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Supplementary Information

Synthesis of Novel Quinolines using TsOH/Ionic Liquid under Microwave

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Description of compounds

3-Trifluoroacetyl-2,4-dimethylquinoline (**3a**): brown oil; $C_{13}H_{10}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H, H12), 2.64 (s, 3H, H9), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.6, H6), 7.79 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.6, H7), 7.90-8.06 (dd, 2H, ^3J 8, ^4J 1, H8, H5); ^{13}C NMR ($CDCl_3$) δ 16.1 (C9), 23.7 (C12), 115.6 (q, ^1J 291, CF_3), 123.8, 125.2, 126.9, 127.8, 129.4, 131 (C-Ar), 142.9 (C3), 147.6 (C4), 153 (C2), 189.7 (q, ^2J 37, C10).; GC/MS (EI, 70 eV) *m/z* 253 (M^+, 58), 184 (100), 156 (70), 115 (24).

2-Ethyl-3-trifluoroacetyl-4-methylquinoline (**3b**): brown oil; $C_{14}H_{12}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 3H, H13), 2.62 (s, 3H, H9), 2.84 (q, 2H, H12), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.4, H6), 7.79 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.5, H7), 8.02 (dd, ^3J 8, ^4J 0.7, H5), 8.09 (dd, ^3J 8, ^4J 0.7, H8); ^{13}C NMR ($CDCl_3$) δ 16 (C9), 13.1 (C13), 30.4 (C12), 115.6 (q, ^1J 292, CF_3), 123.7, 125.2, 126.8, 127.5, 129.6, 130.8 (C-Ar), 142.7(C4), 147.8 (C3), 157.8 (C2), 190 (q, ^2J 37, C10); GC/MS (EI, 70 eV) *m/z* 267 (M^+, 4), 198 (100), 170 (16).

3-Trifluoroacetyl-4-methyl-2-propylquinoline (**3c**): mp 81-84 °C; $C_{15}H_{14}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3H, H14), 1.74-1.93 (m, 2H, 13), 2.62 (s, 3H, H9), 2.78 (t, 2H, H12), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.00, H6), 7.79 (ddd, 1H, ^3J 7 ^3J 8, ^4J 1.2, H7), 8.00 (dd, ^3J 8, ^4J 1, H5), 8.01 (dd, ^3J 8, ^4J 1, H8);^{13}C NMR ($CDCl_3$) δ 16.1 (C9), 13.9(C14), 22.6 (C13), 39.4 (C12); 115.6 (q, ^1J 292, CF_3), 123.7, 125, 173, 126.8, 127.7, 129.6, 130.8 (C-Ar), 142.7(C3), 147.8 (C4), 156.8 (C2) 190 (q, ^2J 37, C10); GC/MS (EI, 70 eV) *m/z* 281 (M^+, 19), 253 (100), 212 (75), 184 (32).

2-Butyl-3-trifluoroacetyl-4-methylquinoline (**3d**): brown oil; $C_{16}H_{16}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, H15), 1.32-1.47 (m, 2H, H14), 1.65-1.85 (m, 2H, H13), 2.62 (s, 3H, H9), 2.80 (t, 2H, H12), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1, H6), 7.80 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.10, H7), 8.02 (dd, ^3J 8, ^4J 1, H5), 8.08 (dd, ^3J 8, ^4J 1, H8); ^{13}C NMR ($CDCl_3$) δ 16.1 (C9), 13.7 (C15), 22.6 (C14), 31.4 (C13), 37.2 (C12); 115.5 (q, ^1J 292, CF_3), 123.7, 125.2, 126.8, 127.7, 129.6, 130.9, 142.7(C3), 147.8 (C4), 157 (C2), 190 (q, ^2J 37, C10); GC/MS (EI, 70 eV) *m/z* 295 (M^+, 4), 253 (100), 226 (16), 198 (10), 184 (26).

3-Trifluoroacetyl-4-methyl-2-(3-methylbutyl) quinoline (**3e**): brown oil; $C_{17}H_{18}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3H, H15), 0.96 (s, 3H, H15'), 1.64-1.70 (m, 1H, H14), 1.64-1.70 (m, 2H, H13), 2.61 (s, 3H, H9), 2.80 (t, 2H, H12), 7.59 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.4, H6), 7.78 (ddd, 1H,, ^3J 7 ^3J 8, ^3J 1.4 H7), 8.02 (dd, ^3J 8, ^4J 1, H5), 8.08 (dd, ^3J 8, ^4J 1, H8);^{13}C NMR ($CDCl_3$) δ 16.1 (C9), 22.3 (C15, C15'), 28.2 (C14), 35.6 (C13), 38.3 (C12), 115.6 (q, ^1J 292, CF_3), 123.7, 125.2, 126.8, 127.6, 129.6, 130.8, 142.8 (C3), 147.9 (C4), 157.3 (C2), 190 (q, ^2J 37, C10); GC/MS (EI, 70 eV) *m/z* 309 (M^+, 4), 294 (23), 167 (34), 253 (100), 238 (11), 184 (29).

3-Trifluoroacetyl-4-methyl-2-(2-methylpropyl) quinoline (**3f**): brown oil; $C_{16}H_{16}F_3NO$ ^{1}H NMR ($CDCl_3$) δ 0.93 (d, 6H, H14,14'), 2.25-2.41 (m, 1H, H13), 2.62 (s, 3H, H9), 2.68 (d, 2H, H12), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.3, H6), 7.79 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.5, H7), 8.03 (dd, ^3J 8, ^4J 0.7, H5), 8.08 (dd, ^3J 8, ^4J 0.7, H8) ^{13}C NMR ($CDCl_3$) δ 16 (C9), 22.2 (C14,C14'), 28.6 (C13), 46 (C12), 115.5 (q, ^1J 292, CF_3), 123.6, 125.1, 126.8, 129.7, 130.7 (C-Ar), 142.5 (C3), 147.7 (C4), 156.2 (C2), 189.9 (q, ^2J 37, C10); GC/MS (EI, 70 eV) *m/z* 236 (MH^+, 7), 166 (40), 99 (100), 69 (30).

3-Trichloroacetyl-2,4-dimethylquinoline (**8a**): mp 84-85 °C; $C_{13}H_{10}Cl_3NO$ ^{1}H NMR ($CDCl_3$) δ 2.81 (s, 3H, H12), 2.91 (s, 3H, H9), 7.58 (ddd, 1H, ^3J 7 ^3J 8, ^3J 0.9, H6), 7.76 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.2, H7), 8.04 (dd, ^3J 8, ^4J 1, H5), 8.14 (dd, ^3J 8, ^4J 1, H8); ^{13}C NMR ($CDCl_3$) δ 18.3 (C9), 22.9 (C12), 94.2 (C11), 124.2, 125.5, 126.5, 128.3,

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129.9, 132.7 (C-Ar), 143.3 (C3), 146.2 (C4), 152.6 (C2), 190 (C10); GC/MS (EI, 70 eV) *m/z* 302 (M^+, 4), 184 (100), 156 (98), 115 (14).

3-Dichloroacetyl-2,4-dimethylquinoline (**9a**): mp > 200 °C; $C_{13}H_{11}Cl_2NO$ ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3H, H12), 2.70 (s, 3H, H9), 6.40 (s, 1H, H11), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.5, H6), 7.80 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.5, H7), 8.00-8.08 (dd, ^3J 8, ^4J 0.9, H5, H8); ^{13}C NMR ($CDCl_3$) δ 16.7 (C9), 23.6 (C12), 70.4 (C11), 123.9, 125.7, 127.2, 129, 130.5, 131.5 (C-Ar), 143 (C3), 146.7 (C4), 153.2 (C2), 192.8 (C10); GC/MS (EI, 70 eV) *m/z* 267 (M^+ 9), 184 (100), 170 (9), 156 (69), 143 (27).

