Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information:

Ni-Catalyzed Dehydrogenative Coupling of Primary and Secondary Alcohols with Methyl-*N*-Heteroaromatics

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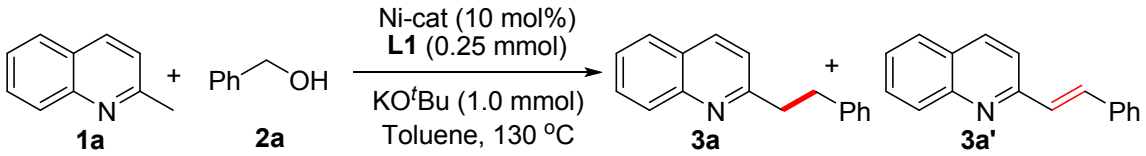
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. Unless otherwise stated reaction were conducted in flame-dried glassware under an atmosphere of nitrogen and commercially obtained reagent were used as received. All solvents were reagent grade or better. Toluene was refluxed over sodium/benzophenone, followed by distilled under argon atmosphere and stored over sodium. Chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated aluminium foil which was visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^1H NMR (500, 200 MHz), ^{13}C NMR (126, 50 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform ($CDCl_3$) was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.27 for ^1H (chloroform-d), δ 77.0 for $^{13}C\{^1H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; tt, triplet of triplet; td, triplet of doublet; q, quartet; br, broad; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

2. Optimization of the reaction condition

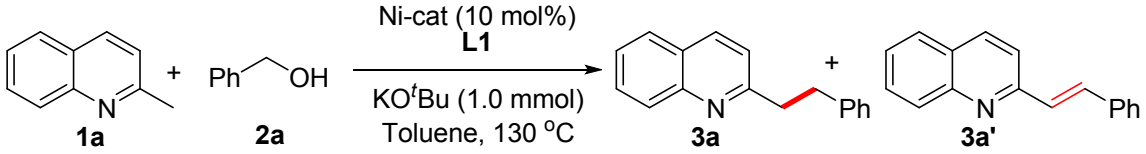
Table S1: Screening of catalyst[a,b]



Entry	Ni-Catalyst	Product	
		3a	**3a'**
1	$NiBr_2$+TMEDA(**L1**)	88	6
2	$NiCl_2$(DME)	72	25
3	$NiBr_2$	0	0
4	Nickel(II) bromide 2-methoxyethyl ether complex	65	25
5	Bis(cyclopentadienyl)nickel(II)	37	63

[a]Reaction conditions: **1a** (0.5 mmol), benzyl alcohol **2a** (1.5 mmol), Ni-catalyst (10 mol%), TMEDA (0.25 mmol), KO^{t}Bu (1.0 mmol) using 2 ml of toluene as solvent at 130 °C. [b]Conversion based on GC analysis using *m*-xylene as an internal standard.

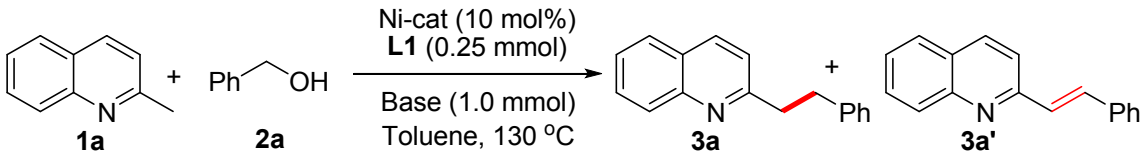
Table S2: Screening of Ni-catalyst and ligand ratio[a,b]



Entry	$NiBr_2$:**L1**	Product	
		3a	**3a'**
1	1:5	88	6
2	1:3	69	25
3	1:2	55	45
4	1:1	51	49

[a]Reaction conditions: **1a** (0.5 mmol), benzyl alcohol **2a** (1.5 mmol), Ni-catalyst (10 mol%), KO^{t}Bu (1.0 mmol) using 2 ml of toluene as solvent at 130 ^{o}C. [b]Conversion based on GC analysis using *m*-xylene as an internal standard.

Table S3: Screening of base[a,b]

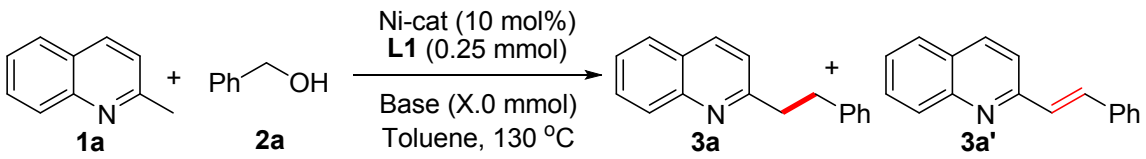


1a **2a** **3a** **3a'**

Entry	**Base**	**Product**	
		3a	**3a'**
1	KO^{t}Bu	88	6
2	LiO^{t}Bu	50	25
	NaO^{t}Bu	55	15
3	KOH	NR	NR
4	KHMDS	trace	trace
5	KH	NR	NR
6	K_2CO_3	NR	NR

[a]Reaction conditions: **1a** (0.5 mmol), benzyl alcohol **2a** (1.5 mmol), Ni-catalyst (10 mol%), TMEDA (0.25 mmol), base (1.0 mmol) using 2 mL of toluene as solvent at 130 ^{o}C. [b]Conversion based on GC analysis using *m*-xylene as an internal standard. NR = No reaction.

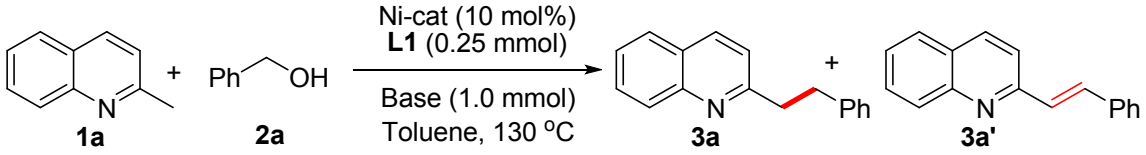
Table S4: Screening of amount of base amount[a,b]



Entry	**Base**	GC-Conversion	
		3a	**3a'**
1	KO^{t}Bu (2.0 equiv)	88	6
2	KO^{t}Bu (1.0 equiv)	56	34
3	KO^{t}Bu (0.5 equiv)	25	45
4	KO^{t}Bu (0.2 equiv)	NR	NR

[a]Reaction conditions: **1a** (0.5 mmol), benzyl alcohol **2a** (1.5 mmol), Ni-catalyst (10 mol%), TMEDA (0.25 mmol), using 2 ml of toluene as solvent at 130 °C. [b]Conversion based on GC analysis using *m*-xylene as an internal standard. NR = No reaction.

Table S5: Screening of alcohol amount[a,b]



Entry	Benzyl alcohol (**2a**, equiv)	GC-Conversion	
		3a	**3a'**
1	3	88	6
2	2	75	15
3	1	60	18

[a]Reaction conditions: **1a** (0.5 mmol), benzyl alcohol **2a**, Ni-catalyst (10 mol%), TMEDA (0.25 mmol), KO^{t}Bu (1.0 mmol) using 2 mL of toluene as solvent at 130 °C. [b]Conversion based on GC analysis using *m*-xylene as an internal standard.

3. General experimental procedure

In a 10 mL oven dried sealed tube, alcohol **2** (1.5 mmol), and methyl *N*-Heteroaromatics **1** (0.5 mmol), $NiBr_2$ (10 mol%), TMEDA (0.25 mmol) KO^{t}Bu (1.0 mmol) were added under an argon atmosphere in toluene (2.0 mL). The flask was sealed tightly with a teflon plug under an argon atmosphere, and the solution was stirred at 130^{o}C (oil bath temperature) for 24 h. Then the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The organic layer was combined, washed with brine (20 mL) and then dried over Na_2SO_4. After concentration under reduced pressure, the residue was purified by 230-400 mesh silica-gel column chromatography using petroleum ether/ethyl acetate (50/1) to afford the pure product **3**.

4. Mechanistic Studies

3a. Detection of H_2 gas liberation

In a 10 ml head space vial, **1a** (0.5 mmol), **2a (**1.5 mmol), $NiBr_2$ (10 mol%), TMEDA (0.25 mmol), KO^{t}Bu (1.0 mmol) were added under an argon atmosphere in toluene (2.0 mL). After 4 h of reaction, the gaseous phase of the crude reaction mixture was analyzed through gas phase GC analysis. The evolution of H_2 gas during the alkylation process was qualitatively observed using GC analysis which reveals the reaction takes place *via* Ni-catalyzed hydrogen auto-transfer pathway.

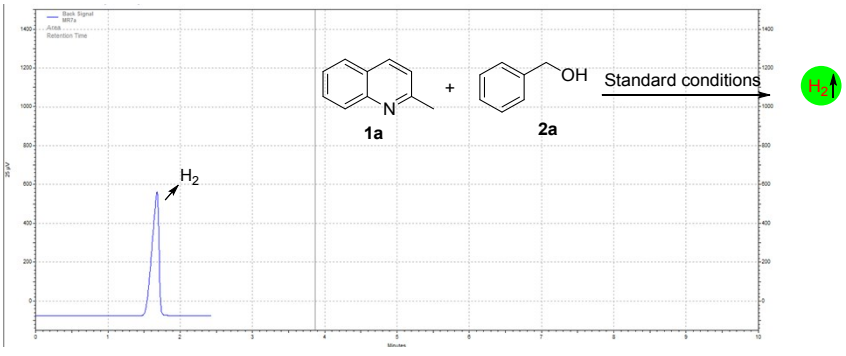
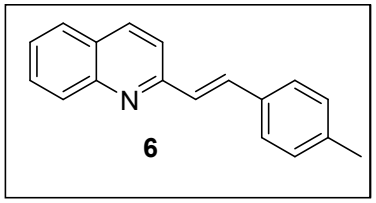


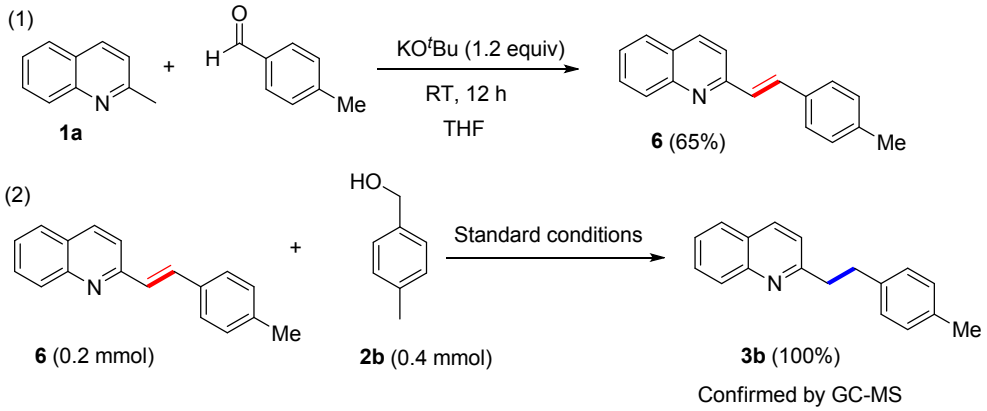
Figure S1. Gas phase GC for the identification of molecular hydrogen

3b. Intermediate Determination



(E)-2-(4-methylstyryl)quinoline (6)

To a reaction mixture of 2-methyl quinoline **1a** and KO^{t}Bu in THF, *p*-tolualdehyde was added slowly under argon atmosphere at room temperature. The reaction mixture was stirred for 12 h. The reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The organic layer was combined, washed with brine (20 mL) and then dried over Na_2SO_4. After concentration under reduced pressure, residue was purified by 230-400 mesh silica-gel column chromatography using petroleum ether/ethyl acetate (50/1) to afford the pure product **6** as colourless solid. Isolated yield: 65%. Next, α,β-unsaturated quinoline derivative **6** was applied under standard catalytic conditions in the presence of 4-methyl benzyl alcohol **2b** as hydrogen donor. The GC analysis of crude mixture showed the formation of alkylated quinoline derivative **3b** confirmed by GC-MS, which confirmed the formation of **6** as a key intermediate in the catalytic process.



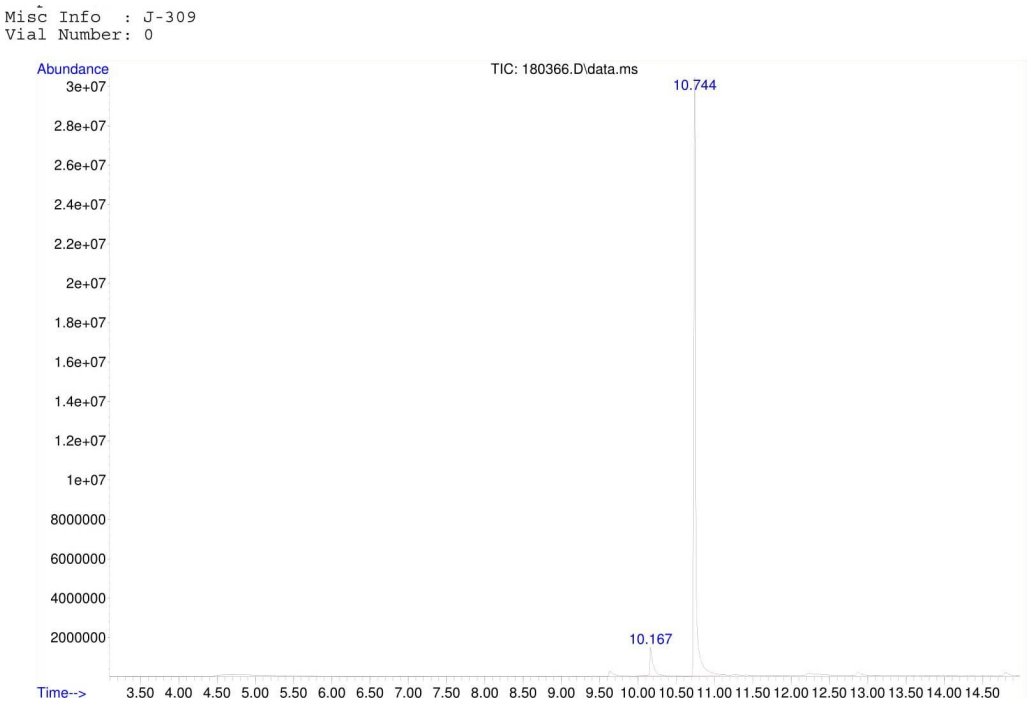


Figure S2.GC of the crude reaction mixture.

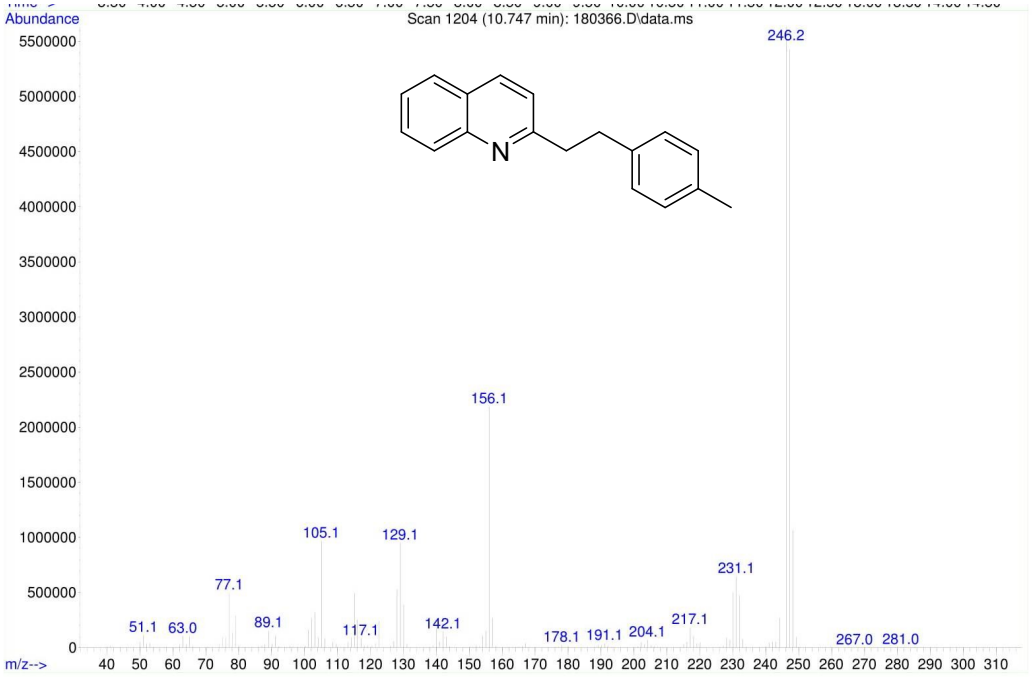
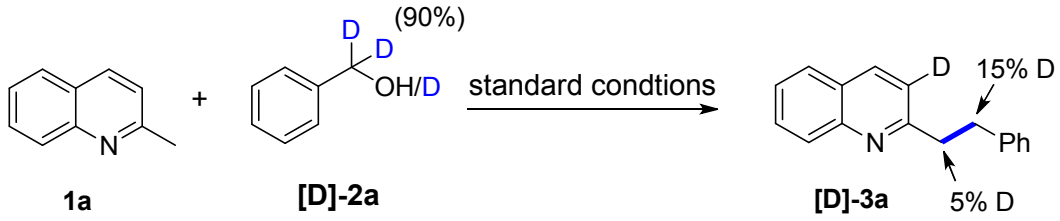


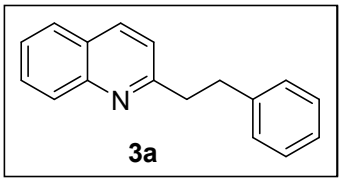
Figure S3.GC-MS data of the crude reaction mixture

3c. Deuterium experiment

a) To a 15 mL clean and oven-dried screw cap reaction tube, **1a** (0.3 mmol) and **2a-[d]** (90%) (0.3 mmol) were added under standard reaction conditions. Then the reaction was performed under standard condition for 24 h. The percentage of deuterium incorporation in the product was calculated based on NMR analysis.



