Electronic Supplementary Material (ESI) for Chemical Communications.

Nickel-Catalysed Alkylation of C(sp^3)-H Bond with Alcohols: Direct Access to Functionalised *N*-Heteroaromatics

Mari Vellakkaran,[‡] Jagadish Das,[‡] Sourajit Bera, and Debasis Banerjee*

Department of Chemistry
Laboratory of Catalysis and Organic Synthesis
Indian Institute of Technology Roorkee, Roorkee-247667, India
E-mail: dbane.fcy@iitr.ac.in

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[1.1] General Experimental Details:

All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, F_{254} plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh) using a gradient of ethyl acetate and hexane as mobile phase. ^{1}H NMR spectral data were collected at, 400 MHz (JEOL), 500 MHz (Bruker) and ^{13}C NMR were recorded at 100 MHz. ^{1}H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ^{13}C NMR chemical shifts are expressed in ppm. Elemental analysis data were recorded in Vario Micro Cube. GC-MS were recorded using Agilent GC Mass Spectrometer. HRMS (ESI) spectral data were collected using Bruker High Resolution Mass Spectrometer. All the reactions were performed in a close system using Schlenk tube. All nickel salts were purchased from Sigma Aldrich. Nickel(II) bromide (Assay- 98%; CAS Number 13462-88-9; EC Number 236-665-0; Pack Size- No 217891-10G). Potassium *tert*-butoxide was purchased from Avra Synthesis Pvt. Ltd., India. (Purity-98%, CAS No: 865-47-4, Catalog No- ASP2012).

[1.2] General Procedure for Nickel Catalysed Alkylation of Methylquinolines with Primary Alcohols:

Procedure A:

In a 15 mL oven dried Schlenk tube, quinaldine (0.25 mmol), *t*-BuOK (0.25 mmol), $NiBr_2$ (10 mol%), Phen (50 mol%), and alcohols (0.50 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 °C for 24 h in closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo.* The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

Procedure B:

In a 15 mL oven dried Schlenk tube, quinaldine (0.25 mmol), *t*-BuOK (0.375 mmol), $NiBr_2$ (10 mol%), Phen (50 mol%), and alcohols (0.50 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 °C for 24 h in close system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo.* The residue was purified by column

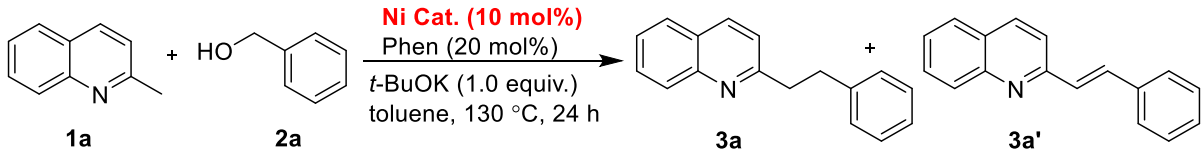
chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

Procedure C:

In a 15 mL oven dried Schlenk tube, quinaldine (0.25 mmol), *t*-BuOK (0.50 mmol), $NiBr_2$ (20 mol%), Phen (100 mol%), and alcohols (1.0 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 °C for 24 h in close system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo*. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

[1.3] Alkylation of 2-methylquinolines with alcohols:

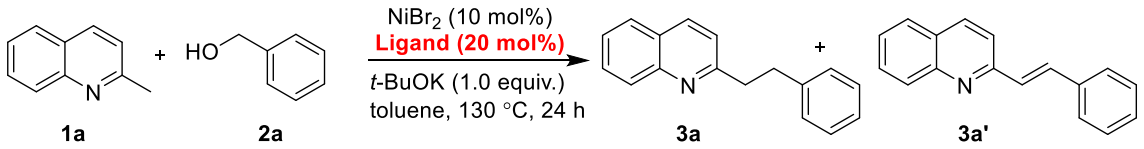
Table S1: Screening of catalyst[a]

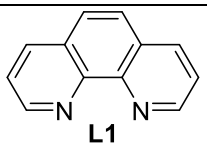
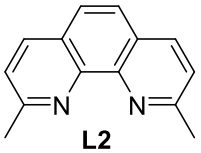
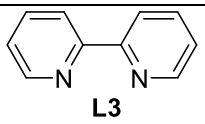
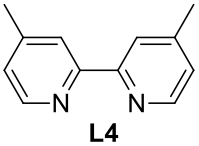
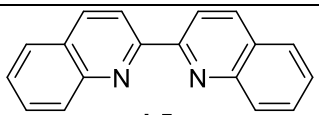


Entry	Ni-Catalyst	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	$NiCl_2$	53	47
2	**$NiBr_2$**	**73 (70%)**[b]	**25**
2	$Ni(acac)_2$	30	34
3	$NiCl_2(DME)$	13	48
4	$Ni(COD)_2$	8	22
5	No Catalyst	0	0

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), **Ni Cat. (10 mol%)**, Phen (20 mol%), *t*-BuOK (0.25 mmol), Toluene (2.0 mL), Schlenk tube under nitrogen atmosphere, 130 °C oil bath, 24 h reaction time. [b] Isolated yield average of two run.

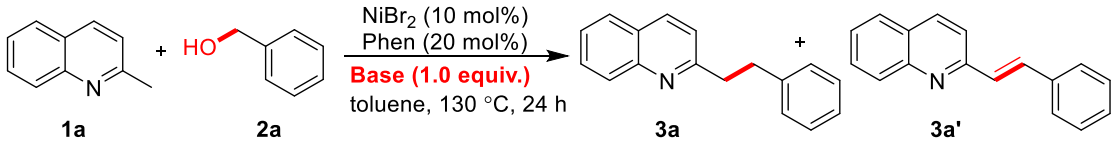
Table S2: Screening of ligands[a]



Entry	Ligand	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	 L1	**73 (70%)**[b]	**25**
2	 L2	1	9
3	 L3	0	12
4	 L4	2	47
5	 L5	0	10
9	No Ligand	8	22

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), $NiBr_2$ (10 mol%), **Ligand (20 mol%)**, *t*-BuOK (0.25 mmol), Toluene (2.0 mL), Schlenk tube under nitrogen atmosphere, 130 ºC oil bath, 24 h reaction time. [b] Isolated yield average of two run.

Table S3: Screening of base[a]

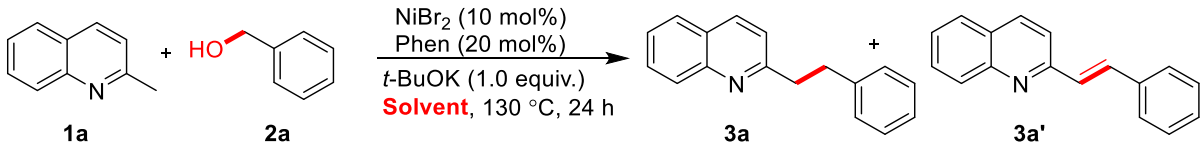


Entry	Base	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	***t*-BuOK**	**73 (70%)** [b]	**25**

2	*t*-BuONa	14	39
3	K_3PO_4	0	18
4	Na_2CO_3	2	12

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), $NiBr_2$ (10 mol%), Phen (20 mol%), **Base (0.25 mmol)**, Toluene (2.0 mL), Schlenk tube under nitrogen atmosphere, 130 ºC oil bath, 24 h reaction time. [b] Isolated yield average of two run.

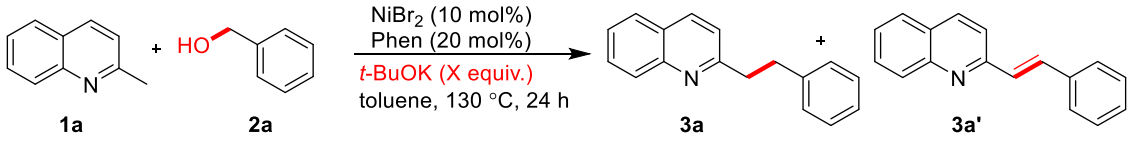
Table S4: Screening of solvents [a]



Entry	**Solvent**	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	**Toluene**	**73 (70%)** [b]	**25**
2	*p*-Xylene	34	40
3	1,4-Dioxane	1	5
4	DMA	0	0
5	*t*-Amylalcohol	0	1

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), $NiBr_2$ (10 mol%), Phen (20 mol%), *t*-BuOK (0.25 mmol), **Solvent (2.0 mL)**, Schlenk tube under nitrogen atmosphere, 130 ºC oil bath, 24 h reaction time. [b] Isolated yield average of two run.

Table S5: Screening of base equivalents[a]

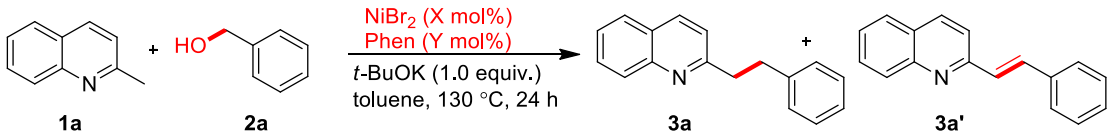


Entry	**Base Equivalent (X equiv.)**	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	***t*-BuOK (1.0 equiv.)**	**73 (70%)** [b]	**25**
2	*t*-BuOK (0.75 equiv.)	12	35

3	*t*-BuOK (0.50 equiv.)	9	29
4	*t*-BuOK (0.25 equiv.)	0	1
5	-	0	0

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), $NiBr_2$ (10 mol%), Phen (20 mol%), *t*-BuOK (**X equiv.**), Toluene (2.0 mL), Schlenk tube under nitrogen atmosphere, 130 ºC oil bath, 24 h reaction time. [b] Isolated yield average of two run.

Table S6: Screening of Catalyst and Ligand Loading [a]

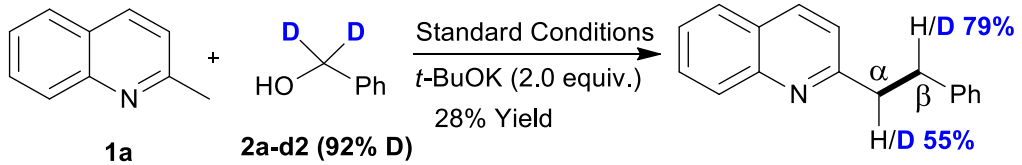


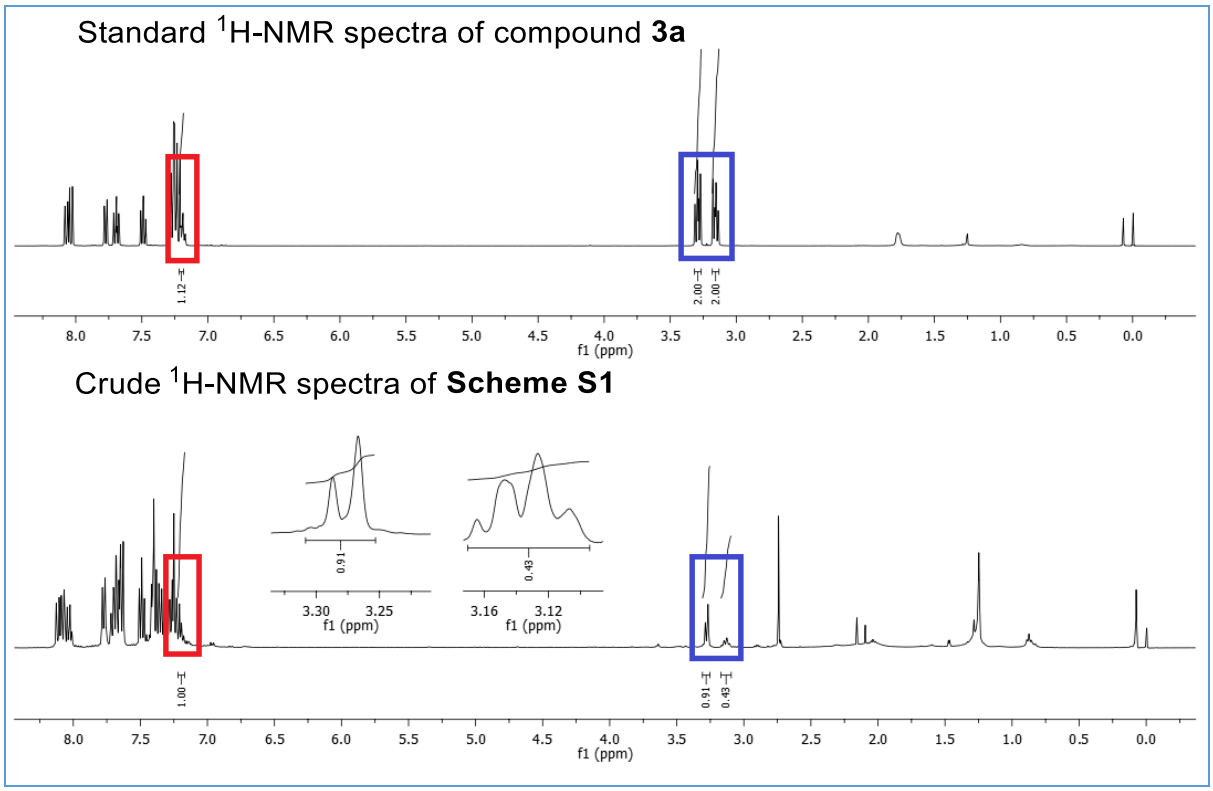
Entry	**Cat. (X mol%)**	**Ligand (Y mol%)**	GC-MS Conversion **3a** (%)	GC-MS Conversion **3a'** (%)
1	**$NiBr_2$ (10 mol%)**	**Phen (20 mol%)**	**73 (70%)** [b]	**25**
2	$NiBr_2$ (10 mol%)	Phen (30 mol%)	27	58
3	$NiBr_2$ (10 mol%)	Phen (40 mol%)	65	34
4	**$NiBr_2$ (10 mol%)**	**Phen (50 mol%)**	**100 (96%)** [b]	**0**
5 [c]	**$NiBr_2$ (10 mol%)**	**Phen (50 mol%)**	**100 (97%)** [b]	**0**
6	$NiBr_2$ (5.0 mol%)	Phen (25 mol%)	13	18
7	$NiBr_2$ (2.5 mol%)	Phen (12.5 mol%)	8	36
8	-	-	0	0

Reaction condition:[a] Quinaldine **1a** (0.25 mmol), Benzyl alcohol **2a** (0.50 mmol), **$NiBr_2$ (X mol%), Phen (Y mol%)**, *t*-BuOK (0.25 mmol), Toluene (2.0 mL), Schlenk tube under nitrogen atmosphere, 130 ºC oil bath, 24 h reaction time. [b] Isolated yield average of two run. [c] 140 ºC, 24 h.

