Supporting Information

Copper-Catalyzed Asymmetric Silyl Addition to Alkenyl-Substituted N-Heteroarenes

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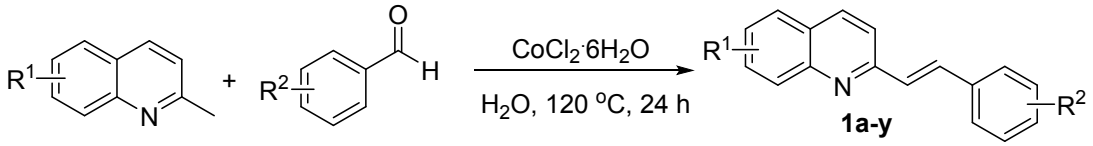
1. General information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All the reagents were obtained from commercial supplier and used as received, without further purification unless otherwise noted. Solvents used in the reactions were distilled from appropriate drying agents prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded respectively at 400 MHz and 100 MHz on a Bruker AVANCE 400. The chiral phosphoramidite ligands were prepared according to the literature procedures.[1] Enantiomeric excess (*ee*) were determined by HPLC analysis on a Shimadzu LC-20A, using Daicel Chiralcel AD or OD columns. Optical rotations were measured at PerkinElmer Model 341LC Polarimeter and concentrations (c) were reported in g×(100 mL)$^{-1}$. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spectrometer in ESI mode.

2. Preparation of alkenyl *N*-heteroarenes 1

The alkenyl *N*-heteroarenes **1a-y**[2a], **1z**[2b] and **1za**[2c], **1zb**[2d], **1zc-zd**[2e] were prepared according to the literature procedures.

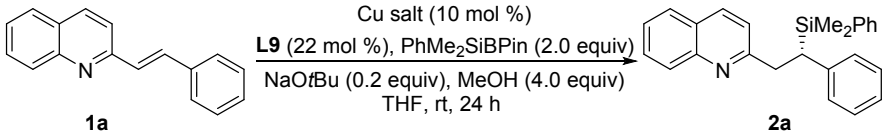
General experimental procedure for the synthesis of alkenyl quinolines 1a-y



To a 50 mL screw-capped reaction vial equipped with a magnetic stir bar, $CoCl_2.6H_2O$ (1.0 mol%, 0.05 mmol, 13.7 mg), 2-methylquinoline (5 mmol，0.7 mL), aldehyde (10 mmol, 1 mL) and H_2O (3 mL) were added. The resulting mixture was placed into a preheated oil bath at 120 °C with vigorous stirring. After 24 h, the reaction mixture was taken out of the oil bath, allowed to cool to room temperature and poured into H_2O (10 mL). The organic layer was then extracted with ethyl acetate (20 mL x 3), washed with brine (40 mL), dried over Na_2SO_4 and solvent removed under reduced pressure. The crude product was then loaded onto a column of silica gel suspended in petroleum ether. Purification by flash chromatography (petroleum ether/EtOAc = 50:1→30:1, v/v) then gave the alkenylation product **1a-y**.

3. Enantioselective silyl addition to alkenyl *N*-heteroarenes

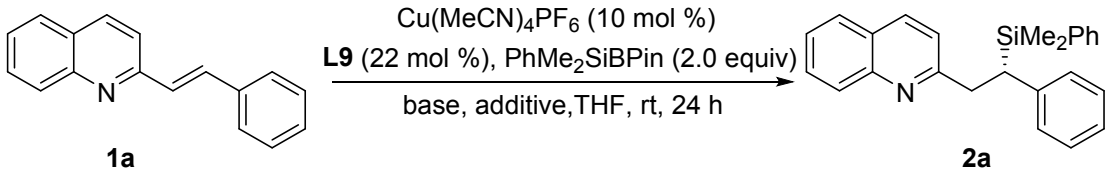
3.1. The screening of copper salts[a]



entry	Cu salt	yield (%)[b]	ee (%)[c]
1	CuCl	87%	89%
2	CuI	90%	90%
3	CuBr	81%	89%
4	$Cu(ClO_4)_2 \cdot O_2H6$	92%	91%
5	$Cu(OTf)_2$	92%	89%
6	$Cu(CH_3CN)_4PF_6$	86%	93%

[a]Reaction conditions: **1a** (0.1 mmol), $PhMe_2SiBpin$ (0.2 mmol), NaO*t*Bu (0.2 equiv), Cu salt (10 mol %), **L9** (22 mol %), MeOH (4.0 equiv), solvent (0.05 M). [b]Isolated yield. [c]Determined by chiral HPLC.

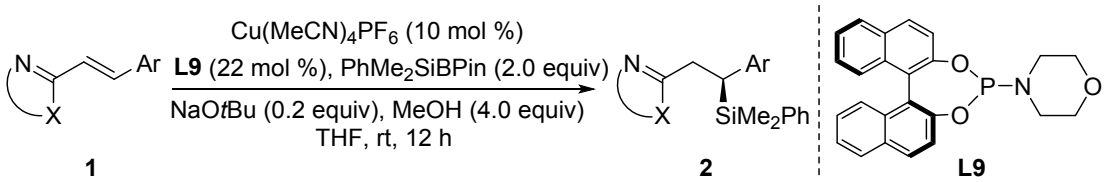
3.2. The screening of bases and additives[a]



entry	base (equiv)	additive (equiv)	yield (%)[b]	ee (%)[c]
1	LiOH (0.2)	MeOH (4.0)	63	93
2	NaOH (0.2)	MeOH (4.0)	58	94
3	KOH (0.2)	MeOH (4.0)	74	92
4	Na_2CO_3 (0.2)	MeOH (4.0)	95	91
5	K_2CO_3 (0.2)	MeOH (4.0)	90	80
6	Cs_2CO_3 (0.2)	MeOH (4.0)	62	93
7	Et_3N (0.2)	MeOH (4.0)	32	91
8	NaHMDS (0.2)	MeOH (4.0)	80	93
9	LiO*t*Bu (0.2)	MeOH (4.0)	85	89
10	KO*t*Bu (0.2)	MeOH (4.0)	77	91
11	NaO*t*Bu (0.2)	MeOH (4.0)	86	93
12	NaO*t*Bu (2.0)	-	trace	
13	NaO*t*Bu (0.2)	EtOH (4.0)	87	89
14	NaO*t*Bu (0.2)	*i*PrOH (4.0)	88	85
15	NaO*t*Bu (0.2)	*t*BuOH (4.0)	73	93
16	NaO*t*Bu (0.2)	H_2O (4.0)	94	90
17	NaO*t*Bu (0.2)	MeOH (2.0)	74	92
18	NaO*t*Bu (0.2)	MeOH (6.0)	82	93

[a]Reaction conditions: **1a** (0.1 mmol), $PhMe_2SiBpin$ (0.2 mmol), base, $Cu(MeCN)_4PF_6$ (10 mol %), **L9** (22 mol %), additive, solvent (0.05 M). [b]Isolated yield. [c]Determined by chiral HPLC.

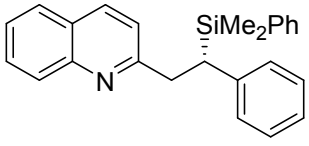
3.3. Typical procedure for the enantioselective silyl addition to alkenyl *N*-heteroarenes



An oven-dried vial was charged with $[Cu(CH_3CN)_4]PF_6$ (3.8 mg, 0.01 mmol, 10 mol%) and chiral phosphoramidite ligand **L9** (8.8 mg, 0.022 mmol, 22 mol%) and sealed with a septum. The vial was connected to an argon-vacuum line, evacuated and backfilled with argon (×3). THF (1.0 mL) was added and the mixture was stirred for 5 min. $PhMe_2SiBpin$ (55 uL, 0.20 mmol, 2.0 equiv) was added followed by a solution of NaO*t*Bu (2 mmg, 0.02 mmol, 0.2 equiv) in THF (0.5 mL). The dark brown solution was stirred for 15 min at room temperature and a solution of **1** (1.0 equiv) in THF (0.5 mL) was added followed by methanol (16 μL, 0.4 mmol, 4.0 equiv). Then, the reaction mixture was stirred overnight at room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x3) and the combined organic layers were washed with saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20:1→10:1).

3.4. Characterization data for the products 2a-2za

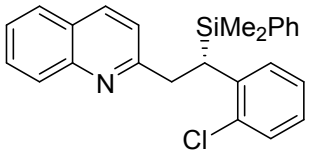
(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-phenylethyl)quinoline (2a)



Colorless oil, 31.6 mg, yield 86%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –56.5 (*c* = 0.1, THF). 93% *ee* determined by HPLC analysis (Chiralpak AD-H , 1% IPA in hexane, rate: 1.0 mL/min, 220 nm). Retention time: t (minor) = 8.9 min, t (major) = 11.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.64-7.58 (m, 2H), 7.44-7.27 (m, 6H), 7.11-7.04 (m, 3H), 6.99-6.96 (m, 3H), 3.50-3.39 (m, 2H), 3.05 (dd, J_1 = 5.6 Hz, J_2 = 10.8 Hz, 1H), 0.31 (s, 3H), 0.26 (s, 3H). **^{13}C NMR** (100 MHz,

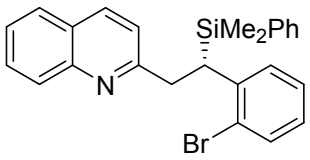
$CDCl_3$, ppm): δ 162.1, 147.7, 142.0, 141.9，137.0, 135.6, 134.2, 129.0, 128.7, 128.1, 127.9, 127.6, 127.3, 126.6, 125.5, 124.6, 121.0, 38.7, 36.0, –3.9, –5.0. **HRMS (ESI)**: calcd for $C_{25}H_{26}NSi$ $[M+H]^+$ 368.1829, found 368.1830.

(*S*)-2-(2-(2-chlorophenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2b)



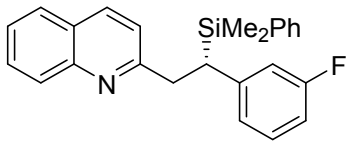
Light yellow solid, 36.2 mg, yield 90%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 103-105 °C, $[\alpha]_D^{25}$ = +19.9 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 21.2 min, t (minor) = 23.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.65-7.58 (m, 2H), 7.50-7.46 (m, 2H), 7.41-7.29 (m, 4H), 7.21 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.14-7.09 (m, 2H), 7.05-7.01 (m, 1H), 6.93-6.88 (m, 1H), 3.79 (t, *J* = 8.4 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 2H), 0.37 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.5, 147.6, 140.1, 136.7, 135.9, 134.2, 133.7, 129.24, 129.21, 129.1, 128.7, 128.3, 127.7, 127.3, 126.6, 126.5, 125.6, 125.5, 120.3, 38.8, 30.6, –3.7, –5.5. **HRMS (ESI)**: calcd for $C_{25}H_{25}ClNSi$ $[M+H]^+$ 402.1439, found 402.1440.

(*S*)-2-(2-(2-bromophenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2c)



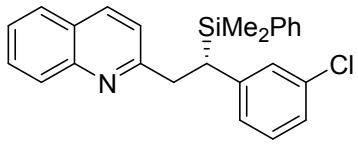
Light yellow oil, 36.6 mg, yield 82%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = +23.8 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 38.0 min, t (major) = 40.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.94 (d, *J* = 8.4, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.64-7.57 (m, 2H), 7.50-7.49 (m, 2H), 7.41-7.30 (m, 5H), 7.15-7.05 (m, 3H), 6.84-6.80 (m, 1H), 3.79 (t, *J* = 8.4 Hz, 1H), 3.45 (d, *J* = 8.4 Hz, 2H), 0.38 (s, 3H), 0.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.4, 147.6, 141.8, 136.7, 135.9, 134.3, 132.6, 129.2, 129.1, 128.7, 128.3, 127.7, 127.3, 127.1, 126.6, 126.0, 125.5, 125.3, 120.4, 39.1, 33.5, –3.6, –5.5. **HRMS (ESI)**: calcd for $C_{25}H_{25}BrNSi$ $[M+H]^+$ 446.0934, found 446.0934.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(3-fluorophenyl)ethyl)quinoline (2d)



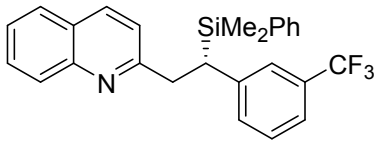
White solid, 36.6 mg, yield 95%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 77-80 °C, $[\alpha]_D^{25}$ = –83.3 (*c* = 0.1, THF). 91% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 24.1 min, t (major) = 28.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 8.8, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.43-7.29 (m, 6H), 7.06-7.00 (m, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.68-6.65 (m, 2H), 3.44-3.36 (m, 2H), 3.09 (t, *J* = 8.4 Hz, 1H), 0.32 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.7 (d, *J* = 243.0 Hz), 161.6, 147.8, 145.0 (d, *J* = 7.2 Hz), 136.6, 135.8, 134.2, 129.3, 129.149，129.148 (d, *J* = 8.3 Hz), 128.7, 127.7, 127.4, 126.6, 125.6, 123.8, 121.0, 114.8 (d, *J* = 21.2 Hz), 111.4 (d, *J* = 21.0 Hz), 38.6, 36.1, –4.0, –5.1. **HRMS (ESI)**: calcd for $C_{25}H_{25}FNSi$ $[M+H]^+$ 386.1735, found 386.1736.

(*S*)-2-(2-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2e)



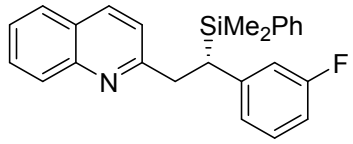
Light yellow oil, 37.8 mg, yield 94%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –81.5 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 25.8 min, t (major) = 35.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 8.4, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.43-7.29 (m, 6H), 7.07-6.94 (m, 4H), 6.84 (d, *J* = 7.6, 1H), 3.43-3.35 (m, 2H), 3.07 (dd, J_1 = 6.8 Hz, J_2 = 9.6 Hz, 1H), 0.32 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.5, 147.8, 144.4, 136.4, 135.8, 134.2, 133.7, 129.3, 129.2, 129.0, 128.8, 128.1, 127.7, 127.4, 126.6, 126.2, 125.6, 124.8, 121.0, 38.5, 36.0, –4.1, –5.1. **HRMS (ESI)**: calcd for $C_{25}H_{25}ClNSi$ $[M+H]^+$ 402.1439, found 402.1439.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(3-(trifluoromethyl)phenyl)ethyl)quinoline (2f)



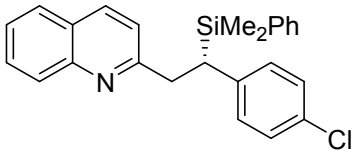
Colorless oil, 40.1 mg, yield 92%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –61.8 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 13.7 min, t (major) = 18.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 8.4, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.43-7.28 (m, 6H), 7.23-7.11 (m, 4H), 7.06 (d, *J* = 8.8 Hz, 1H), 3.50-3.40 (m, 2H), 3.18 (dd, J_1 = 6.8 Hz, J_2 = 10.0 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.3, 147.7, 143.1, 136.2, 136.0, 134.2, 131.3, 130.0 (q, *J* = 31.7 Hz), 129.4, 129.3, 128.7, 128.2, 127.7, 127.4, 126.6, 125.7, 124.8 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.8 Hz), 121.4 (q, *J* = 3.7 Hz), 121.1, 38.4, 36.3, –4.3, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{25}F_3NSi$ $[M+H]^+$ 436.1703, found 436.1703.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(3-fluorophenyl)ethyl)quinoline (2g)



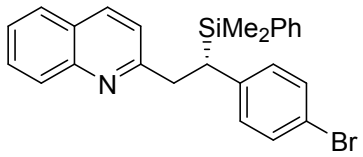
White solid, 36.2 mg, yield 94%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 80-82 °C, $[\alpha]_D^{25}$ = –62.4 (*c* = 0.1, THF). 97% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 26.0 min, t (major) = 30.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) : δ 7.96 (d, *J* = 8.4, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.65-7.59 (m, 2H), 7.42-7.28 (m, 6H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.90-6.87 (m, 2H), 6.79-6.75 (m, 2H), 3.46-3.34 (m, 2H), 3.04 (dd, J_1 = 5.6 Hz, J_2 = 10.8 Hz,1H), 0.31 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 161.8, 160.4 (d, *J* = 240.8 Hz), 147.8, 137.5 (d, *J* = 2.9 Hz), 136.7, 135.7, 134.2, 129.3, 129.2, 129.1, 128.7, 127.7, 127.4, 126.6, 125.6, 121.0, 114.6 (d, *J* = 20.9 Hz), 38.9, 35.3, –4.1, –5.0. **HRMS (ESI)**: calcd for $C_{25}H_{25}FNSi$ $[M+H]^+$ 386.1735, found 386.1735.

(*S*)-2-(2-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2h)



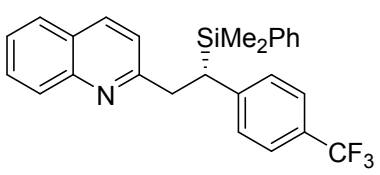
Light yellow oil, 33.0 mg, yield 82%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –80.6 (*c* = 0.1, THF). 94% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 26.5 min, t (major) = 30.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.95 (d, *J* = 8.8, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.43-7.29 (m, 6H), 7.05-7.03 (m, 3H), 6.90-6.86 (m, 2H), 3.45-3.34 (m, 2H), 3.06 (dd, J_1 = 6.0 Hz, J_2 = 10.4 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.6, 147.8, 140.6, 136.6, 135.8, 134.2, 130.1, 129.4, 129.3, 129.2, 128.7, 128.0, 127.7, 127.4, 126.6, 125.6, 121.0, 38.6, 35.7, –4.1, –5.0. **HRMS (ESI)**: calcd for $C_{25}H_{25}ClNSi$ $[M+H]^+$ 402.1439, found 402.1438.

(*S*)-2-(2-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2i)



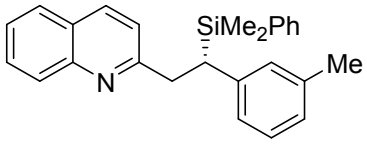
Light yellow oil, 42.4 mg, yield 95%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –98.8 (*c* = 0.1, THF). 94% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t(minor) = 28.3 min, t (major) = 31.9 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.66-7.60 (m, 2H), 7.43-7.29 (m, 6H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.45-3.31 (m, 2H), 3.05 (dd, J_1 = 6.0 Hz, J_2 = 10.4 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.6, 147.7, 141.1, 136.5, 135.8, 134.2, 130.9, 129.8, 129.3, 129.2, 128.7, 127.7, 127.4, 126.6, 125.6, 121.0, 118.1, 38.5, 35.7, –4.1, –5.1. **HRMS (ESI)**: calcd for $C_{25}H_{25}BrNSi$ $[M+H]^+$ 446.0934, found 446.0934.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(4-(trifluoromethyl)phenyl)ethyl)quinoline (2j)



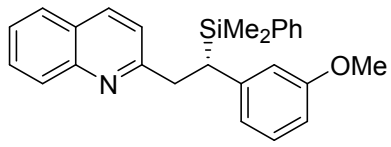
Light yellow oil, 38.8 mg, yield 89%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –89.2 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H, 1% IPA in hexane, rate: 1.0 mL/min, 254 nm). Retention time: t (minor) = 13.7 min, t (major) = 18.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.95 (d, *J* = 8.4, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.67-7.61 (m, 2H), 7.44-7.30 (m, 8H), 7.05 (d, *J* = 8.4 Hz, 3H), 3.45 (d, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 1H), 0.32 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.3, 147.7, 146.6, 136.2, 135.9, 134.2, 129.4, 129.2, 128.7, 128.2, 127.7, 127.4, 126.8 (q, *J* = 31.9 Hz), 126.6, 125.7, 124.8 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 269.6 Hz), 120.9, 38.4, 36.4, –4.1, –5.1. **HRMS (ESI)**: calcd for $C_{26}H_{25}F_3NSi$ $[M+H]^+$ 436.1703, found 436.1703.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(m-tolyl)ethyl)quinoline (2k)



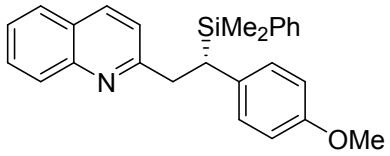
Light yellow oil, 33.2 mg, yield 87%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –53.4 (*c* = 0.1, THF). 91% *ee* determined by HPLC analysis (Chiralpak AD-H, 1% IPA in hexane, rate: 1 mL/min, 254 nm). Retention time: t (minor) = 5.5 min, t (major) = 7.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 8.4, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.64-7.59 (m, 2H), 7.43-7.27 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.01-6.97 (m, 1H), 6.80-6.75 (m, 3H), 3.49-3.38 (m, 2H), 3.00 (dd, J_1 = 5.6 Hz, J_2 = 10.8 Hz, 1H), 2.17 (s, 3H), 0.30 (s, 3H), 0.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.2, 147.6, 141.7, 137.2, 137.1, 135.7, 134.3, 129.0, 128.7, 127.7, 127.5, 127.3, 126.6, 125.5, 125.4, 125.1, 121.1, 38.6, 35.8, 21.4, –3.9, –5.1. **HRMS (ESI)**: calcd for $C_{26}H_{28}NSi$ $[M+H]^+$ 382.1986, found 382.1986.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(3-methoxyphenyl)ethyl)quinoline (2l)



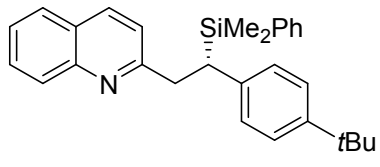
Light yellow oil, 35.4 mg, yield 89%. R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –76.9 (*c* = 0.1, THF). 88% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 32.9 min, t (major) = 38.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 8.4, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.65-7.59 (m, 2H), 7.45-7.28 (m, 6H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.03-6.99 (m, 1H), 6.60-6.48 (m, 3H), 3.61 (s, 3H), 3.49-3.38 (m, 2H), 3.03 (dd, J_1 = 6.0 Hz, J_2 = 10.4 Hz, 1H), 0.32 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.1, 159.2, 147.7, 143.6, 137.1, 135.7, 134.3, 129.1, 128.73, 128.69, 127.6, 127.4, 126.6, 125.5, 121.1, 120.7, 113.6, 110.4, 54.9, 38.7, 36.2, –3.9, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{28}NOSi$ $[M+H]^+$ 398.1935, found 398.1935.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(4-methoxyphenyl)ethyl)quinoline (2m)



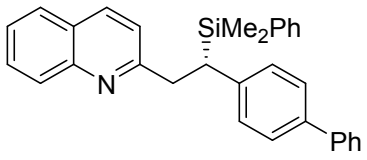
Light yellow oil, 35.8 mg, yield 90%. R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –75.6 (*c* = 0.1, THF). 94% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 36.6 min, t (major) = 40.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 8.4, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.65-7.59 (m, 2H), 7.45-7.28 (m, 6H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.89-6.86 (m, 2H), 6.67-6.63 (m, 2H), 3.69 (s, 3H), 3.42-3.35 (m, 2H), 2.97 (t, *J* = 8.8 Hz, 1H), 0.31 (s, 3H), 0.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.3, 156.9, 147.8, 137.3, 135.6, 134.3, 133.8, 129.03, 128.97, 128.7, 127.6, 127.4, 126.7, 125.5, 121.1, 113.4, 55.1, 39.0, 35.0, –3.8, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{28}NOSi$ $[M+H]^+$ 398.1935, found 398.1935.

(*S*)-2-(2-(4-(tert-butyl)phenyl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2n)



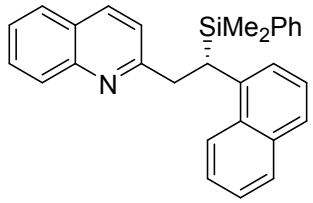
Light yellow solid, 34.3 mg, yield 81%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 81-84 °C, $[\alpha]_D^{25}$ = –66.8 (*c* = 0.1, THF). 93% *ee* determined by HPLC analysis (Chiralpak AD-H × 2 , 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 19.2 min, t (major) = 20.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 8.4, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.64-7.58 (m, 2H), 7.41-7.37 (m, 3H), 7.32-7.26 (m, 3H), 7.12-7.06 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.49-3.37 (m, 2H), 3.00 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1H), 1.23 (s, 9H), 0.30 (s, 3H), 0.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.3, 147.7, 147.3, 138.6, 137.4, 135.6, 134.2, 129.0, 128.9, 128.7, 127.6, 127.5, 127.3, 126.6, 125.4, 124.7, 121.1, 38.9, 35.2, 34.1, 31.4, –3.7, –5.1. **HRMS (ESI)**: calcd for $C_{29}H_{34}NSi$ $[M+H]^+$ 424.2455, found 424.2455.

(*S*)-2-(2-([1,1'-biphenyl]-4-yl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2o)



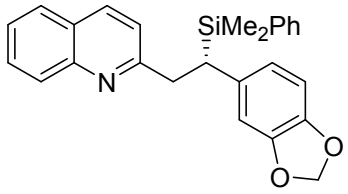
Light yellow solid, 38.2 mg, yield 86%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 120-122 °C, $[\alpha]_D^{25}$ = –117.5 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H × 2 , 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 35.1 min, t (minor) = 40.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 8.4, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.53-7.25 (m, 11H), 7.07 (dd, J_1 = 8.4 Hz, J_2 = 24.4 Hz, 3H), 3.53-3.42 (m, 2H), 3.10 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1H), 0.34 (s, 3H), 0.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.0, 147.7, 141.2, 140.9, 137.2, 137.0, 135.8, 134.3, 129.1, 128.7, 128.6, 128.5, 127.6, 127.4, 126.8, 126.6, 126.5, 125.5, 121.1, 38.7, 35.8, –3.9, –5.0. **HRMS (ESI)**: calcd for $C_{31}H_{30}NSi$ $[M+H]^+$ 444.2142, found 444.2142.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(naphthalen-1-yl)ethyl)quinoline (2p)



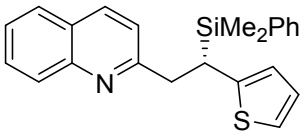
Light yellow oil, 33.8 mg, yield 81%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 93-95 °C, $[\alpha]_D^{25}$ = +50.7 (*c* = 0.1, THF). 89% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 39.8 min, t (minor) = 44.9 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.75-7.67 (m, 2H), 7.59-7.51 (m, 4H), 7.45-7.29 (m, 8H), 7.25-7.24 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.08 (dd, J_1 = 6.0 Hz, J_2 = 9.6 Hz, 1H), 3.69-3.58 (m, 2H), 0.27 (s, 3H), 0.16 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.9, 147.6, 138.9, 137.2, 135.7, 134.2, 133.8, 132.3, 129.1, 129.0, 128.7, 127.6, 127.3, 126.6, 125.4, 125.2, 125.1,125.0, 124.1, 123.7, 120.7, 39.5, 28.7, –3.4, –5.1. **HRMS (ESI)**: calcd for $C_{29}H_{28}NSi$ $[M+H]^+$ 418.1986, found 418.1986.

(*S*)-2-(2-(benzo[d][1,3]dioxol-5-yl)-2-(dimethyl(phenyl)silyl)ethyl)quinoline (2q)



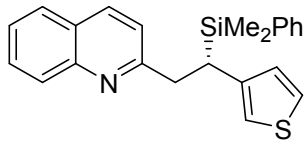
Colorless oil, 32.9 mg, yield 80%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –90.9 (*c* = 0.1, THF). 88% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 37.8 min, t (major) = 44.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.47-7.29 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H). 6.48 (d, J = 1.6 Hz, 1H), 6.41 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 5.82 (d, *J* = 0.8 Hz, 2H), 3.41-3.31 (m, 2H), 2.97 (dd, J_1 = 6.0 Hz, J_2 = 10.4 Hz, 1H), 0.32 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.0, 147.8, 147.2, 144.7, 137.1, 135.9, 135.8, 134.2, 129.11, 129.08, 128.8, 127.6, 127.4, 126.7, 125.5, 121.1, 120.9, 108.6, 107.8, 100.5, 39.1, 35.7, –3.8, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{26}NO_2Si$ $[M+H]^+$ 412.1727, found 412.1726.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(thiophen-2-yl)ethyl)quinoline (2r)



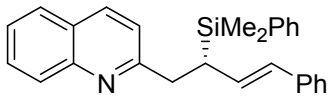
Light yellow oil, 29.9 mg, yield 80%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –75.5 (*c* = 0.1, THF). 85% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 33.0 min, t (minor) = 35.5 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.68-7.61 (m, 2H), 7.49-7.40 (m, 3H), 7.35-7.29 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 5.2 Hz, 1H), 6.76 (dd, J_1 = 3.2 Hz, J_2 = 4.8 Hz, 1H), 6.53 (d, *J* = 3.2 Hz, 1H), 3.45-3.30 (m, 3H), 0.40 (s, 3H), 0.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.6, 147.9, 145.8, 136.9, 135.7, 134.2, 129.2, 129.1, 128.9, 127.7, 127.4, 126.7, 126.6, 125.6, 123.5, 121.4, 121.2, 40.8, 31.3, –3.8, –5.0. **HRMS (ESI)**: calcd for $C_{23}H_{24}NSSi$ $[M+H]^+$ 374.1393, found 374.1393.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(thiophen-3-yl)ethyl)quinoline (2s)



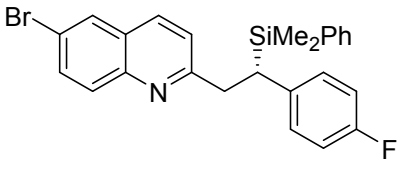
Light yellow oil, 35.9 mg, yield 96%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –72.3 (*c* = 0.1, THF). 91% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 37.1 min, t (minor) = 39.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.98 (d, *J* = 8.4, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44-7.28 (m, 6H), 7.08-7.04 (m, 2H), 6.73 (dd, J_1 = 0.8 Hz, J_2 = 4.8 Hz, 1H), 6.61 (d, *J* = 2 Hz, 1H), 3.43-3.31 (m, 2H), 3.18 (dd, J_1 = 5.6 Hz, J_2 = 10.8 Hz, 1H), 0.32 (s, 3H), 0.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.1, 147.7, 142.1, 137.1, 135.7, 134.2, 129.1, 128.7, 128.1, 127.6, 127.4, 126.6, 125.5, 124.4, 121.0, 118.8, 39.4, 31.5, –4.0, –4.9. **HRMS (ESI)**: calcd for $C_{23}H_{24}NSSi$ $[M+H]^+$ 374.1393, found 374.1394.

(*S, E*)-2-(2-(dimethyl(phenyl)silyl)-4-phenylbut-3-en-1-yl)quinoline (2t)



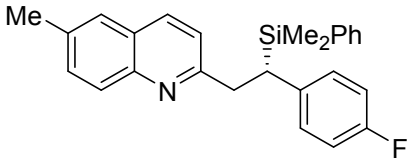
Light yellow oil, 29.9 mg, yield 76%. R_f = 0.2 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –107.8 (*c* = 0.1, THF). 85% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 20.6 min, t (major) = 24.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (dd, J_1 = 8.4 Hz, J_2 = 18.4 Hz, 2H), 7.71-7.55 (m, 4H), 7.45-7.34 (m, 4H), 7.23-7.08 (m, 6H), 6.19-6.08 (m, 2H), 3.27-3.10 (m, 2H), 2.67-2.61 (m, 1H), 0.40 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.3, 147.8, 138.1, 137.0, 135.9, 134.2, 131.2, 129.2, 128.7, 128.6, 128.3, 127.8, 127.4, 126.7, 126.3, 125.65, 125.58, 121.2, 38.6, 33.9, –4.3, –4.9. **HRMS (ESI)**: calcd for $C_{27}H_{28}NSi$ $[M+H]^+$ 394.1986, found 394.1987.

(*S*)-6-bromo-2-(2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)ethyl)quinoline (2u)



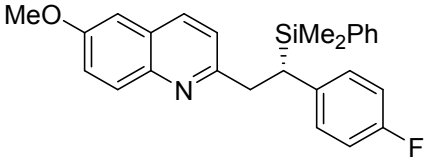
Light yellow oil, 32.1 mg, yield 69%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –49.4 (*c* = 0.1, THF). 87% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 21.6 min, t (major) = 27.6 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.82-7.80 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, J_1 = 2.0 Hz, J_2 = 9.2 Hz, 1H), 7.42-7.29 (m, 5H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.89-6.85 (m, 2H), 6.80-6.75 (m, 2H), 3.42-3.31 (m, 2H), 3.01 (dd, J_1 = 5.6 Hz, J_2 = 10.8 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.4, 160.5 (d, *J* = 241.1 Hz), 146.4, 137.4 (d, *J* = 3.2 Hz), 136.7, 134.7, 134.2, 132.6, 130.5, 129.4, 129.3 (d, *J* = 4.7 Hz), 129.2, 127.8, 127.7, 122.0, 119.3, 114.7 (d, *J* = 20.9 Hz), 39.0, 35.4, –4.0, –5.0. **HRMS (ESI)**: calcd for $C_{25}H_{24}BrFNSi$ $[M+H]^+$ 464.0840, found 464.0839.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)ethyl)-6-methylquinoline (2v)



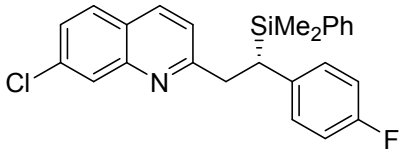
Light yellow oil, 36.0 mg, yield 90%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –45.2 (*c* = 0.1, THF). 91% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 31.9 min, t (major) = 41.2 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.46-7.29 (m, 7H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.89-6.86 (m, 2H), 6.78-6.74 (m, 2H), 3.43-3.31 (m, 2H), 3.02 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1H), 2.46 (s, 3H), 0.30 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.8, 160.4 (d, *J* = 240.6 Hz), 146.3, 137.5 (d, *J* = 2.9 Hz), 136.8, 135.3, 135.1, 134.2, 131.4, 129.24 (d, *J* = 13.0 Hz), 129.23, 128.4, 127.7, 126.6, 126.3, 121.0, 114.6 (d, *J* = 20.9 Hz), 38.8, 35.4, 21.4, –4.1, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{27}FNSi$ $[M+H]^+$ 400.1891, found 400.1891.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)ethyl)-6-methoxyquinoline (2w)



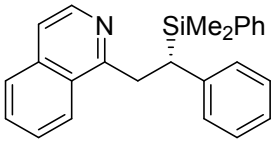
Light yellow solid, 32.4 mg, yield 78%. R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), mp = 95-98 °C, $[\alpha]_D^{25}$ = –4.0 (*c* = 0.1, THF). 86% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 49.2 min, t (major) = 51.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.42-7.40 (m, 2H), 7.35-7.25 (m, 4H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.89-6.86 (m, 2H), 6.79-6.75 (m, 2H), 3.86 (s, 3H), 3.42-3.30 (m, 2H), 3.00 (dd, J_1 = 5.2 Hz, J_2 = 11.2 Hz, 1H), 0.30 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.5 (d, *J* = 240.6 Hz), 159.2, 157.2, 143.8, 137.7 (d, *J* = 2.9 Hz), 136.9, 134.6, 134.2, 130.1, 129.3, 129.2 (d, *J* = 17.3 Hz), 127.6, 127.5, 121.6, 121.3, 114.6 (d, *J* = 20.9 Hz), 105.2, 55.5, 38.7, 35.4, –4.0, –5.0. **HRMS (ESI)**: calcd for $C_{26}H_{27}FNOSi$ $[M+H]^+$ 416.1840, found 416.1840.

(*S*)-7-chloro-2-(2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)ethyl)quinoline (2x)



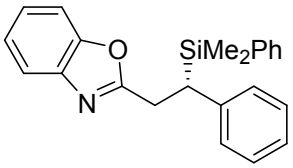
Light yellow solid, 37.0 mg, yield 88%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 98-100 °C, $[\alpha]_D^{25}$ = –58.8 (*c* = 0.1, THF). 93% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 21.8 min, t (major) = 23.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.42-7.29 (m, 6H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.90-6.86 (m, 2H), 6.80-6.76 (m, 2H), 3.43-3.31 (m, 2H), 3.03 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1H), 0.31 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.0, 160.5 (d, *J* = 241.0 Hz), 148.1, 137.4 (d, *J* = 2.8 Hz), 136.7, 135.5, 135.0, 134.2, 129.3, 129.2 (d, *J* = 3.3 Hz), 128.6, 127.9, 127.7, 126.6, 125.0, 121.4, 114.7 (d, *J* = 20.9 Hz), 39.0, 35.3, –4.0, –5.1. **HRMS (ESI)**: calcd for $C_{25}H_{24}ClFNSi$ $[M+H]^+$ 420.1345, found 420.1344.

(*S*)-1-(2-(dimethyl(phenyl)silyl)-2-phenylethyl)isoquinoline (2y)



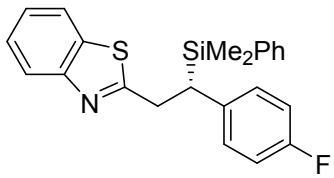
Light yellow oil, 32.3 mg, yield 88%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –3.3 (*c* = 0.1, THF). 95% *ee* determined by HPLC analysis (Chiralpak OD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (major) = 29.0 min, t (minor) = 36.3 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.26 (d, *J* = 5.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H) , 7.68 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.46-7.41 (m, 3H), 7.37-7.28 (m, 4H), 7.11-7.07 (m, 2H), 7.00-6.97 (m, 3H), 3.76-3.66 (m, 2H), 3.17 (dd, J_1 = 6.0 Hz, J_2 = 9.2 Hz, 1H), 0.32 (s, 3H), 0.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.1, 142.6, 141.5, 137.4, 136.1, 134.2, 129.4, 129.0, 128.2, 127.8, 127.6, 127.3, 127.0, 126.6, 125.1, 124.6, 119.0, 36.3, 35.4, –3.7, –5.1. **HRMS (ESI)**: calcd for $C_{25}H_{26}NSi$ $[M+H]^+$ 368.1829, found 368.1835.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-phenylethyl)benzo[d]oxazole (2*z*)



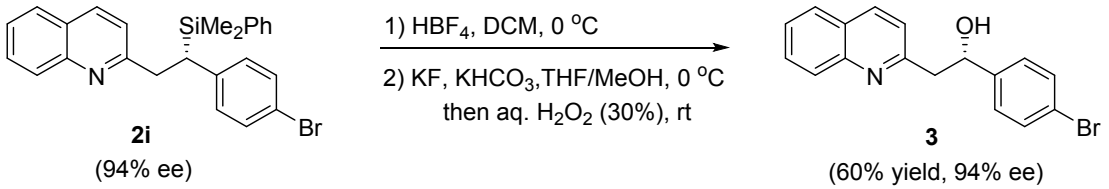
Red solid, 29.0 mg, yield 81%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), mp = 90-93 °C, $[\alpha]_D^{25}$ = –25.7 (*c* = 0.1, THF). 85% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 26.5 min, t (major) = 30.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.54-7.52 (m, 1H), 7.42-7.40 (m, 2H), 7.33-7.25 (m, 4H), 7.20-7.13 (m, 4H), 7.06-7.00 (m, 3H), 3.40-3.27 (m, 2H), 3.10 (dd, J_1 = 5.6 Hz, J_2 = 10.4 Hz, 1H), 0.29 (s, 3H), 0.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 166.5, 150.6, 141.2, 141.1, 136.1, 134.1, 129.3, 128.1, 127.7, 127.6, 125.1, 124.2, 123.8, 119.4, 110.1, 34.1, 29.4, –4.0, –5.6. **HRMS (ESI)**: calcd for $C_{23}H_{24}NOSi$ $[M+H]^+$ 358.1622, found 358.1623.

