Supporting information

Photocatalytic C-H Silylation of Heteroarenes by Using Trialkylhydrosilanes

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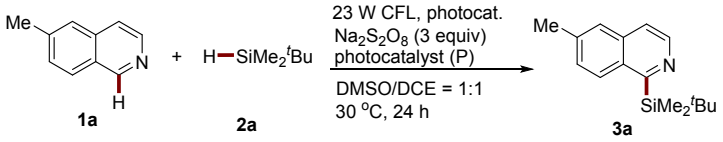
1. The optimization of $Na_2S_2O_8$-mediated photocatalytic C-H silylation.

Table S1. The optimization of photocatalyst. [a]



entry	photocat.	yield [b]
1	**P1** (100 mol%)	20% [c]
2	**P1** (100 mol%)	23%
3	**P2** (5 mol%)	25%
4	**P3** (5 mol%)	31%
5	**P4** (5 mol%)	40%
6	**P5** (5 mol%)	trace
7	**P6** (1 mol%)	55%
8	**P7** (1 mol%)	trace
9	**P8** (1 mol%)	trace
10	**P9** (1 mol%)	60%
11	**P9** (0.5 mol%)	53%
12	**P9** (2 mol%)	49%

[a] Conditions employed 23 W CFL, **1a** (0.5 mmol), **2a** (2.5 mmol), photocat. (1 - 100 mol%), $Na_2S_2O_8$ (1.5 mmol), a solvent mixture (2.5 mL, DMSO : DCE = 1 : 1), air, 30 °C, 24 h, unless otherwise noted; [b] Isolated yields were reported; [c] The reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with N_2.

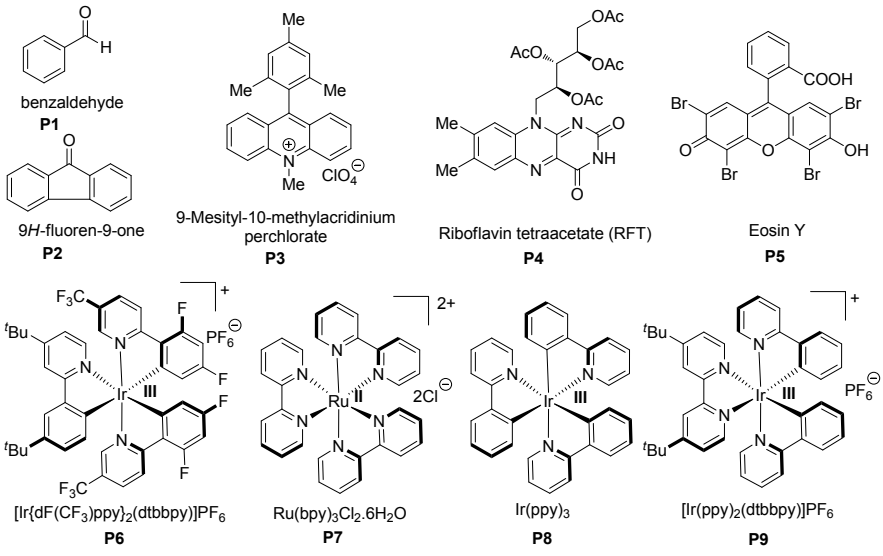
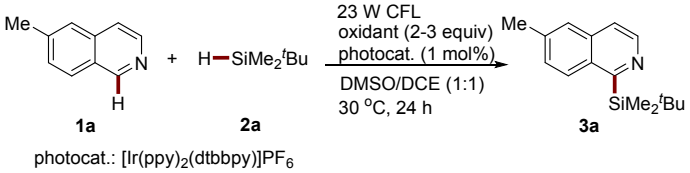


Table S2. The optimization of the oxidant. [a]

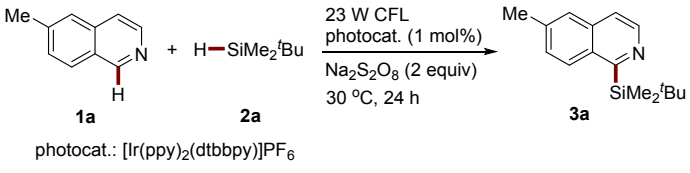


photocat.: $[Ir(ppy)_2(dtbbpy)]PF_6$

entry	oxidant	yield [b]
1	$Na_2S_2O_8$ (3 equiv)	60%
2	$(NH_4)_2S_2O_8$ (3 equiv)	40%
3	$K_2S_2O_8$ (3 equiv)	51%
4	PIDA (3 equiv)	n.d [c]
5	BPO (75%) (3 equiv)	46%
6	O_2	n.d [c]
7	H_2O_2(30%) (3 equiv)	6%
8	TBHP (70%) (3 equiv)	35%
9	$Na_2S_2O_8$ (2 equiv)	67%
10	$Na_2S_2O_8$ (1 equiv)	54%

[a] Conditions employed **1a** (0.5 mmol), **2a** (2.5 mmol), photocat. (1 mol%), 30 °C, oxidant (1.0 - 1.5 mmol), a solvent mixture (1.5 mL, DMSO:DCE = 1:1), air, 30 °C, 24 h, unless otherwise noted; [b] Isolated yields were reported; [c] not detected.

Table S3. The optimization of the reaction solvent. [a]

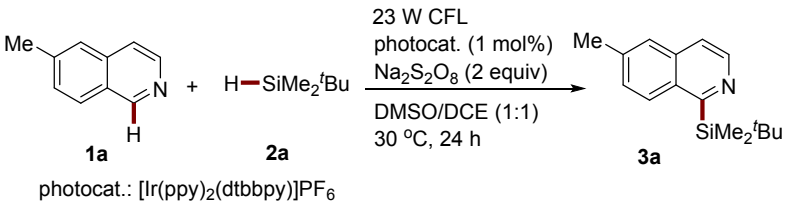


photocat.: $[Ir(ppy)_2(dtbbpy)]PF_6$

entry	solvent	yield [b]
1	DMSO/DCE (1:1)	67%
2	DMSO	32%
3	DCE	n.d [c]
4	MeCN	trace
5	EtOH	n.d [c]
6	DMSO/$CH_3COOC_2H_5$ (1:1)	19%
7	DMSO/MeCN (1:1)	10%
8	DMSO/Acetone (1:1)	25%
9	DMSO/DCE (1:1)	77% [d]
10	DMSO/DCE (3:1)	67% [d]
11	DMSO/DCE (1:3)	33% [d]

[a] Conditions employed **1a** (0.5 mmol), **2a** (2.5 mmol), photocat. (1 mol%), $Na_2S_2O_8$ (1.0 mmol) , solvent (2.5 mL), 30 °C, 24 h, air, unless otherwise noted; [b] Isolated yields were reported; [c] not detected; [d] 5.0 mL of solvent mixture (DMSO:DCE = 1:1) was employed as the reaction solvent.

Table S4. The optimization of the amount of trialkylhydrosilane. [a]

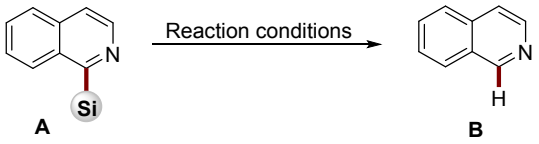


entry	*tert*-butyldimethylsilane	yield [b]
1	5 equiv	77%
2	10 equiv	79%
3	5 equiv	70% [c]
4	5 equiv	66% [d]

[a] Conditions employed 23 W CFL, **1a** (0.5 mmol), **2a** (1.0 - 5.0 mmol), photocat. (1 mol%), $Na_2S_2O_8$ (1.0 mmol), a solvent mixture (5 mL, DMSO : DCE = 1:1), 30 °C, 24 h, air, unless otherwise noted; [b] Isolated yields were reported; [c] The reaction time was extended to 48 h; [d] The reaction time was shorten to 12 h.

2. The chemical stability study of heteroaryltrialkylsilanes

Table S5. The chemical stability study of heteroaryltrialkylsilanes. [a]



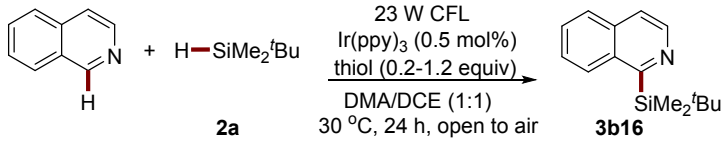
Reaction conditions	**Si** = ^{t}BuMe$_2$Si	**Si** = Et$_3$Si
Standard reaction conditions ($Na_2S_2O_8$) [b]	**A** (100%)	**A** (21%)，**B** (74%)
Standard reaction conditions (^{i}Pr$_3$SiSH) [b]	**A** (100%)	**A** (70%)，**B** (30%)
HCl (1 mol/L), 25 °C, 24 h	**A** (100%)	**A** (80%) + **B** (20%)
HCl (1 mol/L), 50 °C, 24 h	**A** (100%)	**A** (10%) + **B** (90%)
HCl (1 mol/L), 80 °C, 24 h	**A** (92%) + **B** (8%)	**B** (100%)
NaOH (1 mol/L), 25 °C, 24 h	**A** (100%)	**A** (100%)
NaOH (1 mol/L), 50 °C, 24 h	**A** (100%)	**A** (70%) + **B** (30%)
NaOH (1 mol/L), 80 °C, 24 h	**A** (100%)	**A** (30%) + **B** (70%)
TBAF (1 mol/L), 25 °C, 24 h	**A** (95%) + **B** (5%)	**B** (100%)
TBAF (1 mol/L), 50 °C, 24 h	**A** (30%) + **B** (70%)	-
TBAF (1 mol/L), 80 °C, 24 h	**B** (100%)	-

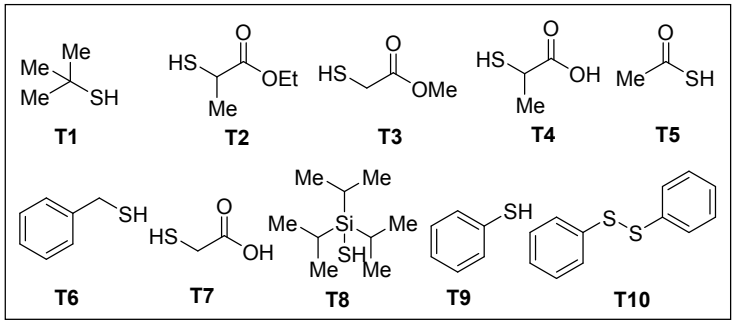
[a] Isolated yields were reported for the each reaction; [b] See general procedure **A** and **B** for the experimental details unless otherwise noted.

Notes: Heteroaryltriethylsilane was prepared according to the known procedure, and spectroscopic data is in accordance with literature.[1]

3. The study of thiol-mediated photocatalytic Minisci-type C-H silylation of heteroarenes

Table S6. The optimization of the reaction conditions. [a]





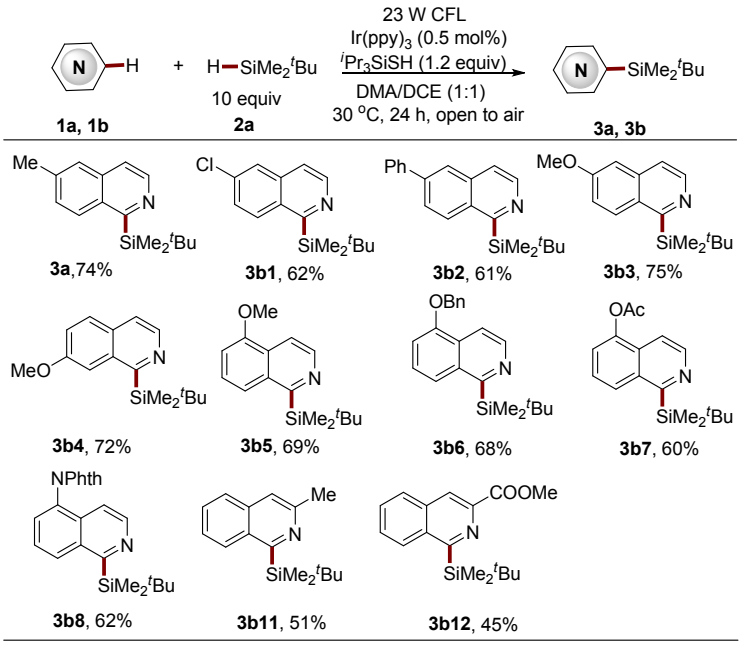
entry	thiol	**2a**	additive	yield [b]
1	**T1** (0.2 equiv)	5 equiv (1 batch)	-	38%
2	**T2** (0.2 equiv)	5 equiv (1 batch)	-	33%
3	**T3** (0.2 equiv)	5 equiv (1 batch)	-	32%
4	**T4** (0.2 equiv)	5 equiv (1 batch)	-	25%
5	**T5** (0.2 equiv)	5 equiv (1 batch)	-	31%
6	**T6** (0.2 equiv)	5 equiv (1 batch)	-	18%
7	**T7** (0.2 equiv)	5 equiv (1 batch)	-	23%
8	**T8** (0.2 equiv)	5 equiv (1 batch)	-	43%
9	**T9** (0.2 equiv)	5 equiv (1 batch)	-	15%
10	**T10** (0.2 equiv)	5 equiv (1 batch)	-	0%
11	**T8** (1.0 equiv)	5 equiv (1 batch)	-	53%
12	**T8** (1.2 equiv)	5 equiv (1 batch)	-	58%
13	**T8** (1.6 equiv)	5 equiv (1 batch)	-	52%
14	**T8** (1.2 equiv)	5 equiv (3 batches)	-	64%
15	**T8** (1.2 equiv)	10 equiv (3 batches)	-	71%
16	**T8** (1.2 equiv)	10 equiv (3 batches)	-	71% [c]
17	**T8** (1.2 equiv)	10 equiv (3 batches)	-	72% [d]
18	**T8** (1.2 equiv)	10 equiv (3 batches)	CF_3SO_3H	70%
19	**T8** (1.2 equiv)	10 equiv (3 batches)	$Sc(OTf)_3$	63%
20	**T8** (1.2 equiv)	10 equiv (3 batches)	-	n.d [e, f]
21	**T8** (1.2 equiv)	10 equiv (3 batches)	-	71% [g]
22	**T8** (1.2 equiv)	10 equiv (3 batches)	-	n.d [f, h]
23	**T8** (1.2 equiv)	10 equiv (3 batches)	-	n.d [f, i]
24	-	10 equiv (3 batches)	-	n.d [f]

[a] Conditions employed 23 W CFL, isoquinoline (0.5 mmol), **2a** (2.5 - 5.0 mmol), $Ir(ppy)_3$ (0.0025 mmol), thiol (0.1 - 0.6 mmol), 30 °C, 24 h, air, a solvent mixture (2.0 mL, DMA:DCE = 1:1), unless otherwise noted; [b] Isolated yields were reported; [c] The reaction time was extended to 36h; [d] 34 W blue LED was used as light source; [e] The reaction mixture was degassed via freeze pump thaw (× 3 times) and refilled with N_2; [f] Not detected; [g] Performed under oxygen (1atm); [h] Performed in darkness; [i] Performed in the absence of $Ir(ppy)_3$.

Notes: The initial screening campaign identified $Ir(ppy)_3$ (0.5 mol%) and the solvent mixture (DMA/DCE = 1 : 1, 0.25M) as the optimal reaction conditions (data not shown here). Various thiol additives were then screened using 5 equiv of ^{t}BuMe$_2$SiH (**2a**) as coupling partner. The thiol with large

steric hindrance displayed better reaction efficiency (entry 1 and entry 8, 38% - 43% yield). $^{i}Pr_3SiSH$ (1.2 equiv) provided the best reaction outcome (entry 12, 58% yield). The stability of thiol additives under oxidation might help to explain this result. The use of 10 equiv of $^{t}BuMe_2SiH$ in three batches showed the best reaction efficiency (entry 15, 71% yield). The extension of reaction time to 36 h, the use of 34 W blue LED as an alternative light source, as well as the addition of acid as additives, have little effect on the reaction efficiency (entries 16 - 19, 63% - 71% yield). The oxygen was proved essential for this transformation, while the running of the reaction under O_2 cannot further improve the yield (entry 21, 71% yield). Furthermore, control reactions show that visible light, $Ir(ppy)_3$, and thiol, are also essential for this process (entries 22 - 24, Table 1). Therefore, the reaction conditions screening campaign identified the optimal conditions as: in the prescene of 23 W CFL, 0.5 mol% of $Ir(ppy)_3$, 1.2 equiv of $^{i}Pr_3SiSH$, treating heteroarenes with 10 equiv of $^{t}BuMe_2SiH$ (three batches) in solvent mixture (DMA : DCE = 1:1, 0.25 M) for 24 h at 30 ^{o}C under air (entry 15).

Scheme S1. Direct C-H silylation of substituted isoquinolines via thiol-mediated photocatalytic Minisci-type reaction. [a]



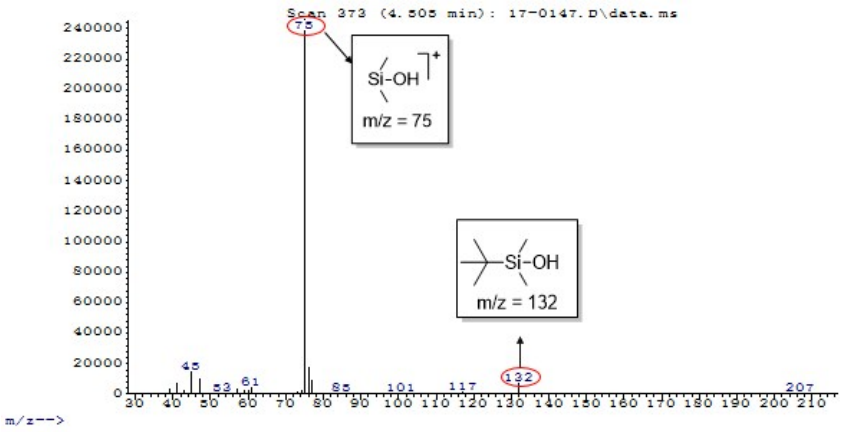
[a] See general procedure **B** for the experimental details unless otherwise noted; the isolated yields were reported.

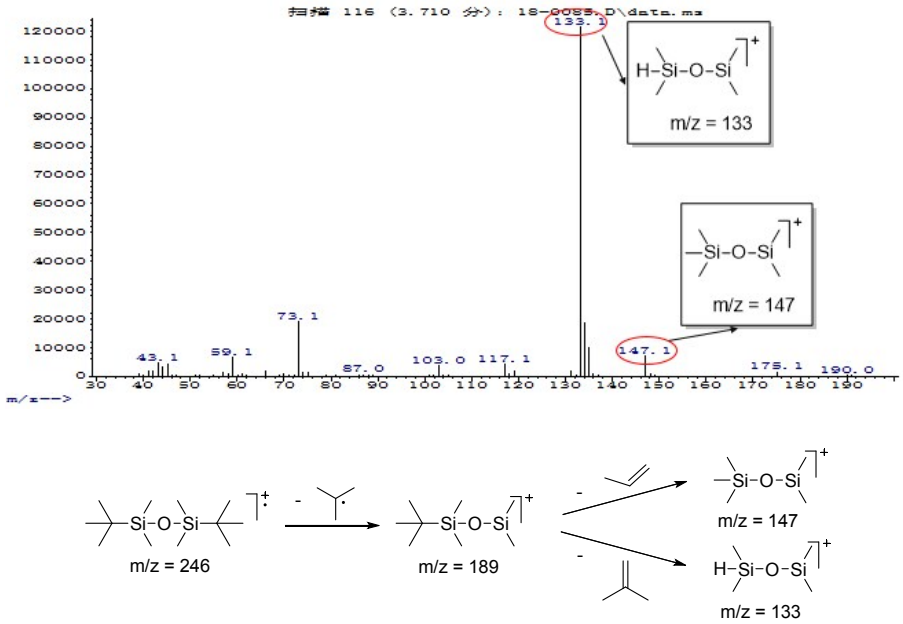
Notes: Only C-1 *mono*-silylation products were detected.

4. The study of the mechanism of $Na_2S_2O_8$-mediated photocatalytic C-H silylation

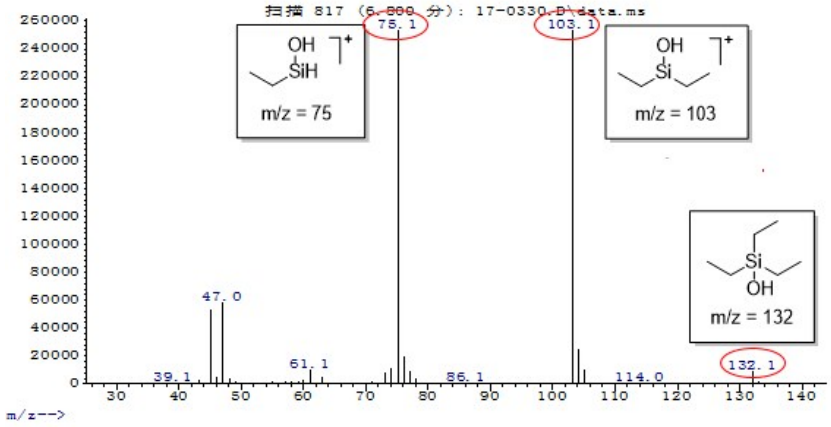
Figure S1. The GC-MS study of the reaction mixture.

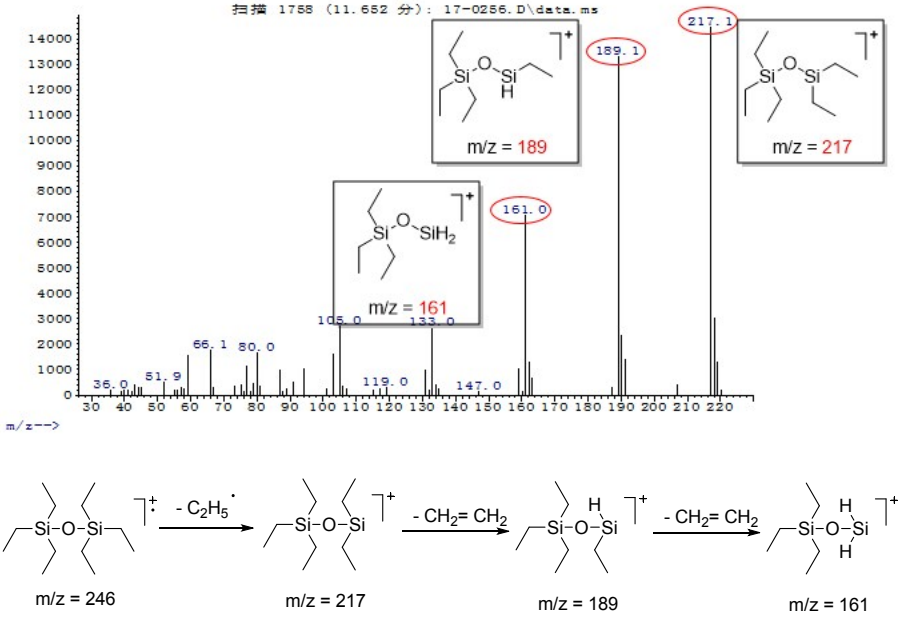
GC-MS data of the coupling reaction of 6-methylisoquinoline **1a** with *tert*-butyldimethylsilane **2a**.





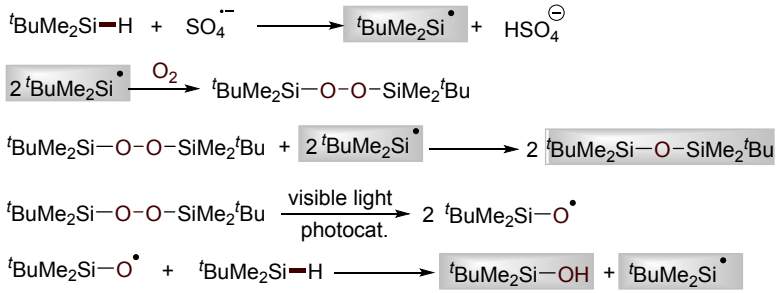
GC-MS data of the coupling reaction of 6-methylisoquinoline **1a** with triethylsilane **2d**



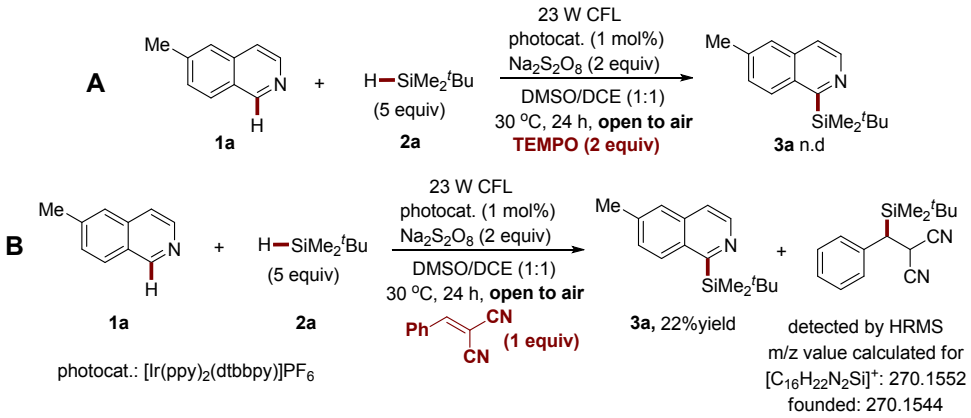


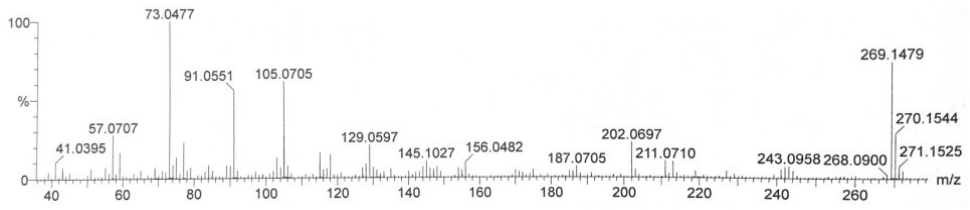
Notes: The reaction solution was directly used for GC-MS analysis. The formation of silanol and siloxane was observed by GC-MS, which indicates that silyl radicals were formed in this process and further validates the radical based mechanism (sila-Minisci-type reaction).[3]

Scheme S2. The proposed mechanisms of the formation of silanol and siloxane.



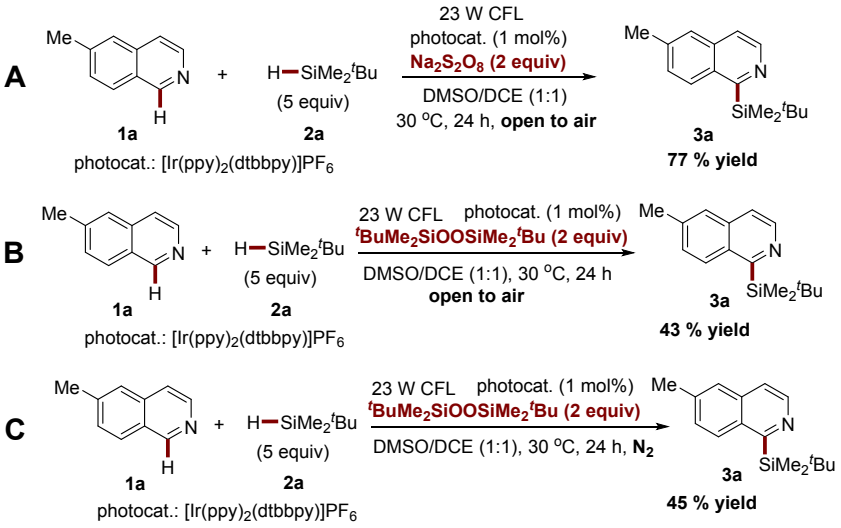
Scheme S3. The radical trapping experiment.





Notes: TEMPO, (*E*)-(2-(phenylsulfonyl)vinyl)benzene, methyl acrylate, and 2-benzylidenemalononitrile were employed to trap the silyl radial. The reaction was shut down by the presence of TEMPO, which is indicative of a radical engaged pathway (Scheme 3A). However, only the radial trapping product was detected using 2-benzylidenemalononitrile as additive (Scheme 3B).

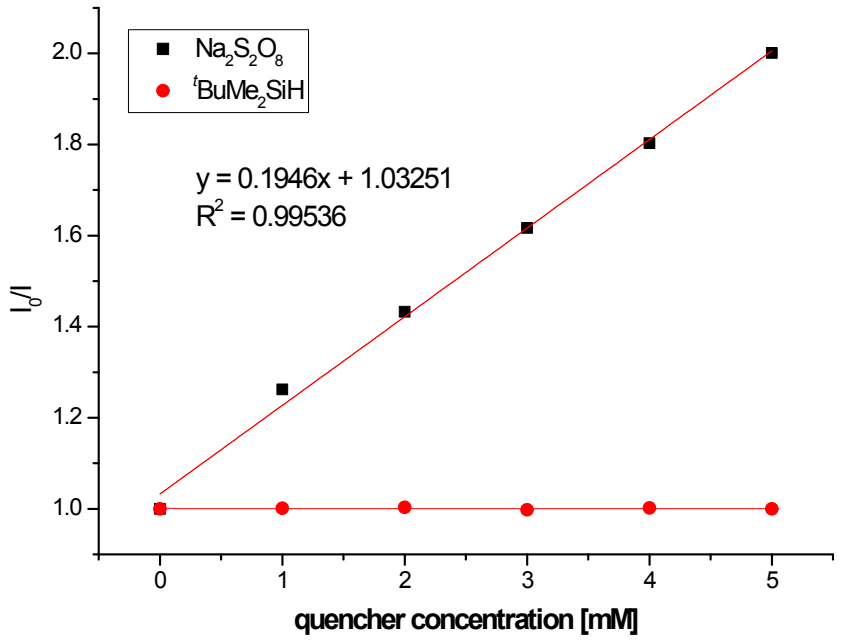
Scheme S4. The control reactions employing $^{t}BuMe_2SiOOSiMe_2{}^{t}Bu$ as the radical initiator.



Notes: $^{t}BuMe_2SiOOSiMe_2{}^{t}Bu$ was prepared according to known procedure, and spectroscopic data is in accordance with literature.[3]

Figure S2. Emission Quenching Experiment

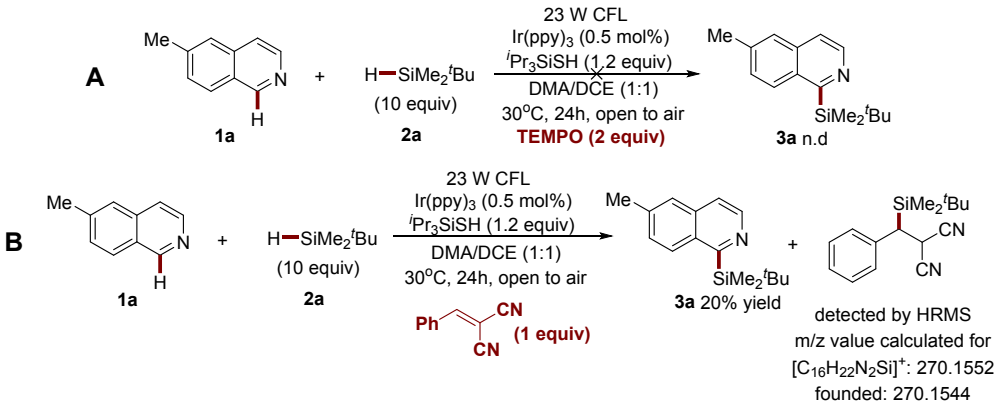
Emission intensities were recorded using a FluoroMax-4 (Horiba Scientific) fluorescence spectrophotometer. All $Ir(ppy)_2(dtbbpy)PF_6$ solutions were excited at 337 nm and the emission intensity was collected at 603 nm. In a typical experiment, to a 1×10^{-6} M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in DMSO was added the appropriate amount of a quencher in a screw-top quartz cuvette.

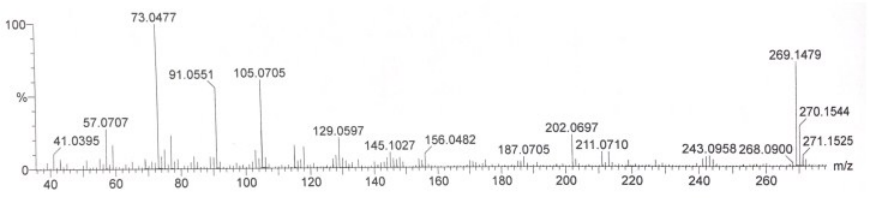


5. The study of the mechanism of thiol-mediated photocatalytic C-H silylation

Figure S3. GC-MS study of the reaction mixture.

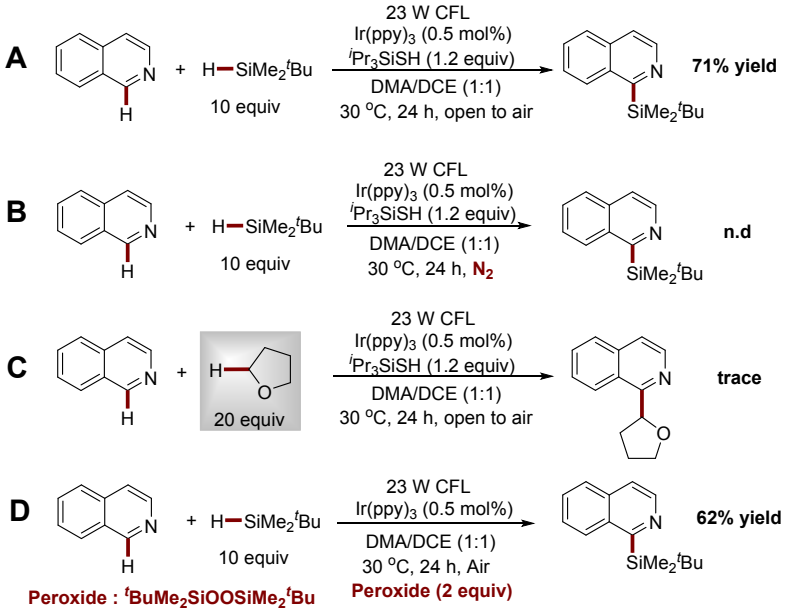
Scheme S5. The radical quenching and trapping experiments.





Notes: The reaction was completely inhibited by the presence of TEMPO, further suggesting the radical based mechanism (Scheme S5A). However, only the use of 2-benzylidenemalononitrile as additive is able to produce the radial trapping product accompanied with the formation of little target product **3a** (Scheme S5B).

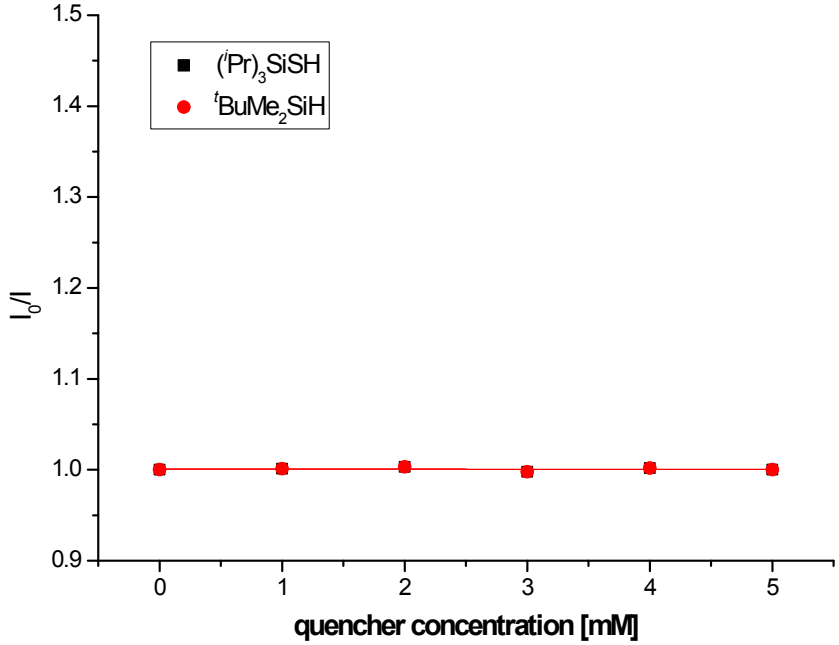
Scheme S6. The control reactions.



Notes: No product was detected in the absence of air (O_2) (Scheme S6B). Furthermore, the use of THF (20 equiv) as coupling partner in place of ^{t}BuMe$_2$SiH resulted in the generation of trace desired product (Scheme S6C). These results, as well as the fact that the use of ^{t}BuMe$_2$SiOOSiMe$_2{}^t$Bu (2 equiv) as radical initiator led to comparable yield (62% yield, Scheme S6D), indicate that the *in-situ* generated ^{t}BuMe$_2$SiOOSiMe$_2{}^t$Bu might be involved in this process to mediate the sila-Minisci-type reaction.

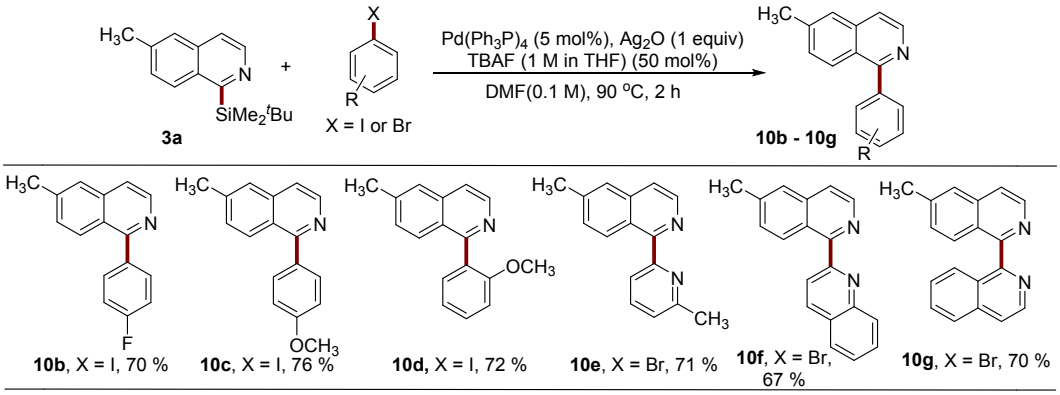
Figure S4. Emission Quenching Experiment.

Emission intensities were recorded using a FluoroMax-4 (Horiba Scientific) fluorescence spectrophotometer. All Ir(ppy)$_3$ solutions were excited at 350 nm and the emission intensity was collected at 527 nm. In a typical experiment, to a 1×10^{-6} M solution of Ir(ppy)$_3$ in DMSO was added the appropriate amount of a quencher in a screw-top quartz cuvette.



6. The synthetic application of our method

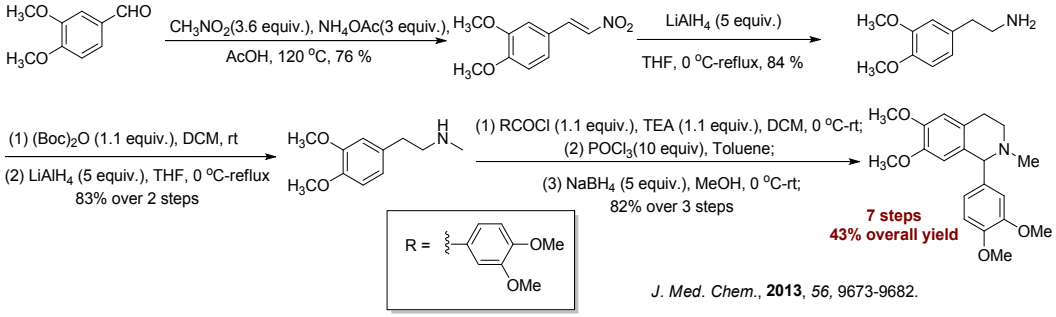
Scheme S7. The study of Hiyama-Denmark cross-coupling of heteroaryl(*tert*-butyldimethyl)silane. [a]



[a] See General procedure **D** for the experimental details unless otherwise noted; isolated yields were reported.

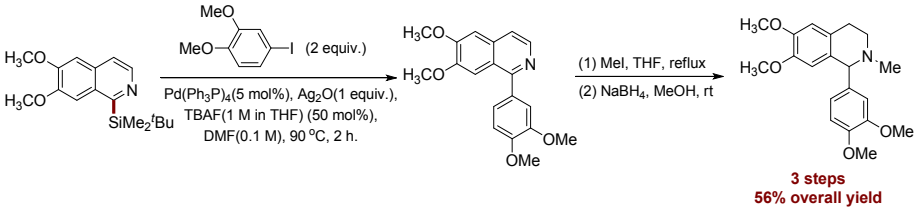
Scheme S8. The comparison of two synthetic routes for the synthesis of norcryptostylines.

Reported synthetic route: [2]



J. Med. Chem., **2013**, *56*, 9673-9682.

Our synthetic route:



7. Experiment Procedures and Product Characterization

Commercial reagents and solvents were used as received, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography was performed on silica gel 200–300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 Spectrometer (400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.00 ppm in ^{1}H and ^{13}C NMR, respectively; d^6-DMSO referenced at 2.50 and 39.52 ppm in ^{1}H and ^{13}C NMR, respectively). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

General Procedure A:

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (2.5 mmol, 5.0 equiv.), $Na_2S_2O_8$ (1.0 mmol, 2.0 equiv.) and $Ir(ppy)_2(dtbpy)PF_6$ (0.005 mmol, 0.01 equiv.) The vial was sealed and placed under atmosphere, then DMSO/DCE (1:1) (5 mL, 0.1 M) were added. The reaction was placed in between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. The reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

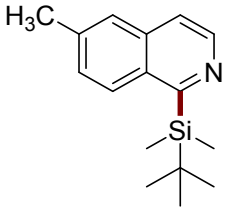
General Procedure B:

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (1.67 mmol, 3.33 equiv.), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.) and $Ir(ppy)_3$ (0.0025 mmol, 0.005 equiv.) The vial was sealed and placed under atmosphere, then DMA/DCE (1:1) (2 mL, 0.25 M) were added. The reaction was placed in between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. In this period, another two batch (1.67 mmol, 3.33 equiv.) added after every 8 hours. The reaction mixture was diluted with saturated $NaHCO_3$ aqueous solution, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

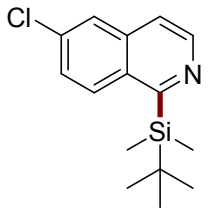
General Procedure C:

To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding heterocycles (0.5 mmol, 1.0 equiv.), the corresponding silane (2.5 mmol, 5.0 equiv.), BTMSPO (1.0

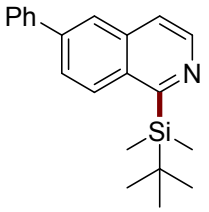
mmol, 2.0 equiv.) and $Ir(ppy)_2(dtbpy)PF_6$ (0.005 mmol, 0.01 equiv.) The vial was sealed and placed under atmosphere, then DMSO/DCE (1:1) (5 mL, 0.1 M) were added. The reaction was placed in between 2 × 23 W fluorescent lamps (approximately 5 cm from each lamp) and irradiated for 24 hours. The reaction mixture was diluted with H_2O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



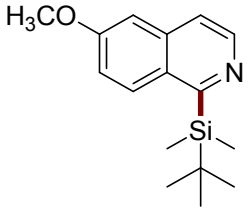
1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline (3a): According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (100 mg, 77 %). And according to the general procedure B, the product was obtained (96 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 5.6 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 7.56 (s, 1H), 7.47 (d, J = 5.6 Hz, 1H), 7.39 (dd, J = 8.6, 1.7 Hz, 1H), 2.53 (s, 3H), 0.97 (s, 9H), 0.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.49, 142.63, 139.24, 134.83, 132.53, 128.59, 128.41, 126.37, 119.41, 27.09, 21.75, 17.96, -3.08; HRMS (ESI) Calcd. for $C_{16}H_{24}NSi$ [$(M+H)^+$] 258.1678, found 258.1676.



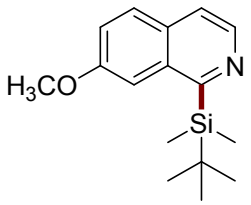
1-(*tert*-butyldimethylsilyl)-6-chloroisoquinoline (3b1): According to the general procedure A, 6-chloroisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (72 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid(85 mg, 61 %). And according to the general procedure B, the product was obtained (86 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 5.6 Hz, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 1.7 Hz, 1H), 7.49 (dd, J = 12.6, 3.8 Hz, 2H), 0.95 (s, 9H), 0.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.43, 143.40, 135.44, 135.23, 132.10, 130.31, 127.41, 126.25, 118.88, 27.00, 17.92, -3.13; HRMS (ESI) Calcd. for $C_{15}H_{21}ClNSi$ [$(M+H)^+$] 278.1132, found 278.1124.



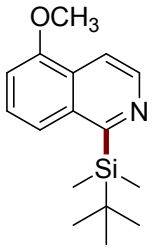
1-(*tert*-butyldimethylsilyl)-6-phenylisoquinoline (3b2): According to the general procedure A, 6-phenylisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (115 mg, 72 %). And according to the general procedure B, the product was obtained (97 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 5.6 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 1.7 Hz, 1H), 7.84 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.73 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.62 (d, *J* = 5.6 Hz, 1H), 7.51 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.43 (ddd, *J* = 7.4, 3.8, 1.2 Hz, 1H), 0.99 (s, 9H), 0.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.87, 142.82, 141.80, 140.14, 134.96, 133.03, 129.22, 128.98, 128.03, 127.49, 126.19, 125.18, 120.18, 27.10, 18.01, -3.06; HRMS (ESI) Calcd. for $C_{21}H_{26}NSi$ [$(M+H)^+$] 320.1835, found 320.1841.



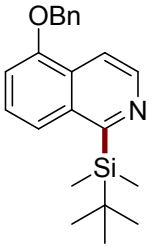
1-(*tert*-butyldimethylsilyl)-6-methoxyisoquinoline (3b3): According to the general procedure A, 6-methoxyisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (94 mg, 69 %). And according to the general procedure B, the product was obtained (102 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.46 (d, *J* = 5.7 Hz, 1H), 7.18 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 0.95 (s, 9H), 0.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.99, 159.71, 143.01, 136.59, 130.37, 130.12, 119.29, 119.21, 104.83, 55.37, 27.07, 17.96, -3.06; HRMS (ESI) Calcd. for $C_{16}H_{24}NOSi$ [$(M+H)^+$] 274.1627, found 274.1624.



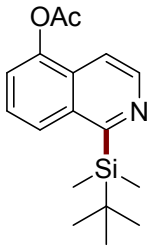
1-(*tert*-butyldimethylsilyl)-7-methoxyisoquinoline (3b4): According to the general procedure A, 7-methoxyisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (95 mg, 71 %). And according to the general procedure B, the product was obtained (96 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.5 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 5.5 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.94 (s, 3H), 0.98 (s, 9H), 0.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.78, 157.51, 141.13, 135.10, 130.01, 128.91, 122.21, 119.67, 106.62, 55.27, 27.14, 18.29, -3.20; HRMS (ESI) Calcd. for $C_{16}H_{24}NOSi$ [$(M+H)^+$] 274.1627, found 274.1625.



1-(*tert*-butyldimethylsilyl)-5-methoxyisoquinoline (3b5): According to the general procedure A, 5-methoxyisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (100 mg, 73 %). And according to the general procedure B, the product was obtained (95 mg, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.8 Hz, 1H), 7.97 (dd, J = 5.8, 0.6 Hz, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.49 – 7.42 (m, 1H), 6.94 (d, J = 7.7 Hz, 1H), 3.99 (s, 3H), 0.96 (s, 9H), 0.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.11, 154.84, 142.32, 134.61, 127.15, 126.20, 120.58, 113.92, 106.41, 55.57, 27.10, 18.01, -3.03; HRMS (ESI) Calcd. for $C_{16}H_{24}NOSi$ [$(M+H)^+$] 274.1627, found 274.1620.

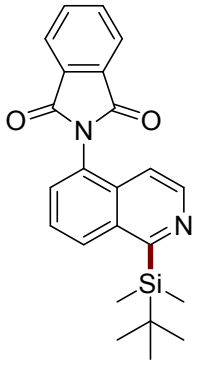


5-(benzyloxy)-1-(*tert*-butyldimethylsilyl)isoquinoline (3b6): According to the general procedure A, 5-(benzyloxy)isoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (123 mg, 70 %). And according to the general procedure B, the product was obtained (119 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.8 Hz, 1H), 8.06 (d, J = 5.7 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 7.3 Hz, 2H), 7.46 - 7.41 (m, 3H), 7.37 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 5.25 (s, 2H), 0.96 (s, 9H), 0.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.18, 153.91, 142.37, 136.67, 134.70, 128.65, 128.09, 127.35, 126.20, 120.91, 114.10, 107.87, 70.24, 27.12, 18.03, -3.02; HRMS (ESI) Calcd. for $C_{22}H_{28}NOSi$ [$(M+H)^+$] 350.1940, found 350.1943.

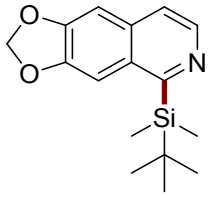


1-(*tert*-butyldimethylsilyl)isoquinolin-5-yl acetate (3b7): According to the general procedure A, isoquinolin-5-yl acetate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2%

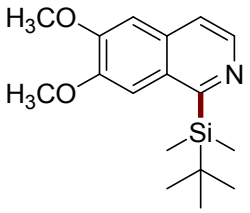
ethyl acetate/hexane) as a colorless oil (95 mg, 63 %). And according to the general procedure B, the product was obtained (90 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 5.8 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.56 (dd, *J* = 15.2, 7.2 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H), 0.97 (s, 9H), 0.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.54, 169.27, 145.97, 142.93, 134.63, 128.32, 126.65, 125.80, 121.23, 112.91, 27.05, 20.95, 17.97, -3.05; HRMS (ESI) Calcd. for $C_{17}H_{24}NO_2Si$ [$(M+H)^+$] 302.1576, found 302.1578.



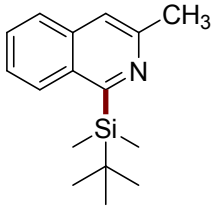
2-(1-(*tert*-butyldimethylsilyl)isoquinolin-5-yl)isoindoline-1,3-dione (3b8): According to the general procedure A, 2-(isoquinolin-5-yl)isoindoline-1,3-dione (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2 % ethyl acetate/hexane) as a colorless solid (128 mg, 66 %). And according to the general procedure B, the product was obtained (120 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.6 Hz, 1H), 8.01 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.87 – 7.77 (m, 4H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 7.3, 0.9 Hz, 1H), 0.98 (s, 9H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.03, 167.62, 149.12, 135.58, 132.08, 131.82, 128.05, 127.74, 127.50, 127.05, 126.65, 124.48, 123.95, 26.60, 17.16, -6.25; HRMS (ESI) Calcd. for $C_{23}H_{25}N_2O_2Si$ [$(M+H)^+$] 389.1685, found 389.1891.



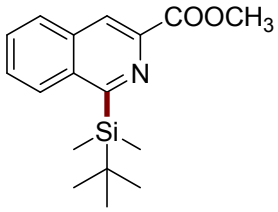
5-(*tert*-butyldimethylsilyl)-[1,3]dioxolo[4,5-g]isoquinoline (3b9): According to the general procedure A, [1,3]dioxolo[4,5-g]isoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (83 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.5 Hz, 1H), 7.50 (s, 1H), 7.40 (d, *J* = 5.5 Hz, 1H), 7.04 (s, 1H), 6.08 (s, 2H), 0.95 (s, 9H), 0.53 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 147.73, 141.79, 133.01, 119.70, 104.48, 103.10, 101.42, 29.69, 27.07, 18.02, -3.00; HRMS (ESI) Calcd. for $C_{16}H_{22}NO_2Si$ [$(M+H)^+$] 288.1420, found 288.1431.



1-(*tert*-butyldimethylsilyl)-6,7-dimethoxyisoquinoline (3b10): According to the general procedure A, 6,7-dimethoxyisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10 % ethyl acetate/hexane) as a colorless solid (92 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 5.5 Hz, 1H), 7.54 (s, 1H), 7.42 (d, J = 5.5 Hz, 1H), 7.03 (s, 1H), 4.01 (d, J = 2.6 Hz, 6H), 0.96 (s, 9H), 0.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.25, 151.8, 149.21, 141.76, 131.27, 130.28, 118.79, 107.19, 105.16, 55.91, 55.77, 27.09, 18.28, -3.26; HRMS (ESI) Calcd. for $C_{17}H_{26}NO_2Si$ [$(M+H)^+$] 304.1733, found 304.1740.

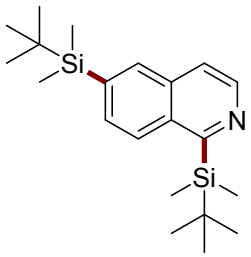


1-(*tert*-butyldimethylsilyl)-3-methylisoquinoline (3b11): According to the general procedure A, 3-methylisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (90 mg, 70 %). And according to the general procedure B, the product was obtained (66 mg, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.36 (s, 1H), 2.70 (s, 3H), 0.98 (s, 9H), 0.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.37, 150.80, 135.32, 132.03, 128.83, 128.30, 127.02, 125.24, 117.54, 27.06, 24.46, 17.91, -3.16; HRMS (ESI) Calcd. for $C_{16}H_{24}NSi$ [$(M+H)^+$] 258.1678, found 258.1676.

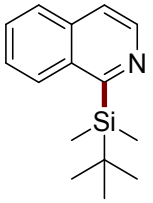


methyl 1-(*tert*-butyldimethylsilyl)isoquinoline-3-carboxylate (3b12): According to the general procedure A, methyl isoquinoline-3-carboxylate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (93 mg, 62 %). And according to the general procedure B, the product was obtained (83 mg, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.33 – 8.22 (m, 1H), 7.93 (dd, J = 6.6, 2.8 Hz, 1H), 7.76 – 7.62 (m, 2H), 4.02 (s, 3H), 1.00 (s, 9H), 0.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.98, 167.04, 141.05, 134.86, 134.23, 129.70, 129.07, 128.57, 128.41, 123.07, 52.46, 27.00, 17.94, -3.39; HRMS (ESI) Calcd. for $C_{17}H_{24}NO_2Si$

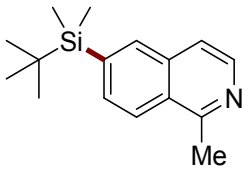
[(M+H)$^+$] 302.1576, found 302.1567.



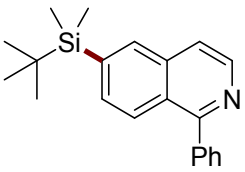
1,6-bis(*tert*-butyldimethylsilyl)isoquinoline (3b13'): According to the general procedure A, isoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (72 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (107 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.6 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 7.68 (dd, J = 8.4, 1.1 Hz, 1H), 7.55 (d, J = 5.6 Hz, 1H), 0.97 (s, 9H), 0.92 (s, 9H), 0.55 (s, 6H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 142.58, 134.61, 133.94, 133.49, 131.48, 126.91, 119.90, 27.11, 26.51, 18.00, 17.05, -3.06, -6.18. HRMS (ESI) Calcd. for $C_{16}H_{24}NOSi$ [(M+H)$^+$] 358.2381, found 358.2387.



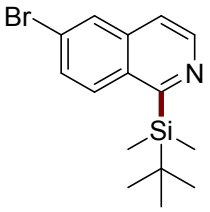
1-(*tert*-butyldimethylsilyl)isoquinoline (3b13): According to the general procedure B, isoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (87 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.6 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.63 (dd, J = 7.9, 7.0 Hz, 1H), 7.60 – 7.51 (m, 2H), 0.97 (s, 9H), 0.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.17, 142.50, 134.52, 133.98, 129.16, 128.63, 127.55, 126.35, 119.86, 27.08, 17.98, -3.04; HRMS (ESI) Calcd. for $C_{15}H_{22}NSi$ [(M+H)$^+$] 244.1522, found 244.1509.



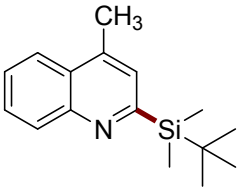
6-(*tert*-butyldimethylsilyl)-1-methylisoquinoline (3b14): According to the general procedure A, 1-methylisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (45 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 5.8 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.72 (dd, J = 8.3, 0.9 Hz, 1H), 7.52 (d, J = 5.7 Hz, 1H), 2.96 (s, 3H), 0.91 (s, 9H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.47, 141.40, 134.91, 134.14, 132.27, 123.94, 119.41, 29.69, 26.47, 17.01, -6.21; HRMS (ESI) Calcd. for $C_{16}H_{24}NSi$ [(M+H)$^+$] 258.1678, found 258.1687.



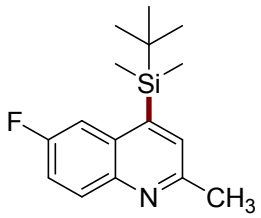
6-(*tert*-butyldimethylsilyl)-1-phenylisoquinoline (3b15): According to the general procedure A, 1-phenylisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (98 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.7 Hz, 1H), 8.10 – 7.99 (m, 2H), 7.70 (dd, J = 7.9, 1.4 Hz, 2H), 7.66 (dd, J = 6.6, 3.1 Hz, 2H), 7.57 – 7.47 (m, 3H), 0.92 (s, 9H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.57, 142.13, 141.26, 139.45, 135.83, 133.90, 132.31, 129.89, 128.55, 128.30, 126.67, 125.76, 119.95, 26.48, 17.03, -6.20; HRMS (ESI) Calcd. for $C_{21}H_{26}NSi$ [$(M+H)^+$] 320.1835, found 320.1837.



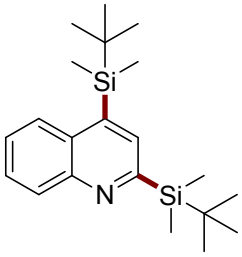
6-bromo-1-(*tert*-butyldimethylsilyl)isoquinoline (3b16): According to the general procedure B, 6-bromoisoquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (103 mg, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.7 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 9.0, 2.0 Hz, 1H), 7.47 (d, J = 5.6 Hz, 1H), 0.94 (s, 9H), 0.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.57, 143.38, 135.77, 132.26, 130.29, 129.93, 129.64, 123.79, 118.71, 27.00, 17.93, -3.13; HRMS (ESI) Calcd. for $C_{15}H_{21}BrNSi$ [$(M+H)^+$] 322.0627, found 322.0628.



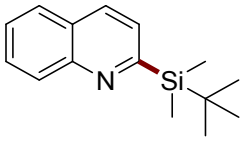
2-(*tert*-butyldimethylsilyl)-4-methylquinoline (3c): According to the general procedure A, 4-methylquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (94 mg, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.4, 0.5 Hz, 1H), 7.99 (dd, J = 8.3, 0.7 Hz, 1H), 7.70 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.55 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.44 (d, J = 0.6 Hz, 1H), 2.71 (d, J = 0.8 Hz, 3H), 1.02 (s, 9H), 0.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.52, 148.37, 140.21, 130.82, 128.38, 127.26, 126.97, 126.03, 123.59, 26.73, 18.61, 17.21, -6.15; HRMS (ESI) Calcd. for $C_{16}H_{24}NSi$ [$(M+H)^+$] 258.1678, found 258.1668.



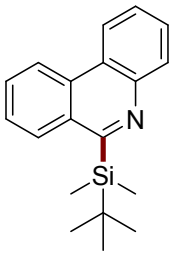
4-(*tert*-butyldimethylsilyl)-6-fluoro-2-methylquinoline (3d): According to the general procedure A, 6-fluoro-2-methylquinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (97 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 9.2, 5.8 Hz, 1H), 7.62 (dd, J = 10.6, 2.8 Hz, 1H), 7.46 – 7.36 (m, 2H), 2.72 (s, 3H), 0.93 (s, 9H), 0.50 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.70, 158.26, 156.42, 156.40, 146.31, 146.25, 144.39 (s), 131.60, 131.51, 131.12, 131.03, 130.92, 118.65, 118.40, 112.28, 112.06, 26.96, 25.07, 17.57, -3.53; HRMS (ESI) Calcd. for $C_{16}H_{23}FNSi$ [(M+H)$^+$] 276.1584, found 276.1589.



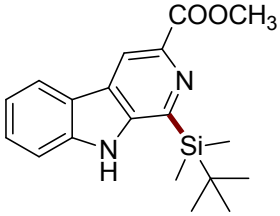
2,4-bis(*tert*-butyldimethylsilyl)quinolone (3e'): According to the general procedure A, quinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (123 mg, 75 %, mixture of **3e'** and **3e**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, J = 7.6 Hz, 1.3 H), 8.08 – 8.00 (m, 1.3 H), 7.79 (s, 0.3 H), 7.76 (s, 1H), 7.73 – 7.63 (m, 1.3 H), 7.61 (d, J = 8.2 Hz, 0.3 H), 7.56 – 7.46 (m, 1.3 H), 1.00 (s, 12H), 0.96 (s, 11 H), 0.54 (s, 6 H), 0.45 (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.54, 148.11, 141.84, 134.27, 132.61, 131.34, 131.21, 130.19, 128.91, 128.77, 128.04, 127.61, 127.15, 126.27, 126.05, 125.71, 26.98, 26.68, 17.70, 17.21, -3.33, -6.17, -6.23. HRMS (ESI) Calcd. for $C_{21}H_{36}NSi_2$ [(M+H)$^+$] 358.2381, found 358.2387.



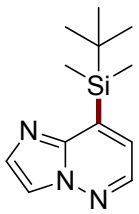
2-(*tert*-butyldimethylsilyl)quinolone (3e): According to the general procedure B, quinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (81 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.53 – 7.48 (m, 1H), 0.97 (s, 9H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.05, 148.73, 132.60, 130.20, 128.77, 127.61, 127.16, 126.26, 126.06, 26.67, 17.20, -6.18; HRMS (ESI) Calcd. for $C_{15}H_{22}NSi$ [(M+H)$^+$] 244.1522, found 244.1526.



6-(*tert*-butyldimethylsilyl)phenanthridine (3f): According to the general procedure A, phenanthridine (0.5 mmol, 1 equiv.) , *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (120 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.75 – 7.70 (m, 1H), 7.66 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 2H), 1.03 (s, 9H), 0.61 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.63, 130.88, 130.69, 129.56, 129.49, 128.16, 126.97, 126.56, 123.06, 122.27, 121.78, 27.19, 18.10, -3.07; HRMS (ESI) Calcd. for $C_{19}H_{24}NSi$ [$(M+H)^+$] 294.1678, found 294.1676.

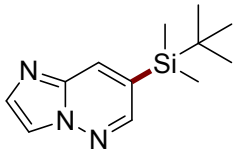


Methyl 1-(*tert*-butyldimethylsilyl)-9H-pyrido[3,4-b]indole-3-carboxylate (3g): According to the general procedure A, Methyl-9H-pyrido[3,4-b]indole-3-carboxylate (this substrate was prepared according to known procedure [4]) (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (111mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.35 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.34 (ddd, *J* = 8.0, 6.4, 1.7 Hz, 1H), 4.02 (s, 3H), 1.00 (s, 9H), 0.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.23, 148.86, 142.80, 140.06, 128.63, 126.68, 121.89, 121.66, 120.83, 116.86, 111.67, 52.36, 26.64, 17.83, -5.05; HRMS (ESI) Calcd. for $C_{19}H_{25}N_2O_2Si$ [$(M+H)^+$] 341.1685, found 341.1683.

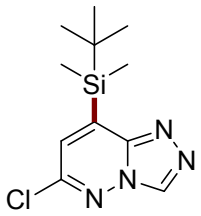


8-(*tert*-butyldimethylsilyl)imidazo[1,2-*b*]pyridazine (3h): According to the general procedure A, imidazo[1,2-*b*]pyridazine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10 % ethyl acetate/hexane) as a colorless solid (41 mg, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.3 Hz, 1H), 7.92 (d, *J* = 1.2 Hz, 1H), 7.78 (d, *J* = 1.1 Hz, 1H), 7.04 (d, *J* = 4.3 Hz, 1H), 0.95 (s, 9H),

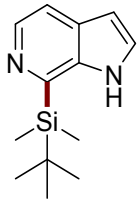
0.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.16, 141.80, 138.56, 133.20, 123.30, 115.73, 26.88, 17.33, -5.47; HRMS (ESI) Calcd. for $C_{12}H_{20}N_3Si$ [$(M+H)^+$] 234.1421, found 234.1427.



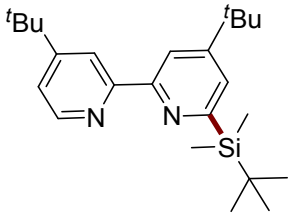
7-(*tert*-butyldimethylsilyl)imidazo[1,2-*b*]pyridazine (3h'): According to the general procedure A, imidazo[1,2-*b*]pyridazine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % ethyl acetate/hexane) as a colorless solid (20 mg, 17 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 1.4 Hz, 1H), 8.05 (d, J = 0.9 Hz, 1H), 7.95 (s, 1H), 7.76 (d, J = 0.7 Hz, 1H), 0.91 (s, 9H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.56, 138.72, 133.67, 132.19, 126.61, 116.32, 26.24, 16.96, -6.53; HRMS (ESI) Calcd. for $C_{12}H_{20}N_3Si$ [$(M+H)^+$] 234.1421, found 234.1427.



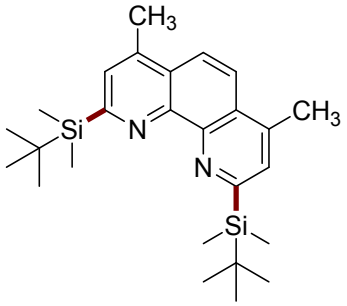
8-(*tert*-butyldimethylsilyl)-6-chloro-[1,2,4]triazolo[4,3-*b*]pyridazine (3i): According to the general procedure A, 6-chloro-[1,2,4]triazolo[4,3-*b*]pyridazine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % ethyl acetate/hexane) as a colorless solid (72 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.07 (s, 1H), 0.98 (s, 9H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.12, 145.49, 142.08, 137.92, 128.52, 26.76, 17.30, -5.75; HRMS (ESI) Calcd. for $C_{11}H_{18}ClN_4Si$ [$(M+H)^+$] 269.0984, found 269.0988.



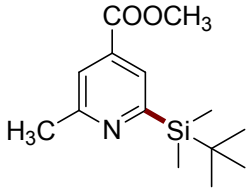
7-(*tert*-butyldimethylsilyl)-1H-pyrrolo[2,3-c]pyridine (3j): According to the general procedure B, 1H-pyrrolo[2,3-c]pyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv., 3 batches), triisopropylsilanethiol (0.6 mmol, 1.2 equiv.), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.005 equiv.) and 2 mL DMA/DCE (1:1) (0.25 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (68 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 5.4 Hz, 1H), 8.39 (s, 1H), 7.50 (d, J = 5.4 Hz, 1H), 7.35 (d, J = 3.1 Hz, 1H), 6.55 (d, J = 3.1 Hz, 1H), 0.95 (s, 9H), 0.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.88, 139.66, 139.32, 130.46, 127.24, 114.64, 101.69, 26.59, 17.84, -5.01; HRMS (ESI) Calcd. for $C_{13}H_{21}N_2Si$ [$(M+H)^+$] 233.1474, found 233.1477.



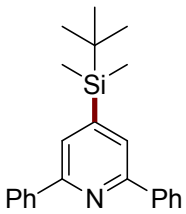
4,4'-di-*tert*-butyl-6-(*tert*-butyldimethylsilyl)-2,2'-bipyridine (3k): According to the general procedure A, 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (103 mg, 54 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.6 Hz, 1H), 8.58 (d, *J* = 5.2 Hz, 1H), 8.33 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.28 (dd, *J* = 5.3, 2.0 Hz, 1H), 1.38 (d, *J* = 5.0 Hz, 18H), 1.01 (s, 9H), 0.37 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.24, 160.51, 158.06, 157.13, 155.46, 148.76, 126.39, 120.41, 118.64, 116.59, 34.84, 34.80, 30.70, 30.51, 26.65, 16.95, -6.10; HRMS (ESI) Calcd. for $C_{24}H_{39}N_2Si$ [$(M+H)^+$] 383.2883, found 383.2887.



