Electronic Supplementary Information

for

Organic photoredox catalyzed C–H silylation of quinoxalinones or electron-deficient heteroarenes under ambient air conditions

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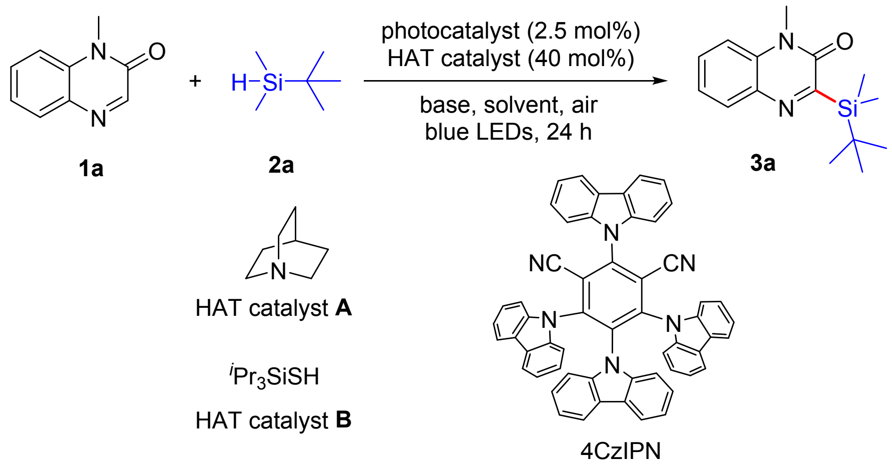
1 General information

All reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography. Column chromatography was performed using silica gel (300−400 mesh). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, q = quartet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected.

2. Reaction optimization

Table S1 Optimization of the reaction conditions[a]



Entry	Photocatalyst	Base (equiv.)	Solvent	Yield[b] (%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	DMSO	<10
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	DMF	trace
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	^{t}BuOH	0
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	THF	trace
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	DCM	0
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	1,4-dioxene	0
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	DCE	trace
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	acetone	25
9	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	K_2CO_3 (1)	CH_3CN	31
10	$Ir(ppy)_2(dtbbpy)PF_6$	K_2CO_3 (1)	CH_3CN	0
11	4CzIPN	K_2CO_3 (1)	CH_3CN	47

12	none	K_2CO_3 (1)	CH_3CN	0
13[c]	4CzIPN	K_2CO_3 (1)	CH_3CN	trace
14[d]	4CzIPN	K_2CO_3 (1)	CH_3CN	31
15[e]	4CzIPN	K_2CO_3 (1)	CH_3CN	41
16	4CzIPN	none	CH_3CN	0
17	4CzIPN	DBU (1)	CH_3CN	41
18	4CzIPN	$CsCO_3$ (1)	CH_3CN	32
19	4CzIPN	2,4,6-Collidine (1)	CH_3CN	52
20	4CzIPN	Et_3N (1)	CH_3CN	0
21	4CzIPN	Pyridine (1)	CH_3CN	65
22	4CzIPN	Pyridine (0.5)	CH_3CN	50
23	4CzIPN	Pyridine (2)	CH_3CN	73
24	4CzIPN	Pyridine (4)	CH_3CN	63
25[f]	4CzIPN	Pyridine (2)	CH_3CN	0
26[g]	4CzIPN	Pyridine (2)	CH_3CN	0
27	4CzIPN	Pyridine (2)	CH_3CN:H_2O (3:1 v/v)	30
28	4CzIPN	Pyridine (2)	DMSO:CH_3CN (1:3, v/v)	74
29	**4CzIPN**	**Pyridine (2)**	**DMSO:CH_3CN (3:1, v/v)**	**77**
30[h]	4CzIPN	Pyridine (2)	DMSO:CH_3CN (3:1, v/v)	55
31[i]	4CzIPN	Pyridine (2)	DMSO:CH_3CN (3:1, v/v)	78

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (1.0 mmol, 5.0 equiv.), photocatalyst (2.5 mol%), HAT catalyst (40 mol%), base and solvent (4 mL) were stirred under irradiation (12 W blue LEDs) at room temperature under open air, 24 h. [b]Isolated yield based on **1a**. [c]Triisoproplysilylthiol (**B**) was used as the HAT catalyst. [d]HAT catalyst **A** (20 mol%). [e]HAT catalyst **A** (30 mol%). [f]Without light. [g]Under Ar (1 atm). [h]12 h. [i]36 h.

3 Experimental procedures

3.1 General procedure for the preparation of 3, 5 and 6

To a tube were added quinoxalin-2(1*H*)-ones **1** (0.2 mmol, 1.0 equiv.), silanes (1.0 mmol, 5.0 equiv), 4CzIPN (4.0 mg, 0.005 mmol, 2.5 mol%), quinuclidine (9.1 mg, 0.08 mmol, 40 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LEDs) at room temperature in the presence of open air for 24 h. The resulting solution was diluted with brine (20 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired products **3**, **5** or **6**.

3.2 Gram-scale synthesis of 3a

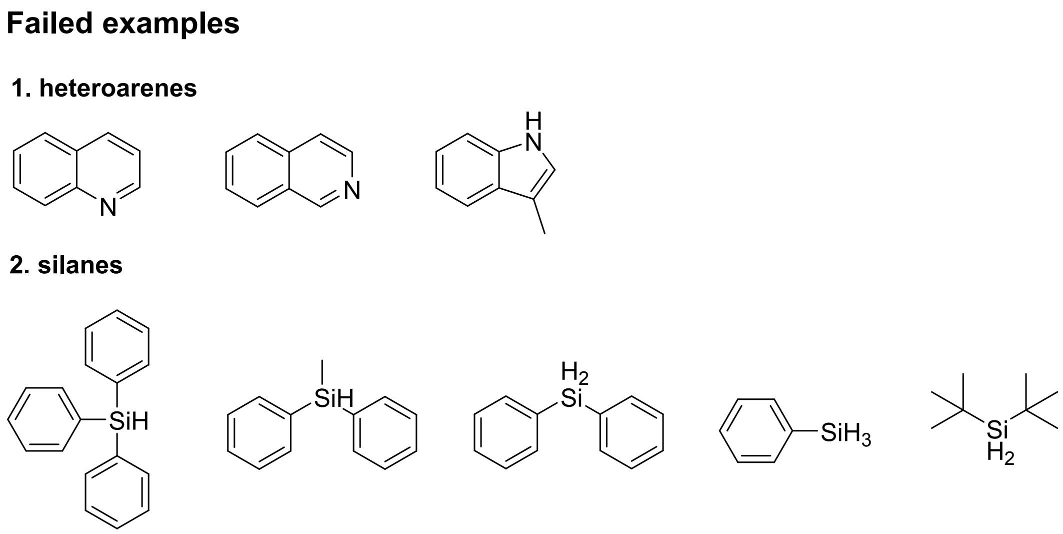
To a tube were added 1-methylquinoxalin-2(1*H*)-one (0.96 g, 6.0 mmol, 1.0 equiv), *tert*-butyldimethylsilane (4.95 mL, 30.0 mmol, 5.0 equiv), 4CzIPN (118.3 mg, 0.15 mmol, 2.5 mol%), quinuclidine (266.7 mg, 2.4 mmol, 40 mol%), pyridine (384 μL, 12 mmol, 2.0 equiv) and CH_3CN (30 mL). The reaction mixture was stirred under irradiation (2 × 30 W blue LEDs) at room temperature in the presence of open air for 60 h. The resulting solution was diluted with brine (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent to afford the desired product **3a** (1.04 g, 63%).

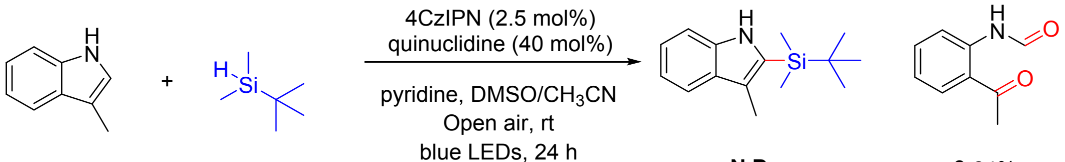
3.3 General procedure for the preparation of 7

A mixture of 1-methylquinoxalin-2(1*H*)-one **3a** (64.0 mg, 0.4 mmol, 1.0 equiv.), $PhI(OAc)_2$ (193.3 mg, 0.6 mmol, 1.5 equiv.), and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 5 mol%) in AcOH (1.0 mL) was stirred at 100 °C for 24 h, followed by the addition of water (1 mL) and heating at 100 °C for another 24 h. After cooling to room temperature, the reaction mixture was poured into aqueous $NaHCO_3$ solution (20 mL) and extract with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with methane dichloride/ethyl acetate (1:1) as eluent to afford the product **7** (37.0 mg, 53% yield, yellow solid).

4 Failed substrates

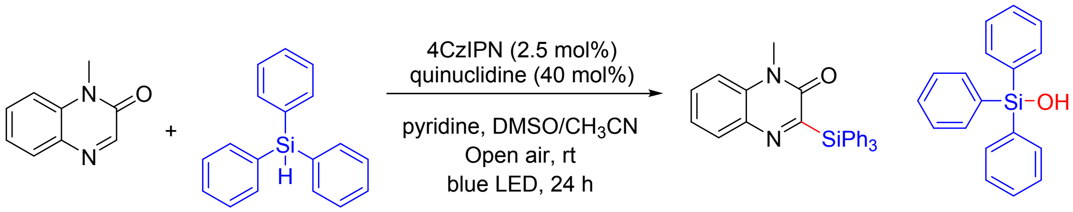
Some substrates did not yield desired products under standard reaction conditions.





2a **N.D.** **9**,64%

To a tube were added 3-methyl-1*H*-indole (26.4 mg, 0.2 mmol, 1.0 equiv.), **2a** (165 μL, 1.0 mmol, 5.0 equiv.), 4CzIPN (3.94 mg, 0.005 mmol, 2.5 mol%), quinuclidine (9.1 mg, 0.08 mmol, 40 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LEDs) at room temperature in the presence of open air for 24 h. After the reaction was stopped, no desired product was detected. The byproduct *N*-(2-acetylphenyl)formamide **(9)** was obtained in 64% yield.



1a **N.D.** **10**, 71%

To a tube were added **1a** (32.0 mg, 0.2 mmol, 1.0 equiv.), triphenylsilane (260.4 mg, 1.0 mmol, 5.0 equiv.), 4CzIPN (3.94 mg, 0.005 mmol, 2.5 mol%), quinuclidine (9.1 mg, 0.08 mmol, 40 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LEDs) at room temperature in the presence of open air for 24 h. After the reaction was stopped, no desired product was detected. The byproduct triphenylsilanol (**10**) was obtained in 71% yield (isolated yield based on triphenylsilane). Meanwhile, the byproduct **10** was observed through the GC-MS analysis from the reaction solution (Figure S1).

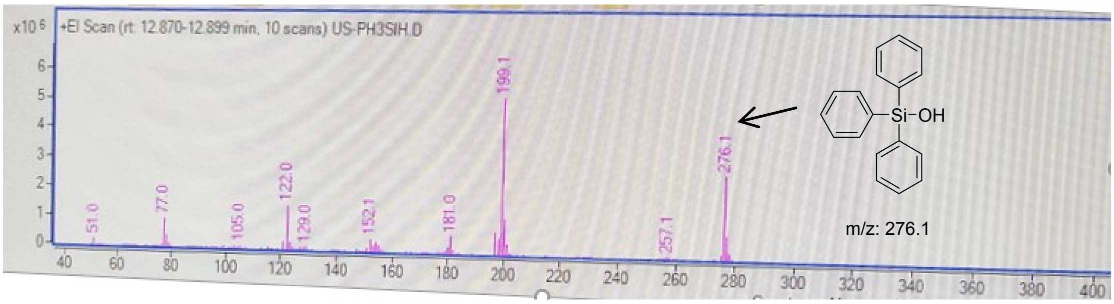


Figure S1 GC-MS analysis of the byproduct **10**.

5 Mechanistic studies

5.1 The LC-MS study of byproducts in the model reaction

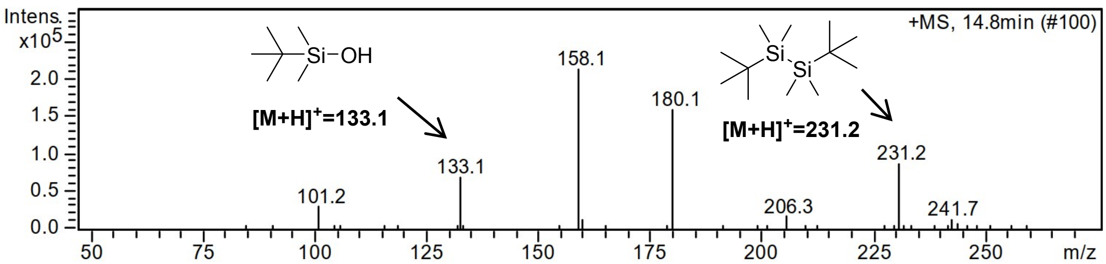


Figure S2 LC-MS analysis of the model reaction.

The model reaction solution was directly used for LC-MS analysis. The formation of *tert*-butyldimethylsilanol and 1,2-di-*tert*-butyl-1,1,2,2-tetramethyldisilane were observed by LC-MS, which indicated that *tert*-butyldimethylsilyl radical was formed in this process.

5.2 Stern-Volmer quenching experiments

Ex: 363 nm, Em: 430 nm–710 nm, PMT voltage: 750 V. Fluorescence studies were operated on an F-7100 fluorescence spectrophotometer (Hitachi).

4CzIPN	Quinuclidine (HAT)-quencher	Ratio (4CzIPN :Quinuclidine)
0.00001 M	0.001 M	1:100
0.00001 M	0.002 M	1:200

0.00001 M	0.004 M	1:400
0.00001 M	0.006 M	1:600
0.00001 M	0.008 M	1:800

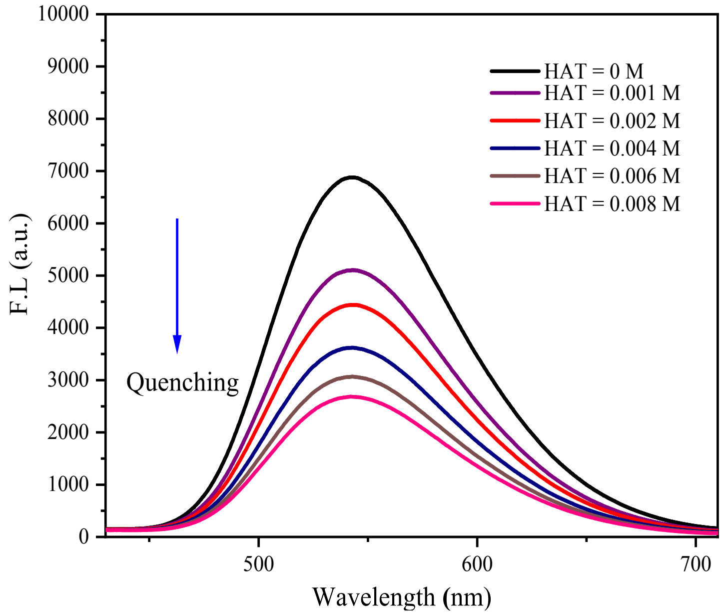


Fig. S3 Emission spectra of 4CzIPN at different concentration of quinuclidine

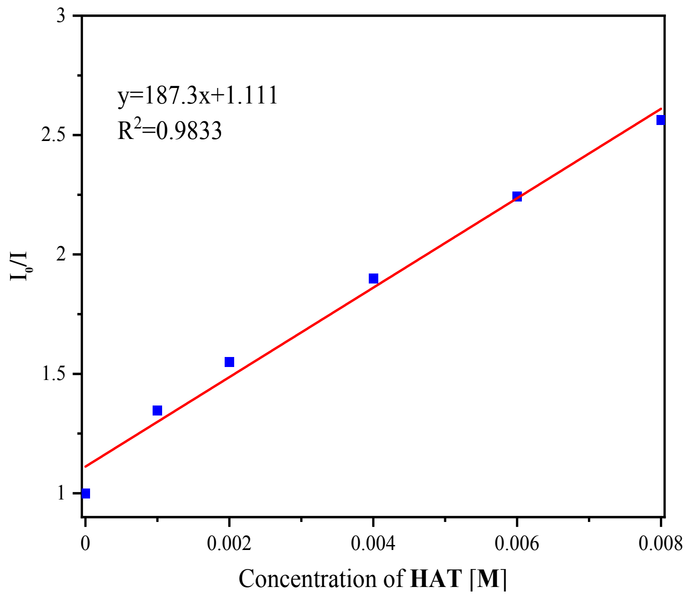
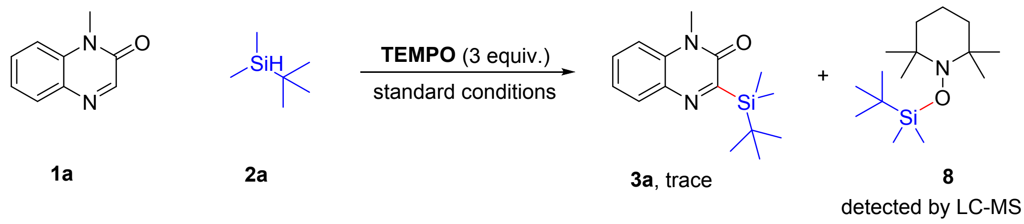


Fig. S4 Stern-Volmer plot of 4CzIPN at different concentrations of quinuclidine

5.3 The radical quenching and trapping experiments



To a tube were added **1a** (32.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (165 μL, 1.0 mmol, 5.0 equiv.), 4CzIPN (3.94 mg, 0.005 mmol, 2.5 mol%), quinuclidine (9.1 mg, 0.08 mmol, 40 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.), TEMPO (94.5 mg, 0.6 mmol, 3.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LED) at room temperature in the presence of open air for 24 h. After the reaction was stopped, no desired product **3a** was detected by TLC and LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **8** was observed through the LC-MS analysis from the reaction solution (Figure S5).

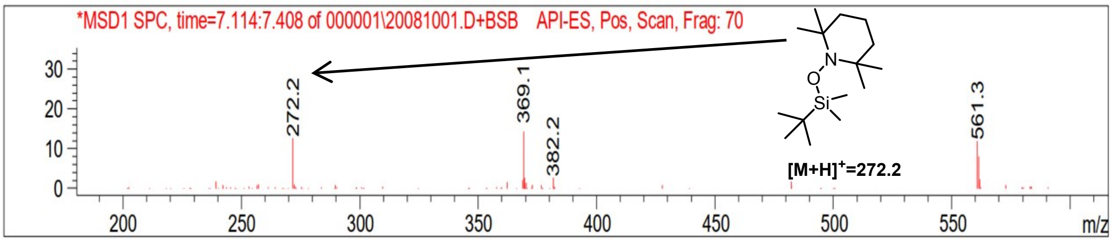
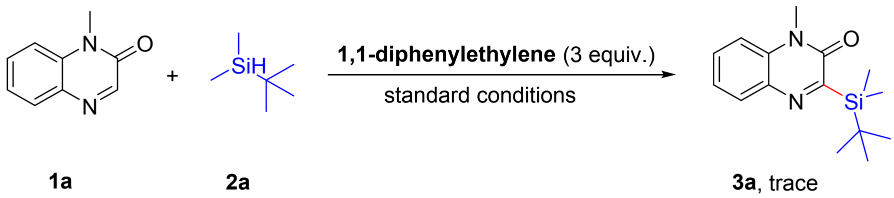
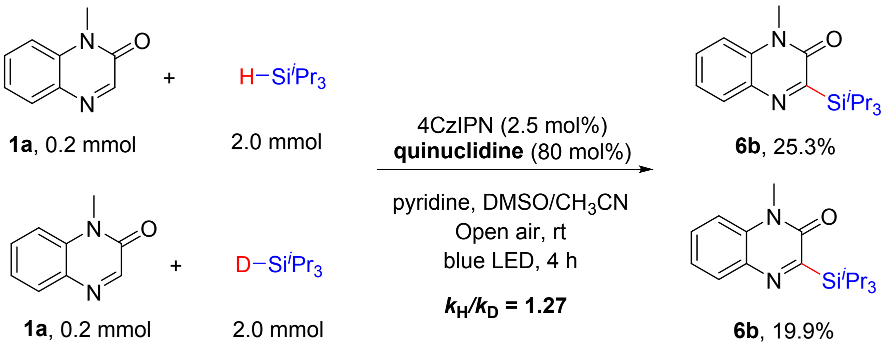


Figure S5 LC-MS analysis of the radical-trapping product **8**.



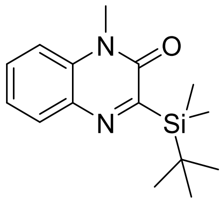
To a tube were added **1a** (32.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (165 μL, 1.0 mmol, 5.0 equiv.), 4CzIPN (3.94 mg, 0.005 mmol, 2.5 mol%), quinuclidine (9.1 mg, 0.08 mmol, 40 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.), 1,1-diphenylethylene (106 μL, 0.6 mmol, 3.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LED) at room temperature in the presence of open air for 24 h. The reaction was completely inhibited, indicating that a radical process might be involved in the catalytic cycle.

5.4 Kinetic isotope effect experiment

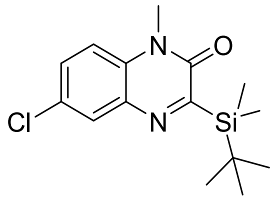


Triisopropylsilane-*d* was prepared according to the procedures of literature.[1] To a tube were added **1a** (32.0 mg, 0.2 mmol, 1.0 equiv.), triisopropylsilane or triisopropylsilane-*d* (410 μL, 2.0 mmol, 10.0 equiv.), 4CzIPN (4.0 mg, 0.005 mmol, 2.5 mol%), quinuclidine (18.2 mg, 0.16 mmol, 80 mol%), pyridine (32 μL, 0.4 mmol, 2.0 equiv.) and DMSO/CH_3CN (3:1, 4 mL). The reaction mixture was stirred under irradiation (12 W blue LEDs) at room temperature in the presence of open air for 4 h. The two reaction mixtures were separately isolated by flash silica gel column chromatography (petroleum ether/EtOAc = 30/1) to give **6b** in 25.3% and 19.9% yields, respectively. The value of k_H/k_D (1.27) from two parallel reactions indicated that Si−H bond cleavage might not be the kinetically rate-determining step in this reaction.

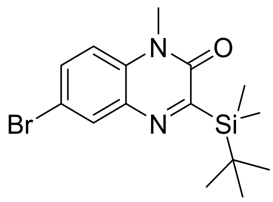
6 Experimental data for the products 3, 5, 6 and 7



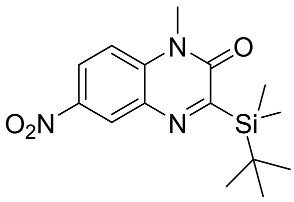
3-(*tert*-Butyldimethylsilyl)-1-methylquinoxalin-2(1*H*)-one (**3a**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (42.2 mg, 77% yield). mp 81−83 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.94 (dd, J = 8.0, 1.6 Hz, 1H), 7.55−7.51 (m, 1H), 7.34−7.27 (m, 2H), 3.64 (s, 3H), 1.05 (s, 9H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.0, 157.0, 134.3, 132.9, 130.8, 130.5, 123.0, 113.5, 28.4, 27.1, 17.7, -5.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{23}N_2OSi^+$ 275.1574; Found 275.1579.



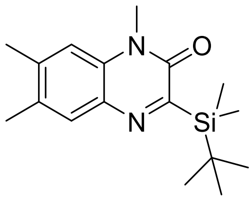
3-(*tert*-Butyldimethylsilyl)-6-chloro-1-methylquinoxalin-2(1*H*)-one (**3b**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (44.4 mg, 72% yield). mp 112−114 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.93 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 8.9, 2.4 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 3.63 (s, 3H), 1.03 (s, 9H), 0.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 174.0, 156.6, 134.6, 131.6, 130.4, 130.1, 128.4, 114.7, 28.5, 27.0, 17.7, -5.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{22}ClN_2OSi^+$ 309.1184; Found 309.1182.



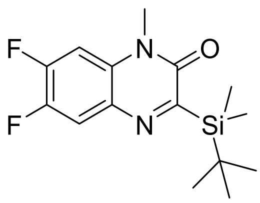
6-Bromo-3-(*tert*-butyldimethylsilyl)-1-methylquinoxalin-2(1*H*)-one (**3c**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (33.1 mg, 47% yield). mp 109−111 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.11 (d, J = 2.4 Hz, 1H), 7.63 (dd, J = 8.8, 2.3 Hz, 1H), 7.18 (d, J = 8.9 Hz, 1H), 3.63 (s, 3H), 1.03 (s, 9H), 0.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.0, 156.6, 134.9, 133.2, 133.1, 132.1, 115.6, 115.0, 28.5, 27.0, 17.7, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}BrN_2OSi^+$ 353.0679; Found 353.0682.



3-(*tert*-Butyldimethylsilyl)-1-methyl-6-nitroquinoxalin-2(1*H*)-one (**3d**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (25.5 mg, 40% yield). mp 187−189 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.81−8.80 (m, 1H), 8.40 (dd, J = 9.2, 2.6 Hz, 1H), 7.40 (d, J = 9.2 Hz, 1H), 3.70 (s, 3H), 1.04 (s, 9H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.9, 156.4, 142.9, 137.7, 133.0, 126.4, 125.0, 114.2, 29.0, 27.0, 17.7, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}N_3O_3Si^+$ 320.1425; Found 320.1424.

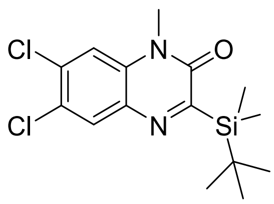


3-(*tert*-Butyldimethylsilyl)-1,6,7-trimethylquinoxalin-2(1*H*)-one (**3e**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (46.5 mg, 77% yield). mp 89−91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (s, 1H), 7.06 (s, 1H), 3.63 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H), 1.04 (s, 9H), 0.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.0, 157.2, 140.4, 132.9, 131.9, 130.9, 130.9, 114.0, 28.3, 27.1, 20.6, 19.1, 17.7, -5.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}N_2OSi^+$ 303.1887; Found 303.1888.

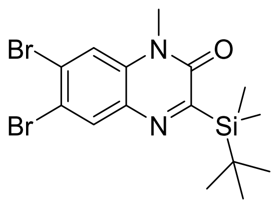


3-(*tert*-Butyldimethylsilyl)-6,7-difluoro-1-methylquinoxalin-2(1*H*)-one (**3f**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v).

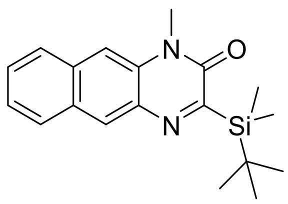
Yellow solid (40.3 mg, 65% yield). mp 92−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77−7.73 (m, 1H), 7.11−7.06 (m, 1H), 3.60 (s, 3H), 1.02 (s, 9H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.9 (d, J = 3.6 Hz), 156.5, 151.7 (dd, J = 253.6, 14.4 Hz), 146.3 (dd, J = 246.6, 14.0 Hz), 130.5 (dd, J = 9.0, 2.9 Hz), 130.2 (dd, J = 9.1, 1.8 Hz), 118.3 (dd, J = 17.5, 2.3 Hz), 102.0 (d, J = 22.9 Hz), 28.9, 27.0, 17.6, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}F_2N_2OSi^+$ 311.1386; Found 311.1383.



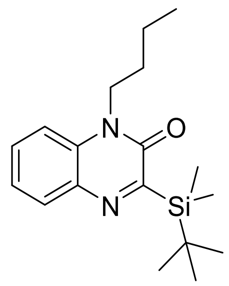
3-(*tert*-Butyldimethylsilyl)-6,7-dichloro-1-methylquinoxalin-2(1*H*)-one (**3g**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (43.8 mg, 64% yield). mp 121−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (t, J = 1.4 Hz, 1H), 7.37 (s, 1H), 3.60 (s, 3H), 1.02 (s, 9H), 0.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.3, 156.3, 134.5, 133.1, 132.4, 131.5, 126.8, 115.0, 28.2, 27.0, 17.7, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}Cl_2N_2OSi^+$ 343.0795; Found 343.0796.



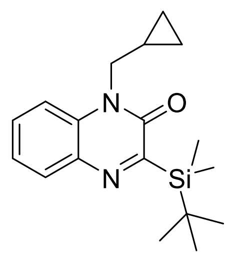
6,7-Dibromo-3-(*tert*-butyldimethylsilyl)-1-methylquinoxalin-2(1*H*)-one (**3h**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (26.8 mg, 31% yield). mp 181−183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (s, 1H), 7.57 (s, 1H), 3.60 (s, 3H), 1.02 (s, 9H), 0.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.6, 156.3, 134.7, 133.8, 132.9, 126.8, 118.2, 118.2, 28.6, 27.0, 17.7, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}Br_2N_2OSi^+$ 430.9784; Found 430.9786.



3-(*tert*-Butyldimethylsilyl)-1-methylbenzo[*g*]quinoxalin-2(1*H*)-one (**3i**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow solid (42.8 mg, 66% yield). mp 185−186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.42 (s, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.55 (t, J = 6.9 Hz, 1H), 7.49−7.44 (m, 2H), 3.67 (s, 3H), 1.10 (s, 9H), 0.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.3, 156.6, 133.9, 133.4, 131.4, 130.1, 129.4, 128.6, 127.9, 127.1, 125.1, 109.6, 28.3, 27.1, 17.7, -5.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}N_2OSi^+$ 325.1731; Found 325.1731.

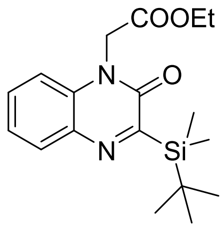


1-Butyl-3-(*tert*-butyldimethylsilyl)quinoxalin-2(1*H*)-one (**3j**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow oil (44.9 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 7.9, 1.6 Hz, 1H), 7.56−7.51 (m, 1H), 7.33−7.29 (m, 2H), 4.21−4.17 (m, 2H), 1.77−1.69 (m, 2H), 1.53−1.45 (m, 2H), 1.04 (s, 9H), 1.01 (d, J = 7.4 Hz, 3H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.0, 156.7, 134.6, 132.1, 131.1, 130.4, 122.8, 113.5, 41.4, 29.3, 27.1, 20.4, 17.7, 13.9, -5.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{29}N_2OSi^+$ 317.2044; Found 317.2042.

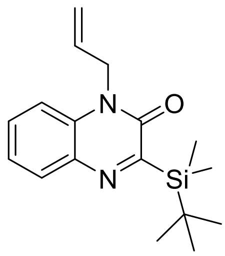


1-(*tert*-Butyldimethylsilyl)-1-(cyclopropylmethyl)quinoxalin-2(1*H*)-one (**3k**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Light yellow oil (39.6 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 8.0, 1.6 Hz, 1H), 7.54−7.50 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.31−7.28 (m, 1H), 4.15 (d, J = 7.0 Hz, 2H), 1.32−1.25 (m, 1H), 1.04 (s, 9H), 0.56−0.52 (m, 4H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

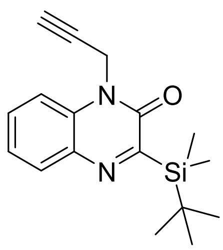
(ppm) 172.2, 156.9, 134.5, 132.3, 131.1, 130.4, 122.8, 113.7, 45.2, 27.1, 17.7, 9.8, 4.1, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2OSi^+$ 315.1887; Found 315.1886.



