

Electronic Supplementary Information

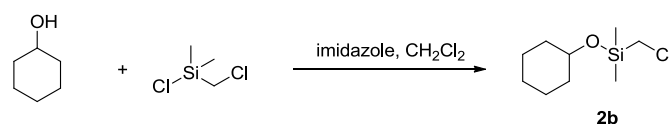
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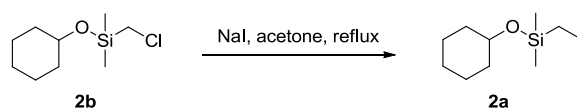
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General Information

Nuclear magnetic resonance spectra were recorded on Bruker-300 and 400MHz instruments internally referenced to tetramethylsilane (0.0 ppm) or residue of CDCl₃ (7.26 ppm for ¹H, and 77.00 ppm for ¹³C) signal. HRMS spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. All reactions were performed under an inert atmosphere of dry nitrogen in dried glassware, unless otherwise stated. Solvents were distilled using standard techniques. Tetrahydrofuran and diethyl ether were distilled over sodium under an atmosphere of nitrogen. Toluene, dichloromethane, dioxane, triethylamine were distilled over calcium hydride under an atmosphere of nitrogen. Acetone was distilled over calcium chloride under an atmosphere of nitrogen. Methanol was dried by magnesium. Room temperature reactions were performed between 25-30 °C.

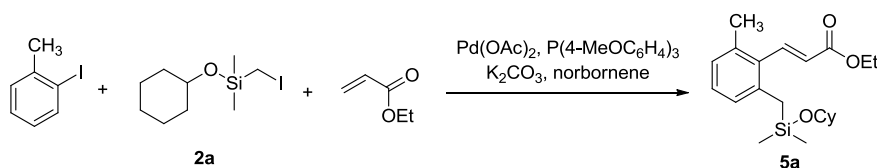


Chloro(chloromethyl)dimethylsilane (2.50 ml, 18.7 mmol, 1.3 eq.) was added dropwise to a solution of cyclohexanol (1.50 ml, 14.4 mmol, 1.0 eq.) and imidazole (1.10 g, 15.8 mmol, 1.1 eq.) in dichloromethane (90 ml) at 0 °C. The mixture was stirred at room temperature overnight before being filtered through a plug of Celite eluting with dichloromethane (10 ml). The filtrate was concentrated and the residue was distilled under vacuo (70 °C, 4 mm Hg) to give **2b** as a colorless oil (2.22 g, 75%). ¹H NMR (400 MHz, CDCl₃) δ 3.72-3.57 (m, 1 H), 2.78 (s, 2 H), 1.85-1.76 (m, 2 H), 1.76-1.66 (m, 2 H), 1.56-1.46 (m, 1 H), 1.35-1.08 (m, 5 H), 0.24 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 71.8, 35.9, 30.1, 25.4, 24.3, -2.9; HRMS (ESI) calcd for C₉H₁₉ClOSiNa [M+Na]⁺ 229.0238, found 229.0235.

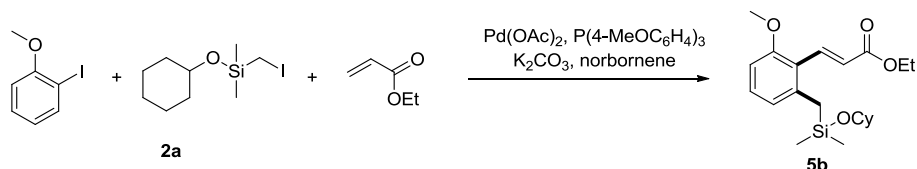


NaI (4.0 g, 29.9 mmol, 8.0 eq.) was added to a solution of **2b** (0.77 g, 3.74 mmol, 1.0 eq.) in acetone (40 ml). The mixture was refluxed for 2d before being filtered through a plug of Celite eluting with acetone (10 ml). The filtrate was concentrated and dichloromethane (30 ml) was added. The resulting mixture was filtered and the filtrate was concentrated and the crude product was purified by flash column chromatography (1.5% ethyl acetate/hexanes) to give **2a** as a colorless oil (0.892 g, 80 %). ¹H NMR (400 MHz, CDCl₃) δ 3.73-3.50 (m, 1 H), 2.02 (s, 2 H), 1.86-1.76 (m, 2 H), 1.76-1.67 (m, 2 H), 1.56-1.45 (m, 1 H), 1.36-1.05 (m, 5 H), 0.28 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 71.7, 35.9, 25.4, 24.3, -2.0, -13.8; HRMS (ESI) calcd for C₉H₁₉IOSiNa [M+Na]⁺ 321.0148, found 321.0150.

General procedure for the Heck reaction-terminated Catellani reaction (**General Procedure A**): To a solution of aryl iodide (0.157 mmol, 1.0 eq.), **2a** (0.392 mmol, 2.5 eq.), MeCN (2 ml) in a Schlenk tube was added Pd(OAc)₂ (0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (0.0314 mmol, 20 mol%), K₂CO₃ (0.471 mmol, 3.0 eq.), norbornene (0.628 mmol, 4.0 eq.), and ethyl acrylate (0.550 mmol, 3.5 eq.). The mixture was allowed to stir at 95 °C for 30 h before being cooled to room temperature. The mixture was filtered through a plug of silica gel eluting with ethyl acetate (15 ml). The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give **5**.

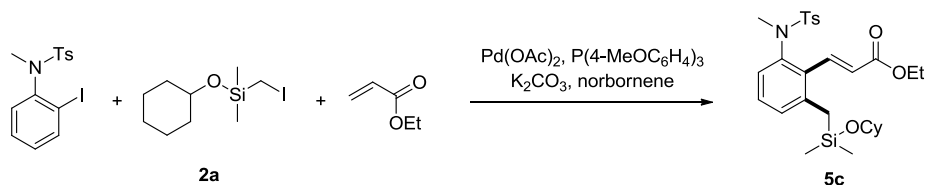


The reaction of 2-iodotoluene (34.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5a** (46.0 mg, 81%) (33% dichloromethane/hexanes then 1.25% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 16.4 Hz, 1 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 7.6 Hz, 2 H), 6.07 (d, *J* = 16.4 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 3.62-3.48 (m, 1 H), 2.33 (s, 3 H), 2.26 (s, 2 H), 1.78-1.61 (m, 4 H), 1.54-1.44 (m, 1 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.31-1.07 (m, 5 H), 0.064 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 144.4, 138.6, 136.3, 133.0, 127.9, 127.2, 126.8, 124.0, 71.3, 60.4, 35.9, 25.5, 25.1, 24.2, 21.5, 14.3, -1.1; HRMS (ESI) calcd for C₂₁H₃₂O₃SiNa [M+Na]⁺ 383.2018, found 383.2020.

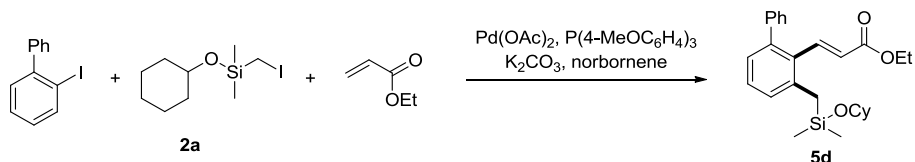


Compound **5b** was prepared following the **General Procedure A**. The reaction of 2-iodoanisole (36.7 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg,

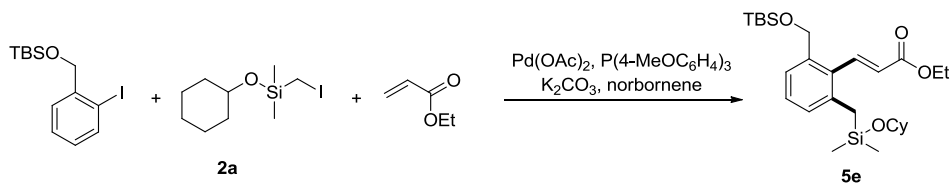
0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5b** (52.0 mg, 88%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.86 (d, $J = 16.2$ Hz, 1 H), 7.15 (t, $J = 7.8$ Hz, 1 H), 6.78-6.64 (m, 3 H), 4.26 (q, $J = 4.2$ Hz, 2 H), 3.86 (s, 3 H), 3.65-3.49 (m, 1 H), 2.38 (s, 2 H), 1.82-1.62 (m, 4 H), 1.56-1.42 (m, 1 H), 1.34 (t, $J = 4.2$ Hz, 3 H), 1.30-1.04 (m, 5 H), 0.076 (s, 6 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 168.2, 159.6, 142.3, 139.4, 129.7, 122.6, 121.7, 120.9, 107.0, 71.3, 60.1, 55.3, 35.9, 25.5, 24.2, 14.4, -1.2; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{32}\text{O}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 399.1968, found 399.1966.



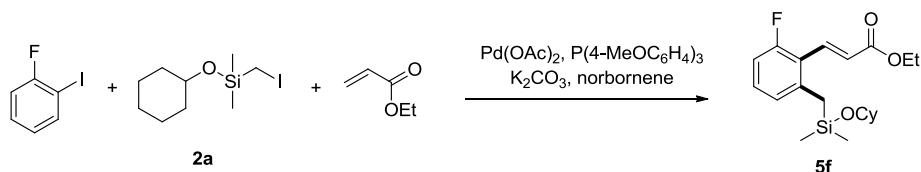
Compound **5c** was prepared following the **General Procedure A**. The reaction of N-(2-Iodophenyl)-N,4-dimethylbenzenesulfonamide (60.8 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), $\text{Pd}(\text{OAc})_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5c** (71.4 mg, 86%) (40% dichloromethane/hexanes then 10% ethyl acetate/hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 16.4$ Hz, 1 H), 7.61 (d, $J = 8.4$ Hz, 2 H), 7.28 (d, $J = 8.0$ Hz, 2 H), 7.14-7.01 (m, 2 H), 6.62 (dd, $J = 2.0, 6.8$ Hz, 1 H), 6.25 (d, $J = 16.4$ Hz, 1 H), 4.27 (q, $J = 6.8$ Hz, 2 H), 3.61-3.46 (m, 1 H), 3.08 (s, 3 H), 2.44 (s, 3 H), 2.30 (s, 2 H), 1.75-1.63 (m, 4 H), 1.56-1.45 (m, 1 H), 1.35 (t, $J = 6.8$ Hz, 3 H), 1.30-1.11 (m, 5 H), 0.071 (s, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.6, 143.5, 141.5, 140.7, 140.1, 135.2, 134.0, 129.7, 129.4, 128.3, 128.1, 124.3, 123.8, 71.3, 60.4, 39.2, 35.8, 25.4, 25.3, 24.2, 21.6, 14.3, -1.1; **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{39}\text{NO}_5\text{SSiNa}$ $[\text{M}+\text{Na}]^+$ 552.2216, found 552.2213.



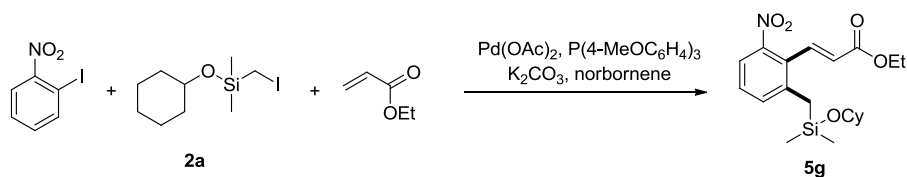
Compound **5d** was prepared following the **General Procedure A**. The reaction of 2-iodobiphenyl (44.0 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), $\text{Pd}(\text{OAc})_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5d** (61.0 mg, 92%) (33% dichloromethane/hexanes then 1.25% ethyl acetate/hexanes). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.75 (d, $J = 16.2$ Hz, 1 H), 7.40-7.19 (m, 6 H), 7.12 (d, $J = 7.2$ Hz, 1 H), 7.06 (d, $J = 4.5$ Hz, 1 H), 5.64 (d, $J = 16.2$ Hz, 1 H), 4.14 (q, $J = 7.2$ Hz, 2 H), 3.69-3.48 (m, 1 H), 2.36 (s, 2 H), 1.81-1.62 (m, 4 H), 1.54-1.43 (m, 1 H), 1.34-1.10 (m, 8 H), 0.11 (s, 6 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.6, 144.0, 142.2, 141.8, 139.2, 131.8, 129.7, 128.8, 128.1, 128.0, 126.93, 126.89, 124.8, 71.3, 60.2, 35.9, 25.5, 25.3, 24.2, 14.2, -1.0; **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 445.2175, found 445.2173.



Compound **5e** was prepared following the **General Procedure A**. The reaction of 2-(*O*-TBS)-hydroxymethyl iodobenzene (54.6 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5e** (49.0 mg, 62%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 16.4 Hz, 1 H), 7.27-7.23 (m, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 6.8 Hz, 1 H), 6.17 (d, *J* = 16.4 Hz, 1 H), 4.63 (s, 2 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 3.61-3.46 (m, 1 H), 2.26 (s, 2 H), 1.79-1.63 (m, 4 H), 1.54-1.43 (m, 1 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.29-1.14 (m, 5 H), 0.92 (s, 9 H), 0.082 (s, 6 H), 0.060 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 143.2, 139.2, 138.4, 132.2, 128.5, 128.0, 124.5, 124.4, 71.3, 63.7, 60.4, 35.9, 25.9, 25.5, 25.0, 24.2, 18.3, 14.3, -1.1, -5.3; HRMS (ESI) calcd for C₂₇H₄₆O₄Si₂Na [M+Na]⁺ 513.2832, found 513.2836.

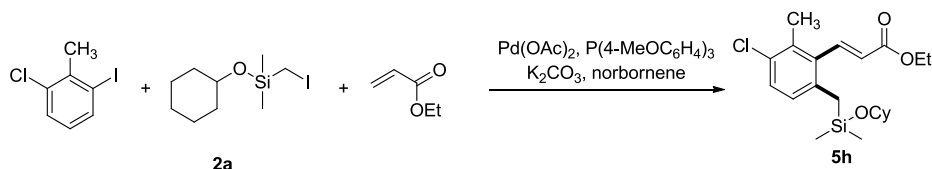


Compound **5f** was prepared following the **General Procedure A**. The reaction of 1-fluoro-2-iodobenzene (34.8 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5f** (37.9 mg, 66%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, *J* = 21.6 Hz, 1 H), 7.22-7.07 (m, 1 H), 6.95-6.77 (m, 2 H), 6.57 (d, *J* = 21.6 Hz, 1 H), 4.27 (q, *J* = 9.6 Hz, 2 H), 3.64-3.48 (m, 1 H), 2.36 (s, 2 H), 1.80-1.62 (m, 4 H), 1.53-1.44 (m, 1 H), 1.37-1.13 (m, 8 H), 0.082 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 162.2 (d, *J* = 251 Hz), 142.8 (d, *J* = 2.7 Hz), 137.0, 129.9 (d, *J* = 10.2 Hz), 125.6 (d, *J* = 3.1 Hz), 123.2 (d, *J* = 14.8 Hz), 120.4 (d, *J* = 11.2 Hz), 112.1 (d, *J* = 23.2 Hz), 71.4, 60.4, 35.8, 29.7, 25.5, 24.2, 14.3, -1.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.7; HRMS (ESI) calcd for C₂₀H₂₉FO₃SiNa [M+Na]⁺ 387.1768, found 387.1766.

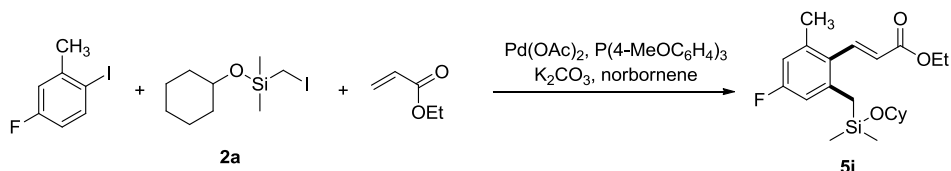


Compound **5g** was prepared following the **General Procedure A**. The reaction of 1-iodo-2-nitrobenzene (39.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%),

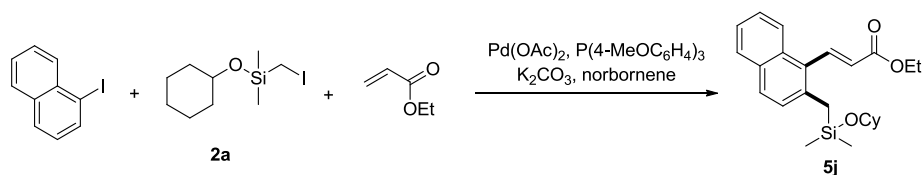
K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5g** (30.5 mg, 50%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 16.4 Hz, 1 H), 7.59 (d, J = 7.2 Hz, 1 H), 7.41-7.27 (m, 2 H), 5.95 (d, J = 16.4 Hz, 1 H), 4.26 (q, J = 7.2 Hz, 2 H), 3.61-3.46 (m, 1 H), 2.28 (s, 2 H), 1.76-1.61 (m, 4 H), 1.52-1.44 (m, 1 H), 1.33 (t, J = 7.2 Hz, 3 H), 1.28-1.15 (m, 5 H), 0.095 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 149.7, 141.1, 140.7, 133.5, 128.3, 128.1, 124.6, 120.2, 71.4, 60.7, 35.8, 29.7, 25.4, 25.3, 24.1, 14.2, -1.0; HRMS (ESI) calcd for $C_{20}H_{29}NO_5SiNa$ $[M+Na]^+$ 414.1713, found 414.1716.



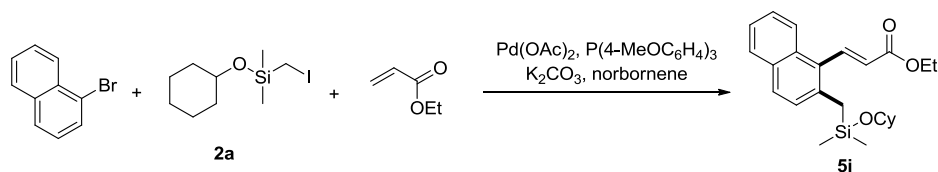
Compound **5h** was prepared following the **General Procedure A**. The reaction of 2-chloro-6-iodotoluene (39.6 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), $Pd(OAc)_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $P(4-MeOC_6H_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5h** (60.6 mg, 98%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). 1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 16.2 Hz, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 1 H), 6.00 (d, J = 16.2 Hz, 1 H), 4.28 (q, J = 6.9 Hz, 2 H), 3.59-3.45 (m, 1 H), 2.34 (s, 3 H), 2.17 (s, 2 H), 1.78-1.62 (m, 4 H), 1.56-1.43 (m, 1 H), 1.34 (t, J = 6.9 Hz, 3 H), 1.28-1.14 (m, 5 H), 0.056 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 144.3, 136.8, 135.1, 133.6, 131.1, 128.5, 127.8, 125.4, 71.3, 60.6, 35.8, 18.2, 14.3, -1.1; HRMS (ESI) calcd for $C_{21}H_{31}ClO_3SiNa$ $[M+Na]^+$ 417.1629, found 417.1631.



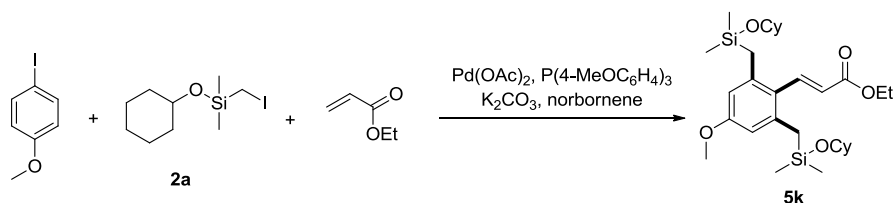
Compound **5i** was prepared following the **General Procedure A**. The reaction of 5-fluoro-2-iodotoluene (37.0 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), $Pd(OAc)_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $P(4-MeOC_6H_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55.0 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5i** (44.5 mg, 75%) (33% dichloromethane/hexanes then 2% ethyl acetate/hexanes). 1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 16.4 Hz, 1 H), 6.70 (s, 1 H), 6.67 (s, 1 H), 6.03 (d, J = 16.4 Hz, 1 H), 4.27 (q, J = 7.2 Hz, 2 H), 3.64-3.45 (m, 1 H), 2.32 (s, 3 H), 2.24 (s, 2 H), 1.75-1.64 (m, 4 H), 1.53-1.45 (m, 1 H), 1.34 (t, J = 7.2 Hz, 3 H), 1.31-1.12 (m, 5 H), 0.074 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.9 (d, J = 245 Hz), 143.4, 141.5 (d, J = 8.4 Hz), 138.8 (d, J = 8.5 Hz), 128.9 (d, J = 2.9 Hz), 124.2, 113.7 (d, J = 2.3 Hz), 113.5 (d, J = 2.2 Hz), 71.3, 60.5, 35.8, 25.6, 25.5, 24.2, 21.7, 14.3, -1.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7; HRMS (ESI) calcd for $C_{21}H_{31}FO_3SiNa$ $[M+Na]^+$ 401.1924, found 401.1920.



Compound **5j** was prepared following the **General Procedure A**. The reaction of 1-iodonaphthalene (39.9 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) and ethyl acrylate (55 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5j** (60.3 mg, 97%) (33% dichloromethane/hexanes then 1.25% ethyl acetate/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, *J* = 16.5 Hz, 1 H), 8.04 (d, *J* = 8.1 Hz, 1 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.51-7.34 (m, 2 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 6.28 (d, *J* = 16.2 Hz, 1 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 3.64-3.49 (m, 1 H), 2.43 (s, 2 H), 1.81-1.63 (m, 4 H), 1.54-1.43 (m, 1 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 1.32-1.13 (m, 5 H), 0.087 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 166.7, 143.4, 136.4, 131.6, 131.4, 129.1, 128.4, 128.3, 128.2, 126.4, 125.6, 124.7, 124.6, 71.3, 60.5, 35.9, 25.9, 25.5, 24.2, 14.3, -0.9; HRMS (ESI) calcd for C₂₄H₃₂O₃SiNa [M+Na]⁺ 419.2018, found 419.2014.



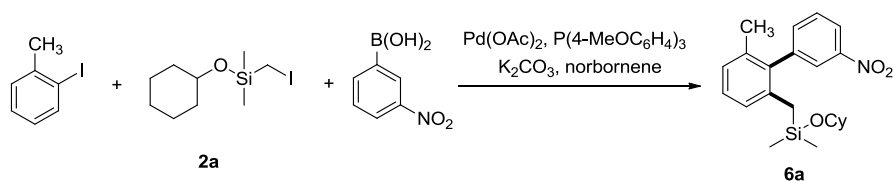
Compound **5j** was prepared following the **General Procedure A**. The reaction of 1-bromonaphthalene (32.5 mg, 0.157 mmol, 1.0 equiv), **2a** (0.117 g, 0.392 mmol, 2.5 equiv), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 equiv), norbornene (59.3 mg, 0.628 mmol, 4.0 equiv) and ethyl acrylate (55 mg, 0.550 mmol, 3.5 eq.) in MeCN (2 mL) delivered **5j** (16.0 mg, 26%) (33% dichloromethane/hexanes then 1.25% ethyl acetate/hexanes).



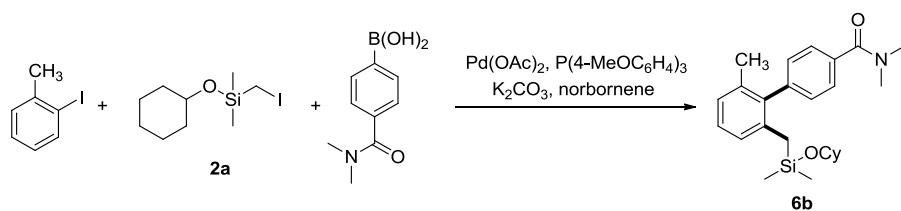
Compound **5k** was prepared following the **General Procedure A**. The reaction of 4-iodoanisole (36.7 mg, 0.157 mmol, 1.0 equiv), **2a** (0.234 g, 0.784 mmol, 5.0 equiv), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (97.5 mg, 0.706 mmol, 4.5 equiv), norbornene (59.3 mg, 0.628 mmol, 4.0 equiv) and ethyl acrylate (55 mg, 0.550 mmol, 3.5 equiv) in MeCN (2 mL) delivered **5k** (21.3 mg, 25%) (33% dichloromethane/hexanes then 1.5% ethyl acetate/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, *J* = 16.5 Hz, 1 H), 6.44 (s, 2 H), 6.07 (d, *J* = 16.2 Hz, 1 H), 4.25 (q, *J* = 6.9 Hz, 2 H), 3.76 (s, 3 H), 3.63-3.49 (m, 2 H), 2.25 (s, 4 H), 1.80-1.65 (m, 8 H), 1.56-1.45 (m, 2 H), 1.33 (t, *J* = 6.9 Hz, 3 H), 1.29-1.13 (m, 10 H), 0.06 (s, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 158.7, 145.0, 140.3, 124.9,

123.0, 111.3, 71.3, 60.2, 54.9, 35.9, 25.6, 25.5, 24.3, 14.3, -1.0; **HRMS** (ESI) calcd for $C_{30}H_{50}O_5Si_2Na$ $[M+Na]^+$ 569.3094, found 569.3098.

General procedure for the Suzuki reaction-terminated Catellani reaction (**General Procedure B**): To a solution of aryl iodide (0.157 mmol, 1.0 eq.), **2a** (0.392 mmol, 2.5 eq.) and aryl boronic acid (0.314 mmol, 2 eq.) in MeCN (2 ml) in a Schlenk tube was added $Pd(OAc)_2$ (0.0157 mmol, 10 mol%), $P(4-MeOC_6H_4)_3$ (0.0314 mmol, 20 mol%), K_2CO_3 (0.471 mmol, 3.0 eq.), norbornene (0.628 mmol, 4.0 eq.), and the mixture was allowed to stir at 95 °C for 30 h before being cooled to rt. The mixture was filtered through a plug of silica gel eluting with ethyl acetate (15 ml). The filtrate was concentrated and the residue was purified by column chromatography to give **6**.

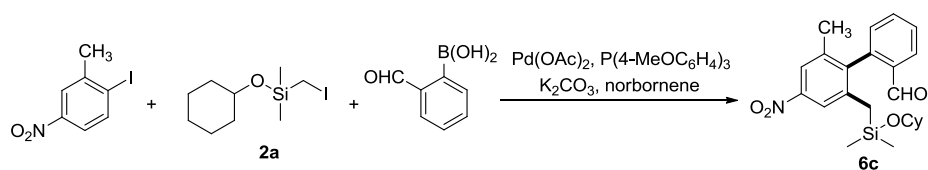


Compound **6a** was prepared following the **General Procedure B**. The reaction of 2-iodotoluene (34.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 3-nitrophenylboronic acid (52.4 mg, 0.314 mmol, 2 eq.), $Pd(OAc)_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $P(4-MeOC_6H_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6a** (43.1 mg, 72%) (1% ethyl acetate/hexanes). **1H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1 H), 8.08 (s, 1 H), 7.60 (t, J = 8.0 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H), 7.18 (t, J = 7.6 Hz, 1 H), 7.10 (d, J = 7.6 Hz, 1 H), 7.03 (d, J = 7.6 Hz, 1 H), 3.45-3.32 (m, 1 H), 1.98 (s, 3 H), 1.92 (s, 2 H), 1.71-1.57 (m, 4 H), 1.52-1.43 (m, 1 H), 1.23-1.04 (m, 5 H), -0.023 (s, 3 H), -0.034 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 143.0, 138.0, 137.5, 136.4, 135.9, 129.2, 127.7, 126.9, 126.2, 125.0, 121.8, 71.3, 35.82, 35.79, 25.4, 24.5, 24.3, 21.3, -0.8, -0.9; **HRMS** (ESI) calcd for $C_{22}H_{29}NO_3SiNa$ $[M+Na]^+$ 406.2528, found 406.2523.

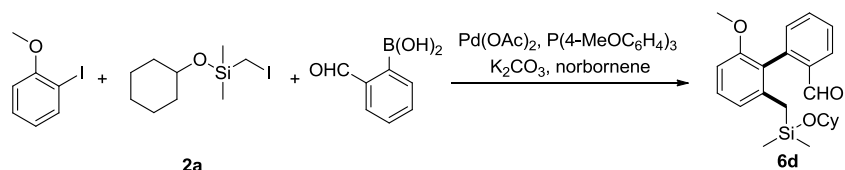


Compound **6b** was prepared following the **General Procedure B**. The reaction of 2-iodotoluene (34.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 4-(*N,N*-dimethylaminocarbonyl)phenylboronic acid (60.6 mg, 0.314 mmol, 2 eq.), $Pd(OAc)_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $P(4-MeOC_6H_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6b** (59.3 mg, 92%) (20% ethyl acetate/hexanes). **1H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.16-7.06 (m, 2 H), 7.00 (d, J = 7.2 Hz, 1 H), 3.50-3.37 (m, 1 H), 3.14 (s, 3 H), 3.04 (s, 3 H), 1.97 (s, 5 H), 1.72-1.59 (m, 4 H), 1.51-1.42 (m, 1 H), 1.25-1.04 (m, 5 H), -0.051 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 142.8, 139.8, 137.4, 136.1, 134.4, 129.8,

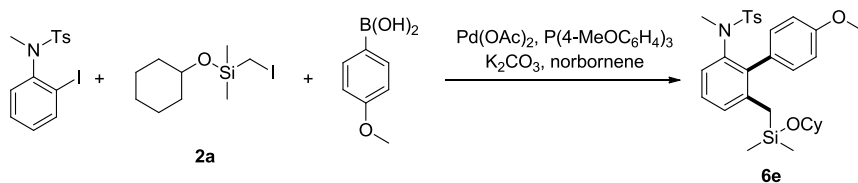
127.2, 127.0, 126.7, 125.9, 71.1, 39.7, 35.8, 35.4, 25.4, 24.3, 24.2, 21.3, -0.9; **HRMS** (ESI) calcd for $C_{25}H_{35}NO_2SiNa$ $[M+Na]^+$ 432.2335, found 432.2336.



