Supporting Information

Cp*Rh(III)-Catalysed Regioselective C(sp^3)-H Methylation of 8-Methylquinolines with Organoborons

Rakesh Kumar, Ritika Sharma, Rohit Kumar and Upendra Sharma*

Natural Product Chemistry and Process Development Division and AcSIR, CSIR-IHBT, Palampur, India
*upendra@ihbt.res.in; upendraihbt@gmail.com

Web address: http://www.ihbt.res.in/en/staff/scientificstaff?chronoform=sctdetail&task=detail&id=41

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1. General consideration

Reagent information. Unless otherwise stated, all reactions were carried out under air atmosphere in screw cap reaction vials. All solvents were bought from Aldrich in sure-seal bottle and used as such. All chemicals were bought from Sigma Aldrich, Alfa-aesar and TCI. For column chromatography, silica gel (230-400 mesh) from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

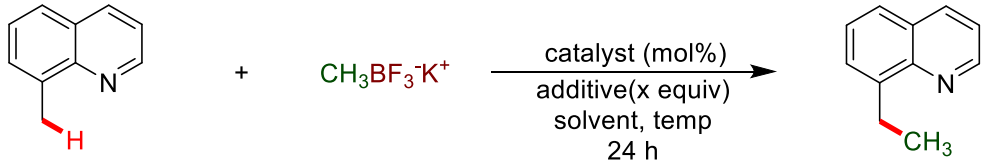
Analytical information. The melting points were recorded on a Bronsted Electro thermal 9100. All isolated compounds are characterized by ^{1}H NMR, ^{13}C NMR, LC-MS and IR. In addition, all the compounds are further characterized by HRMS. Mass spectra were recorded on Q-TOF-Micromass and maXis Impact mass spectrometers. Copies of ^{1}H, ^{13}C NMR are provided in this supporting information file. IR was analyzed by Shimadzu IR Prestige-21with ZnSe Single reflection ATR accessory. Nuclear magnetic resonance spectra were recorded either on a Bruker-Avance 600 or 300 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26) in the deuterated solvents. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.16) and all were obtained with ^{1}H decoupling. Optimization studies were done by NMR and NMR yield were calculated by using TCE as internal standard.

2. Preparation of substituted 8-methyl quinolines.

Substituted 8-methyl quinolines **1b** and **1c** were synthesized according to the literature procedure,[1] **1q** and **1r** were synthesized according to the literature procedure from corresponding 6-bromo-8-methylquinoline,[2] compound **1d**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1m**, **1n**, **1t** and **1u** were synthesized according to the literature procedure,[3] compound **1o** and **1p** were synthesized according to the literature procedure,[4] and all other substituted 8-methyl quinolines were used from commercially available sources.

3. Reaction of 8-methyl quinoline with potassium methyltrifluoroborate

3.1 Optimization study (Table S1)



1a **2a** **3a**

entry	catalyst (mol%)	additive (x equiv)	solvent (0.5 mL)	temp. (°C)	NMR yield (%)	conversion
1	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	AgF (3)	DME	100	45	70
2	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	AgF (3)	DME	50	37	57
3	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	-	DME	65	14	17
4	$[RhCp^*Cl_2]_2$ (5)	-	DME	100	Nd	-
5	-	AgF (3)	DME	100	Nd	-
6	$[CoCOCp^*I_2]$ (5)/$AgSbF_6$ (20)	AgF (3)	DME	100	Nd	-
7	$[RuCl_2(p\text{-cymene})]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	Nd	-
8	$[IrCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	Nd	-
9	$[RhCp^*Cl_2]_2$ (5)/$AgBF_4$ (20)	Ag_2CO_3 (2)	DME	100	Traces	-
10	$[RhCp^*Cl_2]_2$ (5)/$AgNTF_2$ (20)	Ag_2CO_3 (2)	DME	100	51	60
11	$[RhCp^*Cl_2]_2$ (5)/Xanthphos (20)	Ag_2CO_3 (2)	DME	100	Nd	-
12	$[RhCp^*Cl_2]_2$ (5)/Johnphos (20)	Ag_2CO_3 (2)	DME	100	Nd	-
13	$[RhCp^*Cl_2]_2$ (5)/bisphenylphosphinoethane (20)	Ag_2CO_3 (2)	DME	100	Nd	-
14	$[RhCp^*Cl_2]_2$ (5)/$AgCOCF_3$ (20)	Ag_2CO_3 (2)	DME	100	13	25
15	$[RhCp^*Cl_2]_2$ (5)/$AgCF_3SO_3$ (20)	Ag_2CO_3 (2)	DME	100	55	62
16	$[RhCp^*Cl_2]_2$ (5)/AgCl (20)	Ag_2CO_3 (2)	DME	100	Nd	-
17	$[RhCp^*Cl_2]_2$ (5)/AgBr (20)	Ag_2CO_3 (2)	DME	100	Nd	-
18	$[RhCp^*Cl_2]_2$ (5)/AgCN (20)	Ag_2CO_3 (2)	DME	100	Nd	-
19	$[RhCp^*Cl_2]_2$ (5)/$AgClO_4$ (20)	Ag_2CO_3 (2)	DME	100	44	-
20	$[RhCp^*Cl_2]_2$ (5)/$AgCO_2Bz$ (20)	Ag_2CO_3 (2)	DME	100	Nd	-
21	$[RhCp^*Cl_2]_2$ (5)/$AgCO_2C_3F_7$ (20)	Ag_2CO_3 (2)	DME	100	Nd	-
22	$[RhCp^*Cl_2]_2$ (5)/$AgNO_2$(20)	Ag_2CO_3 (2)	DME	100	Nd	-
23	$[RhCp^*Cl_2]_2$ (5)/$AgNO_3$(20)	Ag_2CO_3 (2)	DME	100	Nd	-
24	$[RhCp^*Cl_2]_2$ (5)/AgI (20)	Ag_2CO_3 (2)	DME	100	Nd	-
25	$[RhCp^*Cl_2]_2$ (5)/Ag_3PO_4 (20)	Ag_2CO_3 (2)	DME	100	Nd	-
26	**$[RhCp^*Cl_2]_2$ (10)/$AgSbF_6$ (40)**	**Ag_2CO_3 (2)**	**DME**	**100**	**69**	**72**
27	$[RhCp^*Cl_2]_2$ (15)/$AgSbF_6$ (60)	Ag_2CO_3 (2)	DME	100	64	68
28	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (1)	DME	100	52	55
29	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	Ag_2CO_3 (3)	DME	100	57	60
30[a]	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	60	62
31[b]	**$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)**	**Ag_2CO_3 (2)**	**DME**	**100**	**66**	**70**
32[c]	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	50	52

33	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2O (2)	DME	100	50	50
34	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	MnO_2 (2)	DME	100	30	35
35	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	$AgBF_4$ (2)	DME	100	20	50
36	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	$CuOAc.H_2O$ (2)	DME	100	25	30
37	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	NaOAc (2)	DME	100	traces	-
38	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	K_2CO_3 (2)	DME	100	Nd	-
39	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	O_2	DME	100	traces	-
40	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2O (1)	DME	100	43	53
41	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	62	70
42	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	$K_2S_2O_8$ (2)	DME	100	Nd	-
43	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	$AgClO_4$ (2)	DME	100	30	43
44	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	$AgCF_3SO_3$ (2)	DME	100	40	50
45	$[RhCp^*Cl_2]_2$ (5)	$AgSbF_6$ (2)	DME	100	52	60
46	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	tetrabutyl ammonium iodide (2)	DME	100	Nd	-
47	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	tetrabutyl ammonium bromide (2)	DME	100	Nd	-
48	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	tetrabutyl ammonium chloride (2)	DME	100	Nd	-
49	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	sod. tert butoxide (2)	DME	100	Nd	-
50	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	pot. tert butoxide (2)	DME	100	Nd	-
51	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	benzoquinone (2)	DME	100	nd	-
52	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	-	DME	100	38	40
53[b]	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	50	52
54[a]	$[RhCp^*Cl_2]_2$ (10), $AgSbF_6$ (40)	Ag_2CO_3 (2)	DME	100	67	-
55[b]	$[RhCp^*Cl_2]_2$ (10), $AgSbF_6$ (40)	Ag_2CO_3 (2)	DME	100	65	-
56	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DMSO	100	Nd	-
57	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DCE	100	30	33
58	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DMF	100	31	35
59	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DMA	100	25	30
60	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	ACN	100	12	15
61	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	EtOH	100	53	55
62	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	H_2O	100	40	42
63	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	Ag_2CO_3 (2)	MeOH	100	37	40
64	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	acetone	100	48	50
65	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	$CHCl_3$	100	35	40
66	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	50	52
67	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	Ag_2CO_3 (2)	EtOAc	100	53	55
68	$[RhCp^*Cl_2]_2$ (10), $AgSbF_6$ (40)	Ag_2CO_3 (2)	TFE	100	12	18
69	$[RhCp^*Cl_2]_2$ (10), $AgSbF_6$ (40)	Ag_2CO_3 (2)	toulene	100	34	40
70	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	Ag_2CO_3 (2)	THF	100	58	60

71	$[RhCp^*Cl_2]_2$ (5), $AgSbF_6$ (20)	Ag_2CO_3 (2)	1,4-dioxane	100	35	40
72[d]	$[RhCp^*Cl_2]_2$ (5)/$AgSbF_6$ (20)	Ag_2CO_3 (2)	DME	100	61	70

[a]Reaction time 36 h. [b]reaction time 48 h. [c]reaction time 72 h. [d]**2a** (4 equiv). Nd: not detected.

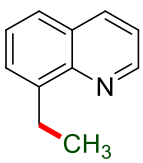
3.2 General procedure for the methylation of 8-methyl quinolines with potassium methyl trifluoroborate

To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.3 mmol), potassium methyl trifluoroborate (0.9 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2.0 equiv) and dimethoxyethane (1.5 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 48 h. Solvent was evaporated under reduced pressure, and the crude mixture was purified by flash chromatography using silica gel (230−400 mesh size) and *n*-hexane: EtOAc as the eluent.

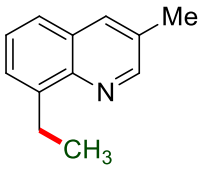
3.3 General procedure for 1.0 mmol scale reaction

To an oven-dried 20 ml schlenk tube charged with a spin vane magnetic stir-bar, 7-methoxy-8-methylquinoline (1.0 mmol), potassium methyltrifluoroborate (3 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol%), Ag_2CO_3 (2.0 equiv) and dimethoxyethane (5.0 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 48 h. Solvent was evaporated under reduced pressure, and the crude mixture was purified by flash chromatography using silica gel (230−400 mesh size) and *n*-hexane: EtOAc (5:95) as the eluent provided product (**3h**) in 63% (117.9 mg) isolated yield.

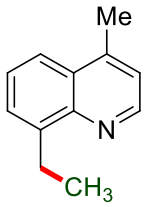
3.4 Characterization data.



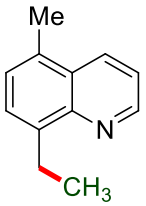
*8-ethylquinoline (Scheme 2, Entry **3a**)*.[5] Colourless liquid, yield = 28.8 mg (61%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.94 – 8.95 (m, 1H), 8.15 (dd, J = 7.8 Hz, 1H), 7.67 (dd, J = 7.8 Hz, 1H), 7.58 (dd, J = 7.2 Hz, 1H), 7.46 – 7.48 (m, 1H), 7.36 – 7.38 (m, 1H), 3.31 – 3.34 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 149.3, 146.9, 143.0, 136.5, 128.5, 128.0, 126.5, 125.9, 120.9, 24.7, 15.1. IR (ZnSe) ν_{max} (cm^{-1}): 2953, 2924, 2853, 1742, 1462, 1377, 1283, 1244, 1163, 1098, 1034, 802. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{12}N$, 158.0964; found 158.0964.



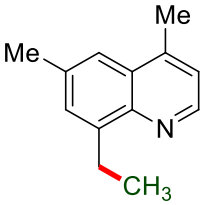
*8-ethyl-3-methylquinoline (Scheme 2, Entry **3b**)*. Yellow liquid, yield = 20.0 mg (39%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.79 (d, J = 2.4 Hz, 1H), 7.89 (d, J = 2.4 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.41– 7.51 (m, 2H), 3.30 (q, J = 7.5 Hz, 2H), 2.51 (s, 3H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 151.4, 145.2, 142.9, 135.2, 130.2, 128.4, 127.1, 126.6, 125.3, 24.7, 18.8, 15.2. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2926, 2870, 1605, 1489, 1452, 1366, 1337, 1234, 1159, 1059, 970, 881, 764, 704. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}N$, 172.1121; found 172.1120.



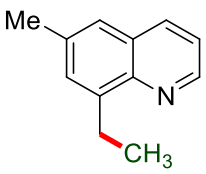
*8-ethyl-4-methylquinoline (Scheme 2, Entry **3c**)*.[6] Colourless liquid, yield = 20.5 mg (40%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.80 (d, J = 4.5 Hz, 1H), 7.86 (dd, J = 8.1, 1.5 Hz, 1H), 7.57 (d, J = 6.6 Hz, 1H), 7.47 – 7.52 (m, 1H), 7.22 (d, J = 4.2 Hz, 1H), 3.32 (q, J = 7.5 Hz, 2H), 2.70 (s, 3H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 149.0, 146.6, 144.5, 143.6, 128.5, 127.8, 126.2, 121.8, 25.1, 19.2, 15.3. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2924, 2870, 2326, 1597, 1574, 1508, 1452, 1439, 1406, 1395, 1308, 1103, 835, 810, 758. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}N$, 172.1121; found 172.1126.



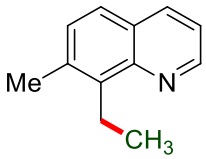
*8-ethyl-5-methylquinoline (Scheme 2, Entry **3d**)*. Colourless liquid, yield = 20.0 mg (39%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.31 (dd, J = 8.4, 1.2 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.41 (dd, J = 8.4, 4.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 3.26 – 3.30 (m, 2H), 2.65 (s, 3H), 1.37 – 1.40 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 148.8, 147.1, 141.0, 132.8, 132.3, 127.8, 127.6, 127.0, 120.5, 24.7, 18.7, 15.2. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2924, 2868, 2336, 1599, 1503, 1452, 1356, 1152, 1069, 1030, 970, 835, 785, 683. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}N$, 172.1121; found 172.1129.



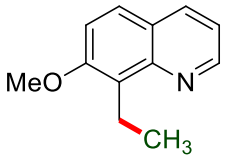
*8-ethyl-4,6-dimethylquinoline (Scheme 2, Entry **3e**)*. Colourless liquid, yield = 26.7 mg (48%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.73 (d, J = 4.5 Hz, 1H), 7.61 (s, 1H), 7.40 (s, 1H), 7.17 (d, J = 4.2 Hz, 1H), 3.28 (q, J = 7.5 Hz, 2H), 2.66 (s, 3H), 2.54 (s, 3H), 1.38 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 148.1, 145.2, 143.7, 143.2, 135.8, 130.0, 128.5, 121.8, 120.8, 25.0, 22.1, 19.1, 15.3. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2922, 2326, 1595, 1501, 1437, 1375, 854, 829, 517. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{13}H_{16}N$, 186.1277; found 186.1279.



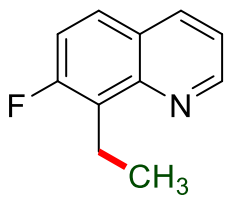
*8-ethyl-6-methylquinoline (Scheme 2, Entry **3f**).* Yellow liquid, yield = 23.6 mg (46%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.87 (dd, J = 4.2, 1.8 Hz, 1H), 8.03 (dd, J = 8.1, 1.8 Hz, 1H), 7.41 (s, 2H), 7.34 (dd, J = 8.4, 4.2 Hz, 1H), 3.28 (q, J = 7.5 Hz, 2H), 2.51 (s, 3H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 148.5, 145.5, 142.7, 136.2, 135.8, 130.4, 128.7, 124.7, 120.9, 24.6, 21.8, 15.2. IR (ZnSe) ν_{max} (cm^{-1}): 2961, 2924, 2855, 1726, 1609, 1493, 1454, 1369, 1260, 1036, 860, 808, 783. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}N$, 172.1121; found 172.1128.



*8-ethyl-7-methylquinoline (Scheme 2, Entry **3g**).* Colourless liquid, yield = 34.4 mg (67%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.92 (dd, J = 4.2, 1.8 Hz, 1H), 8.08 (dd, J = 7.8, 1.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.32 (dd, J = 7.8, 4.2 Hz, 1H), 3.32 – 3.36 (m, 2H), 2.55 (s, 3H), 1.25 – 1.28 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 149.4, 146.8, 140.3, 136.4, 136.2, 130.0, 126.9, 125.1, 120.0, 20.8, 20.0, 14.5. IR (ZnSe) ν_{max} (cm^{-1}): 3426, 2926, 1726, 1503, 1462, 1362, 1096, 1084, 1055, 1038, 831, 800, 478, 432. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}N$, 172.1121; found 172.1124.

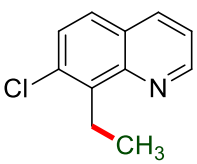


*8-ethyl-7-methoxyquinoline (Scheme 2, Entry **3h**).* Reaction time 60 h. Yellow liquid, yield = 41.0 mg (73%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.91 (dd, J = 4.2, 1.8 Hz, 1H), 8.06 (dd, J = 7.8, 1.8 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.24 (dd, J = 7.8, 4.2 Hz, 1H), 3.98 (s, 3H), 3.29 – 3.33 (m, 2H), 1.25 – 1.27 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 157.1, 150.2, 147.4, 136.3, 128.4, 126.5, 123.8, 118.7, 114.0, 56.6, 17.7, 14.6. IR (ZnSe) ν_{max} (cm^{-1}): 2967, 2932, 2870, 1603, 1589, 1487, 1456, 1443, 1422, 1369, 1312, 1234, 1175, 1123, 1086, 1059, 1028, 955, 847, 829, 795, 775, 696, 664, 640, 596, 584, 557, 550, 534, 500, 467, 453, 426. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{12}H_{14}NO$, 188.1070; found 188.1073.

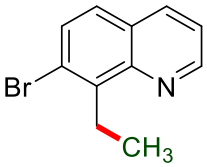


*8-ethyl-7-fluoroquinoline (Scheme 2, Entry **3i**).* Reaction time 60 h. Colourless liquid, yield = 27.9 mg (53%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.12 (dd, J = 8.4, 1.8 Hz, 1H), 7.64 (dd, J = 9.0, 6.0 Hz, 1H), 7.36 (dd, J = 8.4, 4.2 Hz, 1H), 7.31 (t, J = 9.0 Hz, 1H), 3.28 – 3.32 (m, 2H), 1.31 – 1.33 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 160.59 (d, J_{CF} = 244.5 Hz).150.3,

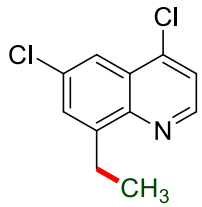
147.68 (d, J_{CF} = 10.5 Hz), 136.5, 127.25 (d, J_{CF} = 15.4 Hz), 126.95 (d, J = 10.5 Hz), 125.6, 120.08 (d, J_{CF} = 1.5 Hz), 117.08 (d, J_{CF} = 27.0 Hz) 17.23 (d, J = 3.0 Hz), 14.8. ^{19}F NMR (565 MHz, $CDCl_3$, δ): -114.09. IR (ZnSe) ν_{max} (cm^{-1}): 2941, 2926, 2832, 1423, 1101, 1022, 962, 939, 835, 800, 687, 592, 565, 550, 527, 490, 453, 430, 401. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{11}FN$, 176.0870; found 176.0871.



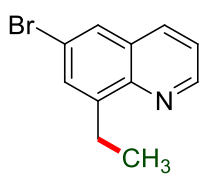
*7-chloro-8-ethylquinoline (Scheme 2, Entry **3j**).* Colourless liquid, yield = 32.2 mg (56%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.96 (dd, J = 4.2, 1.8 Hz, 1H), 8.11 (dd, J = 8.4, 1.8 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 8.4, 4.2 Hz, 1H), 3.45 – 3.48 (m, 2H), 1.29 – 1.31 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 150.3, 147.3, 140.5, 136.4, 134.3, 128.4, 127.2, 126.5, 121.0, 22.0, 13.9. IR (ZnSe) ν_{max} (cm^{-1}): 2968, 2932, 2872, 2326, 1607, 1587, 1489, 1458, 1373, 1362, 1314, 1125, 1088, 1061, 1042, 955, 870, 829, 799, 625, 471. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{11}ClN$, 192.0575; found 192.0579.



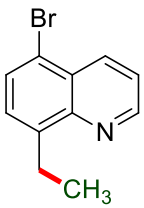
*7-bromo-8-ethylquinoline (Scheme 2, Entry **3k**).* Colourless liquid, yield = 65.2 mg (92%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.94 (dd, J = 4.2, 1.8 Hz, 1H), 8.09 (dd, J = 8.2, 1.8 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.40 (dd, J = 7.8, 4.2 Hz, 1H), 3.47 – 3.51 (m, 2H), 1.28 – 1.31 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 150.2, 147.2, 142.6, 136.4, 131.2, 127.6, 126.7, 125.1, 121.1, 24.9, 13.9. IR (ZnSe) ν_{max} (cm^{-1}): 2961, 2932, 2870, 2837, 1611, 1595, 1570, 1501, 1460, 1427, 1360, 1317, 1260, 1234, 1171, 1138, 1107, 1084, 1055, 1032, 957, 908, 826, 799, 772, 692, 677, 573, 550, 490, 430. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{11}BrN$, 236.0069; found 236.0066.



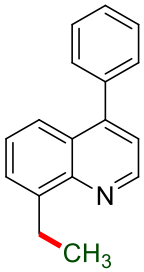
*4,6-dichloro-8-ethylquinoline (Scheme 2, Entry **3l**).* White solid, yield = 31.1 mg (46%). Mp = 49–51°C. Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.76 (d, J = 4.8 Hz, 1H), 8.07 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 4.2 Hz, 1H), 3.25 – 3.29 (m, 2H), 1.35 – 1.38 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ): 148.8, 146.3, 146.0, 141.9, 133.7, 129.9, 127.5, 121.9, 121.0, 24.9, 14.9. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2926, 2851, 2326, 1580, 1474, 1364, 1321, 1285, 1190, 1119, 1092, 1063, 1038, 959, 862, 837, 800, 758, 685, 637, 521, 419. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{10}Cl_2N$, 226.0185; found 226.0181.