Deuterium incorporation studies:

Scheme S1:

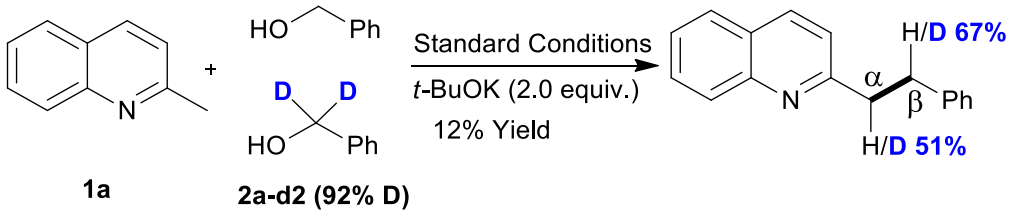




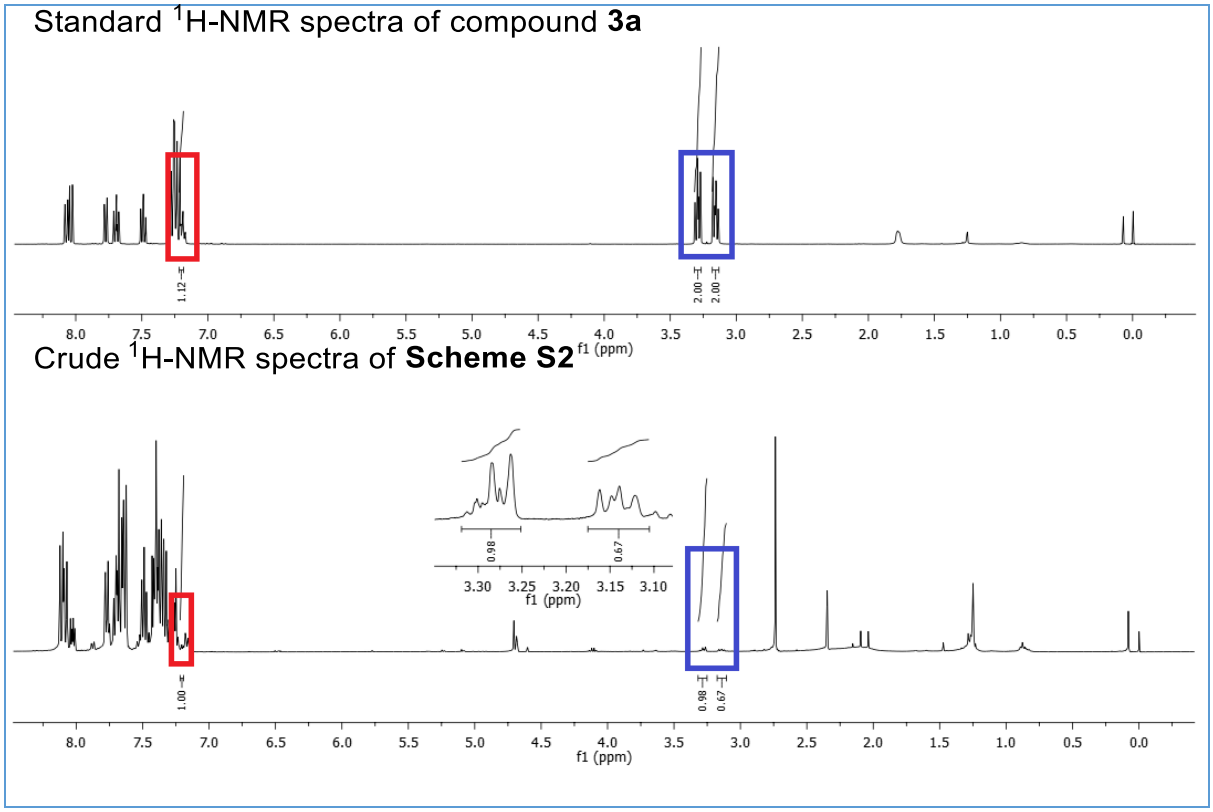
Conversion was calculated by ^{1}H-NMR integration value

		Deuterium incorporation in **α** position	Deuterium incorporation in **β** position
Signal δ ppm	7.21 (1H)	3.29 (2H)	3.15 (2H)
Integral Value	1.0	0.91	0.43
Calculated ratio		{(2-0.91)/2}×100 = **55%**	{(2-0.43)/2}×100 = **79%**

Scheme S2:



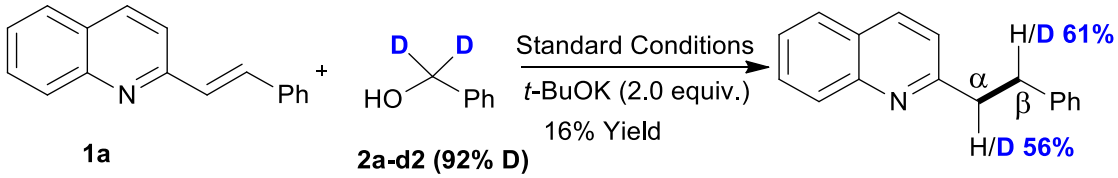
1a **2a-d2 (92% D)**

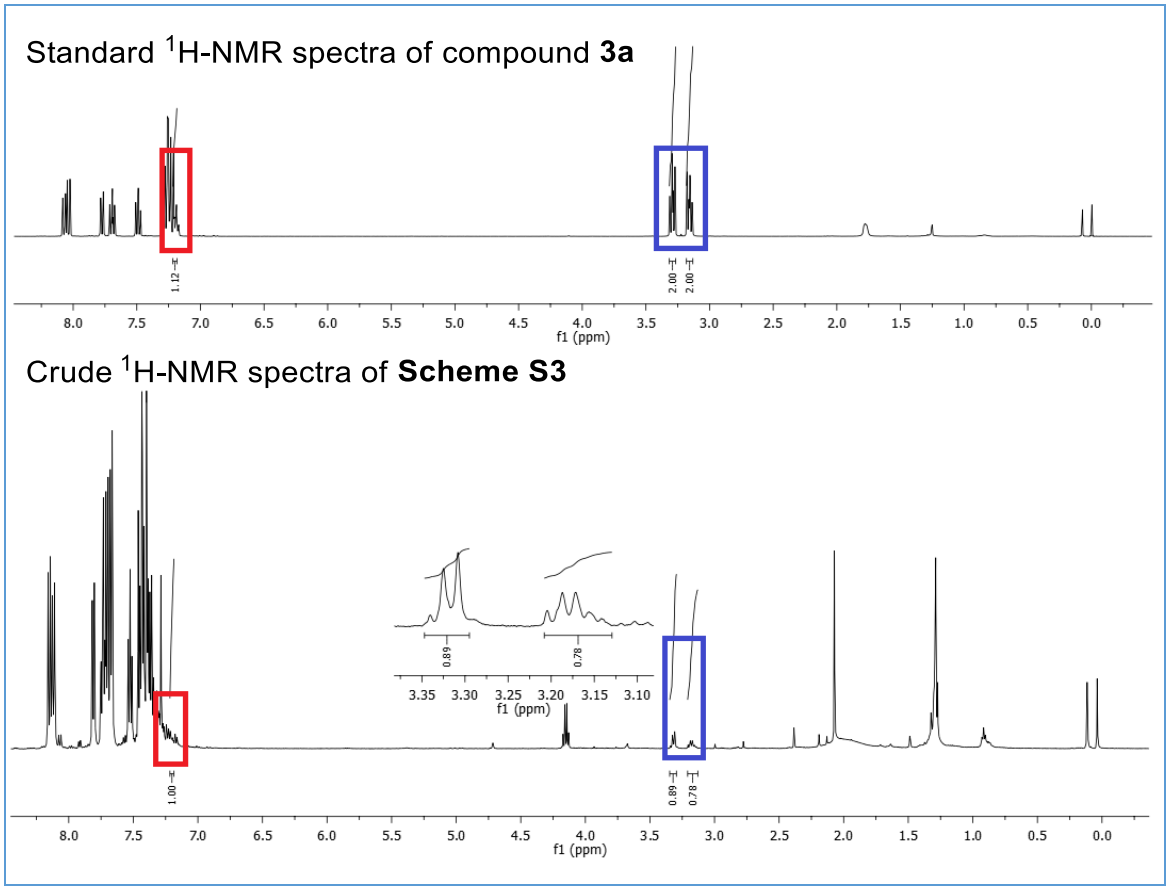


Conversion was calculated by ^{1}H-NMR integration value

		Deuterium incorporation in **α** position	Deuterium incorporation in **β** position
Signal δ ppm	7.21 (1H)	3.29 (2H)	3.15 (2H)
Integral Value	1.0	0.98	0.67
Calculated ratio		{(2-0.98)/2}×100 = **51%**	{(2-0.67)/2}×100 = **67%**

Scheme S3:





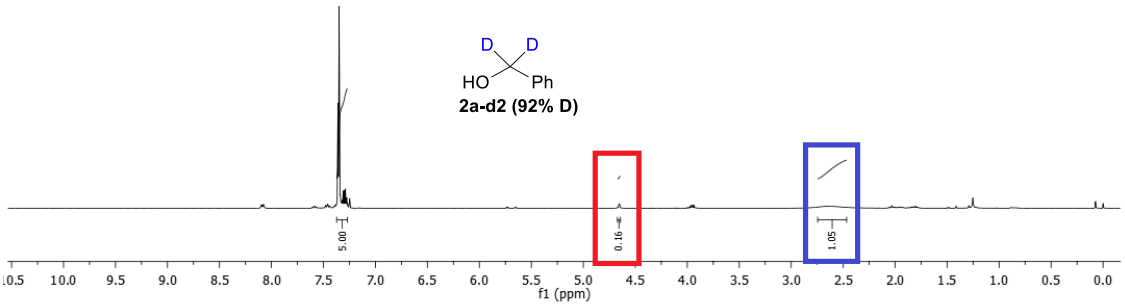
Conversion was calculated by ^{1}H-NMR integration value

		Deuterium incorporation in **α** position	Deuterium incorporation in **β** position
Signal δ ppm	7.21 (1H)	3.29 (2H)	3.15 (2H)
Integral Value	1.0	0.89	0.78

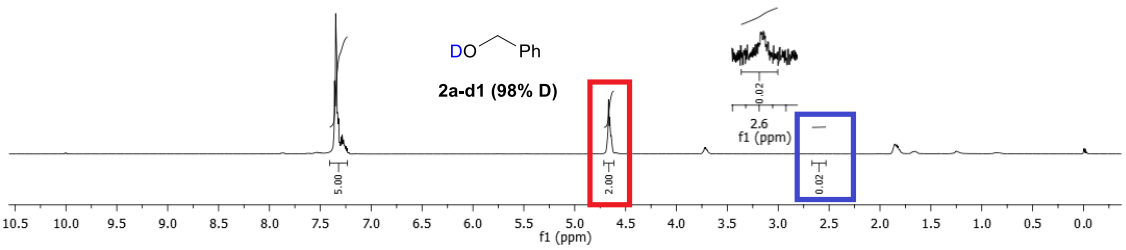
Calculated ratio		{(2-0.89)/2}×100 = **56%**	{(2-0.78)/2}×100 = **61%**

Scheme S4:

Scheme S4a: ^{1}H-NMR spectra of compound **2a-d2**



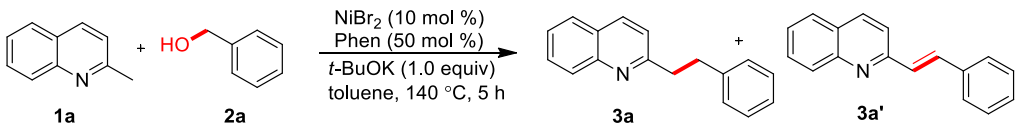
Scheme S4b: ^{1}H-NMR spectra of compound **2a-d1**

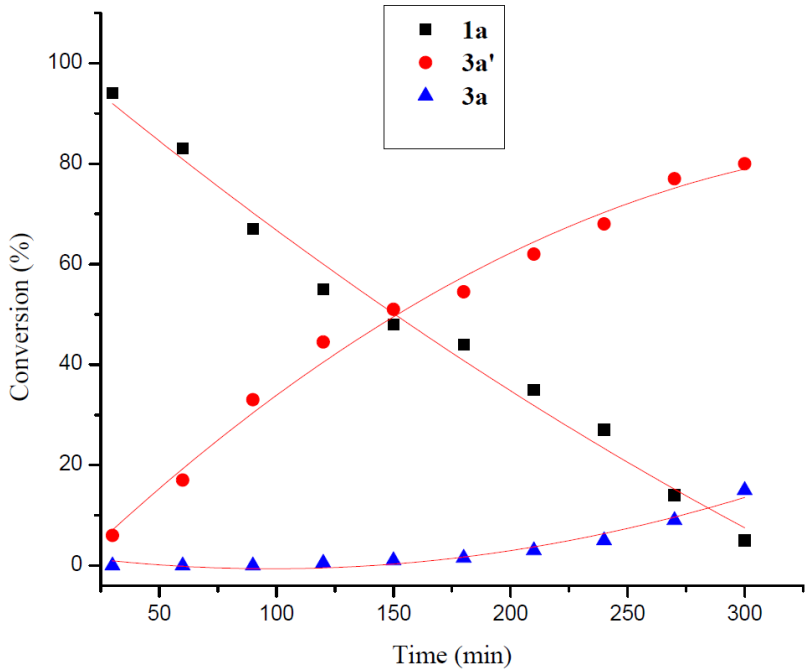


Conversion was calculated by ^{1}H-NMR integration value

		Deuterium incorporation in **CH_2** position	Deuterium incorporation in **OH** position
Signal δ ppm (Standard)	7.24-7.36 (5H)	4.65 (2H)	2.65 (1H)
Integral Value (**Scheme S4a**)	5.0	0.16	1.05
Calculated ratio		{(2-0.16)/2}×100 = **92%**	{(1-1)}×100 = **0%**
Integral Value (**Scheme S4b**)	5.0	2.0	0.02
Calculated ratio		{(2.0-2.0)/2}×100 = **0%**	{(1-0.02)}×100 = **98%**

Scheme S5: Studies for the progress of the reaction over time

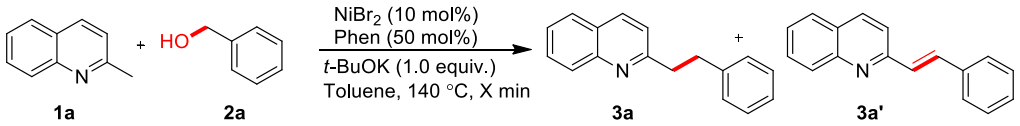




Graphical representation for GC Conversion of **1a, 3a** and **3a'** vs time

Scheme S6: Determination of rate and order of reaction

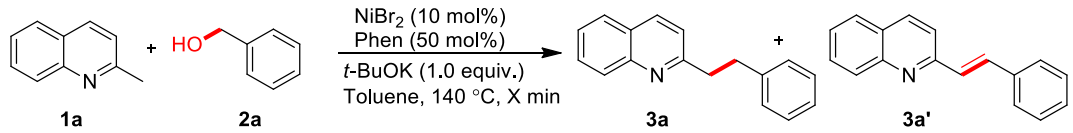
Run 1: Reaction was carried out in 2 mL of toluene and yield was calculated by GC



No.	**1a** (mmol)	**2a** (mmol)	$NiBr_2$ (mmol)	Phen (mmol)	*t*-BuOK (mmol)	Toluene (mL)
Run 1	0.2	0.4	0.02	0.1	0.2	2.0

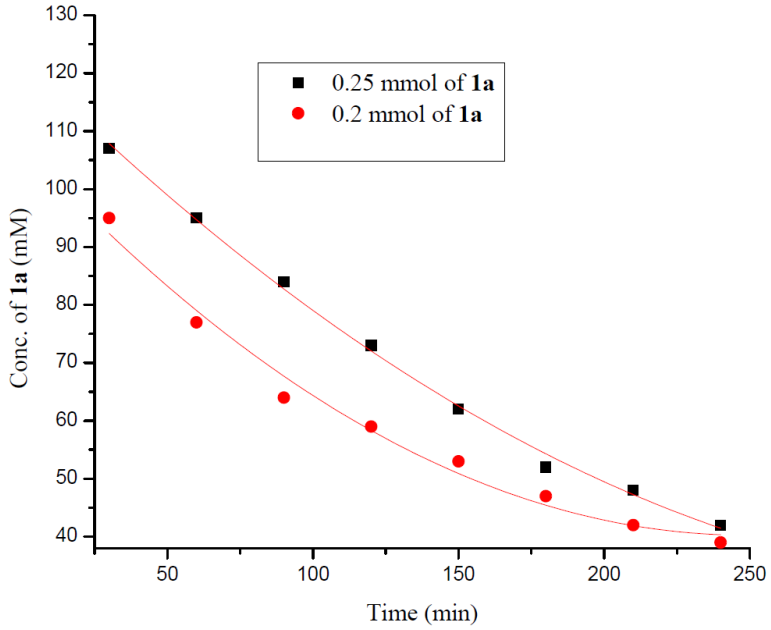
Sl. No.	Time (min)	Concentration of **1a** (mM)
1	30	95
2	60	77
3	90	64
4	120	59
5	150	53
6	180	47
7	210	42
8	240	39

Run 2: Reaction was carried out in 2 mL of toluene and yield was calculated by GC



No.	**1a** (mmol)	**2a** (mmol)	$NiBr_2$ (mmol)	Phen (mmol)	*t*-BuOK (mmol)	Toluene (mL)
Run 2	0.25	0.5	0.025	0.125	0.25	2.0

Sl. No.	Time (min)	Concentration of **1a** (mM)
1	30	107
2	60	95
3	90	84
4	120	73
5	150	62
6	180	52
7	210	48
8	240	42



Graphical representation for determination of rate and order of reaction

Considering steady state approximation for benzyl alcohol

From Run 1: Slope = k $[1a]^x$

$-0.248 = k\,[0.2]^x$

From Run 2: Slope = k $[1a]^x$

$-0.316 = k\,[0.25]^x$

$-0.316 / -0.248 = [0.25]^x / [0.2]^x$

$1.27 = [1.25]^x$

$\text{Log}(1.27) = x.\ \text{Log}(1.25)$

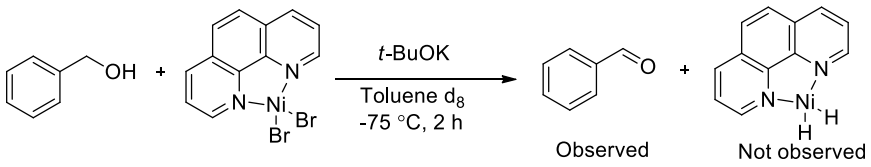
$x = 0.103 / 0.097$

$= 1.06 \approx 1$

Rate = k $[1a]^1$

Scheme S7:

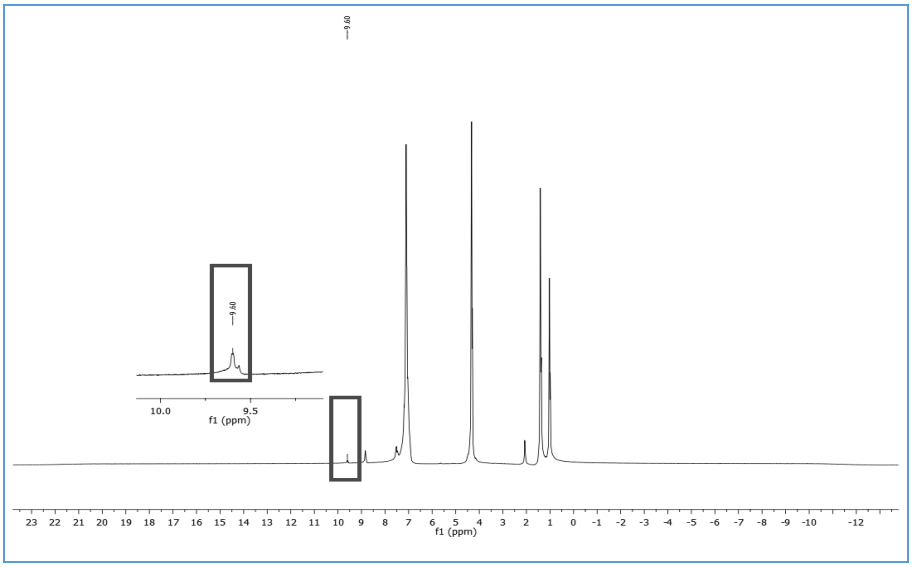
(i) Metal hydride trapping studies using *in situ* ^{1}H NMR:



Reaction condition: [a] Benzyl alcohol (0.2 mmol), $NiBr_2$.Phen complex (0.02 mmol), *t*-BuOK (0.2 mmol), toluene d_8 (0.4 mL), in NMR tube under nitrogen atmosphere, ^{1}H NMR was recorded at -75 °C.

