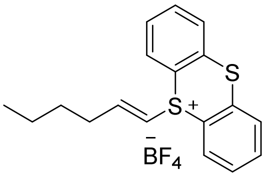
CuCl (49.5 mg, 0.500 mmol, 10.0 mol%), Me_2PhSi-Bpin (**2**) (2.62 g, 10.0 mmol), alkenyl thianthrenium salt **1a** (2.07 g, 5.00 mmol), and LiO^{t}Bu (440 mg, 5.50 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (25 mL) was added, and the mixture was stirred at 50 °C in a pre-heated oil bath for 1 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (petroleum ether) to give the corresponding product **3a** (1.06 g, 86%) and thianthrene (1.07 g, 99%).

b) Gram scale experiment for the borylation

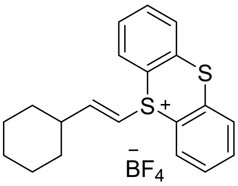


CuCl (39.6 mg, 0.400 mmol, 10.0 mol%), $B_2(pin)_2$ (**4**) (2.03 g, 8.00 mmol), alkenyl thianthrenium salt **1p** (1.94 g, 4.00 mmol), and LiO*t*-Bu (352 mg, 4.40 mmol) were placed in a Schlenk tube under nitrogen. Distilled DCM (25 mL) was added, and the mixture was stirred at 25 ˚C in for 2 h. The reaction mixture was passed through a short column of silica-gel with DCM as eluent. After further removal of solvent by vacuum pump, the crude ^{1}H NMR was taken for analysis. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/petroleum ether = 1/20) to give the corresponding product **5p** (1.04 g, 84%) and thianthrene (857 mg, 99%).

3 Characterization Data of the Products

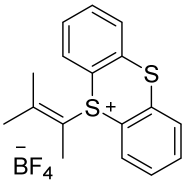


Compound 1b. Following **GPA,** the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a yellow oil (695 mg, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 1.1 Hz, 7.9 Hz, 2H), 7.83 (dd, *J* = 1.1 Hz, 7.9 Hz, 2H), 7.74 (td, *J* = 1.2 Hz, 7.7 Hz, 2H), 7.65 (td, *J* = 1.2 Hz, 7.7 Hz, 2H), 7.28-7.21 (m, 1H), 6.55 (dt, *J* = 1.3 Hz, 14.8 Hz, 1H), 2.27-2.21 (m, 2H), 1.41-1.33 (m, 2H), 1.27-1.19 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 135.5, 134.4, 133.6, 130.3, 130.0, 120.5, 109.1, 33.0, 29.2, 22.0, 13.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.74 (brs), -150.80 (brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{19}S_2^+$ 299.0923; found 299.0918.

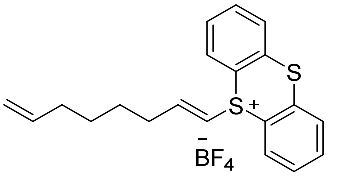


Compound 1f. Following **GPA**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a

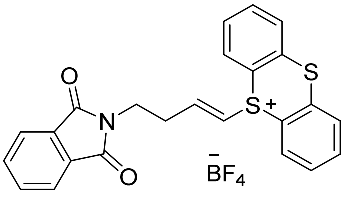
white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 1.0 Hz, 7.9 Hz, 2H), 7.82 (dd, *J* = 1.0 Hz, 7.9 Hz, 2H), 7.73 (td, *J* = 1.1 Hz, 7.7 Hz, 2H), 7.66 (td, *J* = 1.1 Hz, 7.7 Hz, 2H), 7.17 (dd, *J* = 6.8 Hz, 14.9 Hz, 1H), 6.48 (dd, *J* = 1.2 Hz, 14.9 Hz, 1H), 2.24-2.15 (m, 1H), 1.72-1.65 (m, 4H), 1.22-1.14 (m, 3H), 1.14-1.02 (m, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 161.3, 135.5, 134.3, 134.0, 130.4, 130.0, 120.8, 107.7, 42.0, 30.8, 25.5, 25.3. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -150.62 (brs), -150.68 (brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{21}S_2^+$ 325.1079; Found 325.1086.



Compound 1g. Following **GPA**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a white solid (220 mg, 19%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.75-7.67 (m, 6H), 2.54 (d, *J* = 1.4 Hz, 3H), 2.19 (d, *J* = 0.8 Hz, 3H), 2.03 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 163.4, 133.6, 133.5, 131.3, 130.4, 129.6, 119.7, 115.0, 24.2, 24.0, 15.9. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -152.64 (brs), -152.69(brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{17}S_2^+$ 285.0766.0923; found 285.0775.

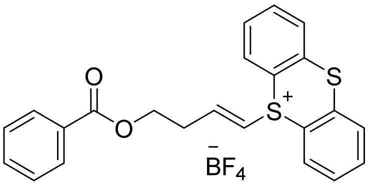


Compound 1h. Following **GPA**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 1.1 Hz, 7.9 Hz, 2H), 7.82 (dd, *J* = 1.1 Hz, 7.9 Hz, 2H), 7.73 (td, *J* = 1.1 Hz, 7.6 Hz, 2H), 7.68 (td, *J* = 1.1 Hz, 7.6 Hz, 2H), 7.33-7.26 (m, 1H), 6.56 (d, *J* = 14.8 Hz, 1H), 5.75-5.66 (m, 1H), 4.96-4.87 (m, 2H), 2.28-2.21 (m, 2H), 1.98 (q, *J* = 7.1 Hz, 2H), 1.46-1.39 (m, 2H), 1.35-1.28 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 157.2, 138.1, 135.4, 134.3, 133.9, 130.3, 129.9, 120.8, 114.9, 109.2, 33.2, 33.1, 28.2, 26.6. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -150.63 (brs), -150.69(brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{21}S_2^+$ 325.1079; Found 325.1072.

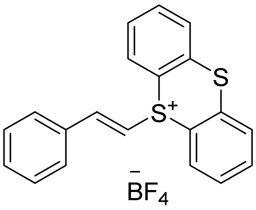


Compound 1i. Following **GPA**, the product was

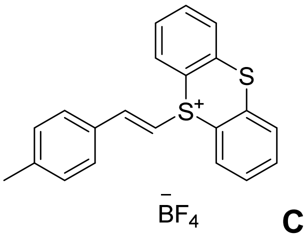
prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a white solid (1.237 g, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.78-7.64 (m, 10H), 7.03 (dt, *J* = 7.2Hz, 14.9 Hz, 1H), 6.56 (d, *J* = 14.9 Hz, 1H), 3.76 (t, *J* = 6.7 Hz, 2H), 2.71-2.64 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.9, 151.0, 135.6, 134.4, 134.2, 134.1, 131.6, 130.3, 130.0, 123.4, 119.7, 111.9, 35.4, 32.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.47 (brs), -150.53(brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{18}NO_2S_2^+$ 416.0773; Found 416.0780.



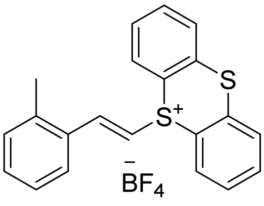
Compound 1j. Following **GPA**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a sticky yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 1.2 Hz, 7.8 Hz, 2H), 7.83 (dd, *J* = 1.2 Hz, 7.8 Hz, 2H), 7.74-7.66 (m, 4H), 7.63 (td, *J* = 1.4 Hz, 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.25-7.17 (m, 1H), 6.67 (d, *J* = 14.9 Hz, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 2.75 (q, *J* = 6.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 151.5, 135.4, 134.3, 133.9, 133.2, 130.3, 129.9, 129.5, 128.4, 120.0, 111.8, 61.4, 32.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.33 (brs), -150.38(brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{19}O_2S_2^+$ 391.0821; Found 391.0809.



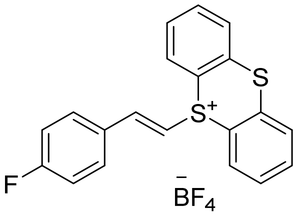
Compound 1p. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a white solid (877 mg, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 1.3 Hz, 8.0 Hz, 2H), 8.09 (d, *J* = 15.1 Hz, 1H), 7.85 (dd, *J* = 1.3 Hz, 8.0 Hz, 2H), 7.74 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.66 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.51-7.47 (m, 2H), 7.42-7.36 (m, 1H) 7.33 (t, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 15.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.8, 135.6, 134.4, 133.9, 132.3, 132.0, 130.4, 130.0, 129.1, 129.0, 120.9, 106.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.12 (brs), -150.17 (d, *J* = 1.6 Hz). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{15}S_2^+$ 319.061; Found 319.0599.



Compound 1q. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a pale-yellow solid (857 mg, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 8.05 (d, *J* = 15.1 Hz, 1H), 7.77 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.65 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.59 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 15.1 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.2, 143.4, 135.6, 134.2, 133.8, 130.4, 129.9, 129.9, 129.4, 129.1, 121.3, 104.3, 21.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.28 (brs), -150.34 (d, *J* = 1.1 Hz). **HRMS** (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0758.

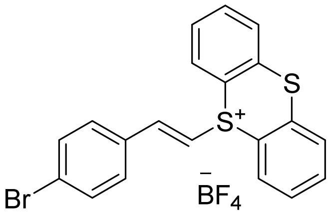


Compound 1r. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a pale-yellow solid (756 mg, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 8.09 (d, *J* = 15.0 Hz, 1H), 7.84 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.74 (td, *J* = 1.3 Hz, 7.6 Hz, 2H), 7.68 (td, *J* = 1.3 Hz, 7.6 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.31-7.26 (m, 1H) 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.3, 139.5, 135.6, 134.3, 134.0, 132.1, 131.3, 131.1, 130.4, 130.0, 126.8, 126.4, 121.0, 106.7, 19.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.07 (brs), -150.12 (brs). **HRMS** (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{21}H_{17}S_2^+$ 333.0766; Found 333.0756.

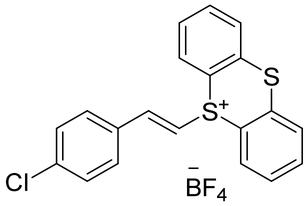


Compound 1s. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a pale-yellow solid (952 mg, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 1.3 Hz, 7.9 Hz, 2H), 8.18 (d, *J* = 15.2 Hz, 1H), 7.85 (dd, *J* = 1.3 Hz, 7.9 Hz, 2H),

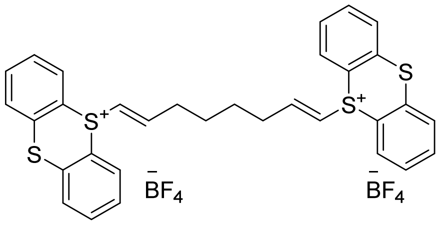
7.74 (td, *J* = 1.4 Hz, 7.6 Hz, 2H), 7.66 (td, *J* = 1.4 Hz, 7.6 Hz, 2H), 7.57-7.52 (m, 2H), 7.08-7.00 (m, 3H) . **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.0, 135.6, 134.3, 134.0, 131.4, 131.37, 130.5, 130.0, 128.4, 121.1, 116.6, 116.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.26 (m), -150.03 (brs), -150.09 (brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20} H_{14}F S_2^+$ 337.0515; Found 337.0523.



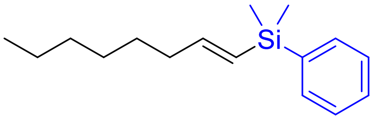
Compound 1t. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a pale-yellow solid (972 mg, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 1.1 Hz, 8.0 Hz, 2H), 8.01 (d, *J* = 15.1 Hz, 1H), 7.85 (dd, *J* = 1.1 Hz, 8.0 Hz, 2H), 7.74 (td, *J* = 1.2 Hz, 7.7 Hz, 2H), 7.66 (td, *J* = 1.2 Hz, 7.7 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 15.1 Hz, 1H),. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.3, 135.7, 134.5, 133.8, 132.3, 131.0, 130.4, 130.2, 126.9, 120.4, 107.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -149.89 (brs), -149.94 (brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20} H_{14}BrS_2^+$ 396.9715; Found 396.9710.



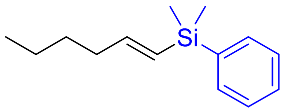
Compound 1u. Following **GPB**, the product was prepared and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a pale-yellow solid (850 mg, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 1.3 Hz, 7.9 Hz, 2H), 8.01 (d, *J* = 15.2 Hz, 1H), 7.78 (dd, *J* = 1.3 Hz, 7.9 Hz, 2H), 7.68 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.61 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 15.2 Hz, 1H),. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 138.5, 135.7, 134.4, 133.9, 130.6, 130.4, 130.3, 130.1, 129.4, 120.6, 106.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -149.93 (brs), -149.98 (brs). **HRMS** (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{20} H_{14}Cl S_2^+$ 353.0220; Found 353.0219.



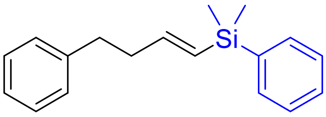
Compound 1w. Prepared from octa-1,7-diene (330mg, 3.00 mmol, 1.00 equiv), thianthrene S-oxide (1) (1.44 g, 6.18 mmol, 2.06 equiv), trifluoroacetic anhydride (2.52 mL, 3.78 g, 18.00 mmol, 6.00 equiv) and HOTf (1.25 mL, 2.12 g, 14.40 mmol, 4.80 equiv), according to GPA and purified by flash column chromatography (eluent: CH_2Cl_2/MeOH = 100/1) as a white solid (1.35g, 63%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.84 (dd, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.73 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.66 (td, *J* = 1.3 Hz, 7.7 Hz, 2H), 7.14 (dt, *J* = 7.2 Hz, 14.8 Hz, 1H), 6.58 (d, *J* = 14.8 Hz, 1H), 2.28-2.22 (m, 2H), 1.46-1.41 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8, 135.6, 134.3, 133.3, 130.2, 120.6, 109.7, 32.7, 26.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -150.63 (brs), -150.68 (brs). **HRMS** (ESI-TOF) m/z: $[M]^{2+}$ Calcd for $C_{32}H_{28}S_4^{2+}$ 270.0531; Found 270.0528



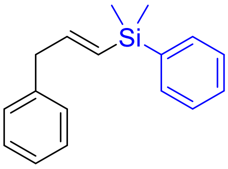
. **Compound 3a (CAS: 116488-00-7**, known compound**)**[2]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a yellow oil (24.3 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.37-7.33 (m, 3H), 6.13 (dt, *J* = 6.3 Hz, 18.6 Hz, 1H), 5.76 (dt, *J* = 1.4 Hz, 18.6 Hz, 1H), 2.19-2.12 (m, 2H), 1.44-1.38 (m, 2H), 1.34-1.28 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.33 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 139.4, 133.8, 128.8, 127.7, 127.2, 36.9, 31.7, 28. 9, 28.6, 22.6, 14.1, -2.4.



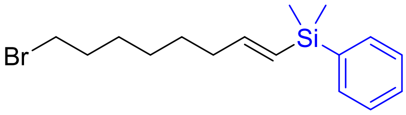
Compound 3b (CAS: 64545-10-4, known compound**)**[3]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a yellow oil (16.1 mg, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.38-7.33 (m, 3H), 6.13 (dt, *J* = 6.3 Hz, 18.6 Hz, 1H), 5.76 (dt, *J* = 1.5 Hz, 18.6 Hz, 1H), 2.20-2.12 (m, 2H), 1.45-1.37 (m, 2H), 1.37-1.30 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.32 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 139.4, 133.8, 128.8, 127.7, 127.2, 36.5, 30.8, 22.3, 14.0, -2.4.



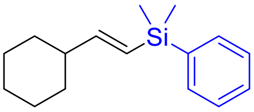
Compound 3c (CAS: 852064-26-7, known compound**)**[4]**.** Following **GPC**, the product was prepared as a colorless oil (21.3 mg, 80%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.51-7.48 (m, 2H), 7.37-7.34 (m, 3H), 7.31-7.27 (m, 2H), 7.23-7.17 (m, 3H), 6.17 (dt, *J* = 6.2 Hz, 18.6 Hz, 1H), 5.80 (dt, *J* = 1.5 Hz, 18.6 Hz, 1H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.52-2.45 (m, 2H), 0.32 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 148.1, 141.9, 139.1, 133.8, 128.8, 128.5, 128.3, 128.2, 127.7, 125.8, 38.5, 35.1, -2.5.



Compound 3d (CAS: 773121-40-7, known compound**)**[2]**.** Following **GPC***,* the product was prepared as a colorless oil (20.2 mg, 80%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.54-7.50 (m, 2H), 7.37-7.33 (m, 3H), 7.32-7.28 (m, 2H), 7.23-7.17 (m, 3H), 6.25 (dt, *J* = 6.3 Hz, 18.4 Hz, 1H), 5.84(dt, *J* = 1.4 Hz, 18.4 Hz, 1H), 3.50 (d, *J* = 6.1 Hz, 2H), 0.33 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 147.1, 139.8, 139.0, 133.8, 129.2, 128.9, 128.7, 128.4, 127.7, 126.1, 43.3, -2.5.

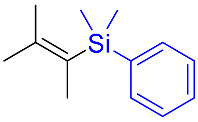


Compound 3e. Following **GPC**, the product was prepared as a colorless oil (29.2 mg, 90%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.54-7.50 (m, 2H), 7.37-7.33 (m, 3H), 6.11 (dt, *J* = 6.2 Hz, 18.5 Hz, 1H), 5.76(d, *J* = 18.5 Hz, 1H), 3.41 (d, *J* = 6.9 Hz, 2H), 2.19-2.12 (m, 2H), 1.90-1.82 (m, 2H), 1.49-1.40 (m, 4H), 1.36-1.30 (m, 2H), 0.32 (s, 6H). ^{13}C **NMR** (126 MHz, CDCl$_3$) δ 149.0, 139.3, 133.8, 128.8, 127.7, 127.5, 36.6, 33.9, 32.7, 28.3, 28.3, 28.0, -2.5. **HRMS** (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{16}$H$_{25}$BrSi Na$^+$ 347.0801; Found 347.0799.

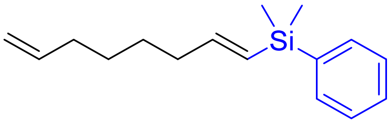


Compound 3f (CAS: 148991-59-7, known compound**)**[2]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a yellow oil (21.1 mg, 86%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.54-7.50 (m, 2H), 7.38-7.33 (m, 3H), 6.09 (dd, *J* = 6.0 Hz, 18.8 Hz, 1H), 5.71 (dd, *J* = 1.4 Hz, 18.8 Hz, 1H), 2.06-1.97 (m, 1H), 1.80-1.70 (m, 4H), 1.69-1.62 (m, 1H), 1.34-1.25 (m, 2H), 1.21-1.08 (m, 3H), 0.32 (s,

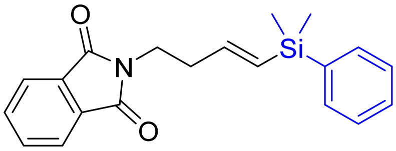
6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 154.9, 139.5, 133.8, 128.7, 127.7, 123.8, 44.0, 32.3, 26.2, 26.0, -2.4.



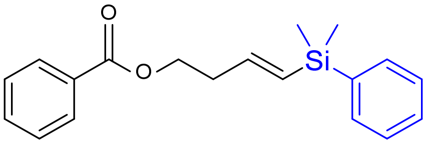
Compound 3g (CAS: 129156-01-0, known **compound)**[5]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a yellow oil (6.5 mg, 32%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.34-7.31 (m, 3H), 1.76 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 0.37 (s, 6H).



Compound 3h. Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a colorless oil (18.8 mg, 77%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.49 (m, 2H), 7.37-7.33 (m, 3H), 6.12 (dt, *J* = 6.3 Hz, 18.5 Hz, 1H), 5.86-5.73 (m, 2H), 5.00(dd, *J* = 1.5 Hz, 17.1 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 2.19-2.13 (m, 2H), 1.90-1.82 (m, 2H), 1.49-1.40 (m, 4H), 1.36-1.30 (m, 2H), 0.32 (s, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 149.0, 139.3, 133.8, 128.8, 127.7, 127.5, 36.6, 33.9, 32.7, 28.3, 28.3, 28.0, -2.5. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{24}SiNa^+$ 267.1539; Found 267.1530.

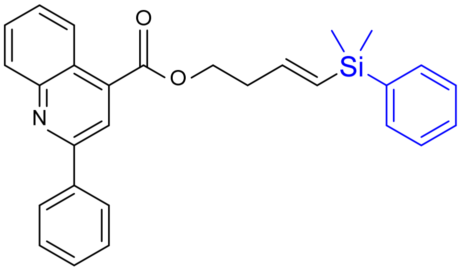


Compound 3i (CAS: 1138502-22-3, known **compound)**[6]**.** According to **GPC** at 25 °C in DCM (1 mL) for 2 h. The product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (26.1 mg, 78%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.72-7.69 (m, 3H), 7.42-7.38 (m, 2H), 7.32-7.29 (m, 1H), 7.28-7.24 (m, 1H), 6.07 (dt, *J* = 6.6 Hz, 18.5 Hz, 1H), 5.79 (dt, *J* = 1.2 Hz, 18.5 Hz, 1H), 3.80 (t, *J* = 7.0 Hz, 2H), 2.57-2.51 (m, 2H), 0.24 (s, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.3, 144.2, 138.5, 133.8, 133.7, 132.0, 131.6, 128.8, 127.6, 123.1, 37.0, 35.6, -2.8.

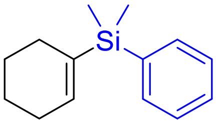


Compound 3j. Following **GPC**, the product was prepared and purified by flash column chromatography (eluent:

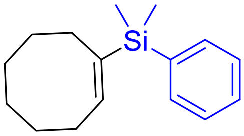
EtOAc/petroleum ether = 1/20) as a yellow oil (14.6 mg, 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 1.1 Hz, 8.2 Hz, 2H), 7.59-7.54 (m, 1H), 7.52-7.48 (m, 2H),7.43 (t, *J* = 7.8 Hz, 2H), 7.37-7.29 (m, 3H), 6.16 (dt, *J* = 6.3 Hz, 18.6 Hz, 1H), 5.96 (dt, *J* = 1.3 Hz, 18.6 Hz, 1H), 4.42 (t, *J* = 6.7 Hz, 2H), 2.73 (qd, *J* = 1.3 Hz, 6.6 Hz, 2H), 0.33 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 143.7, 138.7, 133.8, 132.8, 131.3, 130.4, 129.5, 128.9, 128.3, 127.7, 63.6, 36.0, -2.7. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{22}O_2SiNa^+$ 333.1281; Found 333.1275.



Compound 3k. Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid (20.5 mg, 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.5 Hz, 1H), 8.38 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 7.2 Hz, 2H), 7.80-7.75 (m, 1H), 7.62-7.57 (m, 1H), 7.56-7.52 (m, 2H), 7.51-7.46 (m, 3H), 7.32-7.24 (m, 3H), 6.21 (dt, *J* = 6.2 Hz, 18.6 Hz, 1H), 6.03 (d, *J* = 18.6 Hz, 1H), 4.59 (t, *J* = 6.6 Hz, 2H), 2.73 (qd, *J* = 0.91 Hz, 6.5 Hz, 2H), 0.34 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166. 5, 156.8, 149.3, 143.4, 138.9, 138.5, 135.9, 133.8, 131.8, 130.4, 129.9, 129.7, 129.0, 128.97, 127.8, 127.77, 127.5, 125.5, 124.0, 120.3, 64.6, 36.0, -2.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{28}NO_2Si^+$ 438.1884; Found 438.1889.

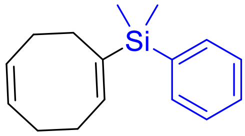


Compound 3l (CAS: 108025-34-9, known compound**)**[2]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as yellow oil (18.2 mg, 84%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.37-7.32 (m, 3H), 6.07-6.05 (m, 1H), 2.10-1.98 (m, 4H), 1.64-1.58 (m, 4H), 0.31 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.8, 137.9, 136.7, 134.0, 128.7, 127.6, 26.9, 26.8, 22.9, 22.4, -3.6.

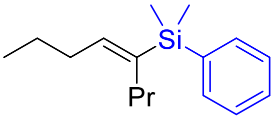


Compound 3m. Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a

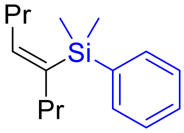
colorless oil (12.9 mg, 53%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.37-7.32 (m, 3H), 6.06 (t, *J* = 6.9Hz, 1H), 2.29-2.25 (m, 2H), 2.25-2.20 (m, 2H), 1.51-1.34 (m, 8H), 0.35 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.7, 140.2, 139.1, 134.0, 128.7, 127.6, 29.7, 28.9, 27.5, 27.0, 26.4, 26.1, -2.9. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{24}Si\ Na^+$ 267.1539; Found 267.1539.



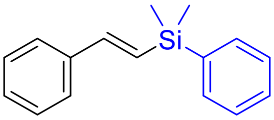
Compound 3n. According to **GPC** at 50 °C in DCM (1 mL) for 2 h. The product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a colorless oil (13.6 mg, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.37-7.32 (m, 3H), 6.01 (t, *J* = 6.0Hz, 1H), 5.62-5.54 (m, 1H), 5.52-5.45(m, 1H), 2.50-2.43 (m, 4H), 2.42-2.35 (m, 2H), 2.27-2.20 (m, 2H), 0.31 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.8, 139.1, 138.3, 134.1, 128.9, 128.7, 128.5, 127.6, 30.8, 29.0, 29.0, 27.6, -2.90. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}Si^+$ 243.1564; Found 243.1559.



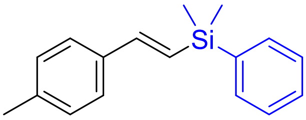
Compound *E*-3o (CAS: 191798-74-0, known compound**)**[7]**.** Following **GPC**, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a colorless oil (19.9 mg, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.36-7.32 (m, 3H), 5.82 (t, *J* = 6.9 Hz, 1H), 2.15-2.06 (m, 4H), 1.41 (q, *J* = 7.4 Hz, 2H), 1.23 (q, *J* = 7.6, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H), 0.34 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 139.5, 138.9, 134.0, 128.6, 127.6, 32.1, 30.7, 23.4, 22.7, 14.4, 13.9, -2.5.



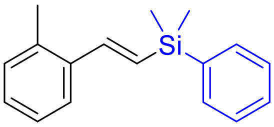
Compound *Z*-3o (CAS: 873663-95-7, known compound**)**[7]**.** Following the general procedure, the product was prepared and purified by flash column chromatography (eluent: petroleum ether) as a colorless oil (14.3 mg, 58%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.35-7.31 (m, 3H), 6.07 (t, *J* = 7.5 Hz, 1H), 2.11-2.06 (m, 2H), 1.93 (dd, *J* = 7.4 Hz, 14.8 Hz, 2H), 1.39-1.33 (m, 2H), 1.26-1.22 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H), 0.38 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.7, 140.1, 136.8, 133.8, 128.6, 127.6, 40.7, 34.4, 24.0, 22.9, 13.8, 13.7, -0.8.



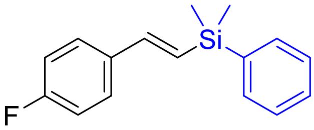
Compound 3p (CAS: 64788-85-8, known compound**)**[2]**.** Following **GPC**, the product was prepared as a colorless oil (19.0 mg, 80%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.59-7.55 (m, 2H), 7.46-7.43 (m, 2H), 7.38-7.35 (m, 3H), 7.34-7.30 (m, 2H), 7.26-7.23 (m, 1H), 6.94 (d, *J* = 19.1 Hz, 1H), 6.58 (d, *J* = 19.1 Hz, 1H), 0.43 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 145.3, 138.6, 138.2, 133.9, 129.0, 128.5, 128.2, 127.8, 127.1, 126.5, -2.5.



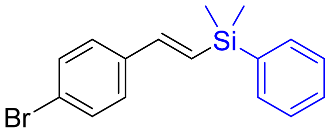
Compound 3q (CAS: 264189-27-7, known compound**)**[2]**.** Following **GPC**, the product was prepared as a colorless oil (24.9 mg, 99%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.60-7.57 (m, 2H), 7.50-7.39 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 19.1 Hz, 1H), 6.53 (d, *J* = 19.1 Hz, 1H), 2.35 (s, 3H), 0.43 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 145.2, 138.8, 138.1, 135.5, 133.9, 129.2, 129.0, 127.8, 126.4, 125.7, 21.2, -2.5.



Compound 3r (CAS: 1440971-96-9, known compound**)**[3]**.** Following **GPC**, the product was prepared as a colorless oil (23.2 mg, 92%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.59-7.55 (m, 2H), 7.55-7.51 (m, 1H), 7.40-7.37 (m, 3H), 7.23-7.12 (m, 4H), 6.49 (d, *J* = 19.0 Hz, 1H), 2.36 (s, 3H), 0.44 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 143.1, 138.7, 137.5, 135.4, 133.9, 130.3, 129.0, 128.9, 127.9, 127.8, 126.1, 125.4, 19.6, -2.5.

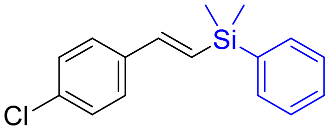


Compound 3s (CAS: 264189-28-8, known compound**)**[2]**.** Following **GPC**, the product was prepared as a colorless oil (21.5 mg, 84%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.59-7.55 (m, 2H), 7.44-7.36 (m, 5H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 19.1 Hz, 1H), 6.50 (d, *J* = 19.1 Hz, 1H), 0.44 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 162.7 (d, *J* = 247.5 Hz), 143.9, 138.4, 134.4 (d, *J* = 3.3 Hz), 133.9, 129.1, 128.0 (d, *J* = 8.1 Hz), 127.8, 126.9 (d, *J* = 2.2 Hz), 115.4 (d, *J* = 21.6 Hz), -2.6. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -113.72 (m).

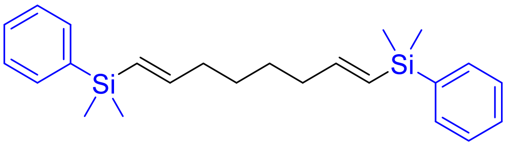


Compound 3t (CAS: 264189-30-2, known compound**)**[2]**.**

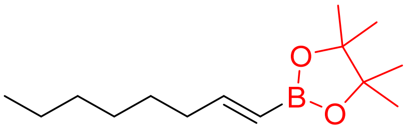
Following **GPC**, the product was prepared as a colorless oil (30.3 mg, 96%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.59-7.55 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.40-7.36 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 19.1 Hz, 1H), 6.58 (d, *J* = 19.1 Hz, 1H), 0.44 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 143.9, 138.2, 137.1, 133.9, 131.6, 129.1, 128.3, 128.0, 127.9, 122.0, -2.6.



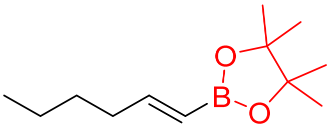
Compound 3u (CAS: 264189-29-9, known compound**)**[2]**.** Following **GPC**, the product was prepared as a colorless oil (26.9 mg, 99%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.58-7.55 (m, 2H), 7.40-7.35 (m, 5H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 19.1 Hz, 1H), 6.56 (d, *J* = 19.1 Hz, 1H), 0.44 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 143.8, 138.3, 136.6, 133.9, 133.8, 129.1, 128.7, 128.1, 127.9, 127.7, -2.6.



Compound 3w (CAS: 461047-17-6, known compound**)**[8]**.** According to general procedure and prepared as a colorless oil (35.5 mg, 94%). **^{1}H NMR** (500 MHz, CDCl3) δ 7.56-7.52 (m, 2H), 7.38-7.33 (m, 3H), 7.32-7.28 (m, 2H), 6.13 (dt, *J* = 6.2 Hz, 18.6 Hz, 1H), 5.78(d, *J* = 18.6 Hz, 1H), 2.20-2.15 (m, 2H), 1.4-1.42 (m, 2H), 0.34 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 149.2, 139.3, 133.8, 128.8, 127.7, 127.4, 36.6, 28.2, -2.4.

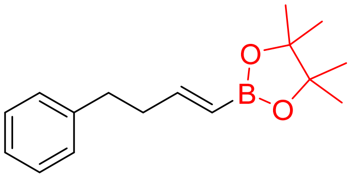


Compound 5a (CAS: 83947-55-1, known compound**)**[9]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow oil (21.4 mg, 90%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 6.63 (dt, *J* = 6.4 Hz, 18.0 Hz, 1H), 5.42 (dt, *J* = 1.5 Hz, 18.0 Hz, 1H), 2.17-2.11 (m, 2H), 1.44-1.37 (m, 2H), 1.30-1.24 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 154.8, 83.0, 35.8, 31.7, 28.9, 28.2, 24.8, 22.58, 14.1.

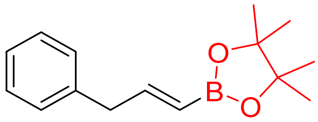


Compound 5b (CAS: 154820-94-7, known compound**)**[9]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow oil (15.1 mg,

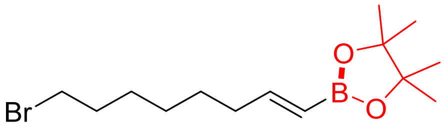
72%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 6.4 Hz, 18.0 Hz, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 2.18-2.12 (m, 2H), 1.43-1.36 (m, 2H), 1.34-1.29 (m, 3H), 1.26 (s, 12H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 154.8, 83.0, 35.5, 30.3, 24.8, 22.2, 13.9.



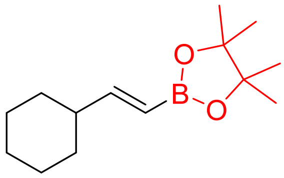
Compound 5c (CAS: 172512-84-4, known compound**)**[10]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (14.7 mg, 57%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.5 (m, 2H), 7.21-7.15 (m, 3H), 6.70 (dt, *J* = 6.2 Hz, 18.0 Hz, 1H), 5.50 (d, *J* = 18.0 Hz, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.50-2.44 (m, 2H), 1.27 (s, 12H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 153.4, 141.8, 128.3, 125.8, 83.1, 37.5, 34.6, 24.8.



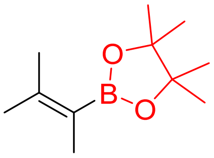
Compound 5d (CAS: 177573-86-3, known compound**)**[9]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (21.2 mg, 87%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.15 (m, 3H), 6.76 (dt, *J* = 6.3 Hz, 17.9 Hz, 1H), 5.44 (dt, *J* = 1.4 Hz, 17.9 Hz, 1H), 3.44 (d, *J* = 6.3 Hz, 2H), 1.25 (s, 12H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 152.4, 139.1, 128.9, 128.4, 126.1, 83.1, 42.3, 24.8.



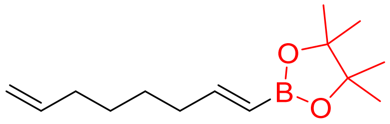
Compound 5e (CAS: 1547450-06-9). Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (24.0 mg, 76%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.61(dt, *J* = 6.4 Hz, 18.0 Hz, 1H), 5.42(d, *J* = 18.0 Hz, 1H), 3.39(t, *J* = 6.8 Hz, 2H), 2.18-2.11 (m, 2H), 1.87-1.81 (m, 2H),1.45-1.39 (m, 4H), 1.35-1.29 (m, 2H), 1.26 (s, 12H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 154.3, 83.0, 35.6, 33.9, 32.7, 28.3, 28.0, 27.9, 24.8. **HRMS** (ESI-TOF) m/z: [M+H]+ Calcd for $C_{14}H_{26}BBrO_2H^+$ 316.1318; Found 316.1308.



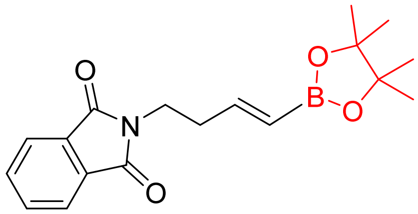
Compound 5f (CAS: 172512-85-5, known compound**)**[11]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (14.2 mg, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 6.2 Hz, 18.2 Hz, 1H), 5.37 (dd, *J* = 1.4 Hz, 18.0 Hz, 1H), 2.06-1.98 (m, 1H), 1.78-1.70 (m, 4H), 1.64-1.60 (m, 1H), 1.26 (s, 12H), 1.19-1.04 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 83.0, 43.2, 31.9, 26.2, 25.9, 24.8.



Compound 5g (CAS: 219488-99-0, known compound**)**[11]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (1.8 mg, 9%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.97 (d, *J* = 1.4 Hz, 3H), 1.72 (brs, 3H), 1.67 (brs, 3H), 1.27 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.2, 82.7, 24.8, 24.4, 21.2, 16.5.

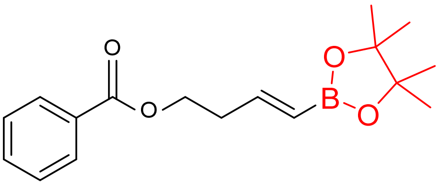


Compound 5h. Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (15.1 mg, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 6.7 Hz, 17.9 Hz, 1H), 5.85-5.73 (m, 1H), 5.43 (dt, *J* = 1.4 Hz, 17.9 Hz, 1H), 2.19-2.13 (m, 2H), 2.08-2.01 (m, 2H), 1.46-1.39 (m, 4H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.5, 138.9, 114.3, 83.0, 35.6, 33.6, 28.4, 27.7, 24.8. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{25}BO_2Na^+$ 258.1876; Found 258.1873.

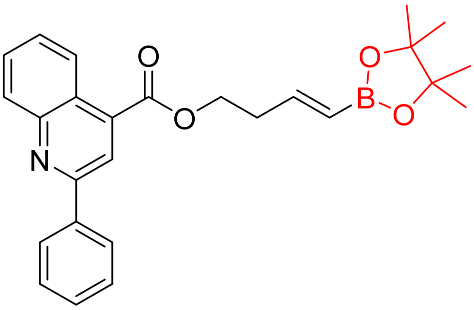


Compound 5i (CAS: 1160924-49-1). Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (25.5 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84-7.81 (m, 2H), 7.71-7.68 (m, 2H), 6.59 (dt, *J* = 6.7

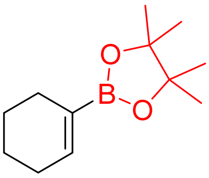
Hz, 18.0 Hz, 1H), 5.52 (dt, *J* = 1.4 Hz, 18.0 Hz, 1H), 3.78 (d, *J* = 7.5 Hz, 2H), 2.57-2.51 (m, 2H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 168.2, 149.2, 133.9, 132.1, 123.2, 83.2, 36.7, 34.6, 24.7. **HRMS** (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{18}H_{22}BNO_4H^+$ 327.1751; Found 327.1756.



. **Compound 5j (CAS: 581802-27-9**, known compound**)**[13]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (25.4 mg, 84%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.66 (dt, *J* = 6.6 Hz, 17.9 Hz, 1H), 5.60 (d, *J* = 17.9 Hz, 1H), 4.39 (t, *J* = 6.7 Hz, 2H), 2.66-2.61 (m, 2H), 1.27 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 166.5, 149.0, 132.9, 130.3, 129.6, 128.3, 83.2, 63.5, 35.0, 24.8.

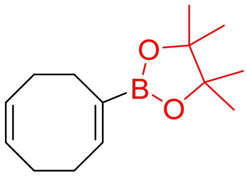


Compound 5k. Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a yellow solid (34.3 mg, 80%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.73 (dd, *J* = 0.7 Hz, 8.6 Hz, 1H), 8.38 (s, 1H), 8.24-8.18 (m, 3H), 7.76 (ddd, *J* = 1.4 Hz, 6.9 Hz, 8.4 Hz, 1H), 7.62 (ddd, *J* = 1.4 Hz, 6.9 Hz, 8.4 Hz, 1H), 7.57-7.52 (m, 2H), 7.51-7.46 (m, 1H), 6.71 (dt, *J* = 6.5 Hz, 18.0 Hz, 1H), 5.68 (dt, *J* = 1.4 Hz, 18.0 Hz, 1H), 4.57 (t, *J* = 6.6 Hz, 2H), 2.73 (qd, *J* = 1.4 Hz, 6.6 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 166.4, 156.7, 149.2, 148.6, 138.8, 135.9, 130.3, 129.9, 129.7, 128.9, 127.7, 127.5, 125.5, 124.0, 120.3, 83.3, 64.3, 34.9, 24.8. **HRMS** (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{26}H_{29}BNO_4^+$ 429.2220; Found 429.2215

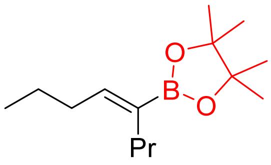


Compound 5l (CAS: 141091-37-4, known compound**)**[14]**.**

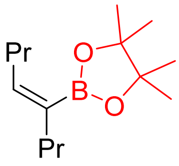
Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (17.3 mg, 83%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 6.59-6.54 (m, 1H), 2.12-2.06 (m, 4H), 1.60-1.56 (m, 4H), 1.25 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 142.9, 83.0, 26.6, 26.1, 24.8, 22.5, 22.1.



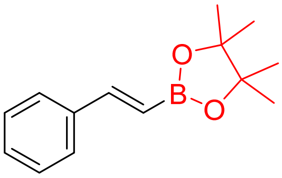
Compound 5n (CAS: 1392323-63-5, known compound**)**[15]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (13.6 mg, 58%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 6.51 (d, J = 5.3 Hz, 1H), 5.56-5.50 (m, 2H), 2.56-2.52 (m, 2H), 2.47-2.38 (m, 4H), 2.36-2.30 (m, 2H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 144.29, 129.28, 127.99, 83.08, 77.25, 77.00, 76.75, 30.57, 29.44, 27.77, 27.01, 24.78.



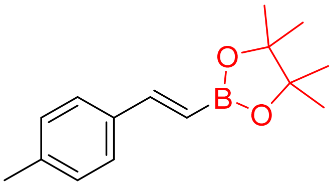
Compound *Z*-5o (CAS: 177949-95-0, known compound**)**[16]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (7.6 mg, 32%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 6.29 (t, J = 7.1 Hz, 1H), 2.13-2.08 (m, 4H), 1.44-1.40 (m, 2H), 1.36-1.32 (m, 2H), 1.25 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 146.0, 83.0, 30.63, 30.56, 24.7, 23.3, 22.4, 14.1, 14.0.



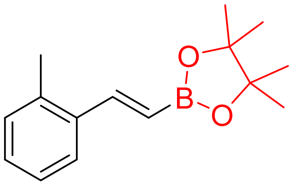
Compound *E*-5o (CAS: 2055824-75-2, known compound**)**[17]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (16.2 mg, 68%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 5.98 (t, J = 7.4 Hz, 1H), 2.27 (q, J = 7.3 Hz, 2H), 2.06 (t, J = 7.4 Hz, 2H), 1.41-1.34 (m, 4H), 1.26 (s, 12H), 0.90-0.84 (m, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 145.9, 82.7, 39.1, 33.1, 24.8, 23.4, 23.2, 13.8, 13.7.



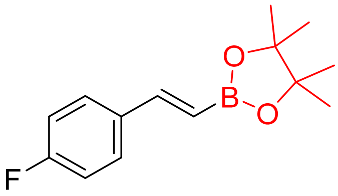
Compound 5p (CAS: 83947-56-2, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (18.4 mg, 80%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.33 (d, *J* = 18.5 Hz, 1H), 7.29-7.19 (m, 3H), 6.10 (d, *J* = 18.5 Hz, 1H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 137.5, 128.9, 128.6, 127.0, 83.3, 24.8.



Compound 5q (CAS: 149777-84-4, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (19.3 mg, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.35 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.5 Hz, 1H), 2.35 (s, 3H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 138.9, 134.8, 129.3, 127.0, 83.3, 24.8, 21.3.

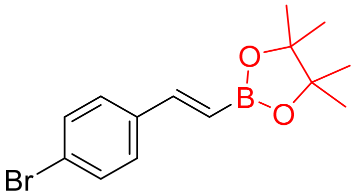


Compound 5r (CAS: 1294009-26-9, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (20.0 mg, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 18.3 Hz, 1H), 7.57-7.54 (m, 1H), 7.21-7.13 (m, 3H), 6.08 (d, *J* = 18.3 Hz, 1H), 2.42 (s, 3H), 1.32 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 136.7, 136.3, 130.4, 128.6, 126.1, 125.8, 83.3, 24.8, 19.8.

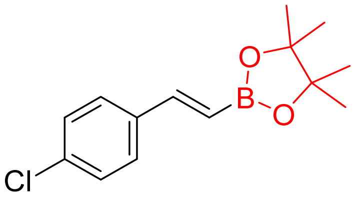


Compound 5s (CAS: 504433-86-7, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid (20.6 mg, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.35 (d, *J* = 18.5 Hz,

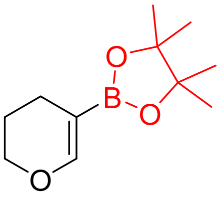
1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.07 (d, *J* = 18.5 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 163.1 (d, *J* = 248.6 Hz), 148.2, 133.7 (d, *J* = 2.9 Hz), 128.7 (d, *J* = 8.3 Hz), 115.5 (d, *J* = 21.7 Hz), 83.4, 24.8. **^{19}F NMR** (471 MHz, CDCl$_3$) δ -112.41 (m).



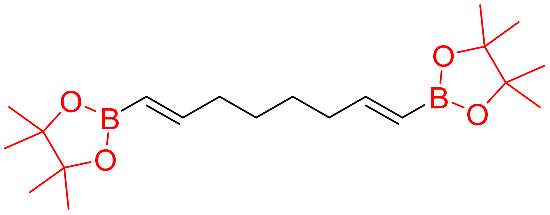
Compound 5t (CAS: 1242770-51-9, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid (26.5 mg, 86%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.36-7.29 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 148.1, 136.4, 131.7, 128.5, 122.9, 83.5, 24.8.



Compound 5u (CAS: 223919-54-8, known compound**)**[18]**.** Following **GPD**, the product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a white solid (21.9 mg, 83%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 18.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.13 (d, *J* = 18.5 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 148.0, 136.0, 134.6, 128.8, 128.2, 83.5, 24.8.



Compound 5v (CAS: 1046811-99-7, known compound**)**[19]**.** According to **GPD** at 25 °C for 3 h. The product was prepared and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (13.2 mg, 63%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 6.97 (s, 1H), 4.01 (t, *J* = 5.2 Hz, 2H), 2.08-2.04 (m, 2H), 1.84-1.79 (m, 2H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 155.1, 82.61, 66.2, 24.7, 22.2, 20.1.



Compound 5w (CAS: 1902952-72-0, known compound**)**[20]**.** According to general procedure and purified by flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) as a colorless oil (19.6 mg, 54%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.61 (dt, J = 6.5 Hz, 18.0 Hz, 1H), 5.41 (d, J = 18.0 Hz, 1H), 2.18-2.12 (m, 2H), 1.45-1.41 (m, 2H), 1.24 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 83.0, 35.6, 27.8, 24.8.

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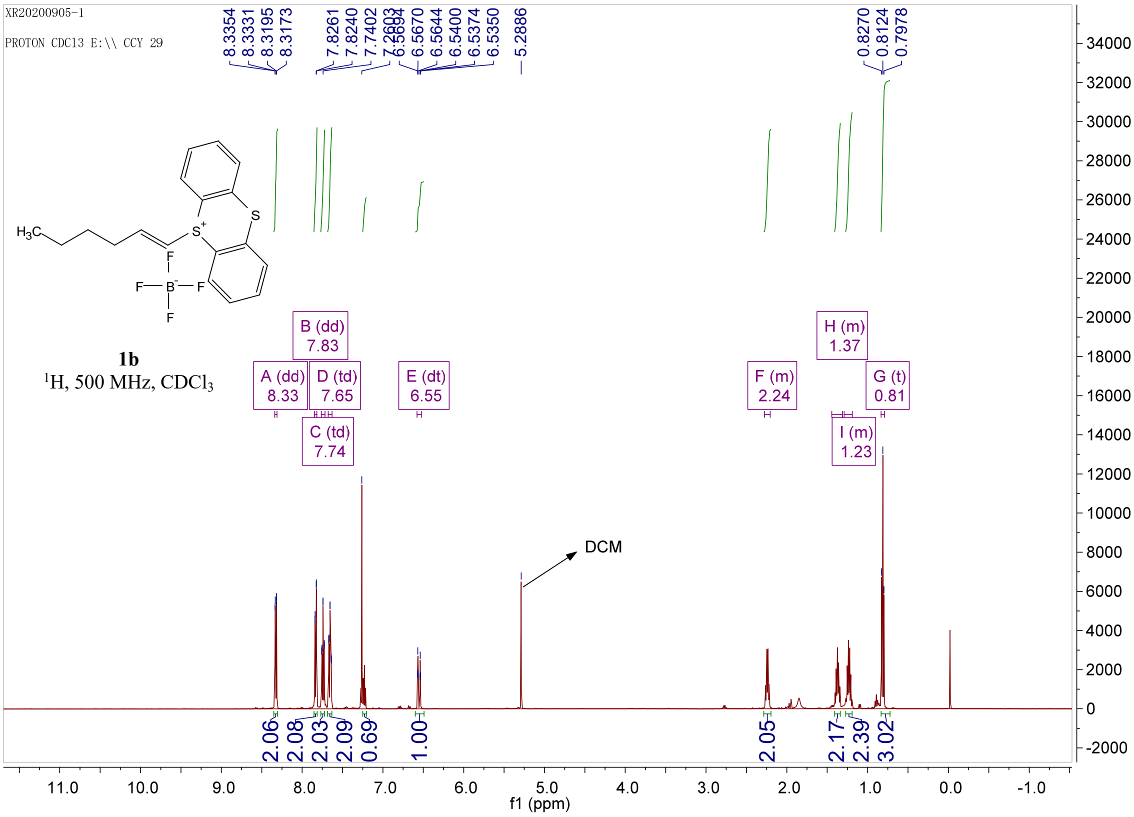
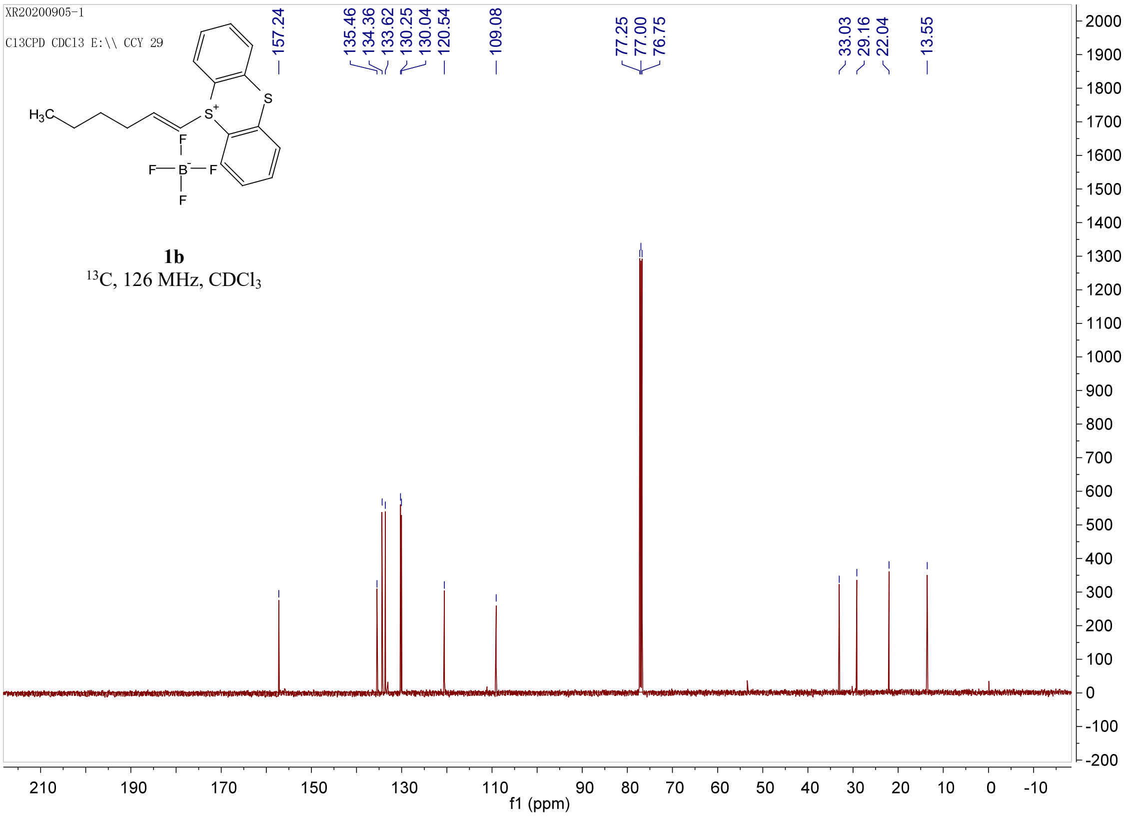
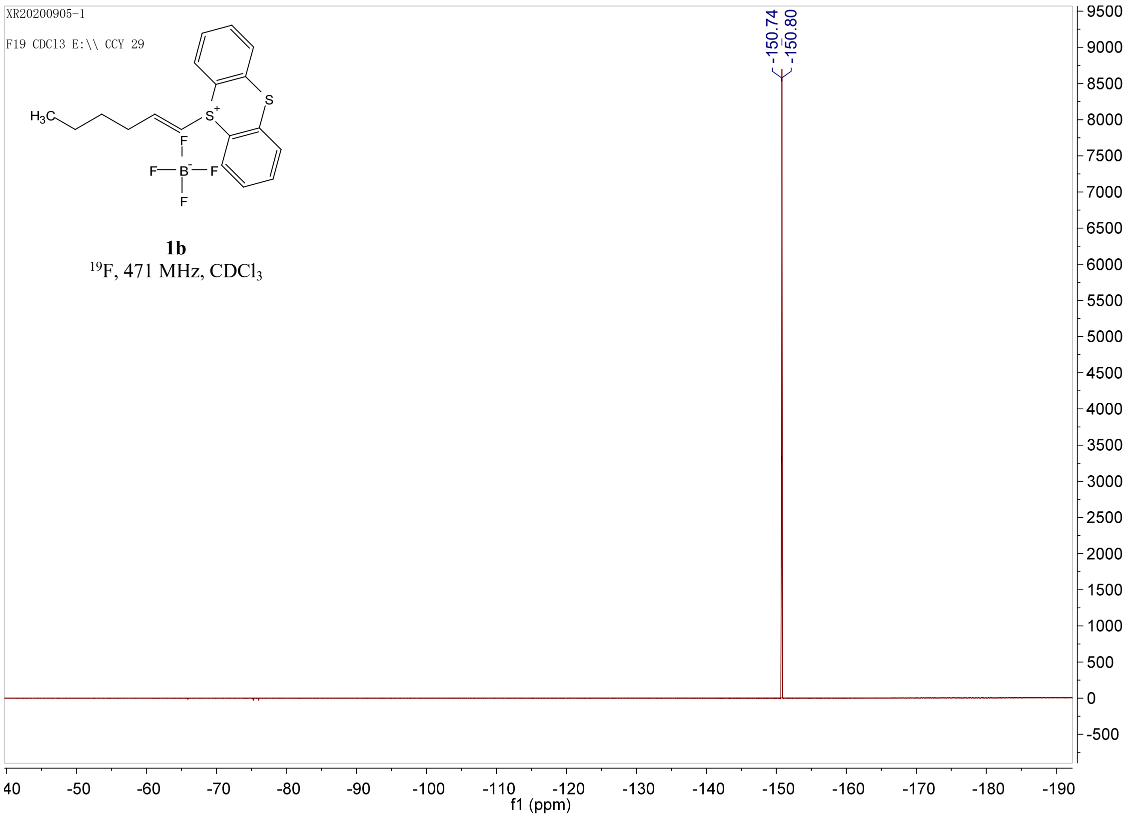
5 NMR Spectra