3-Chlorodifluoroacetyl-2,4-dimethylquinoline (**10a**): brown oil; $C_{13}H_{10}ClF_2NO$ ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 3H, H12), 2.66 (s, 3H, H9), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.2, H6), 7.80 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.5, H7), 7.55-8.07 (dd, ^3J 8, ^4J 1, H5, H8); ^{13}C NMR ($CDCl_3$) δ 16.7 (t, ^6J 2, C9), 23.8 (t, ^6J 2, C9), 120.6 (t, ^1J 305, CF_2Cl), 123.9, 125.2, 125.8, 127.1, 127.7, 128.8, 129.1, 131.4 (C-Ar), 143.4 (C3), 147.1 (C4), 153.1 (C2), 189.6 (t, ^2J 33, C10); GC/MS (EI, 70 eV) *m/z* 269 (M^+ 20), 184 (100), 156 (53), 115 (18).

3-(1,1,1,2,2-Perfluoropropionil)-2,4-dimethylquinoline (**11a**): brown oil; $C_{14}H_{10}F_5NO$ ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3H, H13), 2.63 (s, 3H, H9), 7.60 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.2, H6), 7.80 (ddd, 1H, ^3J 7 ^3J 8, ^3J 1.3, H7), 7.80-8.02 (dd, ^3J 8, ^4J 1, H5, H8); ^{13}C NMR ($CDCl_3$) δ 16 (C9), 23.6 (C13), 104.2, 107.0, 109.5 (t, ^1J 267, CF_2, q ^2J 37, CF_3), 113.7, 116.6, 119.4, 122.3 (q, ^1J 286, CF_3, t, ^2J 33, CF_2), 123.8, 125.1, 126.8, 129.4, 129.9, 131 (C-Ar), 143.2 (C3), 147.6 (C4), 153.1 (C2), 192.4 (t, ^2J 28, C10); GC/MS (EI, 70 eV) *m/z* 303 (M^+, 34), 184 (100), 156 (85), 115 (40).

Table S1. Elemental analyses of quinolones

Compounds	Elemental analyses / % calculated/experimental		
	C	H	N
3a	61.66/60.59	3.98/4.83	5.53/5.88
3b	62.92/61.86	4.53/4.72	5.24/5.54
3c	64.05/63.09	5.02/5.16	4.98/5.59
3d	65.08/64.98	5.46/5.69	4.74/4.69
3e	66.01/66.34	5.87/6.00	4.53/4.50
3f	65.08/64.99	5.46/5.43	4.74/4.97
8a	51.60/50.85	3.33/3.44	4.63/4.69
9a	58.23/58.50	4.13/3.80	5.22/4.96
10a	57.90/57.50	3.74/3.80	5.19/4.75
11a	5.55/5.84	3.32/3.60	4.62/4.94

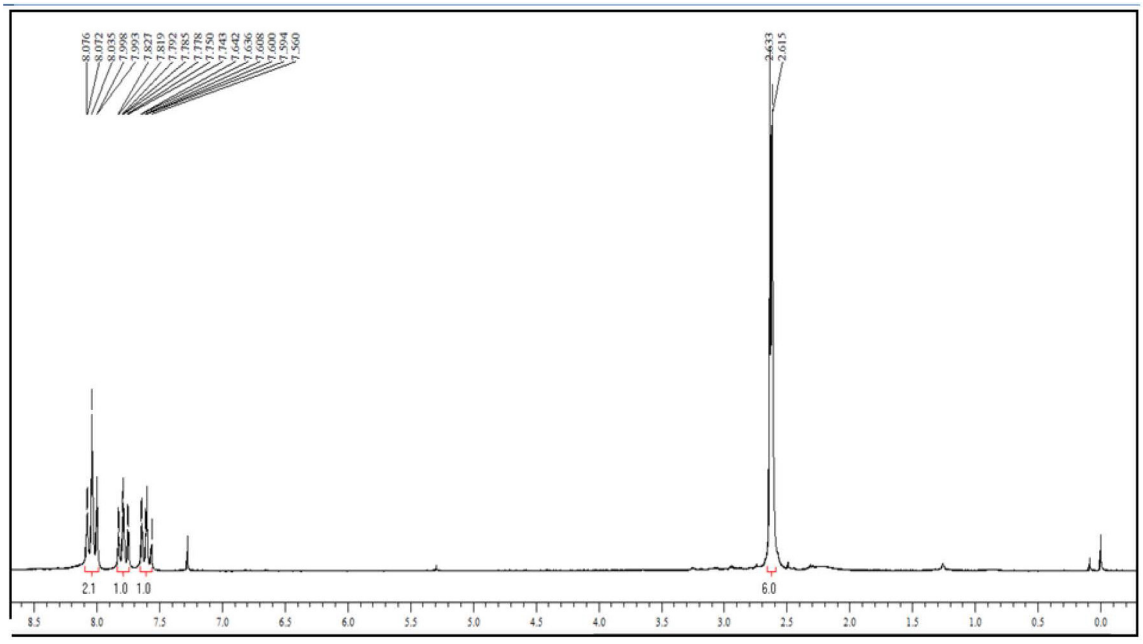

Figure S1. ^{1}H NMR spectrum (200 MHz) of 3-trifluoroacetyl-2,4-dimethylquinoline (**3a**) in $CHCl_3$.

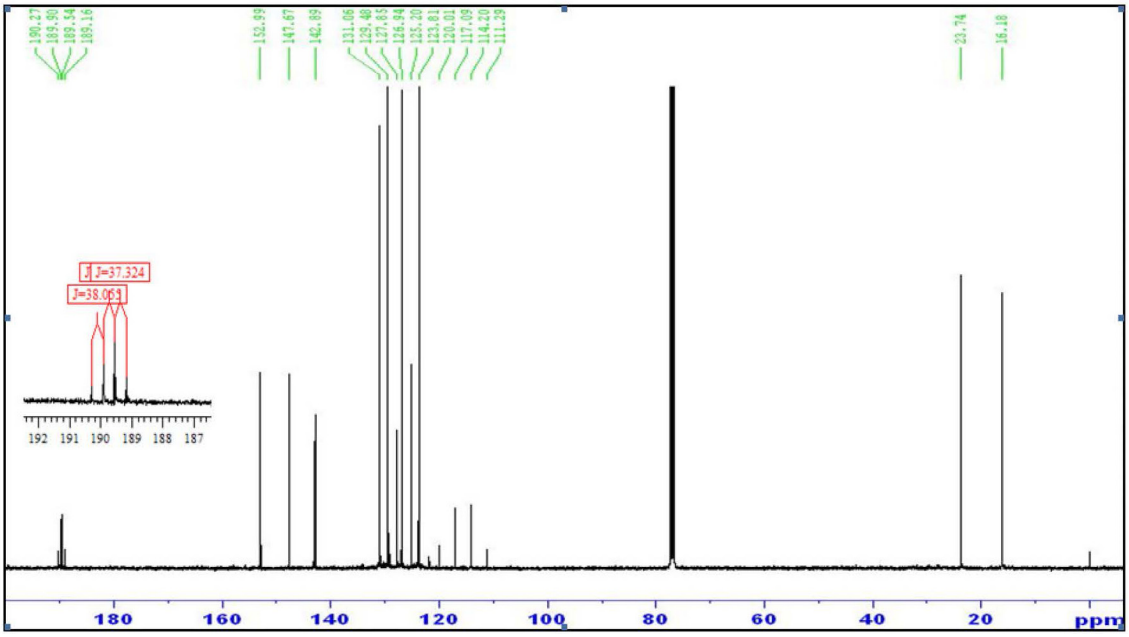

Figure S2. $^{13}C\{^{1}H\}$ spectrum (400 MHz) of 3-trifluoroacetyl-2,4-dimethylquinoline **(3a)** in $CHCl_3$.