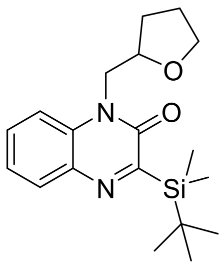
Ethyl 2-(3-(*tert*-butyldimethylsilyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (**3l**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (50.5 mg, 73% yield). mp 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.52−7.47 (m, 1H), 7.34−7.30 (m, 1H), 7.05 (dd, J = 8.4, 1.2 Hz, 1H), 4.98 (s, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.03 (s, 9H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.8, 167.3, 156.3, 134.3, 132.0, 131.2, 130.7, 123.4, 112.9, 62.0, 42.9, 27.0, 17.7, 14.1, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2O_3Si^+$ 347.1785; Found 347.1786.



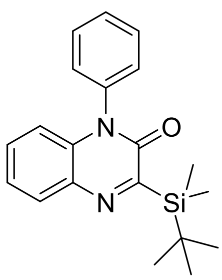
1-Allyl-3-(*tert*-butyldimethylsilyl)quinoxalin-2(1*H*)-one (**3m**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow oil (30.6 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 8.0, 1.6 Hz, 1H), 7.53–7.49 (m, 1H), 7.34–7.30 (m, 1H), 7.26 (dd, J = 8.4, 1.2 Hz, 1H), 6.00–5.90 (m, 1H), 5.28–5.24 (m, 1H), 5.17–5.11 (m, 1H), 4.87–4.85 (m, 2H), 1.04 (s, 9H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.1, 156.5, 134.5, 132.1, 130.9, 130.4, 123.0, 117.7, 114.0, 43.8, 27.1, 17.7, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}N_2OSi^+$ 301.1731; Found 301.1733.



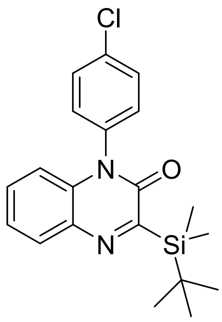
1-(*tert*-Butyldimethylsilyl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (**3n**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow solid (32.8 mg, 55% yield). mp 42−43 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.61–7.56 (m, 1H), 7.45 (dd, J = 8.4, 1.3 Hz, 1H), 7.38–7.34 (m, 1H), 5.01 (d, J = 2.6 Hz, 2H), 2.30 (t, J = 2.5 Hz, 1H), 1.04 (s, 9H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.0, 155.7, 134.5, 131.3, 131.0, 130.6, 123.5, 114.0, 77.1, 73.0, 30.8, 27.0, 17.7, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}N_2OSi^+$ 299.1574; Found 299.1579.



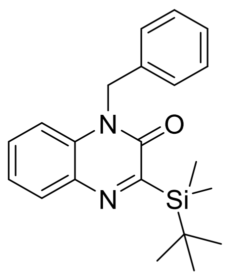
1-(*tert*-Butyldimethylsilyl)-1-((tetrahydrofuran-2-yl)methyl)quinoxalin-2(1*H*)-one (**3o**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow oil (46.1 mg, 67% yield). H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.4 Hz, 1H), 7.54−7.48 (m, 2H), 7.32–7.28 (m, 1H), 4.51−4.47 (m, 1H), 4.36–4.30 (m, 1H), 4.15 (dd, J = 13.9, 7.1 Hz, 1H), 3.92 (dd, J = 14.1, 7.6 Hz, 1H), 3.77−3.71 (m, 1H), 2.13−1.73 (m, 4H), 1.04 (s, 9H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.6, 157.1, 134.5, 132.7, 130.8, 130.3, 123.0, 114.5, 76.9, 68.3, 45.6, 29.6, 27.1, 25.5, 17.7, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{29}N_2O_2Si^+$ 345.1993; Found 345.1996.



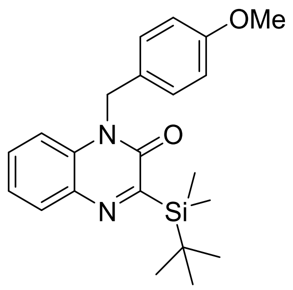
3-(*tert*-Butyldimethylsilyl)-1-phenylquinoxalin-2(1*H*)-one (**3p**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow solid (47.7 mg, 71% yield). mp 110−112 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.03 (dd, J = 7.5, 2.1 Hz, 1H), 7.67−7.63 (m, 2H), 7.59−7.55 (m, 1H), 7.38–7.31 (m, 4H), 6.72 (dd, J = 7.8, 1.8 Hz, 1H), 1.12 (s, 9H), 0.48 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 173.1, 156.6, 135.8, 134.1, 133.6, 130.5, 130.4, 130.2, 129.3, 128.5, 123.3, 115.4, 27.2, 17.8, -5.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{25}N_2OSi^+$ 337.1731; Found 337.1731.



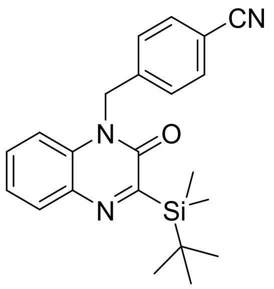
3-(*tert*-Butyldimethylsilyl)-1-(4-chlorophenyl)quinoxalin-2(1*H*)-one (**3q**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow oil (54.0 mg, 73% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.01 (dd, J = 7.8, 1.7 Hz, 1H), 7.62−7.59 (m, 2H), 7.40−7.31 (m, 2H), 7.29−7.26 (m, 2H), 6.71 (dd, J = 8.1, 1.5 Hz, 1H), 1.07 (s, 9H), 0.43 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 173.0, 156.4, 135.3, 134.2, 134.0, 133.2, 130.6, 130.6, 130.3, 130.0, 123.5, 115.0, 27.1, 17.7, -5.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{24}ClN_2OSi^+$ 371.1341; Found 371.1342.



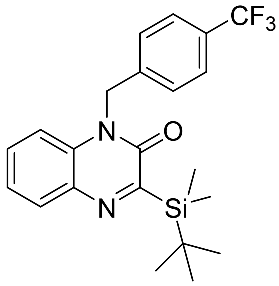
1-Benzyl-3-(*tert*-butyldimethylsilyl)quinoxalin-2(1*H*)-one (**3r**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (53.9 mg, 77% yield). mp 72−73 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.97 (dd, J = 7.9, 1.6 Hz, 1H), 7.44–7.39 (m, 1H), 7.36−7.21 (m, 7H), 5.47 (s, 2H), 1.09 (s, 9H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.2, 157.0, 135.6, 134.6, 132.2, 131.0, 130.5, 128.9, 127.6, 126.8, 123.1, 114.3, 45.2, 27.1, 17.8, -5.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{21}H_{27}N_2OSi^+$ 351.1887; Found 351.1885.



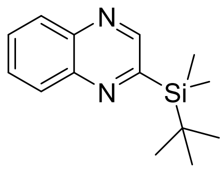
3-(*tert*-Butyldimethylsilyl)-1-(4-methoxybenzyl)quinoxalin-2(1*H*)-one (**3s**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (54.0 mg, 71% yield). mp 60−61 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.96 (dd, J = 8.3, 1.5 Hz, 1H), 7.45−7.41 (m, 1H), 7.30−7.26 (m, 2H), 7.23−7.19 (m, 2H), 6.88−6.85 (m, 2H), 5.40 (s, 2H), 3.78 (s, 3H), 1.09 (s, 9H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.2, 159.0, 157.0, 134.6, 132.2, 131.0, 130.5, 128.3, 127.7, 123.1, 114.3, 114.3, 55.3, 44.6, 27.2, 17.8, -5.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{22}H_{29}N_2O_2Si^+$ 381.1993; Found 381.1994.



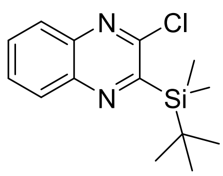
4-((3-(*tert*-Butyldimethylsilyl)-2-oxoquinoxalin-1(2*H*)-yl)methyl)benzonitrile (**3t**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Yellow oil (51.0 mg, 68% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.99 (dd, J = 7.9, 1.6 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.46–7.41 (m, 1H), 7.34–7.30 (m, 3H), 7.08 (dd, J = 8.3, 1.2 Hz, 1H), 5.50 (s, 2H), 1.06 (s, 9H), 0.44 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 172.2, 156.7, 141.0, 134.5, 132.8, 131.8, 131.3, 130.8, 127.5, 123.6, 118.5, 113.7, 111.6, 44.9, 27.1, 17.7, -5.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{22}H_{26}N_3OSi^+$ 376.1840; Found 376.1842.



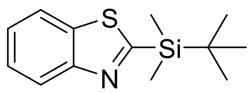
3-(*tert*-Butyldimethylsilyl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (**3u**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (67.7 mg, 81% yield). mp 89−91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.46−7.42(m, 1H), 7.36−7.30 (m, 3H), 7.13 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.52 (s, 2H), 1.08 (s, 9H), 0.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 172.3, 156.8, 139.6, 134.5, 131.9, 131.2, 130.7, 129.9 (q, *J* = 32.5 Hz), 124.0 (q, *J* = 272.1 Hz), 127.1, 126.0 (q, *J* = 3.8 Hz), 123.4, 113.9, 44.8, 27.1, 17.7, -5.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}F_3N_2OSi^+$ 419.1761; Found 419.1762.



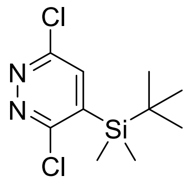
2-(*tert*-Butyldimethylsilyl)quinoxaline (**5a**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Yellow oil (24.9 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.93 (s, 1H), 8.21−8.17 (m, 1H), 8.11−8.07 (m, 1H), 7.78−7.73 (m, 2H), 1.00 (s, 9H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 164.0, 148.4, 143.8, 141.5, 130.1, 129.9, 129.4, 129.4, 26.6, 17.2, -6.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}N_2Si^+$ 245.1469; Found 245.1469.



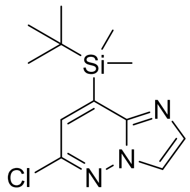
2-(*tert*-Butyldimethylsilyl)-3-chloroquinoxaline (**5b**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Colorless solid (30.6 mg, 55% yield). mp 41−42 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.18−8.14 (m, 1H), 8.00–7.96 (m, 1H), 7.80−7.73 (m, 2H), 1.05 (s, 9H), 0.54 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm) 164.0, 152.3, 141.4, 140.6, 131.0, 129.7, 129.5, 128.2, 26.9, 18.2, -4.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}ClN_2Si^+$ 279.1079; Found 279.1082.



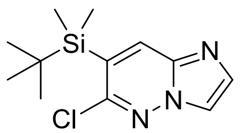
2-(*tert*-Butyldimethylsilyl)benzo[*d*]thiazole (**5c**).[2] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v). Colorless oil (32.4 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 8.1 Hz, 1H), 8.01–7.99 (m, 1H), 7.54–7.50 (m, 1H), 7.45–7.41 (m, 1H), 1.05 (s, 9H), 0.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.9, 156.1, 136.1, 125.7, 125.1, 123.4, 121.5, 26.4, 17.0, -5.4.



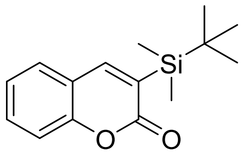
4-(*tert*-Butyldimethylsilyl)-3,6-dichloropyridazine (**5d**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Colorless solid (40.3 mg, 77% yield). mp 98−99 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (s, 1H), 0.96 (s, 9H), 0.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.8, 155.6, 143.1, 137.2, 26.8, 17.9, -4.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}Cl_2N_2Si^+$ 263.0533; Found 263.0536.



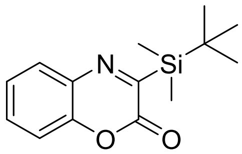
8-(*tert*-Butyldimethylsilyl)-6-chloroimidazo[1,2-*b*]pyridazine (**5ea**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless solid (28.8 mg, 54% yield). mp 96−98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, J = 1.2 Hz, 1H), 7.79 (d, J = 1.3 Hz, 1H), 7.03 (s, 1H), 0.97 (s, 9H), 0.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.2, 141.4, 140.8, 133.9, 124.7, 116.2, 26.9, 17.4, -5.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}ClN_3Si^+$ 268.1031; Found 268.1035.



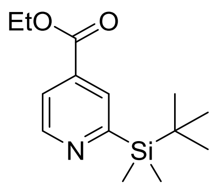
7-(*tert*-Butyldimethylsilyl)-6-chloroimidazo[1,2-*b*]pyridazine (**5eb**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Yellow oil (2.7 mg, 5% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (s, 1H), 7.93 (s, 1H), 7.81 (s, 1H), 0.98 (s, 9H), 0.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 151.6, 141.4, 135.0, 134.4, 128.7, 116.8, 27.0, 17.9, -4.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}ClN_3Si^+$ 268.1031; Found 268.1036.



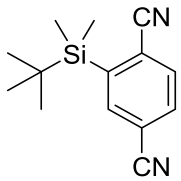
3-(*tert*-Butyldimethylsilyl)-2*H*-chromen-2-one (**5f**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). White solid (22.9 mg, 44% yield). mp 98−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (s, 1H), 7.54–7.48 (m, 2H), 7.32–7.24 (m, 2H), 0.98 (s, 9H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.8, 154.8, 151.6, 131.8, 128.0, 127.7, 124.0, 119.2, 116.6, 27.0, 17.3, -5.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}O_2Si^+$ 261.1305; Found 261.1307.



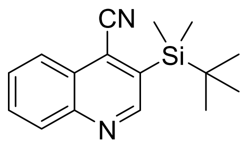
3-(*tert*-Butyldimethylsilyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**5g**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). Yellow solid (11.0 mg, 21% yield). mp 44−45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (dd, J = 7.9, 1.7 Hz, 1H), 7.52–7.48 (m, 1H), 7.39–7.34 (m, 1H), 7.27 (dd, J = 8.2, 1.4 Hz, 1H), 1.04 (s, 9H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.7, 153.6, 146.0, 132.3, 131.4, 129.8, 125.0, 116.5, 26.8, 17.6, -6.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}NO_2Si^+$ 262.1258; Found 262.1259.



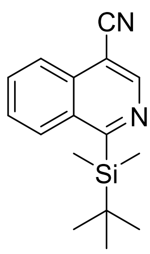
Ethyl 2-(*tert*-butyldimethylsilyl)isonicotinate (**5h**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Light yellow oil (17.5 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.84 (s, 1H), 8.67 (d, J = 5.1 Hz, 1H), 7.52 (d, J = 5.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H), 0.96 (s, 9H), 0.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 168.0, 156.8, 149.9, 145.9, 131.1, 122.3, 61.8, 27.3, 17.9, 14.2, -3.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{24}NO_2Si^+$ 266.1571; Found 266.1572.



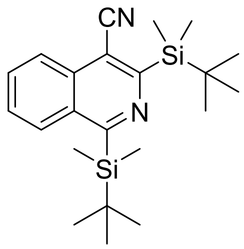
2-(*tert*-Butyldimethylsilyl)terephthalonitrile (**5i**).[2] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Colorless solid (31.5 mg, 65% yield). mp 93−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.75 (dd, J = 8.0, 1.7 Hz, 1H), 0.95 (s, 9H), 0.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 139.4, 134.2, 132.3, 122.0, 119.1, 117.7, 115.4, 26.5, 18.0, -5.1.



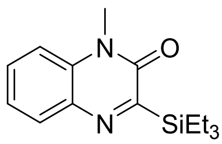
3-(*tert*-Butyldimethylsilyl)quinoline-4-carbonitrile (**5j**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v). White solid (36.5 mg, 68% yield). mp 55−57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.08 (s, 1H), 8.27–8.25 (m, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.86–7.82 (m, 1H), 7.76–7.72 (m, 1H), 0.98 (s, 9H), 0.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.4, 147.6, 135.6, 131.3, 130.0, 129.0, 126.5, 125.1, 125.1, 117.0, 26.5, 18.4, -5.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2Si^+$ 269.1469; Found 269.1465.



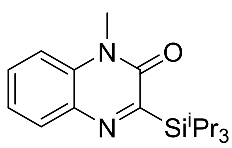
1-(*tert*-Butyldimethylsilyl)isoquinoline-4-carbonitrile (**5ka**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). White solid (30.0 mg, 56% yield). mp 35−36 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.03 (s, 1H), 8.37 (d, J = 8.5 Hz, 1H), 8.21 (d, J = 8.3 Hz, 1H), 7.90–7.86 (m, 1H), 7.77–7.72 (m, 1H), 0.97 (s, 9H), 0.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.4, 146.7, 132.8, 132.7, 131.8, 129.4, 128.3, 124.9, 116.7, 104.7, 27.0, 18.0, -3.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2Si^+$ 269.1469; Found 269.1466.



1,3-Bis(*tert*-butyldimethylsilyl)isoquinoline-4-carbonitrile (**5kb**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v). White solid (14.5 mg, 19% yield). mp 78−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.31 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.3 Hz, 1H), 7.87–7.82 (m, 1H), 7.74–7.70 (m, 1H), 1.01 (s, 9H), 0.96 (s, 9H), 0.58 (s, 1H), 0.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.8, 163.1, 132.4, 131.3, 131.1, 129.1, 128.2, 124.9, 118.2, 111.4, 27.1, 26.8, 18.2, 17.9, -3.0, -4.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{35}N_2Si_2^+$ 383.2333; Found 383.2332.

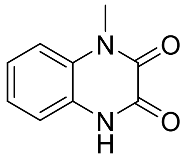


1-Methyl-3-(triethylsilyl)quinoxalin-2(1*H*)-one (**6a**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Orange oil (28.0 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (dd, J = 7.9, 1.5 Hz, 1H), 7.57–7.53 (m, 1H), 7.36−7.28 (m, 2H), 3.66 (s, 3H), 1.07−0.97 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.2, 157.0, 134.5, 132.8, 130.8, 130.5, 123.1, 113.5, 28.3, 7.6, 3.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{23}N_2OSi^+$ 275.1574; Found 275.1575.

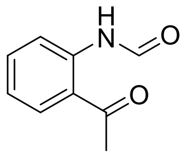


1-Methyl-3-(triisopropylsilyl)quinoxalin-2(1*H*)-one (**6b**). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow solid (41.7 mg, 66%

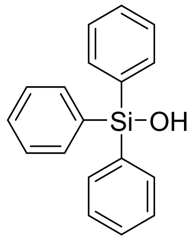
yield). mp 67−69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.36−7.30 (m, 2H), 3.67 (s, 3H), 1.70−1.62 (m, 3H), 1.17 (d, J = 7.5 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.7, 157.0, 134.4, 132.8, 130.8, 130.4, 123.0, 113.5, 28.5, 19.0, 11.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{29}N_2OSi^+$ 317.2044; Found 317.2043.



1-Methyl-1,4-dihydroquinoxaline-2,3-dione (**7**).[3] Yellow solid (37.3 mg, 53% yield). mp 285−286 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.02 (s, 1H), 7.35 (s, 1H), 7.18 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 155.7, 154.1, 127.7, 126.0, 124.0, 123.7, 115.8, 115.5, 30.1.



***N*-(2-acetylphenyl)formamide** (**9**).[4] White solid (28.2 mg, 64% yield). mp 70−71 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.64 (brs, 1H), 8.84–8.64 (m, 1H), 8.50 (brs, 1H), 7.93 (dd, J = 8.0, 1.6 Hz, 1H), 7.59–7.55 (m, 1H), 7.22–7.14 (m, 1H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.9, 160.0, 139.9, 135.2, 131.7, 123.1, 121.9, 121.6, 28.7.



Triphenylsilanol (**10**).[5] White solid (196.0 mg, 71% yield). mp 52−53 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75−7.71 (m, 6H), 7.45−7.40 (m, 8H), 7.37−7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.6, 135.1, 130.0, 127.9.

7 References

(1) R. Zhou, J. Li, H. W. Cheo, R. Chua, G. Zhan, Z. Hou and J. Wu, *Chem. Sci*., 2019, **10**, 7340–7344.

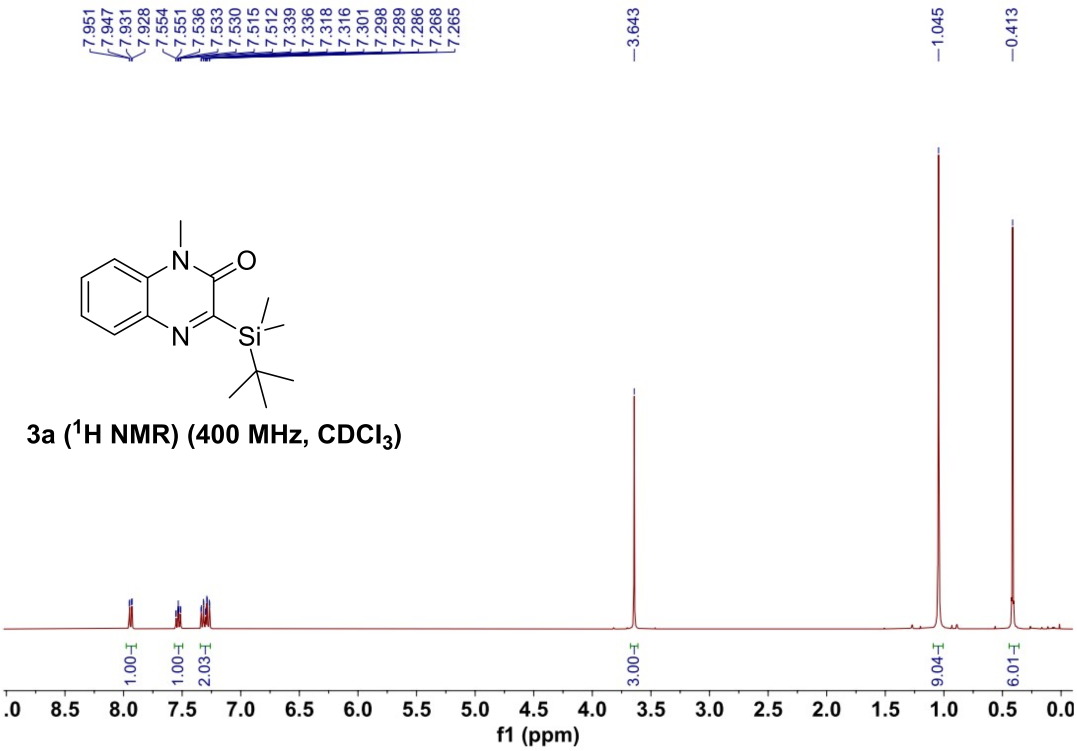
(2) S. Liu, P. Pan, H. Fan, H. Li, W. Wang and Y. Zhang, *Chem. Sci*., 2019, **10**, 3817–3825.

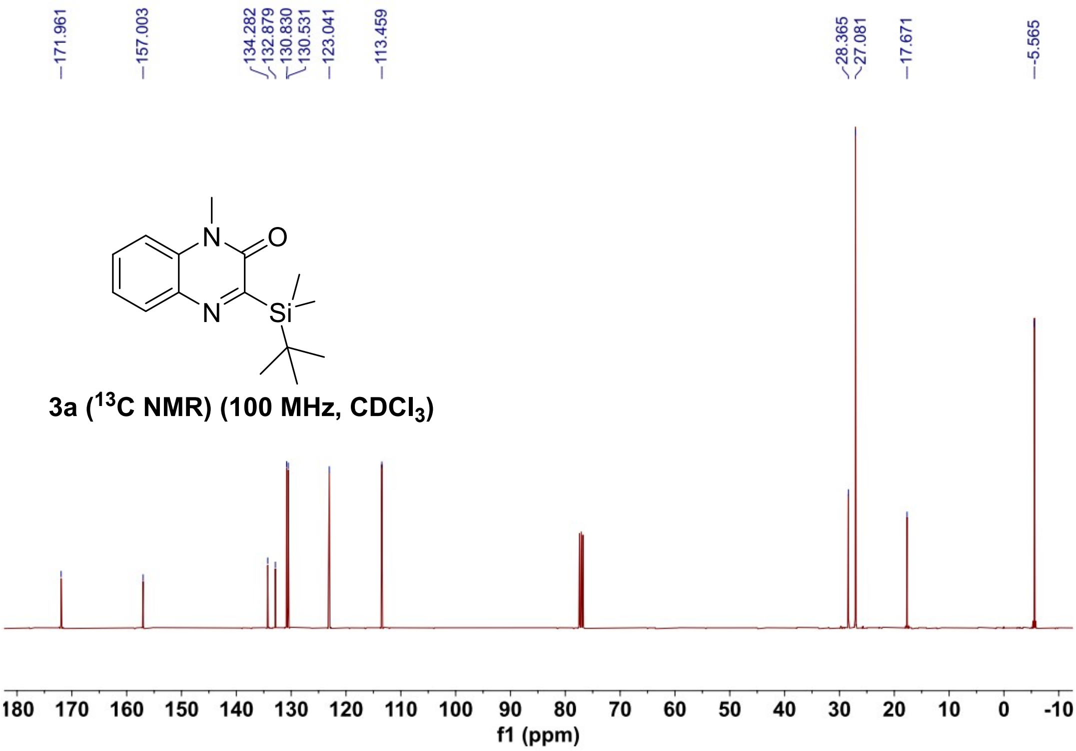
(3) S. Peng, D. Hu, J.-L. Hu, Y.-W. Lin, S.-S. Tang, H.-S. Tang, J.-Y. He, Z. Cao and W.-M. He, *Adv. Synth. Catal*., 2019, **361**, 5721–5726.

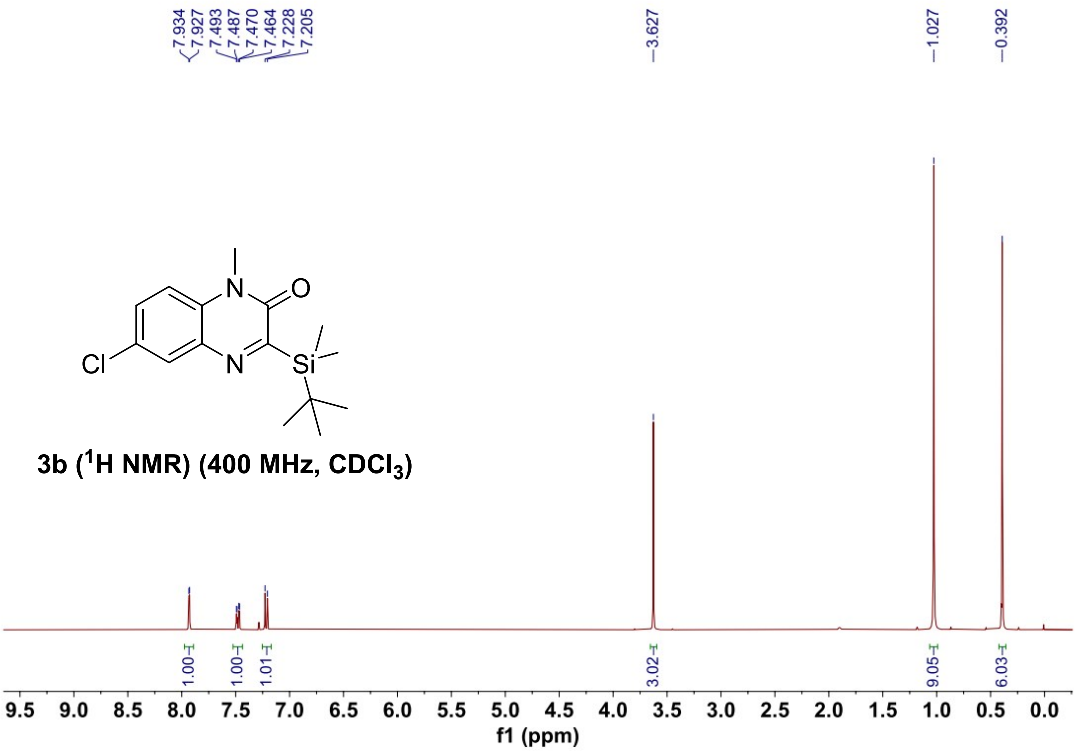
(4) W. Schilling, Y. Zhang, R. Daniel and S. Das, *Chem. Eur. J.*, 2020, **26**, 390–395.

(5) K. Wang, J. Zhou, Y. Jiang, M. Zhang, C. Wang, D. Xue, W. Tang, H. Sun, J. Xiao and C. Li, *Angew. Chem., Int. Ed*., 2019, **58**, 6380–6384.