1b
^1H, 500 MHz, $CDCl_3$

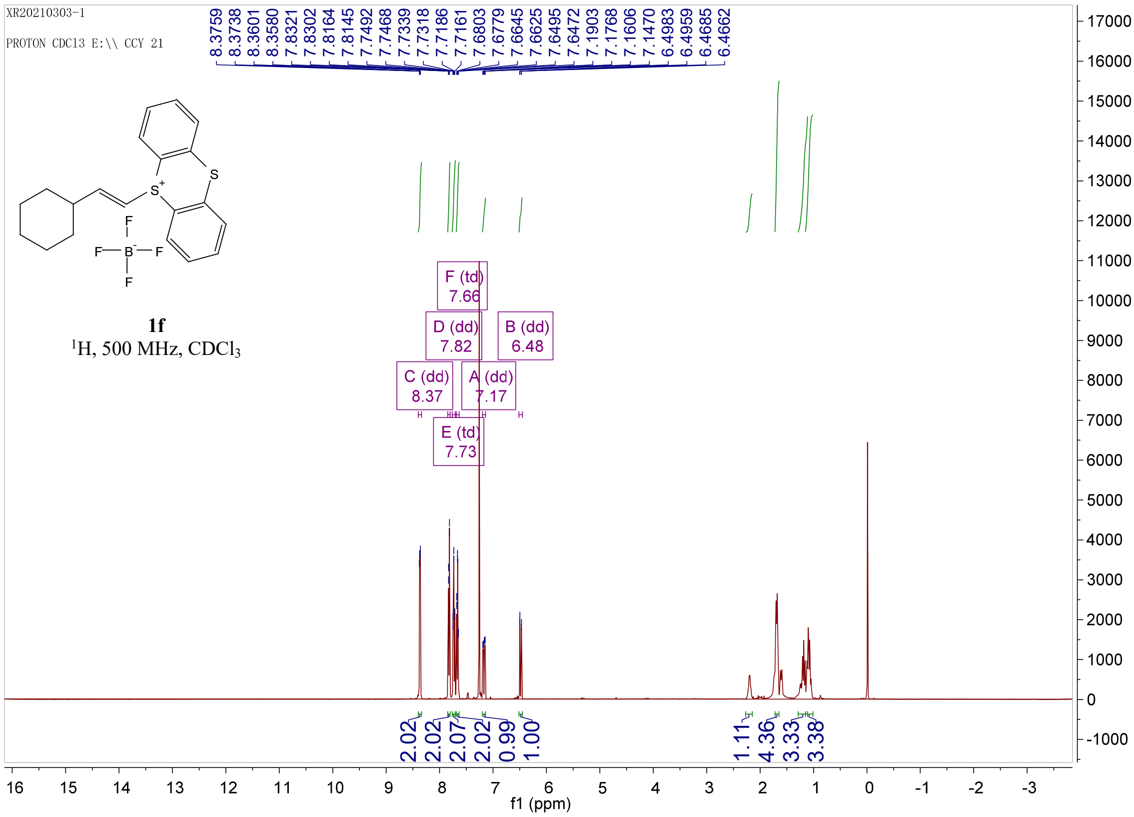


1b
^{13}C, 126 MHz, $CDCl_3$



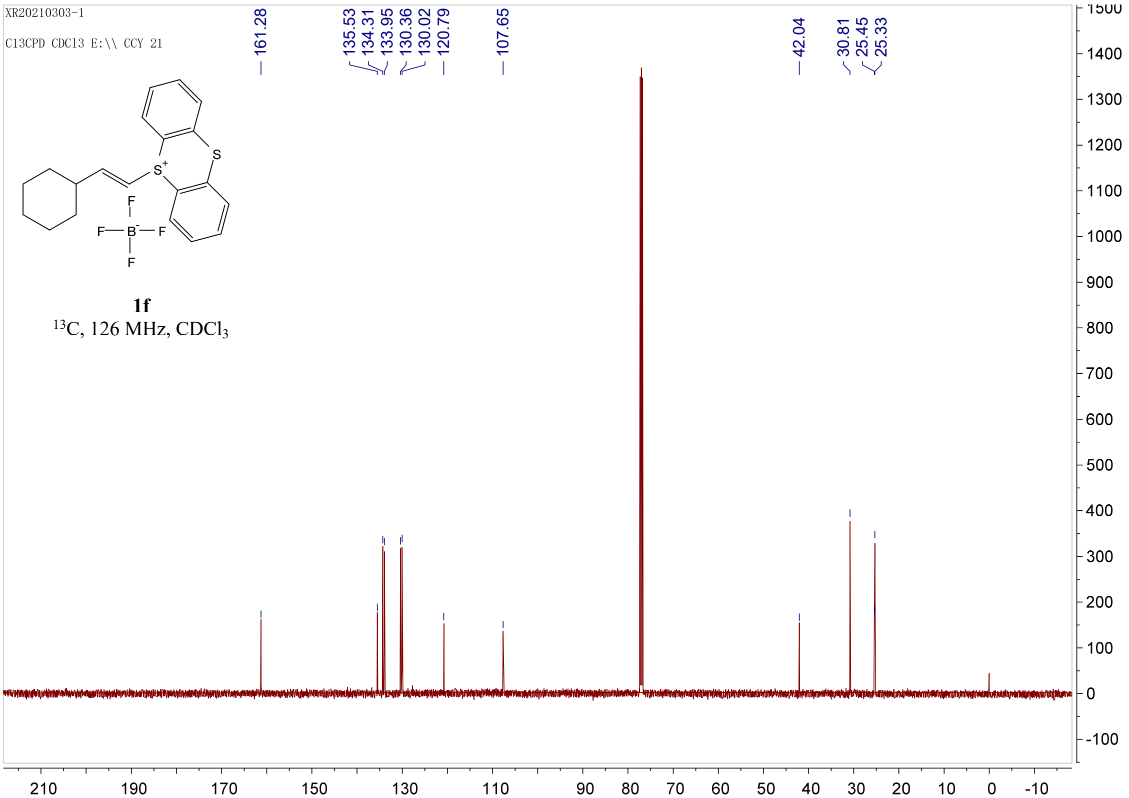
1b

^{19}F, 471 MHz, CDCl$_3$



1f

^{1}H, 500 MHz, CDCl$_3$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C13CPD CDCl3 E:\\ CCY 21
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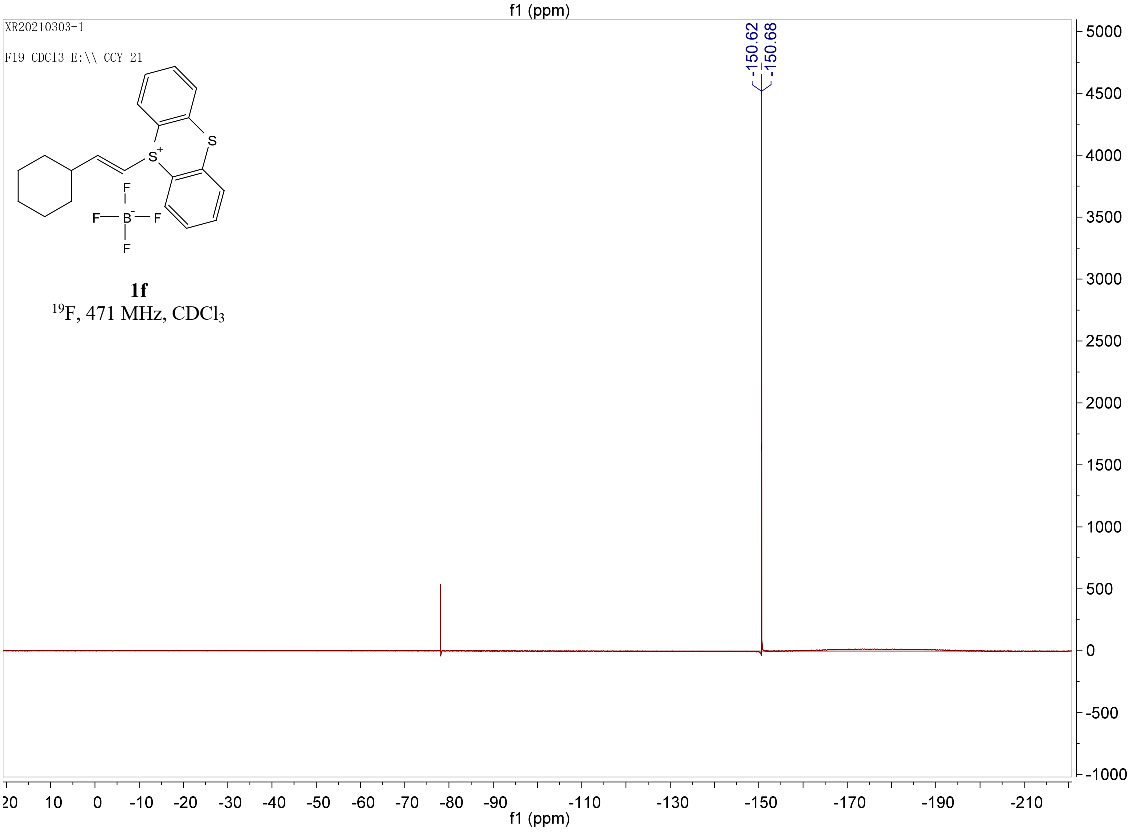
135.53
134.31
133.95
130.36
130.02
120.79
107.65
42.04
30.81
25.45
25.33
1f
13C, 126 MHz, CDCl3
S+
S
F
B-
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100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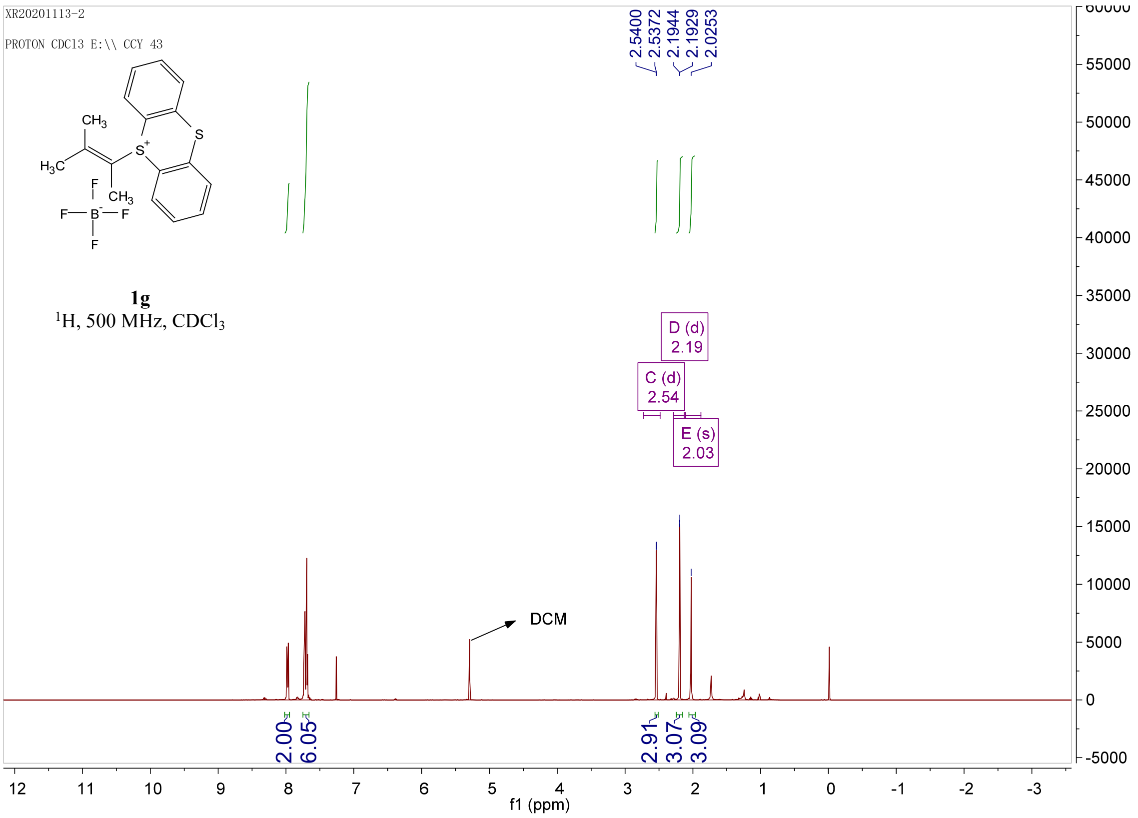
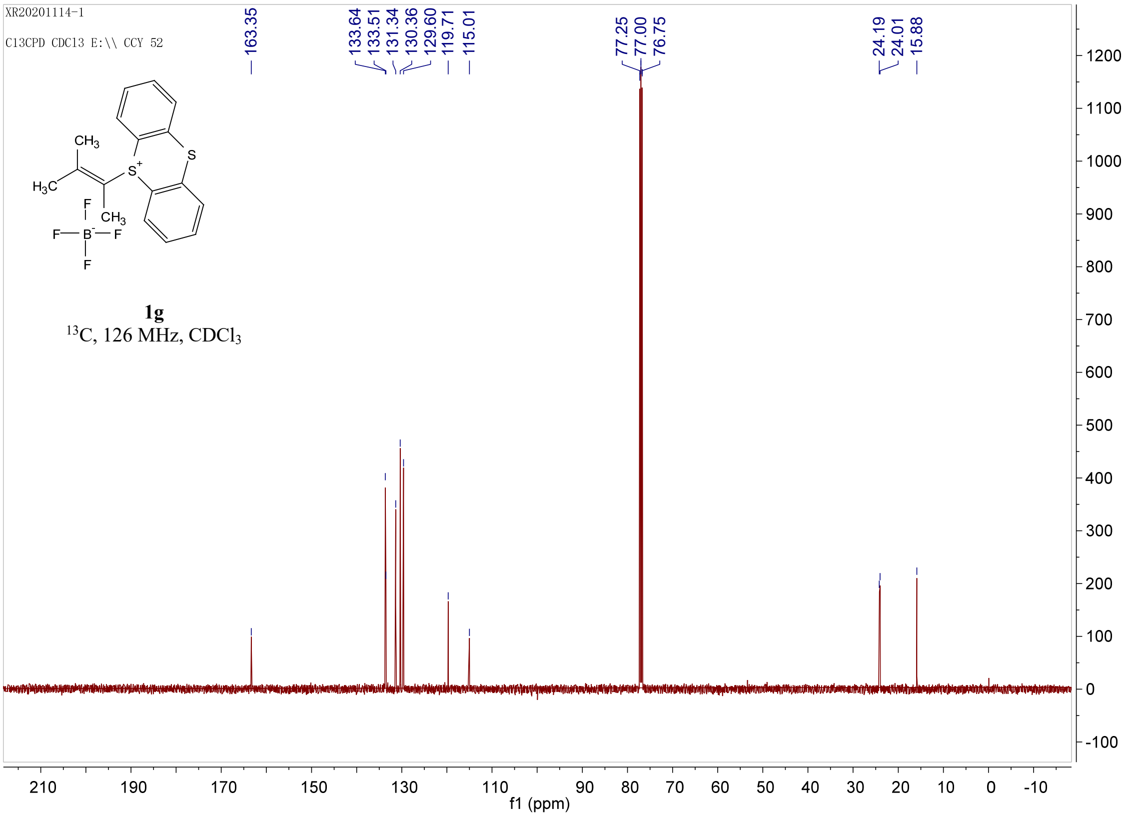
F19 CDCl3 E:\\ CCY 21
-150.62
-150.68
1f
19F, 471 MHz, CDCl3
S+
S
F
B-
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500 -1000



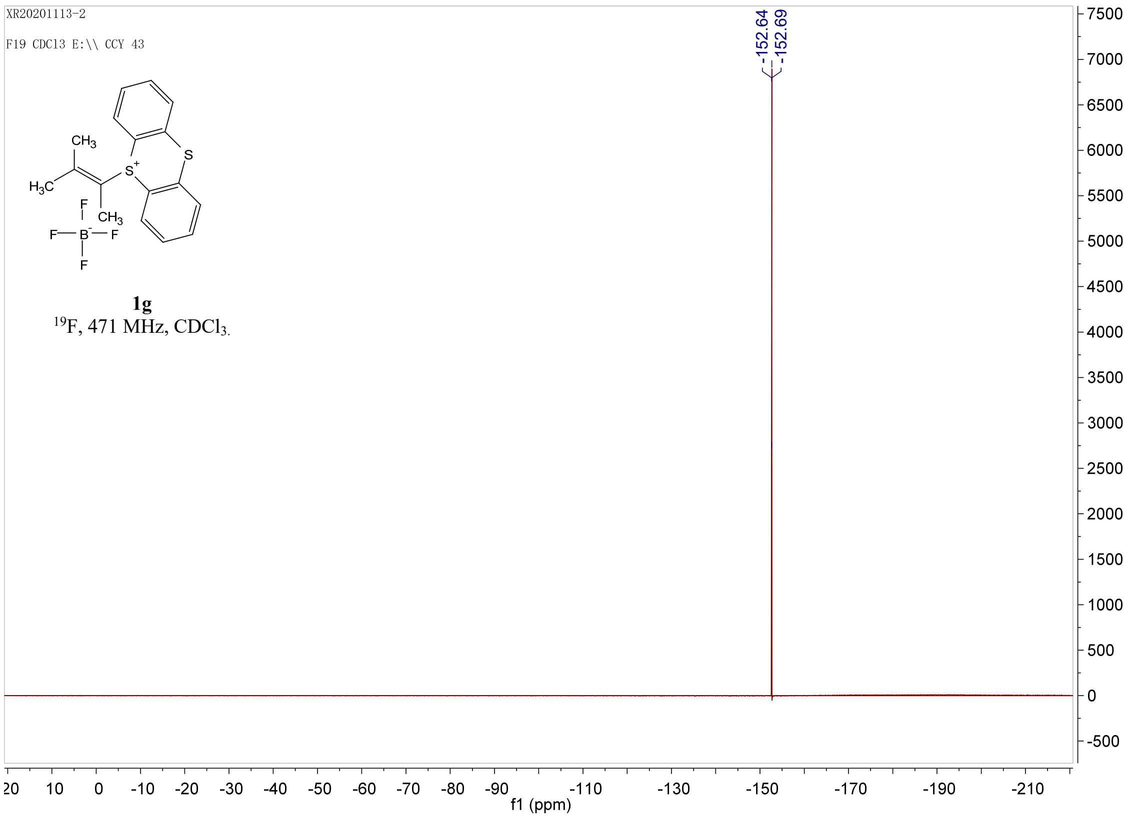
1g

^{1}H, 500 MHz, CDCl$_3$



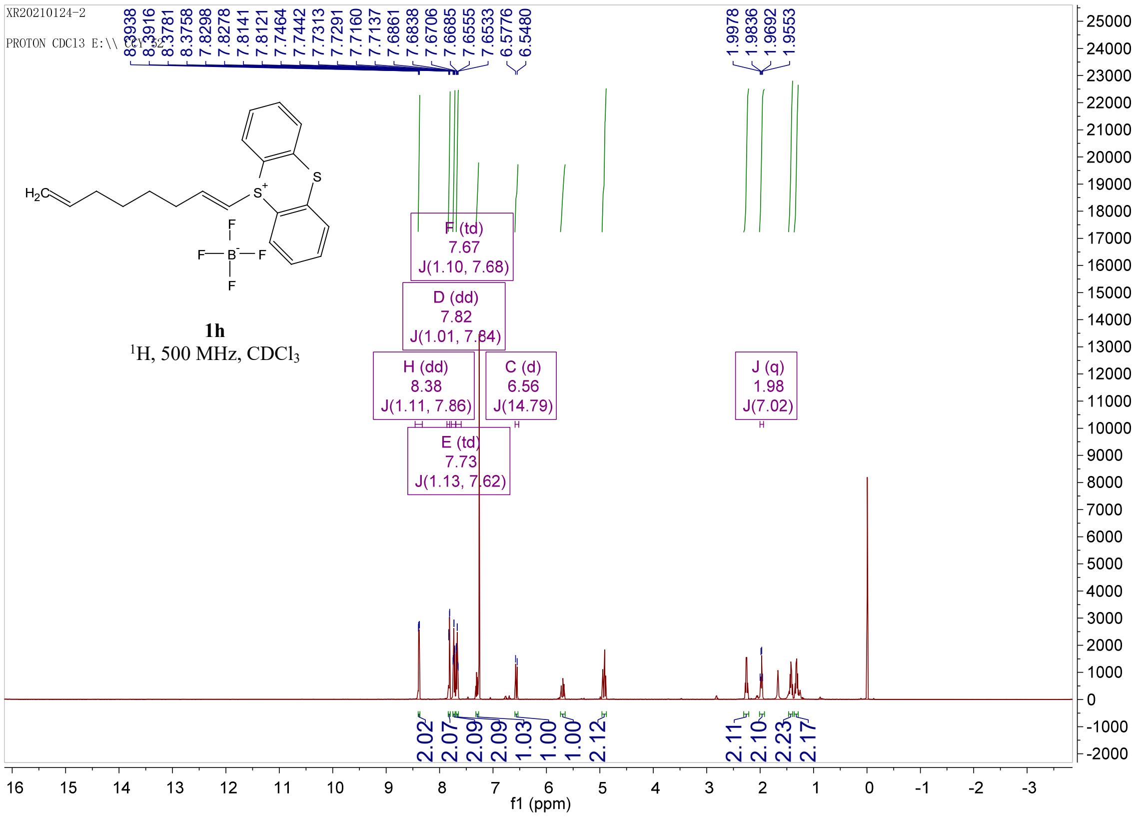
1g

^{13}C, 126 MHz, CDCl$_3$



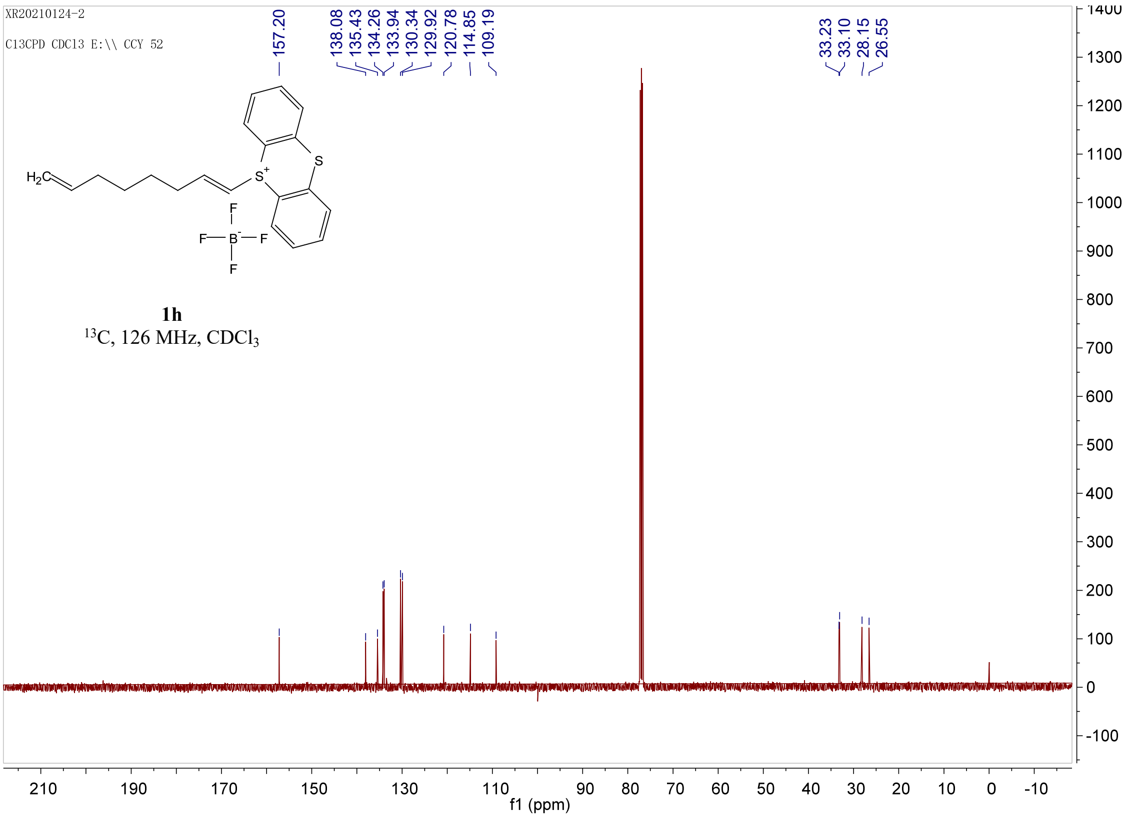
1g

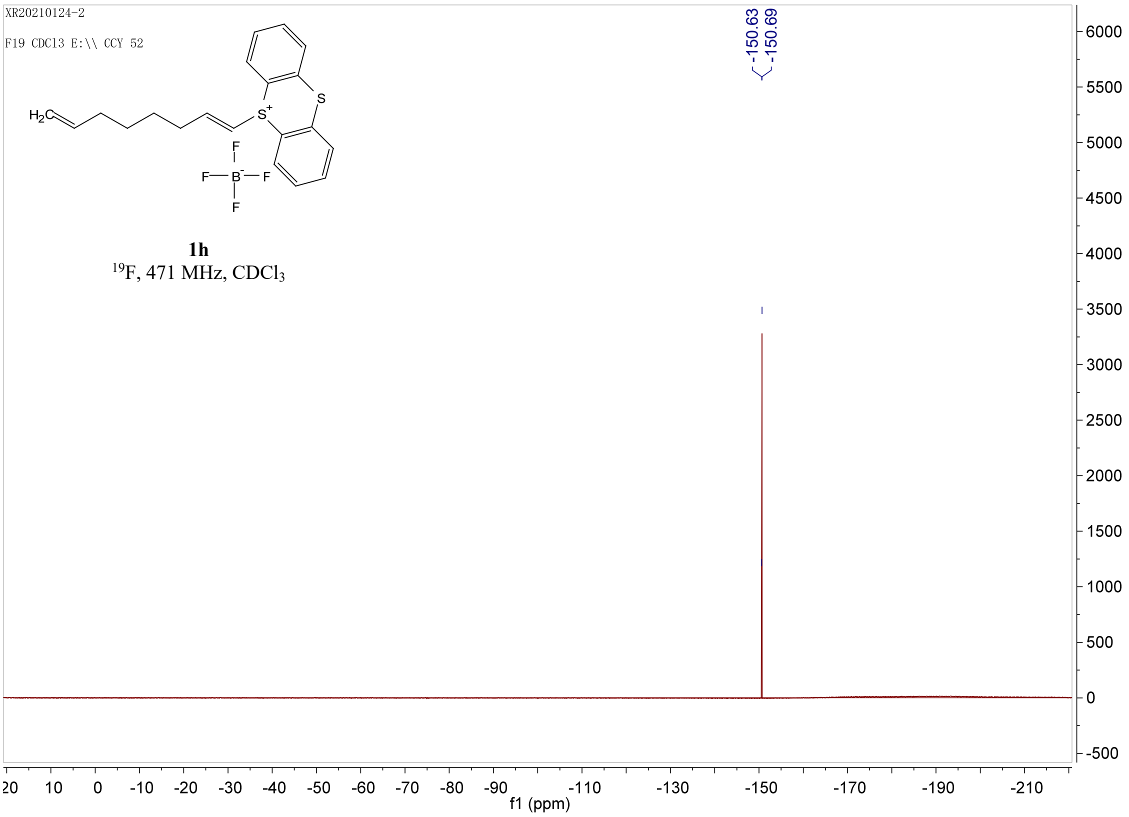
^{19}F, 471 MHz, CDCl$_3$.

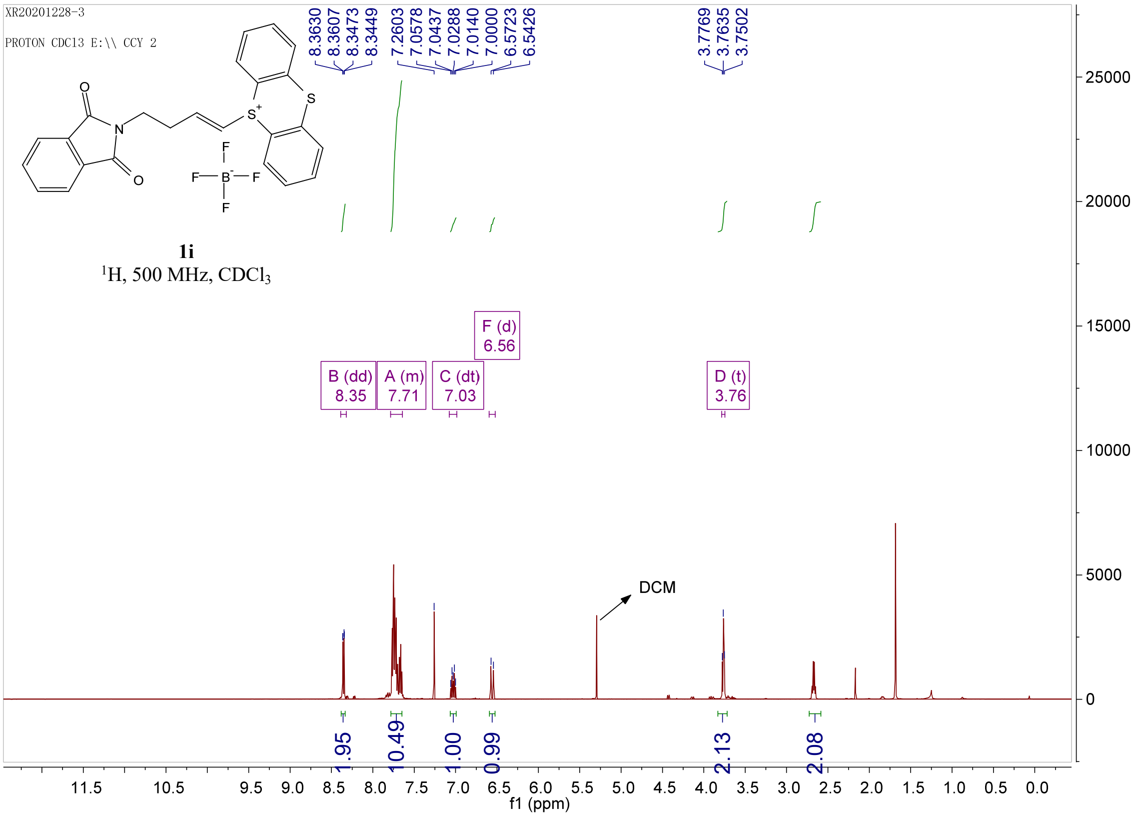


1h

^{1}H, 500 MHz, CDCl$_3$


XR20210124-2
C13CPD CDCl3 E:\\ CCY 52
157.20
138.08
135.43
134.26
133.94
130.34
129.92
120.78
114.85
109.19
33.23
33.10
28.15
26.55
H2C
S+
S
F
F—B—F
F
1h
13C, 126 MHz, CDCl3
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20210124-2
F19 CDCl3 E:\\ CCY 52
-150.63
-150.69
H2C
S+
S
F
F—B—F
F
1h
19F, 471 MHz, CDCl3
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



1i

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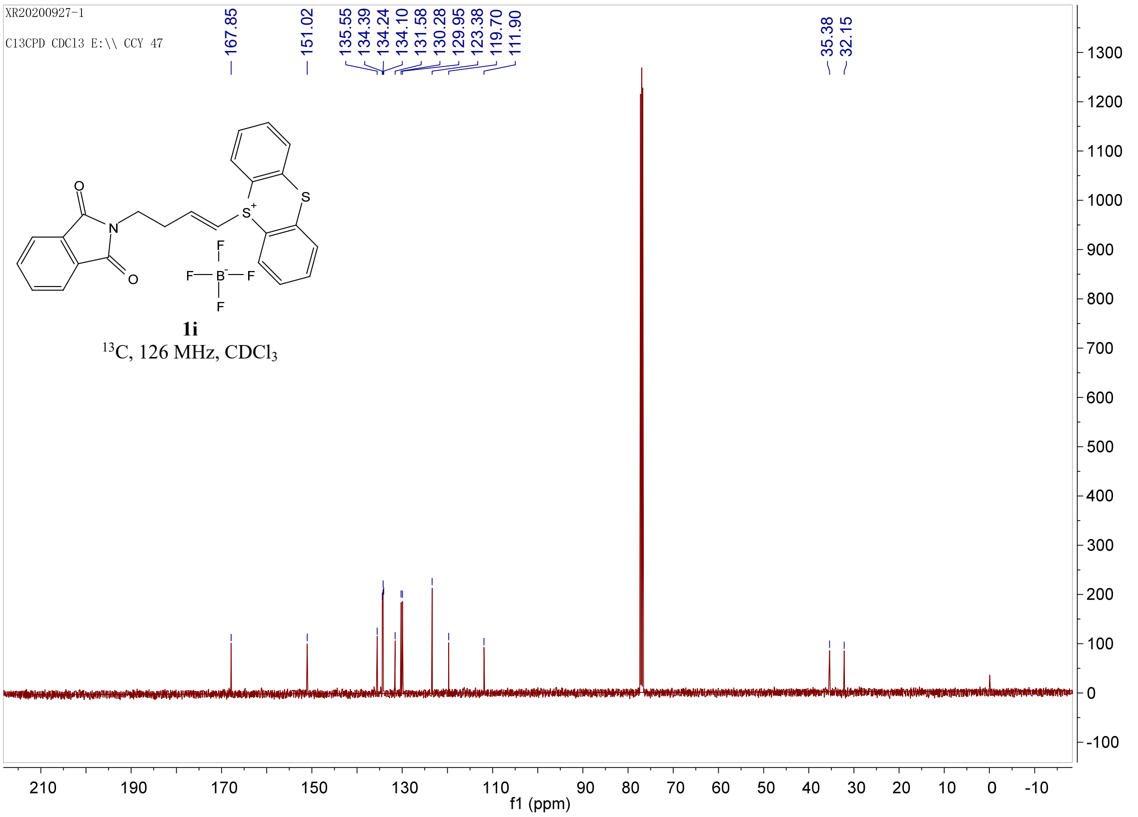
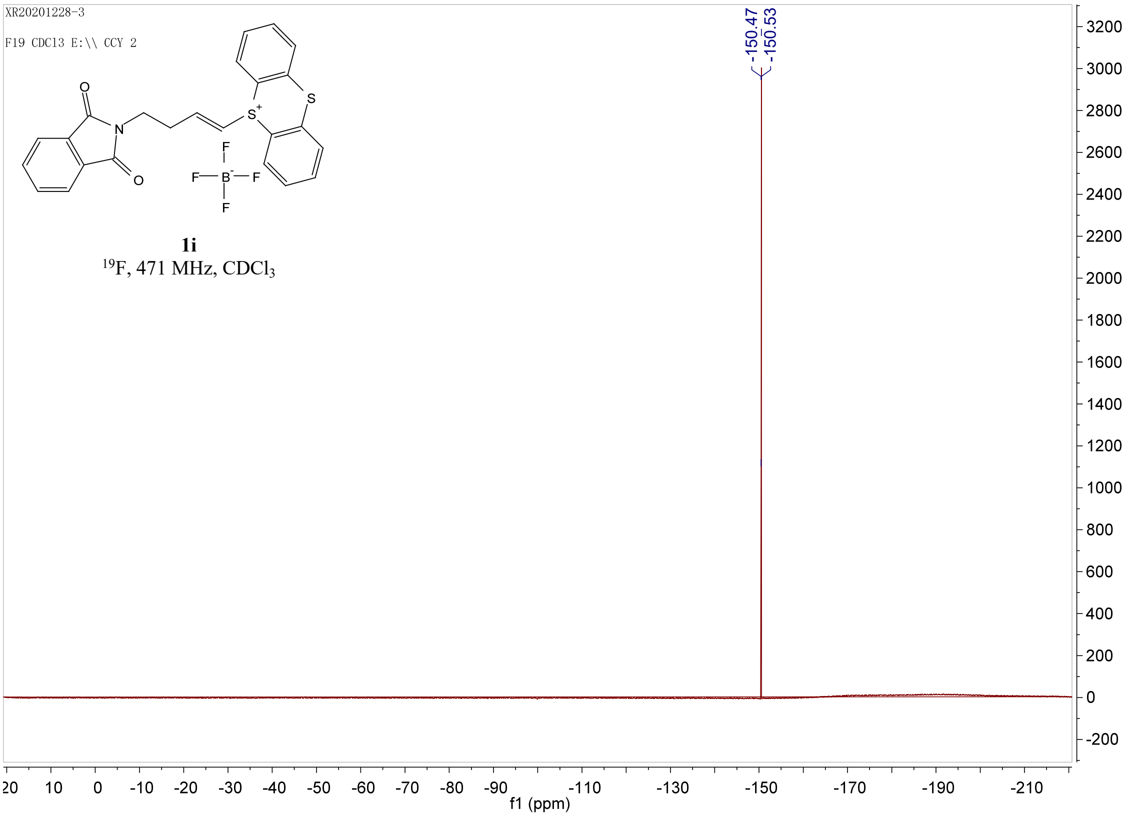


1i

^{13}C, 126 MHz, CDCl$_3$



1i
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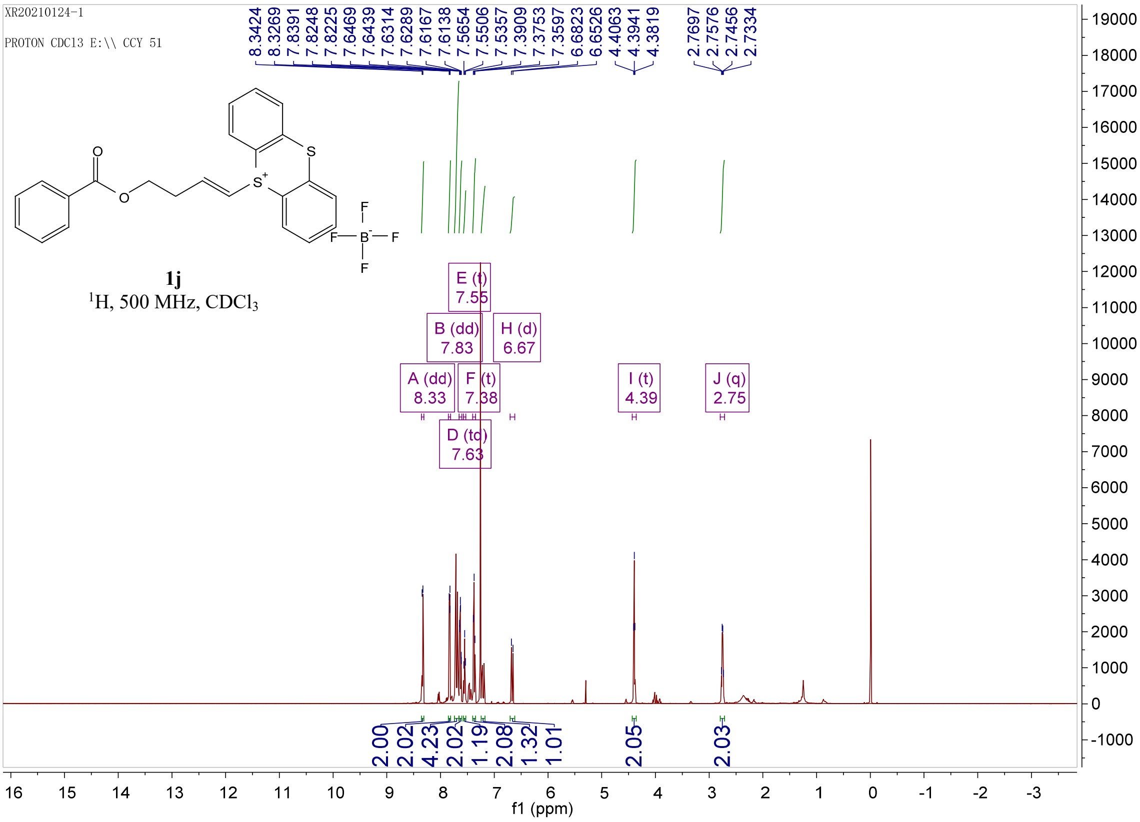

1j
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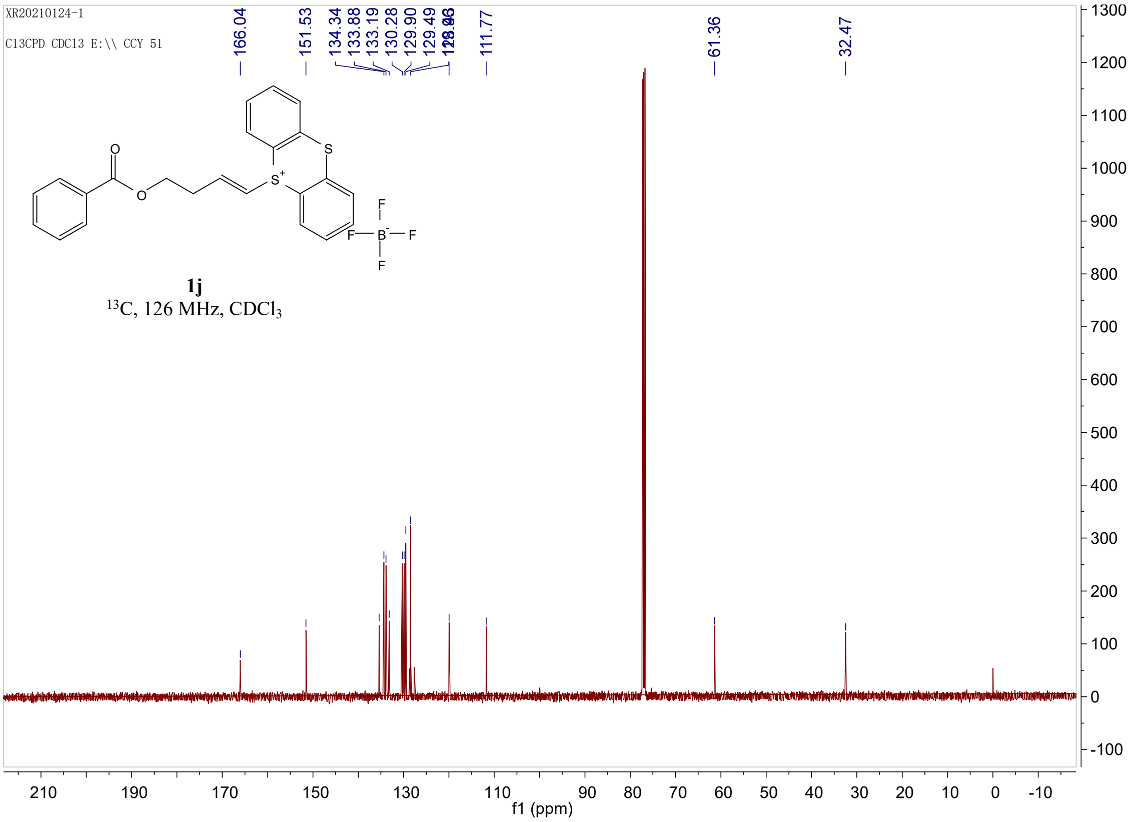

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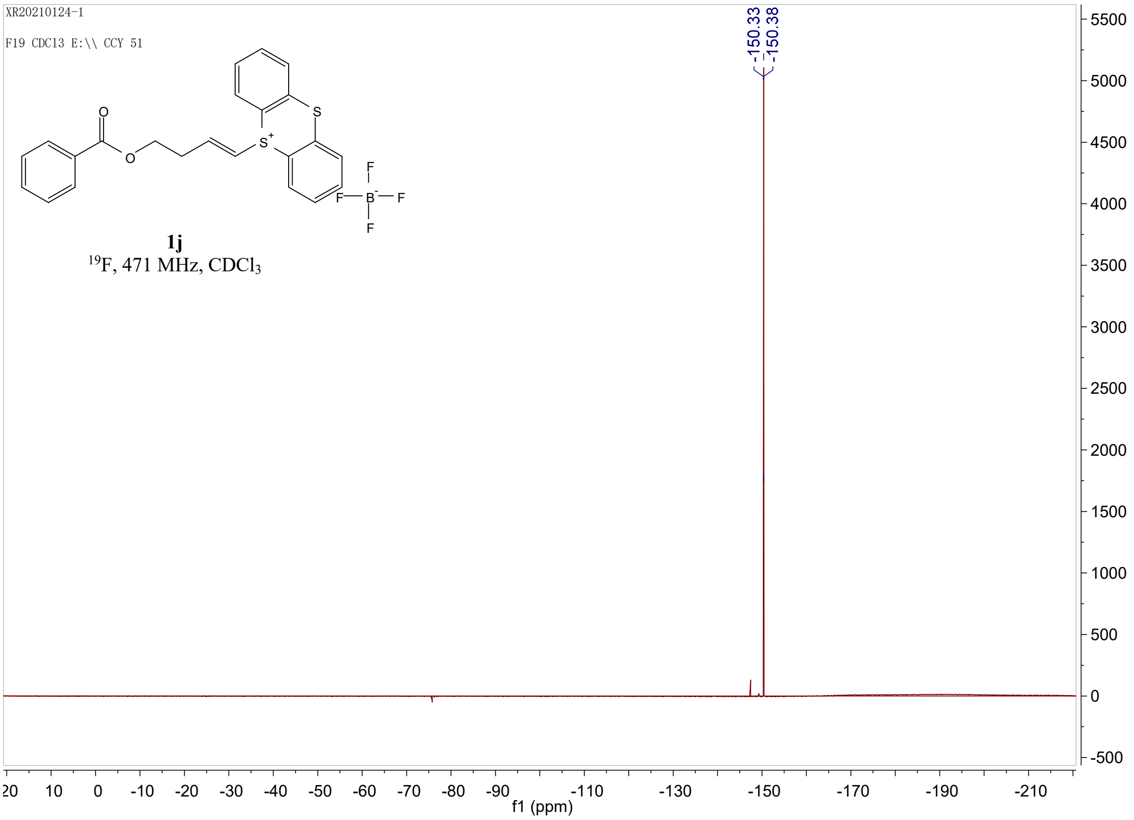

1j
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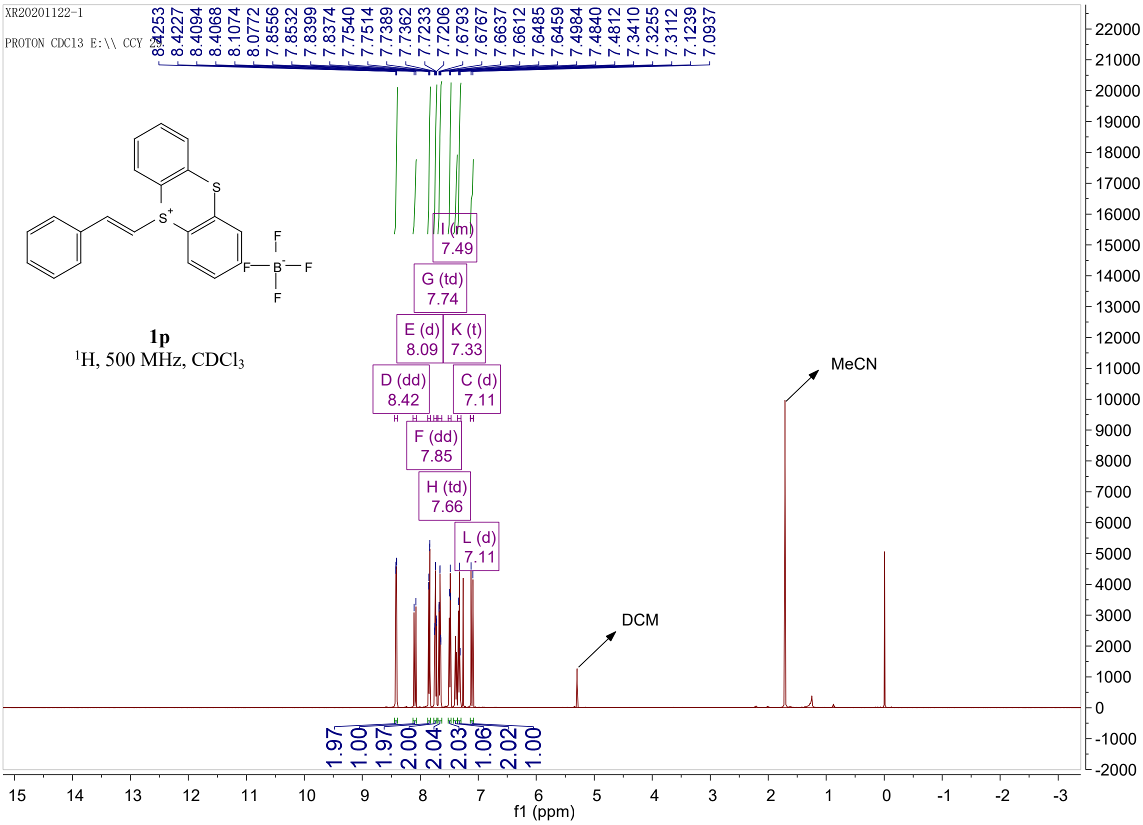

1p

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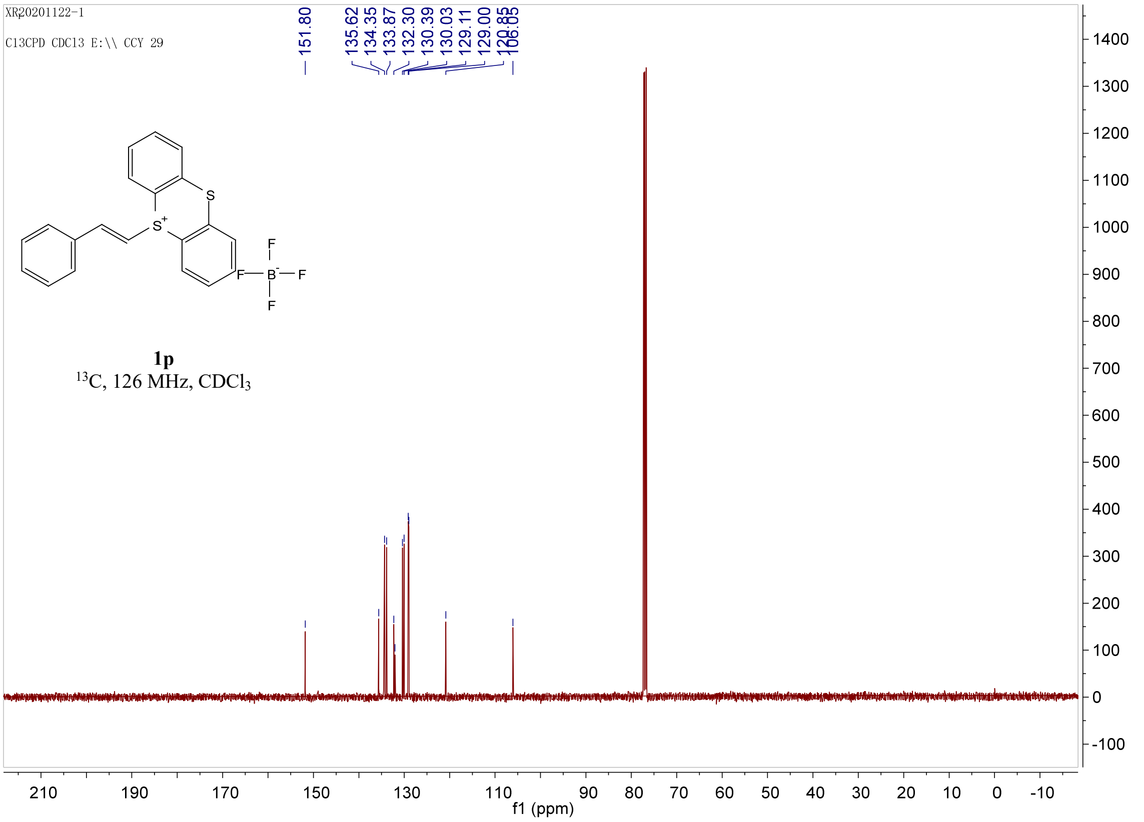
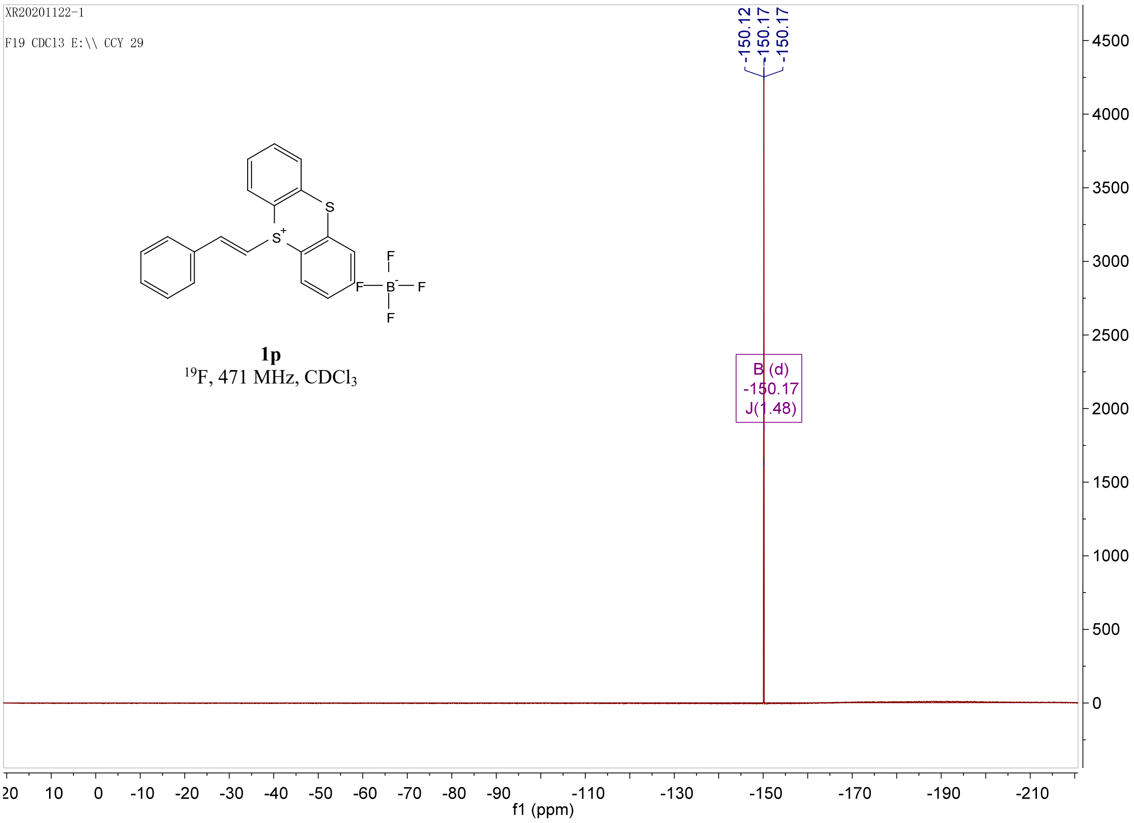


1p

^{13}C, 126 MHz, CDCl$_3$



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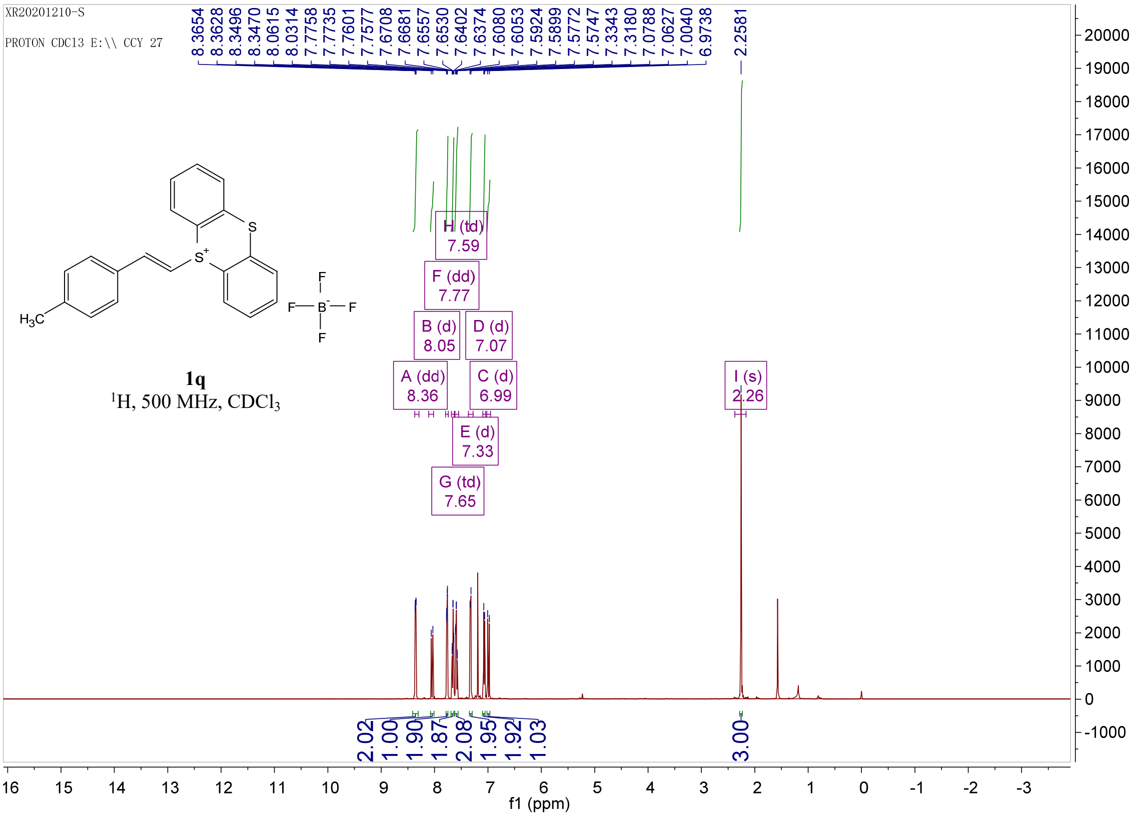

1q
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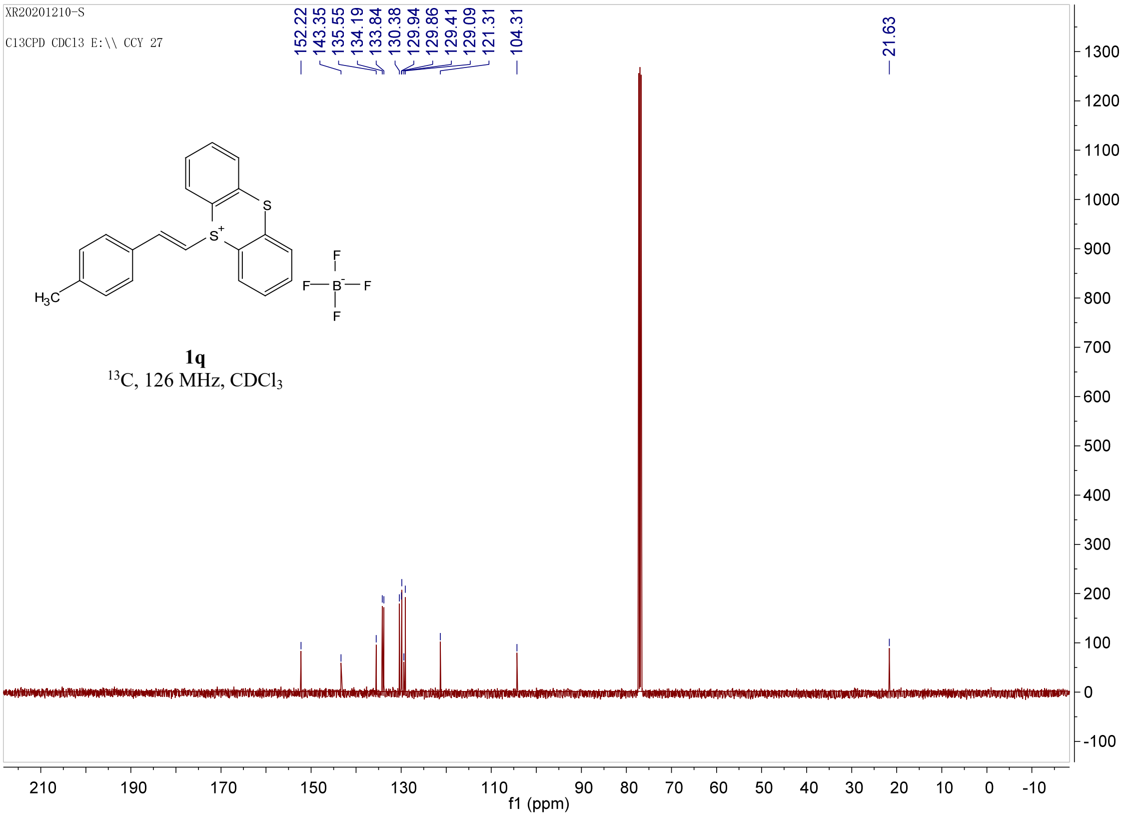

