Cascade synthesis of 3-quinolinecarboxylic ester via benzylation propargylation-cyclization

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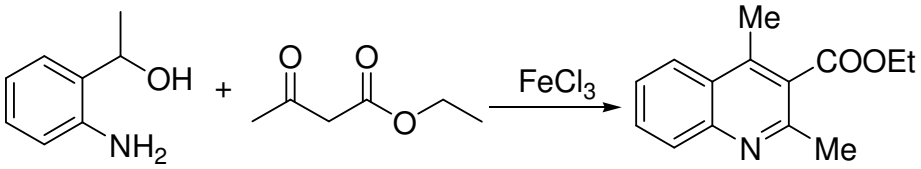
General Remarks: ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC-300 FT (^{1}H: 300 MHz, ^{13}C: 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer. Toluene and THF were distilled from sodium/benzophenone and stored over 4 Å molsieves in screw-cap flask. Chlorobenzene was predried over 4 Å molsieves and stored in screw-cap flasks. 4 Å molsieves was predried in oven at 250 °C for 48 h. All commercially available reagents were used as received.

1 Optimization of reaction conditions

Table S1 Reaction of 1-(2-aminophenyl)ethanol (1b) with ethyl 3-oxobutanoate (2a) [a]



1b **2a** **3ba**

Entry	Catalysts (10 mol%)	Solvent	Yield(%)[c]
1	—	CH_3NO_2	0
2	HOAc	CH_3NO_2	Trace
3	HCl	CH_3NO_2	Trace
4	*p*-TSA[b]	CH_3NO_2	12
5	TfOH	CH_3NO_2	Trace
6	$BF_3{\cdot}OEt_2$	CH_3NO_2	18
7	$InCl_3 \cdot 4H_2O$	CH_3NO_2	38
8	$FeCl_3$	CH_3NO_2	47
9	$CoCl_2$	CH_3NO_2	0
10	$NiCl_2$	CH_3NO_2	0
11	$Cu(OTf)_2$	CH_3NO_2	50
12	$ZrOCl_2$	CH_3NO_2	32
13	$La(OTf)_3$	CH_3NO_2	31
14	$BiCl_3$	CH_3NO_2	15
15	$Cu(OTf)_2$	EtOH	12
16	$Cu(OTf)_2$	CH_3CN	41
17	$Cu(OTf)_2$	DMF	N.D
18	$Cu(OTf)_2$	THF	N.D
19	$Cu(OTf)_2$	PhCl	55
20	$FeCl_3$	PhCl	58
21[d]	$FeCl_3$,$ZnCl_2$(100 mol%)	PhCl	64
22[d]	$FeCl_3$,$ZnCl_2$(20 mol%)	PhCl	46
23[d]	$FeCl_3$	PhCl	38
24[d]	$ZnCl_2$(100 mol%)	PhCl	22
25[d,i]	$FeCl_3$, $ZnCl_2$(100 mol%)	PhCl	75
26[d,e,i]	$FeCl_3$,$ZnCl_2$(100 mol%)	PhCl	32
27[d,f,i]	$FeCl_3$,$ZnCl_2$(100 mol%)	PhCl	Trace
28[d,g,i]	$FeCl_3$,$ZnCl_2$(100 mol%)	PhCl	40
29[d,h,i]	$FeCl_3$,$ZnCl_2$(100 mol%)	PhCl	78

[a] Reaction conditions: 1-(2-aminophenyl)ethanol (**1a**) (0.5 mmol), ethyl 3-oxobutanoate (**2a**) (2 mmol), 3 mL of solvents, 90 ℃, 10 h. [b] *p*-TSA = *p*-toluene sulfonic acid. [c] Isolated yield. [d] 6 h. [e] 50 ℃. [f] Room temperature. [g] **2a** (0.75 mmol). [h] **2a** (5 mmol). [i] 0.5 g of 4 Å MS.

2 General procedure

2.1 General procedure A for benzylation and cyclization

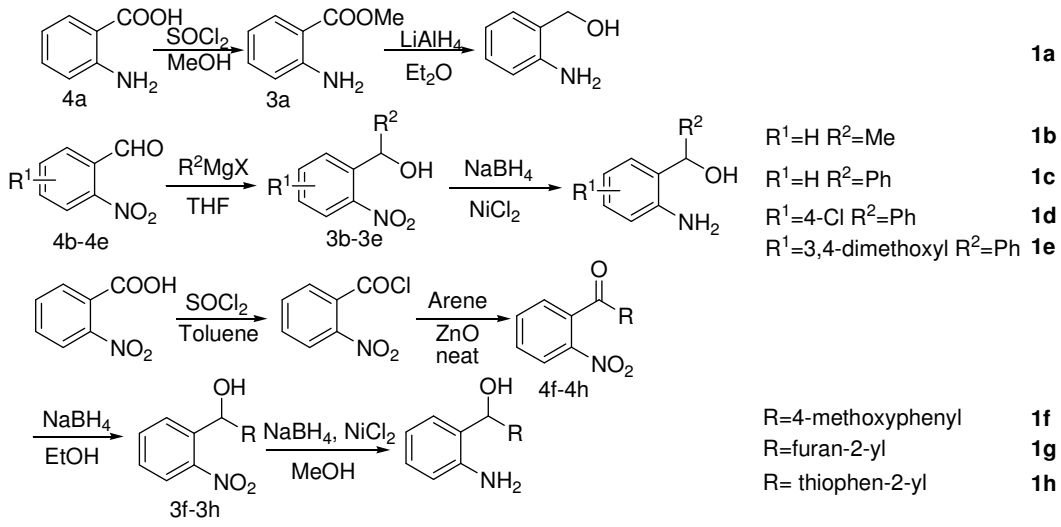
$FeCl_3$ (8.1 mg, 0.05 mmol), anhydrous $ZnCl_2$ (68.0 mg, 0.50 mmol) and 0.50 g of 4 Å MS were added to a solution of 1-(2-aminophenyl)ethanol **1b** (68.5 mg, 0.5 mmol) and ethyl 3-oxobutanoate **2a** (260.0 mg, 2.0 mmol) in freshly distilled PhCl (1.5 mL). The resulting mixture was stirred at 90 ˚C for 12 h in the atmosphere of air. The reaction mixture was then cooled to room temperature and quenched with saturated $NaHCO_3$, and the mixture was extracted with ethyl acetate. The combined organic extracts were washed with water and saturated brine, dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **3b** (97.3 mg, 85%).

2.2 General procedure B for propargylation and cyclization

$FeCl_3$ (8.1 mg, 0.05 mmol) and 0.50 g of 4 Å MS were added to a solution of 1-(2-nitrophenyl)-3-phenylprop-2-yn-1-ol **1j** (126.5 mg, 0.5 mmol) and ethyl 3-oxobutanoate **2a** (260.0 mg, 2.0 mmol) in freshly distilled PhCl (1.5 mL). The mixture was stirred at 70 ˚C for 4 h. Then $SnCl_2{\cdot}2H_2O$ (337.5 mg, 1.50 mmol) was added and the result mixture was stirred at 70 ˚C for another 6 h. After Cooled to room temperature, the system was rendered basic (pH 8) with 10% aqueous $NaHCO_3$, then transferred to a separatory funnel, and extracted with ethyl acetate. The combined organic extracts were washed with water and saturated brine, dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **4a** (108.7 mg, 69%).

3 Preparation of Precursors

3.1 Preparation of Precursors for benzylation and cyclization (*Scheme 1*)



Scheme S1 Synthesis of substrates **1a-1h**

Procedure for preparation of substrates 1a-1h:

3.1.1 Synthesis of 1a (2-aminophenyl)methanol was according to literature[1]

3.1.2 General procedure C for synthesis of 1b-1e: synthesis of (2-aminophenyl)-(phenyl)methanol (1c)

Step1: 2-Nitrobenzaldehyde (5 mmol), was dissolved in anhydrous tetrahydrofuran (25 mL) and the solution was cooled to –78°C. Phenylmagnesium bromide (1M solution in THF, 5 mL) was added to the stirred solution by syringe during 10 minutes. After 10 minutes at -78°C the mixture was stirred at -15 °C for 15 minutes. Saturated NH_4Cl was added dropwise followed by evaporated THF in vacuo. Then the resulting solution was extracted with dichliromethane (50 mL × 2). The combined organic extracts were dried with anhydrous sodium sulphate and concentrated in vacuo. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1) to give **3c** (2-nitrophenyl)(phenyl)methanol as a yellow oil.

Step 2: To a stirred solution of (2-nitrophenyl)(phenyl)methanol and $NiCl_2{\cdot}6H_2O$ (1.0 equiv) in EtOH was added $NaBH_4$ (10 equiv) at 0 °C. The reaction was stirred at 0 °C for 2 h. The solution was extracted with EtOAc twice, dried with sodium sulphate and concentrated in vacuo to afford **1c** (2-aminophenyl)(phenyl)methanol as a light orange solid, which was used directly without further purification.

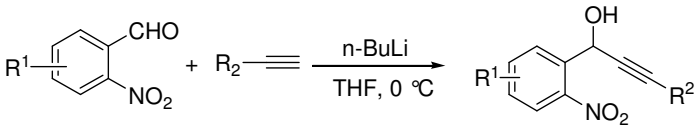
3.1.3 General procedure D for synthesis of 1f-1h: synthesis of (2-aminophenyl)(4-methoxyphenyl)methanol (1f)

Compound **4f-4h** was synthesis according to literature[2]

$NaBH_4$ (228 mg, 6.0 mmol) was added dropwise over 0.5 h to a solution of **4f** (515 mg, 2.0 mmol) in a mixture solution (MeOH/dioxane = 3:2, 10 mL) at 0 °C. The resulting mixture was stirred at room temperature for 3 h. Then $NiCl_2{\cdot}6H_2O$ (2.0 mmol) was to the solution, after 10 minutes, $NaBH_4$ (760 mg, 20.0 mmol) was added at 0 °C. The reaction was stirred at 0 °C for 2 h before quenched with water. After evaporated MeOH in vacuo, the solution was extracted with EtOAc (40 mL × 2), dried with sodium sulphate and concentrated in vacuo. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (1:1) to give **1f** (2-aminophenyl)(4-methoxyphenyl)methanol (361 mg, 79% yield over the two steps) as a yellow solid.

3.1.4 1i (2-aminopyridin-3-yl)(phenyl)methanol was synthesized using 2-aminonicotinaldehyde and 5 equiv of phenylmagnesium bromide at room temperature according to the synthetic procedure of **3b**-**3e**.

3.2 Preparation of precursors for propargylation and cyclization (*Scheme 2*)



R^1=H R^2=Ph **1j**

R^1=4-Cl R^2=Ph **1k**

R^1=H R^2=n-Bu **1l**

R^1=H R^2=4-methoxyphenyl **1m**

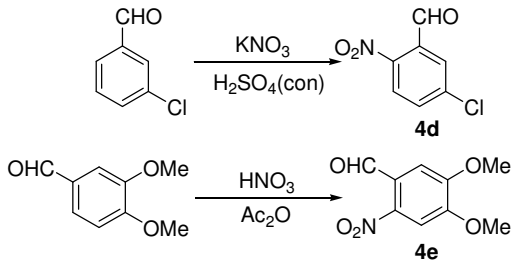
R^1=H R^2=TMS **1n**

Scheme S2 synthesis of substrates **1j**-**1n**

General procedure E for synthesis of 1j-1n: synthesis of 1-(2-nitrophenyl)-3-phenylprop-2-yn-1-ol (1j)

A solution of 357 mg (3.5 mmol) of ethynylbenzene in 5 mL of anhydrous THF was cooled to 0 °C, and 1.3 mL (3.2 mmol) of 2.5 M n-butyl lithium was added dropwise. The resulting solution was stirred for 30 min at 0 °C, and then 302 mg (2.0 mmol) of *o*-nitrobenzaldehyde dissolved in 2 mL of anhydrous THF was added dropwise via cannula. The mixture was stirred at 0 °C for a subsequent 60 min, then quenched with water. THF was removed in vacuo, and the residue was extracted with EtOAc (25 mL × 2), dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel eluting with chloroform to give **1j** 1-(2-nitrophenyl)-3-phenylprop-2-yn-1-ol as a pale red oil

Synthesis of 4d[3], 4e[4] (*Scheme 3*)



Scheme S3 synthesis of **4d**, **4e**

1 B. B. Snider, Y. Ahn, S. M. O'Hare, *Org. Lett.* **2001**, *3*, 4217-4220.

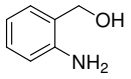
2. M. H. Sarvari, H. Sharghi, *J. Org. Chem*. **2004**, *69*, 6953-6956.

3. F. Benington, R. D. Morin, L. C. Clark. Jr. J. Org. Chem. 1960, 25, 1542-1547.

4. W. Guo, Q.-J. Jiang, F. Lu, D.-Q. Yang, Chinese Journal of Synthetic Chemistry. 2005, 27, 415-416.

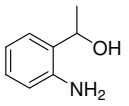
4 ^{1}H-NMR data for substrates 1a-1n

(2-aminophenyl)methanol (1a)



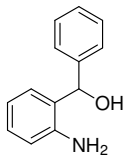
Literature[1] was followed using 2-aminobenzoic acid. The title compound was a light brown solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.16-7.07 (m, 2 H), 6.76-6.71 (m, 2 H), 4.68 (s, 2 H), 3.11 (br, 3 H).

1-(2-aminophenyl)ethanol (1b)



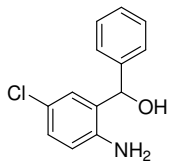
General procedure C was followed using 2-nitrobenzaldehyde. The title compound was a light yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.11-7.07 (m, 2 H), 6.75-6.66 (m, 2 H), 4.93 (q, J = 6.6 Hz, 1 H), 3.34 (br, 3 H), 1.59 (d, J = 6.6 Hz, 3 H).

(2-aminophenyl)(phenyl)methanol (1c)



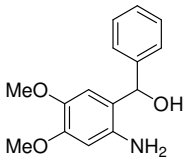
The title compound was a light yellow solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.40-7.28 (m, 5 H), 7.14-7.09 (m, 1 H), 7.02 (d, J = 7.2 Hz, 1 H), 6.77-6.66 (m, 2 H), 5.85 (s, 1 H), 3.30 (br, 3 H).

(2-amino-5-chlorophenyl)(phenyl)methanol (1d)



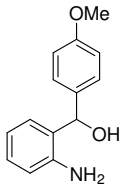
General procedure C was followed using 5-chloro-2-nitrobenzaldehyde. The title compound was a light brown solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.39-7.32 (m, 5 H), 7.09-7.06 (m, 2 H), 6.59 (d, J = 8.1 Hz, 1 H), 5.79 (s, 1 H), 3.39 (br, 3 H).

(2-amino-4,5-dimethoxyphenyl)(phenyl)methanol (1e)



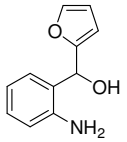
General procedure C was followed using 4,5-dimethoxy-2-nitrobenzaldehyde. The title compound was a brown solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.36-7.28 (m, 5 H), 6.62 (s, 1 H), 6.26 (s, 1 H), 5.78 (s, 1 H), 3.80 (s, 3 H), 3.72 (s, 1 H), 3.07 (br, 3 H).

(2-aminophenyl)(4-methoxyphenyl)methanol (1f)



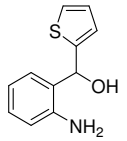
The title compound was a brown solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30-7.24 (m, 2 H), 7.11-7.03 (m, 2 H), 6.89-6.86 (m, 2 H), 6.74-6.66 (m, 2 H), 5.81 (s, 1 H), 3.79 (s, 3 H), 3.30 (br, 3 H).

(2-aminophenyl)(furan-2-yl)methanol (1g)



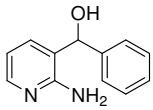
General procedure D was followed using 2-aminobenzoic acid. The title compound was a brown oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.42-7.30 (m, 1 H), 7.16-7.06 (m, 2 H), 6.78-6.66 (m, 2 H), 6.40-6.35 (m, 1 H), 6.23 (d, J = 2.7 Hz, 1 H), 5.84 (s, 1 H), 3.45 (br, 3 H).

(2-aminophenyl)(thiophen-2-yl)methanol (1h)



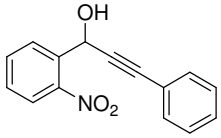
General procedure D was followed using 2-aminobenzoic acid. The title compound was a light black solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.28-7.25 (m, 1 H), 7.17-7.12 (m, 2 H), 6.97-6.80 (m, 2 H), 6.80-6.75 (m, 1 H), 6.70-6.67 (d, J = 7.8 Hz, 1 H), 6.02 (s, 1 H), 3.58 (br, 3 H).

(2-aminopyridin-3-yl)(phenyl)methanol (1i)



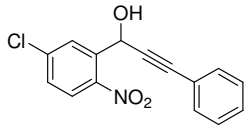
General procedure C was followed using 2-aminonicotinaldehyde. The title compound was a brown oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.77 (d, J = 3.6 Hz, 1 H). 7.33-7.30 (m, 5 H), 7.17 (d, J = 6.6 Hz, 1 H), 6.53 (dd, J = 6.8, 5.1 Hz, 1 H), 5.71 (s, 1 H), 4.89 (br, 2 H), 4.30 (br, 1 H).

1-(2-nitrophenyl)-3-phenylprop-2-yn-1-ol (1j)



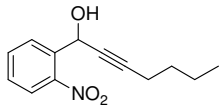
The title compound was a pale red oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.02-7.97 (m, 2 H), 7.71-7.66 (m, 1 H), 7.54-7.49 (m, 1 H), 7.46-7.44 (m, 2 H), 7.42-7.32 (m, 3 H), 6.21 (s, 1 H), 3.23 (br, 1 H).

1-(5-chloro-2-nitrophenyl)-3-phenylprop-2-yn-1-ol (1k)



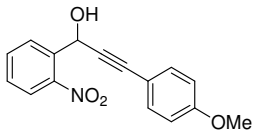
General procedure E was followed using 5-chloro-2-nitrobenzaldehyde and ethynylbenzene. The title compound was a light brown solid. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.99-7.94 (m, 2 H), 7.46-7.40 (m, 3 H), 7.38-7.30 (m, 3 H), 6.23 (s, 1 H), 3.10 (br, 1 H).

1-(2-nitrophenyl)hept-2-yn-1-ol (1l)



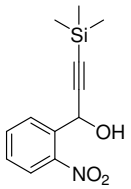
General procedure E was followed using 2-nitrobenzaldehyde and 1-hexyne. The title compound was a dark red oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.95-7.93 (m, 2 H), 7.69-7.64 (m, 1 H), 7.51-7.46 (m, 1 H), 5.97 (s, 1 H), 3.11 (br, 1 H), 2.27-2.22 (m, 2 H), 1.55-1.46 (m, 2 H), 1.43-1.36 (m, 2 H), 0.91 (t, J = 7.2 Hz, 3 H).

3-(4-methoxyphenyl)-1-(2-nitrophenyl)prop-2-yn-1-ol (1m)



General procedure E was followed using 2-nitrobenzaldehyde and 1-ethynyl-4-methoxybenzene. The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.01-7.96 (m, 2 H), 7.71-7.65 (m, 1 H), 7.53-7.50 (m, 1 H), 7.38 (d, J = 8.7 Hz, 2 H), 6.83 (d, J = 8.7 Hz, 2 H), 6.19 (d, J = 4.5 Hz, 1 H), 3.80 (s, 3 H), 3.27 (s, 1 H).

1-(2-nitrophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1n)

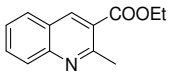


General procedure E was followed using 2-nitrobenzaldehyde and ethynyltrimethylsilane. The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.96-7.92 (m, 2 H), 7.67 (m, 1 H), 7.53 (m, 1 H), 5.97 (s, 1 H), 3.20 (br, 1 H), 0.18 (s, 9 H).

5 Characterization data for the products

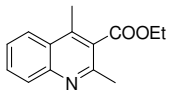
5.1 Characterization data for the products via benzylation and cyclization

ethyl 2-methylquinoline-3-carboxylate (3a)



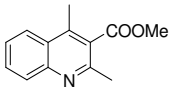
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.73 (s, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 1 H), 7.80-7.75 (m, 1 H), 7.56-7.51 (m, 1 H), 4.44 (q, J = 7.2 Hz, 2 H), 2.30 (s, 3 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 166.7, 158.6, 148.7, 140.1, 131.8, 128.6, 126.7, 125.9, 124.2, 61.6, 25.7, 14.5; IR (liquid film, cm^{-1}): v = 2971, 2928, 2540, 2413, 2253, 2134, 1925, 1727, 1621, 1596, 1565, 1425, 1378, 1320, 1246, 1202, 1128, 1060, 882, 790, 751; HRMS calc. $C_{13}H_{13}NO_2$ (M^+): 215.0946. Found: 215.0937.

ethyl 2,4-dimethylquinoline-3-carboxylate (3b)



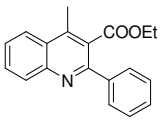
Yellow oil .^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.03-7.97 (m, 2 H), 7.73-7.68 (m, 1 H), 7.56-7.51 (m, 1 H), 4.48 (q, J = 7.2 Hz, 2 H), 2.70 (s, 3 H), 2.65 (s, 3 H), 1.45-1.41 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 169.3, 154.5, 147.1, 141.7, 130.2, 129.3, 128.1, 126.5, 126.0, 124.1, 61.8, 23.8, 15.8, 14.4; IR (liquid film, cm^{-1}): v = 3068, 2959, 1951, 1726, 1614, 1589, 1566, 1498, 1446, 1403, 1337, 1341, 1287, 1233, 1162, 1129, 1081, 1056, 852, 758, 645; HRMS calc. $C_{14}H_{15}NO_2$ (M^+): 229.1103. Found: 229.1114.

methyl 2,4-dimethylquinoline-3-carboxylate (3c)



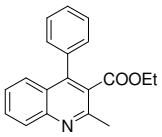
Yellow oil .^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.02-7.99 (m, 2 H), 7.73-7.70 (m, 1 H), 7.55-7.53 (m, 1 H), 4.02 (s, 3 H), 2.68 (s, 3 H), 2.63 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 169.8, 154.5, 147.3, 141.8, 130.2, 129.4, 127.9, 126.5, 125.9, 124.1, 52.6, 23.9, 15.9; IR (liquid film, cm^{-1}): v = 3068, 2952, 1927, 1729, 1614, 1589, 1566, 1498, 1437, 1400, 1343, 1298, 1235, 1161, 1130, 1081, 1058, 951, 867, 836, 786, 647; HRMS calc. $C_{13}H_{13}NO_2$ (M^+): 215.0946. Found: 215.0933.

ethyl 4-methyl-2-phenylquinoline-3-carboxylate (3d)



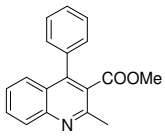
Yellow oil .^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.17 (d, J = 8.1 Hz, 1 H), 8.06 (d, J = 8.1 Hz, 1 H), 7.77-7.68 (m, 3 H), 7.61-7.58 (m, 1 H), 7.46-7.44 (m, 3 H), 4.16 (q, J = 7.2 Hz, 2 H), 2.75 (s, 3 H), 1.01 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 169.1, 156.3, 147.3, 142.8,140.7, 130.3, 128.7, 128.4, 127.5, 127.0, 126.1, 124.1, 61.6, 15.7, 13.7; IR (liquid film, cm^{-1}): v = 3064, 2980, 1958, 1725, 1615, 1579, 1558, 1495, 1447, 1400, 1350, 1292, 1233, 1166, 1112, 1055, 1023, 914, 841, 763, 733, 698; HRMS calc. $C_{19}H_{17}NO_2$ (M^+): 291.1259. Found: 291.1267.

ethyl 2-methyl-4-phenylquinoline-3-carboxylate (3e)



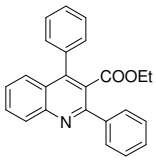
Pale yellow solid, mp: 97-98°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.08 (d, J = 8.4 Hz, 1 H), 7.76-7.70 (m, 1 H), 7.57 (d, J = 8.1 Hz, 1 H), 7.48-7.43 (m, 3 H), 7.41-7.35 (m, 3 H), 4.06 (q, J = 7.2 Hz, 2 H), 2.79 (s, 3 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.5, 154.7, 147.8, 146.3, 135.8, 130.3, 129.5, 128.9, 128.5, 128.3, 127.5, 126.54, 126.47, 125.2, 61.4, 23.9, 14.4; IR (liquid film, cm^{-1}): ν = 3062, 2982, 1956, 1726, 1646, 1613, 1567, 1486, 1444, 1400, 1295, 1229, 1178, 1124, 1066, 914, 862, 766, 735, 703, 602; HRMS calc. $C_{19}H_{17}NO_2$ (M^+): 291.1259. Found: 291.1252.

methyl 2-methyl-4-phenylquinoline-3-carboxylate (3f)



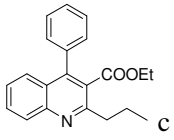
Pale yellow solid, mp: 95-96°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.06 (d, J = 8.4 Hz, 1 H), 7.70-7.60 (m, 1 H), 7.57 (d, J = 8.1 Hz, 1 H), 7.45-7.37 (m, 4 H), 7.35-7.33 (m, 2 H), 3.56 (s, 3 H), 2.77 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 169.0, 154.6, 147.8, 146.5, 135.8, 130.4, 129.3, 129.0, 128.6, 128.3, 127.4, 126.6, 126.5, 125.1, 52.2, 23.9; IR (liquid film, cm^{-1}): ν = 3062, 2951, 1959, 1730, 1647, 1612, 1568, 1487, 1438, 1397, 1296, 1231, 1174, 1126, 1068, 964, 917, 869, 767, 736, 704, 602; HRMS calc. $C_{18}H_{15}NO_2$ (M^+): 277.1103. Found: 277.1108.

ethyl 2,4-diphenylquinoline-3-carboxylate (3g)



Pale yellow solid, mp: 105-107°C ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.25 (d, J = 8.1 Hz, 1 H), 7.77-7.76 (m, 3 H), 7.63 (d, J = 8.1 Hz, 1 H), 7.51-7.42 (m, 9 H), 3.89 (q, J = 7.2 Hz, 2 H), 0.83 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.3, 156.1, 147.9, 147.3, 140.3, 135.7, 130.6, 129.9, 129.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.3, 127.2, 126.7, 125.7, 61.4, 13.5; IR (liquid film, cm^{-1}): ν = 3062, 2930, 1958, 1729, 1611, 1567, 1553, 1485, 1445, 1399, 1349, 1298, 1230, 1156, 1106, 911, 766, 732, 700, 602; HRMS calc. $C_{24}H_{19}NO_2$ (M^+): 353.1416. Found: 353.1408.