5. Characterization data



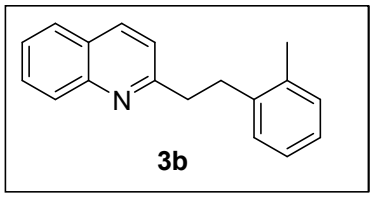
2-phenethylquinoline (3a)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 82%, 95 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.76-7.68 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.34-7.28 (m, 4H), 7.26-7.22 (m, 1H), 3.36-3.31 (m, 2H), 3.23-3.18 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 147.9, 141.5, 136.2, 129.4, 128.8, 128.5, 128.4, 127.5, 126.7, 125.9, 125.7, 121.5, 40.9, 35.9.

HRMS(EI) m/z Calcd for $C_{17}H_{16}N$ $[M+H]^+$: 234.1277; Found: 234.1279.



3b

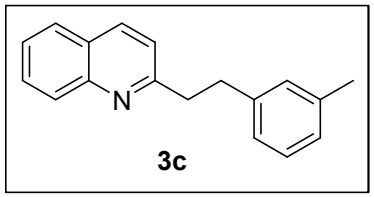
2-(2-methylphenethyl)quinoline (3b)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 69%, 85 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 6.7 Hz, 1H), 7.52 (t, *J* = 6.7 Hz, 1H), 7.25-7.21 (m, 2H), 7.20-7.14 (m, 3H), 3.30-3.26 (m, 2H), 3.19-3.15 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 147.9, 139.6, 136.1, 135.9, 130.1, 129.3, 128.9, 128.8, 127.5, 126.7, 126.1, 125.9, 125.7, 121.4, 39.6, 33.2, 19.3.

HRMS(EI) m/z Calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; Found: 248.1436.



3c

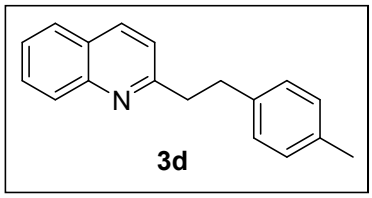
2-(3-methylphenethyl)quinoline (3c)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 71%, 87 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.05 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 6.7 Hz, 1H), 7.30-7.26 (m, 1H), 7.20 (t, *J* = 6.7 Hz, 1H), 7.15-7.03 (m, 3H), 3.37-3.28 (m, 2H), 3.20-3.11 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 147.9, 141.4, 137.9, 136.2, 129.4, 129.3, 128.8, 128.3, 127.5, 126.8, 126.7, 125.5, 121.5, 41.1, 35.9, 21.4.

HRMS(EI) m/z Calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; Found: 248.1436.



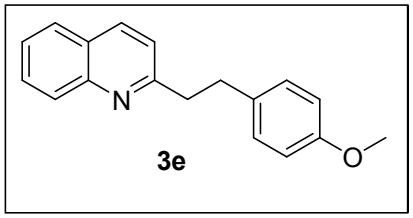
2-(4-methylphenethyl)quinoline (3d)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 73%, 90 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.20-8.09 (m, 2H), 7.90-7.74 (m, 2H), 7.62-7.54 (m, 1H), 7.36-7.20 (m, 1H), 7.26-7.05 (m, 4H), 3.42-3.31 (m, 2H), 3.27-3.12 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 161.8, 147.9, 138.3, 136.1, 135.3, 129.3, 128.9, 128.8, 128.3, 127.4, 126.7, 125.6, 121.5, 41.1, 35.4, 20.9.

HRMS(EI) m/z Calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; Found: 248.1436.



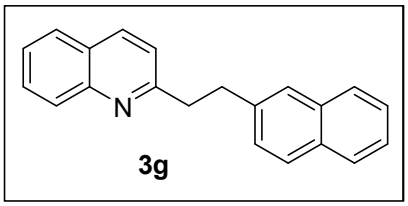
2-(4-methoxyphenethyl)quinoline (3e)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 70%, 92 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.13-8.05 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* =7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.31-3.26 (m, 2H), 3.15-3.10 (m, 2H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 161.9, 157.9, 147.9, 136.1, 133.6, 129.4, 129.3, 128.8, 127.5, 126.8, 125.7, 121.6, 113.8, 55.2, 41.3, 35.1.

HRMS(EI) m/z Calcd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383; Found: 264.1379.



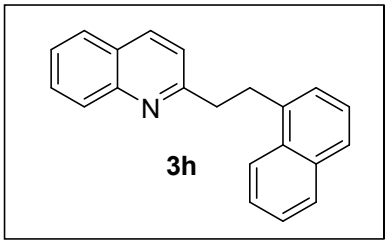
2-(2-(Naphthalen-2-yl)ethyl)quinoline (3g)

The general procedure was followed to afford the title compound as pale yellow solid, isolated yield: 91%, 128 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.93-7.68 (m, 6H), 7.60-7.37 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 1H), 3.40 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 147.9, 138.9, 136.2, 133.6, 132.0, 129.4, 128.8, 127.9, 127.6, 127.5, 127.4, 127.3, 126.8, 126.5, 125.8, 125.7, 125.2, 121.5, 40.8, 36.0.

HRMS(EI) m/z Calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1434; Found: 284.1433.



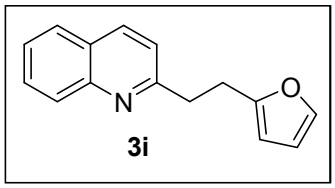
2-(2-(Naphthalen-1-yl)ethyl)quinoline (3h)

The general procedure was followed to afford the title compound as pale yellow solid, isolated yield: 83%, 117 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26-8.11 (m, 2H), 8.03(d, *J* = 8.3 Hz, 1H), 7.95-7.85 (m, 1H), 7.84-7.69 (m, 3H), 7.62-7.47 (m, 3H), 7.43-7.35 (m, 2H), 7.22 (d, *J* = 6.8 Hz, 1H), 3.70-3.63 (m, 2H), 3.51-3.39 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 148.0, 137.5, 136.1, 133.8, 131.8, 129.4, 128.9, 128.8, 127.5, 126.8, 126.1, 125.9, 125.7, 125.5, 125.4, 123.7, 121.5, 40.0, 32.9.

HRMS(EI) m/z Calcd for $C_{21}H_{18}N$ $[M+H]^+$: 284.1434; Found: 284.1433.



3i

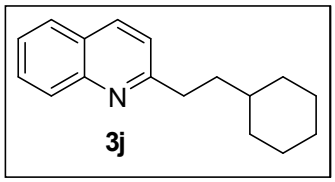
2-(2-(furan-2-yl)ethyl)quinoline (3i)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 72%, 80 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.83(d, *J* = 8.8 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.39-7.29 (m, 2H), 6.30 (br, 1H), 6.04 (br, 1H), 3.37 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 140.9, 136.3, 129.4, 128.8, 127.5, 126.8, 125.9, 121.3, 110.1, 105.4, 37.4, 27.9.

HRMS(EI) m/z Calcd for $C_{15}H_{14}ON$ $[M+H]^+$: 224.1070; Found: 224.1069.



3j

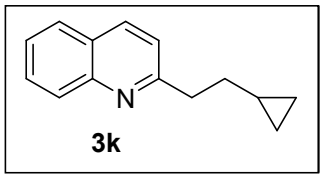
2-(2-cyclohexylethyl)naphthalene (3j)

The general procedure was followed to afford the title compound as colorless liquid, isolated yield: 71%, 85 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-7.97 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.85-7.61 (m, 2H), 7.54-7.41 (m, 1H), 7.33-7.25 (m, 1H), 3.07-2.87 (m, 2H), 1.88-1.64 (m, 7H), 1.46-1.10 (m, 4H), 1.07-0.85 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 147.9, 136.2, 129.3, 128.8, 127.5, 126.7, 125.6, 121.4, 37.8, 37.7, 36.9, 33.3, 26.7, 26.4.

HRMS(EI) m/z Calcd for $C_{17}H_{22}N$ $[M+H]^+$: 240.1747; Found: 240.1746.



3k

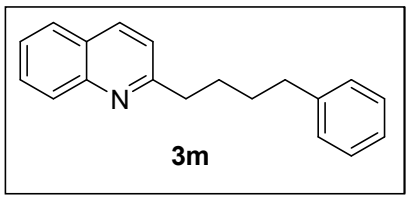
2-(2-cyclopropylethyl)quinoline (3k)

The general procedure was followed to afford the title compound as colorless liquid, isolated yield: 70%, 69 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.80-7.62 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 3.08 (t, *J* = 7.8 Hz, 2H), 1.72 (q, *J* = 7.4 Hz, 2H), 0.85-0.67 (m, 1H), 0.51-0.35 (m, 2H), 0.12-0.03 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 147.9, 136.0, 129.3, 128.8, 127.4, 126.7, 125.6, 121.5, 39.3, 35.0, 10.9, 4.6.

HRMS(EI) m/z Calcd for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277; Found: 198.1179.



3m

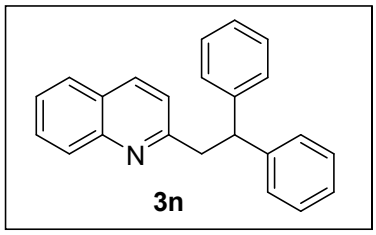
2-(4-phenylbutyl)quinoline (3m)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 68%, 89 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.34-7.13 (m, 6H), 3.00 (t, *J* = 8.5 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.87 (pent, *J* = 8.5 Hz, 2H), 1.75 (pent, *J* = 7.6 Hz, 2H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 147.9, 142.4, 136.2, 129.3, 128.8, 128.4, 128.2, 127.4, 126.7, 125.6, 121.3, 39.1, 35.8, 31.3, 29.6.

HRMS(EI) m/z Calcd for $C_{19}H_{20}N$ $[M+H]^+$: 262.1590; Found: 262.1589.



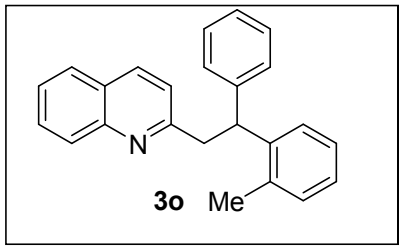
2-(2,2-diphenylethyl)quinoline (3n)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 45%, 69 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.76-7.63 (m, 2H), 7.48-7.32 (m, 6H), 7.24-7.12 (m, 5H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.73 (t, *J* = 7.8 Hz, 1H), 3.74 (d, *J* = 8.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 147.9, 144.3, 135.8, 129.3, 128.8, 128.5, 128.4, 128.1, 127.6, 127.5, 126.6, 126.2, 125.8, 122.1, 51.1, 44.9.

HRMS(EI) m/z Calcd for $C_{23}H_{20}N$ $[M+H]^+$: 310.1590; Found: 310.1591.



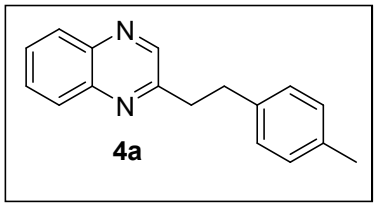
2-(2-phenyl-2-*o*-tolylethyl)quinoline (3o)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 42%, 68 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.69 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.53-7.46 (m, 2H), 7.24-7.18 (m, 5H), 7.16-7.05 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 4.96 (t, *J* = 7.8 Hz, 1H), 3.72 (d, *J* = 7.8 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 147.9, 143.9, 142.1, 136.4, 135.6, 130.4, 129.2, 128.9, 128.2, 128.1, 127.4, 126.9, 126.7, 126.1, 126.0, 125.9, 125.7, 122.0, 46.8, 45.4, 19.8.

HRMS(EI) m/z Calcd for $C_{24}H_{22}N$ $[M+H]^+$: 324.1747; Found: 324.1749.



4a

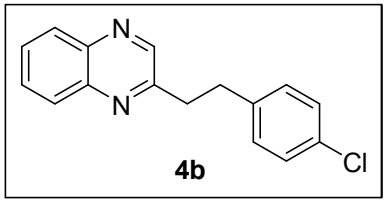
2-(4-methylphenethyl)quinoxaline (4a)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 78%, 97 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.13-8.03 (m, 2H), 7.82-7.68 (m, 2H), 7.20-7.01 (m, 4H), 3.39-3.27 (m, 2H), 3.21-3.09 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 156.6, 145.9, 142.3, 141.3, 137.6, 135.8, 129.9, 129.2, 129.0, 128.9, 128.4, 38.3, 34.9, 21.0.

HRMS(EI) m/z Calcd for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; Found: 249.1385.



4b

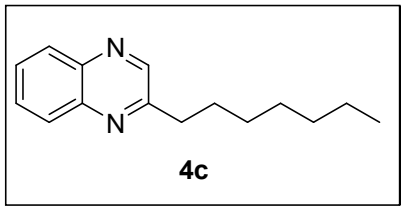
2-(4-chlorophenethyl)quinoxaline (4b)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 71%, 95 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.15-8.02 (m, 2H), 7.81-7.65 (m, 2H), 7.31-7.15 (m, 4H), 3.40-3.27 (m, 2H), 3.16-3.11 (m, 2H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 156.4, 145.8, 142.2, 141.3, 140.7, 129.9, 129.2, 129.0, 128.9, 128.5, 128.4, 126.2, 38.1, 35.2.

HRMS(EI) m/z Calcd for $C_{16}H_{14}N_2Cl$ $[M+H]^+$: 269.0840; Found: 269.0838.



4c

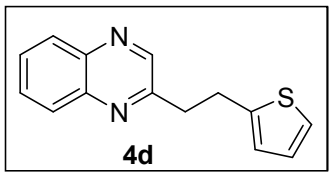
2-heptylquinoxaline (4c)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 70%, 80 mg.

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.12-8.01 (m, 2H), 7.79-7.62 (m, 2H), 3.01 (t, *J* = 8.1 Hz, 2H), 1.94-1.77 (m, 2H), 1.48-1.17 (m, 8H), 0.93-0.77 (m, 3H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 157.7, 145.8, 142.2, 141.2, 129.9, 129.2, 128.9, 36.5, 31.7, 29.5, 29.4, 29.1, 22.6, 14.0.

HRMS(EI) m/z Calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1699; Found: 229.1698.



4d

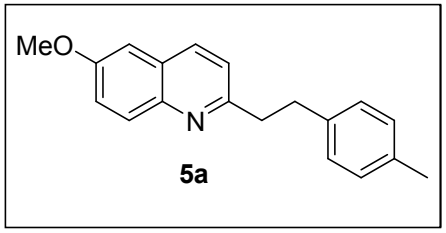
2-(2-(thiophen-2-yl)ethyl)quinoxaline (4d)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 62%, 74 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.6 (s, 1H), 8.07- 8.05 (m, 2H), 7.77-7.68 (m, 2H), 7.11 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.3 Hz, 1H), 6.80 (dd, *J* = 3.3, 1.0 Hz, 1H), 3.45-3.41 (m, 2H), 3.36-3.34 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 145.6, 143.2, 142.1, 141.2, 129.9, 129.1, 129.0, 128.8, 126.7, 124.7, 123.4, 38.0, 28.9.

HRMS(EI) m/z Calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.0794; Found: 241.0793.



5a

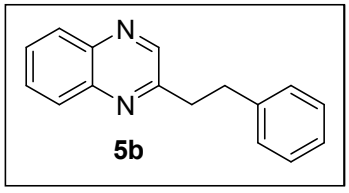
6-methoxy-2-(4-methylphenethyl)quinoline (5a)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 81%, 112 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.93 (m, 2H), 7.37 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 2.8 Hz, 1H), 3.93 (s, 3H), 3.27-3.22 (m, 2H), 3.14-3.09 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 157.2, 144.0, 138.5, 135.4, 134.9, 130.3, 129.0, 128.4, 127.6, 121.8, 121.7, 105.2, 55.5, 40.8, 35.6, 20.9.

HRMS(EI) m/z Calcd for $C_{19}H_{20}ON$ $[M+H]^+$: 278.1539; Found: 278.1542.