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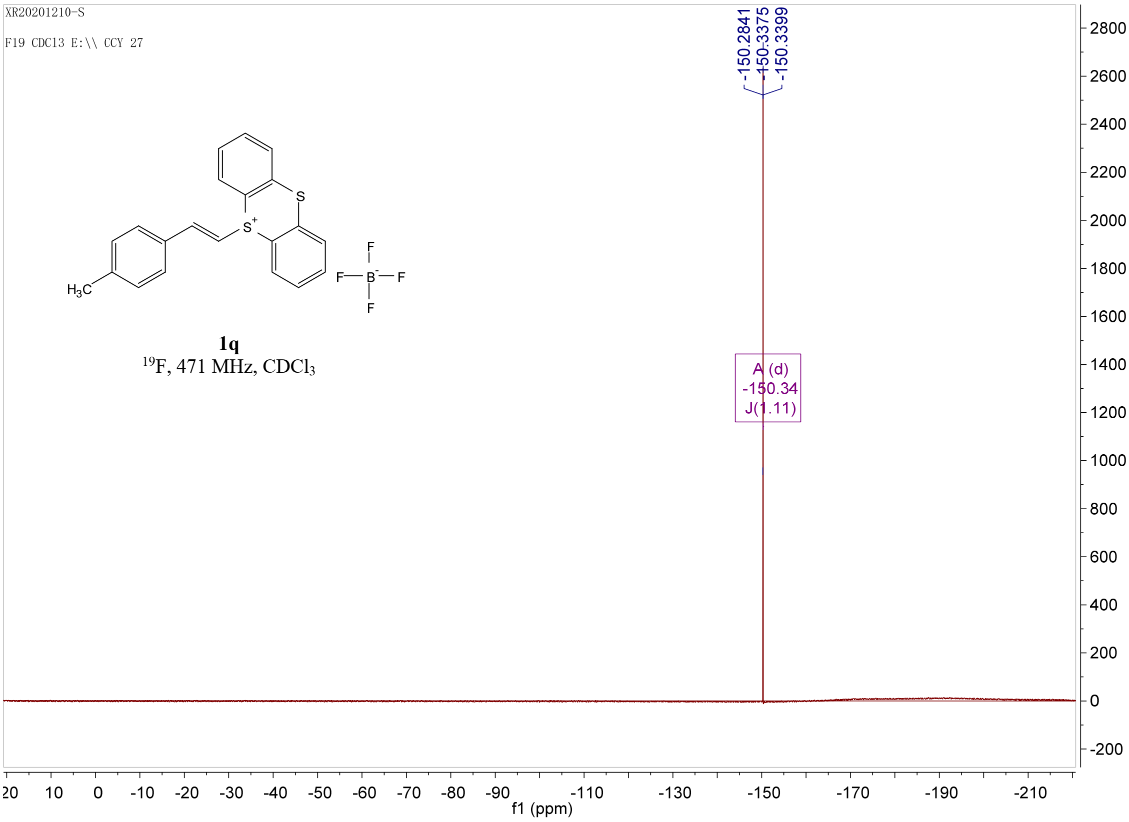

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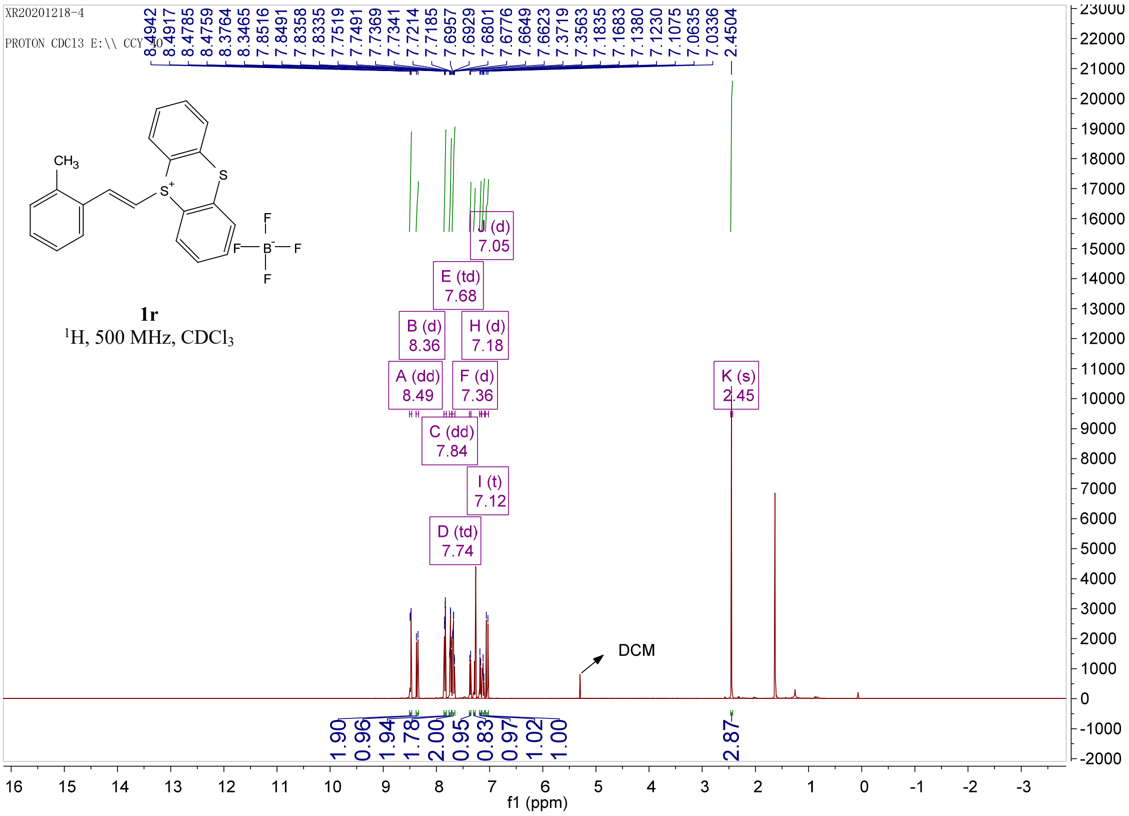
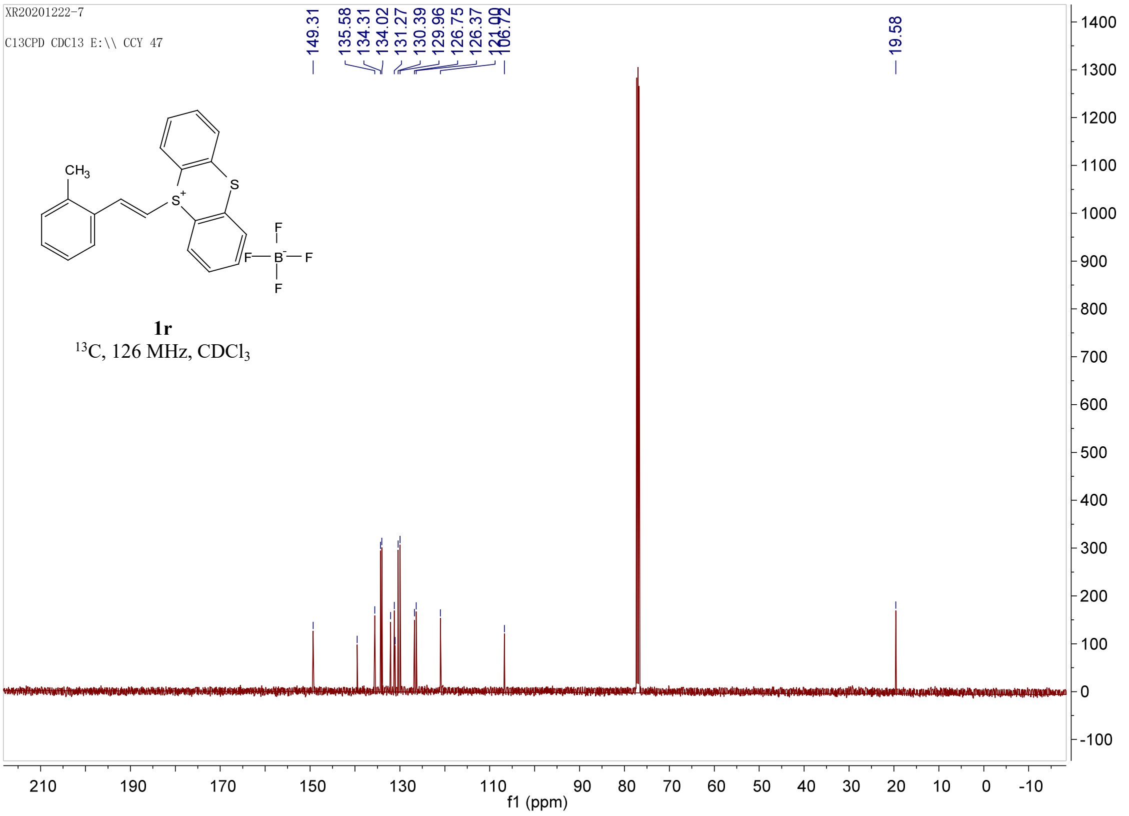


1r

^{1}H, 500 MHz, CDCl$_3$



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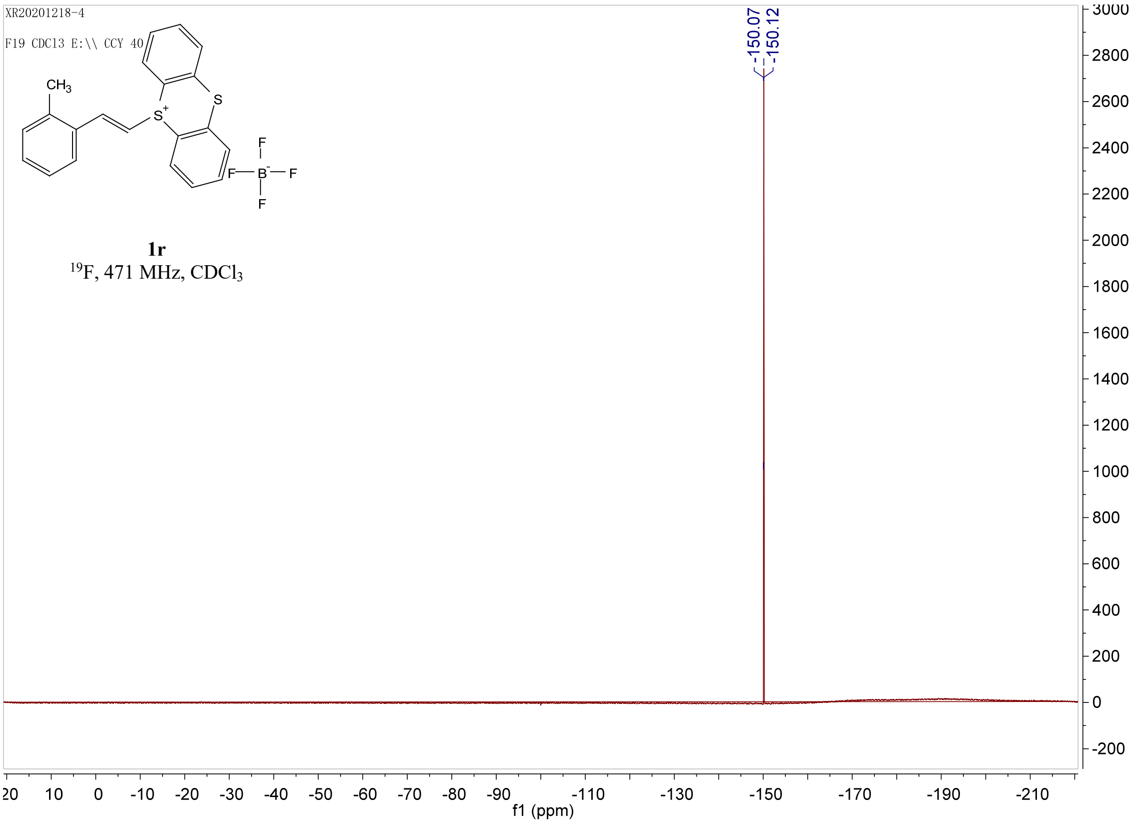
^{13}C, 126 MHz, CDCl$_3$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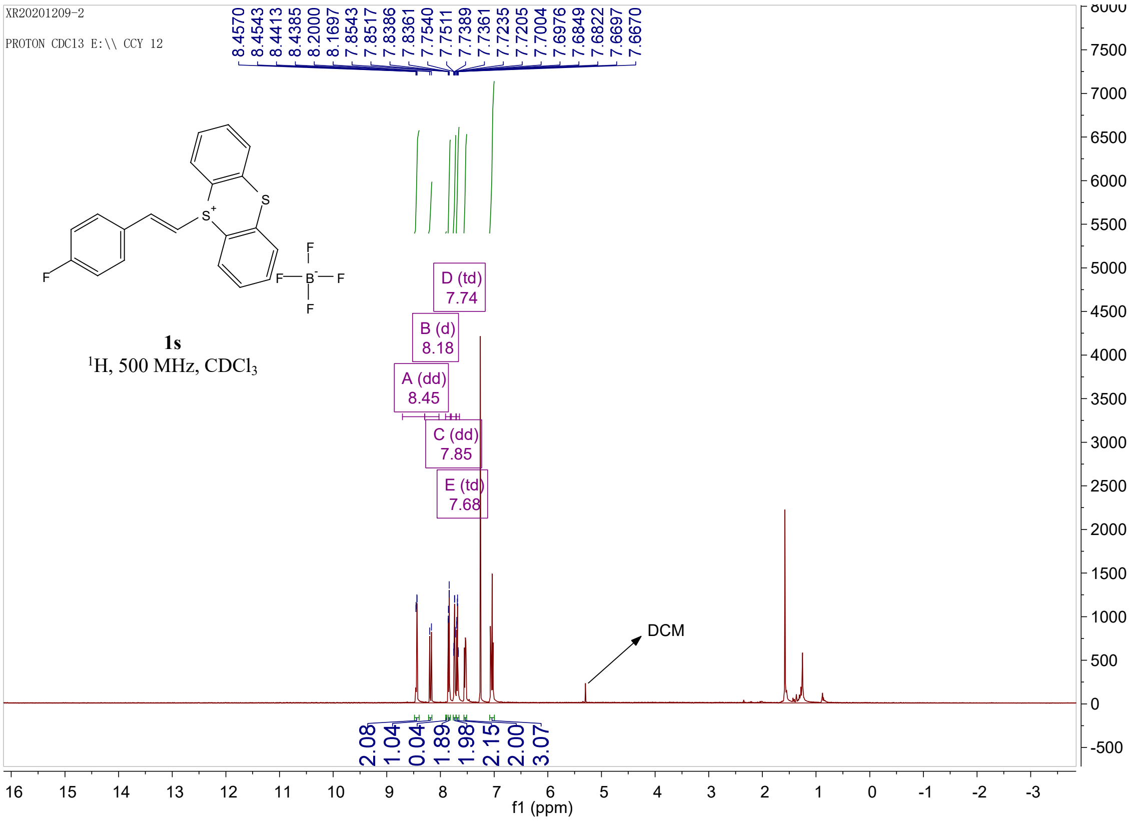
^{19}F, 471 MHz, CDCl$_3$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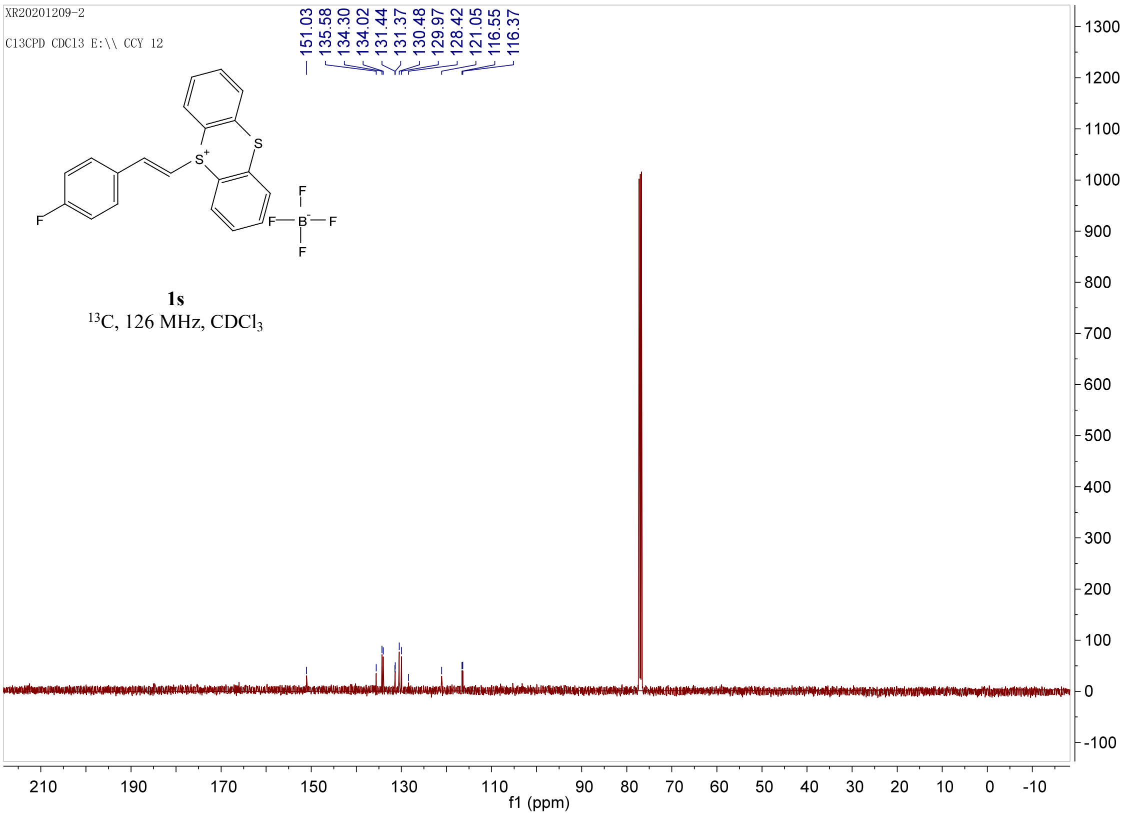
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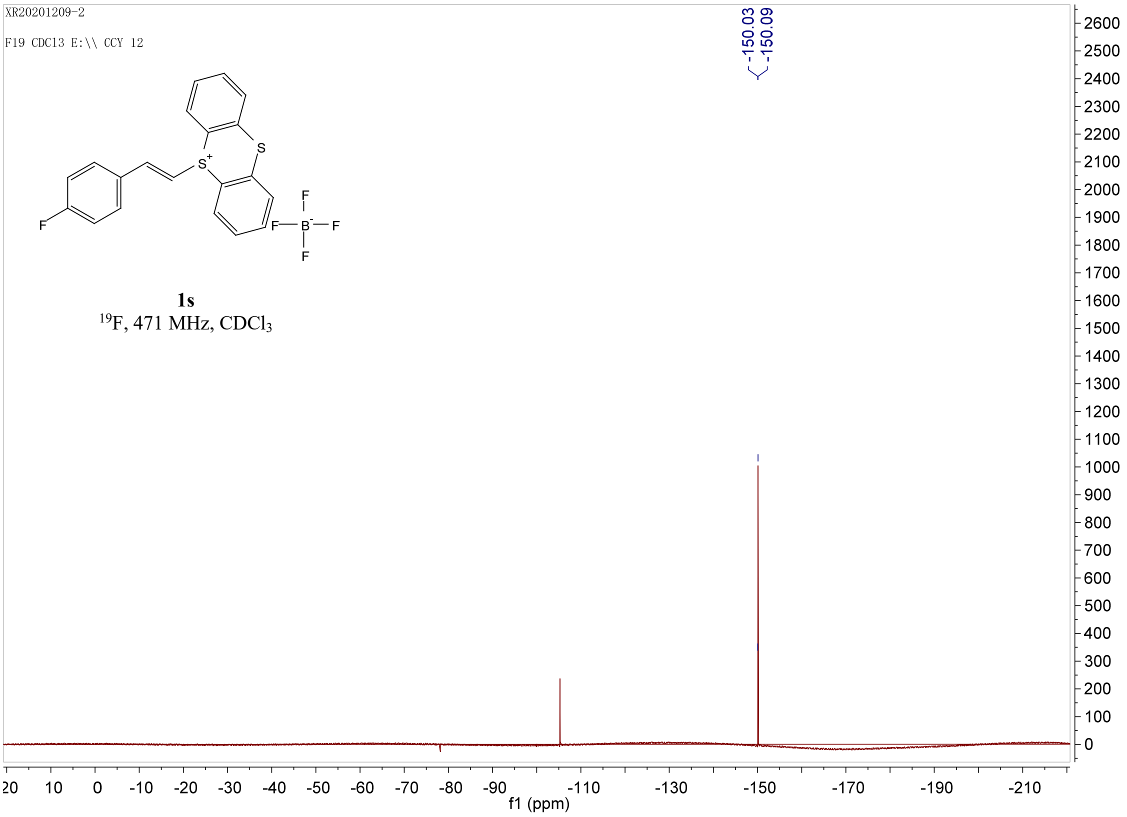
135.58
134.30
134.02
131.44
131.37
130.48
129.97
128.42
121.05
116.55
116.37
S
S+
F
F
F—B−—F
F
1s
^{13}C, 126 MHz, CDCl$_3$
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100


XR20201209-2
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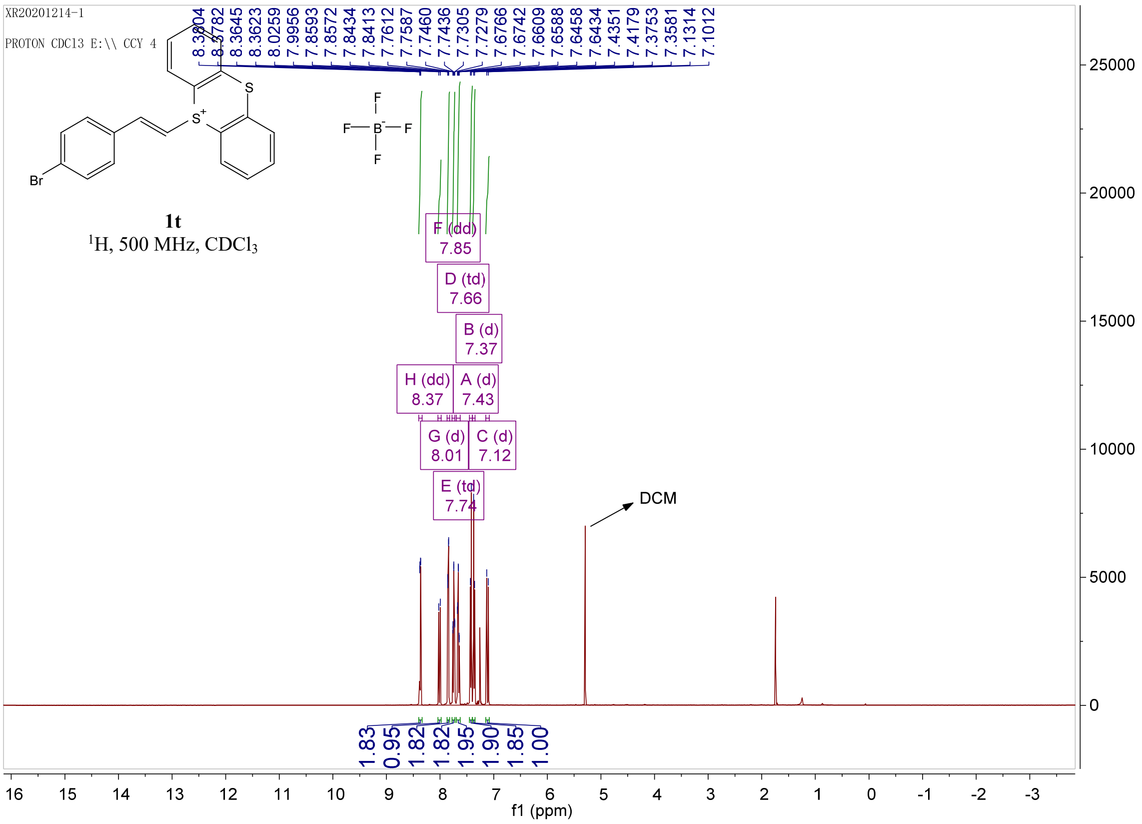
-150.09
S
S+
F
F
F—B−—F
F
1s
^{19}F, 471 MHz, CDCl$_3$
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
2600 2500 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0


XR20201214-1
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7.9956
7.8593
7.8572
7.8434
7.8413
7.7612
7.7587
7.7460
7.7436
7.7305
7.7279
7.6766
7.6742
7.6609
7.6588
7.6458
7.6434
7.4351
7.4179
7.3753
7.3581
7.1314
7.1012
S
S+
Br
F
F—B−—F
F
1t
1H, 500 MHz, CDCl3
F (dd) 7.85
D (td) 7.66
B (d) 7.37
H (dd) 8.37
A (d) 7.43
G (d) 8.01
C (d) 7.12
E (td) 7.74
DCM
1.83
0.95
1.82
1.82
1.95
1.90
1.85
1.00
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
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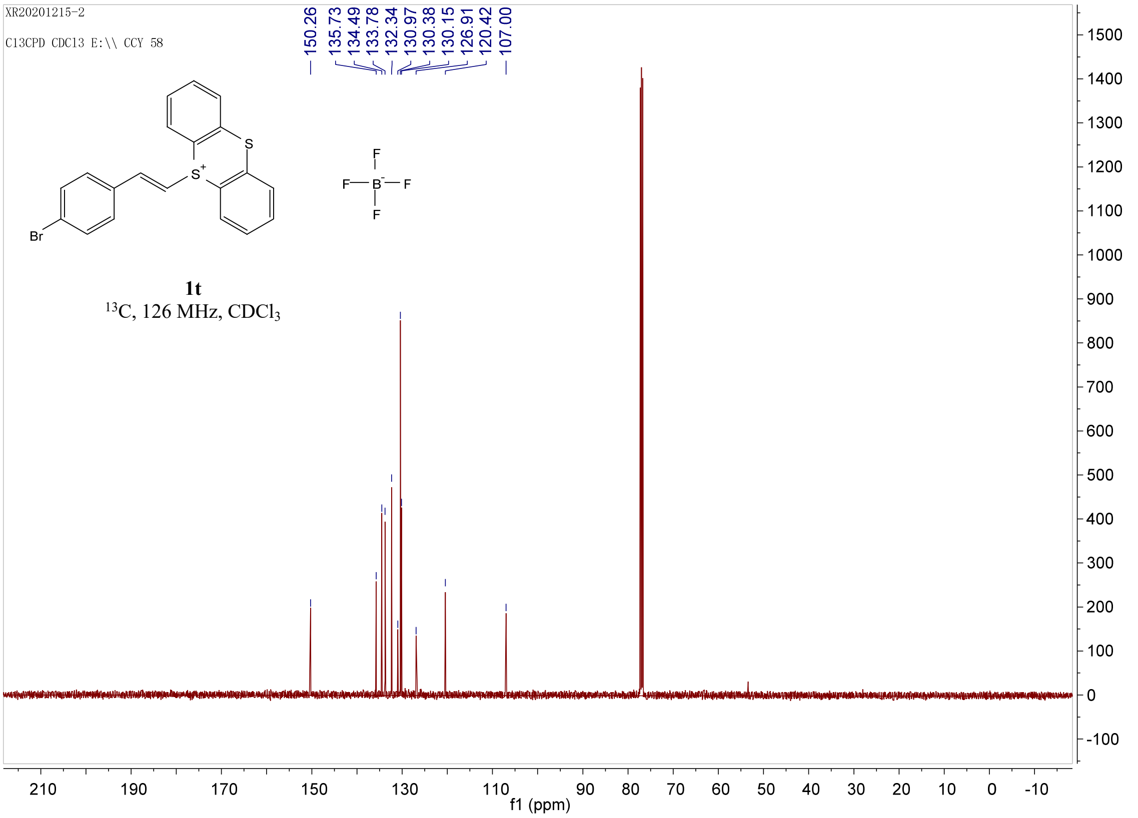
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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150.26
135.73
134.49
133.78
132.34
130.97
130.38
130.15
126.91
120.42
107.00
S
S+
Br
F
F—B−—F
F
1t
13C, 126 MHz, CDCl3
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
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80
70
60
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40
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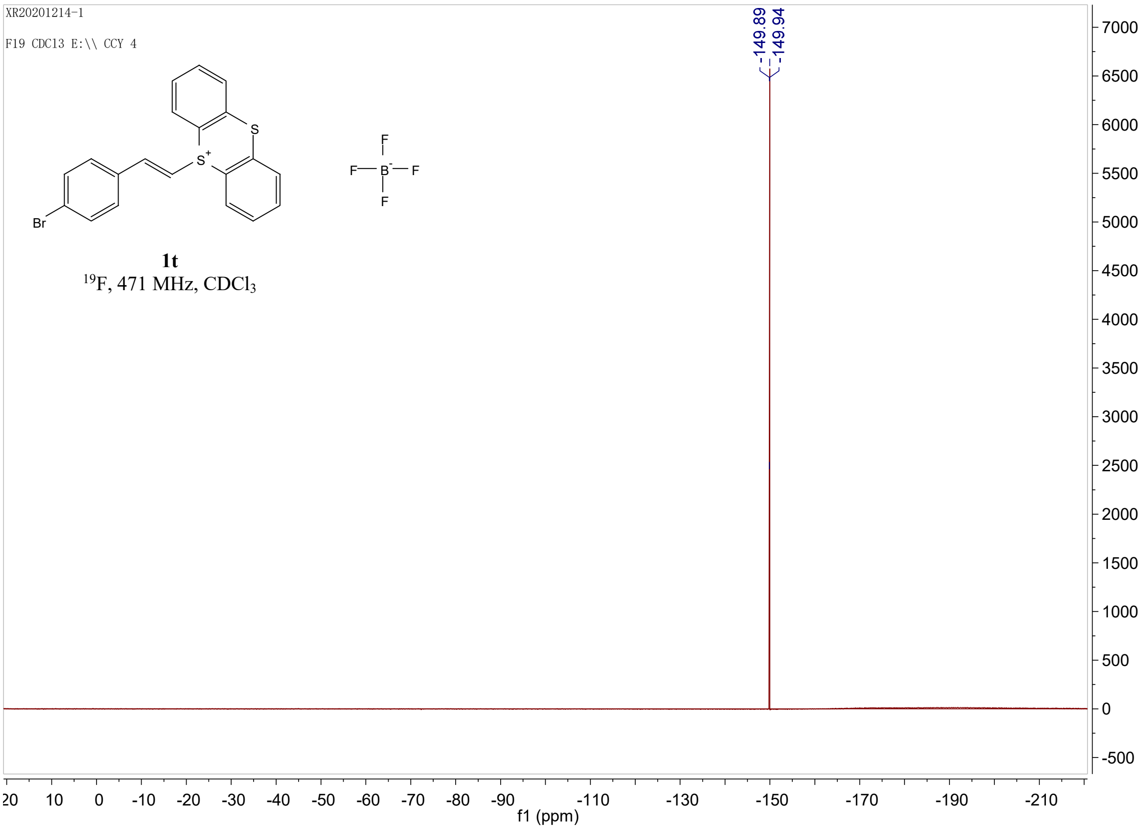
0
-10
f1 (ppm)



1t

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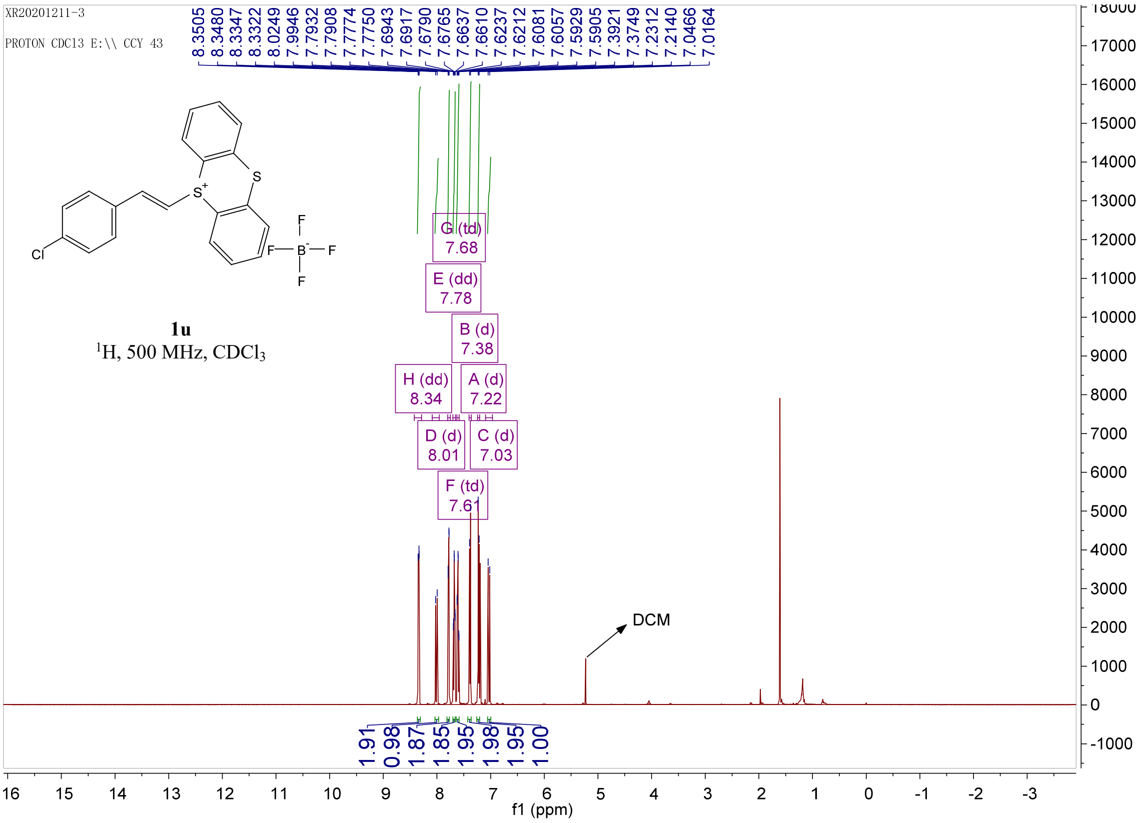

1u

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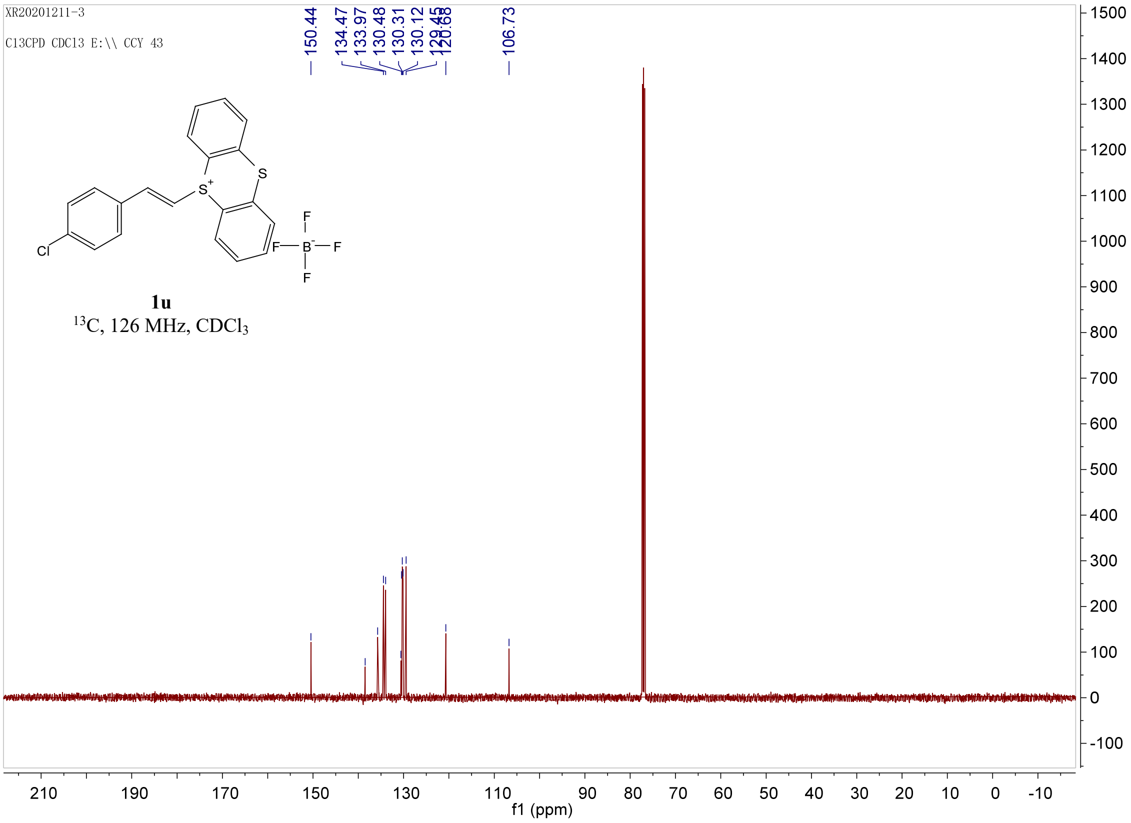

1u

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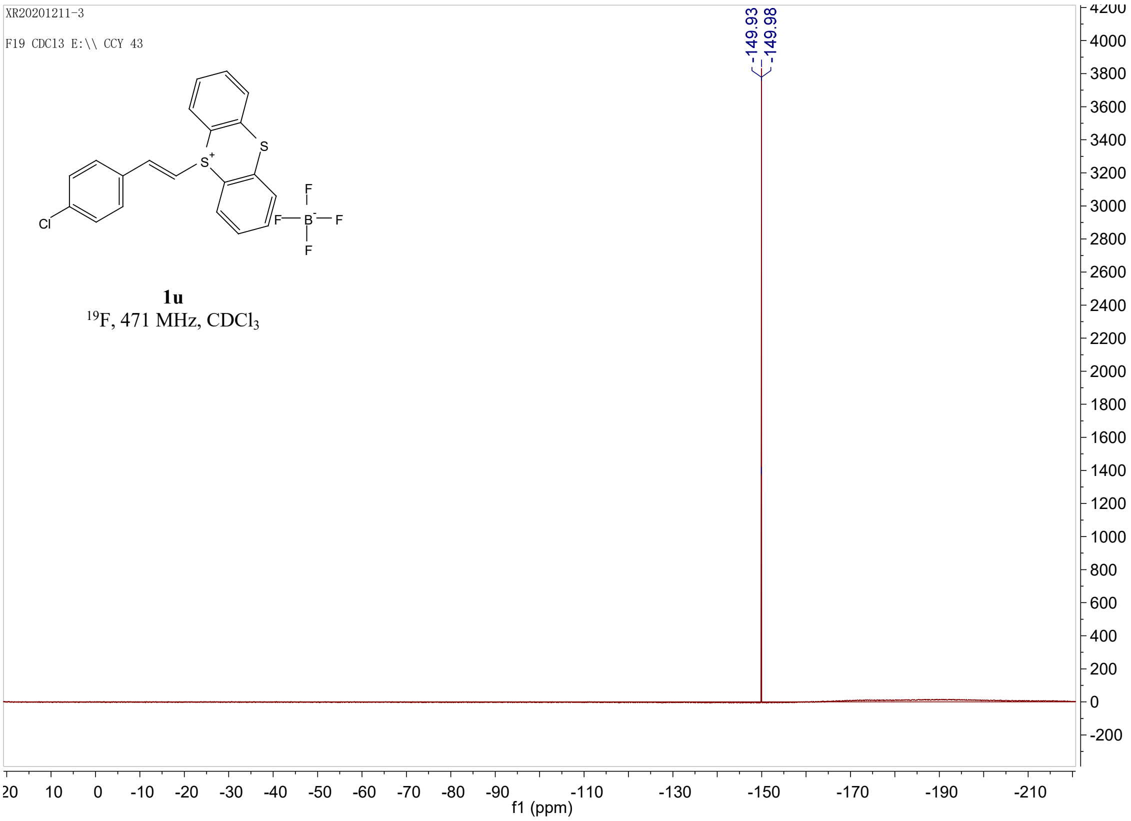
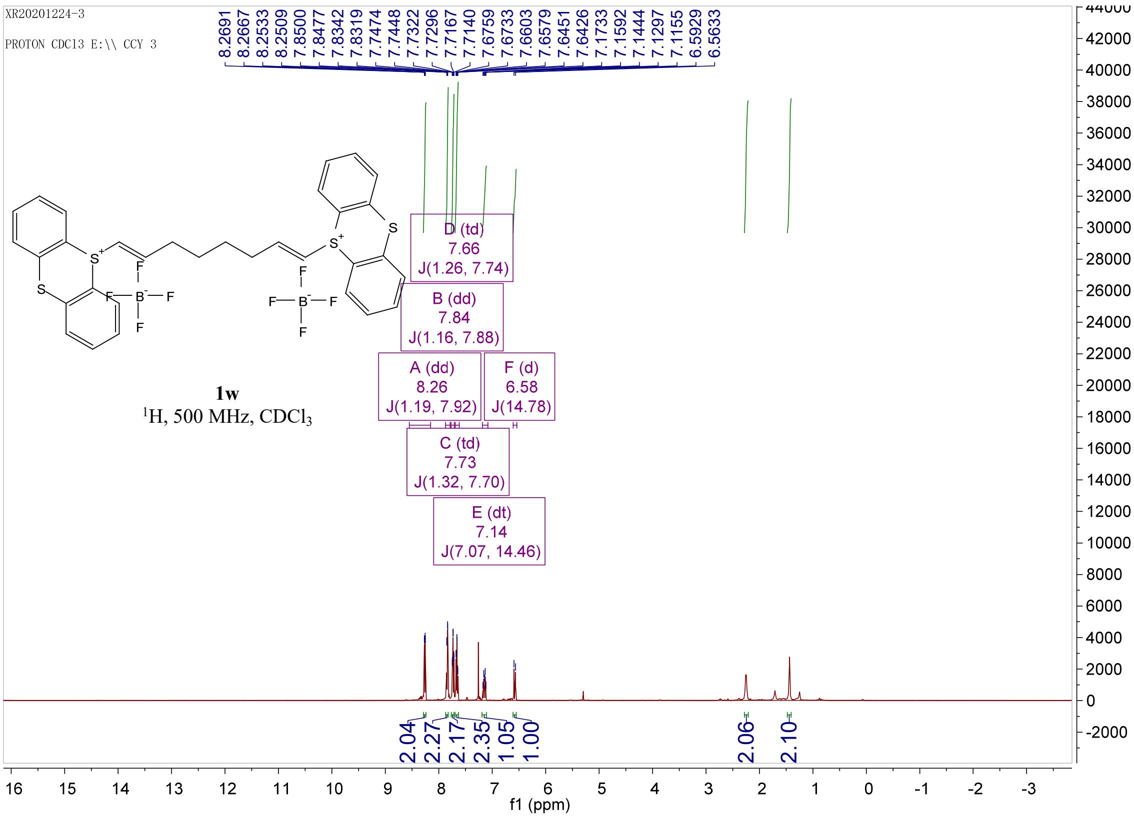
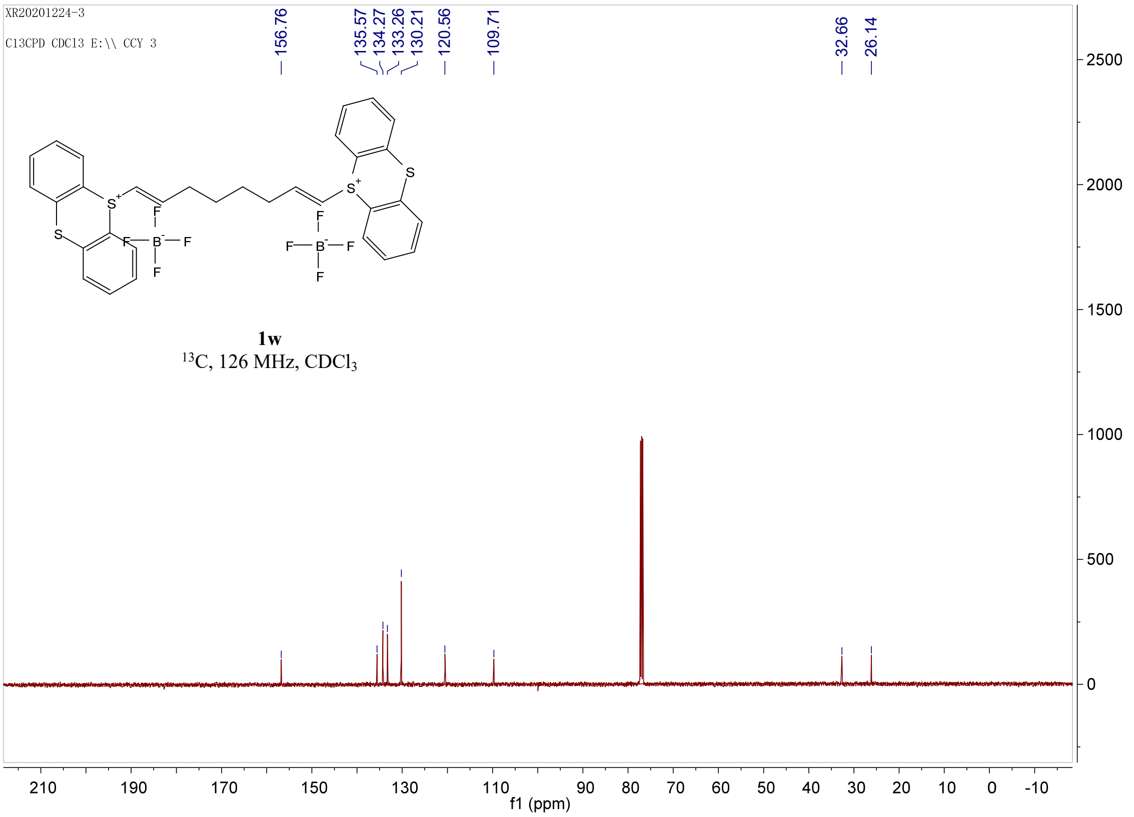
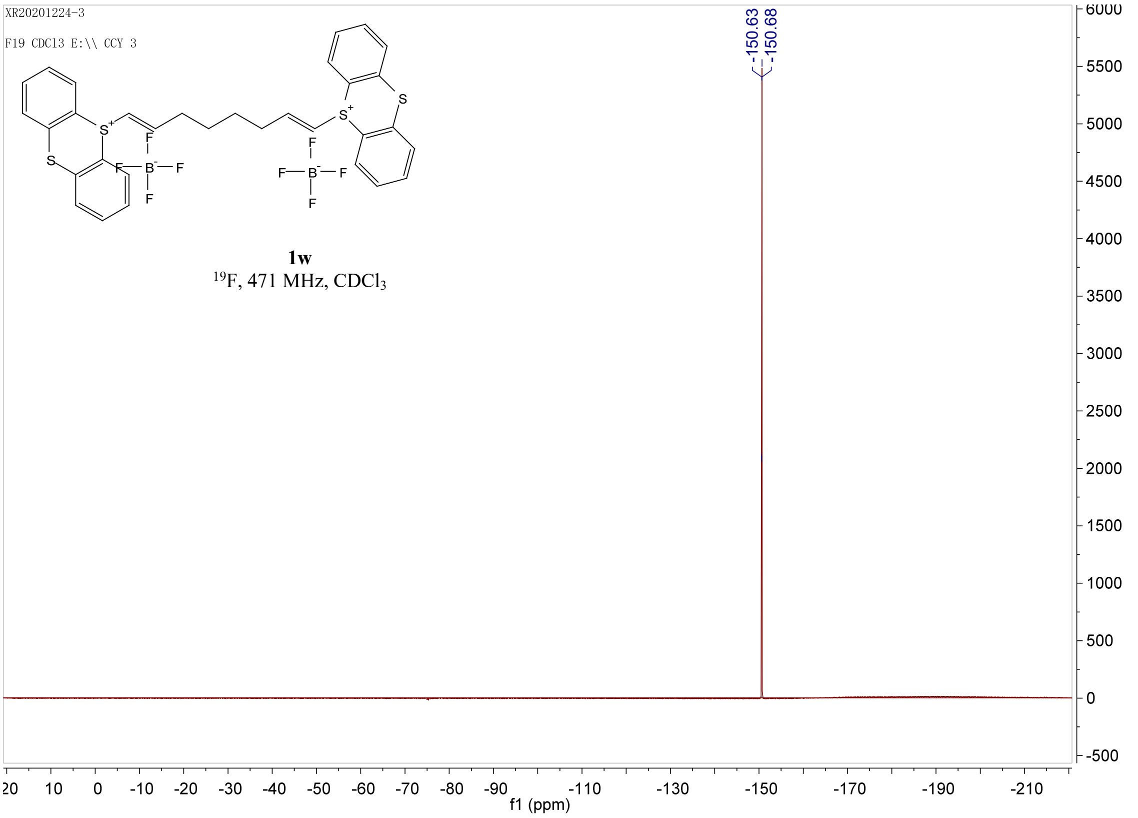


1u

^{19}F, 471 MHz, $CDCl_3$

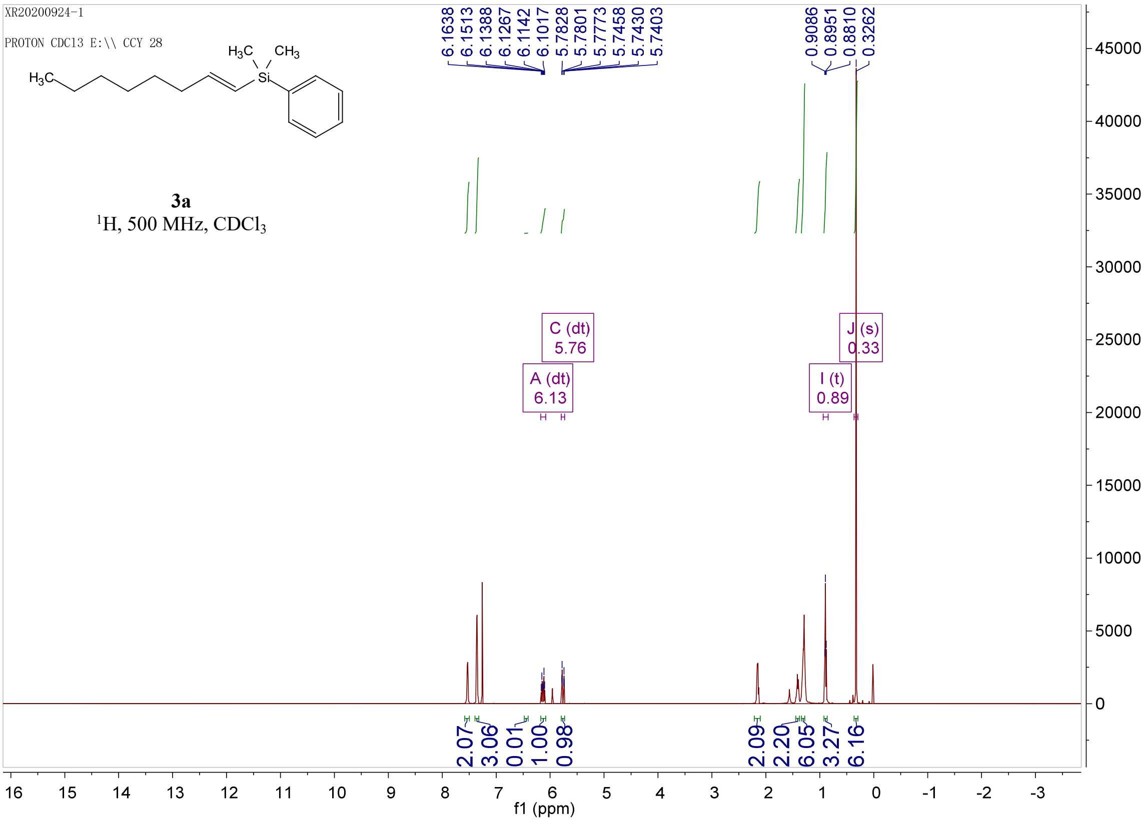

XR20201224-3
PROTON CDCl3 E:\\ CCY 3
8.2691
8.2667
8.2533
8.2509
7.8500
7.8477
7.8342
7.8319
7.7474
7.7448
7.7322
7.7296
7.7167
7.7140
7.6759
7.6733
7.6603
7.6579
7.6451
7.6426
7.1733
7.1592
7.1444
7.1297
7.1155
6.5929
6.5633
D (td) 7.66 J(1.26, 7.74)
B (dd) 7.84 J(1.16, 7.88)
A (dd) 8.26 J(1.19, 7.92)
F (d) 6.58 J(14.78)
C (td) 7.73 J(1.32, 7.70)
E (dt) 7.14 J(7.07, 14.46)
1w
^{1}H, 500 MHz, CDCl$_3$
2.04
2.27
2.17
2.35
1.05
1.00
2.06
2.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
44000 42000 40000 38000 36000 34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


XR20201224-3
C13CPD CDCl3 E:\\ CCY 3
156.76
135.57
134.27
133.26
130.21
120.56
109.71
32.66
26.14
1w
^{13}C, 126 MHz, CDCl$_3$
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2500 2000 1500 1000 500 0



