Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A


# Self-assembled hybrid tinphosphonate nanoparticles with bimodal porosity: An insight towards the efficient and selective catalyst for the synthesis of bioactive 1,4-dihydropyridines reaction under solvent-free conditions

Malay Pramanik and Asim Bhaumik*

## Supporting Information

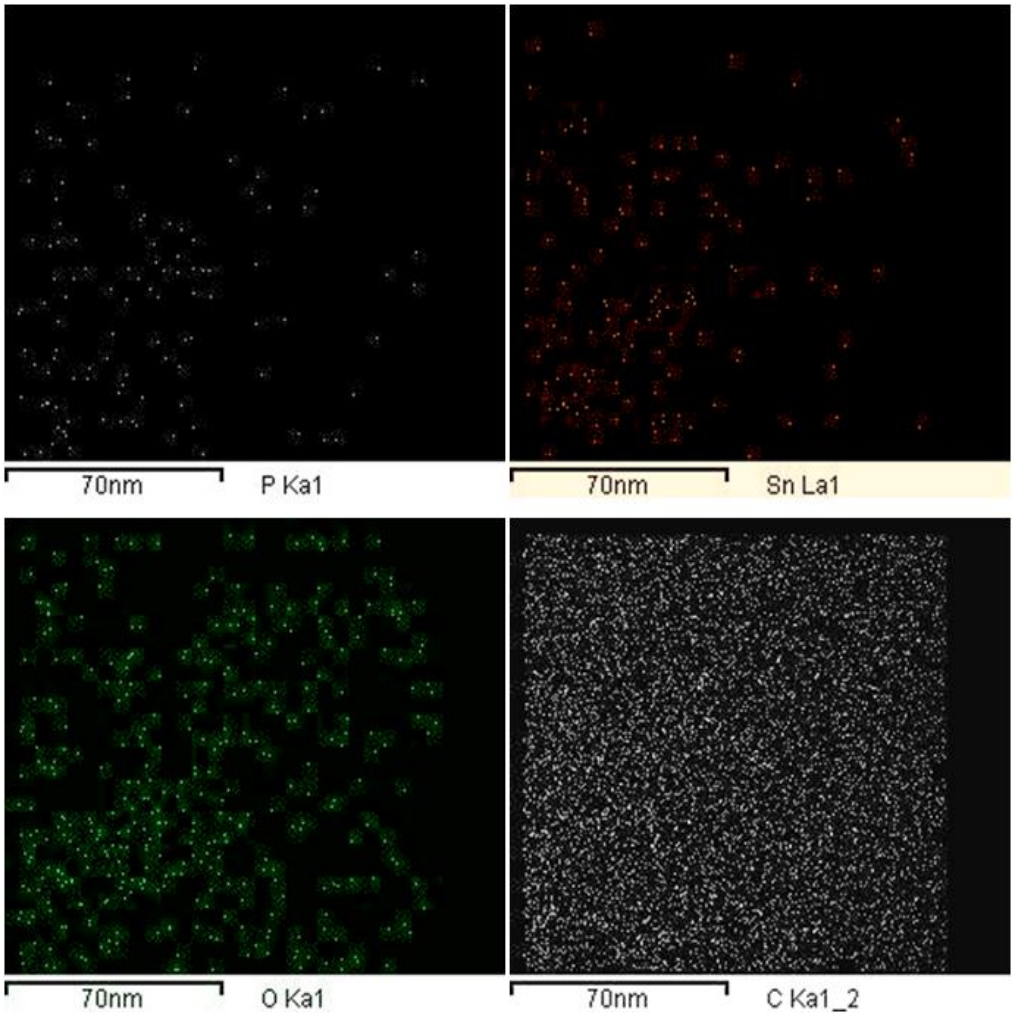



**Figure S1:** Elemental mapping of the material (HSnP-2).

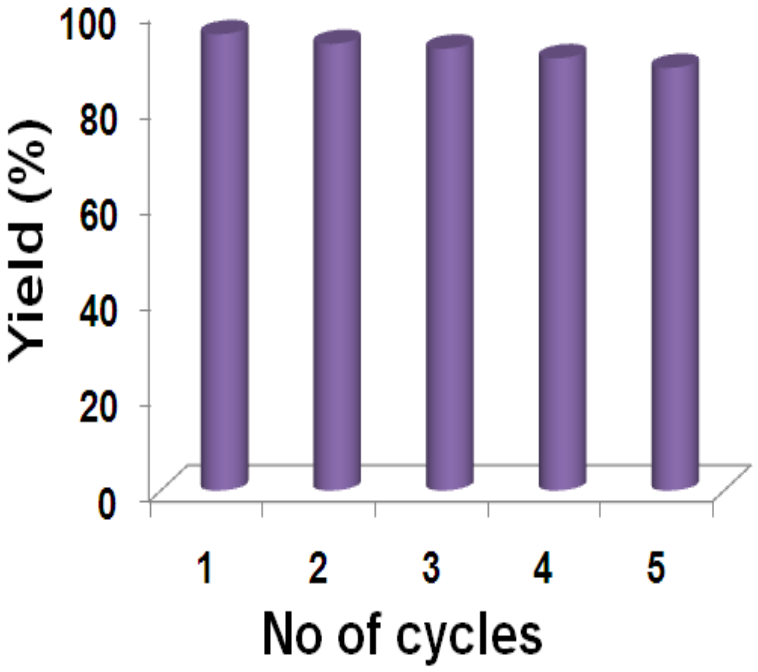
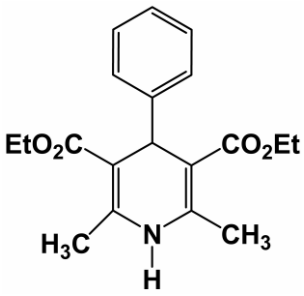


