Electronic Supplementary Information for

Zircon $PrVO_4$: An Efficient Heterogeneous Catalyst for Tandem Oxidative Synthesis of 2,3-Disubstituted Quinoline Derivatives

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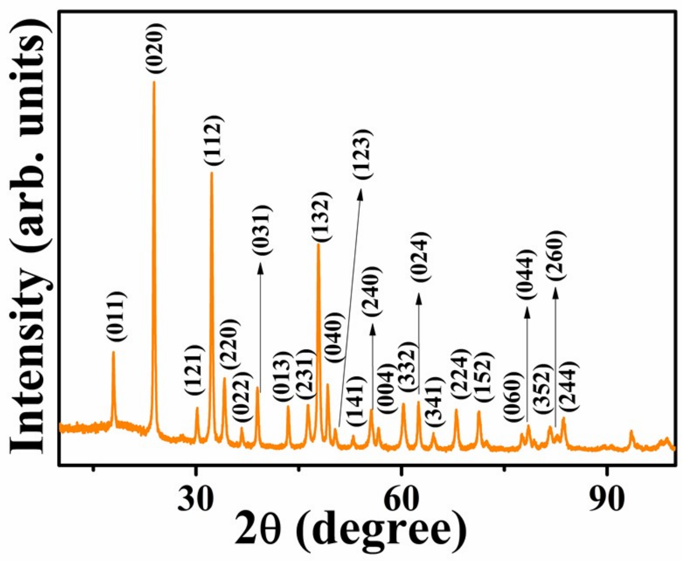


Figure S1. PXRD pattern of $PrVO_4$ sample calcined at 475 °C for 3 h.

Table S1. Crystallographic details from the structural refinement of the PXRD pattern of $PrVO_4$ by the Rietveld method.

Composition	**$PrVO_4$**
a (Å)	7.3599 (9)
c (Å)	6.4660 (1)
Cell volume (Å^3)	350.258 (8)
Formula weight (g/mol)	255.85
Z	4
ρ_{calc} (g/cm^3)	4.851
Temperature (°C)	25
No. of data points	9000
2θ range	10-100°
R_p	0.0684
R_{wp}	0.0919
χ^2	0.7993

Table S2. Atomic parameters from the final cycle of refinement of the PXRD patterns of $PrVO_4$ sample by the Rietveld method.

Composition	**Atoms**	***Wyck***	***x/a***	***y/b***	***z/c***	**SOF**	**U(iso)Å^2**
$PrVO_4$	Pr	4*a*	0.0	0.75	0.125	1.0	0.0249 (3)
	V	4*b*	0.0	0.25	0.375	1.0	0.0227 (5)
	O	16*h*	0.0	0.0711 (4)	0.2186 (5)	1.0	0.0217 (12)

Typical procedure for the synthesis of 3,4-Dihydroacridin-1(2*H*)-one: To the magnetically stirred mixture of the 2-aminobenzylalcohol **1a** (123.07 mg, 1 mmol) and 1,3-cyclohexanedione **2a** (123.25 mg, 1.1 mmol, 1.1 equiv) was added zircon $PrVO_4$ (25.58 mg, 0.1 mmol, 10 mol%) and the mixture was heated at 110 °C under oxygen atmosphere (O_2 balloon) for 12 h. After completion of the reaction (monitored by TLC), the mixture was allowed to cool to the room temperature. The mixture was diluted with ethyl acetate (3 mL), adsorbed on silica gel (2 g) and dried in vacuo. The residue was charged on to chromatography (100-200 mesh silica gel) column and eluted with 10% EtOAc-hexane to afford pure **3a** (179.3 mg, 91%). All the remaining reactions were performed on 1 mmol scale following this general procedure. The spectral data of the synthesised compounds are provided below.

Characterization of quinoline products

3,4-Dihydroacridin-1(2*H*)-one (3a)

Yellow solid; yield: 91%; Melting Point: 104-106 °C (Lit.: 105-106 °C)[1].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.27 (qu, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 161.9, 149.6, 137.1, 132.3, 132.7, 128.5, 126.7, 126.6, 126.2, 39.0, 33.4, 21.7.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{13}H_{11}NO$: 198.0913, found: 198.0914.

3,3-Dimethyl-3,4-dihydroacridin-1(2*H*)-one (3b)

Brown solid; yield: 90%; Melting Point: 112-114 °C (Lit.: 112-113 °C)[1].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.81-7.77 (m, 1H), 7.56-7.52 (m, 1H), 3.18 (s, 2H), 2.64 (s, 2H), 1.13 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 160.8, 149.9, 136.5, 132.2, 129.7, 128.5, 126.7, 125.2, 52.4, 47.1, 32.7, 28.3.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{15}NO$: 226.1226, found: 226.1227.

1-(2-Methylquinolin-3-yl)ethan-1-one (3c)

Pale yellow solid; yield: 93%; Melting Point: 76-77 °C (Lit.: 77-78 °C)[1].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80-7.76 (m, 1H), 7.57-7.53 (m, 1H), 2.91 (s, 3H), 2.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 157.6, 148.3, 138.2, 131.7, 131.1, 128.6, 128.3, 126.6, 125.6, 29.2, 25.6.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{12}H_{11}NO$: 186.0913, found: 186.0911.

(2-Methylquinolin-3-yl)(phenyl)methanone (3d)

Yellow solid; yield: 87%; Melting Point: 133-134 °C (Lit.: 134-136 °C)[2].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.10 (m, 2H), 7.83-7.80 (m, 2H), 7.78-7.73 (m, 2H), 7.62-7.58 (m, 1H), 7.53-7.41 (m, 3H), 2.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 156.6, 147.6, 137.0, 136.9, 133.6, 131.1, 130.0, 129.8, 128.6, 128.1, 127.9, 126.6, 125.2, 23.8.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{13}NO$: 248.1070, found: 248.1064.

Phenyl(2-phenylquinolin-3-yl)methanone (3e)

Yellow solid; yield: 89%; Melting Point: 134-136 °C (Lit.: 135-137 °C)[3].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.86-7.82 (m, 1H), 7.73-7.70 (m, 2H), 7.64-7.60 (m, 3H), 7.49-7.45 (m, 1H), 7.35-7.26 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 157.4, 148.3, 139.6, 137.6, 136.9, 133.3, 132.8, 131.2, 129.9, 129.6, 129.2, 128.8, 128.4, 128.3, 128.1, 127.3, 125.8.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{15}NO$: 310.1226, found: 310.1231.

Ethyl 2-methylquinoline-3-carboxylate (3f)

Pale yellow solid; yield: 95%; Melting Point: 68-70 °C (Lit.: 69-70 °C)[1].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.79-7.74 (m, 1H), 7.55-7.51 (m, 1H), 4.43 (q, J = 7.2 Hz, 2H), 2.98 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 158.4, 148.6, 139.8, 131.6, 128.5, 128.4, 126.5, 125.7, 123.9, 61.4, 25.6, 14.3.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{13}H_{13}NO_2$: 216.1019, found: 216.1019.

Methyl 2-phenylquinoline-3-carboxylate (3g)

Yellow oil (Lit.: yellow viscous liquid)[4]; yield: 94%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.66-7.59 (m, 3H), 7.51-7.43 (m, 3H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 157.9, 148.4, 140.5, 139.2, 131.6, 129.5, 128.6, 128.5, 128.2, 127.2, 125.7, 125.0, 52.4.

HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{13}NO_2$: 264.1019, found: 264.1022.

Methyl 2-(4-chlorophenyl)quinoline-3-carboxylate (3h)

Light yellow solid; yield: 96%; Melting Point: 111-113 °C (Lit.: 111.2-114.4 °C)[4].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.85-7.81 (m, 1H), 7.64-7.56 (m, 3H), 7.46-7.44 (m, 2H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 156.8, 148.4, 139.5, 139.0, 134.8, 131.8, 130.0, 129.5, 128.4, 128.3, 127.5, 125.8, 124.6, 52.5.

HRMS: m/z $[M+H]^+$ calcd for $C_{17}H_{12}ClNO_2$: 298.0629, found: 298.0635.

Methyl 2-(4-methoxyphenyl)quinoline-3-carboxylate (3i)

Pale yellow solid; yield: 93%; Melting Point: 92-96 °C (Lit.: 92.1-95.7 °C)[4].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.82-7.78 (m, 1H), 7.63-7.56 (m, 3H), 7.02-6.99 (m, 2H), 3.87 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 160.2, 157.4, 148.4, 139.1, 132.9, 131.5, 130.0, 129.4, 128.2, 126.9, 125.6, 124.9, 113.7, 55.3, 52.5.

HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{15}NO_3$: 294.1125, found: 294.1132.

Methyl 2-(3-methoxyphenyl)quinoline-3-carboxylate (3j)

Light yellow oil; yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.83-7.79 (m, 1H), 7.61-7.57 (m, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.25-7.24 (m, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.01-6.98 (m, 1H), 3.87 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.5, 157.7, 148.3, 141.8, 138.9, 131.5, 129.4, 129.1, 128.1, 127.2, 125.7, 125.1, 121.0, 114.7, 113.7, 55.2, 52.4.

HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{15}NO_3$: 294.1125, found: 294.1129.

Methyl 2-(2-methoxyphenyl)quinoline-3-carboxylate (3k)

Brown oil; yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.79-7.75 (m, 1H), 7.72-7.70 (m, 1H), 7.59-7.55 (m, 1H), 7.44-7.39 (m, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 156.4, 155.6, 148.7, 138.0, 131.1, 130.3, 130.1, 129.9, 129.4, 128.2, 126.9, 126.2, 125.8, 121.2, 109.9, 54.9, 51.9.

HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{15}NO_3$: 294.1125, found: 294.1127.

1-(2,4-dimethylquinolin-3-yl)ethan-1-one (3l)

Light yellow oil (Lit.: light yellow oil)[5]; yield: 89%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.94 (m, 2H), 7.71-7.67 (m, 1H), 7.55-7.51 (m, 1H), 2.62 (s, 3H), 2.57 (s, 3H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 206.6, 152.6, 146.8, 138.5, 135.6, 129.8, 129.2, 126.3, 125.9, 123.6, 32.6, 23.5, 15.2.

HRMS: m/z $[M+H]^+$ calcd for $C_{13}H_{13}NO$: 200.1070, found: 200.1062.

1-(2-methyl-4-phenylquinolin-3-yl)ethan-1-one (3m)

Light yellow solid; yield: 85%; Melting Point: 112-115 °C (Lit.: 112-114 °C)[5].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 1H), 7.74-7.69 (m, 1H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 3H), 7.46-7.42 (m, 1H), 7.38-7.33 (m, 2H), 2.69 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 153.5, 147.5, 139.9, 135.1, 134.8, 130.1, 130.0, 128.9, 128.8, 128.7, 126.5, 126.1, 124.9, 31.9, 23.9.

HRMS: m/z $[M+H]^+$ calcd for $C_{18}H_{15}NO$: 262.1226, found: 262.1222

References

[1] Z.-H. Yu, H.-F. Zheng, W. Yuan, Z.-L. Tang, A.-D. Zhang, and D.-Q. Shi, *Tetrahedron*, 2013, **69**, 8137-8141.

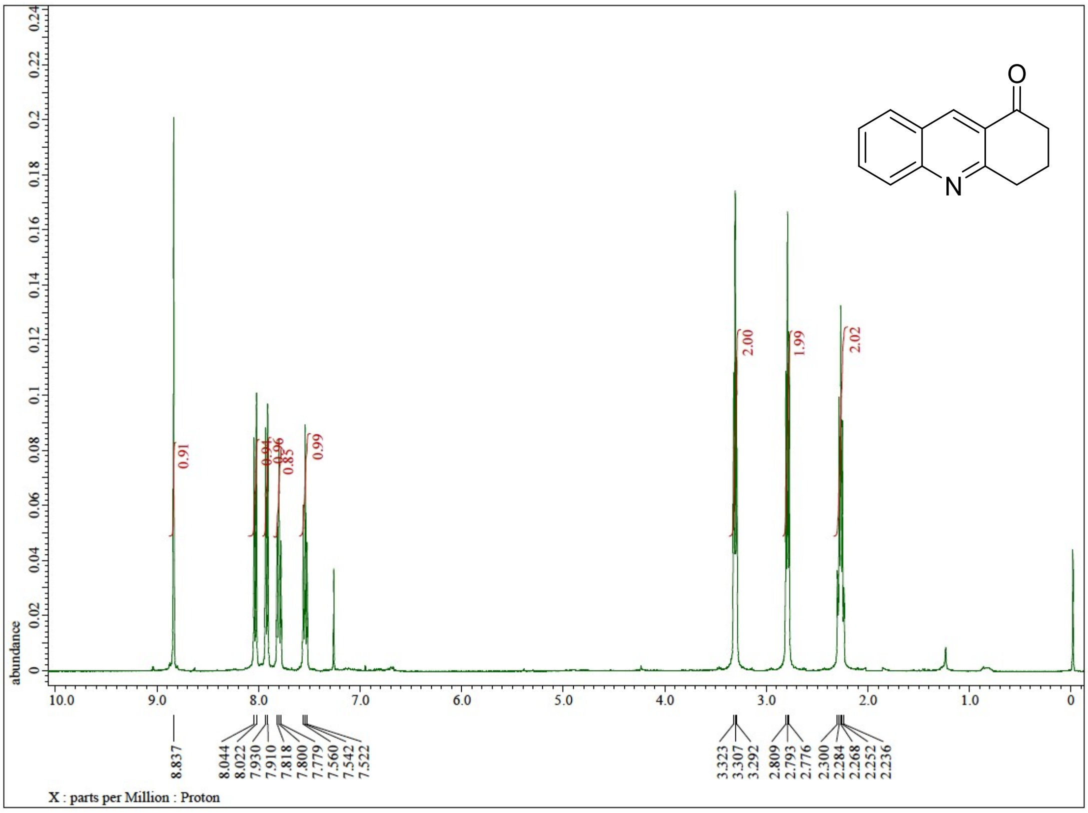
[2] Z. Wang, G. Chen, X. Zhang and X. Fan, *Org. Chem. Front.*, 2017, **4**, 612-616.

[3] N. Anand, T. Chanda, S. Koley, S. Chowdhury and M. S. Sing, *RSC Adv.*, 2015, **5**, 7654-7660.

[4] Y.-F. Li, Z.-G. Wu, J. Shi, Y. Pan, H. Bu, H.-F. Ma, J.-C. Gu, H. Huang, Y.-Z. Wang and L. Wu, *Tetrahedron*, 2014, **70**, 8971-8975.

[5] K. Fobi and R. A. Bunce, *Molecules*, 2022, **27**, 4123.