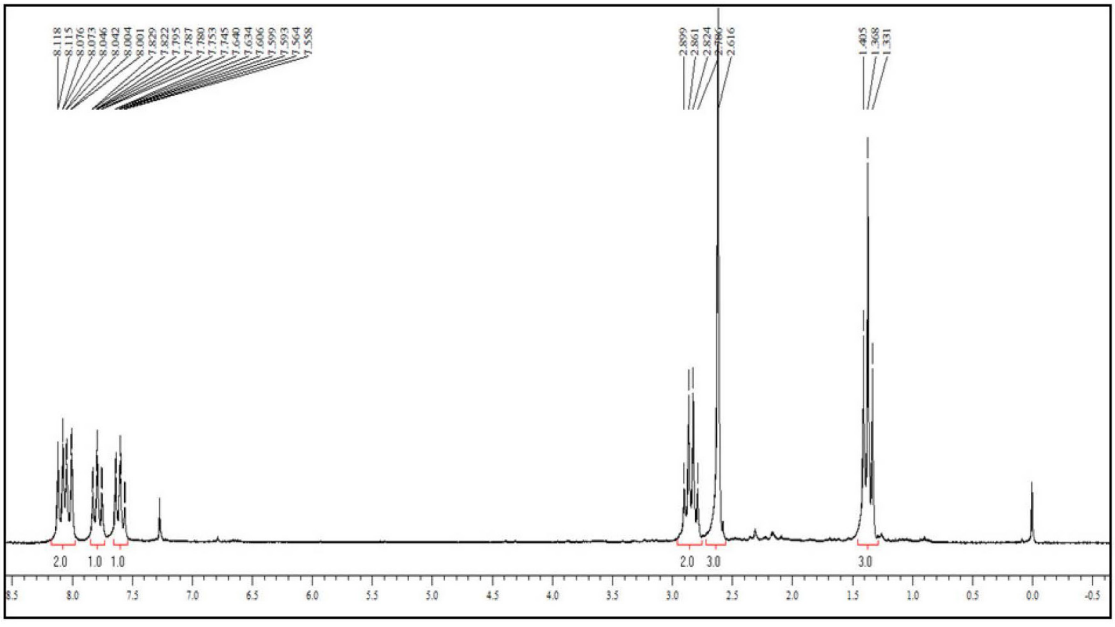

Figure S3. ^{1}H NMR spectrum (200 MHz) of 2-ethyl-3-trifluoroacetyl-4-methylquinoline (**3b**) in $CDCl_3$.

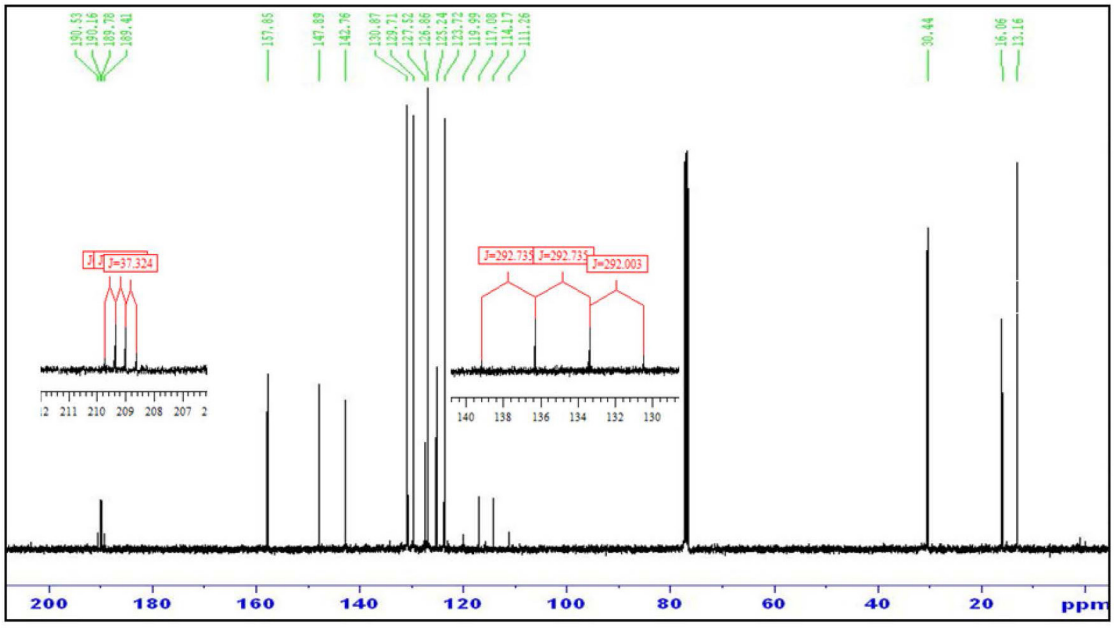

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 2-ethyl-3-trifluoroacetyl-4-methylquinoline (**3b**) in $CDCl_3$.

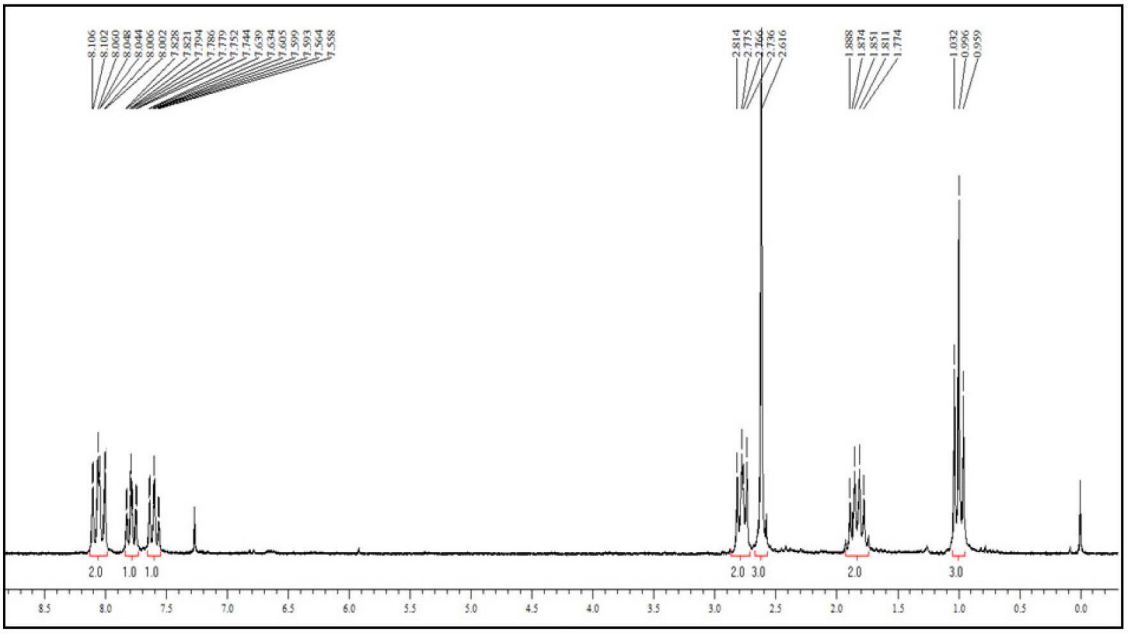

Figure S5. ^{1}H NMR spectrum (200 MHz) of 3-trifluoroacetyl-4-methyl-2-propylquinoline (**3c**) in $CDCl_3$.