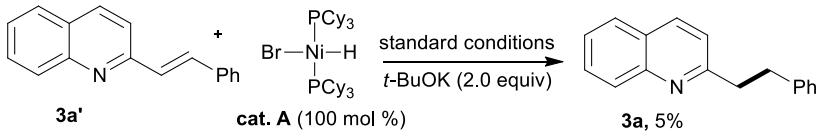
The reaction mixture was turned reddish brown colour indicating the formation of metal hydride species, several attempt made to trace metal hydride by ^{1}H-NMR experiments and it was not successful. We observed the benzaldehyde formation. These results indicating that the nickel-hydride species is not stable under this conditions.

Characterization of $NiBr_2$.Phen complex: Chemical Formula: $C_{12}H_8Br_2N_2Ni$; Elemental Analysis calculated (%): C, 36.15; H, 2.02; Br, 40.08; N, 7.03; Ni, 14.72; Found (%): C, 35.57; H, 2.66; N, 6.91 (Ref: M. Khrizanforov, K.Vera, V. Mamedov, N. Zhukova, S. Strekalova, V. Grinenko, T. Gryaznova, O. Sinyashin, Y. Budnikova, J. Organomet. Chem. 2016, **820**, 82).

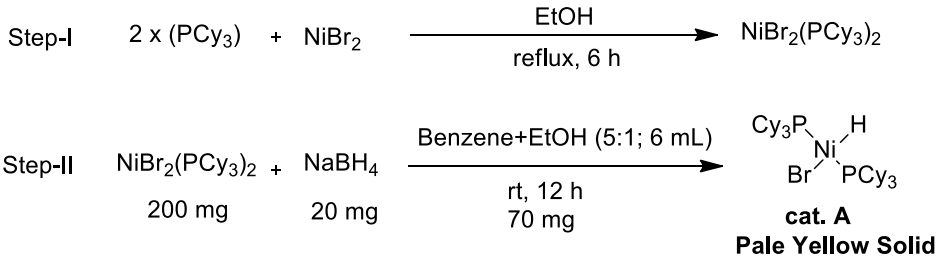


^{1}H NMR spectra at (-75 °C) in toluene d_8

(ii): Experimental evidences for generation of Ni-H species:



Preparation of cat. A: The catalyst was prepared following literature reported procedure. The Ni-H species, **cat. A** was obtained as pale yellow solid and the solid decomposes very fast in solvent. Characterization data are in agreement with the literature reported data.



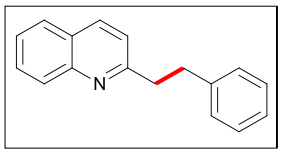
*Characterization of **cat. A:*** IR: Ni-H 1950 cm.$^{-1}$; M.P: (150-151) ^{o}C (decompose).

Ref: 1. M. L. H. Green, T. Saito, P. J. Tanfield, *J. Chem. Soc. A* **1971**, 152-154.

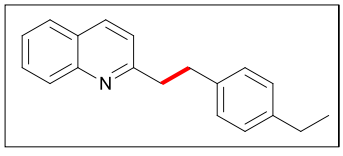
2. M. M. Lindner, U. Beckmann, W. Frank, W. Kläui, *ISRN Inorg. Chem.* **2013**, 1-13.

[1.4] Spectroscopic and analytical data:

2-phenethylquinoline (3a)[1]: Following the general procedure A the title compound was isolated as light brown oil (Yield 97%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.69 (ddt, J = 8.4, 6.9, 1.5 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.30 – 7.17 (m, 6H), 3.32 – 3.27 (m, 2H), 3.18 – 3.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.91, 148.08, 141.61, 136.30, 129.49, 128.96, 128.61, 128.48, 127.61, 126.90, 126.08, 125.88, 121.65, 41.07, 36.02.

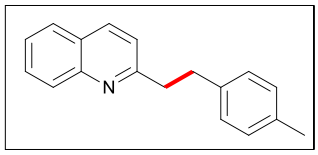


2-(4-ethylphenethyl)quinoline (3b): Following the general procedure A the title compound was isolated as light brown oil (Yield 95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 13.6, 8.5 Hz, 2H), 7.78 (dd, J = 8.1, 1.1 Hz, 1H), 7.70 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.49 (ddd, J = 8.0,



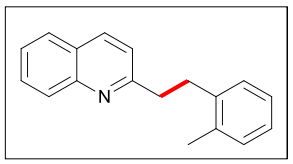
6.9, 1.1 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.30 – 3.26 (m, 2H), 3.14 – 3.10 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.08, 148.06, 141.98, 138.80, 136.33, 129.49, 128.95, 128.53, 127.98, 127.62, 126.90, 125.87, 121.67, 41.22, 35.67, 28.55, 15.74. Elemental Analysis: Calculated C, 87.31; H, 7.33; N, 5.36; Found C, 86.42; H, 7.27; N, 4.08.

2-(4-isopropylphenethyl)quinoline (3c): Following the general procedure A the title compound was isolated as light brown oil (Yield 78%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 15.3, 8.4 Hz, 2H), 7.78 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.17 – 7.15 (m, 2H), 3.31 – 3.27 (m, 2H), 3.15 – 3.11(m, 2H), 2.93 – 2.85 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.11, 148.08, 146.63, 138.95, 136.33, 129.49, 128.97, 128.50, 127.63, 126.90, 126.55, 125.87, 121.66, 41.20, 35.66, 33.80, 24.17; Elemental Analysis: Calculated C, 87.23; H, 7.69; N, 5.09; Found C, 88.02; H, 7.19; N, 4.38.

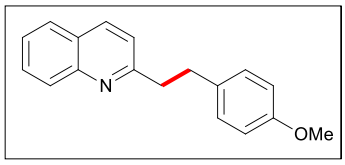


2-(4-methylphenethyl)quinolone (3d)[1]: Following the general procedure A the title compound was isolated as light brown oil (Yield 95%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 12.3, 8.5 Hz, 2H), 7.77 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 3.29 – 3.25 (m, 2H), 3.13 – 3.09 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.05, 148.06, 138.52, 136.34, 135.54, 129.49, 129.18, 128.94, 128.48, 128.02, 127.62, 126.89, 121.68, 41.22, 35.63, 21.13.

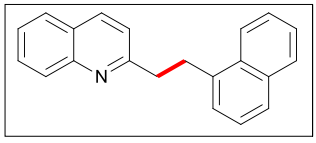
2-(2-methylphenethyl)quinolone (3e)[1]: Following the general procedure A the title compound was isolated as light brown oil (Yield 94%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 13.9, 8.5 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.50 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.25 – 7.10 (m, 5H), 3.27 – 3.23 (m, 2H), 3.15 – 3.11 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.08, 148.09, 139.77, 136.32, 136.12, 130.29, 129.50, 128.98, 128.95, 127.62, 126.89, 126.24, 126.12, 125.90, 121.61, 39.78, 33.35, 19.46.



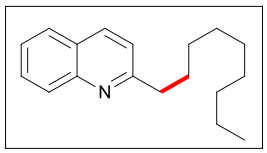
2-(4-methoxyphenethyl)quinolone (3f)[1]: Following the general procedure A the title compound was isolated as light brown oil (Yield 96%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.77 (d, J = 8.1 Hz, 1H), 7.69 (ddt, J = 8.2, 6.9, 1.3 Hz, 1H), 7.48 (ddt, J = 8.1, 7.0, 1.2 Hz, 1H), 7.22 (dd, J = 8.4, 1.0 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 6.81 (dd, J = 8.7, 0.7 Hz, 2H), 3.77 (s, 3H), 3.27 – 3.23 (m, 2H), 3.10 – 3.06 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 162.03, 157.94, 148.04, 136.30, 133.65, 129.52, 129.48, 128.91, 127.63, 126.87, 125.85, 121.72, 113.86, 55.33, 41.38, 31.05.



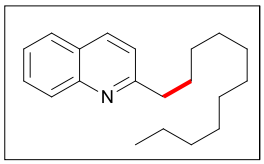
2-(1-(naphthalen-2-yl)ethyl)quinolone (3g)[2]: Following the general procedure A the title compound was isolated as light brown oil (Yield 84%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.89 – 7.85 (m, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.55-7.52 (m, 3H), 7.39 – 7.32 (m, 2H), 7.19 (dd, J = 12.8, 10.3 Hz, 1H), 3.64 – 3.60 (m, 2H), 3.44 – 3.40 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 162.05, 148.08, 137.61, 136.39, 135.19, 133.36, 131.88, 129.57, 128.92, 127.67, 126.94, 126.24, 126.04, 125.95, 125.68, 125.62, 124.90, 123.85, 121.74, 40.16, 33.16.



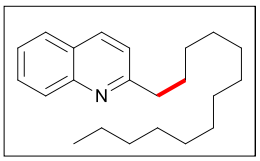
2-nonylquinoline (3h)[1]: Following the general procedure A the title compound was isolated as pale yellow oil (Yield 60%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.2, 1.7 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.27 – 7.25 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 2.90 (t, J = 6.4 Hz, 2H), 1.44-1.40 (m, 2H), 1.30-1.25 (m, 12H), 0.85 (t, J = 8 Hz, 3H); GC-MS (EI) m/z = 255.1.



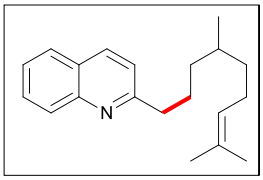
2-undecylquinoline (3i)[3]: Following the general procedure A the title compound was isolated as pale yellow oil (Yield 48%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.2, 1.7 Hz, 1H), 7.99 (dd, J = 8.3, 1.7 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 2.90 (t, J = 6.4 Hz, 2H), 1.46-1.40 (m, 2H), 1.32-1.25 (m, 16H), 0.85 (t, J = 8 Hz, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 161.30, 147.04, 140.75, 135.99, 130.72, 129.15, 127.44, 120.63, 113.19, 40.60, 31.99, 30.99, 30.16, 26.97, 22.77, 14.22.



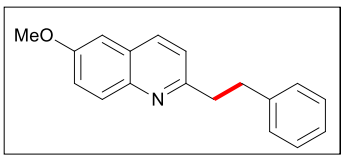
2-Tridecylquinoline (3j)[1]: Following the general procedure A the title compound was isolated as pale yellow oil (Yield 38%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.2, 1.7 Hz, 1H), 7.99 (dd, J = 8.3, 1.7 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 2.91 (t, J = 6.4 Hz, 2H), 1.46 – 1.41 (m, 2H), 1.27-1.24 (m, 20H), 0.85 (t, J = 8 Hz, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 160.80, 147.02, 140.74, 136.00, 130.88, 129.16, 127.44, 120.63, 113.18, 40.60, 32.02, 30.99, 30.17, 29.75, 29.46, 26.97, 22.79, 14.23.



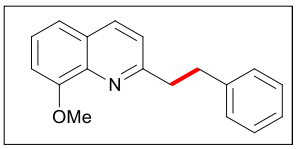
2-(4,8-dimethylnon-7-en-1-yl)quinoline (3k): Following the general procedure A the title compound was isolated as pale yellow oil (Yield 47%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.1, 1.4 Hz, 1H), 8.03 (dd, J = 8.2, 1.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 5.95 (t, J = 6.8 Hz, 1H), 3.57 – 3.54 (m, 2H), 2.95 (t, J = 6.3 Hz, 2H), 2.20 (s, 3H), 2.09 (dd, J = 11.6, 6.0 Hz, 2H), 1.71 – 1.61 (m, 5H), 1.28 (s, 3H), 0.90 (dd, J = 11.6, 5.3 Hz, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 146.94, 140.70, 137.53, 135.85, 129.05, 127.38, 121.24, 120.52, 116.57, 113.10, 41.28, 31.92, 30.88, 29.69, 29.35, 27.04, 22.68, 21.84, 14.09. Elemental Analysis: Calculated C, 85.35; H, 9.67; N, 4.98; Found C, 84.16; H, 9.91; N, 5.19.



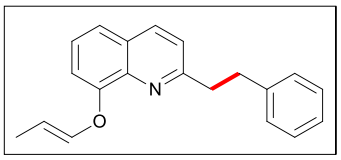
6-methoxy-2-phenethylquinoline (3l)[2]: Following the general procedure B the title compound was isolated as light brown oil (Yield 62%).[1]H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, J = 9.0 Hz, 2H), 7.34 (dd, J = 9.1, 2.9 Hz, 1H), 7.29 – 7.16 (m, 6H), 7.04 (d, J = 2.8 Hz, 1H), 3.91 (s, 3H), 3.26 – 3.22 (m, 2H), 3.14 – 3.10 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 157.64, 155.68, 142.44, 140.03, 133.41, 128.66, 126.90, 126.75, 126.05, 124.32, 120.27, 120.16, 103.64, 53.89, 39.07, 34.40.



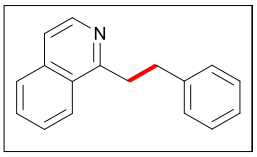
8-methoxy-2-phenethylquinoline (3m)[4]: Following the general procedure B the title compound was isolated as light brown oil (Yield 92%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.35 (dd, J = 8.1, 0.9 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.19 (ddd, J = 8.5, 5.1, 2.0 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 4.08 (s, 3H), 3.38 – 3.34 (m, 2H), 3.17 – 3.13 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 157.65, 151.79, 138.32, 136.57, 132.86, 125.22, 125.08, 124.67, 122.65, 118.66, 116.20, 111.69, 104.54, 52.84, 37.68, 32.76.



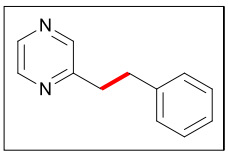
8-(allyloxy)-2-phenethylquinoline (3n): Following the general procedure B the title compound was isolated as pale yellow oil (Yield 60%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.28 – 7.25 (m, 2H), 7.22 – 7.10 (m, 2H), 7.09 – 7.04 (m, 2H), 6.57 – 6.54 (m, 1H), 5.11 – 5.04 (m, 1H), 3.38 – 3.34 (m, 2H), 3.20 – 3.17 (m, 2H), 1.87 – 1.83 (m, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 161.30, 153.13, 141.83, 141.44, 139.84, 136.16, 129.49, 128.70, 128.45, 128.16, 126.01, 121.40, 112.72, 111.30, 109.68, 40.88, 35.70, 9.94; Elemental Analysis: Calculated C, 83.01; H, 6.62; N, 4.84; Found C, 82.36; H, 6.11; N, 4.08.



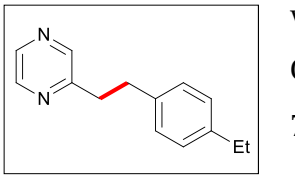
1-phenethylisoquinoline (3o)[5]: Following the general procedure A the title compound was isolated as light brown oil (Yield 80%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 5.7 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.66 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.58 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.53 (d, J = 5.7 Hz, 1H), 7.32 (d, J = 4.3 Hz, 4H), 7.25 – 7.20 (m, 1H), 3.63 – 3.58 (m, 2H), 3.23 – 3.18 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 158.95, 139.89, 134.18, 127.72, 126.40, 126.38, 125.35, 125.00, 124.88, 123.97, 122.98, 117.32, 35.13, 33.38.



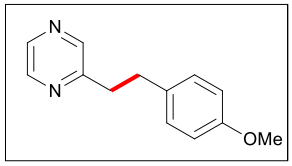
2-phenethylpyrazine (3p)[6]: Following the general procedure A the title compound was isolated as light brown oil (Yield 92%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 2.5, 1.6 Hz, 1H), 8.38 (d, J = 2.6 Hz, 1H), 8.34 (d, J = 1.5 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 3.14 – 3.03 (m, 4H); [13]C NMR (100 MHz, $CDCl_3$) δ 156.83, 144.83, 144.75, 144.25, 144.16, 142.48, 142.39, 140.83, 128.54, 126.36, 37.32, 35.47.