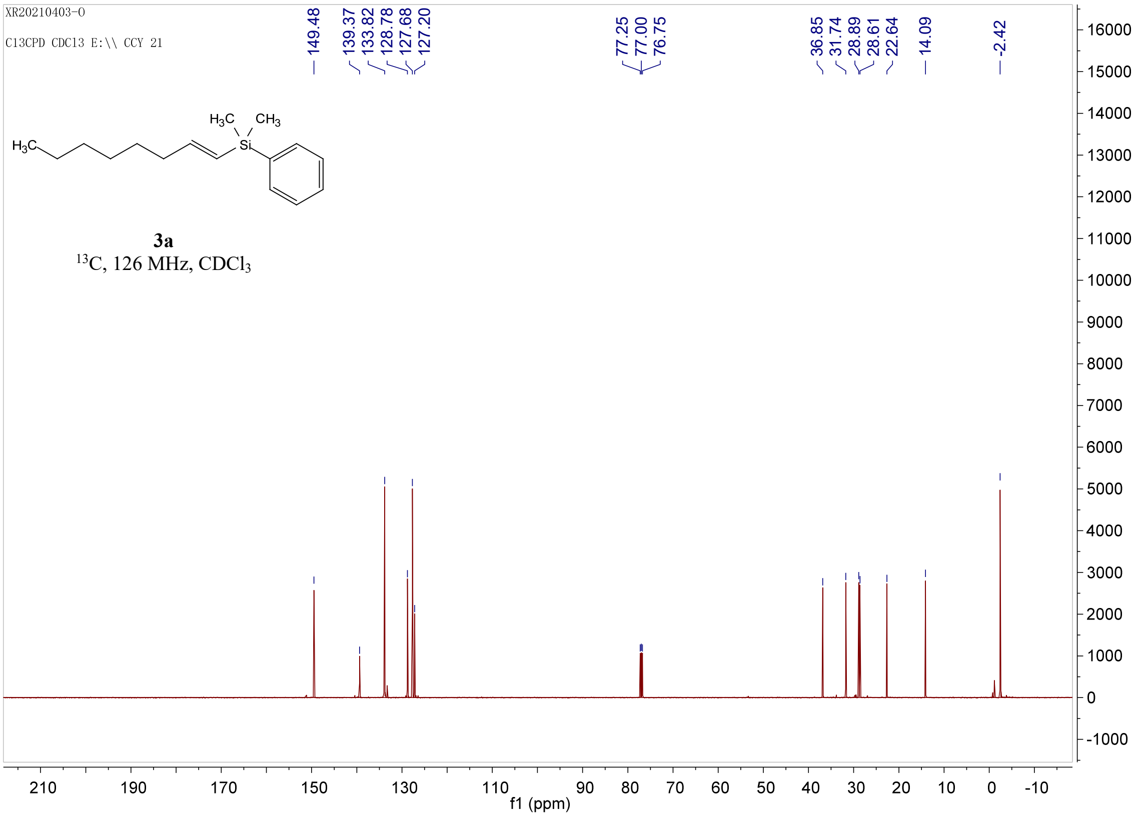
1w

^{19}F, 471 MHz, CDCl$_3$



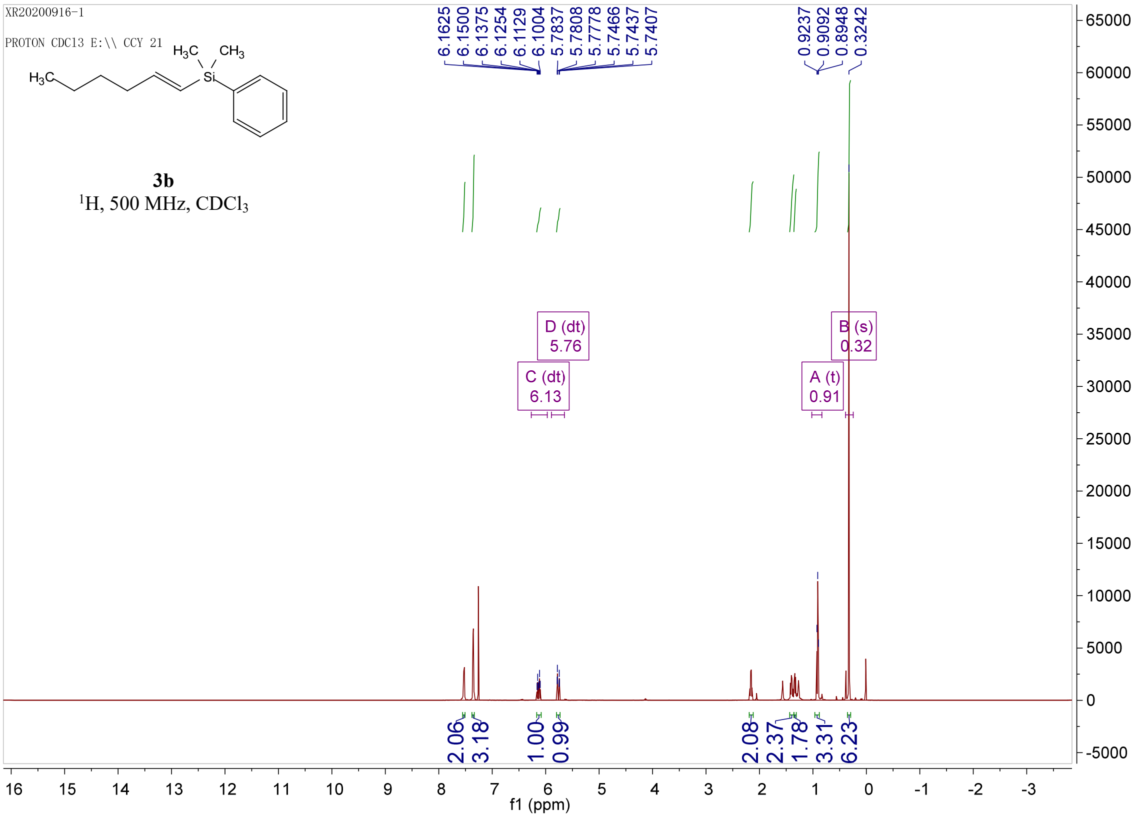
3a

^{1}H, 500 MHz, CDCl$_3$



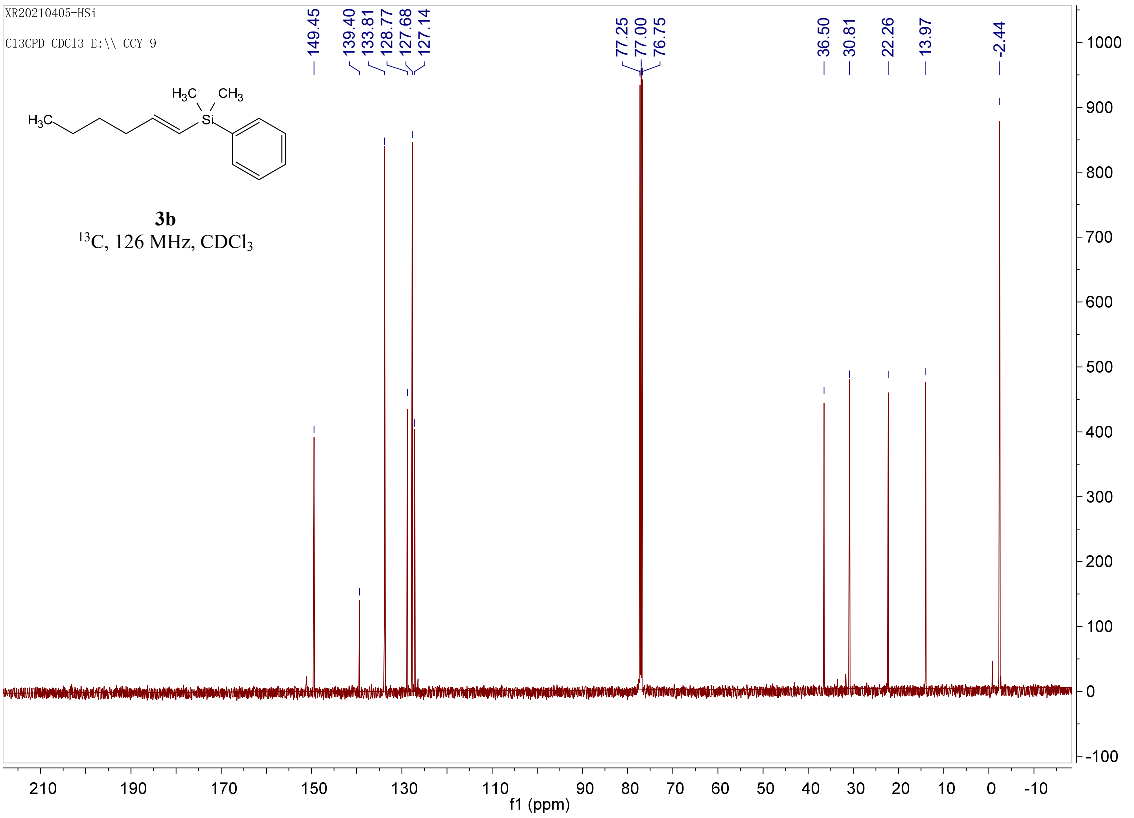
3a

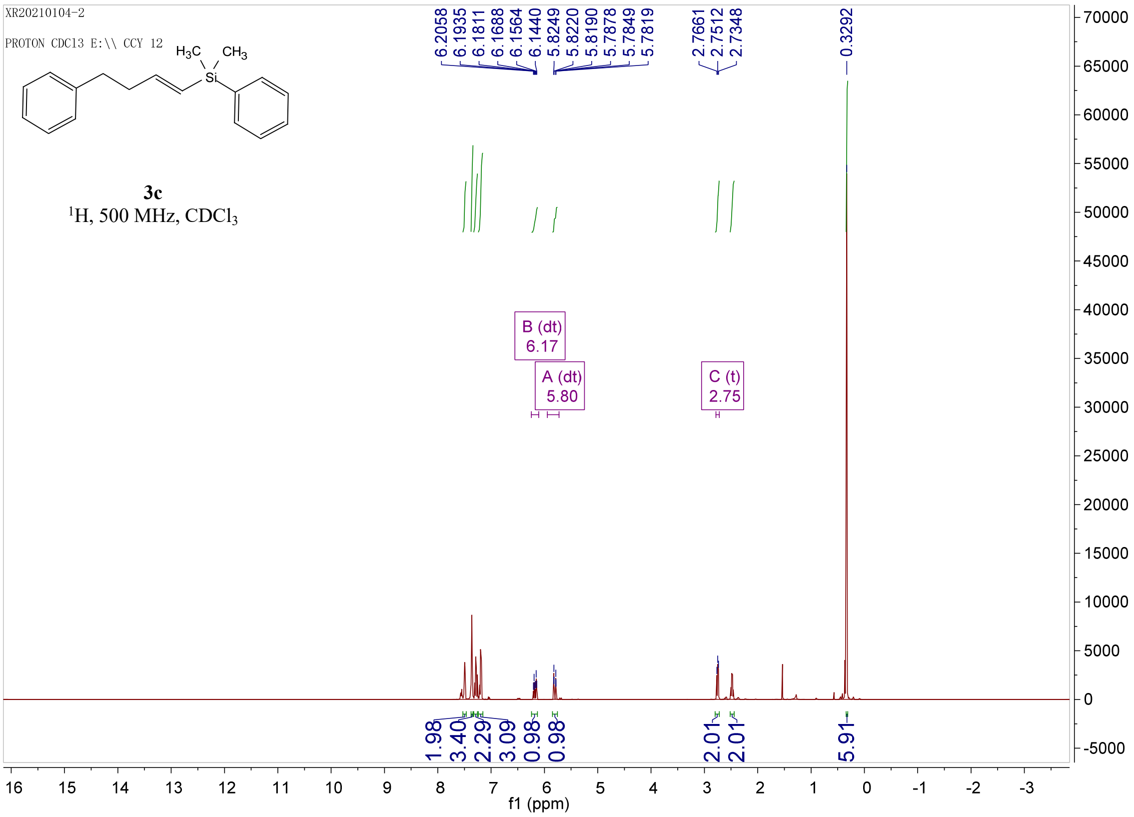
^{13}C, 126 MHz, CDCl$_3$

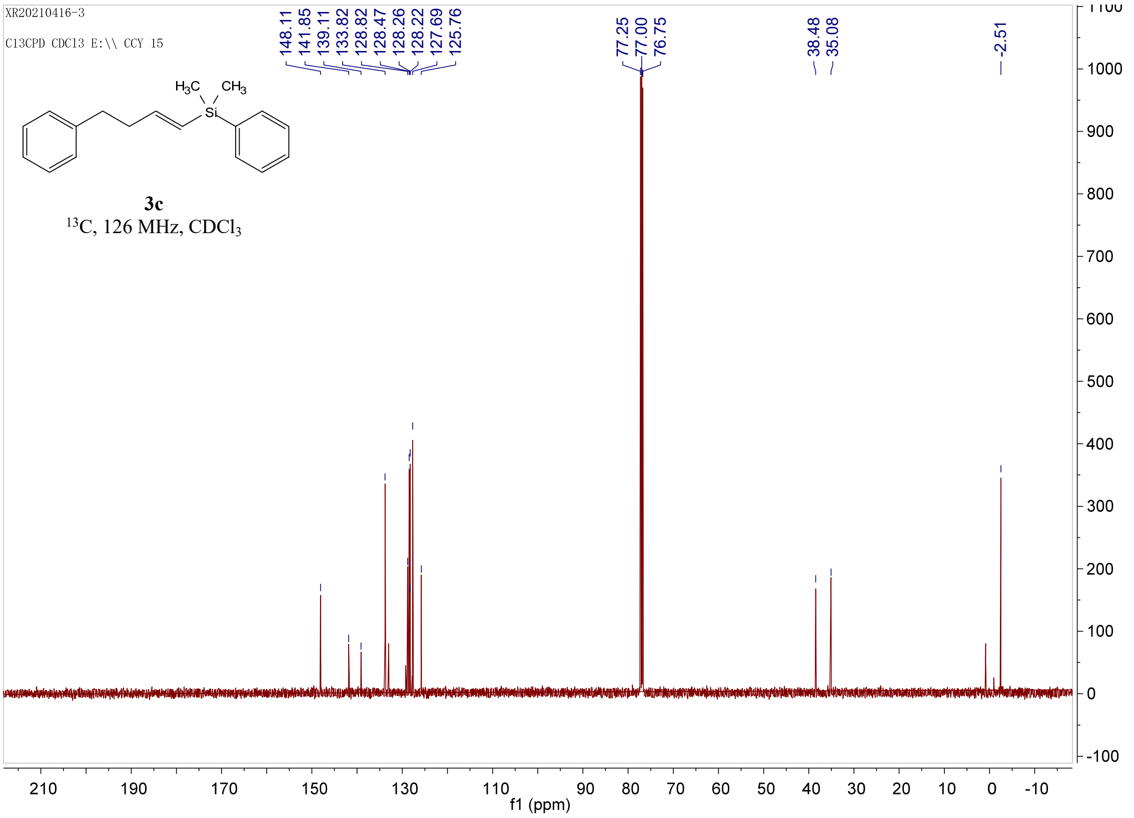


3b

^{1}H, 500 MHz, CDCl$_3$

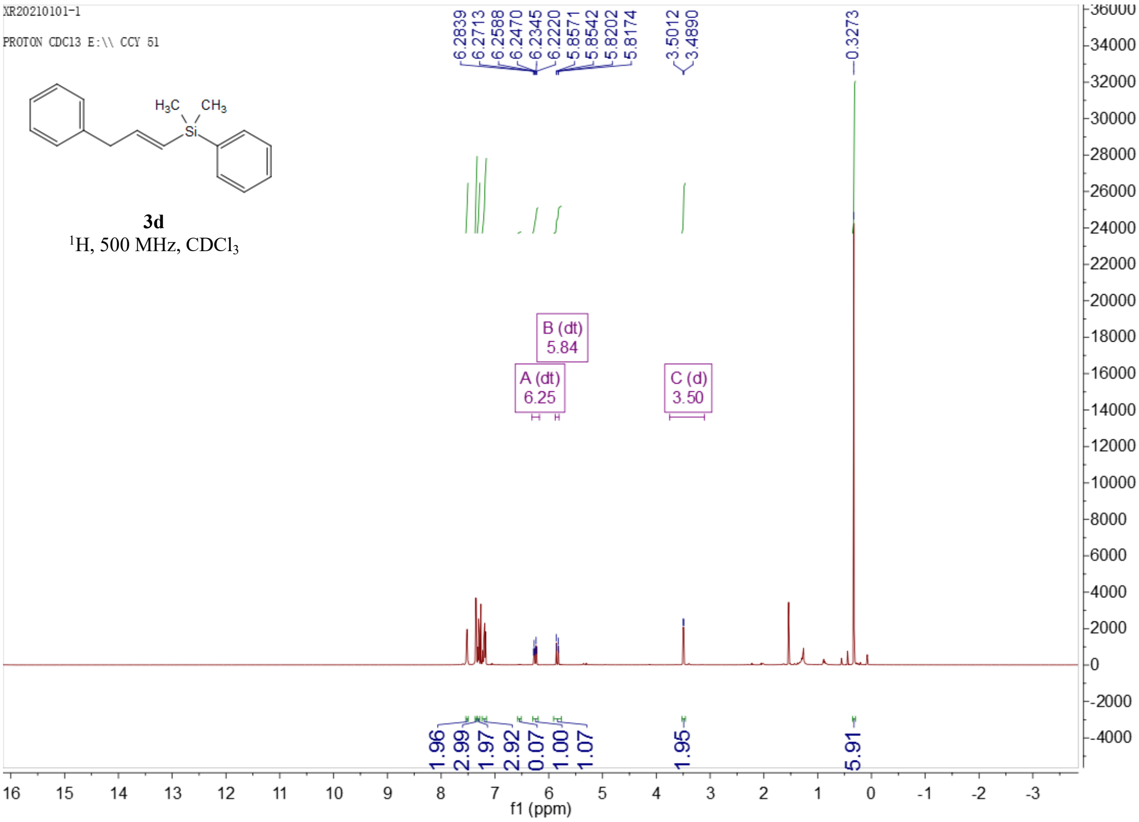

XR20210405-HSi
C13CPD CDCl3 E:\\ CCY 9
149.45
139.40
133.81
128.77
127.68
127.14
77.25
77.00
76.75
36.50
30.81
22.26
13.97
-2.44
H_3C
CH_3
Si
3b
^{13}C, 126 MHz, $CDCl_3$
f1 (ppm)


XR20210104-2
PROTON CDCl3 E:\\ CCY 12
6.2058
6.1935
6.1811
6.1688
6.1564
6.1440
5.8249
5.8220
5.8190
5.7878
5.7849
5.7819
2.7661
2.7512
2.7348
0.3292
H_3C
CH_3
Si
3c
^1H, 500 MHz, $CDCl_3$
B (dt)
6.17
A (dt)
5.80
C (t)
2.75
1.98
3.40
2.29
3.09
0.98
0.98
2.01
2.01
5.91
f1 (ppm)



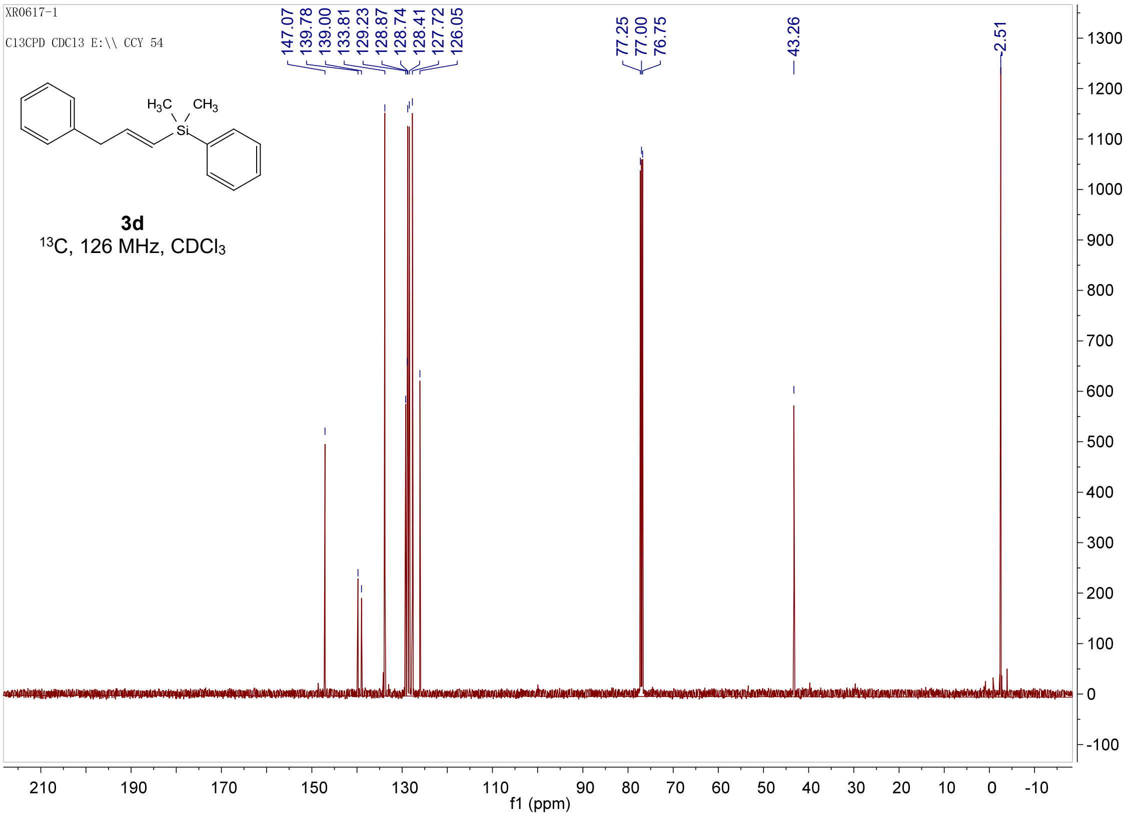
3c

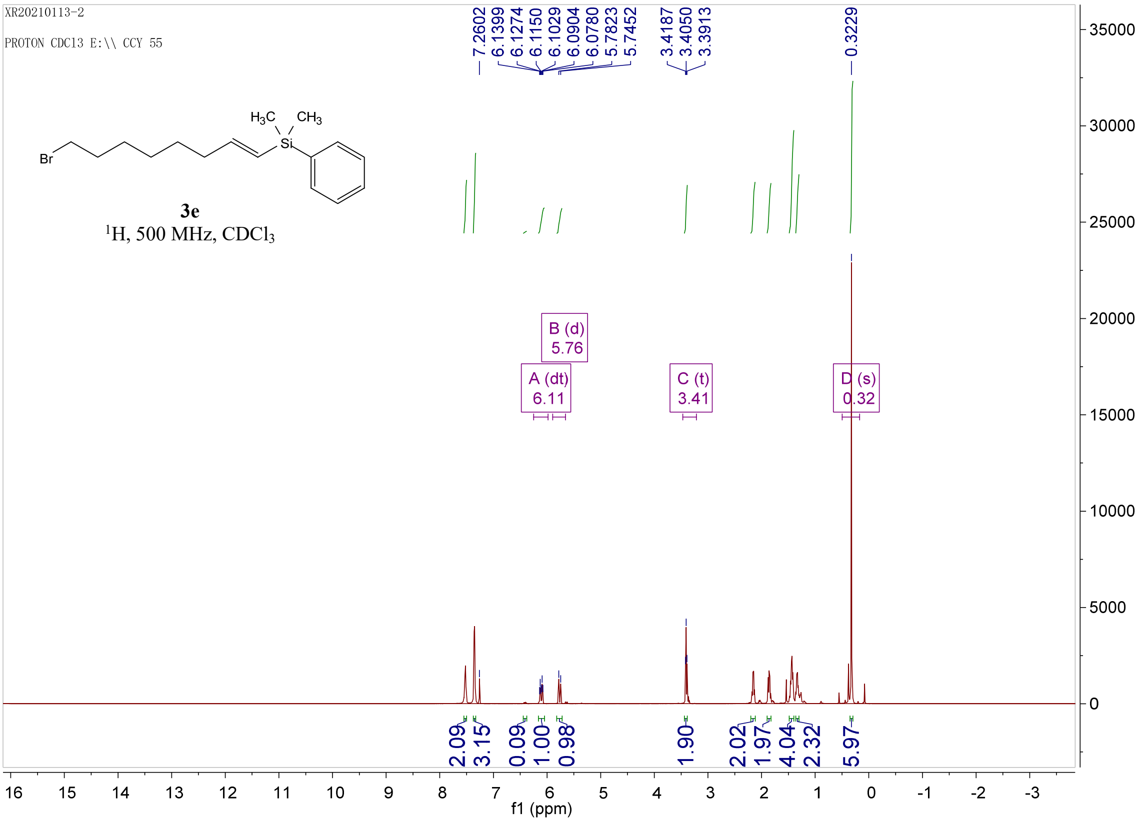
^{13}C, 126 MHz, CDCl$_3$

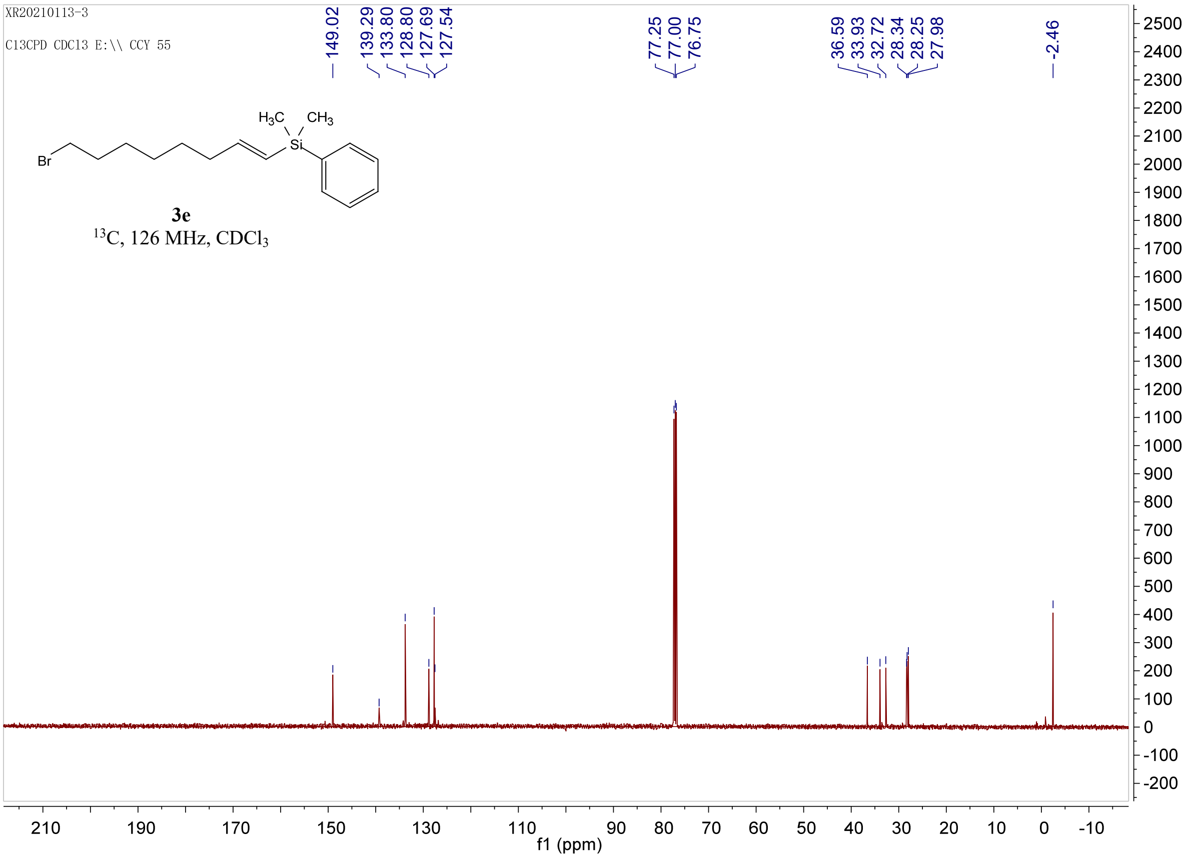


3d

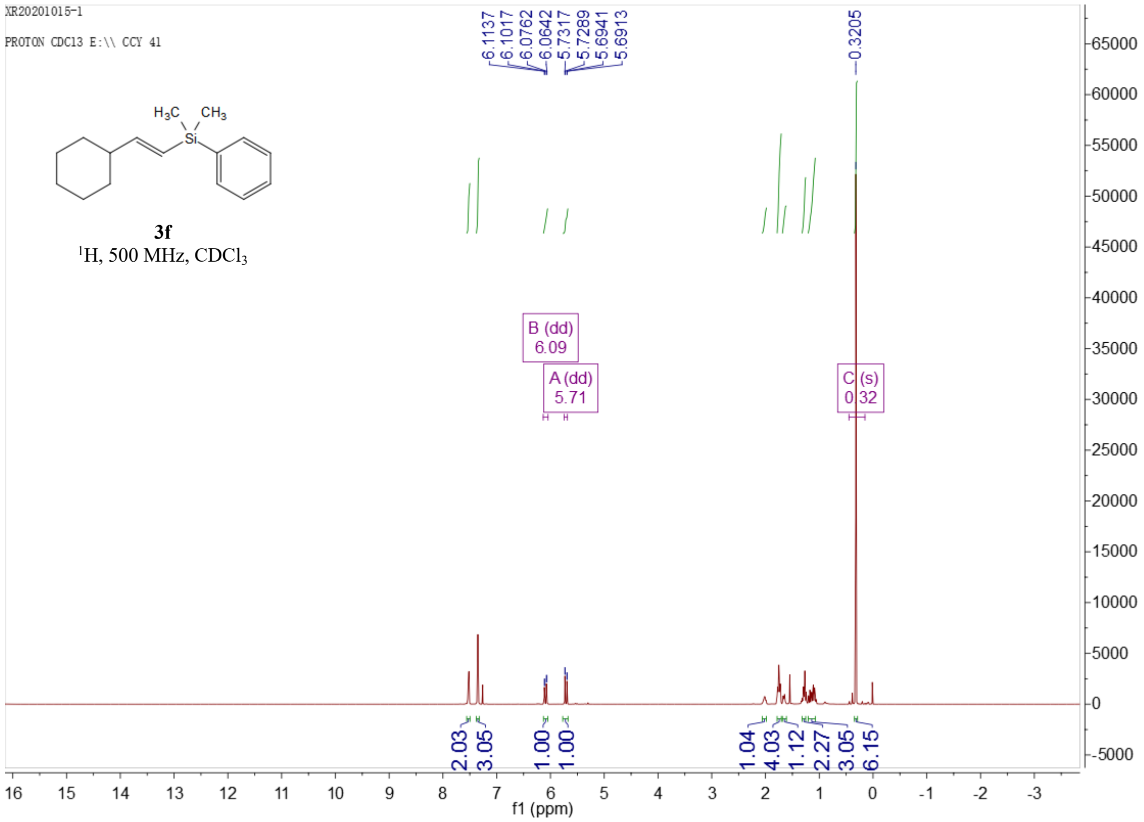
^{1}H, 500 MHz, CDCl$_3$


XR0617-1
C13CPD CDCl3 E:\\ CCY 54
147.07
139.78
139.00
133.81
129.23
128.87
128.74
128.41
127.72
126.05
77.25
77.00
76.75
43.26
-2.51
H3C
CH3
Si
3d
13C, 126 MHz, CDCl3
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

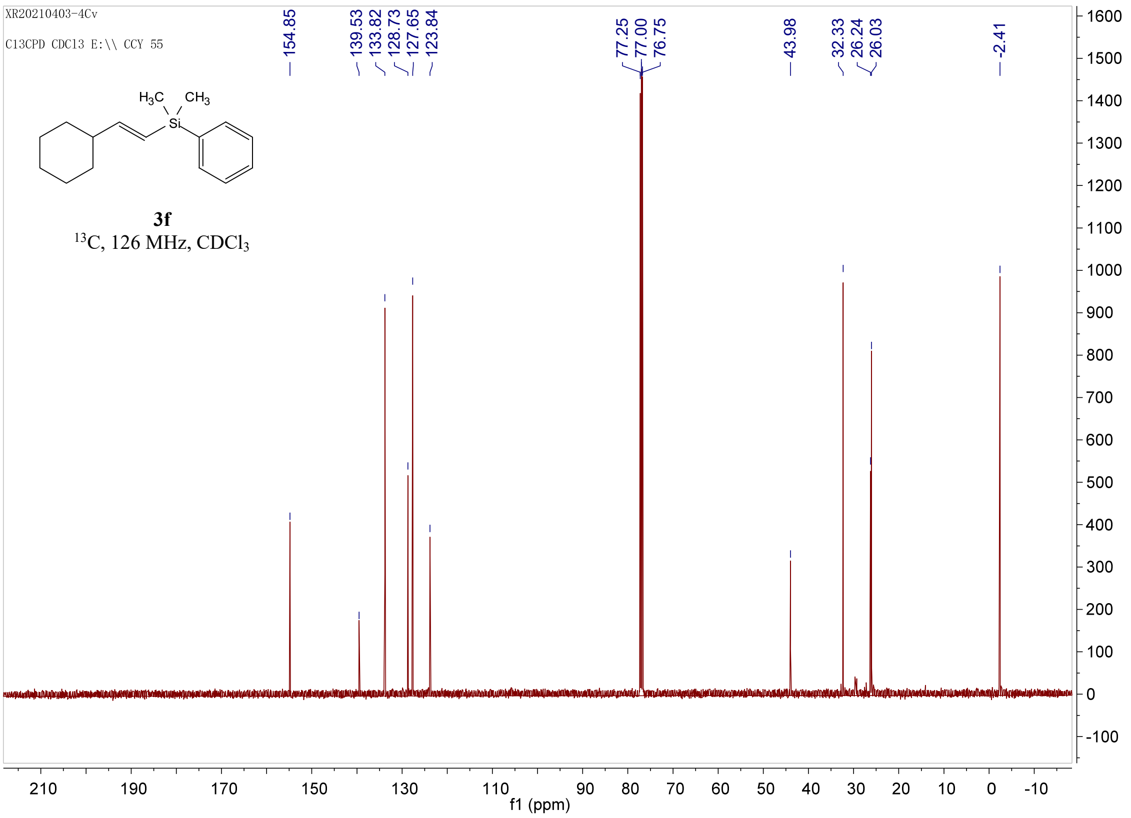

XR20210113-2
PROTON CDCl3 E:\\ CCY 55
7.2602
6.1399
6.1274
6.1150
6.1029
6.0904
6.0780
5.7823
5.7452
3.4187
3.4050
3.3913
0.3229
Br
H3C
CH3
Si
3e
1H, 500 MHz, CDCl3
B (d)
5.76
A (dt)
6.11
C (t)
3.41
D (s)
0.32
2.09
3.15
0.09
1.00
0.98
1.90
2.02
1.97
4.04
2.32
5.97
35000
30000
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

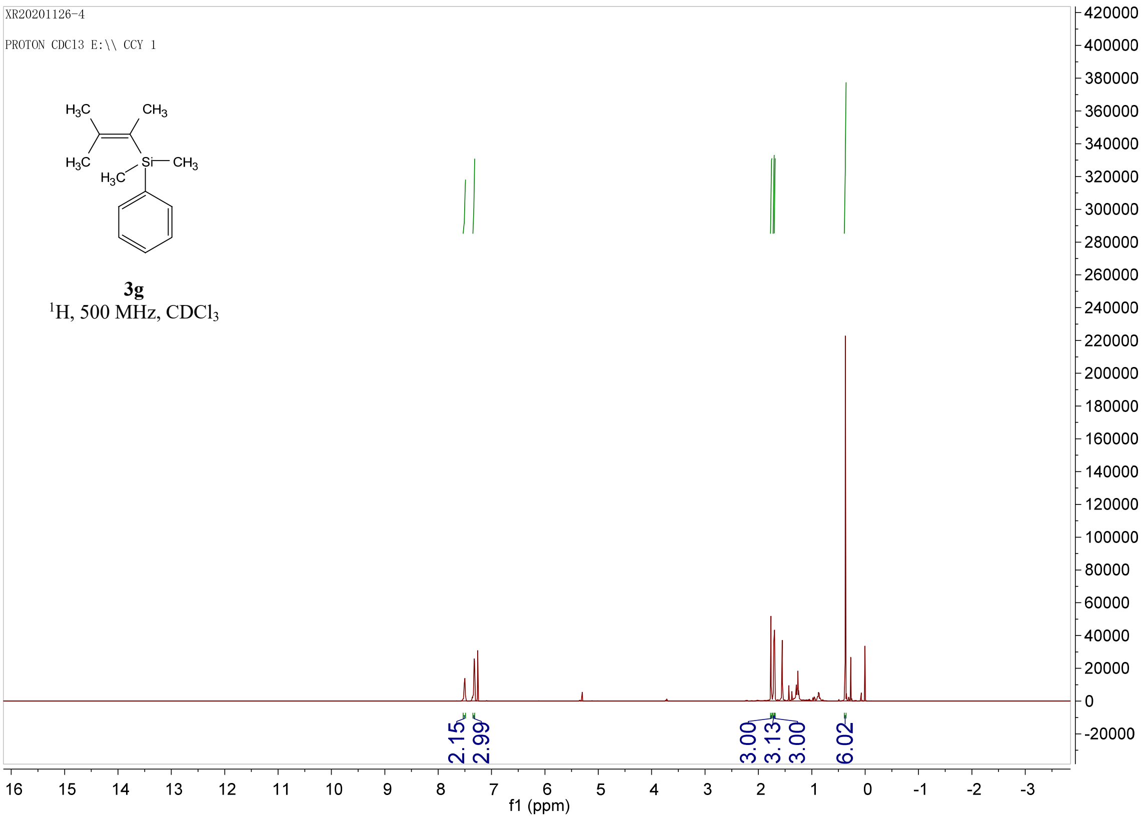

3e

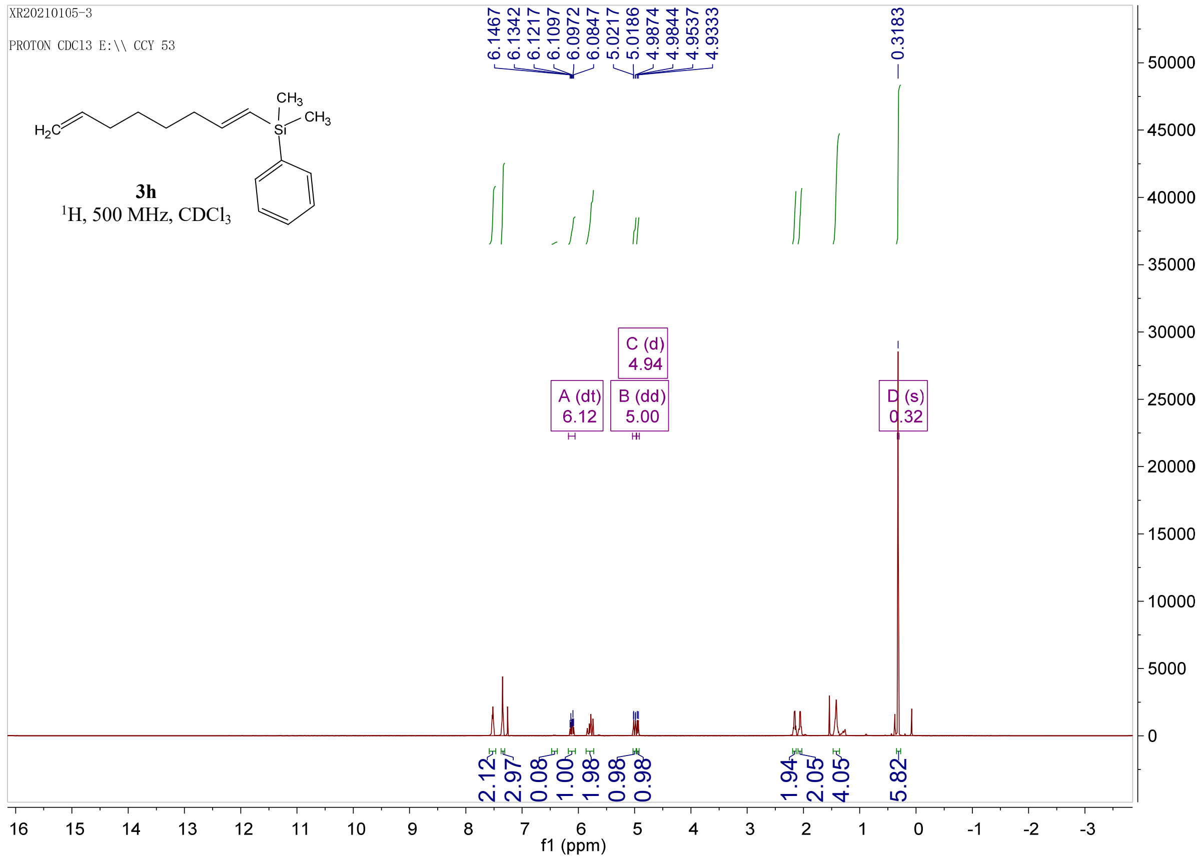
^{13}C, 126 MHz, CDCl$_3$

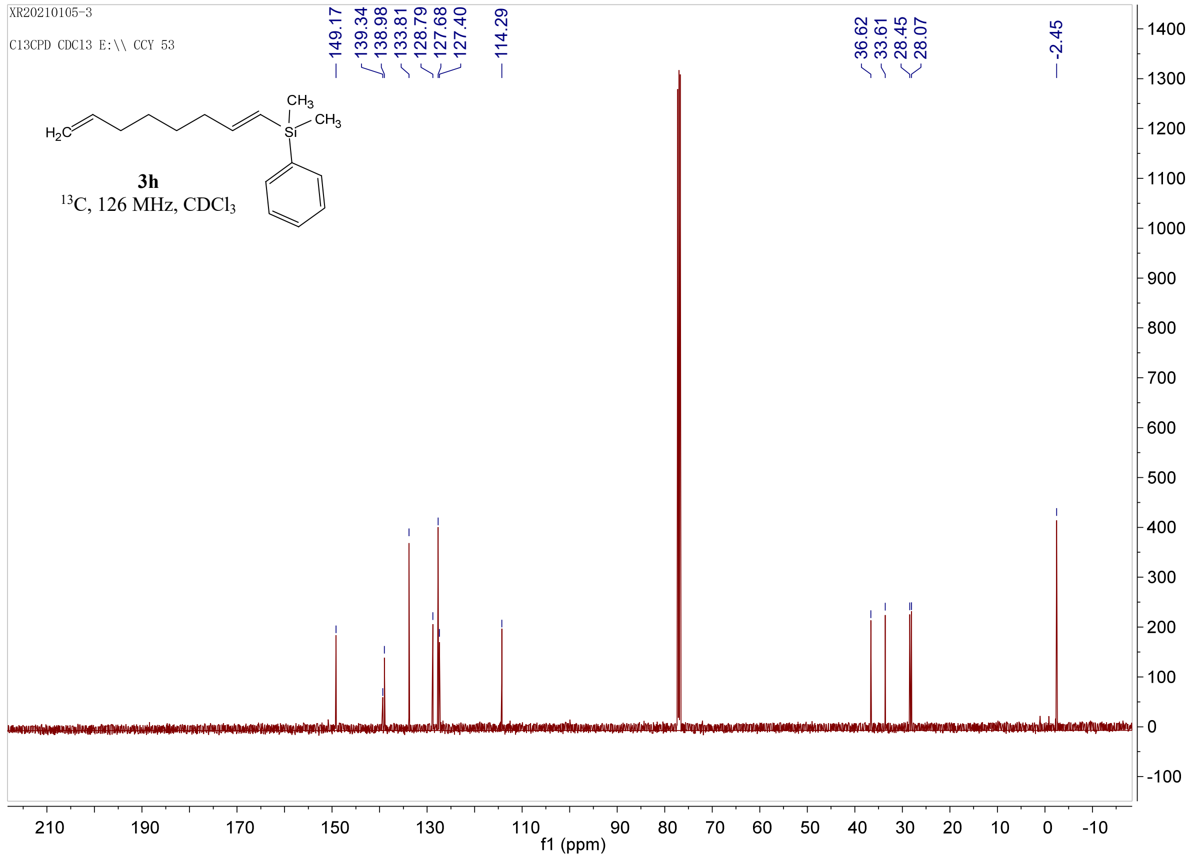

3f

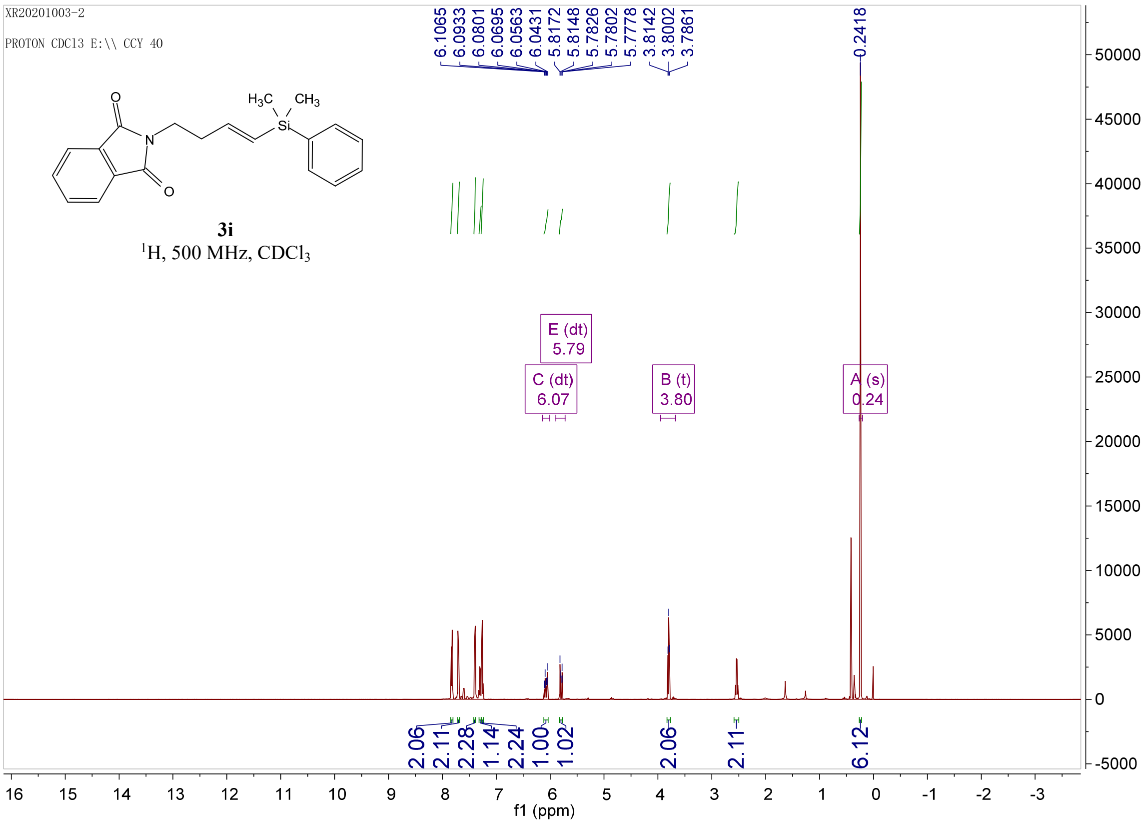
^{1}H, 500 MHz, CDCl$_3$


XR20210403-4Cv
C13CPD CDCl3 E:\\ CCY 55
154.85
139.53
133.82
128.73
127.65
123.84
77.25
77.00
76.75
43.98
32.33
26.24
26.03
-2.41
H3C
CH3
Si
3f
13C, 126 MHz, CDCl3
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20201126-4
PROTON CDCl3 E:\\ CCY 1
H3C
CH3
H3C
Si
CH3
H3C
3g
1H, 500 MHz, CDCl3
2.15
2.99
3.00
3.13
3.00
6.02
420000
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

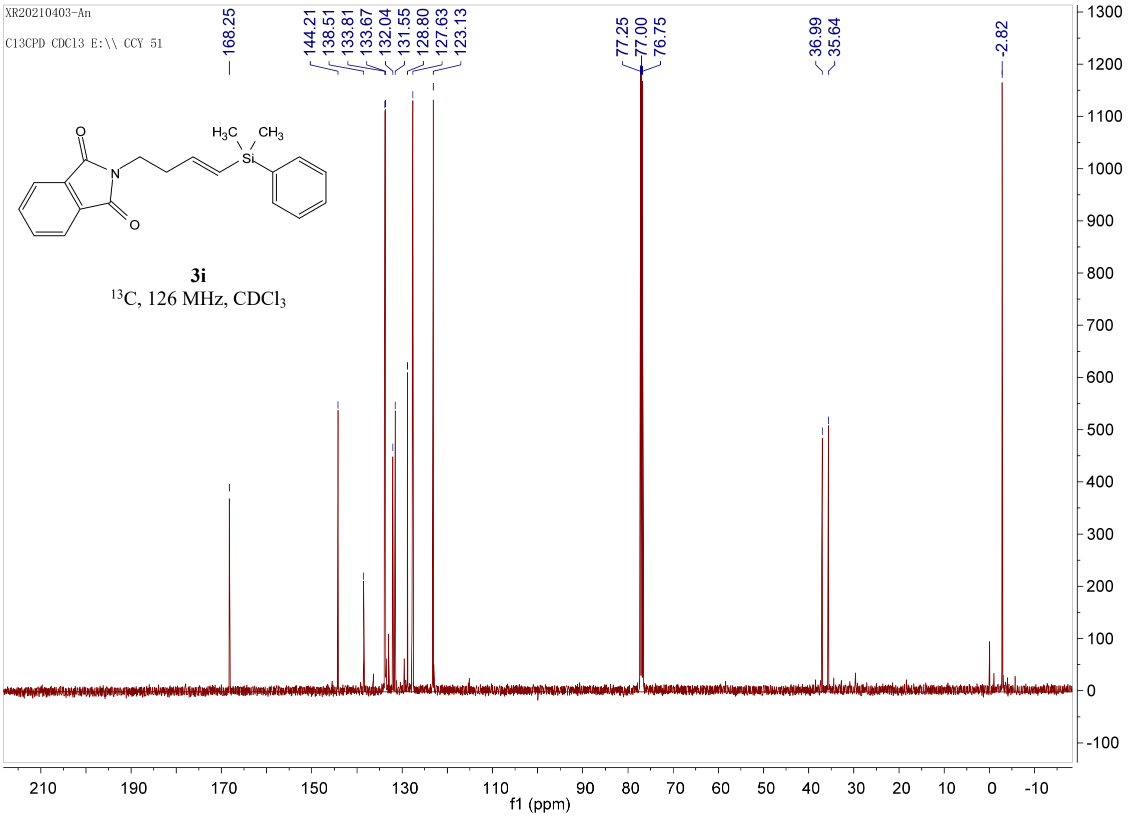

XR20210105-3
PROTON CDCl3 E:\\ CCY 53
CH3
CH3
H2C
Si
3h
1H, 500 MHz, CDCl3
6.1467
6.1342
6.1217
6.1097
6.0972
6.0847
5.0217
5.0186
4.9874
4.9844
4.9537
4.9333
0.3183
C (d)
4.94
A (dt)
6.12
B (dd)
5.00
D (s)
0.32
2.12
2.97
0.08
1.00
1.98
0.98
0.98
1.94
2.05
4.05
5.82
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


XR20210105-3
C13CPD CDCl3 E:\\ CCY 53
CH3
CH3
H2C
Si
3h
13C, 126 MHz, CDCl3
149.17
139.34
138.98
133.81
128.79
127.68
127.40
114.29
36.62
33.61
28.45
28.07
-2.45
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



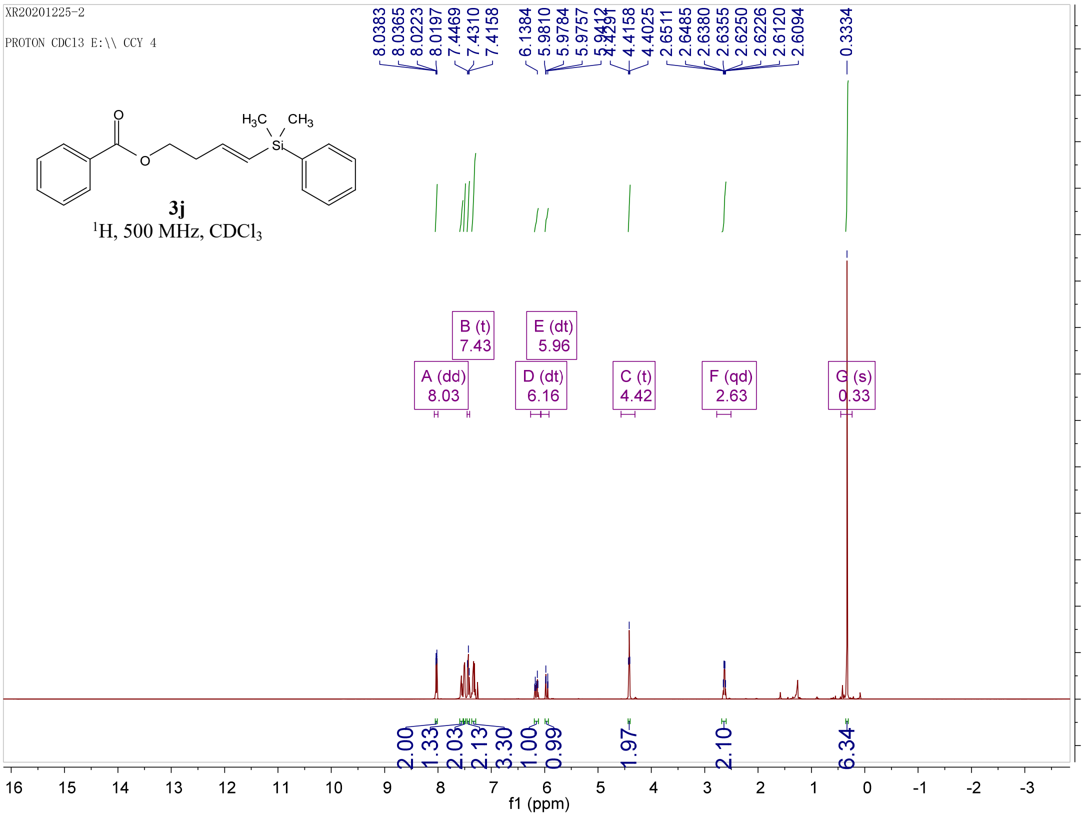
3i

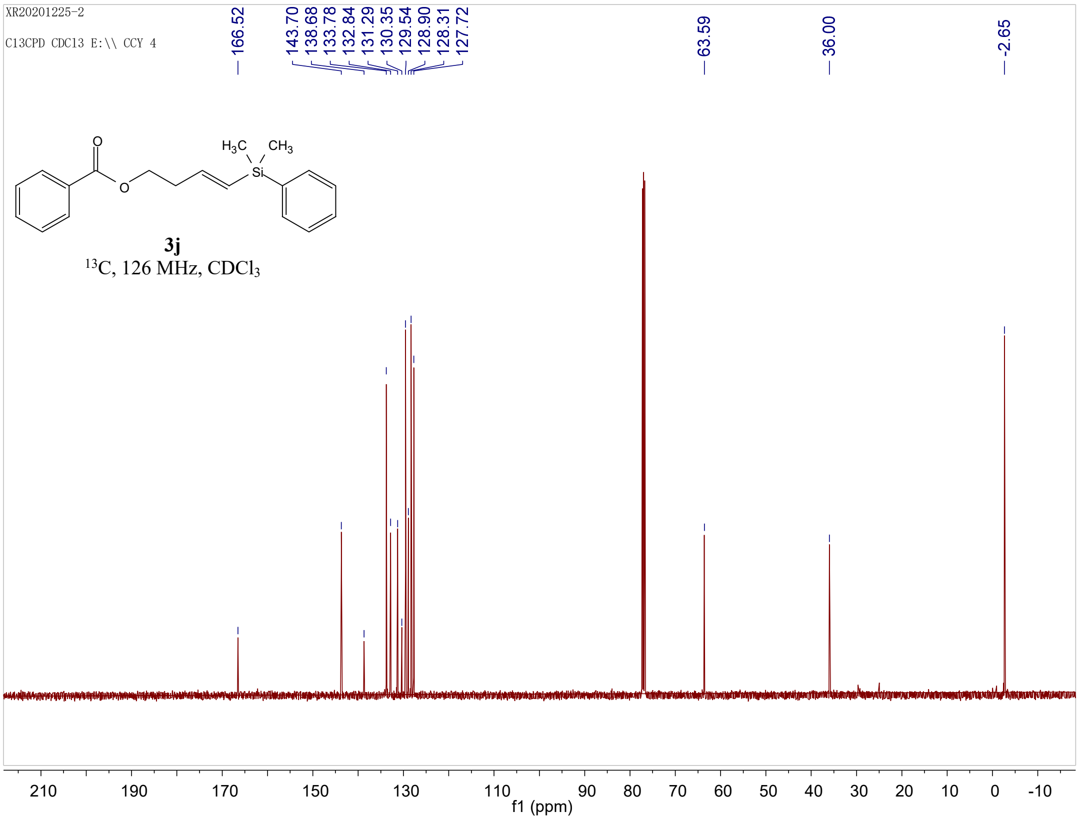
^{1}H, 500 MHz, CDCl$_3$

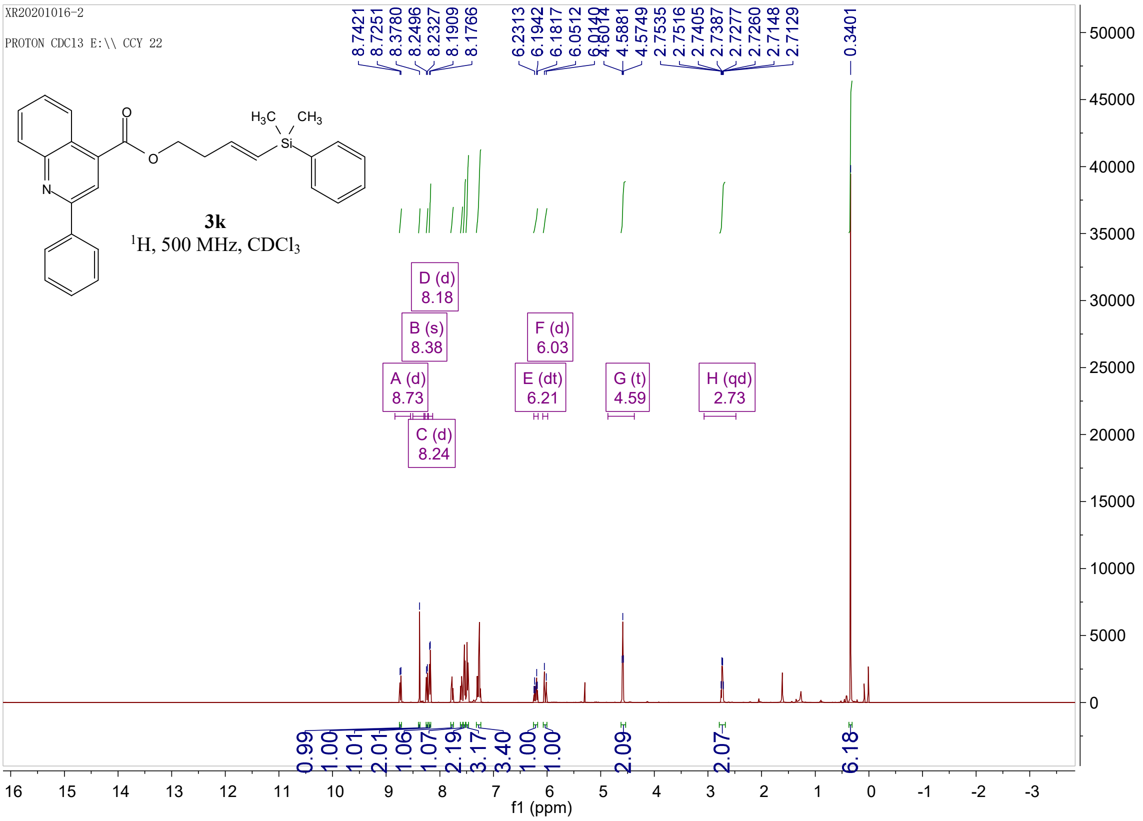


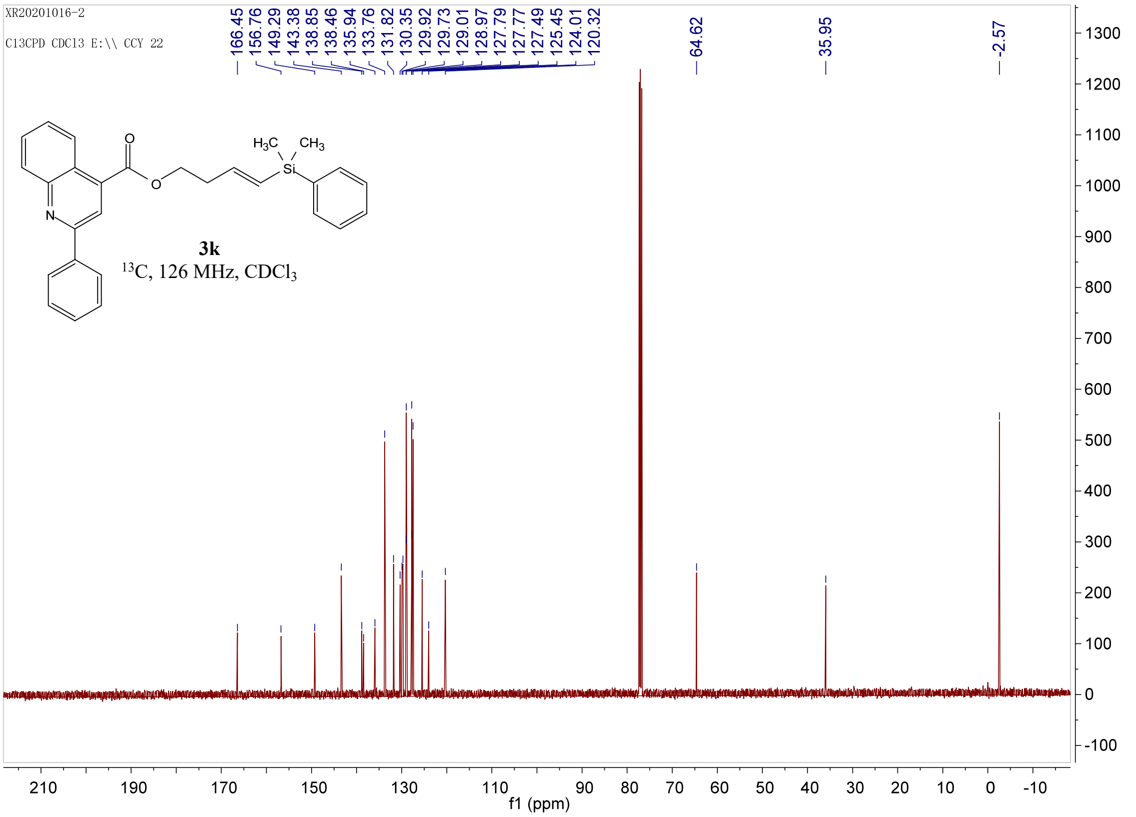
3i

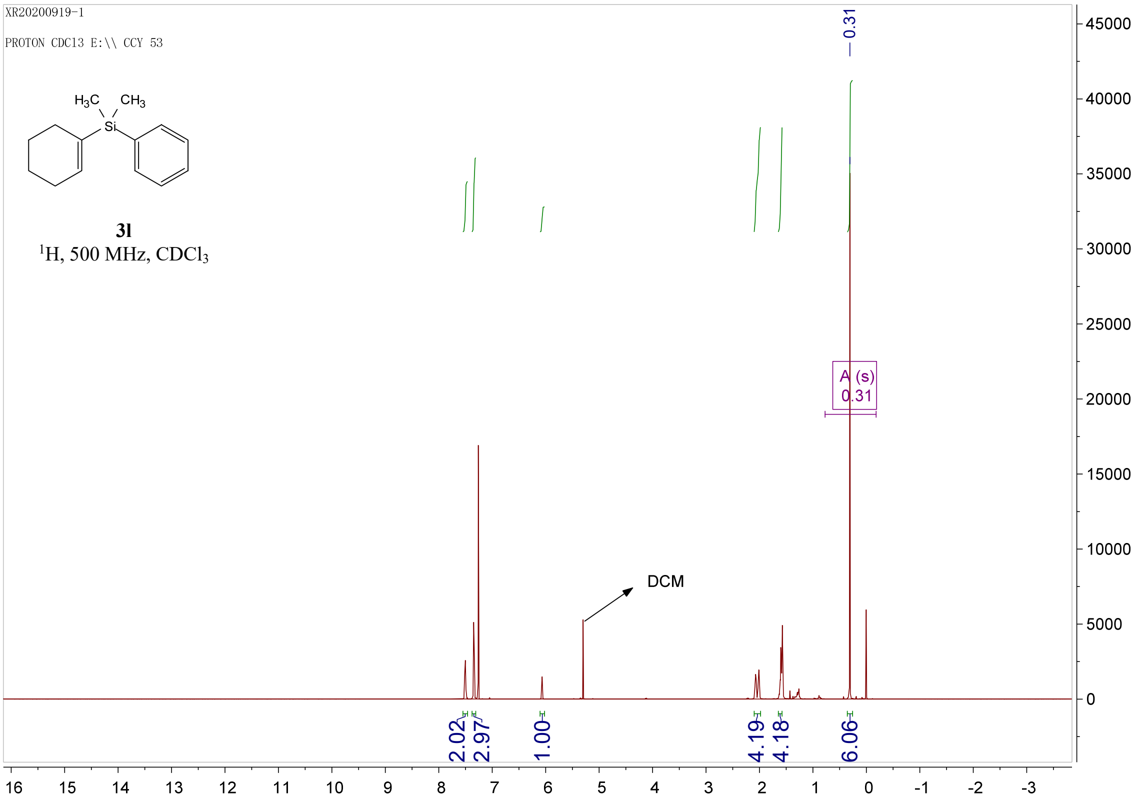
^{13}C, 126 MHz, CDCl$_3$

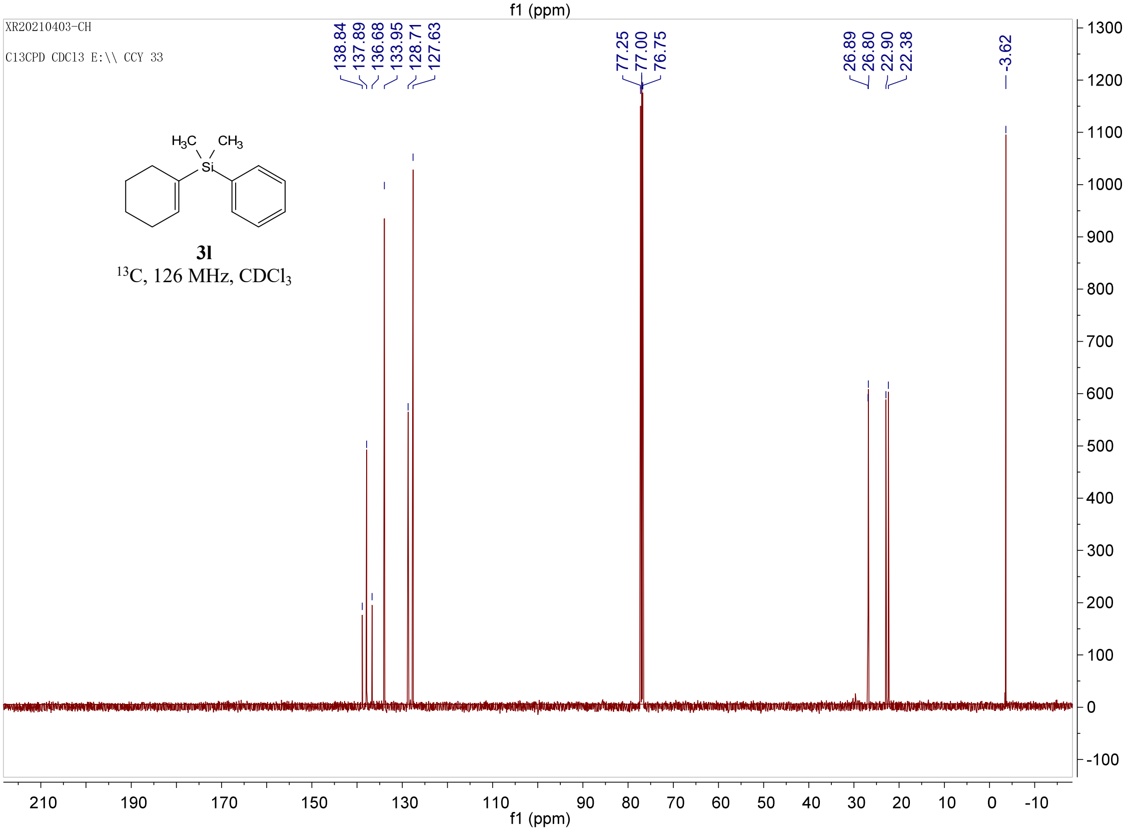

XR20201225-2
PROTON CDCl3 E:\\ CCY 4
8.0383
8.0365
8.0223
8.0197
7.4469
7.4310
7.4158
6.1384
5.9810
5.9784
5.9757
5.9412
4.4291
4.4158
4.4025
2.6511
2.6485
2.6380
2.6355
2.6250
2.6226
2.6120
2.6094
0.3334
H3C
CH3
Si
O
O
3j
1H, 500 MHz, CDCl3
A (dd) 8.03
B (t) 7.43
C (t) 4.42
D (dt) 6.16
E (dt) 5.96
F (qd) 2.63
G (s) 0.33
2.00
1.33
2.03
2.13
3.30
1.00
0.99
1.97
2.10
6.34
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
70000 65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000