5b

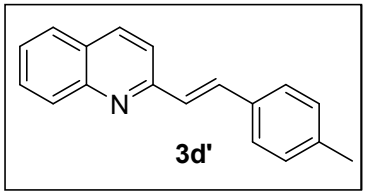
2-phenethylquinoxaline (5b)

The general procedure was followed to afford the title compound as pale yellow liquid, isolated yield: 86%, 100 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.14-8.01 (m, 2H), 7.81-7.65 (m, 2H), 7.31-7.15 (m, 5H), 3.40-3.27 (m, 2H), 3.24-3.11 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 145.8, 142.2, 141.2, 140.7, 129.9, 129.2, 129.0, 128.9, 128.5, 128.4, 126.2, 38.1, 35.2.

HRMS(EI) m/z Calcd for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230; Found: 235.1229.

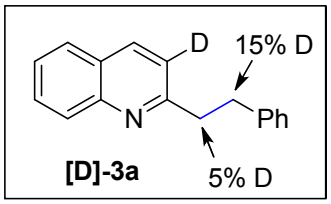


(*E*)-2-(4-methylstyryl)quinoline

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 3H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 16.3 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 2.40 (s, 3H).

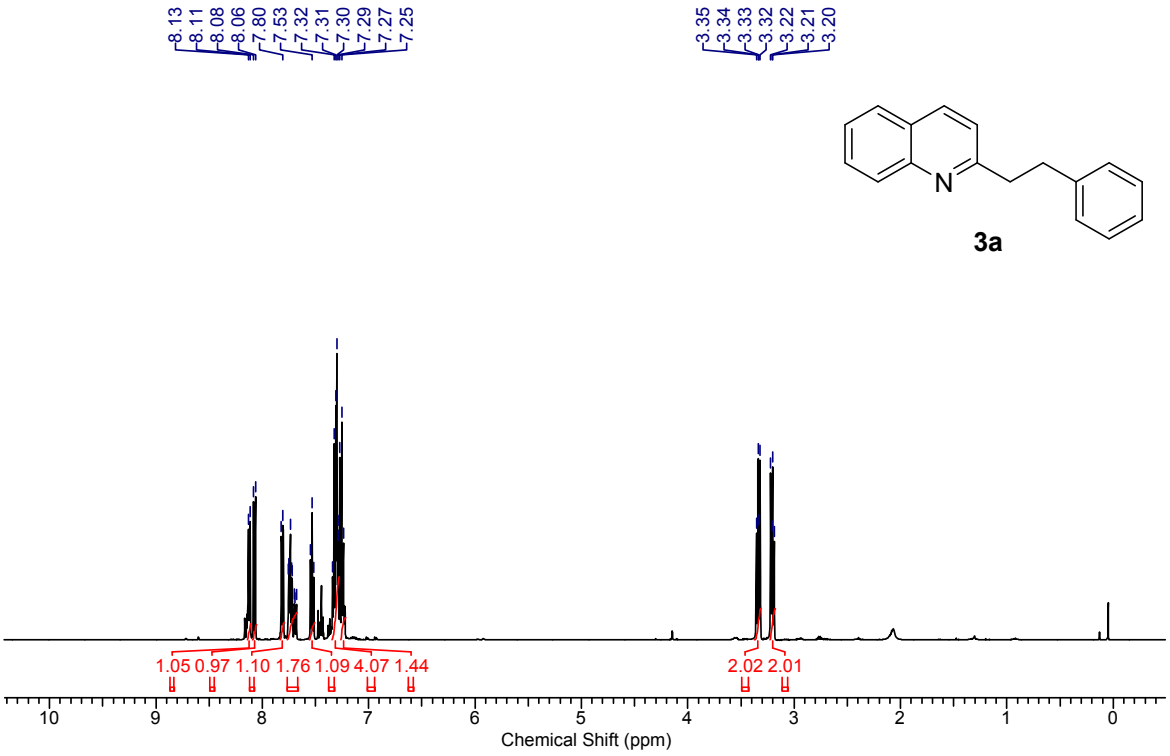
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 148.2, 138.7, 136.3, 134.4, 133.7, 129.7, 129.5, 129.1, 127.9, 127.5, 127.2, 126.0, 119.2, 21.4.

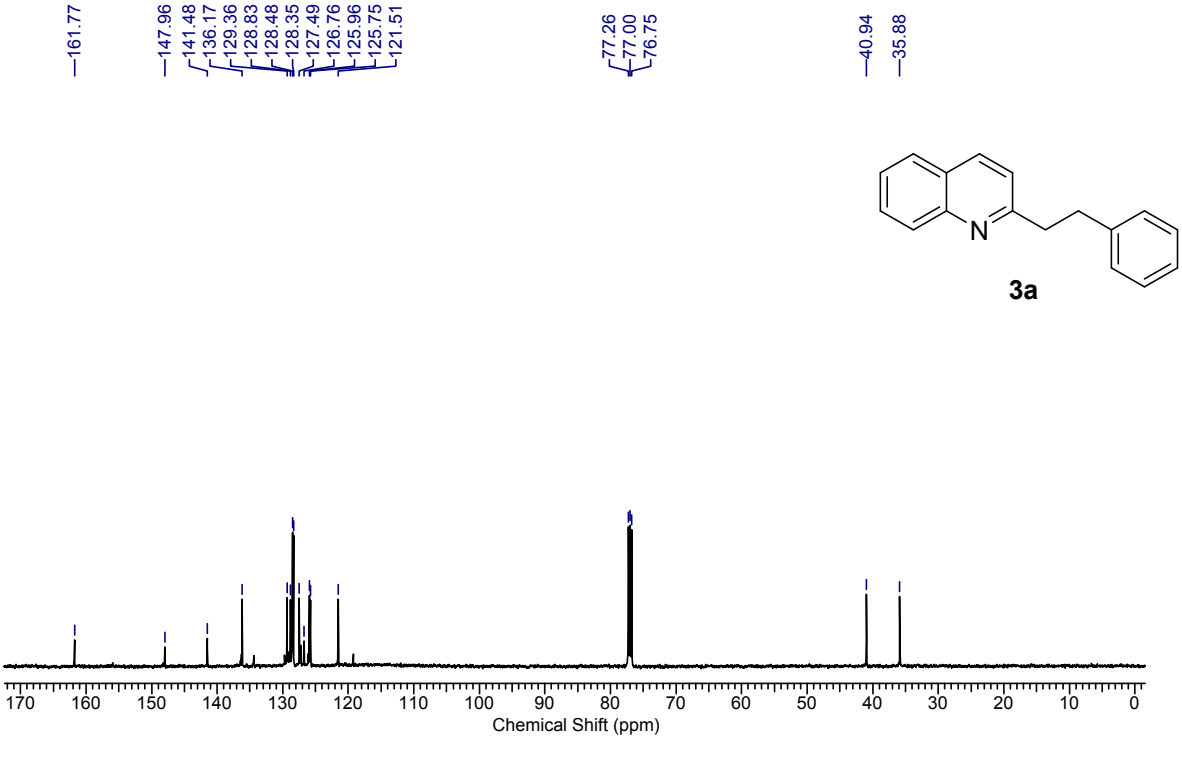
HRMS(EI) m/z Calcd for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277; Found: 246.1275.



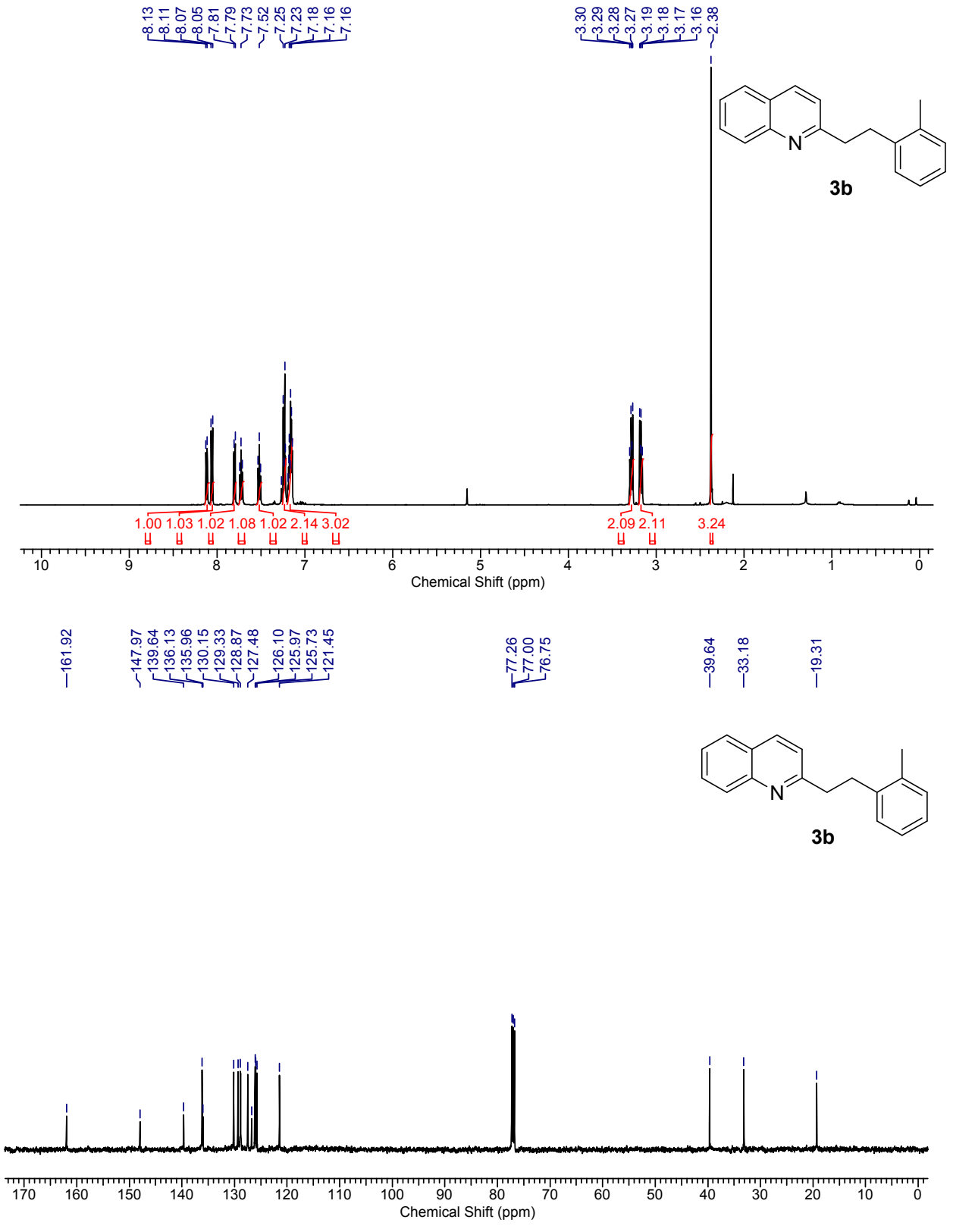
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (t, *J* = 8.7 Hz, 2H), 7.83-7.71 (m, 2H), 7.56 (dt, *J* = 8.5, 1.3 Hz, 1H), 7.37-7.28 (m, 5H), 3.42-3.29 (m, 1.92H), 3.28-3.14 (m, 1.70H).