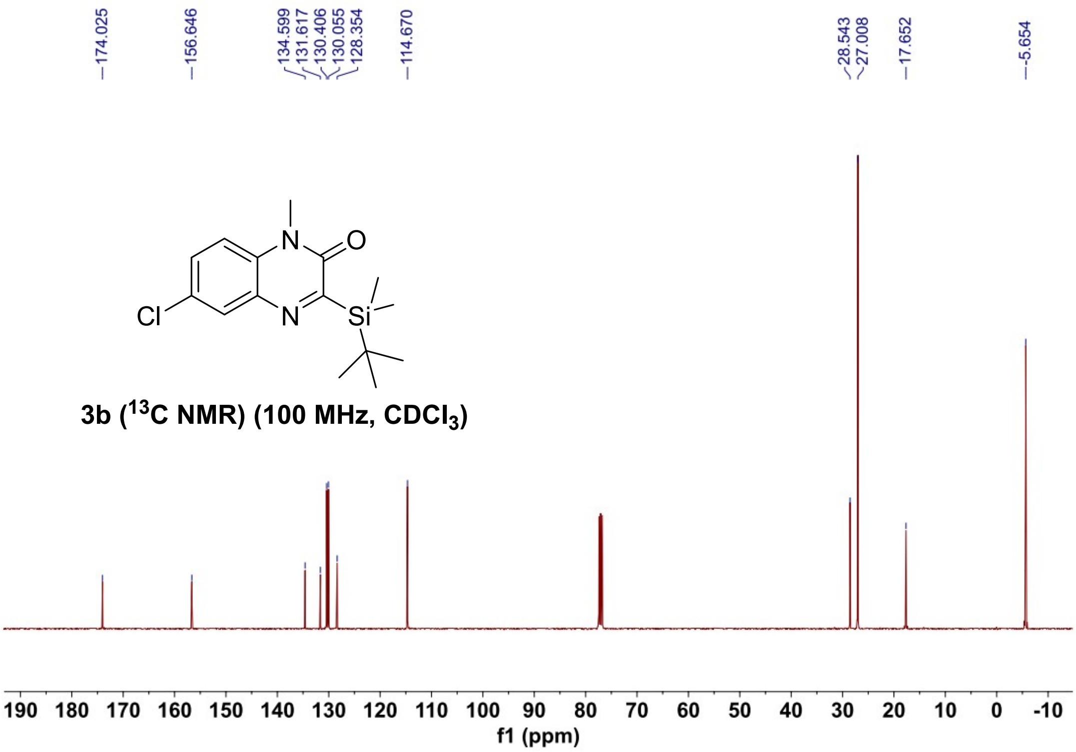
8 ^{1}H and ^{13}C NMR spectra of the products



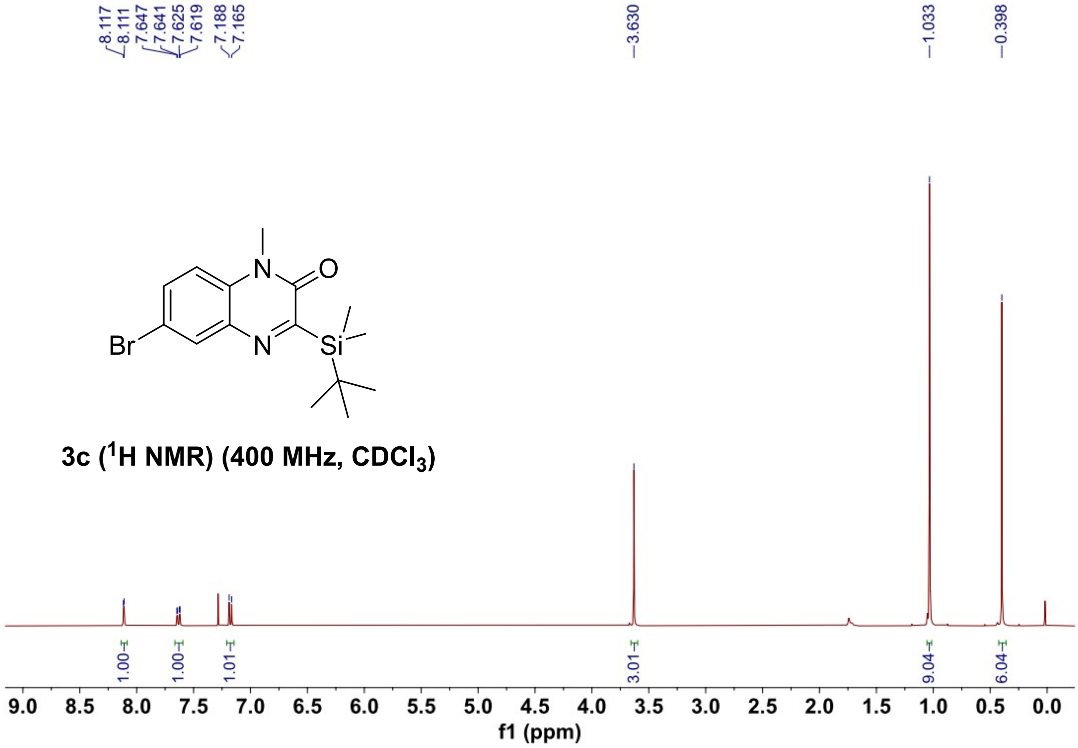




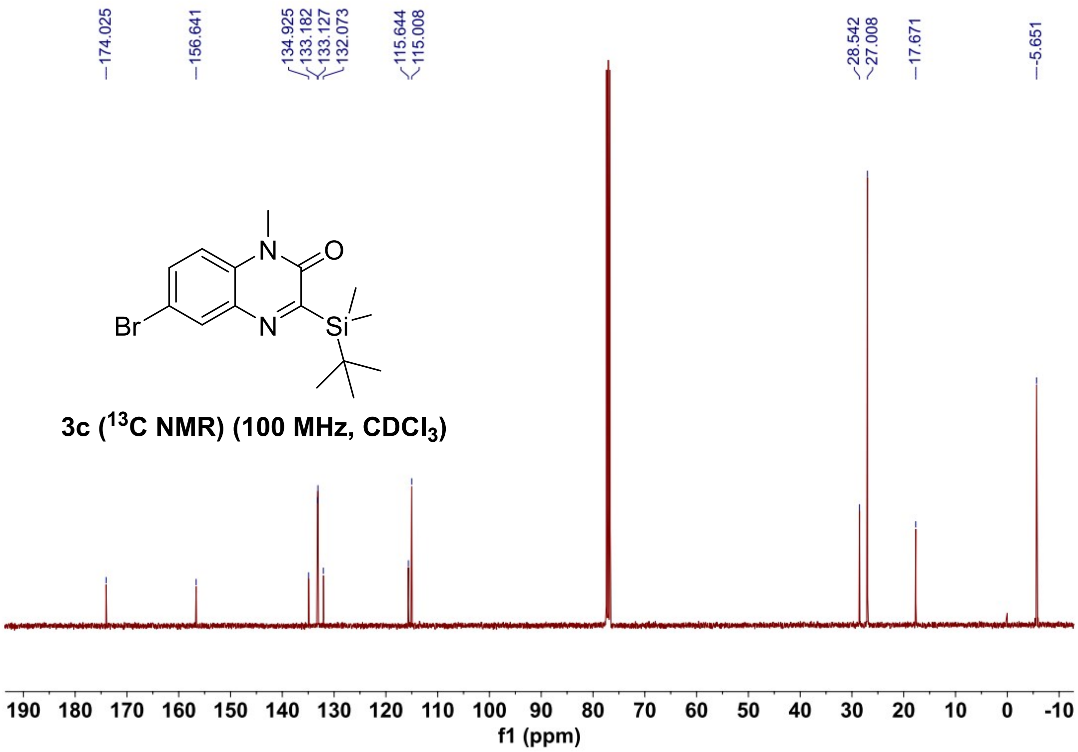
3b (^{1}H NMR) (400 MHz, $CDCl_3$)



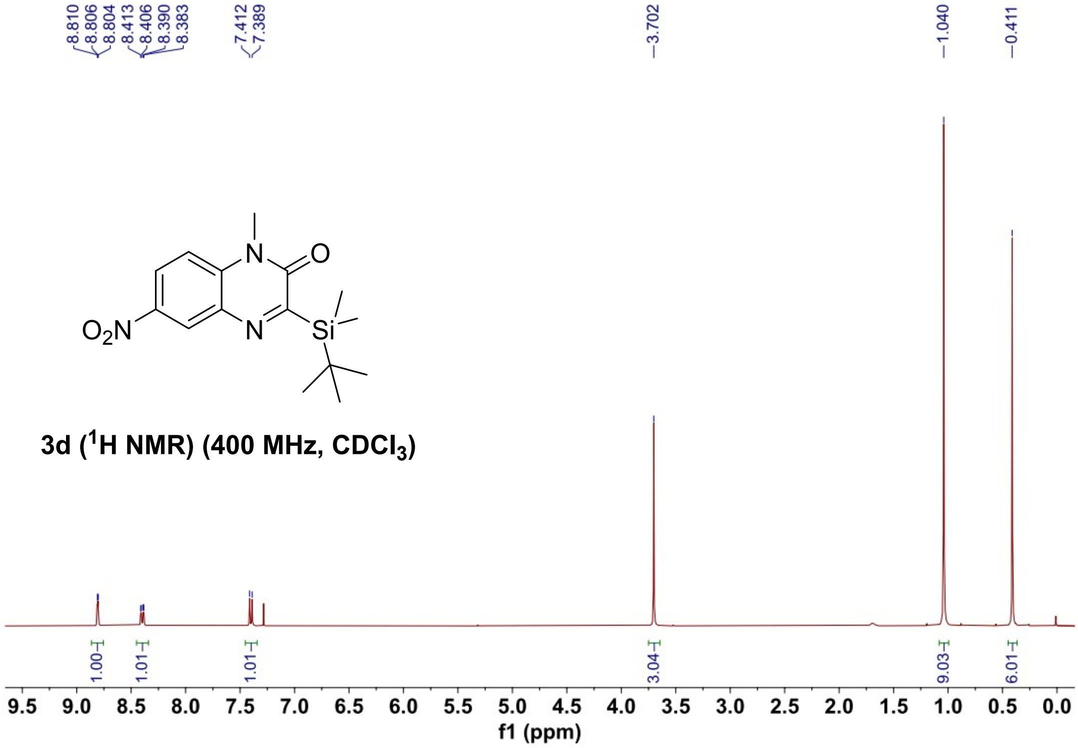
3b (^{13}C NMR) (100 MHz, $CDCl_3$)

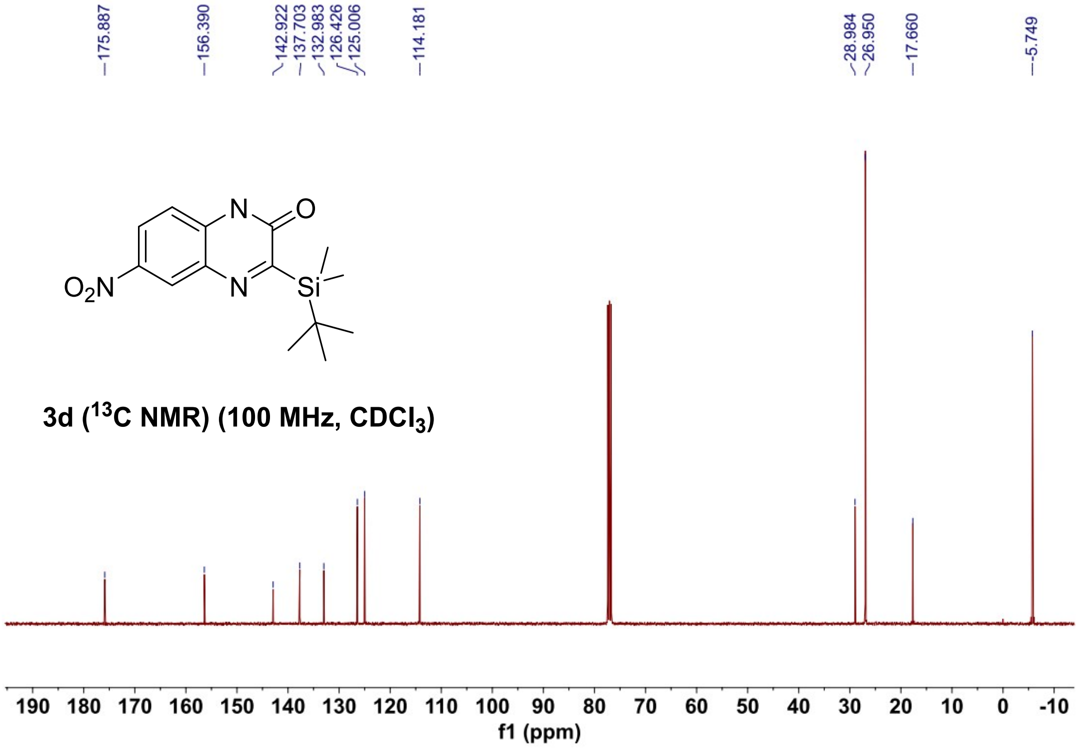


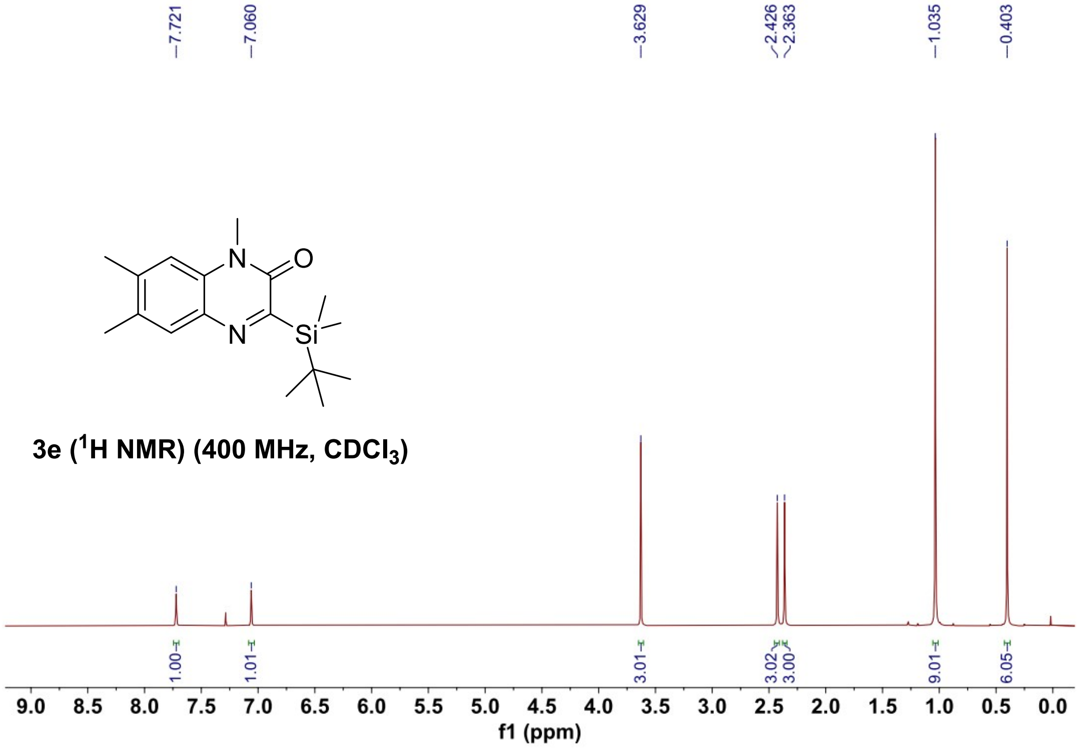
3c (^{1}H NMR) (400 MHz, $CDCl_3$)



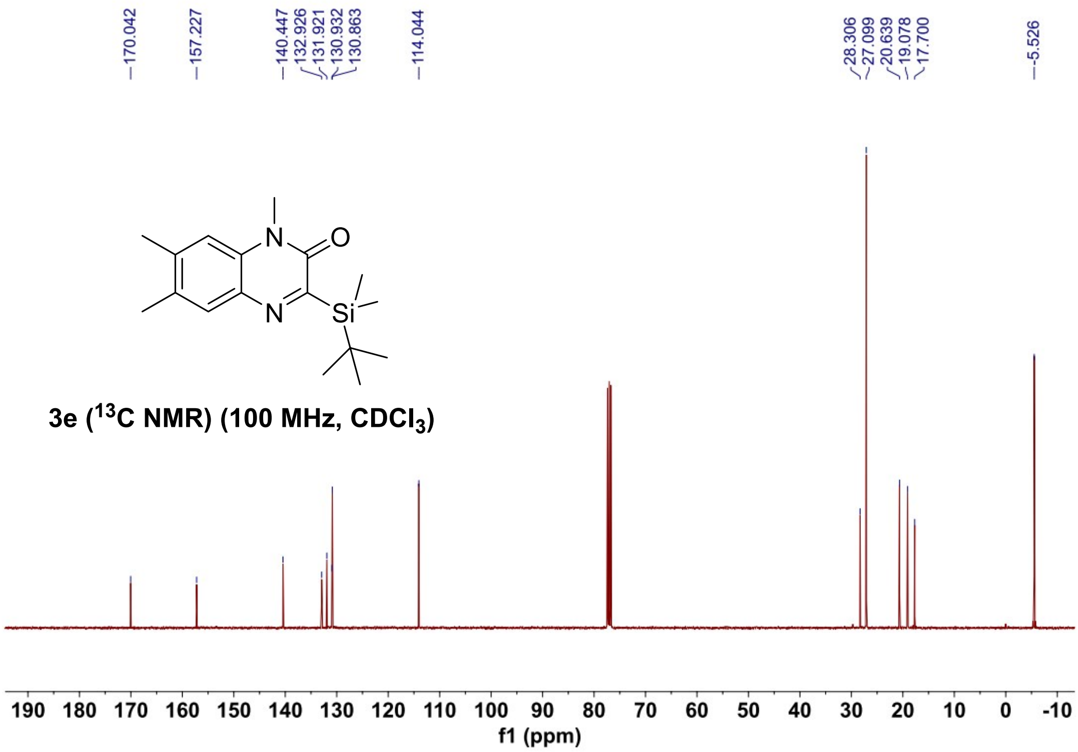
3c (^{13}C NMR) (100 MHz, $CDCl_3$)


8.810
8.806
8.804
8.413
8.406
8.390
8.383
7.412
7.389
3.702
1.040
0.411
O_2N
N
N
O
Si
3d (^{1}H NMR) (400 MHz, $CDCl_3$)
1.00
1.01
1.01
3.04
9.03
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

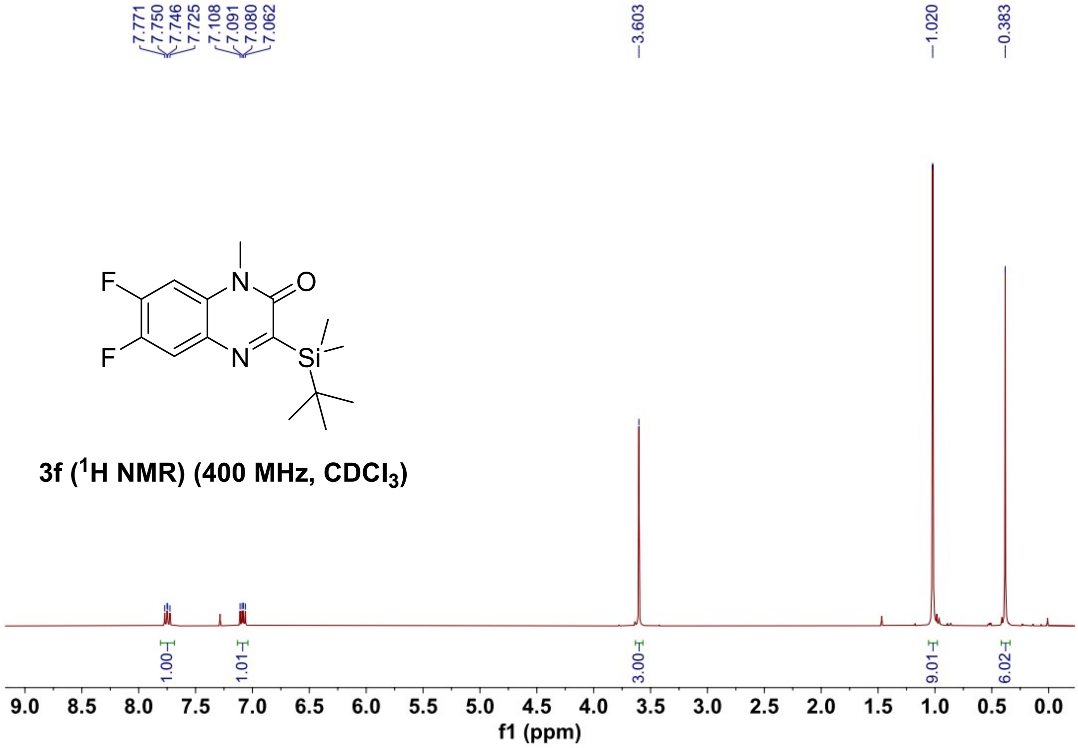

175.887
156.390
142.922
137.703
132.983
126.426
125.006
114.181
28.984
26.950
17.660
-5.749
O_2N
N
N
O
Si
3d (^{13}C NMR) (100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



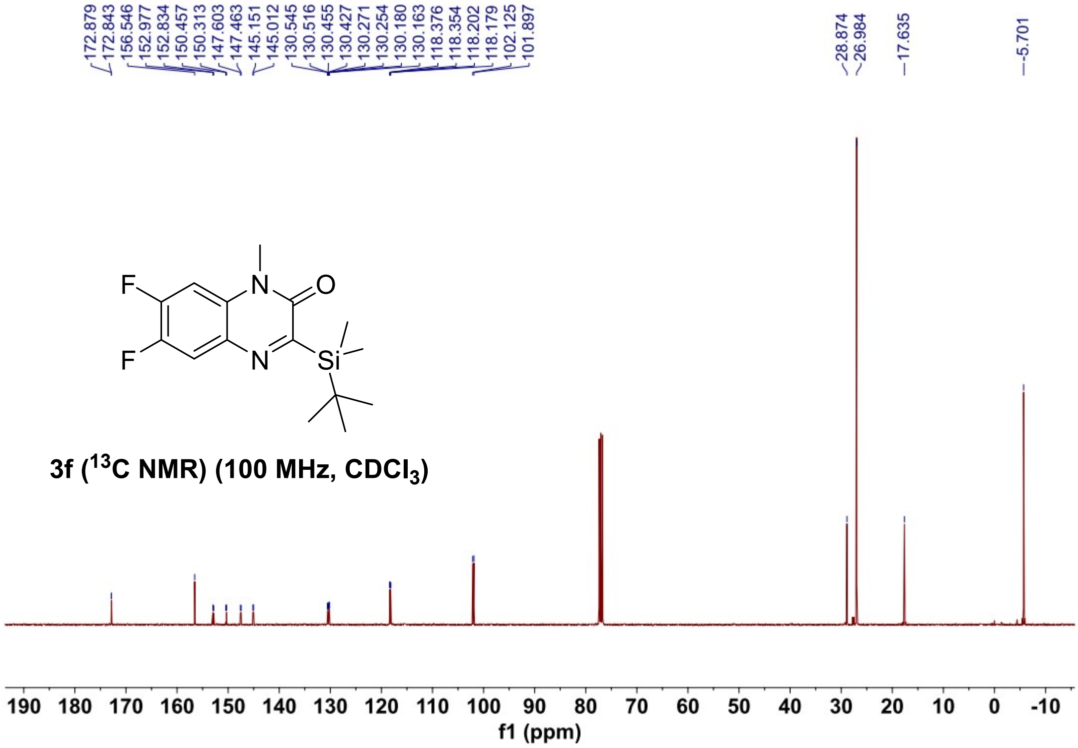
3e (^{1}H NMR) (400 MHz, $CDCl_3$)



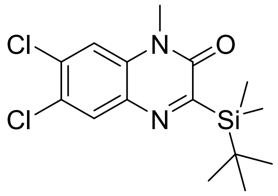
3e (^{13}C NMR) (100 MHz, $CDCl_3$)



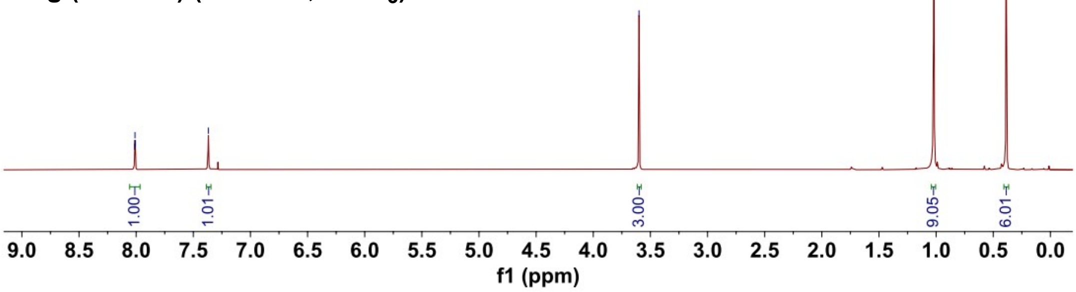
3f (^{1}H NMR) (400 MHz, $CDCl_3$)

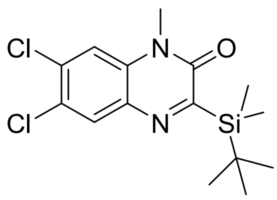


3f (^{13}C NMR) (100 MHz, $CDCl_3$)

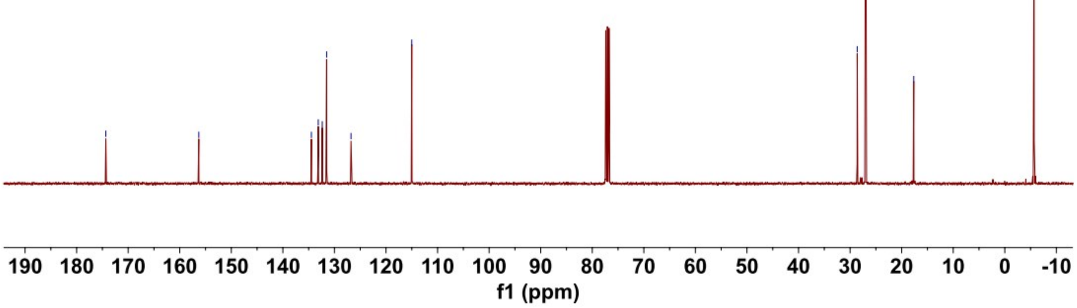


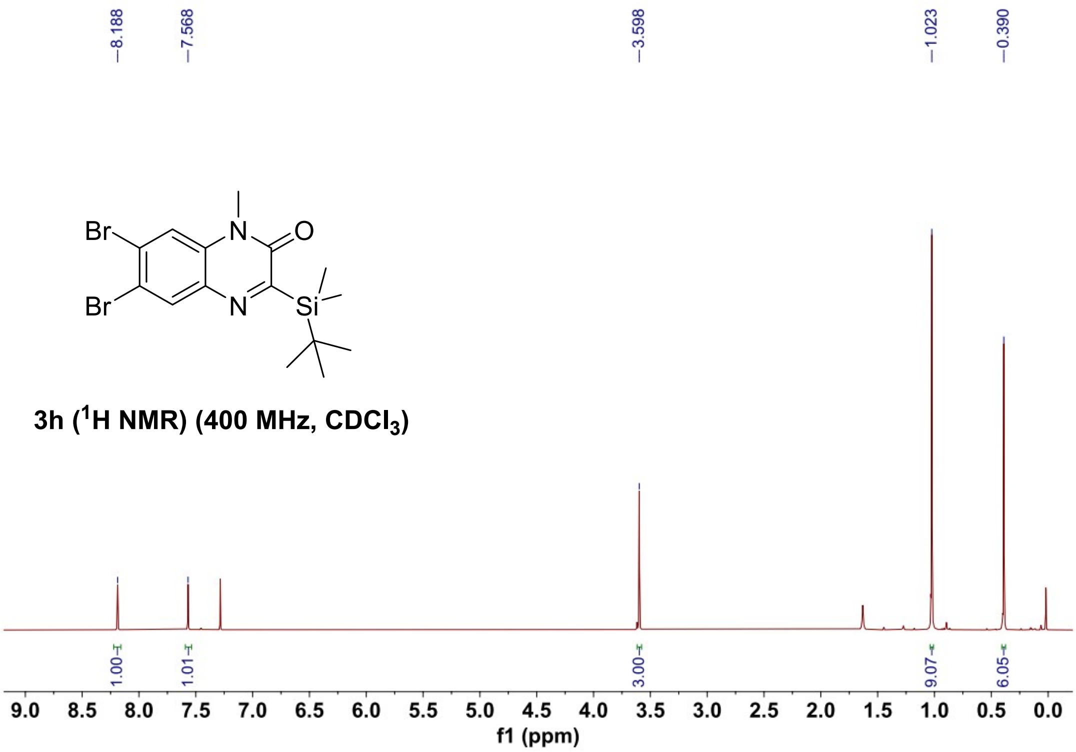
3g (^{1}H NMR) (400 MHz, $CDCl_3$)



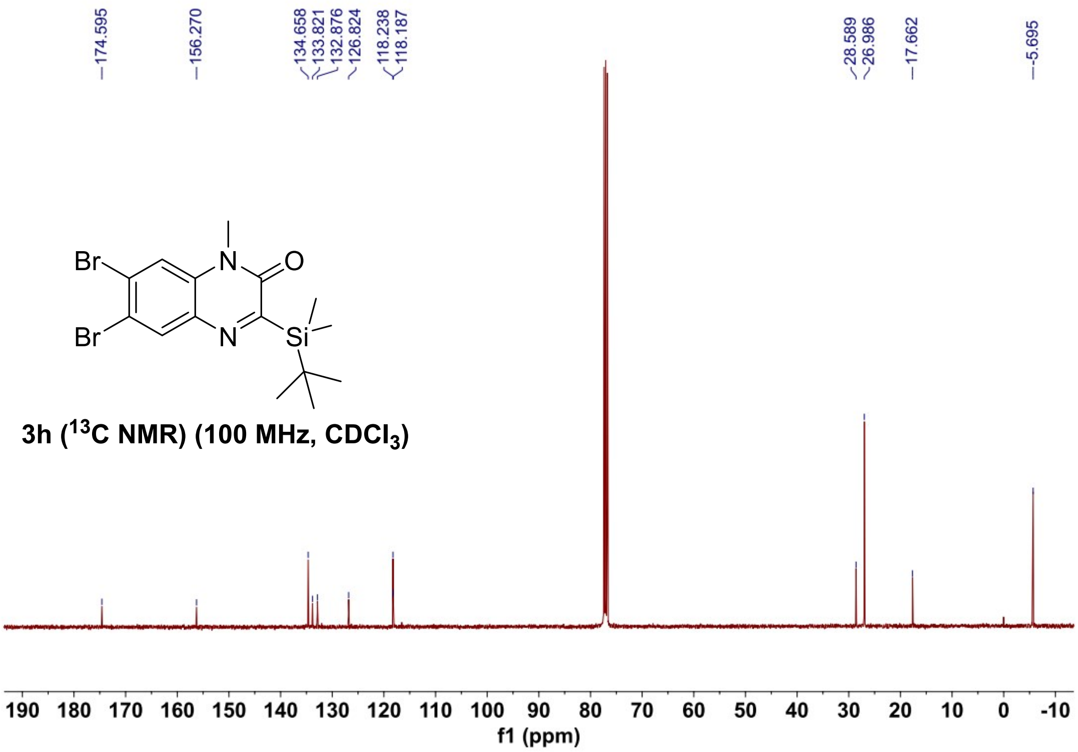


3g (^{13}C NMR) (100 MHz, $CDCl_3$)

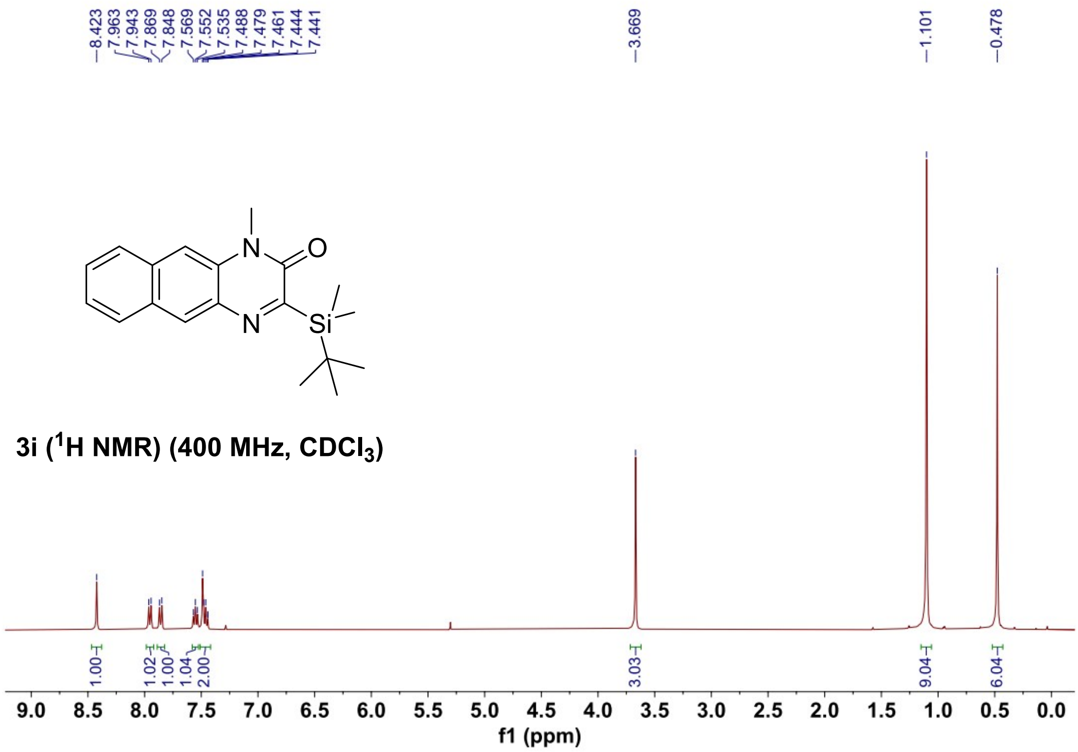




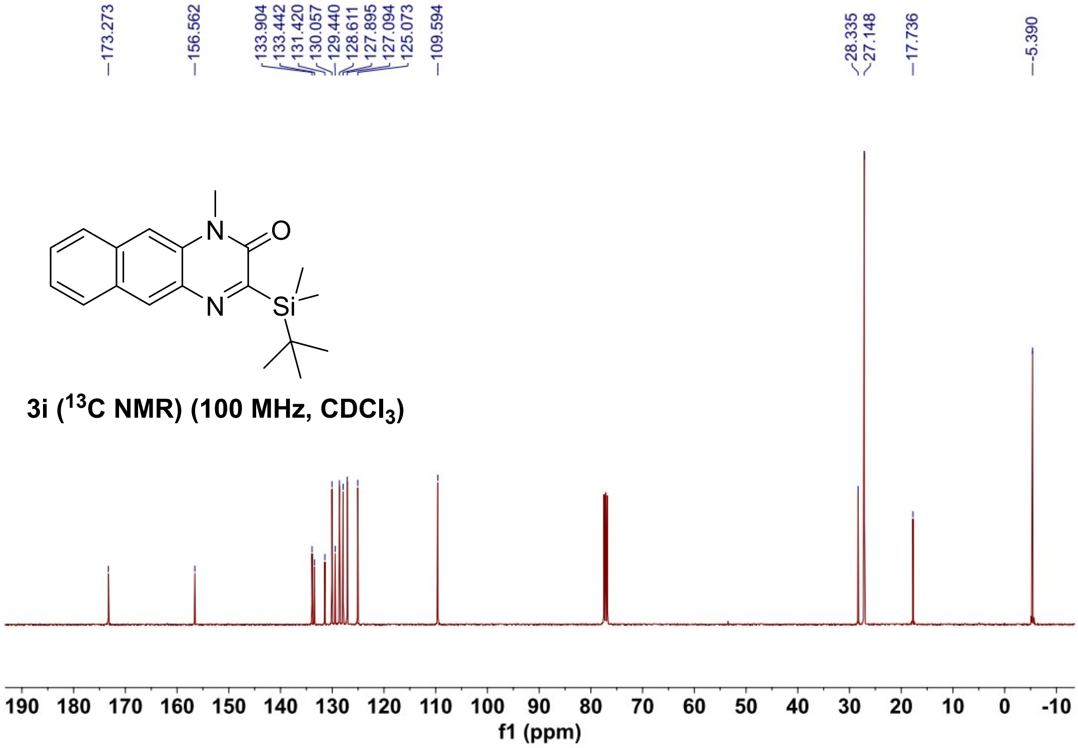
3h (^{1}H NMR) (400 MHz, $CDCl_3$)



