Supporting Information

Organo-photocatalytic dearomative hydrosilylation of indoles with silanes

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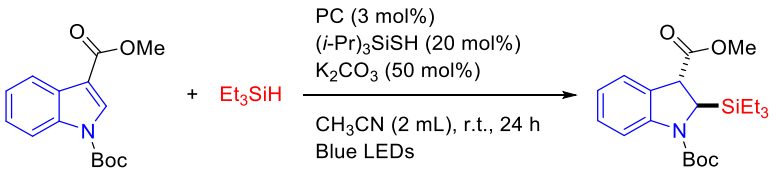
1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. Indole derivatives were prepared concerning literature. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on Bruker AV-III400 (400 MHz) and Bruker AVANCE III HD 600 (600 MHz) spectrometers. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.0 ppm ^{13}C NMR). Multiplicity was indicated as follows: brs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). High-resolution mass spectra (HRMS) were obtained on an Agilent 7200 GC-QTOF spectrometer (EI). Cyclic voltammetry was performed using a CHI660E Chenhua (China).

2. Complementary Reaction Optimization Data

Table S1. Screening of photocatalysts



1a, 0.1 mmol **2a**, 1.5 equiv **3aa**

entry	PC	yield% (3aa)[a]
1	4-CzIPN	46
2	$Ir(ppy)_3$	0
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	0
4	$Ir(ppy)_2(dtbbpy)PF_6$	0
5	**3DPA2FBN**	**65**

[a] The yield was obtained with ^{1}H-NMR using trimethoxybenzene as the internal standard.

Table S2. Screening of bases.

1a, 0.1 mmol **2a**, 1.5 equiv **3aa**

entry	base	yield% (3aa)[a]
1	NaOAc	0
2	K_2HPO_4	0
3	DABCO	0
4	KH_2PO_4	0
5	PhCOONa	0
6	DIPEA	0
7	K_3PO_4	40
8	NaOH	97
9[b]	**Cs_2CO_3**	**92**

[a] The yield was obtained with ^{1}H-NMR using trimethoxybenzene as the internal standard.
[b] Isolated yield.

3. Starting Material Preparation

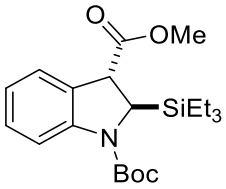
The indole esters (**1a-1B**) were synthesized accordinig to the literature procedures[1].

4. General Procedure for Hydrosilylation of Indole Ester

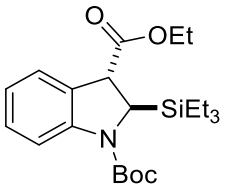
1, 0.2 mmol **2**, 1.5 equiv **3**

In a 20 mL Schlenk tube with a magnetic stir bar were placed 3DPA2FBN (**PC**, 4 mg, 0.006 mmol, 3 mol%), Cs_2CO_3 (32 mg, 0.1 mmol, 0.5 equiv), and silanes (**2**, 0.3 mmol, 1.5 equiv). Under nitrogen atmosphere, indole esters (**1**, 0.2 mmol, 1 equiv), (i-Pr)$_3$SiSH (8 μL, 0.04 mmol, 20 mol%), CH_3CN (4 mL) were added, subsequently. The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction was placed under a blue LED (2-meter strips, 20 W) and irradiated for 24 hrs at rt. The solvent was removed under vacuum. Silica gel chromatography (PE: EA = 20:1) of the crude product afforded the desired compound **3**.

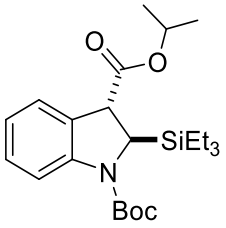
5. Analytical Data of the Products



1-(*tert*-Butyl)-3-methyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3aa): colorless oil (71 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (brs, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.59 (d, J = 2.7 Hz, 1H), 3.86 (d, *J* = 2.7 Hz, 1H), 3.68 (s, 3H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.64, 152.36, 142.75, 129.54, 128.78, 125.37, 122.60, 116.63, 81.04, 52.48, 51.77, 47.59, 28.42, 7.19, 1.95. HRMS (EI): Calcd for $C_{21}H_{34}NO_4Si$ $[M+H]^+$ 392.2252, found 392.2253.

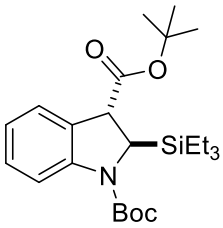


1-(*tert*-Butyl)-3-ethyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ba): colorless oil (49 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (brs, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.58 (d, *J* = 2.8 Hz, 1H), 4.13 (qd, *J* = 7.2, 5.2 Hz, 2H), 3.84 (d, *J* = 2.8 Hz, 1H), 1.57 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.12, 152.36, 142.83, 129.68, 128.69, 125.25, 122.55, 116.59, 80.96, 61.23, 51.67, 47.73, 28.41, 14.05, 7.19, 1.93. HRMS (EI): Calcd for $C_{22}H_{36}NO_4Si$ $[M+H]^+$ 406.2408, found 406.2410.

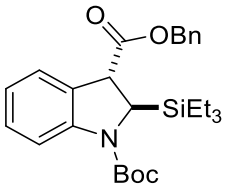


1-(*tert*-Butyl)-3-isopropyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ca): colorless oil (59 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (brs, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J*

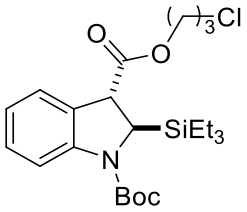
= 7.8 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 4.96 (hept, *J* = 6.3 Hz, 1H), 4.57 (d, *J* = 2.9 Hz, 1H), 3.80 (d, *J* = 2.9 Hz, 1H), 1.56 (s, 9H), 1.19 (dd, *J* = 9.8, 6.3 Hz, 6H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.57, 152.36, 142.81, 129.76, 128.60, 125.07, 122.48, 116.52, 80.86, 68.59, 51.57, 47.91, 28.38, 21.64, 7.16, 1.91. HRMS (EI): Calcd for $C_{23}H_{38}NO_4Si$ $[M+H]^+$ 420.2565, found 420.2565.



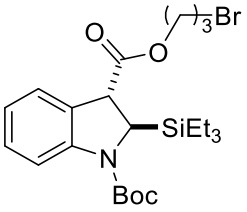
di-*tert*-Butyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3da): colorless oil (58 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (brs, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.8, 1H), 6.94 (t, *J* = 7.5, 1H), 4.52 (d, *J* = 3.0 Hz, 1H), 3.75 (d, *J* = 3.0 Hz, 1H), 1.56 (s, 9H), 1.40 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.24, 152.37, 142.83, 130.08, 128.48, 125.01, 122.42, 116.44, 81.18, 80.83, 51.63, 48.80, 28.40, 27.88, 7.19, 1.94. HRMS (EI): Calcd for $C_{24}H_{40}NO_4Si$ $[M+H]^+$ 434.2721, found 434.2721.



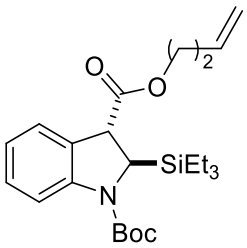
3-Benzyl-1-(*tert*-butyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ea): colorless oil (45 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (brs, 1H), 7.34 (dd, *J* = 8.1, 2.4 Hz, 3H), 7.31 – 7.27 (m, 3H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 5.13 (s, 2H), 4.64 (d, *J* = 2.7 Hz, 1H), 3.93 (d, *J* = 2.7 Hz, 1H), 1.56 (s, 9H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.84, 152.24, 142.78, 135.61, 129.35, 128.78, 128.46, 128.11, 127.77, 125.27, 122.54, 116.55, 80.93, 66.89, 51.59, 47.71, 28.32, 7.15, 1.87. HRMS (EI): Calcd for $C_{27}H_{38}NO_4Si$ $[M+H]^+$ 468.2565, found 468.2566.



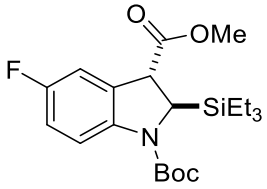
1-(*tert*-Butyl)-3-((dimethyl-λ^3-chloraneyl)methyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3fa): colorless oil (51 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (brs, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 2.5 Hz, 1H), 4.34 – 4.15 (m, 2H), 3.85 (d, *J* = 2.6 Hz, 1H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.04 (p, *J* = 6.3 Hz, 2H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.93, 152.28, 142.79, 129.49, 128.86, 125.12, 122.64, 116.66, 81.08, 61.85, 51.75, 47.74, 40.91, 31.40, 28.38, 7.17, 1.90. HRMS (EI): Calcd for $C_{23}H_{37}ClNO_4Si$ $[M+H]^+$ 454.2175, found 454.2175.



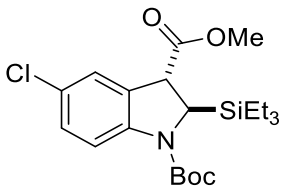
1-(*tert*-Butyl)-3-((dimethyl-λ^3-bromaneyl)methyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ga): colorless oil (71 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (brs, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 2.6 Hz, 1H), 4.23 (td, *J* = 5.7, 4.2 Hz, 2H), 3.85 (d, *J* = 2.6 Hz, 1H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.04 (p, *J* = 6.3 Hz, 2H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.93, 152.29, 142.81, 129.51, 128.86, 125.12, 122.64, 116.68, 81.07, 61.86, 51.79, 47.76, 40.90, 31.42, 28.39, 7.17, 1.92. HRMS (EI): Calcd for $C_{23}H_{37}BrNO_4Si$ $[M+H]^+$ 498.1670, found 498.1672.



1-(*tert*-Butyl)-3-(2-methylallyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ha): colorless oil (34 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (brs, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5, 1H), 5.72 (m, 1H), 5.20 – 4.93 (m, 2H), 4.59 (d, *J* = 2.7 Hz, 1H), 4.13 (tt, *J* = 7.2, 3.7 Hz, 2H), 3.85 (d, *J* = 2.7 Hz, 1H), 2.35 (m, 2H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.06, 152.32, 142.83, 133.73, 129.56, 128.72, 125.36, 122.53, 117.36, 116.55, 80.96, 64.19, 51.63, 47.75, 33.01, 28.41, 7.20, 1.92. HRMS (EI): Calcd for $C_{24}H_{37}NO_4Si$ $[M+H]^+$ 431.2486, found 431.2489.

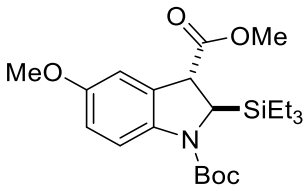


1-**(*tert*-Butyl)-3-methyl-*trans*-5-fluoro-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ia):** colorless oil (43 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (brs, 1H), 7.01 (dd, *J* = 8.0, 2.7 Hz, 1H), 6.91 (td, *J* = 8.9, 2.7 Hz, 1H), 4.60 (d, *J* = 2.6 Hz, 1H), 3.82 (d, *J* = 2.7 Hz, 1H), 3.70 (s, 3H), 1.56 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -120.89 (d, *J* = 230.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.04, 158.65 (d, *J* = 241.2 Hz), 152.29, 138.95, 131.09, 117.29, 115.26 (d, *J* = 23.1 Hz), 112.61 (d, *J* = 24.3 Hz), 81.19, 52.63, 52.10, 47.52, 28.39, 7.17, 1.90. HRMS (EI): Calcd for $C_{21}H_{33}FNO_4Si$ $[M+H]^+$ 410.2157, found 410.2154.

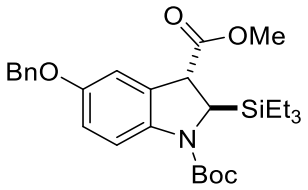


1-(*tert*-Butyl)-3-methyl-*trans*-5-chloro-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ja):

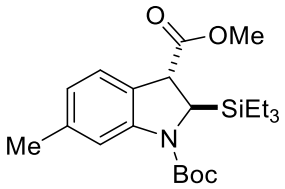
colorless oil (60 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (brs, 1H), 7.26 (d, J = 2.2 Hz, 1H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 4.59 (d, J = 2.8 Hz, 1H), 3.82 (d, J = 2.8 Hz, 1H), 3.70 (s, 3H), 1.55 (s, 9H), 0.87 (t, J = 7.9 Hz, 9H), 0.55 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.99, 152.14, 141.57, 131.17, 128.79, 127.41, 125.48, 117.40, 81.42, 52.68, 52.01, 47.31, 28.34, 7.18, 1.91. HRMS (EI): Calcd for $C_{21}H_{33}ClNO_4Si$ $[M+H]^+$ 426.1862, found 426.1861.



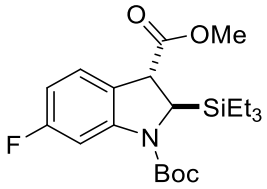
1-(*tert*-Butyl)-3-methyl-*trans*-5-methoxy-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ka): colorless oil (58 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (brs, 1H), 6.85 (s, 1H), 6.75 (d, J = 9.1 Hz, 1H), 4.56 (s, 1H), 3.80 (s, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 1.55 (s, 9H), 0.87 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.45, 155.53, 152.61, 136.45, 130.82, 117.12, 113.65, 111.35, 80.68, 55.63, 52.47, 51.94, 47.69, 28.41, 7.19, 1.88. HRMS (EI): Calcd for $C_{22}H_{36}NO_5Si$ $[M+H]^+$ 422.2357, found 422.2358.



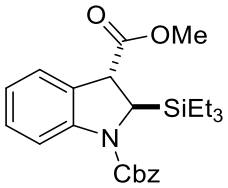
1-(*tert*-Butyl)-3-methyl-*trans*-5-(benzyloxy)-2-(triethylsilyl)indoline-1,3-dicarboxylate (3la): colorless oil (62 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 6H), 6.95 (d, J = 2.6 Hz, 1H), 6.85 (dd, J = 8.9, 2.7 Hz, 1H), 5.03 (s, 2H), 4.59 (d, J = 2.6 Hz, 1H), 3.88 – 3.74 (m, 1H), 3.67 (s, 3H), 1.56 (s, 9H), 0.88 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.38, 154.62, 152.10, 146.17, 136.97, 130.72, 128.47, 127.85, 127.48, 117.09, 114.89, 112.45, 80.71, 70.51, 52.46, 51.83, 47.70, 28.39, 7.20, 1.87. HRMS (EI): Calcd for $C_{28}H_{40}NO_5Si$ $[M+H]^+$ 498.2670, found 498.2672.



1-(*tert*-Butyl)-3-methyl-*trans*-6-methyl-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ma): colorless oil (64 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (brs, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.1 Hz, 1H), 4.57 (d, *J* = 2.6 Hz, 1H), 3.81 (d, *J* = 2.6 Hz, 1H), 3.67 (s, 3H), 2.32 (s, 3H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.78, 152.44, 142.93, 138.78, 126.65, 124.87, 123.42, 117.37, 80.90, 52.40, 52.04, 47.31, 28.38, 21.73, 7.20, 1.92. HRMS (EI): Calcd for $C_{22}H_{36}NO_4Si$ $[M+H]^+$ 406.2408, found 406.2409.

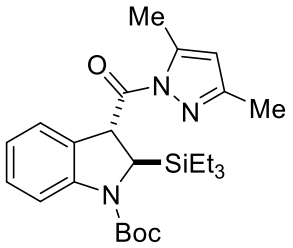


1-(*tert*-Butyl)-3-methyl-*trans*-6-fluoro-2-(triethylsilyl)indoline-1,3-dicarboxylate (3na): colorless oil (54 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (brs, 1H), 7.21 (dd, *J* = 8.3, 5.6 Hz, 1H), 6.64 (td, *J* = 8.6, 2.5 Hz, 1H), 4.61 (d, *J* = 2.7 Hz, 1H), 3.83 (d, *J* = 2.7 Hz, 1H), 3.69 (s, 3H), 1.57 (s, 9H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 8.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.46, 163.38 (d, *J* = 243.5 Hz), 151.99, 144.17, 125.95 (d, *J* = 10.3 Hz), 124.89, 109.15 (d, *J* = 23.2 Hz), 104.56 (d, *J* = 28.8 Hz), 81.58, 52.63,52.53, 46.83, 28.31, 7.16, 1.92; ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.64. HRMS (EI): Calcd for $C_{21}H_{33}FNO_4Si$ $[M+H]^+$ 410.2157, found 410.2155.

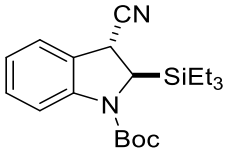


1-Benzyl-3-methyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3oa): colorless oil (45 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88(brs, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.36 (d, *J* = 12.2 Hz, 1H), 5.20 (d, *J* = 12.8 Hz,

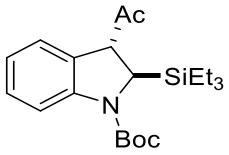
1H), 4.67 (d, *J* = 2.9 Hz, 1H), 3.93 (d, *J* = 3.0 Hz, 1H), 3.69 (s, 3H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.50 (q, *J* = 8.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.42, 152.91, 142.87, 136.12, 128.91, 128.45, 128.31, 128.26, 128.12, 125.33, 123.04, 116.50, 67.28, 52.54, 51.68, 47.72, 7.09, 1.87. HRMS (EI): Calcd for $C_{24}H_{32}NO_4Si$ $[M+H]^+$ 426.2095, found 426.2096.



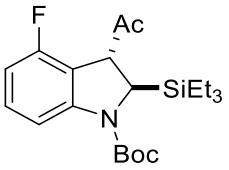
***tert*-Butyl-*trans*-3-(3,5-dimethyl-1*H*-pyrazole-1-carbonyl)-2-(triethylsilyl)indoline-1-carboxylate (3pa):** colorless oil (37 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (brs, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.20 (td, *J* = 7.8, 1.4 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 5.27 (s, 1H), 4.58 (d, *J* = 2.3 Hz, 1H), 2.47 (d, *J* = 0.9 Hz, 3H), 2.30 (s, 3H), 1.58 (s, 9H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.45, 152.05, 144.70, 130.25, 128.65, 125.77, 122.50, 116.49, 111.48, 80.93, 52.70, 46.59, 28.43, 17.67, 14.34, 13.80, 12.23, 7.24, 2.21. HRMS (EI): Calcd for $C_{25}H_{38}N_3O_3Si$ $[M+H]^+$ 456.2677, found 456.2678.



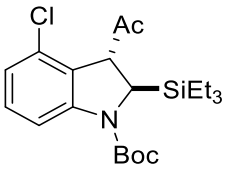
***tert*-Butyl-*trans*-3-cyano-2-(triethylsilyl)indoline-1-carboxylate (3qa):** colorless oil (30 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.59 (brs, 1H), 7.38 – 7.14 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.42 (d, *J* = 2.8 Hz, 1H), 3.98 (d, *J* = 2.8 Hz, 1H), 1.56 (s, 9H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.85, 142.45, 129.97, 125.91, 124.87, 123.36, 119.94, 116.90, 81.92, 53.44, 32.20, 28.32, 7.09, 1.89. HRMS (EI): Calcd for $C_{20}H_{31}N_2O_2Si$ $[M+H]^+$ 359.2149, found 359.2148.



***tert*-Butyl-*trans*-3-acetyl-2-(triethylsilyl)indoline-1-carboxylate (3ra):** colorless oil (54 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.25 – 7.14 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.46 (d, *J* = 2.2 Hz, 1H), 3.77 (d, *J* = 2.2 Hz, 1H), 2.07 (s, 3H), 1.57 (s, 9H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.74, 152.24, 143.14, 130.03, 128.90, 124.93, 122.92, 117.04, 81.24, 56.35, 51.70, 28.39, 25.60, 7.17, 1.90. HRMS (EI): Calcd for $C_{21}H_{34}NO_3Si$ $[M+H]^+$ 376.2302, found 376.2301.

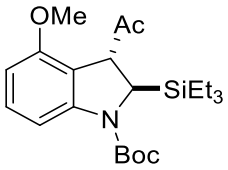


***tert*-Butyl-*trans*-3-acetyl-4-fluoro-2-(triethylsilyl)indoline-1-carboxylate (3sa):** colorless oil (47 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (brs, 1H), 7.19 (td, *J* = 8.2, 5.9 Hz, 1H), 6.69 (t, *J* = 8.6 Hz, 1H), 4.54 (d, *J* = 2.1 Hz, 1H), 3.89 (d, *J* = 2.0 Hz, 1H), 2.14 (d, *J* = 0.8 Hz, 3H), 1.56 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.53, 158.90 (d, *J* = 245.9 Hz), 151.91, 145.44, 130.68 (d, *J* = 8.2 Hz), 116.51, 112.74, 109.58 (d, *J* = 20.0 Hz), 81.56, 52.55, 52.24, 28.31, 26.81, 7.10, 1.86; ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.38. HRMS (EI): Calcd for $C_{21}H_{33}FNO_3Si$ $[M+H]^+$ 394.2208, found 394.2209.

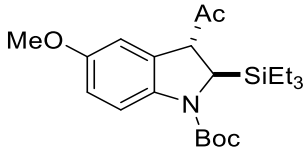


***tert*-Butyl-*trans*-3-acetyl-4-chloro-2-(triethylsilyl)indoline-1-carboxylate (3ta):** colorless oil (25 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (brs, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.28 (d, *J* = 2.7 Hz, 1H), 3.86 (d, *J* = 2.7 Hz, 1H), 2.07 (s, 3H), 1.55 (s, 9H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.91, 151.89, 144.30,

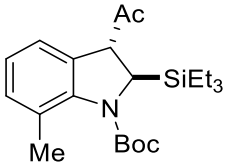
130.78, 130.27, 128.98, 122.92, 115.12, 81.72, 54.81, 53.09, 28.30, 26.78, 7.09, 1.78. HRMS (EI): Calcd for $C_{21}H_{33}ClNO_3Si$ $[M+H]^+$ 410.1913, found 410.1914.



***tert*-Butyl-*trans*-3-acetyl-4-methoxy-2-(triethylsilyl)indoline-1-carboxylate (3ua):** colorless oil (29 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 4.37 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 4H), 2.05 (s, 3H), 1.55 (s, 9H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.54, 155.90, 152.16, 144.43, 130.15, 117.35, 109.83, 105.10, 81.12, 55.34, 52.88, 28.37, 26.59, 19.15, 7.14, 1.85. HRMS (EI): Calcd for $C_{22}H_{36}NO_4Si$ $[M+H]^+$ 406.2408, found 406.2409.

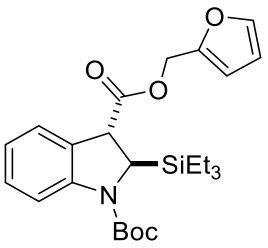


***tert*-Butyl-*trans*-3-acetyl-5-methoxy-2-(triethylsilyl)indoline-1-carboxylate (3va):** colorless oil (28 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (brs, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.75 (s, 1H), 4.42 (s, 1H), 3.76 (d, *J* = 0.8 Hz, 3H), 3.70 (s, 1H), 2.06 (s, 3H), 1.55 (s, 9H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.78, 155.76, 152.38, 136.99, 131.29, 117.60, 113.62, 110.91, 80.91, 56.56, 55.59, 51.98, 28.37, 25.45, 7.17, 1.82. HRMS (EI): Calcd for $C_{22}H_{36}NO_4Si$ $[M+H]^+$ 406.2408, found 406.2409.

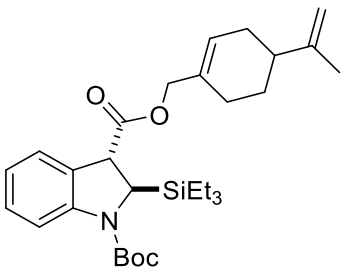


***tert*-Butyl-*trans*-3-acetyl-7-methyl-2-(triethylsilyl)indoline-1-carboxylate (3wa):** colorless oil (42 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.4 Hz, 2H), 6.98 (dd, *J* = 8.3, 6.6 Hz,

1H), 4.56 (d, *J* = 1.5 Hz, 1H), 3.59 (d, *J* = 1.5 Hz, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 1.53 (s, 9H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.47 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.00, 154.22, 142.94, 132.76, 131.09, 129.63, 124.82, 122.06, 80.86, 57.16, 54.63, 28.28, 25.92, 19.81, 7.11, 1.59. HRMS (EI): Calcd for $C_{22}H_{36}NO_3Si$ $[M+H]^+$ 390.2459, found 390.2460.

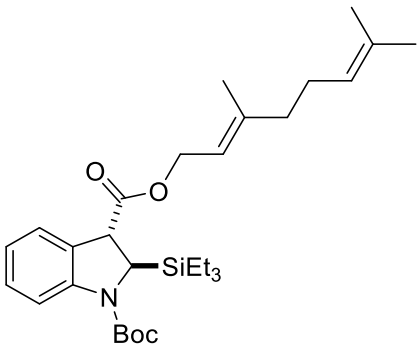


1-(*tert*-Butyl)-3-(furan-2-ylmethyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3xa): colorless oil (53 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (brs, 1H), 7.40 (t, *J* = 1.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.17 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.40 – 6.30 (m, 2H), 5.06 (d, *J* = 3.2 Hz, 2H), 4.58 (d, *J* = 2.8 Hz, 1H), 3.89 (d, *J* = 2.9 Hz, 1H), 1.55 (s, 9H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.68, 152.30, 149.13, 143.18, 142.80, 132.72, 129.17, 128.78, 125.31, 122.57, 116.53, 110.54, 80.97, 58.82, 51.50, 47.51, 28.34, 7.14, 1.88. HRMS (EI): Calcd for $C_{25}H_{36}NO_5Si$ $[M+H]^+$ 458.2357, found458.2359.

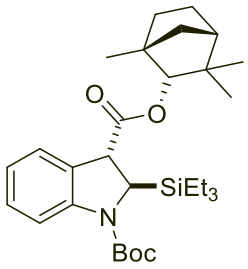


1-(*tert*-Butyl)-3-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3ya): colorless oil (57 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (brs, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.17 (m, 1H), 6.95 (t, *J* = 7.5, 1H), 5.73 – 5.63 (m, 1H), 4.71 (d, *J* = 9.9, 2H), 4.60 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.45 (d, *J* = 3.7 Hz, 2H), 3.87 (d, *J* = 2.7 Hz, 1H), 2.20 – 2.06 (m, 2H), 1.98 (dd, *J* = 7.3, 3.8 Hz, 3H), 1.86 – 1.77 (m, 1H), 1.72 (t, *J* = 1.0 Hz, 3H), 1.57 (s, 9H), 1.51 – 1.38 (m, 1H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz,

6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.97, 152.31, 149.50, 142.84, 132.33, 129.62, 128.74, 125.84, 125.28, 122.52, 116.57, 108.75, 80.94, 69.22, 51.68, 47.86, 40.73, 30.39, 28.40, 27.20, 26.18, 20.70, 7.19, 1.94. HRMS (EI): Calcd for $C_{30}H_{46}NO_4Si$ $[M+H]^+$ 512.3191, found 512.3193.

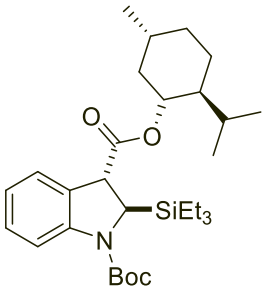


1-(*tert*-Butyl)-3-((*E*)-3,7-dimethylocta-2,6-dien-1-yl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3za): colorless oil (42 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (brs, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.30 (t, *J* = 7.1 Hz, 1H), 5.07 (t, *J* = 6.6 Hz, 1H), 4.70 – 4.50 (m, 3H), 3.86 (d, J = 3.0 Hz, 1H), 2.04 (dd, *J* = 12.2, 6.3 Hz, 4H), 1.71 – 1.58 (m, 9H), 1.57 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.12, 152.34, 142.62, 131.80, 129.62, 128.68, 125.30, 123.69, 122.52, 118.89, 117.96, 116.53, 80.94, 62.17, 51.58, 47.70, 39.46, 28.40, 26.28, 25.66, 17.66, 16.48, 7.21, 1.93. HRMS (EI): Calcd for $C_{30}H_{48}NO_4Si$ $[M+H]^+$ 514.3347, found 514.3348.

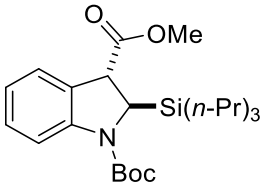


1-(*tert*-Butyl)-3-((1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3A): colorless oil (32 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (brs, 1H), 7.29 – 7.23 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 4.58 (s, 1H), 4.29 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.86 (t, *J* = 2.4 Hz, 1H), 1.75 – 1.60 (m, 3H), 1.56 (s,

9H), 1.53 – 1.47 (m, 1H), 1.42 – 1.33 (m, 1H), 1.25 (s, 1H), 1.18 – 0.95 (m, 7H), 0.88 (t, J = 7.9 Hz, 9H), 0.80 (s, 1H), 0.71 (s, 1H), 0.57 (q, J = 7.6 Hz, 6H), 0.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.79, 152.08, 142.96, 129.82, 128.69, 125.19, 122.47, 116.42, 86.76, 80.92, 52.16, 48.28, 41.23, 39.52, 29.54, 28.39, 26.46, 25.71, 20.11, 19.65, 19.39, 19.00, 7.18, 1.92. HRMS (EI): Calcd for $C_{30}H_{48}NO_4Si$ $[M+H]^+$ 514.3347, found 514.3348.

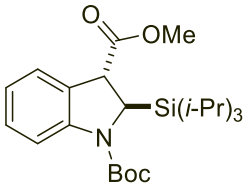


1-(*tert*-Butyl)-3-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (3B): colorless oil (64 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (brs, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 4.62 (td, J = 10.9, 4.3 Hz, 1H), 4.55 (dd, J = 9.5, 2.6 Hz, 1H), 3.83 (d, J = 2.9 Hz, 1H), 1.90 (dd, J = 12.1, 4.7 Hz, 1H), 1.63 (td, J = 10.9, 3.3 Hz, 3H), 1.56 (s, 9H), 1.10 – 0.92 (m, 3H), 0.87 (t, J = 7.6 Hz, 12H), 0.84 (s, 3H), 0.79 (d, J = 7.0 Hz, 2H), 0.59 (dq, J = 27.1, 8.0, 7.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.78, 152.32, 142.92, 129.83, 128.59, 124.79, 122.48, 116.56, 80.80, 74.92, 51.82, 48.13, 47.14, 40.58, 34.18, 31.29, 28.39, 26.12, 23.37, 21.92, 20.60, 16.15, 7.17, 1.89. HRMS (EI): Calcd for $C_{30}H_{50}NO_4Si$ $[M+H]^+$ 516.3504, found 516.3505.

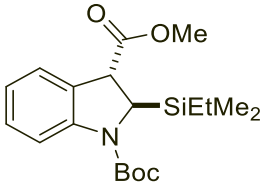


1-(*tert*-Butyl)-3-methyl-*trans*-2-(tripropylsilyl)indoline-1,3-dicarboxylate (3ab): colorless oil (69 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (brs, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 4.56 (d, J = 2.5 Hz, 1H), 3.85 (d, J = 2.6 Hz, 1H), 3.68 (s,

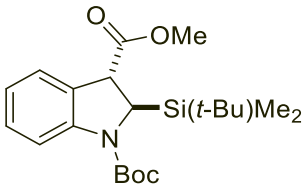
3H), 1.57 (s, 9H), 1.30 – 1.16 (m, 6H), 0.87 (t, J = 7.2 Hz, 9H), 0.69 – 0.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.62, 152.36, 142.80, 129.56, 128.73, 125.28, 122.59, 116.61, 80.94, 52.43, 52.17, 47.61, 28.38, 18.54, 17.20, 13.66. HRMS (EI): Calcd for $C_{24}H_{40}NO_4Si$ $[M+H]^+$ 434.2721, found 434.2723.



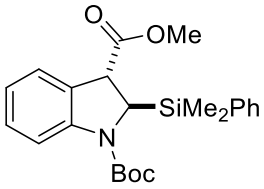
1-(*tert*-Butyl)-3-methyl-*trans*-2-(triisopropylsilyl)indoline-1,3-dicarboxylate (3ac): colorless oil (37 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (brs, 1H), 7.30 (d, J = 7.5 Hz, 1H), 7.25 – 7.21 (t, J = 7.8, 1H), 6.96 (t, J = 7.5, 1H), 4.88 (d, J = 2.4 Hz, 1H), 3.92 (d, J = 2.4 Hz, 1H), 3.68 (s, 3H), 1.55 (s, 9H), 1.24 – 1.14 (m, 3H), 0.99 (dd, J = 11.2, 7.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.60, 152.62, 143.20, 130.38, 128.67, 125.31, 122.82, 117.61, 81.05, 52.45, 51.30, 48.20, 28.38, 18.50, 18.44, 11.01. HRMS (EI): Calcd for $C_{24}H_{40}NO_4Si$ $[M+H]^+$ 434.2721, found 434.2720.



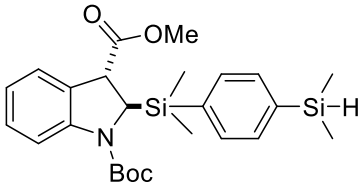
1-(*tert*-Butyl)-3-methyl-*trans*-2-(ethyldimethylsilyl)indoline-1,3-dicarboxylate (3ad): colorless oil (44 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.60 (brs, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.95 (td, J = 7.5, 1.1 Hz, 1H), 4.48 (d, J = 2.9 Hz, 1H), 3.85 (d, J = 3.0 Hz, 1H), 3.69 (s, 3H), 1.57 (s, 9H), 0.88 (t, J = 7.9 Hz, 3H), 0.51 (q, J = 7.9 Hz, 2H), -0.00 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.62, 152.40, 142.69, 129.26, 128.79, 125.31, 122.54, 116.33, 81.02, 52.59, 52.49, 47.44, 28.40, 7.10, 5.05, -5.38. HRMS (EI): Calcd for $C_{19}H_{30}NO_4Si$ $[M+H]^+$ 364.1939, found 364.1941.



1-(*tert*-Butyl)-3-methyl-*trans*-2-(tert-butyldimethylsilyl)indoline-1,3-dicarboxylate (3ae): colorless oil (57 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (brs, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 4.65 (d, J = 2.3 Hz, 1H), 3.89 (d, *J* = 2.3 Hz, 1H), 3.69 (s, 3H), 1.56 (s, 9H), 0.94 (s, 9H), 0.01 (s, 3H), -0.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53, 152.47, 142.84, 129.69, 128.76, 125.33, 122.68, 116.62, 80.96, 52.50, 51.02, 48.64, 28.40, 26.72, 16.98, -7.06, -7.39. HRMS (EI): Calcd for $C_{21}H_{34}NO_4Si$ $[M+H]^+$ 392.2252, found 392.2254.



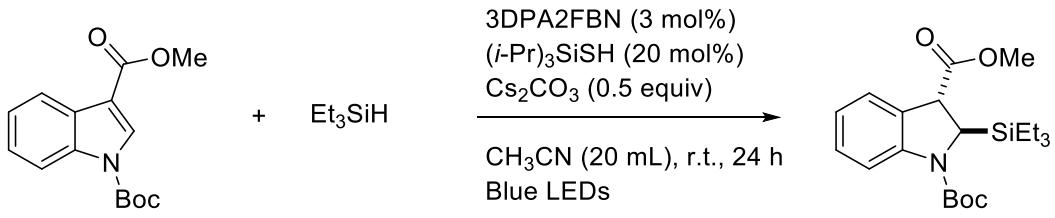
1-(*tert*-Butyl)-3-methyl-*trans*-2-(dimethyl(phenyl)silyl)indoline-1,3-dicarboxylate (3af): colorless oil (58 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (brs, 1H), 7.51 – 7.42 (m, 2H), 7.34 (ddd, *J* = 13.8, 7.5, 5.8 Hz, 3H), 7.26 –7.12 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 4.71 (d, *J* = 3.1 Hz, 1H), 3.80 (d, *J* = 3.2 Hz, 1H), 3.65 (s, 3H), 1.56 (s, 9H), 0.42 (s, 3H), 0.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.29, 152.33, 142.53, 135.72, 133.87, 129.38, 129.07, 128.69, 127.75, 125.24, 122.49, 116.13, 81.00, 52.63, 52.34, 47.67, 28.28, -3.61, -5.50. HRMS (EI): Calcd for $C_{23}H_{30}NO_4Si$ $[M+H]^+$ 412.1939, found 412.1941.



1-(*tert*-Butyl)-3-methyl-*trans*-2-((4-(dimethylsilyl)phenyl)dimethylsilyl)indoline-1,3-dicarboxylate (3ag): colorless oil (68 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.56

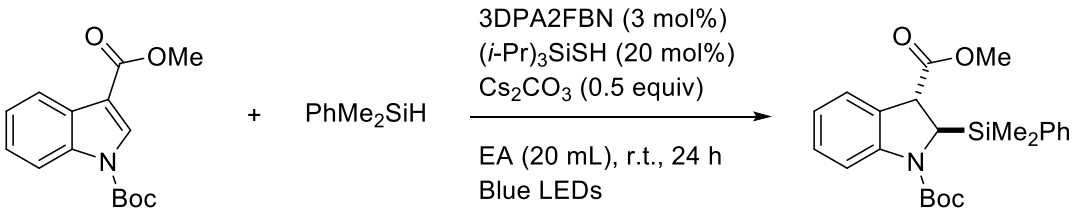
– 7.49 (m, 2H), 7.50 – 7.42 (m, 2H), 7.29 – 7.19 (m, 2H), 6.96 (td, J = 7.5, 1.1 Hz, 1H), 4.72 (dd, J = 3.2, 1.2 Hz, 1H), 4.46 (tt, J = 7.5, 3.7 Hz, 1H), 3.82 (d, J = 3.1 Hz, 1H), 3.68 (s, 3H), 1.56 (s, 9H), 0.50 – 0.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.35, 152.36, 142.59, 140.71, 138.81, 136.79, 133.26, 132.30, 128.75, 125.30, 122.55, 116.19, 81.05, 52.43, 47.72, 28.29, 0.87, -3.94, -5.58. HRMS (EI): Calcd for $C_{25}H_{36}NO_4Si_2$ $[M+H]^+$ 470.2177, found 470.2178.

6. Gram-scale Preparation of 3aa and 3af



1a, 2 mmol **2a**, 1.5 equiv **3aa**, 68%

In a 100 mL Schlenk tube with a magnetic stir bar were placed 3DPA2FBN (**PC**, 40 mg, 0.06 mmol, 3 mol%), Cs_2CO_3 (320 mg, 1 mmol, 0.5 equiv), and Et_3SiH (**2a**, 480 μL, 3 mmol, 1.5 equiv). Under nitrogen atmosphere, 1-(*tert*-butyl) 3-methyl 1*H*-indole-1,3-dicarboxylate (**1a**, 552 mg, 2 mmol, 1 equiv), (*i*-Pr)$_3$SiSH (80 μL, 0.4 mmol, 20 mol%), CH_3CN (20 mL) were added, subsequently. The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction was placed under a blue LED (2-meter strips, 20 W) and irradiated for 24 hrs at room temperature. The solvent was removed under vacuum. Silica gel chromatography (eluent: PE) of the crude product afforded 1-(*tert*-butyl)-3-methyl-*trans*-2-(triethylsilyl)indoline-1,3-dicarboxylate (**3aa**, 0.54 g) as a colorless oil.

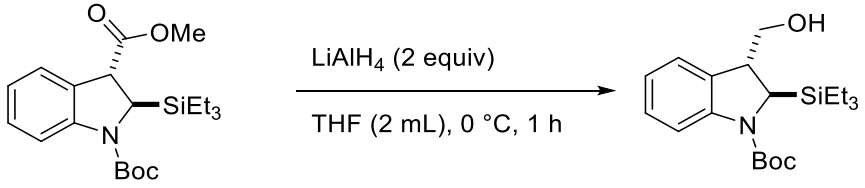


1a, 2 mmol **2e**, 1.5 equiv **3af**, 60%

In a 100 mL Schlenk tube with a magnetic stir bar were placed 3DPA2FBN (**PC**, 40 mg, 0.06 mmol, 3 mol%), Cs_2CO_3 (320 mg, 1 mmol, 0.5 equiv), and $PhMe_2SiH$ (**2f**, 480 μL, 1.5 mmol, 1.5 equiv). Under nitrogen atmosphere, 1-(*tert*-butyl) 3-methyl 1*H*-indole-1,3-dicarboxylate (**1a**, 552

mg, 2 mmol, 1 equiv), (*i*-Pr)$_3$SiSH (80 μL, 0.4 mmol, 20 mol%), EtOAc (20 mL) were added, subsequently. The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction was placed under a blue LED (2-meter strips, 20 W) and irradiated for 24 hrs at room temperature. The solvent was removed under vacuum. Silica gel chromatography (eluent: PE) of the crude product afforded 1-(*tert*-butyl)-3-methyl-*trans*-2-(dimethyl(phenyl)silyl)indoline-1,3-dicarboxylate (**3af**, 0.48 g) as a colorless oil.

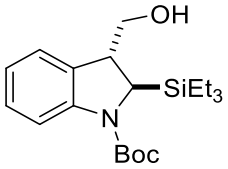
7. Transformations of the Products



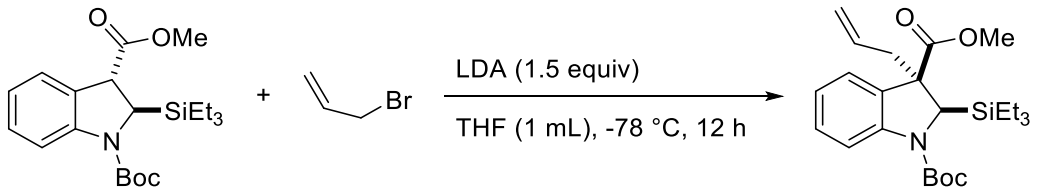
3aa, 0.2 mmol

4, 96%

According to literature report[2], **3aa** (78.3 mg, 0.2 mmol) was added portionwise at 0 ℃ to 0.4 mL (0.4 mmol) of a 1 M $LiAlH_4$ solution (in THF). Then, the reaction mixture was continued to stir at 0 ℃ for 1 hour. The crude product was purified by column chromatography (PE/EA = 3:1) on silica gel to afford colorless oil (70 mg, 96% yield).

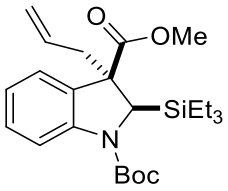


***tert*-Butyl-*trans*-3-(hydroxymethyl)-2-(triethylsilyl)indoline-1-carboxylate (4)**: colorless oil (69 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.16 (d, J = 7.4 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 4.03 (s, 1H), 3.56 (d, J = 6.8 Hz, 2H), 3.17 (td, J = 6.9, 1.8 Hz, 1H), 1.55 (s, 9H), 0.86 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.63, 142.43, 133.34, 128.08, 124.76, 122.43, 116.36, 80.85, 66.28, 52.10, 45.19, 28.36, 7.17, 1.93. HRMS (EI): Calcd for $C_{20}H_{34}NO_3Si$ $[M+H]^+$ 364.2302, found 364.2303.



3aa, 0.2 mmol 1.5 equiv **5**, 60%

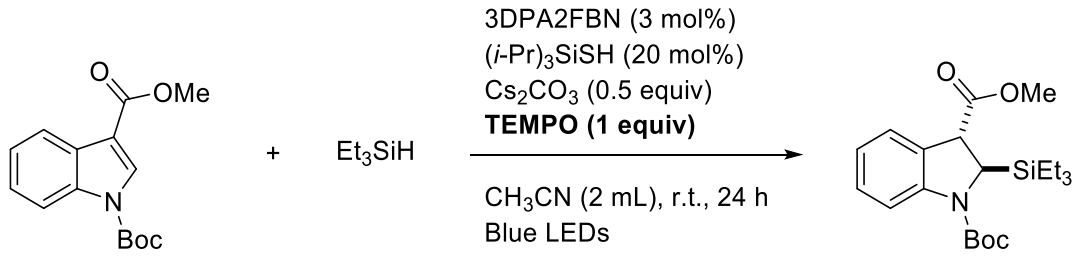
According to literature report[3], to a flame-dried 20 mL flask charged with **3aa** (78 mg, 0.2 mmol) and THF (1 mL) was added LDA (0.15 mL, 2 M in heptane/ethylbenzene, 0.3 mmol, 1.5 equiv) at −78 °C dropwise. The resulting mixture was allowed at the same temperature for 30 min. The allyl bromide (26 μL, 0.3 mmol, 1.5 equiv) was then added slowly at −78 °C. The reaction mixuture was then allowed to warm to room temerature and continued to stir at the same temperature for 12 h. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (30:1) as the eluent to afford **5** as a colorless oil (52 mg, 60% yield).