(*S*)-2-(2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)ethyl)benzo[d]thiazole (2za)

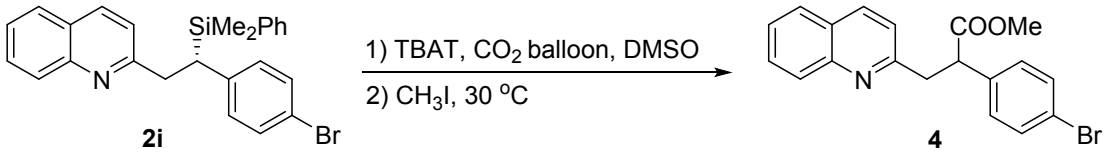


Light yellow oil, 34.9 mg, yield 89%. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{25}$ = –45.4 (*c* = 0.1, THF). 90% *ee* determined by HPLC analysis (Chiralpak AD-H × 2, 1% IPA in hexane, rate: 0.5 mL/min, 254 nm). Retention time: t (minor) = 24.5 min, t (major) = 27.6 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H) , 7.42-7.32 (m, 6H), 7.28-7.23 (m, 1H), 6.93-6.83 (m, 4H), 3.56-3.45 (m, 2H), 2.90 (dd, J_1 = 5.6 Hz, J_2 = 11.2 Hz, 1H), 0.31 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 172.0, 160.8 (d, *J* = 241.7 Hz), 152.7, 136.4 (d, *J* = 3.0 Hz), 135.9, 135.1, 134.2, 129.5, 129.2 (d, *J* = 7.8 Hz), 127.8, 125.7, 124.5, 122.4, 121.4, 115.0 (d, *J* = 21.1 Hz), 36.1, 34.8, –4.2, –5.2. **HRMS (ESI)**: calcd for $C_{23}H_{22}FNSSi$ $[M+H]^+$ 392.1230, found 392.1230.

4. Further derivatization



To a solution of **2i** (44.6 mg, 0.1 mmol) in 0.35 mL of CH_2Cl_2, 0.22 mL of HBF_4 (50-54% solution in Et_2O) was added at 0 °C. The mixture was stirred at ambient temperature for 2 hours. Dropping 2 mL of aqueous solution of 2N NaOH quenched the reaction, and the mixture was extracted with AcOEt, dried over Na_2SO_4, and evaporated under reduced pressure, and the brownish red oil was obtained. Then the flask was charged with 0.25 mL of THF, 0.25 mL of MeOH, KF (13.1 mg, 0.225 mmol), and $KHCO_3$ (12.5 mg, 0.125 mmol). To the stirred mixture was added 0.35 mL of 30% H_2O_2 in one portion at ambient temperature. The mixture was stirred for 8 hours. Dropping 0.25 mL of aqueous saturated solution of $Na_2S_2O_3$ quenched the reaction, and the mixture was extracted with AcOEt, dried over Na_2SO_4, and evaporated under reduced pressure. The remaining oil was purified by silica-gel chromatography (petroleum ether/ethyl acetate, 2:1) and 19.7 mg of alcohol (60%) was obtained as a white powder **3**, mp = 145-147 °C. $[\alpha]_D^{25}$ = –59.8 (*c* = 0.1, THF). 94% *ee* determined by HPLC analysis (Chiralpak AD-H, 5% IPA in hexane, rate: 1 mL/min, 254 nm). Retention time: t (major) = 44.2 min, t (minor) = 60.7 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.07 (dd, J_1 = 8.4 Hz, J_2 = 17.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74-7.70 (m, 1H), 7.55-7.51 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 5.29 (t, *J* = 6.0 Hz, 1H), 3.27 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.1, 147.0, 143.0, 136.9, 131.4, 129.9, 128.7, 127.6, 126.9, 126.3, 122.0, 121.0, 72.3, 45.8. **HRMS (ESI)**: calcd for $C_{17}H_{15}BrNO$ $[M+H]^+$ 328.0332, found 328.0332.



An oven-dried 10 mL sealed tube was charged with a stirring bar and tetrabutylammonium triphenyldifluorosilicate (59.4 mg, 0.11 mmol, 1.1 equiv). Under CO_2 atmosphere, super dry DMSO (0.1 M) was added to make a clear solution. **2i**

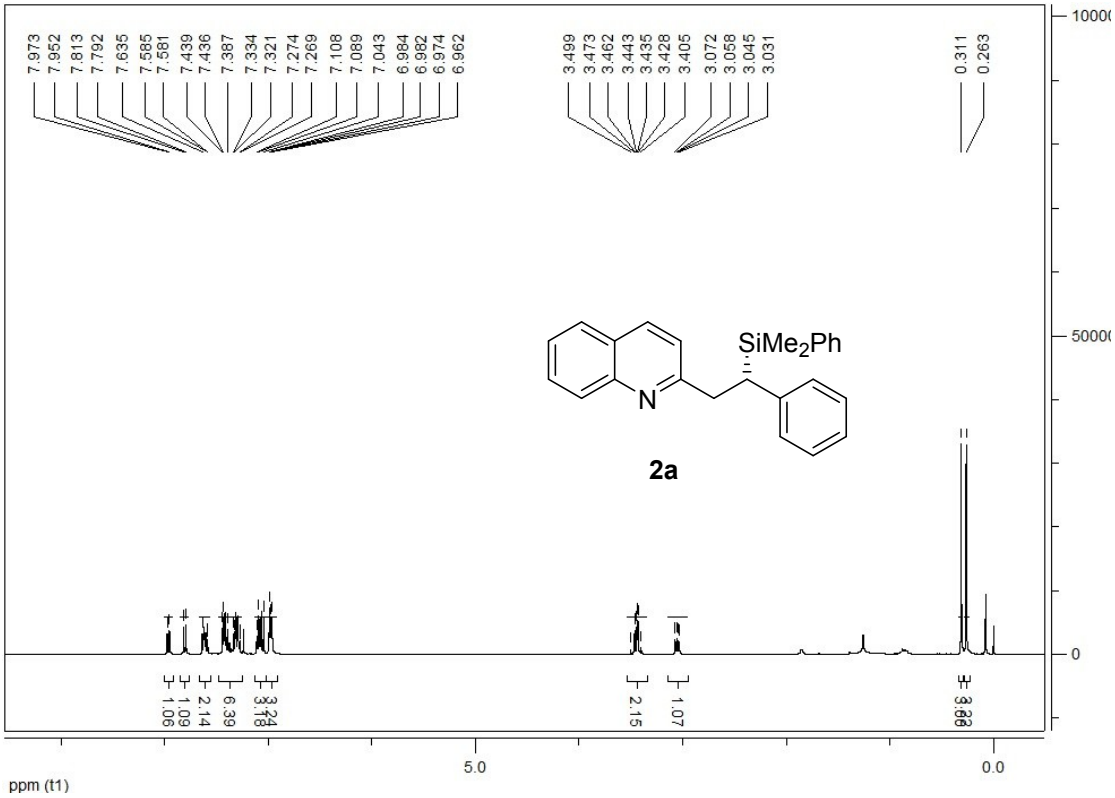
(44.4 mg, 0.1 mmol, 1.0 equiv) in DMSO (0.1 M) was added in one portion via a syringe. The reaction mixture was kept at 30 °C until the total consumption of **2i**. CH_3I (14 uL, 0.14 mmol, 2.4 equiv) was then added and the system was stirred for another 2 hours. Water was added and the resulting mixture was extracted with AcOEt. The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The remaining oil was purified by silica-gel chromatography (petroleum ether/ethyl acetate, 10:1) and 18.5 mg of ester (50%) was obtained as a white powder **4**, mp = 86-88 °C. 0% *ee* determined by HPLC analysis (Chiralpak OD-H, 1% IPA in hexane, rate: 1 mL/min, 254 nm). Retention time: t (major) = 22.2 min, t (minor) = 24.8 min. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.08 (dd, J_1 = 4.0 Hz, J_2 = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.78-7.74 (m, 1H), 7.59-7.49 (m, 3H), 7.34-7.32 (m, 2H), 7.25 (d, J = 8.4 Hz, 1H), 4.51 (dd, J_1 = 6.4 Hz, J_2 = 9.2 Hz, 1H), 3.86 (dd, J_1 = 9.2 Hz, J_2 = 14.8 Hz, 1H), 3.72 (s, 3H), 3.40 (dd, J_1 = 6.0 Hz, J_2 = 15.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 173.7, 158.9, 147.9, 137.8, 136.1, 131.8, 129.8, 129.4, 128.9, 127.5, 126.8, 126.0, 121.8, 121.3, 52.2, 49.9, 41.9. **HRMS (ESI)**: calcd for $C_{19}H_{16}BrNNaO_2$ $[M+Na]^+$ 392.0257, found 392.0258.

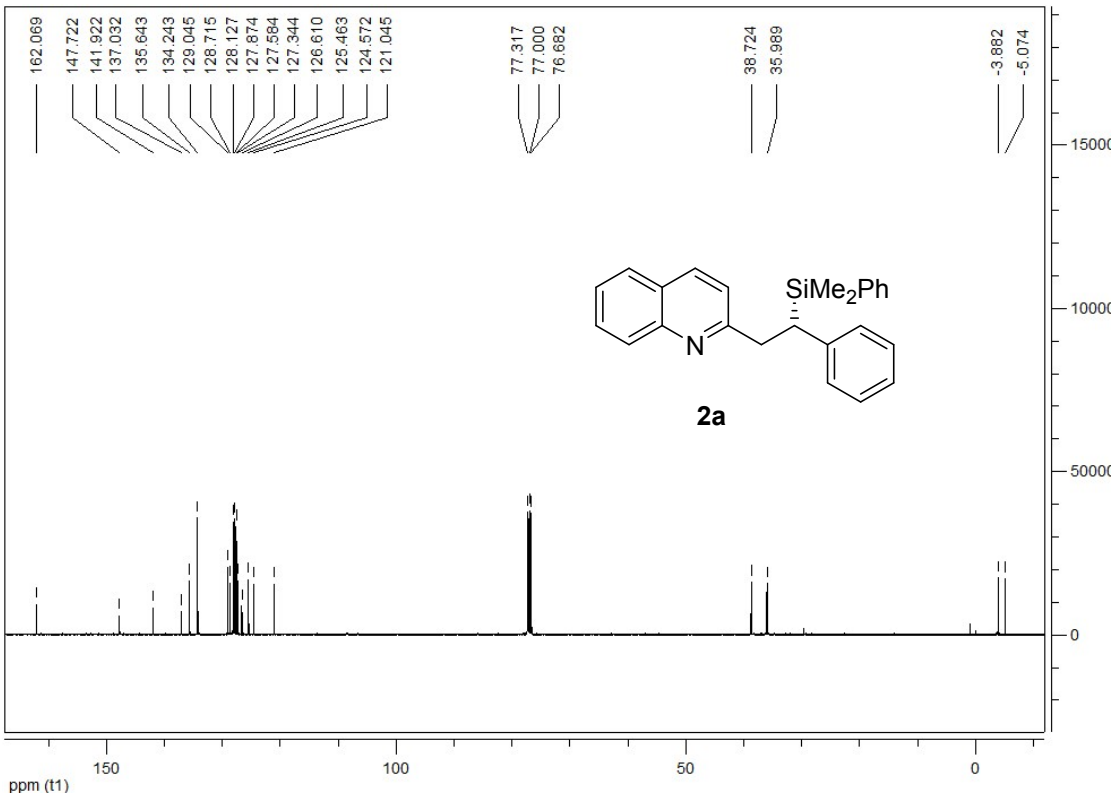
5. References

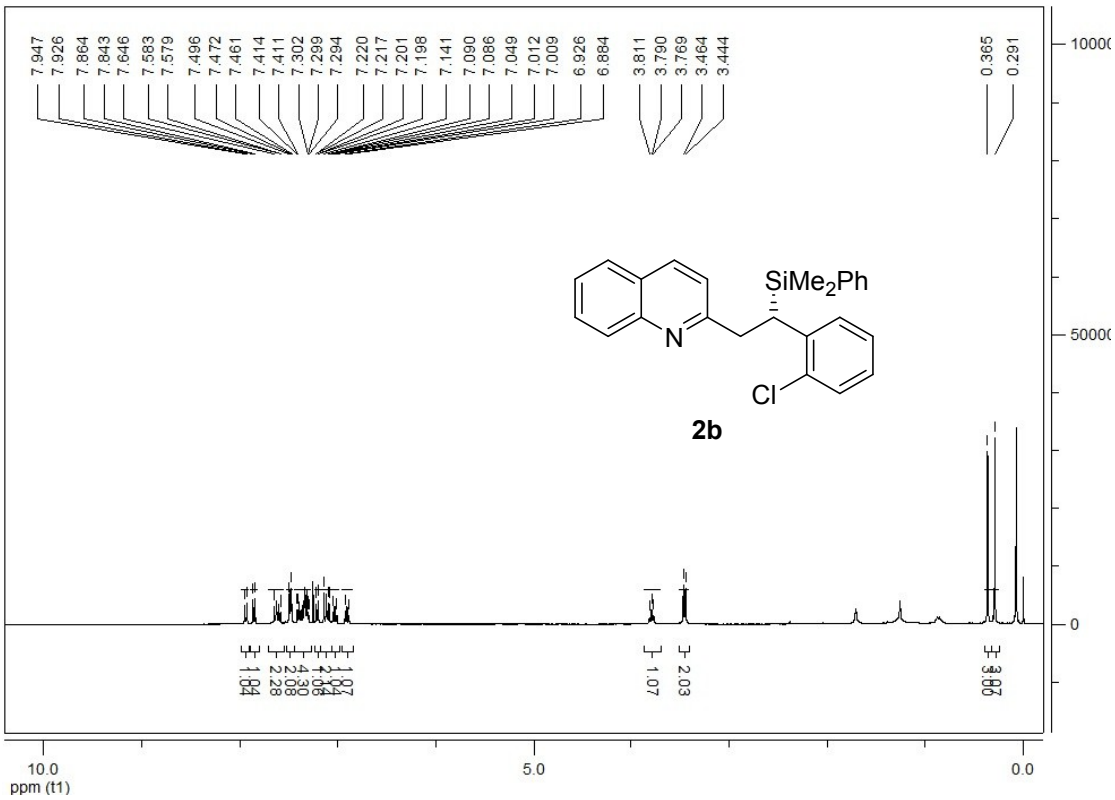
(1) (a) Trost, B. M.; Silverman, S. M.; Stambuli, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 19483. (b) Zhang, Z.; Mao, J.; Zhu, D.; Wu, F.; Chen, H.; Wan, B. *Catal. Comm.* **2005**, *6*, 784. (c) Huang, H.; Wu, Z.; Gao, G.; Zhou, L.; Chang, M. *Org. Chem. Front.* **2017**, *4,* 1976.

(2) (a) Jamal, Z.; Teo, Y.-C. *Synlett.* **2014,** *25,* 2049. (b) Wang, Y.; Wu, C.; Nie, S.; Xu, D.; Yu, M.; Yao, X. *Tetrahedron Lett.* **2015**, *56,* 6827. (c) Patel, U. N.; Jagtap, R. A.; Punji, B. *Organometallics.* **2019**, *38*, 2422. (d) Roy, L. D.; Burns, A. R.; Pattison, G.; Michel, B.; Parker, A. J.; Lam, H. Wai. *Chem. Comm.* **2014**, *50*, 2865. (e) Jamal, Z.; Teo, Y.-C.; Lin, G. S. *Tetrahedron.* **2016**, *72*, 2132.