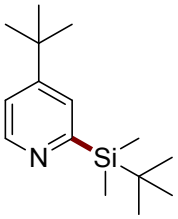
2,9-bis(*tert*-butyldimethylsilyl)-4,7-dimethyl-1,10-phenanthroline (3l'): According to the general procedure A, 4,7-dimethyl-1,10-phenanthroline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a colorless solid (135 mg,62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.60 (s, 2H), 2.75 (s, 6H), 1.05 (s, 18H), 0.46 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.93, 146.32, 140.09, 128.95, 126.71, 122.12, 26.84, 19.03, 17.17, -6.02; HRMS (ESI) Calcd. for $C_{26}H_{41}N_2Si_2$ [$(M+H)^+$] 437.2808, found 437.2811.



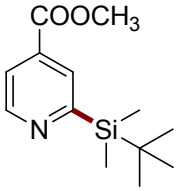
methyl 2-(*tert*-butyldimethylsilyl)-6-methylisonicotinate (3m): According to the general procedure A, methyl 6-methylisonicotinate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (80 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 0.7 Hz, 1H), 7.57 (d, *J* = 1.3 Hz, 1H), 3.93 (s, 3H), 2.63 (s, 3H), 0.91 (s, 9H), 0.32 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.65, 166.83, 159.01, 134.83, 125.20, 120.89, 52.44, 26.58, 24.83, 16.89, -6.27; HRMS (ESI) Calcd. for $C_{14}H_{24}NO_2Si$ [$(M+H)^+$] 266.1576, found 266.1578.



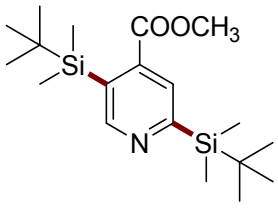
4-(*tert*-butyldimethylsilyl)-2,6-diphenylpyridine (3n): According to the general procedure A, 2,6-diphenylpyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (76 mg, 44 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 4H), 7.77 (s, 2H), 7.51 (t, J = 7.4 Hz, 4H), 7.43 (t, J = 7.3 Hz, 2H), 0.95 (s, 9H), 0.38 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 155.50, 149.22, 139.94, 128.78, 128.64, 127.14, 124.32, 26.43, 16.79, -6.46; HRMS (ESI) Calcd. for $C_{23}H_{28}NSi$ [$(M+H)^+$] 346.1986, found 346.1995.



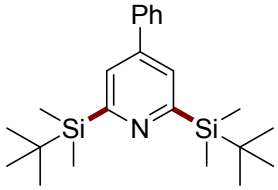
4-(*tert*-butyl)-2-(*tert*-butyldimethylsilyl)pyridine (3o)： According to the general procedure A, 4-(*tert*-butyl)pyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (90 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 5.3, 0.6 Hz, 1H), 7.47 (dd, J = 2.1, 0.7 Hz, 1H), 7.15 (dd, J = 5.3, 2.1 Hz, 1H), 1.28 (s, 9H), 0.89 (s, 9H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 156.84, 149.68, 126.81, 119.48, 34.36, 30.47, 26.50, 16.82, -6.33. HRMS (ESI) Calcd. for $C_{15}H_{28}NSi$ [$(M+H)^+$] 250.1986, found 250.1993.



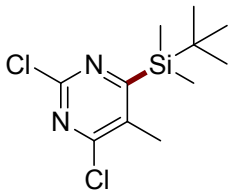
Methyl 2-(*tert*-butyldimethylsilyl)isonicotinate (3p)： According to the general procedure A, 4-(tert-butyl)pyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (50 mg, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 5.0, 0.9 Hz, 1H), 8.00 (dd, J = 1.7, 1.0 Hz, 1H), 7.71 (dd, J = 5.0, 1.8 Hz, 1H), 3.94 (s, 3H), 0.90 (s, 9H), 0.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.41, 166.39, 150.52, 134.68, 128.20, 121.39, 52.59, 26.48, 16.90, -6.36. HRMS (ESI) Calcd. for $C_{13}H_{22}NO_2Si$ [$(M+H)^+$] 252.1414, found 252.1417.



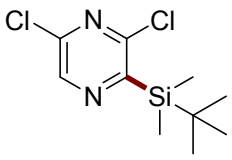
Methyl 2,5-bis(*tert*-butyldimethylsilyl)isonicotinate (3p'): According to the general procedure A, 4-(tert-butyl)pyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (46 mg, 25 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 0.9 Hz, 1H), 7.65 (d, J = 0.9 Hz, 1H), 3.89 (s, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.33 (s, 6H), 0.29 (s, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ 169.22, 167.48, 156.52, 143.00, 129.09, 127.79, 52.43, 27.21, 26.54, 17.95, 16.98, -3.89, -6.44. HRMS (ESI) Calcd. for $C_{19}H_{36}NO_2Si_2$ [$(M+H)^+$] 366.2279, found 366.2283.



2,6-bis(*tert*-butyldimethylsilyl)-4-phenylpyridine (3q'): According to the general procedure A, 4-phenylpyridine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (125 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.55 (s, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 0.94 (s, 18H), 0.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.97, 128.37, 127.24, 126.22, 26.71, 16.96, -6.17; HRMS (ESI) Calcd. for $C_{23}H_{38}NSi_2$ [$(M+H)^+$] 384.2543, found 384.2541.

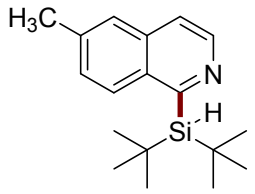


4-(*tert*-butyldimethylsilyl)-2,6-dichloro-5-methylpyrimidine (3r): According to the general procedure A, 2,4-dichloro-5-methylpyrimidine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2 % ethyl acetate/hexane) as a colorless solid (59 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 0.95 (s, 9H), 0.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.59, 162.17, 156.50, 134.59, 26.61, 17.99, 17.19, -4.16; HRMS (ESI) Calcd. for $C_{11}H_{19}Cl_2N_2Si$ [$(M+H)^+$] 277.0689, found 277.0693.

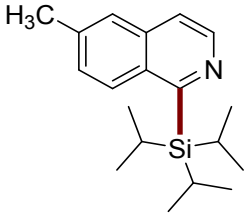


2-(*tert*-butyldimethylsilyl)-3,5-dichloropyrazine (3s): According to the general procedure A, 2,6-dichloropyrazine (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (1 % ethyl

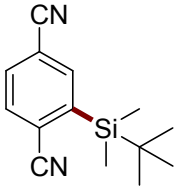
acetate/hexane) as a colorless solid (51 mg, 39 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 0.95 (s, 9H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.02, 153.38, 146.69, 142.32, 26.68, 18.10, -4.80; HRMS (ESI) Calcd. for $C_{10}H_{17}Cl_2N_2Si$ [$(M+H)^+$] 263.0533, found 263.0535.



1-(di-*tert*-butylsilyl)-6-methylisoquinoline (3t): According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), di-*tert*-butylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (73 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 5.6 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.47 (d, J = 5.6 Hz, 1H), 7.40 (dd, J = 8.6, 1.3 Hz, 1H), 4.63 (s, 1H), 2.53 (s, 3H), 1.09 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.66, 142.57, 139.43, 134.42, 128.83, 128.56, 126.14, 119.21, 28.92, 21.83, 19.53. HRMS (ESI) Calcd. for $C_{18}H_{28}NSi$ [$(M+H)^+$] 286.1986, found 286.1989.

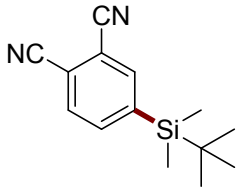


6-**methyl-1-(triisopropylsilyl)isoquinoline (3u):** According to the general procedure A, 6-methylisoquinoline (0.5 mmol, 1 equiv.), triisopropylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (115 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 5.6 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H), 7.56 (s, 1H), 7.46 (d, J = 5.6 Hz, 1H), 7.39 (dd, J = 8.6, 1.6 Hz, 1H), 2.53 (s, 3H), 1.80 - 1.69 (m, 3H), 1.15 (d, J = 7.6 Hz, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.54, 142.70, 139.10, 134.83, 132.83, 128.56, 128.17, 126.48, 119.19, 21.75, 19.03, 13.04. HRMS (ESI) Calcd. for $C_{19}H_{30}NSi$ [$(M+H)^+$] 300.2142, found 300.2144.

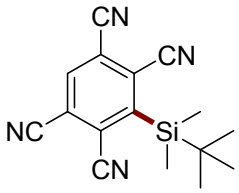


2-(*tert*-butyldimethylsilyl)terephthalonitrile (5a): According to the general procedure A, terephthalonitrile (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (86 mg, 71%). And according to the general procedure B, the product was obtained (79 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 1.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.73 (dd, J = 8.0, 1.6 Hz, 1H), 0.92 (s, 9H), 0.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)

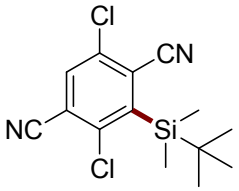
δ 144.45, 139.23, 134.11, 132.18, 121.87, 118.96, 117.53, 115.25, 26.40, 17.85, -5.25; HRMS (ESI) Calcd. for $C_{14}H_{19}N_2Si$ [(M+H)$^+$] 243.1318, found 243.1322.



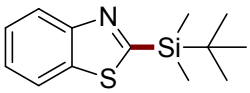
4-(*tert*-butyldimethylsilyl)phthalonitrile (5d): According to the general procedure A, phthalonitrile (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (59 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.84 (dd, J = 7.7, 1.1 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 0.87 (s, 9H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.75, 138.85, 138.54, 131.83, 115.80, 115.52, 114.69, 26.15, 16.79, -6.55; HRMS (ESI) Calcd. for $C_{14}H_{19}N_2Si$ [(M+H)$^+$] 243.1318, found 243.1321.



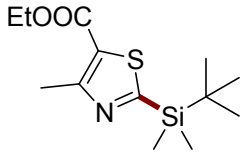
3-(*tert*-butyldimethylsilyl)benzene-1,2,4,5-tetracarbonitrile (5e): According to the general procedure A, 1,2,4,5-tetracarbonitrile (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (72 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (105 mg,72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 1.06 (s, 9H), 0.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.12, 136.64, 126.30, 121.89, 115.18, 113.29, 26.61, 19.81, -2.11; HRMS (ESI) Calcd. for $C_{16}H_{17}N_4Si$ [(M+H)$^+$] 293.1222, found 293.1231.



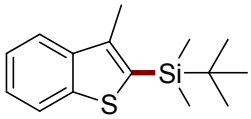
3-(*tert*-butyldimethylsilyl)-2,5-dichloroterephthalonitrile (5f): According to the general procedure A, 2,5-dichloroterephthalonitrile (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless solid (115 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 1.04 (s, 9H), 0.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.43, 141.98, 137.79, 134.62, 124.42, 119.12, 115.60, 114.27, 27.05, 19.84, -0.13; HRMS (ESI) Calcd. for $C_{14}H_{17}Cl_2N_2Si$ [(M+H)$^+$] 311.0538, found 311.0540.



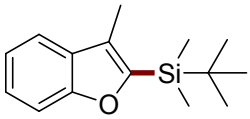
2-(*tert*-butyldimethylsilyl)benzo[*d*]thiazole (7a): According to the general procedure C, benzo[*d*]thiazole (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (50 mg, 41 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 1.02 (s, 9H), 0.47 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.79, 156.17, 136.14, 125.62, 125.00, 123.44, 121.48, 26.34, 16.98, -5.45; HRMS (ESI) Calcd. for $C_{13}H_{20}NSSi$ [$(M+H)^+$] 250.1080, found 250.1085.



ethyl 2-(*tert*-butyldimethylsilyl)-4-methylthiazole-5-carboxylate (7b): According to the general procedure C, ethyl 4-methylthiazole-5-carboxylate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (3 % ethyl acetate/hexane) as a colorless solid (95 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.30, 162.45, 162.33, 124.42, 61.12, 26.20, 17.38, 16.82, 14.31, -5.59; HRMS (ESI) Calcd. for $C_{13}H_{24}NO_2SSi$ [$(M+H)^+$] 286.1292, found 286.1296.

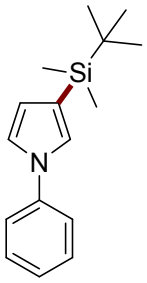


***tert*-butyldimethyl(3-methylbenzo[*b*]thiophen-2-yl)silane (7c):** According to the general procedure C, 3-methylbenzo[*b*]thiophene (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (85 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.43 - 7.34 (m, 2H), 2.55 (s, 3H), 1.00 (s, 9H), 0.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.95, 141.77, 139.40, 132.65, 124.08, 123.55, 121.99, 121.71, 26.70, 18.23, 15.26, -3.83; HRMS (EI) Calcd. for $C_{15}H_{22}SSi$ [M^+] 262.1211, found 262.1214.

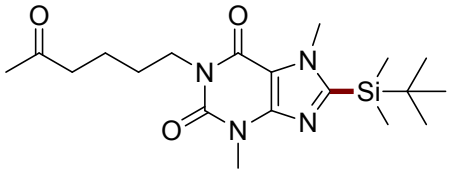


***tert*-butyldimethyl(3-methylbenzofuran-2-yl)silane (7d):** According to the general procedure C, 3-methylbenzo[*b*]thiophene (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography

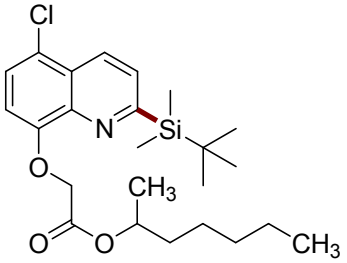
(hexane) as a colorless solid (78 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.30 - 7.20 (m, 2H), 2.33 (s, 3H), 0.97 (s, 9H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.49, 156.29, 129.84, 126.15, 124.14, 121.64, 119.15, 111.09, 26.40, 17.78, 9.22, -5.66; HRMS (EI) Calcd. for $C_{15}H_{22}OSi$ [M^+] 246.1440, found 246.1442.



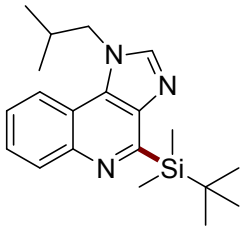
3-(*tert*-butyldimethylsilyl)-1-phenyl-1*H*-pyrrole (7e): According to the general procedure C, 3-methylbenzo[*b*]thiophene (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (hexane) as a colorless solid (66 mg, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 7.26 (s, 1H), 7.17 (dd, *J* = 2.6, 2.1 Hz, 1H), 7.09 (t, *J* = 1.8 Hz, 1H), 6.40 (dd, *J* = 2.7, 1.6 Hz, 1H), 0.93 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.46, 129.46, 125.55, 125.45, 120.53, 120.30, 117.22, 116.20, 26.48, 16.75, -5.32; HRMS (EI) Calcd. for $C_{16}H_{23}NSi$ [M^+] 257.1600, found 257.1602.



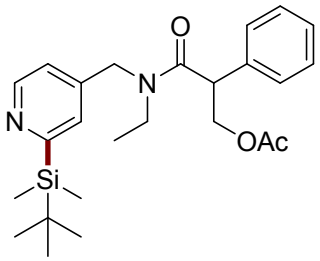
8-(*tert*-butyldimethylsilyl)-3,7-dimethyl-1-(5-oxohexyl)-1*H*-purine-2,6(3*H*,7*H*)-dione (7f): According to the general procedure C, 3,7-dimethyl-1-(5-oxohexyl)-3,4,5,7-tetrahydro-1*H*-purine-2,6-dione (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), TMSOOTMS (138 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (20 % acetone/hexane) as a colorless solid (88 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H), 3.99 (t, *J* = 7.0 Hz, 2H), 3.56 (s, 3H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.13 (s, 3H), 1.63 (dd, *J* = 6.5, 3.2 Hz, 4H), 0.97 (s, 9H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.90, 157.09, 155.33, 151.51, 148.93, 109.45, 43.19, 40.62, 34.18, 29.93, 29.55, 27.42, 26.36, 20.94, 17.69, -4.98; HRMS (ESI) Calcd. for $C_{19}H_{33}N_4O_3Si$ [$(M+H)^+$] 393.2316, found 393.2318.



heptan-2-yl 2-((2-(*tert*-butyldimethylsilyl)-5-chloroquinolin-8-yl)oxy)acetate (8a): According to the general procedure A, heptan-2-yl 2-((5-chloroquinolin-8-yl)oxy)acetate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (5% ethyl acetate/hexane) as a colorless oil (115 mg, 51%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 5.11 (s, 2H), 5.03 (dd, *J* = 7.1, 5.8 Hz, 1H), 1.24 (d, *J* = 6.3 Hz, 8H), 0.96 (s, 10H), 0.88 – 0.82 (m, 4H), 0.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.09, 168.70, 153.26, 141.81, 129.74, 127.05, 126.22, 126.09, 124.69, 115.33, 35.77, 31.54, 26.62, 24.94, 22.47, 19.90, 17.05, 13.94, -6.23. HRMS (ESI) Calcd. for $C_{24}H_{37}ClNO_3Si$ [$(M+H)^+$] 450.2226, found 450.2228.

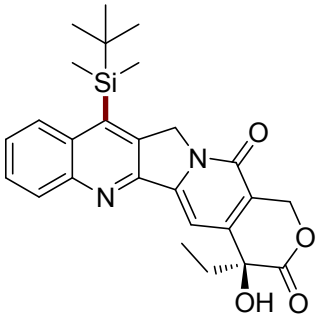


4-(*tert*-butyldimethylsilyl)-1-isobutyl-1H-imidazo[4,5-c]quinolone (8b): According to the general procedure A, 1-isobutyl-1H-imidazo[4,5-c]quinoline (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (136 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.1 Hz, 1H), 8.07 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.88 (s, 1H), 7.65 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 4.30 (d, *J* = 7.4 Hz, 2H), 2.47 – 2.25 (m, 1H), 1.05 (s, 9H), 1.03 (s, 3H), 1.01 (s, 3H), 0.62 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.69, 144.89, 143.60, 142.99, 131.70, 130.00, 126.35, 126.10, 119.80, 117.36, 54.98, 28.71, 27.04, 19.82, 17.67, -4.94. HRMS (ESI) Calcd. for $C_{20}H_{30}N_3Si$ [$(M+H)^+$] 340.2204, found 340.2208.

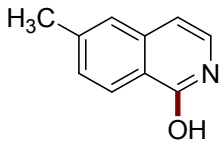


3-(((2-(*tert*-butyldimethylsilyl)pyridin-4-yl)methyl)(ethyl)amino)-3-oxo-2-phenylpropyl acetate (8c): According to the general procedure A, 3-(ethyl(pyridin-4-ylmethyl)amino)-3-oxo-2-phenylpropyl acetate (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (5% ethyl acetate/hexane) as a colorless oil (70 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64(8.69) (d, *J* = 5.1 Hz, 1H), 7.37 – 7.19 (m, 6H), 6.92(6.89) (d, *J* = 5.0 Hz, 1H), 4.87(4.49) (d, *J* = 15.8 Hz, 1H), 4.69 – 4.62 (m, 1H), 4.38 – 4.13(3.92 – 3.88) (m, 3H), 3.43 - 3.36(3.68 – 3.63)(m, 1H), 3.13 – 3.10(3.24- 3.19) (m, 1H), 2.04(2.00) (s, 3H), 1.09 – 1.03 (m, 3H), 0.92 – 0.82 (m, 9H), 0.33 – 0.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.87, 170.67, 166.61, 150.06, 149.75, 144.15, 143.44, 135.53, 135.26, 129.17, 128.57, 128.10, 128.01, 127.97, 127.47, 121.20, 119.97, 66.65, 66.45, 49.48, 48.27,

47.83, 47.59, 41.97, 41.57, 29.67, 26.47, 22.66, 20.93, 20.88, 16.88, 16.85, 14.10, 13.86, 12.40, -6.35, -6.40. HRMS (ESI) Calcd. for $C_{25}H_{37}N_2O_3Si$ [$(M+H)^+$] 441.2568, found 441.2566.



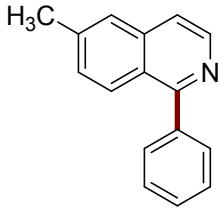
(*S*)-11-(*tert*-butyldimethylsilyl)-4-ethyl-4-hydroxy-1H-pyrano[3',4':6,7]indolizino[1,2-b]quinoline-3,14(4H,12H)-dione (8d): According to the general procedure A, Camptothecin (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (580 mg, 5 mmol, 10 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (4:1) (0.1 M) were used. Then irradiated at 467 nm Blue Led (Kessil Photoredox LED Lights PR160 Series) (25% intensity) for 24 hours. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a yellow solid (51 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 3.5 Hz, 1H), 8.22 (d, J = 3.1 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.68 (s, 1H), 7.65 – 7.60 (m, 1H), 5.76 (d, J = 16.3 Hz, 1H), 5.31 (t, J = 8.1 Hz, 3H), 3.72 (s, 1H), 1.90 (dt, J = 14.3, 6.8 Hz, 2H), 1.07 – 1.04 (m, 3H), 0.99 (s, 9H), 0.70 (s, 6H).
Spectroscopic data in accordance with literature.[5]



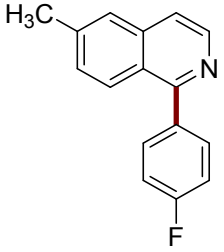
6-methylisoquinolin-1-ol (9): 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** (52 mg, 0.2 mmol) and 30% H_2O_2 (0.5 mL) were placed into a flask in tetrahydrofuran (1 mL). The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated $NaHSO_3$ aqueous solution (10 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to obtain the compound as brown oil, which was purified by column chromatography (20% ethyl acetate/hexane) to yield the title compound (31 mg, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.17 (d, J = 7.1 Hz, 1H), 6.51 (d, J = 7.1 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.46, 143.25, 138.31, 128.43, 127.71, 127.15, 125.93, 123.73, 106.60, 21.83. HRMS (ESI) Calcd. for $C_{10}H_{10}NO$ [$(M+H)^+$] 160.0757, found 160.0762.

General procedure D for Hiyama-Denmark cross-coupling of heteroarylsilane products:
To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added the corresponding aryl silane (0.5 mmol, 1.0 equiv.), the corresponding aryl iodides or bromide (1.0 mmol, 2 equiv.), $Pd(Ph_3P)_4$ (0.025 mmol, 0.05 equiv.) and Ag_2O (0.5 mmol, 1 equiv.). The vial was sealed and placed under an atmosphere of nitrogen, then anhydrous DMF (5 mL, 0.1 M) and TBAF (0.25 mL, 0.5 equiv., 1 mmol/L in THF) were added. The reaction was heated at 90 °C for 4 hours. The reaction mixture was diluted with H_2O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of

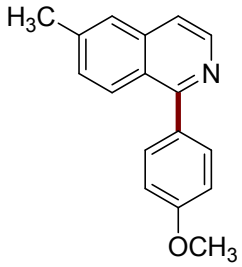
the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



6-methyl-1-phenylisoquinoline (10a): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 4-iodobenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (70 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 5.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.65 (s, 1H), 7.59 – 7.45 (m, 4H), 7.36 (dd, J = 8.7, 1.6 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.32, 142.21, 140.31, 139.61, 137.14, 129.84, 129.39, 128.47, 128.27, 127.36, 125.85, 125.05, 119.43, 21.83. HRMS (ESI) Calcd. for $C_{16}H_{14}N$ [$(M+H)^+$] 220.1121, found 220.1119.

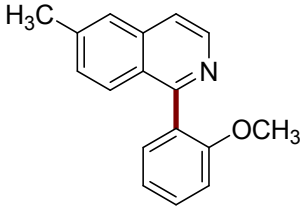


1-(4-fluorophenyl)-6-methylisoquinoline (10b): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 1-fluoro-4-iodobenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (83 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 5.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.60 (d, J = 5.7 Hz, 1H), 7.42 (dd, J = 8.7, 1.6 Hz, 1H), 7.30 – 7.24 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.24, 161.78, 159.18, 142.13), 140.47, 137.18, 135.65, 135.61, 131.68, 131.60, 129.57, 127.05, 125.95, 125.00, 119.58, 115.39, 115.18, 21.83. HRMS (ESI) Calcd. for $C_{16}H_{13}FN$ [$(M+H)^+$] 238.1027, found 238.1029.

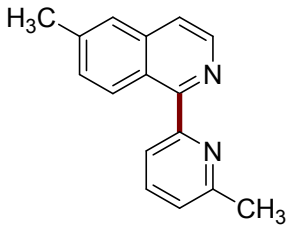


1-(4-methoxyphenyl)-6-methylisoquinoline (10c): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 1-iodo-4-methoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (95 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 5.7 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.71 – 7.59 (m, 3H), 7.52 (d, J = 5.7 Hz, 1H), 7.35 (dd, J = 8.7, 1.5 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz,

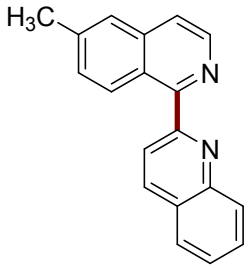
$CDCl_3$) δ 159.91, 142.17, 140.19, 137.21, 132.13, 131.20, 129.27, 127.43, 125.84, 125.06, 119.06, 113.70, 55.34, 21.80. HRMS (ESI) Calcd. for $C_{17}H_{16}NO$ [$(M+H)^+$] 250.1226, found 250.1233.



1-(2-methoxyphenyl)-6-methylisoquinoline (10d): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 1-iodo-2-methoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.7 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.47 (ddd, *J* = 8.3, 7.6, 1.8 Hz, 1H), 7.38 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.30 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.11 (t, *J* = 7.4Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.57, 157.09, 142.20, 140.22, 136.48, 131.17, 129.92, 129.11, 128.64, 127.71, 126.12, 125.58, 120.68, 119.65, 111.05, 55.51, 21.88. HRMS (ESI) Calcd. for $C_{17}H_{16}NO$ [$(M+H)^+$] 250.1226, found 250.1231.

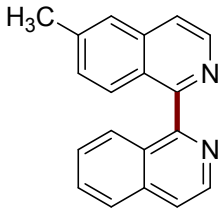


6-methyl-1-(6-methylpyridin-2-yl)isoquinoline (10e): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 2-bromo-6-methylpyridine. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (83 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.7 Hz, 1H), 8.37 (d, *J* = 8.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.40 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.26 (t, *J* = 3.8 Hz, 2H), 2.69 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.63, 141.97, 140.30, 137.44, 136.96, 129.76, 127.48, 125.69, 125.07, 122.68, 122.06, 120.53, 24.62, 21.86. HRMS (ESI) Calcd. for $C_{16}H_{15}N_2$ [$(M+H)^+$] 235.1230, found 235.1227.

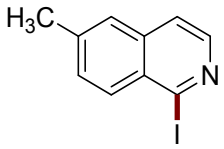


2-(6-methylisoquinolin-1-yl)quinolone (10f): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 2-bromoquinoline. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.7 Hz, 1H), 8.64 (d, *J* = 5.6 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.79 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.70 – 7.58 (m, 3H), 7.45 (dd, *J* = 8.8, 1.5 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.13, 157.15,

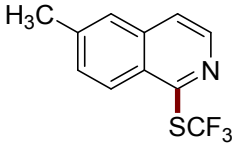
147.30, 142.00, 140.47, 137.61, 136.78, 130.12, 129.83, 129.68, 127.69, 127.62, 127.55, 127.01 (s), 125.77, 125.31, 122.73, 120.94, 21.91. HRMS (ESI) Calcd. for $C_{19}H_{15}N_2$ [$(M+H)^+$] 271.1230, found 271,1234.



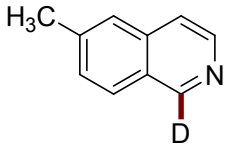
7-**methyl-1,1'-biisoquinoline (10g):** According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** and 1-bromoisoquinoline. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (95 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.7 Hz, 1H), 8.66 (d, *J* = 5.7 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 5.6 Hz, 1H), 7.75 – 7.61 (m, 4H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.46 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.29 (dd, *J* = 8.6, 1.5 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.19, 157.67, 141.98, 141.89, 140.71, 137.12, 136.76, 130.28, 129.80 , 127.75, 127.47, 127.19, 126.90, 126.85, 126.19, 125.73, 120.97, 120.54, 21.95. HRMS (ESI) Calcd. for $C_{19}H_{15}N_2$ [$(M+H)^+$] 271.1230, found 271.1231.



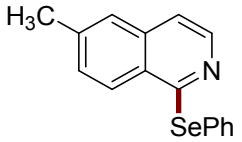
1-iodo-6-methylisoquinoline (11): 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** (52 mg, 0.2 mmol) and NIS (180 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (39 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.6 Hz, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.04, 141.70, 136.39, 132.61, 131.16, 130.42, 127.06, 126.10, 120.86, 21.72. HRMS (ESI) Calcd. for $C_{10}H_9IN$ [$(M+H)^+$] 269.9774, found 269.9781.



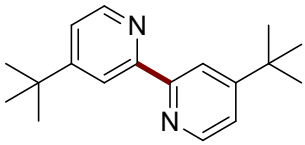
6-methyl-1-((trifluoromethyl)thio)isoquinoline (12): 1-(*tert*-butyldimethylsilyl)-6-methyl isoquinoline **3a** (52 mg, 0.2 mmol) and 1-((trifluoromethyl)thio)pyrrolidine-2,5-dione (159 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (30 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.6 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.52 (dd, *J* = 8.7, 1.5 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.79, 141.71, 137.13, 130.81, 126.21, 125.77, 121.55, 21.89. HRMS (ESI) Calcd. for $C_{11}H_9F_3NS$ [$(M+H)^+$] 244.0402, found 244.0406.



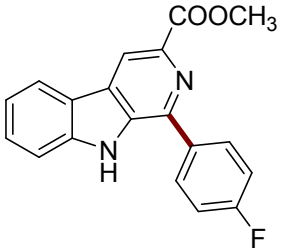
6-methylisoquinoline- 1- d (13): 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** (52 mg, 0.2 mmol) and D_2O (16 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (29 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 0.02H), 8.47 (d, *J* = 5.7 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.43 (dd, *J* = 8.4, 1.3 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.52 (t, *J* = 107.6 Hz), 142.75, 140.79, 136.09, 129.53, 127.36, 126.98, 125.32, 120.02, 22.04. HRMS (ESI) Calcd. for $C_{10}H_8DN$ [$(M+H)^+$] 145.0871, found 145.0880.



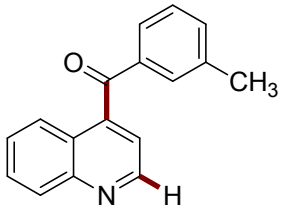
6-methyl-1-(phenylselanyl)isoquinoline (14): 1-(*tert*-butyldimethylsilyl)-6-methylisoquinoline **3a** (52 mg, 0.2 mmol) and phenyl hypochloroselenoite (153 mg, 0.8 mmol) were placed into a Schlenk flask under nitrogen in anhydrous tetrahydrofuran (2 mL). Then anhydrous AgF (105 mg, 0.8 mmol) was added. After this addition, the reaction mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the crude was directly poured into a flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a colorless oil (28 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.6 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.55 (s, 1H), 7.43 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.34 (dd, *J* = 4.2, 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.64, 142.87, 140.85, 136.24, 135.09, 129.73, 129.18, 128.52, 128.01, 127.77, 126.65, 126.17, 118.95, 21.82. HRMS (ESI) Calcd. for $C_{16}H_{14}NSe$ [$(M+H)^+$] 300.0286, found 300.0289.



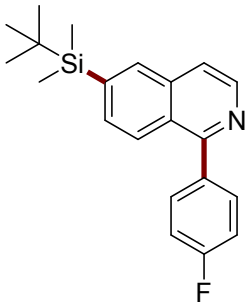
4,4'-di-*tert*-butyl-2,2'-bipyridine (15): According to the general procedure D for Hiyama-Denmark cross-coupling with 4-(*tert*-butyl)-2-(*tert*-butyldimethylsilyl)pyridine **3o** and 2-bromo-4-(*tert*-butyl)pyridine. The crude mixture was purified by flash column chromatography (50% ethyl acetate/hexane) to give the title compound as a white solid (74 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 5.3, 0.4 Hz, 2H), 8.40 (d, *J* = 1.4 Hz, 2H), 7.28 (dd, *J* = 5.2, 2.0 Hz, 2H), 1.36 (s, 19H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.87, 156.44, 148.96, 120.64, 118.20, 34.90, 30.55. HRMS (ESI) Calcd. for $C_{18}H_{25}N_2$ [$(M+H)^+$] 269.2012, found 269.2015.



Methyl 1-(4-fluorophenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (16): According to the general procedure D for Hiyama-Denmark cross-coupling methyl 1-(*tert*-butyldimethylsilyl)-9H-pyrido[3,4-b]indole-3-carboxylate **3g** and 1-fluoro-4-iodobenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (90 mg, 56%). ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 11.96 (s, 1H), 8.93 (s, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.07 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.47 (t, *J* = 8.9 Hz, 2H), 7.37 – 7.29 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, *d*^{6}-DMSO) δ 165.97, 163.79, 161.34, 141.46, 141.05, 136.61, 134.47, 133.93, 130.85, 130.76, 129.23, 128.71, 122.03, 121.10, 120.43, 116.71, 115.76, 115.54, 112.71, 52.03. HRMS (ESI) Calcd. for $C_{19}H_{14}FN_2O_2$ [(M+H)$^+$] 321.1034, found 321.1037.

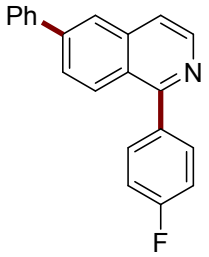


Quinolin-4-yl(m-tolyl)methanone (18): The 3-methylbenzoyl group was introduced according to the known procedure.[6] To a solution of 2-(*tert*-butyldimethylsilyl) quinoline **3e** (0.2 mmol), 3-methylbenzaldehyde (0.8 mmol) and $TMSN_3$ (0.4 mmol) in benzene (1.5 mL) phenyliodinebis(trifluroacetate) (PIFA) (0.4 mmol) was added portionwise in a 5-10 minutes period at room temperature. After stirring the reaction mixture for 2 h at room temperature, Et_3N (0.5 mL) was added and then stirred for 10 min. The solvents were removed under reduced pressure. The crude mixture was added to 1 mL H_2O, then TBAF (1.0 mL, 1 mmol/L in THF) were added, the reaction was heated at 80 °C for 4 hours. The reaction mixture was diluted with H_2O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a colorless oil (22 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 4.3 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 3H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.39 (d, *J* = 4.3 Hz, 1H), 7.26 (s, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.51, 164.49, 149.52, 148.49, 145.12, 132.73, 129.98, 129.87, 129.55, 127.49, 125.47, 125.04, 119.21, 114.04, 55.60. HRMS (ESI) Calcd. for $C_{17}H_{14}NO$ [(M+H)$^+$] 248.1070, found 248.1075.

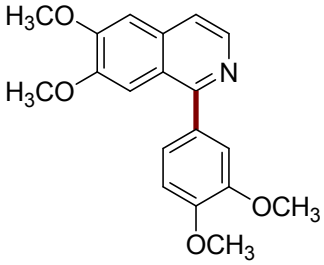


6-(*tert*-butyldimethylsilyl)-1-(4-fluorophenyl)isoquinoline (20): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)isoquinoline **3b13** (1.0 mmol) and 1-fluoro-4-iodobenzene(2.0 mmol, 2 equiv.). The crude mixture was purified by flash column

chromatography (50% ethyl acetate/hexane) to give the compound 1-(4-fluorophenyl)isoquinoline **19** as a white solid (159 mg, 71%). Then according to the general procedure A, 1-(4-fluorophenyl)isoquinoline **19** (0.5 mmol, 1 equiv.), *tert*-butyldimethylsilane (290 mg, 2.5 mmol, 5 equiv.), $Na_2S_2O_8$ (238 mg, 1.0 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbpy)PF_6$ (4.6 mg, 0.005 mmol, 0.01 equiv.) and 5 mL DMSO/DCE (1:1) (0.1 M) were used. The product was isolated by flash chromatography (2% ethyl acetate/hexane) as a colorless oil (101 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.7 Hz, 1H), 8.08 – 7.95 (m, 2H), 7.75 – 7.60 (m, 4H), 7.23 (dd, *J* = 12.1, 5.3 Hz, 2H), 0.92 (s, 9H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.35, 159.46, 142.08, 141.52, 135.91, 135.49, 134.02, 132.53, 131.79, 131.71, 126.65, 125.51, 120.16, 115.47, 115.26, 26.51, 17.07, -6.17; HRMS (ESI) Calcd. for $C_{21}H_{25}FNSi$ [$(M+H)^+$] 338.1740, found 338.1751.

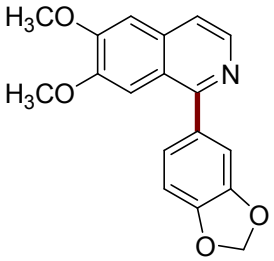


1-(4-fluorophenyl)-6-phenylisoquinoline (21): To a 10 mL vial equipped with a Teflon septum and magnetic stir bar were added 6-(*tert*-butyldimethylsilyl)-1-(4-fluorophenyl)isoquinoline **20** (0.5 mmol, 1.0 equiv.), 1-fluoro-4-iodobenzene (1.0 mmol, 2 equiv.), $PdCl_2$ (0.025 mmol, 0.05 equiv.). The vial was sealed and placed under an atmosphere of nitrogen, then anhydrous DMF (5 mL, 0.1 M) and TBAF (1.0 mL, 2.0 equiv., 1 mmol/L in THF) were added. The reaction was heated at 90 °C for 4 hours. The reaction mixture was diluted with H_2O, extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (10% ethyl acetate/hexane) to give the title compound as a white solid (106 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.7 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 1.5 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.78 – 7.67 (m, 5H), 7.53 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.31 – 7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.32, 161.86, 159.37, 142.71, 142.43, 139.82, 137.25, 135.38, 131.73, 131.64, 129.02, 128.23, 127.85, 127.48, 127.04, 125.64, 124.63, 120.27, 115.48, 115.27. HRMS (ESI) Calcd. for $C_{21}H_{15}FN$ [$(M+H)^+$] 300.1183, found 300.1185.

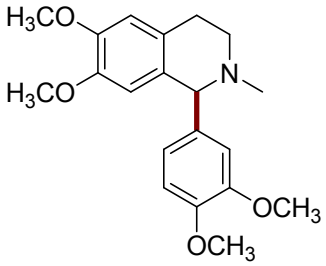


1-(3,4-dimethoxyphenyl)-6,7-dimethoxyisoquinoline (22): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6,7-dimethoxyisoquinoline **3b10** and 4-iodo-1,2-dimethoxybenzene. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (114 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.5 Hz, 1H), 7.49 (d, *J* = 5.6 Hz, 1H), 7.44 (s, 1H), 7.28 (d, *J* = 1.7 Hz, 2H), 7.12 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.94 (s, 3H), 3.88 (s, 3H); ^{13}C

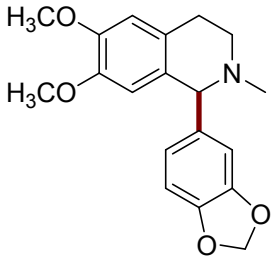
NMR (100 MHz, $CDCl_3$) δ 157.70, 152.66, 149.92, 149.27, 148.89, 140.76, 133.86, 132.24, 122.43, 122.18, 118.55, 112.75, 110.74, 105.64, 104.93, 55.89. HRMS (ESI) Calcd. for $C_{19}H_{20}NO_4$ [$(M+H)^+$] 326.1387, found 326.1391.



1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxyisoquinoline (22'): According to the general procedure D for Hiyama-Denmark cross-coupling with 1-(*tert*-butyldimethylsilyl)-6,7-dimethoxyisoquinoline **3b10** and 5-iodobenzo[d][1,3]dioxole. The crude mixture was purified by flash column chromatography (20% ethyl acetate/hexane) to give the title compound as a white solid (108 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.6 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 7.39 (s, 1H), 7.17 (dd, *J* = 10.4, 2.4 Hz, 2H), 7.10 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.04 (s, 2H), 4.03 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58, 152.63, 149.94, 147.81, 147.76, 141.01, 133.80, 123.46, 122.43, 118.62, 110.11, 108.19, 105.49, 104.94, 101.20, 56.02, 55.89. HRMS (ESI) Calcd. for $C_{18}H_{16}NO_4$ [$(M+H)^+$] 310.1074, found 310.1077.



1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (23): To a stirred solution of 1-(3,4-dimethoxyphenyl)-6,7-dimethoxyisoquinoline (65 mg, 0.2 mmol) in THF (2 mL) at room temperature under nitrogen was added methyl iodide (284 mg, 2 mmol). The resulting solution was stirred in the dark at room temperature for 12 h during which time a yellow precipitate formed. The solvent was removed to dryness to afford the iodide salt as an yellow power. Sodium borohydride (15 mg, 0.4 mmol) was added in portions to the solution of this yellow power in methanol (2 mL) at 0 °C with constant stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to obtain the compound as brown oil, which was purified by column chromatography (10% methanol/dichloromethane) to yield the title compound (55 mg, 80%) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.81 (s, 2H), 6.60 (s, 1H), 6.13 (s, 1H), 4.44 (s, 1H), 3.93 – 3.77 (m, 9H), 3.58 (s, 3H), 3.28 (d, *J* = 7.4 Hz, 2H), 2.91 – 2.70 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.20, 148.85, 147.92, 147.30, 135.53, 125.35, 122.53, 112.11, 111.11, 110.58, 110.30, 70.25, 55.95. 55.76, 51.39, 43.06, 29.61. HRMS (ESI) Calcd. for $C_{20}H_{26}NO_4$ [$(M+H)^+$] 344.1856, found 344.1859.



1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (24): To a stirred solution of 1-(benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxyisoquinoline (62 mg, 0.2 mmol) in THF (2 mL) at room temperature under nitrogen was added methyl iodide (284 mg, 2 mmol). The resulting solution was stirred in the dark at room temperature for 12 hr during which time a yellow precipitate formed. The solvent was removed to dryness to afford the iodide salt as an yellow power. Sodium borohydride (15 mg, 0.4 mmol) was added in portions to the solution of this yellow power in methanol (2 mL) at 0 °C with constant stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to obtain the compound as brown oil, which was purified by column chromatography (10% methanol/dichloromethane) to yield the title compound (49 mg, 75%) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 21.6 Hz, 3H), 6.59 (s, 1H), 6.16 (s, 1H), 5.94 (s, 2H), 4.30 (s, 1H), 3.85 (s, 3H), 3.62 (s, 3H), 3.14 (dd, J = 9.5, 6.5 Hz, 2H), 2.86 – 2.61 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.85, 147.71, 147.22, 147.13,125.93, 123.32, 111.21, 110.62, 109.58, 107.59, 101.02, 69.98, 55.82, 55.77, 51.22, 43.48, 29.65. HRMS (ESI) Calcd. for $C_{19}H_{22}NO_4$ [$(M+H)^+$] 328.1543, found 328.1545.

8. References

1. Komiyama, T.; Minami, Y.; Hiyama, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 15787.

2. Crestey, F.; A. Jensen, A. A.; Borch, M.; Andreasen,J. T.; Andersen, J.; Balle, T.; Kristensen, J. L. *J. Med. Chem.* **2013**, *56*, 9673.

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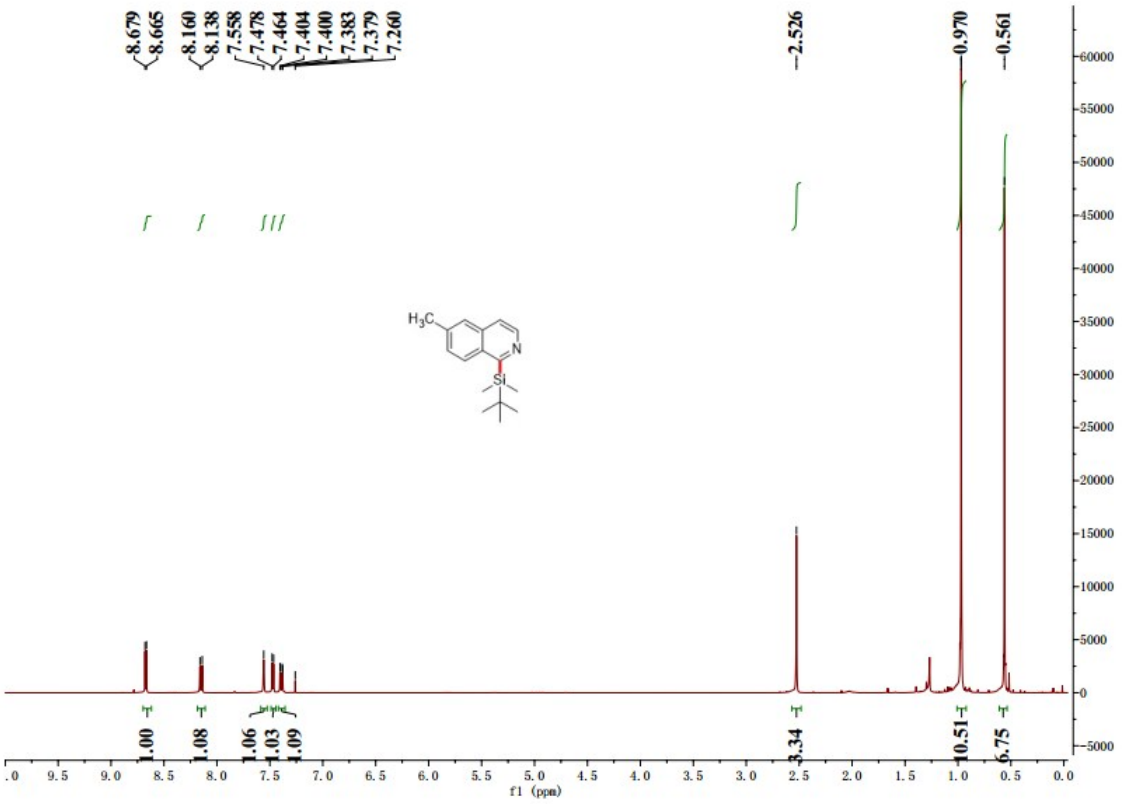
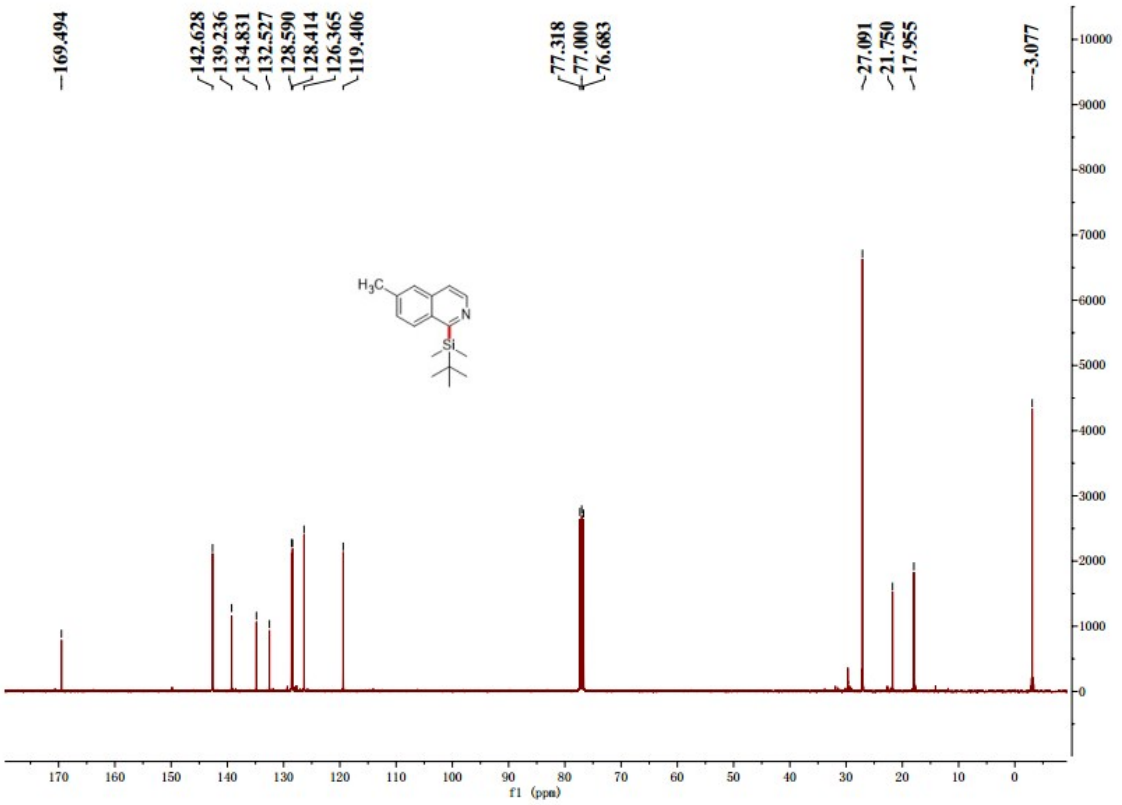
4. Ikeda, R.; Kimura, T.; Tsutsumi, T.; Tamura, S.; Sakai, N.; Konakahara, T. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 3506.

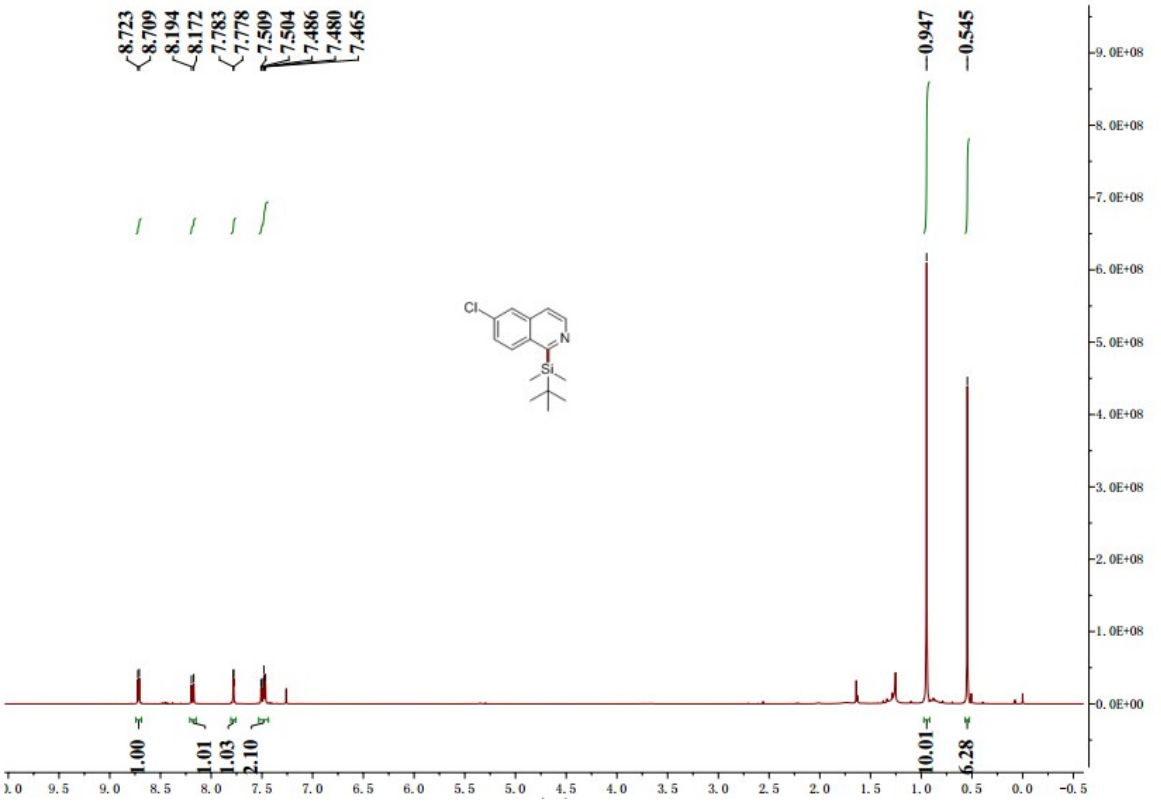
5. Du, W.; Kaskar, B.; Blumbergs, P.; Subramanianb P.-K.; Curran, D. P. *Bioorg. Med. Chem.* **2003***, 11,* 451.