1-(*tert*-Butyl)-3-methyl-*trans*-3-allyl-2-(triethylsilyl)indoline-1,3-dicarboxylate (5): colorless oil (51 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.63 (brs, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.53 (ddt, *J* = 17.3, 10.1, 7.4 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 4.97 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.24 (s, 1H), 3.77 (s, 3H), 2.55 (s, 1H), 2.47 (dd, *J* = 13.1, 6.9 Hz, 1H), 1.56 (s, 9H), 0.79 (t, *J* = 7.9 Hz, 9H), 0.46 (t, *J* = 7.9, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.77, 152.46, 141.63, 133.95, 132.54, 128.03, 125.48, 122.71, 119.00, 116.92, 80.95, 58.04, 57.35, 51.67, 46.04, 28.45, 7.24, 2.87. HRMS (EI): Calcd for $C_{24}H_{38}NO_4Si$ $[M+H]^+$ 432.2565, found 432.2566.

8. Additional Control Experiments to Elucidate the Mechanism

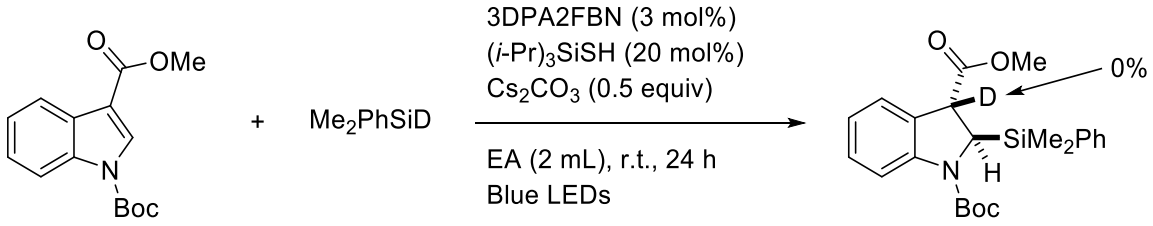
8.1 Radical Inhibition Experiments



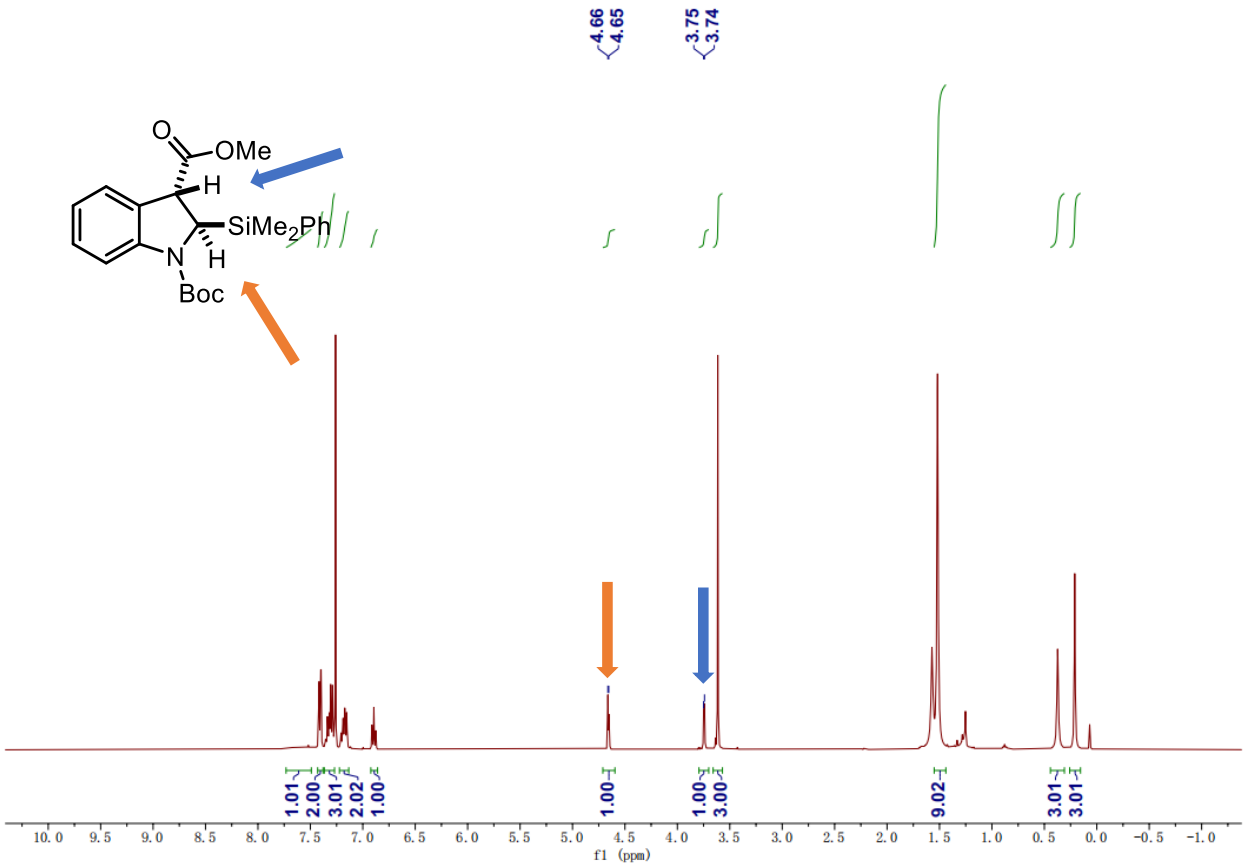
1a, 0.1 mmol **2a**, 1.5 equiv **3aa**, 0%

The radical initiator, TEMPO, can totally inhibit the formation of product, **3aa**, thus supporting a radical-based mechanism.

8.2 Deuterium-Labeling Experiments



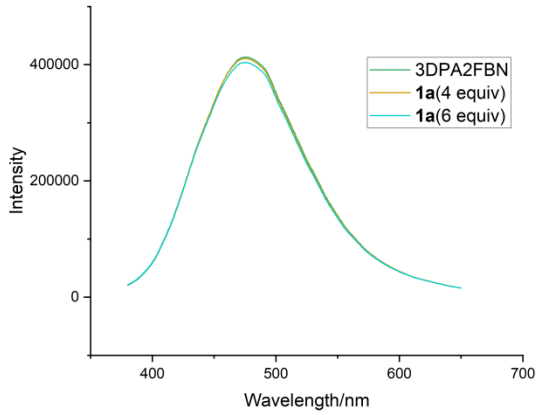
1a, 0.1 mmol **2f-D**, 1.5 equiv **3af-D**, 26%

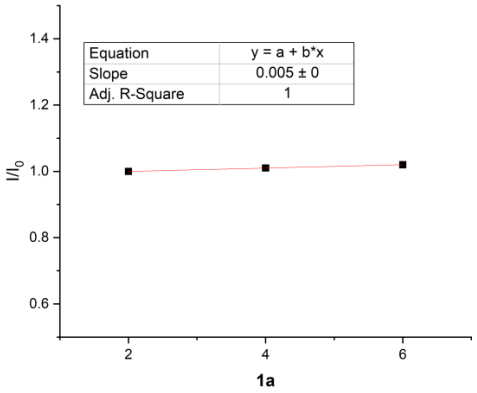


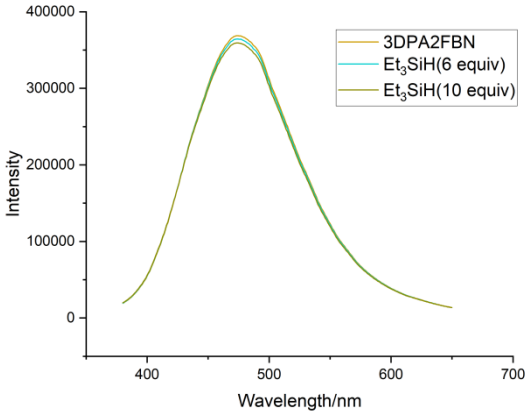
2f-D (20.6 mg, 0.15 mmol) was used to perform dearomatization under the standard conditions. The product (**3af-D**) was analyzed by ^{1}H NMR to determine the ratio of H-D exchange. It was found that 0% of the hydrogen at the C3 position was deuterated, which proved that it generated the carbon anion at the C3 position.

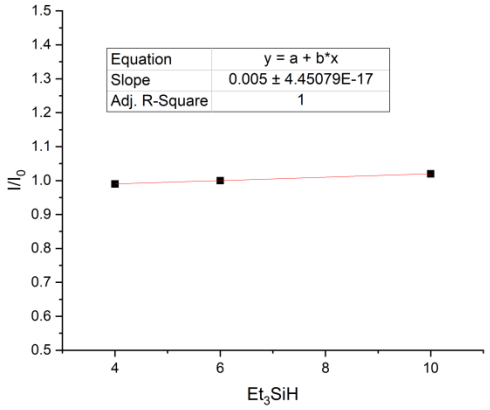
8.3 Stern-Volmer Fluorescence Quenching Experiments

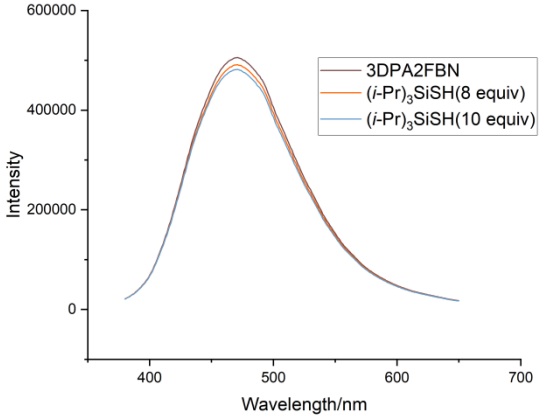
In a typical experiment, a solution of 3DPA2FBN in anhydrous reaction solvent (CH_3CN) (5.0×10^{-6} M) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity was collected with the excited wavelength of photocatalysts, respectively.

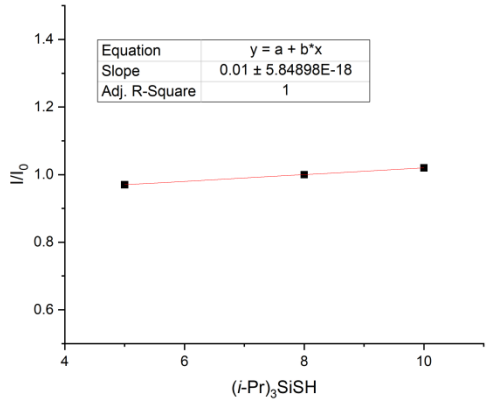

3DPA2FBN
1a(4 equiv)
1a(6 equiv)
Intensity
Wavelength/nm

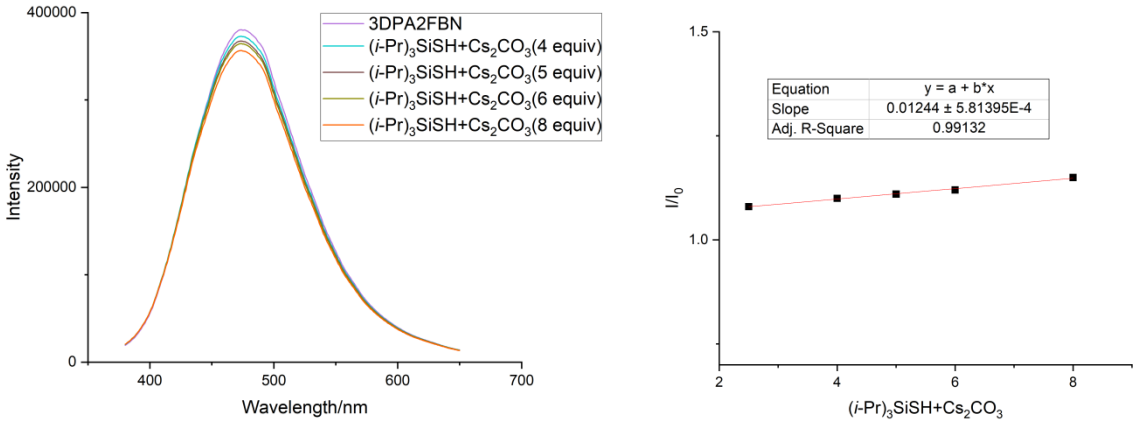

Equation y = a + b*x
Slope 0.005 ± 0
Adj. R-Square 1
I/I0
1a


3DPA2FBN
Et3SiH(6 equiv)
Et3SiH(10 equiv)
Intensity
Wavelength/nm


Equation y = a + b*x
Slope 0.005 ± 4.45079E-17
Adj. R-Square 1
I/I0
Et3SiH


3DPA2FBN
(i-Pr)3SiSH(8 equiv)
(i-Pr)3SiSH(10 equiv)
Intensity
Wavelength/nm


Equation y = a + b*x
Slope 0.01 ± 5.84898E-18
Adj. R-Square 1
I/I0
(i-Pr)3SiSH



8.4 Quantum Yield Measurement

Determination of the light intensity at 470 nm: Following Yoon's protocol,[4] the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 470$ nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq (1).

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{1 \cdot \varepsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq (2).

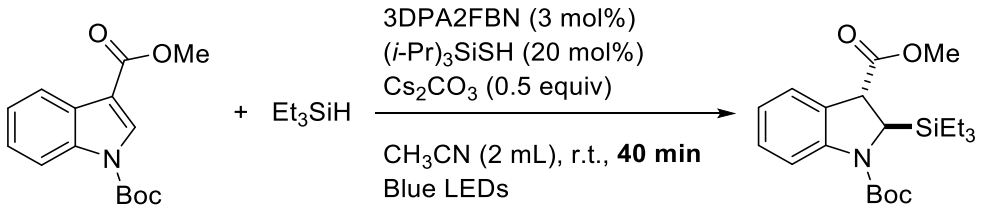
$$Photon\ flux = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ = 468 nm),[5] t is the time (90.0 s), and f is the fraction of light absorbed at λ = 470 nm (0.14, vide infra). The photon flux was calculated (average of three experiments) to be 3.22×10^{-8} einstein s^{-1}.

$$\text{mol } Fe^{2+} = \frac{0.00235\ \text{L} \cdot\ 1.76}{1.000\ \text{cm} \cdot 11100\ \text{L mol}^{-1}\text{cm}^{-1}} = 3.73\ \times\ 10^{-7}\ \text{mol}$$

$$Photon\ flux = \frac{3.73\ \times\ 10^{-7}\ \text{mol}}{0.92 \cdot 90.0\ \text{s} \cdot 0.14} = 3.22\ \times\ 10^{-8}\ \text{mol}$$

Determination of quantum yield:



1a, 0.1 mmol **2a**, 1.5 equiv **3aa**, 50%

A cuvette was charged with **1a** (27.6 mg, 0.1 mmol), **2a** (24 μL, 0.15mmol), 3DPA2FBN (2 mg, 0.03 mmol, 3 mol%), Cs_2CO_3 (16 mg, 0.05 mmol, 0.5 equiv), (*i*-Pr)$_3$SiSH (4 μL, 0.02 mmol, 20 mol%), and CH_3CN (2 mL). The cuvette was then capped with a PTFE stopper. The sample was stirred and irradiated (λ = 470 nm, slit width = 10.0 nm) for 2400 s (40 min). After irradiation, the solvent was removed. The yield of product formed was determined as 50% by crude ^{1}H NMR using a dibromomethane as the internal standard. The quantum yield was determined using eq (3). Essentially all incident light (f > 0.999, vide infra) is absorbed by the 3DPA2FBN at the reaction conditions described above. Φ (50%) = 0.65.

$$\Phi = \frac{mol\ product}{flux \cdot \text{t} \cdot \text{f}} \quad (3)$$

$$\Phi = \frac{0.5 \times 0.1 \times 10^{-3} mol}{3.22\ \times\ 10^{-8}\ \text{mol} \cdot 2400\ \text{s} \cdot 1.00} = 0.65$$

References

1. (a) Zhang, Q., Xu, W., Liu, Q., Xia, C., Shao, Q., Ma, L. and Wu, M., Diastereoselective dearomatization of indoles via photocatalytic hydroboration on hydramine-functionalized carbon nitride, *Nat. Commun.*, 2024, **15**, 4371; (b) Chen, L., Shen, J. J., Gao, Q. and Xu, S., Synthesis of cyclic chiral *α*-amino boronates by copper-catalyzed asymmetric dearomative borylation of indoles, *Chem. Sci.*, 2018, **9**, 5855; (c) Zhang, Y., Ji, P., Gao, F., Dong, Y., Huang, H., Wang, C., Zhou, Z. and Wang, W., Organophotocatalytic dearomatization of indoles, pyrroles and benzo(thio)furans via a giese-type transformation, *Commun. Chem.*, 2021, **4**, 20.
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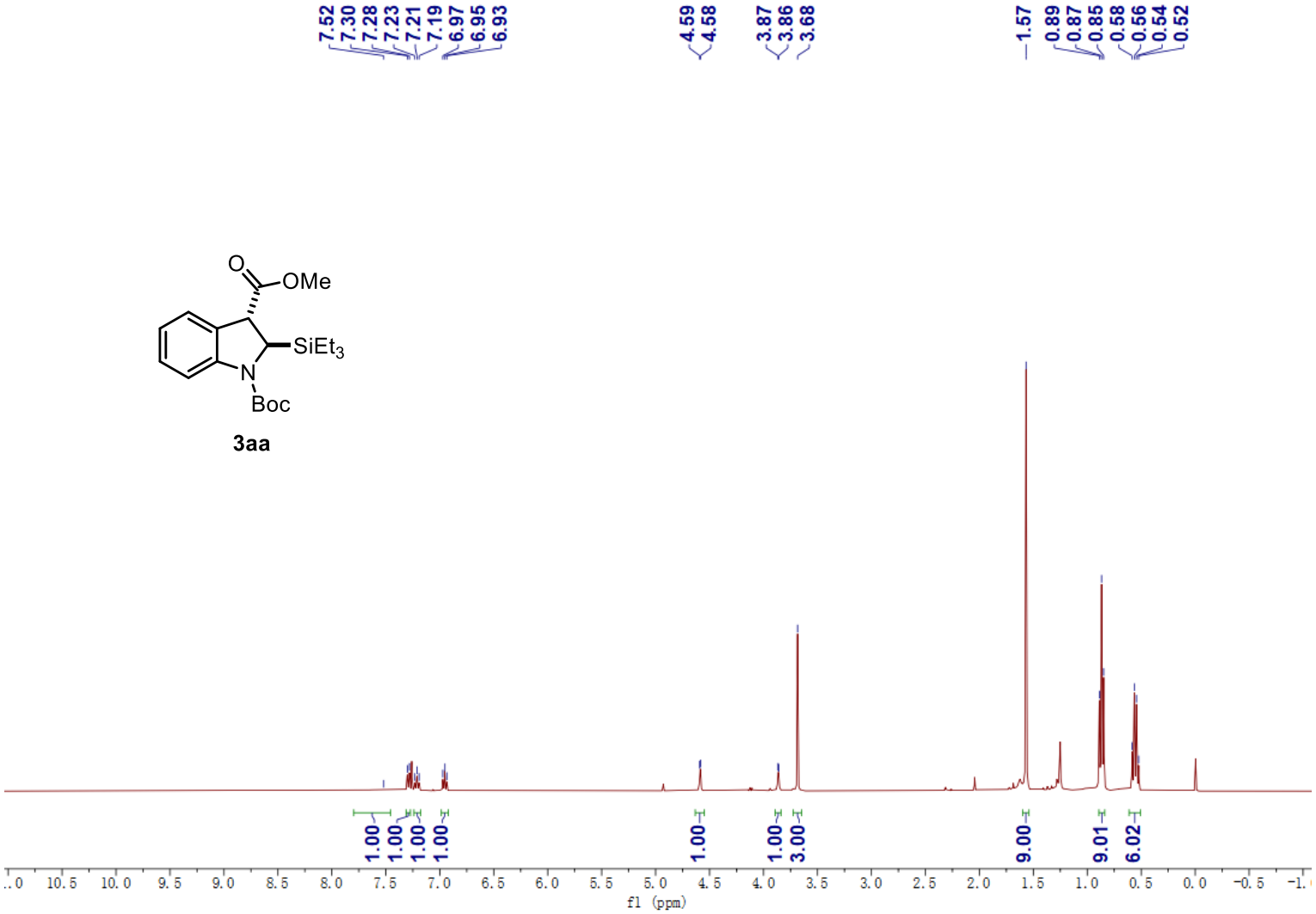
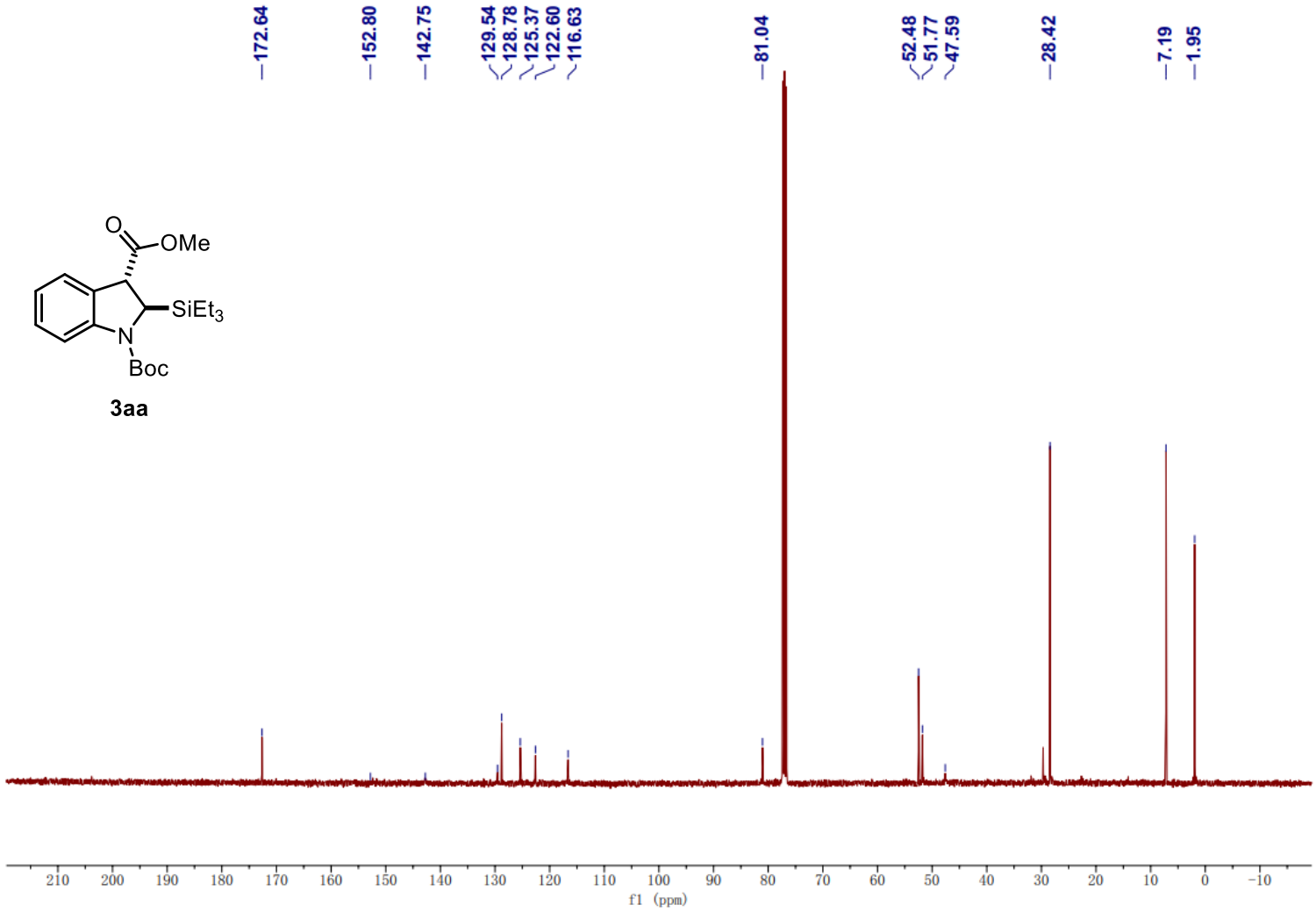
3. Shi, Y., Gao, Q. and Xu, S., NHC-copper-catalyzed asymmetric dearomative silylation of indoles, *J. Org. Chem.*, 2018, **83**, 14758.
4. Cismesia, M. A. and Yoon, T. P., Characterizing chain processes in visible light photoredox catalysis, *Chem. Sci.*, 2015, **6**, 5426.
5. Hatchard C. G. and Parker C. A., A new sensitive chemical actinometer- II potassium ferrioxalate as a standard chemical actinometer, *P. Roy. Soc. A-Math. Phy.*, 1956, **235**, 518.