6. Copies of NMR Spectra

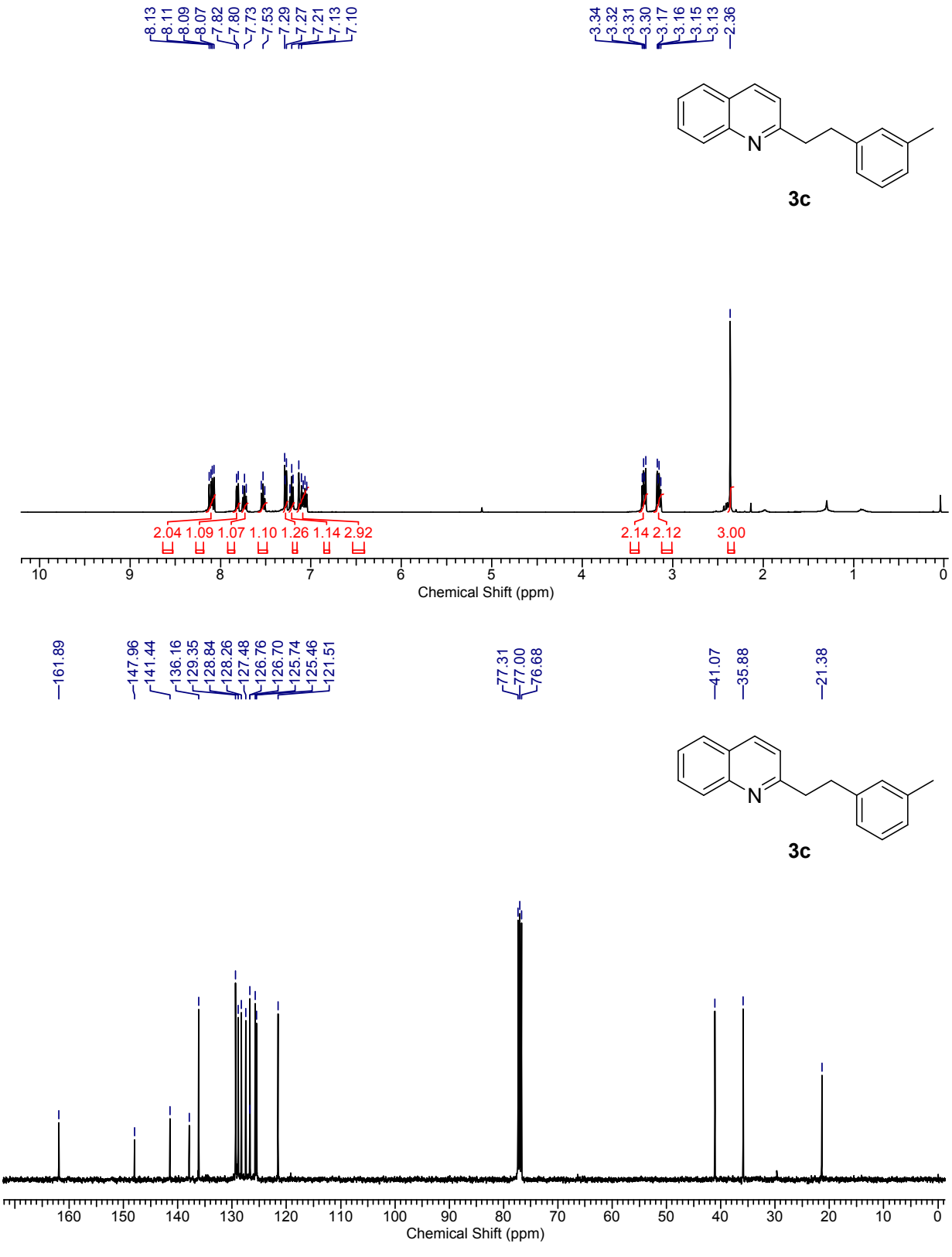




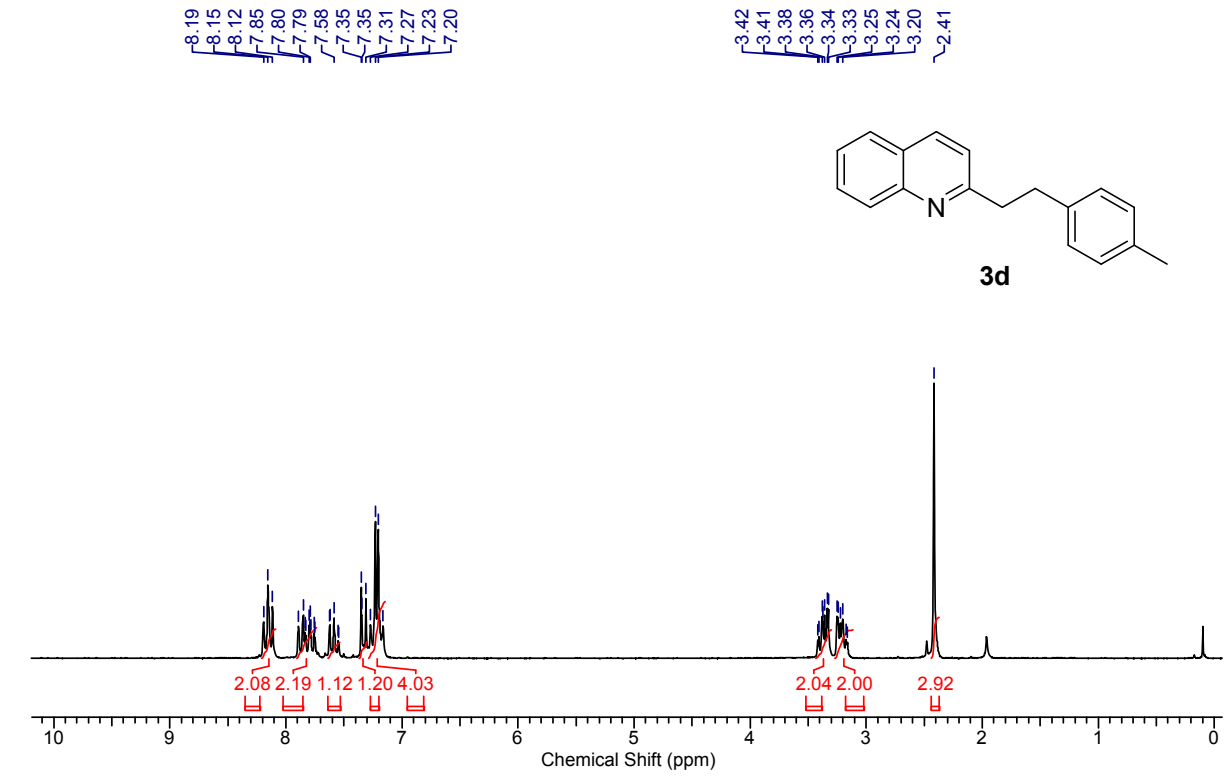
^{1}H &^{13}C NMR of **3a**

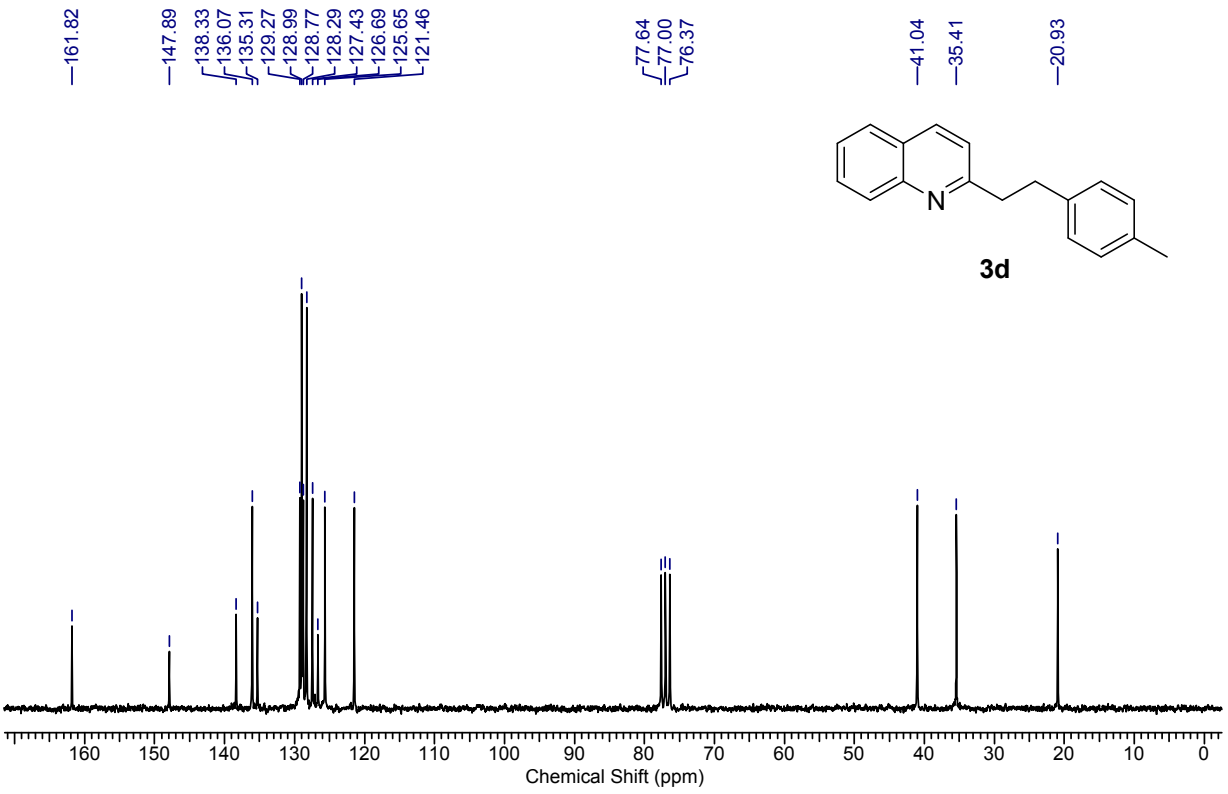


^{1}H &^{13}C NMR of **3b**

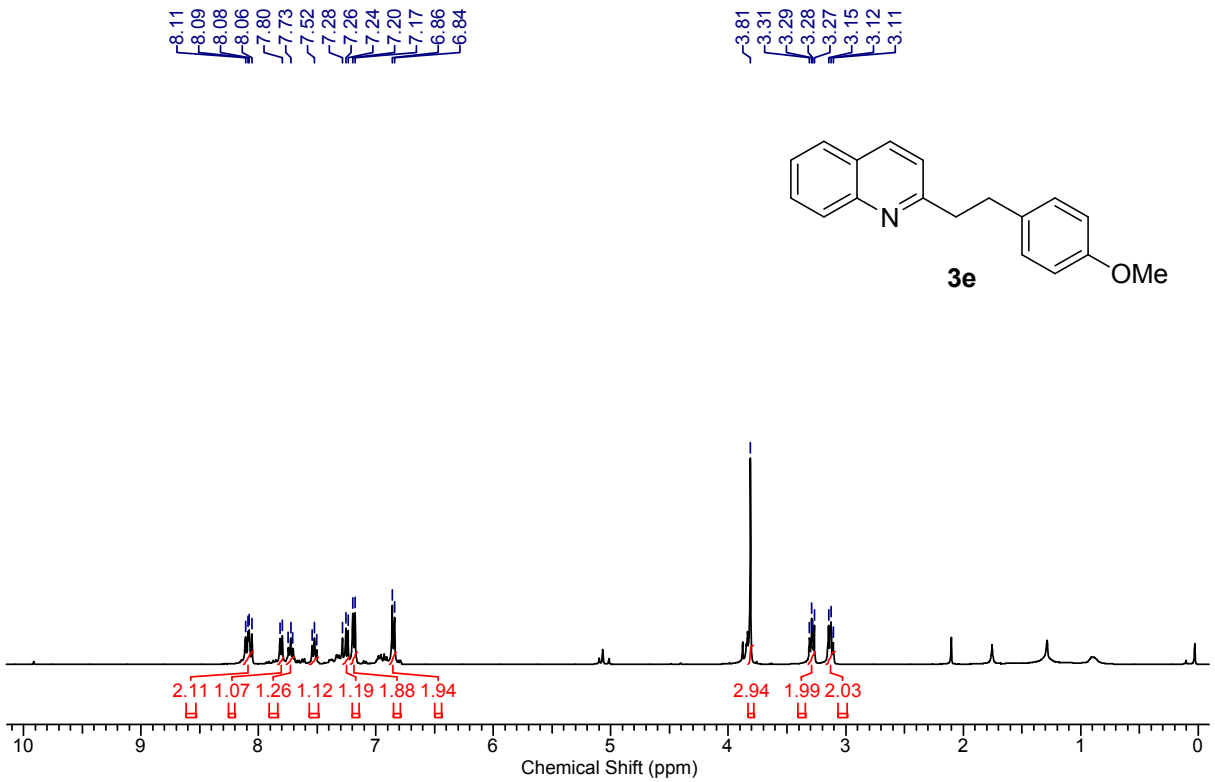


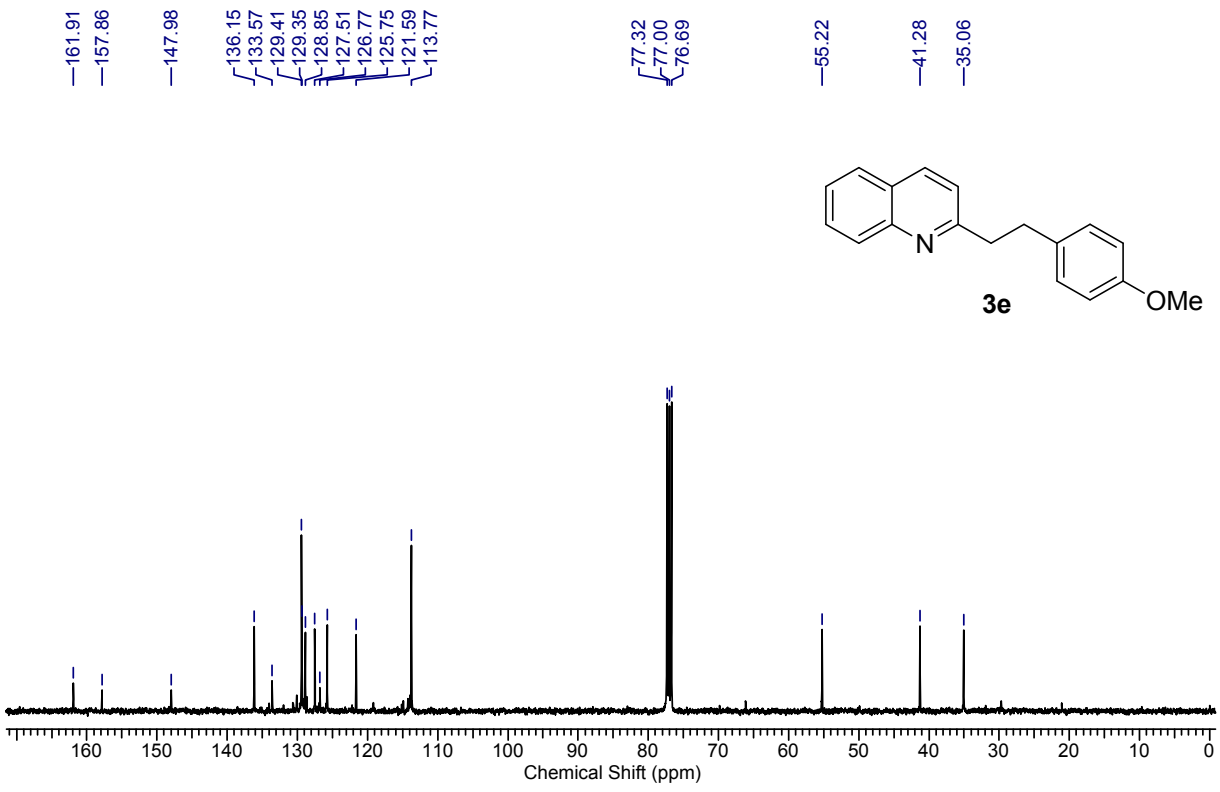
^{1}H &^{13}C NMR of **3c**



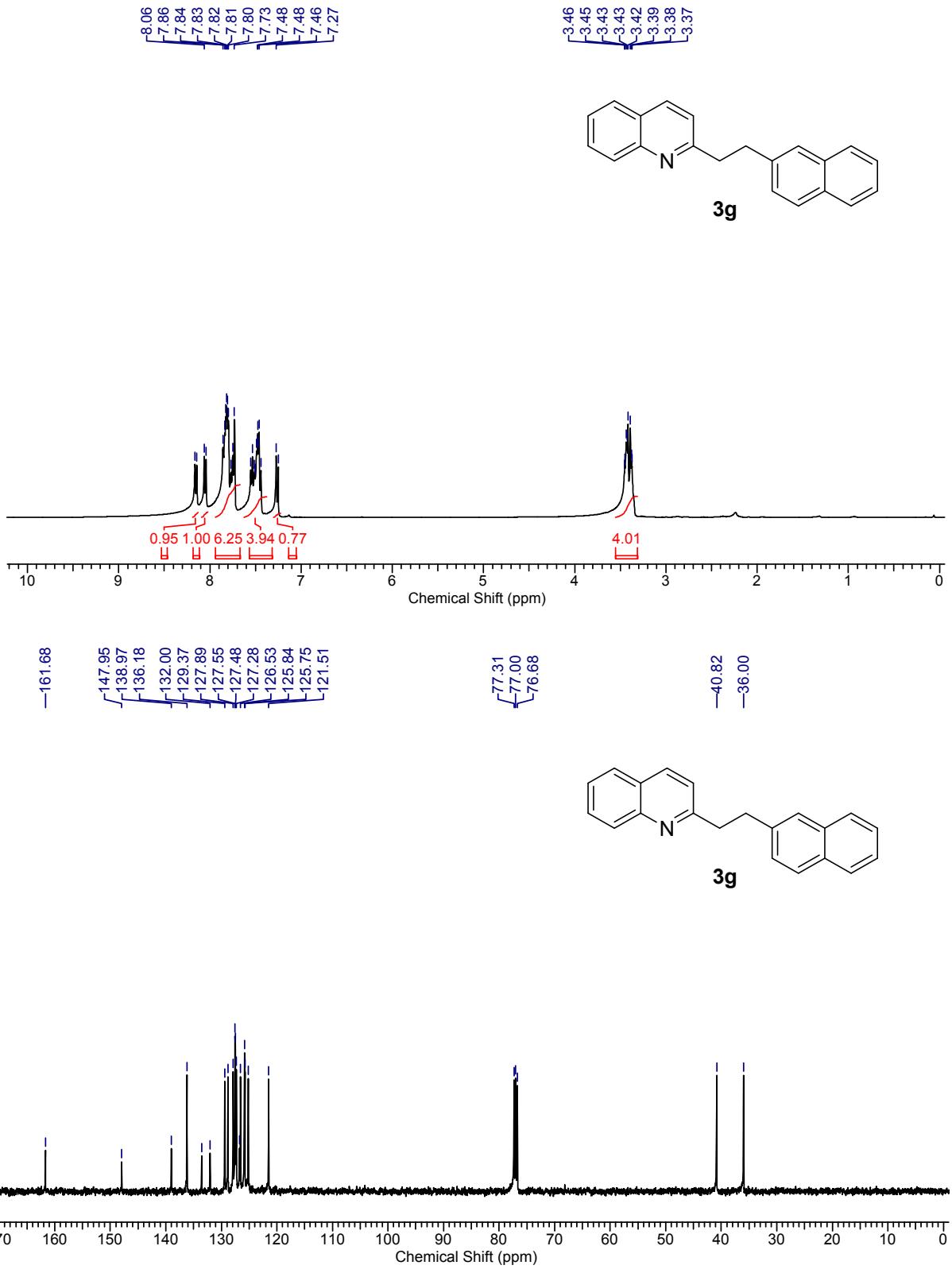


^{1}H &^{13}C NMR of **3d**

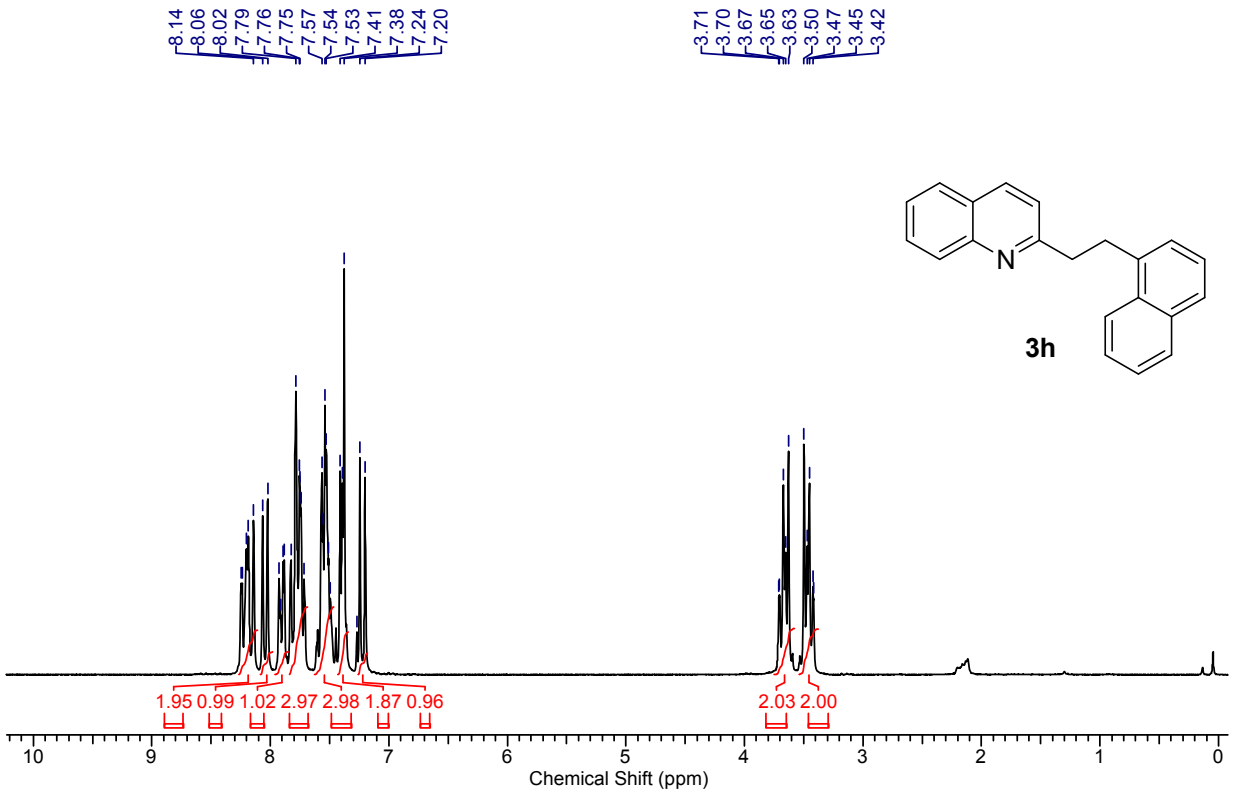