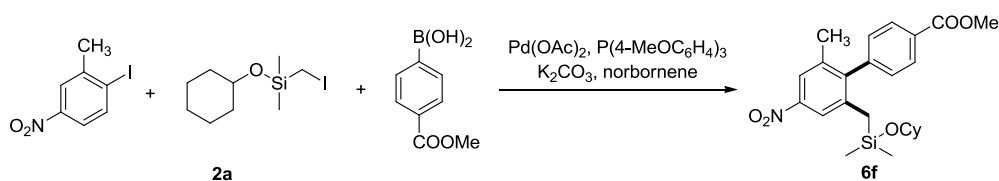
Compound **6c** was prepared following the **General Procedure B**. The reaction of 2-iodo-5-nitrotoluene (41.3 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-formylbenzeneboronic acid (47.1 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6c** (42.4 mg, 66%) (7% ethyl acetate/hexanes). **¹H NMR** (300 MHz, CDCl₃) δ 9.64 (s, 1 H), 8.13-8.00 (m, 2 H), 7.91 (s, 1 H), 7.71 (t, *J* = 6.9 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.19 (d, *J* = 7.5 Hz, 1 H), 3.58-3.34 (m, 1 H), 2.08-1.77 (m, 5 H), 1.73-1.59 (m, 4 H), 1.53-1.40 (m, 1 H), 1.28-1.08 (m, 5 H), -0.016 (s, 3 H), -0.025 (s, 3 H); **¹³C NMR** (75 MHz, CDCl₃) δ 191.1, 147.2, 143.0, 142.6, 140.7, 138.4, 134.4, 133.4, 130.5, 128.6, 128.4, 121.6, 120.6, 71.5, 35.7, 25.4, 25.1, 24.2, 21.6, -0.69, -0.73; **HRMS** (ESI) calcd for $C_{23}H_{29}NO_4SiNa$ $[M+Na]^+$ 434.6519, found 434.6524.



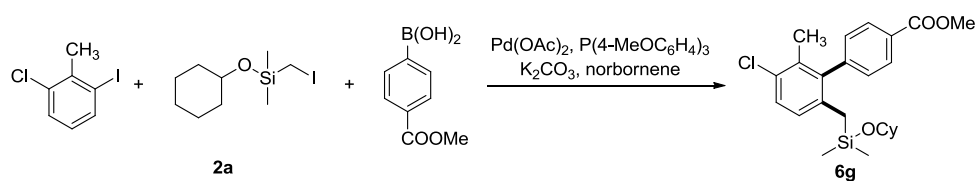
Compound **6d** was prepared following the **General Procedure B**. The reaction of 2-iodoanisole (36.7 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-formylbenzeneboronic acid (47.1 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6d** (43.8 mg, 73%) (7% ethyl acetate/hexanes). **¹H NMR** (400 MHz, CDCl₃) δ 9.69 (d, *J* = 0.8 Hz, 1 H), 8.03 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.64 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.31-7.22 (m, 2 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 3.65 (s, 3 H), 3.42-3.30 (m, 1 H), 2.08 (d, *J* = 14.0 Hz, 1 H), 1.91 (d, *J* = 14.0 Hz, 1 H), 1.71-1.57 (m, 4 H), 1.52-1.42 (m, 1 H), 1.22-1.06 (m, 5 H), -0.058 (s, 3 H), -0.10 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃) δ 193.0, 157.1, 141.7, 140.0, 134.4, 133.7, 132.0, 128.8, 127.6, 126.7, 124.8, 122.1, 106.3, 71.3, 55.5, 35.8, 35.7, 25.4, 24.3, 24.2, -0.7, -0.9; **HRMS** (ESI) calcd for $C_{23}H_{30}O_3SiNa$ $[M+Na]^+$ 405.1862, found 405.1865.



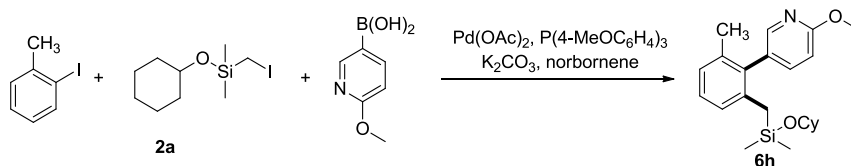
Compound **6e** was prepared following the **General Procedure B**. The reaction of iodobenzene (60.8 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 4-methoxyphenylboronic acid (16.3 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6e** (48.2 mg, 79%) (10% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.28-7.18 (m, 4 H), 7.18-7.08 (m, 2 H), 6.94 (d, *J* = 8.0 Hz, 2 H), 6.78 (dd, *J* = 0.8, 8.0 Hz, 1 H), 3.87 (s, 3 H), 3.43-3.30 (m, 1 H), 2.82 (s, 3 H), 2.42 (s, 3 H), 2.08 (s, 2 H), 1.68-1.57 (m, 4 H), 1.52-1.44 (m, 1 H), 1.23-1.06 (m, 5 H), -0.043 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 143.1, 141.0, 140.7, 140.4, 136.4, 130.5, 129.3, 129.2, 128.0, 127.3, 123.3, 113.3, 71.2, 55.2, 39.3, 35.8, 25.4, 24.5, 24.3, 21.5, -0.9; HRMS (ESI) calcd for C₃₀H₃₉NO₄SSiNa [M+Na]⁺ 560.2267, found 560.2268.



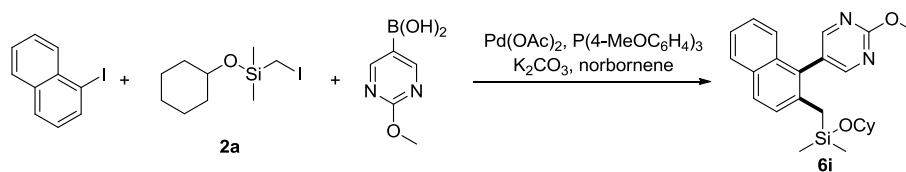
Compound **6f** was prepared following the **General Procedure B**. The reaction of 2-iodo-5-nitrotoluene (41.3 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), boronic acid (56.5 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6f** (59.2 mg, 85%) (2% ethyl acetate/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, *J* = 8.1 Hz, 2 H), 8.01 (s, 1 H), 7.87 (s, 1 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 3.96 (s, 3 H), 3.54-3.37 (m, 1 H), 2.05 (s, 3 H), 1.99 (s, 2 H), 1.73-1.54 (m, 4 H), 1.52-1.38 (m, 1 H), 1.33-1.05 (m, 5 H), -0.028 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 146.9, 146.0, 144.3, 139.9, 137.8, 130.0, 129.4, 129.2, 121.5, 120.5, 71.3, 52.2, 35.7, 25.4, 24.9, 24.1, 21.4, -0.9; HRMS (ESI) calcd for C₂₄H₃₁NO₅SiNa [M+Na]⁺ 464.1869, found 464.1873.



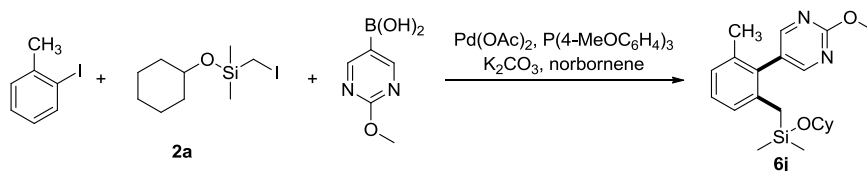
Compound **6g** was prepared following the **General Procedure B**. The reaction of 2-chloro-6-iodotoluene (39.6 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 4-(methoxycarbonyl)benzeneboronic acid (56.5 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6g** (41.8 mg, 62%) (2% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.4 Hz, 2 H), 7.28-7.18 (m, 3 H), 7.04 (d, *J* = 8.4 Hz, 1 H), 3.95 (s, 3 H), 3.44-3.31 (m, 1 H), 2.00 (s, 3 H), 1.87 (s, 2 H), 1.71-1.58 (m, 4 H), 1.52-1.40 (m, 1 H), 1.23-1.07 (m, 5 H), -0.058 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 146.0, 141.2, 136.2, 133.7, 130.7, 129.9, 129.7, 128.8, 128.0, 127.6, 71.2, 52.2, 35.8, 25.4, 24.2, 18.4, -0.9; HRMS (ESI) calcd for C₂₄H₃₁ClO₃SiNa [M+Na]⁺ 453.1629, found 453.1630.



Compound **6h** was prepared following the **General Procedure B**. The reaction of 2-iodotoluene (34.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyridine-5-boronic acid (48.0 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq) in MeCN (2 mL) delivered **6h** (52.0 mg, 90%) (1.5% ethyl acetate/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 1.8 Hz, 1 H), 7.41 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.19-7.05 (m, 2 H), 7.02 (d, *J* = 6.9 Hz, 1 H), 6.82 (d, *J* = 8.4, 1 H), 3.99 (s, 3 H), 3.46-3.32 (m, 1 H), 2.04-1.96 (m, 5 H), 1.73-1.58 (m, 4 H), 1.53-1.42 (m, 1 H), 1.28-1.07 (m, 5 H), -0.026 (s, 3 H), -0.039 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 162.9, 147.3, 140.5, 138.5, 137.0, 136.6, 129.6, 127.3, 126.7, 126.0, 110.4, 71.2, 53.4, 35.9, 35.8, 25.5, 24.3, 21.5, -0.88, -0.91; HRMS (ESI) calcd for C₂₂H₃₂NO₂Si [M+H]⁺ 370.2201, found 370.2205.

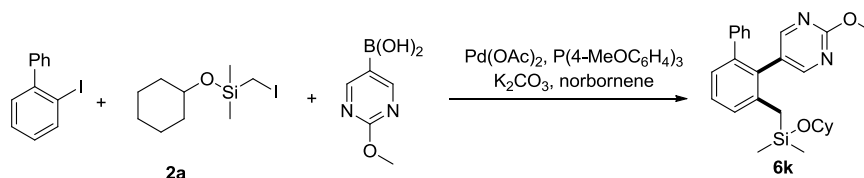


Compound **6i** was prepared following the **General Procedure B**. The reaction of 1-iodonaphthalene (39.9 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyrimidine-5-boronic acid (48.4 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6i** (49.0 mg, 76%) (7% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 2 H), 7.89-7.75 (m, 2 H), 7.45-7.34 (m, 3 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 4.13 (s, 3 H), 3.51-3.42 (m, 1 H), 2.17 (s, 2 H), 1.73-1.62 (m, 4 H), 1.52-1.42 (m, 1 H), 1.25-1.11 (m, 5 H), 0.025 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 160.9, 137.0, 133.5, 131.3, 128.3, 128.1, 126.8, 126.4, 125.0, 124.7, 71.4, 55.0, 35.8, 25.6, 25.4, 24.3, -0.8; HRMS (ESI) calcd for C₂₄H₃₀N₂O₂SiNa [M+Na]⁺ 429.3224, found 429.3221.

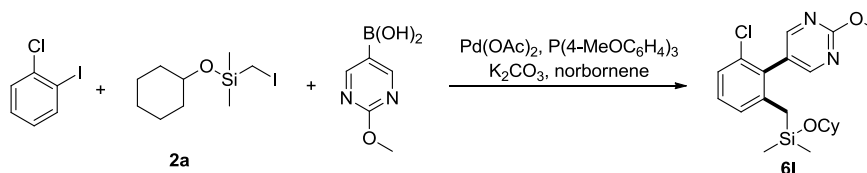


Compound **6j** was prepared following the **General Procedure B**. The reaction of 3-iodotoluene (34.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyrimidine-5-boronic acid (48.4 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6j** (46.9

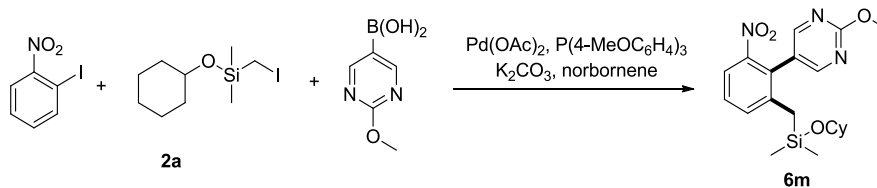
mg, 81%) (7% ethyl acetate/hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.36 (s, 2 H), 7.18 (t, $J = 7.6$ Hz, 1 H), 7.09 (d, $J = 7.6$ Hz, 1 H), 7.04 (d, $J = 7.2$ Hz, 1 H), 4.08 (s, 3 H), 3.49-3.35 (m, 1 H), 2.03 (s, 3 H), 1.96 (s, 2 H), 1.75-1.55 (m, 4 H), 1.55-1.43 (m, 1 H), 1.36-1.03 (m, 5 H), -0.010 (s, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.5, 160.0, 138.8, 137.1, 132.8, 128.0, 127.9, 127.0, 126.2, 71.4, 54.9, 35.8, 25.4, 24.8, 24.3, 21.6, -0.9; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 393.2128, found 393.2123.



Compound **6k** was prepared following the **General Procedure B**. The reaction of 2-iodobiphenyl (44.0 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyrimidine-5-boronic acid (48.4 mg, 0.314 mmol, 2 eq.), $\text{Pd}(\text{OAc})_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6k** (46.8 mg, 69%) (7% ethyl acetate/hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (s, 2 H), 7.33 (t, $J = 7.6$ Hz, 1 H), 7.27 (d, $J = 7.6$ Hz, 1 H), 7.22-7.10 (m, 4 H), 7.00 (d, $J = 7.2$ Hz, 2 H), 3.96 (s, 3 H), 3.51-3.35 (m, 1 H), 2.12 (s, 2 H), 1.74-1.61 (m, 4 H), 1.54-1.42 (m, 1 H), 1.30-1.10 (m, 5 H), -0.010 (s, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.8, 160.6, 142.9, 141.4, 139.0, 131.6, 129.9, 128.6, 127.98, 127.96, 127.6, 126.6, 126.5, 71.4, 54.8, 35.8, 25.4, 24.9, 24.3, -0.9; **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 455.2131, found 455.2130.



Compound **6l** was prepared following the **General Procedure B**. The reaction of 1-chloro-2-iodobenzene (37.4 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyrimidine-5-boronic acid (48.4 mg, 0.314 mmol, 2 eq.), $\text{Pd}(\text{OAc})_2$ (3.5 mg, 0.0157 mmol, 10 mol%), $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ (11.0 mg, 0.0314 mmol, 20 mol%), K_2CO_3 (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6l** (34.3 mg, 56%) (7% ethyl acetate/hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 (s, 2 H), 7.28-7.11 (m, 3 H), 4.08 (s, 3 H), 3.49-3.33 (m, 1 H), 2.03 (s, 2 H), 1.70-1.60 (m, 4 H), 1.52-1.41 (m, 1 H), 1.28-1.04 (m, 5 H), -0.004 (s, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.7, 160.3, 141.3, 134.7, 131.9, 129.1, 127.9, 126.3, 125.6, 71.5, 55.0, 35.8, 25.45, 25.39, 24.2, -0.9; **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{27}\text{ClN}_2\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 413.1428, found 413.1424.

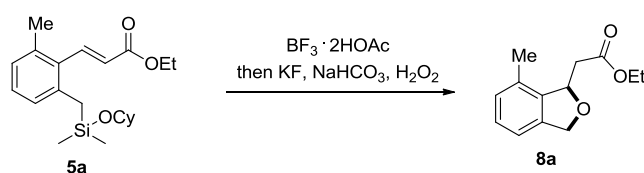


Compound **6m** was prepared following the **General Procedure B**. The reaction of 1-iodo-2-nitrobenzene (39.1 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-methoxypyrimidine-5-boronic acid (48.4 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.) and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **6m** (26.8 mg, 43%) (7% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 2 H), 7.66 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.50 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 4.07 (s, 3 H), 3.50-3.37 (m, 1 H), 2.04 (s, 2 H), 1.70-1.57 (m, 4 H), 1.53-1.43 (m, 1 H), 1.28-1.07 (m, 5 H), -0.021 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 159.3, 151.0, 142.4, 133.4, 128.6, 126.8, 123.7, 120.2, 71.6, 55.1, 35.7, 25.3, 25.1, 24.2, -0.9; HRMS (ESI) calcd for C₂₀H₂₇N₃O₄SiNa [M+Na]⁺ 424.1669, found 424.1667.

General procedure for the Fleming-Tamao Oxidation (**General Procedure C**):

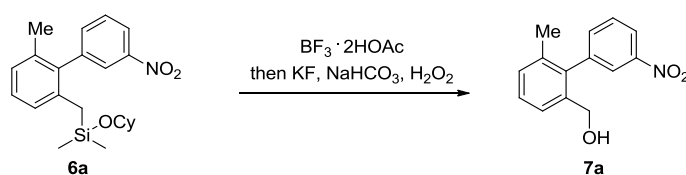
To a solution of substrate (0.160 mmol, 1.0 eq) in dichloromethane (2 mL) was added BF₃·2HOAc (0.480 mmol, 3.0 eq) dropwise at 0 °C, and the solution was stirred at room temperature for 1.5 h before being quenched by addition of saturated sodium bicarbonate (5 mL). The mixture was extracted with dichloromethane (2 × 10 mL) and the combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and concentrated in vacuo. The residue was used for next step without further purification.

THF/MeOH (1.5 mL / 1.5 mL) was added to a solution of the above residue, followed by KF (0.480 mmol, 3.0 eq), NaHCO₃ (1.28 mmol, 8.0 eq) and H₂O₂ (30% w/w, 0.192 mmol, 1.2 eq). The mixture was heated for 1-6 h at 70 °C before being poured into water (15 mL), extracted with ethyl acetate (2 × 10 mL), washed with brine (10 mL), dried (MgSO₄), filtered and concentrated. The crude product was purified by flash column chromatography to give the product.

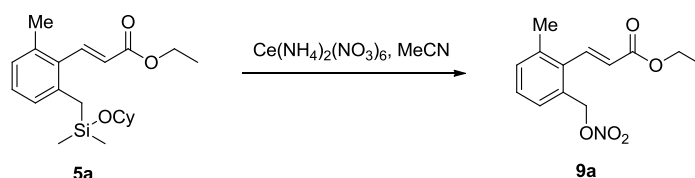


The oxidation of **5a** was followed the **General Procedure C**. The reaction of **5a** (57.6 mg, 0.160 mmol, 1.0 eq.), BF₃·2HOAc (90 mg, 0.480 mmol, 3.0 eq.) in dichloromethane (2 mL) then KF (27.8 mg, 0.480 mmol, 3.0 eq.), NaHCO₃ (0.108 g, 1.28 mmol, 8.0 eq.) and H₂O₂ (30% w/w, 21.8 mg, 0.192 mmol, 1.2 eq.) in THF/MeOH (1.5 mL / 1.5 mL) for 1 h afforded the product **8a** (20.6 mg, 59 %) (5% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, *J* = 7.6 Hz, 1 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 5.73 (d, *J* = 9.2 Hz, 1 H), 5.19 (dd, *J* = 2.4, 12.0 Hz, 1 H), 5.05 (d, *J* = 12.4 Hz, 1 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 2.86 (dd, *J* = 2.4, 15.6 Hz, 1 H), 2.60 (dd, *J* = 9.2, 15.6 Hz, 1 H), 2.30 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 139.2, 138.9, 131.3,

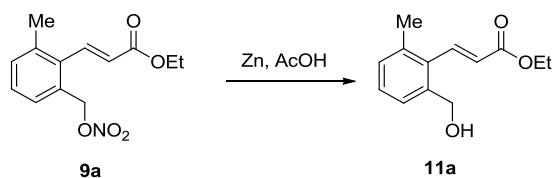
128.8, 128.2, 118.5, 80.4, 72.7, 60.7, 40.2, 18.7, 14.1; **HRMS** (ESI) calcd for C₁₃H₁₆O₃Na [M+Na]⁺ 243.0783, found 243.0781.



Oxidation of **6a** was followed the **General Procedure C**. The reaction of **6a** (61.3 mg, 0.160 mmol, 1.0 eq.), BF₃·2HOAc (90 mg, 0.480 mmol, 3.0 eq.) in dichloromethane (2 mL) then KF (27.8 mg, 0.480 mmol, 3.0 eq.), NaHCO₃ (108 mg, 1.28 mmol, 8.0 eq.) and H₂O₂ (30% w/w, 21.8 mg, 0.192 mmol, 1.2 eq.) in THF/MeOH (1.5 mL / 1.5 mL) for 6 h afforded **7a** (27.2 mg, 70%) (15% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1 H), 8.09 (s, 1 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.26 (d, *J* = 7.2 Hz, 1 H), 4.34 (bs, 2 H), 2.04 (s, 3 H), 1.56 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 141.2, 138.4, 138.2, 136.1, 135.6, 129.6, 129.4, 128.5, 125.5, 124.2, 122.2, 63.2, 20.6; **HRMS** (ESI) calcd for C₁₄H₁₃NO₃Na [M+Na]⁺ 266.0793, found 266.0791.

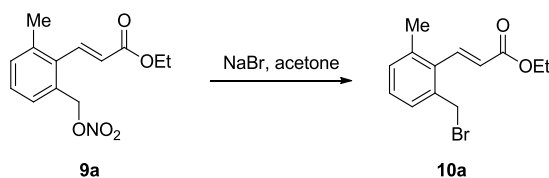


Ce(NH₄)₂(NO₃)₆ (0.263 g, 0.480 mmol, 3.0 eq.) was added to a solution of **5a** (57.6 mg, 0.160 mmol, 1.0 eq.) in MeCN (2 mL), and the mixture was stirred for 40 mins at room temperature before being quenched by addition of saturated sodium bicarbonate (10 mL). The solution was extracted with ethyl acetate (2 × 10 mL) and the combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (5% ethyl acetate/hexanes) to give **9a** (38.6 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 16.4 Hz, 1 H), 7.35-7.19 (m, 3 H), 6.04 (d, *J* = 16.4 Hz, 1 H), 5.43 (s, 2 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 2.32 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 141.4, 137.3, 135.6, 131.7, 129.8, 128.6, 128.3, 125.9, 72.9, 60.9, 20.7, 14.2; **HRMS** (ESI) calcd for C₁₃H₁₅NO₅Na [M+Na]⁺ 288.1687, found 288.1692.

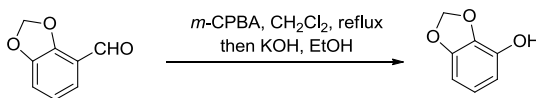


Zn (31.2 mg, 0.480 mmol, 3 eq.) was added to **9a** (42.4 mg, 0.160 mmol, 1.0 eq.) in AcOH (1.5 mL), and the mixture was stirred for 30 mins at room temperature before being quenched by addition of saturated sodium bicarbonate (50 mL). The solution was extracted with ethyl acetate (2×10 mL) and the combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by flash column

chromatography (10 % ethyl acetate/hexanes) to give **11a** (30.5 mg, 87 %). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 16.0 Hz, 1 H), 7.34 (d, *J* = 7.2 Hz, 1 H), 7.29-7.23 (m, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 6.19 (d, *J* = 16.0 Hz, 1 H), 4.70 (s, 2 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 2.36 (s, 3 H), 1.79 (s, 1 H), 1.34 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 142.0, 138.7, 137.0, 133.7, 130.0, 128.6, 126.3, 124.7, 63.4, 60.6, 20.8, 14.3; HRMS (ESI) calcd for C₁₃H₁₆O₃Na [M+Na]⁺ 243.1133, found 243.1138.

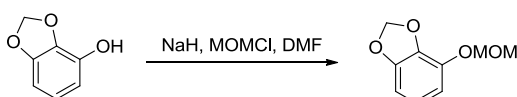


NaBr (0.132 g, 1.280 mmol, 8 eq.) was added to **9a** (42.4 mg, 0.160 mmol, 1.0 eq.) in acetone (3.0 mL), and the mixture was stirred overnight at room temperature before being poured into water (15 mL). The solution was extracted with ethyl acetate (2×10 mL) and the combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and concentrated under vacuo. The crude product was purified by flash column chromatography (2 % ethyl acetate/hexanes) to give **10a** (29.3 mg, 64 %). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 16.4 Hz, 1 H), 7.32-7.15 (m, 3 H), 6.28 (d, *J* = 16.4 Hz, 1 H), 4.52 (s, 2 H), 4.30 (q, *J* = 6.8 Hz, 2 H), 2.33 (s, 3 H), 1.36 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 141.7, 137.2, 135.6, 134.6, 130.8, 128.6, 128.5, 125.0, 60.8, 32.2, 20.9, 14.3; HRMS (ESI) calcd for C₁₃H₁₅BrO₂Na [M+Na]⁺ 305.0127, found 305.0125.



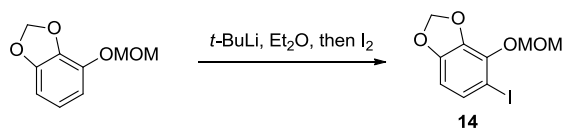
To a solution of aldehyde (0.541 g, 3.60 mmol, 1.0 eq.) in CH₂Cl₂ (30 mL) was added *m*-CPBA (0.722 g, 4.32 mmol, 1.2 eq.), then the mixture was refluxed for 6 h before being filtered and washed with CH₂Cl₂ (10 mL). The filtrate was concentrated in vacuo and used for next step without purification.

KOH (0.605 g, 10.8 mmol, 3.0 eq.) and EtOH (20 mL) was added to the above residue, and the mixture was stirred for 5 min at room temperature before being neutralized by 1 N HCl. The solution was extracted with ethyl acetate (2×60 mL), and the combined organic layers were washed with brine (50 mL), dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (12% ethyl acetate/hexanes) to give the phenol (0.412 g, 83% two steps).

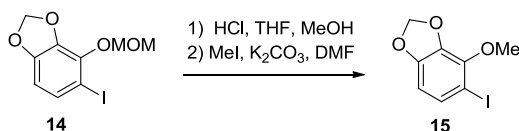


To a solution of phenol (0.280 g, 2.03 mmol, 1.0 eq.) in DMF (20 mL) was added NaH (97.4 mg, 4.06 mmol, 2.0 eq.) slowly at 0 °C, and the mixture was stirred at 0 °C for 5 min. MOMCl (244 mg, 3.04 mmol, 1.5 eq.) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for 1h before being quenched by saturated bicarbonate (10 mL) slowly. The

solution was extracted with ethyl acetate (2×30 mL), and the combined organic layers were washed with brine (20 mL), dried (MgSO₄), filtered and concentrated under vacuo. The crude product was purified by flash column chromatography (10% ethyl acetate/hexanes) to give the product (0.354 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ 6.77 (t, *J* = 8.0 Hz, 1 H), 6.70 (dd, *J* = 1.2, 8.4 Hz, 1 H), 6.57 (dd, *J* = 1.2, 7.6 Hz, 1 H), 5.97 (s, 2 H), 5.23 (s, 2 H), 3.52 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 140.9, 136.1, 122.0, 111.4, 103.4, 101.1, 95.4, 56.3; HRMS (ESI) calcd for C₉H₁₀O₄Na [M+Na]⁺ 205.1691, found 205.1694.

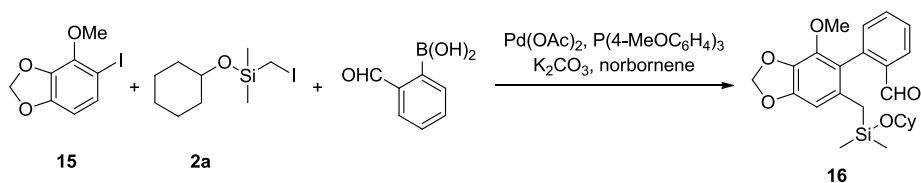


To a solution of substrate (0.385 g, 2.12 mmol, 1 eq.) in Et₂O (15 mL) was added *t*-BuLi (3.82 mmol, 1.8 eq.) dropwise at 0 °C, and the mixture was stirred for 1 h at room temperature, then I₂ (0.807 g, 1.06 mmol, 1.5 eq.) in Et₂O (10 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 5 h before being quenched by saturated NH₄Cl (15 mL). The solution was extracted with Et₂O (2×40 mL), and the combined organic layers were washed with brine (30 mL), dried (MgSO₄), filtered and concentrated under vacuo. The crude product was purified by flash column chromatography (5 % ethyl acetate/hexanes) to give **14** (0.516 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.4 Hz, 1 H), 6.40 (d, *J* = 8.4 Hz, 1 H), 5.97 (s, 2 H), 5.32 (s, 2 H), 3.59 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 139.2, 137.1, 131.7, 105.8, 101.5, 96.8, 80.4, 57.7; HRMS (ESI) calcd for C₉H₉IO₄Na [M+Na]⁺ 331.1243, found 331.1241.

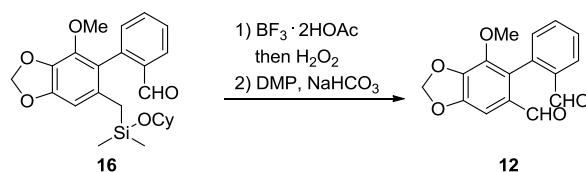


To a solution of **14** (0.280 g, 0.910 mmol, 1.0 eq.) in THF/MeOH (5 mL / 5 mL) was added 12 N HCl (0.758 mL, 9.10 mmol, 10 eq.) dropwise, and the mixture was stirred at 40 °C for 30 mins before being poured into water (20 mL). The solution was extracted with ethyl acetate (2×30 mL), and the combined organic layers were washed with brine (30 mL), dried (MgSO₄), filtered, concentrated under vacuo and used for next step without purification.