NMR spectra of quinoline products



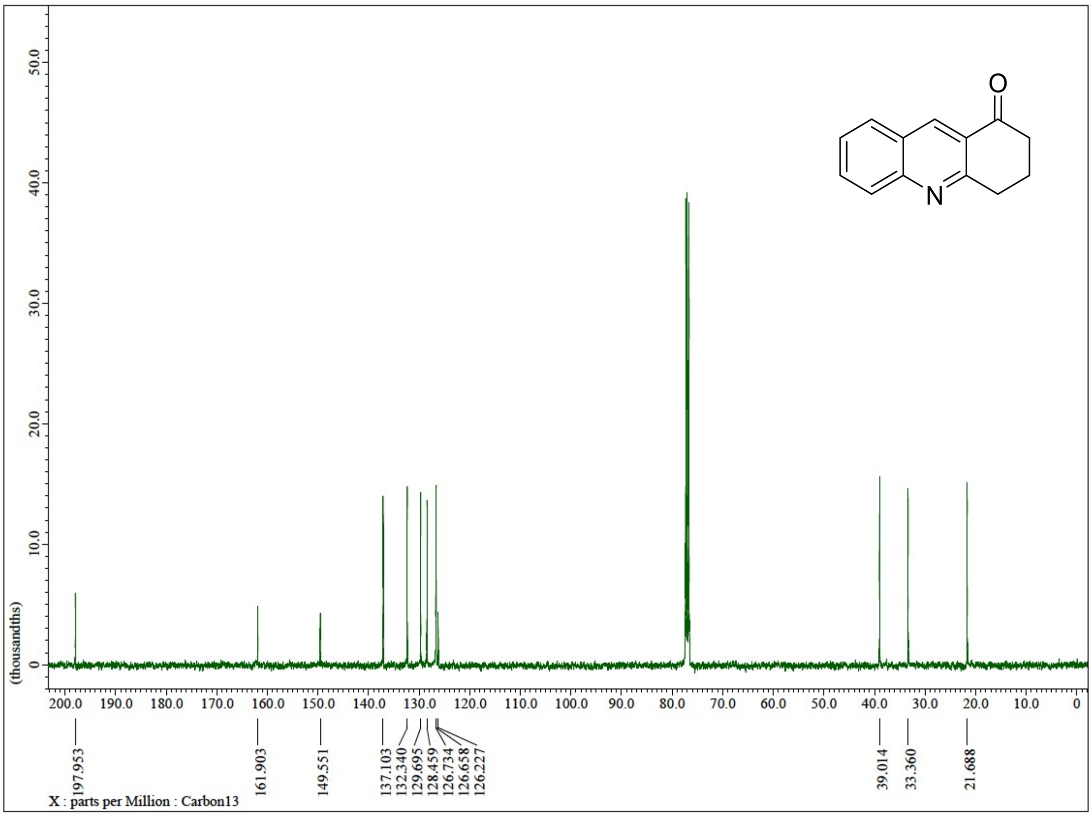
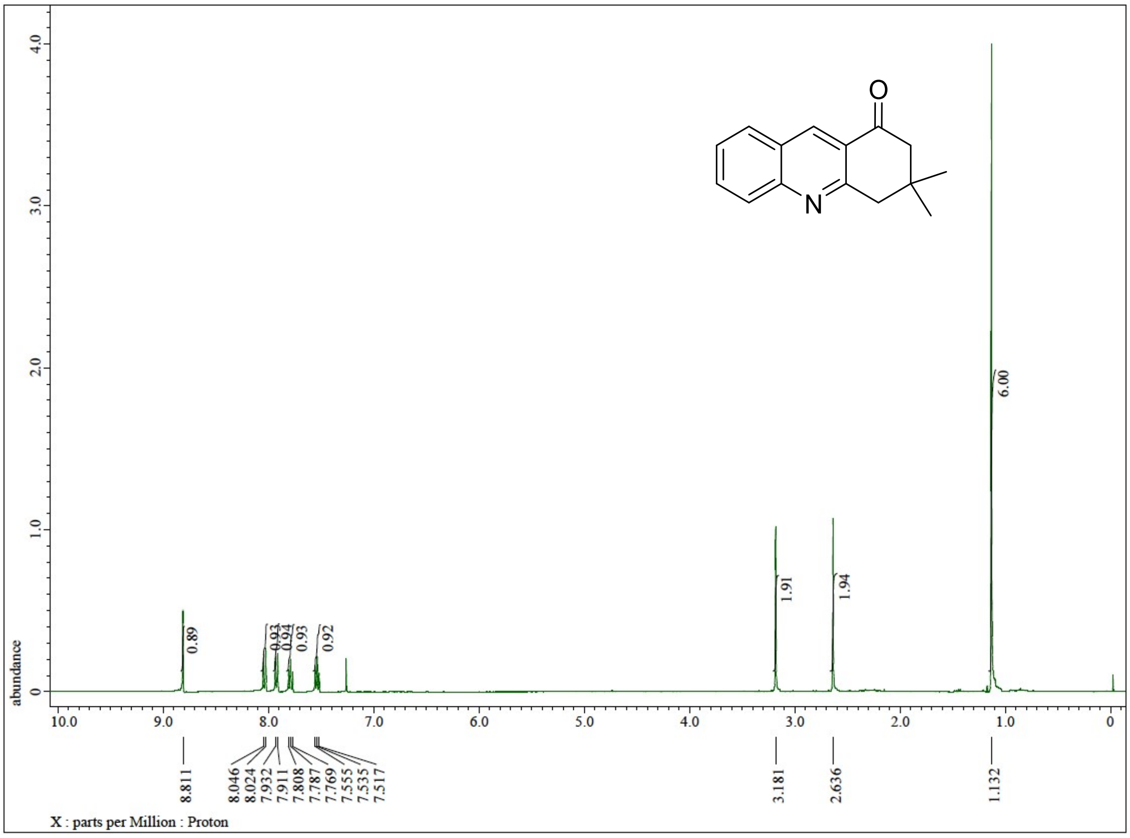


Figure S2. ^{1}H NMR of **3a** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



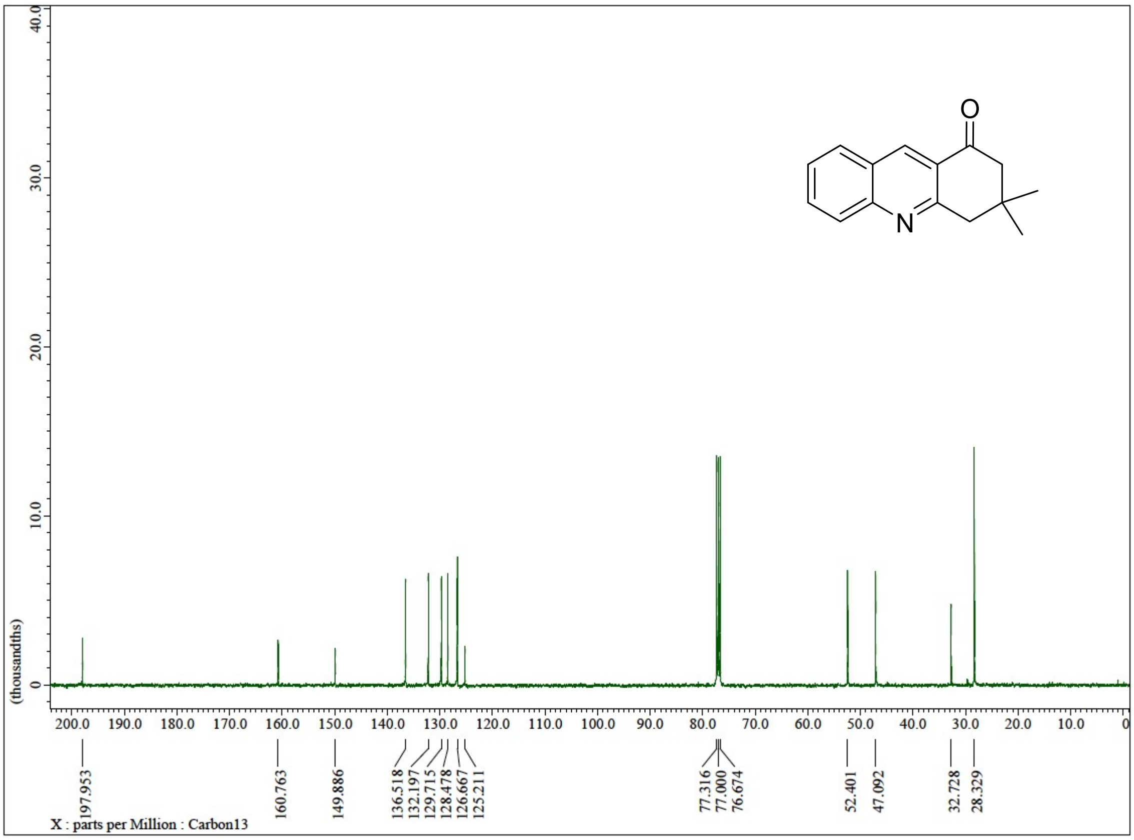
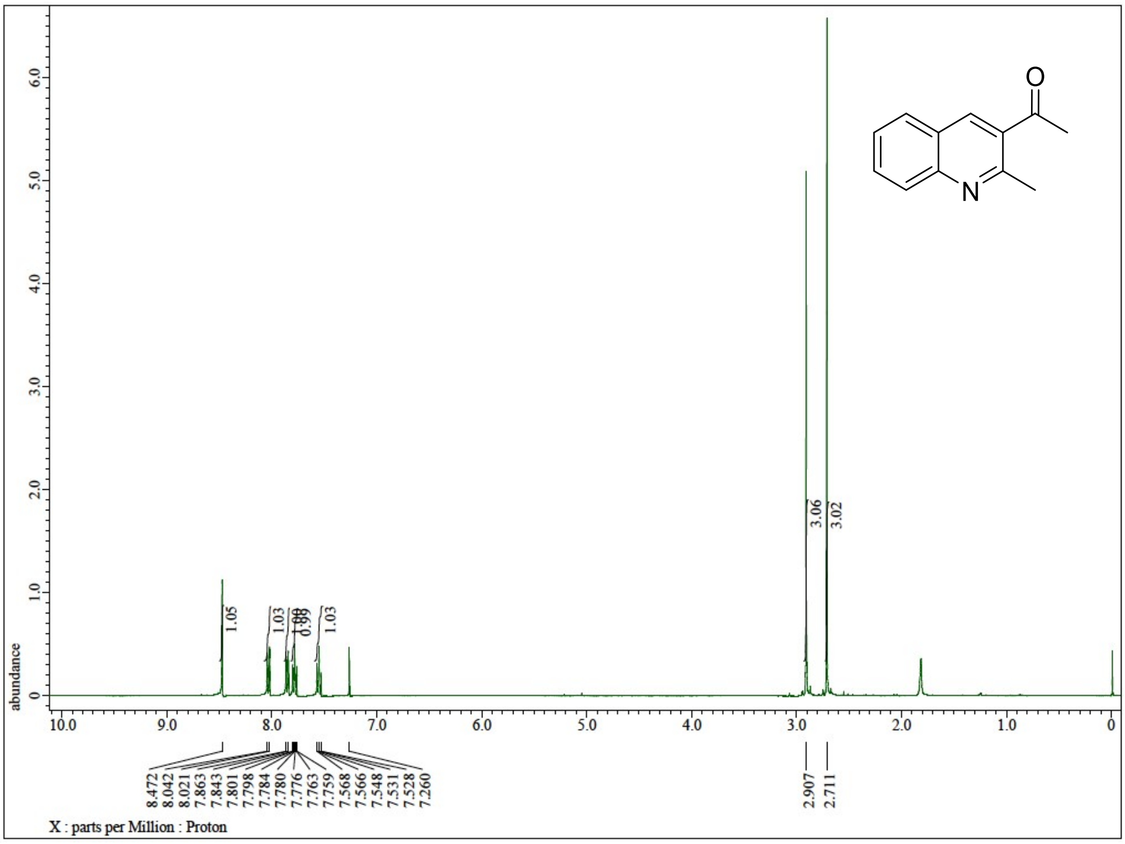


Figure S3. [1]H NMR of **3b** (400 MHz, $CDCl_3$) and [13]C NMR of **3b** (100 MHz, $CDCl_3$)



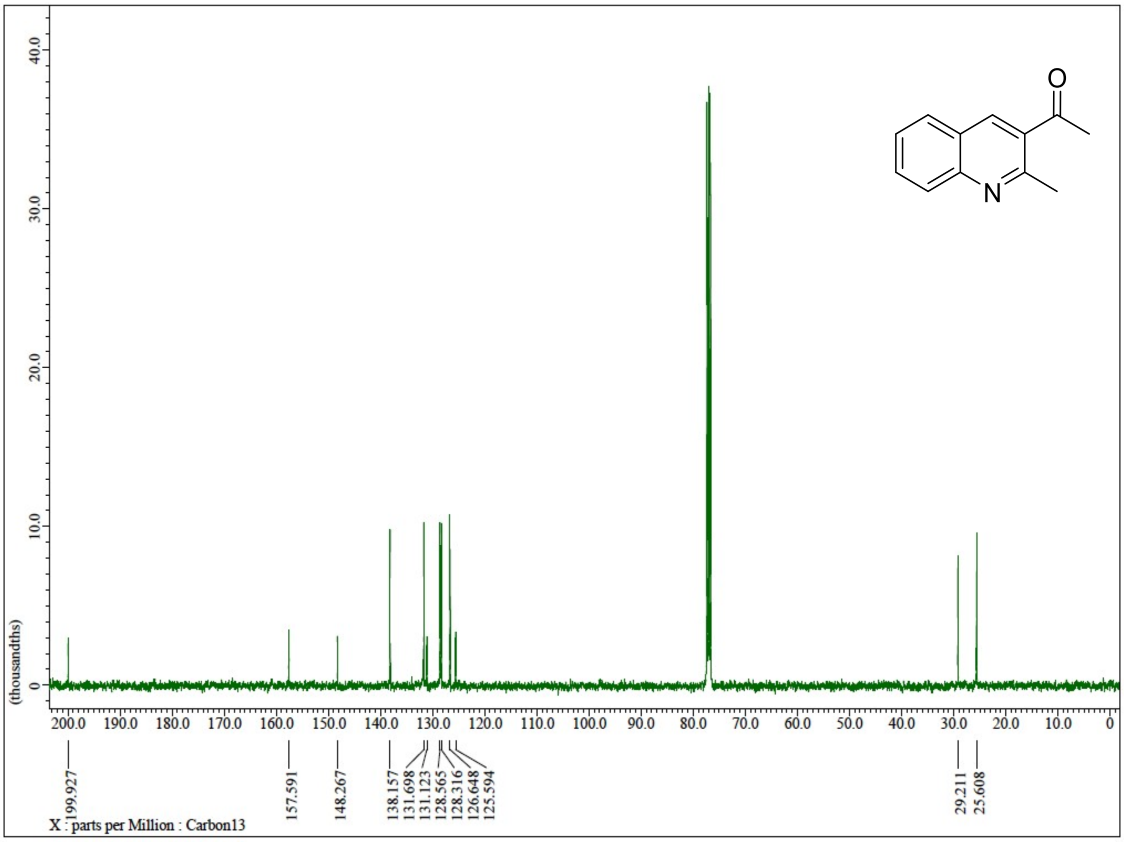
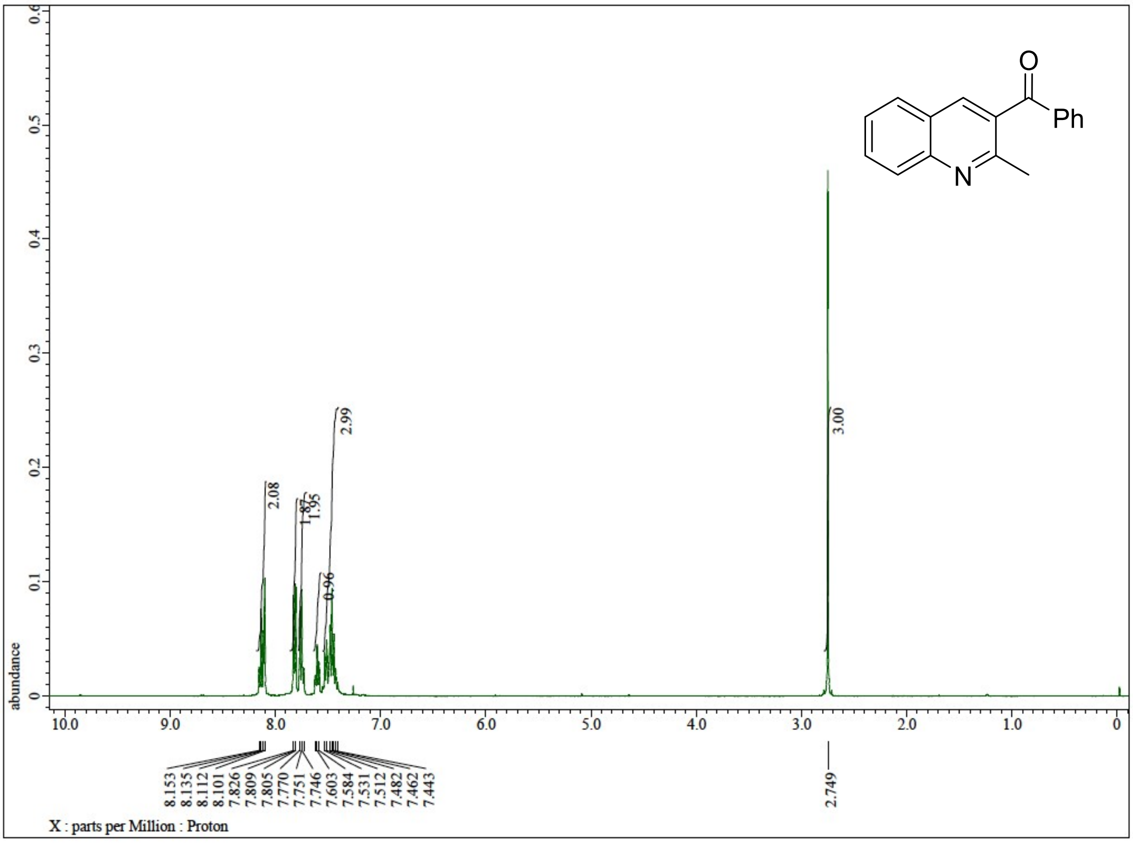