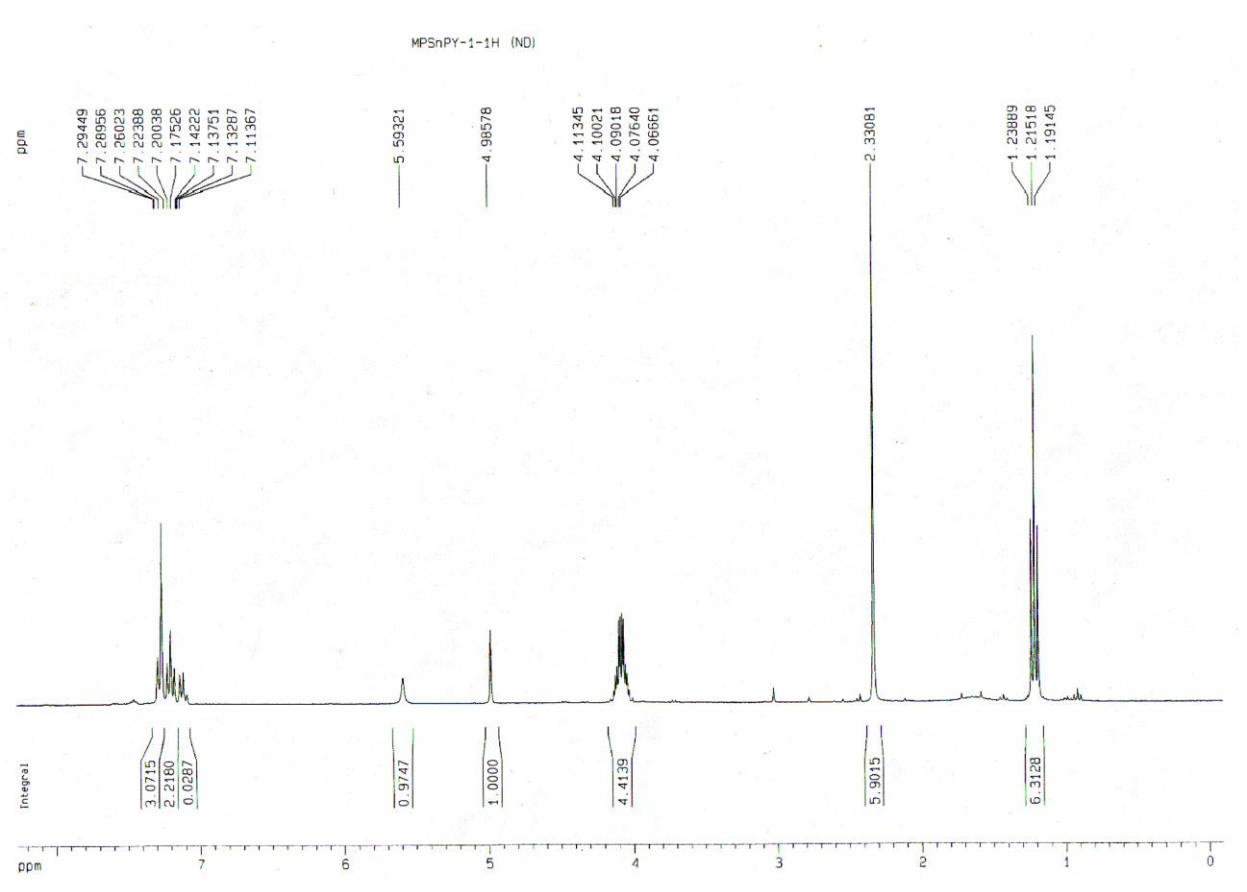

**Figure S2:** Reusability of the catalyst HSnP-2 in the Hantzsch ester reaction.

## Spectral data:

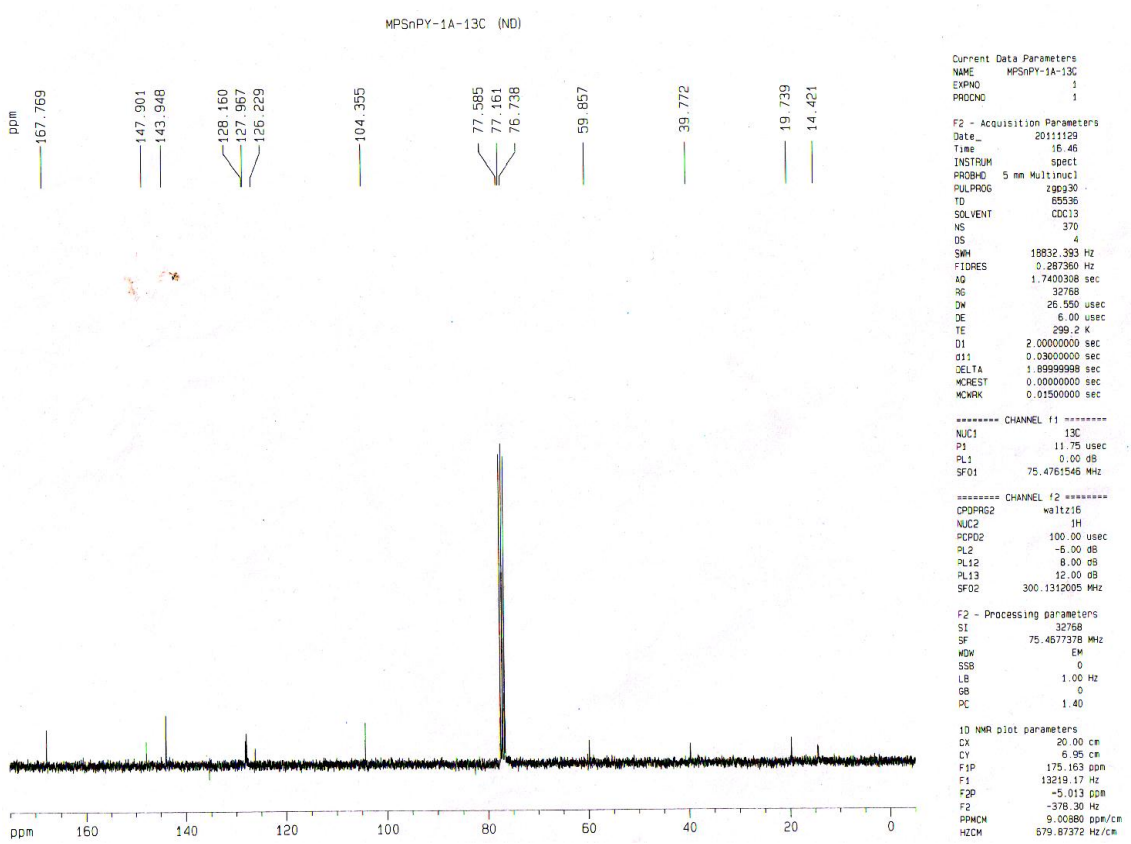
### Diethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate




**Entry 1:** $^{1}$H NMR ($CDCl_3$, 300 MHz) : δ (ppm): 1.12 (t, 6H), 2.33 (s, 6H), 4.09 (m, 4H), 4.98 (s, 1H), 5.59 (b, 1H), 7.11-7.29 (m, 5H); $^{13}$C NMR ($CDCl_3$, 300 MHz) : δ (ppm): 14.42, 19.73, 39.77,59.85, 104.35, 126.22, 127.96, 128.16, 143.94, 147.90, 167.76.