To a solution of the above residue was added DMF (9 mL) followed by MeI (0.324 g, 2.28 mmol, 2.5 eq.) and K₂CO₃ (0.377 g, 2.73 mmol, 3 eq.), and the mixture was heated at 40 °C for 1 h before being poured into water (20 mL). The solution was extracted with ethyl acetate (2×20 mL), and the combined organic layers were washed with brine (20 mL), dried (MgSO₄), filtered and concentrated under vacuo. The crude product was purified by flash column chromatography (5% ethyl acetate/hexanes) to give **15** (207 mg, 82% two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.0 Hz, 1 H), 6.36 (d, *J* = 8.0 Hz, 1 H), 5.96 (s, 2 H), 4.02 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 142.7, 136.5, 131.4, 105.2, 101.4, 79.6, 60.0; HRMS (ESI) calcd for C₈H₇IO₃Na [M+Na]⁺ 301.2322, found 301.2326.



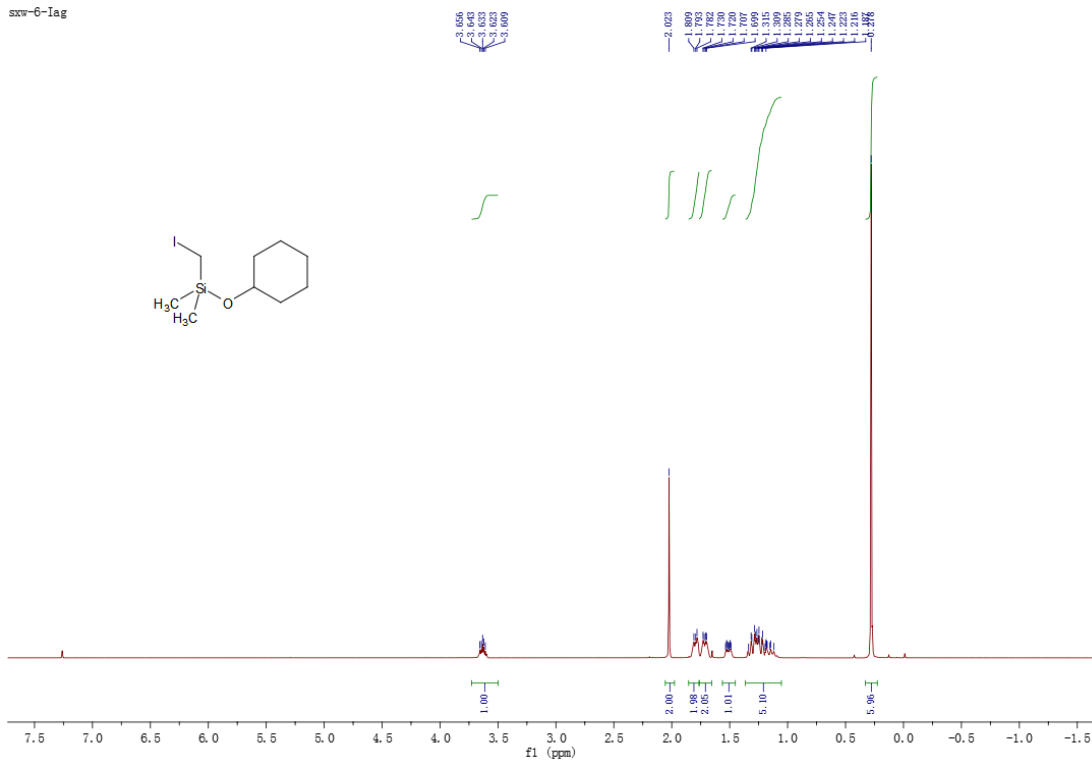
Compound **16** was prepared following the **Typical Procedure B**. The reaction of **15** (43.6 mg, 0.157 mmol, 1.0 eq.), **2a** (0.117 g, 0.392 mmol, 2.5 eq.), 2-formylbenzeneboronic acid **3** (56.5 mg, 0.314 mmol, 2 eq.), Pd(OAc)₂ (3.5 mg, 0.0157 mmol, 10 mol%), P(4-MeOC₆H₄)₃ (11.0 mg, 0.0314 mmol, 20 mol%), K₂CO₃ (65.0 mg, 0.471 mmol, 3.0 eq.), and norbornene (59.3 mg, 0.628 mmol, 4.0 eq.) in MeCN (2 mL) delivered **16** (41.5 mg, 62%) (2% ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 9.79 (d, *J* = 0.4 Hz, 1 H), 8.01 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.62 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.28-7.23 (d, 1 H), 6.54 (s, 1 H), 5.95 (s, 2 H), 3.76 (s, 3 H), 3.45-3.31 (m, 1 H), 1.77 (d, *J* = 14.4 Hz, 1 H), 1.91 (d, *J* = 14.0 Hz, 1 H), 1.71-1.56 (m, 4 H), 1.50-1.44 (m, 1 H), 1.27-1.05 (m, 5 H), -0.065 (s, 3 H), -0.083 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 192.8, 149.1, 141.6, 141.0, 134.7, 133.6, 132.9, 132.5, 127.6, 126.8, 121.2, 103.7, 100.8, 71.3, 59.4, 35.81, 35.77, 25.4, 24.3, 24.1, -0.8, -1.0; HRMS (ESI) calcd for C₂₄H₃₀O₅SiNa [M+Na]⁺ 449.2756, found 449.2752.



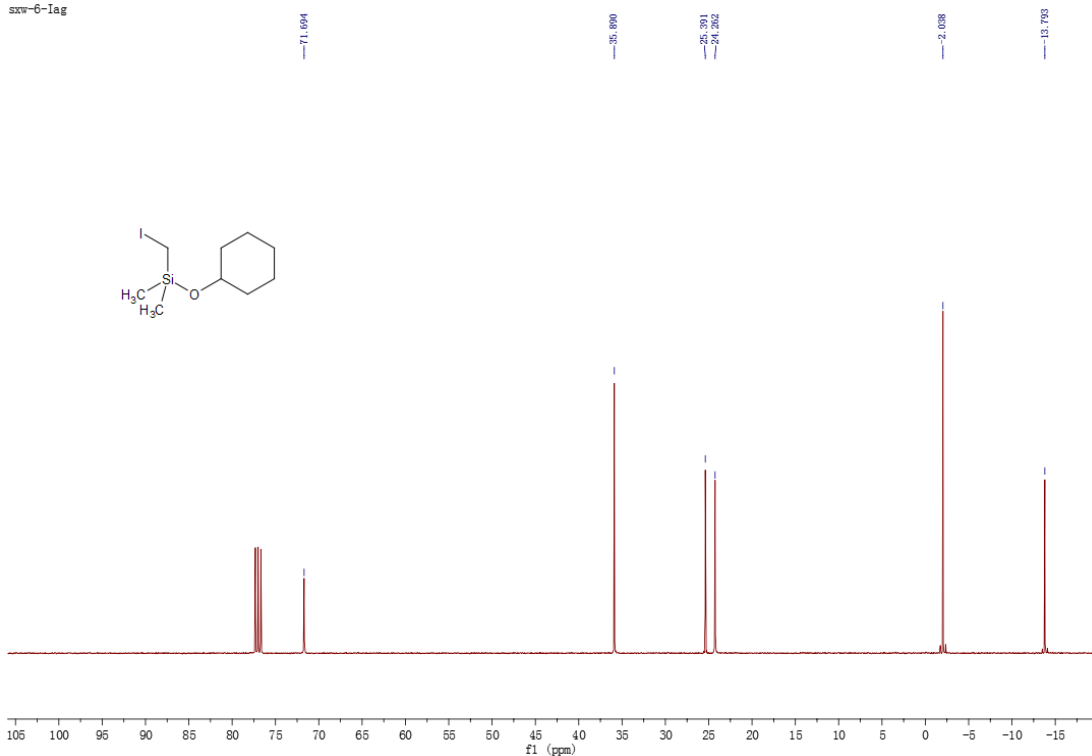
The oxidation of **16** was followed the **Typical Procedure C**. The reaction of **16** (0.256 g, 0.160 mmol, 1.0 eq.), BF₃·2HOAc (90 mg, 0.480 mmol, 3.0 eq.) in dichloromethane (2 mL) then KF (27.8 mg, 0.480 mmol, 3.0 eq.), NaHCO₃ (0.108 g, 1.28 mmol, 8.0 eq.) and H₂O₂ (30% w/w, 21.8 mg, 0.192 mmol, 1.2 eq.) in THF/MeOH (1.5 mL/1.5 mL) afforded the alcohol, which used in the next step without purification.

The above alcohol in dichloromethane (3 mL) was added to a mixture of Dess-Martin periodinane (0.101 g, 0.240 mmol, 1.5 eq.), NaHCO₃ (54.1 mg, 0.640 mmol, 4 eq.) and CH₂Cl₂ (1 mL). The reaction mixture was stirred at room temperature for 30 min before being quenched by addition of saturated sodium thiosulfate (20 mL). The mixture was extracted with dichloromethane (2×10 mL), and the combined organic layers were washed with brine (10 mL), dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (12% ethyl acetate/hexanes) to give **12** (27.3 mg, 60% for two steps). ¹H NMR (400 MHz, CDCl₃) δ 9.86 (d, *J* = 0.8 Hz, 1 H), 9.47 (s, 1 H), 8.05 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.66 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.30-7.24 (m, 2 H), 6.17-6.06 (m, 2 H), 3.83 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 191.3, 189.4, 150.1, 141.4, 140.6, 136.1, 135.3, 133.4, 132.7, 130.6, 130.2, 128.9, 128.4, 102.3, 101.4, 59.8; HRMS (ESI) calcd for C₁₆H₁₂O₅Na [M+Na]⁺ 307.1542, found 307.1547.

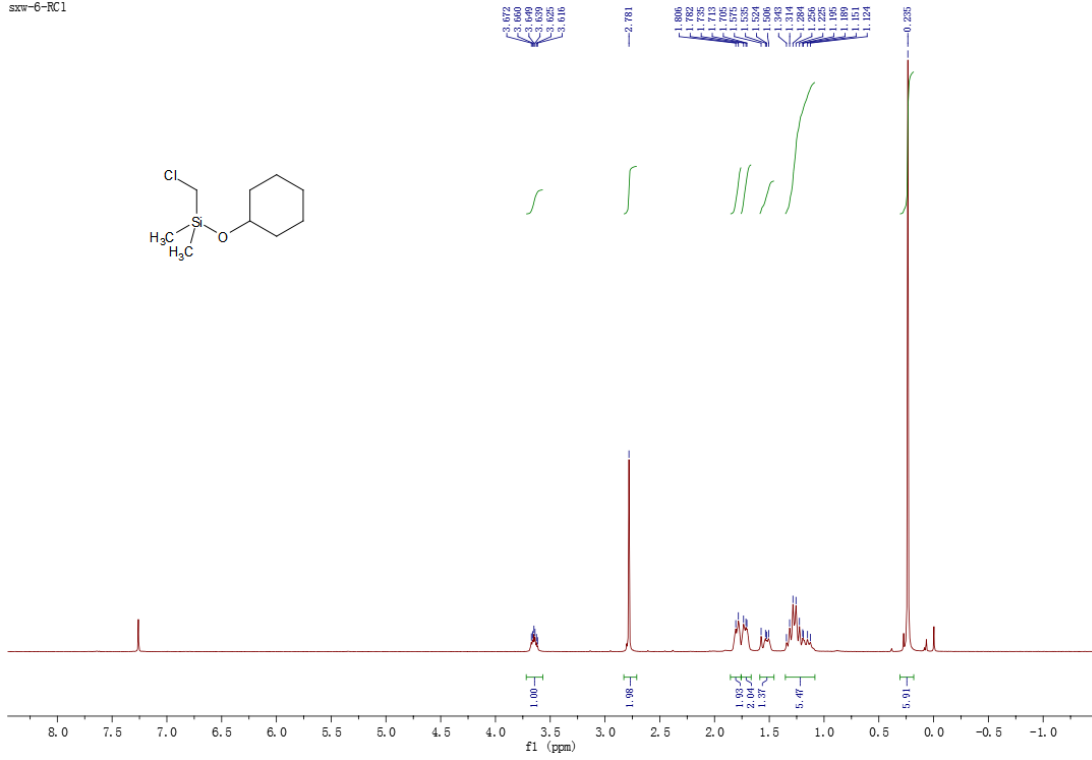
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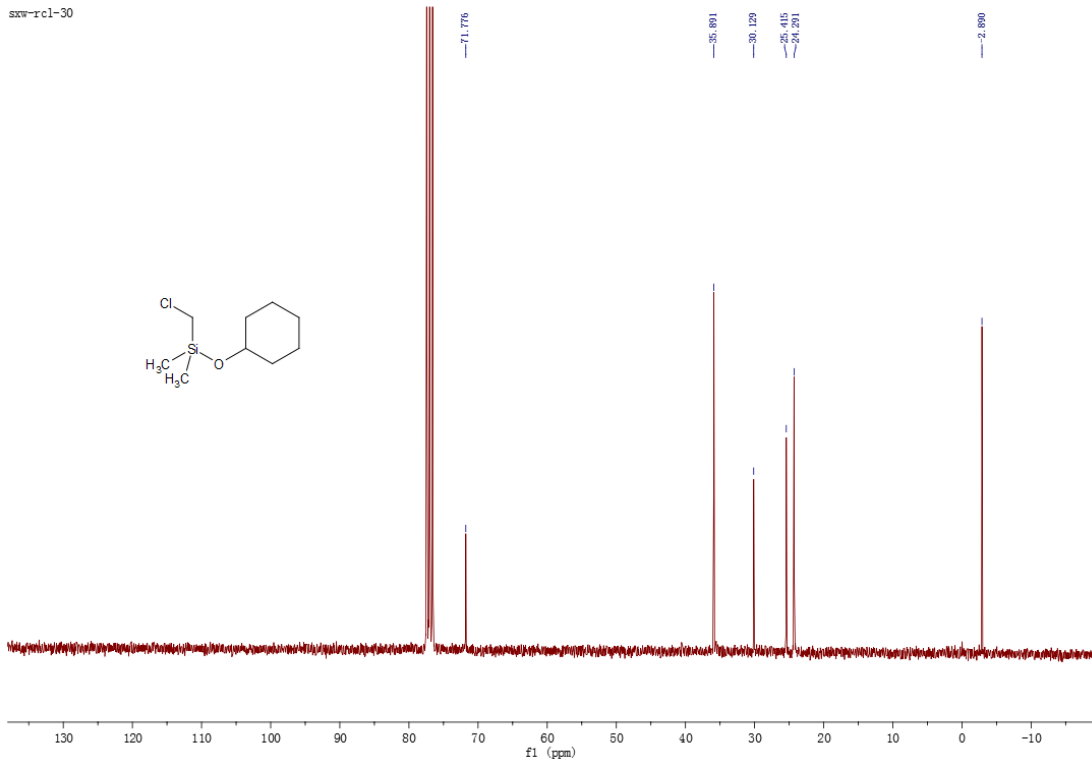
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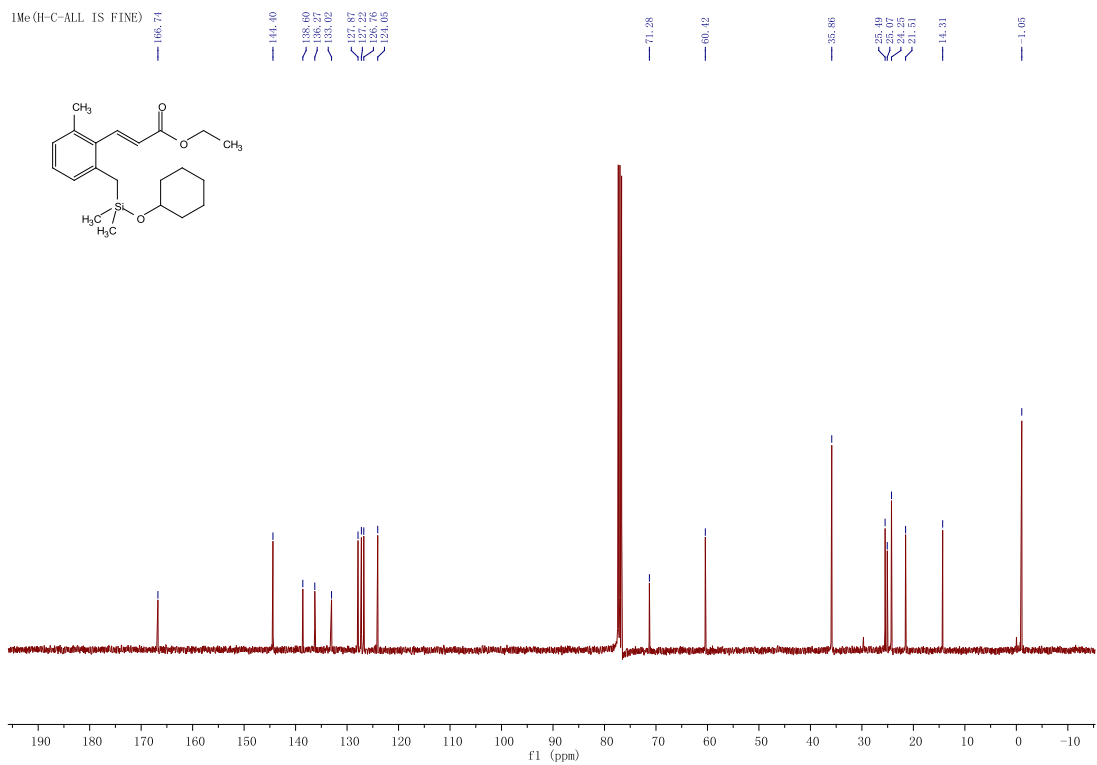
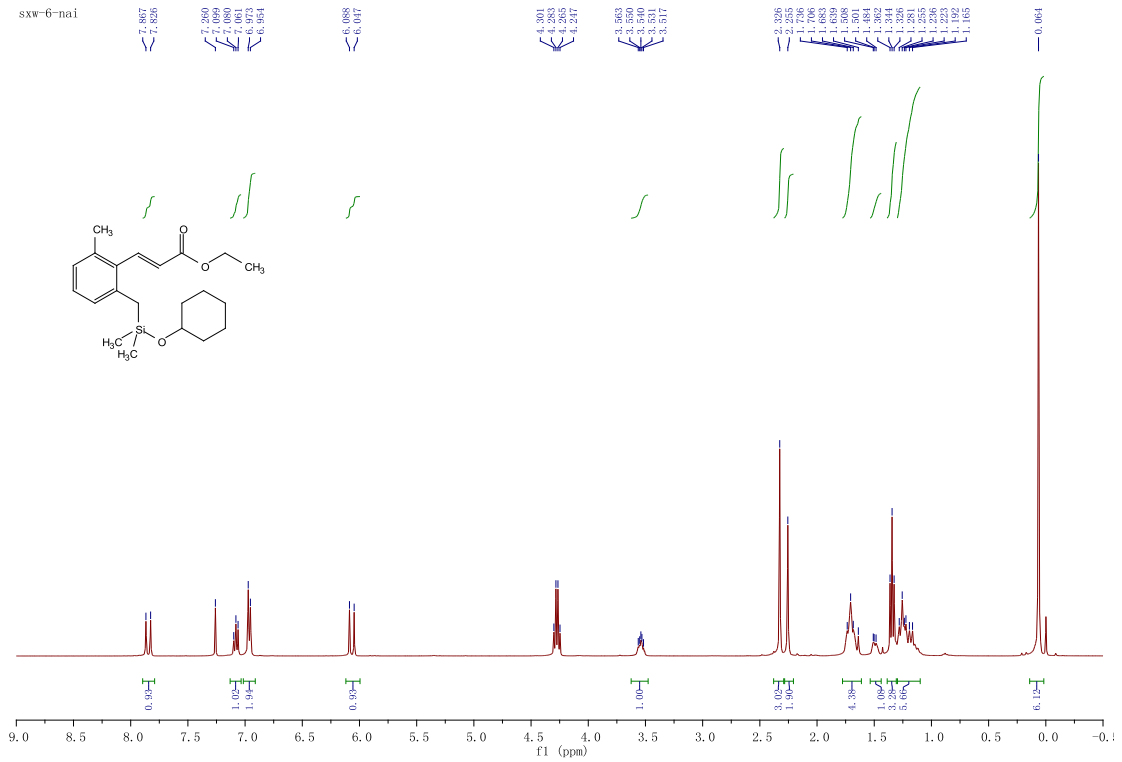


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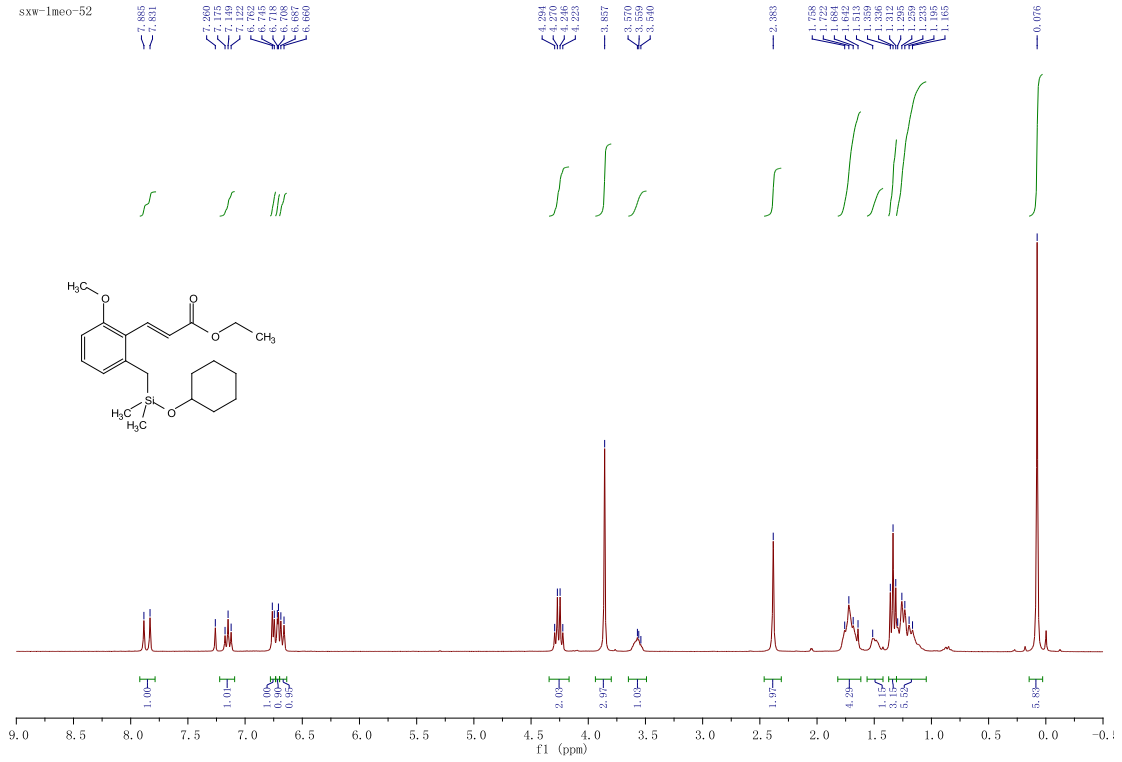


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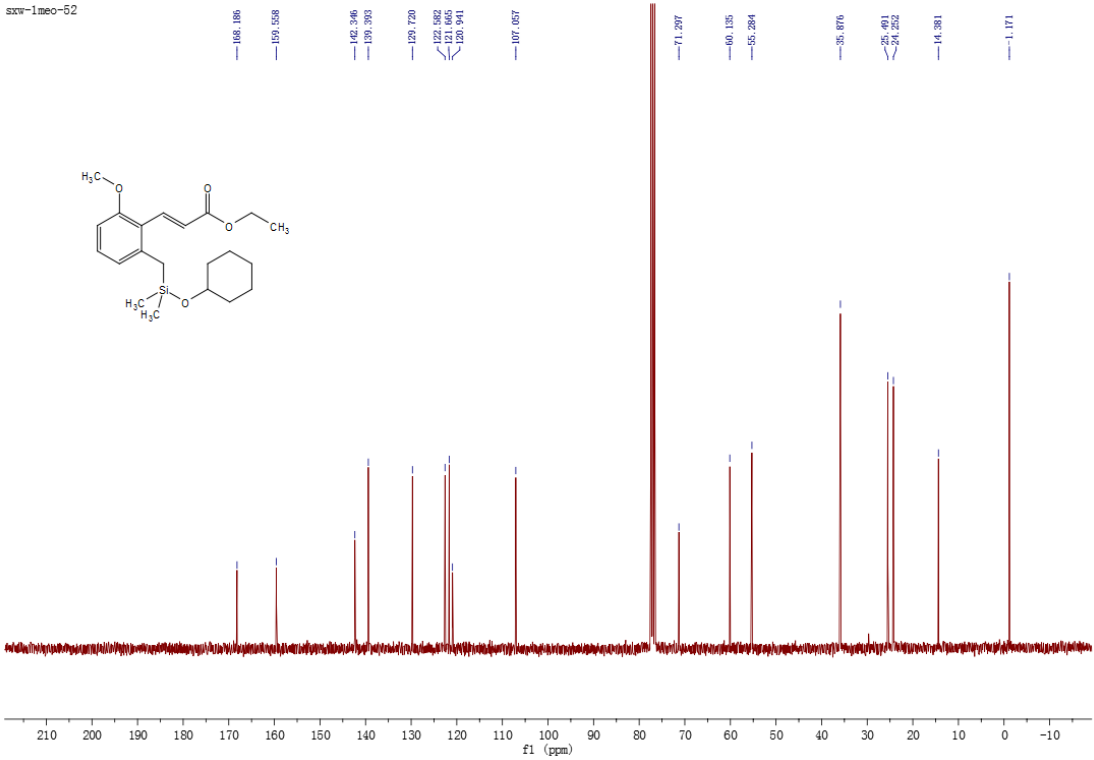