6. NMR spectra of the products



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7.299
7.294
7.220
7.217
7.201
7.198
7.141
7.090
7.086
7.049
7.012
7.009
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6.884
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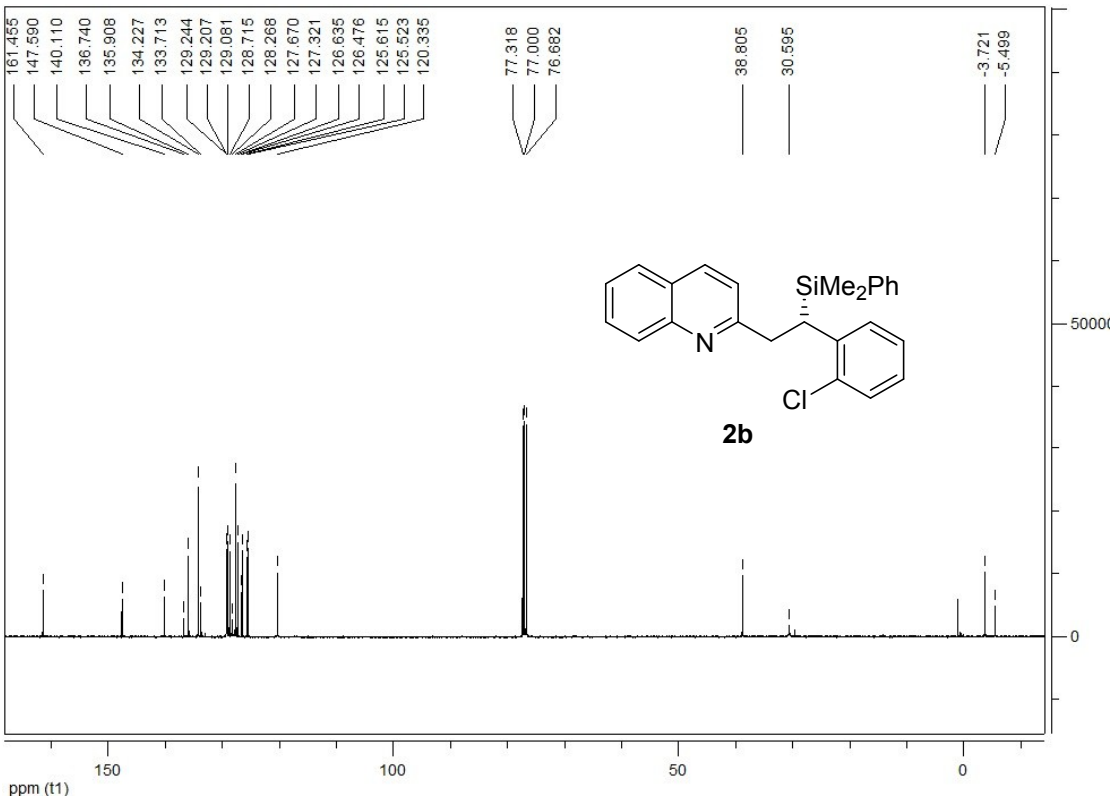
ppm (t1)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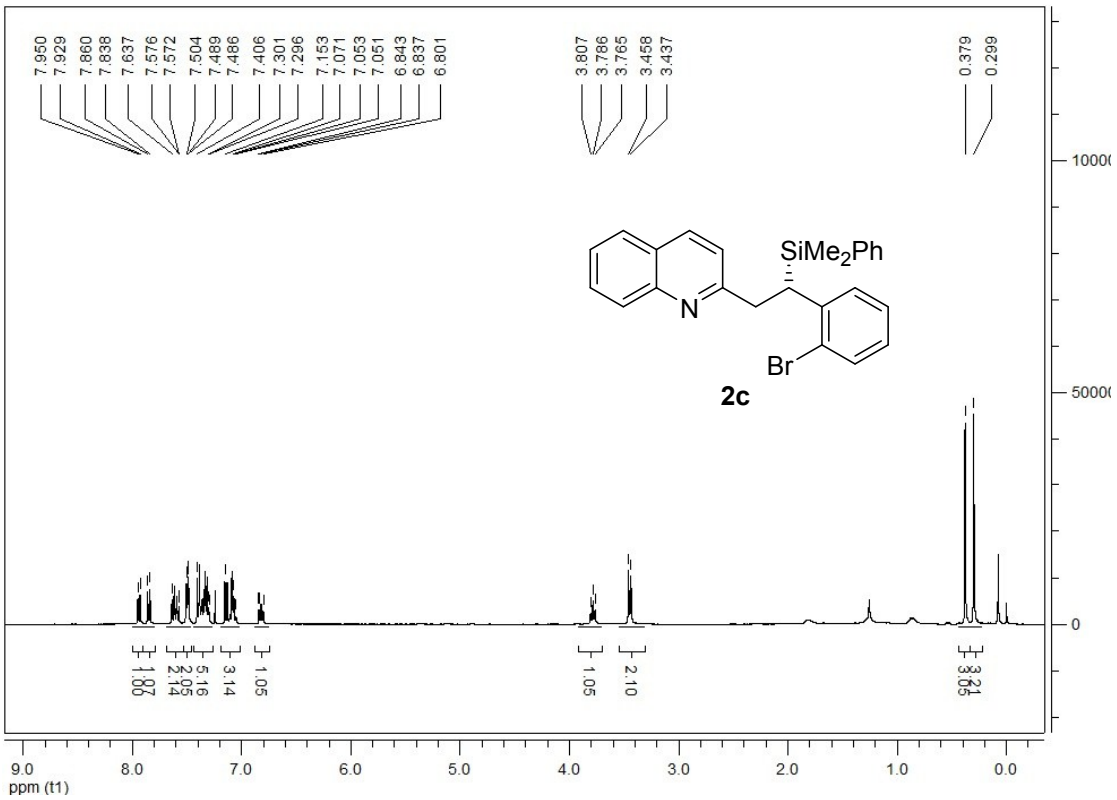
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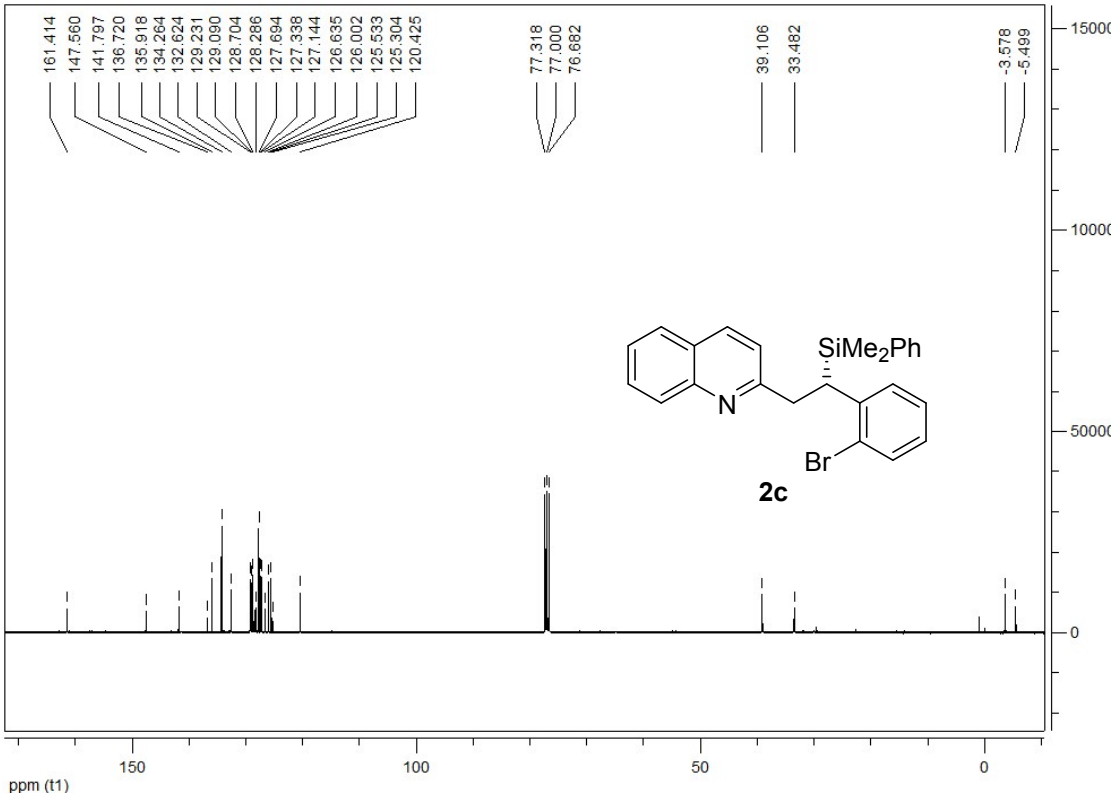
ppm (t1)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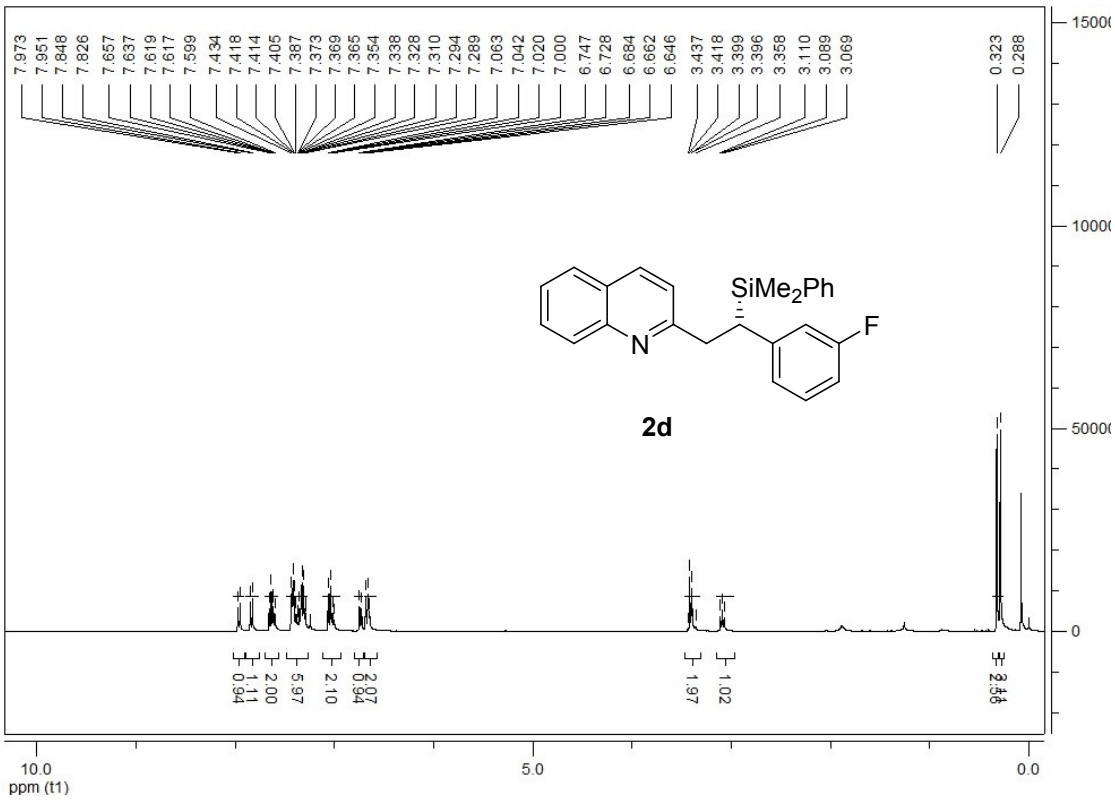
77.000
76.682
39.106
33.482
-3.578
-5.499
SiMe2Ph
N
Br
2c
150
100
50
0
ppm (t1)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7.599
7.434
7.418
7.414
7.405
7.387
7.373
7.369
7.365
7.354
7.338
7.328
7.310
7.294
7.289
7.063
7.042
7.020
7.000
6.747
6.728
6.684
6.662
6.646
3.437
3.418
3.399
3.396
3.358
3.110
3.089
3.069
0.323
0.288
SiMe2Ph
N
F
2d
0.94
1.11
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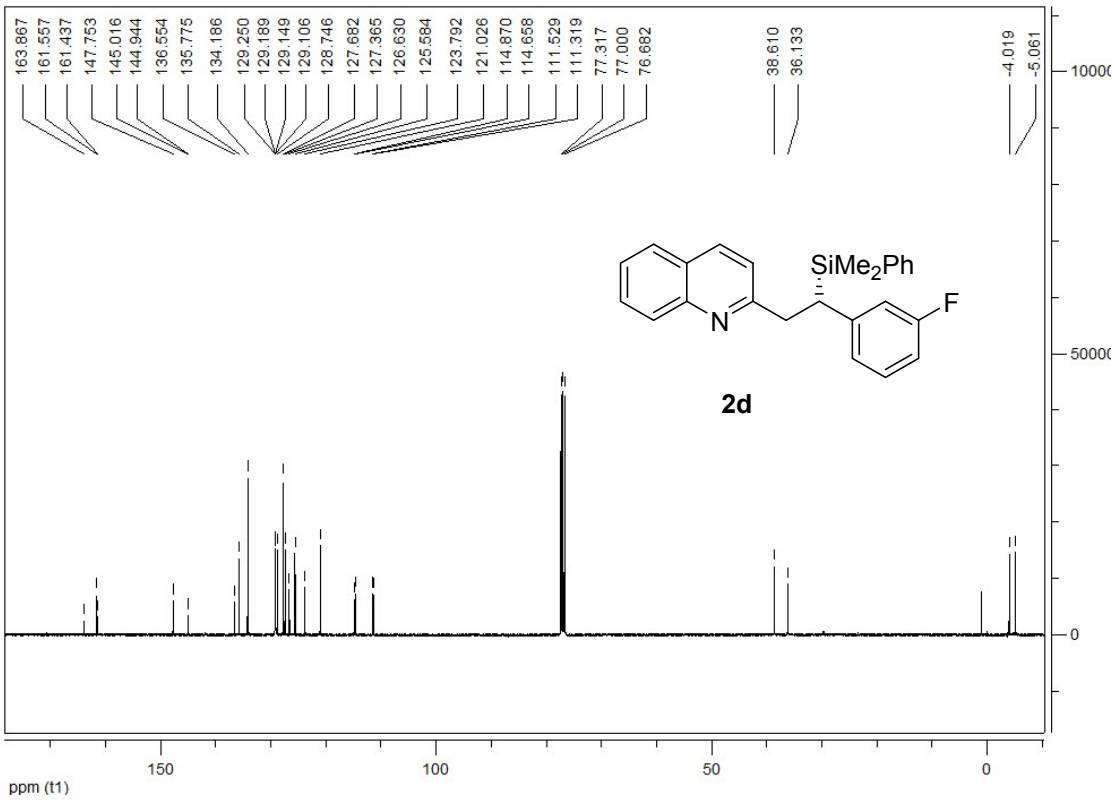
5.97
2.10
2.07
1.97
1.02
10.0
5.0
0.0
ppm (t1)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129.149
129.106
128.746
127.682
127.365
126.630
125.584
123.792
121.026
114.870
114.658
111.529
111.319
77.317
77.000
76.682
38.610
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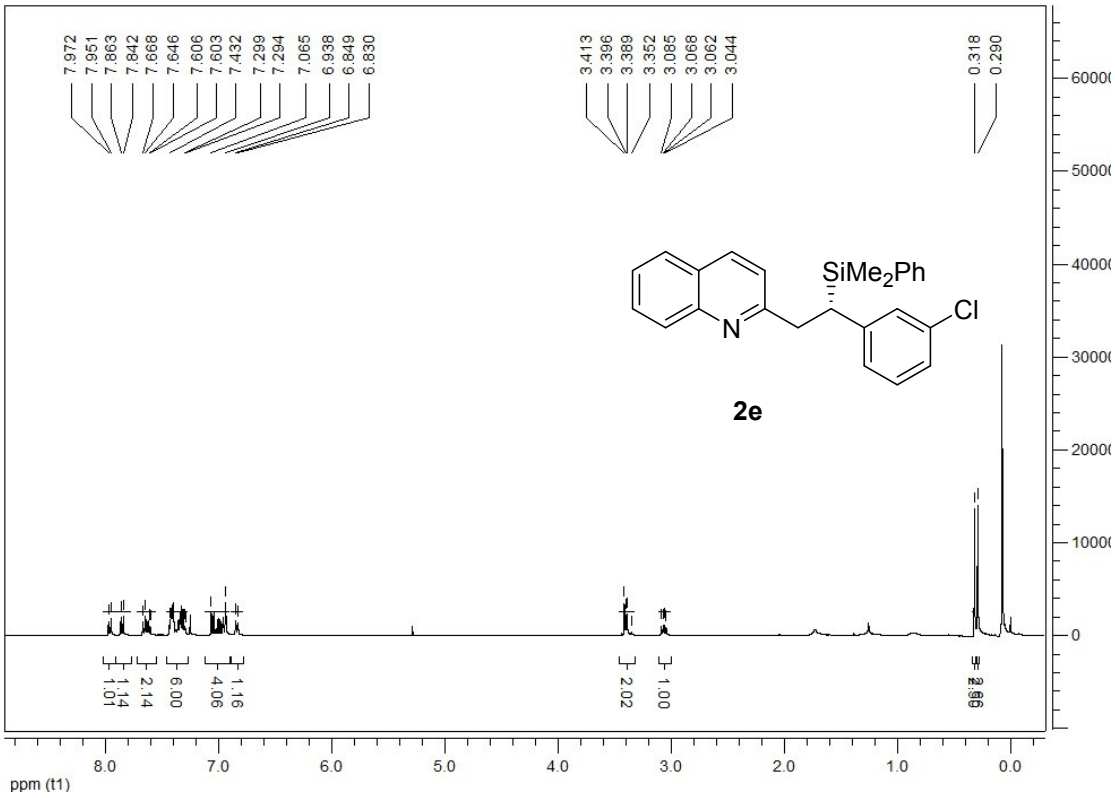
-4.019
-5.061
SiMe2Ph
N
F
2d
150
100
50
0
ppm (t1)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7.603
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7.299
7.294
7.065
6.938
6.849
6.830
3.413
3.396
3.389
3.352
3.085
3.068
3.062
3.044
0.318
0.290
SiMe2Ph
Cl
N
2e
1.01
1.14
2.14
6.00
4.06
1.16
2.02
1.00
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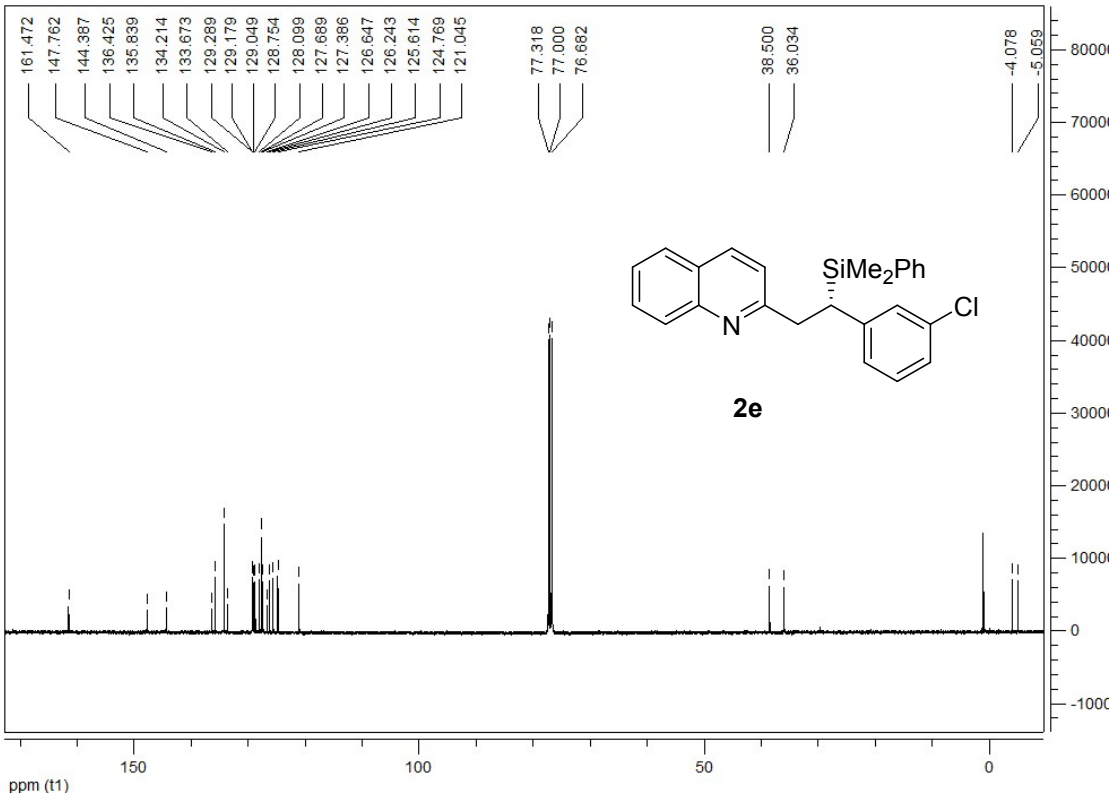
2.0
1.0
0.0
ppm (t1)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128.754
128.099
127.689
127.386
126.647
126.243
125.614
124.769
121.045
77.318
77.000
76.682
38.500
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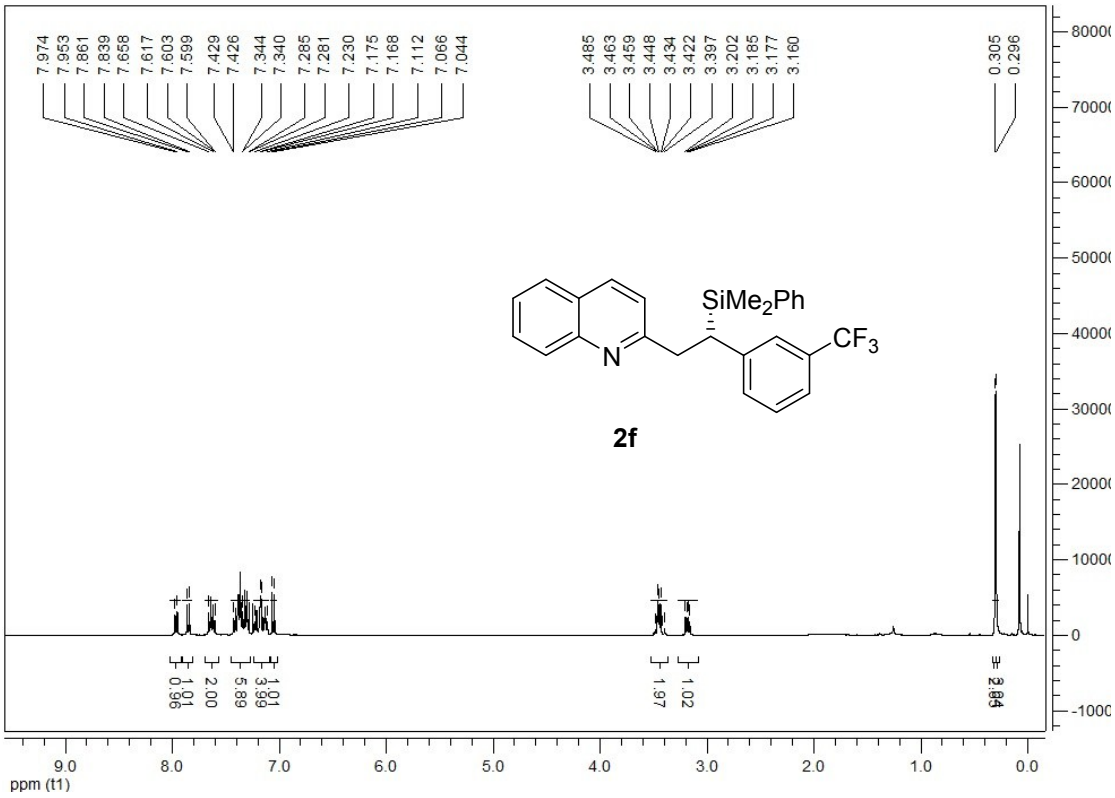
-5.059
SiMe2Ph
Cl
N
2e
150
100
50
0
ppm (t1)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7.603
7.599
7.429
7.426
7.344
7.340
7.285
7.281
7.230
7.175
7.168
7.112
7.066
7.044
3.485
3.463
3.459
3.448
3.434
3.422
3.397
3.202
3.185
3.177
3.160
0.305
0.296
SiMe2Ph
CF3
N
2f
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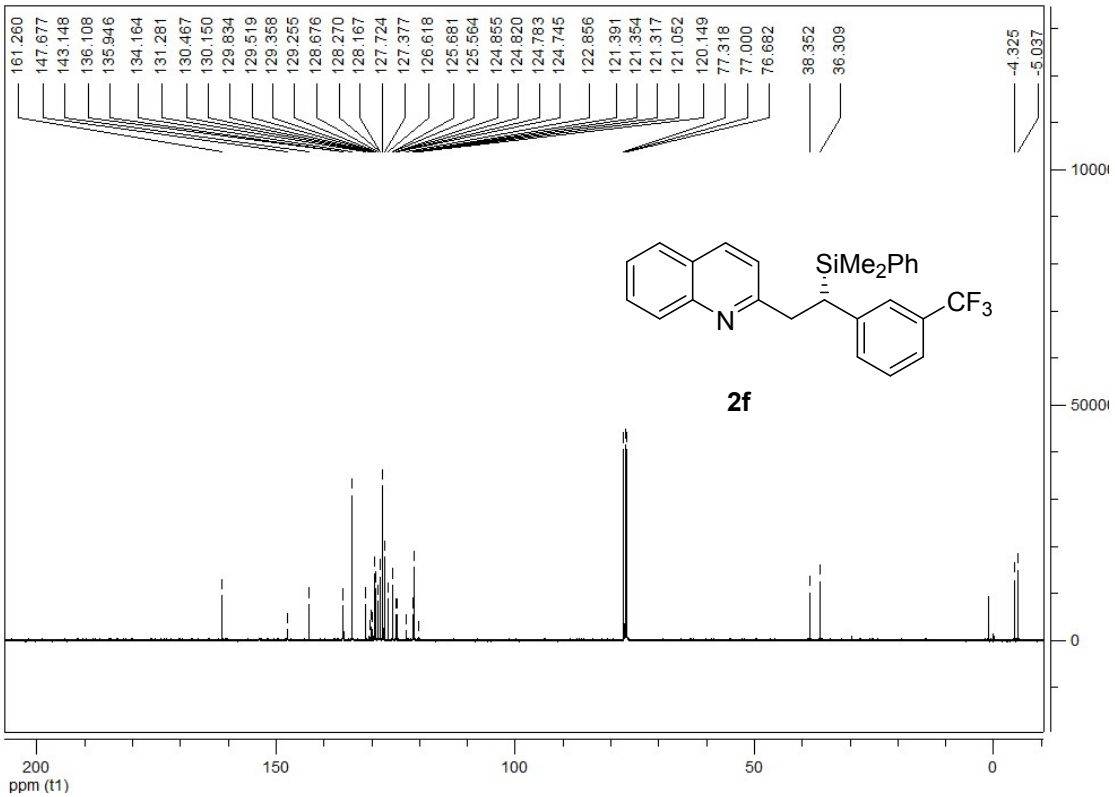
1.01
2.00
5.89
3.99
1.01
1.97
1.02
9.04
ppm (t1)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130.467
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129.834
129.519
129.358
129.255
128.676
128.270
128.167
127.724
127.377
126.618
125.681
125.564
124.855
124.820
124.783
124.745
122.856
121.391
121.354
121.317
121.052
120.149
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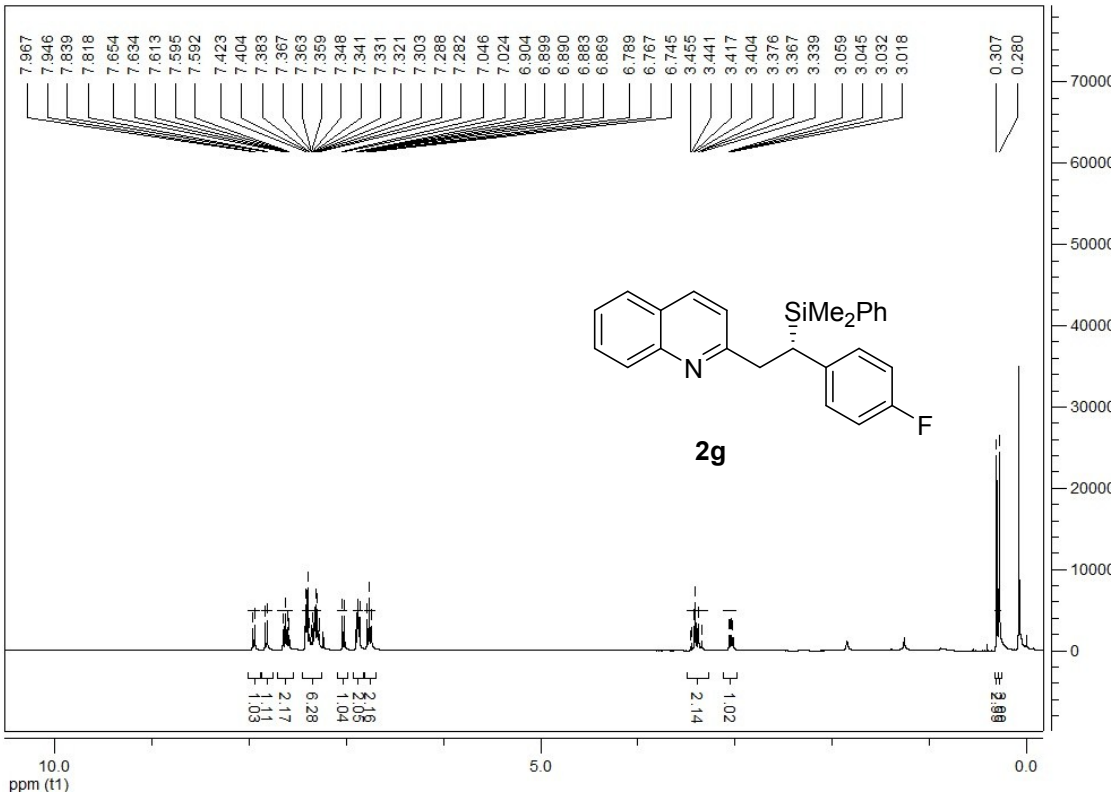
-5.037
SiMe2Ph
CF3
N
2f
ppm (t1)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7.839
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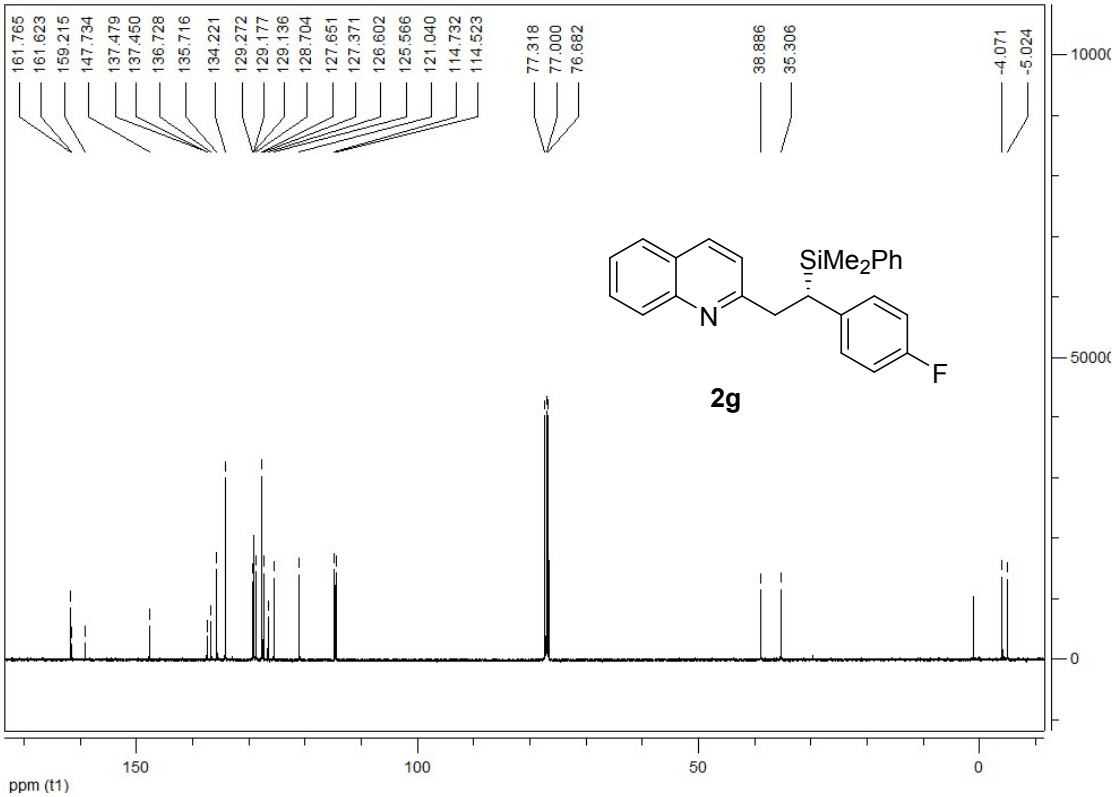
7.654
7.634
7.613
7.595
7.592
7.423
7.404
7.383
7.367
7.363
7.359
7.348
7.341
7.331
7.321
7.303
7.288
7.282
7.046
7.024
6.904
6.899
6.890
6.883
6.869
6.789
6.767
6.745
3.455
3.441
3.417
3.404
3.376
3.367
3.339
3.059
3.045
3.032
3.018
0.307
0.280
SiMe2Ph
N
F
2g
1.03
1.11
2.17
9.28
1.04
2.16
2.05
2.14
1.02
10.0
ppm (t1)
5.0
0.0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129.177
129.136
128.704
127.651
127.371
126.602
125.566
121.040
114.732
114.523
77.318
77.000
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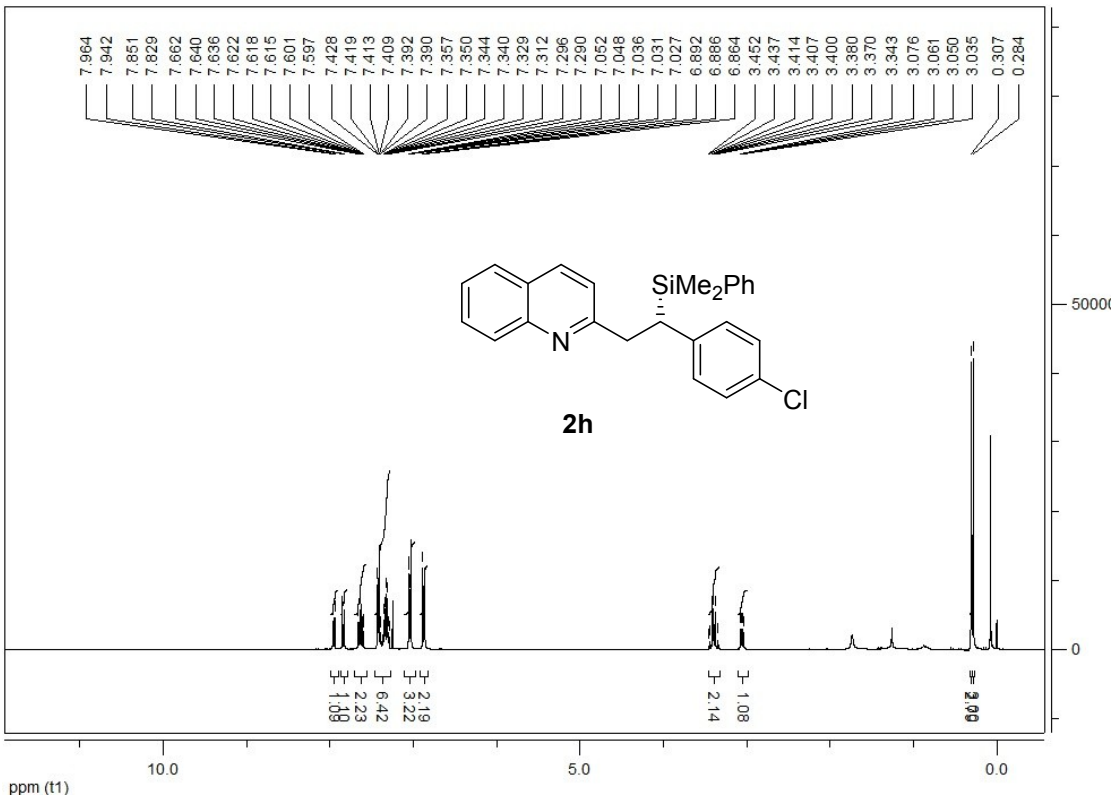
-4.071
-5.024
SiMe2Ph
N
F
2g
150
ppm (t1)
100
50
0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7.615
7.601
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7.428
7.419
7.413
7.409
7.392
7.390
7.357
7.350
7.344
7.340
7.329
7.312
7.296
7.290
7.052
7.048
7.036
7.031
7.027
6.892
6.886
6.864
3.452
3.437
3.414
3.407
3.400
3.380
3.370
3.343
3.076
3.061
3.050
3.035
0.307
0.284
SiMe2Ph
N
Cl
2h
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1.08
2.23
9.42
3.22
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10.0
5.0
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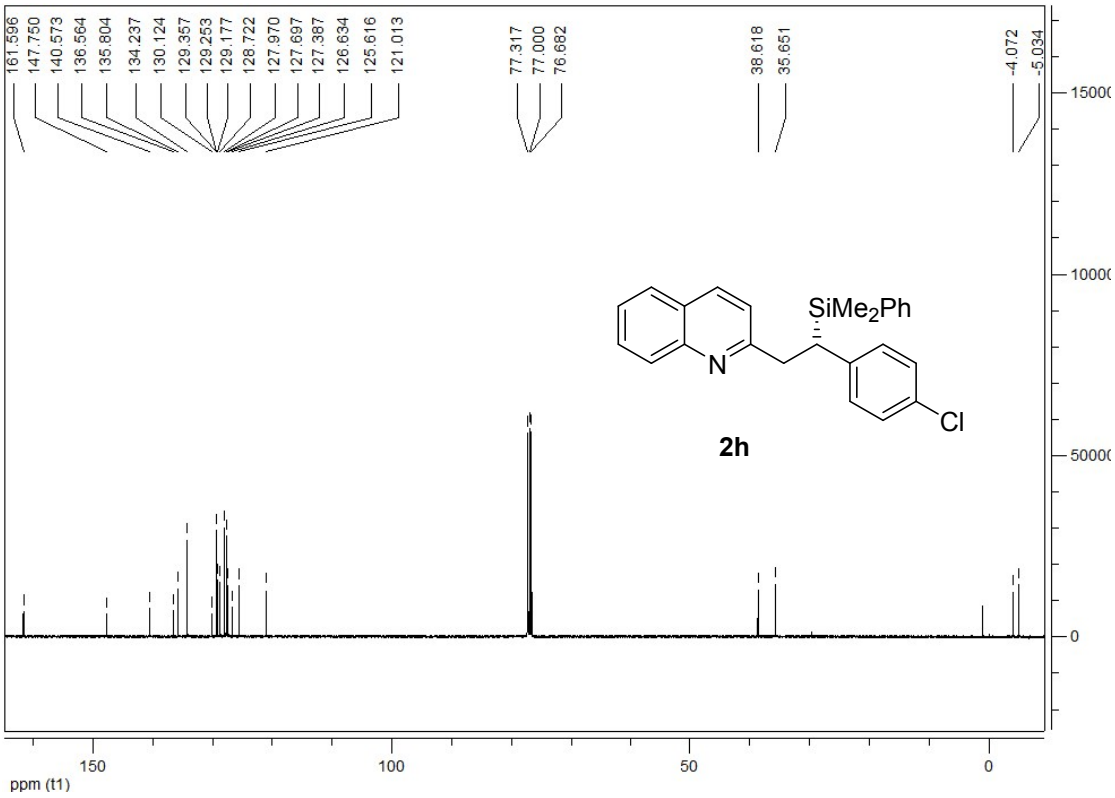
ppm (t1)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127.387
126.634
125.616
121.013
77.317
77.000
76.682
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-4.072
-5.034
SiMe2Ph
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Cl
2h
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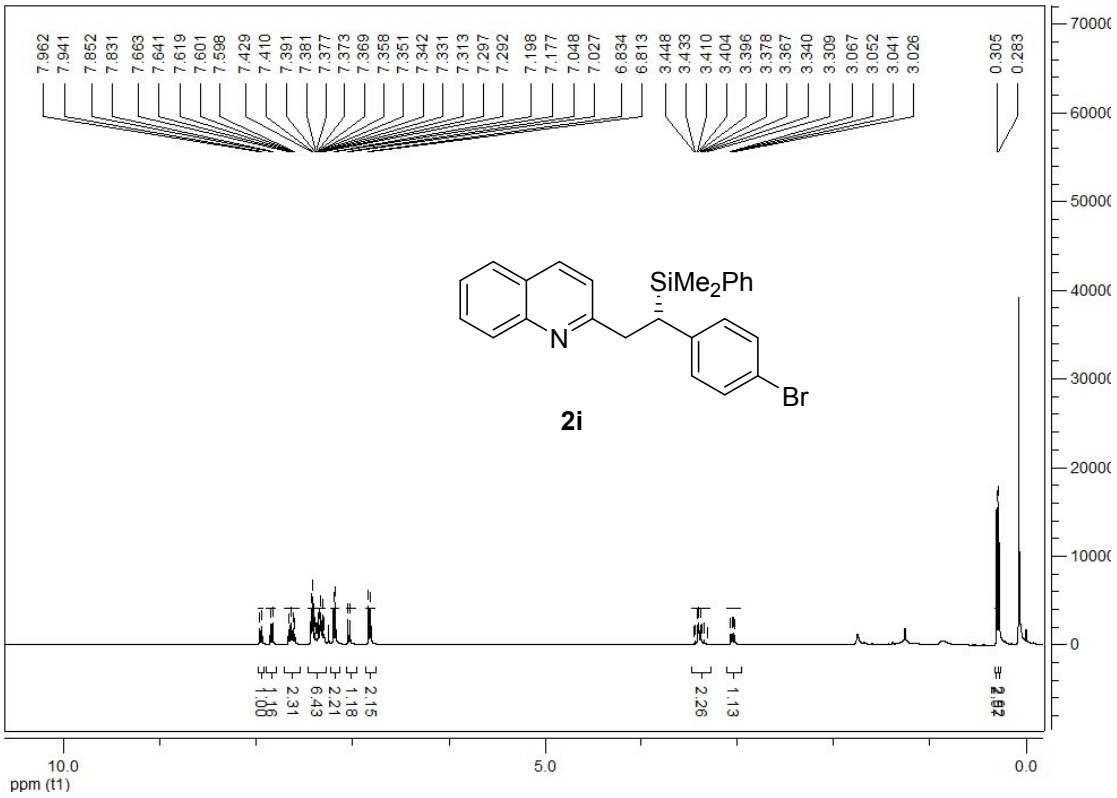
100
50
0
ppm (t1)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7.377
7.373
7.369
7.358
7.351
7.342
7.331
7.313
7.297
7.292
7.198
7.177
7.048
7.027
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6.813
3.448
3.433
3.410
3.404
3.396
3.378
3.367
3.340
3.309
3.067
3.052
3.041
3.026
0.305
0.283
SiMe2Ph
N
Br
2i
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2.21
1.18
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2.26
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10.0
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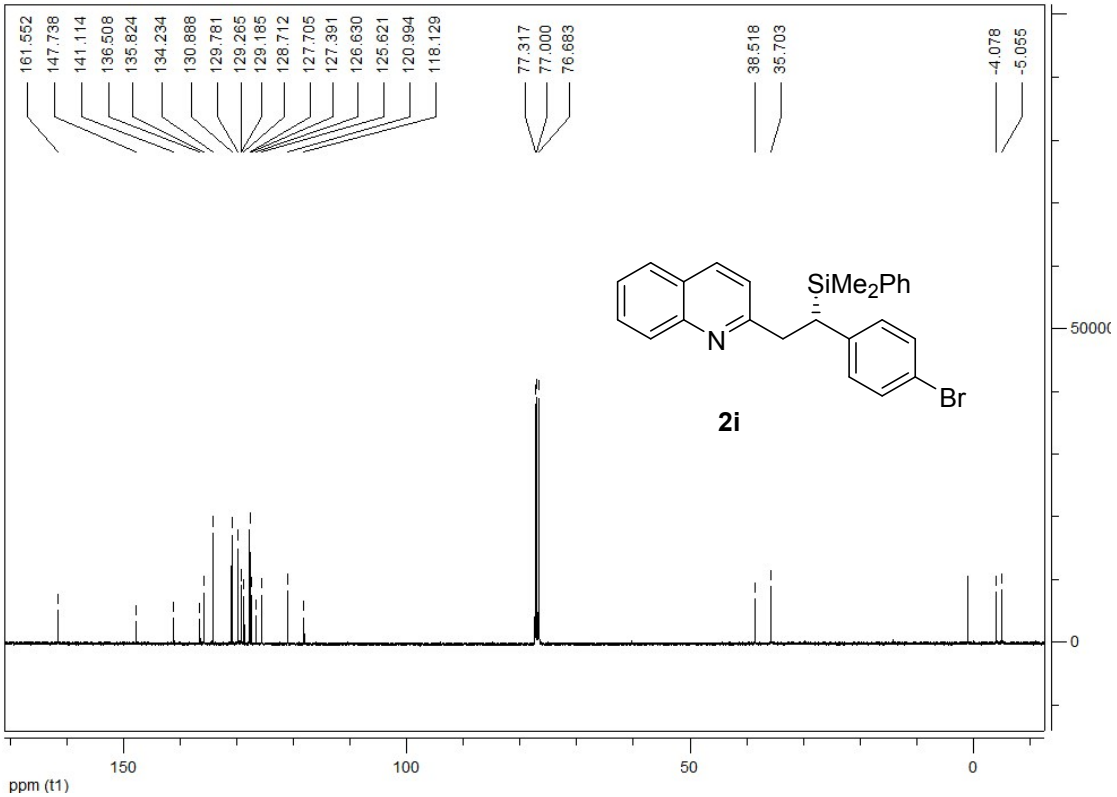
ppm (t1)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125.621
120.994
118.129
77.317
77.000
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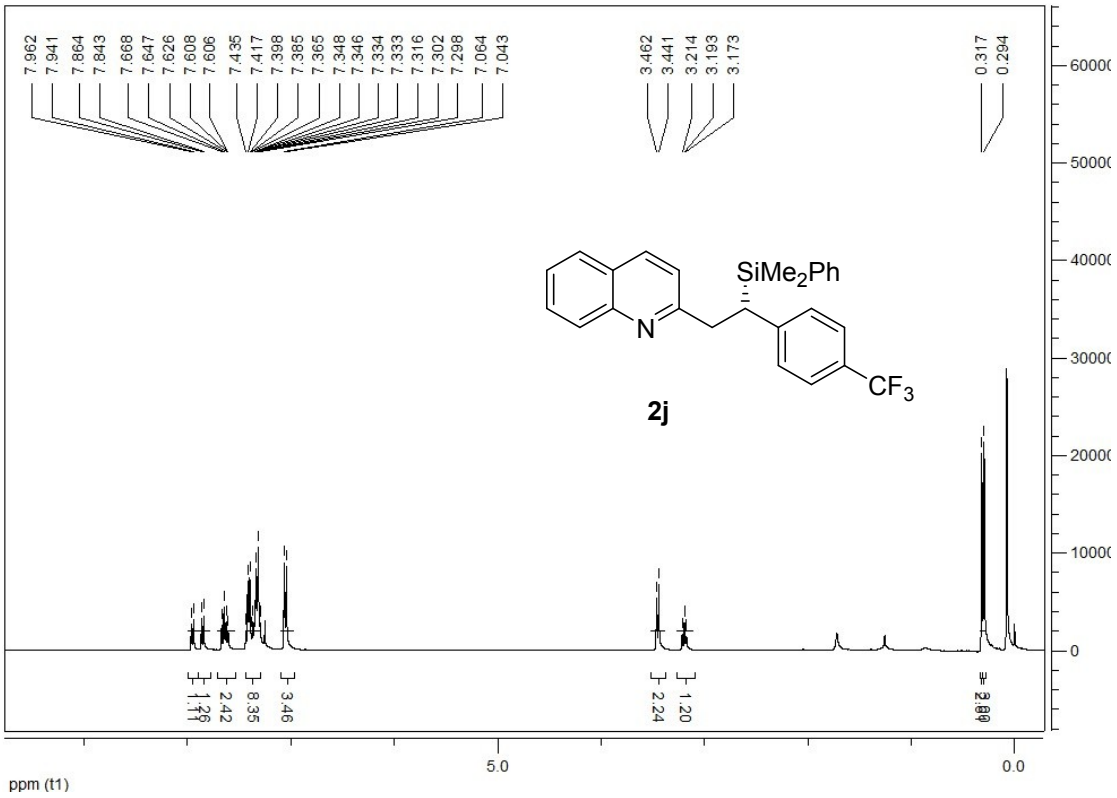
-5.055
SiMe2Ph
N
Br
2i
150
100
50
0
ppm (t1)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7.435
7.417
7.398
7.385
7.365
7.348
7.346
7.334
7.333
7.316
7.302
7.298
7.064
7.043
3.462
3.441
3.214
3.193
3.173
0.317
0.294
SiMe2Ph
N
CF3
2j
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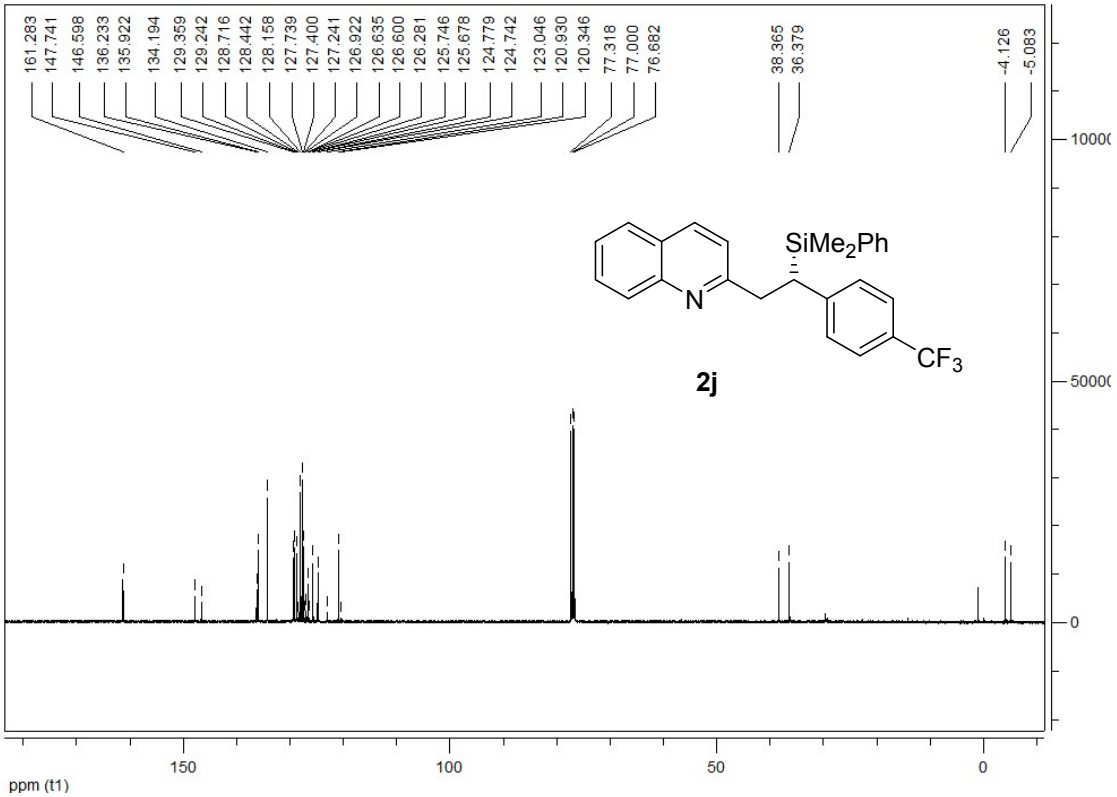
ppm (t1)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127.739
127.400
127.241
126.922
126.635
126.600
126.281
125.746
125.678
124.779
124.742
123.046
120.930
120.346
77.318
77.000
76.682
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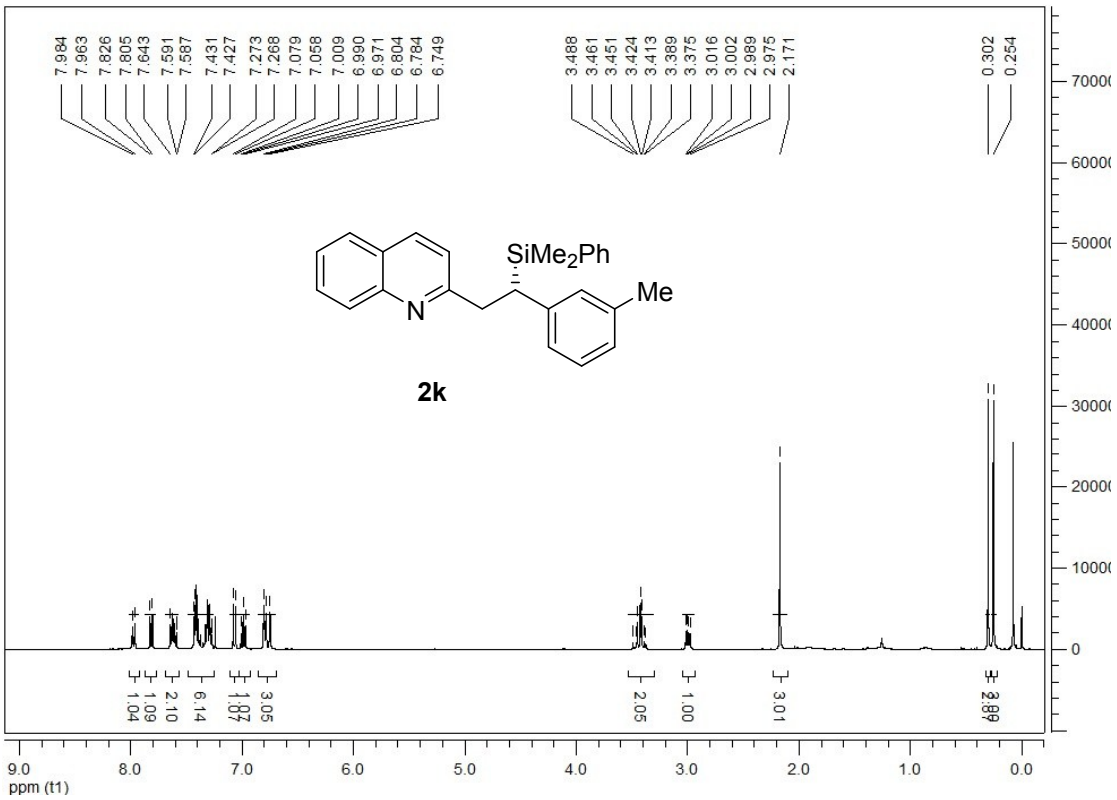
-4.126
-5.083
SiMe2Ph
N
CF3
2j
150
100
50
0
ppm (t1)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7.079
7.058
7.009
6.990
6.971
6.804
6.784
6.749
3.488
3.461
3.451
3.424
3.413
3.389
3.375
3.016
3.002
2.989
2.975
2.171
0.302
0.254
SiMe2Ph
Me
N
2k
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2.10
9.14
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2.05
1.00
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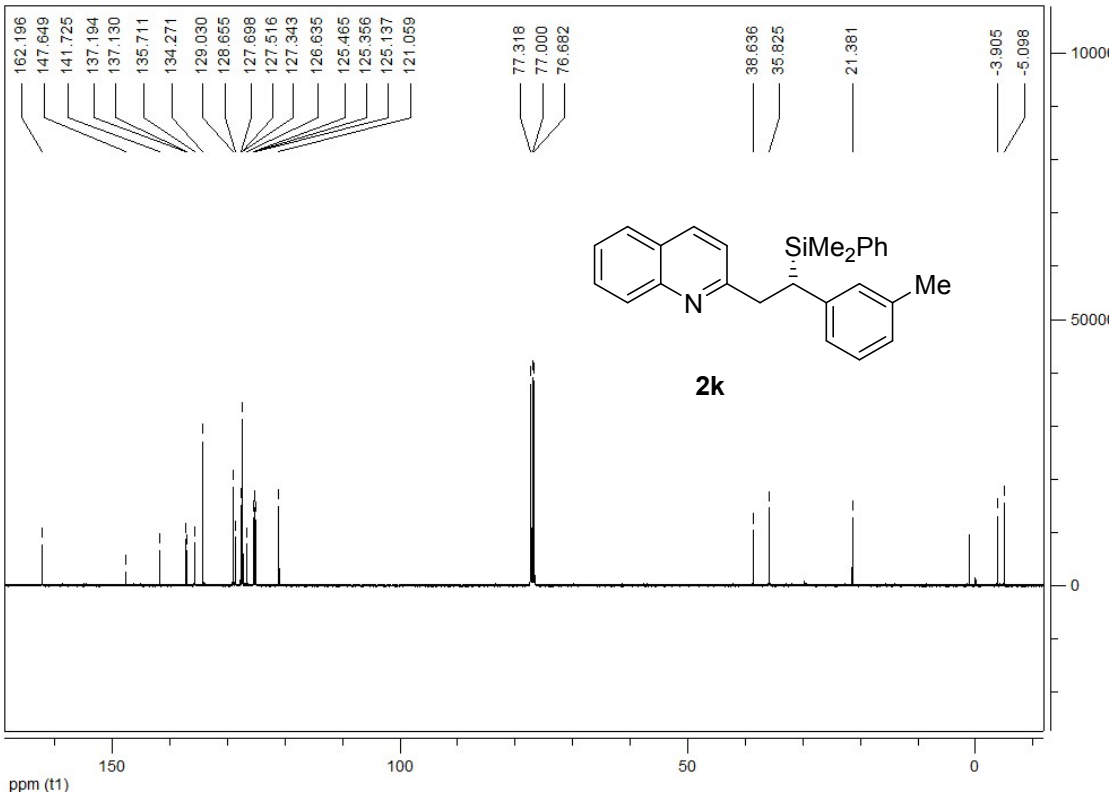
ppm (t1)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127.343
126.635
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125.356
125.137
121.059
77.318
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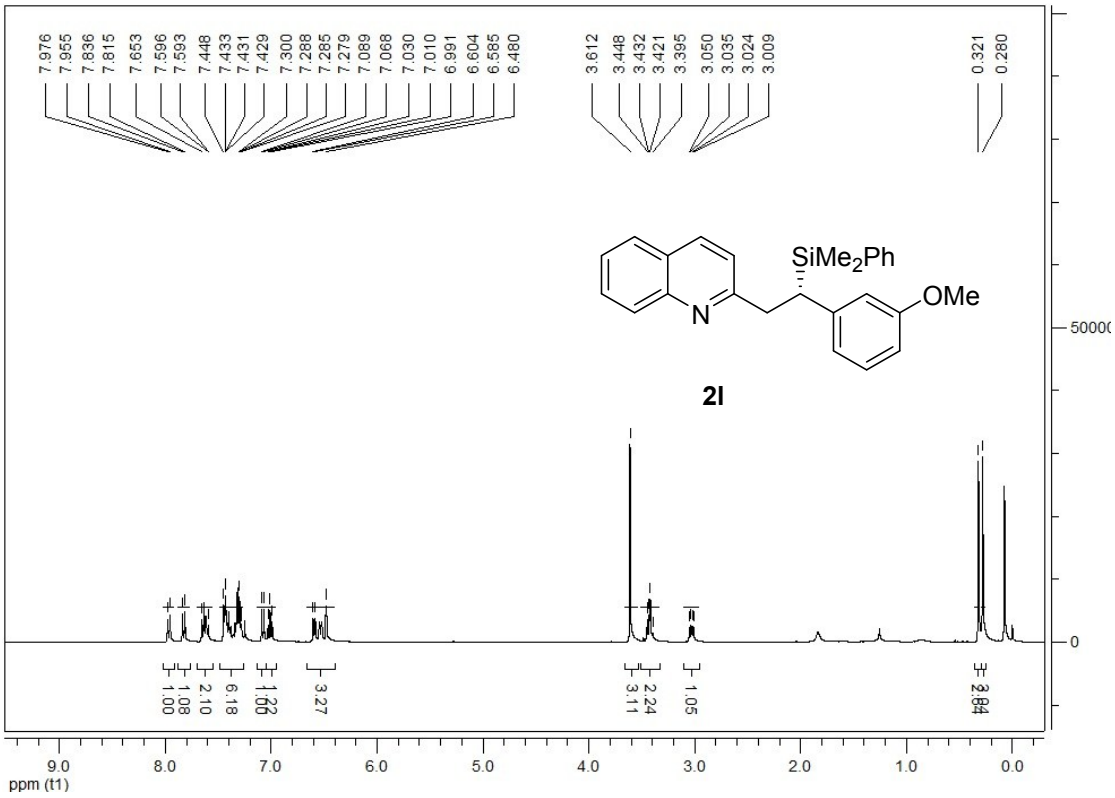
SiMe2Ph
Me
N
2k