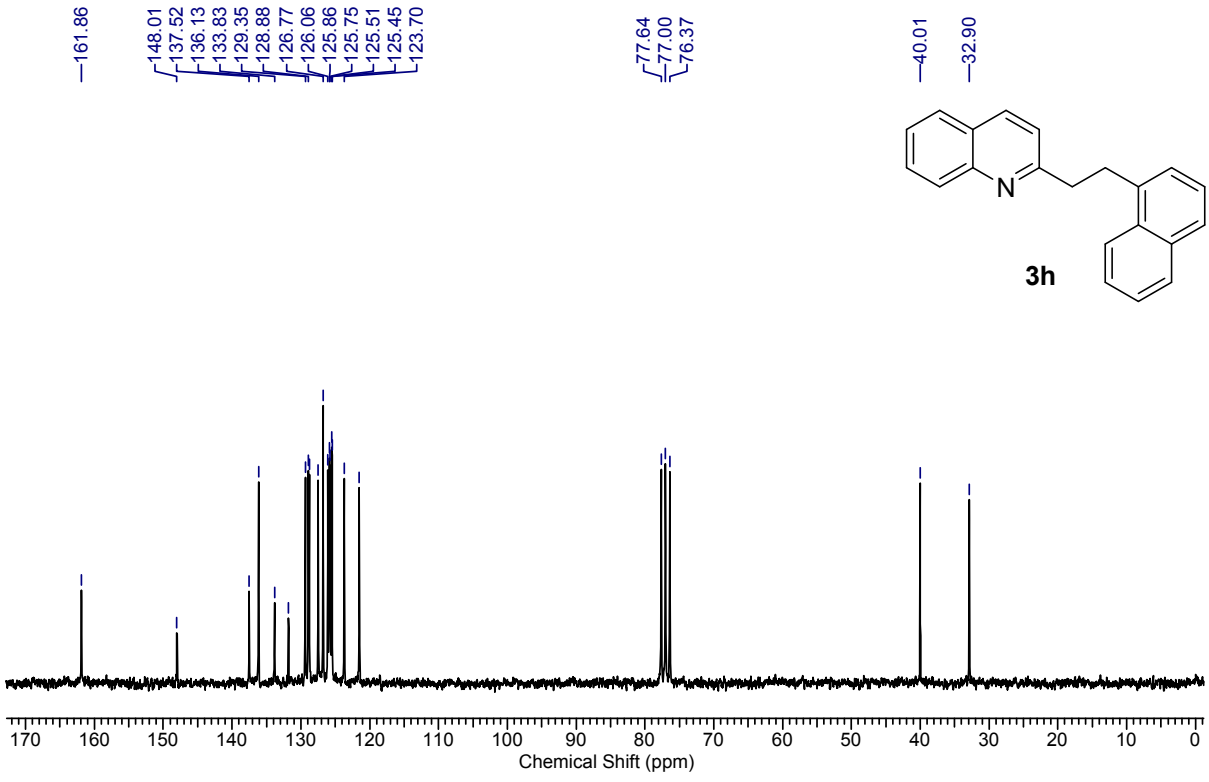


^{1}H &^{13}C NMR of **3e**

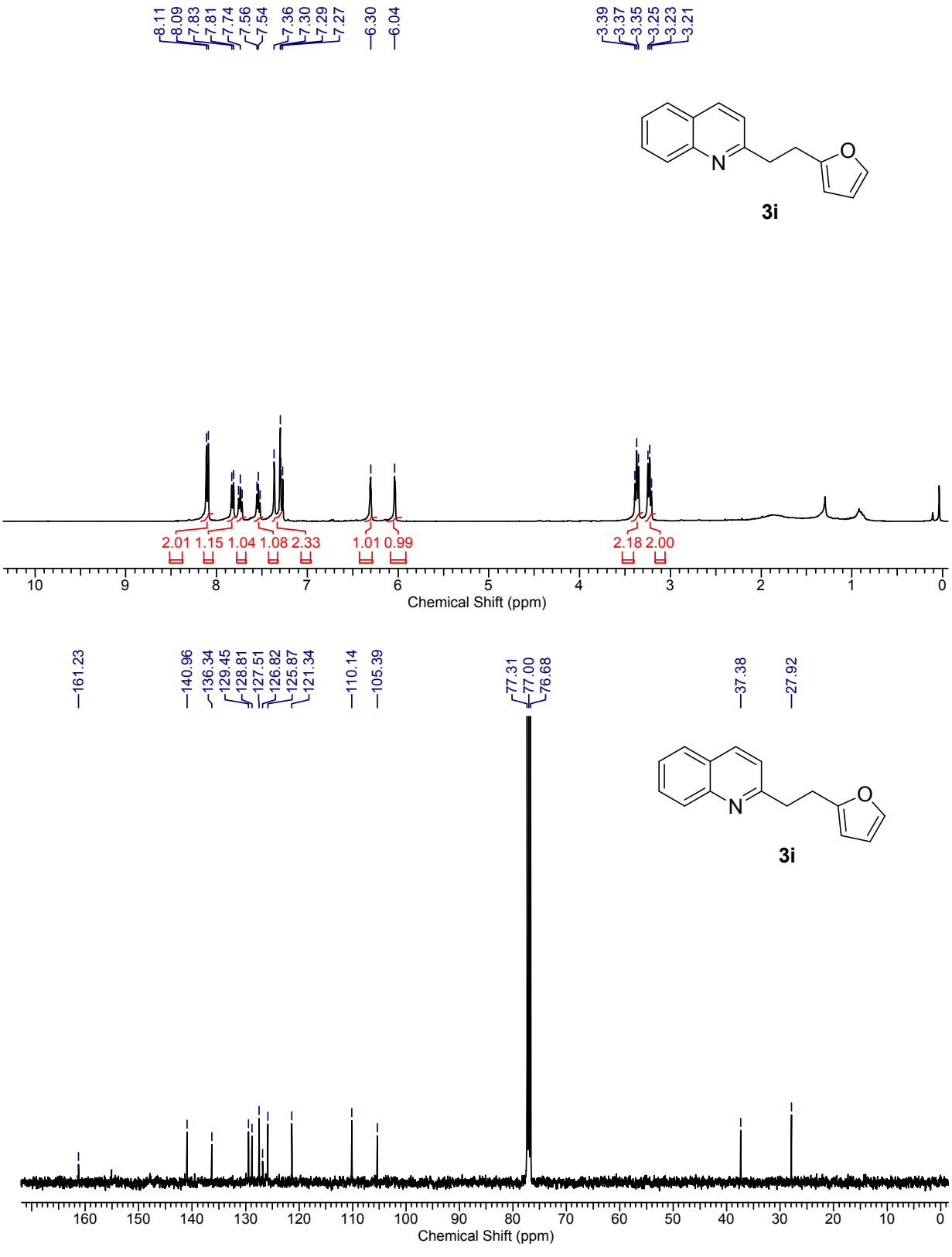


^{1}H &^{13}C NMR of **3g**

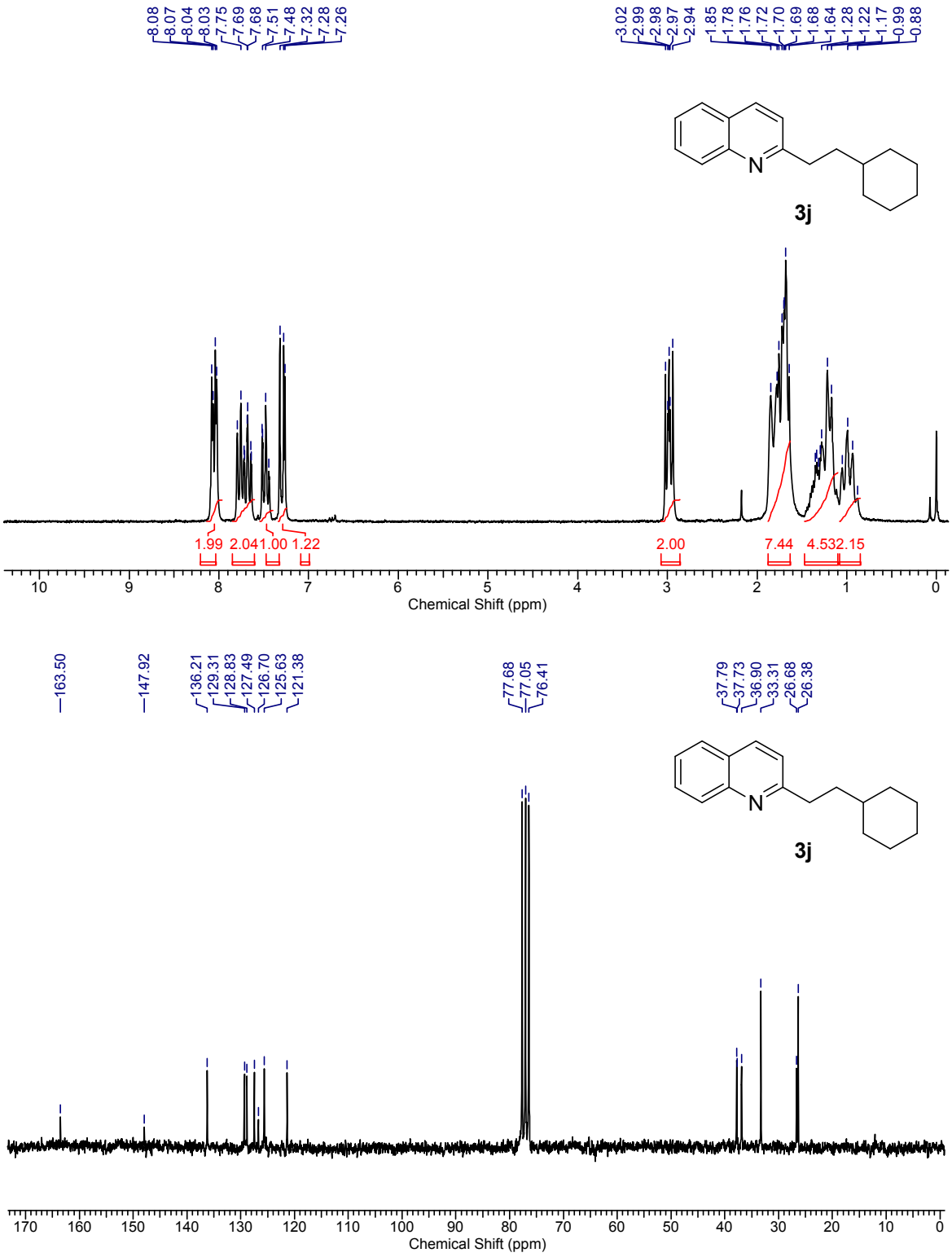




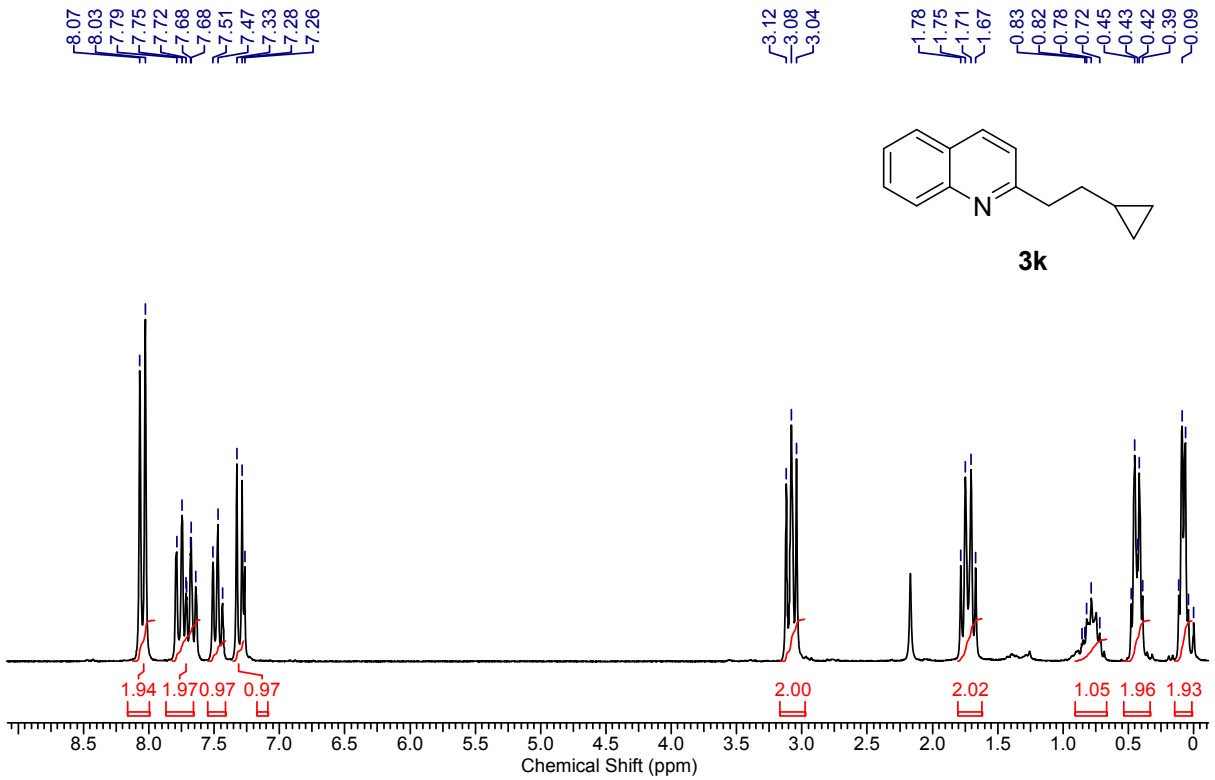
^{1}H &^{13}C NMR of **3h**

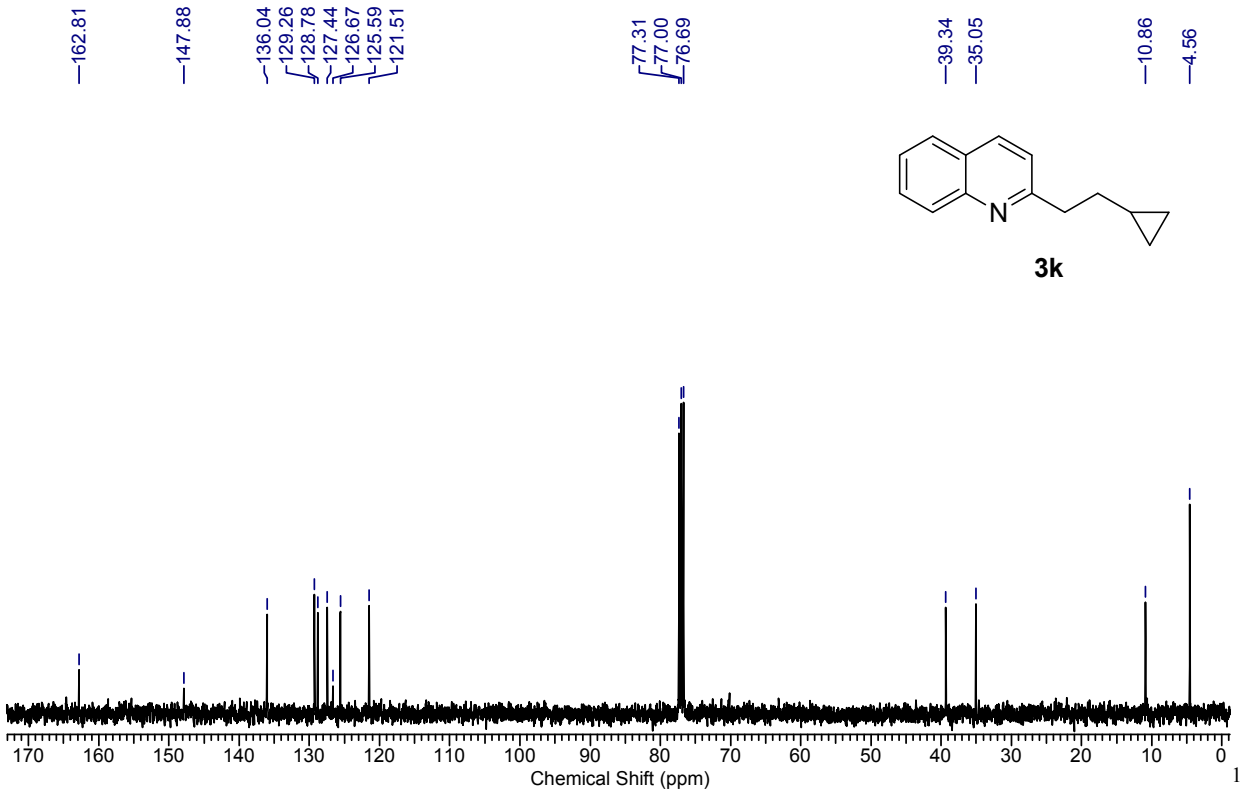


^{1}H &^{13}C NMR of **3i**

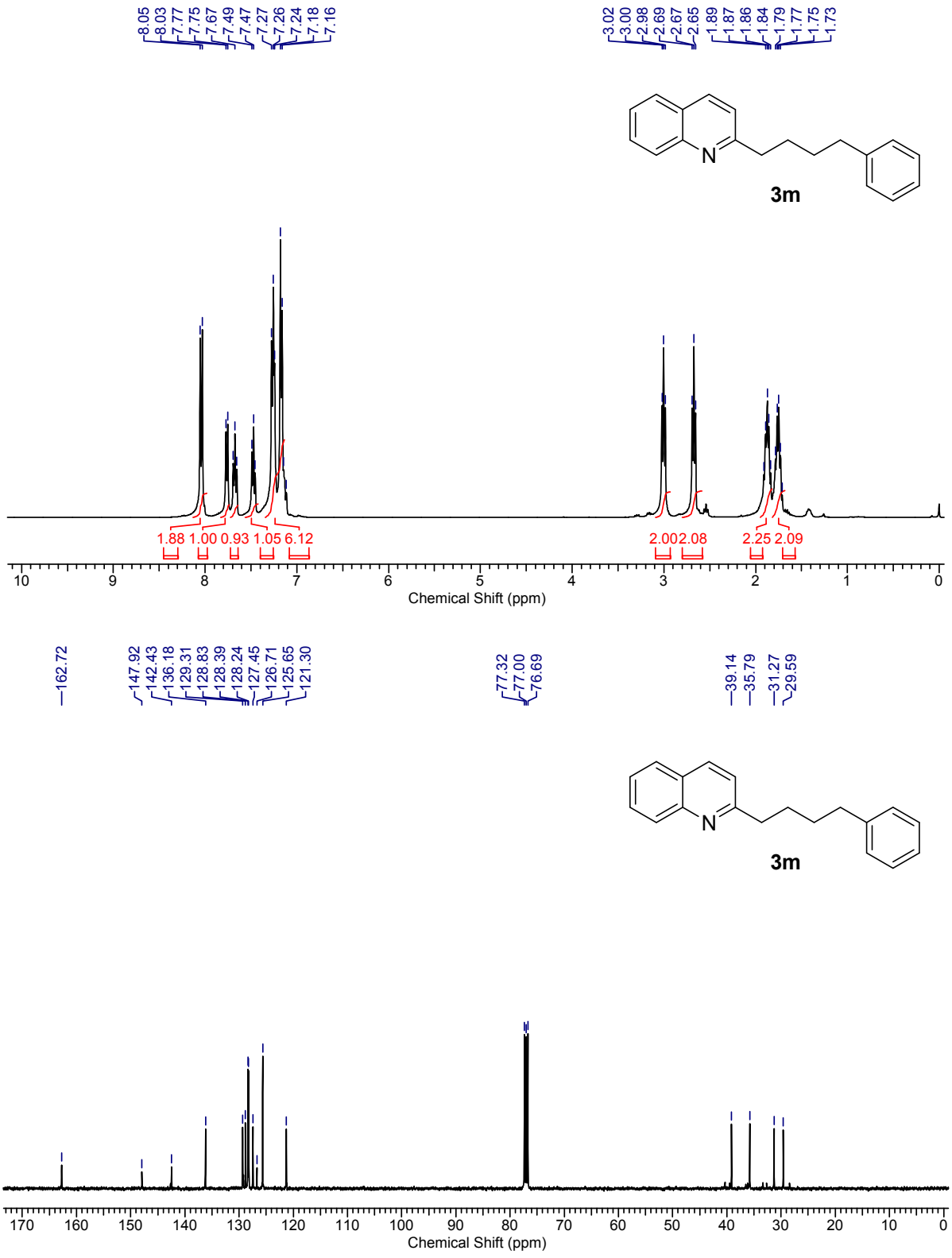


^{1}H &^{13}C NMR of **3j**

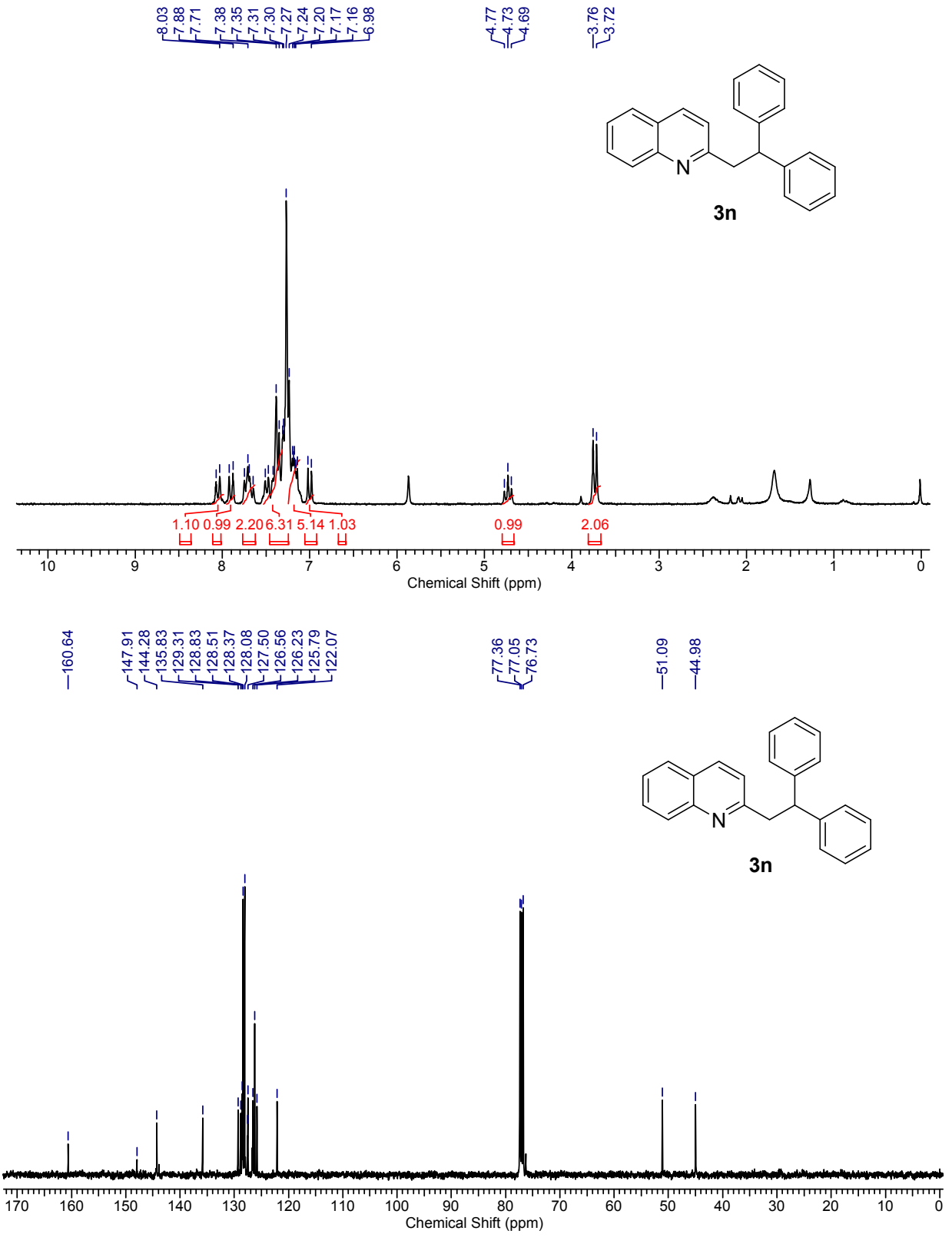