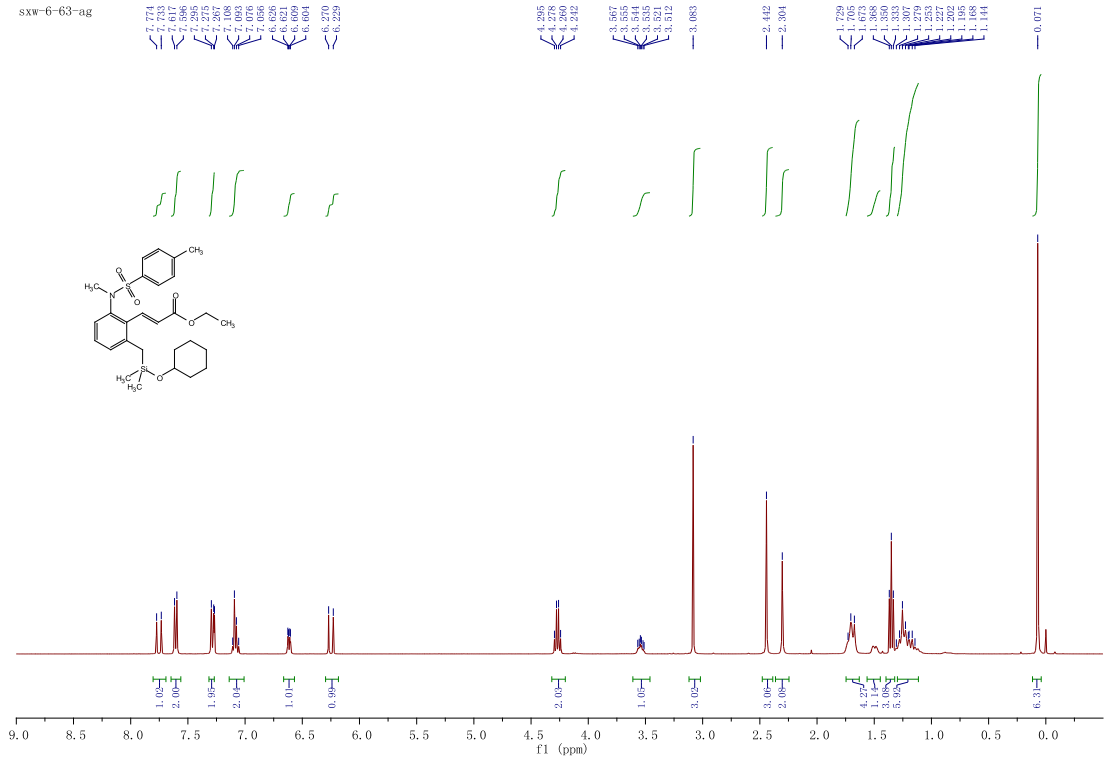
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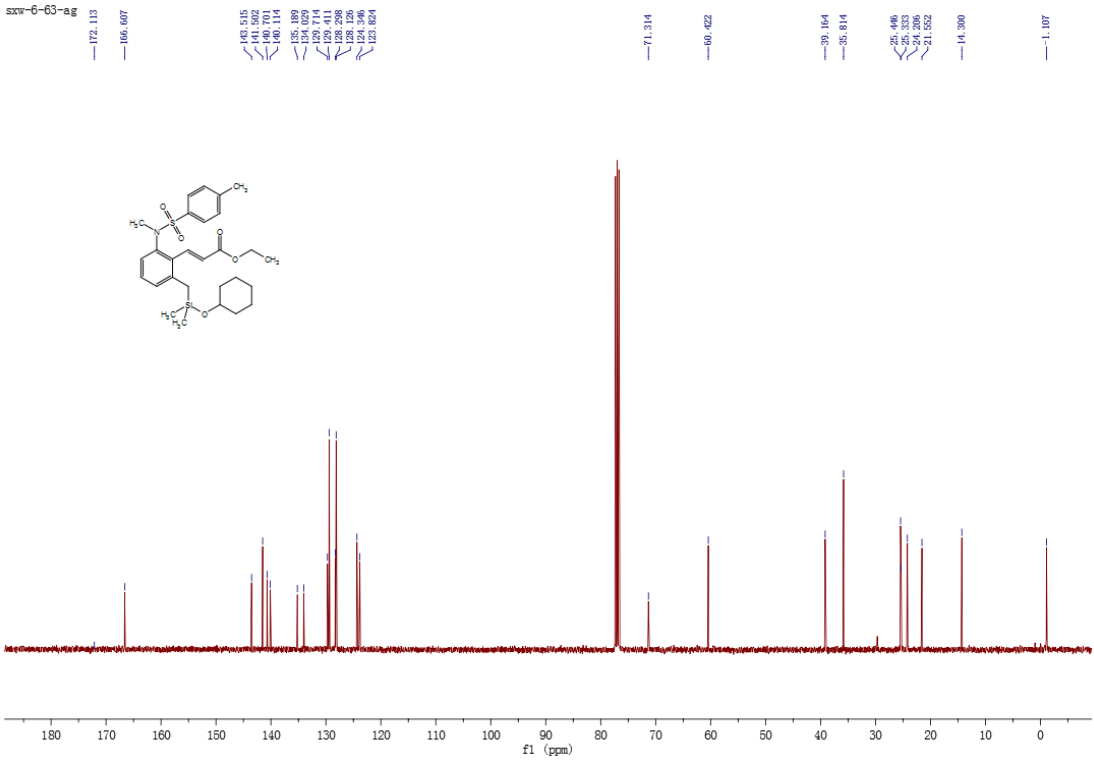
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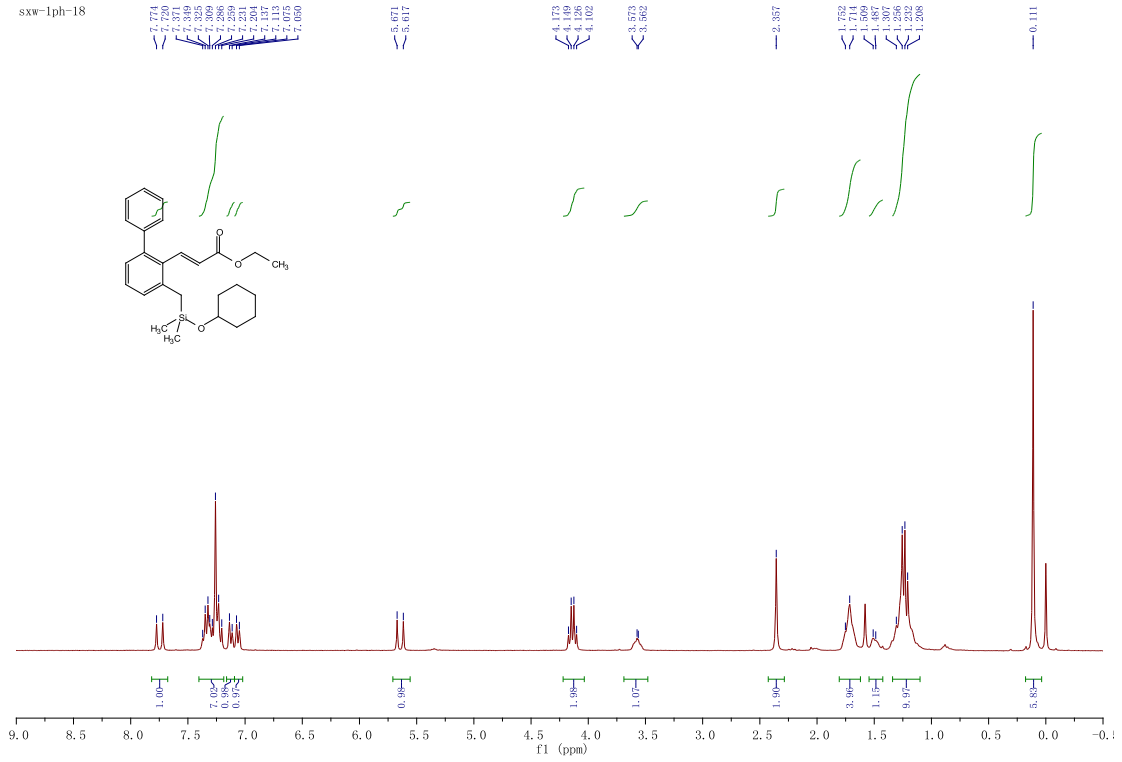
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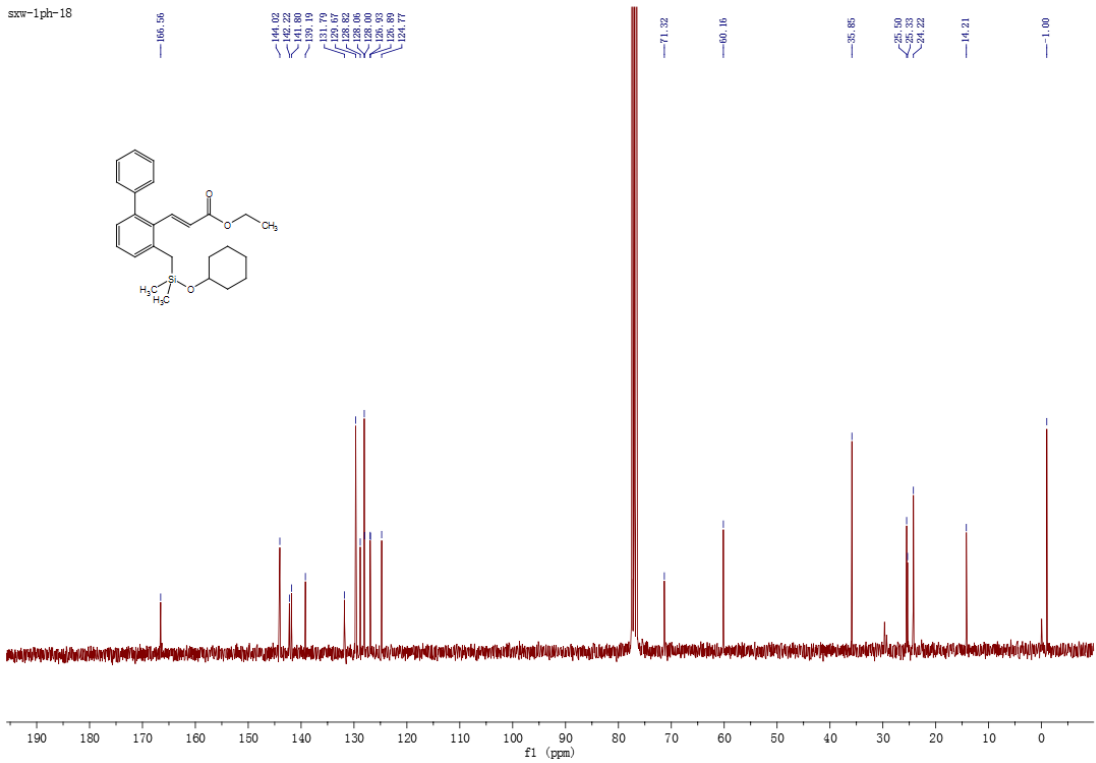
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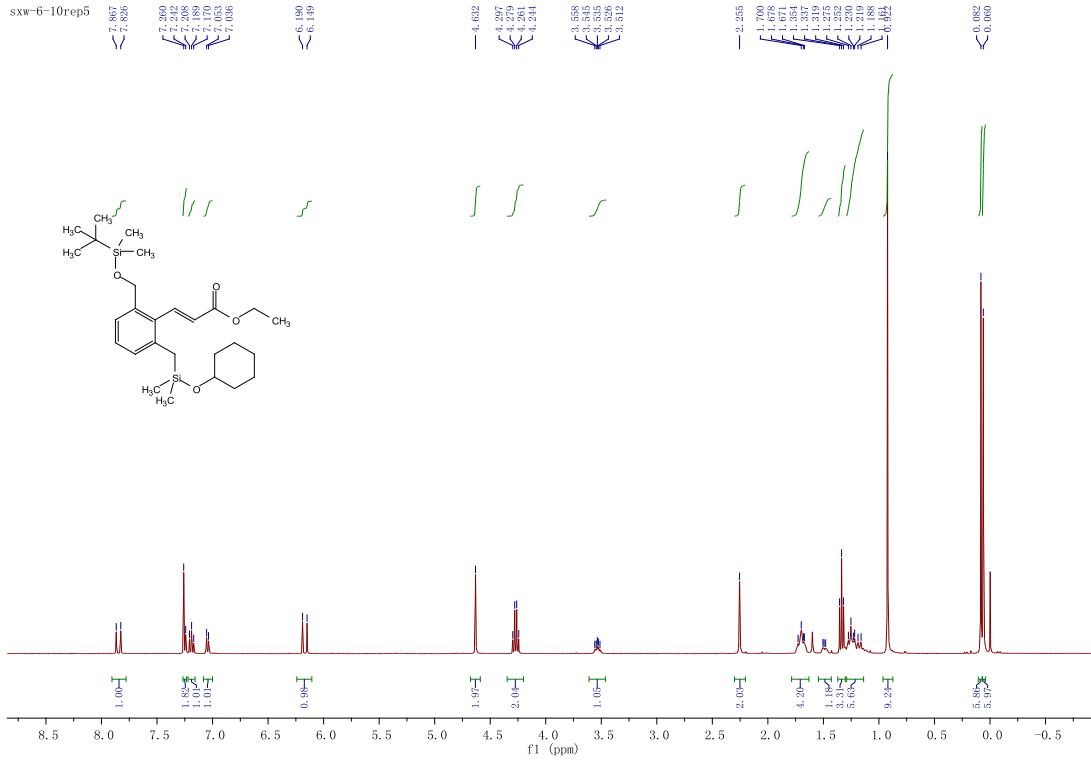
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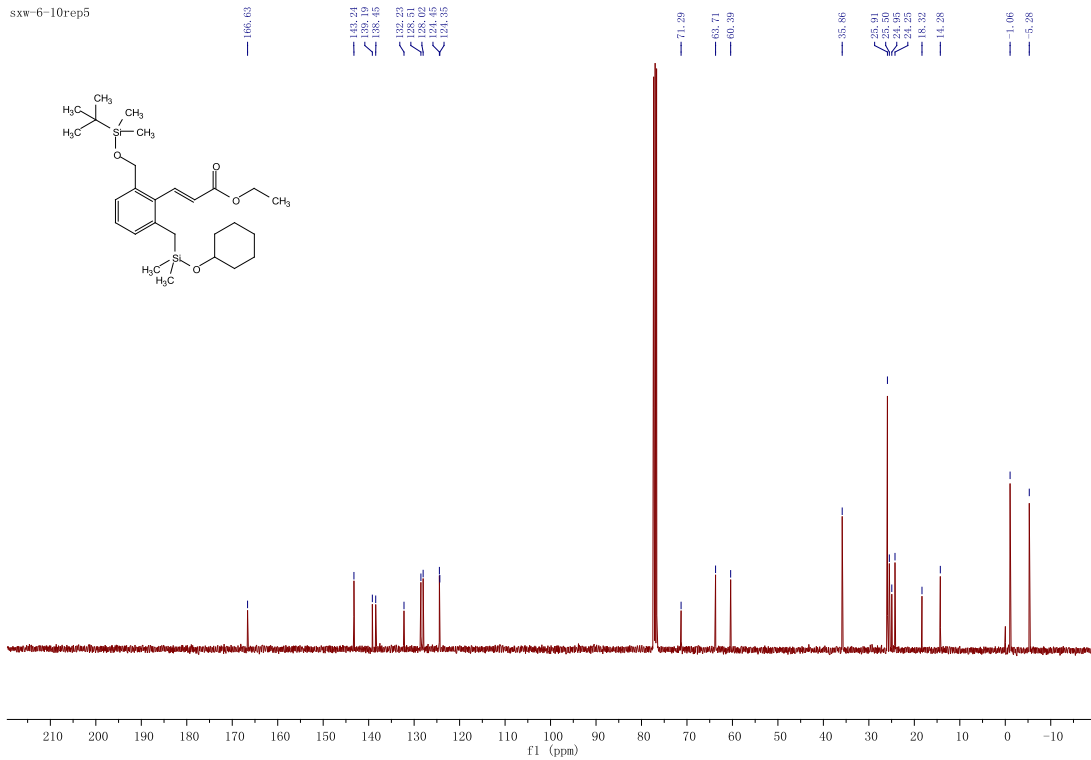
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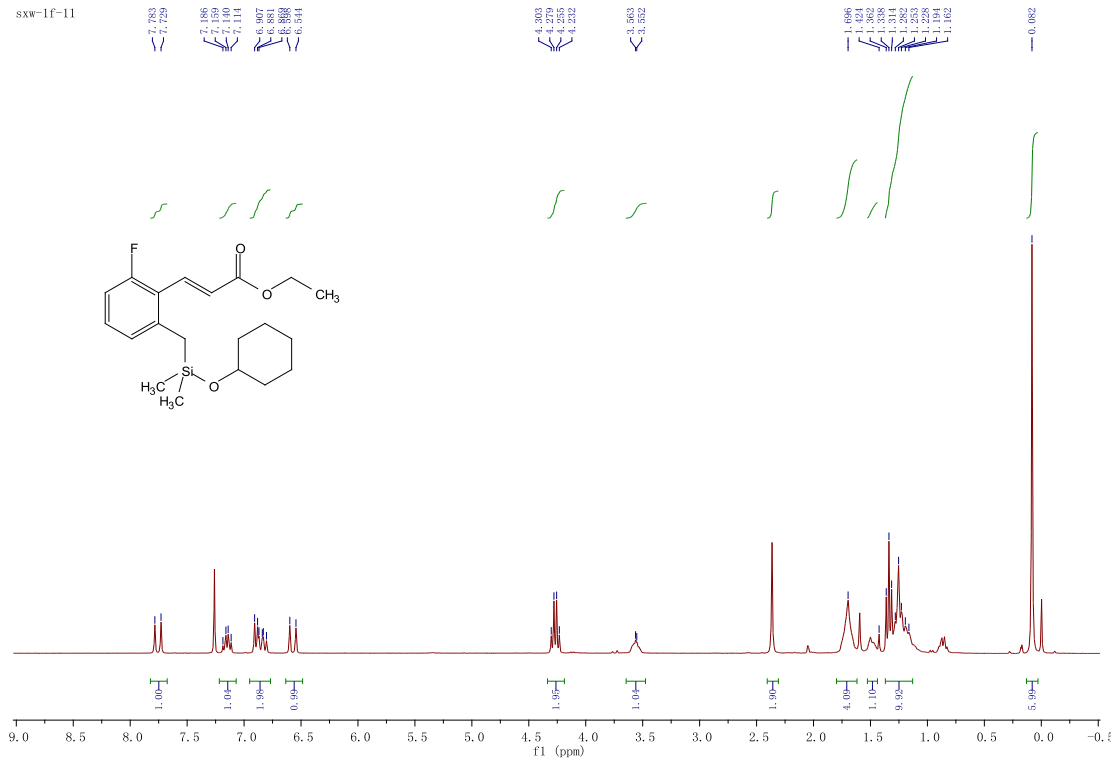
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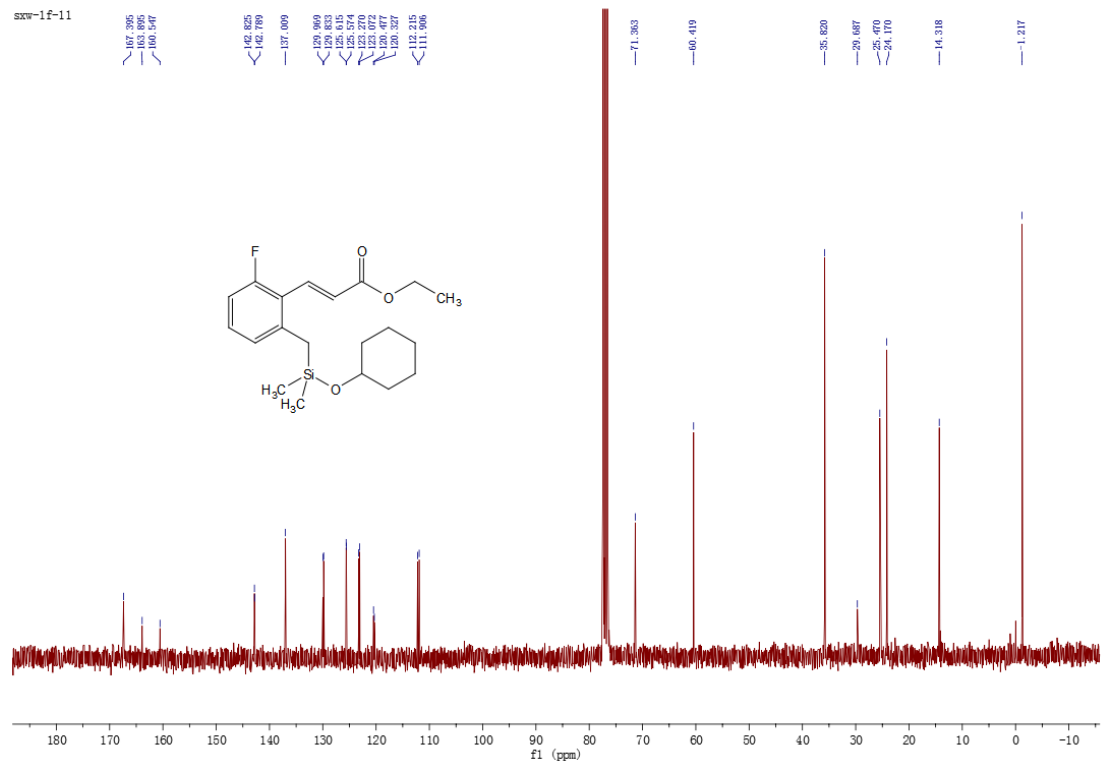
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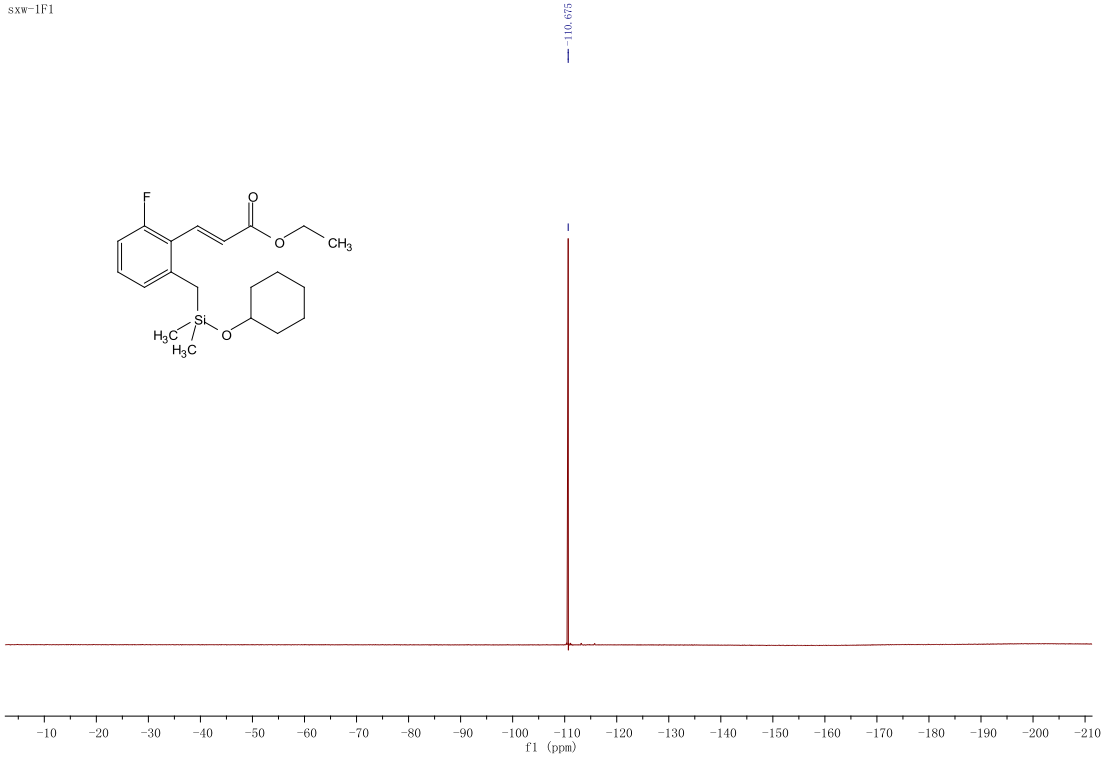
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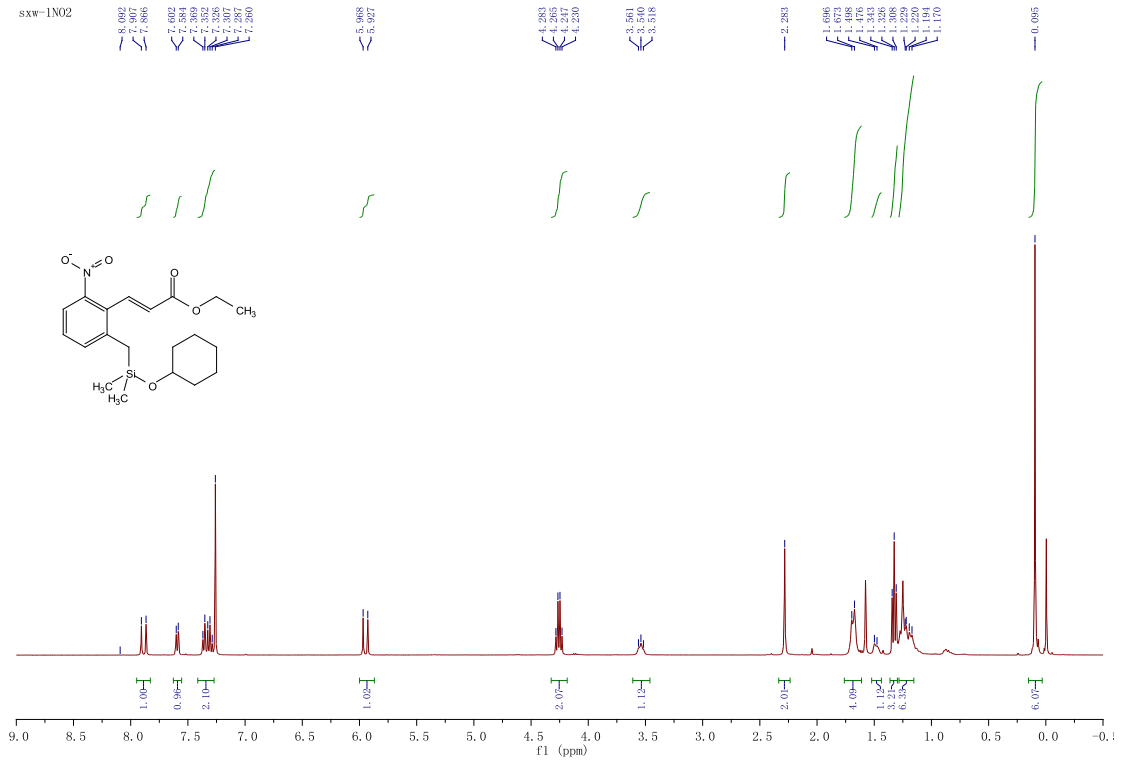
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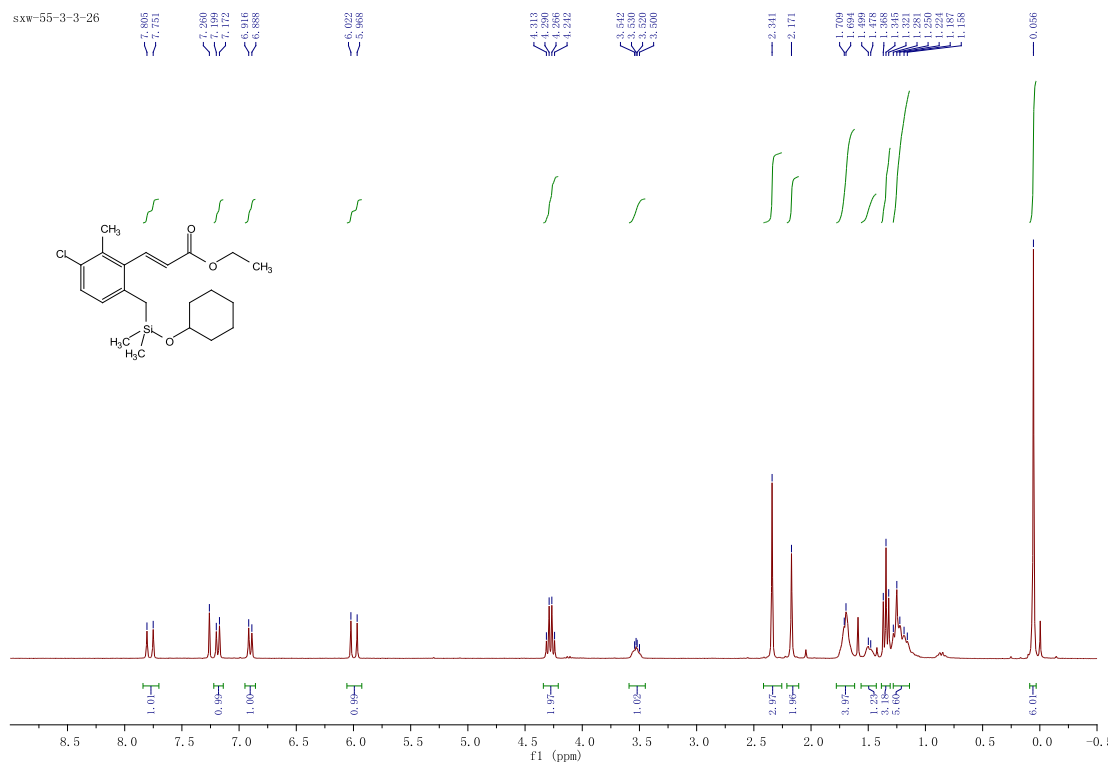
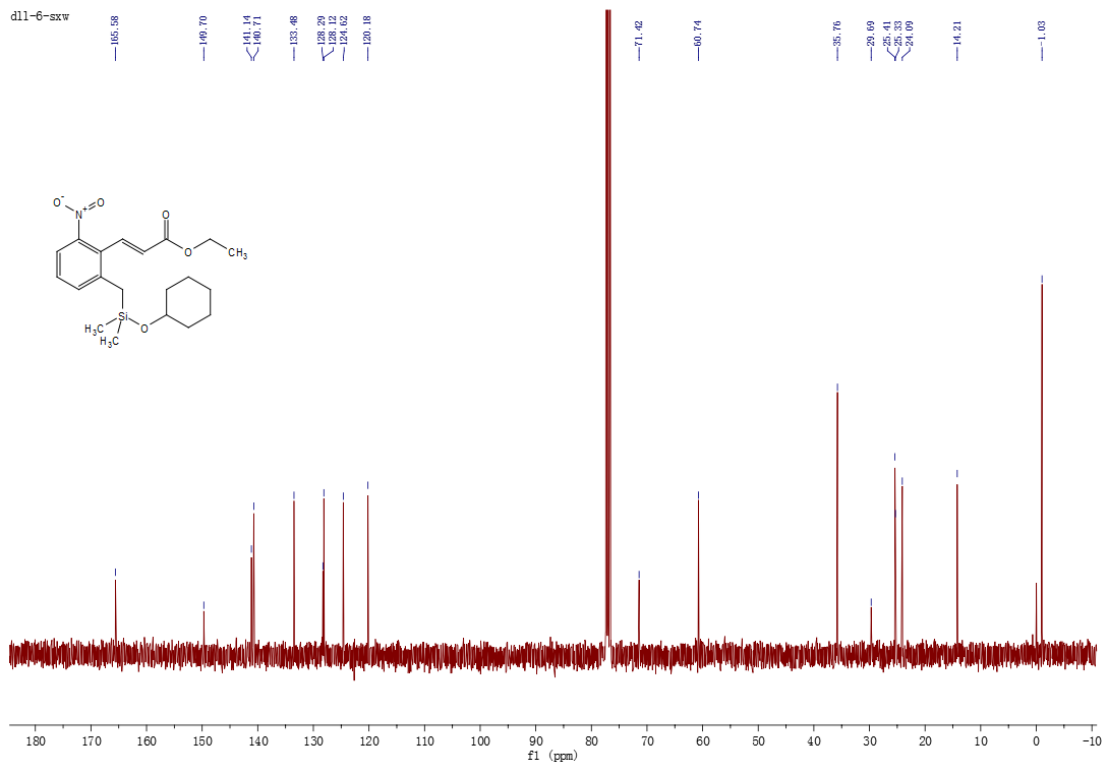