6. Matcha, K.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 2082.

9. Spectral Data for Products



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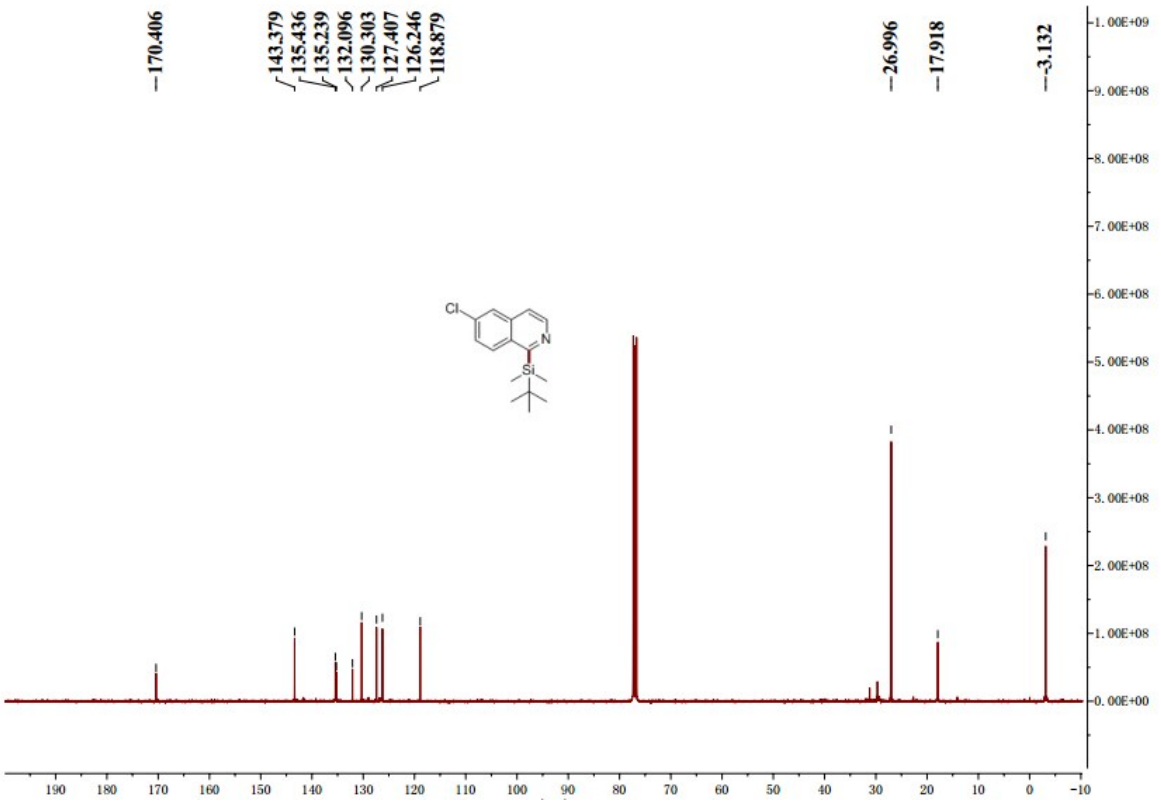
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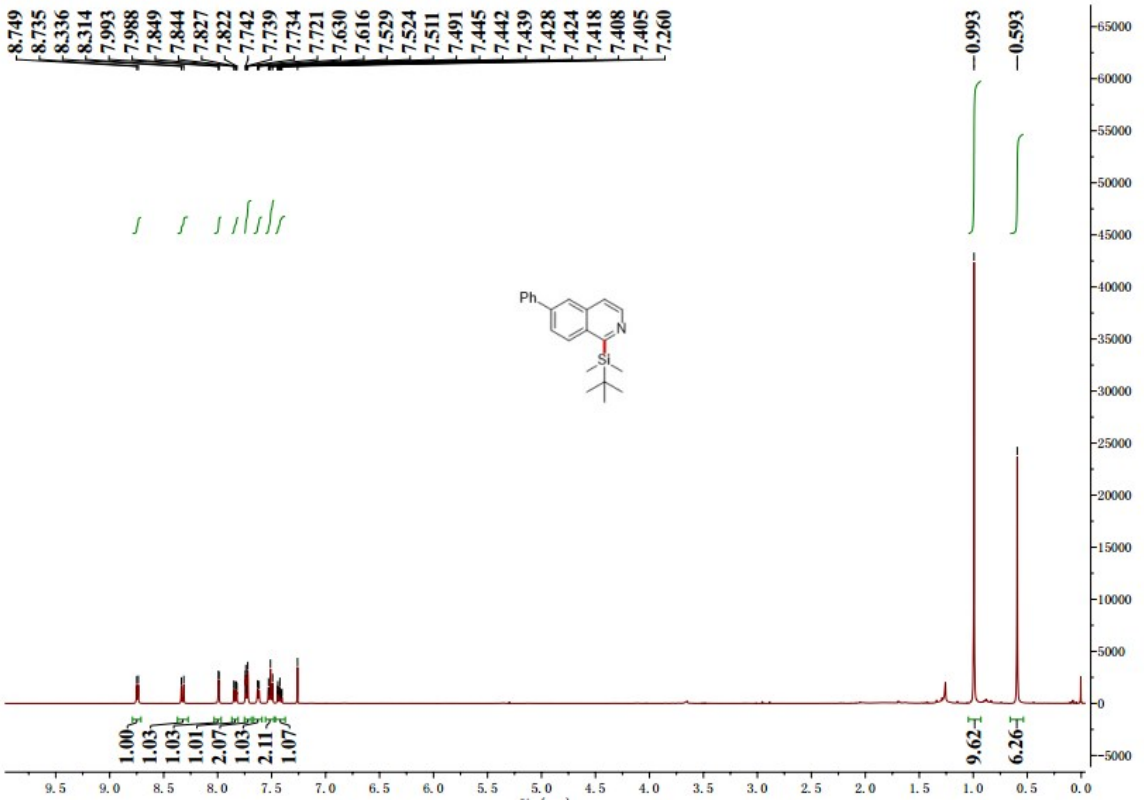
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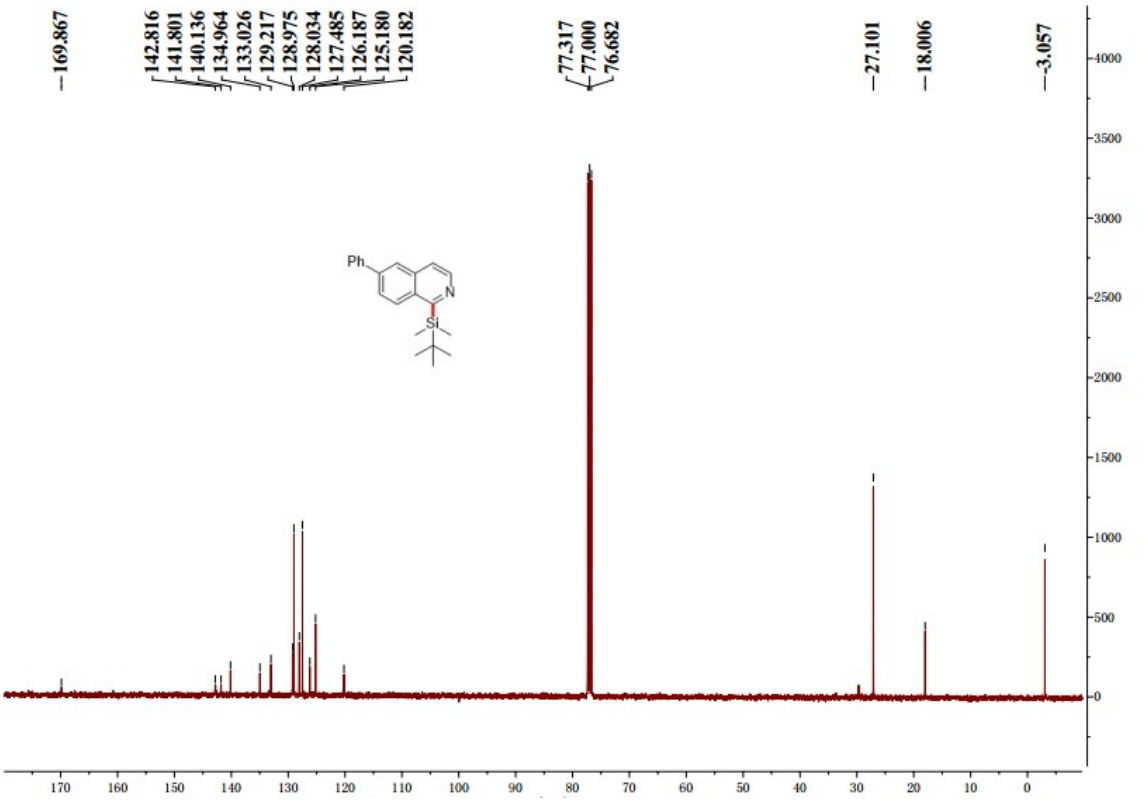
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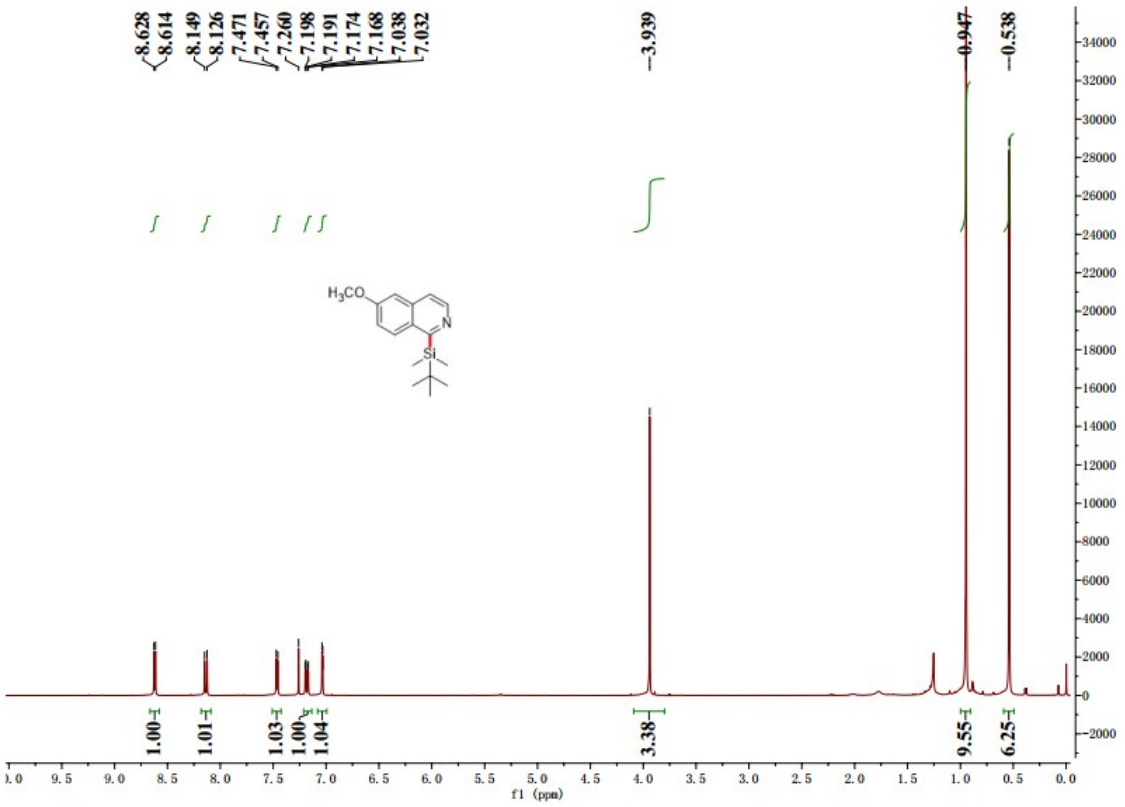
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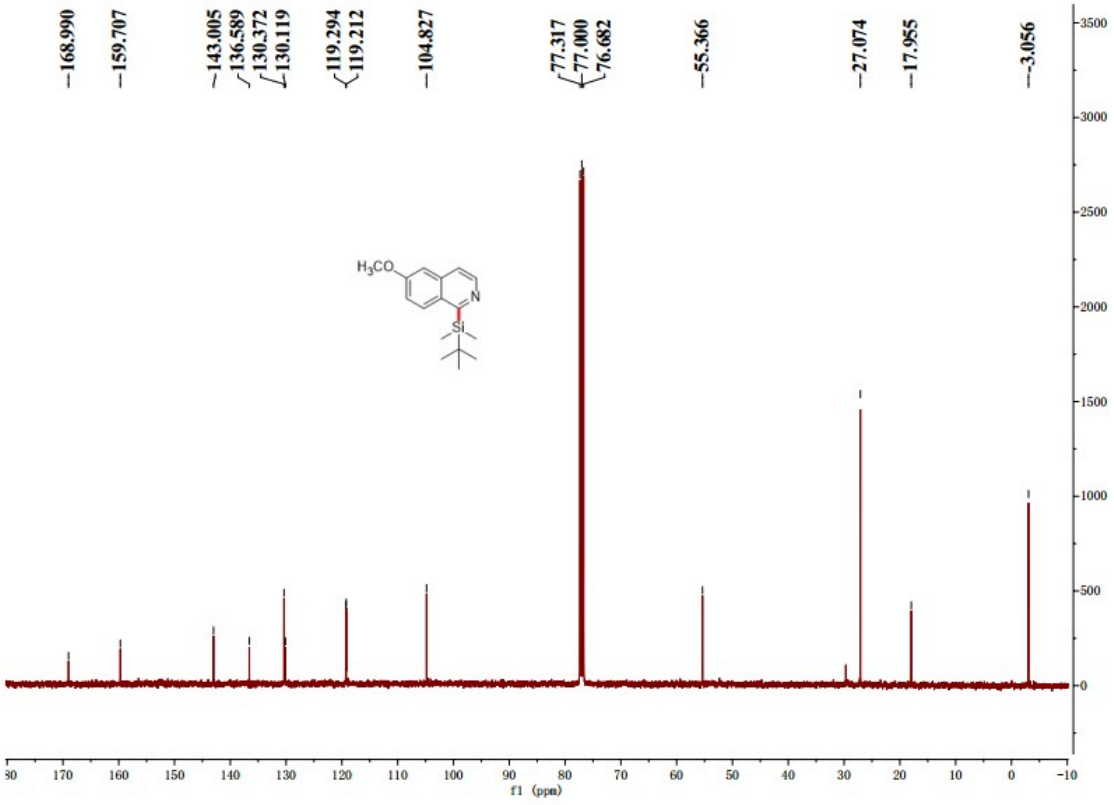
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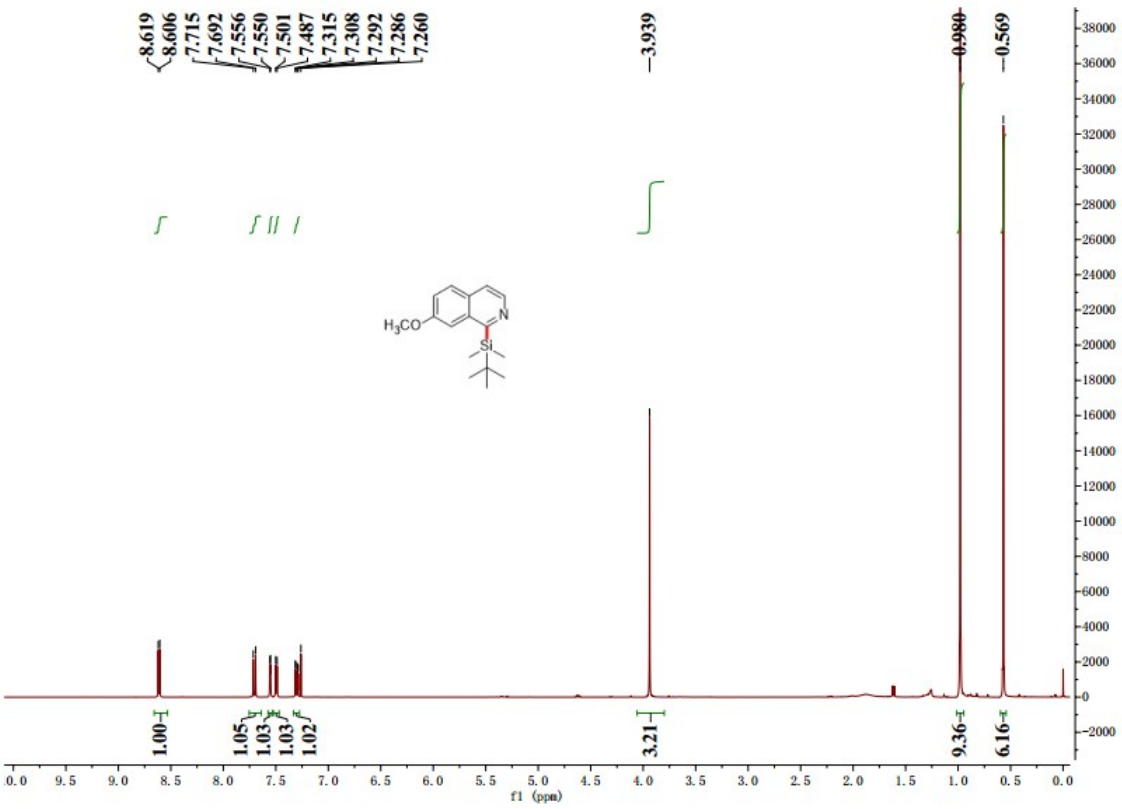
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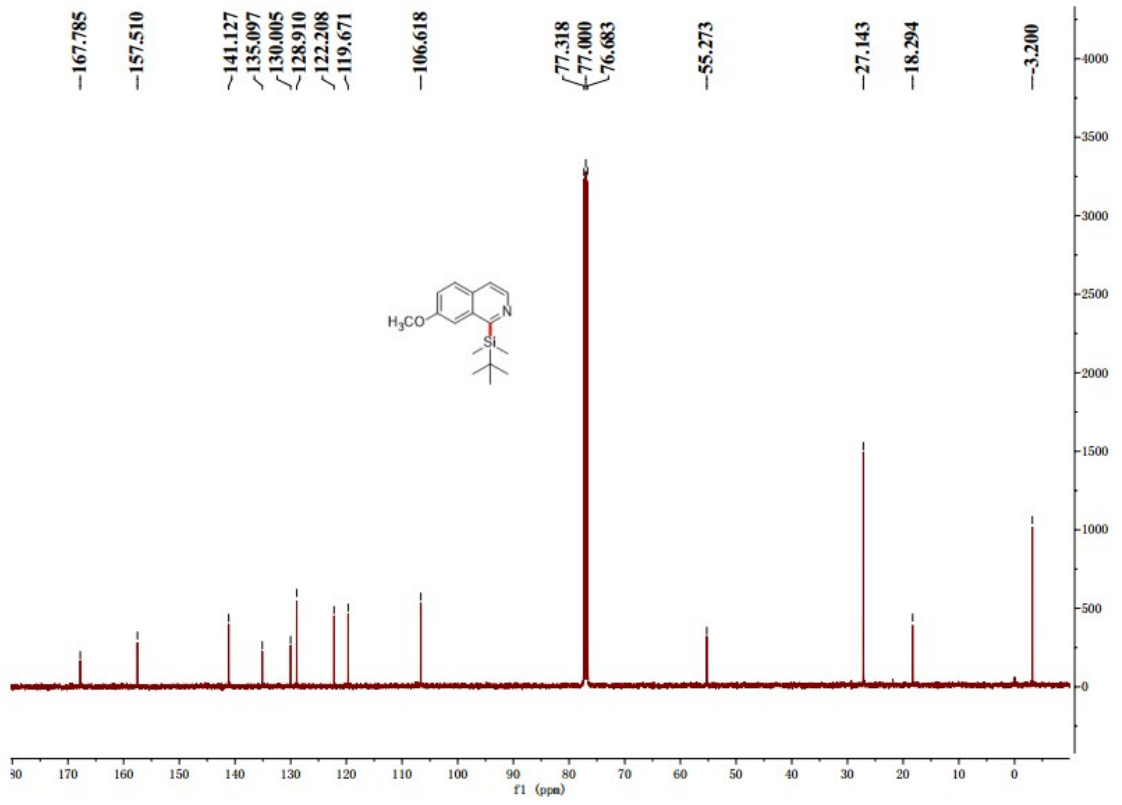
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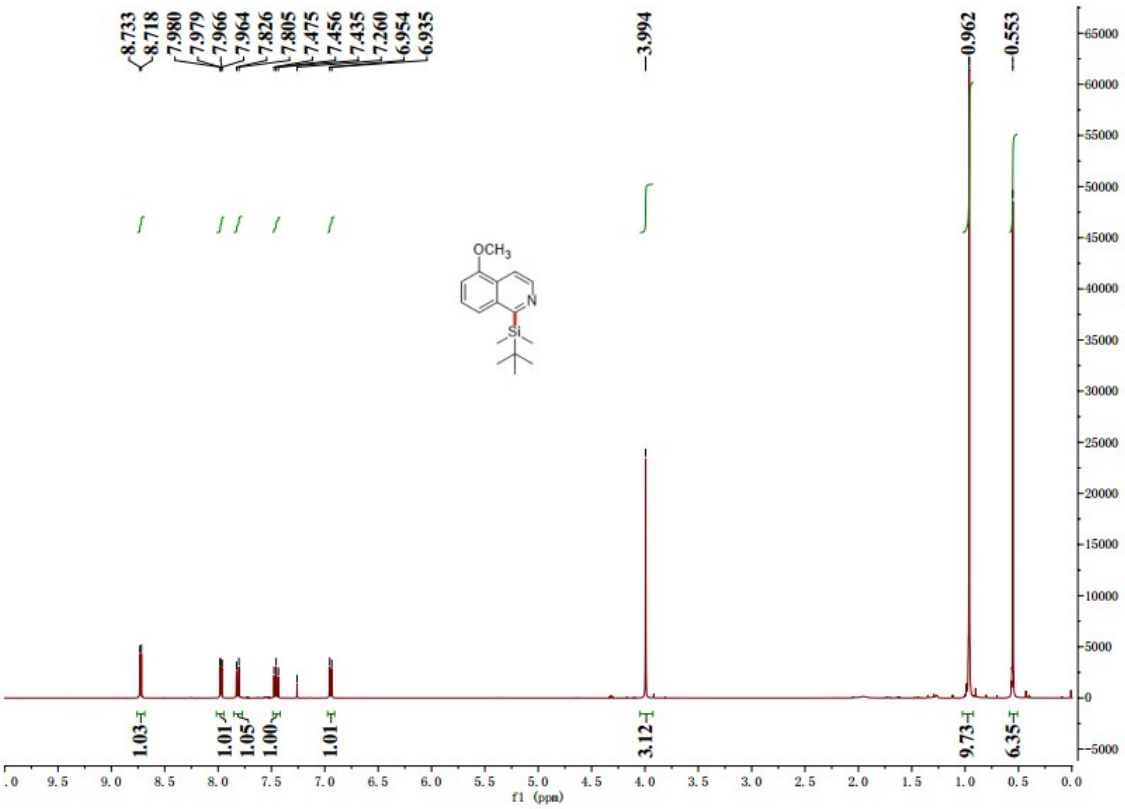
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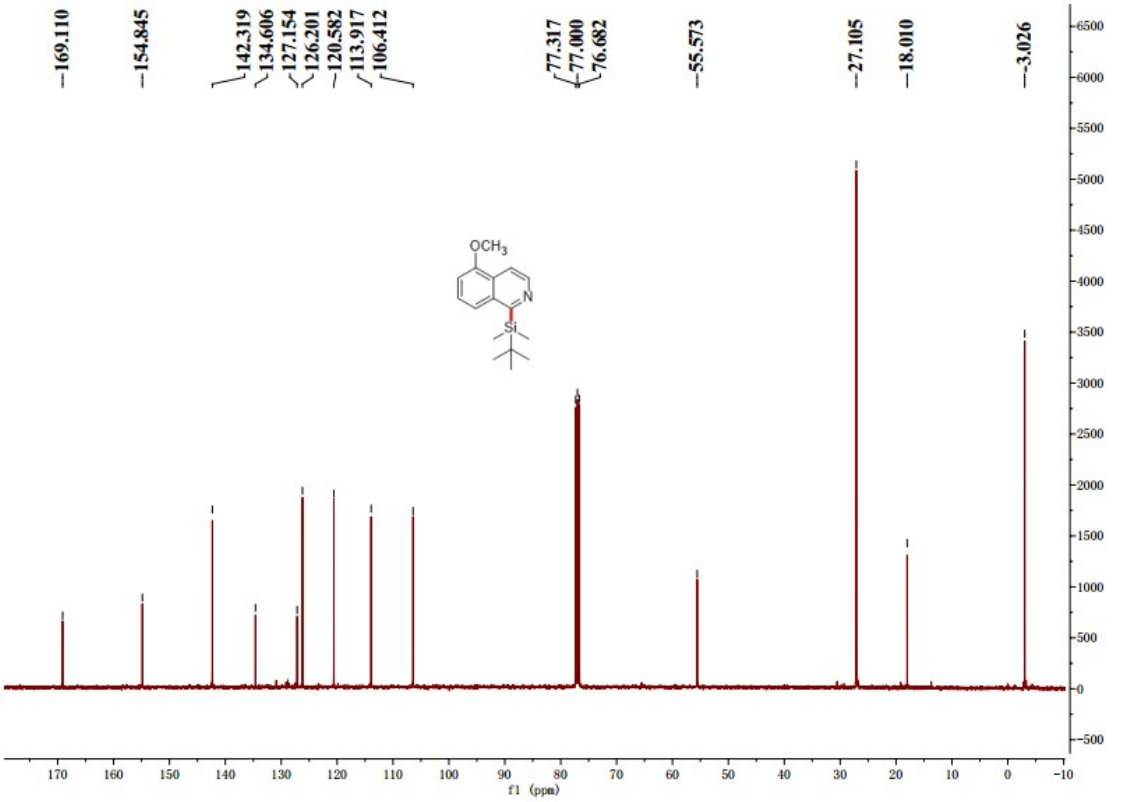
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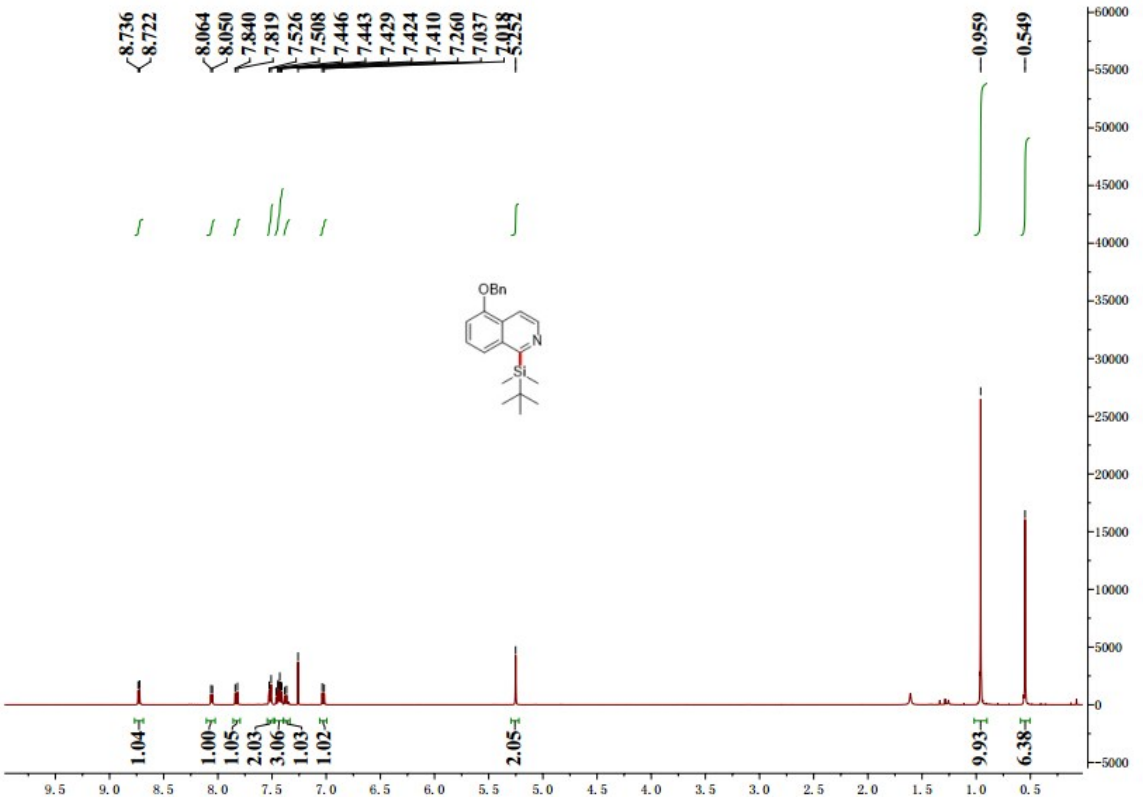
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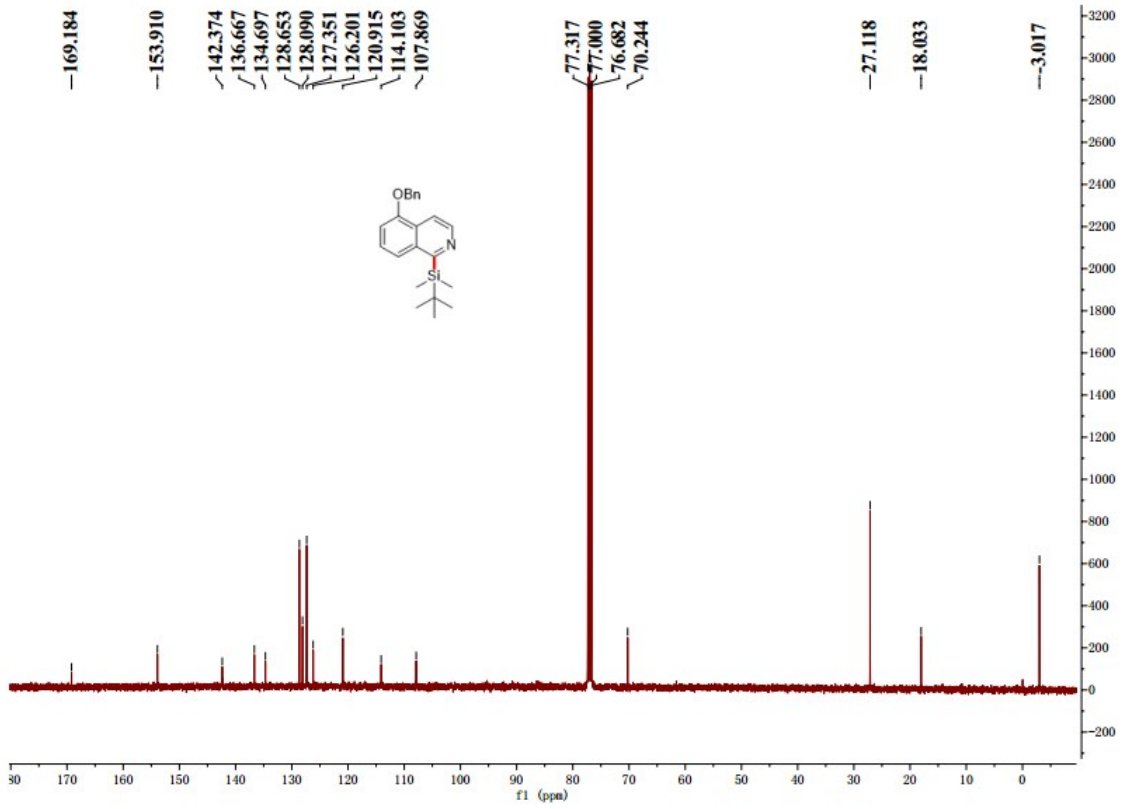
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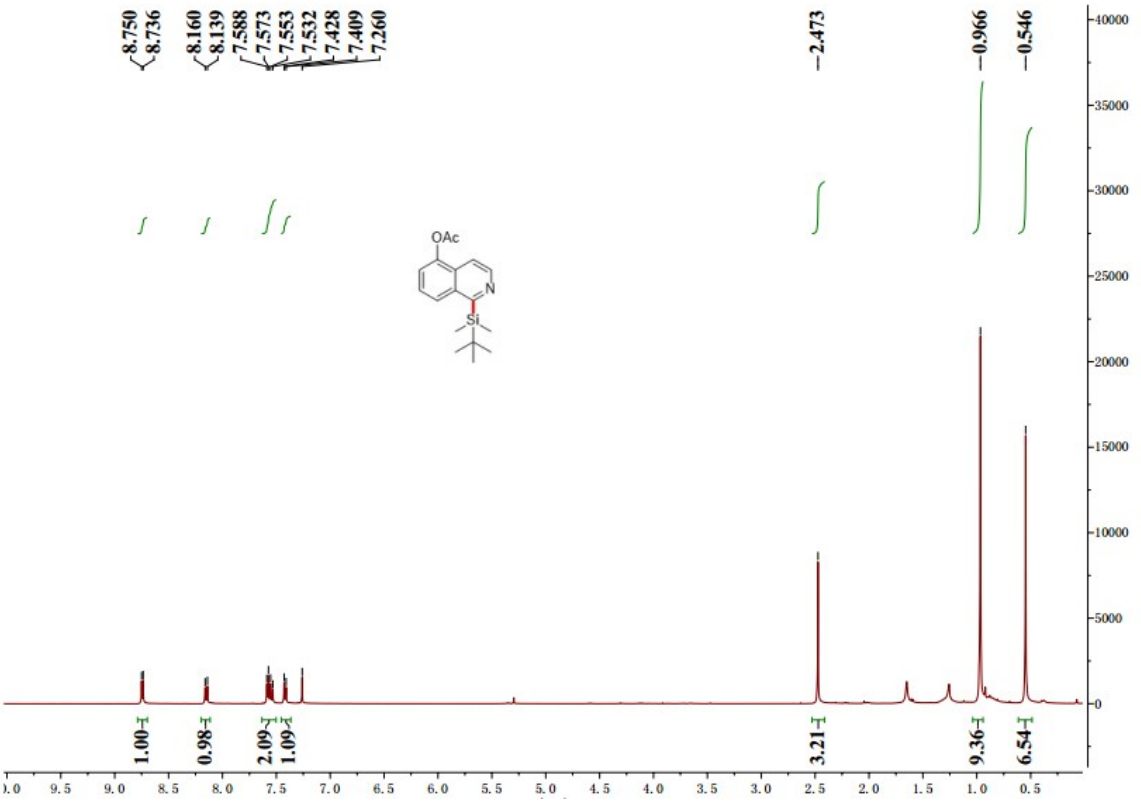
f1 (ppm)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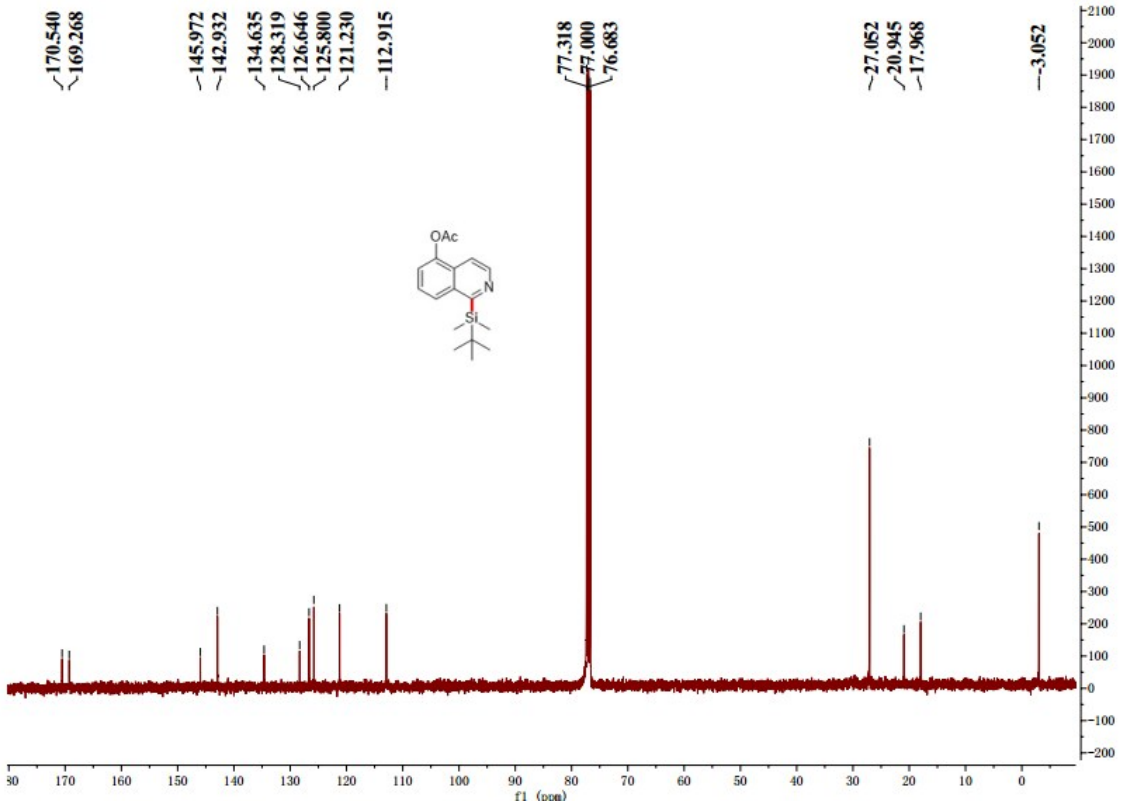
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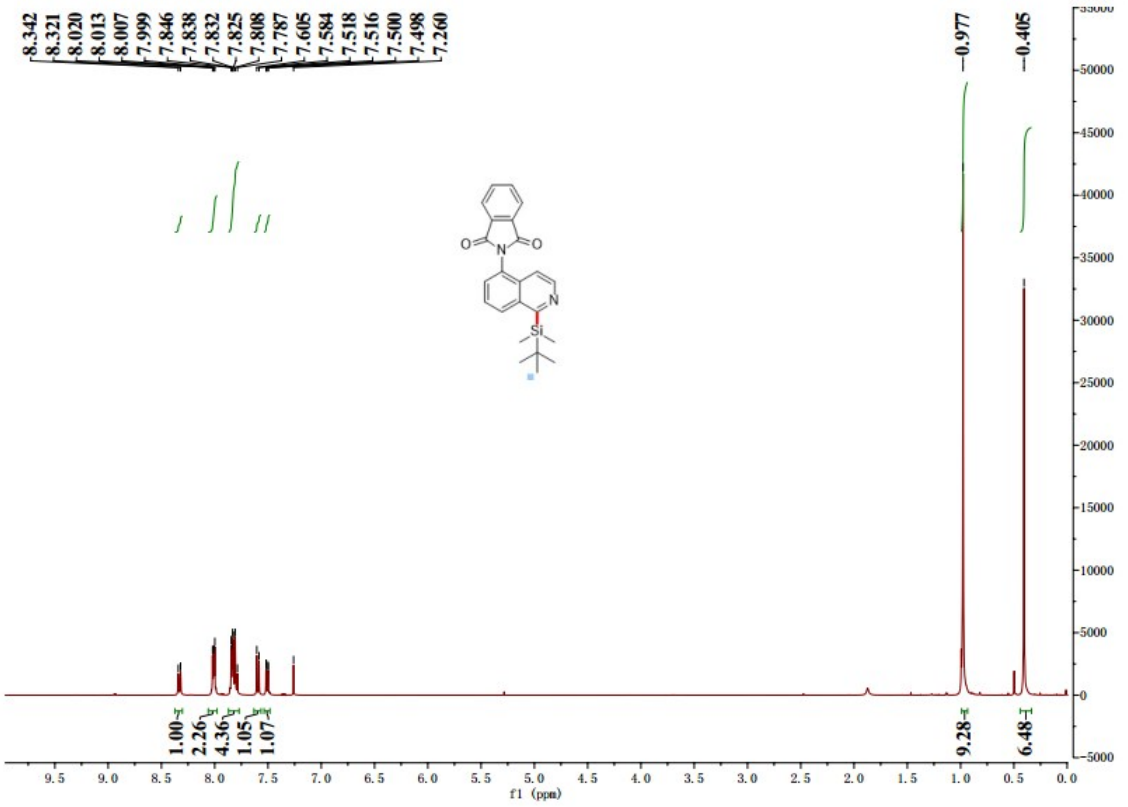
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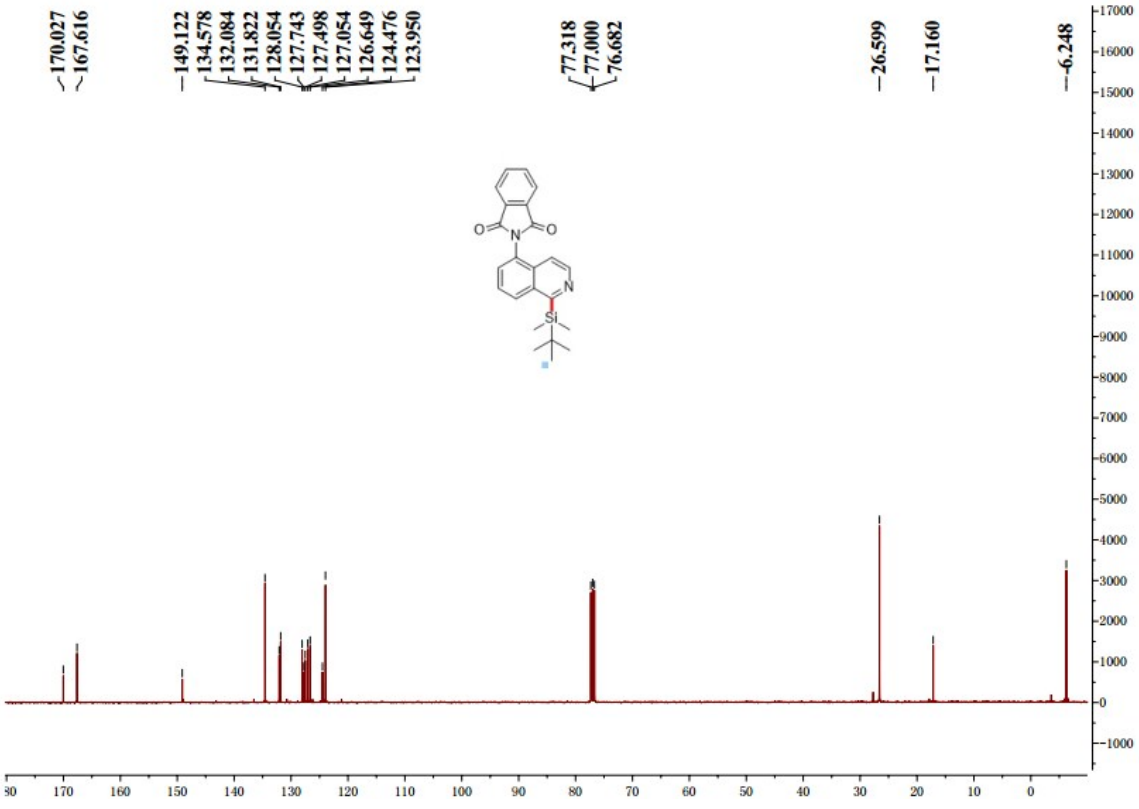
f1 (ppm)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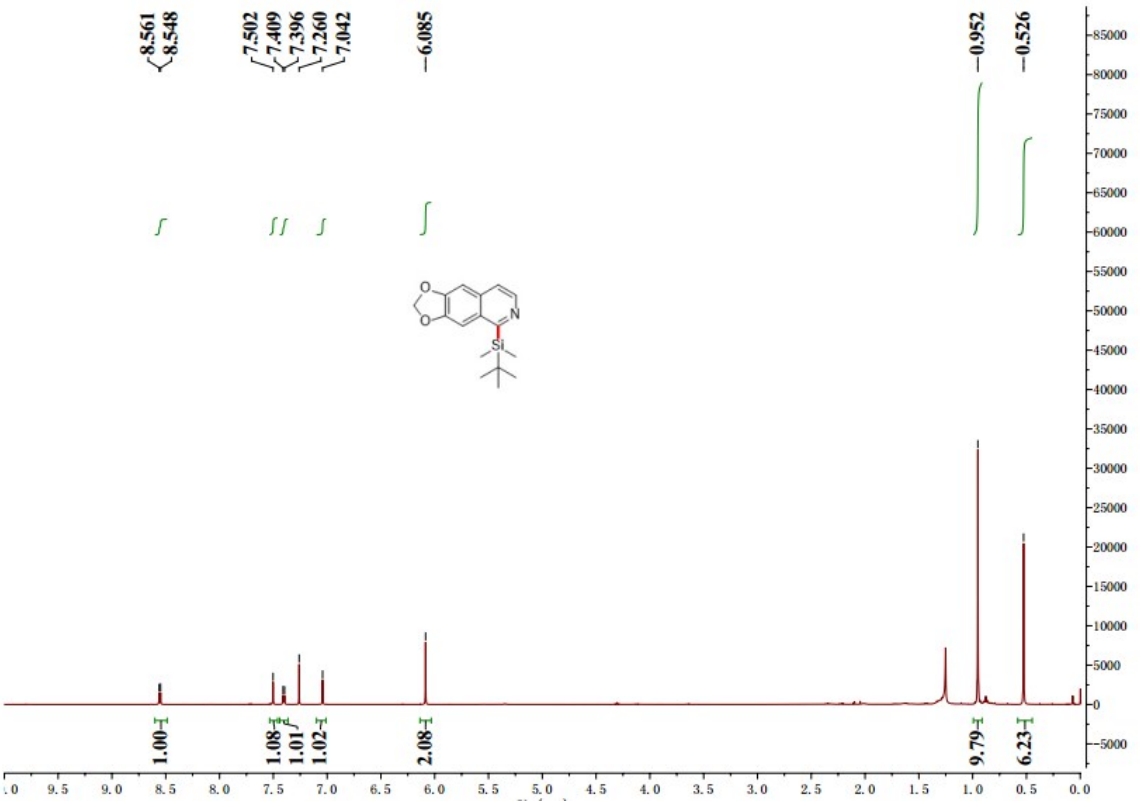
167.616
149.122
134.578
132.084
131.822
128.054
127.743
127.498
127.054
126.649
124.476
123.950
77.318
77.000
76.682
26.599
17.160
6.248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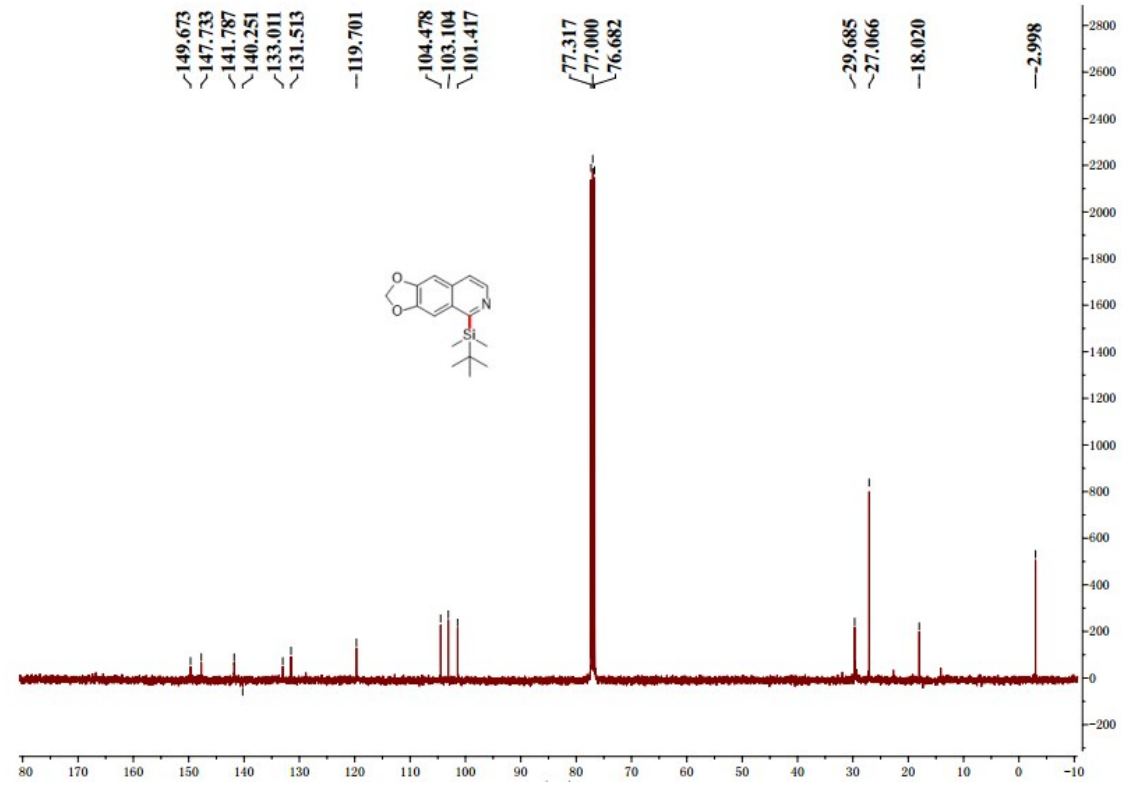
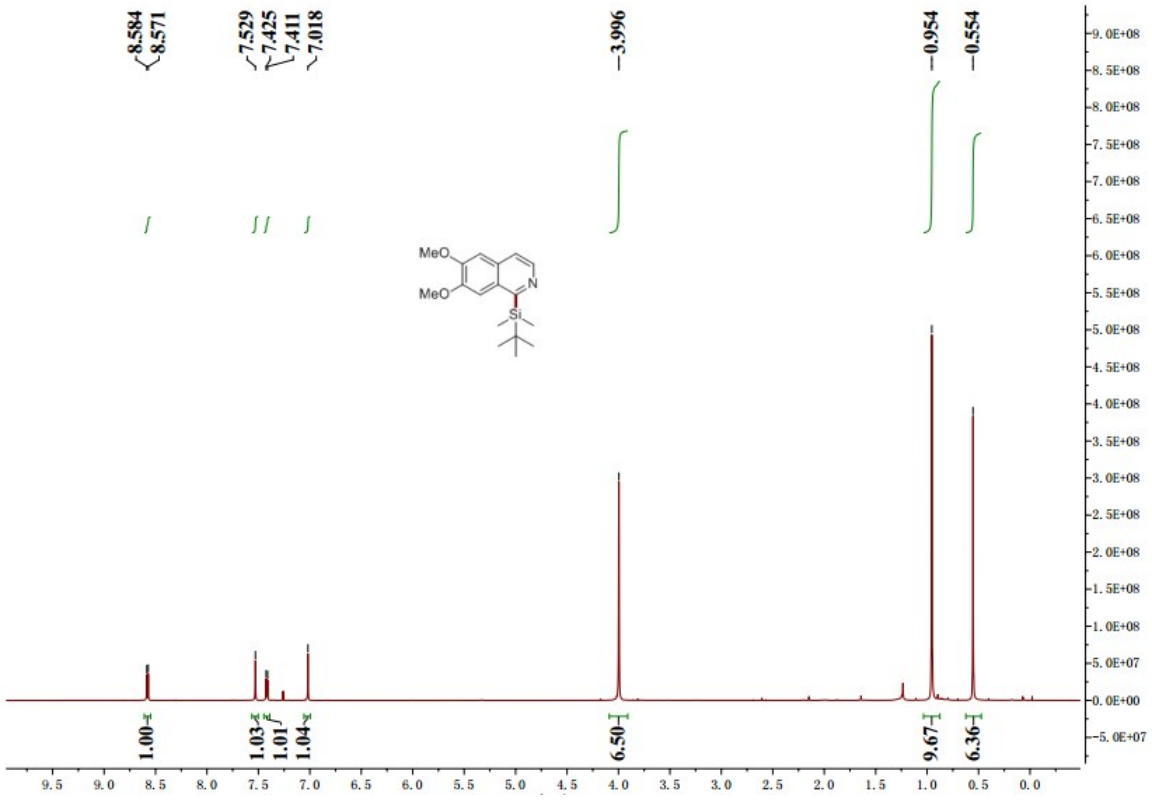
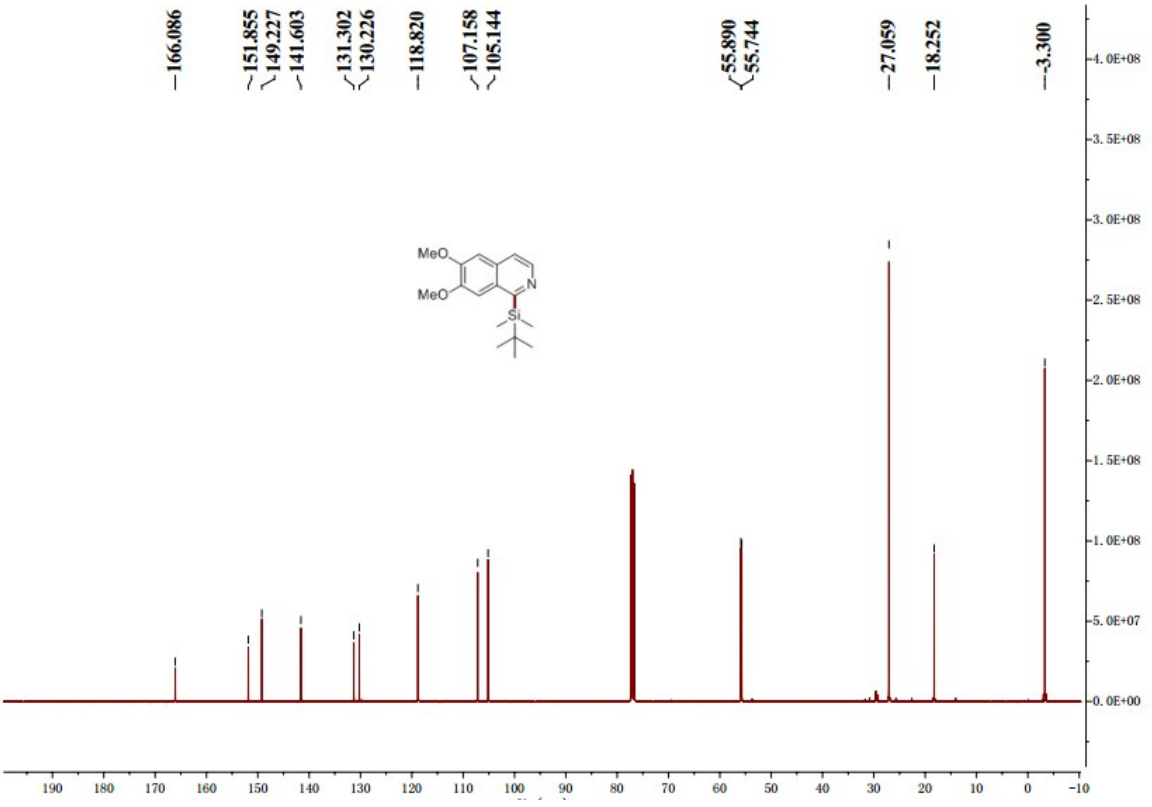
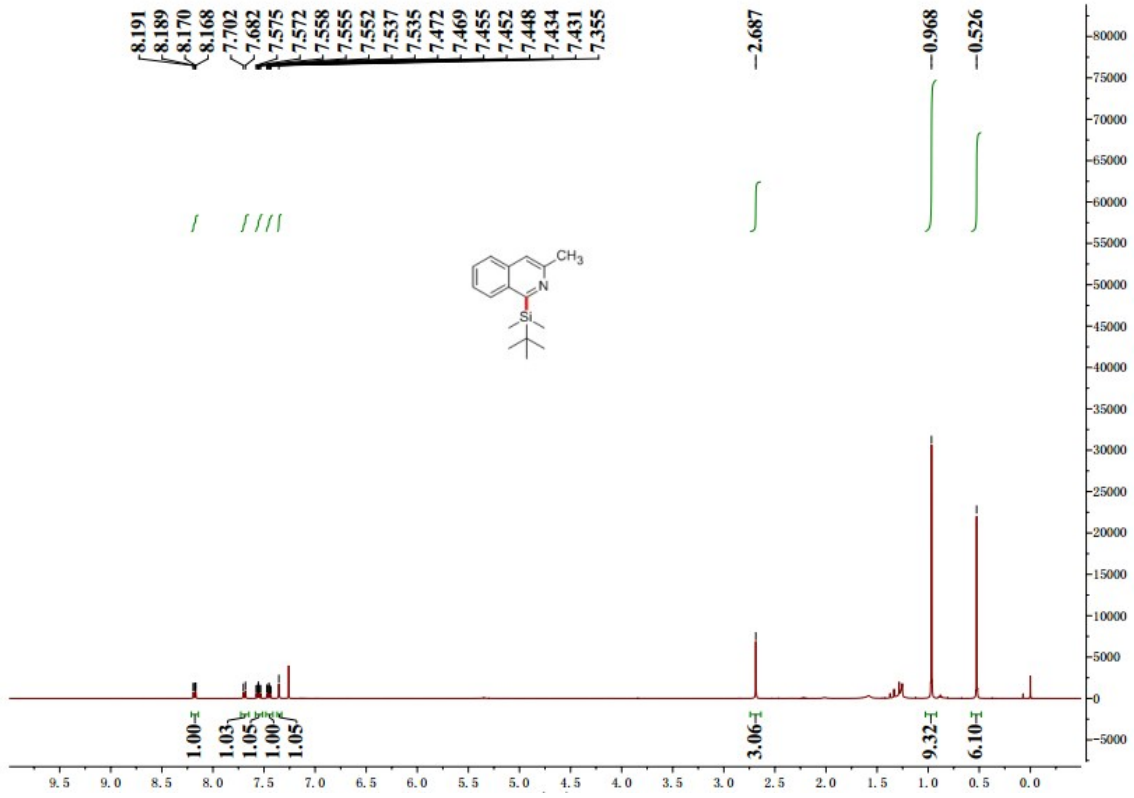
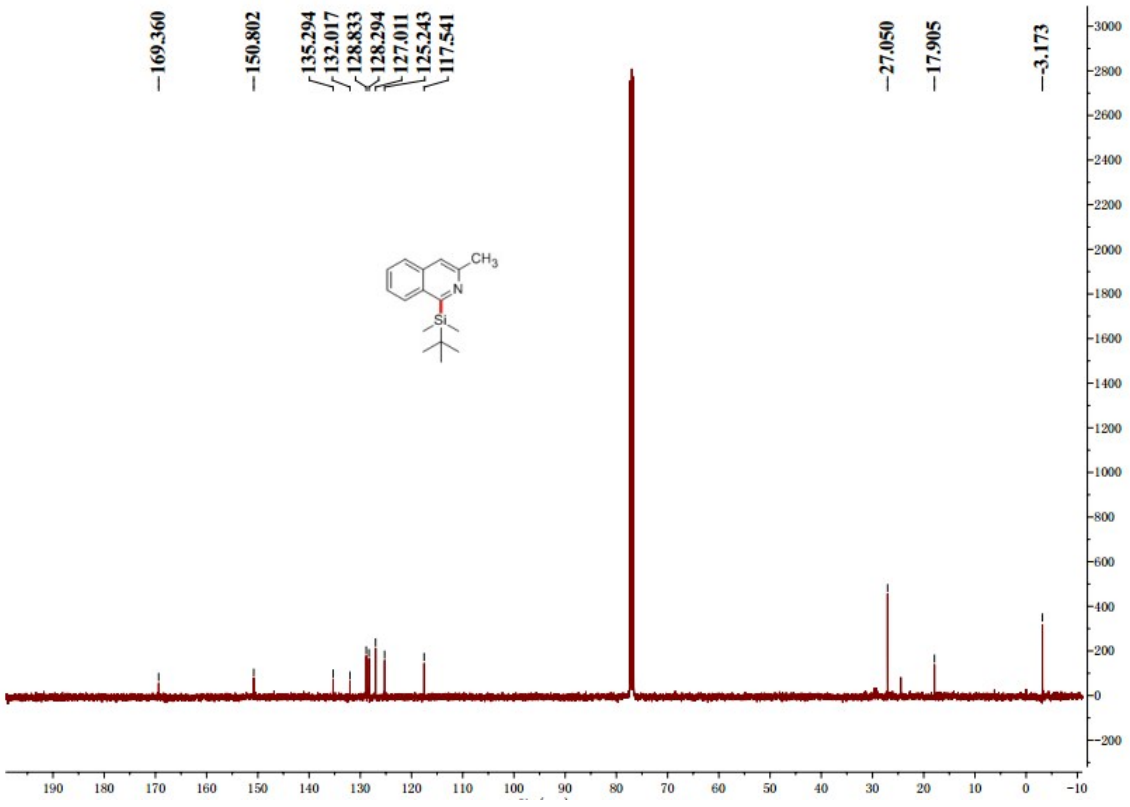
8.548
7.502
7.409
7.396
7.260
7.042
6.085
0.952
0.526
1.00
1.08
1.01
1.02
2.08
9.79
6.23


149.673
147.733
141.787
140.251
133.011
131.513
119.701
104.478
103.104
101.417
77.317
77.000
76.682
29.685
27.066
18.020
2.998


8.584
8.571
7.529
7.425
7.411
7.018
3.996
0.954
0.554
MeO
MeO
Si
1.00
1.03
1.01
1.04
6.50
9.67
6.36


166.086
151.855
149.227
141.603
131.302
130.226
118.820
107.158
105.144
55.890
55.744
27.059
18.252
3.300
MeO
MeO
Si


8.191
8.189
8.170
8.168
7.702
7.682
7.575
7.572
7.558
7.555
7.552
7.537
7.535
7.472
7.469
7.455
7.452
7.448
7.434
7.431
7.355
2.687
0.968
0.526
CH3
N
Si
1.00
1.03
1.05
1.00
1.05
3.06
9.32
6.10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150.802
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128.294
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125.243
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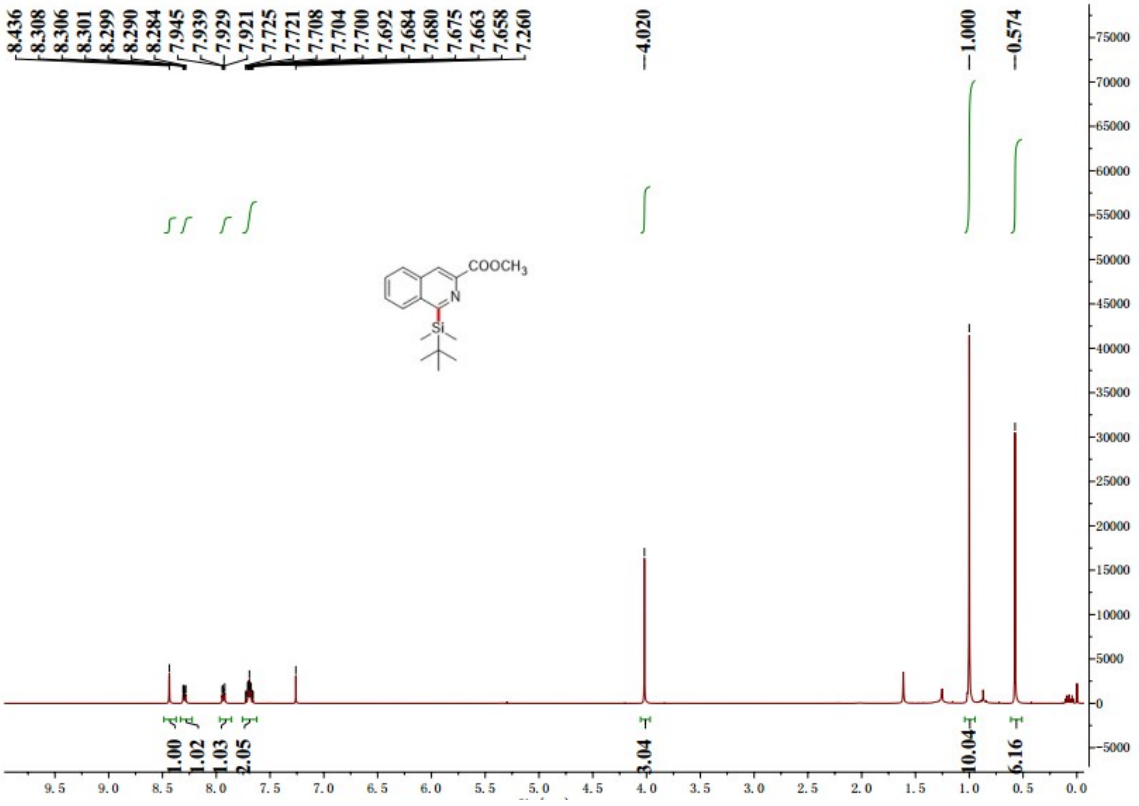
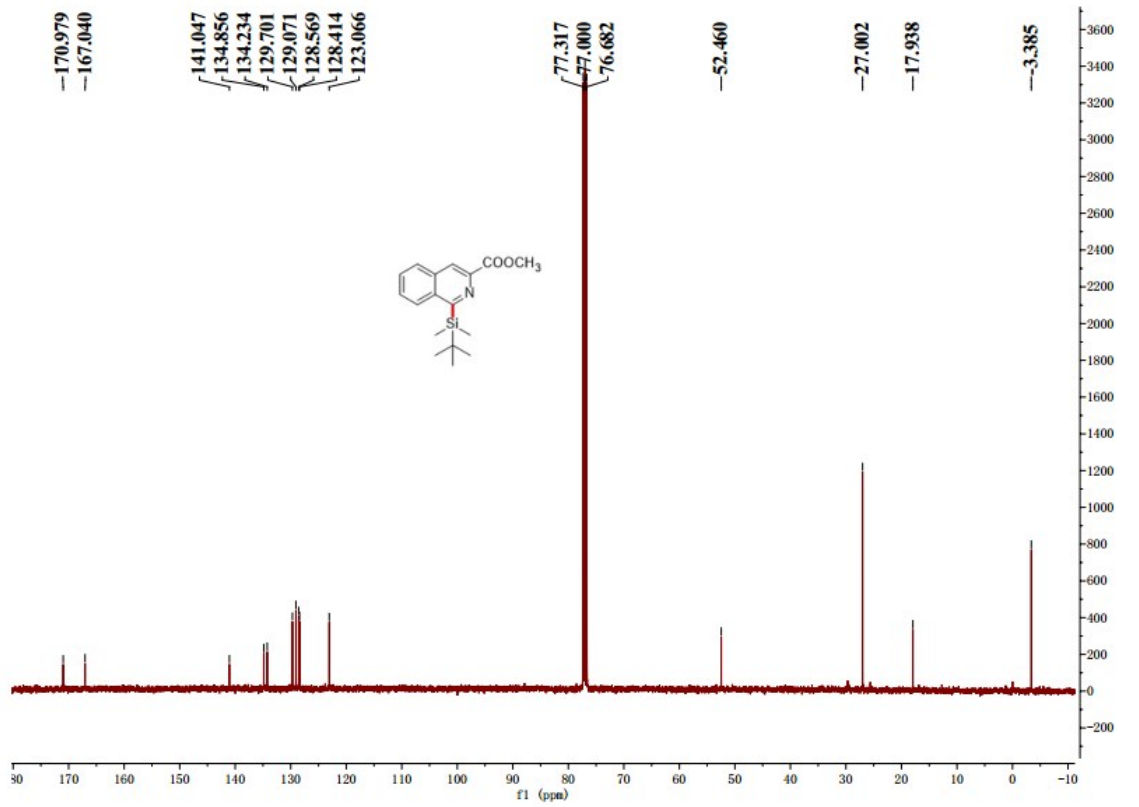
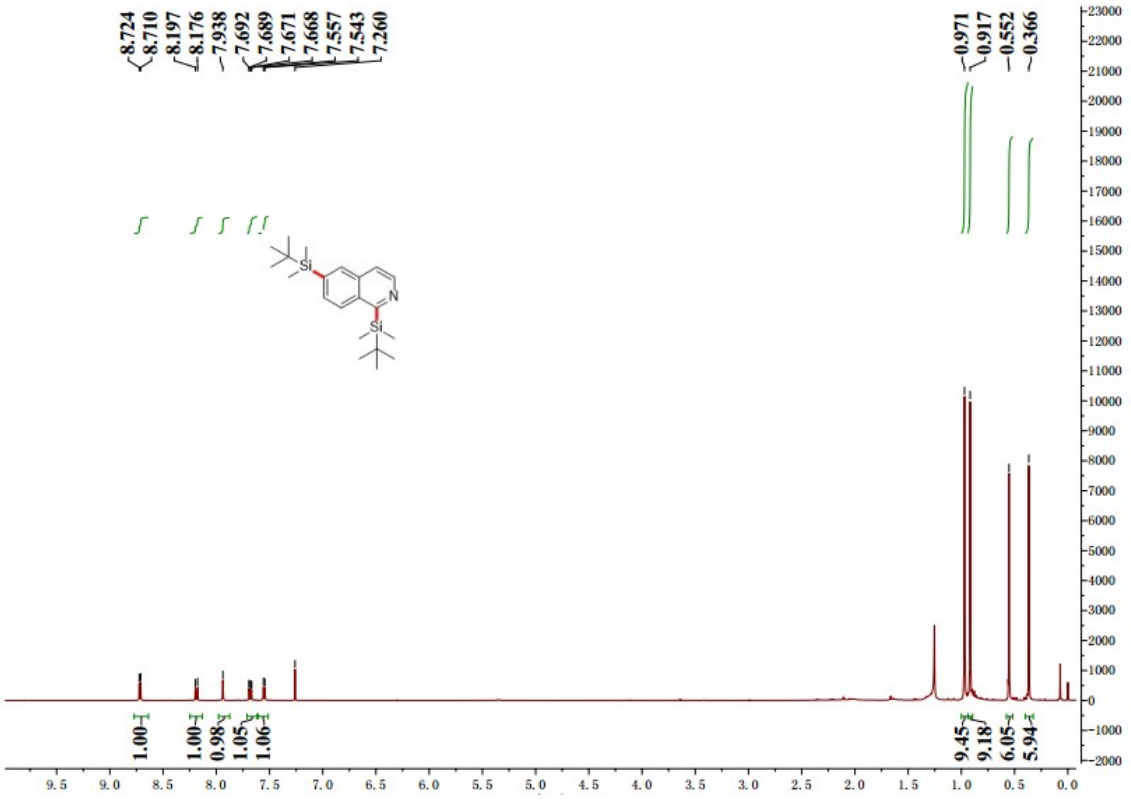
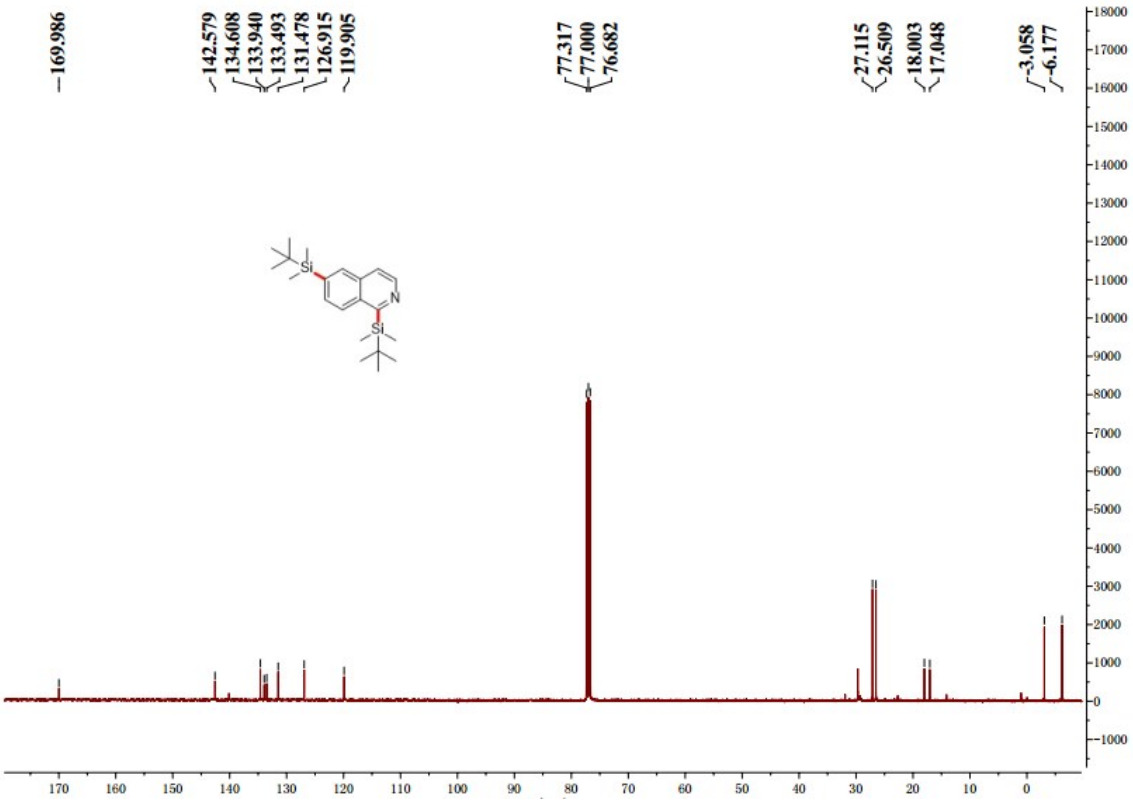
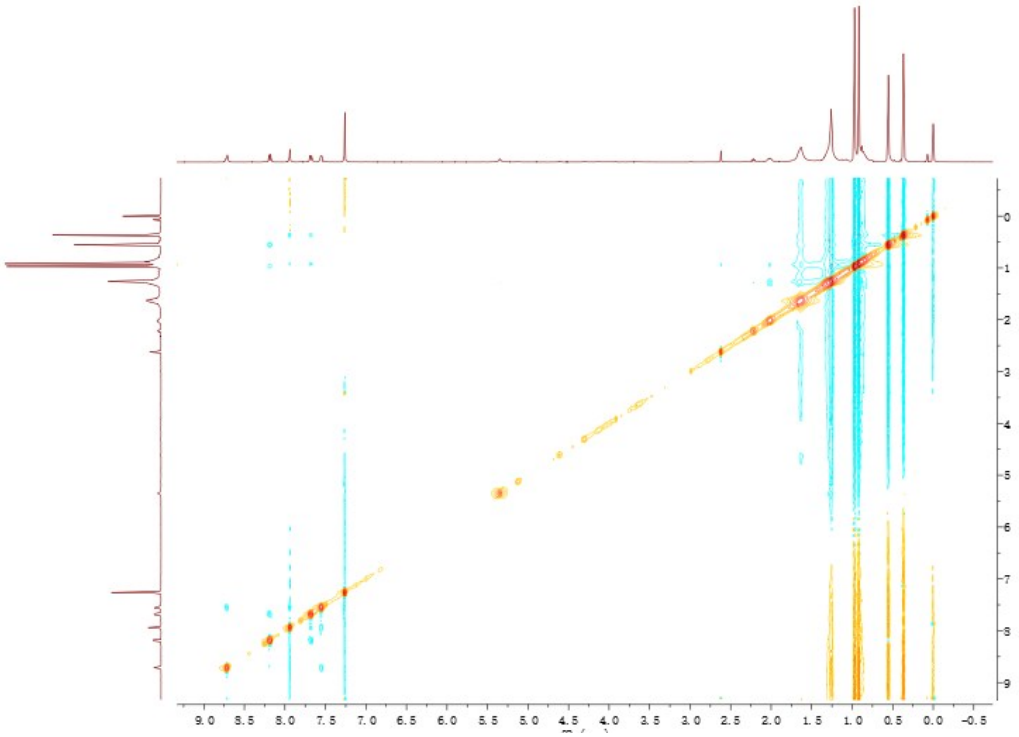
17.905
-3.173
CH3
N
Si

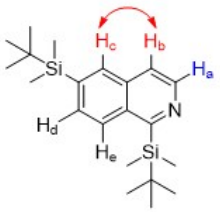

8.436
8.308
8.306
8.301
8.299
8.290
8.284
7.945
7.939
7.929
7.921
7.725
7.721
7.708
7.704
7.700
7.692
7.684
7.680
7.675
7.663
7.658
7.260
4.020
1.000
0.574
COOCH3
N
Si
1.00
1.02
1.03
2.05
3.04
10.04
6.16

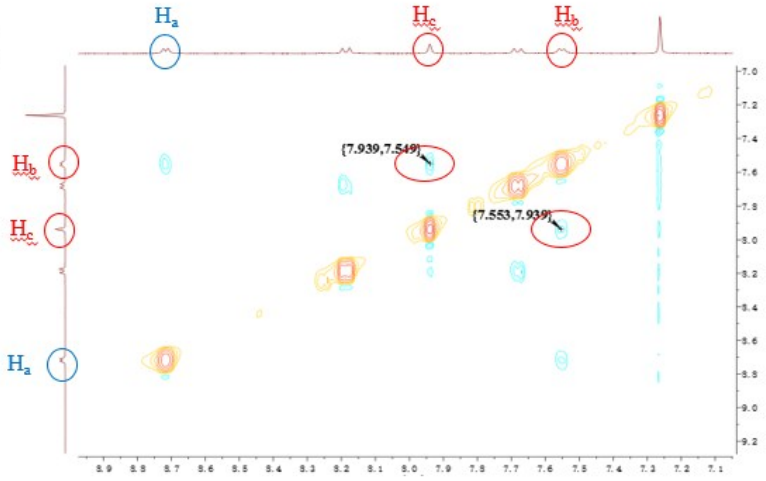

170.979
167.040
141.047
134.856
134.234
129.701
129.071
128.569
128.414
123.066
77.317
77.000
76.682
52.460
27.002
17.938
3.385
COOCH3
N
Si
f1 (ppm)

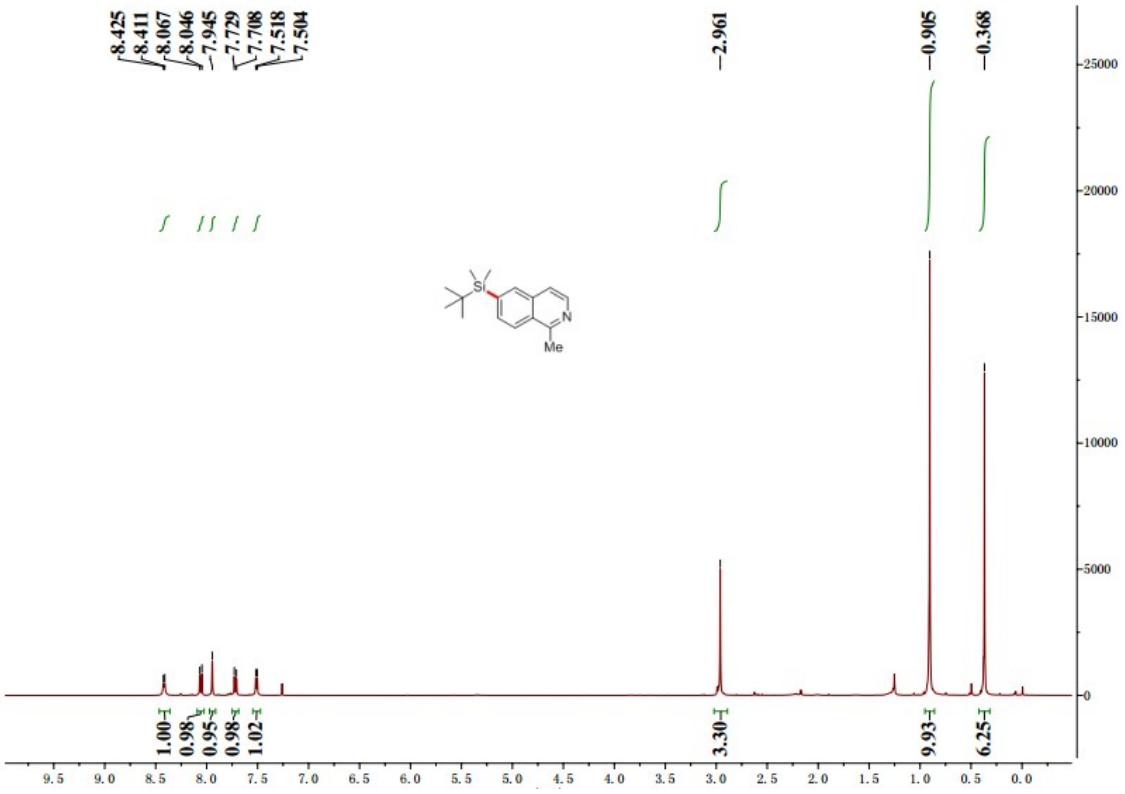

8.724
8.710
8.197
8.176
7.938
7.692
7.689
7.671
7.668
7.557
7.543
7.260
0.971
0.917
0.552
0.366
1.00
1.00
0.98
1.05
1.06
9.45
9.18
6.05
5.94

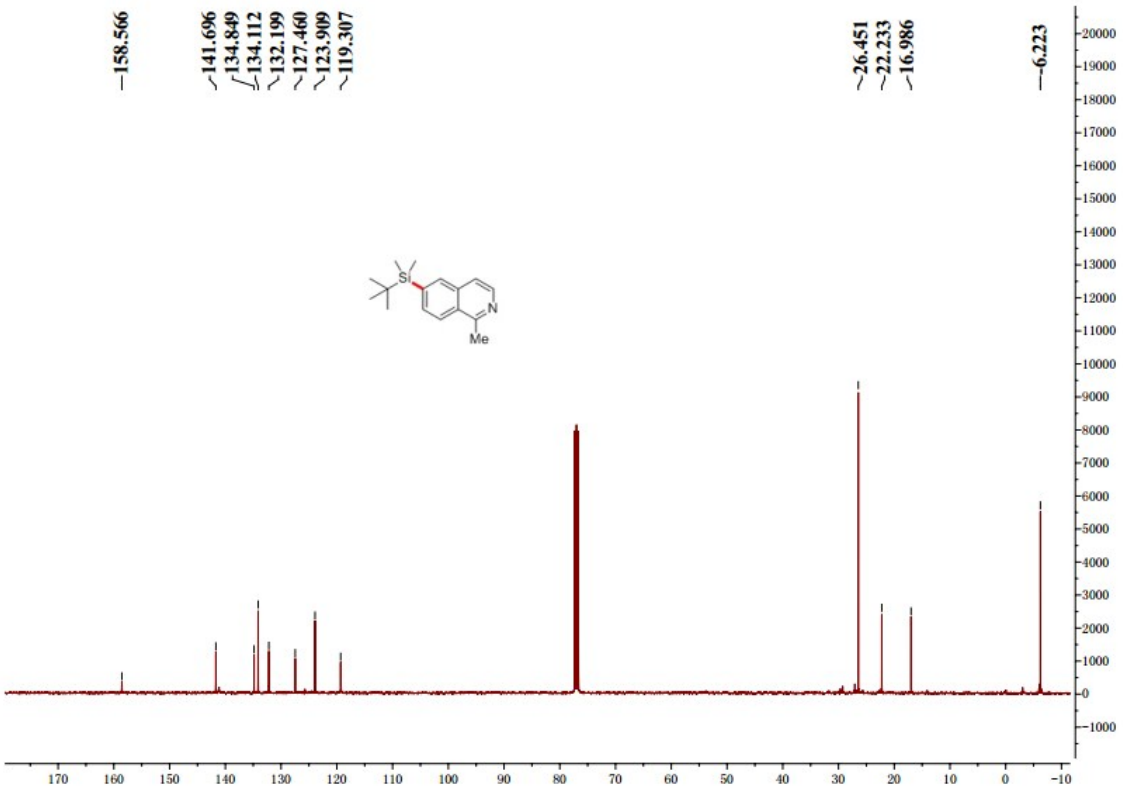

169.986
142.579
134.608
133.940
133.493
131.478
126.915
119.905
77.317
77.000
76.682
27.115
26.509
18.003
17.048
-3.058
-6.177