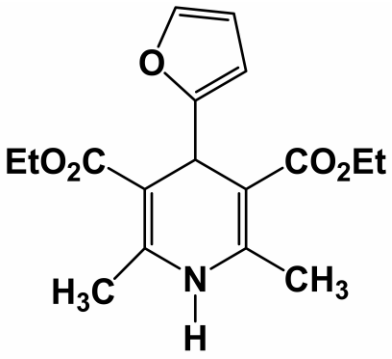



**$^{1}$H NMR**

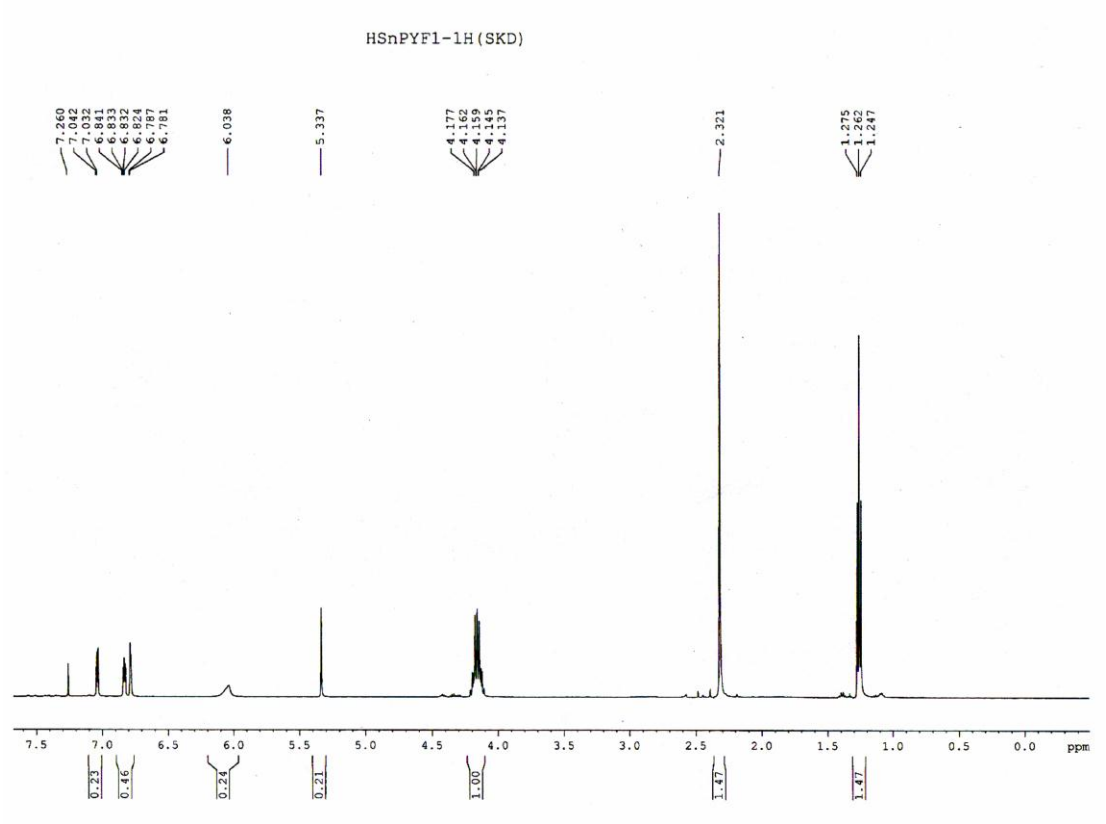



**$^{13}$C NMR**

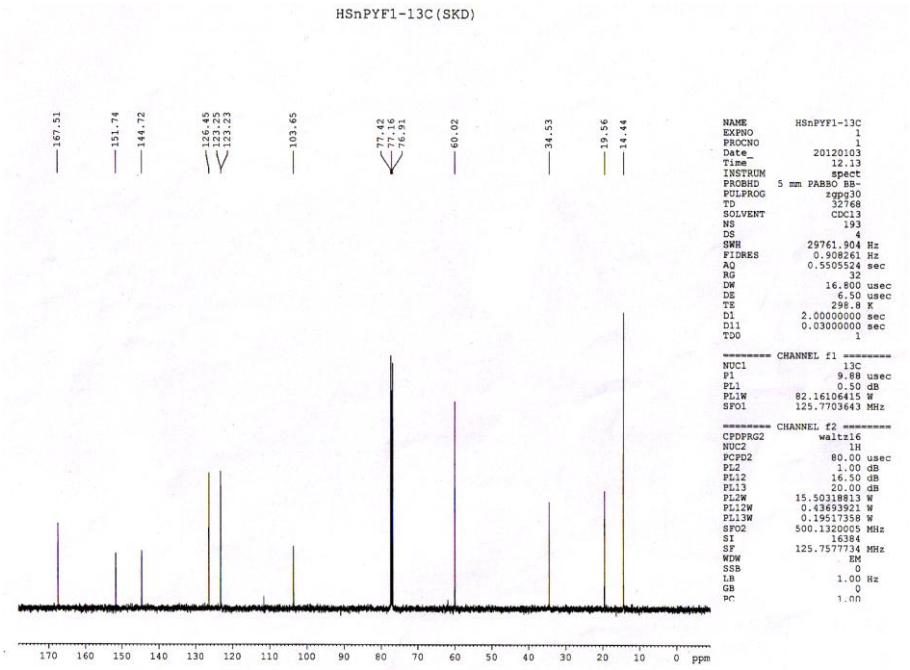
## Diethyl 4-(furan-2-yl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 2:** $^{1}$H NMR ($CDCl_3$, 300 MHz) : δ (ppm): 1.26 (t, 6H), 2.32 (s, 6H), 4.15 (q, 4H), 5.33(s, 1H), 6.03(b, 1H), 6.78 (s, 1H), 6.83 (m, 1H), 7.03 (d, 1H);$^{13}$C NMR ($CDCl_3$, 300 MHz) : δ (ppm): 14.44, 19.56, 34.53, 60.02, 103.65, 123.23, 123.25, 126.45, 144.72, 151.74, 167.51.