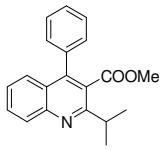
ethyl 4-phenyl-2-propylquinoline-3-carboxylate (3h)



Pale yellow solid, mp: 83-84°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.10 (d, J = 8.4 Hz, 1 H), 7.72-7.67 (m, 1 H), 7.57 (d, J = 8.4 Hz, 1 H), 7.47-7.42 (m, 3 H), 7.40-7.35 (m, 3 H), 4.04 (q, J = 7.2 Hz, 2 H), 3.01 (t, J = 7.5 Hz, 2 H), 1.97-1.84 (m, 2 H), 1.05 (t, J = 7.2 Hz, 3 H), 0.95 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.6, 158.4, 147.9, 146.4, 136.0, 130.2, 129.6, 129.2, 128.5, 128.3, 127.5, 126.5, 126.4, 125.2, 61.3, 39.3, 23.1,

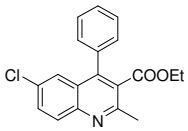
14.3, 13.7; IR (liquid film, cm^{-1}): ν = 3060, 2966, 1962, 1727, 1605, 1579, 1483, 1444, 1423, 1383, 1330, 1299, 1263, 1226, 1175, 1121, 1095, 1003, 934, 856, 765, 703, 602; HRMS calc. $C_{21}H_{21}NO_2$ (M^+): 319.1572. Found: 319.1579.

methyl 2-isopropyl-4-phenylquinoline-3-carboxylate (3i)



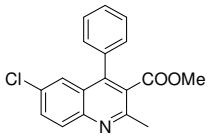
Pale yellow solid, mp: 62-63°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.13 (d, J = 8.1 Hz, 1 H), 7.73-7.68 (m, 1 H), 7.56 (d, J = 8.1 Hz, 1 H), 7.47-7.41 (m, 3 H), 7.38-7.35 (m, 3 H), 3.57 (s, 3 H), 3.27 (sep, J = 6.6 Hz, 1 H), 1.44 (d, J = 6.6 Hz, 6 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 169.4, 162.6, 148.1, 146.2, 136.0, 130.1, 129.5, 128.5, 128.3, 127.1, 126.5, 126.4, 125.3, 52.2, 34.5, 22.5; IR (liquid film, cm^{-1}): ν = 3064, 2968, 2255, 1732, 1651, 1561, 1487, 1436, 1399, 1329, 1280, 1231, 1160, 1125, 1097, 1047, 911, 765, 734, 702, 606; HRMS calc. $C_{20}H_{19}NO_2$ (M^+): 305.1416. Found: 305.1404.

ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3j)



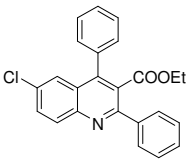
Pale yellow solid, mp: 108-109°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.05 (d, J = 7.5 Hz, 1 H), 7.68 (d, J = 9.0 Hz, 1 H), 7.56-7.52 (m, 4 H), 7.37-7.36 (m, 2 H), 4.09 (q, J = 6.9 Hz, 2 H), 2.80 (s, 3 H), 0.98 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.2, 155.2, 146.2, 145.7, 135.2, 132.6, 131.3, 130.6, 129.5, 128.9, 128.6, 128.4, 126.2, 125.4, 61.6, 23.8, 13.8; IR (liquid film, cm^{-1}): ν = 3063, 2929, 2255, 1727, 1577, 1481, 1445, 1384, 1308, 1280, 1224, 1164, 1069, 1018, 910, 834, 734, 647, 610; HRMS calc. $C_{19}H_{16}ClNO_2$ (M^+): 325.0870. Found: 325.0879.

methyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3k)



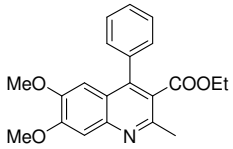
Pale yellow solid, mp: 106-107°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.02 (d, J = 8.7 Hz, 1 H), 7.66 (d, J = 9.0 Hz, 1 H), 7.55-7.49 (m, 4 H), 7.35-7.33 (m, 2 H), 3.58 (s, 3 H), 2.76 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.7, 155.1, 146.2, 145.8, 135.1, 132.6, 131.4, 130.6, 129.3, 128.9, 128.6, 128.2, 126.1, 125.4, 51.4, 23.8; IR (liquid film, cm^{-1}): ν = 3061, 2926, 1733, 1646, 1578, 1482, 1439, 1383, 1309, 1280, 1223, 1163, 1071, 930, 834, 733, 704, 609; HRMS calc. $C_{18}H_{14}ClNO_2$ (M^+): 311.0713. Found: 311.0705.

ethyl 6-chloro-2,4-diphenylquinoline-3-carboxylate (3l)



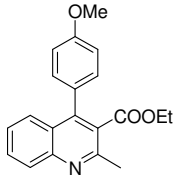
Pale yellow solid, mp: 119-120°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.19-8.10 (m, 1 H), 7.93 (d, J = 7.5 Hz, 1 H), 7.73-7.69 (m, 3 H), 7.56 (s, 1 H), 7.48-7.44 (m, 5 H), 7.39-7.37 (m, 2 H), 3.86 (q, J = 7.2 Hz, 2 H), 0.80 (t, J =7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.9, 167.6, 156.3, 146.5, 146.3, 139.9, 134.9, 133.8, 133.2, 131.5, 131.3, 129.5, 129.2, 128.9, 128.8, 128.6, 128.5, 128.3, 128.1, 126.5, 126.2, 125.4, 61.5, 14.2; IR (liquid film, cm^{-1}): v = 3061, 2981, 1960, 1732, 1689, 1549, 1476, 1447, 1397, 1292, 1214, 1108, 1034, 954, 913, 835, 758, 732, 699, 610; HRMS calc. $C_{24}H_{18}ClNO_2$ (M^+): 387.1026. Found: 387.1036.

ethyl 6,7-dimethoxy-2-methyl-4-phenylquinoline-3-carboxylate (3m)



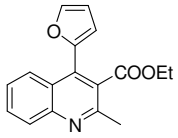
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.56 (s, 1 H), 7.50-7.48 (m, 2 H), 7.38-7.35 (m, 3 H), 6.89 (s, 1 H), 4.05-4.02 (m, 5 H), 3.80 (s, 3 H), 2.78 (s, 3 H), 0.94 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.5, 153.7, 152.3, 150.1, 144.2, 136.2, 129.2, 128.7, 128.5, 128.3, 125.9, 120.7, 106.9, 104.2, 61.5, 56.5, 56.0, 22.9, 13.7; IR (liquid film, cm^{-1}): v = 3059, 2934, 1723, 1619, 1566, 1504, 1468, 1430, 1382, 1229, 1149, 1074, 1025, 915, 853, 758, 731, 703, 608; HRMS calc. $C_{21}H_{21}NO_4$ (M^+): 351.1471. Found: 351.1462.

ethyl 4-(4-methoxyphenyl)-2-methylquinoline-3-carboxylate (3n)



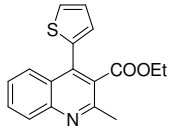
Pale yellow solid, mp: 85-86°C ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.98 (d, J = 8.1 Hz, 1 H), 7.64-7.52 (m, 2 H), 7.36-7.31 (m, 1 H), 7.21 (d, J = 8.1 Hz, 2 H), 6.92 (d, J = 8.1 Hz, 2 H), 4.02 (q, J = 6.9 Hz, 2 H), 3,79 (s, 3 H), 2.69 (s, 3 H), 0.94 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.7, 160.0, 154.6, 147.8, 146.2, 130.8, 130.3, 128.9, 127.9, 126.6, 126.4, 125.7, 113.9, 61.4, 55.5, 23.8, 13.9; IR (liquid film, cm^{-1}): v = 3065, 2937, 2028, 1725, 1610, 1579, 1516, 1492, 1461, 1399, 1293, 1249, 1179, 1125, 1065, 1032, 836, 767, 609; HRMS calc. $C_{20}H_{19}NO_3$ (M^+): 321.1365. Found: 321.1363.

ethyl 4-(furan-2-yl)-2-methylquinoline-3-carboxylate (3o)



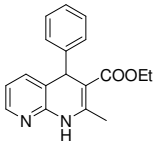
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.09-8.05 (m, 2 H), 7.79-7.70 (m, 1 H), 7.66-7.60 (m, 1 H), 7.58-7.45 (m, 1 H), 6.77 (d, J = 3.0 Hz, 1 H), 6.65-6.55 (m, 1 H), 4.29 (q, J = 7.2 Hz, 2 H), 2.77 (s, 3 H), 1.23 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.7, 154.9, 148.2, 148.1, 144.1, 134.6, 130.5, 129.2, 127.0, 126.8, 126.0, 123.9, 113.4, 111.8, 61.8, 23.8, 14.2; IR (liquid film, cm^{-1}): v = 3066, 2929, 1929, 1726, 1564, 1481, 1444, 1406, 1379, 1294, 1232, 1188, 1064, 1016, 951, 865, 763, 593; HRMS calc. $C_{17}H_{15}NO_3$ (M^+): 281.1052. Found: 281.1057.

ethyl 2-methyl-4-(thiophen-2-yl)quinoline-3-carboxylate (3p)



Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.07 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 1 H), 7.78-7.69 (m, 1 H), 7.54-7.48 (m, 2 H), 7.18-7.16 (m, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 2.78 (s, 3 H), 1.10 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.4, 154.6, 147.8, 139.2, 135.3, 130.5, 129.5, 129.0, 127.7, 127.3, 126.9, 126.3, 125.9, 61.7, 23.8, 13.9; IR (liquid film, cm^{-1}): v = 3068, 2979, 1725, 1612, 1577, 1491, 1438, 1402, 1288, 1229, 1160, 1131, 1062, 1014, 853, 765, 703, 652; HRMS calc. $C_{17}H_{15}NO_2S$ (M^+): 297.0823. Found: 297.0826.

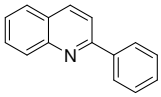
ethyl 2-methyl-4-phenyl-1,4-dihydro-1,8-naphthyridine-3-carboxylate (3q)



Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.02 (d, J = 3.3 Hz, 1 H), 7.79 (s, 1 H), 7.38 (d, J = 7.2 Hz, 1 H), 7.24-7.19 (m, 4 H), 7.13 (d, J = 6.6 Hz, 1 H), 6.85-6.83 (m, 1 H), 5.19 (s, 1 H), 4.06 (q, J = 6.6 Hz, 2 H), 2.49 (s, 3 H), 1.17 (t, J = 6.6 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.5, 149.6, 147.8, 147.0, 146.1, 137.8, 128.6, 127.4, 126.6, 120.8, 119.2, 100.4, 59.7, 44.1, 20.3, 14.4; IR (liquid film, cm^{-1}): v = 2938, 1694, 1629, 1583, 1509, 1445, 1277, 1206, 1108, 1056, 921, 852, 750, 699; HRMS calc. $C_{18}H_{18}N_2O_2$ (M^+): 294.1368. Found: 294.1377.

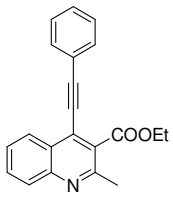
5.2 Characterization data for the products via propargylation and cyclization

2-phenylquinoline (5a)



White solid, mp: 78-79°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.21-8.19 (m, 4 H), 7.89-7.85 (m, 2 H), 7.80-7.70 (m, 1 H), 7.66-7.53 (m, 4 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 157.5, 148.4, 139.8, 137.0, 132.1, 130.2, 129.9, , 129.5, 129.0, 127.6, 127.4, 126.5, 119.2; IR (liquid film, cm^{-1}): v = 3058, 2924, 2204, 1726, 1597, 1553, 1508, 1490, 1423, 1319, 1282, 1241, 1125, 1073, 1024, 829, 768, 691; HRMS calc. $C_{15}H_{11}N$ (M^+): 205.0891. Found: 205.0887.

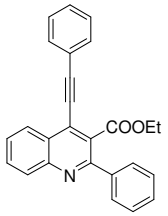
ethyl 2-methyl-4-(phenylethynyl)quinoline-3-carboxylate (4a)



Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.34 (d, J = 8.4 Hz, 1 H), 8.04 (d, J = 8.1 Hz, 1 H), 7.78-7.76 (m, 1 H), 7.63-7.61 (m, 3 H), 7.55-7.30 (m, 3 H), 4.53 (q, J = 7.2 Hz, 2 H), 2.78 (s, 3 H), 1.44 (t, J = 7.2 Hz, 3 H);

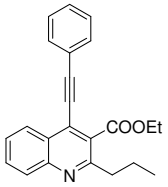
^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.98, 154.8, 147.5, 132.1, 130.3, 129.7, 129.4, 129.1, 128.7, 128.1, 127.2, 126.4, 125.5, 122.2, 102.3, 83.2, 62.0, 23.9, 14.4; IR (liquid film, cm^{-1}): v = 3062, 2981, 2209, 1727, 1567, 1496, 1432, 1405, 1299, 1229, 1153, 1128, 1074, 1033, 865, 760, 690; HRMS calc. $C_{21}H_{17}NO_2$ (M^+): 315.1259. Found: 315.1267.

ethyl 2-phenyl-4-(phenylethynyl)quinoline-3-carboxylate (4b)



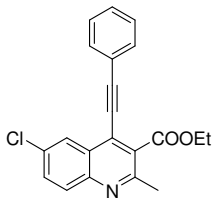
Yellow solid, mp: 103-104°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.45 (d, J = 8.4 Hz, 1 H), 8.22 (d, J = 8.4 Hz, 1 H), 7.86-7.81 (m, 1 H), 7.77-7.75 (m, 2 H), 7.72-7.67 (m, 3 H), 7.50-7.46 (m, 6 H), 4.29 (q, J = 7.2 Hz, 2 H), 1.15 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.0, 156.2, 147.7, 140.0, 139.2, 132.2, 131.2, 130.1, 129.8, 129.3, 129.2, 128.8, 128.6, 128.3, 127.9, 126.5, 125.8, 122.2, 102.9, 83.3, 62.0, 13.9; IR (liquid film, cm^{-1}): v = 3060, 2930, 2211, 1728, 1564, 1493, 1446, 1402, 1353, 1301, 1226, 1155, 1109, 1021, 952, 760, 693; HRMS calc. $C_{26}H_{19}NO_2$ (M^+): 377.1416. Found: 377.1426.

ethyl 4-(phenylethynyl)-2-propylquinoline-3-carboxylate (4c)



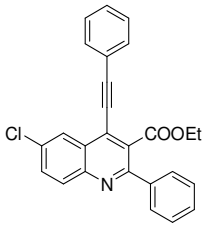
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.35 (d, J = 8.4 Hz, 1 H), 8.07 (d, J = 8.1 Hz, 1 H), 7.78-7.74 (m, 1 H), 7.63-7.58 (m, 3 H), 7.43-7.41 (m, 3 H), 4.53 (q, J = 7.2 Hz, 2 H), 3.00 (t, J = 7.8 Hz, 2 H), 1.91-1.84 (m, 2 H), 1.44 (t, J = 7.2 Hz, 3 H), 1.03 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.1, 158.4, 147.5, 132.1, 130.9, 129.7, 129.5, 129.3, 128.8, 128.2, 127.2, 126.4, 125.5, 122.2, 102.2, 83.3, 62.0, 39.2, 23.1, 14.4, 14.3; IR (liquid film, cm^{-1}): v = 3062, 2962, 2209, 1725, 1612, 1566, 1496, 1445, 1404, 1301, 1227, 1198, 1152, 1127, 1073, 1017, 913, 858, 758, 689; HRMS calc. $C_{23}H_{21}NO_2$ (M^+): 343.1572. Found: 343.1584.

ethyl 6-chloro-2-methyl-4-(phenylethynyl)quinoline-3-carboxylate (4d)



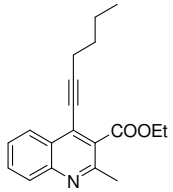
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.31 (s, 1 H), 8.14-8.02 (m, 1 H), 7.73-7.70 (m, 1 H), 7.65-7.63 (m, 3 H), 7.46-7.44 (m, 2 H), 4.54 (q, J = 7.2 Hz, 2 H), 2.79 (s, 3 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.4, 155.2, 145.3, 136.1, 134.1, 133.5, 130.4, 130.0, 128.8, 127.9, 126.8, 126.3, 125.3, 121.8, 103.5, 82.6, 62.3, 23.6, 14.4; IR (liquid film, cm^{-1}): v = 3063, 2936, 2208, 1728, 1666, 1568, 1478, 1400, 1312, 1276, 1220, 1091, 1040, 992, 923, 830, 756, 689; HRMS calc. $C_{21}H_{16}ClNO_2$ (M^+): 349.0870. Found: 349.0861.

ethyl 6-chloro-2-phenyl-4-(phenylethynyl)quinoline-3-carboxylate (4e)



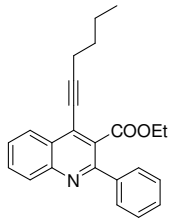
Yellow solid, mp: 115-116°C. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.36 (s, 1 H), 8.15-8.07 (m, 1 H), 7.75-7.72 (m, 3 H), 7.70-7.65 (m, 2 H), 7.48-7.40 (m, 6 H), 4.28 (q, J = 7.2 Hz, 2 H), 1.11 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.7, 156.5, 146.1, 139.7, 133.9, 132.2, 132.1, 130.0, 129.4, 129.2, 129.1, 128.8, 128.7, 127.2, 126.5, 125.3, 121.9, 103.4, 82.7, 62.1, 14.0; IR (liquid film, cm^{-1}): v = 3061, 2980, 2210, 1729, 1598, 1560, 1545, 1493, 1475, 1444, 1384, 1349, 1289, 1225, 1111, 1024, 964, 911, 874, 830, 756, 693; HRMS calc. $C_{26}H_{18}ClNO_2$ (M^+): 411.1026. Found: 411.1024.

ethyl 4-(hex-1-ynyl)-2-methylquinoline-3-carboxylate (4f)



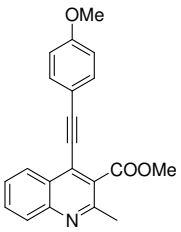
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.22 (d, J = 8.1 Hz, 1 H), 8.05-7.95 (m, 1 H), 7.73-7.65 (m, 1 H), 7.58-7.45 (m, 1 H), 4.46 (q, J = 7.2 Hz, 2 H), 2.70 (s, 3 H), 2.57 (t, J = 7.2 Hz, 2 H), 1.69-1.64 (m, 2 H), 1.56-1.51 (m, 2 H), 1.42 (t, J = 6.9 Hz, 3 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.2, 154.5, 147.4, 131.8, 130.7, 129.7, 129.0, 128.8, 126.9, 126.5, 125.9, 104.7, 74.8, 61.9, 30.6, 23.8, 22.1, 19.7, 14.3, 13.7; IR (liquid film, cm^{-1}): v = 3063, 2959, 2219, 1729, 1613, 1570, 1491, 1404, 1323, 1291, 1229, 1159, 1131, 1065, 862, 764, 697; HRMS calc. $C_{19}H_{21}NO_2$ (M^+): 295.1572. Found: 295.1577.

ethyl 4-(hex-1-ynyl)-2-phenylquinoline-3-carboxylate (4g)



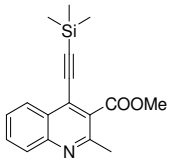
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.33-8.28 (m, 1 H), 8.15-8.05 (m, 1 H), 7.77-7.70 (m, 3 H), 7.65-7.59 (m, 1 H), 7.48-7.44 (m, 3 H), 4.22 (q, J = 7.2 Hz, 2 H), 2.62 (t, J = 6.9 Hz, 2 H), 1.73-1.66 (m, 2 H), 1.59-1.52 (m, 2 H), 1.11 (t, J = 7.2 Hz, 3 H), 0.99 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.2, 156.1, 147.7, 140.2, 130.9, 130.0, 129.8, 129.6, 129.0, 128.6, 128.5, 127.6, 126.5, 126.3, 105.3, 74.9, 61.8, 30.6, 22.2, 19.8, 13.9, 13.7; IR (liquid film, cm^{-1}): v = 3062, 2932, 2223, 1729, 1615, 1548, 1486, 1460, 1401, 1296, 1226, 1157, 1103, 1033, 923, 846, 766, 699; HRMS calc. $C_{24}H_{23}NO_2$ (M^+): 357.1729. Found: 357.1739.

methyl 4-((4-methoxyphenyl)ethynyl)-2-methylquinoline-3-carboxylate (4h)



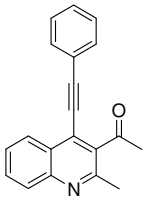
Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.35 (d, J = 8.1 Hz, 1 H), 8.03 (d, J = 8.4 Hz, 1 H), 7.85-7.76 (m, 1 H), 7.63-7.56 (m, 3 H), 6.94 (d, J = 8.4 Hz, 2 H), 4.05 (s, 3 H), 3.86 (s, 3 H), 2.76 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 168.6, 160.9, 154.9, 147.6, 133.8, 132.7, 131.0, 129.2, 128.9, 127.1, 126.6, 125.4, 114.5, 114.2, 103.0, 82.4, 55.6, 52.8, 24.0; IR (liquid film, cm^{-1}): ν = 2998, 2932, 2203, 1723, 1654, 1603, 1566, 1511, 1433, 1400, 1294, 1251, 1170, 1075, 1034, 822, 767, 707; HRMS calc. $C_{21}H_{17}NO_3$ (M^+): 331.1208. Found: 331.1216.

methyl 2-methyl-4-((trimethylsilyl)ethynyl)quinoline-3-carboxylate (4i)



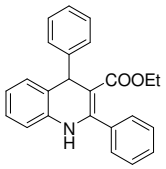
Colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.24 (d, J = 8.1 Hz, 1 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.74-7.72 (m, 1 H), 7.62-7.57 (m, 1 H), 4.49 (q, J = 7.2 Hz, 2 H), 2.74 (s, 3 H), 1.46 (t, J = 7.2 Hz, 3 H), 0.34 (s, 9 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.9, 154.7, 147.5, 130.9, 129.9, 129.1, 127.7, 127.3, 126.4, 125.5, 109.1, 98.0, 62.0, 23.8, 14.3, 0.12; IR (liquid film, cm^{-1}): ν = 3064, 2960, 2159, 1730, 1569, 1491, 1404, 1291, 1250, 1230, 1155, 1128, 1081, 1045, 846, 763, 674; HRMS calc. $C_{17}H_{19}NO_2Si$ (M^+): 297.1185. Found: 297.1189.

1-(2-methyl-4-(phenylethynyl)quinolin-3-yl)ethanone (4j)



Yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.36-8.28 (m, 1 H), 8.09-8.01 (m, 1 H), 7.81-7.72 (m, 1 H), 7.63-7.61 (m, 3 H), 7.43-7.42 (m, 3 H), 2.77 (s, 3 H), 2.68 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 204.4, 153.6, 147.3, 137.2, 132.0, 130.8, 129.9, 129.2, 128.8, 127.3, 126.0, 125.7, 125.4, 121.8, 103.4, 83.2, 31.8, 23.7; IR (liquid film, cm^{-1}): ν = 3025, 2910, 2206, 1698, 1613, 1565, 1495, 1291, 1198, 1124, 1025, 954, 872, 758, 689, 644; HRMS calc. $C_{20}H_{15}NO$ (M^+): 285.1154. Found: 285.1141.

ethyl 2,4-diphenyl-1,4-dihydroquinoline-3-carboxylate ($3c_1$)

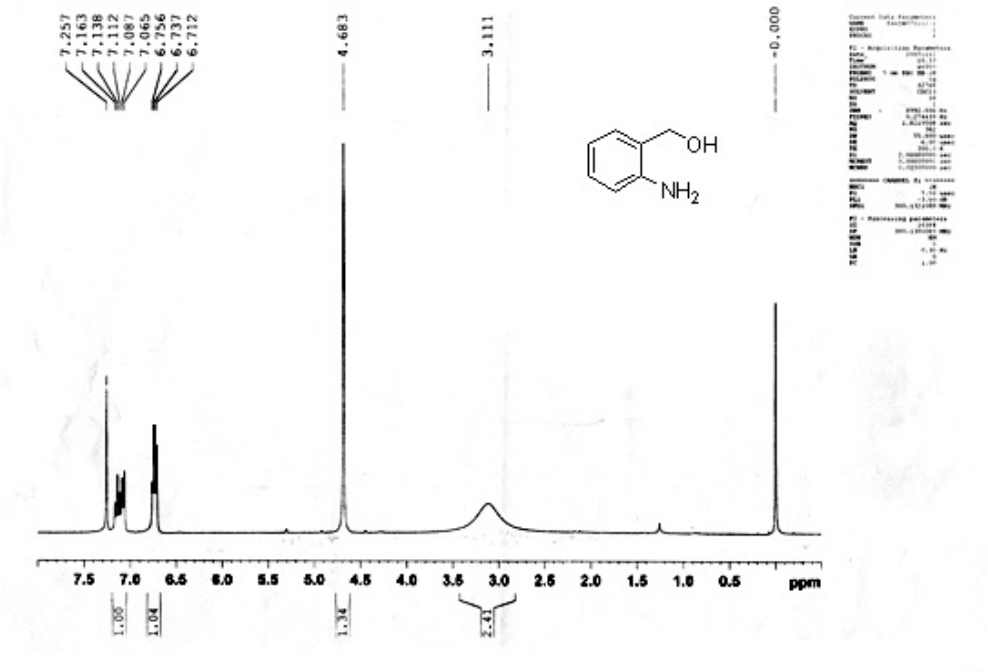


^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.45-7.31 (m, 7 H), 7.26-7.22 (m, 2 H), 7.15 (d, J = 6.6 Hz, 2 H), 7.10-7.05 (m, 1 H), 6.96-6.93 (m, 1 H), 6.70 (d, J = 7.5 Hz, 1 H), 6.21 (s, 1 H), 5.29 (s, 1 H), 3.80 (q, J = 6.9 Hz, 2 H), 0.81 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.3, 148.4, 138.4, 136.2, 129.7, 128.9, 128.5, 128.3, 128.2, 127.4, 127.1, 126.3, 125.5, 123.7, 114.8, 100.4, 59.4, 44.1, 13.8; IR (liquid film, cm^{-1}): ν = 3380, 3013,

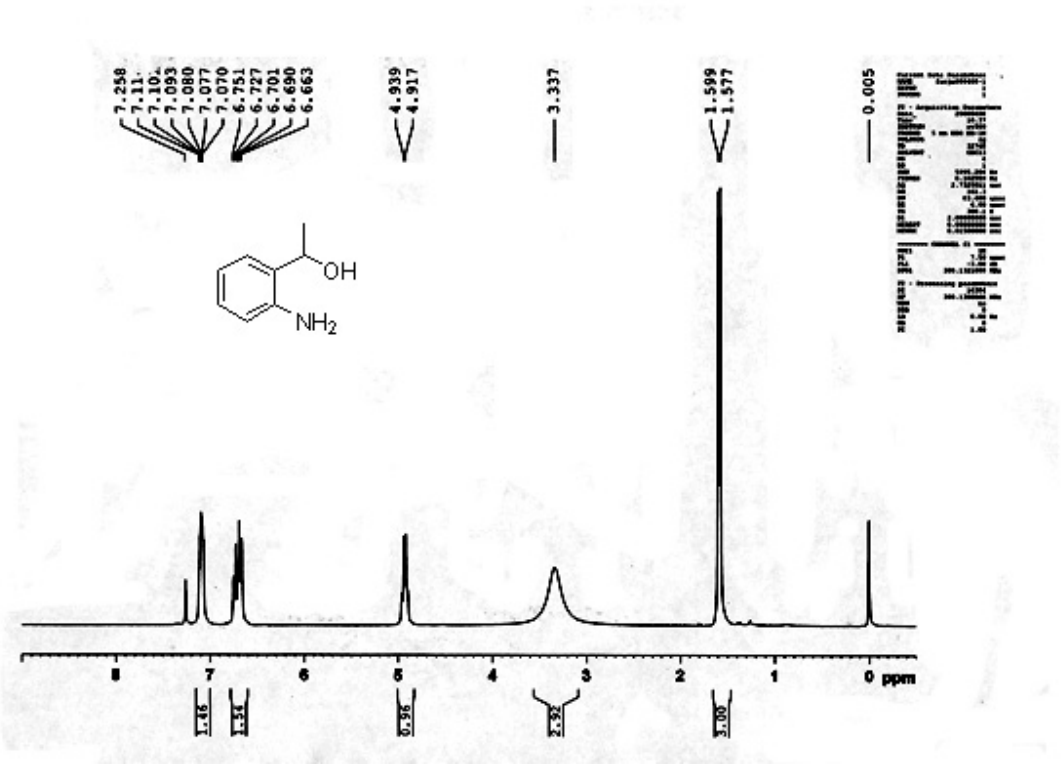
2901,, 1678, 1567, 1458, 1421, 1376, 1349, 1230, 1156, 1076, 934, 766, 723, 700, 642; HRMS calc. $C_{24}H_{21}NO_2$ (M^+): 355.1572. Found: 355.1569.