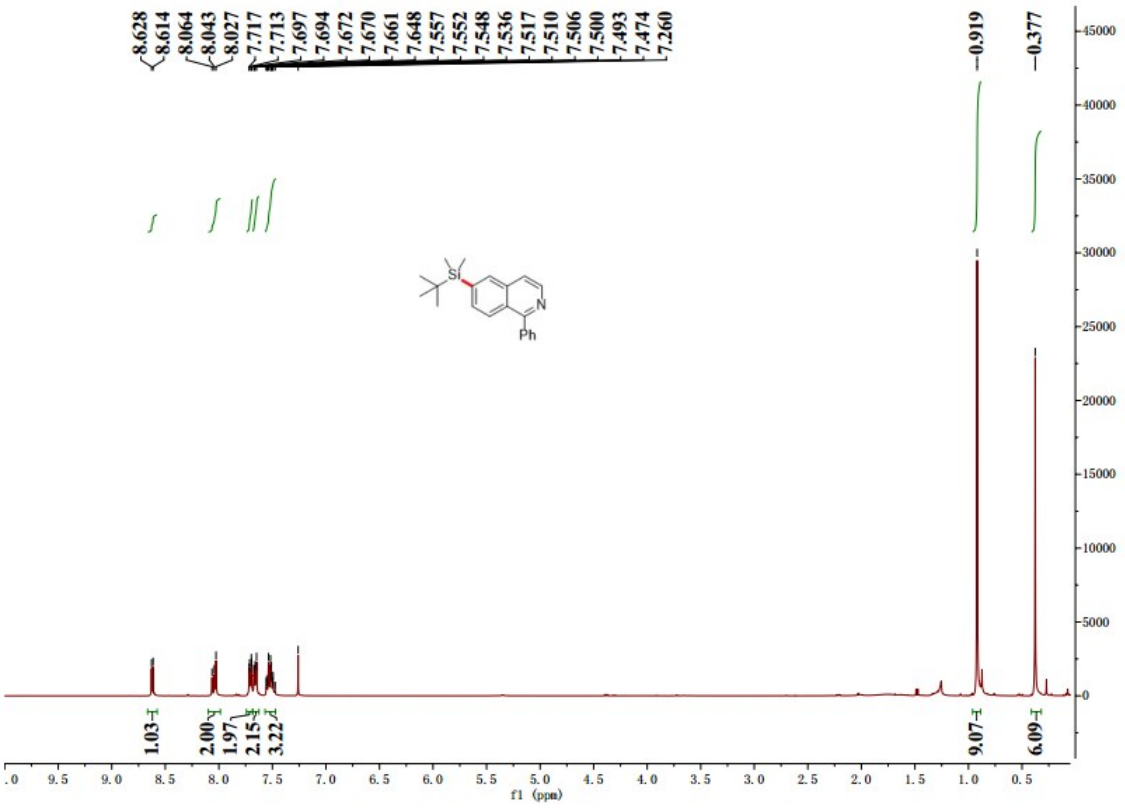


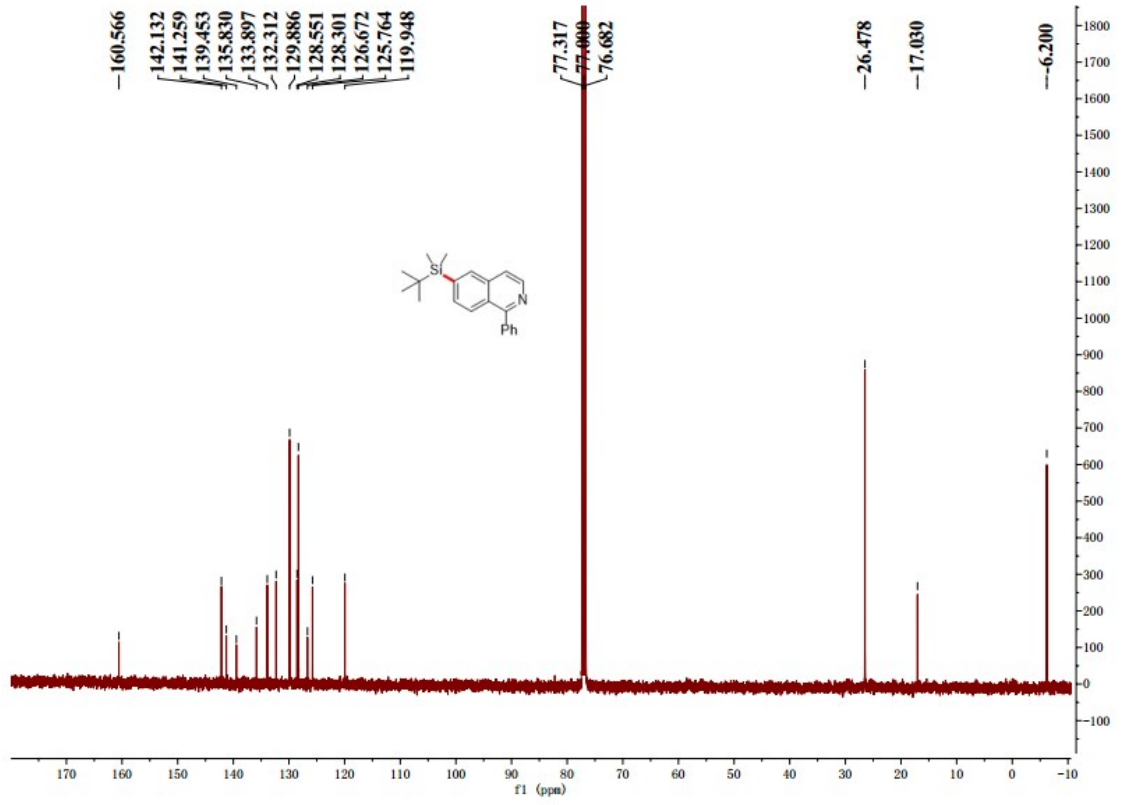

Hc
Hb
Ha
Si
N
Hd
He
Si


Ha
Hc
Hb
Hb
Hc
Ha
{7.939,7.549}
{7.553,7.939}


8.425
8.411
8.067
8.046
7.945
7.729
7.708
7.518
7.504
2.961
0.905
0.368
Me
1.00
0.98
0.95
0.98
1.02
3.30
9.93
6.25


158.566
141.696
134.849
134.112
132.199
127.460
123.909
119.307
26.451
22.233
16.986
6.223
Me


8.628
8.614
8.064
8.043
8.027
7.717
7.713
7.697
7.694
7.672
7.670
7.661
7.648
7.557
7.552
7.548
7.536
7.517
7.510
7.506
7.500
7.493
7.474
7.260
0.919
0.377
1.03
2.00
1.97
2.15
3.22
9.07
6.09
Si
N
Ph
f1 (ppm)


160.566
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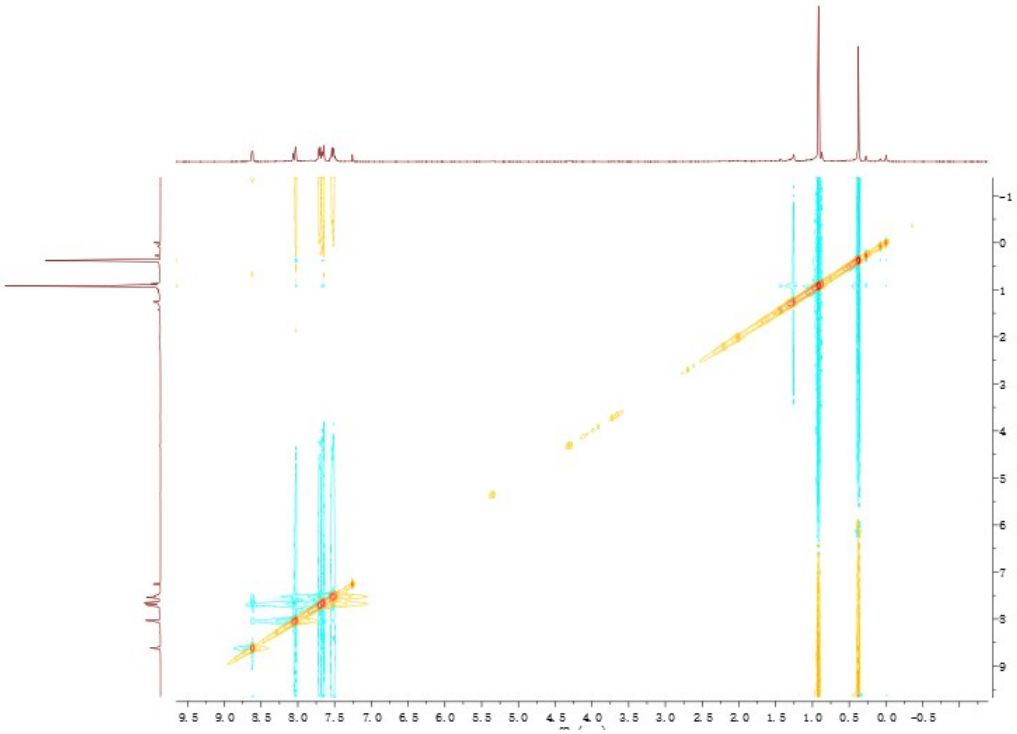
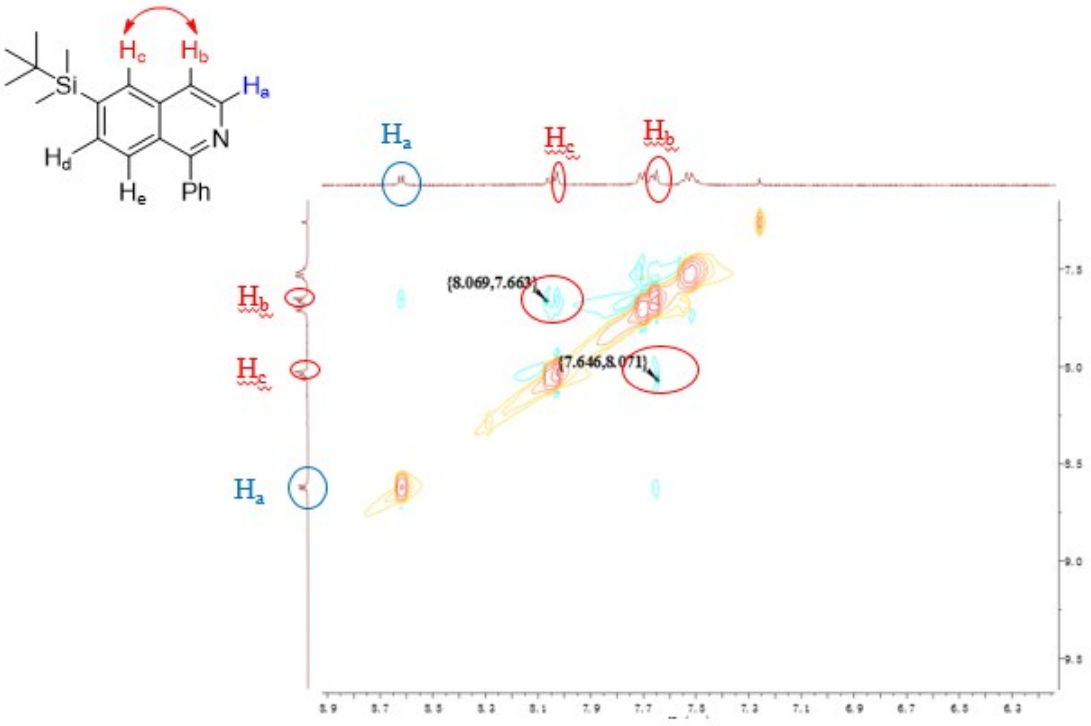
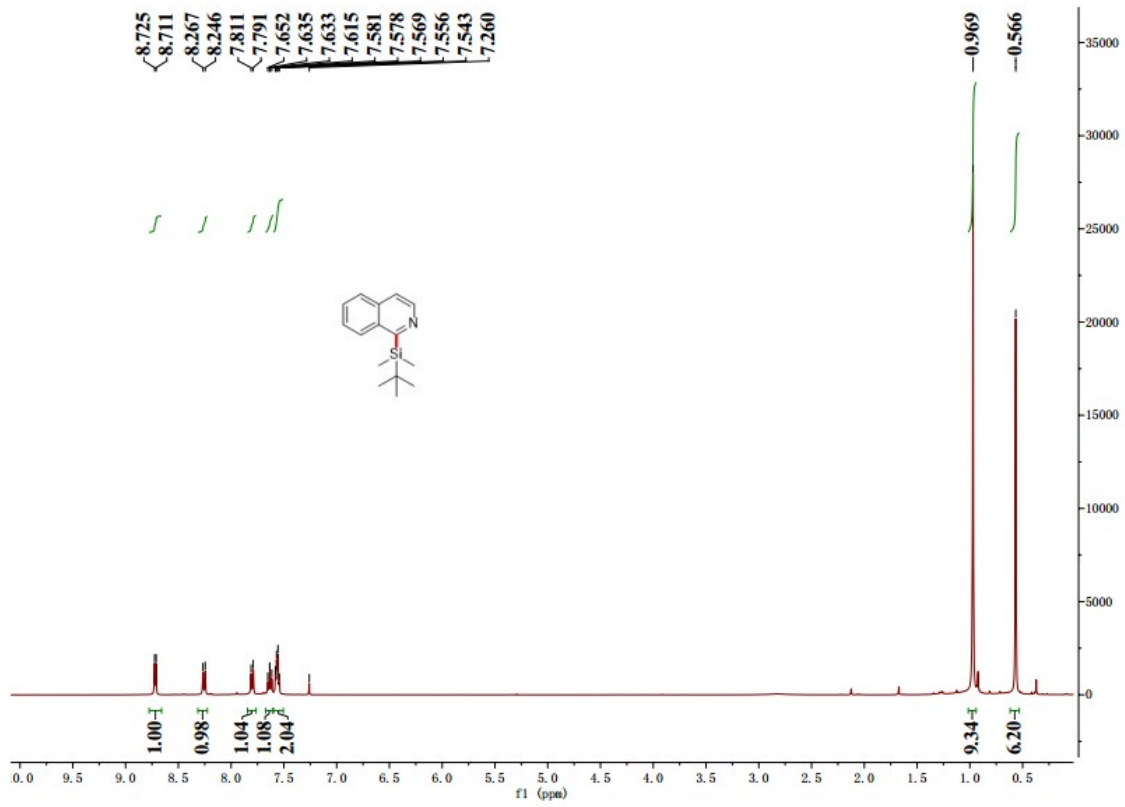
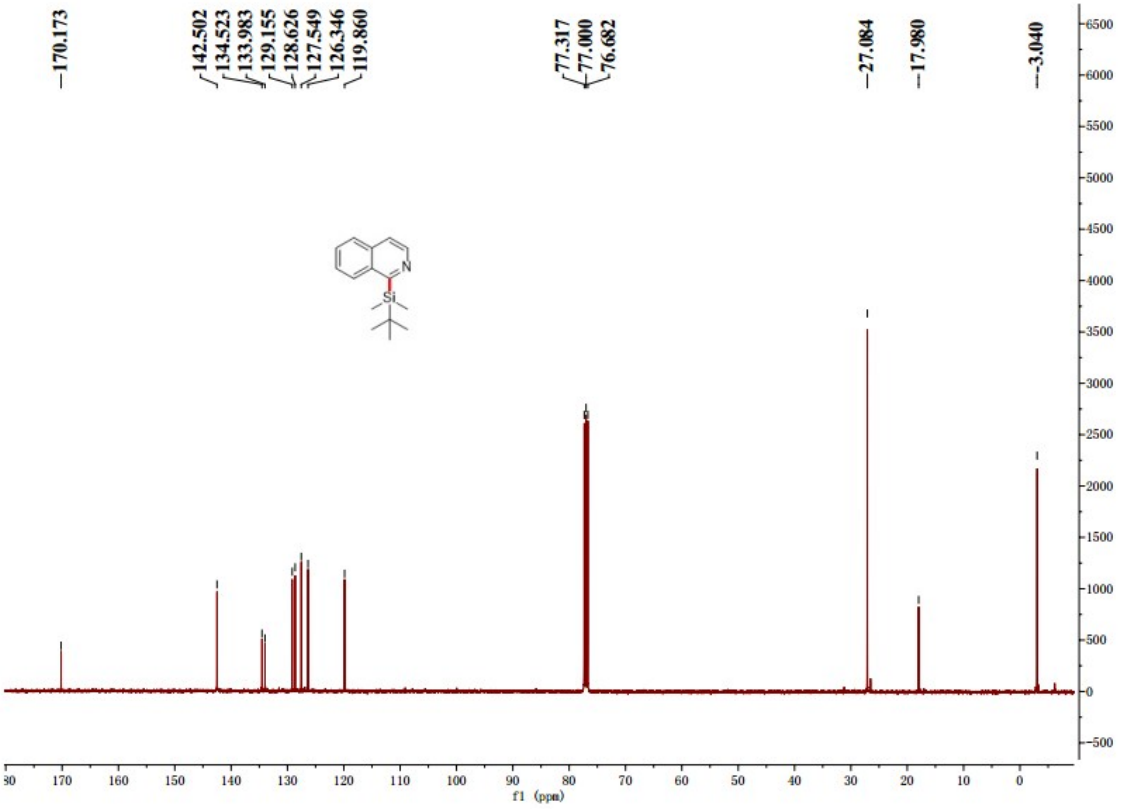
141.259
139.453
135.830
133.897
132.312
129.886
128.551
128.301
126.672
125.764
119.948
77.317
77.000
76.682
26.478
17.030
6.200
Si
N
Ph
f1 (ppm)




Hc
Hb
Ha
Si
N
Hd
He
Ph
Ha
Hc
Hb
{8.069,7.663}
{7.646,8.071}
Hb
Hc
Ha


8.725
8.711
8.267
8.246
7.811
7.791
7.652
7.635
7.633
7.615
7.581
7.578
7.569
7.556
7.543
7.260
0.969
0.566
1.00
0.98
1.04
1.08
2.04
9.34
6.20
f1 (ppm)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142.502
134.523
133.983
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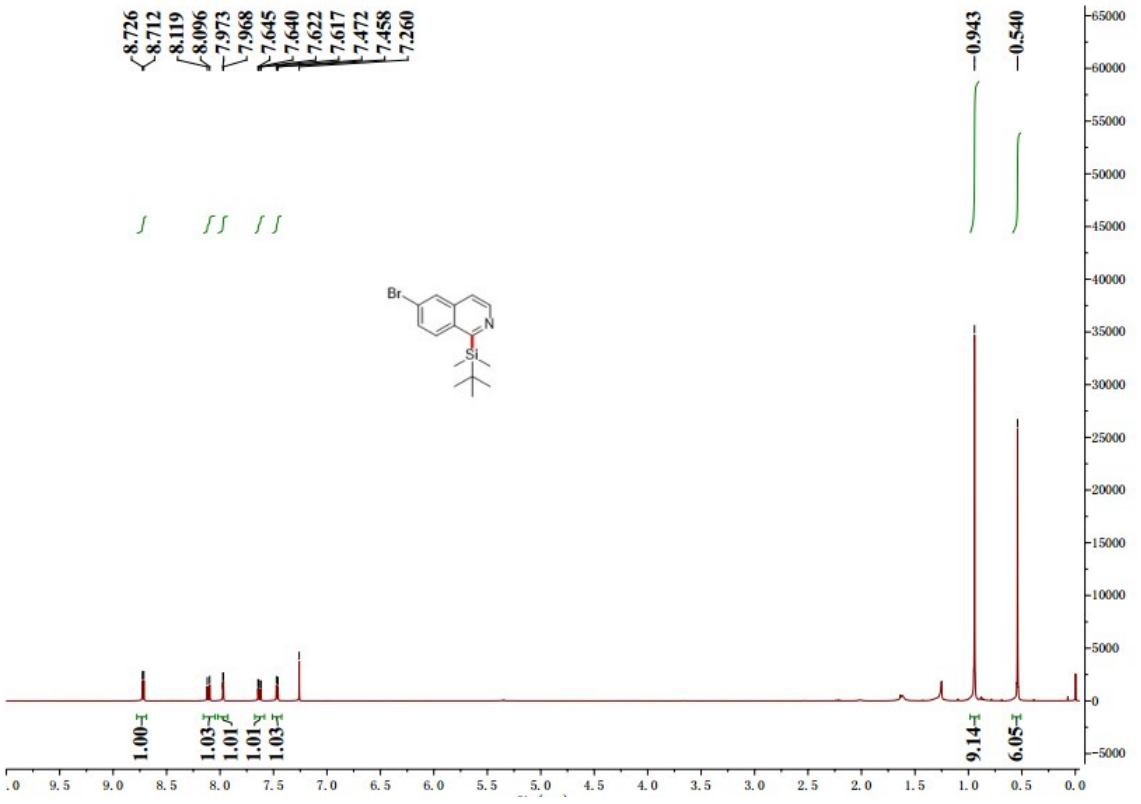
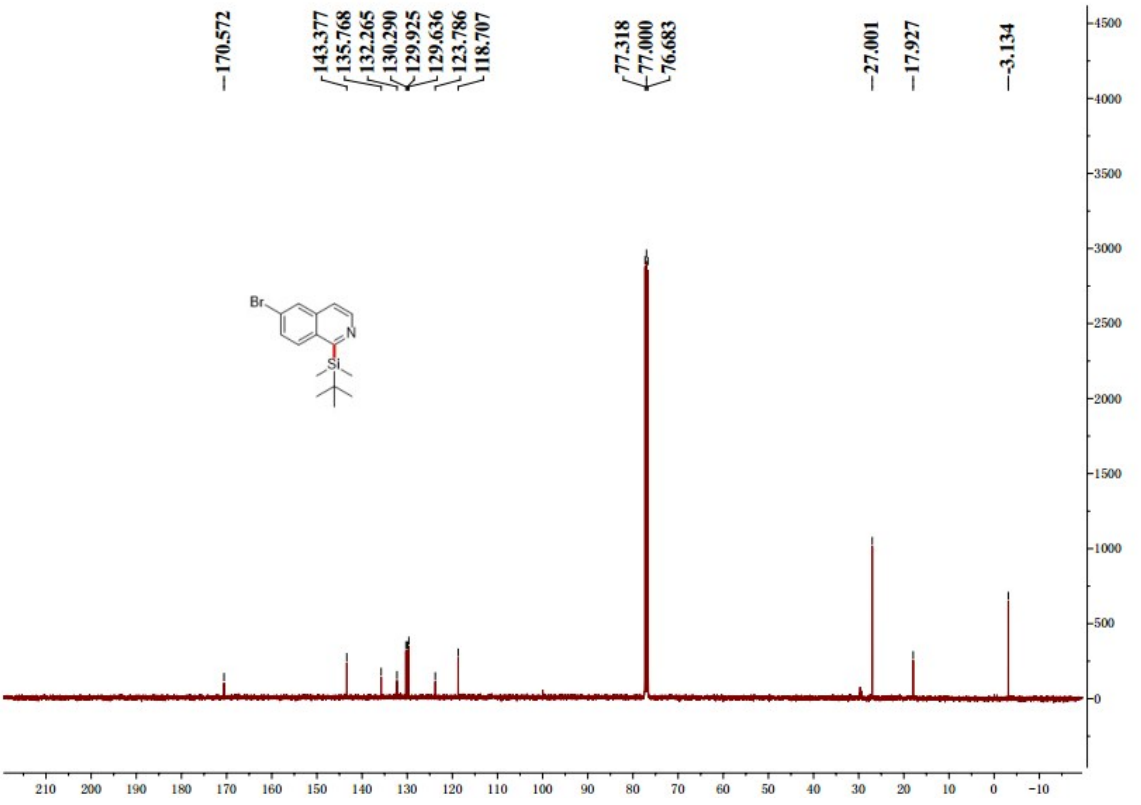
126.346
119.860
77.317
77.000
76.682
27.084
17.980
3.040
f1 (ppm)


8.726
8.712
8.119
8.096
7.973
7.968
7.645
7.640
7.622
7.617
7.472
7.458
7.260
0.943
0.540
Br
N
Si
1.00
1.03
1.01
1.01
1.03
9.14
6.05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130.290
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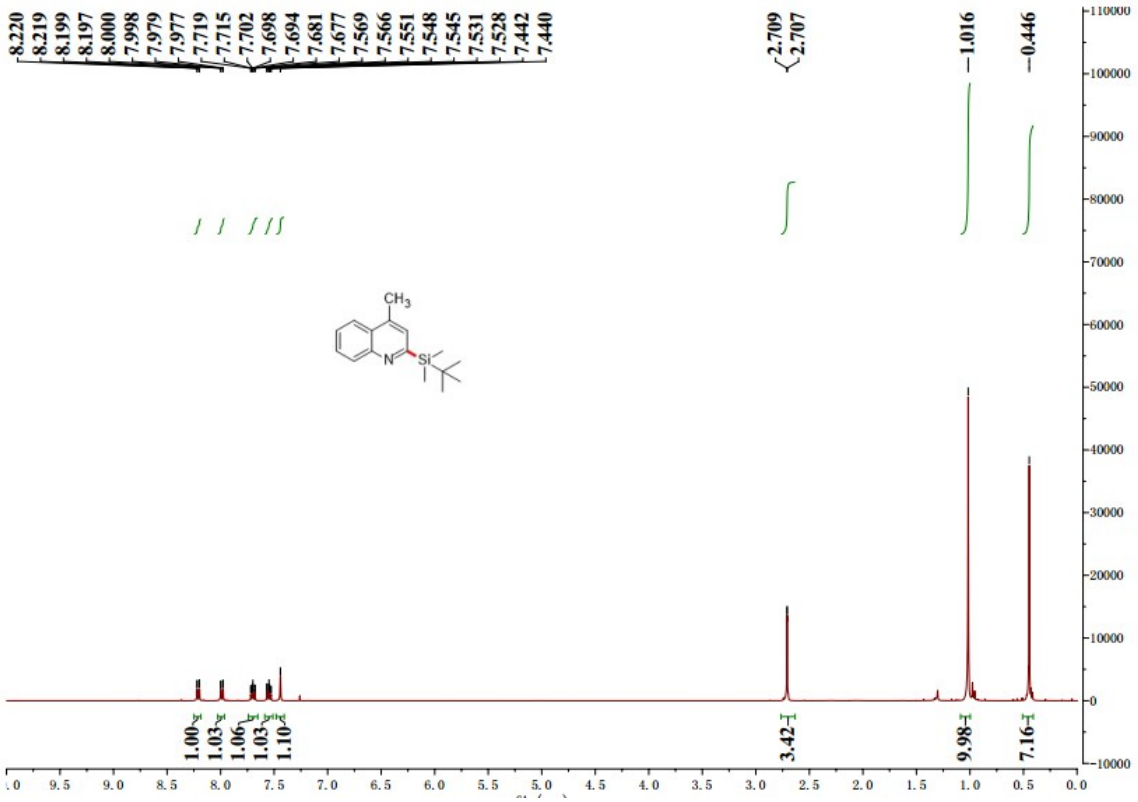
77.318
77.000
76.683
27.001
17.927
3.134
Br
N
Si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8.197
8.000
7.998
7.979
7.977
7.719
7.715
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7.694
7.681
7.677
7.569
7.566
7.551
7.548
7.545
7.531
7.528
7.442
7.440
2.709
2.707
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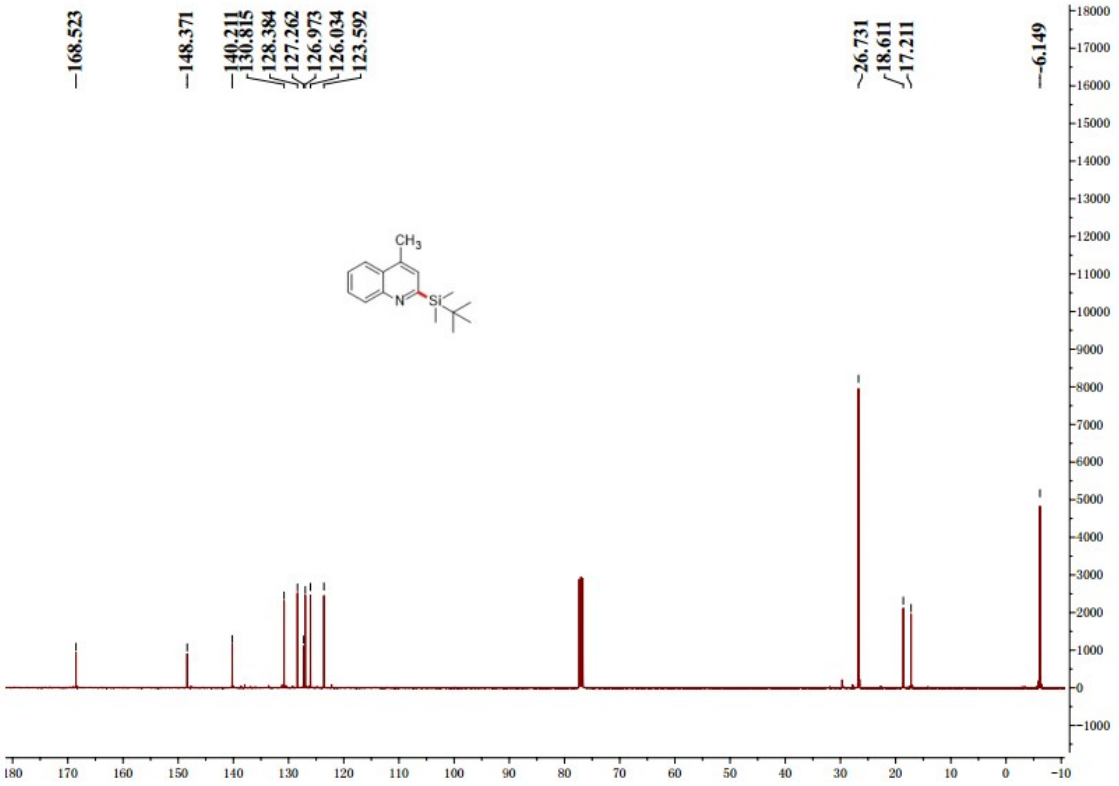
CH3
N
Si
1.00
1.03
1.06
1.03
1.10
3.42
9.98
7.16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140.211
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126.973
126.034
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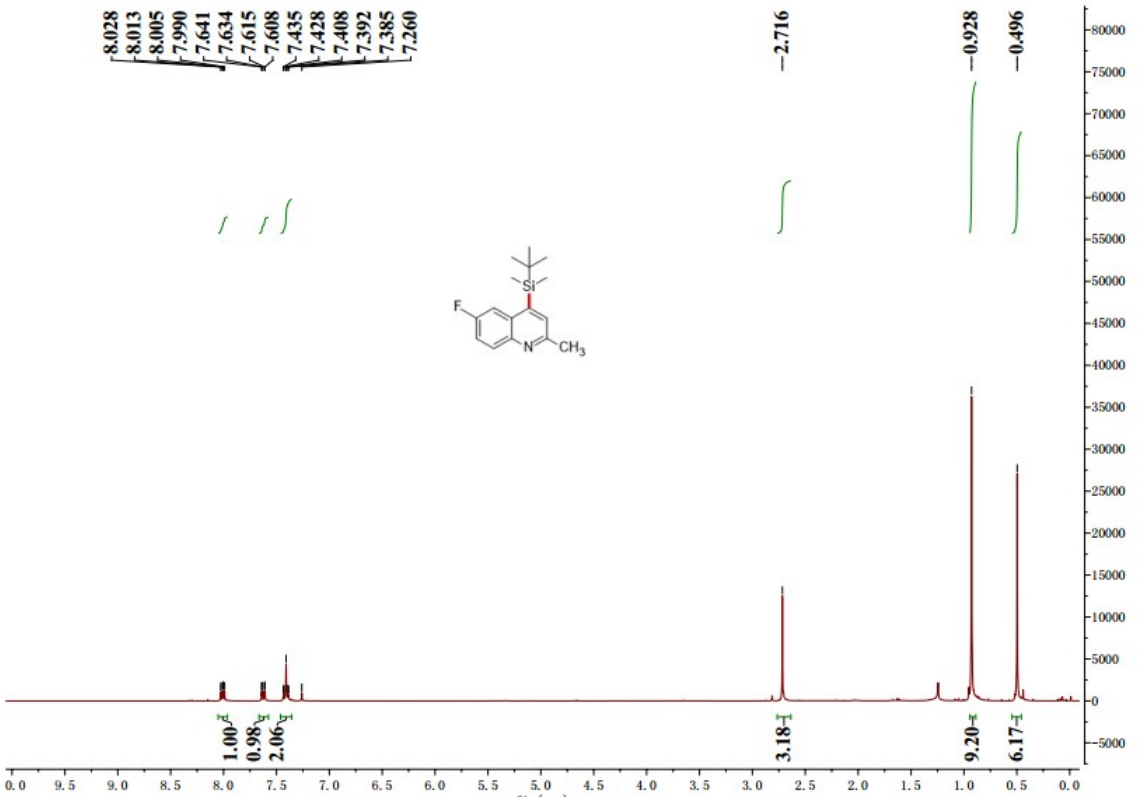
26.731
18.611
17.211
6.149
CH3
N
Si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7.641
7.634
7.615
7.608
7.435
7.428
7.408
7.392
7.385
7.260
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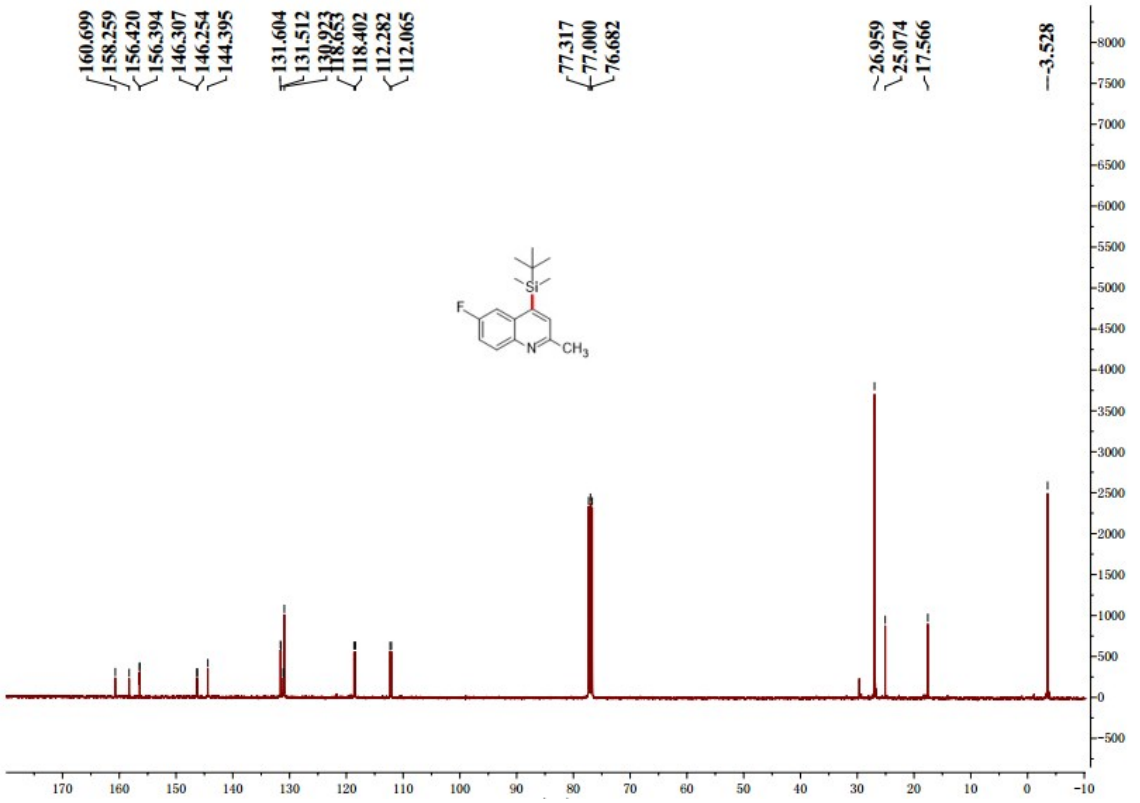
0.496
1.00
0.98
2.06
3.18
9.20
6.17
Si
F
N
CH3


160.699
158.259
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131.604
131.512
130.923
118.853
118.402
112.282
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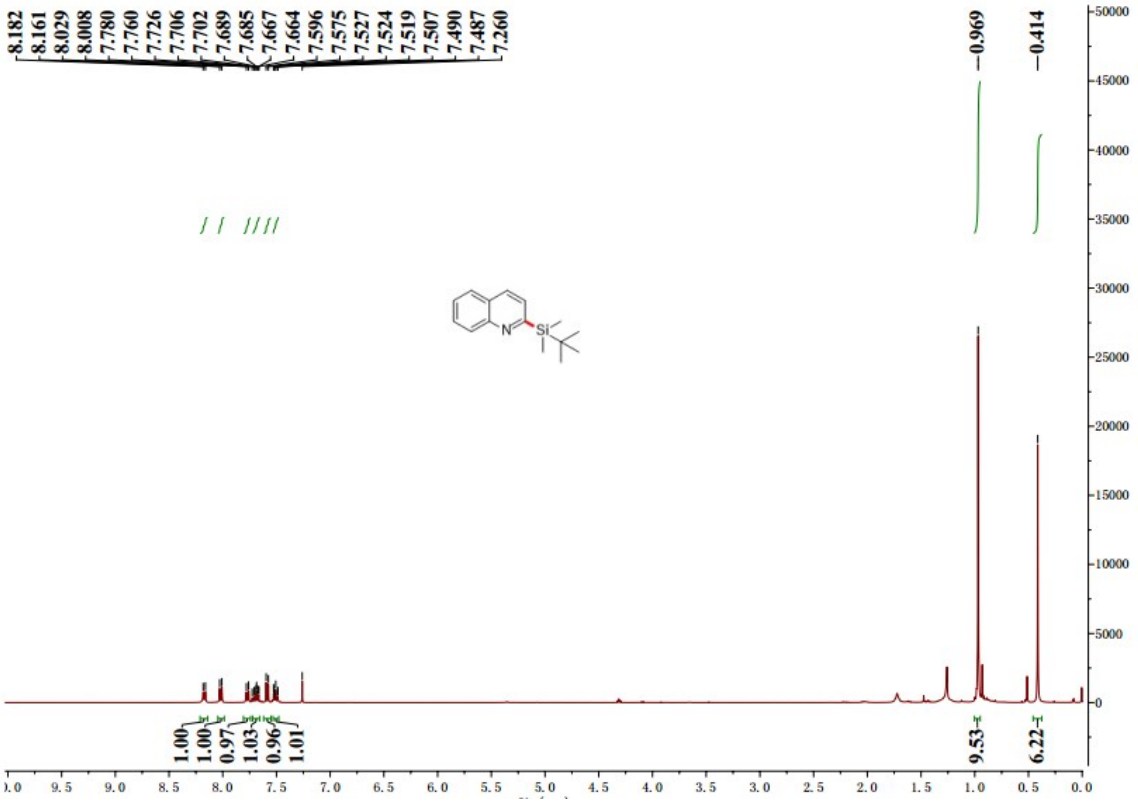
77.317
77.000
76.682
26.959
25.074
17.566
3.528
Si
F
N
CH3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7.760
7.726
7.706
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7.689
7.685
7.667
7.664
7.596
7.575
7.527
7.524
7.519
7.507
7.490
7.487
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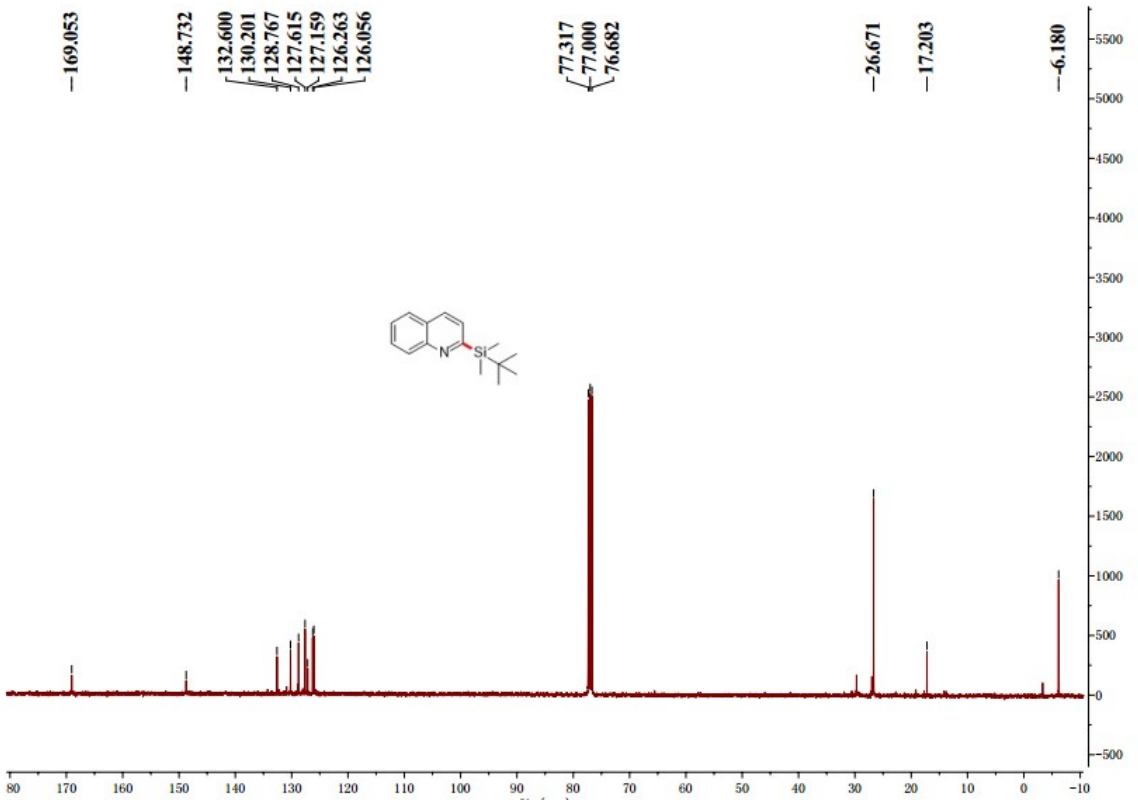
1.00
0.97
1.03
0.96
1.01
9.53
6.22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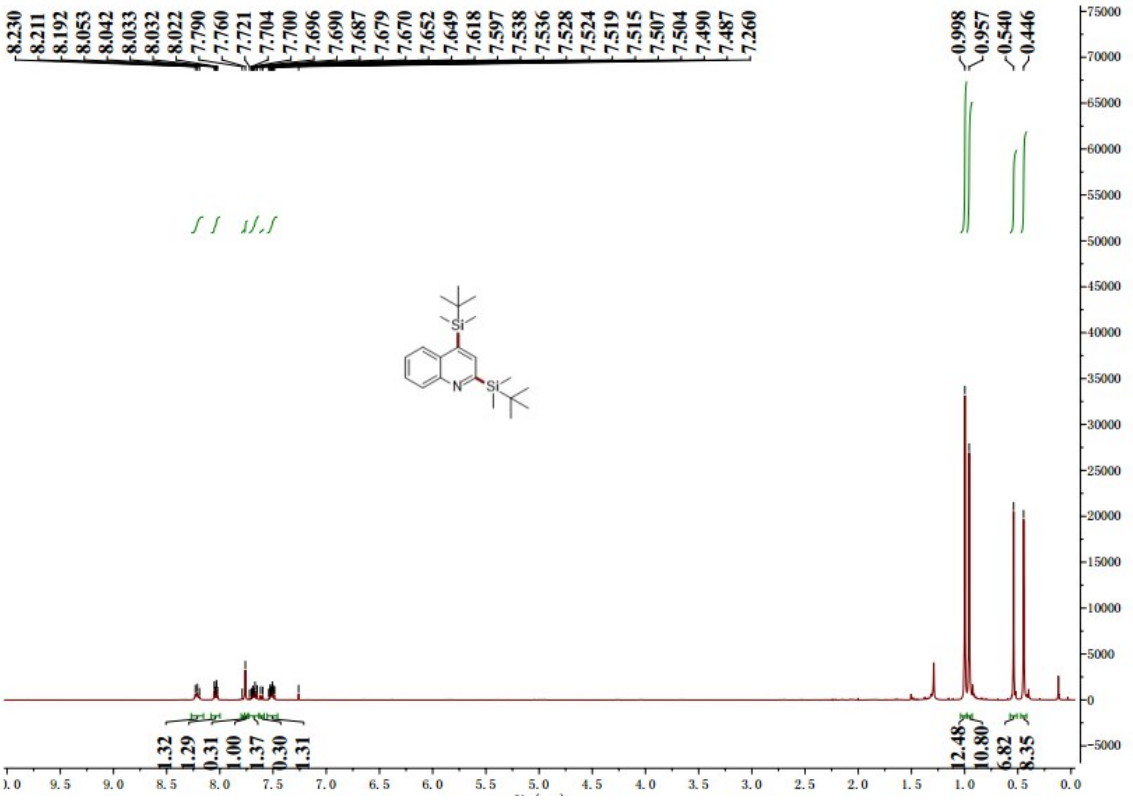
127.159
126.263
126.056
77.317
77.000
76.682
26.671
17.203
6.180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8.211
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8.033
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7.760
7.721
7.704
7.700
7.696
7.690
7.687
7.679
7.670
7.652
7.649
7.618
7.597
7.538
7.536
7.528
7.524
7.519
7.515
7.507
7.504
7.490
7.487
7.260
0.998
0.957
0.540
0.446
Si
N
Si
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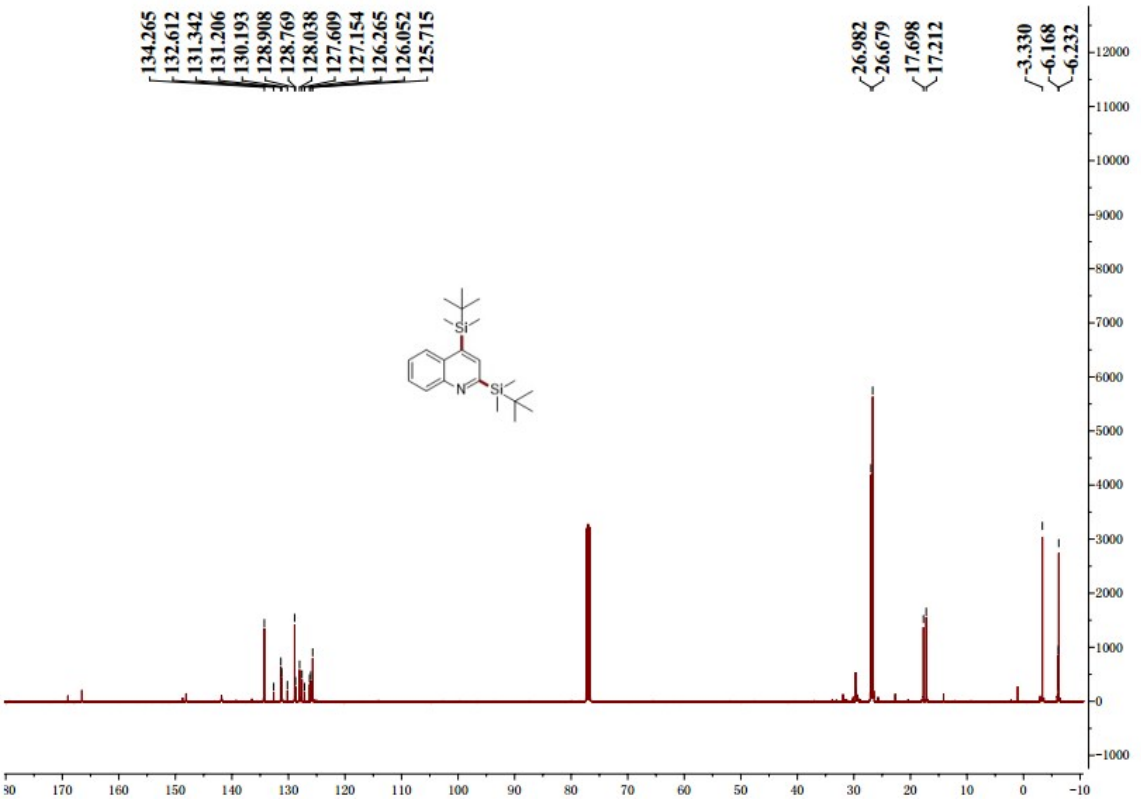
0.31
1.00
1.37
0.30
1.31
12.48
10.80
6.82
8.35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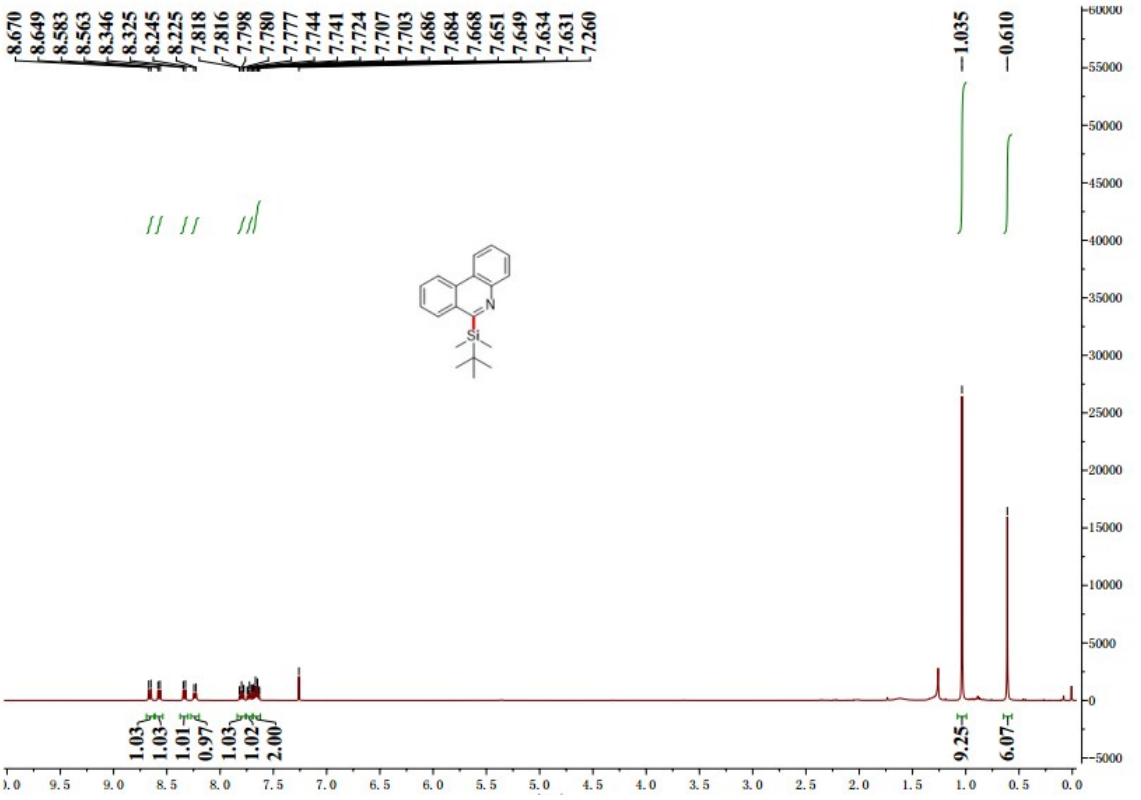
132.612
131.342
131.206
130.193
128.908
128.769
128.038
127.609
127.154
126.265
126.052
125.715
26.982
26.679
17.698
17.212
-3.330
-6.168
-6.232
Si
N
Si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8.225
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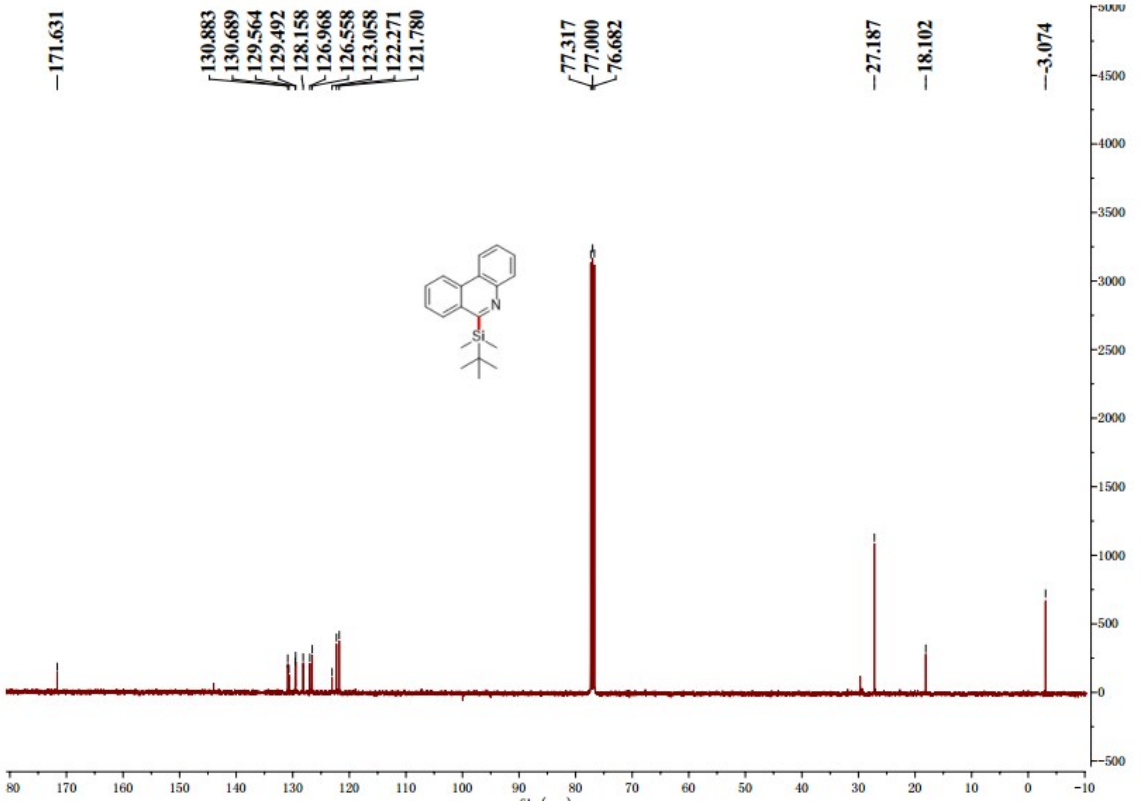
7.741
7.724
7.707
7.703
7.686
7.684
7.668
7.651
7.649
7.634
7.631
7.260
1.035
0.610
1.03
1.03
1.01
0.97
1.03
1.02
2.00
9.25
6.07
Si
N