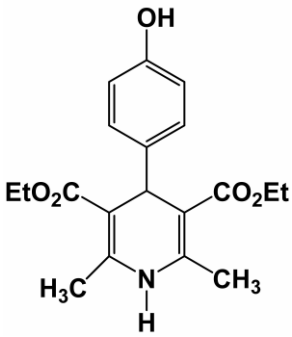



**$^{1}$H NMR**

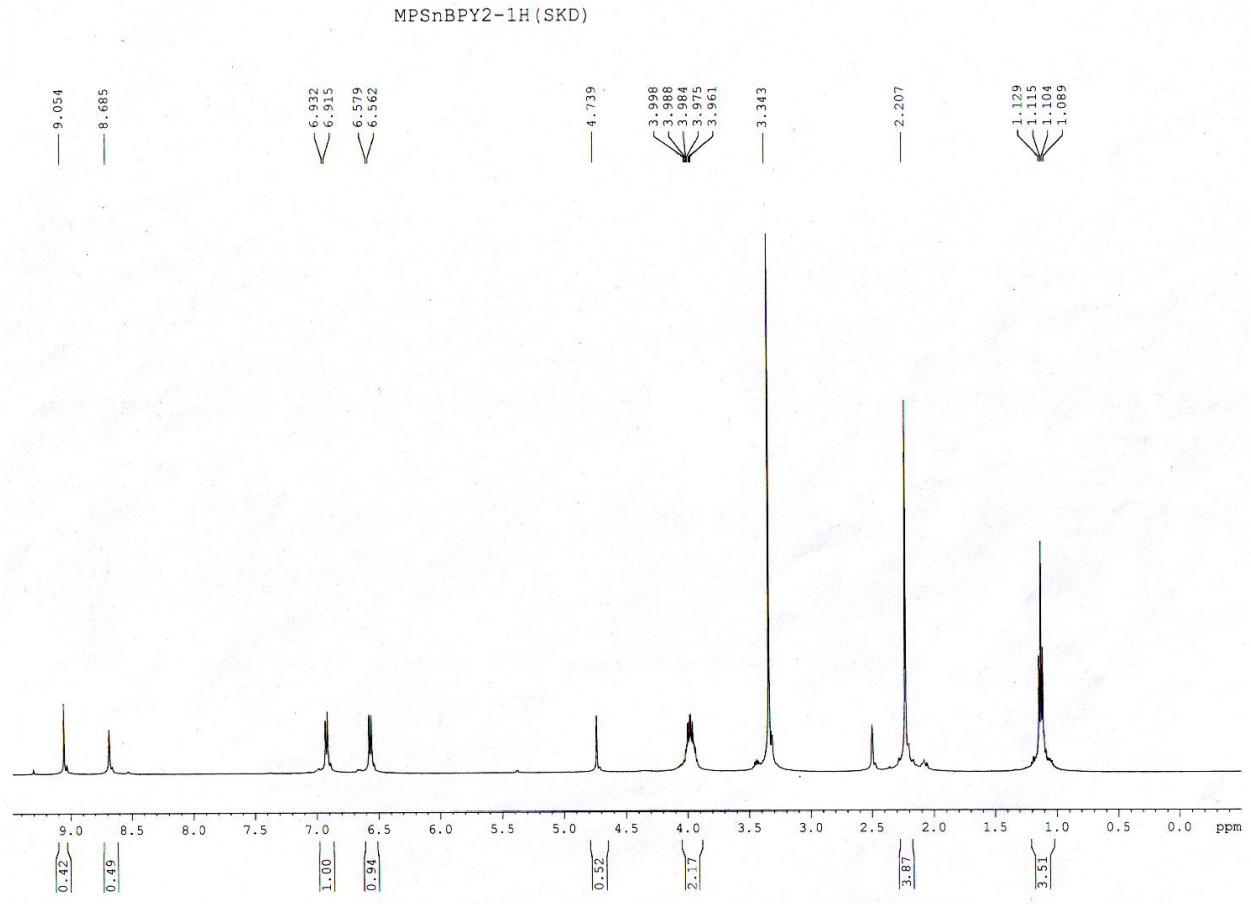



**$^{13}$C NMR**

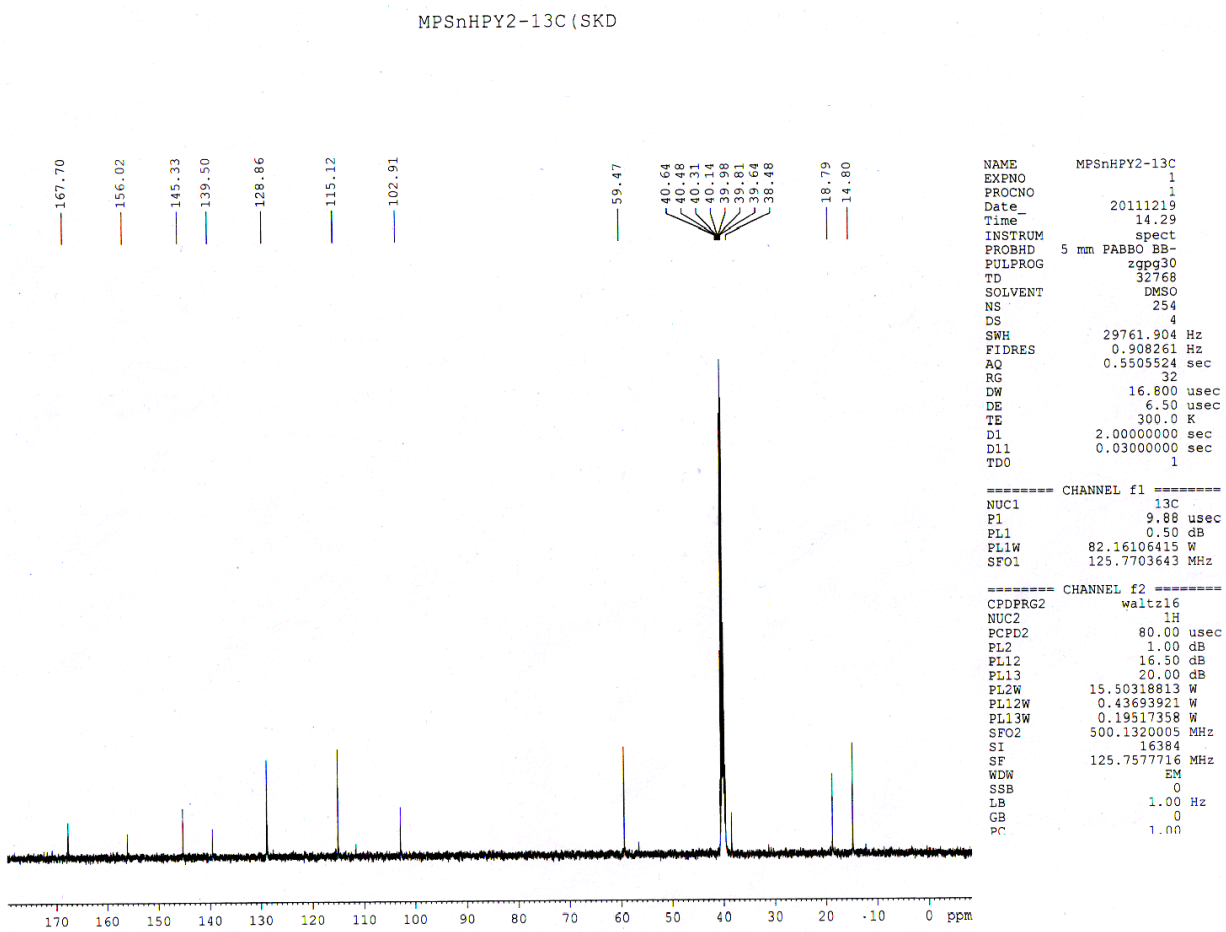
# Diethyl 1,4-dihydro-4-(4-hydroxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 3:** $^{1}$H NMR (DMSO-$d_6$, 500 MHz) : δ (ppm): 1.04-1.19 (t, 6H), 2.20 (s, 6H), 3.93-4.01 (m, 4H), 4.73 (s, 1H), 6.56 (d, 2H), 6.91 (d, 2H); 8.68 (s, 1H), 9.05 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 500 MHz) : δ (ppm): 14.80, 18.79, 59.47, 102.91, 115.12, 128.86, 139.50, 145.33, 156.02, 167.70.

