

Supporting Information

Rh(III)-catalyzed C–H alkenylation of *NH*-sulfoximine with vinylsilanes

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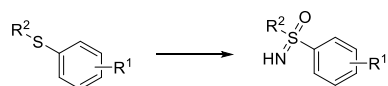
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1. General Methods

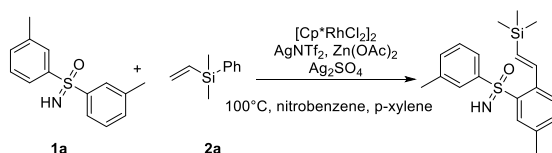
All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. NMR data were obtained for ^1H at 400 MHz, ^{19}F NMR at 376 MHz, and for ^{13}C at 100 or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl_3 solution. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. TLC was performed on glass-backed silica plates. UV detection was monitored at 254 nm. Column chromatography was performed on silica gel (300-400 mesh), eluting with ethyl acetate and petroleum ether. *NH*-sulfoximines were obtained according to the literature procedures.¹⁻³

2. General Procedure for the Synthesis of *NH*-sulfoximines



Add the sulfide (10 mmol), (diacetoxyiodo) benzene (21 mmol, 2.1 equiv.) and ammonium bicarbonate (3.0 equiv) to a flask containing a stirrer bar. Add MeOH (25 mL, 0.4 M) and stir the reaction at room temperature for 3 hours. Remove the solvent under reduced pressure. Subsequent flash column chromatography of the obtained residue on silica gel with pure petroleum ether/ethyl acetate (1:1) / ethyl acetate as eluent.

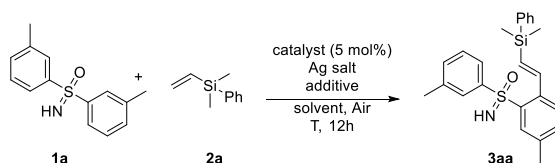
3. General Procedure for the Synthesis of **3aa**



NH-sulfoximines **1a** (24.5mg, 0.1 mmol), vinylsilane **2a** (64.8 mg, 4.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.0 mg, 5 mol %), AgNTf_2 (11.6 mg, 0.3 equiv), $\text{Zn}(\text{OAc})_2$ (9.8 mg, 1.0 equiv), Ag_2SO_4 (46 mg, 1.5 equiv) were stirred in *p*-xylene: Nitrobenzene = 4:1 (1 mL) in preheated oil bath at 100 °C for 4 h, under Air. After completion, using vacuum-rotary and evaporation procedure to remove solvent, and the reaction mixture was purified by flash chromatography (eluent: petroleum ether /EtOAc = 5:1, v/v) to give the product **3aa** as a yellow oil (24.6 mg, 72%).

4. Optimization of Reaction Conditions

Table S1. The effect of oxidative for **3aa**



Entry	Oxidative /equiv.	Yield/%
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1	Ag ₂ SO ₄ /1.5	72%
2	Ag ₂ SO ₄ /1	64%
3	Ag ₂ SO ₄ /2	62%
4	Ag ₂ O/1.5	46%
5	Ag ₂ CO ₃ /1.5	Mess
6	CuSO ₄ /1.5	Mess
7	Cu(OAc) ₂ /1.5	Mess
8	/	48%

^aReaction conditions: **1a** (0.1 mmol), **2a** (4.0 equiv), [Cp*RhCl₂]₂ (5 mol %), AgNTf₂ (0.3 equiv), Zn(OAc)₂ (1.0 equiv), oxidative (1.5 equiv), *p*-xylene: Nitrobenzene = 4:1 (1 mL) at 100 °C for 4 h, under Air.

Table S2. The effect of solvents for **3aa**

Entry	Solvent	Yield/%	Entry	Solvent	Yield/%
1	PhNO ₂ : xylene	71%	9	<i>t</i> -AmylOH	Messy
2	PhNO ₂	60%	10	MeOH	NR
3	xylene	45%	11	<i>i</i> -PrOH	trace
4	toluene	23%	12	CHCl ₃	32%
5	DCE	42%	13	MeCN	trace
6	TFE	32%	14	PhNO ₂ :DCE	41%
7	HFIP	27%	15	PhNO ₂ : DCM	35%
8	DMF	29%	16	PhNO ₂ :TFE	33%

^aReaction conditions: **1a** (0.1 mmol), **2a** (4.0 equiv), [Cp*RhCl₂]₂ (5 mol %), AgNTf₂ (0.3 equiv), Zn(OAc)₂ (1.0 equiv), Ag₂SO₄ (1.5 equiv), other solvents: Nitrobenzene = 4:1 (1 mL) at 100 °C for 4 h, under Air.

Table S3. The effect of Ag salts for **3aa**

Entry	Additive/equiv.	Yield/%
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1	AgNTf ₂ /0.2	69%
2	AgNTf ₂ /0.1	42%
3	AgNTf ₂ /0.4	54%
4	AgNTf ₂ /0.3	72%
5	AgSbF ₆ /0.2	28%
6	AgBF ₄ /0.2	NR
7	AgOTf/0.2	36%
8	AgSO ₃ CH ₃ /0.2	NR
9	/	NR

^aReaction conditions: follows: **1a** (0.1 mmol), **2a** (4.0 equiv), [Cp*RhCl₂]₂ (5 mol %), Ag salt, Zn(OAc)₂ (1.0 equiv), Ag₂SO₄ (1.5 equiv), *p*-xylene: Nitrobenzene = 4:1 (1 mL) at 100 °C for 4 h, under Air.

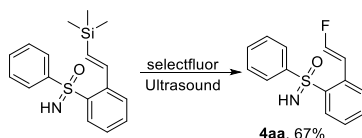
Table S4. The effect of bases for **3aa**

Entry	Additive/ equiv.	Yield/%
1	AgNTf ₂ /0.3 + MesCO ₂ Na/0.1	39%
2	AgNTf ₂ /0.3 + Na ₂ HPO ₄ /0.5	Trace
3	AgNTf ₂ /0.3 + NaOPiv·H ₂ O/0.5	Trace
5	AgNTf ₂ /0.3 + NaOAc/0.5	42%
6	AgNTf ₂ /0.3 + Na ₂ S ₂ O ₈ /0.5	32%
7	AgNTf ₂ /0.3 + NaOH/0.5	43%
8	AgNTf ₂ /0.3 + Na ₂ S/0.5	NR
9	AgNTf ₂ /0.3 + NaF/0.5	41%
10	AgNTf ₂ /0.3 + NaI/0.5	NR
11	AgNTf ₂ /0.3 + AgOAc/0.5	42%
12	AgNTf ₂ /0.3 + Zn(OAc) ₂ /0.5	44%
13	AgNTf ₂ /0.3 + CsOAc/0.5	37%
14	AgNTf ₂ /0.3 + KOAc/0.5	Trace
15	AgNTf ₂ /0.3 + LiOH/0.5	NR
16	AgNTf ₂ /0.3 + TBAB/0.5	NR
17	AgNTf ₂ /0.3 + Zn(OAc) ₂ /1	48%

^aReaction conditions: **1a** (0.1 mmol), **2a** (4.0 equiv), [Cp*RhCl₂]₂ (5 mol %), AgNTf₂ (0.3 equiv.), *p*-xylene: Nitrobenzene = 4:1 (1 mL) at 100 °C for 4 h, under Air.

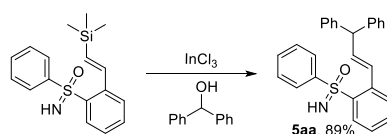
5. Synthetic Applications of Corresponding Product

5.1 Procedure for the synthesis of compound **4aa**:



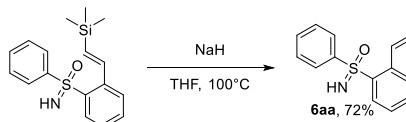
To a solution of the appropriate alkenyltrimethylsilane compound (0.03 mmol) in dry CH_3CN (0.3 mL) was added selectfluor (0.03 mmol 10.2 mg). The reaction mixture was irradiated with ultrasound for 25–35 min. The mixture was filtered and poured into saturated aqueous sodium hydrogen carbonate (2 mL) and extracted with diethyl ether (2 mL $\times$ 2). The organic layer was separated, washed with brine (5 mL), dried over MgSO_4 , filtered and the solvent was removed. The product was purified on a silica column eluted with a 1:8 mixture of dichloromethane and hexane. to give the product **4aa** as a yellow oil (5.2mg, 67%).

5.2 Procedure for the synthesis of compound 5aa:



To a mixture of InCl_3 (0.01 mmol) and benzhydrol (0.05 mmol, 1equiv.) was added **3ac** (0.1 mmol, 2equiv.) in dichloroethane (0.5 mL) under Ar. The reaction mixture was stirred at 70°C for 8h. The resulting mixture was poured into EA (10 mL) and aqueous NaHCO_3 (10 mL). The solution was extracted with EA and the organic layer was dried over Na_2SO_4 . The evaporation of the ether solution gave the crude product, purified by column chromatography to afford the desired product **5aa** as clear oil (18 mg, 89%).

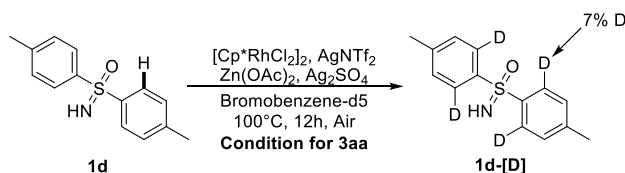
5.3 Procedure for the synthesis of compound 6aa:

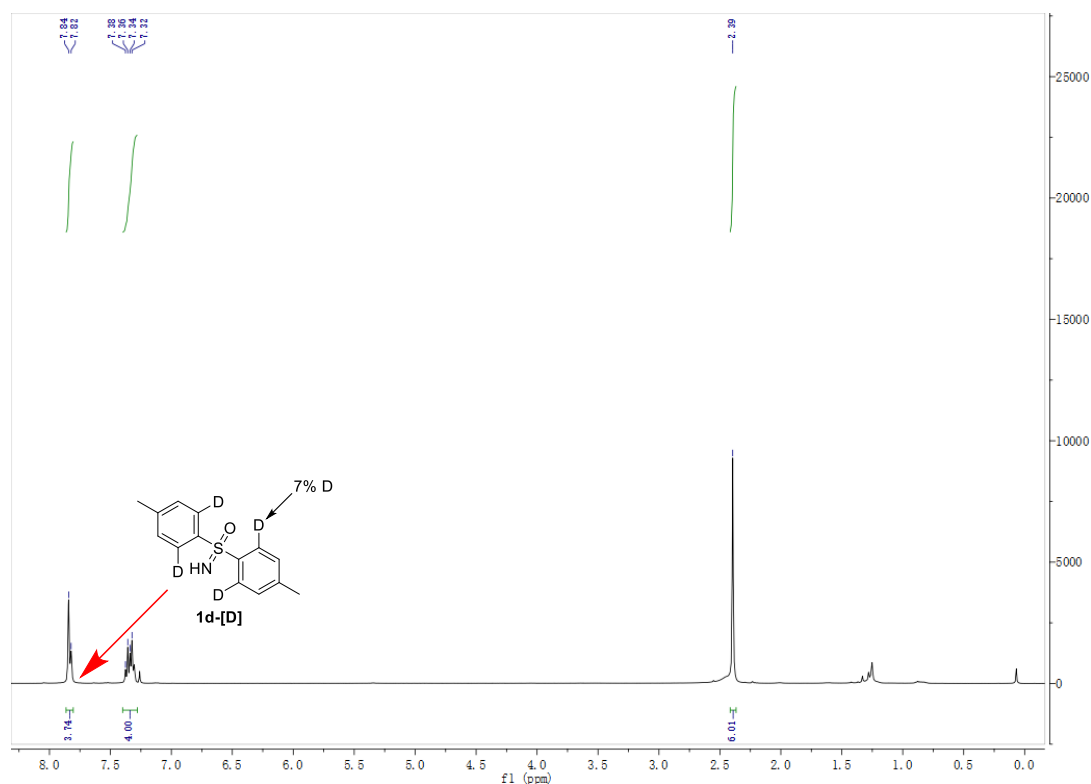


To a mixture of NaH (0. 1 mmol) was added **3ac** (0.1 mmol) in THF (0.5 mL) under Ar. The reaction mixture was stirred at 100°C for 18h. The resulting mixture was poured into EA (10 mL) and aqueous NaHCO_3 (10 mL). The solution was extracted with EA and the organic layer was dried over Na_2SO_4 . The evaporation of the ether solution gave the crude product, purified by column chromatography to afford the desired product **6aa** as yellow solid (18 mg, 72%).

6. Control Experiments and Mechanistic Studies

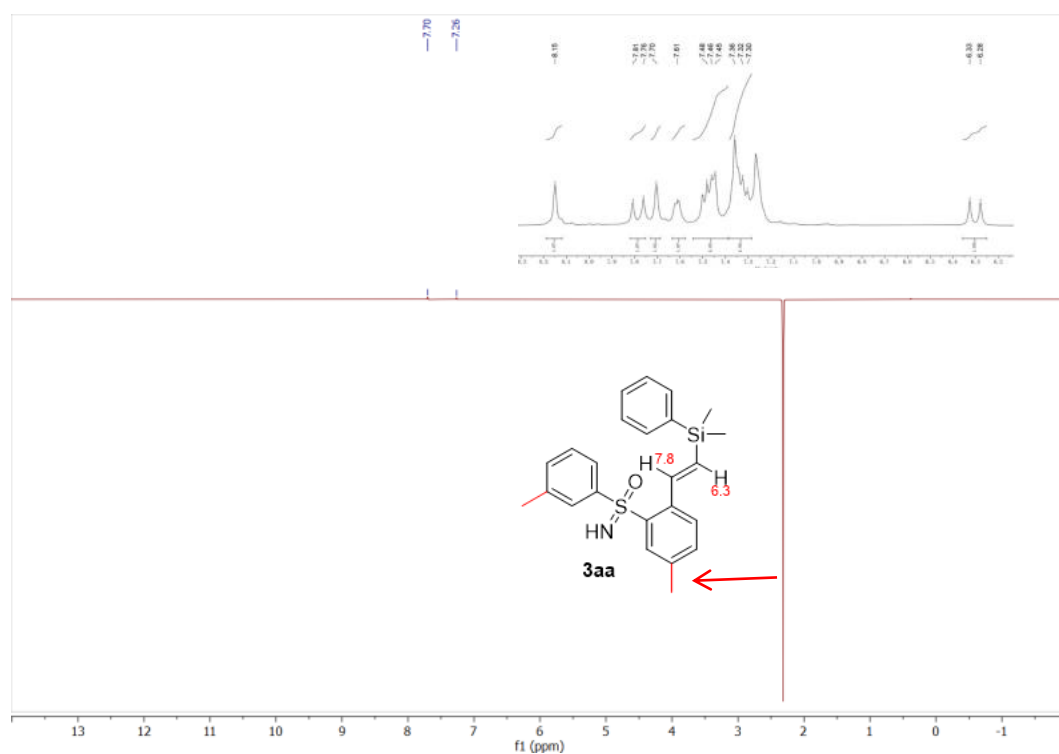
6.1 H/D exchange experiments



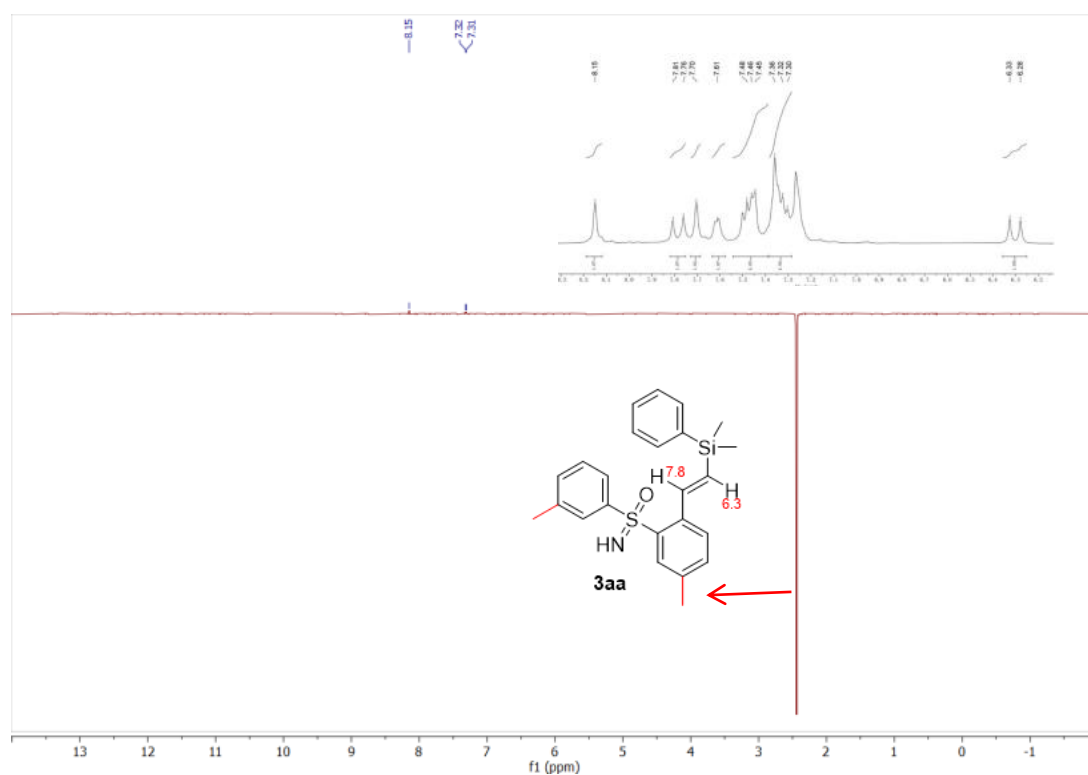


Deuterium-labelling experiments were performed to probe the mechanism of this coupling reaction. Firstly, we applied the condition of affording **3aa** to explore H/D exchange experiment. *NH*-sulfoximines **1a** (24.5 mg, 0.1 mmol), vinylsilane **2a** (64.8 mg, 4.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.0 mg, 5 mol %), AgNTf_2 (11.6 mg, 0.3 equiv), $\text{Zn}(\text{OAc})_2$ (9.8 mg, 1.0 equiv), Ag_2SO_4 (46 mg, 1.5 equiv) were stirred in Bromobenzene- d_5 in preheated oil bath at 100 $^\circ\text{C}$ for 4 h, under Air. After completion, the reaction mixture was purified by flash chromatography eluting to give the product **1a**-[D] as a yellow oil. The deuterium rate (7%) was obtained from ^1H NMR. Deuterium was observed at *ortho*-positions of phenyl ring, which indicated the possibility of the reaction pathway via *ortho* C–H activation.

6.2 NOE of **3aa**

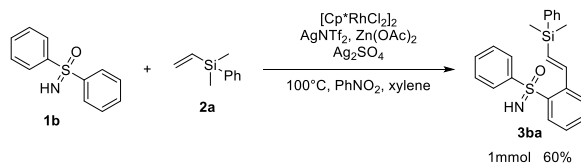


NOE OF δ 2.32



NOE OF δ 2.44

6.3 Scale-up experiments



NH-sulfoximines **1b** (217mg, 1 mmol), vinylsilane **2a** (648 mg, 4.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (15 mg, 2.5 mol %), AgNTf_2 (116 mg, 0.3 equiv), $\text{Zn}(\text{OAc})_2$ (98 mg, 1.0 equiv), Ag_2SO_4 (460 mg, 1.5 equiv) were stirred in p -xylene: Nitrobenzene = 4:1 (10 mL) in preheated oil bath at 100°C for 16 h, under Air. After completion, using vacuum-rotary and evaporation procedure to remove solvent, and the reaction mixture was purified by flash chromatography (eluent: petroleum ether /EtOAc = 5:1, v/v) to give the product **3aa** as a yellow oil (226 mg, 60%).

References

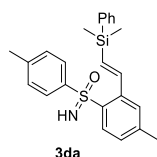
- [1] Y. M. Li, C. P. Nie, H. F. Wang, X. Y. Li, F. Verpoort, C. Y. Duan, *Eur. J. Org. Chem.*, **2011**, 7331.
- [2] M. Zenzola, R. Doran, L. Degennaro, R. Luisi, J. A. Bull, *Angew. Chem. Int. Ed.*, 2016, **55**, 7203.
- [3] M. Harmata, N. K. O. Rayanil, M. G. Gomes, P. Zheng, N. L. Calkins, S. Y. Kim, Y. Fan, V. Bumbu, D. Y. Lee, S. Wacharasindhu, X. Hong, *Org. Lett.*, 2005, **7**, 143.