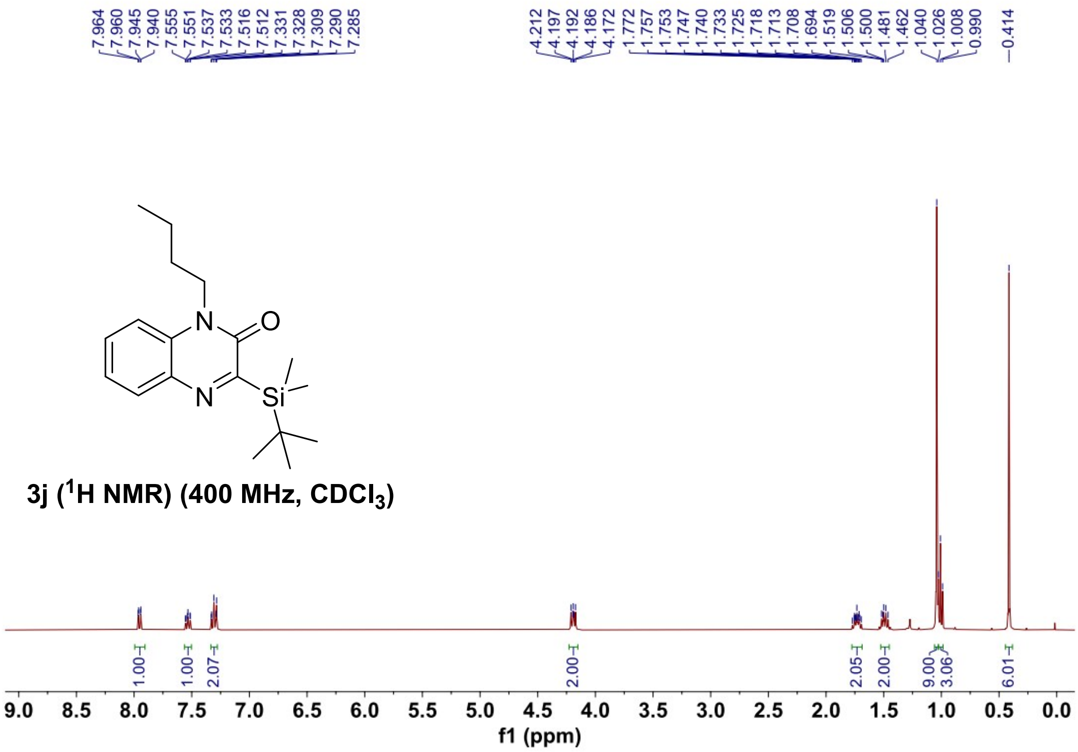
3h (^{13}C NMR) (100 MHz, $CDCl_3$)



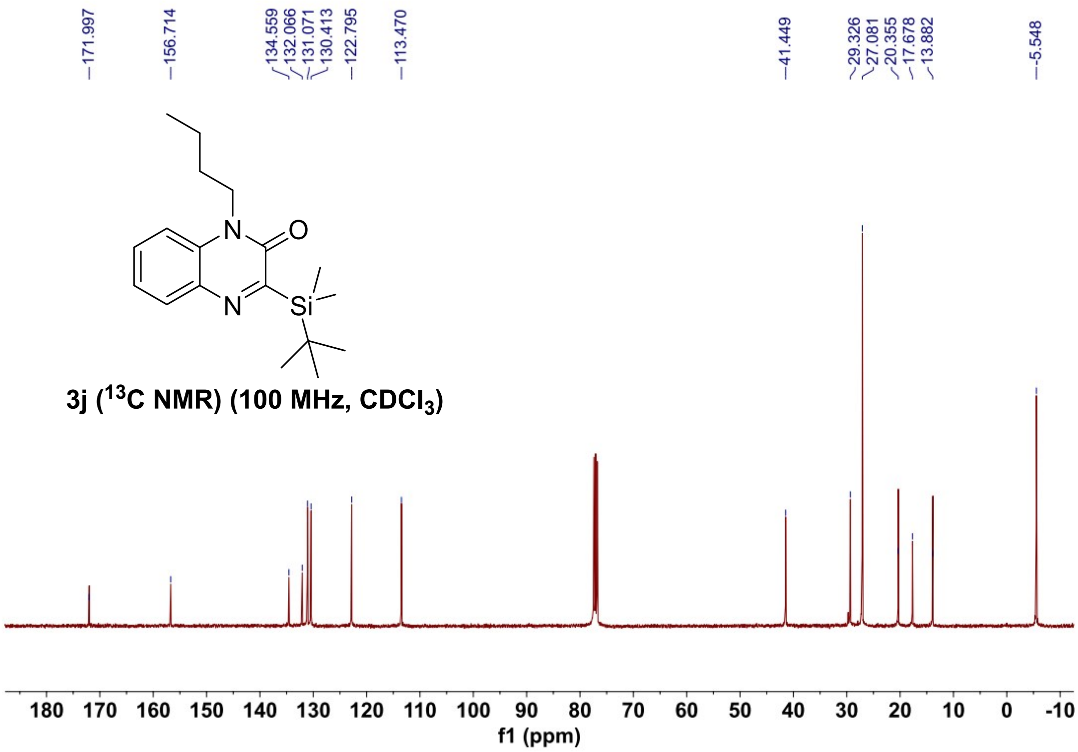
3i (^{1}H NMR) (400 MHz, $CDCl_3$)



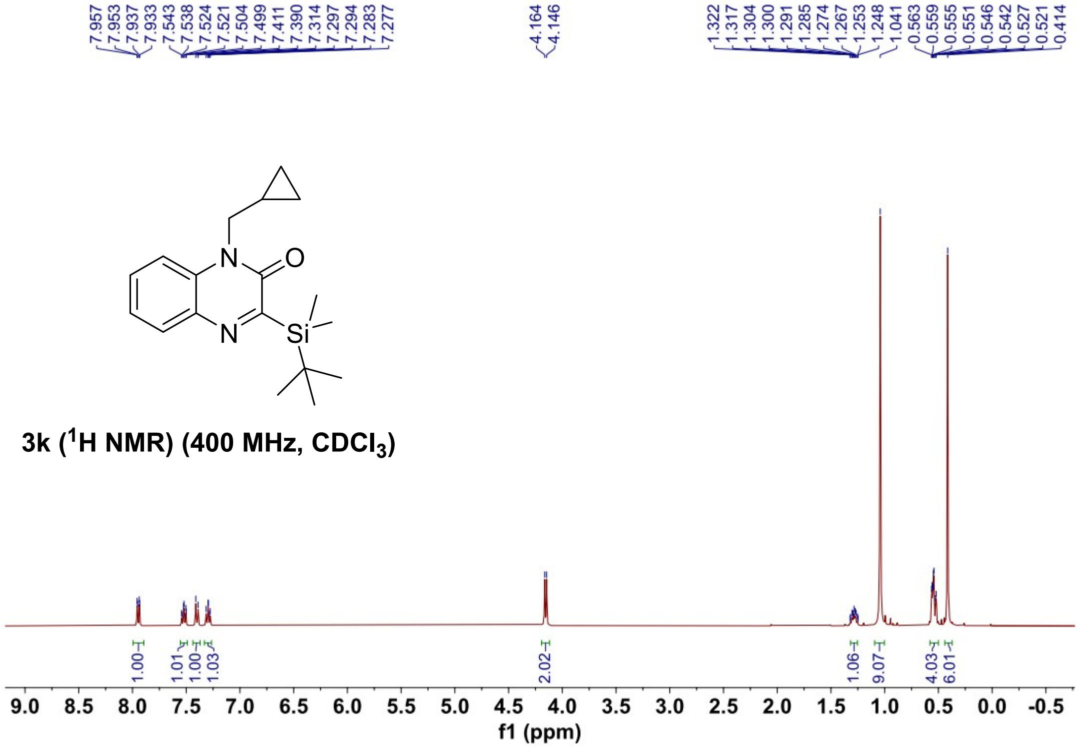
3i (^{13}C NMR) (100 MHz, $CDCl_3$)



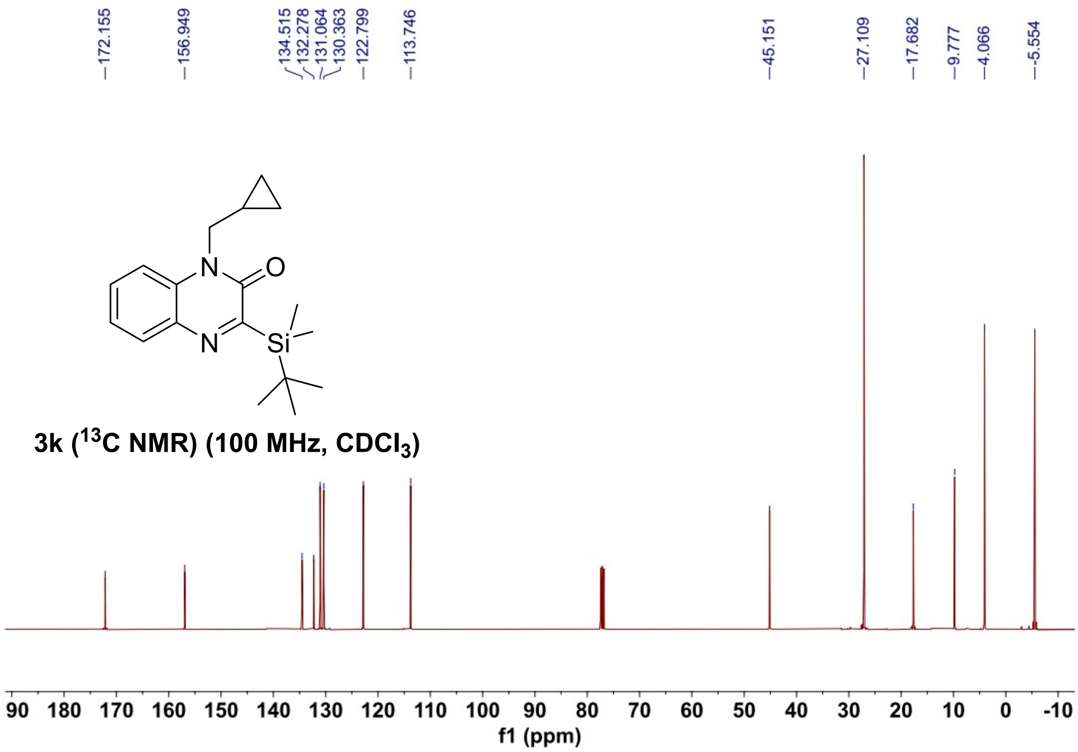
3j (^{1}H NMR) (400 MHz, $CDCl_3$)



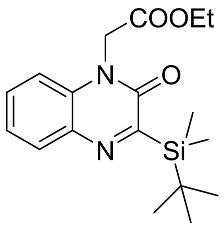
3j (^{13}C NMR) (100 MHz, $CDCl_3$)



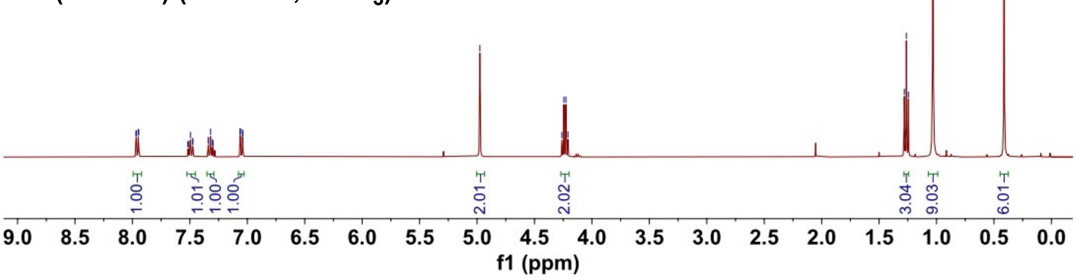
3k (^{1}H NMR) (400 MHz, $CDCl_3$)

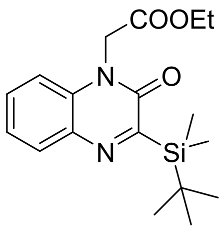


3k (^{13}C NMR) (100 MHz, $CDCl_3$)

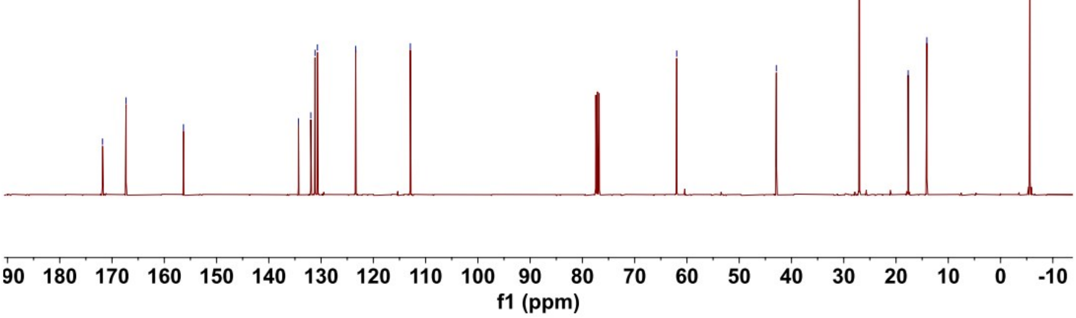


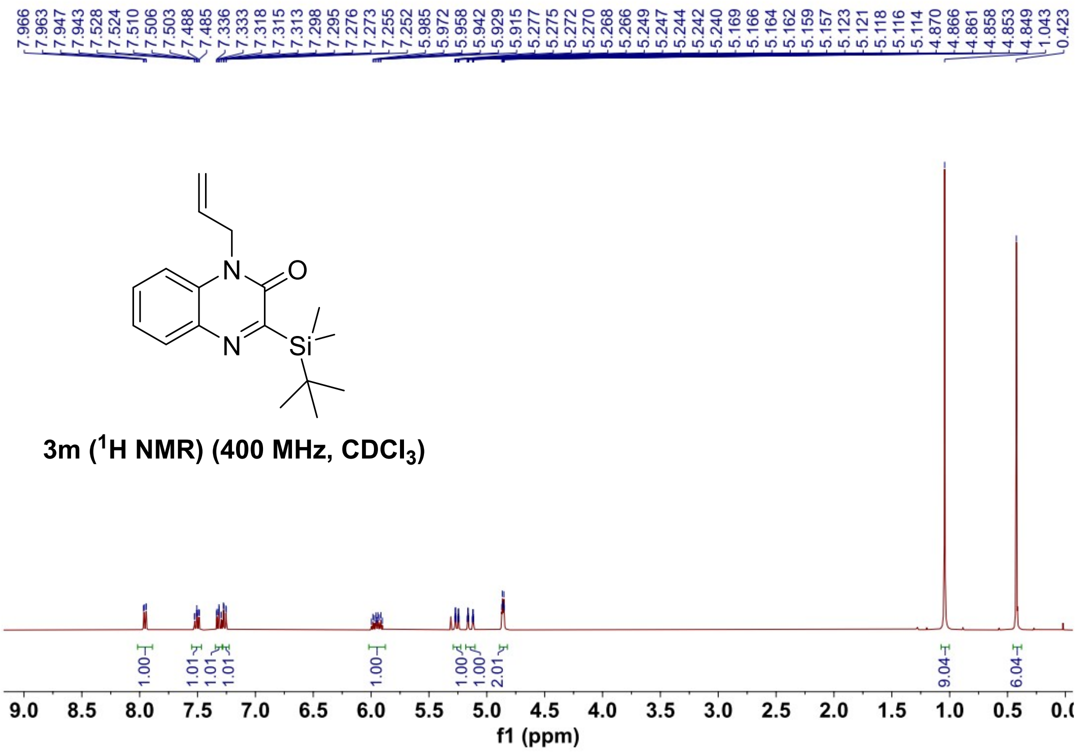
3l (^{1}H NMR) (400 MHz, CDCl$_3$)



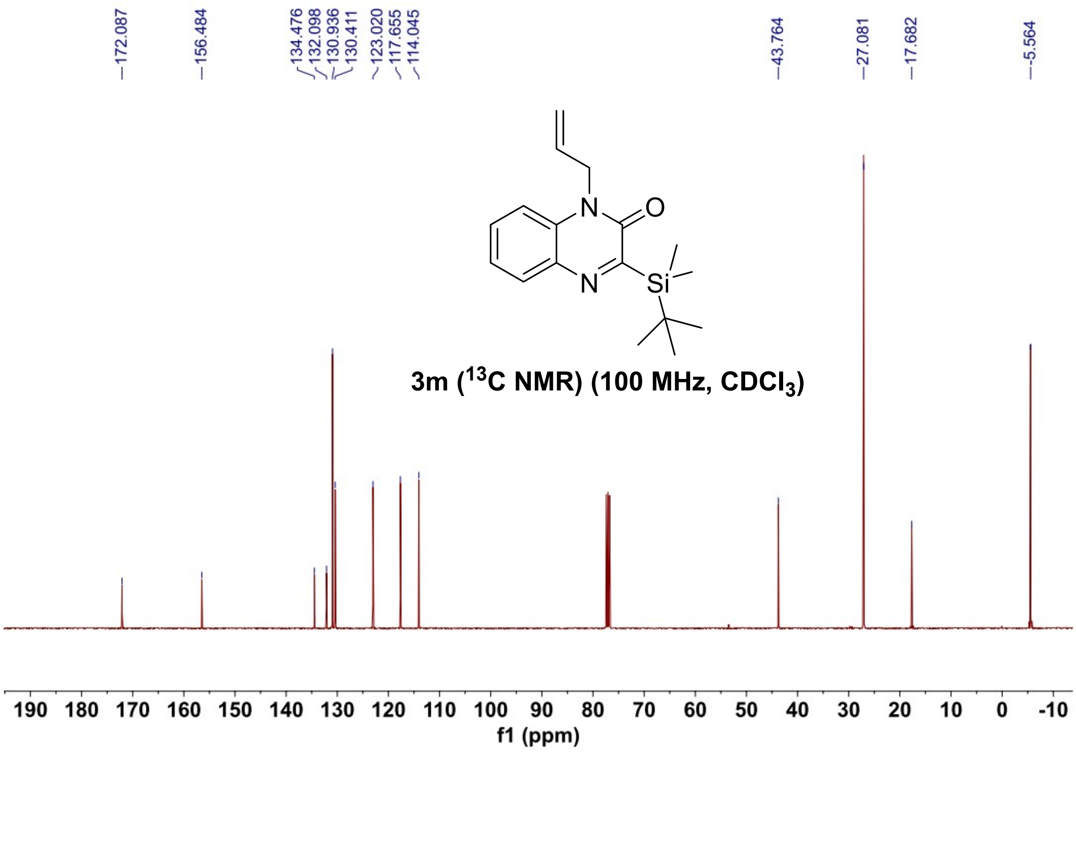


3l (^{13}C NMR) (100 MHz, CDCl$_3$)

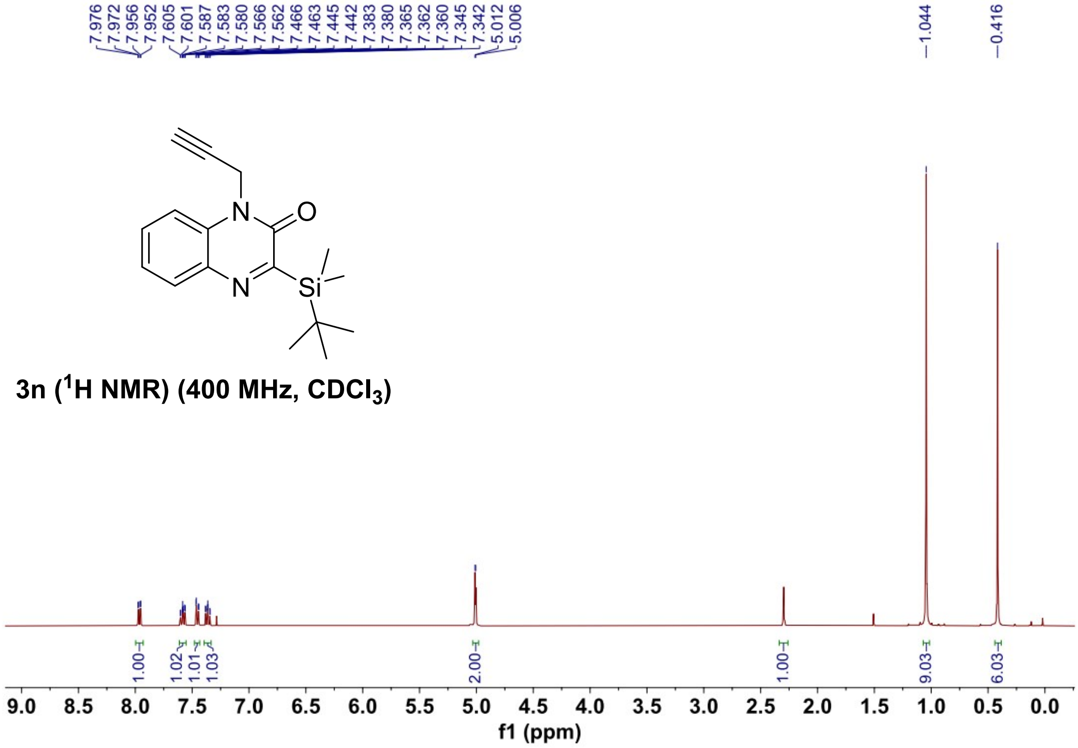




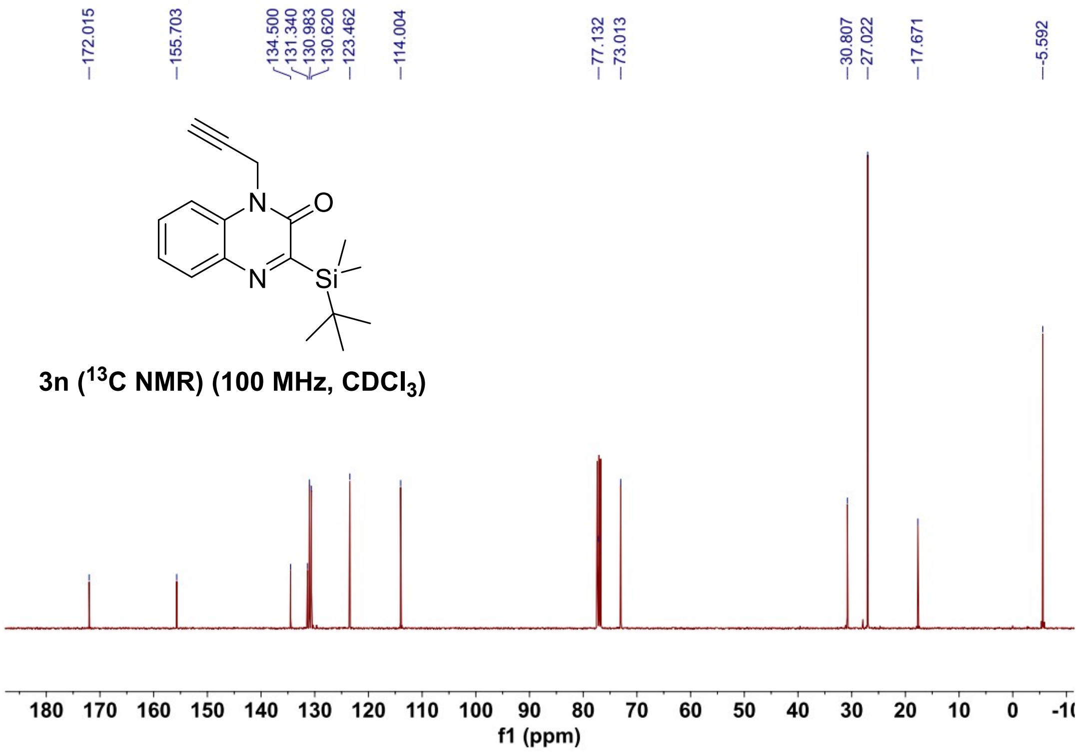
3m (^{1}H NMR) (400 MHz, $CDCl_3$)



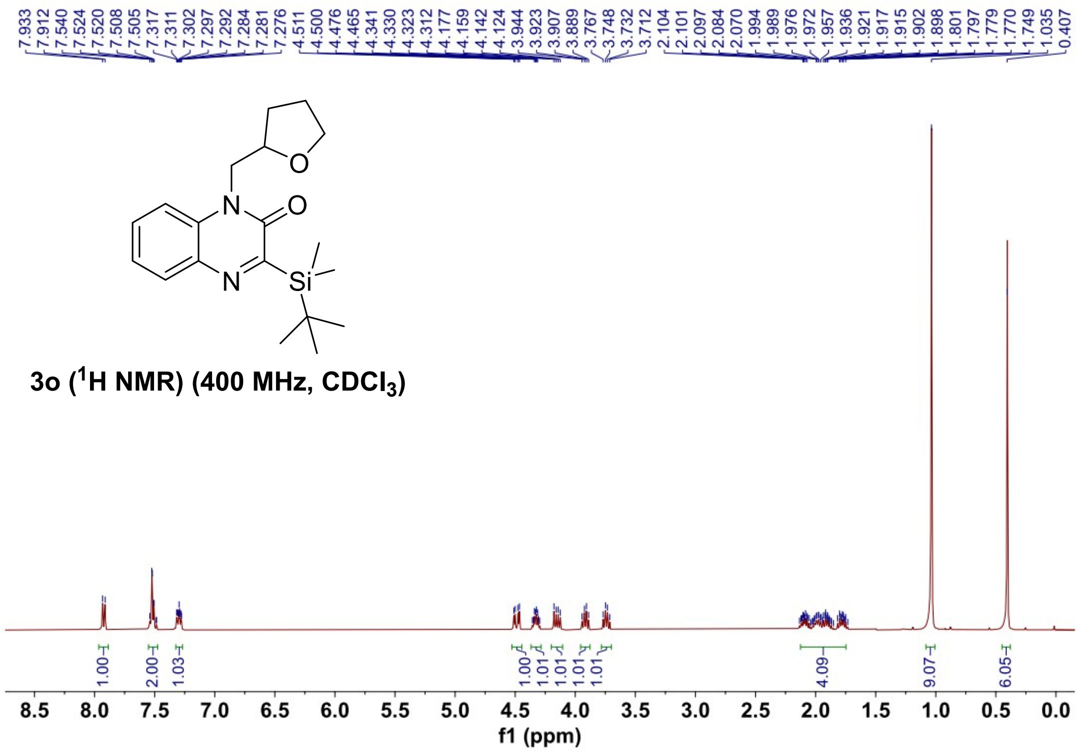
3m (^{13}C NMR) (100 MHz, $CDCl_3$)



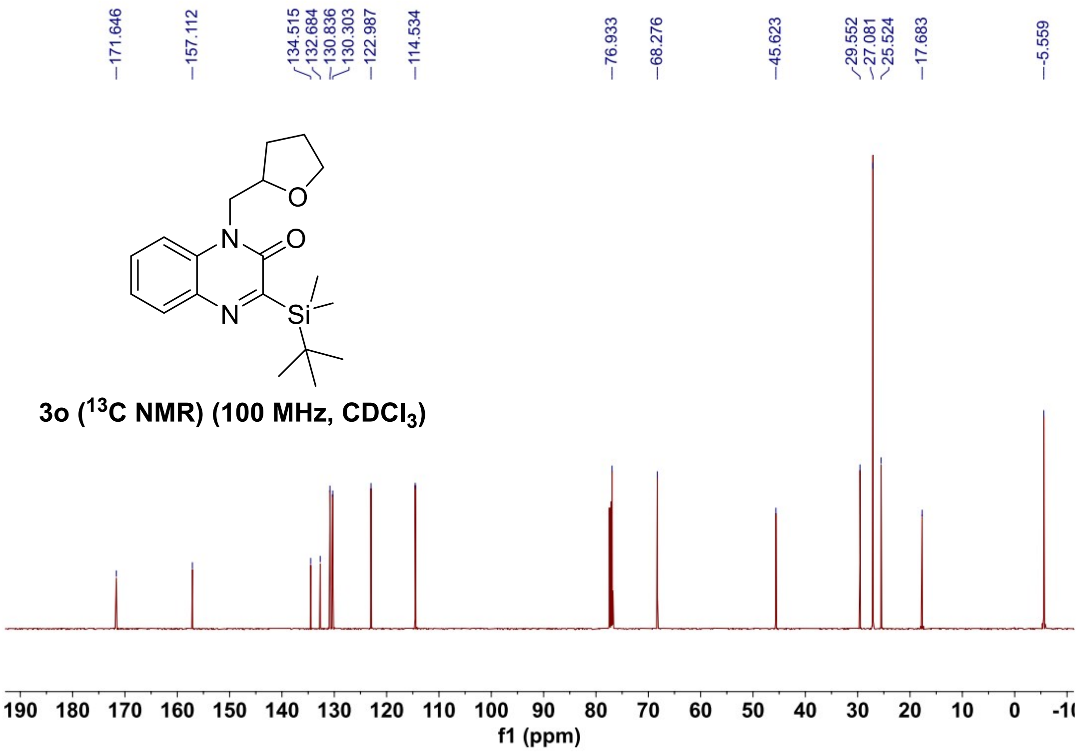
3n (^{1}H NMR) (400 MHz, $CDCl_3$)