Figure S4. [1]H NMR of **3c** (400 MHz, $CDCl_3$) and [13]C NMR of **3c** (100 MHz, $CDCl_3$)



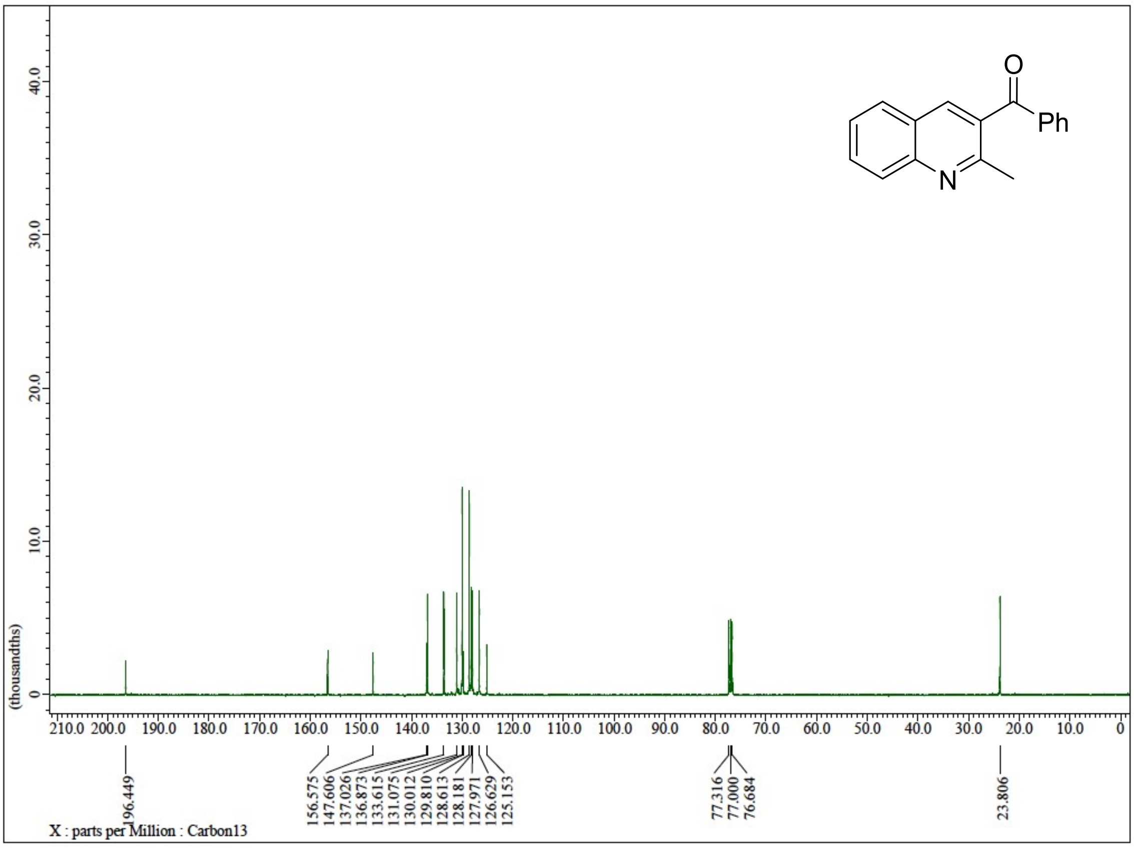
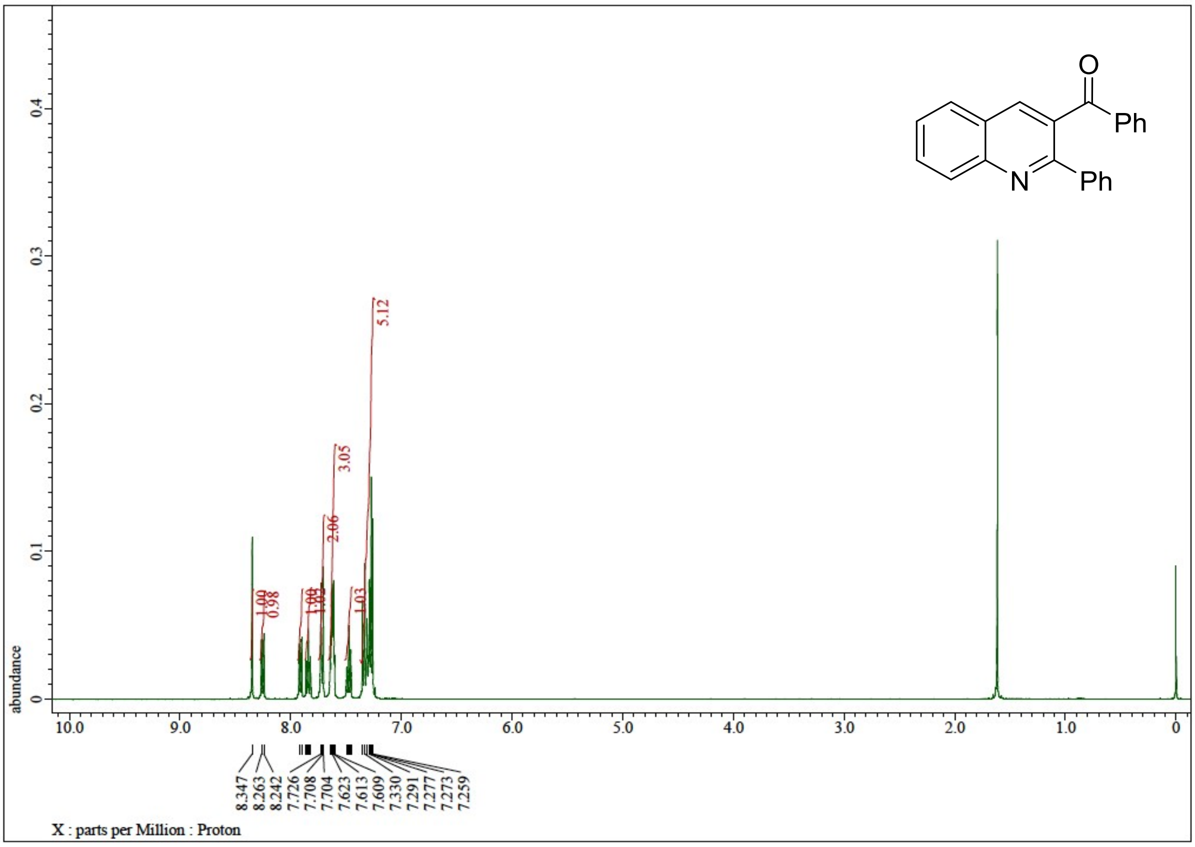


Figure S5. [1]H NMR of **3d** (400 MHz, $CDCl_3$) and [13]C NMR of **3d** (100 MHz, $CDCl_3$)



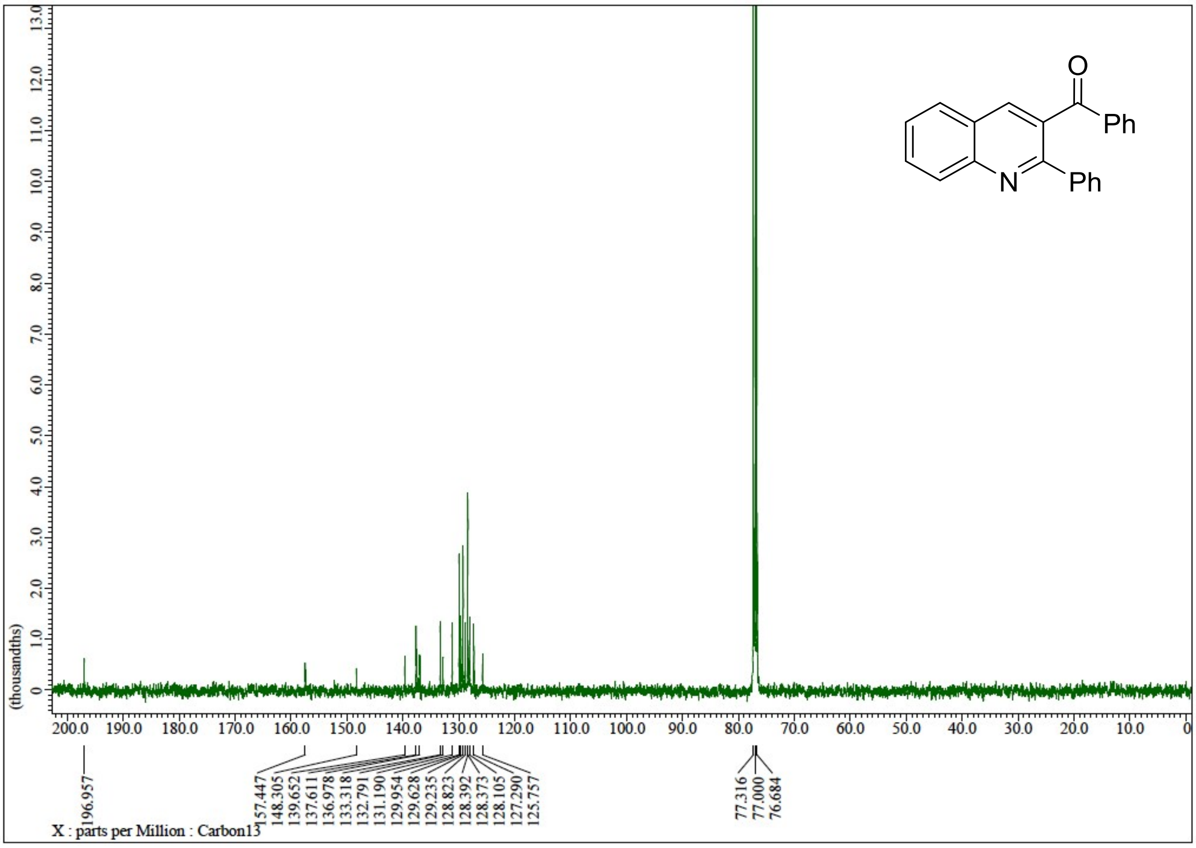
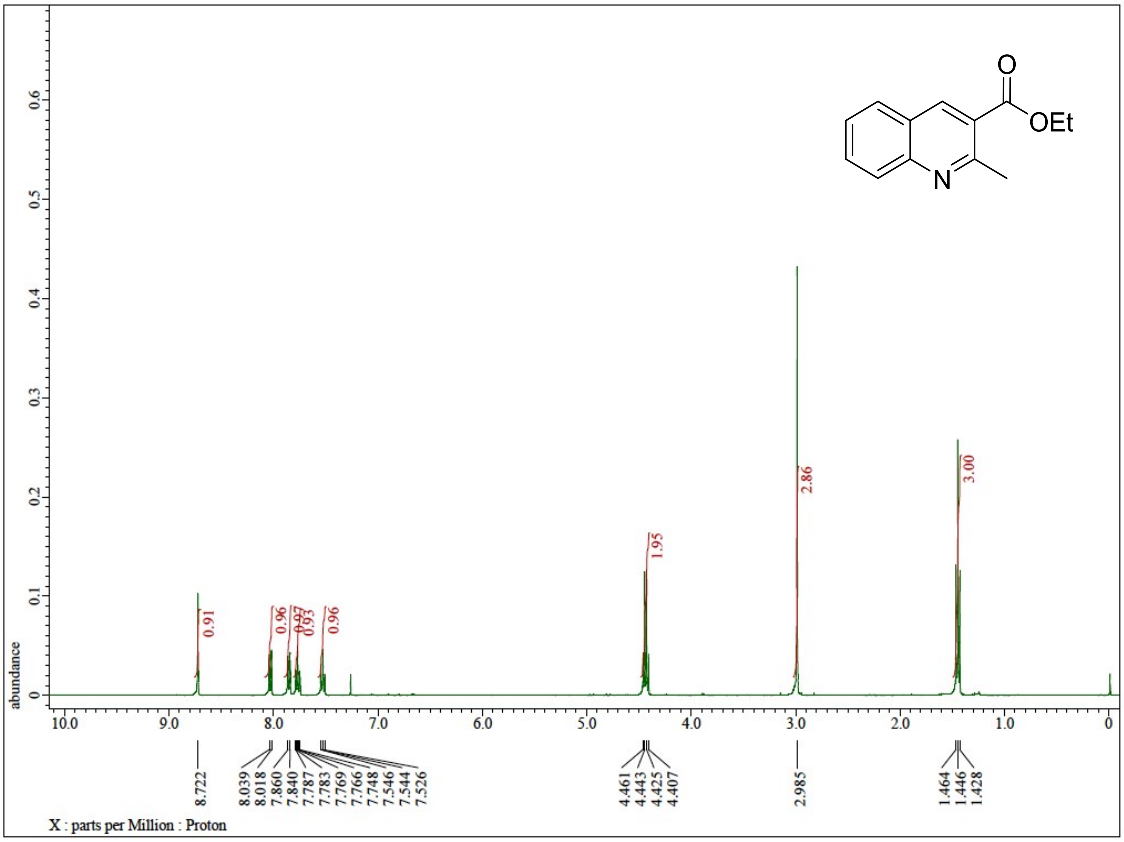


Figure S6. ^{1}H NMR of **3e** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3e** (100 MHz, $CDCl_3$)