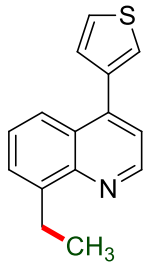
*6-bromo-8-ethylquinoline (Scheme 2, Entry **3m**)*. Colourless liquid, yield = 36.8 mg (52%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.93 (dd, J = 4.2, 1.8 Hz, 1H), 8.04 (dd, J = 8.4, 1.8 Hz, 1H), 7.82 (d, J = 1.8 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.40 (dd, J = 8.4, 4.2 Hz, 1H), 3.26 – 3.30 (m, 2H), 1.37 – 1.39 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, CDCl3, δ): 149.6, 145.6, 145.5, 135.5, 131.4, 129.7, 127.8, 121.8, 120.6, 24.5, 14.9. IR (ZnSe) ν_{max} (cm^{-1}): 2965, 2928, 1726, 1589, 1570, 1487, 1454, 1360, 1314, 1190, 1134, 1030, 959, 860, 839, 806, 781, 758, 714, 596, 586, 505, 461. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{11}BrN$, 236.0069; found 236.0064.



5-bromo-8-ethylquinoline *(Scheme 2, Entry **3n**)*. Colourless liquid, yield = 29.7 mg (42%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.94 – 8.96 (m, 1H), 8.52 – 8.55 (m, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.49 (dd, J = 8.7, 4.2 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 3.23 – 3.30 (m, 2H), 1.37 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 149.9, 147.6, 143.4, 135.9, 130.3, 128.4, 127.7, 122.1, 119.4, 24.7, 15.0. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2928, 2870, 2336, 1589, 1564, 1491, 1460, 1379, 1348, 1148, 1038, 1018, 957, 895, 831, 787, 752, 617, 488. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{11}BrN$, 236.0069; found 236.0062.

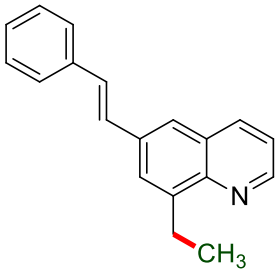


*8-ethyl-4-phenylquinoline (Scheme 2, Entry **3o**)*. Colourless liquid, yield = 39.2 mg (56%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.97 (d, J = 4.5 Hz, 1H), 7.76 (dd, J = 8.4, 1.5 Hz, 1H), 7.59 (d, J = 6.9 Hz, 1H), 7.40 – 7.52 (m, 6H), 7.33 (d, J = 4.5 Hz, 1H), 3.33 – 3.41 (m, 2H), 1.44 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 148.9, 148.8, 147.3, 143.3, 138.7, 129.7, 128.6, 128.4, 128.0, 127.0, 126.5, 124.0, 121.3, 25.2, 15.3. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2928, 2336, 1585, 1566, 1508, 1489, 1464, 1445, 1404, 1395, 1260, 1074, 1059, 1032, 853, 826, 800, 762, 700, 656, 584, 565, 550, 449. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{16}N$, 234.1277; found 234.1273.

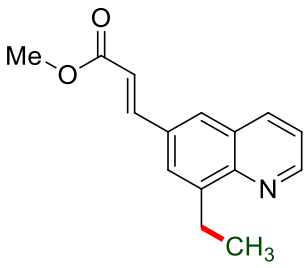


*8-ethyl-4-(thiophen-3-yl)quinoline (Scheme 2, Entry **3p**)*. Colourless liquid, yield = 28.7 mg (40%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.95 (d, J = 4.2 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 6.9 Hz, 1H), 7.34 – 7.51 (m, 3H), 7.38 (d, J = 4.2 Hz, 1H), 7.32 – 7.34 (m, 1H), 3.36 (q, J = 7.5 Hz, 2H), 1.43 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 148.8, 147.2, 143.7, 143.3, 139.1, 129.1, 128.1, 127.1, 126.7, 126.2,

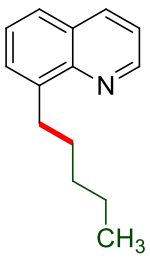
125.0, 123.8, 121.1, 25.1, 15.3. IR (ZnSe) ν_{max} (cm^{-1}): 2963, 2926, 2868, 2326, 1587, 1570, 1501, 1466, 1452, 1416, 1356, 1256, 1200, 1082, 1059, 1024, 849, 826, 787, 766, 729, 683, 654, 583. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{14}NS$, 240.0841; found 240.0838.



*(E)-8-ethyl-6-styrylquinoline (Scheme 2, Entry **3q**)*. White solid, yield = 34.2 mg (44%). Mp = 97–99 °C. Isolated from flash chromatography (5% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.89 (dd, J = 4.2, 1.8 Hz, 1H), 8.11 (dd, J = 8.4, 1.8 Hz, 1H), 7.83 (d, J = 1.8 Hz, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.35 – 7.42 (m, 3H), 7.26 – 7.32 (m, 3H), 3.33 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 149.1, 146.9, 143.3, 137.35, 136.38, 135.4, 129.9, 128.9, 128.9, 128.4, 128.0, 126.8, 125.8, 124.3, 121.4, 24.9, 15.2. IR (ZnSe) ν_{max} (cm^{-1}): 3026, 2959, 2924, 2862, 2328, 1726, 1585, 1574, 1493, 1445, 1377, 1364, 1076, 1034, 966, 881, 843, 791, 750, 692, 613. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{18}N$, 260.1434; found 260.1438.



*(E)-methyl 3-(8-ethylquinolin-6-yl)acrylate (Scheme 2, Entry **3r**)*. White solid, yield = 30.4 mg (42%). Mp = 68–70 °C. Isolated from flash chromatography (5% EtOAc/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.94 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 8.4, 1.8 Hz, 1H), 7.83 (d, J = 15.9 Hz, 1H), 7.74 (s, 2H), 7.41 (dd, J = 8.4, 4.2 Hz, 1H), 6.60 (d, J = 15.9 Hz, 1H), 3.84 (s, 3H), 3.30 (q, J = 7.5 Hz, 2H), 1.40 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 167.5, 150.3, 147.9, 144.5, 144.0, 136.9, 132.4, 128.5, 127.6, 125.7, 121.7, 118.9, 51.9, 24.8, 15.0. IR (ZnSe) ν_{max} (cm^{-1}): 2965, 2924, 2841, 1703, 1638, 1589, 1489, 1429, 1377, 1308, 1283, 1238, 1194, 1165, 1128, 1069, 1022, 980, 853, 791, 762, 729, 606, 575, 436. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{16}NO_2$, 242.1176; found 242.1176.

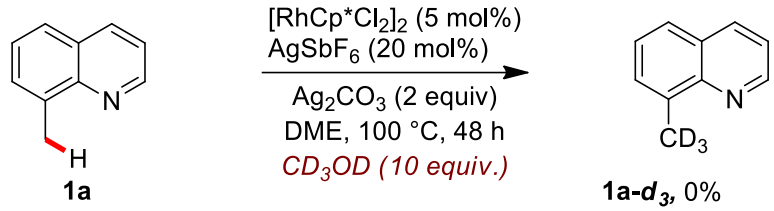


*8-pentylquinoline (Scheme 2, Entry **3s**)*.[7] Yellow liquid, yield = 6.0 mg (10%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.94 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 7.8, 1.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.45 – 7.48 (m, 1H), 7.38 (dd, J = 8.4, 4.2 Hz, 1H), 3.27 (t, J = 7.8 Hz, 2H), 1.77 – 1.82 (m, 2H), 1.36 – 1.46 (m, 4H), 0.89 – 0.91 (m, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 149.4, 147.1, 141.9, 136.5, 128.8, 128.6, 126.4, 125.9, 120.9, 32.1, 31.5, 30.5, 22.8, 14.2. IR (ZnSe) ν_{max} (cm^{-1}): 2955, 2924,

2857, 1597, 1499, 1466, 1366, 1261, 1163, 1078, 1026, 966, 826, 793, 758, 729. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}N$, 200.1434; found 200.1433.

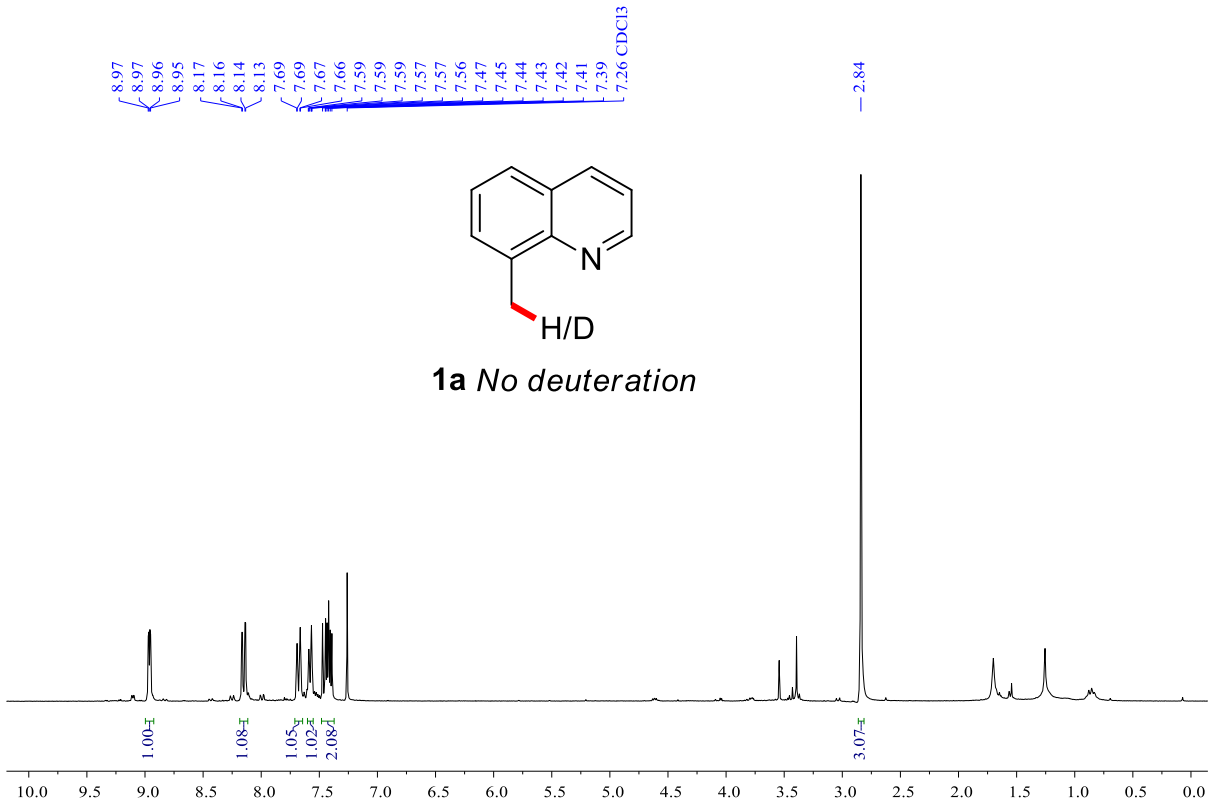
4. Mechanistic study

4.1 Deuterium lebling experiments under methylation condition (Scheme S1)

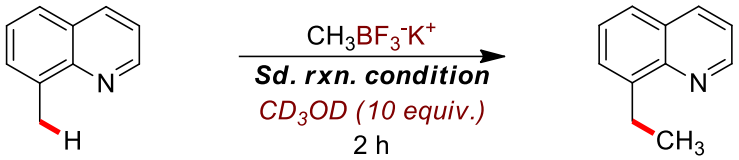


To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.1 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2 equiv), CD_3OD (10 equiv) and dimethoxyethane (0.5 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 48 h. Solvent was evaporated under reduced pressure, and the crude mixture was analysed by ^1H NMR. No deuteration was observed.

^{1}H NMR



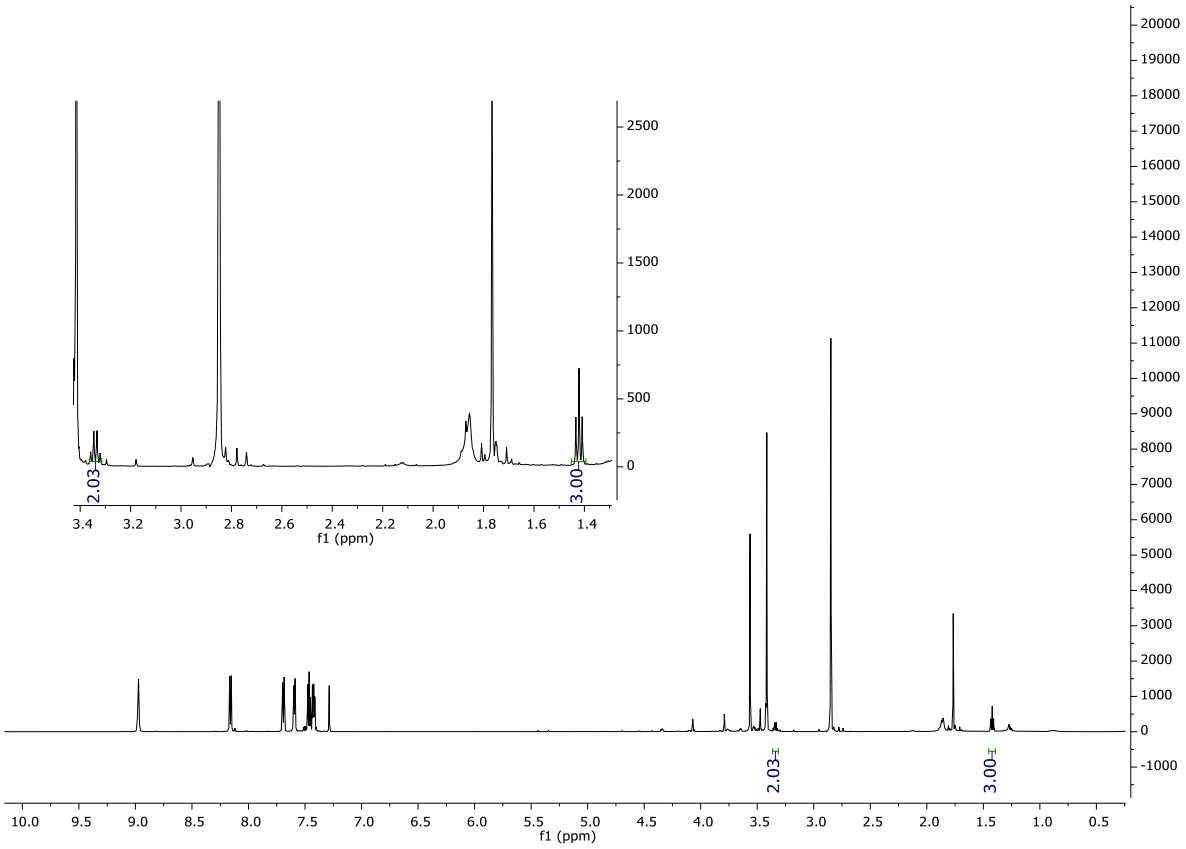
4.2 Deuterium lebling experiments under methylation condition (Scheme S2)



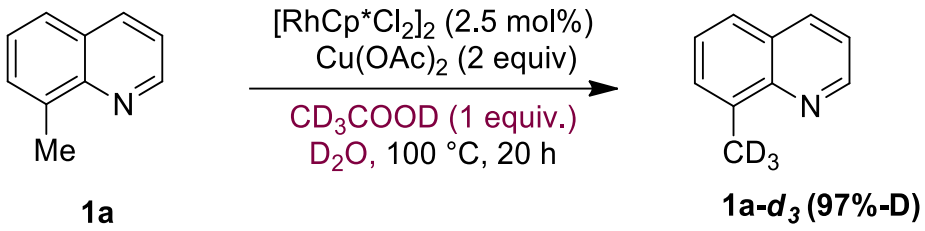
3a, *No deuteration*

To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.1 mmol), potassium methyltrifluoroborate (3 equiv), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2 equiv), CD_3OD (10 equiv) and dimethoxyethane (0.5 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 2 h. Solvent was evaporated under reduced pressure, and the crude mixture was analysed by ^1H NMR. No deuteration was observed.

^{1}H NMR



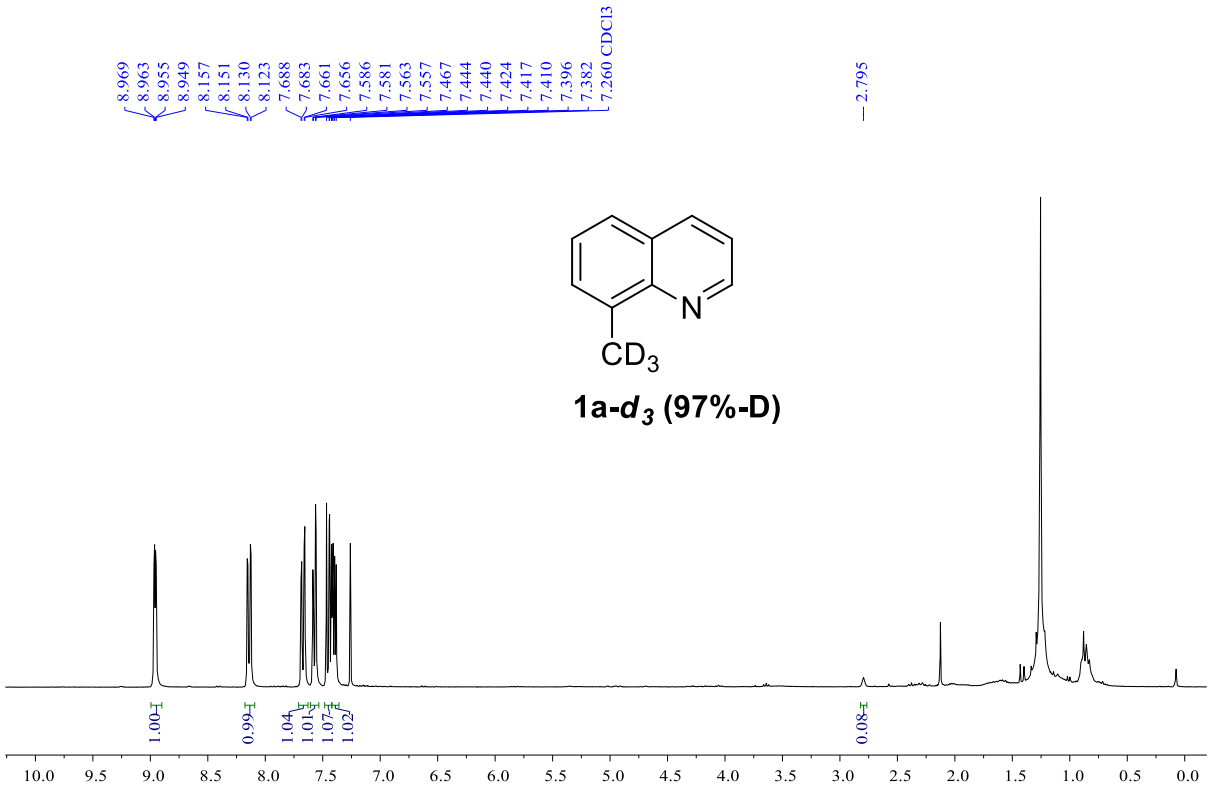
*4.3 Synthesis of **1a-d3** (Scheme S3)*[8]



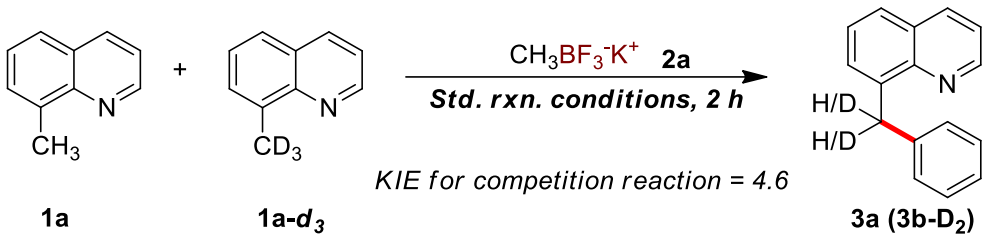
1a **1a-*d*$_3$ (97%-D)**

To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (**1a**) (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), CD_3COOD (1 equiv.) and $Cu(OAc)_2$ (2 equiv.) were added in D_2O (1 mL) under air at room temperature subsequent reaction mixture was stir at 100 ℃ for 20 h. The reaction mixture was extracted with EtOAc and the organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography using silica gel (230-400 mesh size) and *n*-hexane: EtOAc as eluent.