ppm (t1)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7.448
7.433
7.431
7.429
7.300
7.288
7.285
7.279
7.089
7.068
7.030
7.010
6.991
6.604
6.585
6.480
3.612
3.448
3.432
3.421
3.395
3.050
3.035
3.024
3.009
0.321
0.280
SiMe2Ph
OMe
N
2l
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9.18
1.00
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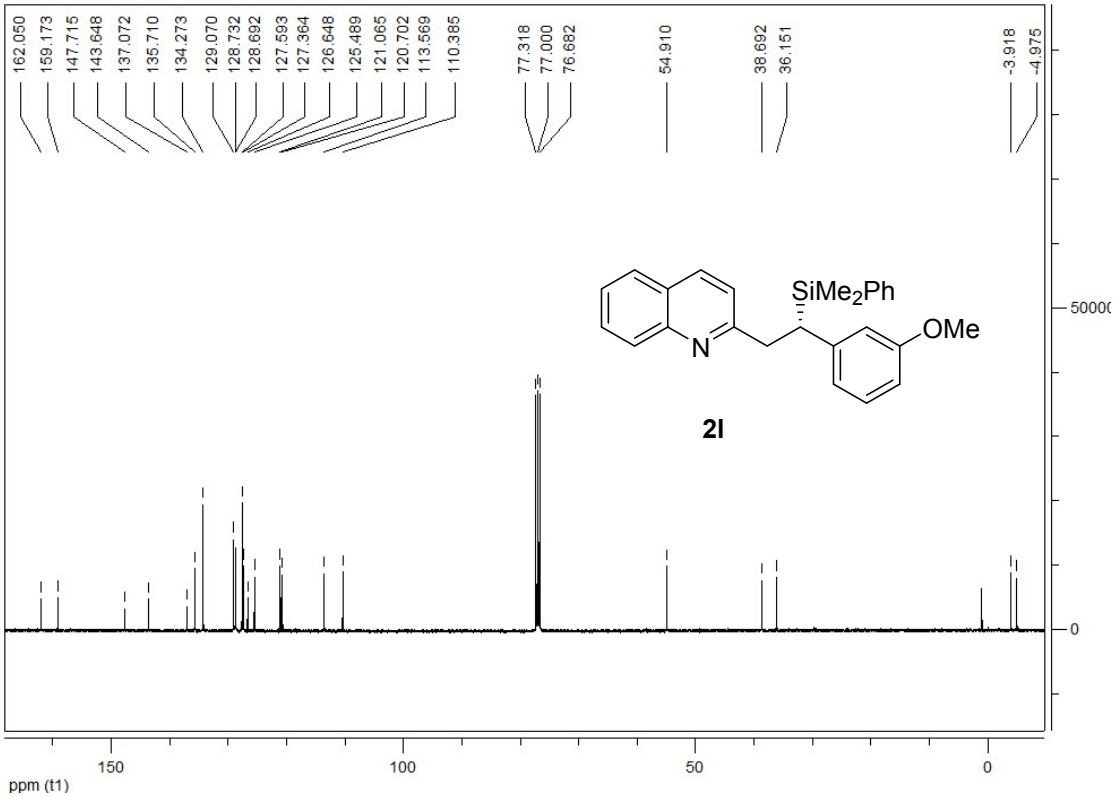
2.24
1.05
3.84
ppm (t1)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126.648
125.489
121.065
120.702
113.569
110.385
77.318
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38.692
36.151
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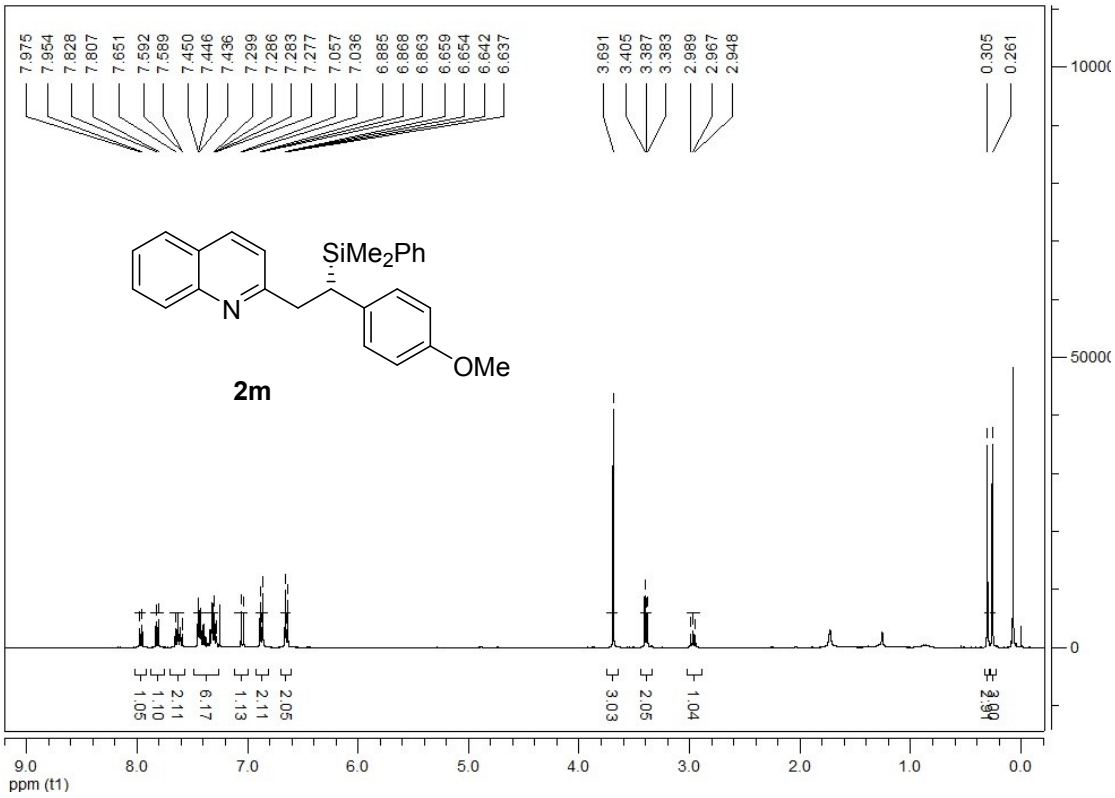
-4.975
SiMe2Ph
OMe
N
2l
ppm (t1)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7.283
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7.057
7.036
6.885
6.868
6.863
6.659
6.654
6.642
6.637
3.691
3.405
3.387
3.383
2.989
2.967
2.948
0.305
0.261
SiMe2Ph
N
OMe
2m
1.05
1.10
2.11
9.17
1.13
2.11
2.05
3.03
2.05
1.04
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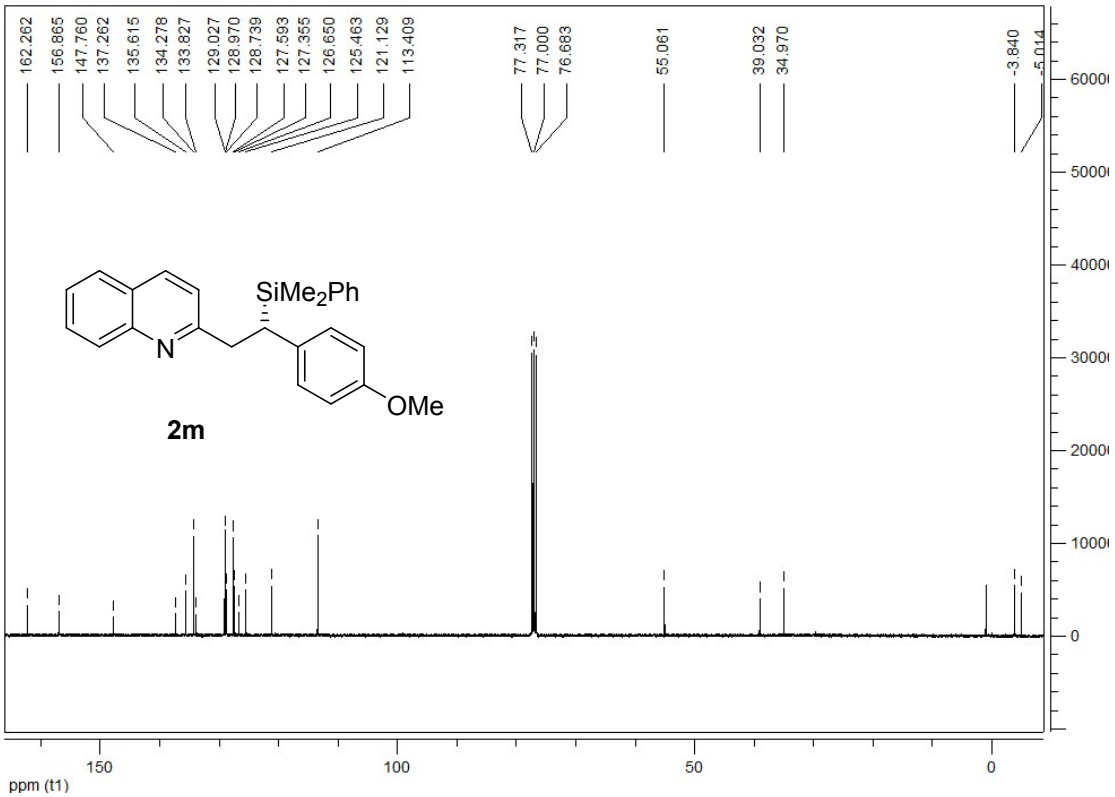
2.0
1.0
0.0
ppm (t1)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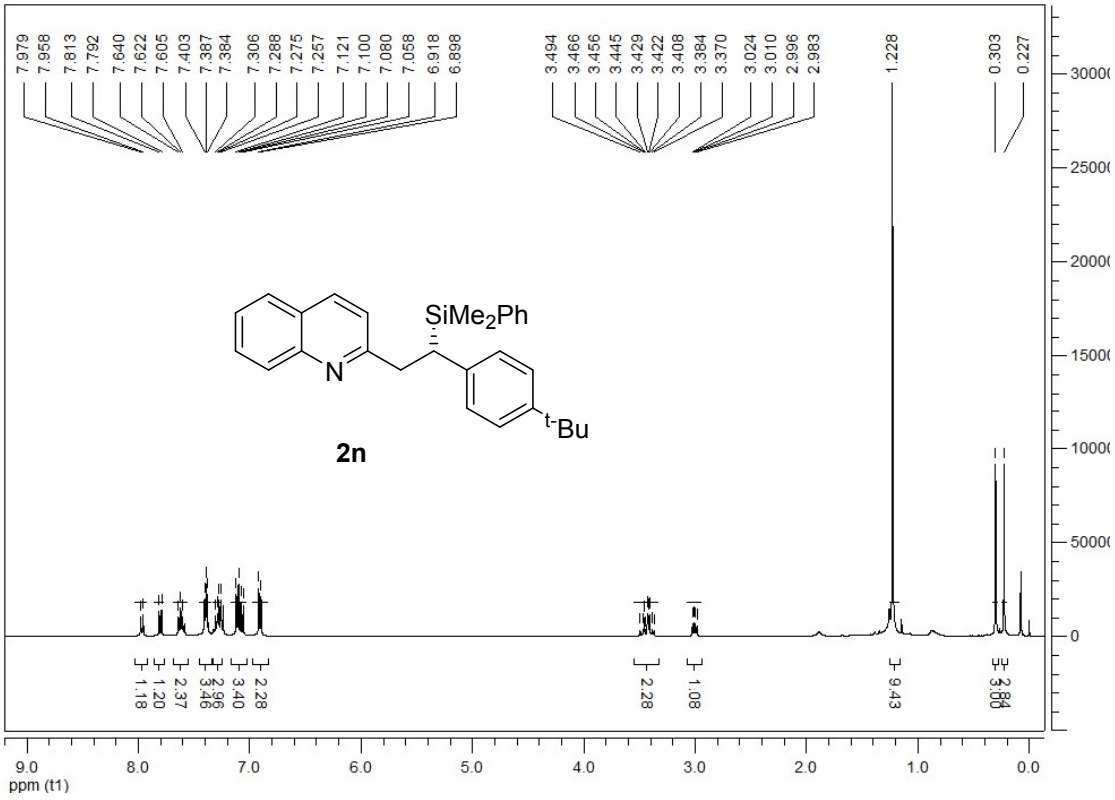
127.355
126.650
125.463
121.129
113.409
77.317
77.000
76.683
55.061
39.032
34.970
-3.840
SiMe2Ph
N
OMe
2m
150
100
50
0
ppm (t1)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7.384
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7.288
7.275
7.257
7.121
7.100
7.080
7.058
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6.898
3.494
3.466
3.456
3.445
3.429
3.422
3.408
3.384
3.370
3.024
3.010
2.996
2.983
1.228
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0.227
SiMe2Ph
N
t-Bu
2n
1.18
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2.28
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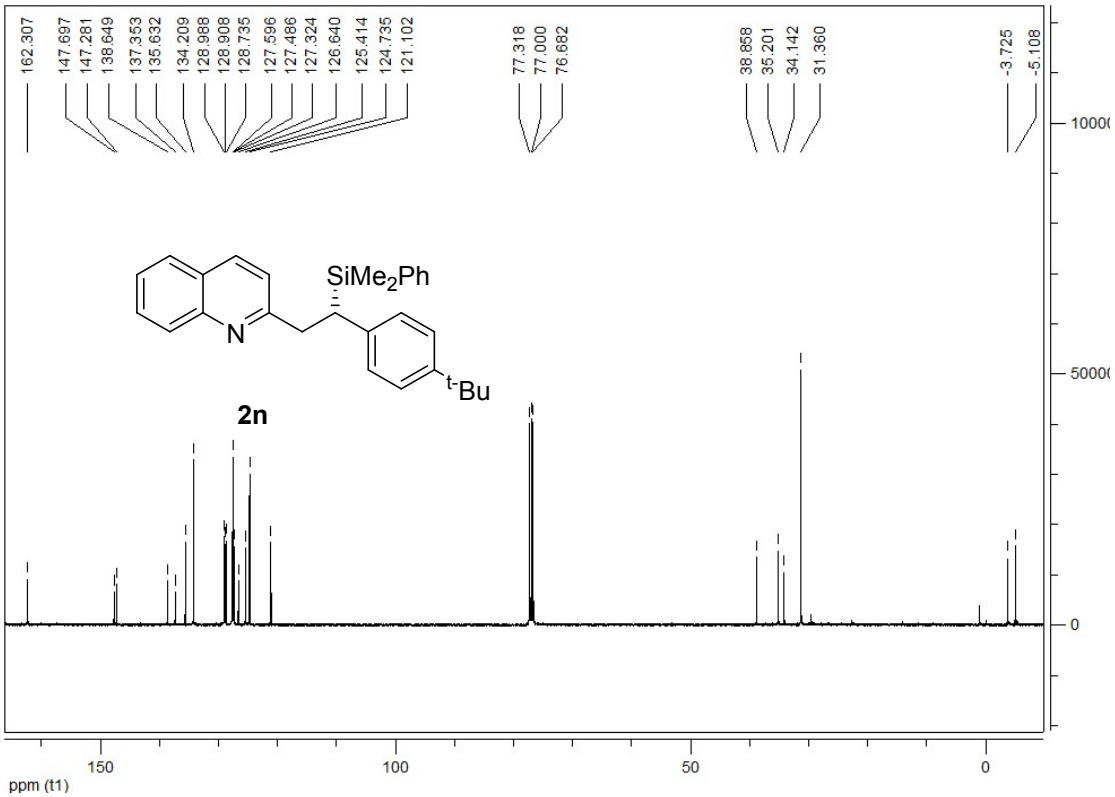
3.04
ppm (t1)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126.640
125.414
124.735
121.102
77.318
77.000
76.682
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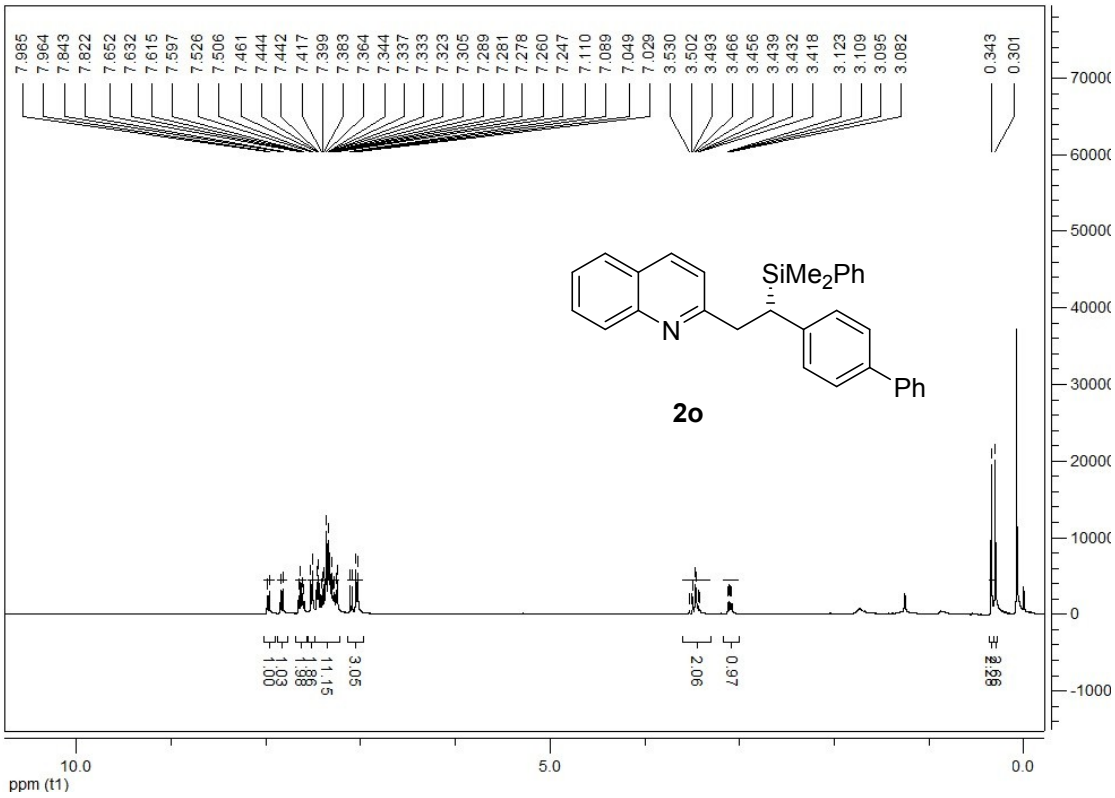
34.142
31.360
-3.725
-5.108
SiMe2Ph
N
t-Bu
2n
ppm (t1)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7.337
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7.323
7.305
7.289
7.281
7.278
7.260
7.247
7.110
7.089
7.049
7.029
3.530
3.502
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3.439
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3.418
3.123
3.109
3.095
3.082
0.343
0.301
SiMe2Ph
N
Ph
2o
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1.03
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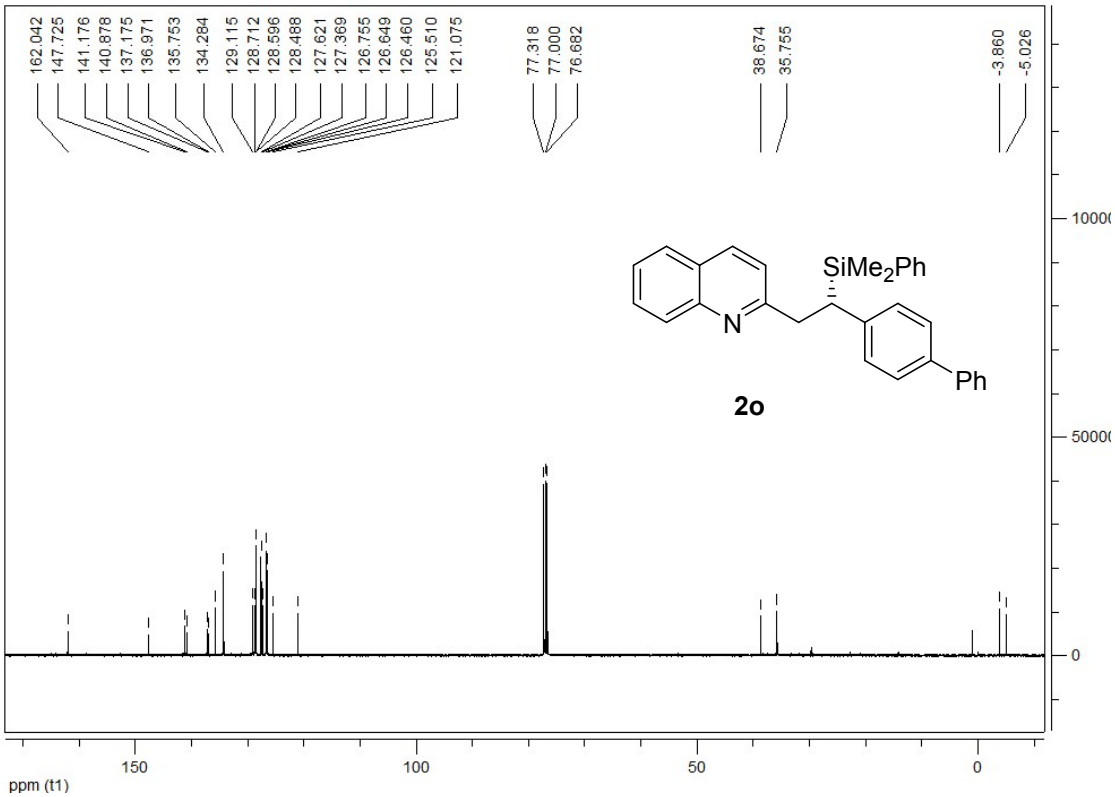
ppm (t1)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127.369
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125.510
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77.000
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N
Ph
2o
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50
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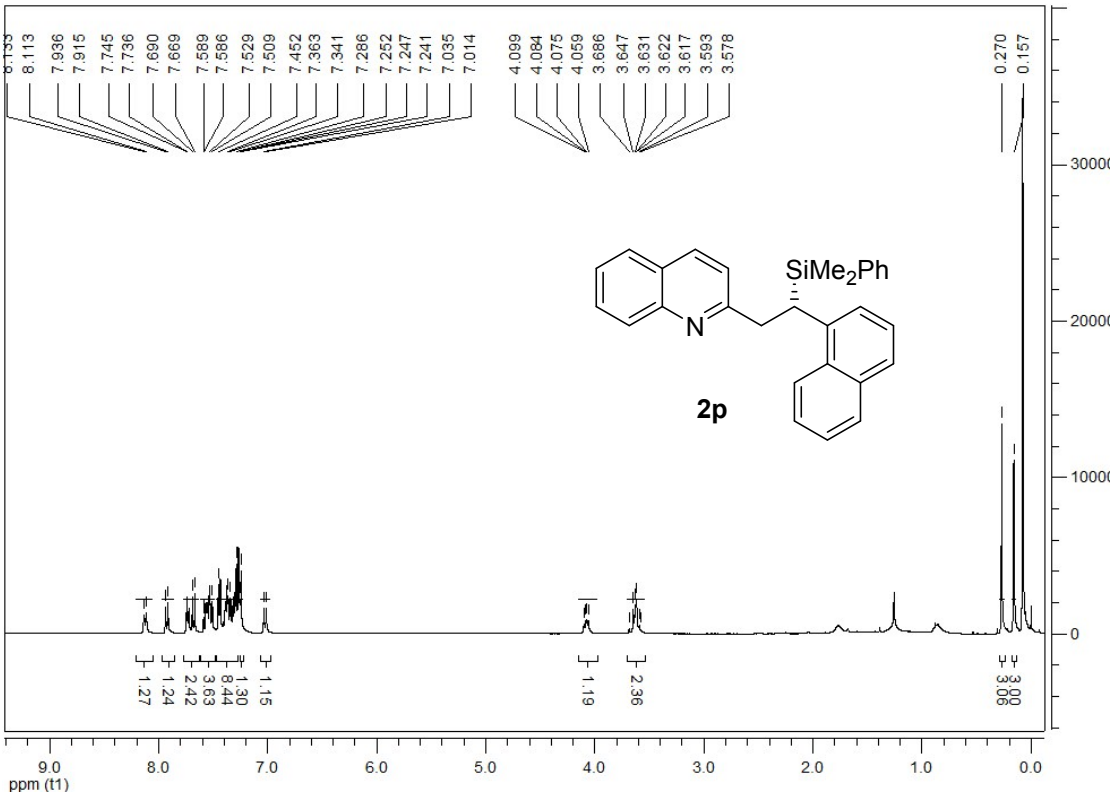
ppm (t1)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7.452
7.363
7.341
7.286
7.252
7.247
7.241
7.035
7.014
4.099
4.084
4.075
4.059
3.686
3.647
3.631
3.622
3.617
3.593
3.578
0.270
0.157
SiMe2Ph
N
2p
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1.15
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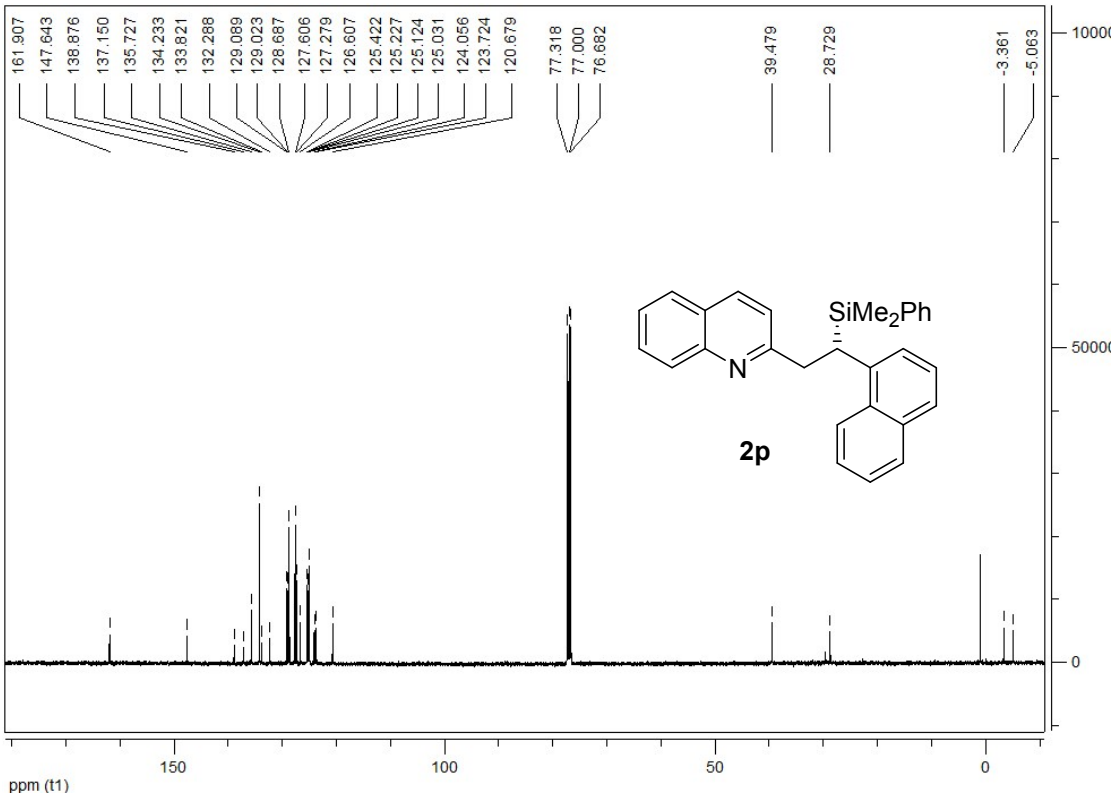
ppm (t1)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127.279
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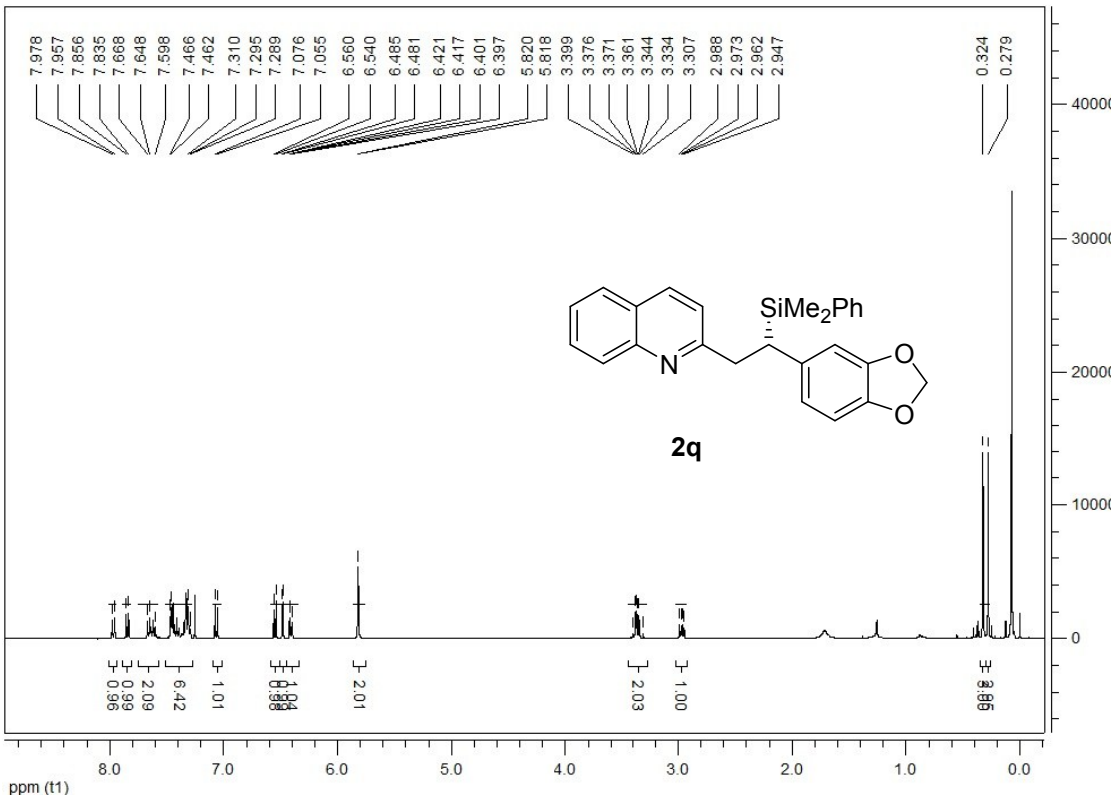
SiMe2Ph
N
2p
ppm (t1)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7.055
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6.540
6.485
6.481
6.421
6.417
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6.397
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5.818
3.399
3.376
3.371
3.361
3.344
3.334
3.307
2.988
2.973
2.962
2.947
0.324
0.279
SiMe2Ph
N
O
O
2q
0.96
0.99
2.09
6.42
1.01
1.04
2.01
2.03
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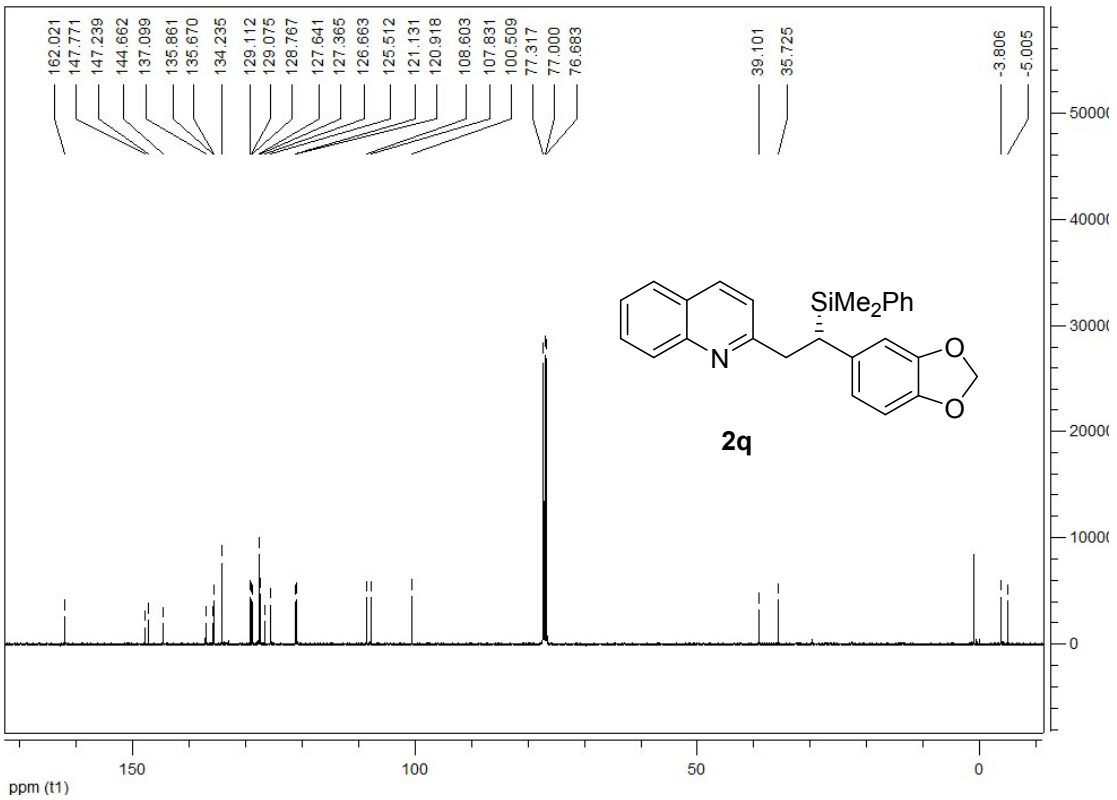
ppm (t1)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125.512
121.131
120.918
108.603
107.831
100.509
77.317
77.000
76.683
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-5.005
SiMe2Ph
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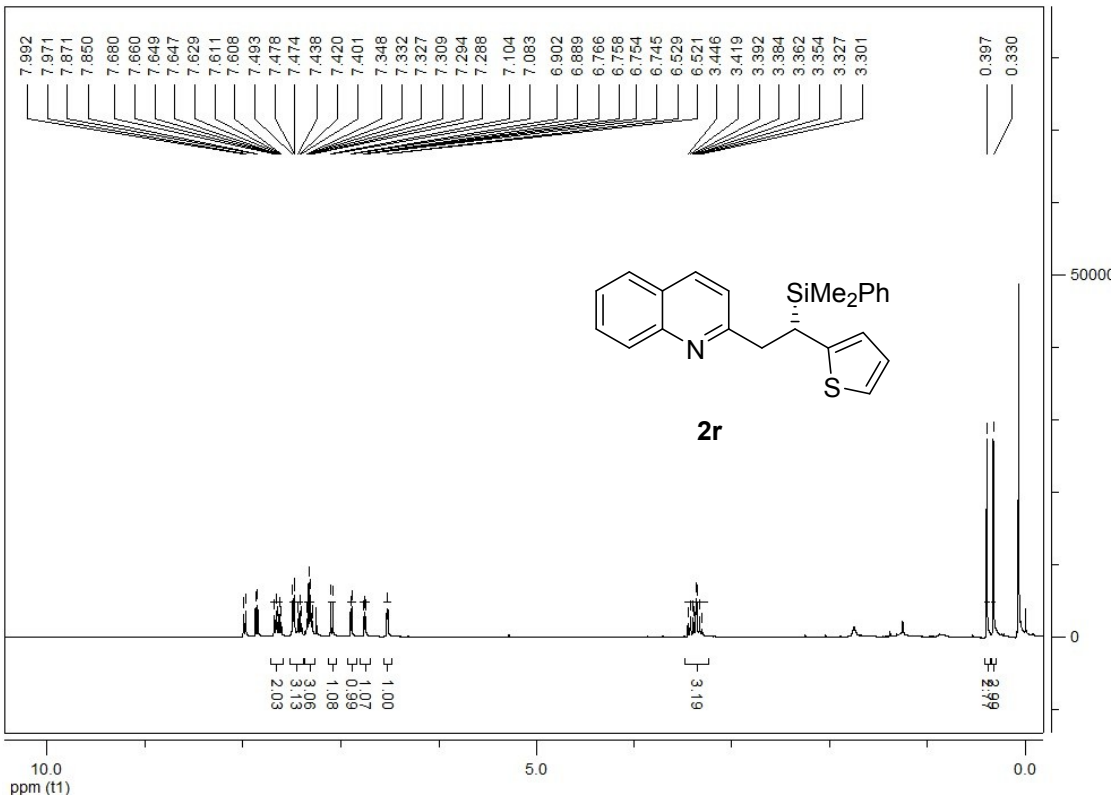
O
O
2q
150
100
50
0
ppm (t1)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7.647
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7.478
7.474
7.438
7.420
7.401
7.348
7.332
7.327
7.309
7.294
7.288
7.104
7.083
6.902
6.889
6.766
6.758
6.754
6.745
6.529
6.521
3.446
3.419
3.392
3.384
3.362
3.354
3.327
3.301
0.397
0.330
SiMe2Ph
N
S
2r
2.03
3.13
3.06
1.08
0.99
1.07
1.00
3.19
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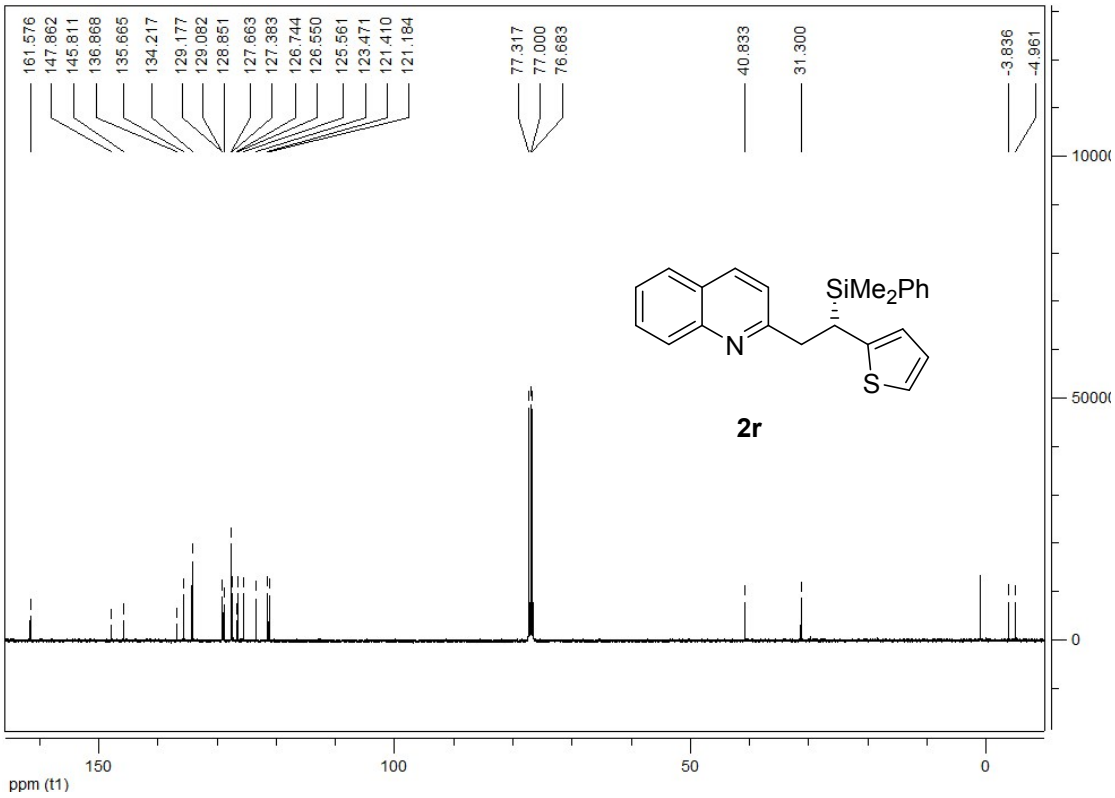
5.0
0.0
ppm (t1)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126.550
125.561
123.471
121.410
121.184
77.317
77.000
76.683
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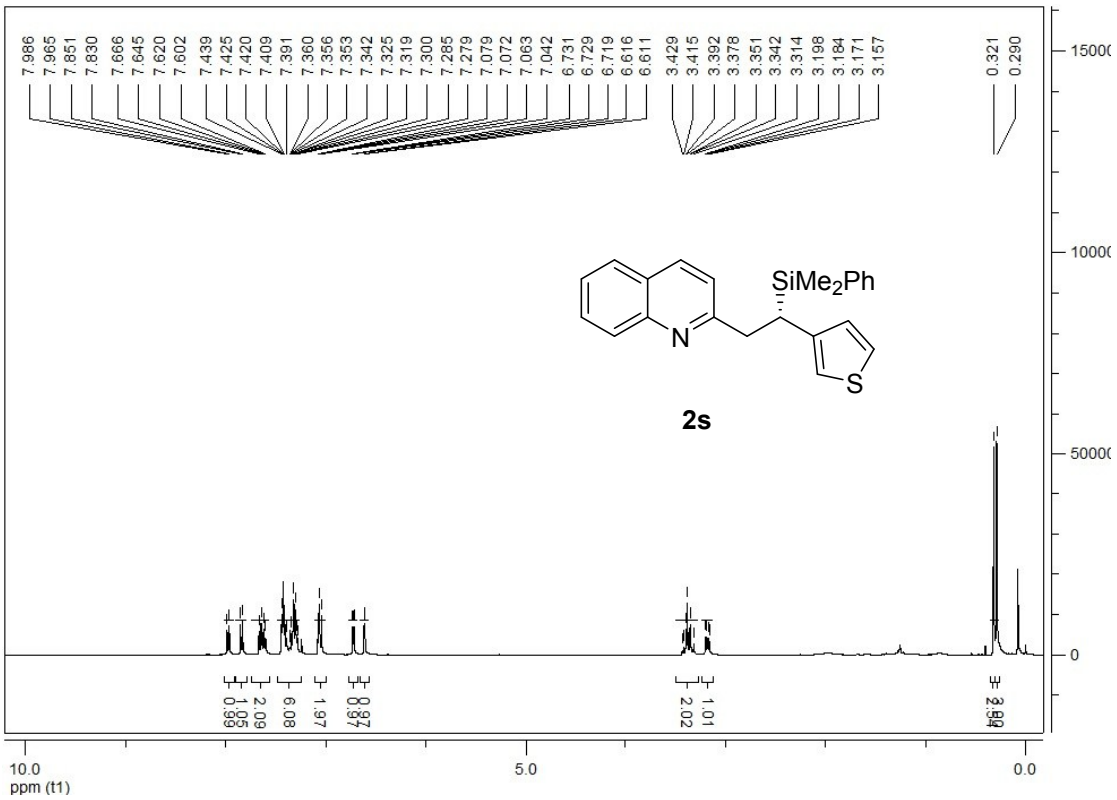
-4.961
SiMe2Ph
N
S
2r
150
100
50
0
ppm (t1)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7.830
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7.620
7.602
7.439
7.425
7.420
7.409
7.391
7.360
7.356
7.353
7.342
7.325
7.319
7.300
7.285
7.279
7.079
7.072
7.063
7.042
6.731
6.729
6.719
6.616
6.611
3.429
3.415
3.392
3.378
3.351
3.342
3.314
3.198
3.184
3.171
3.157
0.321
0.290
SiMe2Ph
N
S
2s
0.99
1.05
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0.97
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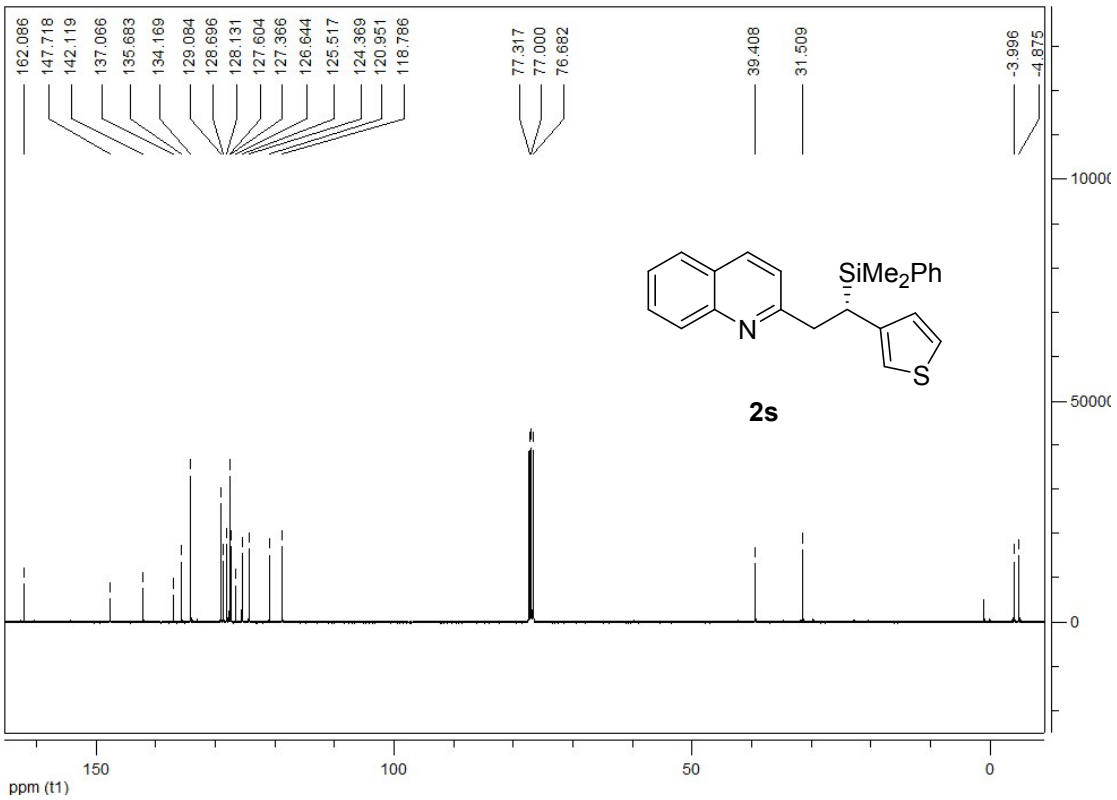
ppm (t1)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127.366
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125.517
124.369
120.951
118.786
77.317
77.000
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-3.996
-4.875
SiMe2Ph
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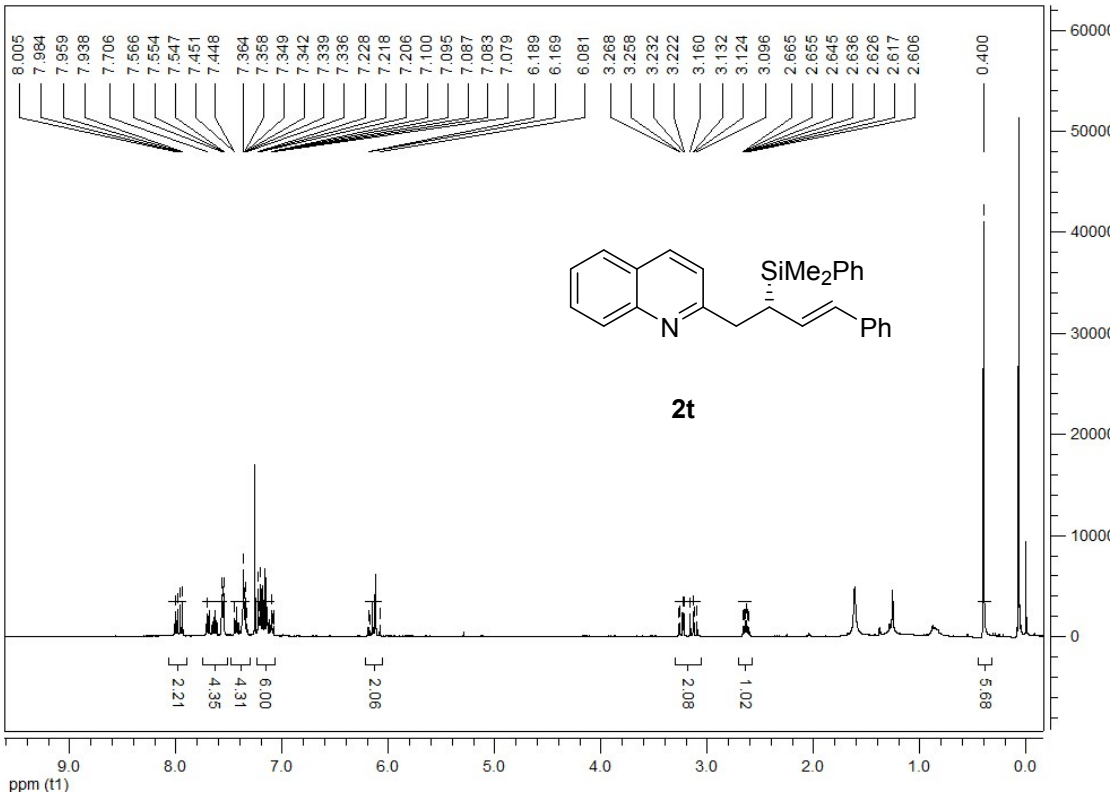
S
2s
150
100
50
0
ppm (t1)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7.349
7.342
7.339
7.336
7.228
7.218
7.206
7.100
7.095
7.087
7.083
7.079
6.189
6.169
6.081
3.268
3.258
3.232
3.222
3.160
3.132
3.124
3.096
2.665
2.655
2.645
2.636
2.626
2.617
2.606
0.400
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N
Ph
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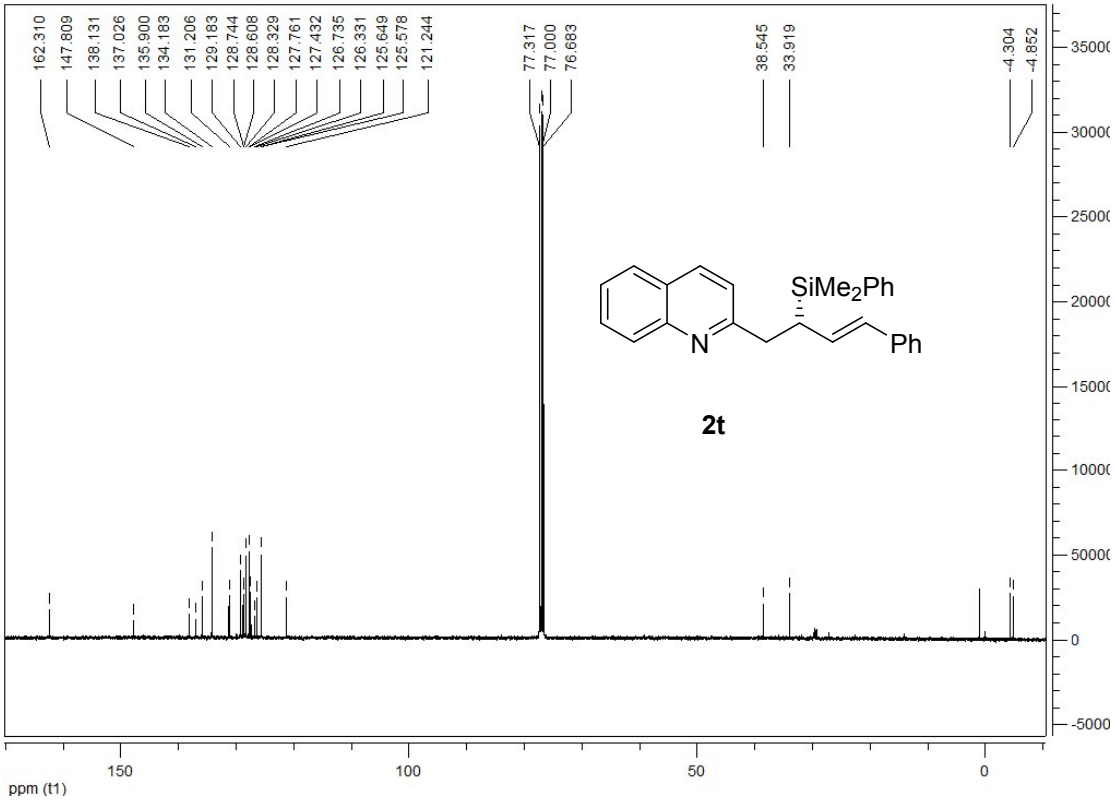
2.08
1.02
5.68
ppm (t1)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127.432
126.735
126.331
125.649
125.578
121.244
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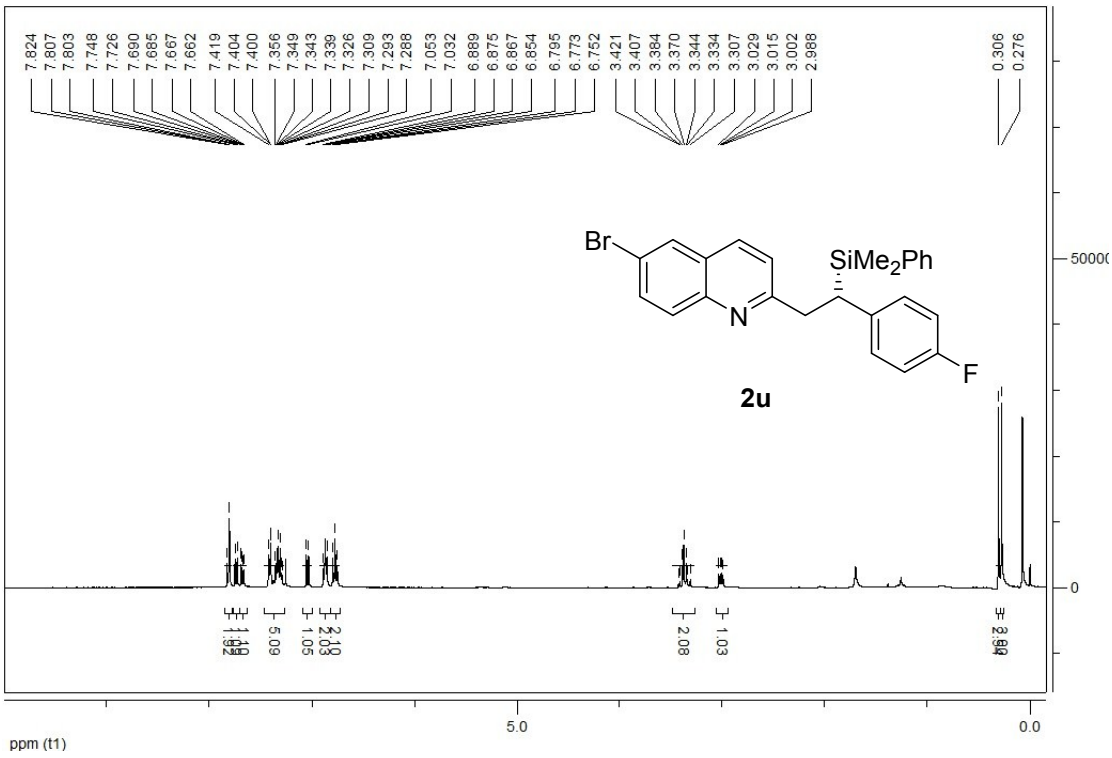
-4.852
SiMe2Ph
N
Ph
2t
ppm (t1)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7.400
7.356
7.349
7.343
7.339
7.326
7.309
7.293
7.288
7.053
7.032
6.889
6.875
6.867
6.854
6.795
6.773
6.752
3.421