7. Characterization Data and NMR Spectra of Sulfonylimine Silanes Derivatives

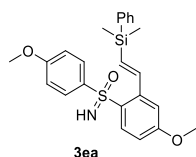
(E)-(2-(2-(dimethyl(phenyl)silyl)vinyl)-5-methylphenyl)(imino)(m-tolyl)-sulfanone (**3aa**). 29.1 mg, 72% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 7.78 (d, $J = 18.8$ Hz, 1H), 7.70 (s, 1H), 7.61 (d, $J = 6.8$ Hz, 1H), 7.47 (dd, $J = 15.4, 7.2$ Hz, 4H), 7.34 (d, $J = 14.2$ Hz, 5H), 6.30 (d, $J = 18.9$ Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 141.5, 139.3, 139.0, 138.3, 138.2, 135.7, 133.9, 133.8, 133.2, 131.5, 129.4, 129.1, 128.7, 128.3, 127.8, 124.9, 21.4, -2.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{28}\text{NOSSi}^+$ 406.1655; Found 406.1624.

(E)-(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)(imino)(phenyl)-sulfanone (**3ba**). 25.3 mg, 68% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.33 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.84 – 7.76 (m, 3H), 7.61 – 7.56 (m, 1H), 7.49 (dt, $J = 8.6, 2.4$ Hz, 5H), 7.41 – 7.32 (m, 5H), 6.34 (d, $J = 18.9$ Hz, 1H), 0.40 (d, $J = 1.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 141.7, 139.4, 138.7, 137.9, 134.0, 133.1, 133.1, 132.4, 129.2, 129.1, 128.8, 128.5, 128.0, 127.9, 127.8, -2.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{24}\text{NOSSi}^+$ 378.1342; Found 378.1347

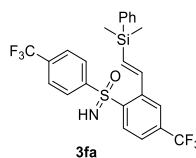
(E)-(2-(2-(E)-(5-chloro-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)(3-chlorophenyl)(imino)-sulfanone (**3ca**). 10.2 mg, 23% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 2.1$ Hz, 1H), 7.85 (t, $J = 2.0$ Hz, 1H), 7.70 (d, $J = 18.9$ Hz, 1H), 7.65 – 7.60 (m, 1H), 7.53 – 7.42 (m, 5H), 7.36 (td, $J = 4.7, 2.3$ Hz, 3H), 6.34 (d, $J = 18.8$ Hz, 1H), 0.39 (d, $J = 2.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 139.2, 139.0, 136.5, 136.1, 134.0, 133.5, 133.1, 132.8, 132.3, 130.6, 129.7, 129.1, 128.9, 128.3, 128.1, 126.9, 126.8, 125.0, 123.4, 121.7, -3.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{NOSSi}^+$ 446.0563; Found 446.0578



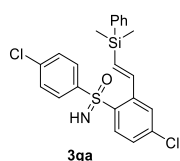
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)-4-methylphenyl(imino)(p-tolyl)-sulfanone (**3da**). 26.3 mg, 65% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 19.0 Hz, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.37 (q, J = 4.2 Hz, 4H), 7.23 – 7.20 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 18.9 Hz, 1H), 2.35 (d, J = 12.3 Hz, 6H), 0.42 – 0.33 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 143.0, 142.0, 139.9, 138.5, 138.1, 137.01, 133.9, 132.4, 130.0, 129.4, 129.2, 129.0, 128.7, 127.9, 127.8, 124.9, 21.5, 21.4, -2.70. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{24}\text{H}_{28}\text{NOSSi}^+$ 406.1655; Found 406.1673



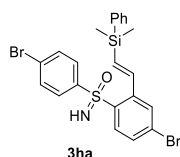
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)-4-methoxyphenyl(imino)(4-methoxyphenyl)-sulfanone (**3ea**). 25.0 mg, 57% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 18.8 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.53 – 7.47 (m, 2H), 7.41 – 7.35 (m, 3H), 7.03 (d, J = 2.7 Hz, 1H), 6.89 (dd, J = 8.9, 2.7 Hz, 1H), 6.81 – 6.77 (m, 2H), 6.31 (d, J = 18.8 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 162.5, 142.1, 140.5, 138.0, 134.8, 134.0, 132.7, 132.3, 131.4, 129.8, 129.2, 127.9, 113.9, 113.7, 112.7, 55.6, -2.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{24}\text{H}_{22}\text{F}_6\text{NO}_3\text{SSi}^+$ 514.1090; Found 514.1108



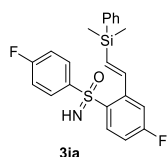
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)-4-(trifluoromethyl)phenyl(imino)(4-(trifluoromethyl)phenyl)-sulfanone (**3fa**). 20 mg, 39% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 9.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.43 (d, J = 7.2 Hz, 3H), 6.45 (d, J = 18.9 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 140.99, 138.9, 138.7, 136.0, 135.3, 134.1 (d, $J_{\text{C-F}}$ = 22.0 Hz), 133.3 (d, $J_{\text{C-F}}$ = 22.0 Hz), 132.9, 129.0, 128.5, 127.4, 127.0, 125.0, 124.7, 123.6, 123.0, 121.2, -3.9. ^{19}F NMR (376 MHz, CDCl_3) δ -63.17 (d, J = 45.1 Hz). HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{24}\text{H}_{22}\text{F}_6\text{NOSSi}^+$ 514.1090; Found 514.2001



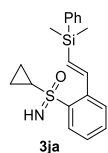
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl(4-chlorophenyl)(imino)-sulfanone (**3ga**). 19.1 mg, 43% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 8.27 – 8.22 (m, 1H), 7.78 – 7.70 (m, 3H), 7.50 (d, J = 7.7 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.37 (dd, J = 7.7, 3.5 Hz, 2H), 7.31 (q, J = 4.2 Hz, 3H), 7.26 (s, 1H), 6.26 (d, J = 18.9 Hz, 1H), 0.32 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 140.8, 140.3, 139.7, 139.2, 137.7, 135.2, 133.9, 130.8, 129.8, 129.4, 129.3, 129.1, 128.5, 128.0, 126.0, -2.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{NOSSi}^+$ 446.0563; Found 446.0572



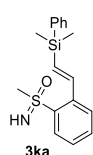
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl(4-bromophenyl)(imino)-sulfanone (**3ha**). 23 mg, 43% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.5 Hz, 1H), 7.69 (dd, J = 10.4, 8.4 Hz, 2H), 7.57 (dd, J = 13.4, 7.4 Hz, 3H), 7.50 (dd, J = 6.8, 2.6 Hz, 2H), 7.44 (d, J = 8.0 Hz, 5H), 6.38 (d, J = 18.9 Hz, 1H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 141.7, 141.5, 139.5, 138.6, 136.7, 135.3, 133.5, 132.8, 132.3, 132.1, 130.8, 130.7, 129.6, 129.4, 129.0, -1.44. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{21}\text{Br}_2\text{NOSSi}^+$ 533.9553; Found 533.9642



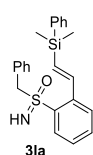
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)-4-fluorophenyl(4-fluorophenyl)(imino)-sulfanone (**3ia**). 18.6mg, 45% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 8.33 (dd, J = 8.9, 5.6 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.51 – 7.48 (m, 2H), 7.44 – 7.38 (m, 3H), 7.10 (m, J = 8.9, 7.5, 2.7 Hz, 1H), 6.99 (t, J = 8.5 Hz, 2H), 6.38 (d, J = 18.8 Hz, 1H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0 (d, $J_{\text{C-F}}$ = 46.0 Hz), 164.4 (d, $J_{\text{C-F}}$ = 46.0 Hz), 141.7, 140.6, 138.4, 137.3, 134.9, 134.2, 133.0, 132.2, 130.5, 129.4, 128.4, 128.0, 116.1, 116.0, 115.4, 115.2, -2.8. ^{19}F NMR (376 MHz, CDCl_3) δ -105.42 (d, J = 48.1 Hz). HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{22}\text{F}_2\text{NOSSi}^+$ 414.1154; Found 414.1160



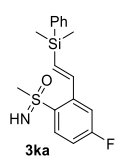
(E)-cyclopropyl(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)(imino)-sulfanone (**3ja**). 19.4 mg, 57% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 19.0 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.54 (d, J = 1.4 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.24 (q, J = 2.7 Hz, 3H), 6.44 (d, J = 19.0 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.27 – 1.22 (m, 1H), 0.90 (m, 1H), 0.84 – 0.79 (m, 1H), 0.68 – 0.61 (m, 1H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 139.9, 138.9, 138.2, 133.8, 133.6, 132.8, 129.2, 128.90, 128.4, 128.0, 33.6, 5.91, 5.70, -2.63. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{24}\text{NOSSi}^+$ 342.1342; Found 342.1355



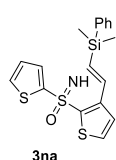
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl(imino)(methyl)-sulfanone (**3ka**). 17.6 mg, 56% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 6:1). ^1H NMR (400 MHz, CDCl_3) δ 8.16 – 8.04 (m, 2H), 7.68 (dd, J = 7.8, 1.4 Hz, 1H), 7.57 (m, 3H), 7.43 (dd, J = 7.6, 1.4 Hz, 1H), 7.38 (dd, J = 4.1, 2.2 Hz, 3H), 6.60 (d, J = 19.0 Hz, 1H), 3.04 (s, 3H), 0.48 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.0, 140.0, 138.8, 138.0, 134.8, 133.8, 133.1, 129.3, 128.8, 128.4, 128.14, 128.0, 44.8, -2.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{22}\text{NOSSi}^+$ 316.1186; Found 316.1190



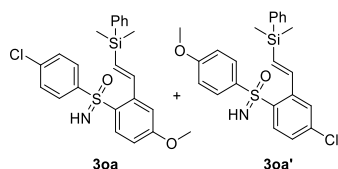
(E)-benzyl(2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)(imino)-sulfanone (**3la**). 17.2 mg, 44% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 7:1). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 19.0 Hz, 1H), 7.81 (dd, J = 8.0, 1.4 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.53 (dd, J = 6.5, 3.0 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.28 – 7.21 (m, 2H), 7.19 (dd, J = 5.6, 2.2 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.53 (d, J = 19.0 Hz, 1H), 4.28 (d, J = 13.2 Hz, 1H), 4.19 (d, J = 13.2 Hz, 1H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 139.5, 138.0, 137.2, 134.4, 133.9, 133.3, 131.1, 130.3, 129.3, 128.7, 128.5, 128.3, 128.2, 128.0, 63.1, -2.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{23}\text{H}_{26}\text{NOSSi}^+$ 392.1499; Found 392.1487



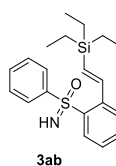
(E)-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl(imino)(methyl)-sulfanone (**3ma**). 18.3 mg, 55% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 6:1). ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.02 (m, 2H), 7.61 – 7.53 (m, 2H), 7.43 – 7.31 (m, 4H), 7.08 (m, 1H), 6.65 (s, 1H), 3.02 (s, 3H), 0.48 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4 (d, $J_{\text{C-F}}$ = 46.0 Hz), 142.4 (d, $J_{\text{C-F}}$ = 101.0 Hz), 140.5 (d, $J_{\text{C-F}}$ = 101.0 Hz), 137.6, 136.3, 133.8, 133.8, 132.0, 131.9, 129.4, 128.0, 128.0, 127.9, 115.1, 115.0, 114.8, 45.0, -2.8. ^{19}F NMR (376 MHz, CDCl_3) δ -105.83 (d, J = 7.5 Hz). HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{21}\text{FNOSSi}^+$ 334.1092; Found 334.1110



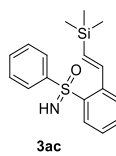
(E)-3-(2-(dimethyl(phenyl)silyl)vinyl)thiophen-2-yl(imino)(thiophen-2-yl)-sulfanone (**3na**). 12.8 mg, 33% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 19.2 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.44 (s, 1H), 7.39 (dd, J = 5.1, 1.9 Hz, 3H), 7.29 (d, J = 5.5 Hz, 2H), 7.00 (dd, J = 5.0, 3.8 Hz, 1H), 6.49 (d, J = 19.1 Hz, 1H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 145.3, 140.9, 140.7, 139.6, 137.4, 135.8, 135.3, 134.8, 133.2, 132.6, 131.8, 131.1, 130.8, 129.7, 129.1, -0.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+ \text{C}_{18}\text{H}_{20}\text{NOS}_3\text{Si}^+$ 390.0471; Found 390.0478



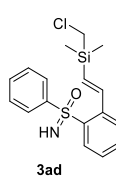
(E)-(4-chlorophenyl)(2-(2-(dimethyl(phenyl)silyl)vinyl)-4-methoxyphenyl)(imino)-sulfanone + (E)-(4-chloro-2-(2-(dimethyl(phenyl)silyl)vinyl)phenyl)(imino)(4-methoxyphenyl)-sulfanone (**3oa+3oa'**). 21.6 mg, 49% total yield of the mixture (3oa:3oa'=1:1); Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ^1H NMR (400 MHz, CDCl_3) δ 8.46 (t, J = 8.3 Hz, 1H), 8.06 – 7.89 (m, 3H), 7.77 – 7.69 (m, 3H), 7.62 (t, J = 5.7 Hz, 3H), 7.49 (d, J = 7.8 Hz, 1H), 7.22 – 7.11 (m, 1H), 7.03 (d, J = 8.5 Hz, 1H), 4.07 (s, 2H), 4.00 (s, 2H), 0.65 (d, J = 5.6 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 161.8, 140.7, 139.8, 139.6, 139.0, 138.0, 137.7, 137.5, 136.6, 136.6, 132.9, 130.7, 130.0, 129.5, 129.0, 128.4, 128.3, 128.3, 128.0, 128.0, 127.3, 127.0, 126.9, 126.7, 126.2, 113.9, 113.0, 112.7, 111.9, 54.6, 54.6, -3.7, -3.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{25}\text{ClNO}_2\text{SSi}^+$ 422.1058; Found 422.1069



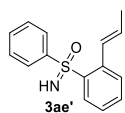
(E)-imino(phenyl)(2-(2-(triethylsilyl)vinyl)phenyl)-sulfanone (**3ab**). 19.3 mg, 54% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, J = 8.0, 1.4 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.76 (d, J = 19.0 Hz, 1H), 7.59 (dd, J = 7.8, 1.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.42 (m, 3H), 6.24 (d, J = 19.0 Hz, 1H), 0.93 (t, J = 7.9 Hz, 9H), 0.61 (d, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.7, 141.2, 139.4, 139.0, 133.0, 132.4, 132.2, 129.3, 129.1, 128.8, 128.4, 127.8, 127.6, 124.8, 7.4, 3.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+ \text{C}_{20}\text{H}_{28}\text{NOSSi}^+$ 358.1655; Found 358.1660



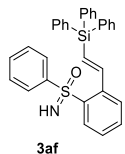
(E)-imino(phenyl)(2-(2-(trimethylsilyl)vinyl)phenyl)-sulfanone (**3ac**). 18.3 mg, 58% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ^1H NMR (400 MHz, CDCl_3) δ 8.31 (dd, J = 8.0, 1.3 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.74 (d, J = 18.9 Hz, 1H), 7.64 (dd, J = 4.9, 2.6 Hz, 1H), 7.54 (dd, J = 6.2, 1.5 Hz, 2H), 7.50 (dd, J = 7.2, 1.3 Hz, 2H), 7.47 – 7.43 (m, 4H), 6.20 (d, J = 18.9 Hz, 1H), 0.10 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 141.5, 140.8, 140.4, 136.8, 134.4, 133.8, 130.4, 130.2, 129.8, 129.2, 0.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+ \text{C}_{17}\text{H}_{22}\text{NOSSi}^+$ 316.1186; Found 316.1200



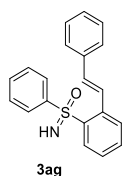
(E)-(2-(2-((chloromethyl)dimethylsilyl)vinyl)phenyl)(imino)(phenyl)-sulfanone (**3ad**). 21.7 mg, 62% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ^1H NMR (400 MHz, CDCl_3) δ 8.21 – 8.16 (m, 1H), 7.85 (d, J = 43.1 Hz, 2H), 7.73 (d, J = 19.1 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.32 (s, 2H), 6.06 (d, J = 19.0 Hz, 1H), 2.65 (s, 2H), 0.12 (d, J = 1.6 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 138.6, 137.3, 132.1, 131.5, 129.4, 127.8, 127.4, 127.2, 126.7, 29.1, -5.53, -5.54. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+ \text{C}_{17}\text{H}_{21}\text{ClNOSSi}^+$ 350.0796; Found 350.0802



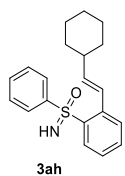
((E)-imino(phenyl)(2-(prop-1-en-1-yl)phenyl)-sulfanone (**3ae'**). 7.7 mg, 30% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 4:1). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.53 – 7.44 (m, 4H), 7.43 – 7.35 (m, 2H), 5.92 – 5.79 (m, 1H), 1.79 (dd, *J* = 6.6, 1.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 139.2, 138.3, 133.0, 132.4, 130.4, 128.8, 128.7, 128.6, 128.0, 127.0, 18.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₆NOS⁺ 258.0947; Found 258.0942



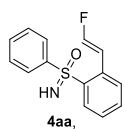
(E)-imino(phenyl)(2-(2-(triphenylsilyl)vinyl)phenyl)-sulfanone (**3af**). 26 mg, 52% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 3:1). ¹H NMR (400 MHz, CDCl₃) δ 8.33 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.81 (d, *J* = 18.8 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.50 (m, 7H), 7.47 – 7.44 (m, 4H), 7.42 (s, 4H), 7.40 (s, 4H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 18.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 142.5, 139.9, 138.3, 136.1, 133.9, 133.1, 132.1, 129.8, 129.3, 128.9, 128.5, 128.5, 128.4, 128.0, 127.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₂H₂₈NOSSi⁺ 502.1655; Found 502.1643



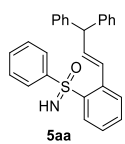
(E)-imino(phenyl)(2-styrylphenyl)-sulfanone (**3ag**). 22.6 mg, 71% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 6:1). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.92 (d, *J* = 16.2 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.25 (s, 1H), 7.19 – 7.15 (m, 3H), 7.11 (dd, *J* = 7.1, 1.7 Hz, 1H), 6.55 (d, *J* = 16.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 142.5, 140.0, 137.6, 136.9, 133.1, 132.6, 132.5, 129.6, 129.2, 128.8, 128.3, 128.2, 128.0, 127.9, 127.6, 126.9, 125.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₁₈NOS⁺ 320.1104; Found 320.1096



(E)-2-(2-(cyclohexylvinyl)phenyl)(imino)(phenyl)-sulfanone (**3ah**). 14.3 mg, 44% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 6:1). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.38 (m, 6H), 7.22 (d, *J* = 15.8 Hz, 1H), 5.83 (dd, *J* = 15.8, 6.8 Hz, 1H), 3.73 – 3.42 (m, 1H), 2.02 (d, *J* = 6.0 Hz, 2H), 1.77 – 1.68 (m, 2H), 1.53 – 1.43 (m, 2H), 1.27 (m, 2H), 1.20 – 1.13 (m, 1H), 1.05 (td, *J* = 12.0, 3.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 138.4, 133.0, 132.4, 128.9, 128.7, 128.5, 128.0, 127.8, 126.9, 126.2, 124.2, 41.3, 37.1, 32.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₄NOS⁺ 326.1573; Found 326.1564

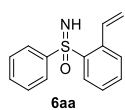


(E)-2-(2-(2-fluorovinyl)phenyl)(imino)(phenyl)-sulfanone (**4aa**). 5.2 mg, 67% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 8.29 – 8.22 (m, 1H), 7.87 (m, 2H), 7.68 – 7.45 (m, 2H), 7.40 (m, 4H), 6.83 – 6.36 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.9 (d, *J*_{C-F} = 175.0 Hz), 148.1, 133.2, 132.7 (d, *J*_{C-F} = 15.0 Hz), 132.7, 129.7, 129.4, 128.9, 128.07, 127.8, 111.8, 107.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -121.58 (d, *J* = 3 Hz). HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₃FNOS⁺ 262.0696; Found 262.0702

