Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Direct and co-catalytic oxidative aromatization of 1,4-dihydropyridines and related substrates using gold nanoparticles supported on carbon nanotubes

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1. Synthesis and characterization of carbon nanotubes:

Multi-walled carbon nanotubes were prepared by catalytic decomposition of methane (P. Chen, H. B. Zhang, G. D. Lin, Q. Hong, K. R. Tsai, *Carbon* **1997**, *35*, 1495-1501) at the University of Xiamen and purified by treatment with HNO_3. The nanotubes were characterized by Raman spectroscopy (Figure S1) and X-ray photoelectron spectroscopy (Figure S2).

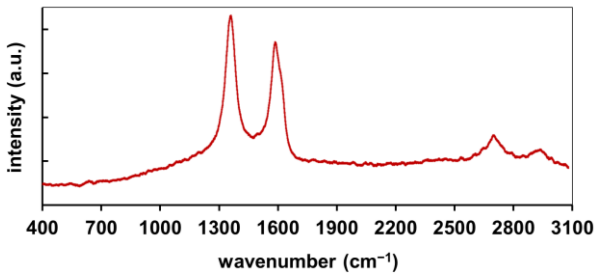


Figure S1: Raman of the purified CNT (ex. 514 nm)

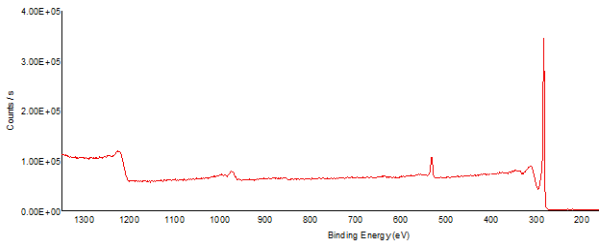


Figure S2: XPS of the purified CNT

2. Assembly of the CNT-gold nanohybrid and characterization:

Step 1: Amphiphilic DANTA (20 mg) was dissolved in 2 mL of 25 mM pH 8 aqueous Tris-buffer before multiwalled carbon nanotubes (50 mg) were added. The dispersion was sonicated and the stable suspension transferred into two tubes. The tubes were centrifuged at 5000×g and the supernatants were collected. The latter were centrifuged at 15000×g for 45 min. The supernatant was discarded and the pellets taken in buffer and centrifuged again at 15000×g for 45 min. The pellets were finally resuspended in 1.5 mL of buffer and submitted to UV irradiation at 254 nm for 6 h.

Step 2: After polymerization, the buffer volume was adjusted to 1.5 mL. The suspension was stirred in the presence of the cationic polymer PDADMAC (700 µL of a 20% water solution) for 1 h. The ensuing centrifugation at 15000×g for 30 min permitted to get rid of the polymer in excess. The pellets were taken in 2 mL of buffer. This operation was repeated twice using the buffer solution and two more times using pure water.

Step 3: The final pellets were resuspended in 1 mL of water. 50 µL of the latter suspension was transfered to Eppendorf tubes (× 20). To each tube was added 1 mL of a 1 mM colloid suspension of the gold nanoparticles (D. G. Duff, A. Baiker, P. P. Edwards. *Langmuir* **1993**, *9*, 2301-2309) and the mixture was vortex-stirred at room temperature for 1 min every 30 min (during 4 h). The suspension was then centrifuged at 3000×g for 5 min. The supernatant was discarded and 1 mL of a fresh gold colloid suspension was added. The same process was repeated two more times. The pellets were washed 3 times by centrifugation/redispersion in water. The 20 pellets were combined and 4 mL of water was finally added. Gold concentration of the aqueous suspension was assessed by ICP-MS, [Au] = 3.4 mM. The AuCNT nanohybrid was further characterized by higher resolution transmission electron microscopy (TEM, Figure

S3), X-ray photoelectron spectroscopy (XPS, Figure S4), energy-dispersive X-ray spectroscopy (EDX, Figure S5), and thermogravimetric analysis (TGA, Figure S6).

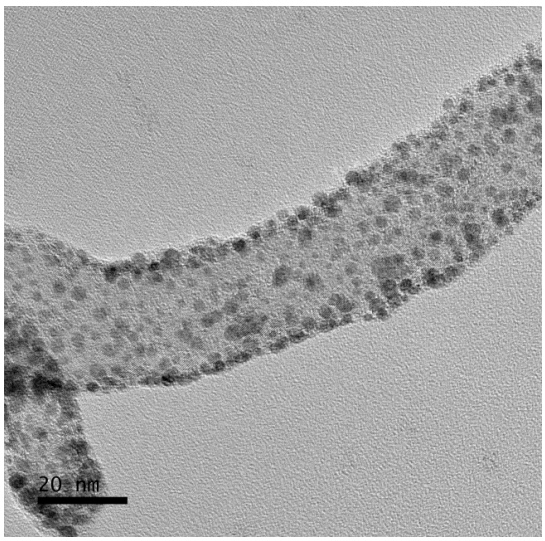


Figure S3: Higher resolution TEM of AuCNT

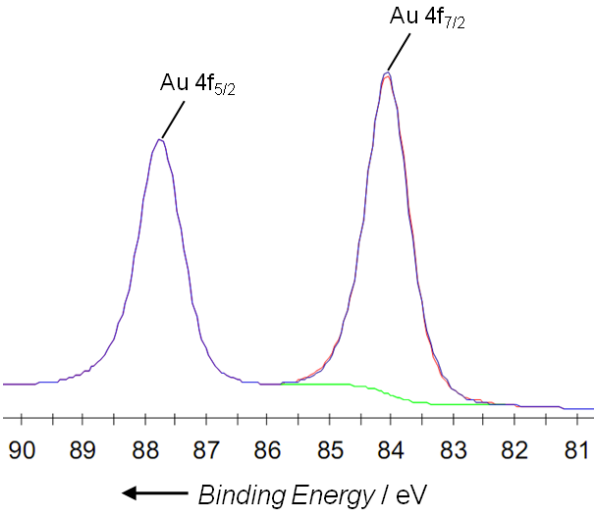


Figure S4: Narrow scan XPS analysis of AuCNT

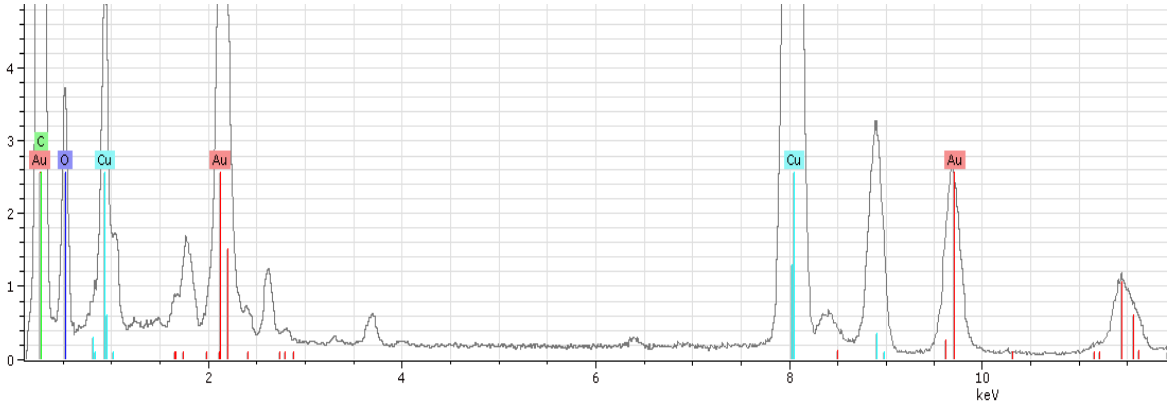


Figure S5: EDX spectrum of AuCNT

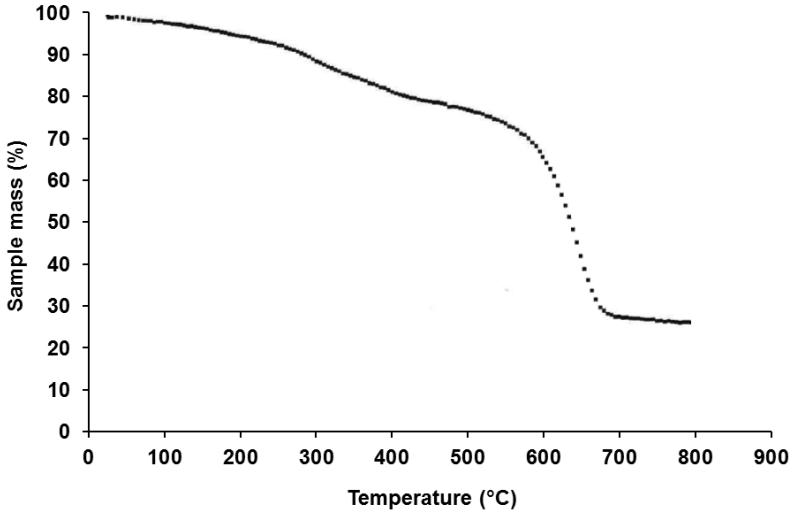


Figure S6: TGA of AuCNT (scan rate 5 °C/min)

3. General procedure for the direct oxidation of 1,4-dihydropyridines:

The preparation of **2a** is given as a representative example. To a solution of 1,4-dihydropyridine **1a** (25 mg, 0.1 mmol) in $CHCl_3/H_2O$ 3:1 (2 mL), was added AuCNT (3.4 mM aqueous suspension, 145 µL, 0.5 mol%). The reaction mixture was stirred at room temperature under oxygen atmosphere for 11 h. After completion of the reaction (confirmed by TLC), the catalyst was removed by filtration and the aqueous phase was extracted with $CHCl_3$ (3 × 2 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum to afford the pure product in 99% yield.