2-(4-ethylphenethyl)pyrazine (3q)[6]: Following the general procedure B the title compound was isolated as light brown oil (Yield 71%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.42 (d, J = 15.6 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.13 – 7.10 (m, 2H), 3.14 – 3.11 (m, 2H), 3.05 – 3.01 (m, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 156.65, 144.81, 144.20, 142.28, 140.97, 137.90, 130.33, 128.43, 37.40, 35.15, 28.52, 15.72.

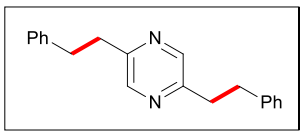


2-(4-methoxyphenethyl)pyrazine (3r)[7]: Following the general procedure B the title

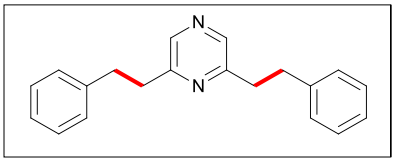


compound was isolated as light brown oil (Yield 55%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.52 (m, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.37 (d, J = 1.0 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.13 – 3.10 (m, 2H), 3.05-3.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.06, 156.93, 144.81, 144.19, 142.36, 132.83, 129.44, 113.95, 55.33, 37.64, 34.67.

2,5-diphenethylpyrazine (3t)[8]: Following the general procedure A the title compound was

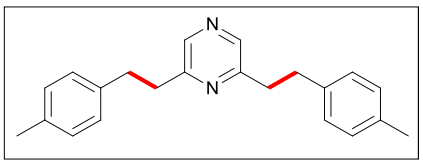


isolated as colorless solid (Yield 52%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 2H), 7.33 – 7.29 (m, 4H), 7.21 (dd, J = 11.3, 7.2 Hz, 6H), 3.19 – 3.14 (m, 4H), 3.13 – 3.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.66, 142.86, 140.91, 128.61, 128.53, 126.31, 37.11, 35.61.



2,6-diphenethylpyrazine (3u): Following the general procedure C the title compound was isolated as colorless oil (Yield 38%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.27 (dd, J = 11.1, 3.9 Hz, 4H), 7.18 (dd, J = 12.7, 7.2 Hz, 6H), 3.13 – 3.03 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.67, 141.77, 140.94, 128.46, 128.44, 126.15, 37.09, 35.44. HRMS (ESI): Calculated for $[C_{20}H_{21}N_2]^+$ 289.1699; Found 289.1700.

2,6-bis(4-methylphenethyl)pyrazine (3v): Following the general procedure C the title



compound was isolated as colorless oil (Yield 30%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.07 – 7.04 (m, 8H), 3.10 – 3.06 (m, 4H), 3.03 – 2.99 (m, 4H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.76, 141.76, 137.86, 135.59, 129.12, 128.34, 37.27, 35.06, 21.00. HRMS (ESI): Calculated for $[C_{22}H_{25}N_2]^+$ 317.2012; Found 317.2014.

[1.5] References:

1 Y. Obora, S. Ogawa and N. Yamamoto, *J. Org. Chem.*, 2012, **77**, 9429−9433.

2 T. Feng, H. Li, D. J. Young and J. Lang, *J. Org. Chem*., 2017, **82**, 4113−4120.

3 M. A. Fakhfakh, X. Franck, A. Fournet, R. Hocquemillera and B. Figadere, *Tetrahedron Letters*., 2001, **42**, 3847–3850.

4 Z. Tan, H. Jiang and M. Zhang, *Chem. Commun*., 2016, **52**, 9359.

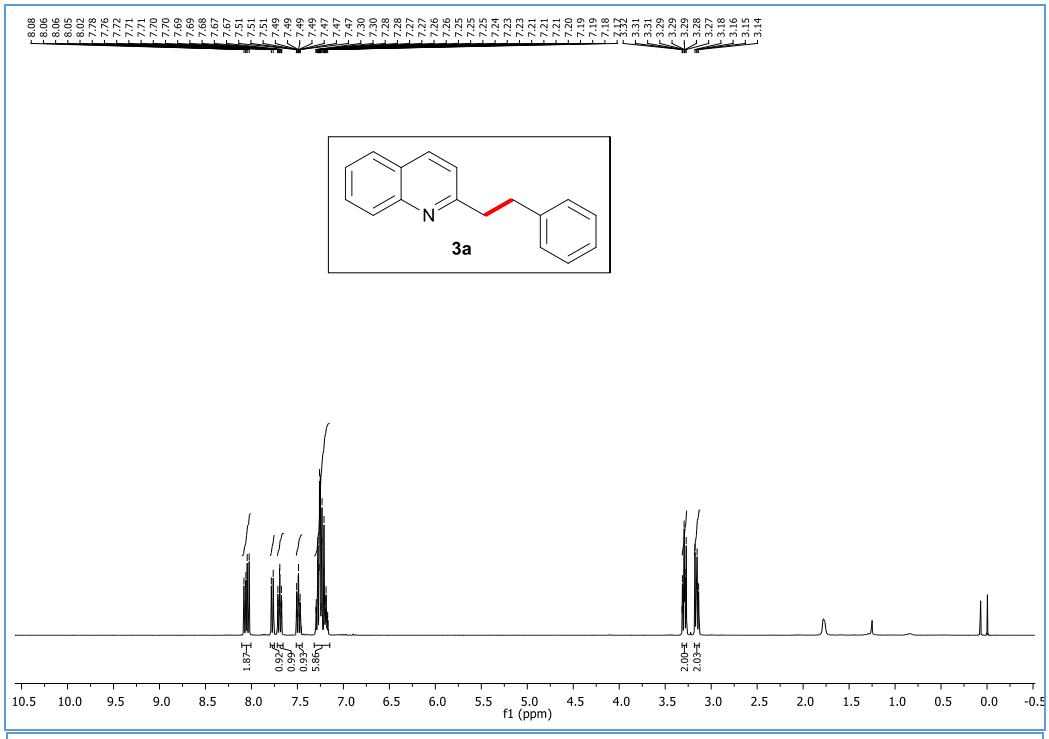
5 P. Basnet, S. Thapa, D. A. Dickie and R. Giri, *Chem. Commun*., 2016, **52**, 11072.

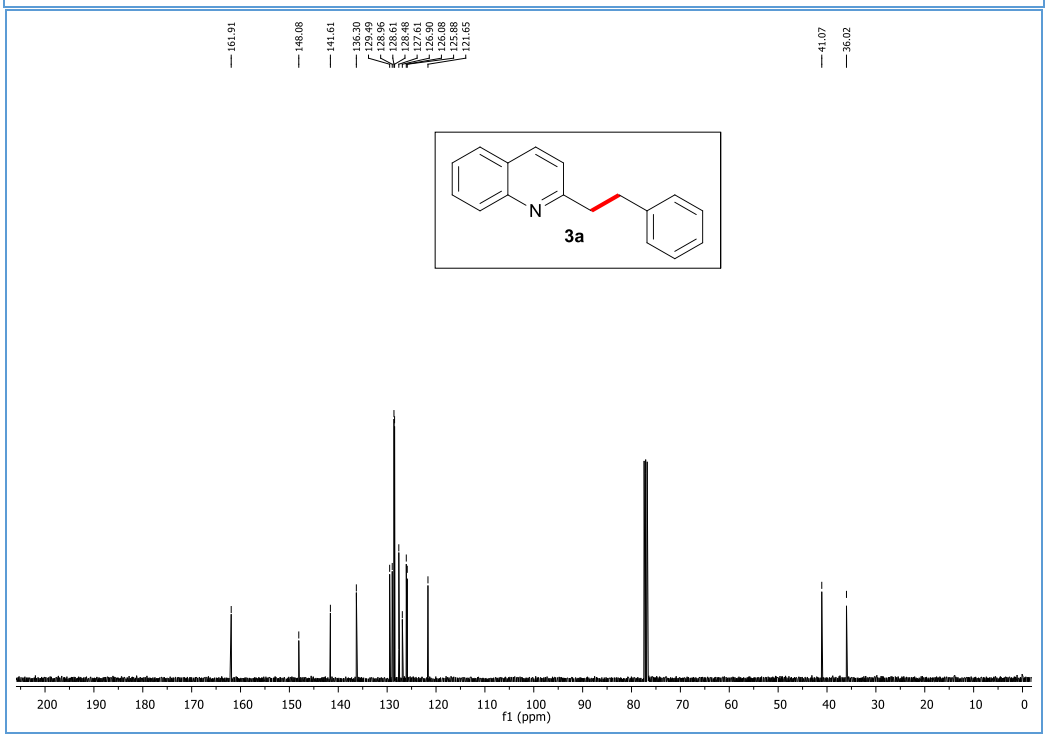
6 Y. Zhang, J. Briski, Y. Zhang, R. Rendy and D. A. Klumpp, *Org. Lett*., 2005, **7**, 12.

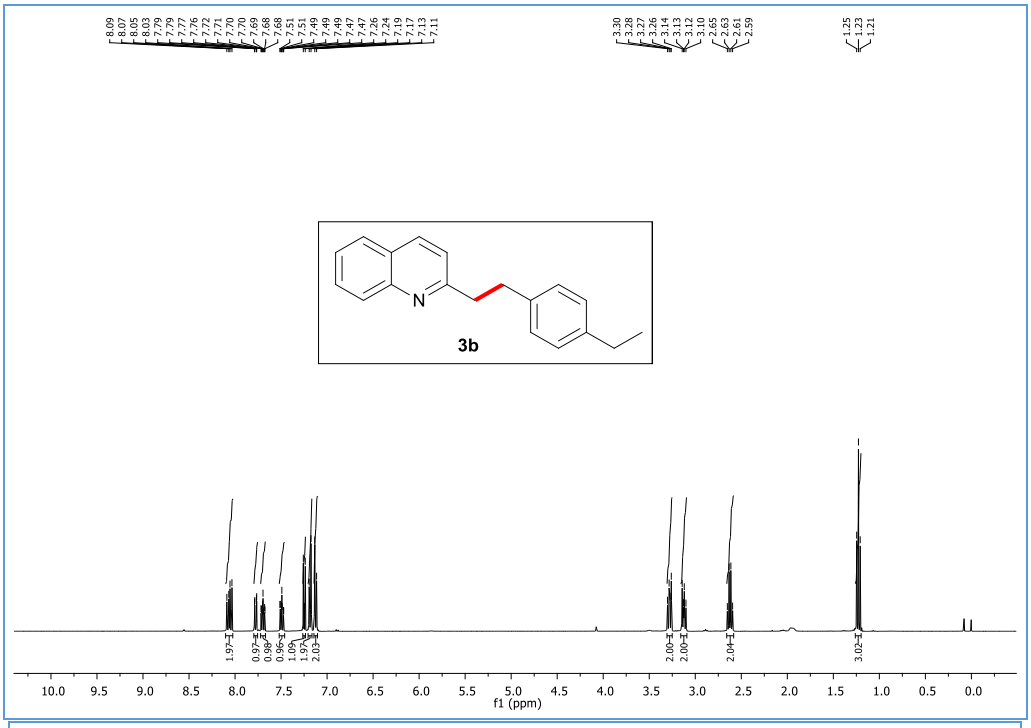
7 B. Blank and Rhett Kempe, *J. Am. Chem. Soc.* 2010, **132**, 924–925.