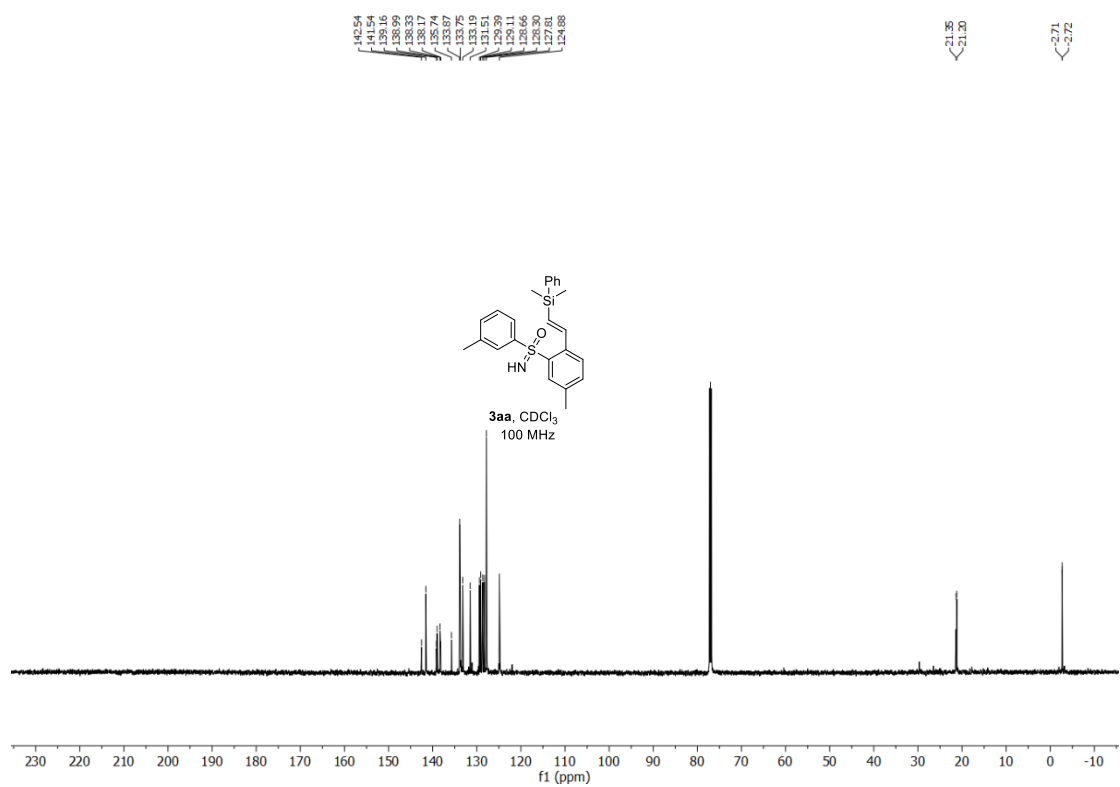
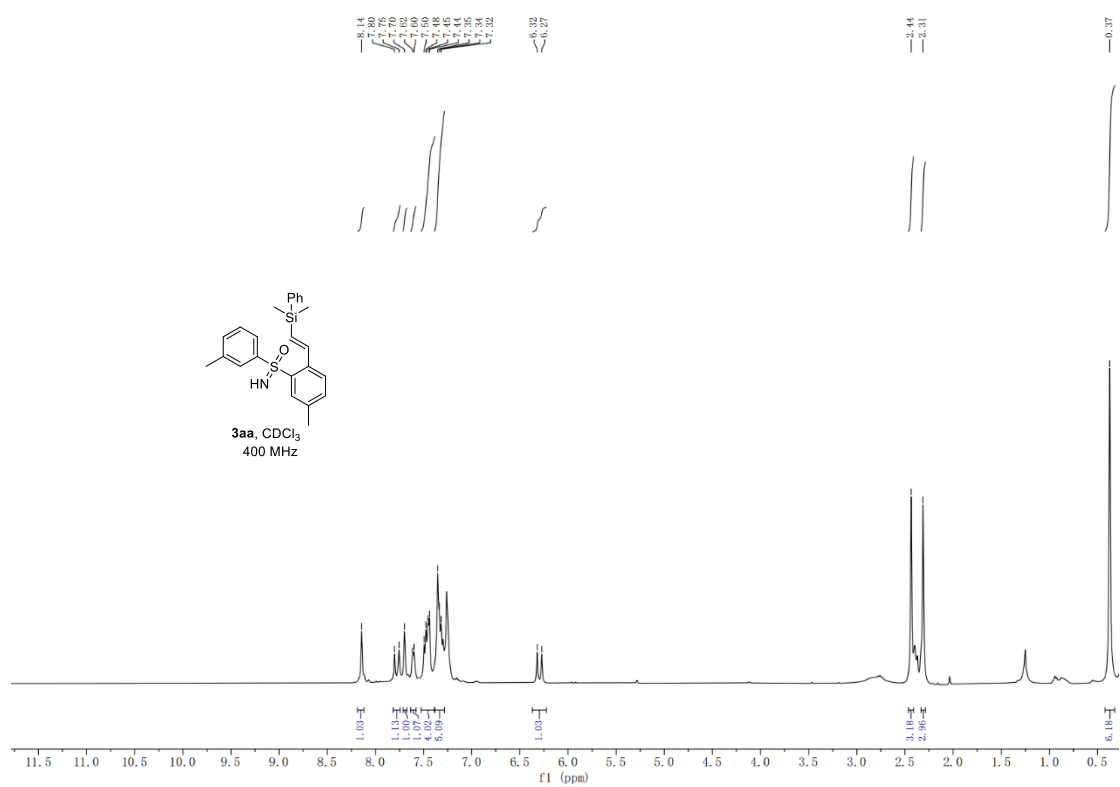


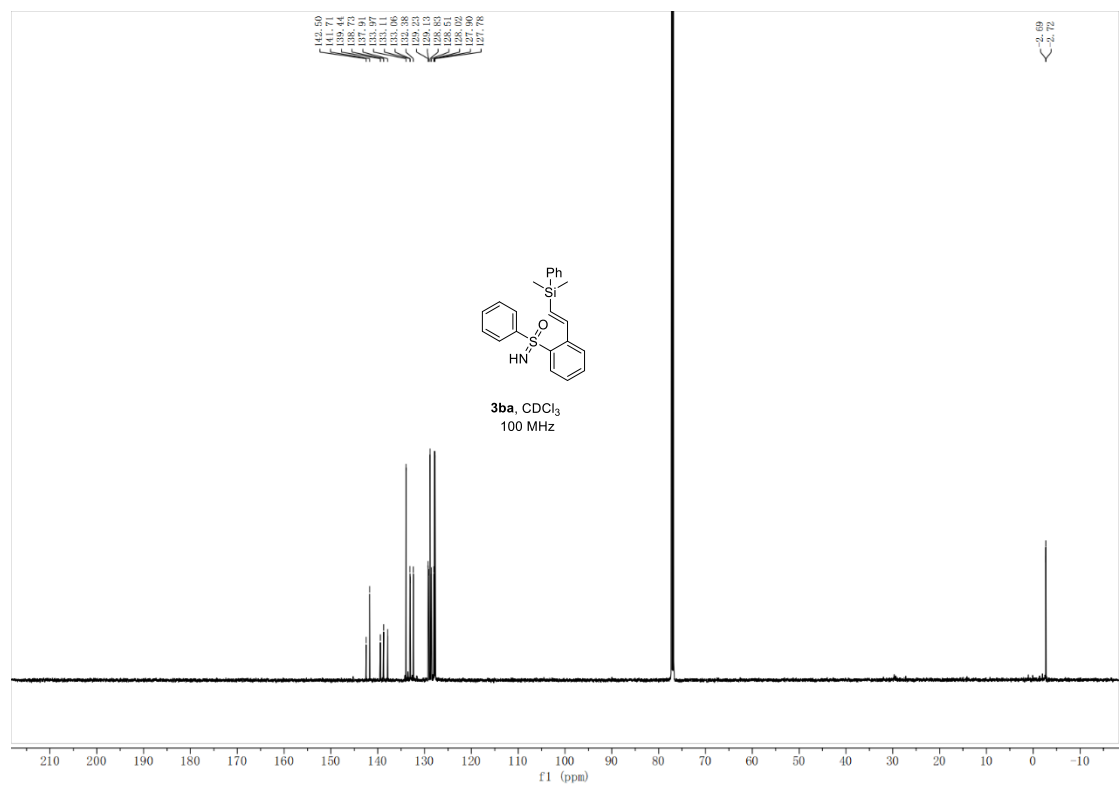
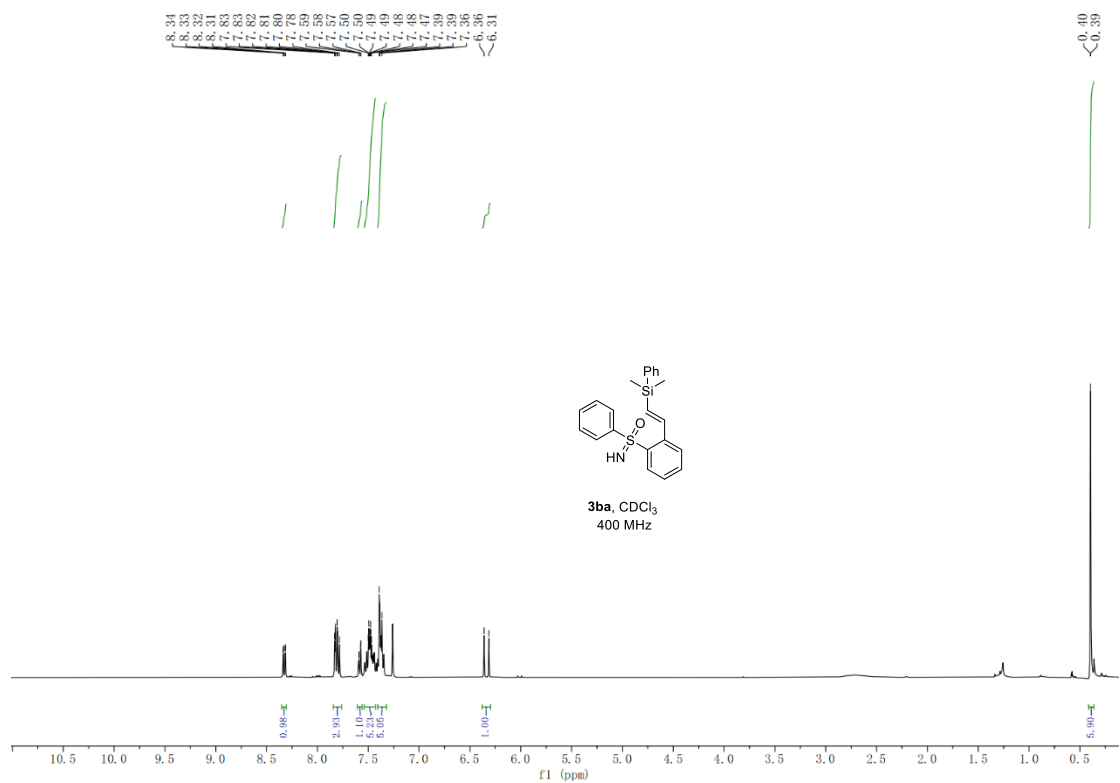
(E)-2-(3,3-diphenylprop-1-en-1-yl)phenyl(imino)(phenyl)-sulfanone (**5aa**). 18 mg, 89% yield; Yellow oil; eluent (petroleum ether/ethyl acetate = 15:1). ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 7.8 Hz, 1H), 8.02 – 7.93 (m, 2H), 7.53 (q, *J* = 5.8 Hz, 3H), 7.49 – 7.43 (m, 5H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 3H), 7.24 (t, *J* = 7.2 Hz, 3H), 7.19 – 7.14

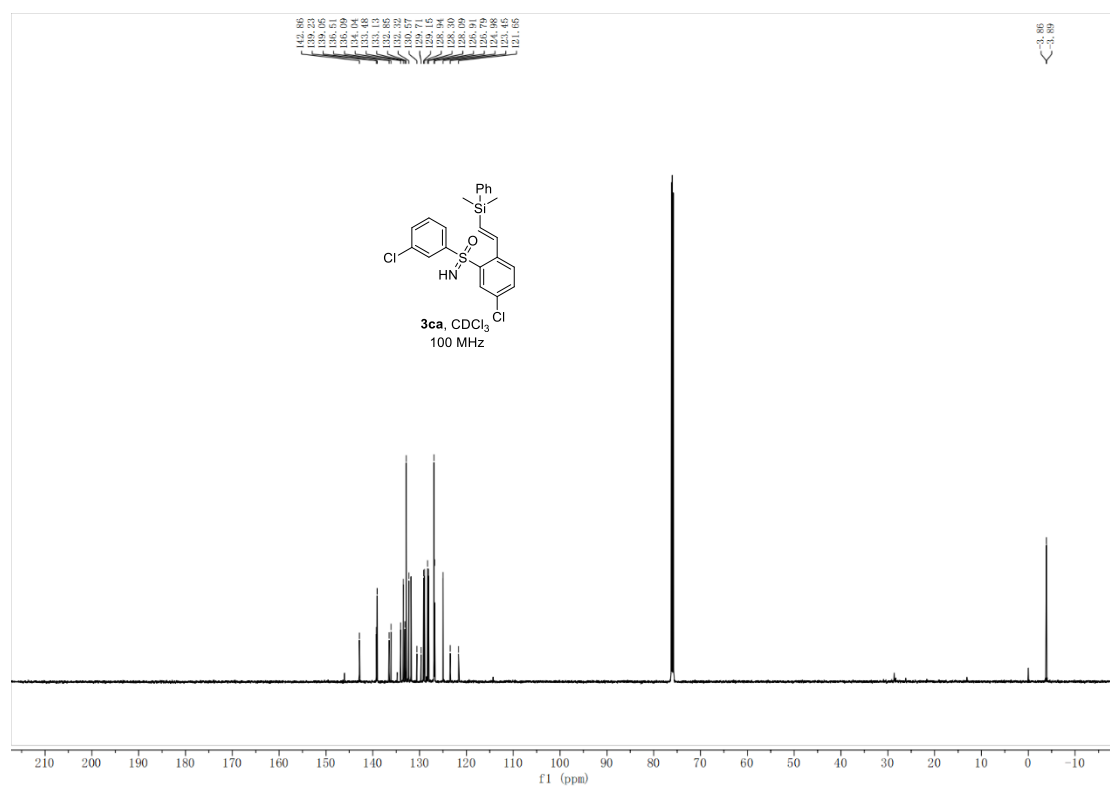
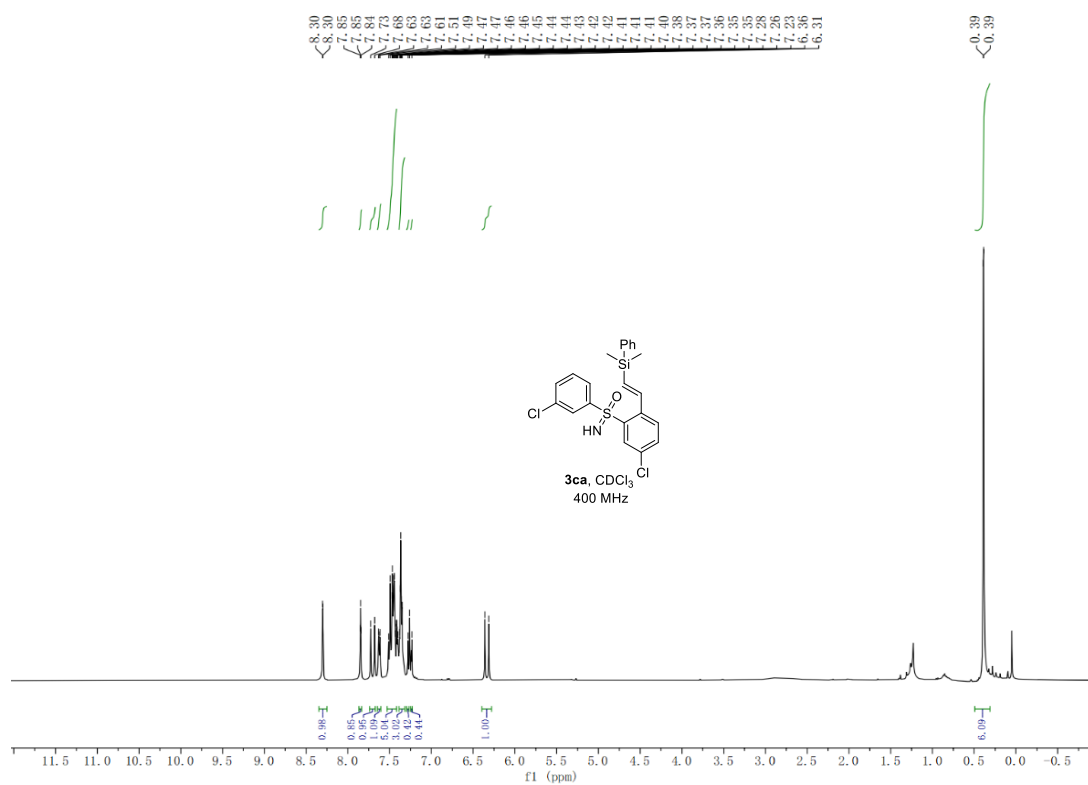
(m, 1H), 6.11 (d, $J = 19.0$ Hz, 1H), 5.48 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 144.0, 140.1, 138.5, 137.9, 135.3, 133.5, 131.5, 130.8, 129.4, 127.3, 127.3, 127.2, 126.8, 126.4, 126.3, 126.1, 125.1, 60.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{24}\text{NOS}^+$ 410.1573; Found 410.1564

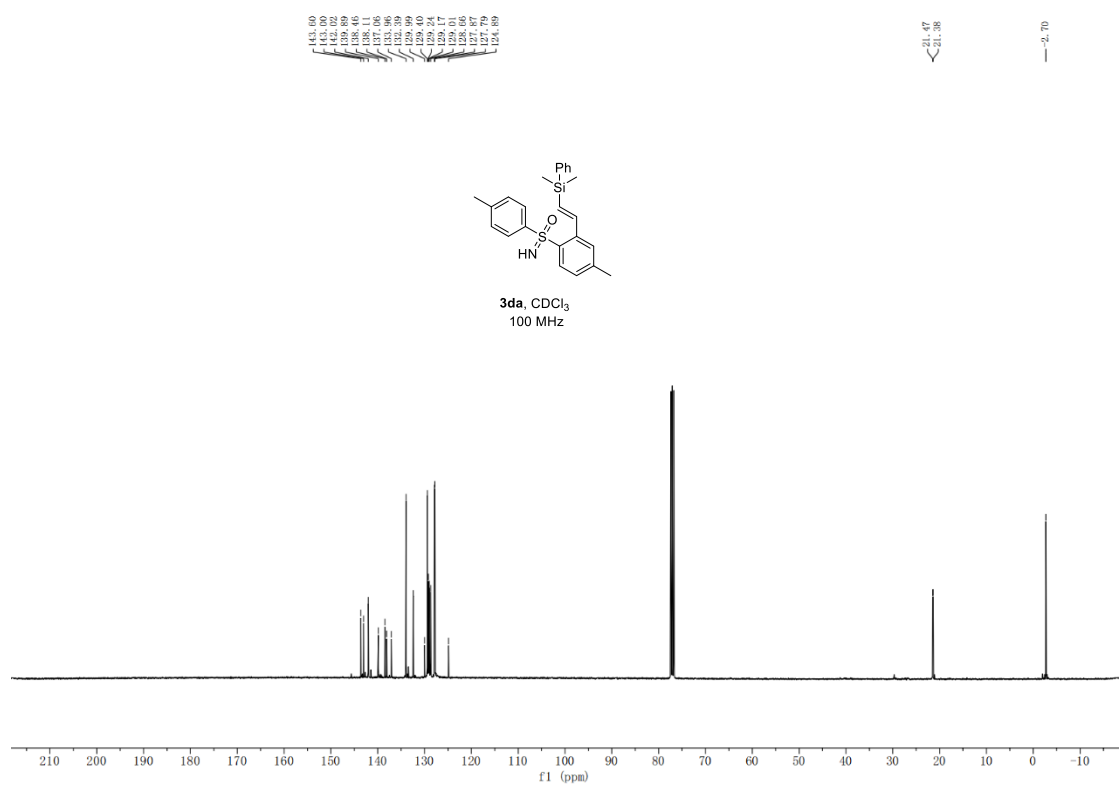
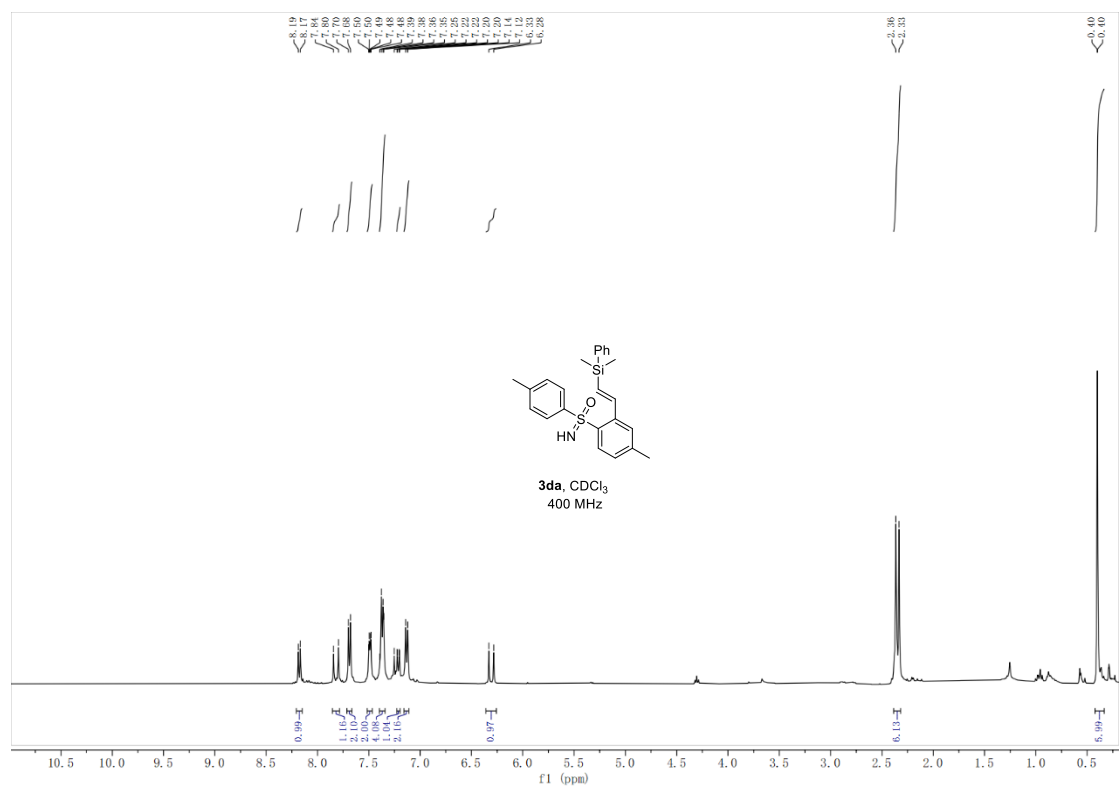