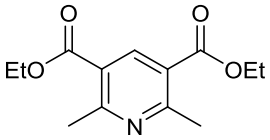
4. General procedure for the co-catalytic oxidation of C-4 sustituted 1,4-dihydropyridines:

Dihydropyridine **1f** (33 mg, 0.1 mmol), 2,5-dichloro-1,4-benzoquinone **5** (3.5 mg, 0.02 mmol) and AuCNT (3.4 mM aqueous suspension, 290 µL, 1 mol%) were stirred in a biphasic mixture of $CHCl_3$ (1.5 mL) and H_2O (0.5 mL) at room temperature for 36 h under oxygen atmosphere. The catalyst was removed by filtration and the aqueous phase was extracted with $CHCl_3$ (3 × 2 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was subjected to column chromatography (silica gel, cyclohexane/ethyl acetate) to afford the desired product **2f** (78%).

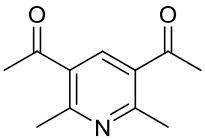
5. Recycling experiment:

To a solution of 1,4-dihydropyridine **1a** (25 mg, 0.1 mmol) in $CHCl_3/H_2O$ 3:1 (2 mL), was added AuCNT (3.4 mM aqueous suspension, 145 µL, 0.5 mol%). The reaction mixture was stirred at room temperature under oxygen atmosphere and the progress of the reaction monitored by TLC. After 11 h of reaction, the catalyst was recovered by centrifugation and the supernatant was worked up as described in the corresponding procedure to afford pure product **2a**. The recovered catalyst was washed with water and reused in subsequent oxidation reactions. This process was repeated over 5 consecutive cycles and showed no significant decrease in yields of oxidized product **2a** (Table 2).

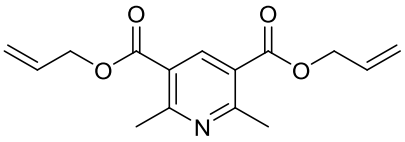
6. Spectral data for compounds 2a-j:



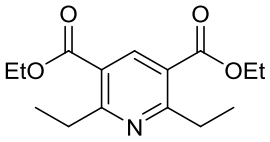
2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63 (s, 1H), 4.40 (q, J = 8 Hz, 4H), 2.85 (s, 6H), 1.42 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.9, 162.2, 140.9, 123.0, 61.4, 24.9, 14.3.



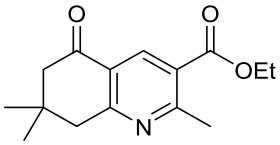
2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25 (s, 1H), 2.78 (s, 6H), 2.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 160.2, 137.8, 130.1, 29.3, 24.9.



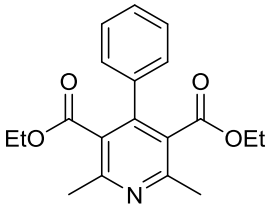
2c: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.77 (s, 1H), 6.11-6.01 (m, 2H), 5.44 (d, J = 16 Hz, 2H), 5.34 (d, J = 8 Hz, 2H), 4.85 (d, J = 4 Hz, 4H), 2.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.4, 162.6, 141.0, 131.7, 122.7, 118.8, 65.9, 24.9.



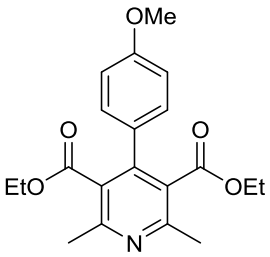
2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62 (s, 1H), 4.41 (q, J = 8 Hz, 4H),), 3.21 (q, J = 8 Hz, 4H), 1.42 (t, J = 8 Hz, 6H), 1.32 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.8, 166.1, 141.1, 122.6, 61.4, 30.4, 14.2, 13.8.



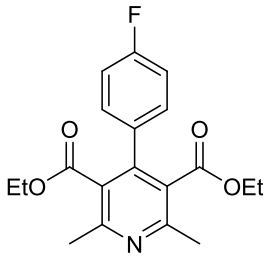
2e: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.74 (s, 1H), 4.40 (q, J = 8 Hz, 2H),), 3.04 (s, 2H), 2.89 (s, 3H), 2.57 (s, 2H), 1.42 (t, J = 8 Hz, 3H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.2, 165.8, 164.6, 164.3, 137.1, 124.9, 124.5, 61.5, 51.9, 46.4, 32.9, 28.3, 25.2, 14.3, 1.0.



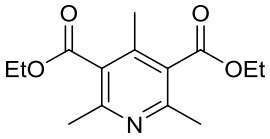
2f: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.37 (m, 3H), 7.29-7.26 (m, 2H), 4.02 (q, J = 8 Hz, 4H),), 2.62 (s, 6H), 0.92 (t, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.9, 155.4, 146.3, 136.5, 128.5, 128.1, 128.0, 127.8, 127.0, 61.4, 22.8, 13.6.



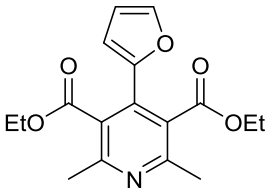
2g: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (d, *J*=12Hz , 2H), 6.91 (d, *J* = 8 Hz , 2H), 4.07 (q, *J* = 8 Hz, 4H),), 3.84 (s, 3H), 2.60 (s, 6H), 1.00 (t, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.1, 159.8, 155.1, 145.6, 129.4, 128.6, 127.4, 113.6, 61.4, 55.3, 22.7, 13.8.



2h: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26-7.23 (m, 2H), 7.11-7.07 (m, 2H), 4.06 (q, *J* = 8 Hz, 4H),), 2;61 (s, 6H), 0.99 (t, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.7, 164.1, 155.4, 145.5, 132.4, 130.1, 127.1, 115.1, 61.5, 22.8, 13.7.

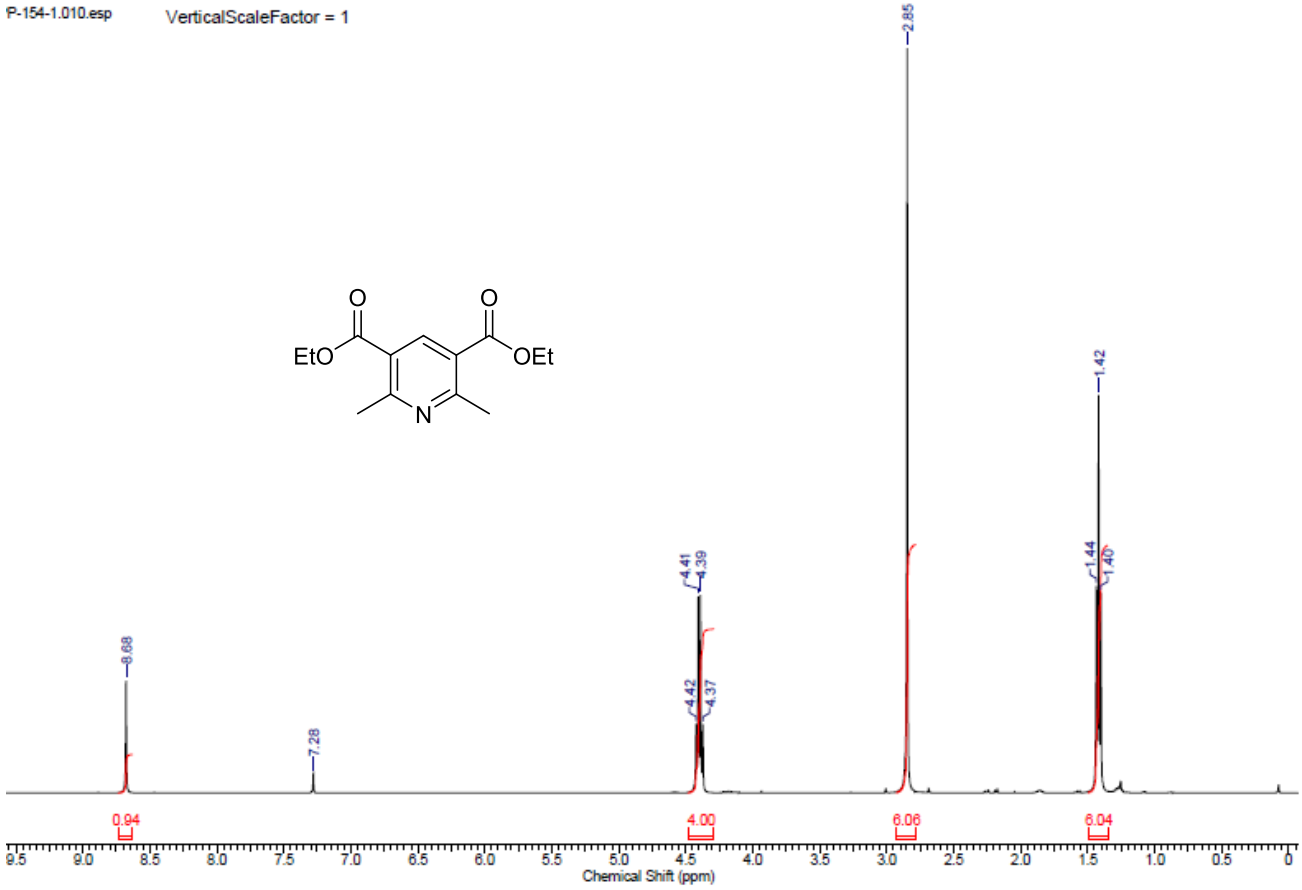


2i: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.43 (q, *J* = 8 Hz, 4H), 2.53 (s, 6H), 2.29 (s, 3H), 1.41 (t, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.3, 154.8, 142.2, 127.7, 61.6, 22.7, 16.9, 14.1.