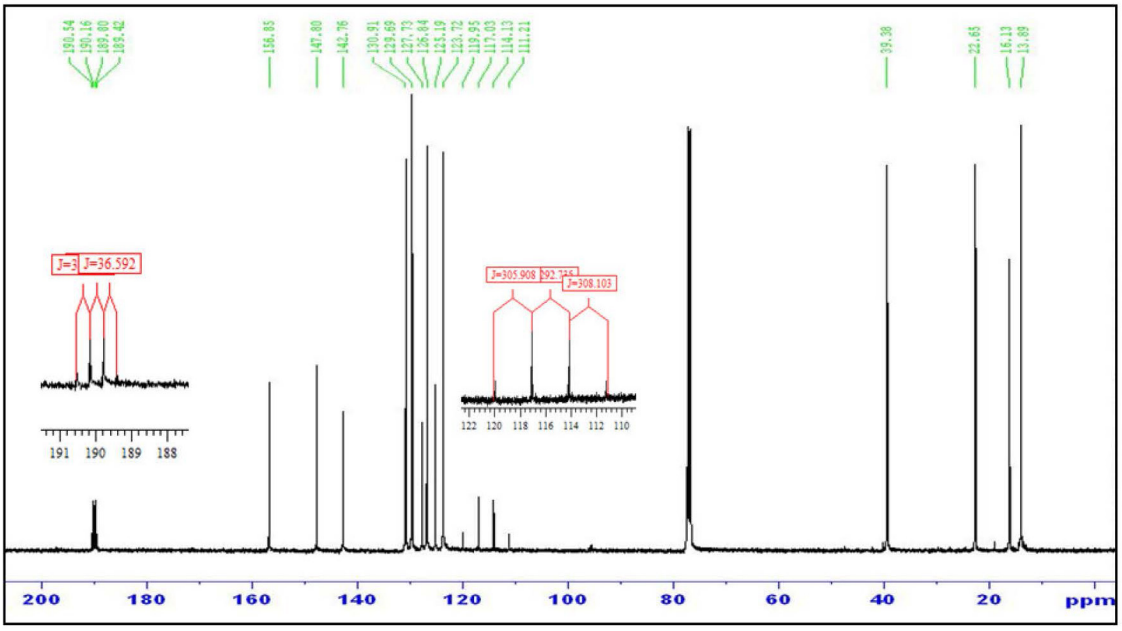

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 3-trifluoroacetyl-4-methyl-2-propylquinoline (**3c**) in $CDCl_3$.

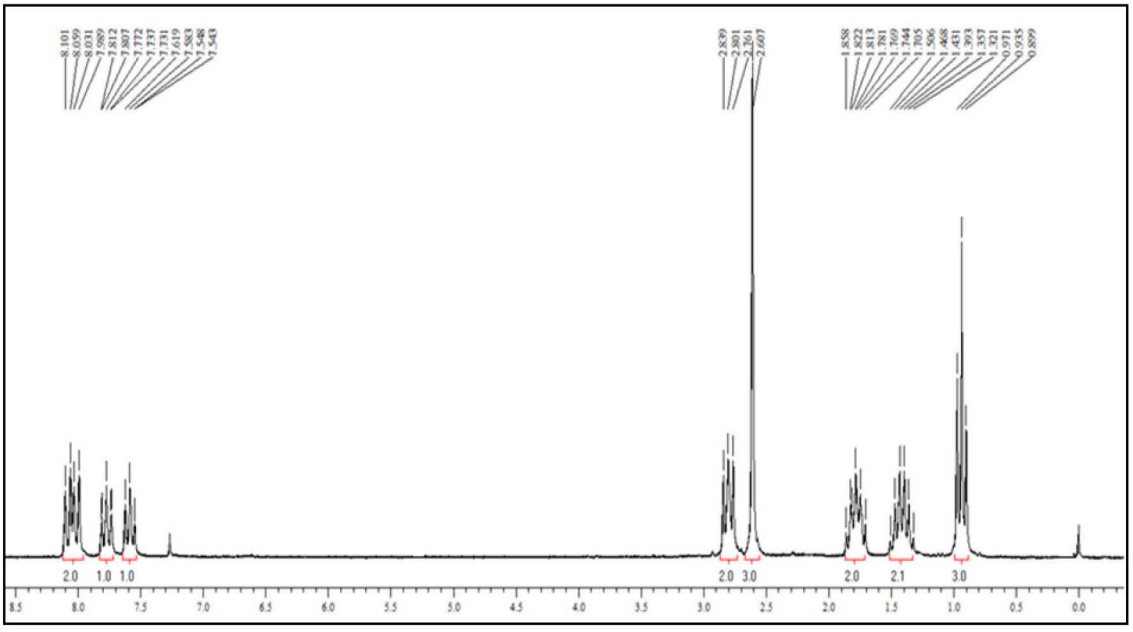

Figure S7. ^{1}H NMR spectrum (200 MHz) of 2-butyl-3-trifluoroacetyl-4-methylquinoline (**3d**) in $CDCl_3$.

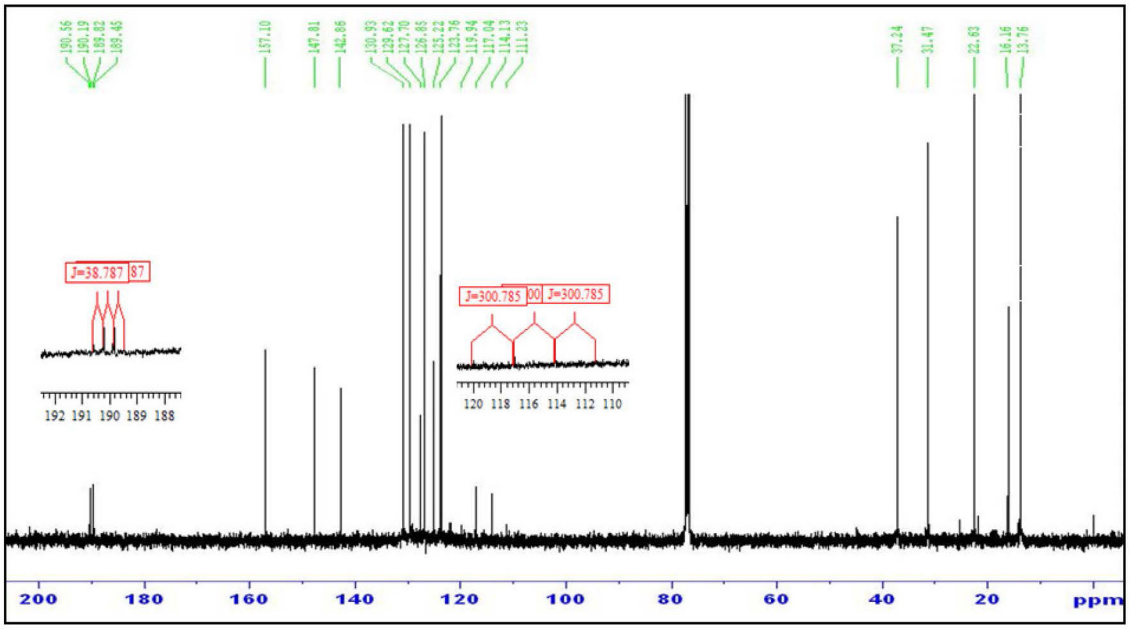

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 5-2-butyl-3-trifluoroacetyl-4-methylquinoline **(3d)** in $CDCl_3$.

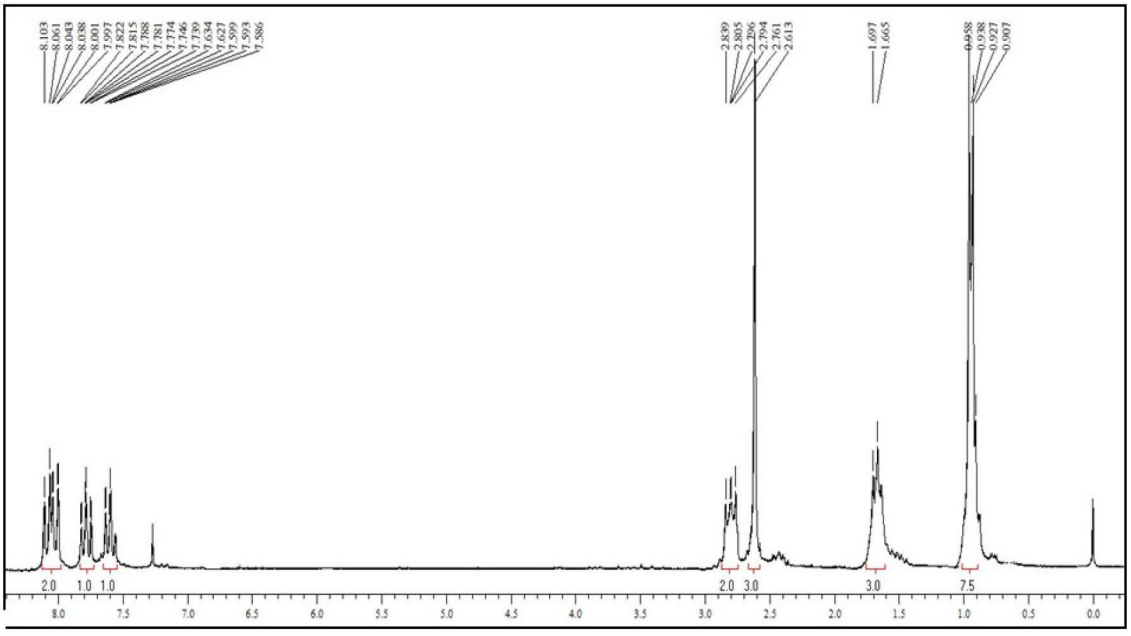

Figure S9. ^{1}H NMR spectrum (200 MHz) of 3-trifluoroacetyl-4-methyl-2-(3-methylbutyl)quinoline (**3e**) in $CDCl_3$.