^{1}H, ^{19}F, ^{13}C-NMR Spectra

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N
Boc
3aa
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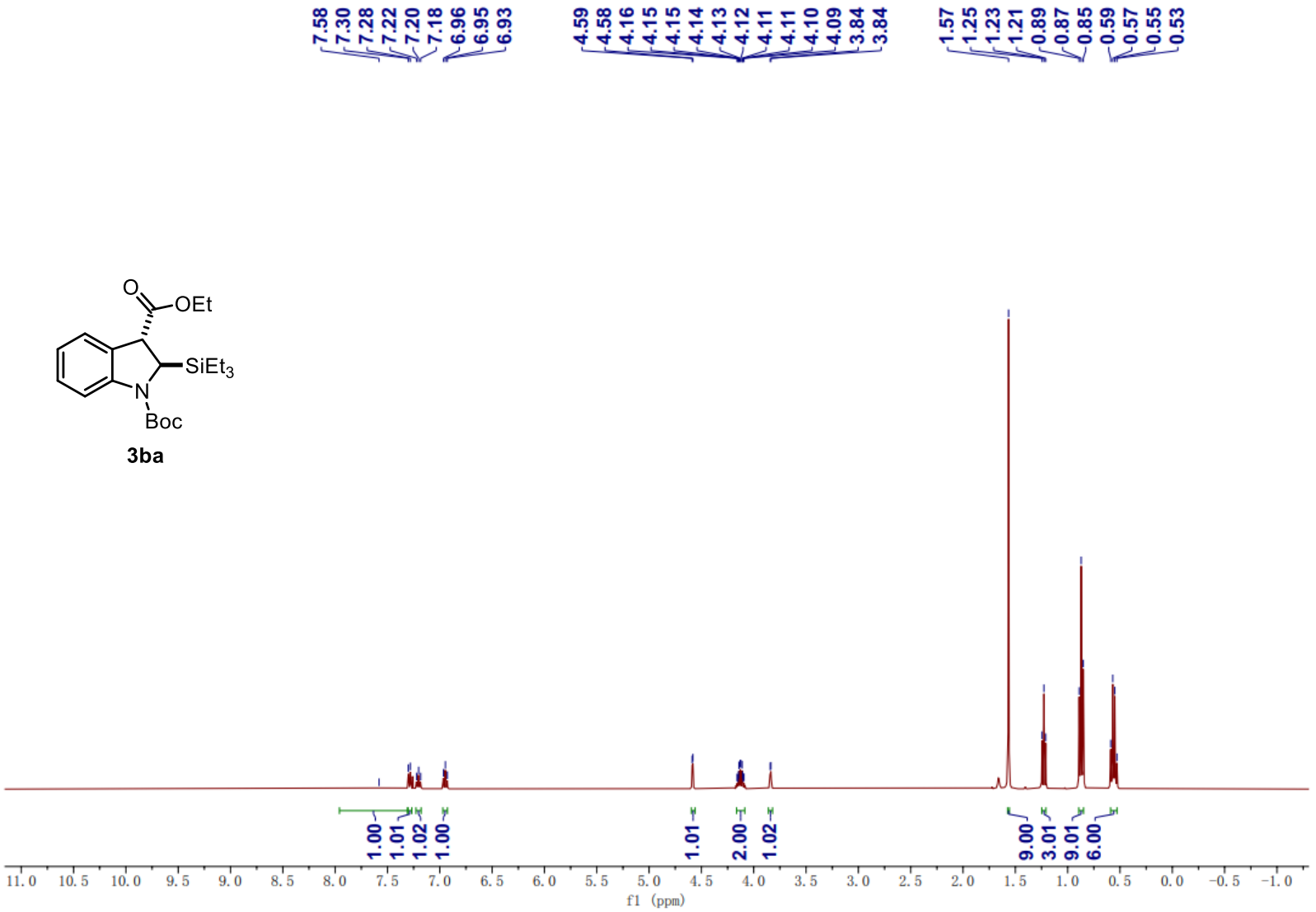
f1 (ppm)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N
Boc
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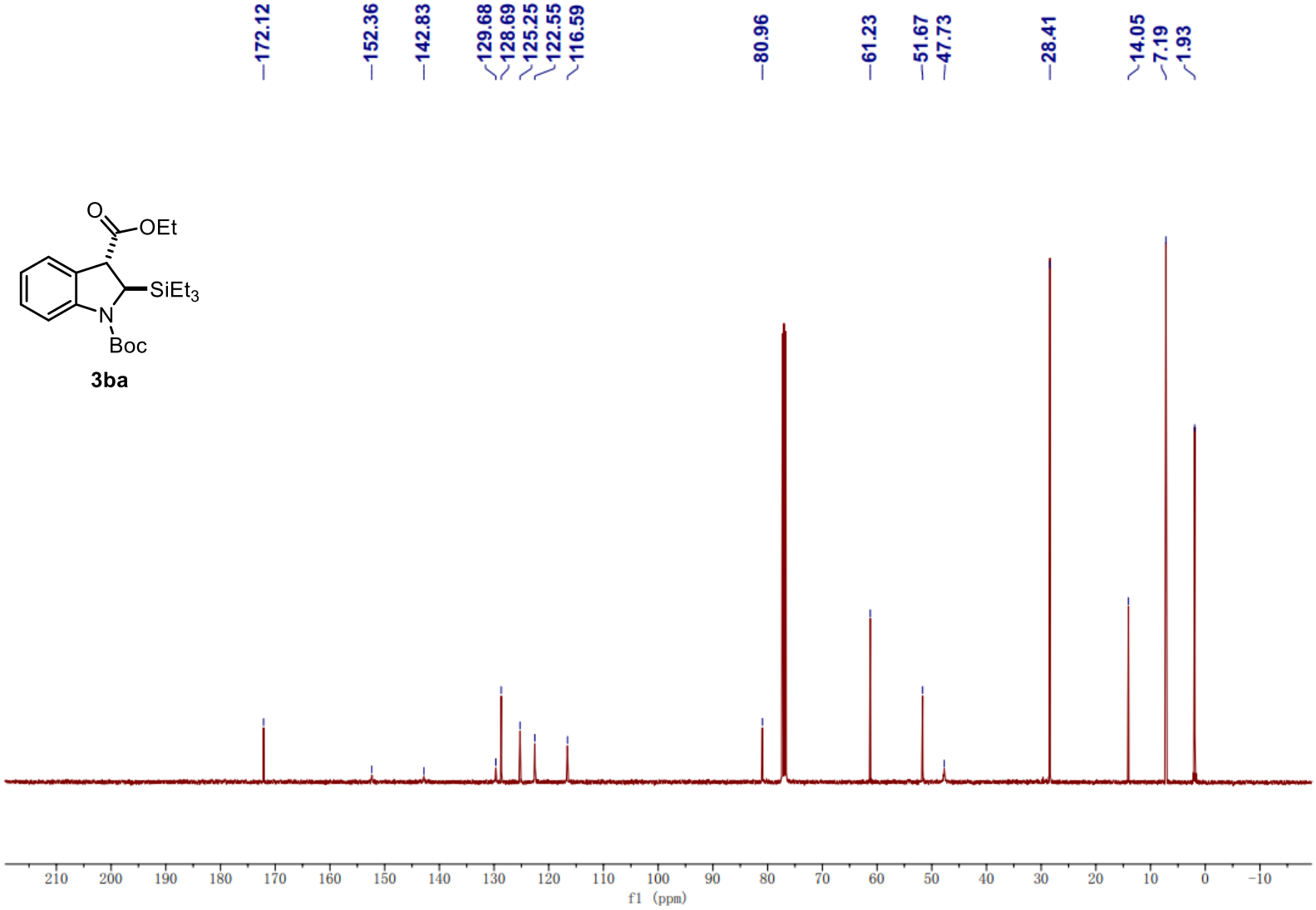
3ba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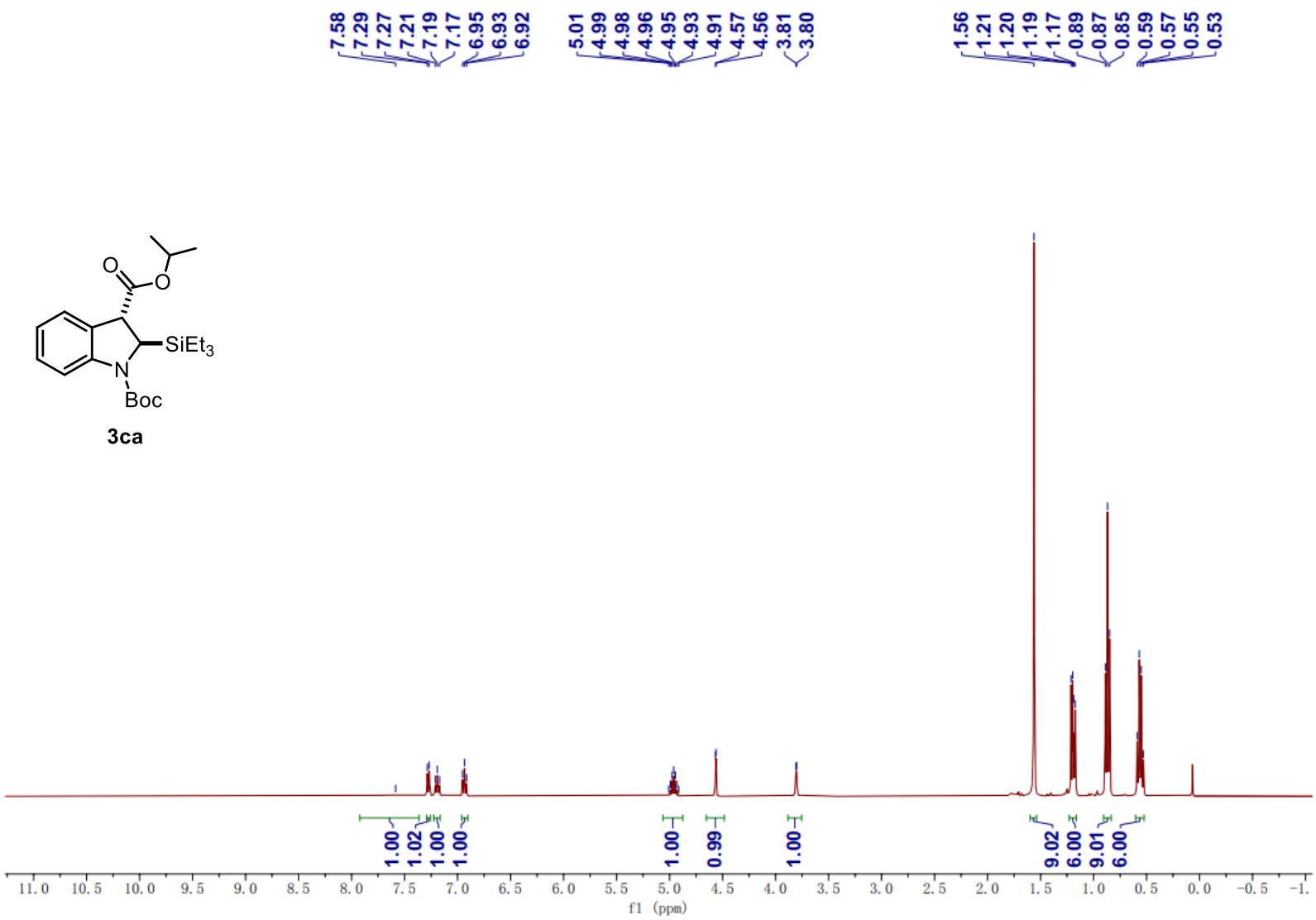
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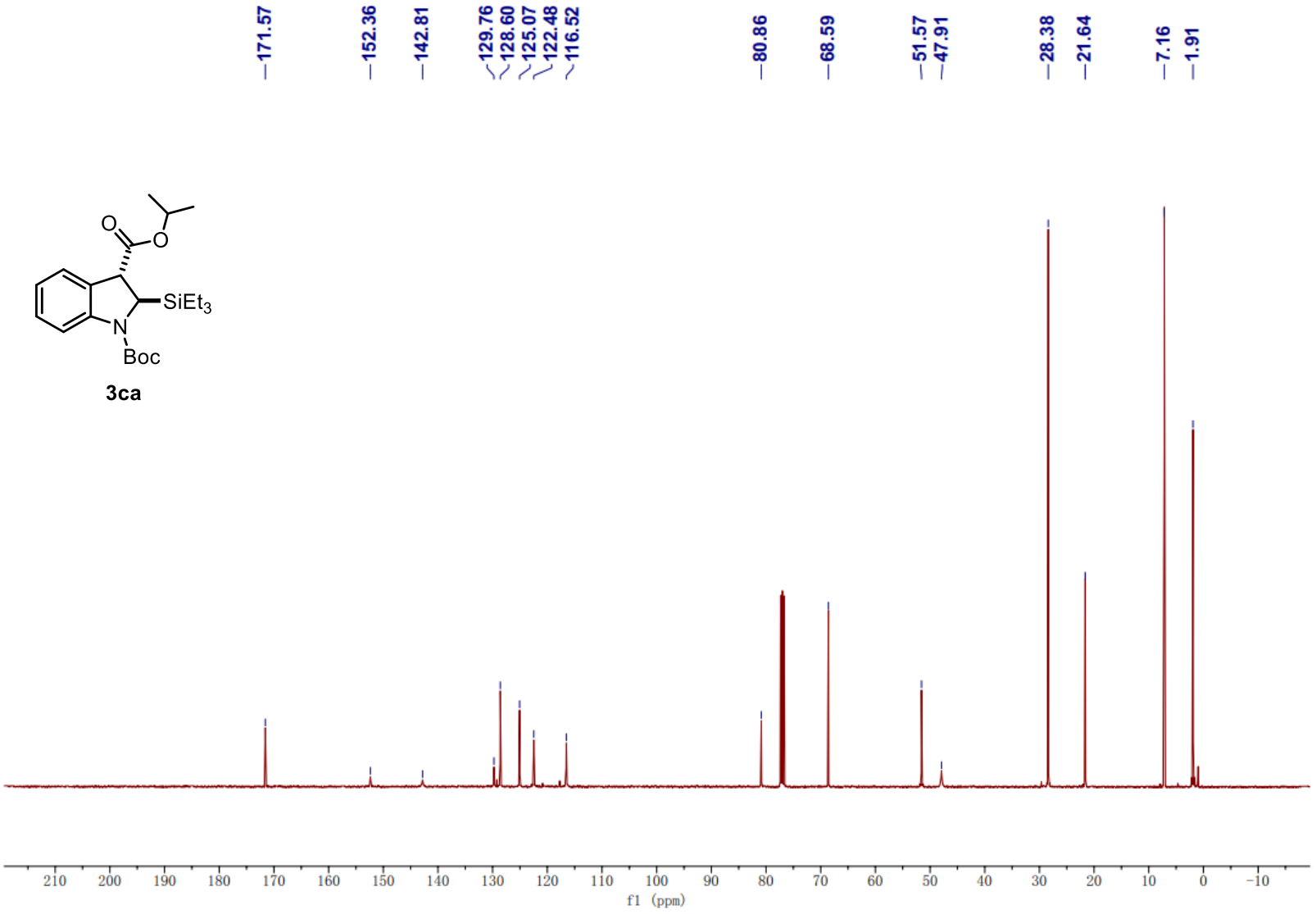
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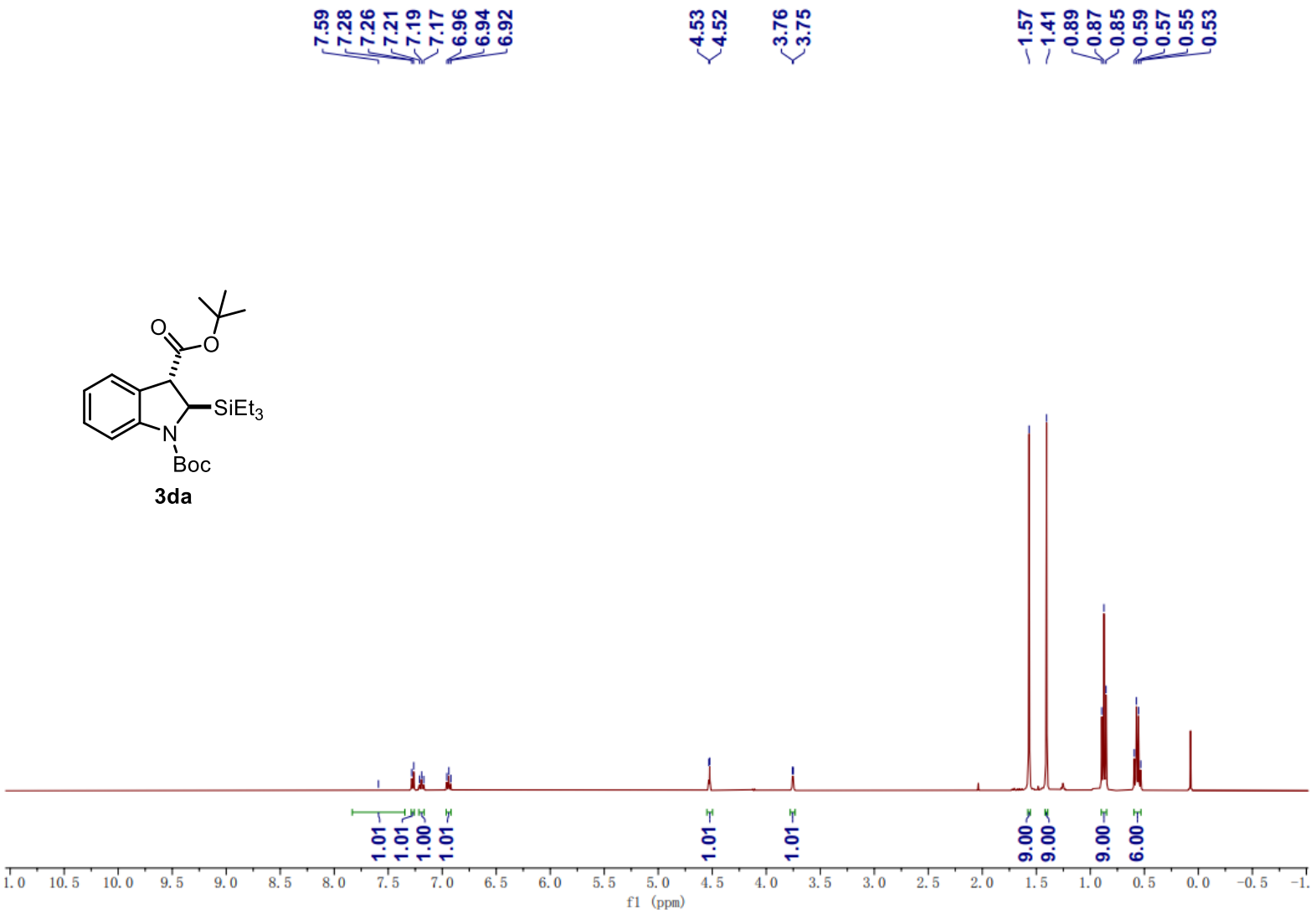
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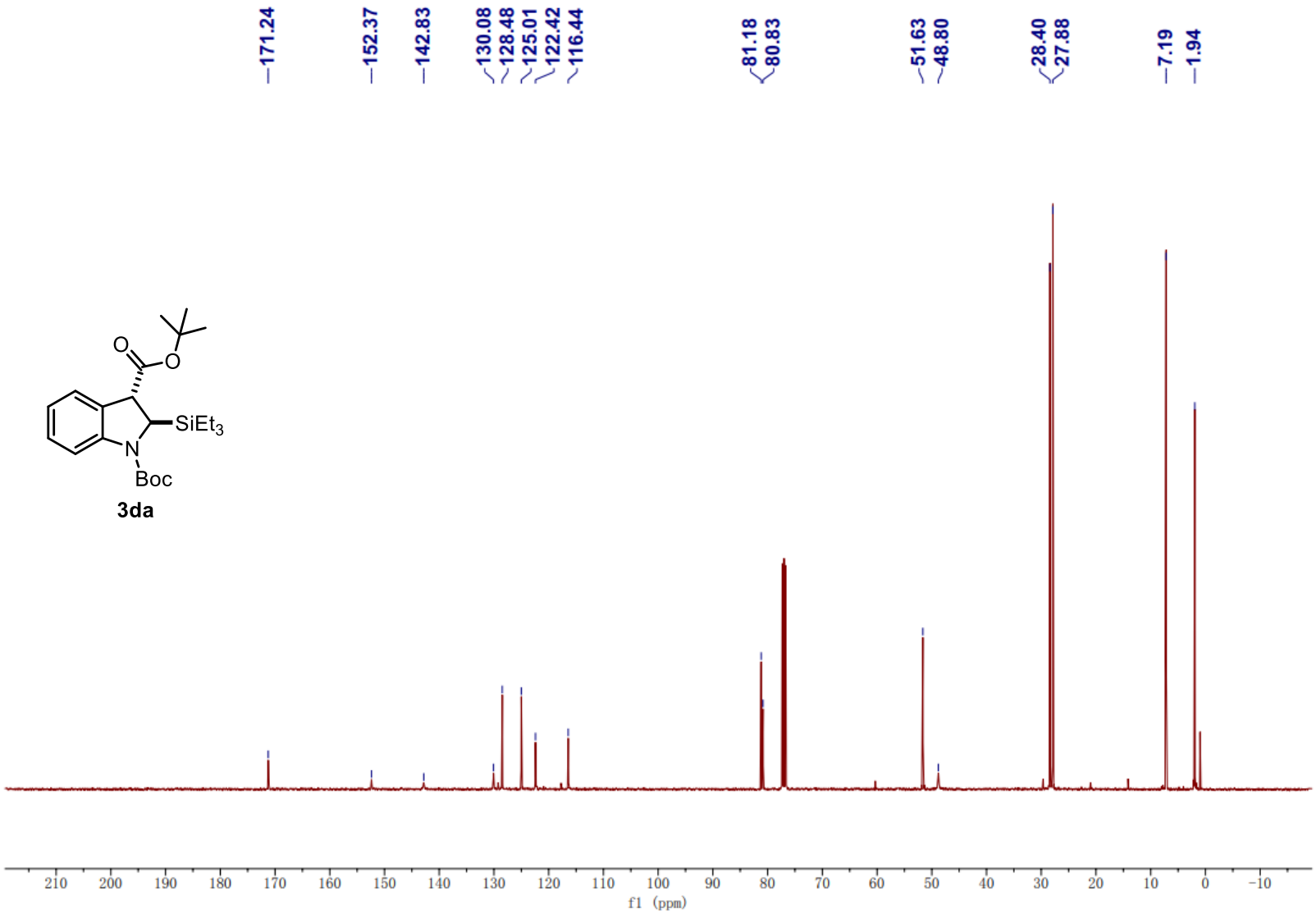
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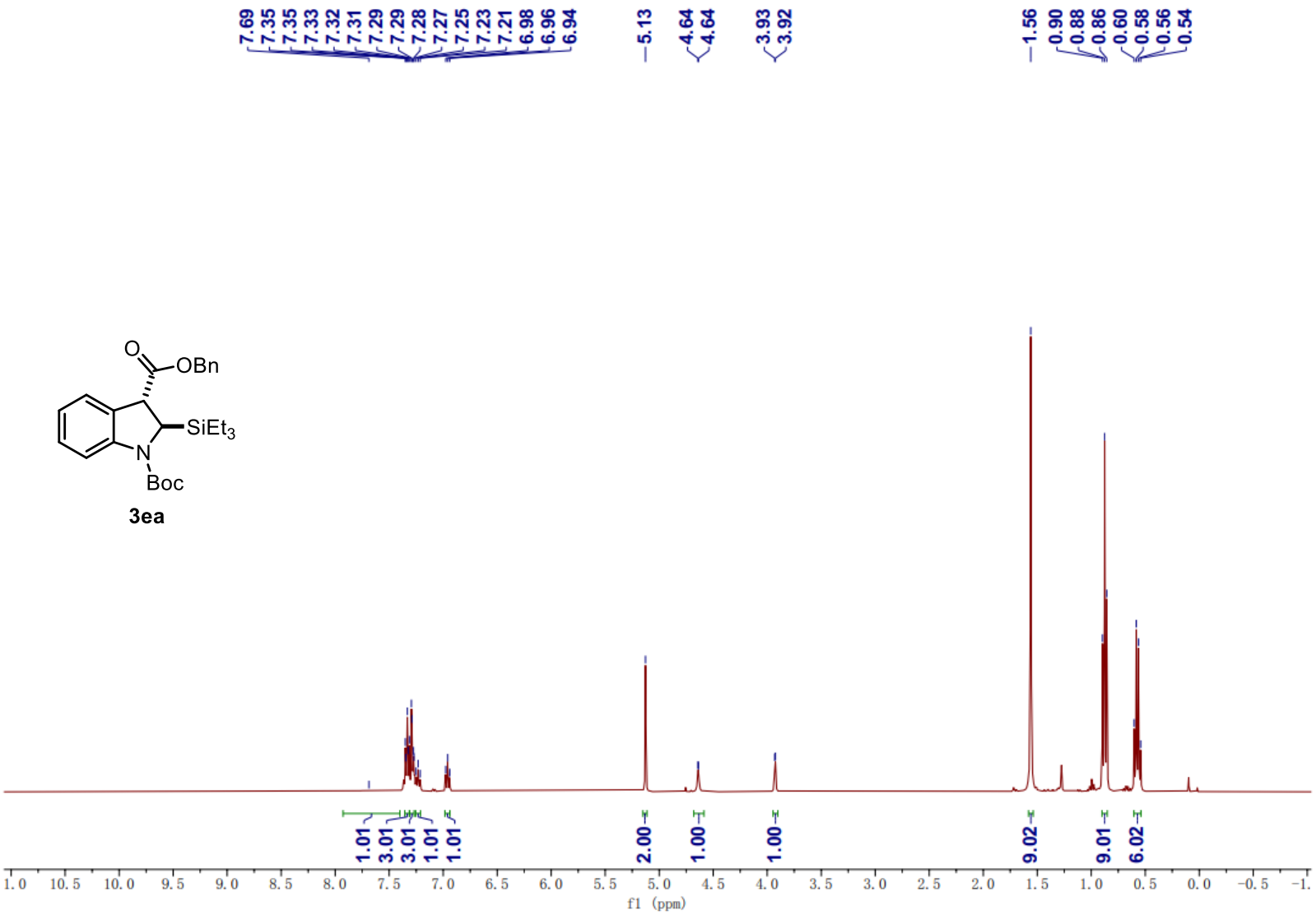
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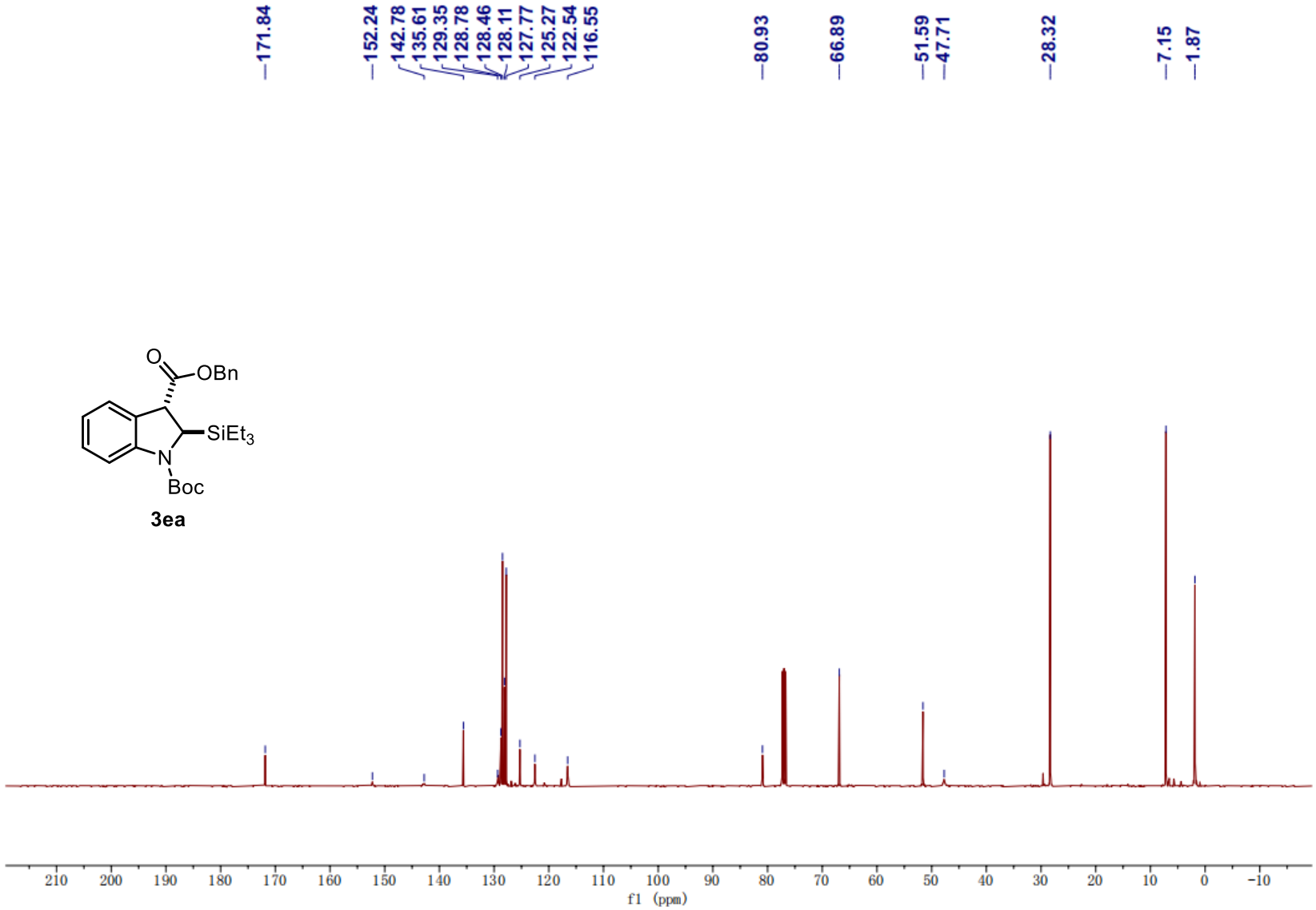
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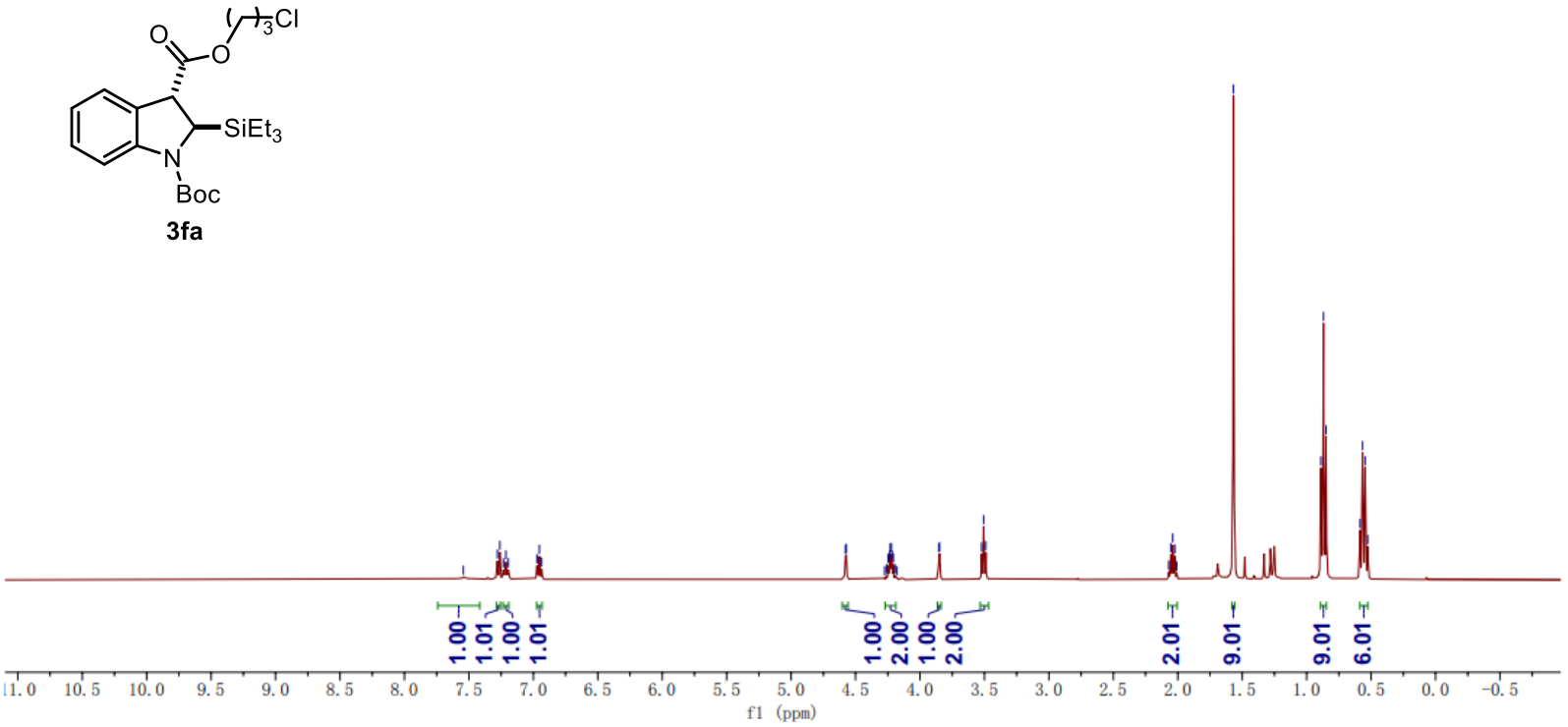
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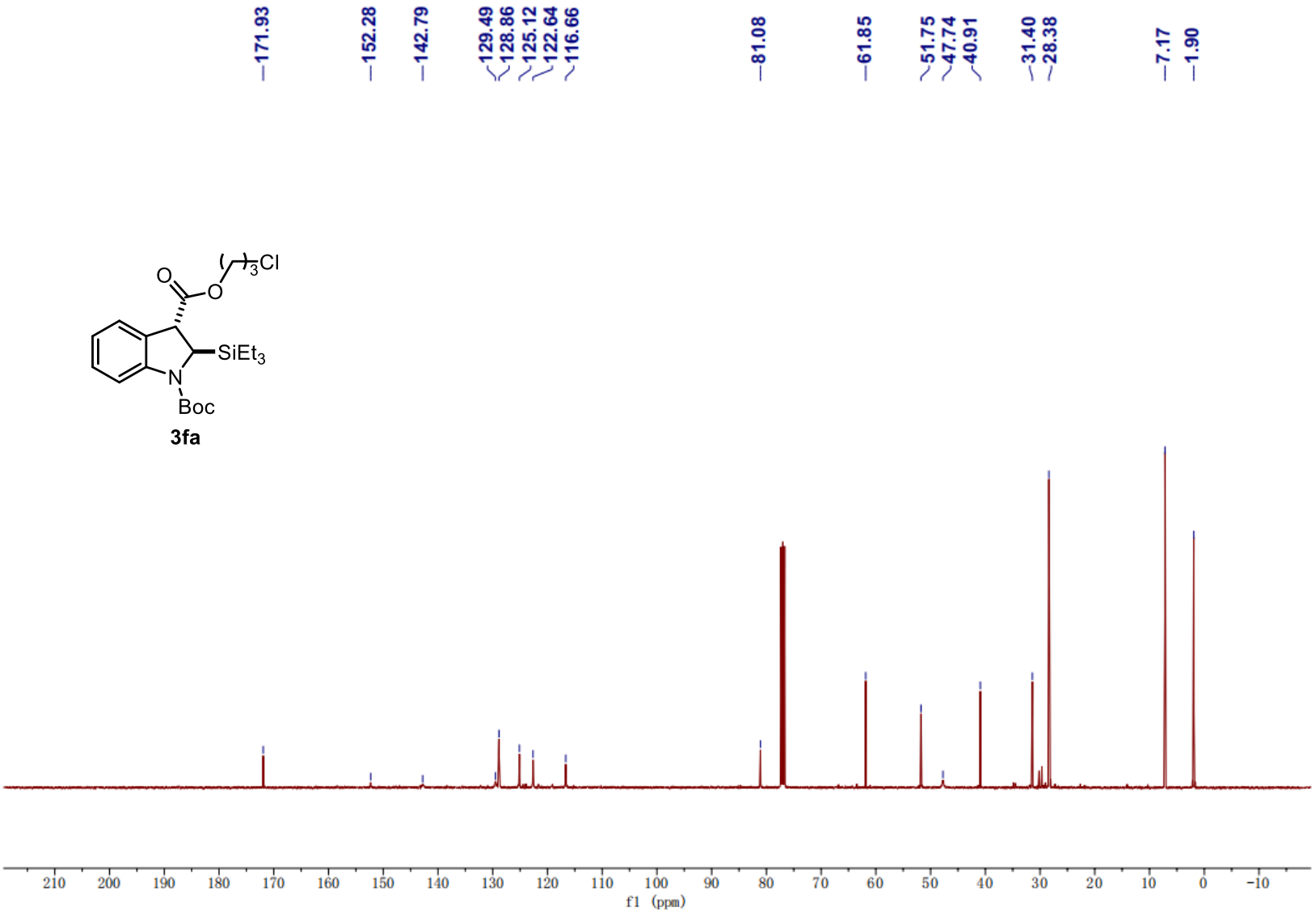
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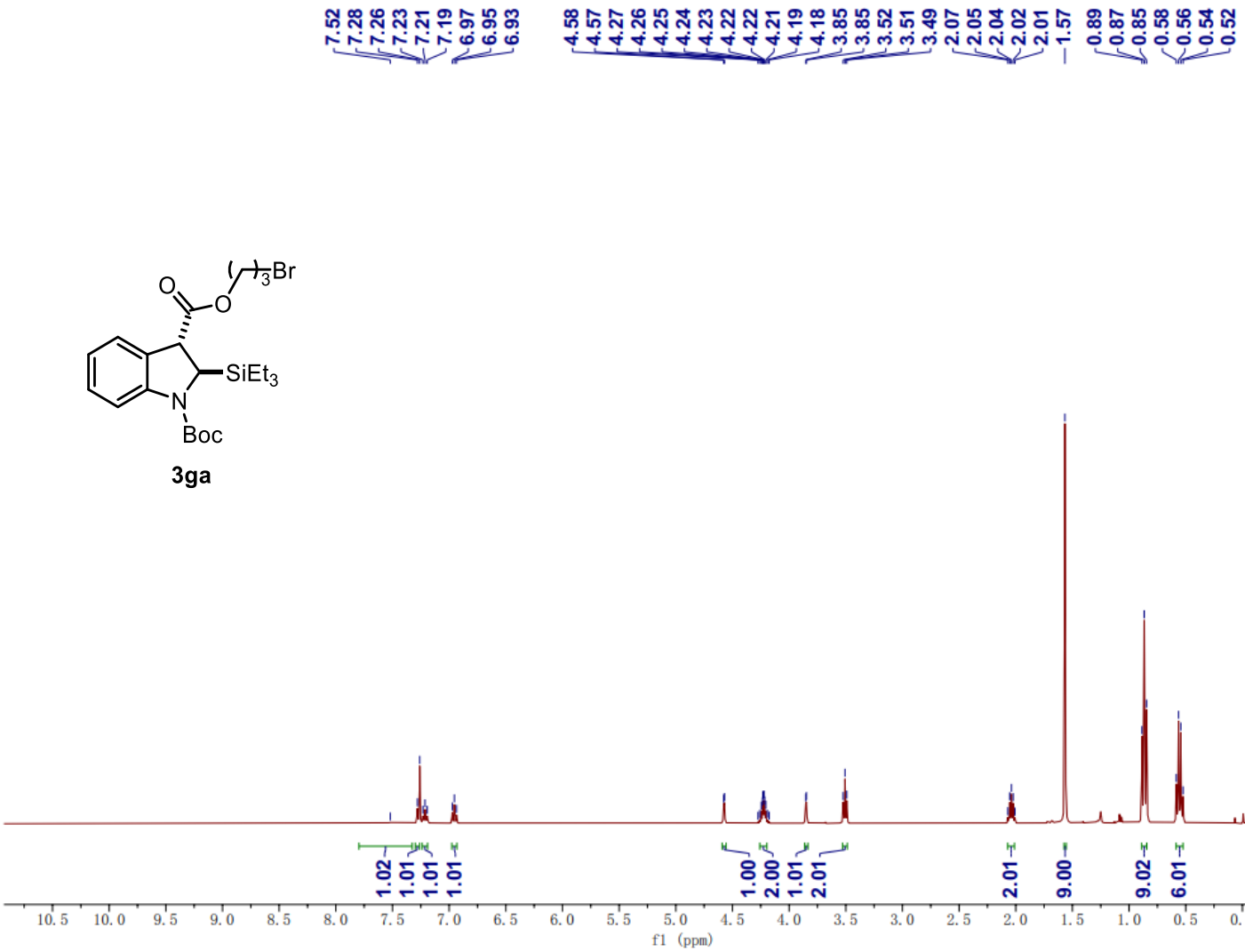
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f1 (ppm)