^{1}H NMR

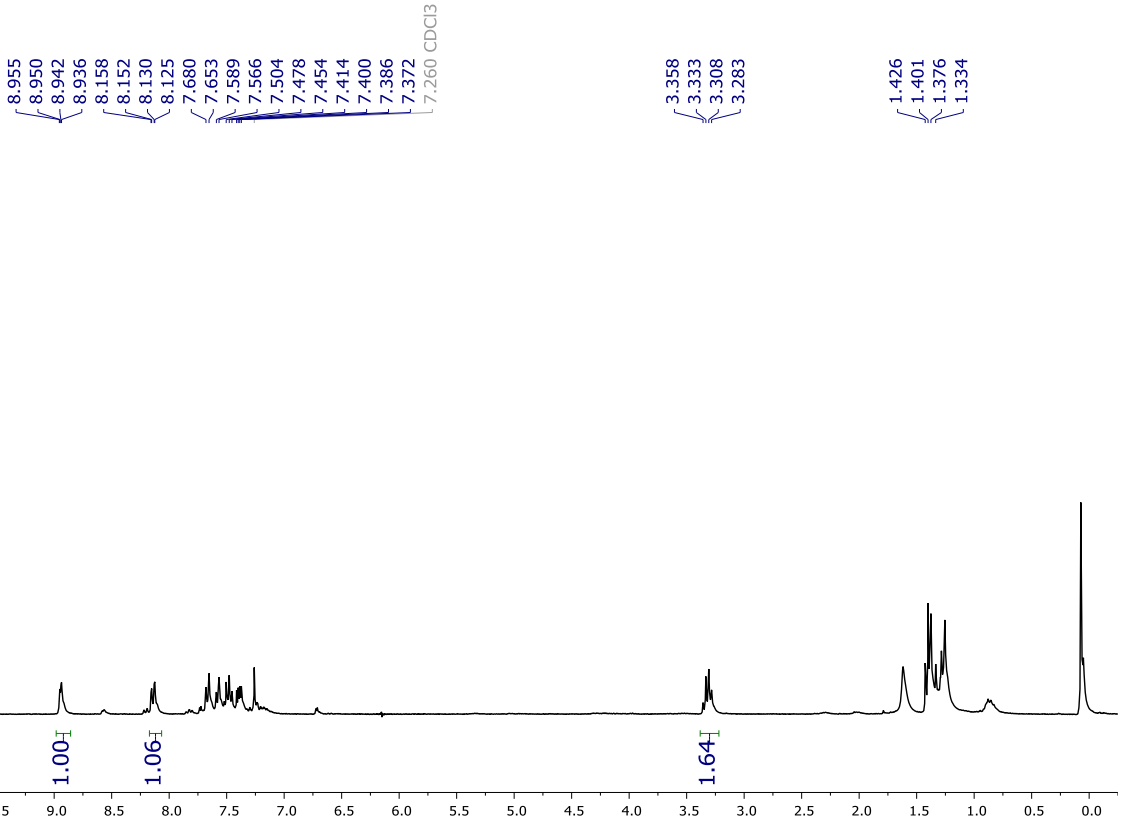


4.4 Competition experiment under methylation condition for KIE (Kinetic Isotopic Effect) (Scheme S4)

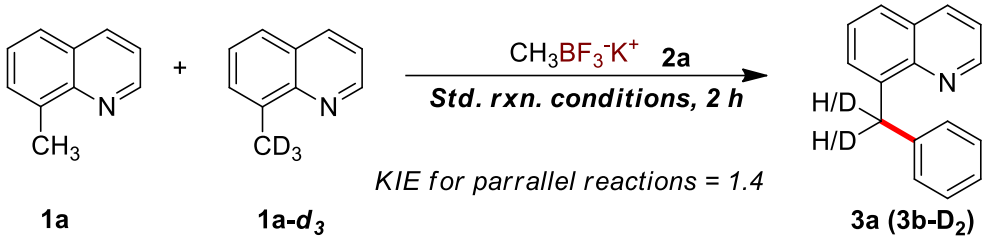


To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.1 mmol), 8-methyl quinoline-d_3 (0.1 mmol), potassium methyltrifluoroborate (0.6 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2 equiv) and dimethoxyethane (1.0 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 2 h. Solvent was evaporated under reduced pressure, and the crude mixture was purified by flash chromatography using silica gel (230−400 mesh size) and *n*-hexane: EtOAc as the eluent. The kinetic isotope effect value (k_H/k_D) was found 4.6.

^{1}H NMR

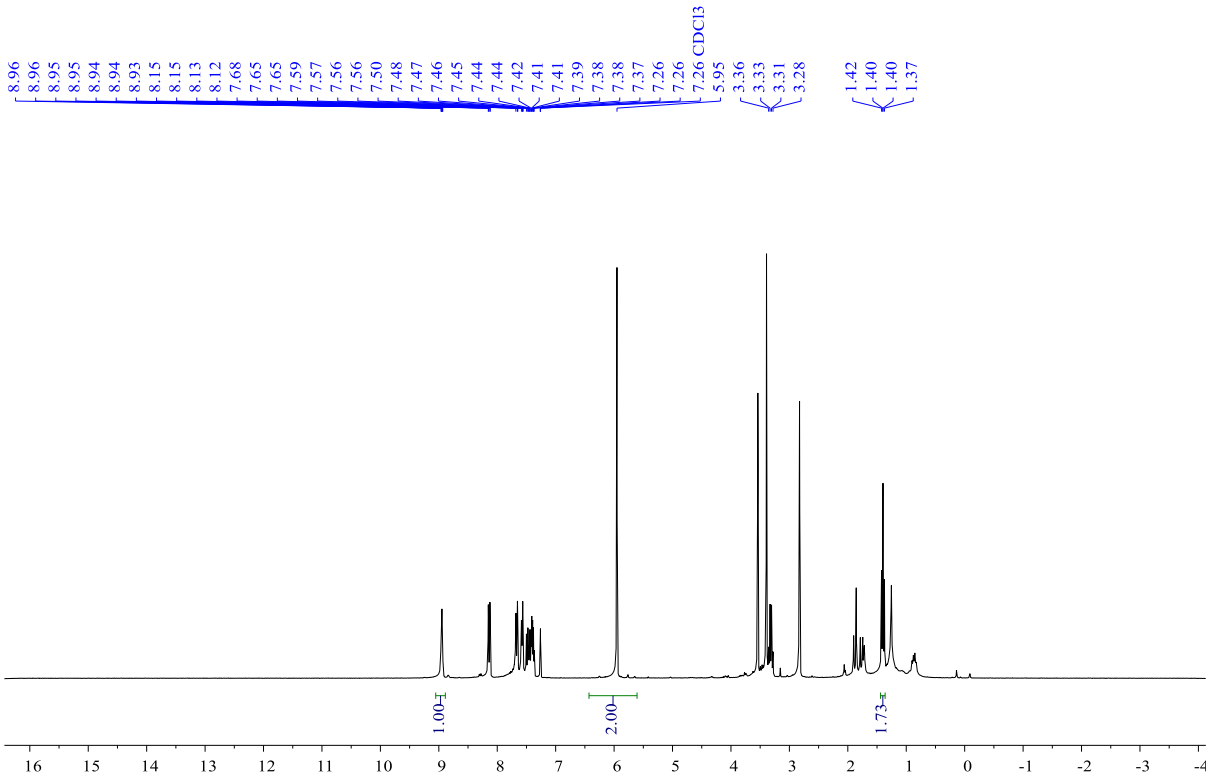


4.5 Parallel experiment under methylation condition for KIE (Kinetic Isotopic Effect) (Scheme S5)

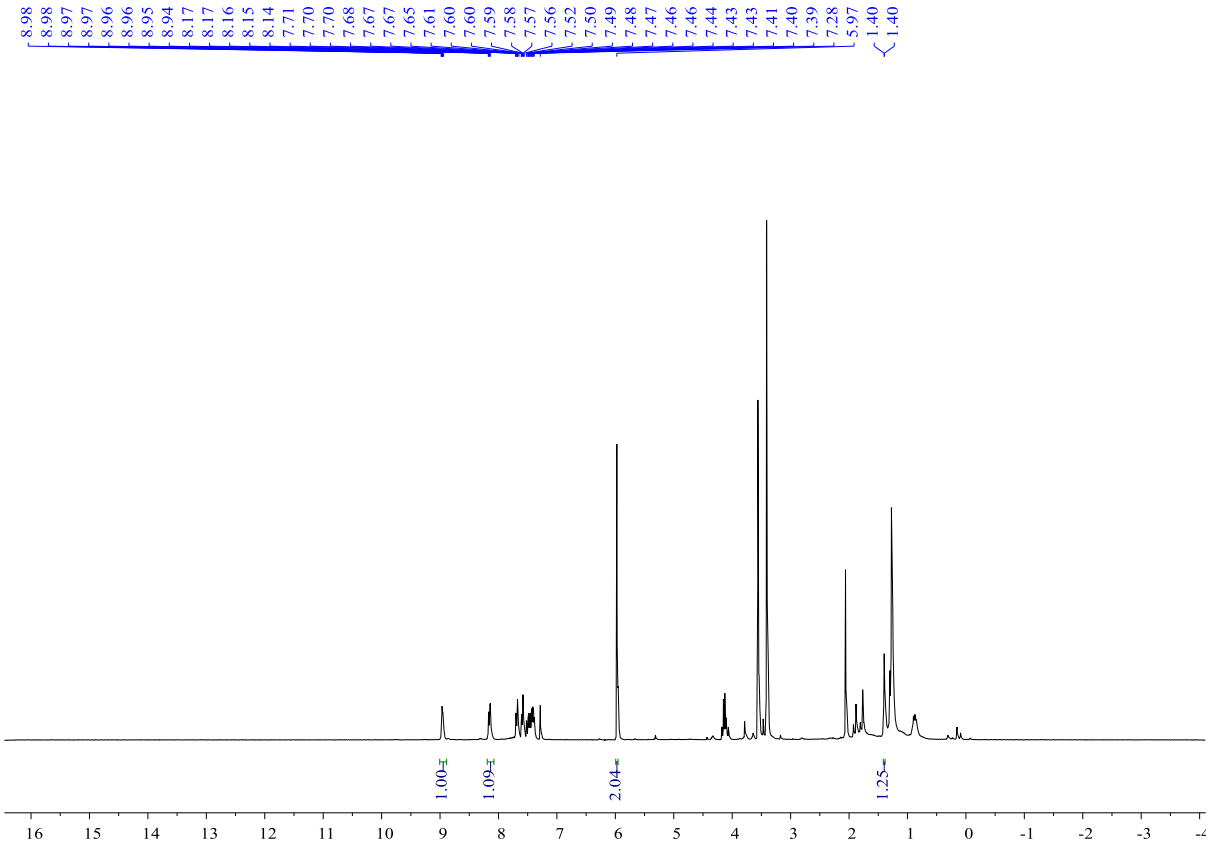


To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.1 mmol), potassium methyl trifluoroborate (0.3 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2 equiv) and dimethoxyethane (0.5 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 2 h. In another reaction tube 8-methyl quinoline-d_3 (0.1 mmol) was used instead of 8-methyl quinoline. The two-reaction mixtures were allowed to stir at 100 ℃ for 2h. Both reaction mixtures were analyzed through ^{1}HNMR using TCE as an internal standard and the calculated NMR yields of products **3aa** and **3aa-D$_2$** was 57% and 41%, respectively. The kinetic isotope effect value (k_H/k_D) was found 1.4.

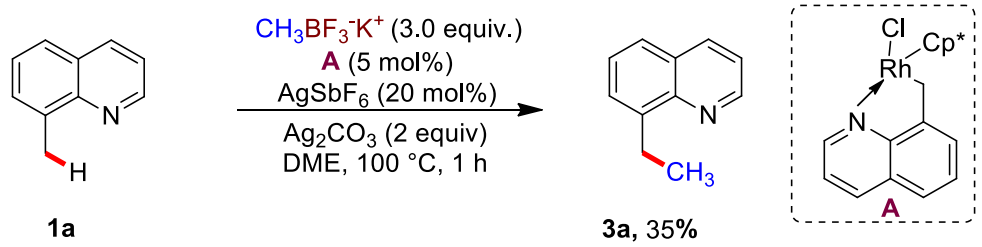
^{1}H NMR



^{1}H NMR


8.98
8.98
8.97
8.97
8.96
8.96
8.95
8.94
8.17
8.17
8.16
8.15
8.14
7.71
7.70
7.70
7.68
7.67
7.67
7.65
7.61
7.60
7.60
7.59
7.58
7.57
7.56
7.52
7.50
7.49
7.48
7.47
7.46
7.46
7.44
7.43
7.43
7.41
7.40
7.39
7.28
5.97
1.40
1.40
1.00
1.09
2.04
1.25
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

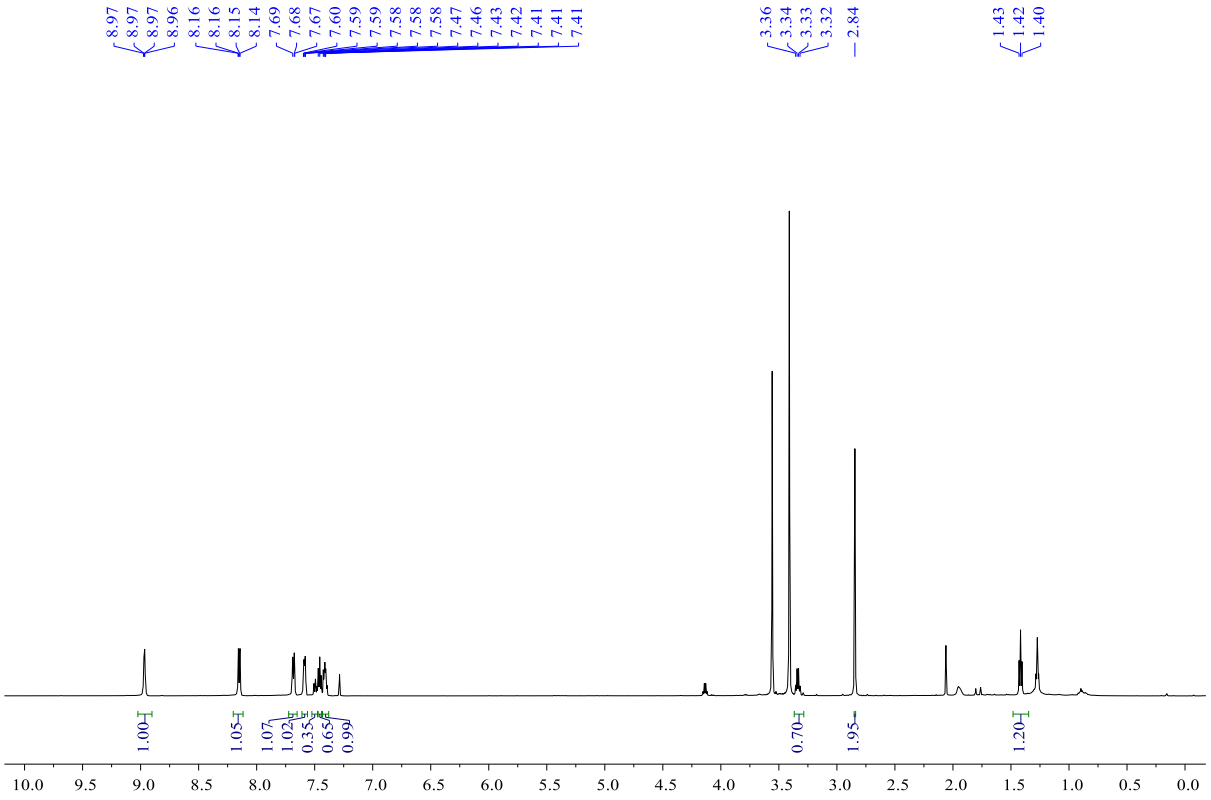
4.6 Intermediate study (Scheme S6)



1a **3a**, 35%

To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (0.1 mmol), potassium methyl trifluoroborate (0.3 mmol), rhodacycle **A** (5 mol %), $AgSbF_6$ (20 mol%), Ag_2CO_3 (2.0 equiv) and dimethoxyethane (0.5 mL) were added. The subsequent reaction mixture was stirred at 100 °C for 48 h. Solvent was evaporated under reduced pressure, and the crude mixture was analysed by ^{1}HNMR the calculated NMR yield of product **3a** was 35%, and 65% reactant remains as such.

^{1}H NMR



5. References

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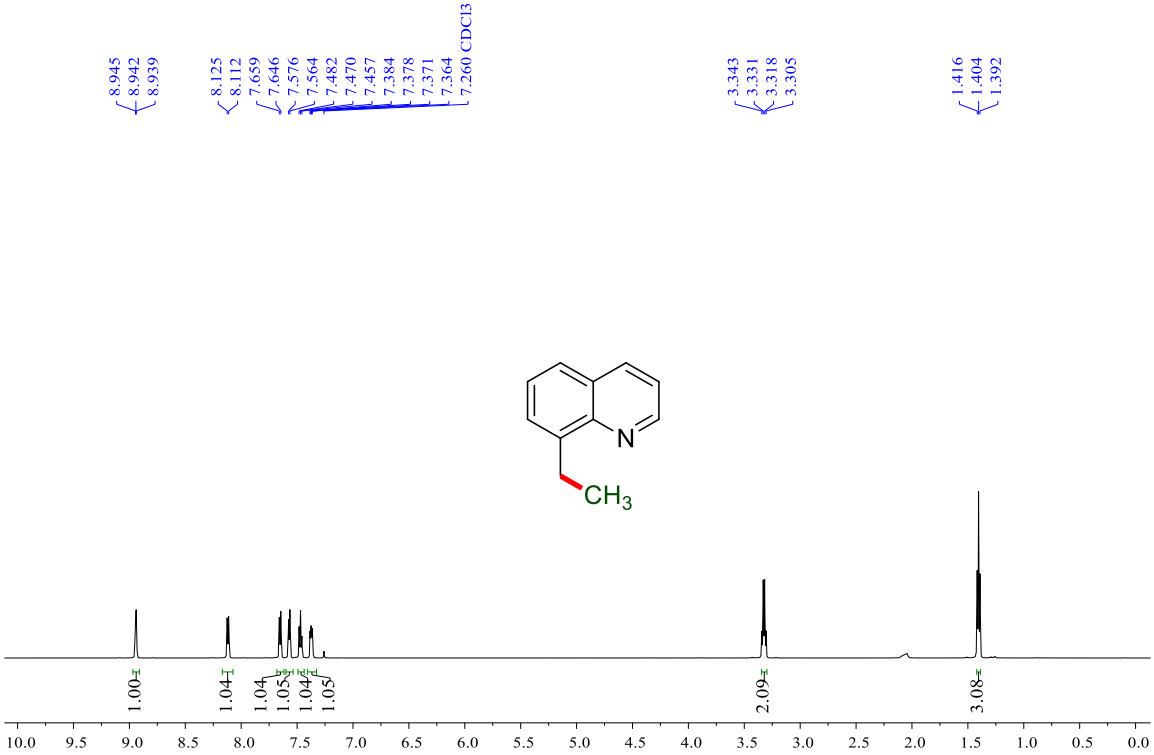
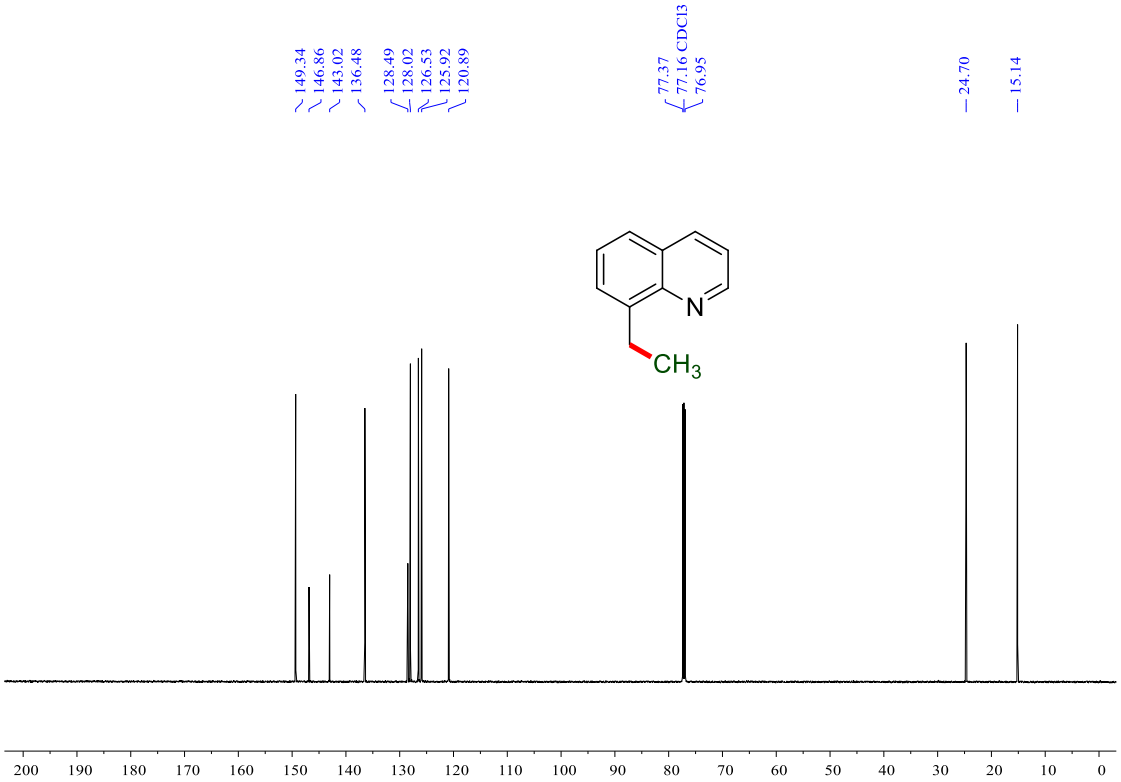
6. ^{1}H and ^{13}C Spectra of Synthesized Compounds

*8-ethylquinoline (Scheme 2, Entry **3a**)*

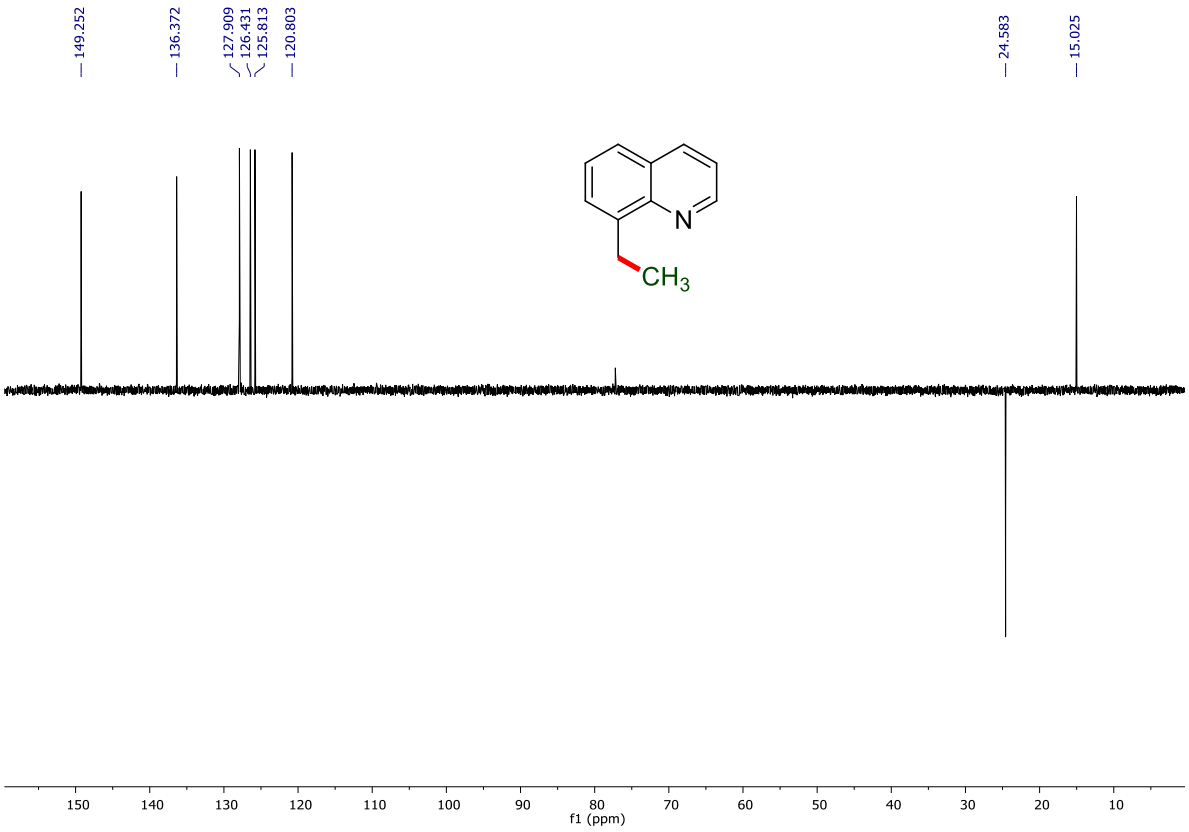
^{1}H NMR (600 MHz)