171.631
130.883
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128.158
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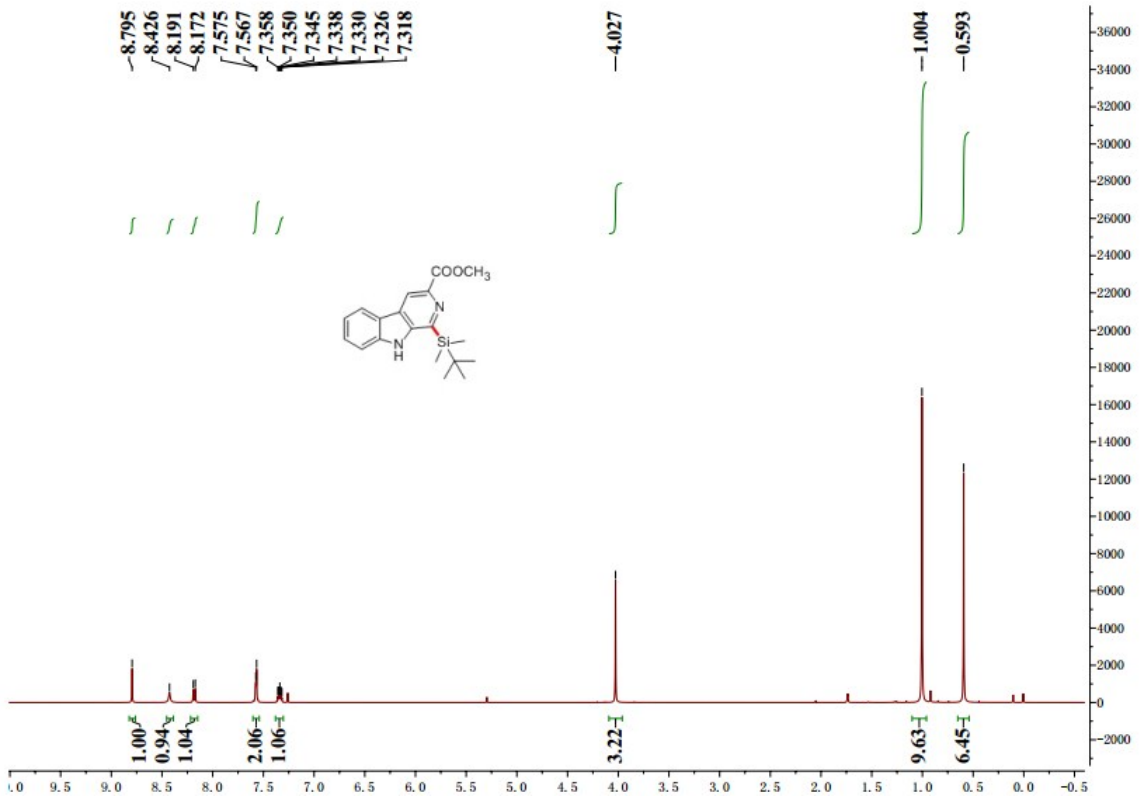
126.558
123.058
122.271
121.780
77.317
77.000
76.682
27.187
18.102
-3.074
Si
N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7.350
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7.330
7.326
7.318
4.027
1.004
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N
Si
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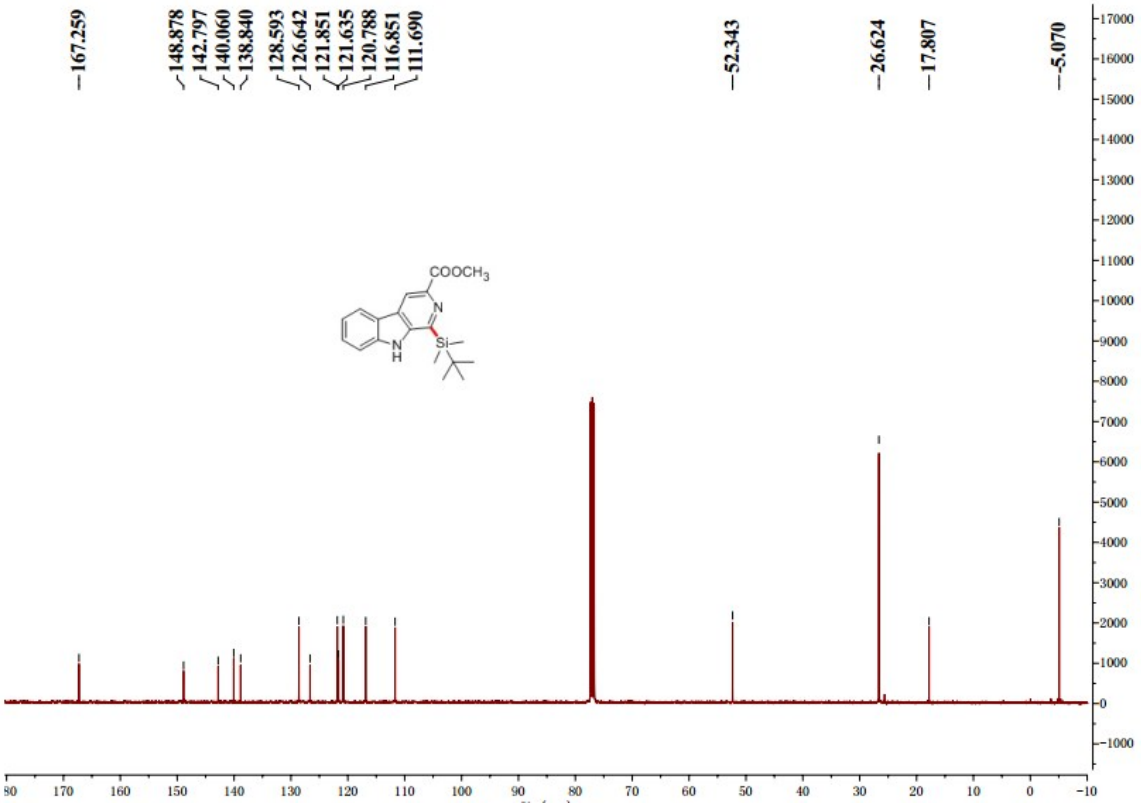
0.94
1.04
2.06
1.06
3.22
9.63
6.45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116.851
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52.343
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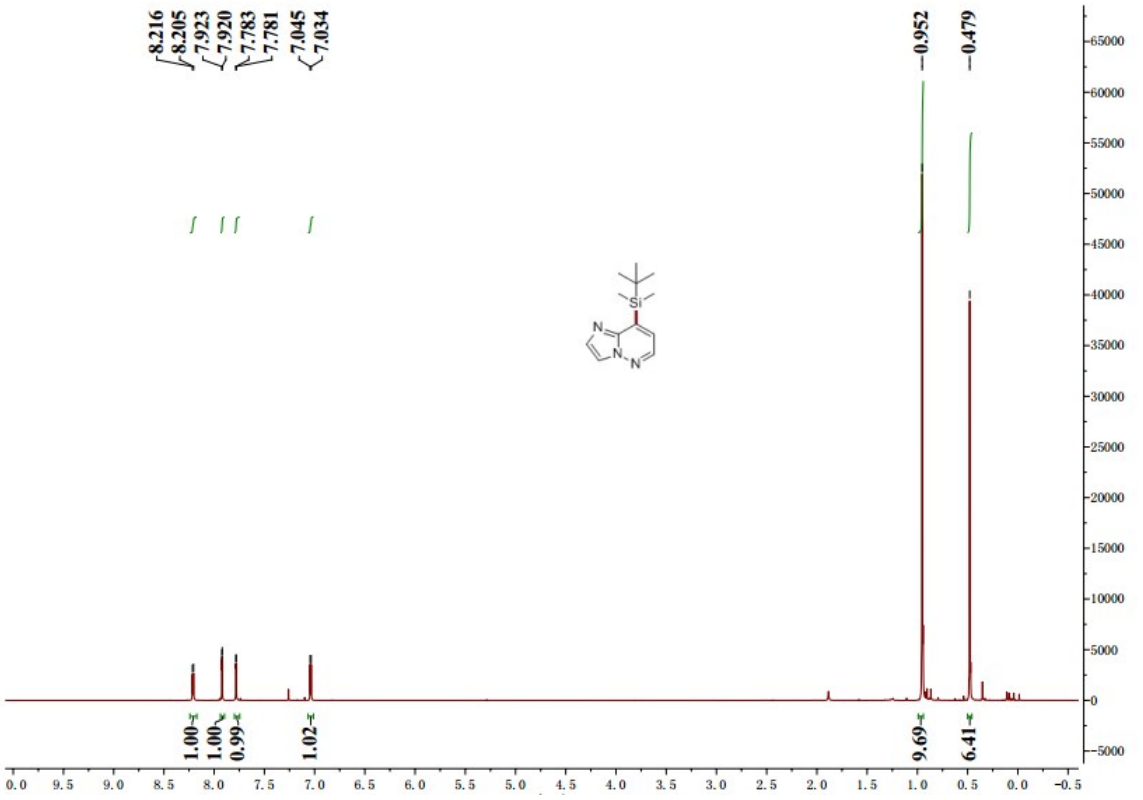
17.807
-5.070
COOCH3
N
Si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7.920
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7.034
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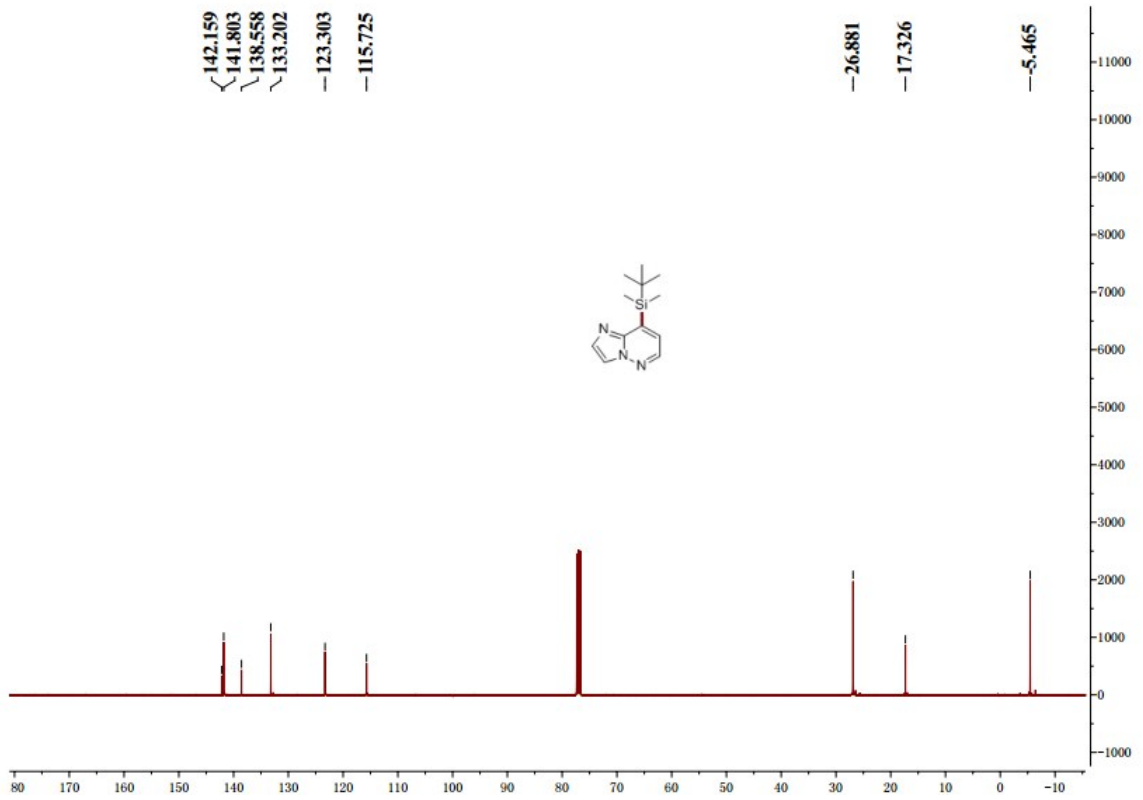
1.00
0.99
1.02
9.69
6.41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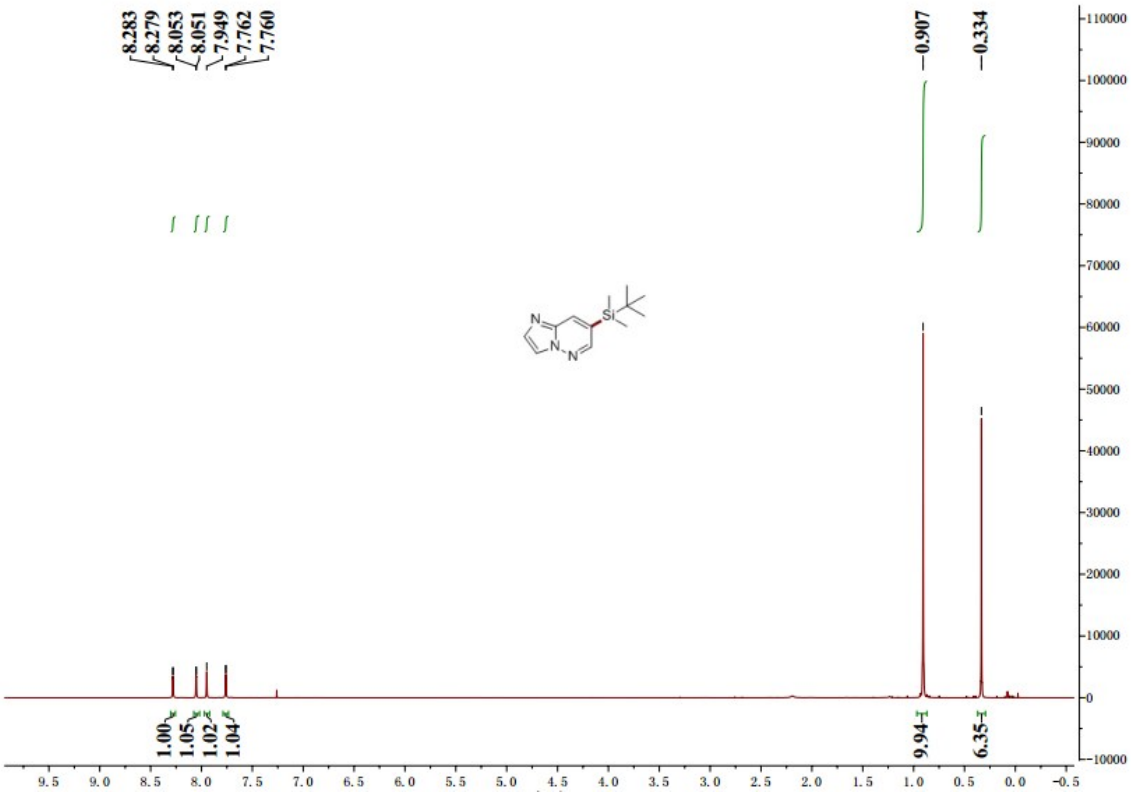
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0.907
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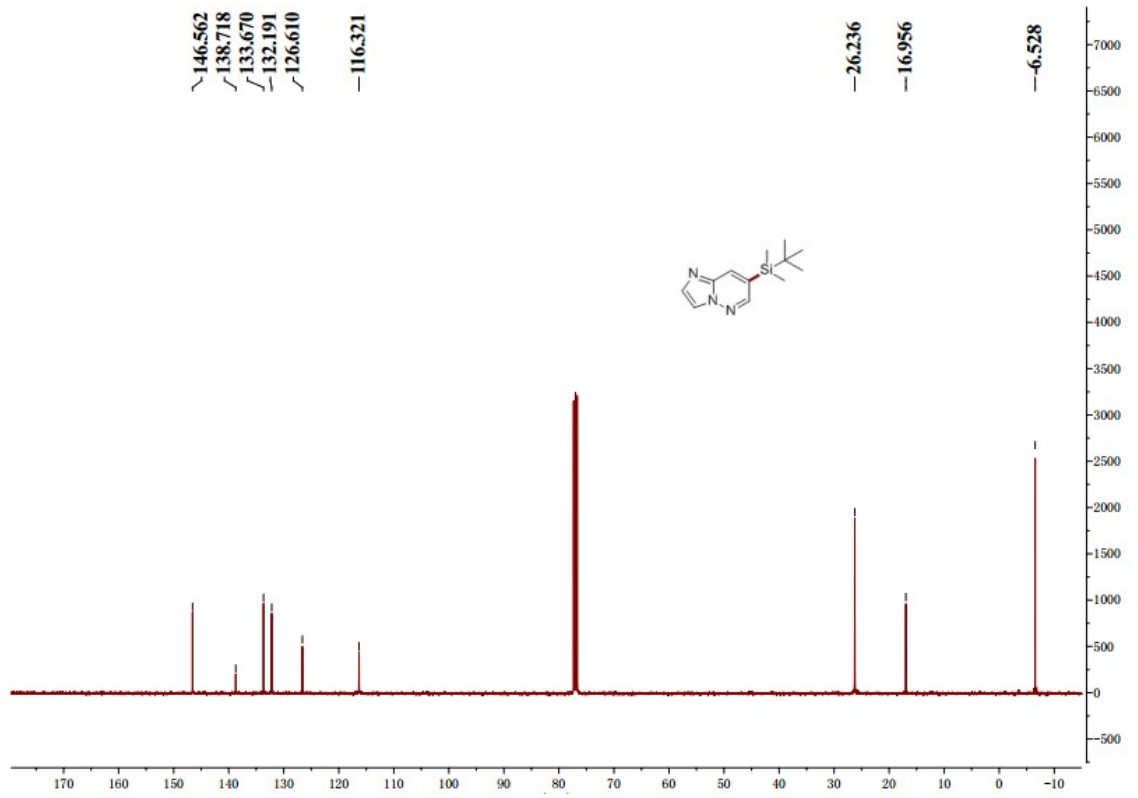
1.05
1.02
1.04
9.94
6.35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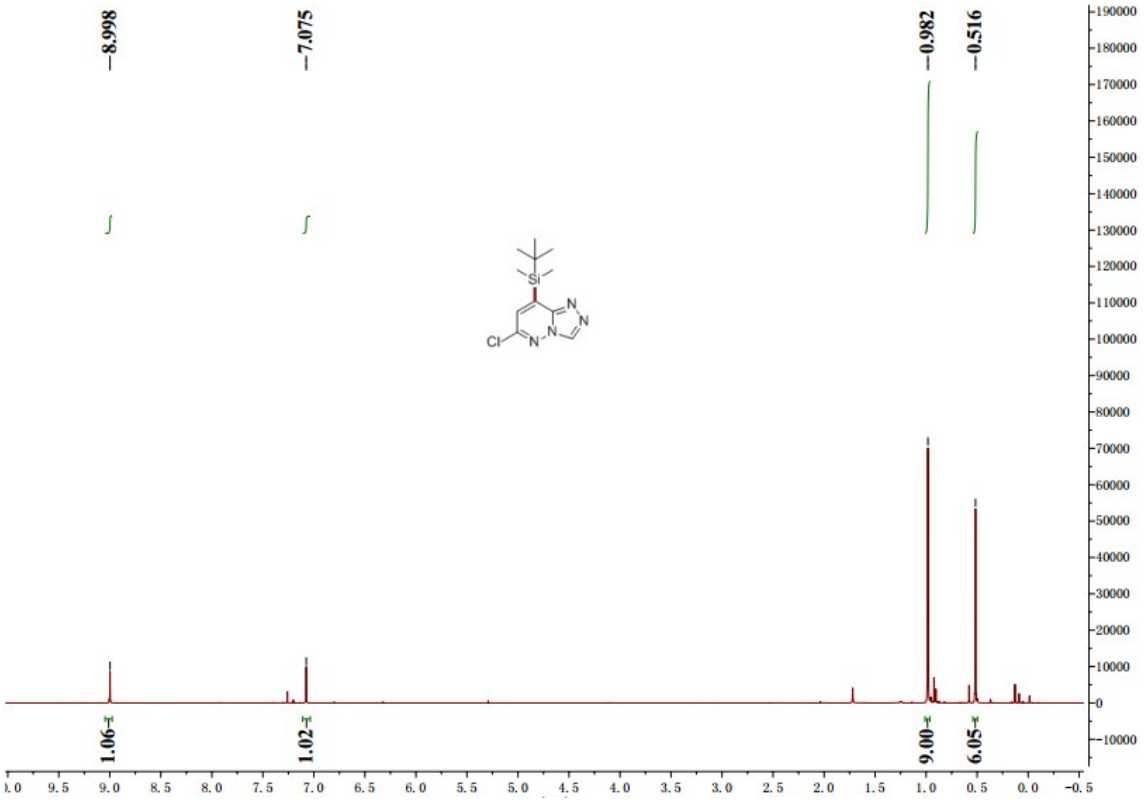
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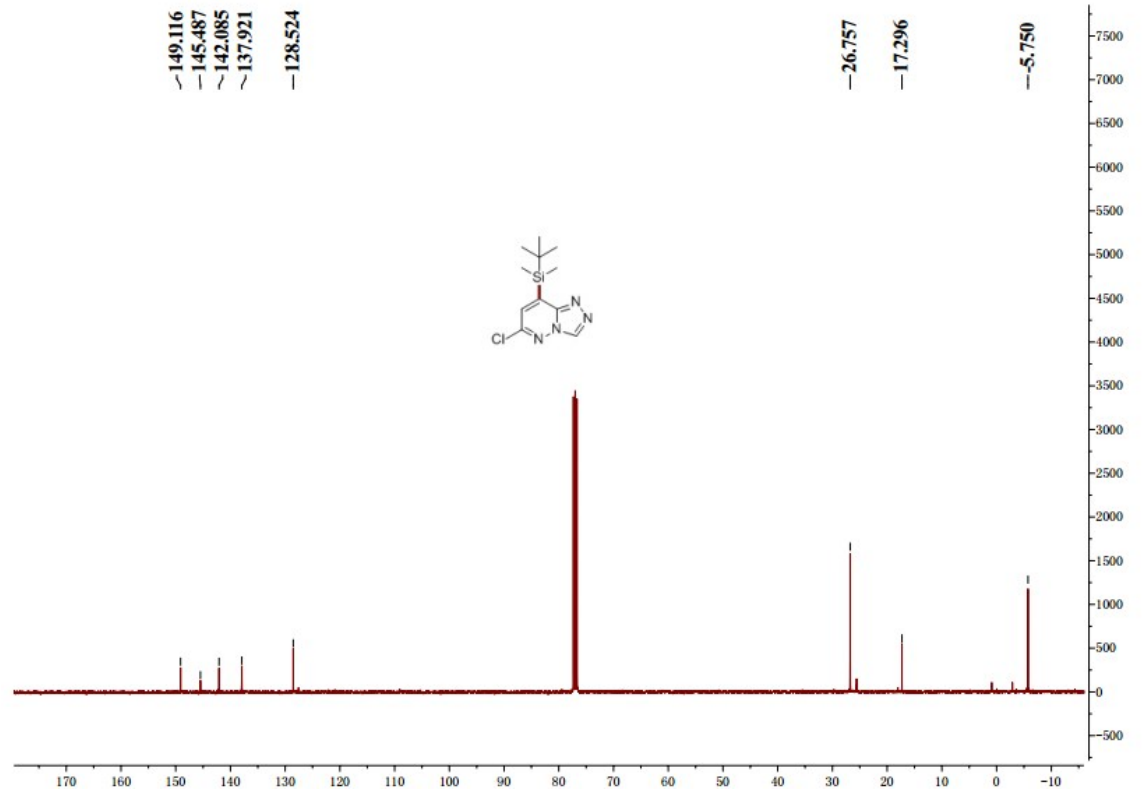
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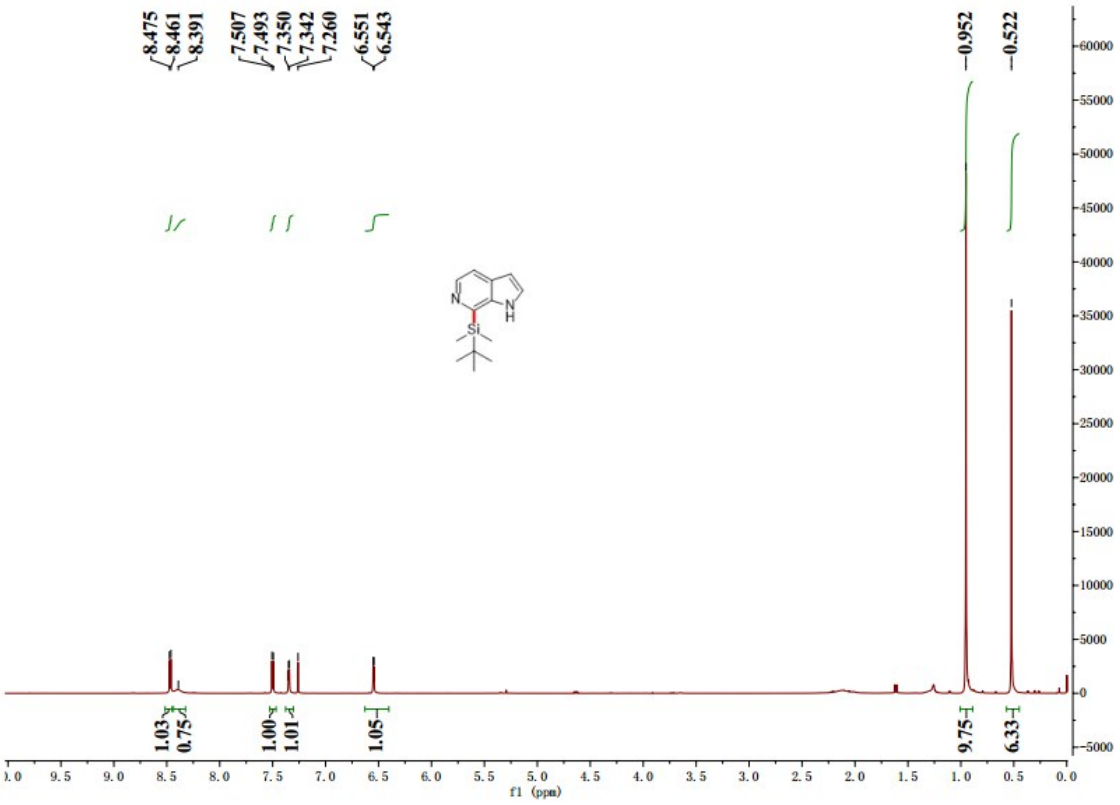
-5.750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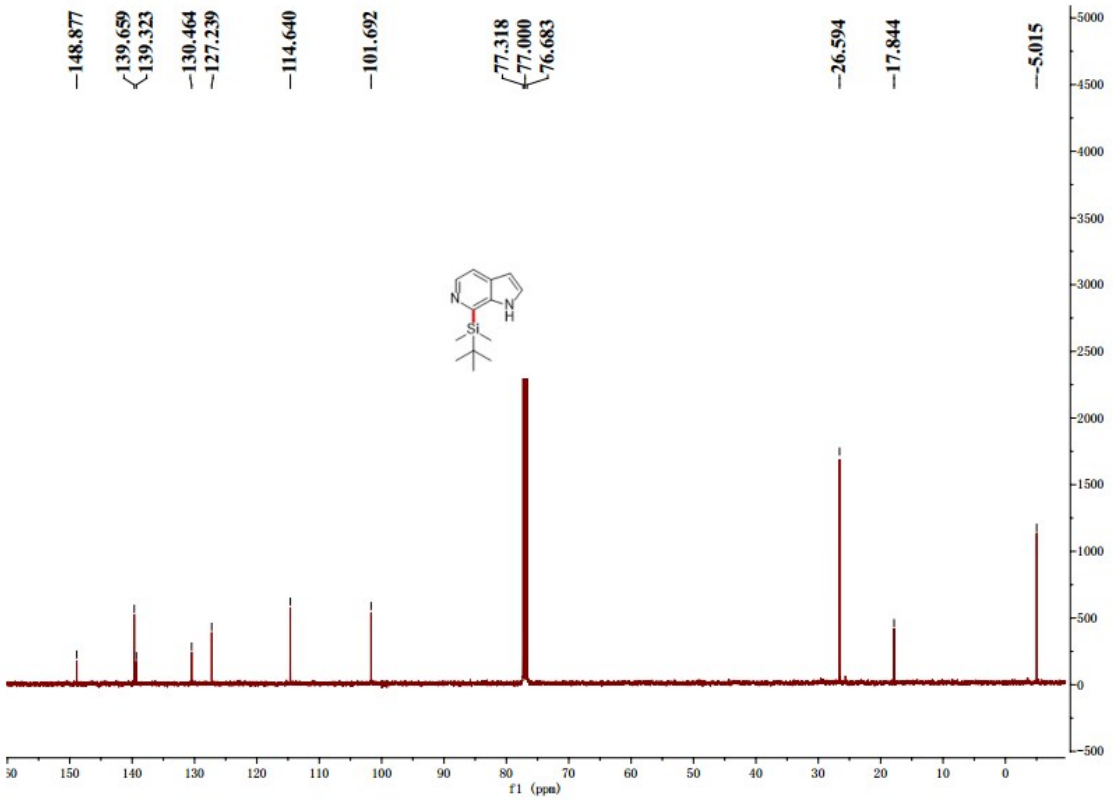
8.461
8.391
7.507
7.493
7.350
7.342
7.260
6.551
6.543
0.952
0.522
1.03
0.75
1.00
1.01
1.05
9.75
6.33
f1 (ppm)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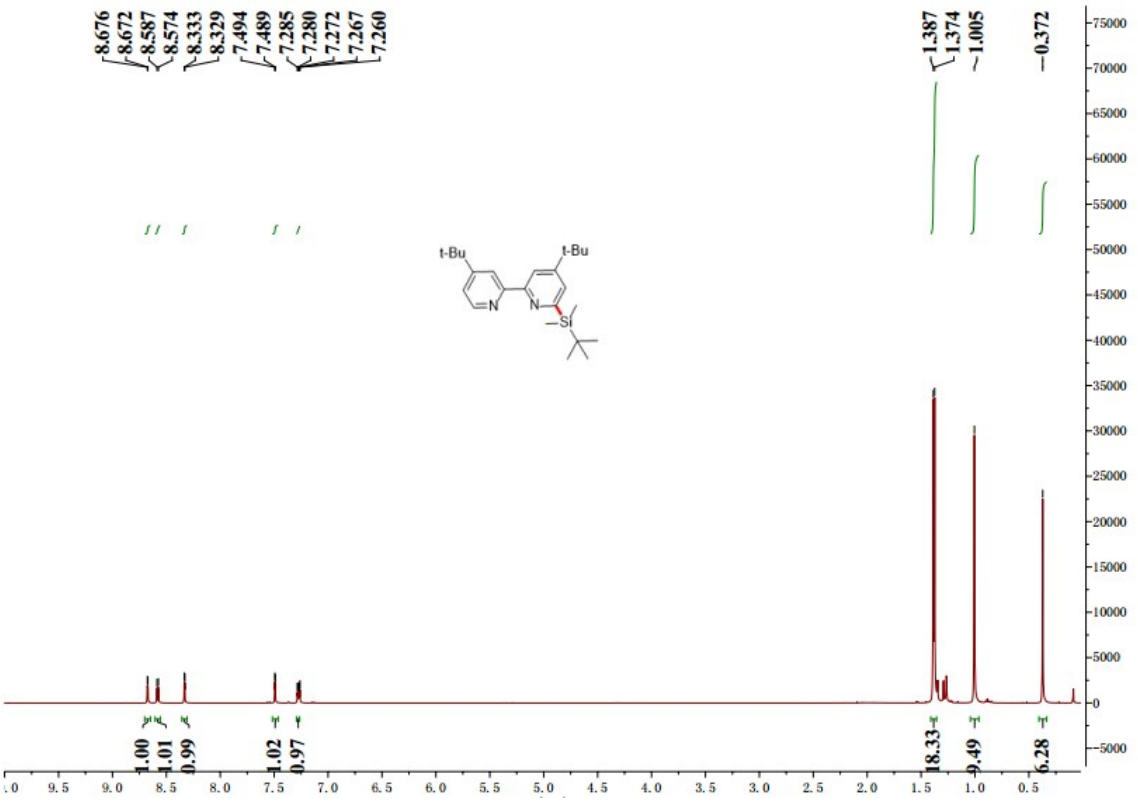
77.318
77.000
76.683
26.594
17.844
5.015
f1 (ppm)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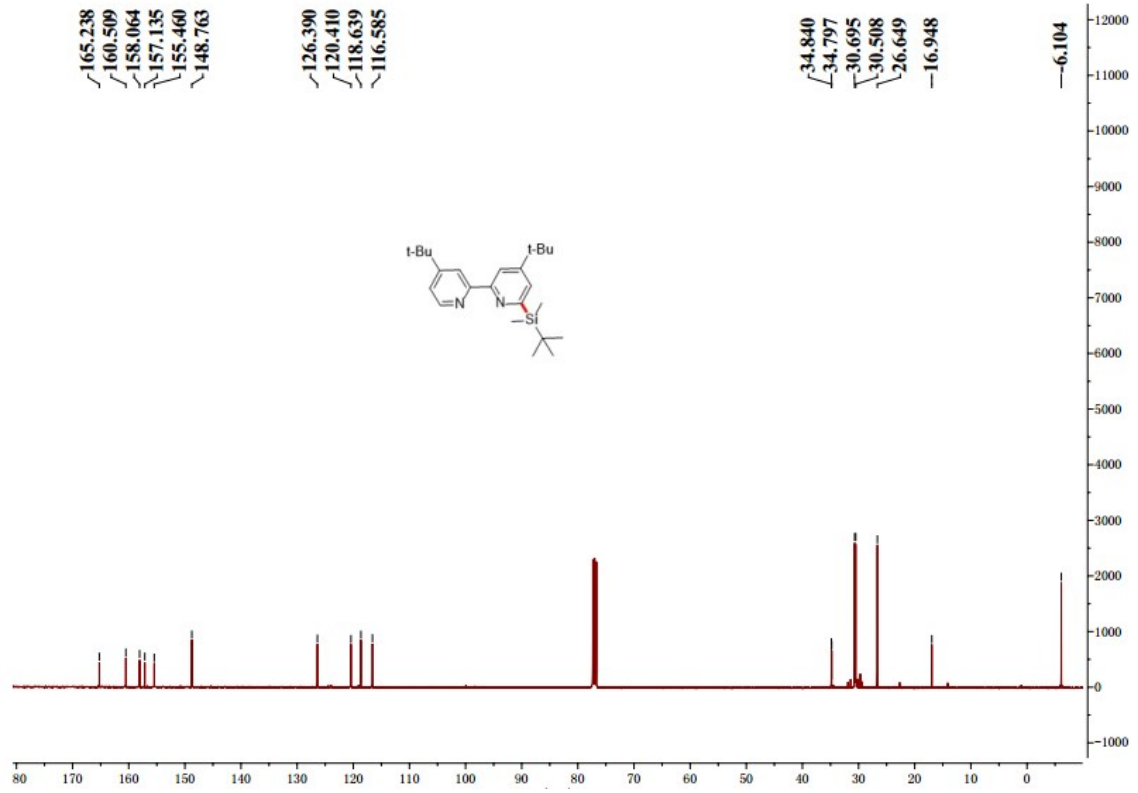
8.574
8.333
8.329
7.494
7.489
7.285
7.280
7.272
7.267
7.260
1.387
1.374
1.005
0.372
t-Bu
t-Bu
N
N
Si
1.00
1.01
0.99
1.02
0.97
18.33
9.49
6.28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157.135
155.460
148.763
126.390
120.410
118.639
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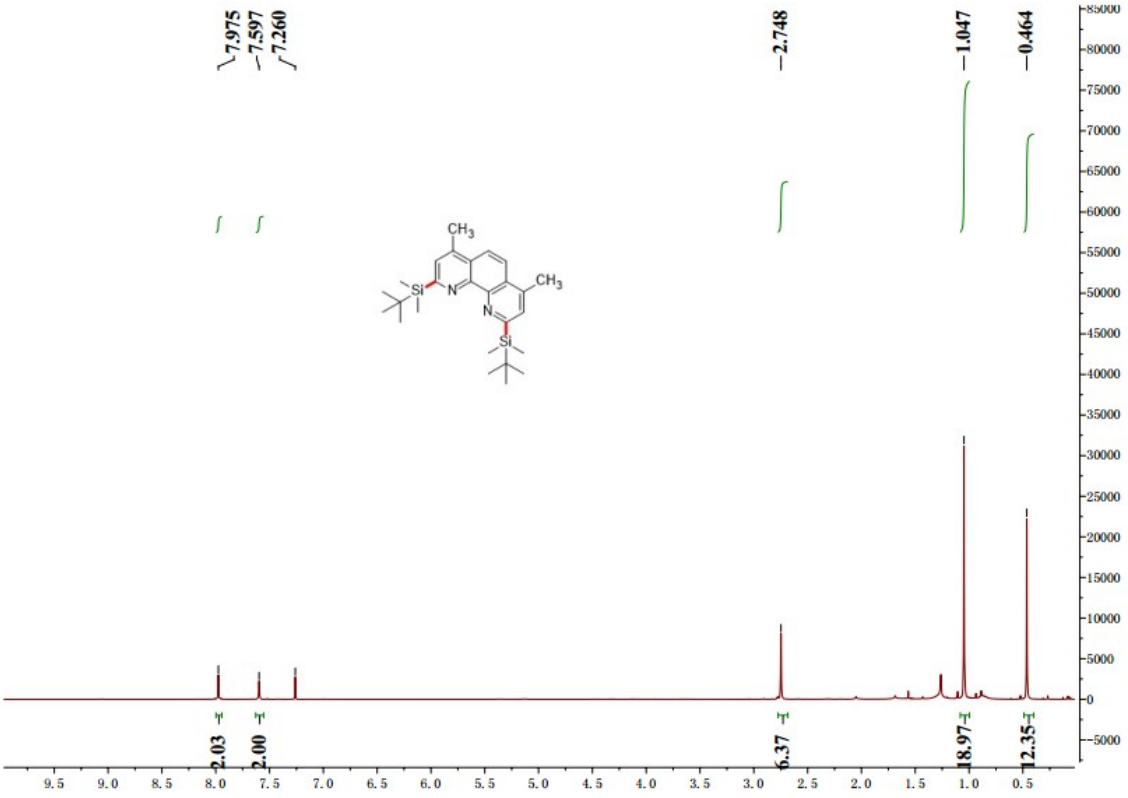
34.797
30.695
30.508
26.649
16.948
6.104
t-Bu
t-Bu
N
N
Si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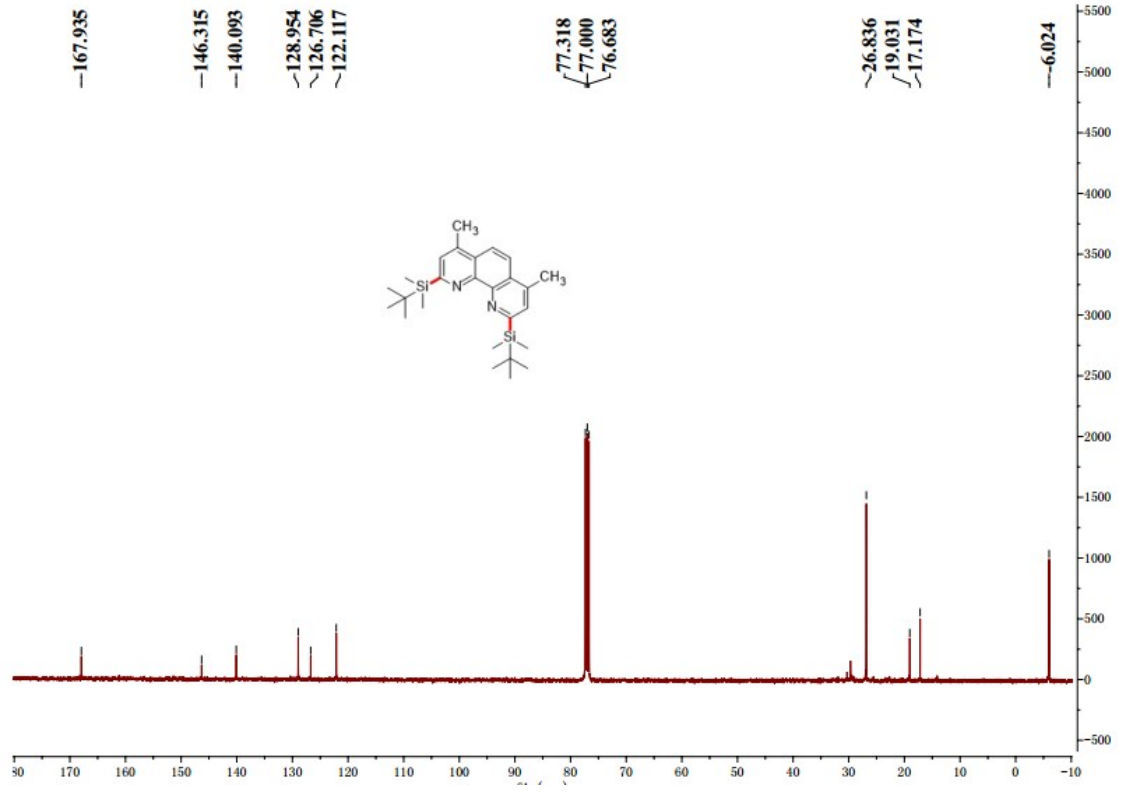
2.03
2.00
6.37
18.97
12.35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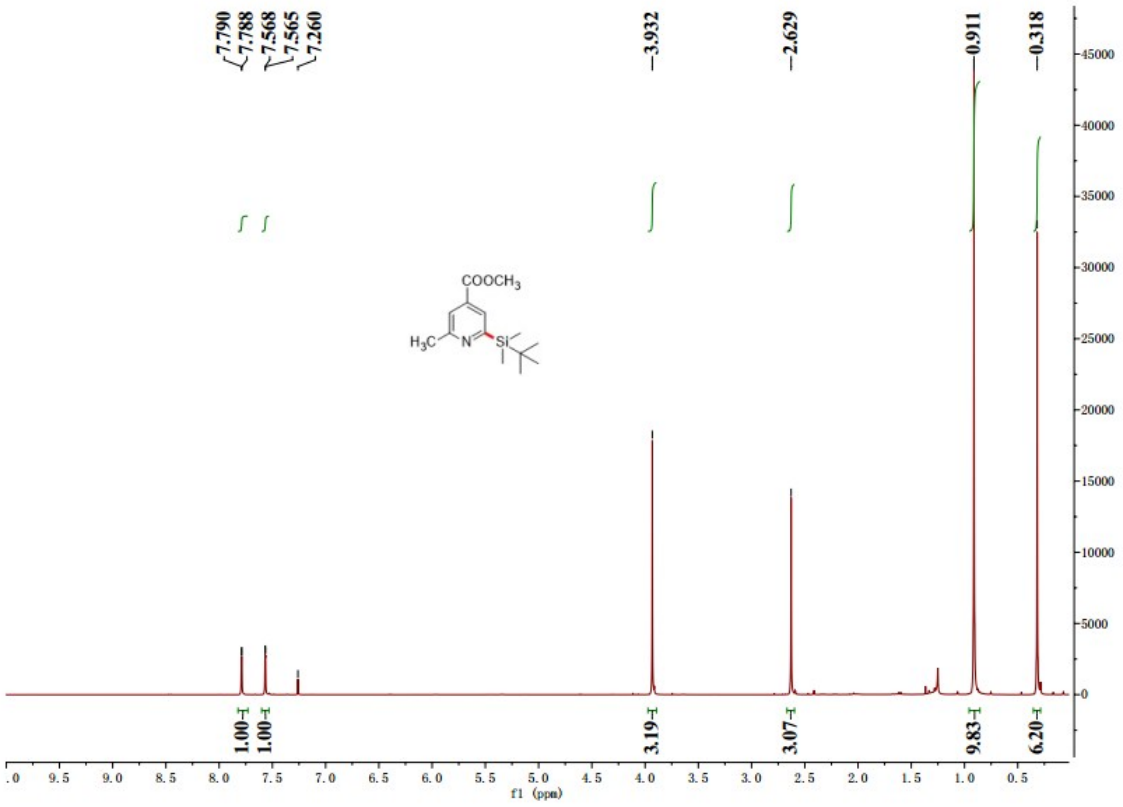
77.000
76.683
26.836
19.031
17.174
6.024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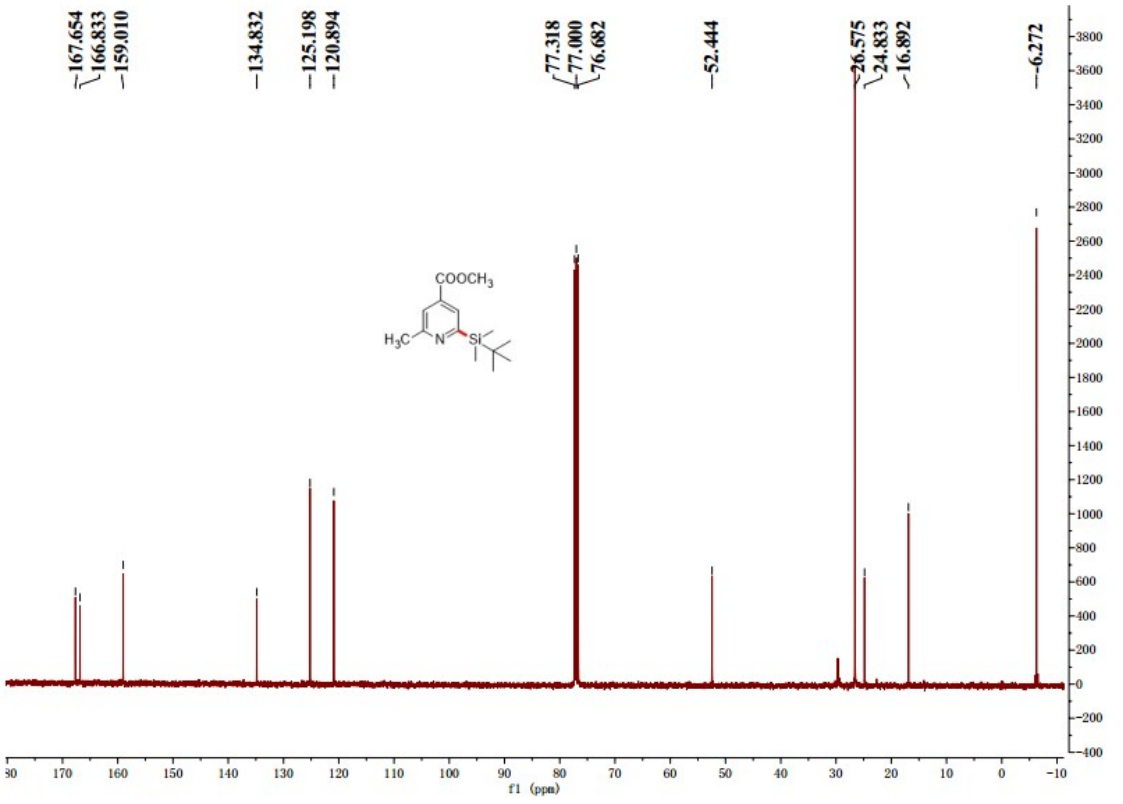
7.788
7.568
7.565
7.260
3.932
2.629
0.911
0.318
COOCH3
H3C
N
Si
1.00
1.00
3.19
3.07
9.83
6.20
f1 (ppm)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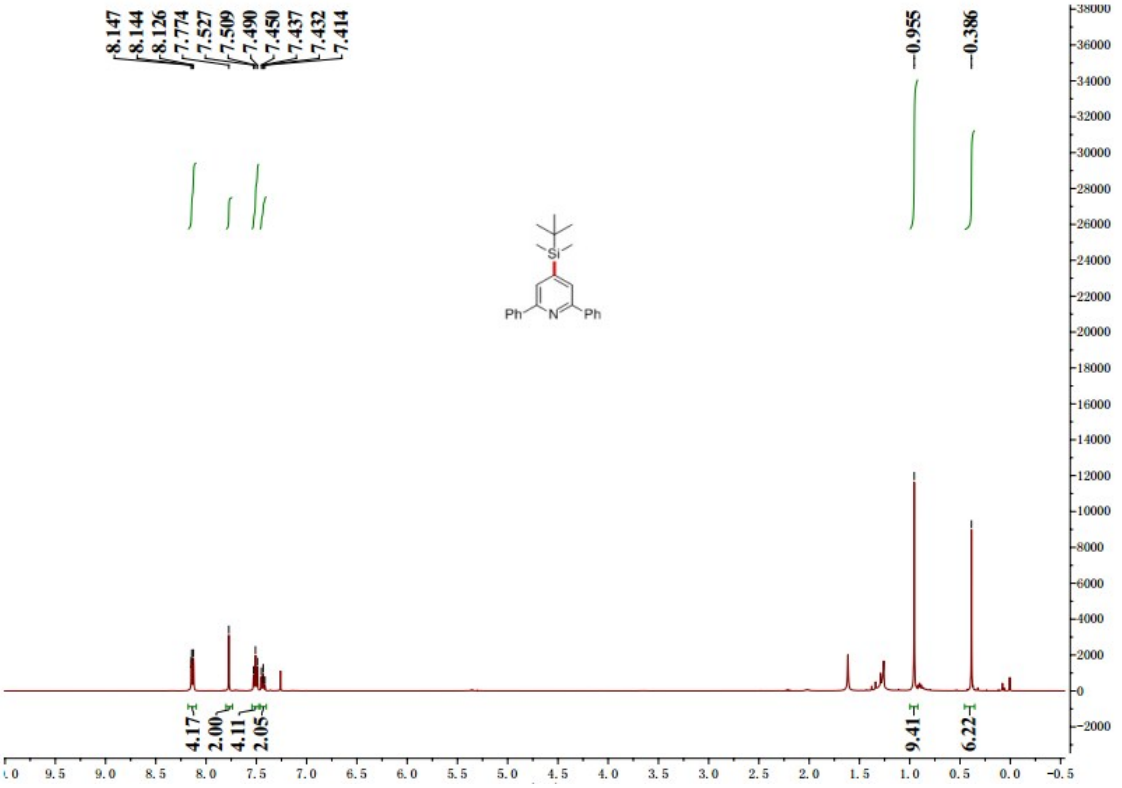
24.833
16.892
-6.272
COOCH3
H3C
N
Si
f1 (ppm)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8.144
8.126
7.774
7.527
7.509
7.490
7.450
7.437
7.432
7.414
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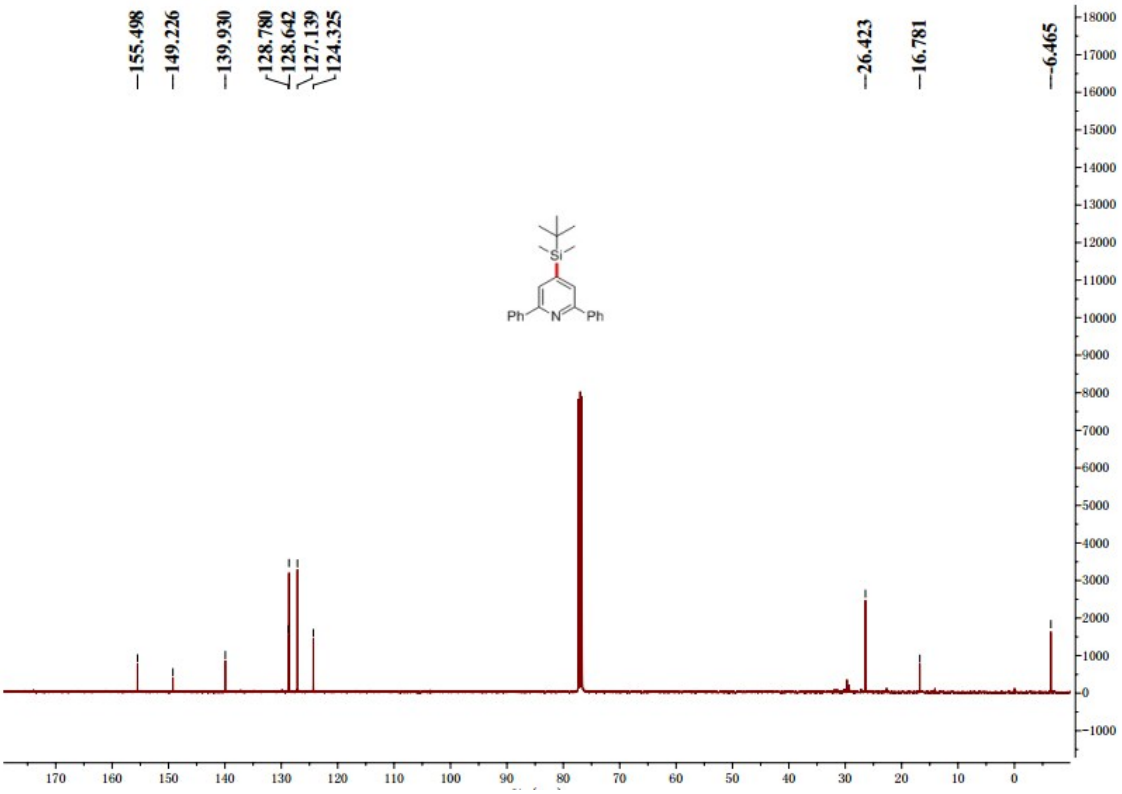
0.386
Si
Ph
N
Ph
4.17
2.00
4.11
2.05
9.41
6.22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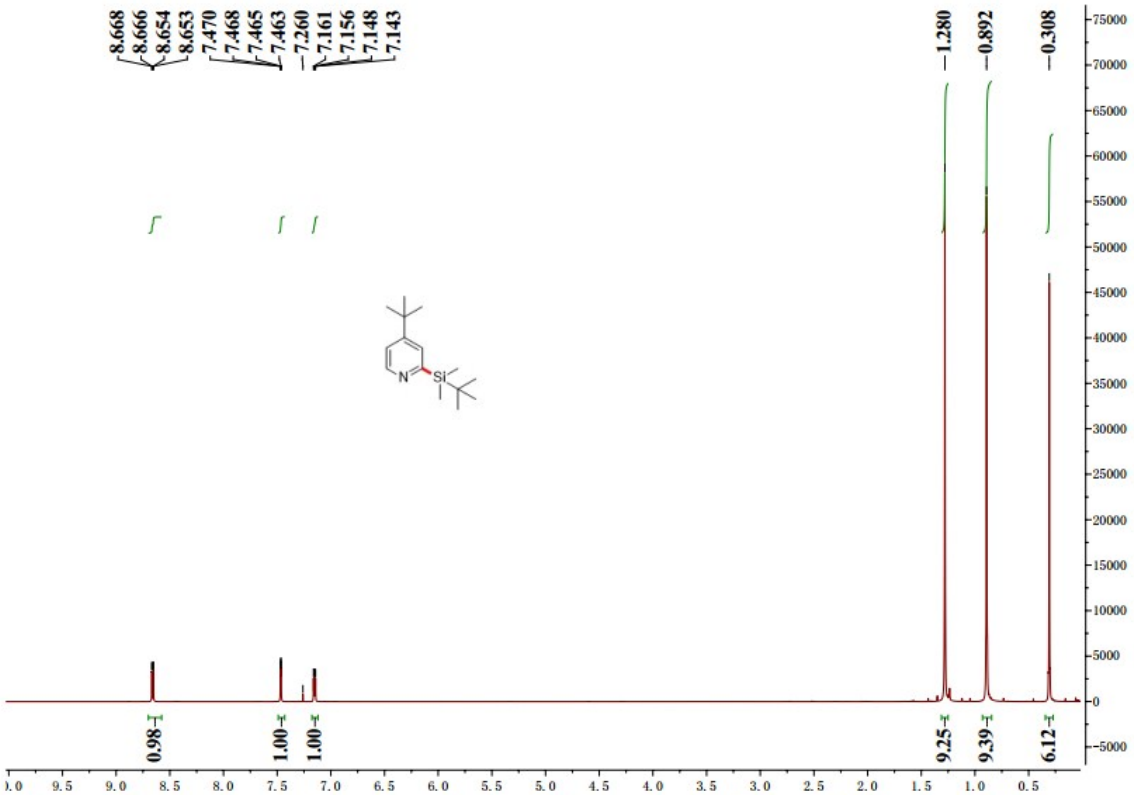
127.139
124.325
26.423
16.781
6.465
Si
Ph
N
