

## Electronic Supplementary Information

### Gas-phase synthesis of 3-carboethoxy-quinolin-4-ones. A comprehensive computational mechanistic study to uncover the dark side of the Gould-Jacobs reaction

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**Abstract.** A set of 3-carboethoxy-quinolin-4-ones has been synthesized from diethyl 2-((arylamino)methylene) malonates through a Gould-Jacobs (G-J) cyclization using the flash vacuum pyrolysis (FVP) method. Mechanistic studies including calculations at first principles DFT and Coupled Cluster (CCSD(T)) levels of theory, along with insightful experiments, have been gathered to shed light on the complex multi-step process to afford quinolones. The G-J cyclization proceeded through a unimolecular process involving reactive species as iminoketenes, an azetinone and a quinolin-4(4*aH*)-one intermediates. The reaction was rate limited by a proton shift step in the pathway which leads to the final tautomeric product. In the gas phase pyrolysis of starting malonates, along with the expected 3-carboethoxy-quinolin-4-ones, 3-unsubstituted-quinolin-4-ones were obtained, and the ratio between these products was strongly dependent on the nature of the arylamino group. In order to explain the deethoxycarbonylation reaction, DFT and *ab initio* calculations were also accomplished.

## PART I. Experimental details and substance characterization data

### General procedure for the study of diethyl 2-((phenylamino)methylene) malonates (3a-f) cyclization under FVP conditions.

FVP reactions were carried out in a Thermolyne 21100 furnace using a vycor glass of 30 cm long and a 1.2 cm i.d. reactor (Figure 1). Temperatures were 250-500°C, being 330°C the optimized temperature, pressures of  $10^{-2}$  Torr, contact times were  $10^{-2}$  s, total reaction time 1 h and sample amounts were ~20 mg (0.076 – 0.051 mmol). After the experiments were completed, the pyrolysate was collected in a liquid N<sub>2</sub> trap and extracted with acetone. The solid product/s was/were filtered. Finally, both solid and soluble products were submitted to conventional analysis (<sup>1</sup>H NMR, <sup>13</sup>C NMR and GC/MS).

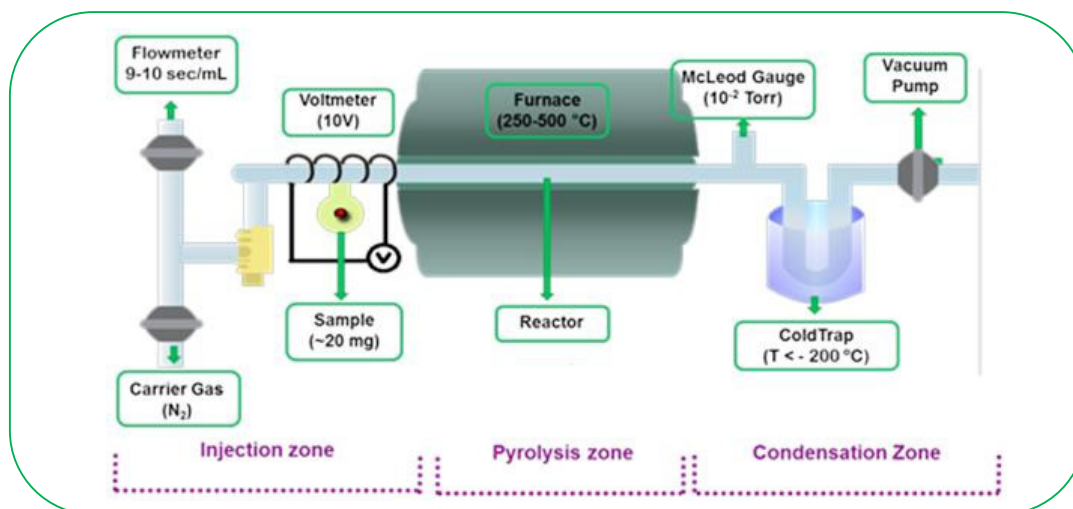
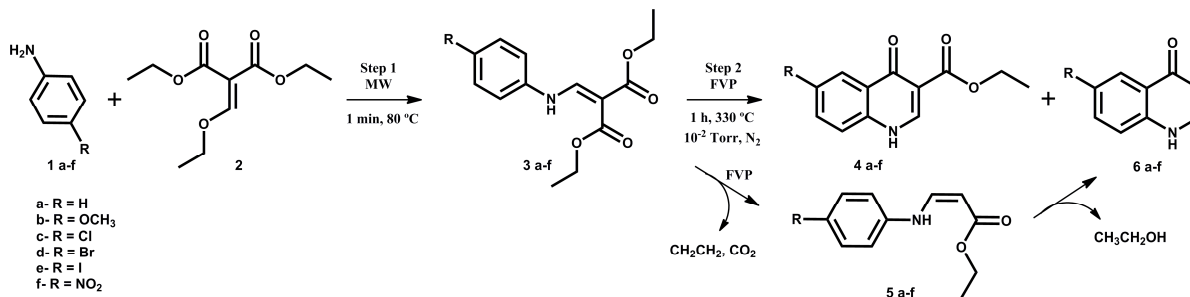


Figure S1. Flash Vacuum Pyrolysis reactor.

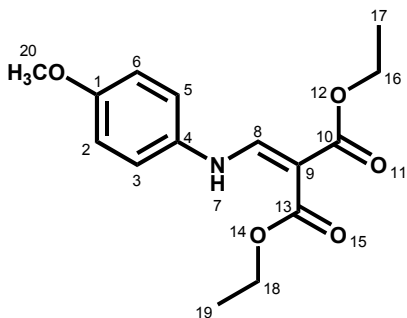


Scheme S1. Formation of 4-quinolone derivatives under FVP.

## CHARACTERIZATION OF FVP REACTANTS

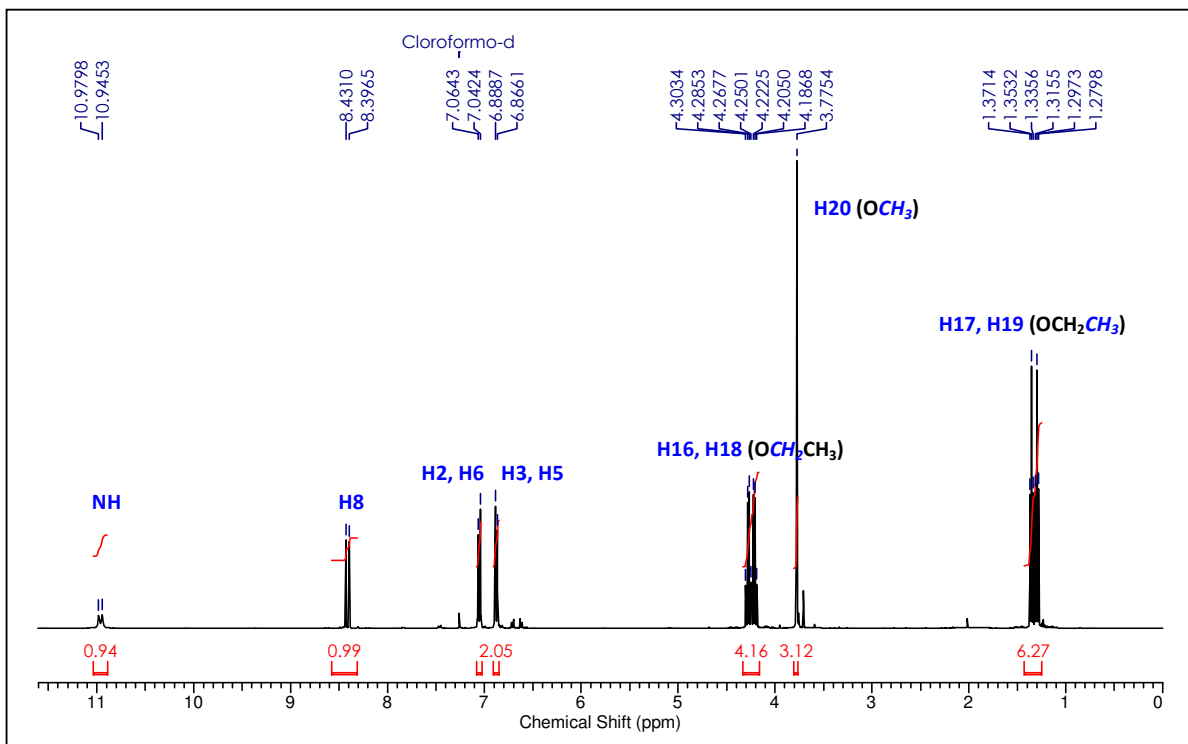
$^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advance II 400 ( $^1\text{H}$  at 400,  $^{13}\text{C}$  at 100 MHz) using  $\text{CDCl}_3$ ,  $\text{DMSO-}d_6$  and  $\text{TFA-}d_1$  as solvents. Chemical shifts are reported in parts per million (ppm) downfield from TMS.

### Diethyl 2-(((4-methoxyphenyl)amino)methylene)malonate (**3b**)



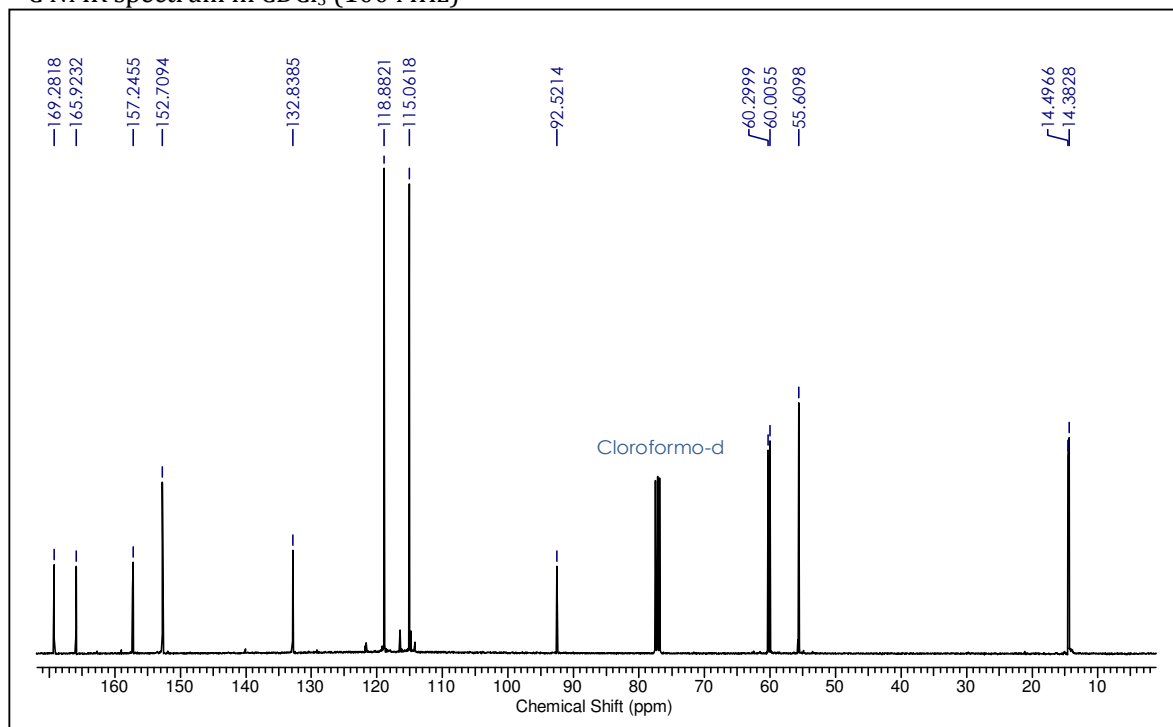
$\text{C}_{15}\text{H}_{19}\text{NO}_5$   
Molecular Weight: 293.32 g/mol  
Description: yellow liquid

$^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  (400 MHz)



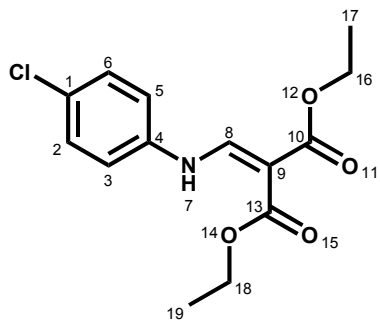
$\delta$  (ppm) : 1.29 (t, 3H,  $J=7.14$  Hz); 1.35 (t, 3H,  $J=7.16$  Hz); 3.77 (s, 3H); 4.21 (q, 2H,  $J=7.14$  Hz); 4.27 (q, 2H,  $J=7.11$  Hz); 6.87 (d, 2H,  $J=9.04$  Hz); 7.05 (d, 2H,  $J=8.76$  Hz); 8.41 (d, 1H,  $J=13.80$  Hz); 10.95 (d, 1H,  $J=13.80$  Hz).

<sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> (100 MHz)



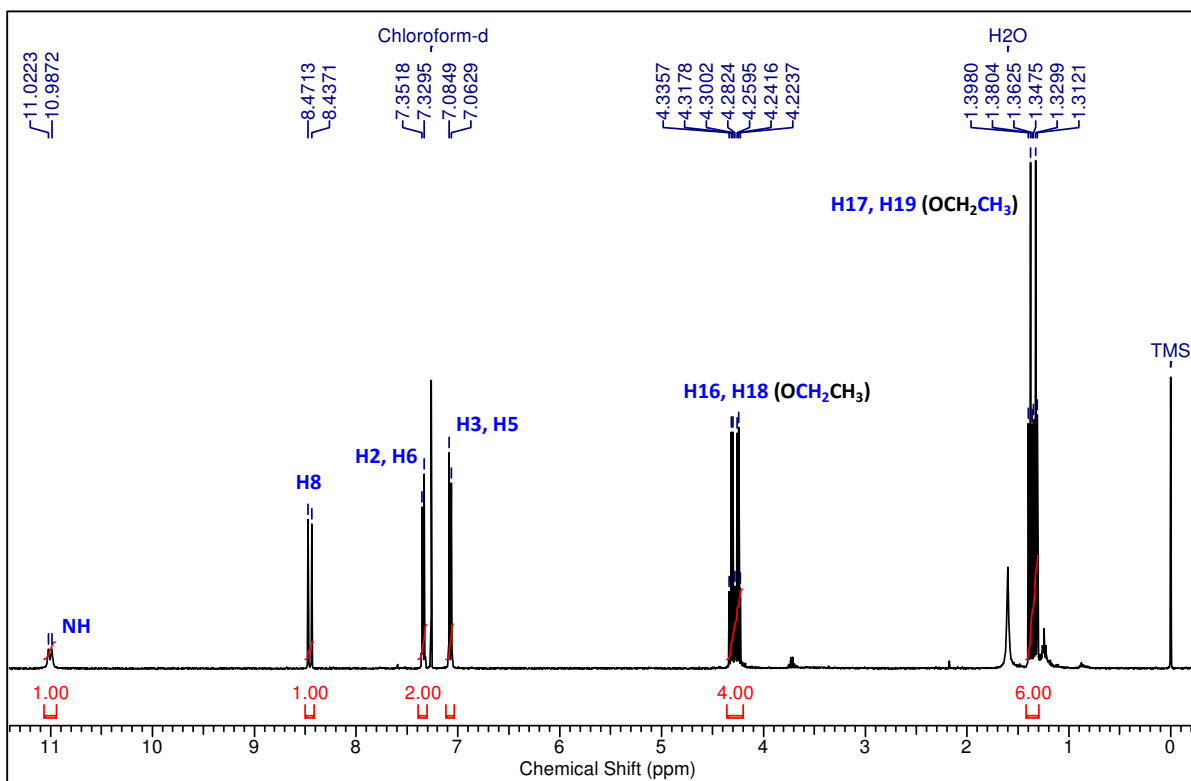
$\delta$  (ppm) : 14.38; 14.50; 55.61; 60.00; 60.30; 92.52; 115.06; 118.88; 132.84; 152.71; 157.24; 165.92; 169.28.

### Diethyl 2-(((4-chlorophenyl)amino)methylene)malonate (3c)



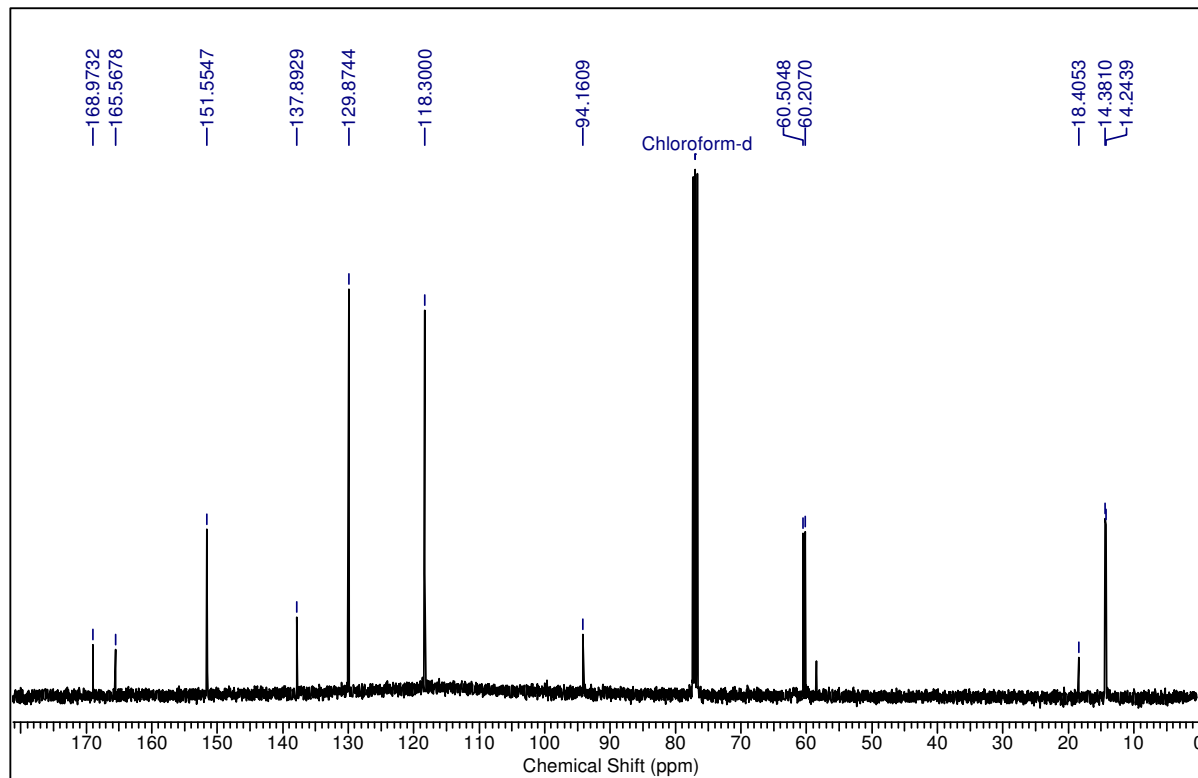
$C_{14}H_{16}ClNO_4$   
Molecular Weight: 297.73 g/mol  
Description: beige solid

$^1H$  NMR spectrum in  $CDCl_3$  (400 MHz)



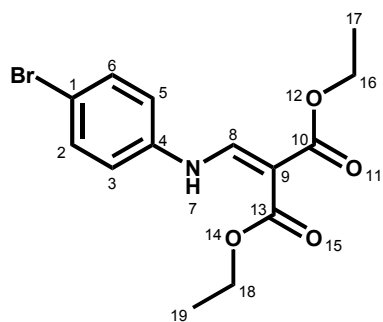
$\delta$  (ppm) : 1.33 (t, 3H,  $J$ = 7.08 Hz); 1.38 (t, 3H,  $J$ = 7.10 Hz); 4.25 (q, 2H,  $J$ = 7.15 Hz); 4.31 (q, 2H,  $J$ = 7.11 Hz); 7.07 (d, 2H,  $J$ = 8.80 Hz); 7.34 (d, 2H,  $J$ = 8.92 Hz); 8.45 (d, 1H,  $J$ = 13.68 Hz); 11.00 (d, 1H,  $J$ = 14.04 Hz).

$^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  (100 MHz)



$\delta$  (ppm): 14.24; 14.38; 18.40; 60.21; 60.50; 94.16; 118.30; 129.87; 137.89; 151.55; 165.57; 168.97.