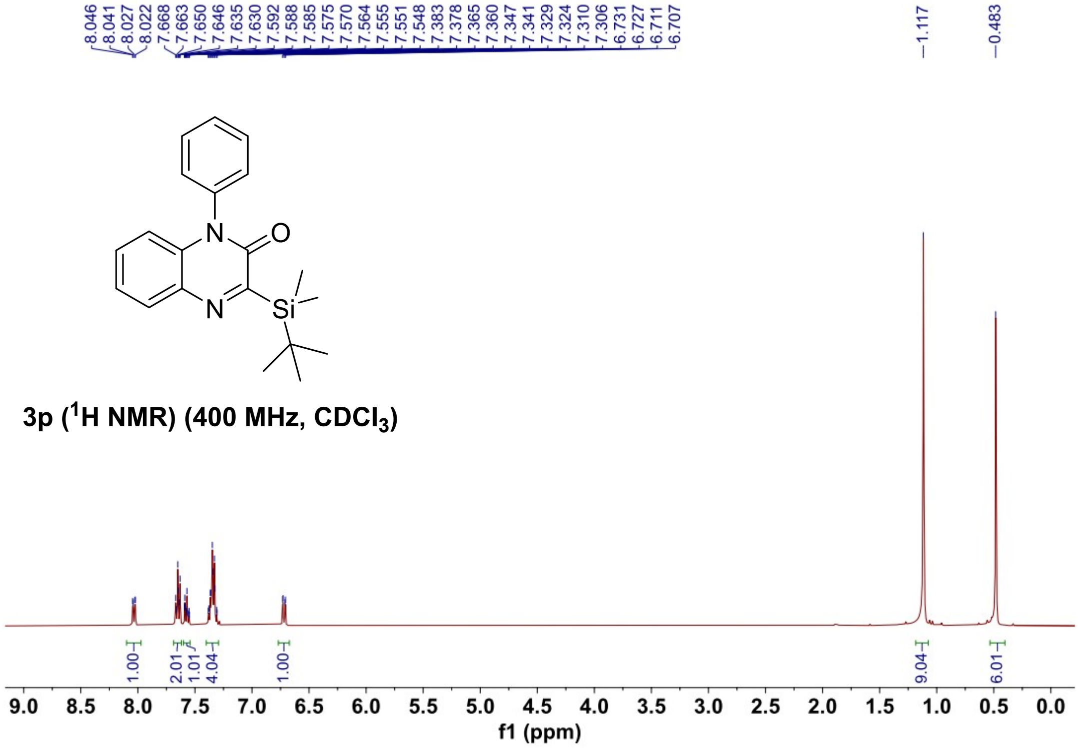
3n (^{13}C NMR) (100 MHz, $CDCl_3$)

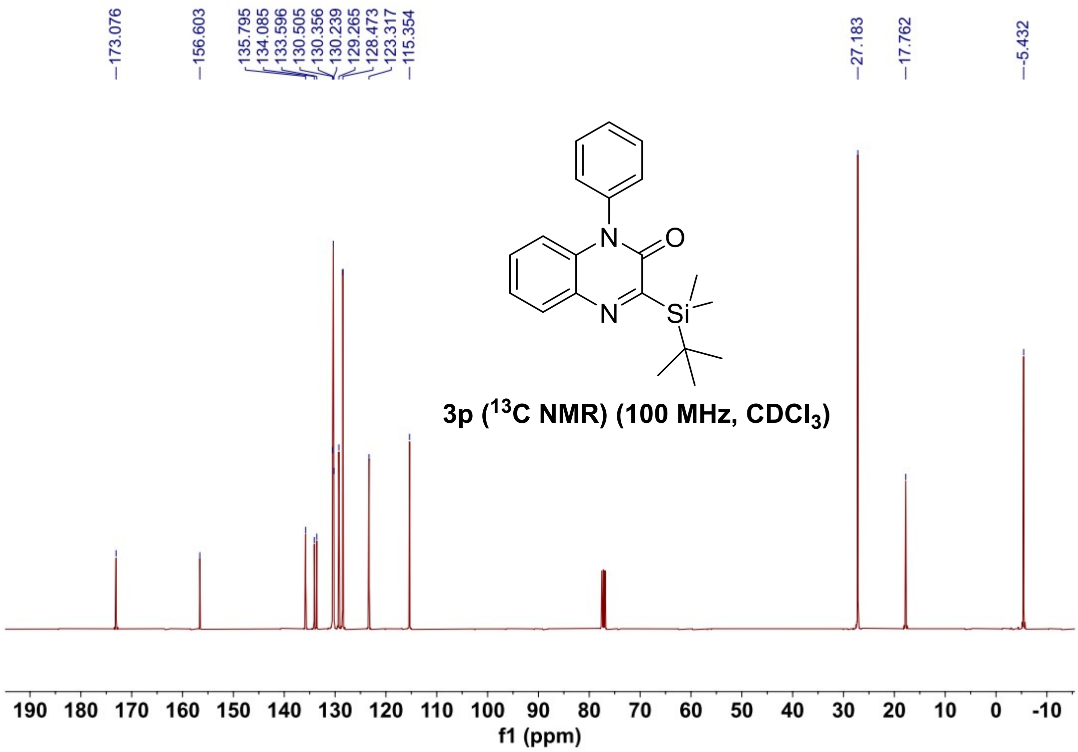


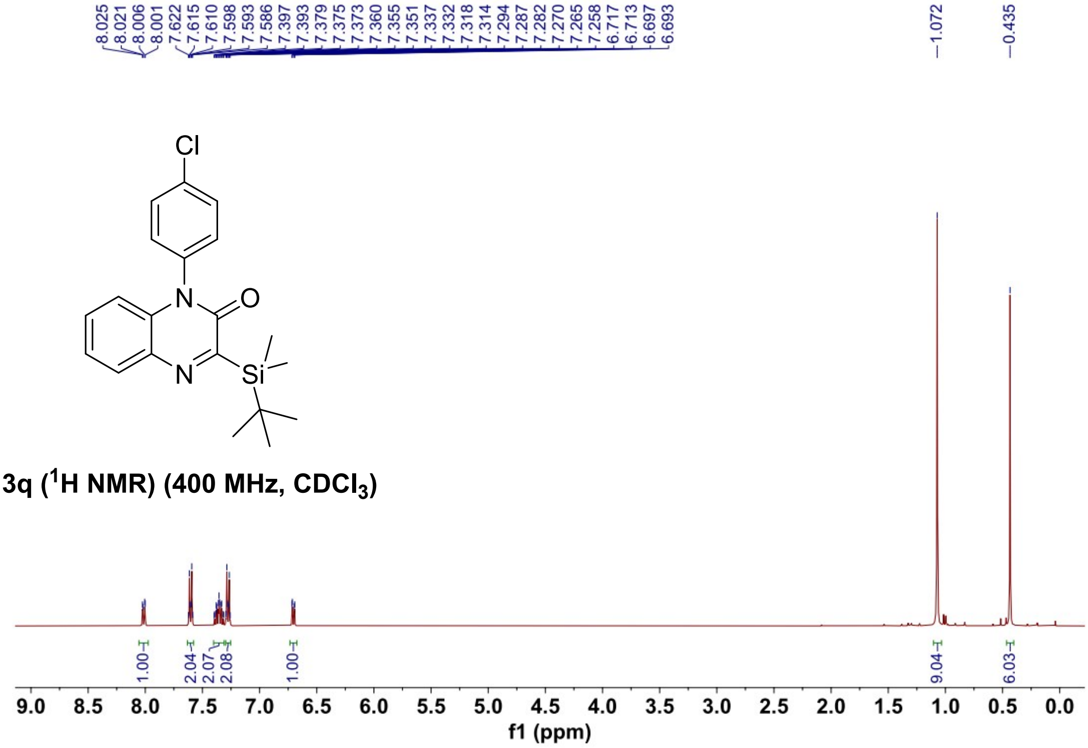
3o (^{1}H NMR) (400 MHz, $CDCl_3$)



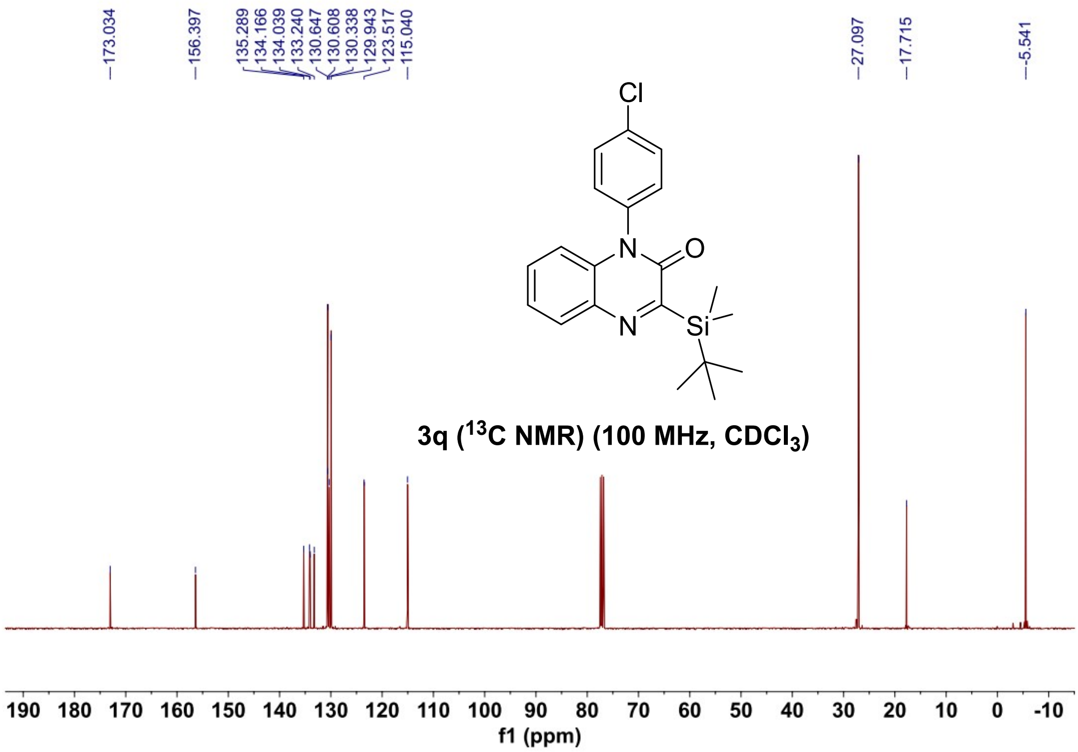
3o (^{13}C NMR) (100 MHz, $CDCl_3$)


8.046
8.041
8.027
8.022
7.668
7.663
7.650
7.646
7.635
7.630
7.592
7.588
7.585
7.575
7.570
7.564
7.555
7.551
7.548
7.383
7.378
7.365
7.360
7.347
7.341
7.329
7.324
7.310
7.306
6.731
6.727
6.711
6.707
1.117
0.483
N
O
N
Si
3p (^{1}H NMR) (400 MHz, $CDCl_3$)
1.00
2.01
1.01
4.04
1.00
9.04
6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

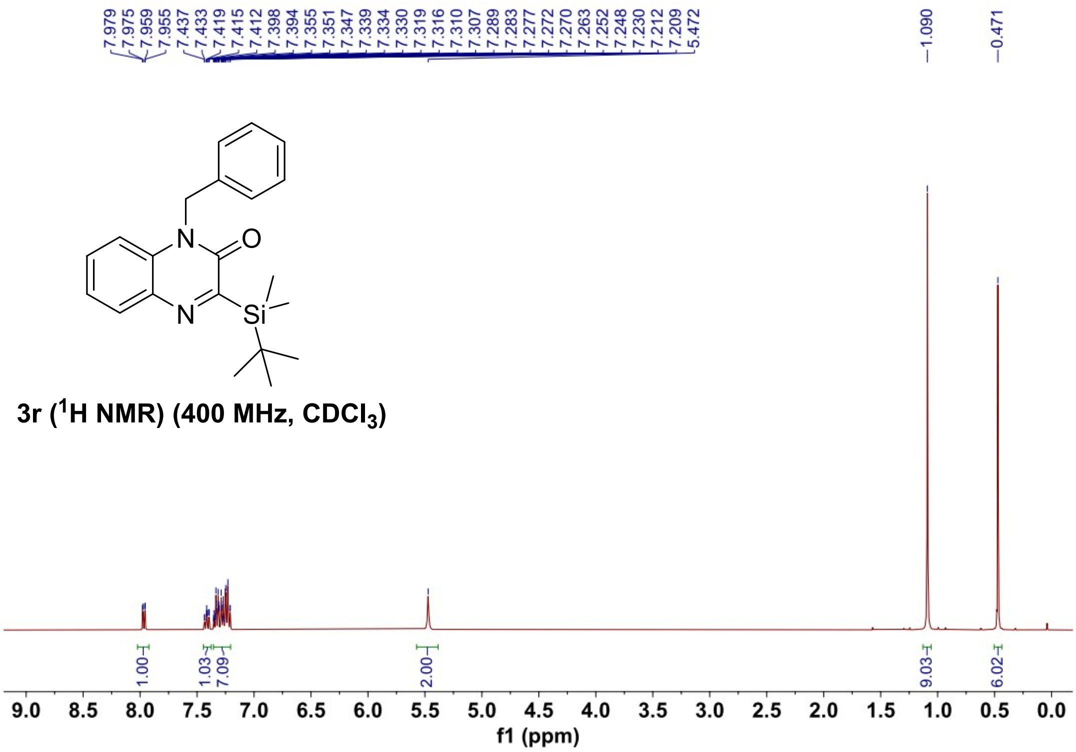

173.076
156.603
135.795
134.085
133.596
130.505
130.356
130.239
129.265
128.473
123.317
115.354
27.183
17.762
-5.432
N
O
N
Si
3p (^{13}C NMR) (100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



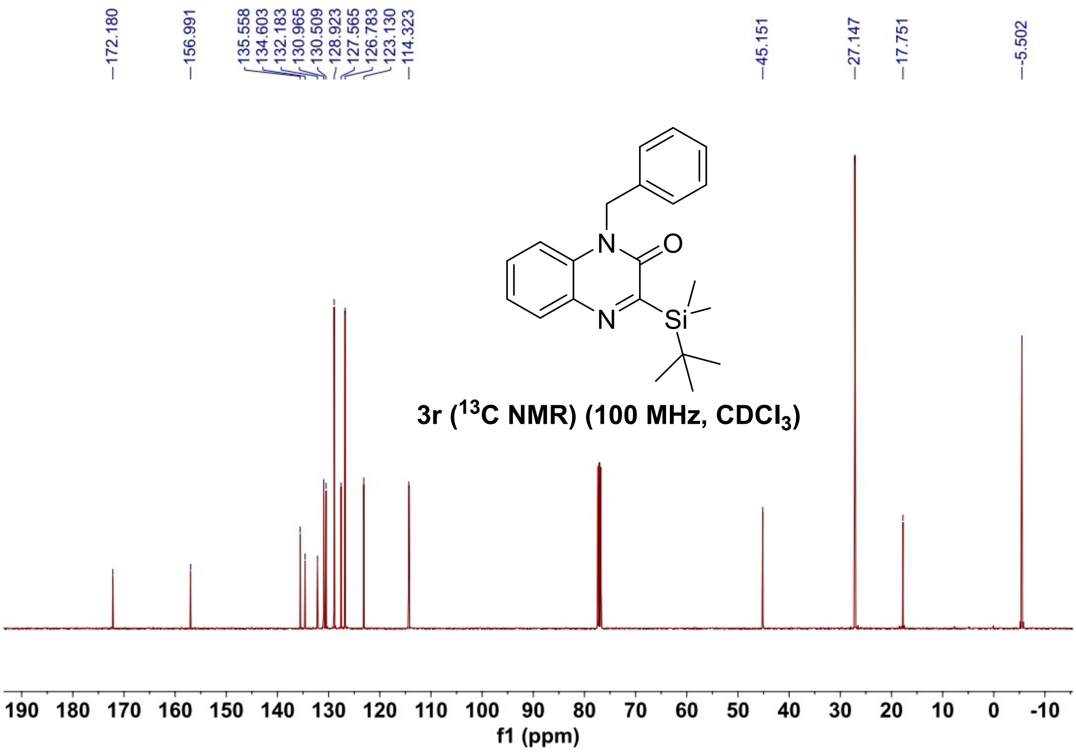
3q (^{1}H NMR) (400 MHz, $CDCl_3$)



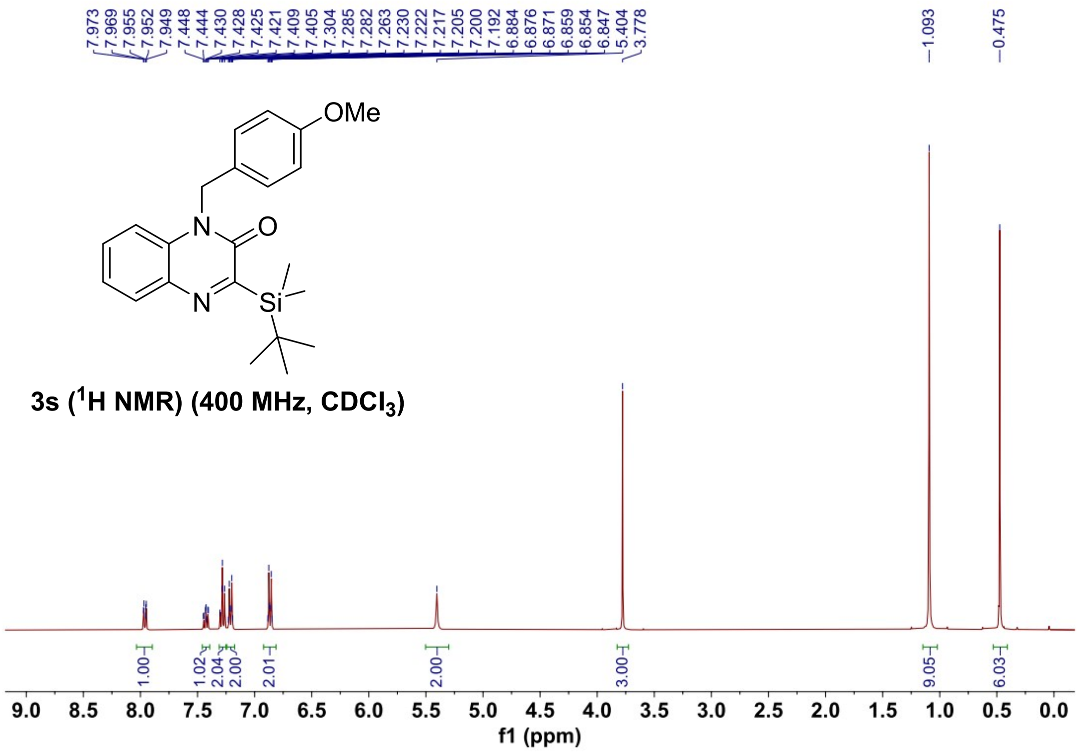
3q (^{13}C NMR) (100 MHz, $CDCl_3$)

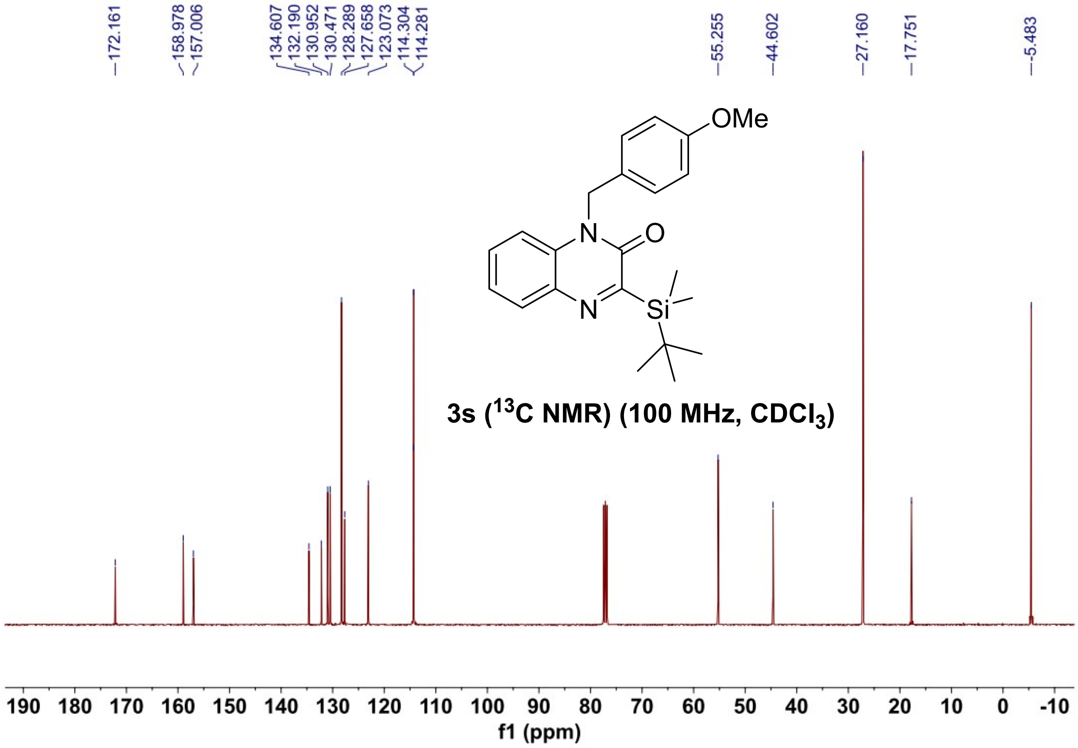


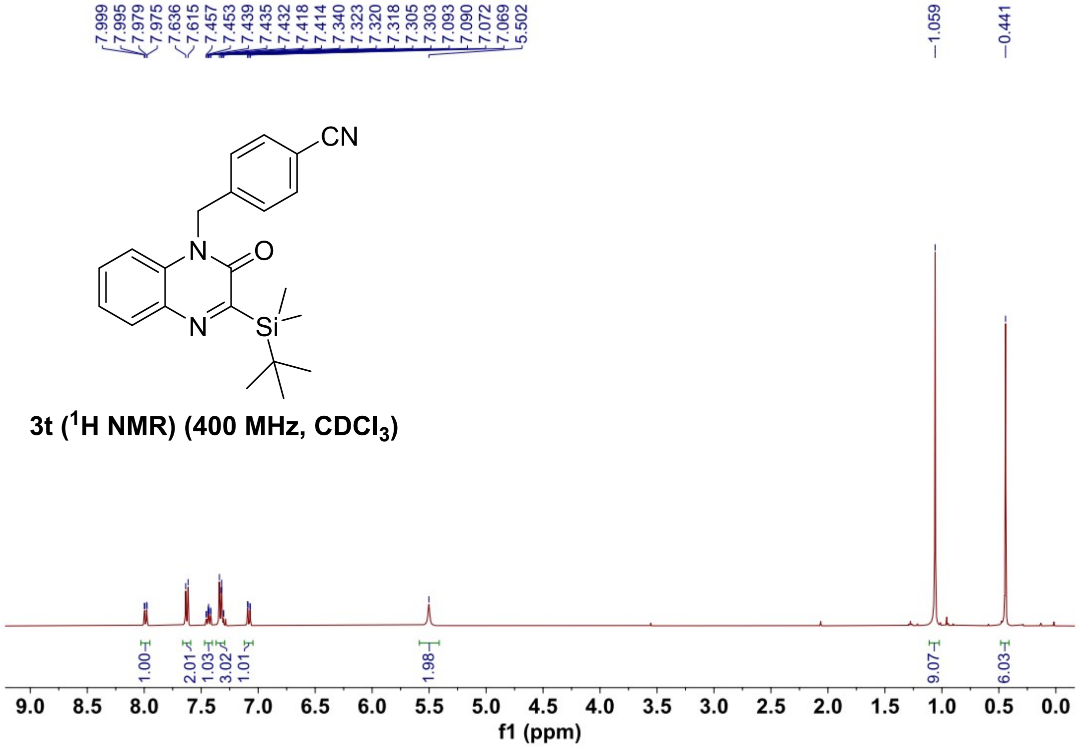
3r (^{1}H NMR) (400 MHz, $CDCl_3$)



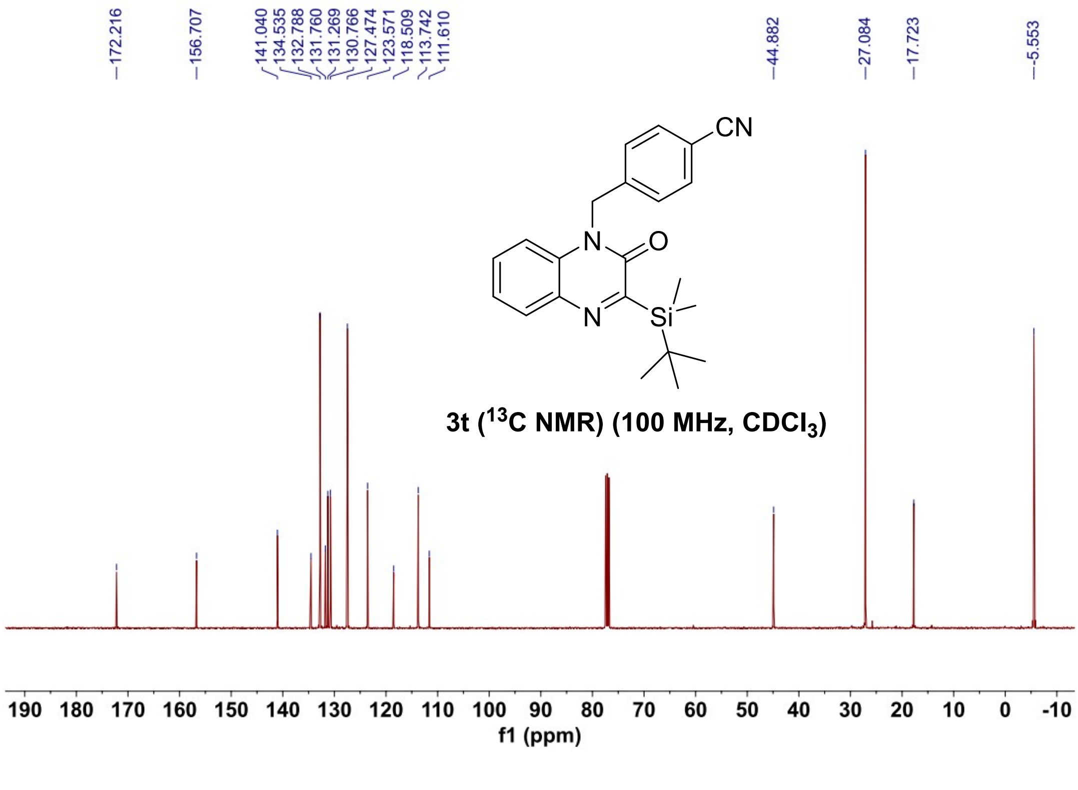
3r (^{13}C NMR) (100 MHz, $CDCl_3$)


7.973
7.969
7.955
7.952
7.949
7.448
7.444
7.430
7.428
7.425
7.421
7.409
7.405
7.304
7.285
7.282
7.263
7.230
7.222
7.217
7.205
7.200
7.192
6.884
6.876
6.871
6.859
6.854
6.847
5.404
3.778
1.093
0.475
OMe
N
O
N
Si
3s (^{1}H NMR) (400 MHz, CDCl$_3$)
1.00
1.02
2.04
2.00
2.01
2.00
3.00
9.05
6.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

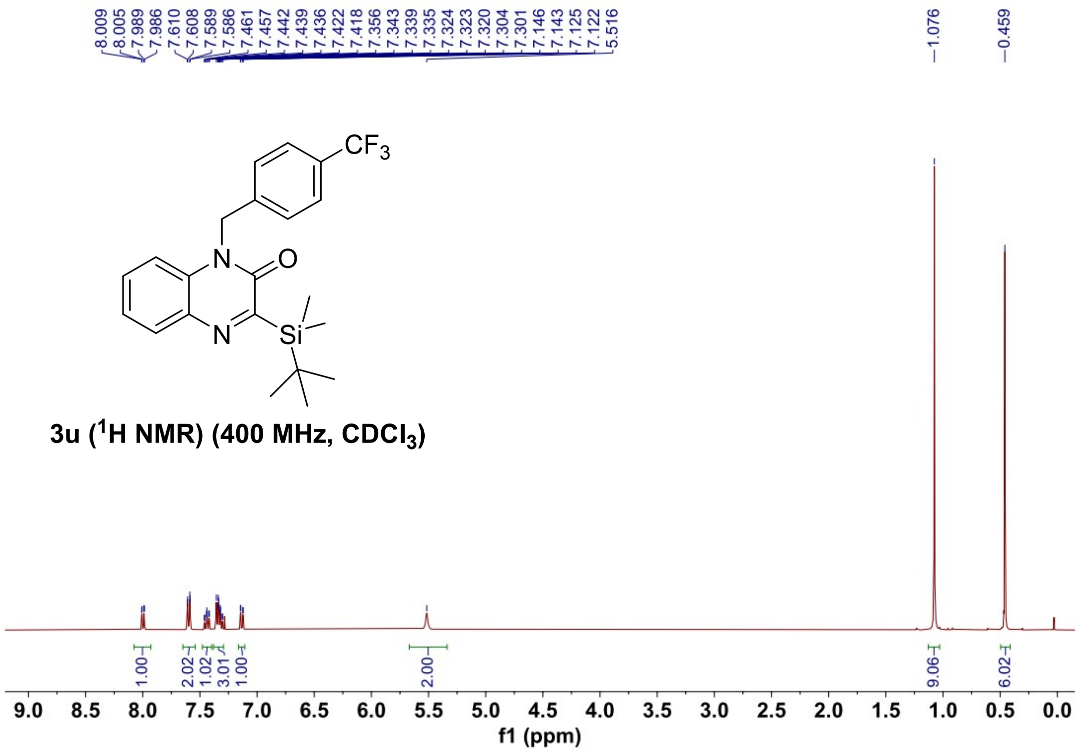

172.161
158.978
157.006
134.607
132.190
130.952
130.471
128.289
127.658
123.073
114.304
114.281
55.255
44.602
27.160
17.751
-5.483
OMe
N
O
N
Si
3s (^{13}C NMR) (100 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



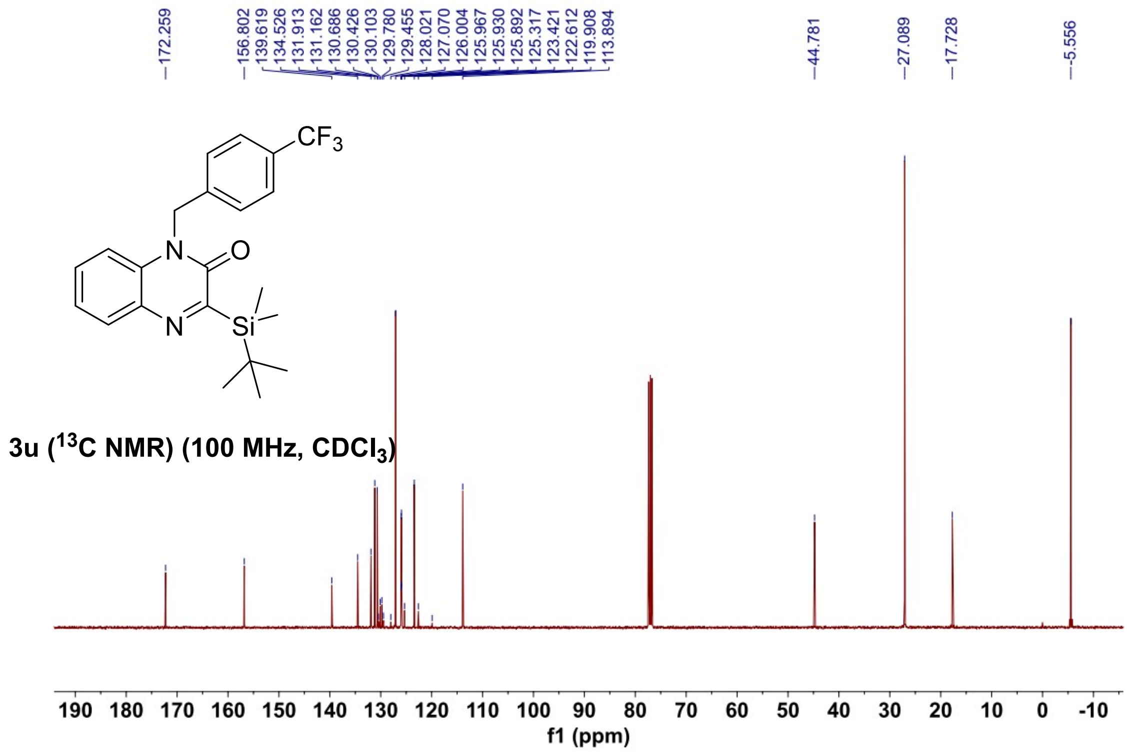
3t (^{1}H NMR) (400 MHz, CDCl$_3$)