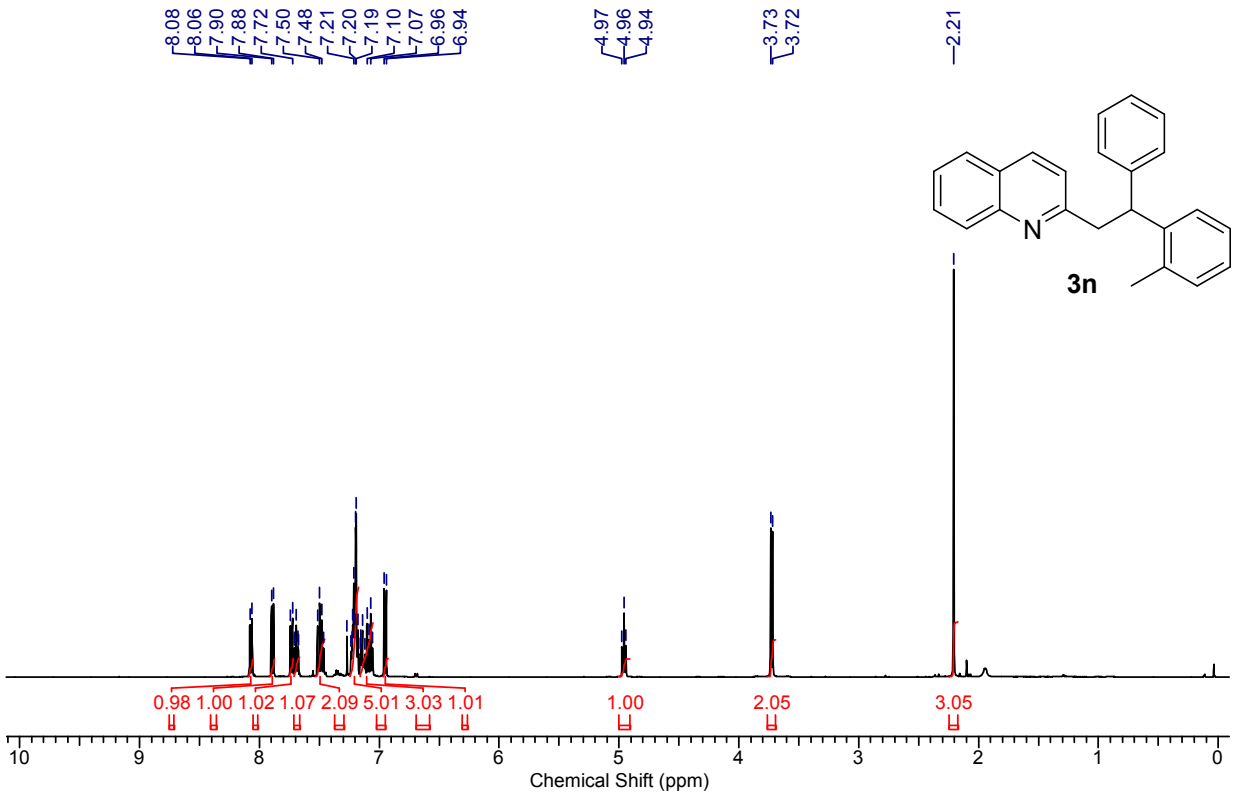
H &^{13}C NMR of **3k**

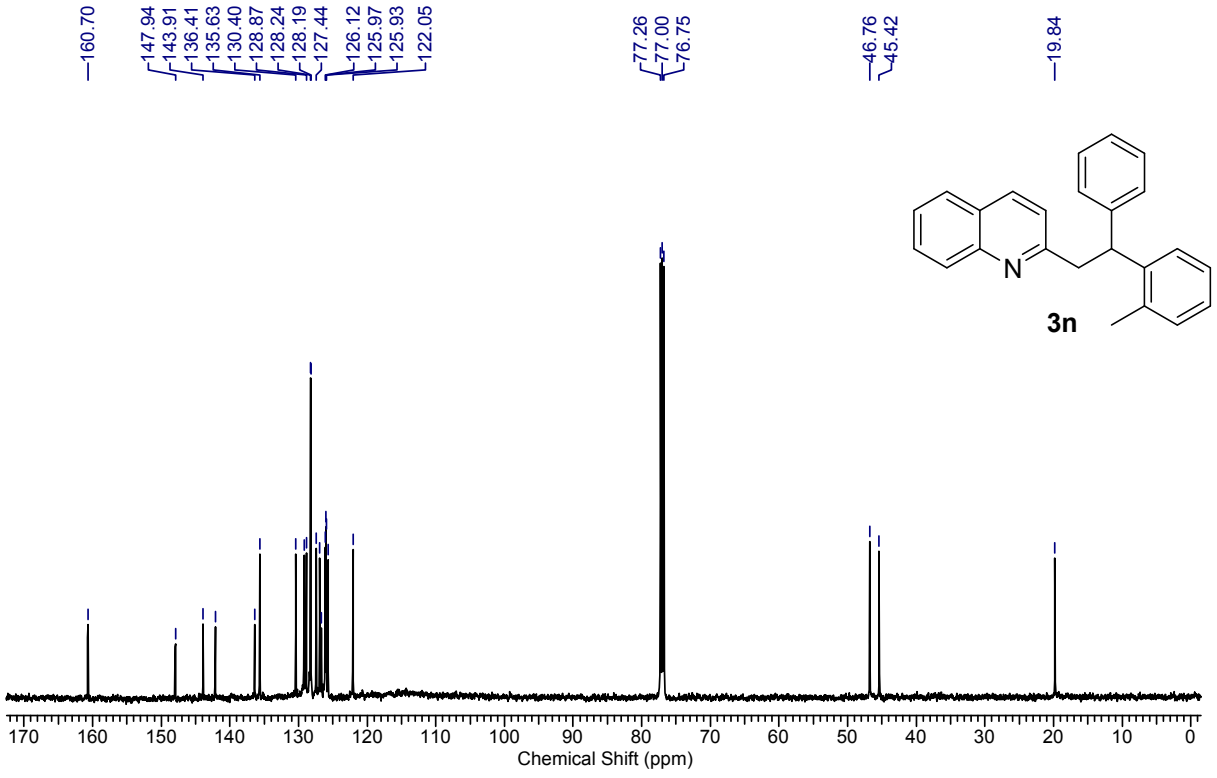


^{1}H &^{13}C NMR of **3m**

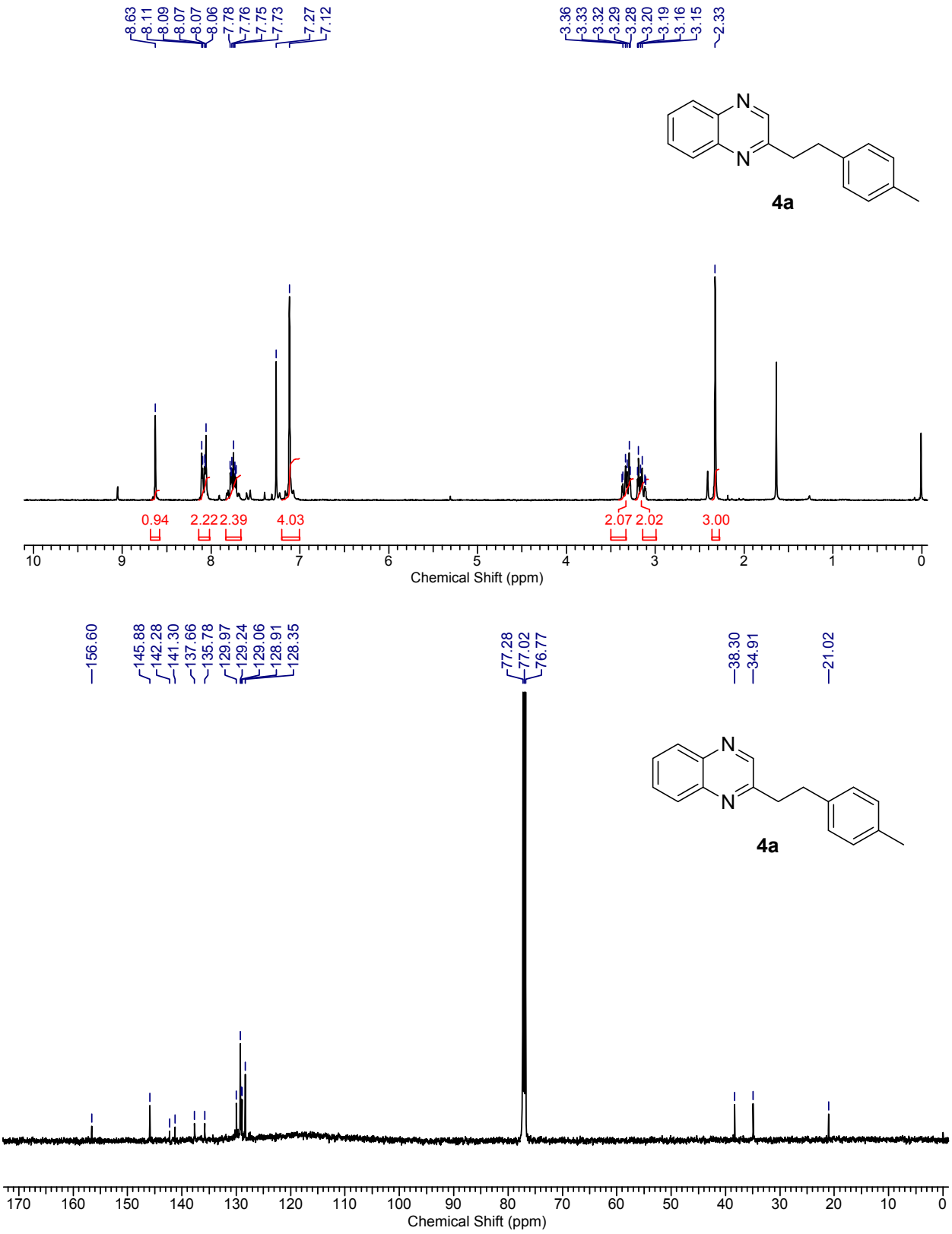


^{1}H &^{13}C NMR of **3n**

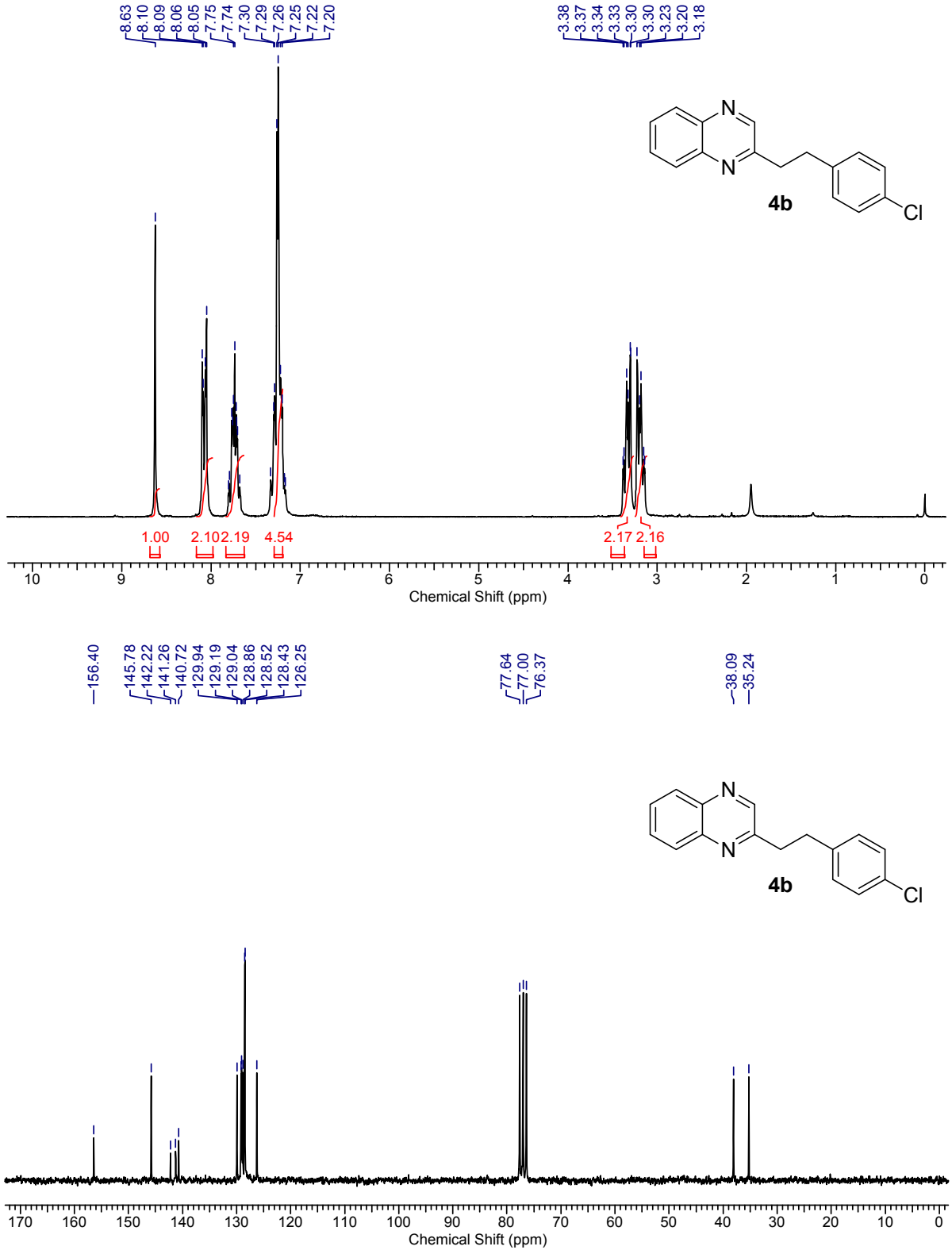




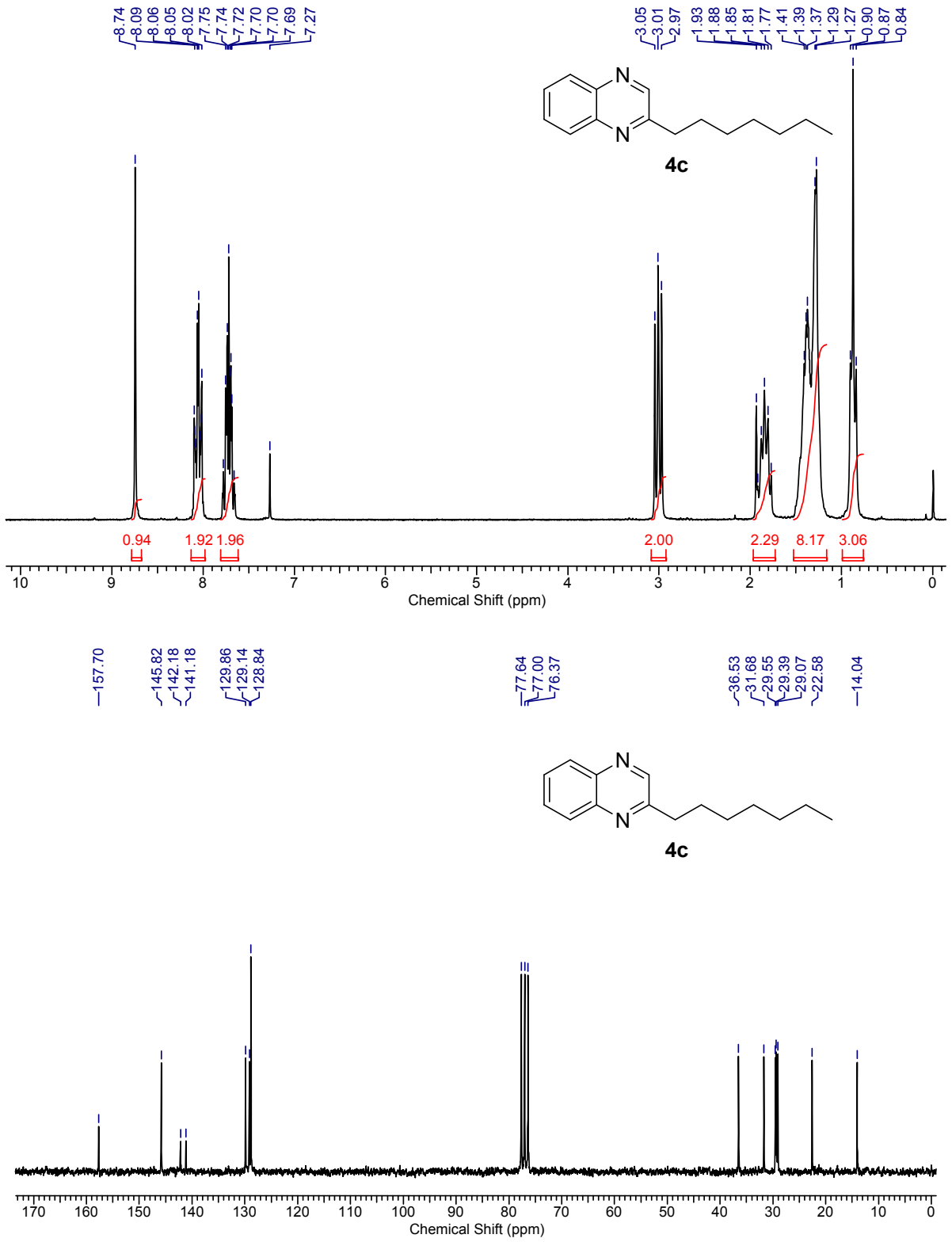
^{1}H &^{13}C NMR of **3n**



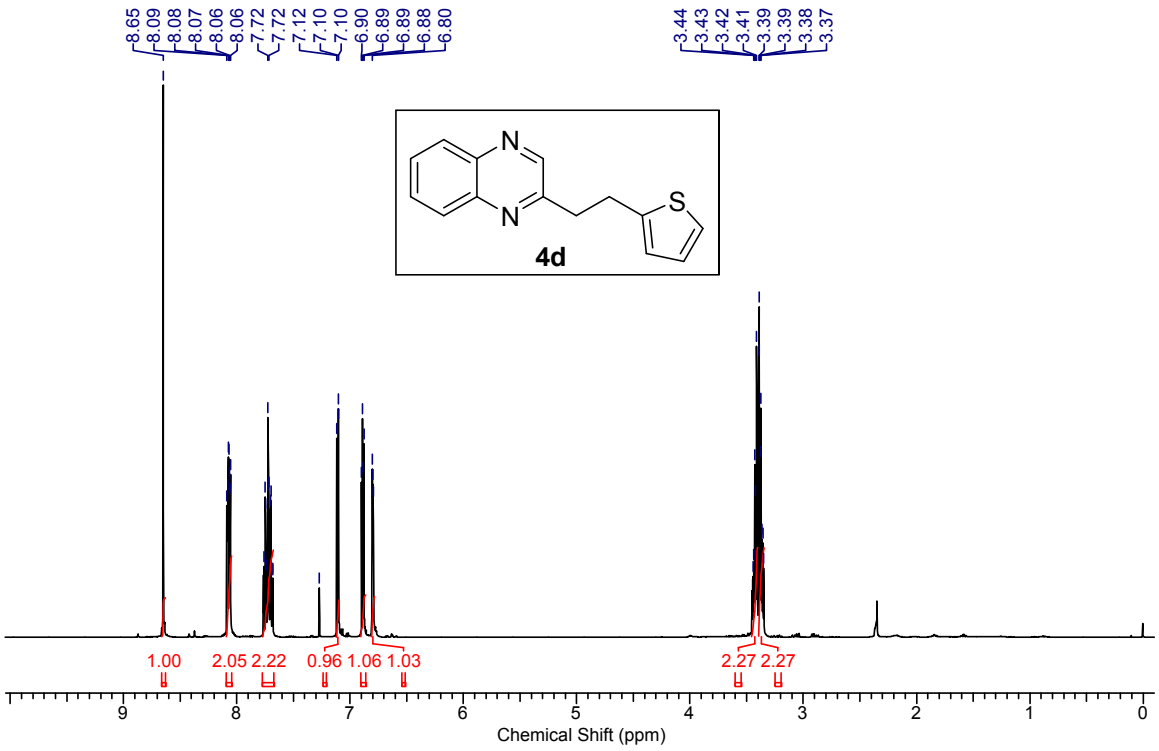
^{1}H &^{13}C NMR of **4a**