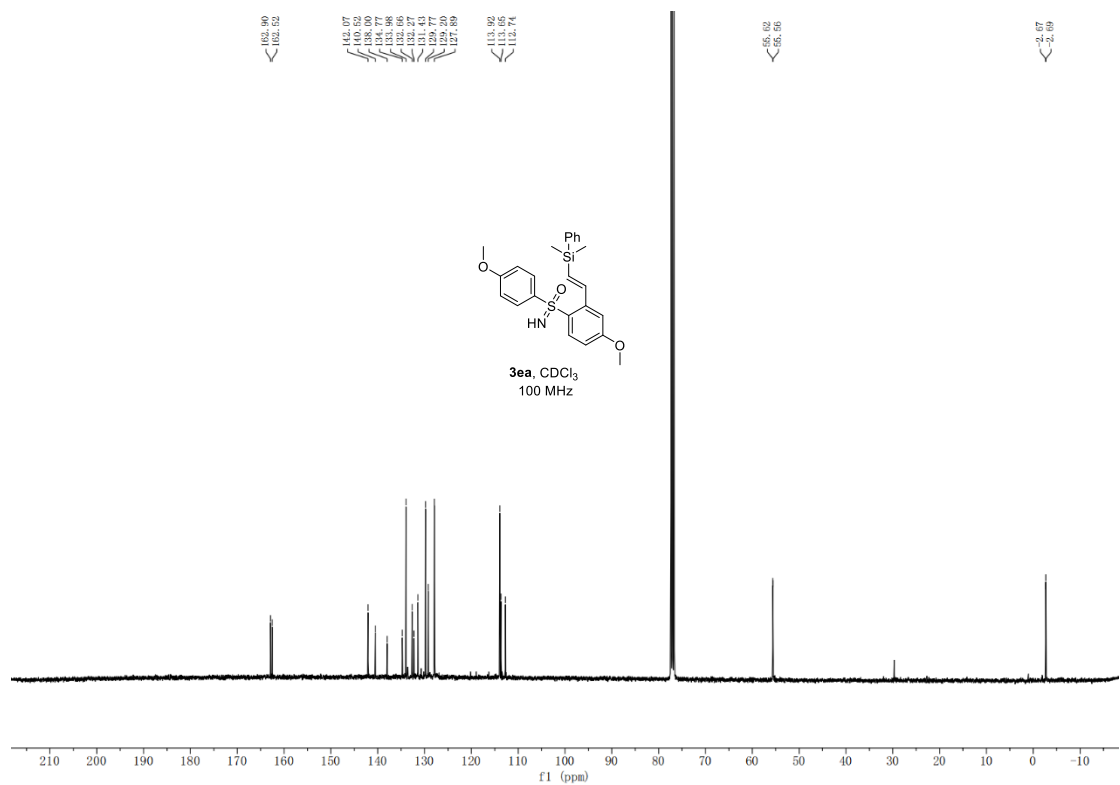
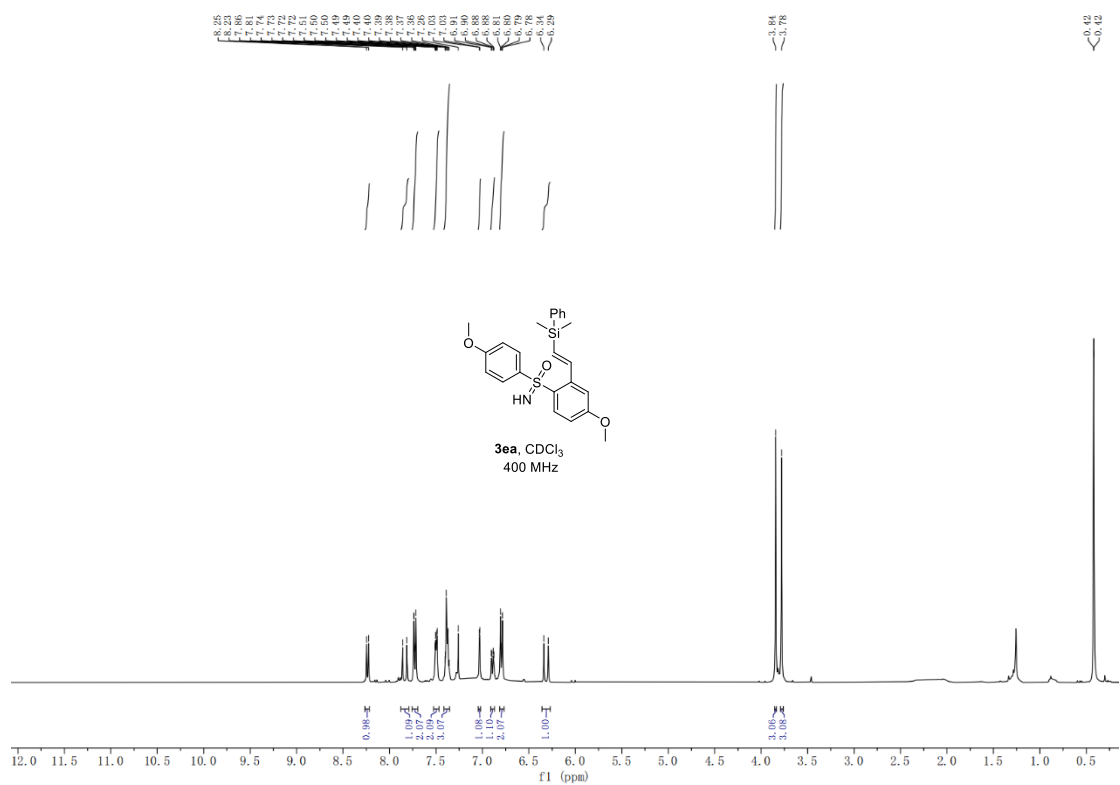
imino(phenyl)(2-vinylphenyl)-sulfanone (**6aa**). 17.5 mg, 72% yield; Yellow solid; eluent (petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 7.6$ Hz, 2H), 7.61 (m, $J = 17.3, 11.0$ Hz, 1H), 7.54 – 7.51 (m, 3H), 7.49 – 7.44 (m, 3H), 5.49 (d, $J = 17.2$ Hz, 1H), 5.28 (d, $J = 10.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.2, 139.6, 138.1, 133.9, 133.2, 129.2, 128.9, 128.6, 128.0, 118.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{14}\text{NOS}^+$ 244.0971; Found 244.0678

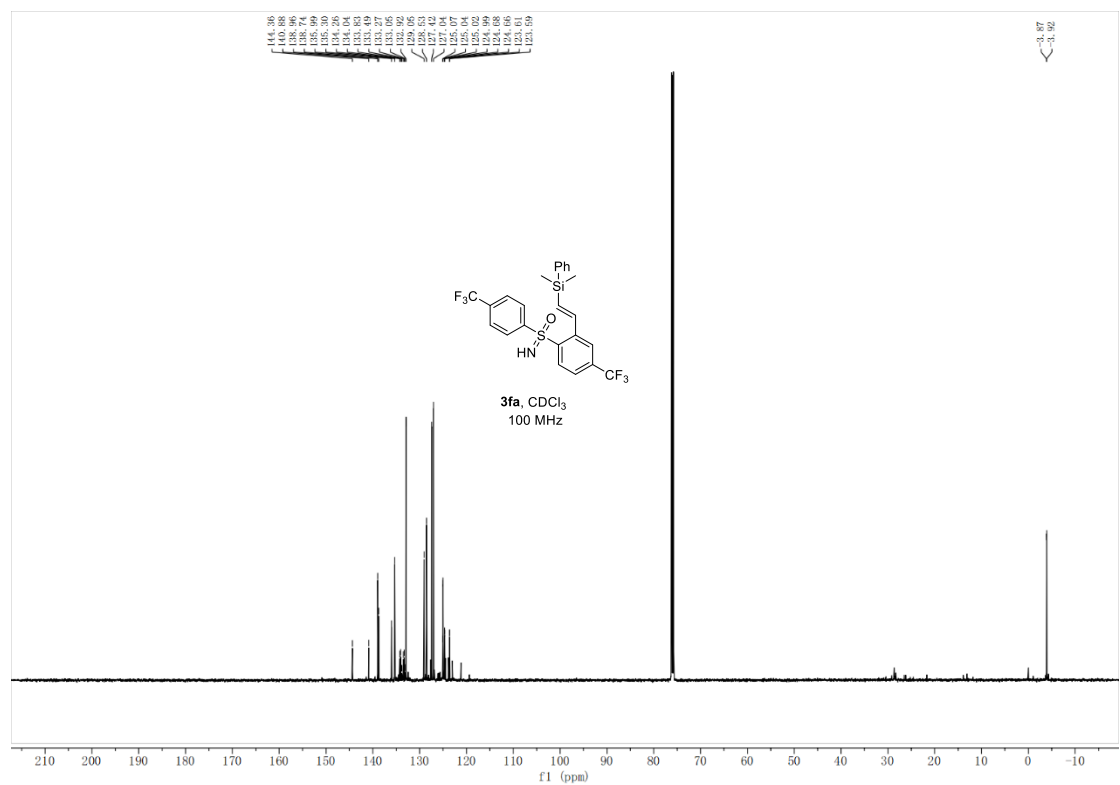


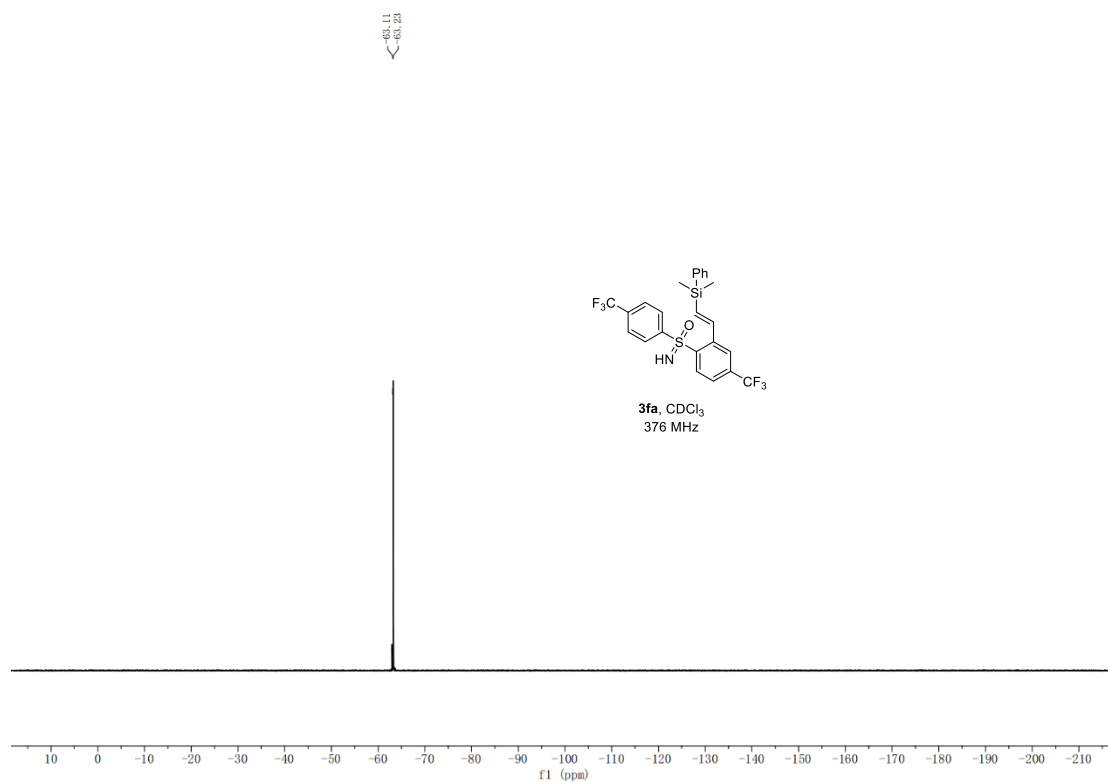


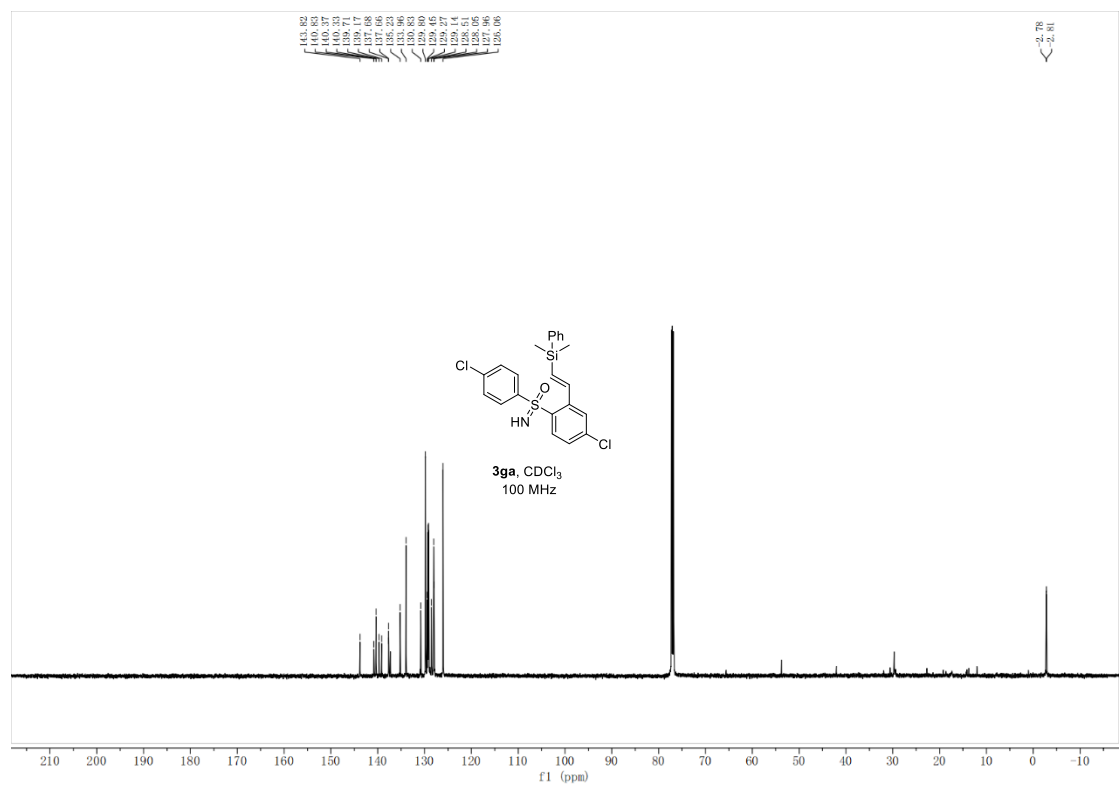
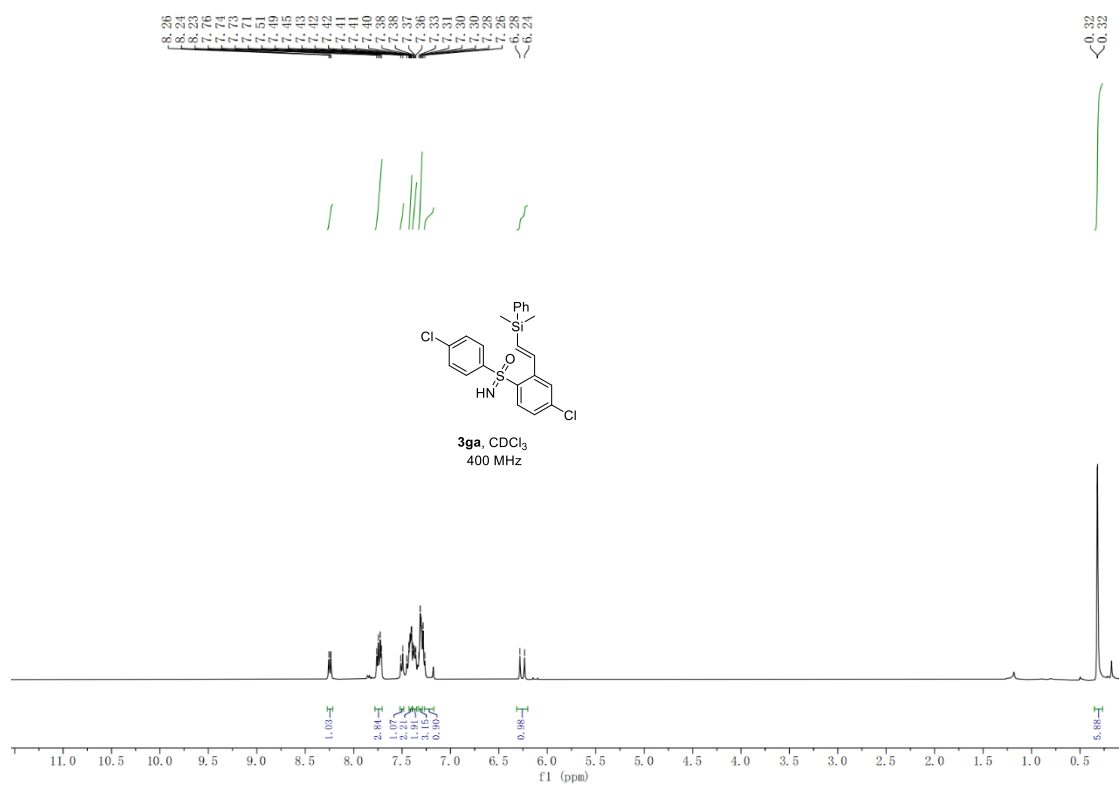