^{13}C NMR (150 MHz)

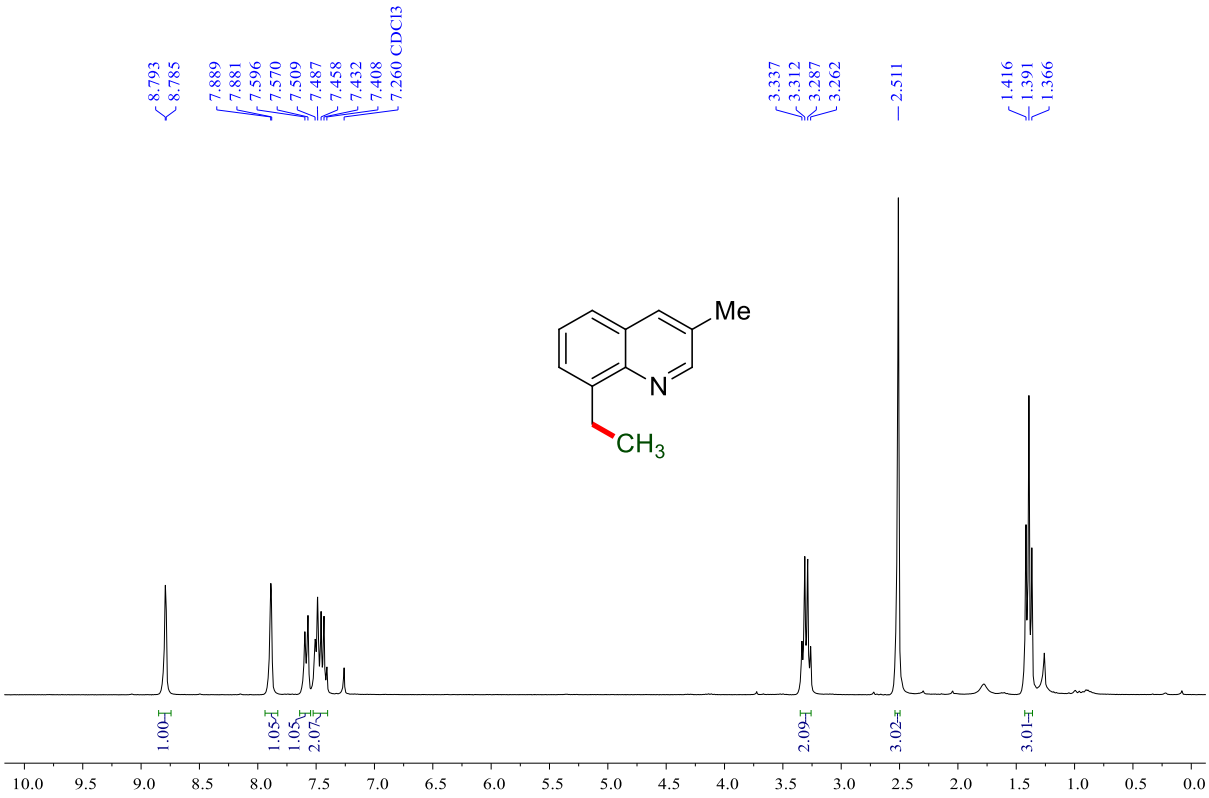


DEPT NMR

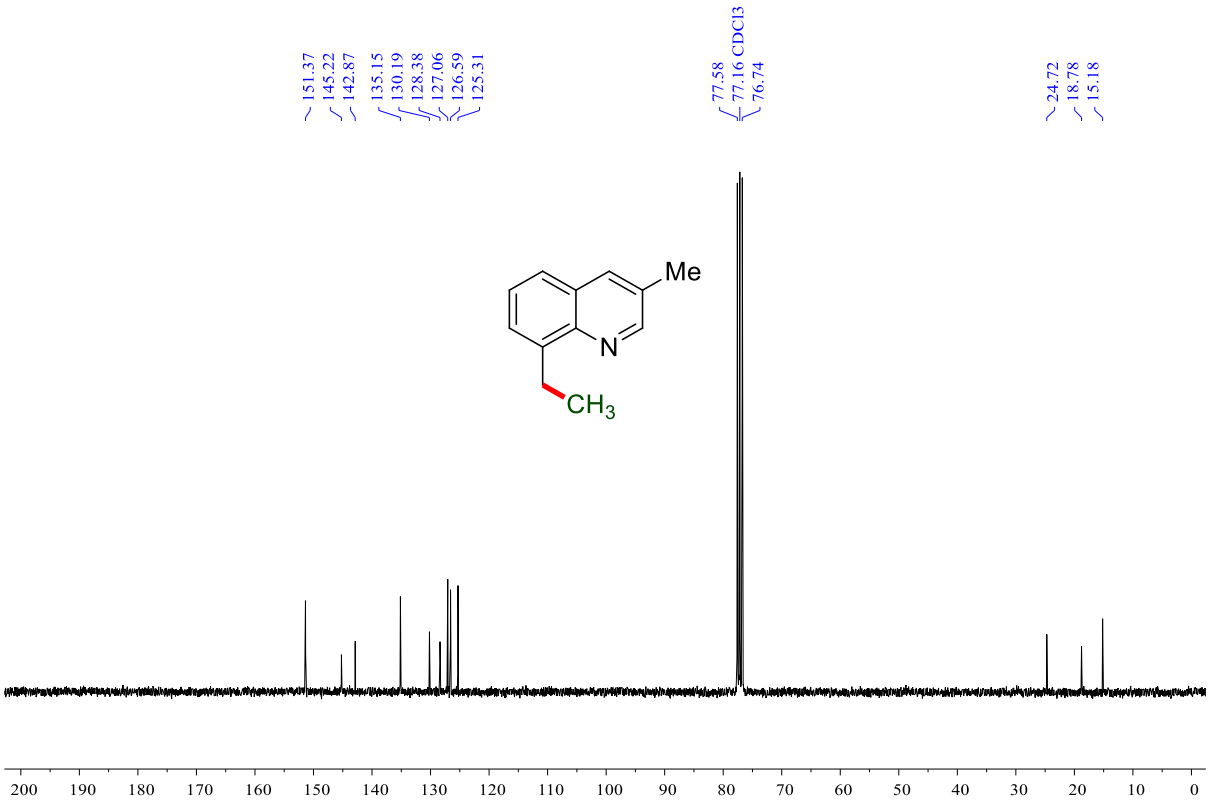

149.252
136.372
127.909
126.431
125.813
120.803
24.583
15.025
N
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

*8-ethyl-3-methylquinoline (Scheme 2, Entry **3b**)*

^{1}H NMR (300 MHz)

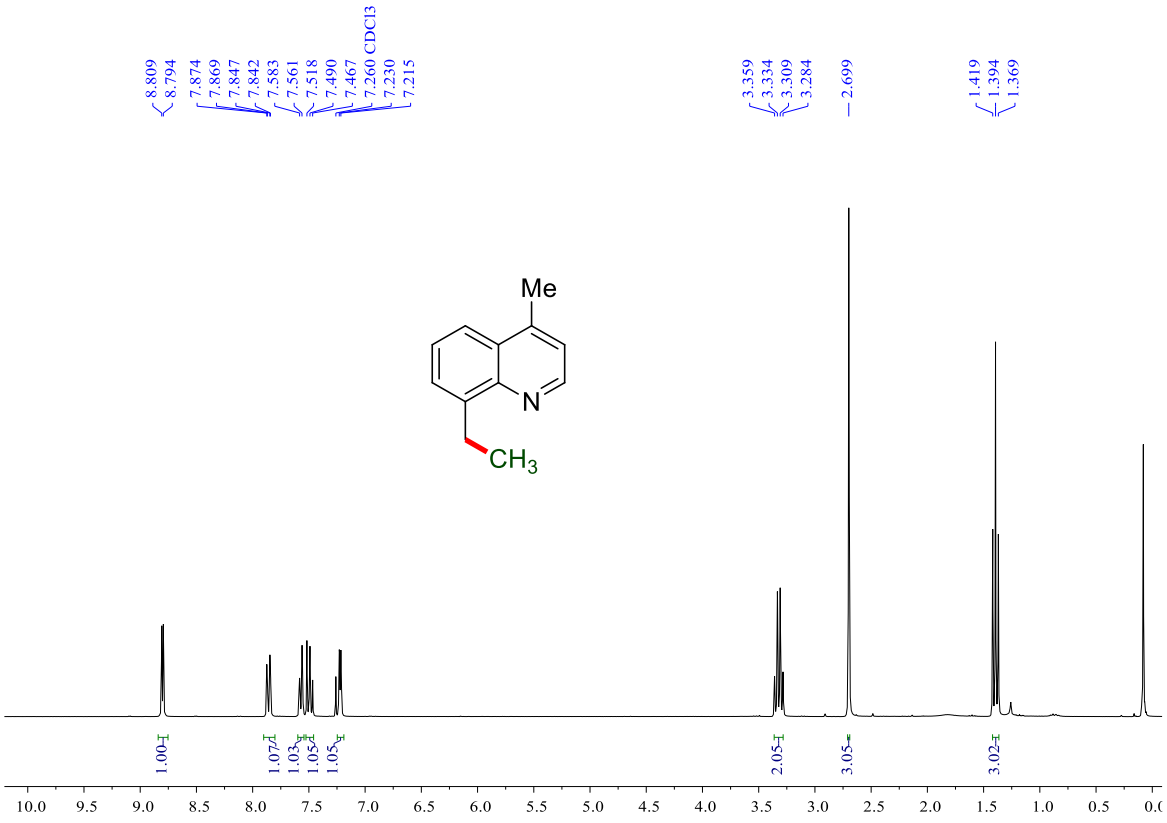


^{13}C NMR (75 MHz)

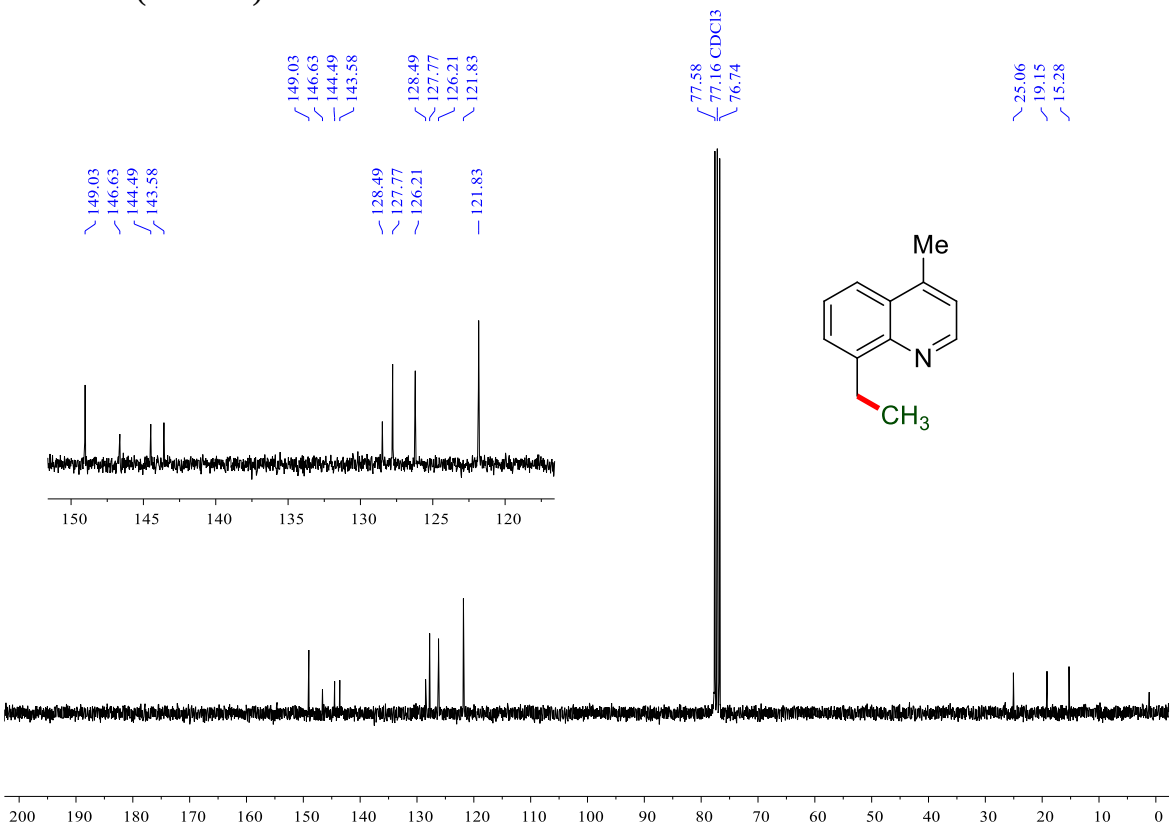


*8-ethyl-4-methylquinoline (Scheme 2, Entry **3c**)*

^{1}H NMR (300 MHz)

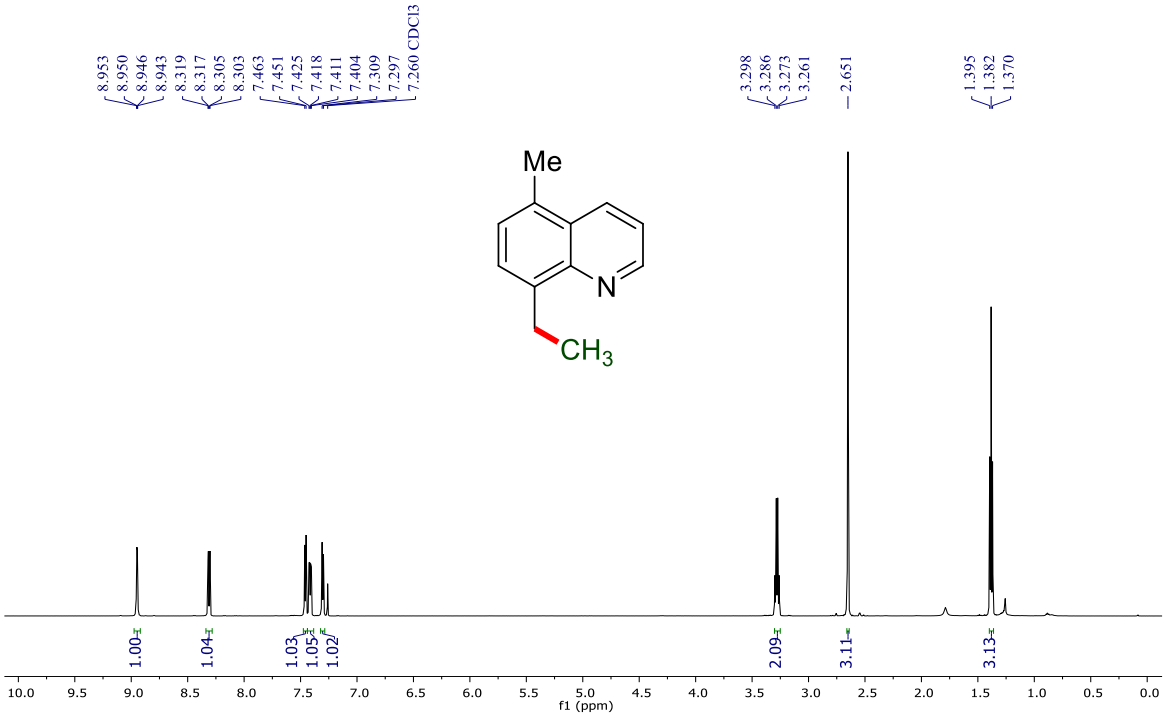


^{13}C NMR (75 MHz)

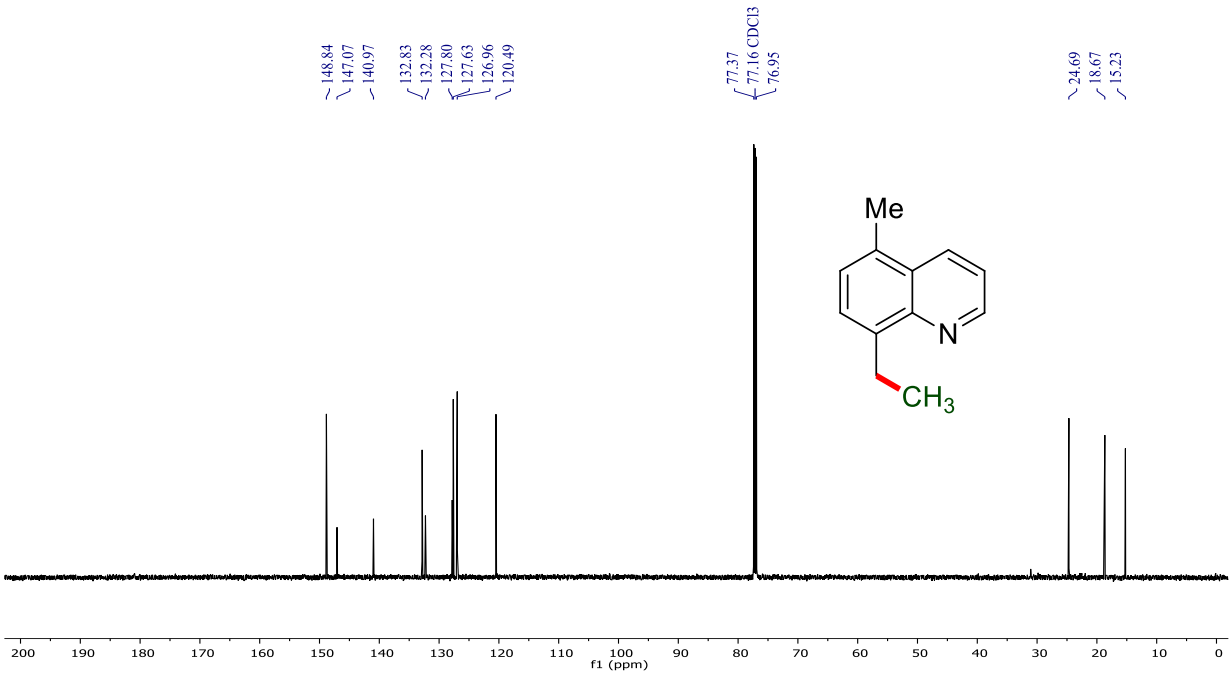


*8-ethyl-5-methylquinoline (Scheme 2, Entry **3d**)*

^{1}H NMR (600 MHz)

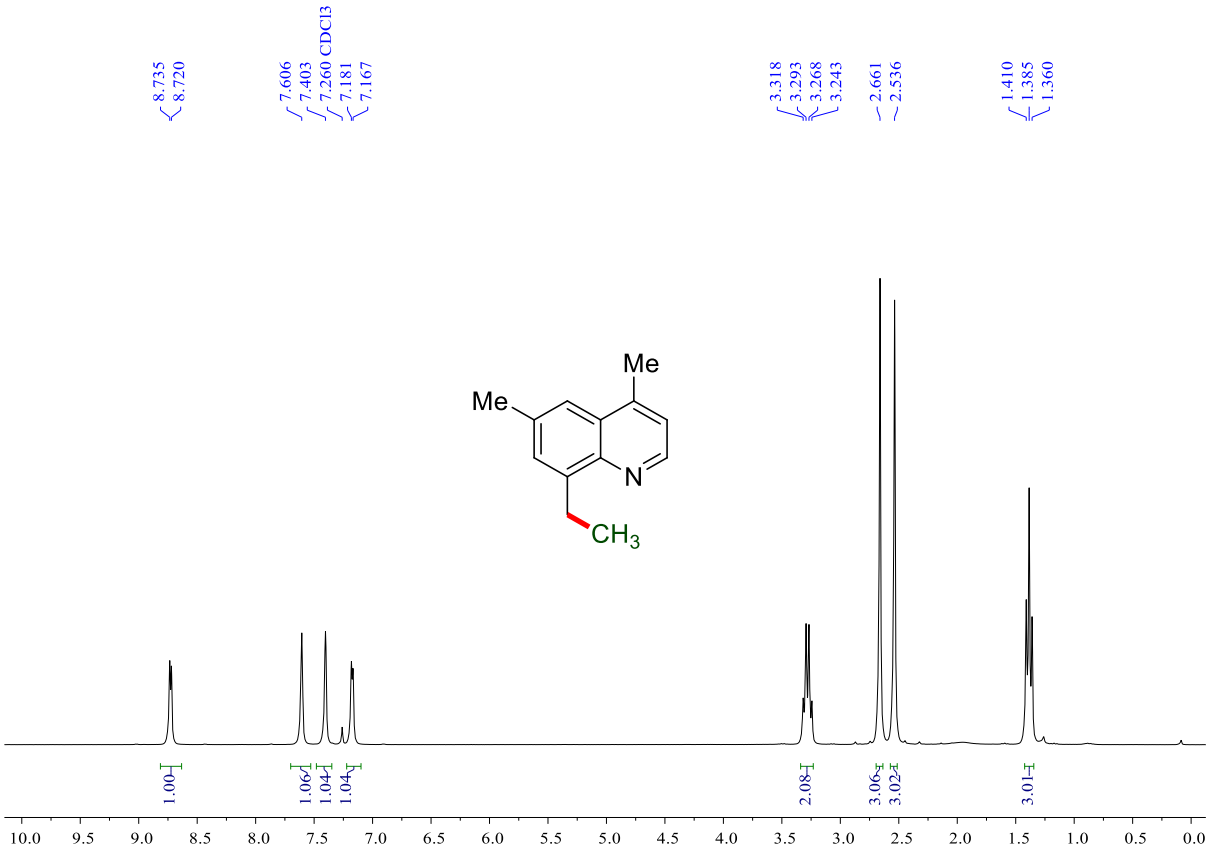


^{13}C NMR (150 MHz)