### Diethyl 2-(((4-bromophenyl)amino)methylene)malonate (3d)

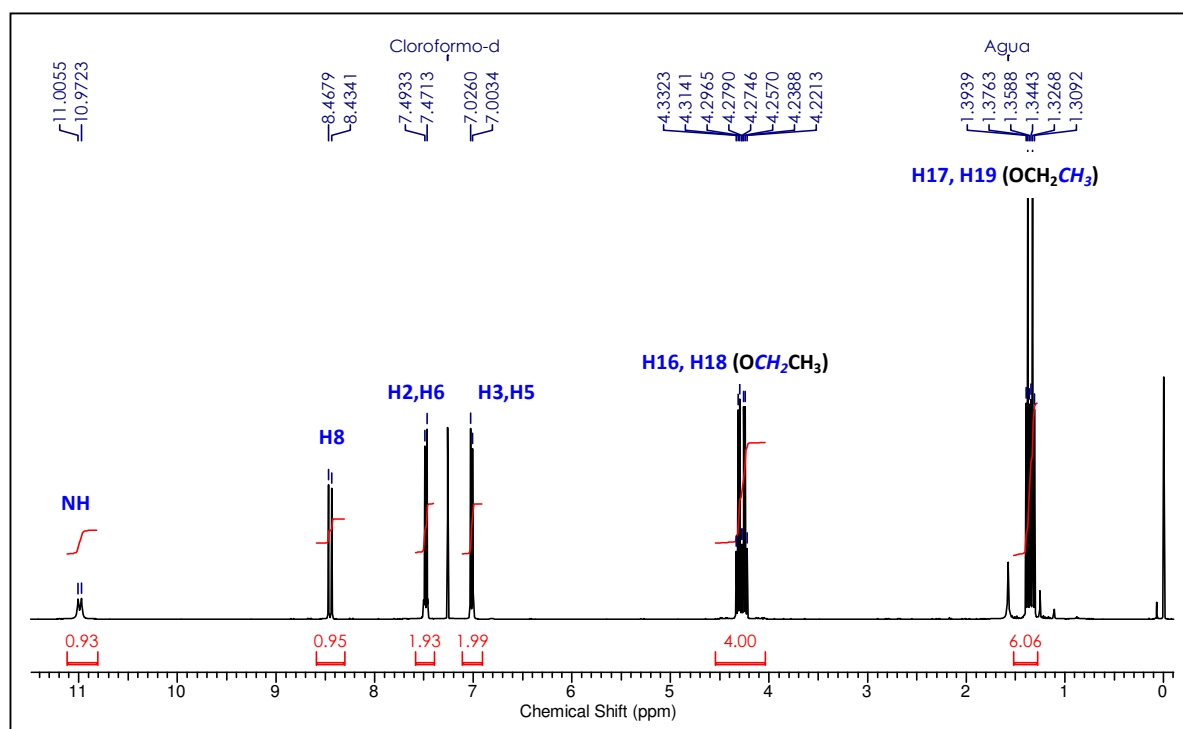


C<sub>14</sub>H<sub>16</sub>BrNO<sub>4</sub>

Molecular Weight: 342.19 g/mol

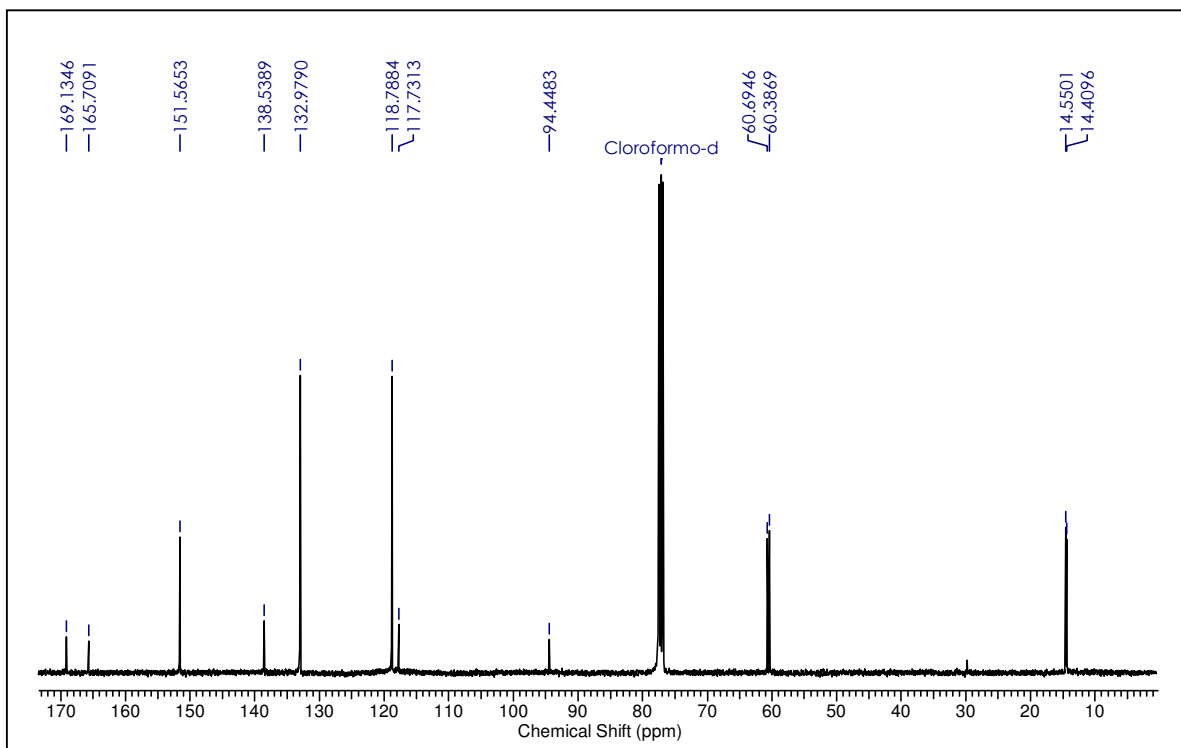
Description: beige solid

<sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> (400 MHz)



$\delta$  (ppm) : 1.32 (t, 3H,  $J=7.02$  Hz); 1.37 (t, 3H,  $J=7.02$  Hz); 4.24 (q, 2H,  $J=7.11$  Hz); 4.30 (q, 2H,  $J=7.11$  Hz); 7.01 (d, 2H,  $J=9.04$  Hz); 7.48 (d, 2H,  $J=8.80$  Hz); 8.44 (d, 2H,  $J=13.52$  Hz); 10.99 (d, 1H,  $J=13.28$  Hz)

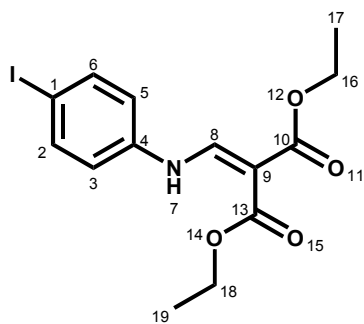
$^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  (100 MHz)



$\delta$  (ppm): 14.41; 14.55; 60.39; 60.69; 94.44; 117.73; 118.78; 132.98; 138.54; 151.56; 165.71; 169.13.

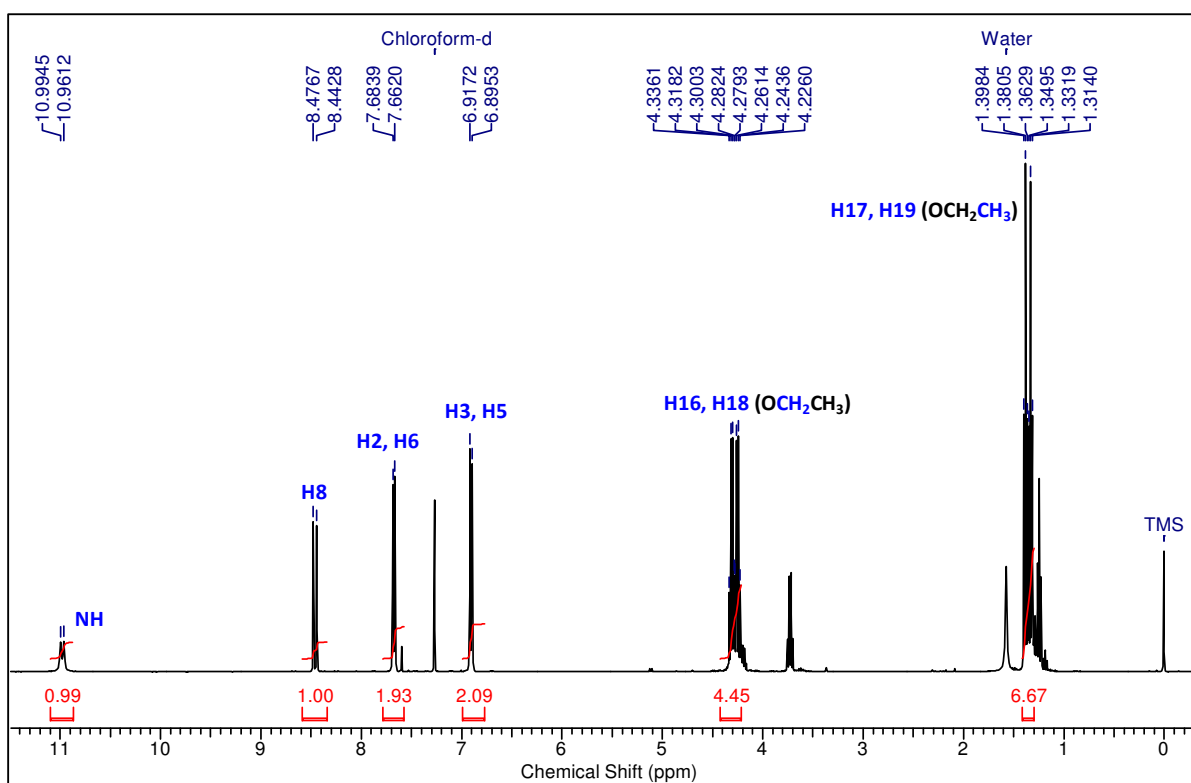


### Diethyl 2-(((4-iodophenyl)amino)methylene)malonate (3e)



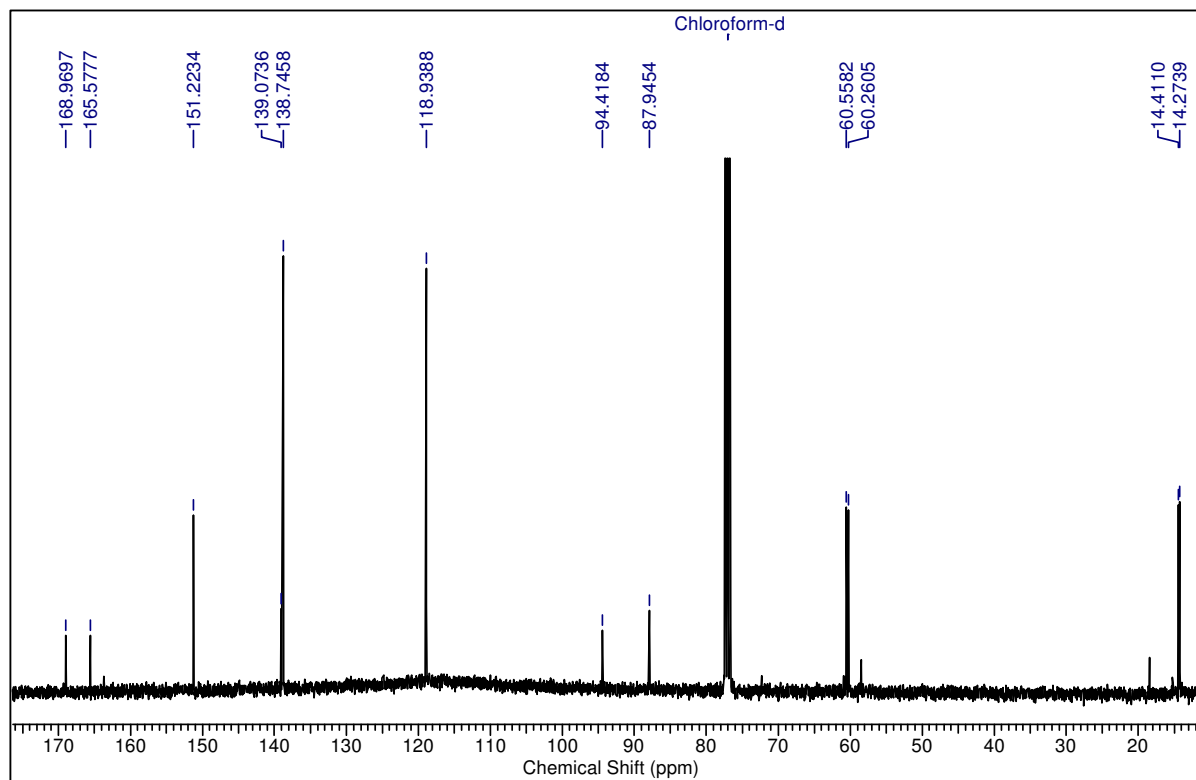
$C_{14}H_{16}INO_4$   
Molecular Weight: 389.19 g/mol  
Description: beige solid

$^1H$  NMR spectrum in  $CDCl_3$  (400 MHz)



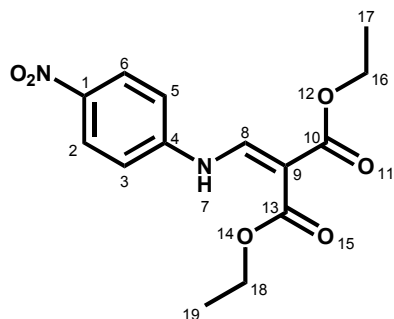
$\delta$  (ppm) : 1.33 (t, 3H,  $J=7.10$  Hz); 1.38 (t, 3H,  $J=7.10$  Hz); 4.25 (q, 2H,  $J=7.11$  Hz); 4.31 (q, 2H,  $J=7.16$  Hz); 6.91 (d, 2H,  $J=8.76$  Hz); 7.67 (d, 2H,  $J=8.76$  Hz); 8.46 (d, 2H,  $J=13.56$  Hz); 10.98 (d, 1H,  $J=13.32$  Hz)

$^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  (100 MHz)



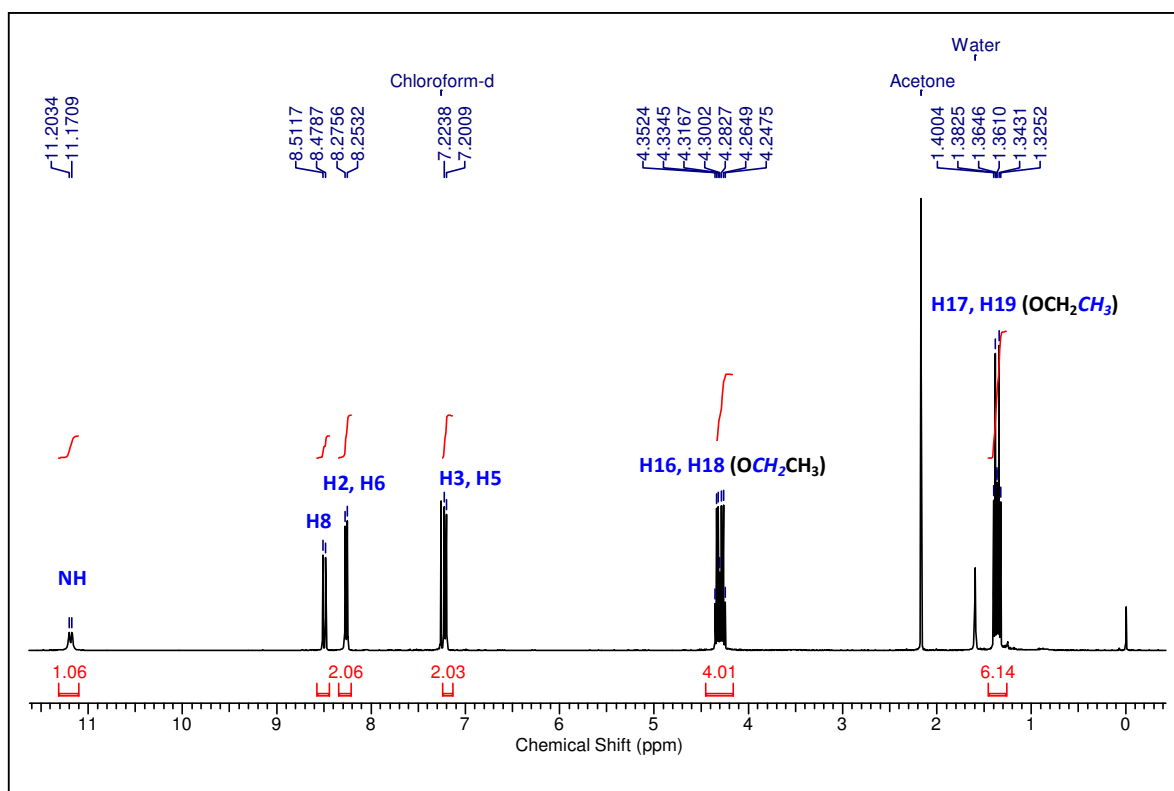
$\delta_{(\text{ppm})}$ : 14.27; 14.41; 60.26; 60.56; 87.94; 94.42; 118.94; 138.74; 139.07; 151.22; 165.58; 168.97.

## Diethyl 2-(((4-nitrophenyl)amino)methylene)malonate (3f)



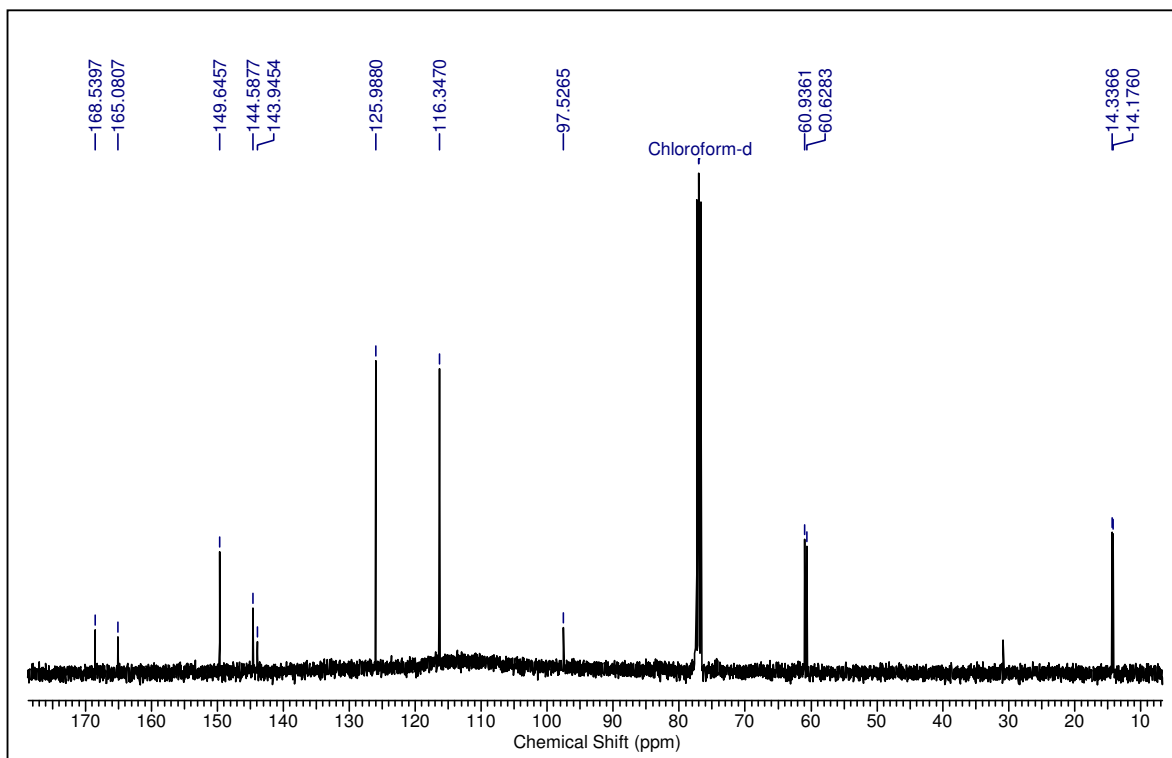
$C_{14}H_{16}N_2O_6$   
Molecular Weight: 308.29 g/mol  
Description: yellow solid

$^1H$  NMR spectrum in  $CDCl_3$  (400 MHz)



$\delta$  (ppm) : 1.34 (t, 3H,  $J=7.16$  Hz); 1.38 (t, 3H,  $J=7.16$  Hz); 4.27 (q, 2H,  $J=7.05$  Hz); 4.32 (q, 2H,  $J=6.96$  Hz); 7.21 (d, 2H,  $J=9.16$  Hz); 8.26 (d, 2H,  $J=8.96$  Hz); 8.49 (d, 1H,  $J=13.20$  Hz); 11.18 (d, 1H,  $J=13.00$  Hz).

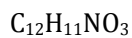
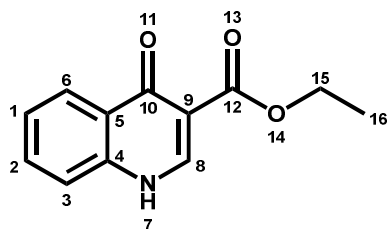
$^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  (100 MHz)



$\delta$  (ppm) : 14.18; 60.63; 60.94; 97.53; 116.35; 125.99; 143.94; 144.59; 149.64; 165.08; 168.54.

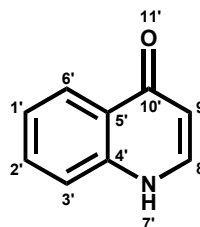
## CHARACTERIZATION OF PRODUCTS IN THE INSOLUBLE FRACTION (IF)

### Ethyl 4-oxo-1,4-dihydroquinoline-3-carboxylate (4a) and quinolin-4(1H)-one (6a)



Molecular Weight: 217.22 g/mol

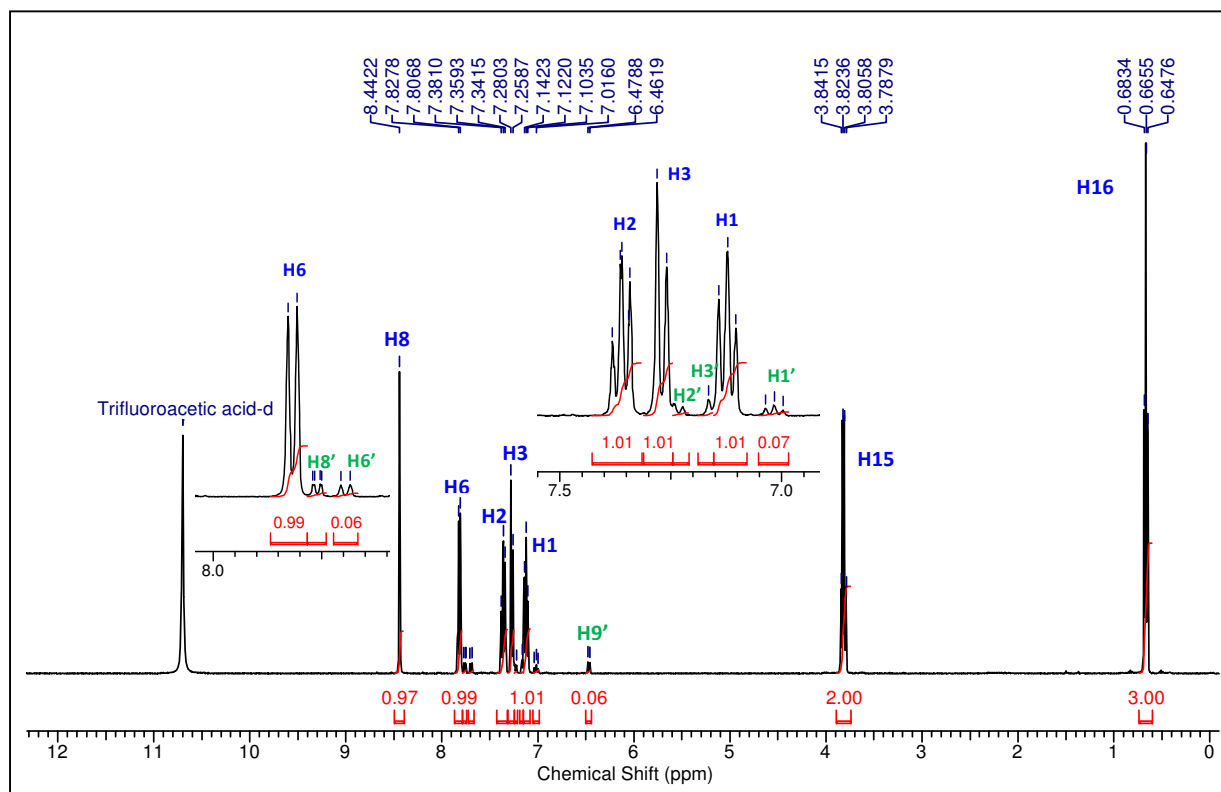
Description: white solid



Molecular Weight: 145.16 g/mol

Description: white solid

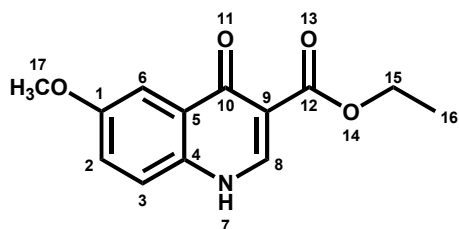
$^1H$  NMR spectrum in TFA-*d* (400 MHz)



$\delta$  (ppm) **4a**: 0.67 (t, 3H,  $J$  = 7.16 Hz); 3.82 (q, 2H,  $J$  = 7.15 Hz); 7.12 (t, 1H,  $J$  = 7.76 Hz); 7.27 (d, 1H,  $J$  = 8.64 Hz); 7.36 (t, 1H,  $J$  = 7.50 Hz); 7.82 (d, 1H,  $J$  = 8.29 Hz); 8.44 (s, 1H).