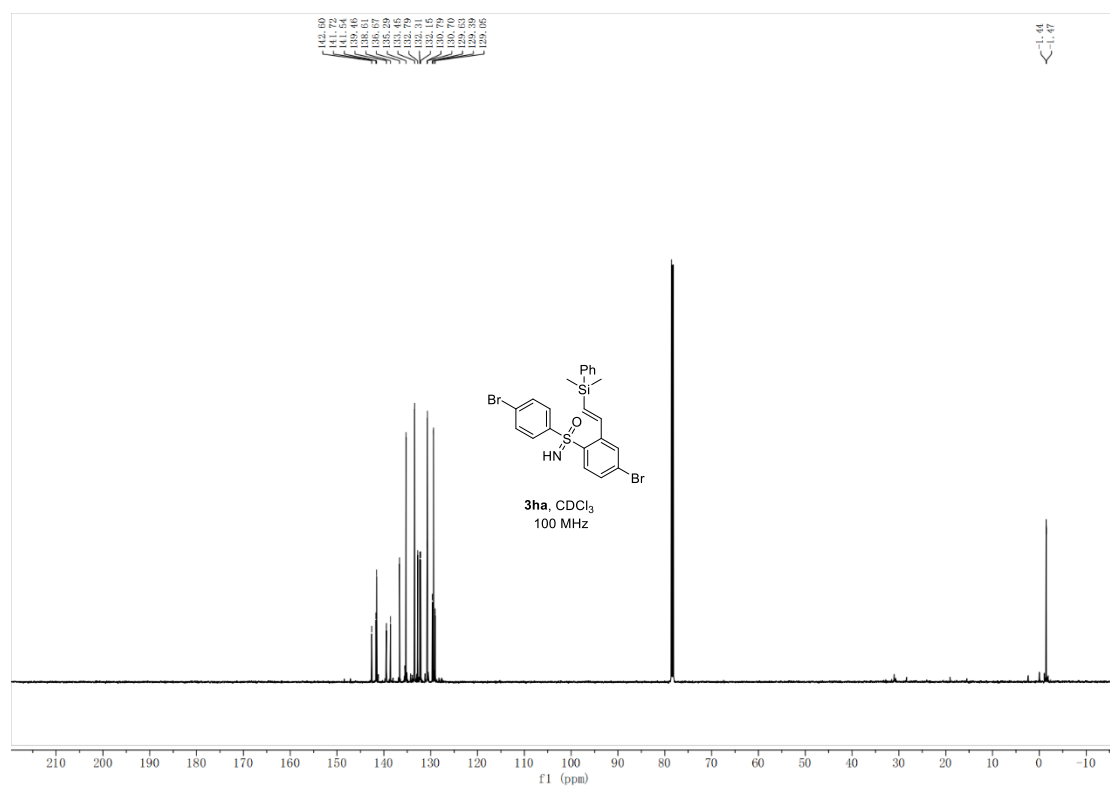
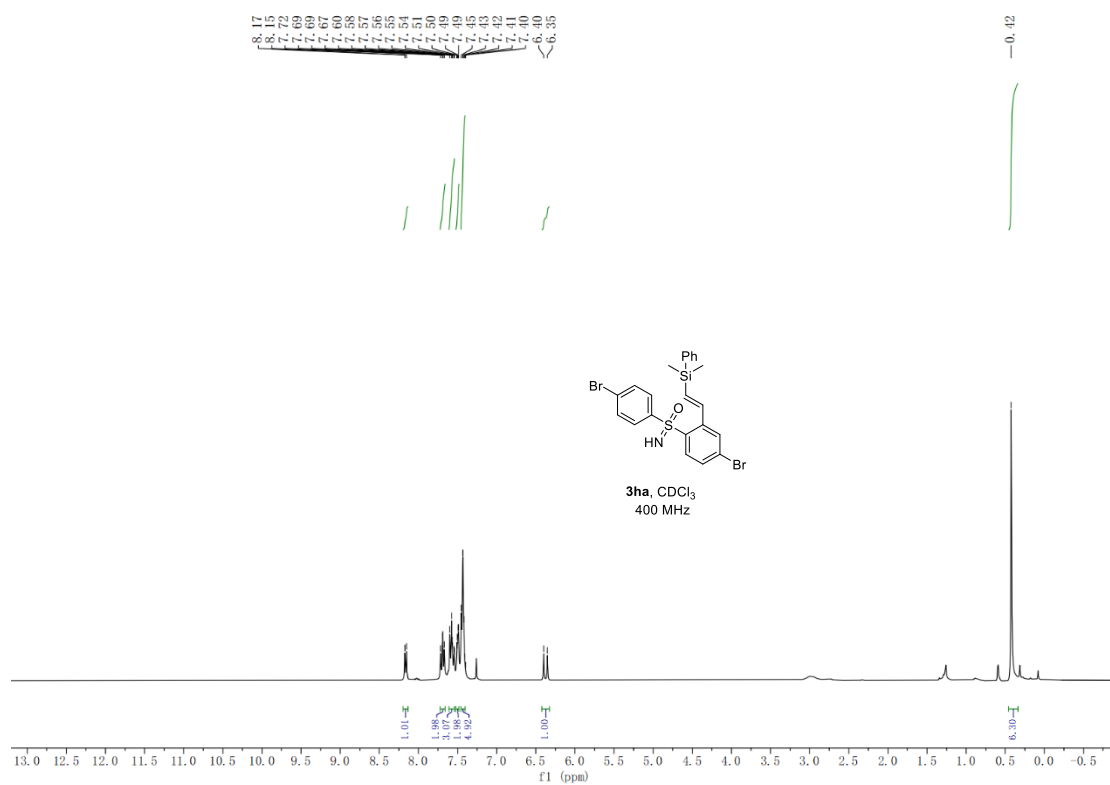


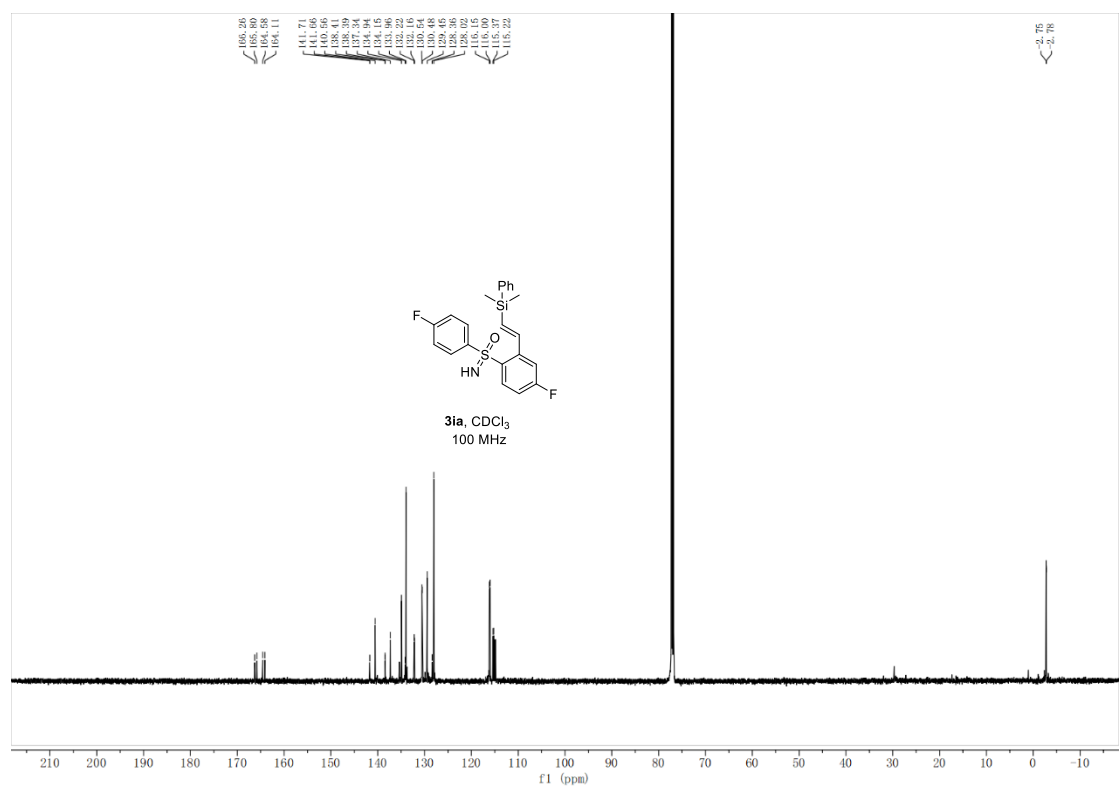
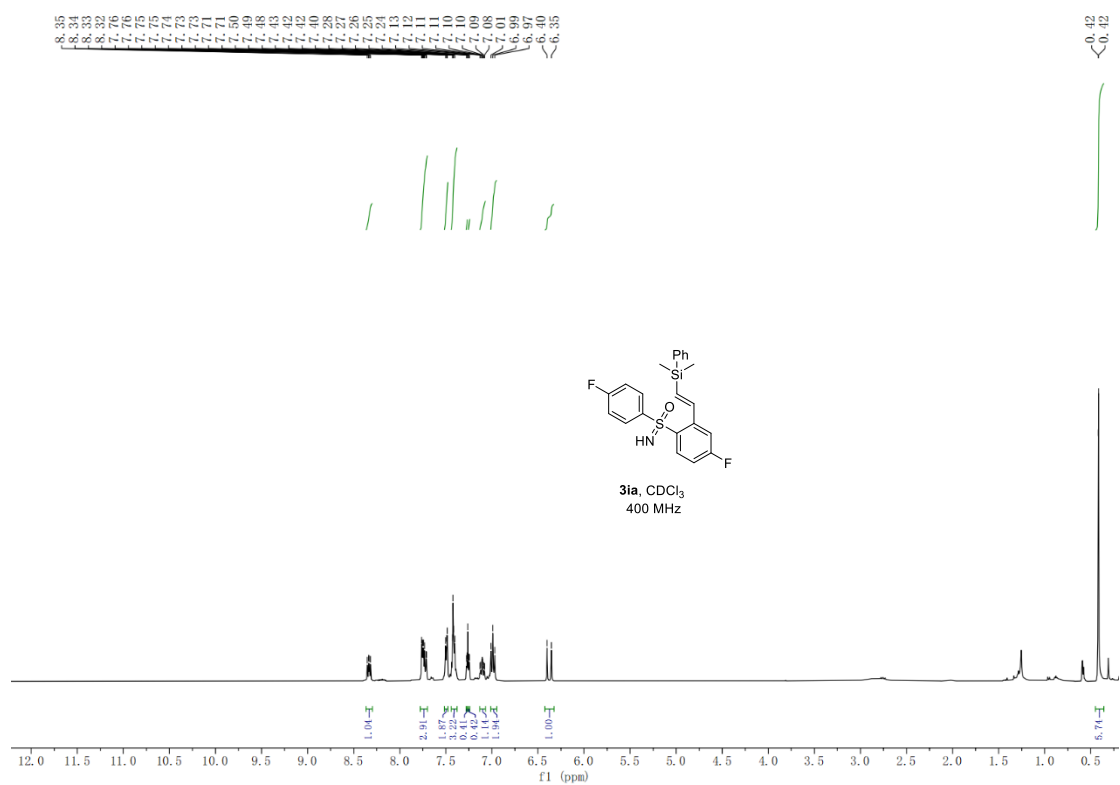


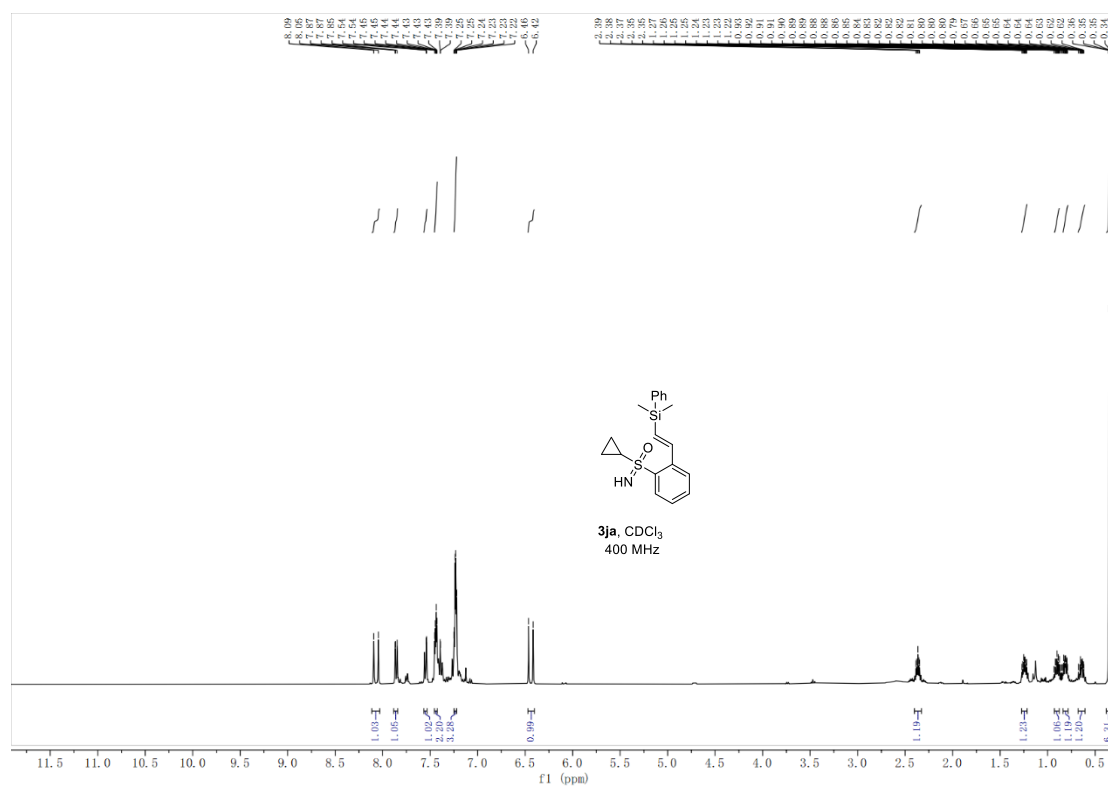
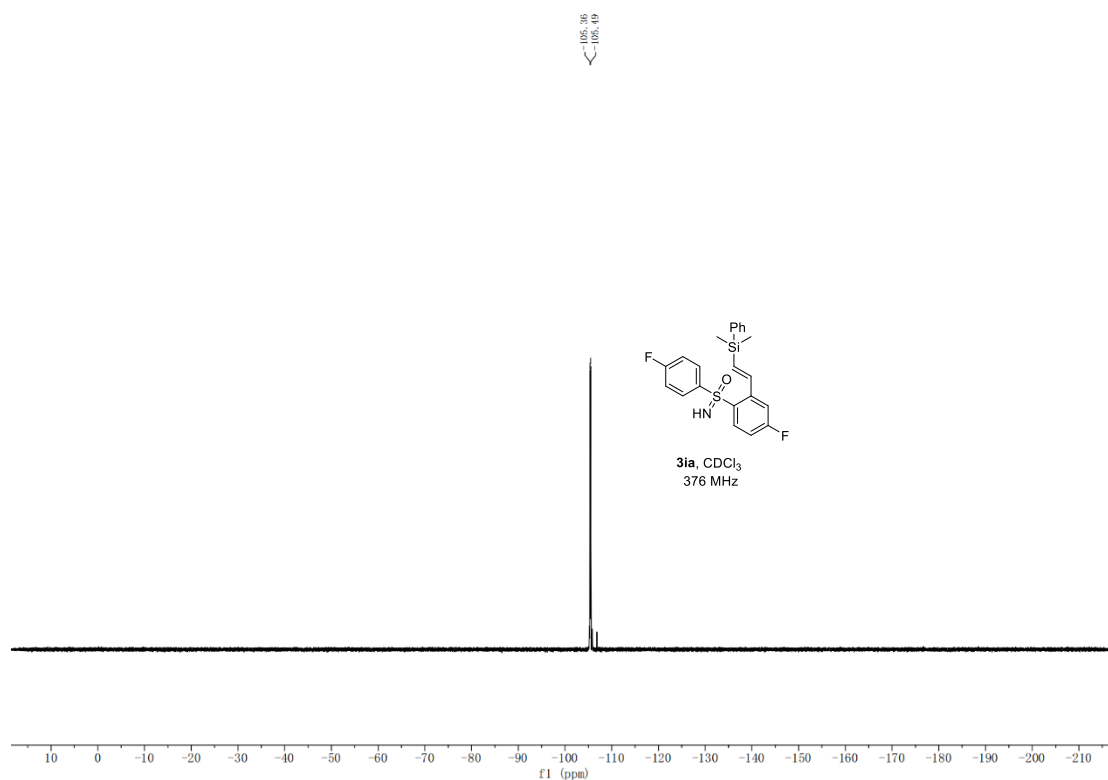


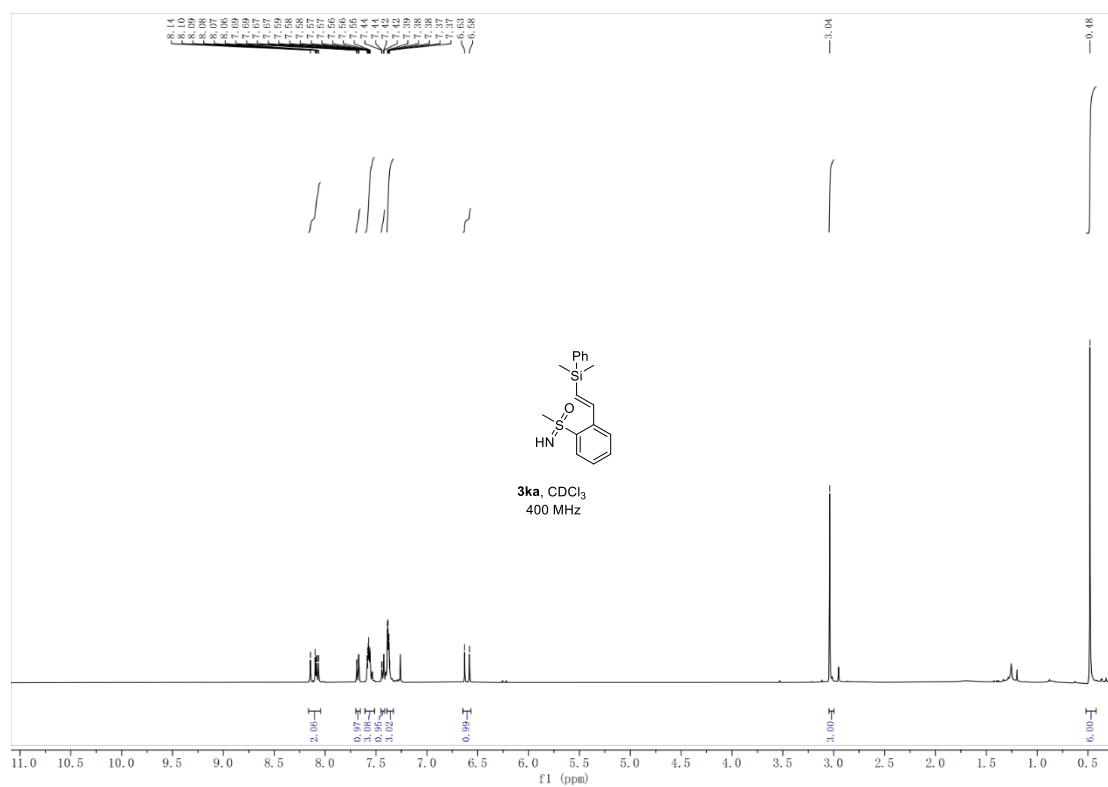
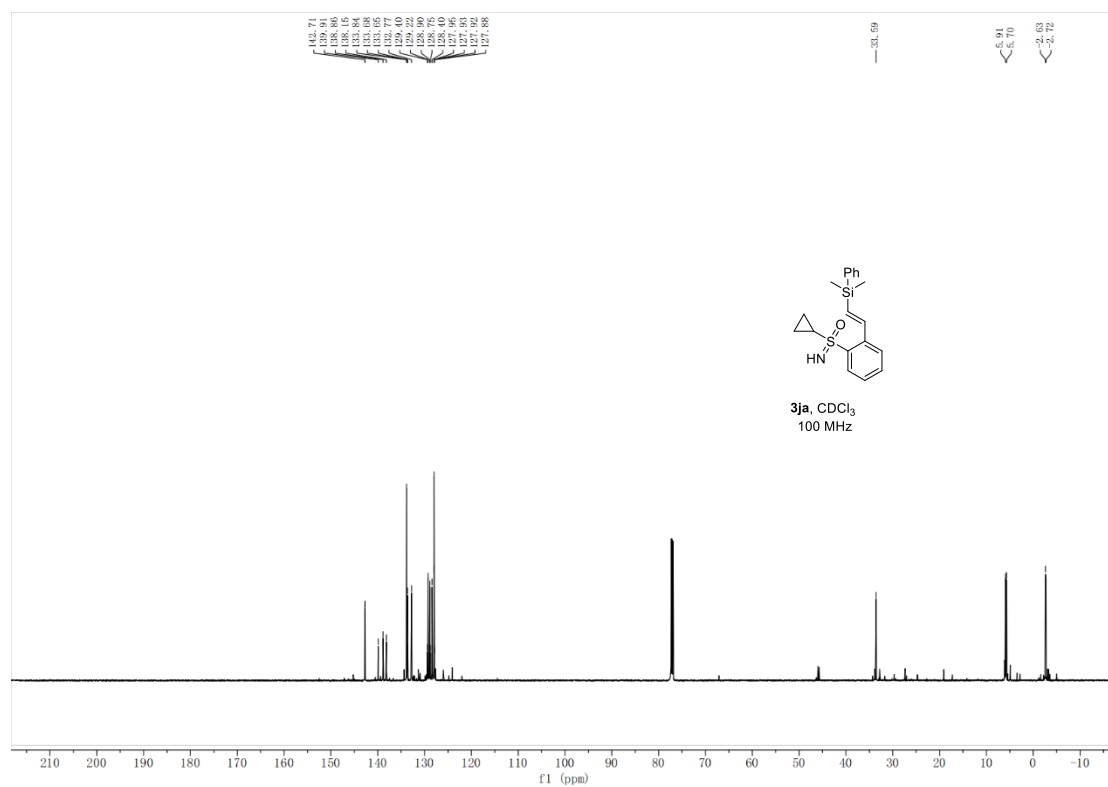