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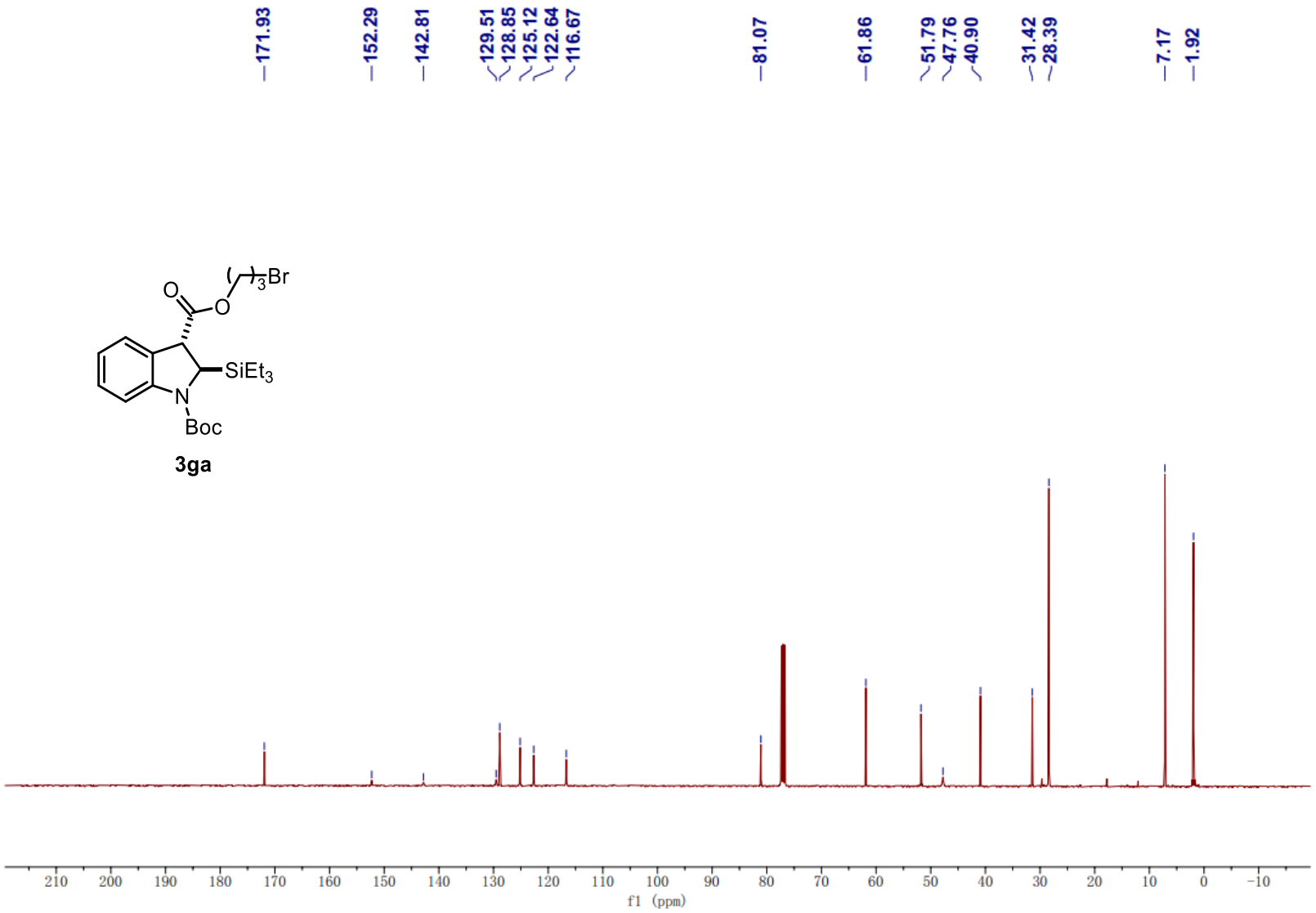
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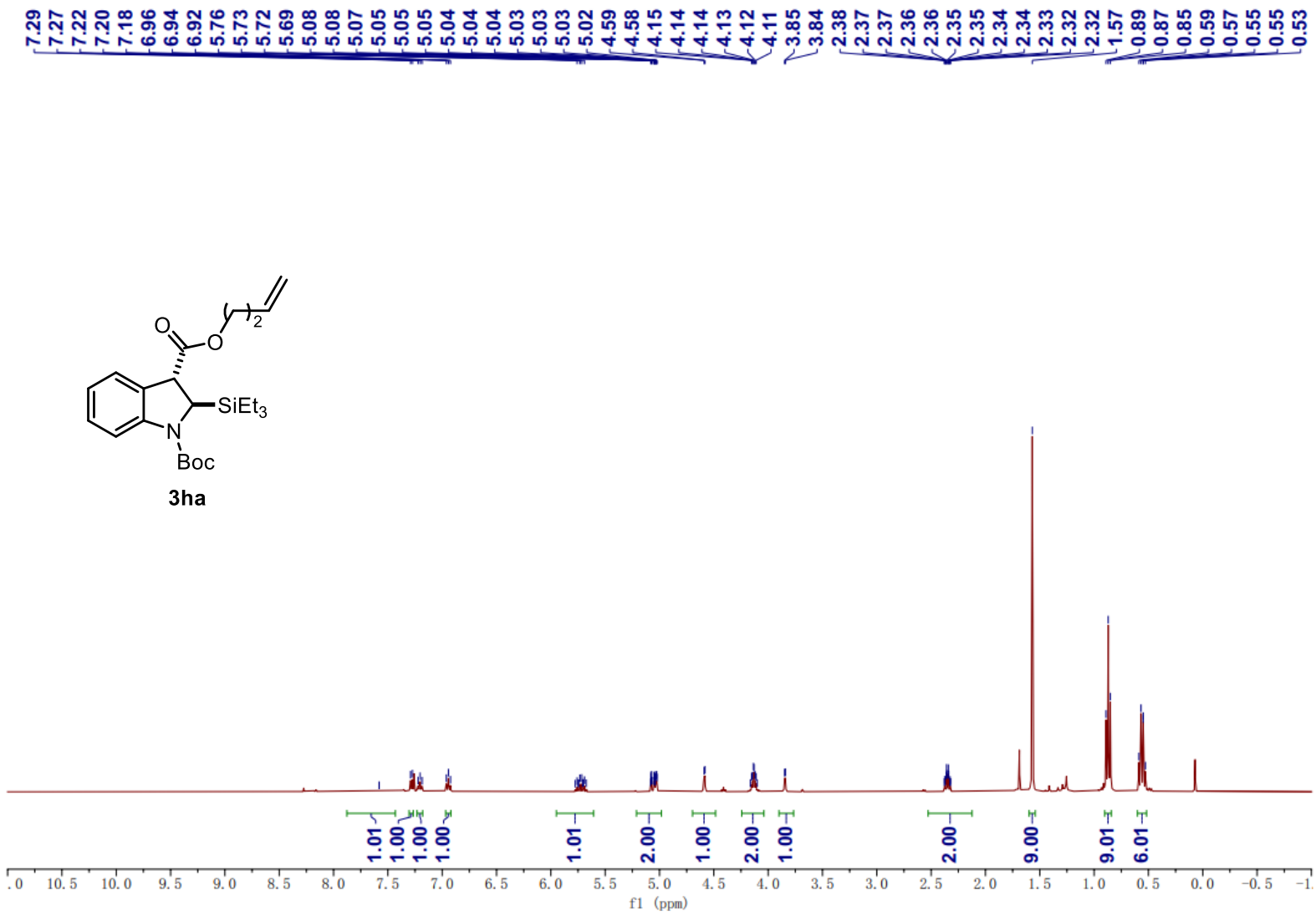
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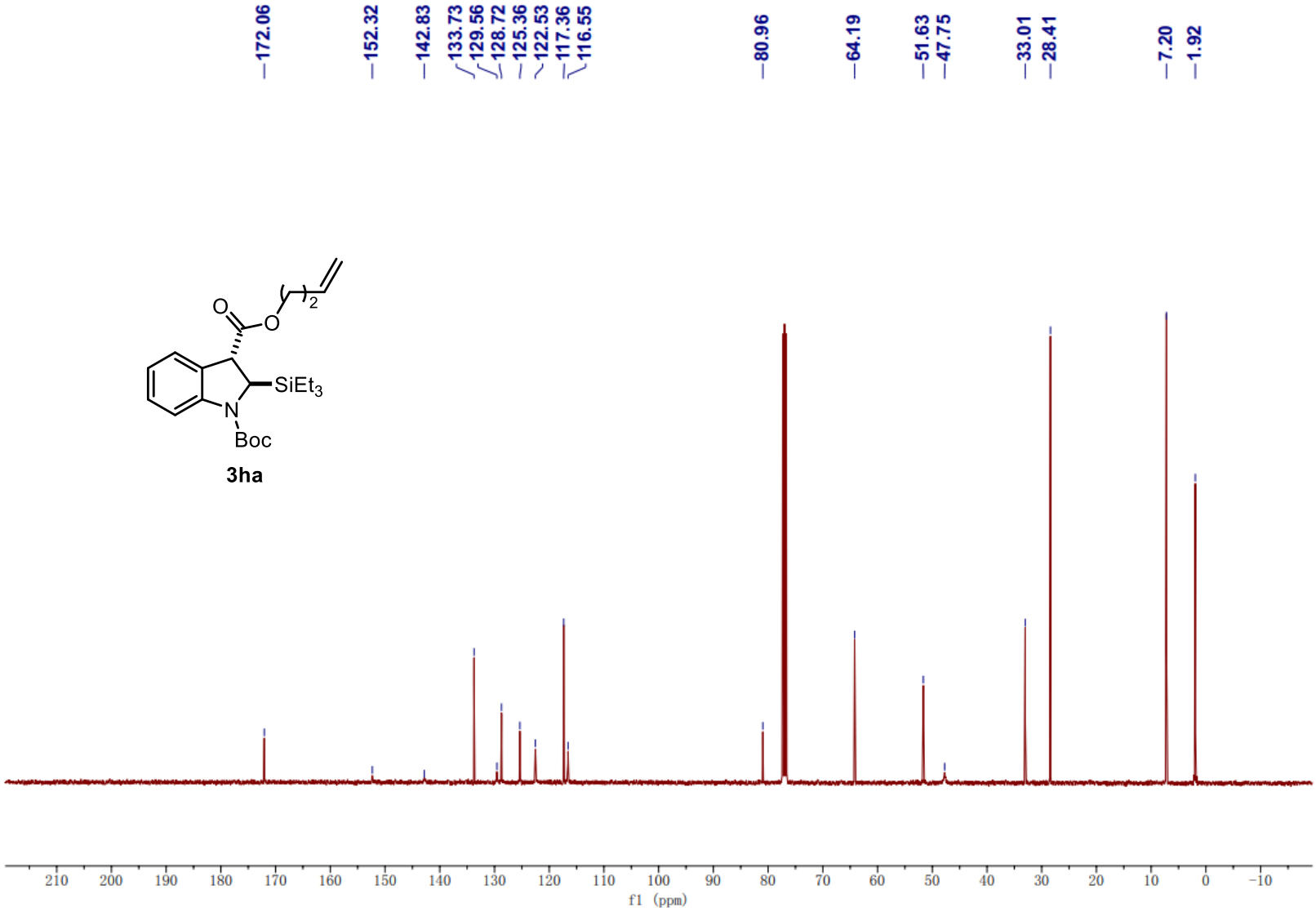
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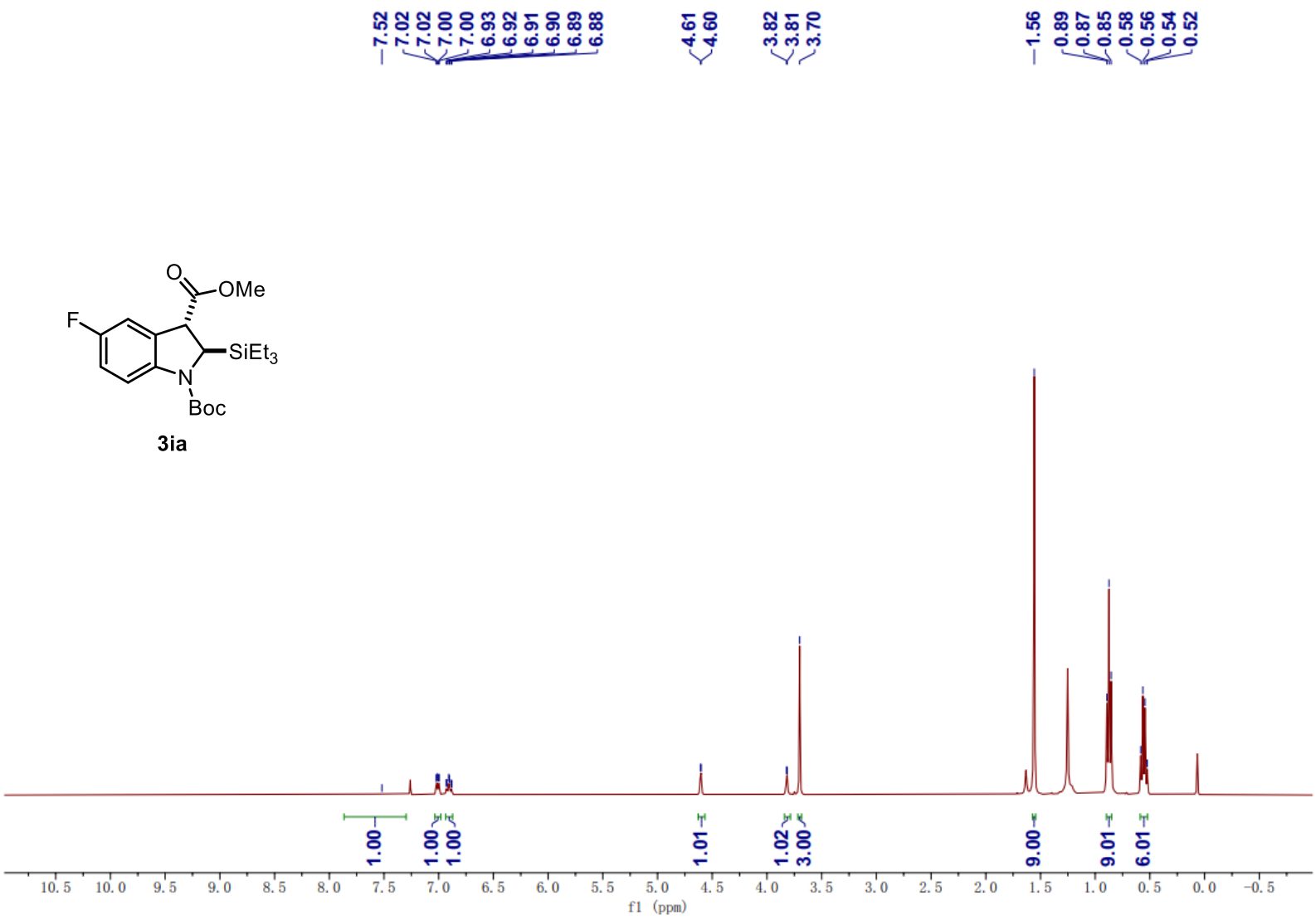
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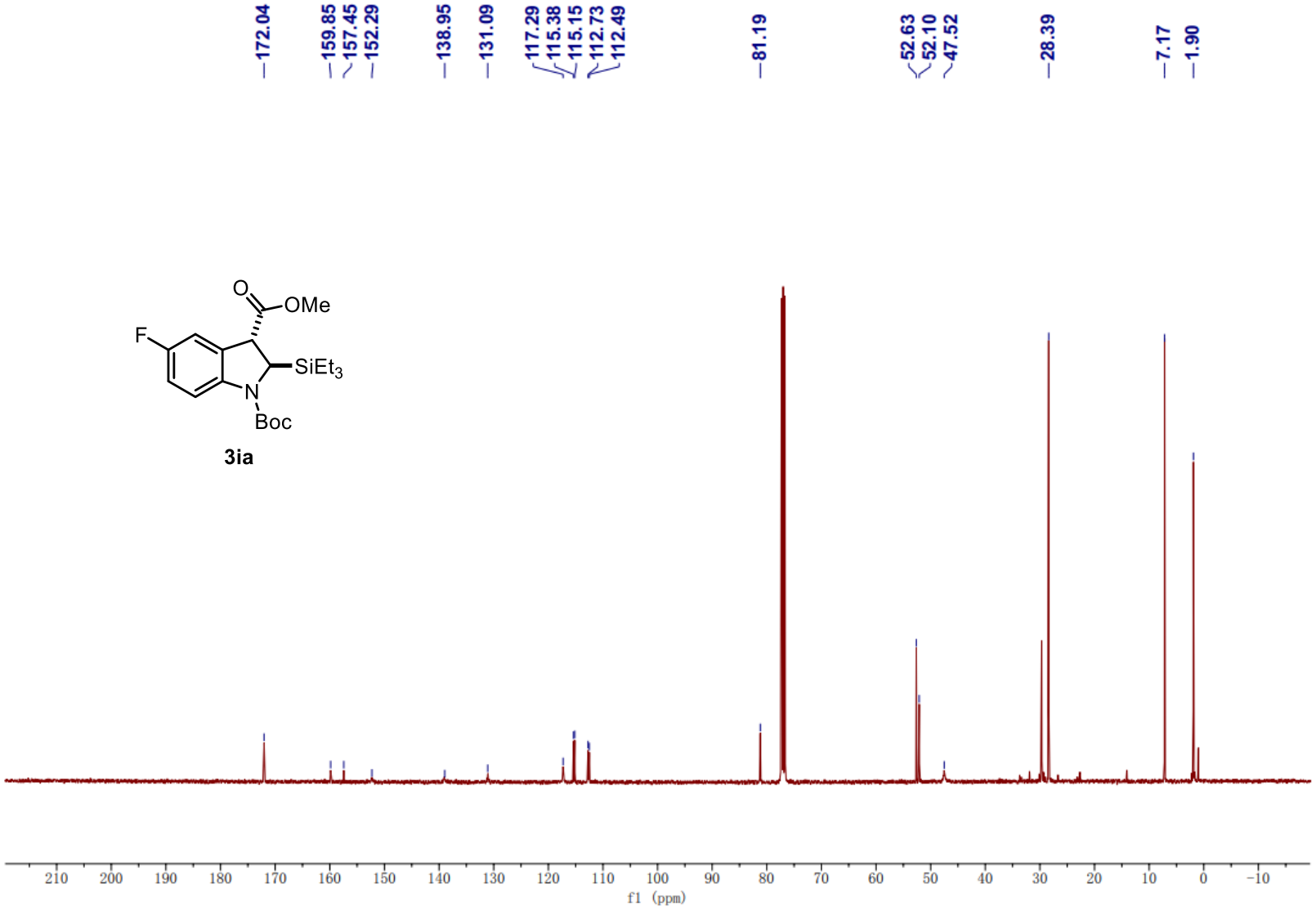
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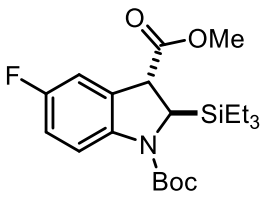
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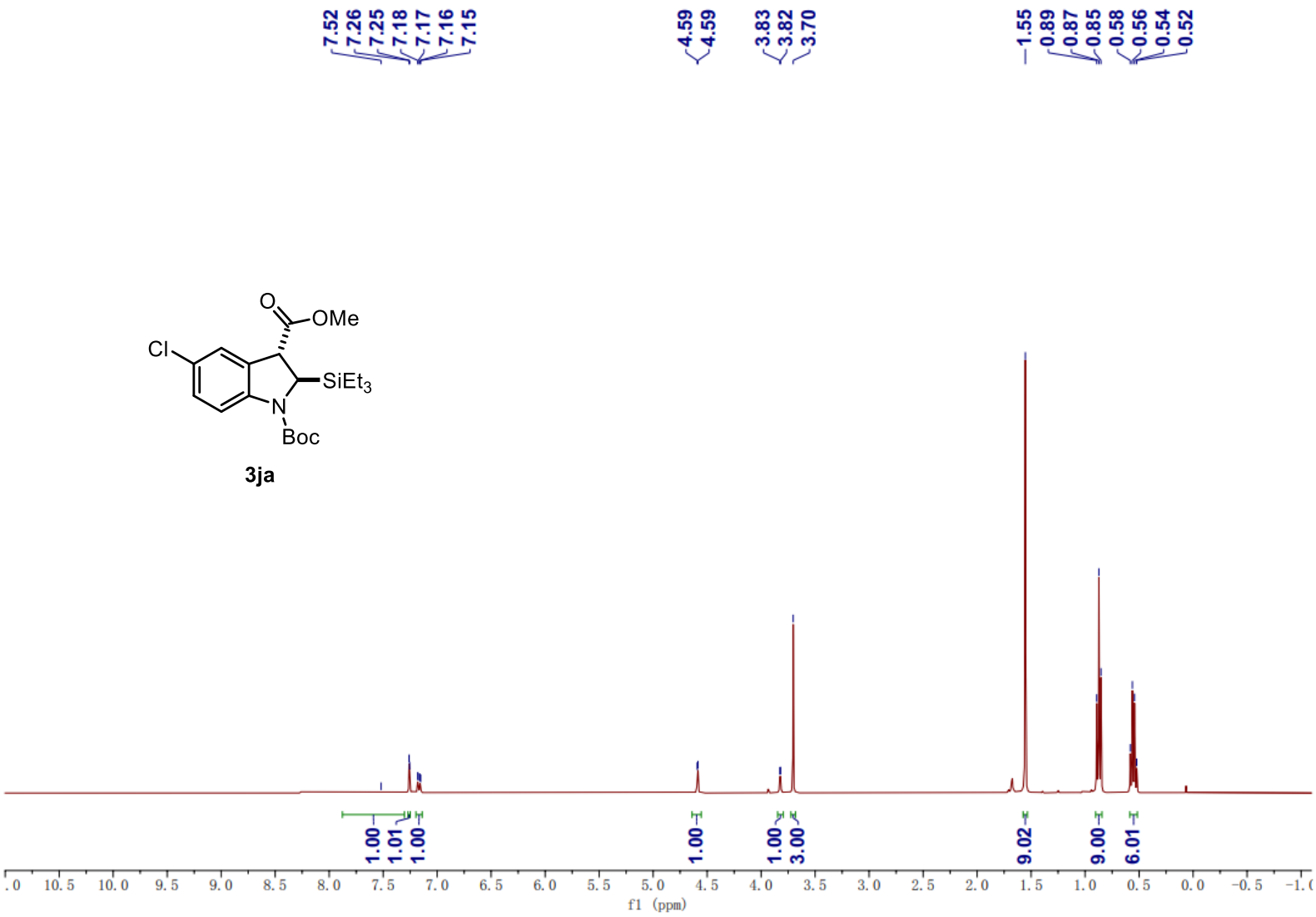
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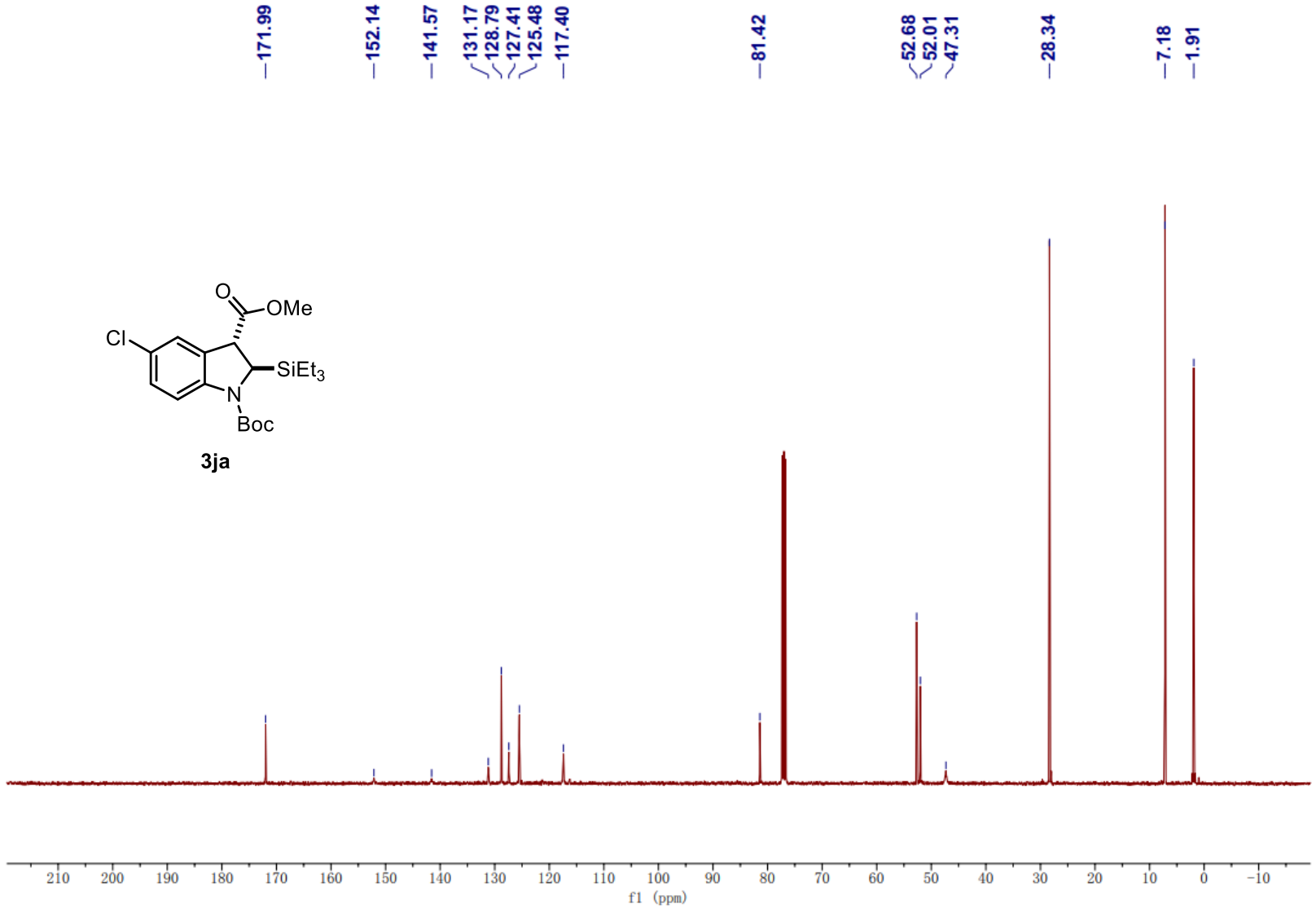
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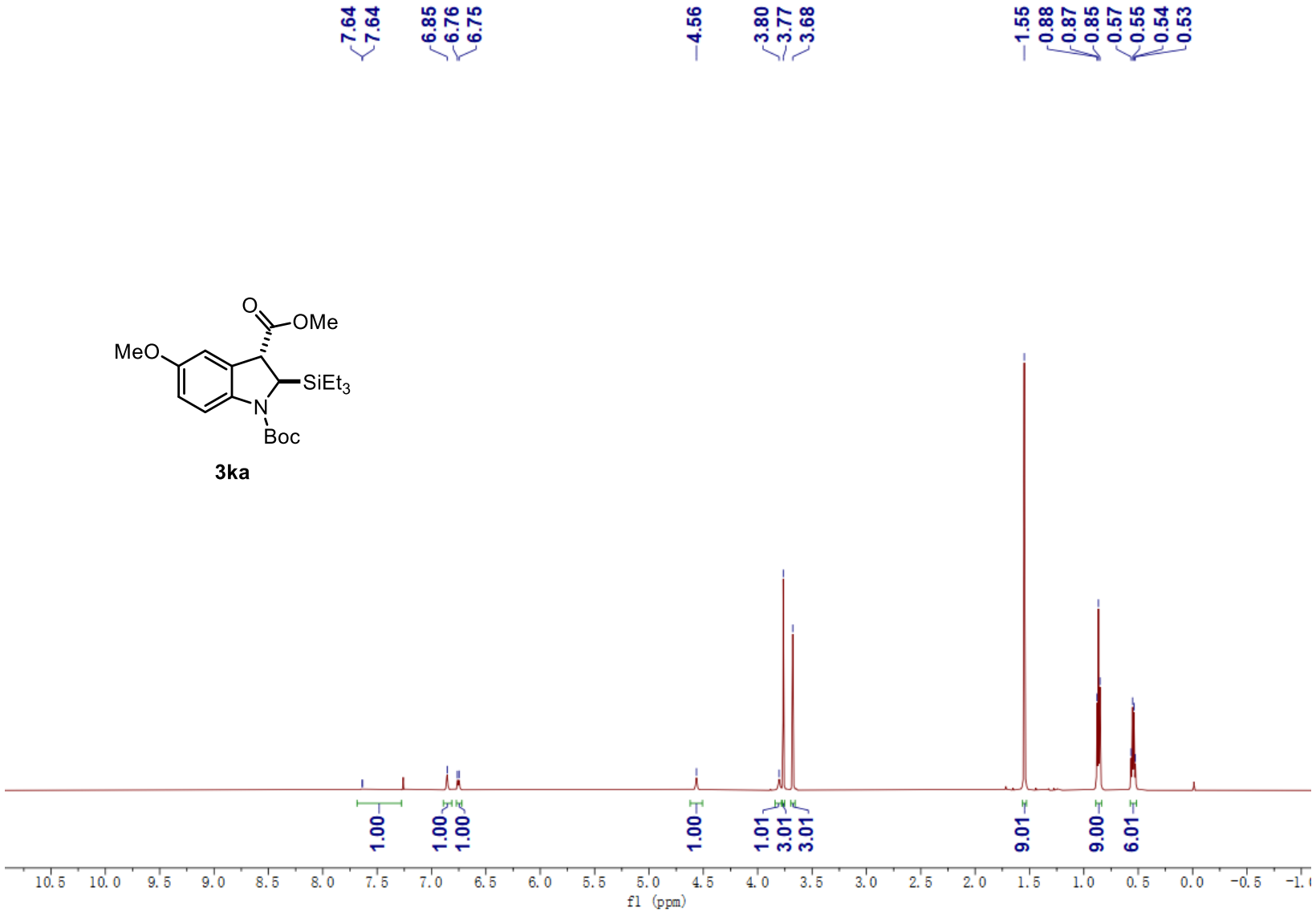
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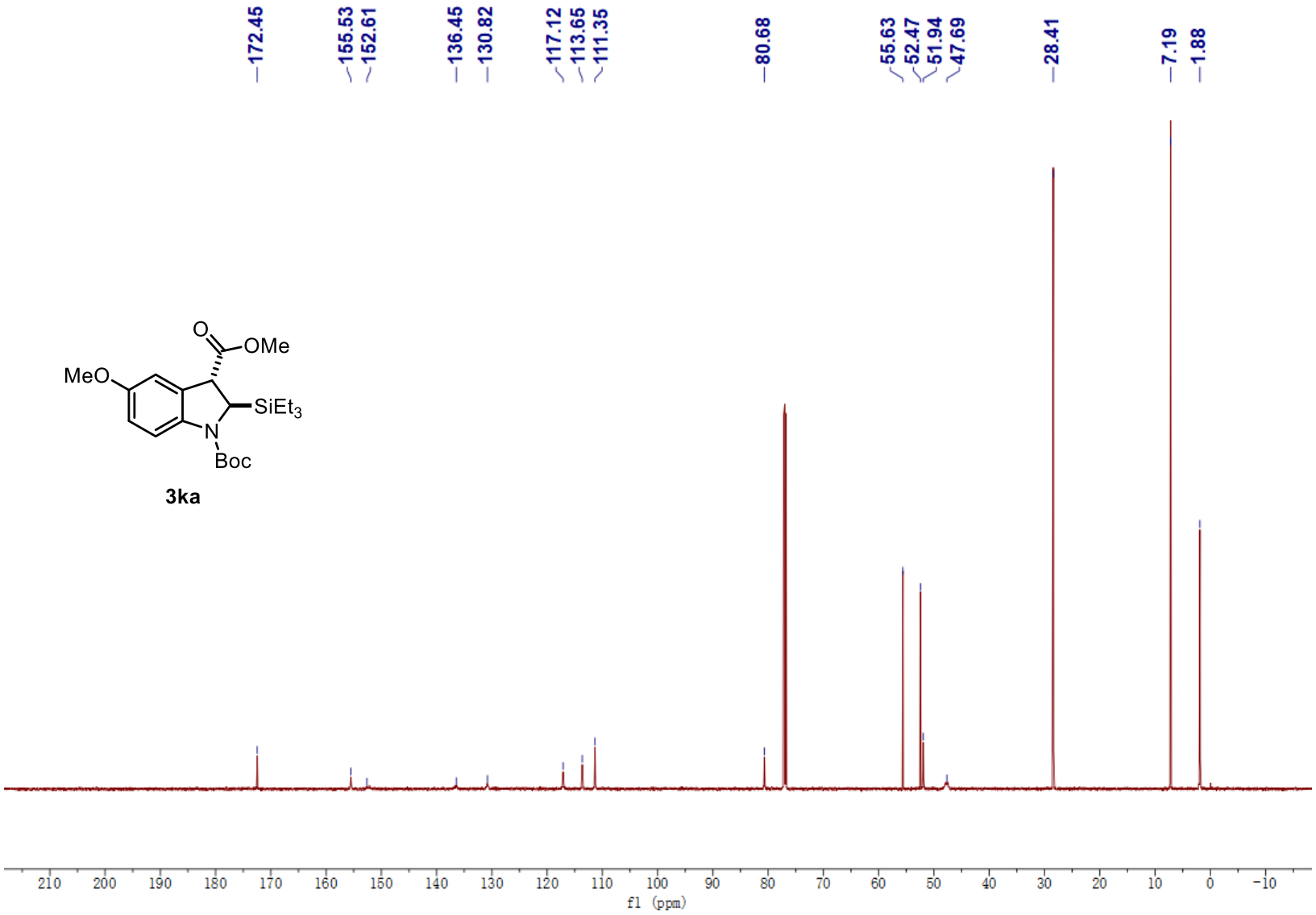
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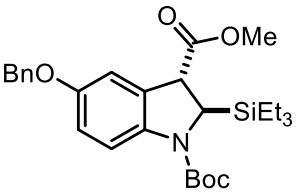
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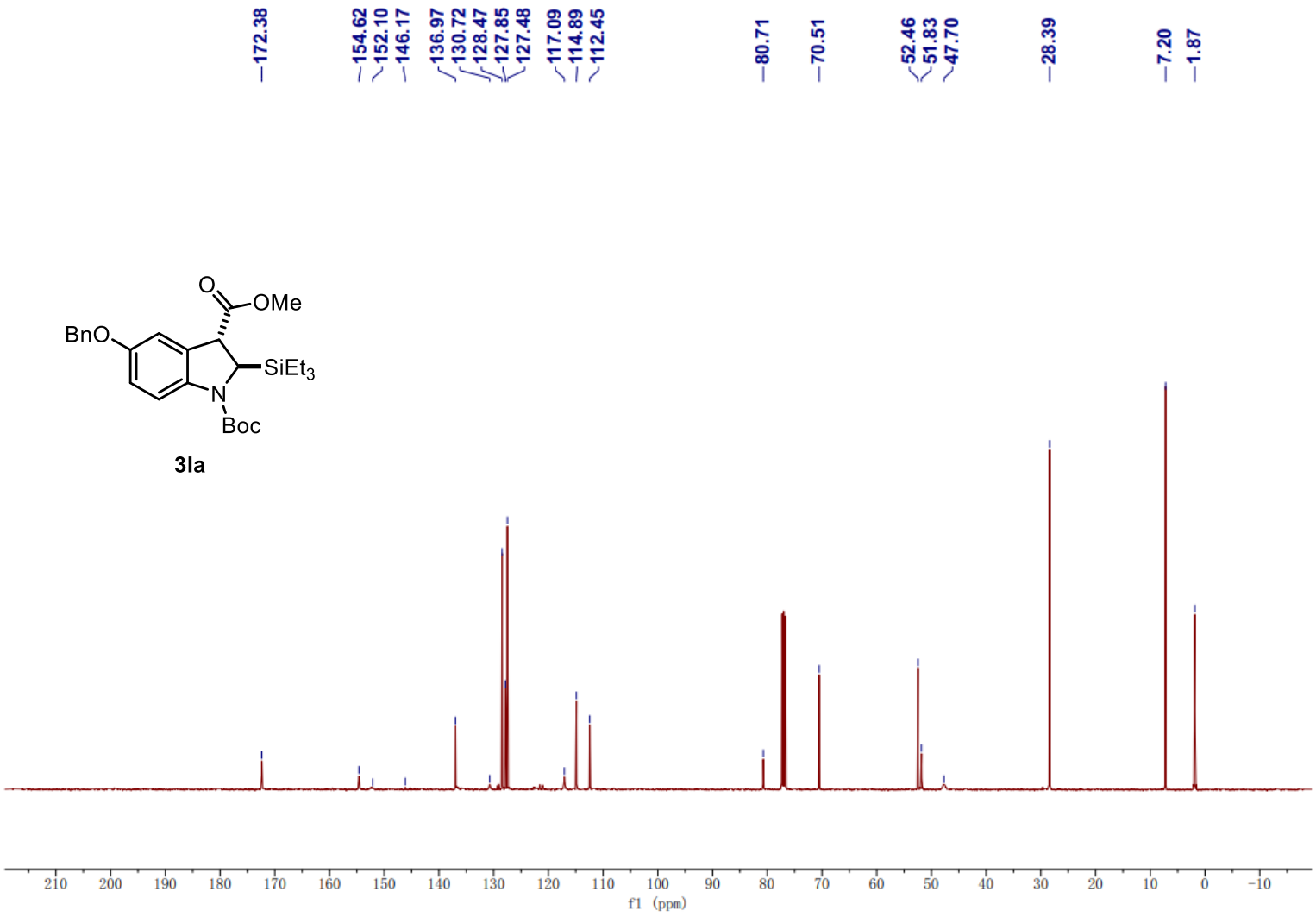
7.40
7.39
7.38
7.37
7.36
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
6.95
6.94
6.87
6.86
6.85
6.84
5.03
4.59
4.58
3.82
3.81
3.81
3.67
1.56
0.90
0.88
0.86
0.59
0.57
0.55
0.53
6.00
1.00
1.00
2.00
1.00
1.00
3.00
9.00
9.00
6.00
f1 (ppm)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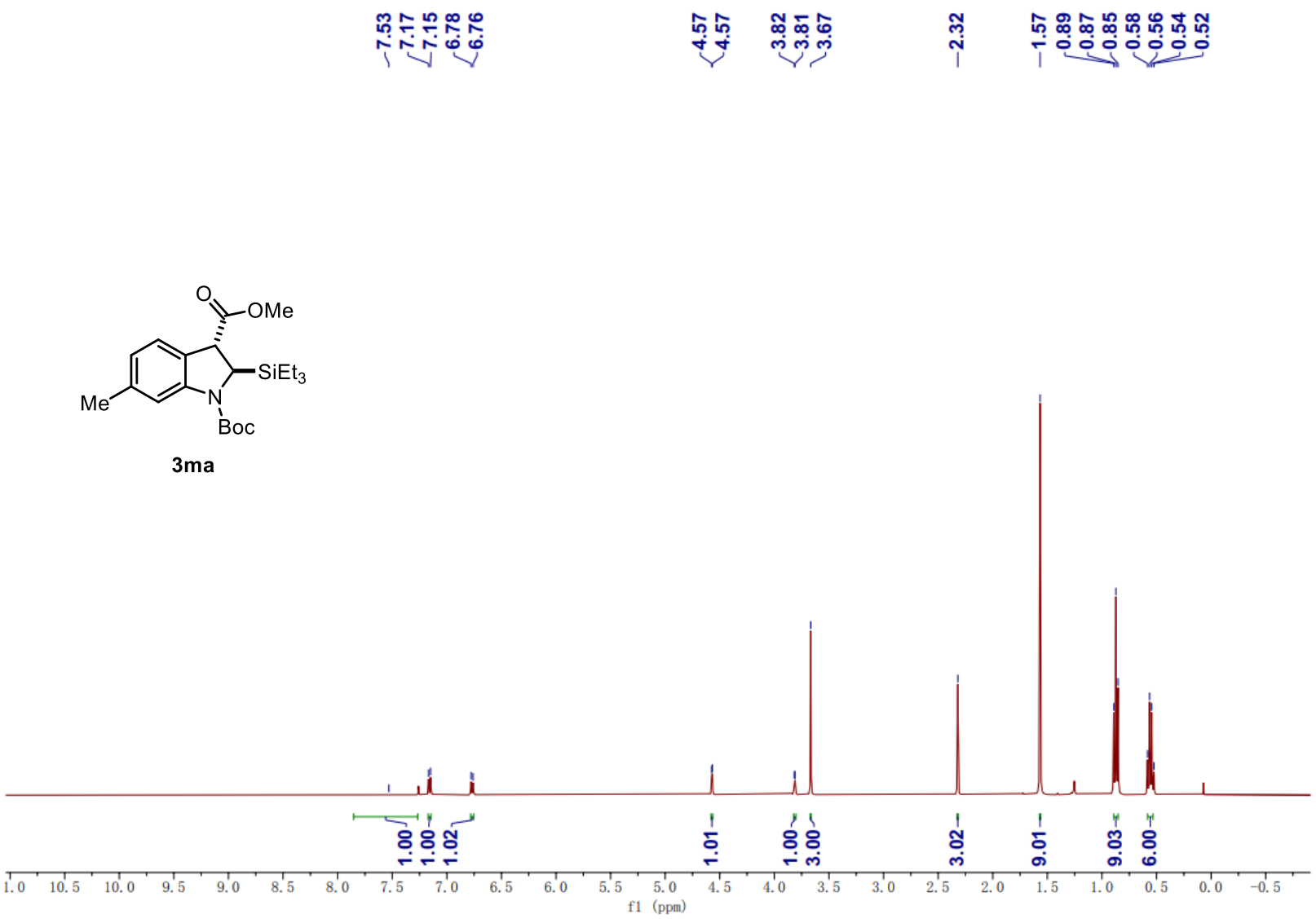
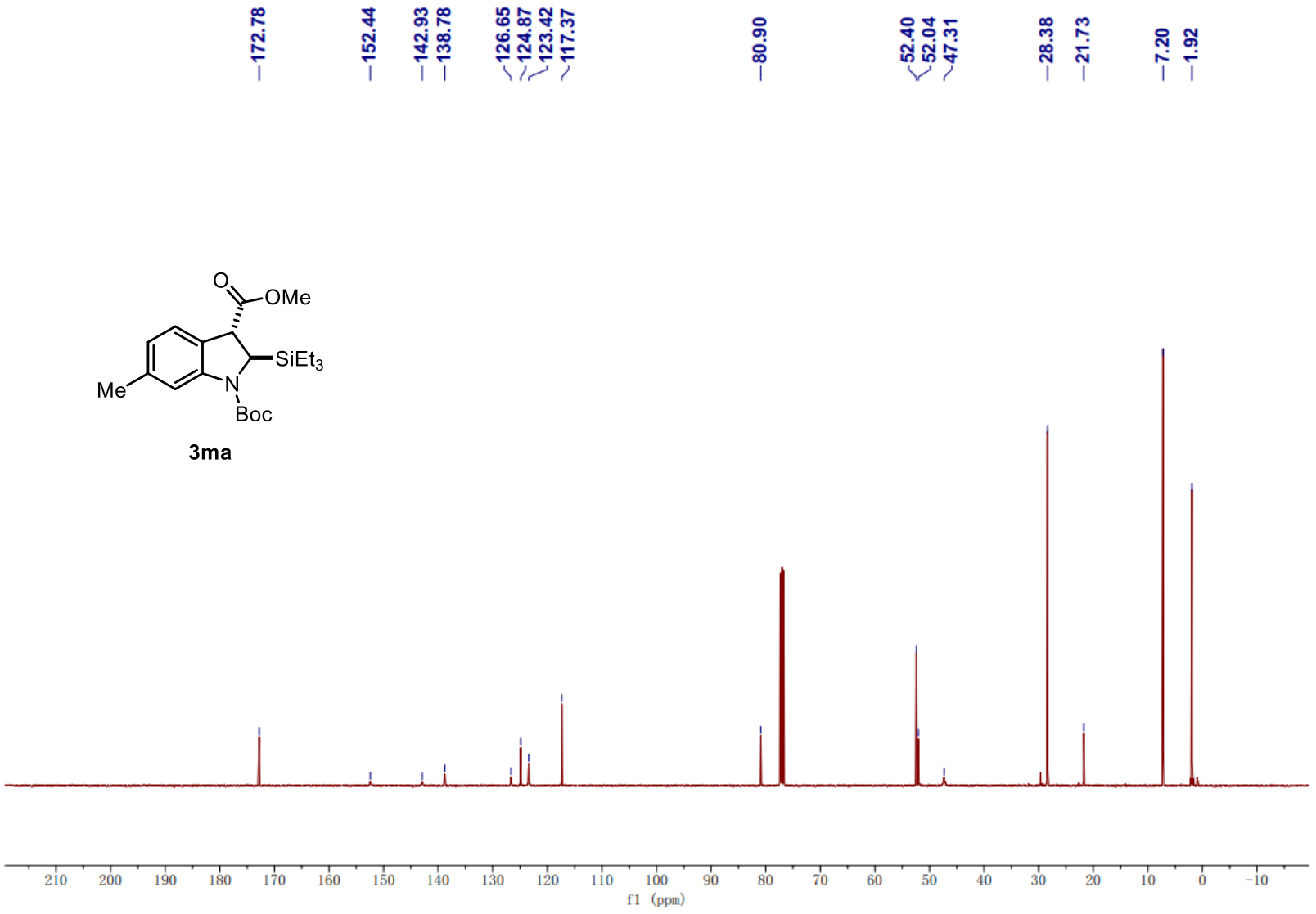
154.62
152.10
146.17
136.97
130.72
128.47
127.85
127.48
117.09
114.89
112.45
80.71
70.51
52.46
51.83
47.70
28.39
7.20
1.87
O
OMe
BnO
SiEt3
N
Boc
3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.53
7.17
7.15
6.78
6.76
4.57
4.57
3.82
3.81
3.67
2.32
1.57
0.89
0.87
0.85
0.58
0.56
0.54
0.52
O
OMe
SiEt3
Me
N
Boc
1.00
1.00
1.02
1.01
1.00
3.00
3.02
9.01
9.03
6.00
f1 (ppm)

3ma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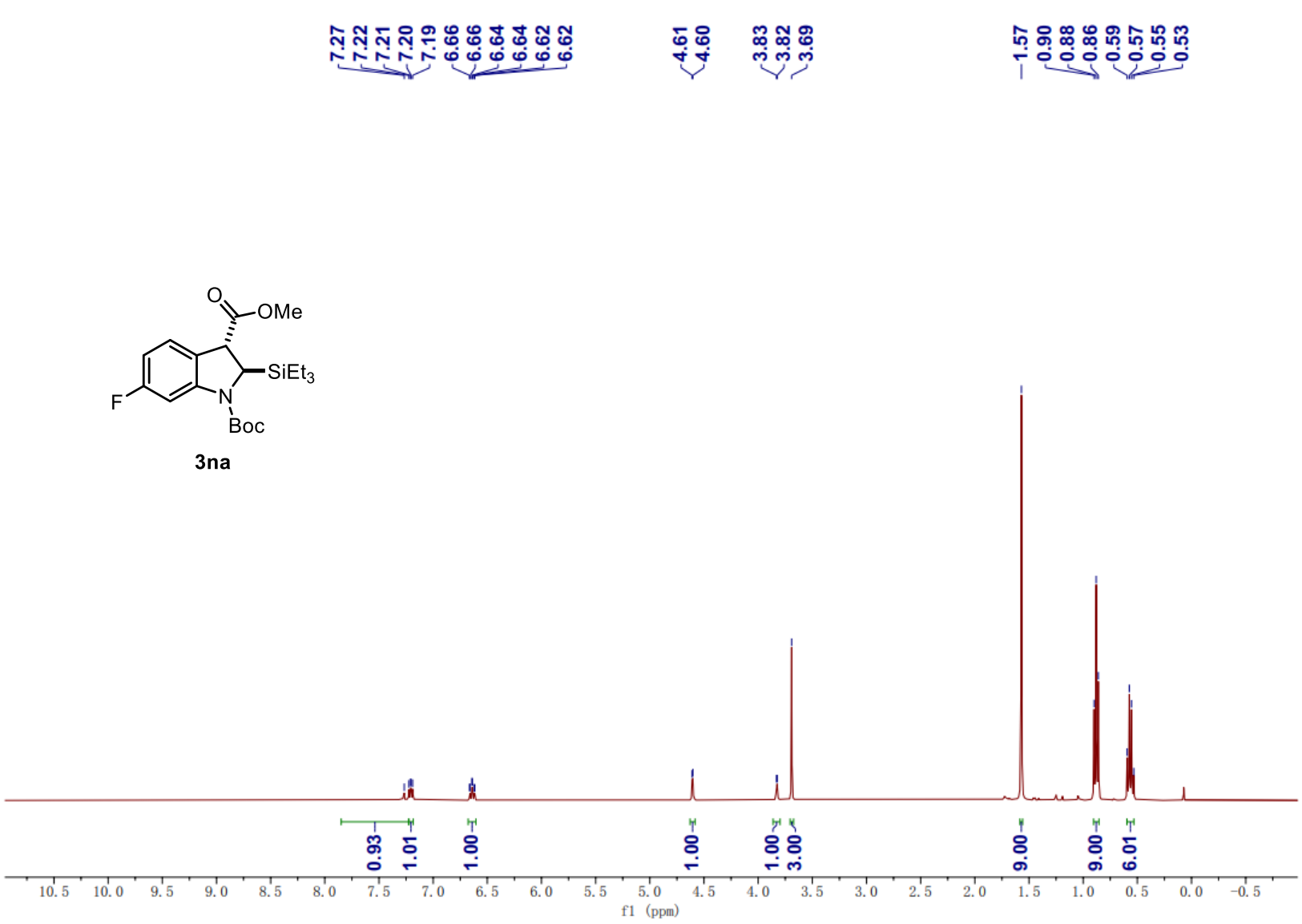
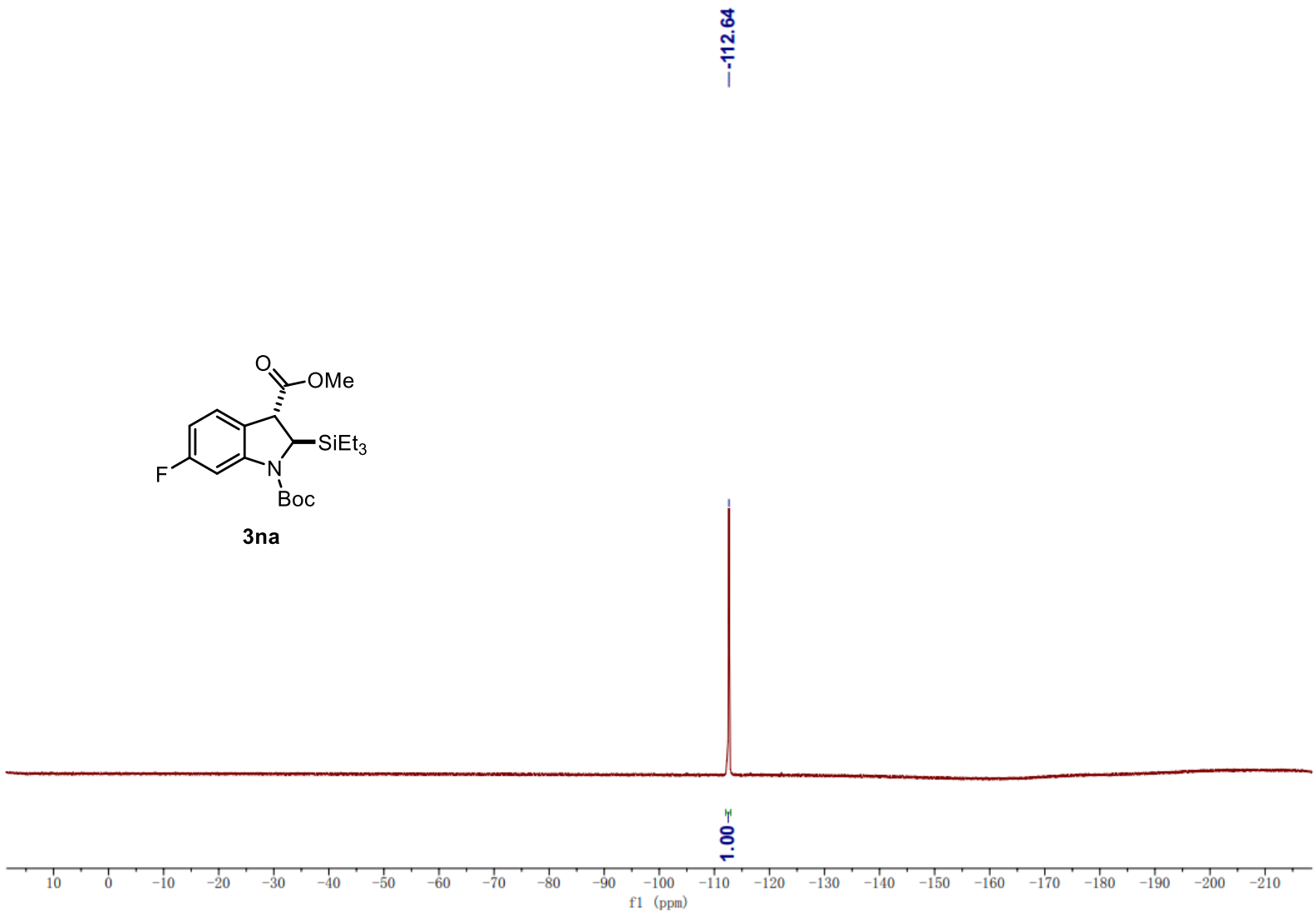
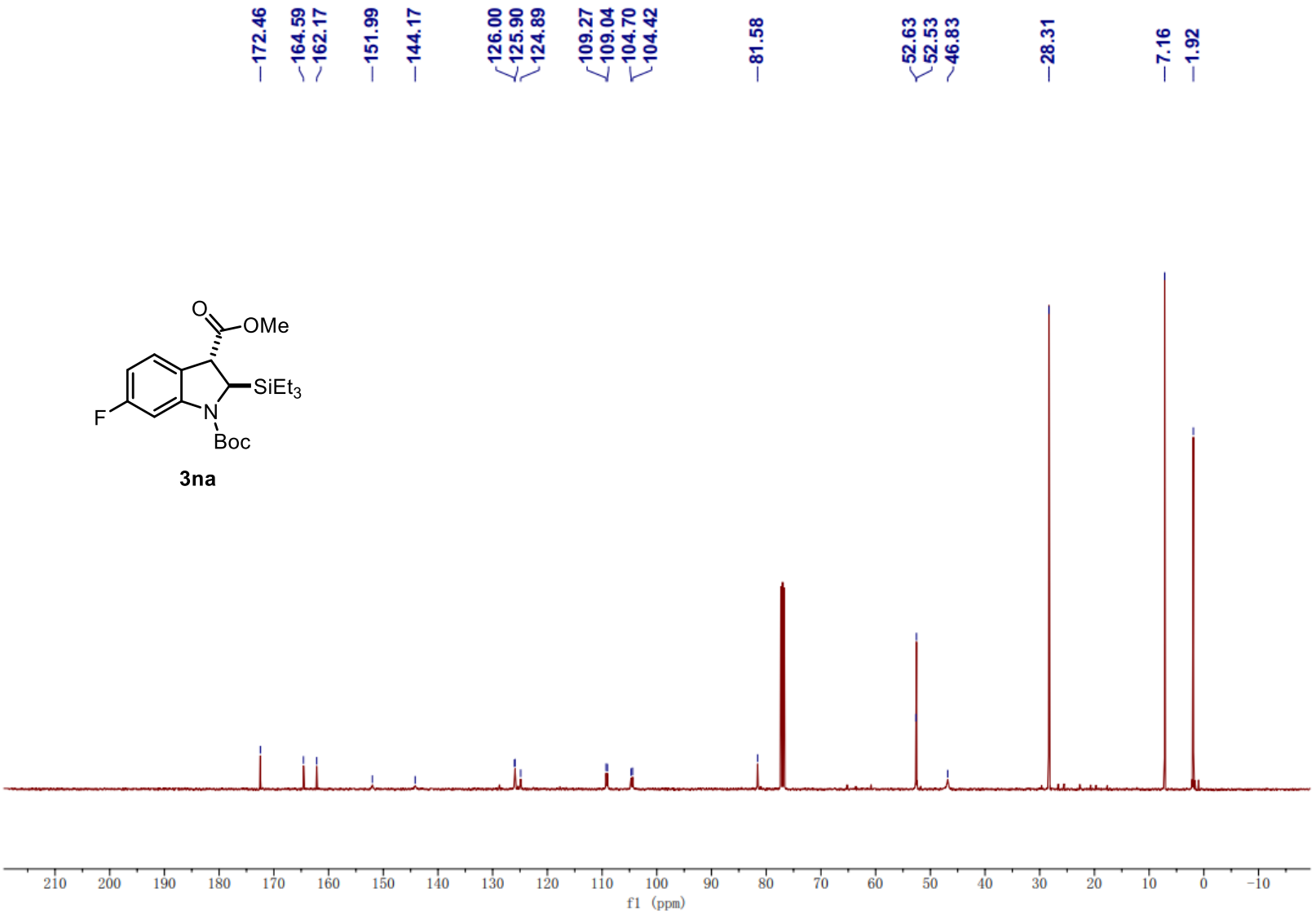
152.44
142.93
138.78
126.65
124.87
123.42
117.37
80.90
52.40
52.04
47.31
28.38
21.73
7.20
1.92
O
OMe
SiEt3
Me
N
Boc
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.27
7.22
7.21
7.20
7.19
6.66
6.66
6.64
6.64
6.62
6.62
4.61
4.60
3.83
3.82
3.69
1.57
0.90
0.88
0.86
0.59
0.57
0.55
0.53
O
OMe
SiEt3
F
N
Boc
0.93
1.01
1.00
1.00
1.00
3.00
9.00
9.00
6.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3na


-112.64
O
OMe
SiEt3
F
N
Boc
3na
1.00
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)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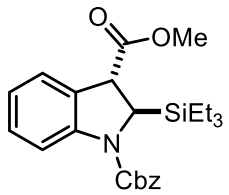
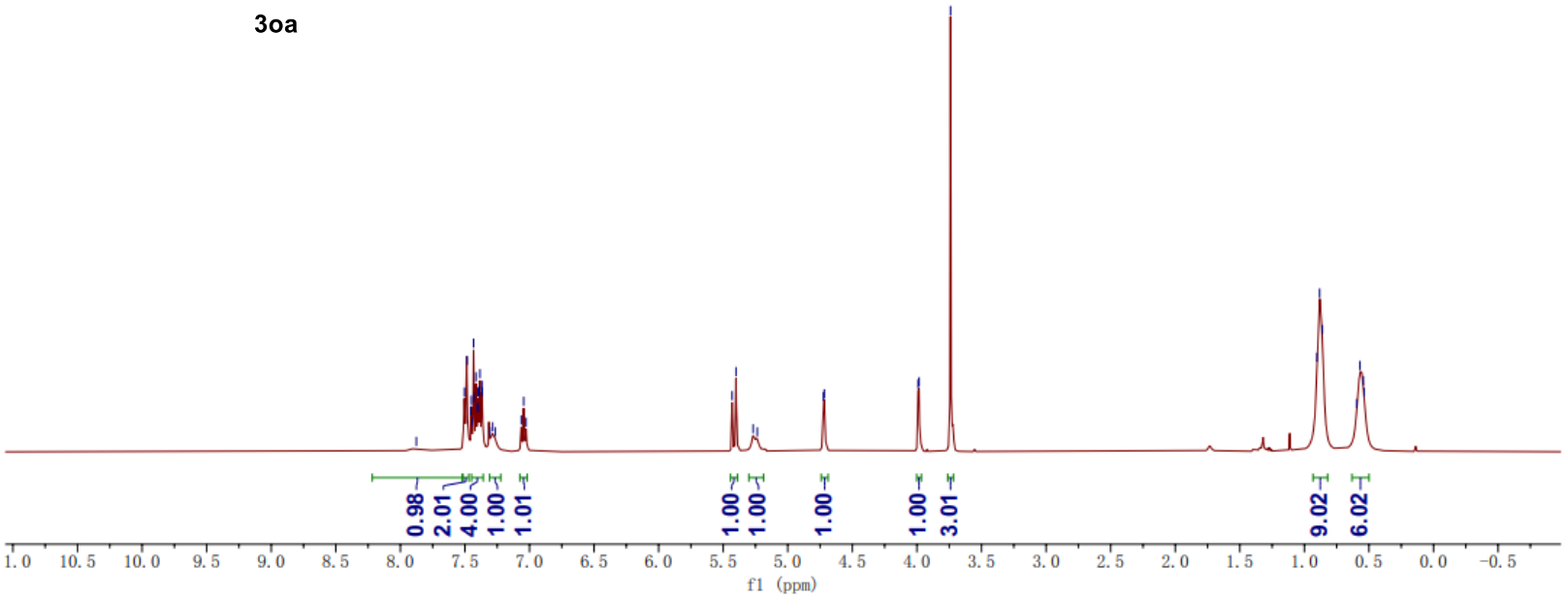
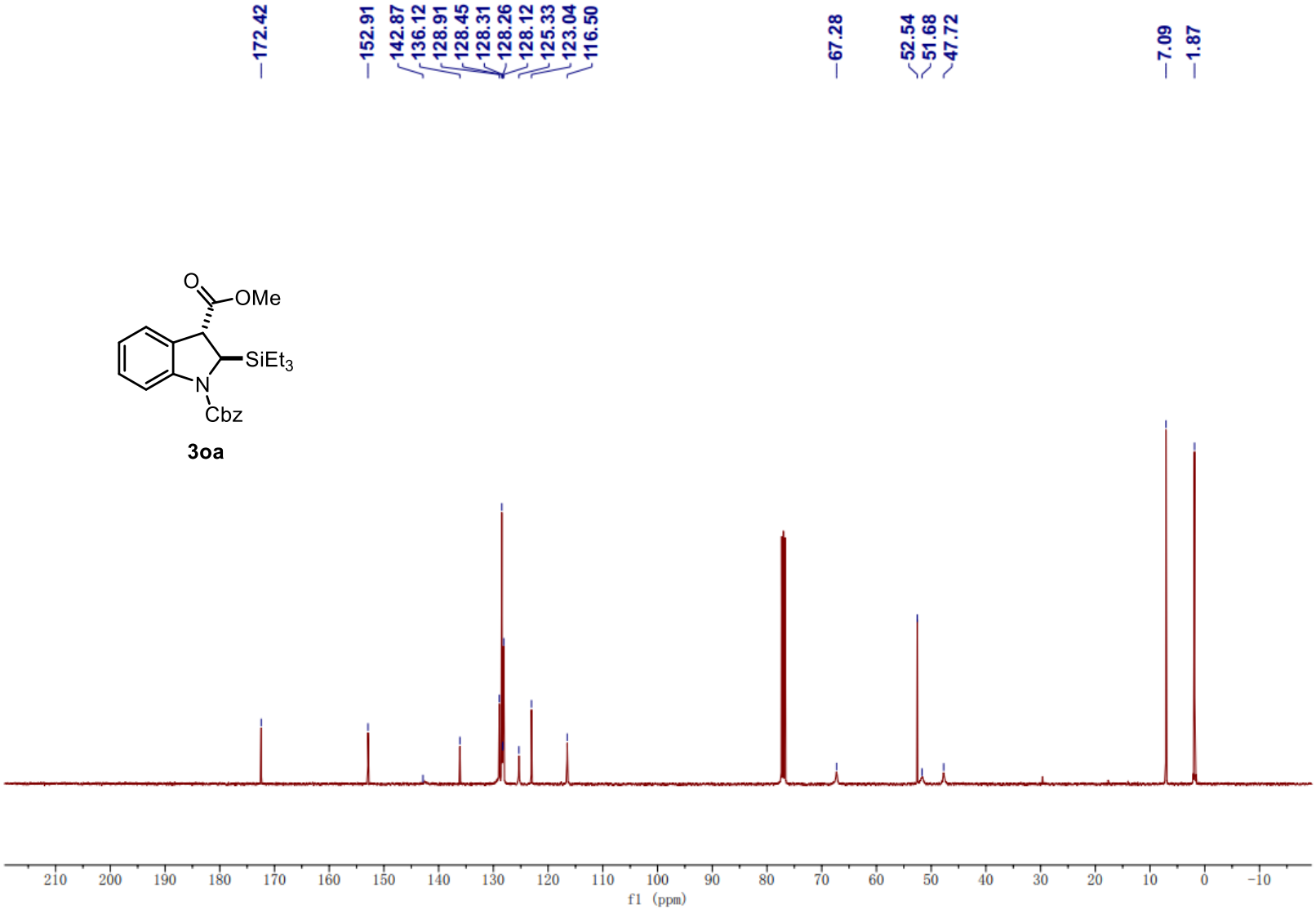
164.59
162.17
151.99
144.17
126.00
125.90
124.89
109.27
109.04
104.70
104.42
81.58
52.63
52.53
46.83
28.31
7.16
1.92
O
OMe
SiEt3
F
N
Boc
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.88
7.50
7.48
7.45
7.45
7.44
7.43
7.43
7.41
7.40
7.40
7.40
7.39
7.38
7.37
7.37
7.31
7.29
7.27
7.06
7.05
7.03
5.43
5.40
5.27
5.24
4.72
4.72
3.99
3.98
3.74
0.90
0.88
0.86
0.60
0.57
0.54
0.54