$\delta$  (ppm) **6a**: 6.47 (dd, 1H,  $J$  = 1.63 and 6.66 Hz); 7.02 (t, 1H,  $J$  = 7.64 Hz); 7.14-7.17 (m, 1H); 7.21-7.24 (m, 1H); 7.69 (d, 1H,  $J$  = 8.45 Hz); 7.76 (dd, 1H,  $J$  = 1.60 and 6.80 Hz).

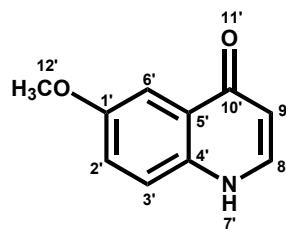
**Ethyl 6-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylate (4b) and 6-methoxyquinolin-4(1H)-one (6b)**



$C_{13}H_{13}NO_4$

Molecular Weight: 247.25 g/mol

Description: white solid

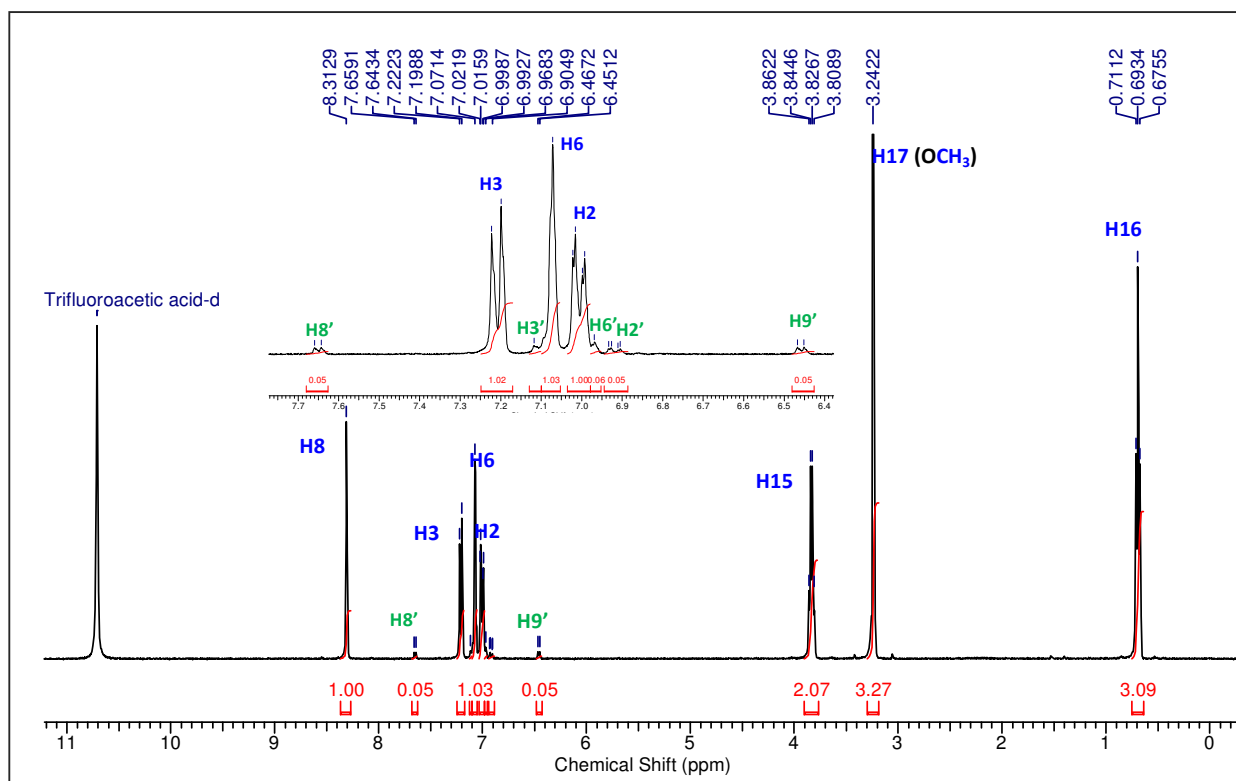


$C_{10}H_9NO_2$

Molecular Weight: 175.18 g/mol

Description: white solid

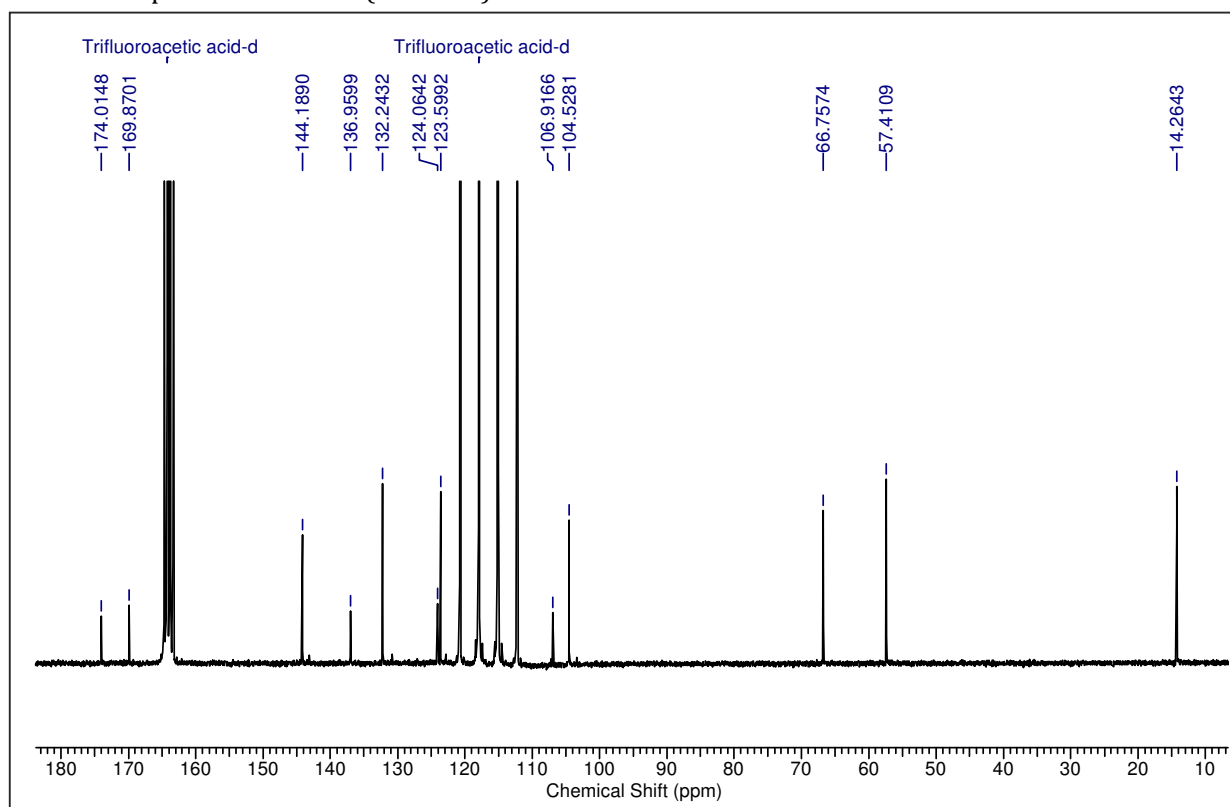
$^1H$  NMR spectrum in TFA-*d* (400 MHz)



$\delta$  (ppm) **4b**: 0.69 (t, 3H,  $J$  = 7.14 Hz); 3.24 (s, 3H); 3.83 (q, 2H,  $J$  = 7.11 Hz); 7.00 (dd, 1H,  $J$  = 2.63 and 9.44 Hz); 7.07 (s, 1H); 7.21 (dd, 1H,  $J$  = 2.27 and 9.36 Hz); 8.31 (s, 1H).

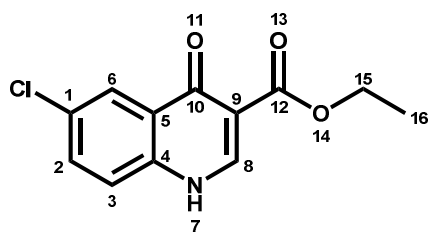
$\delta$  (ppm) **6b**: 6.46 (d, 1H,  $J$  = 6.40 Hz); 6.92 (dd, 1H,  $J$  = 2.58 and 8.70 Hz); 6.95-6.98 (m, 1H); 7.10-7.12 (m, 1H); 7.65 (d, 1H,  $J$  = 6.46 Hz).

<sup>13</sup>C NMR spectrum in TFA-d (100 MHz)

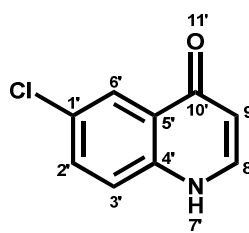


$\delta$  (ppm) : 14.26; 57.41; 66.75; 104.53; 106.92; 123.60; 124.06; 132.24; 136.96; 144.19; 169.87; 174.01.

**Ethyl 6-chloro-4-oxo-1,4-dihydroquinoline-3-carboxylate (4c) and 6-chloroquinolin-4(1H)-one (6c)**

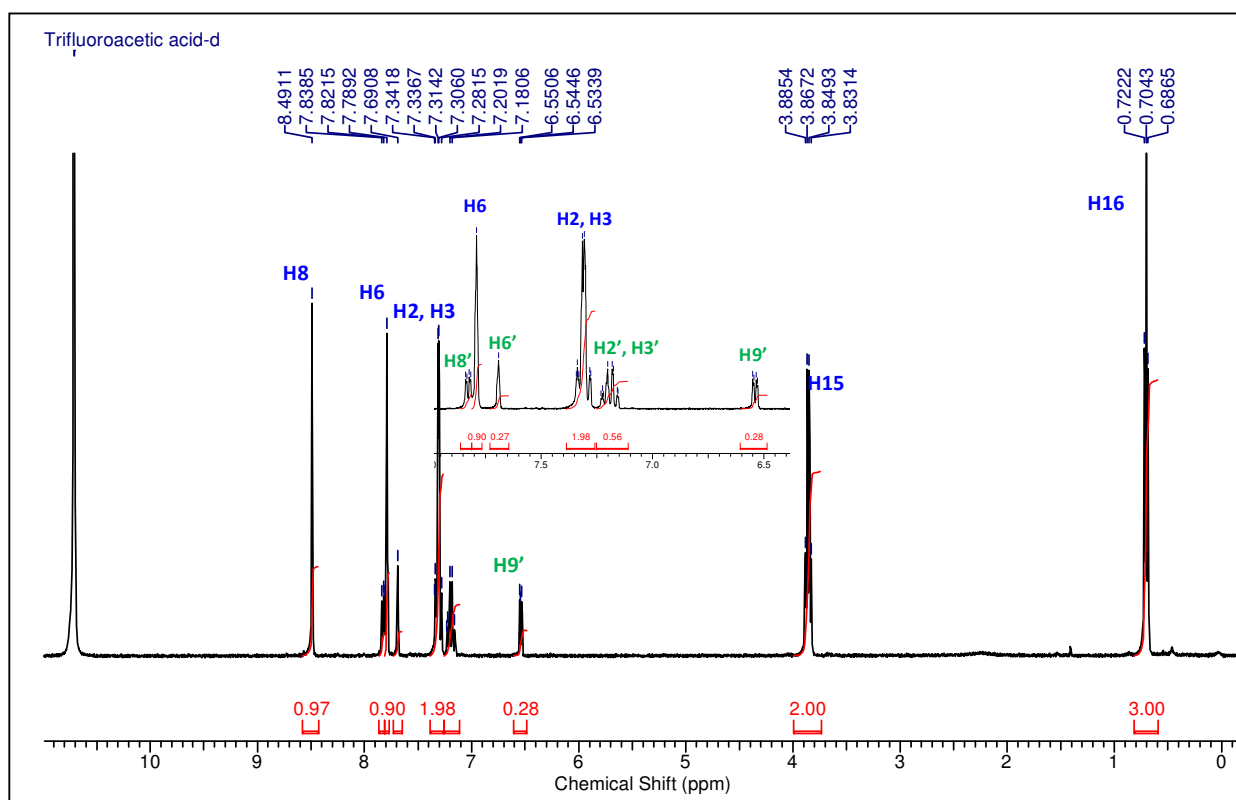


$C_{12}H_{10}ClNO_3$   
Molecular Weight: 251.67 g/mol  
Description: white solid



$C_9H_6ClNO$   
Molecular Weight: 179.60 g/mol  
Description: white solid

$^1H$  NMR spectrum in TFA-*d* (400 MHz)

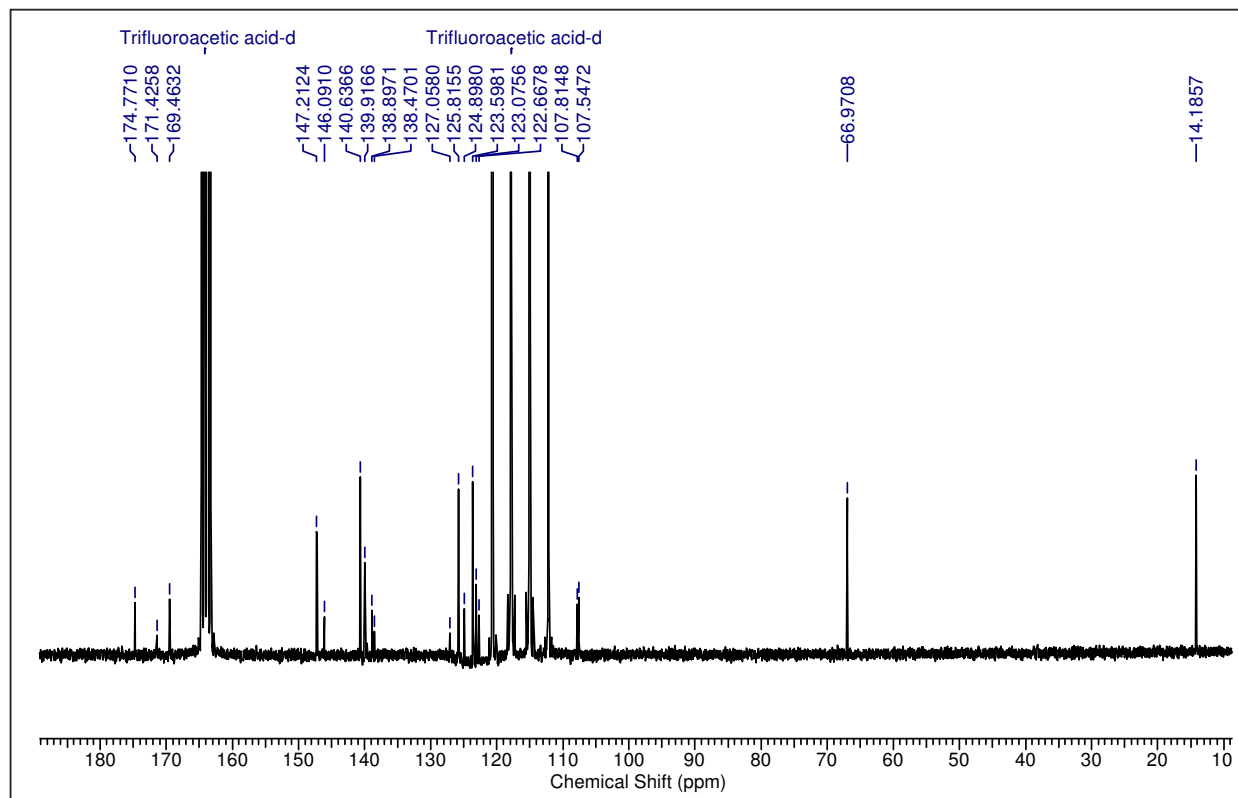


$\delta_{(ppm)}$  **4c**: 0.70 (t, 3H,  $J=7.14$  Hz); 3.86 (q, 2H,  $J=7.20$  Hz); 7.27-7.35 (m, 2H); 7.79 (s, 1H); 8.49 (s, 1H).

$\delta_{(ppm)}$  **6c**: 6.54 (dd, 1H,  $J=1.94$  and 7.00 Hz); 7.20 (q, 2H,  $J=8.94$  Hz); 7.69 (t, 1H,  $J=2.20$ ); 7.83 (dd, 1H,  $J=2.18$  and 6.90 Hz).

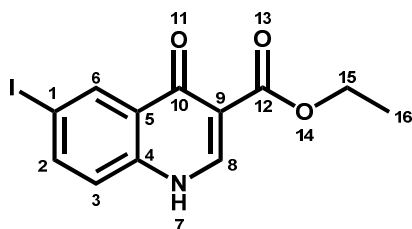


<sup>13</sup>C NMR spectrum in TFA-d (100 MHz)



$\delta$  (ppm) : 14.19; 66.97; 107.55; 107.84; 122.67; 123.07; 123.60; 124.90; 125.81; 127.06; 138.47; 138.90; 139.92; 140.64; 146.09; 147.21; 169.46; 171.42; 174.77.

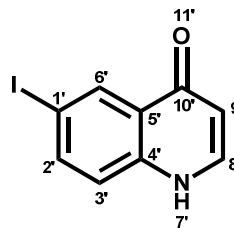
**Ethyl 6-iodo-4-oxo-1,4-dihydroquinoline-3-carboxylate (4e) and 6-iodoquinolin-4(1H)-one (6e)**



$C_{12}H_{10}INO_3$

Molecular Weight: 343.12 g/mol

Description: white solid

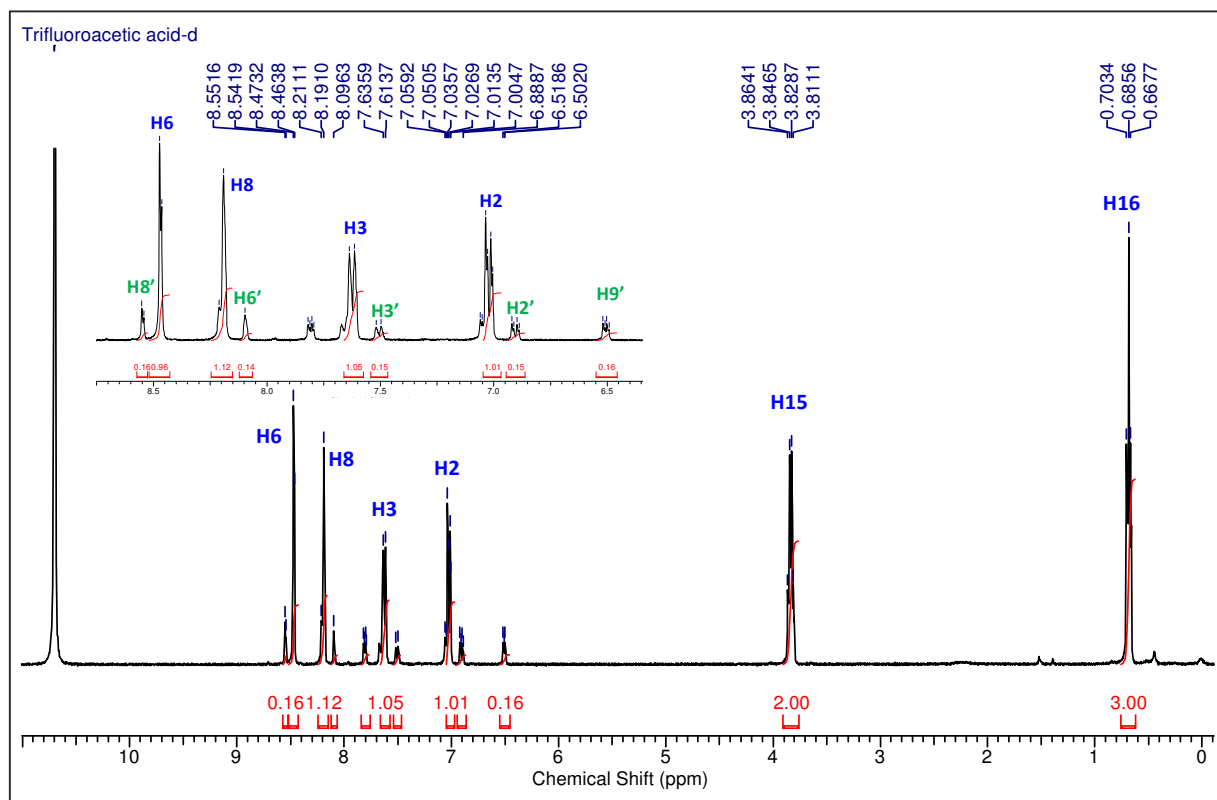


$C_9H_6INO$

Molecular Weight: 271.05 g/mol

Description: white solid

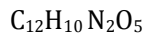
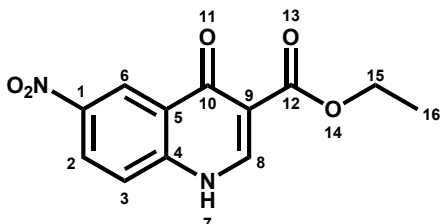
$^1H$  NMR spectrum in TFA-*d* (400 MHz)



$\delta$  (ppm) **4e**: 0.68 (t, 3H,  $J$ = 7.14 Hz); 3.84 (q, 2H,  $J$ = 7.07 Hz); 7.02 (dd, 1H,  $J$ = 3.52 and 8.88 Hz); 7.62 (d, 1H,  $J$ = 8.87 Hz); 8.19 (s, 1H); 8.47 (d, 1H,  $J$ = 3.58 Hz).

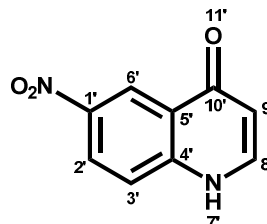
$\delta$  (ppm) **6e**: 6.50 (dd, 1H,  $J$ = 3.33 and 6.40 Hz); 6.90 (dd, 1H,  $J$ = 3.40 and 9.10 Hz); 7.51 (d, 1H,  $J$ = 8.74 Hz); 8.10 (s, 1H); 8.55 (d, 1H,  $J$ = 3.60 Hz).