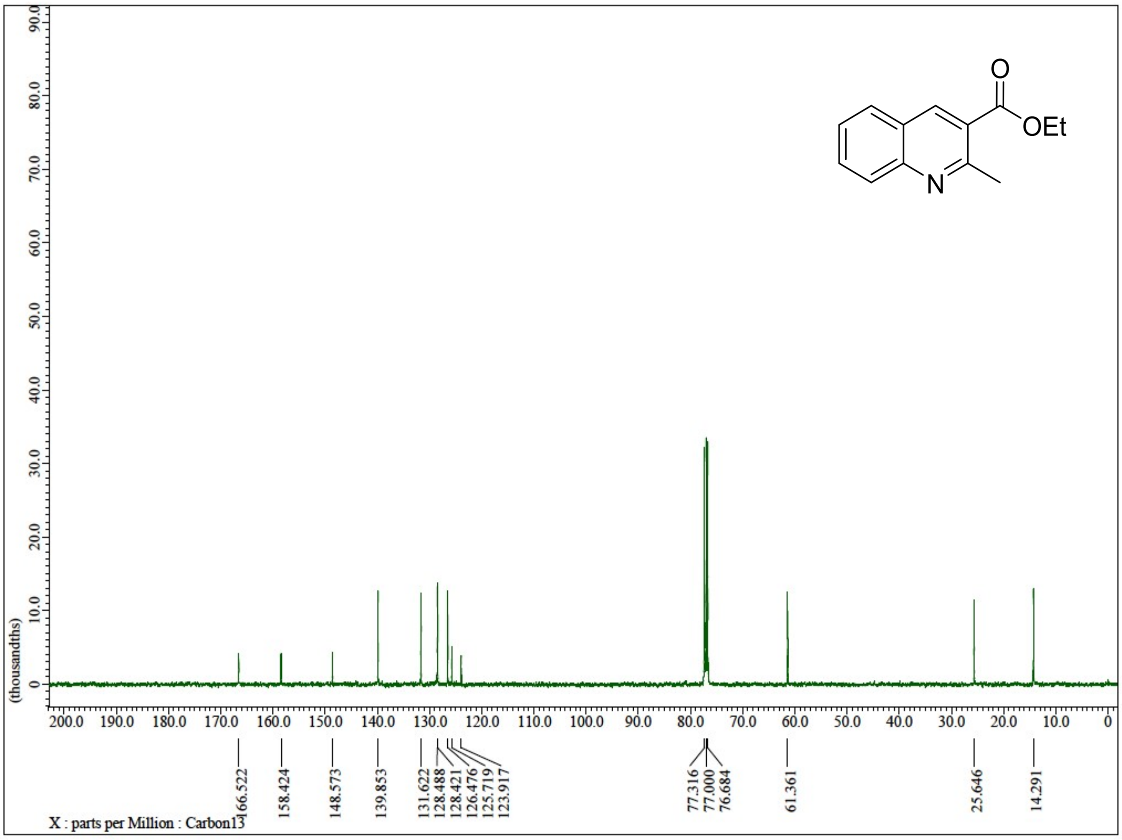
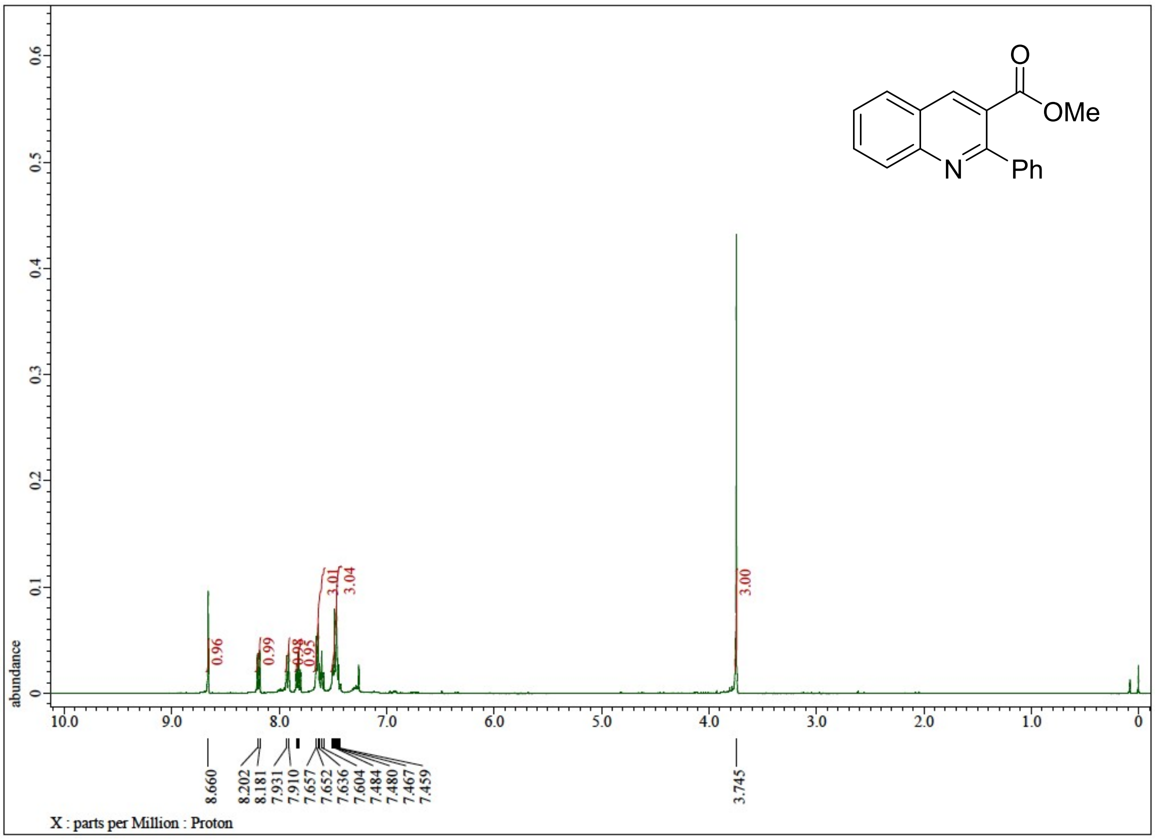


Figure S7. ^{1}H NMR of **3f** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3f** (100 MHz, $CDCl_3$)



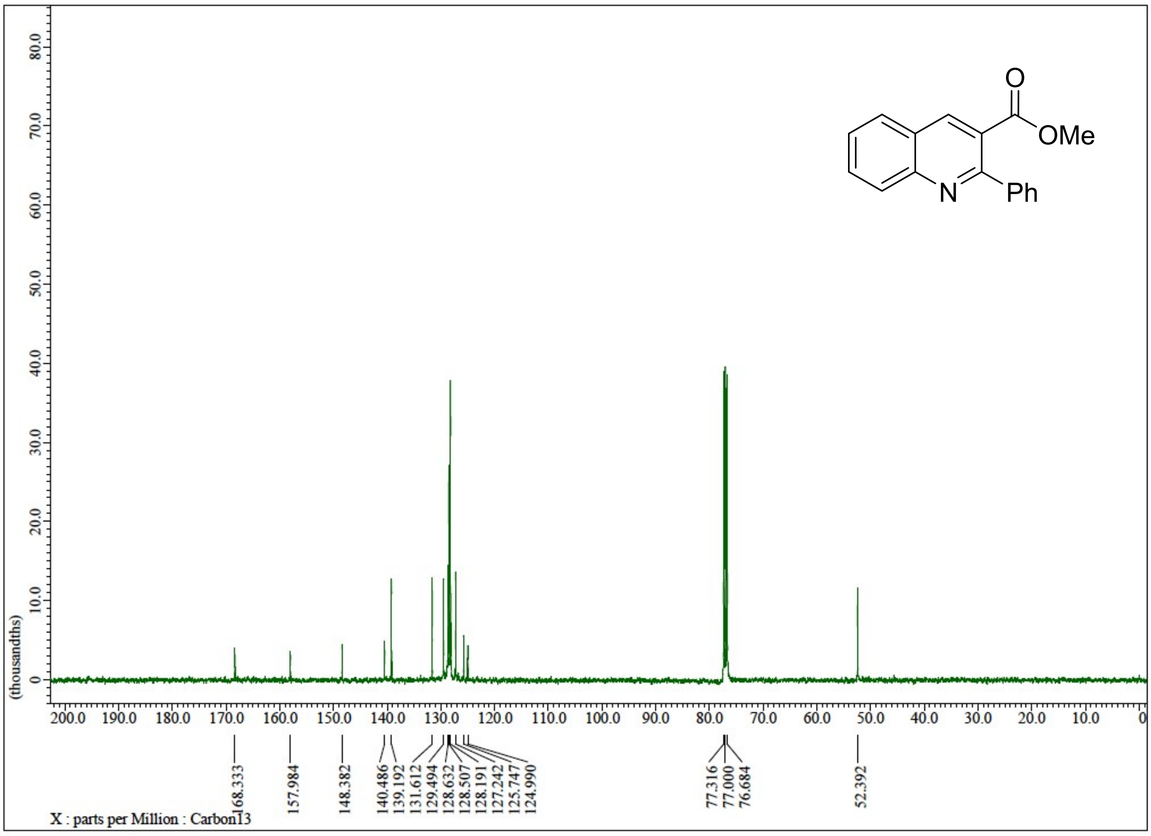
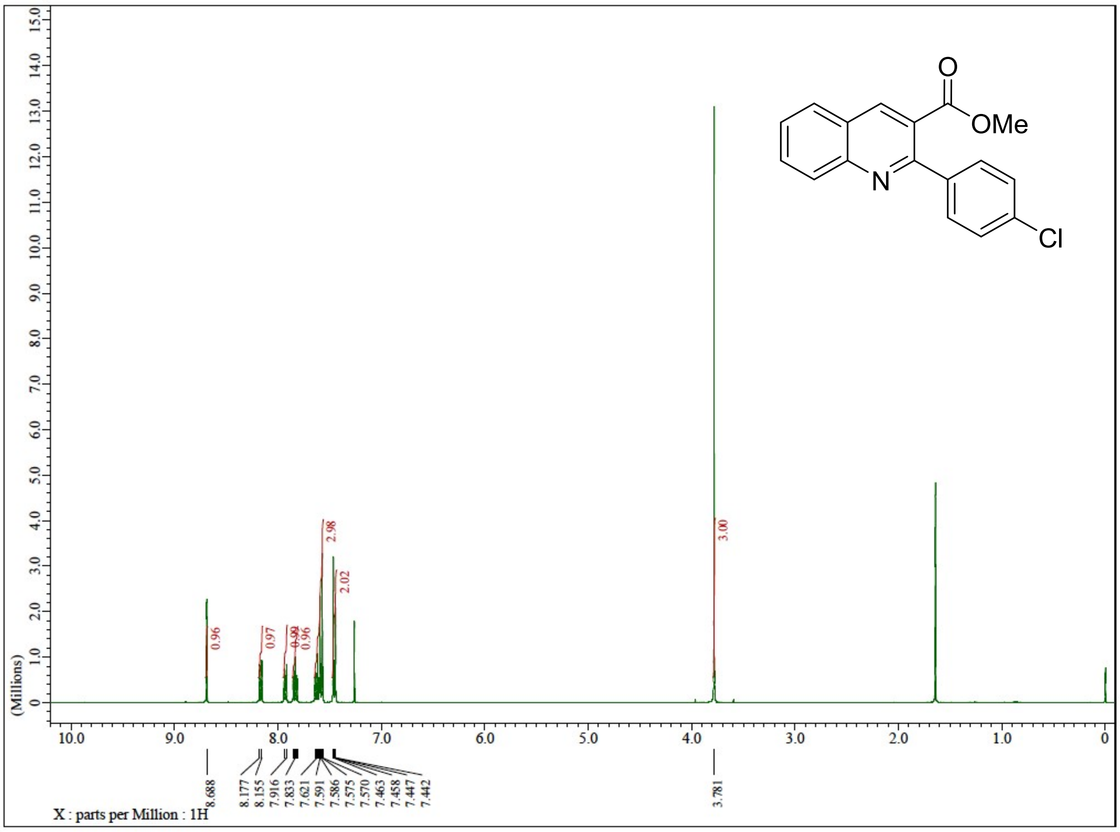


Figure S8. ^{1}H NMR of **3g** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3g** (100 MHz, $CDCl_3$)



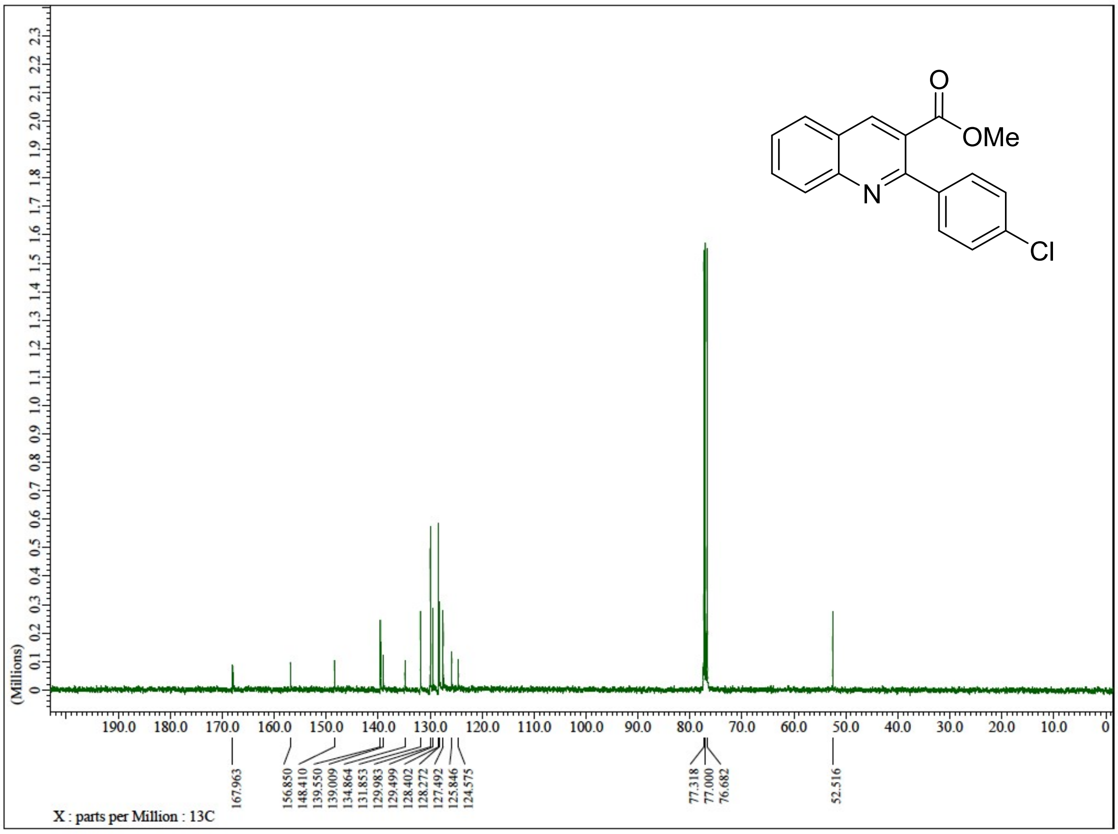
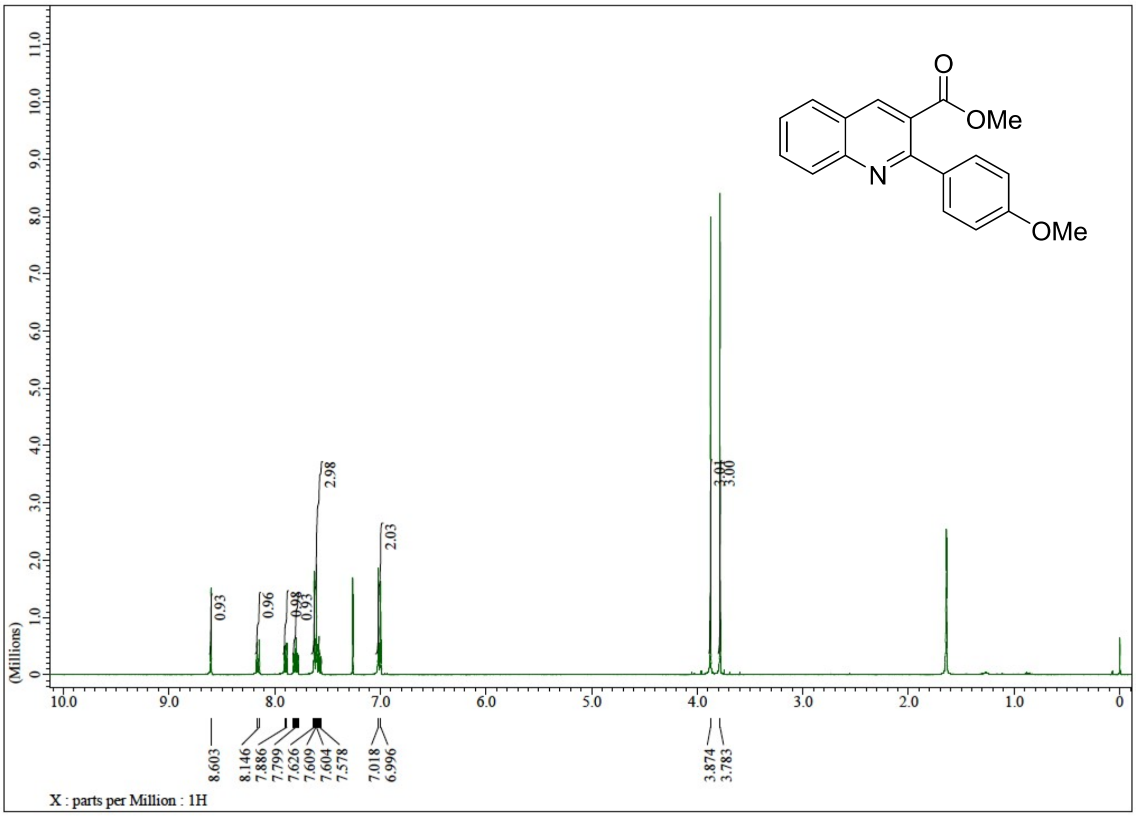


Figure S9. ^{1}H NMR of **3h** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