6 NMR Spectra

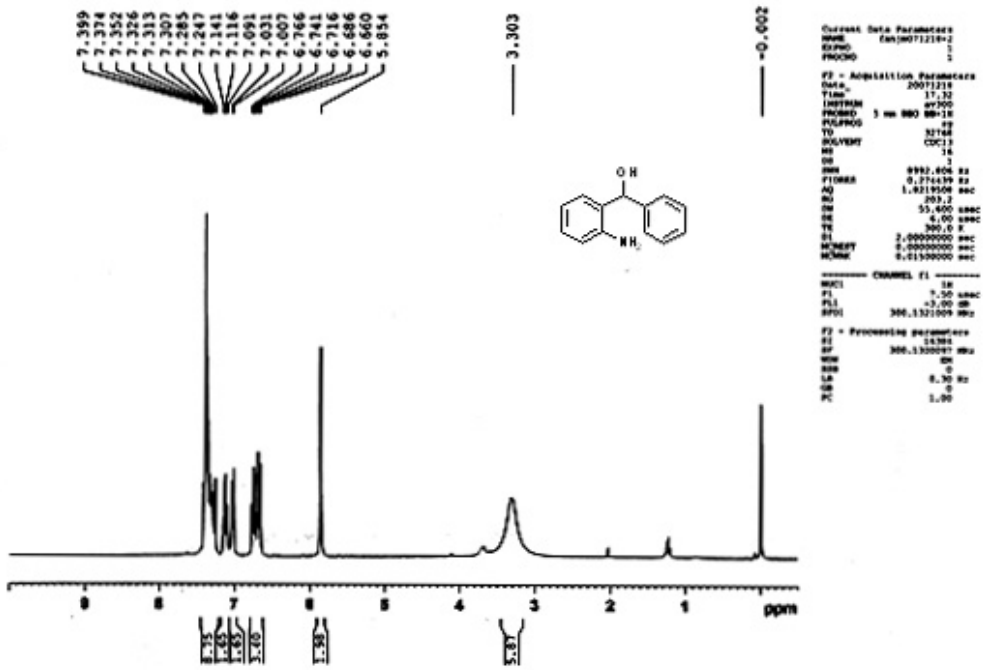
1a (^{1}H-NMR)



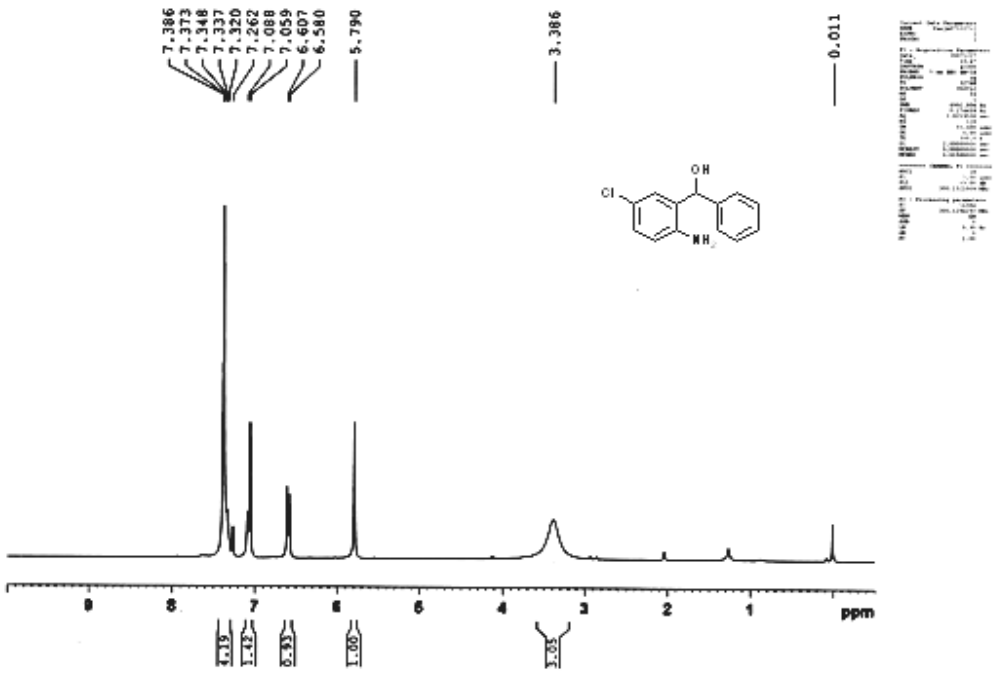
1b (^{1}H-NMR)



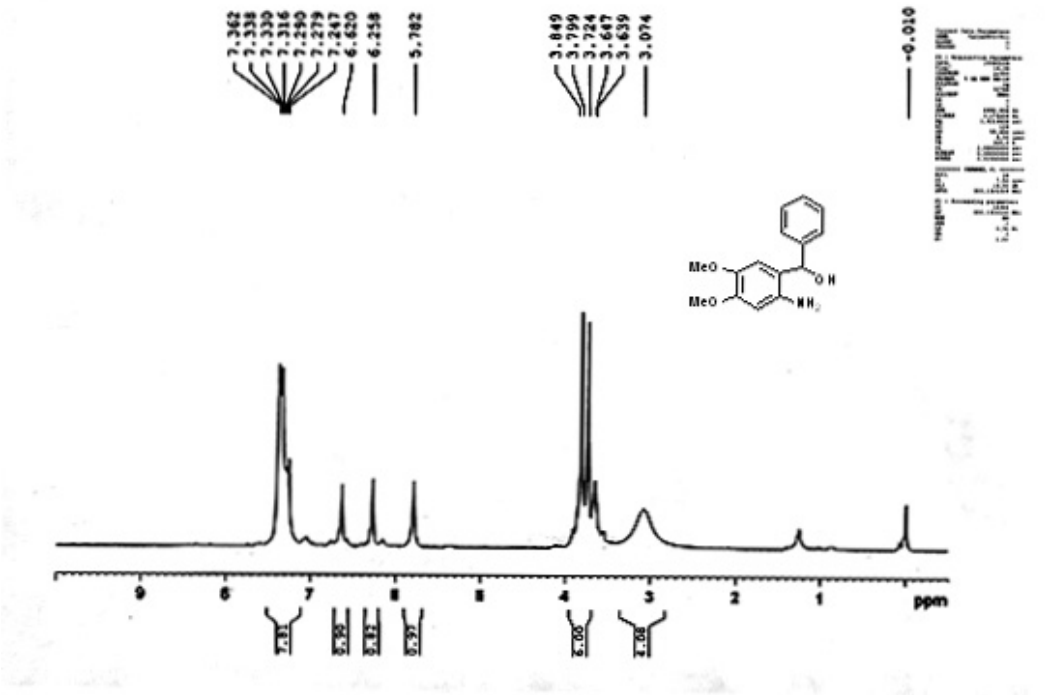
1c (^{1}H-NMR)



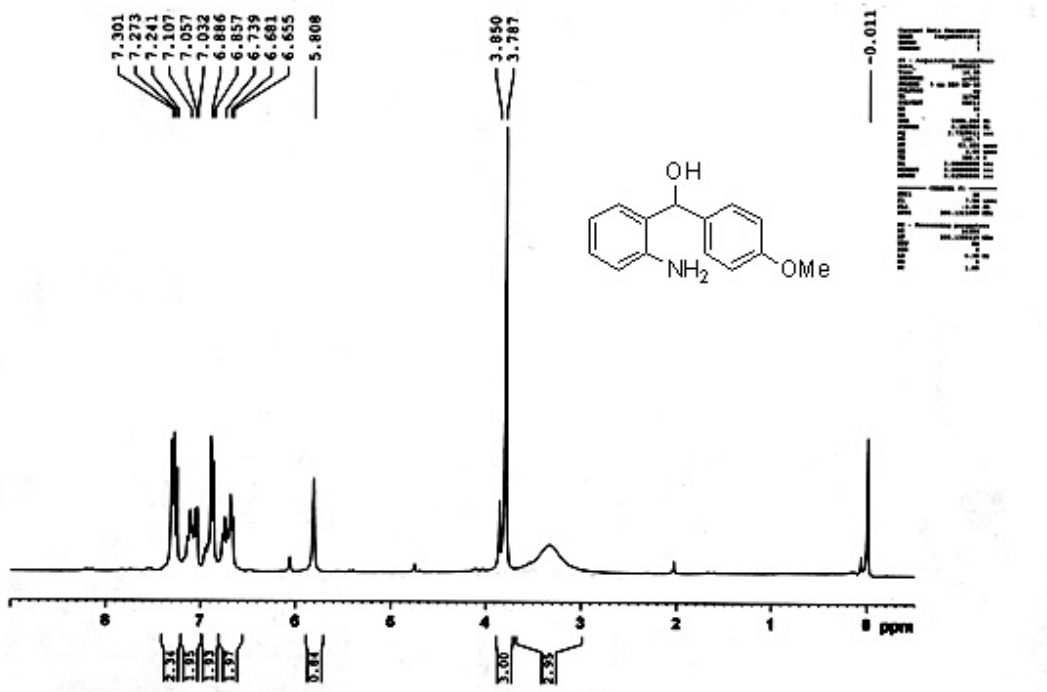
1d (^{1}H-NMR)



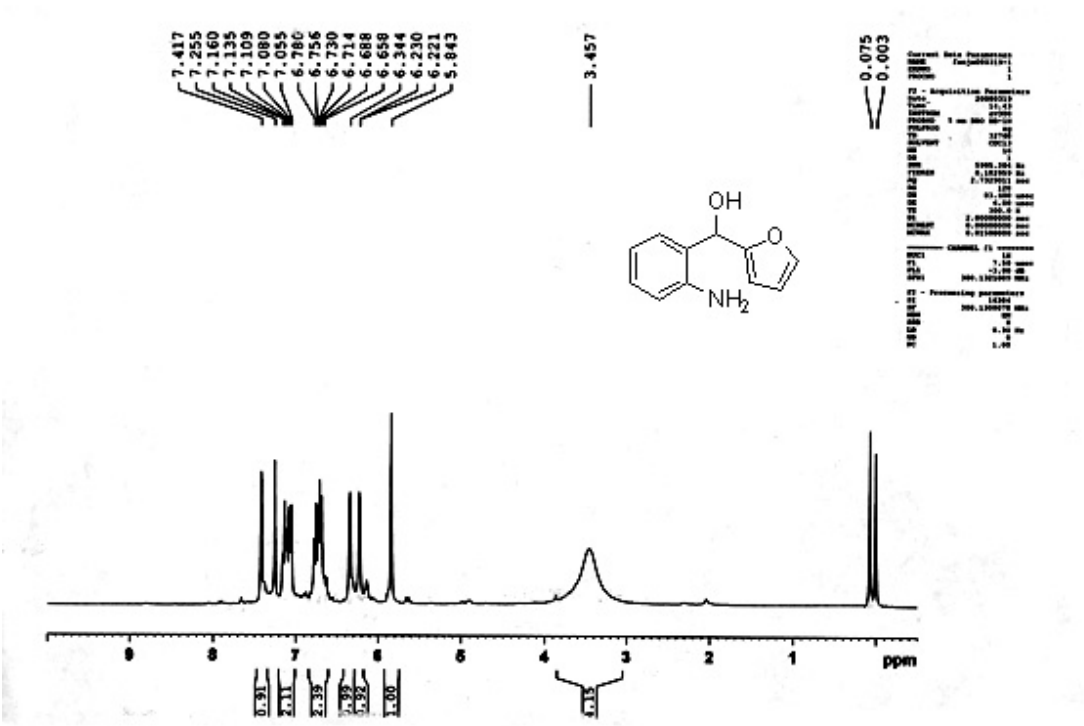
1e (^{1}H-NMR)



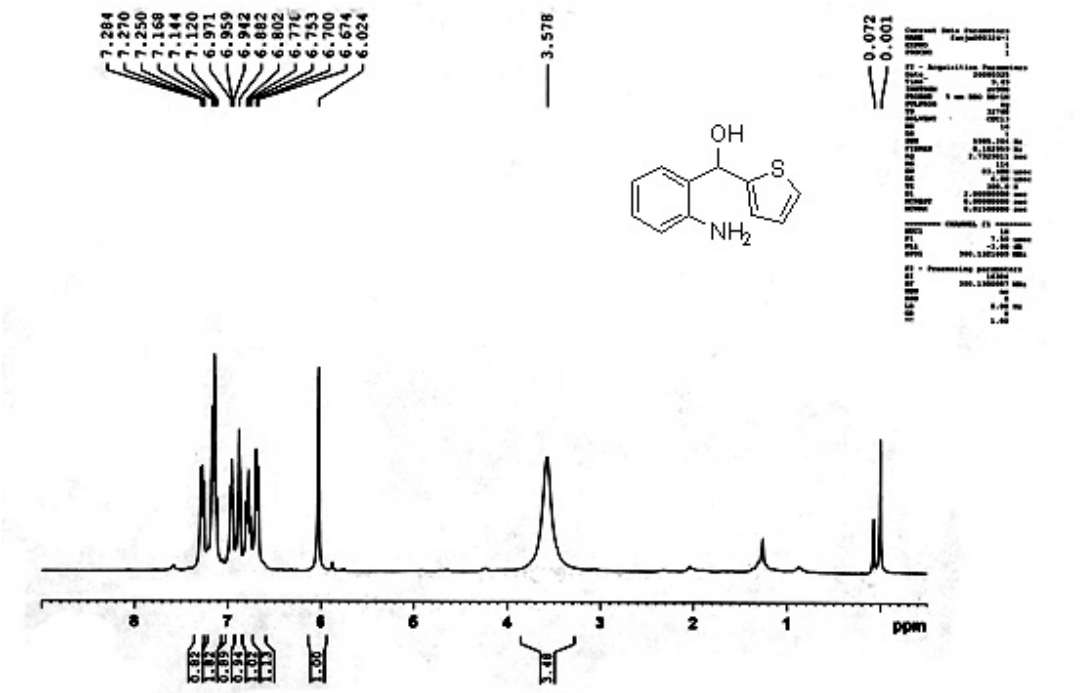
1f (^{1}H-NMR)



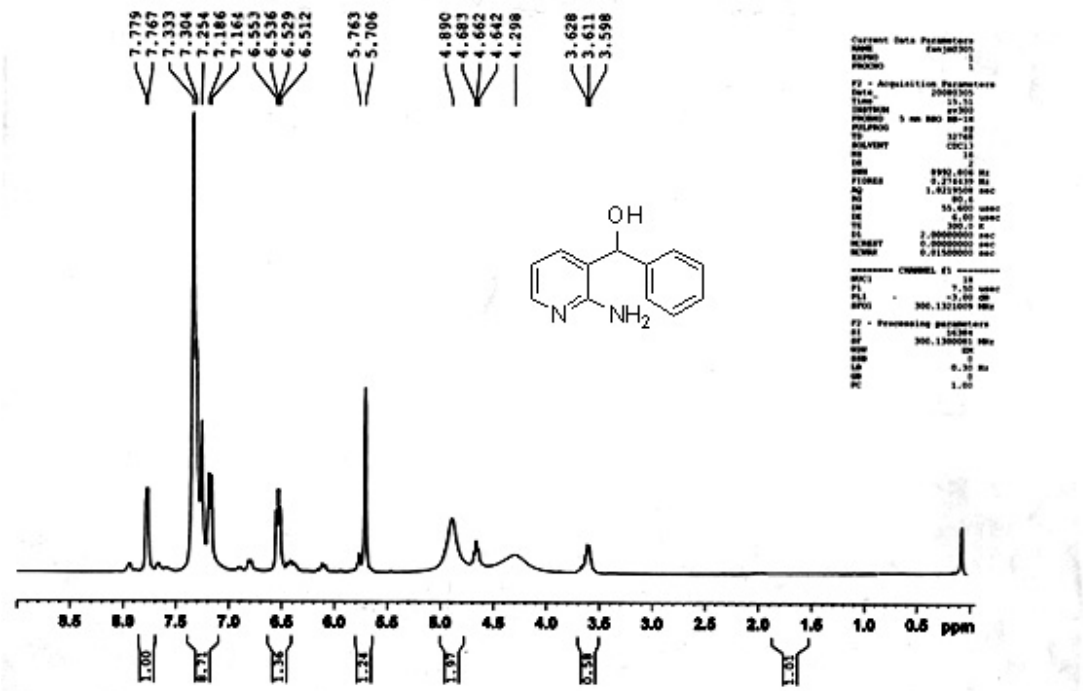
1g (^{1}H-NMR)



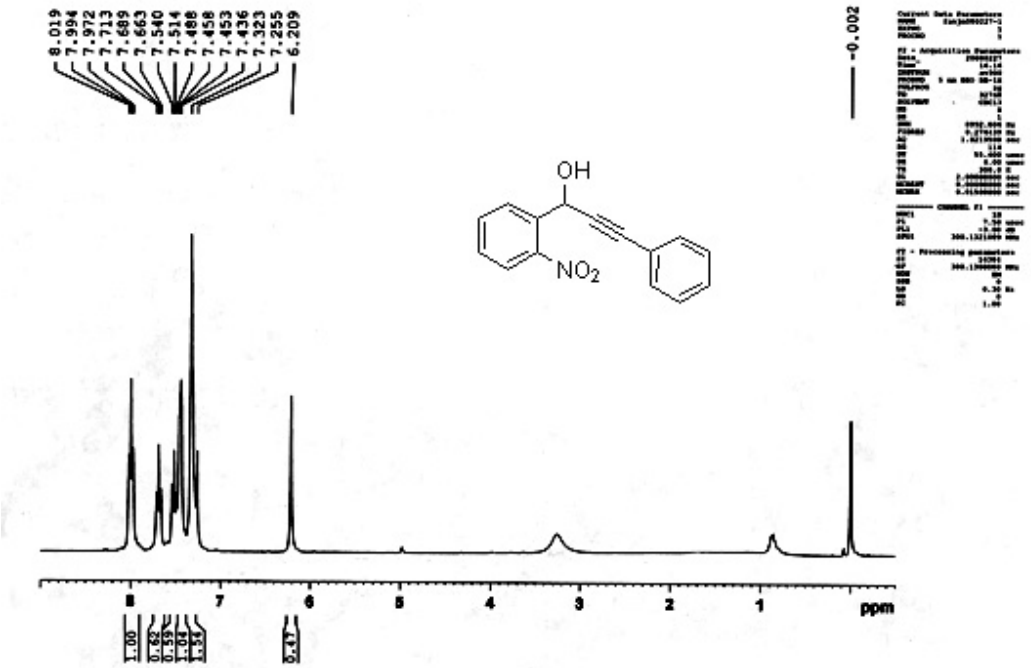
1h (^{1}H-NMR)



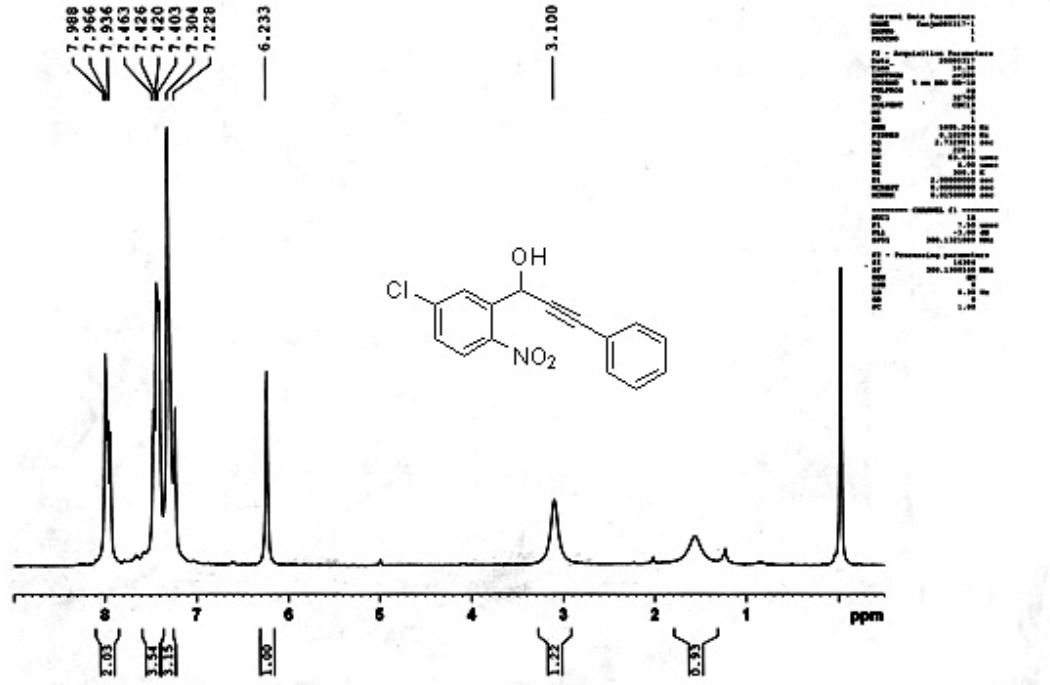
1i (^{1}H-NMR)



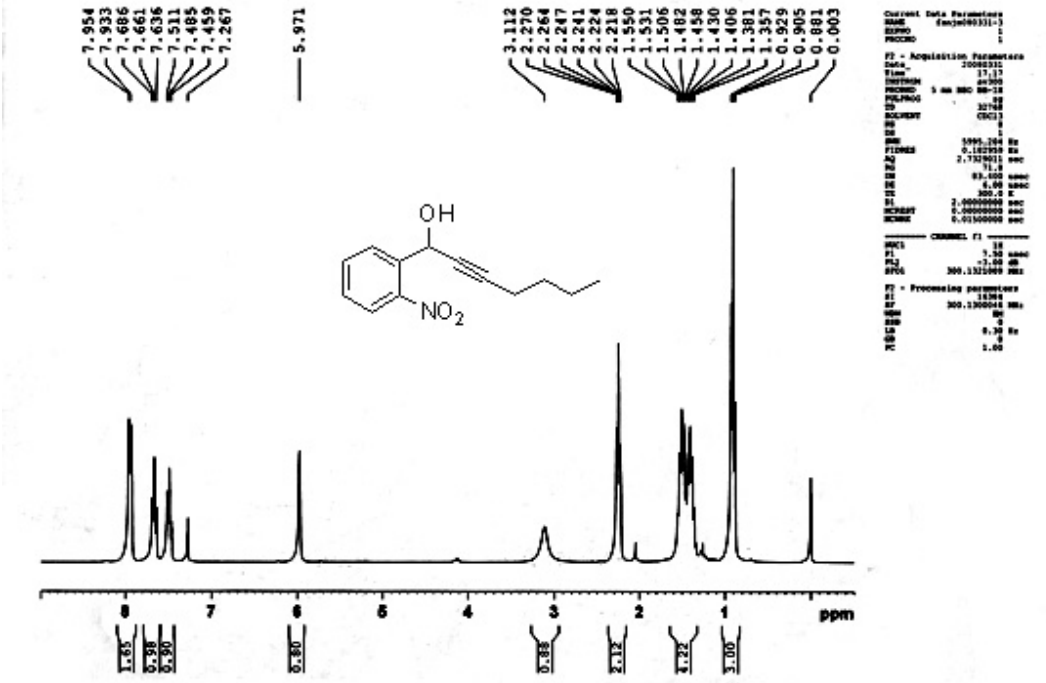
1j (^{1}H-NMR)