**Ethyl 6-nitro-4-oxo-1,4-dihydroquinoline-3-carboxylate (4f) and 6-nitroquinolin-4(1H)-one (6f)**



Molecular Weight: 262.22 g/mol

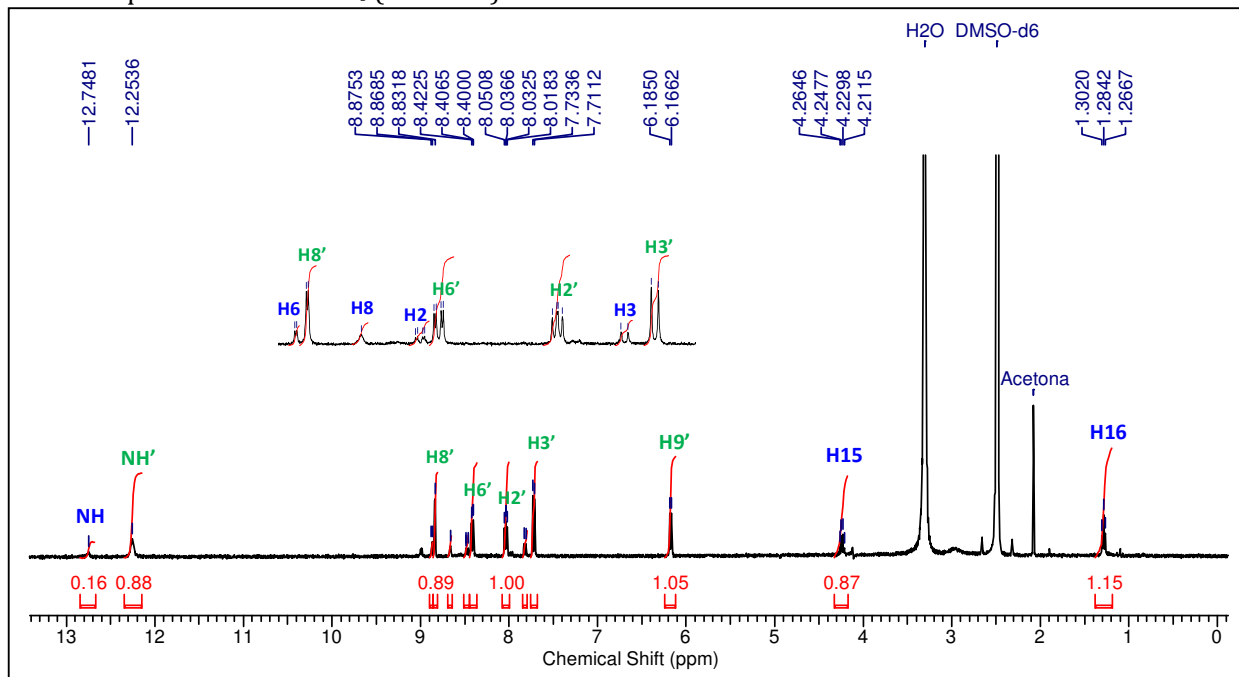
Description: yellow solid



Molecular Weight: 190.16 g/mol

Description: yellow solid

$^1H$  NMR spectrum in DMSO- $d_6$  (400 MHz)



$\delta$  (ppm) **4f**: 1.28 (t, 3H,  $J$  = 7.06 Hz); 4.24 (q, 2H,  $J$  = 7.08 Hz); 7.82 (d, 1H,  $J$  = 8.97 Hz); 8.47 (dd, 1H,  $J$  = 2.70 and 9.18 Hz); 8.65 (s, 1H); 8.87 (d, 1H,  $J$  = 2.72 Hz); 12.75 (s, 1H).

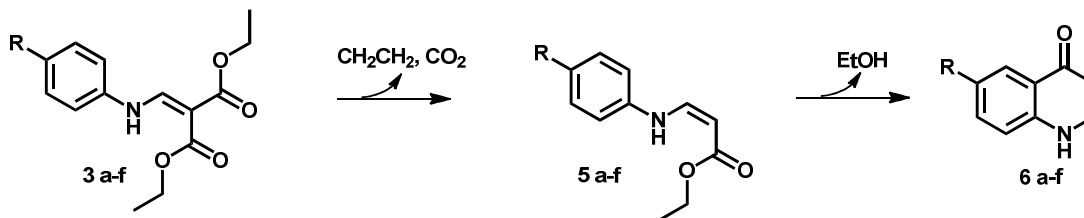
$\delta$  (ppm) **6f**: 6.17 (d, 1H,  $J$  = 7.61 Hz); 7.72 (d, 1H,  $J$  = 9.15 Hz); 8.03 (dd, 1H,  $J$  = 5.65 and 7.72 Hz); 8.41 (dd, 1H,  $J$  = 2.68 and 9.08 Hz); 8.83 (d, 1H,  $J$  = 2.56); 12.25 (s, 1H).

## CHARACTERIZATION OF PRODUCTS IN THE SOLUBLE FRACTION (SF)

### Minority products found in FVP reactions

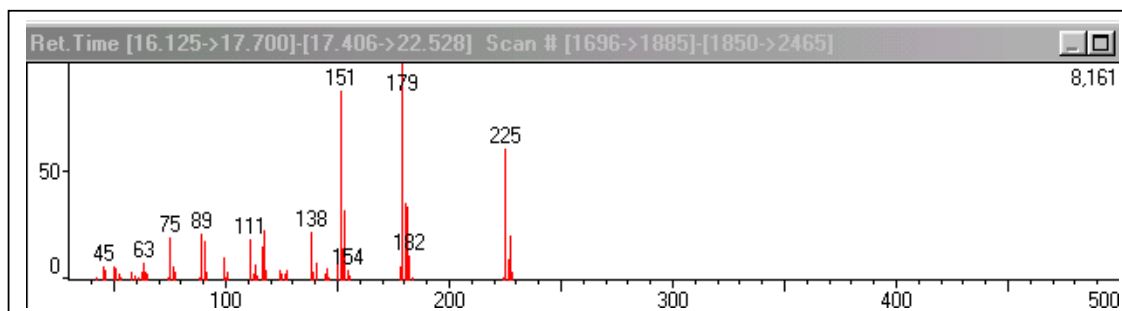
In some reactions, especially at high temperatures, **5c** was detected by GC/MS.

The decarboxylated quinolone **6c** was characterized by <sup>1</sup>H NMR analysis after collecting enough mass from 16 reactions and running preparative TLC to isolate it.

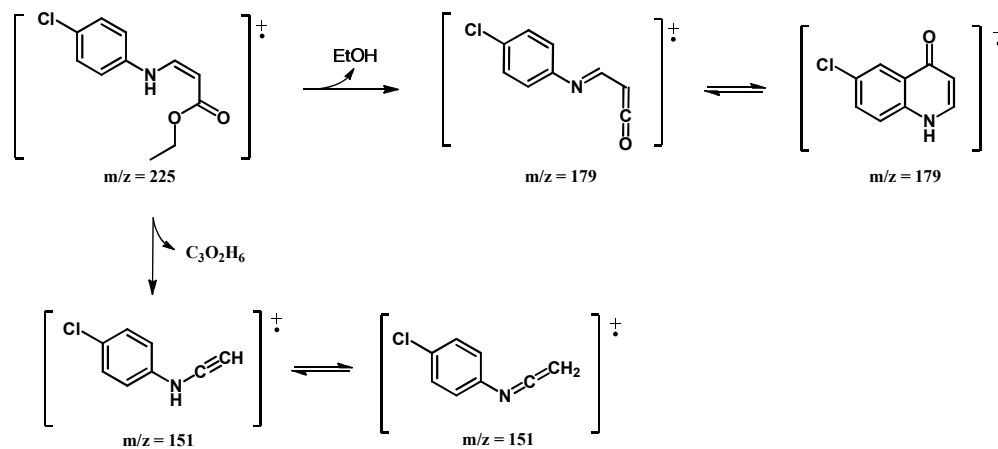


**Scheme S2.** Secondary reaction observed under FVP conditions.

Gas chromatography/mass spectrometry (GC/MS) analyses were performed in a Shimadzu CG-MS-QP 5050A spectrometer equipped with a VF column, using Helium as eluent at a flow rate of 1.1 mL/min with a heating ramp of 15 °C/min from 80 °C to 280 °C. Mass spectra were obtained in electron impact mode (EI) with 70 eV ionization energy.

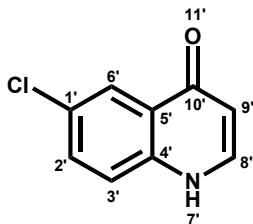


**Figure S2.** GC-MS spectrum for **5c** (R = Cl).

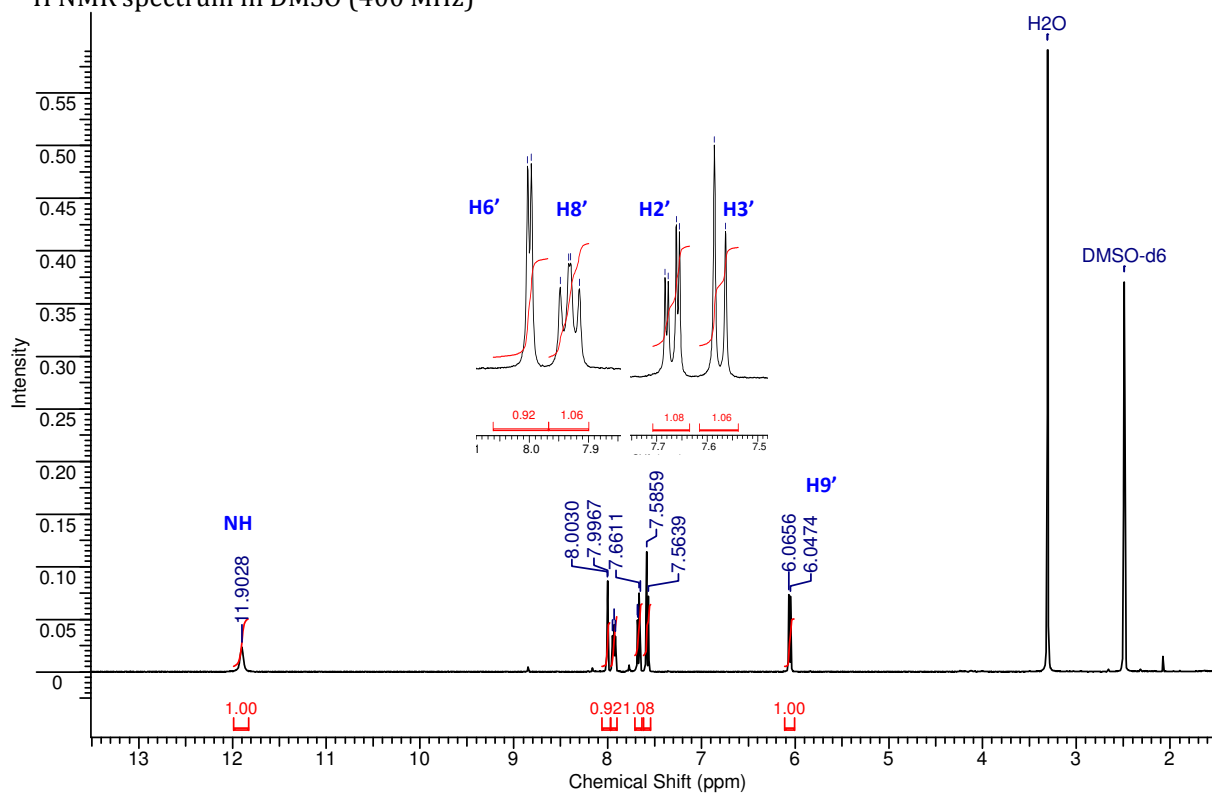


**Ethyl 3-((4-chlorophenyl)amino)acrylate (**5c**).** m/z (%): 225 (62, M<sup>+</sup>); 179 (100); 151 (88).

### 6-chloroquinolin-4(1H)-one (6c)

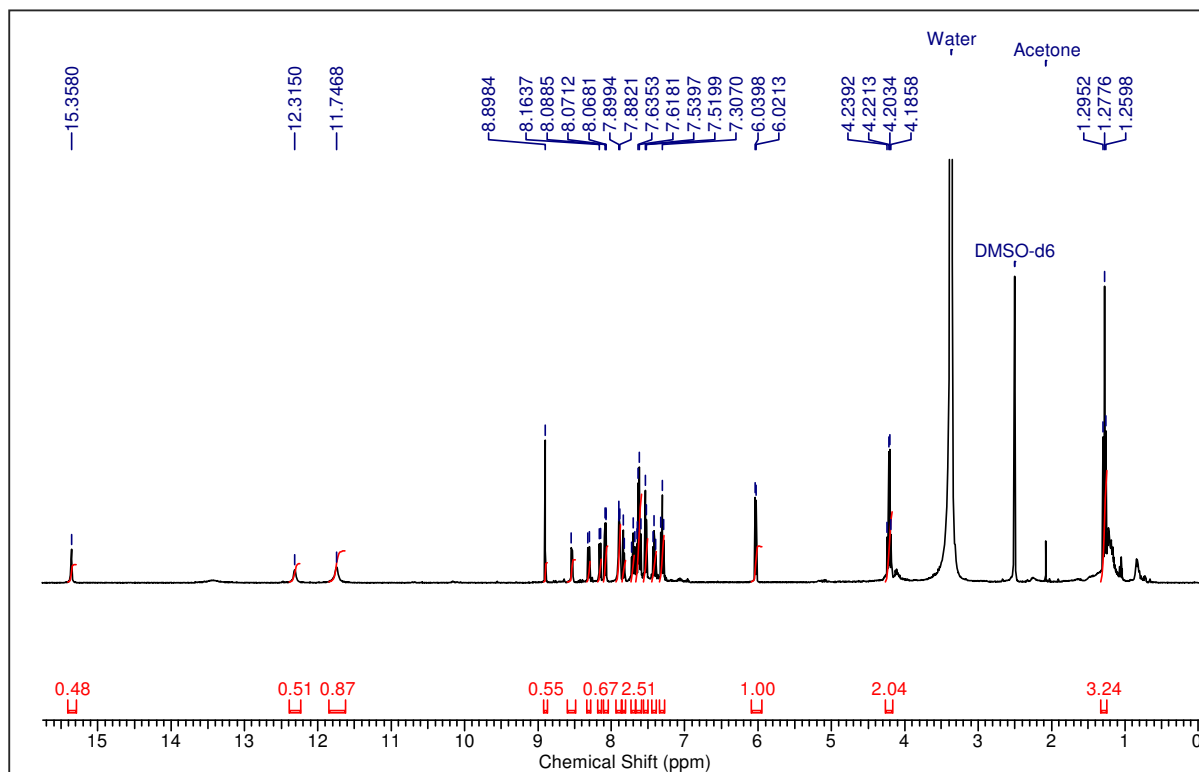


$^1\text{H}$  NMR spectrum in DMSO (400 MHz)

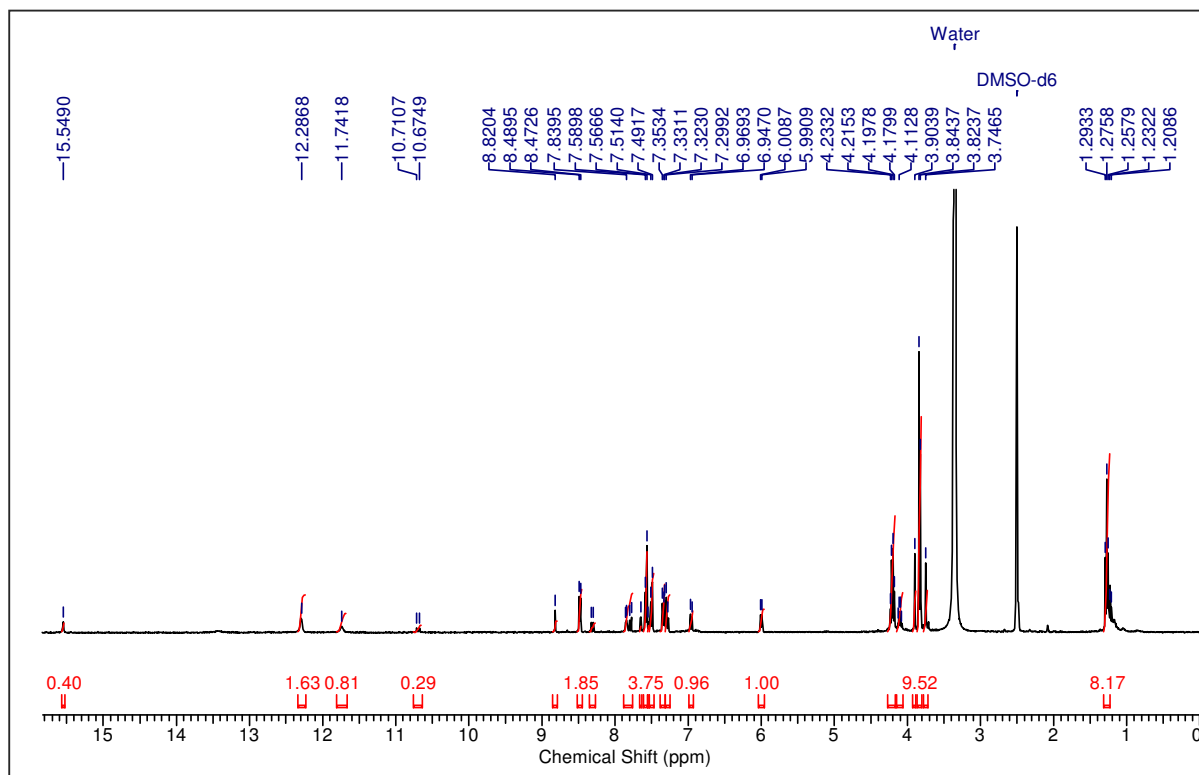


$\delta$  (ppm) : 6.06 (d, 1H,  $J$ = 7.28 Hz); 7.57 (d, 1H,  $J$ = 8.80 Hz); 7.67 (dd, 1H,  $J$ = 9.04 Hz and  $J$ = 2.48 Hz); 7.93 (t, 1H,  $J$ = 7.04 Hz); 8.00 (d, 1H,  $J$ = 2.52 Hz); 11.90 (s, 1H).

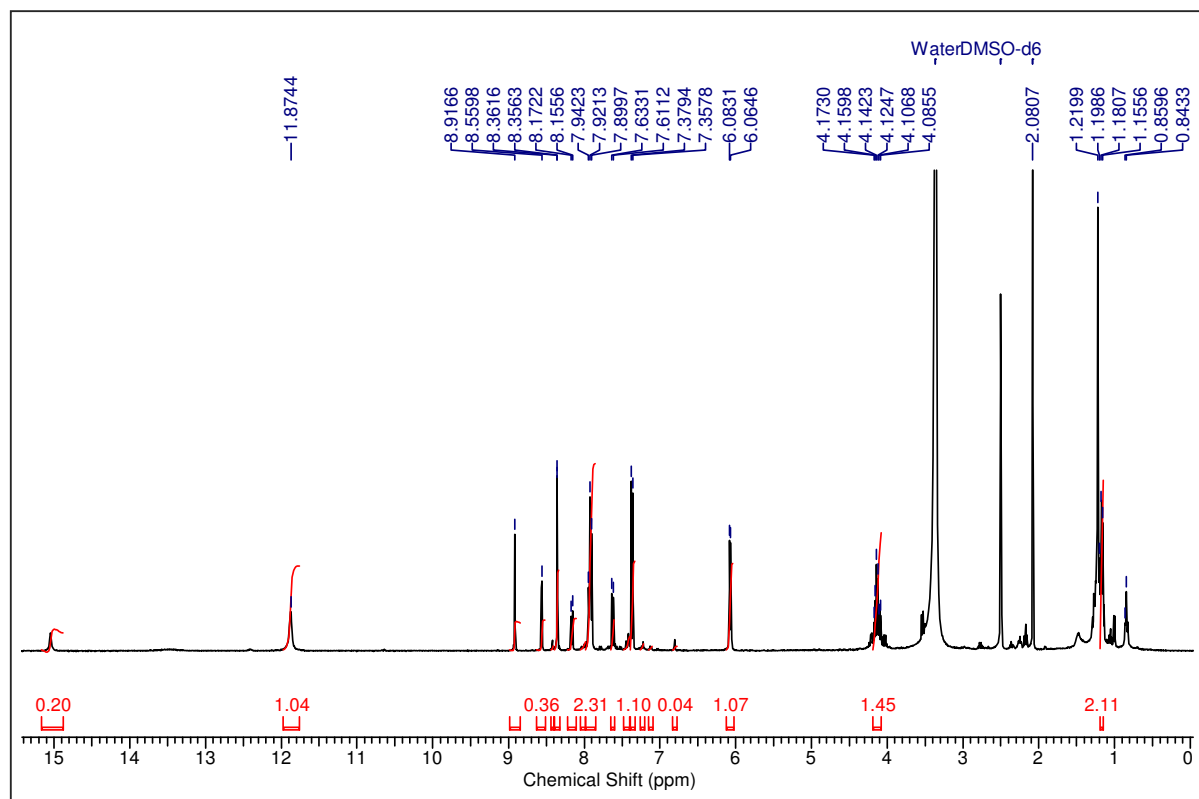
$^1\text{H}$  NMR spectrum in DMSO (400 MHz) of soluble products from FVP of **3a**.