O
OMe
SiEt3
N
Cbz

3oa


0.98
2.01
4.00
1.00
1.01
1.00
1.00
1.00
1.00
3.01
9.02
6.02
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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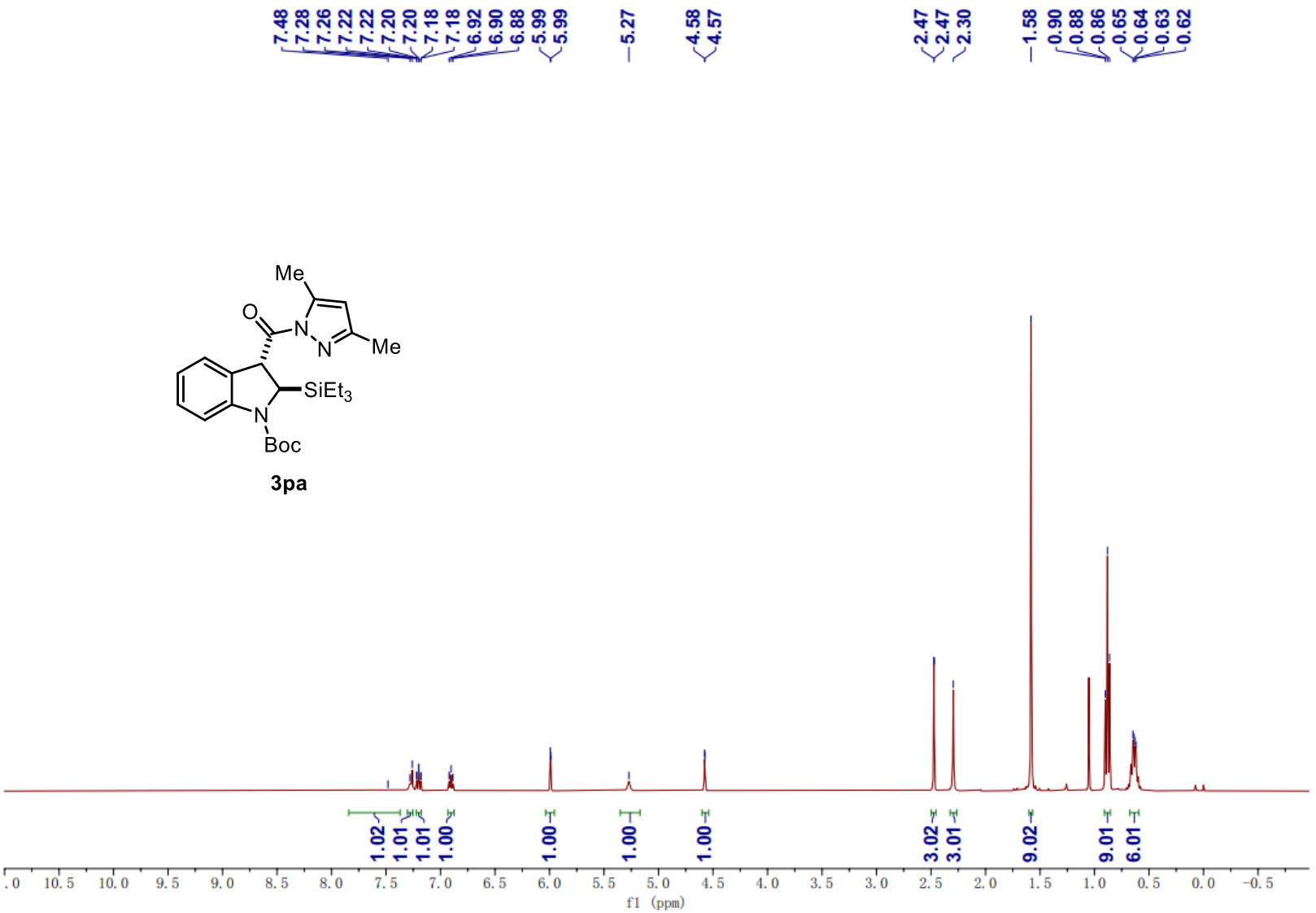
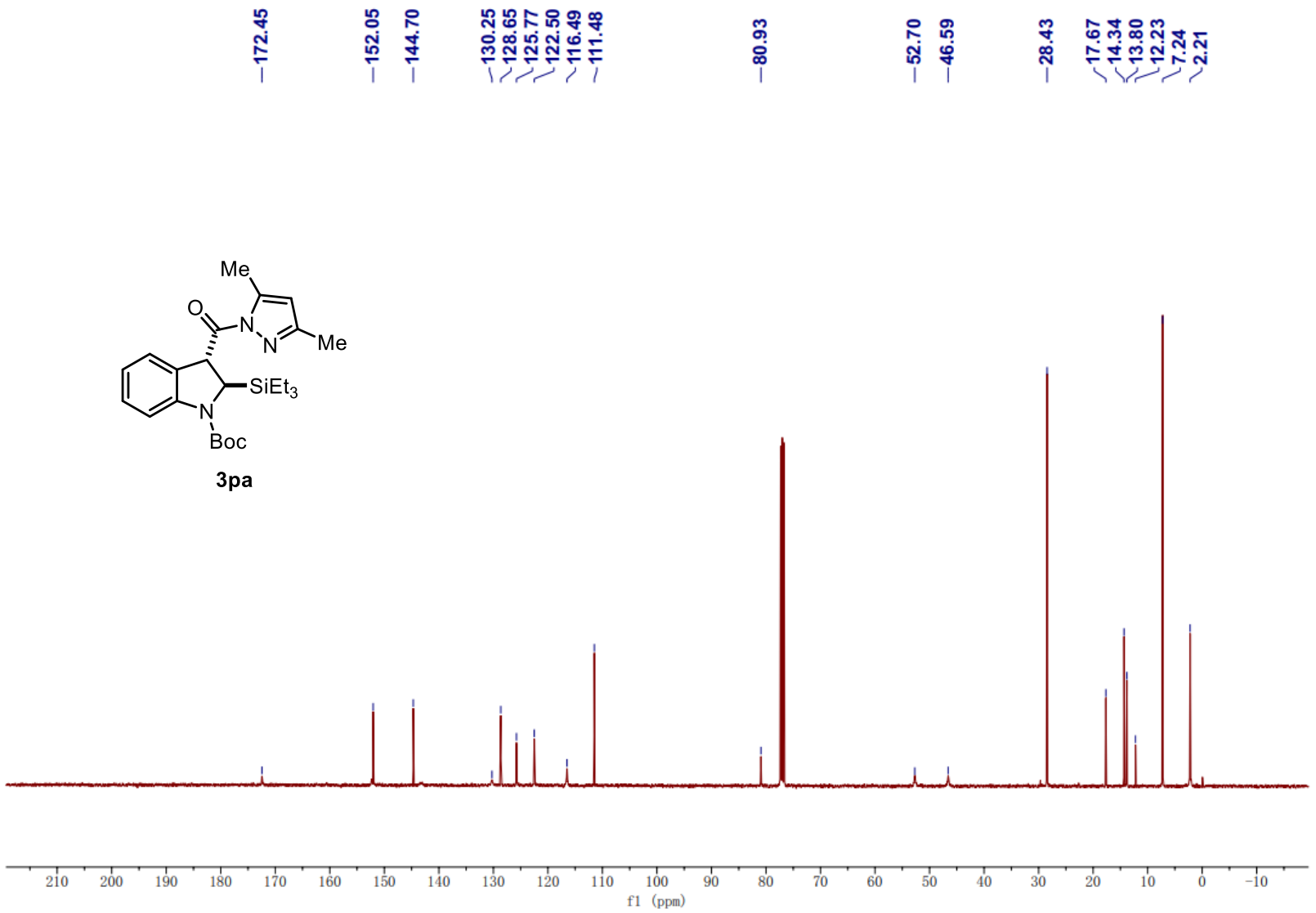
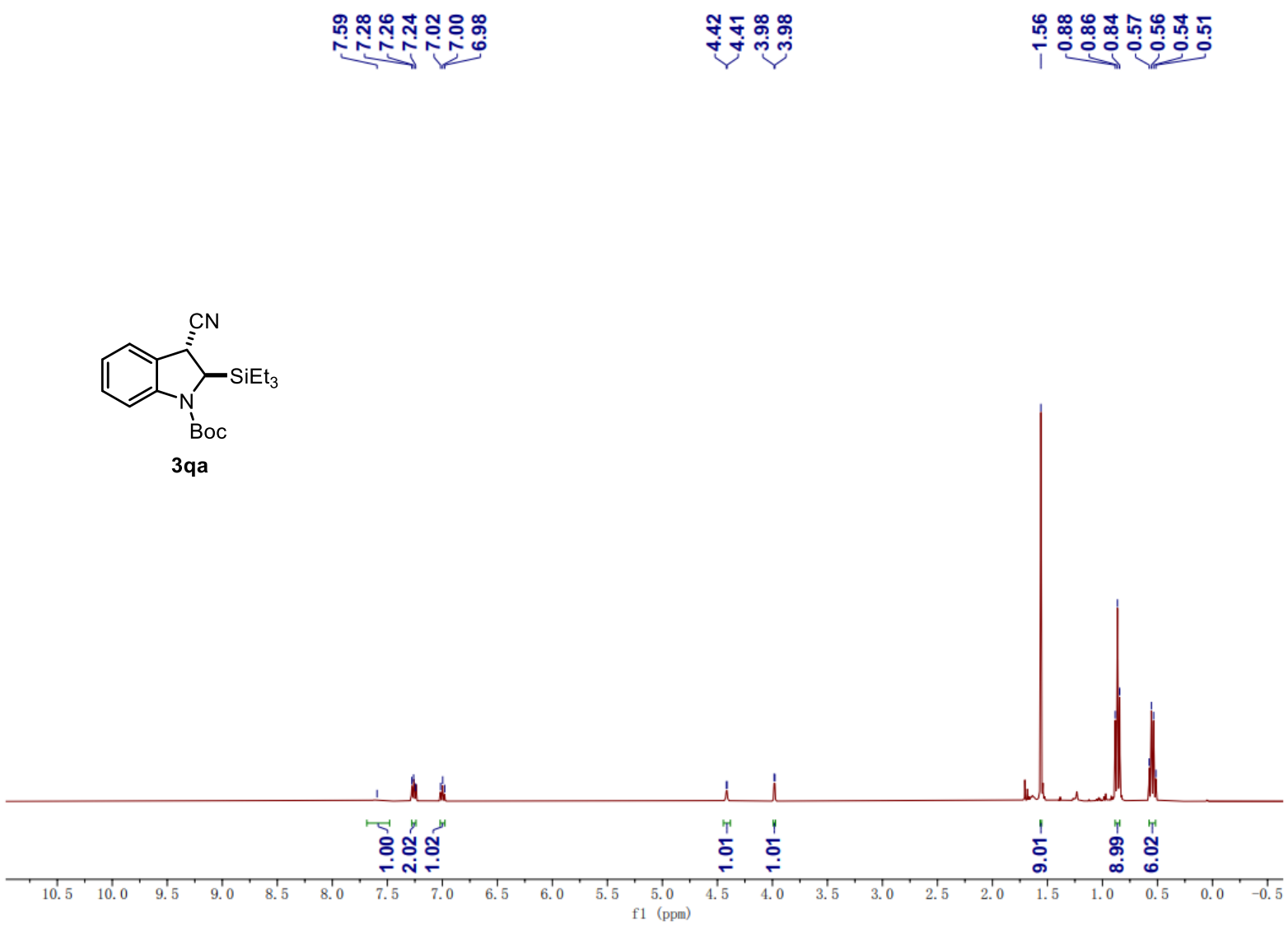
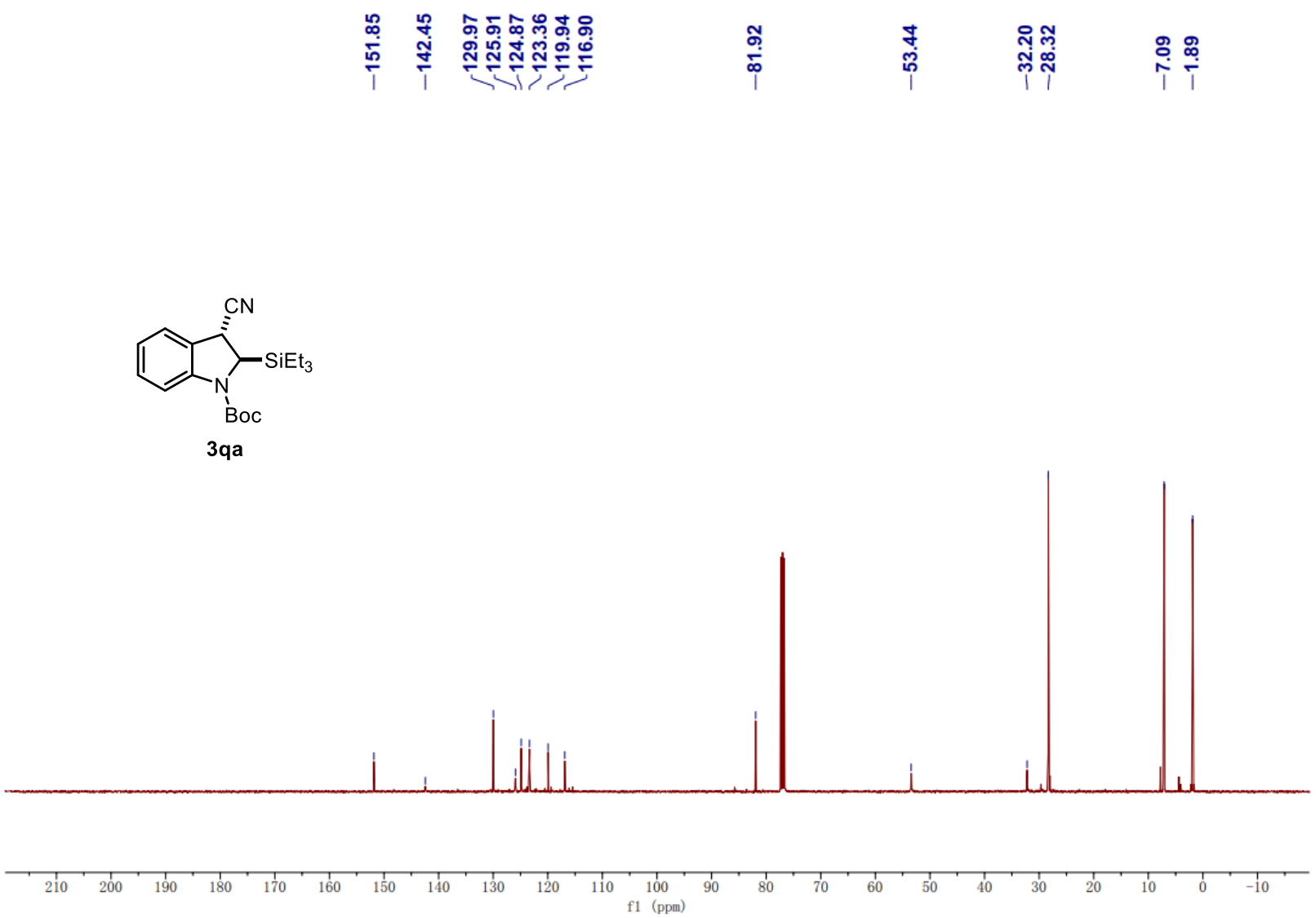
152.91
142.87
136.12
128.91
128.45
128.31
128.26
128.12
125.33
123.04
116.50
67.28
52.54
51.68
47.72
7.09
1.87
O
OMe
SiEt3
N
Cbz
3oa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.48
7.28
7.26
7.22
7.22
7.20
7.20
7.18
7.18
6.92
6.90
6.88
5.99
5.99
5.27
4.58
4.57
2.47
2.47
2.30
1.58
0.90
0.88
0.86
0.65
0.64
0.63
0.62
Me
O
N
N
Me
SiEt3
N
Boc
1.02
1.01
1.01
1.00
1.00
1.00
1.00
3.02
3.01
9.02
9.01
6.01
f1 (ppm)

3pa


172.45
152.05
144.70
130.25
128.65
125.77
122.50
116.49
111.48
80.93
52.70
46.59
28.43
17.67
14.34
13.80
12.23
7.24
2.21
Me
O
N
N
Me
SiEt3
N
Boc
3pa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.59
7.28
7.26
7.24
7.02
7.00
6.98
4.42
4.41
3.98
3.98
1.56
0.88
0.86
0.84
0.57
0.56
0.54
0.51
CN
SiEt3
N
Boc
3qa
1.00
2.02
1.02
1.01
1.01
9.01
8.99
6.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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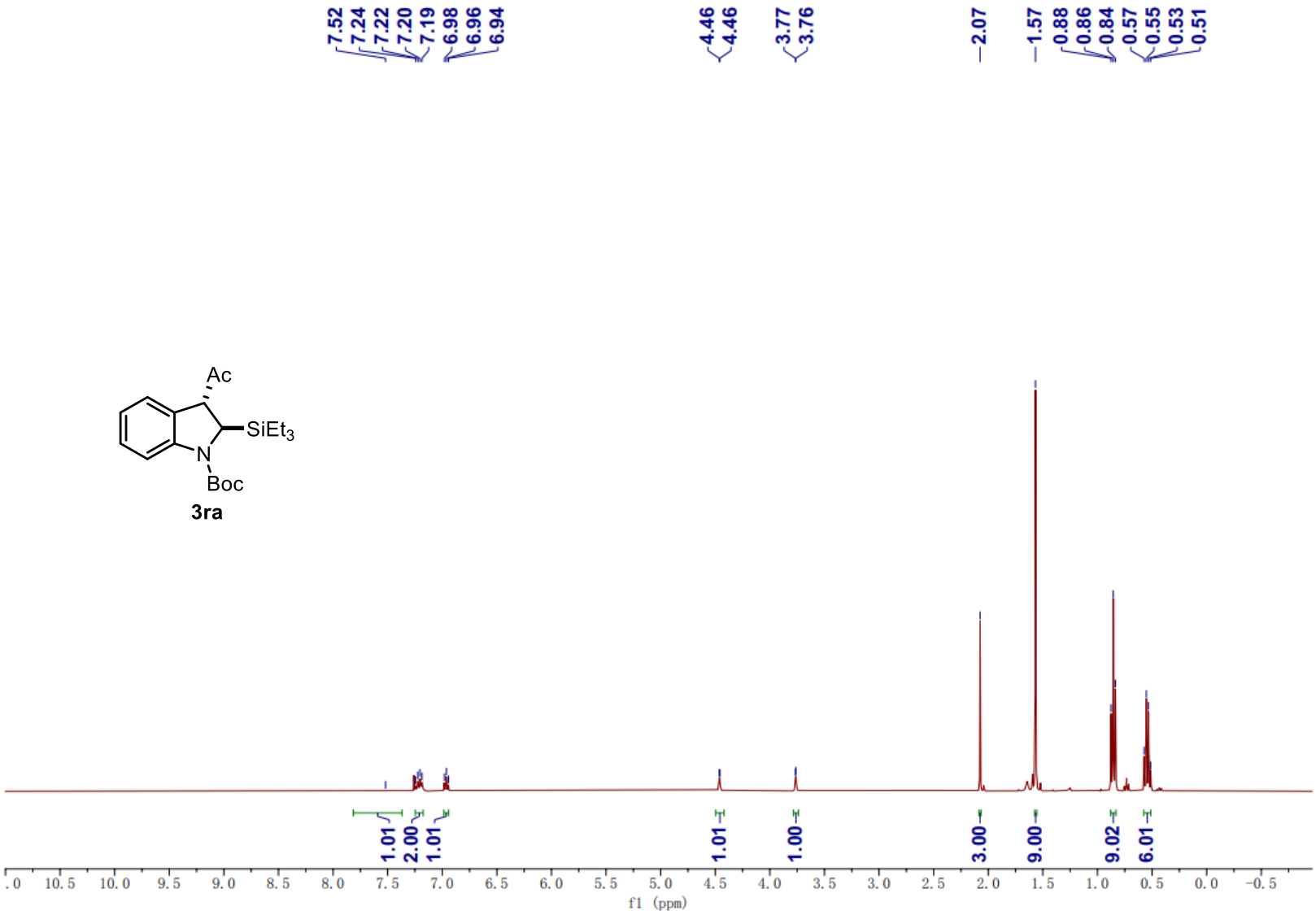
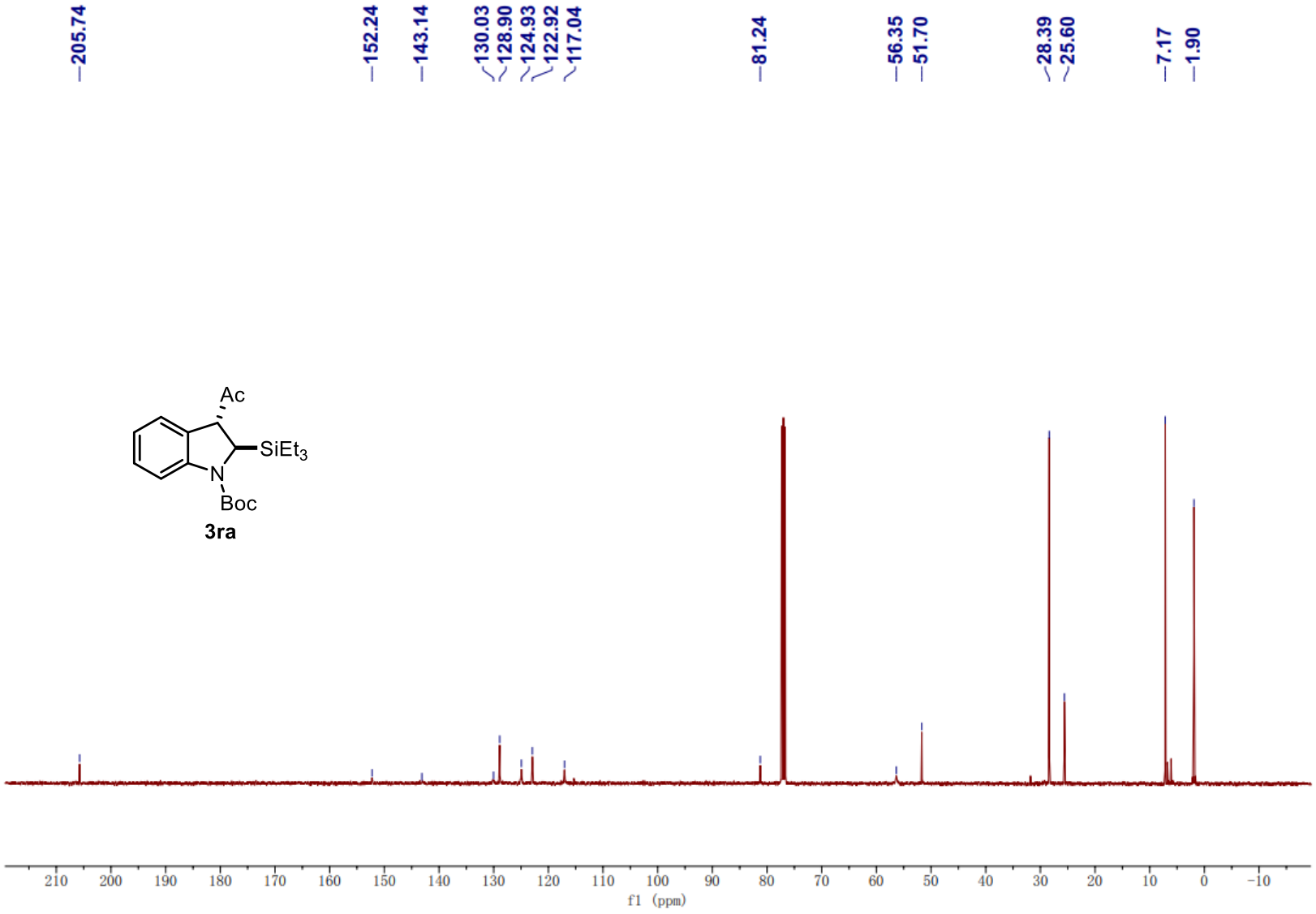
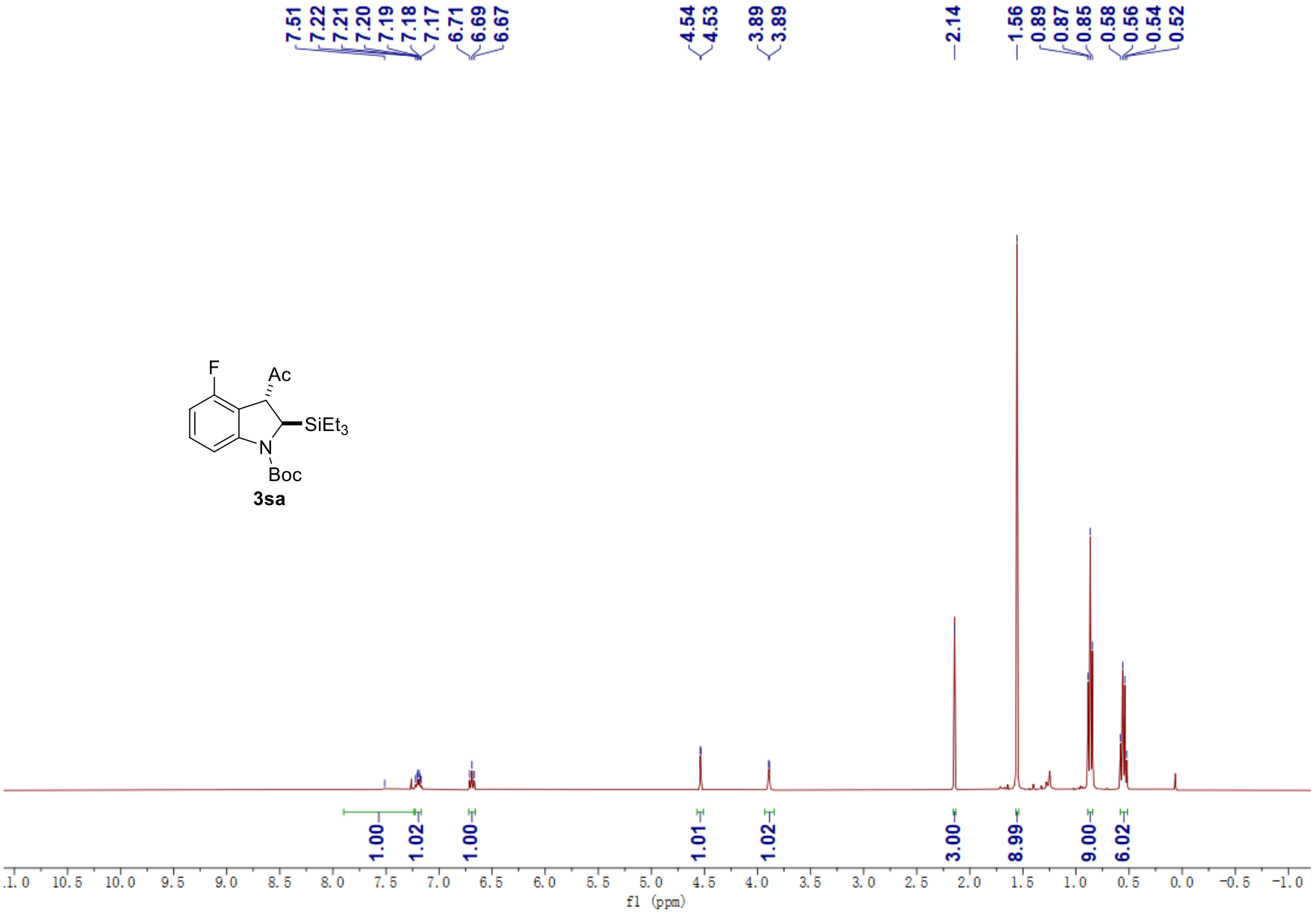
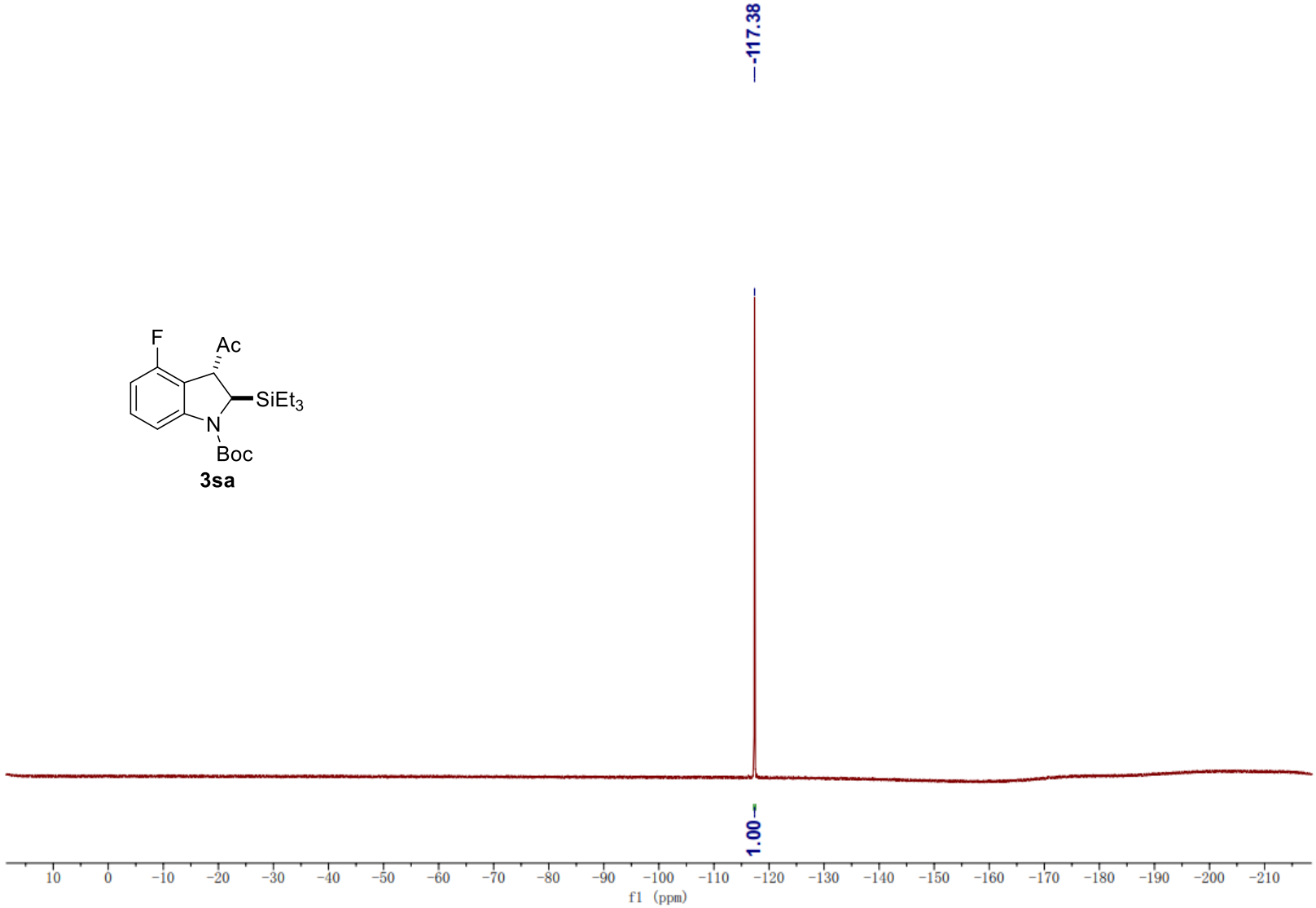
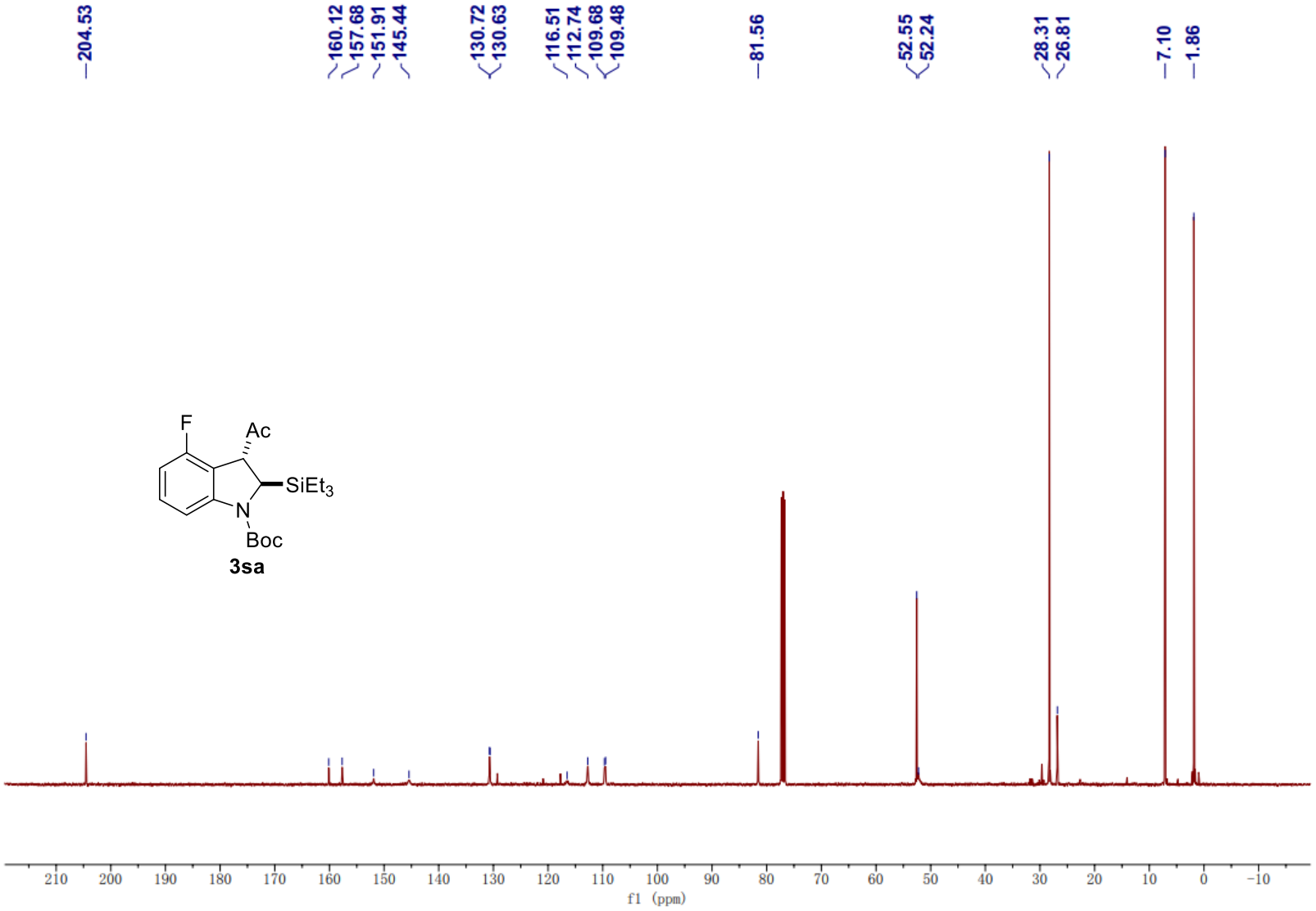
142.45
129.97
125.91
124.87
123.36
119.94
116.90
81.92
53.44
32.20
28.32
7.09
1.89
CN
SiEt3
N
Boc
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.52
7.24
7.22
7.20
7.19
6.98
6.96
6.94
4.46
4.46
3.77
3.76
2.07
1.57
0.88
0.86
0.84
0.57
0.55
0.53
0.51
Ac
SiEt3
N
Boc
3ra
1.01
2.00
1.01
1.01
1.00
3.00
9.00
9.02
6.01
f1 (ppm)


205.74
152.24
143.14
130.03
128.90
124.93
122.92
117.04
81.24
56.35
51.70
28.39
25.60
7.17
1.90
Ac
SiEt3
N
Boc
3ra
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.51
7.22
7.21
7.20
7.19
7.18
7.17
6.71
6.69
6.67
4.54
4.53
3.89
3.89
2.14
1.56
0.89
0.87
0.85
0.58
0.56
0.54
0.52
F
Ac
SiEt3
N
Boc
3sa
1.00
1.02
1.00
1.01
1.02
3.00
8.99
9.00
6.02
f1 (ppm)