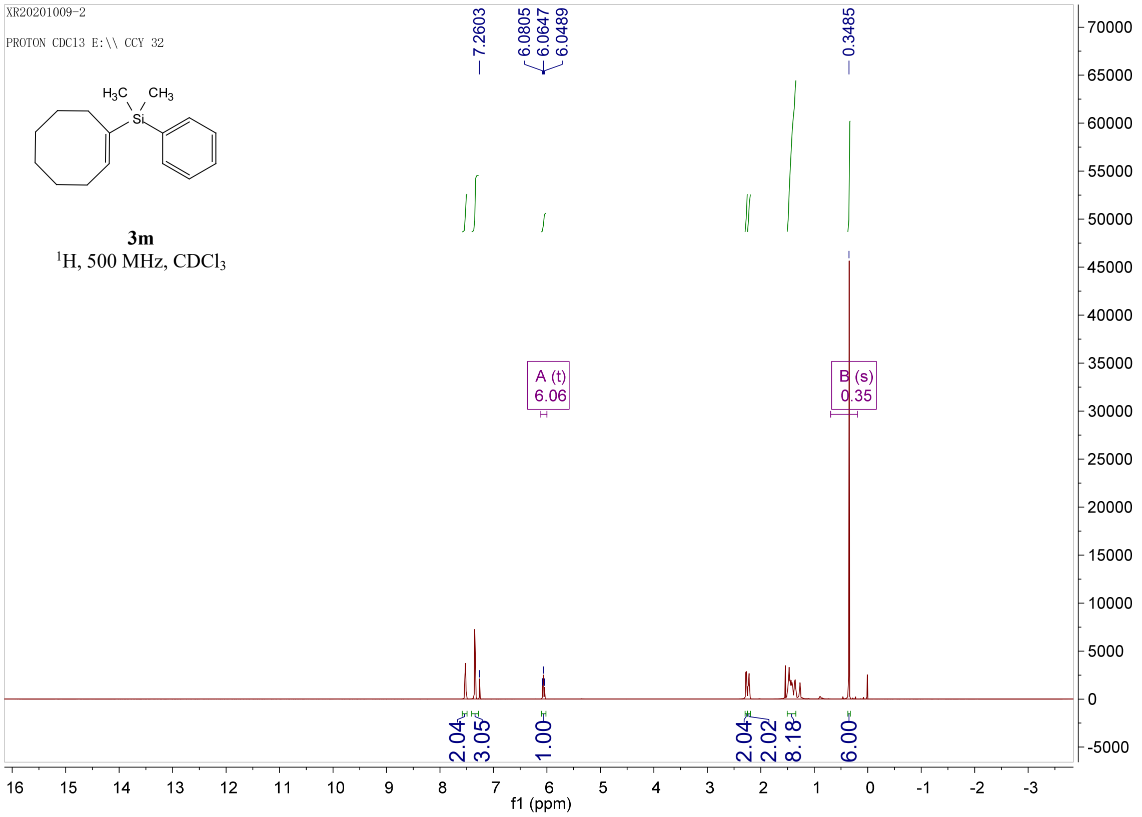

XR20201225-2
C13CPD CDCl3 E:\\ CCY 4
166.52
143.70
138.68
133.78
132.84
131.29
130.35
129.54
128.90
128.31
127.72
63.59
36.00
-2.65
H3C
CH3
Si
O
O
3j
13C, 126 MHz, CDCl3
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

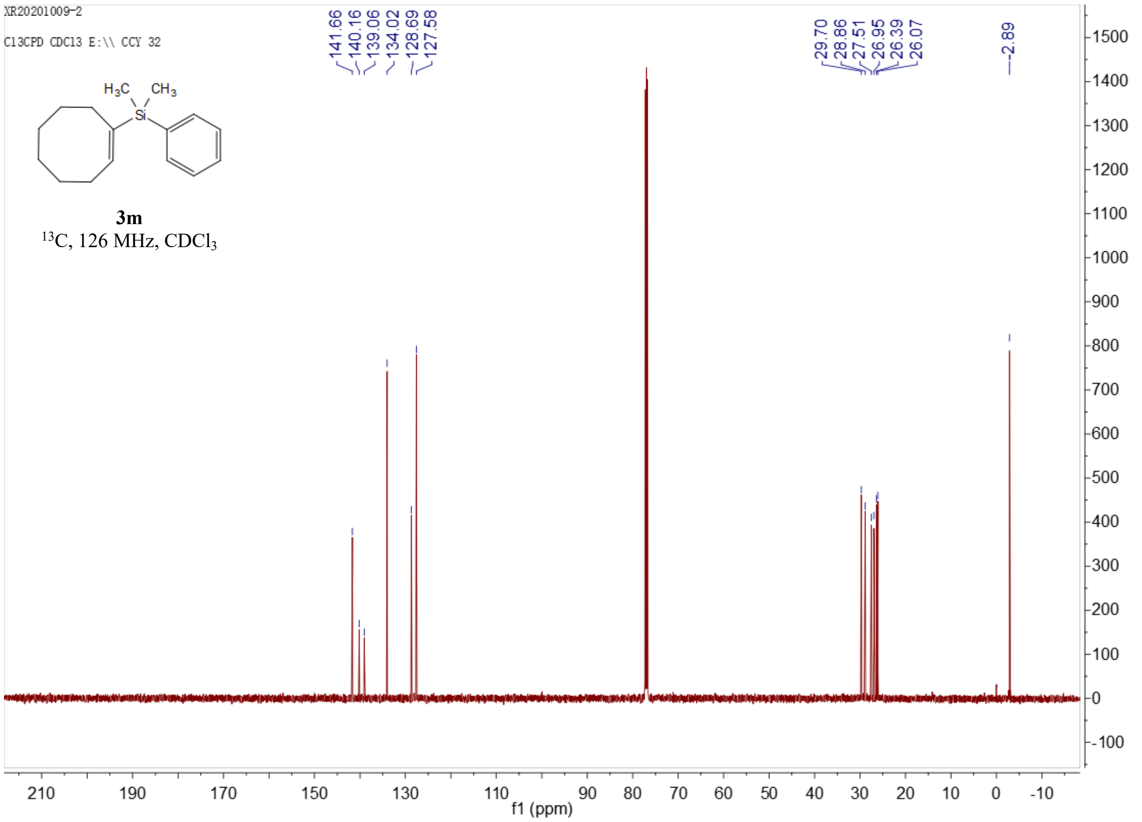

XR20201016-2
PROTON CDCl3 E:\\ CCY 22
8.7421
8.7251
8.3780
8.2496
8.2327
8.1909
8.1766
6.2313
6.1942
6.1817
6.0512
6.0140
4.6014
4.5881
4.5749
2.7535
2.7516
2.7405
2.7387
2.7277
2.7260
2.7148
2.7129
0.3401
O
O
N
H3C
CH3
Si
3k
1H, 500 MHz, CDCl3
D (d)
8.18
B (s)
8.38
F (d)
6.03
A (d)
8.73
E (dt)
6.21
G (t)
4.59
H (qd)
2.73
C (d)
8.24
0.99
1.00
1.01
2.01
1.06
1.07
2.19
3.17
3.40
1.00
1.00
2.09
2.07
6.18
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

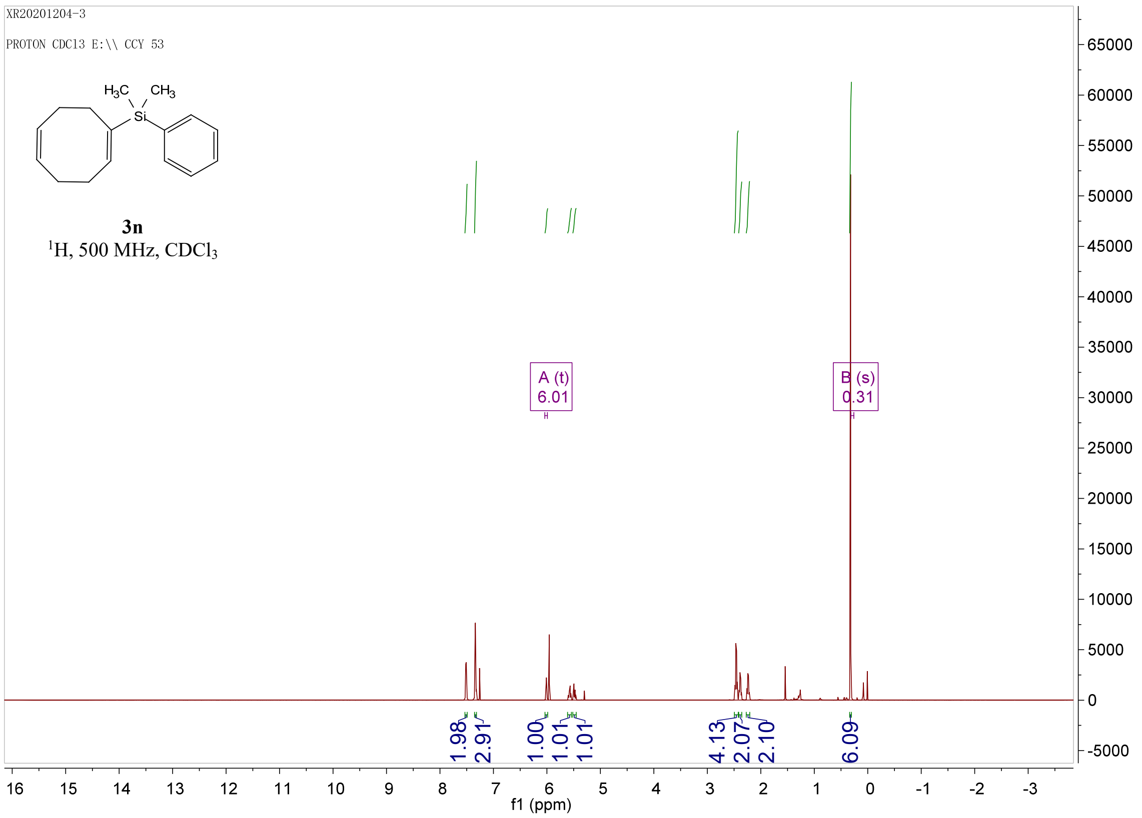

XR20201016-2
C13CPD CDCl3 E:\\ CCY 22
166.45
156.76
149.29
143.38
138.85
138.46
135.94
133.76
131.82
130.35
129.92
129.73
129.01
128.97
127.79
127.77
127.49
125.45
124.01
120.32
64.62
35.95
-2.57
O
O
N
H3C
CH3
Si
3k
13C, 126 MHz, CDCl3
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20200919-1
PROTON CDCl3 E:\\ CCY 53
H3C CH3
Si
3l
1H, 500 MHz, CDCl3
0.31
A (s)
0.31
DCM
2.02
2.97
1.00
4.19
4.18
6.06
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
45000 40000 35000 30000 25000 20000 15000 10000 5000 0


XR20210403-CH
C13CPD CDCl3 E:\\ CCY 33
138.84
137.89
136.68
133.95
128.71
127.63
77.25
77.00
76.75
26.89
26.80
22.90
22.38
-3.62
H3C CH3
Si
3l
13C, 126 MHz, CDCl3
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

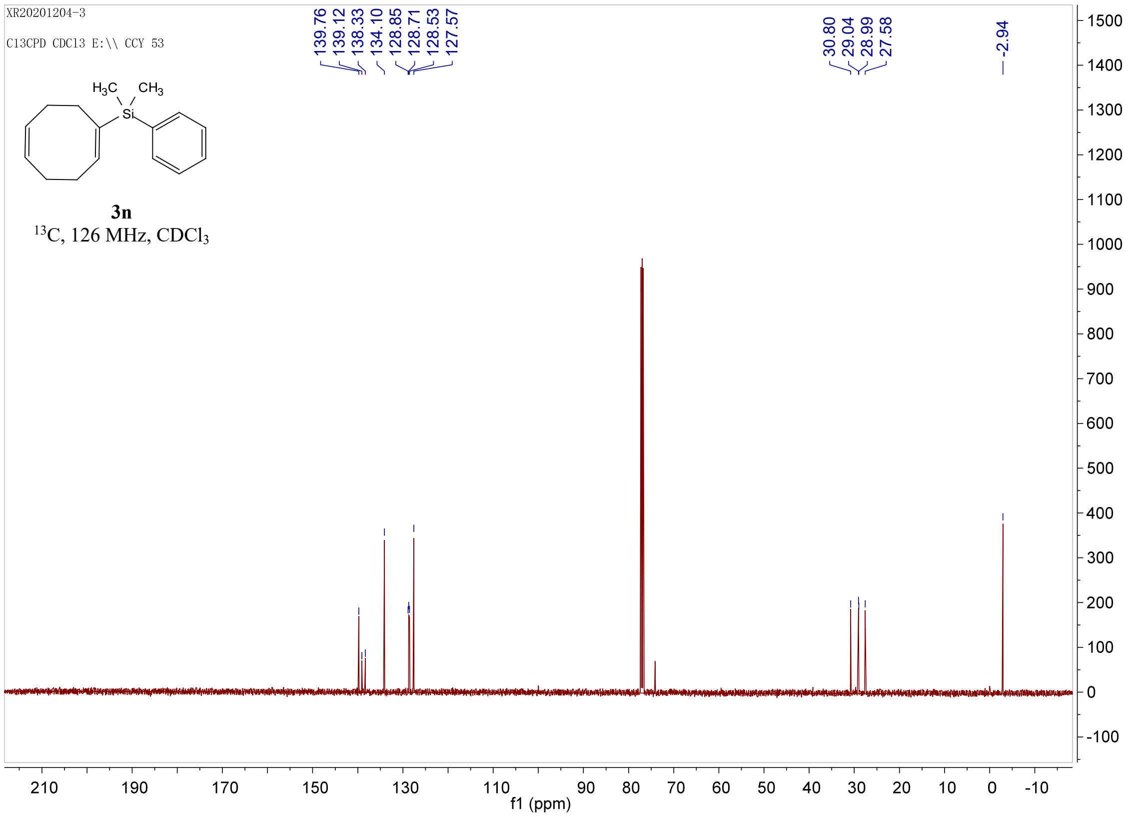

XR20201009-2
PROTON CDCl3 E:\\ CCY 32
3m
^{1}H, 500 MHz, CDCl$_3$
7.2603
6.0805
6.0647
6.0489
0.3485
A (t)
6.06
B (s)
0.35
2.04
3.05
1.00
2.04
2.02
8.18
6.00
f1 (ppm)


XR20201009-2
C13CPD CDCl3 E:\\ CCY 32
3m
^{13}C, 126 MHz, CDCl$_3$
141.66
140.16
139.06
134.02
128.69
127.58
29.70
28.86
27.51
26.95
26.39
26.07
-2.89
f1 (ppm)



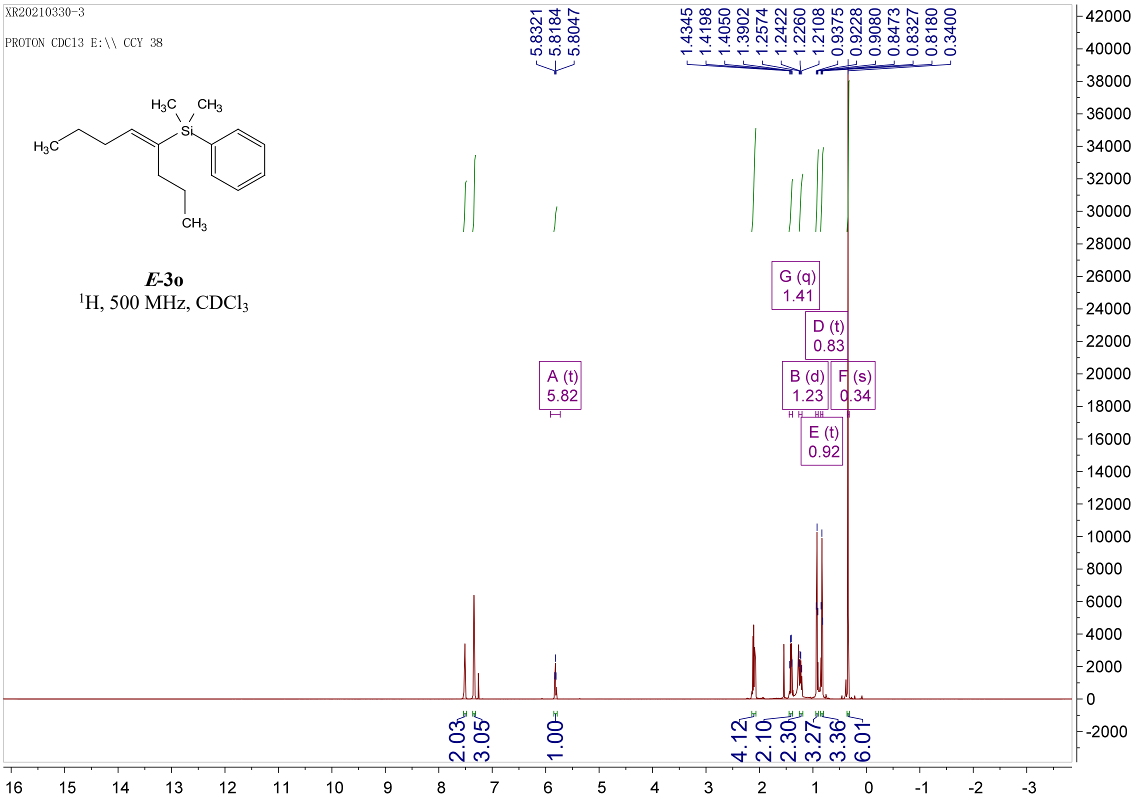
3n

^{1}H, 500 MHz, CDCl$_3$



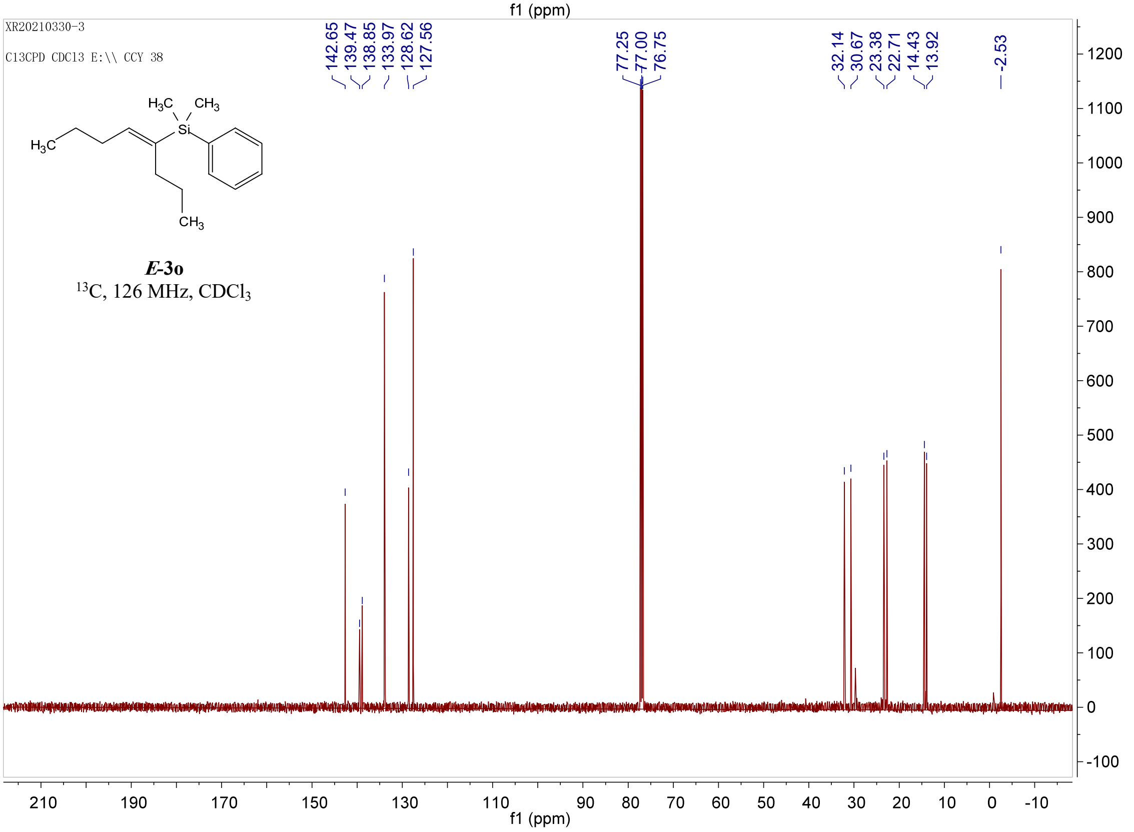
3n

^{13}C, 126 MHz, CDCl$_3$



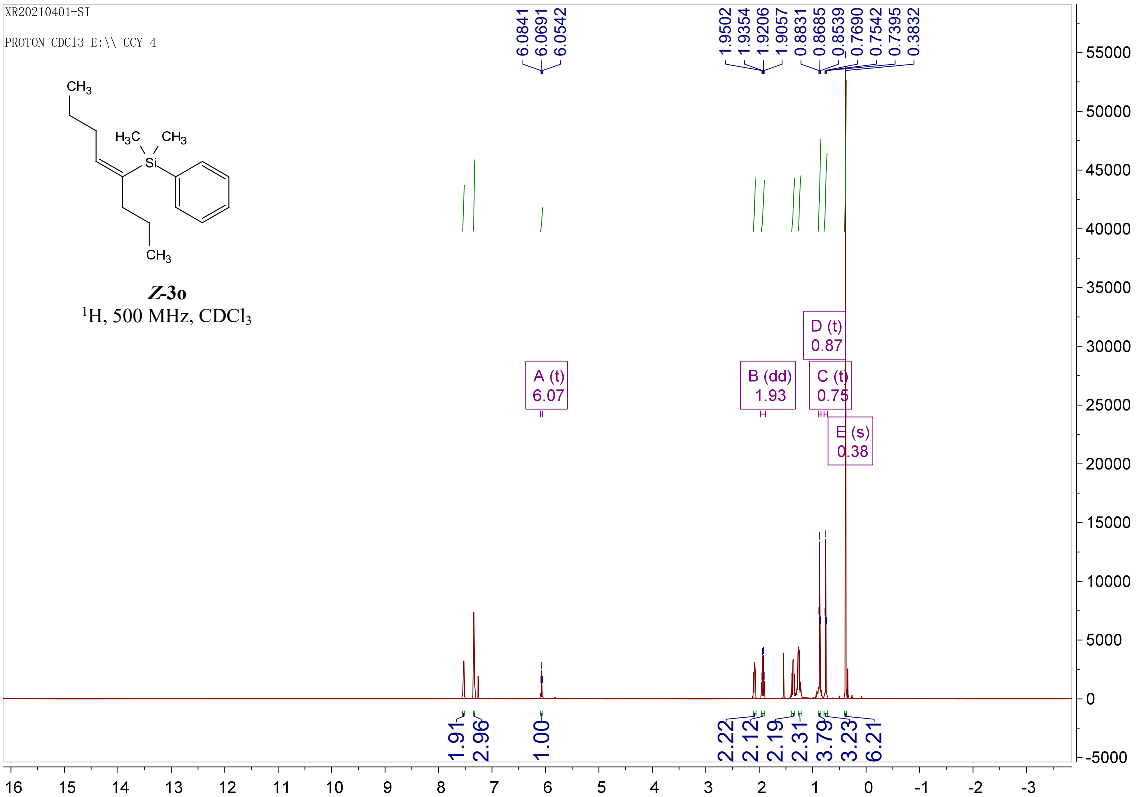
***E*-3o**

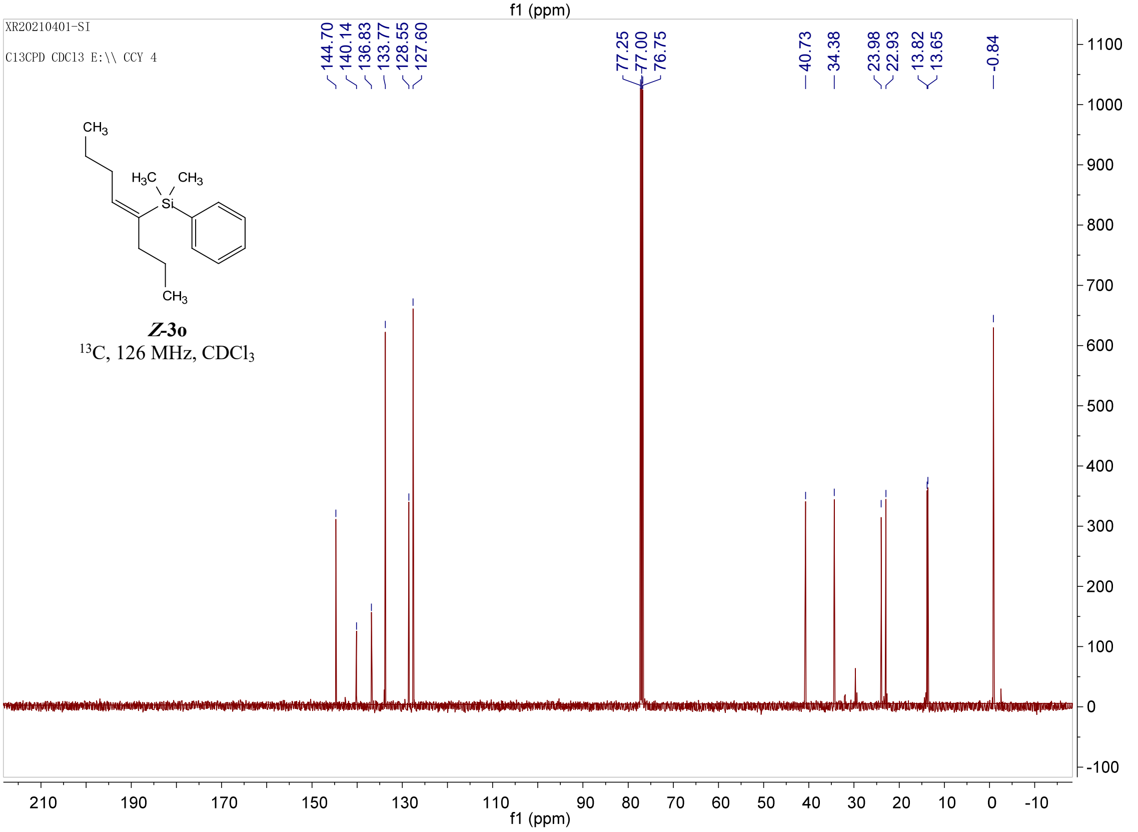
^1H, 500 MHz, $CDCl_3$

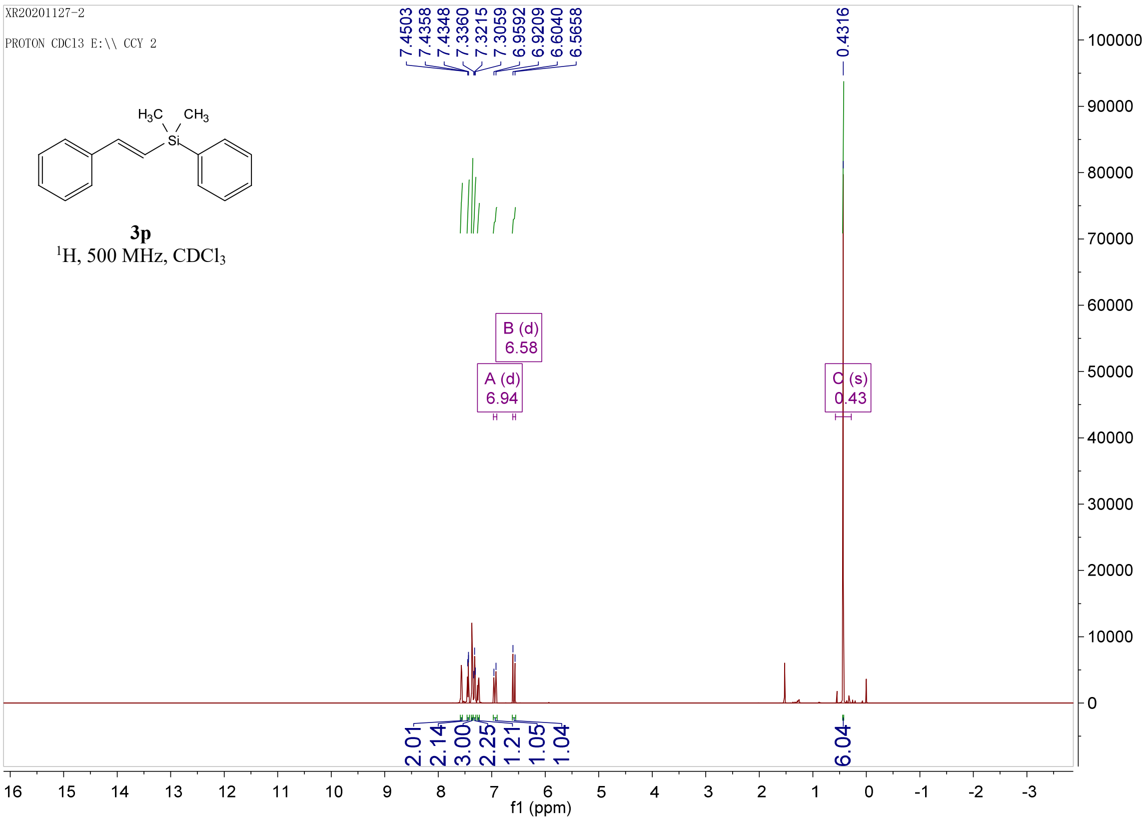


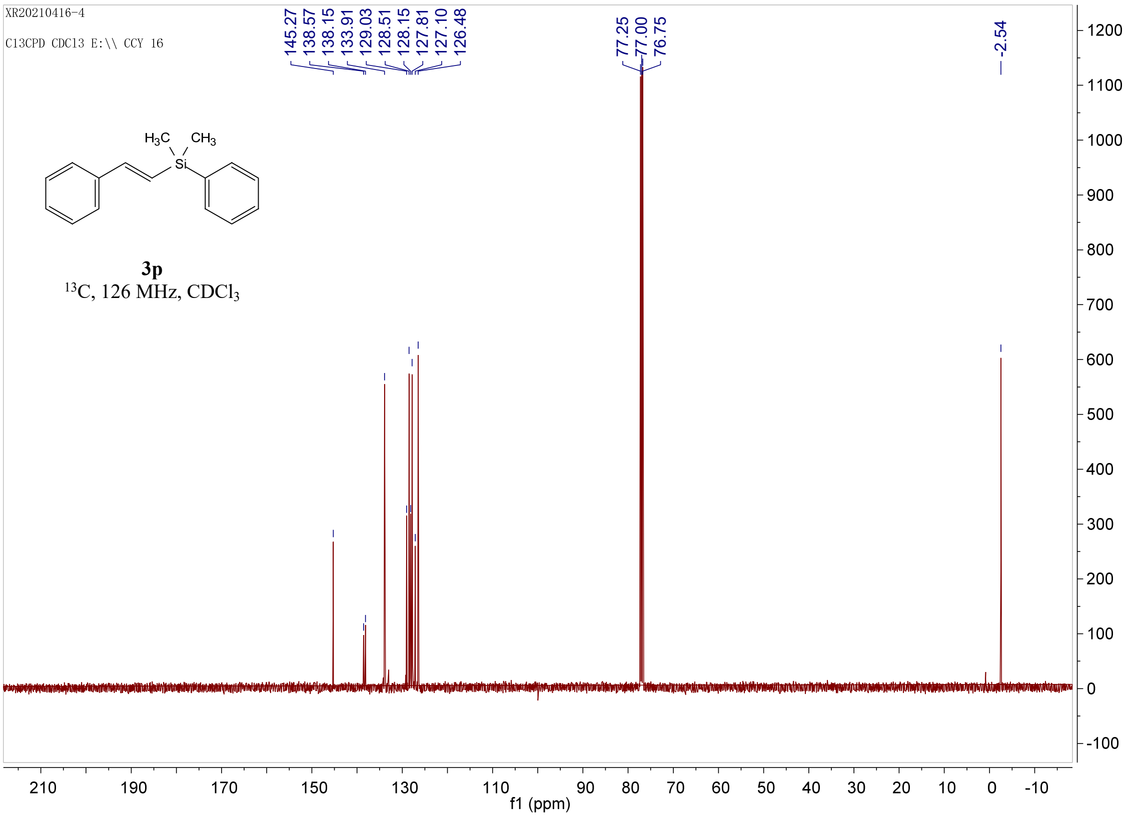
***E*-3o**

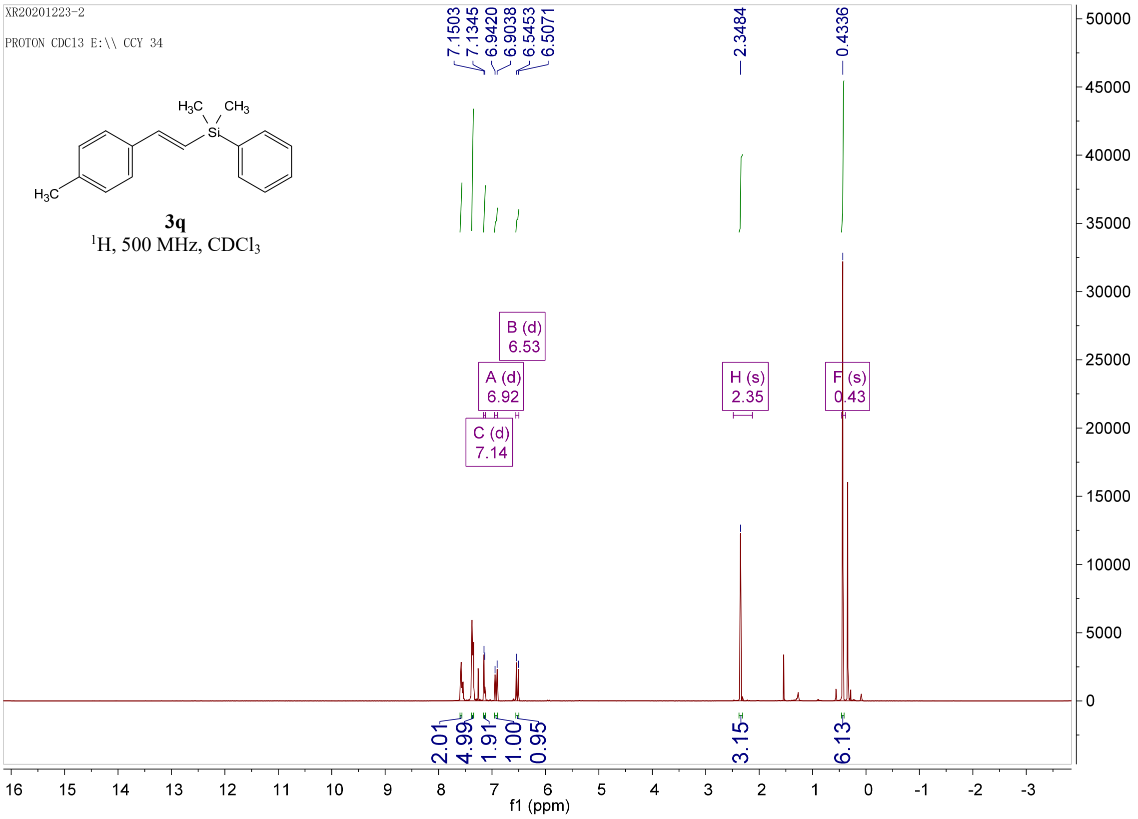
^{13}C, 126 MHz, $CDCl_3$


XR20210401-SI
PROTON CDCl3 E:\\ CCY 4
CH3
H3C
CH3
Si
CH3
Z-3o
1H, 500 MHz, CDCl3
6.0841
6.0691
6.0542
1.9502
1.9354
1.9206
1.9057
0.8831
0.8685
0.8539
0.7690
0.7542
0.7395
0.3832
A (t)
6.07
B (dd)
1.93
C (t)
0.75
D (t)
0.87
E (s)
0.38
1.91
2.96
1.00
2.22
2.12
2.19
2.31
3.79
3.23
6.21
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

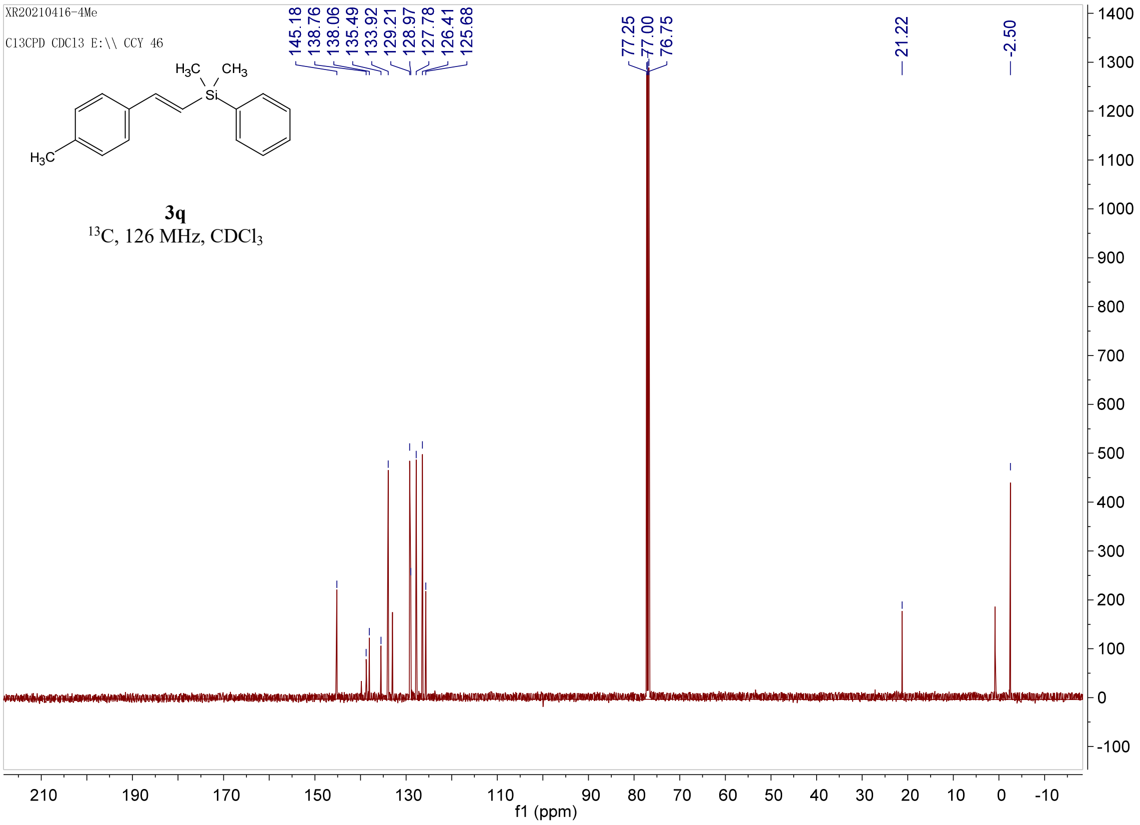

XR20210401-SI
C13CPD CDCl3 E:\\ CCY 4
CH3
H3C
CH3
Si
CH3
Z-3o
13C, 126 MHz, CDCl3
144.70
140.14
136.83
133.77
128.55
127.60
77.25
77.00
76.75
40.73
34.38
23.98
22.93
13.82
13.65
-0.84
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20201127-2
PROTON CDCl3 E:\\ CCY 2
7.4503
7.4358
7.4348
7.3360
7.3215
7.3059
6.9592
6.9209
6.6040
6.5658
0.4316
H_3C
CH_3
Si
3p
^1H, 500 MHz, $CDCl_3$
B (d)
6.58
A (d)
6.94
C (s)
0.43
2.01
2.14
3.00
2.25
1.21
1.05
1.04
6.04
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

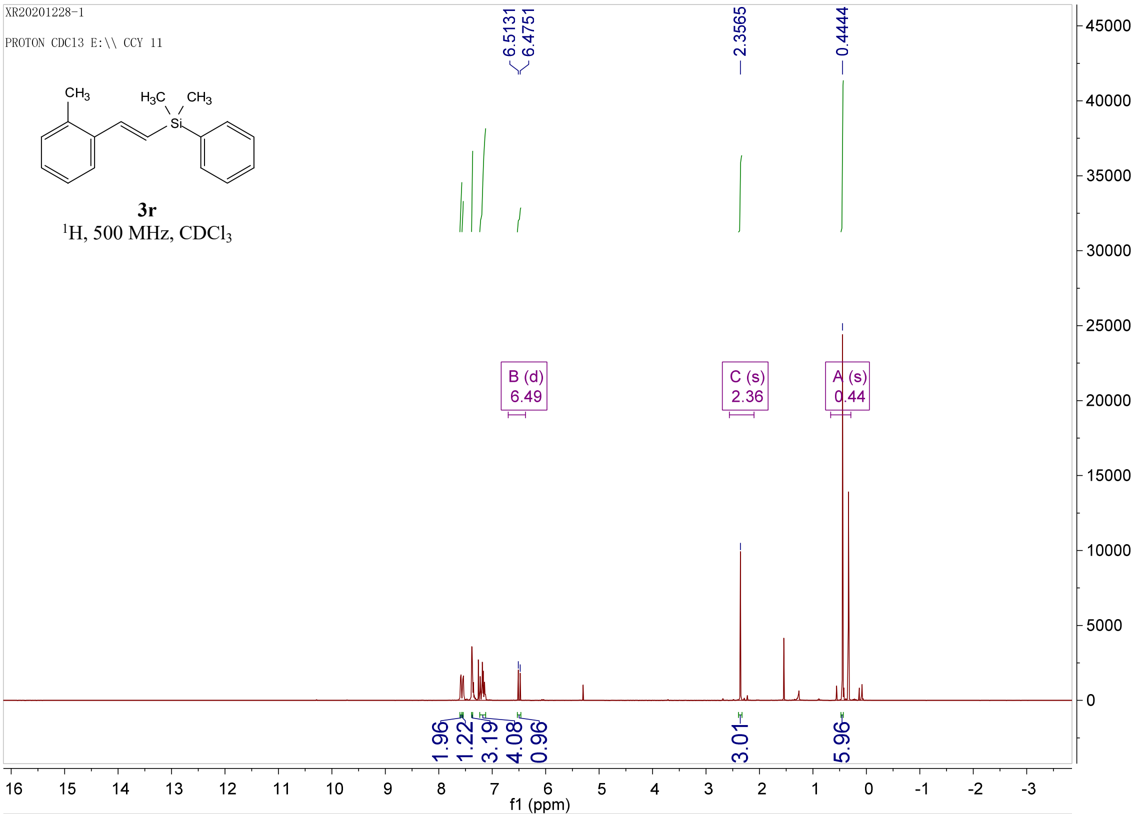

XR20210416-4
C13CPD CDCl3 E:\\ CCY 16
145.27
138.57
138.15
133.91
129.03
128.51
128.15
127.81
127.10
126.48
77.25
77.00
76.75
-2.54
H_3C
CH_3
Si
3p
^{13}C, 126 MHz, $CDCl_3$
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

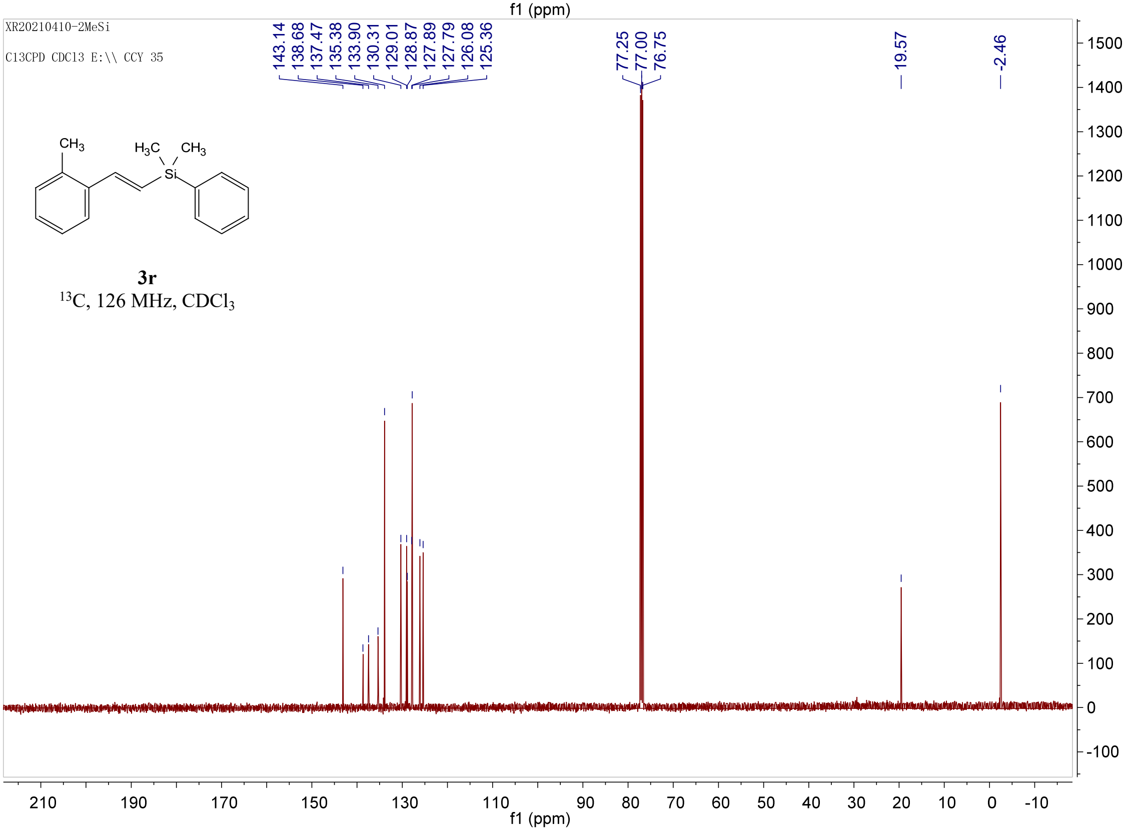

3q

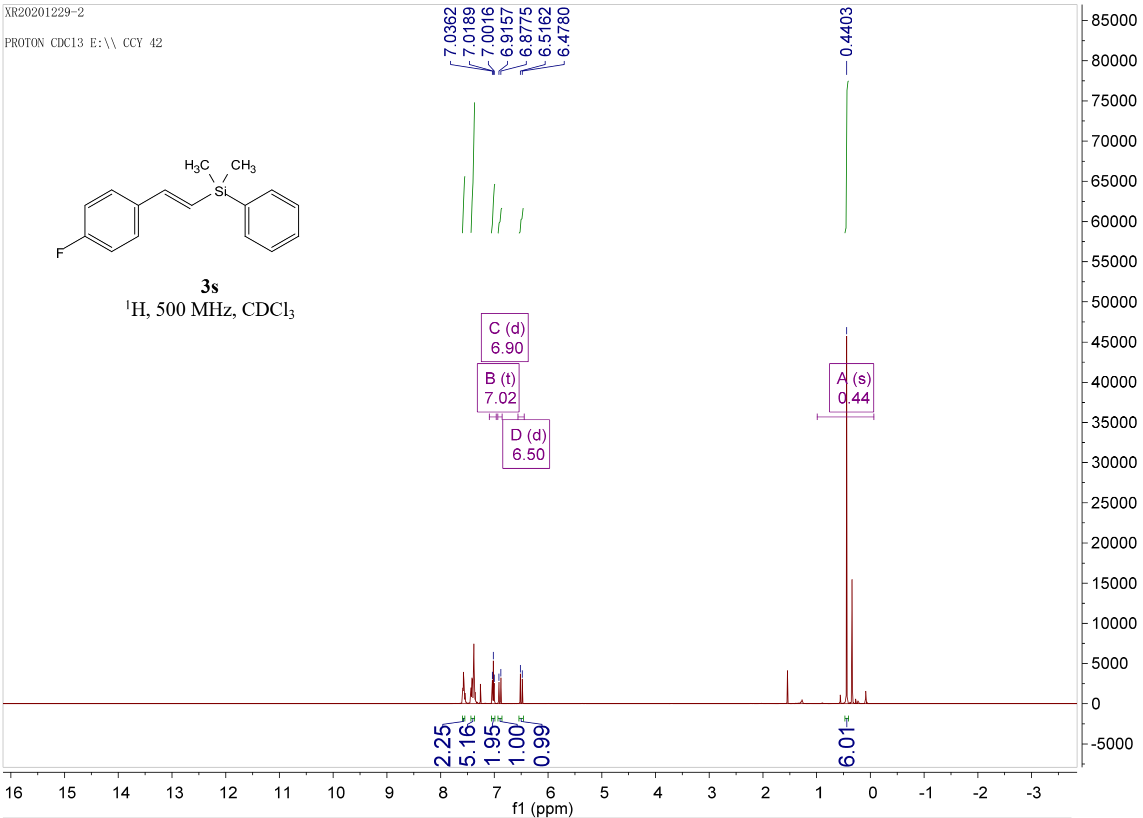
^{1}H, 500 MHz, CDCl$_3$


3q

^{13}C, 126 MHz, CDCl$_3$

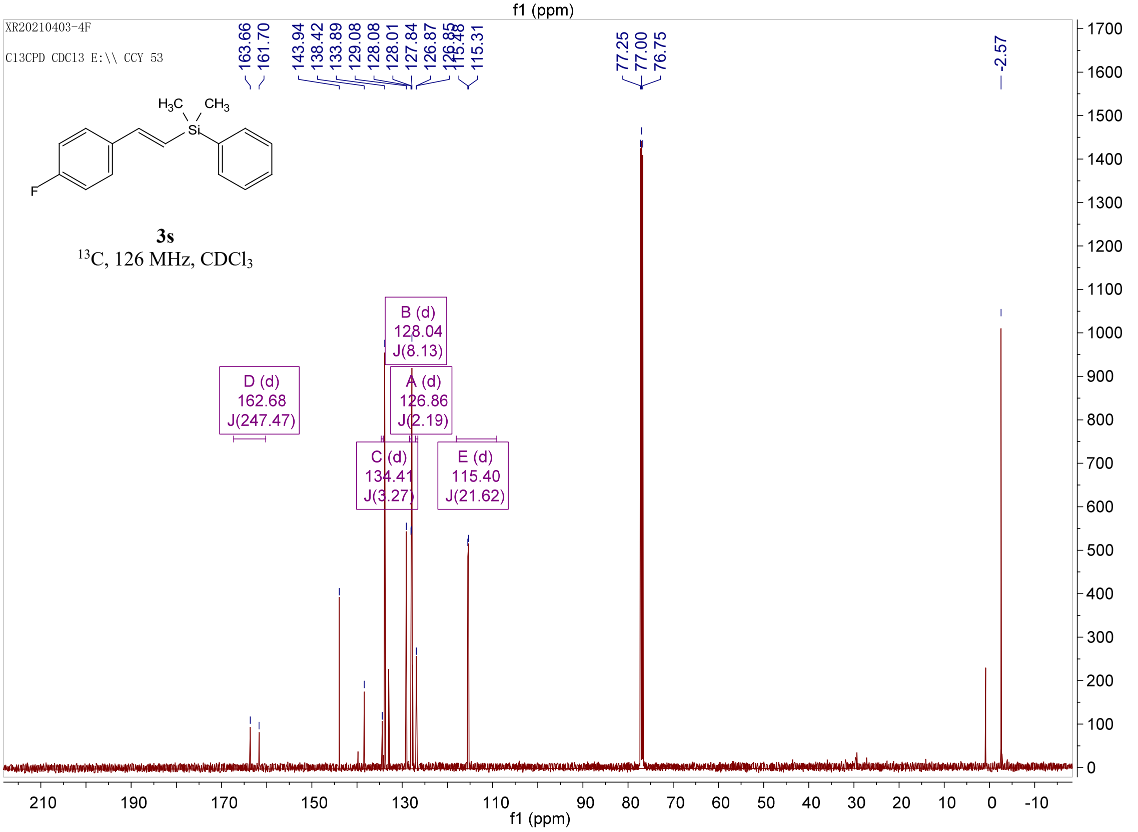

XR20201228-1
PROTON CDCl3 E:\\ CCY 11
6.5131
6.4751
2.3565
0.4444
CH3
H3C
CH3
Si
3r
¹H, 500 MHz, CDCl₃
B (d)
6.49
C (s)
2.36
A (s)
0.44
1.96
1.22
3.19
4.08
0.96
3.01
5.96
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