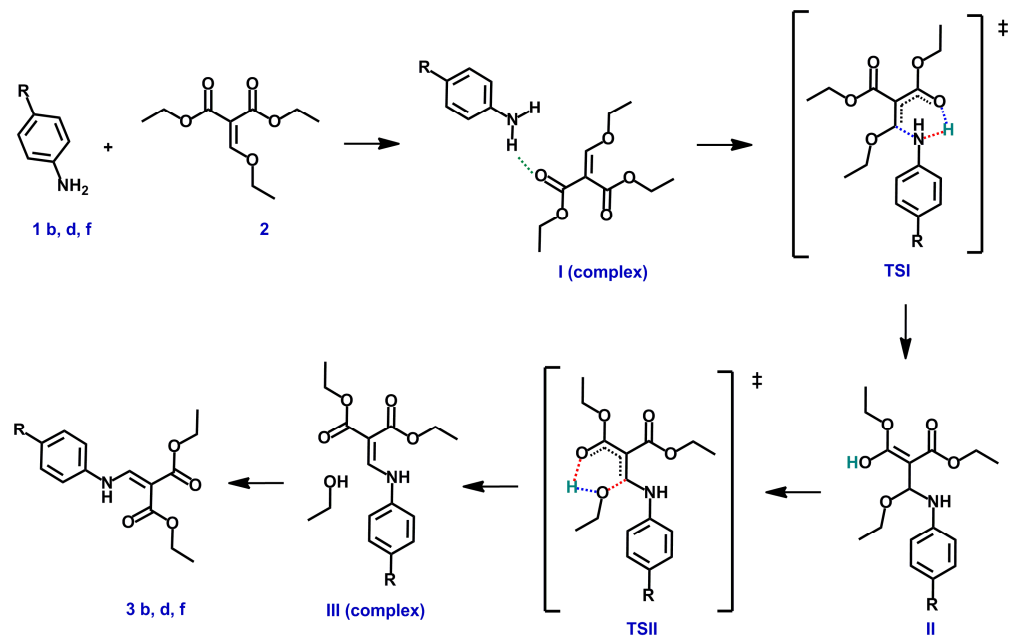
$^1\text{H}$  NMR spectrum in DMSO (400 MHz) of soluble products from FVP of **3b**.



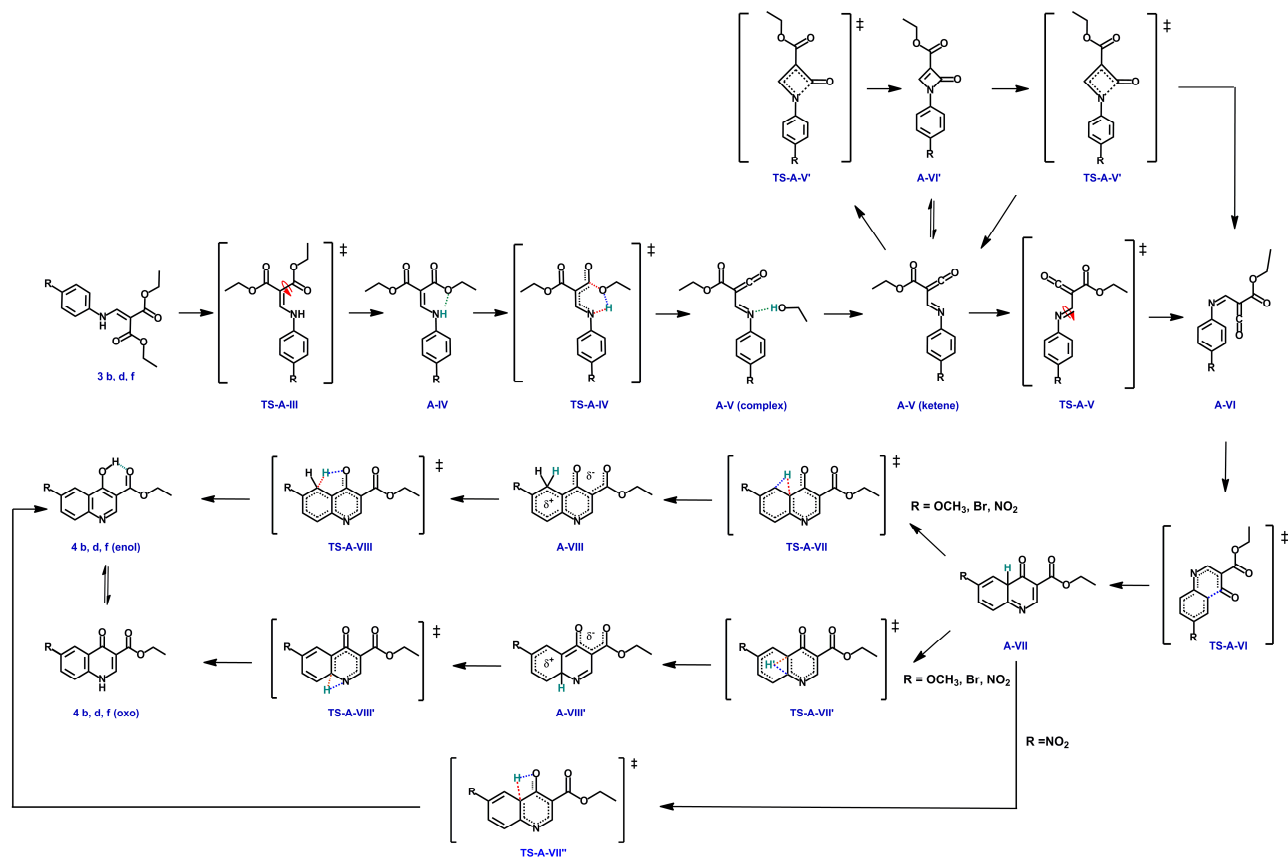
$^1\text{H}$  NMR spectrum in DMSO (400 MHz) of soluble products from FVP of **3e**.



**PART II. COMPUTATIONAL MECHANISM STUDY**



**Scheme S3.** First step of the G-J reaction mechanism.



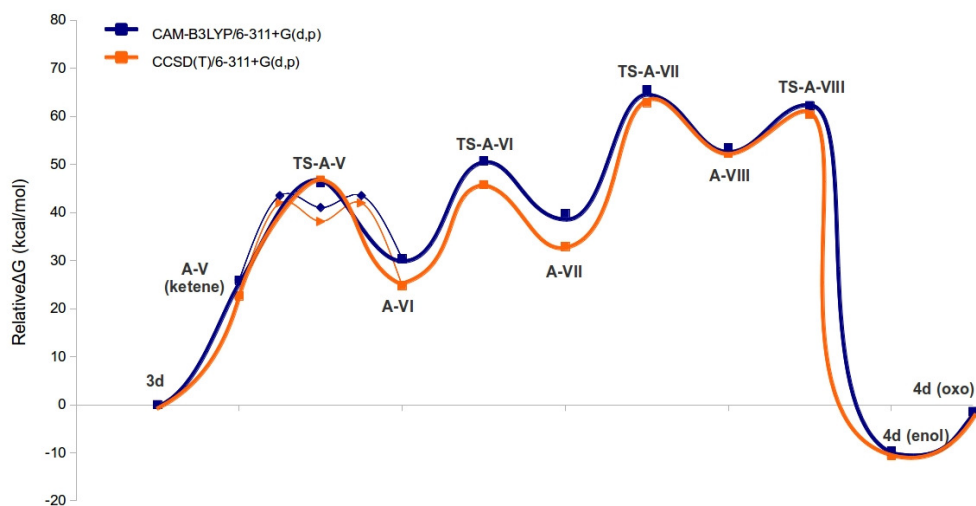
**Scheme S4.** Main reaction (**Path A**) leading to the formation of quinolone 4.



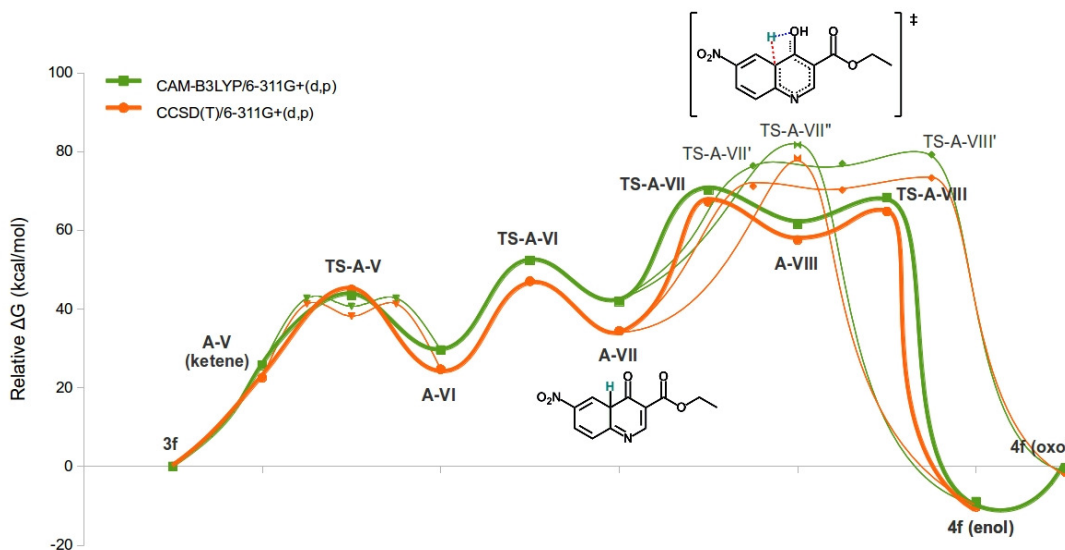
**Table S1.** Thermochemistry calculations details. Example (for R=Br) of data source for main text tables. CAM-B3LYP/6-311+G(d,p) level of theory and CCSD(T) energy refinement.

	CAM-B3LYP				CCSD(T) G <sup>d,e</sup>
	E <sup>a</sup>	E + ZPE <sup>b</sup>	H <sup>c</sup>	G <sup>d</sup>	
<b>Path A</b>					
3d	-3472.8721	-3472.5863	-3472.5648	-3472.6406	-3469.0116
A-IV	-3472.8638	-3472.5780	-3472.5565	-3472.6319	-3468.9654
TS-A-IV	-3472.8105	-3472.5285	-3472.5065	-3472.5835	
A-V (+ EtOH)	-3472.8058	-3472.5260	-3472.5032	-3472.5993	-3468.9714
TS-A-V	-3317.7554	-3317.5578	-3317.5404	-3317.6060	-3314.3058
A-VI	-3317.7835	-3317.5835	-3317.5664	-3317.6310	-3314.3408
TS-A-VI	-3317.7526	-3317.5536	-3317.5374	-3317.5987	-3314.3074
A-VII	-3317.7716	-3317.5708	-3317.5545	-3317.6162	-3314.3278
TS-A-VII	-3317.7268	-3317.5299	-3317.5139	-3317.5751	-3314.2801
A-VIII	-3317.7481	-3317.5486	-3317.5321	-3317.5943	-3314.2970
TS-A-VIII	-3317.7327	-3317.5361	-3317.5204	-3317.5803	-3314.2841
4d (keto)	-3317.8541	-3317.6507	-3317.6350	-3317.6948	-3314.3972
4d (enol)	-3317.8390	-3317.6361	-3317.6199	-3317.6817	-3314.3832
TS-A-V'	-3317.7606	-3317.5625	-3317.5455	-3317.6102	-3314.3134
A-VI'	-3317.7663	-3317.5667	-3317.5496	-3317.6141	-3314.3195
TS-A-VII'	-3317.7192	-3317.5221	-3317.5060	-3317.5678	
A-VIII'	-3317.7206	-3317.5219	-3317.5056	-3317.5674	
TS-A-VIII'	-3317.7113	-3317.5145	-3317.4984	-3317.5596	
<b>Path B</b>					
B-II	-3472.8721	-3472.5856	-3472.5645	-3472.6395	
B-II'	-3472.8669	-3472.5809	-3472.5595	-3472.6345	
TS-B-II	-3472.7640	-3472.4866	-3472.4651	-3472.5411	-3468.9050
B-III (hereafter + ethene)	-3472.8467	-3472.5653	-3472.5432	-3472.6350	-3469.0040
TS-B-III	-3472.8179	-3472.5380	-3472.5161	-3472.6075	
TS-B-III'	-3472.7616	-3472.4842	-3472.4626	-3472.5381	
B-IV	-3472.8460	-3472.5645	-3472.5425	-3472.6339	
B-IV'	-3472.7577	-3472.4816	-3472.4572	-3472.5567	
TS-B-IV	-3472.7606	-3472.4833	-3472.4604	-3472.5549	-3468.9289
TS-B-IV'	-3472.7558	-3472.4795	-3472.4563	-3472.5516	
B-V (complex)	-3472.7688	-3472.4920	-3472.4675	-3472.5676	
B-V (hereafter + CO <sub>2</sub> + ethene)	-3472.7634	-3472.4892	-3472.4649	-3472.5738	
TS-B-V	-3472.7227	-3472.4521	-3472.4286	-3472.5353	-3468.8666
5d	-3472.8443	-3472.5685	-3472.5459	-3472.6491	-3468.9939
TS-B-VI	-3472.7862	-3472.5150	-3472.4907	-3472.5997	
B-VI (hereafter + CO <sub>2</sub> + C <sub>2</sub> H <sub>2</sub> + EtOH)	-3472.7793	-3472.5101	-3472.4853	-3472.6123	-3468.9939
TS-B-VI'	-3472.7565	-3472.4816	-3472.4572	-3472.5572	
B-VI' (complex)	-3472.7775	-3472.5030	-3472.4768	-3472.5829	
TS-B-VII	-3472.7460	-3472.4785	-3472.4539	-3472.5808	-3468.9545
B-VII	-3472.7751	-3472.5057	-3472.4810	-3472.6075	-3468.9903
TS-B-VIII	-3472.7446	-3472.4755	-3472.4521	-3472.5749	-3468.9569
B-VIII	-3472.7702	-3472.4989	-3472.4754	-3472.5983	-3468.9826
TS-B-IX	-3472.7234	-3472.4560	-3472.4328	-3472.5549	-3468.9312
B-IX	-3472.7457	-3472.4756	-3472.4520	-3472.5751	-3468.9504
TS-B-X	-3472.7277	-3472.4606	-3472.4377	-3472.5590	-3468.9356
6d	-3472.8318	-3472.5588	-3472.5354	-3472.6576	-3469.0351

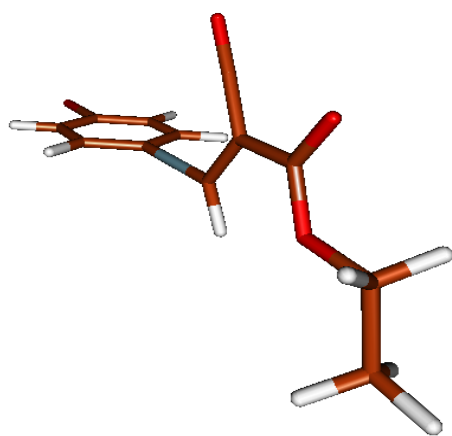
a) Total electronic energy in Hartrees; b) E plus zero point energy; c) Sum of the electronic and thermal enthalpies; d) Sum of the electronic and thermal free energies; e) From frequencies at CAM-B3LYP level of theory.



**Figure S3.** Comparison of energy profiles at CAM-B3LYP/6-311+G(d,p) and CCSD(T)/6-311+G(d,p) level of theory for Step 2 (**Path A**)



**Figure S4.** Thermochemistry of Step 2 (**Path A**) for R=NO<sub>2</sub> studied at the CAM-B3LYP/6-311+G(d,p) and CCSD(T)/6-311+G(d,p) level of theory.



**Figure S5.** 3D view of **TS-A-V** for R=Br.

## X,Y,Z coordinates of main stationary points

### Step 1 (R = Br)

#### 1 (bromoaniline)

C	-0.000125	0.000678	0.000000
C	0.003239	0.000246	1.400936
C	1.198722	0.000119	2.105517
C	2.409102	0.000721	1.425086
C	2.422496	0.001417	0.036629
C	1.229255	0.001250	-0.671750
N	-1.185914	0.000732	-0.701404
H	-0.938342	-0.000177	1.943452
H	1.184440	-0.000454	3.190192
Br	4.037228	0.000213	2.388150
H	3.366213	0.001738	-0.498277
H	1.251242	0.001629	-1.758219
H	-2.072418	0.000194	-0.225752
H	-1.196017	0.001004	-1.707402

## 2 (diethyl-ethoxymethylenmalonate)

C	0.272782	0.437920	0.407139
C	-0.171789	0.022066	1.795524
H	1.355256	0.596202	0.376545
H	-0.217897	1.376480	0.127927
H	0.001826	-0.320699	-0.331799
O	0.528760	-1.156315	2.240076
H	-1.244611	-0.177510	1.829445
H	0.080340	0.778240	2.540858
C	-0.002482	-2.341528	1.925846
C	0.707194	-3.462281	2.608986
O	-0.953257	-2.479719	1.185012
C	0.676962	-3.397513	4.087912
O	1.446188	-4.330300	4.683559
C	1.394210	-4.366966	6.121465
C	2.306822	-5.481769	6.580404
H	0.357725	-4.529178	6.429972
H	1.709267	-3.393163	6.505617
H	1.978259	-6.447188	6.184087
H	2.298503	-5.539076	7.673563
H	3.335726	-5.305178	6.253352
O	0.010858	-2.600936	4.714252
C	1.245588	-4.551185	2.015339
O	1.431643	-4.861455	0.738971
C	1.196613	-3.924569	-0.326651
C	1.807686	-4.512139	-1.578323
H	1.670065	-2.972927	-0.059009
H	0.121957	-3.764523	-0.428143
H	2.883929	-4.664376	-1.456939
H	1.645274	-3.832338	-2.420736
H	1.345295	-5.473632	-1.818916
H	1.636078	-5.340000	2.648580

## I (complex)

C	0.026993	0.019492	-0.017911
C	0.004785	0.012926	1.369306
C	1.197290	0.006562	2.105724
C	2.411851	0.007090	1.408007
C	2.434033	0.013459	0.019818
C	1.241968	0.019510	-0.691579
N	1.166553	-0.052160	3.490684
Br	1.270582	0.030554	-2.585927
O	-1.301018	0.816125	5.094524
C	-1.508750	0.178367	6.113020
C	-0.578240	-0.857594	6.637556
C	-1.157937	-2.215967	6.756766
O	-0.333353	-3.095490	7.352598
C	-0.799921	-4.457617	7.415162
C	0.274033	-5.274167	8.097232
O	-2.595579	0.322091	6.862182
C	-3.654606	1.163941	6.356395
C	-3.452598	2.608525	6.767108
C	0.749186	-0.689985	6.826141
O	1.499699	0.407146	6.808238
C	0.935408	1.729906	6.882962
C	2.032105	2.659194	7.351094
O	-2.256140	-2.516277	6.340346
H	-3.373257	2.696612	7.854932
H	-4.308542	3.206861	6.437741
H	-2.551602	3.023428	6.307736
H	-3.695099	1.055461	5.271054
H	-4.558516	0.741950	6.797864
H	-0.998389	-4.804269	6.397454
H	-1.743602	-4.474927	7.966537
H	1.210651	-5.241560	7.532853
H	-0.046826	-6.318271	8.168342
H	0.464847	-4.903746	9.108713
H	0.099097	1.706621	7.590821
H	0.553148	2.013028	5.900430
H	2.398290	2.369352	8.339859
H	1.647065	3.682198	7.408064
H	2.873269	2.649047	6.652141
H	1.357304	-1.559745	7.048135
H	3.348619	-0.005171	1.959338
H	3.382435	0.013689	-0.506847
H	-0.904169	0.024721	-0.574419
H	-0.945828	0.008580	1.895124
H	2.002661	0.247700	3.972798
H	0.310470	0.253561	3.944575

**TSI**

C	-0.008939	-0.004776	-0.047754
C	-0.030392	0.088091	1.337498
C	1.170687	0.130527	2.035758
C	2.377303	0.077398	1.348112
C	2.390084	-0.011988	-0.038607
C	1.193823	-0.055104	-0.742209
N	3.623990	0.135731	2.068779
C	4.245464	-1.198863	2.521254
C	5.643709	-0.899436	2.975641
C	6.378277	0.061141	2.270798
O	7.656035	0.259706	2.562635
C	8.377446	1.288733	1.863661
C	8.938922	0.777376	0.551167
Br	-1.635956	-0.073627	-1.002905
O	4.060406	-2.131518	1.494994
C	5.087699	-2.326682	0.522873
C	4.625333	-3.438979	-0.394342
C	6.202049	-1.656410	4.080284
O	7.315427	-1.566858	4.561880
O	5.290953	-2.550753	4.579660
C	5.741680	-3.354767	5.675051
C	4.602166	-4.270301	6.067737
O	5.848260	0.783396	1.338023
H	9.561080	-0.107005	0.717841
H	9.558841	1.552136	0.086645
H	8.133950	0.520179	-0.142053
H	7.725114	2.150454	1.710495
H	9.176880	1.558337	2.556334
H	6.042520	-2.701081	6.499306
H	6.626452	-3.917568	5.363248
H	3.726217	-3.694216	6.382133
H	4.908554	-4.910446	6.901703
H	4.309495	-4.911342	5.230694
H	6.021919	-2.594324	1.026405
H	5.265148	-1.401895	-0.040451
H	4.455687	-4.357945	0.174089
H	5.385164	-3.637284	-1.157446
H	3.690619	-3.170155	-0.895831
H	3.636583	-1.568408	3.344834
H	3.335457	-0.042563	-0.569760
H	1.196679	-0.125281	-1.823963
H	-0.974850	0.126774	1.868210
H	1.161047	0.198597	3.120397
H	4.615125	0.607315	1.515392
H	3.512568	0.692844	2.917164

## II

C	-0.043460	0.062369	0.018161
C	-0.048974	0.071047	1.407989
C	1.155507	0.045825	2.094145
C	2.373570	0.003472	1.407488
C	2.363184	-0.002626	0.012516
C	1.154178	0.027410	-0.678104
N	3.563562	-0.025245	2.191255
C	4.866588	-0.354042	1.566203
C	5.926353	-0.468292	2.643048
C	5.943048	0.394277	3.715674
O	6.906331	0.382863	4.613928
C	6.870420	1.281464	5.740947
C	7.448323	2.637538	5.388250
Br	-1.682942	0.094169	-0.928266
O	5.168577	0.559089	0.531000
C	5.455750	1.911316	0.860755
C	5.814221	2.627922	-0.424772
C	6.994528	-1.457700	2.474898
O	7.954573	-1.631322	3.198468
O	6.797742	-2.220942	1.366441
C	7.799439	-3.212594	1.101375
C	7.407458	-3.924558	-0.174705
O	4.992809	1.304281	3.939704
H	8.459885	2.530189	4.986318
H	7.499762	3.259112	6.288673
H	6.826202	3.153052	4.652152
H	5.847931	1.360063	6.114572
H	7.485064	0.772415	6.484838
H	7.854660	-3.897351	1.952648
H	8.770581	-2.717505	1.011974
H	6.434193	-4.413423	-0.068580
H	8.151536	-4.690649	-0.416165
H	7.351103	-3.222822	-1.012142
H	6.291456	1.953920	1.569382
H	4.580482	2.381626	1.328679
H	6.684285	2.159767	-0.894156
H	6.051455	3.676773	-0.218718
H	4.981071	2.595694	-1.133085
H	4.796605	-1.305350	1.037912
H	3.295122	-0.017273	-0.536723
H	1.154419	0.019939	-1.762539
H	-0.986782	0.099512	1.951653
H	1.152331	0.063550	3.181177
H	4.251397	1.141665	3.288593
H	3.429302	-0.666173	2.971107