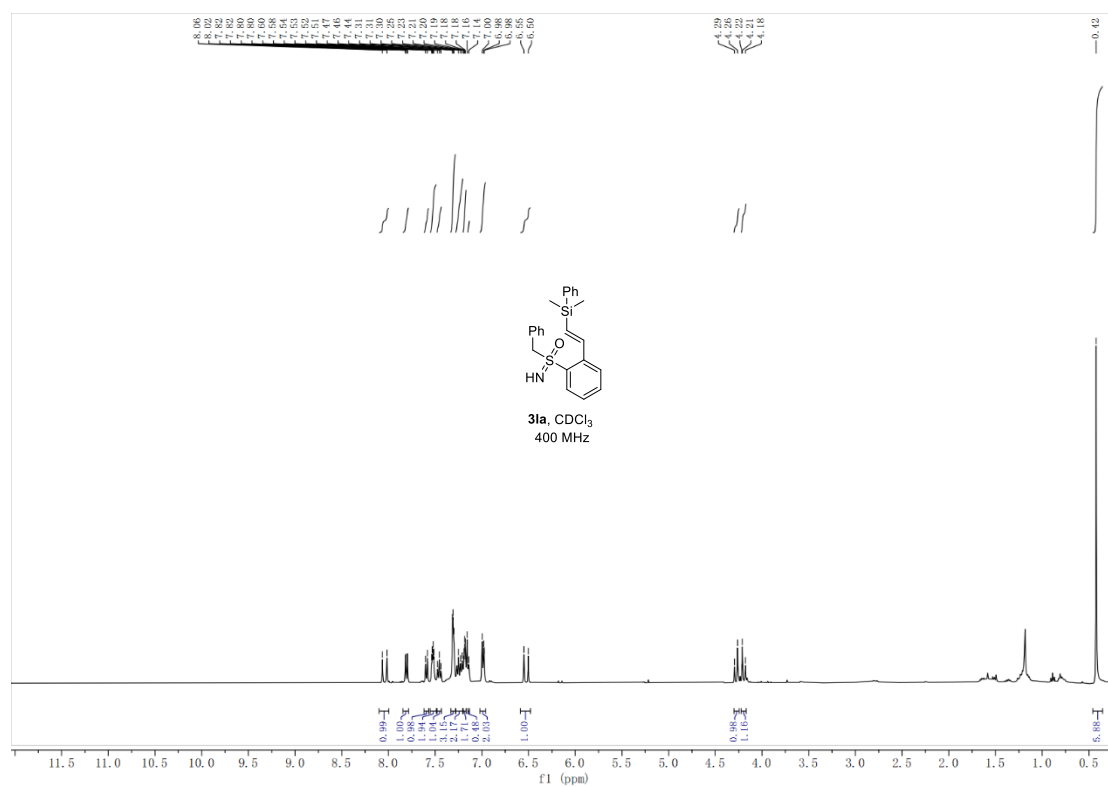
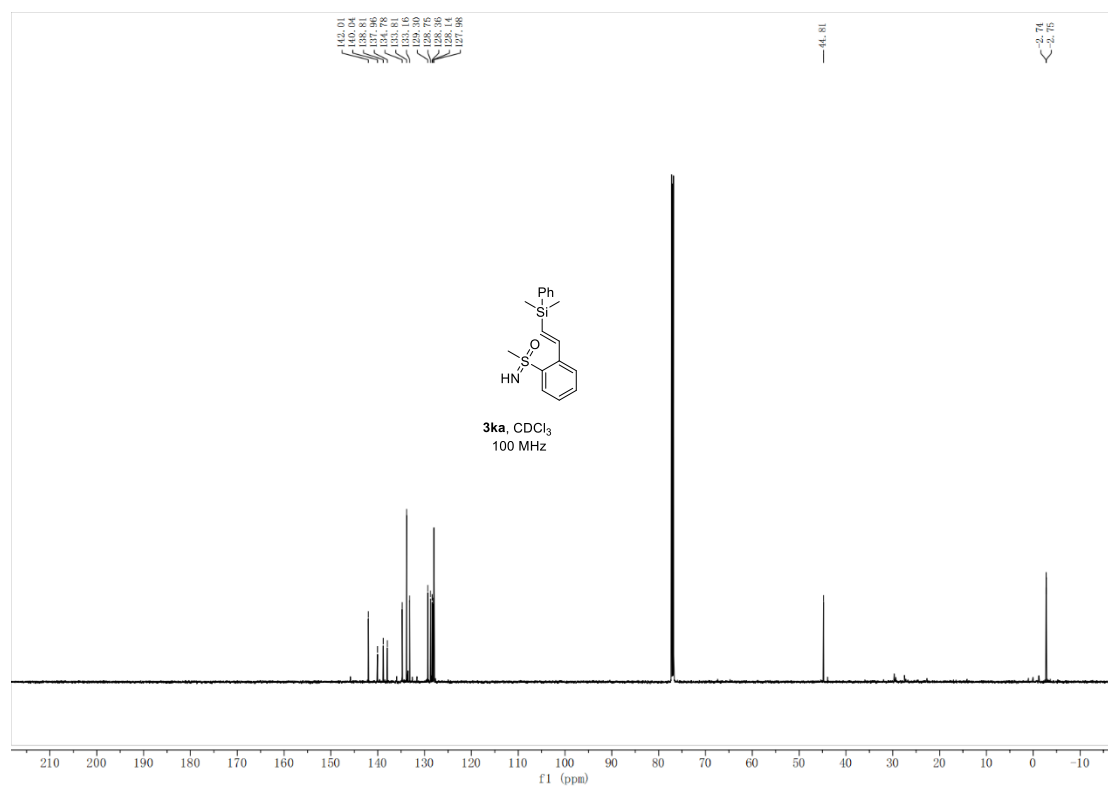


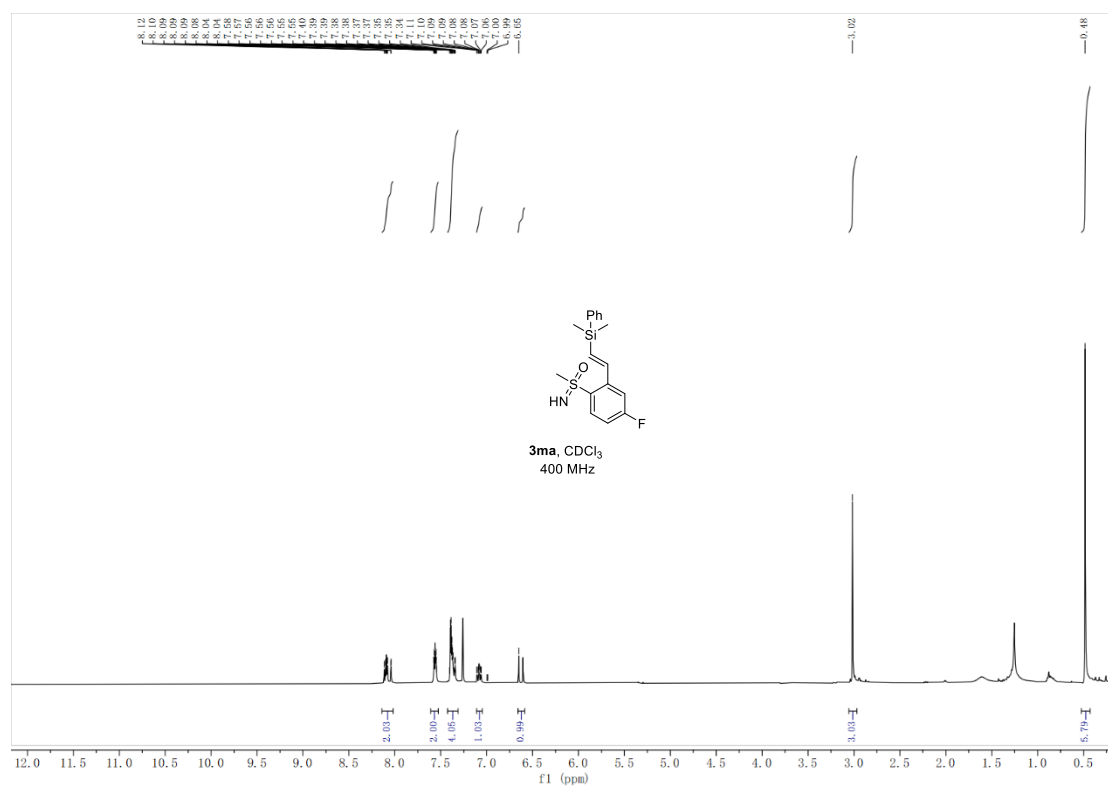
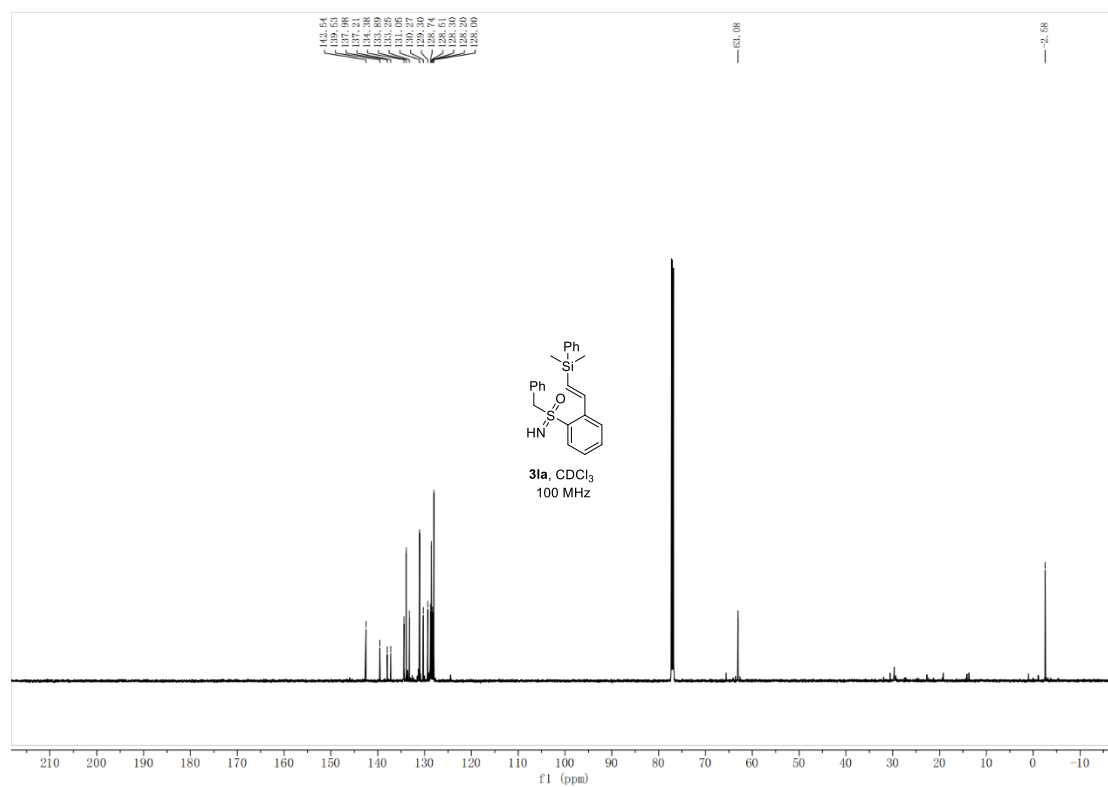


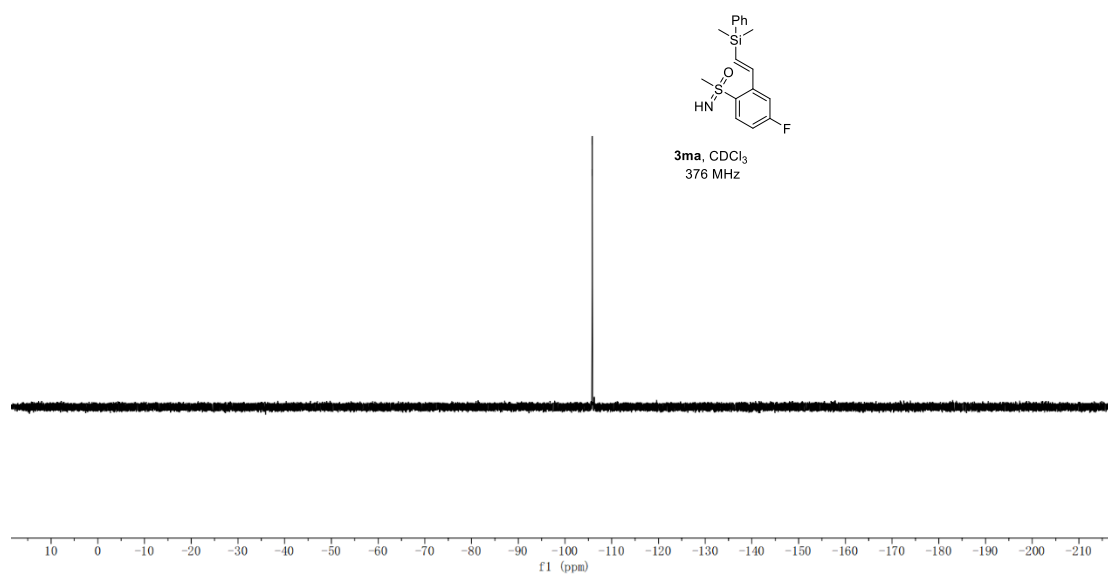
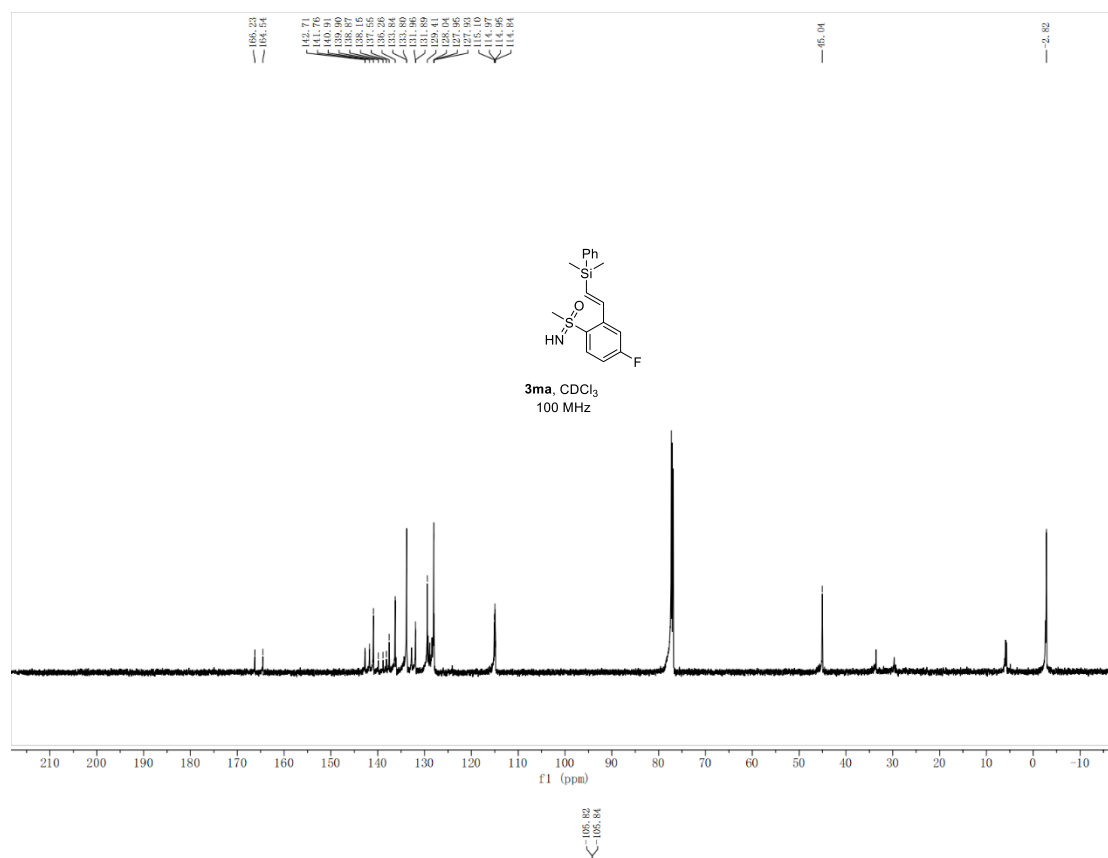


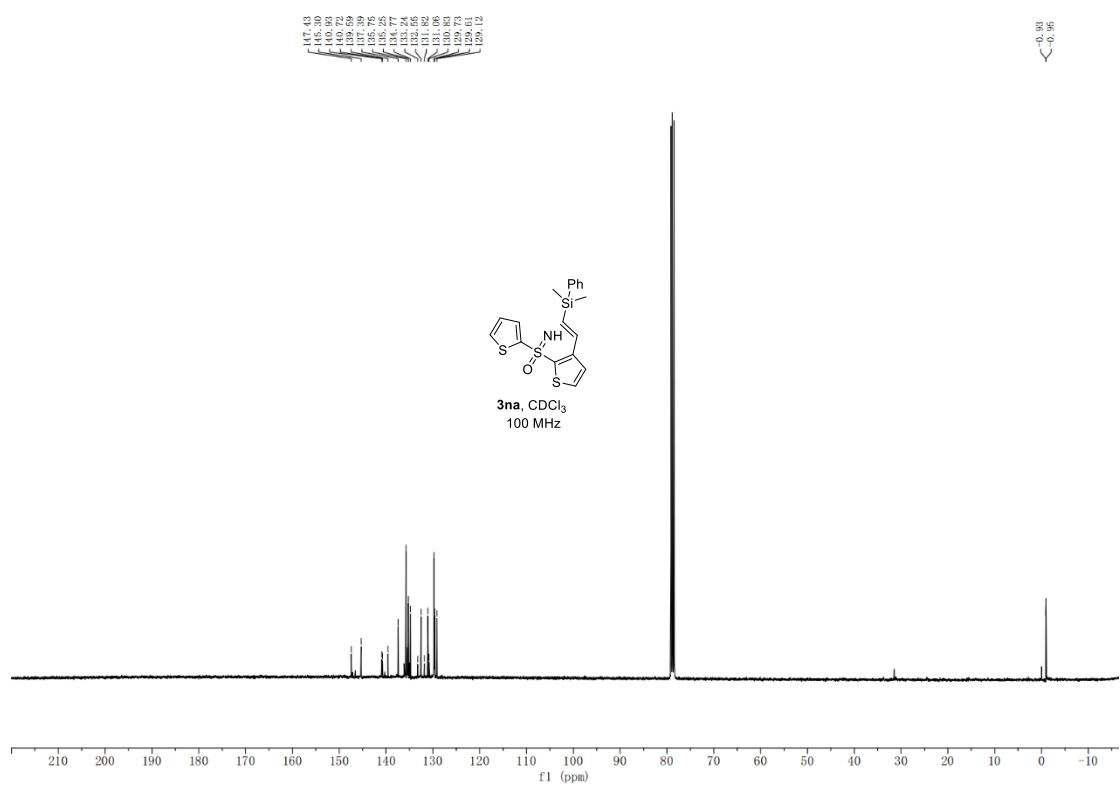
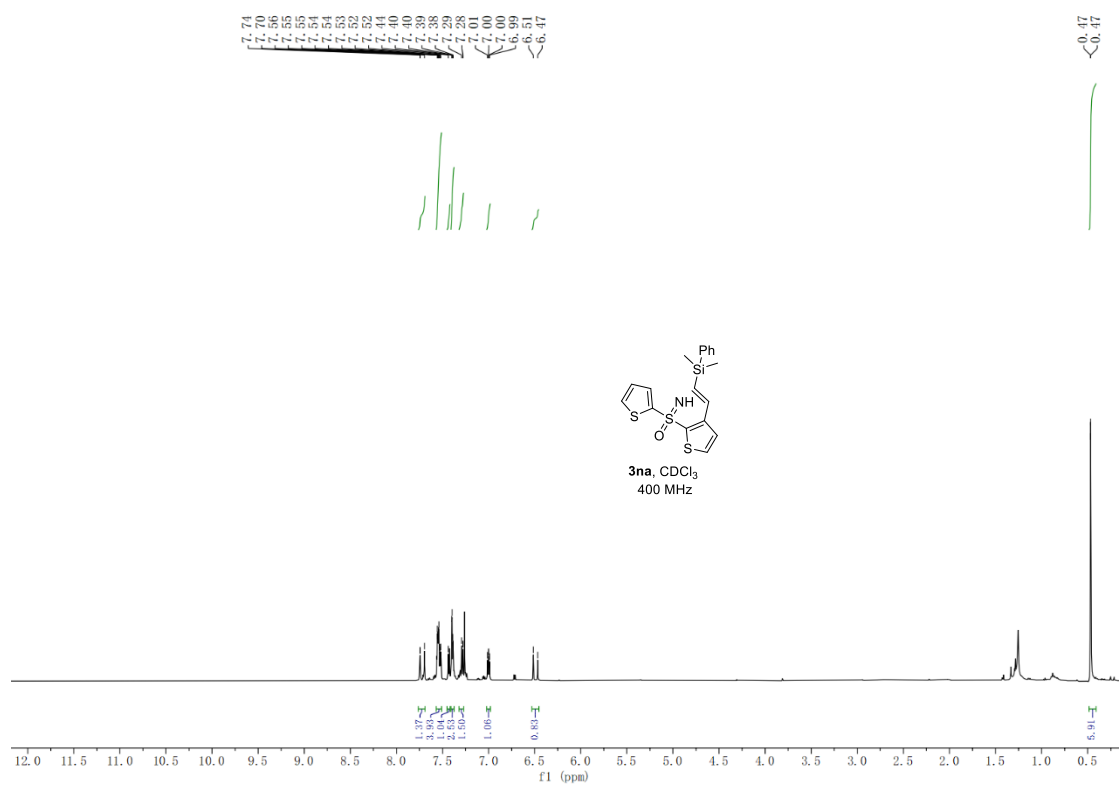