XR20210410-2MeSi
C13CPD CDCl3 E:\\ CCY 35
143.14
138.68
137.47
135.38
133.90
130.31
129.01
128.87
127.89
127.79
126.08
125.36
77.25
77.00
76.75
19.57
-2.46
CH3
H3C
CH3
Si
3r
¹³C, 126 MHz, CDCl₃
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



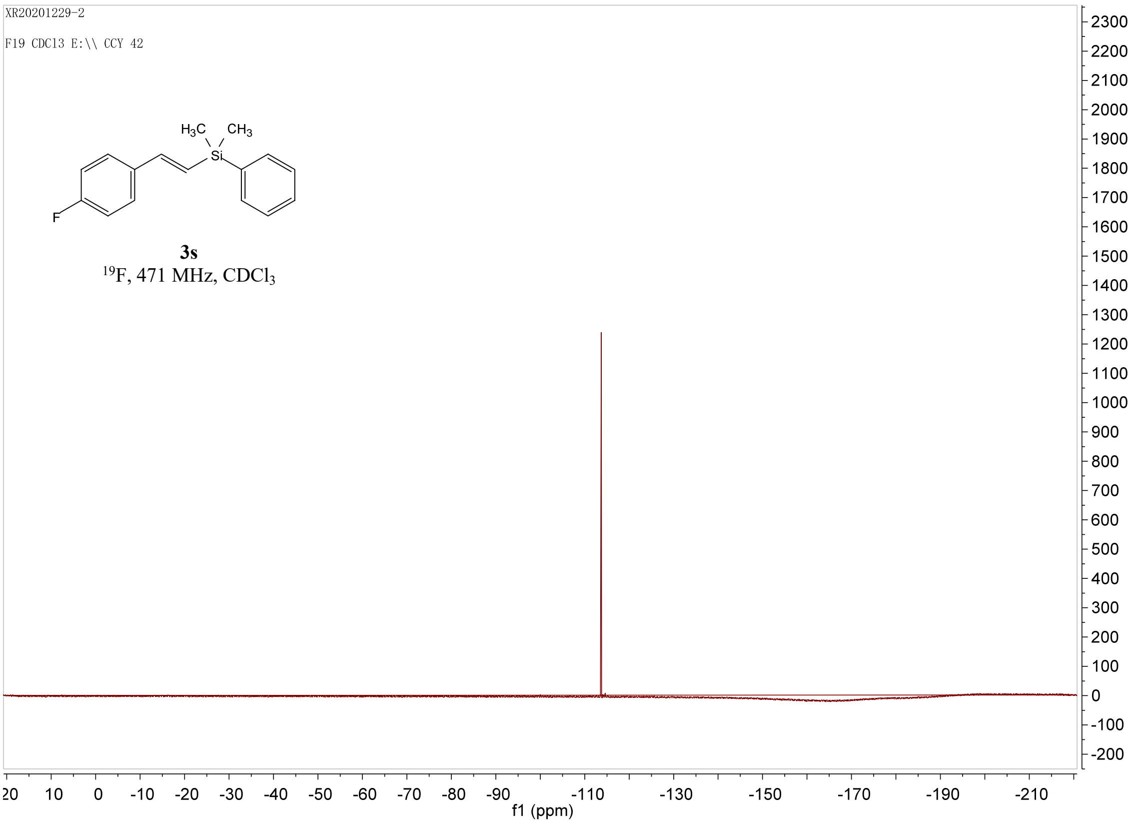
3s

^{1}H, 500 MHz, CDCl$_3$



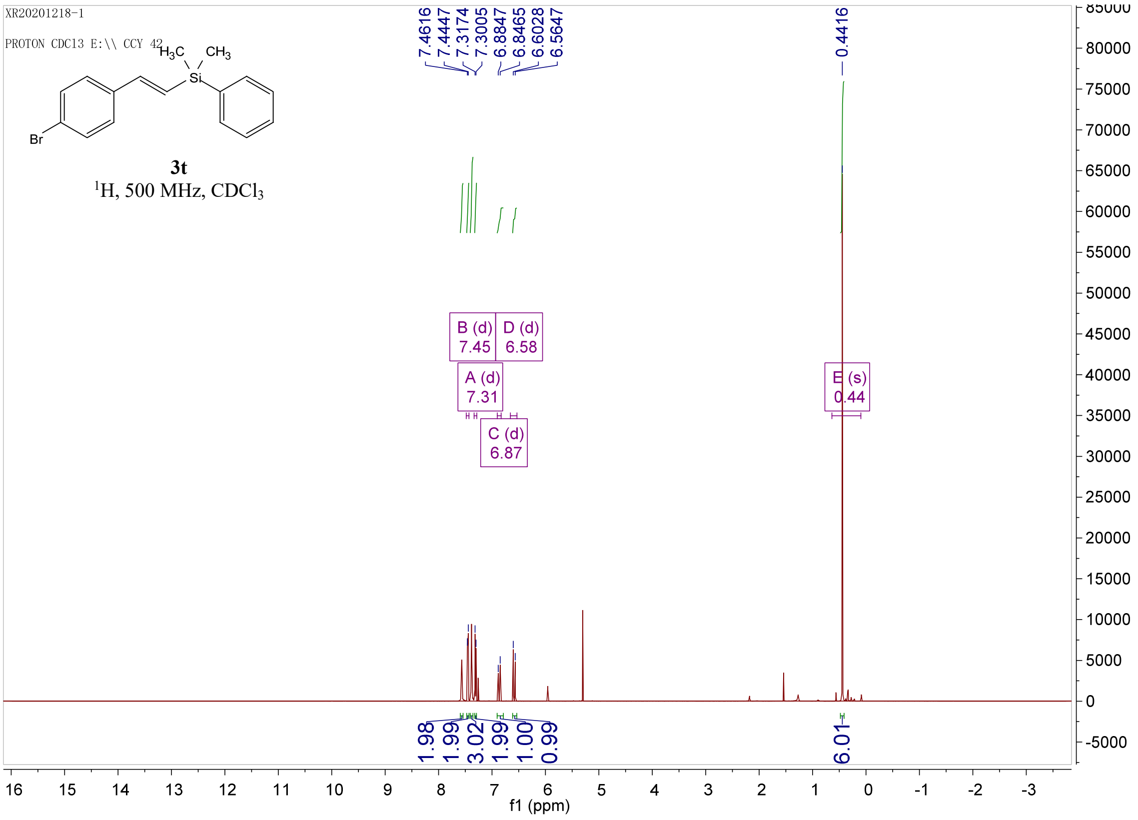
3s

^{13}C, 126 MHz, CDCl$_3$



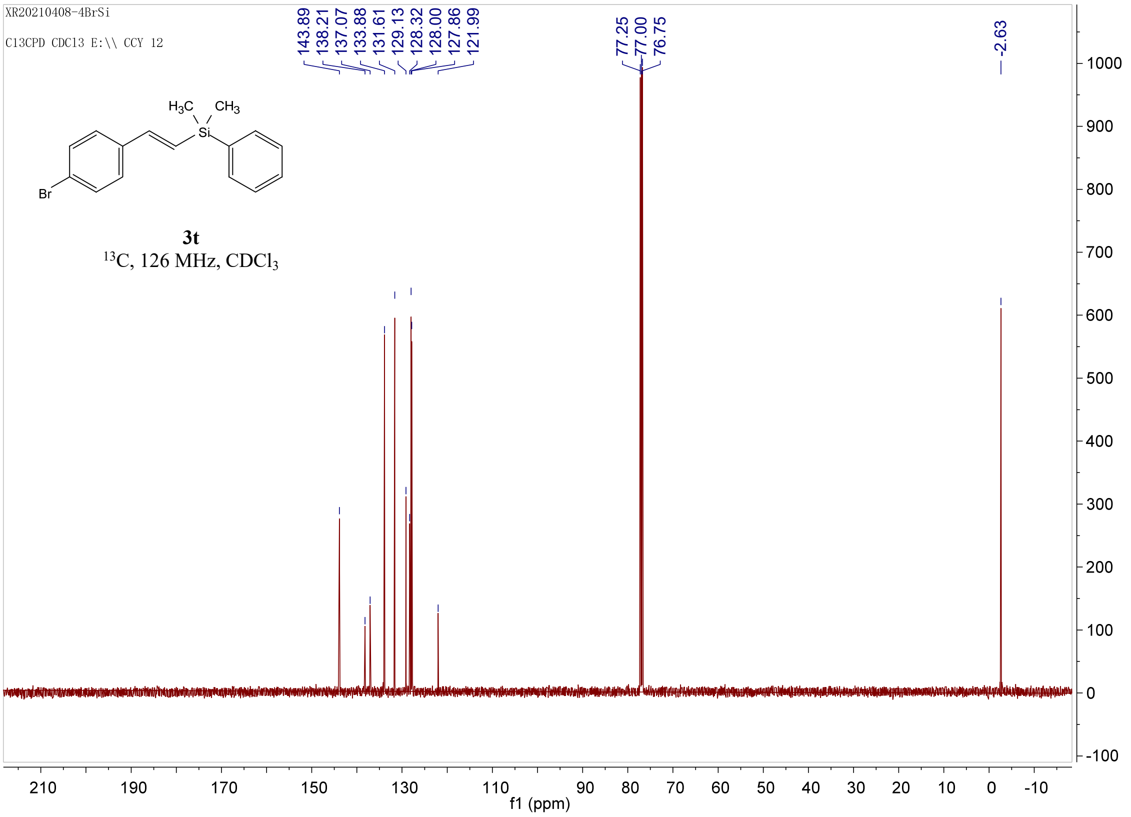
3s

^{19}F, 471 MHz, CDCl$_3$

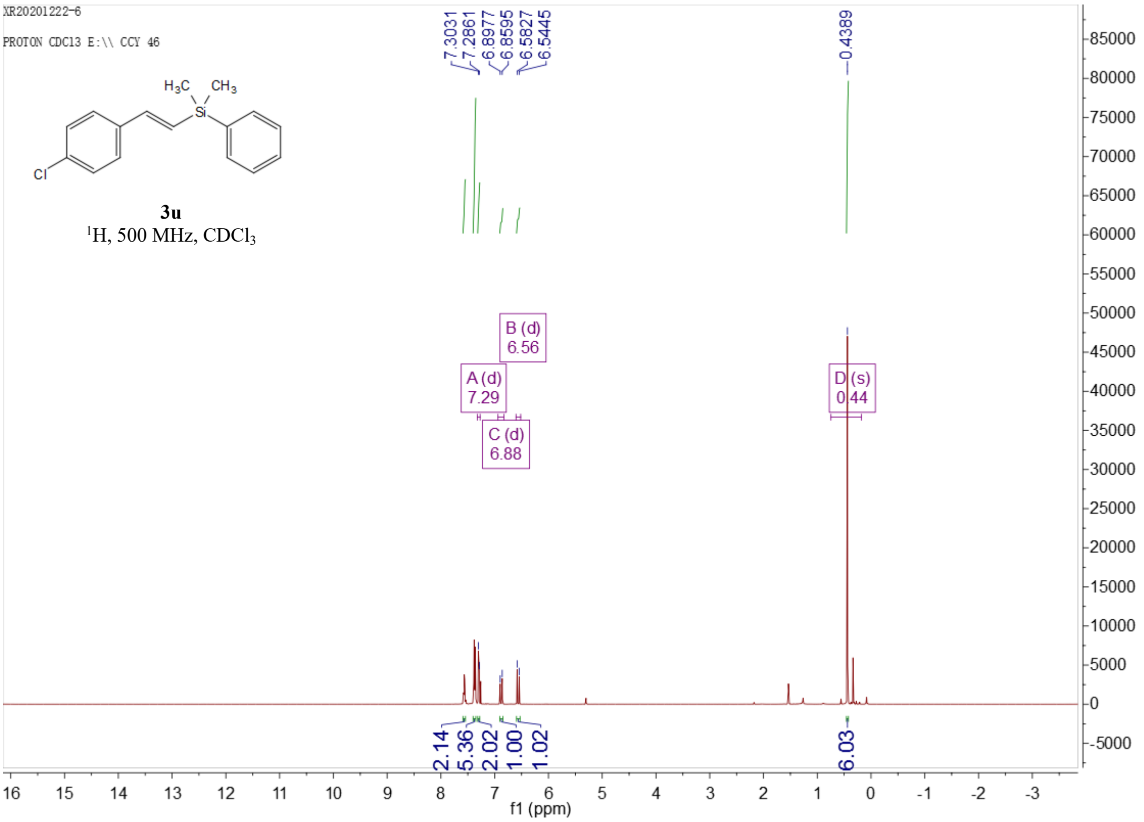


3t

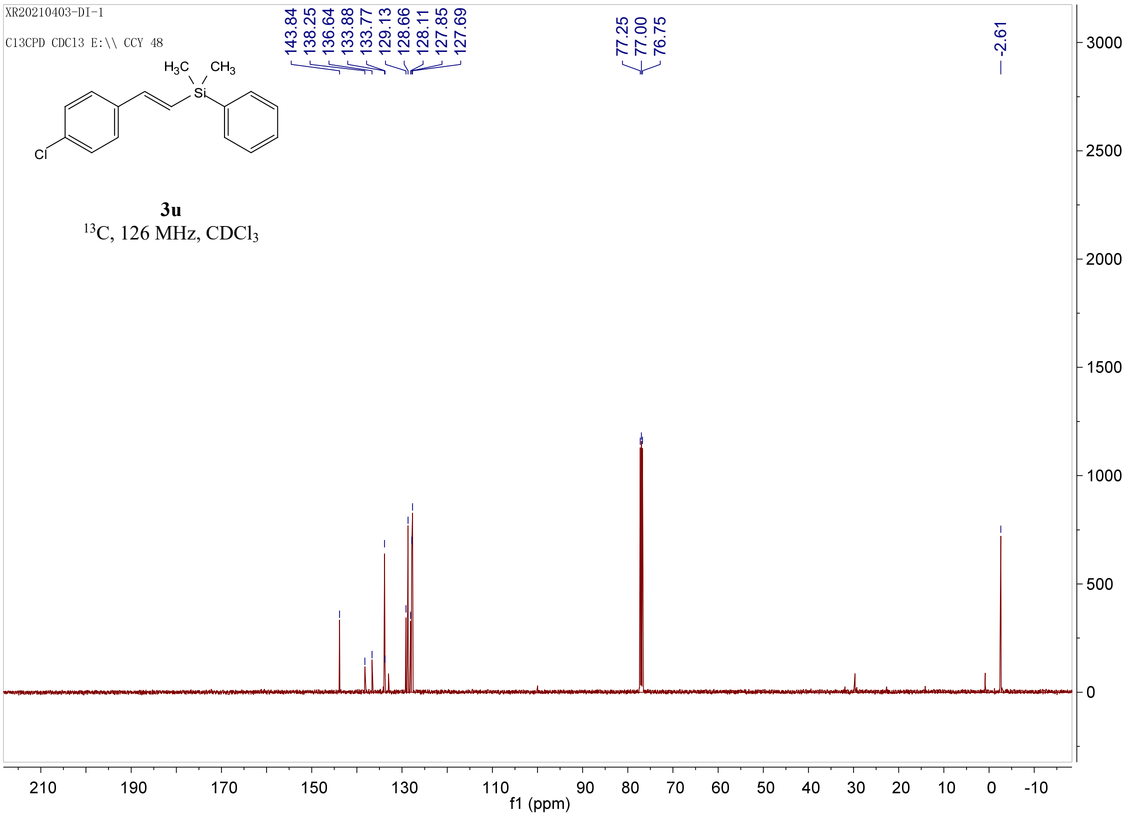
^{1}H, 500 MHz, CDCl$_3$



3t
^{13}C, 126 MHz, CDCl$_3$

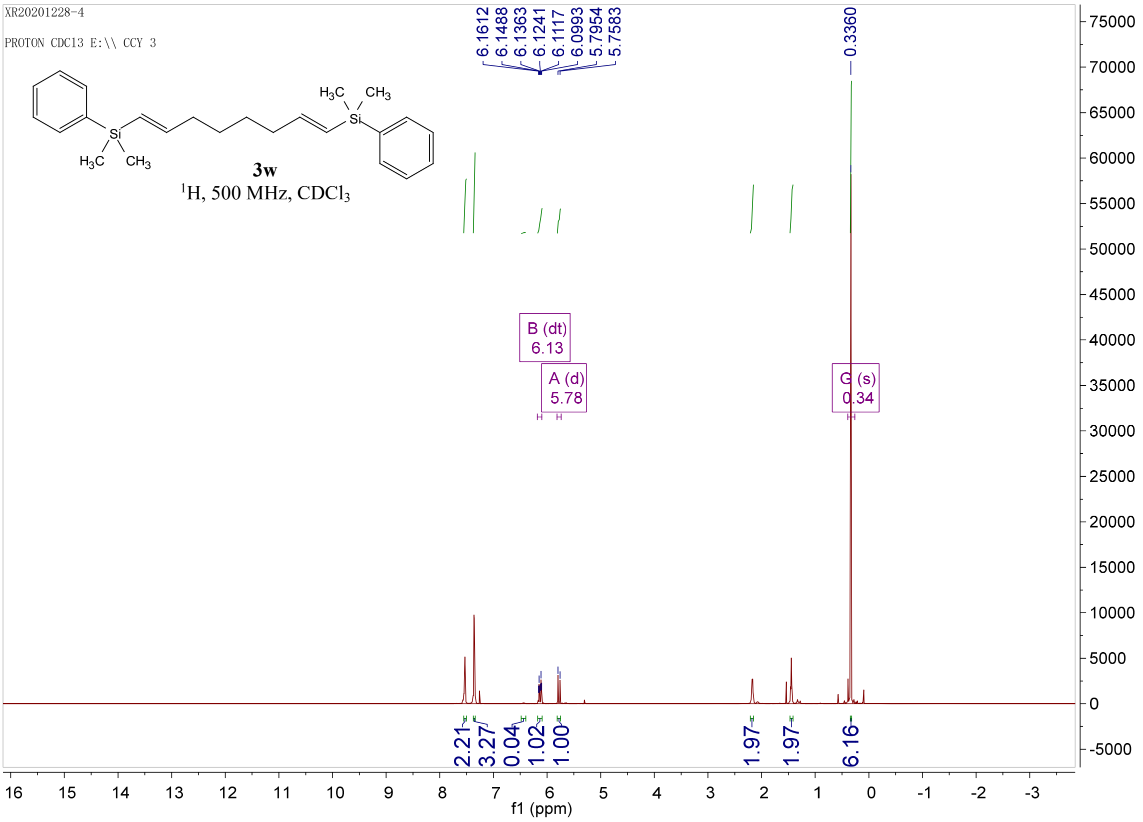


3u
^{1}H, 500 MHz, CDCl$_3$



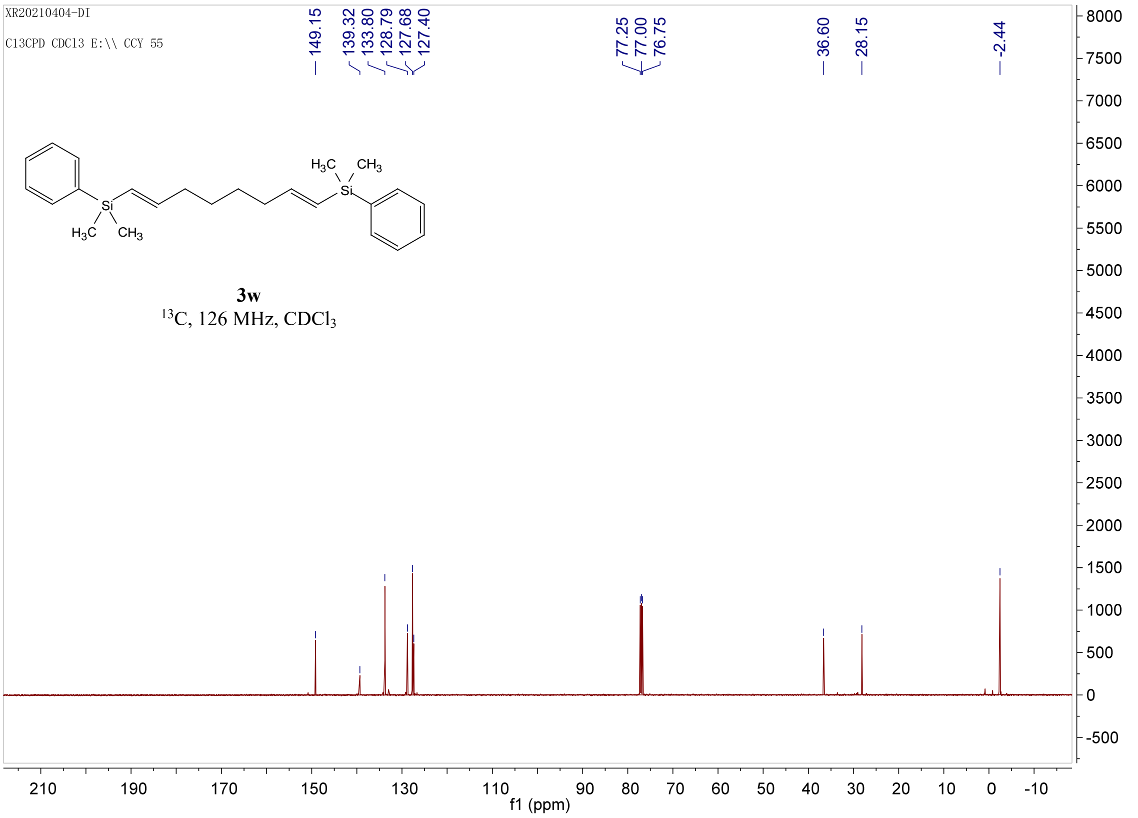
3u

^{13}C, 126 MHz, $CDCl_3$



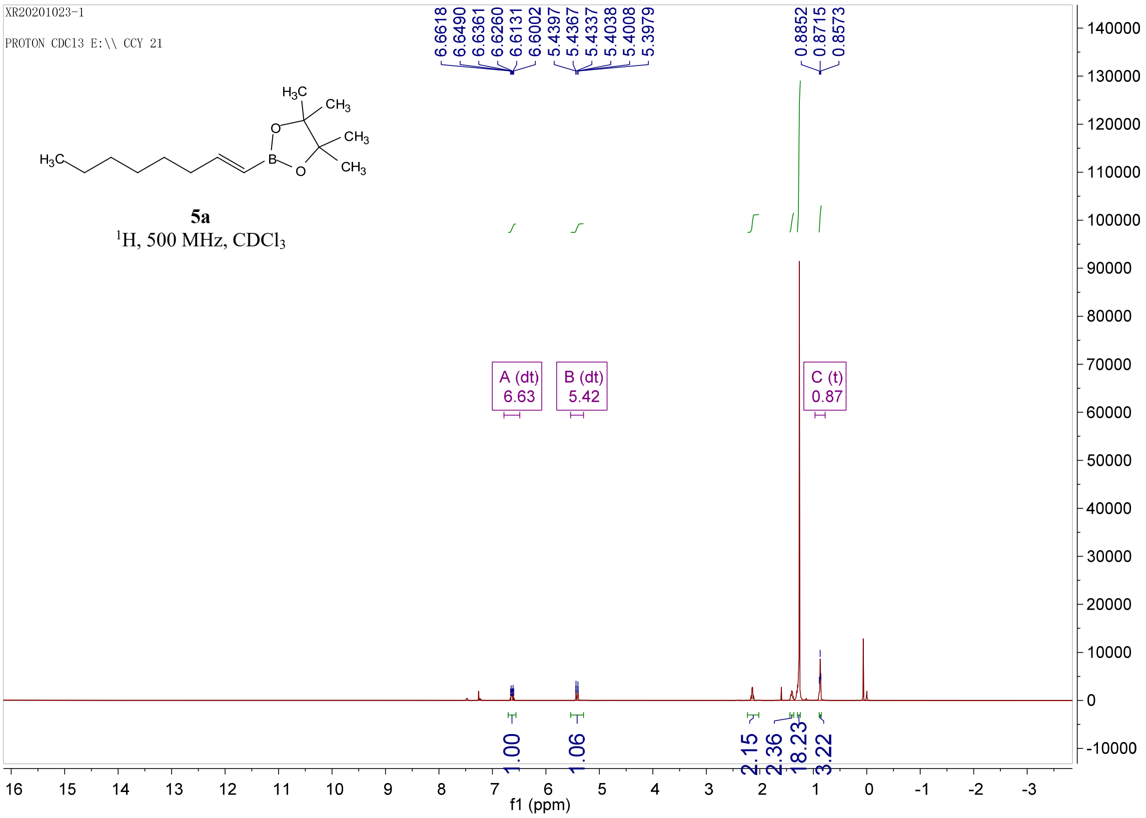
3w

^{1}H, 500 MHz, $CDCl_3$



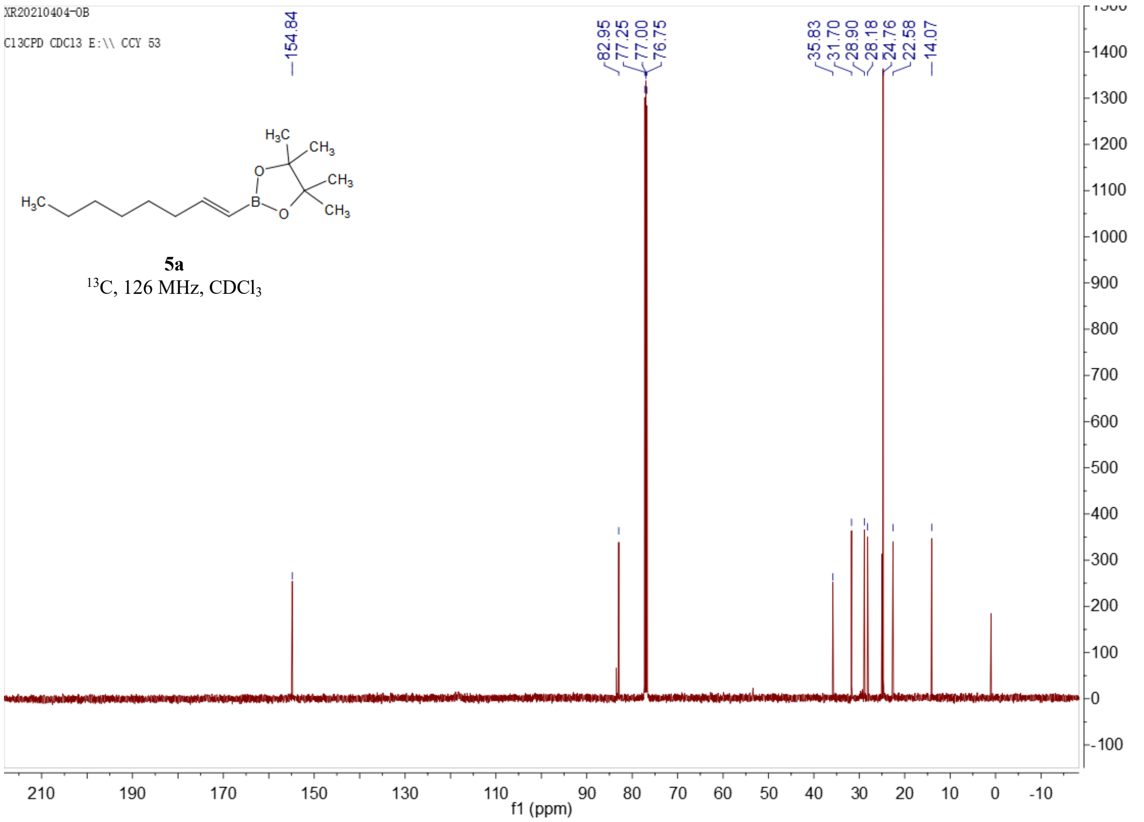
3w

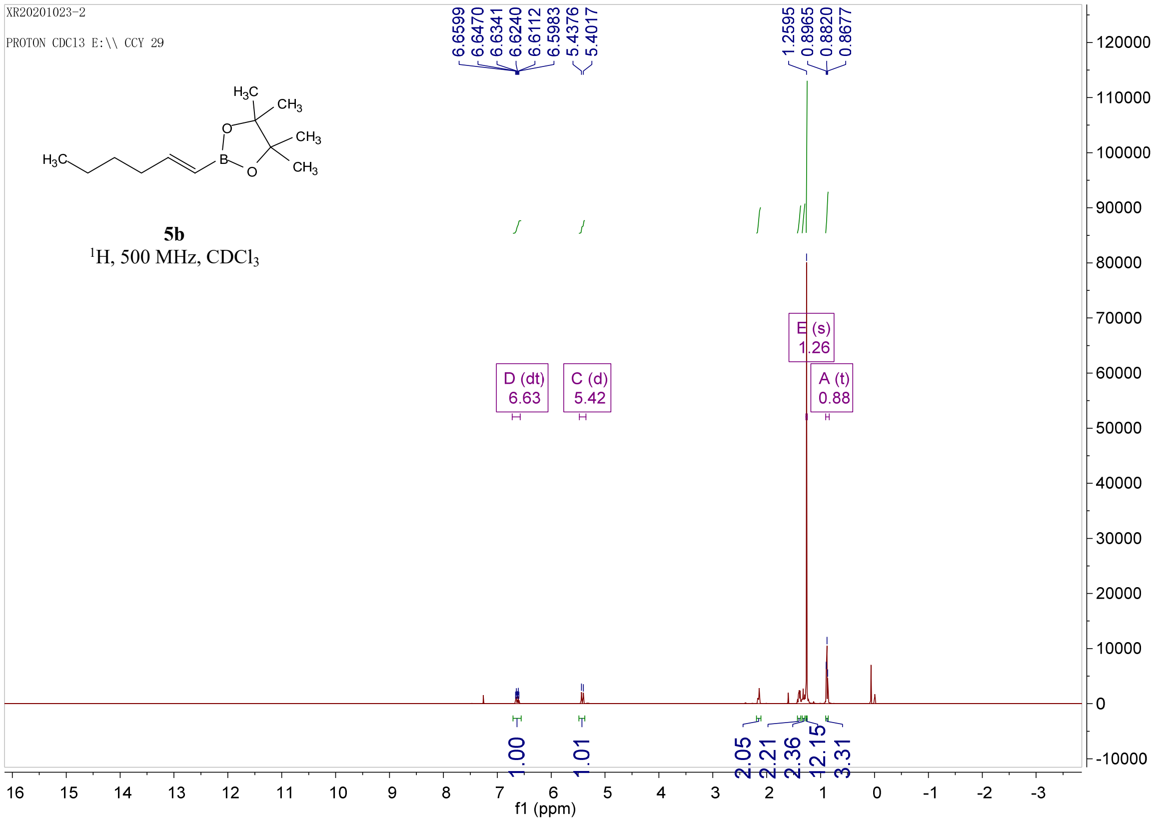
^{13}C, 126 MHz, CDCl$_3$

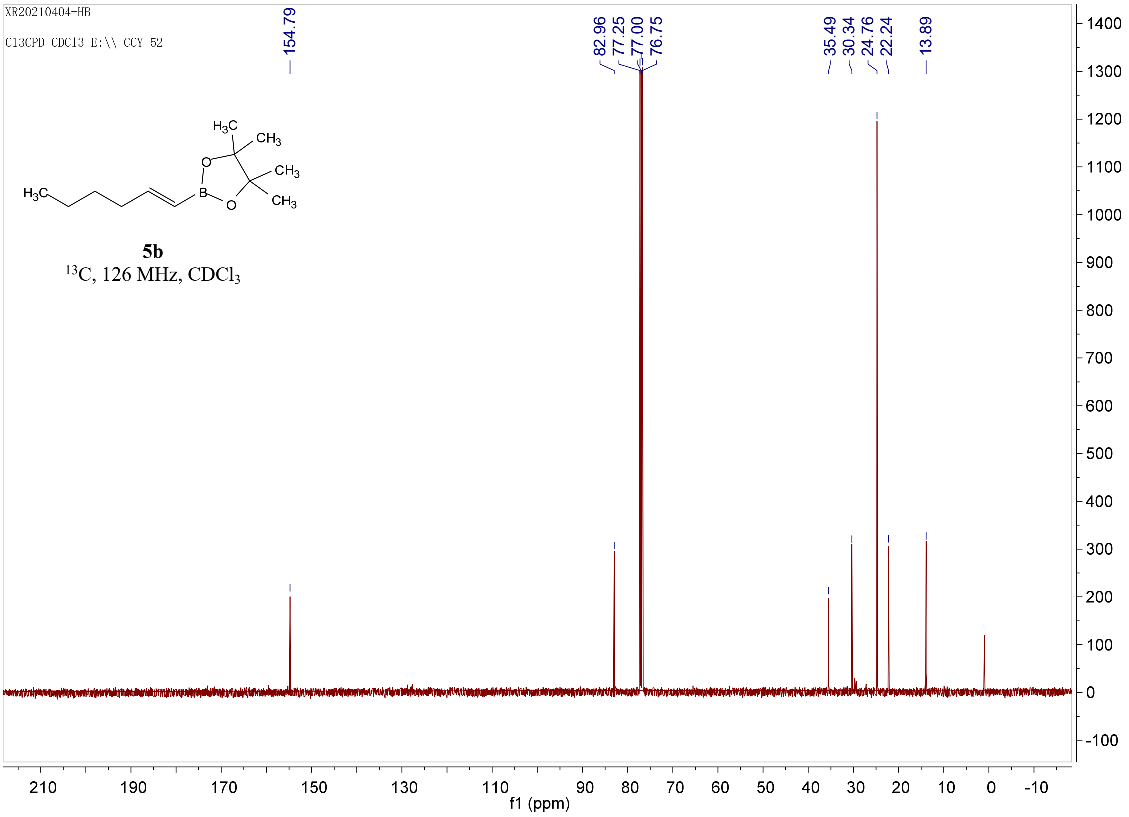


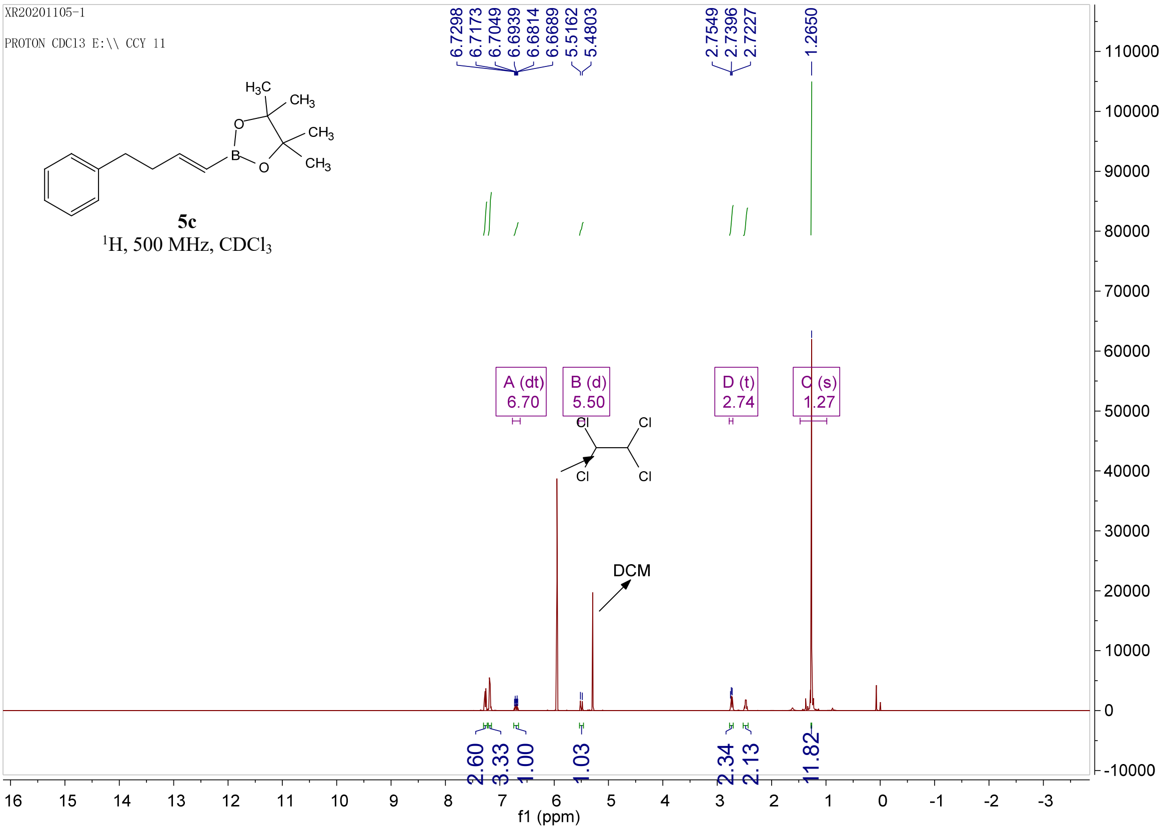
5a

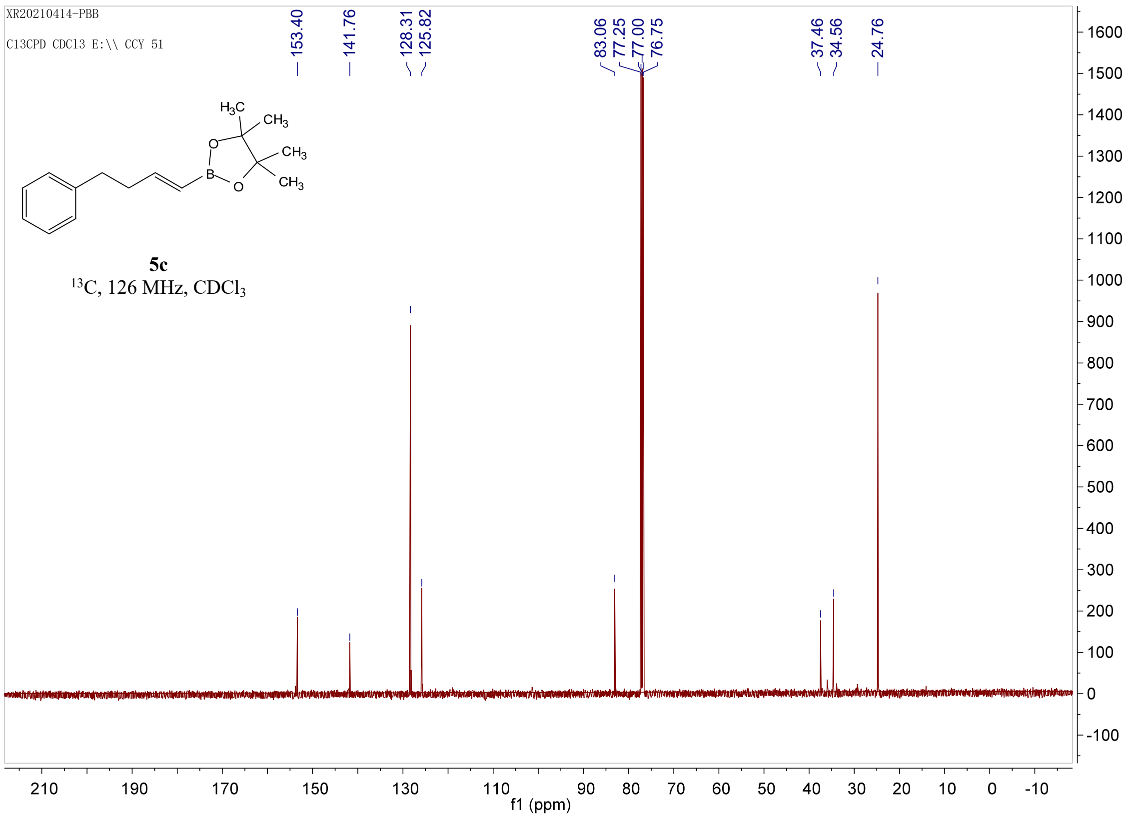
^{1}H, 500 MHz, CDCl$_3$


XR20210404-0B
C13CPD CDCl3 E:\\ CCY 53
154.84
82.95
77.25
77.00
76.75
35.83
31.70
28.90
28.18
24.76
22.58
14.07
H3C
CH3
CH3
CH3
O
O
B
H3C
5a
13C, 126 MHz, CDCl3
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20201023-2
PROTON CDCl3 E:\\ CCY 29
6.6599
6.6470
6.6341
6.6240
6.6112
6.5983
5.4376
5.4017
1.2595
0.8965
0.8820
0.8677
H3C
CH3
CH3
CH3
O
O
B
H3C
5b
1H, 500 MHz, CDCl3
E (s)
1.26
D (dt)
6.63
C (d)
5.42
A (t)
0.88
1.00
1.01
2.05
2.21
2.36
12.15
3.31
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

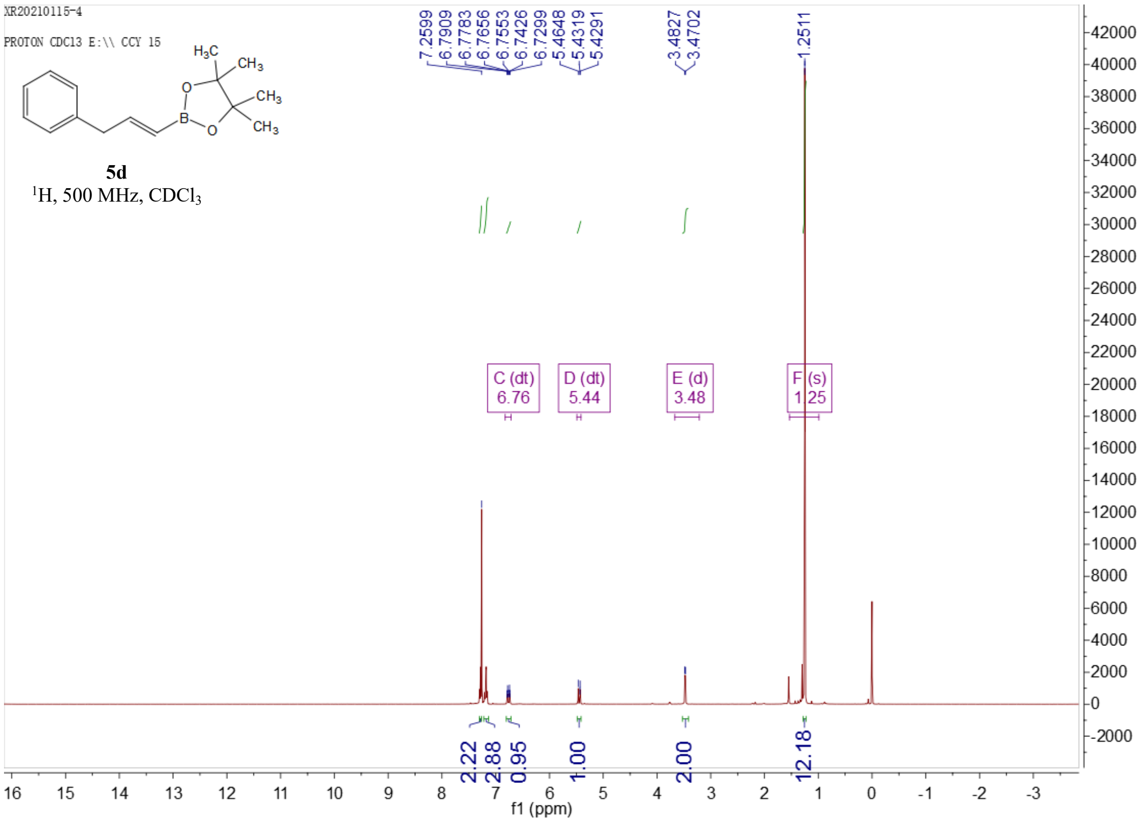

XR20210404-HB
C13CPD CDCl3 E:\\ CCY 52
154.79
82.96
77.25
77.00
76.75
35.49
30.34
24.76
22.24
13.89
5b
13C, 126 MHz, CDCl3
H3C
CH3
CH3
CH3
O
B
O
H3C
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


XR20201105-1
PROTON CDCl3 E:\\ CCY 11
6.7298
6.7173
6.7049
6.6939
6.6814
6.6689
5.5162
5.4803
2.7549
2.7396
2.7227
1.2650
5c
1H, 500 MHz, CDCl3
H3C
CH3
CH3
CH3
O
B
O
A (dt)
6.70
B (d)
5.50
D (t)
2.74
C (s)
1.27
Cl
Cl
Cl
Cl
DCM
2.60
3.33
1.00
1.03
2.34
2.13
11.82
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