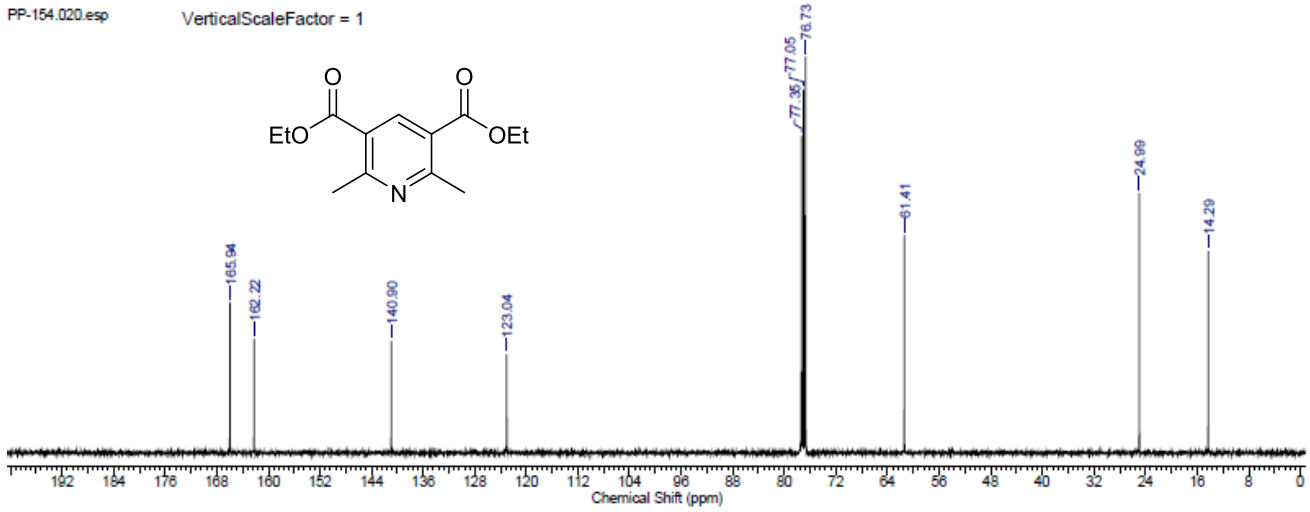


2j: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (s, 1H), 6.65 (d, *J* = 4 Hz, 1H), 6.50-6.49 (m, 1H), 4.30 (q, *J* = 8 Hz, 4H),), 2.59 (s, 6H), 1.24 (t, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.2, 155.7, 144.0, 140.9, 133.9, 124.9, 111.9, 61.9. 22.6, 14.0.

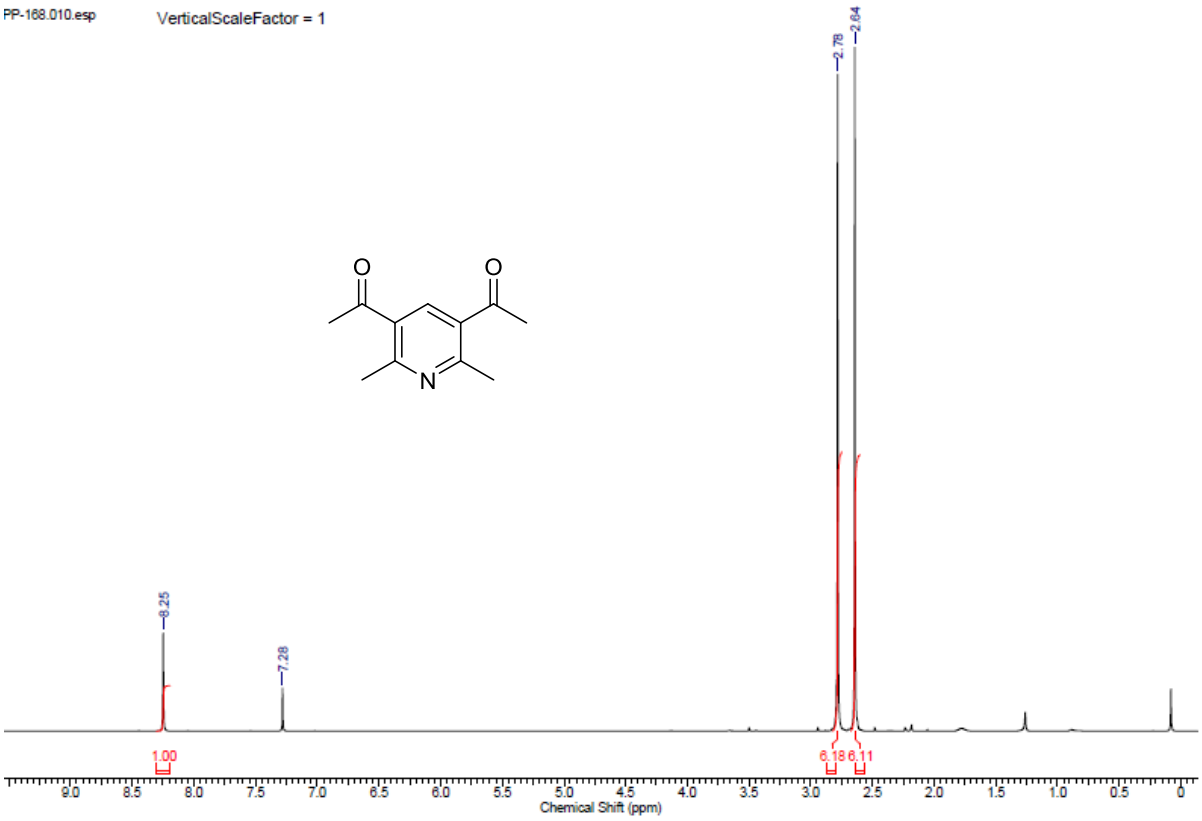
7. ^{1}H and ^{13}C spectra of compounds 2a-j:



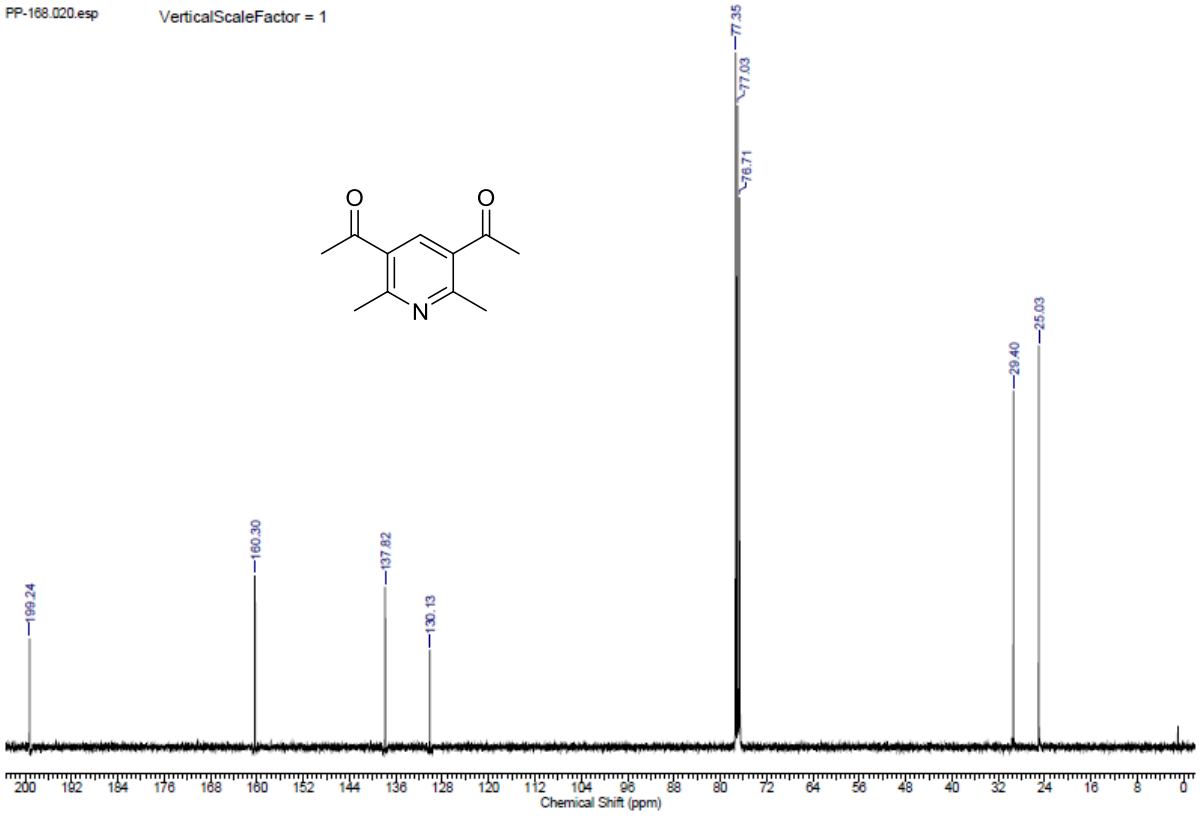
^{1}H NMR of **2a**



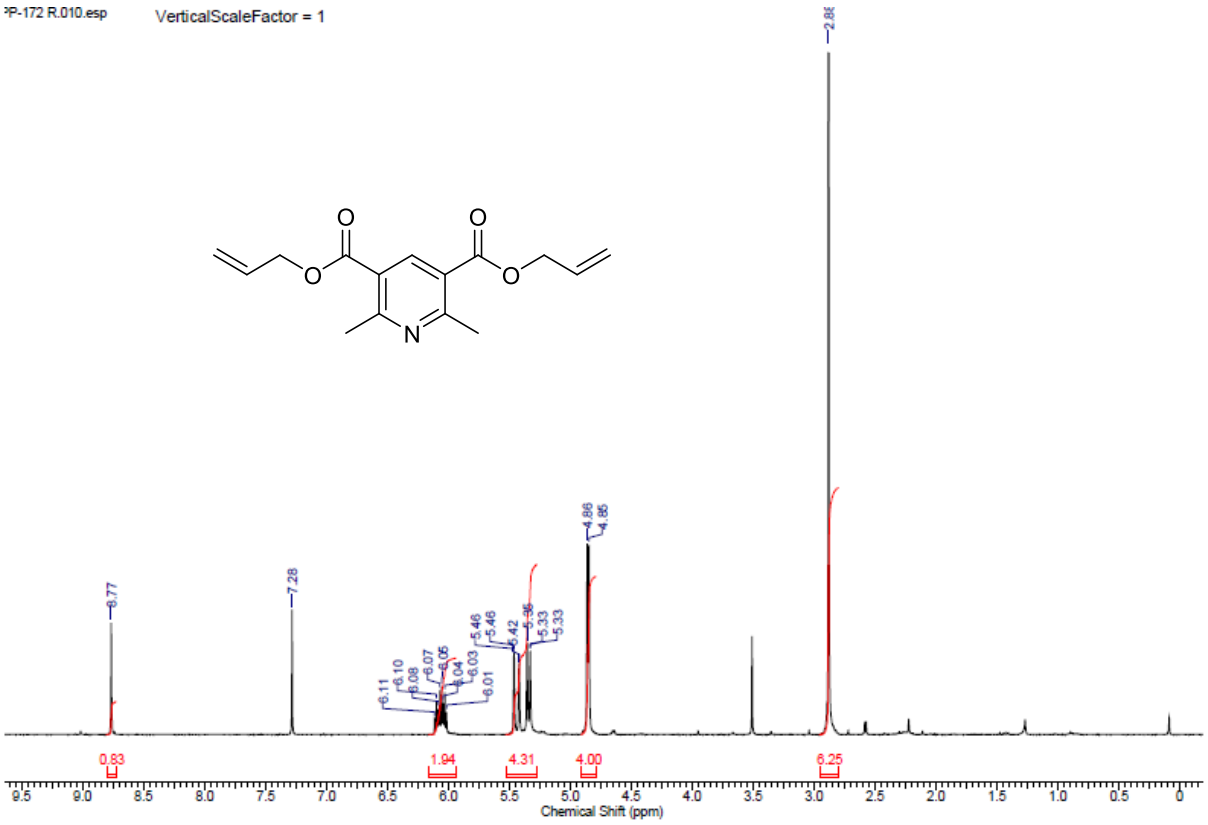
^{13}C NMR of **2a**



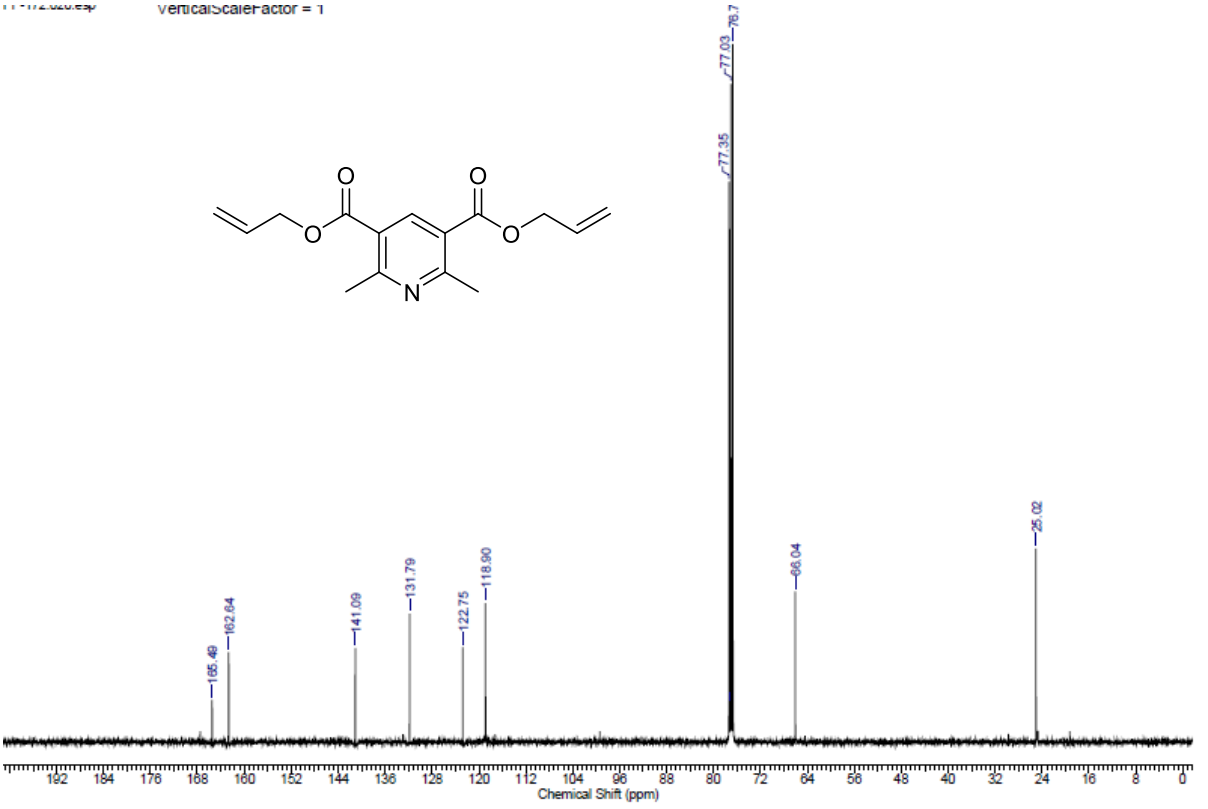
^{1}H NMR of **2b**



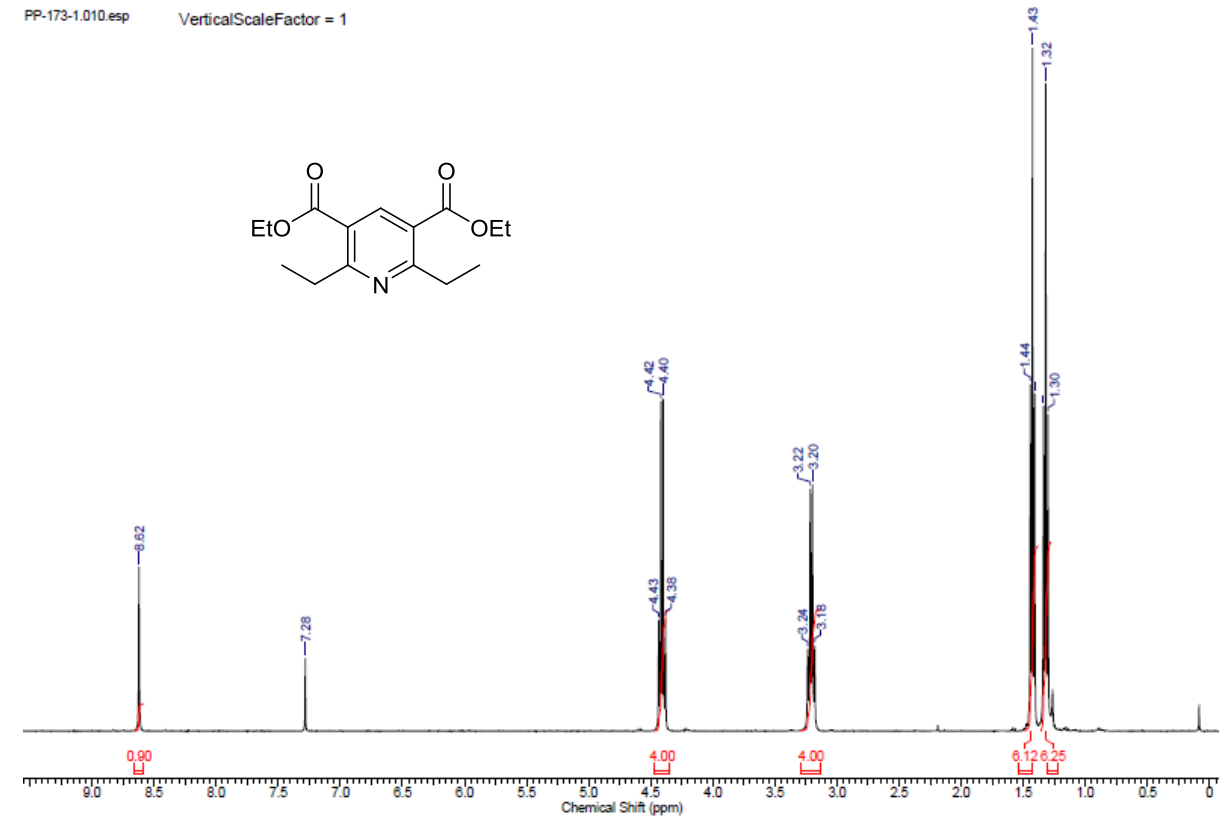