3.407
3.384
3.370
3.344
3.334
3.307
3.029
3.015
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0.276
Br
SiMe2Ph
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F
2u
5000
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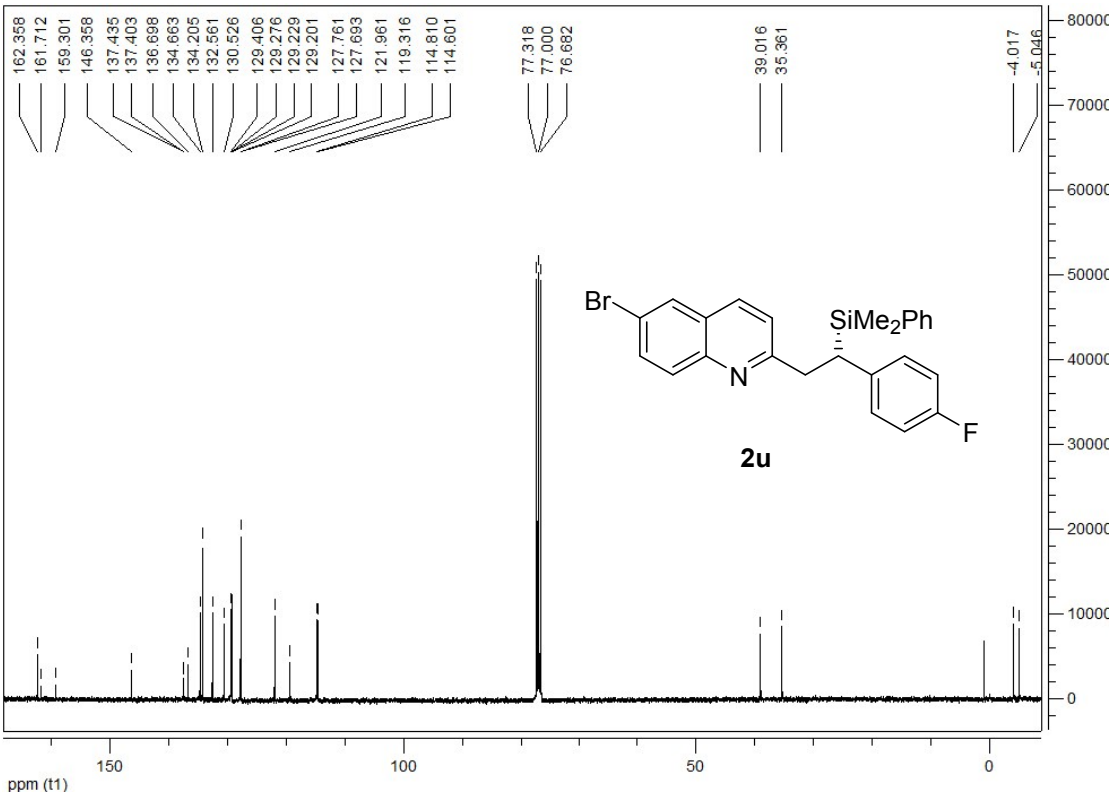
ppm (t1)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129.229
129.201
127.761
127.693
121.961
119.316
114.810
114.601
77.318
77.000
76.682
39.016
35.361
-4.017
-5.046
Br
SiMe2Ph
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F
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60000
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30000
20000
10000
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100
50
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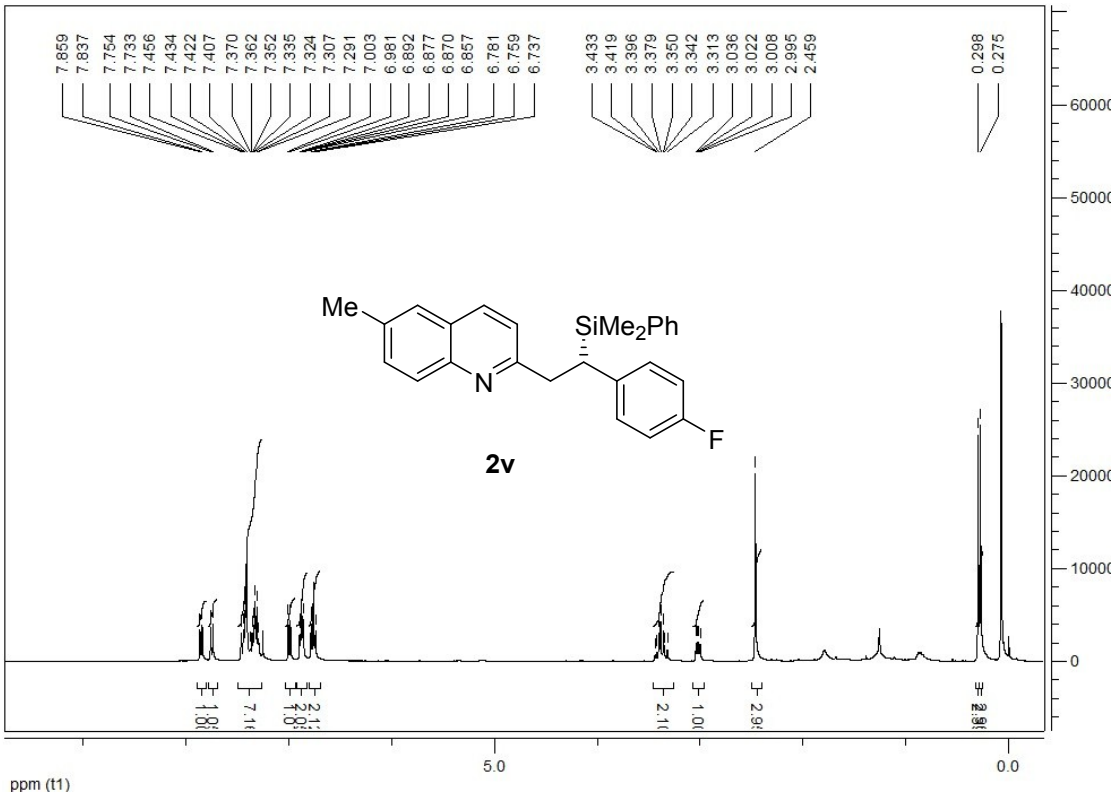
ppm (t1)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7.335
7.324
7.307
7.291
7.003
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6.892
6.877
6.870
6.857
6.781
6.759
6.737
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3.419
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3.379
3.350
3.342
3.313
3.036
3.022
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0.275
Me
SiMe2Ph
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F
2v
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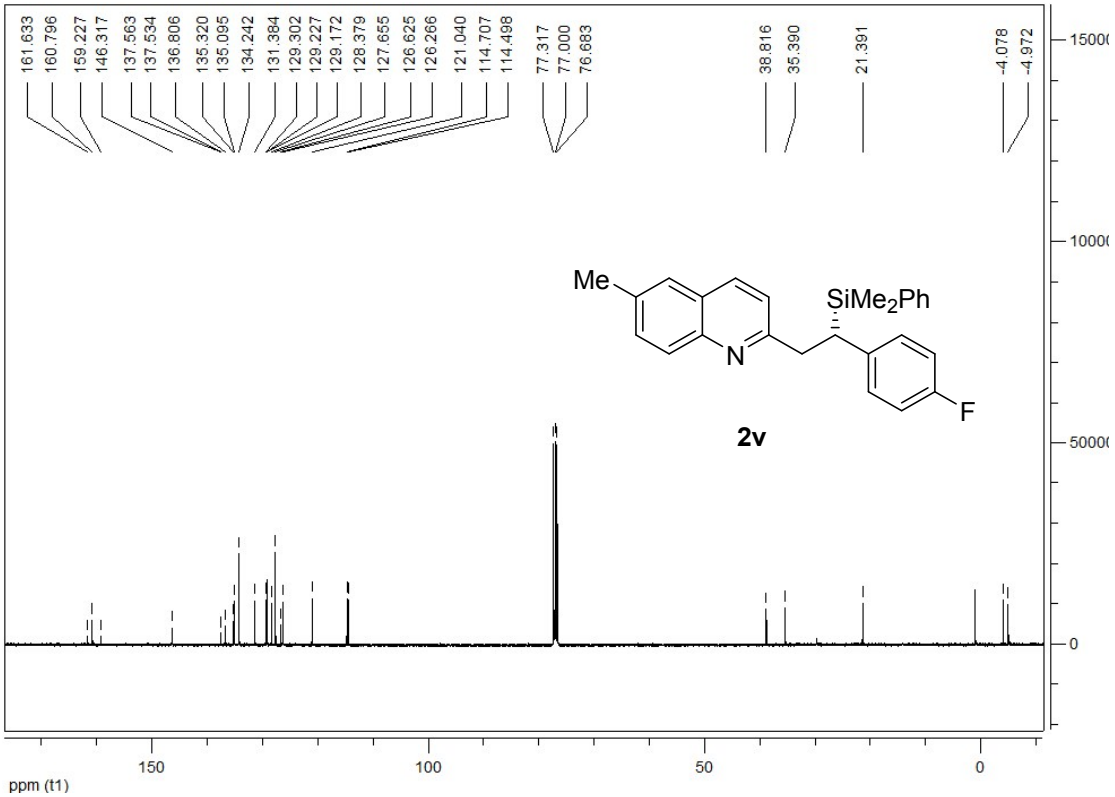
0.0
ppm (t1)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129.227
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128.379
127.655
126.625
126.266
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77.000
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Me
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F
2v
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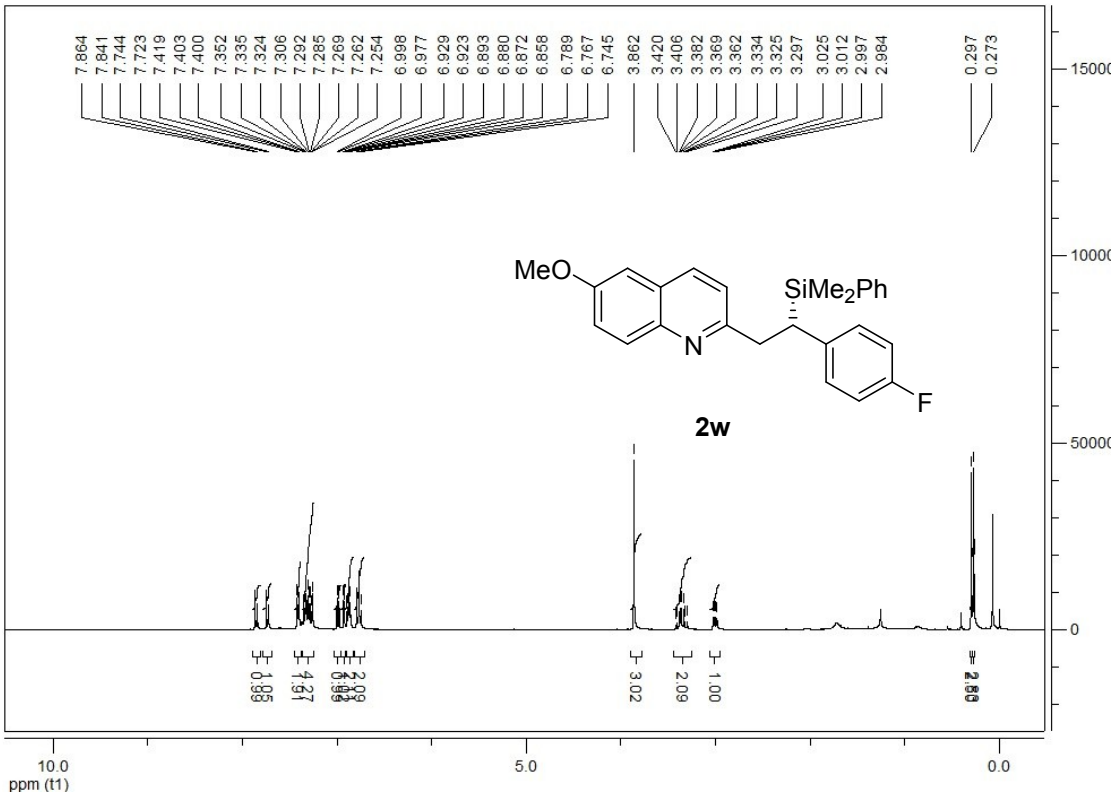
50
0
ppm (t1)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7.269
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7.254
6.998
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6.929
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6.893
6.880
6.872
6.858
6.789
6.767
6.745
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3.420
3.406
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3.369
3.362
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3.325
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2.984
0.297
0.273
MeO
SiMe2Ph
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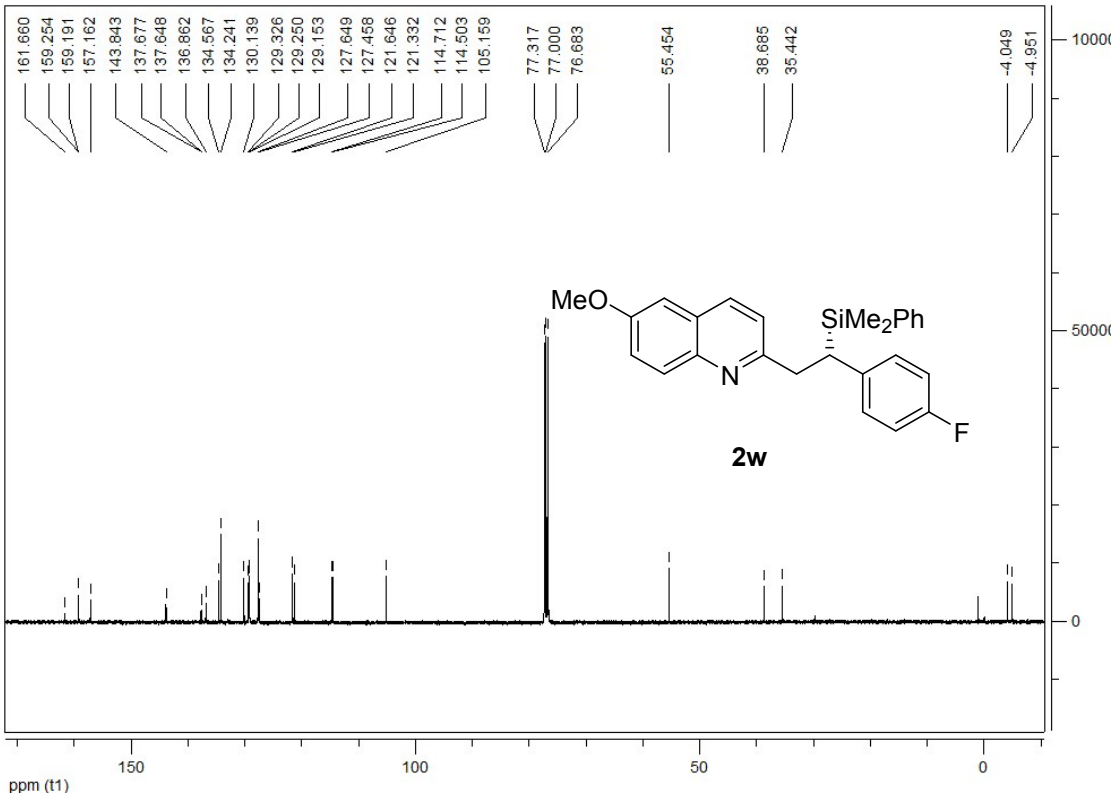
ppm (t1)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129.153
127.649
127.458
121.646
121.332
114.712
114.503
105.159
77.317
77.000
76.683
55.454
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-4.951
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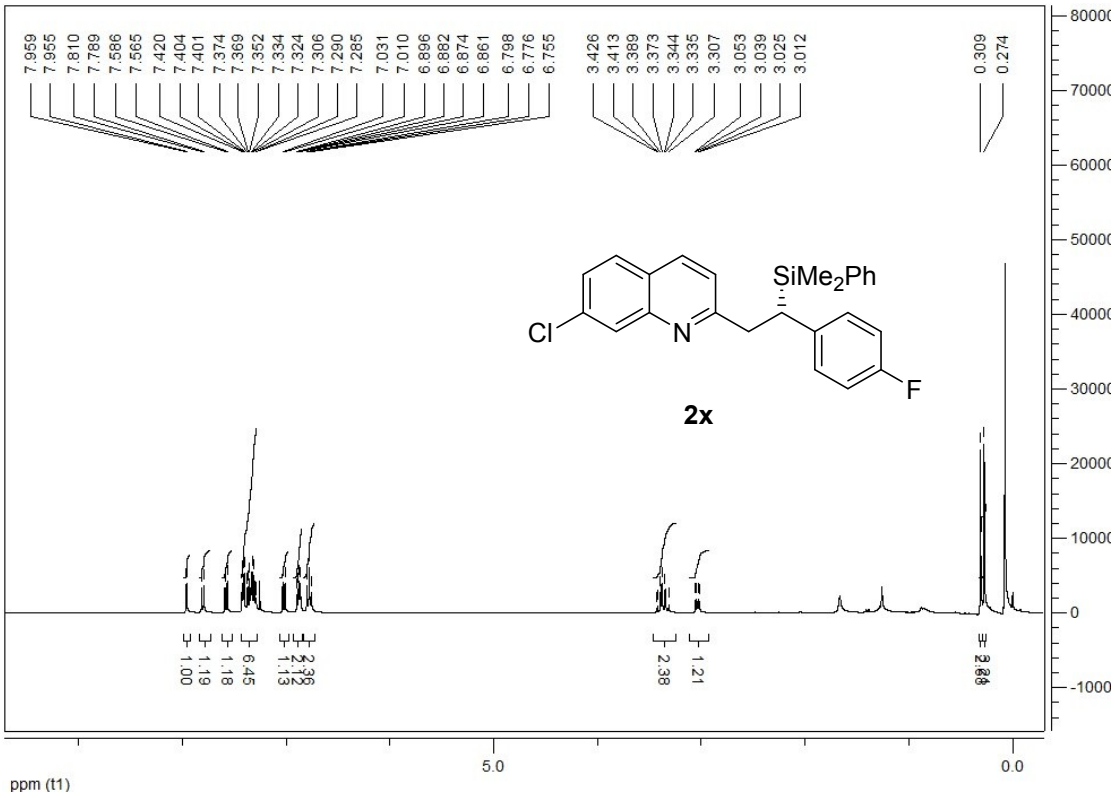
SiMe2Ph
N
F
2w
150
100
50
0
ppm (t1)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0.274
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Cl
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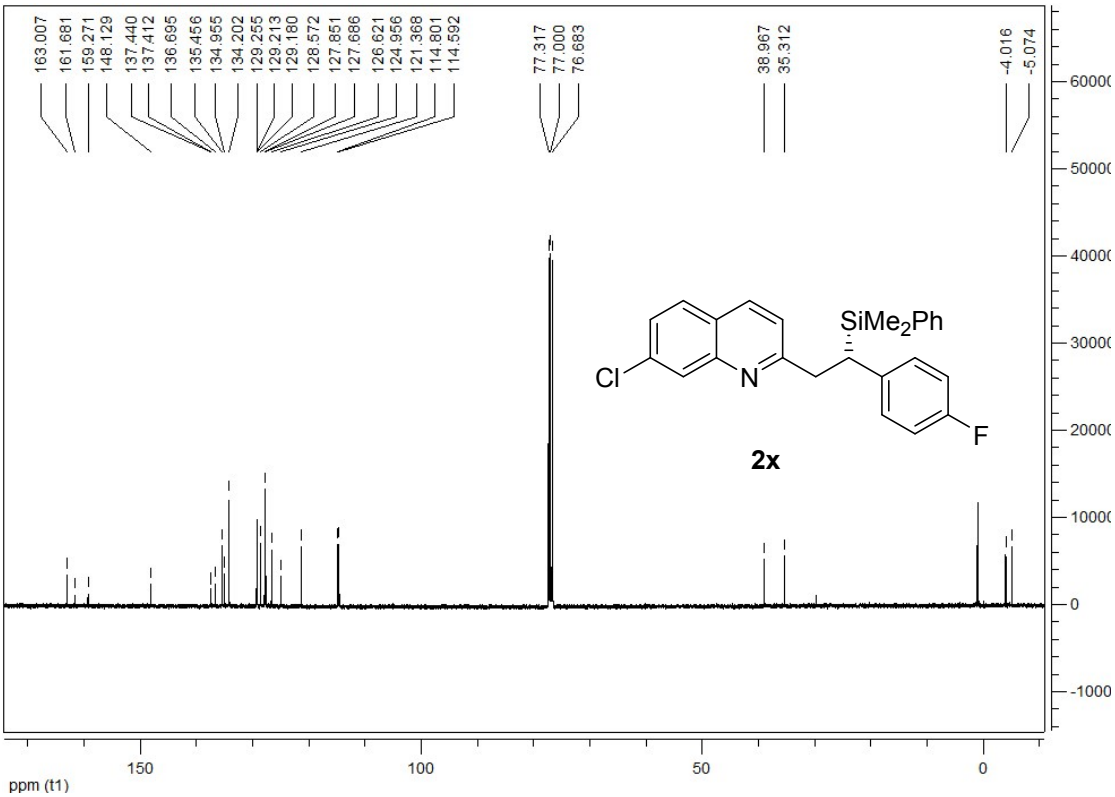
ppm (t1)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127.686
126.621
124.956
121.368
114.801
114.592
77.317
77.000
76.683
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-5.074
SiMe2Ph
Cl
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F
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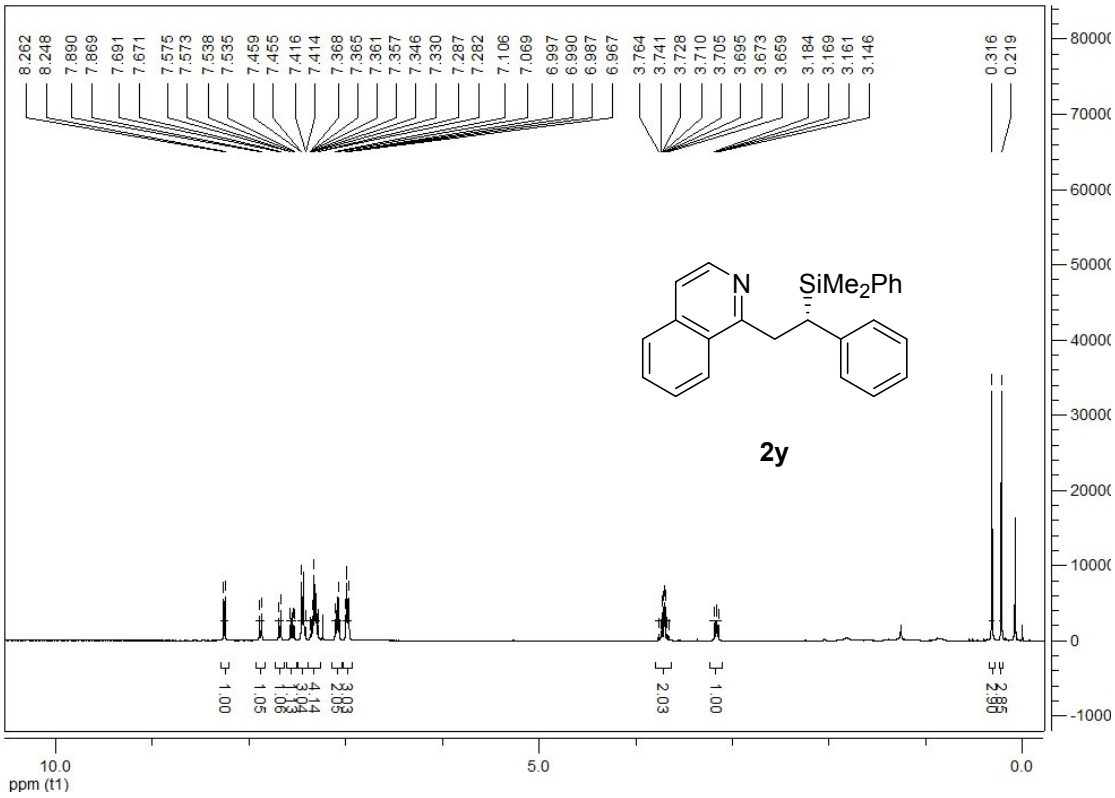
50
0
ppm (t1)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7.414
7.368
7.365
7.361
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7.282
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3.184
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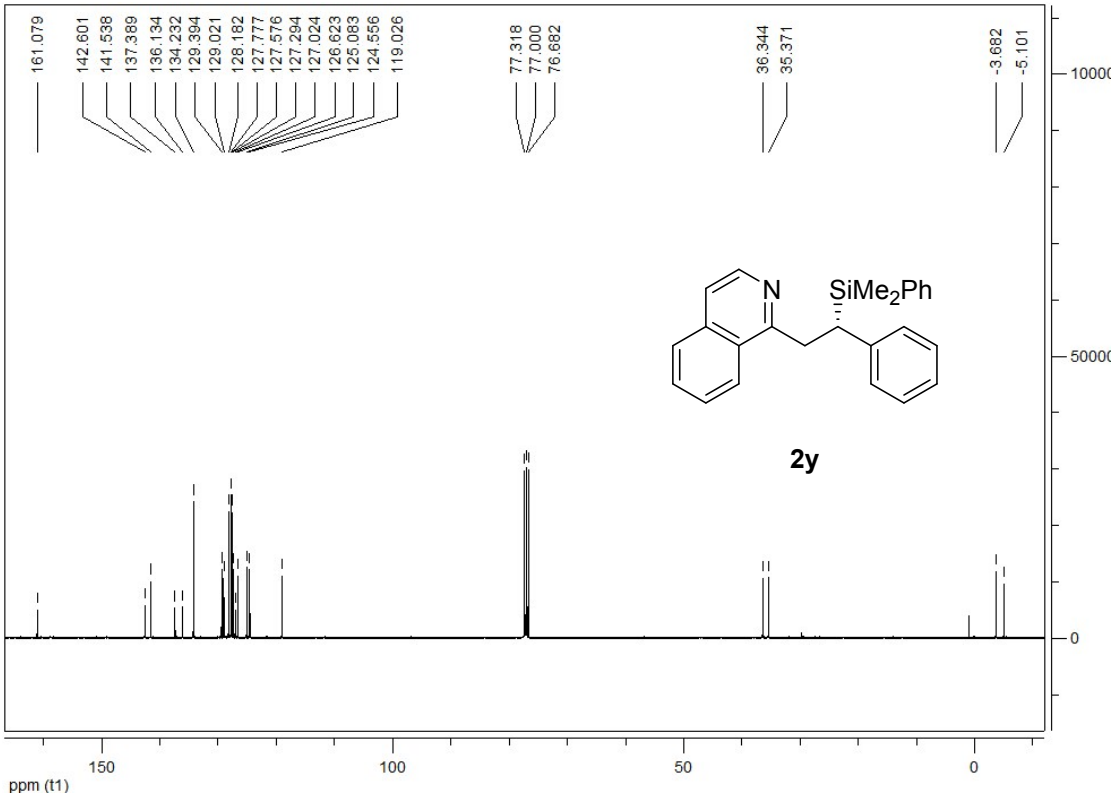
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125.083
124.556
119.026
77.318
77.000
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2y
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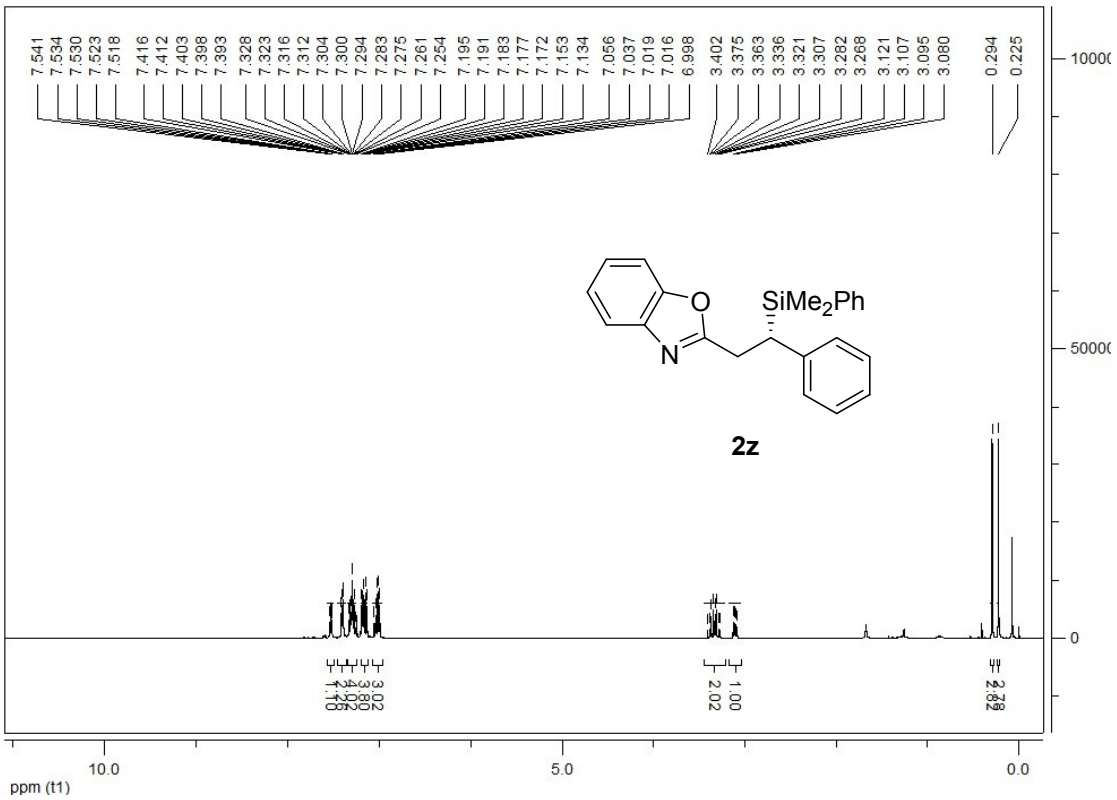
ppm (t1)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7.275
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7.191
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3.375
3.363
3.336
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3.307
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3.268
3.121
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3.080
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O
N
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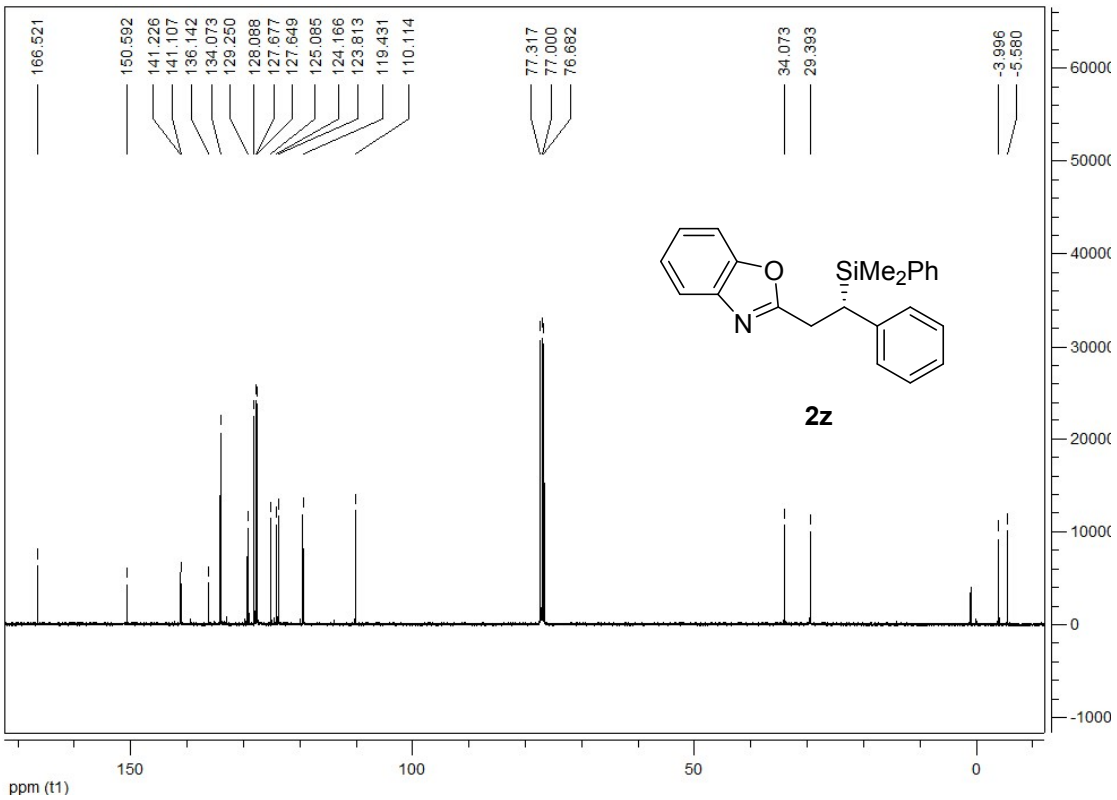
ppm (t1)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123.813
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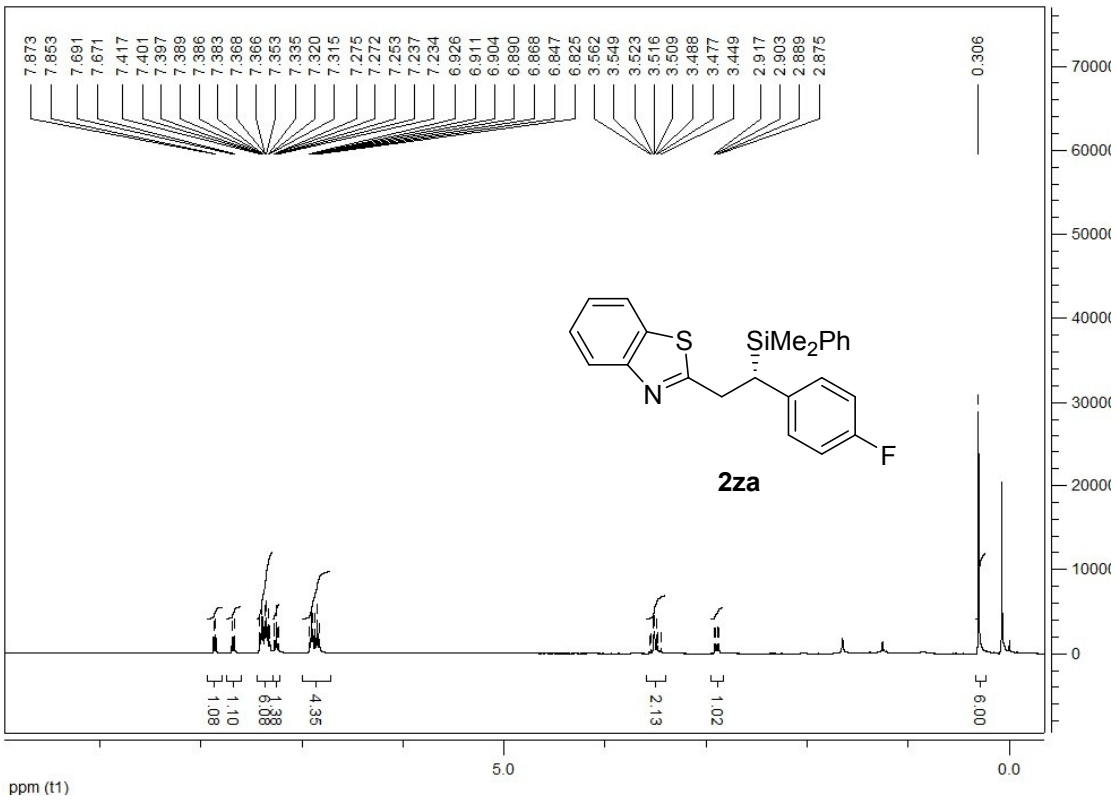
110.114
77.317
77.000
76.682
34.073
29.393
-3.996
-5.580
O
N
SiMe2Ph
2z
150
100
50
0
ppm (t1)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7.671
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7.401
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7.383
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7.366
7.353
7.335
7.320
7.315
7.275
7.272
7.253
7.237
7.234
6.926
6.911
6.904
6.890
6.868
6.847
6.825
3.562
3.549
3.523
3.516
3.509
3.488
3.477
3.449
2.917
2.903
2.889
2.875
0.306
S
N
SiMe2Ph
F
2za
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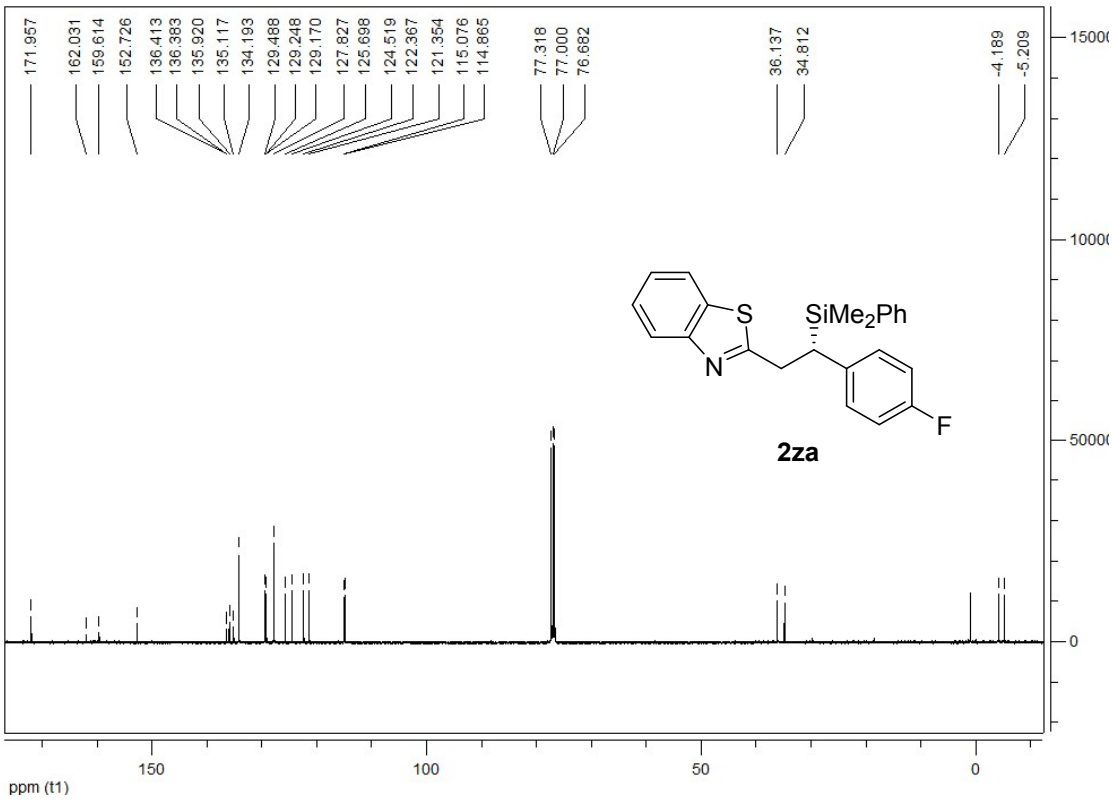
1.10
1.88
6.08
4.35
2.13
1.02
6.00
5.0
0.0
ppm (t1)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152.726
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136.383
135.920
135.117
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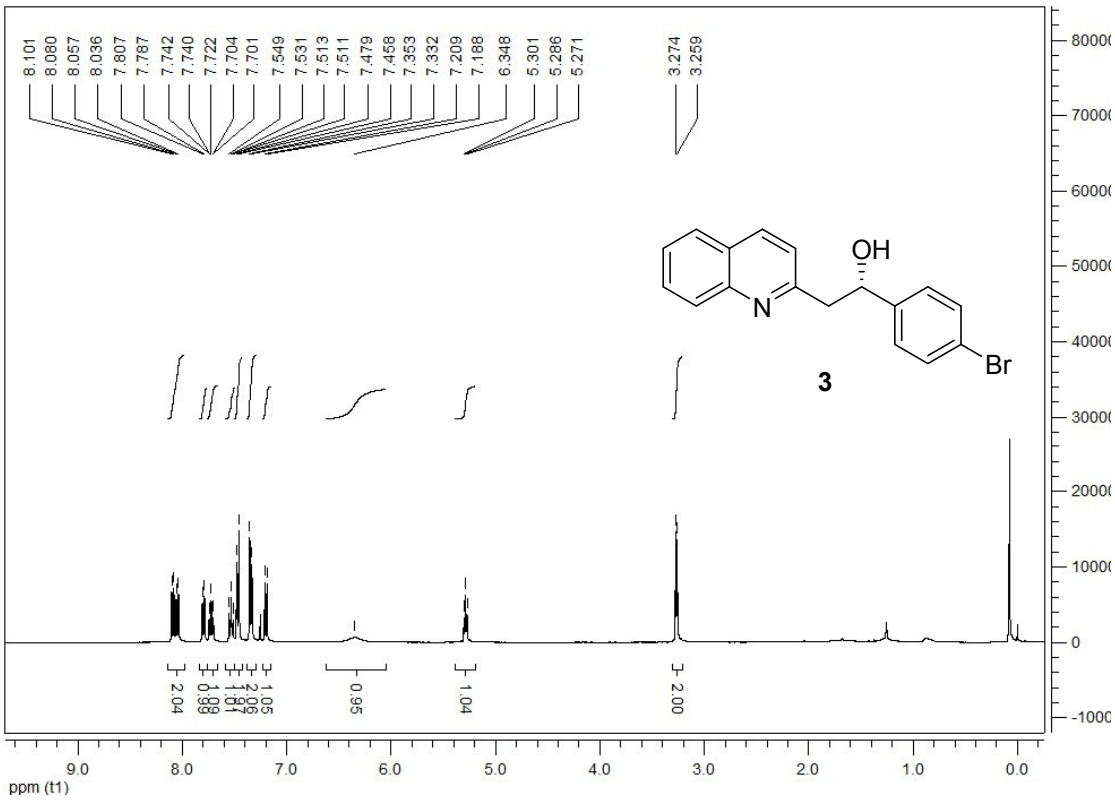
129.248
129.170
127.827
125.698
124.519
122.367
121.354
115.076
114.865
77.318
77.000
76.682
36.137
34.812
-4.189
-5.209
S
N
SiMe2Ph
F
2za
150
100
50
0
ppm (t1)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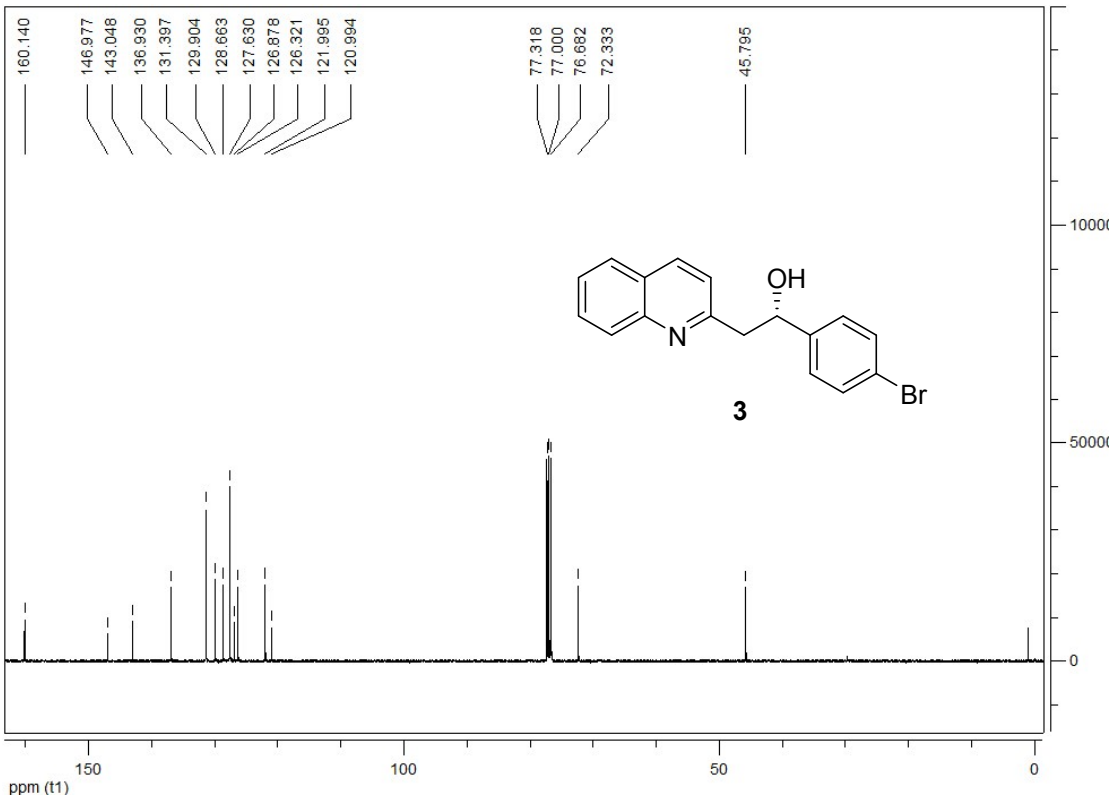
7.787
7.742
7.740
7.722
7.704
7.701
7.549
7.531
7.513
7.511
7.479
7.458
7.353
7.332
7.209
7.188
6.348
5.301
5.286
5.271
3.274
3.259
OH
N
Br
3
2.04
0.98
1.01
1.07
2.06
1.05
0.95
1.14
2.00
ppm (t1)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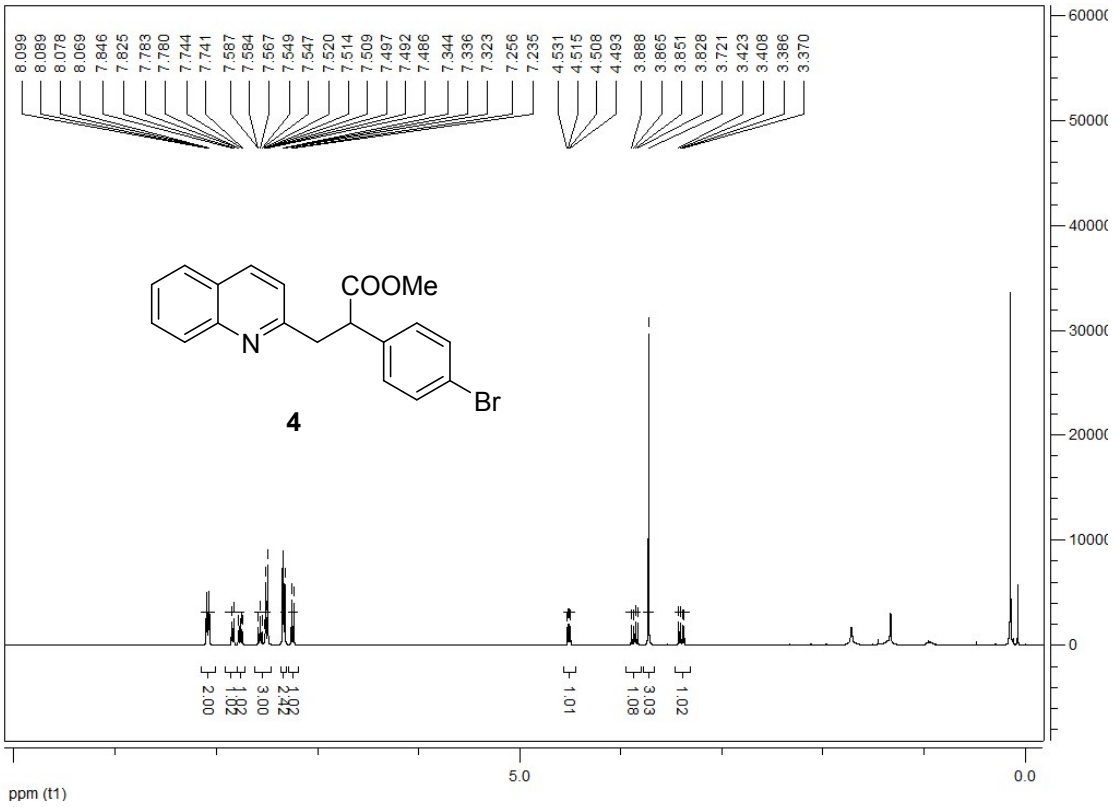
129.904
128.663
127.630
126.878
126.321
121.995
120.994
77.318
77.000
76.682
72.333
45.795
OH
N
Br
3
ppm (t1)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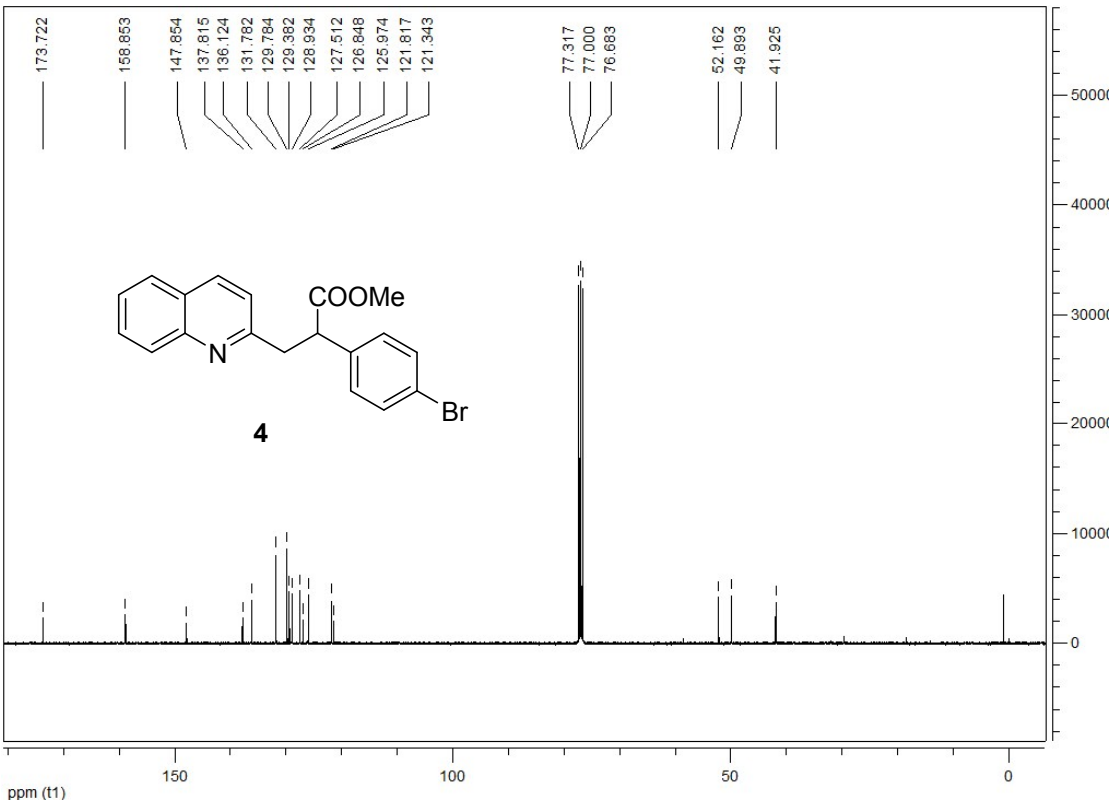
7.783
7.780
7.744
7.741
7.587
7.584
7.567
7.549
7.547
7.520
7.514
7.509
7.497
7.492
7.486
7.344
7.336
7.323
7.256
7.235
4.531
4.515
4.508
4.493
3.888
3.865
3.851
3.828
3.721
3.423
3.408
3.386
3.370
COOMe
N
Br
4
2.00
2.02
3.00
2.22
1.01
3.03
1.08
1.02
5.0
0.0
ppm (t1)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129.784
129.382
128.934
127.512
126.848
125.974
121.817
121.343
77.317
77.000
76.683
52.162
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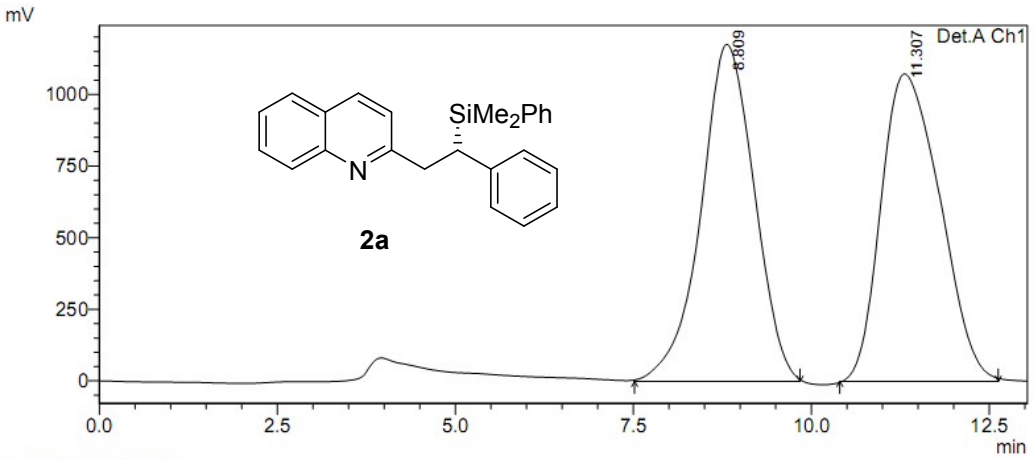
41.925
COOMe
N
Br
4
150
100
50
0
ppm (t1)