8 H. R. Henze and J. H. Shown Jr., *J. Am. Chem. Soc.*, 1947, **69** , 1662–1666.

[1.6] Copies of ^{1}H NMR and ^{13}C NMR Spectra for selected compounds



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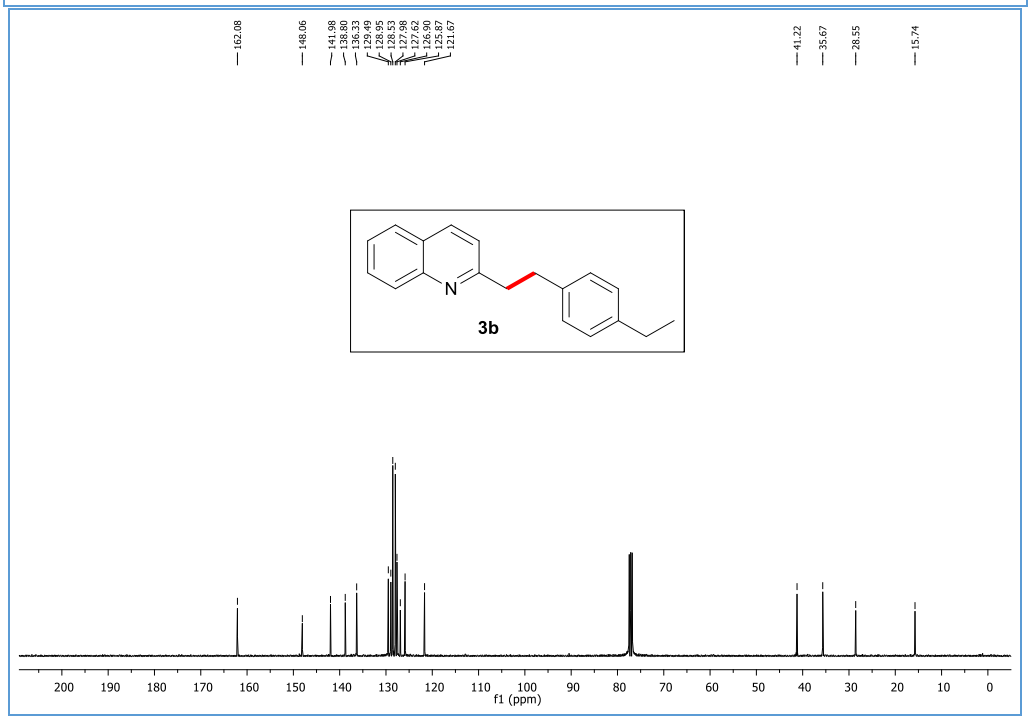
8.07
8.05
8.03
7.79
7.79
7.77
7.77
7.76
7.72
7.71
7.70
7.70
7.69
7.68
7.68
7.51
7.51
7.49
7.49
7.49
7.47
7.47
7.26
7.24
7.19
7.17
7.13
7.11
3.30
3.28
3.27
3.26
3.14
3.13
3.12
3.10
2.65
2.63
2.61
2.59
1.25
1.23
1.21
N
3b
1.97
0.97
0.98
0.96
1.09
1.97
2.03
2.00
2.00
2.04
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.98
138.80
136.33
129.49
128.95
128.55
127.98
127.62
126.90
125.87
121.67
41.22
35.67
28.55
15.74
N
3b
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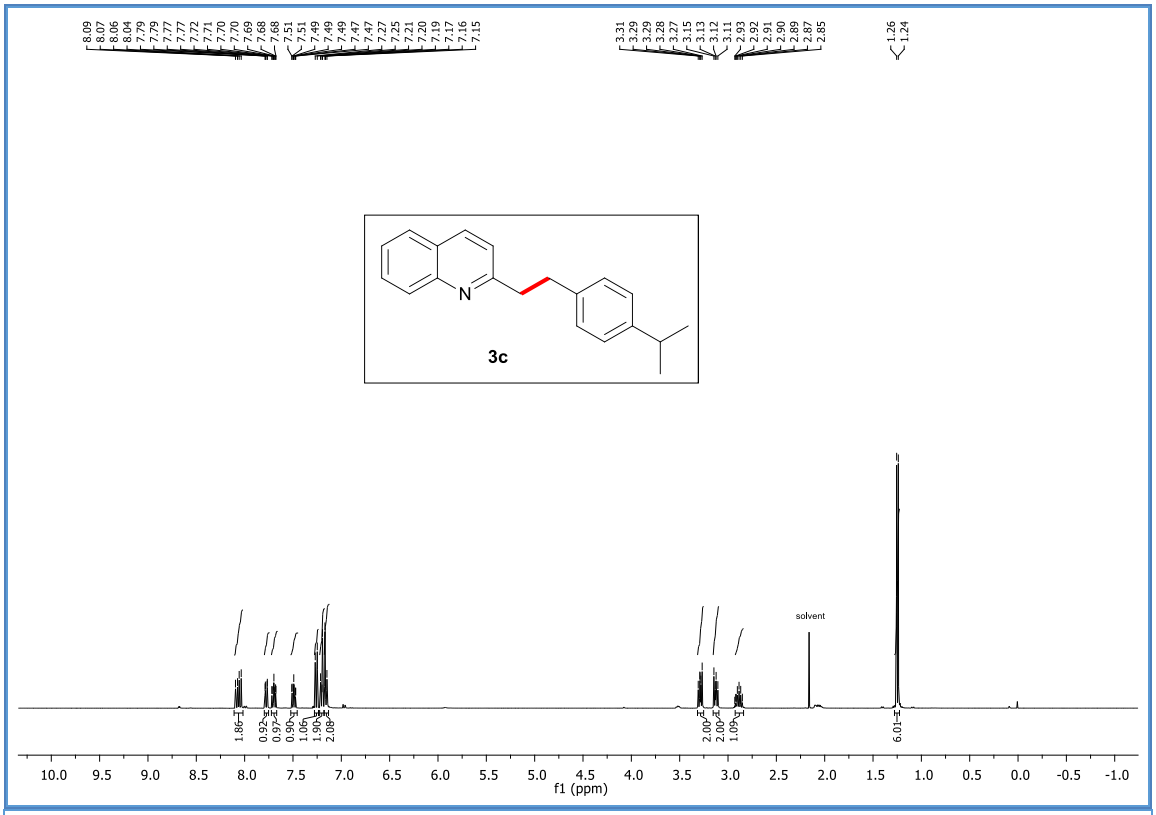
f1 (ppm)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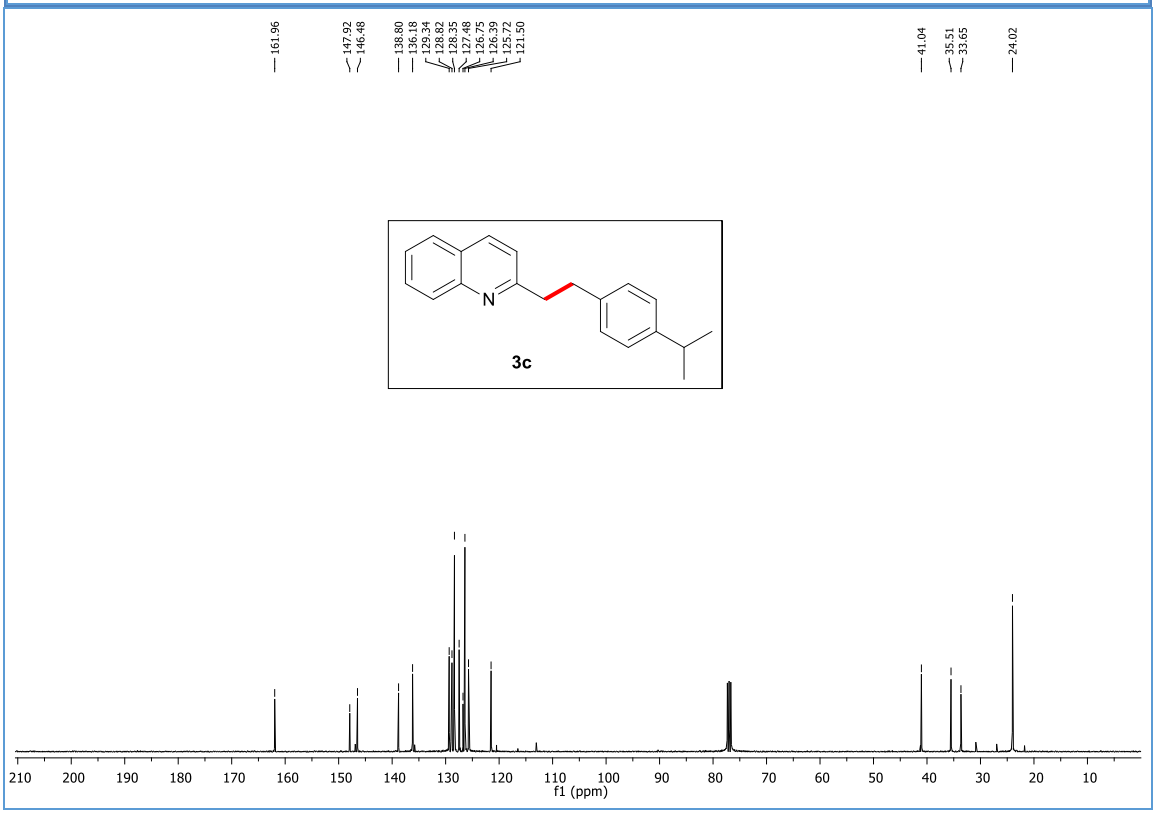
8.07
8.06
8.04
7.79
7.79
7.77
7.77
7.72
7.71
7.70
7.70
7.69
7.68
7.68
7.51
7.51
7.49
7.49
7.47
7.47
7.27
7.25
7.21
7.20
7.19
7.17
7.16
7.15
3.31
3.29
3.29
3.28
3.27
3.15
3.13
3.12
3.11
2.93
2.92
2.91
2.90
2.89
2.87
2.85
1.26
1.24
N
3c
solvent
1.86
0.92
0.97
0.90
1.06
1.90
2.08
2.00
2.00
1.09
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.35
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126.39
125.72
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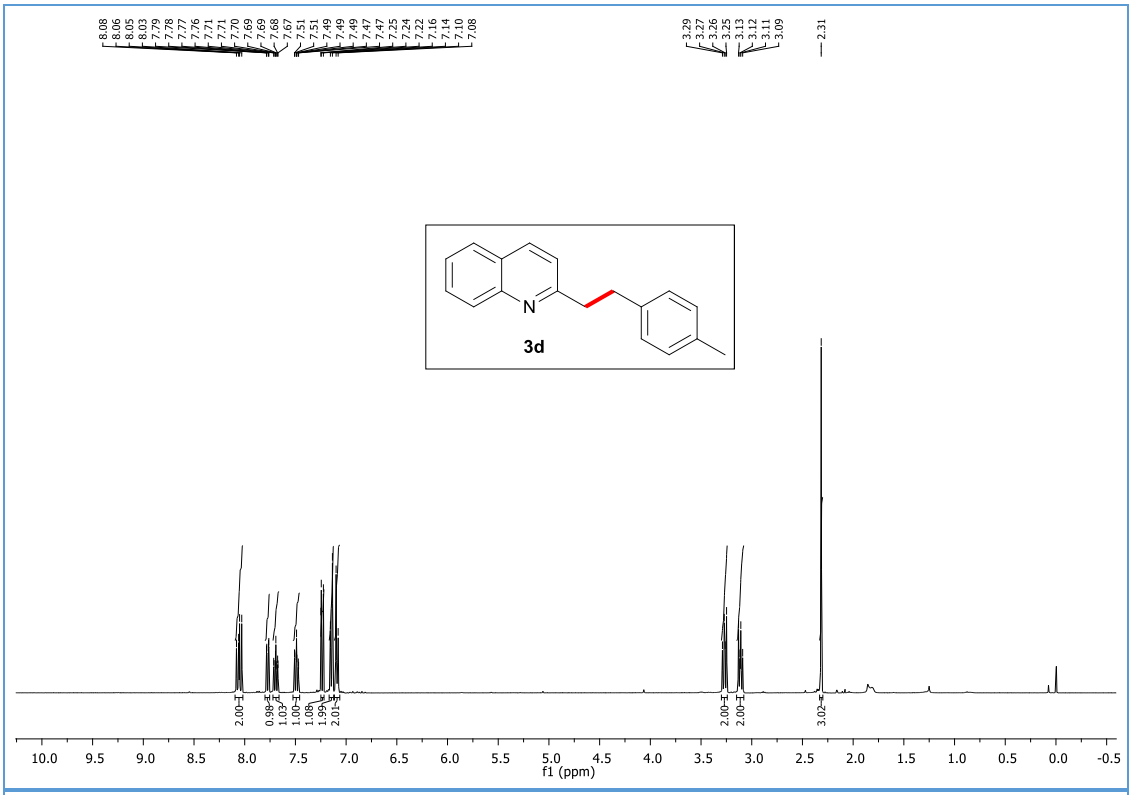
33.65
24.02
N
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.10
7.08
3.29
3.27
3.26
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3.13
3.12
3.11
3.09
2.31
N
3d
2.00
0.98
1.03
1.00
1.08
1.99
2.01
2.00
2.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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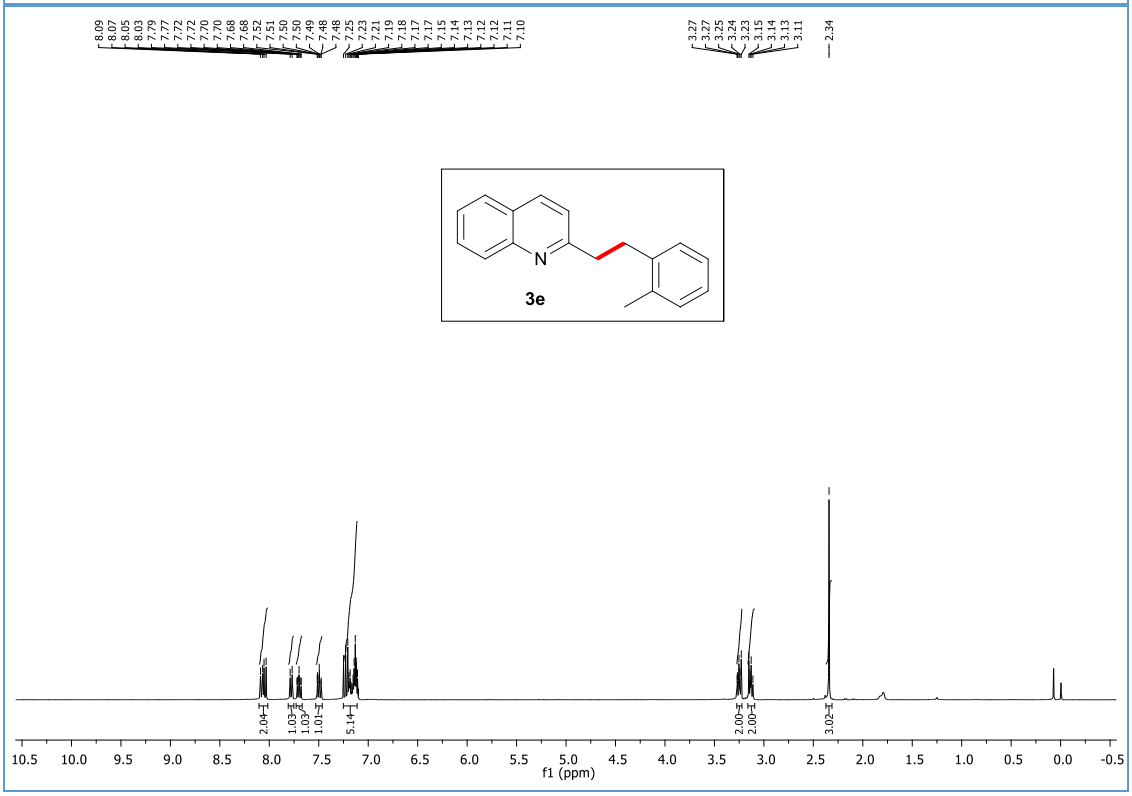
0.5
0.0
-0.5
f1 (ppm)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7.51
7.50
7.50
7.49
7.48
7.48
7.25
7.23
7.21
7.19
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7.17
7.15
7.14
7.13
7.12
7.12
7.11
7.10