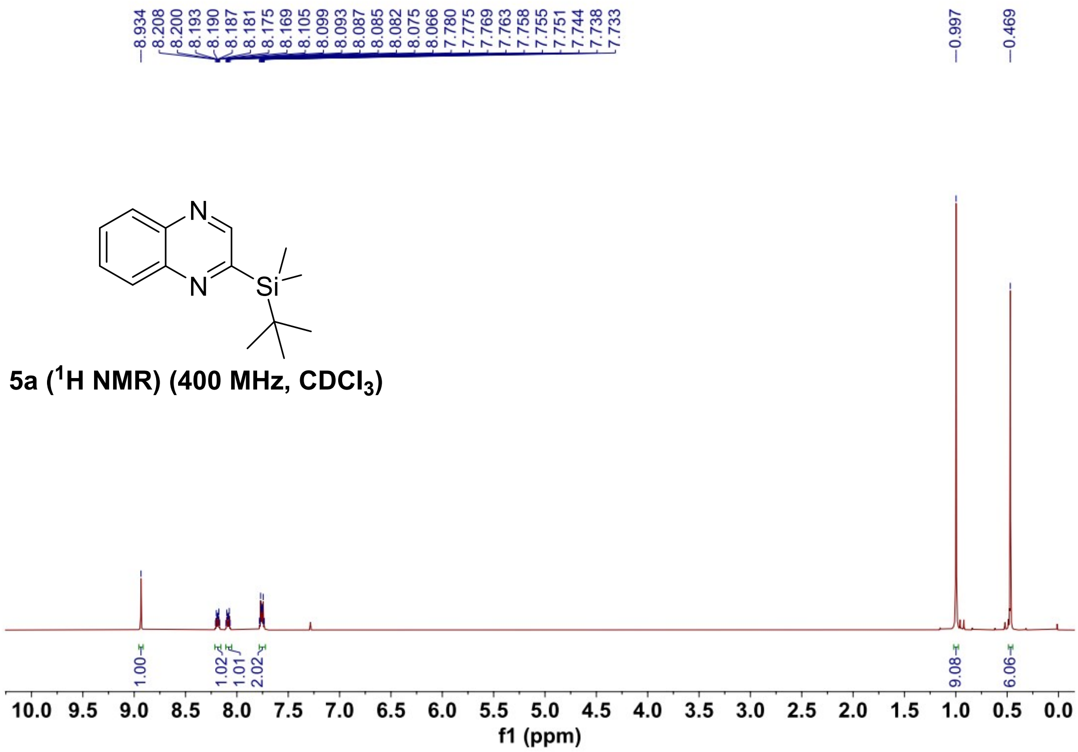
3t (^{13}C NMR) (100 MHz, CDCl$_3$)



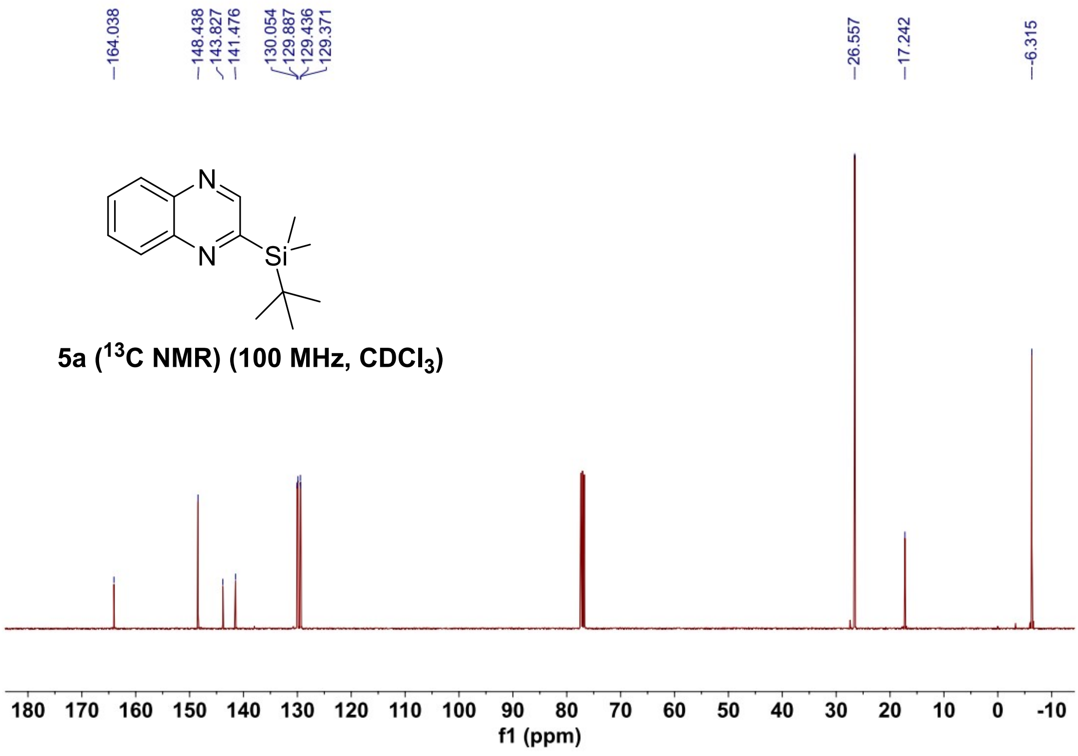
3u (^{1}H NMR) (400 MHz, $CDCl_3$)



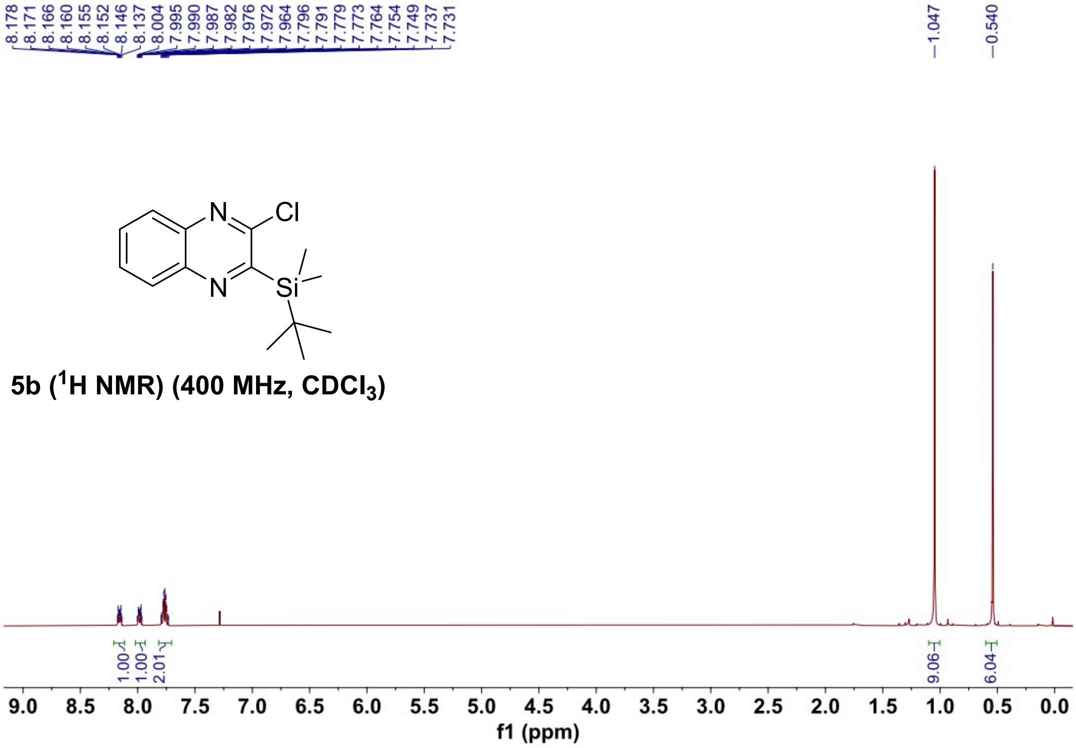
3u (^{13}C NMR) (100 MHz, $CDCl_3$)



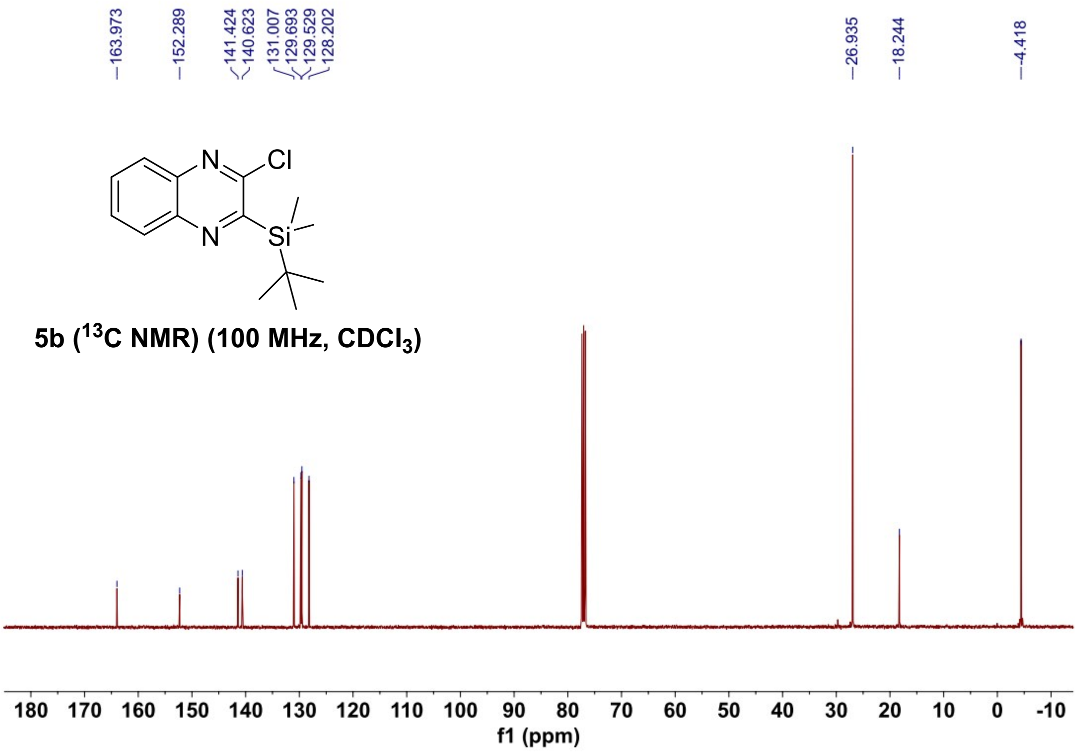
8.934
8.208
8.200
8.193
8.190
8.187
8.181
8.175
8.169
8.105
8.099
8.093
8.087
8.085
8.082
8.075
8.066
7.780
7.775
7.769
7.763
7.758
7.755
7.751
7.744
7.738
7.733
0.997
0.469
N
N
Si
5a (1H NMR) (400 MHz, CDCl3)
1.00
1.02
1.01
2.02
9.08
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



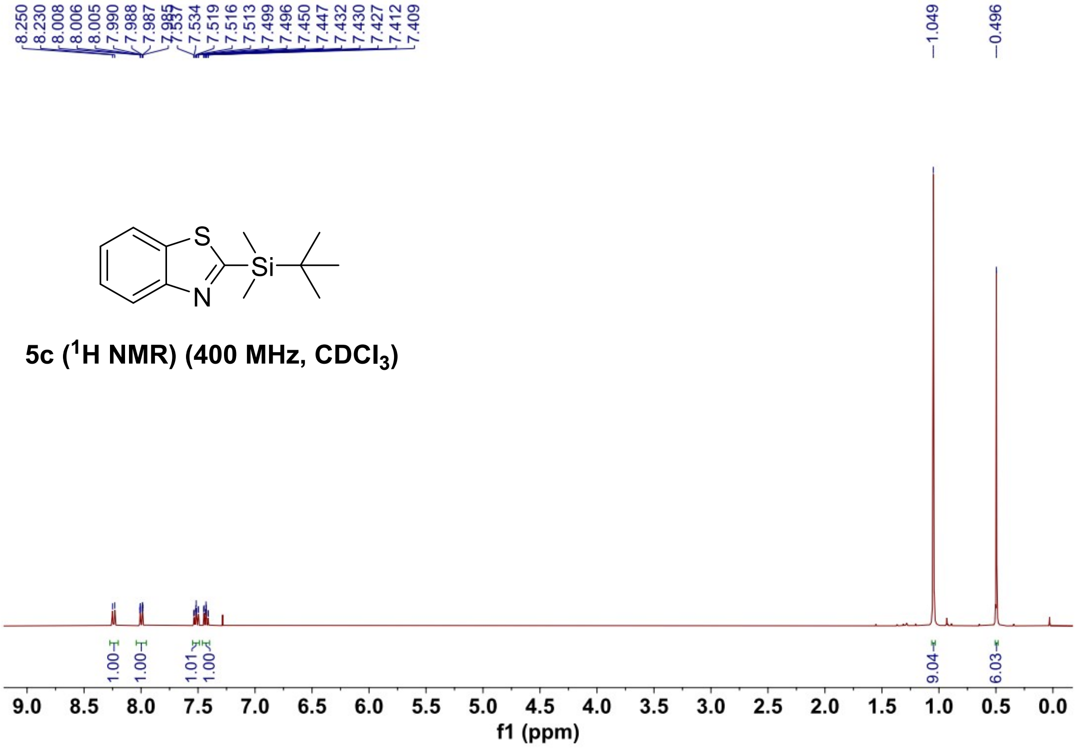
164.038
148.438
143.827
141.476
130.054
129.887
129.436
129.371
26.557
17.242
-6.315
N
N
Si
5a (13C NMR) (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



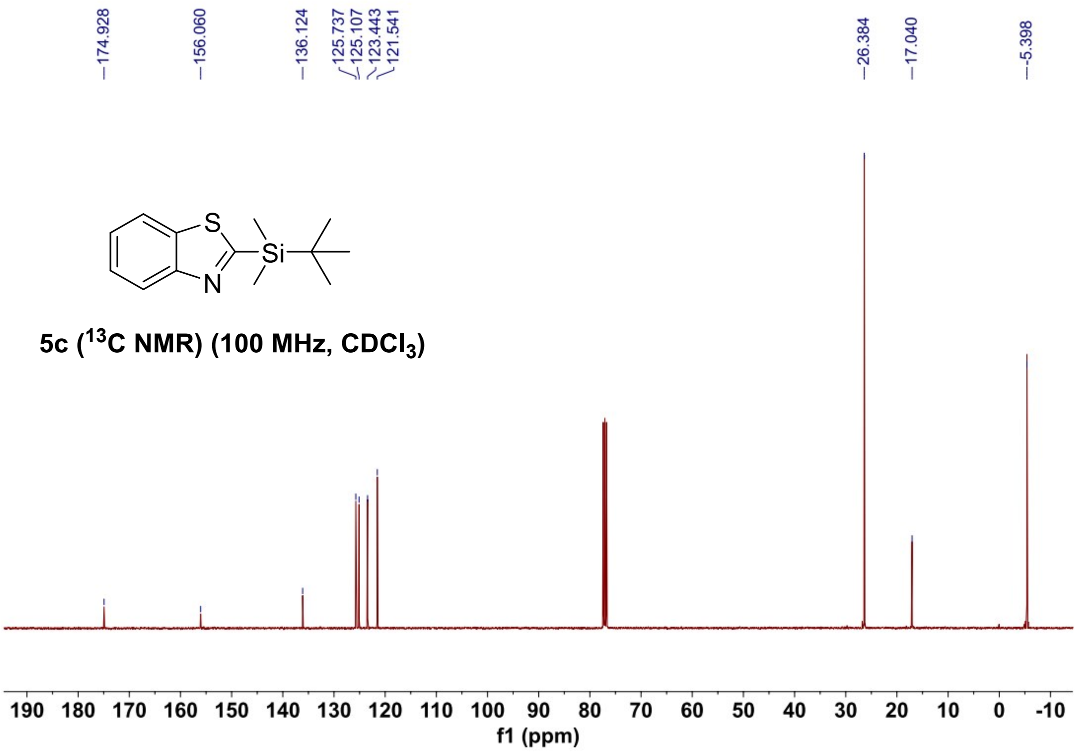
5b (^{1}H NMR) (400 MHz, $CDCl_3$)



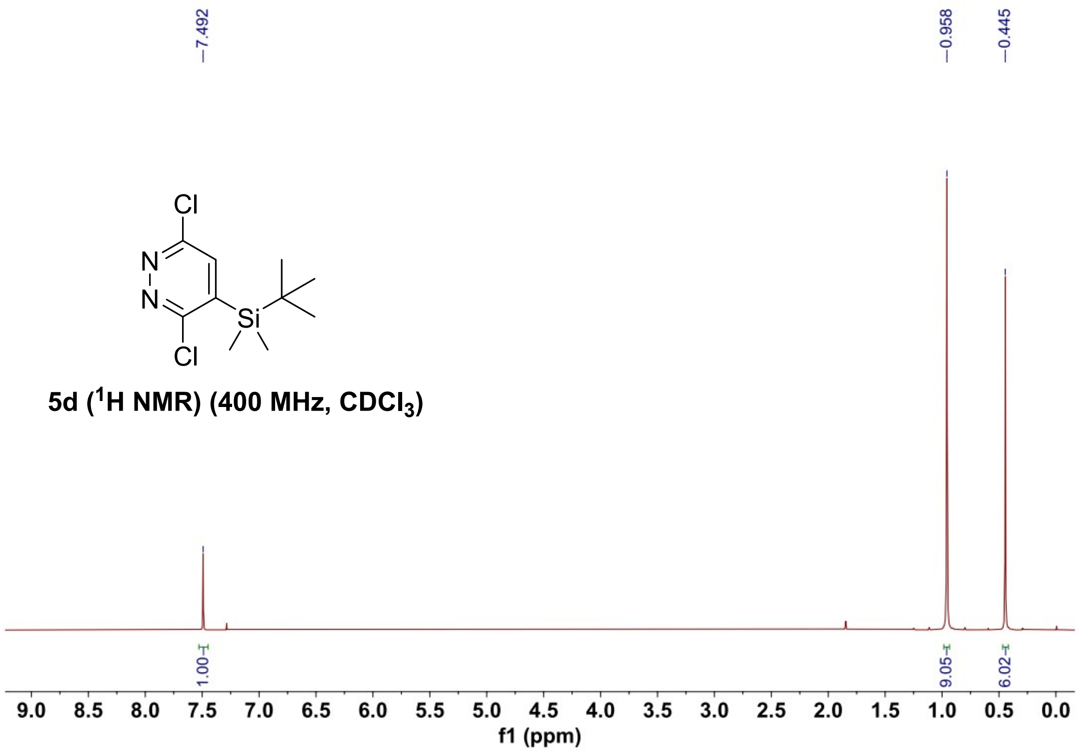
5b (^{13}C NMR) (100 MHz, $CDCl_3$)



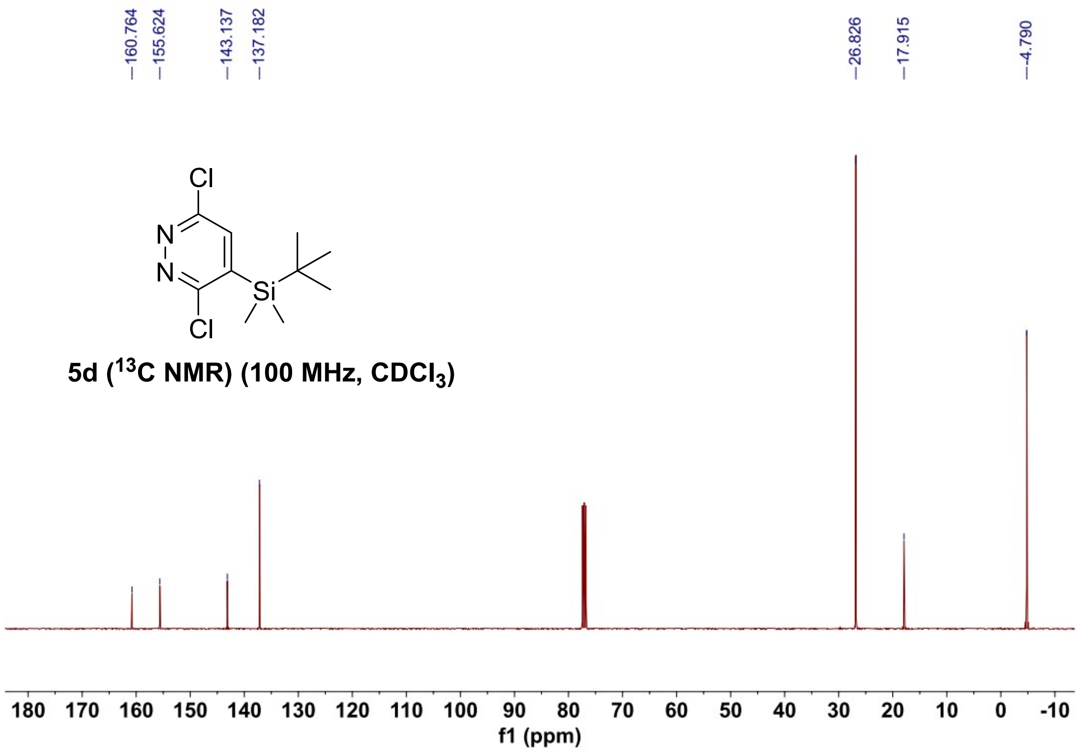
5c (^{1}H NMR) (400 MHz, $CDCl_3$)



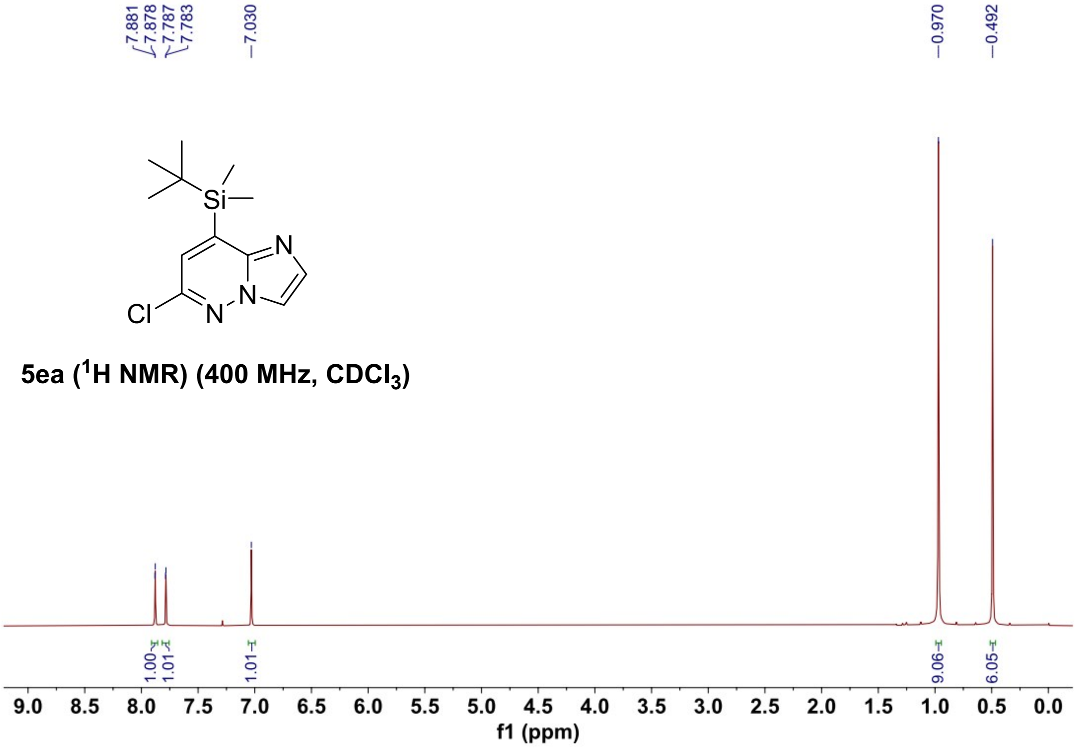
5c (^{13}C NMR) (100 MHz, $CDCl_3$)



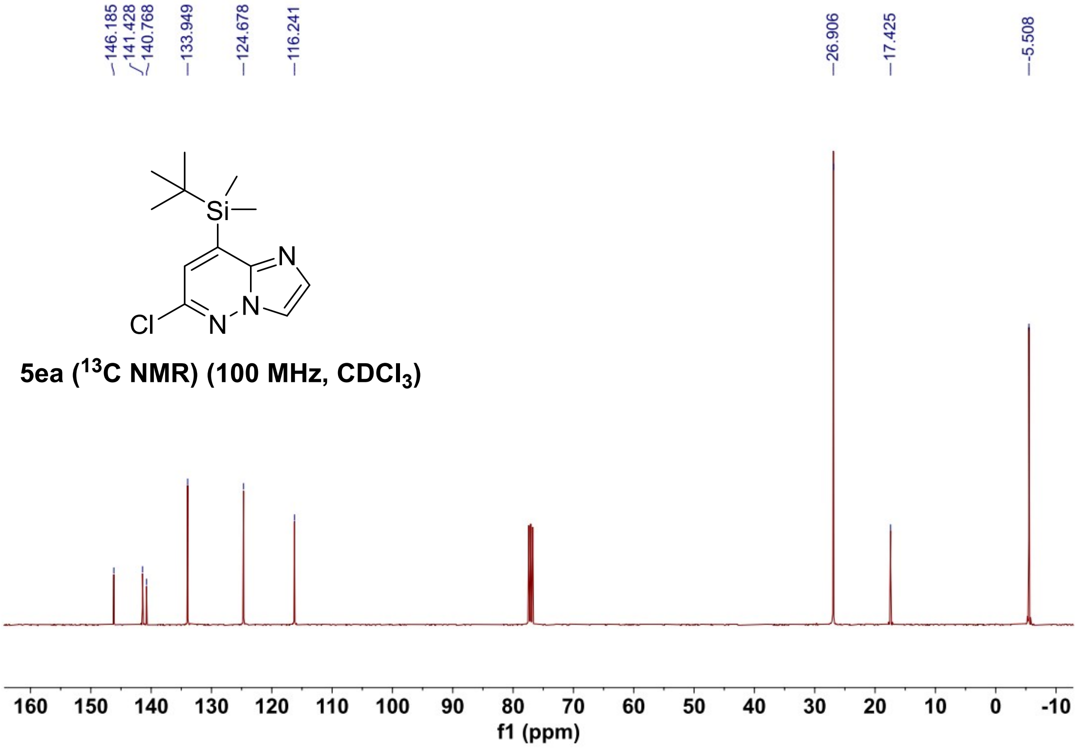
5d (^{1}H NMR) (400 MHz, $CDCl_3$)



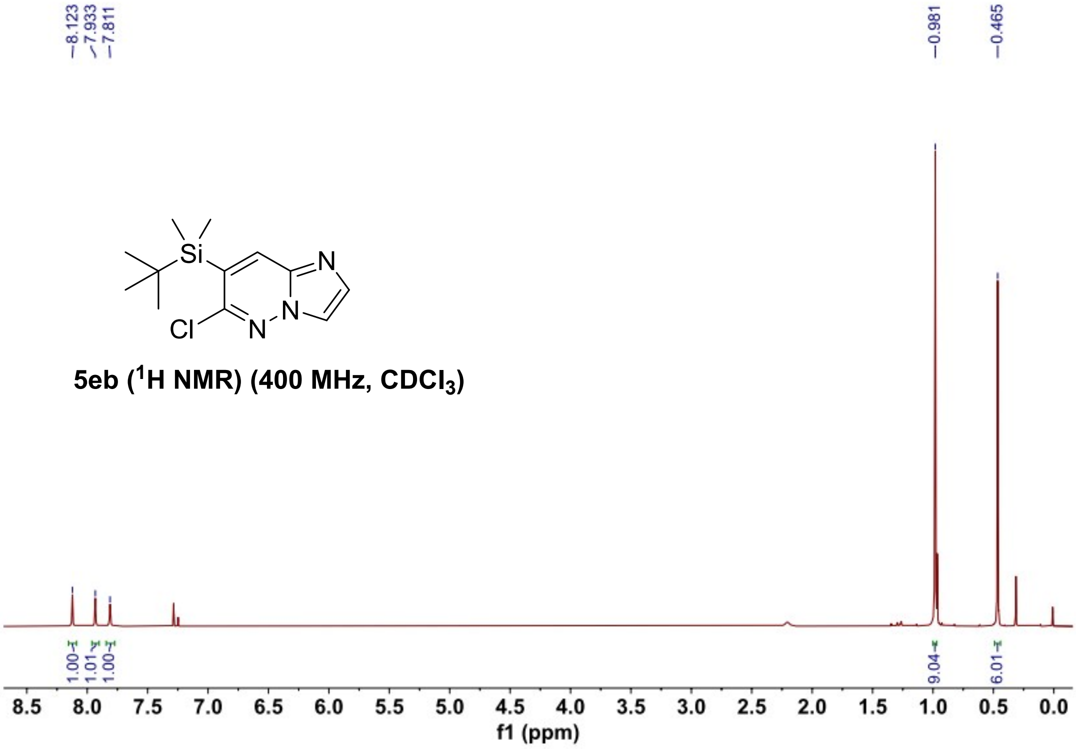
5d (^{13}C NMR) (100 MHz, $CDCl_3$)



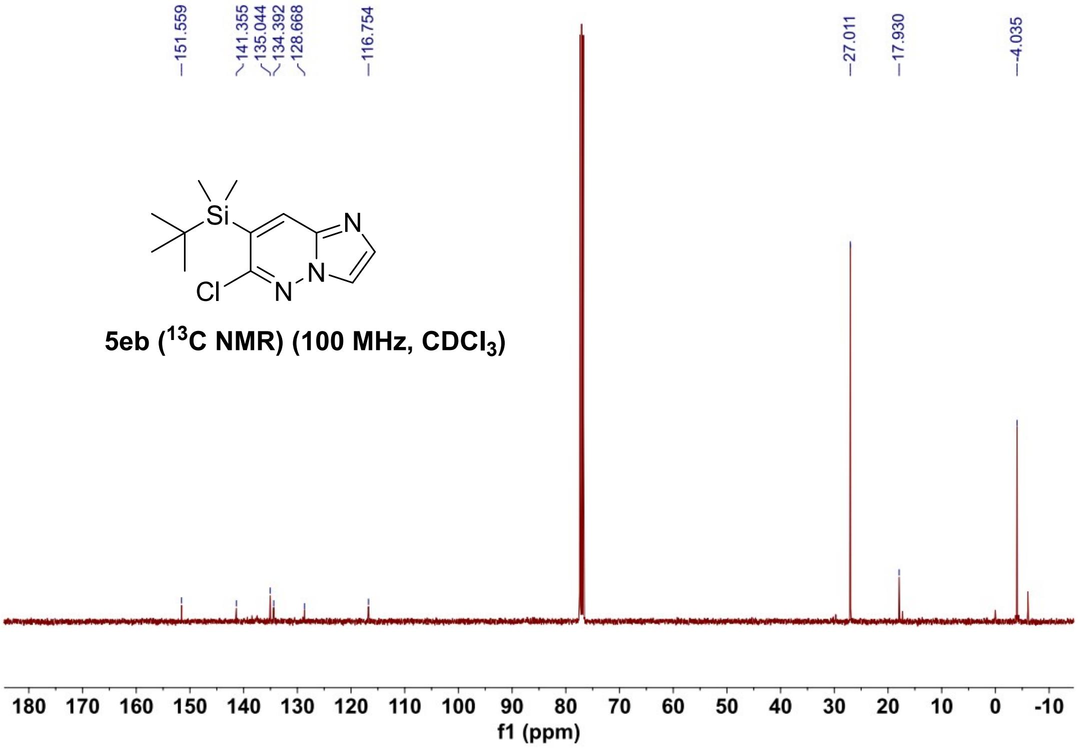
5ea (^{1}H NMR) (400 MHz, $CDCl_3$)