-117.38
F
Ac
SiEt3
N
Boc
3sa
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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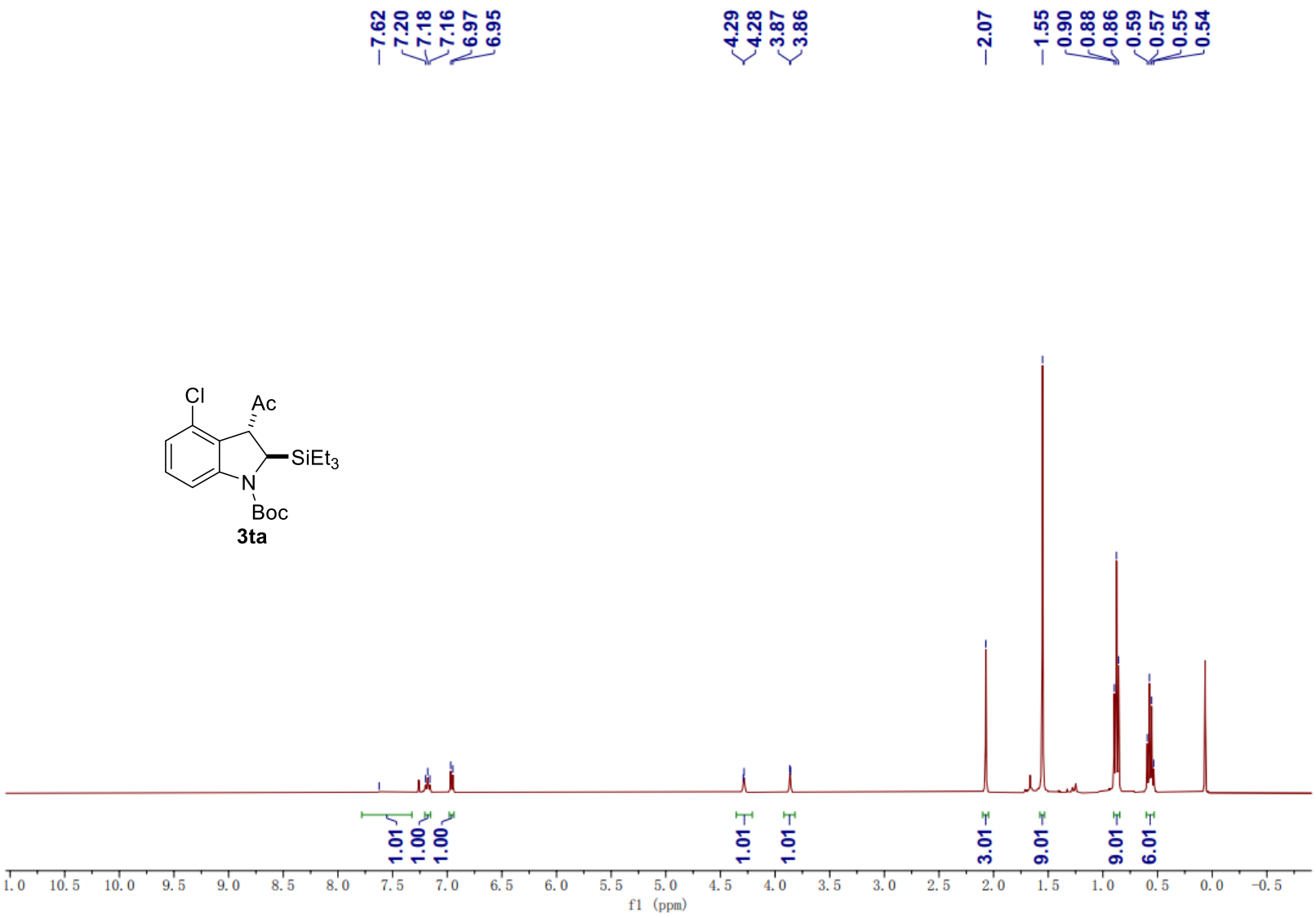
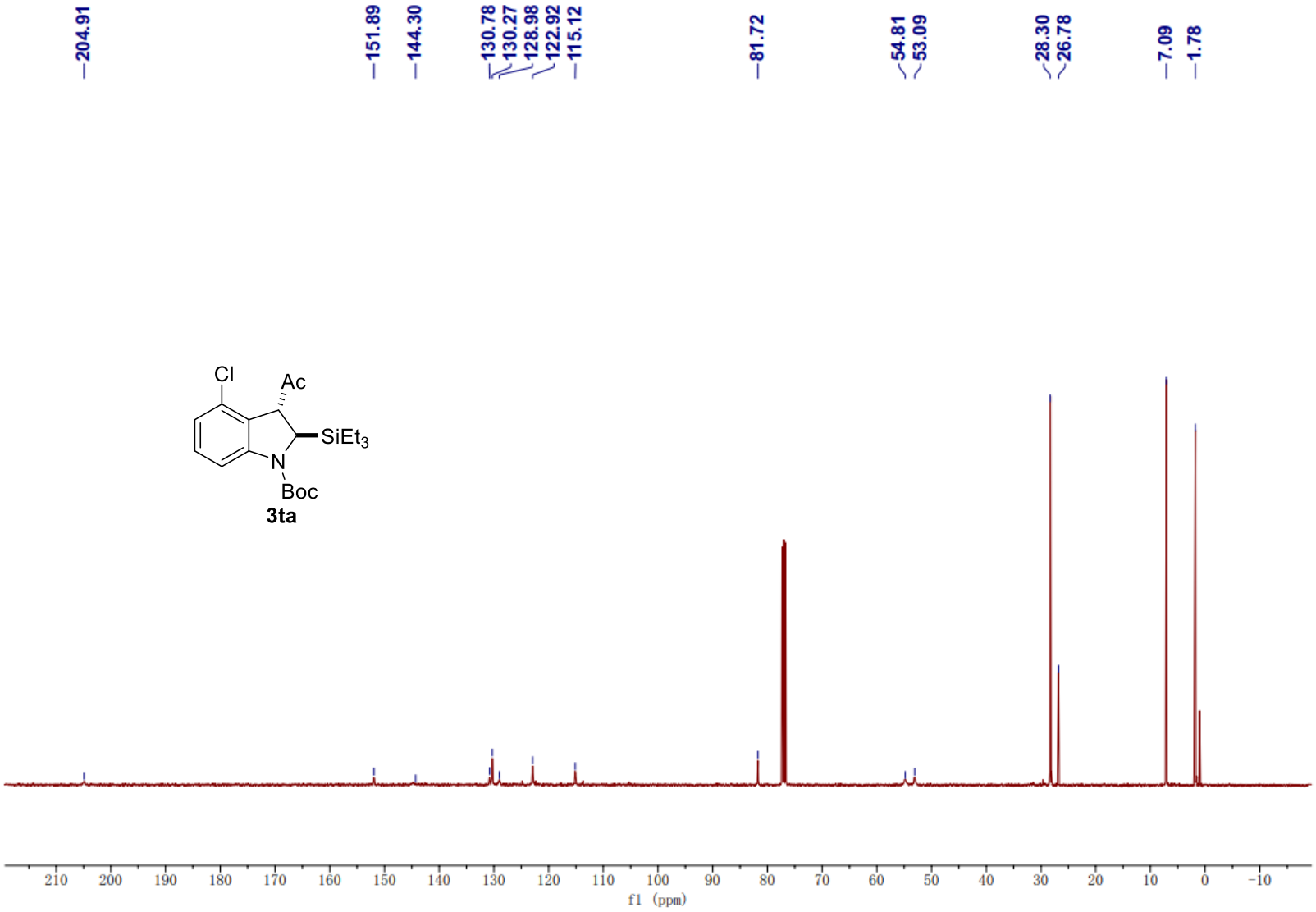
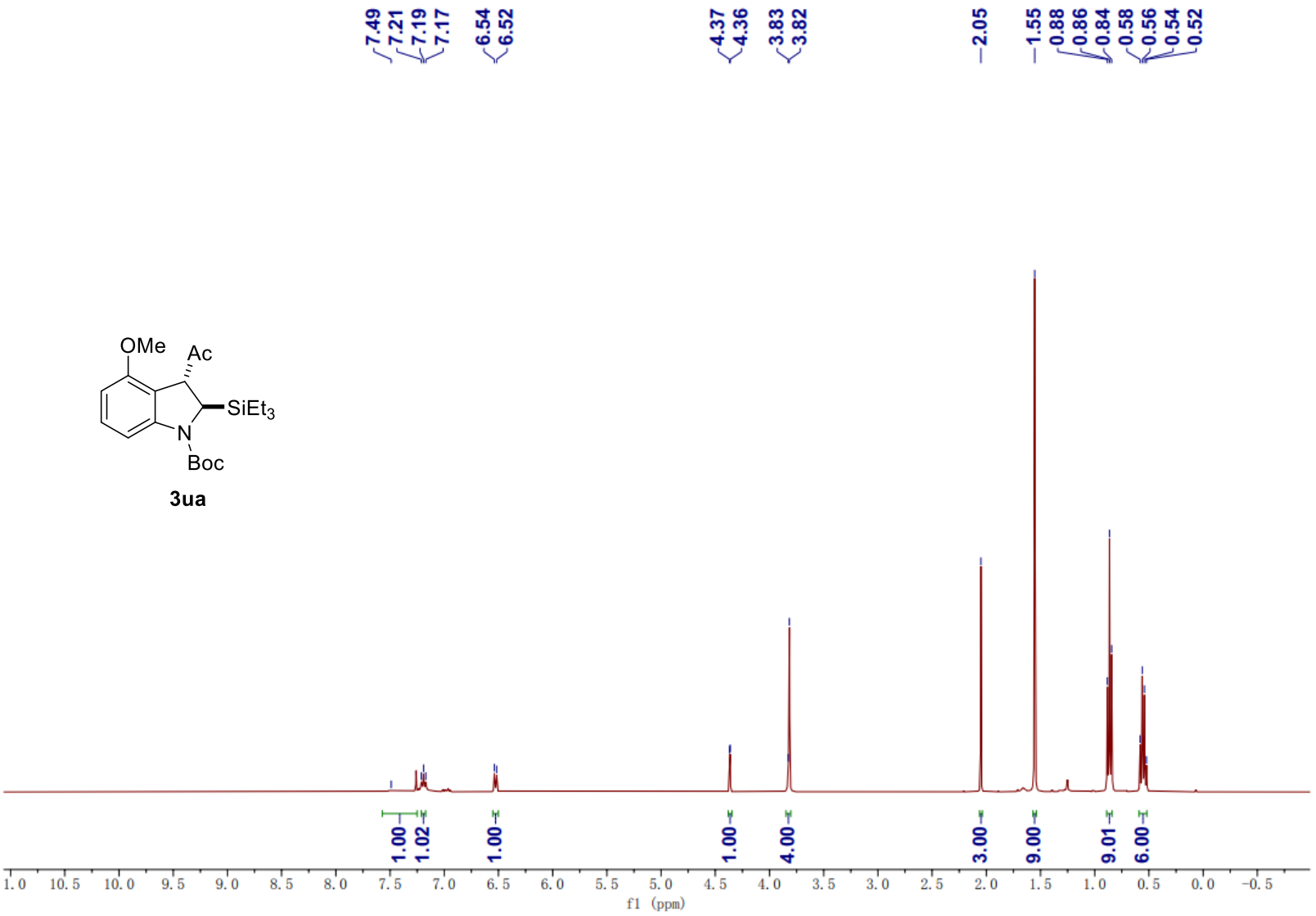
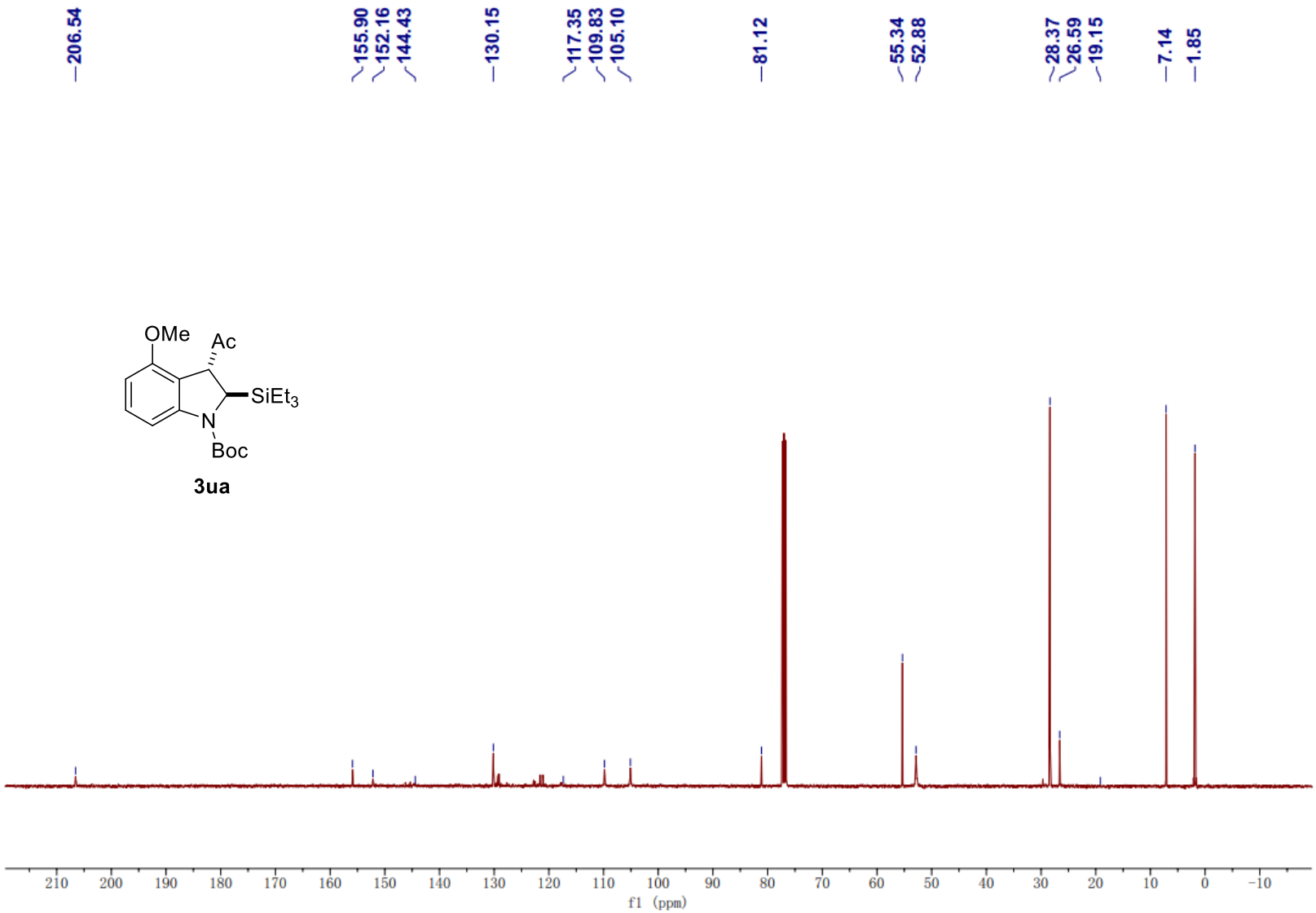
130.72
130.63
116.51
112.74
109.68
109.48
81.56
52.55
52.24
28.31
26.81
7.10
1.86
F
Ac
SiEt3
N
Boc
3sa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.62
7.20
7.18
7.16
6.97
6.95
4.29
4.28
3.87
3.86
2.07
1.55
0.90
0.88
0.86
0.59
0.57
0.55
0.54
Cl
Ac
SiEt3
N
Boc
3ta
1.01
1.00
1.00
1.01
1.01
3.01
9.01
9.01
6.01
f1 (ppm)


204.91
151.89
144.30
130.78
130.27
128.98
122.92
115.12
81.72
54.81
53.09
28.30
26.78
7.09
1.78
Cl
Ac
SiEt3
N
Boc
3ta
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.49
7.21
7.19
7.17
6.54
6.52
4.37
4.36
3.83
3.82
2.05
1.55
0.88
0.86
0.84
0.58
0.56
0.54
0.52
OMe
Ac
SiEt3
N
Boc
3ua
1.00
1.02
1.00
1.00
4.00
3.00
9.00
9.01
6.00
f1 (ppm)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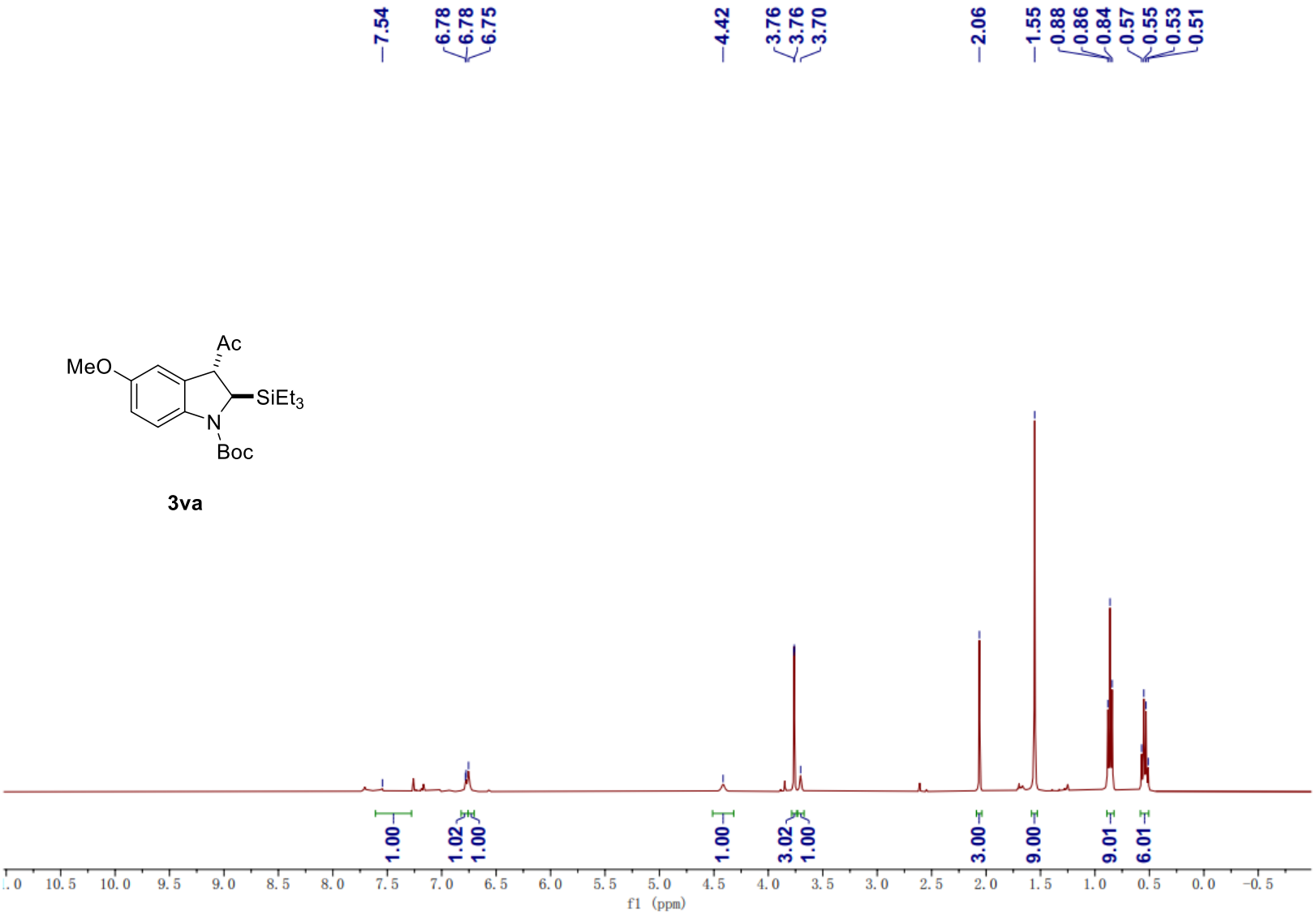
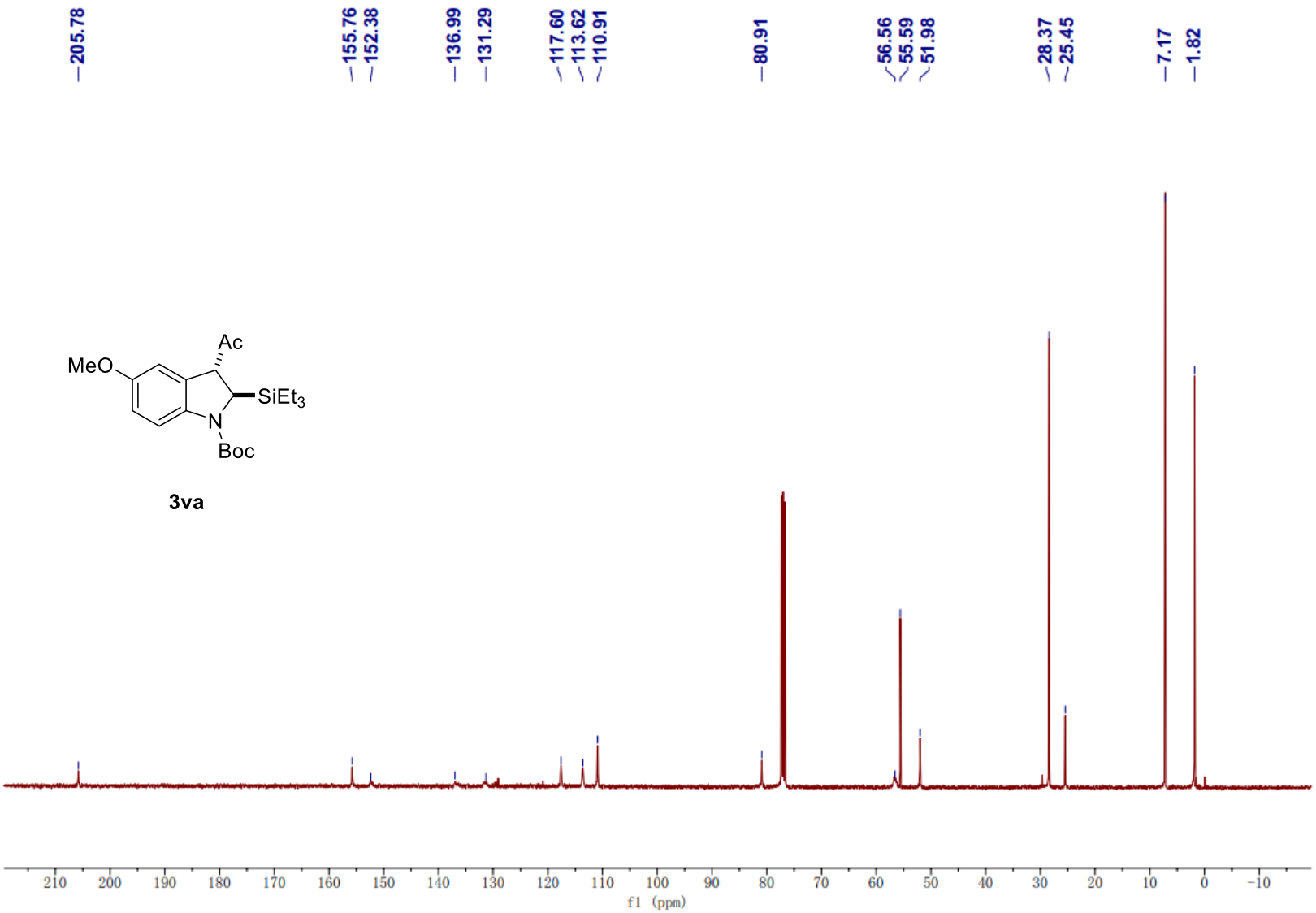
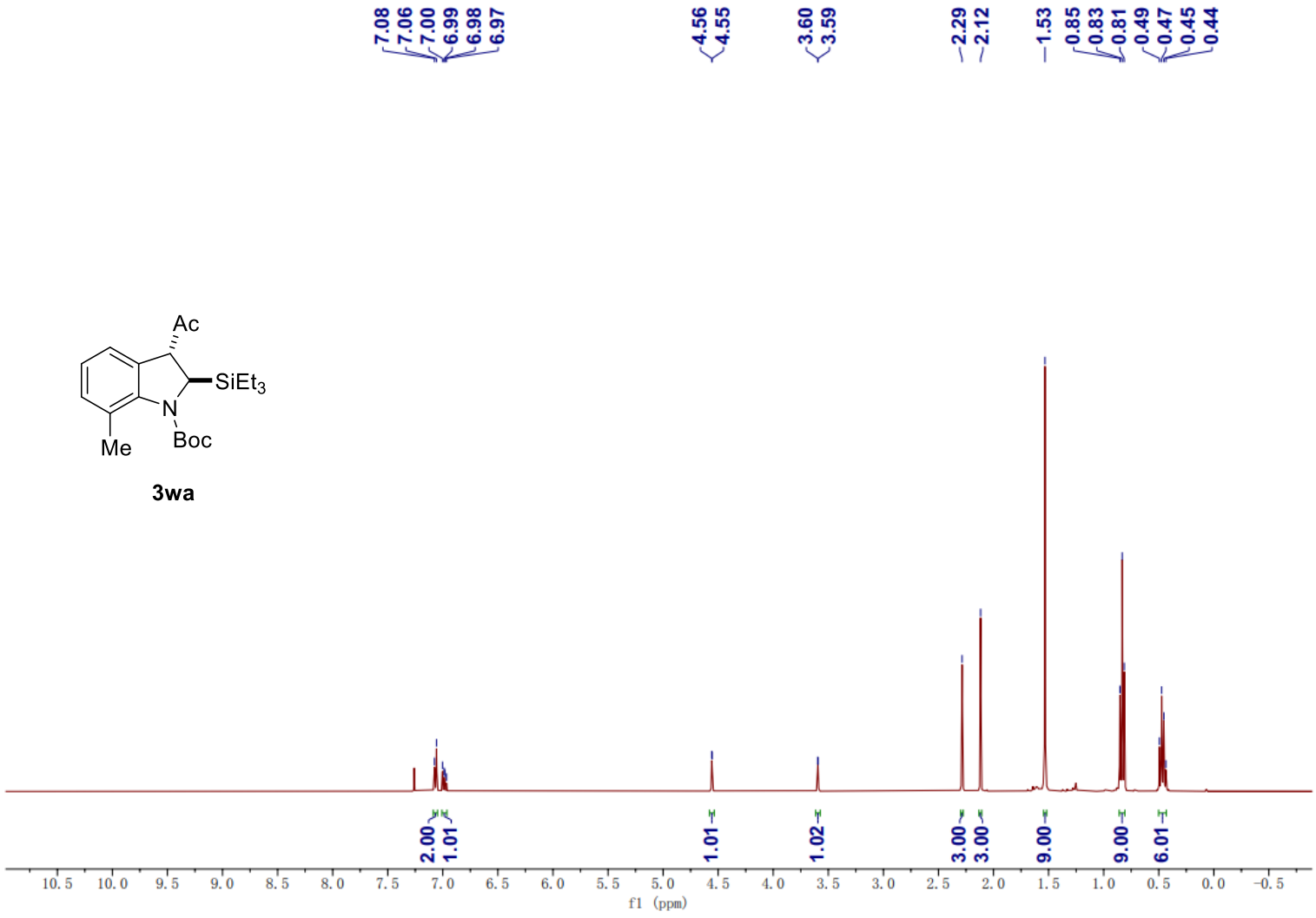
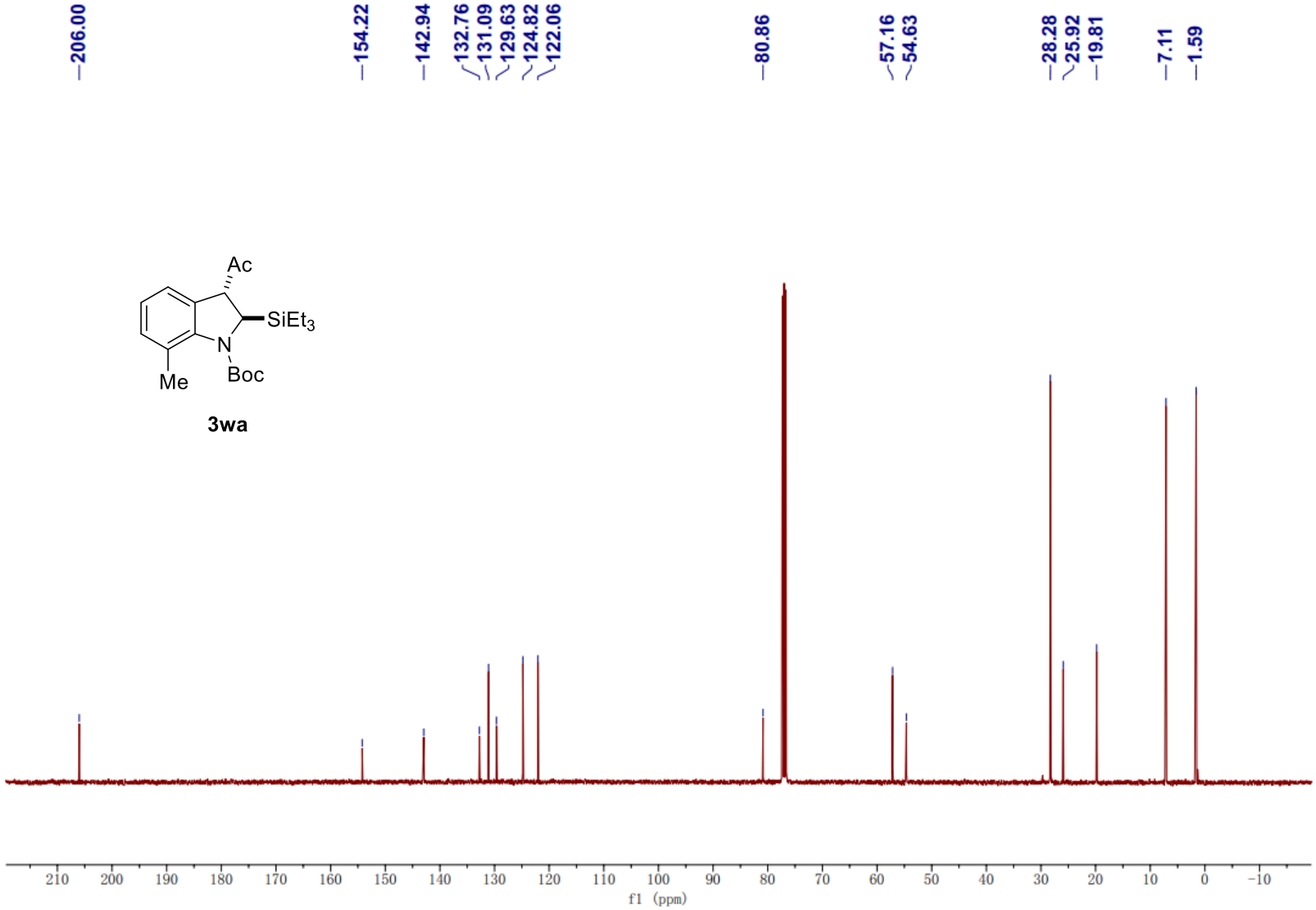
152.16
144.43
130.15
117.35
109.83
105.10
81.12
55.34
52.88
28.37
26.59
19.15
7.14
1.85
OMe
Ac
SiEt3
N
Boc
3ua
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

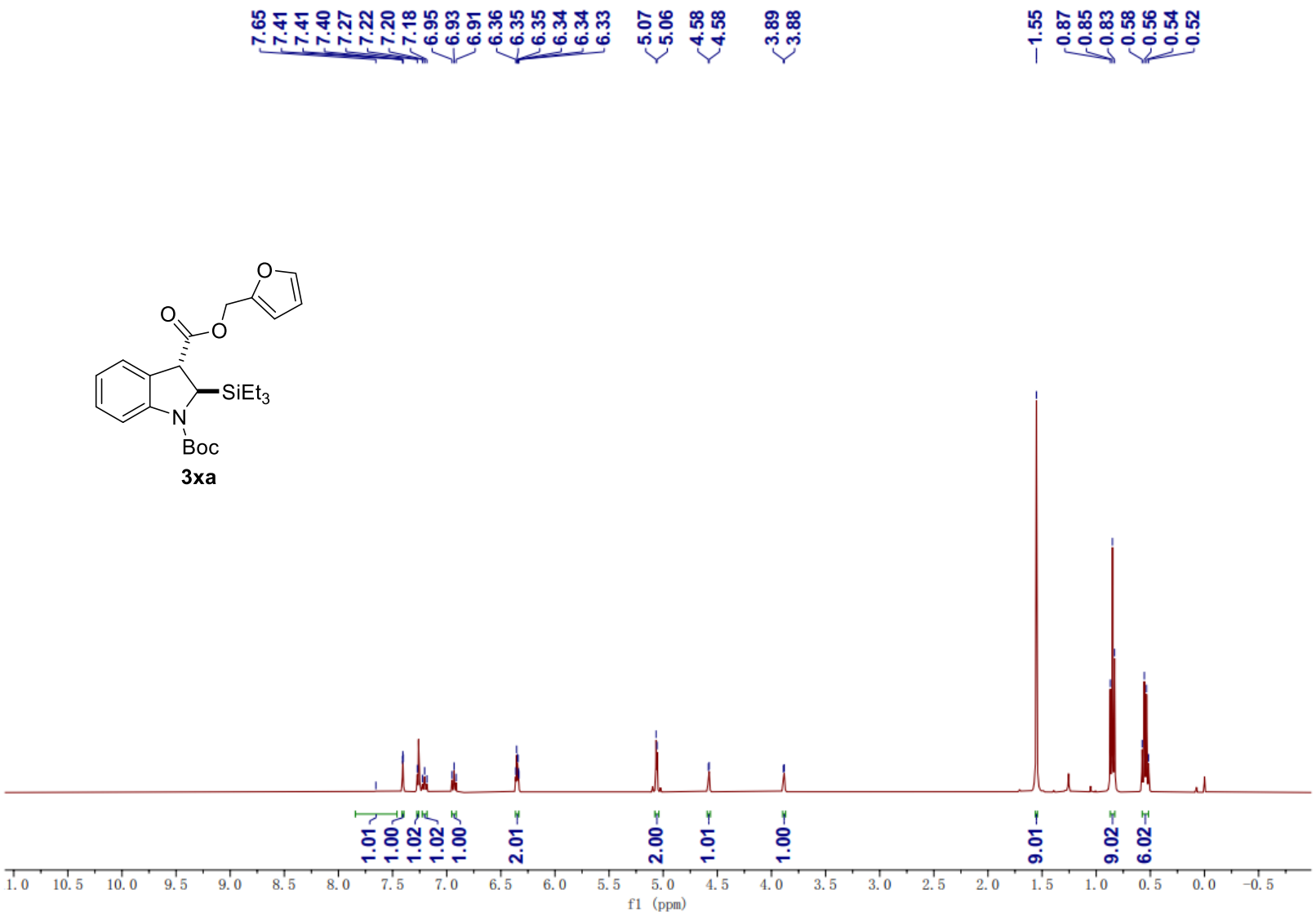

7.54
6.78
6.78
6.75
4.42
3.76
3.76
3.70
2.06
1.55
0.88
0.86
0.84
0.57
0.55
0.53
0.51
Ac
MeO
SiEt3
N
Boc
1.00
1.02
1.00
1.00
3.02
1.00
3.00
9.00
9.01
6.01
f1 (ppm)

3va


205.78
155.76
152.38
136.99
131.29
117.60
113.62
110.91
80.91
56.56
55.59
51.98
28.37
25.45
7.17
1.82
MeO
Ac
SiEt3
N
Boc
3va
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.08
7.06
7.00
6.99
6.98
6.97
4.56
4.55
3.60
3.59
2.29
2.12
1.53
0.85
0.83
0.81
0.49
0.47
0.45
0.44
Ac
SiEt3
N
Me
Boc
3wa
2.00
1.01
1.01
1.02
3.00
3.00
9.00
9.00
6.01
f1 (ppm)


206.00
154.22
142.94
132.76
131.09
129.63
124.82
122.06
80.86
57.16
54.63
28.28
25.92
19.81
7.11
1.59
Ac
SiEt3
N
Boc
Me
3wa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.41
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7.18
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6.93
6.91
6.36
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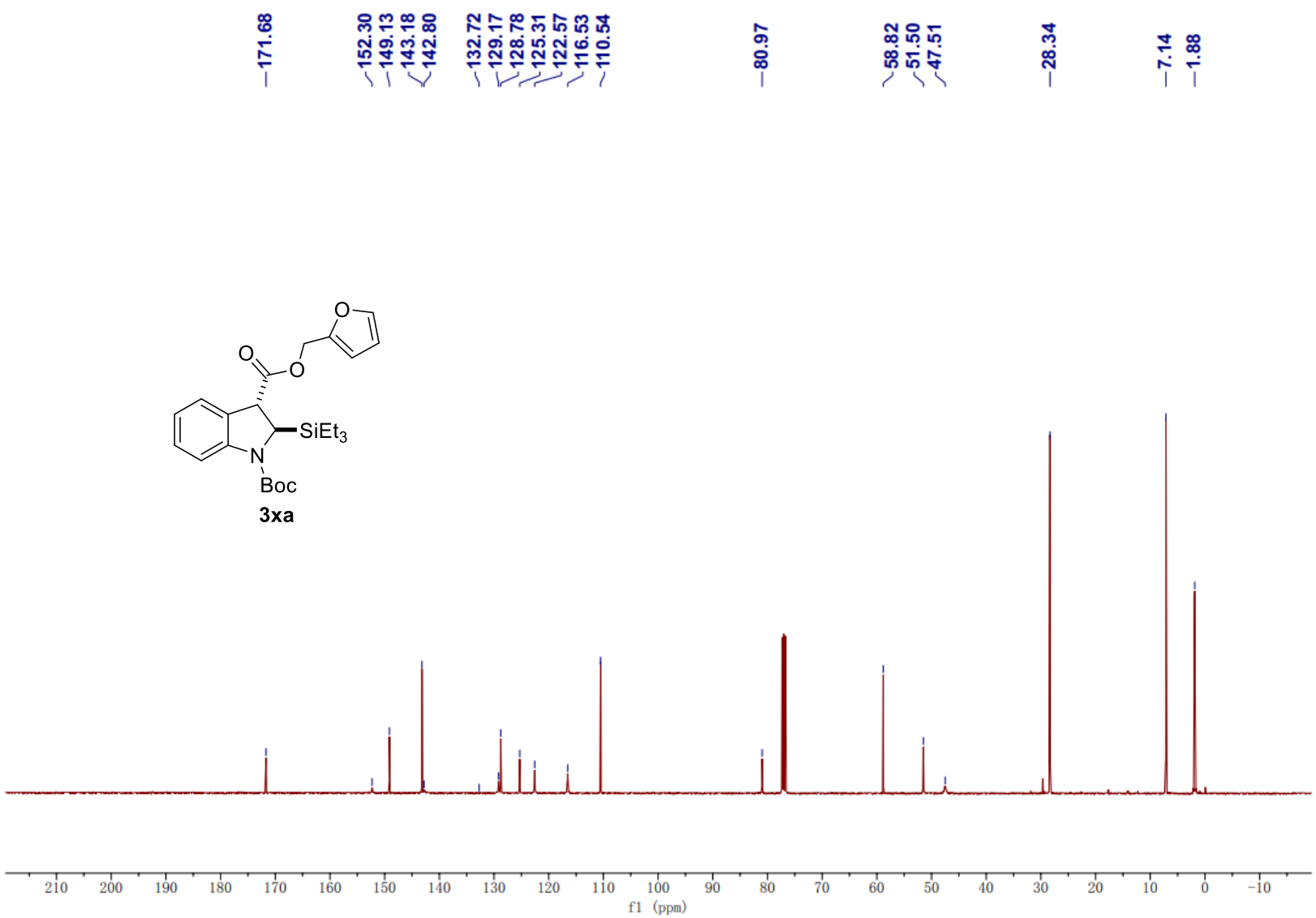
6.35
6.34
6.34
6.33
5.07
5.06
4.58
4.58
3.89
3.88
1.55
0.87
0.85
0.83
0.58
0.56
0.54
0.52
O
O
O
SiEt3
N
Boc
3xa
1.01
1.00
1.02
1.02
1.00
2.01
2.00
1.01
1.00
9.01
9.02
6.02
f1 (ppm)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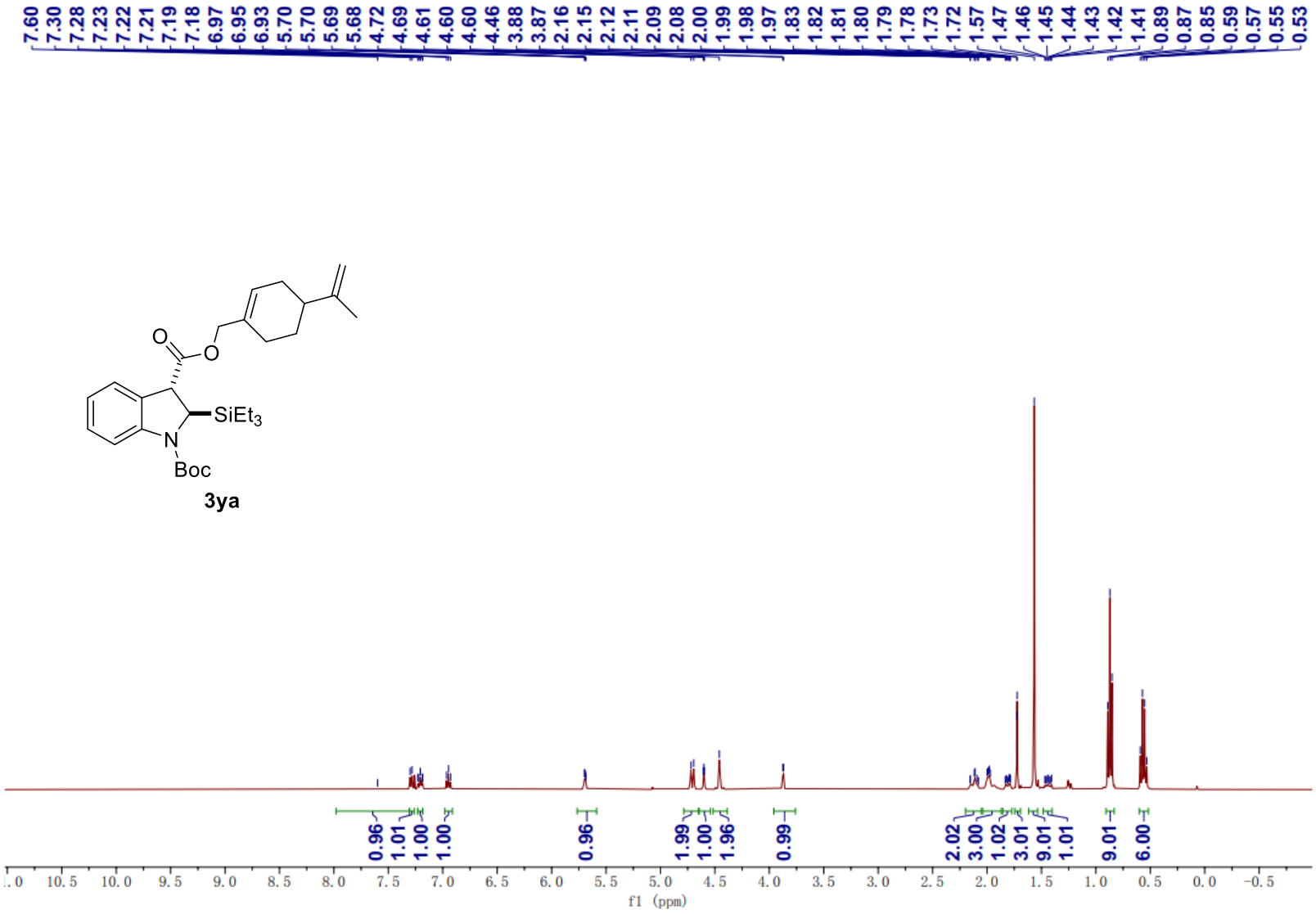
129.17
128.78
125.31
122.57
116.53
110.54
80.97
58.82
51.50
47.51
28.34
7.14
1.88
O
O
O
SiEt3
N
Boc
3xa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.18
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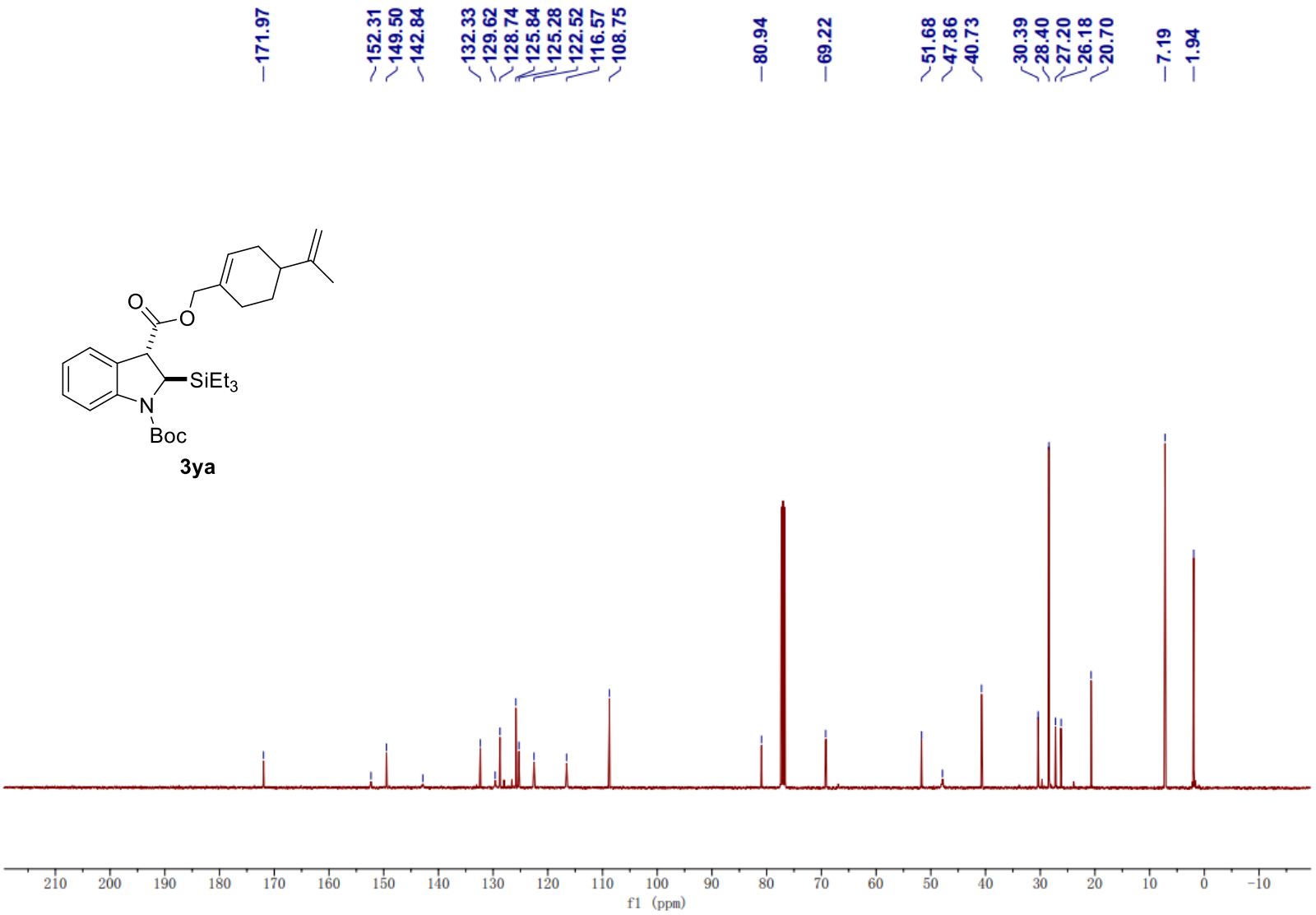
6.95
6.93
5.70
5.70
5.69
5.68
4.72
4.69
4.61
4.60
4.60
4.46
3.88
3.87
2.16
2.15
2.12
2.11
2.09
2.08
2.00
1.99
1.98
1.97
1.83
1.82
1.81
1.80
1.79
1.78
1.73
1.72
1.57
1.47
1.46
1.45
1.44
1.43
1.42
1.41
0.89
0.87
0.85
0.59
0.57
0.55
0.53
O
O
SiEt3
N
Boc
3ya
0.96
1.01
1.00
1.00
0.96
1.99
1.00
1.96
0.99
2.02
3.00
1.02
3.01
9.01
1.01
9.01
6.00
f1 (ppm)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108.75
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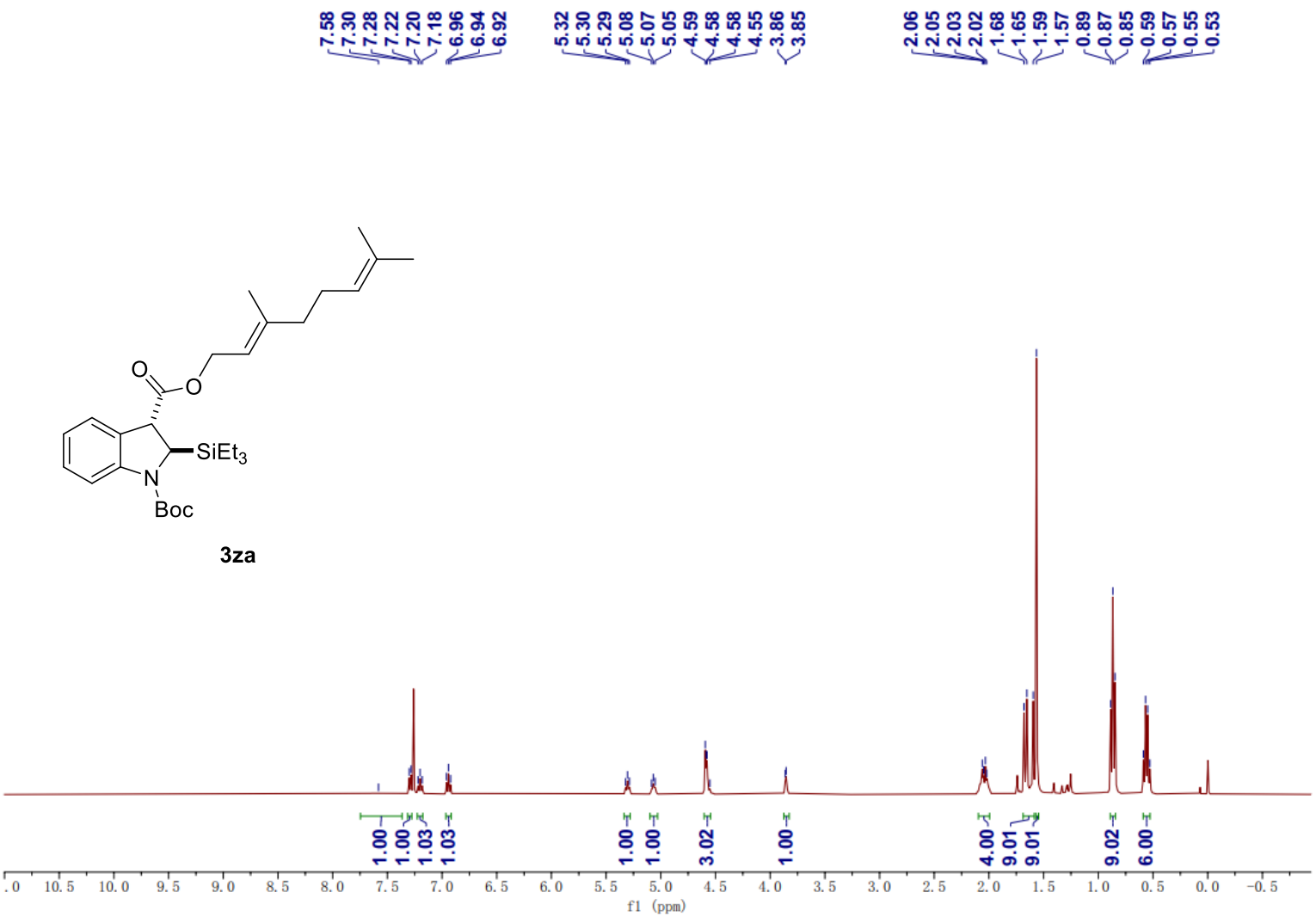
69.22
51.68
47.86
40.73
30.39
28.40
27.20
26.18
20.70
7.19
1.94
O
O
SiEt3
N
Boc
3ya
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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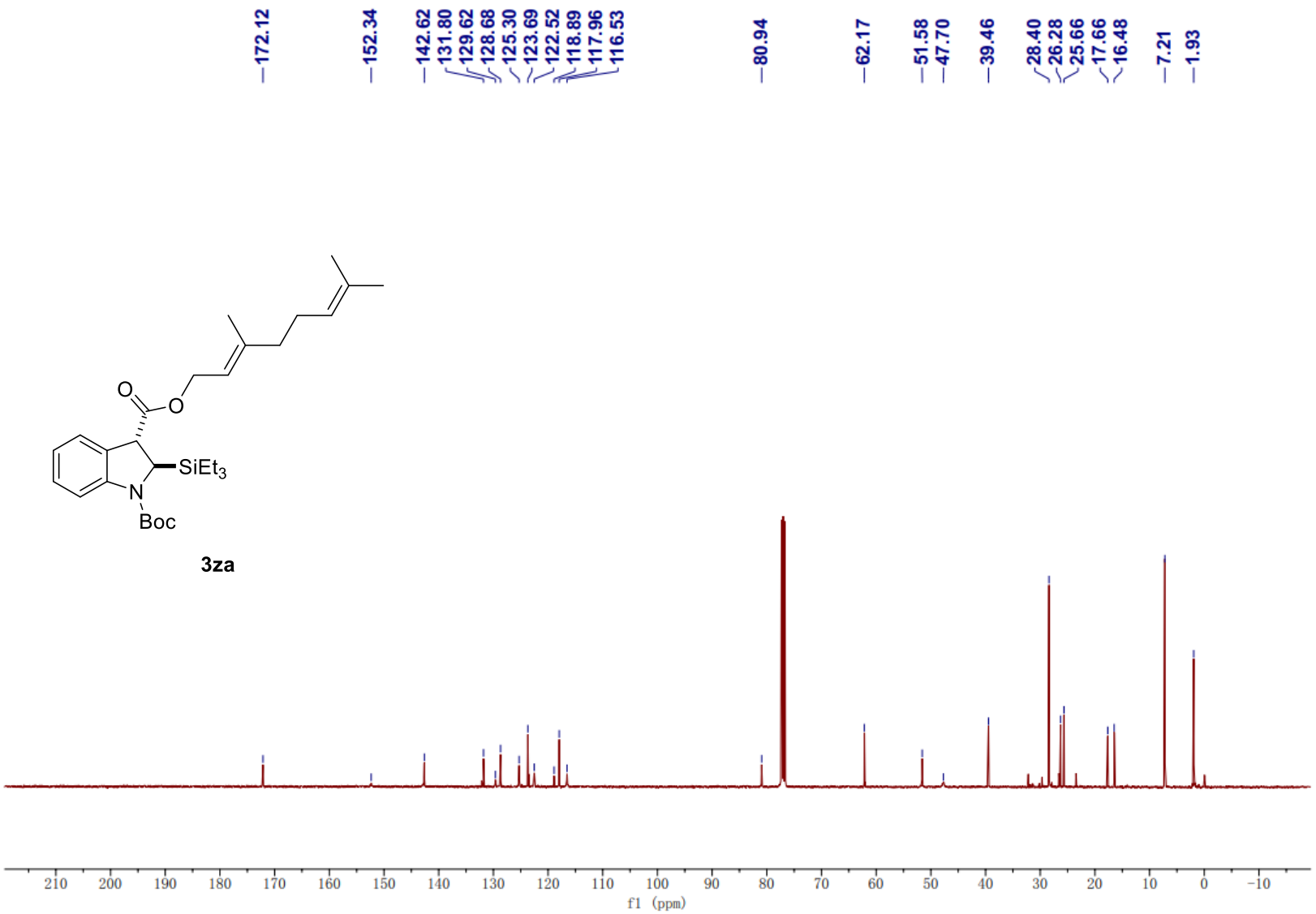
5.30
5.29
5.08
5.07
5.05
4.59
4.58
4.58
4.55
3.86
3.85
2.06
2.05
2.03
2.02
1.68
1.65
1.59
1.57
0.89
0.87
0.85
0.59
0.57
0.55
0.53
O
O
SiEt3
N
Boc
1.00
1.00
1.03
1.03
1.00
1.00
3.02
1.00
4.00
9.01
9.01
9.02
6.00
f1 (ppm)