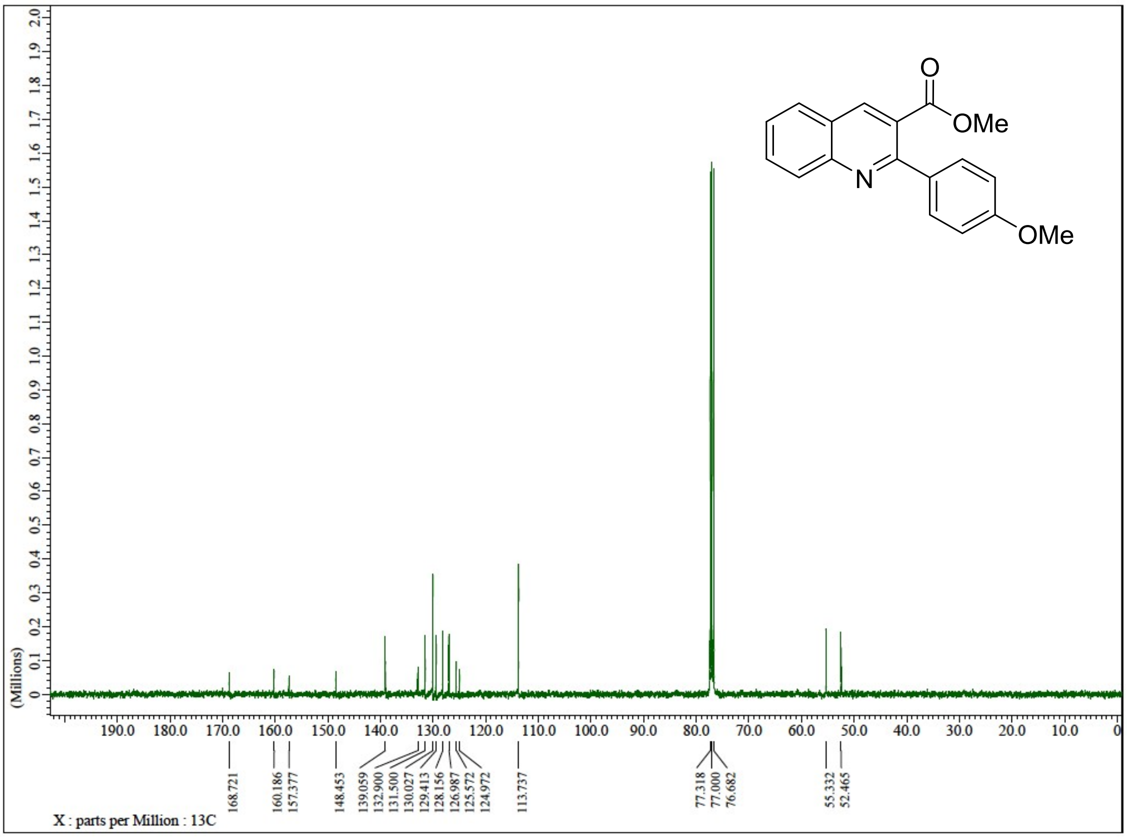
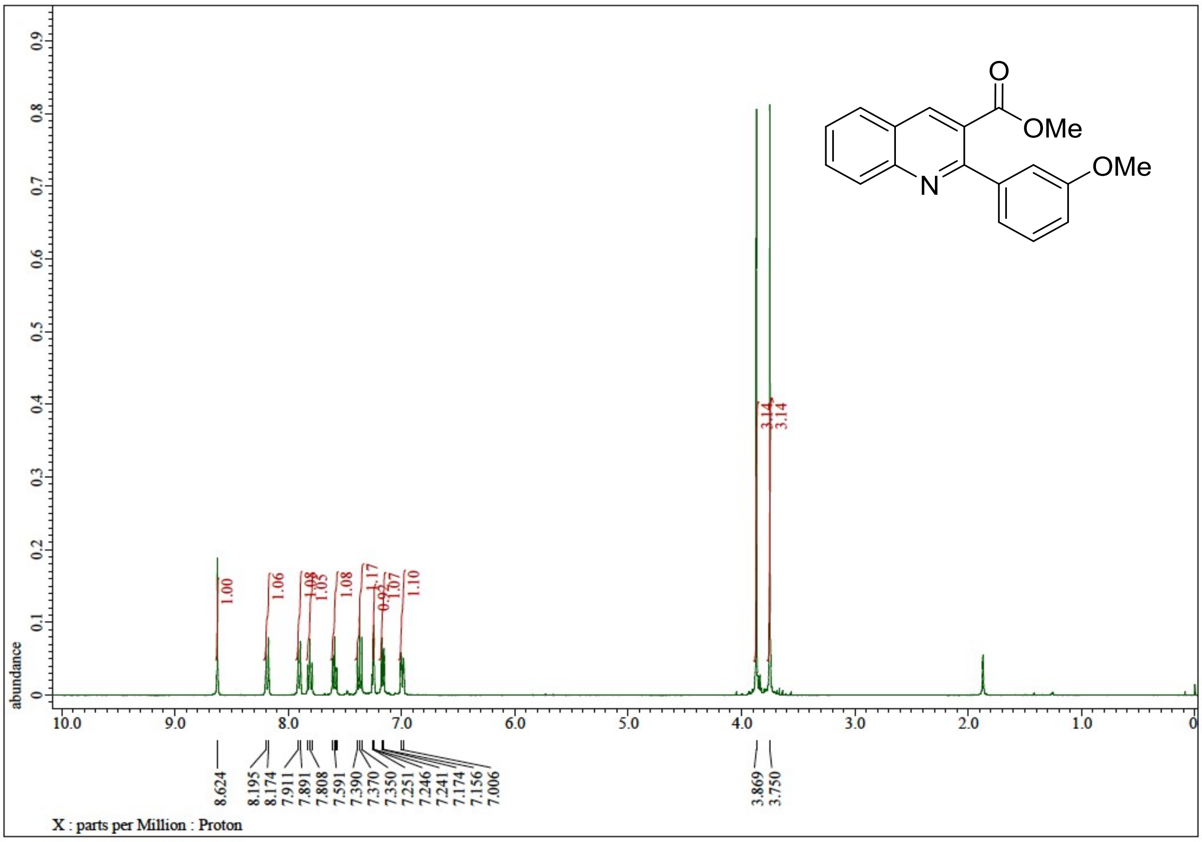


Figure S10. ^{1}H NMR of **3i** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



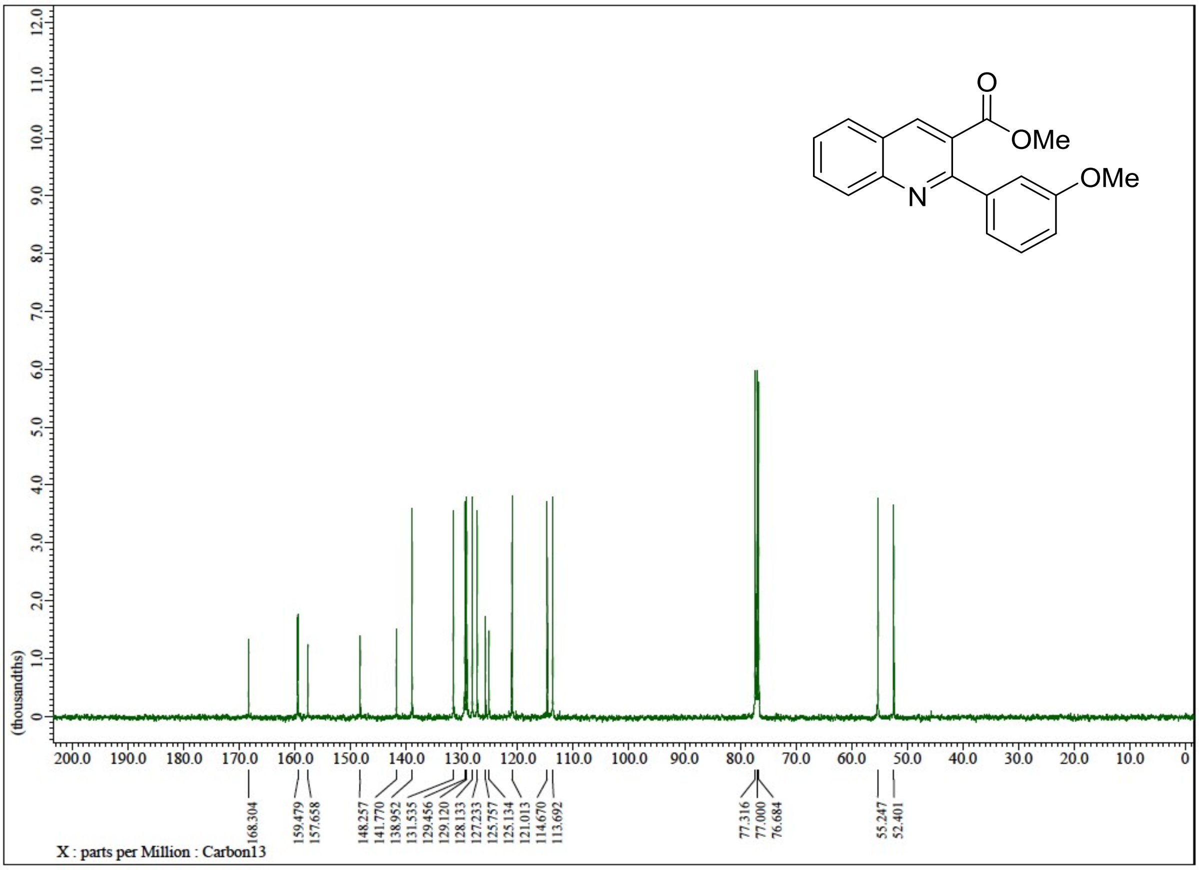
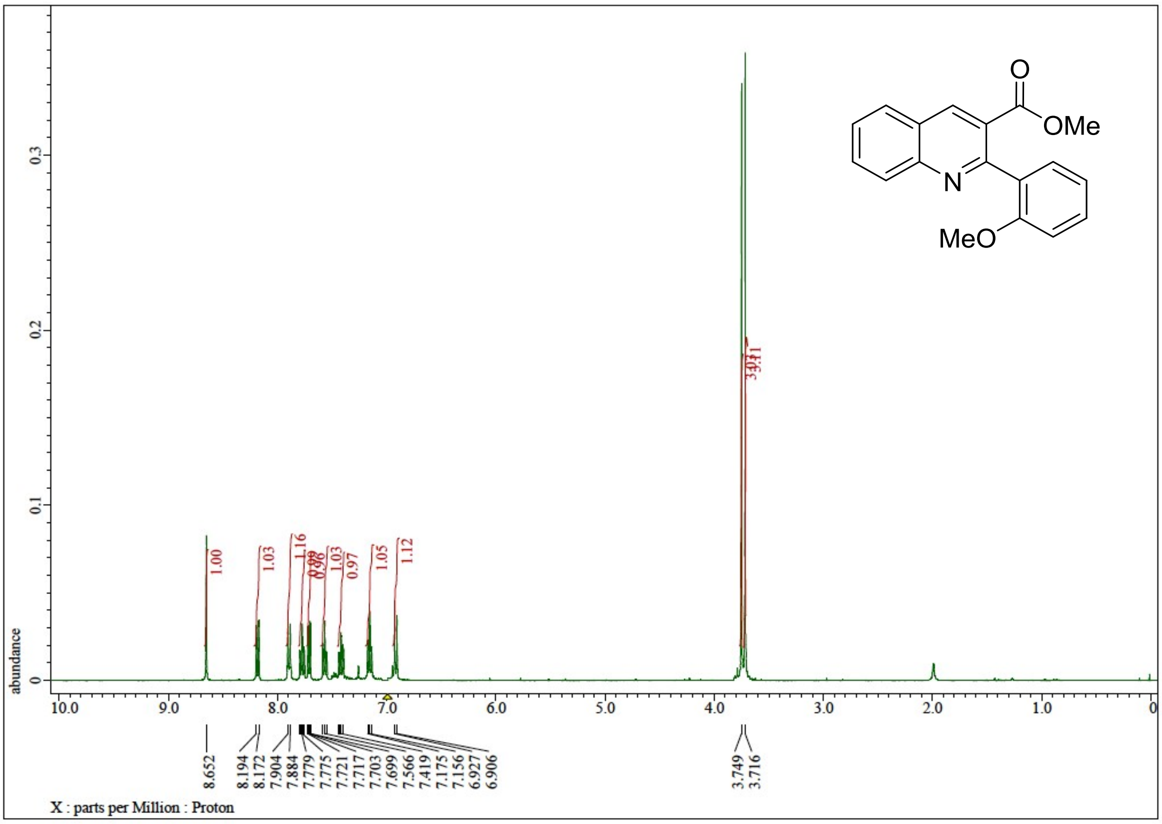


Figure S11. ^{1}H NMR of **3j** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3j** (100 MHz, $CDCl_3$)



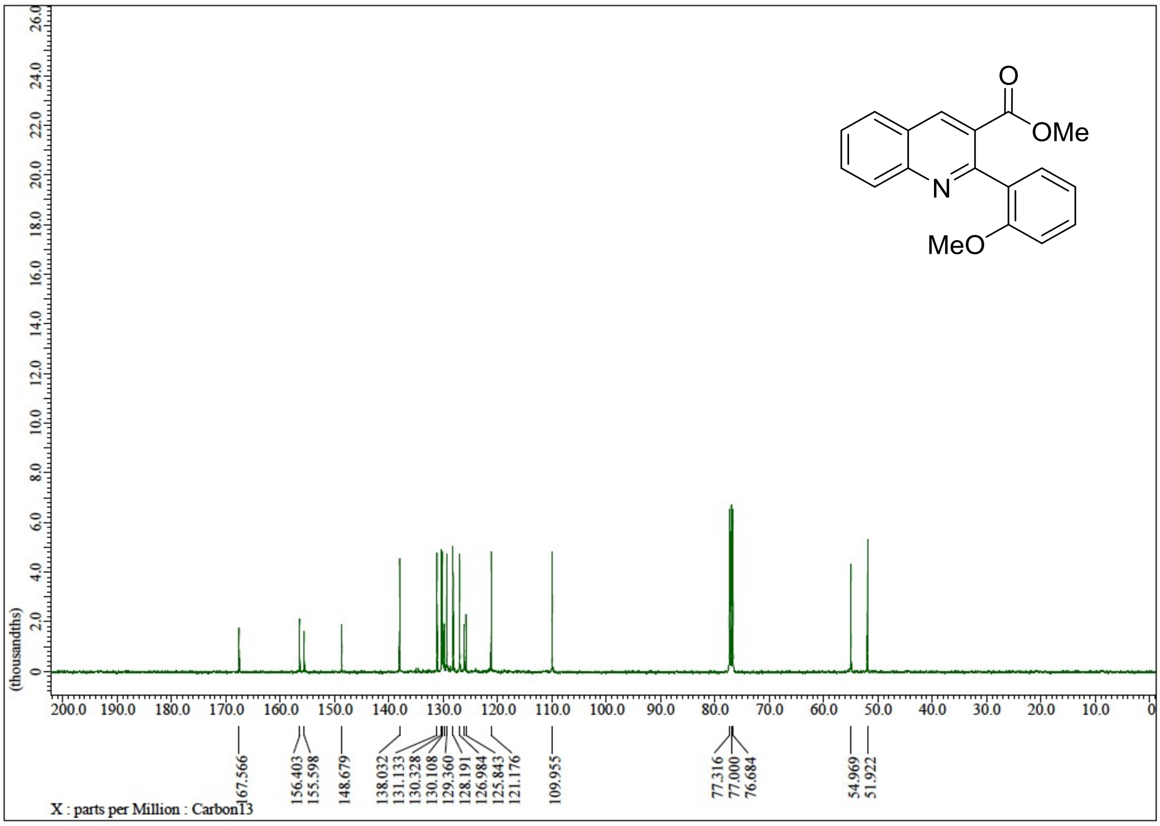
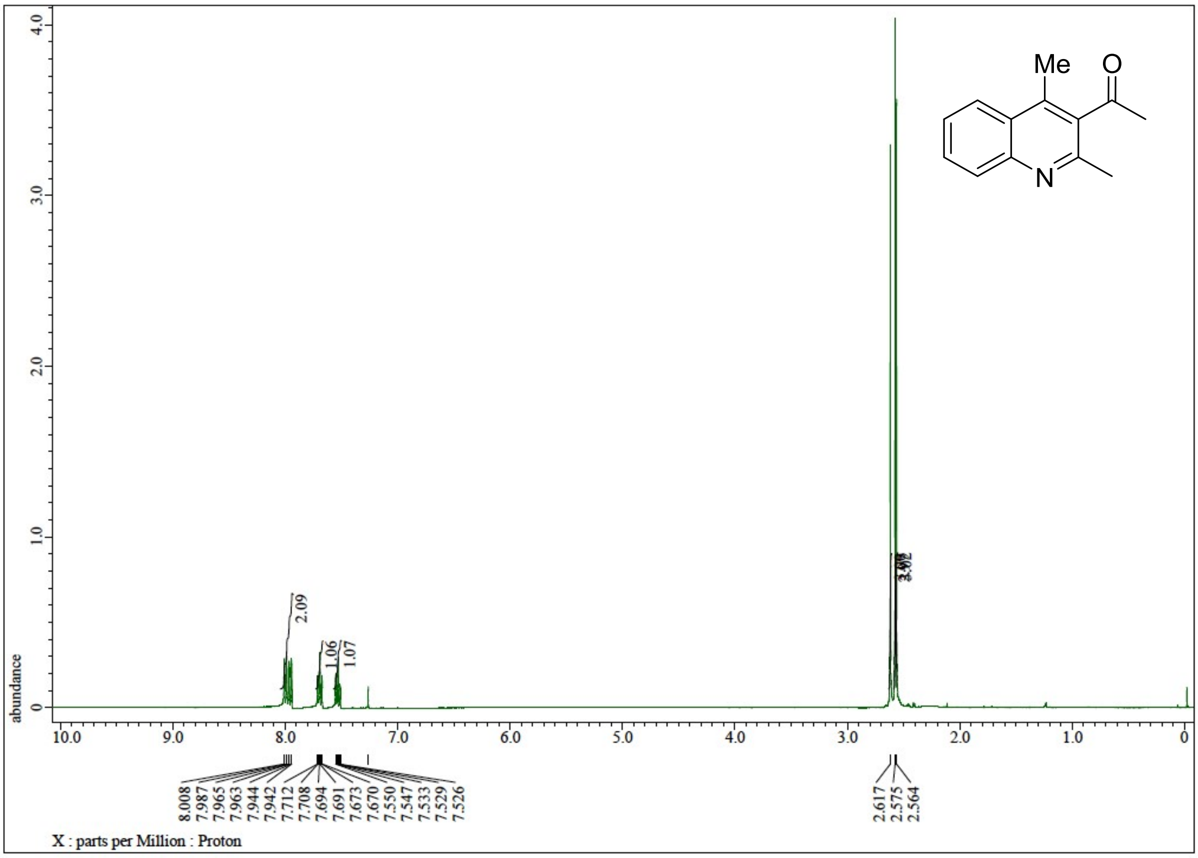