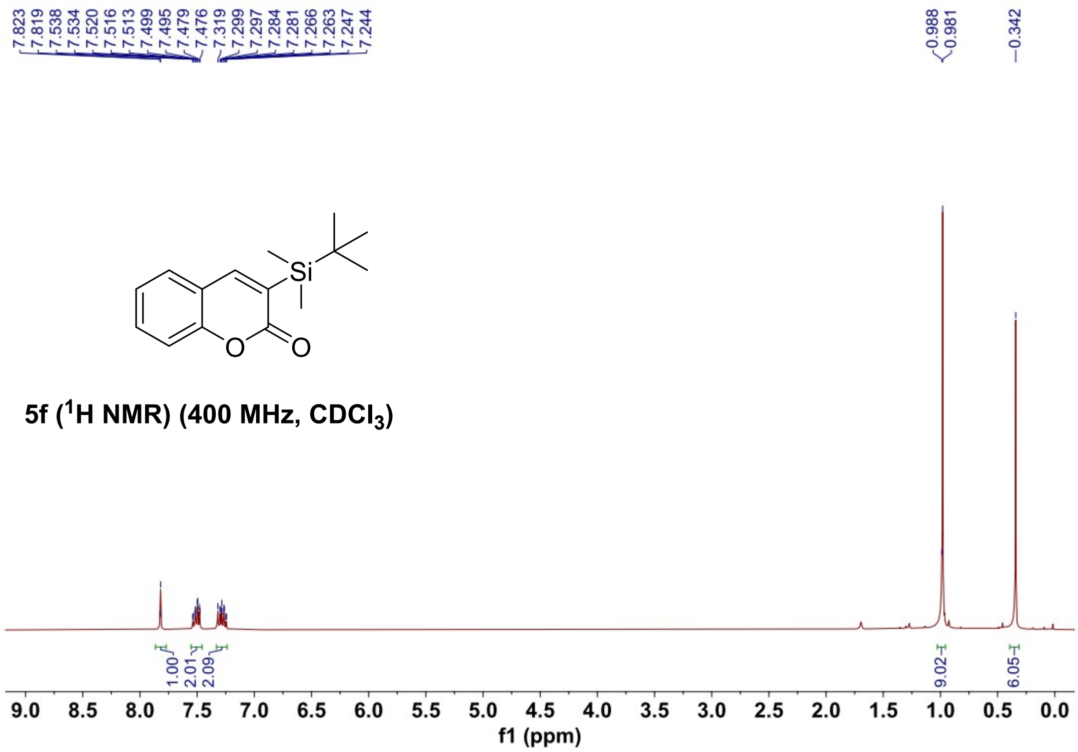
5ea (^{13}C NMR) (100 MHz, $CDCl_3$)



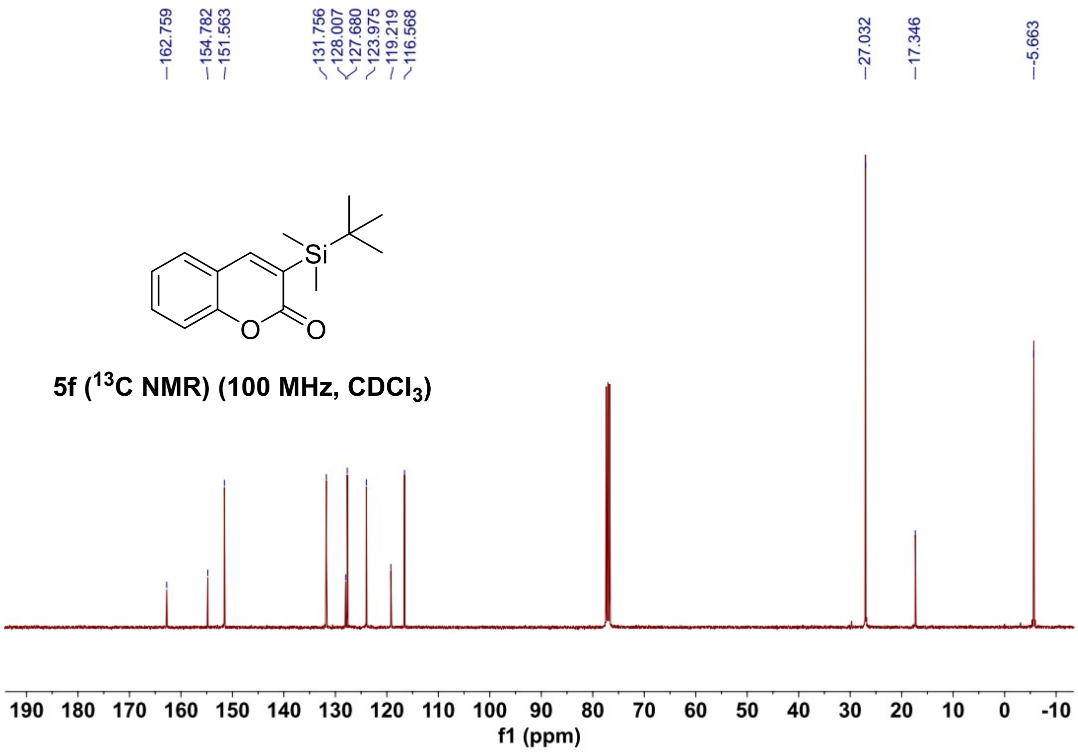
5eb (^{1}H NMR) (400 MHz, $CDCl_3$)



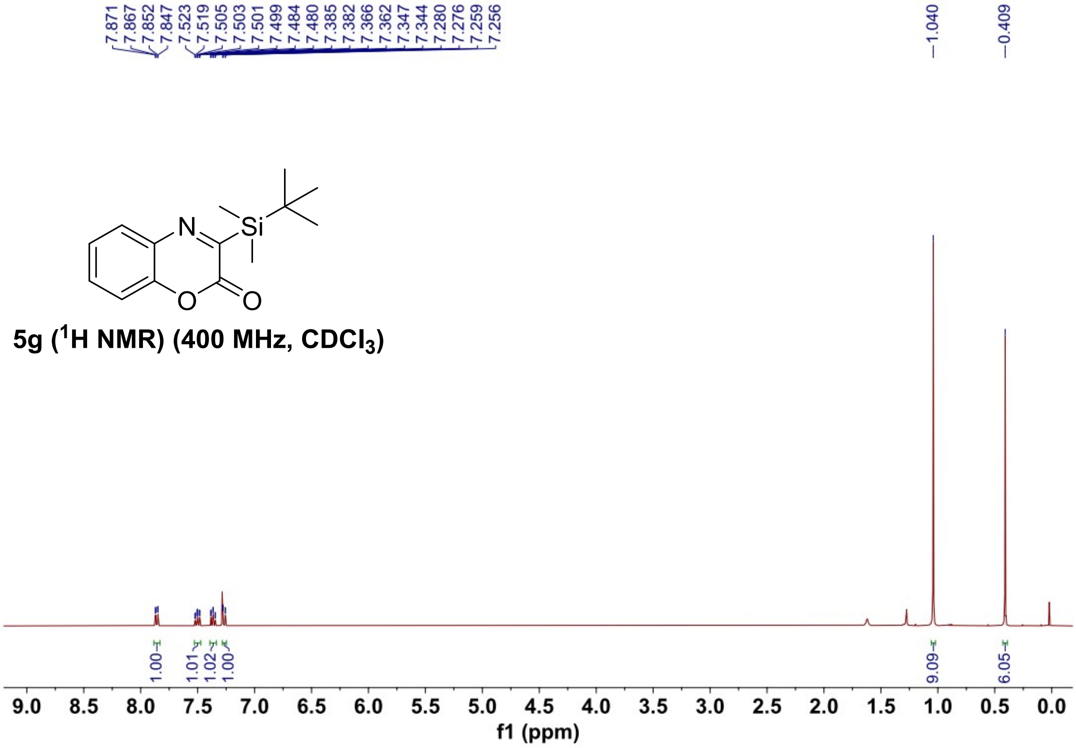
5eb (^{13}C NMR) (100 MHz, $CDCl_3$)



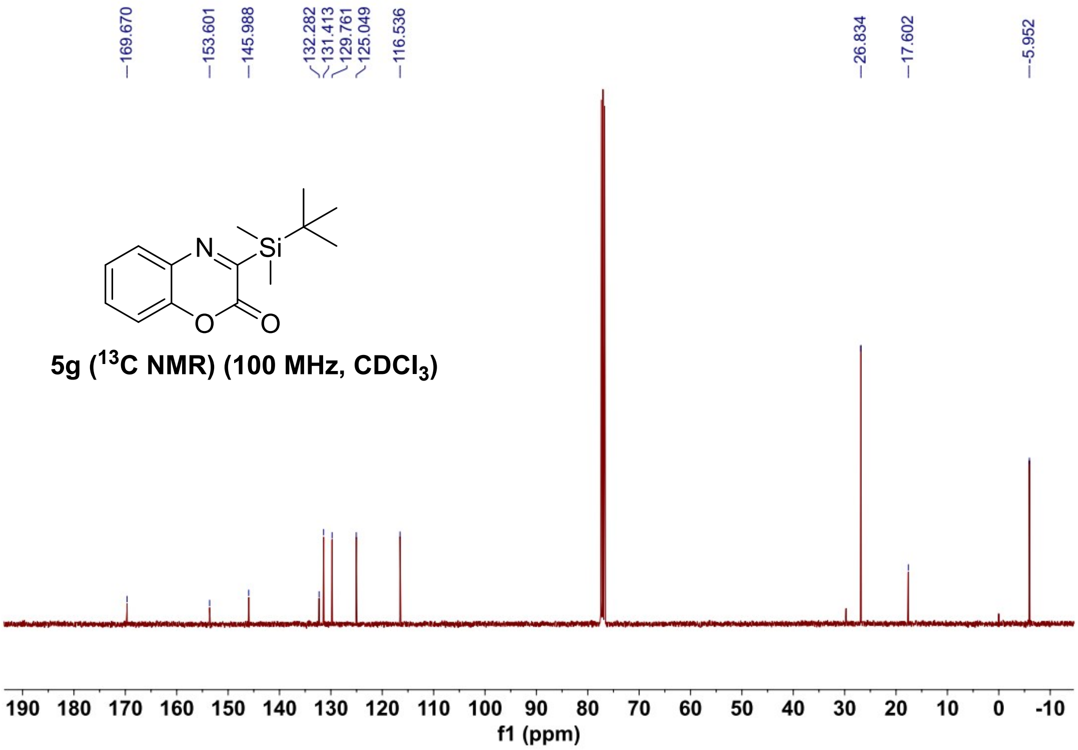
5f (^{1}H NMR) (400 MHz, $CDCl_3$)



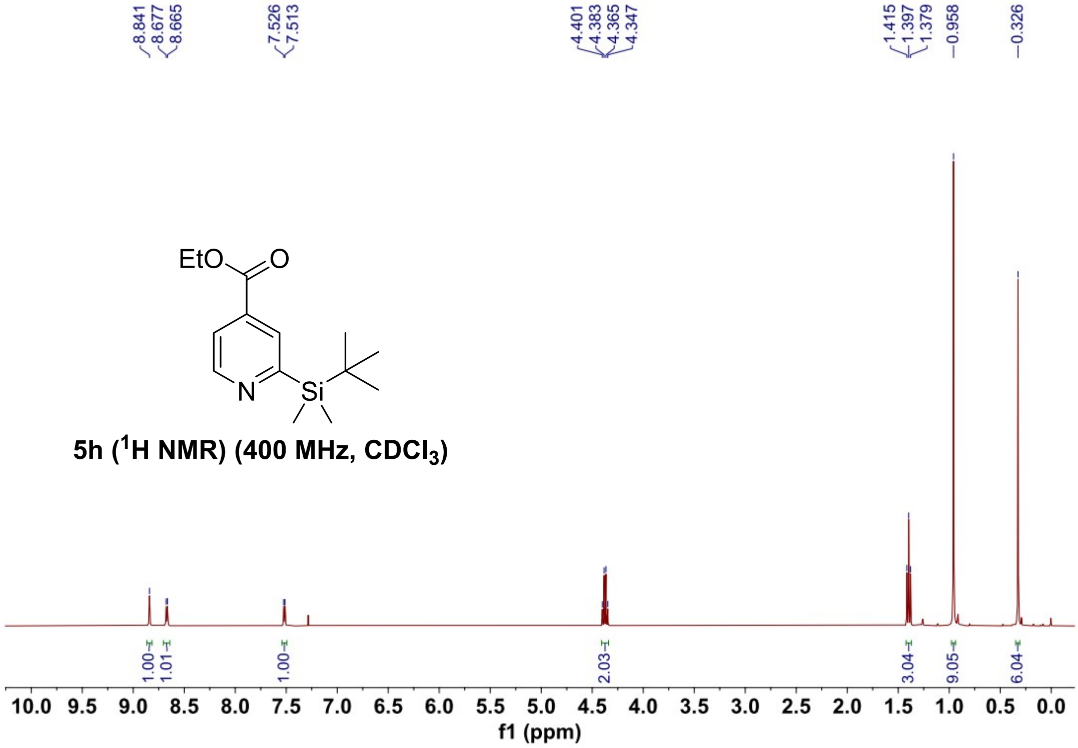
5f (^{13}C NMR) (100 MHz, $CDCl_3$)

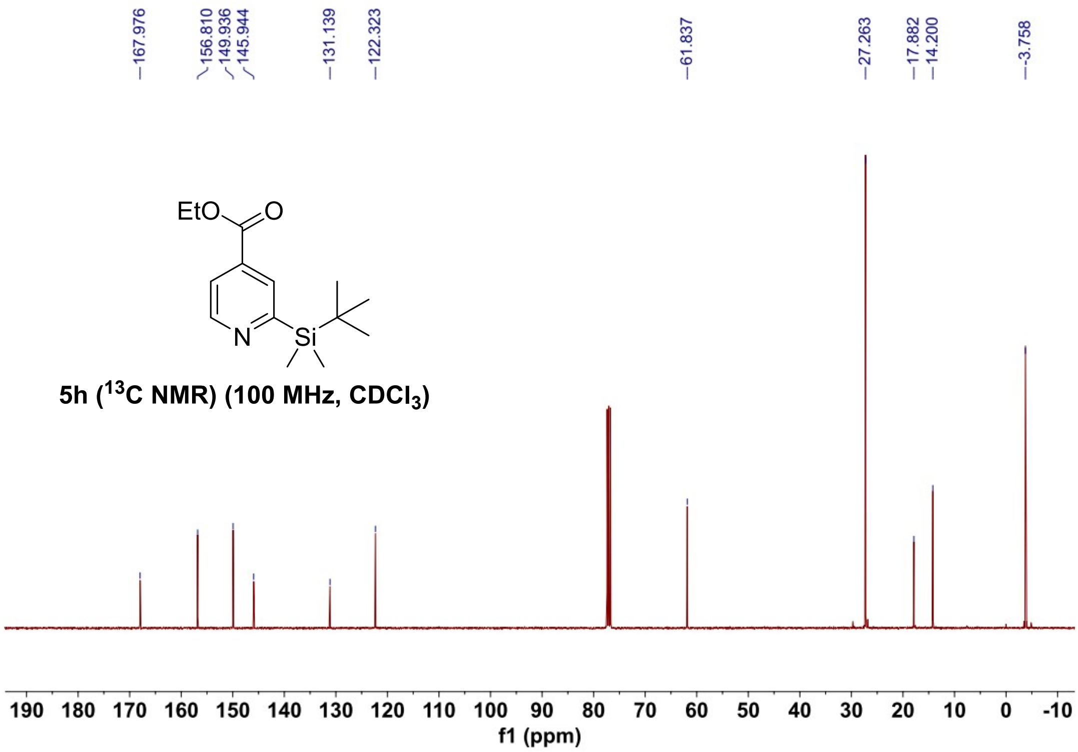


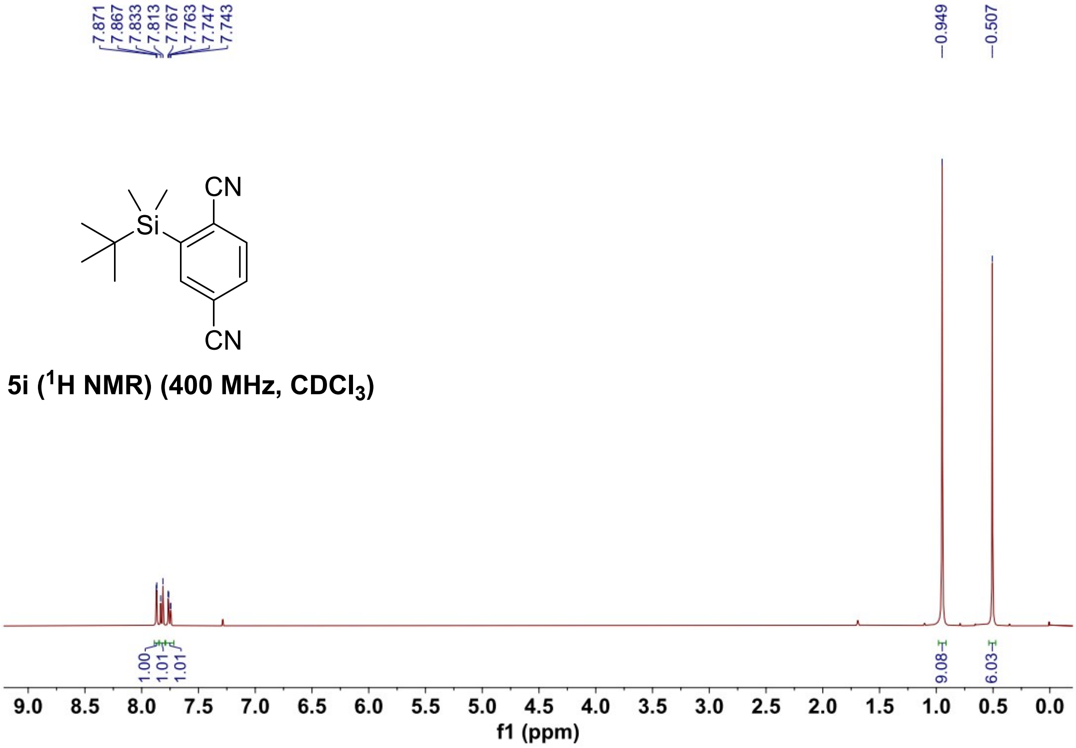
5g (^{1}H NMR) (400 MHz, $CDCl_3$)



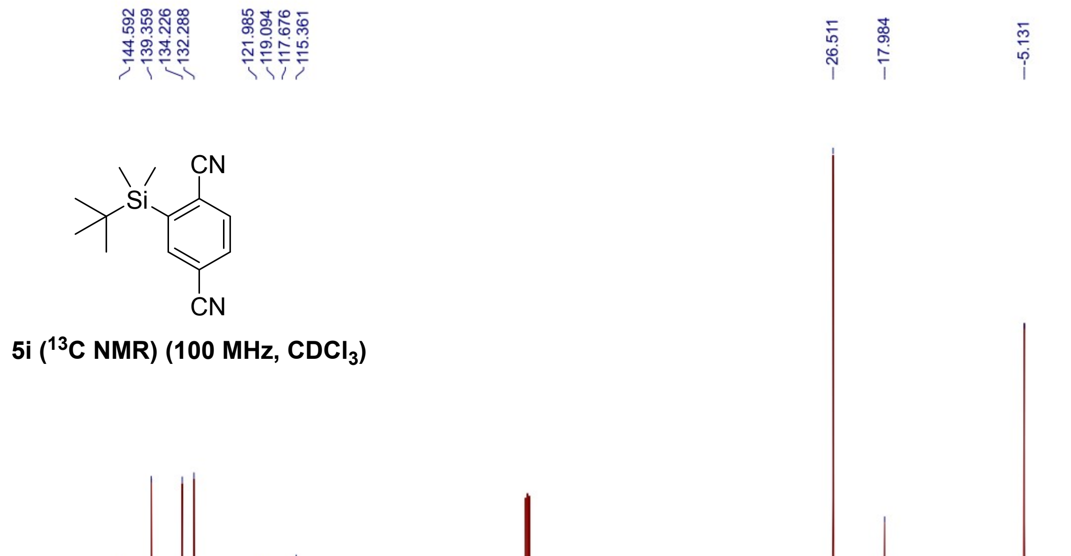
5g (^{13}C NMR) (100 MHz, $CDCl_3$)


8.841
8.677
8.665
7.526
7.513
4.401
4.383
4.365
4.347
1.415
1.397
1.379
0.958
0.326
EtO
O
N
Si
5h (^{1}H NMR) (400 MHz, $CDCl_3$)
1.00
1.01
1.00
2.03
3.04
9.05
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

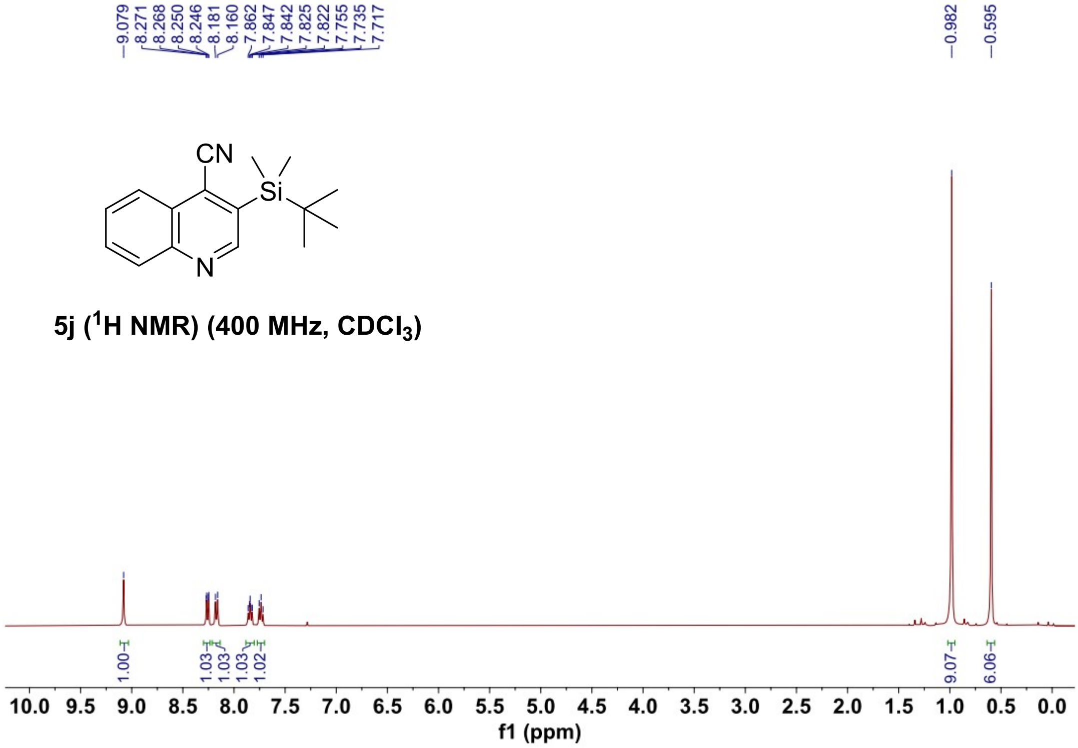

167.976
156.810
149.936
145.944
131.139
122.323
61.837
27.263
17.882
14.200
-3.758
EtO
O
N
Si
5h (^{13}C NMR) (100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

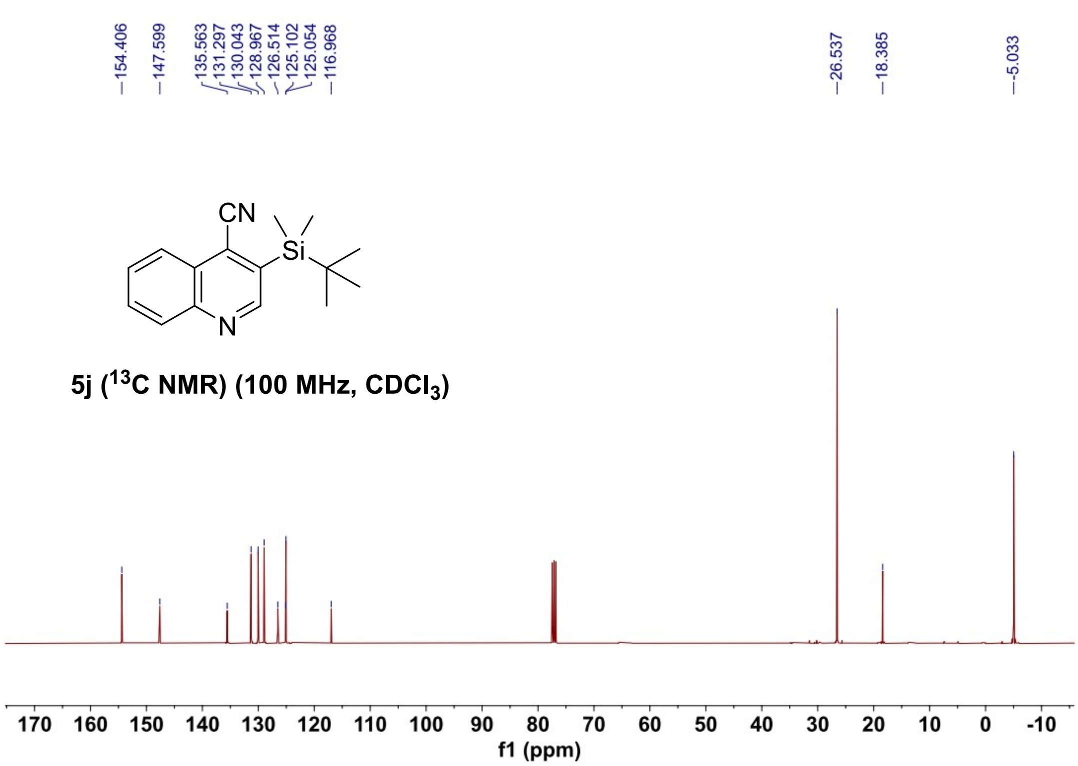


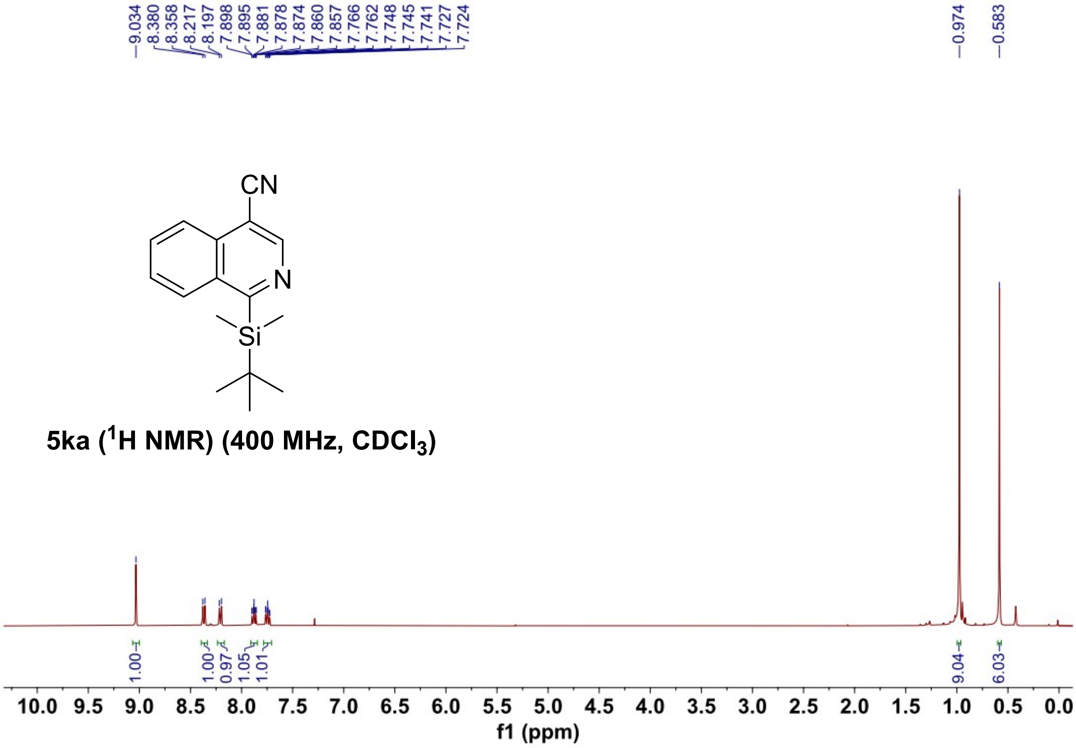
5i (^{1}H NMR) (400 MHz, $CDCl_3$)



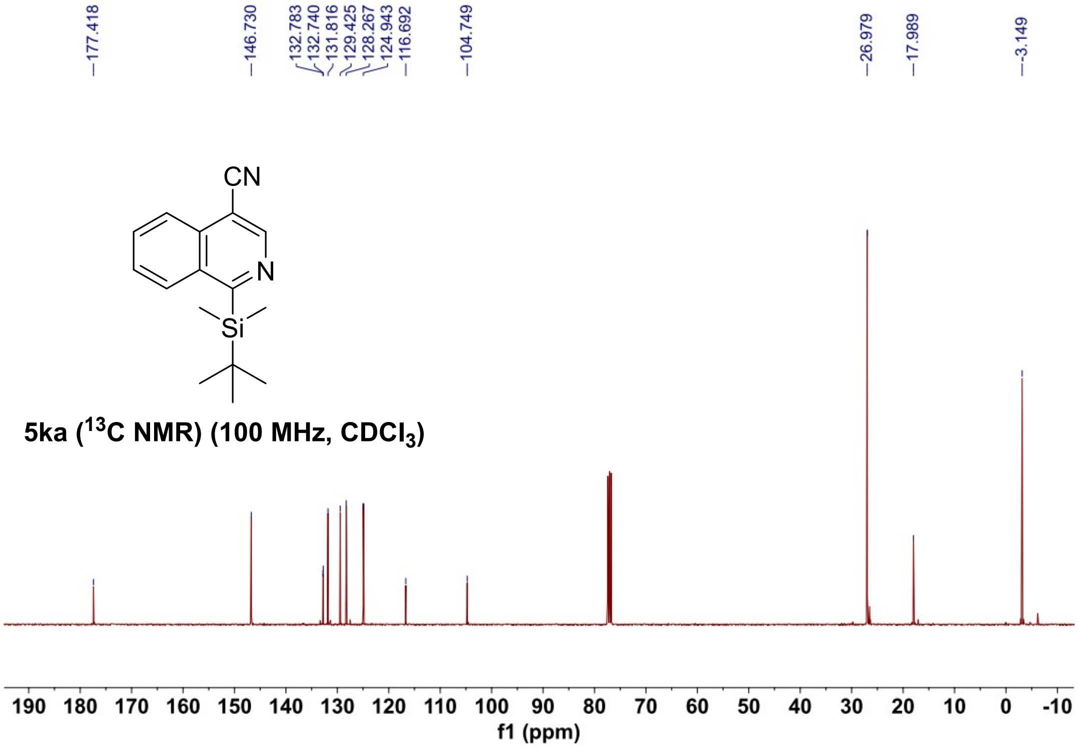
5i (^{13}C NMR) (100 MHz, $CDCl_3$)


9.079
8.271
8.268
8.250
8.246
8.181
8.160
7.862
7.847
7.842
7.825
7.822
7.755
7.735
7.717
0.982
0.595
CN
Si
N
5j (^{1}H NMR) (400 MHz, $CDCl_3$)
1.00
1.03
1.03
1.03
1.02
9.07
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