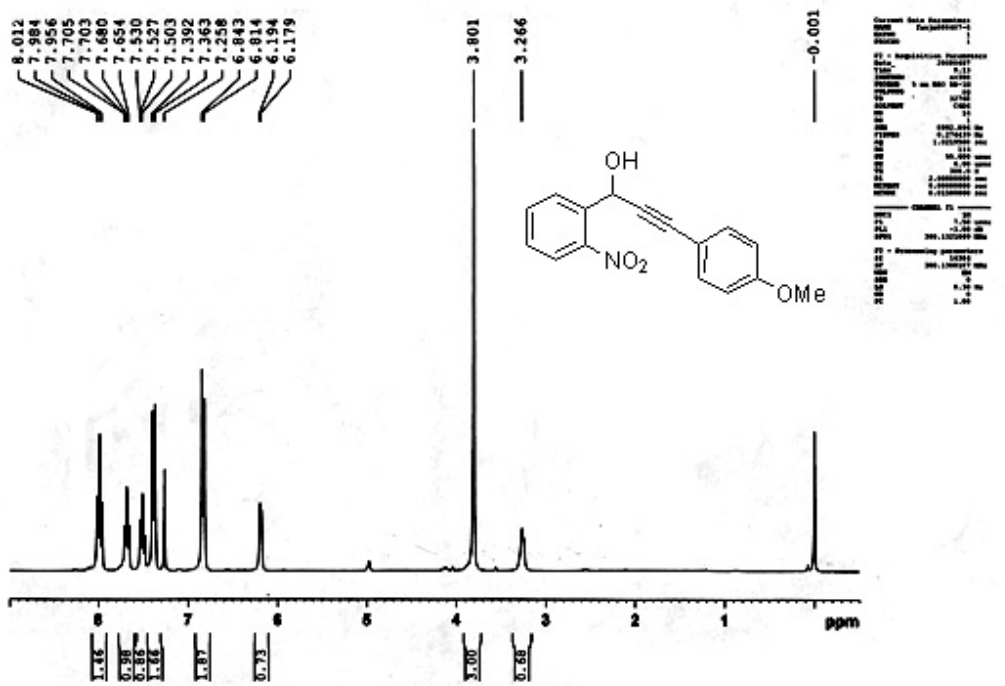
1k (^{1}H-NMR)



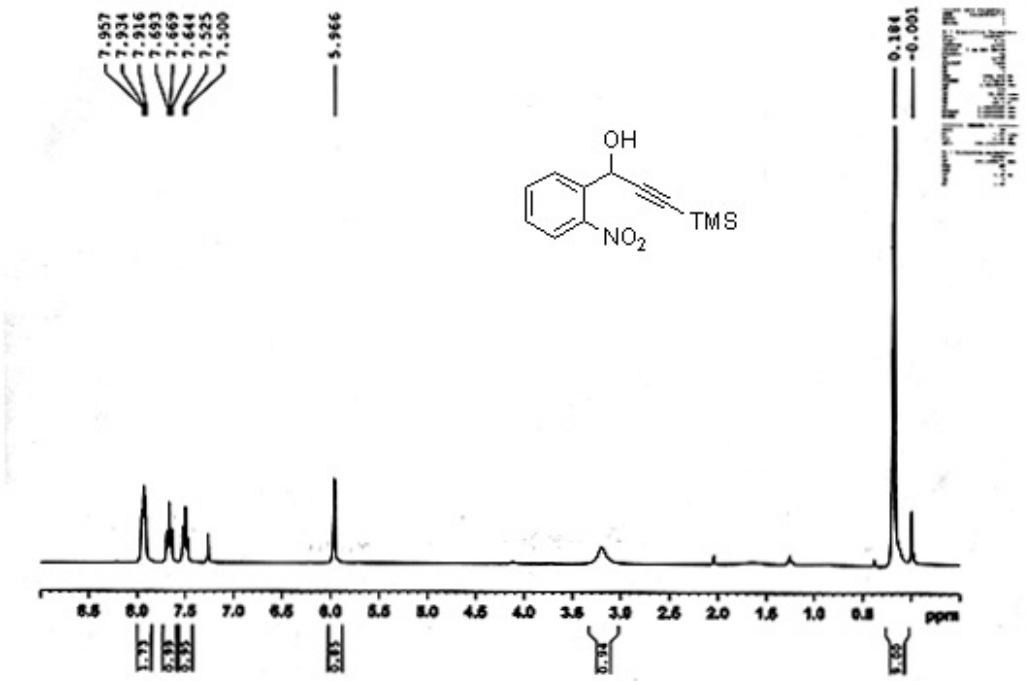
1l (^{1}H-NMR)



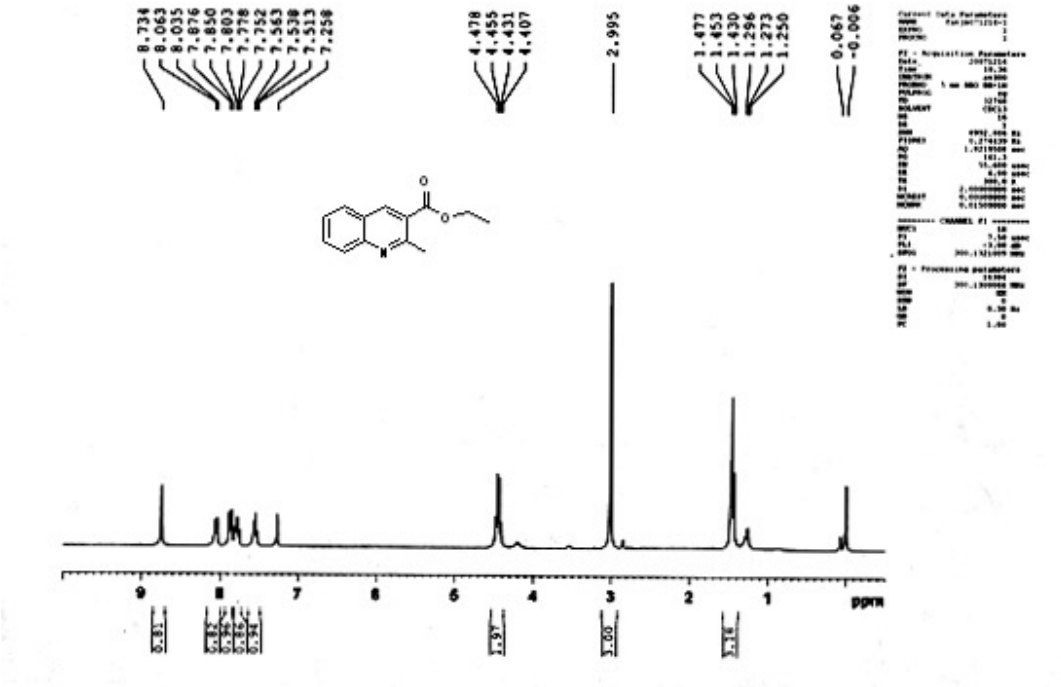
1m (^{1}H-NMR)



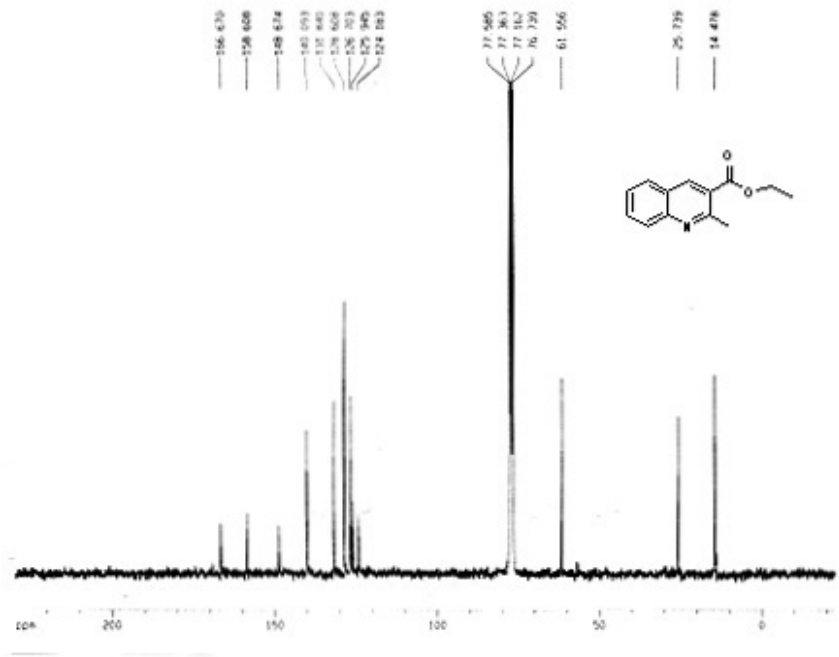
1n (^{1}H-NMR)



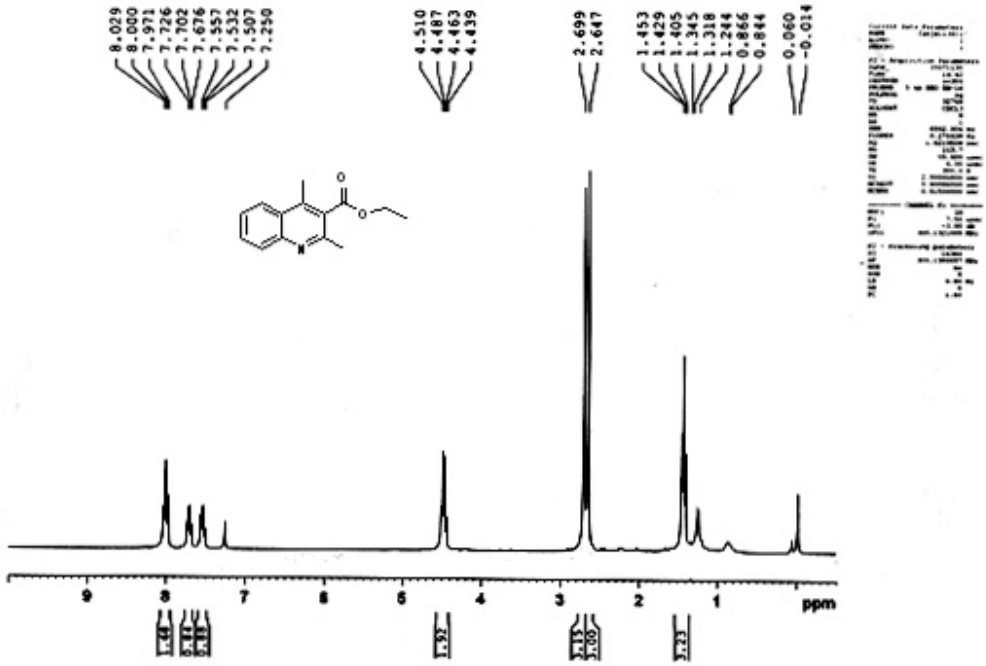
3a (^{1}H-NMR)



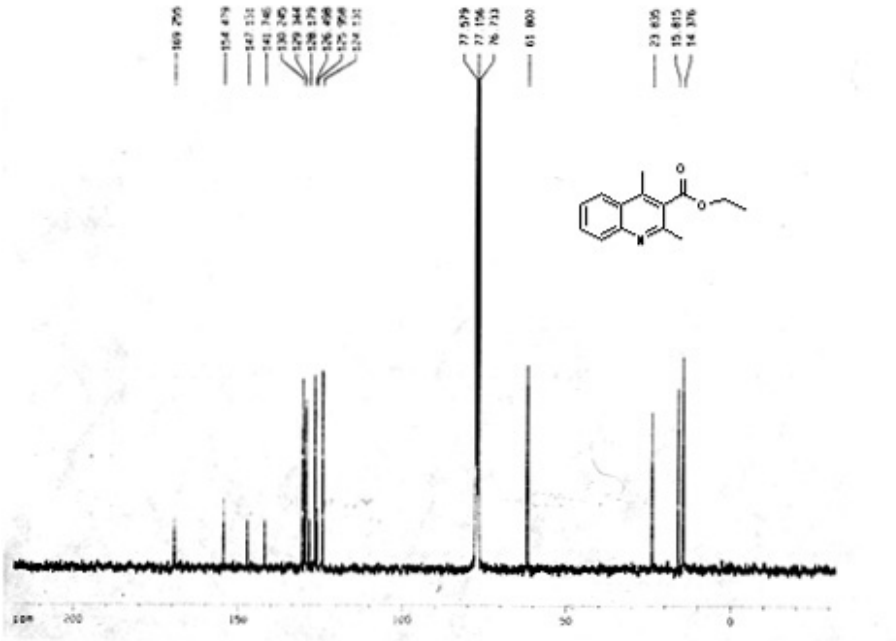
3a (^{13}C-NMR)



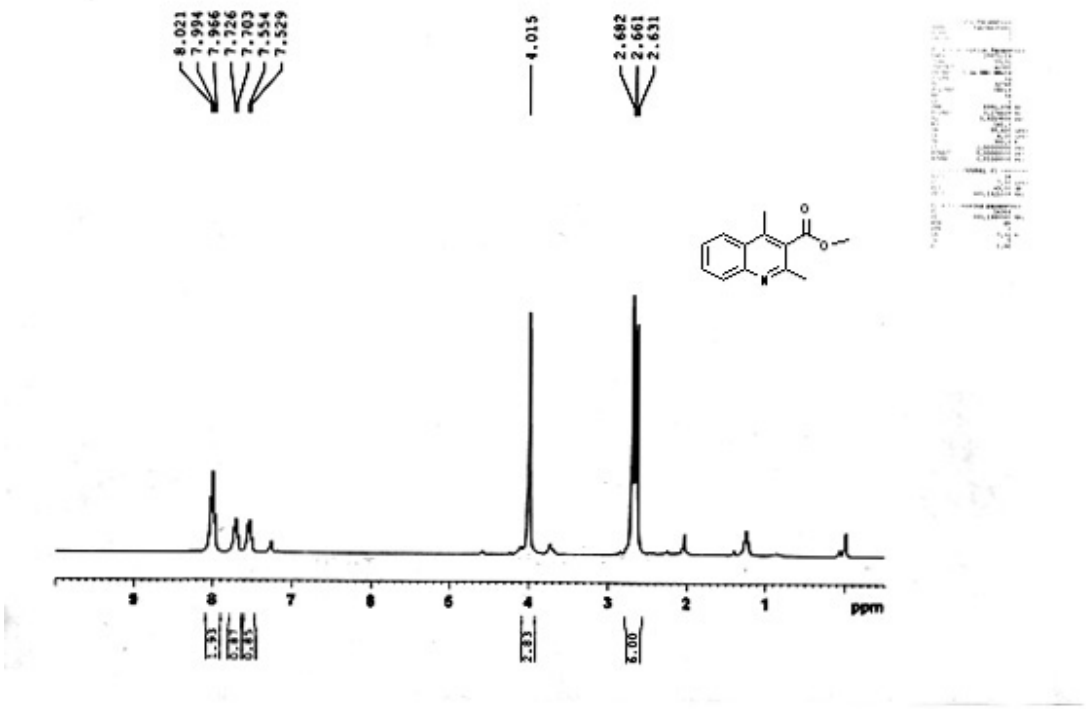
3b (^{1}H-NMR)



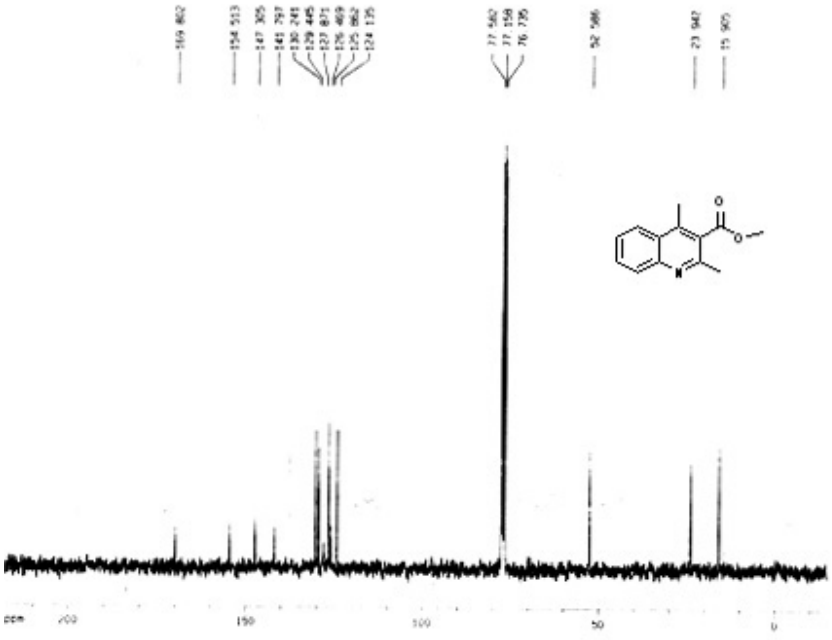
3b (^{13}C-NMR)



3c (^{1}H-NMR)



3c (^{13}C-NMR)



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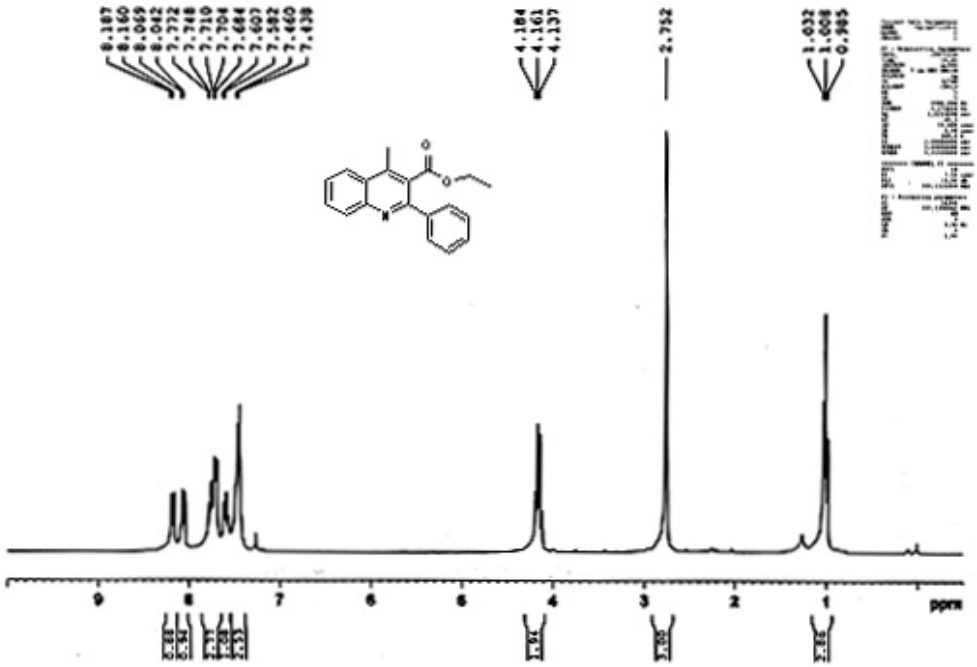

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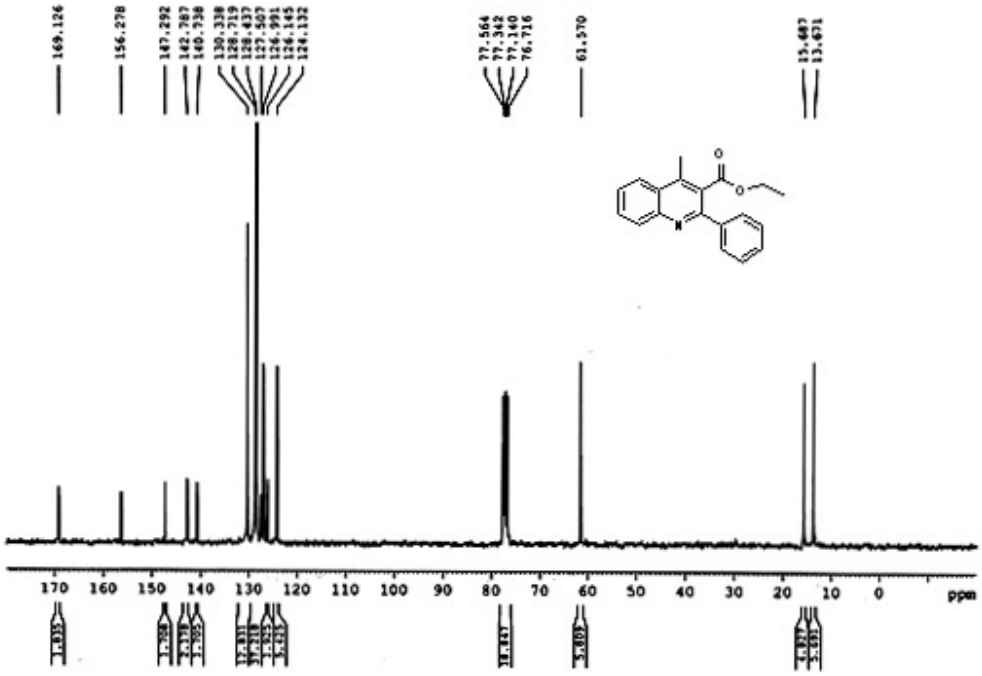

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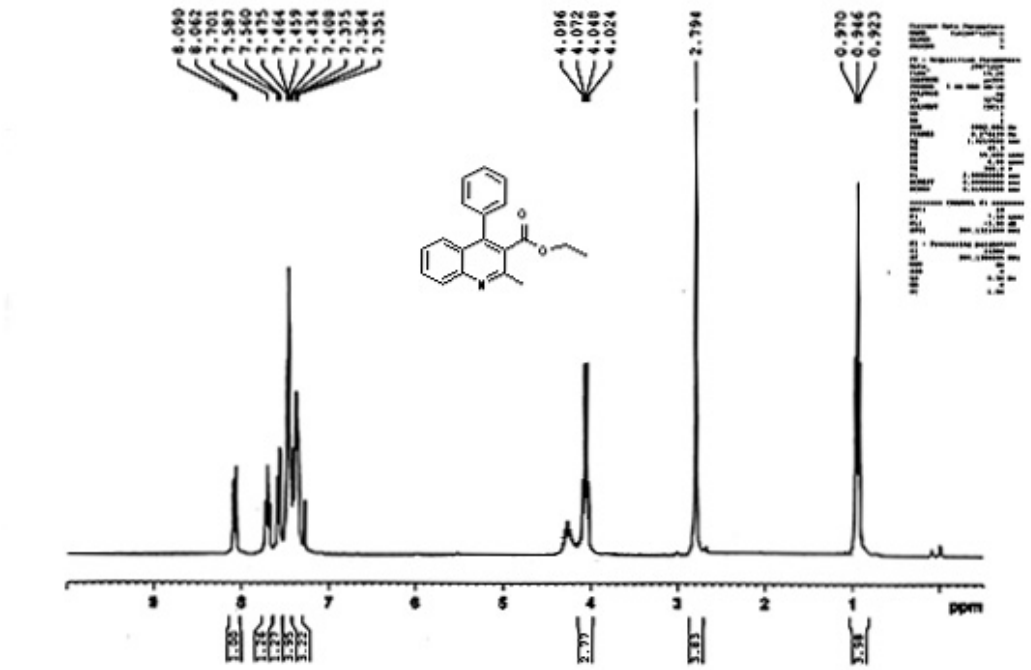

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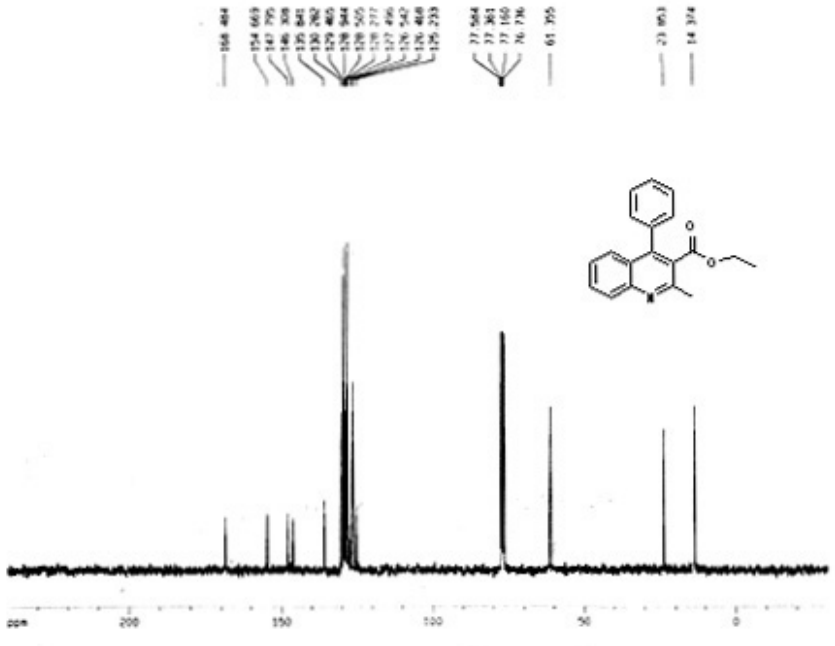

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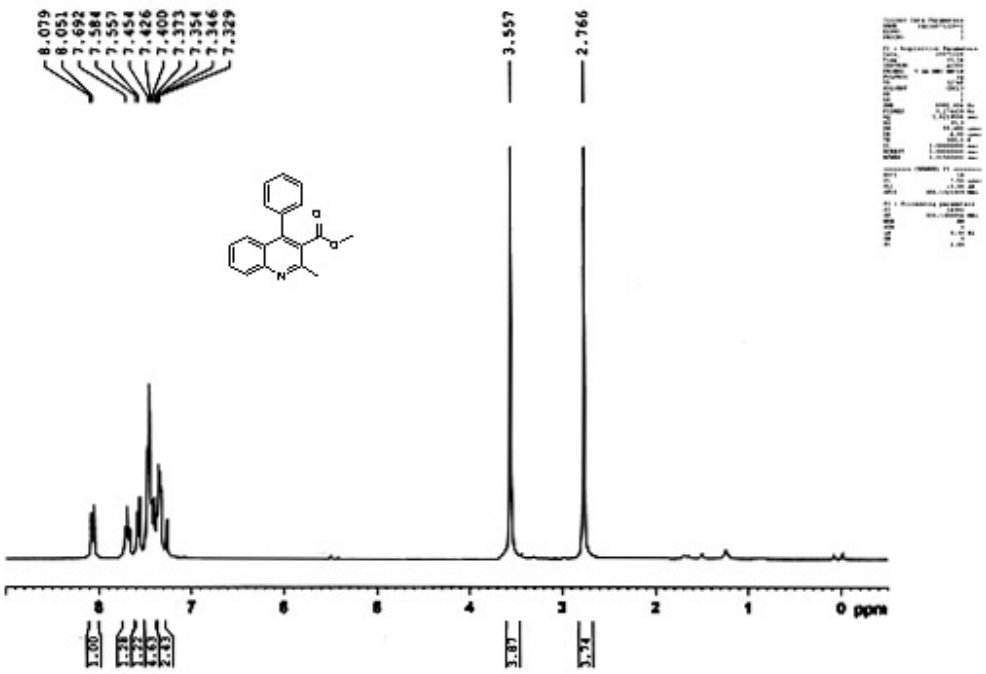