Ph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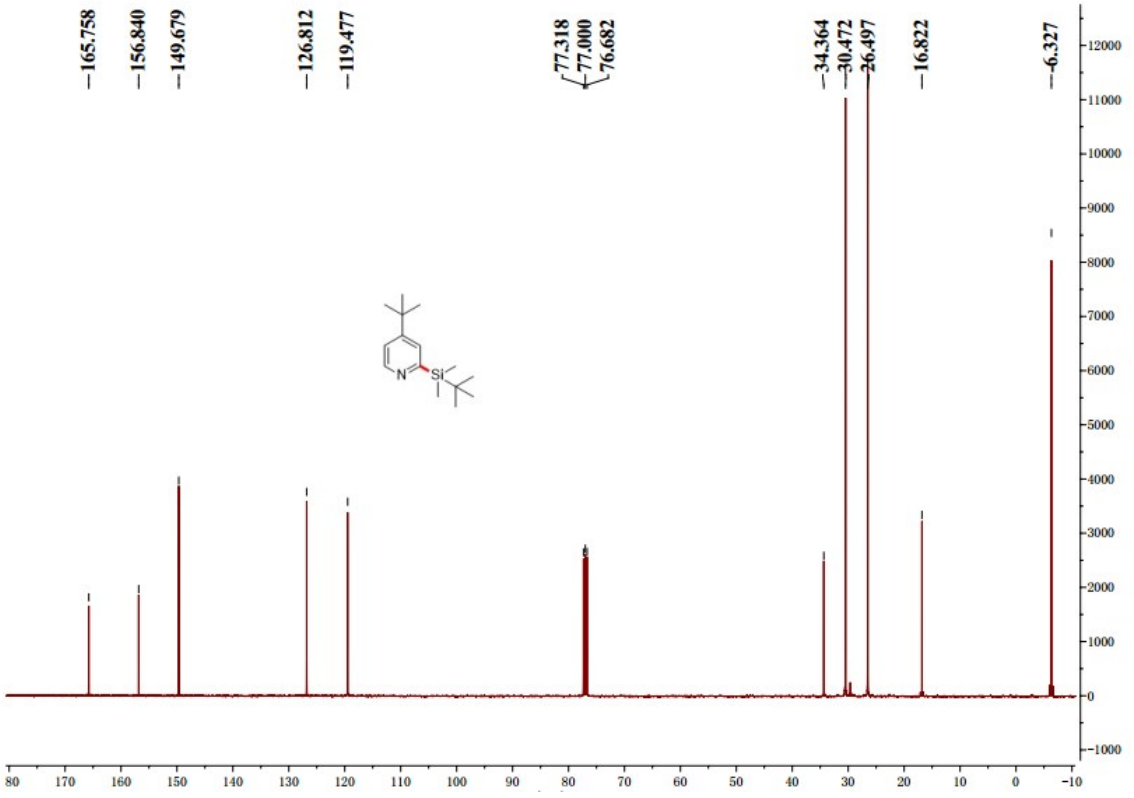
8.653
7.470
7.468
7.465
7.463
7.260
7.161
7.156
7.148
7.143
1.280
0.892
0.308
0.98
1.00
1.00
9.25
9.39
6.12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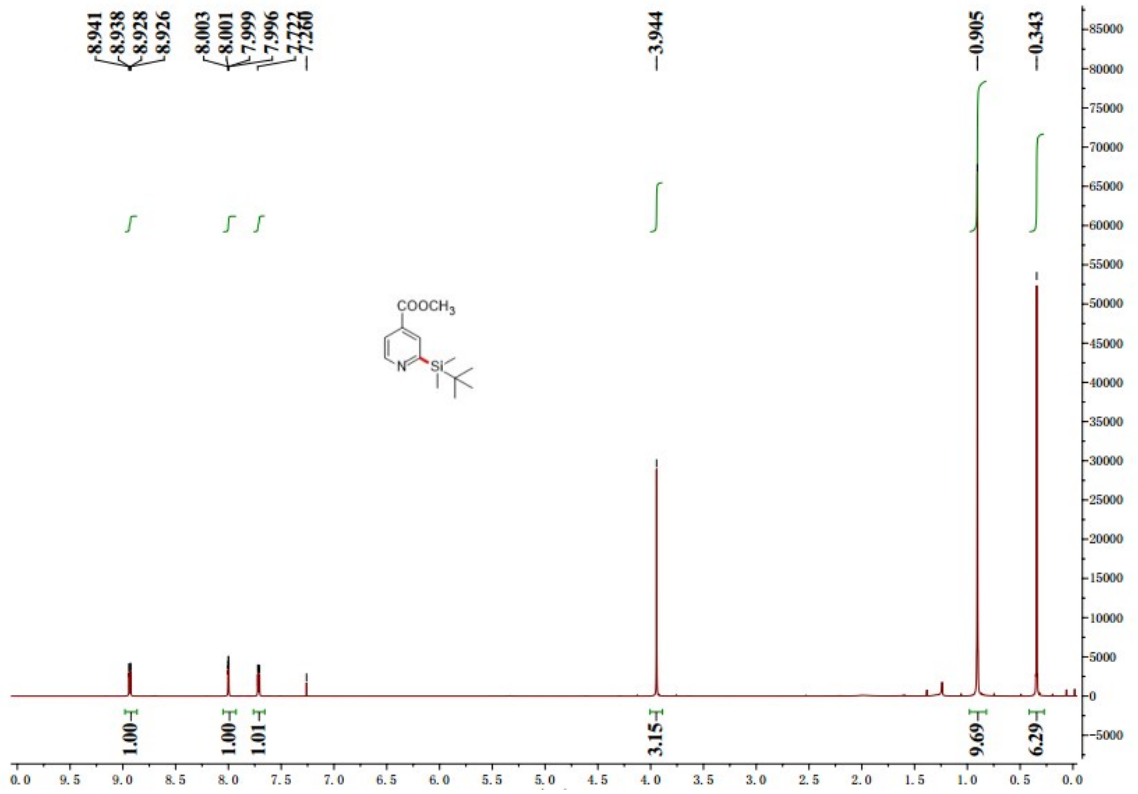
6.327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8.938
8.928
8.926
8.003
8.001
7.999
7.996
7.722
7.260
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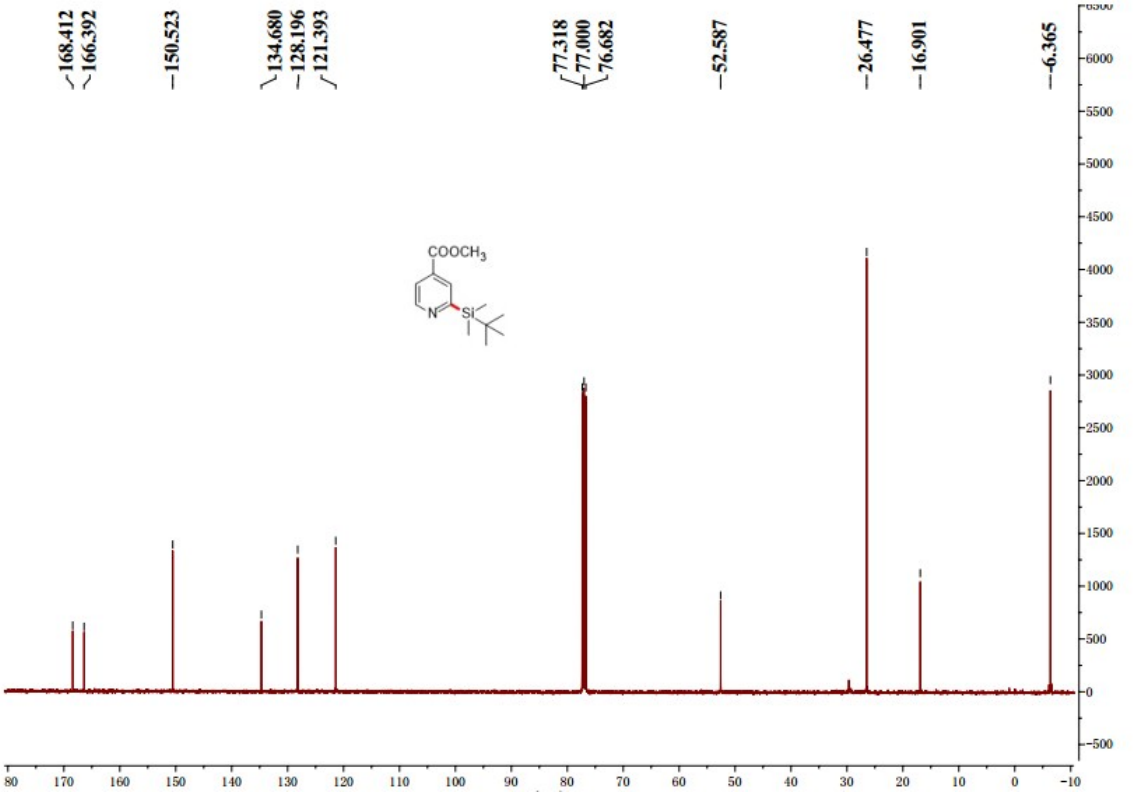
0.343
COOCH3
N
Si
1.00
1.00
1.01
3.15
9.69
6.29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76.682
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16.901
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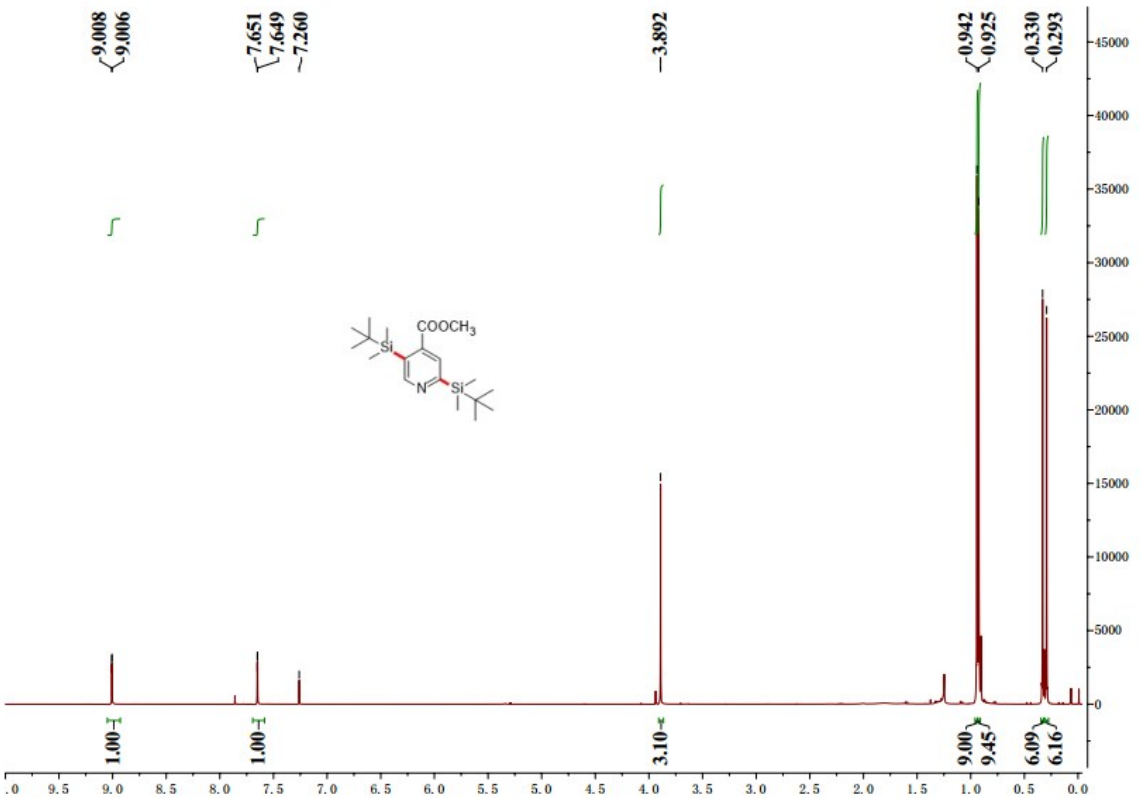
COOCH3
N
Si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9.006
7.651
7.649
7.260
3.892
0.942
0.925
0.330
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COOCH3
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N
Si
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1.00
3.10
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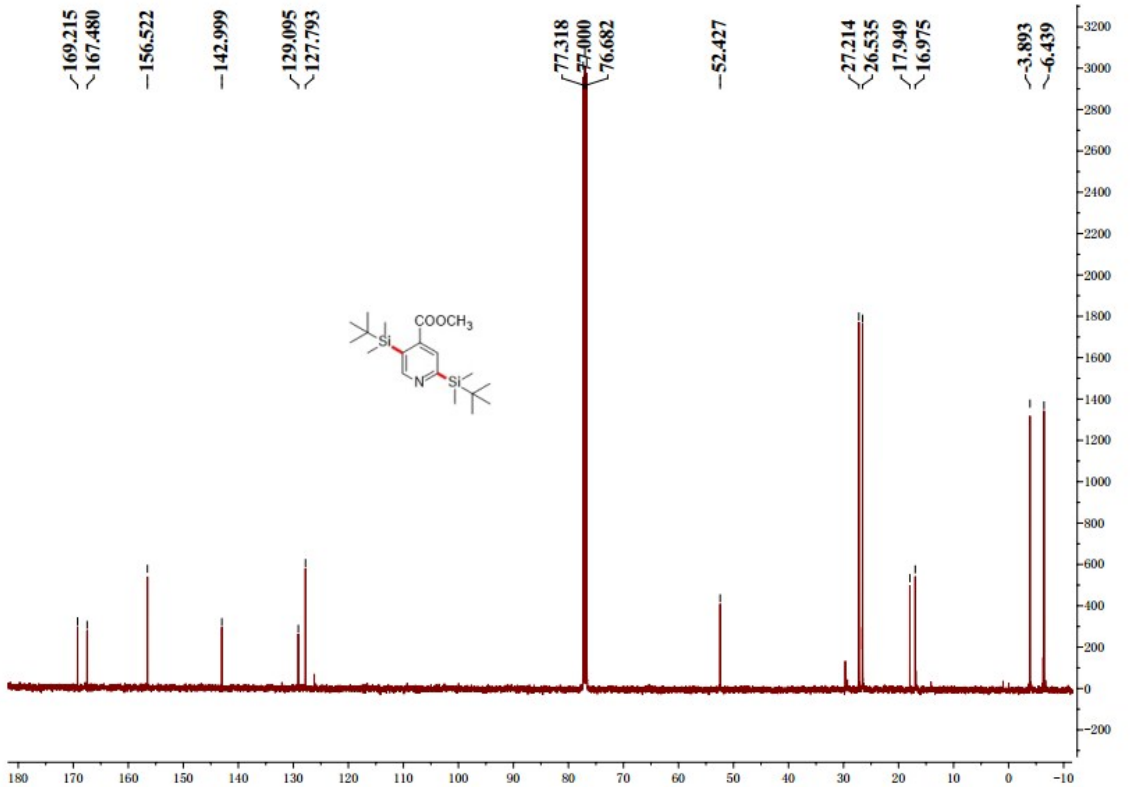
9.45
6.09
6.16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127.793
77.318
77.000
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27.214
26.535
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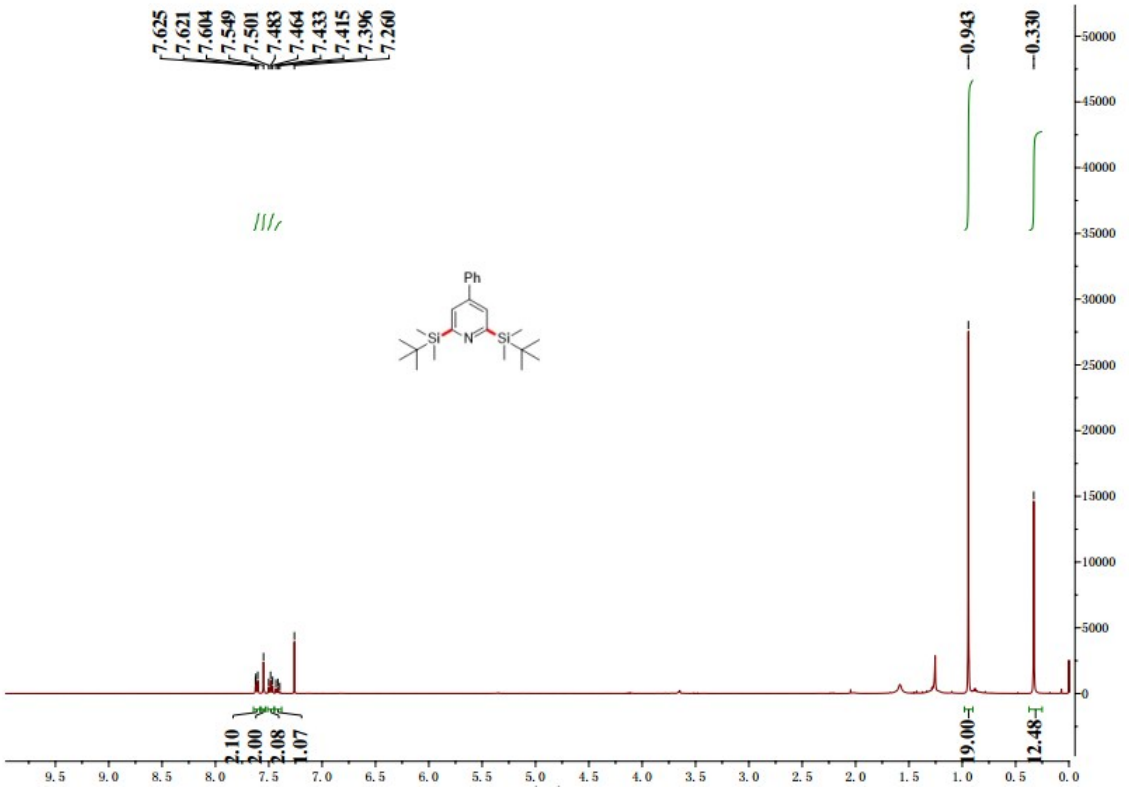
-6.439
COOCH3
Si
N
Si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7.549
7.501
7.483
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7.433
7.415
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0.330
Ph
Si
N
Si
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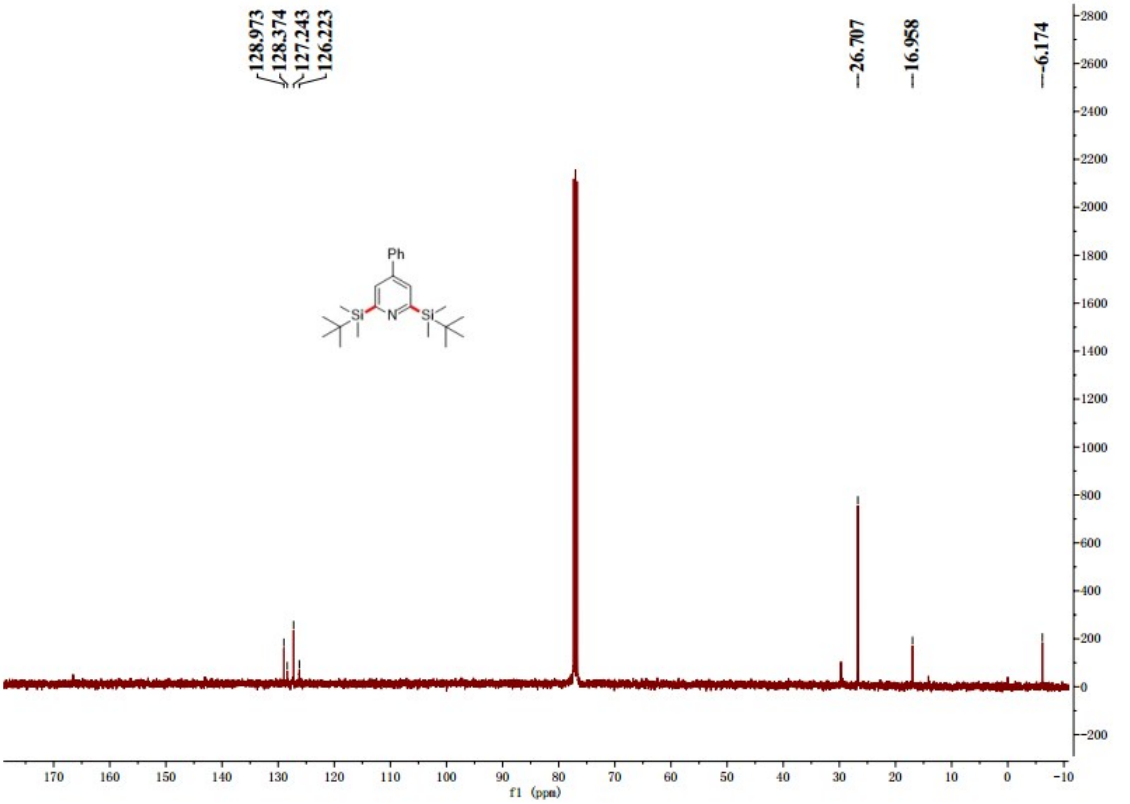
2.00
2.08
1.07
19.00
12.48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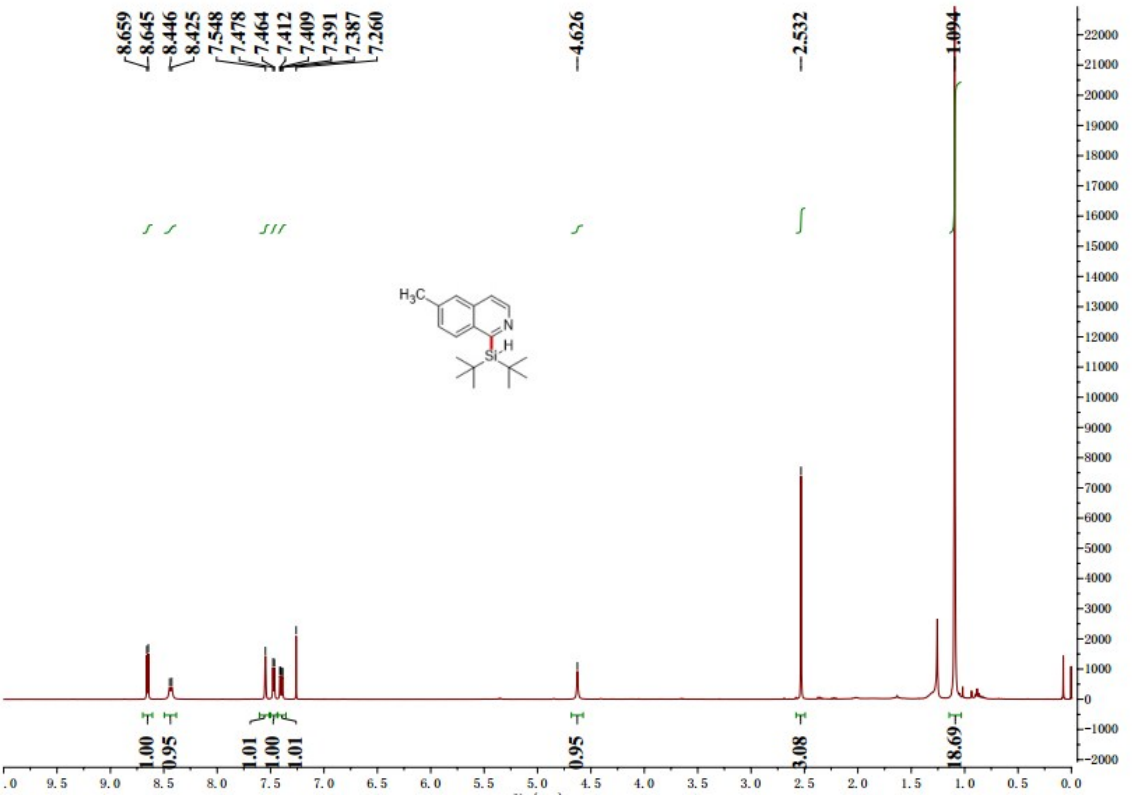
16.958
6.174
Ph
Si
N
Si
f1 (ppm)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7.478
7.464
7.412
7.409
7.391
7.387
7.260
4.626
2.532
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N
H
Si
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1.00
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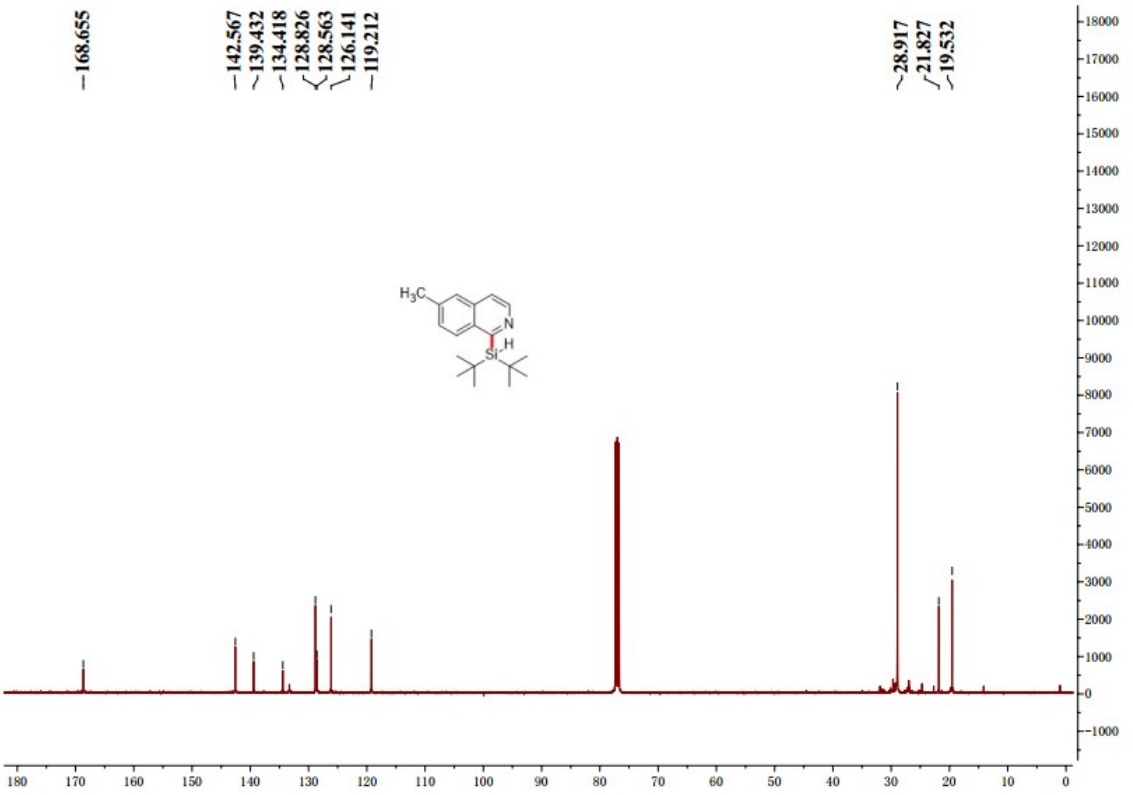
18.69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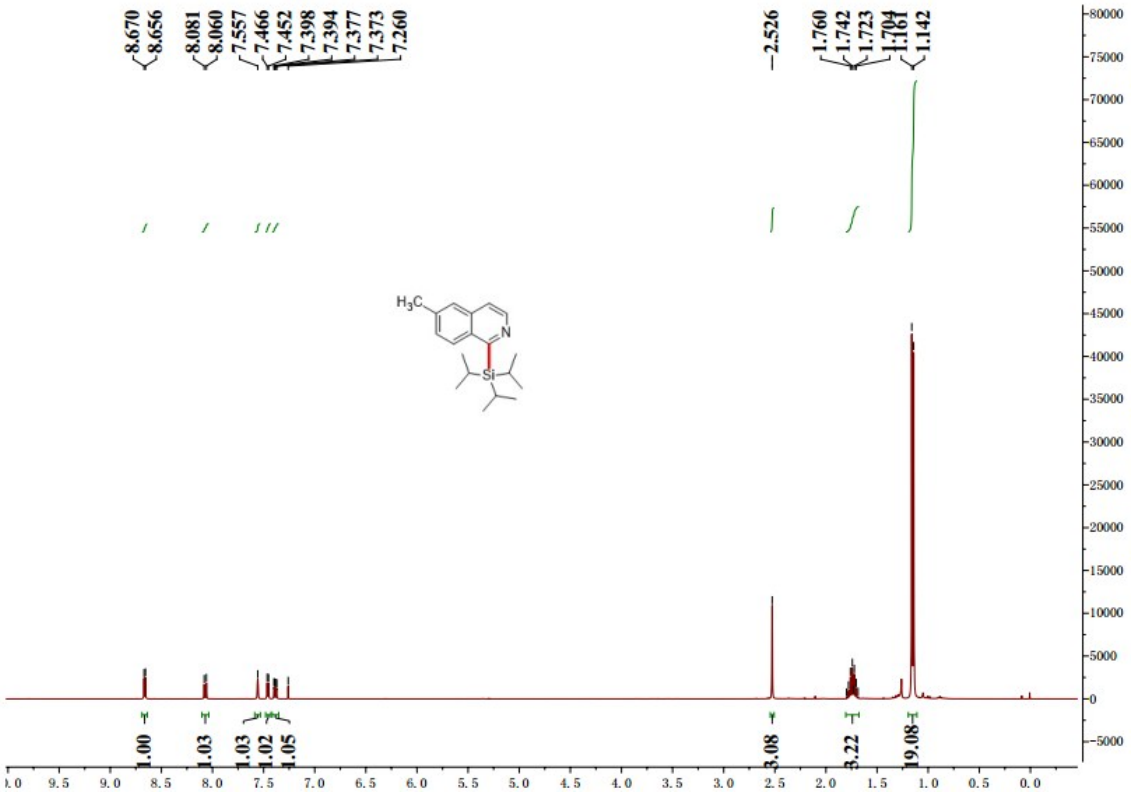
H
Si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7.377
7.373
7.260
2.526
1.760
1.742
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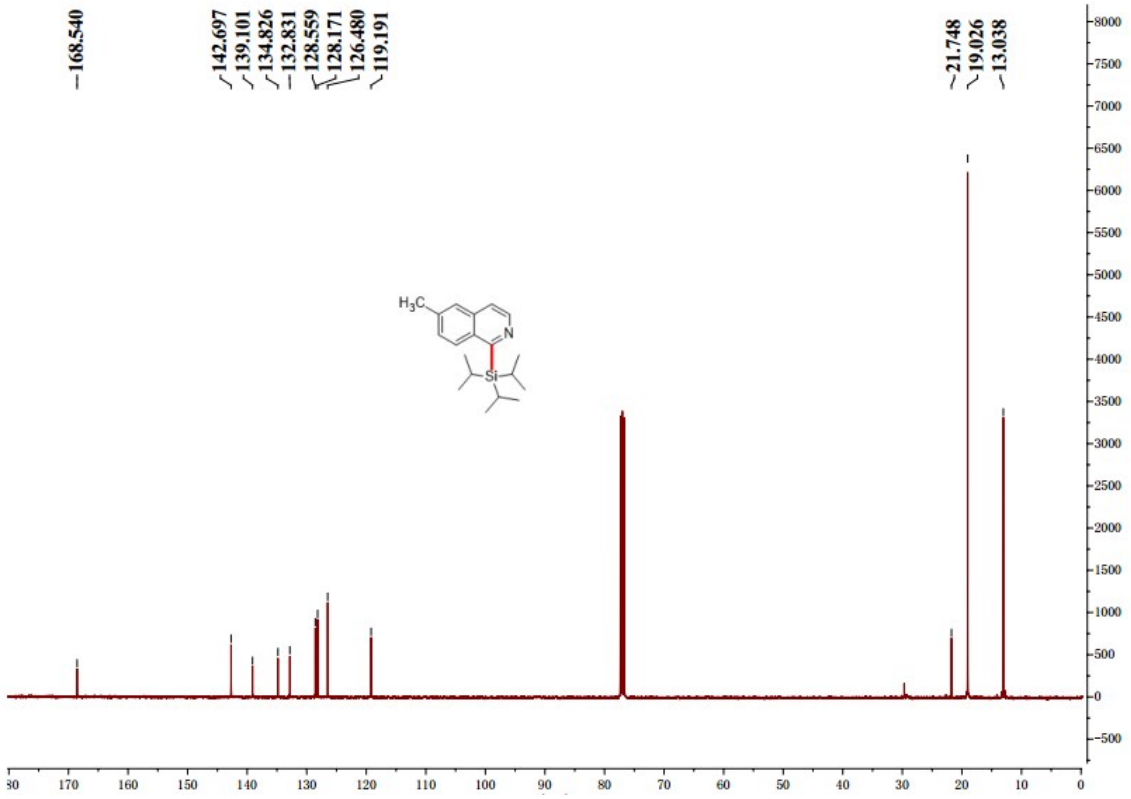
1.03
1.03
1.02
1.05
3.08
3.22
19.08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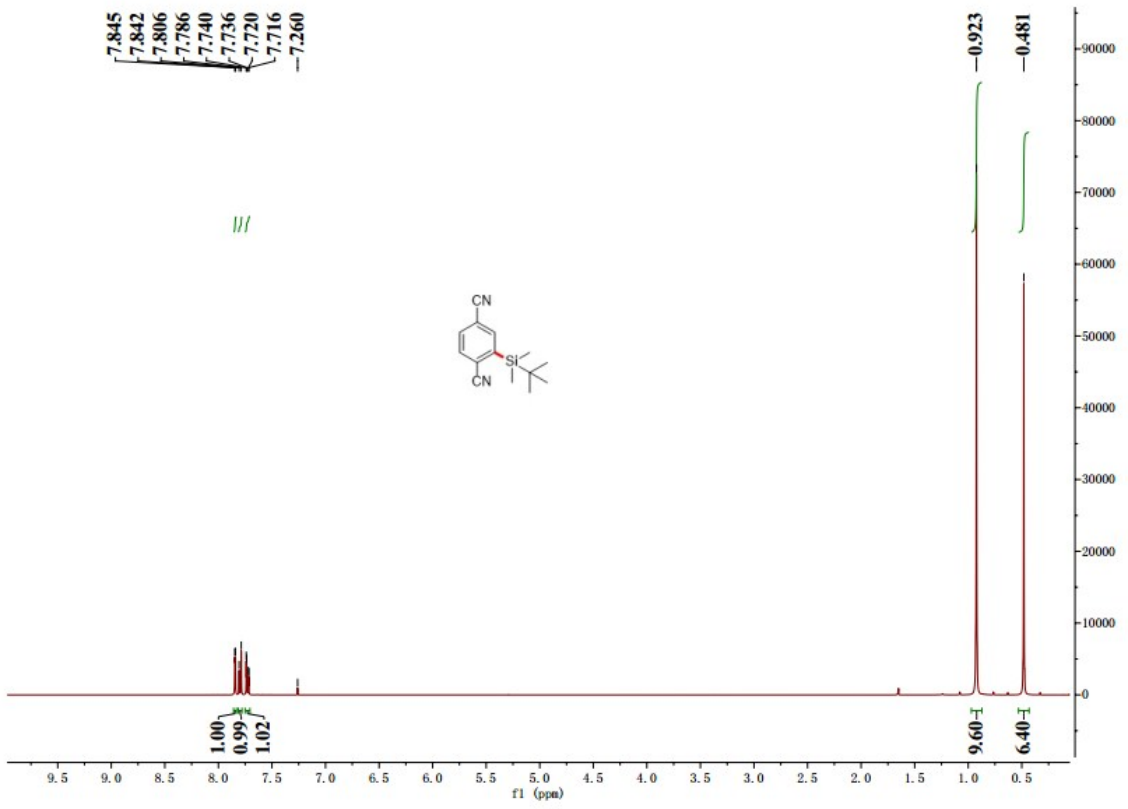
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7.806
7.786
7.740
7.736
7.720
7.716
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CN
Si
CN
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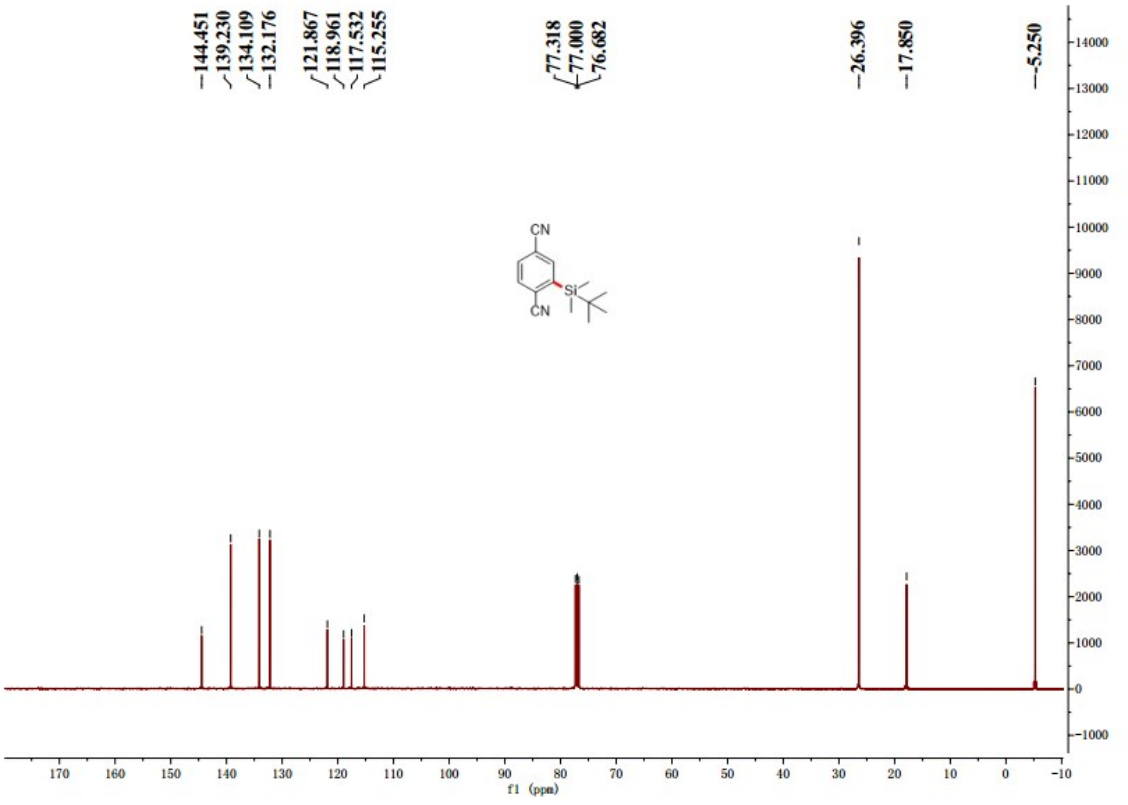
0.99
1.02
9.60
6.40
f1 (ppm)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26.396
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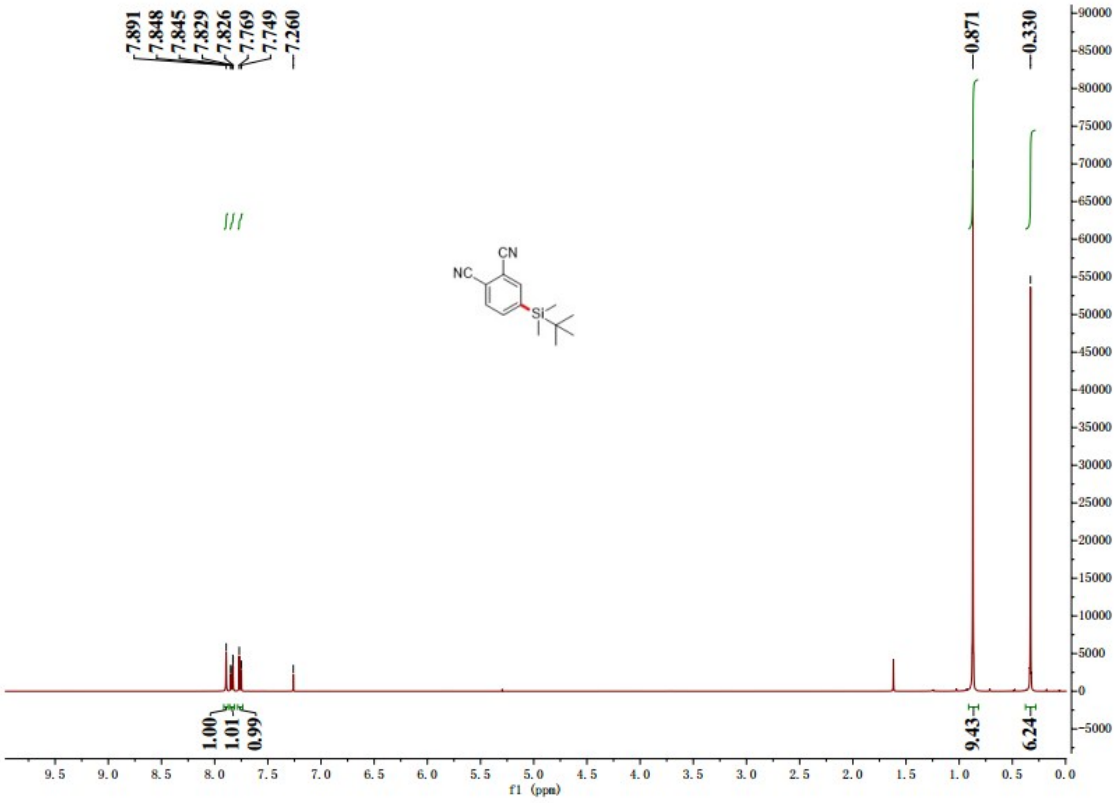
CN
Si
CN
f1 (ppm)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7.826
7.769
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NC
Si
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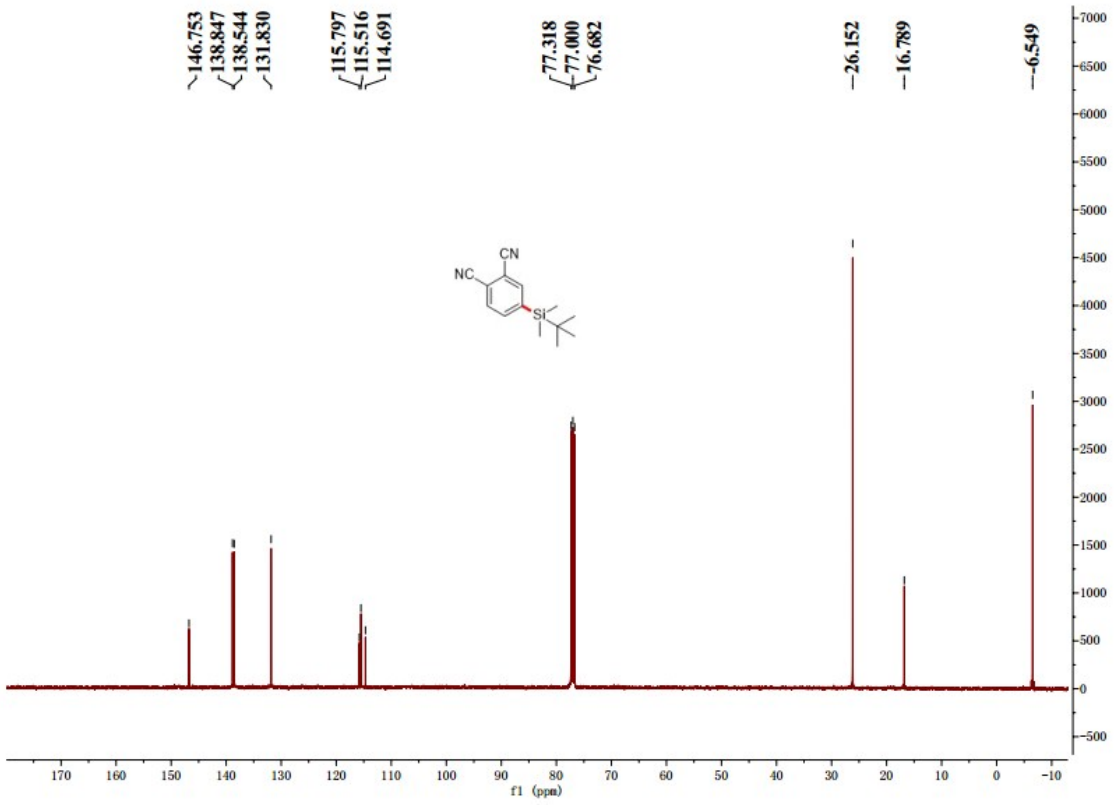
0.99
9.43
6.24
f1 (ppm)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77.318
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76.682