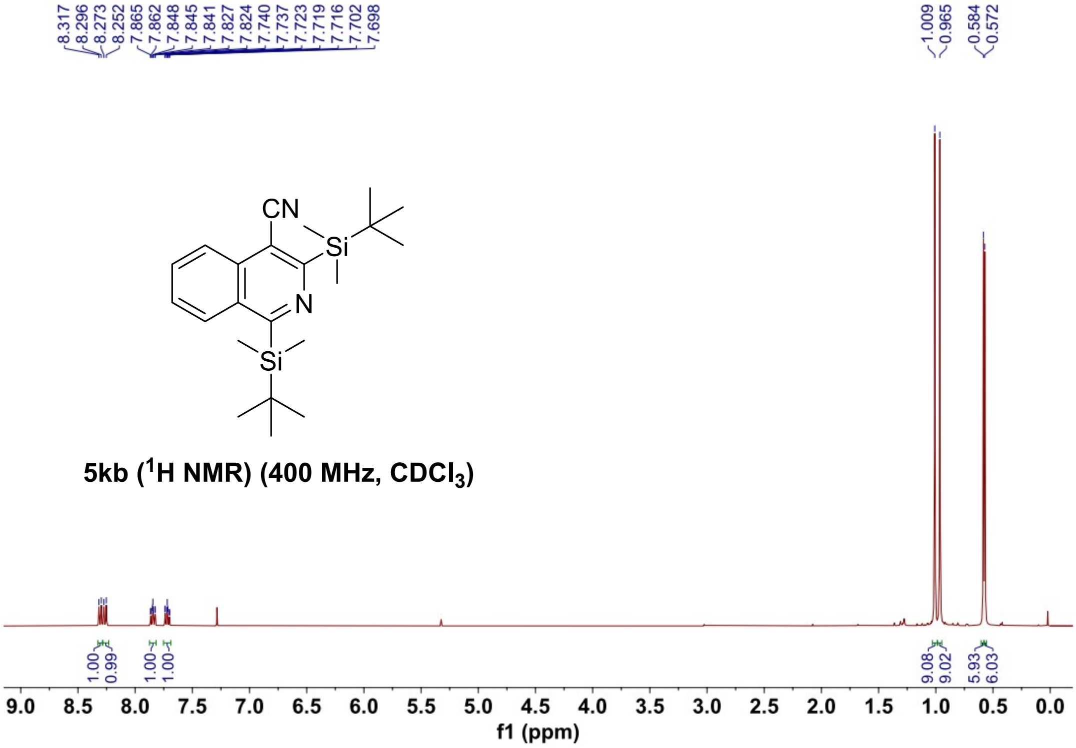

154.406
147.599
135.563
131.297
130.043
128.967
126.514
125.102
125.054
116.968
26.537
18.385
-5.033
CN
Si
N
5j (^{13}C NMR) (100 MHz, $CDCl_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



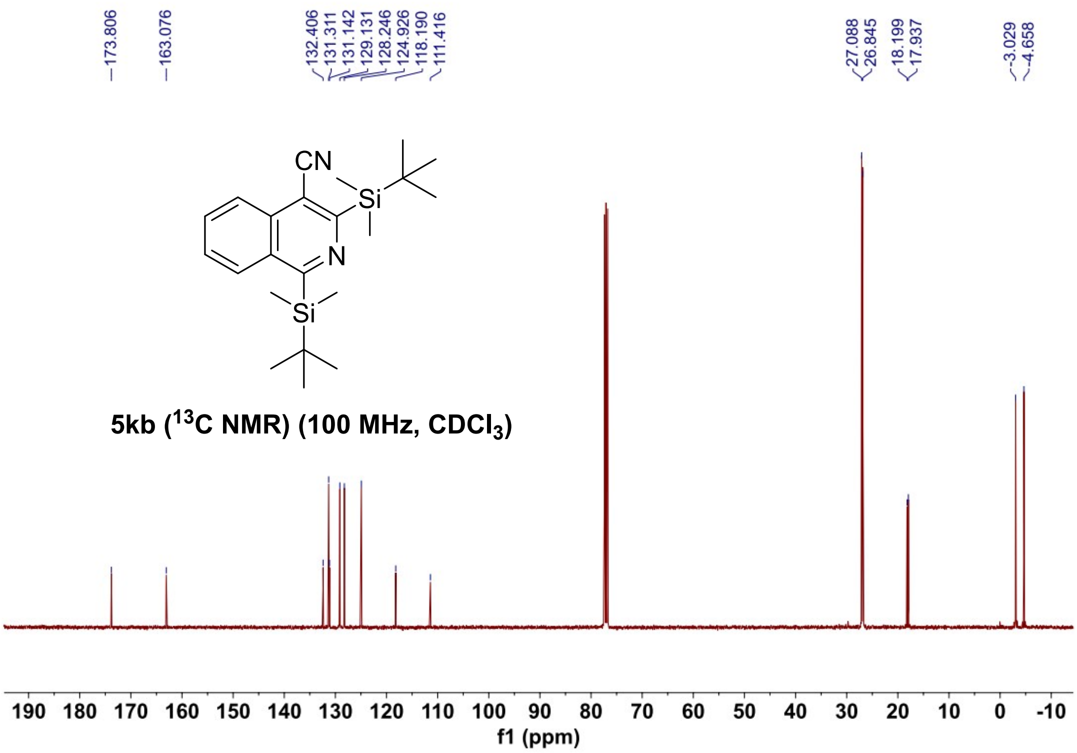
5ka (^{1}H NMR) (400 MHz, $CDCl_3$)



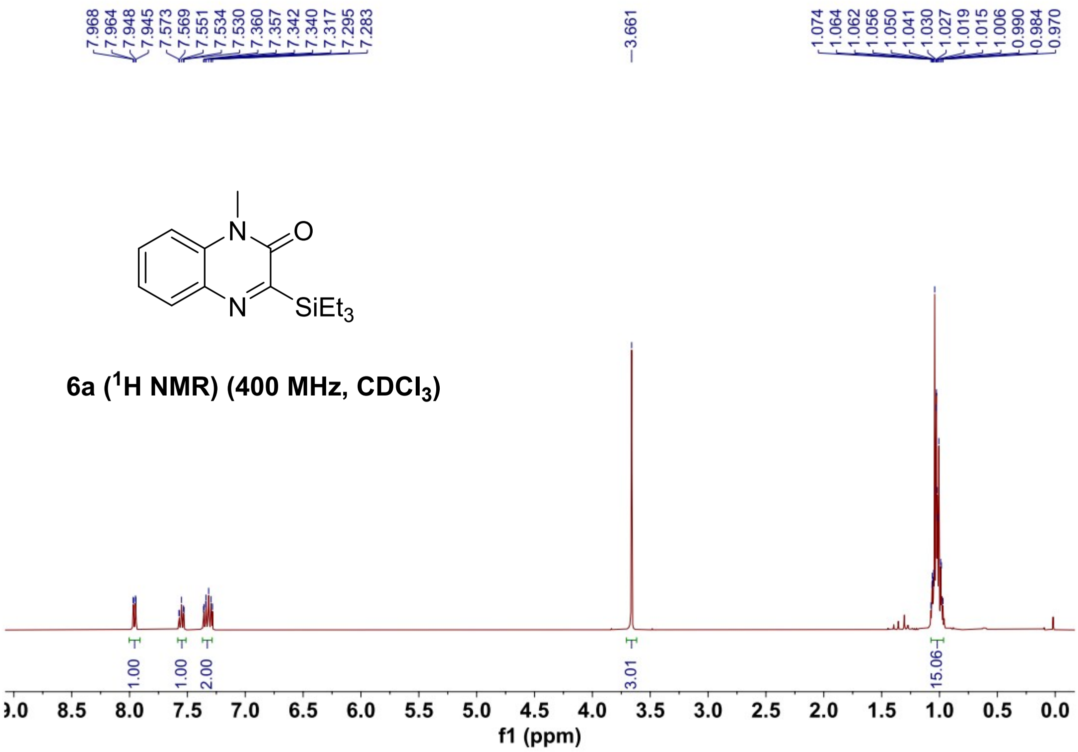
5ka (^{13}C NMR) (100 MHz, $CDCl_3$)



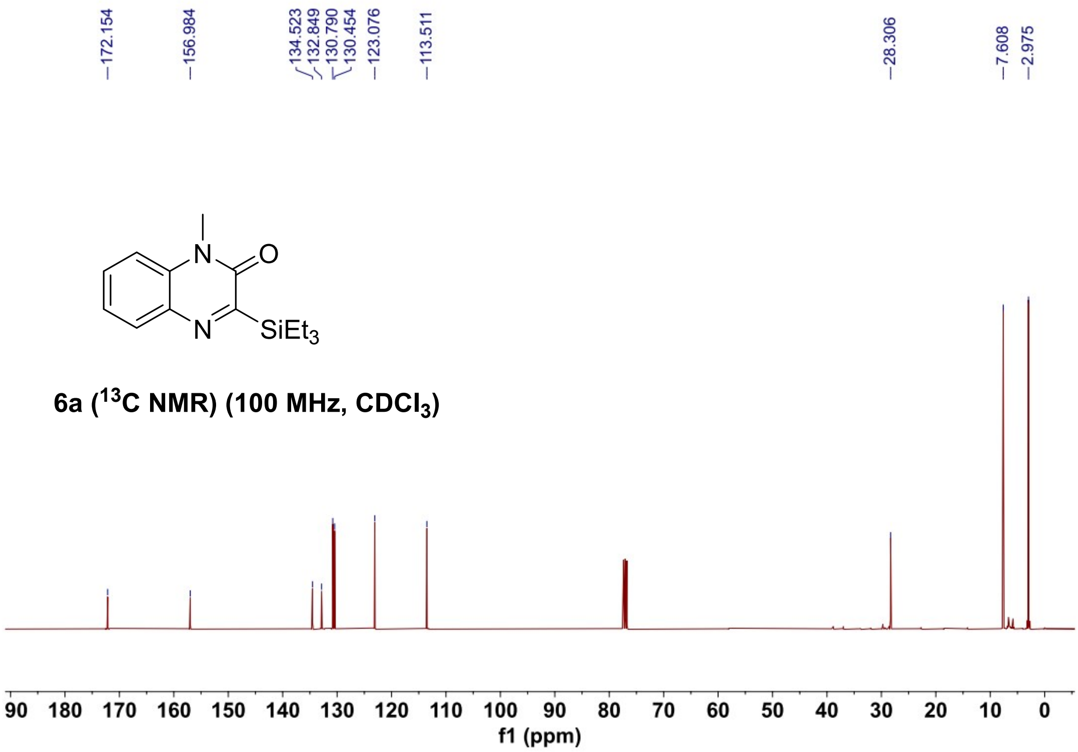
5kb (^{1}H NMR) (400 MHz, $CDCl_3$)



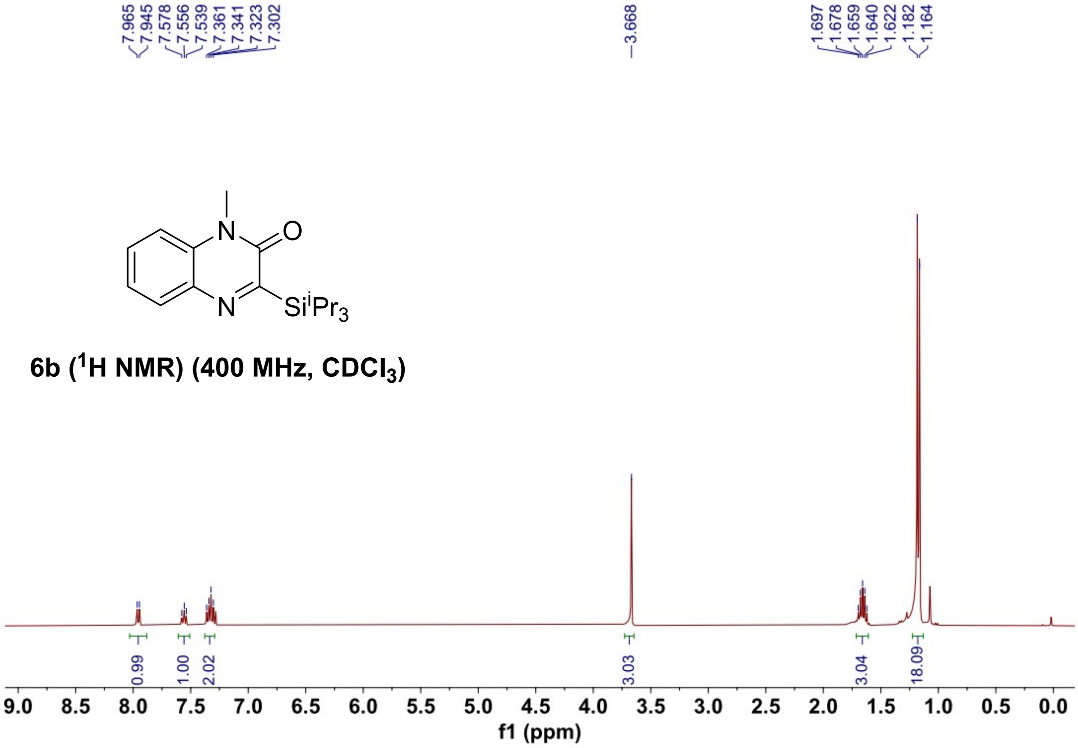
5kb (^{13}C NMR) (100 MHz, $CDCl_3$)



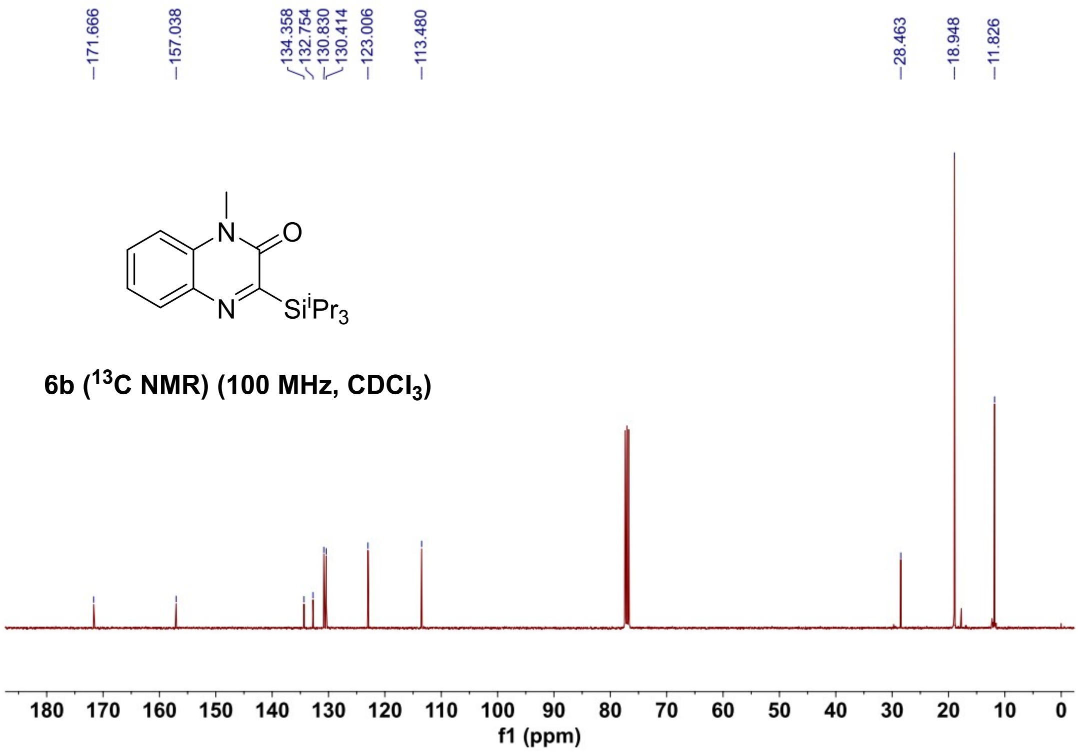
6a (^{1}H NMR) (400 MHz, $CDCl_3$)



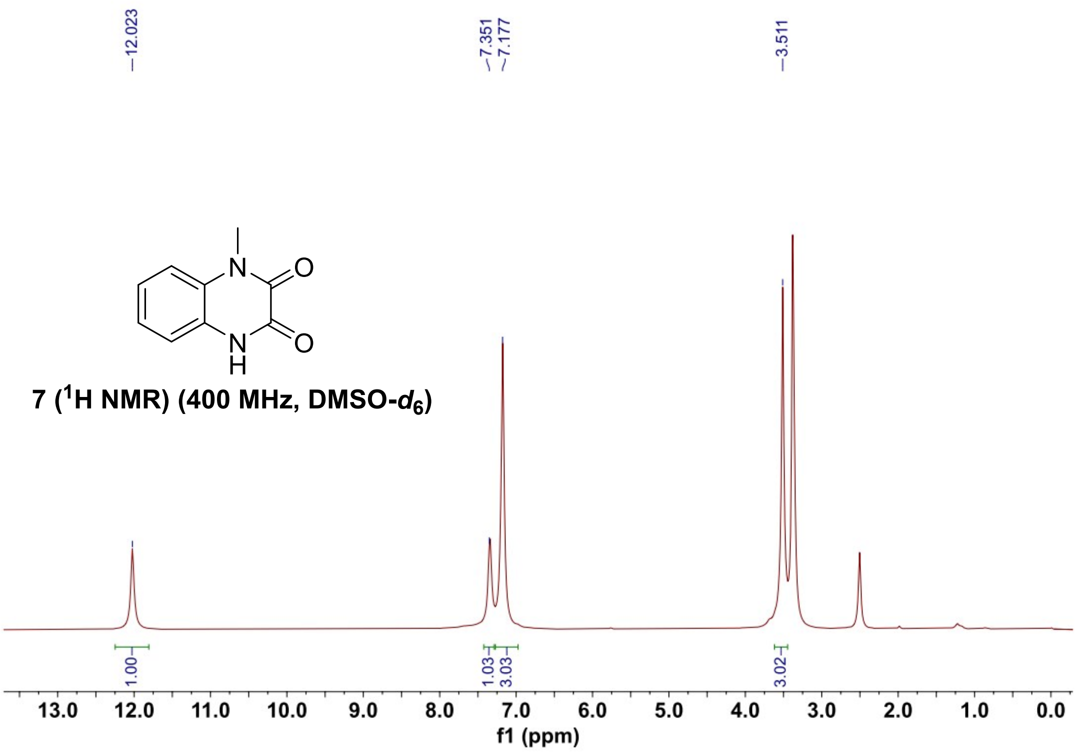
6a (^{13}C NMR) (100 MHz, $CDCl_3$)

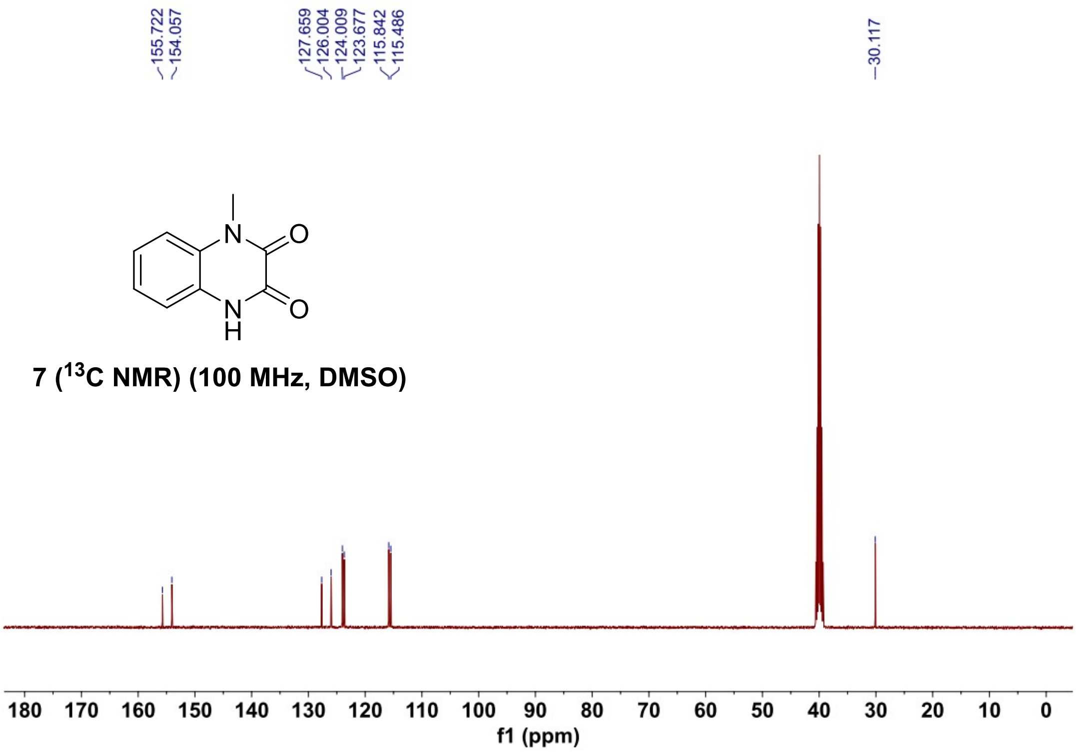


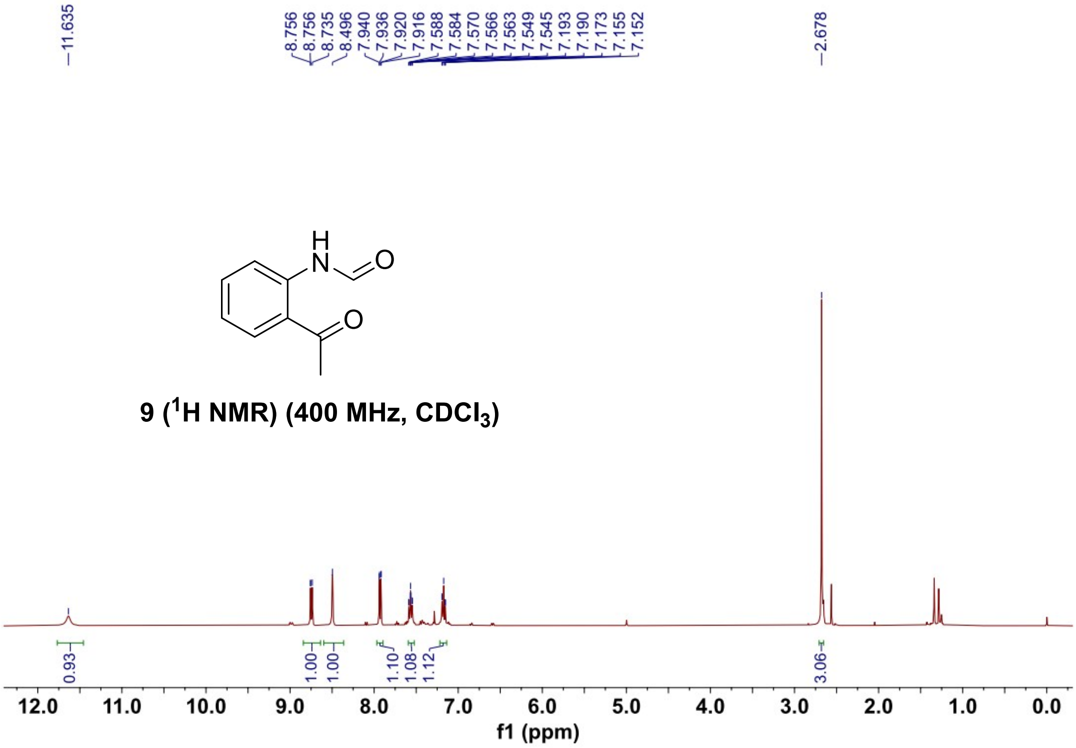
6b (^{1}H NMR) (400 MHz, $CDCl_3$)



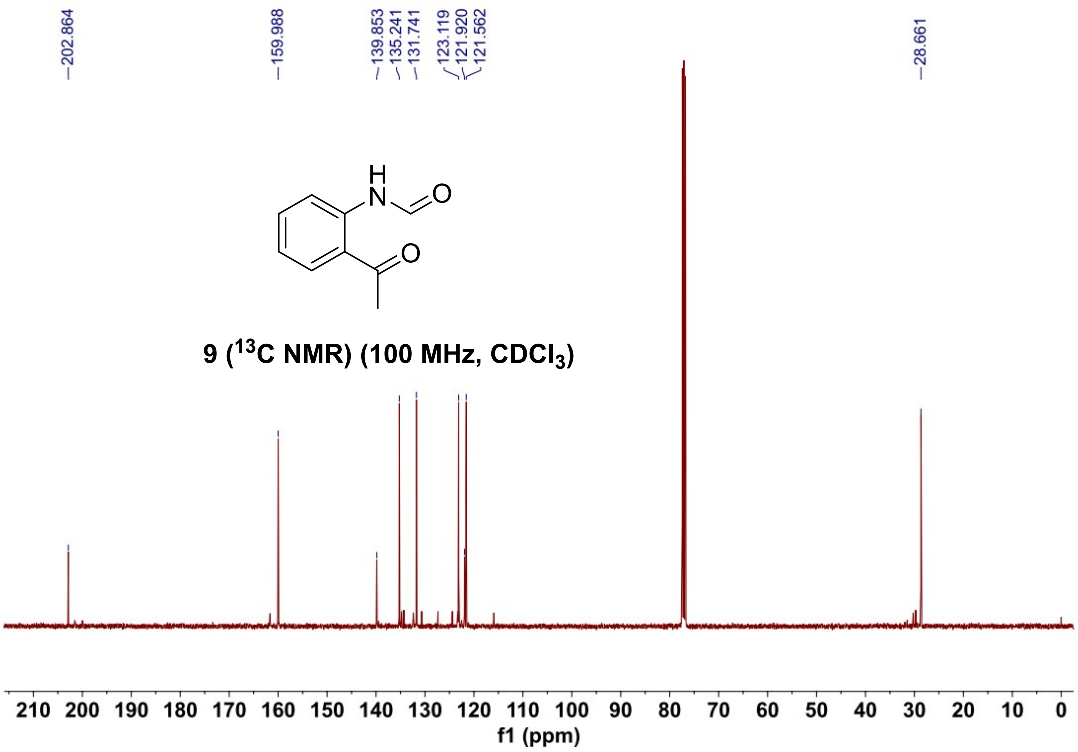
6b (^{13}C NMR) (100 MHz, $CDCl_3$)


12.023
7.351
7.177
3.511
7 (1H NMR) (400 MHz, DMSO-d6)
1.00
1.03
3.03
3.02
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

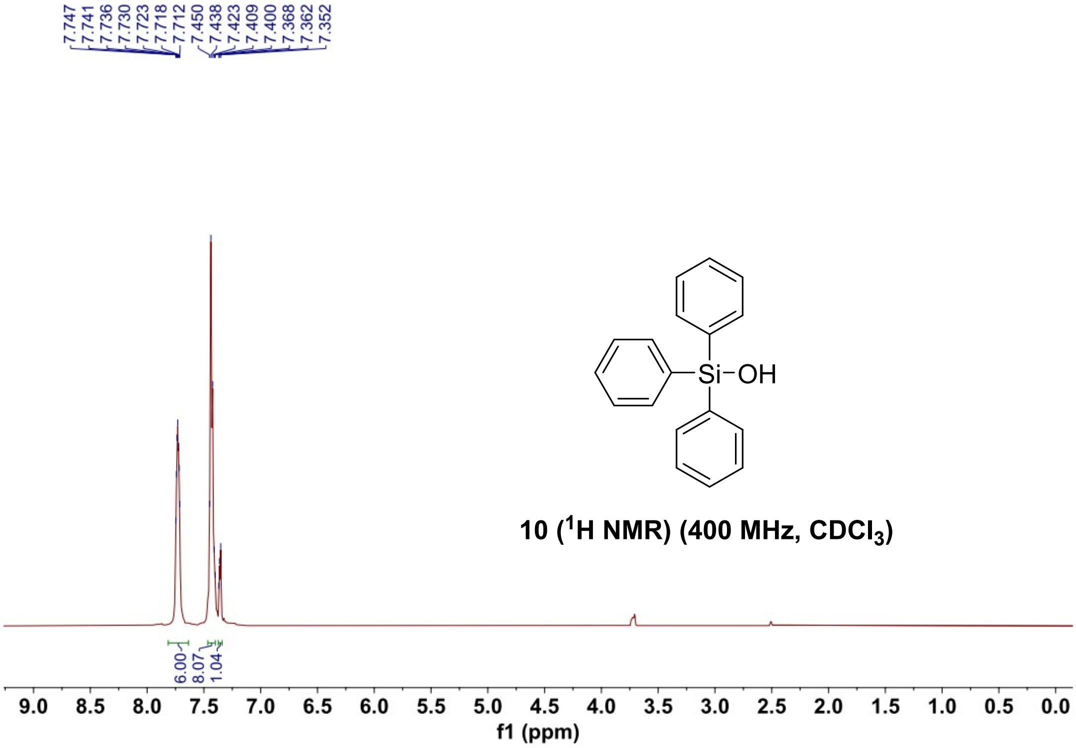

155.722
154.057
127.659
126.004
124.009
123.677
115.842
115.486
30.117
7 (13C NMR) (100 MHz, DMSO)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



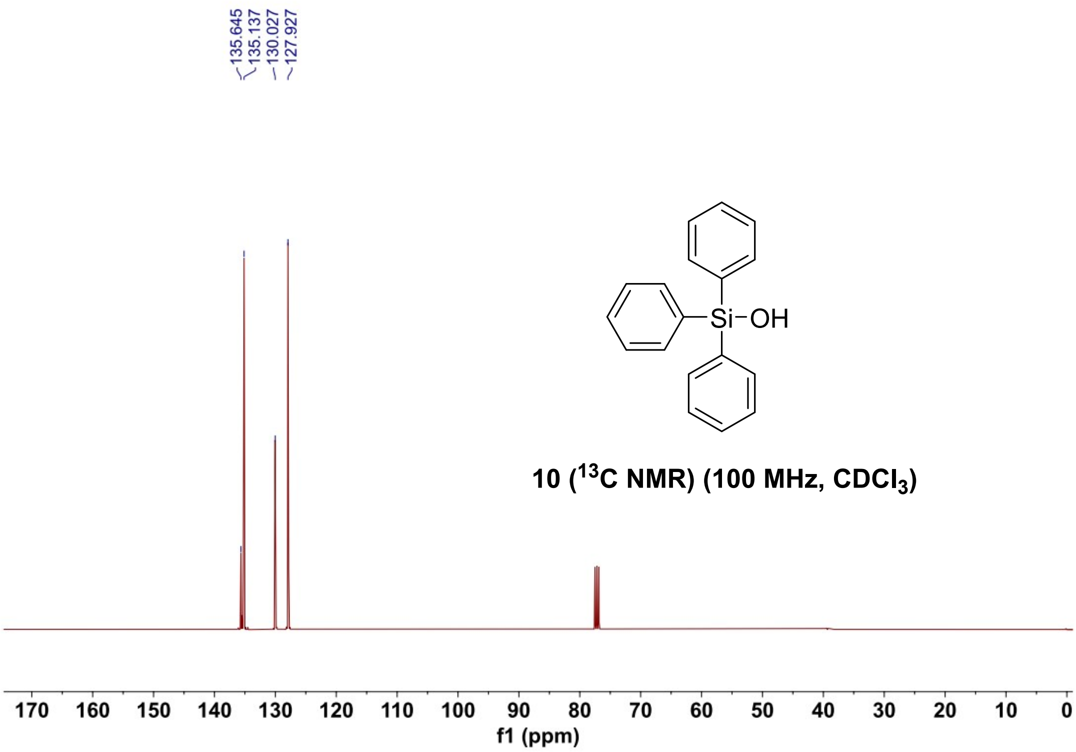
9 (^{1}H NMR) (400 MHz, $CDCl_3$)



9 (^{13}C NMR) (100 MHz, $CDCl_3$)



10 (^{1}H NMR) (400 MHz, $CDCl_3$)



10 (^{13}C NMR) (100 MHz, $CDCl_3$)