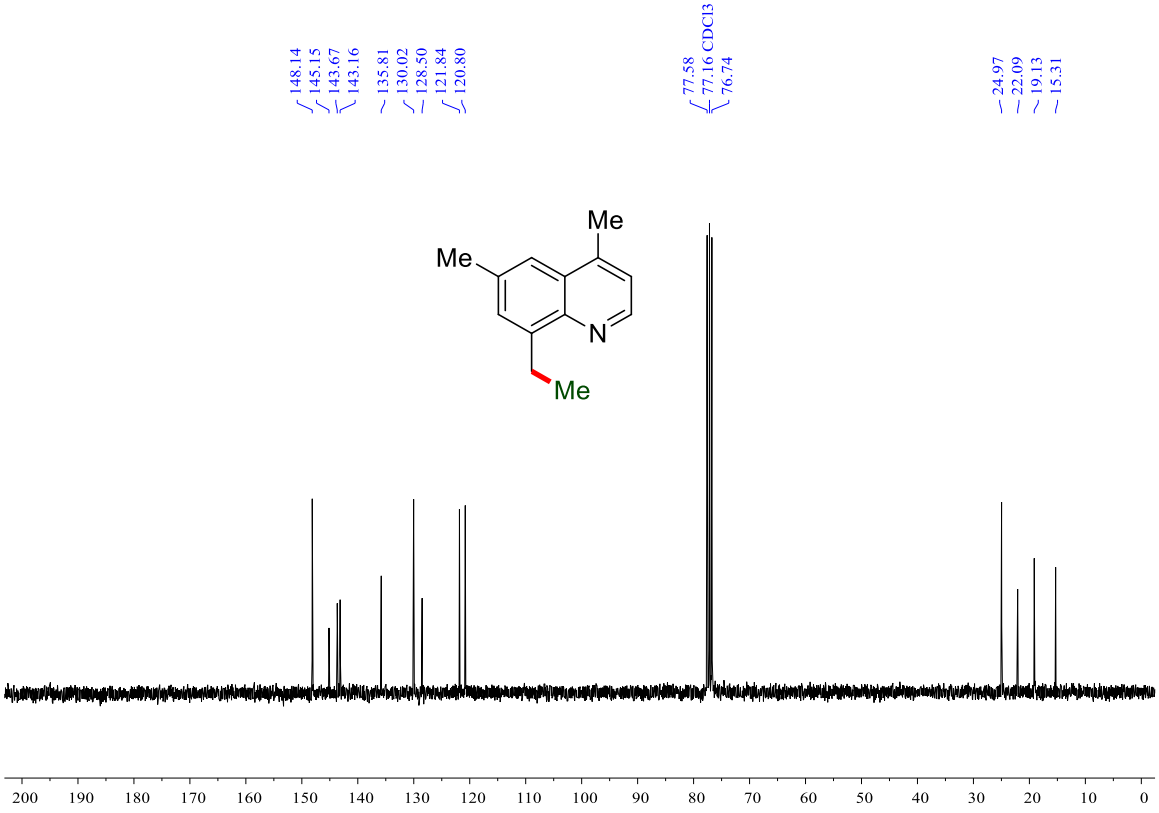


*8-ethyl-4,6-dimethylquinoline (Scheme 2, Entry **3e**)*

^{1}H NMR (300 MHz)

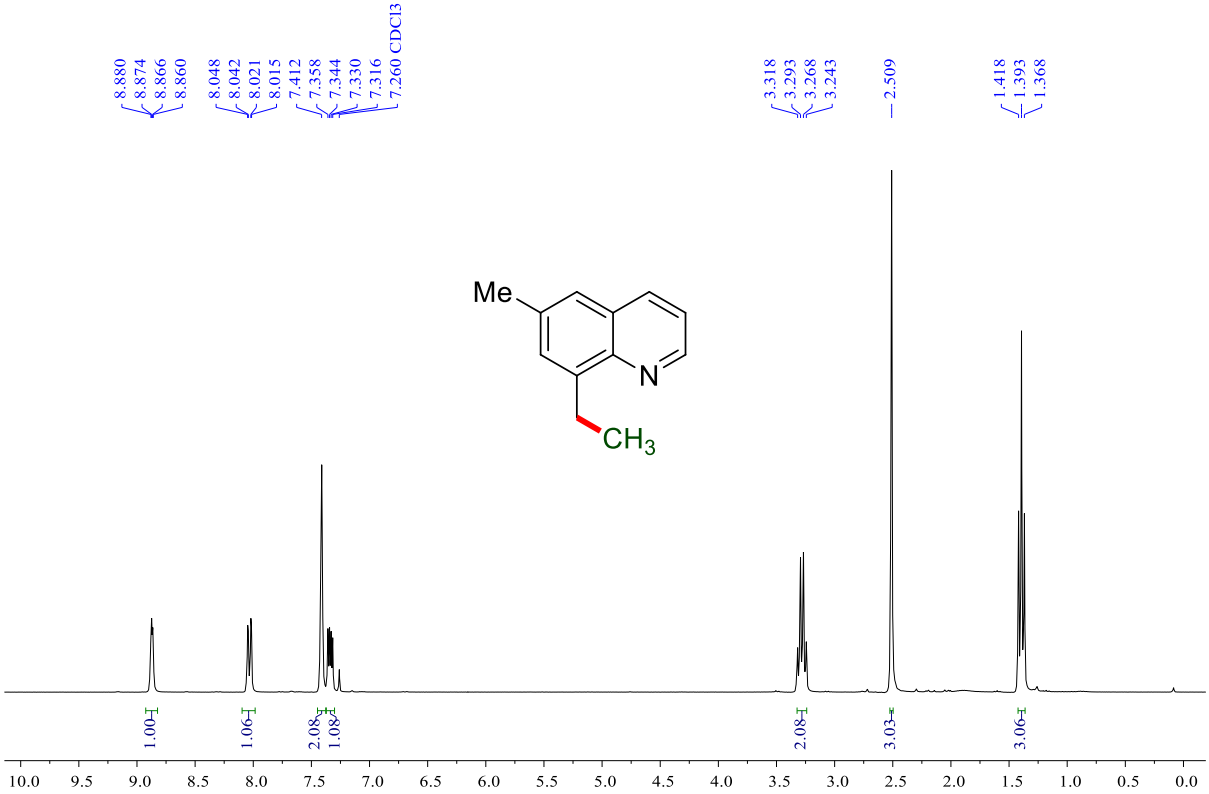


^{13}C NMR (75 MHz)

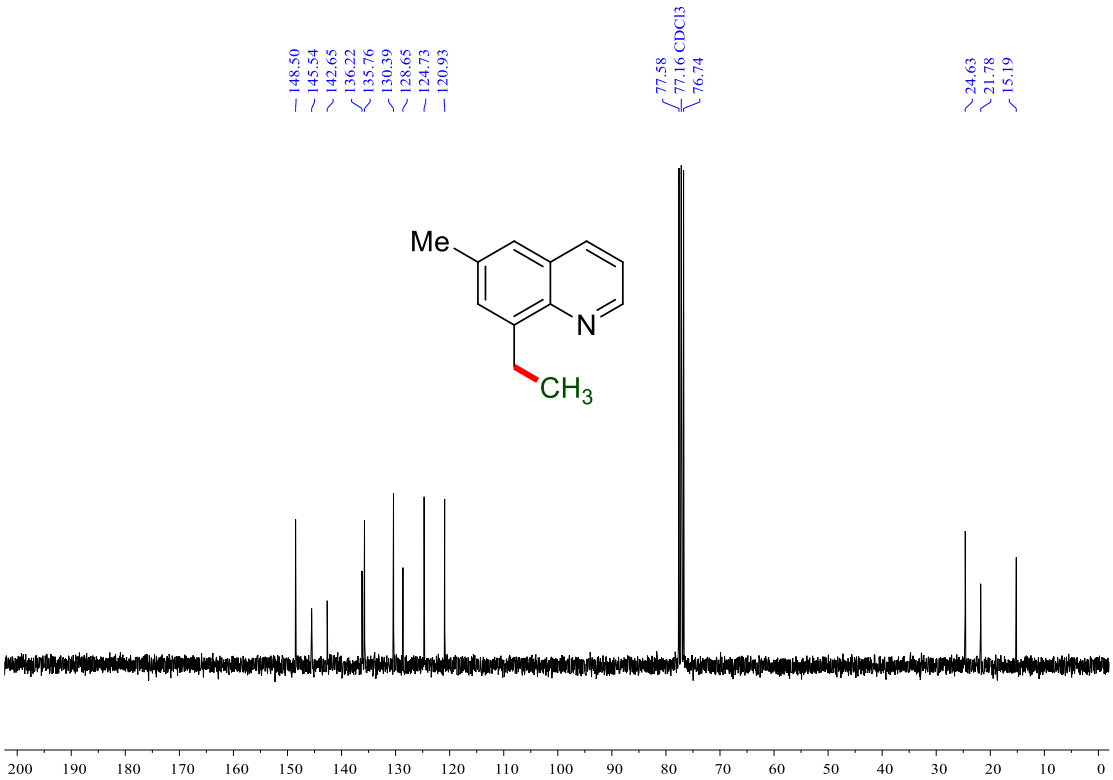


*8-ethyl-6-methylquinoline (Scheme 2, Entry **3f**)*

^{1}H NMR (300 MHz)

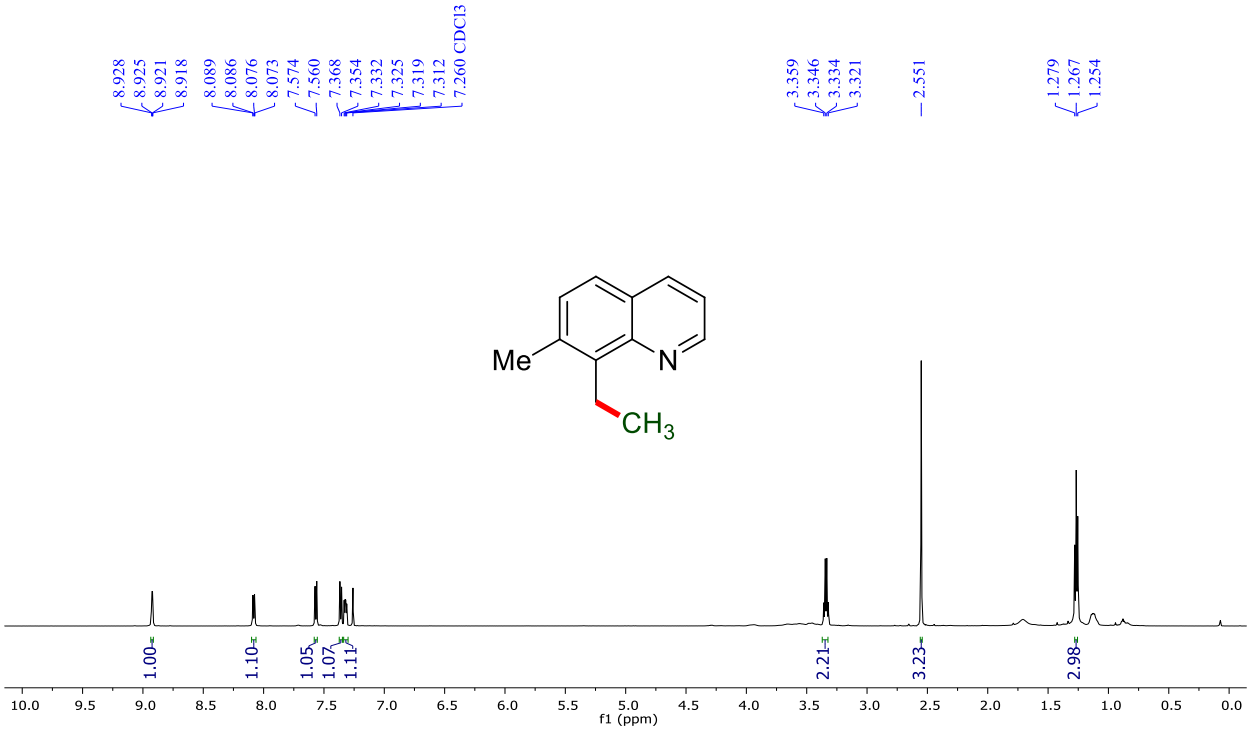


^{13}C NMR (75 MHz)

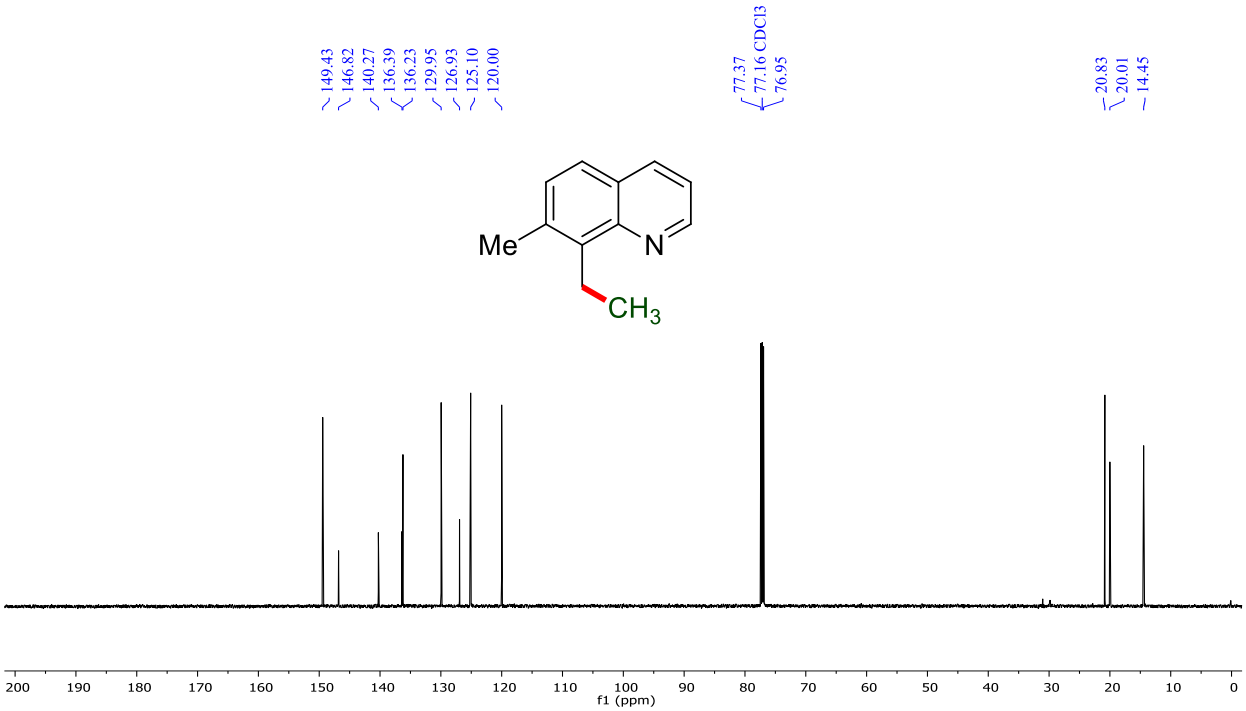


*8-ethyl-7-methylquinoline (Scheme 2, Entry **3g**)*

^{1}H NMR (600 MHz)

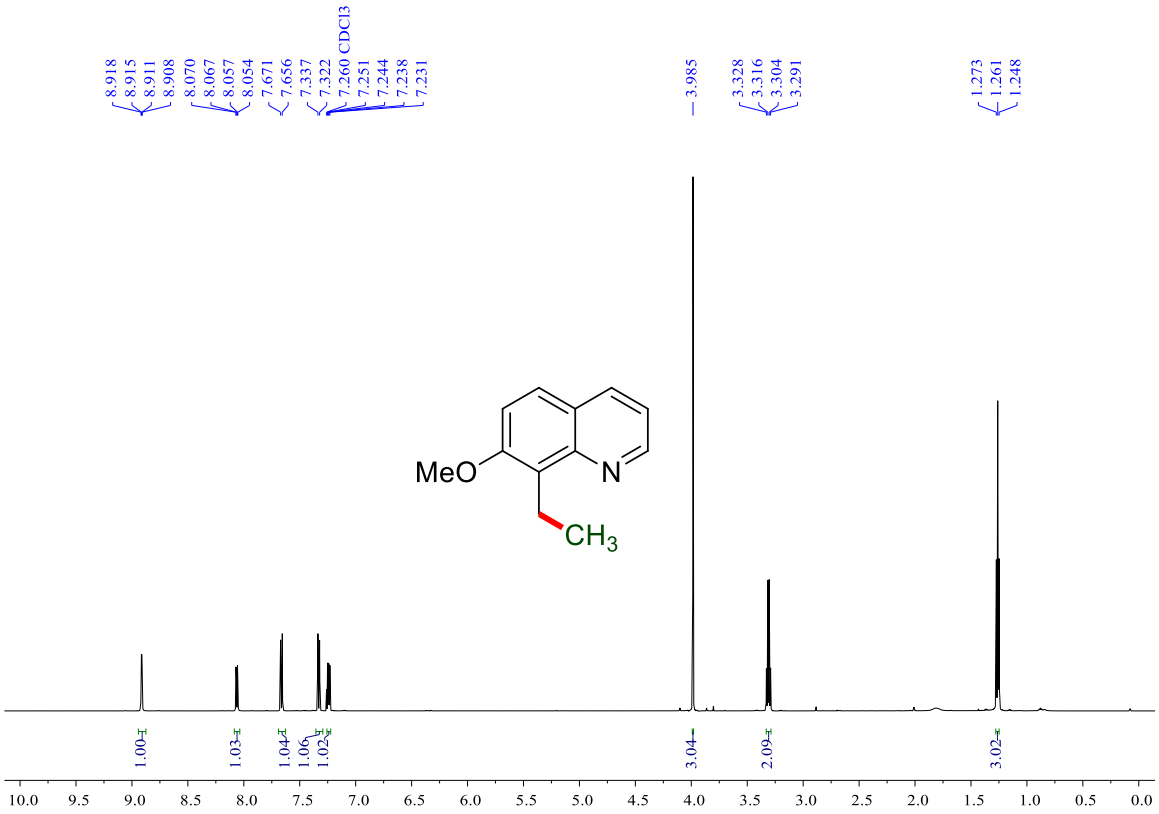


^{13}C NMR (150 MHz)

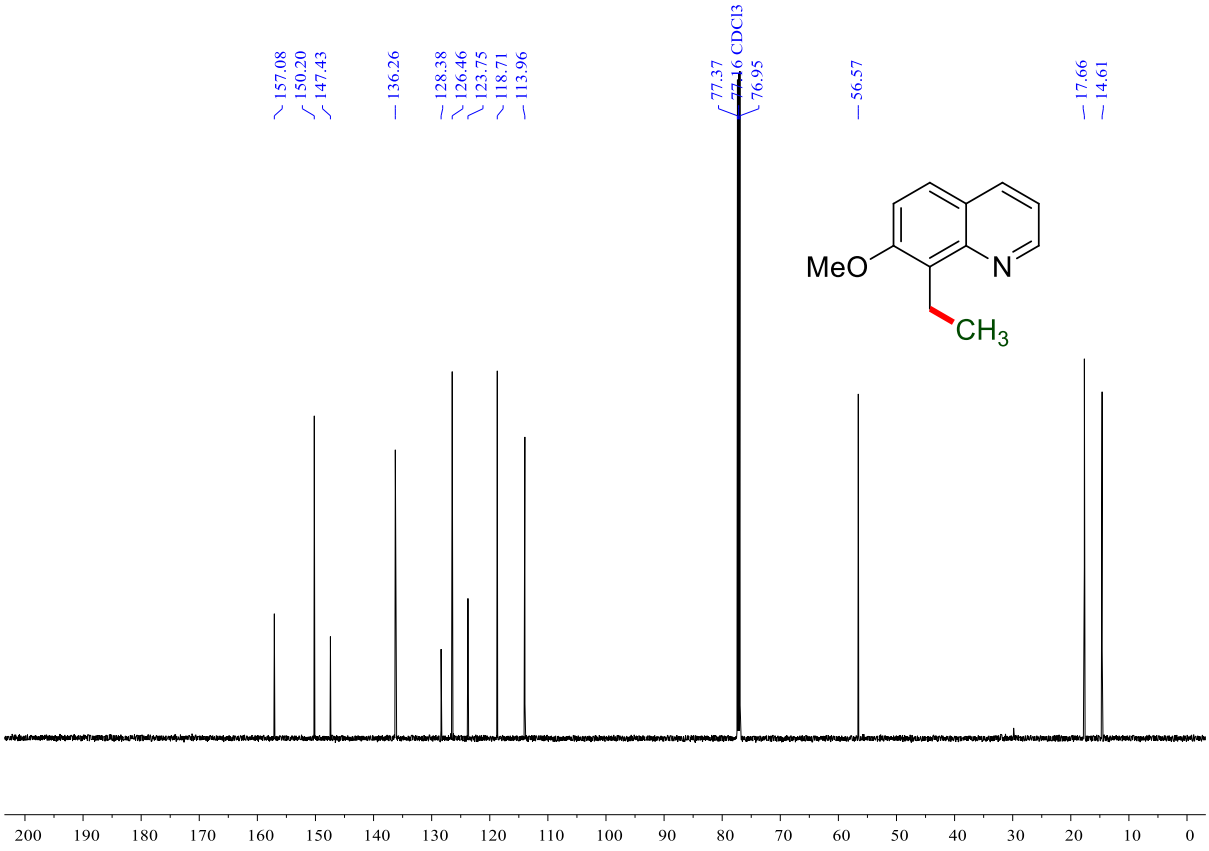


*8-ethyl-7-methoxyquinoline (Scheme 2, Entry **3h**)*

^{1}H NMR (600 MHz)