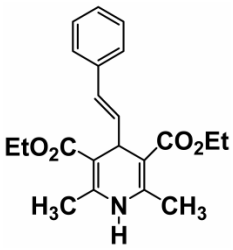



**$^{1}$H NMR**

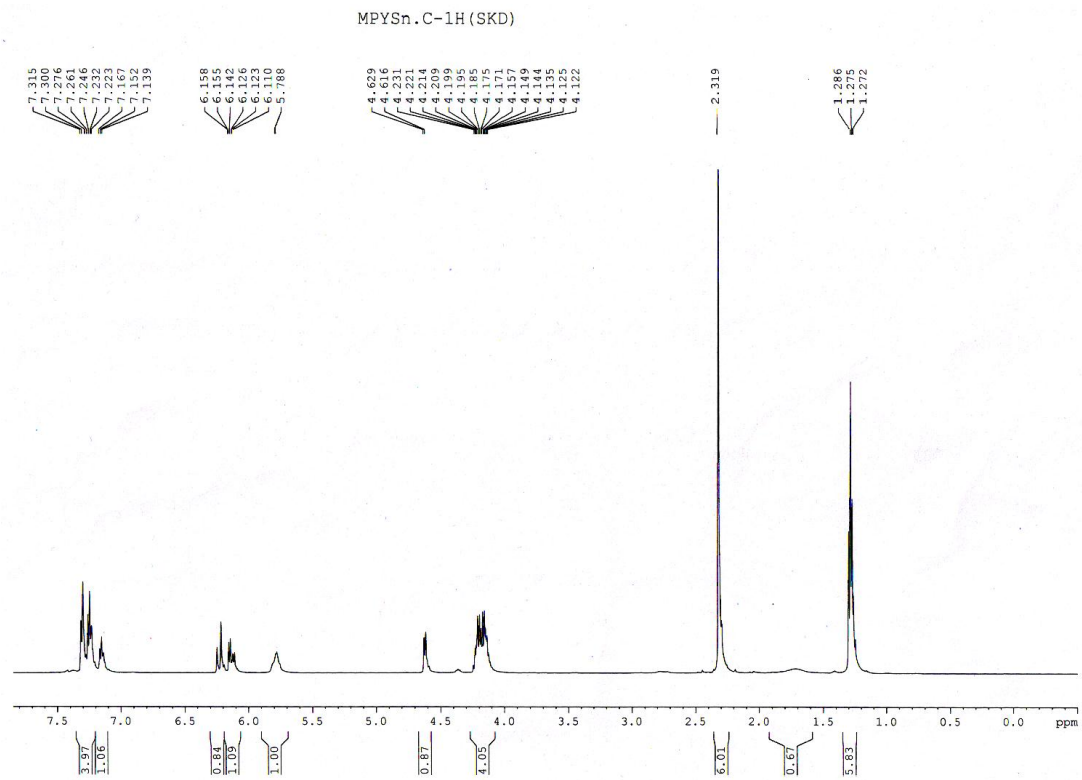



## $^{13}$C NMR

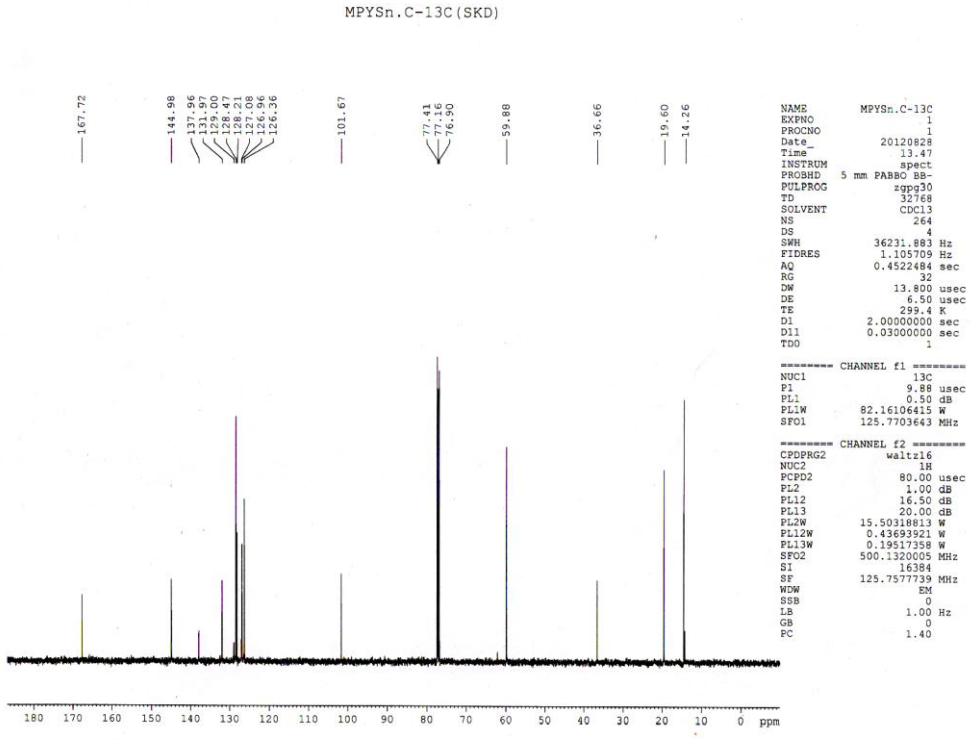
## Diethyl 1,4-dihydro-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylate




**Entry 4:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 1.27 (t, 6H), 2.31(s, 6H), 4.12-4.23 (m, 4H), 4.61 (d, 1H), 5.78 (b, 1H), 6.11-6.15 (m, 2H), 7.13-7.16 (m, 1H), 7.22-7.31 (m. 3H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : δ (ppm):14.26, 19.60, 36.66, 59.88, 101.67, 126.36, 126.96, 127.08, 128.21, 128.47, 129.0, 131.97, 137.96, 144.98, 167.72.

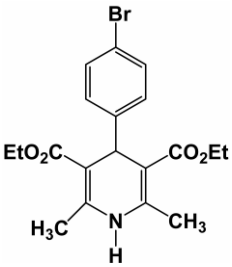



**$^{1}$H NMR**

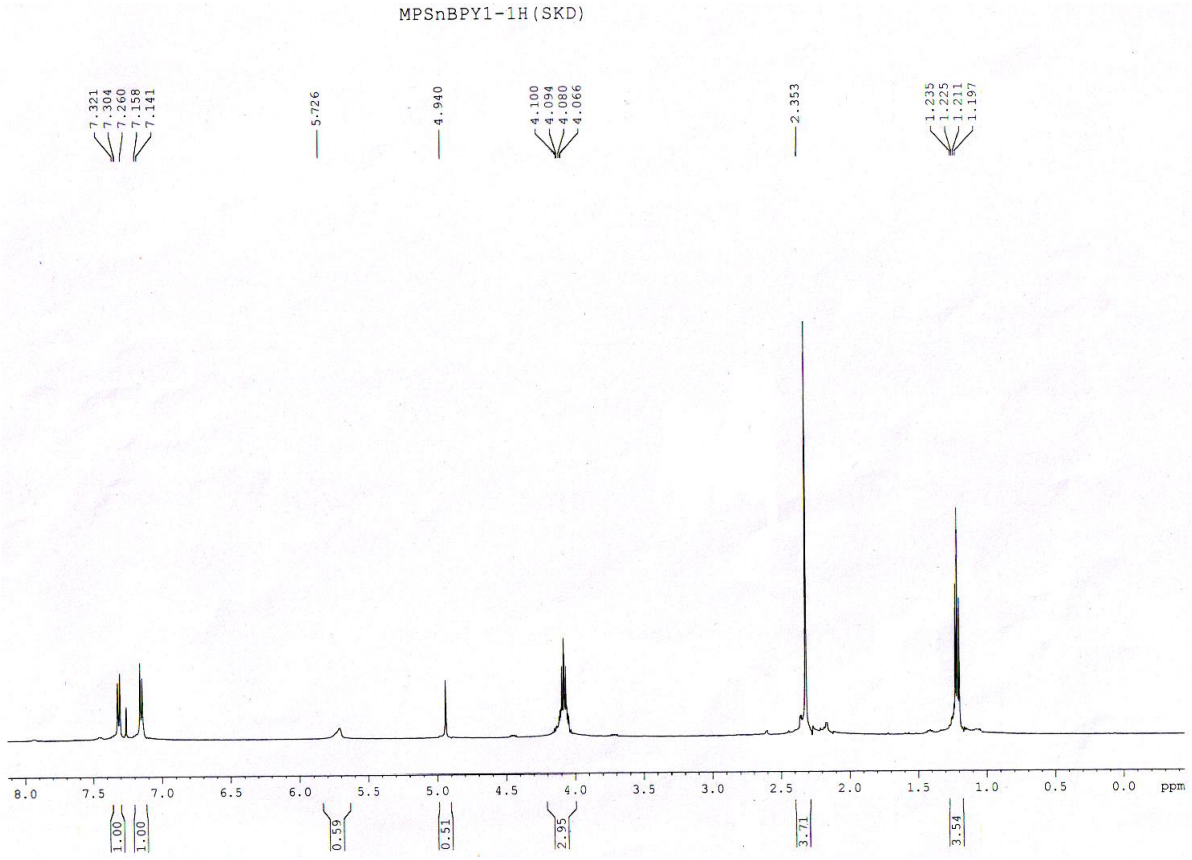



**$^{13}$C NMR**

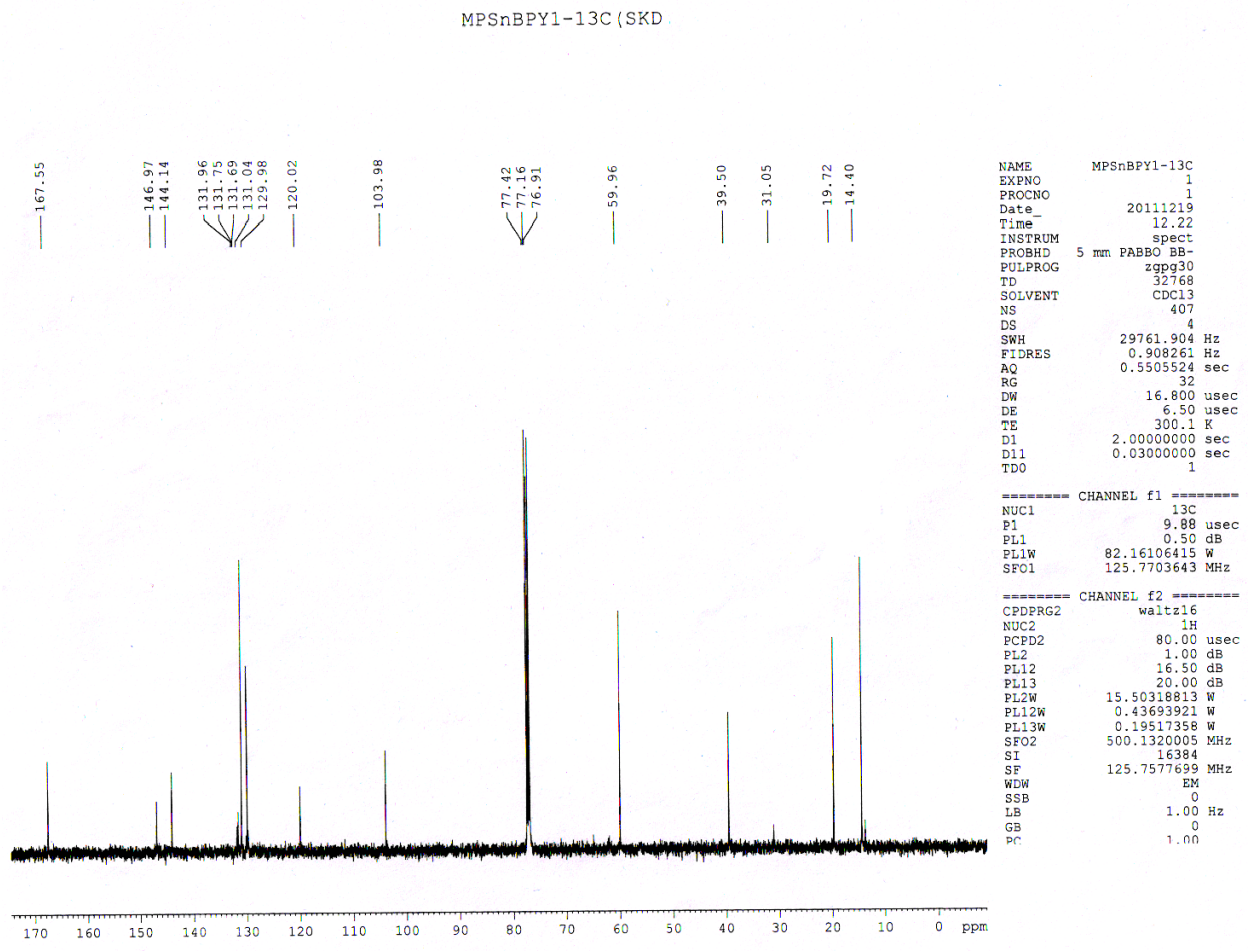
# Diethyl 4-(4-bromophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 5:** $^{1}$H NMR ($CDCl_3$, 300 MHz) : δ (ppm): 1.19-1.23 (6H), 2.33 (s, 6H), 4.08(q, 4H), 4.94 (s, 1H), 5.72(b, 1H), 7.14 (d, 2H), 7.30 (d, 2H); $^{13}$C NMR ($CDCl_3$, 300 MHz) : δ (ppm): 14.40, 19.72, 31.05, 39.50, 59.96, 103.98, 120.02, 129.98, 131.04, 131.69, 131.75, 131.96, 144.14, 146.97, 167.55.