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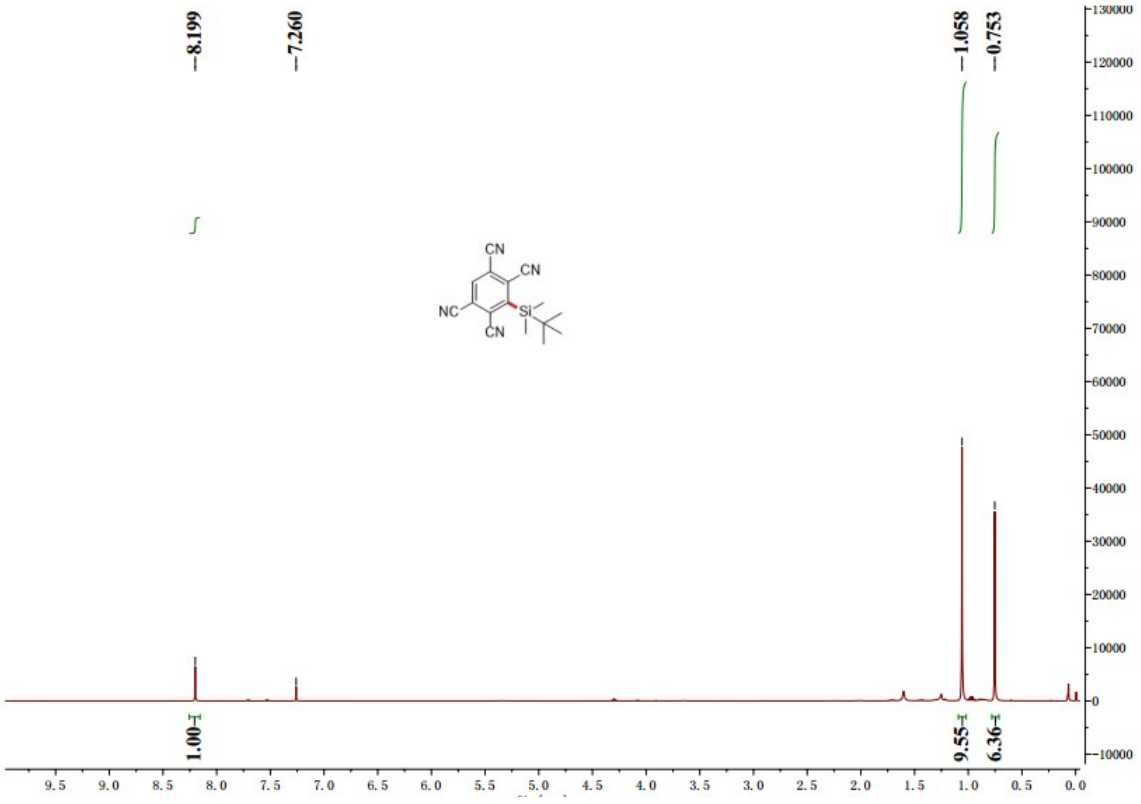
NC
Si
f1 (ppm)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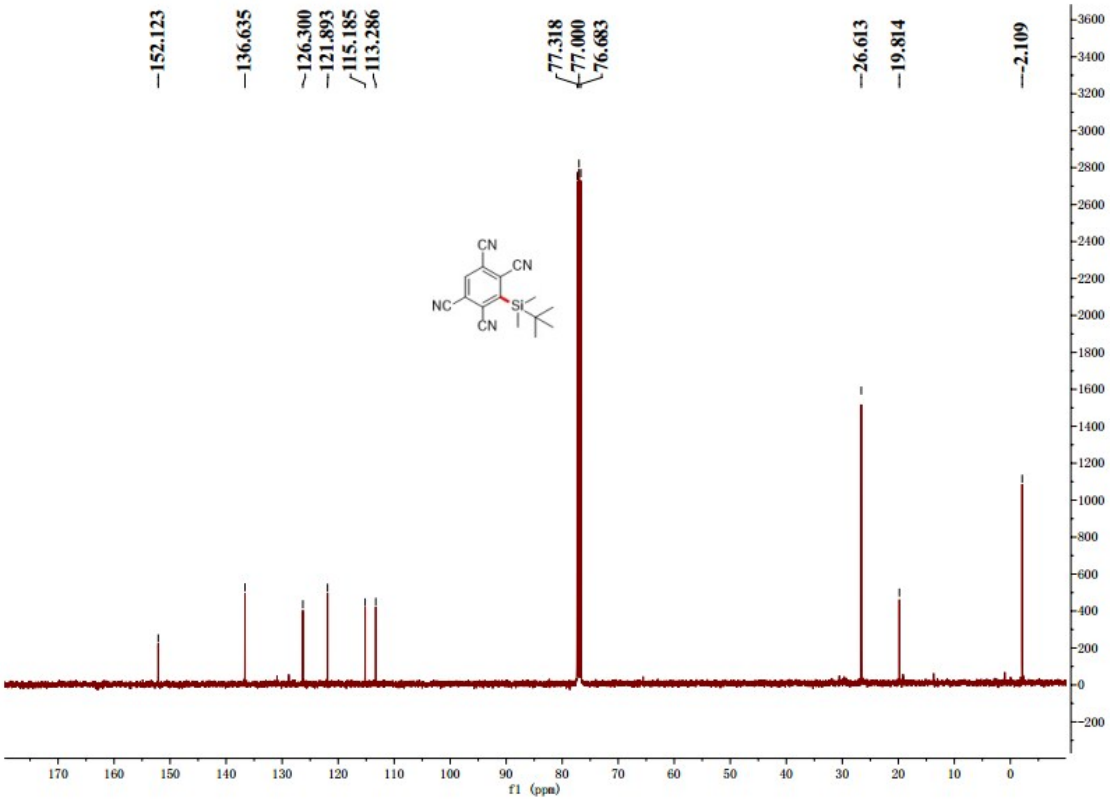
CN
NC
Si
CN
1.00
9.55
6.36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77.000
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19.814
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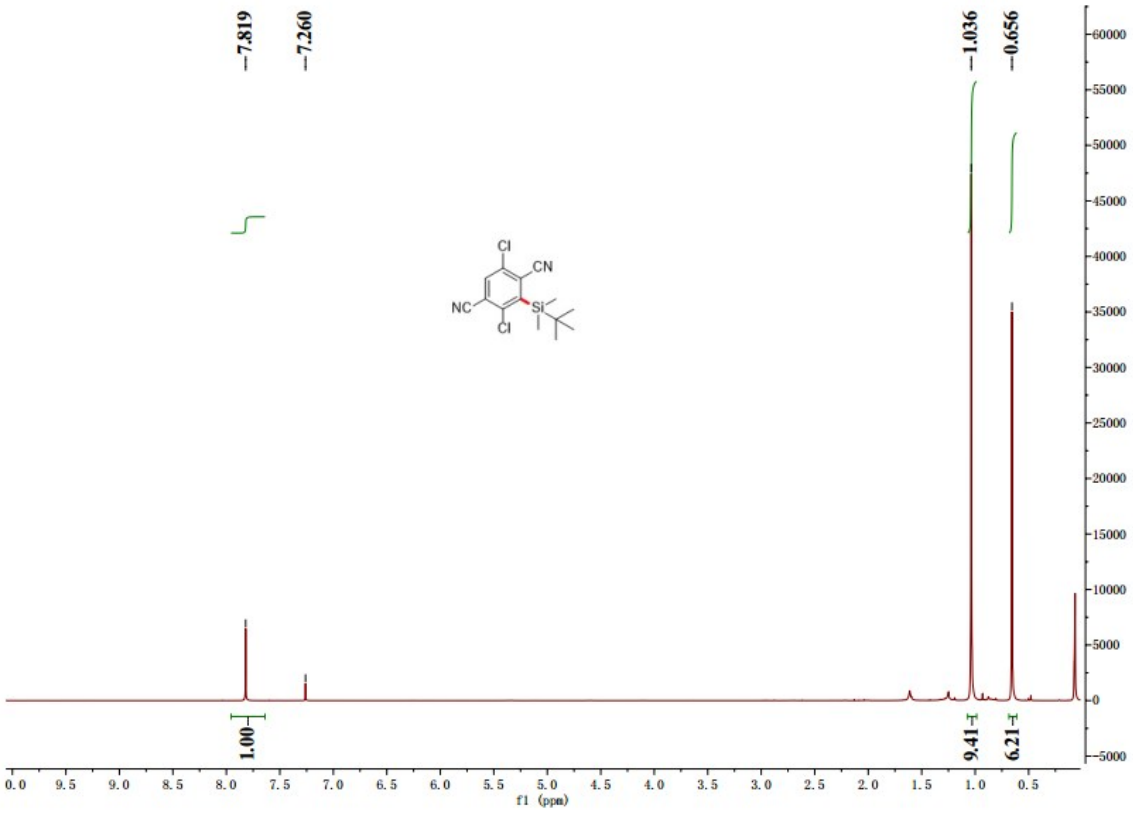
CN
NC
Si
CN
f1 (ppm)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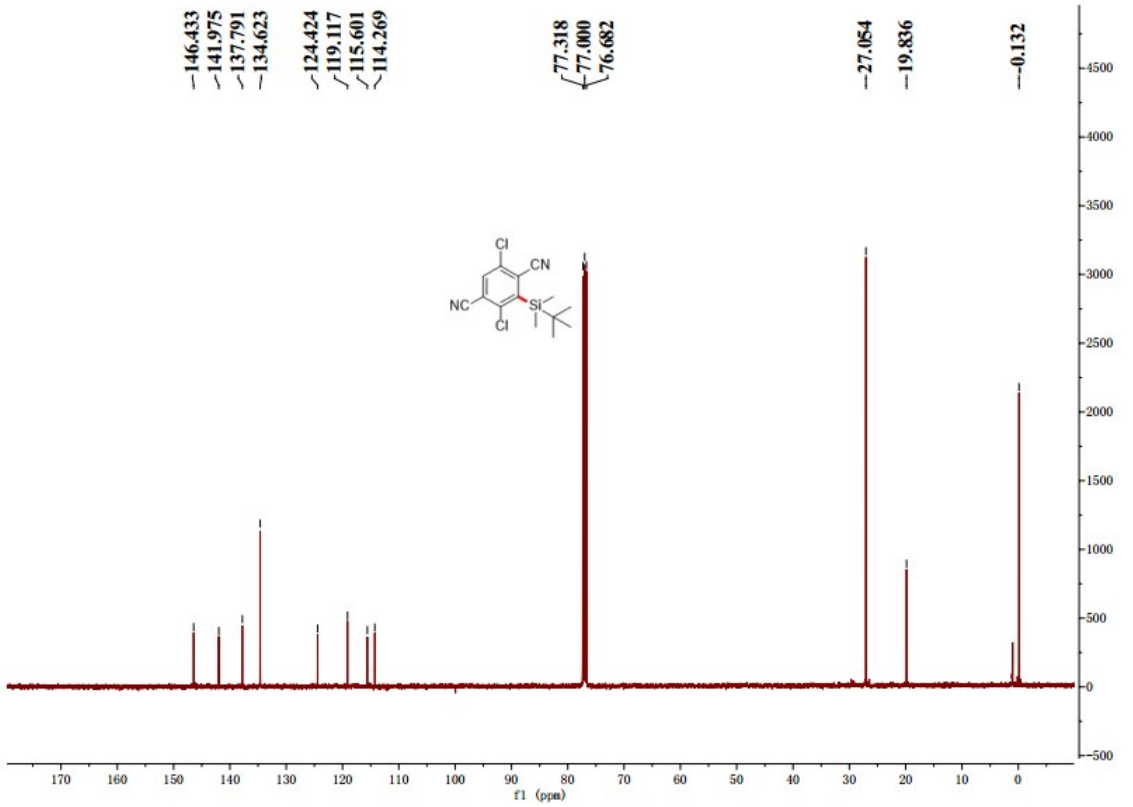
CN
NC
Si
Cl
1.00
9.41
6.21
f1 (ppm)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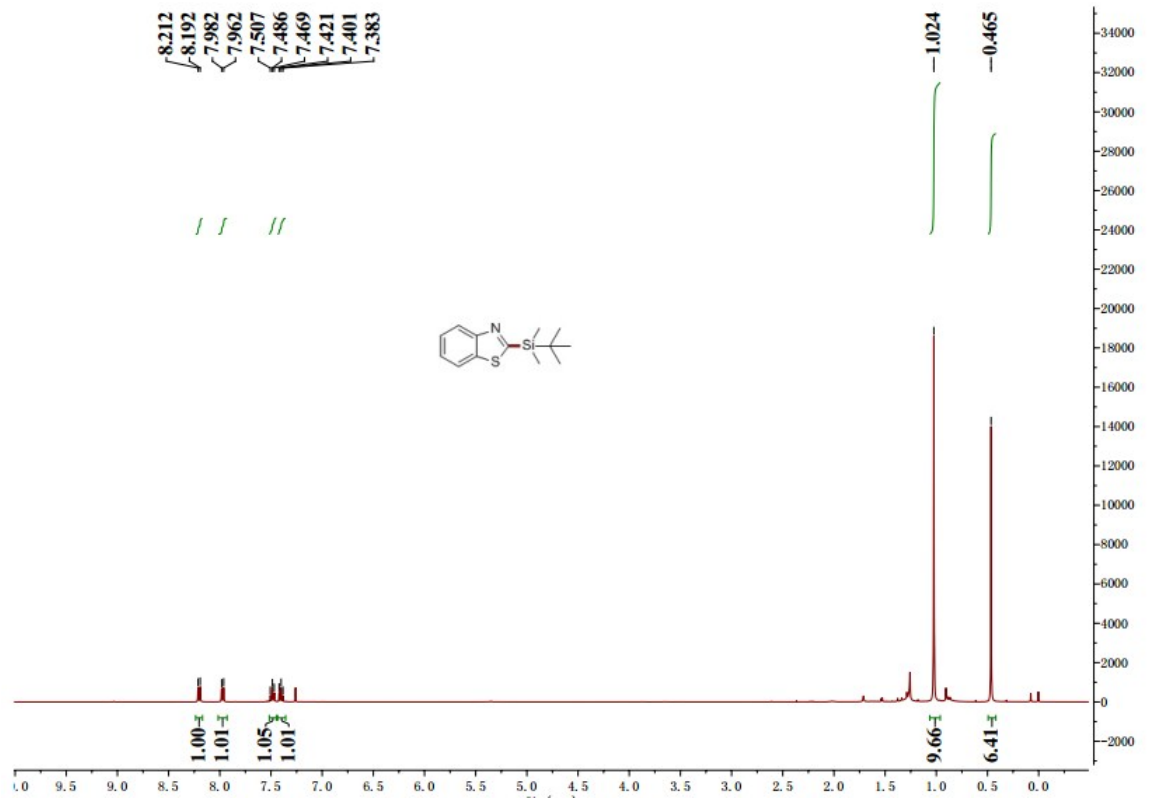
f1 (ppm)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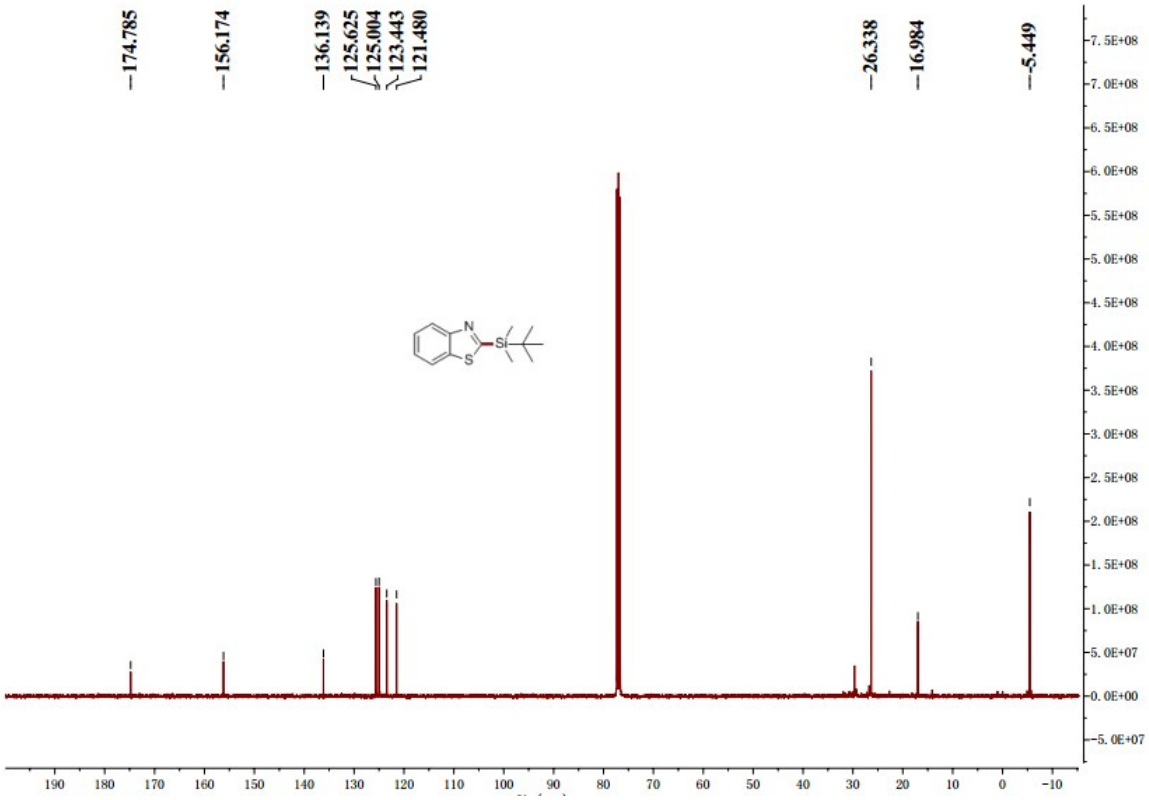
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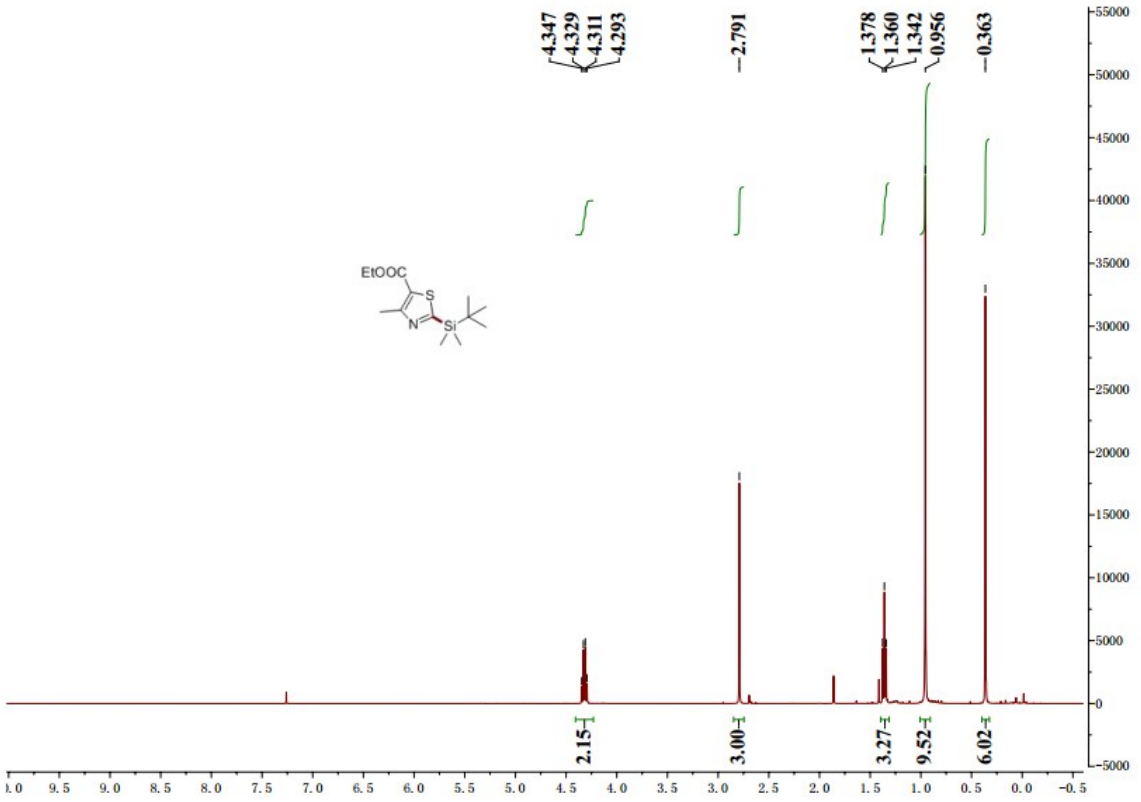
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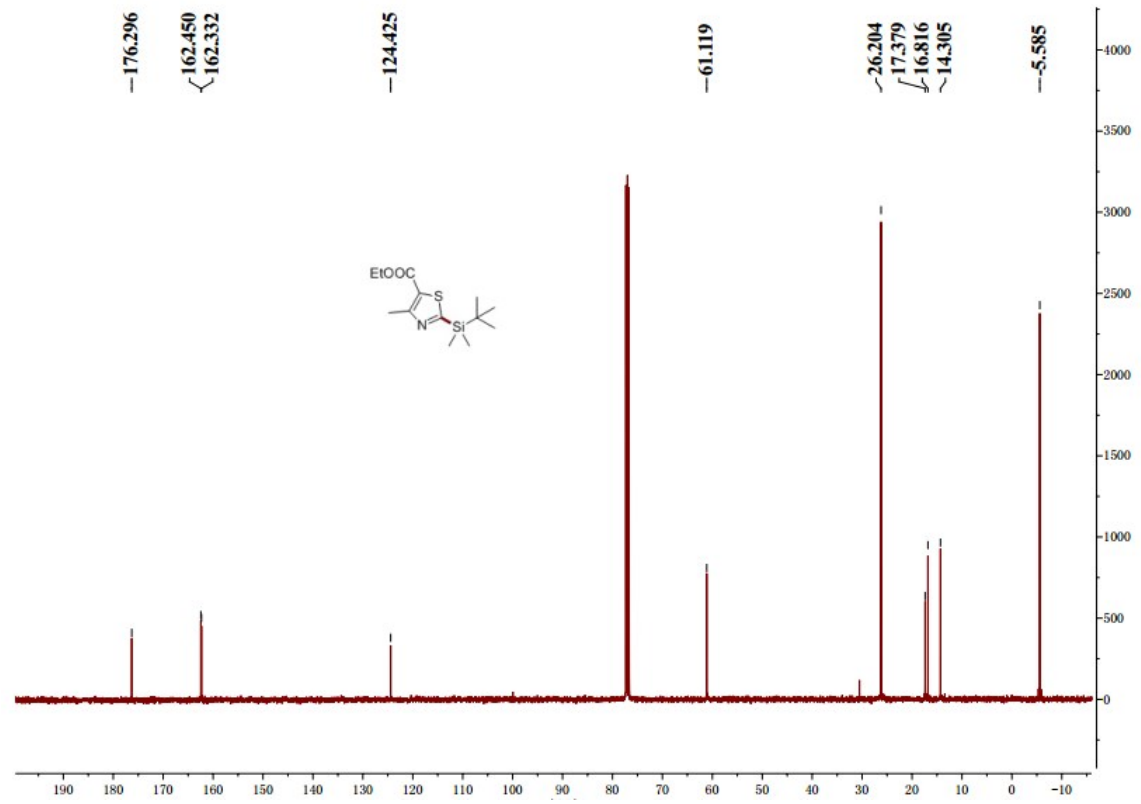
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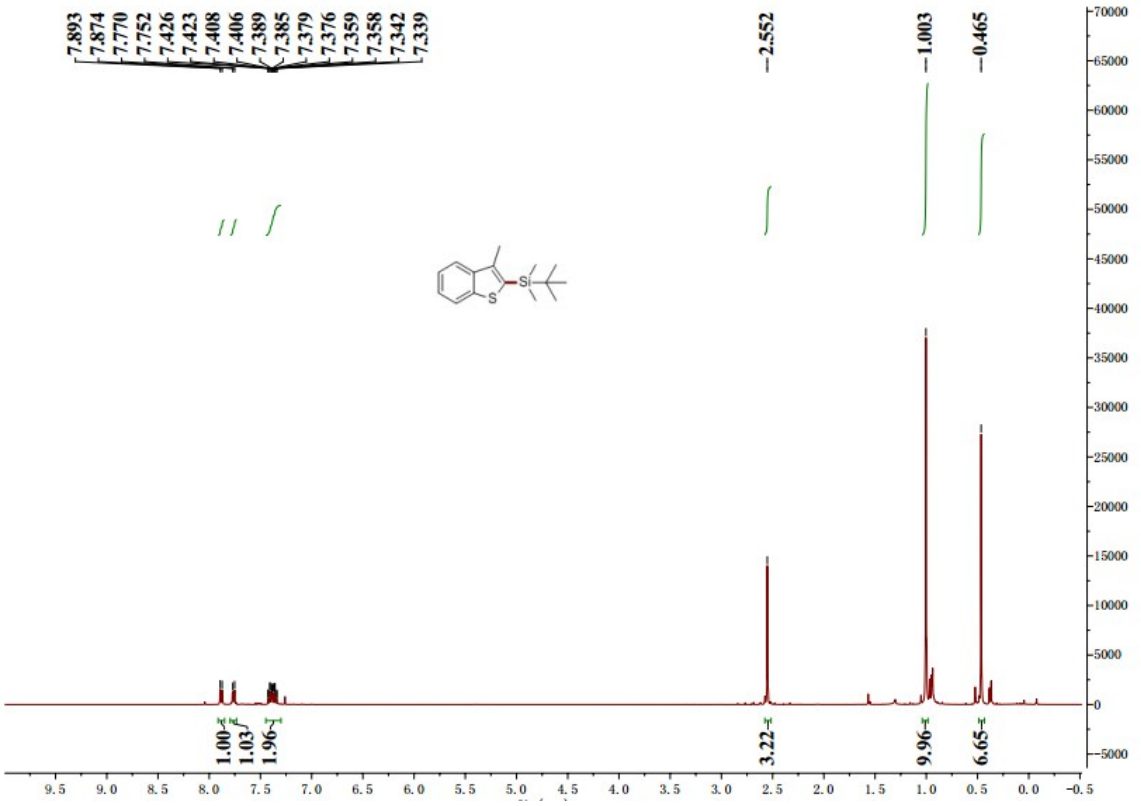
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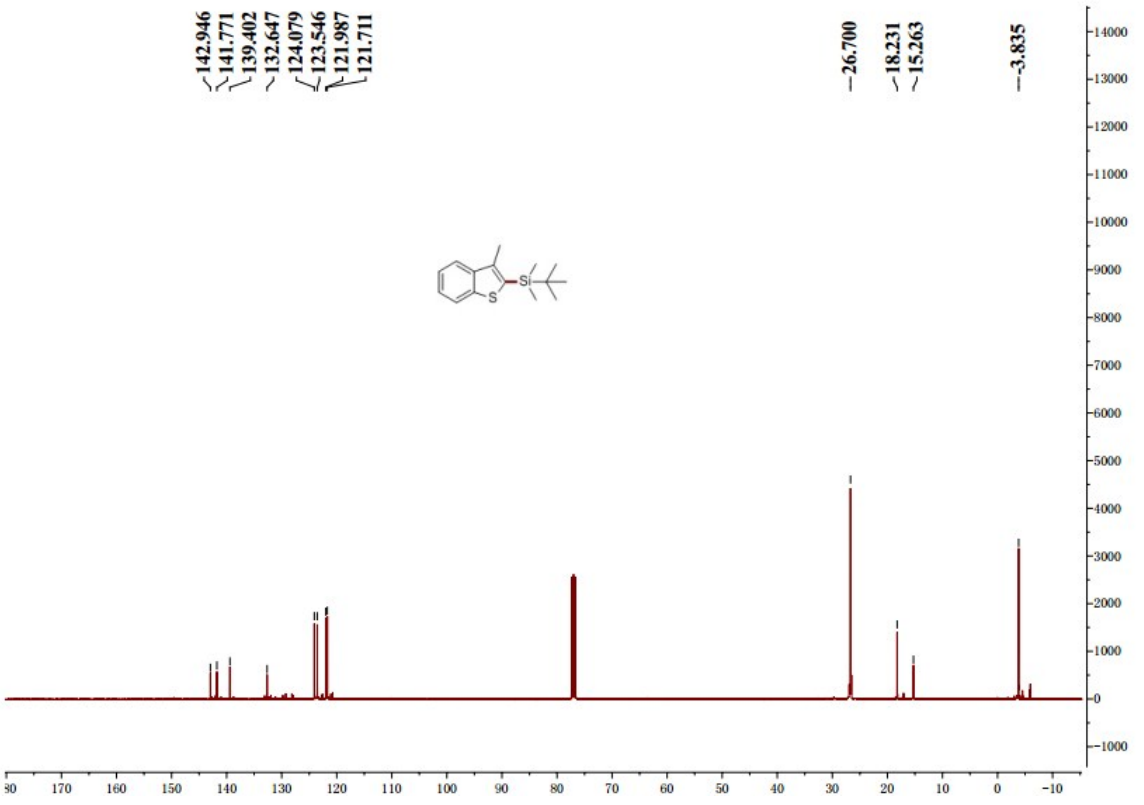
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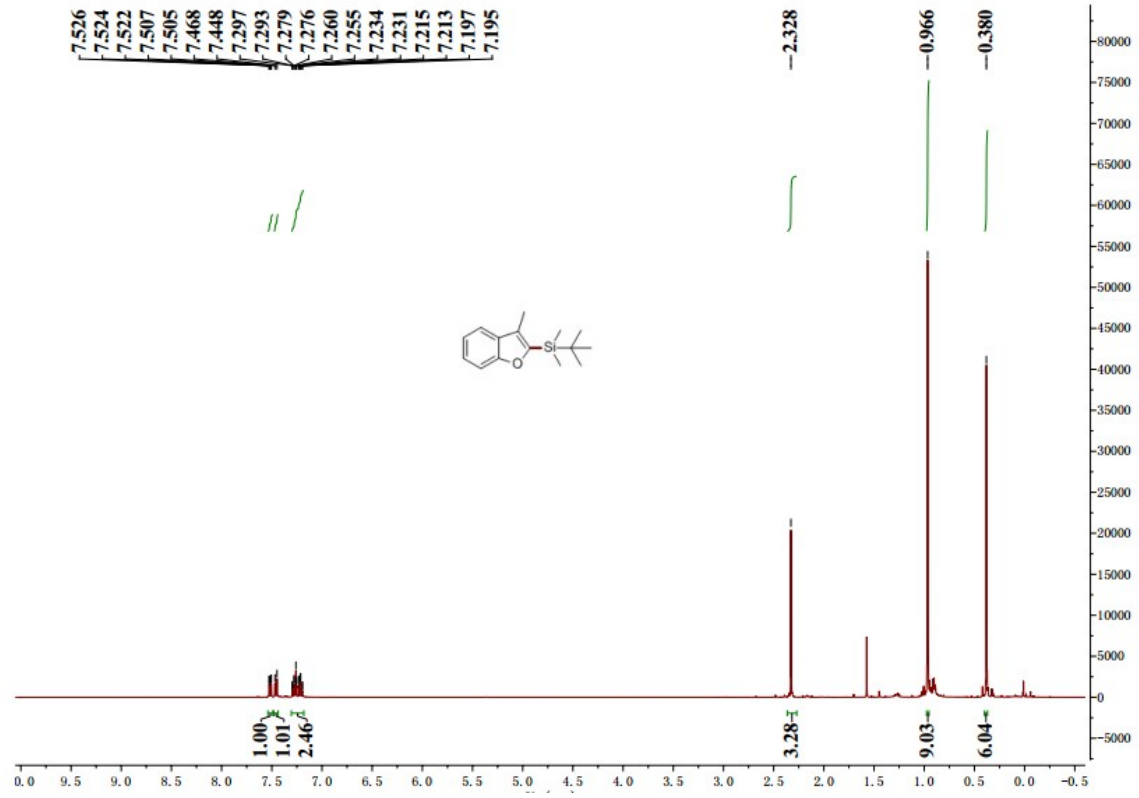
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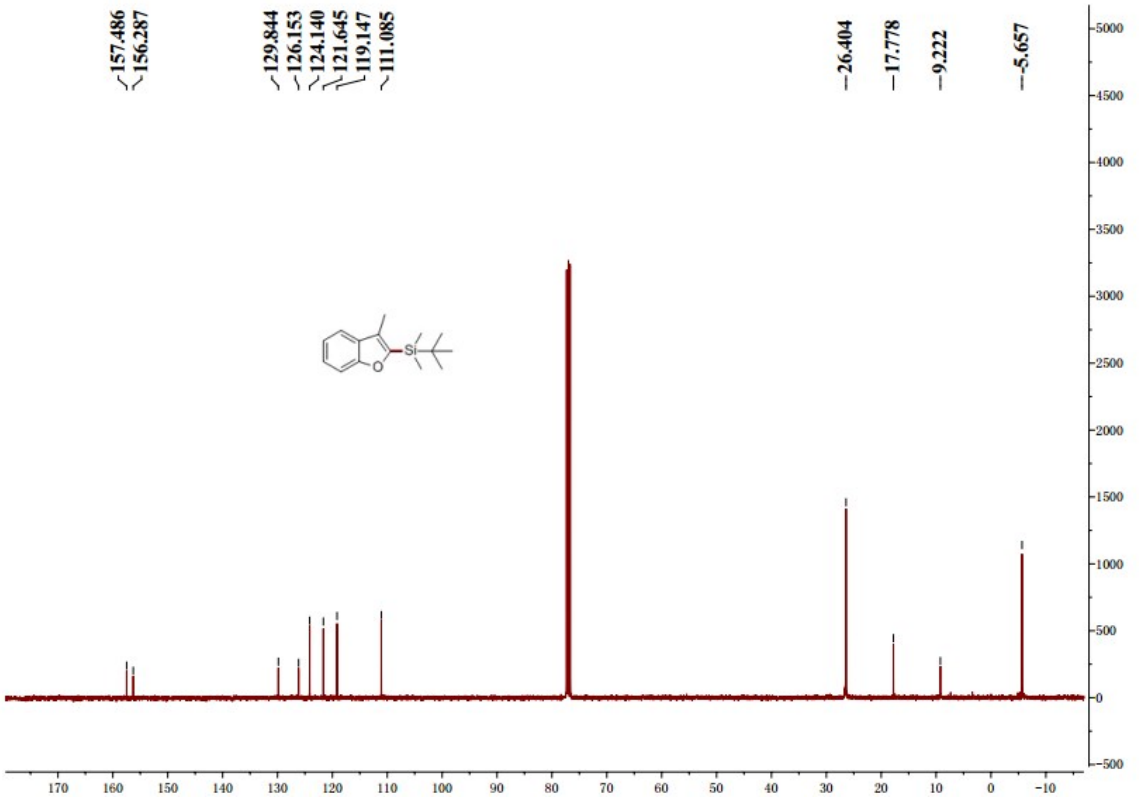
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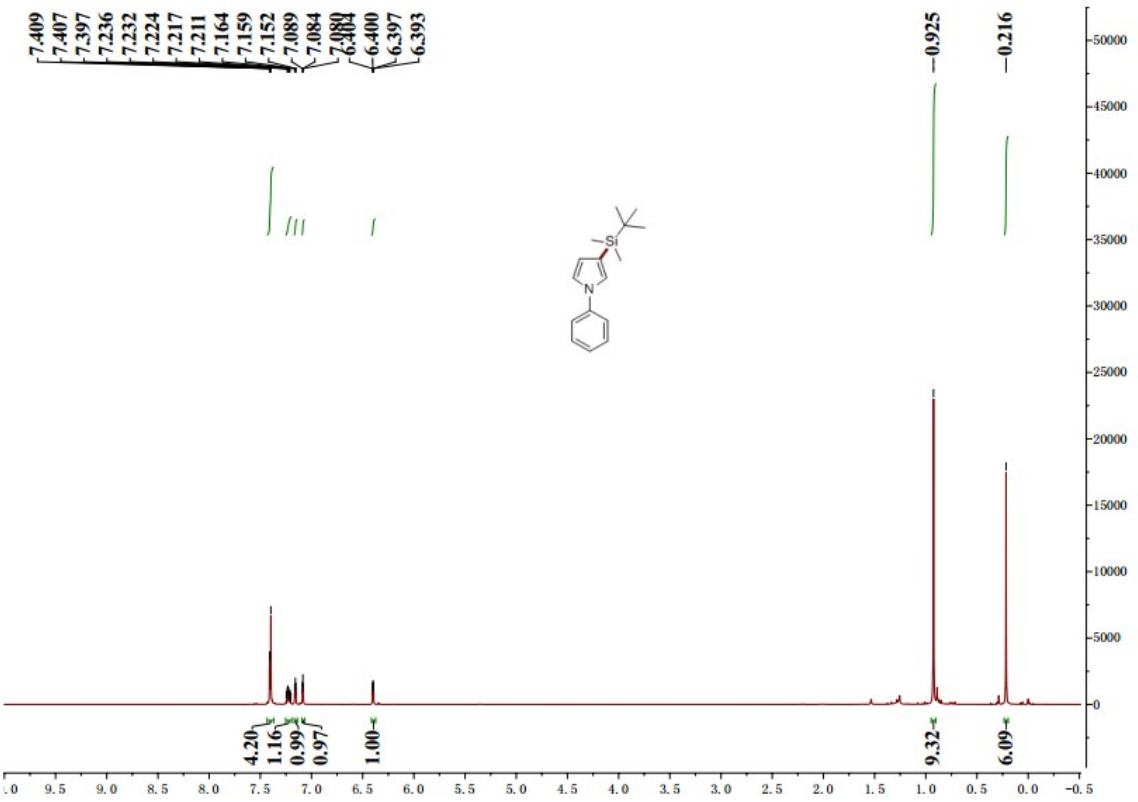
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7.084
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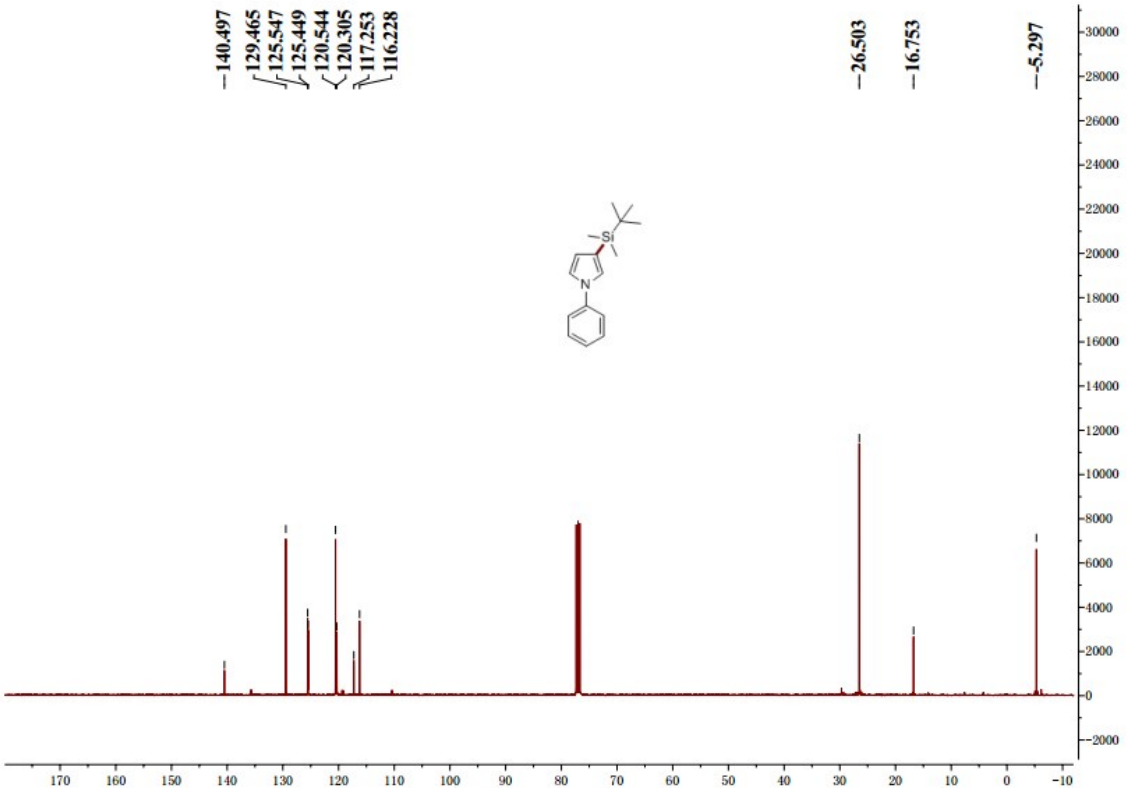
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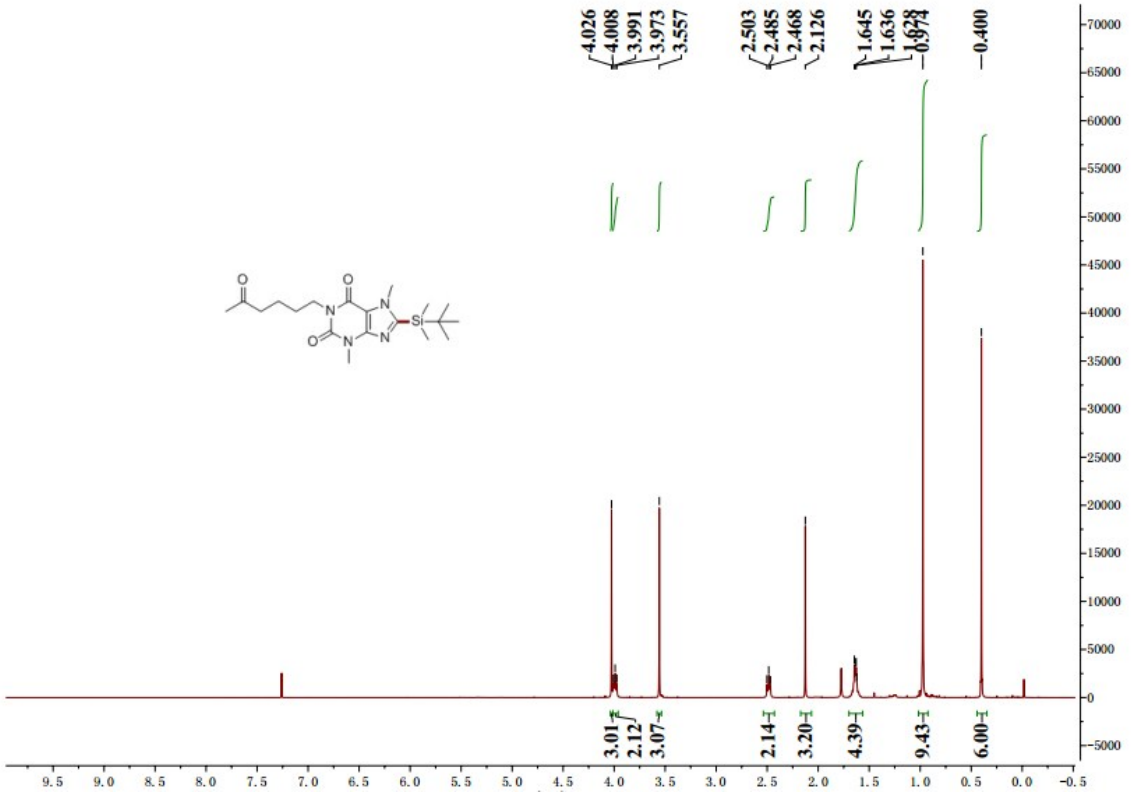
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2.14
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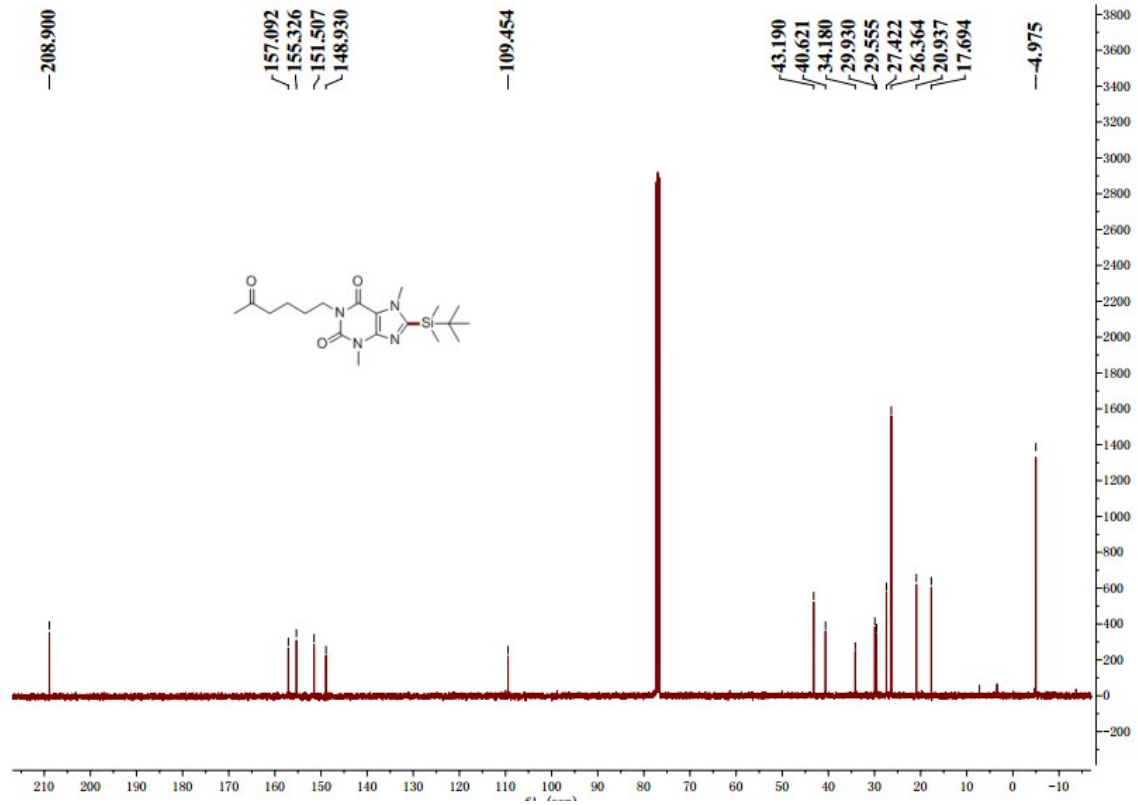
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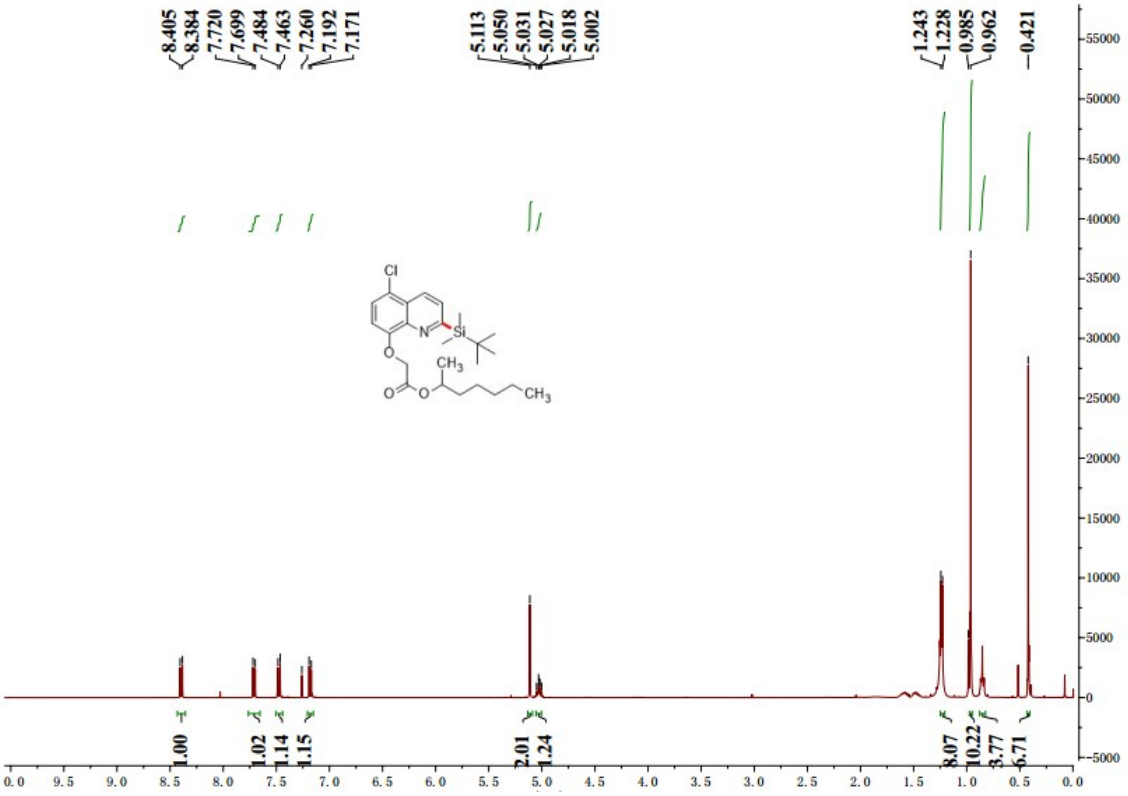
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5.002
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1.228
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0.962
0.421
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Si
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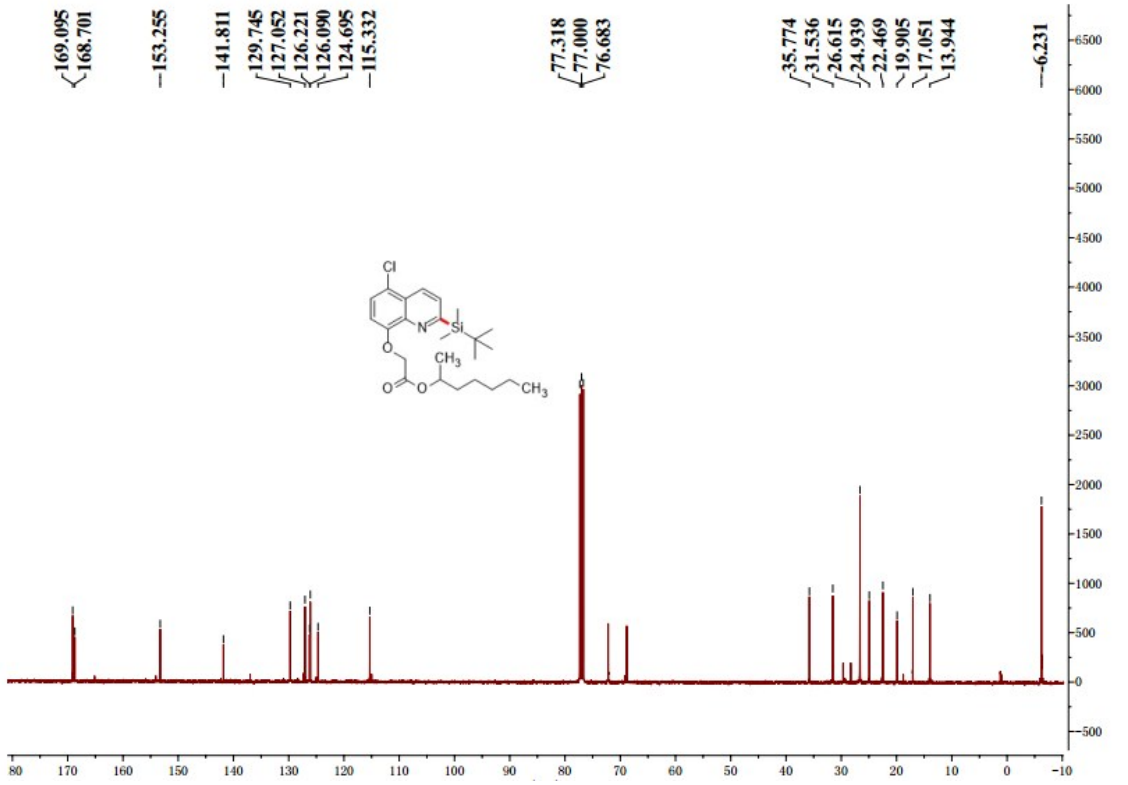
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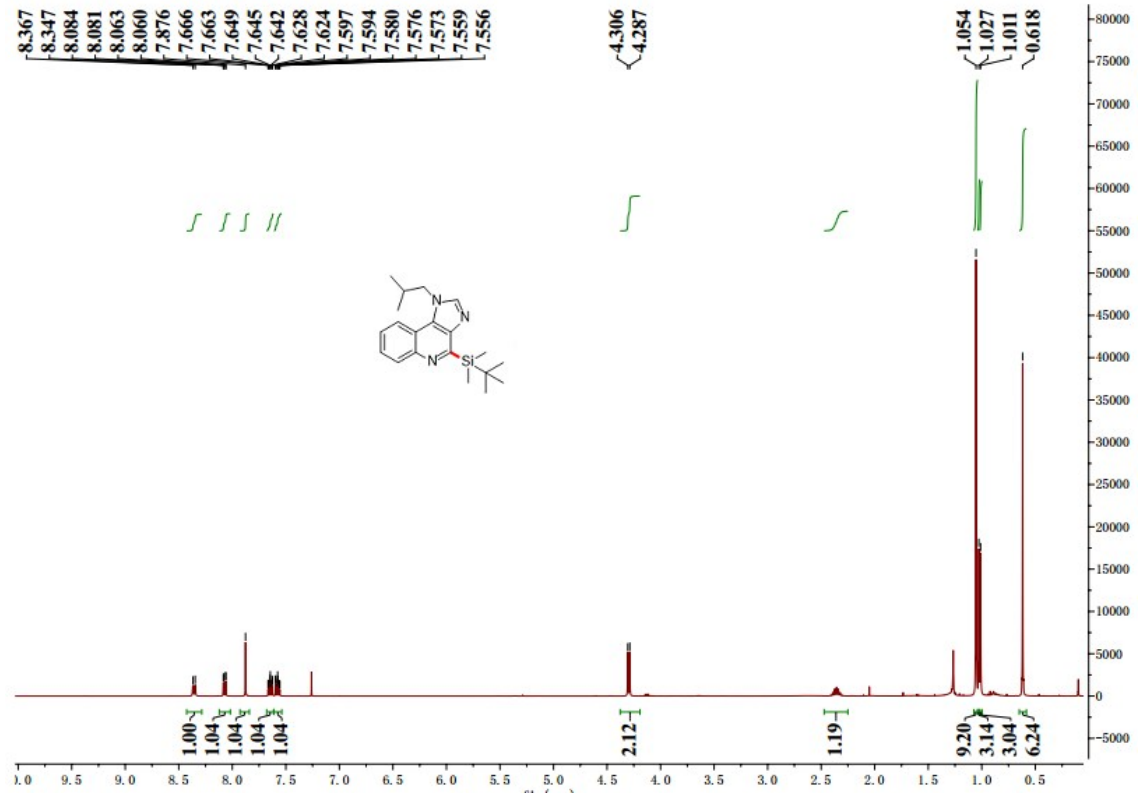
Cl
N
Si
CH3
O
CH3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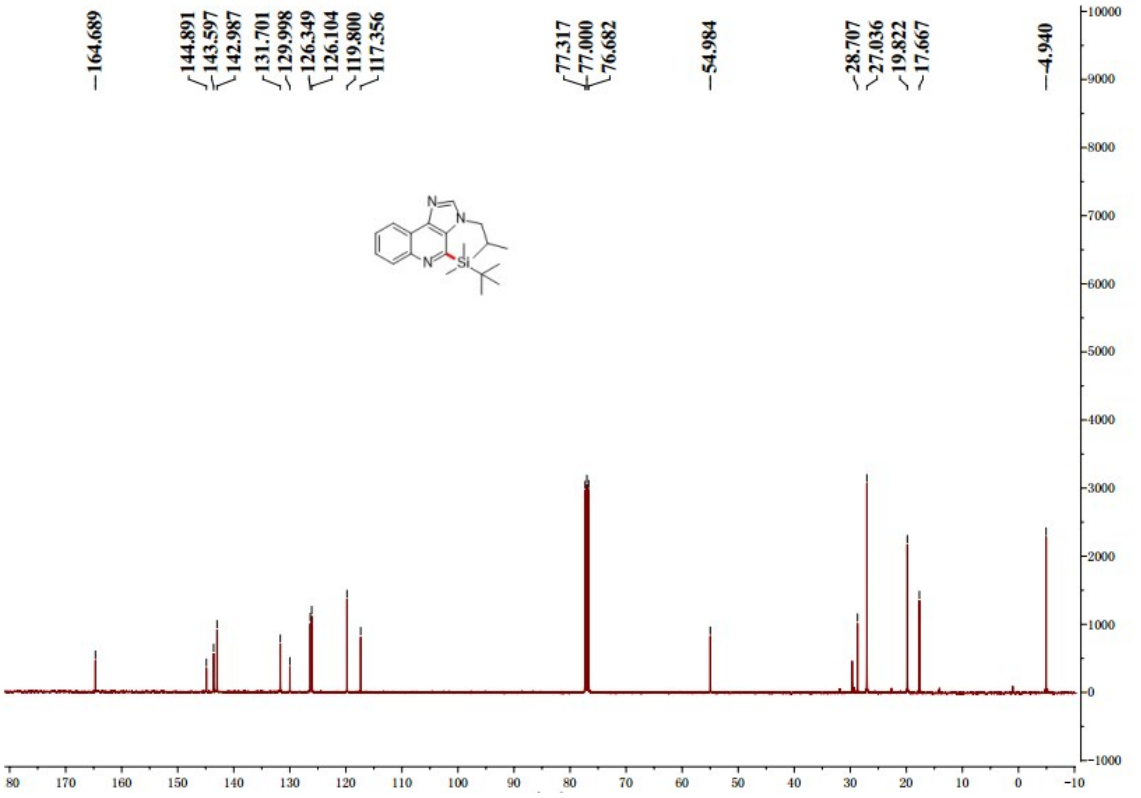
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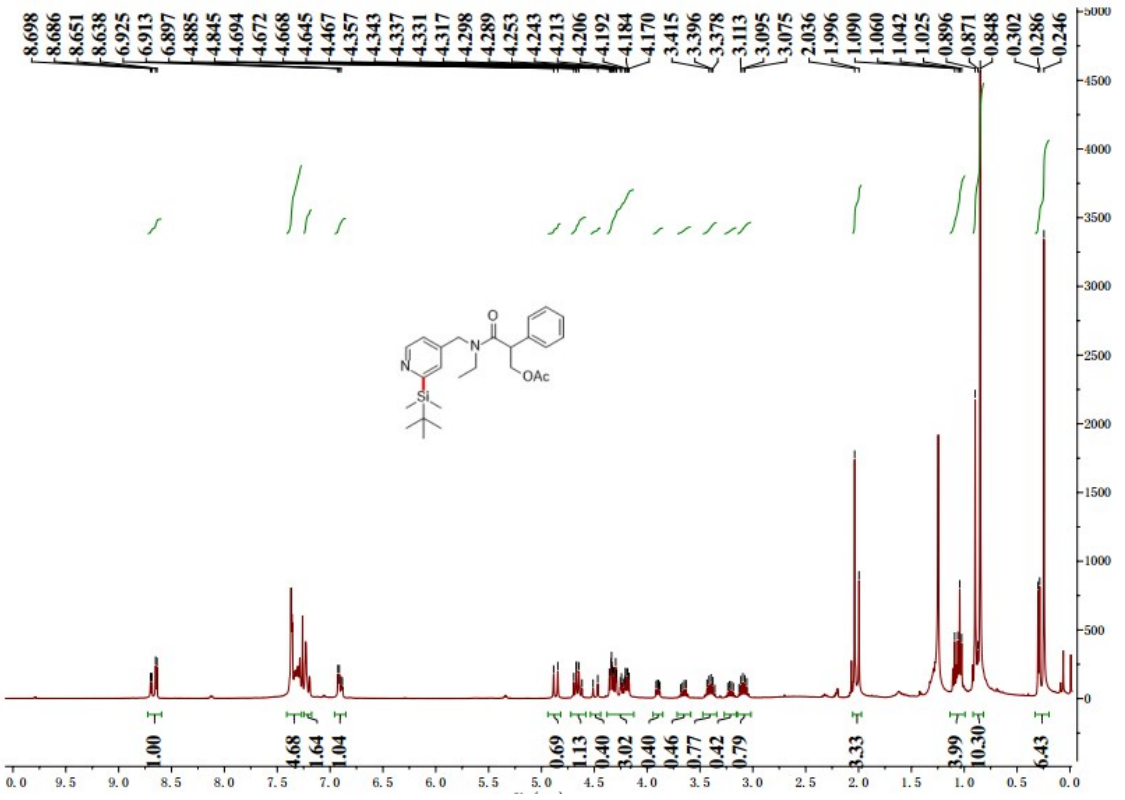
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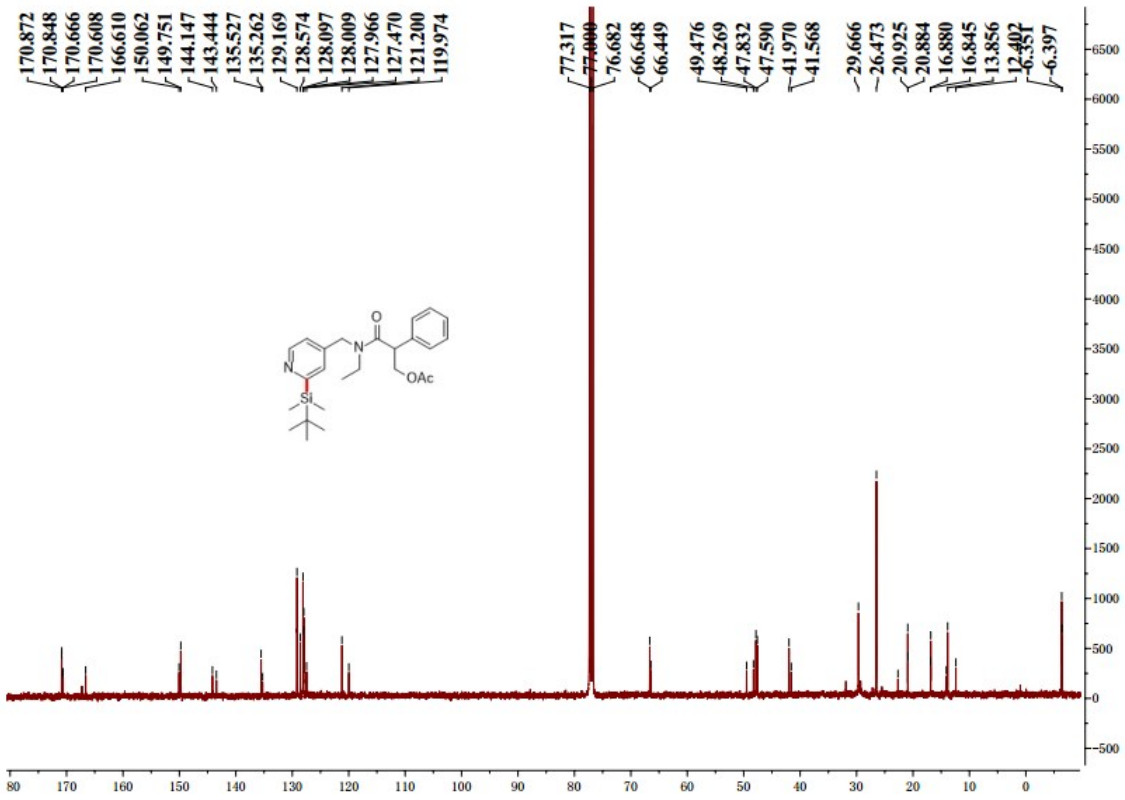
OAc
Si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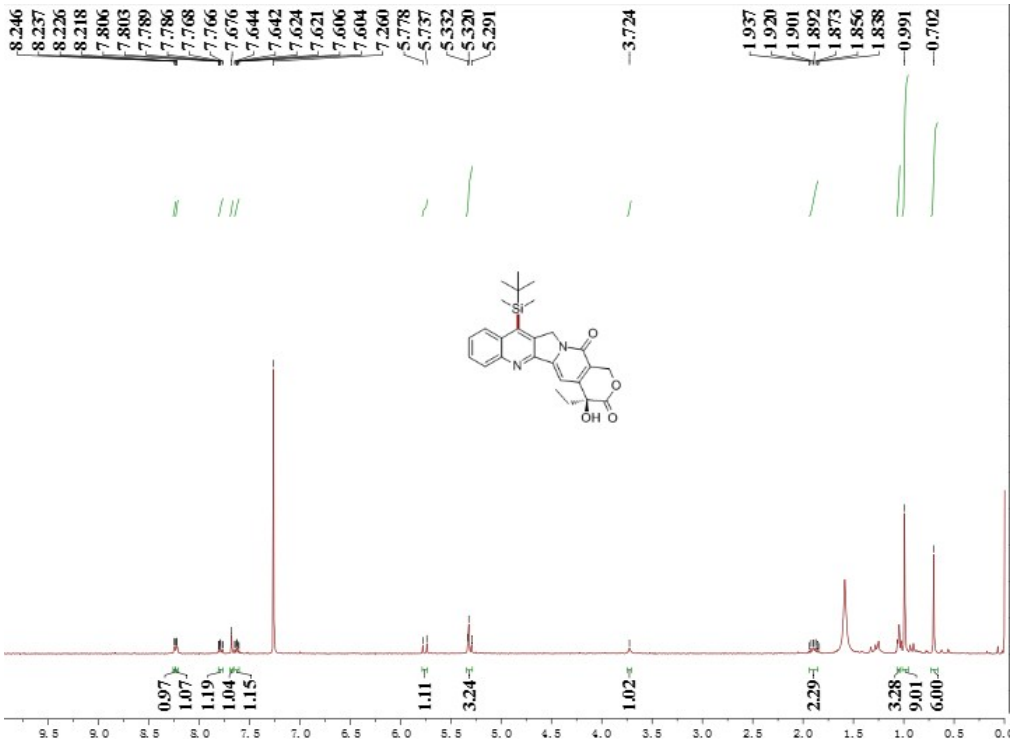
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OH
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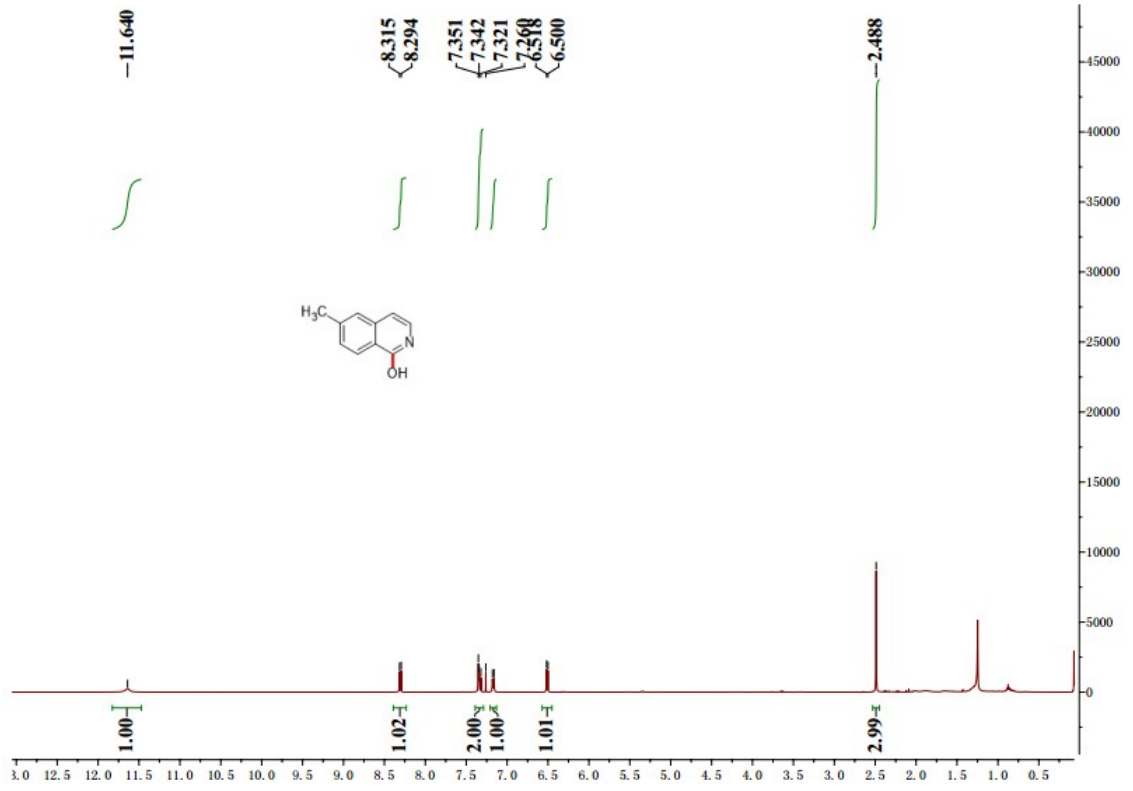
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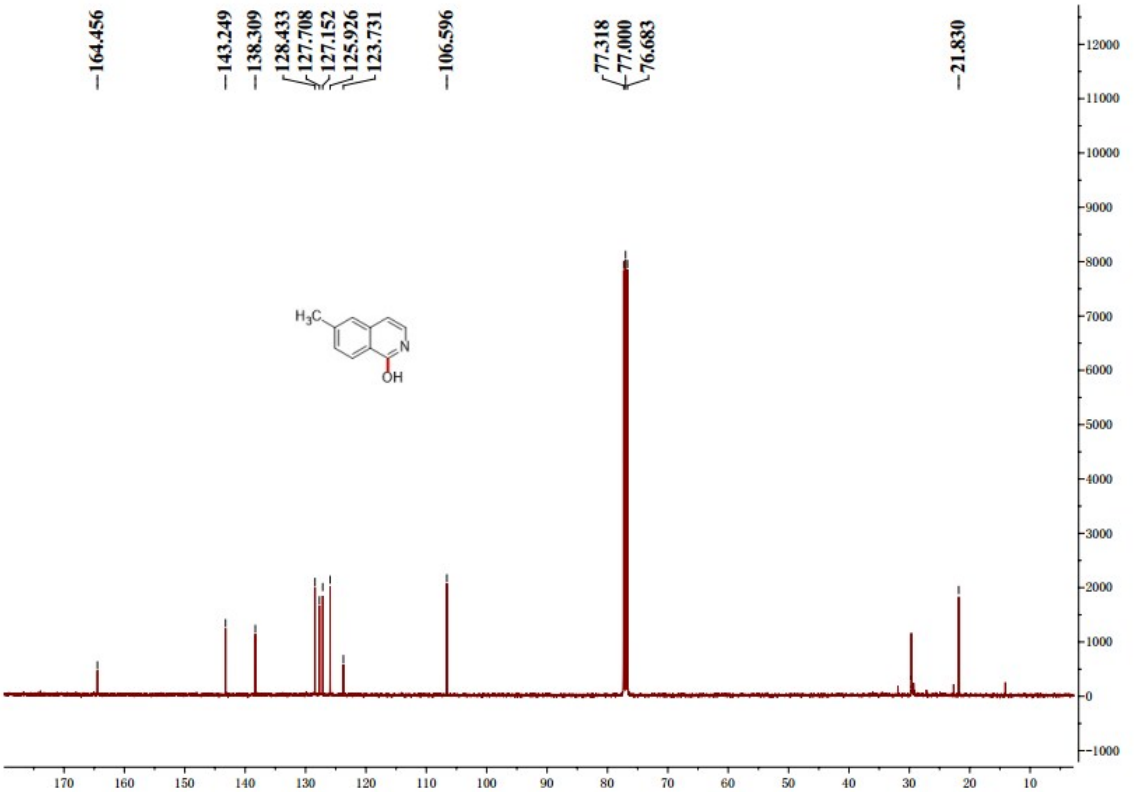
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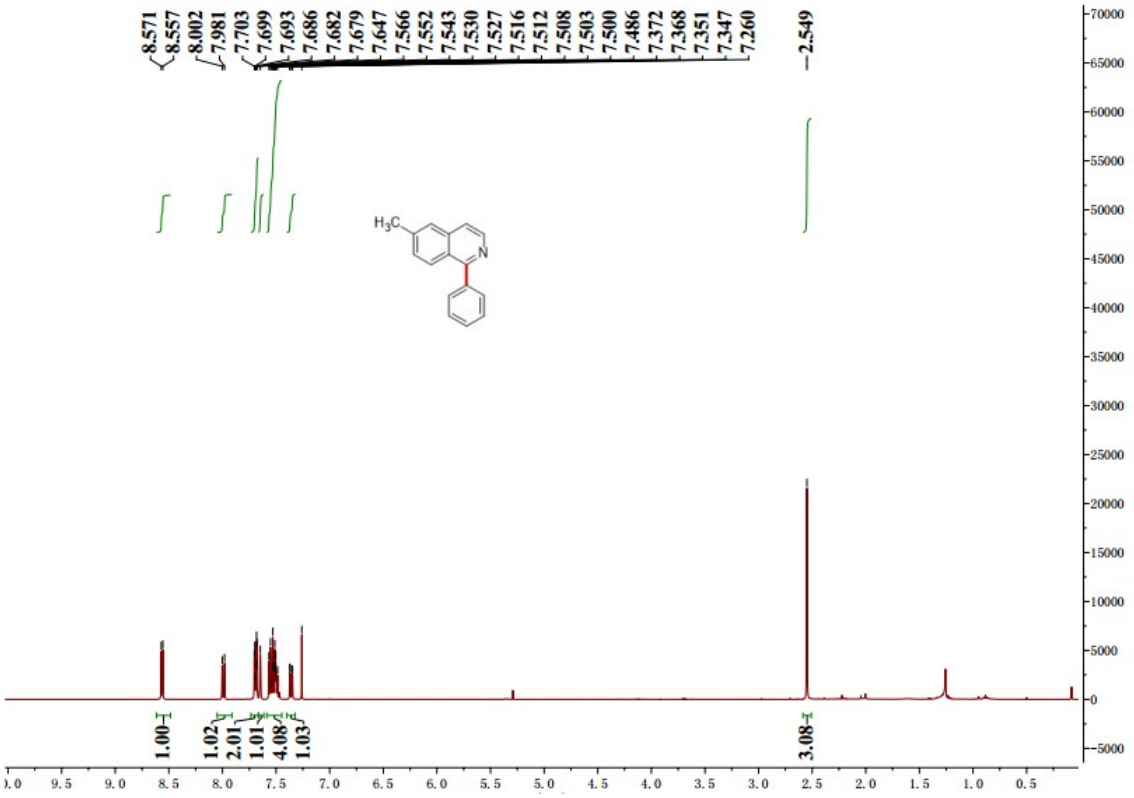
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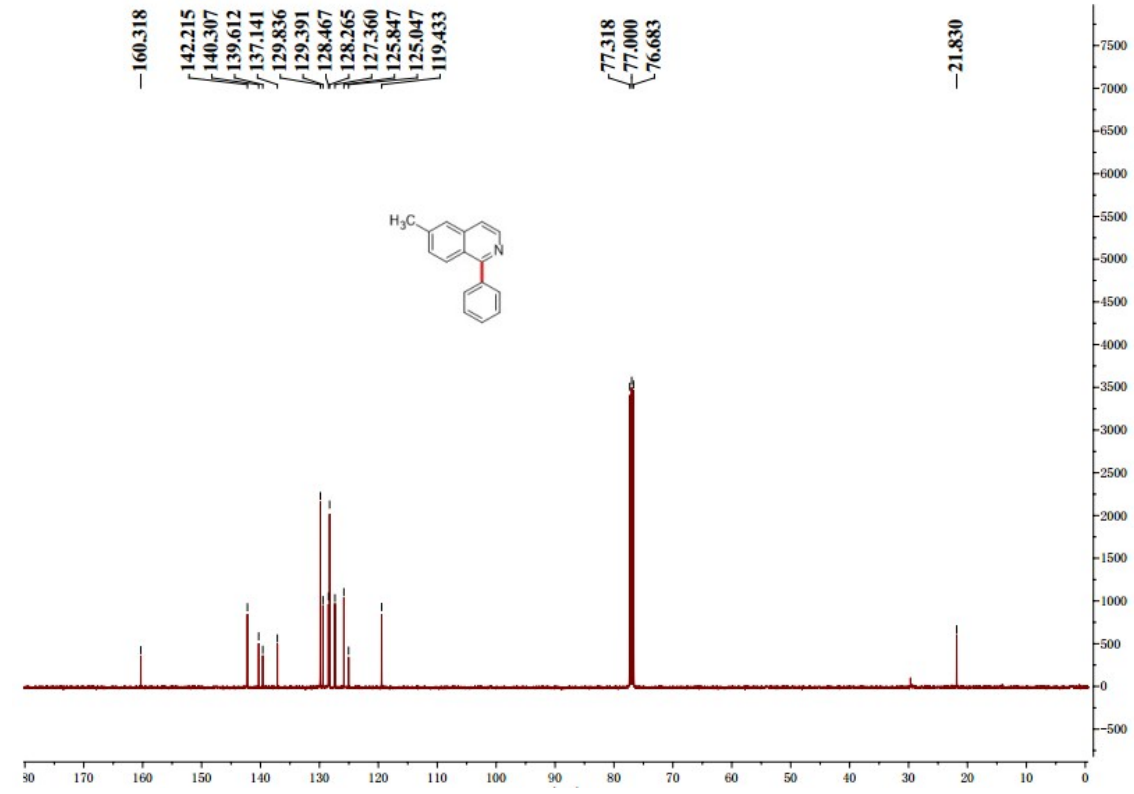
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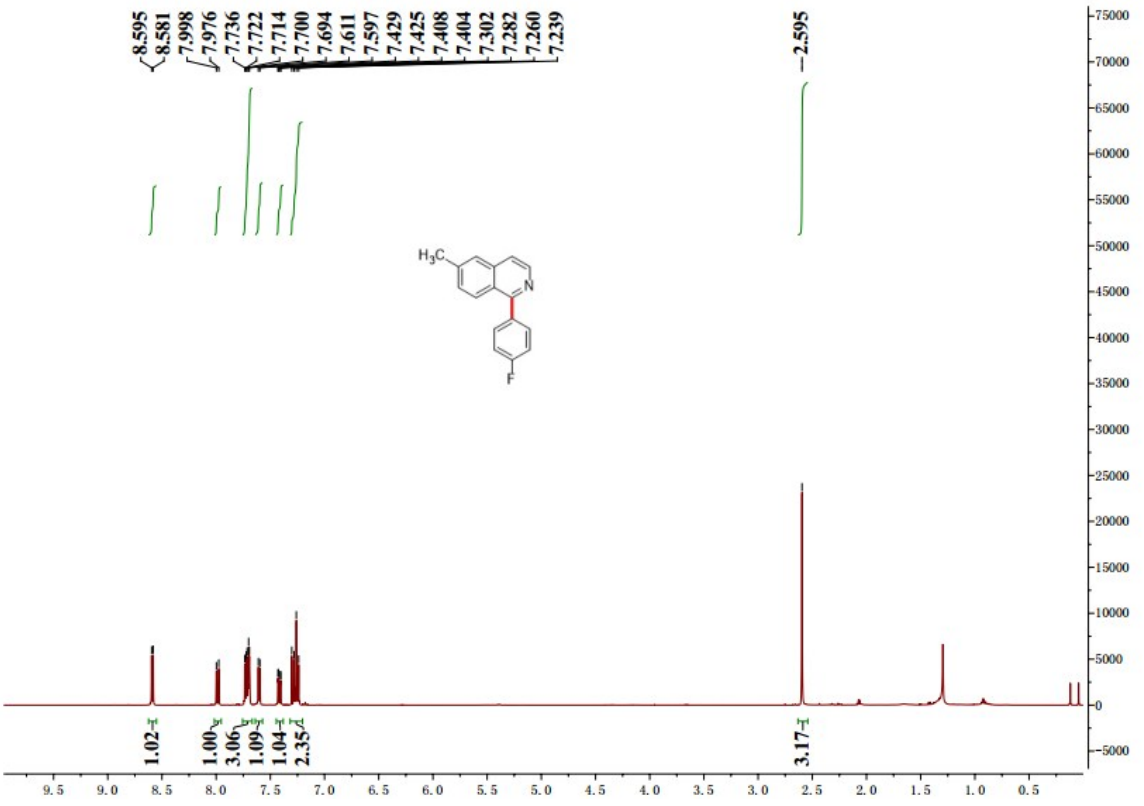
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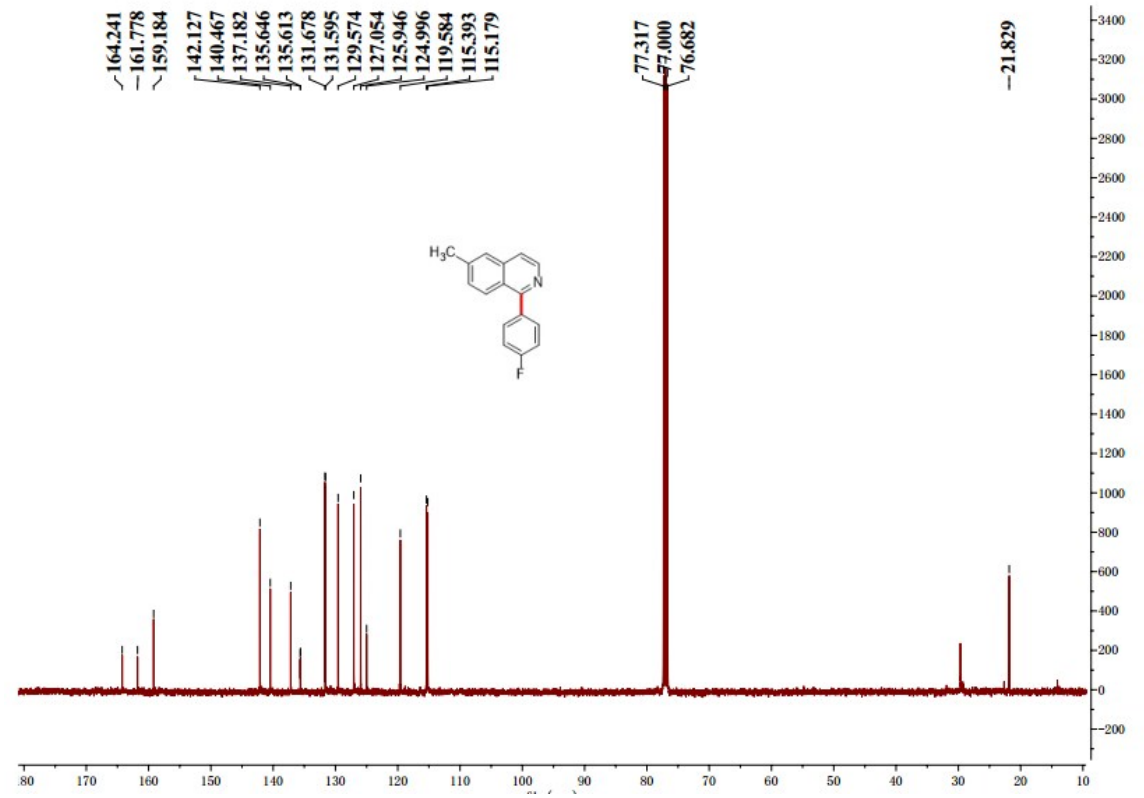
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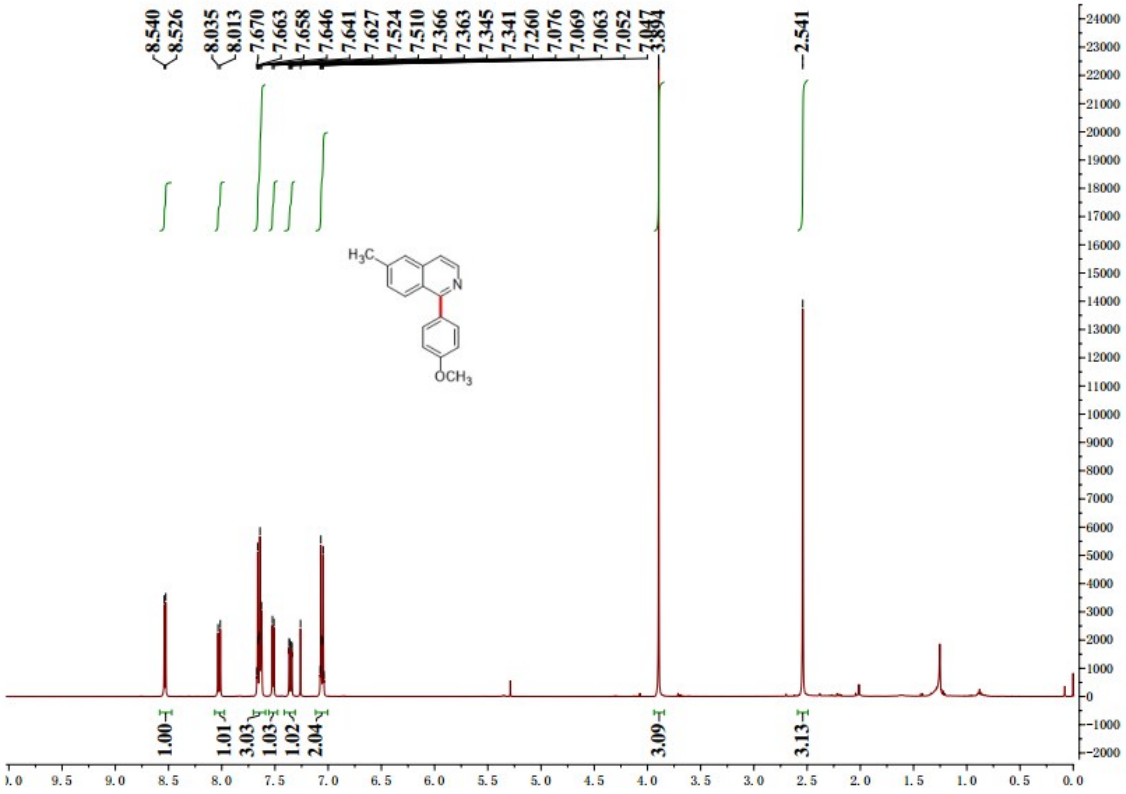