**TSII**

C	-0.062584	-0.619227	-0.002814
C	-0.022809	-0.742439	1.381457
C	1.175661	-0.569792	2.057391
C	2.340177	-0.274499	1.358609
C	2.303051	-0.168042	-0.023195
C	1.103554	-0.345161	-0.719794
Br	1.224570	-0.738212	3.941794
N	1.118994	-0.258887	-2.115677
C	0.072490	-0.553772	-2.952563
C	0.347092	-0.580917	-4.395750
C	0.643701	0.658331	-5.004077
O	1.108336	0.662711	-6.247726
C	1.253328	1.926066	-6.920175
C	-0.052053	2.363272	-7.556016
C	0.216624	-1.827120	-5.119571
O	0.386420	-2.023315	-6.307385
O	-0.153213	-2.850096	-4.280580
C	-0.311597	-4.134715	-4.894666
C	-0.699363	-5.114906	-3.808689
O	0.457370	1.762223	-4.395399
O	-1.002147	0.777172	-2.705516
C	-2.329842	0.597607	-3.233160
C	-3.103218	1.895367	-3.122180
H	-0.431638	1.587003	-8.226632
H	0.107019	3.277585	-8.138122
H	-0.806683	2.572668	-6.792903
H	1.626199	2.670926	-6.215084
H	2.013982	1.730254	-7.677971
H	0.628329	-4.414622	-5.378864
H	-1.075842	-4.067125	-5.674690
H	0.072207	-5.166991	-3.034537
H	-0.824733	-6.114920	-4.236684
H	-1.642948	-4.824878	-3.335710
H	-2.791649	-0.195716	-2.638041
H	-2.253347	0.255502	-4.270834
H	-3.165270	2.225705	-2.081560
H	-4.119804	1.753385	-3.502942
H	-2.628078	2.685756	-3.711194
H	-0.562890	-1.354071	-2.585668
H	-1.012814	-0.717708	-0.513034
H	-0.931965	-0.960393	1.930653
H	3.275684	-0.137494	1.889427
H	3.217384	0.045358	-0.570299
H	-0.436844	1.423961	-3.345091
H	1.929518	0.165067	-2.546422

### III (complex)

C	-0.005876	-0.051854	-0.031105
C	-0.017729	-0.055418	1.358725
C	1.179280	-0.009783	2.060768
C	2.394420	0.037100	1.388964
C	2.408227	0.022385	0.001114
C	1.211155	-0.034155	-0.713195
Br	1.157301	-0.025165	3.952234
N	1.267495	-0.027666	-2.122106
C	0.362571	-0.582497	-2.934736
C	0.359118	-0.516319	-4.311038
C	1.423048	0.213496	-4.998878
O	1.384295	0.153799	-6.328123
C	2.414962	0.846413	-7.056164
C	2.069823	2.311556	-7.239084
C	-0.740049	-1.180154	-5.037327
O	-1.130251	-0.917037	-6.154015
O	-1.323207	-2.152527	-4.288630
C	-2.440532	-2.825346	-4.889269
C	-2.870651	-3.927163	-3.946245
O	2.317650	0.812064	-4.397133
O	-2.300844	1.001724	-2.254903
C	-3.474904	0.811241	-3.046127
C	-4.361593	-0.183651	-2.329106
H	1.096215	2.419346	-7.726074
H	2.826002	2.793077	-7.868572
H	2.046052	2.829145	-6.276750
H	3.366014	0.721121	-6.534500
H	2.452729	0.324793	-8.013982
H	-2.132949	-3.216825	-5.862343
H	-3.240355	-2.098478	-5.062935
H	-2.057261	-4.640311	-3.783434
H	-3.722386	-4.467574	-4.371743
H	-3.172772	-3.522281	-2.975680
H	-3.200825	0.438081	-4.041626
H	-3.999743	1.767406	-3.173365
H	-3.843870	-1.139916	-2.205807
H	-5.279641	-0.357982	-2.899639
H	-4.635495	0.190405	-1.337952
H	-0.435684	-1.129855	-2.449604
H	-0.942614	-0.017399	-0.578893
H	-0.962106	-0.070124	1.891276
H	3.325147	0.074668	1.943743
H	3.354191	0.041460	-0.532263
H	-1.717341	1.633138	-2.699597

**3d (diethyl 2-((4-bromophenyl)amino)methylene)malonate)**

C	0.106828	-0.759347	0.267698
C	0.051556	-0.071466	1.472028
C	1.171602	0.595076	1.951862
C	2.349474	0.569709	1.219939
C	2.419680	-0.118534	0.006233
C	1.286729	-0.783564	-0.465501
Br	-1.557973	-0.043740	2.464972
N	3.644356	-0.095824	-0.680593
C	3.935663	-0.707458	-1.833872
C	5.144100	-0.665367	-2.493051
C	5.278441	-1.417171	-3.757640
O	4.120793	-2.049196	-4.094368
C	4.154957	-2.813293	-5.310127
C	2.790516	-3.440492	-5.491973
C	6.243369	0.117615	-1.918510
O	6.131103	0.732911	-0.855450
O	7.372552	0.121151	-2.616848
C	8.478440	0.880825	-2.092929
C	8.387651	2.337857	-2.502312
O	6.266749	-1.499954	-4.450729
H	8.324241	2.429005	-3.590624
H	9.281851	2.872189	-2.163515
H	7.512949	2.815498	-2.053698
H	8.503832	0.770254	-1.007055
H	9.354287	0.398418	-2.529916
H	4.944467	-3.565641	-5.230973
H	4.412791	-2.146540	-6.137605
H	2.547756	-4.102084	-4.654829
H	2.775318	-4.033678	-6.411948
H	2.012564	-2.674530	-5.566600
H	3.145285	-1.291377	-2.285758
H	1.302183	-1.323518	-1.405061
H	-0.769663	-1.277704	-0.104698
H	1.127712	1.131871	2.892824
H	3.226890	1.089705	1.593833
H	4.421930	0.437962	-0.284585

**EtOH**

C	-0.005212	-0.001510	-0.016497
C	0.013313	-0.018628	1.503319
O	1.330709	0.010670	2.038000
H	-1.034897	0.027467	-0.390387
H	0.472759	-0.898406	-0.428967
H	0.528236	0.874971	-0.396513
H	-0.534767	-0.891831	1.885314
H	-0.473752	0.874647	1.902287
H	1.807458	-0.779500	1.746896

## Step 2 - Pathway A (R = Br)

### TS-A-III

C	1.091938	-0.327951	0.112431
C	1.628566	0.947562	-0.075085
C	3.005543	1.125690	-0.125088
C	3.855893	0.036178	0.005628
C	3.335421	-1.237781	0.191928
C	1.961666	-1.415723	0.246101
Br	5.728633	0.290837	-0.065427
N	-0.285189	-0.580527	0.168004
C	-1.290567	0.334545	0.107063
C	-2.609946	0.061454	0.174030
C	-3.629582	1.111620	0.075907
O	-3.110184	2.354082	0.004146
C	-4.062013	3.426435	-0.124303
C	-3.279942	4.718881	-0.202931
C	-3.136163	-1.325659	0.369701
O	-3.530403	-1.769110	1.425348
O	-3.091336	-2.037728	-0.772710
C	-3.642950	-3.370328	-0.736887
C	-2.606074	-4.386352	-0.290424
O	-4.822725	0.889478	0.048586
H	-1.724200	-4.356888	-0.941640
H	-3.030597	-5.394118	-0.343566
H	-2.300550	-4.205157	0.744786
H	-4.513368	-3.367483	-0.077477
H	-3.966669	-3.553428	-1.764132
H	-4.730731	3.403740	0.740126
H	-4.662546	3.255541	-1.020167
H	-2.678193	4.871061	0.698496
H	-3.970767	5.563428	-0.298320
H	-2.613746	4.724294	-1.068247
H	-0.987203	1.370219	0.008110
H	0.992182	1.813919	-0.186397
H	3.414487	2.120666	-0.272385
H	3.998016	-2.088290	0.298502
H	1.559044	-2.414594	0.396528
H	-0.550158	-1.554305	0.241266

**A-IV**

C	0.014185	0.318106	-0.039456
C	-0.080305	0.337737	1.346606
C	1.033171	0.046631	2.122455
C	2.244891	-0.268605	1.520885
C	2.336293	-0.297962	0.137093
C	1.222598	-0.011188	-0.655896
Br	0.895263	0.066518	4.007476
N	1.381892	-0.036700	-2.050971
C	0.393790	-0.078228	-2.963210
C	0.498772	-0.044222	-4.327309
C	1.759292	0.133696	-5.068691
O	2.858813	-0.046239	-4.267851
C	4.146166	0.134611	-4.895942
C	4.599784	-1.127973	-5.600628
C	-0.742105	-0.191363	-5.122556
O	-0.802030	-0.486403	-6.292644
O	-1.857511	0.017778	-4.374839
C	-3.109593	-0.174740	-5.054004
C	-4.214884	0.085067	-4.054694
O	1.869984	0.432451	-6.231888
H	4.635205	-1.972487	-4.905442
H	5.604188	-0.979195	-6.011477
H	3.925768	-1.374146	-6.424425
H	4.078172	0.975380	-5.588306
H	4.814338	0.396853	-4.072478
H	-3.143449	-1.194281	-5.448273
H	-3.155303	0.511943	-5.903448
H	-4.156691	-0.611767	-3.212830
H	-5.188576	-0.044333	-4.538003
H	-4.159058	1.106049	-3.665226
H	-0.606398	-0.160251	-2.557292
H	-0.856813	0.585291	-0.626913
H	-1.021868	0.593954	1.819168
H	3.113564	-0.496574	2.128276
H	3.280942	-0.555968	-0.333513
H	2.325811	-0.048358	-2.423402

**TS-A-IV**

C	-0.205792	-0.774420	0.005670
C	-0.369917	-0.366163	1.331487
C	0.695024	0.253440	1.990621
C	1.915649	0.427308	1.348277
C	2.068327	-0.010402	0.039926
C	1.012495	-0.609232	-0.638055
N	-1.636188	-0.544577	1.927206
C	-1.702509	-0.927232	3.147240
C	-2.900000	-1.133022	3.938929
C	-4.205583	-1.035222	3.567548
O	-4.149768	0.230895	1.510129
C	-4.379121	1.628542	1.623264
C	-4.400293	2.313991	0.266616
Br	3.737616	0.197545	-0.824864
C	-2.806153	-1.580327	5.348428
O	-3.760898	-1.799007	6.064282
O	-1.532545	-1.713869	5.753894
C	-1.345232	-2.152773	7.116325
C	0.143560	-2.230256	7.365040
O	-5.349667	-1.110116	3.541146
H	-3.430468	2.221992	-0.234389
H	-4.625709	3.380938	0.376805
H	-5.161540	1.861227	-0.375649
H	-5.347728	1.739115	2.120742
H	-3.618208	2.086175	2.272520
H	-1.835931	-3.121829	7.237060
H	-1.839600	-1.439065	7.780126
H	0.619676	-2.941681	6.684033
H	0.327005	-2.562948	8.391525
H	0.615813	-1.252429	7.232569
H	-0.792103	-1.162130	3.702787
H	0.564596	0.626000	3.001979
H	2.740051	0.909325	1.862119
H	1.141034	-0.942841	-1.661837
H	-1.042702	-1.234375	-0.510096
H	-3.193326	0.051563	1.345651

## A-V (complex)

C	-0.373321	0.574124	0.444069
C	-0.319465	0.279109	1.798996
C	0.907038	0.226407	2.465263
C	2.079288	0.518260	1.762906
C	2.030203	0.820712	0.406933
C	0.804283	0.843924	-0.244193
N	0.893694	-0.041069	3.851010
C	1.803155	-0.783150	4.356652
C	1.889335	-1.089326	5.773565
C	2.957354	-1.892519	6.389025
O	3.867579	-2.287985	5.488601
C	4.954837	-3.093043	5.995807
C	5.853999	-3.425695	4.827718
Br	0.737949	1.232252	-2.093479
C	0.935917	-0.683900	6.636733
O	0.119612	-0.387767	7.382081
O	3.006439	-2.164400	7.571022
O	0.149881	2.124653	5.619657
C	0.700218	3.344077	5.150474
C	-0.104857	3.955539	4.013439
H	-0.113077	3.296398	3.137797
H	0.325221	4.916166	3.706571
H	-1.140567	4.121492	4.325829
H	0.710318	4.016630	6.013134
H	1.745805	3.198037	4.838117
H	4.532552	-3.987023	6.461482
H	5.474000	-2.521635	6.769275
H	5.312220	-3.988538	4.062087
H	6.692869	-4.037591	5.173788
H	6.258092	-2.517282	4.371593
H	2.574025	-1.260565	3.745541
H	3.032925	0.538466	2.281513
H	2.940824	1.049119	-0.135831
H	-1.325573	0.600200	-0.073993
H	-1.228995	0.080287	2.356654
H	0.220115	1.449130	4.916712



**A-V (ketene)**

C	-0.146950	0.095469	0.039635
C	-0.059369	-0.027678	1.418653
C	1.184592	-0.035371	2.055087
C	2.341742	0.129701	1.287994
C	2.259244	0.264129	-0.093233
C	1.015621	0.240495	-0.709218
N	1.204093	-0.143834	3.457204
C	2.115049	-0.830666	4.024533
C	2.208586	-0.918875	5.477901
C	3.174223	-1.731323	6.229917
O	3.994563	-2.407522	5.414883
C	4.981428	-3.244582	6.056651
C	5.786765	-3.911480	4.965607
Br	0.902035	0.398874	-2.590384
C	1.348400	-0.204410	6.221479
O	0.609591	0.405094	6.854907
O	3.222402	-1.782802	7.442164
H	4.460130	-3.968386	6.688178
H	5.599195	-2.615362	6.702394
H	5.147686	-4.527131	4.326115
H	6.547656	-4.557564	5.414525
H	6.292415	-3.169455	4.340907
H	2.868076	-1.404166	3.475308
H	3.311362	0.186371	1.773119
H	3.158599	0.396807	-0.684538
H	-1.113668	0.086130	-0.451452
H	-0.955428	-0.124966	2.022762

**TS-A-V**

C	-0.544382	-0.222254	1.009926
C	0.159984	0.031353	2.179699
C	1.529015	0.260181	2.132454
C	2.200085	0.236651	0.919019
C	1.501007	-0.021078	-0.274735
C	0.113842	-0.248760	-0.210474
Br	-0.746609	0.058916	3.842397
N	2.145309	-0.041736	-1.455915
C	2.738017	-0.061075	-2.545747
C	3.354661	-1.253962	-3.173893
C	4.055941	-1.266280	-4.467022
O	4.079821	-0.054186	-5.032949
C	4.748279	0.039364	-6.310962
C	4.658342	1.478150	-6.763741
C	3.288607	-2.433541	-2.543483
O	3.209453	-3.426068	-1.969338
O	4.552370	-2.259338	-4.958722
H	4.257102	-0.645988	-7.006221
H	5.781923	-0.291516	-6.182721
H	5.147031	2.146442	-6.048942
H	3.616126	1.790568	-6.875763
H	5.155754	1.588794	-7.732350
H	2.859883	0.842476	-3.160678
H	-0.436768	-0.444264	-1.124473
H	-1.613914	-0.400429	1.046175
H	2.079618	0.458971	3.045840
H	3.268978	0.417949	0.881785

**TS-A-V'**

C	0.053636	-0.000477	-0.032970
C	-0.009141	-0.000156	1.355472
C	1.153185	0.000289	2.116276
C	2.388968	0.000414	1.484498
C	2.466576	0.000092	0.089112
C	1.288573	-0.000353	-0.665581
Br	-1.694263	-0.000324	2.212403
N	3.729003	0.000231	-0.495131
C	4.140107	0.000031	-1.740716
C	5.542332	0.000407	-1.607778
C	6.668054	0.000439	-2.514772
O	6.248643	0.000010	-3.800248
C	7.284712	0.000001	-4.800286
C	6.610223	-0.000490	-6.153481
C	5.522032	0.000759	-0.187902
O	6.040102	0.001146	0.855101
O	7.836480	0.000799	-2.186791
H	7.911830	-0.883492	-4.653181
H	7.911424	0.883854	-4.653619
H	5.983690	-0.888550	-6.279119
H	7.367780	-0.000527	-6.943626
H	5.983304	0.887233	-6.279571
H	3.526805	-0.000331	-2.637323
H	1.328269	-0.000610	-1.750262
H	-0.857784	-0.000823	-0.620228
H	1.096196	0.000539	3.198981
H	3.303797	0.000762	2.067803

**A-VI**

C	-0.028727	0.035098	0.030993
C	0.002313	0.030413	1.420312
C	1.212077	-0.003959	2.103305
C	2.402614	-0.043725	1.389594
C	2.385667	-0.063434	-0.008503
C	1.161915	-0.004665	-0.682540
Br	-1.615042	0.133047	2.390641
N	3.591381	-0.070728	-0.730563
C	4.112442	-1.182966	-1.063325
C	3.632508	-2.547131	-0.801497
C	4.359728	-3.749165	-1.259344
O	5.478924	-3.436574	-1.923488
C	6.261289	-4.547982	-2.412644
C	7.465291	-3.973307	-3.122509
C	2.506649	-2.856376	-0.133271
O	1.569553	-3.227301	0.420793
O	3.986117	-4.886361	-1.056969
H	5.632641	-5.144590	-3.078466
H	6.540982	-5.173090	-1.560900
H	7.161687	-3.343756	-3.963861
H	8.085934	-4.787653	-3.509288
H	8.073551	-3.372368	-2.440400
H	5.045436	-1.155860	-1.621422
H	1.152234	0.014119	-1.767836
H	-0.977760	0.078100	-0.492117
H	1.225519	0.008748	3.187654
H	3.354780	-0.055221	1.910711

**A-VI'**

C	-0.020382	0.062879	0.025502
C	0.007733	-0.014565	1.410784
C	1.218925	-0.080820	2.088999
C	2.412602	-0.055641	1.382078
C	2.392795	0.014210	-0.013831
C	1.171695	0.069728	-0.687960
Br	-1.615569	-0.049702	2.379572
N	3.603909	0.070620	-0.712522
C	4.917025	-0.551675	-0.454396
O	5.420916	-0.890071	0.564961
C	3.903391	-0.036596	-2.077625
C	5.152827	-0.543485	-1.941764
C	6.270314	-0.842195	-2.822094
O	5.944835	-0.622754	-4.111545
C	6.976671	-0.901392	-5.078803
C	6.417169	-0.580165	-6.445876
O	7.352549	-1.242643	-2.454796
H	7.263389	-1.952530	-4.987103
H	7.852202	-0.292379	-4.838376
H	5.538300	-1.193895	-6.664242
H	7.174424	-0.780702	-7.210341
H	6.130943	0.473455	-6.514678
H	3.274351	0.257813	-2.907469
H	1.140516	0.119162	-1.771682
H	-0.967321	0.108159	-0.500554
H	1.233978	-0.144569	3.171248
H	3.360577	-0.095227	1.905998

TS-A-VI

C	-1.256534	0.642176	1.135473
C	0.066044	0.183136	2.454175
C	1.326614	0.396587	1.823255
N	1.602136	1.555008	1.179856
C	0.615476	2.163472	0.571339
C	-0.720229	1.706235	0.401745
C	2.276433	-0.652439	1.807085
C	1.974475	-1.859425	2.378277
C	0.723006	-2.073264	3.016126
C	-0.203652	-1.080416	3.076385
Br	0.383451	-3.759256	3.789586
C	-1.587616	2.268844	-0.652666
O	-1.020957	3.340059	-1.247885
C	-1.802378	3.976362	-2.276035
C	-0.998626	5.146209	-2.797176
O	-2.272323	0.070216	1.317256
O	-2.683271	1.850427	-0.953977
H	-2.756367	4.291413	-1.844759
H	-2.014617	3.241372	-3.057164
H	-0.790963	5.865843	-1.999750
H	-1.561113	5.658683	-3.584157
H	-0.046092	4.811594	-3.218582
H	0.871049	3.088084	0.062916
H	3.228428	-0.479269	1.317637
H	2.692326	-2.672352	2.345735
H	-1.157503	-1.235346	3.568211
H	-0.359999	1.051955	2.964609

**A-VII**

C	-0.035983	0.022744	-0.052405
C	-0.029815	0.008043	1.475006
C	1.342772	0.022662	2.087191
N	2.376476	0.519101	1.480099
C	2.224208	0.908737	0.166181
C	1.125380	0.723881	-0.617161
C	1.475137	-0.477469	3.434804
C	0.467033	-1.161742	4.016144
C	-0.779859	-1.417776	3.315541
C	-1.017496	-0.918346	2.098476
Br	-2.030427	-2.538935	4.178030
C	1.114885	1.155371	-2.040757
O	2.358425	1.267542	-2.544744
C	2.449105	1.752419	-3.898510
C	3.915104	1.812478	-4.262840
O	-0.946151	-0.470530	-0.682567
O	0.117237	1.414683	-2.670510
H	1.969507	2.733900	-3.949874
H	1.889995	1.072492	-4.546744
H	4.457241	2.494736	-3.601333
H	4.024965	2.171927	-5.290906
H	4.376490	0.823145	-4.193334
H	3.105230	1.372944	-0.264677
H	2.429993	-0.333474	3.928576
H	0.584649	-1.566475	5.015682
H	-1.924144	-1.125945	1.542358
H	-0.399166	1.036430	1.693015

TS-A-VII

C	-0.189933	-0.366105	-0.042147
C	-0.032410	-0.196812	1.435713
C	1.250549	-0.258219	2.072649
N	2.382264	-0.474665	1.387899
C	2.247651	-0.652885	0.071785
C	1.070554	-0.636209	-0.681981
C	1.277876	-0.109288	3.476348
C	0.131607	0.069000	4.232720
C	-1.123506	0.116855	3.628799
C	-1.233092	0.014464	2.232742
Br	-2.671091	0.320748	4.665324
C	1.118417	-0.908920	-2.135609
O	2.390416	-0.955212	-2.603619
C	2.531988	-1.241113	-4.003912
C	4.011085	-1.245087	-4.320447
O	-1.312346	-0.250277	-0.532600
O	0.160644	-1.082761	-2.852993
H	1.992313	-0.479635	-4.573915
H	2.064118	-2.207007	-4.214928
H	4.461917	-0.273747	-4.096197
H	4.161880	-1.457047	-5.383937
H	4.534642	-2.010903	-3.740227
H	3.176181	-0.834917	-0.459449
H	2.249772	-0.149567	3.958317
H	0.207969	0.171017	5.309688
H	-2.183337	-0.063244	1.712325
H	-0.664345	0.995974	1.741663