Figure S12. ^{1}H NMR of **3k** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3k** (100 MHz, $CDCl_3$)



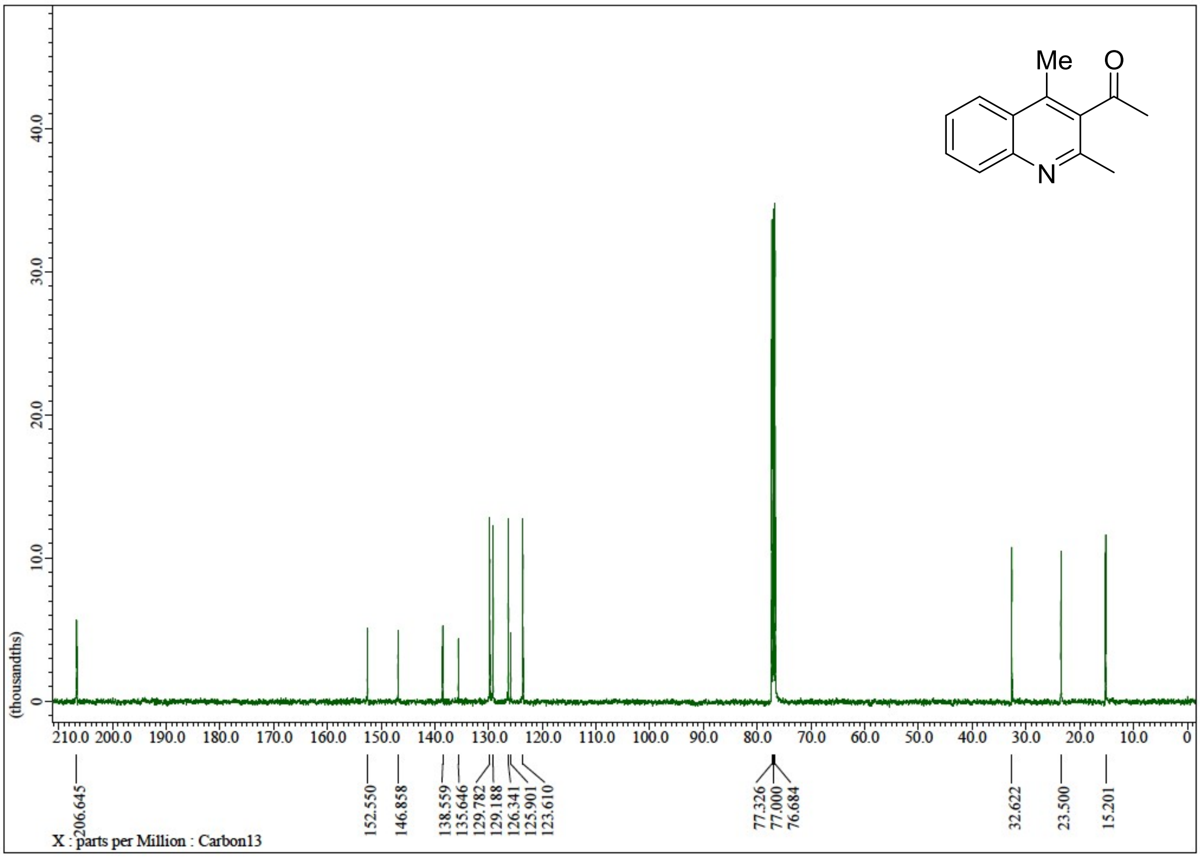
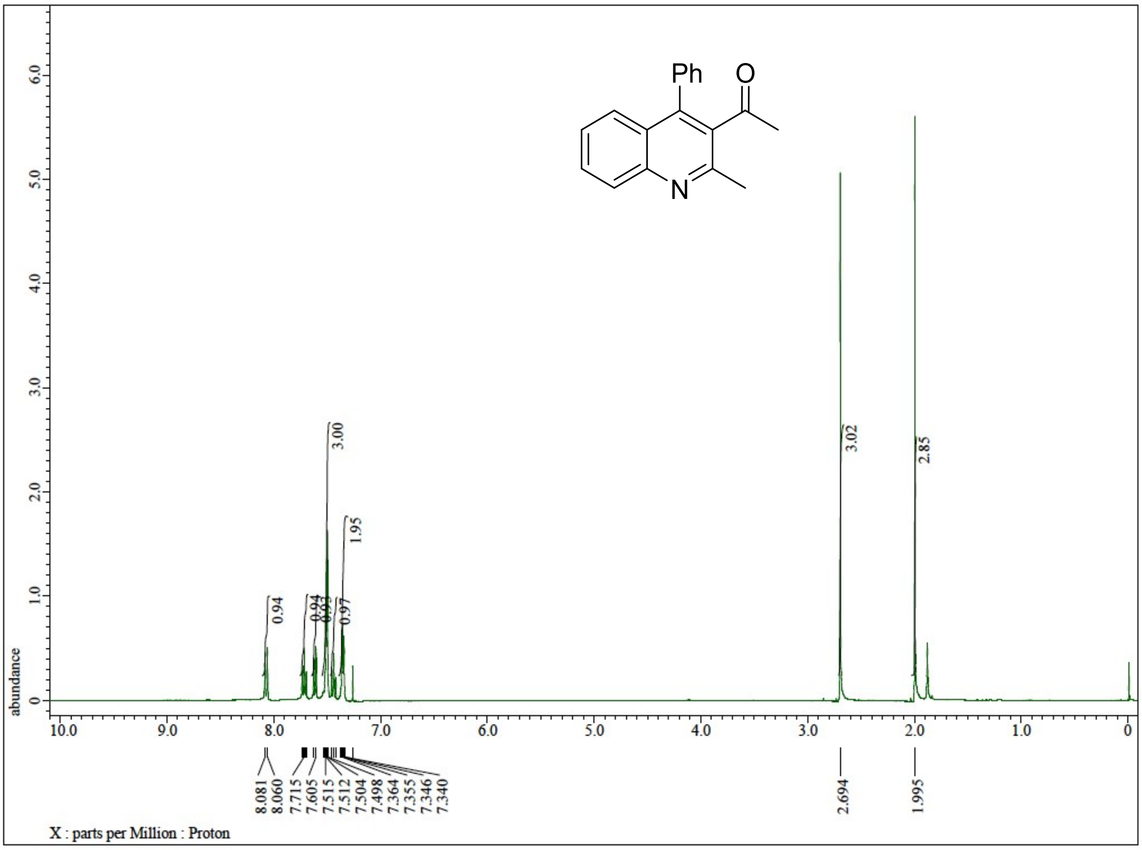


Figure S13. ^{1}H NMR of **3l** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



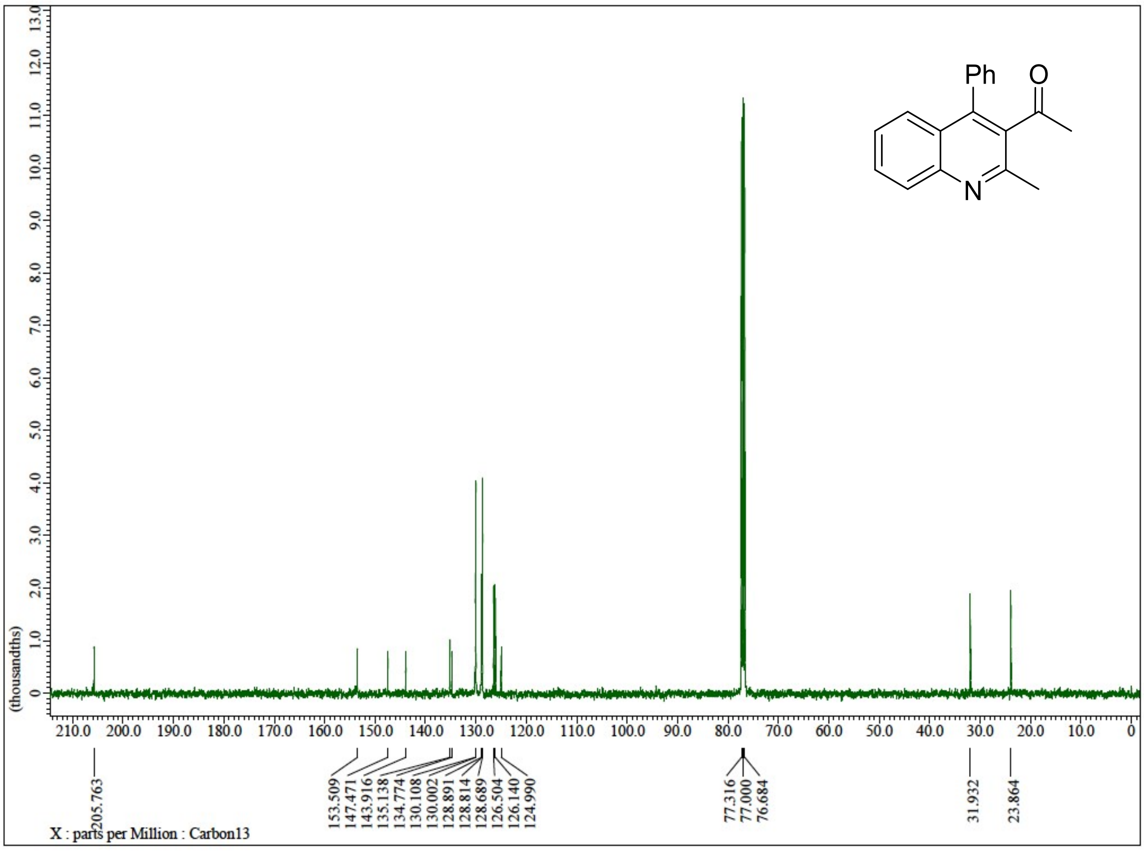


Figure S14. [1]H NMR of **3m** (400 MHz, $CDCl_3$) and [13]C NMR of **3m** (100 MHz, $CDCl_3$)