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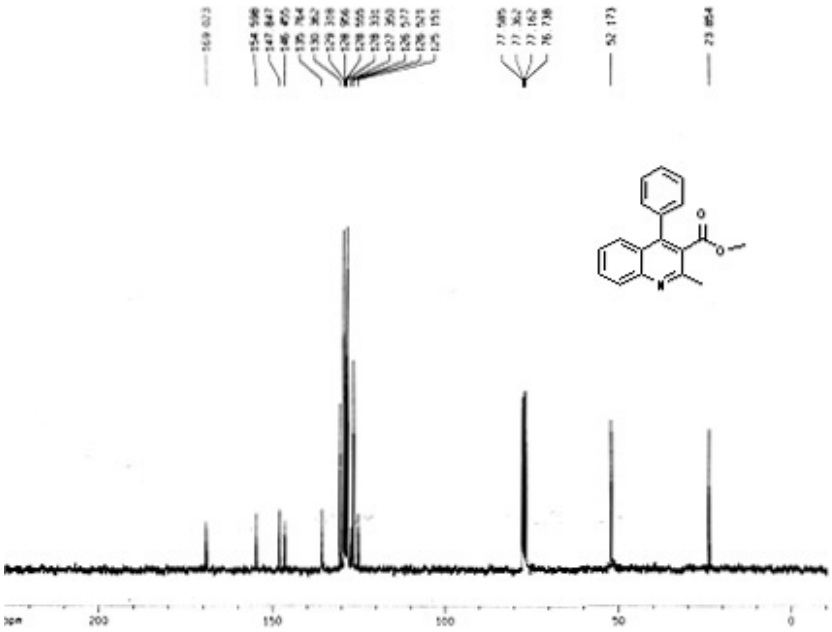
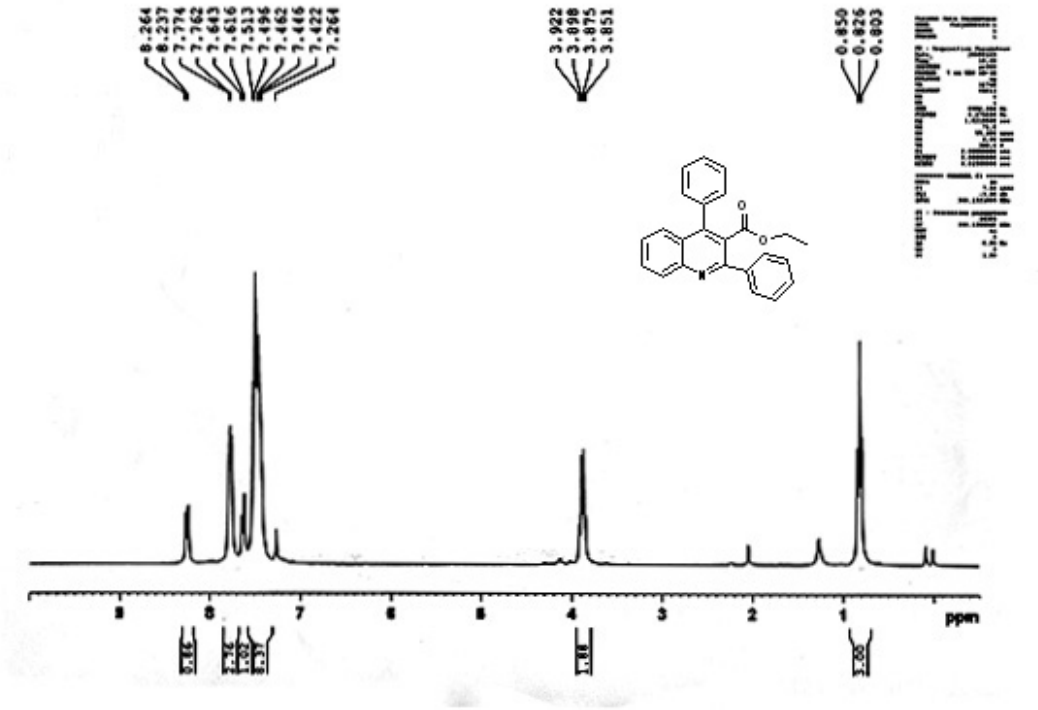


3g (^{1}H-NMR)



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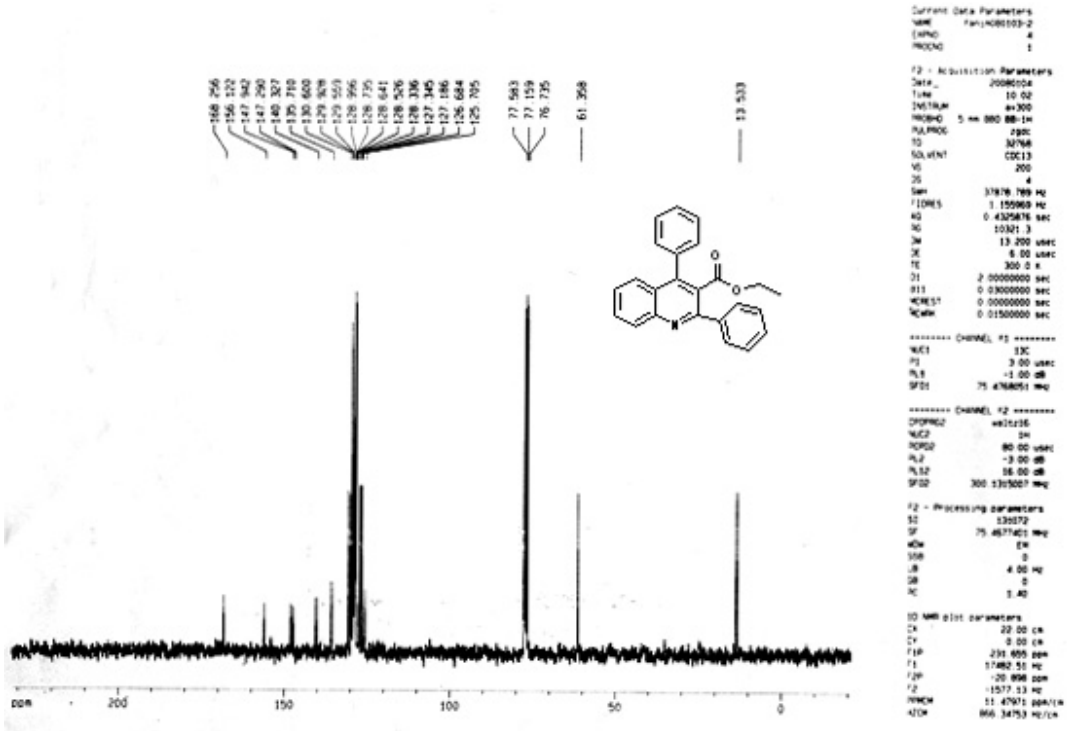
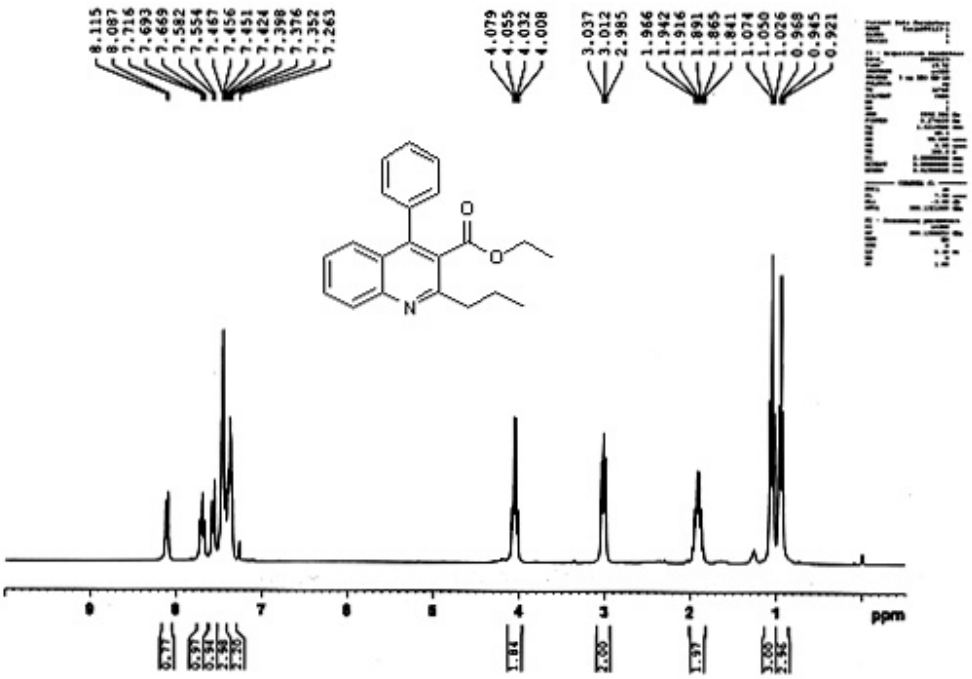
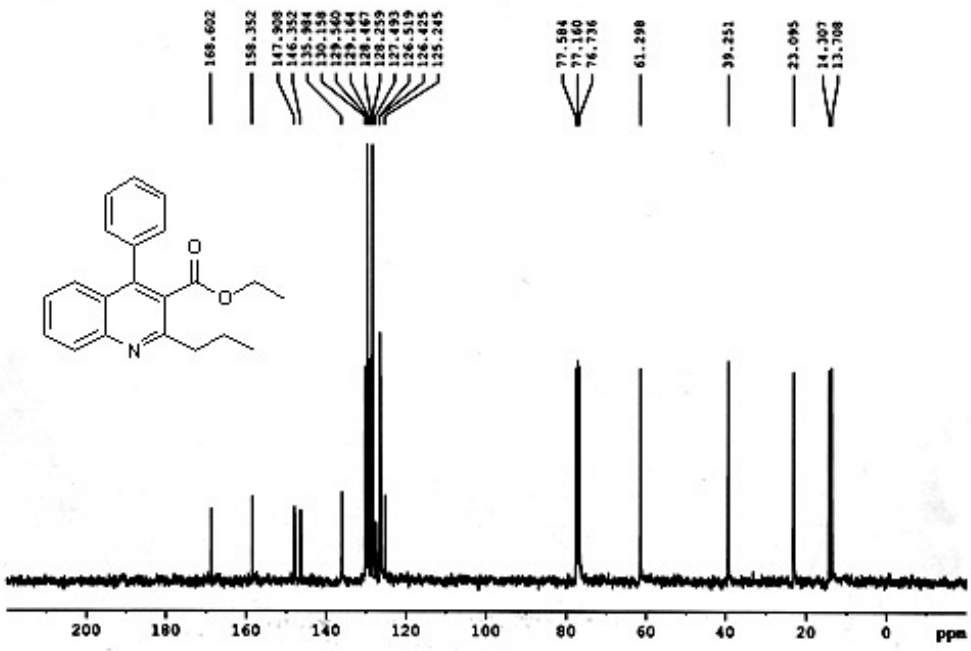


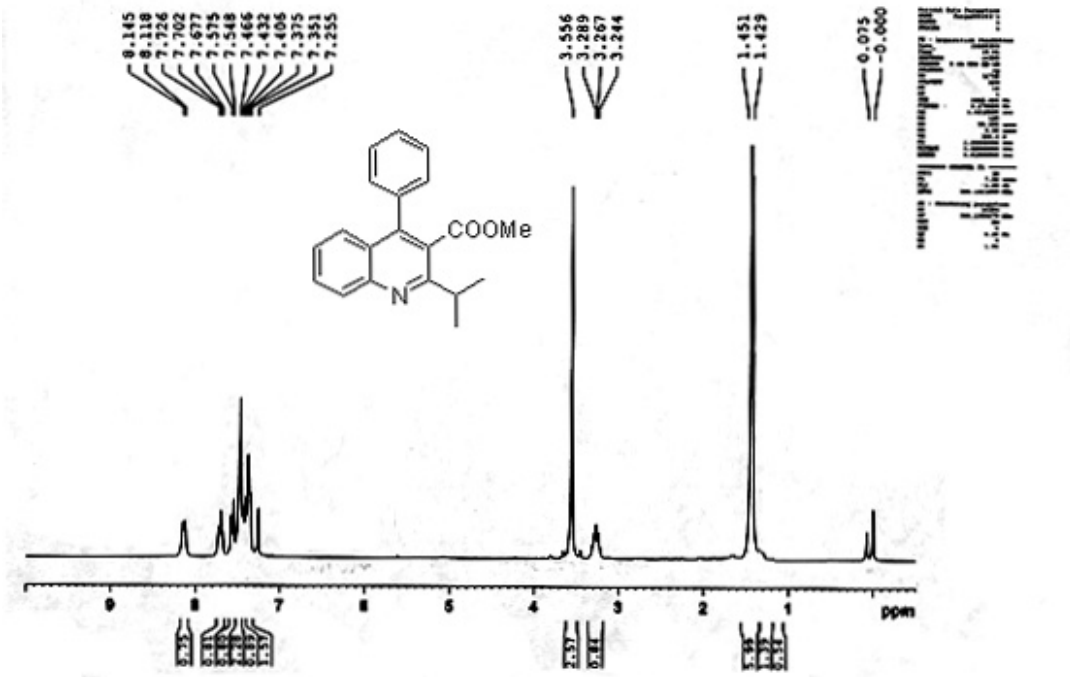
3h (^{1}H-NMR)



3h (^{13}C-NMR)



3i (^{1}H-NMR)



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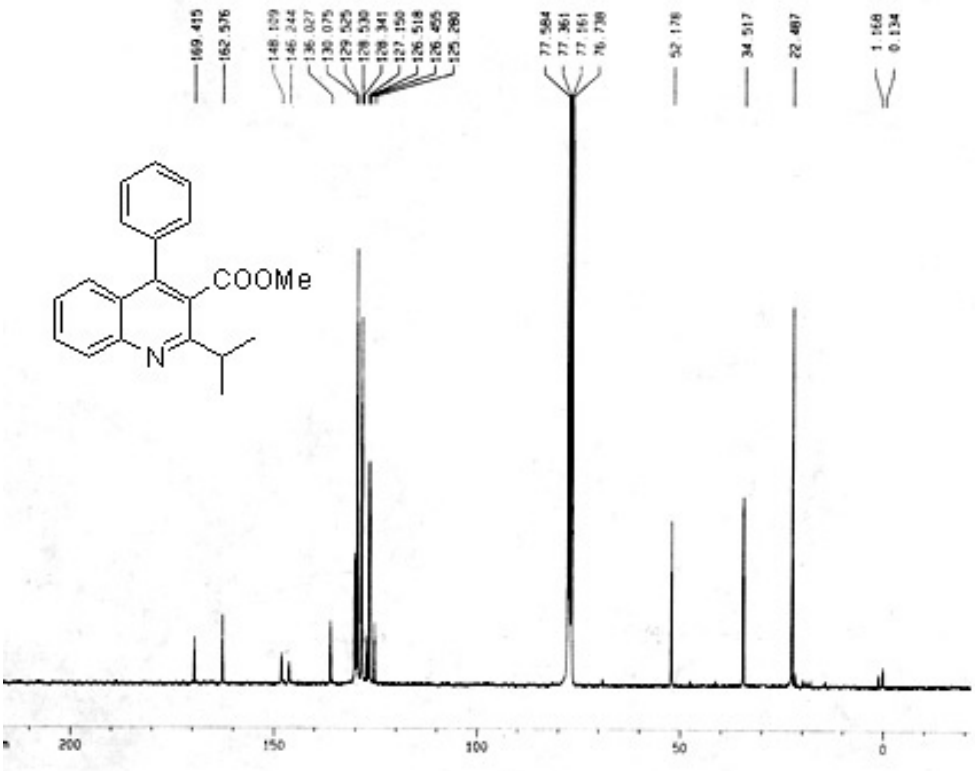

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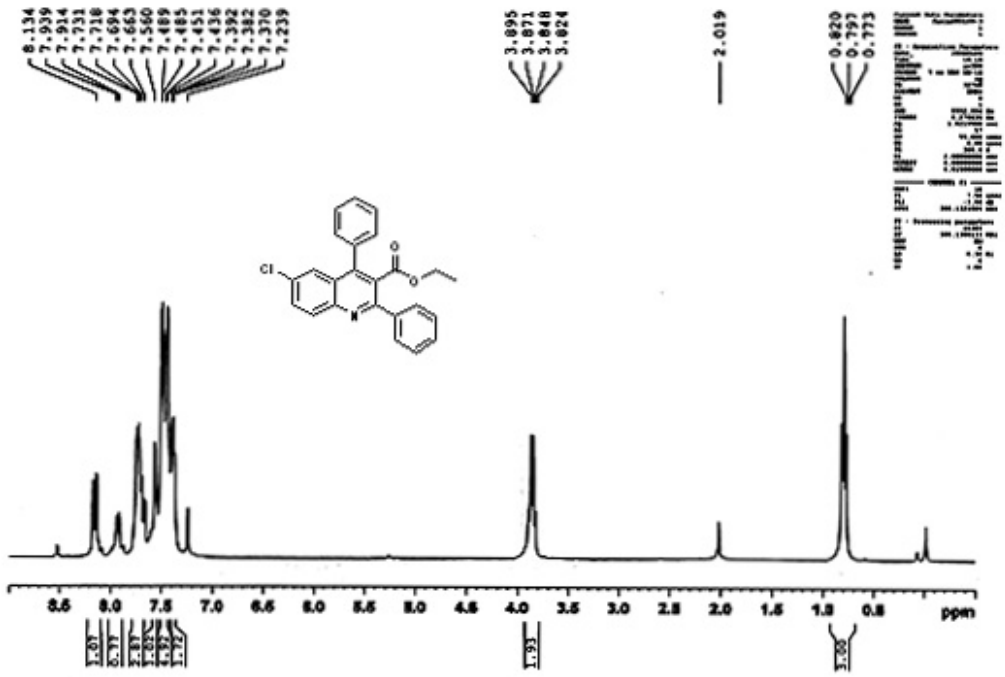

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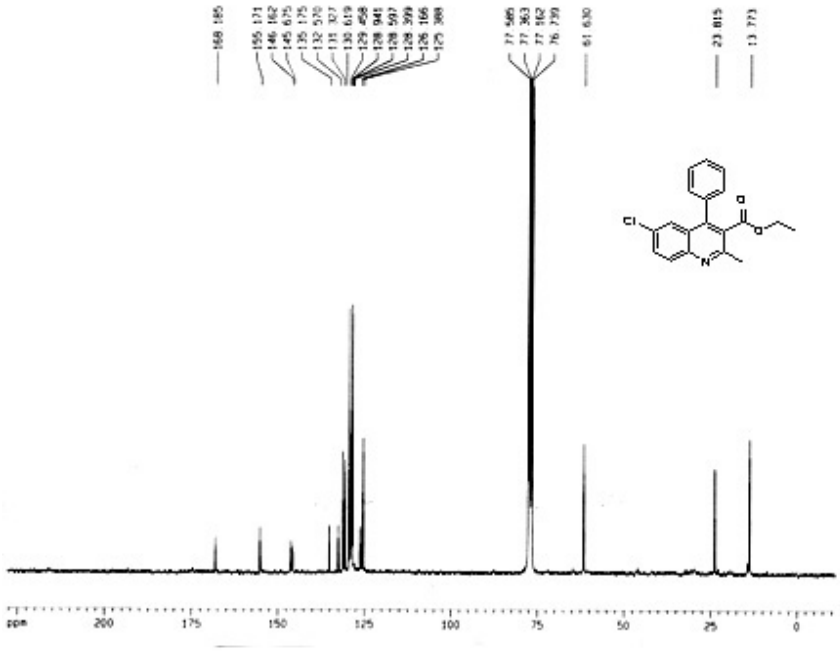

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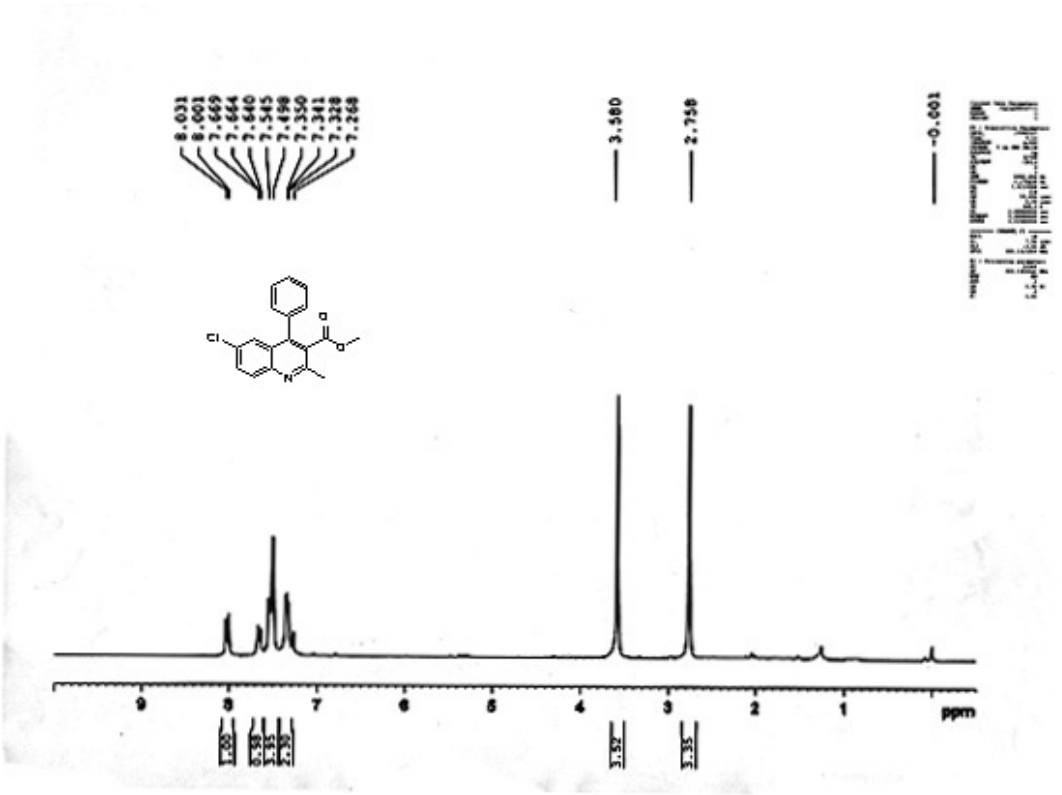

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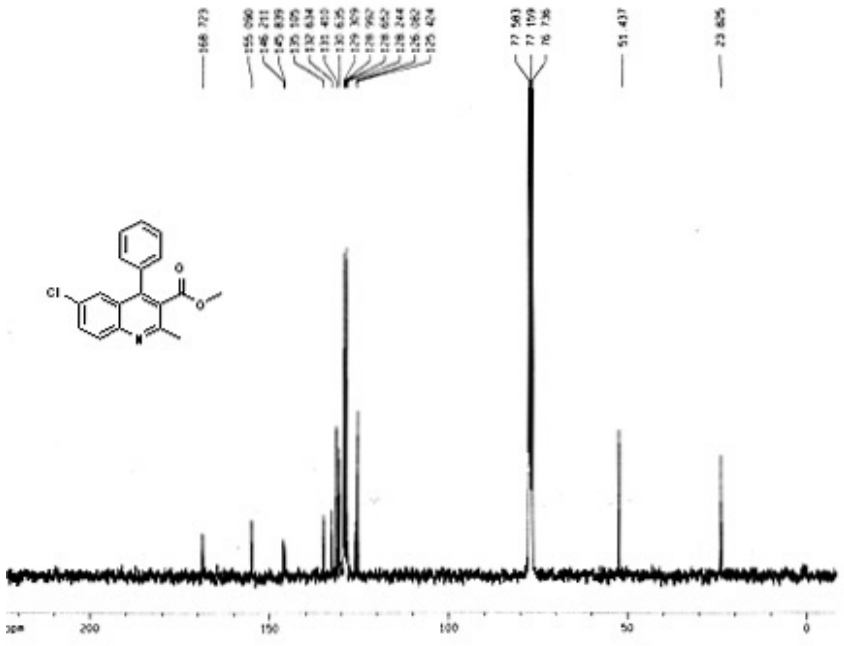

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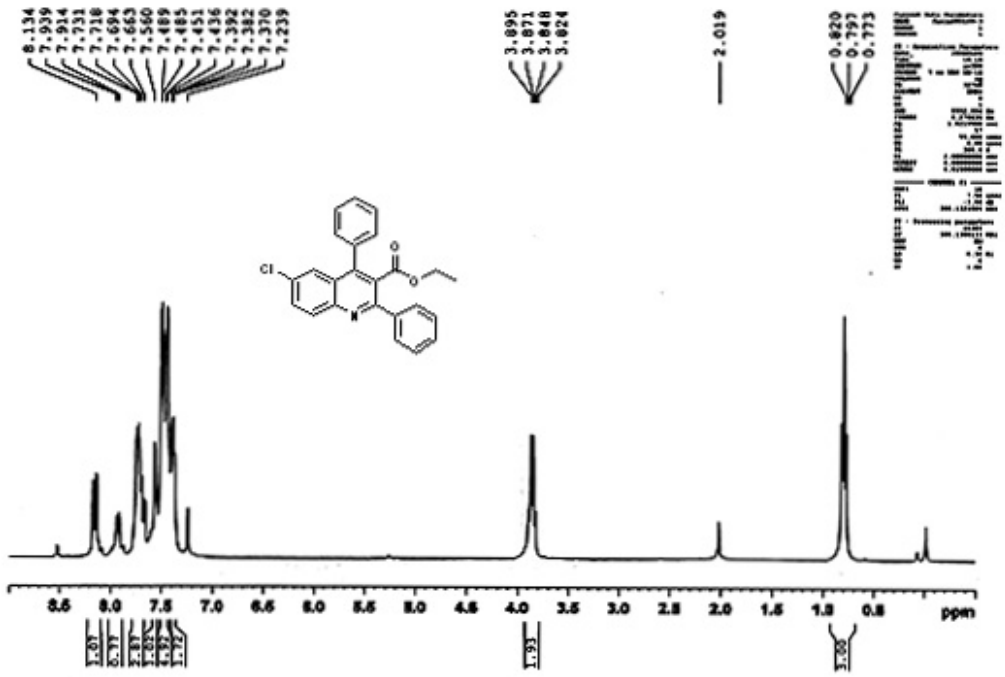