3za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131.80
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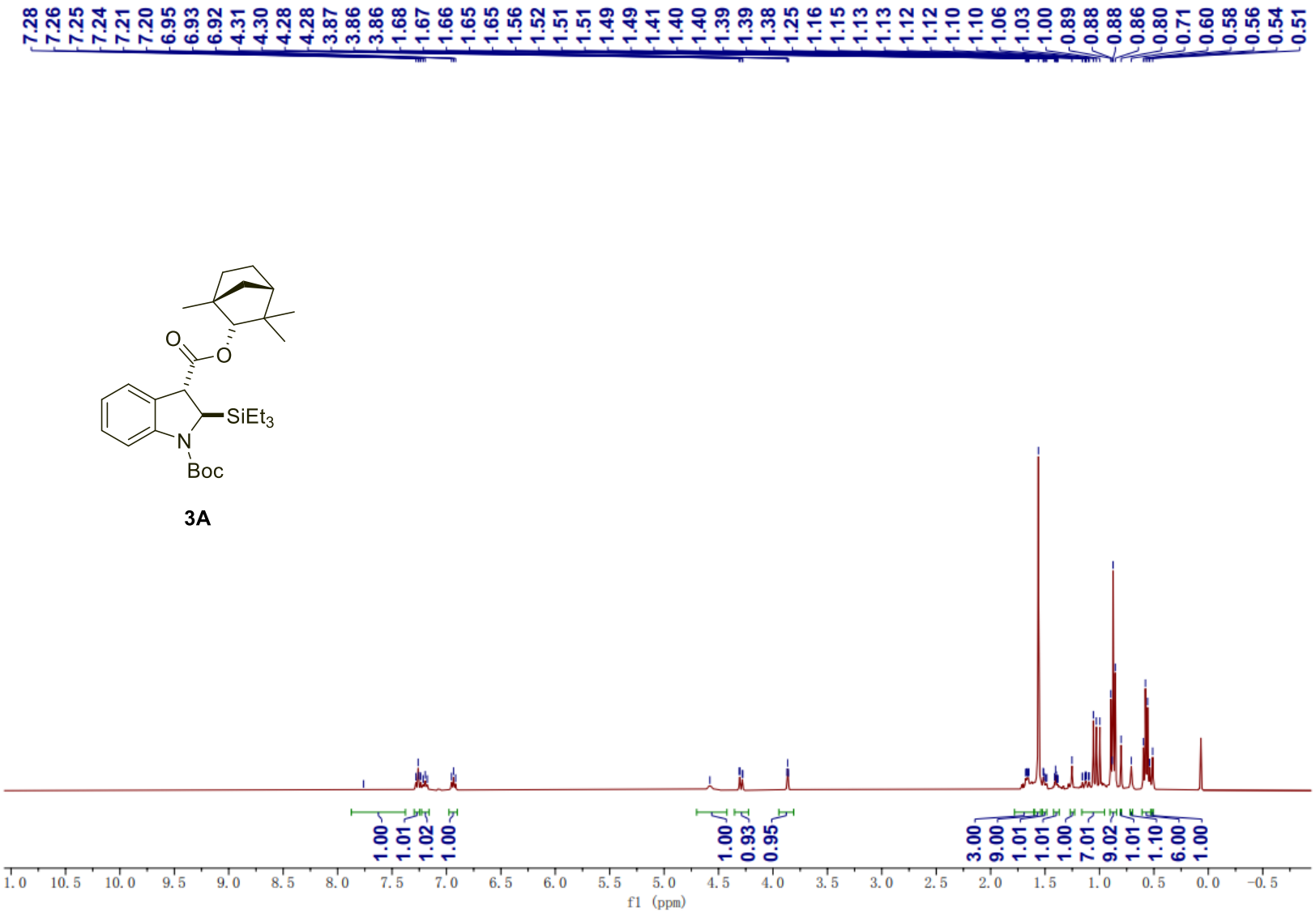
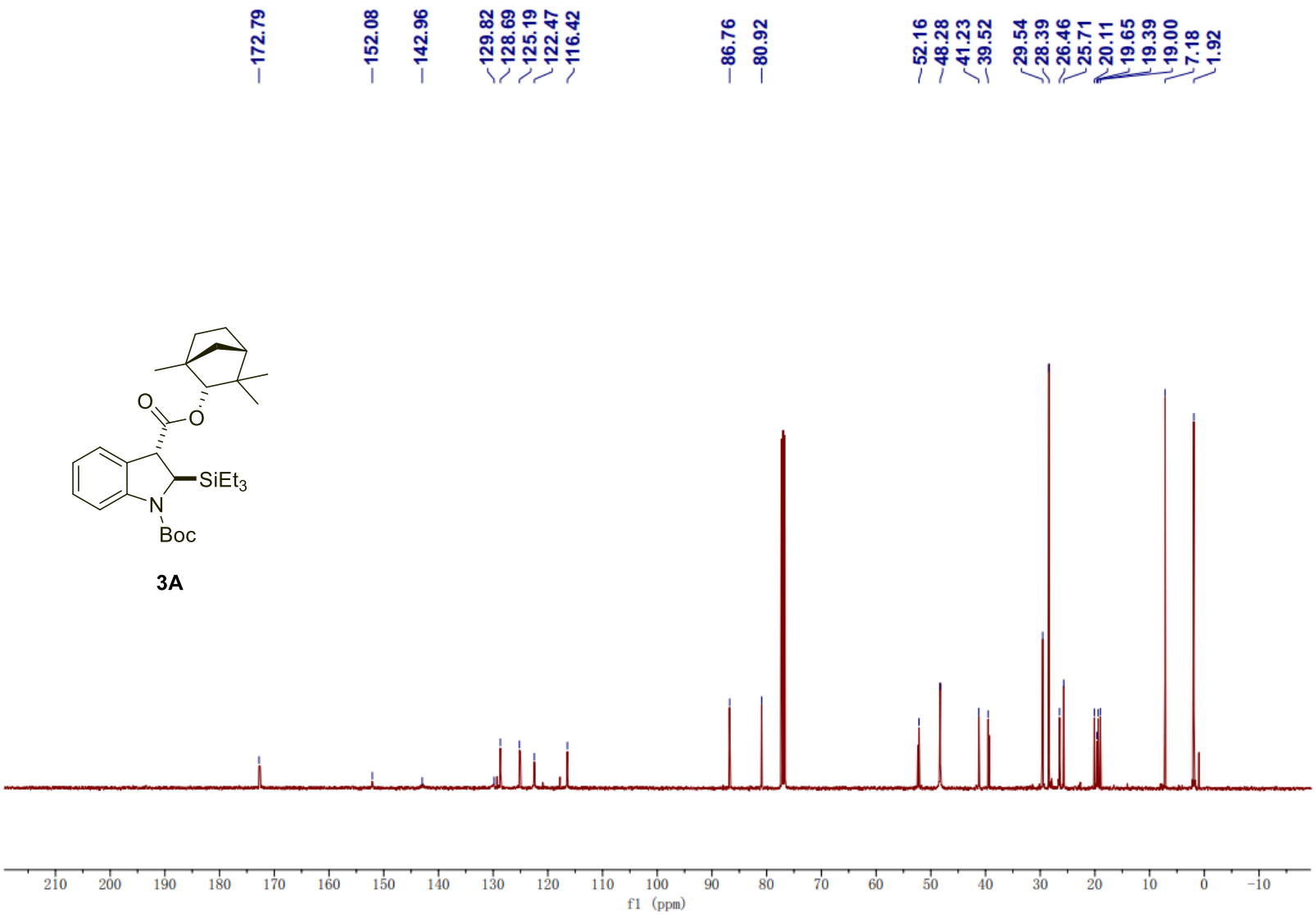
128.68
125.30
123.69
122.52
118.89
117.96
116.53
80.94
62.17
51.58
47.70
39.46
28.40
26.28
25.66
17.66
16.48
7.21
1.93
O
O
SiEt3
N
Boc
3za
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.28 7.26 7.25 7.24 7.21 7.20 6.95 6.93 6.92 4.31 4.30 4.28 4.28 3.87 3.86 3.86 1.68 1.67 1.66 1.65 1.65 1.56 1.52 1.51 1.51 1.49 1.49 1.41 1.40 1.40 1.39 1.39 1.38 1.25 1.16 1.15 1.13 1.13 1.12 1.12 1.10 1.10 1.06 1.03 1.00 0.89 0.88 0.88 0.86 0.80 0.71 0.60 0.58 0.56 0.54 0.51
O
O
SiEt3
N
Boc
3A
1.00 1.01 1.02 1.00 1.00 0.93 0.95 3.00 9.00 1.01 1.01 1.00 7.01 9.02 1.01 1.10 6.00 1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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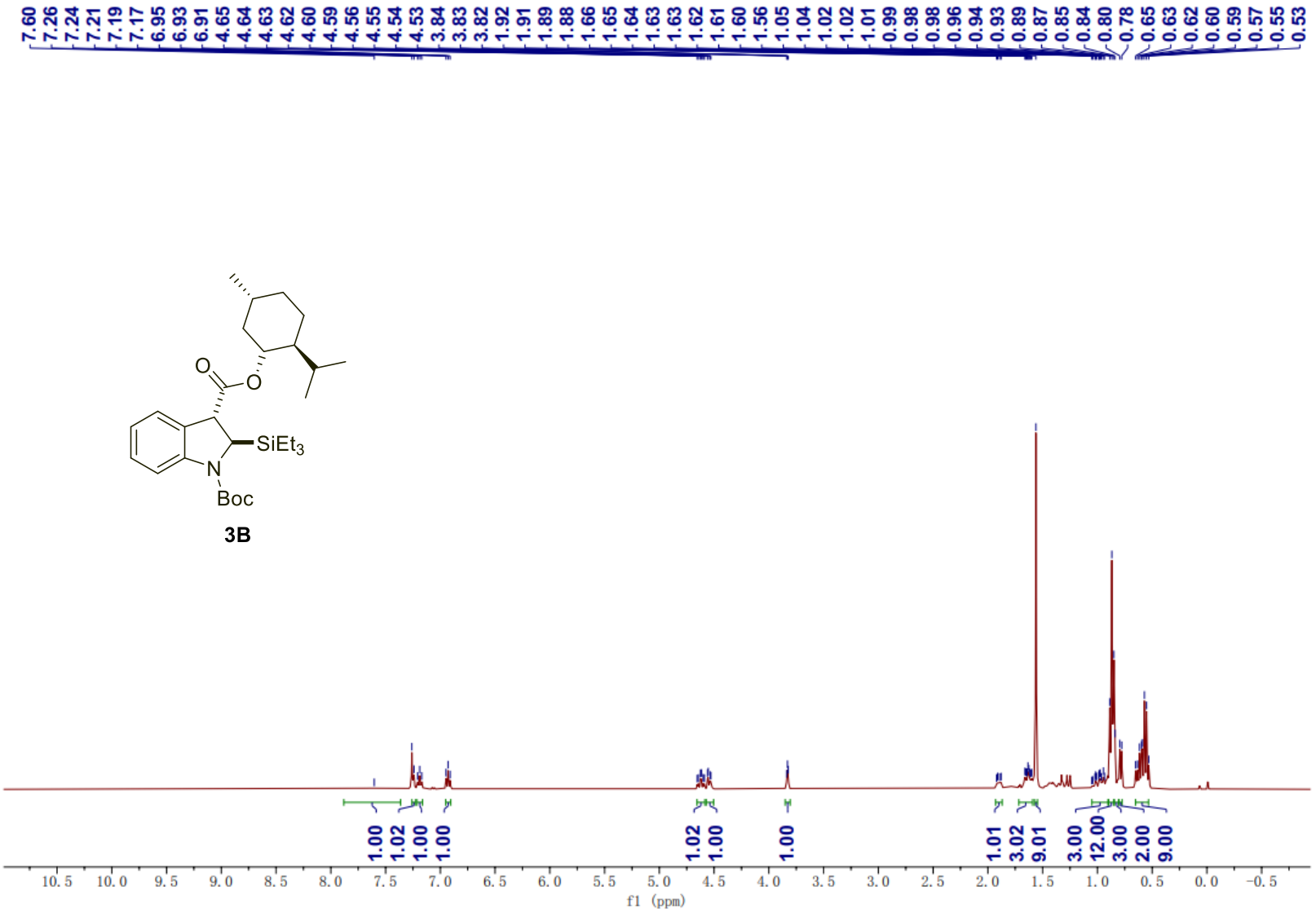
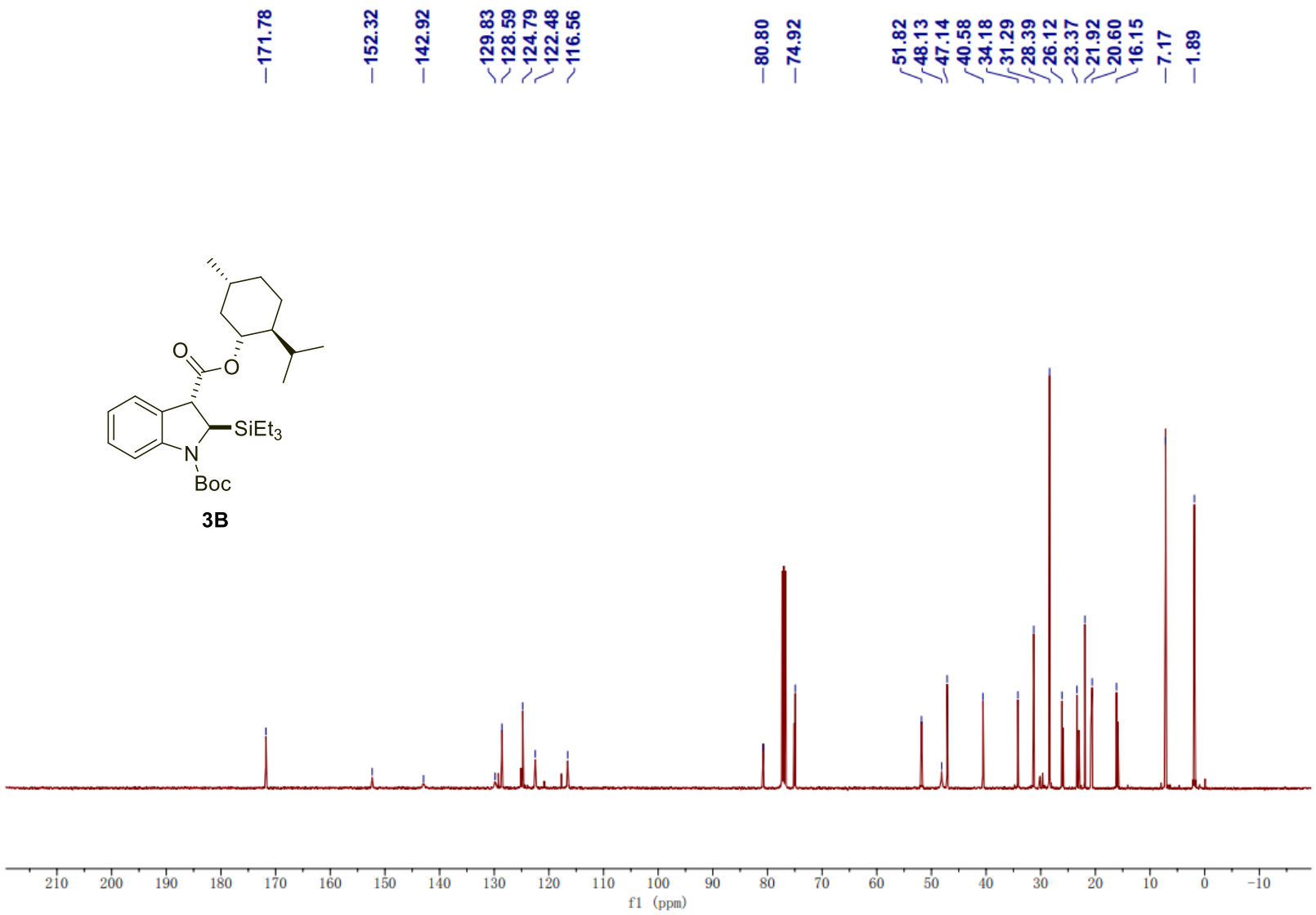
125.19
122.47
116.42
86.76
80.92
52.16
48.28
41.23
39.52
29.54
28.39
26.46
25.71
20.11
19.65
19.39
19.00
7.18
1.92
O
O
SiEt3
N
Boc
3A
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.60 7.26 7.24 7.21 7.19 7.17 6.95 6.93 6.91 4.65 4.64 4.63 4.62 4.60 4.59 4.56 4.55 4.54 4.53 3.84 3.83 3.82 1.92 1.91 1.89 1.88 1.66 1.65 1.64 1.63 1.63 1.62 1.61 1.60 1.56 1.05 1.04 1.02 1.02 1.01 0.99 0.98 0.98 0.96 0.94 0.93 0.89 0.87 0.85 0.84 0.80 0.78 0.65 0.63 0.62 0.60 0.59 0.57 0.55 0.53
O
O
SiEt3
N
Boc
3B
1.00 1.02 1.00 1.00 1.02 1.00 1.00 1.01 3.02 9.01 3.00 12.00 3.00 2.00 9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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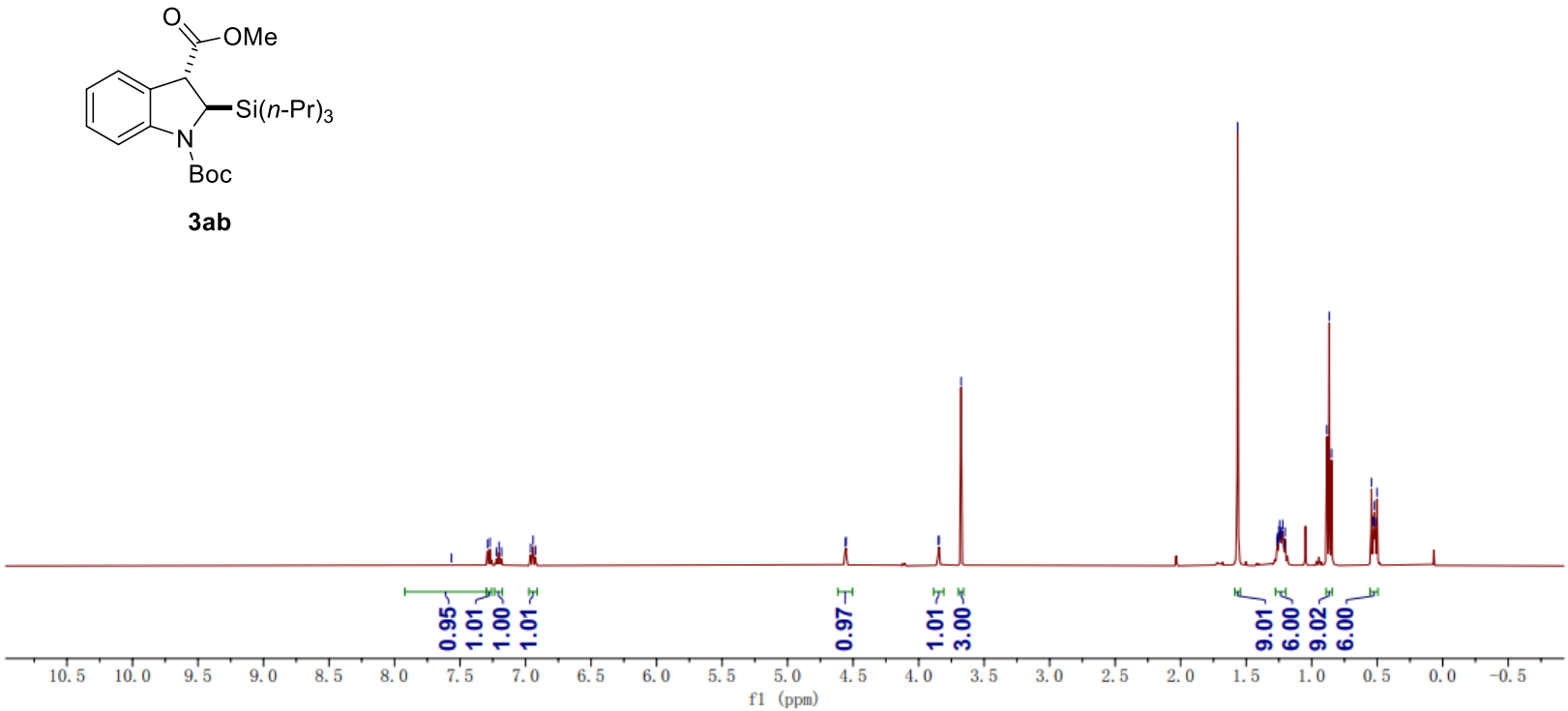
124.79
122.48
116.56
80.80
74.92
51.82
48.13
47.14
40.58
34.18
31.29
28.39
26.12
23.37
21.92
20.60
16.15
7.17
1.89
O
O
SiEt3
N
Boc
3B
f1 (ppm)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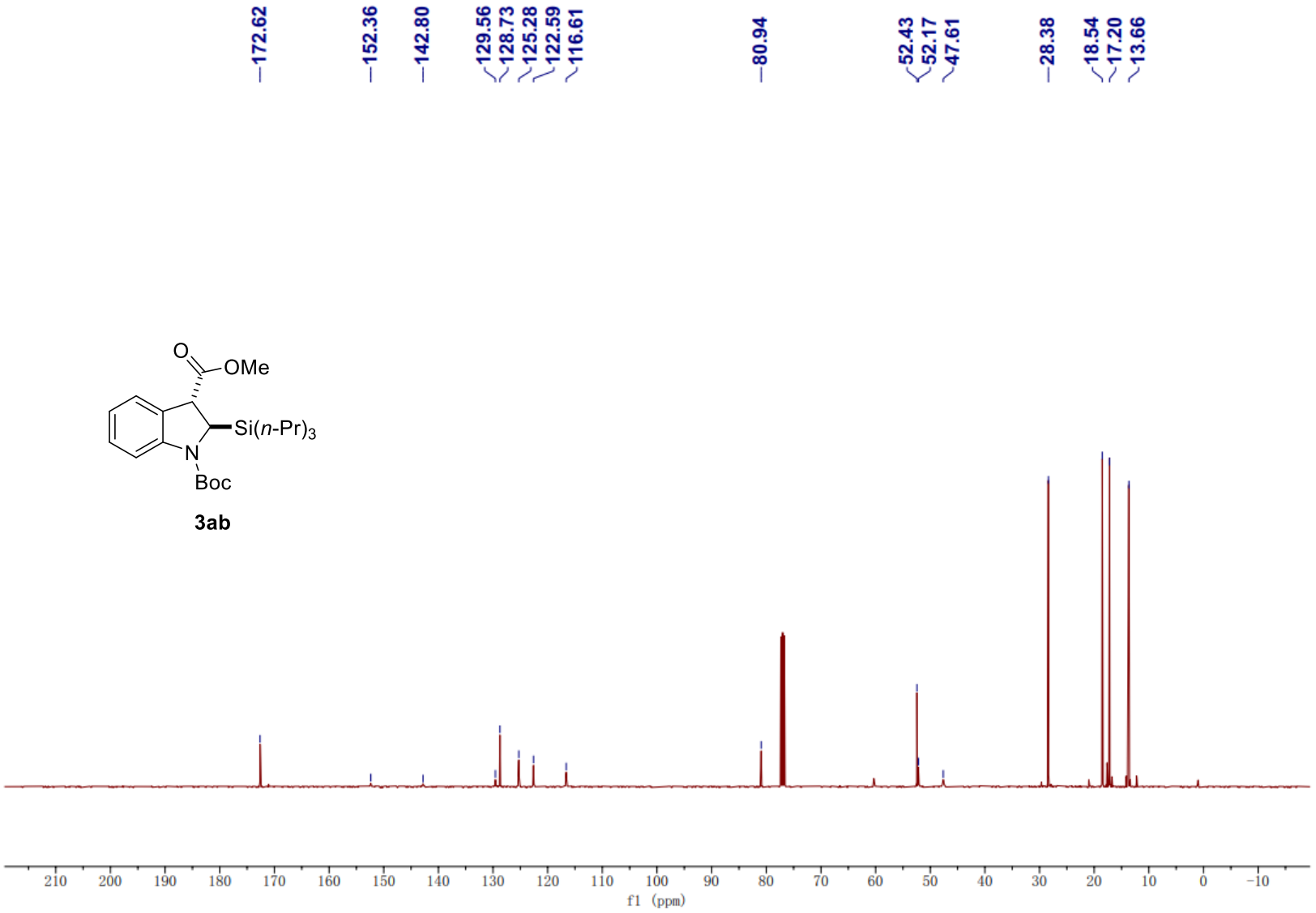
7.29
7.27
7.22
7.20
7.18
6.96
6.94
6.92
4.56
4.55
3.85
3.84
3.68
1.57
1.27
1.26
1.25
1.25
1.24
1.24
1.24
1.23
1.22
1.21
1.20
0.88
0.87
0.85
0.54
0.53
0.52
0.51
0.50
O
OMe
Si(n-Pr)3
N
Boc
3ab
0.95
1.01
1.00
1.01
0.97
1.01
3.00
9.01
6.00
9.02
6.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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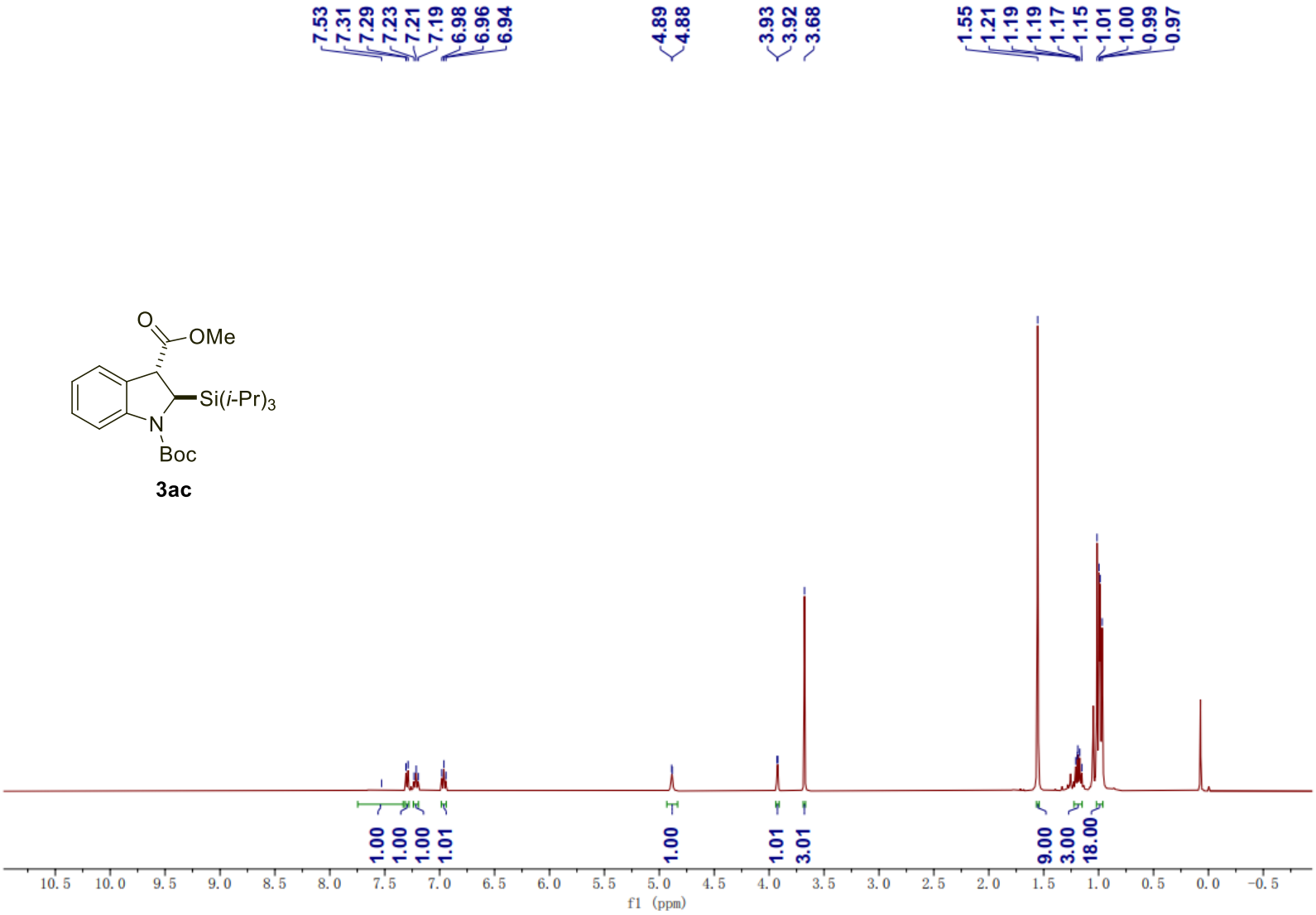
125.28
122.59
116.61
80.94
52.43
52.17
47.61
28.38
18.54
17.20
13.66
O
OMe
Si(n-Pr)3
N
Boc
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.31
7.29
7.23
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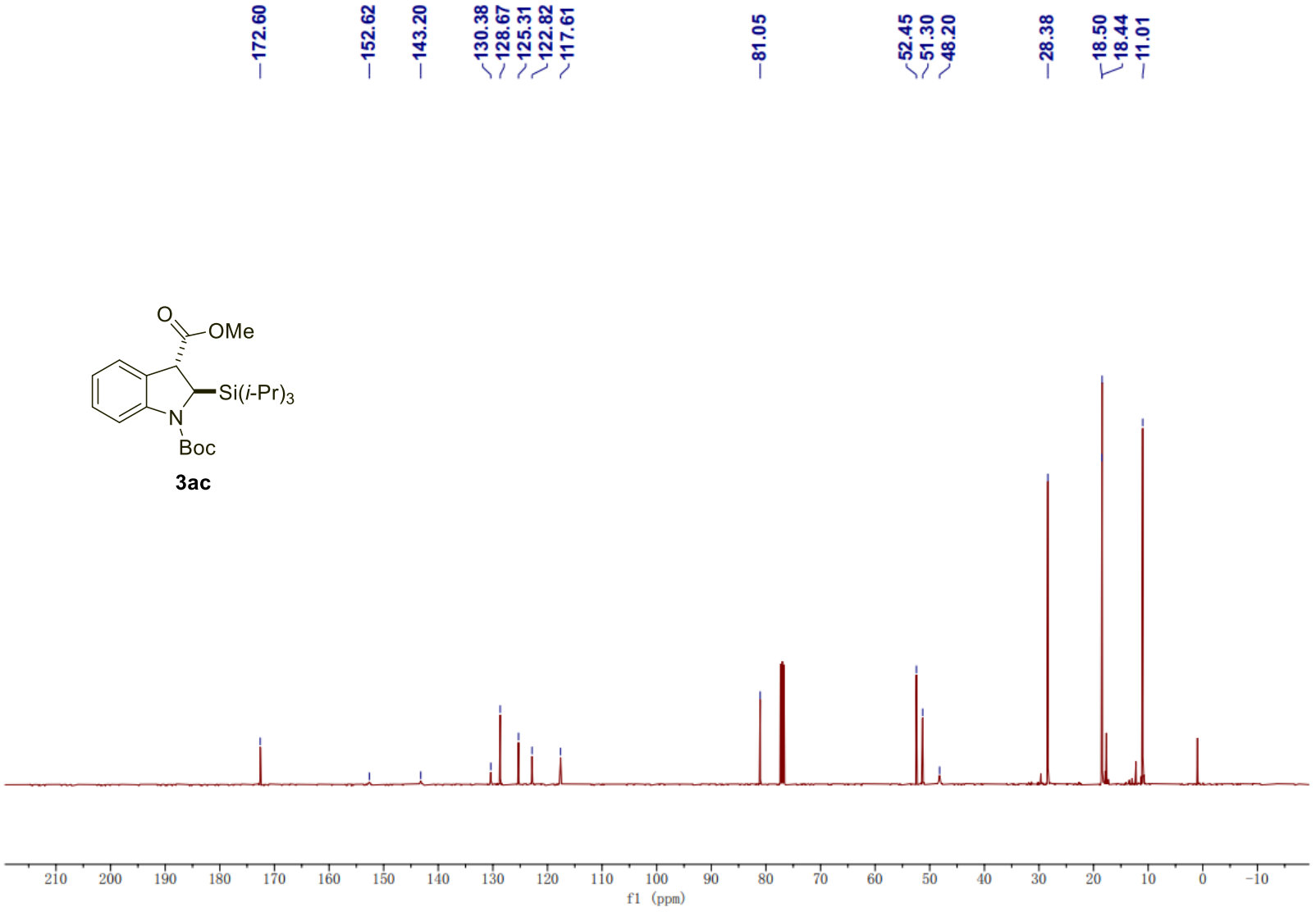
7.19
6.98
6.96
6.94
4.89
4.88
3.93
3.92
3.68
1.55
1.21
1.19
1.19
1.17
1.15
1.01
1.00
0.99
0.97
O
OMe
Si(i-Pr)3
N
Boc
3ac
1.00
1.00
1.00
1.01
1.00
1.01
3.01
9.00
3.00
18.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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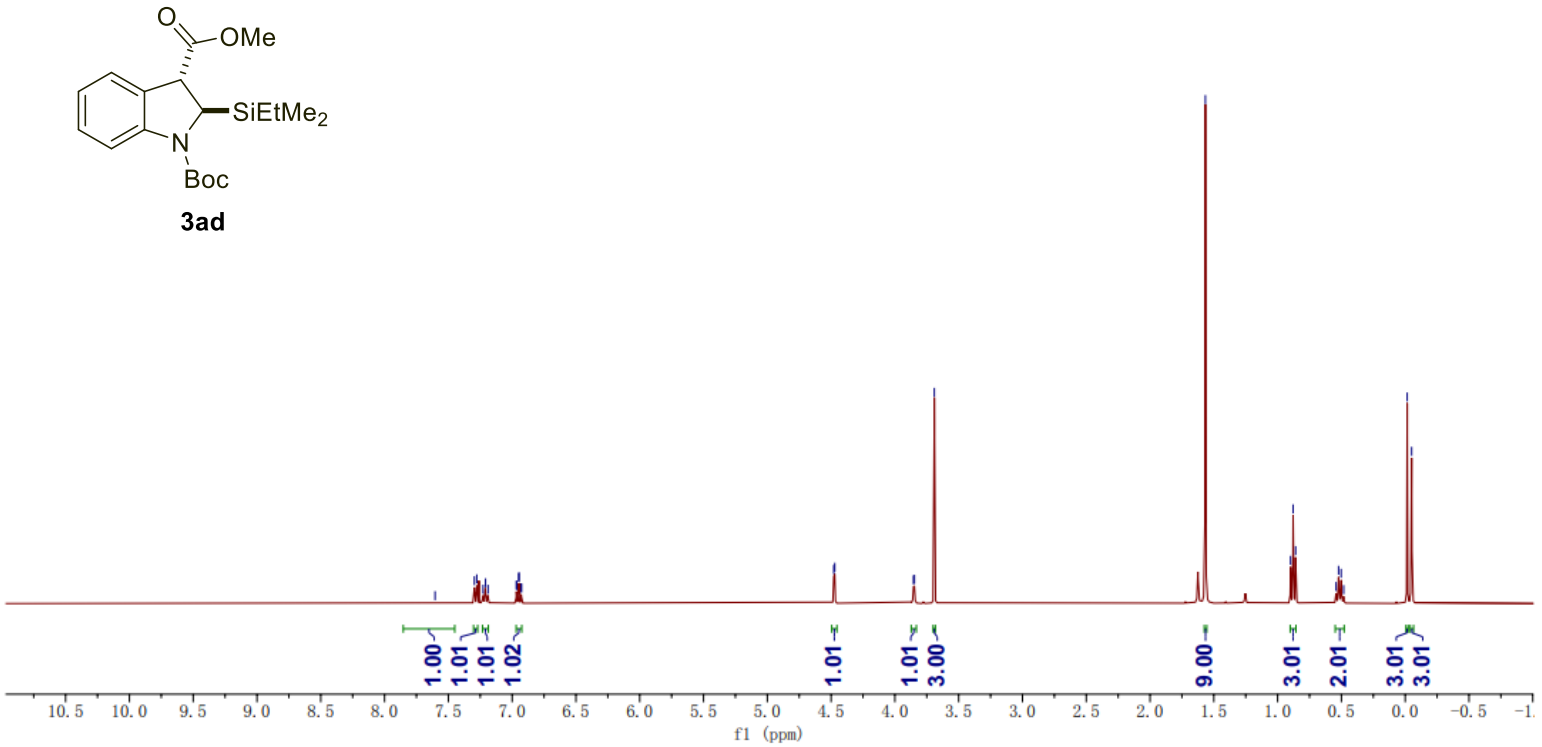
125.31
122.82
117.61
81.05
52.45
51.30
48.20
28.38
18.50
18.44
11.01
O
OMe
Si(i-Pr)3
N
Boc
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.30
7.28
7.23
7.21
7.19
6.97
6.96
6.95
6.95
6.93
6.93
4.48
4.47
3.85
3.85
3.69
1.57
0.90
0.88
0.86
0.54
0.52
0.50
0.48
-0.02
-0.05
O
OMe
SiEtMe2
N
Boc
3ad
1.00
1.01
1.01
1.02
1.01
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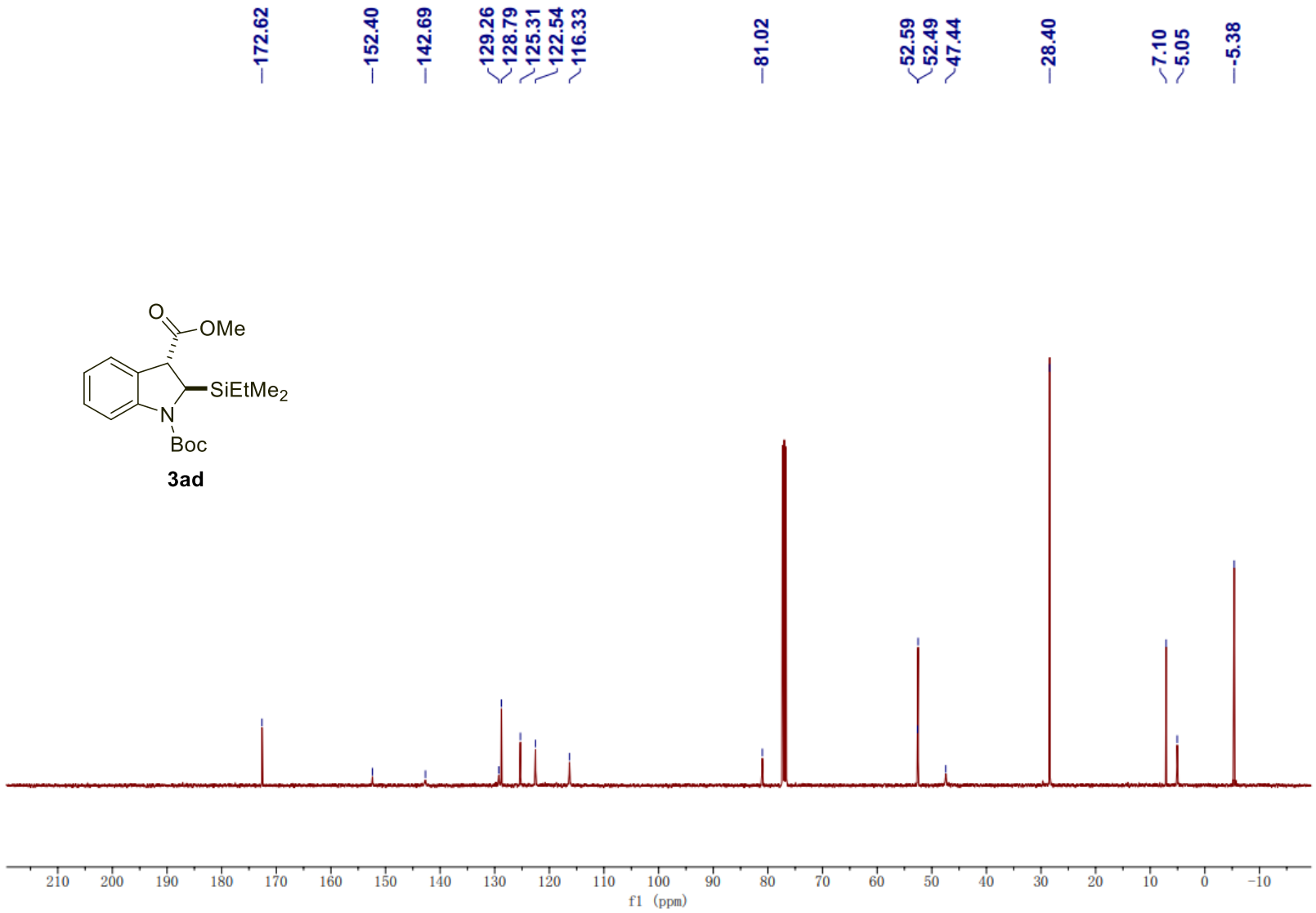
3.01
2.01
3.01
3.01
f1 (ppm)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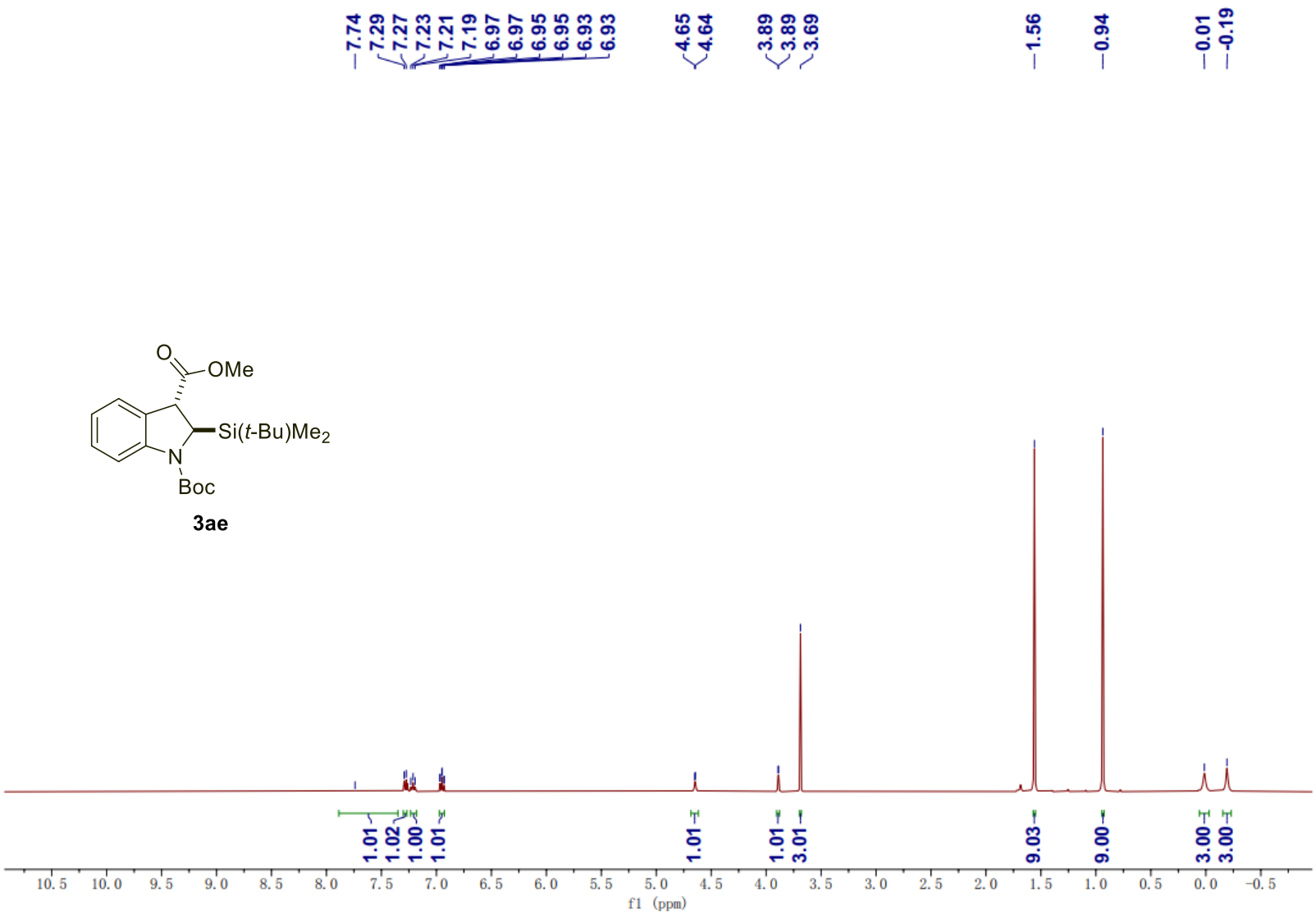
122.54
116.33
81.02
52.59
52.49
47.44
28.40
7.10
5.05
-5.38
O
OMe
SiEtMe2
N
Boc
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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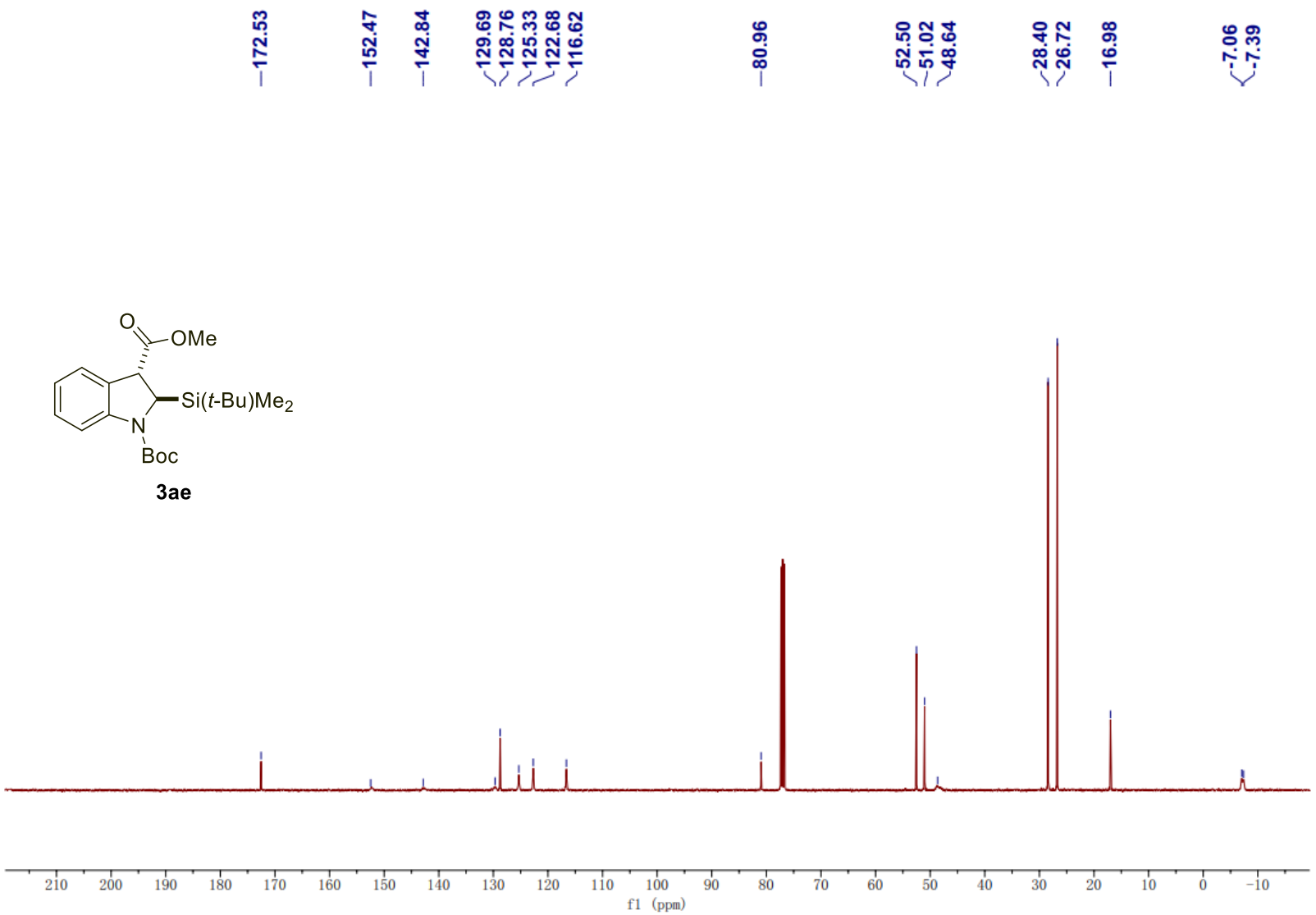
6.95
6.95
6.93
6.93
4.65
4.64
3.89
3.89
3.69
1.56
0.94
0.01
-0.19
O
OMe
Si(t-Bu)Me2
N
Boc
3ae
1.01
1.02
1.00
1.01
1.01
1.01
3.01
9.03
9.00
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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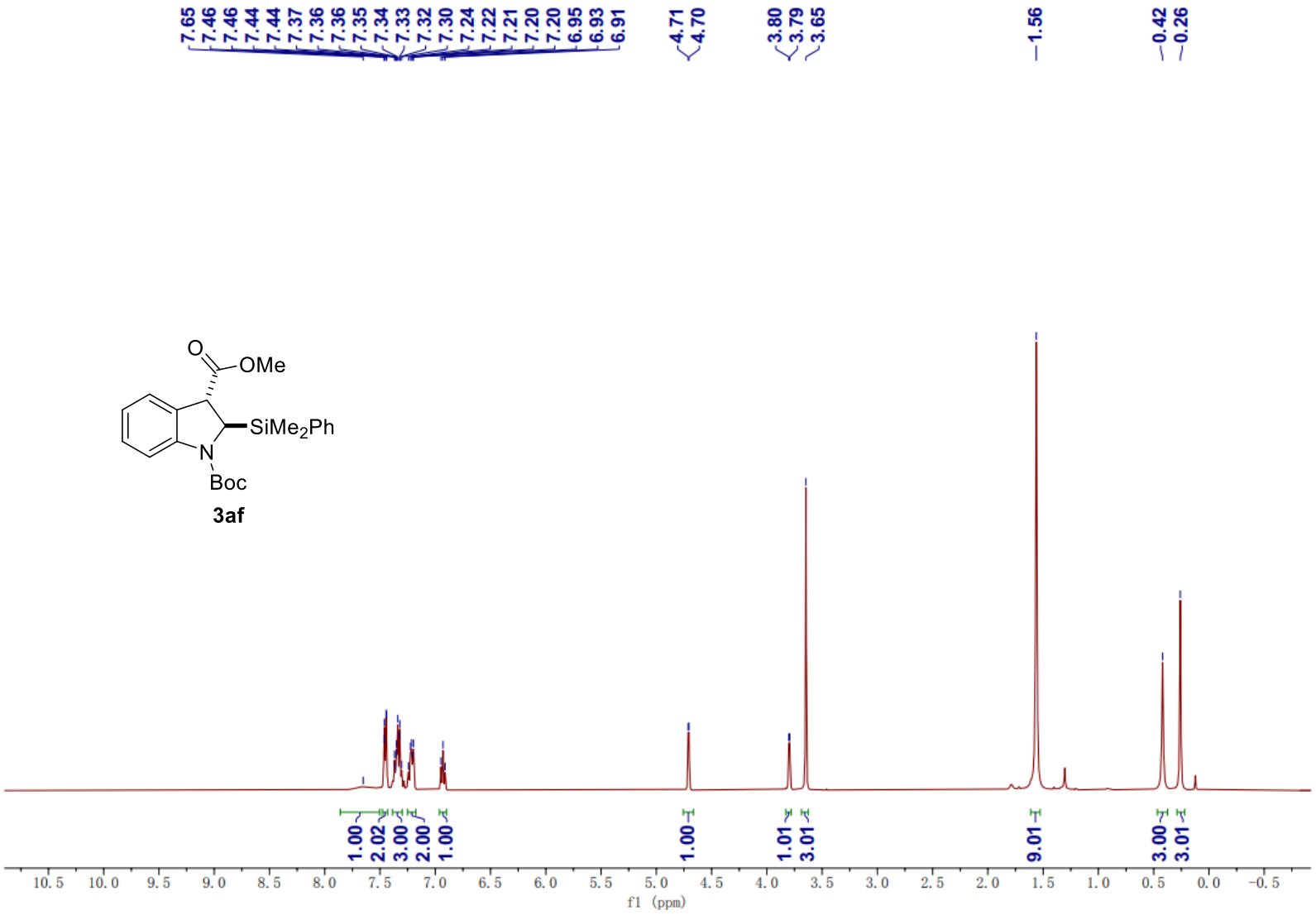
122.68
116.62
80.96
52.50
51.02
48.64
28.40
26.72
16.98
7.06
7.39
O
OMe
Si(t-Bu)Me2
N
Boc
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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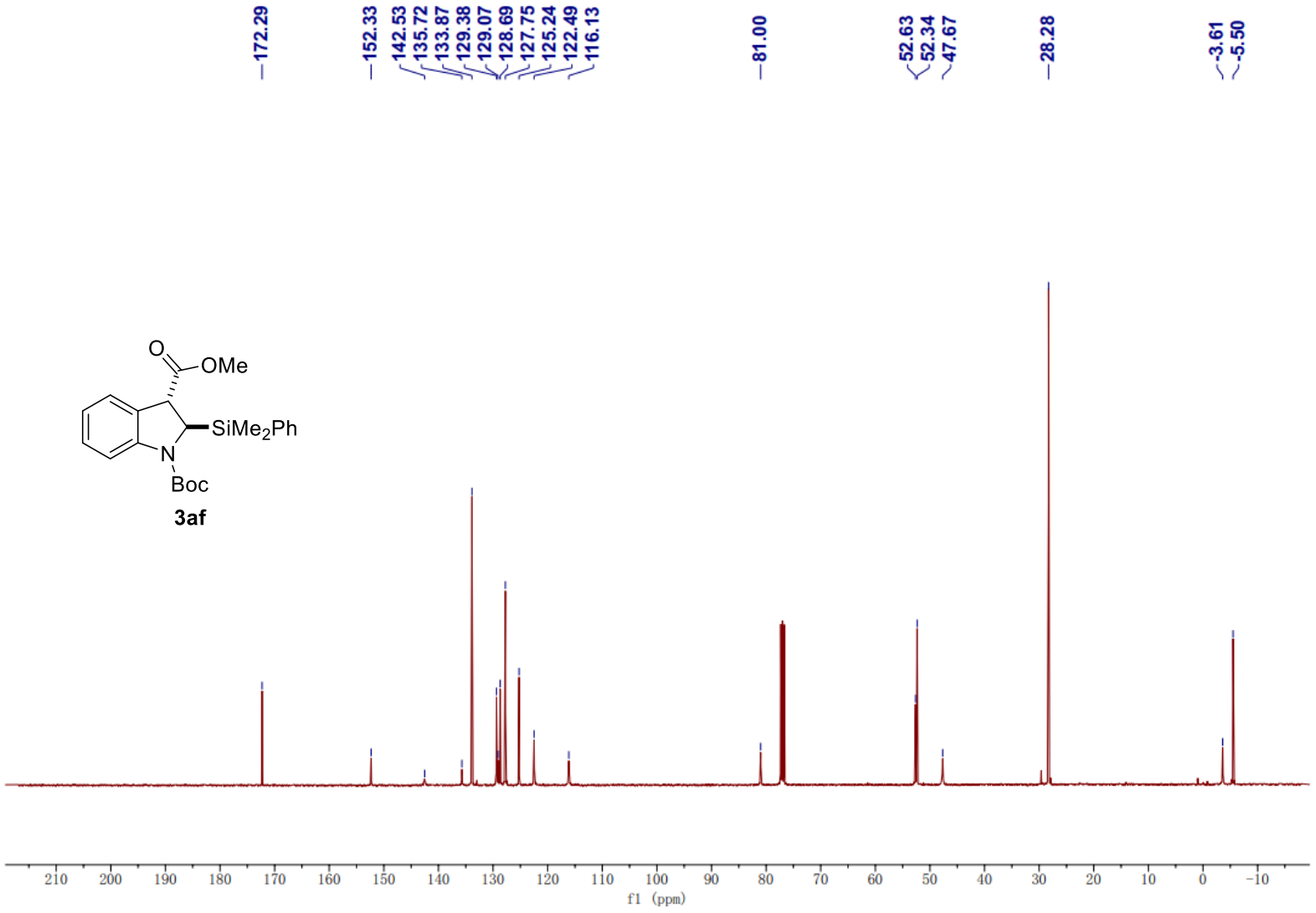
7.35
7.34
7.33
7.32
7.30
7.24
7.22
7.21
7.20
7.20
6.95
6.93
6.91
4.71
4.70
3.80
3.79
3.65
1.56
0.42
0.26
O
OMe
SiMe2Ph
N
Boc
3af
1.00
2.02
3.00
2.00
1.00
1.00
1.01
3.01
9.01
3.00
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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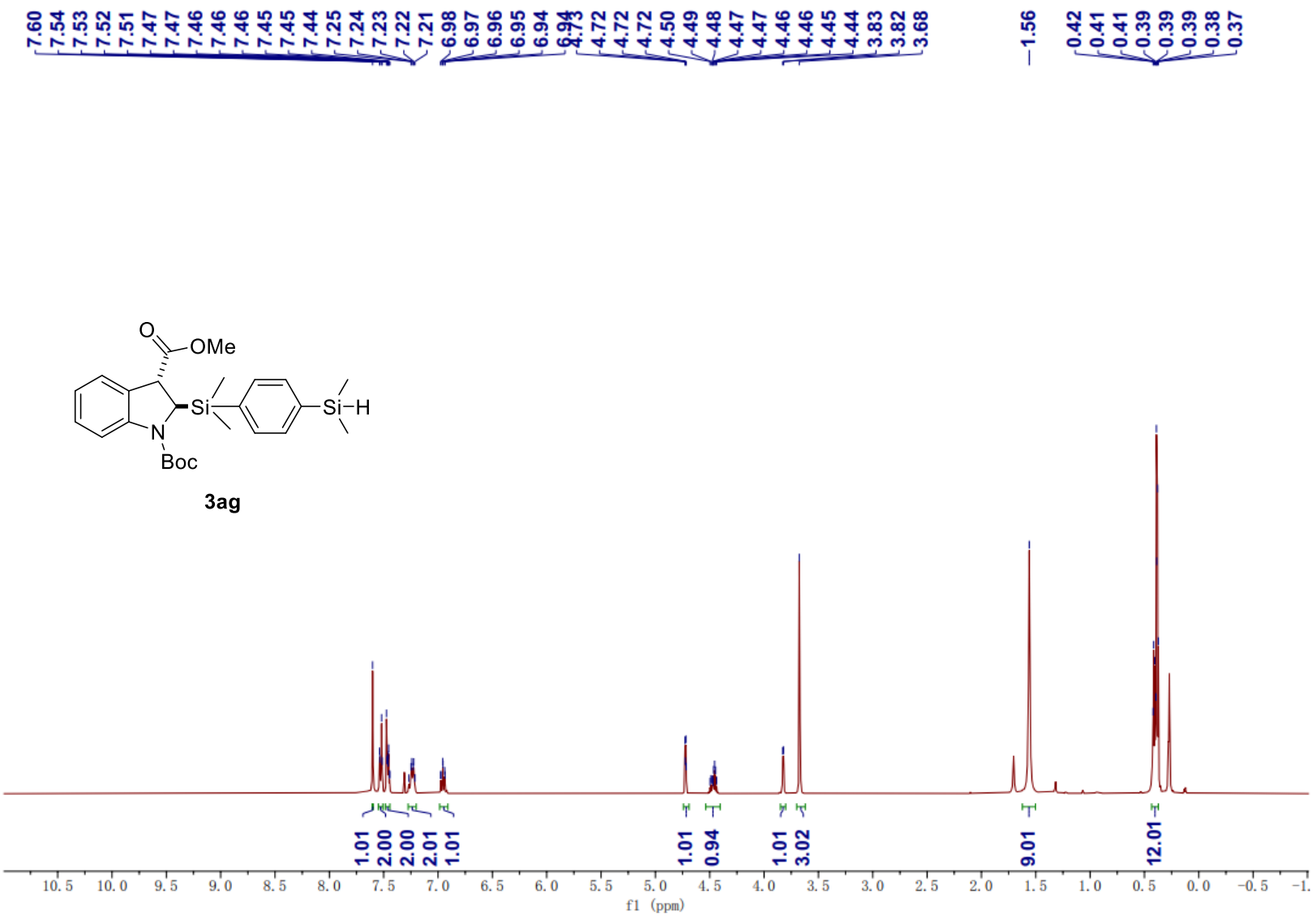
128.69
127.75
125.24
122.49
116.13
81.00
52.63
52.34
47.67
28.28
-3.61
-5.50
O
OMe
SiMe2Ph
N
Boc
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.52
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7.46
7.46
7.45
7.45
7.44
7.25
7.24
7.23
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7.21
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6.97
6.96
6.95
6.94
6.94
4.73
4.72
4.72
4.72
4.50
4.49
4.48
4.47
4.47
4.46
4.46
4.45
4.44
3.83
3.82
3.68
1.56
0.42
0.41
0.41
0.39
0.39
0.39
0.38
0.37
O
OMe
Si
Si
H
N
Boc
3ag
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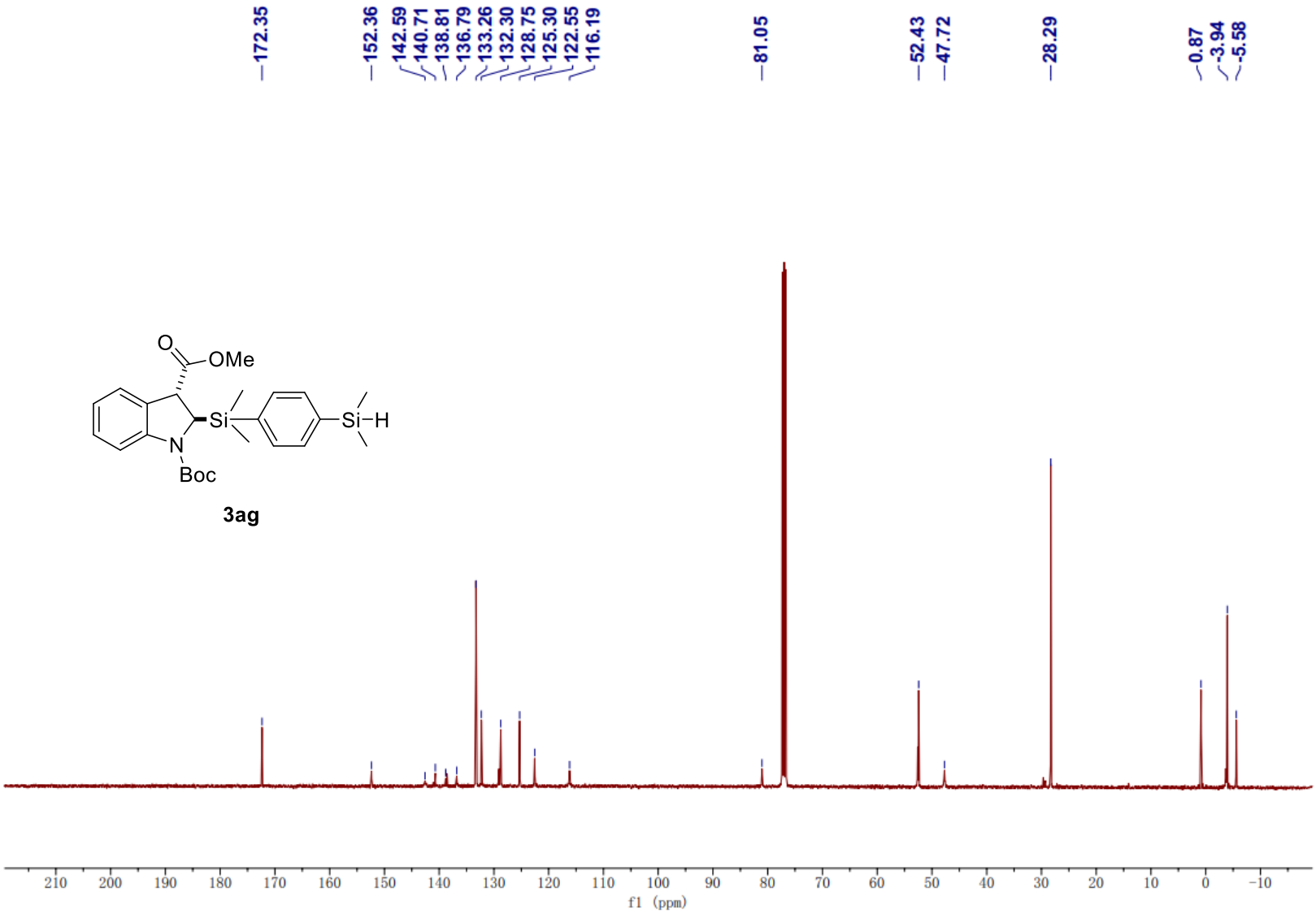
2.00
2.00
2.01
1.01
1.01
0.94
1.01
3.02
9.01
12.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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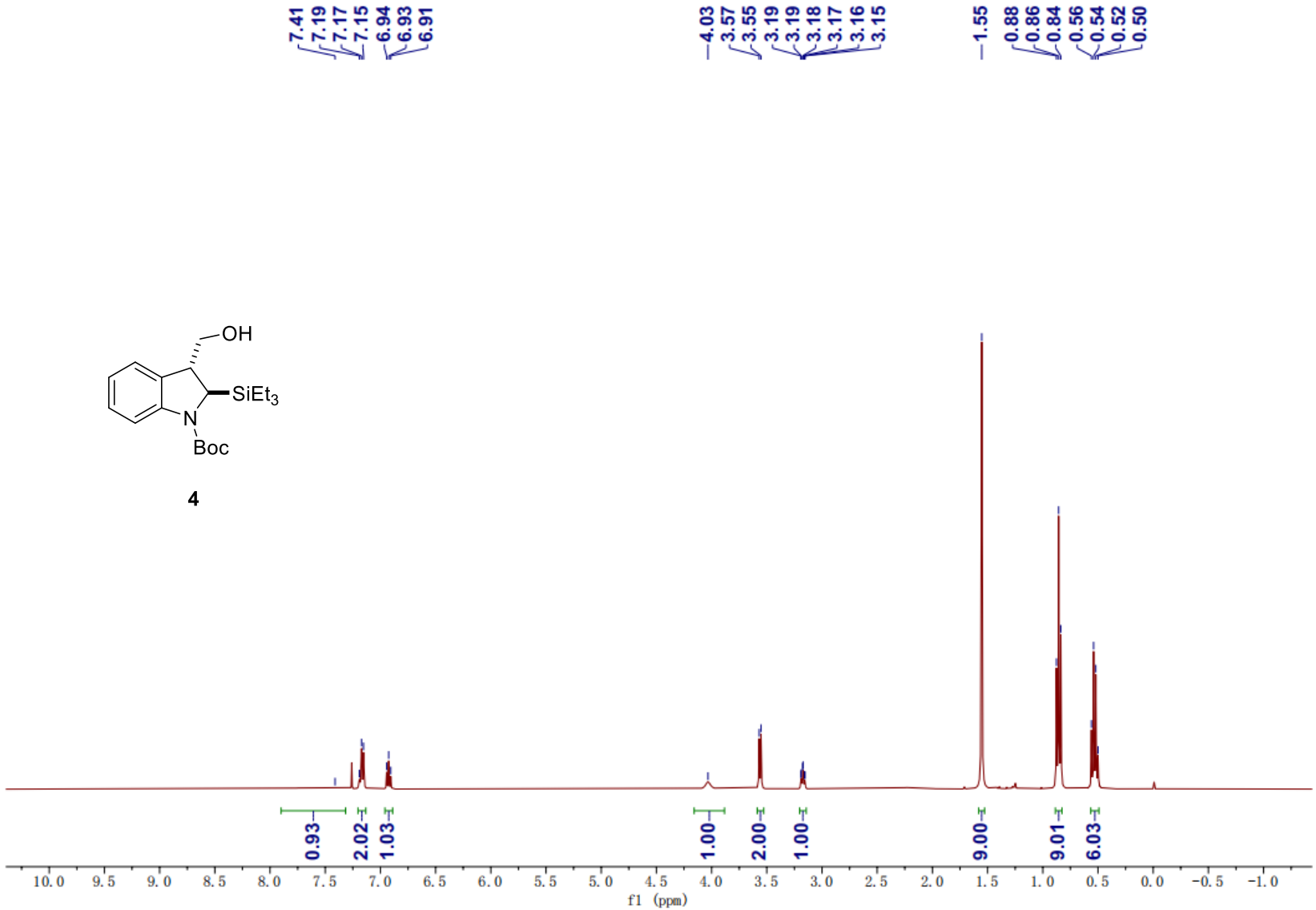
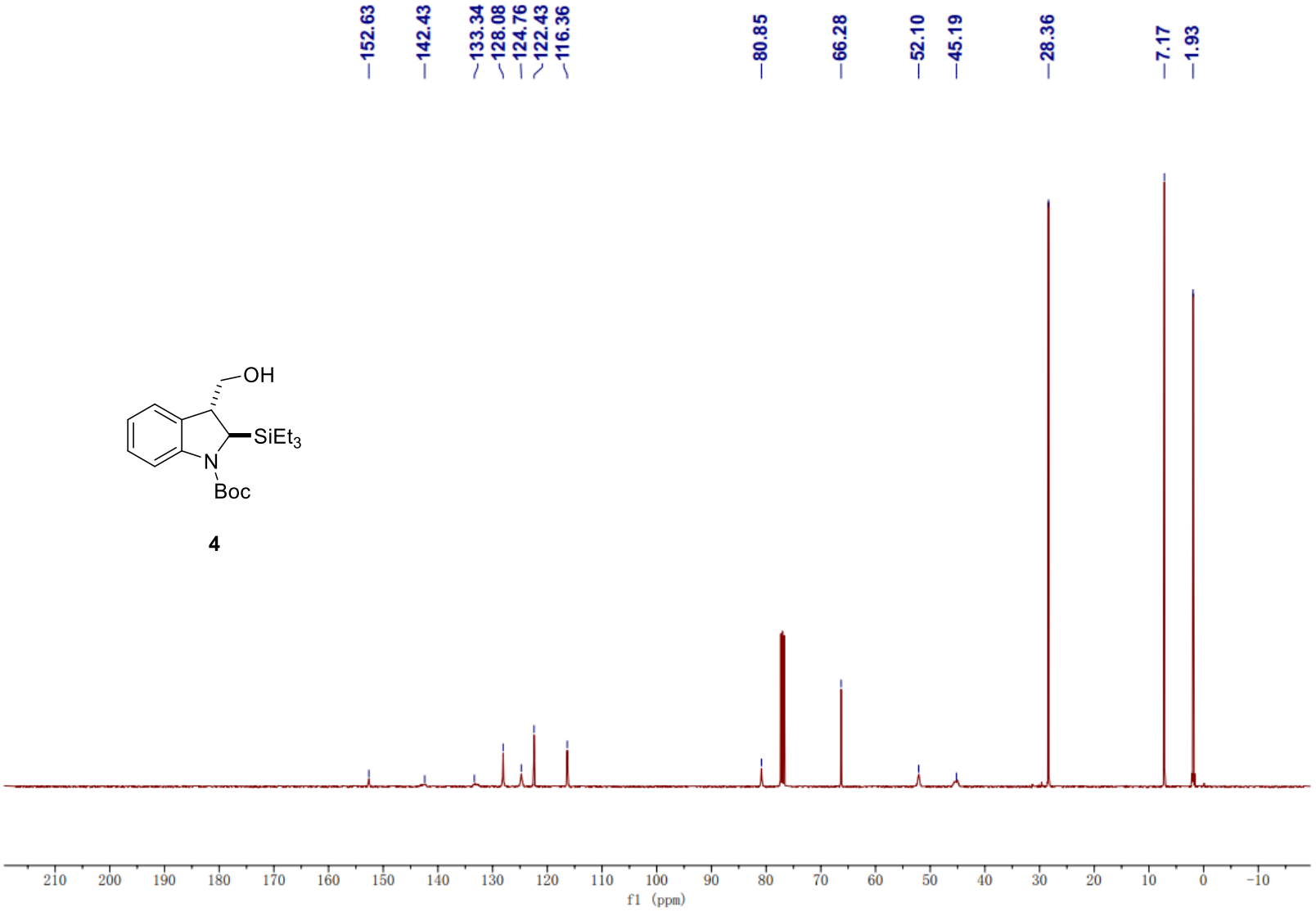
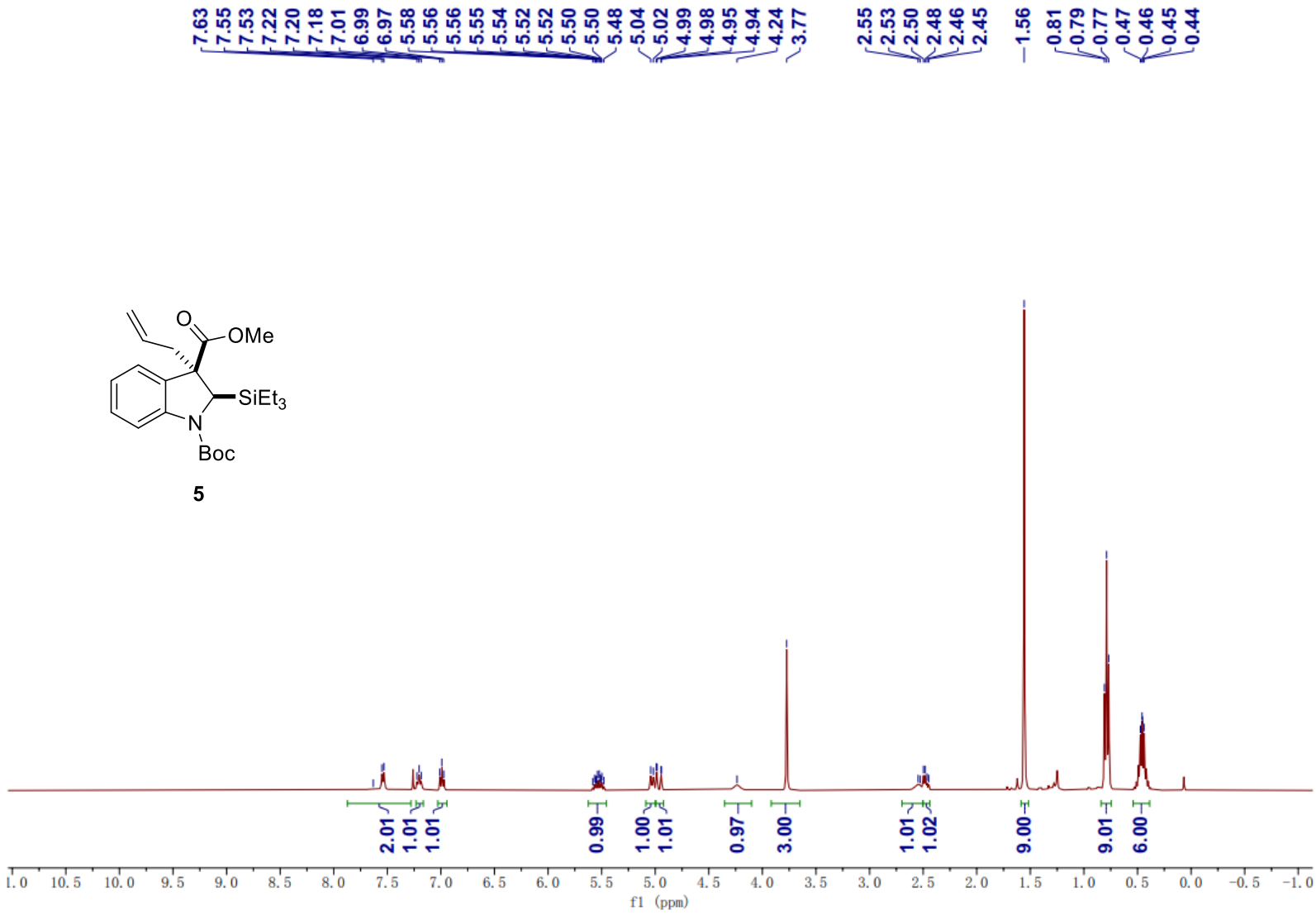
136.79
133.26
132.30
128.75
125.30
122.55
116.19
81.05
52.43
47.72
28.29
0.87
-3.94
-5.58
O
OMe
Si
Si–H
N
Boc
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.41
7.19
7.17
7.15
6.94
6.93
6.91
4.03
3.57
3.55
3.19
3.19
3.18
3.17
3.16
3.15
1.55
0.88
0.86
0.84
0.56
0.54
0.52
0.50
OH
SiEt3
N
Boc
0.93
2.02
1.03
1.00
2.00
1.00
9.00
9.01
6.03
f1 (ppm)