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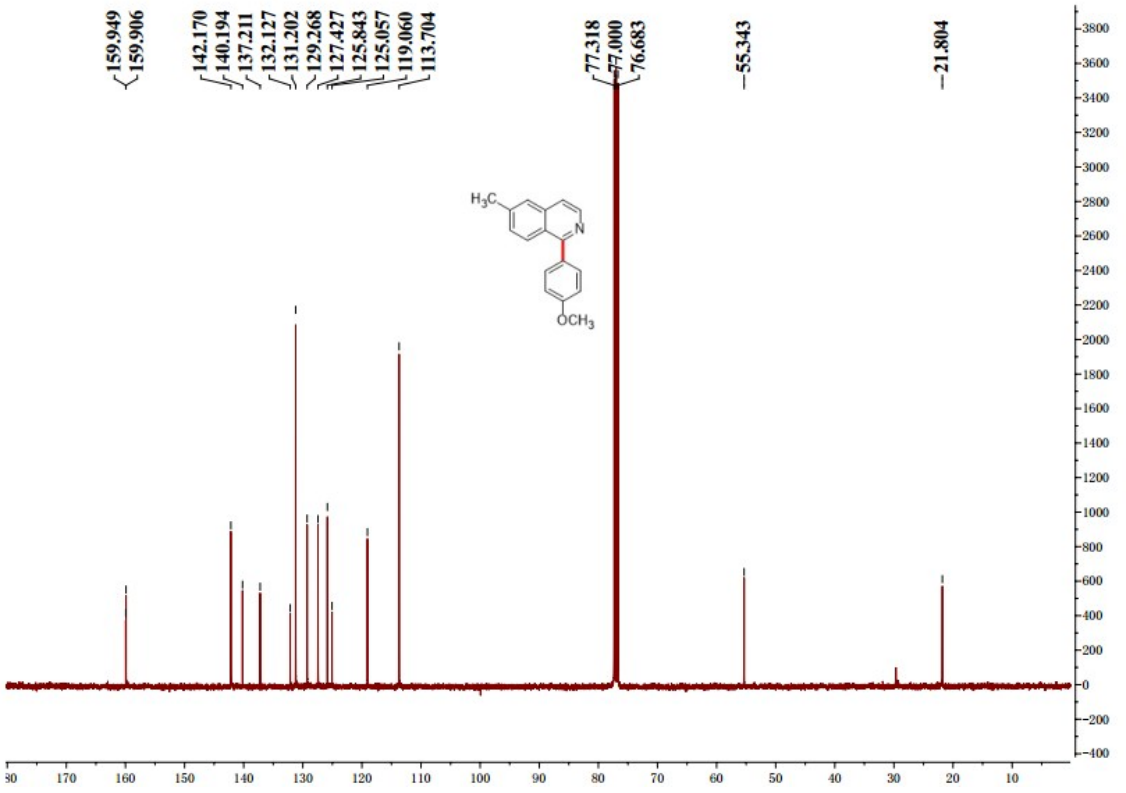
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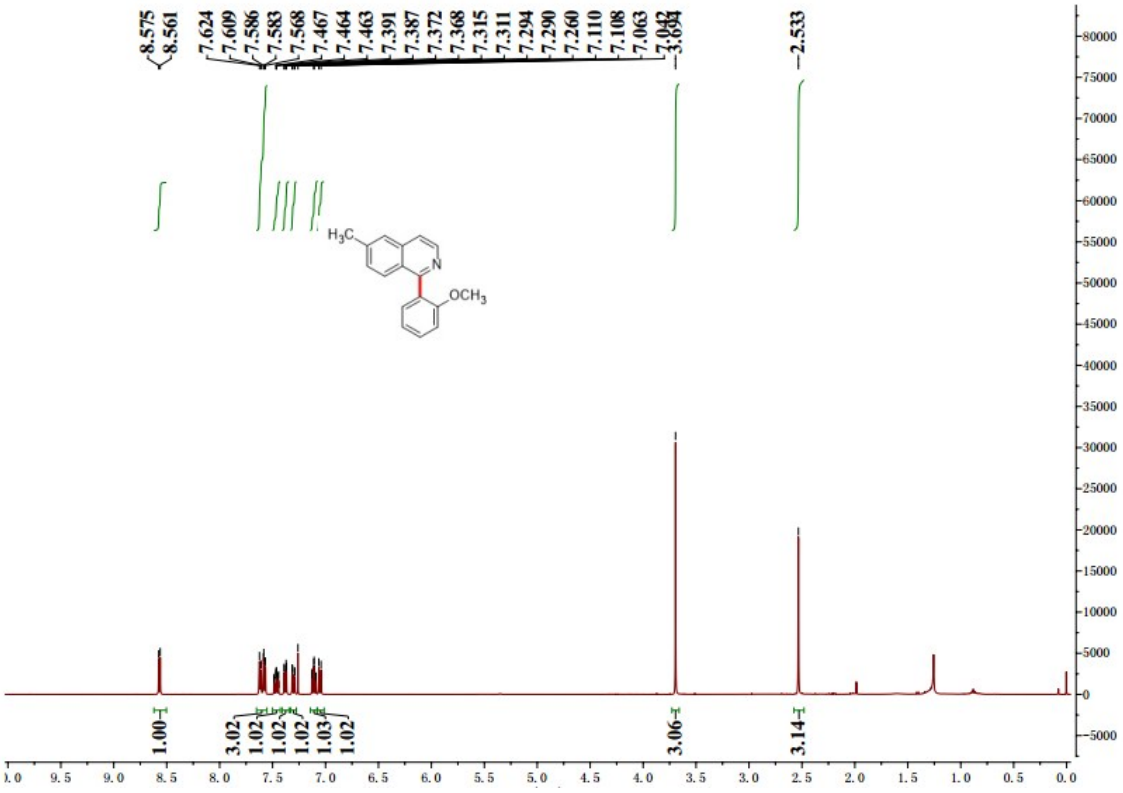
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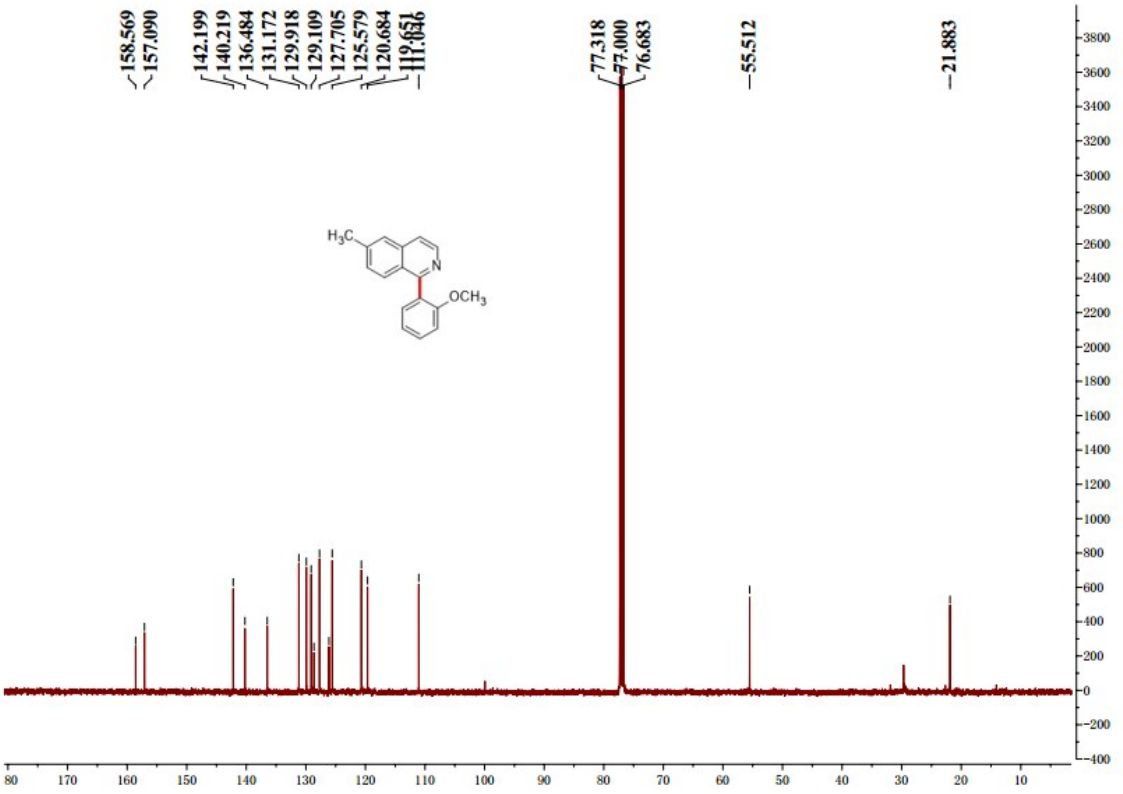
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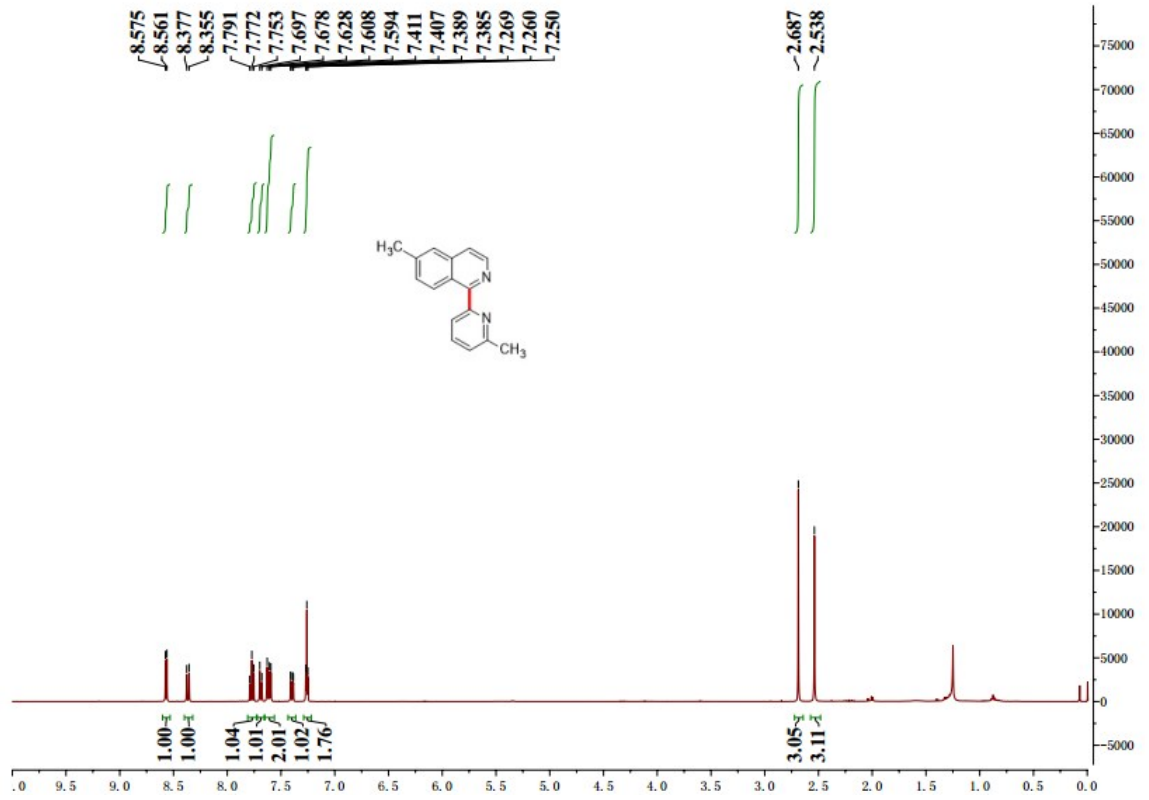
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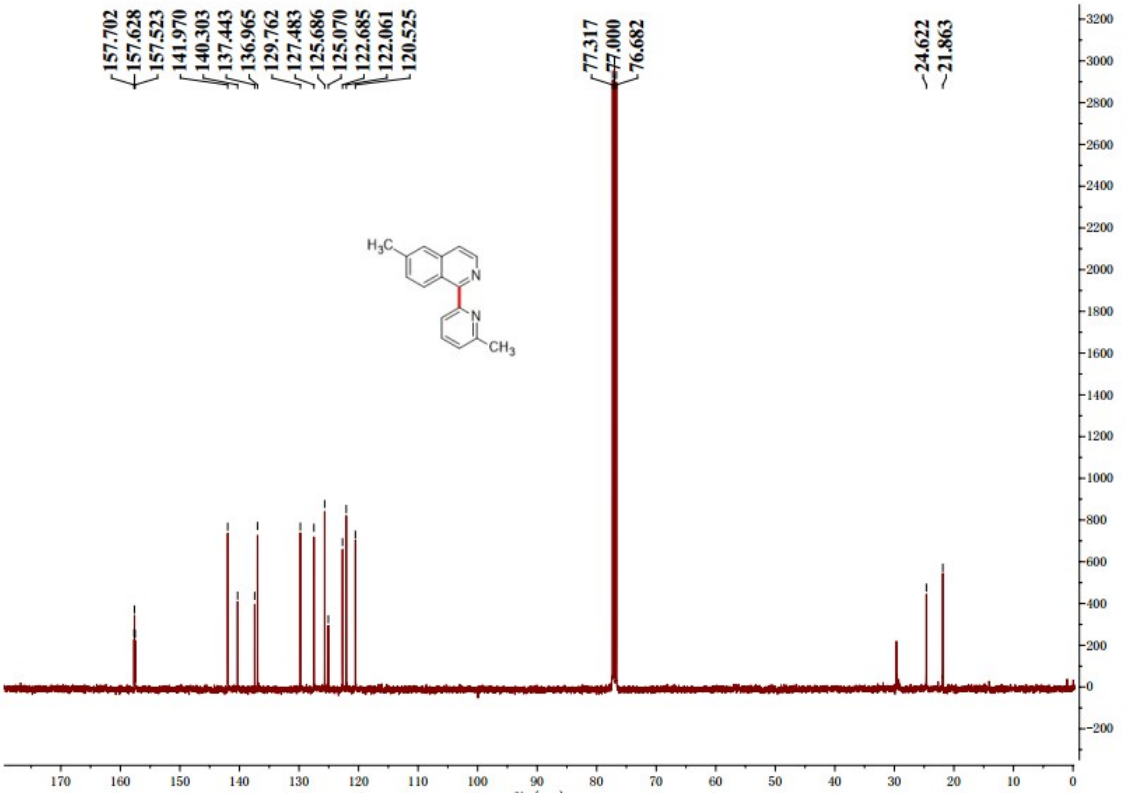
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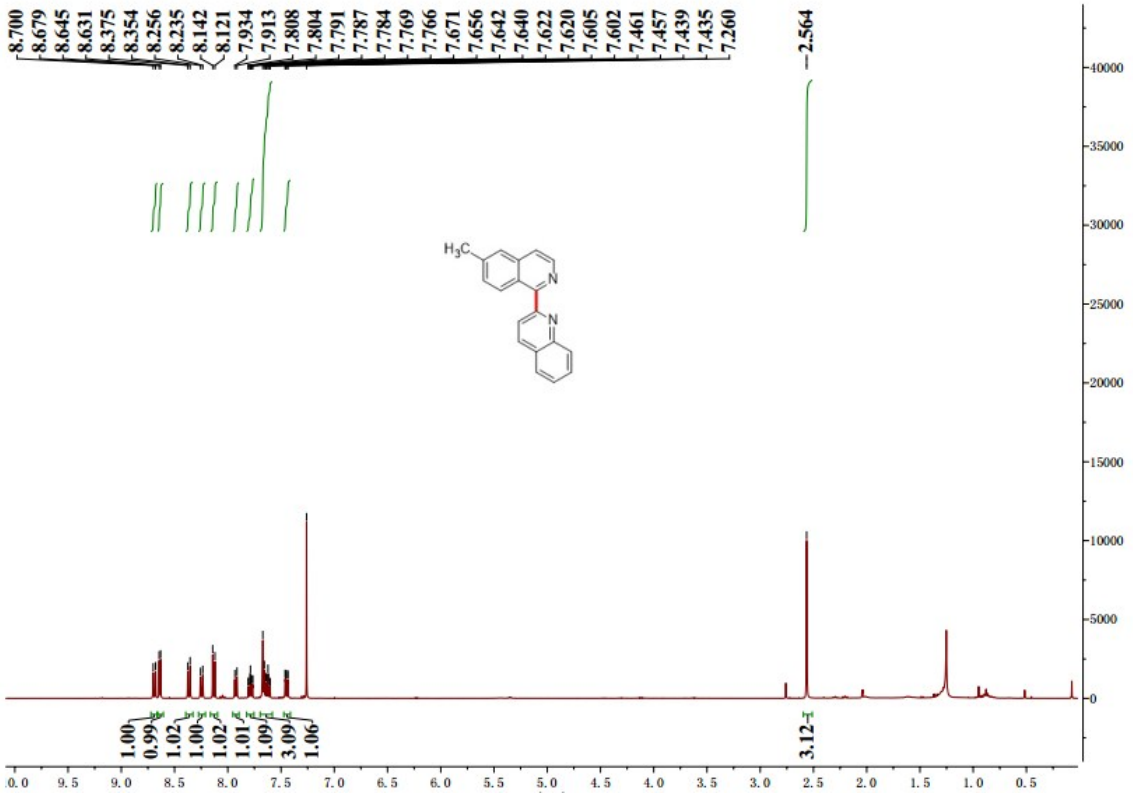
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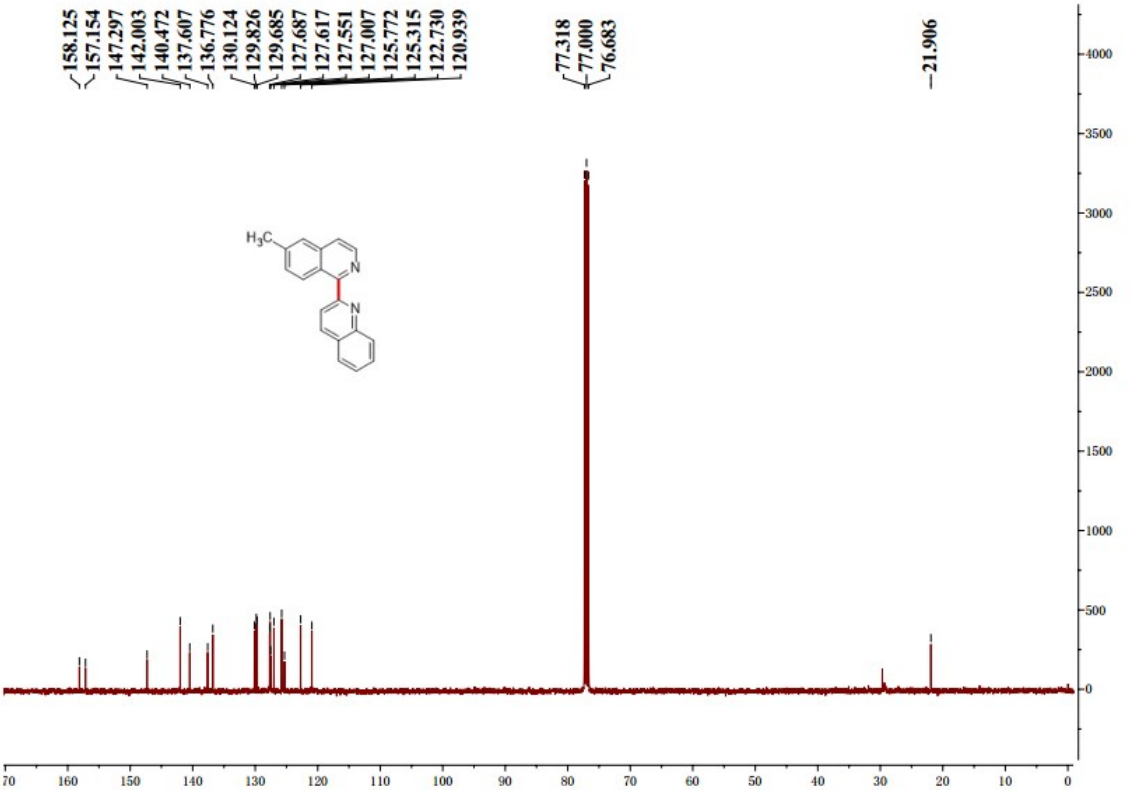
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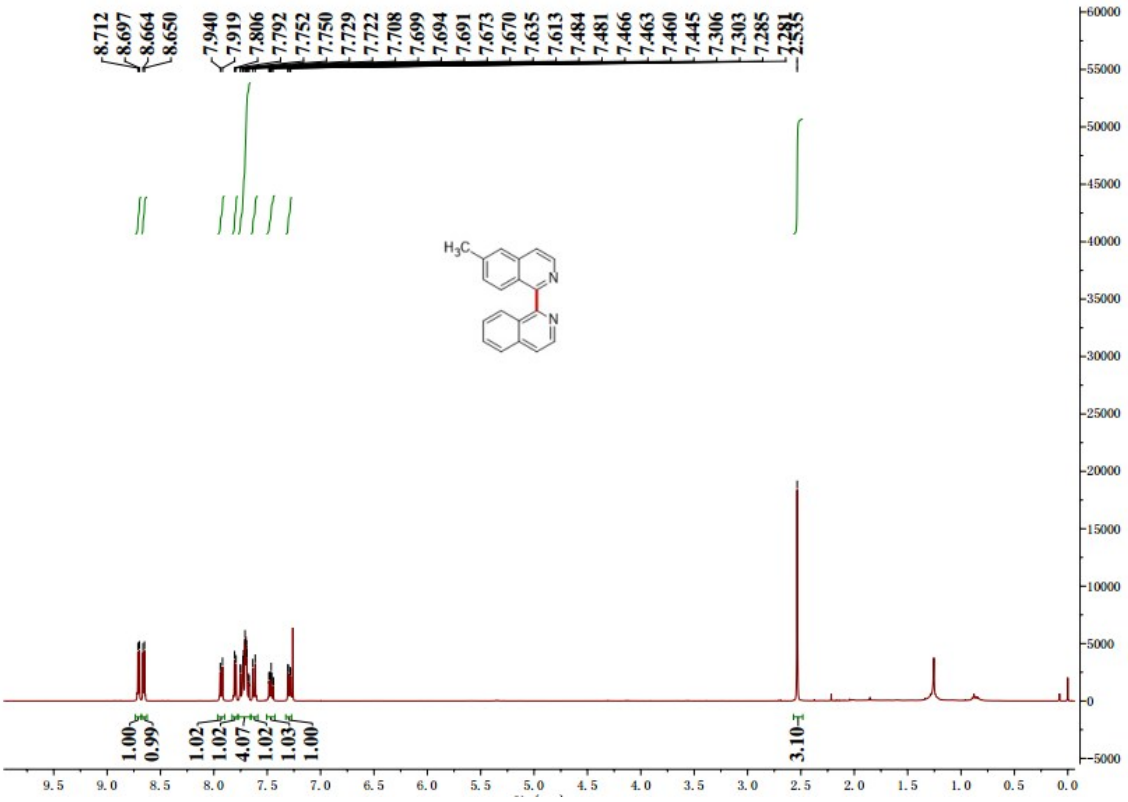
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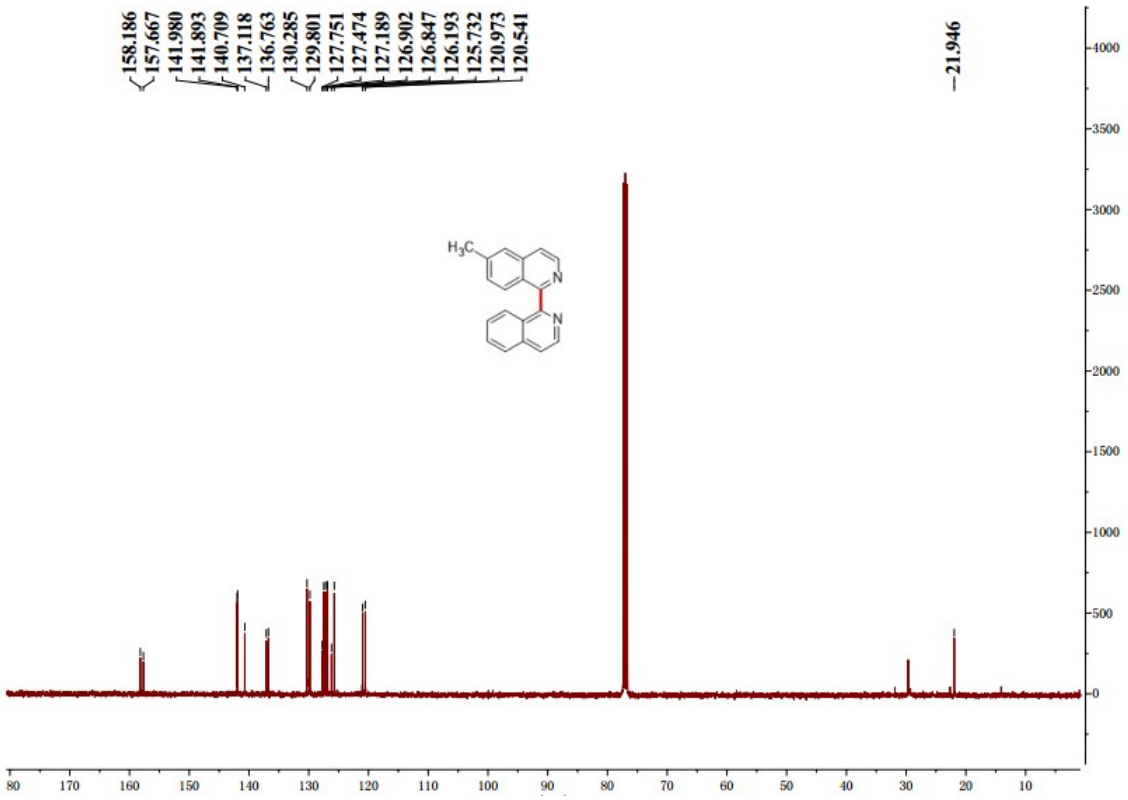
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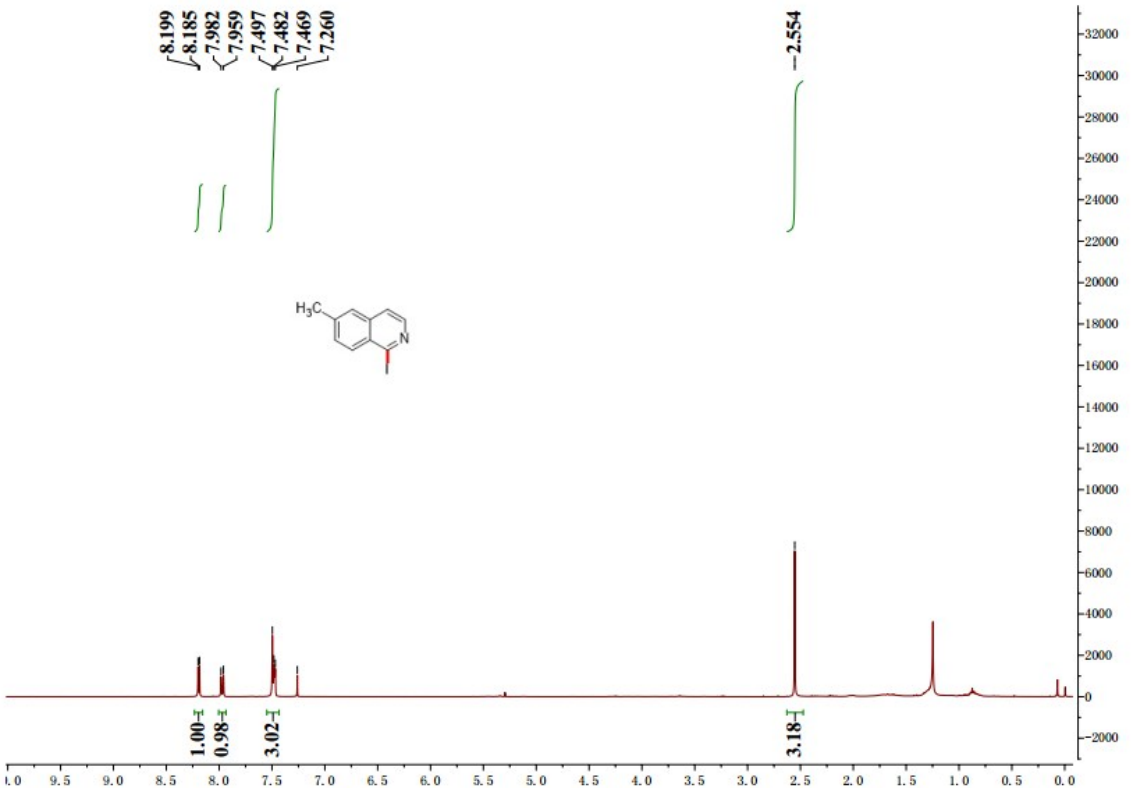
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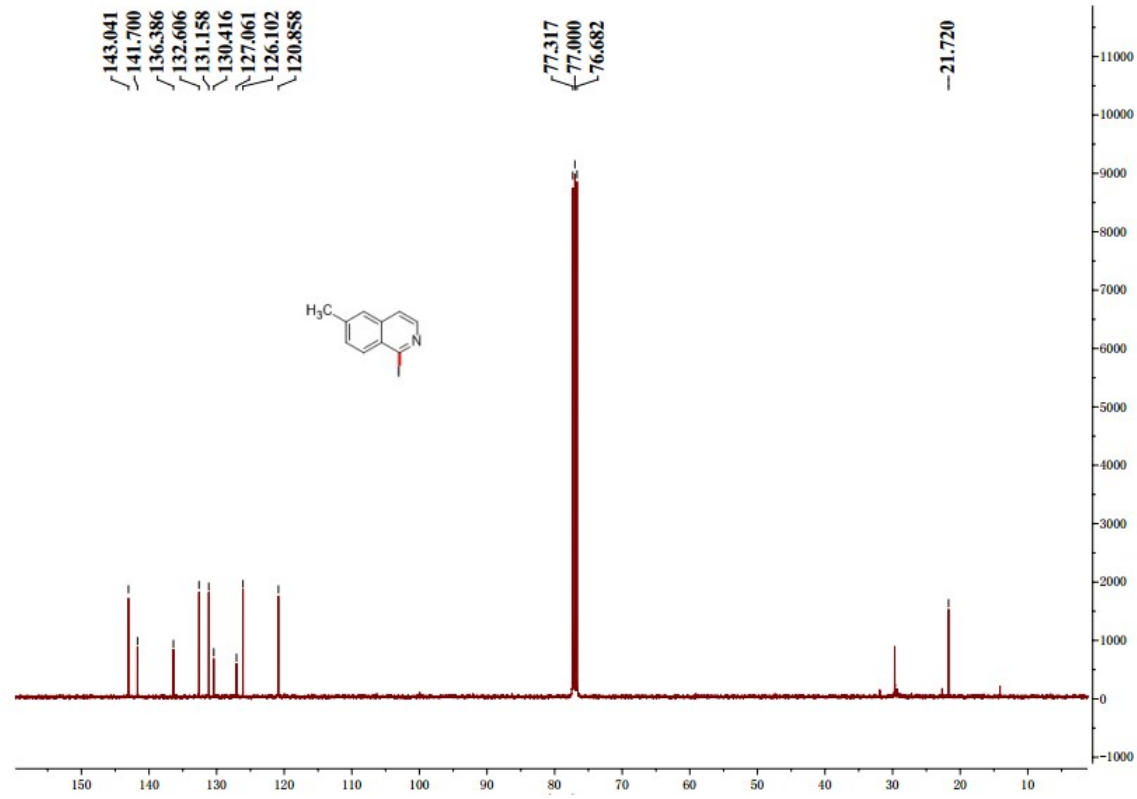
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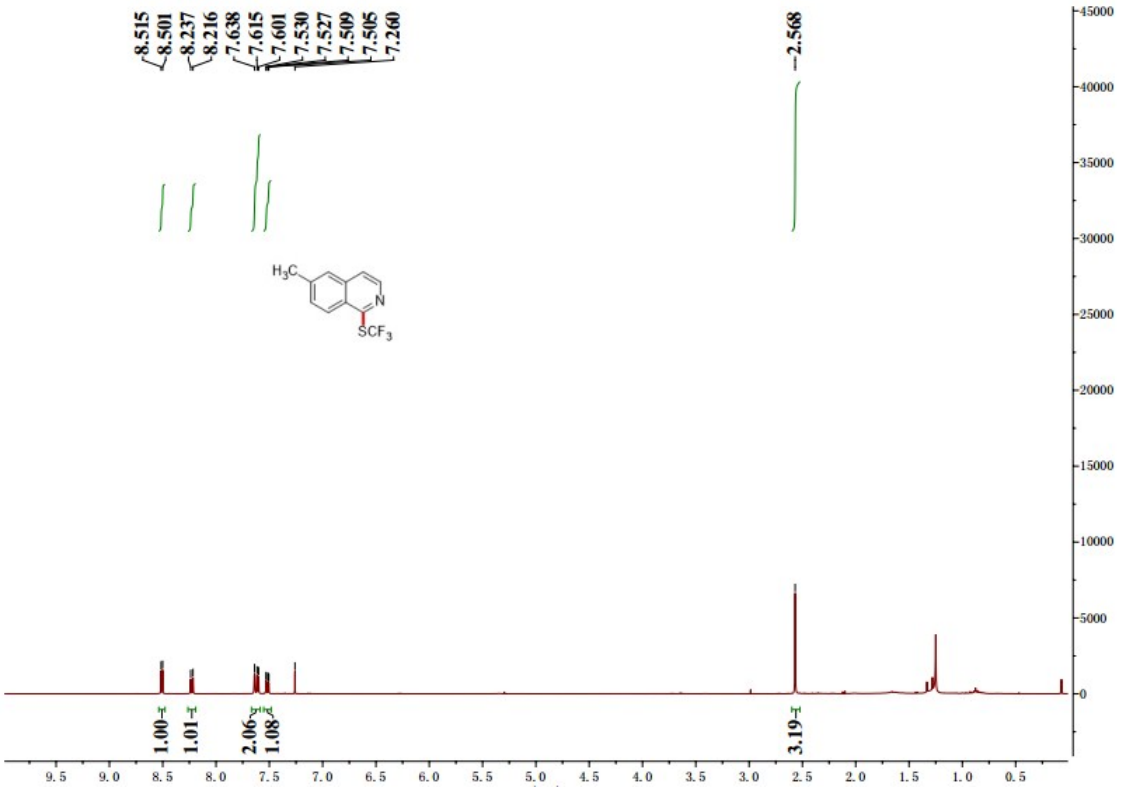
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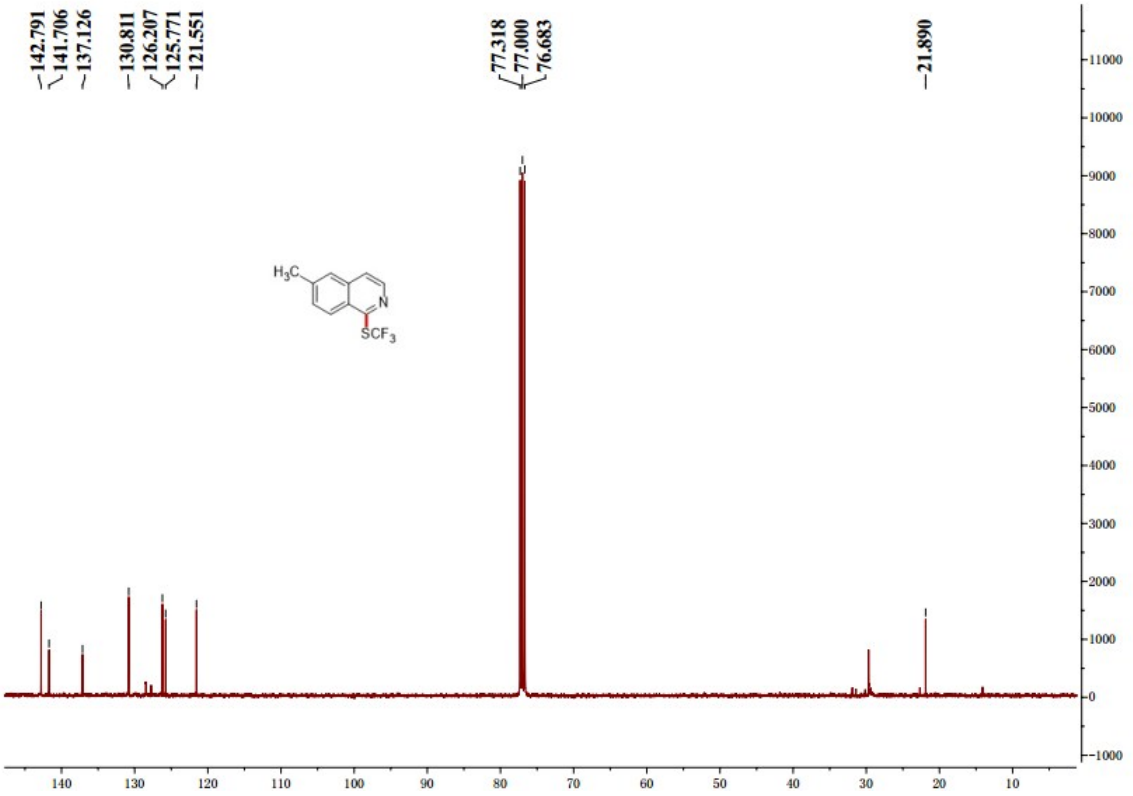
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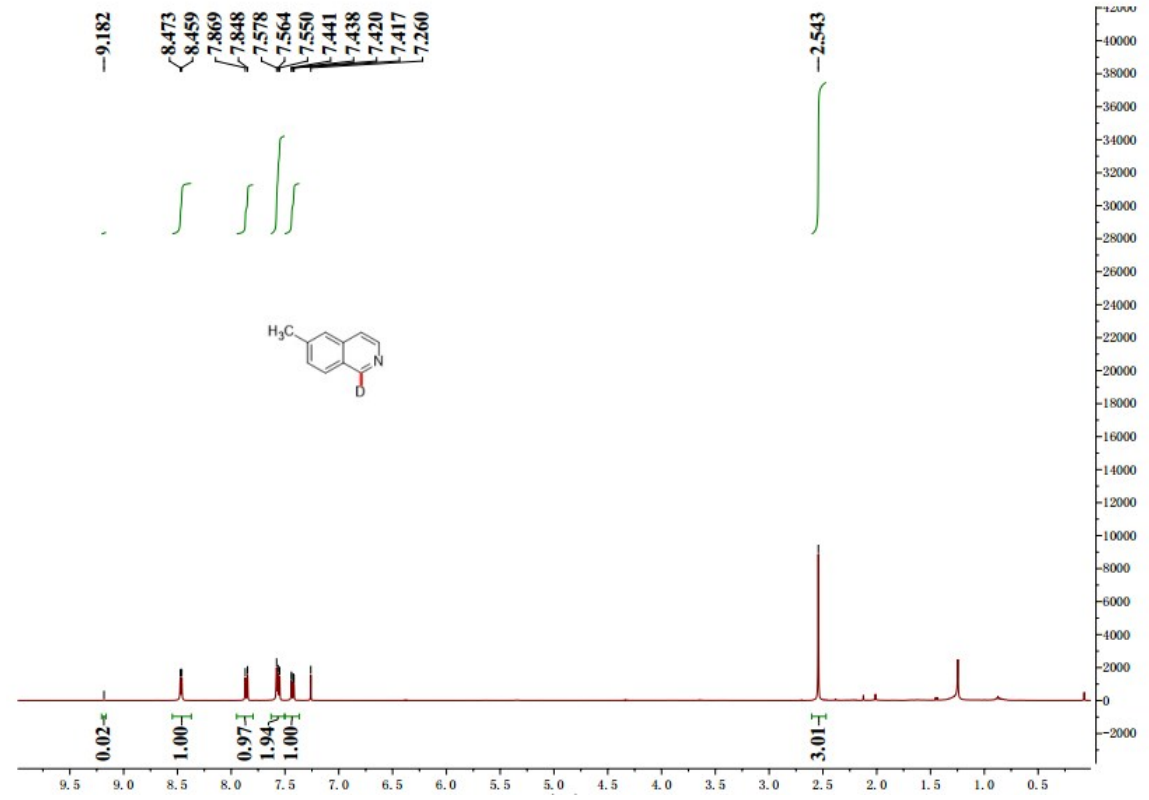
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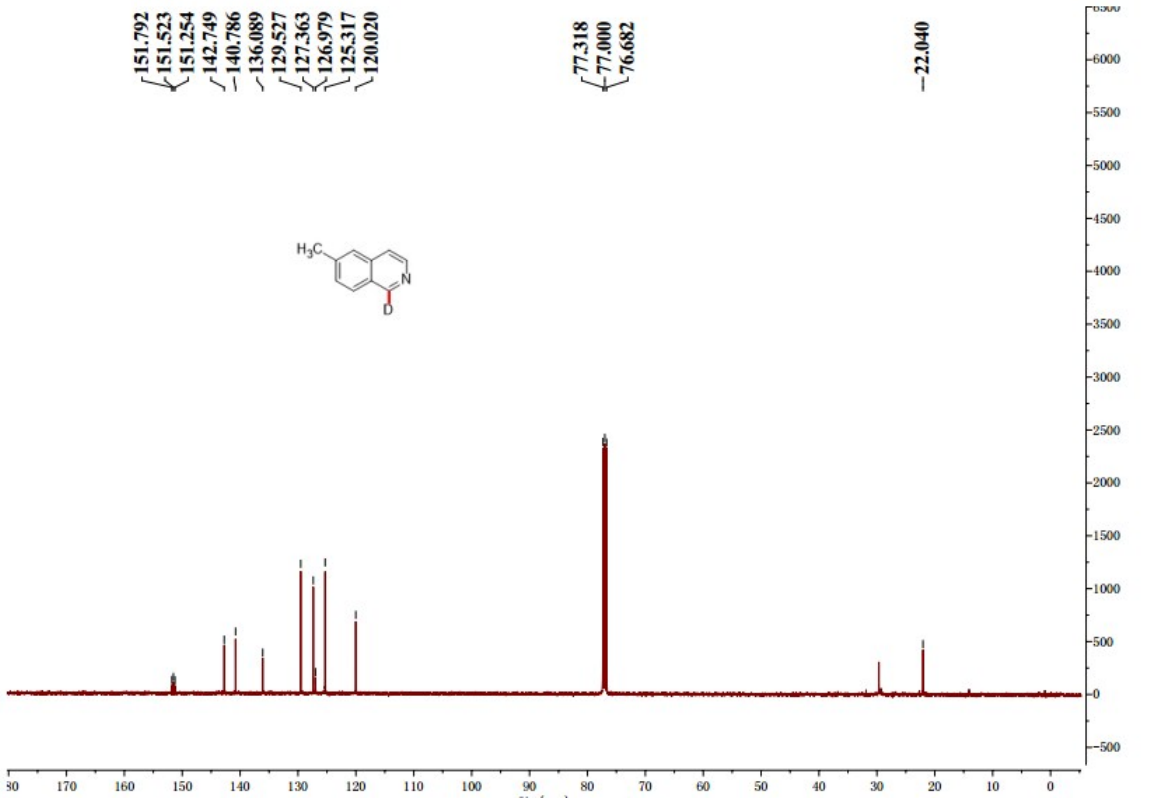
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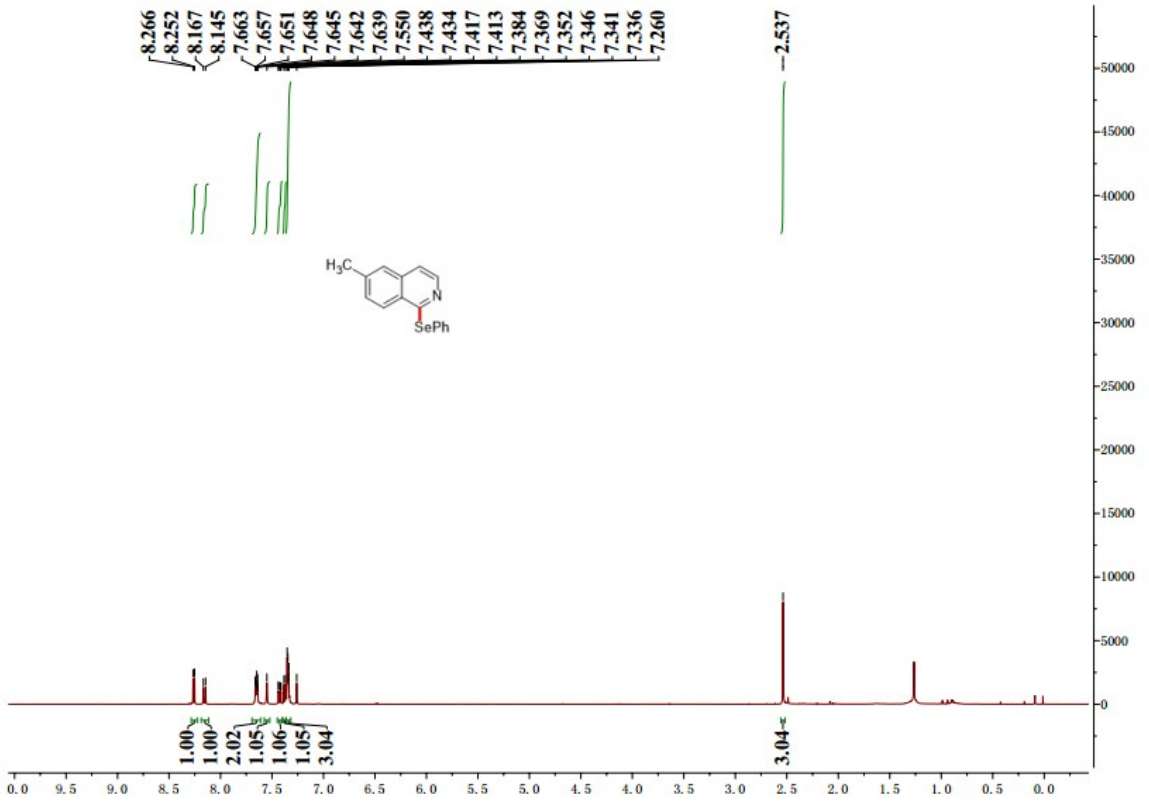
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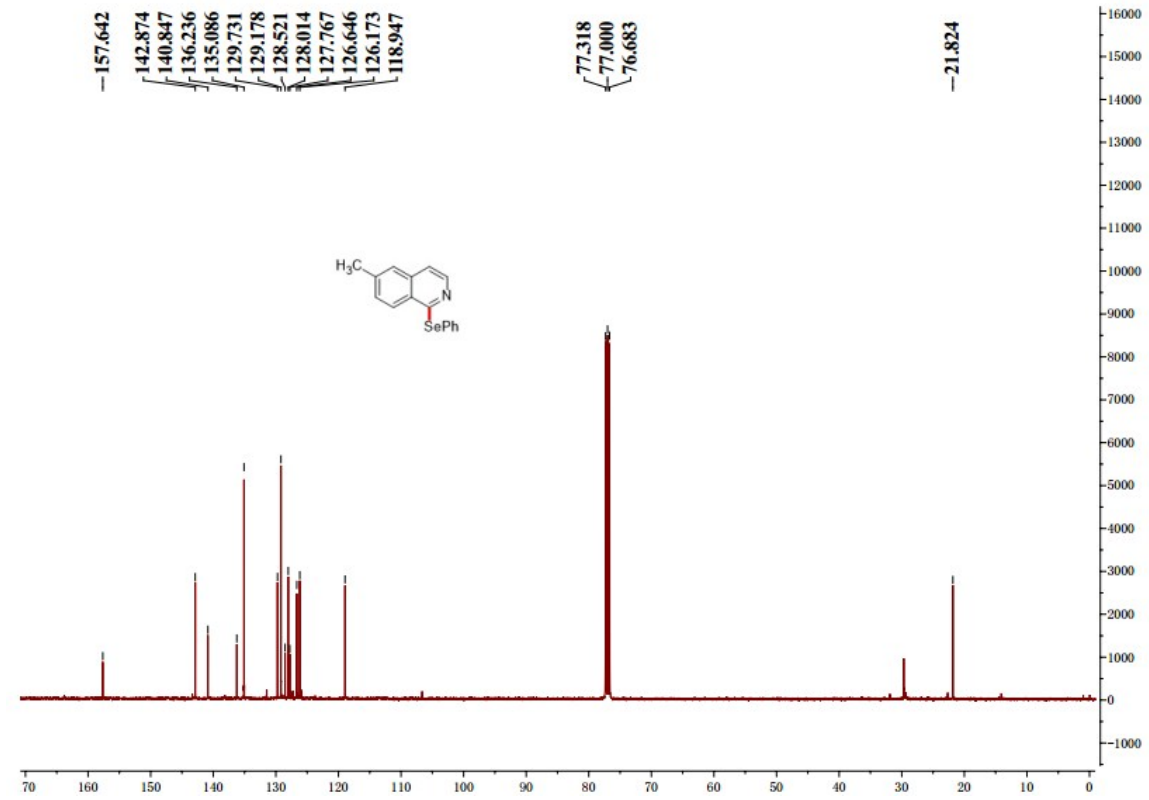
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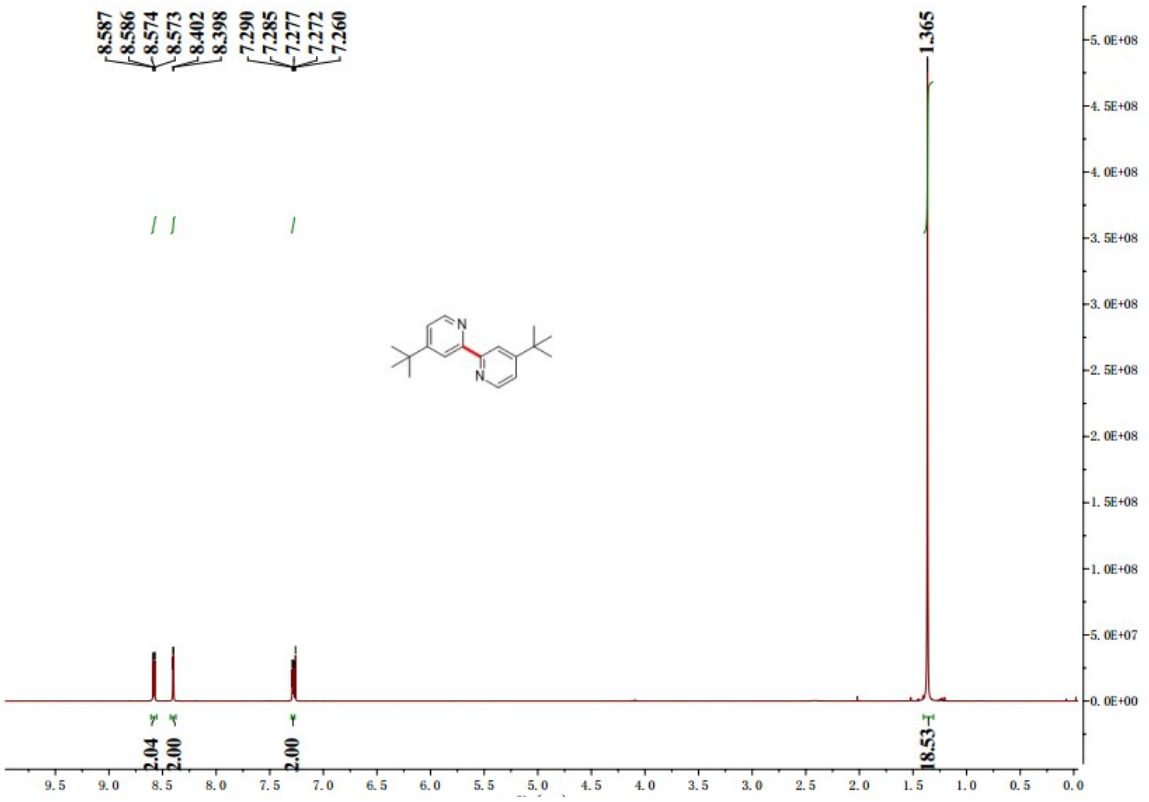
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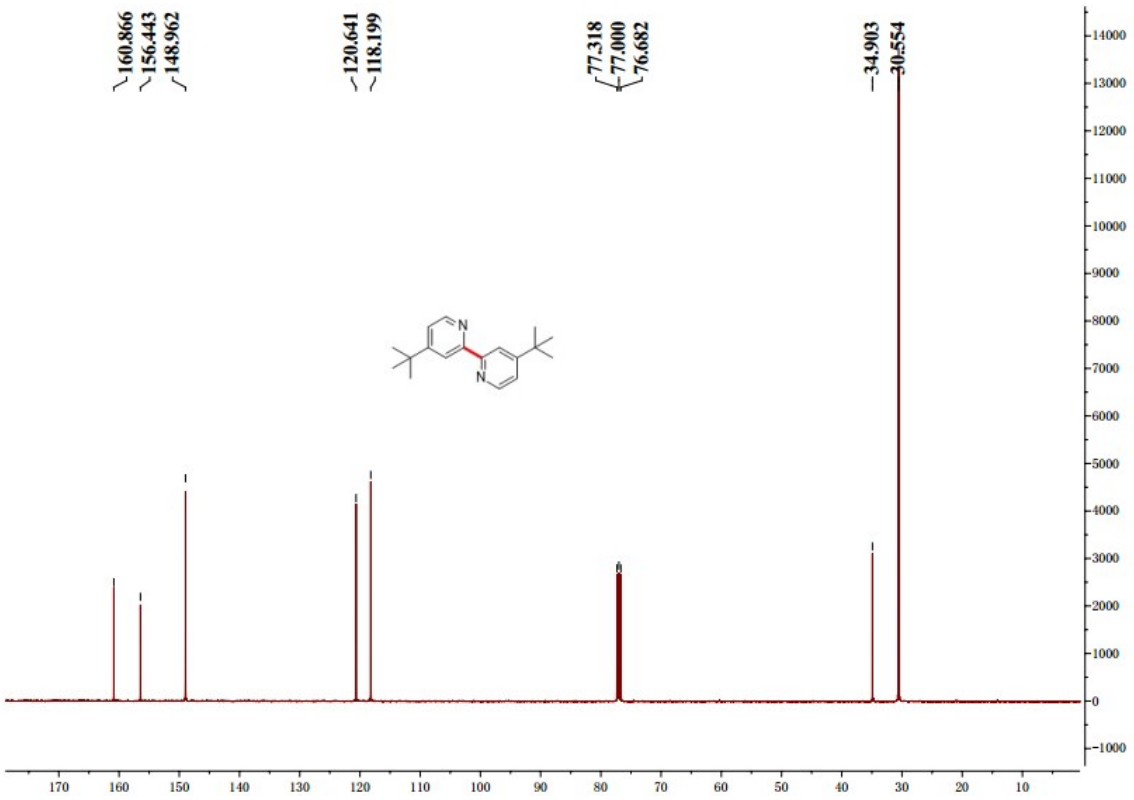
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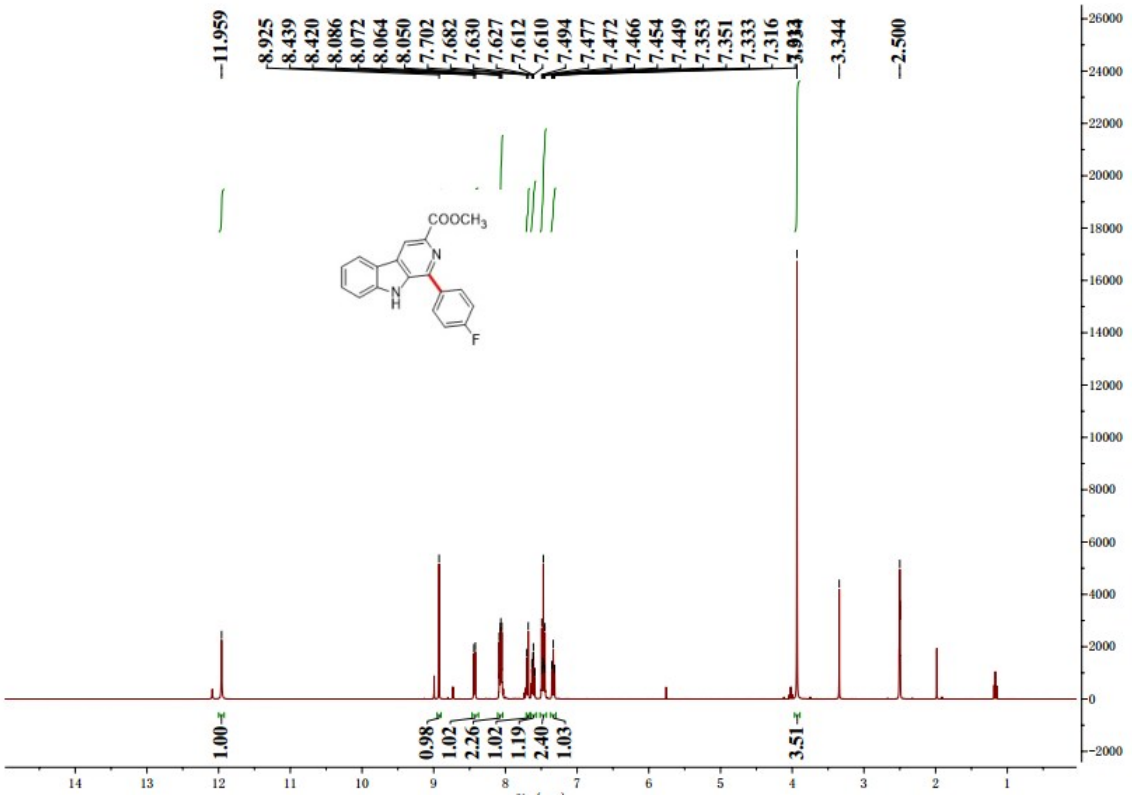
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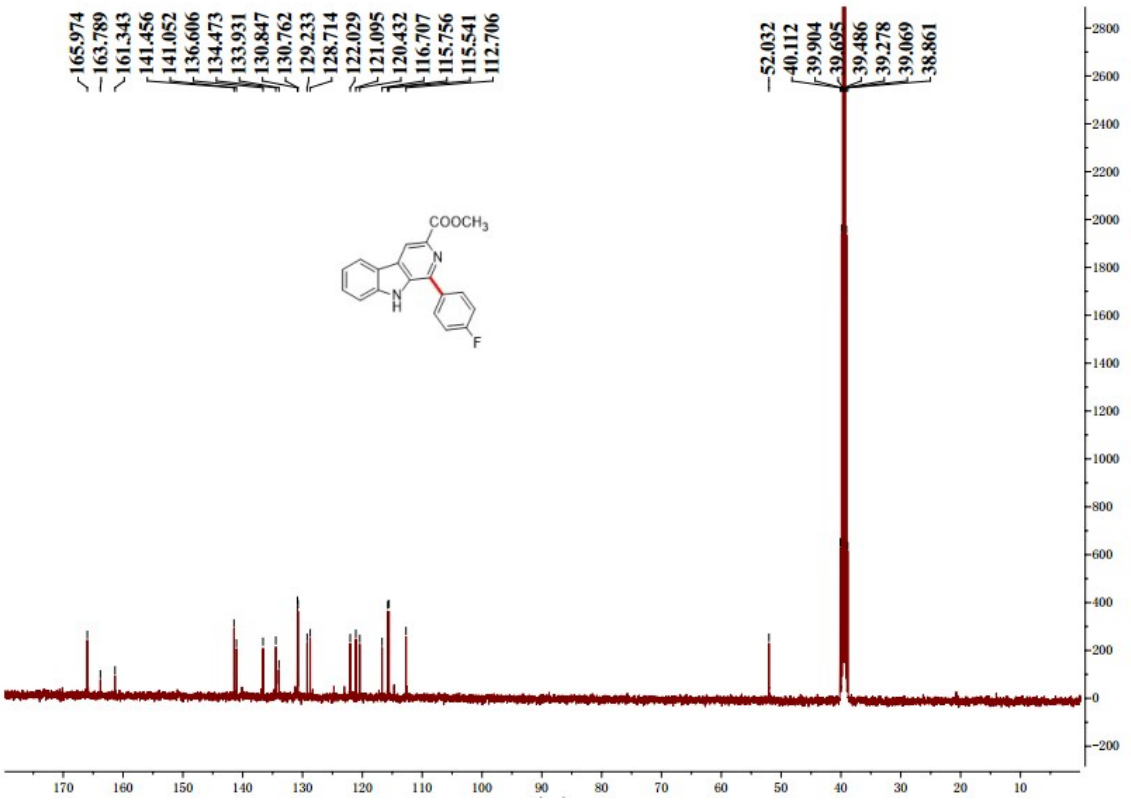
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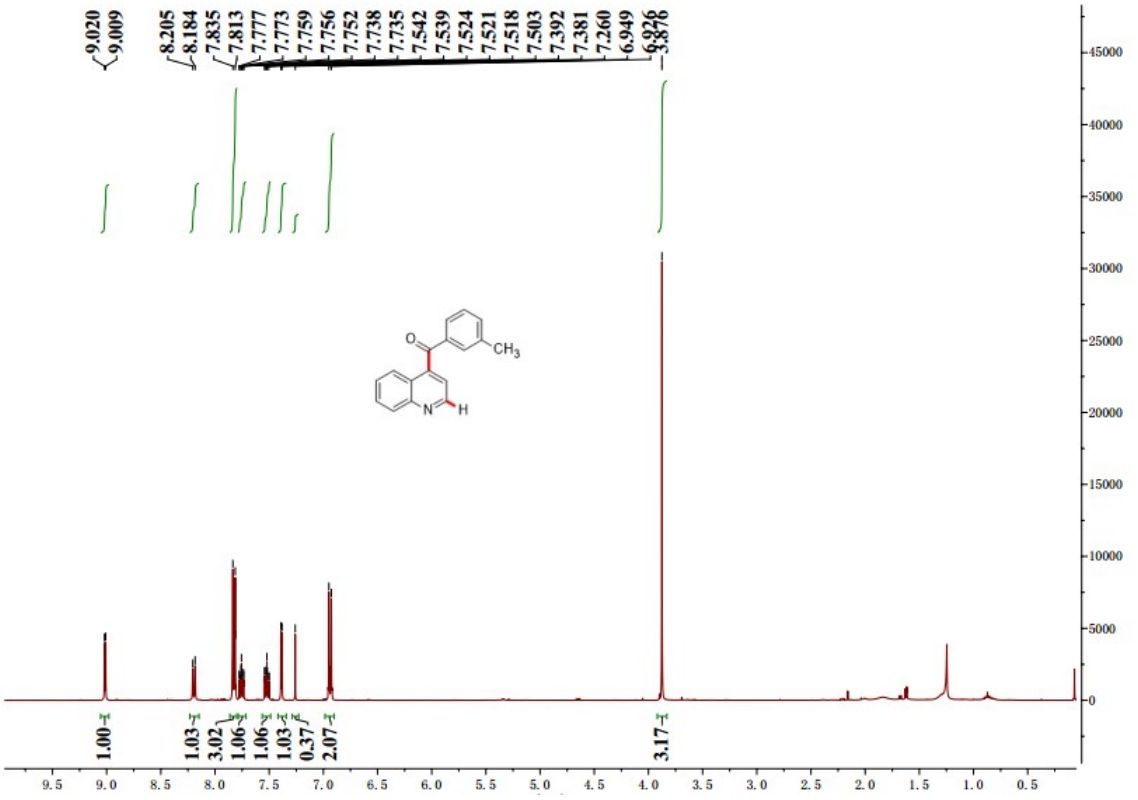
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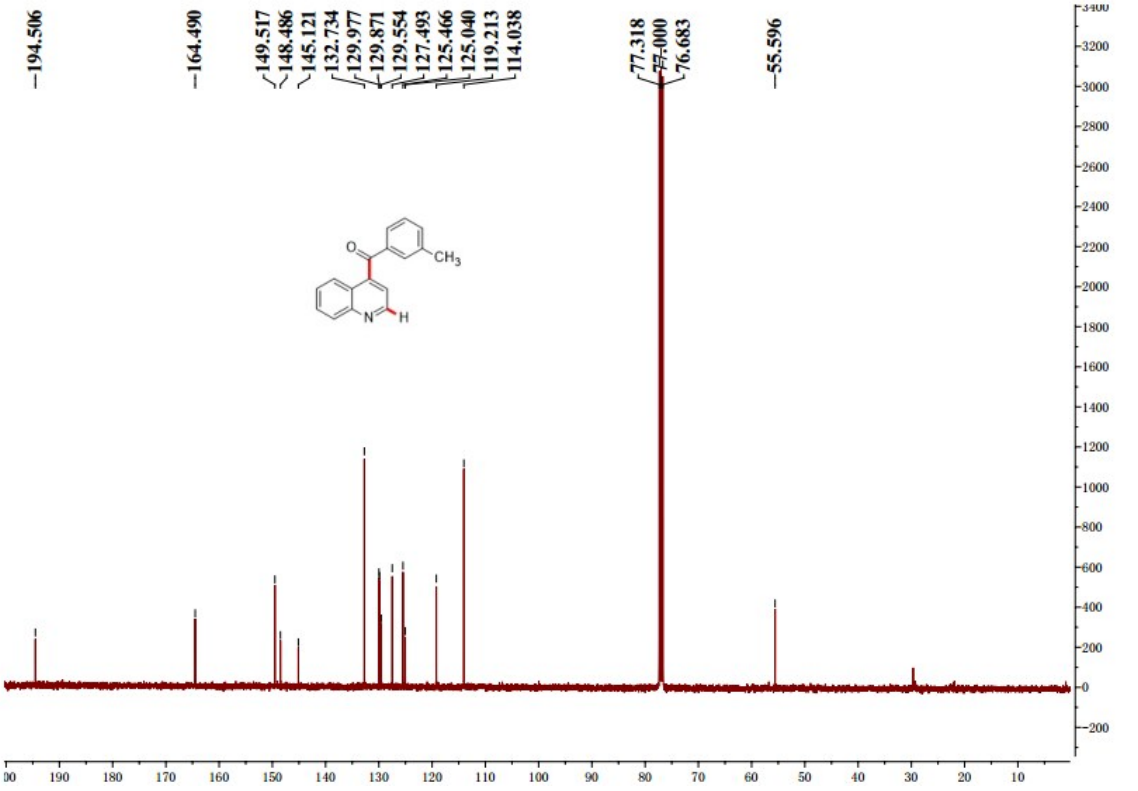
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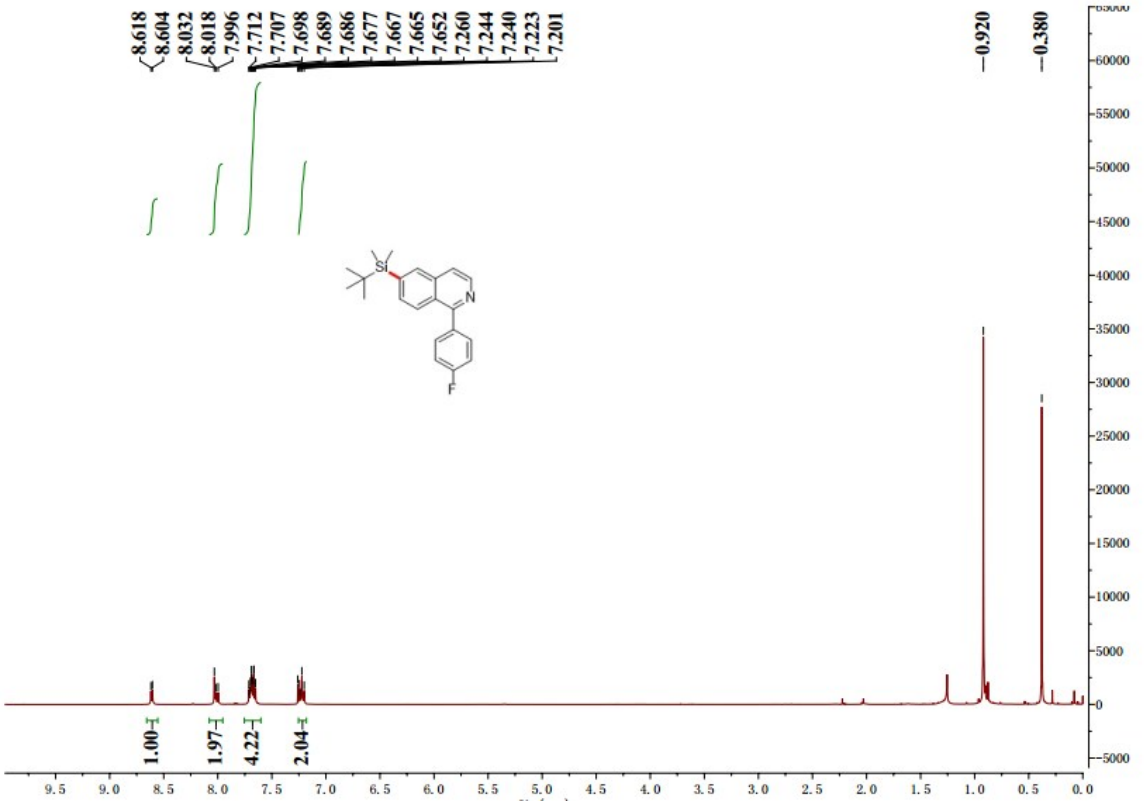
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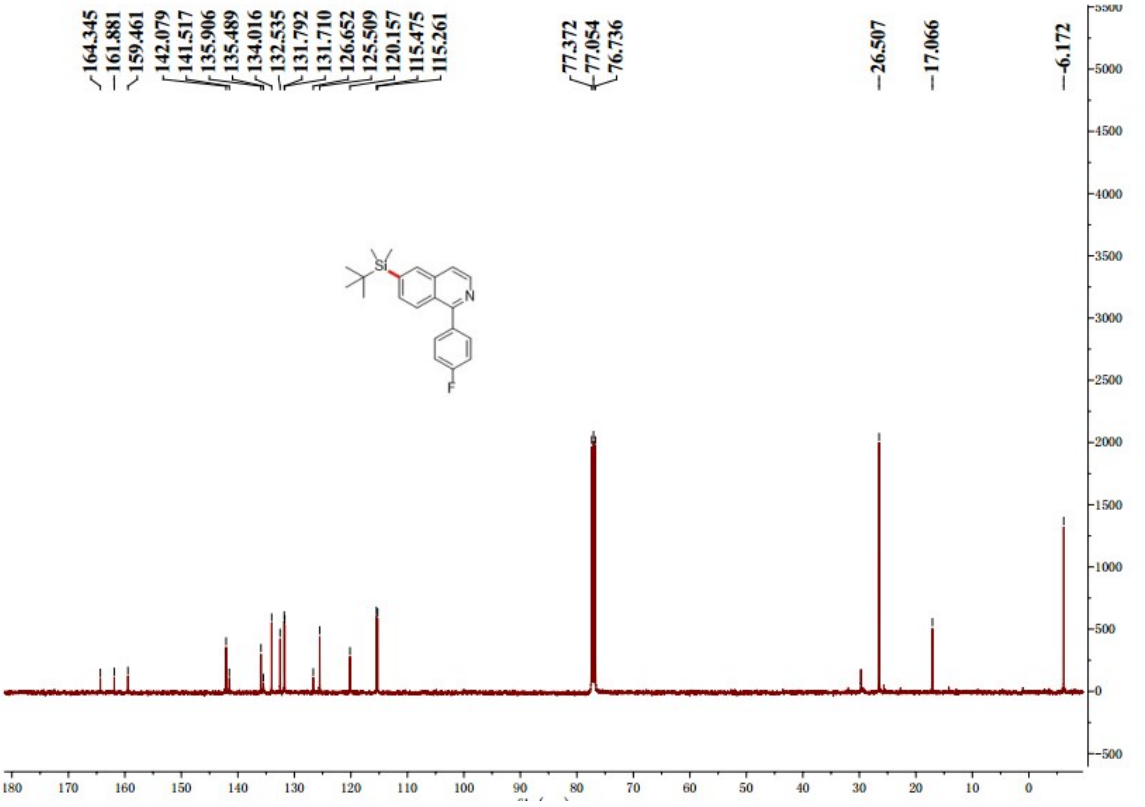
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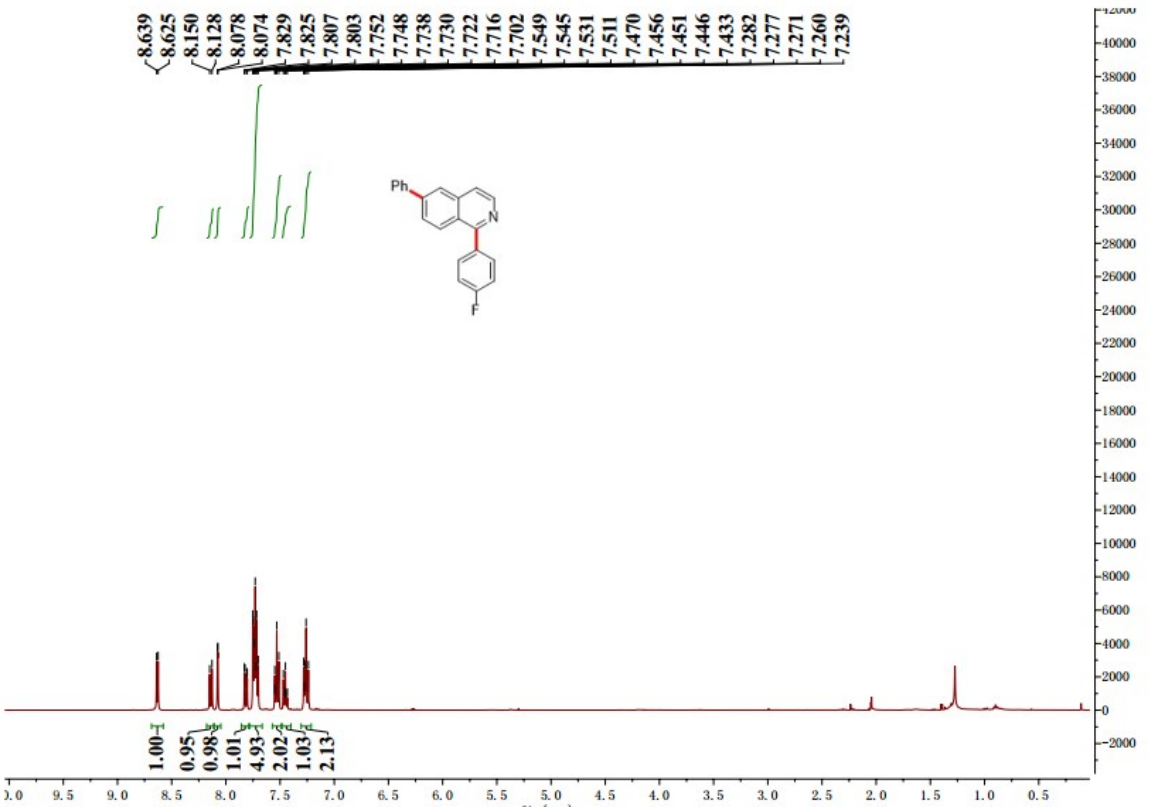
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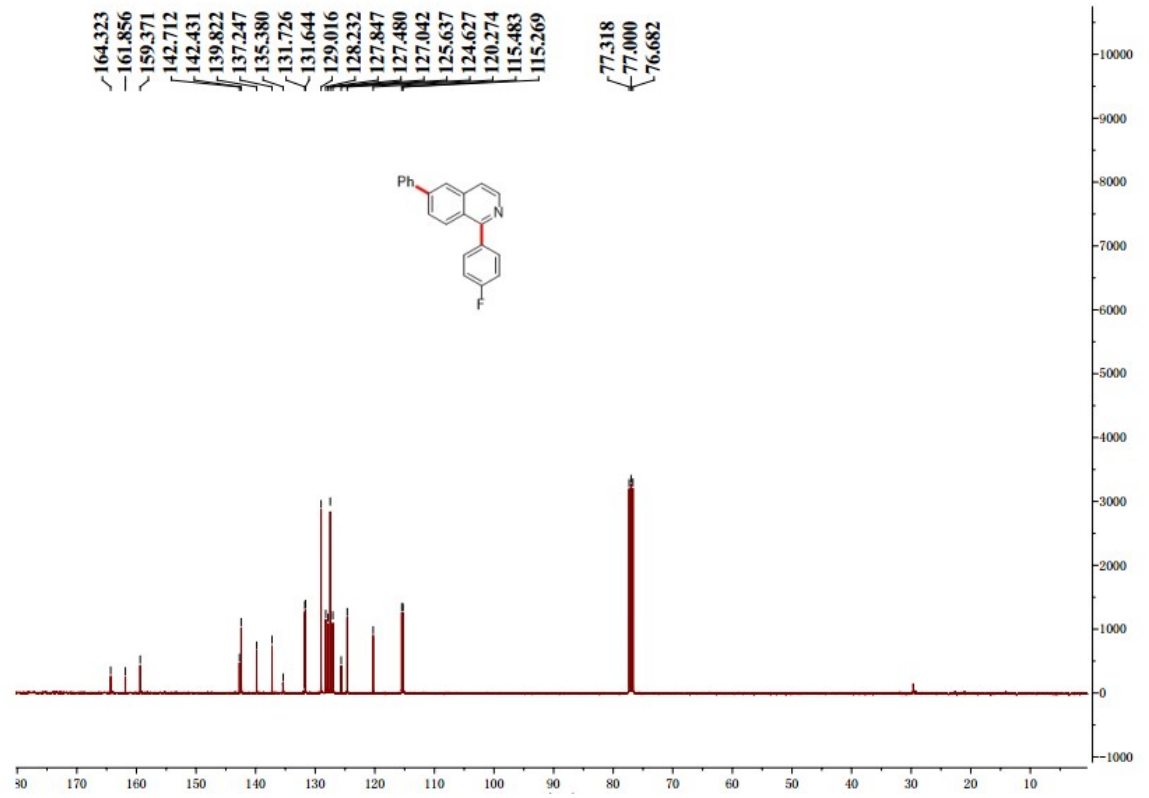
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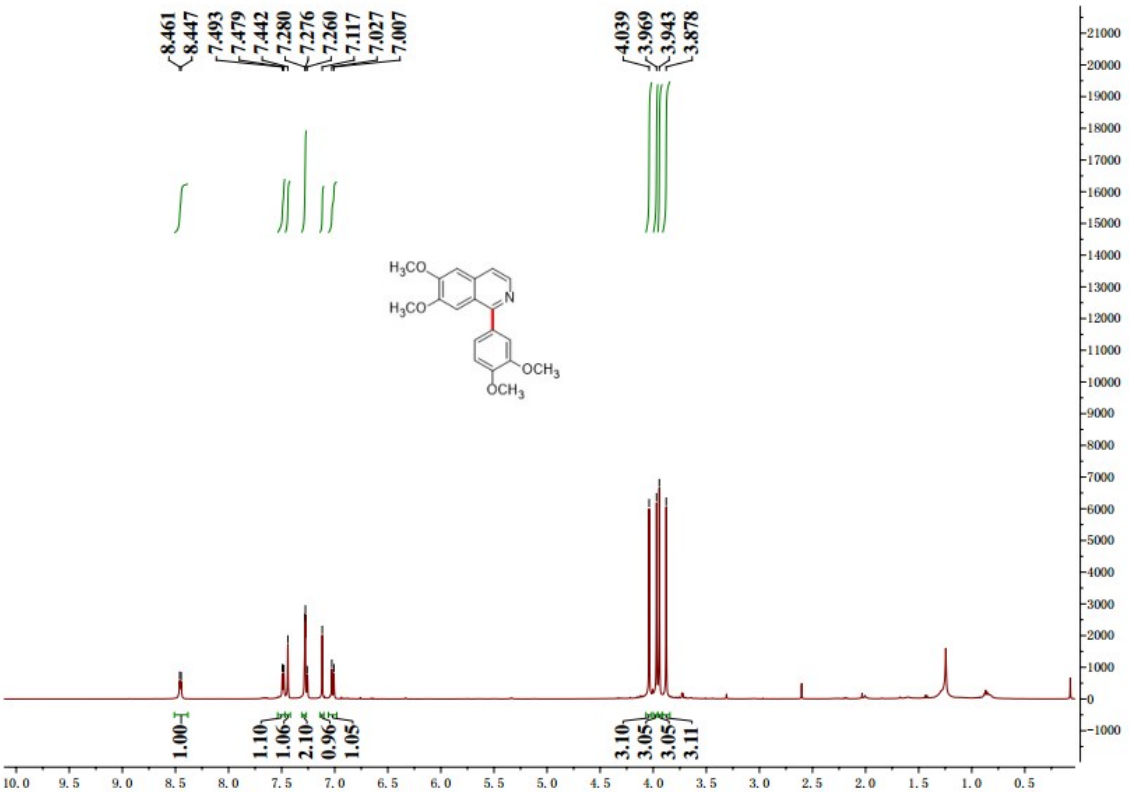
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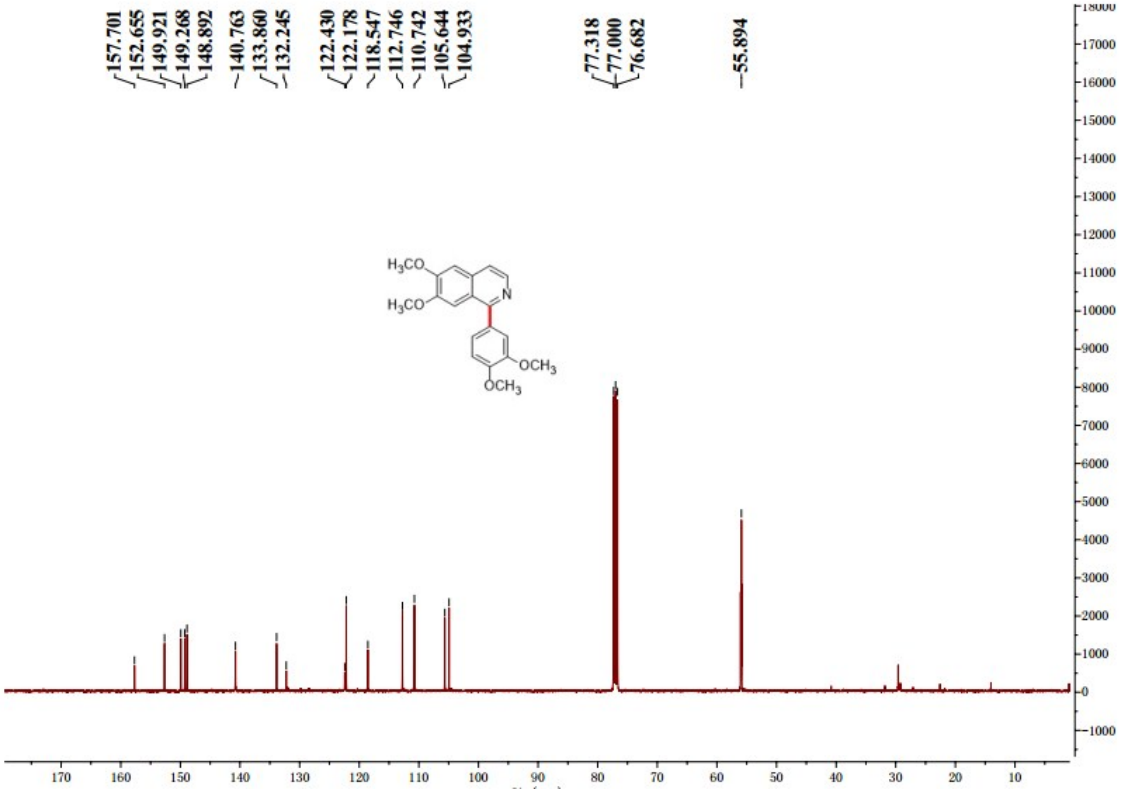
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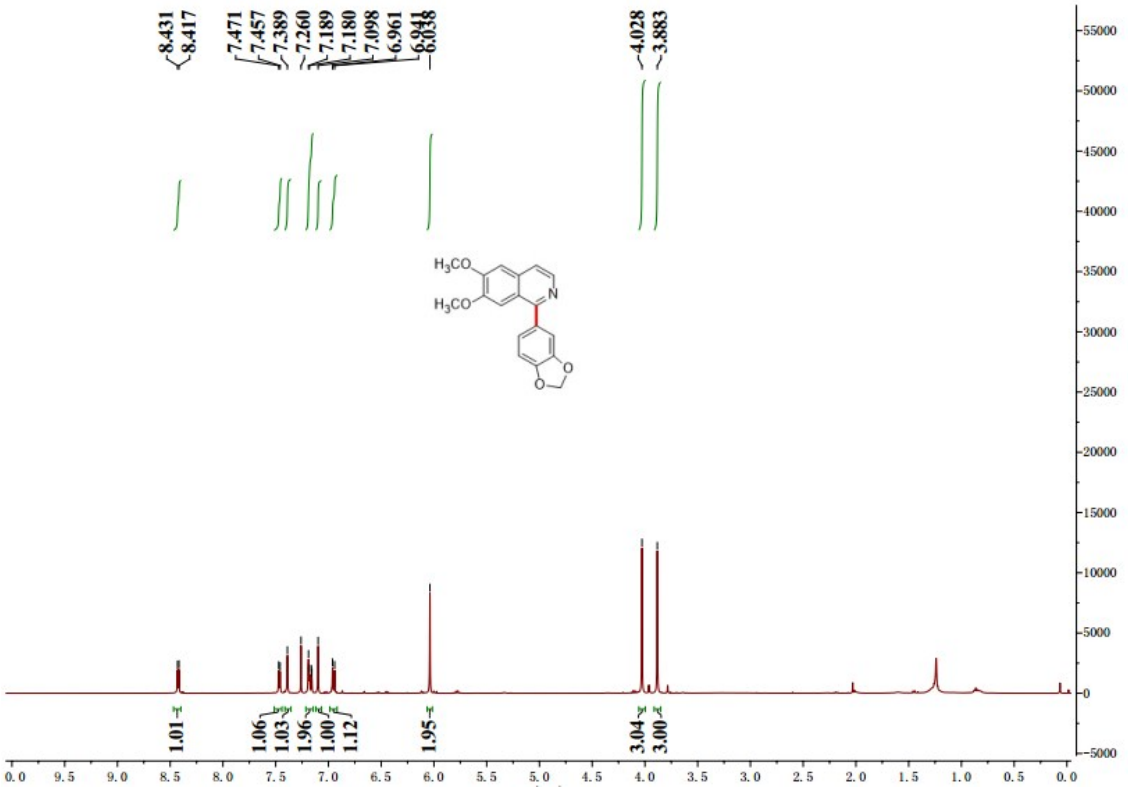
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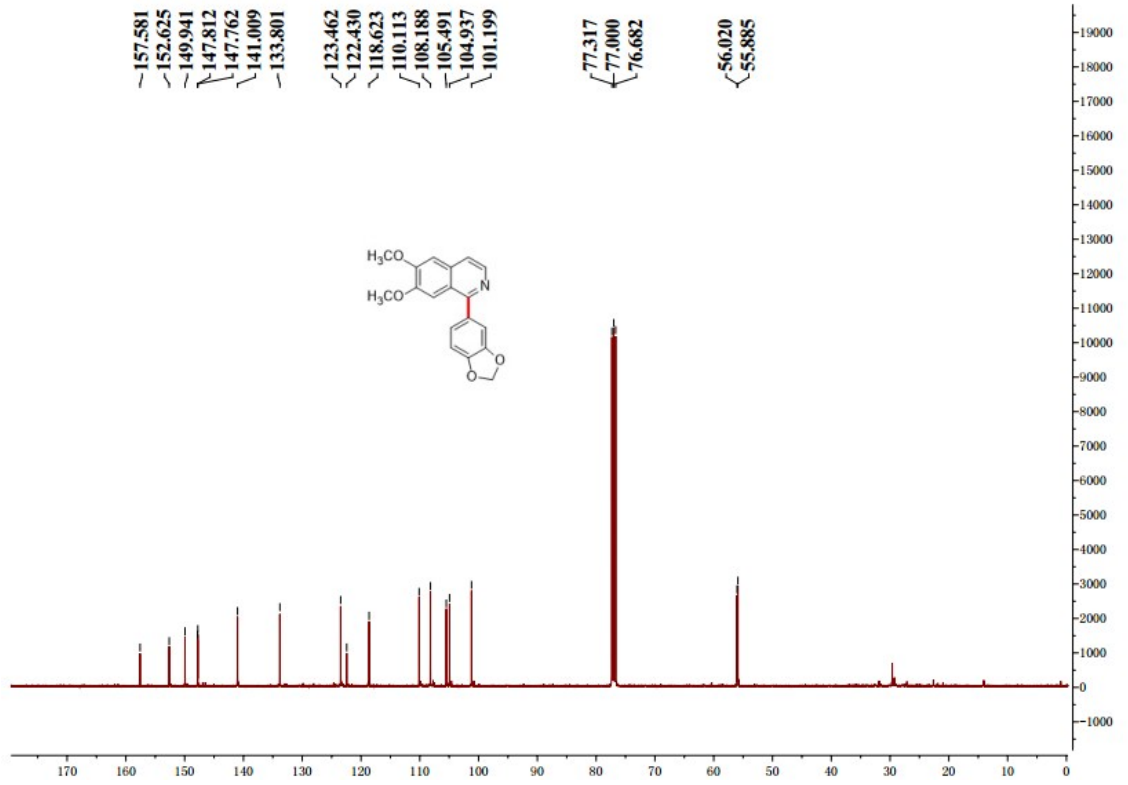
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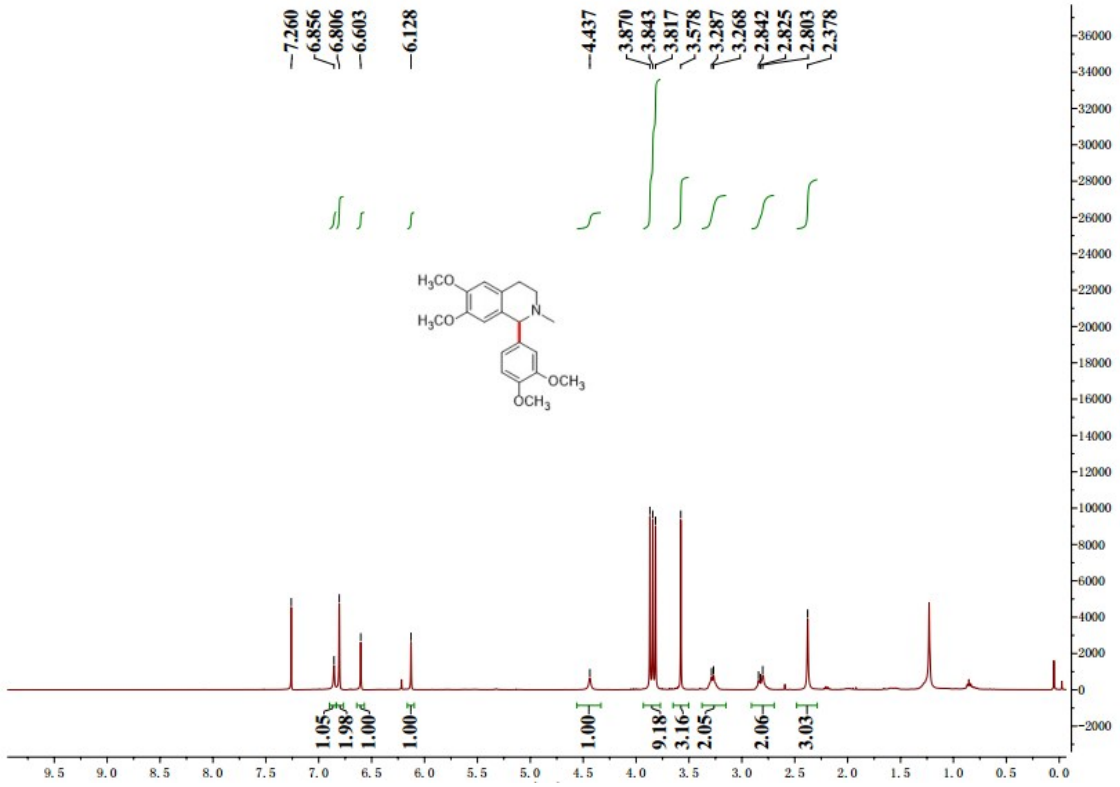
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H3CO
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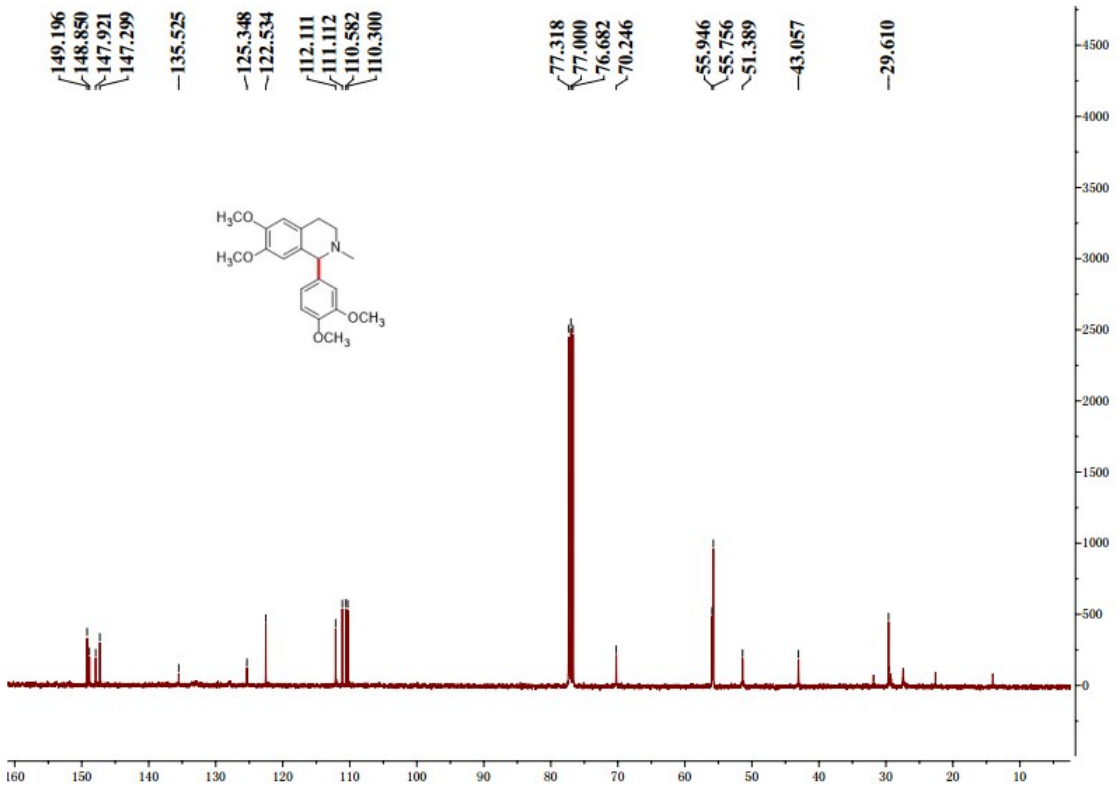
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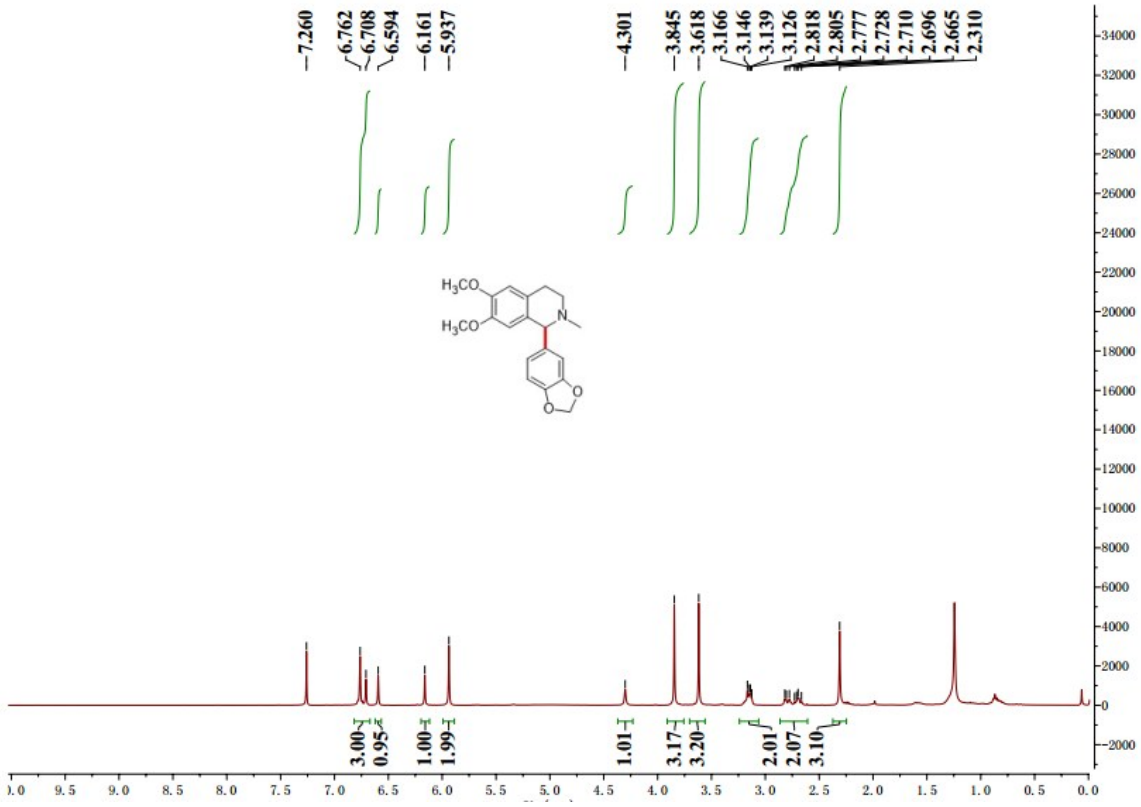
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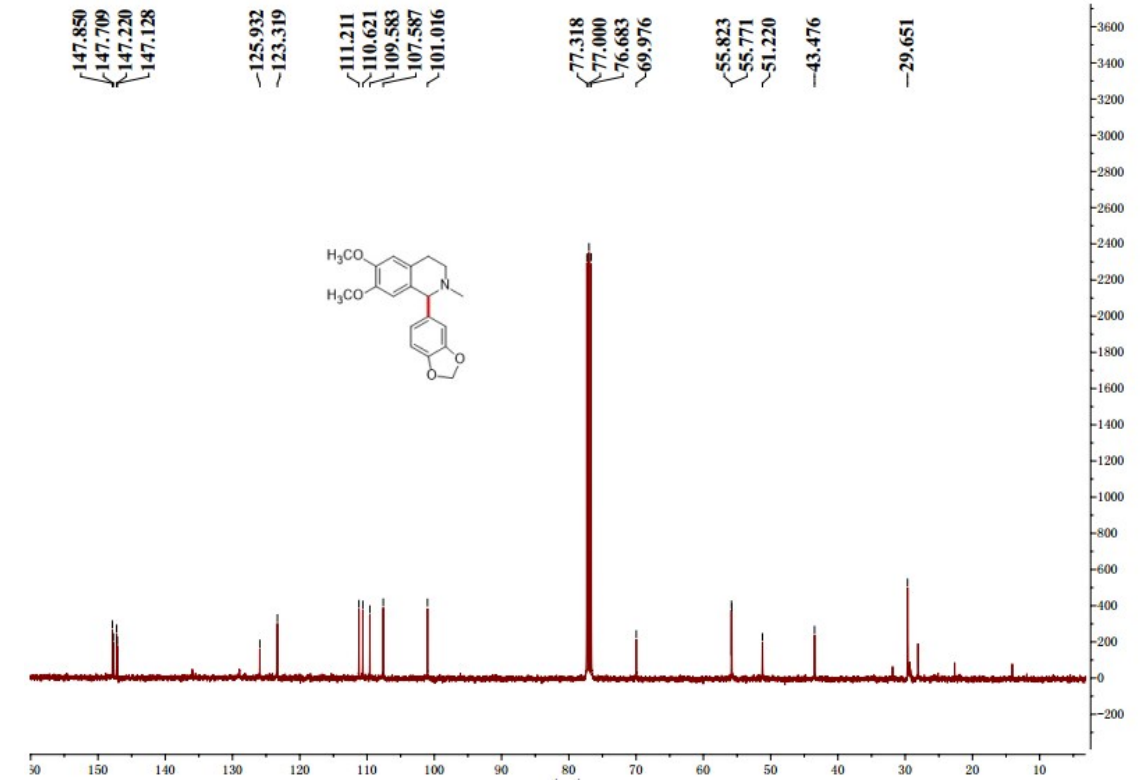
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