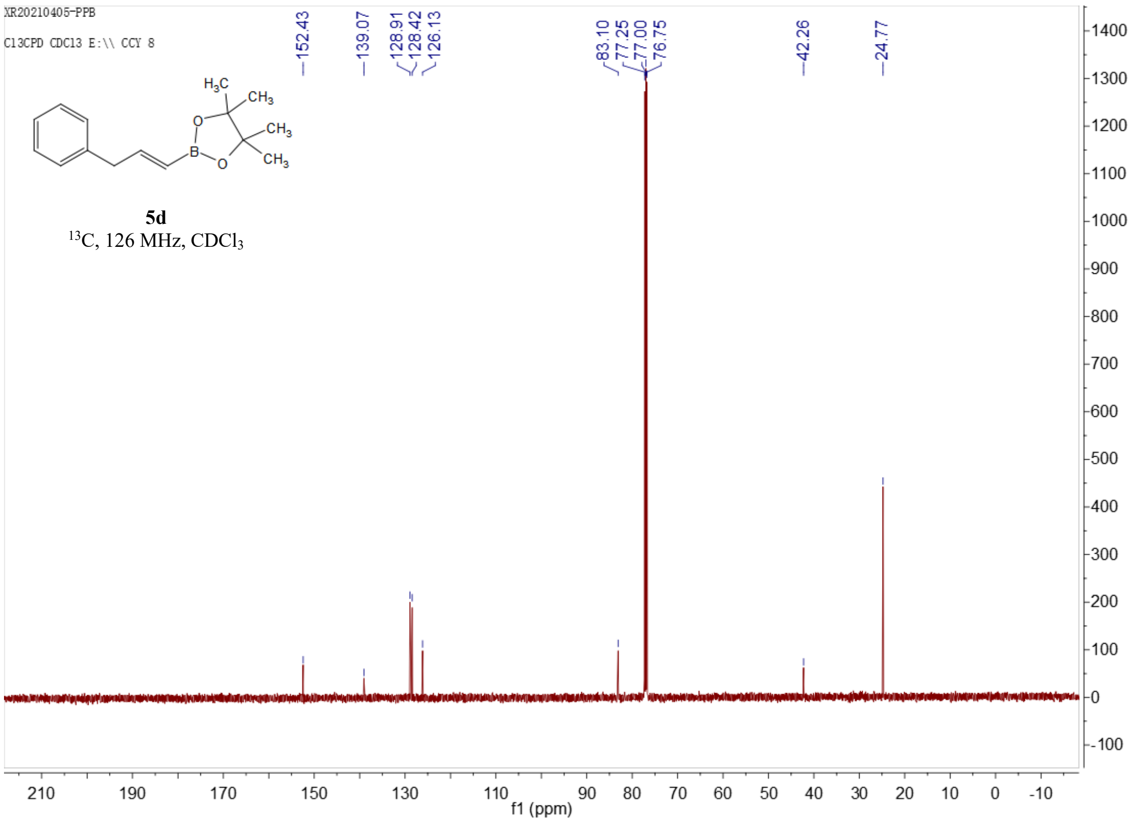
5c

^{13}C, 126 MHz, CDCl$_3$



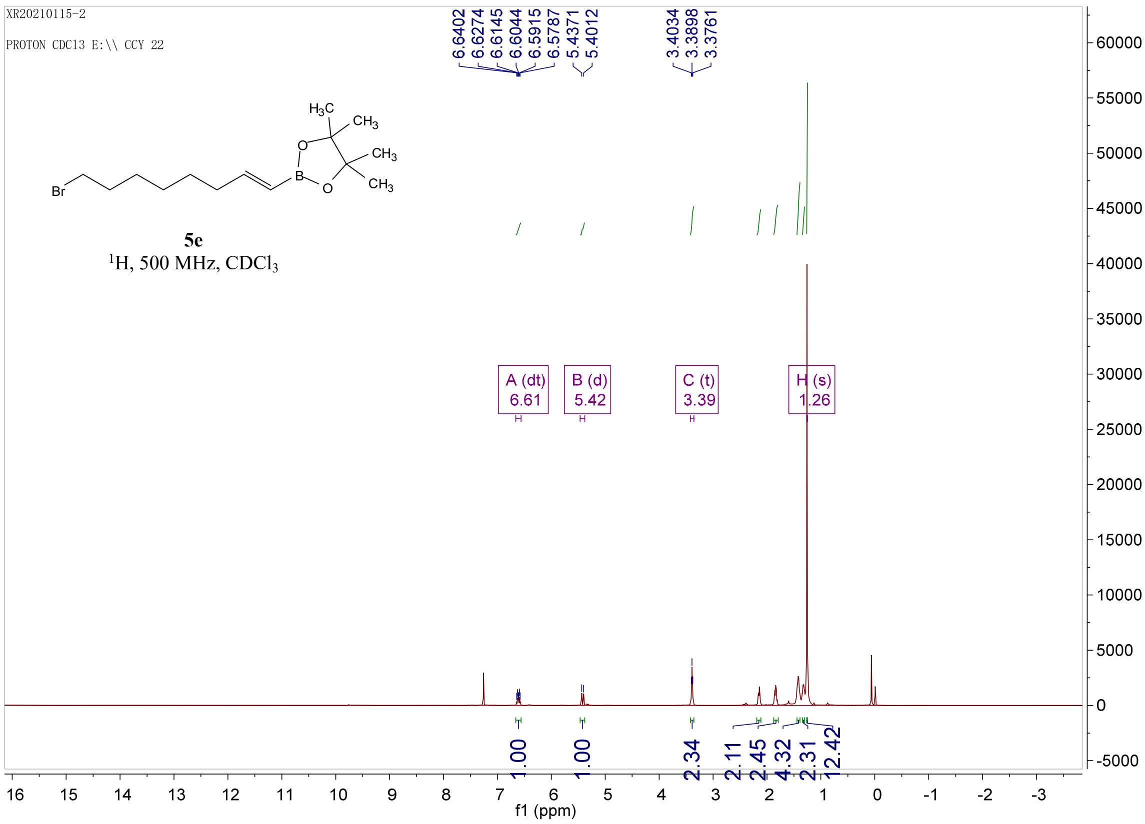
5d

^{1}H, 500 MHz, CDCl$_3$



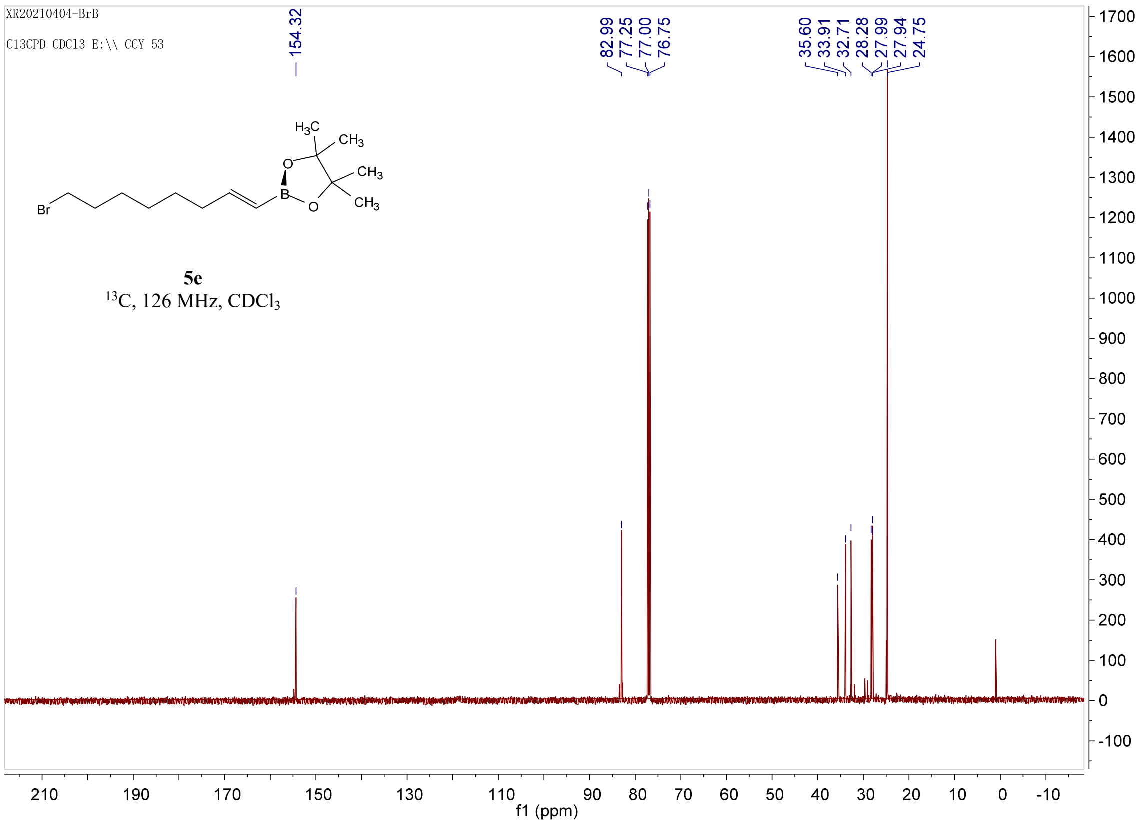
5d

^{13}C, 126 MHz, CDCl$_3$

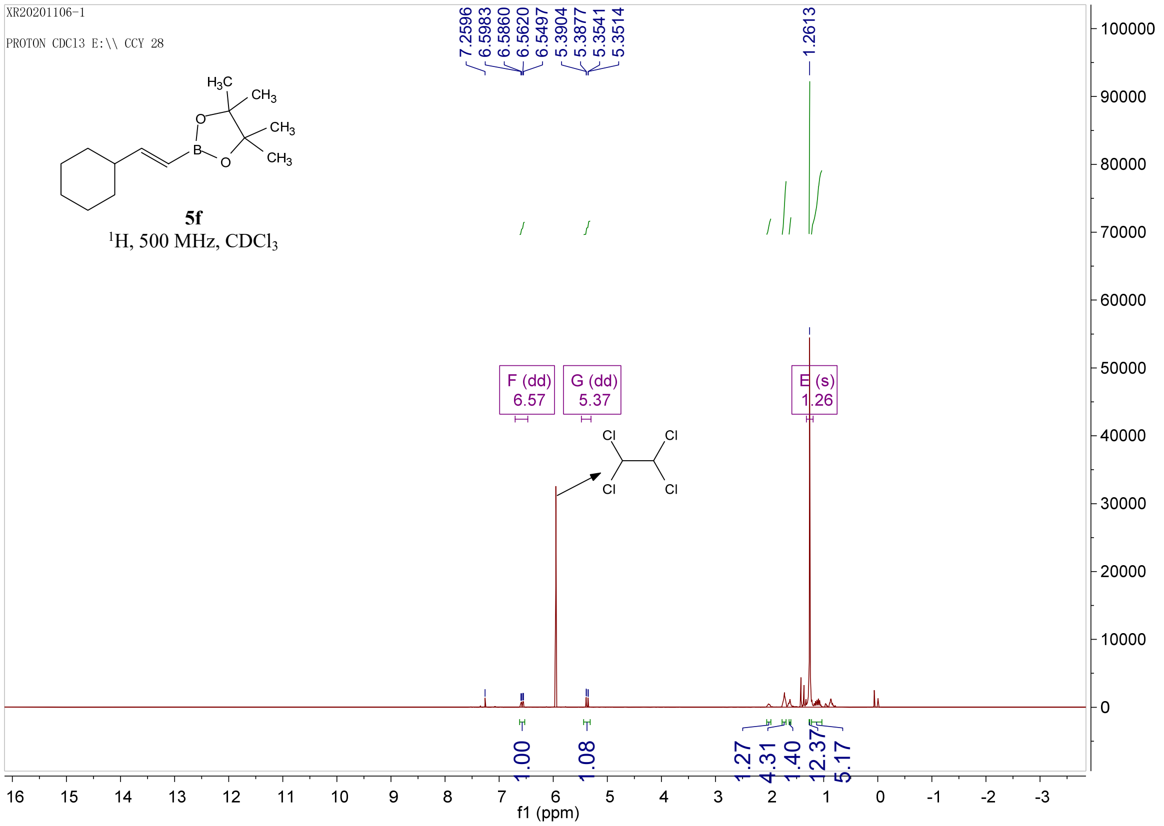


5e

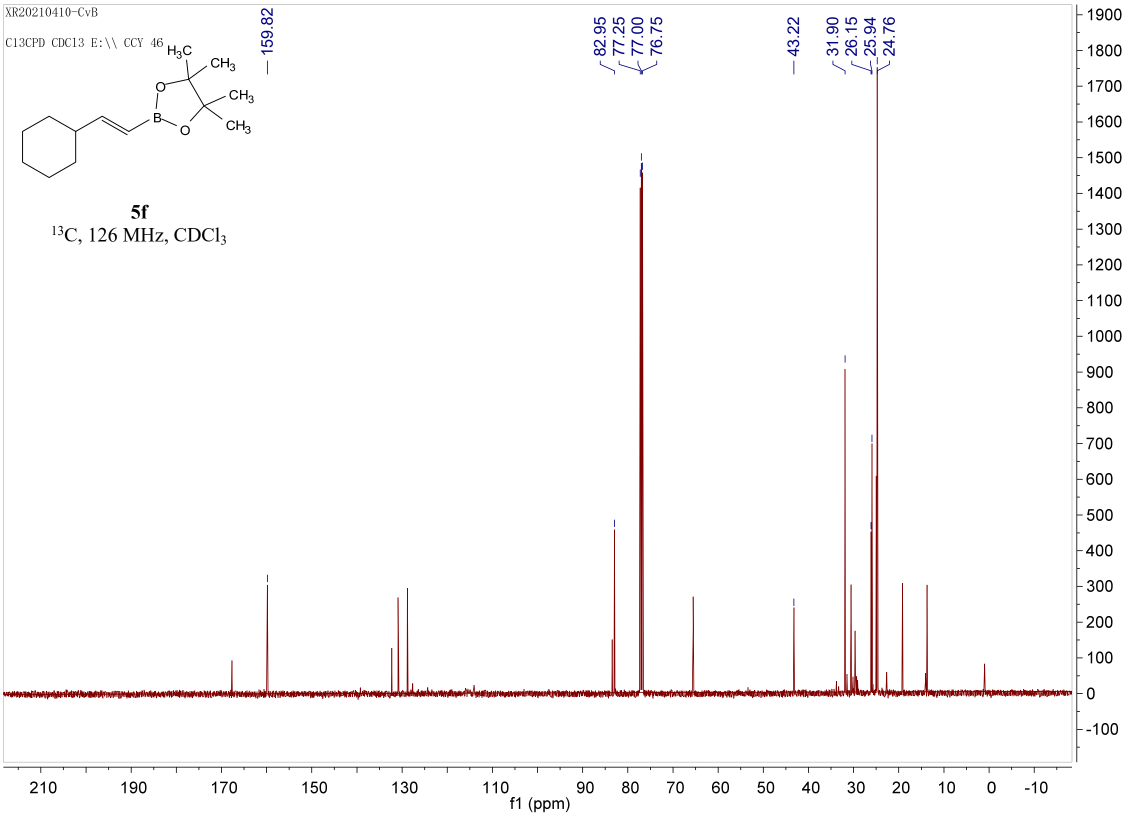
^{1}H, 500 MHz, CDCl$_3$


5e

^{13}C, 126 MHz, CDCl$_3$

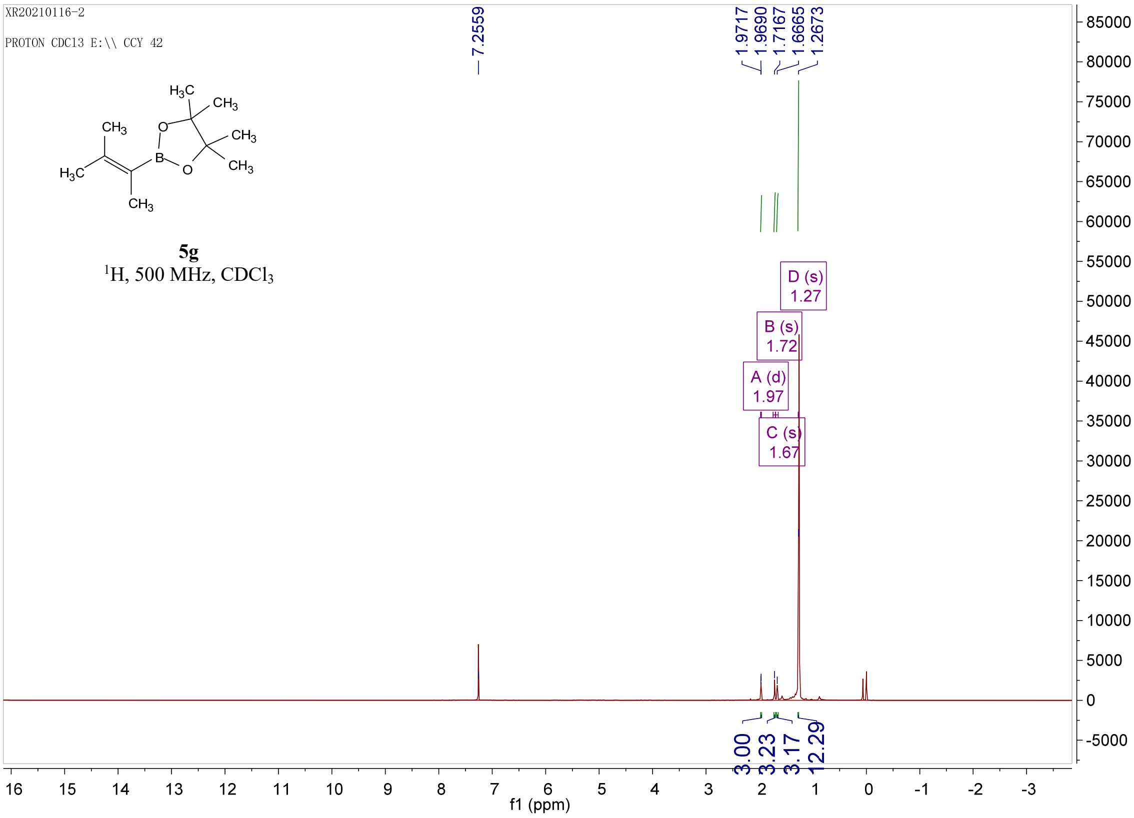

5f

^{1}H, 500 MHz, CDCl$_3$



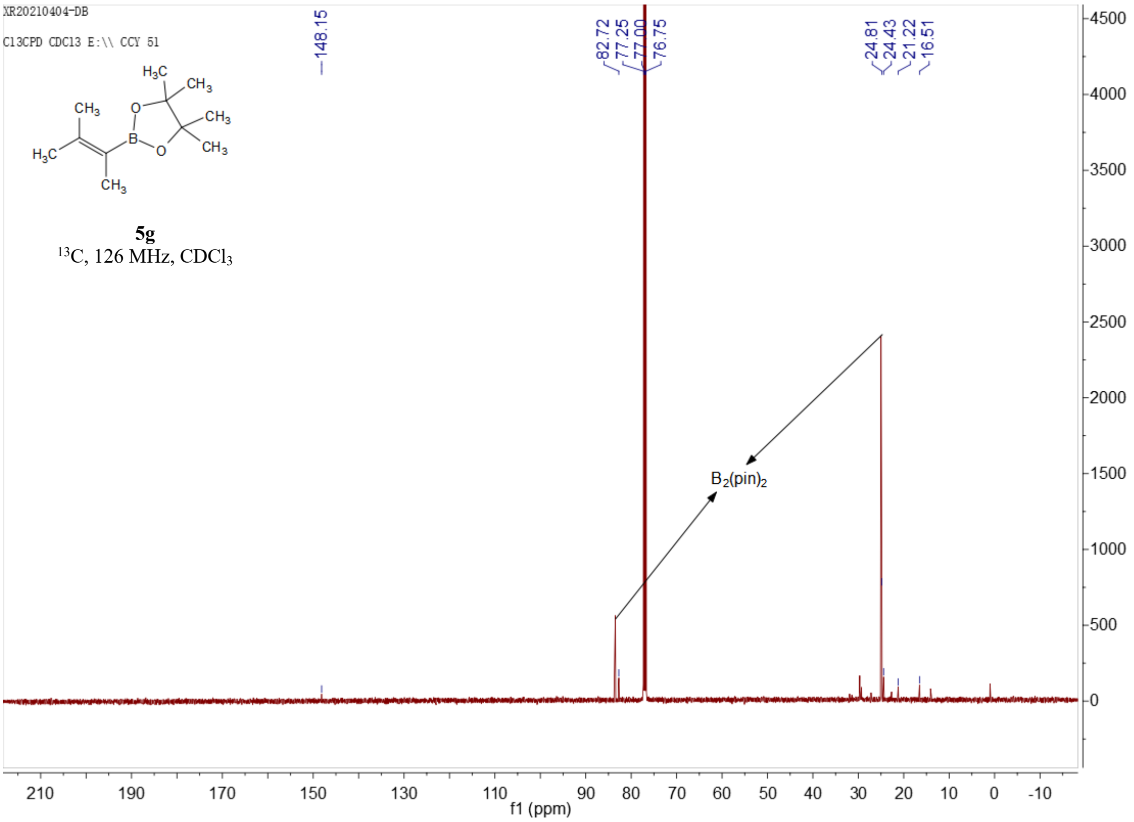
5f

^{13}C, 126 MHz, $CDCl_3$



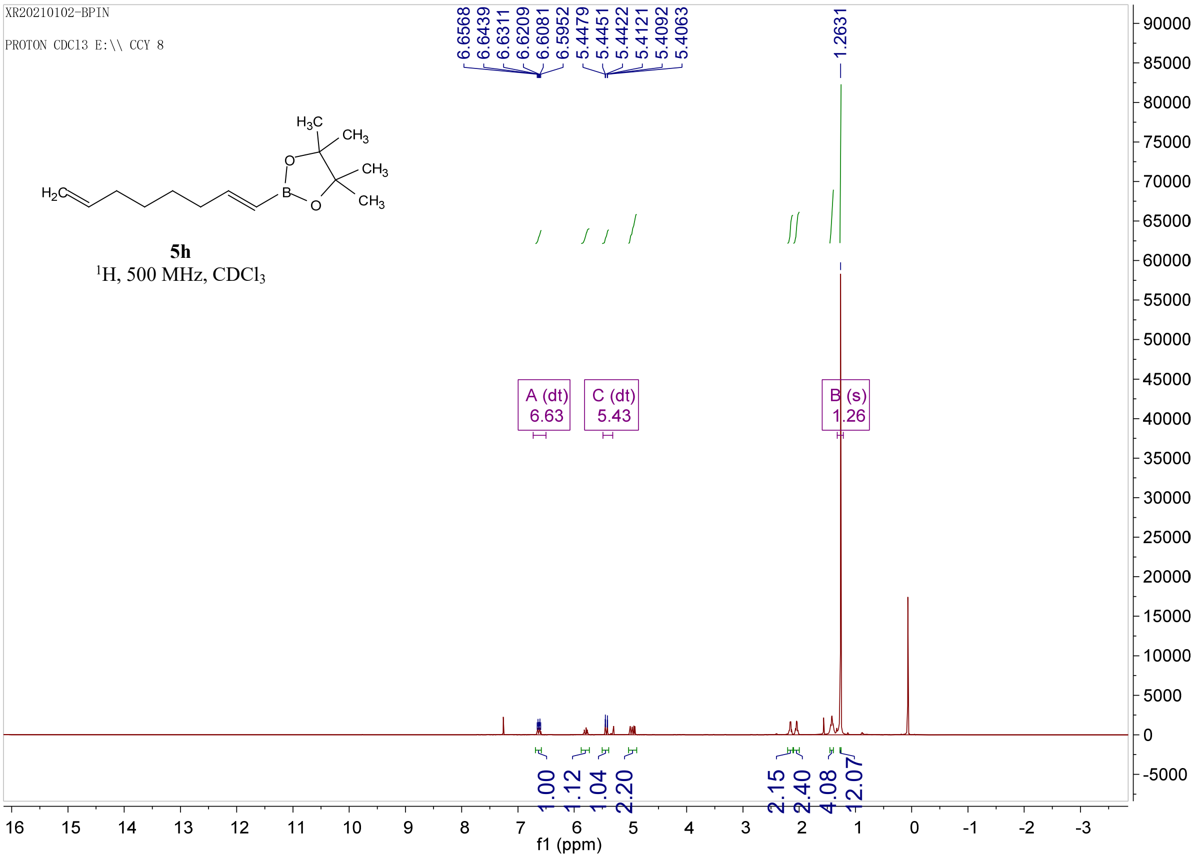
5g

^{1}H, 500 MHz, $CDCl_3$



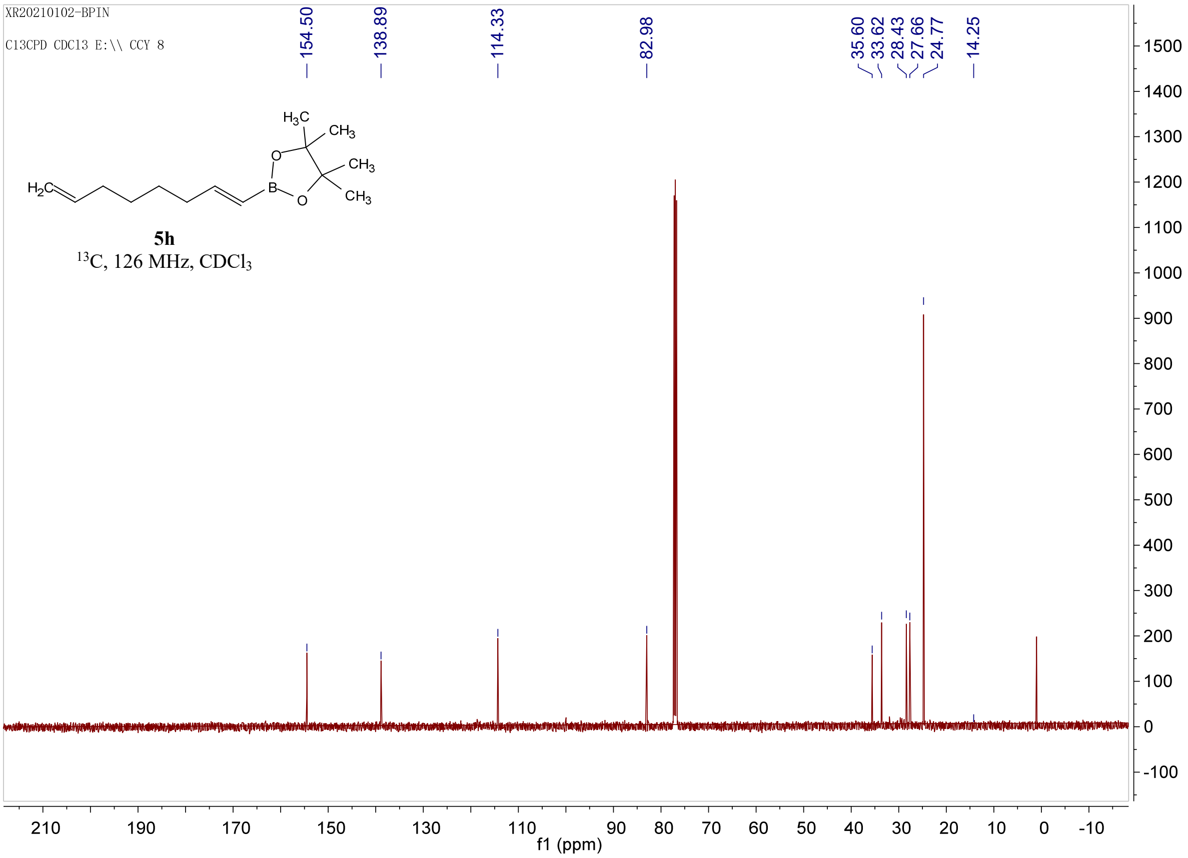
5g

^{13}C, 126 MHz, $CDCl_3$



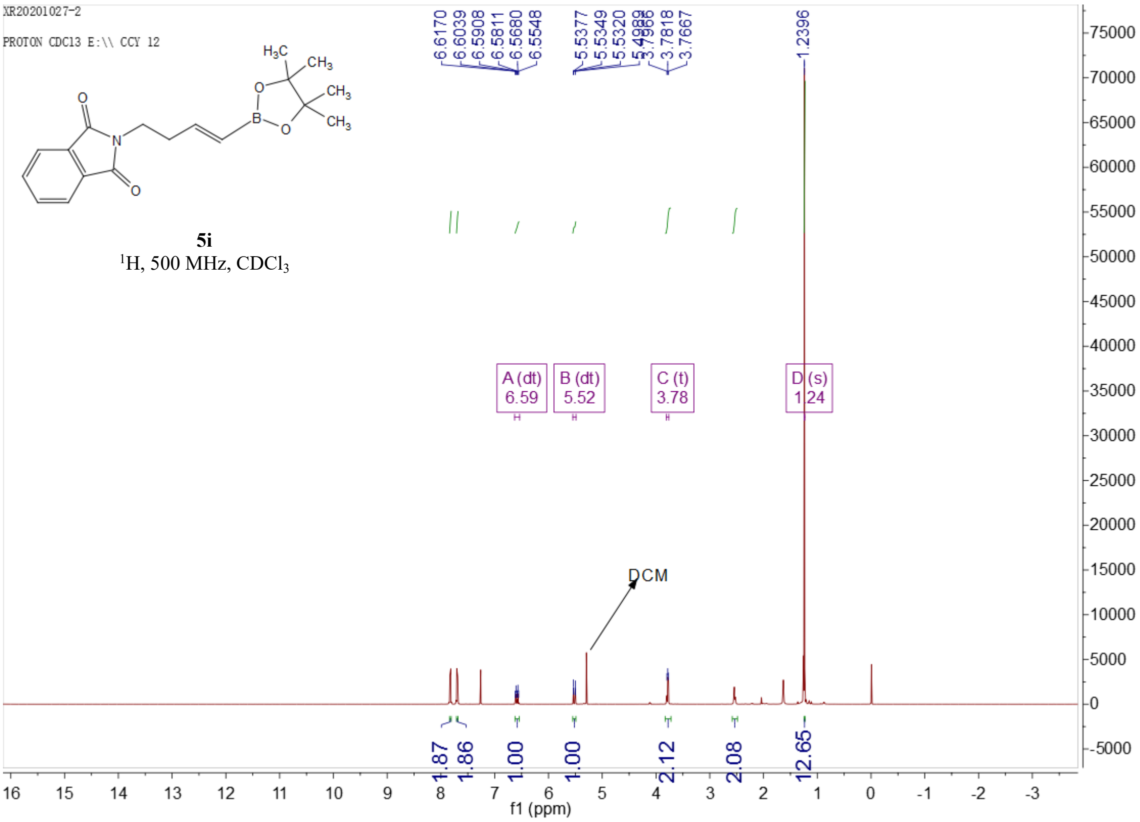
5h

^{1}H, 500 MHz, $CDCl_3$



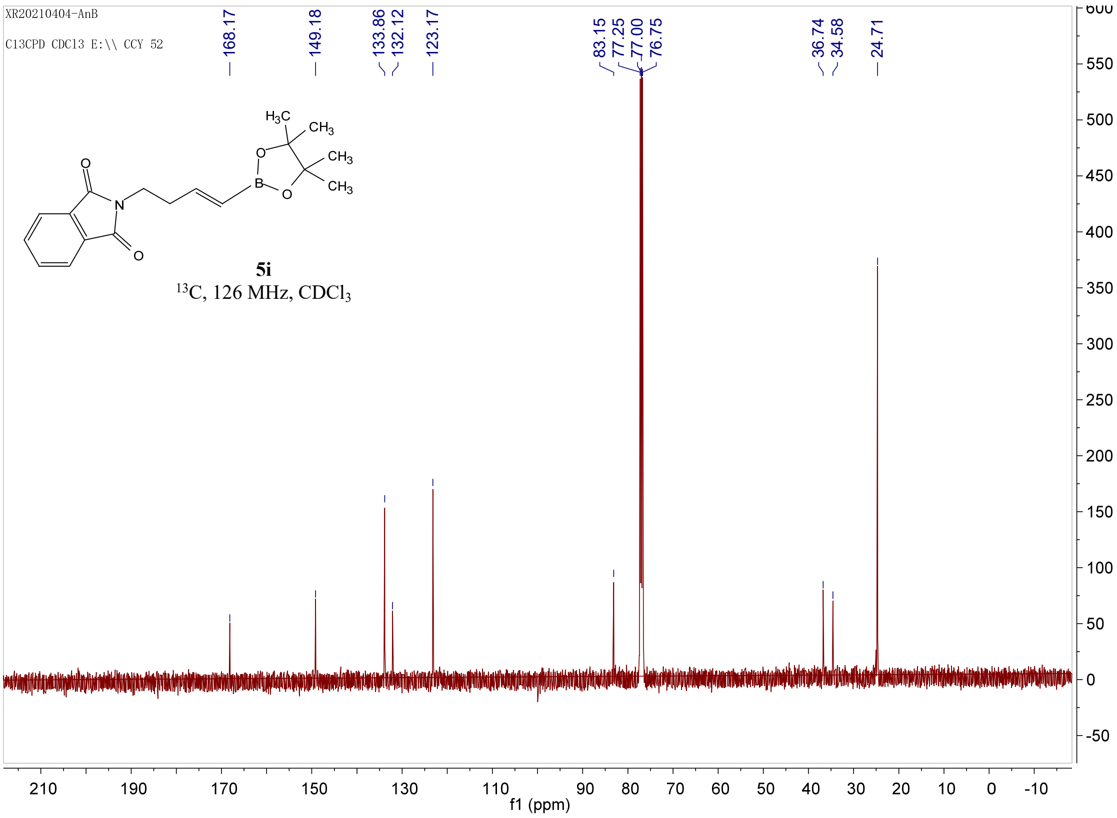
5h

^{13}C, 126 MHz, $CDCl_3$



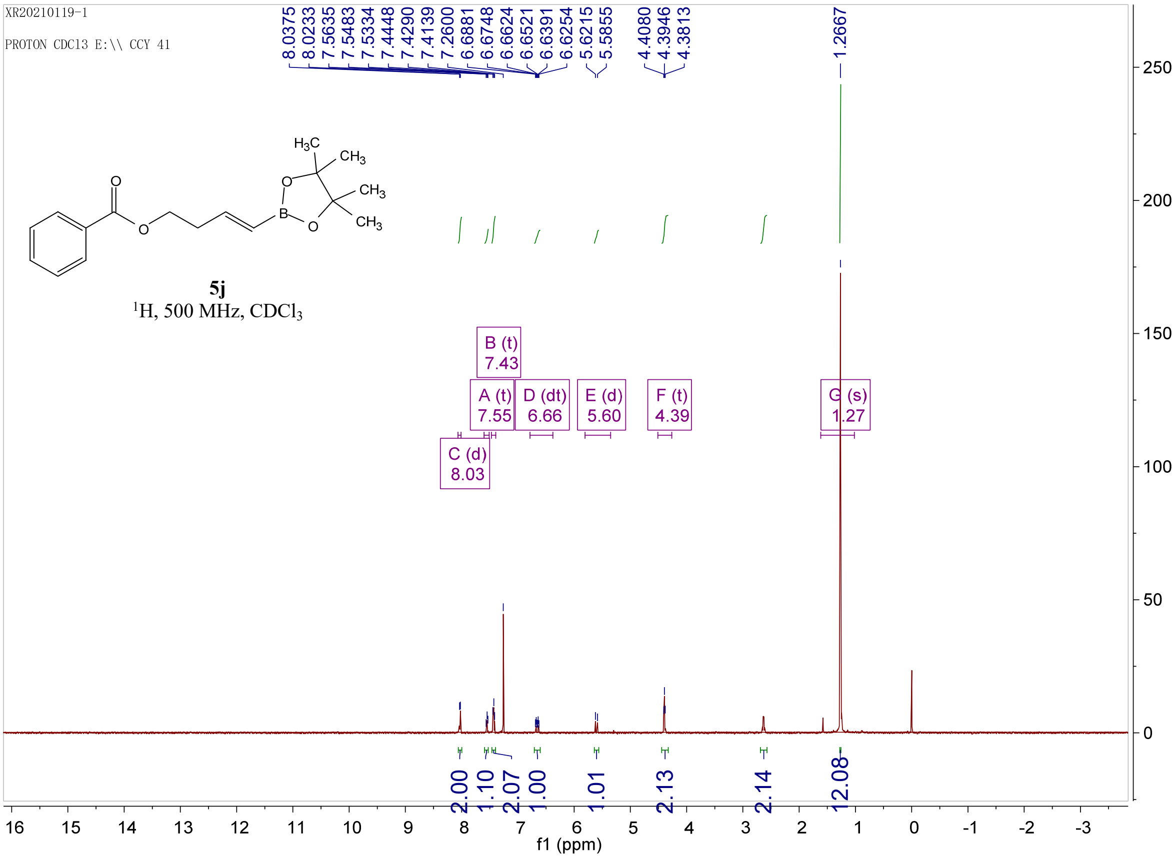
5i

^{1}H, 500 MHz, $CDCl_3$



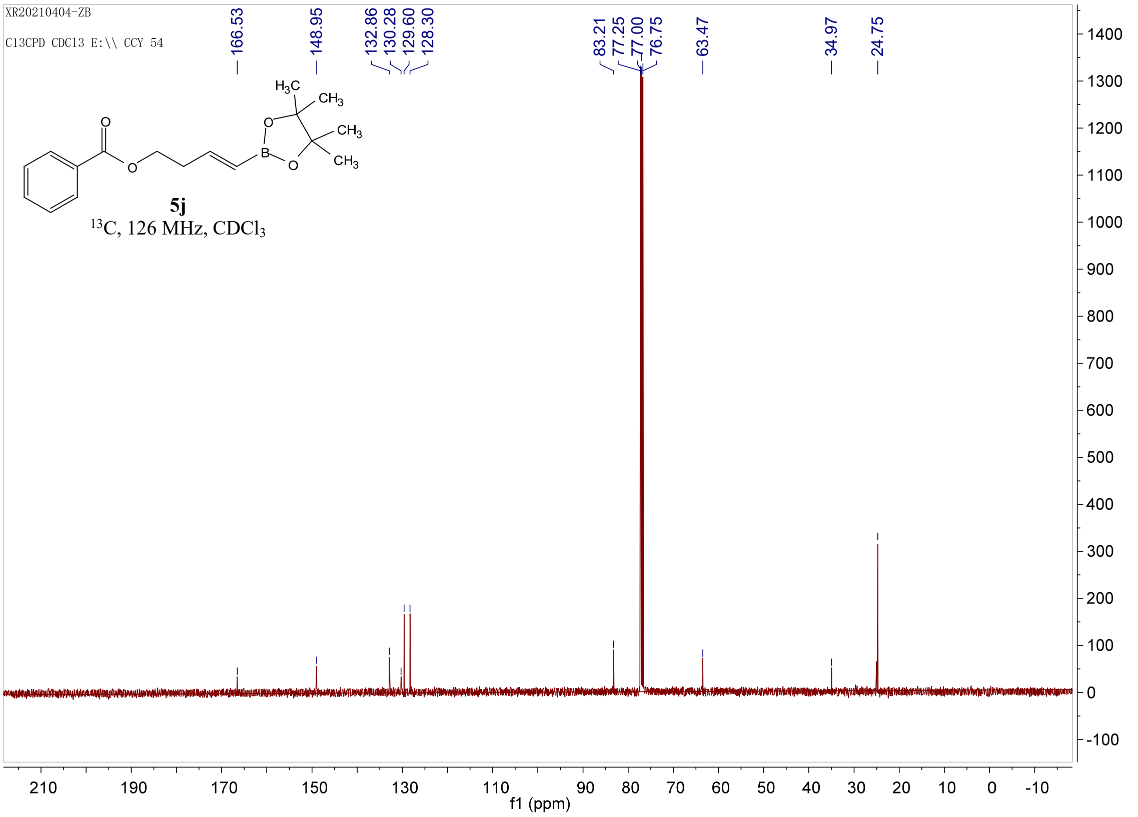
5i

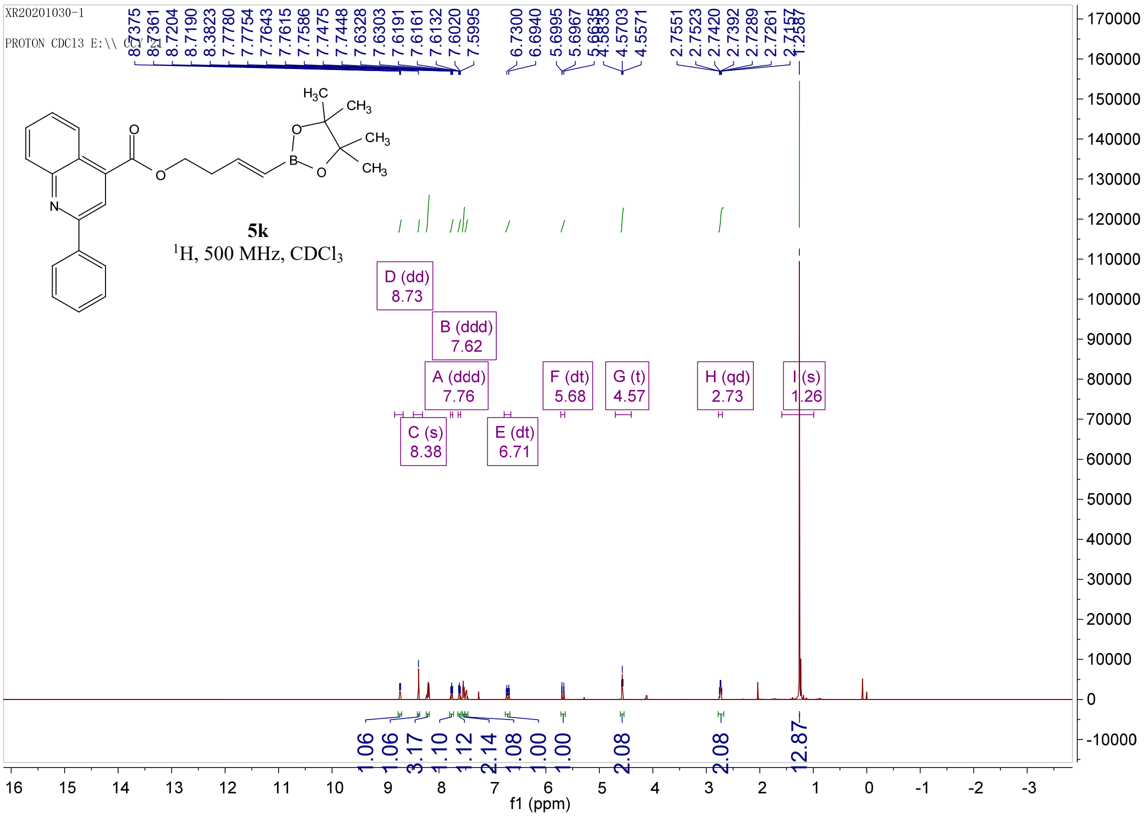
^{13}C, 126 MHz, CDCl$_3$

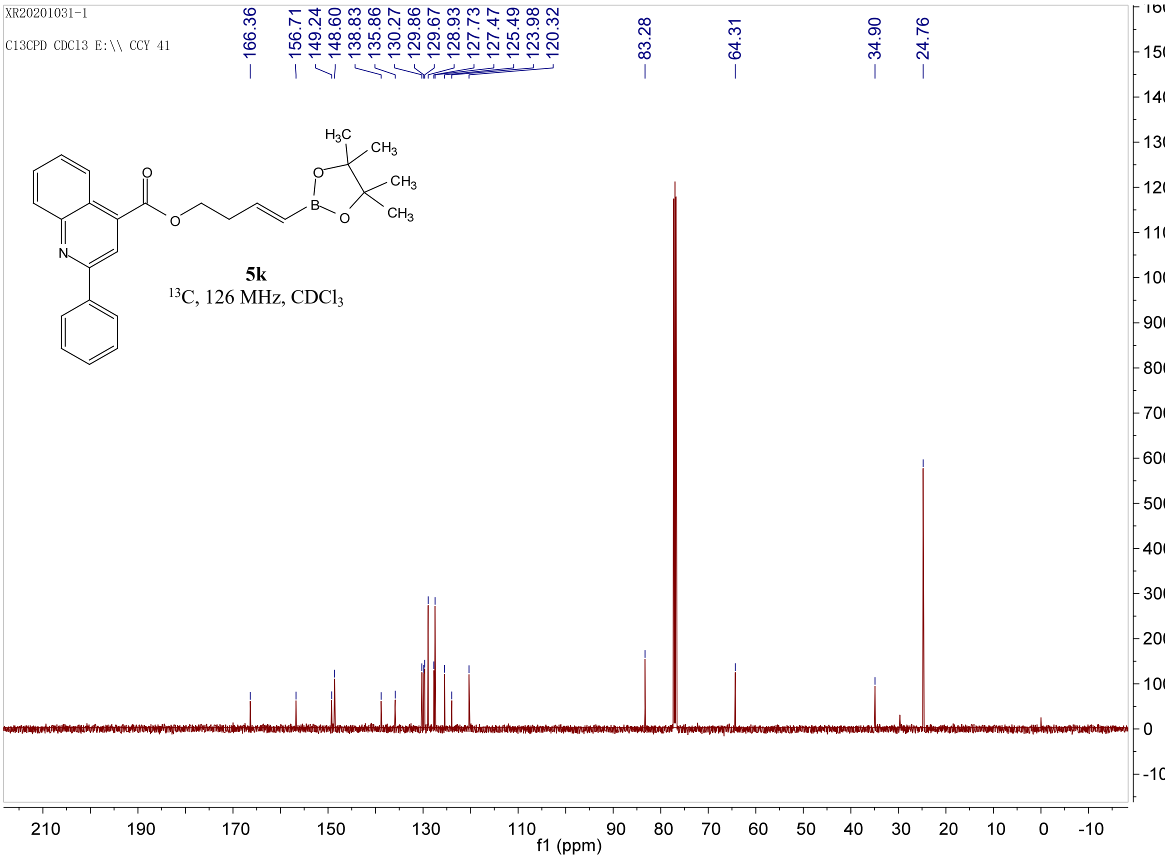


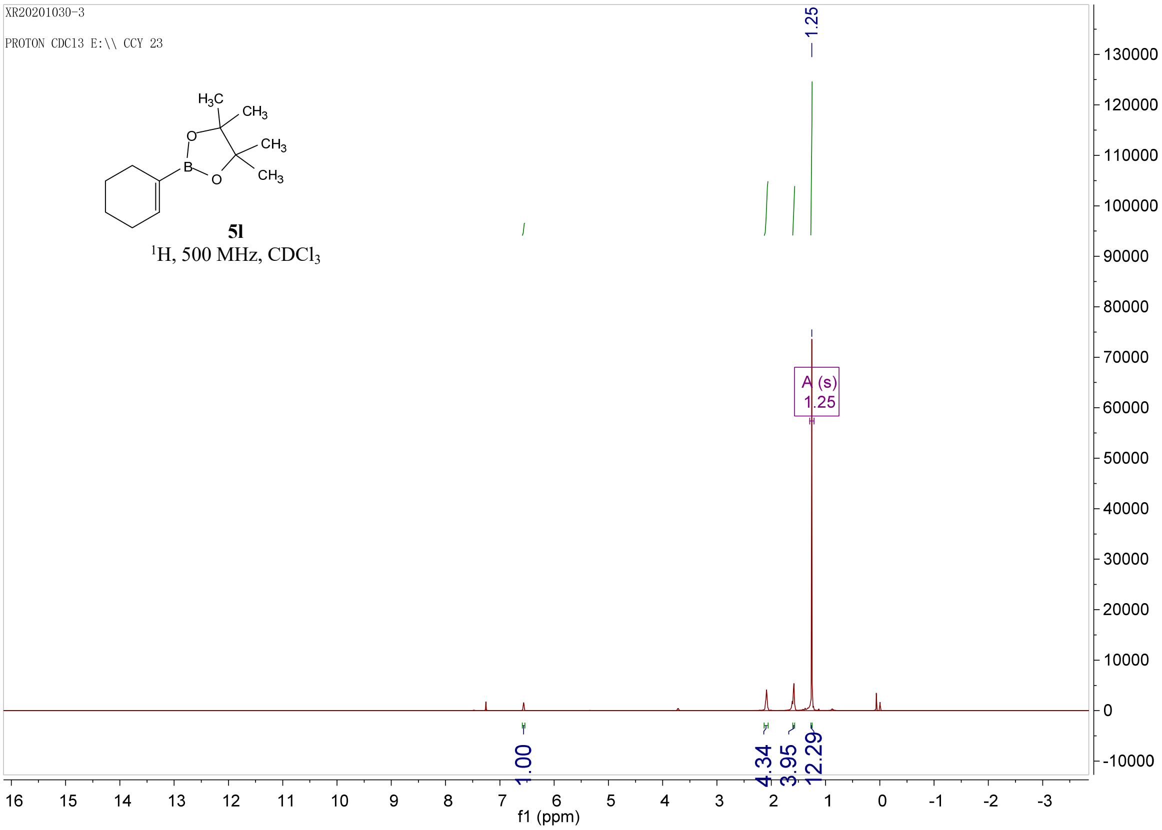
5j

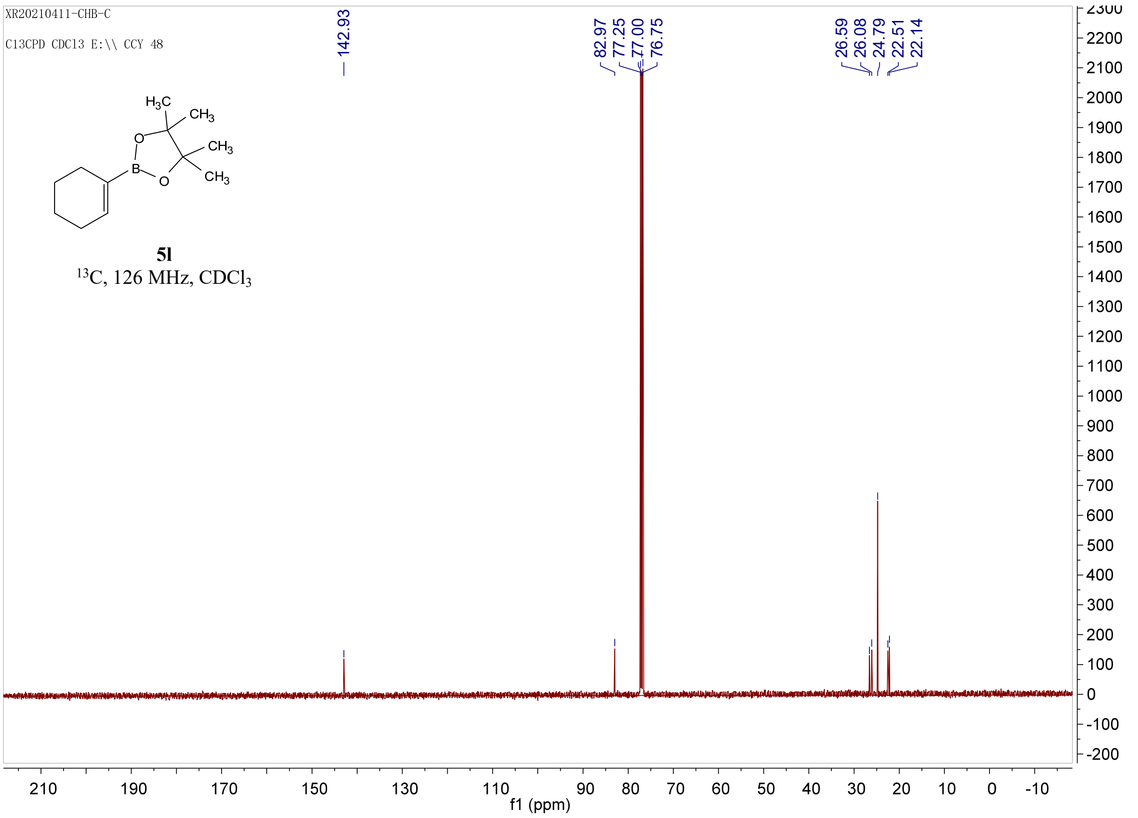
^{1}H, 500 MHz, CDCl$_3$

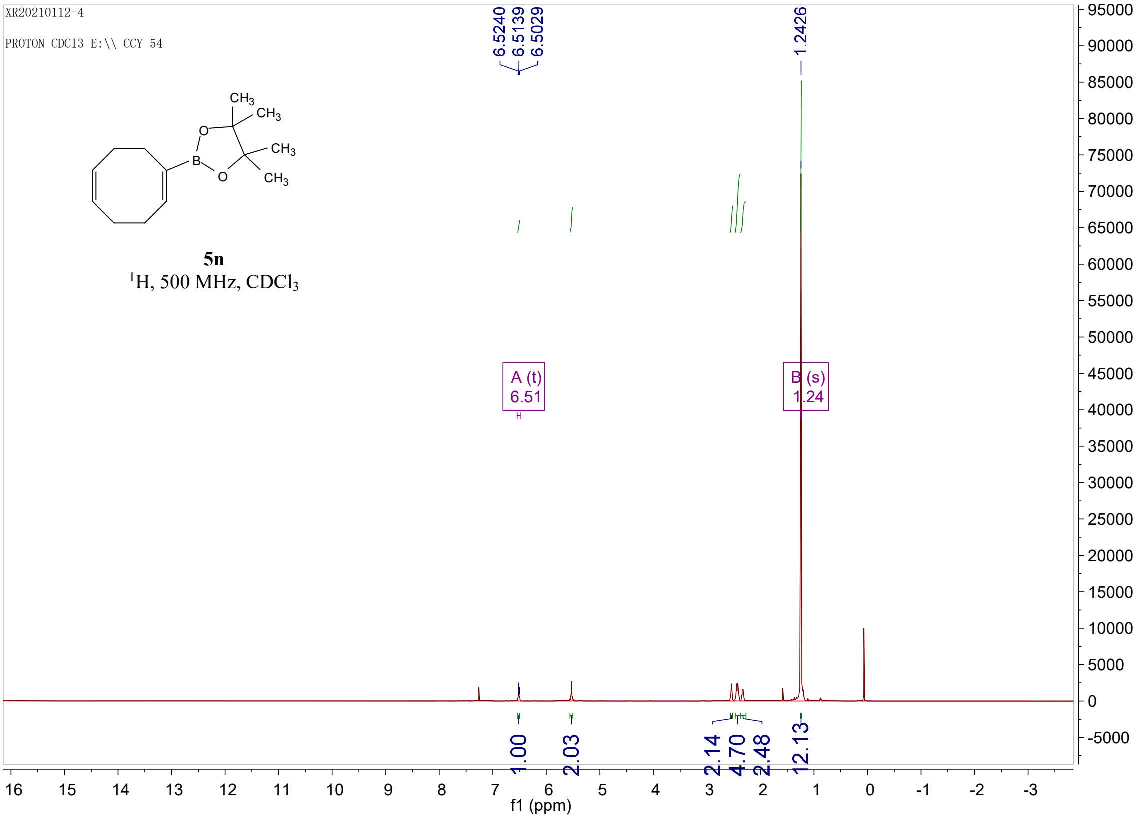

XR20210404-ZB
C13CPD CDCl3 E:\\ CCY 54
166.53
148.95
132.86
130.28
129.60
128.30
83.21
77.25
77.00
76.75
63.47
34.97
24.75
H3C
CH3
CH3
CH3
O
O
B
O
O
5j
13C, 126 MHz, CDCl3
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

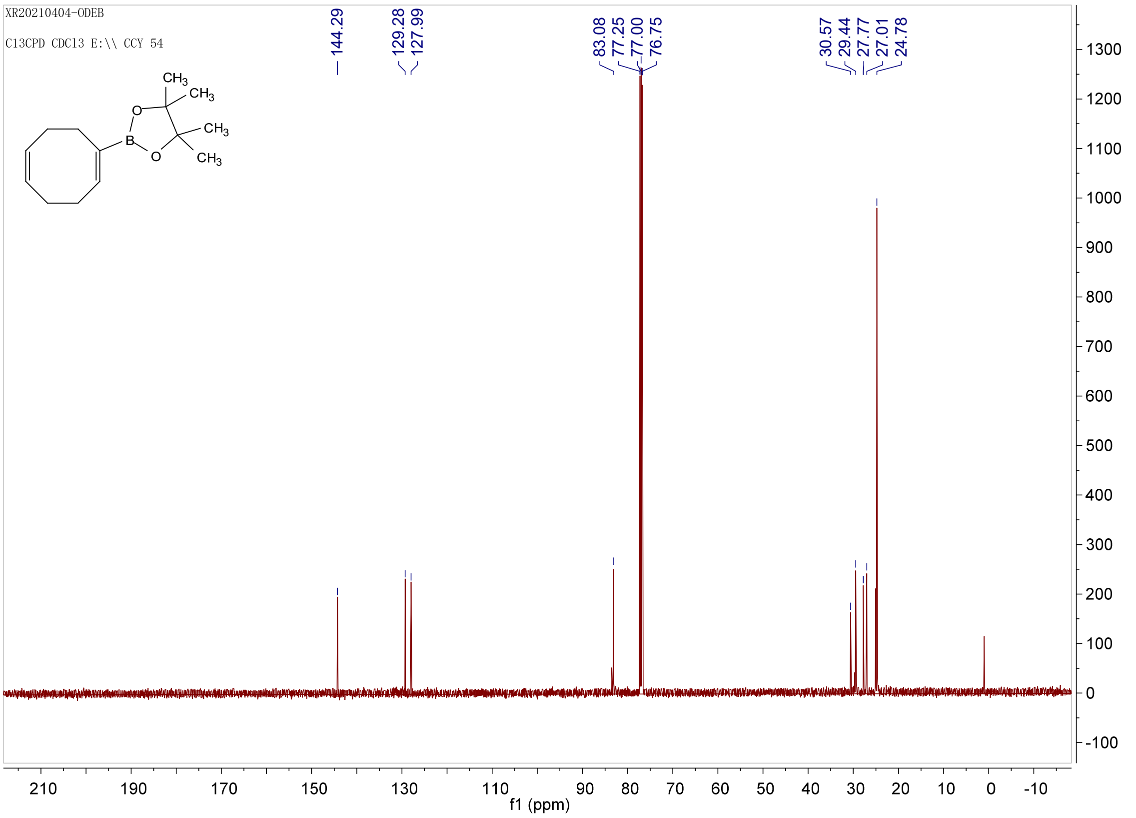

XR20201030-1
PROTON CDCl3 E:\\ CCY 21
8.7375
8.7361
8.7204
8.7190
8.3823
7.7780
7.7754
7.7643
7.7615
7.7586
7.7475
7.7448
7.6328
7.6303
7.6191
7.6161
7.6132
7.6020
7.5995
6.7300
6.6940
5.6995
5.6967
5.6635
4.5835
4.5703
4.5571
2.7551
2.7523
2.7420
2.7392
2.7289
2.7261
2.7157
1.2587
H3C
CH3
CH3
CH3
O
O
B
O
O
N
5k
1H, 500 MHz, CDCl3
D (dd)
8.73
B (ddd)
7.62
A (ddd)
7.76
F (dt)
5.68
G (t)
4.57
H (qd)
2.73
I (s)
1.26
C (s)
8.38
E (dt)
6.71
1.06
1.06
3.17
1.10
1.12
2.14
1.08
1.00
1.00
2.08
2.08
12.87
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

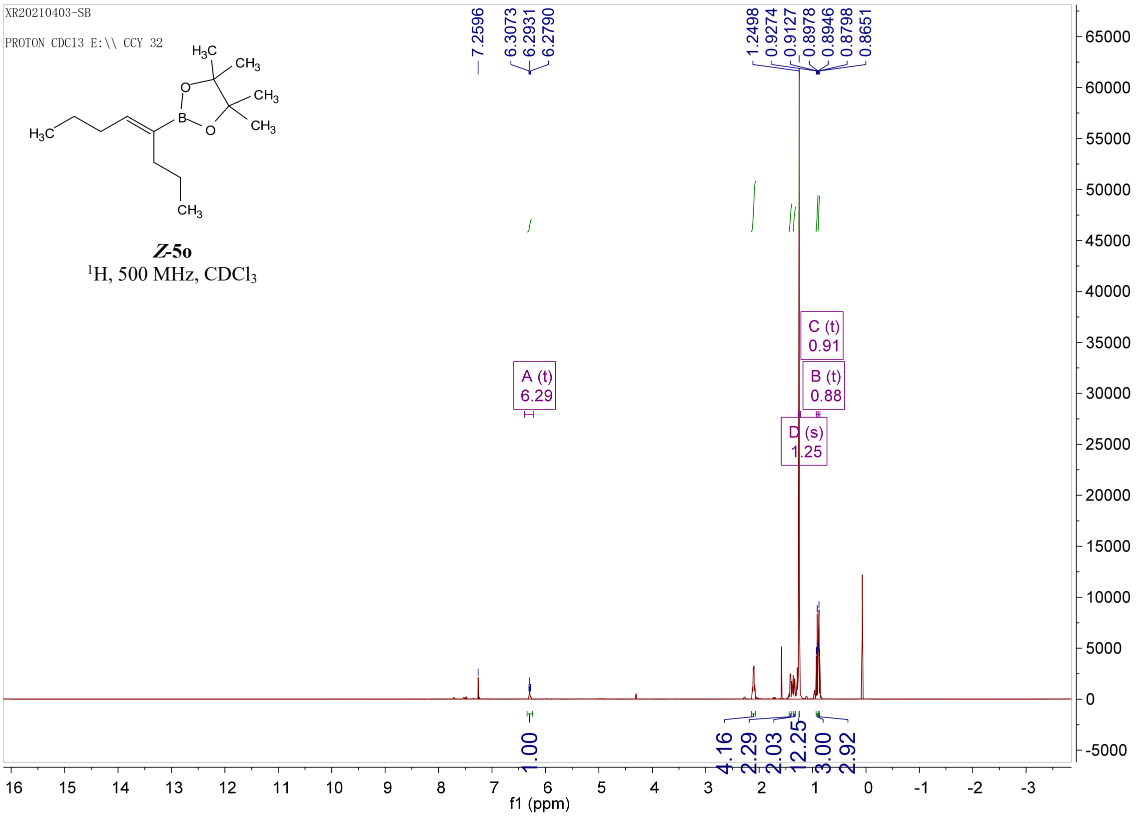

XR20201031-1
C13CPD CDCl3 E:\\ CCY 41
166.36
156.71
149.24
148.60
138.83
135.86
130.27
129.86
129.67
128.93
127.73
127.47
125.49
123.98
120.32
83.28
64.31
34.90
24.76
5k
^{13}C, 126 MHz, CDCl$_3$
f1 (ppm)

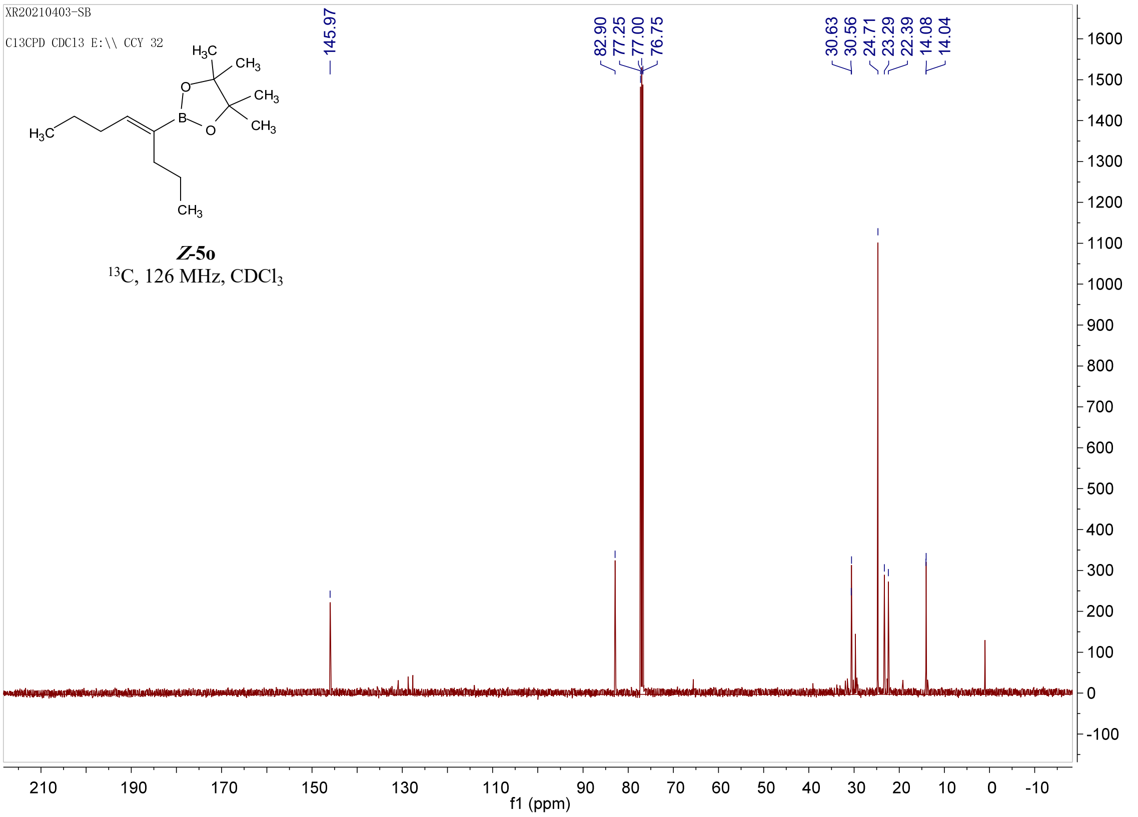

XR20201030-3
PROTON CDCl3 E:\\ CCY 23
1.25
5l
^{1}H, 500 MHz, CDCl$_3$
A (s)
1.25
1.00
4.34
3.95
12.29
f1 (ppm)


XR20210411-CHB-C
C13CPD CDCl3 E:\\ CCY 48
142.93
82.97
77.25
77.00
76.75
26.59
26.08
24.79
22.51
22.14
H_3C
CH_3
CH_3
CH_3
O
B
O
5l
^{13}C, 126 MHz, $CDCl_3$
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200


XR20210112-4
PROTON CDCl3 E:\\ CCY 54
6.5240
6.5139
6.5029
1.2426
CH_3
CH_3
CH_3
CH_3
O
B
O
5n
^1H, 500 MHz, $CDCl_3$
A (t)
6.51
B (s)
1.24
1.00
2.03
2.14
4.70
2.48
12.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
95000 90000 85000 80000 75000 70000 65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000

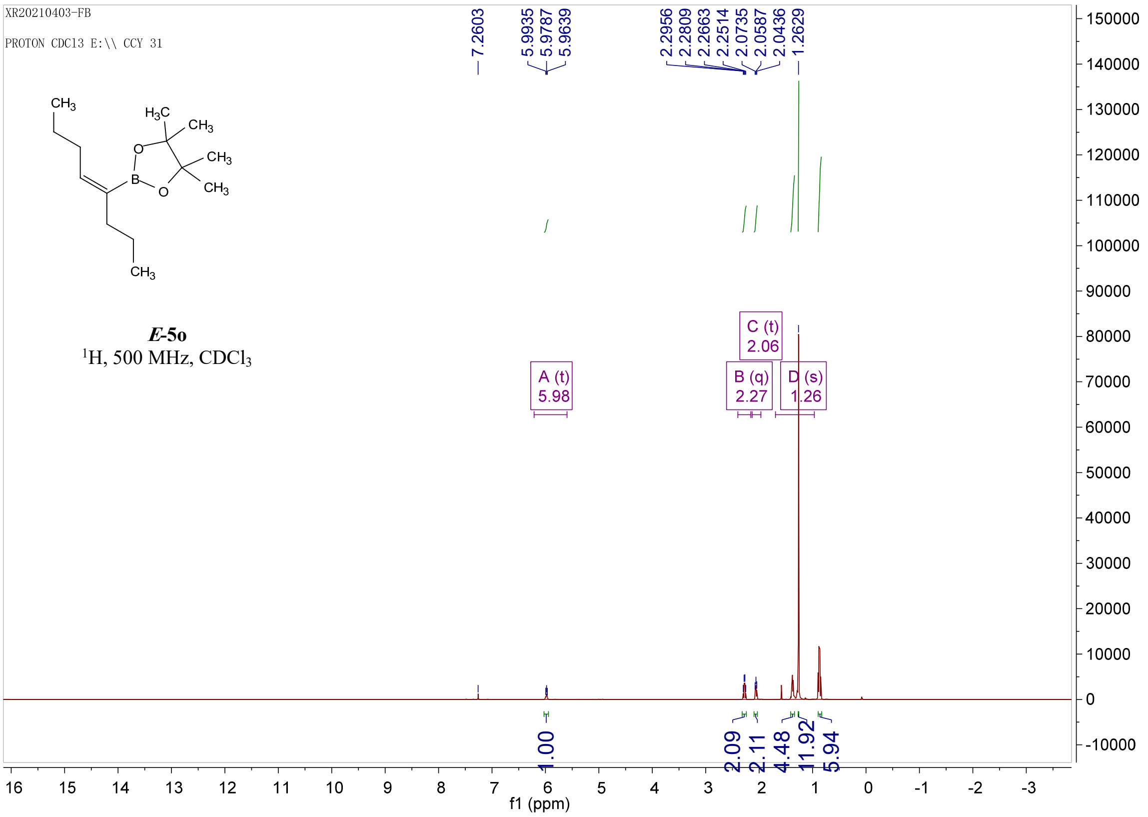

XR20210404-ODEB
C13CPD CDCl3 E:\\ CCY 54
144.29
129.28
127.99
83.08
77.25
77.00
76.75
30.57
29.44
27.77
27.01
24.78
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