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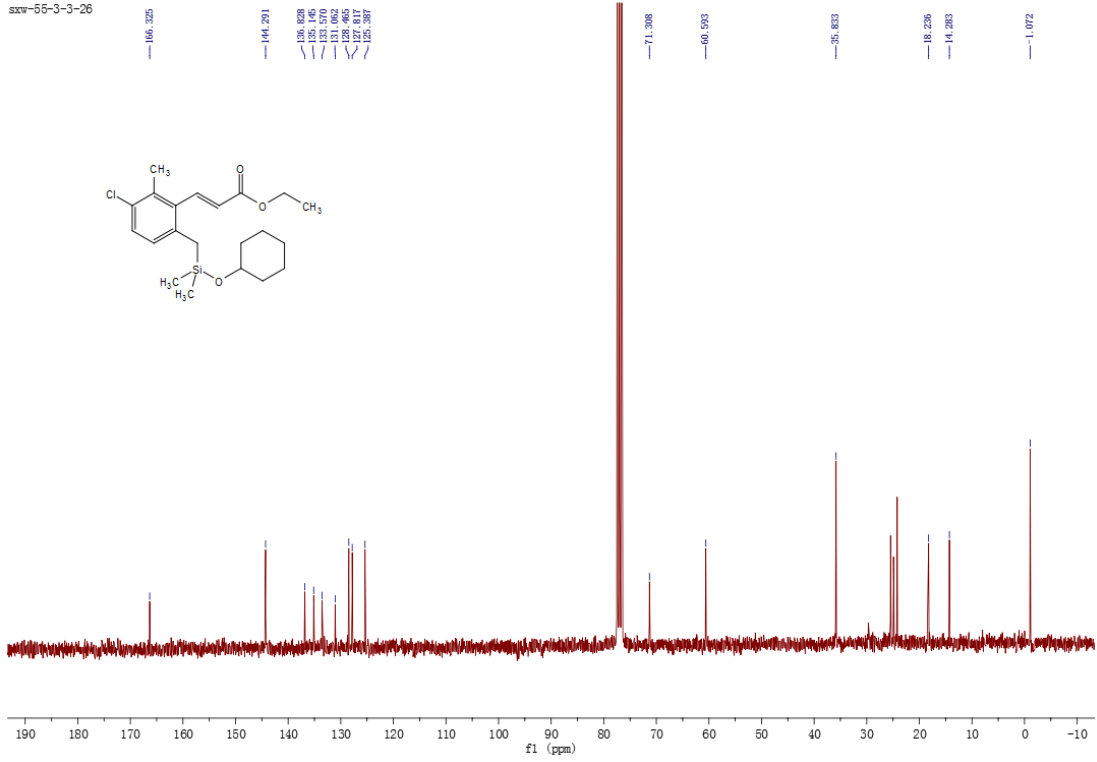


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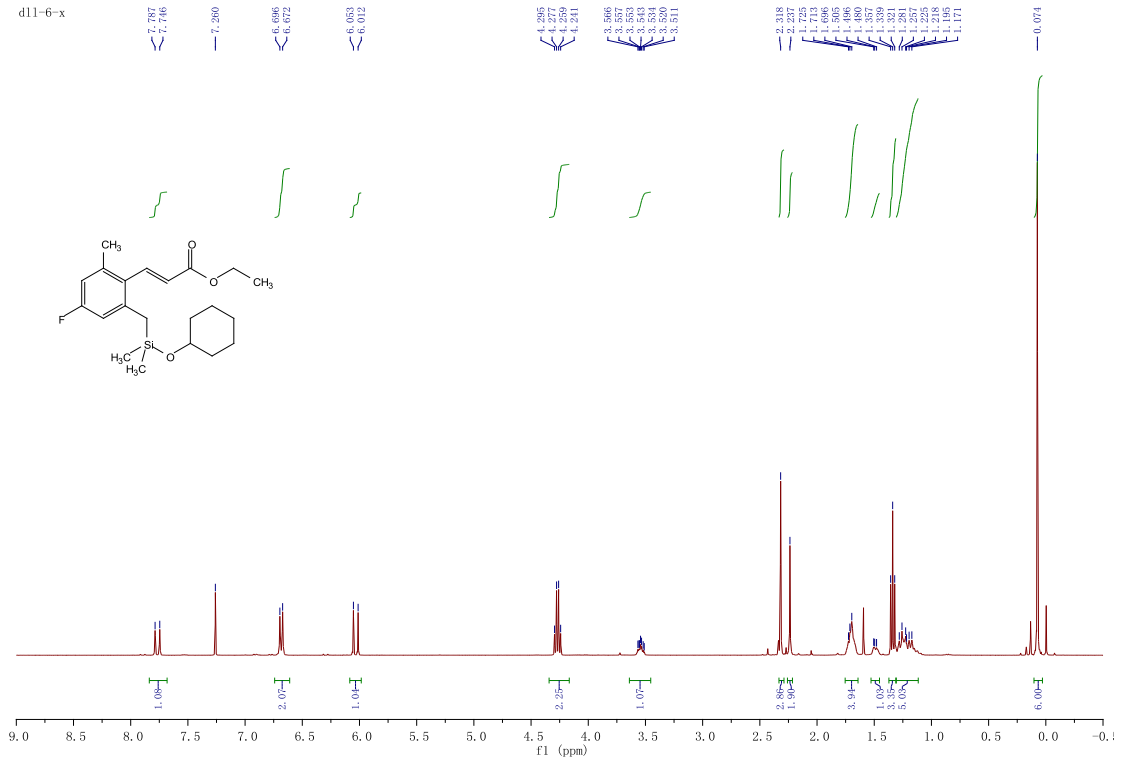




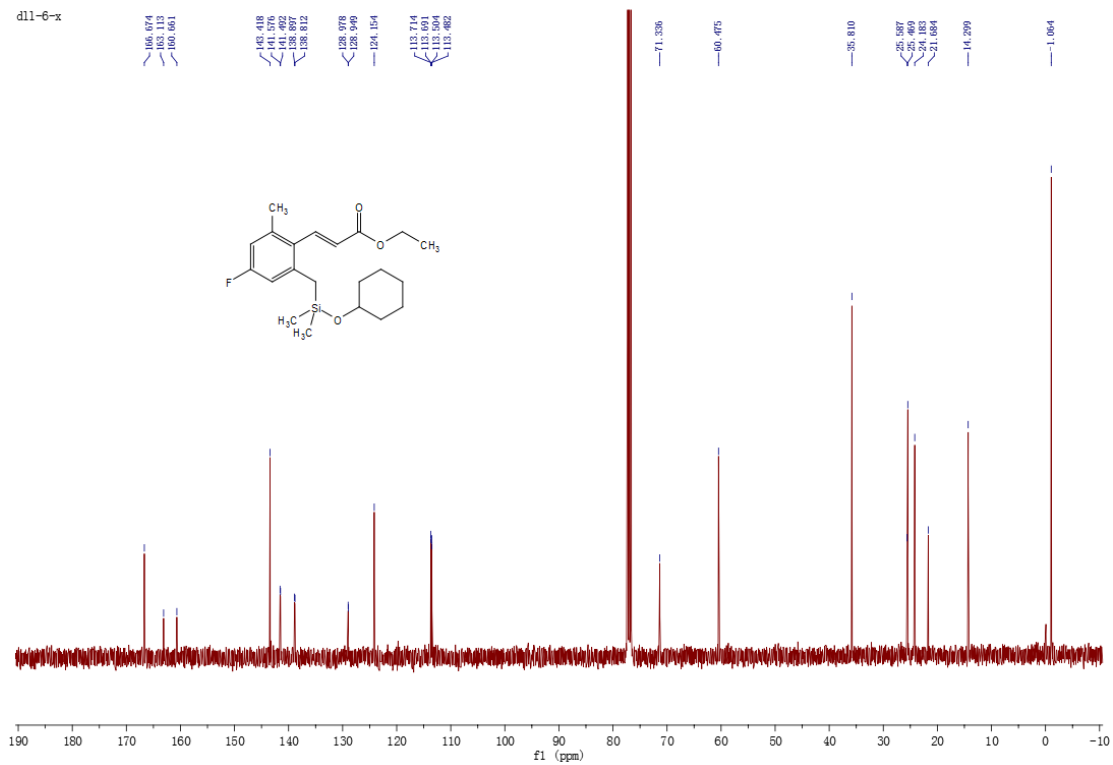
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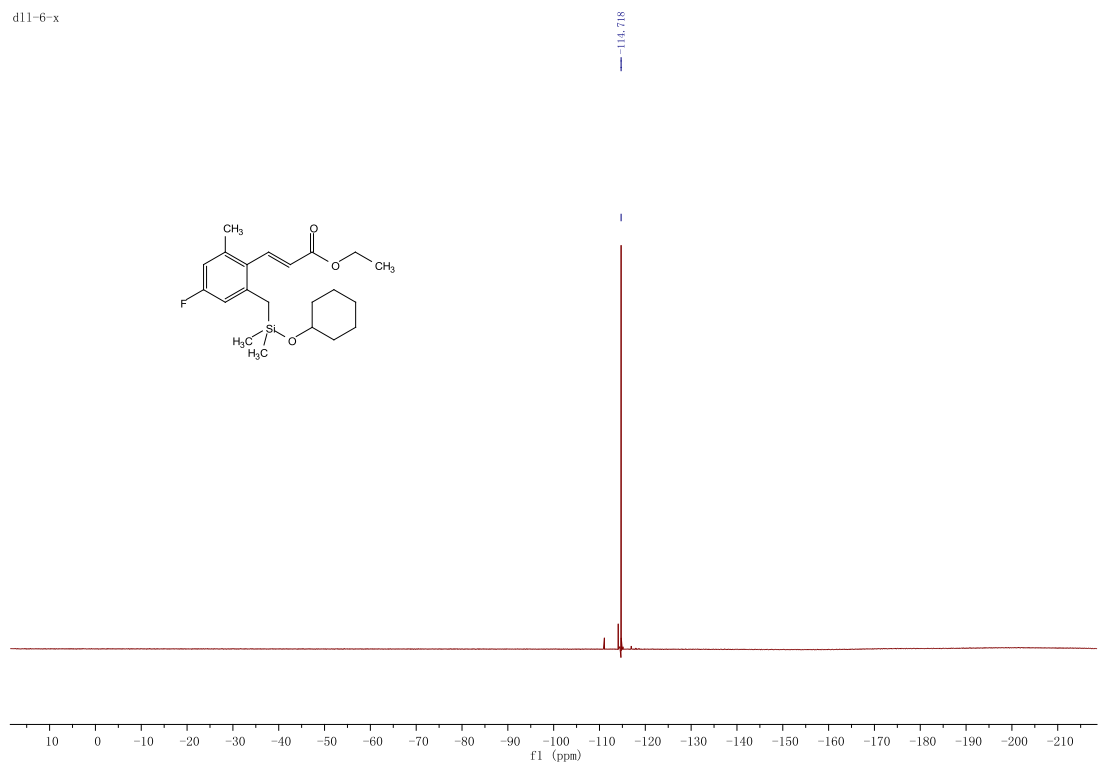
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d11-6-x

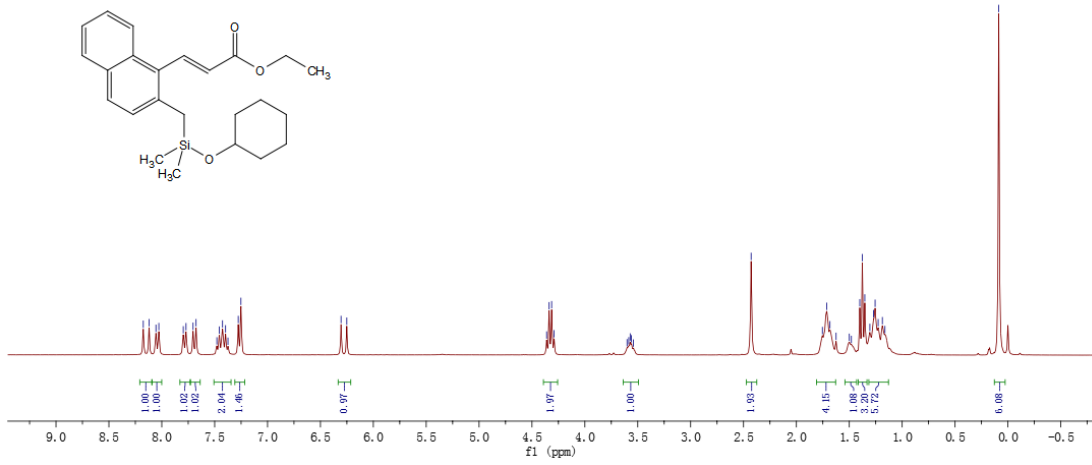
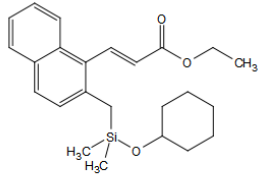


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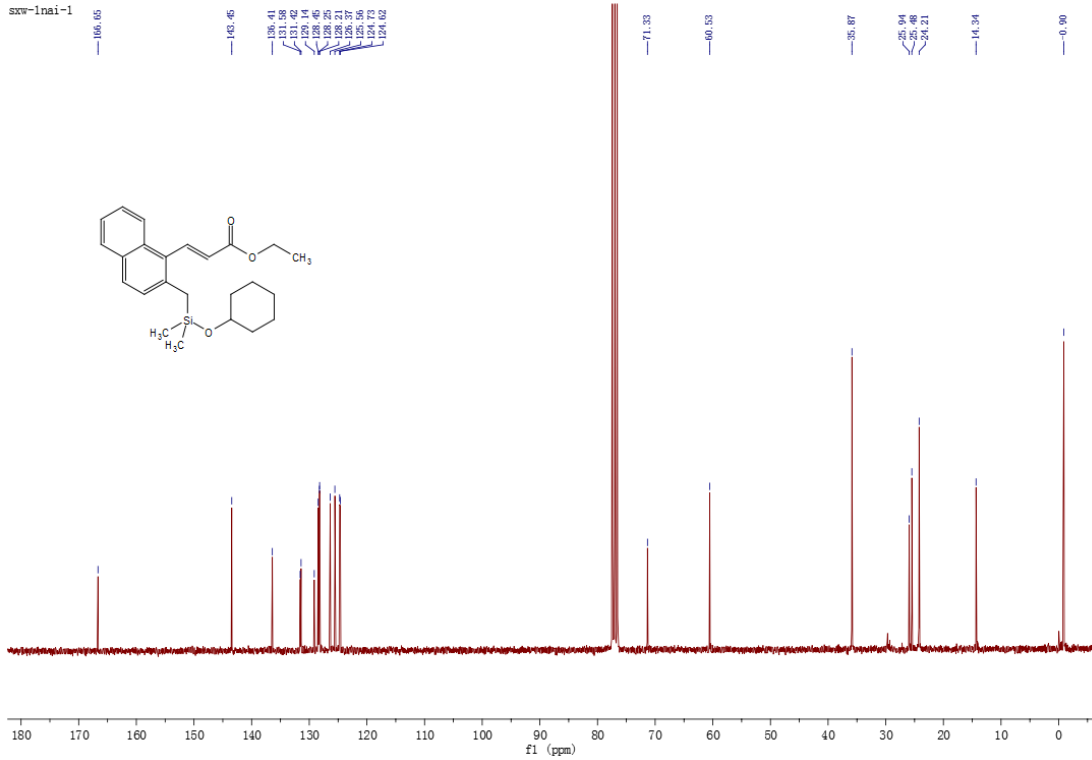
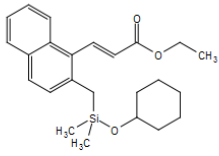
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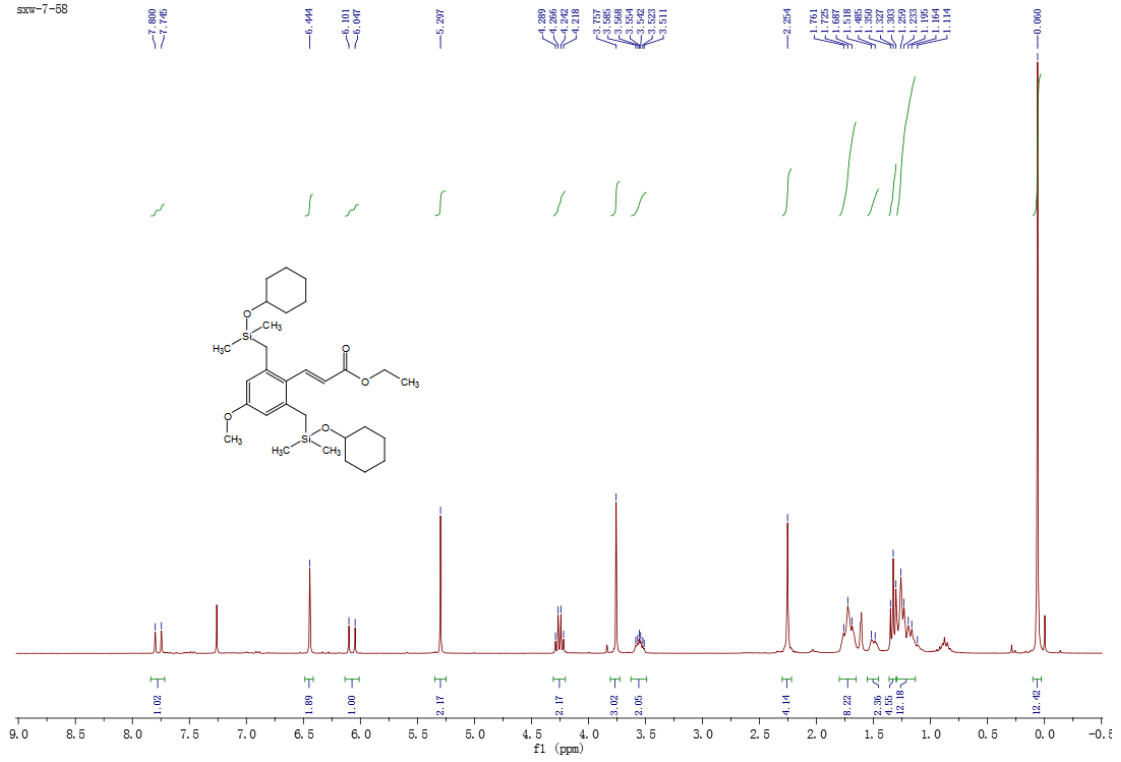