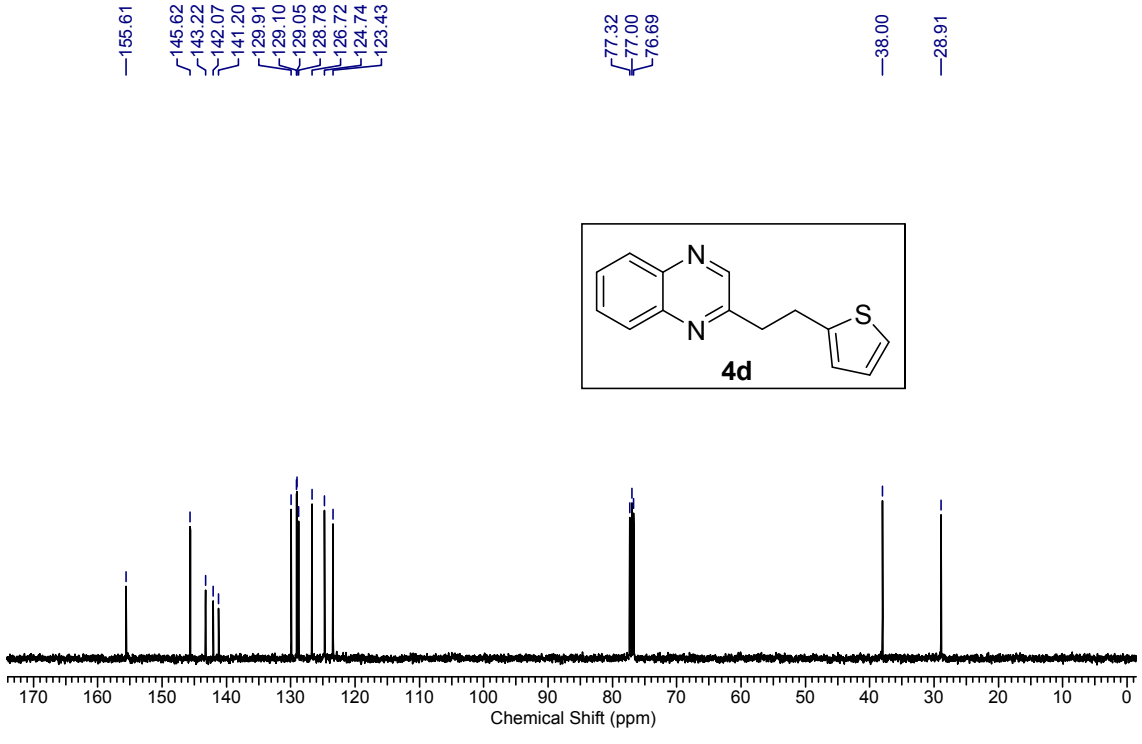
^{1}H &^{13}C NMR of **4b**



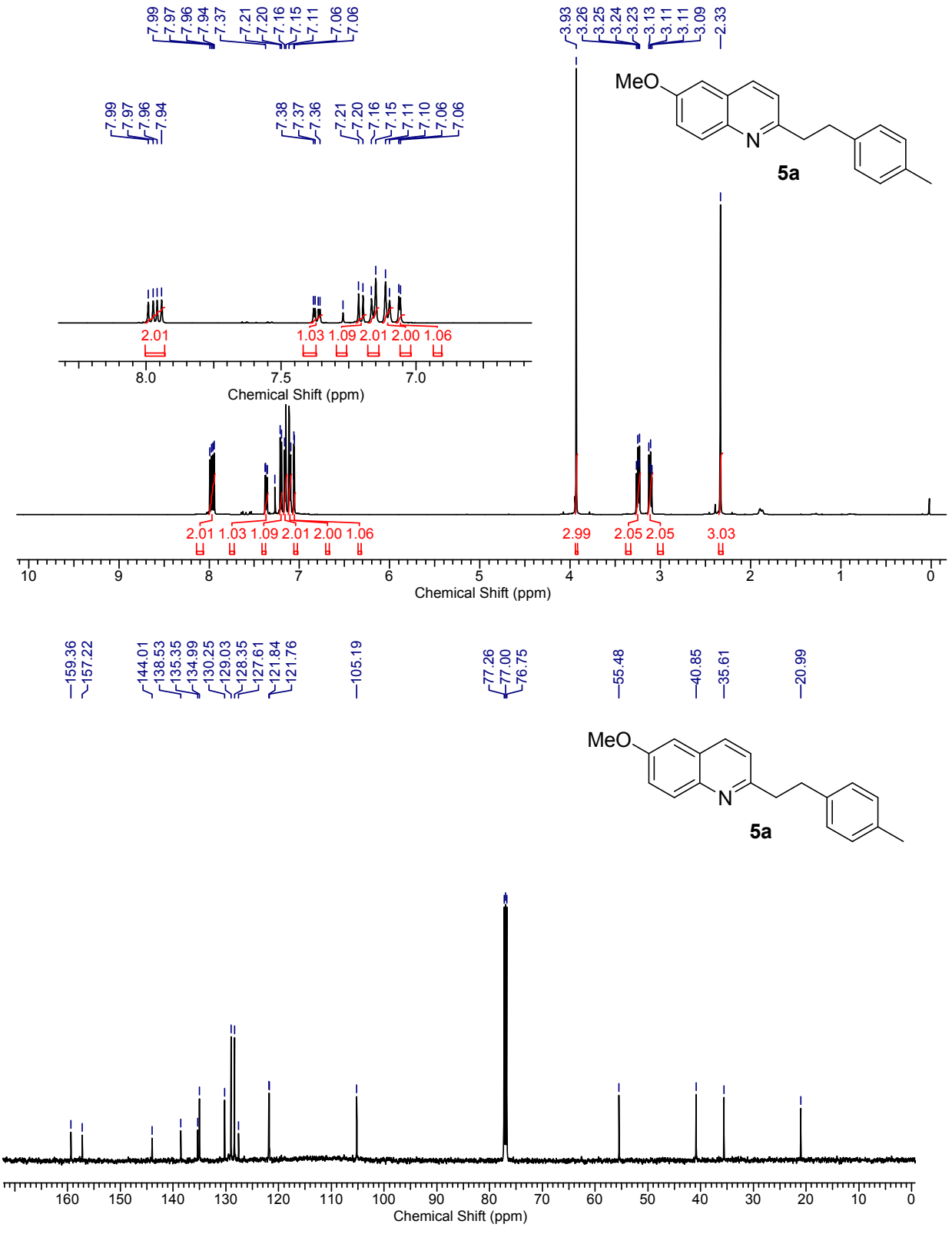
^{1}H &^{13}C NMR of **4c**



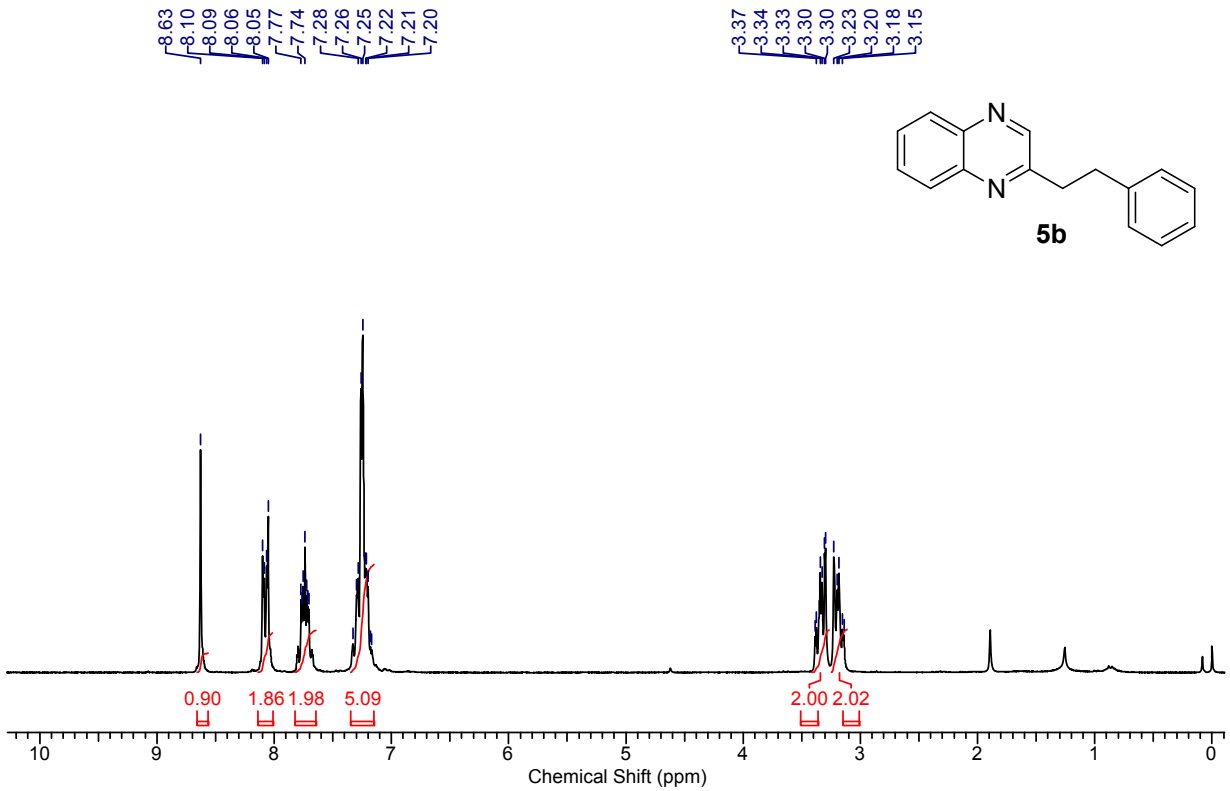
^{1}H NMR of **4d**

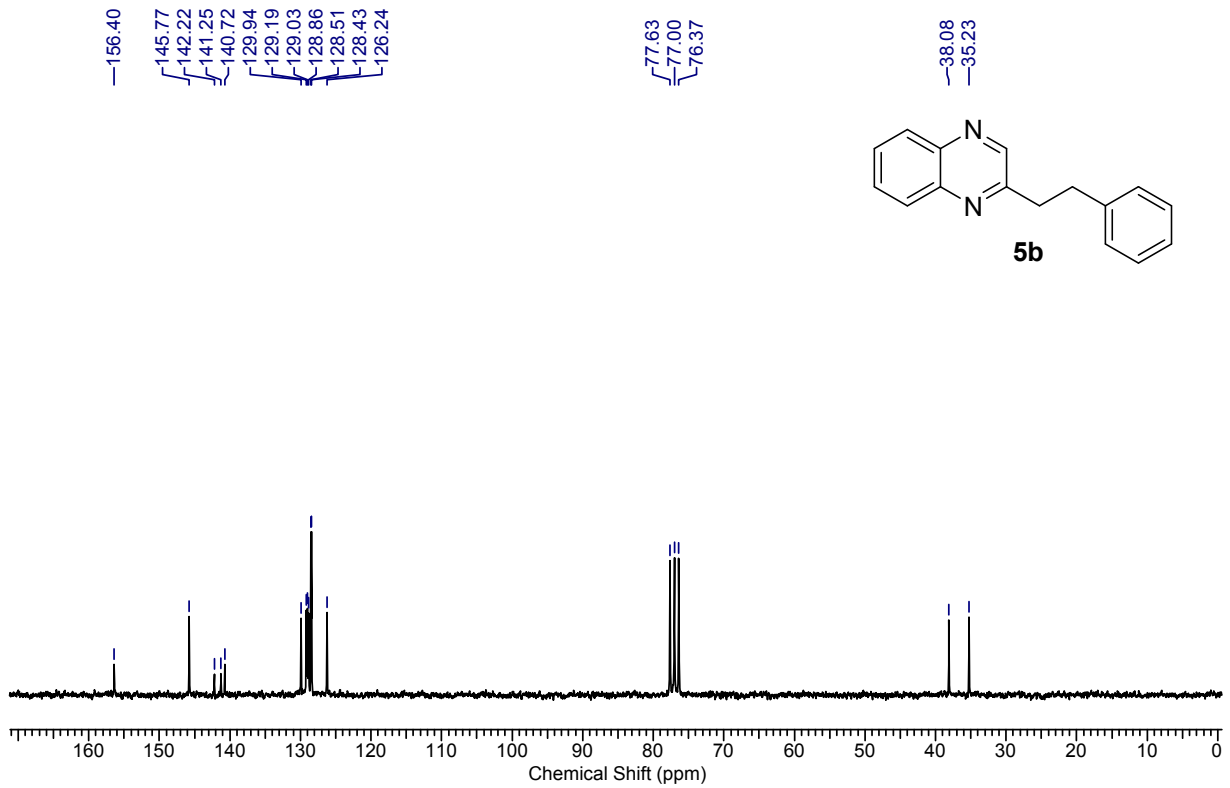


^{13}C NMR of **4d**

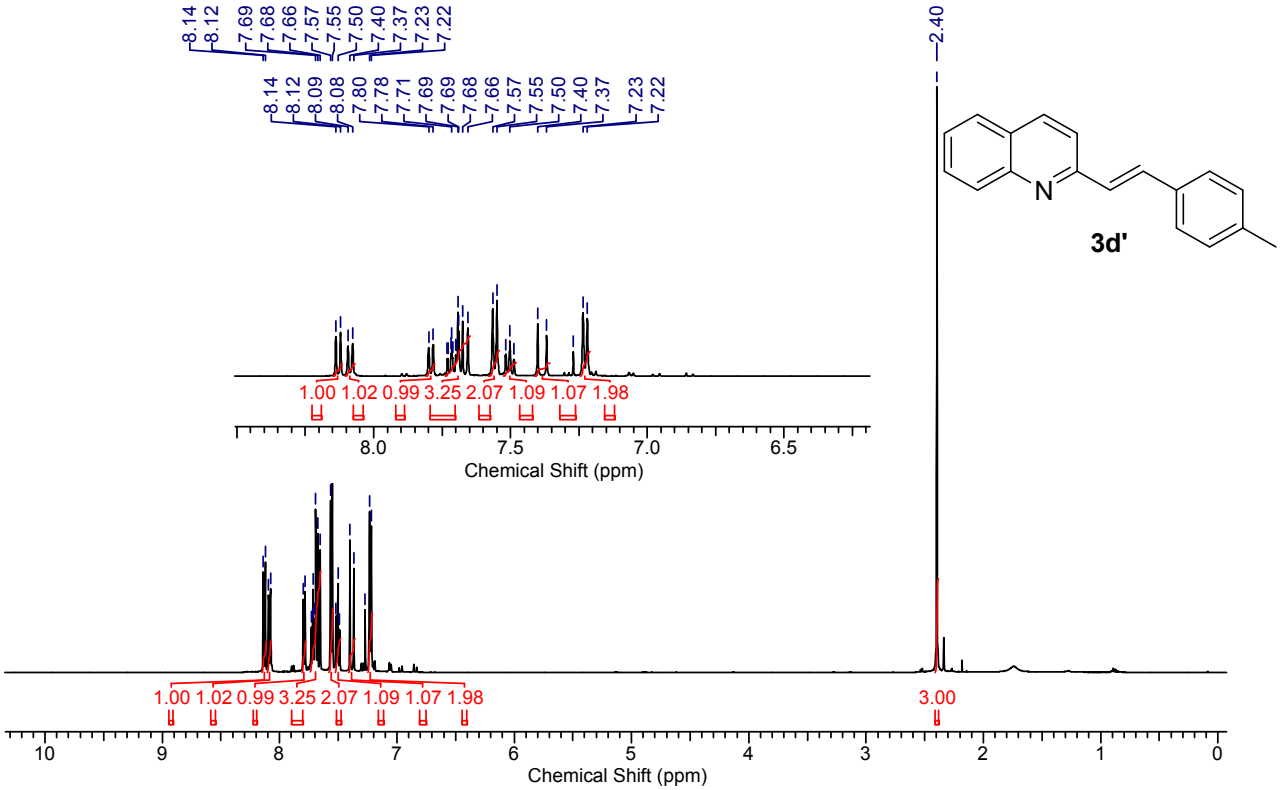


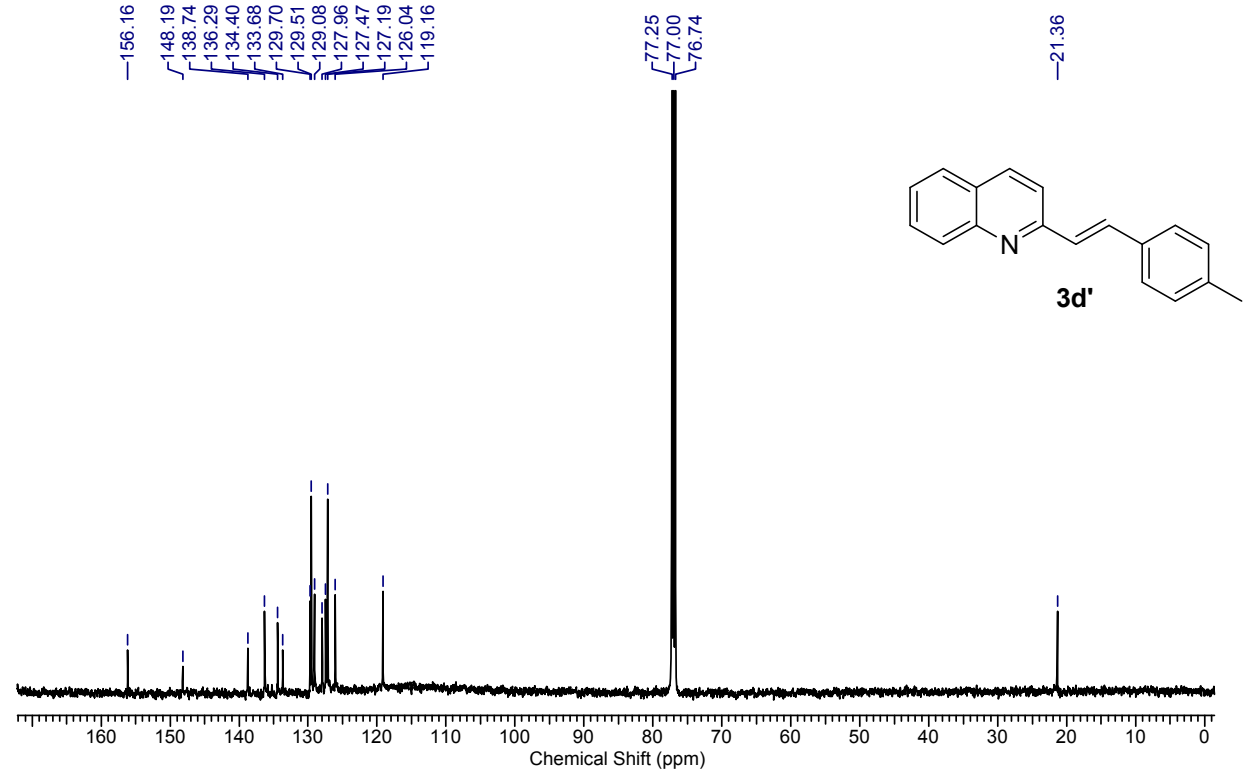
^{1}H &^{13}C NMR of **5a**


8.63
8.10
8.09
8.06
8.05
7.77
7.74
7.28
7.26
7.25
7.22
7.21
7.20