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3.25
3.24
3.23
3.15
3.14
3.13
3.11
2.34
N
3e
2.04
1.03
1.09
1.01
5.14
2.00
2.00
3.02
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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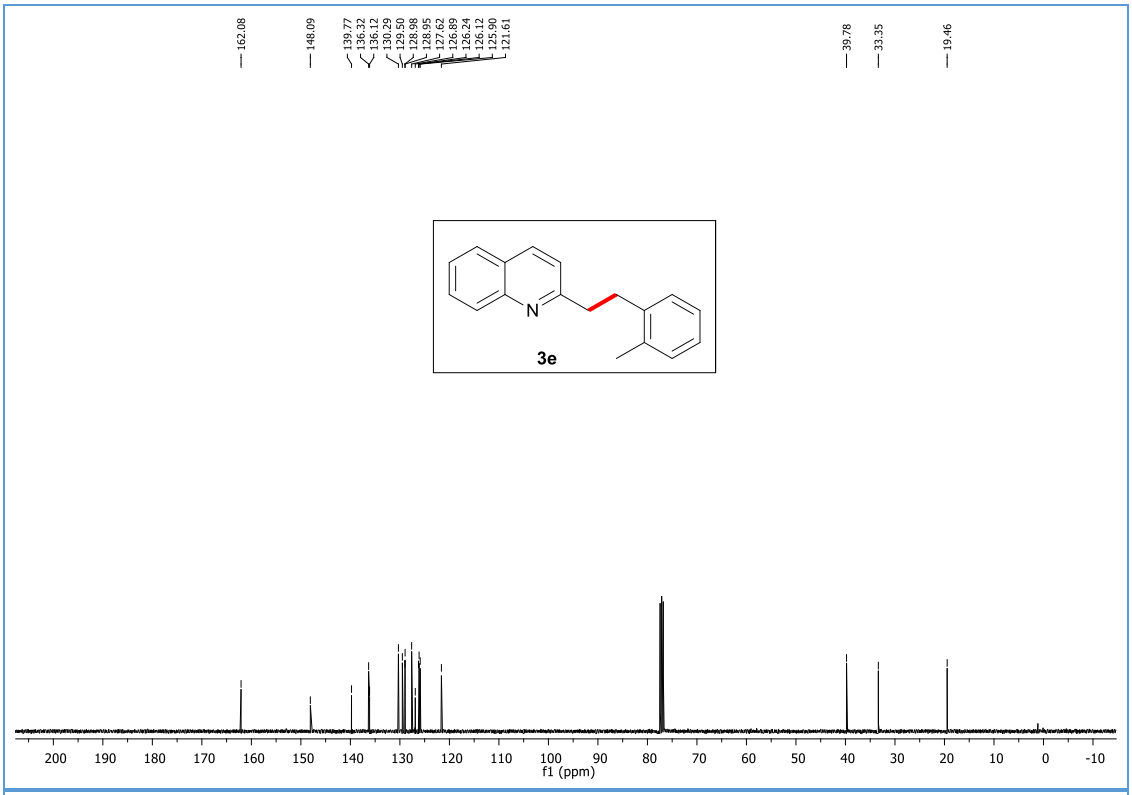
-0.5
f1 (ppm)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148.09
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136.32
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128.98
128.95
127.62
126.89
126.24
126.12
125.90
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33.35
19.46
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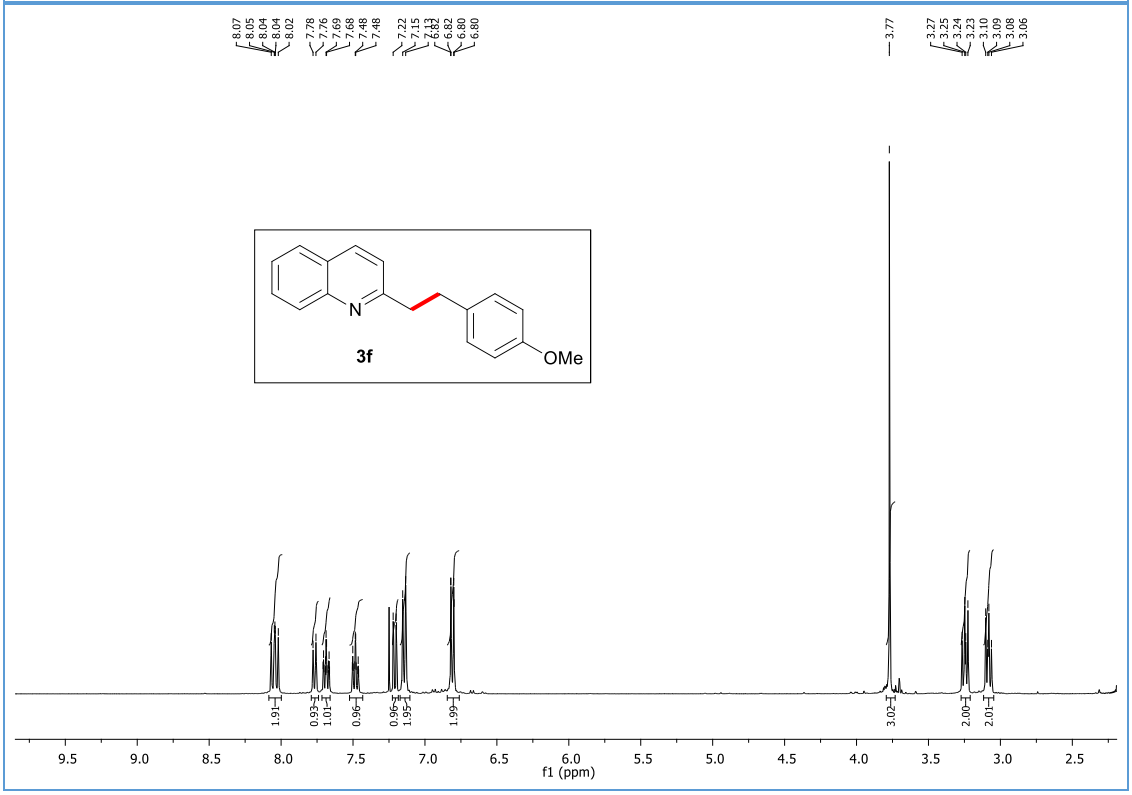
f1 (ppm)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8.05
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8.04
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7.69
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7.48
7.48
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3.77
3.27
3.25
3.24
3.23
3.10
3.09
3.08
3.06
N
3f
OMe
1.91
0.93
1.01
0.96
0.96
1.95
1.99
3.02
2.00
2.01
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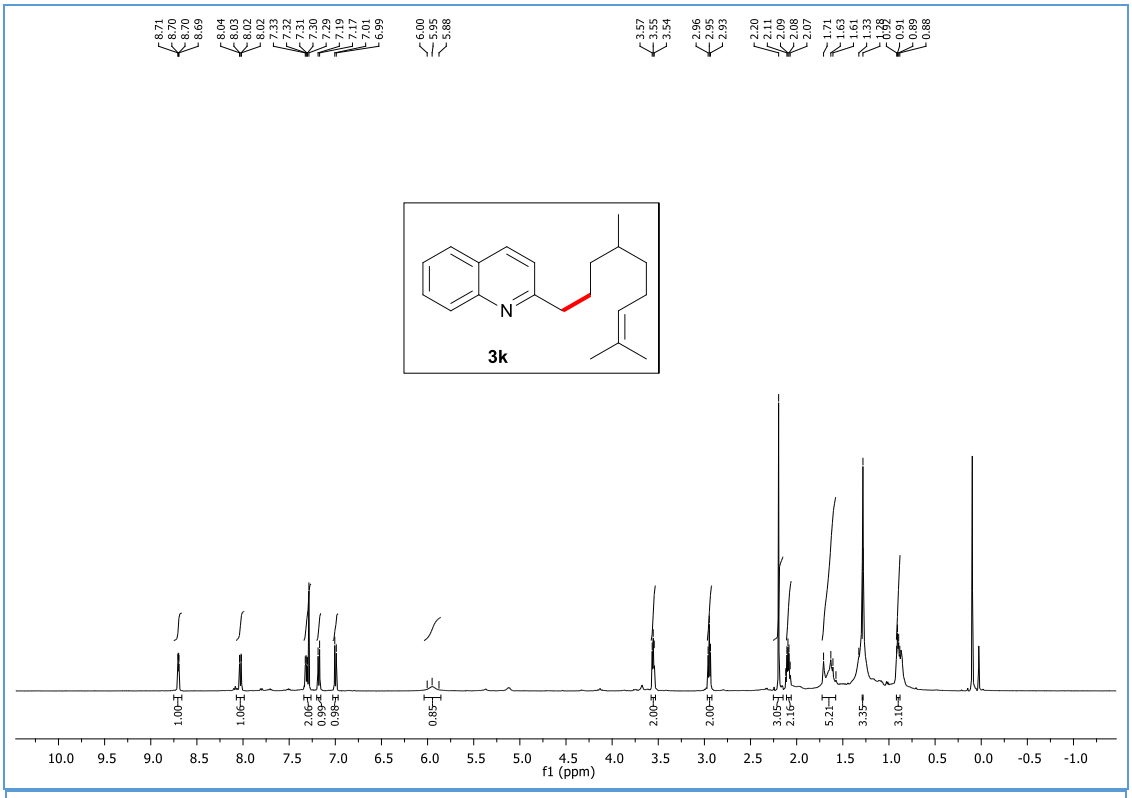
f1 (ppm)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8.03
8.02
8.02
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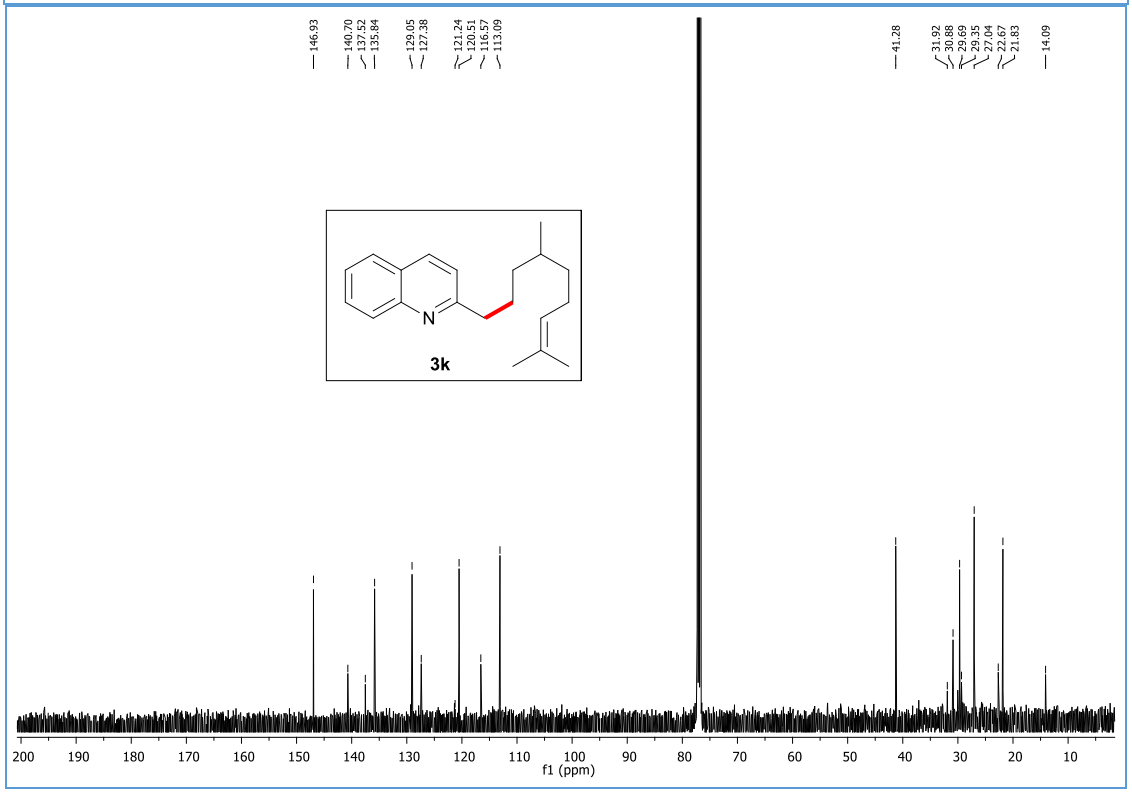
7.32
7.31
7.30
7.29
7.19
7.17
7.01
6.99
6.00
5.95
5.88
3.57
3.55
3.54
2.96
2.95
2.93
2.20
2.11
2.09
2.08
2.07
1.71
1.63
1.61
1.33
0.92
0.91
0.89
0.88
N
3k
1.00
1.06
2.06
0.99
0.98
0.85
2.00
2.00
3.05
2.16
5.21
3.35
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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113.09
41.28
31.92
30.88
29.69
29.35
27.04
22.67
21.83
14.09
N
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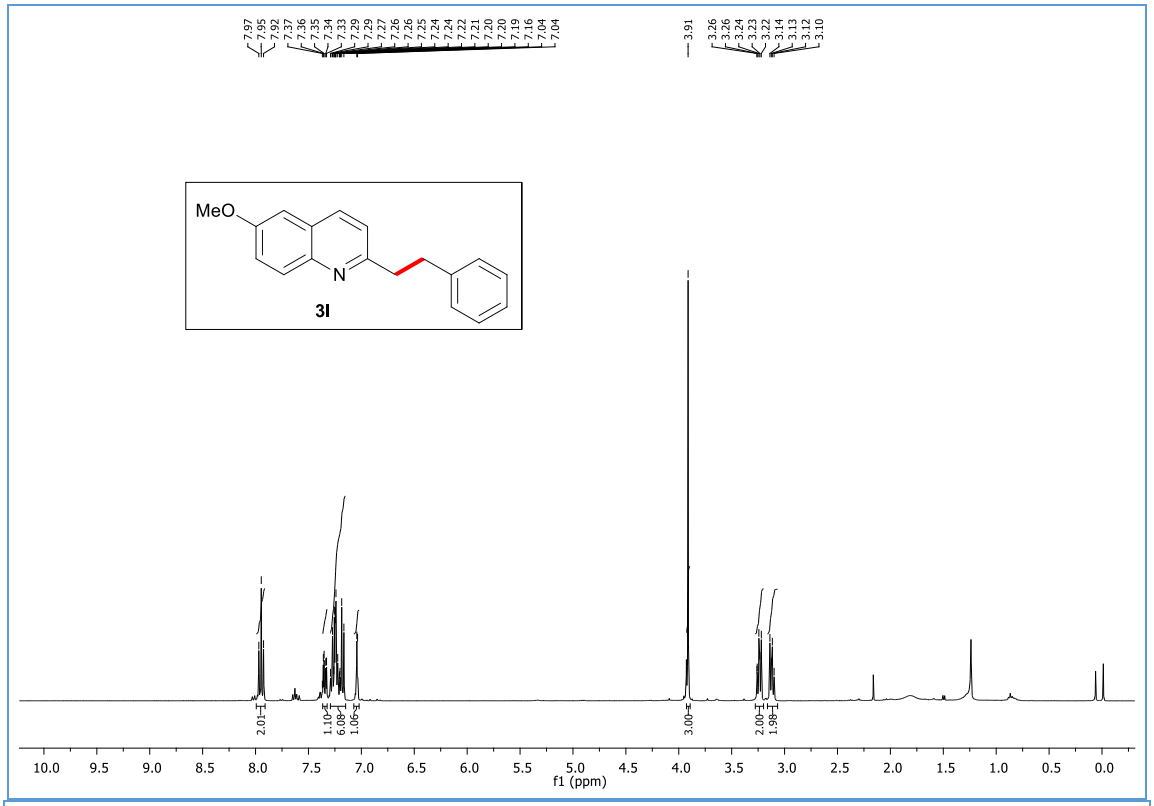
f1 (ppm)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3l
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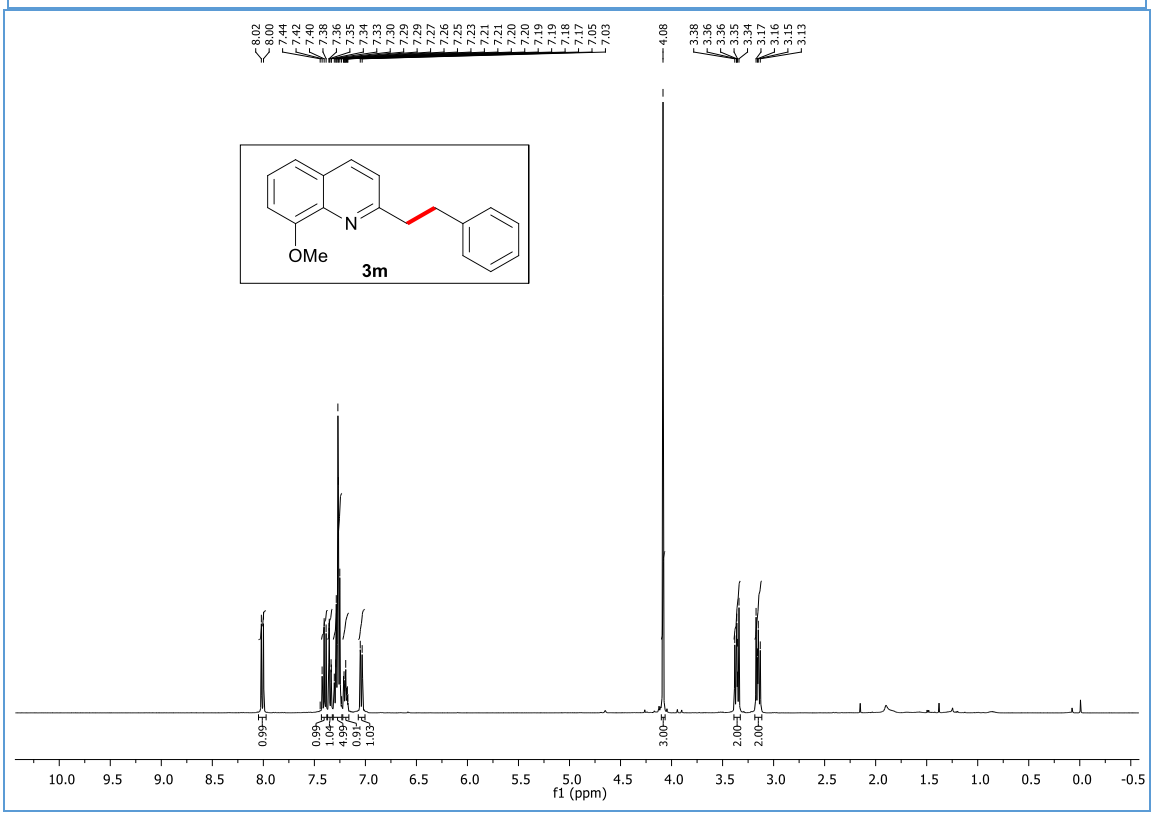
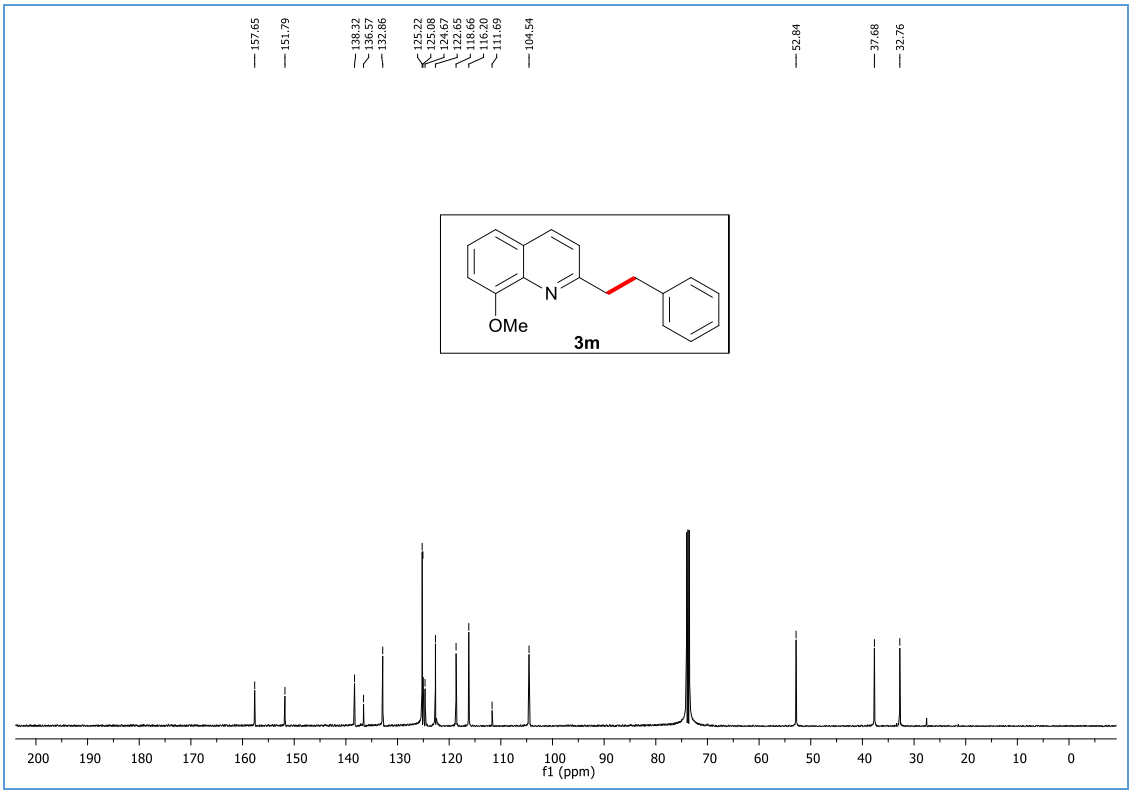