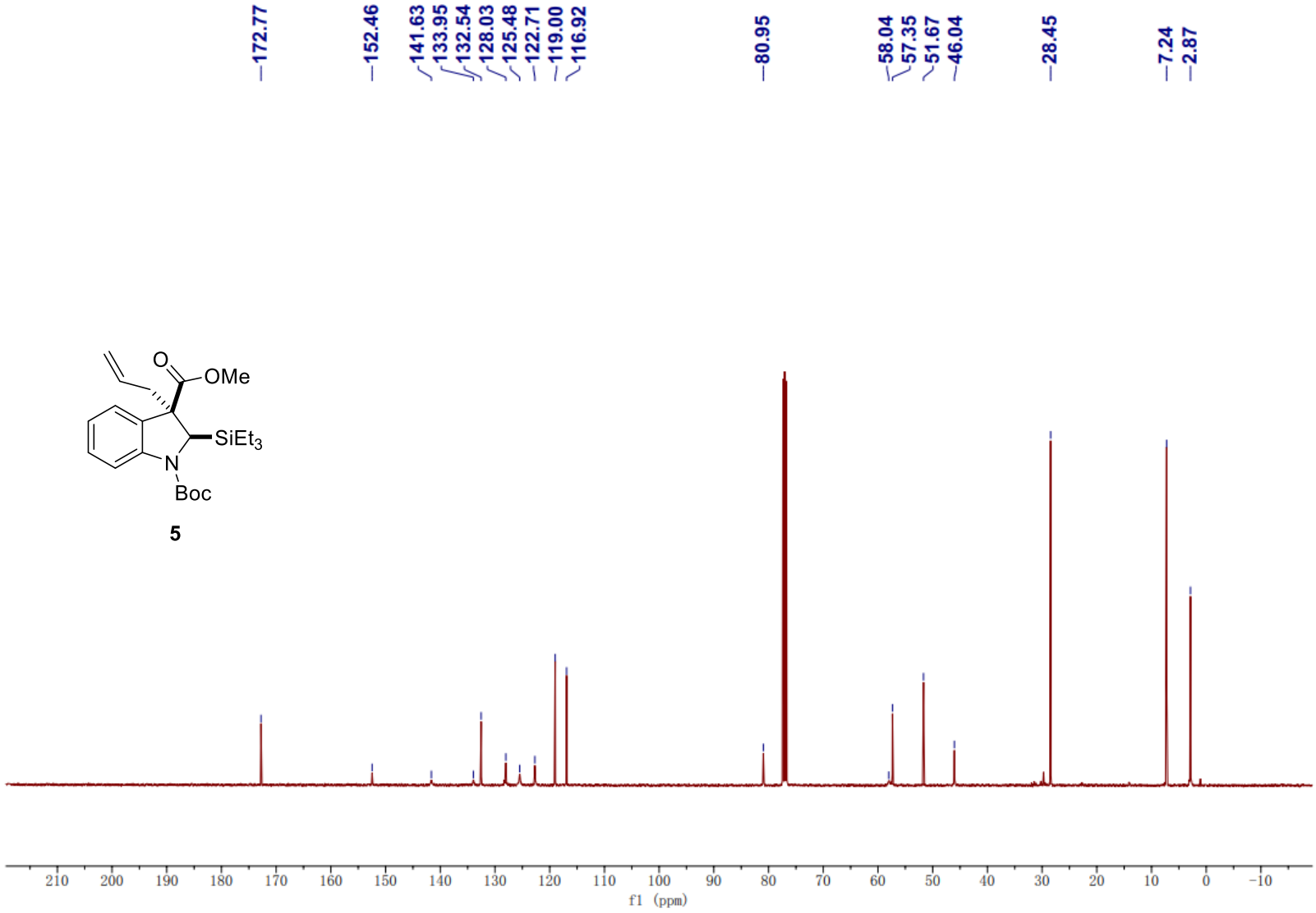
4


152.63
142.43
133.34
128.08
124.76
122.43
116.36
80.85
66.28
52.10
45.19
28.36
7.17
1.93
OH
SiEt3
N
Boc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4


7.63
7.55
7.53
7.22
7.20
7.18
7.01
6.99
6.97
5.58
5.56
5.56
5.55
5.54
5.52
5.52
5.50
5.50
5.48
5.04
5.02
4.99
4.98
4.95
4.94
4.24
3.77
2.55
2.53
2.50
2.48
2.46
2.45
1.56
0.81
0.79
0.77
0.47
0.46
0.45
0.44
O
OMe
SiEt3
N
Boc
2.01
1.01
1.01
0.99
1.00
1.01
0.97
3.00
1.01
1.02
9.00
9.01
6.00
f1 (ppm)

5


172.77
152.46
141.63
133.95
132.54
128.03
125.48
122.71
119.00
116.92
80.95
58.04
57.35
51.67
46.04
28.45
7.24
2.87
O
OMe
SiEt3
N
Boc
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)