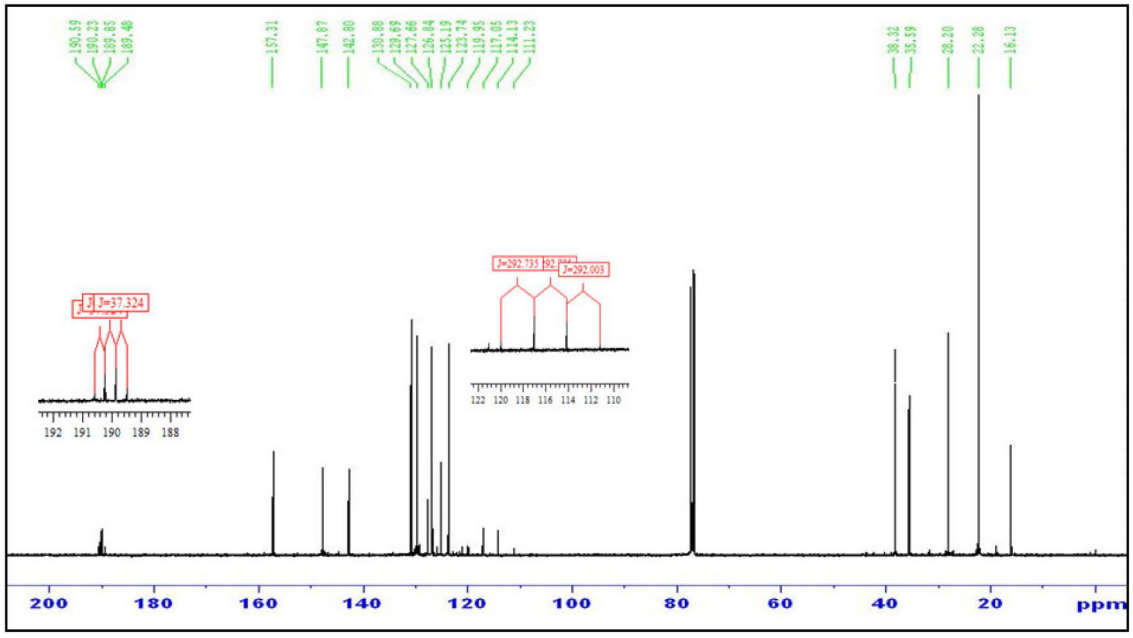

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 3-trifluoroacetyl-4-methyl-2-(3-methylbutyl)quinoline (**3e**) in $CDCl_3$.

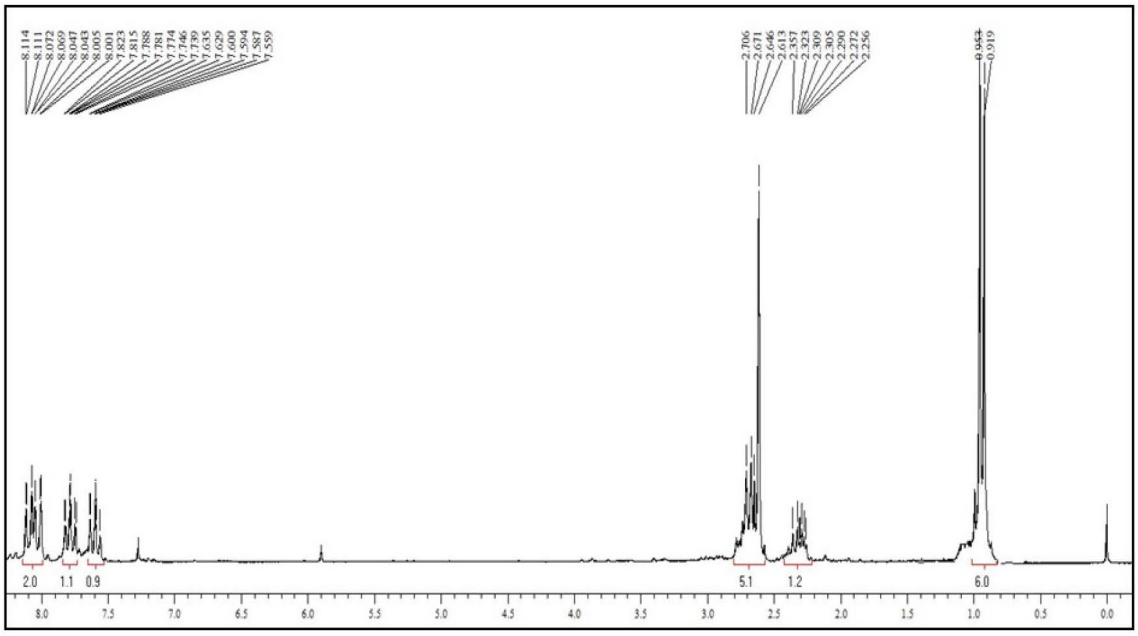

Figure S11. ^{1}H NMR spectrum (200 MHz) of 3-trifluoroacetyl-4-methyl-2-(2-methylpropyl)quinoline (**3f**) in $CDCl_3$.

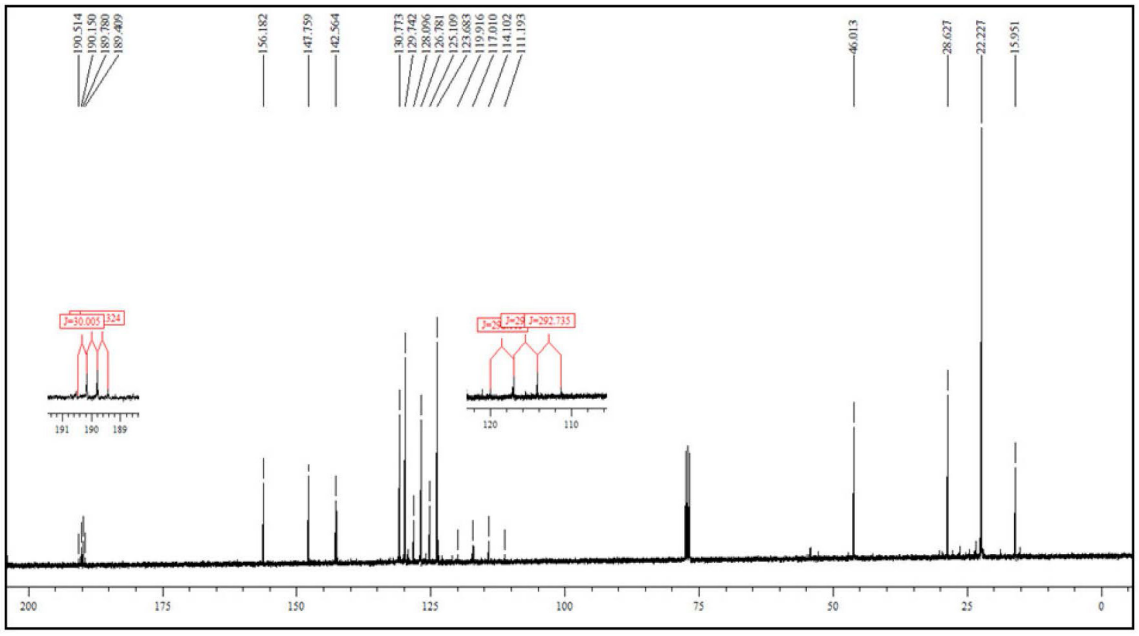

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of of 3-trifluoroacetyl-4-methyl-2-(2-methylpropyl)quinoline (**3f**) in $CDCl_3$.