^{13}C NMR of **2b**



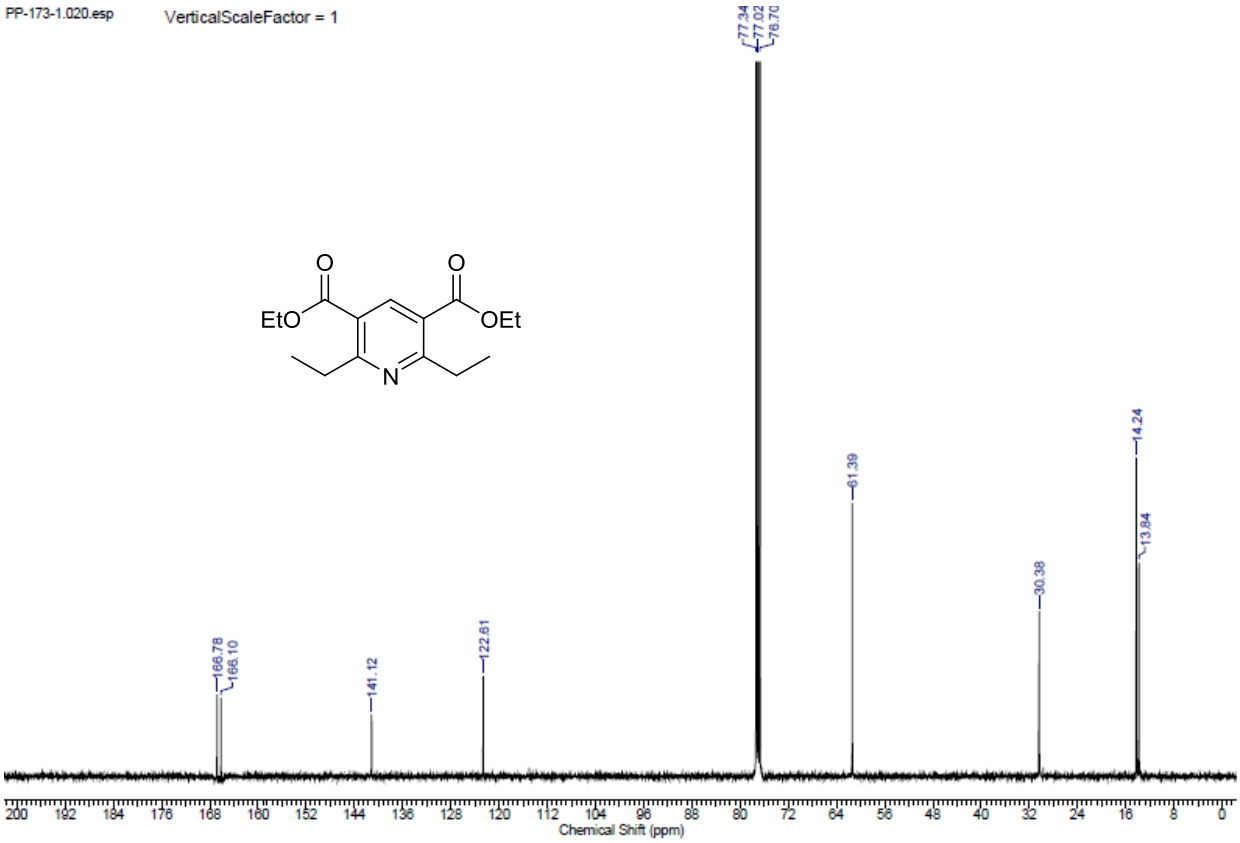
^{1}H NMR of **2c**



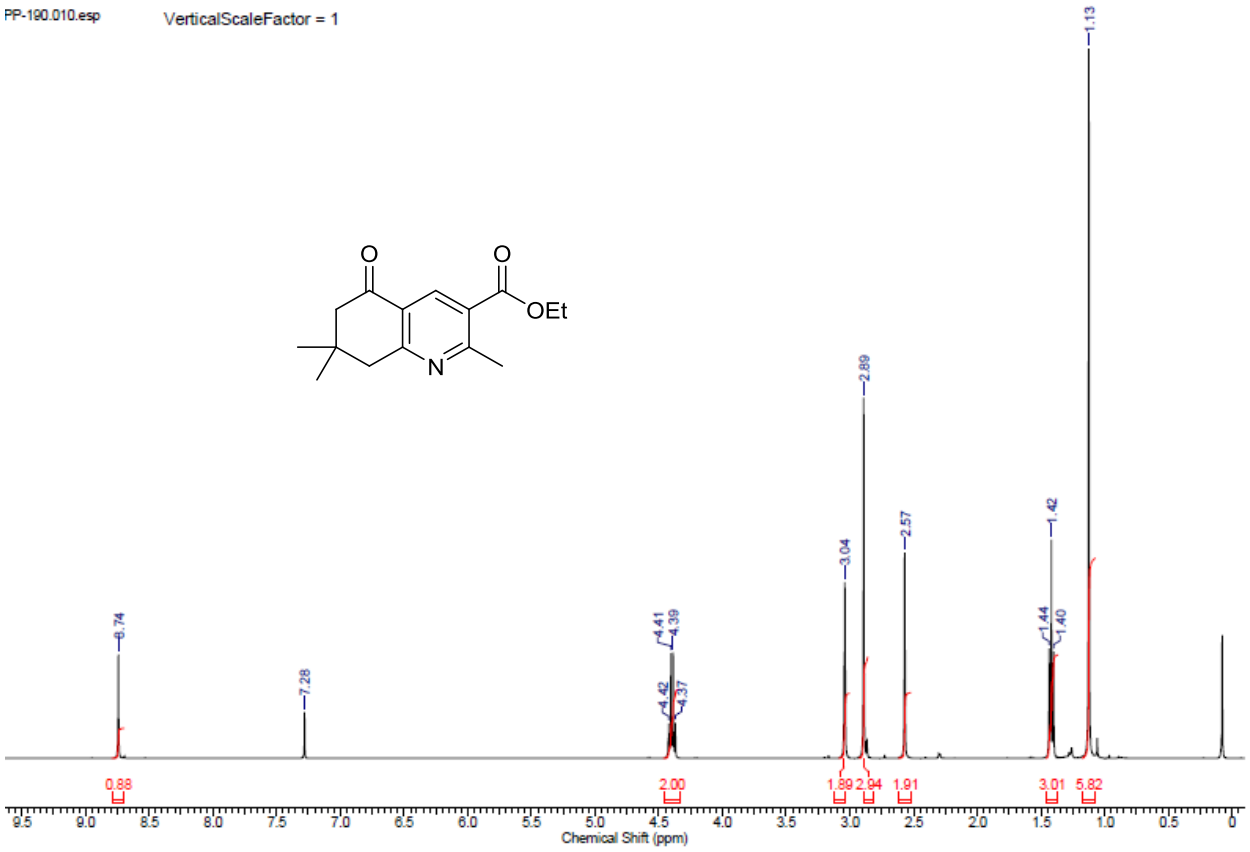
^{13}C NMR of **2c**



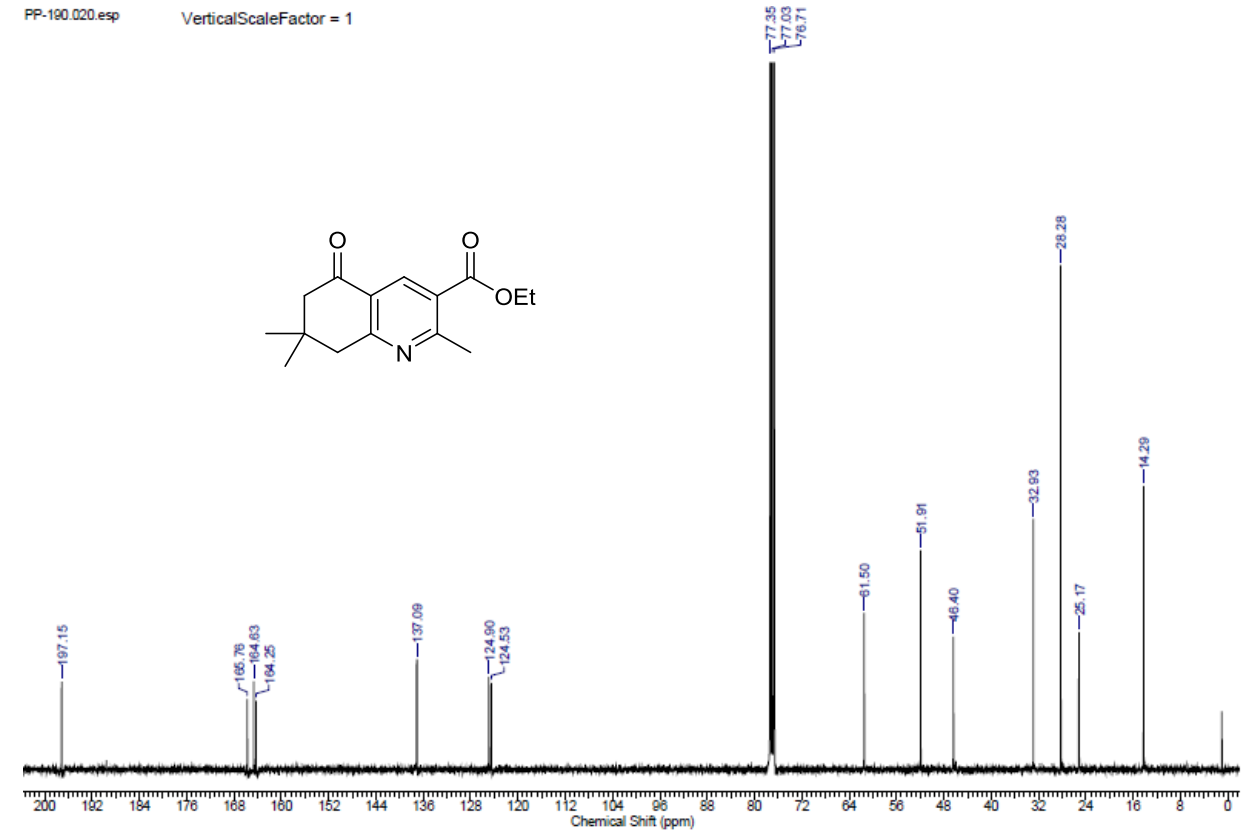
^{1}H NMR of **2d**