FTIR spectra of quinoline products

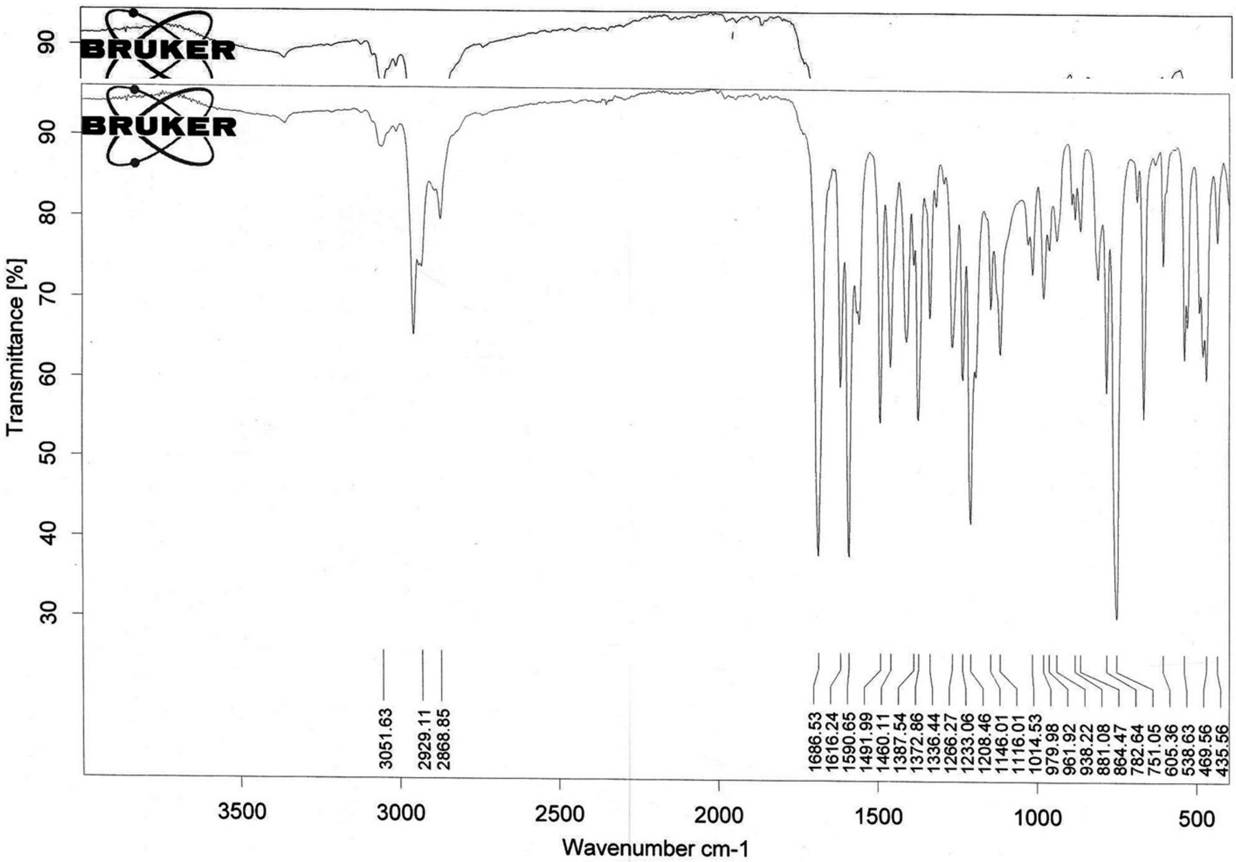


Figure S17. FTIR spectrum of **3a**

Figure S18. FTIR spectrum of **3b**

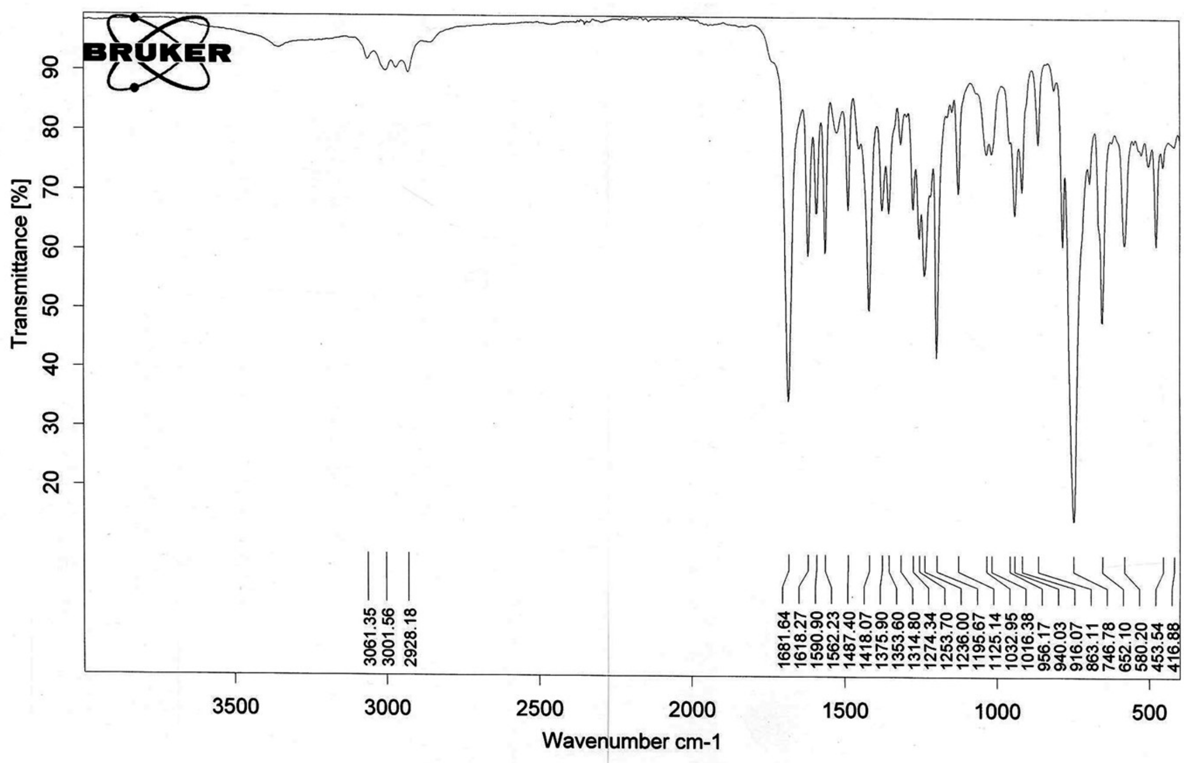


Figure S19. FTIR spectrum of **3c**

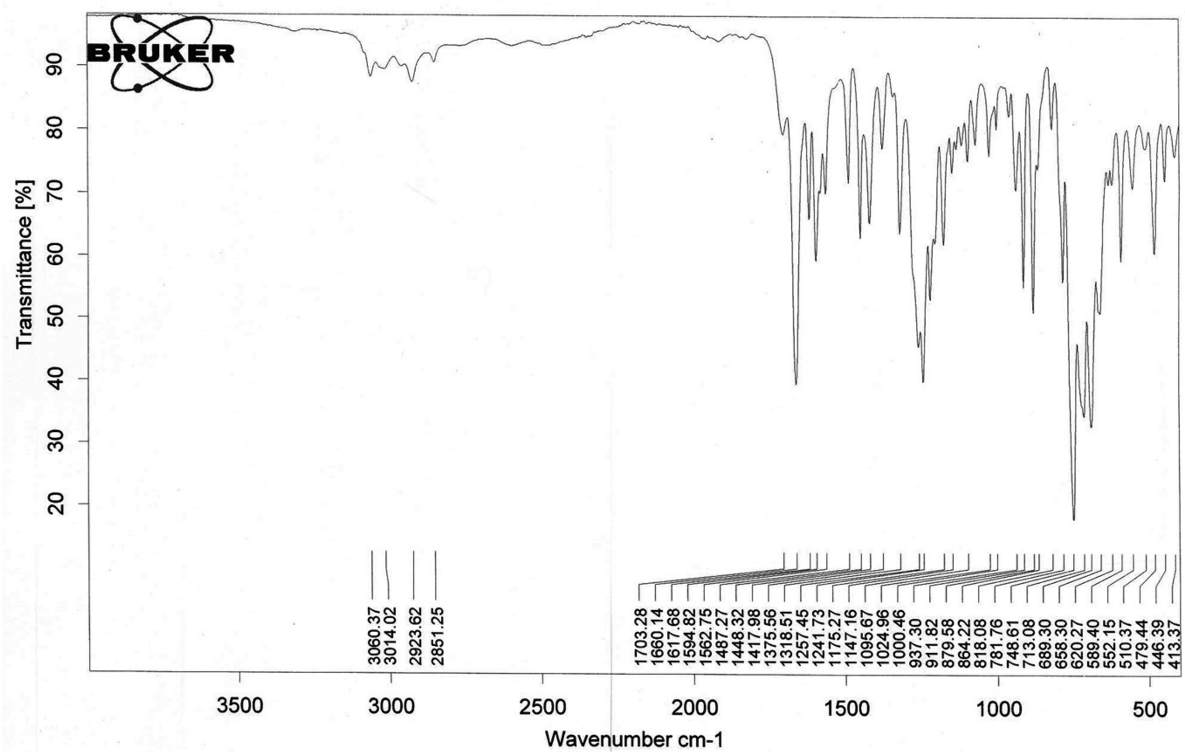


Figure S20. FTIR spectrum of **3d**

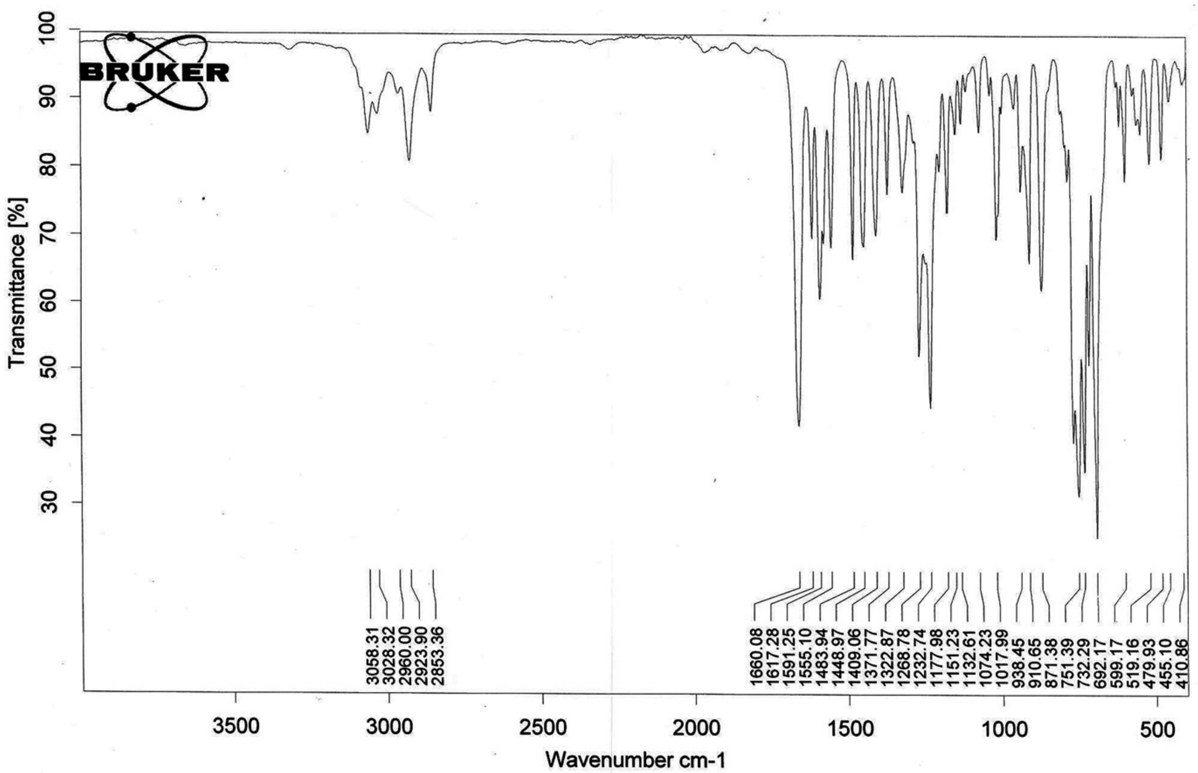


Figure S21. FTIR spectrum of **3e**

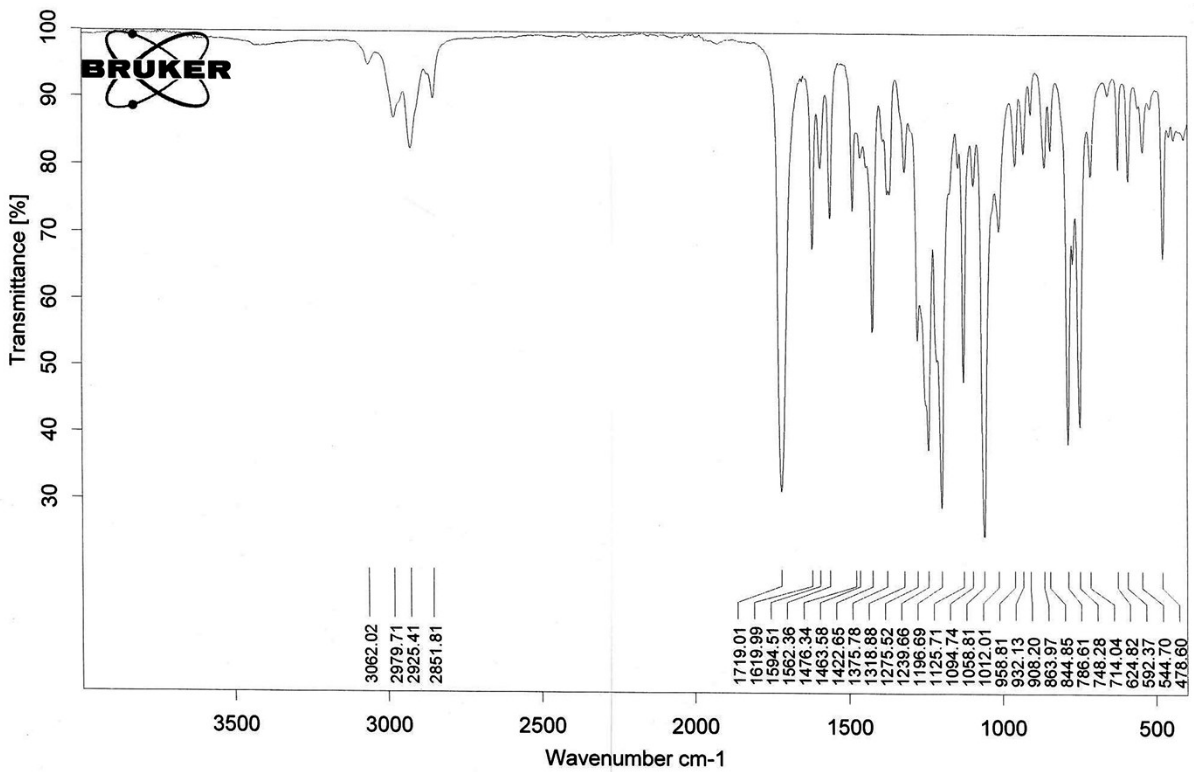


Figure S22. FTIR spectrum of **3f**

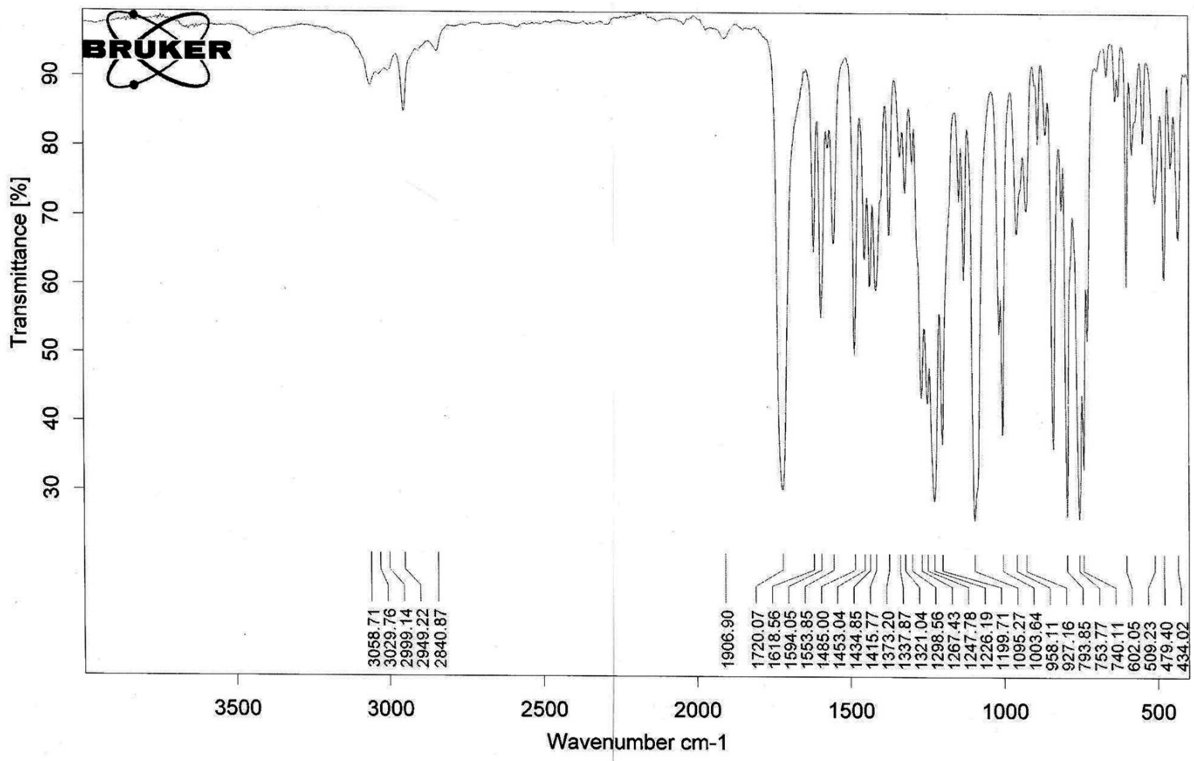