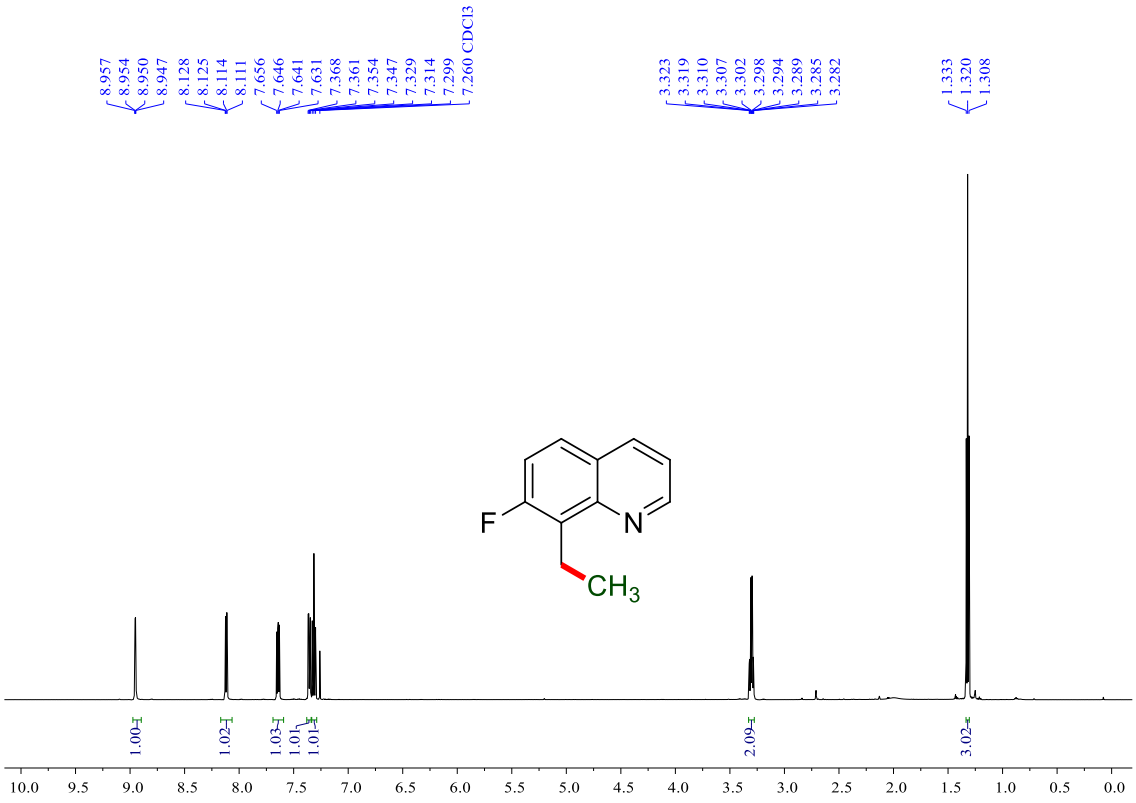


^{13}C NMR (150 MHz)

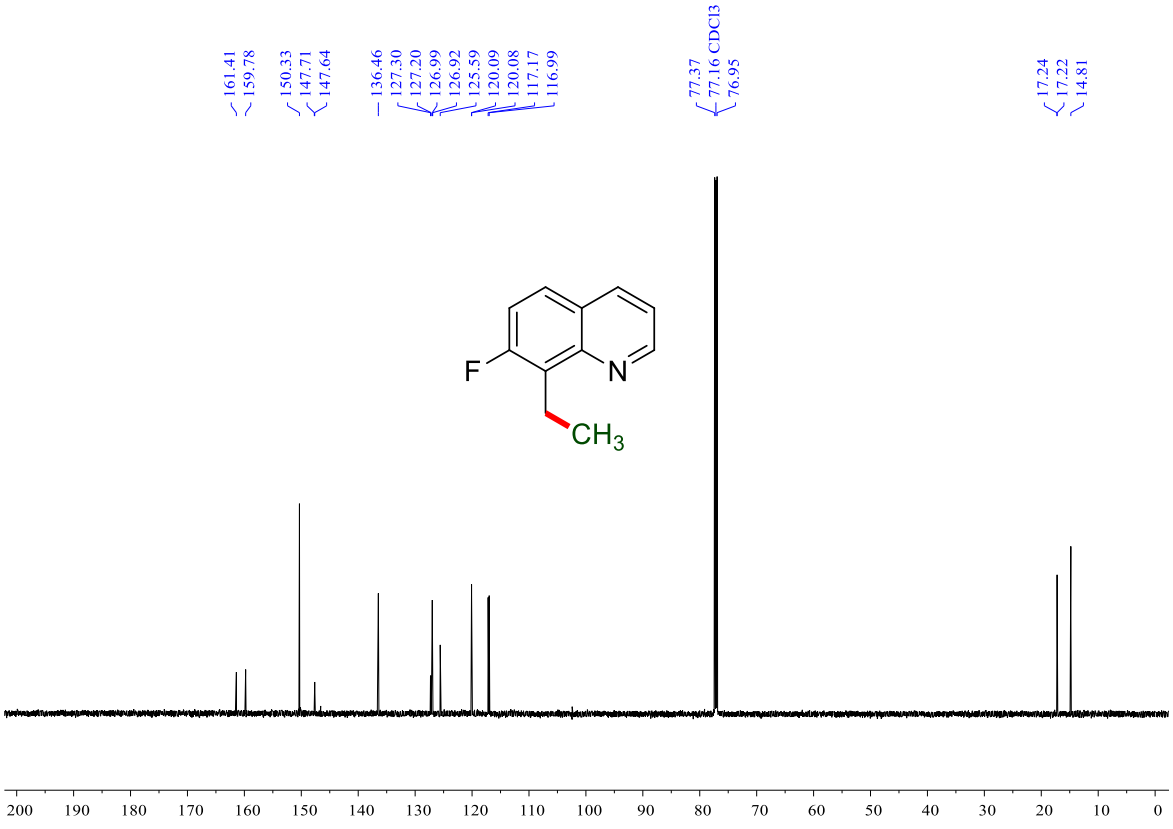


*7-fluoro-8-ethylquinoline (Scheme 2, Entry **3i**)*

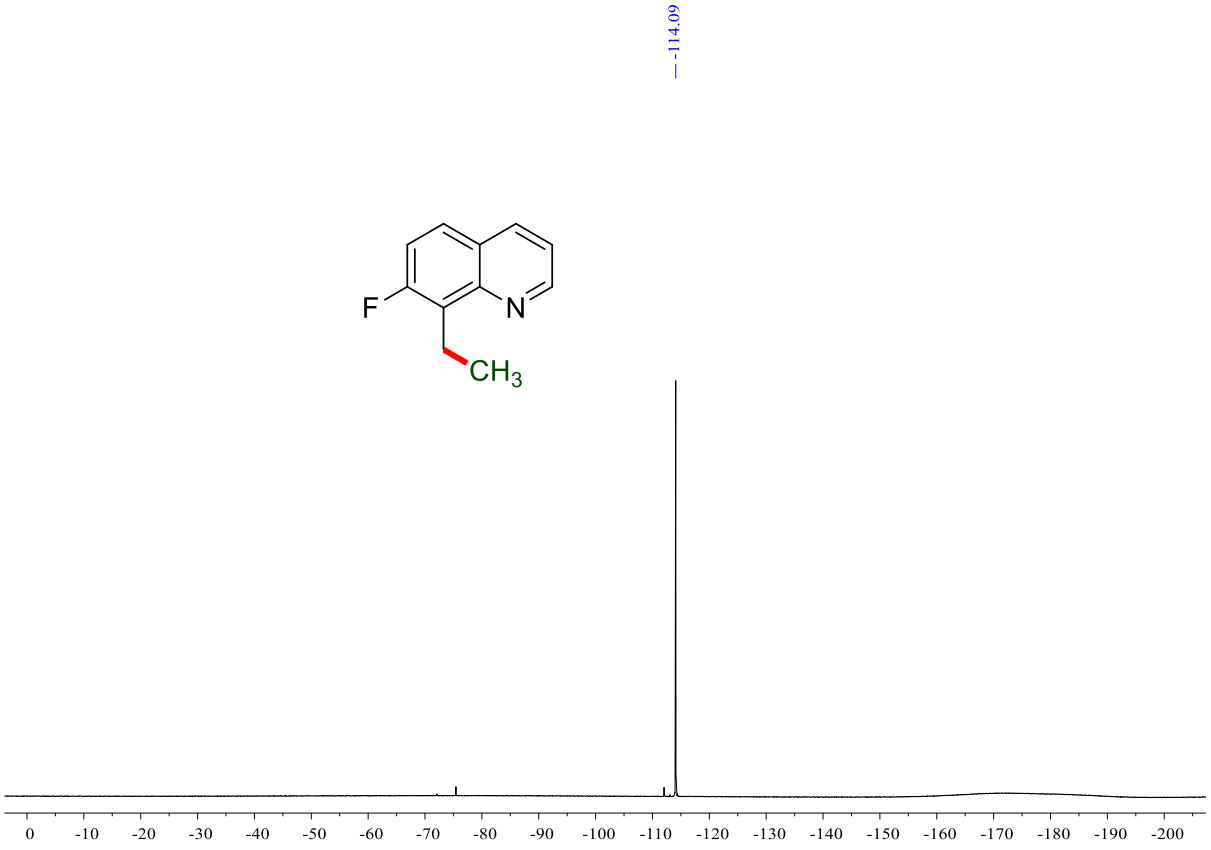
^{1}H NMR (600 MHz)



^{13}C NMR (150 MHz)

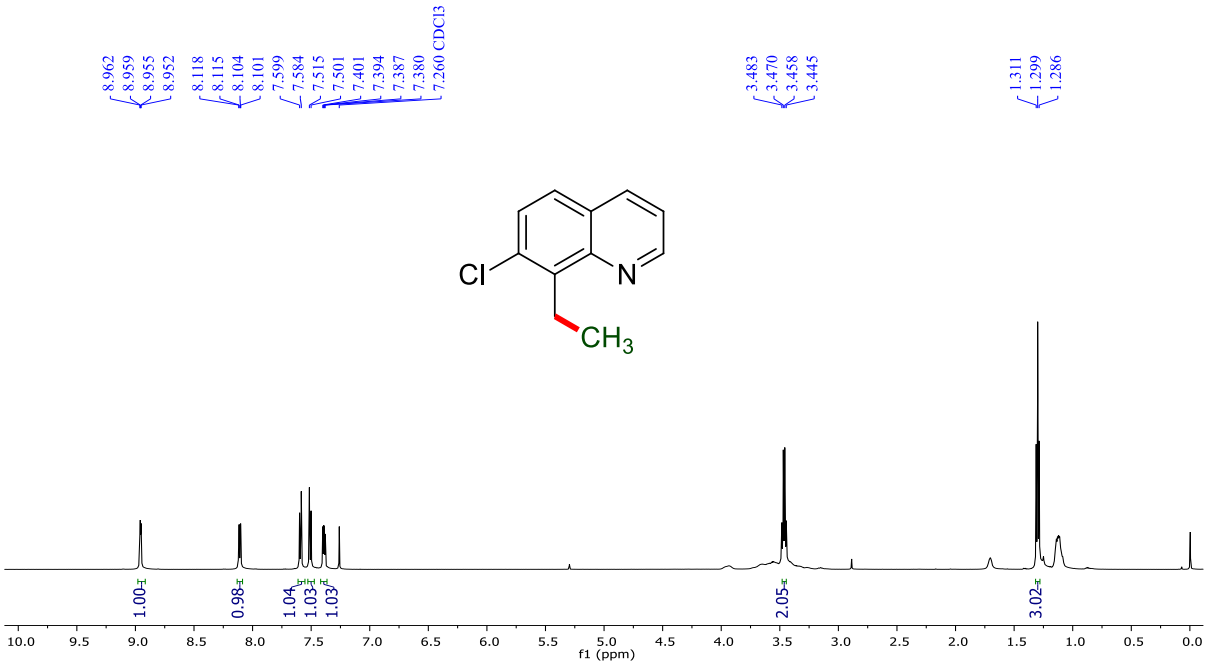


^{19}F NMR (565 MHz)

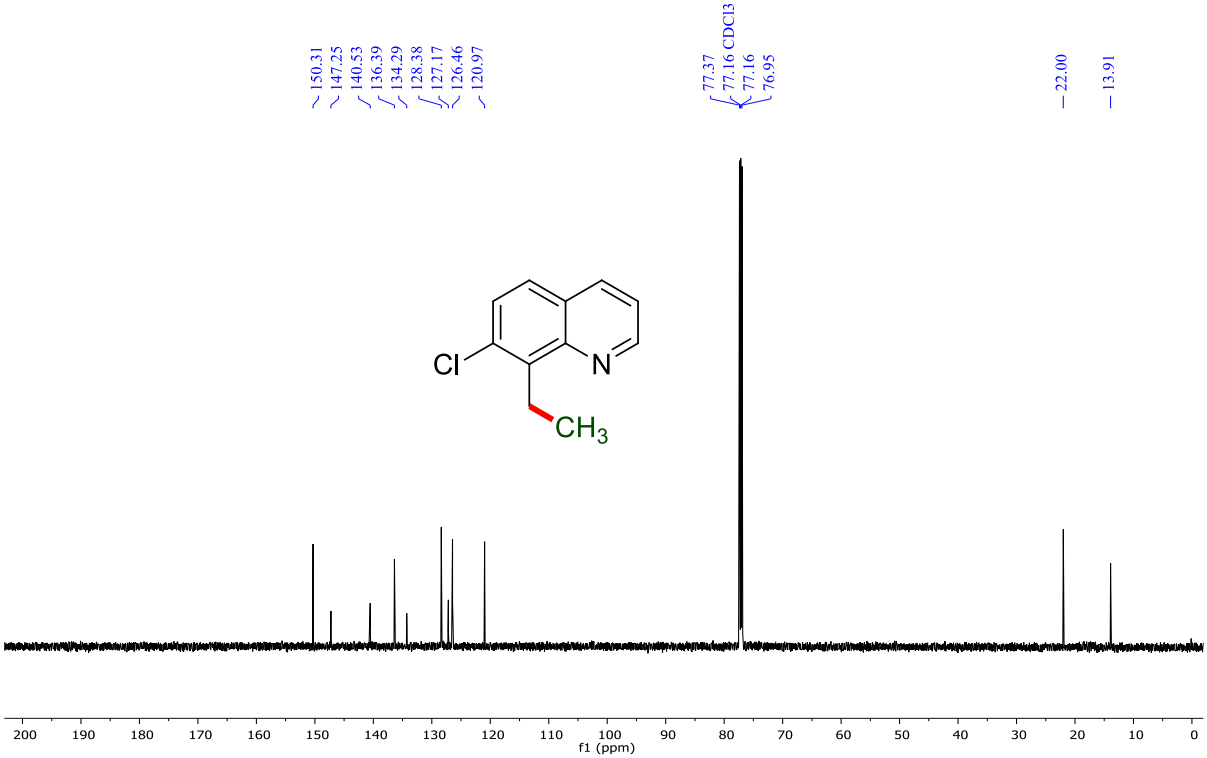


*7-chloro-8-ethylquinoline (Scheme 2, Entry **3j**)*

^{1}H NMR (600 MHz)

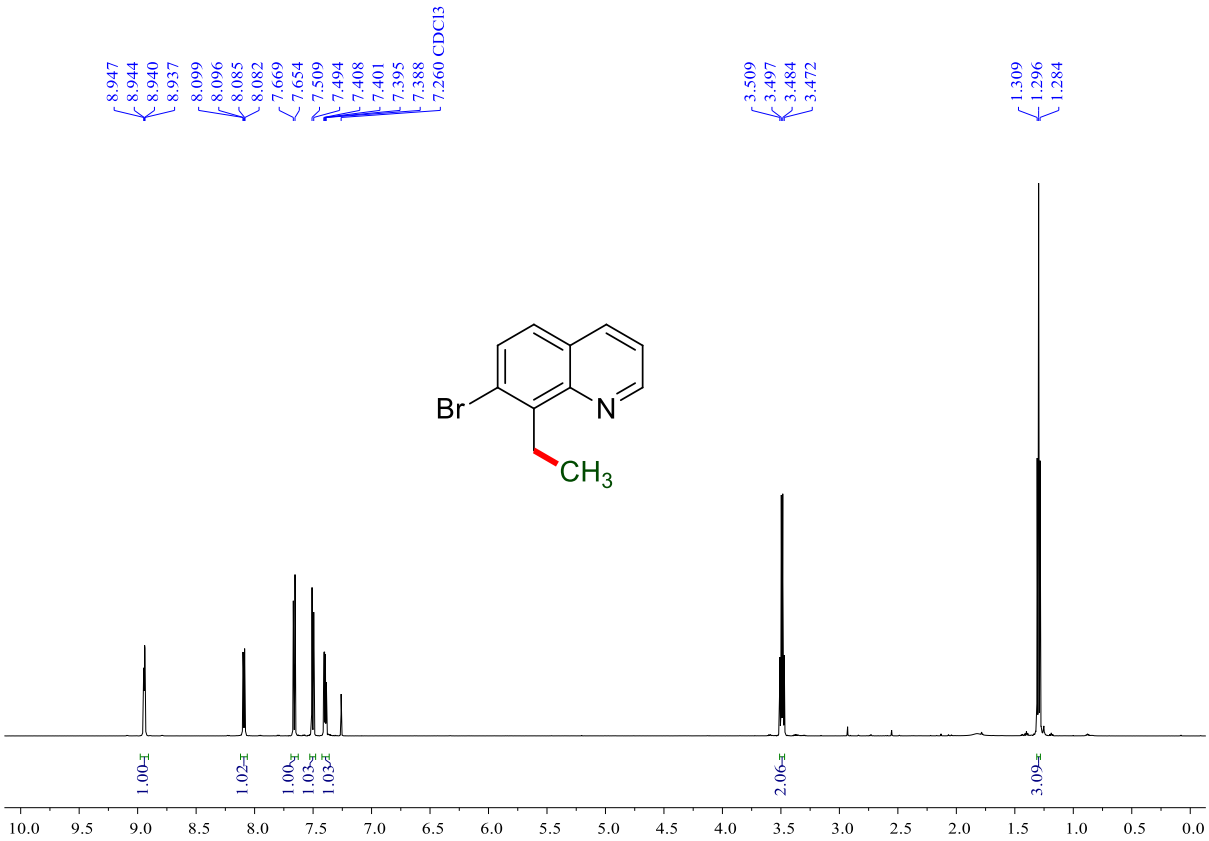


^{13}C NMR (150 MHz)

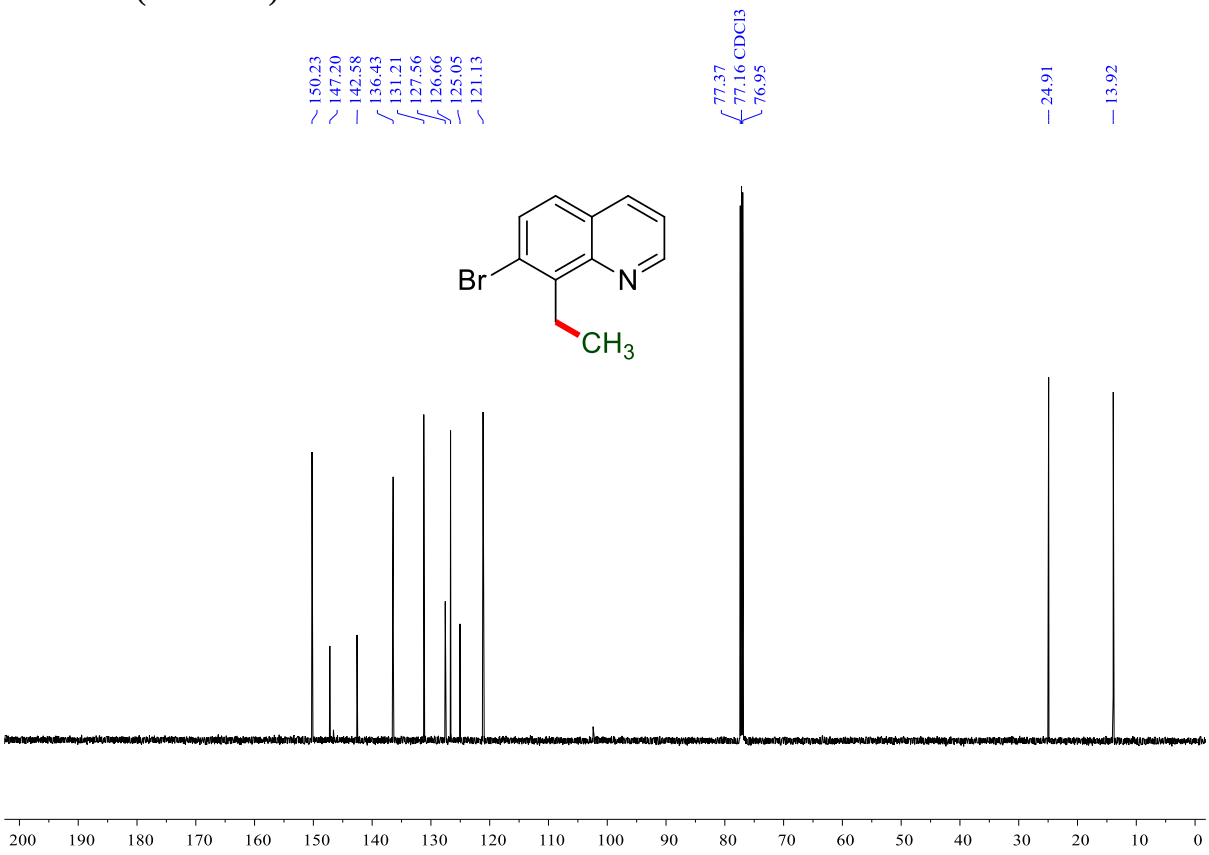


*7-bromo-8-ethylquinoline (Scheme 2, Entry **3k**)*

^{1}H NMR (600 MHz)