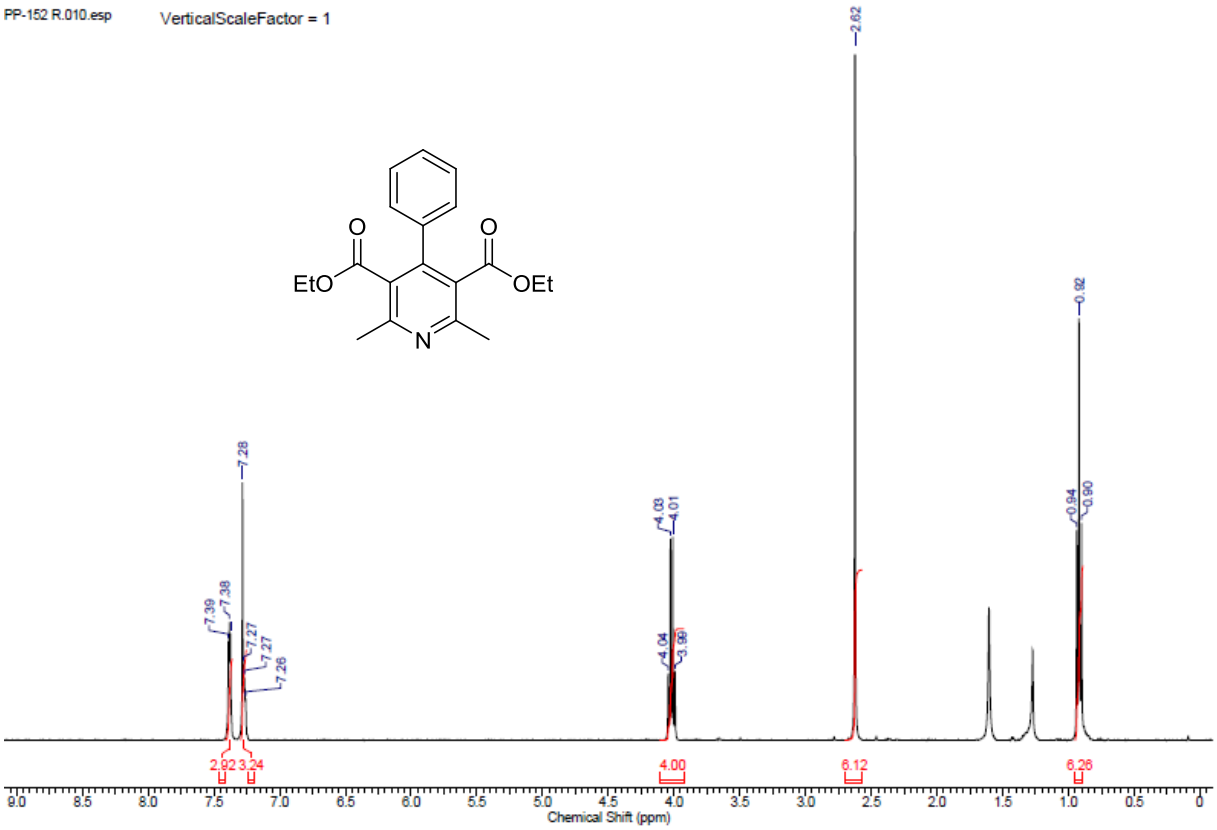
^{13}C NMR of **2d**



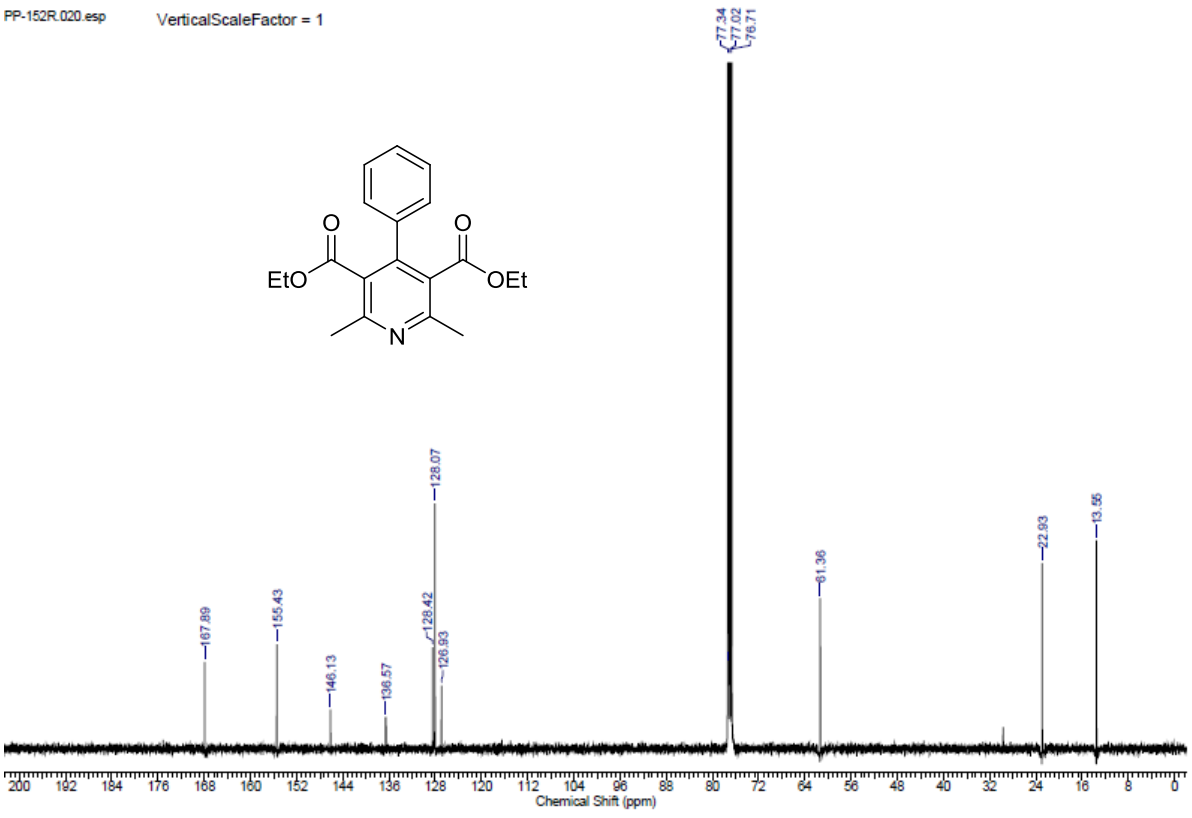
^{1}H NMR of **2e**



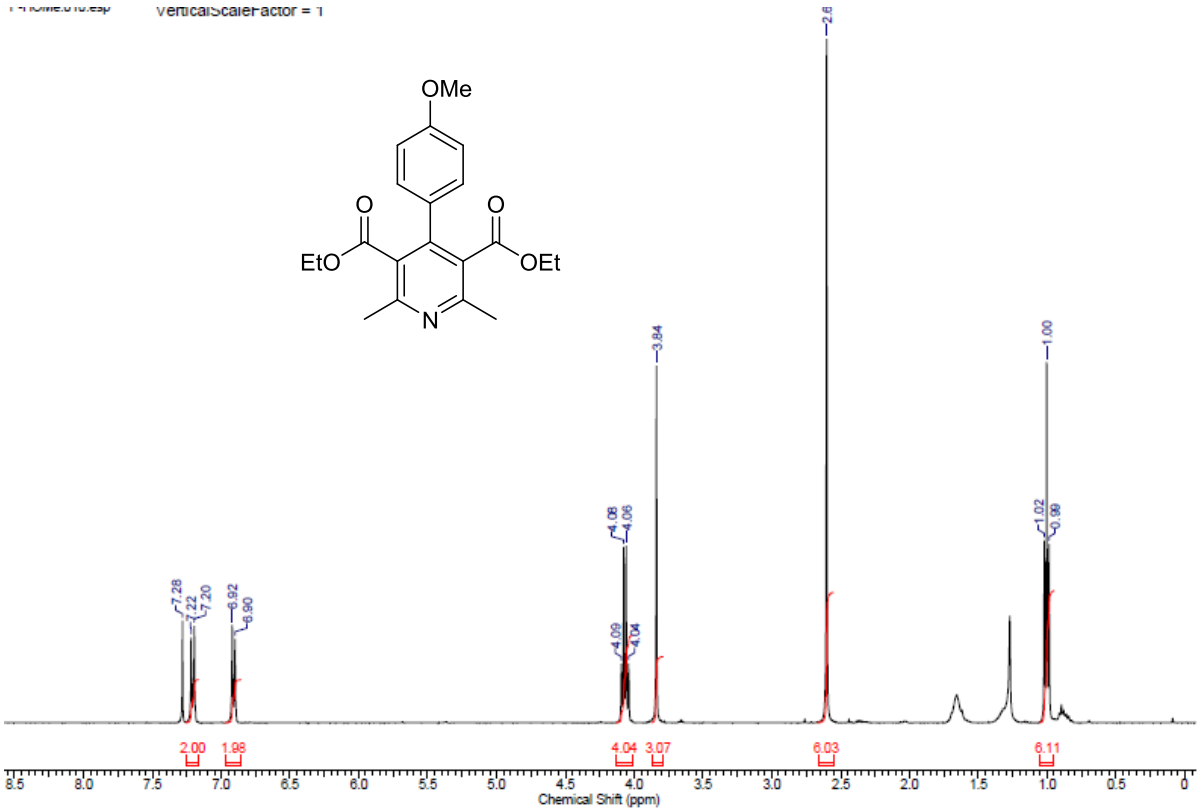
^{13}C NMR of **2e**



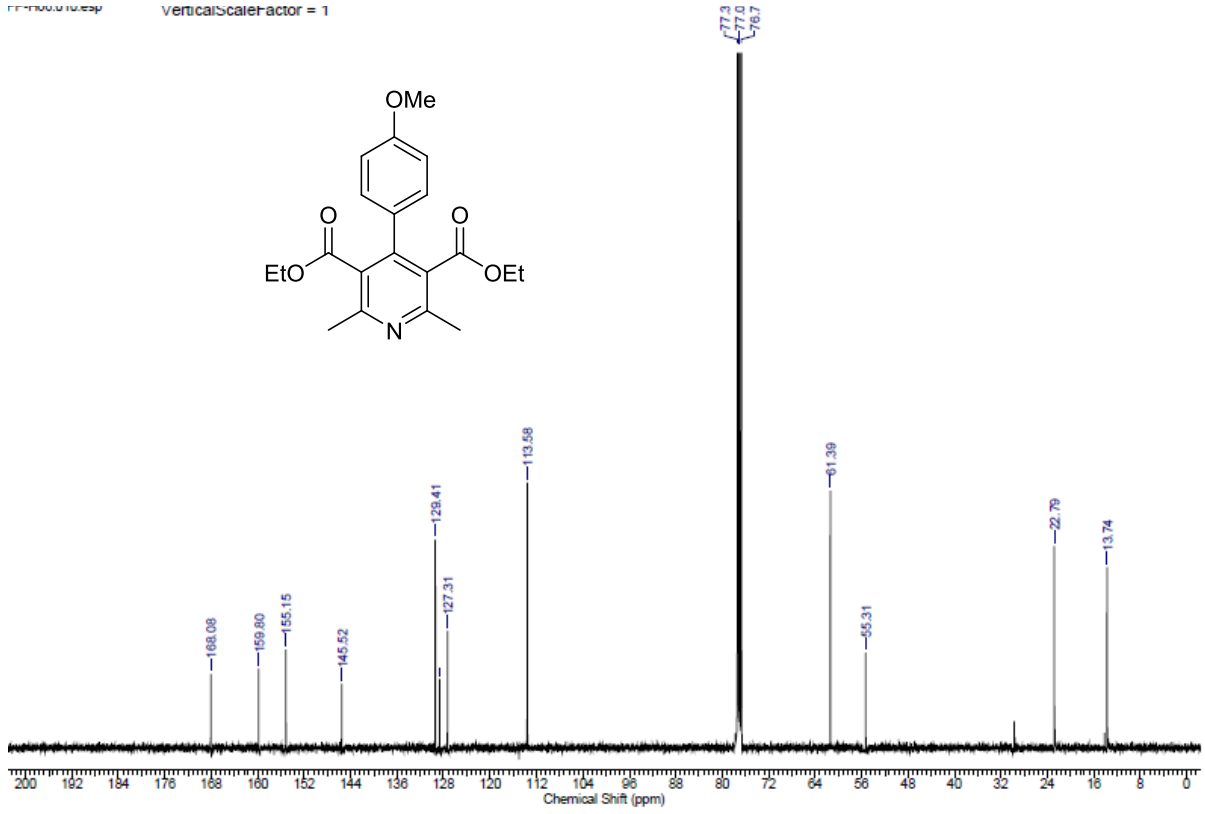
^{1}H NMR of **2f**