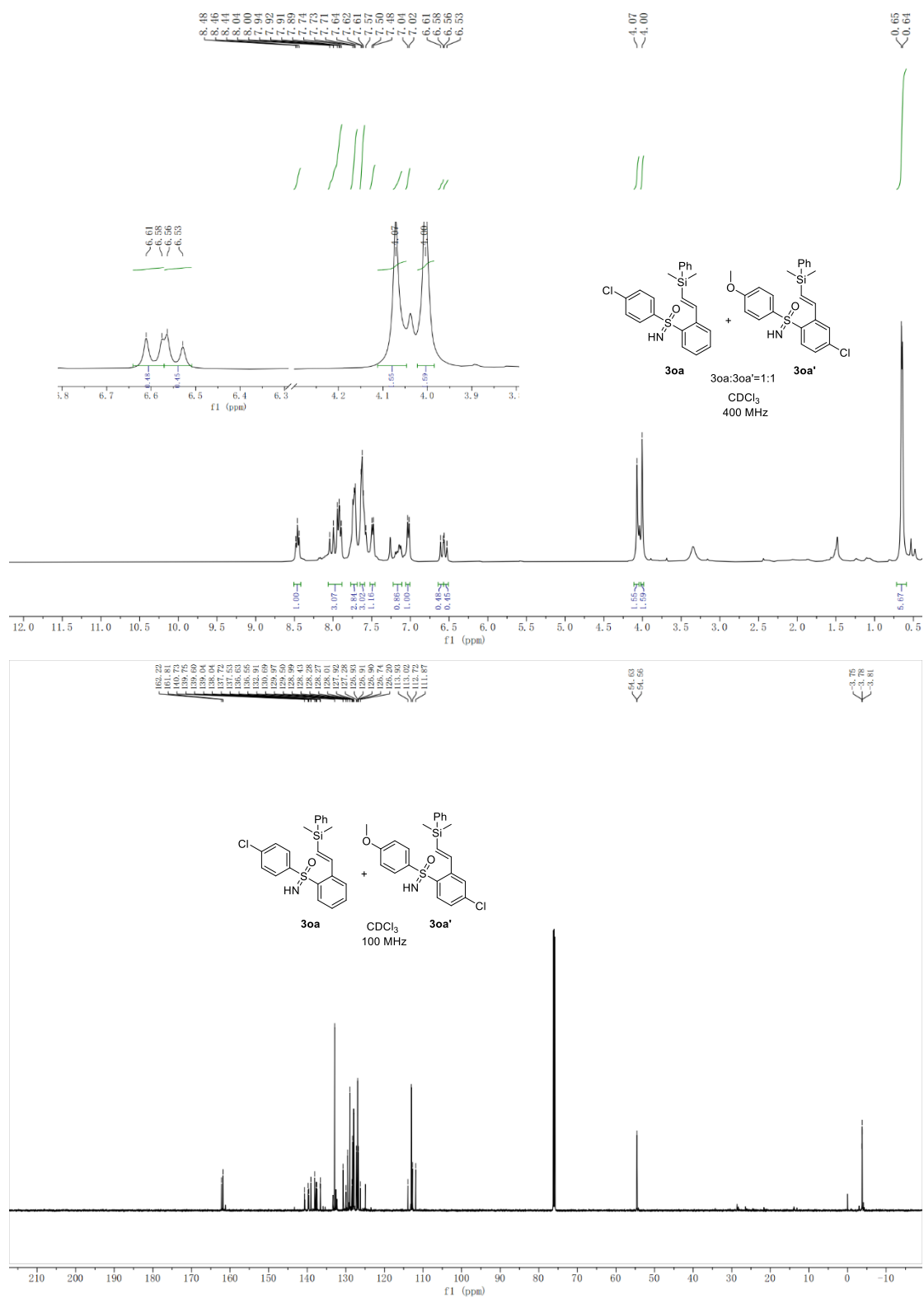


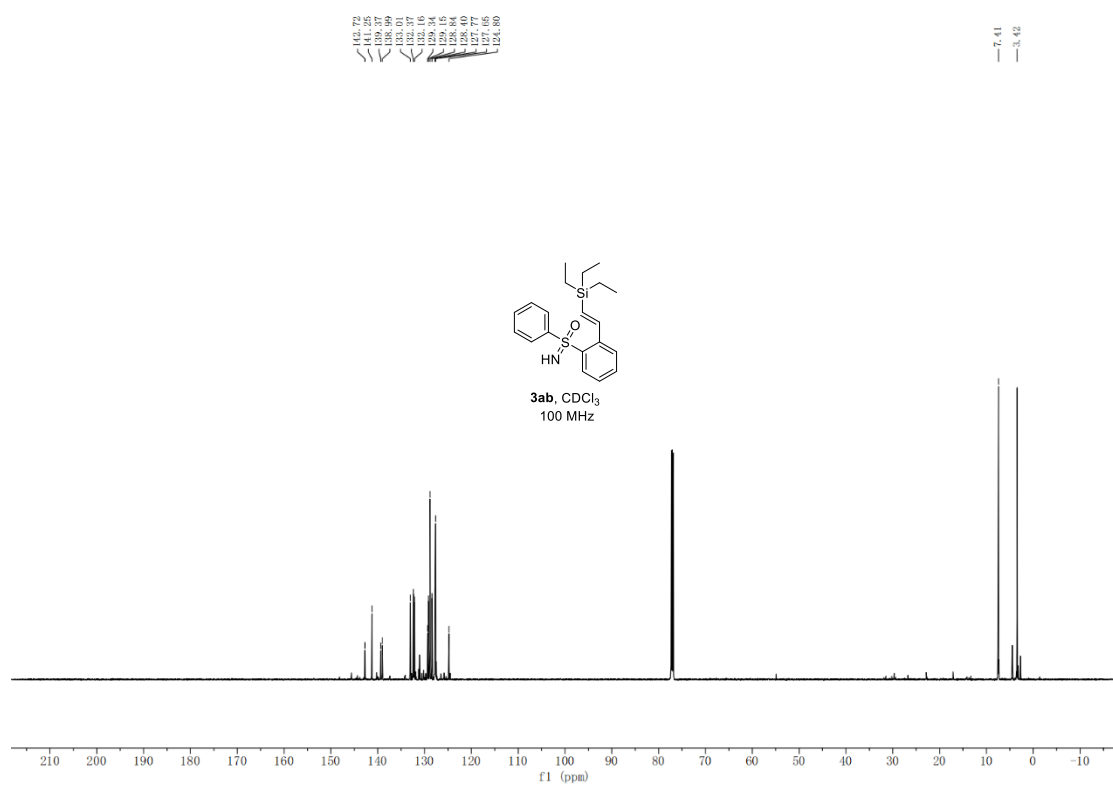
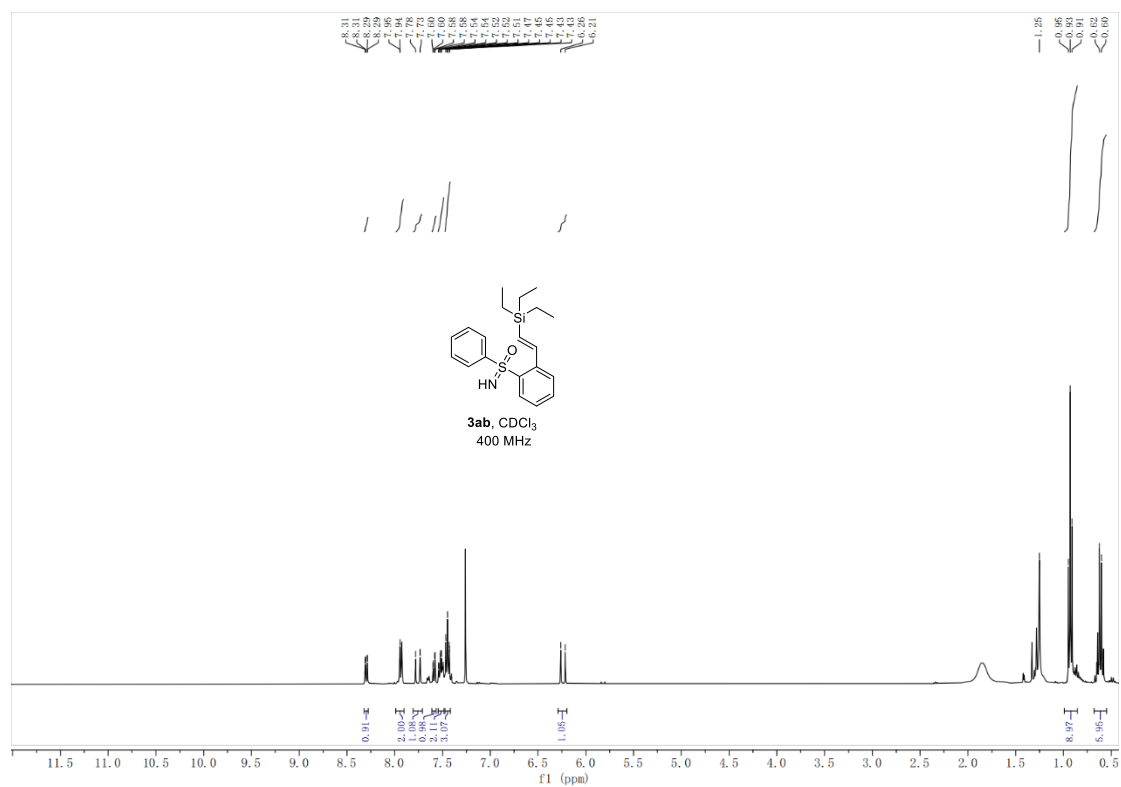


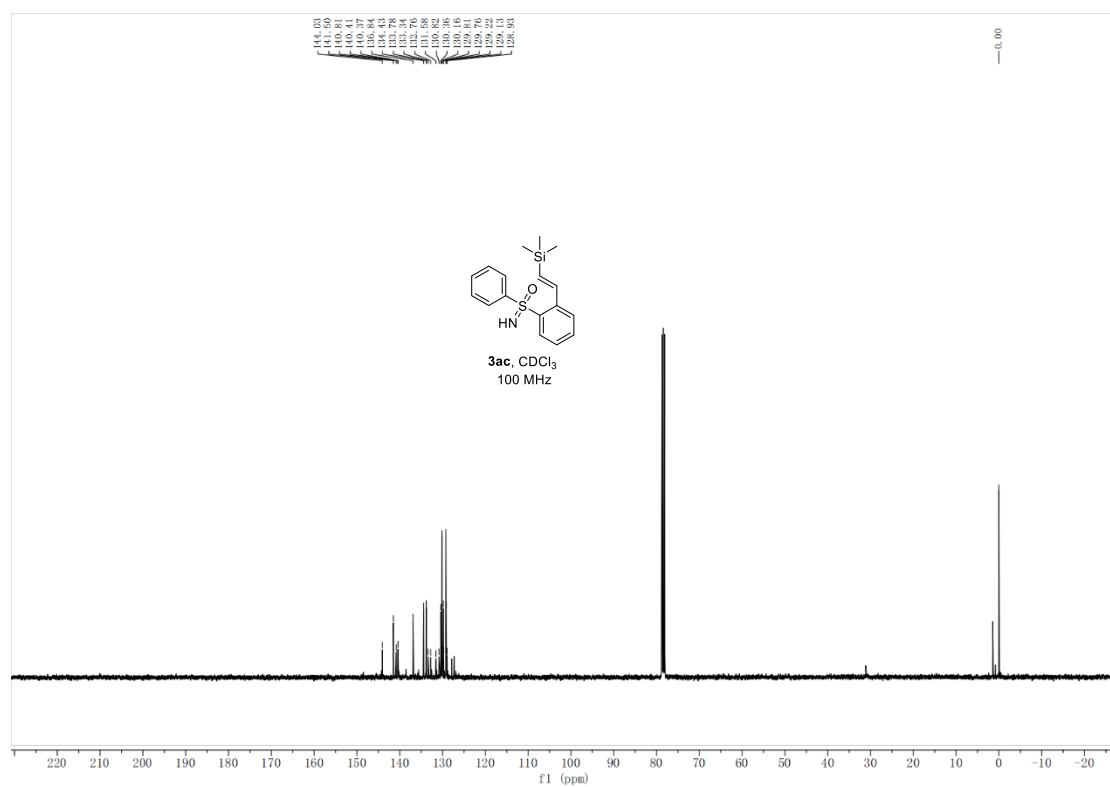
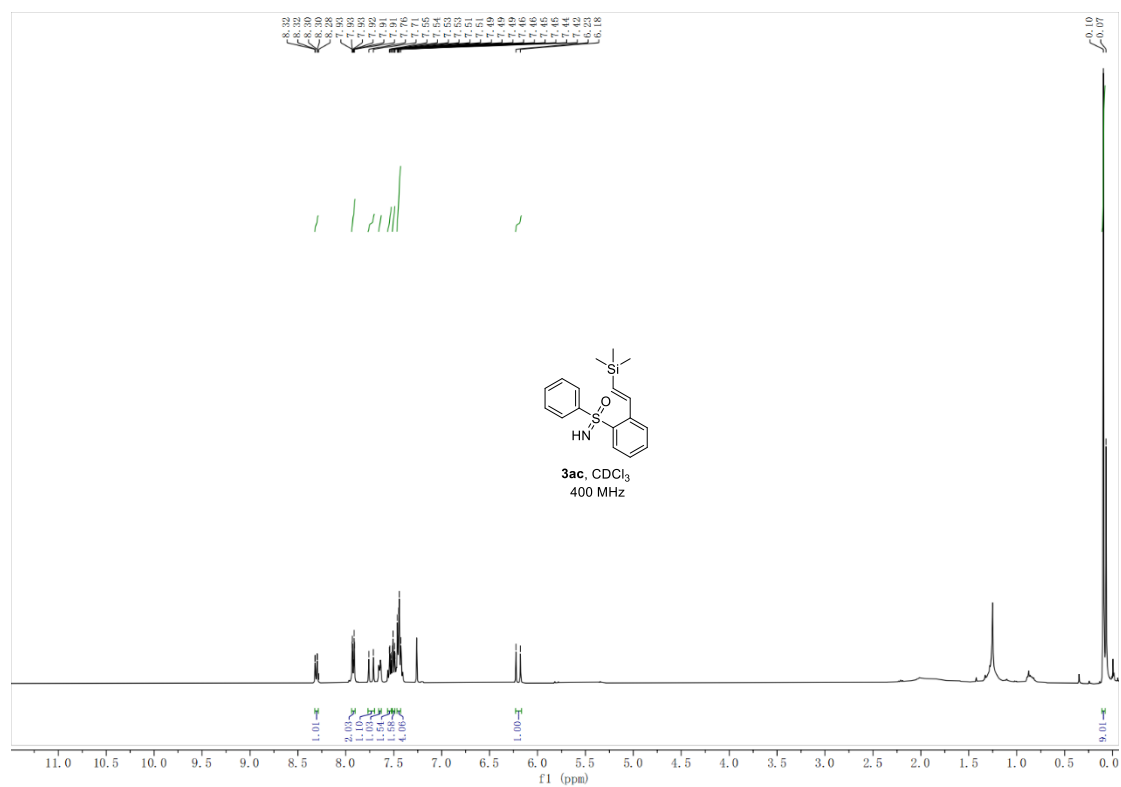


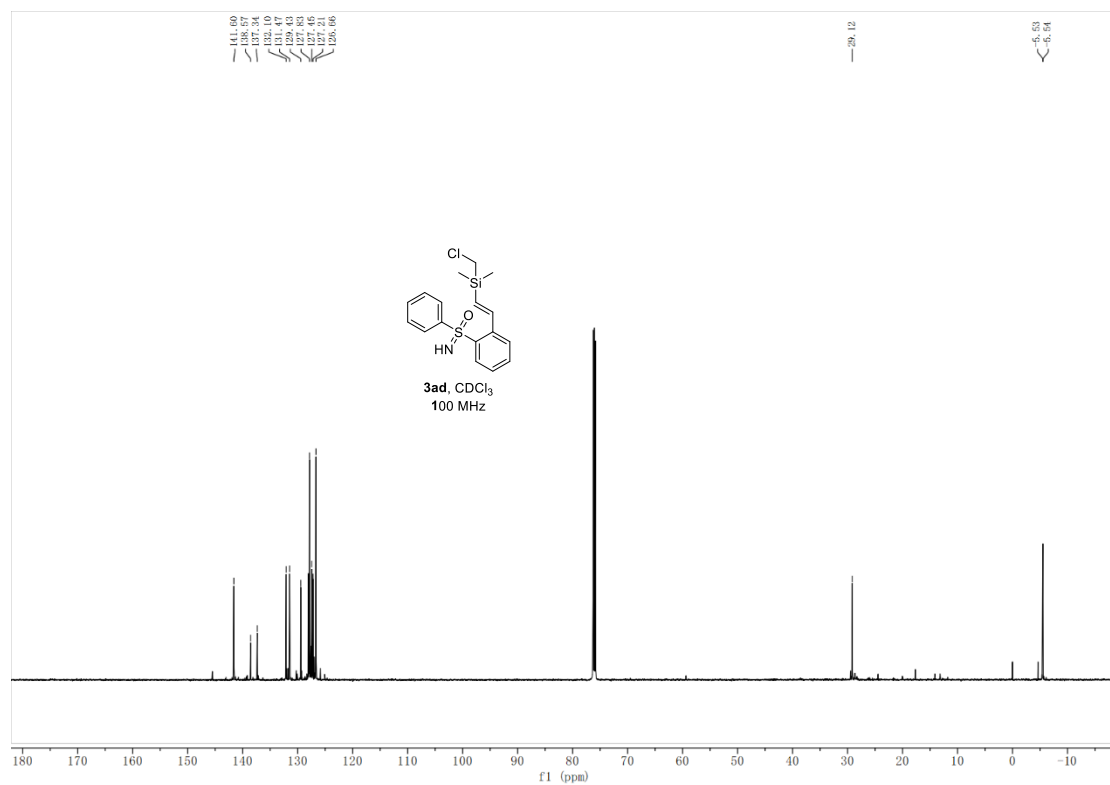
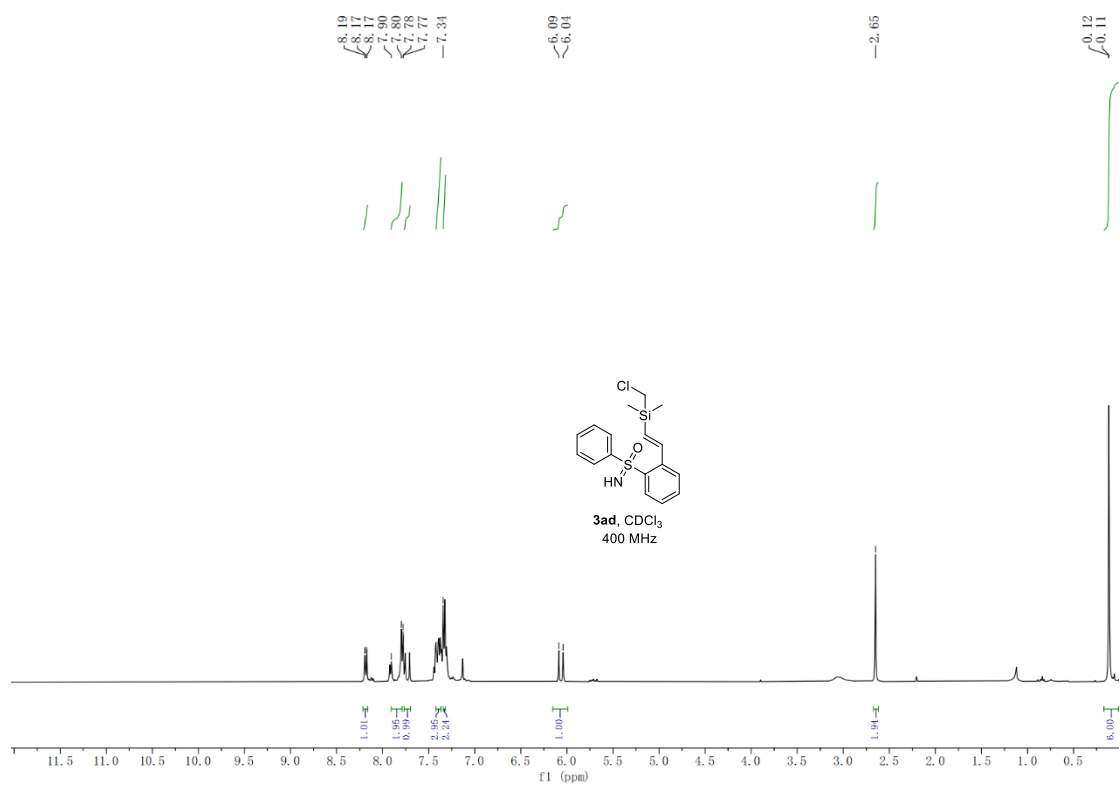