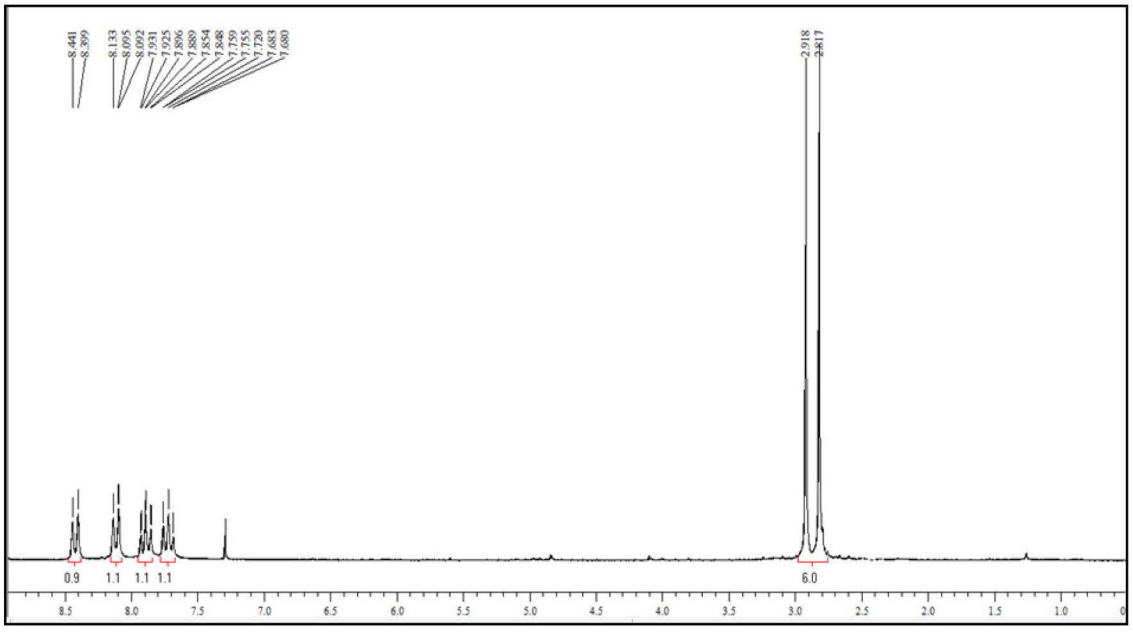

Figure S13. ^{1}H NMR (200 MHz) spectrum of 3-trichloroacetyl-2,4-dimethylquinoline (**8a**) in $CDCl_3$.

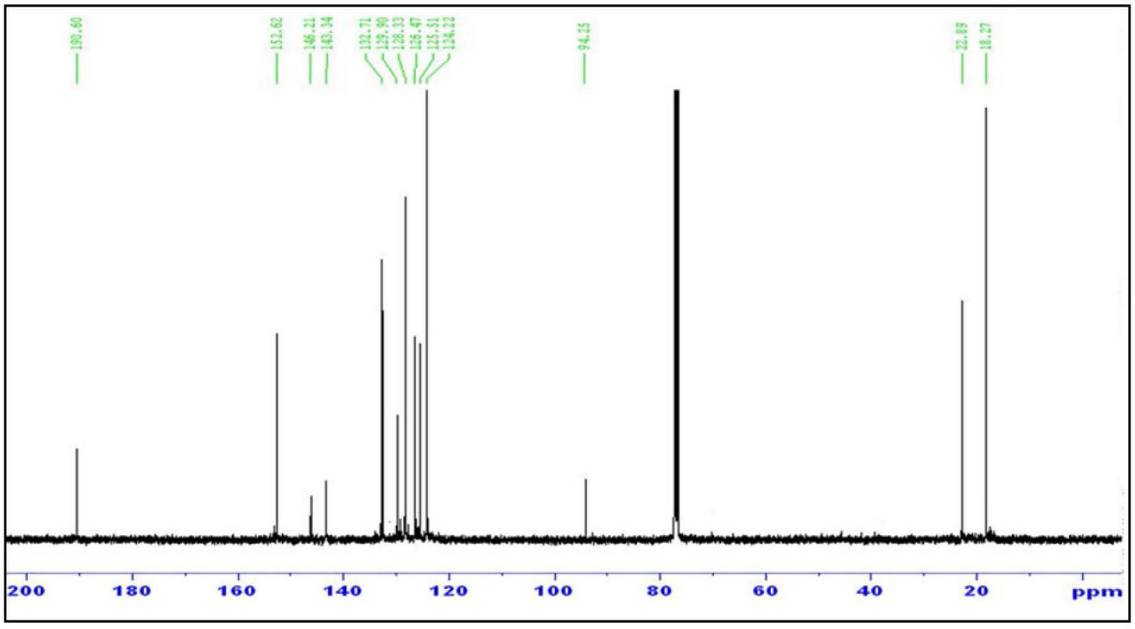

Figure Figure S14. ^{13}C {^{1}H} NMR spectrum (400 MHz) of 3-trichloroacetyl-2,4-dimethylquinoline (**8a**) in $CDCl_3$.

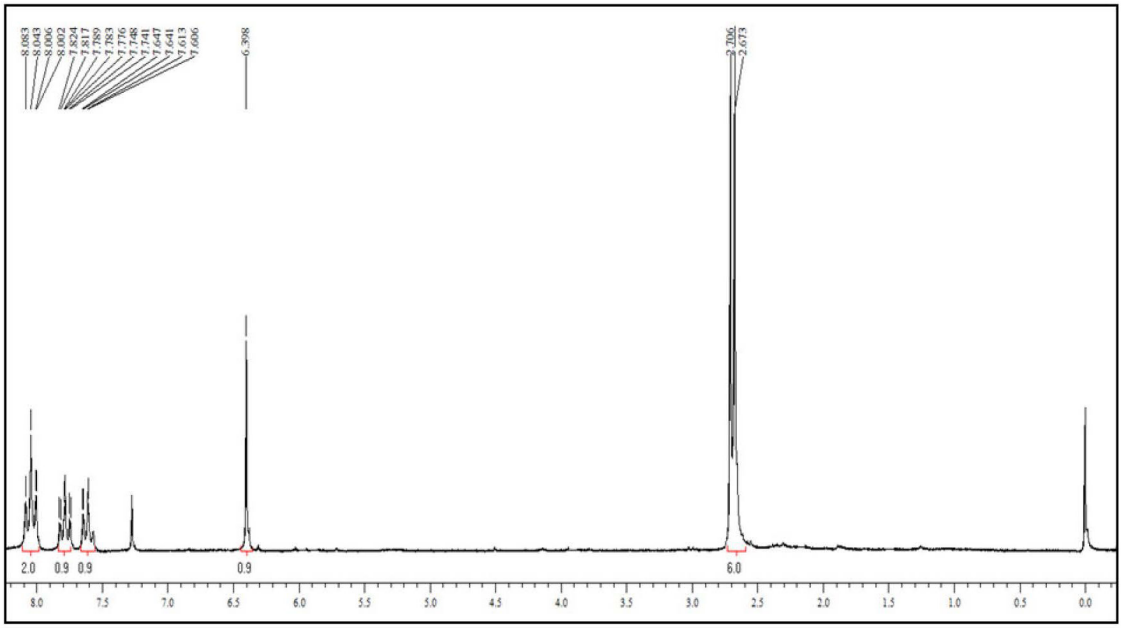

Figure S15. ^{1}H NMR spectrum (200 MHz) of 3-dichloroacetyl-2,4-dimethylquinoline (**9a**) in $CDCl_3$.