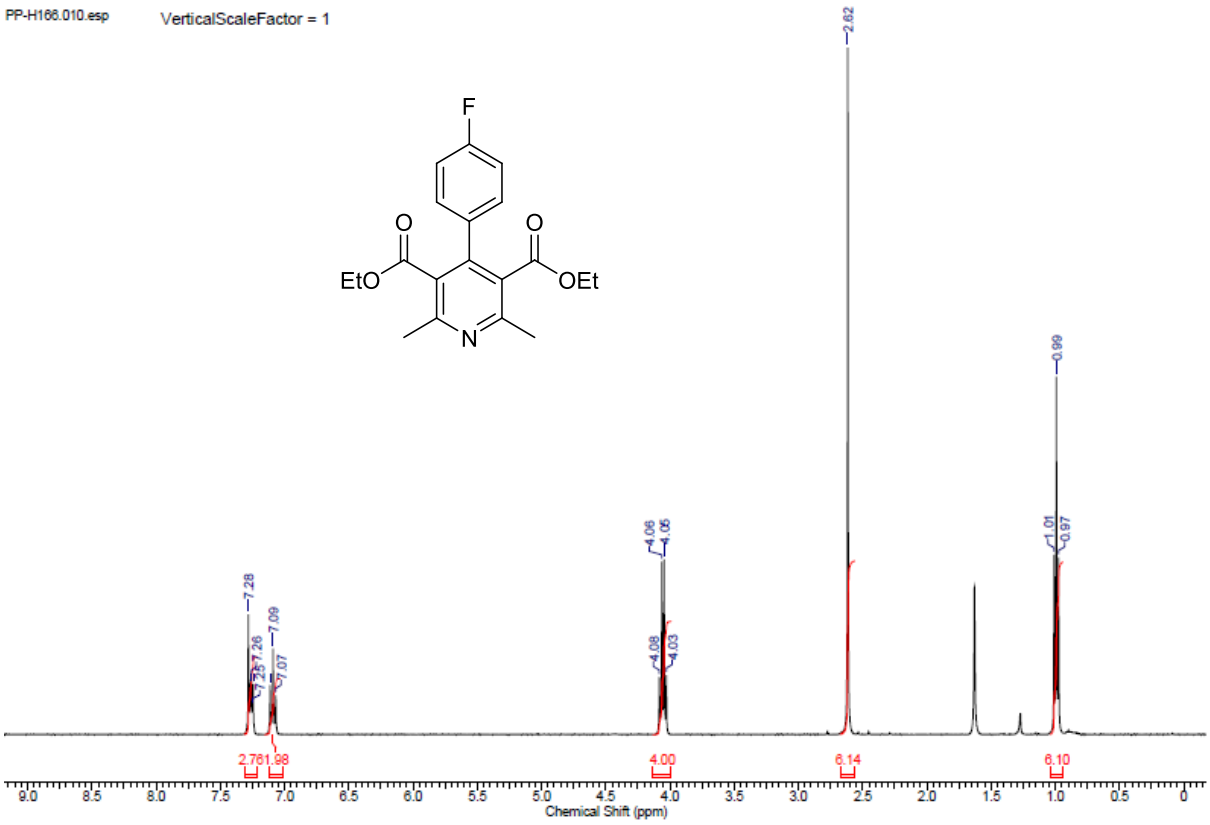
^{13}C NMR of **2f**



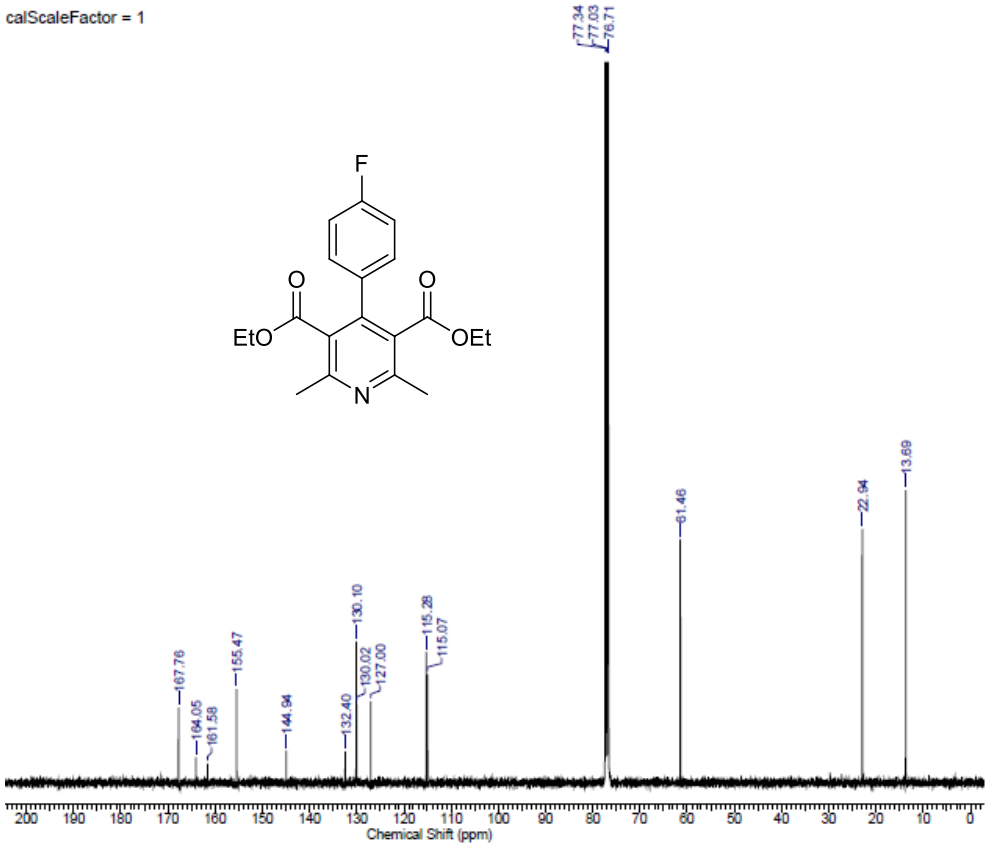
^{1}H NMR of **2g**



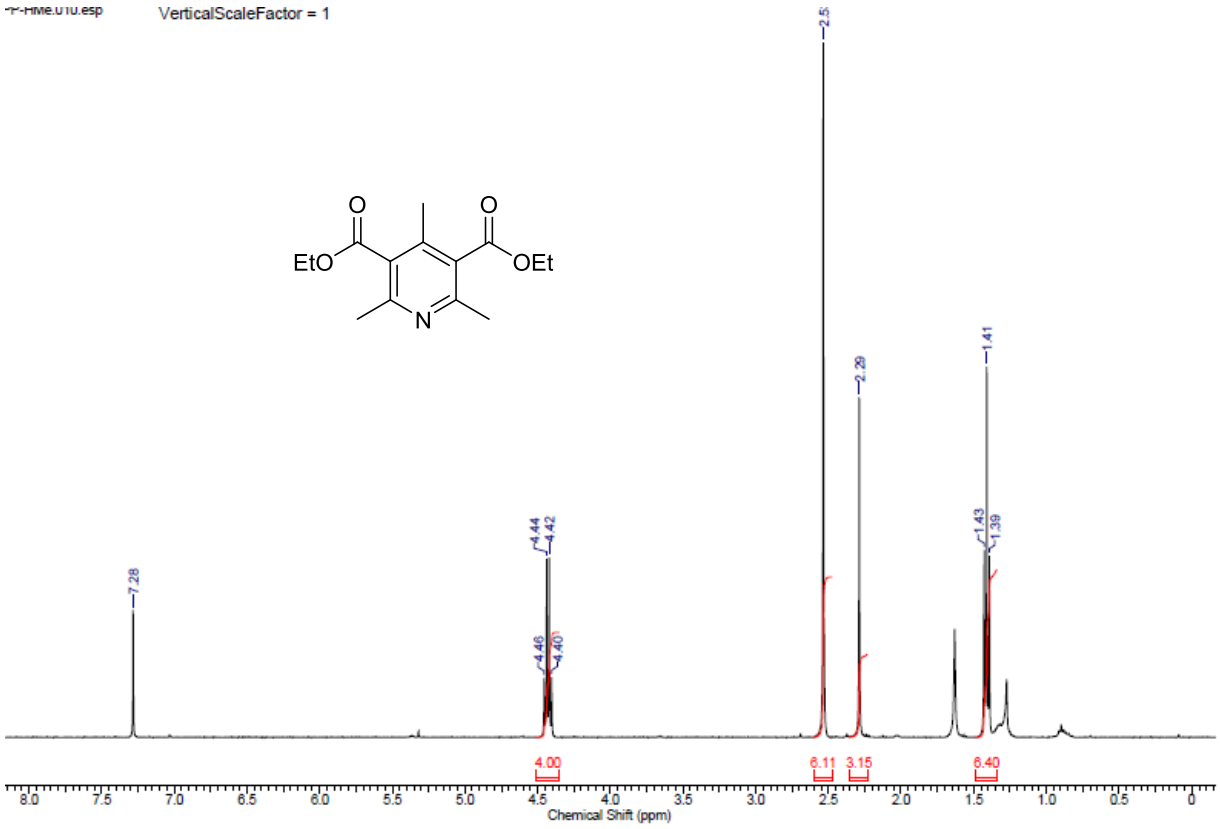
^{13}C NMR of **2g**



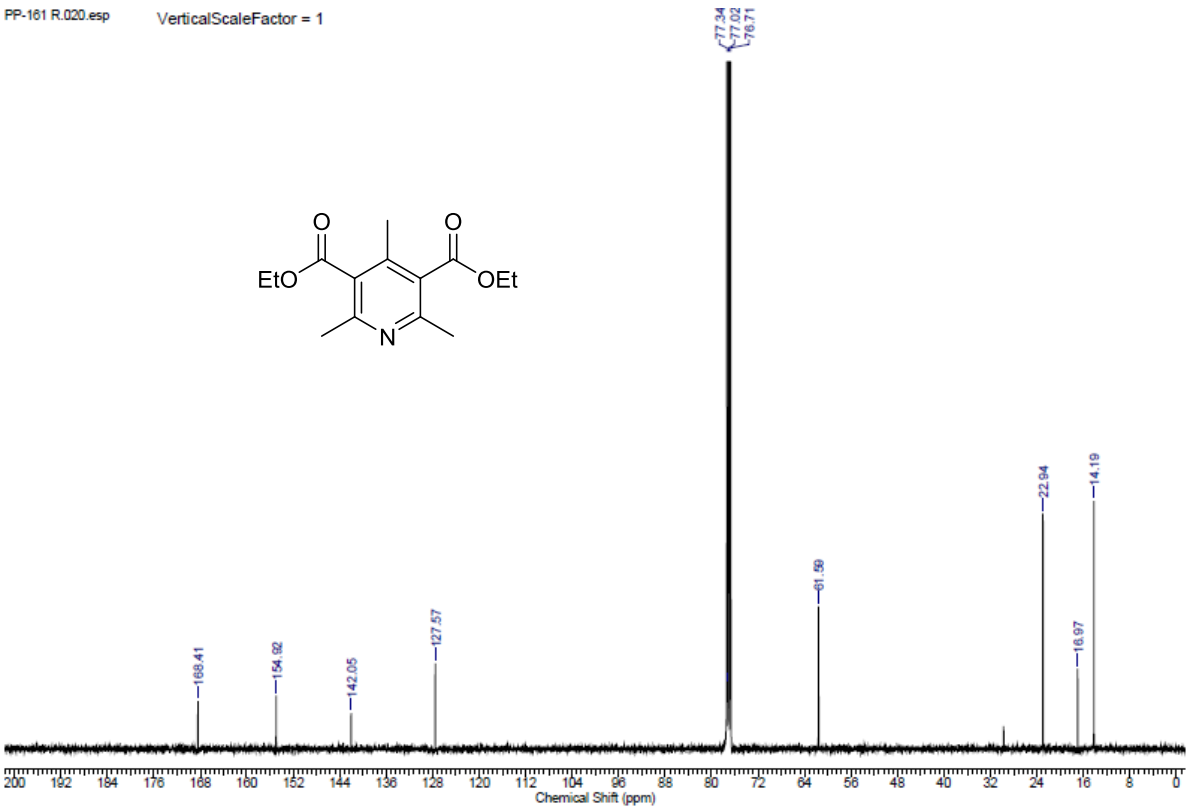