N
OMe
3m
f1 (ppm)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32.76
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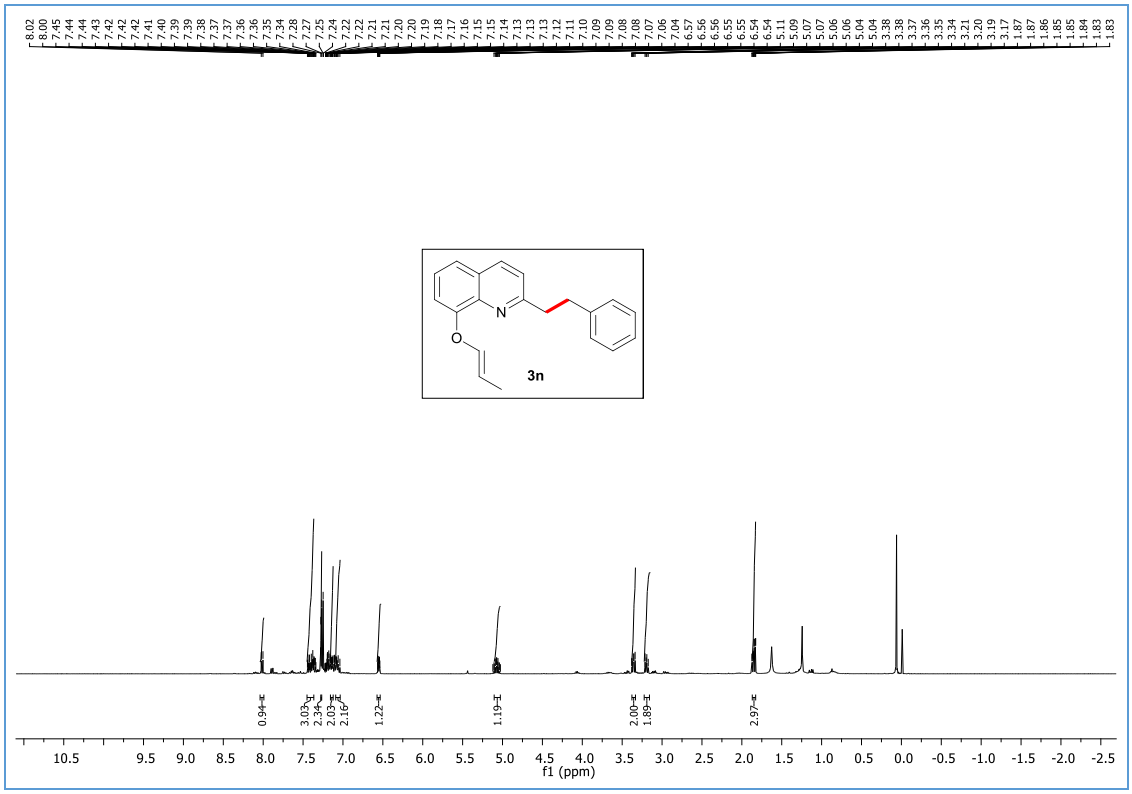
OMe
3m
f1 (ppm)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O
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1.19
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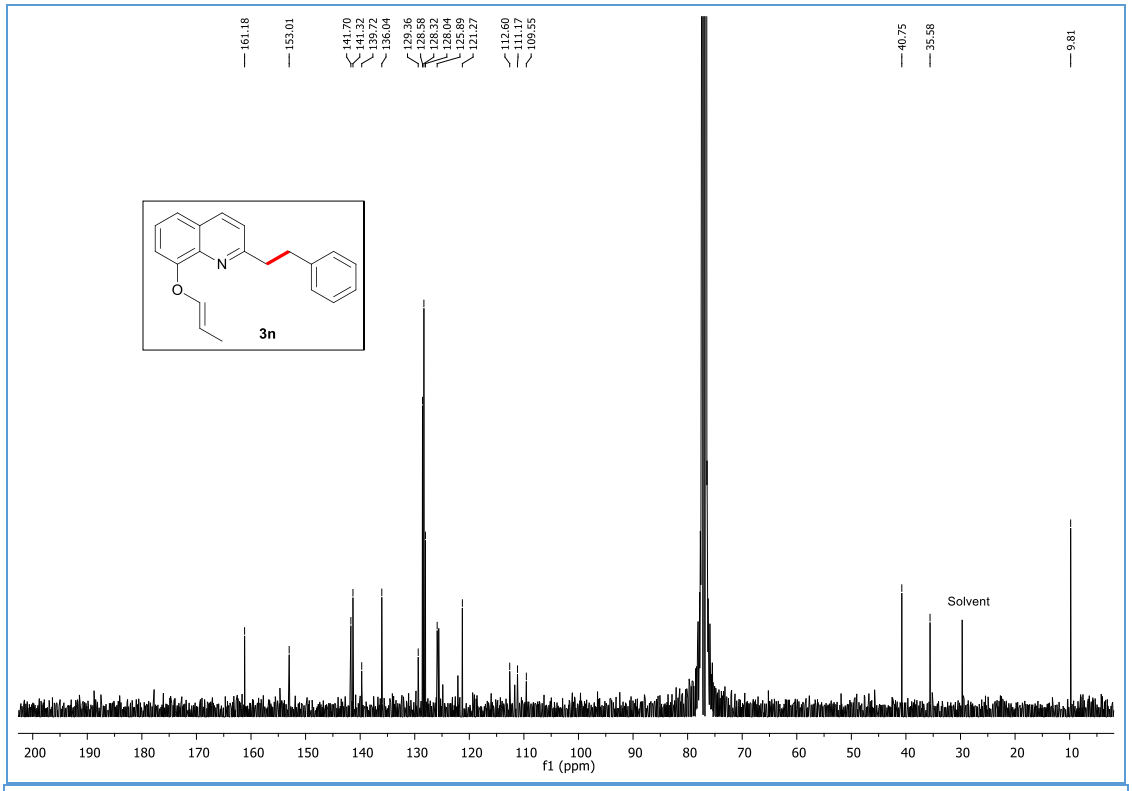
2.97
f1 (ppm)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128.58
128.32
128.04
125.89
121.27
112.60
111.17
109.55
40.75
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9.81
N
O
3n
Solvent
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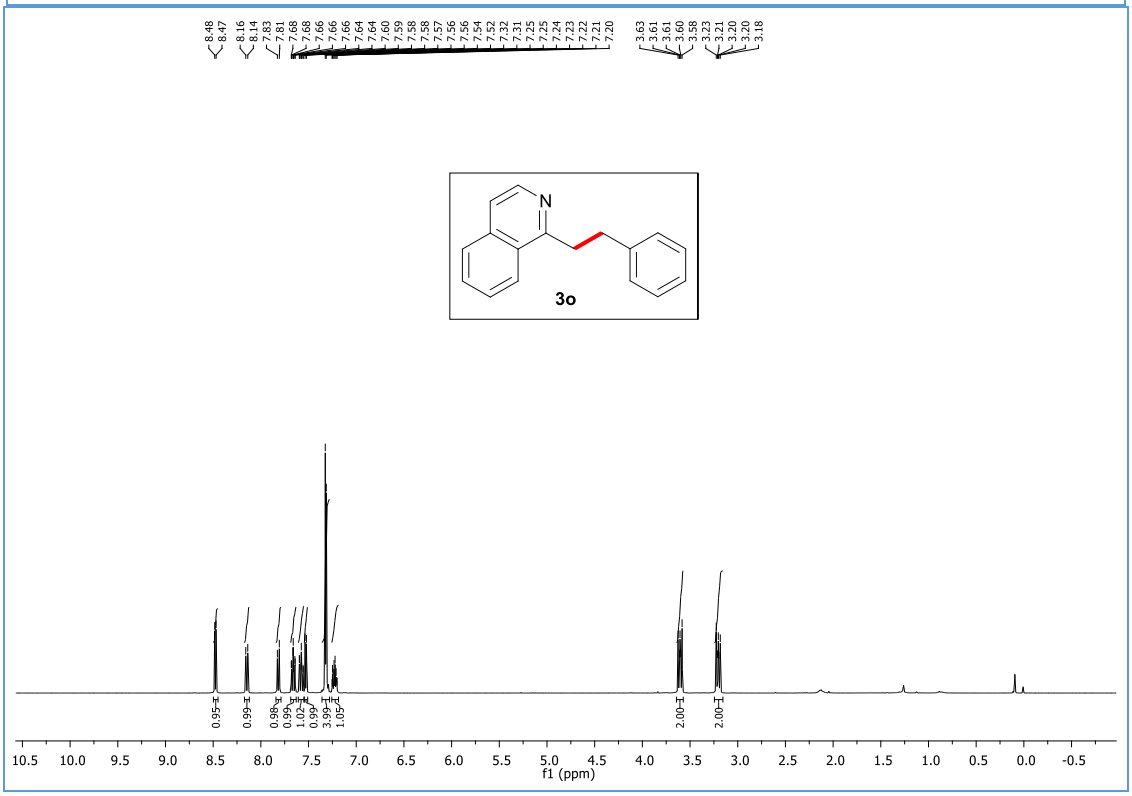
f1 (ppm)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3.18
N
3o
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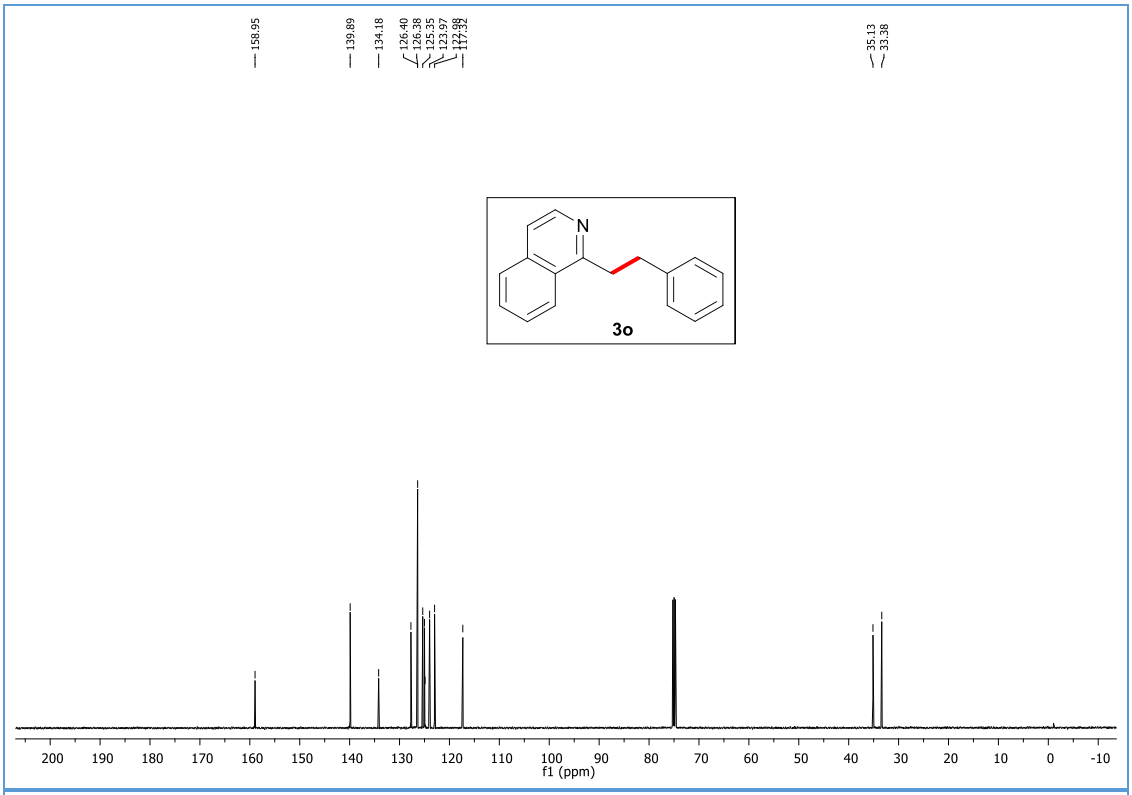
0.98
0.99
1.02
0.99
3.99
1.05
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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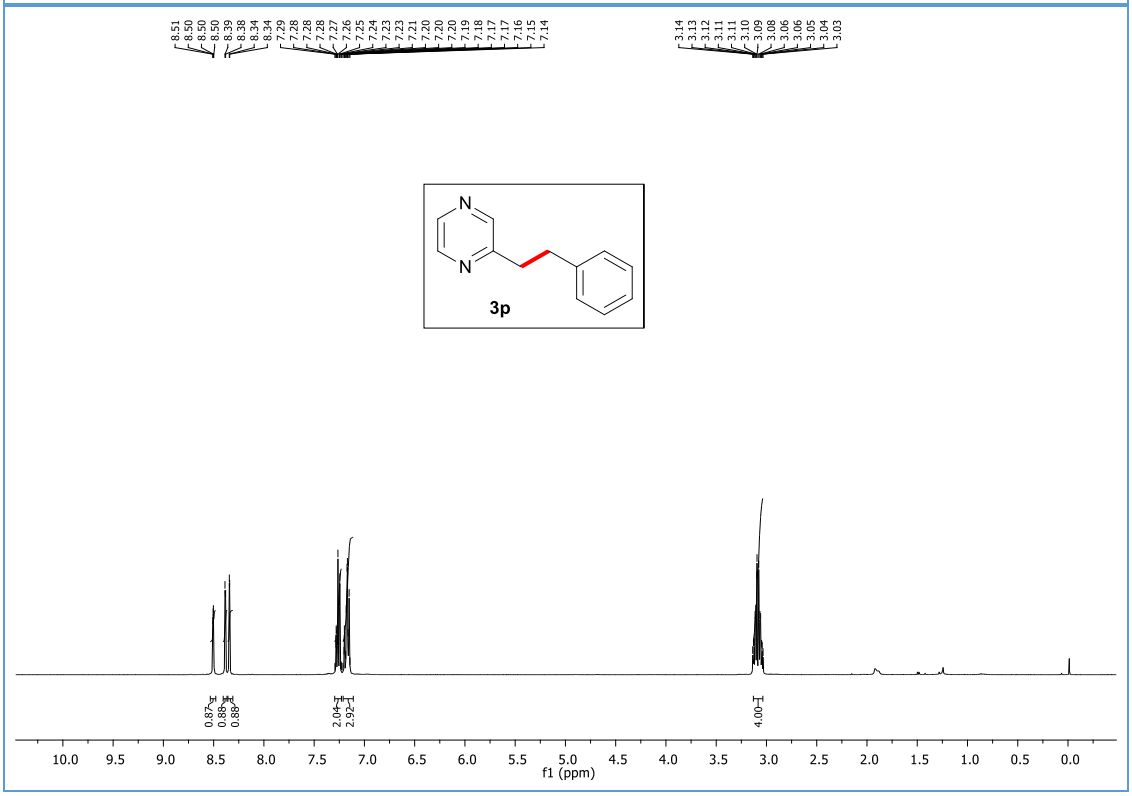
126.40
126.38
123.35
123.27
117.32
117.32
35.13
33.38
N
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.50
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8.38
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8.34
7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.24
7.23
7.23
7.21
7.20
7.20
7.20
7.19
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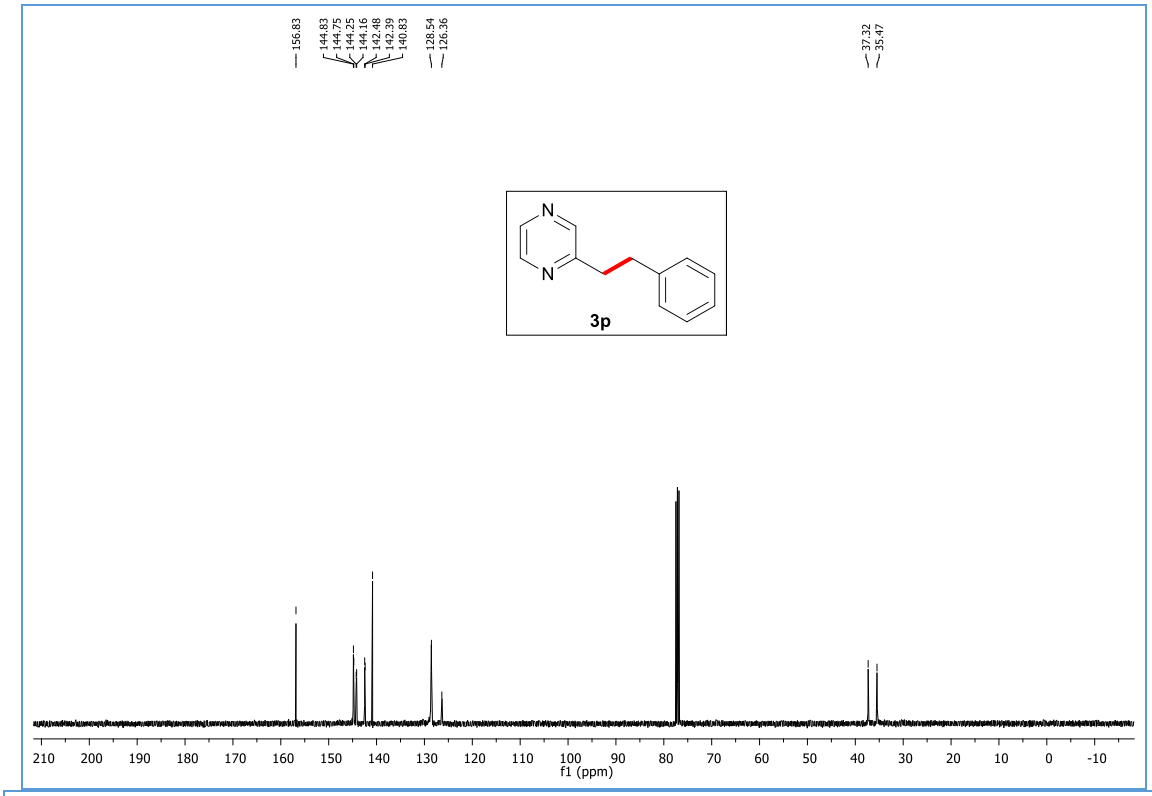
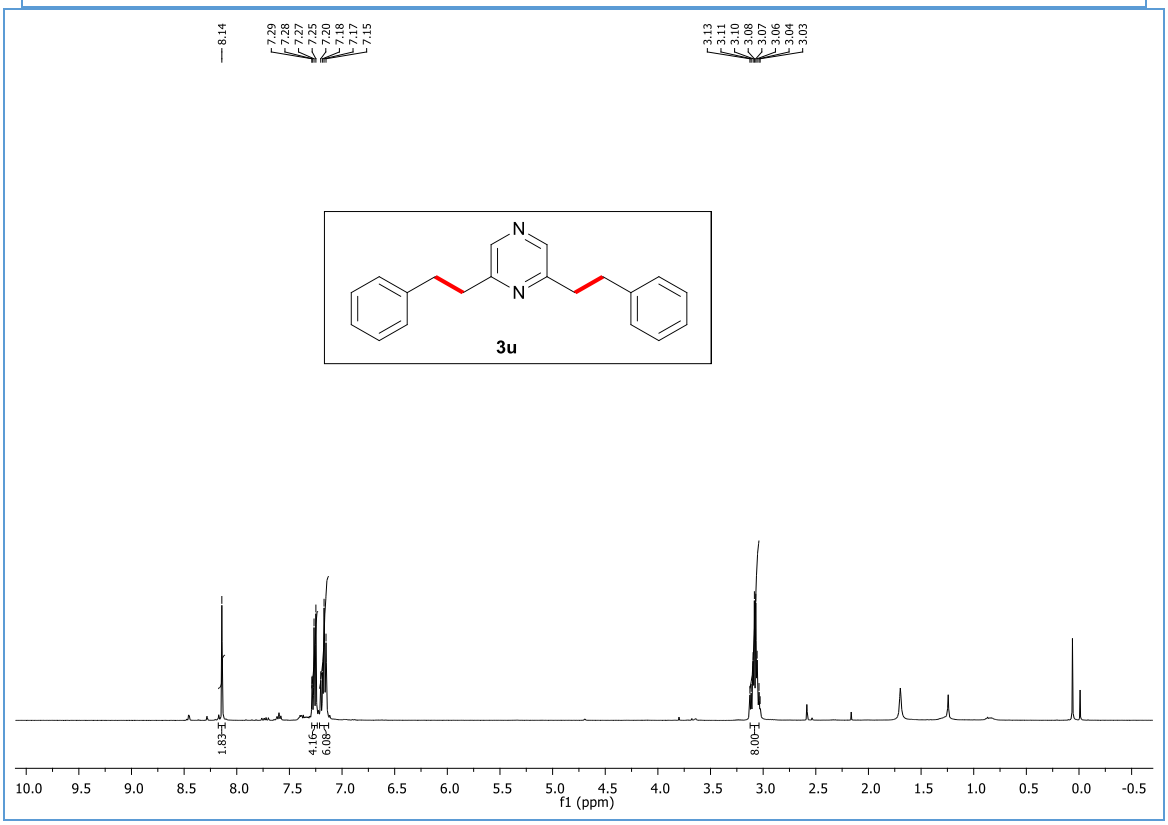
7.17
7.17
7.16
7.15
7.14
3.14
3.13
3.12
3.11
3.11
3.10
3.09
3.08
3.06
3.06
3.05
3.04
3.03
N
N
3p
0.87
0.89
0.88
2.04
2.92
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.83
144.83