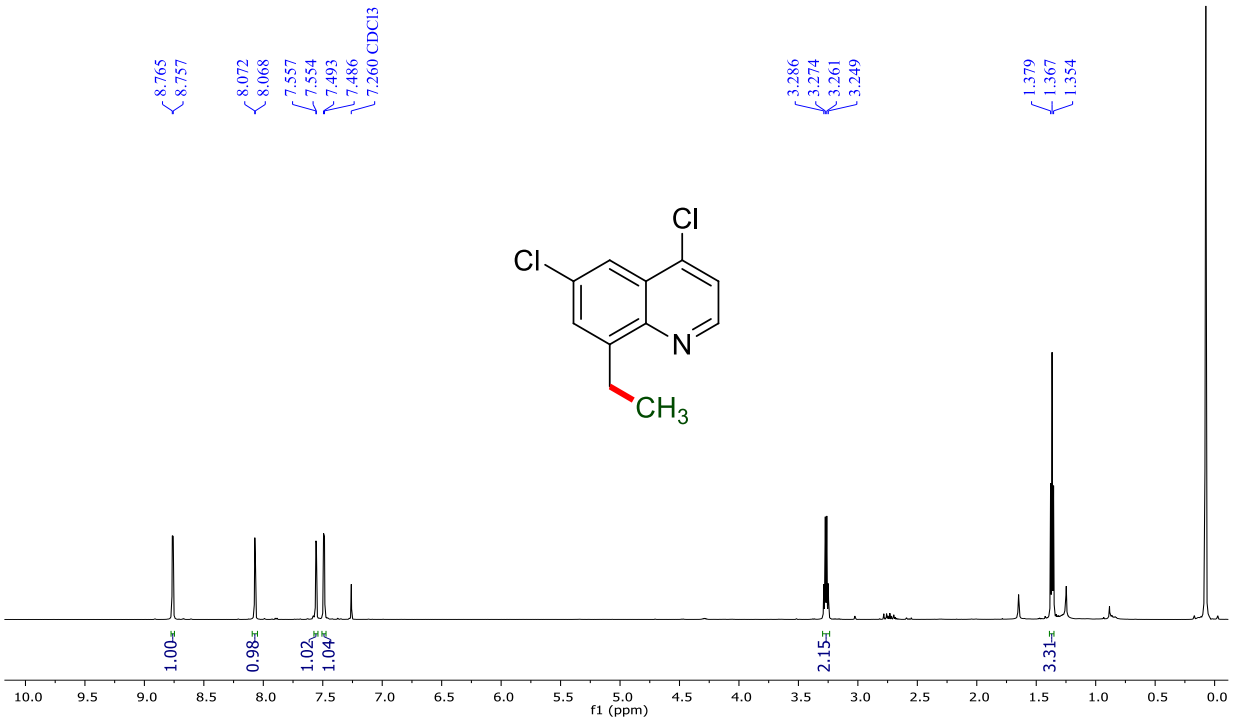


^{13}C NMR (150 MHz)

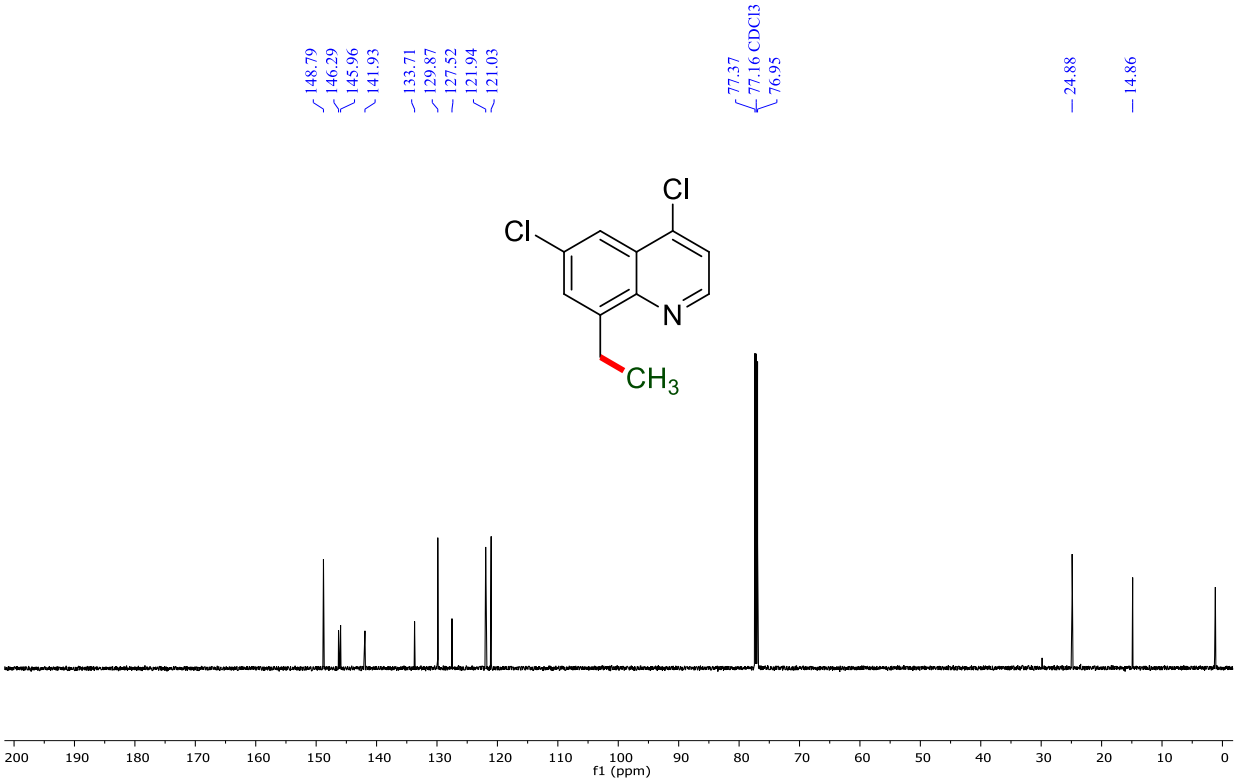


*4,6-dichloro-8-ethylquinoline (Scheme 2, Entry **3l**)*

^{1}H NMR (600 MHz)

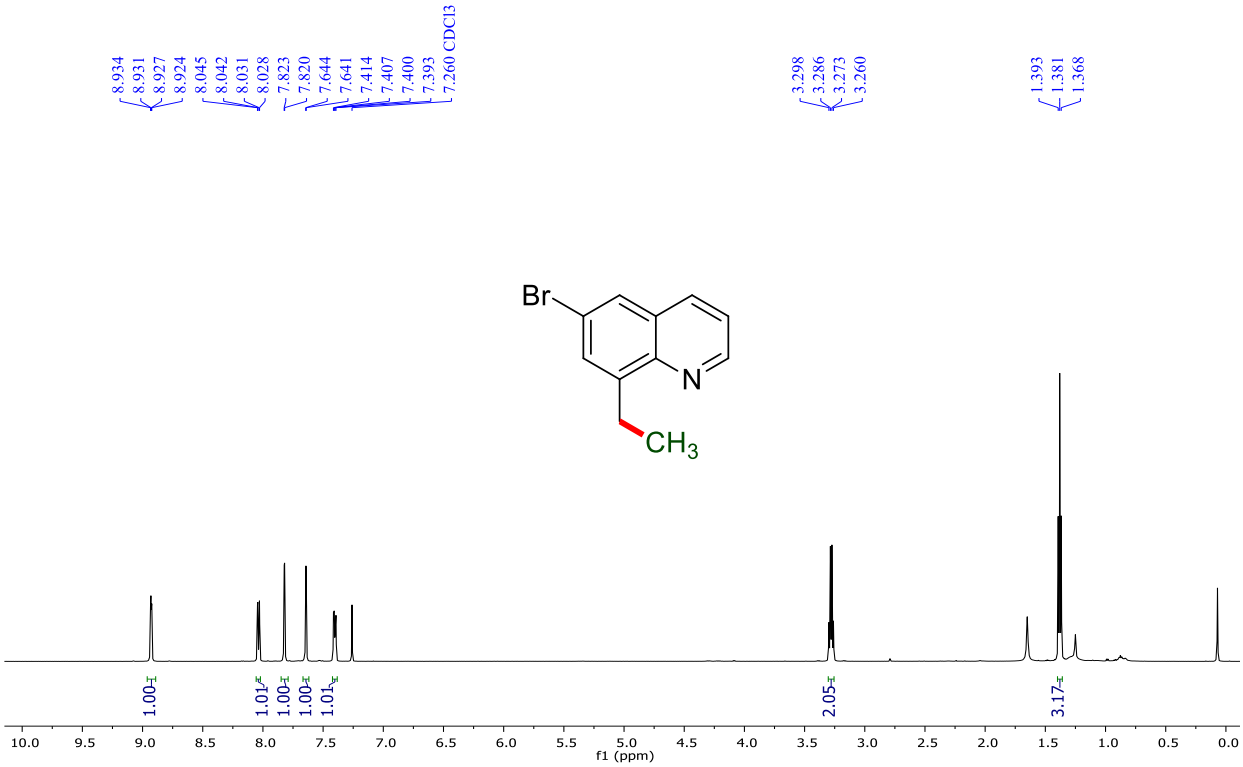


^{13}C NMR (150 MHz)

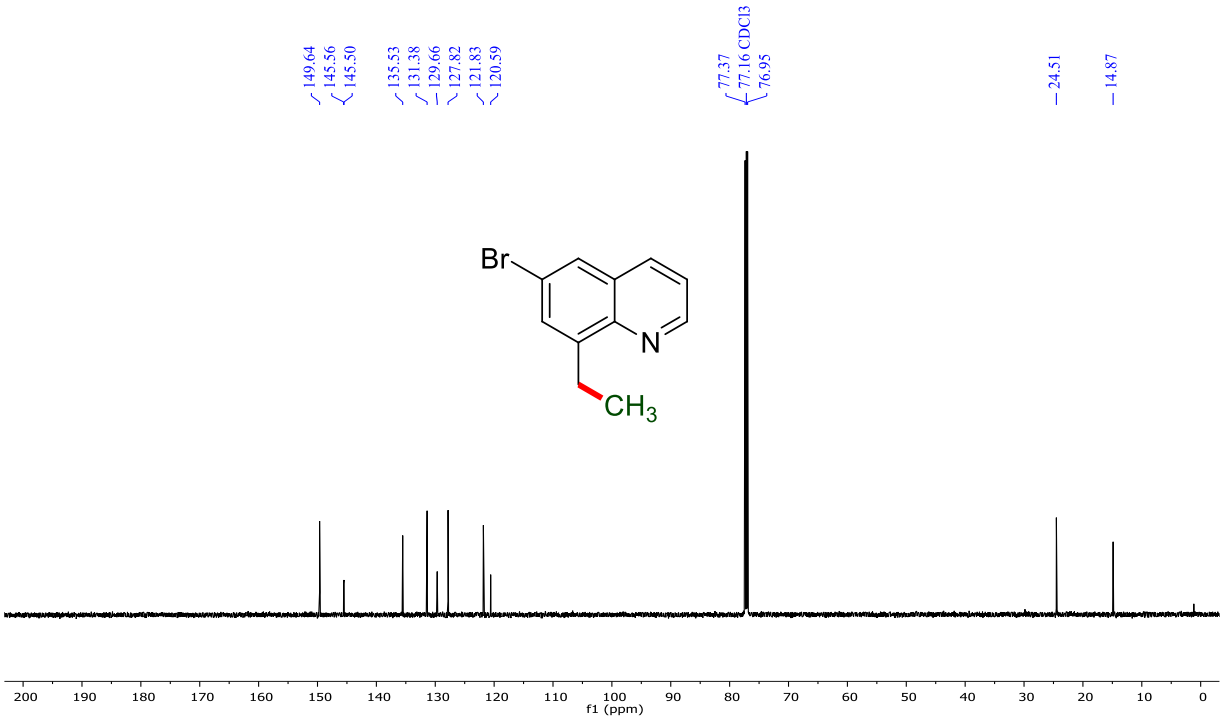


*6-bromo-8-ethylquinoline (Scheme 2, Entry **3m**)*

^{1}H NMR (600 MHz)

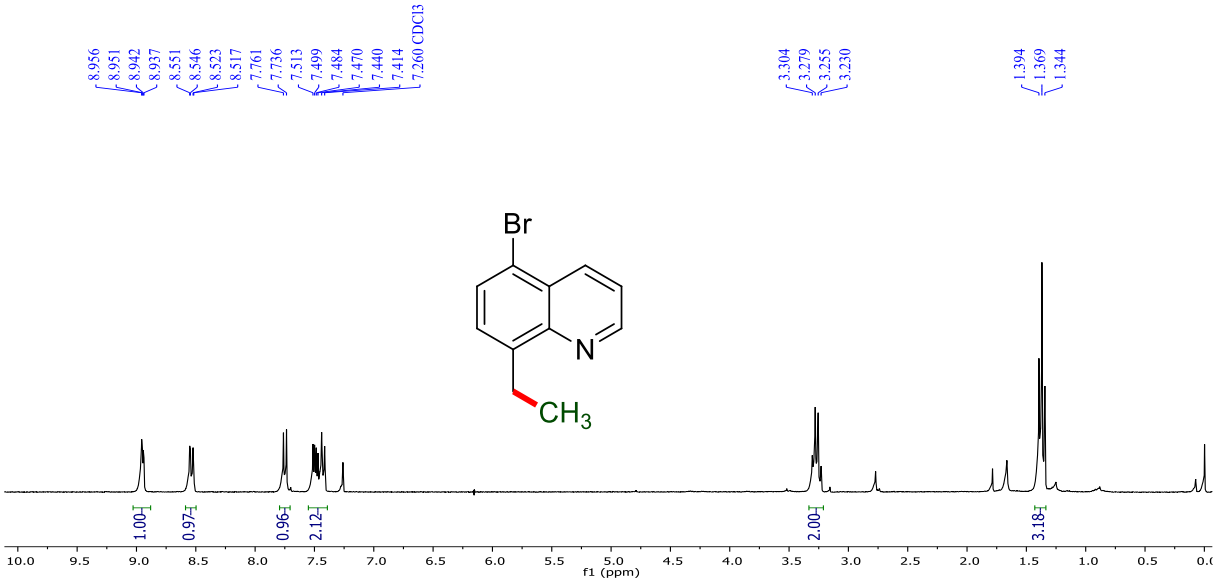


^{13}C NMR (150 MHz)

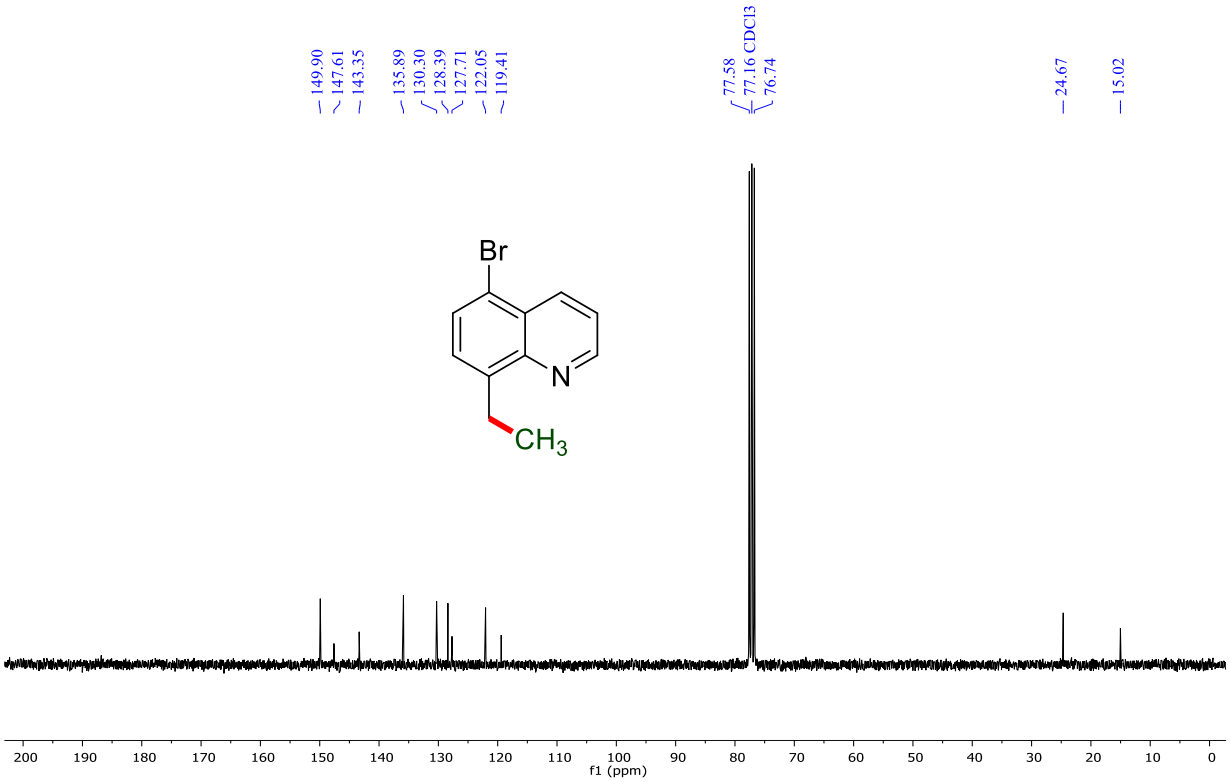


*5-bromo-8-ethylquinoline (Scheme 2, Entry **3n**)*

^{1}H NMR (300 MHz)

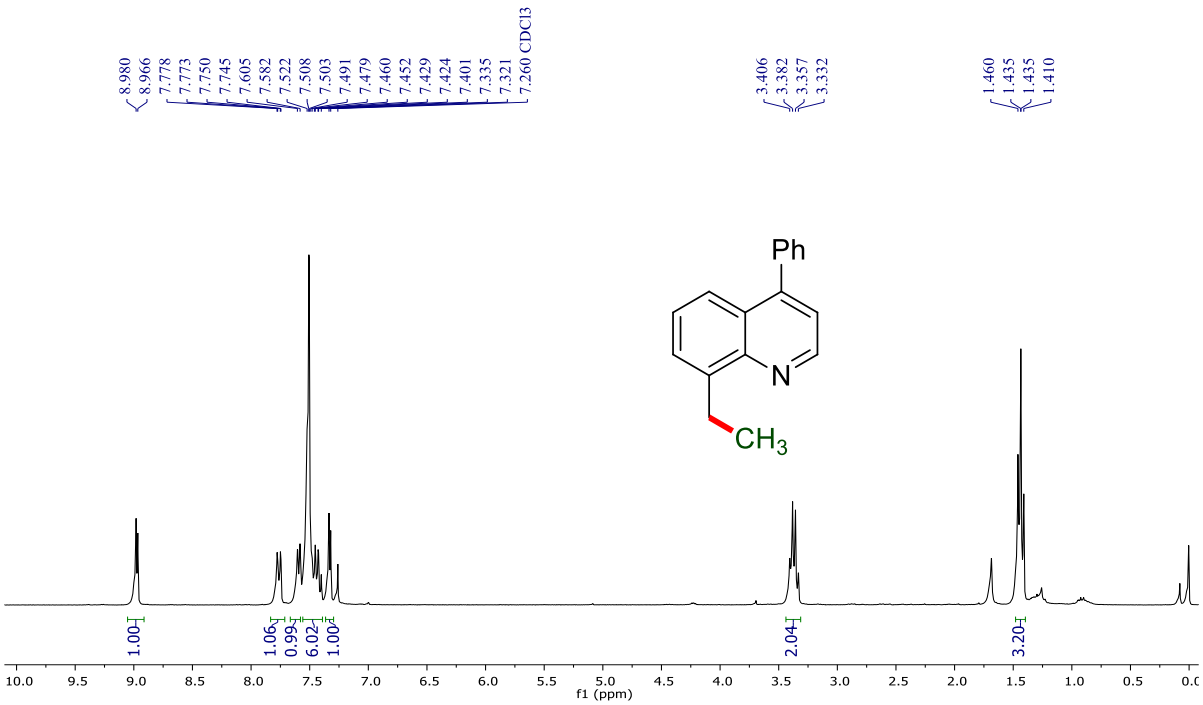


^{13}C NMR (75 MHz)

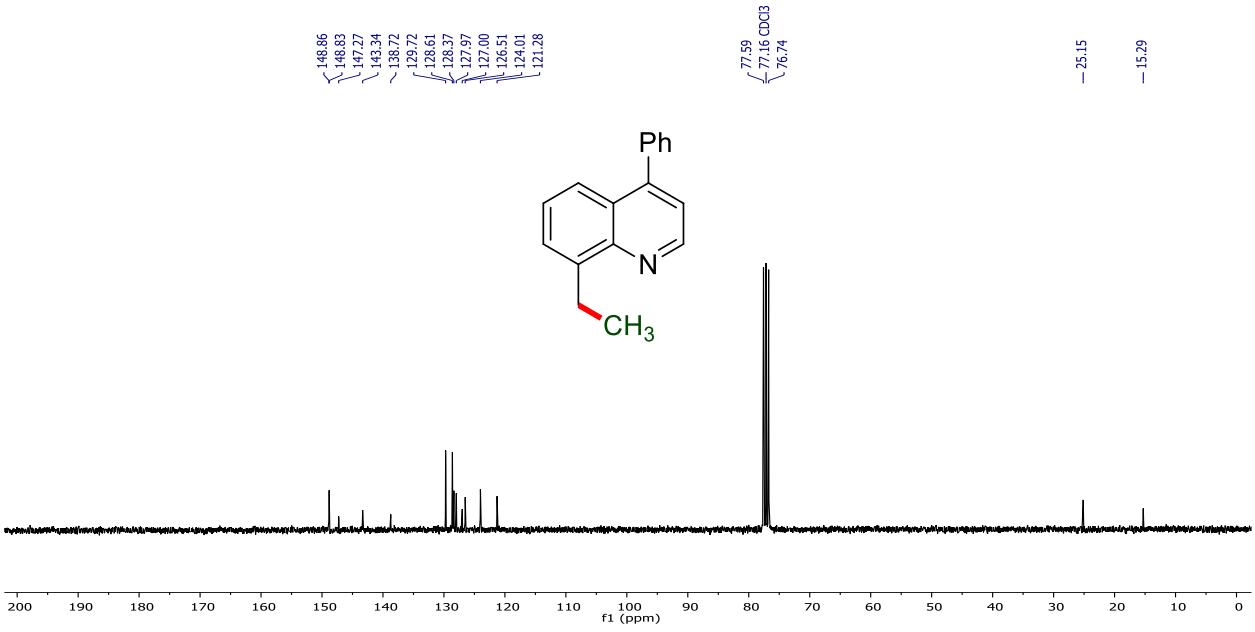


*8-ethyl-4-phenylquinoline (Scheme 2, Entry **3o**)*

^{1}H NMR (300 MHz)