XR20210403-SB
PROTON CDCl3 E:\\ CCY 32
Z-5o
¹H, 500 MHz, CDCl₃
7.2596
6.3073
6.2931
6.2790
1.2498
0.9274
0.9127
0.8978
0.8946
0.8798
0.8651
A (t)
6.29
B (t)
0.88
C (t)
0.91
D (s)
1.25
1.00
4.16
2.29
2.03
12.25
3.00
2.92
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000



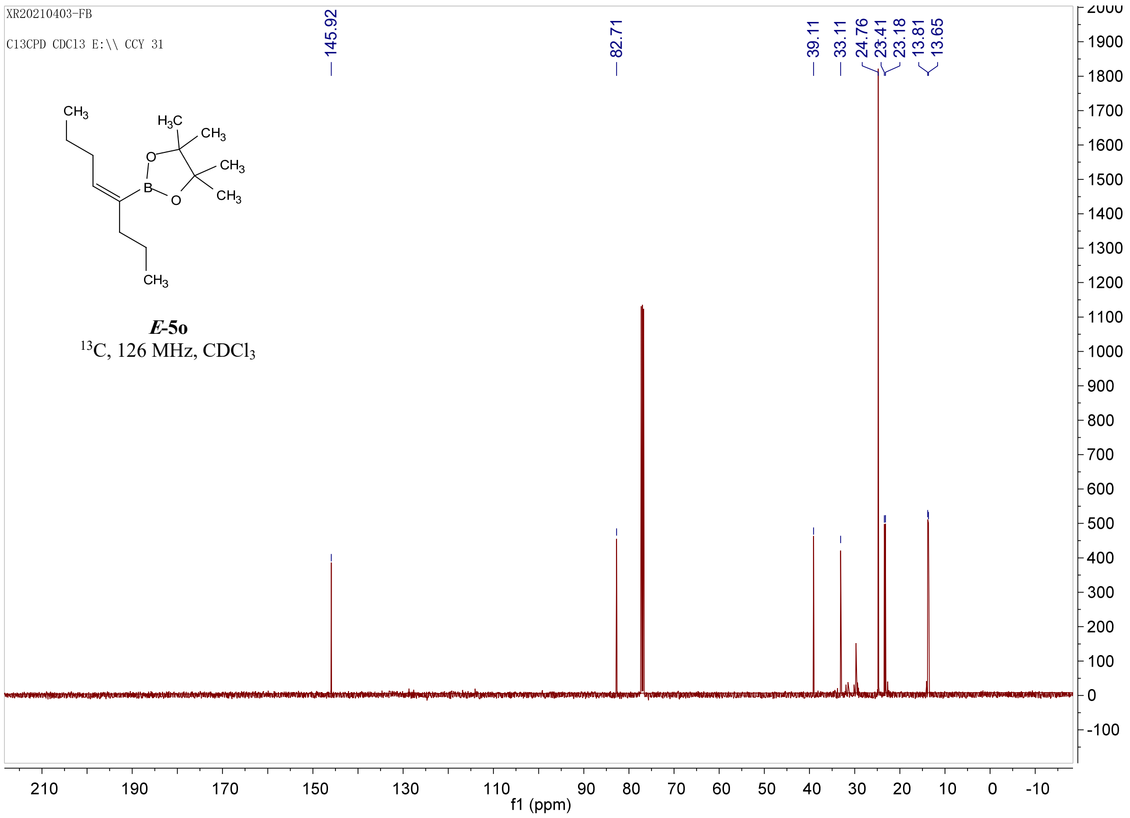
***Z*-5o**

^{13}C, 126 MHz, CDCl$_3$



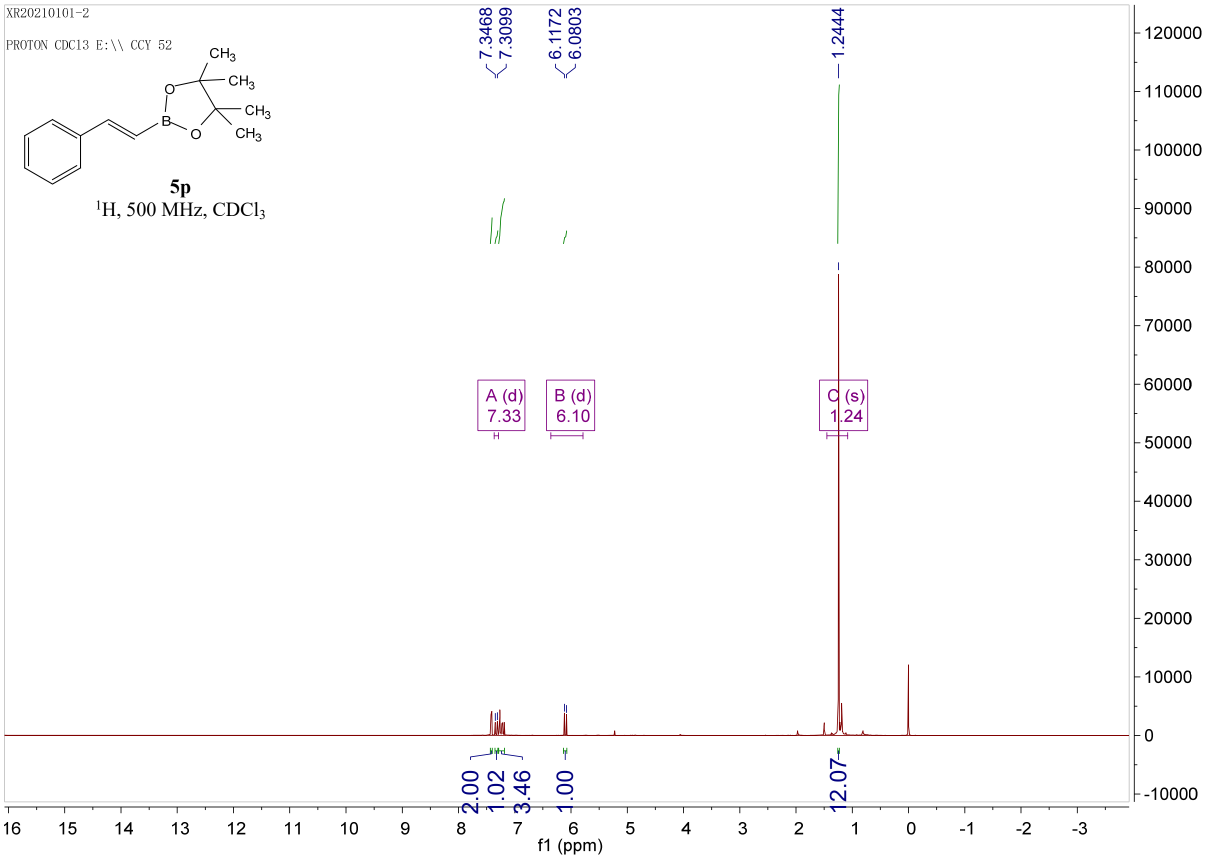
***E*-5o**

^{1}H, 500 MHz, CDCl$_3$



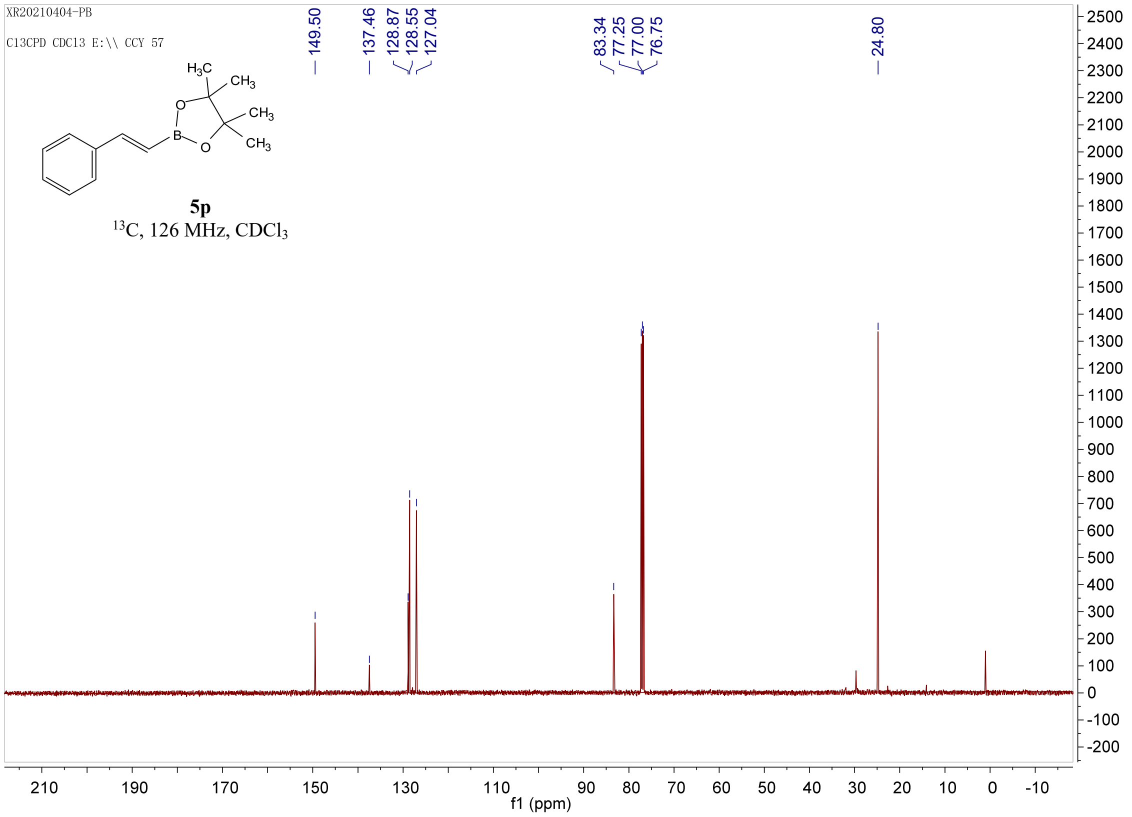
***E*-5o**

^{13}C, 126 MHz, CDCl$_3$



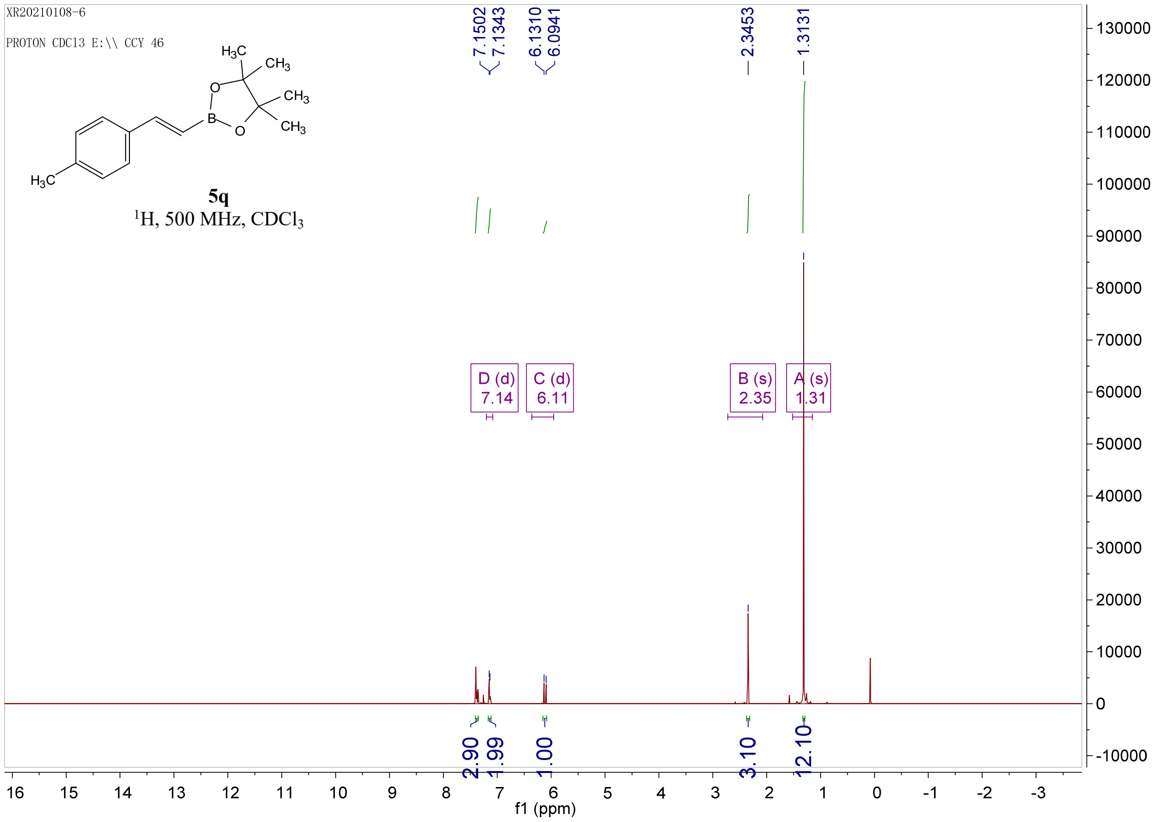
5p

^{1}H, 500 MHz, CDCl$_3$



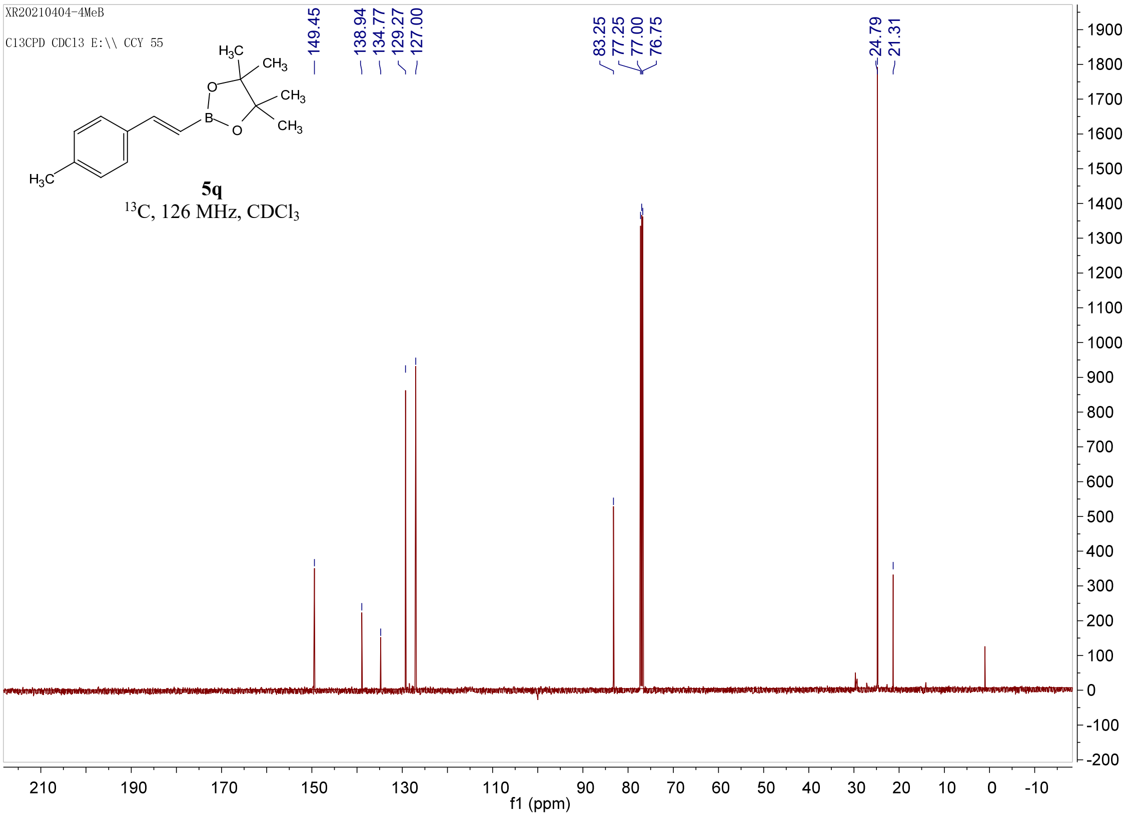
5p

^{13}C, 126 MHz, CDCl$_3$



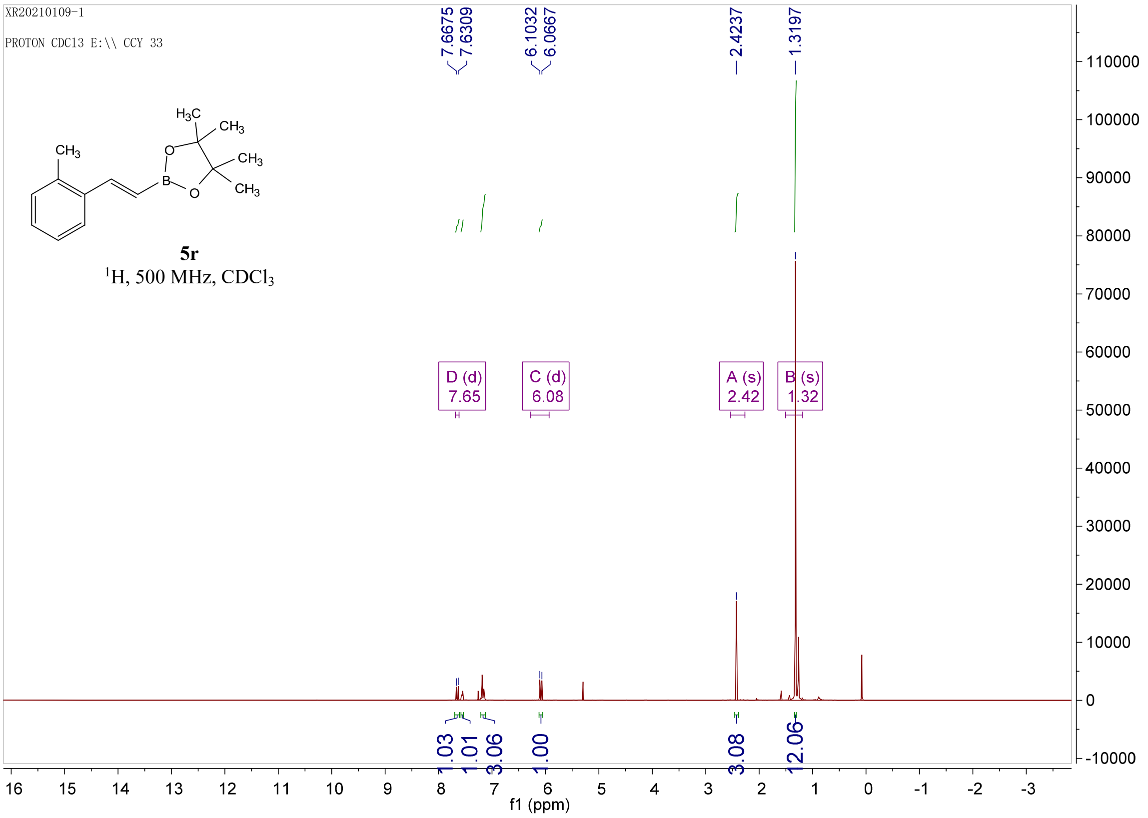
5q

^{1}H, 500 MHz, CDCl$_3$



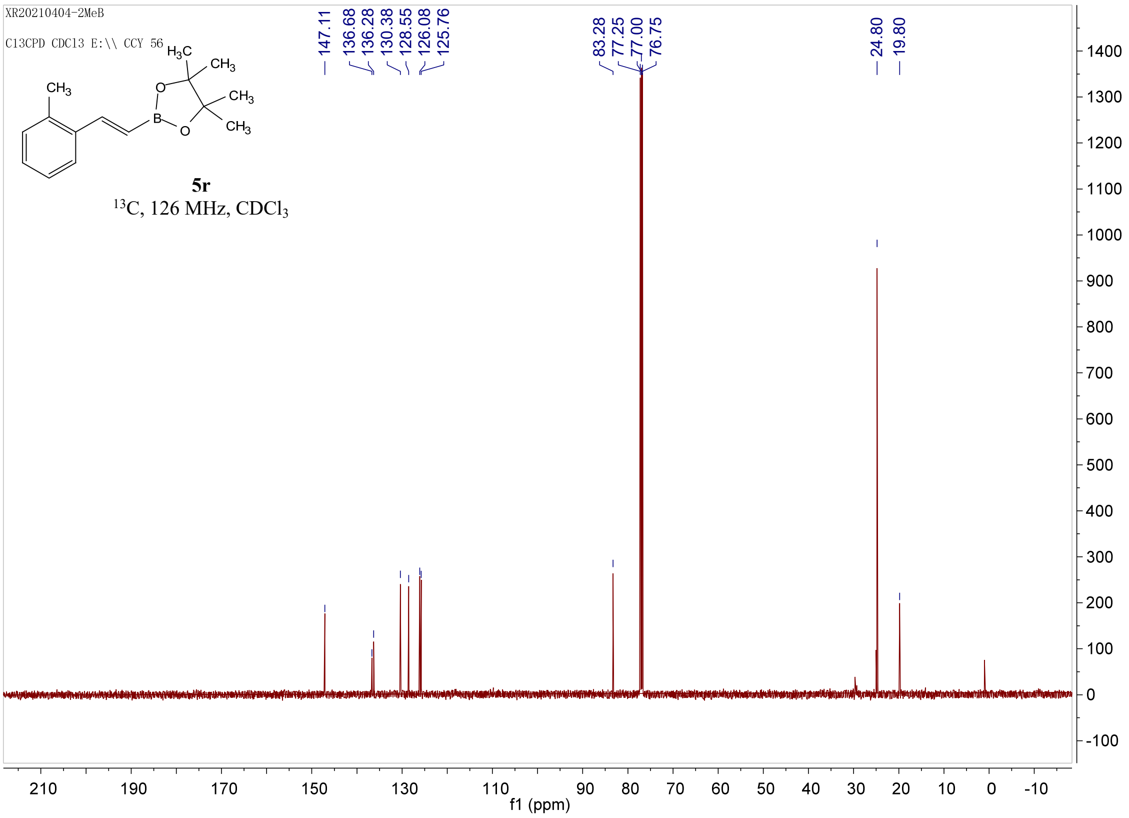
5q

^{13}C, 126 MHz, CDCl$_3$

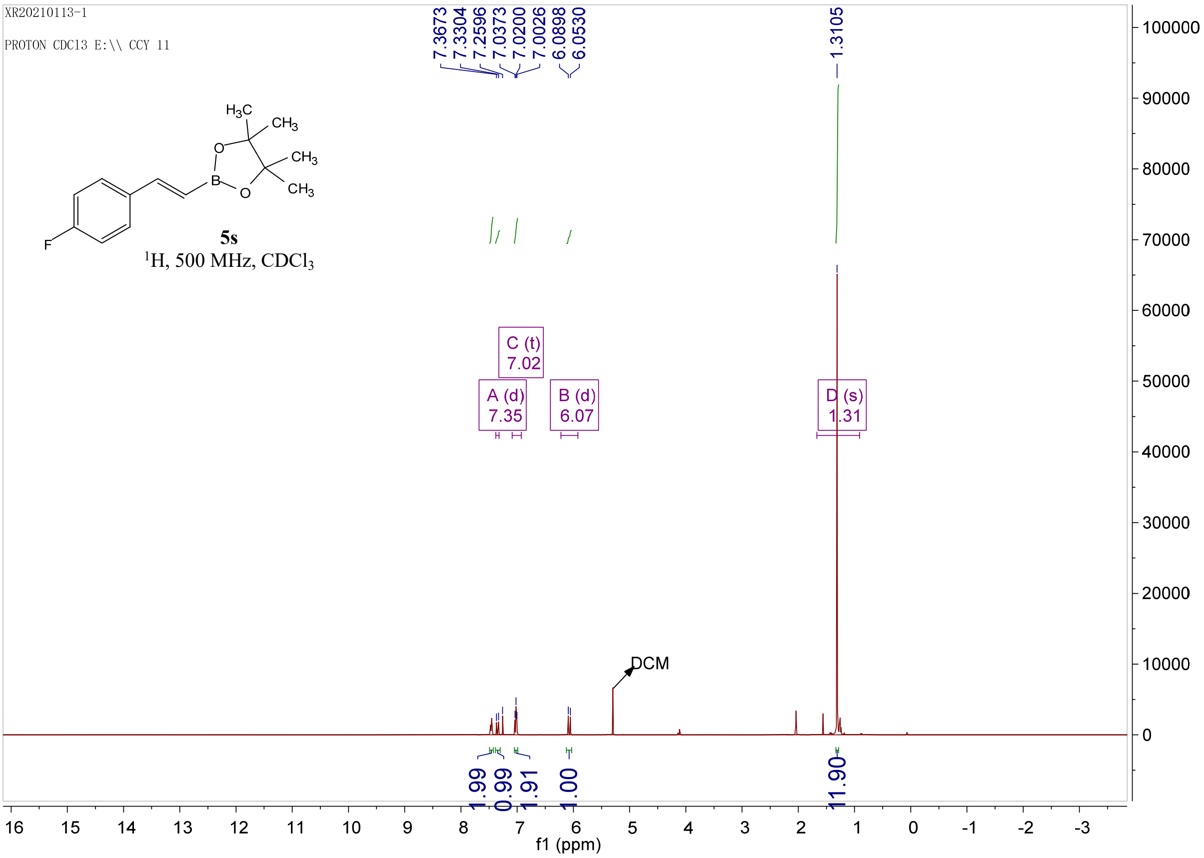


5r

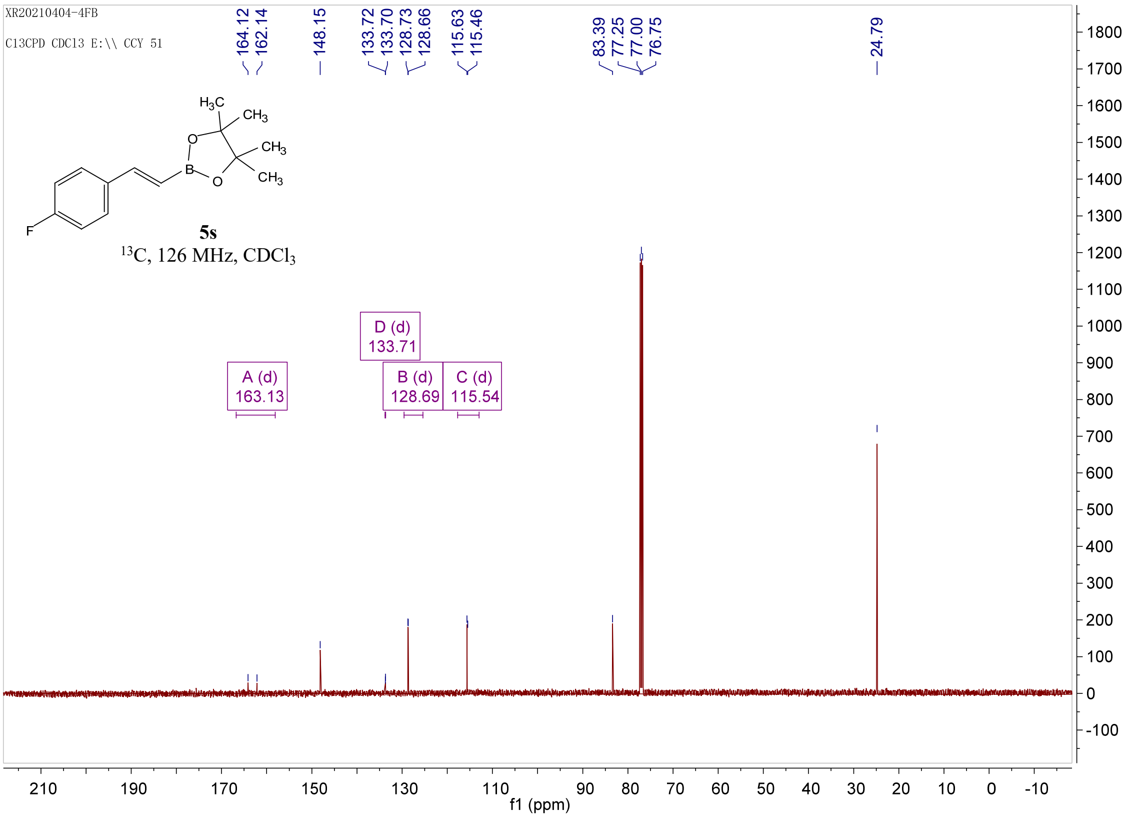
^{1}H, 500 MHz, CDCl$_3$


5r

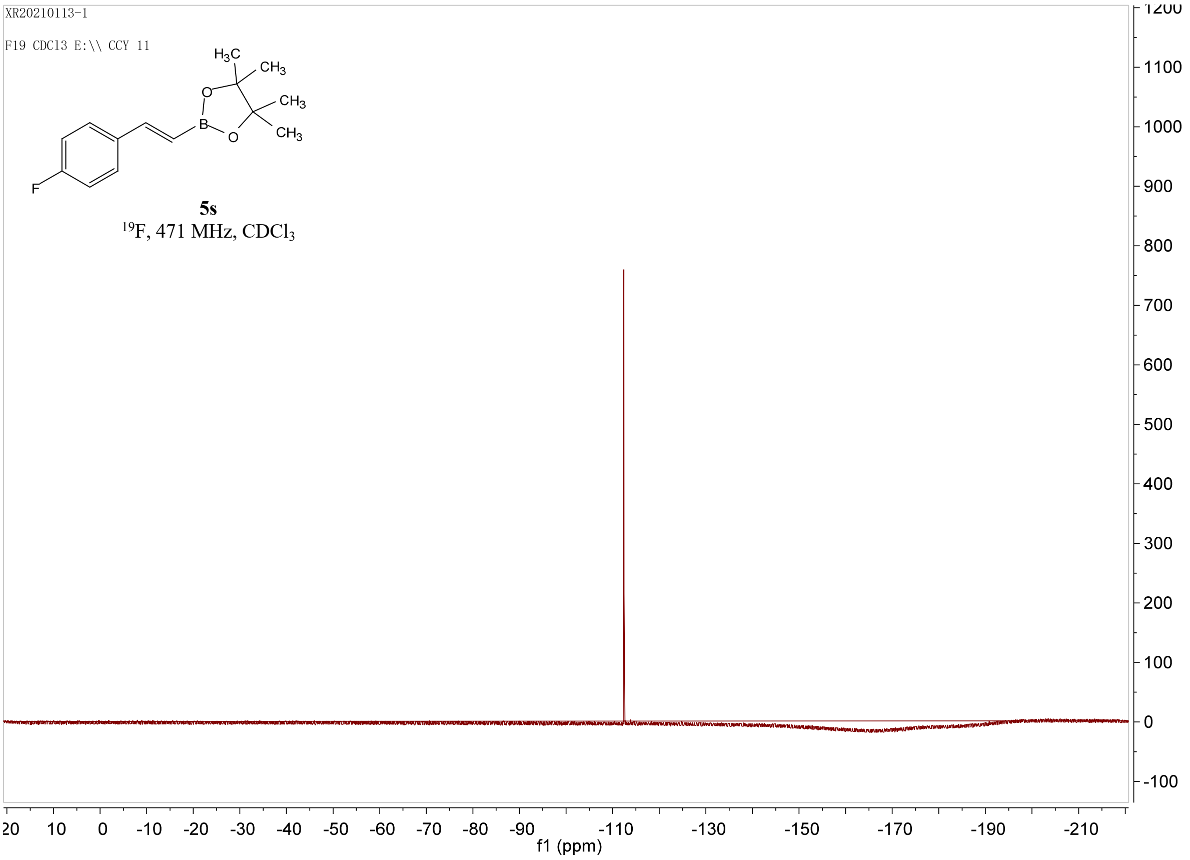
^{13}C, 126 MHz, CDCl$_3$


5s

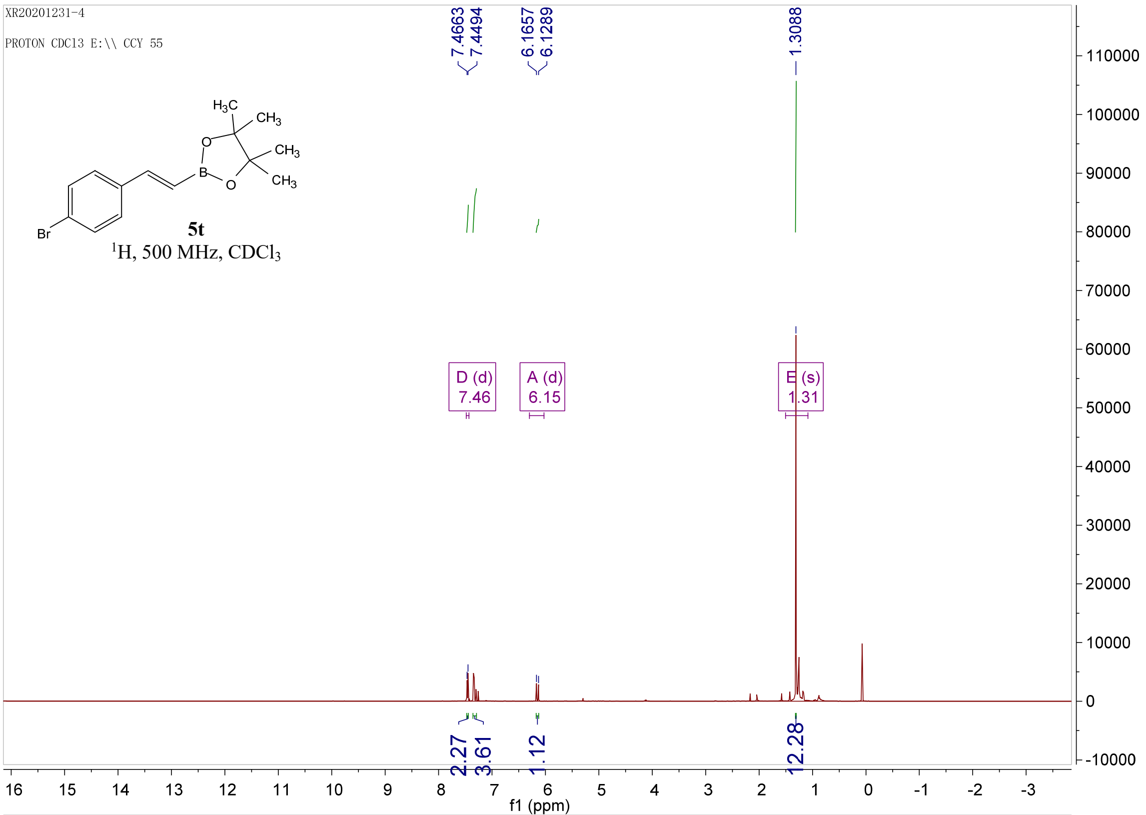
^{1}H, 500 MHz, CDCl$_3$

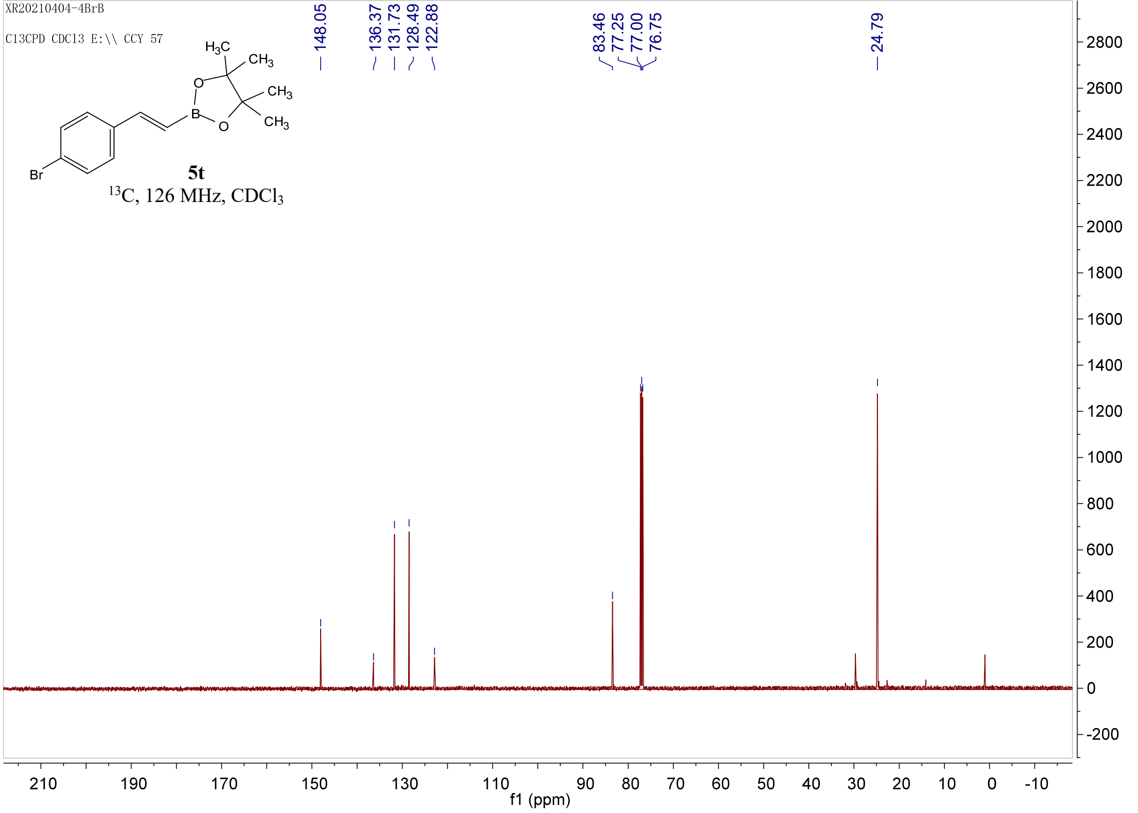

5s

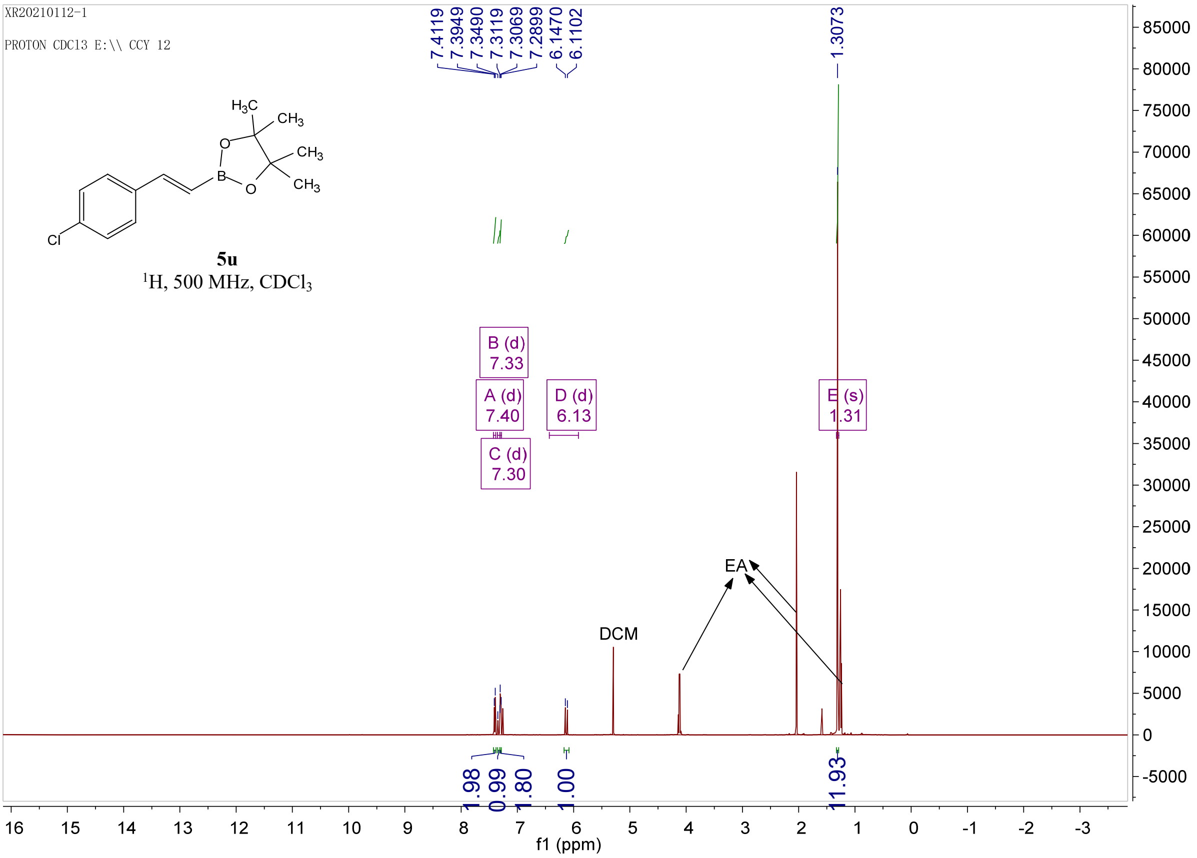
^{13}C, 126 MHz, CDCl$_3$


5s

^{19}F, 471 MHz, CDCl$_3$

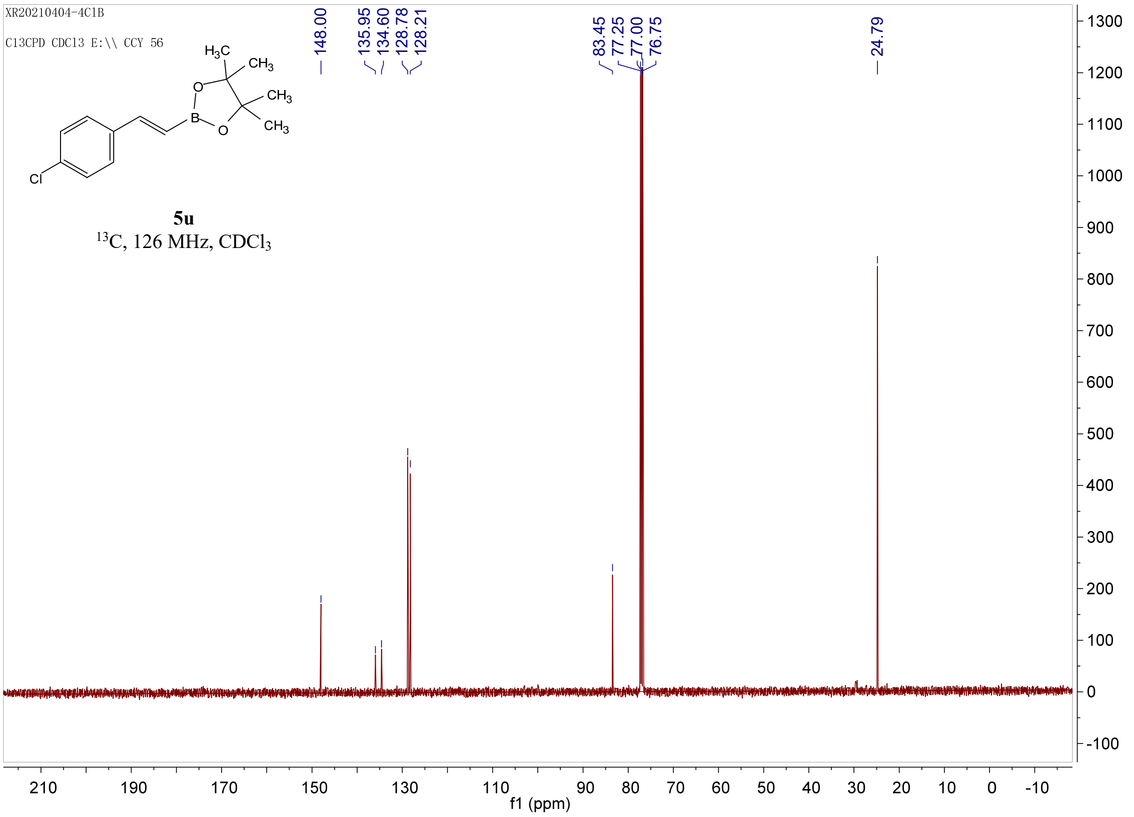

XR20201231-4
PROTON CDCl3 E:\\ CCY 55
7.4663
7.4494
6.1657
6.1289
1.3088
D (d)
7.46
A (d)
6.15
E (s)
1.31
2.27
3.61
1.12
12.28
5t
^{1}H, 500 MHz, CDCl$_3$
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000


XR20210404-4BrB
C13CPD CDCl3 E:\\ CCY 57
148.05
136.37
131.73
128.49
122.88
83.46
77.25
77.00
76.75
24.79
5t
^{13}C, 126 MHz, CDCl$_3$
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200



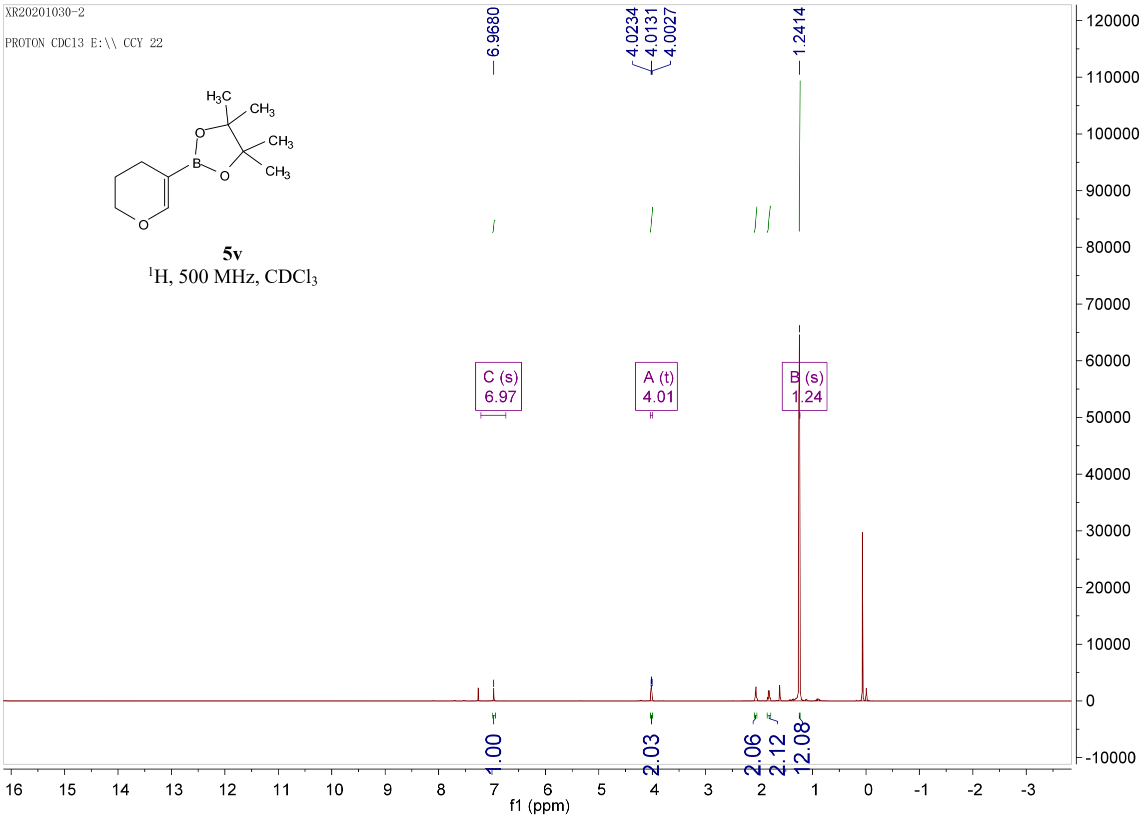
5u

^{1}H, 500 MHz, CDCl$_3$



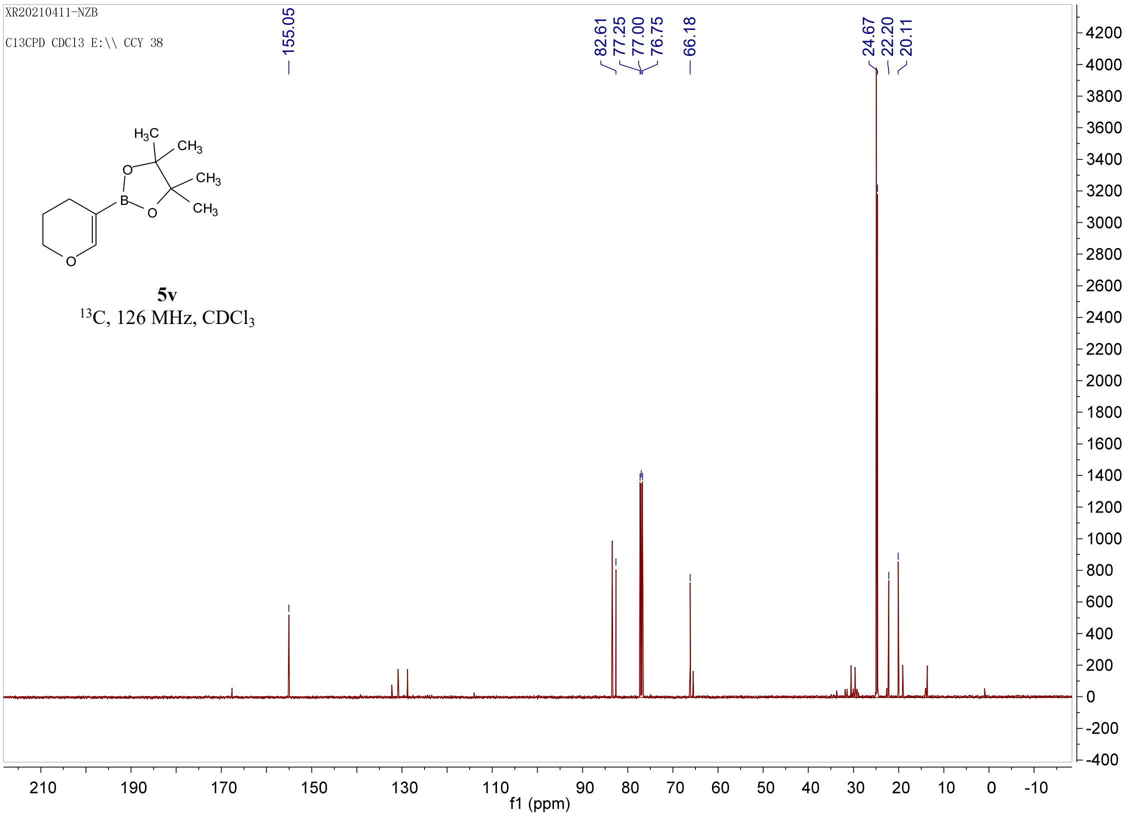
5u

^{13}C, 126 MHz, CDCl$_3$



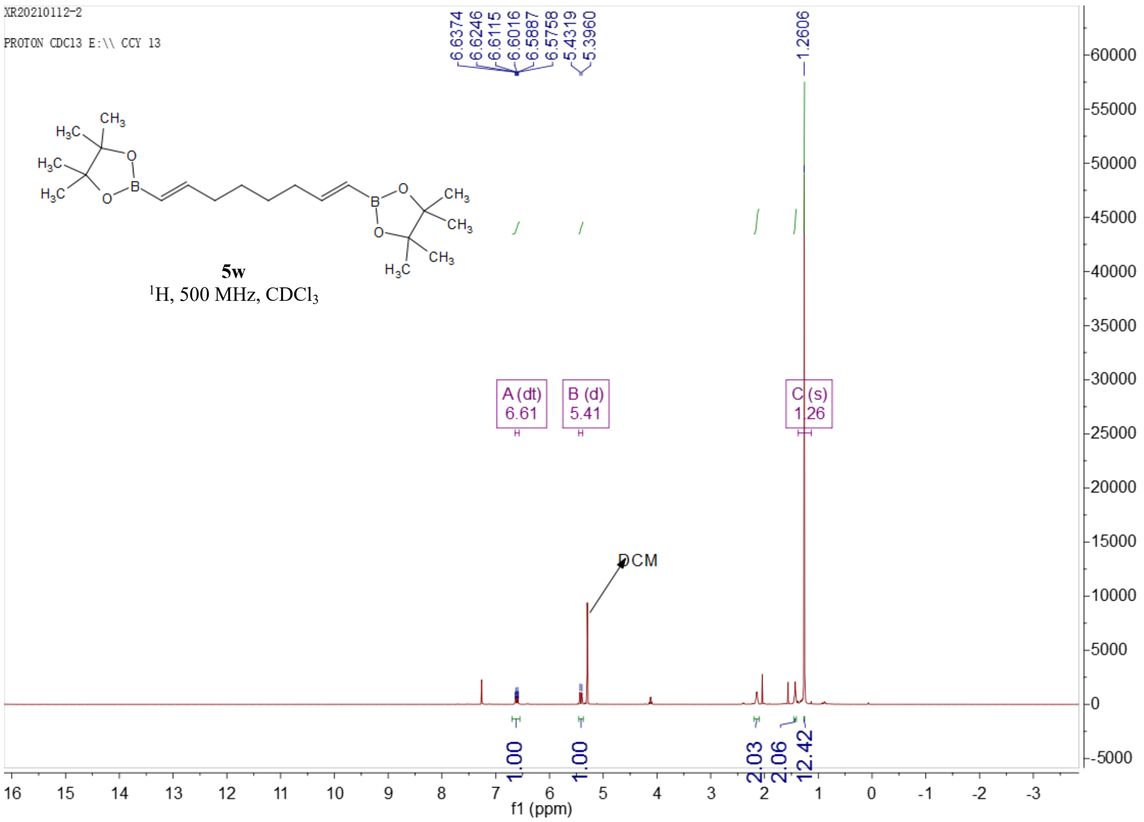
5v

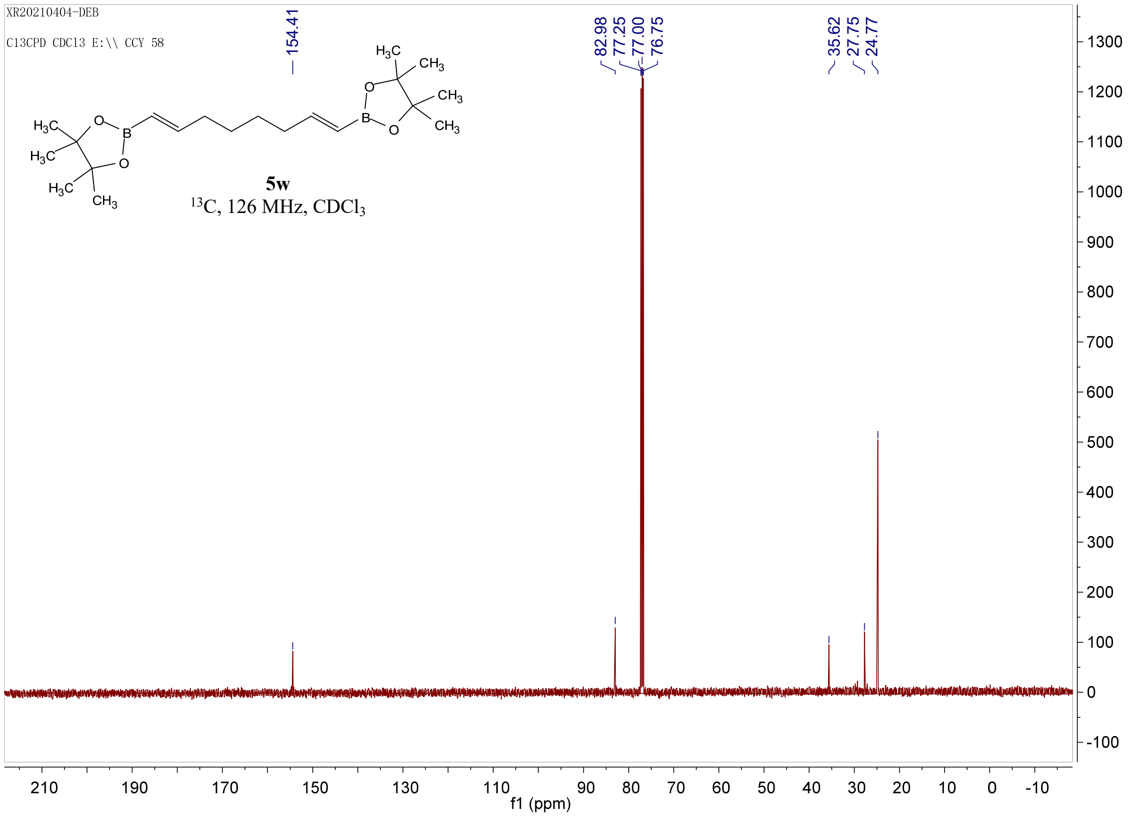
^{1}H, 500 MHz, CDCl$_3$



5v

^{13}C, 126 MHz, CDCl$_3$


XR20210112-2
PROTON CDCl3 E:\\ CCY 13
6.6374
6.6246
6.6115
6.6016
6.5887
6.5758
5.4319
5.3960
1.2606
5w
^{1}H, 500 MHz, CDCl$_3$
A (dt) 6.61
B (d) 5.41
C (s) 1.26
DCM
1.00
1.00
2.03
2.06
12.42
f1 (ppm)


XR20210404-DEB
C13CPD CDCl3 E:\\ CCY 58
154.41
82.98
77.25
77.00
76.75
35.62
27.75
24.77
5w
^{13}C, 126 MHz, CDCl$_3$
f1 (ppm)