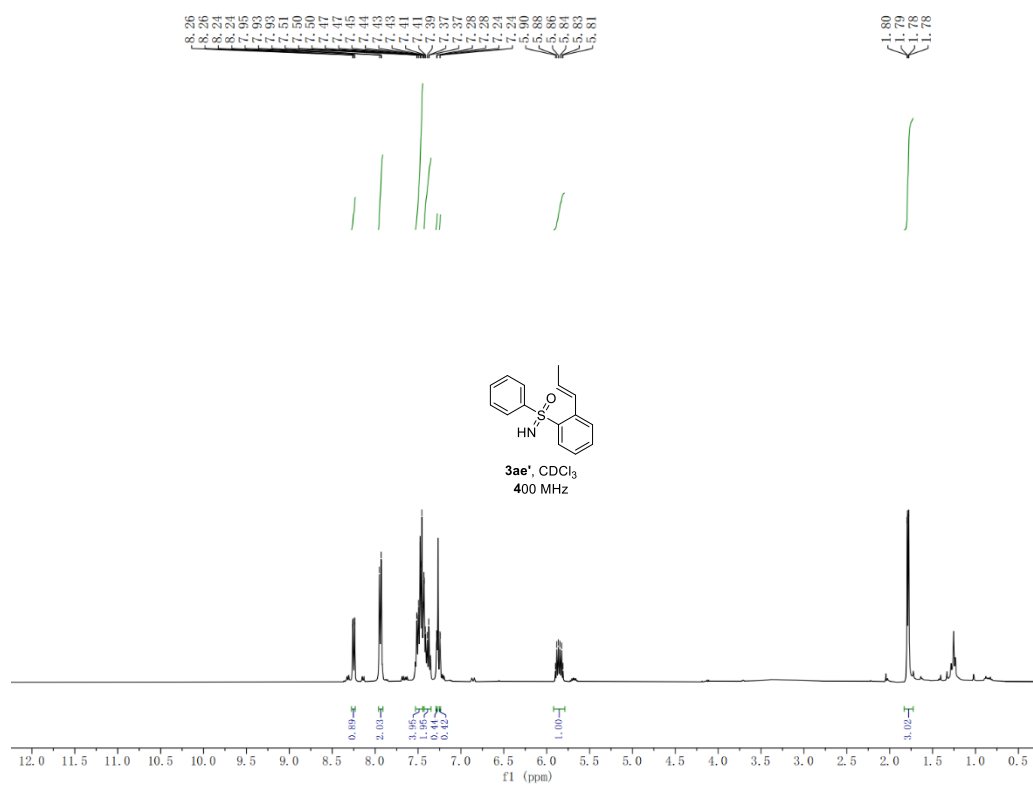


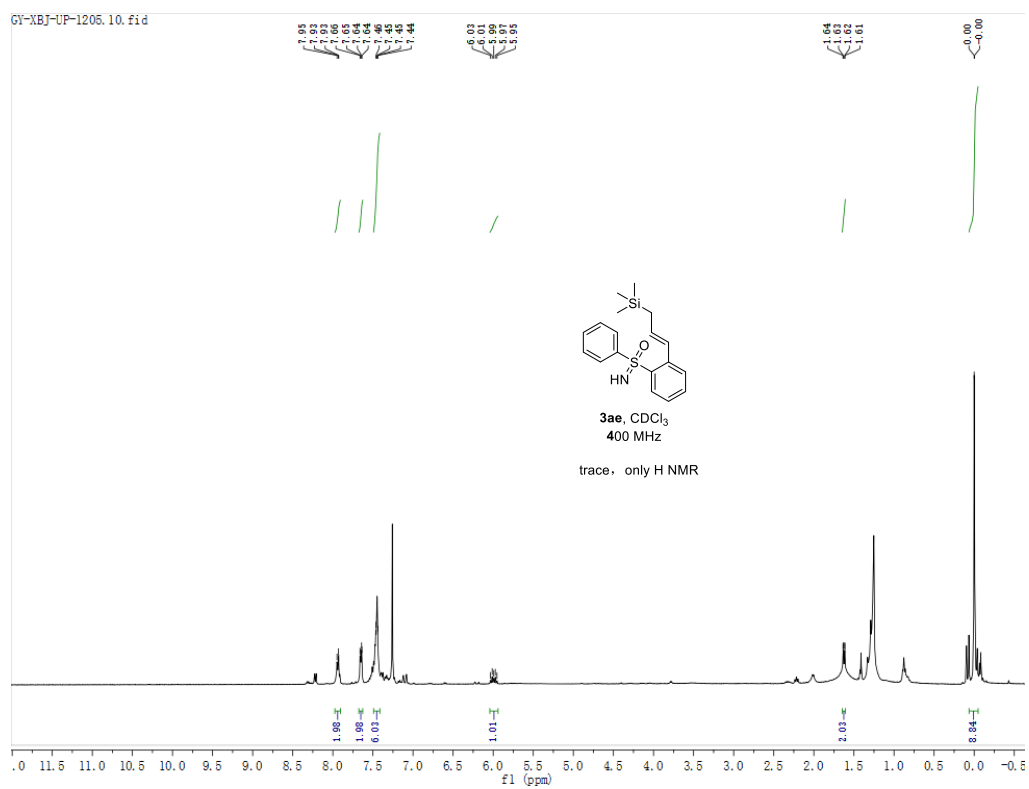
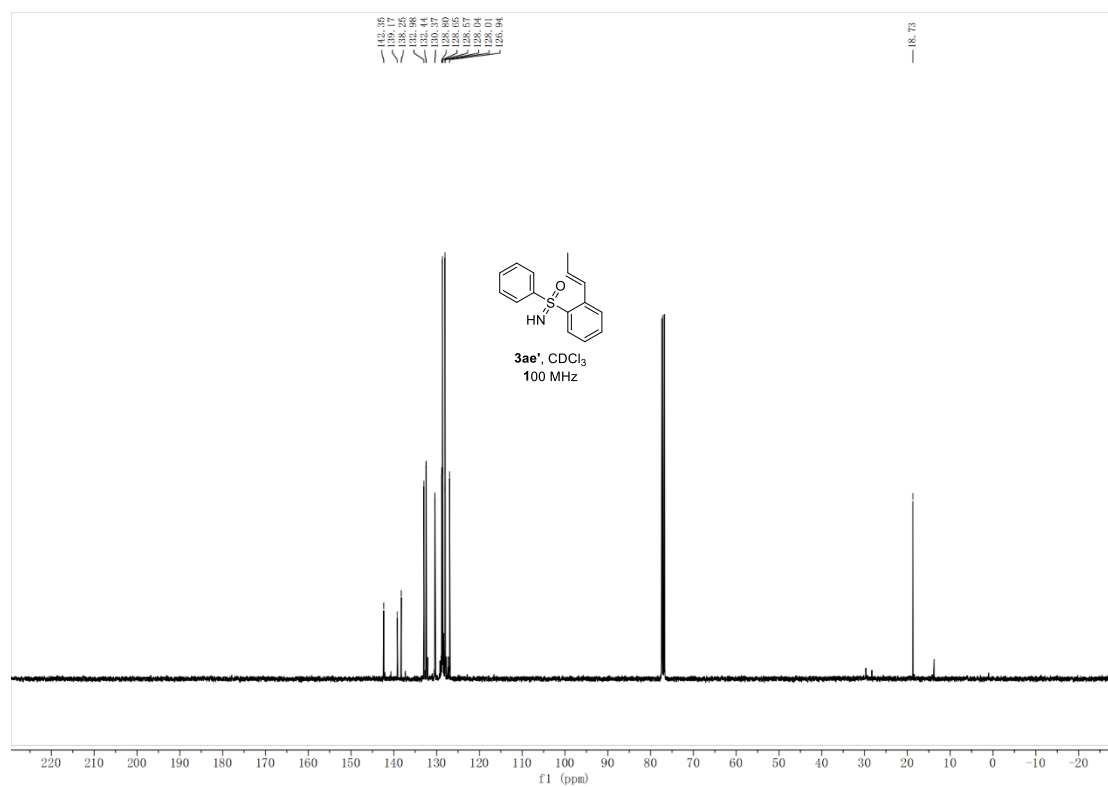


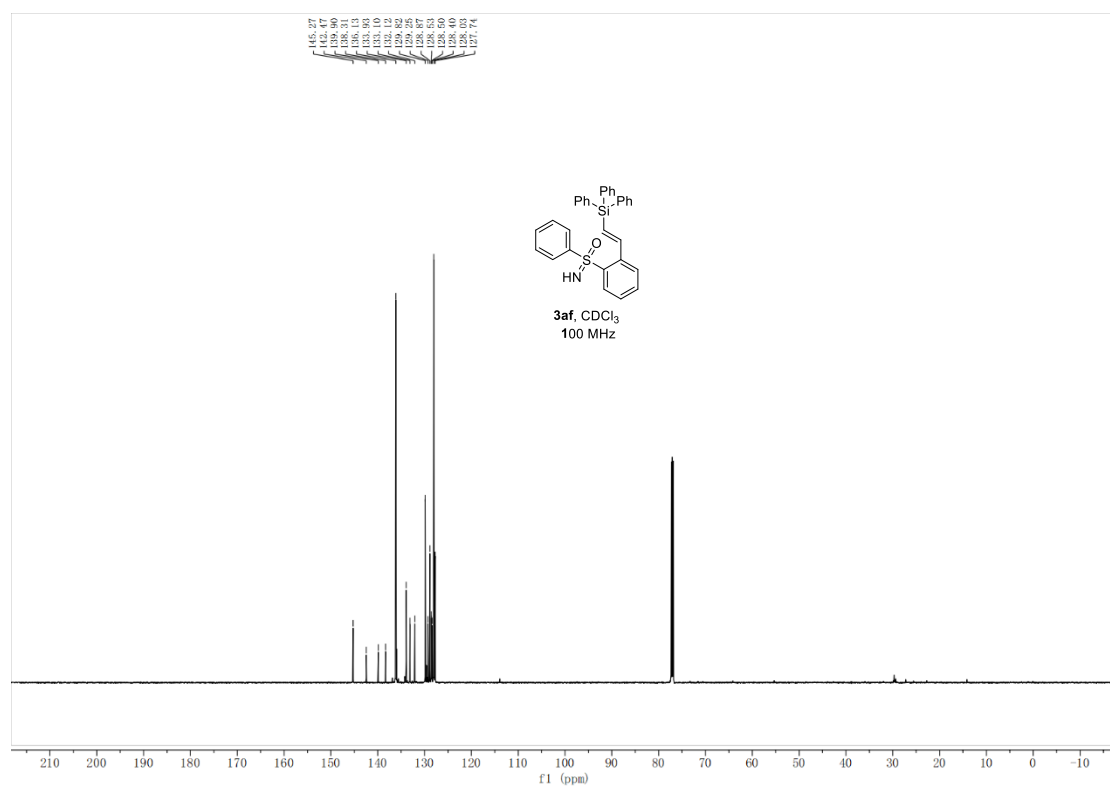
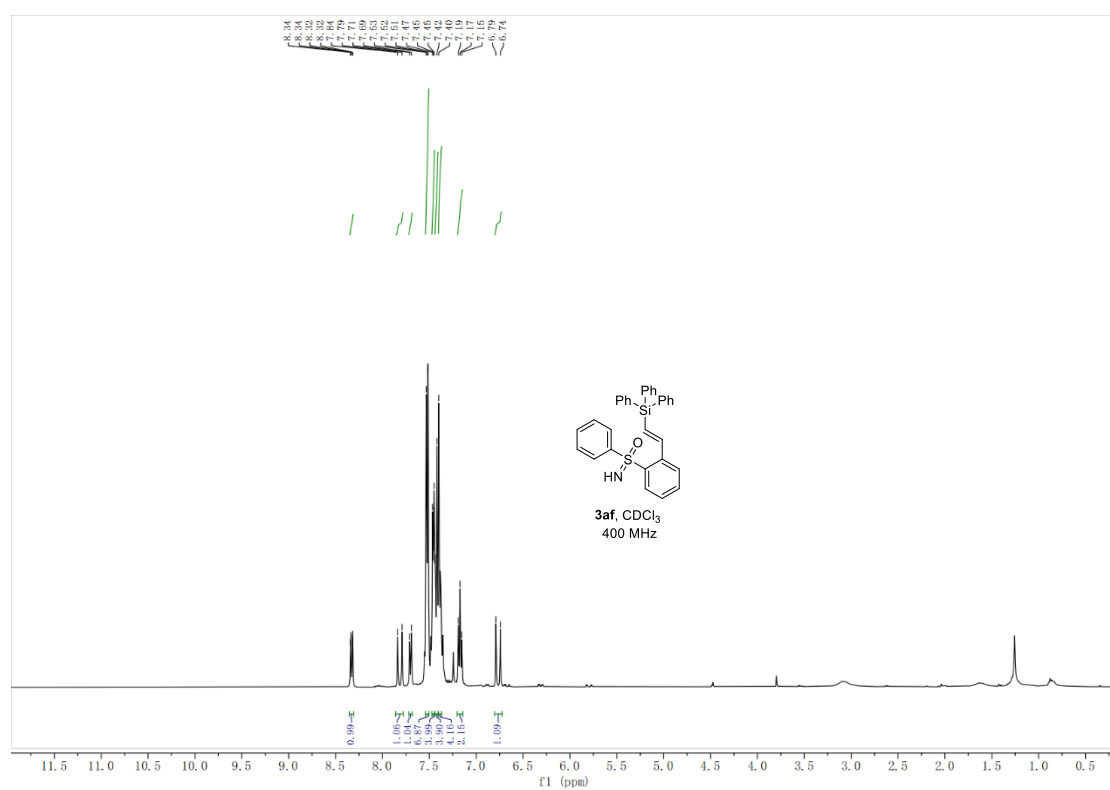


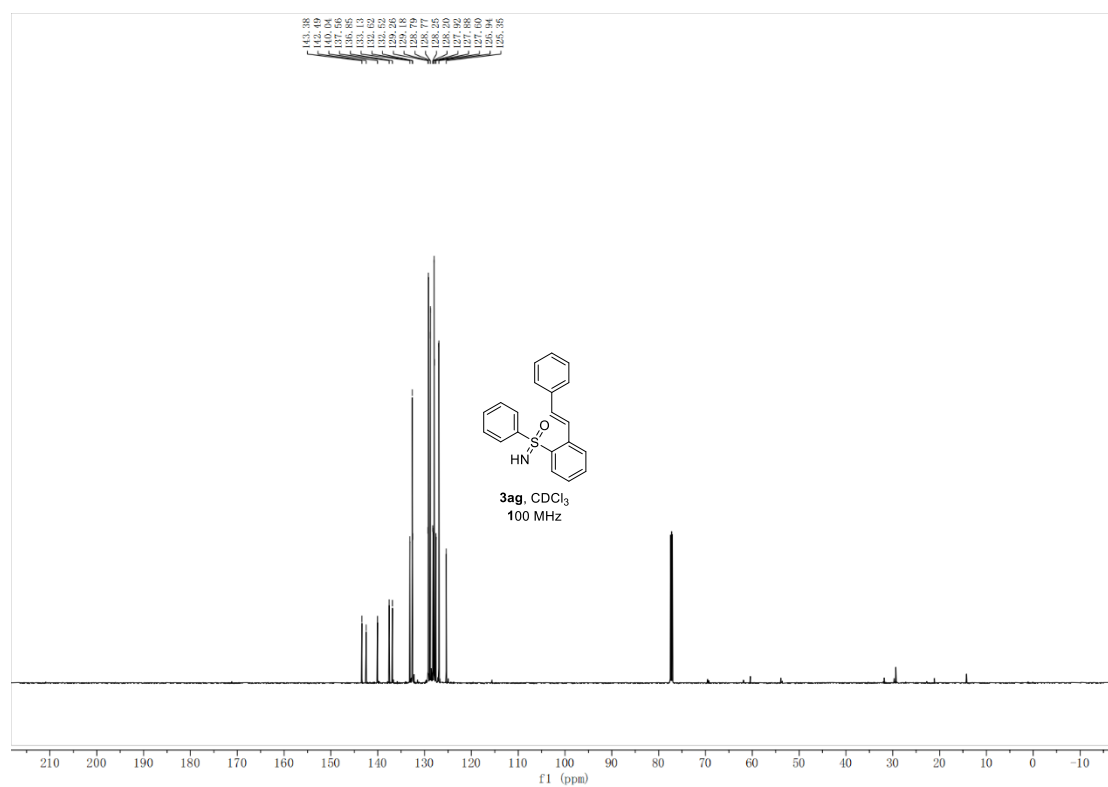
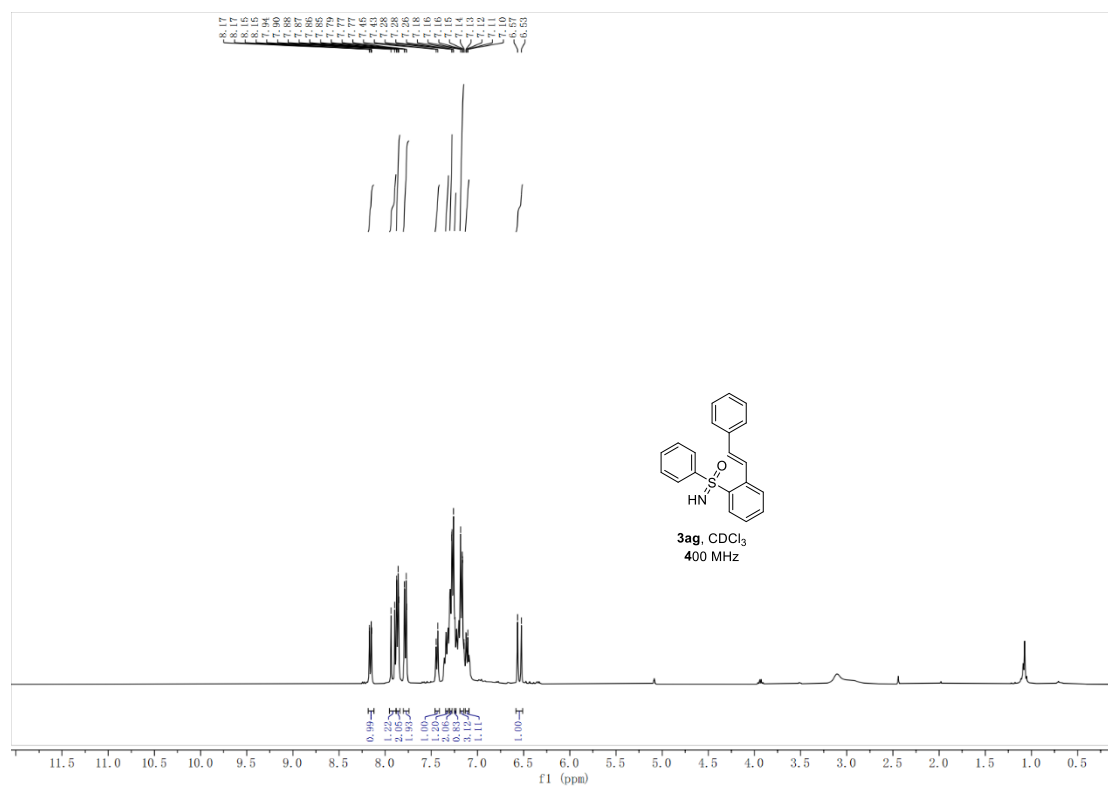












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