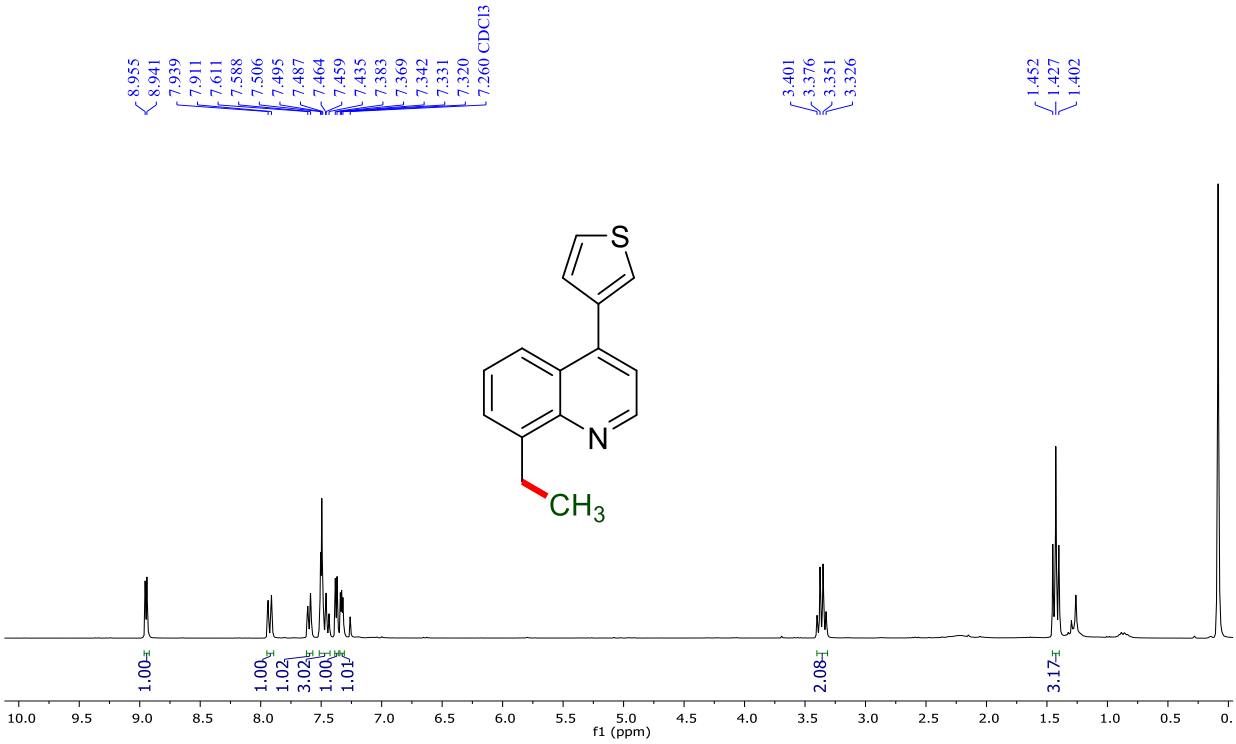


^{13}C NMR (75 MHz)

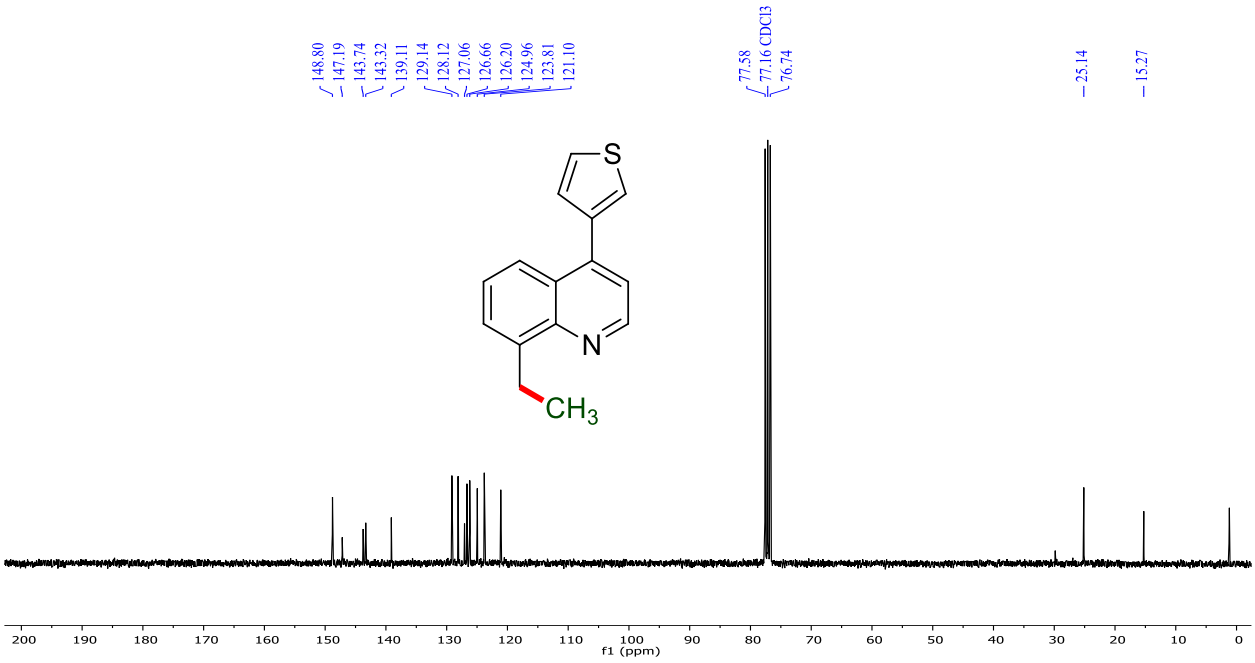


*8-ethyl-4-(thiophen-3-yl)quinoline (Scheme 2, Entry **3p**)*

^{1}H NMR (300 MHz)

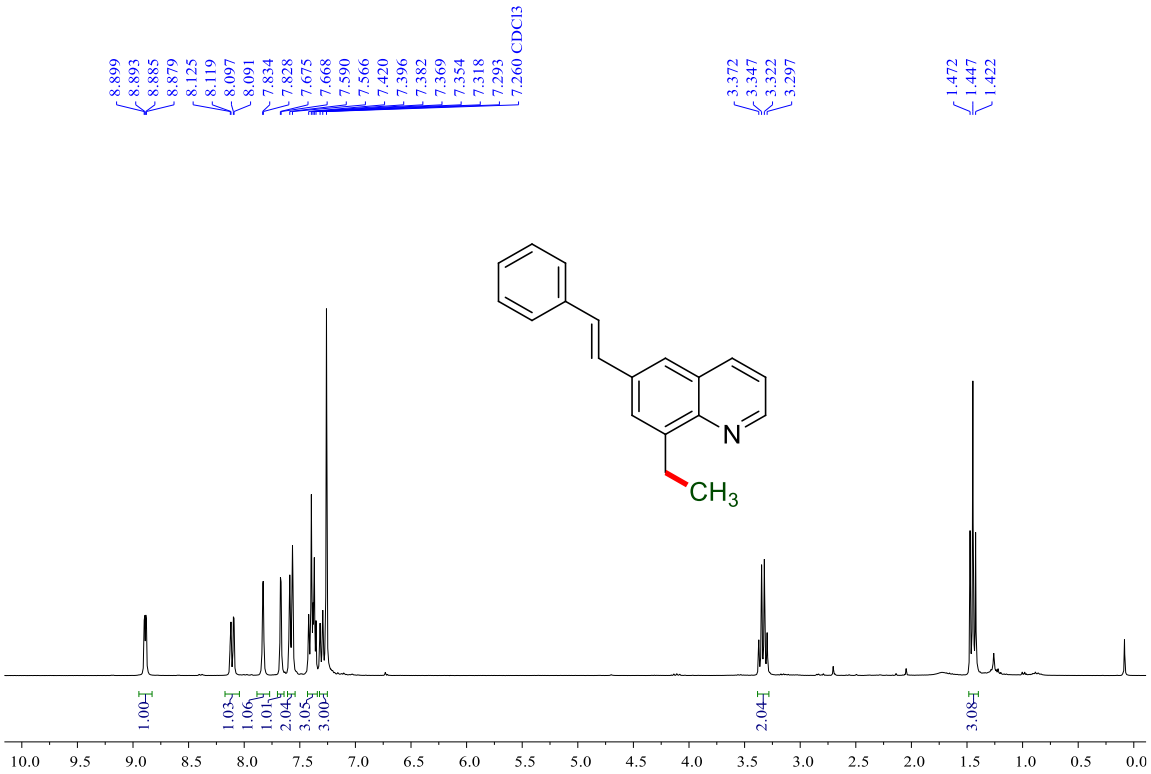


^{13}C NMR (75 MHz)

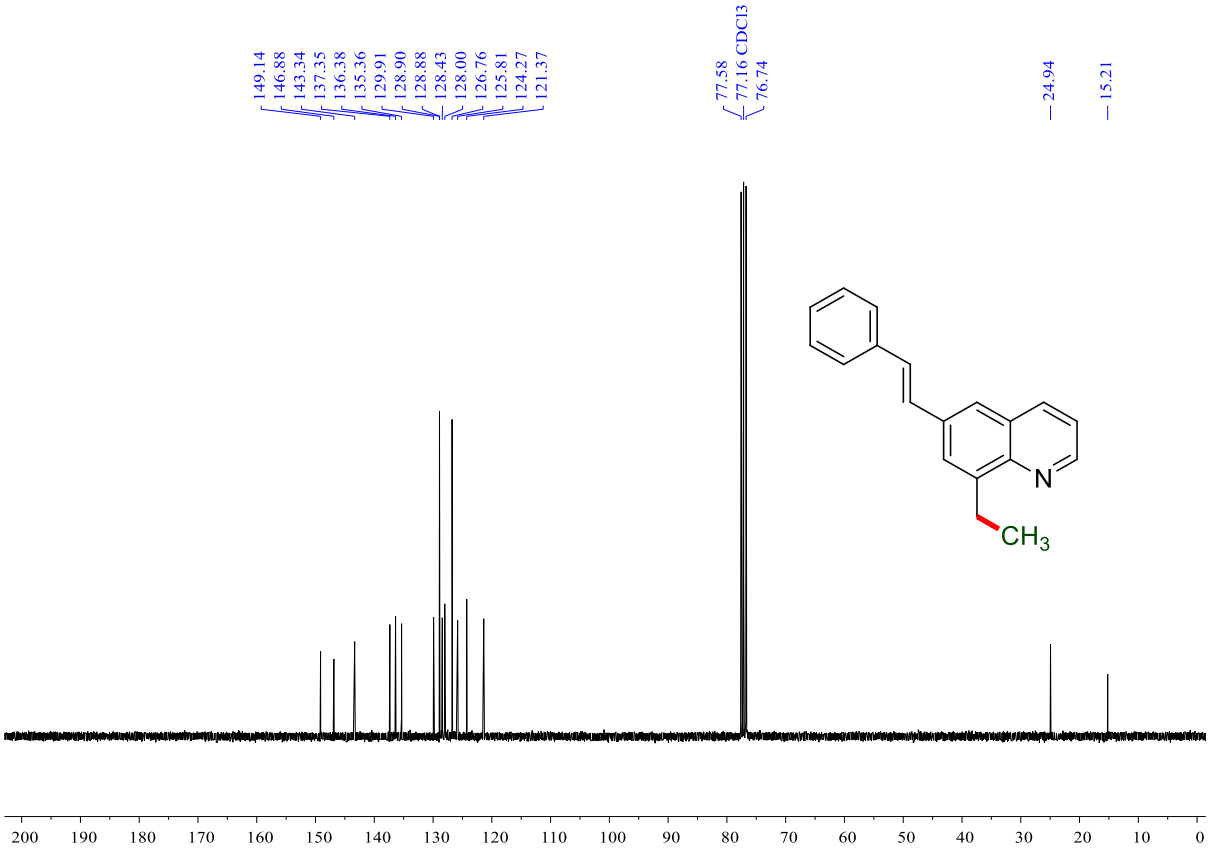


*(E)-8-ethyl-6-styrylquinoline (Scheme 2, Entry **3q**)*

^{1}H NMR (300 MHz)

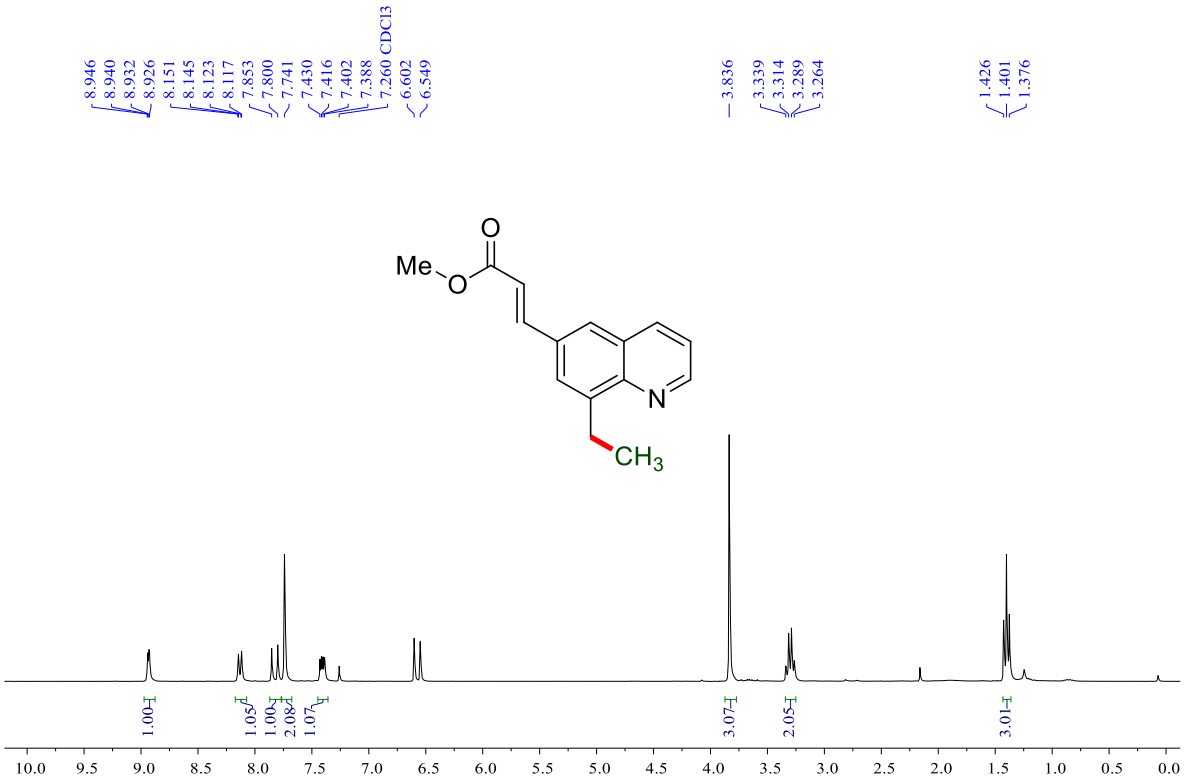


^{13}C NMR (75 MHz)

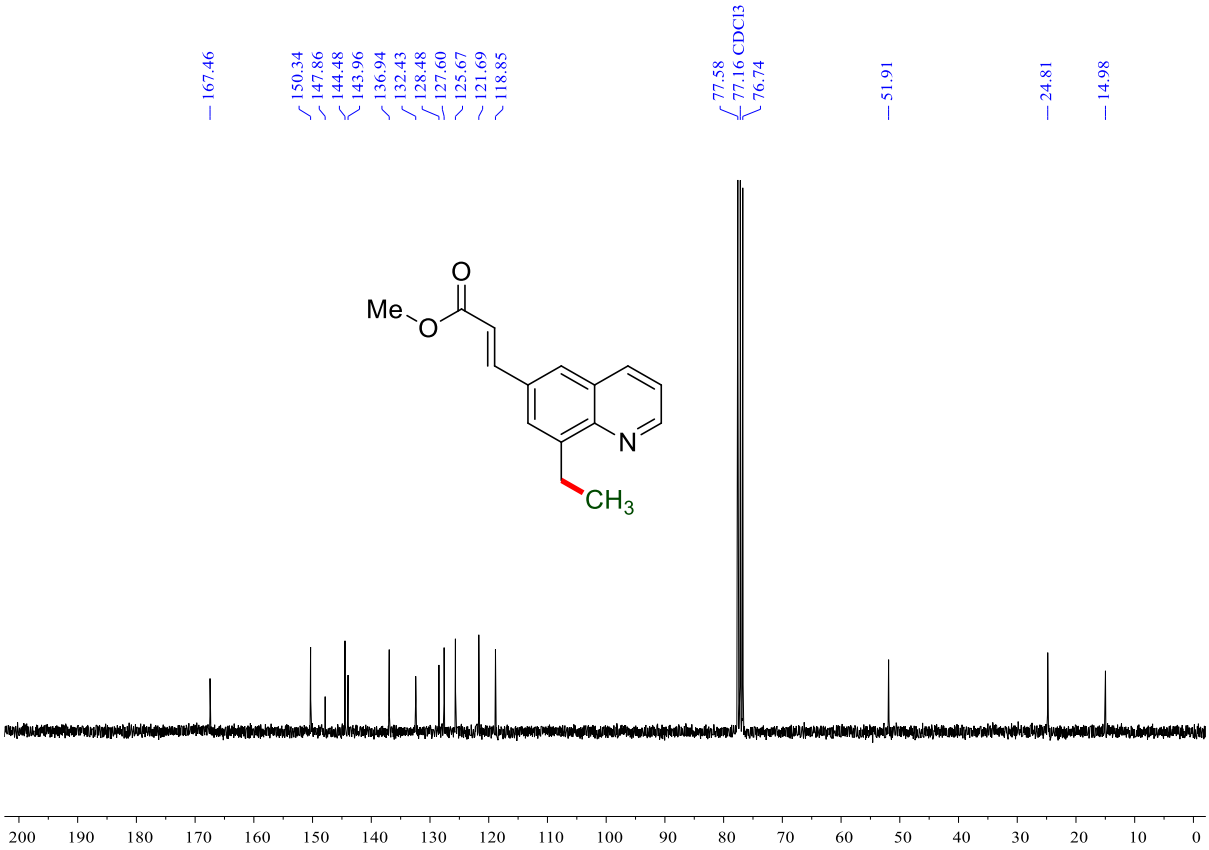


*(E)-methyl 3-(8-ethylquinolin-6-yl)acrylate (Scheme 2, Entry **3r**)*

^{1}H NMR (300 MHz)

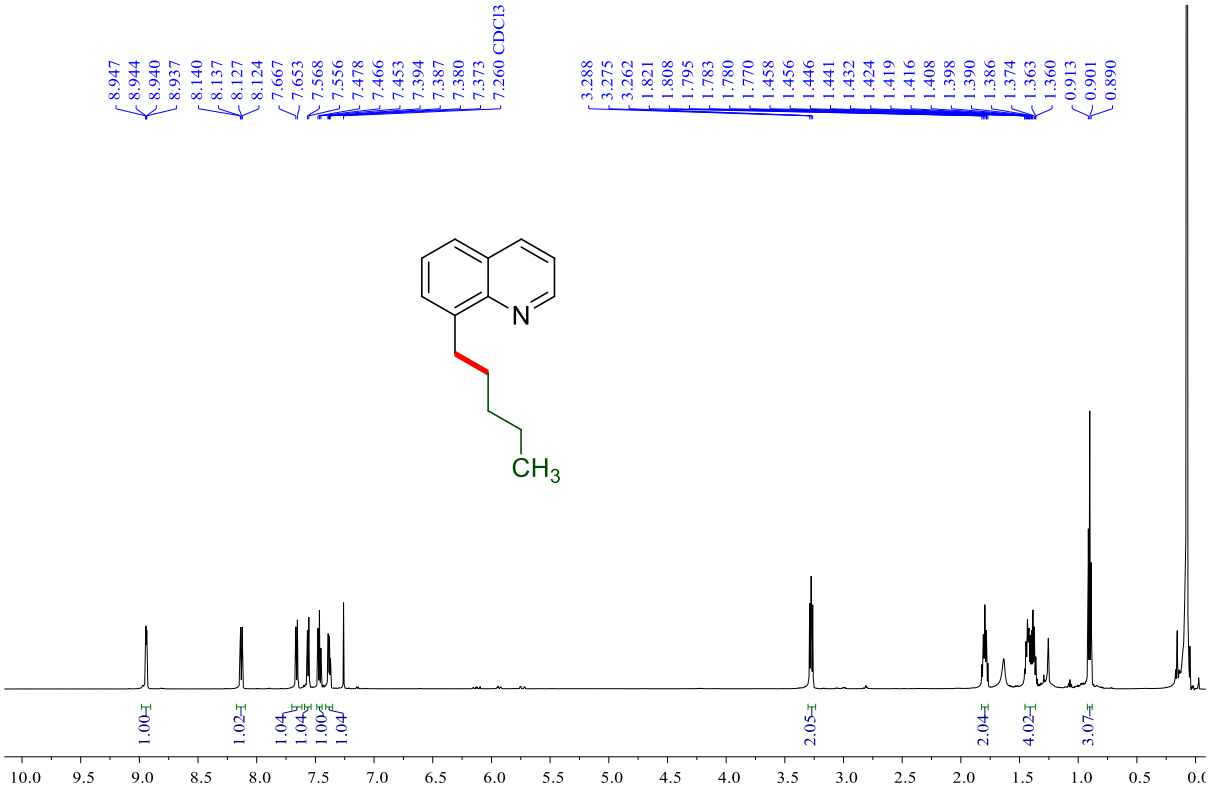


^{13}C NMR (75 MHz)



*8-pentylquinoline (Scheme 2, Entry **3s**)*

^{1}H NMR (600 MHz)



^{13}C NMR (150 MHz)