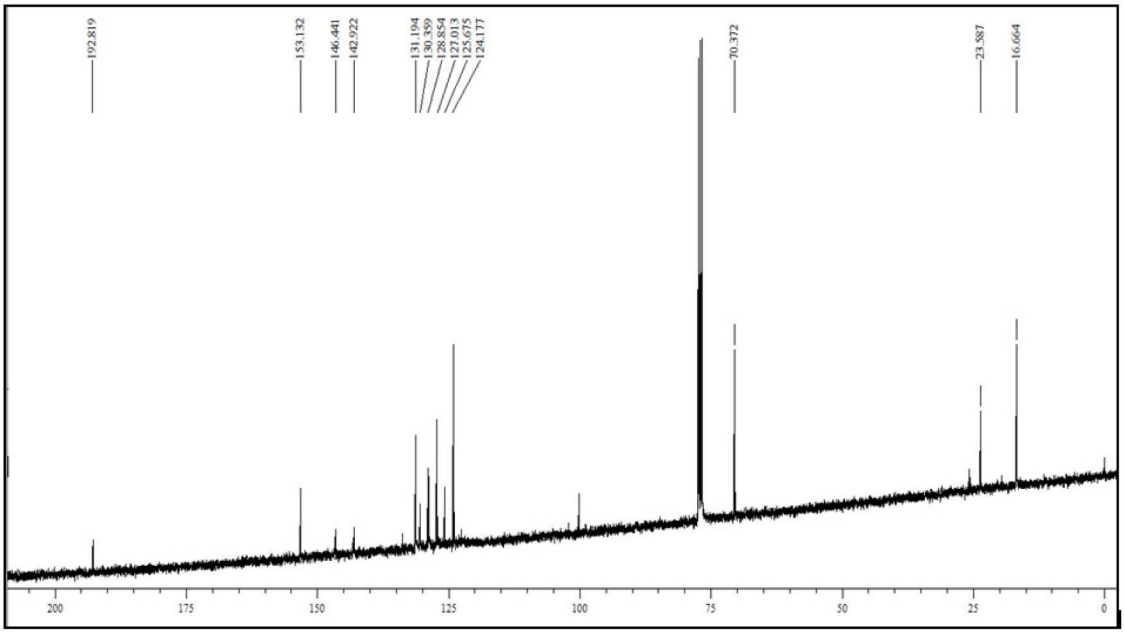

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 3-dichloroacetyl-2,4-dimethylquinoline (**9a**) in $CDCl_3$.

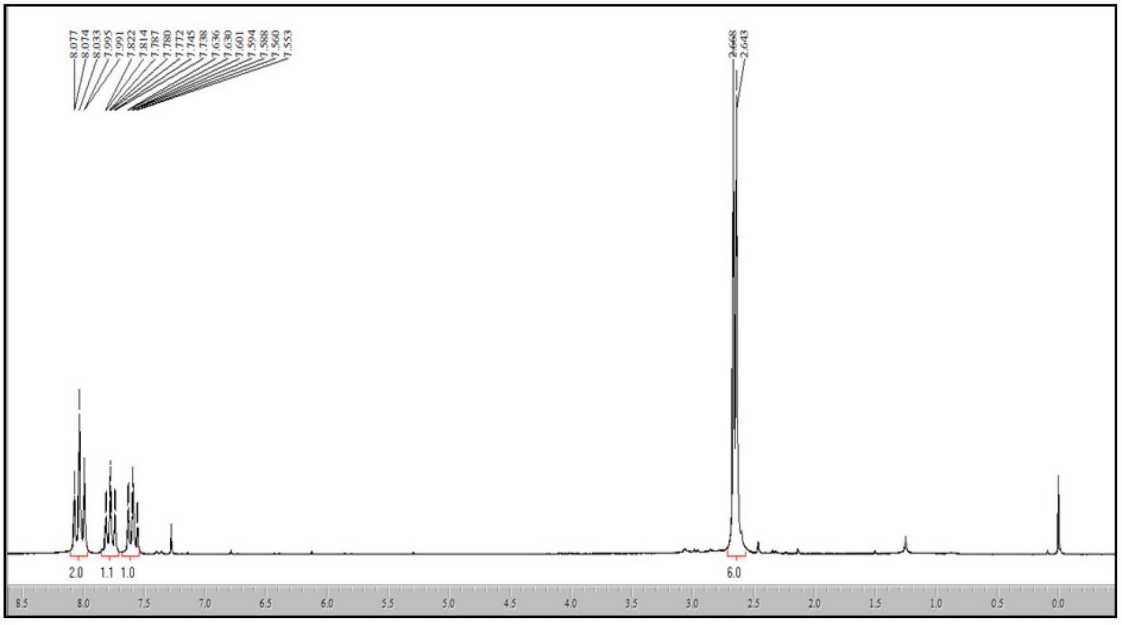

Figure S17. ^{1}H NMR spectrum (200 MHz) of 3-chlorodifluoroacetyl-2,4-dimethylquinoline (**10a**) in $CDCl_3$.

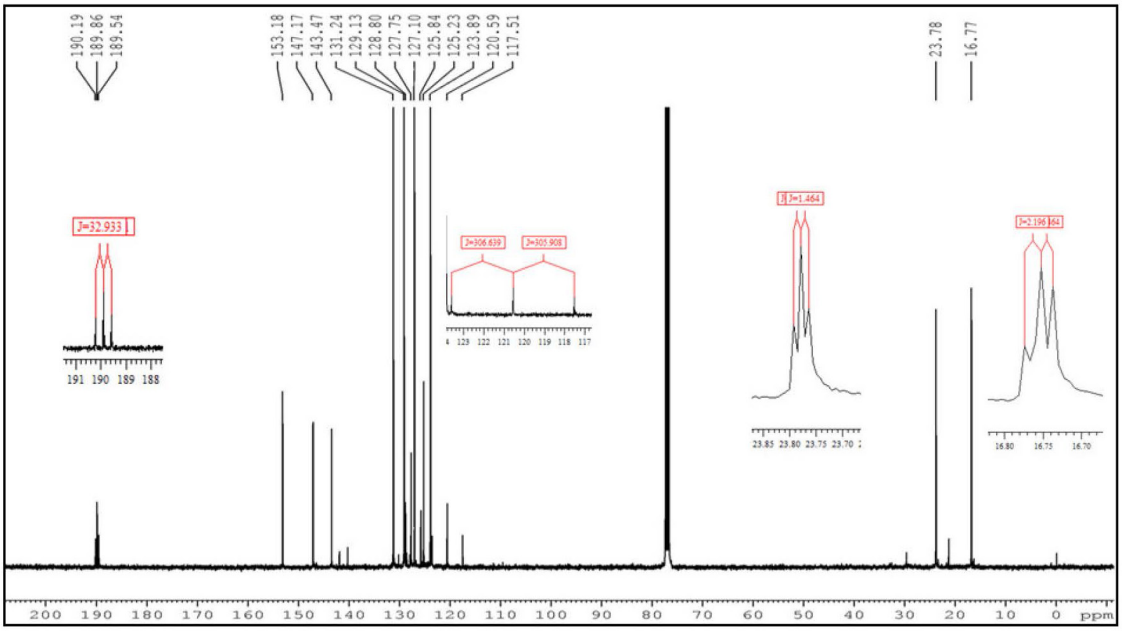

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 3-chlorodifluoroacetyl-2,4-dimethylquinoline (**10a**) in $CDCl_3$.