A-VIII

C	-0.005081	-0.062680	0.014577
C	-0.018768	-0.063249	1.475642
C	1.167654	-0.130272	2.221118
N	2.414615	-0.210335	1.684609
C	2.442531	-0.230709	0.362772
C	1.334995	-0.183682	-0.505519
C	1.055799	-0.109205	3.621581
C	-0.166184	-0.029072	4.314320
C	-1.328552	0.033156	3.599615
C	-1.336161	0.023301	2.130886
Br	-2.968632	0.135398	4.482073
C	1.557923	-0.283833	-1.966282
O	2.830179	0.038272	-2.309506
C	3.149161	-0.076740	-3.704804
C	4.596599	0.327712	-3.876370
O	-1.070742	0.047131	-0.608884
O	0.735062	-0.625353	-2.783340
H	2.472713	0.567601	-4.273390
H	2.969813	-1.107924	-4.023186
H	4.755999	1.358576	-3.546410
H	4.879173	0.256208	-4.931729
H	5.257782	-0.325390	-3.298778
H	3.429731	-0.298893	-0.083714
H	1.985491	-0.157122	4.183830
H	-0.175450	-0.018467	5.398039
H	-1.983110	-0.787245	1.753761
H	-1.870665	0.906551	1.739939

TS-A-VIII

C	-0.006288	0.049847	-0.011229
C	0.075575	-0.167923	1.410552
C	1.283858	-0.131919	2.090388
N	2.480444	-0.200524	1.440436
C	2.400005	-0.245658	0.124890
C	1.228196	-0.126681	-0.674229
C	1.196851	0.127935	3.477723
C	-0.026518	0.286911	4.126037
C	-1.220113	0.116386	3.432488
C	-1.226362	-0.143237	2.032655
Br	-2.838971	0.138595	4.370461
C	1.314676	-0.090810	-2.148649
O	2.592750	-0.061869	-2.588758
C	2.765512	-0.043062	-4.015705
C	4.251517	-0.004418	-4.293920
O	-1.164061	0.387903	-0.413918
O	0.364590	-0.094346	-2.898206
H	2.248601	0.832274	-4.418616
H	2.290703	-0.933351	-4.437844
H	4.708131	0.889110	-3.858079
H	4.425251	0.012726	-5.374689
H	4.751430	-0.885100	-3.879696
H	3.346116	-0.333463	-0.400091
H	2.123194	0.259379	4.030735
H	-0.047663	0.506861	5.187244
H	-1.927871	-0.940434	1.747716
H	-1.672434	0.527279	1.062755

4 (enol) - (Ethyl 6-bromo-4-hydroxyquinoline-3-carboxylate)

C	-0.001513	0.001645	0.005186
C	-0.000763	0.000099	1.437373
C	1.254369	0.009439	2.093844
N	2.442427	0.019698	1.428202
C	2.397632	0.020855	0.122136
C	1.212409	0.012026	-0.662255
C	1.283740	0.008156	3.509649
C	0.126410	-0.001742	4.241386
C	-1.116335	-0.010915	3.575396
C	-1.188325	-0.010170	2.208814
Br	-2.704145	-0.024431	4.601008
C	1.296567	0.013545	-2.146434
O	2.576644	0.033920	-2.569051
C	2.770999	0.036233	-3.995034
C	4.260998	0.064268	-4.250409
O	-1.147184	-0.006313	-0.688584
O	0.357245	-0.001500	-2.907990
H	2.264074	0.909836	-4.413942
H	2.297602	-0.856827	-4.412205
H	4.715845	0.961059	-3.819643
H	4.450318	0.066870	-5.328578
H	4.749728	-0.813737	-3.818025
H	3.350392	0.029129	-0.396290
H	2.256122	0.015362	3.990201
H	0.154453	-0.002618	5.325153
H	-2.171815	-0.017722	1.749351
H	-1.911090	-0.011745	-0.095418

**TS-A-VII'**

C	-0.049278	0.140891	-0.003582
C	-0.025443	-0.072720	1.479466
C	1.141567	0.343730	2.255205
N	2.336680	0.714197	1.663936
C	2.298413	0.843215	0.353357
C	1.204686	0.629897	-0.511313
C	1.136334	0.012050	3.677588
C	0.042261	-0.535293	4.262002
C	-1.110445	-0.841911	3.475919
C	-1.155351	-0.608774	2.128407
Br	-2.595928	-1.580527	4.351126
C	1.359336	0.881992	-1.959566
O	2.638927	1.192842	-2.290388
C	2.876114	1.467091	-3.679803
C	4.345407	1.790839	-3.835848
O	-1.072513	-0.166183	-0.610322
O	0.475253	0.836525	-2.783632
H	2.237092	2.299420	-3.988334
H	2.584491	0.590755	-4.265518
H	4.619154	2.668223	-3.242112
H	4.568401	2.003877	-4.886350
H	4.967944	0.949710	-3.516348
H	3.232171	1.158406	-0.101562
H	2.037498	0.240319	4.236779
H	0.034390	-0.762345	5.321870
H	-2.016400	-0.844952	1.513254
H	0.407191	1.273149	2.218227

A-VIII'

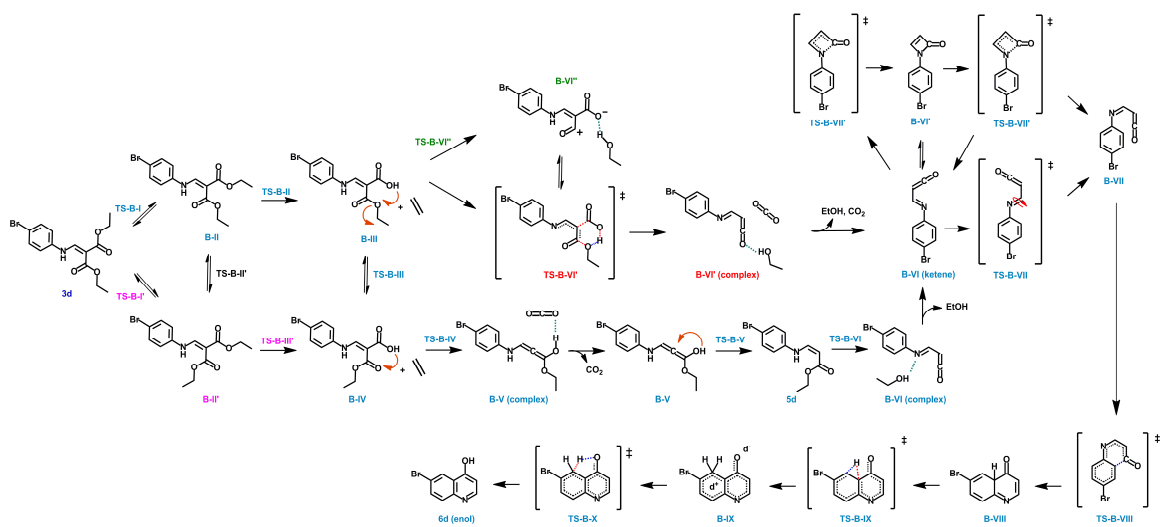
C	-0.028957	-0.120099	0.025427
C	-0.010051	-0.123861	1.417695
C	1.268236	-0.091799	2.141370
C	2.453432	0.266729	1.337605
C	2.396331	0.295473	-0.015215
C	1.145465	0.083817	-0.667437
N	1.321241	0.212774	3.524169
C	0.163414	0.235048	4.126957
C	-1.126584	0.027832	3.565247
C	-1.291288	-0.254705	2.165591
O	-2.318923	-0.519239	1.541300
C	-2.315145	0.125261	4.436673
O	-3.463707	0.192059	4.063041
Br	1.123140	0.111628	-2.536976
O	-1.981780	0.146472	5.753514
C	-3.077095	0.275476	6.672842
C	-2.501523	0.266612	8.071671
H	-3.771760	-0.553261	6.509487
H	-3.612579	1.204106	6.454774
H	-1.965094	-0.666508	8.268099
H	-3.308826	0.360253	8.805274
H	-1.808013	1.100550	8.216473
H	0.204765	0.438629	5.193065
H	3.379215	0.429322	1.880474
H	3.278132	0.502096	-0.610393
H	-0.985261	-0.243243	-0.471162
H	1.422726	-1.215685	2.135377

**TS-A-VIII'**

C	0.041145	-0.000385	0.005313
C	0.011024	-0.001639	1.485889
C	1.227139	-0.087472	2.242959
N	2.505653	-0.328167	1.624940
C	2.472097	-0.393217	0.289670
C	1.357868	-0.305009	-0.532283
C	1.129876	-0.224051	3.678201
C	-0.080550	-0.119689	4.296399
C	-1.254065	0.056907	3.524347
C	-1.213279	0.106603	2.148896
Br	-2.898260	0.205136	4.422441
C	1.519419	-0.530737	-1.992345
O	2.755613	-0.191404	-2.420238
C	3.025596	-0.436057	-3.812868
C	4.442638	0.013750	-4.088430
O	-0.973856	0.229457	-0.643560
O	0.673652	-0.990299	-2.720764
H	2.294412	0.115575	-4.409798
H	2.884184	-1.501832	-4.013891
H	4.563610	1.079529	-3.873543
H	4.685026	-0.154275	-5.142629
H	5.158559	-0.545674	-3.478761
H	3.443643	-0.550187	-0.168812
H	2.048811	-0.368123	4.236949
H	-0.155326	-0.188388	5.375626
H	-2.108881	0.214431	1.547303
H	1.831187	0.924683	2.116430

4 (keto) (Ethyl 6-bromo-4-oxo-1,4-dihydroquinoline-3-carboxylate)

C	0.010800	0.005564	0.005718
C	0.012089	0.002161	1.498172
C	1.201669	-0.006745	2.231844
N	2.405409	-0.015073	1.542351
C	2.457024	-0.021550	0.192469
C	1.348832	-0.019594	-0.603746
C	1.175082	-0.006352	3.631649
C	-0.037642	0.004125	4.291006
C	-1.228794	0.013885	3.557312
C	-1.209719	0.012757	2.179303
Br	-2.877740	0.030716	4.483613
C	1.523676	-0.049077	-2.075827
O	2.831039	0.072706	-2.428127
C	3.102625	0.034099	-3.839511
C	4.595259	0.194877	-4.022065
O	-1.042203	0.035732	-0.611544
O	0.645294	-0.171433	-2.892895
H	2.540962	0.836498	-4.325350
H	2.739492	-0.916237	-4.240598
H	4.940417	1.147883	-3.609856
H	4.841682	0.173814	-5.088433
H	5.141708	-0.615157	-3.529271
H	3.449762	-0.030766	-0.239895
H	2.103268	-0.013582	4.196953
H	-0.068277	0.005033	5.374728
H	-2.119855	0.021590	1.590566
H	3.267695	-0.020540	2.068024



**Scheme S5.** Mechanism proposed for the formation of quinolone **6d** (Path B).



## Step 2 - Pathway B (R = Br)

### B-II

C	0.088304	0.300518	0.003165
C	0.053141	-0.017756	1.350727
C	1.220206	-0.329541	2.029939
C	2.425367	-0.330965	1.348862
C	2.475783	-0.017622	-0.007814
C	1.297662	0.308314	-0.674466
Br	-1.606712	-0.018034	2.276730
N	3.731220	-0.029568	-0.638520
C	3.958949	-0.008735	-1.952335
C	5.183579	0.005416	-2.574165
C	5.097233	-0.005961	-4.051388
O	6.267343	-0.139740	-4.678052
C	6.236846	-0.156691	-6.117211
C	6.216416	1.245734	-6.687444
C	6.394184	0.032043	-1.752781
O	6.356231	-0.039943	-0.529388
O	7.543548	0.157271	-2.408574
C	8.750860	0.198522	-1.623941
C	9.036889	1.598012	-1.122656
O	4.043104	0.075440	-4.647726
H	9.997129	1.612543	-0.601731
H	8.265474	1.925893	-0.425844
H	9.088434	2.302869	-1.954309
H	8.662995	-0.508487	-0.799807
H	9.522789	-0.142130	-2.312681
H	7.148739	-0.684344	-6.394081
H	5.371341	-0.730586	-6.447048
H	7.067700	1.823151	-6.322501
H	5.294523	1.760120	-6.415975
H	6.274785	1.200540	-7.777553
H	3.095569	-0.011814	-2.605671
H	1.306602	0.585284	-1.720086
H	-0.823523	0.554513	-0.520473
H	1.191378	-0.574999	3.083036
H	3.339013	-0.584020	1.874198
H	4.574813	-0.072736	-0.065927

**B-II'**

C	0.142733	-0.047625	-0.190895
C	0.085952	-0.415333	1.144093
C	1.241491	-0.395828	1.906039
C	2.456099	-0.003323	1.347297
C	2.495338	0.380913	0.009480
C	1.341958	0.349028	-0.759149
N	3.593210	0.005936	2.172669
C	4.866721	0.025592	1.757344
C	6.011269	0.077062	2.502079
C	6.053301	0.204077	3.965078
O	4.818235	-0.008032	4.525217
C	4.731533	0.118113	5.959784
C	5.130526	-1.165758	6.654488
Br	-1.437203	-0.080980	-1.246346
C	7.248375	0.041611	1.684205
O	7.251314	0.158106	0.476790
O	8.356945	-0.169247	2.388175
C	9.588474	-0.206794	1.646943
C	10.703256	-0.424299	2.641181
O	7.002226	0.484029	4.644809
H	6.179847	-1.394296	6.468768
H	4.518179	-2.001533	6.310604
H	4.989160	-1.058998	7.732539
H	5.360278	0.950195	6.273497
H	3.686929	0.366222	6.148686
H	9.531027	-1.009123	0.909024
H	9.698813	0.734077	1.105073
H	10.570979	-1.367347	3.173569
H	10.730204	0.382453	3.374662
H	11.662599	-0.453458	2.120052
H	5.018867	-0.008740	0.685451
H	3.415569	0.724539	-0.443668
H	1.379855	0.647921	-1.798084
H	-0.851683	-0.723139	1.587037
H	1.201747	-0.698446	2.946248
H	3.457609	-0.038311	3.175473

TS-B-II

C	0.018436	-0.145947	0.059568
C	0.044901	0.101180	1.422876
C	1.261917	0.178588	2.077777
C	2.457911	0.005935	1.382743
C	2.415119	-0.255662	0.015257
C	1.197773	-0.324028	-0.644376
N	3.656955	0.089813	2.106274
C	4.889903	0.180880	1.594593
C	6.068561	0.234754	2.290473
C	6.030225	0.138411	3.743806
O	7.217419	0.001915	4.353035
C	7.208214	-0.099213	5.789607
C	7.141267	1.264436	6.444062
Br	-1.648352	-0.248089	-0.849841
C	7.281914	0.390954	1.426932
O	7.209082	0.225870	0.219484
O	8.397572	0.740529	2.014731
C	10.411614	0.156182	1.812758
C	10.427371	-0.091808	3.179041
O	4.988911	0.135261	4.388757
H	7.217462	1.155756	7.528562
H	6.196444	1.757147	6.215533
H	7.962352	1.898249	6.104321
H	6.372615	-0.727404	6.095785
H	8.143994	-0.605948	6.024729
H	10.186147	-0.617882	1.090417
H	10.693902	1.116173	1.402613
H	9.183444	0.275395	3.047476
H	10.903291	0.627868	3.835586
H	10.397566	-1.120083	3.522214
H	4.980959	0.222331	0.516459
H	3.322927	-0.421346	-0.548915
H	1.172694	-0.526870	-1.706659
H	-0.876943	0.237920	1.972180
H	1.286395	0.381350	3.142284
H	3.618627	0.101843	3.124288

**B-III**

C	0.023282	-0.002035	0.086354
C	0.094205	0.229018	1.450951
C	1.328245	0.228211	2.078634
C	2.492273	-0.007679	1.352183
C	2.406980	-0.254875	-0.014499
C	1.173596	-0.243715	-0.647041
N	3.716077	-0.001797	2.049640
Br	-1.664988	0.005359	-0.783984
H	1.111960	-0.435544	-1.709866
H	3.290806	-0.472847	-0.598939
H	1.389210	0.420012	3.143706
H	-0.805612	0.414529	2.021893
C	4.930664	0.080353	1.513003
C	6.128425	0.067954	2.188440
C	7.329735	0.178084	1.309959
C	6.116624	-0.038960	3.635963
H	3.697237	-0.051791	3.067183
H	4.998205	0.174437	0.435878
O	7.234034	0.267302	0.111706
O	8.535203	0.174850	1.888569
O	5.107289	-0.109101	4.316302
O	7.343027	-0.059290	4.209135
C	7.418052	-0.138433	5.653009
H	6.633807	-0.809797	5.997985
H	8.390794	-0.589455	5.842423
C	7.301188	1.230847	6.283599
H	6.320704	1.665676	6.089647
H	7.428490	1.144811	7.364996
H	8.071442	1.903128	5.902080
H	8.440860	0.092922	2.852238

TS-B-III

C	-2.906199	1.023824	0.788835
C	-1.525641	1.013849	0.888554
C	-0.772028	0.055713	0.213539
C	-1.422548	-0.891676	-0.572423
C	-2.806458	-0.893821	-0.659293
C	-3.542926	0.062881	0.018987
N	0.626821	0.089560	0.332082
C	1.463942	-0.955982	0.118982
C	2.808496	-0.914301	0.147184
C	3.554124	0.362954	0.352117
O	3.922256	0.906391	-0.808456
C	4.687539	2.133311	-0.764700
C	3.781627	3.341389	-0.672177
Br	-5.438372	0.065705	-0.114419
C	3.542110	-2.185283	-0.017179
O	3.058520	-3.190795	-0.457943
O	4.841548	-2.174887	0.367933
O	3.812560	0.845725	1.429410
H	0.999604	-1.915992	-0.071944
H	-0.859698	-1.620903	-1.139907
H	-3.305737	-1.633405	-1.270799
H	-3.482976	1.770846	1.317402
H	-1.029257	1.752973	1.507469
H	5.250245	2.125039	-1.696359
H	5.376619	2.085131	0.077918
H	3.063610	3.349962	-1.493895
H	4.380119	4.252822	-0.733103
H	3.243774	3.355788	0.276487
H	1.021730	0.942789	0.699697
H	5.045957	-1.400280	0.905010

TS-B-III'

C	0.102874	-0.252016	0.027409
C	0.046246	-0.002521	1.397924
C	1.219022	0.325956	2.074449
C	2.425236	0.382263	1.393513
C	2.465038	0.128351	0.032618
C	1.304313	-0.184139	-0.656754
N	-1.202019	-0.076331	2.033728
C	-1.410408	-0.150502	3.359533
C	-2.587434	-0.174789	4.046337
C	-3.906884	-0.032670	3.435579
O	-3.866072	-0.139189	2.071426
C	-5.113878	0.019906	1.367100
C	-5.892752	-1.276919	1.318703
Br	4.121109	0.215970	-0.897238
C	-2.424597	-0.312786	5.535778
O	-1.342489	-0.108705	6.063773
O	-3.483781	-0.686035	6.193100
C	-4.550194	-0.078014	7.937172
C	-5.693461	-0.002190	7.156585
O	-4.950836	0.189190	4.002577
H	-6.798930	-1.139544	0.723983
H	-6.185233	-1.587915	2.321416
H	-5.299819	-2.070468	0.860168
H	-5.688162	0.809526	1.849650
H	-4.823090	0.347016	0.368679
H	-4.270513	-0.983425	8.458287
H	-3.911935	0.780147	8.104106
H	-4.864112	-0.327075	6.236161
H	-6.062854	0.971214	6.855159
H	-6.419893	-0.805111	7.211077
H	-0.525854	-0.199472	3.983038
H	1.205404	0.555579	3.131298
H	3.331290	0.637163	1.926715
H	1.335826	-0.381118	-1.719970
H	-0.803260	-0.510801	-0.508614
H	-2.030417	-0.101688	1.453249

**B-IV**

C	-0.103099	-0.024099	-0.062479
C	-0.032079	0.333059	1.280493
C	1.188815	0.329129	1.936883
C	2.342168	-0.012470	1.249335
C	2.286240	-0.352551	-0.092952
C	1.063696	-0.361106	-0.742896
N	-1.317450	-0.040593	-0.777879
Br	4.013585	-0.007369	2.150765
C	-2.540088	-0.088205	-0.244645
C	-3.752034	-0.075979	-0.881072
C	-3.936105	-0.000210	-2.319143
H	-2.596301	-0.154207	0.835799
H	-0.917618	0.632377	1.824973
H	1.239019	0.606156	2.981304
H	3.188281	-0.617226	-0.628004
H	1.015523	-0.642764	-1.788640
O	-2.785688	0.032037	-3.024852
C	-2.896187	0.099833	-4.468452
C	-3.100182	-1.271689	-5.071961
H	-1.953468	0.544057	-4.785012
H	-3.713632	0.773668	-4.718504
H	-2.291739	-1.948161	-4.788764
H	-3.111184	-1.190874	-6.161111
H	-4.050432	-1.698868	-4.752731
H	-1.269028	-0.030399	-1.789104
O	-5.018277	0.034483	-2.880940
H	-6.043371	-0.059521	-1.502302
C	-4.933684	-0.145612	0.036116
O	-4.806975	-0.215328	1.233516
O	-6.138329	-0.126235	-0.528129

TS-B-IV

C	0.368750	0.424584	-0.079698
C	0.148181	0.096470	1.258938
C	1.215405	-0.379765	2.019630
C	2.465925	-0.546573	1.444303
C	2.665698	-0.220237	0.113759
C	1.620059	0.273287	-0.650811
N	-1.132586	0.270903	1.791298
C	-1.613650	-0.264812	2.953384
C	-2.746534	0.079486	3.570600
C	-2.496930	-0.273175	5.837984
O	-3.237353	0.547958	6.251243
Br	4.385770	-0.441512	-0.666672
C	-3.938027	0.618469	3.250655
O	-4.633289	1.407493	4.070527
O	-4.568973	0.337661	2.110737
C	-6.003143	0.503833	2.020363
C	-6.735582	-0.611495	2.733200
O	-1.714665	-1.136903	5.842946
H	-0.963543	-1.006214	3.408917
H	1.088847	-0.605643	3.069630
H	3.287077	-0.917703	2.042984
H	1.776862	0.530927	-1.689806
H	-0.452363	0.794095	-0.683870
H	-6.193215	0.481739	0.948518
H	-6.277752	1.483162	2.409076
H	-6.434223	-1.584436	2.342183
H	-7.811382	-0.497690	2.581709
H	-6.541352	-0.586916	3.806128
H	-1.771800	0.843586	1.260497
H	-4.192629	1.399279	4.941090