3.37
3.34
3.33
3.30
3.30
3.23
3.20
3.18
3.15
N
N
5b
0.90
1.86
1.98
5.09
2.00
2.02
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

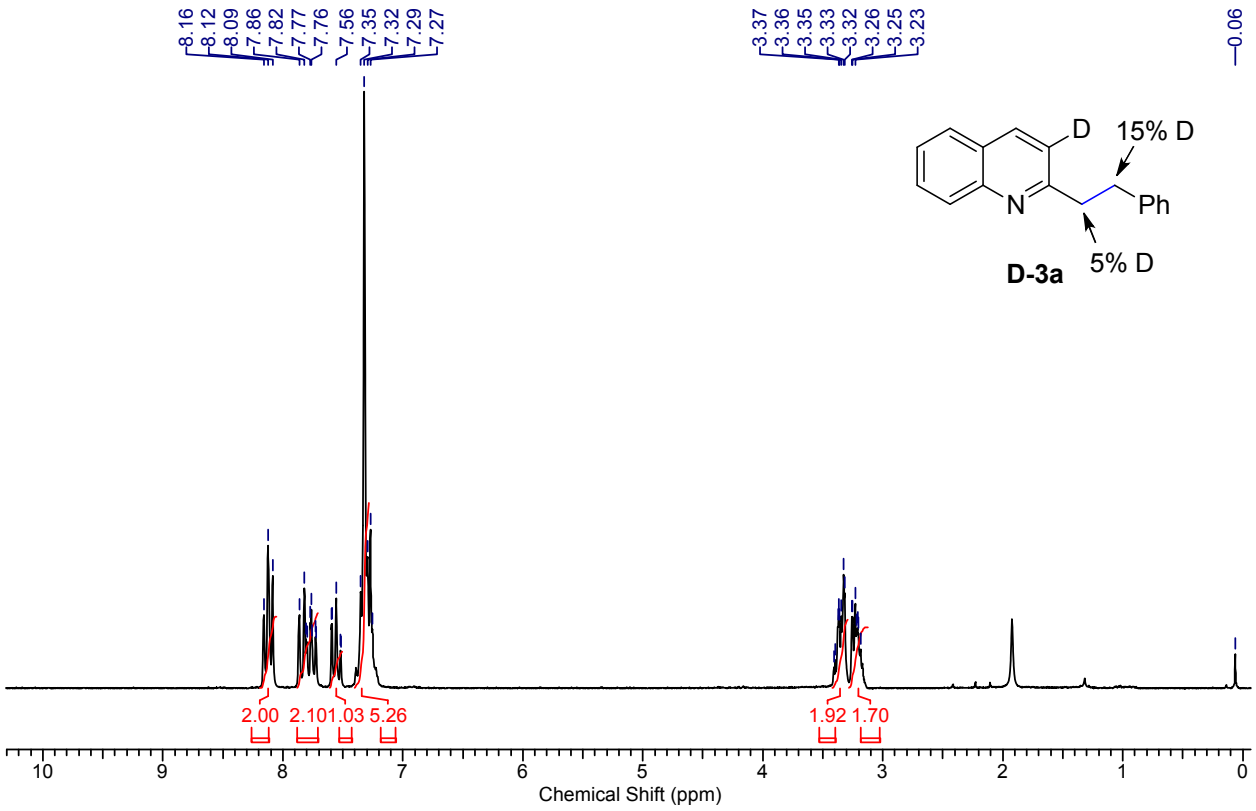

156.40
145.77
142.22
141.25
140.72
129.94
129.19
129.03
128.86
128.51
128.43
126.24
77.63
77.00
76.37
38.08
35.23
N
N
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{1}H &^{13}C NMR of **5b**





^{1}H &^{13}C NMR of **3d'**



^{1}H NMR of **[D]-3a**