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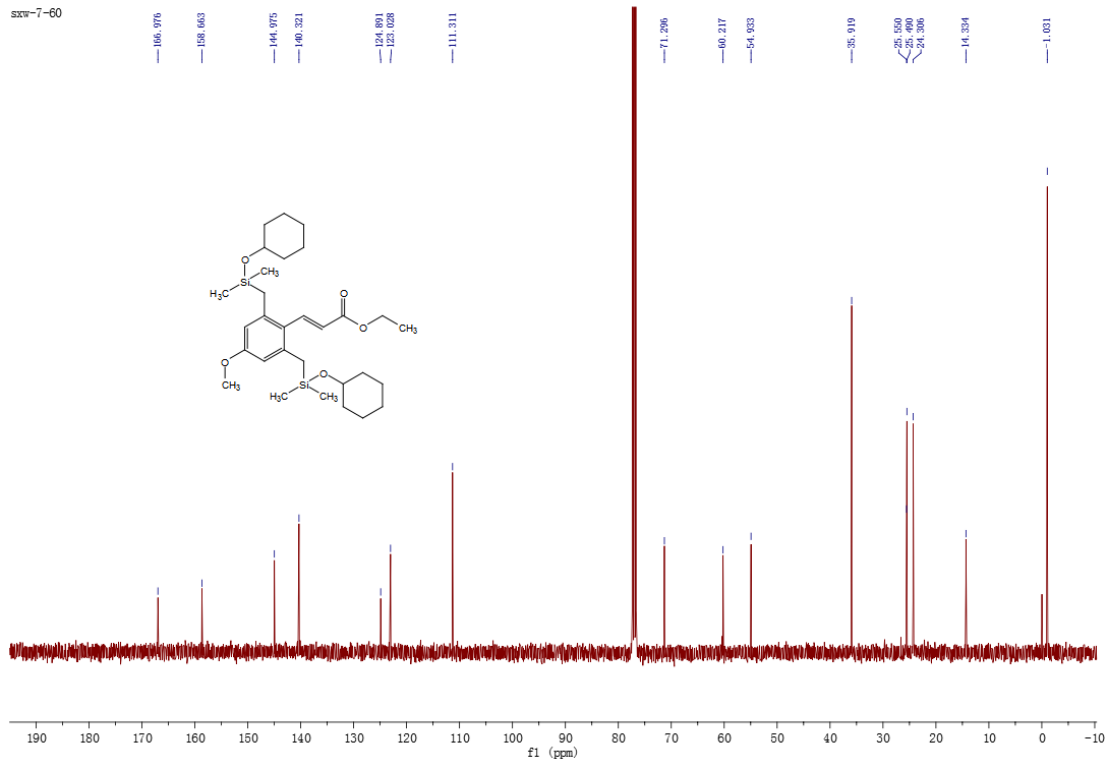
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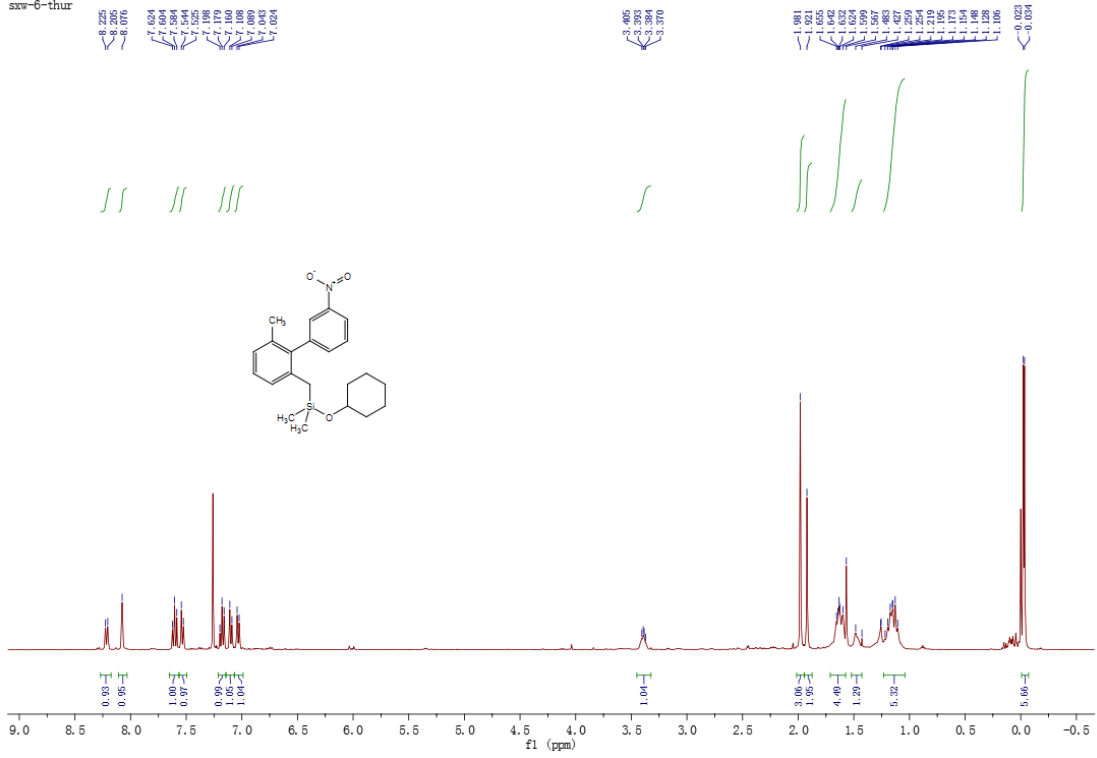
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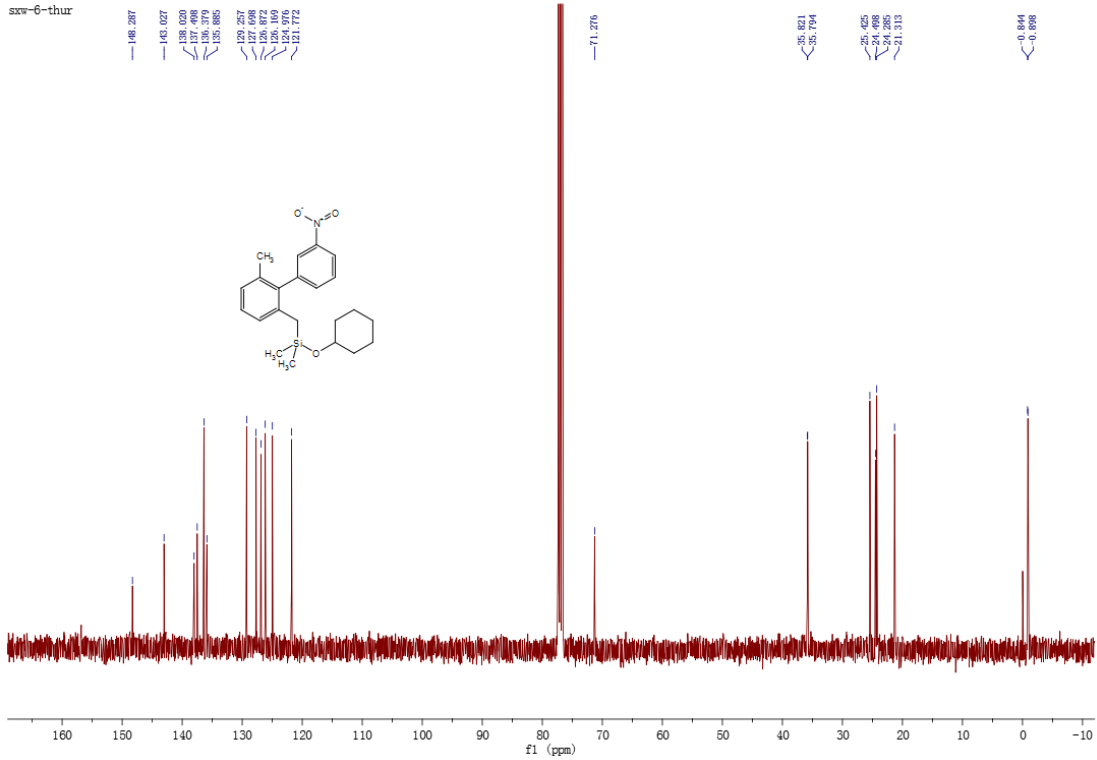
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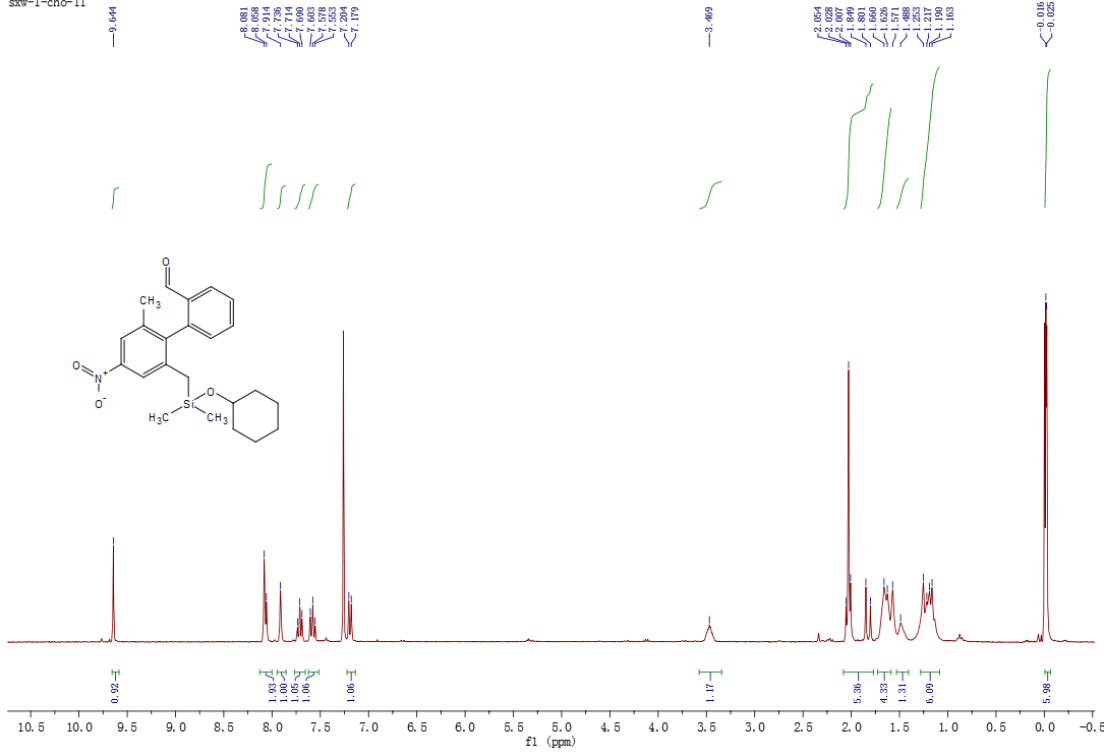
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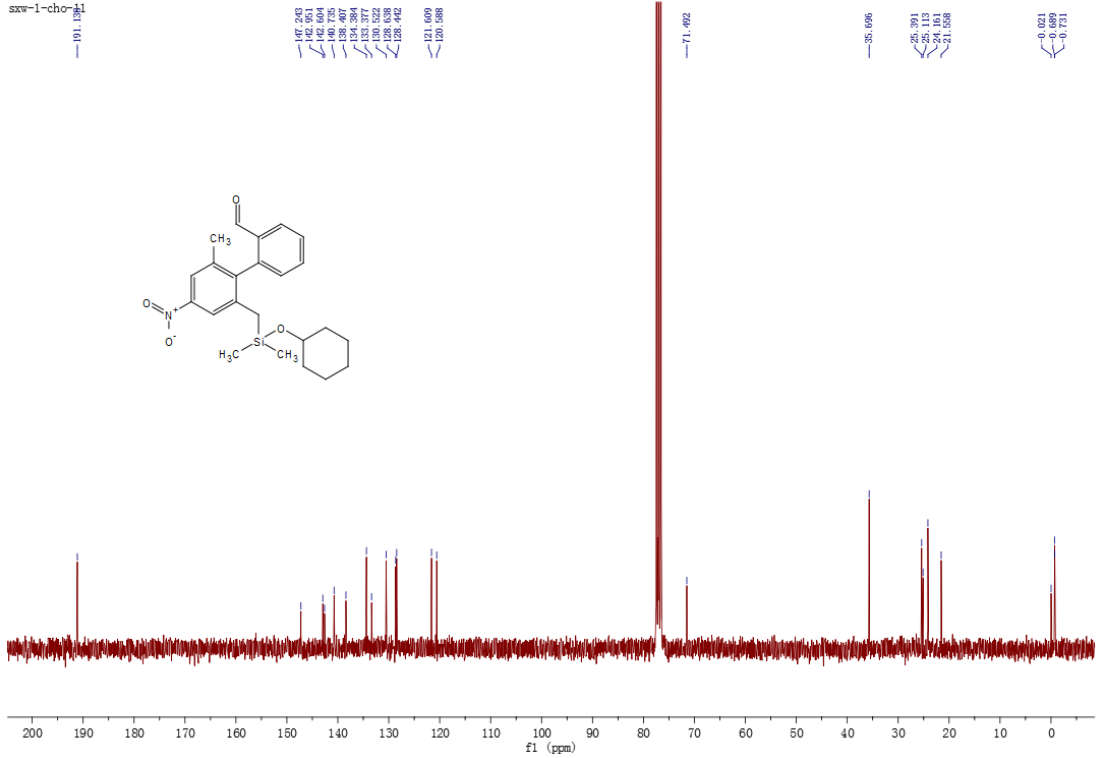
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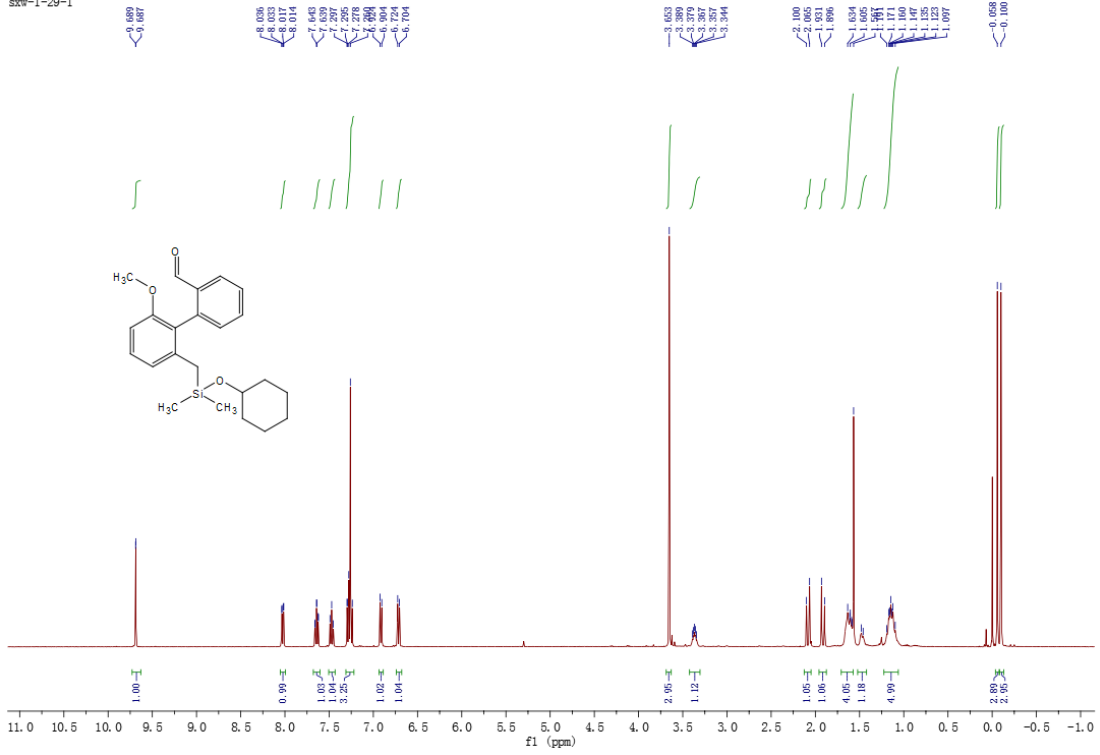
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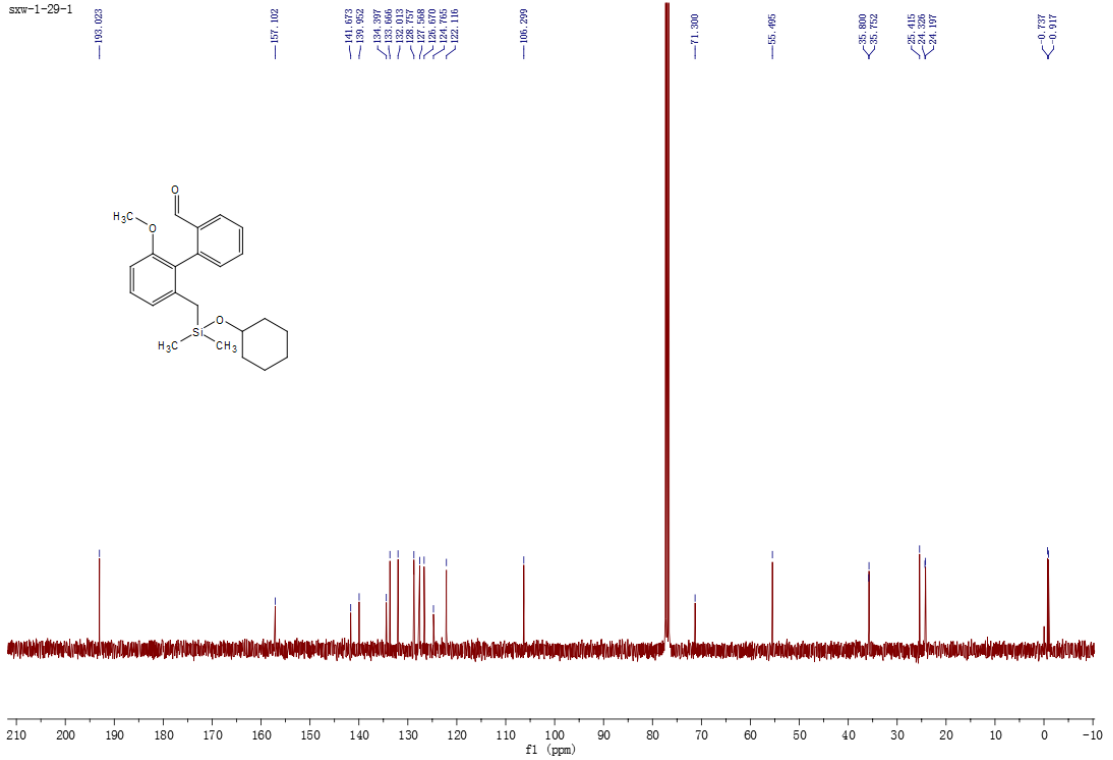
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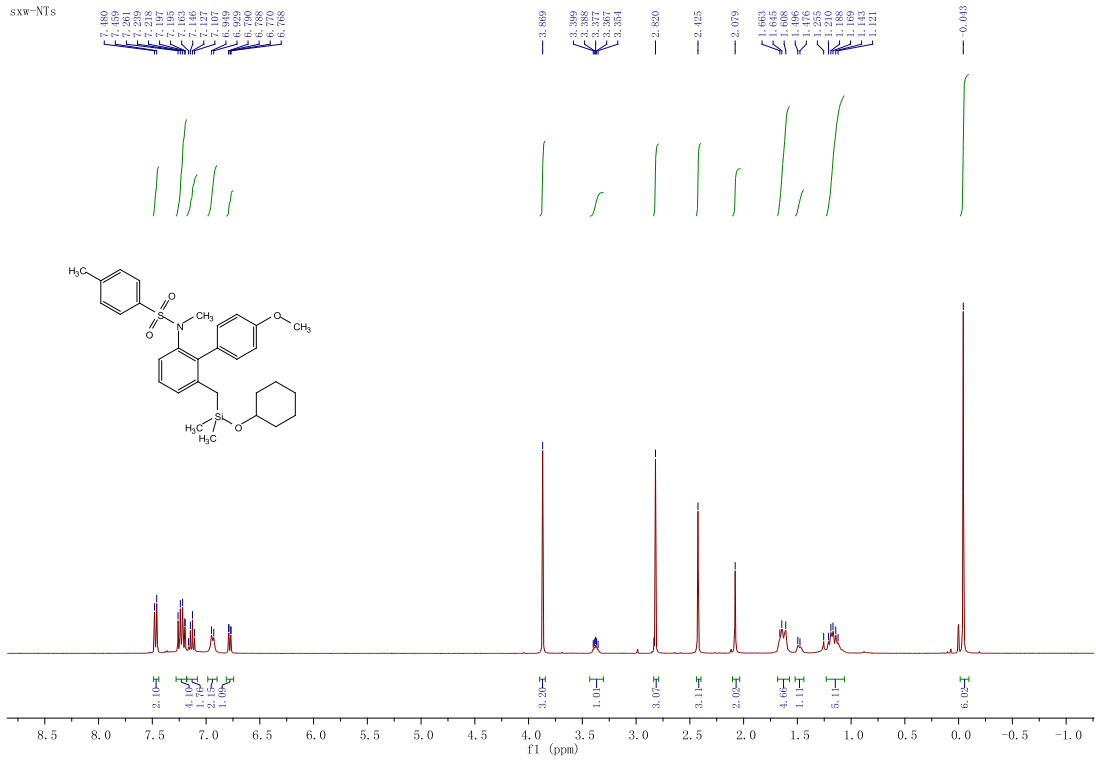
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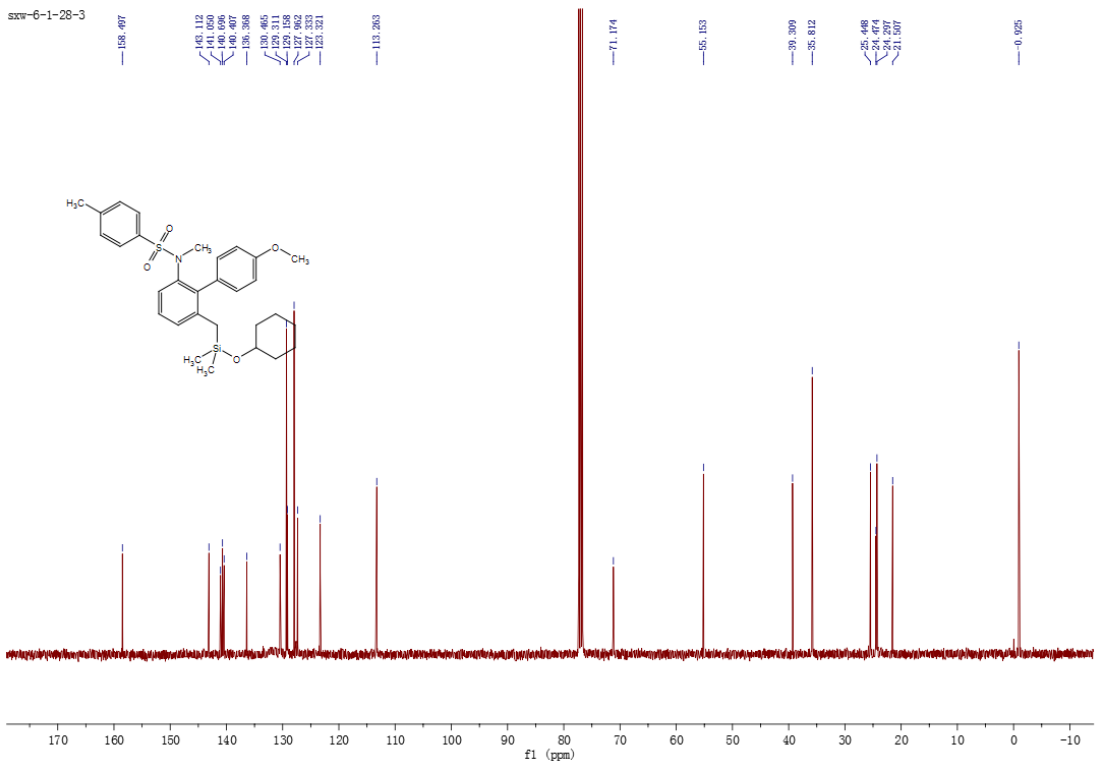
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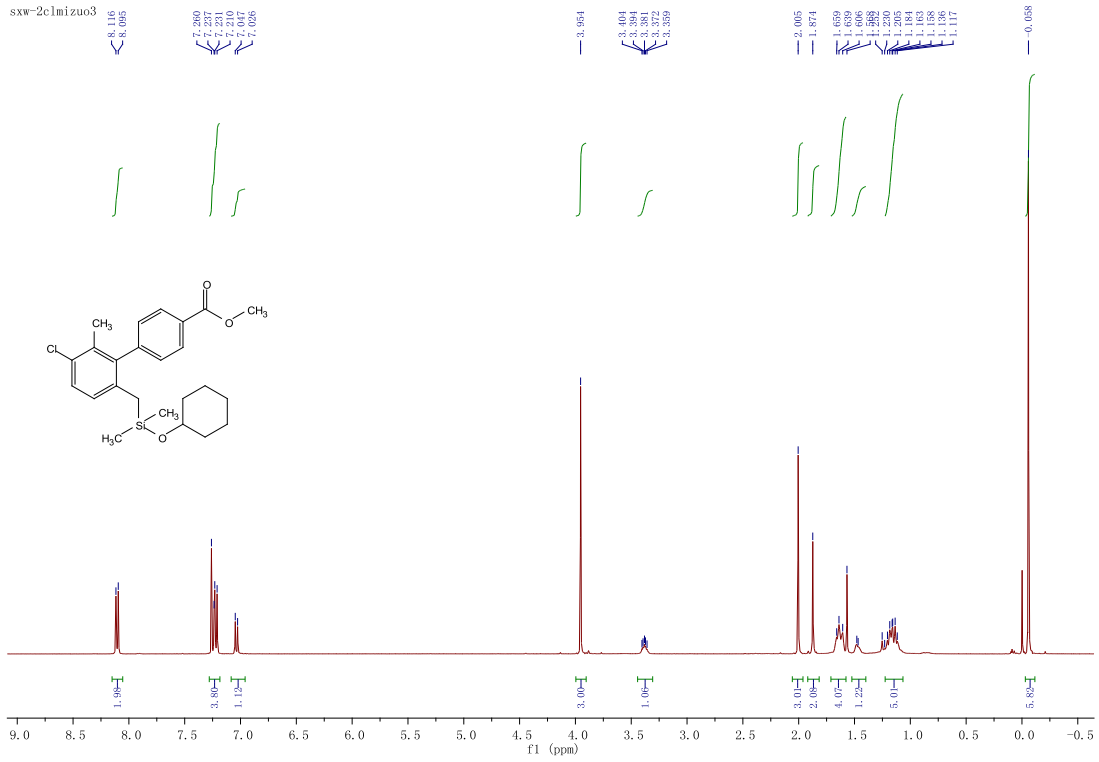
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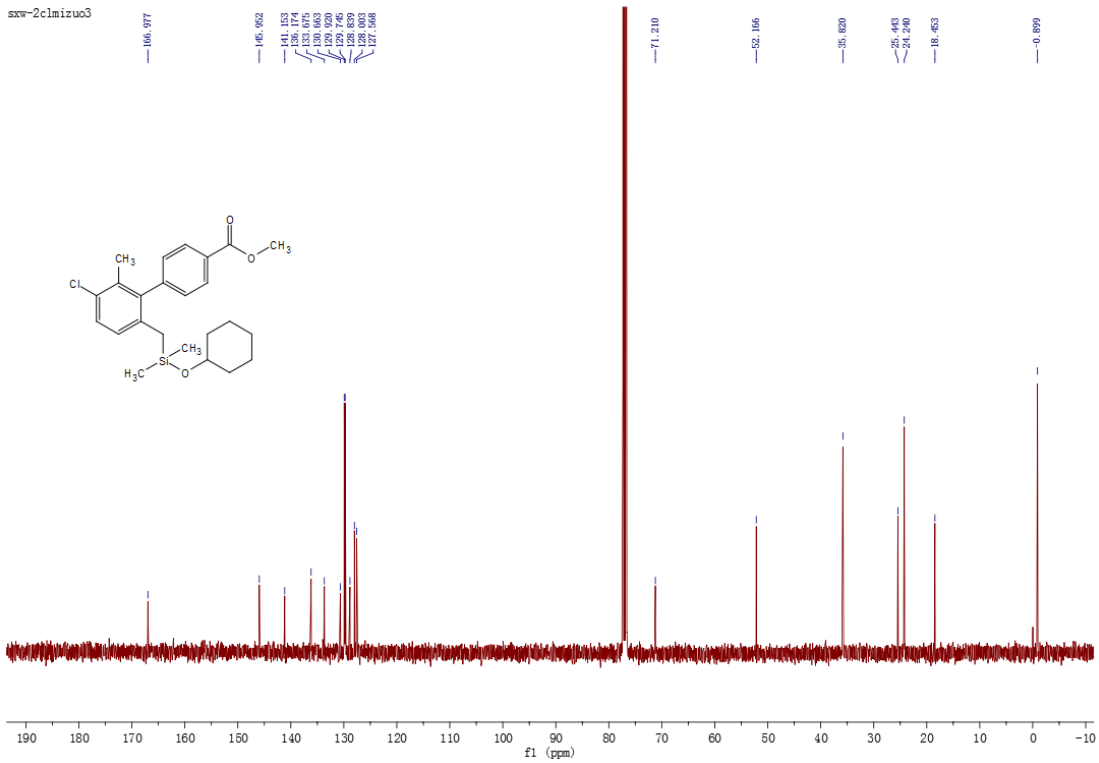
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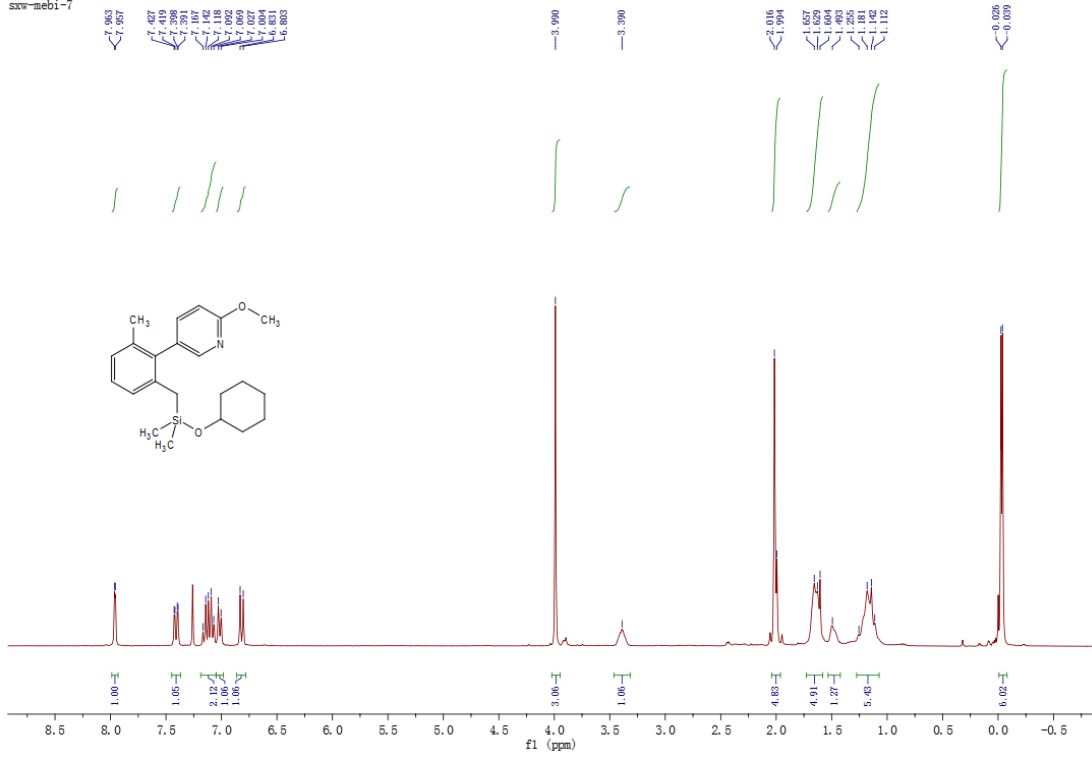
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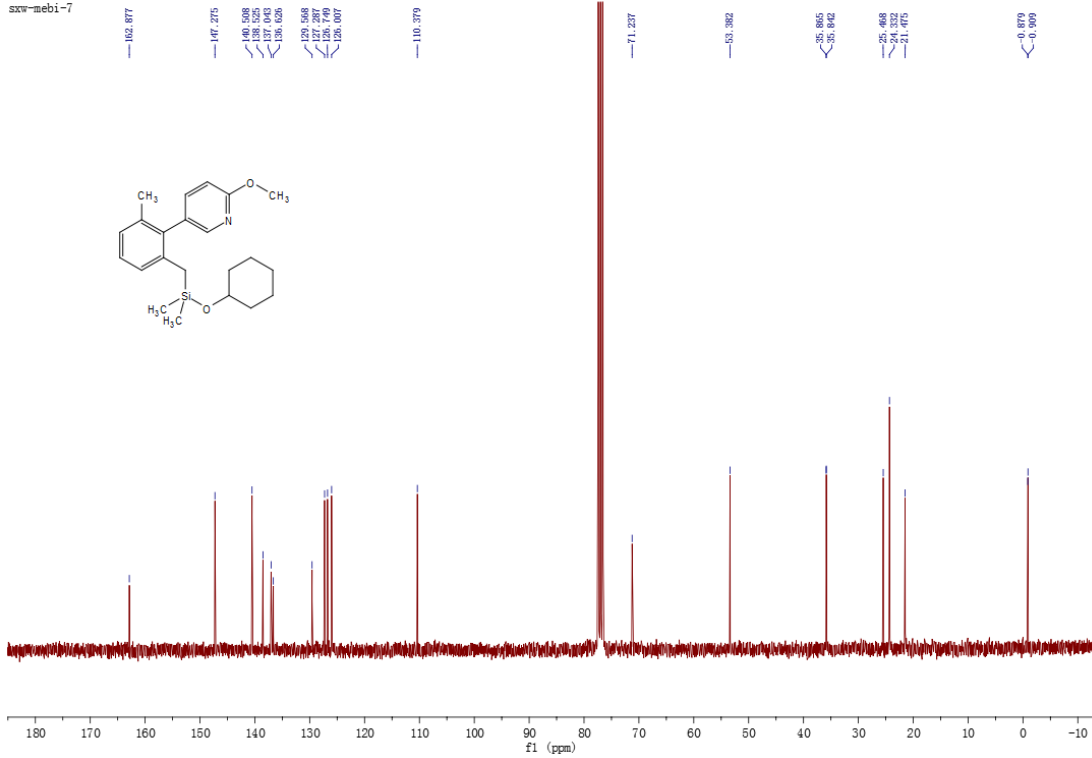
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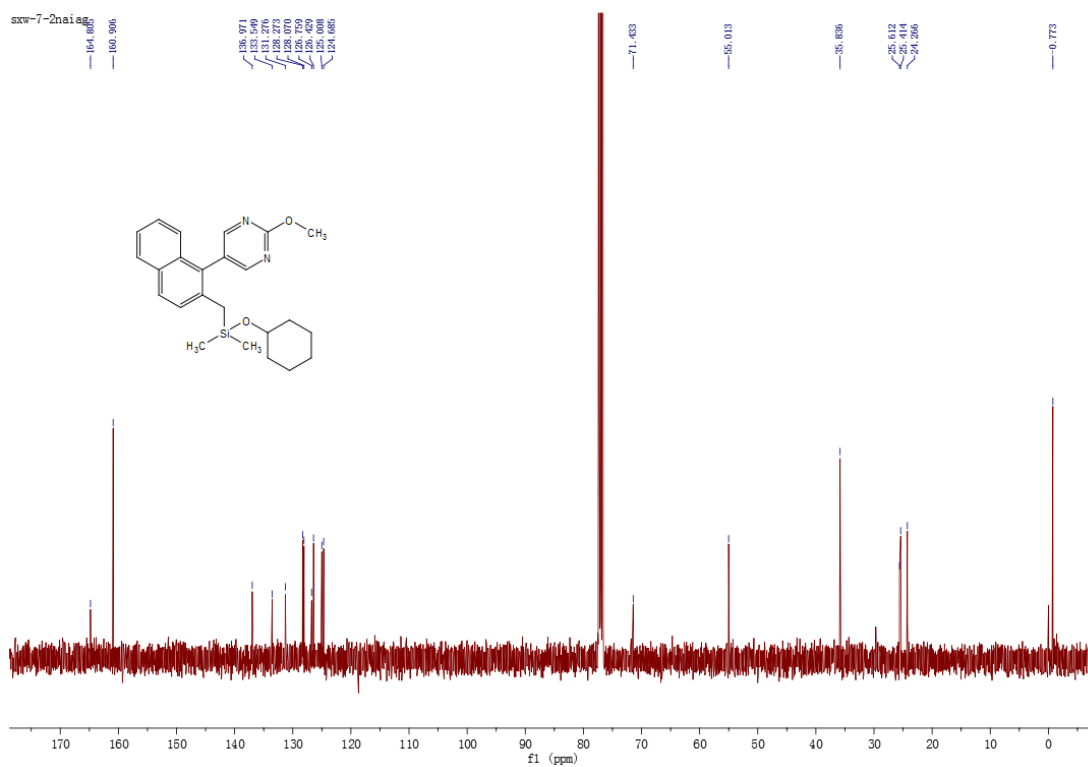
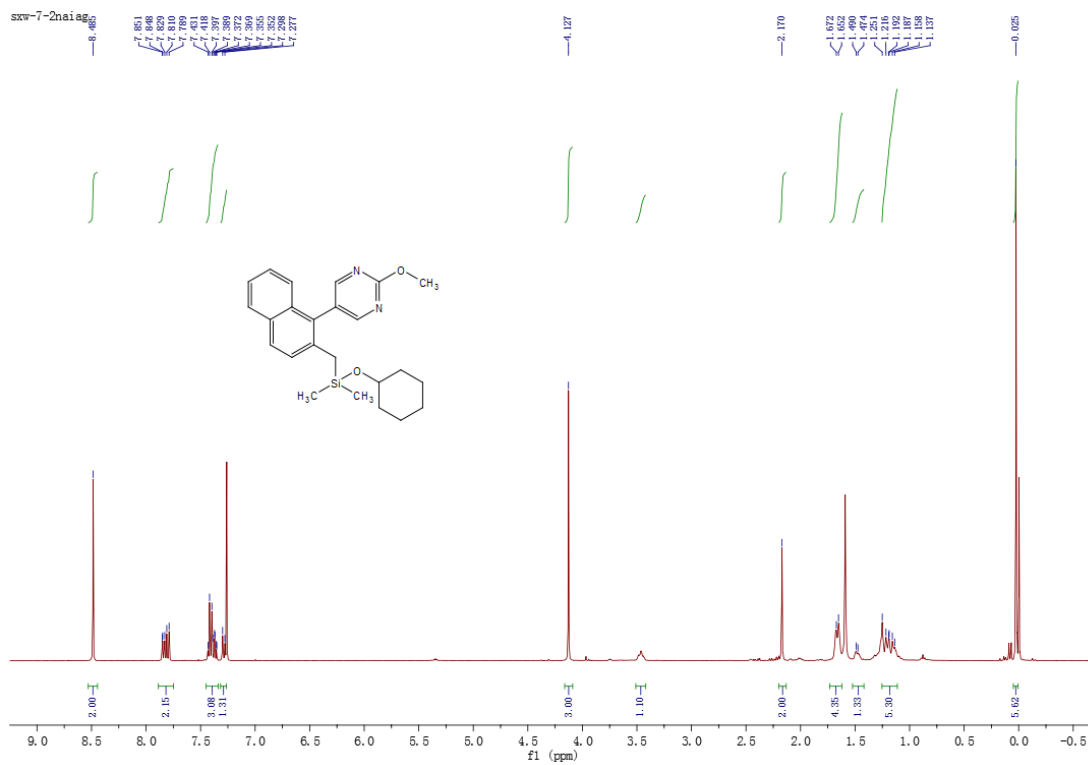