144.75
144.25
144.15
142.48
142.39
140.83
128.54
126.36
37.32
35.47
N
N
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.29
7.28
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7.25
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7.18
7.17
7.15
3.13
3.11
3.10
3.08
3.07
3.06
3.04
3.03
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N
3u
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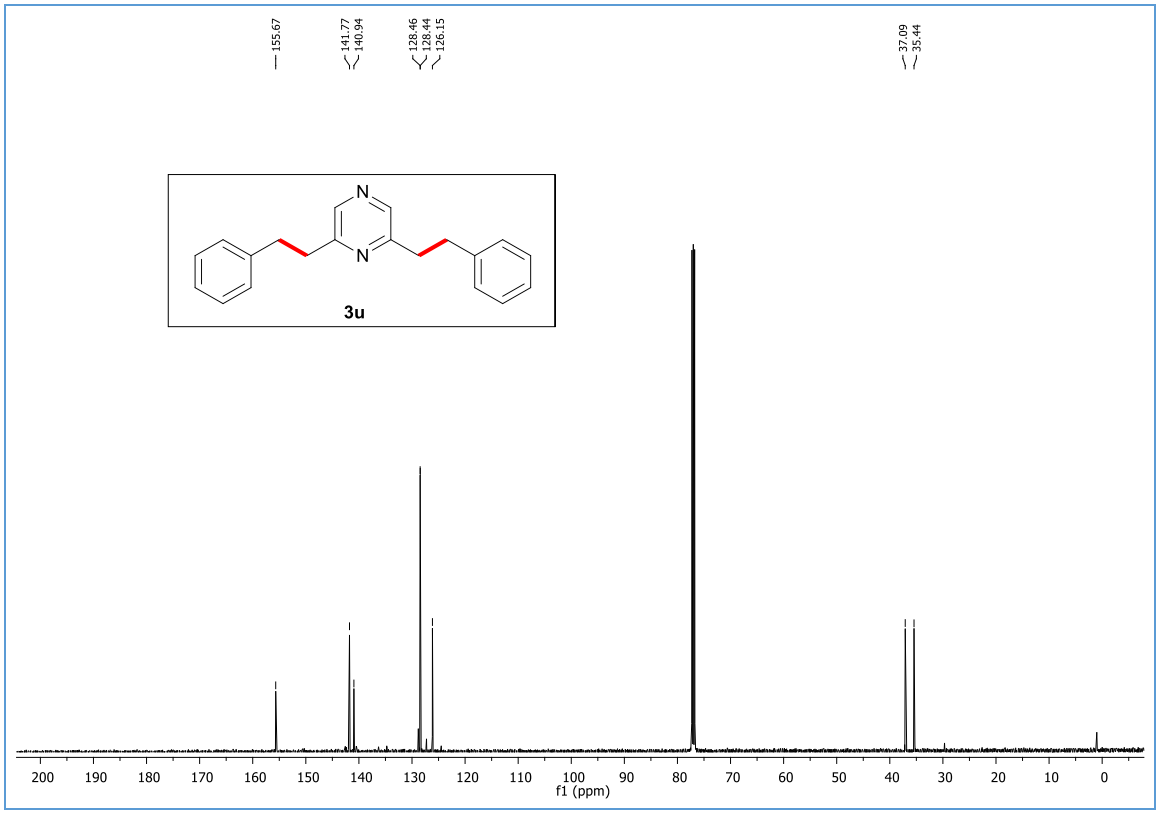
f1 (ppm)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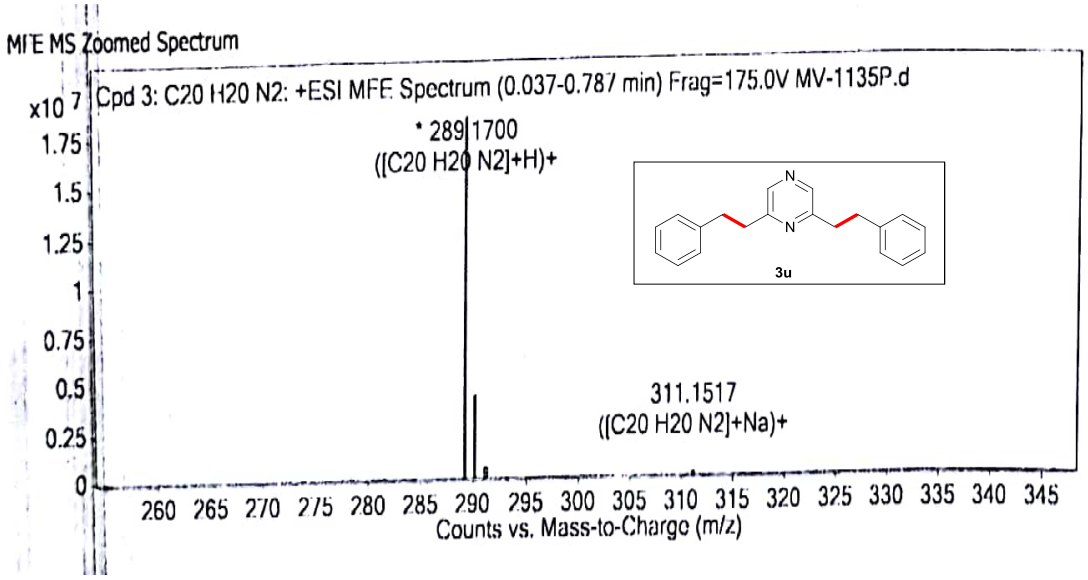
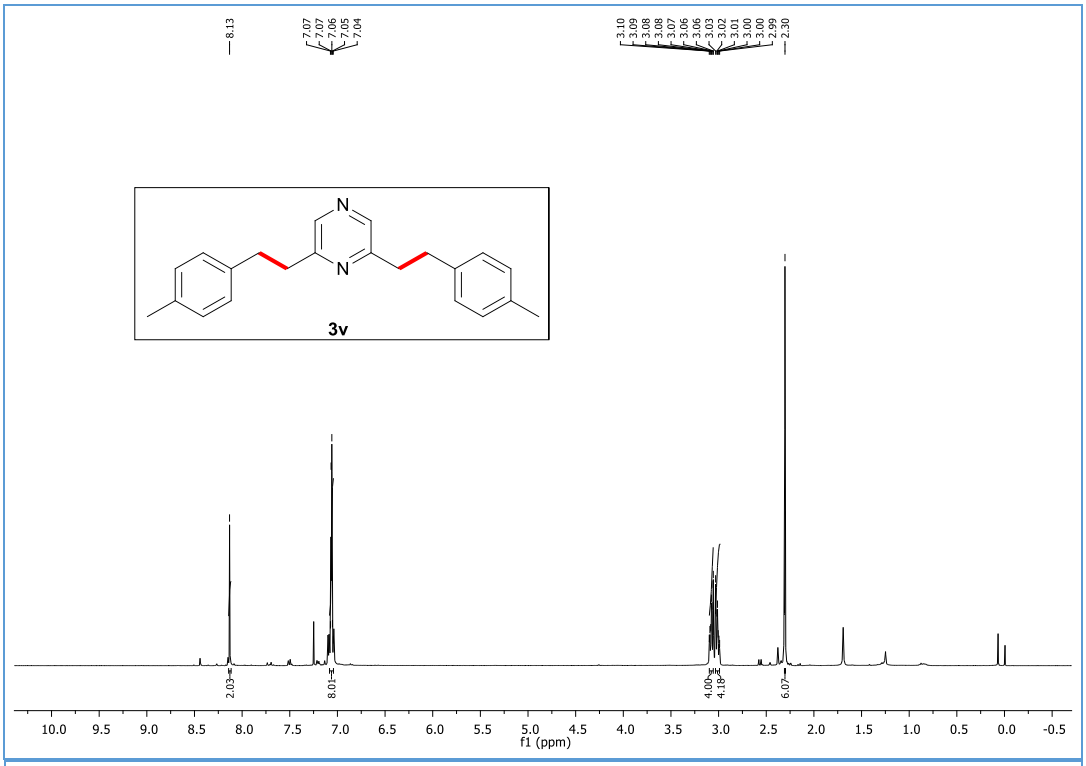
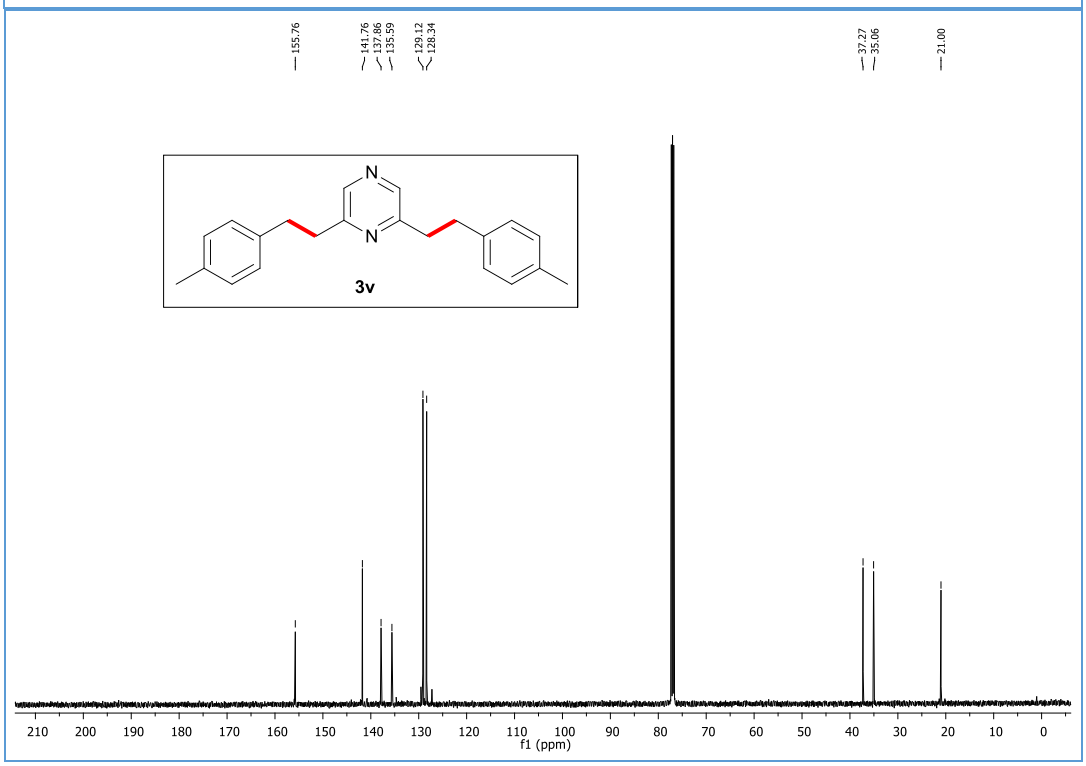
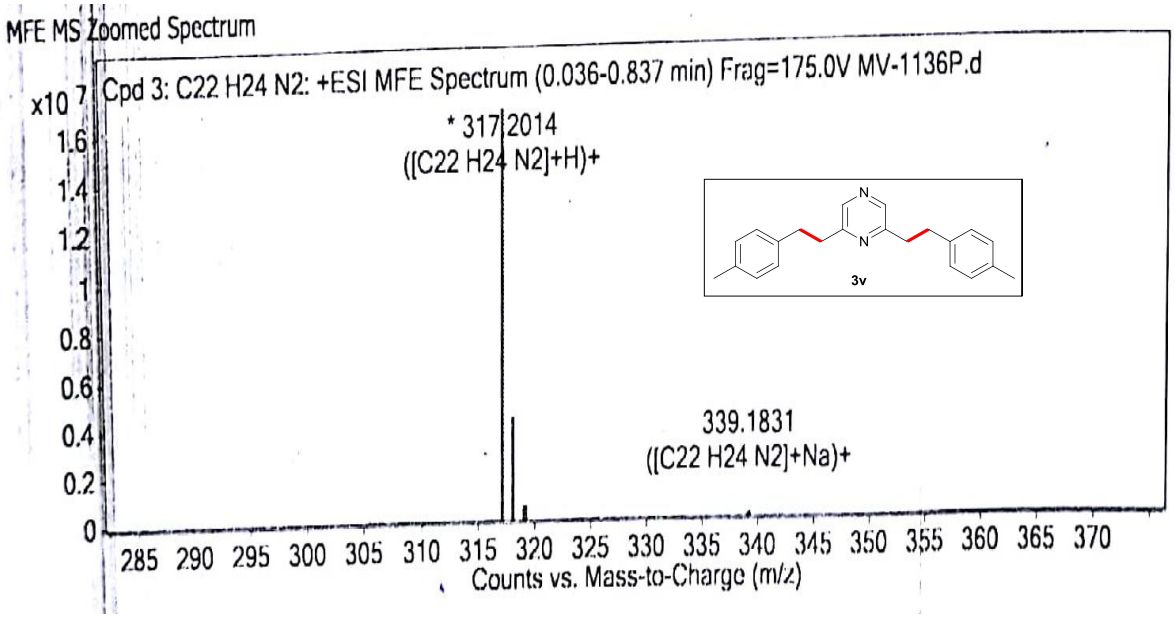
128.44
126.15
37.09
35.44
N
N
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MFE MS Zoomed Spectrum
Cpd 3: C20 H20 N2: +ESI MFE Spectrum (0.037-0.787 min) Frag=175.0V MV-1135P.d
x10 7
1.75
1.5
1.25
1
0.75
0.5
0.25
0
* 289.1700
([C20 H20 N2]+H)+
311.1517
([C20 H20 N2]+Na)+
N
N
3u
260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345
Counts vs. Mass-to-Charge (m/z)


8.13
7.07
7.07
7.06
7.05
7.04
3.10
3.09
3.08
3.08
3.07
3.07
3.06
3.06
3.03
3.02
3.01
3.00
3.00
2.99
2.30
N
N
3v
2.03
8.01
4.00
4.18
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.76
141.76
137.86
135.59
129.12
128.34
37.27
35.06
21.00
N
N
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MFE MS Zoomed Spectrum
Cpd 3: C22 H24 N2: +ESI MFE Spectrum (0.036-0.837 min) Frag=175.0V MV-1136P.d
x10 7
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
* 317.2014
([C22 H24 N2]+H)+
339.1831
([C22 H24 N2]+Na)+
N
N
3v
285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370
Counts vs. Mass-to-Charge (m/z)