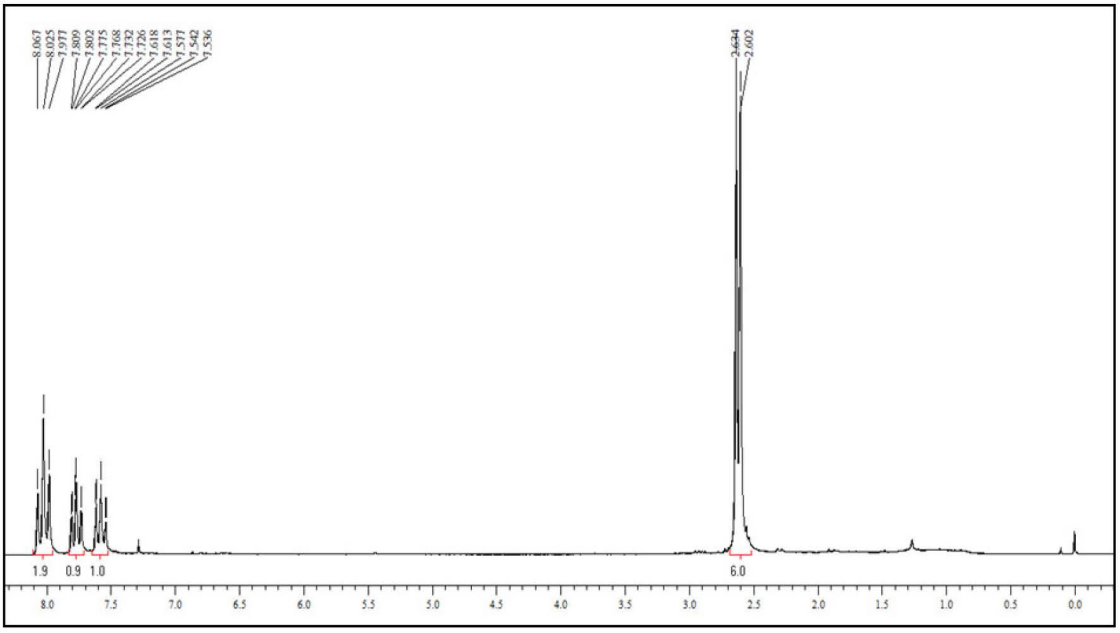

Figure S19. ^{1}H NMR spectrum (200 MHz) of 3-(1,1,1,2,2-perfluoropropionil)-2,4-dimethylquinoline (**11a**) in $CDCl_3$.

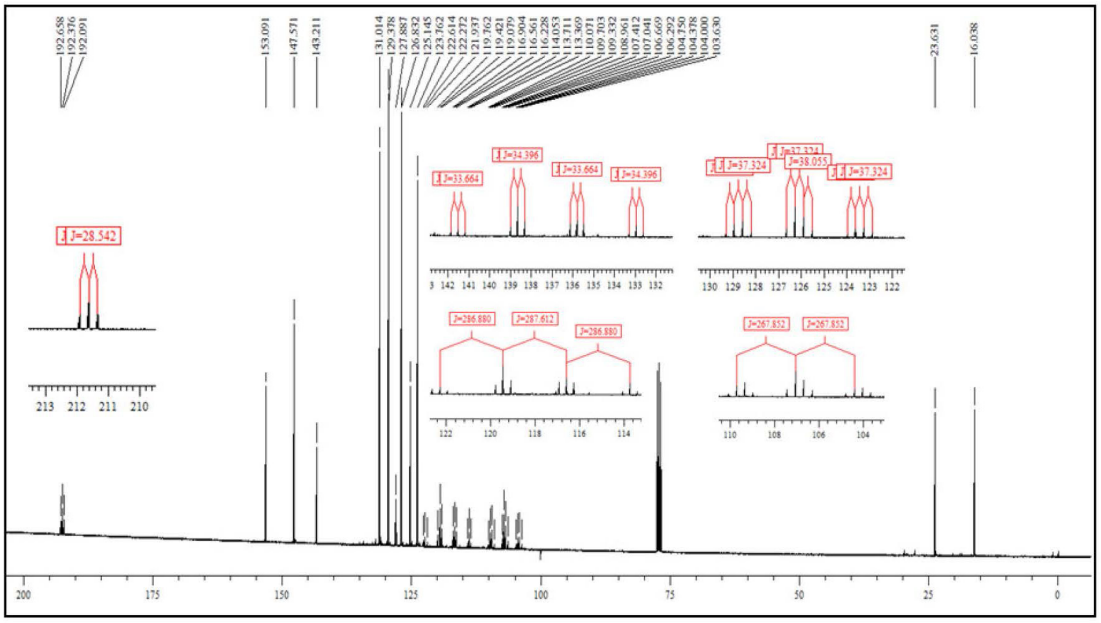

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz) of 3-(1,1,1,2,2-perfluoropropionil)-2,4-dimethylquinoline **(11a)** in $CDCl_3$.

Table S1. General and crystal data and summary of intensity data collection and structure refinement for compound **3c**

Compound	**3c**
Formula	$C_{15}H_{14}F_3NO$
M	281.27
CCDC	836125
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	
a / Å	13.6049(8)
b / Å	13.5737(7)
c / Å	7.5195(4)
α / degree	90
β / degree	91.742(4)
γ / degree	90
V / Å^3	13879.98(13)
Z	4
Density (calculated) / (g cm^{-3})	1.346
Absorption coefficient / mm^{-1}	0.112
F(000)	584
Crystal size / mm	0.76 × 0.42 × 0.26
θ range for data collection / degree	3.00 to 27.13
h, k, l range	−9 ≤ h ≤ 9; −17 ≤ k ≤ 17; −17 ≤ l ≤ 17
T_{max}/T_{min}	0.9715 and 0.9199
Reflections collected	19531
Independent reflections	3046 [R(int) = 0.00294]
Data/restraints/parameters	3051 / 0 / 208
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0720, wR2 = 0.2026
R indices (all data)	R1 = 0.1192, wR2 = 0.2436
Goodness of fit F^2	1.036
Largest diffraction peak and hole / (e Å^{-3})	0.296 and −0.287

Table S2. Selected bond lengths (Å) and bond angles (degree) for compound **3c**

Bond length / Å		Angle / degree	
F(1)-C(32)	1.311(5)	C(2)-N(1)-C(8A)	118.9(2)
F(2)-C(32)	1.322(5)	C(21)-C(22)-C(23)	112.9(4)
F(3)-C(32)	1.281(4)	C(2)-C(21)-C(22)	113.8(3)
O(31)-C(31)	1.187(4)	N(1)-C(2)-C(3)	121.7(3)
N(1)-C(2)	1.314(4)	N(1)-C(2)-C(21)	116.3(3)
N(1)-C(8A)	1.352(3)	C(3)-C(2)-C(21)	122.0(3)
C(23)-C(22)	1.522(5)	C(4)-C(3)-C(2	120.7(3)
C(22)-C(21)	1.500(6)	C(4)-C(3)-C(31)	119.7(3)
C(21)-C(2)	1.498(4)	C(2)-C(3)-C(31)	119.5(3)
C(2)-C(3)	1.436(4)	C(3)-C(4)-C(4A)	117.7(2)
C(3)-C(4)	1.371(4)	C(3)-C(4)-C(41)	122.2(3)
C(3)-C(31)	1.494(4)	C(4A)-C(4)-C(41)	120.2(3)
C(4)-C(4A)	1.426(4)	C(5)-C(4A)-C(8A)	118.8(3)
C(4)-C(41)	1.506(4)	F(1)-C(32)-F(2)	106.1(4)
C(4A)-C(5)	1.409(4)	F(3)-C(32)-C(31)	113.0(3)
C(4A)-C(8A)	1.421(4)	O(31)-C(31)-C(3)	123.2(3)
C(32)-C(31)	1.526(5)	O(31)-C(31)-C(32)	117.7(3)
C(7)-C(8)	1.358(4)	C(3)-C(31)-C(32)	119.0(3)
C(8)-C(8A)	1.410(4)	C(8)-C(7)-C(6)	119.9(3)
		C(7)-C(8)-C(8A)	121.2(3)