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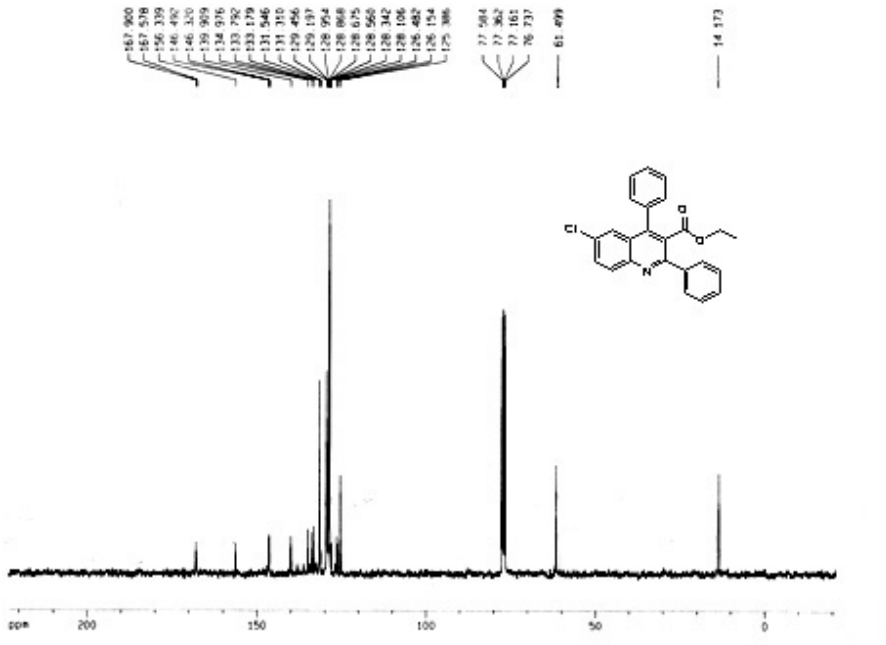
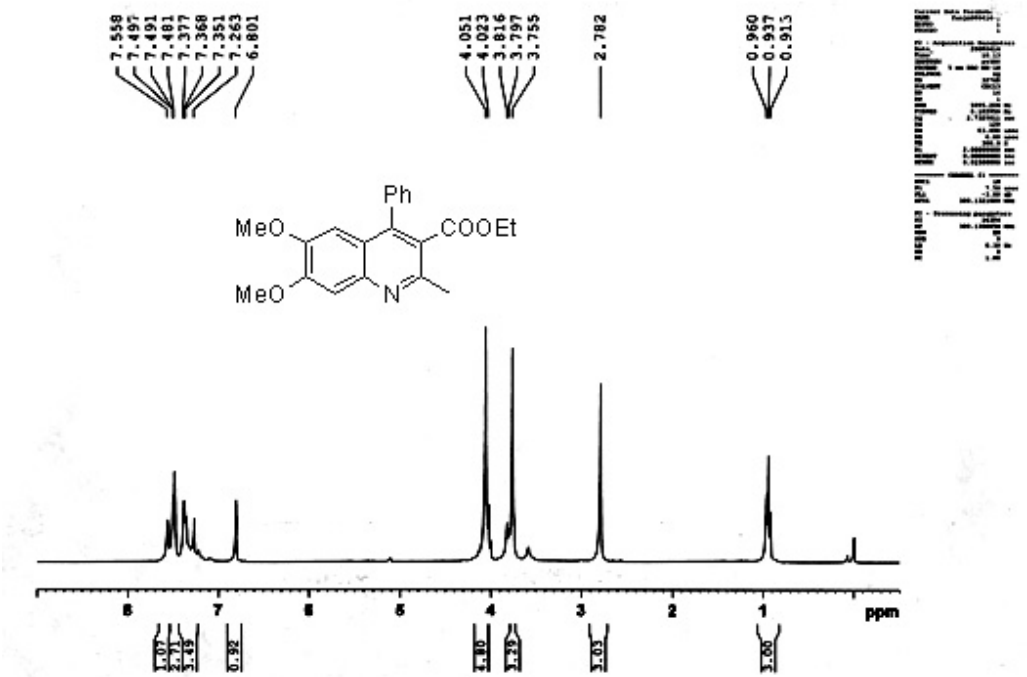


3m (^{1}H-NMR)



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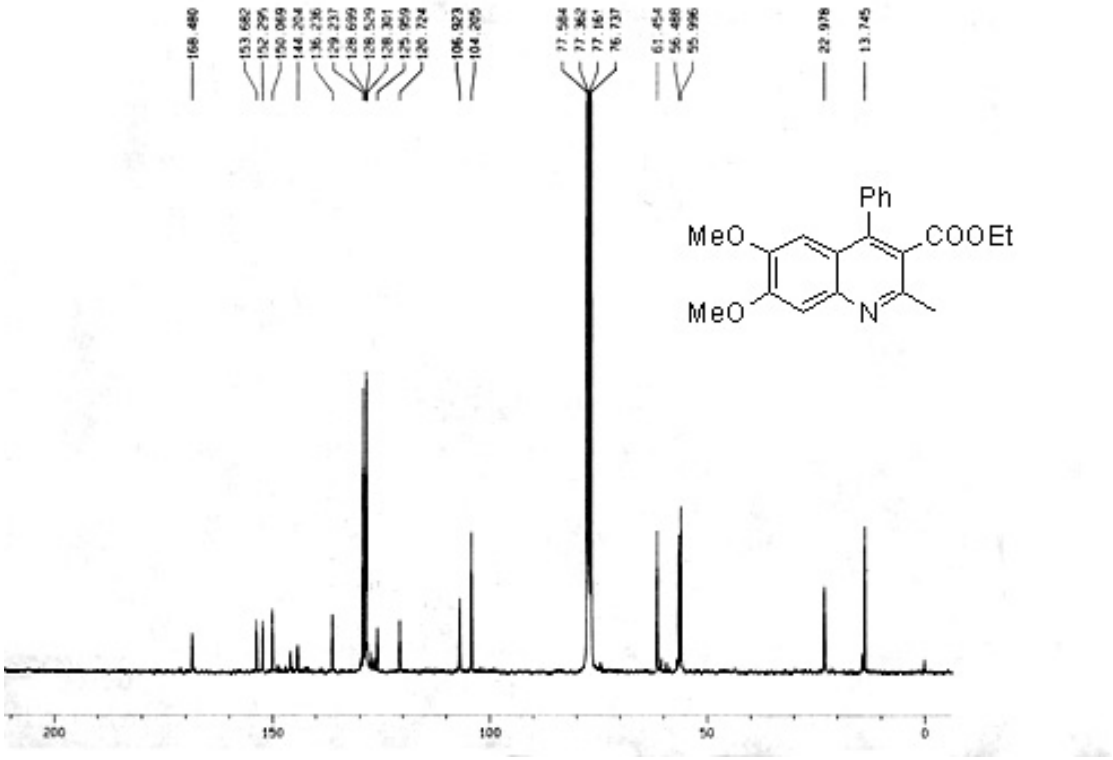

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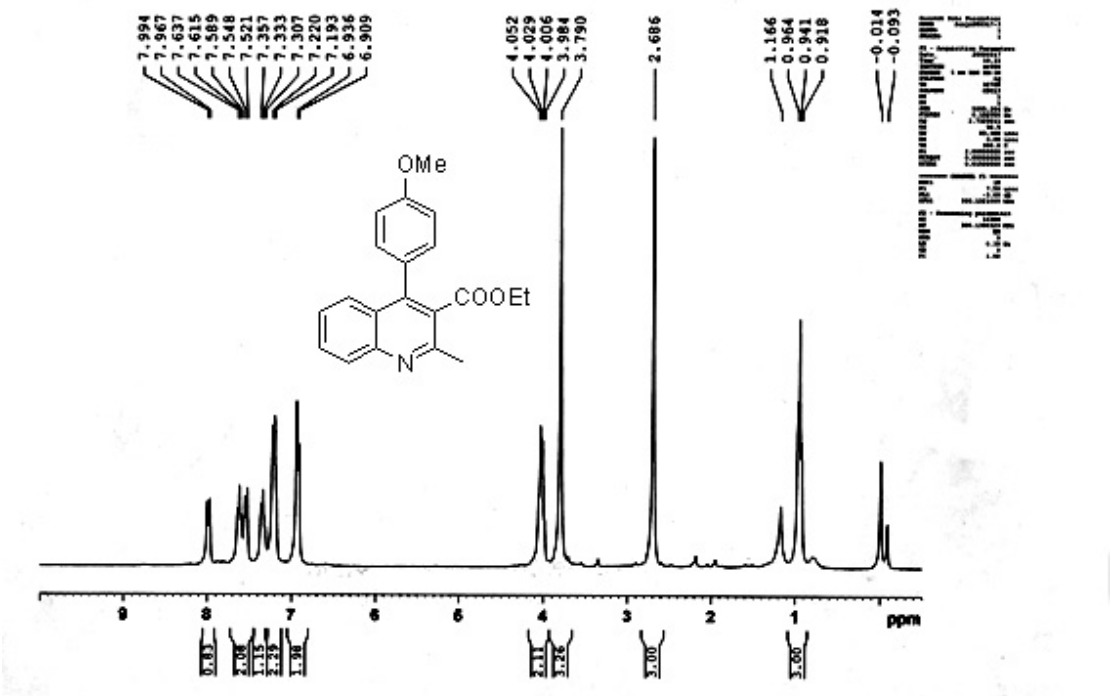

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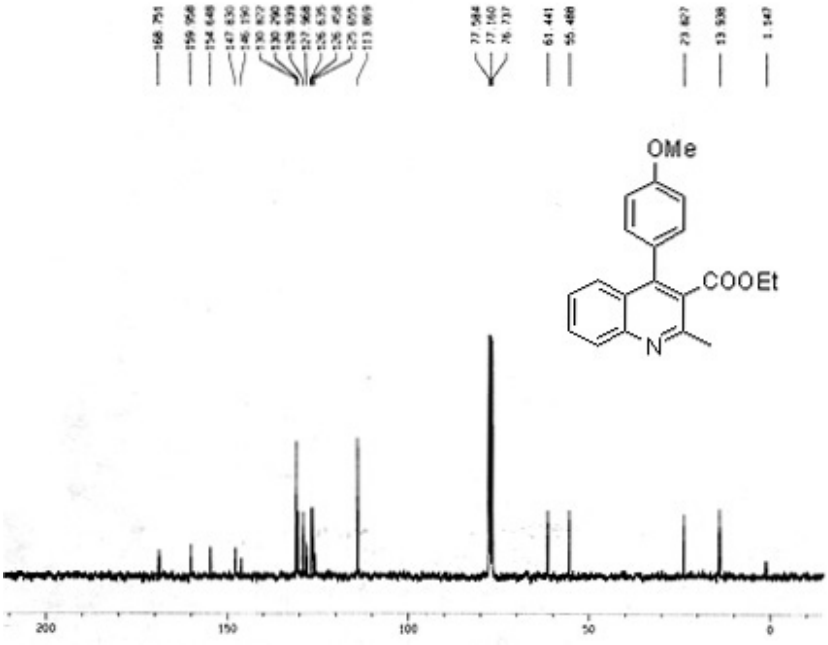

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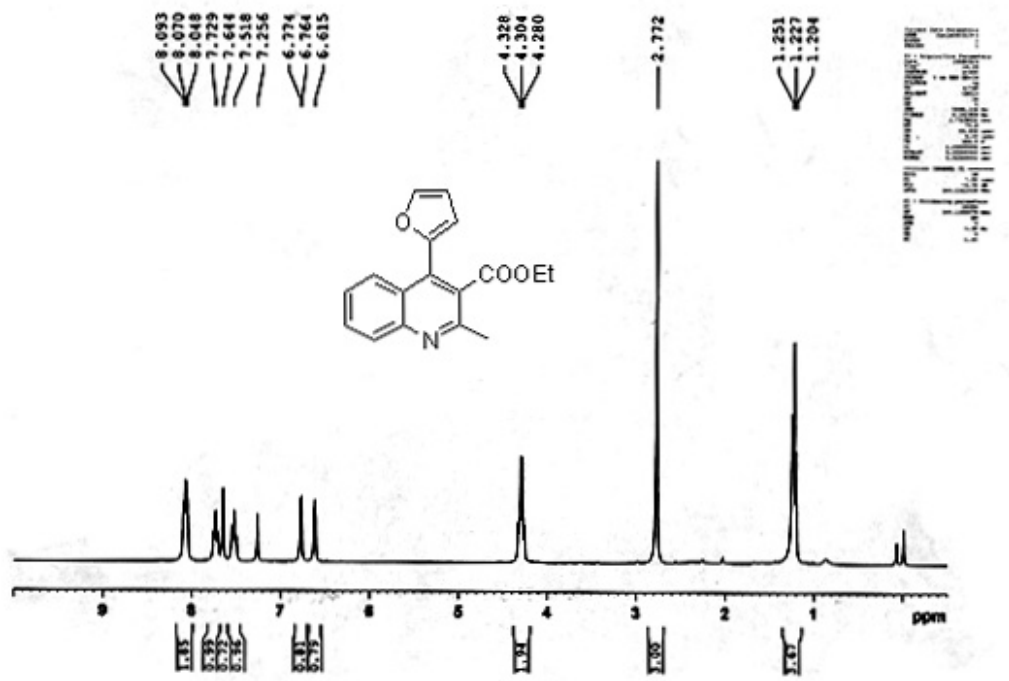
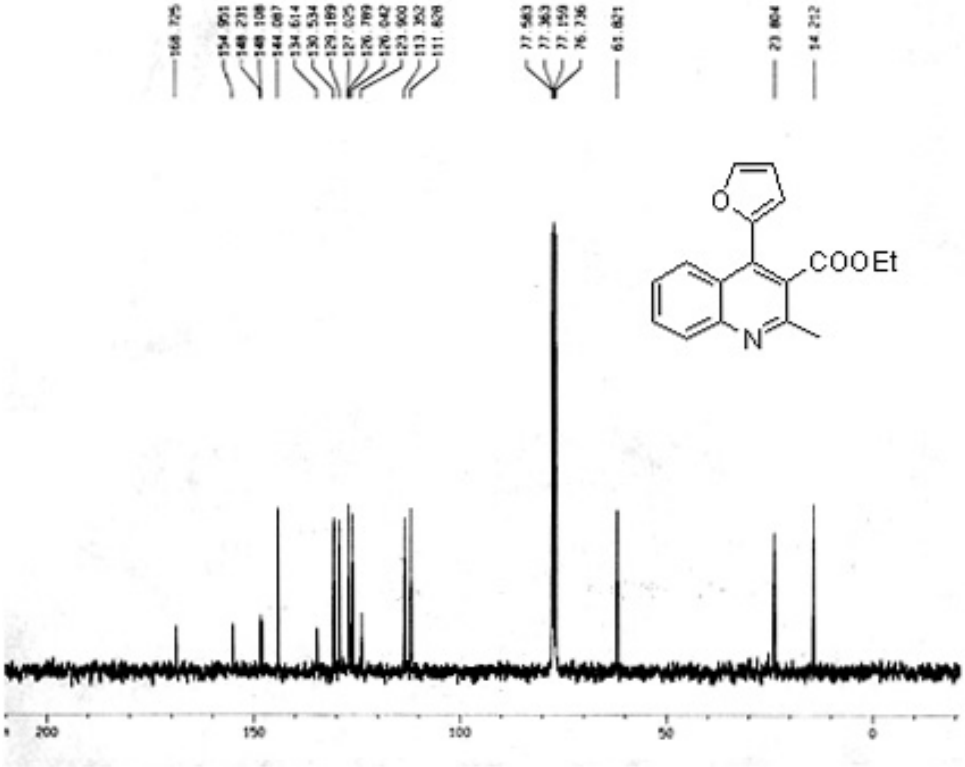


3o (^{13}C-NMR)



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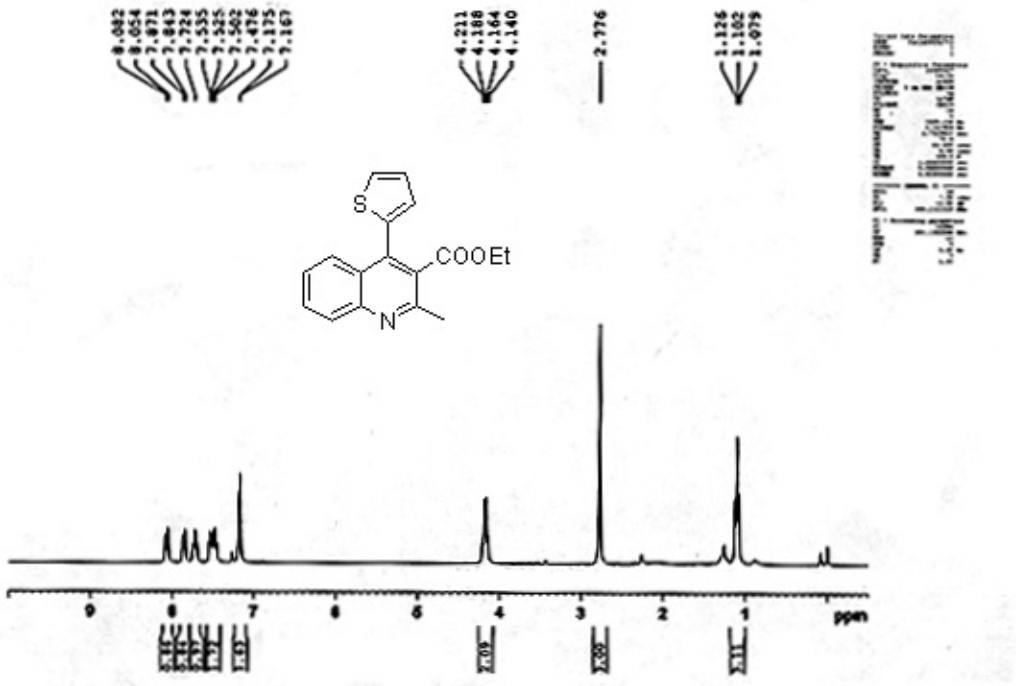

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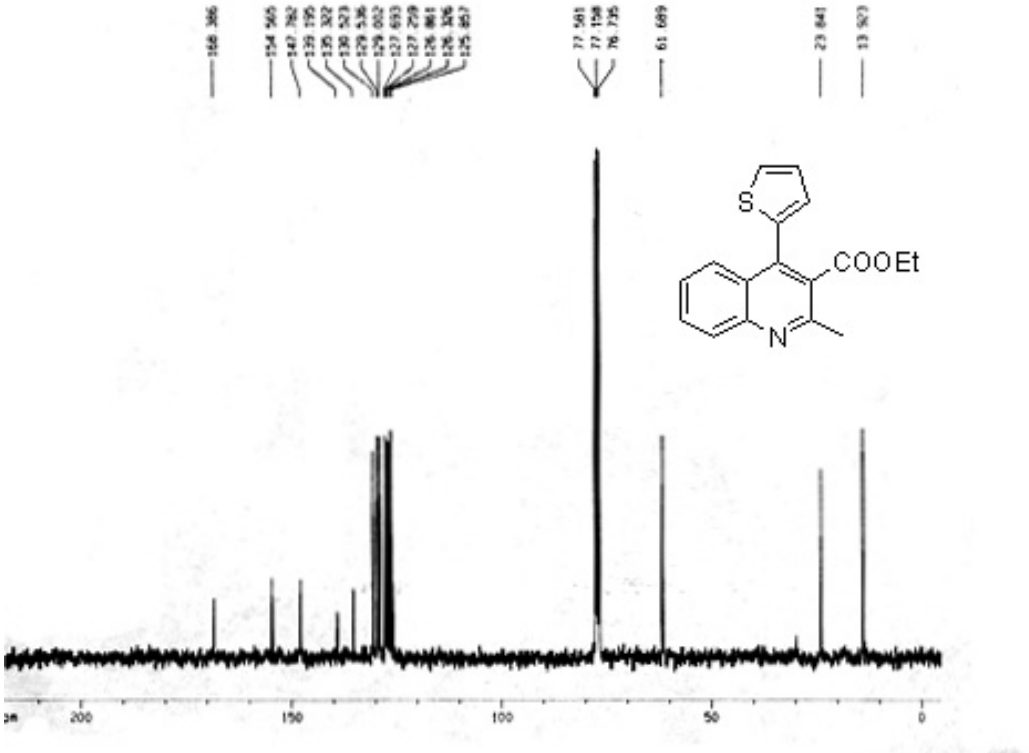

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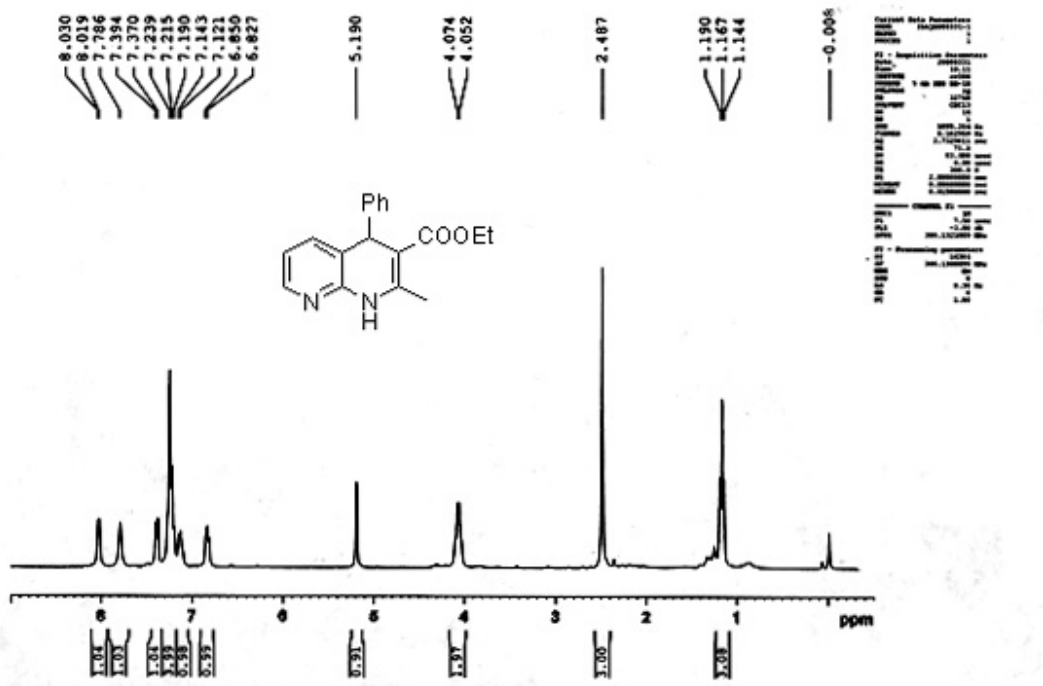

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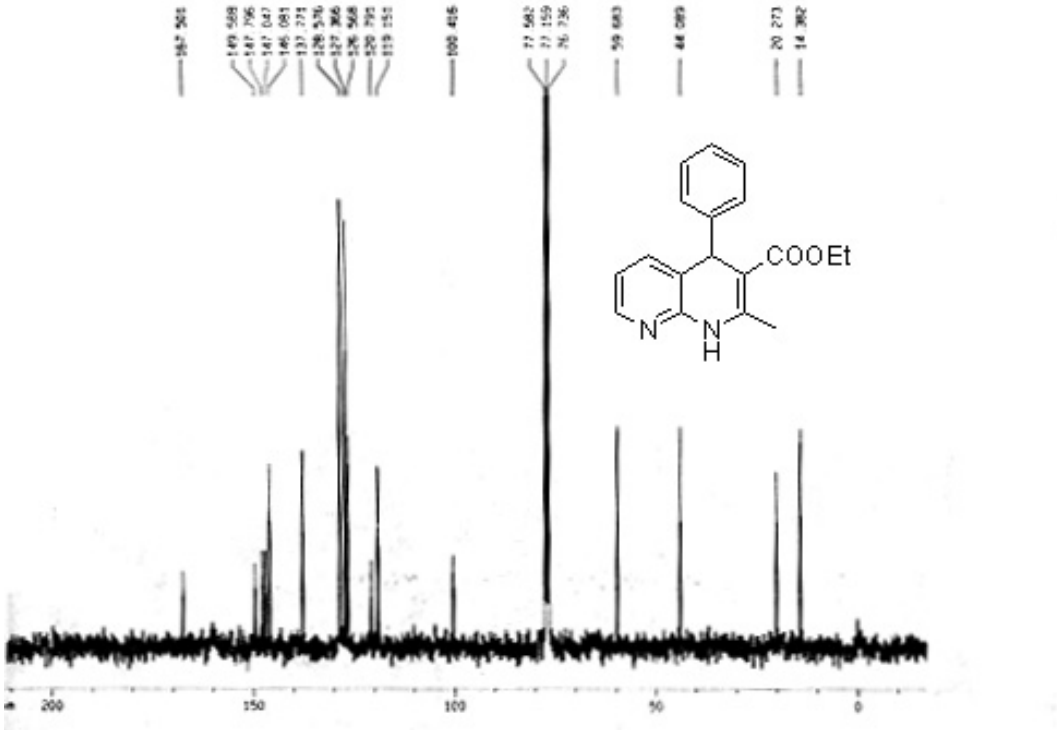
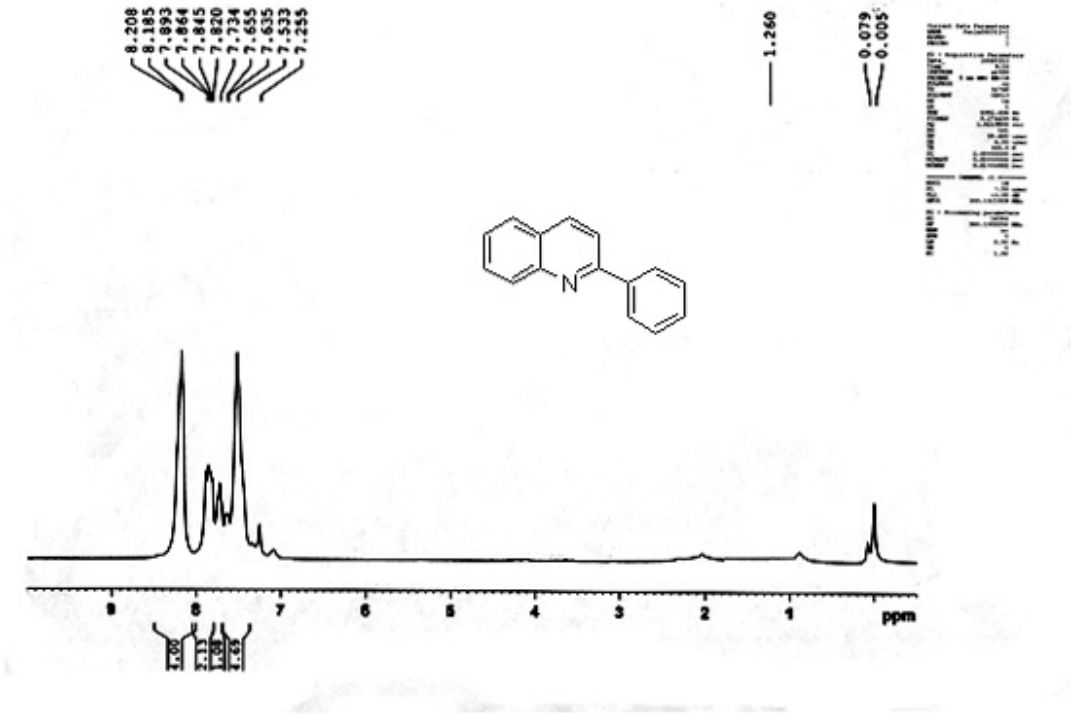
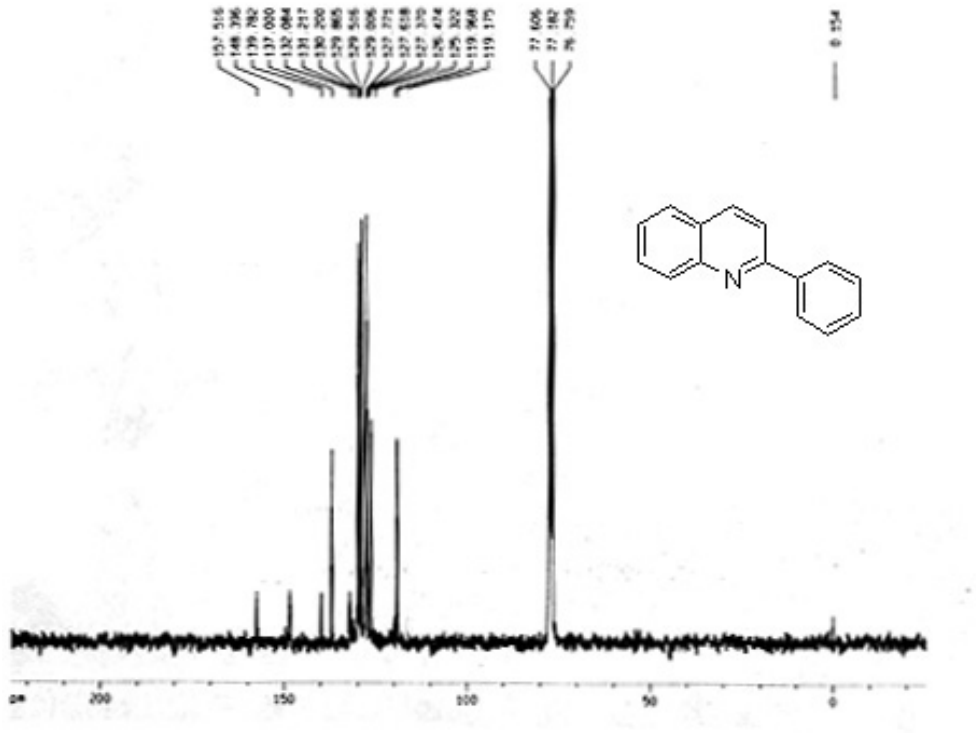