## B-V (complex)

C	2.798518	0.564448	0.642390	-0.962671
C	3.667874	-0.304339	0.006673	0.596314
C	3.174932	-1.329402	-0.786522	-0.339377
C	1.808470	-1.490014	-0.926131	-0.527576
C	0.912689	-0.626171	-0.288242	-0.296571
C	1.428113	0.413648	0.488499	1.057141
Br	5.547678	-0.086548	0.211979	-0.121964
N	-0.452459	-0.822093	-0.462412	0.022010
C	-1.464278	-0.284833	0.321568	-0.528008
C	-2.739808	-0.303990	0.020909	1.051050
C	-3.980500	-0.498847	-0.348928	-1.116050
O	-4.623699	-1.664938	-0.144351	-0.077287
C	-6.019363	-1.614725	0.200020	-0.257299
C	-6.242395	-1.051113	1.587657	-0.361003
C	-2.147312	3.003272	-0.194129	0.485970
O	-1.194745	3.102563	0.447784	-0.199524
O	-3.105578	2.925480	-0.841272	-0.262856
O	-4.759504	0.409850	-0.997339	-0.235275
H	-1.110742	0.150040	1.252255	0.150783
H	0.768664	1.131768	0.956656	0.144653
H	3.184126	1.374662	1.247114	0.153341
H	3.853683	-2.007704	-1.286391	0.153673
H	1.426574	-2.304710	-1.531284	0.123415
H	-6.335842	-2.655357	0.143081	0.157877
H	-6.560212	-1.043724	-0.554727	0.171765
H	-5.692254	-1.627142	2.333562	0.152627
H	-7.305810	-1.090226	1.835161	0.144316
H	-5.921994	-0.009250	1.646152	0.149953
H	-0.741931	-1.428952	-1.213036	0.266481
H	-4.279186	1.243213	-1.072102	0.304054

**B-V**

C	0.000919	-0.088583	-0.021743
C	-0.026873	-0.098806	1.365119
C	1.152454	-0.020390	2.084200
C	2.367528	0.068109	1.421917
C	2.395781	0.064749	0.039582
C	1.215682	-0.017365	-0.707268
Br	1.107924	-0.027373	3.986818
N	1.300325	-0.010408	-2.093431
C	0.283873	-0.313633	-2.987631
C	0.352562	-0.154016	-4.285223
C	0.494409	-0.018301	-5.575780
O	0.065492	1.063528	-6.296259
O	1.128190	-0.918596	-6.351782
C	0.566331	-1.198899	-7.645943
C	-0.757304	-1.927500	-7.545378
H	-0.602807	-0.735701	-2.524796
H	-0.936962	-0.117903	-0.558875
H	-0.976042	-0.155396	1.881471
H	3.291213	0.131765	1.981742
H	3.349709	0.119092	-0.473247
H	1.321617	-1.819413	-8.126234
H	0.468977	-0.270251	-8.208924
H	-0.648117	-2.854667	-6.980337
H	-1.120919	-2.172278	-8.546094
H	-1.511616	-1.308765	-7.055542
H	2.195138	0.216162	-2.497785
H	-0.415943	1.647853	-5.702718

TS-B-V

C	0.789043	-0.885400	-0.472094
C	0.225484	0.335947	-0.095503
C	1.071615	1.355624	0.341385
C	2.443769	1.160633	0.381499
C	2.983474	-0.056438	0.001636
C	2.156981	-1.085594	-0.421203
N	-1.161985	0.475379	-0.159098
C	-1.883203	1.635955	-0.075097
C	-3.231220	1.755116	-0.086953
C	-4.120461	0.661700	-0.177111
O	-5.324929	1.110776	-0.131059
Br	4.865904	-0.321073	0.068251
O	-3.868063	-0.622227	-0.302034
C	-4.985927	-1.552198	-0.357699
C	-5.484115	-1.886681	1.029058
H	-1.272092	2.529089	-0.004821
H	0.672082	2.304421	0.671233
H	3.089334	1.959228	0.722251
H	2.577195	-2.037609	-0.717053
H	0.145741	-1.687462	-0.816758
H	-4.575162	-2.424481	-0.863224
H	-5.765473	-1.107806	-0.974714
H	-4.681622	-2.299792	1.642217
H	-6.278586	-2.632729	0.957395
H	-5.890591	-1.002697	1.520328
H	-1.693190	-0.371976	-0.302034
H	-4.749082	2.141336	-0.052707

## 5 (ethyl 3-((4-bromophenyl)amino)acrylate)

C	0.123940	0.100893	0.020543
C	0.085105	0.023864	1.414486
C	1.290740	-0.019555	2.113813
C	2.499158	0.015240	1.434050
C	2.517067	0.091777	0.052242
C	1.328114	0.134196	-0.659077
N	-1.166559	-0.006702	2.033124
C	-1.420804	-0.050257	3.365225
C	-2.627376	-0.084744	3.970789
C	-3.938997	-0.084730	3.340365
O	-4.988138	-0.108935	3.934879
Br	4.177036	0.137451	-0.873727
O	-3.884220	-0.049758	1.975294
C	-5.145346	-0.058332	1.275322
C	-5.678715	-1.464720	1.107268
H	-0.545157	-0.055510	4.001049
H	1.310802	-0.082674	3.192866
H	3.427267	-0.019159	1.988956
H	1.339011	0.193898	-1.739177
H	-0.804398	0.136031	-0.538451
H	-4.924958	0.403560	0.313098
H	-5.848673	0.568748	1.821715
H	-4.956202	-2.096601	0.587088
H	-6.598180	-1.440632	0.517680
H	-5.906298	-1.908654	2.076238
H	-1.984880	0.004916	1.437990
H	-2.655857	-0.114011	5.049767

**TS-B-VI**

C	0.058222	-0.573592	0.064130
C	0.018119	-0.112588	1.372033
C	1.151579	0.403682	1.976502
C	2.337112	0.471600	1.258481
C	2.393880	0.031097	-0.063341
C	1.246673	-0.509711	-0.642981
Br	-1.609108	-0.210478	2.352932
N	3.578608	0.062450	-0.822668
C	4.302739	1.114524	-0.796462
C	5.562402	1.337345	-1.453263
C	6.338899	0.566707	-2.215870
O	5.364487	-1.698515	-1.800188
C	5.211023	-2.723496	-2.765168
C	4.411932	-2.284844	-3.981110
O	7.145715	0.143035	-2.910870
H	3.959230	1.991608	-0.238580
H	1.294627	-0.869663	-1.663227
H	-0.830808	-0.983141	-0.396688
H	1.116626	0.740041	3.004264
H	3.233212	0.841060	1.742102
H	4.745108	-3.602902	-2.303697
H	6.220961	-3.013868	-3.061857
H	3.396920	-1.992824	-3.699749
H	4.338137	-3.100624	-4.704879
H	4.888460	-1.434074	-4.472425
H	4.502217	-1.354639	-1.492325
H	5.994191	2.328476	-1.358399

**B-VI (complex)**

C	-0.219953	0.466700	0.742981
C	0.052259	0.579107	2.095894
C	1.223357	0.040349	2.628904
C	2.096420	-0.651218	1.790467
C	1.824236	-0.774191	0.435400
C	0.670542	-0.207994	-0.079757
N	1.453069	0.178561	4.013192
C	2.622514	0.480423	4.420942
C	2.993573	0.591110	5.812348
C	2.162666	0.303716	6.803147
O	-1.112046	0.582340	5.340361
C	-1.975715	-0.538813	5.331494
C	-1.503685	-1.656880	6.245961
Br	0.291238	-0.375861	-1.936333
O	1.472248	0.049475	7.680127
H	3.431279	0.688962	3.714191
H	2.980080	-1.124124	2.201826
H	2.500947	-1.317927	-0.210298
H	-1.122716	0.897723	0.331056
H	-0.636155	1.094544	2.755027
H	-2.102528	-0.919812	4.308972
H	-2.949681	-0.171047	5.661024
H	-0.541904	-2.055357	5.912191
H	-2.222892	-2.480518	6.252531
H	-1.385300	-1.290556	7.267471
H	-0.251236	0.331815	4.964673
H	3.983625	0.918118	6.098616

**TS-B-VI'**

C	0.110422	-0.680926	-0.235292
C	-0.018805	-1.124472	1.071408
C	1.009684	-0.913335	1.976317
C	2.169018	-0.260103	1.588118
C	2.289596	0.197210	0.286445
C	1.261017	-0.006491	-0.626078
Br	0.834436	-1.534889	3.759788
N	1.431348	0.469778	-1.950438
C	0.453655	0.798942	-2.793511
C	0.556673	1.218114	-4.087322
C	-1.102198	1.354210	-4.978637
O	-0.924710	1.363170	-6.165867
C	1.621568	1.511378	-4.802156
O	2.458711	1.861877	-5.502818
O	1.051086	-0.600338	-6.737672
C	1.732652	-0.551652	-7.980328
C	2.894590	-1.518626	-7.928162
O	-1.923799	1.375269	-4.111784
H	-0.559079	0.727945	-2.405682
H	-0.682269	-0.884774	-0.943087
H	-0.914330	-1.648803	1.376303
H	2.970002	-0.099887	2.296976
H	3.187097	0.725375	-0.014948
H	2.096596	0.465502	-8.175300
H	1.054202	-0.823417	-8.798226
H	3.583968	-1.244495	-7.126759
H	3.444243	-1.512612	-8.872225
H	2.537485	-2.532995	-7.740401
H	2.386905	0.566054	-2.266724
H	0.283836	-0.010259	-6.768872

**B-VI' (complex)**

C	-2.928231	-0.017827	1.922836
C	-2.429425	-0.400925	0.688151
C	-1.179232	0.037897	0.280769
C	-0.414373	0.841821	1.121846
C	-0.927259	1.219963	2.359581
C	-2.184179	0.798657	2.759735
Br	-4.647567	-0.611085	2.468672
N	0.864420	1.302784	0.755096
C	1.694500	0.743098	-0.145271
C	2.892934	1.256839	-0.464787
H	1.217615	2.119302	1.235450
H	1.318118	-0.175506	-0.591968
H	-0.820220	-0.240269	-0.701519
H	-3.021360	-1.023112	0.030505
H	-2.574723	1.095302	3.723868
H	-0.338049	1.846681	3.019384
C	3.962774	1.089180	-1.129919
O	5.005567	1.018068	-1.662775
C	6.608387	-2.569420	-3.316405
C	5.258753	-2.510050	-2.625836
O	4.418232	-1.498536	-3.163451
H	4.717922	-3.448115	-2.762450
H	5.389284	-2.359475	-1.547185
H	7.214236	-3.382269	-2.907411
H	6.483668	-2.734024	-4.388205
H	7.160158	-1.636358	-3.174902
H	4.833183	-0.644573	-2.988624
C	2.044081	-0.152383	-3.638128
O	2.703447	0.565205	-4.257698
O	1.339808	-0.838413	-3.024811



TS-B-VI''

C	-0.004916	-0.508559	-0.454896
C	-0.254315	-0.131640	0.855493
C	0.809909	0.112801	1.707604
C	2.115178	-0.028255	1.253357
C	2.359117	-0.425572	-0.055035
C	1.295310	-0.655466	-0.912881
N	3.175021	0.225317	2.165231
C	4.407933	0.584329	1.834845
C	5.496853	0.814357	2.649930
C	6.883478	1.196009	1.876982
O	7.890563	1.185487	2.586464
Br	-1.456339	-0.836617	-1.630138
C	5.326370	0.811759	3.984720
O	4.984605	0.942393	5.065776
O	7.299731	-0.518626	4.484728
C	8.041120	-0.589835	5.692121
C	8.453818	0.774765	6.217582
O	6.672068	1.429009	0.698978
H	4.630828	0.734816	0.780560
H	3.368947	-0.575795	-0.413681
H	1.482838	-0.963620	-1.932458
H	-1.270370	-0.020398	1.208938
H	0.618341	0.425926	2.727794
H	8.927209	-1.217516	5.539152
H	7.403592	-1.103385	6.415636
H	9.073974	1.300220	5.488097
H	9.029124	0.668343	7.140860
H	7.579612	1.393788	6.429990
H	2.937341	0.125536	3.144093
H	7.778853	0.025399	3.818479

**B-VI''**

C	0.006554	0.018914	-0.010869
C	0.003468	0.030375	1.375607
C	1.193881	0.040201	2.086051
C	2.401620	0.035904	1.406119
C	2.410119	0.045999	0.017208
C	1.213891	0.031809	-0.689136
Br	-1.646497	0.022653	2.309333
N	3.627219	0.053831	-0.714921
C	4.774281	0.568979	-0.293480
C	5.995576	0.582660	-0.922300
C	7.191637	1.491481	-0.213437
O	6.906099	1.736677	0.941703
C	6.294047	-0.099462	-2.029698
O	6.618709	-0.746920	-2.908887
O	8.112614	1.751905	-0.980611
O	6.869343	2.221258	-3.388995
C	7.634922	2.383040	-4.570210
C	8.300760	3.745529	-4.647435
H	3.580276	-0.329149	-1.650198
H	4.774721	1.071061	0.671349
H	3.326525	0.007740	1.967681
H	1.183733	0.034933	3.167577
H	-0.925332	0.010485	-0.559703
H	1.220275	0.045346	-1.773148
H	6.941052	2.252259	-5.403757
H	8.390185	1.589778	-4.646317
H	8.859591	3.850023	-5.581432
H	7.553285	4.539707	-4.598475
H	8.998966	3.882580	-3.818161
H	7.462712	2.252408	-2.615109

**B-VI (ketene)**

C	0.142698	-0.616604	0.076474
C	0.047934	-0.135095	1.370973
C	1.159116	0.445976	1.965228
C	2.364141	0.552448	1.270102
C	2.444578	0.030976	-0.021216
C	1.337537	-0.539871	-0.624882
Br	-1.378312	-1.414555	-0.742973
N	3.519825	1.116824	1.832161
C	3.428747	2.188857	2.509385
C	4.566842	2.796289	3.169967
H	1.404188	-0.930635	-1.631587
H	3.389315	0.087559	-0.547053
H	-0.881341	-0.221292	1.918441
H	1.095206	0.791257	2.990082
H	2.481525	2.726848	2.624267
H	4.482884	3.729320	3.708737
C	5.759021	2.225098	3.130271
O	6.799308	1.742869	3.102984

B-VI'

C	-0.006754	0.061781	-0.027284
C	-0.015773	0.028331	1.364960
C	1.175895	-0.022148	2.073964
C	2.378025	-0.054786	1.389679
C	2.400572	-0.030341	0.003028
C	1.213176	0.037680	-0.704634
Br	4.013943	-0.133277	2.358105
N	-1.197570	0.158711	-0.763519
C	-2.530842	-0.108943	-0.306773
C	-2.951116	-0.773520	-1.388754
C	-1.560914	-0.642062	-1.940570
O	-0.908636	-1.004047	-2.857938
H	1.224585	0.068152	-1.785702
H	3.343692	-0.055563	-0.526454
H	1.161828	-0.043532	3.155564
H	-0.951337	0.040605	1.909931
H	-2.966025	0.231275	0.620498
H	-3.885621	-1.157189	-1.757336

TS-B-VII

C	0.357152	-0.541413	1.207459
C	-0.995285	-0.249263	1.201019
C	-1.671268	-0.104298	0.000119
C	-0.995446	-0.252586	-1.200463
C	0.356984	-0.544784	-1.206274
C	1.060456	-0.694051	0.000754
Br	-3.532887	0.300382	-0.000315
N	2.372257	-0.983741	0.001048
C	3.588608	-1.223061	0.001068
C	4.678342	-0.237086	0.000043
C	4.439732	1.060954	-0.001062
O	4.216792	2.186800	-0.002017
H	3.961762	-2.259167	0.001958
H	-1.522369	-0.135026	2.139422
H	0.883557	-0.655974	2.146241
H	-1.522656	-0.140954	-2.139109
H	0.883258	-0.661965	-2.144805
H	5.711702	-0.554983	0.000141

**TS-B-VII'**

C	0.029954	-0.101428	-0.072212
C	-0.019209	0.038189	1.317122
C	1.148921	0.105767	2.060749
C	2.373853	0.067901	1.415082
C	2.443141	-0.041760	0.033843
C	1.275672	-0.133038	-0.702892
Br	3.977652	0.181841	2.431499
N	-1.109432	-0.206243	-0.863794
C	-2.370326	-0.377895	-0.485710
C	-3.112147	0.195639	-1.508370
C	-1.990912	0.682937	-2.209183
O	-1.492433	1.296318	-3.057517
H	-2.696347	-0.848128	0.436846
H	-0.972981	0.110350	1.825622
H	1.102997	0.207382	3.137010
H	3.403868	-0.065278	-0.463006
H	1.314505	-0.235987	-1.779951
H	-4.151964	0.214550	-1.781860

**B-VII**

C	-0.064064	0.042593	0.058867
C	-0.075940	0.089106	1.453250
C	1.134362	0.043231	2.145834
C	2.332370	-0.081588	1.460344
C	2.322642	-0.149818	0.075955
C	1.131852	-0.082237	-0.630261
N	-1.286549	0.235642	2.148379
C	-1.918479	-0.804290	2.511796
C	-1.579195	-2.208506	2.317579
C	-0.513661	-2.701827	1.705759
O	0.370612	-3.231191	1.198064
Br	3.965568	-0.322120	-0.867432
H	-2.853044	-0.649331	3.048434
H	3.268444	-0.123485	2.001330
H	1.128656	0.108557	3.226985
H	1.136438	-0.124639	-1.711388
H	-1.000731	0.107422	-0.481169
H	-2.252303	-2.963756	2.704511

**TS-B-VIII**

C	0.009609	0.006074	0.013064
C	0.012515	0.002128	1.377972
C	1.234377	-0.003717	2.091922
C	2.451976	0.039685	1.358447
C	2.420013	0.070631	-0.069443
C	1.226744	0.029282	-0.713560
N	1.211078	-0.123562	3.436313
C	2.195744	-0.779475	4.004106
C	3.265441	-1.457776	3.395203
C	3.601940	-1.368697	2.058734
O	4.408064	-1.710369	1.272606
Br	1.148813	0.023250	-2.611551
H	2.121854	-0.876623	5.084535
H	3.351894	0.103467	-0.618413
H	3.259365	0.609241	1.824080
H	-0.926668	-0.018060	-0.529832
H	-0.909621	-0.021840	1.943849
H	3.790321	-2.222373	3.955024



**B-VIII**

C	-0.007118	-0.016745	0.000267
C	-0.003063	-0.023253	1.445392
C	1.152476	-0.000661	2.132783
C	2.434262	0.028370	1.450130
C	2.530013	-0.070410	0.124981
C	1.301160	-0.288582	-0.688374
Br	3.980033	0.253925	2.532348
N	-1.112453	0.173965	-0.637549
C	-1.049339	0.298207	-2.015037
C	0.074554	0.337771	-2.761046
C	1.377321	0.213295	-2.127739
O	2.439678	0.406599	-2.674866
H	-2.016735	0.424754	-2.489226
H	-0.963551	0.017787	1.942610
H	1.146720	0.034311	3.214646
H	3.472116	-0.028357	-0.404569
H	1.245554	-1.383563	-0.872079
H	0.041281	0.549558	-3.821819

**TS-B-IX**

C	-0.005202	0.008052	-0.004997
C	-0.000169	0.003416	1.407936
C	1.158271	-0.004189	2.157318
C	2.406582	-0.004348	1.540020
C	2.499318	-0.046626	0.143579
C	1.277044	-0.013830	-0.654667
Br	3.979771	0.047316	2.573459
N	-1.152184	0.063051	-0.677881
C	-1.042808	0.104872	-2.015157
C	0.119831	0.087837	-2.756794
C	1.395758	-0.000953	-2.132942
O	2.503907	-0.059923	-2.668352
H	3.432112	0.058275	-0.398022
H	1.100207	-0.000338	3.237910
H	-0.965557	0.011807	1.899903
H	-1.990562	0.155491	-2.543925
H	2.020811	-1.117855	-0.213670
H	0.080316	0.136127	-3.837074

**B-IX**

C	0.001467	0.010524	0.001491
C	0.003807	0.000883	1.361959
C	1.236659	-0.009117	2.040315
C	2.482929	-0.009848	1.405881
C	2.496589	-0.000118	-0.001404
C	1.244082	0.011514	-0.778251
Br	-1.623075	0.023763	-0.934586
N	3.586235	-0.020390	2.194522
C	4.729865	-0.021061	1.526332
C	4.868432	-0.012208	0.139654
C	3.743893	-0.000922	-0.738920
O	3.764181	0.007605	-1.980051
H	5.628355	-0.029375	2.137743
H	1.247662	-0.017001	3.125730
H	-0.921526	0.000661	1.921647
H	1.252343	-0.830544	-1.488271
H	1.259068	0.866593	-1.472609
H	5.858721	-0.013791	-0.299536

TS-B-X

C	-0.004552	0.014101	-0.003281
C	-0.004211	0.010413	1.406768
C	1.172489	-0.004152	2.150550
C	2.404398	0.058149	1.517473
C	2.504211	0.070650	0.098224
C	1.247712	-0.032459	-0.604117
Br	3.955883	0.288368	2.556991
N	-1.154238	-0.085608	-0.717923
C	-0.985941	-0.305712	-2.010203
C	0.231654	-0.544050	-2.676635
C	1.421346	-0.507733	-1.942762
O	2.613243	-0.847840	-2.235761
H	-1.901619	-0.367084	-2.592388
H	-0.962298	-0.039641	1.913167
H	1.124082	-0.024316	3.230863
H	3.207519	0.829218	-0.268291
H	3.027575	-0.726031	-0.712814
H	0.228089	-0.823048	-3.722147

6(enol) (6-bromoquinolin-4(1H)-one)

C	-0.003206	0.000003	-0.002302
C	-0.006840	0.000001	1.412477
C	1.210505	-0.000006	2.130342
C	2.386979	-0.000012	1.440128
C	2.416415	-0.000013	0.030387
C	1.244138	-0.000006	-0.670033
Br	4.038239	-0.000021	2.383799
N	-1.140124	0.000008	-0.749841
C	-2.278275	0.000009	-0.109071
C	-2.407709	0.000017	1.294548
C	-1.271880	0.000009	2.057097
O	-1.268431	0.000009	3.407870
H	1.191401	-0.000005	3.210874
H	3.367891	-0.000018	-0.484625
H	1.235266	-0.000005	-1.752386
H	-3.178042	0.000027	-0.718282
H	-2.168538	0.000039	3.747117
H	-3.392483	0.000026	1.747971