^{1}H NMR of **2h**



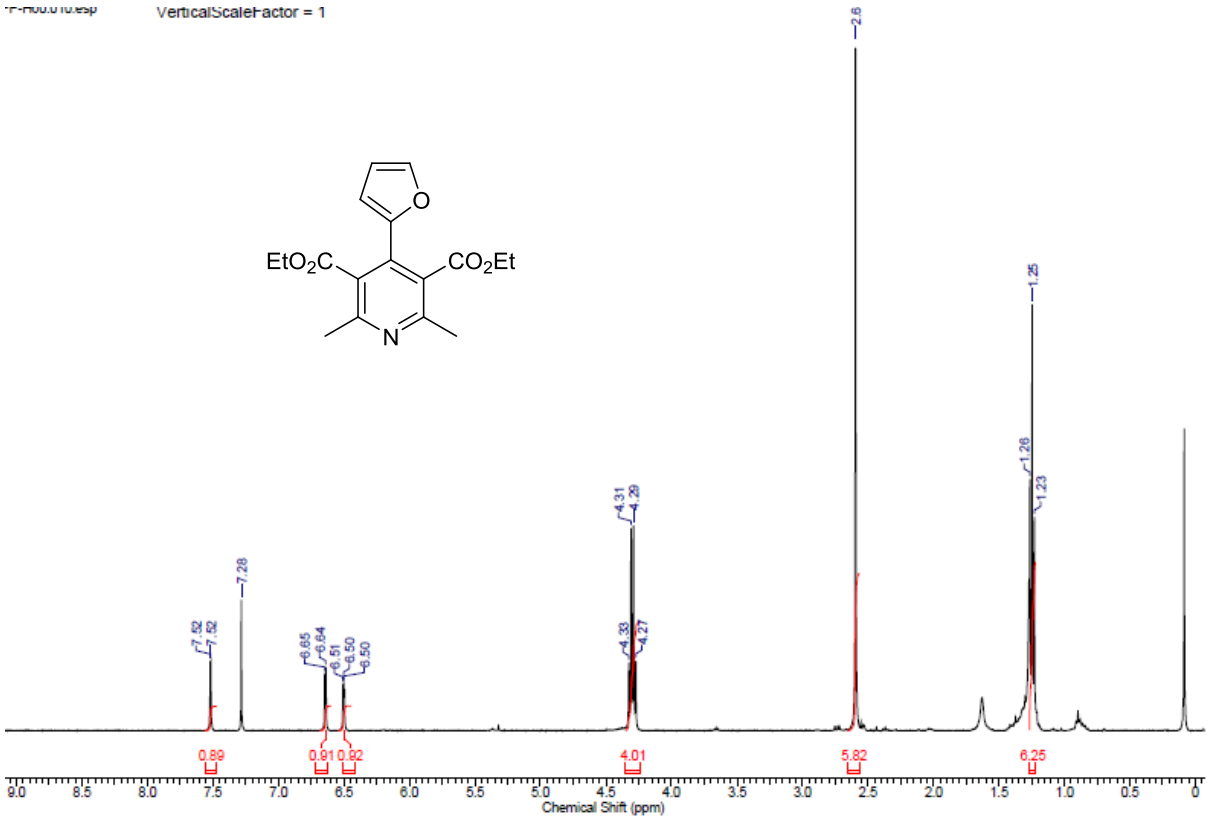
^{13}C NMR of **2h**



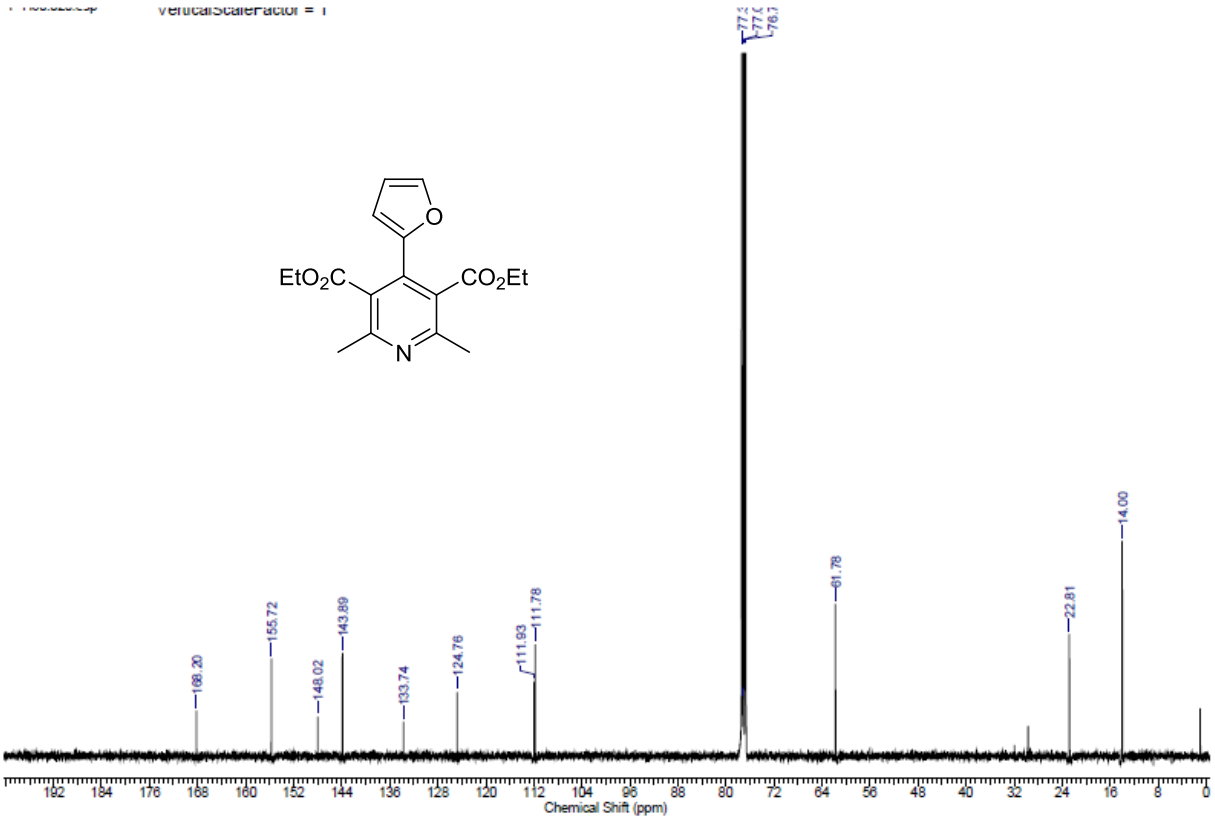
^{1}H NMR of **2i**



^{13}C NMR of **2i**



^{1}H NMR of **2j**



^{13}C NMR of **2j**