5a (^{1}H-NMR)



5a (^{13}C-NMR)



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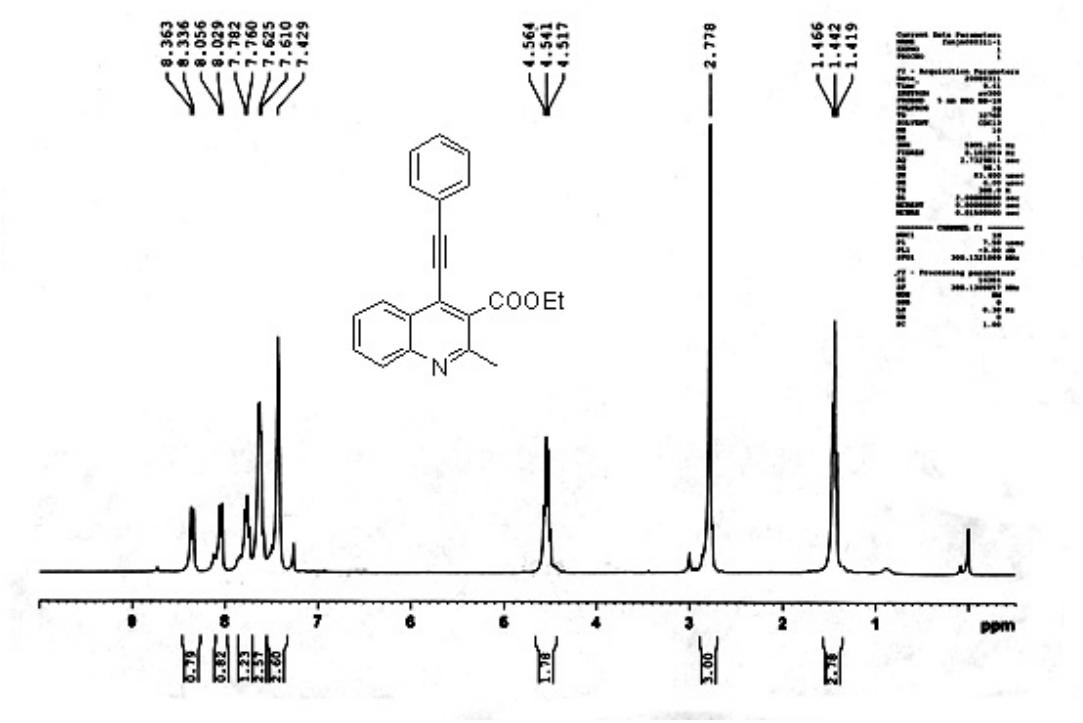

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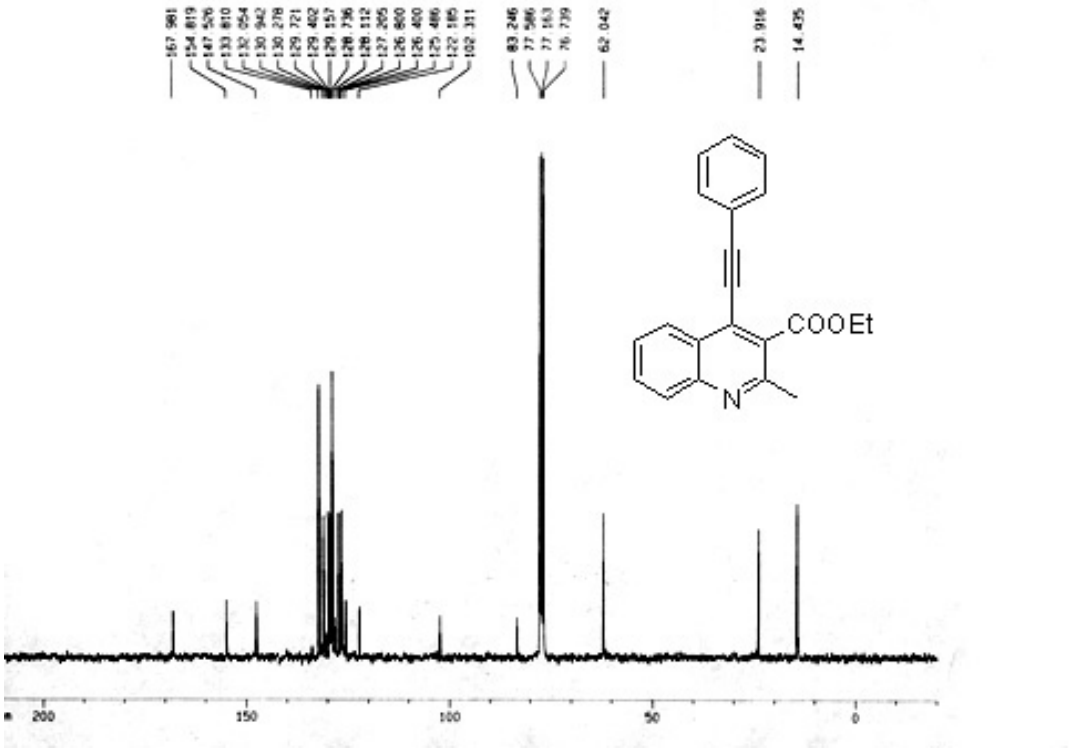
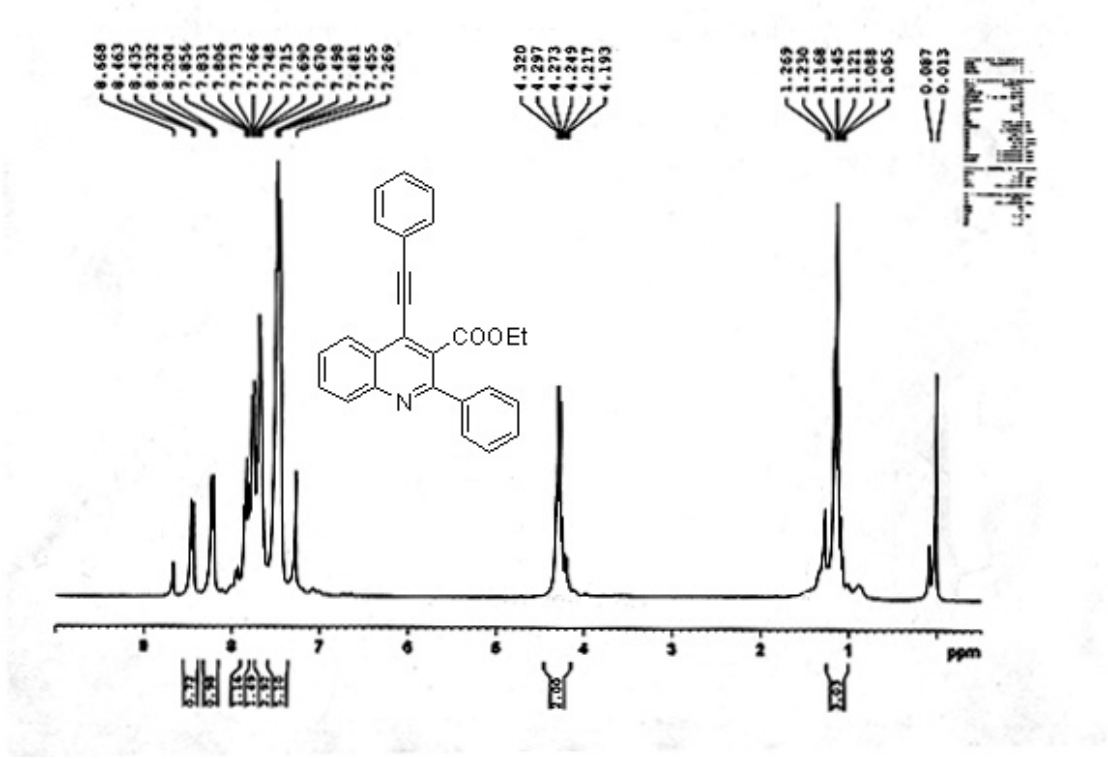


4b (^{1}H-NMR)



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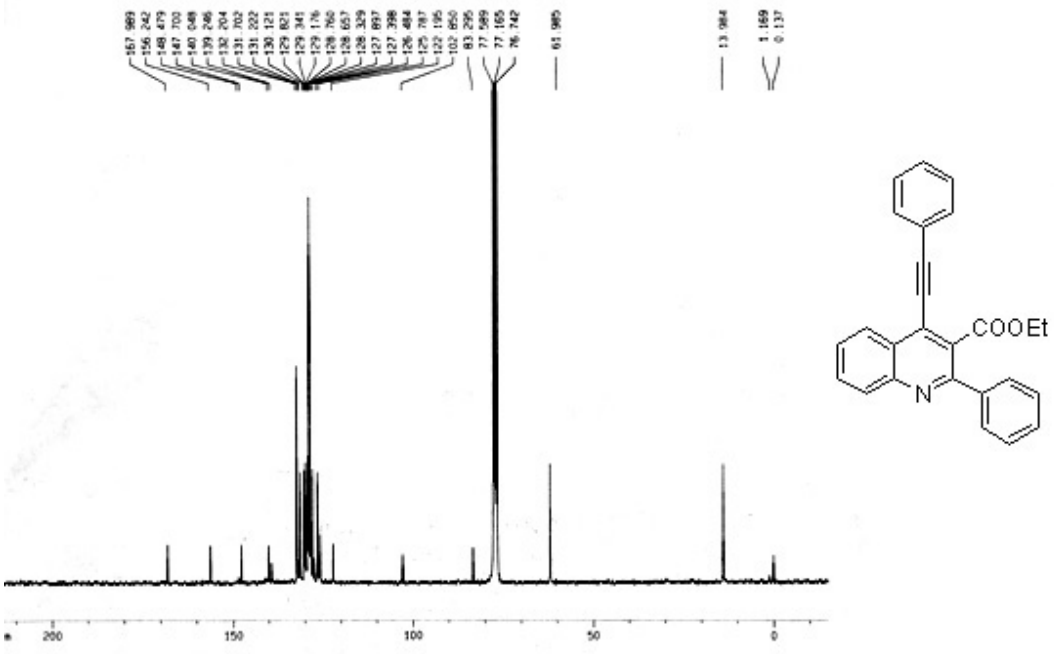
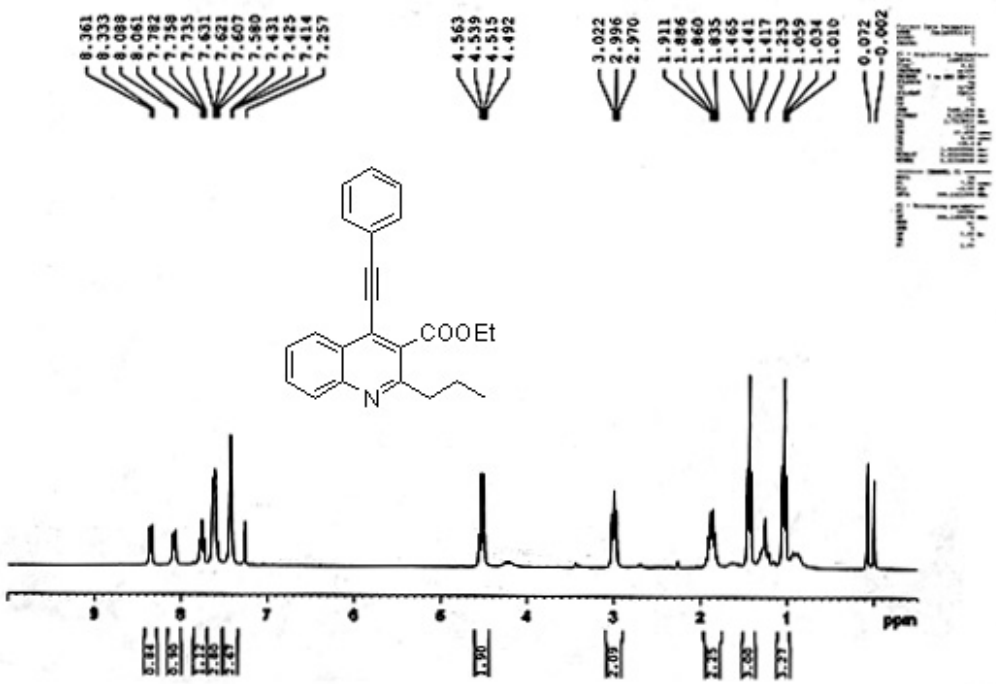
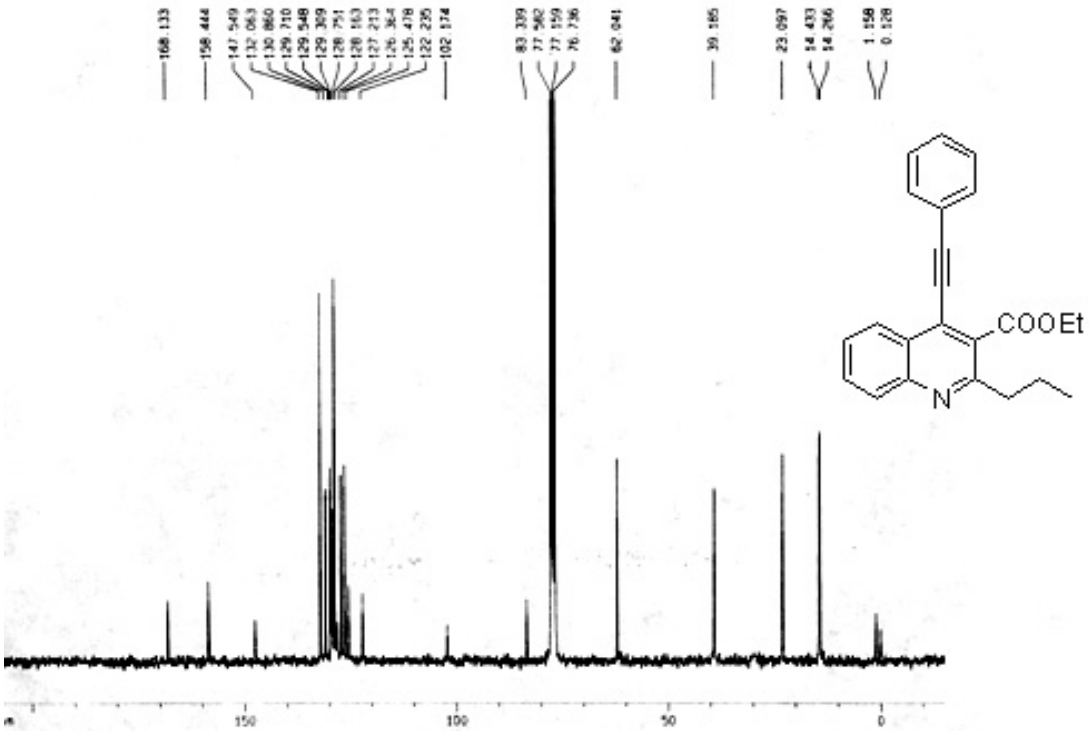


4c (^{1}H-NMR)



4c (^{13}C-NMR)



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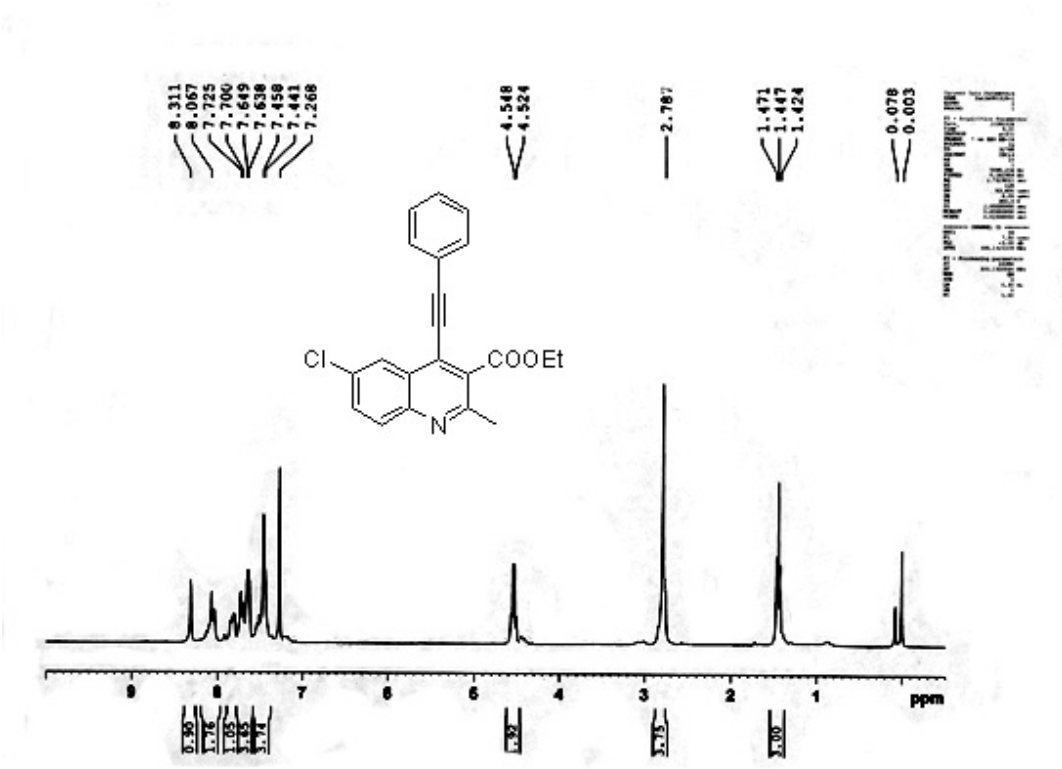

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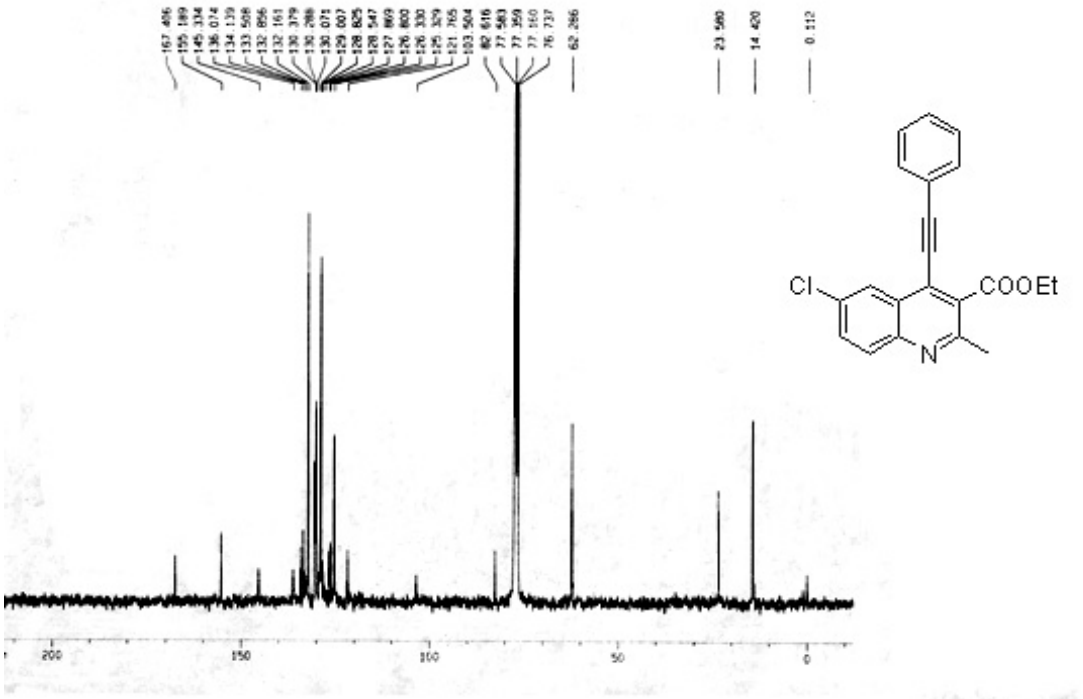

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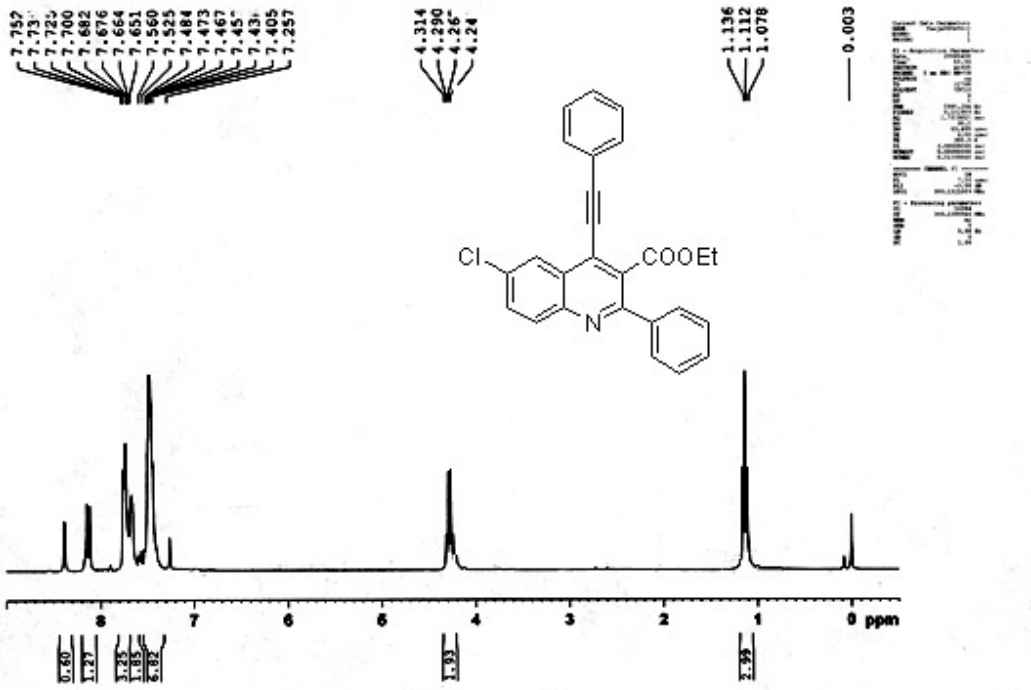