7. HPLC spectra of the products

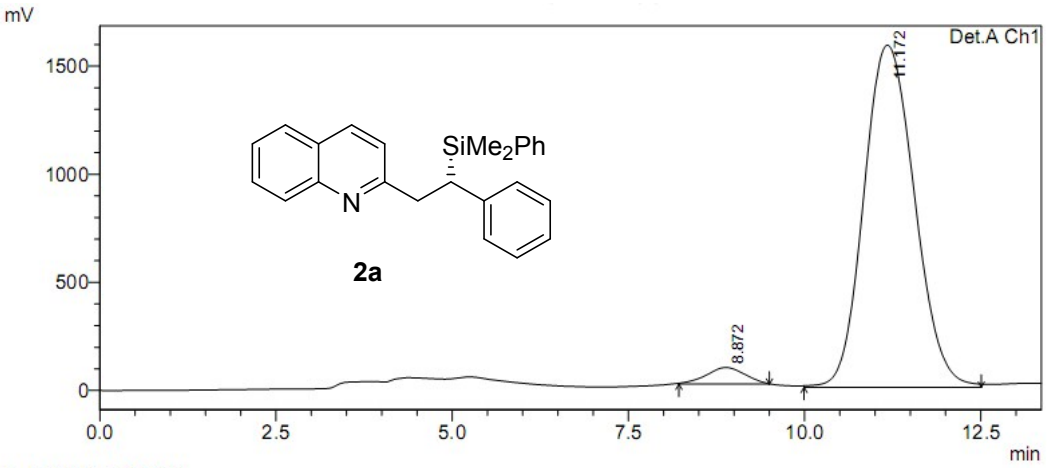


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.809	61341943	1175782	49.813
2	11.307	61802338	1073191	50.187
Total		123144281	2248973	100.000

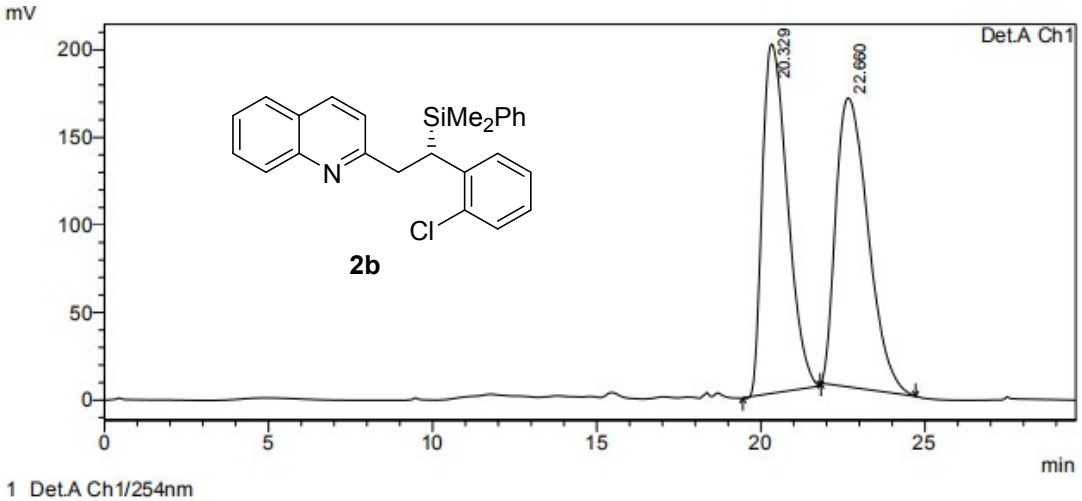


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.872	2981302	77463	3.629
2	11.172	79175218	1582481	96.371
Total		82156520	1659944	100.000

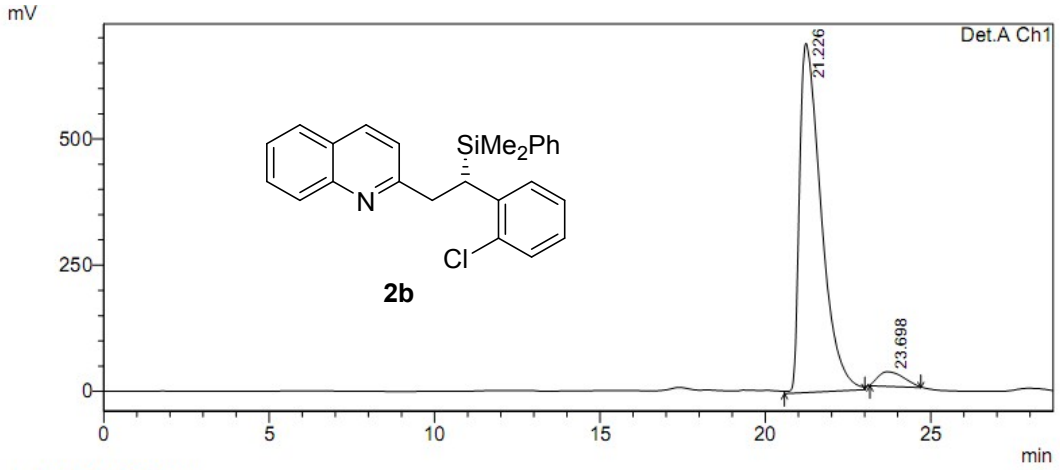


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.329	10624456	199537	48.413
2	22.660	11320950	165079	51.587
Total		21945406	364616	100.000

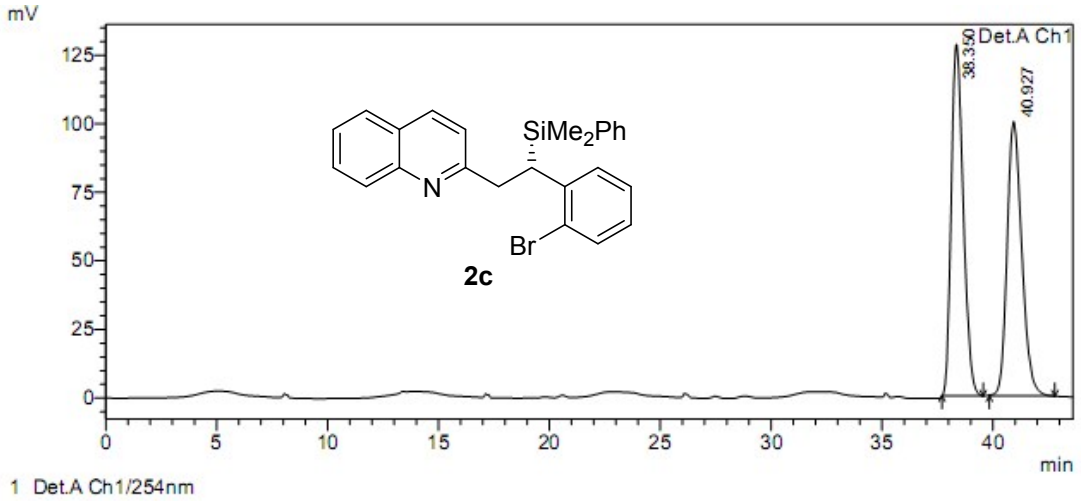


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

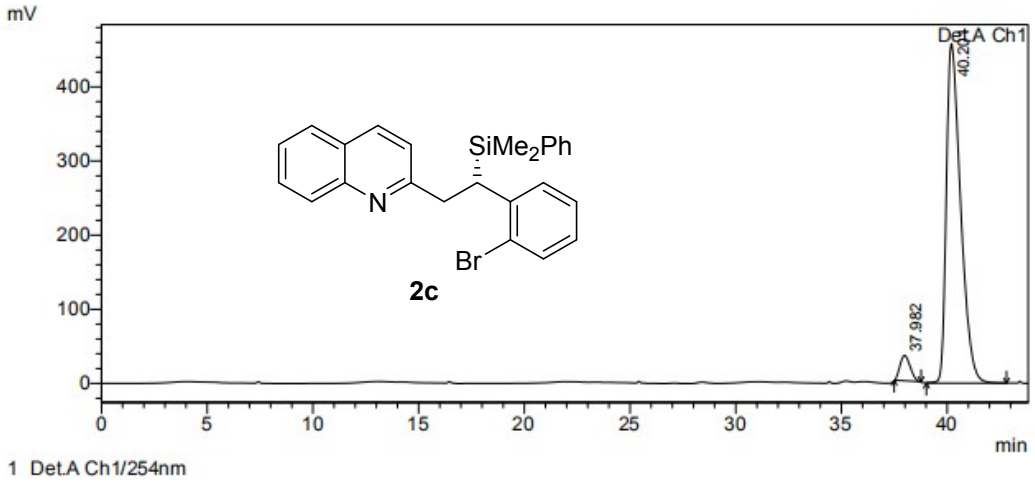
Peak#	Ret. Time	Area	Height	Area %
1	21.226	31421030	691717	95.141
2	23.698	1604667	29156	4.859
Total		33025697	720873	100.000



PeakTable

Detector A Ch1 254nm

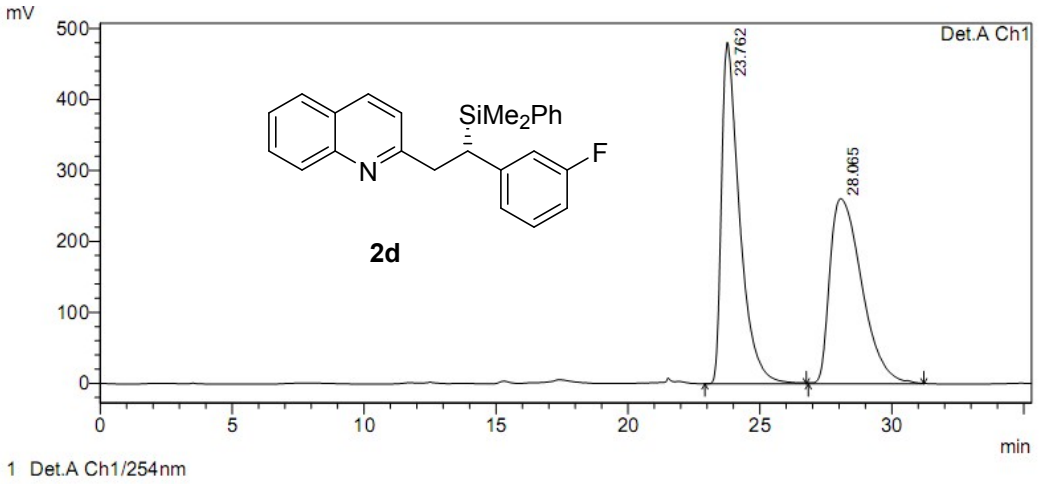
Peak#	Ret. Time	Area	Height	Area %
1	38.350	4808891	128150	51.129
2	40.927	4596550	99997	48.871
Total		9405441	228147	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	37.982	1125600	33980	4.975
2	40.201	21500549	457912	95.025
Total		22626148	491892	100.000

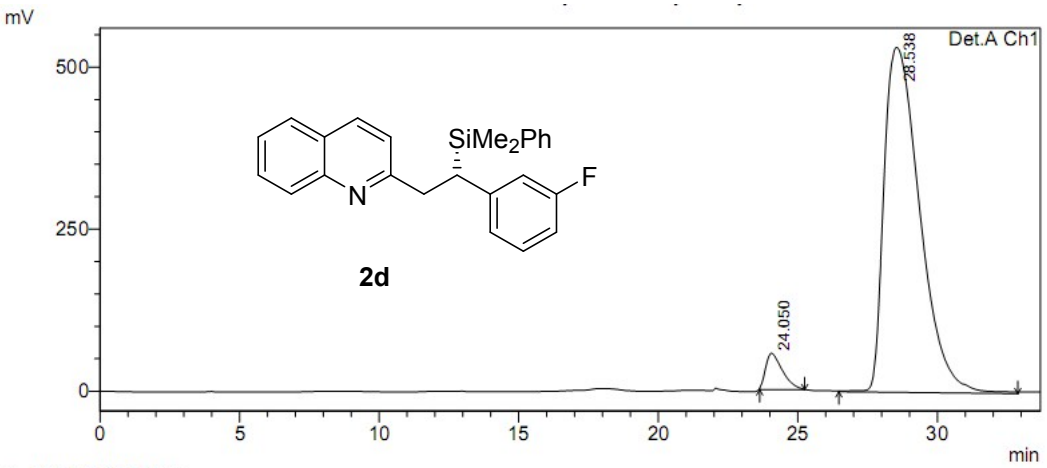


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	23.762	23023348	481203	51.085
2	28.065	22044989	260852	48.915
Total		45068337	742055	100.000

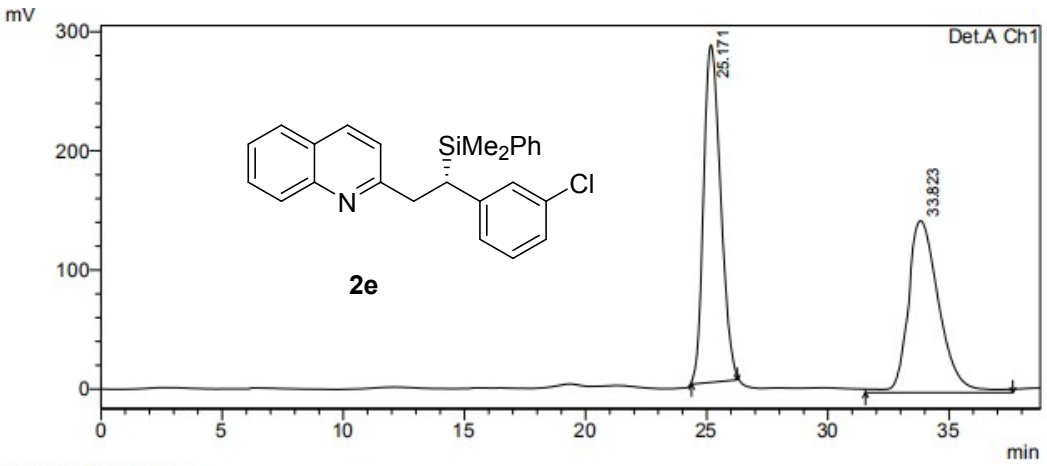


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.050	2366159	56198	4.749
2	28.538	47461393	532405	95.251
Total		49827552	588603	100.000

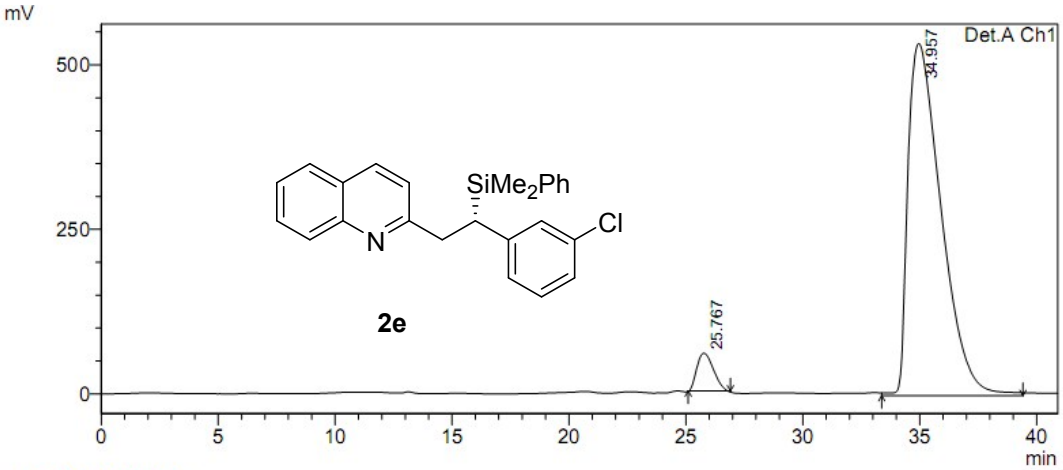


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.171	13818656	283326	51.874
2	33.823	12820095	144318	48.126
Total		26638751	427644	100.000

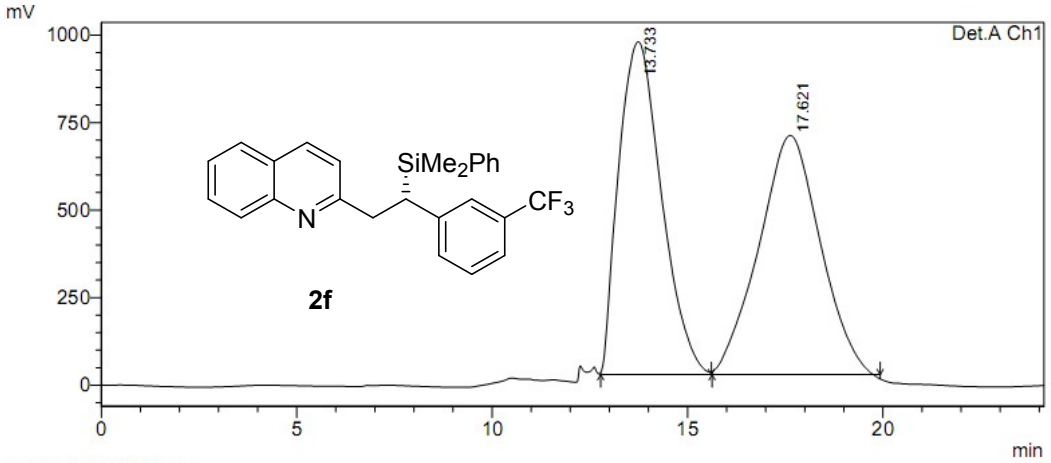


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.767	2800646	57209	5.033
2	34.957	52850048	535031	94.967
Total		55650694	592240	100.000