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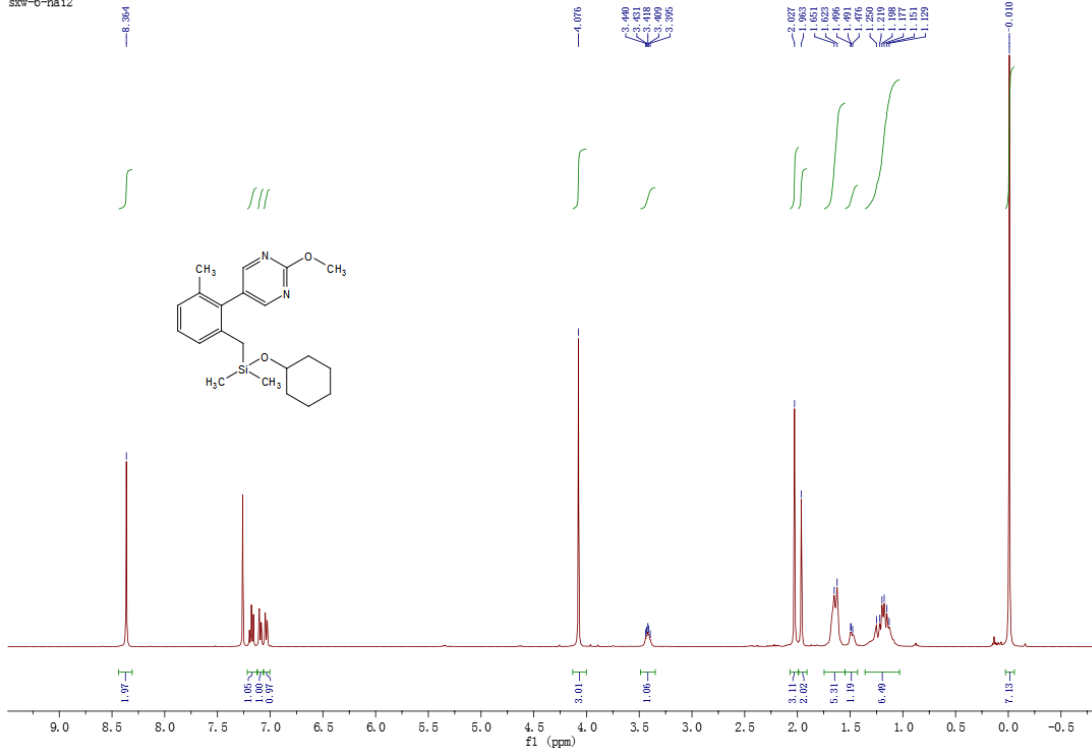


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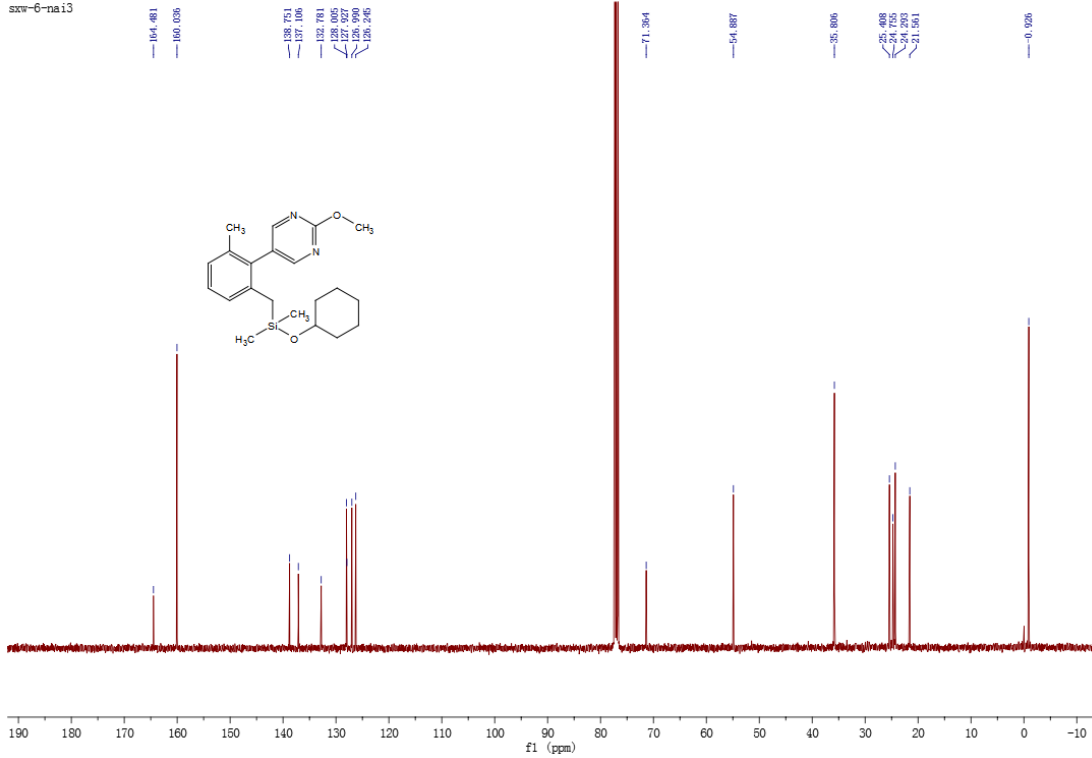




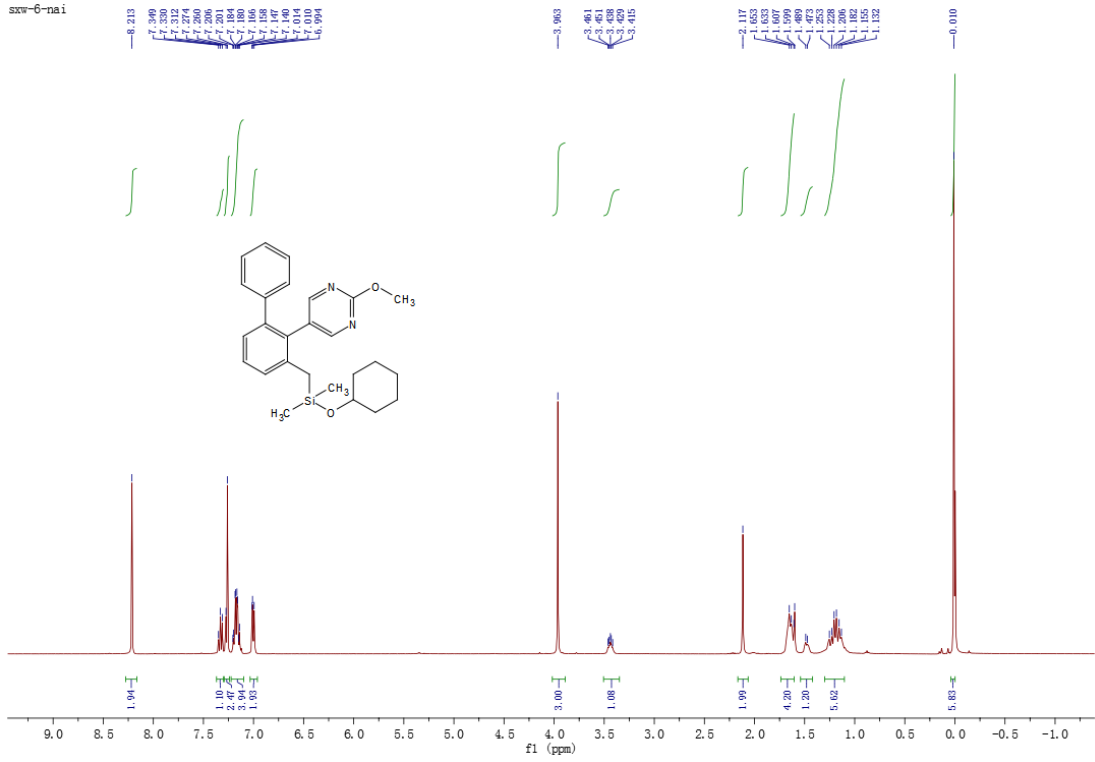
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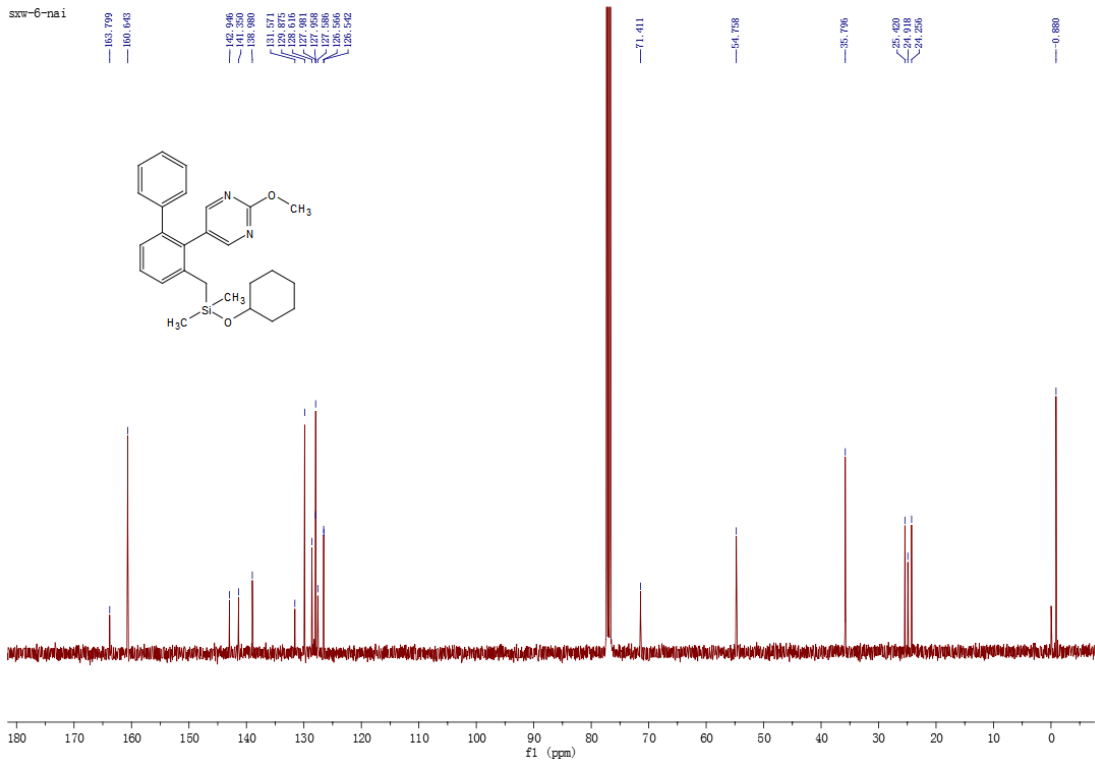
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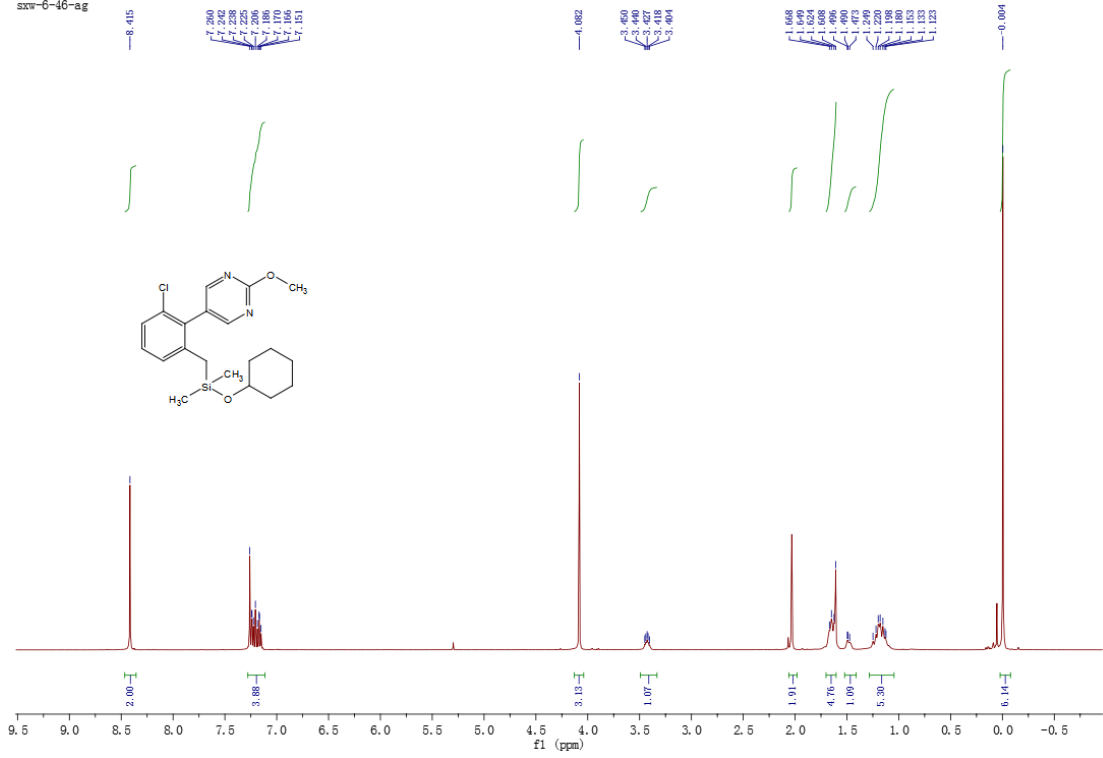
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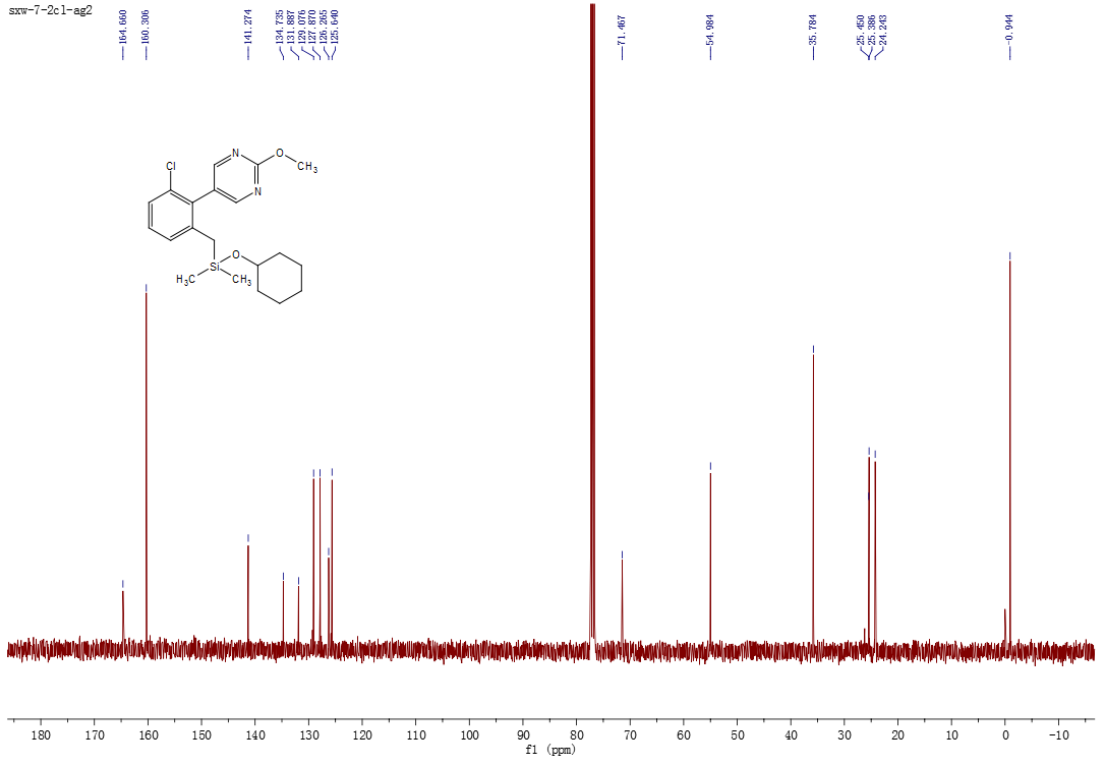
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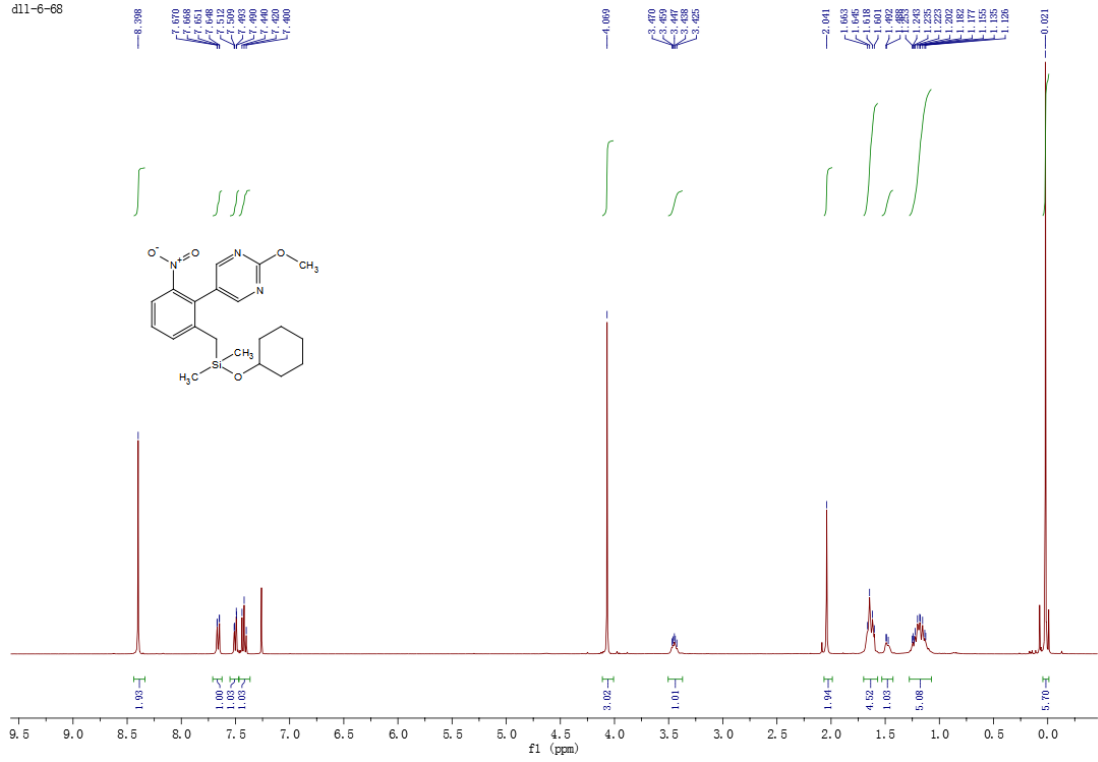
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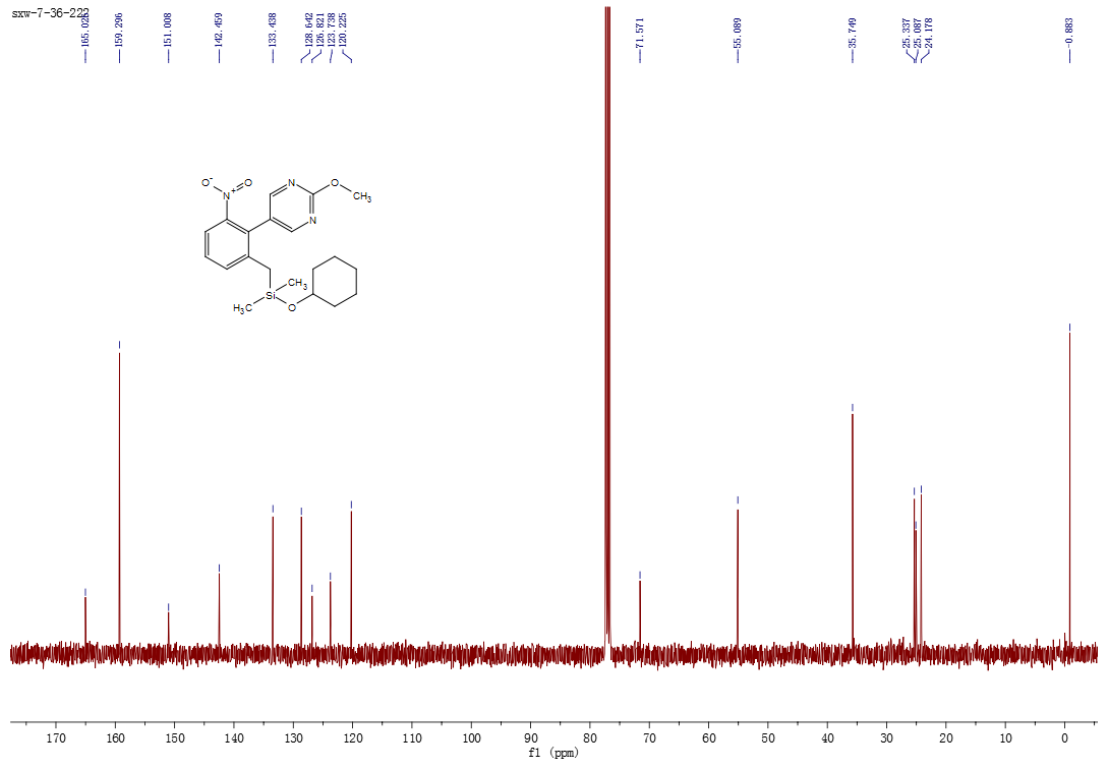
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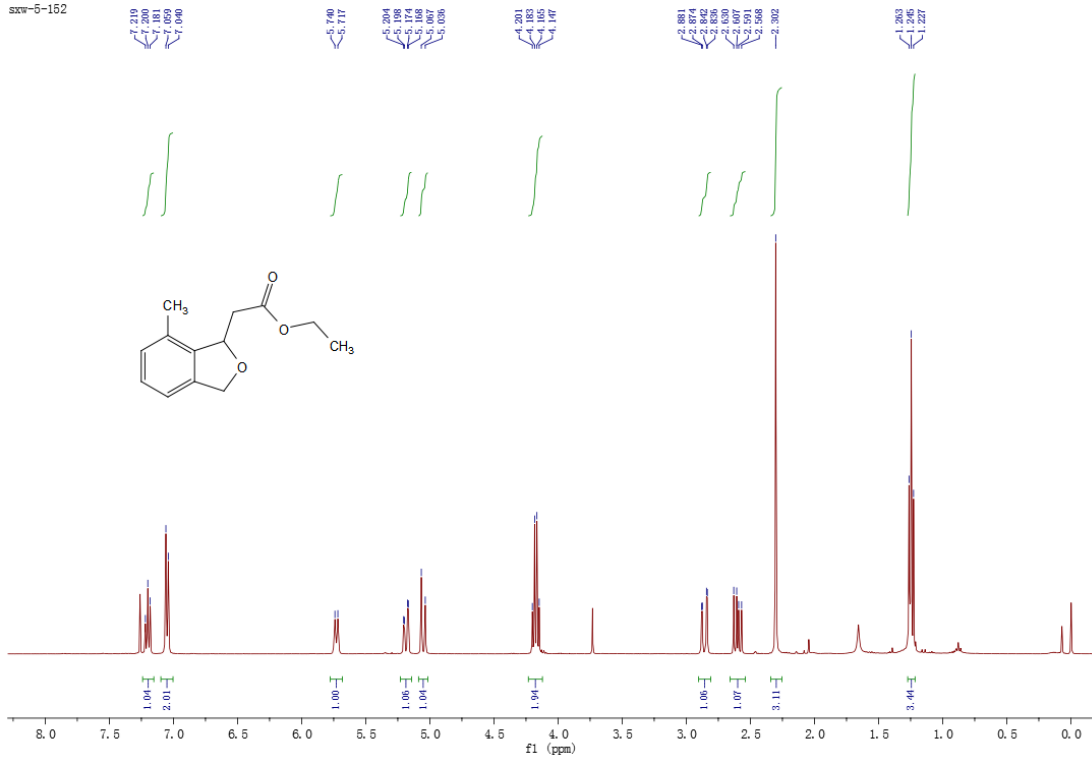
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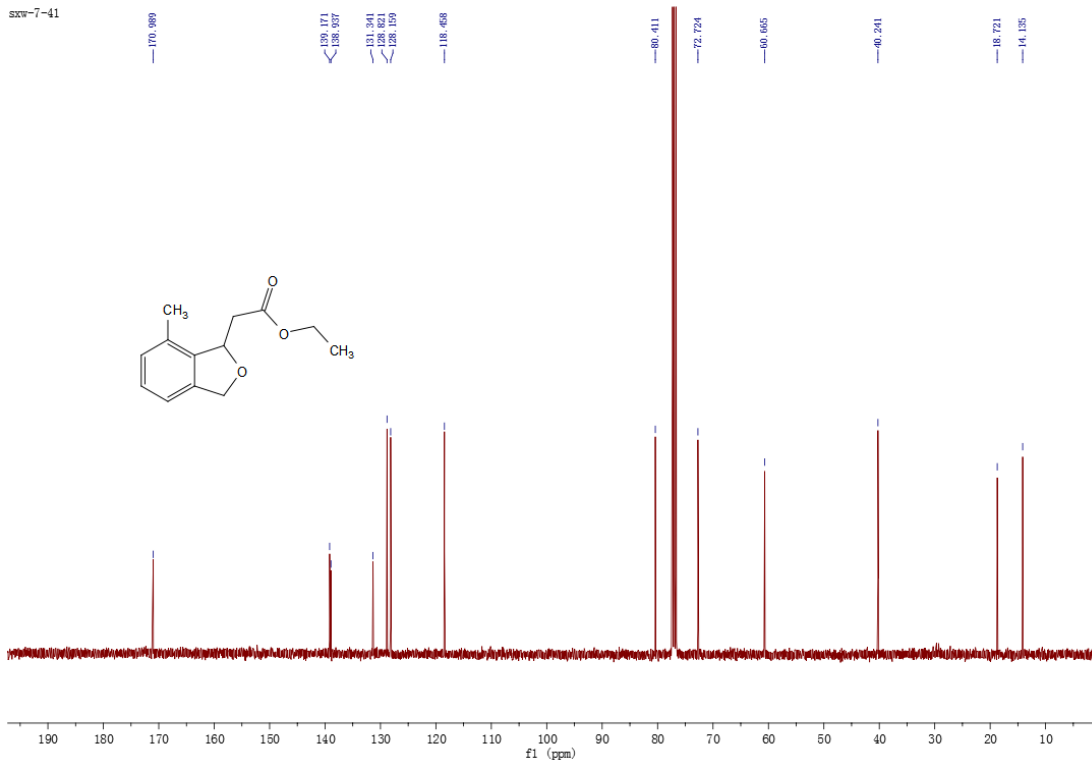
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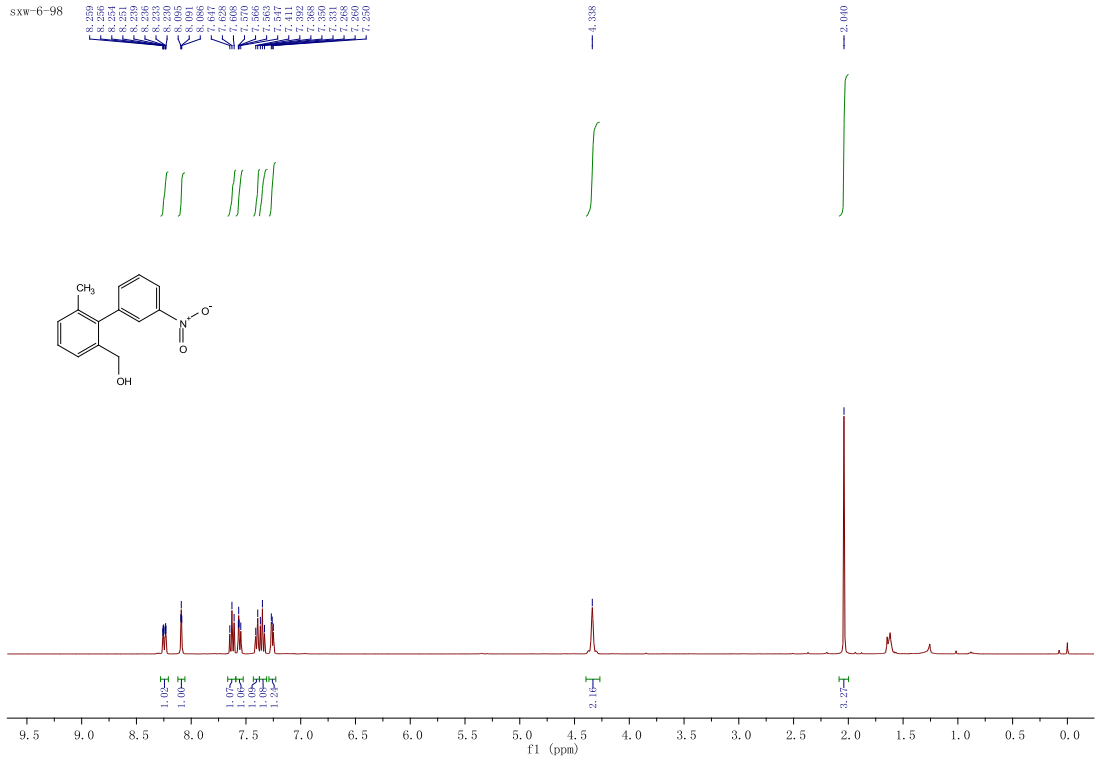
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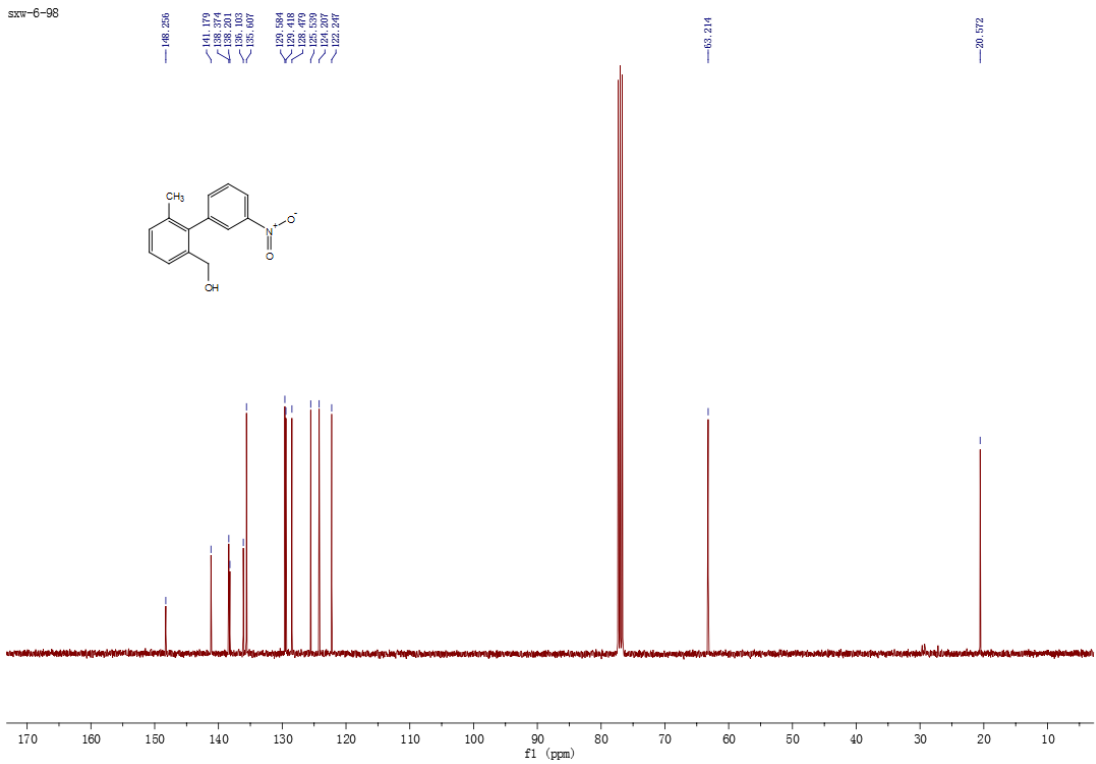
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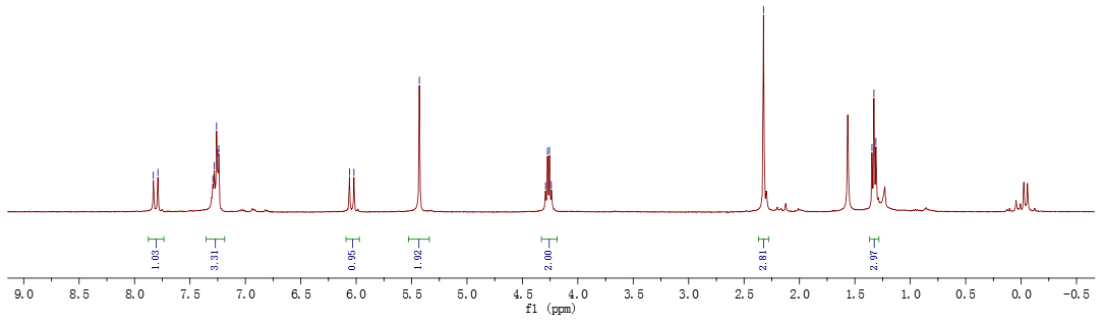
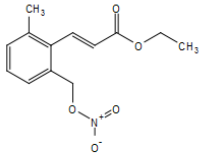
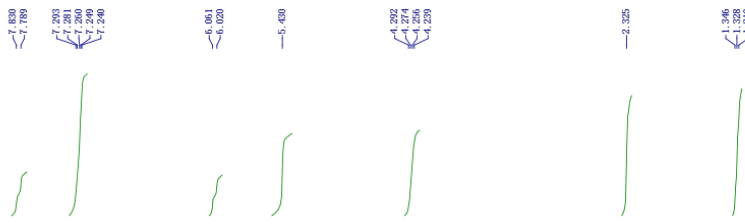
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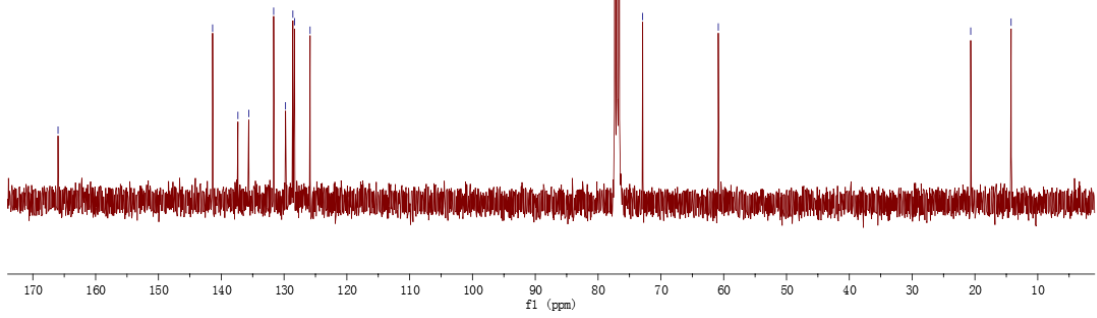
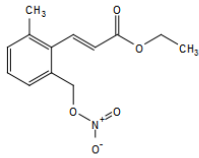
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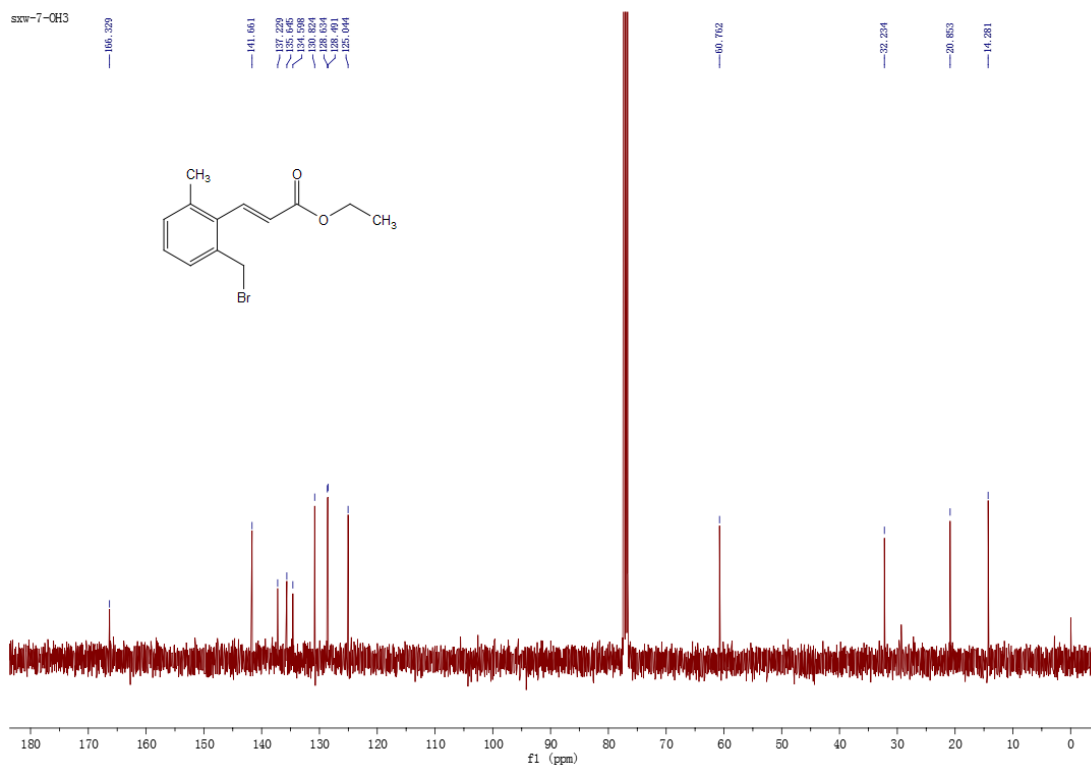
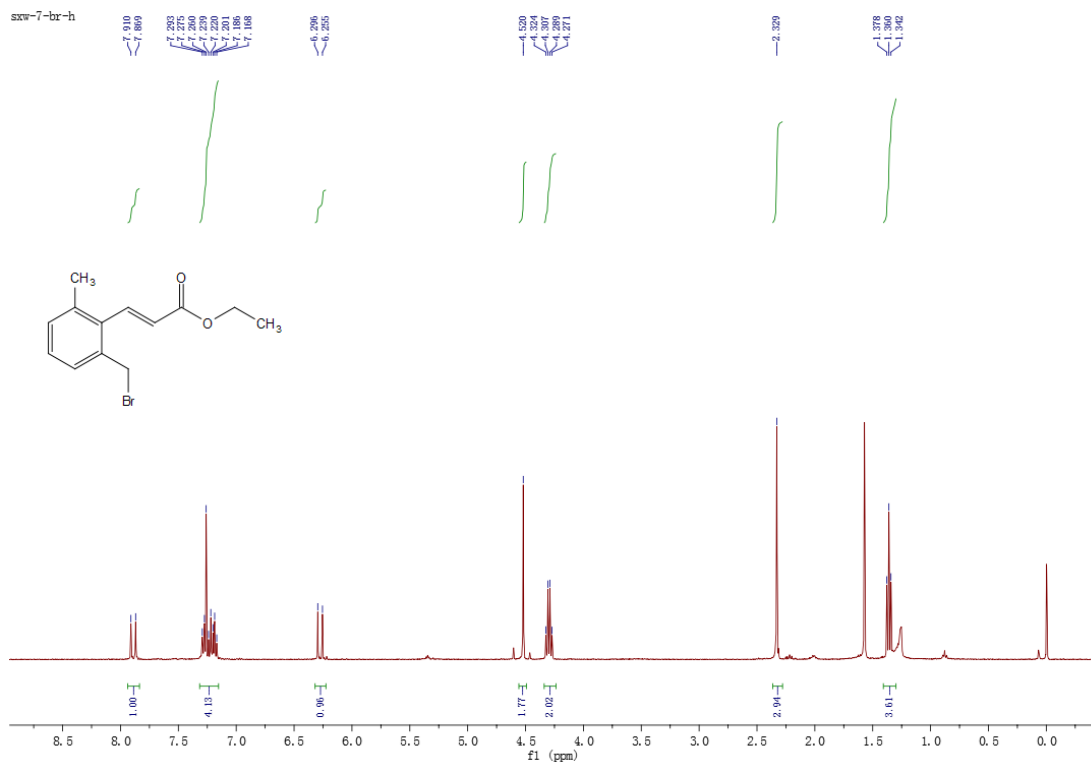