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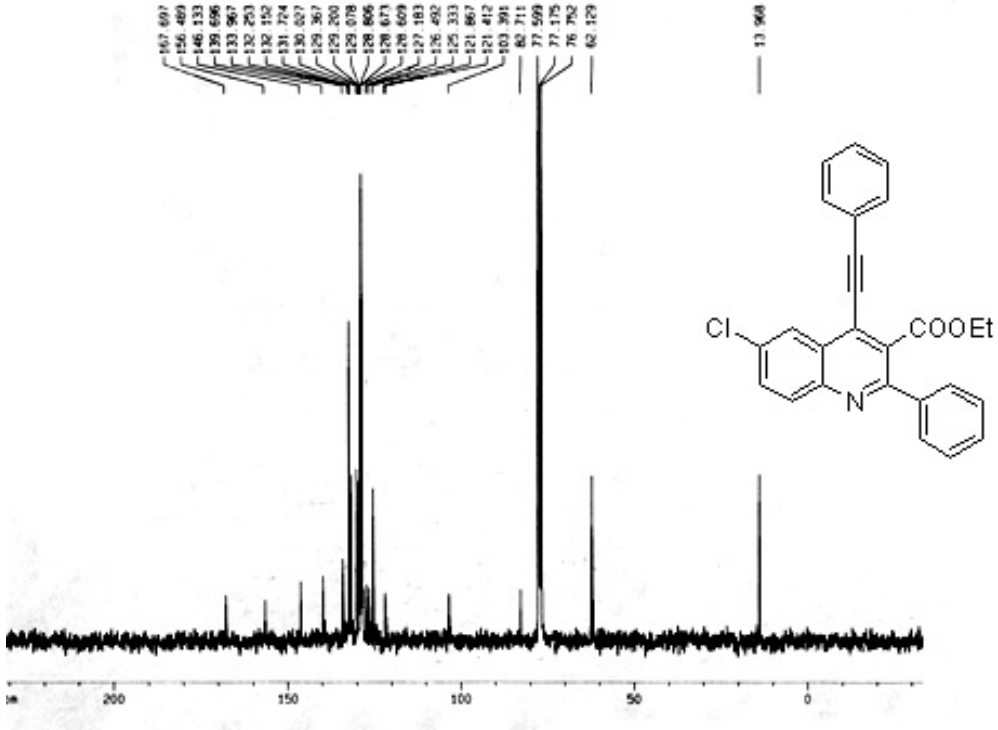
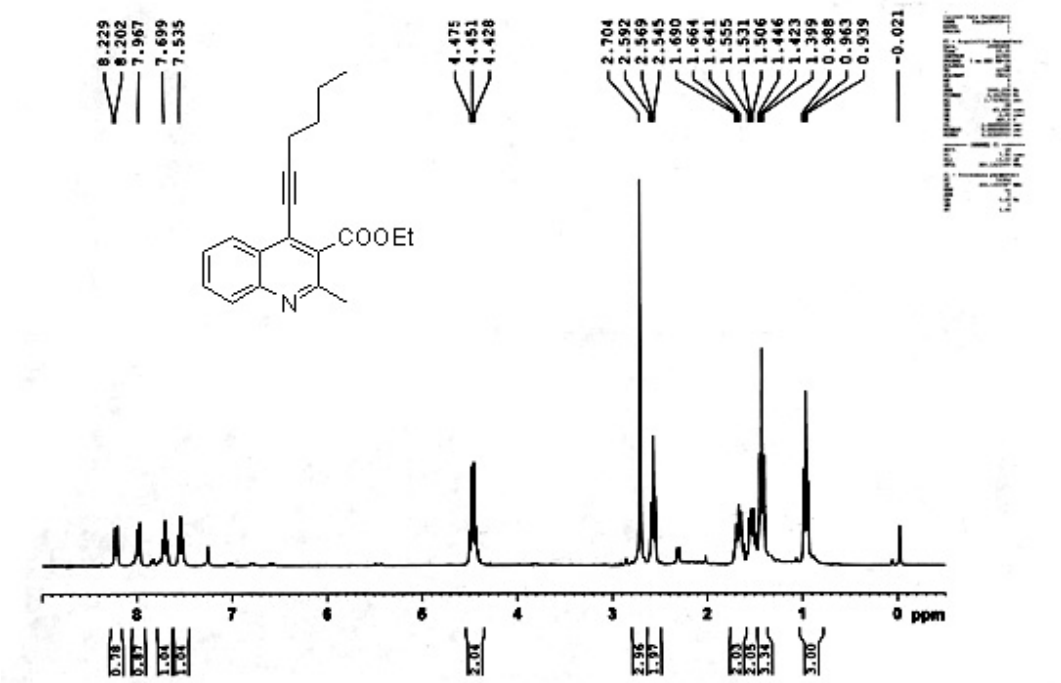
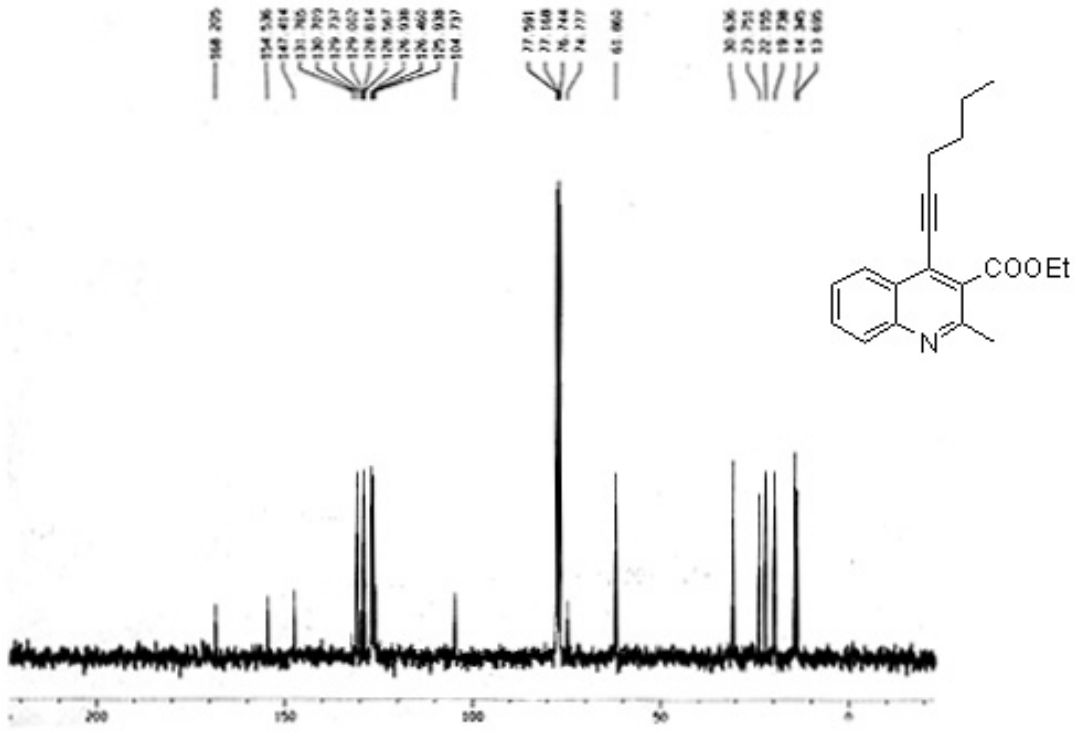


4f (^{1}H-NMR)



4f (^{13}C-NMR)



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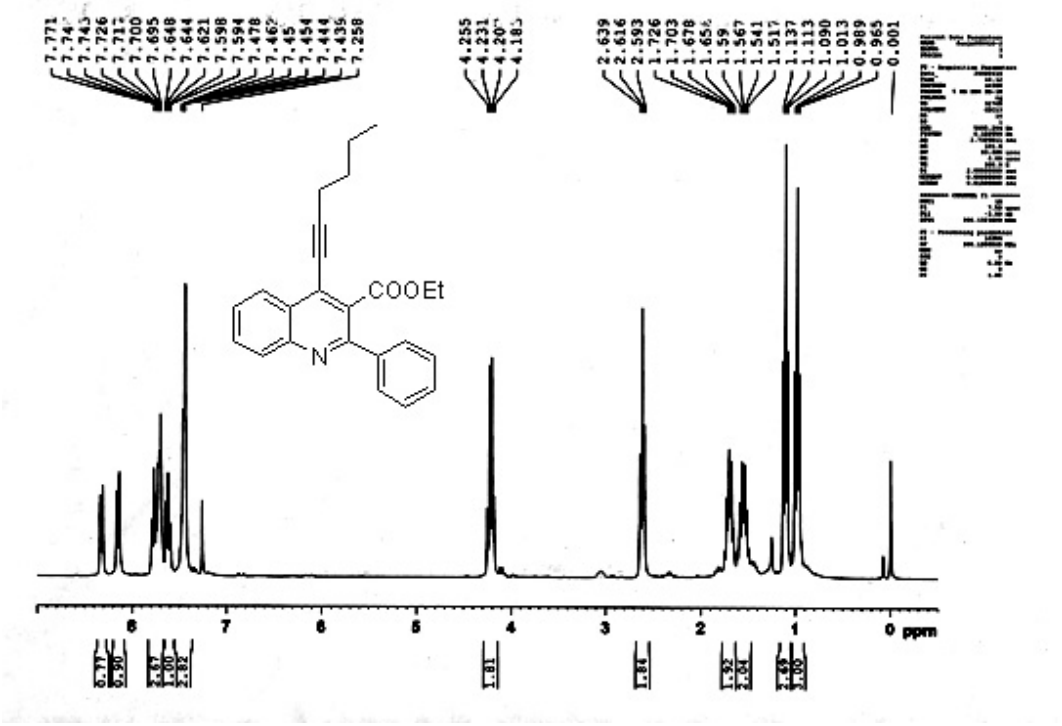
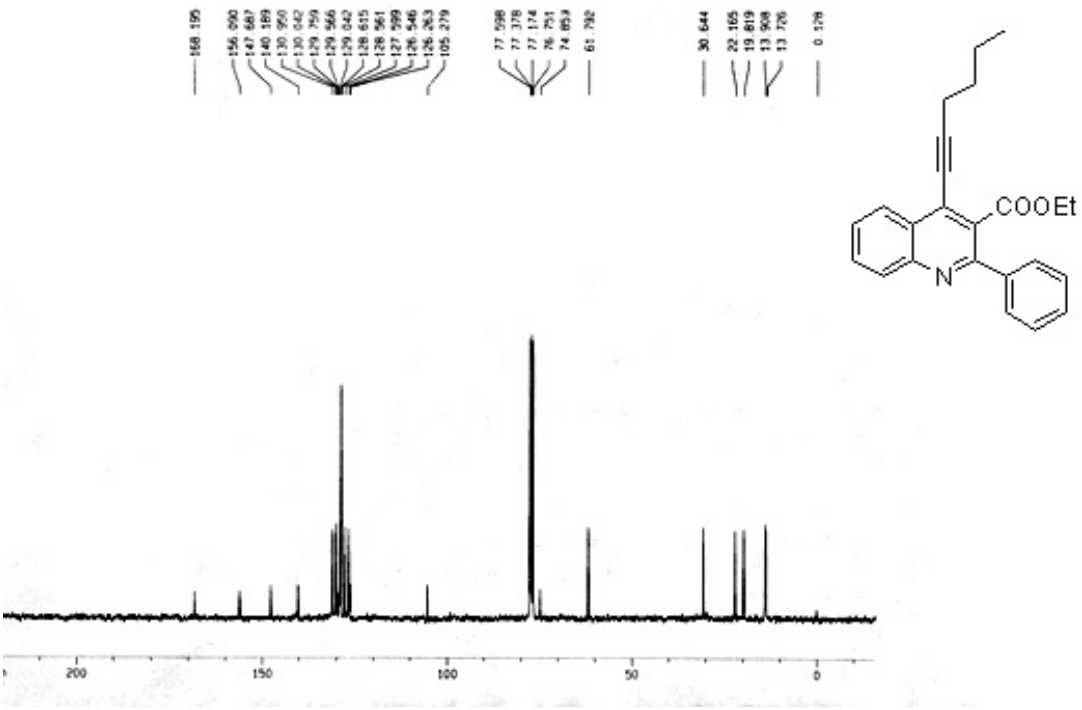


4g (^{13}C-NMR)



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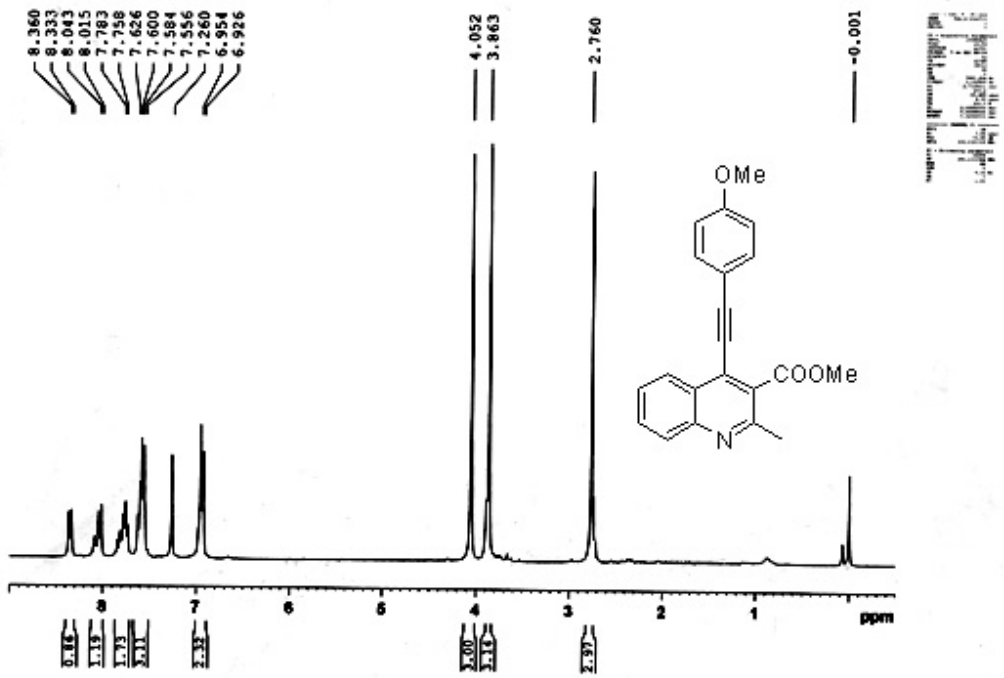

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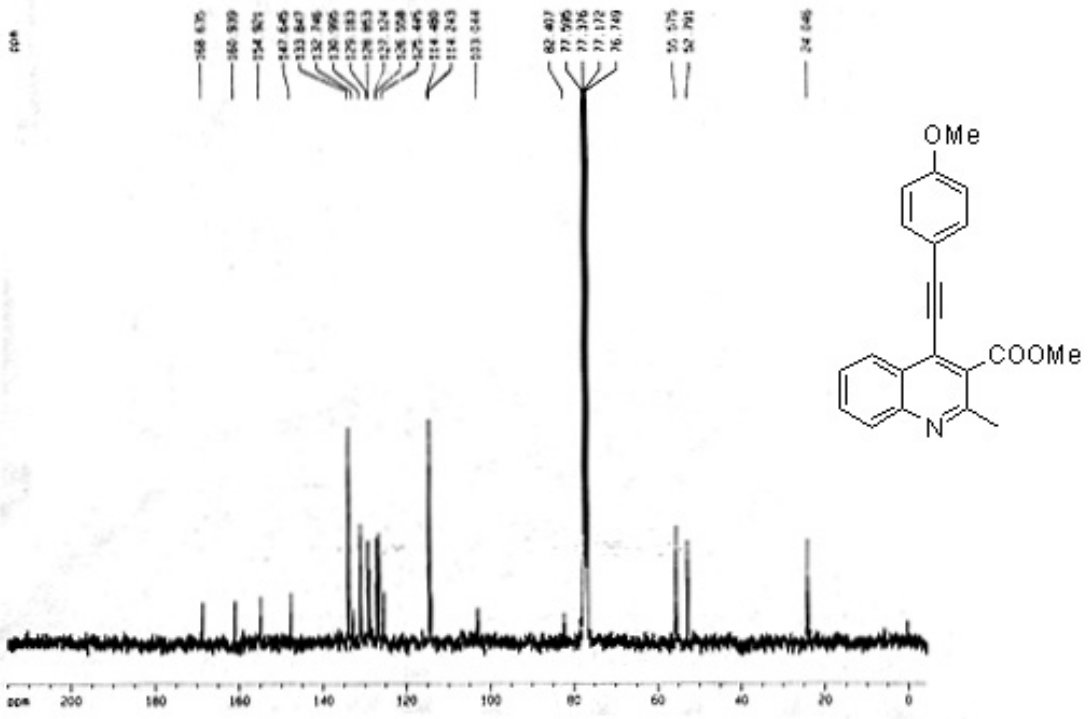
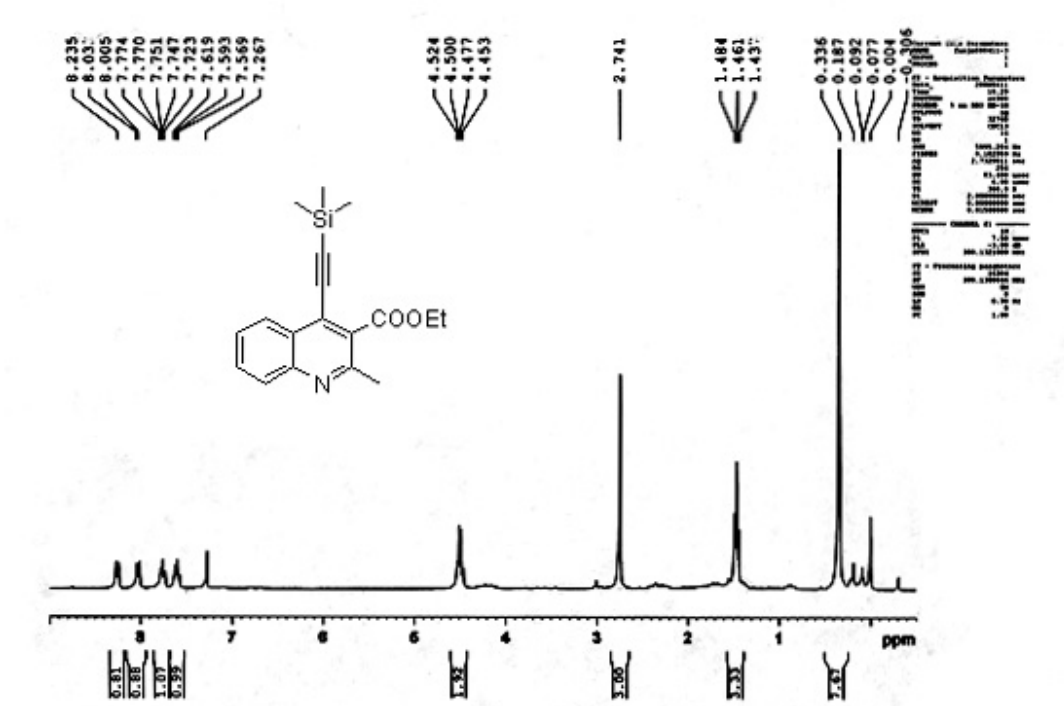


4i (^{1}H-NMR)



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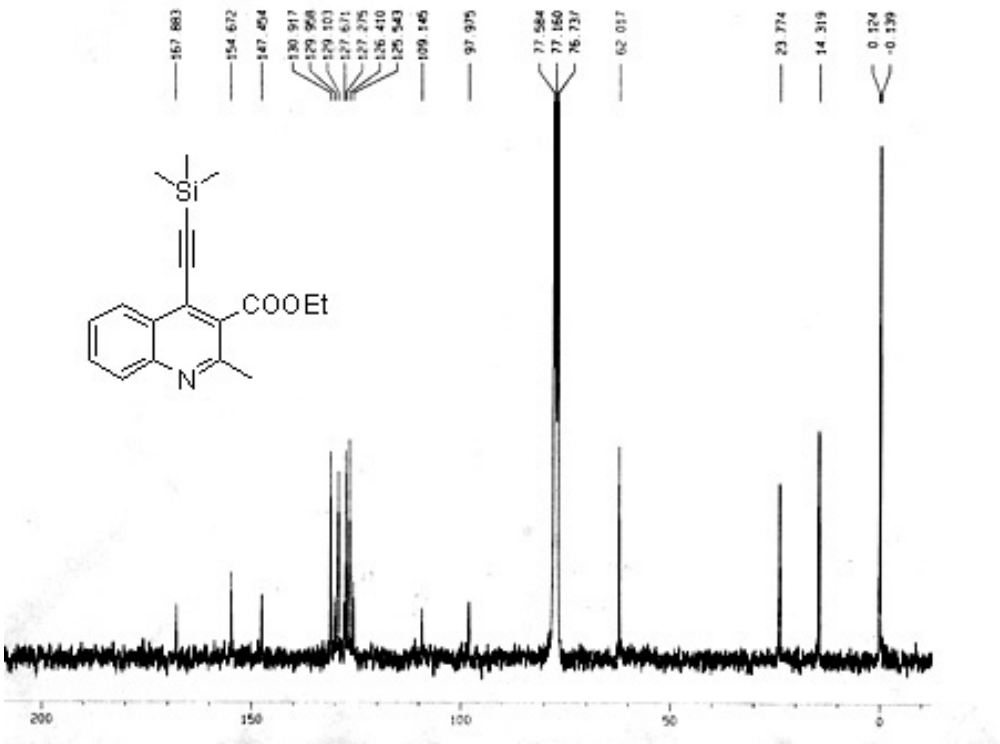

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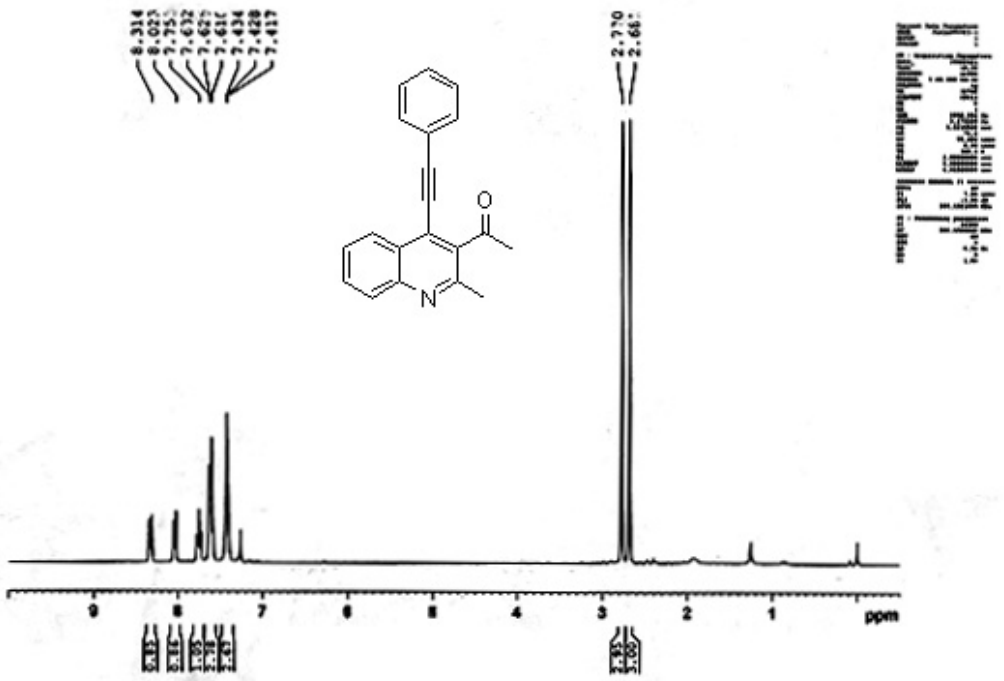

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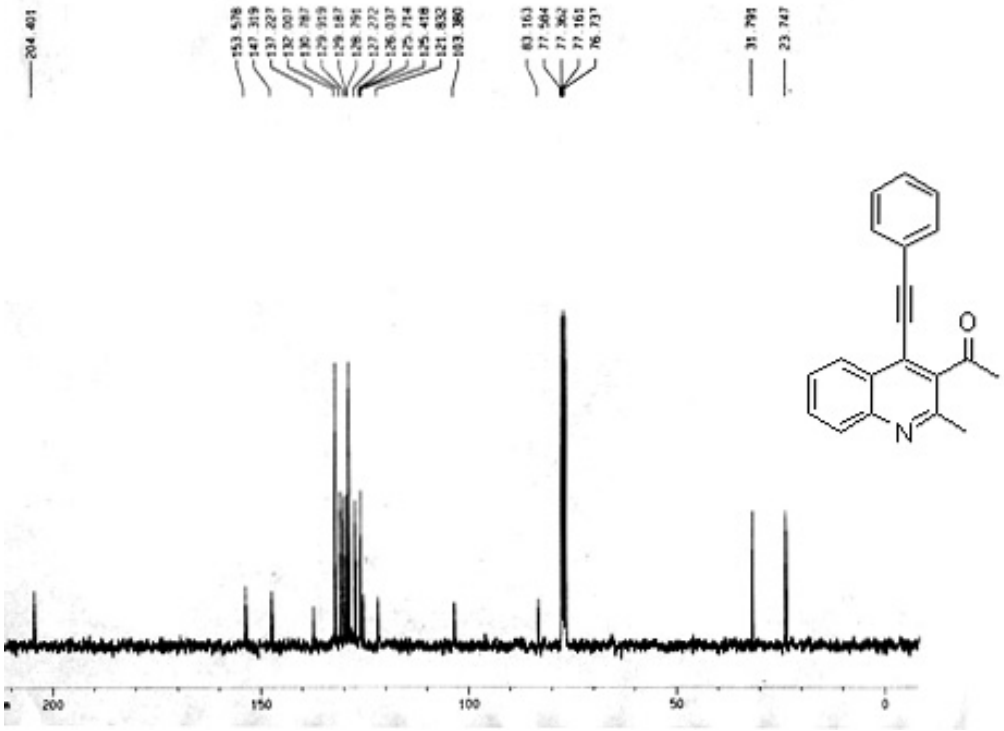
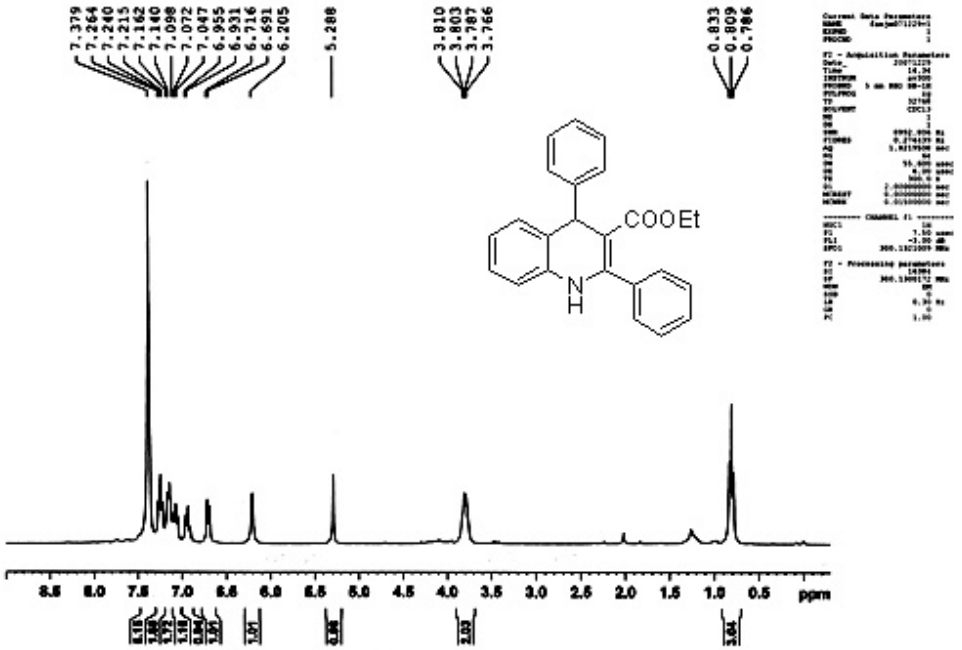


$3c_1$ (^{1}H-NMR)



$3c_1$(^{13}C-NMR)