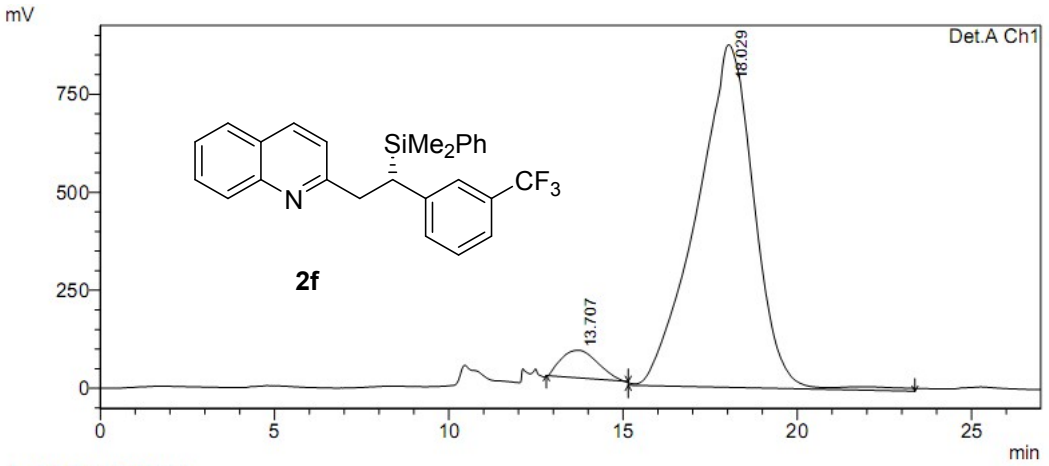


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	13.733	72317421	951323	49.211
2	17.621	74635723	683964	50.789
Total		146953144	1635287	100.000

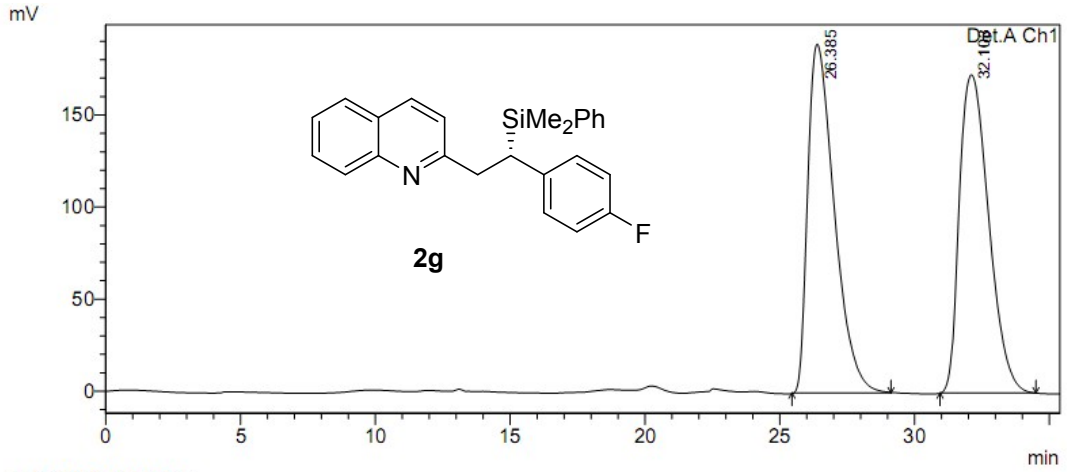


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	13.707	5112914	70116	4.859
2	18.029	100108132	873996	95.141
Total		105221046	944113	100.000

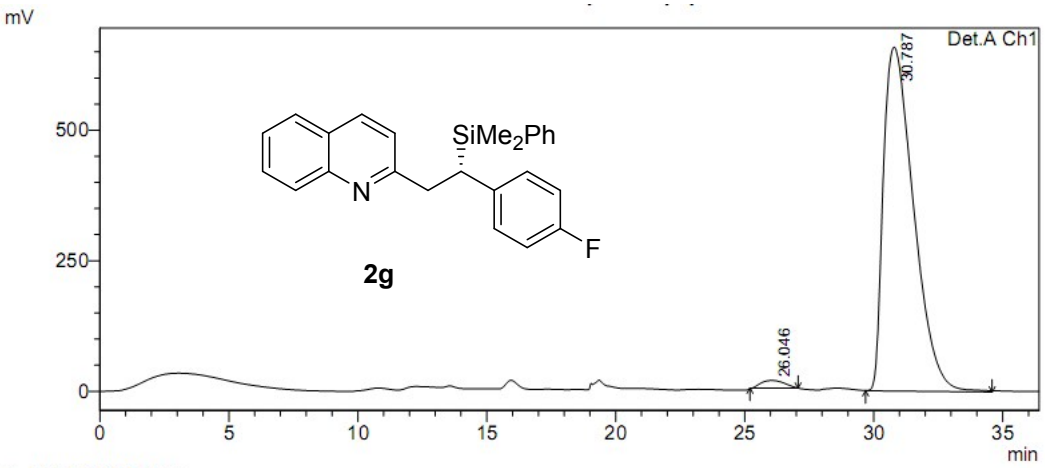


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.385	12952546	189352	49.787
2	32.103	13063408	172725	50.213
Total		26015953	362078	100.000

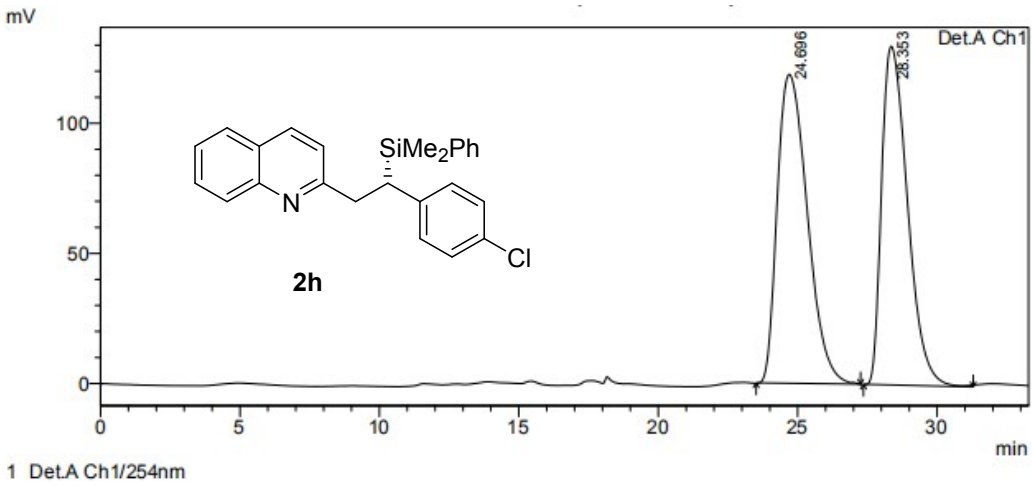


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.046	923519	14569	1.688
2	30.787	53782841	658733	98.312
Total		54706359	673302	100.000

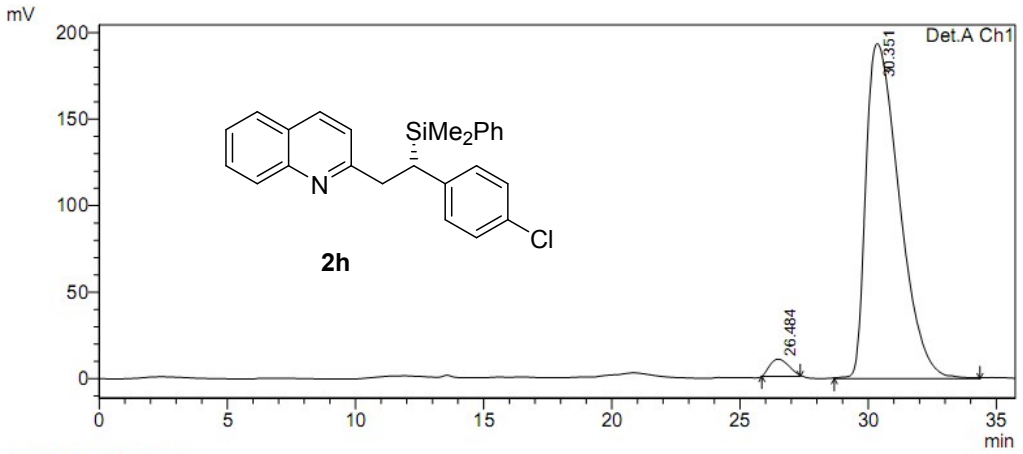


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.696	8899837	118685	51.475
2	28.353	8389854	130104	48.525
Total		17289691	248789	100.000

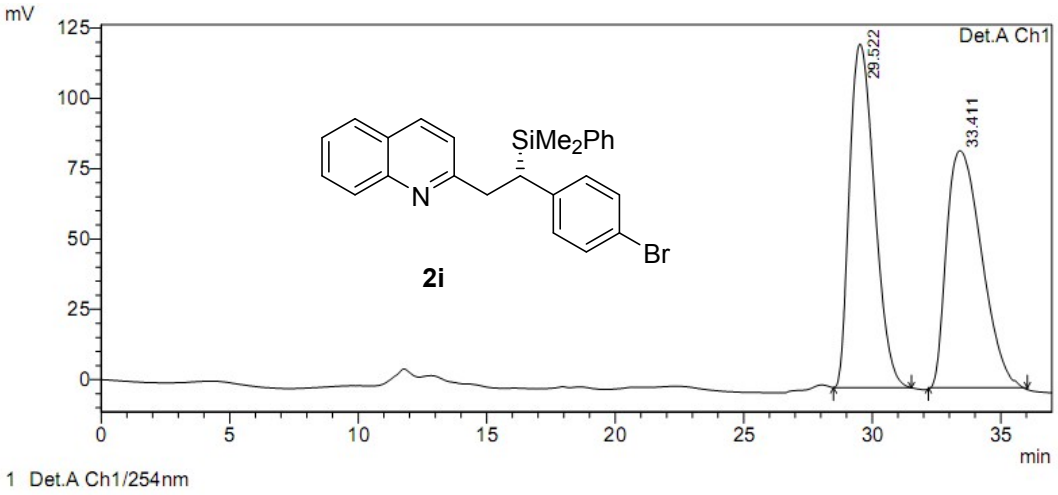


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.484	518284	9899	2.864
2	30.351	17580742	193657	97.136
Total		18099027	203556	100.000

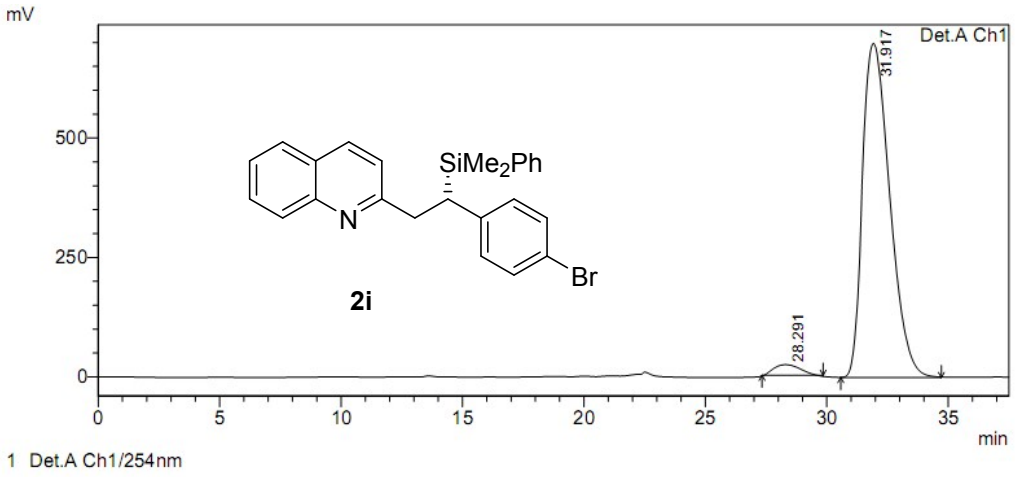


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	29.522	8295180	122218	50.871
2	33.411	8011273	84298	49.129
Total		16306453	206516	100.000

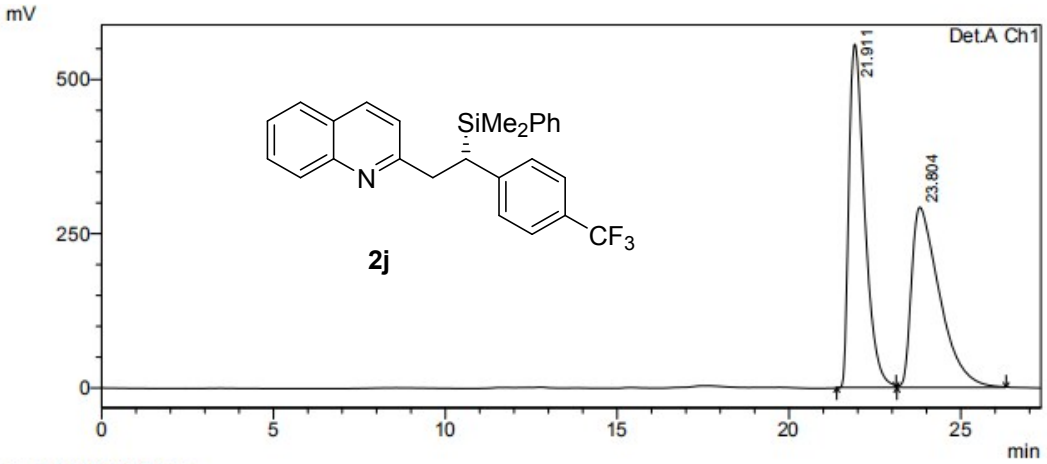


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	28.291	1609273	21806	2.860
2	31.917	54660389	699549	97.140
Total		56269662	721356	100.000

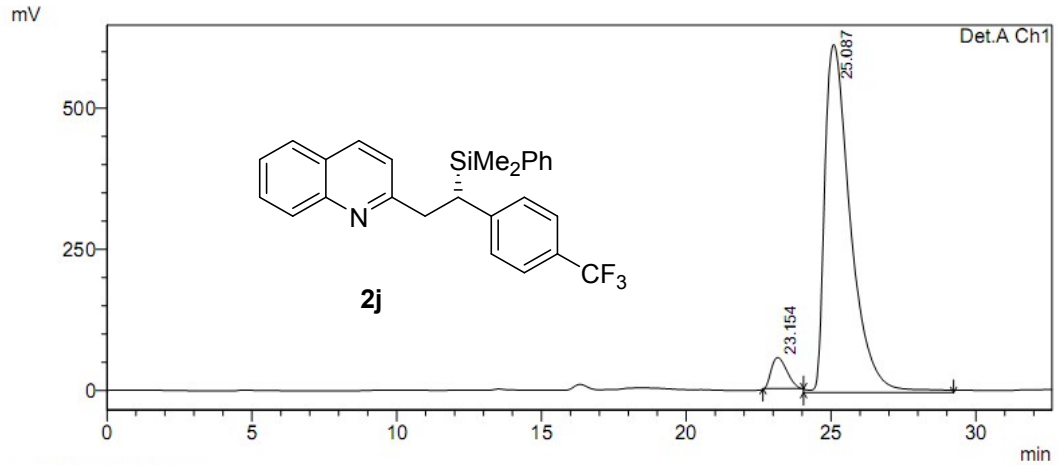


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.911	17821789	556530	51.710
2	23.804	16642991	292129	48.290
Total		34464780	848659	100.000

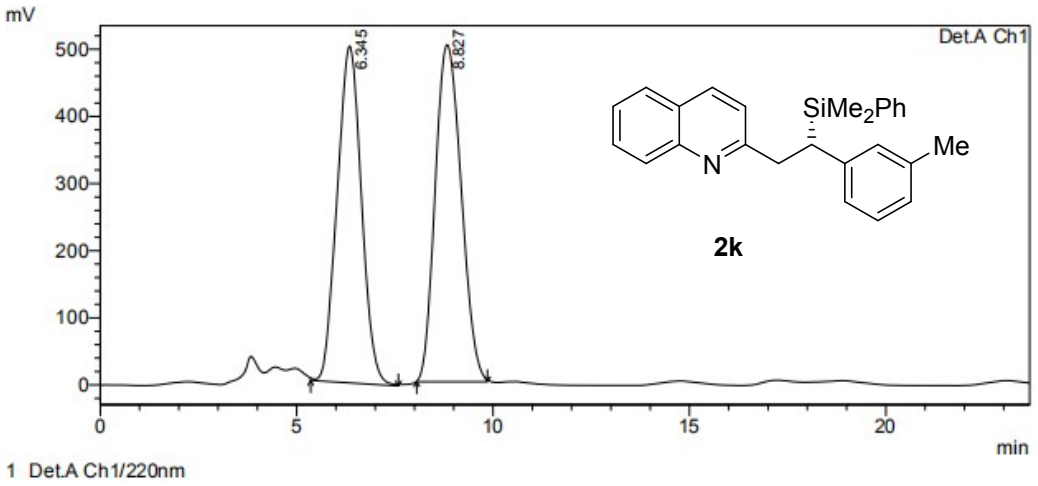


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	23.154	2037464	54943	5.049
2	25.087	38314376	616748	94.951
Total		40351840	671691	100.000

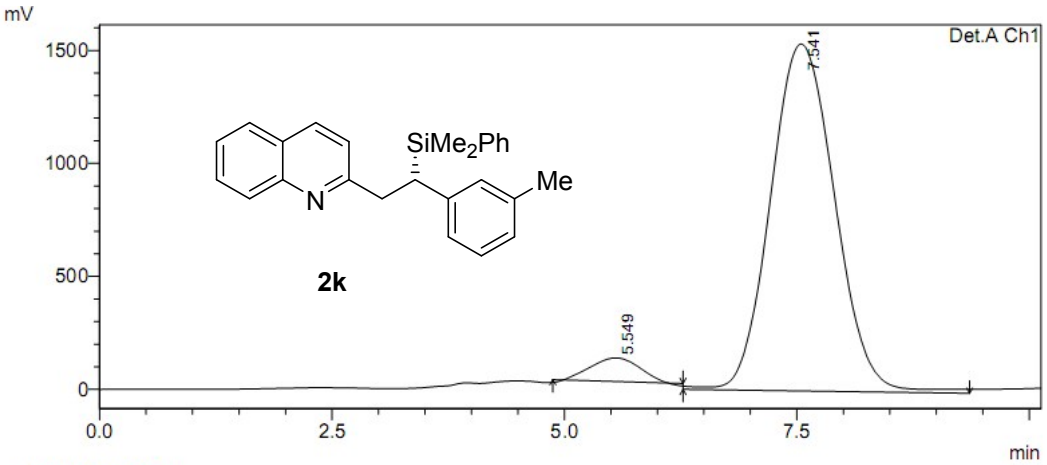


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	6.345	21532736	501630	48.248
2	8.827	23096626	502055	51.752
Total		44629362	1003686	100.000

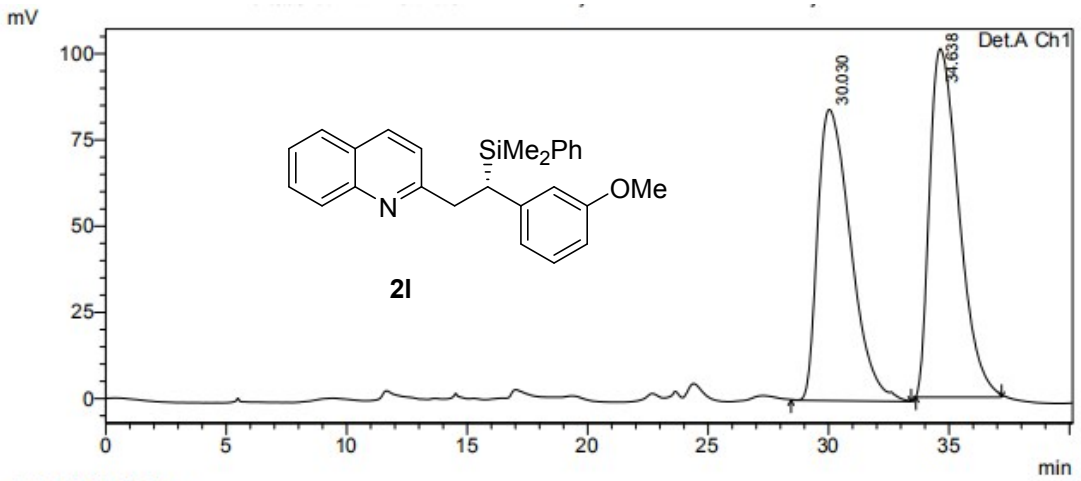


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	5.549	3682440	104513	4.748
2	7.541	73882802	1535053	95.252
Total		77565242	1639567	100.000

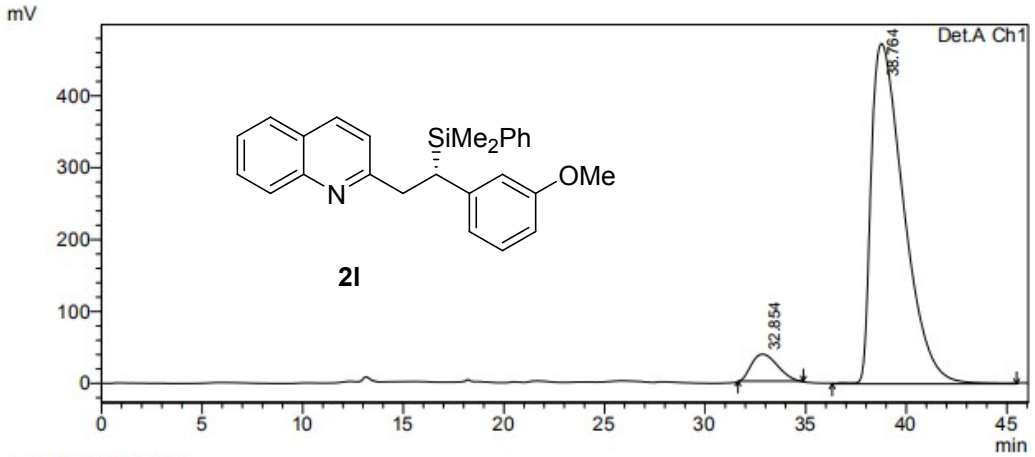


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	30.030	8071309	84450	48.395
2	34.638	8606623	101084	51.605
Total		16677932	185534	100.000

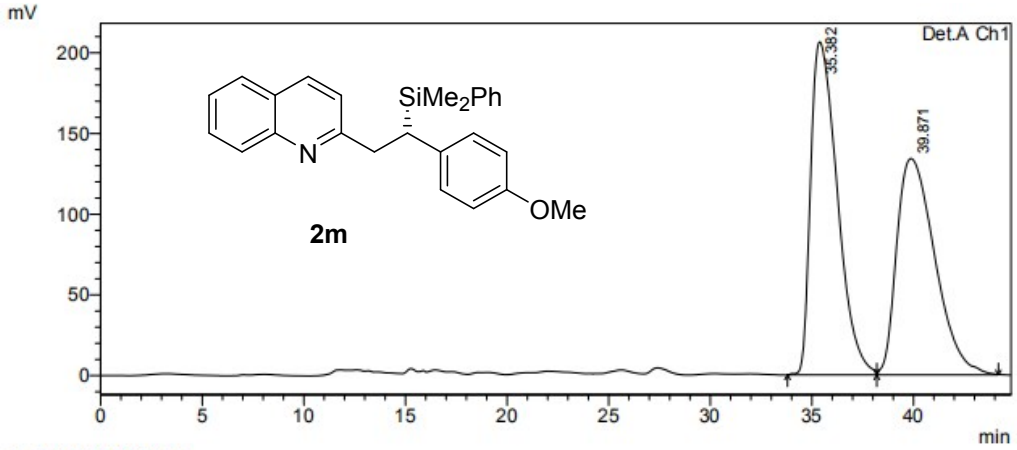


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	32.854	3361406	37353	5.933
2	38.764	53290659	473389	94.067
Total		56652065	510743	100.000

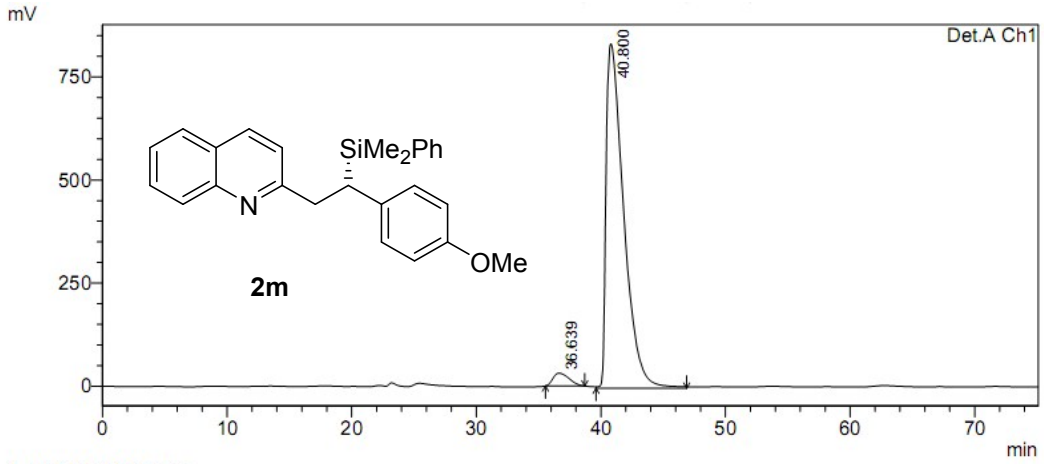


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	35.382	18891960	206397	51.856
2	39.871	17539860	134120	48.144
Total		36431820	340517	100.000

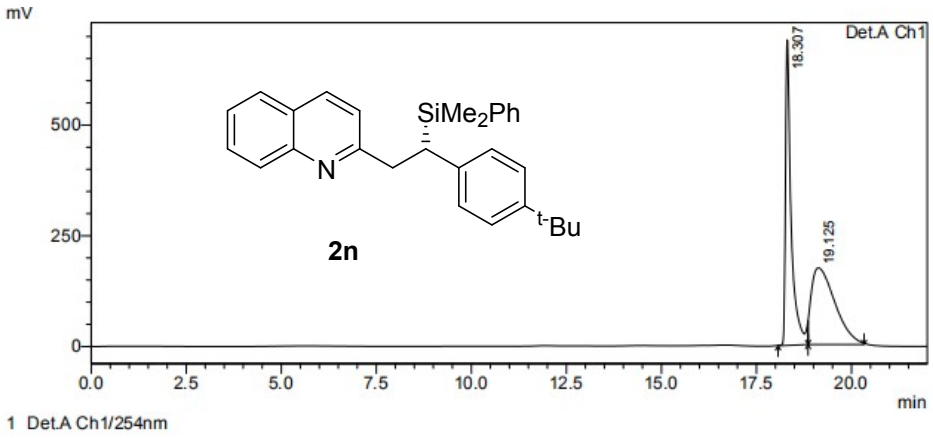


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	36.639	2728117	30840	3.225
2	40.800	81862475	835310	96.775
Total		84590592	866150	100.000

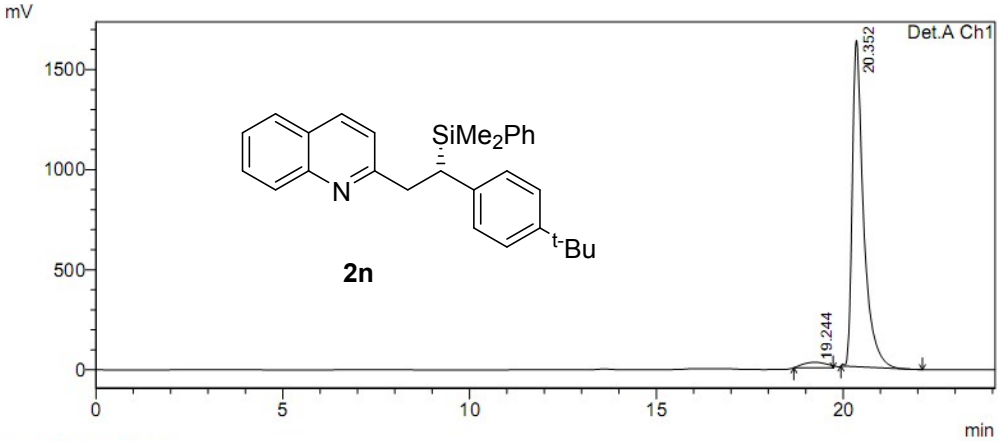


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.307	7212884	690110	49.209
2	19.125	7444908	172957	50.791
Total		14657791	863068	100.000

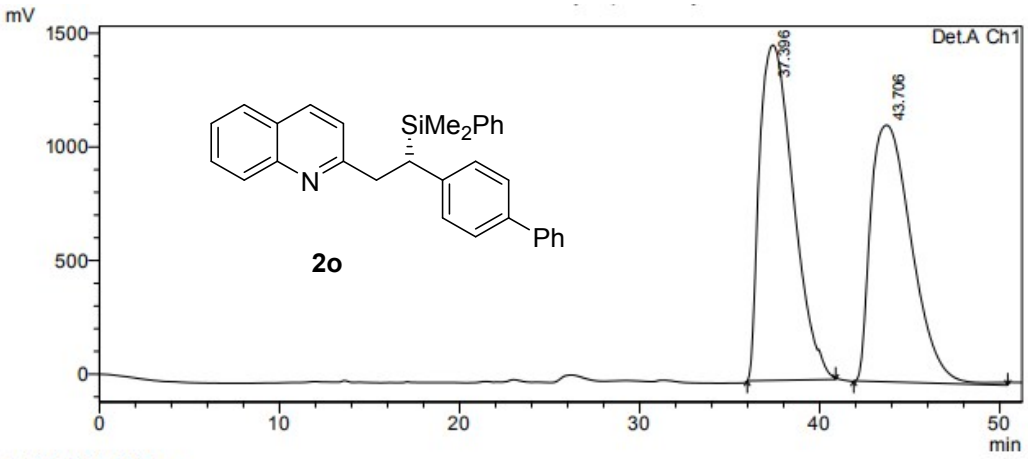


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.244	1235601	27809	3.483
2	20.352	34241174	1630819	96.517
Total		35476775	1658628	100.000

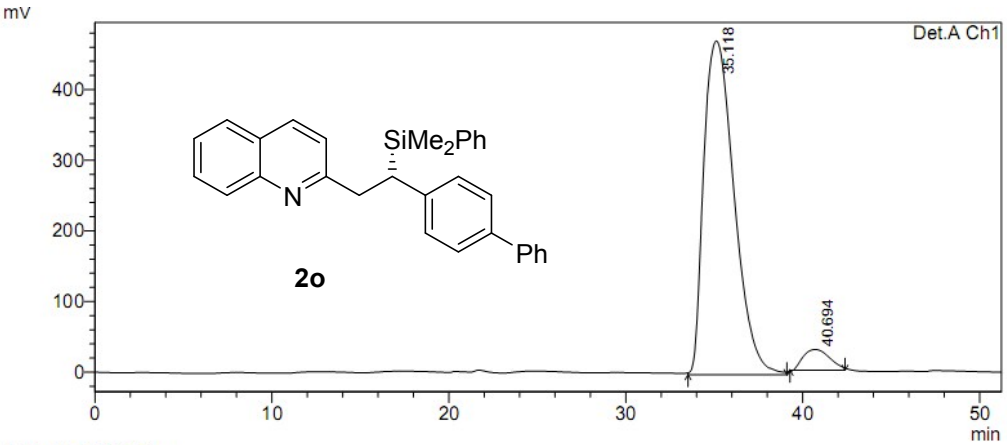


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	37.396	193184758	1476095	51.939
2	43.706	178759048	1129305	48.061
Total		371943806	2605400	100.000

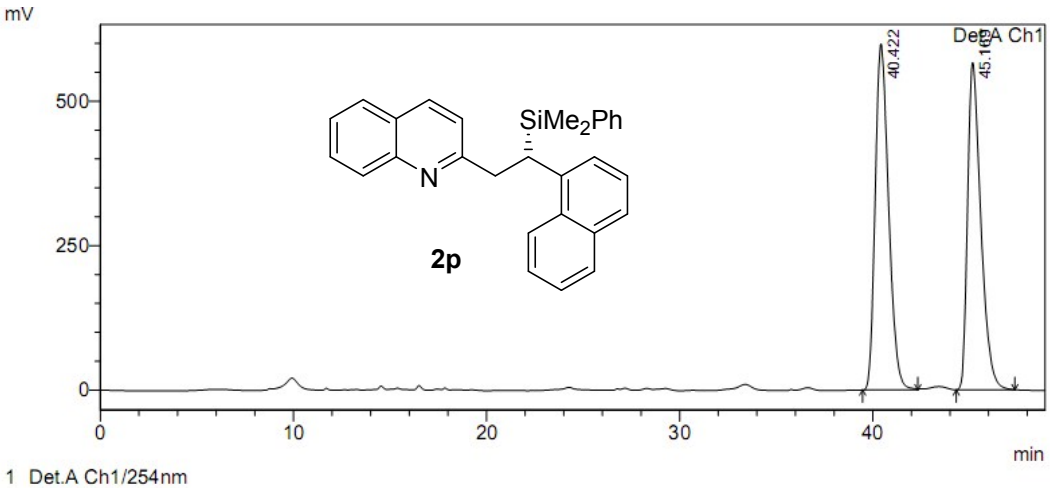


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	35.118	56541248	472309	94.872
2	40.694	3055902	29227	5.128
Total		59597149	501536	100.000

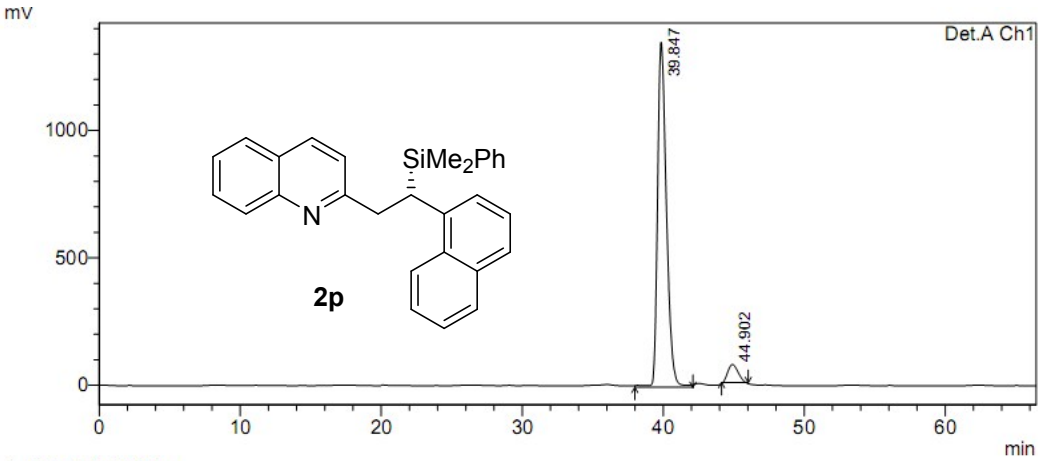


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	40.422	28820891	598481	51.709
2	45.169	26915935	566339	48.291
Total		55736826	1164820	100.000

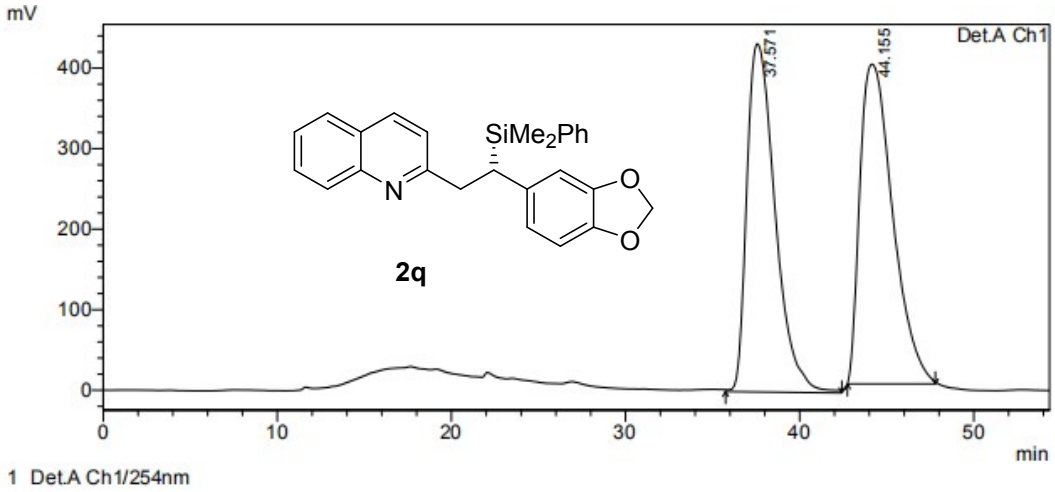


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	39.847	59324465	1354780	94.422
2	44.902	3504536	70741	5.578
Total		62829001	1425520	100.000

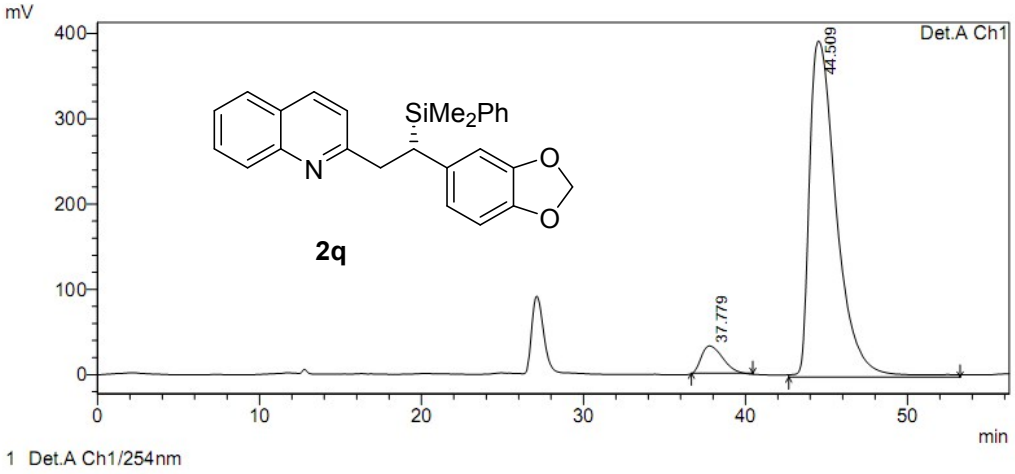


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	37.571	48903727	432270	48.446
2	44.155	52040054	396893	51.554
Total		100943780	829164	100.000

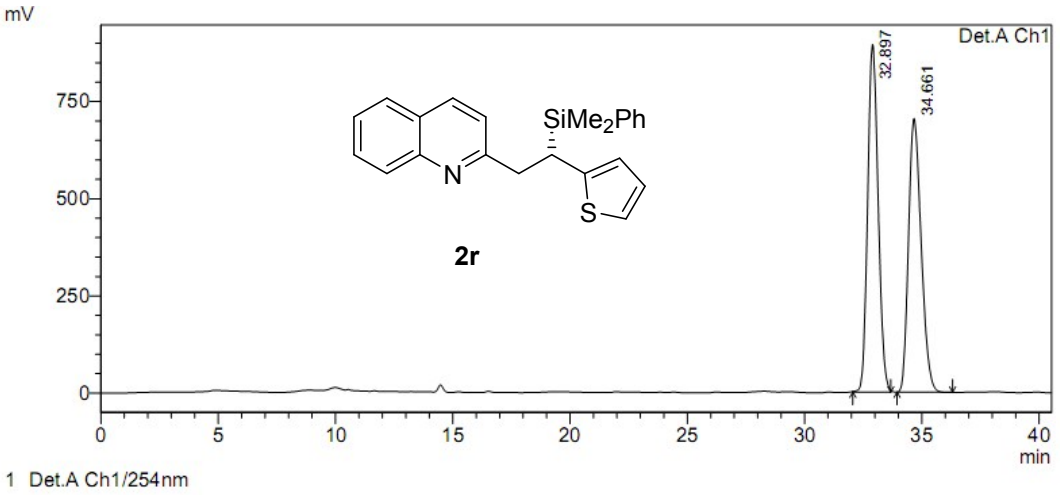


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	37.779	2885905	31954	5.929
2	44.509	45786610	393760	94.071
Total		48672515	425714	100.000