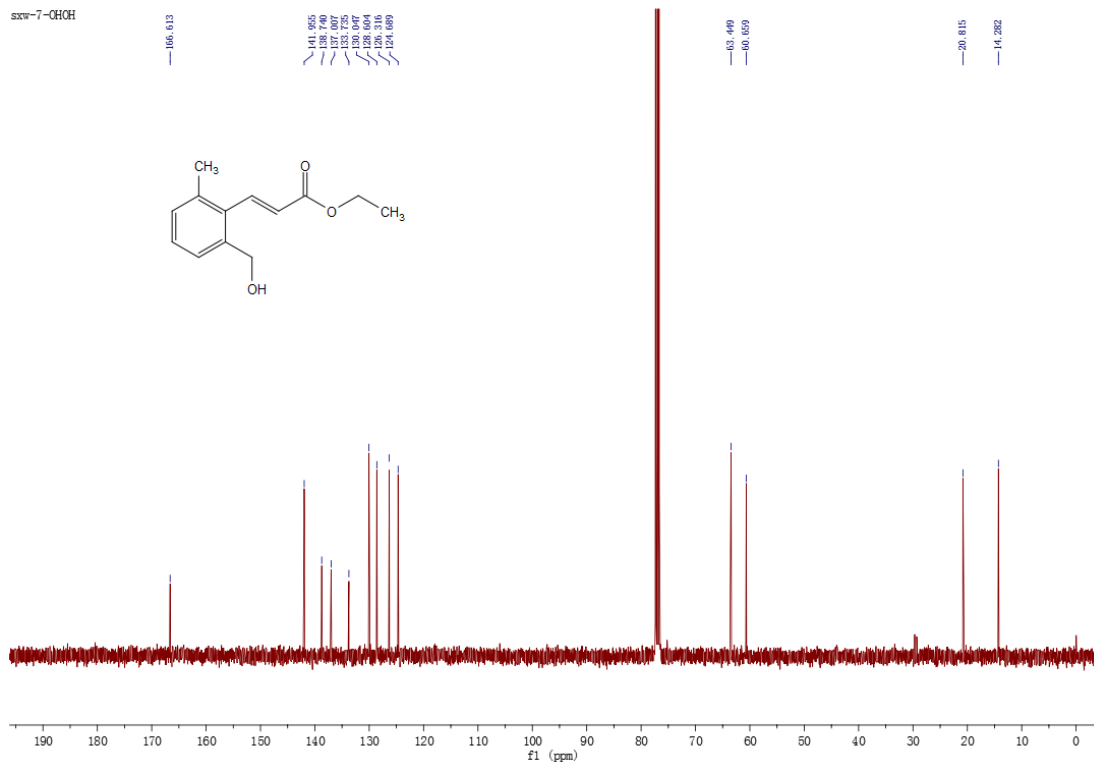
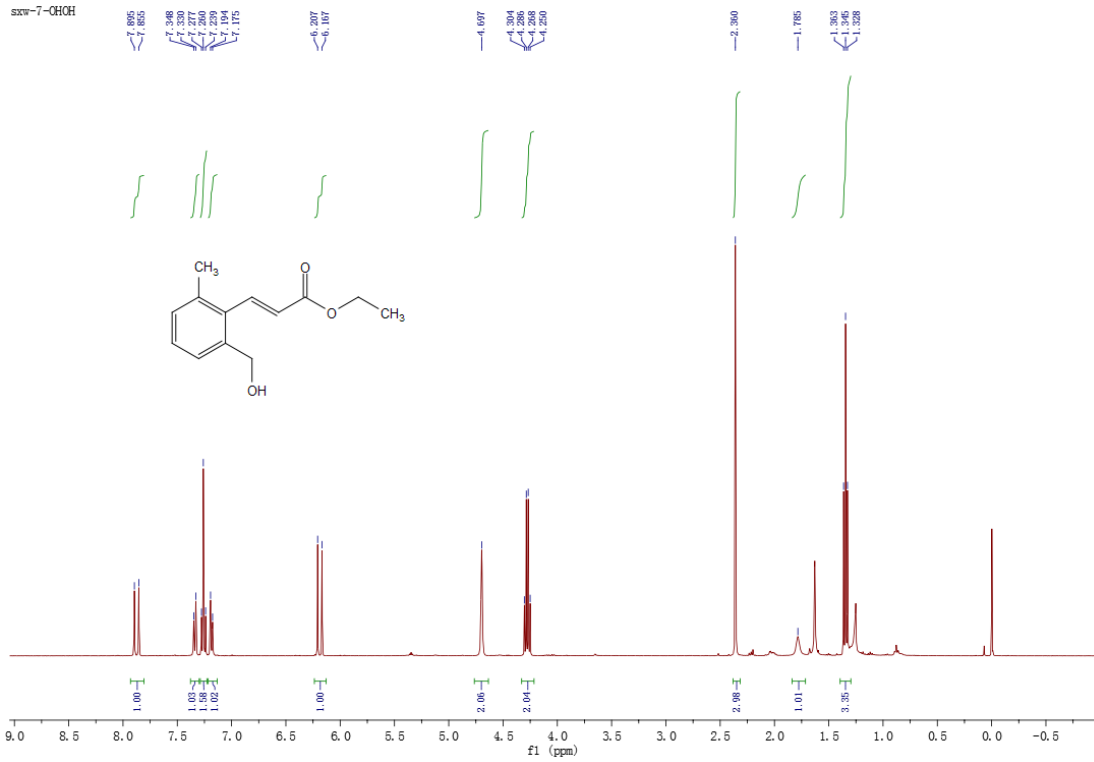
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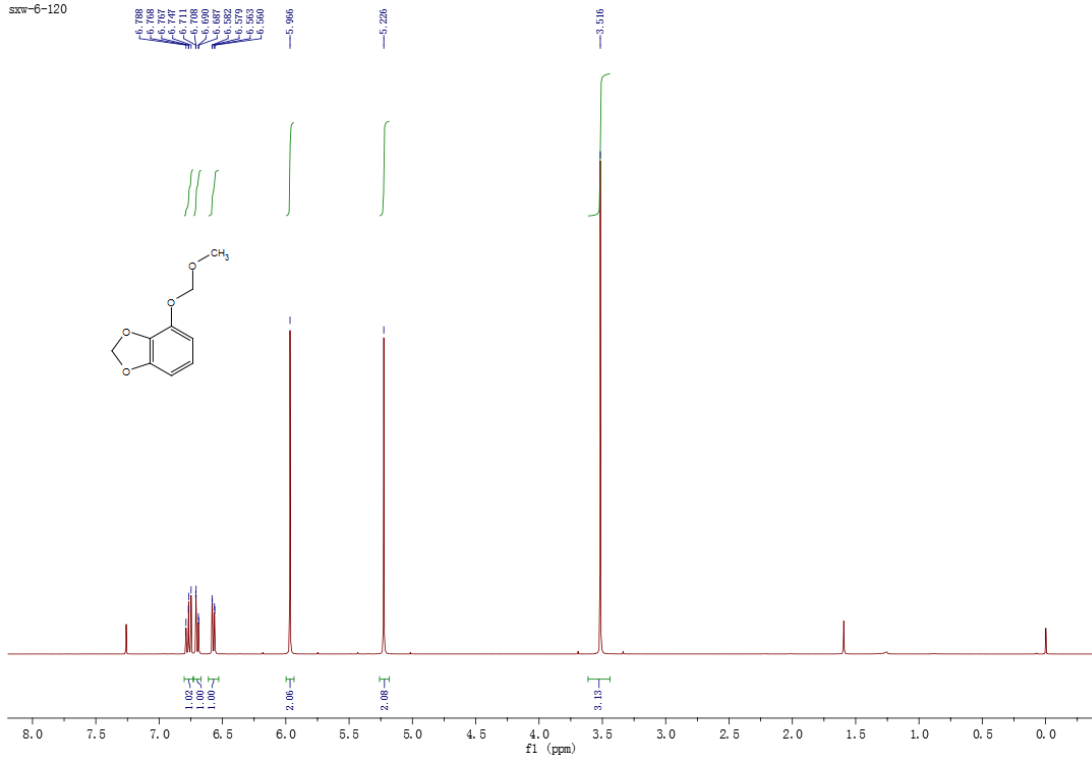
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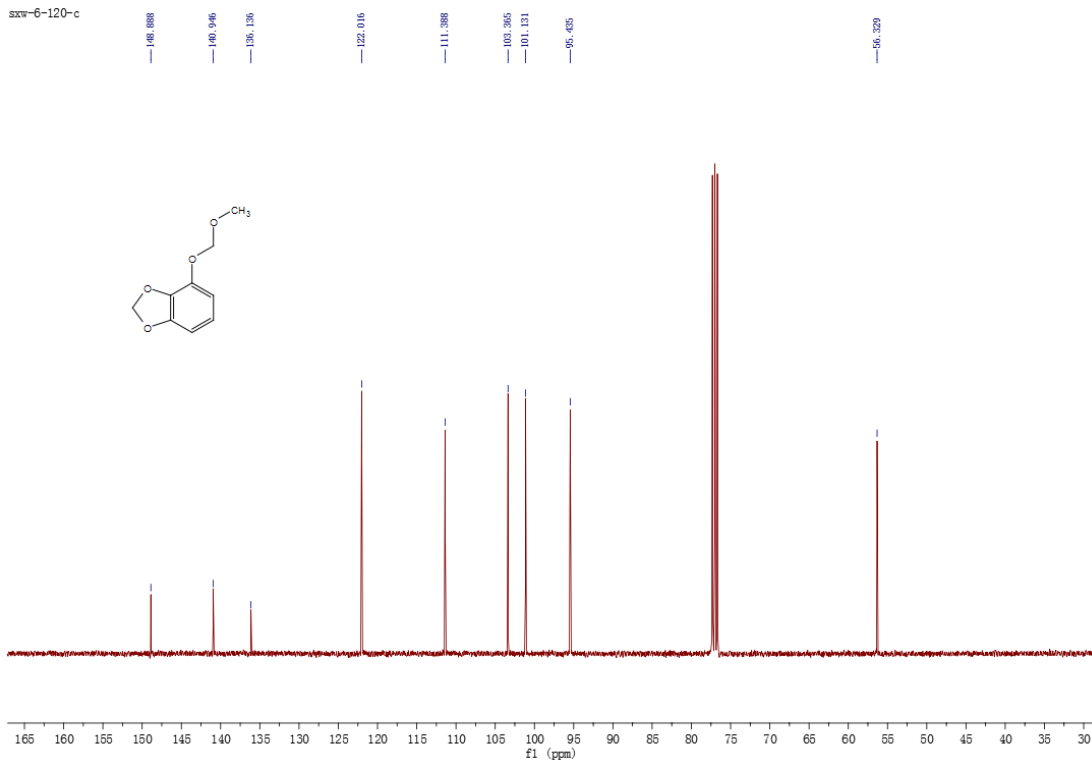




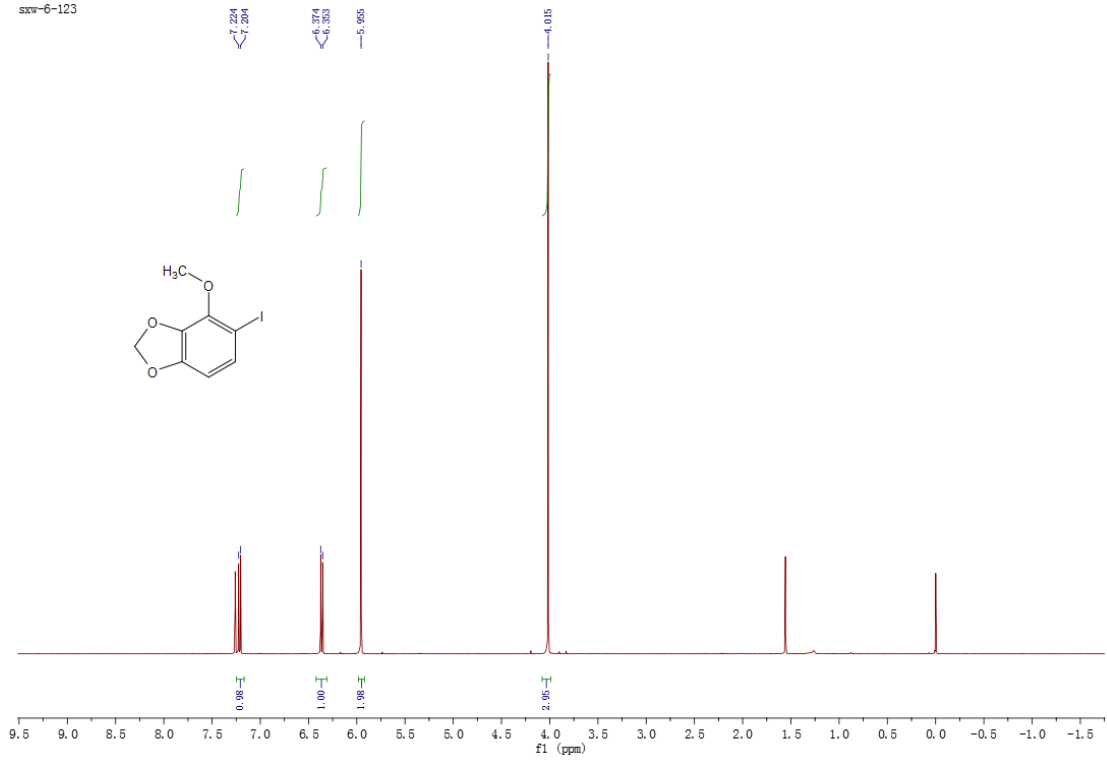
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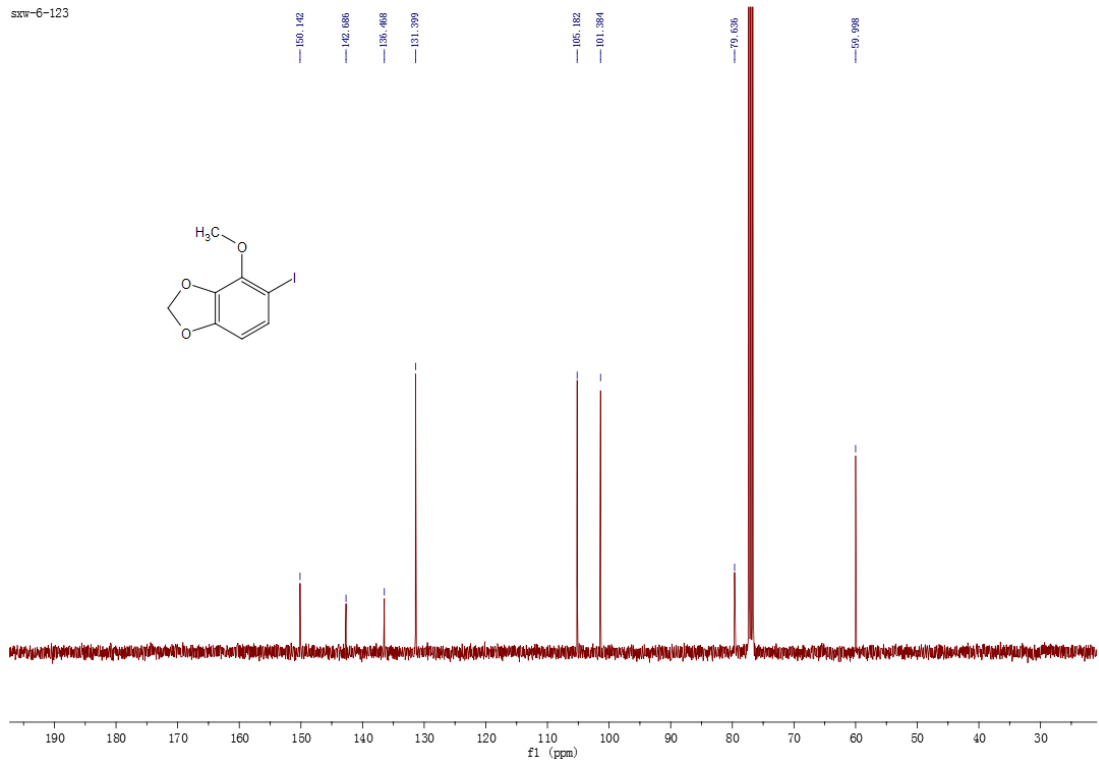
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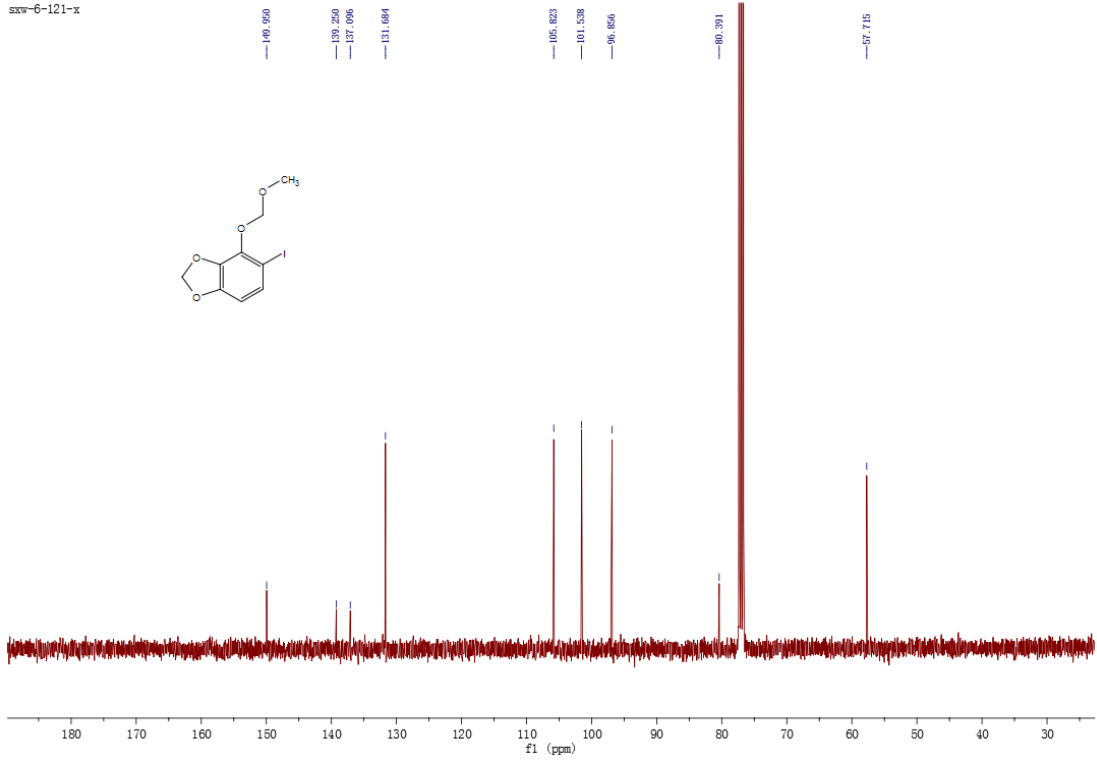
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SKW-6-123



szw-6-121-x



szw-6-121-x