Figure S23. FTIR spectrum of **3g**

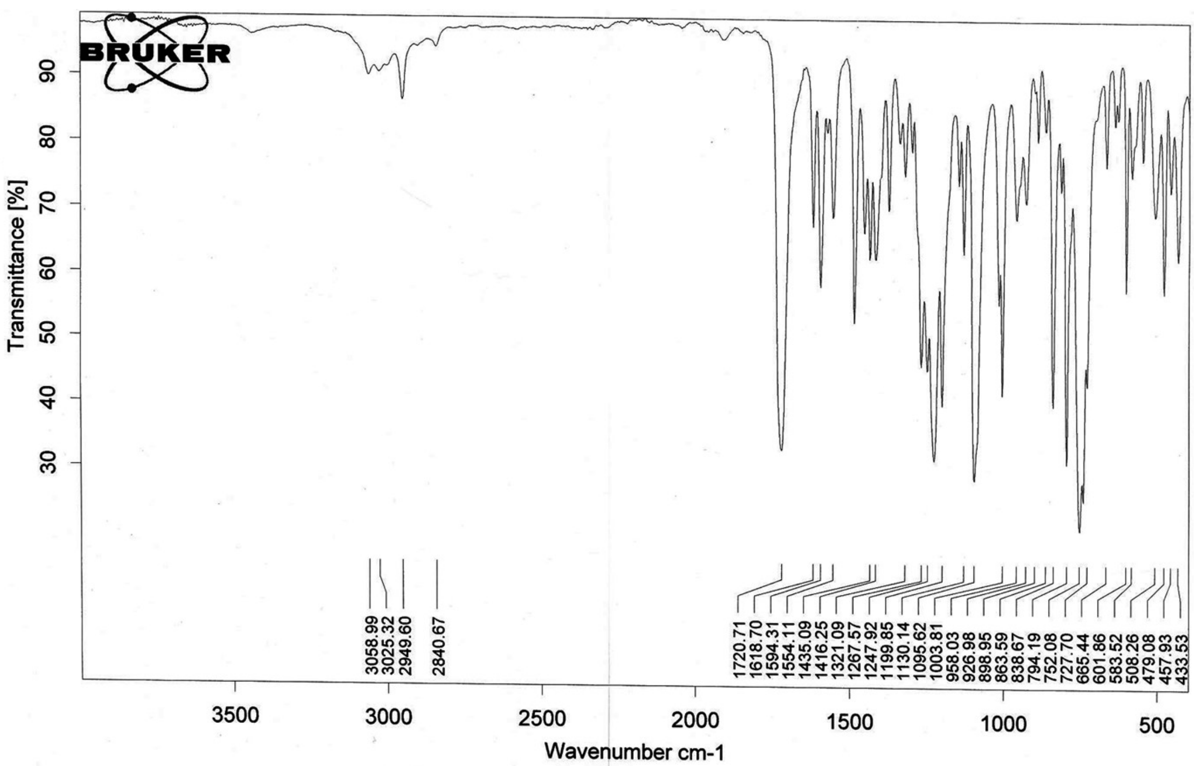


Figure S24. FTIR spectrum of **3h**

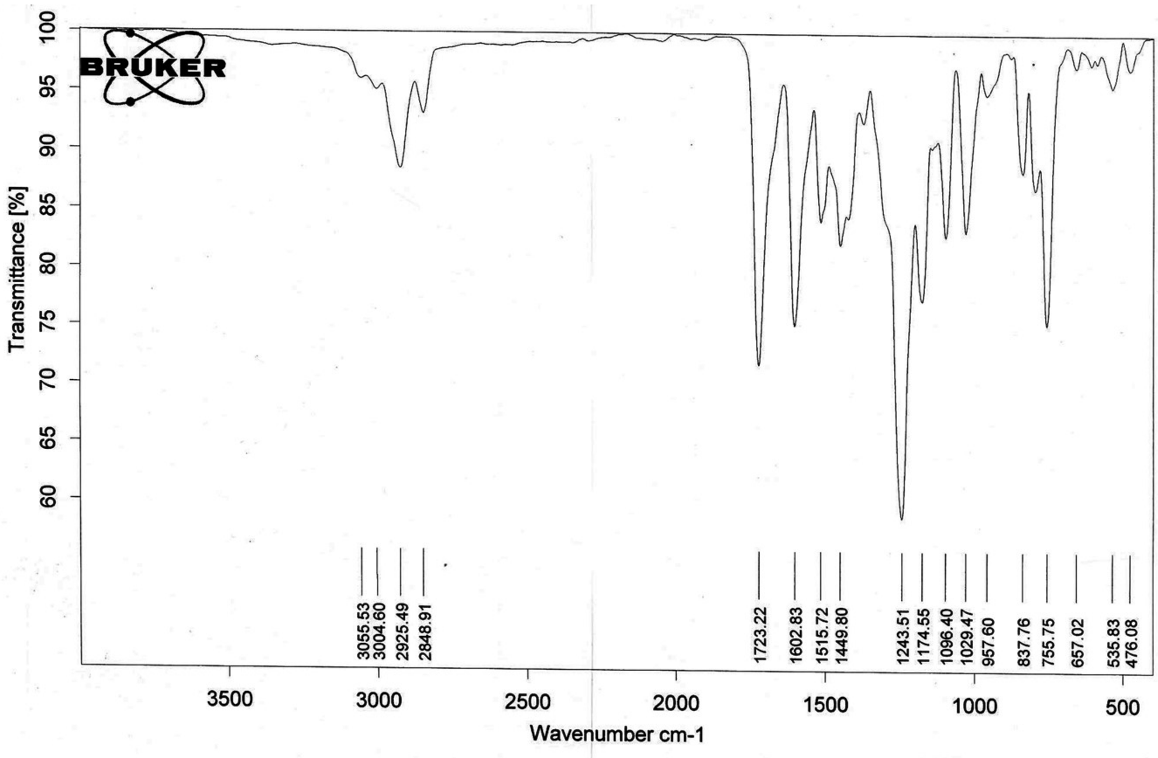


Figure S25. FTIR spectrum of **3i**

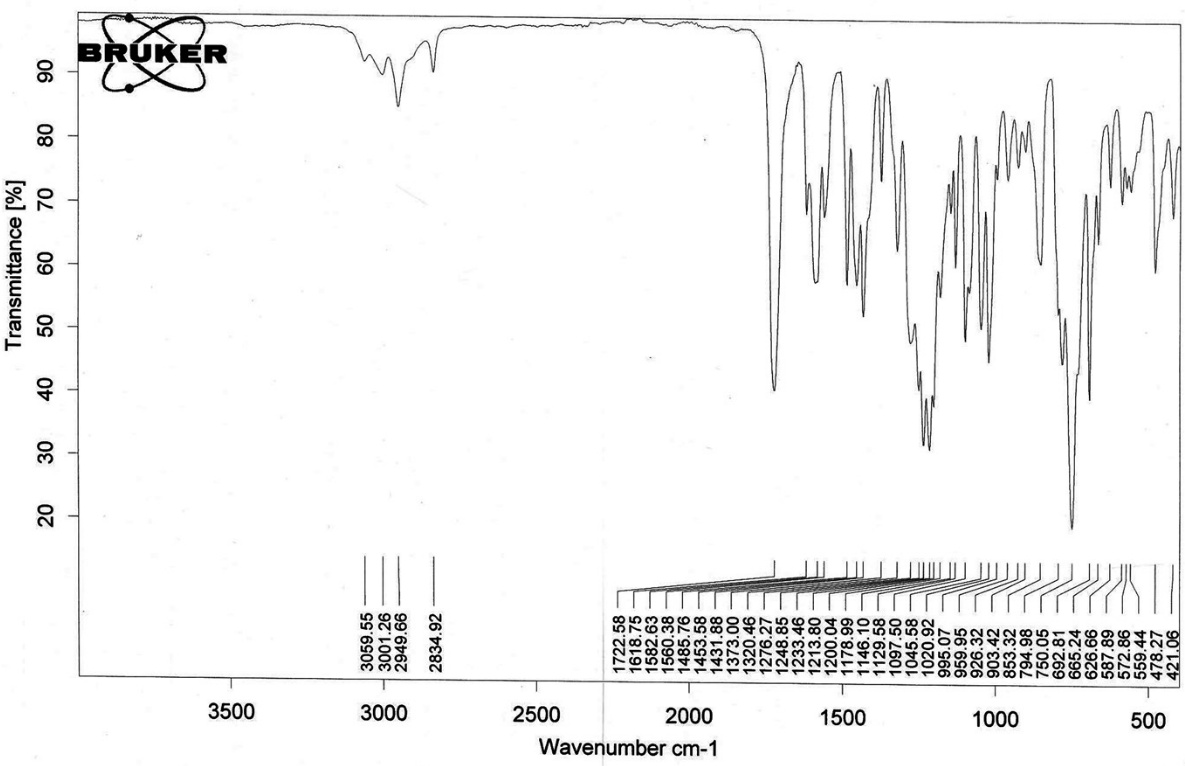


Figure S26. FTIR spectrum of **3j**

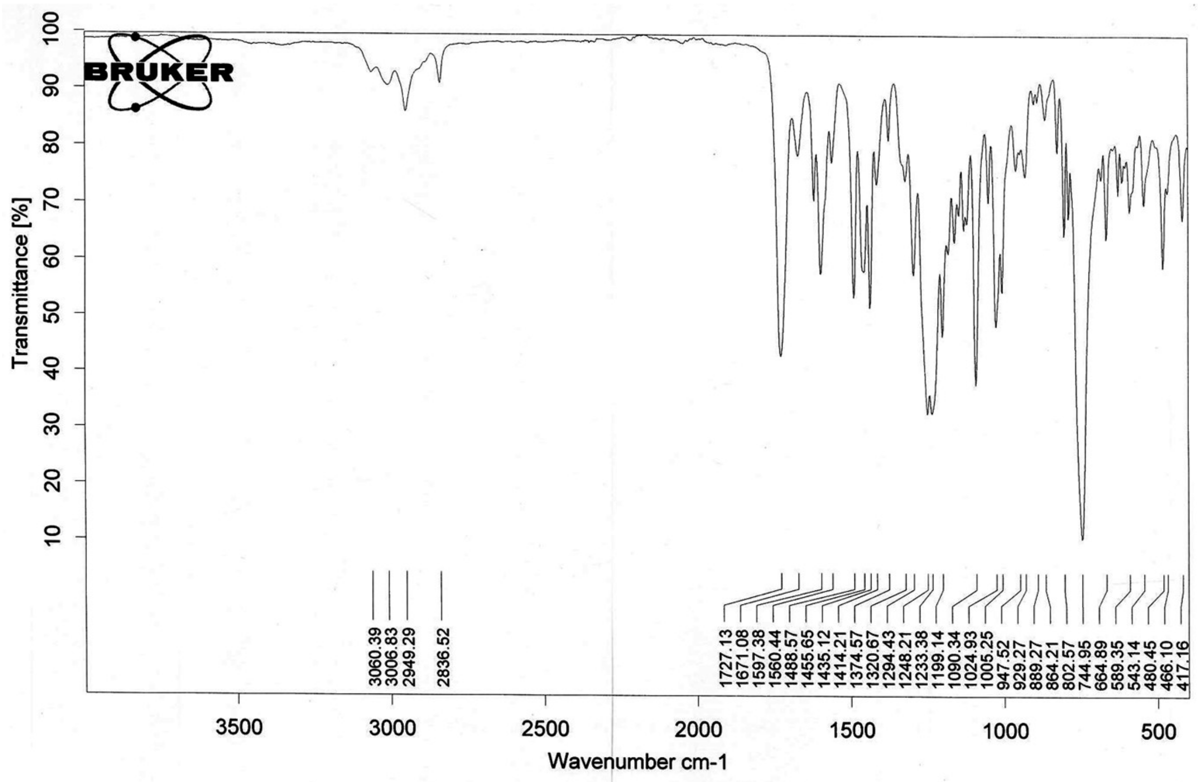


Figure S27. FTIR spectrum of **3k**

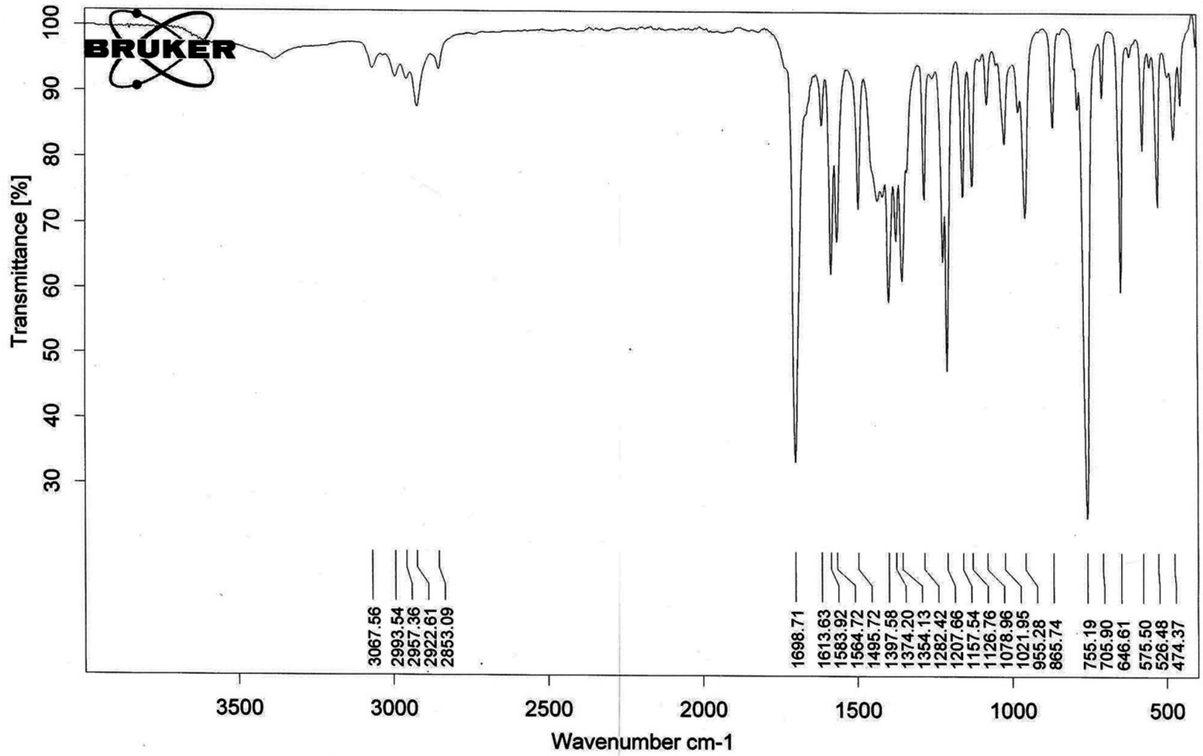


Figure S28. FTIR spectrum of **3l**

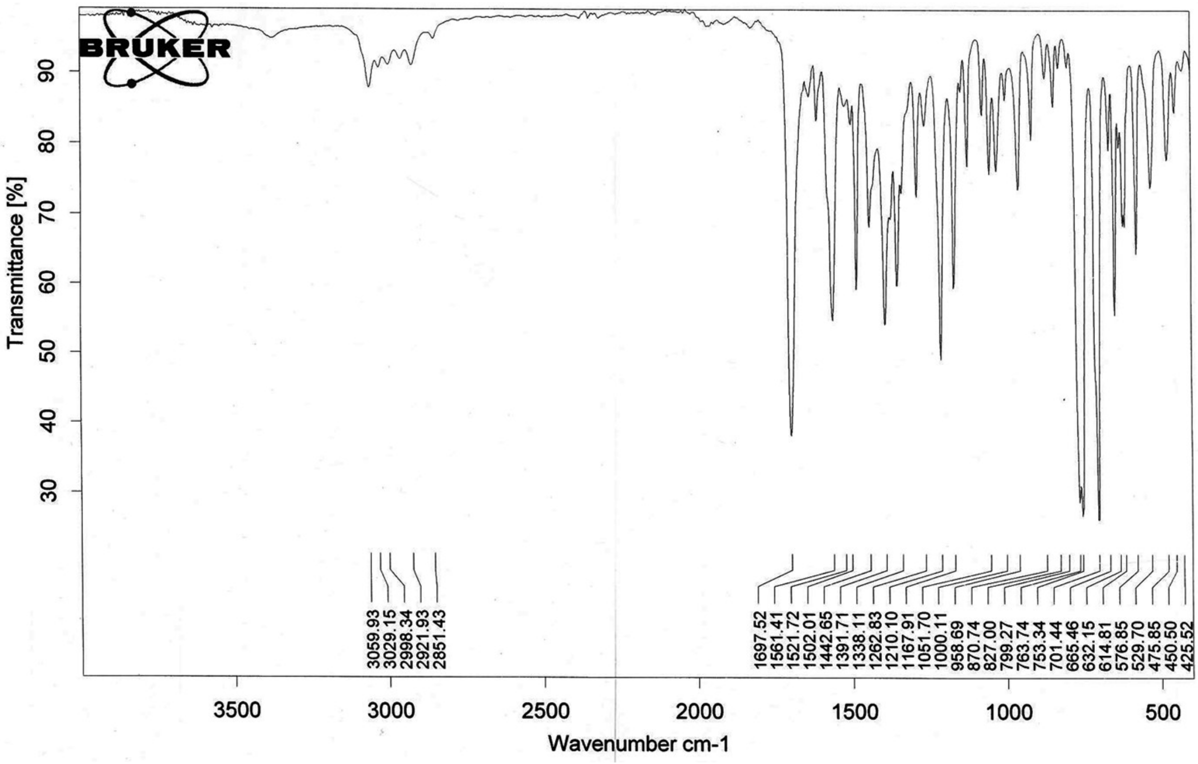


Figure S29. FTIR spectrum of **3m**