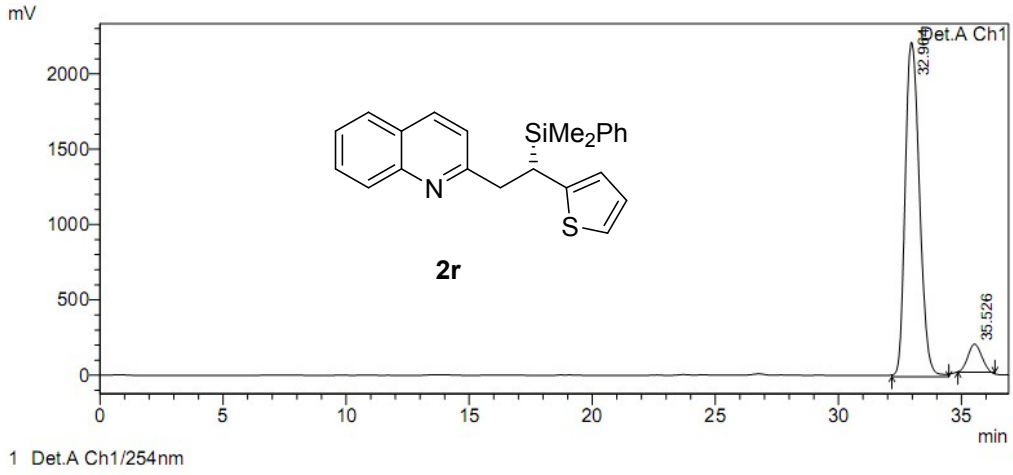


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	32.897	27817601	894501	51.417
2	34.661	26284382	703956	48.583
Total		54101982	1598457	100.000

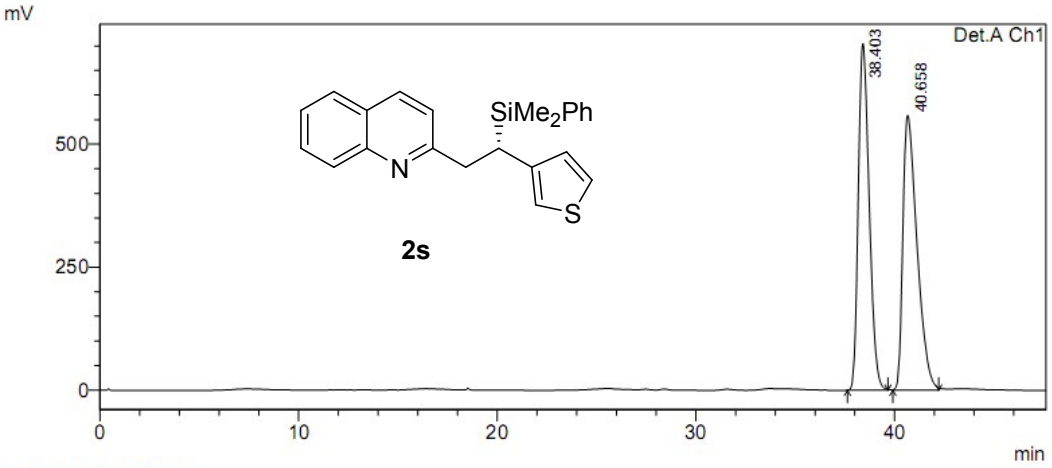


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	32.964	89784668	2219468	92.610
2	35.526	7164429	186933	7.390
Total		96949098	2406401	100.000

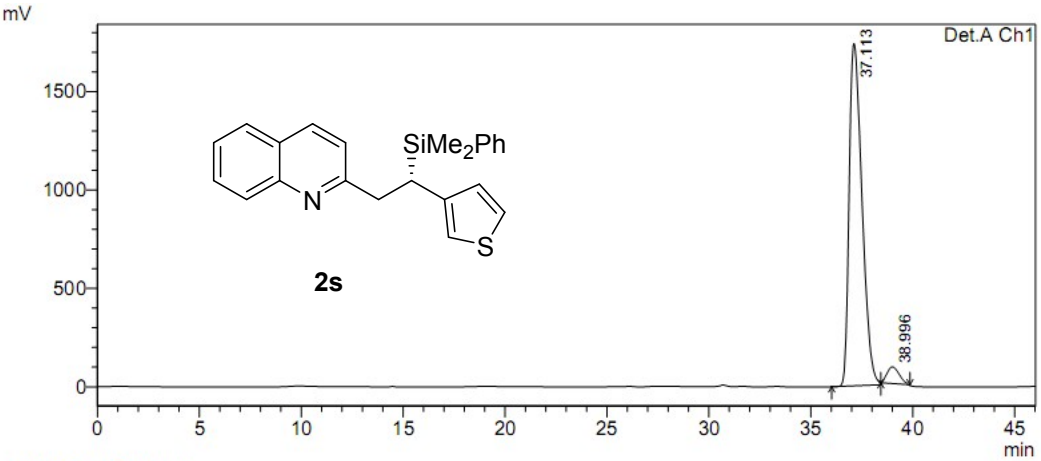


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	38.403	26846230	705175	49.218
2	40.658	27699436	558985	50.782
Total		54545665	1264160	100.000

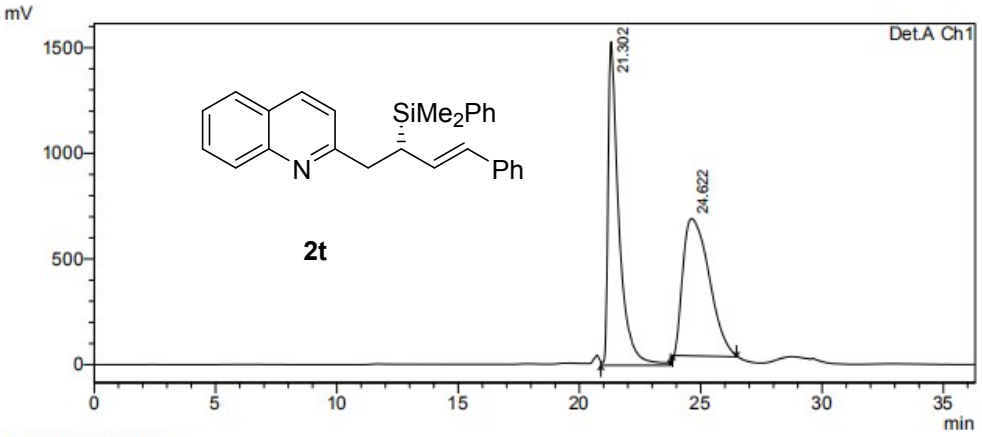


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	37.113	75813194	1739620	95.505
2	38.996	3567801	84862	4.495
Total		79380995	1824482	100.000

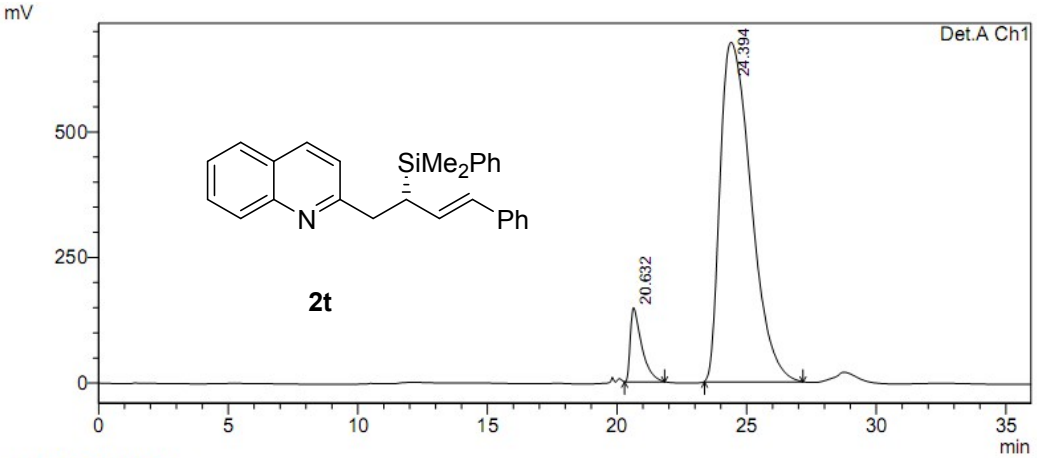


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.302	47464003	1531440	49.159
2	24.622	49087131	649286	50.841
Total		96551133	2180726	100.000

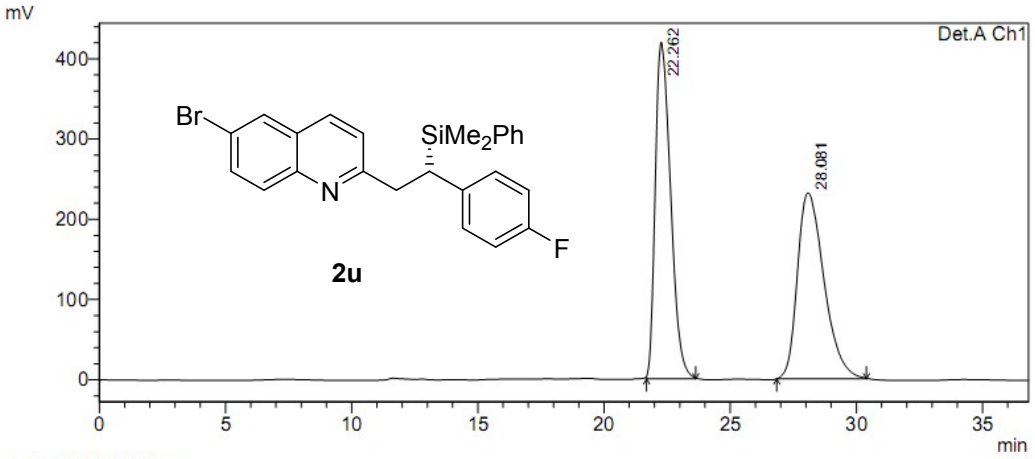


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.632	4555525	147946	7.485
2	24.394	56304119	676223	92.515
Total		60859644	824168	100.000

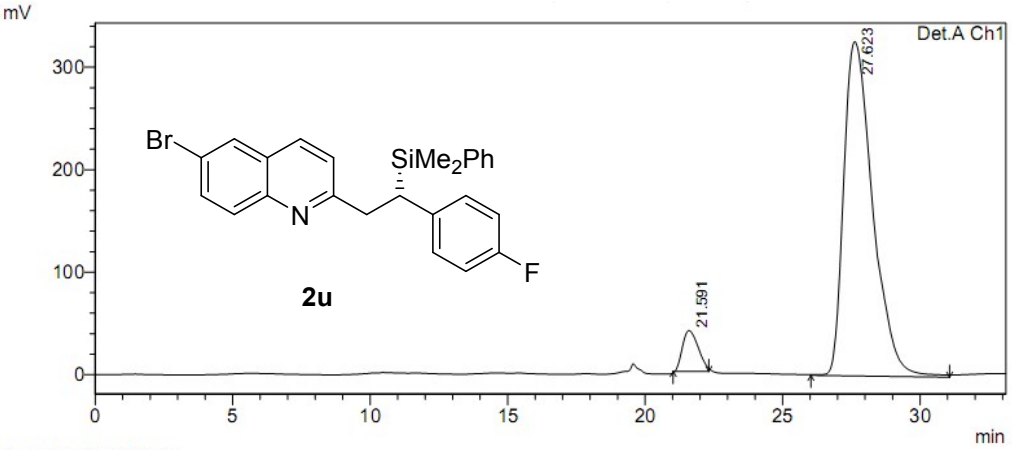


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.262	17773321	419650	51.040
2	28.081	17048700	231659	48.960
Total		34822021	651309	100.000

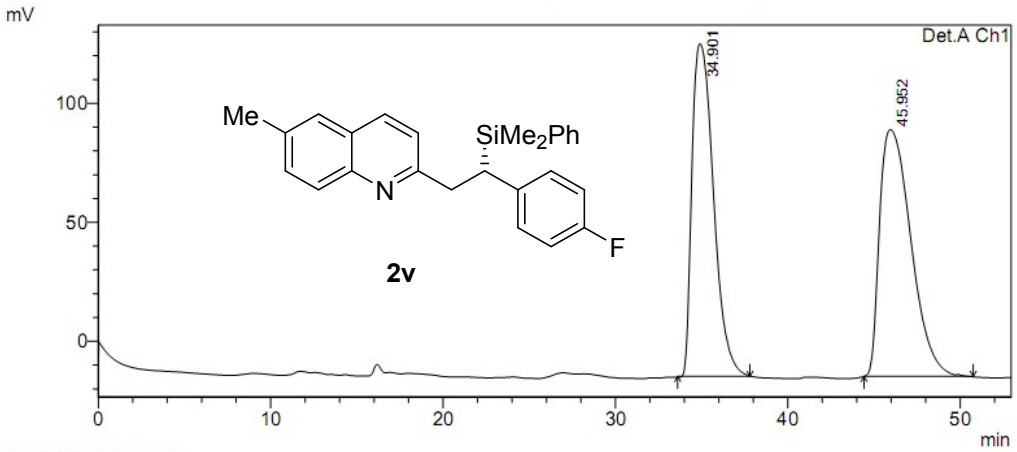


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.591	1598542	40020	6.260
2	27.623	23939143	326249	93.740
Total		25537684	366269	100.000

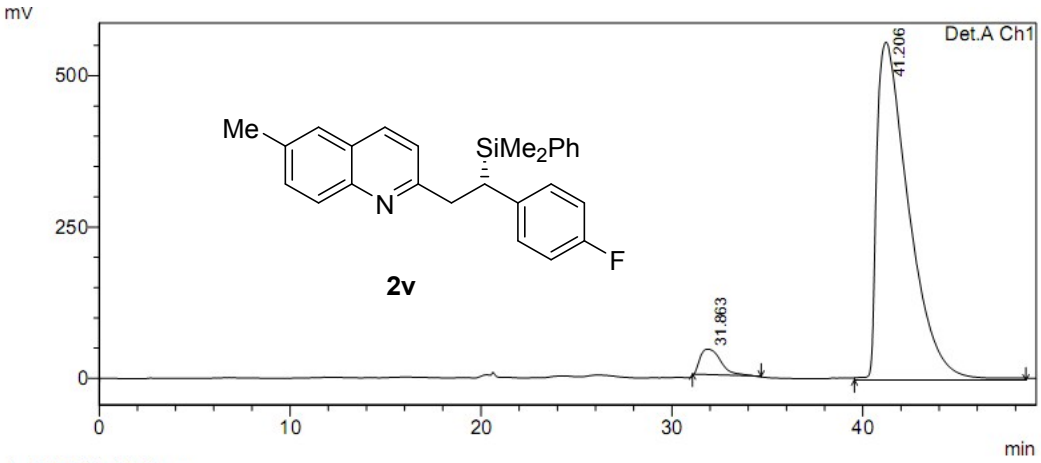


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	34.901	12145475	139796	48.081
2	45.952	13115209	103753	51.919
Total		25260684	243549	100.000

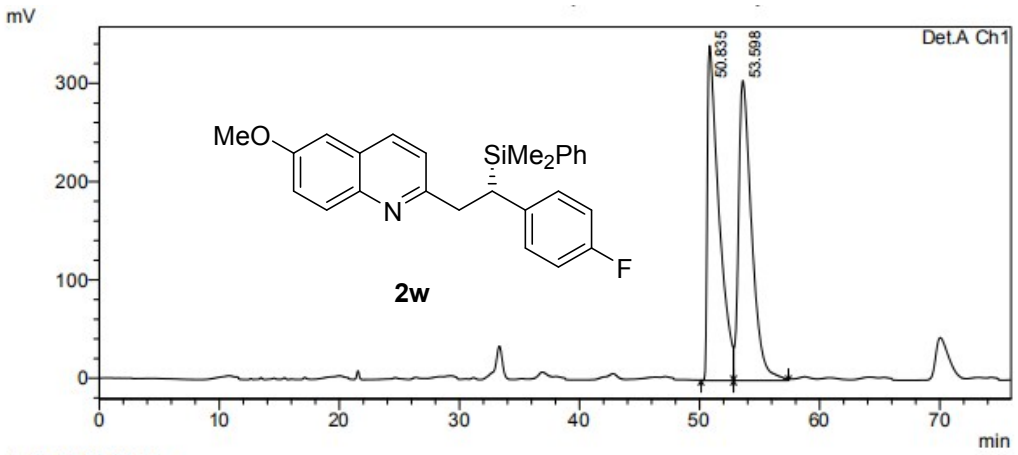


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	31.863	3104263	41798	4.554
2	41.206	65061523	558056	95.446
Total		68165786	599854	100.000

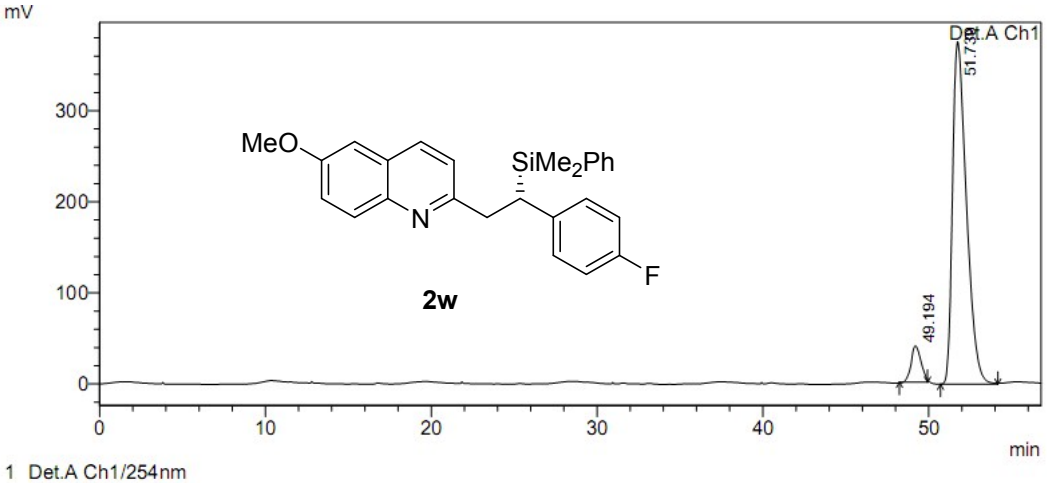


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	50.835	22861112	340645	49.670
2	53.598	23164945	305010	50.330
Total		46026057	645655	100.000

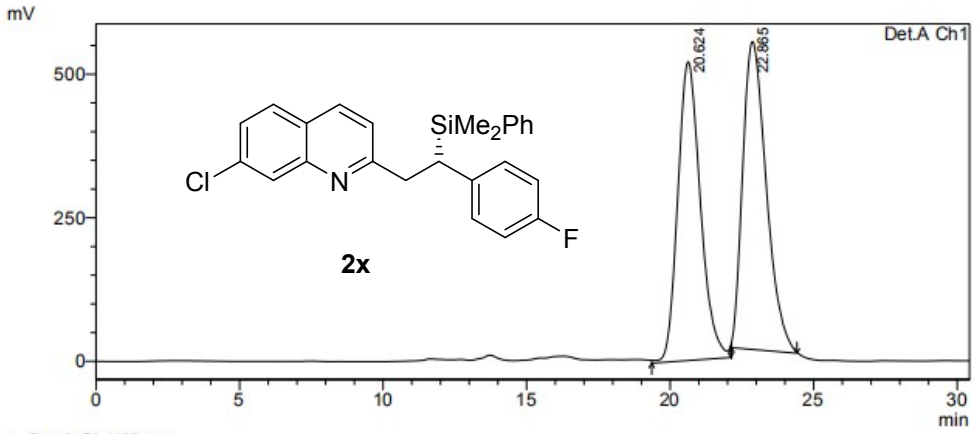


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	49.194	1647655	39950	6.989
2	51.739	21927003	376216	93.011
Total		23574659	416166	100.000

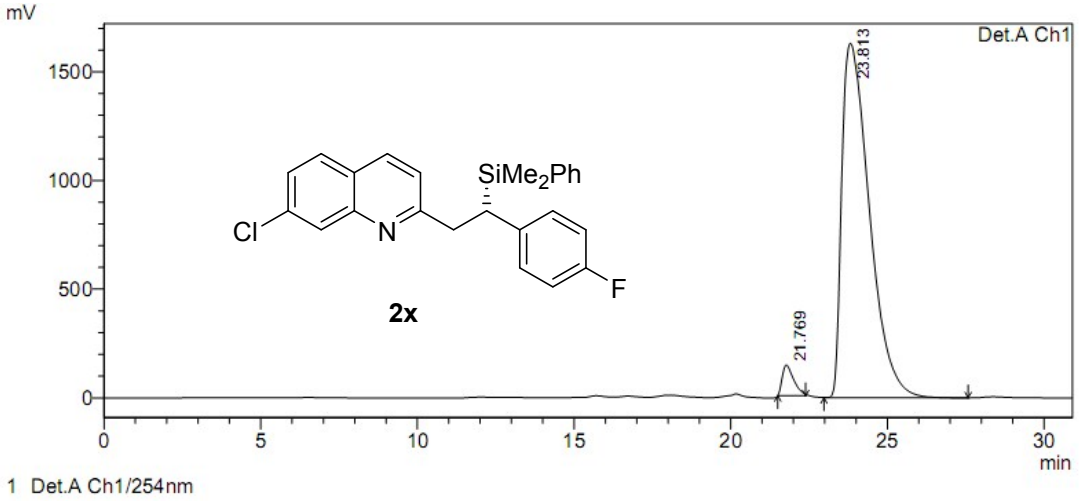


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	20.624	28568518	520066	48.310
2	22.865	30567128	535860	51.690
Total		59135646	1055926	100.000

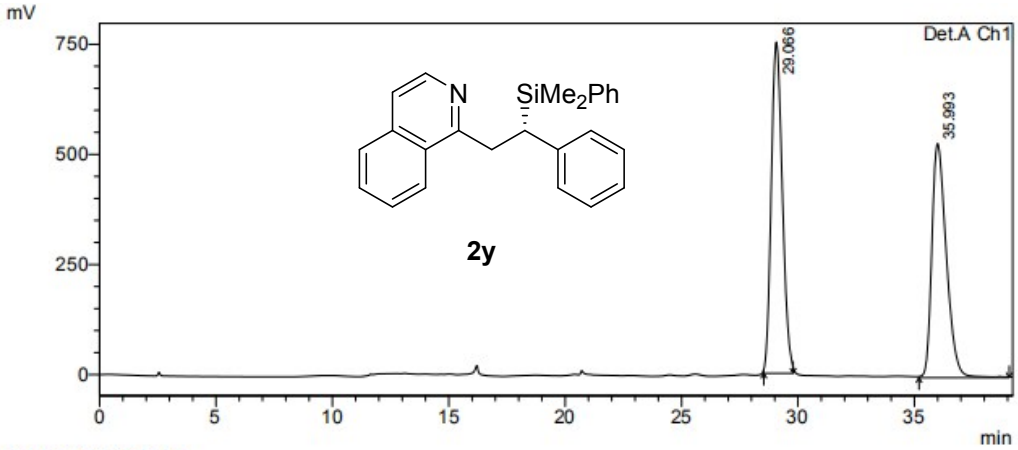


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.769	3564751	141682	3.447
2	23.813	99845652	1630303	96.553
Total		103410402	1771985	100.000

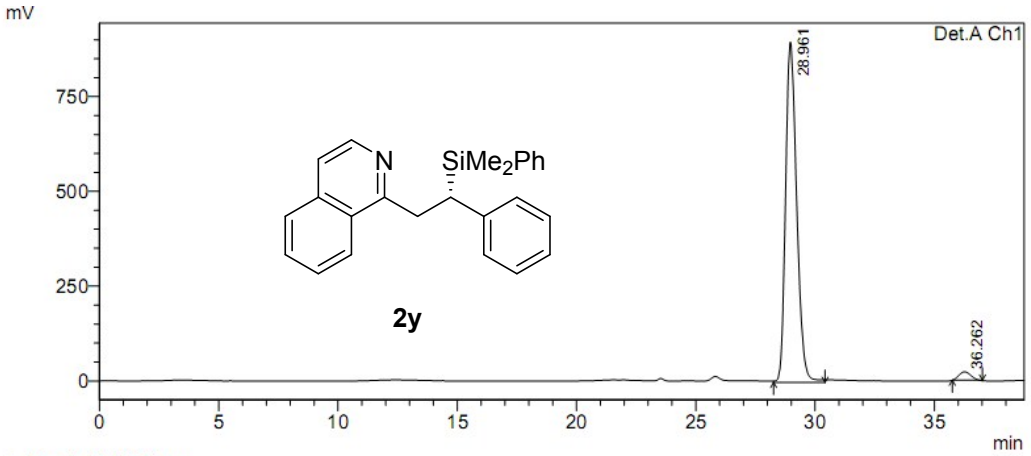


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	29.066	24837278	751856	51.853
2	35.993	23062028	531307	48.147
Total		47899306	1283163	100.000

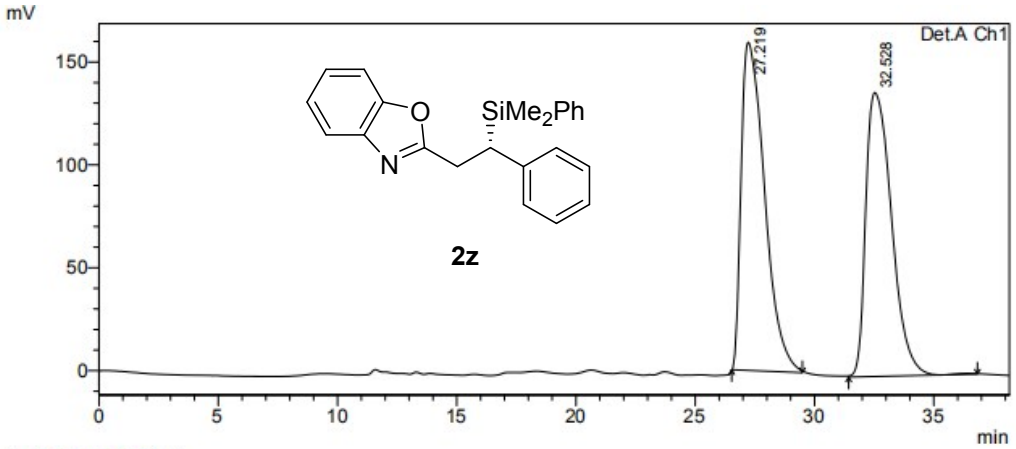


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	28.961	29033165	897762	97.585
2	36.262	718358	21642	2.415
Total		29751522	919404	100.000

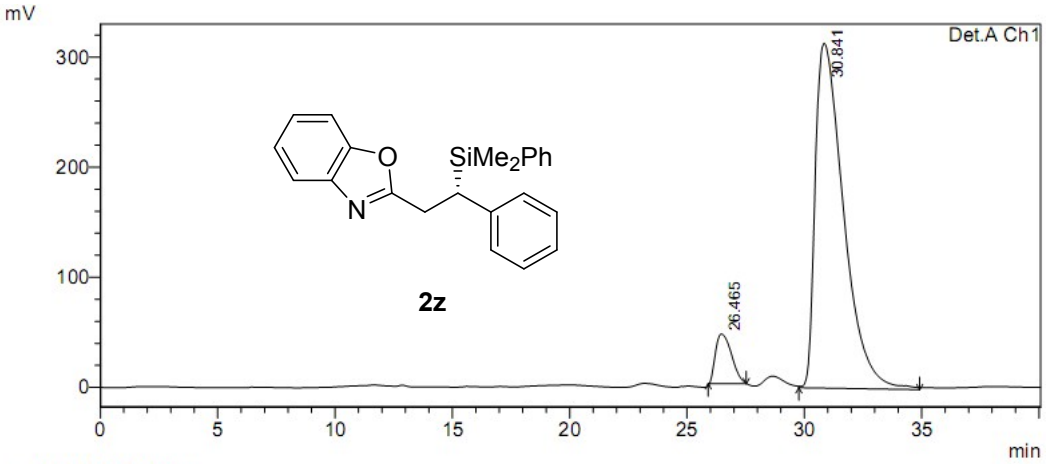


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	27.219	10898829	159452	51.159
2	32.528	10405175	137969	48.841
Total		21304004	297421	100.000

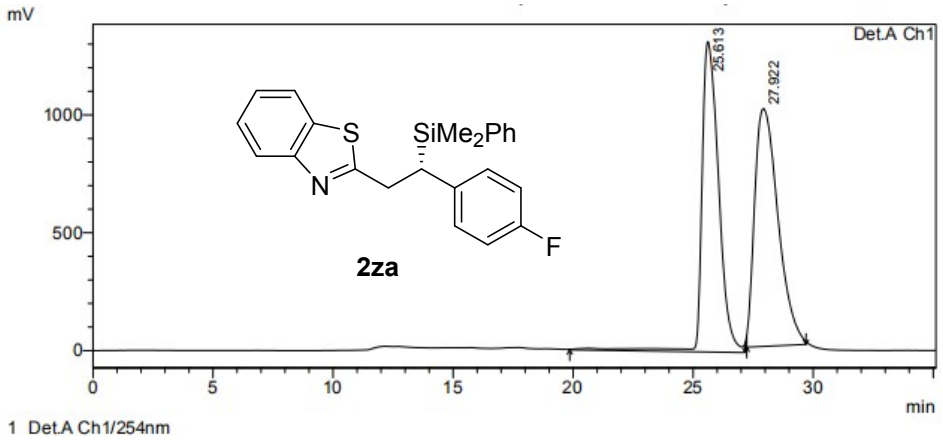


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	26.465	2153470	45214	7.565
2	30.841	26311905	313129	92.435
Total		28465376	358343	100.000

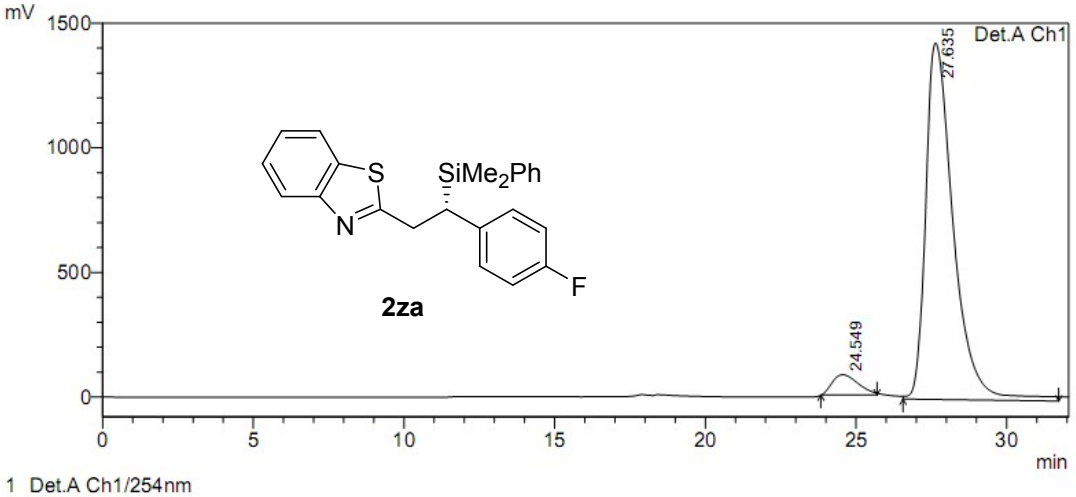


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.613	64434295	1317279	48.507
2	27.922	68401629	1009034	51.493
Total		132835924	2326313	100.000

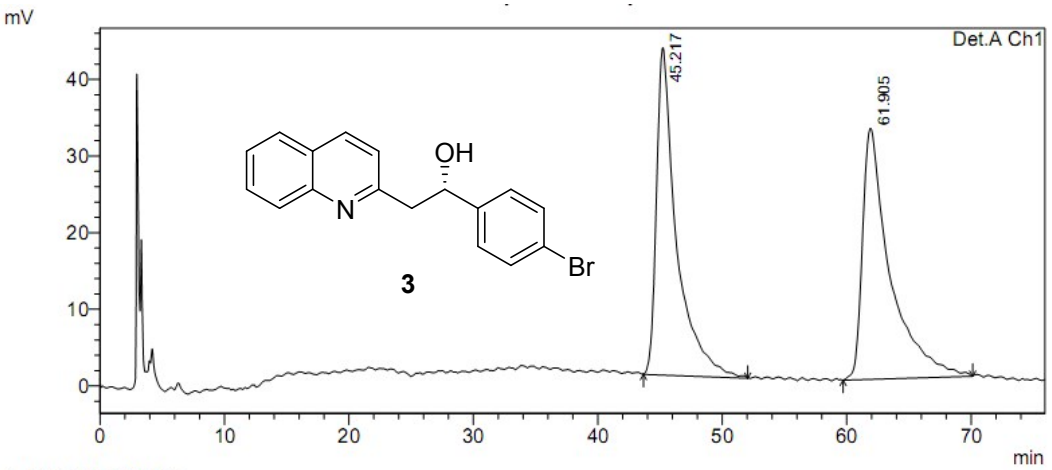


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	24.549	4914273	81452	5.121
2	27.635	91050645	1430197	94.879
Total		95964918	1511649	100.000

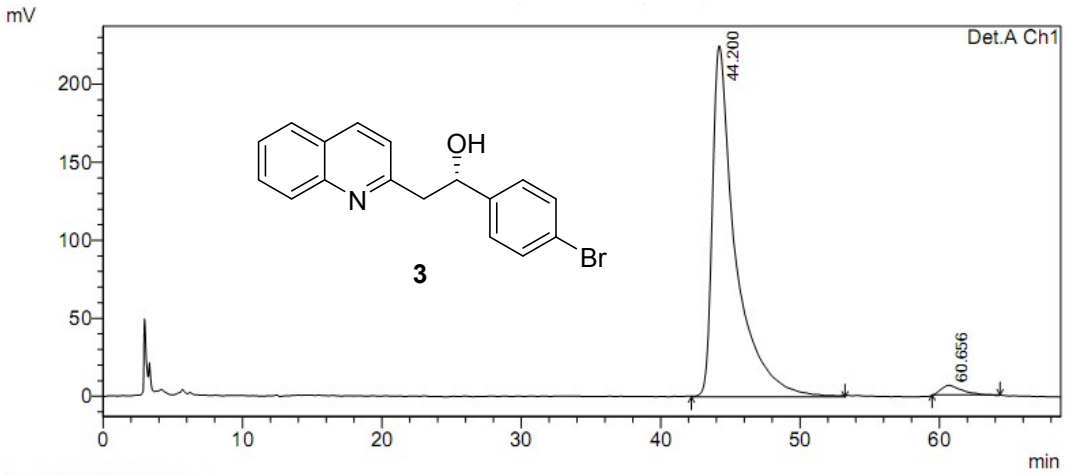


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	45.217	4756402	42748	48.509
2	61.905	5048878	32766	51.491
Total		9805280	75515	100.000

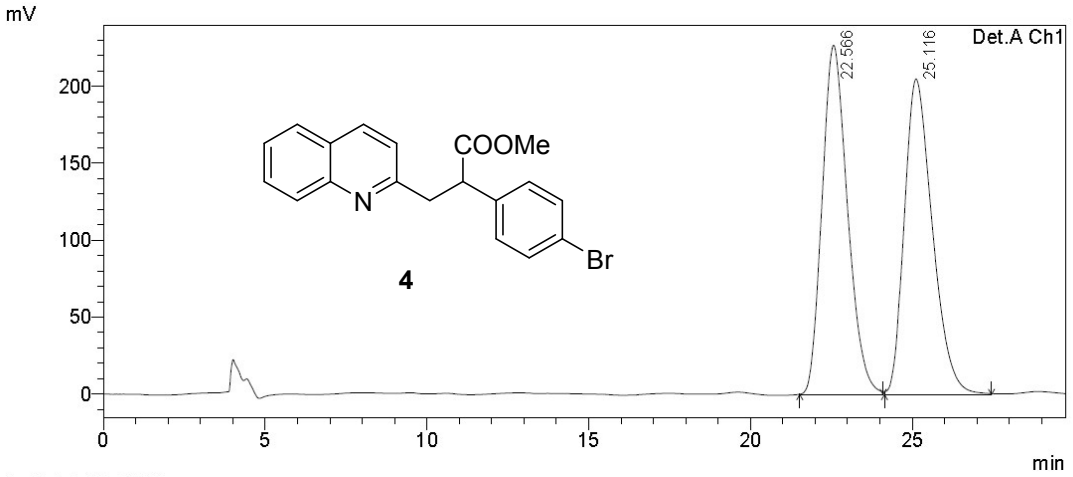


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	44.200	25869239	225164	97.682
2	60.656	613802	6094	2.318
Total		26483040	231258	100.000

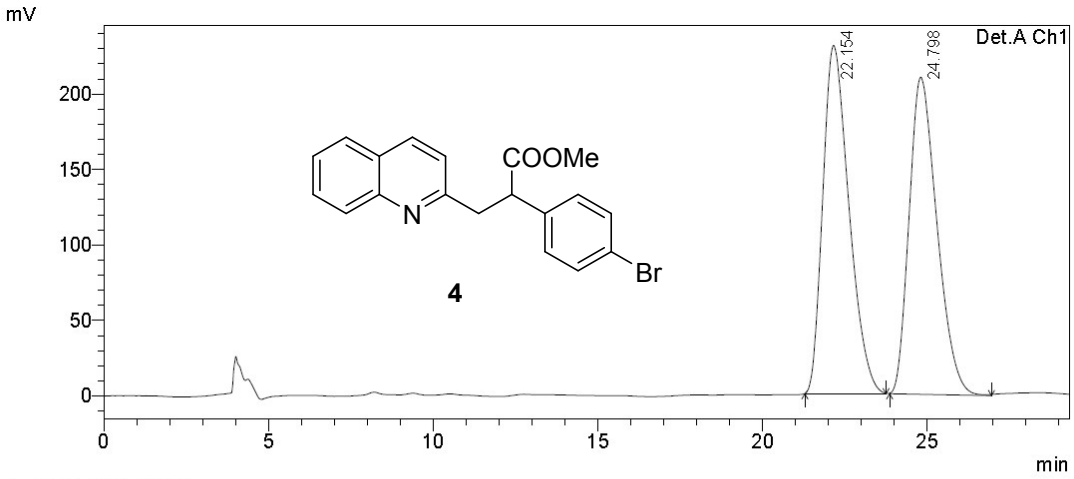


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.566	12433502	226993	50.115
2	25.116	12376592	205050	49.885
Total		24810094	432043	100.000



1 Det.A Ch1/254nm

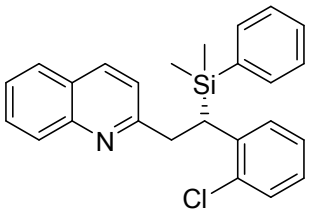
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	22.154	12766979	230776	50.834
2	24.798	12347870	210099	49.166
Total		25114849	440875	100.000

8. X-ray crystallographic data of (1b)

The structure of **1b** were determined by the X-ray diffraction analysis. CCDC 1955733 (**1b**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



1b

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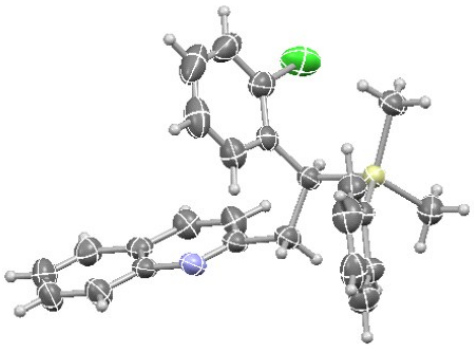

Table 1 Crystal data and structure refinement for **1b**.

Identification code	1ab
CCDC Deposit number	1955733
Empirical formula	$C_{25}H_{24}ClNSi$
Formula weight	402.01
Temperature (K)	293.15
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	a = 8.346(4)
Å	b = 9.916(4)
	c = 13.969(6)
(°)	α = 86.705(12)
	β = 77.173(11)
	γ = 71.341(14)
Volume/ Å^3	1067.8(8)
Z	2
ρ_{calc}g/cm^3	1.2502
μ /mm^{-1}	0.245
F(000)	424.6
Crystal size/mm^3	0.18 × 0.15 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.24 to 50.84

Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$
Reflections collected	44494
Goodness-of-fit on F^2	1.069
Independent reflections	3917 [R_{int} = 0.0463, R_{sigma} = 0.0209]
Data/restraints/parameters	3917/0/255
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1025
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.38