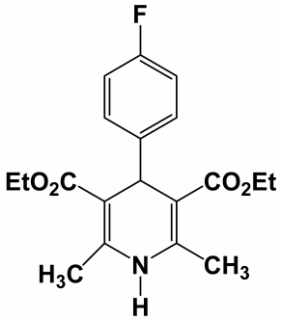



**$^{1}$H NMR**

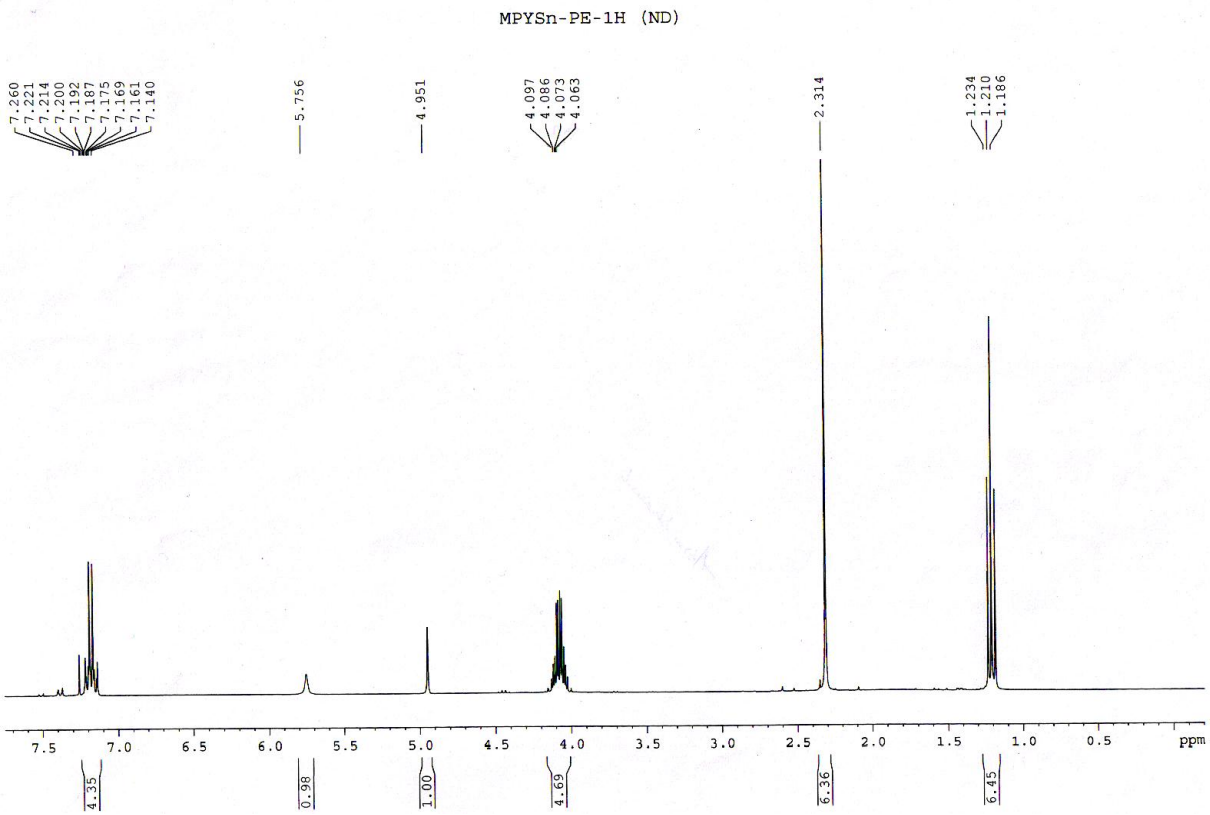



## $^{13}$C NMR

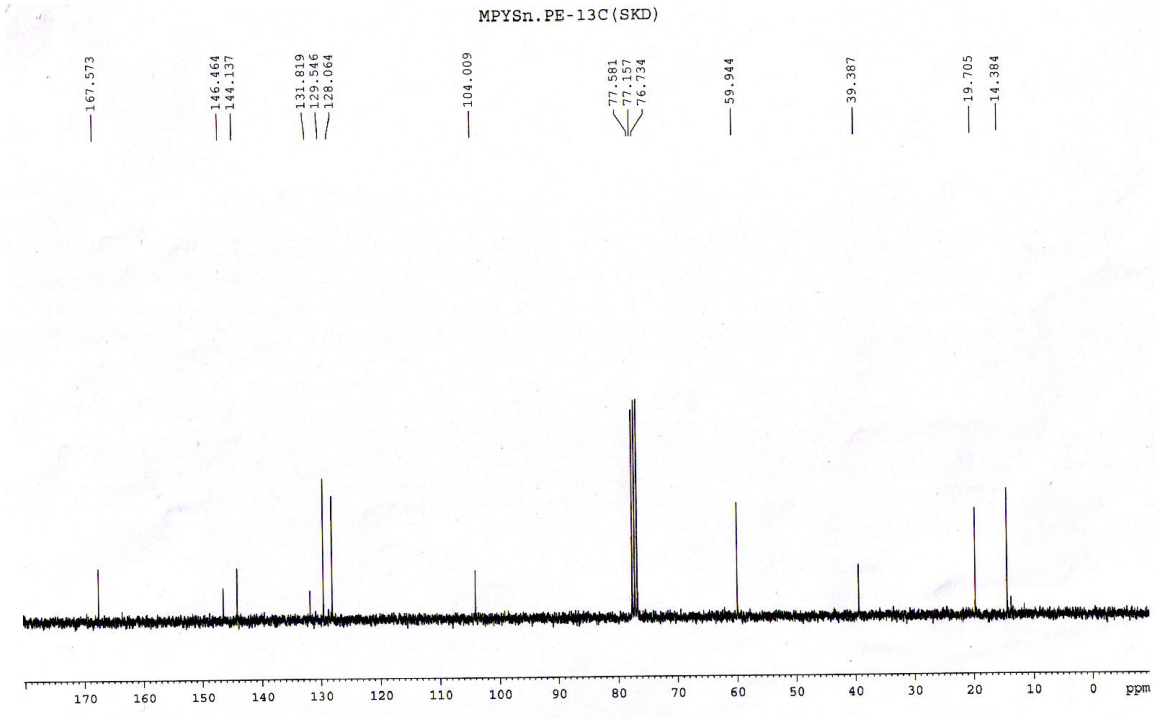
## Diethyl 4-(4-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 6:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 1.21 (t, 6H), 2.31 (s, 6H), 4.07 (q, 4H), 4.95 (s, 1H), 5.75 (b, 1H), 7.14-7.26 (m, 4H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : δ (ppm): 14.39, 19.69, 39.19, 59.90, 104.30, 114.54, 129.55, 129.61, 143.82, 161.22, 167.77.

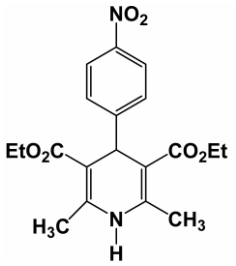



**$^{1}$H NMR**

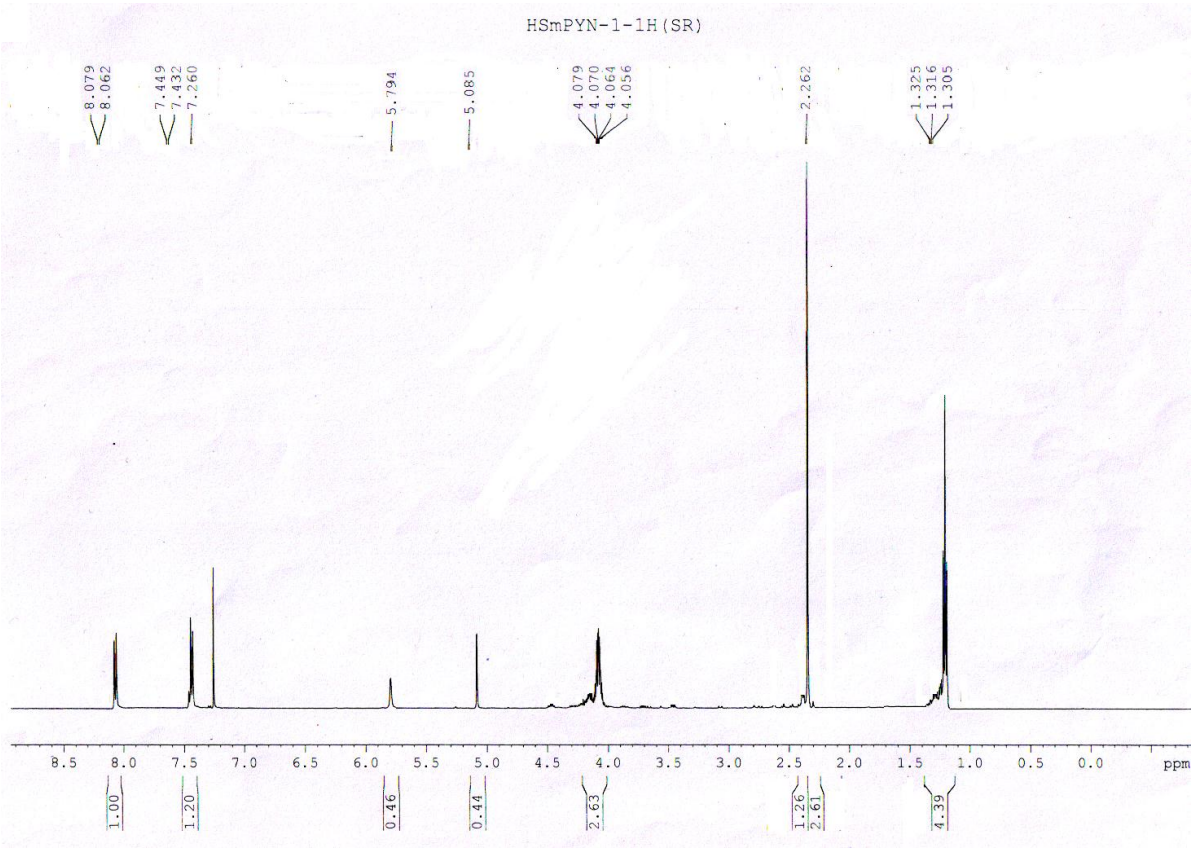



**$^{13}$C NMR**

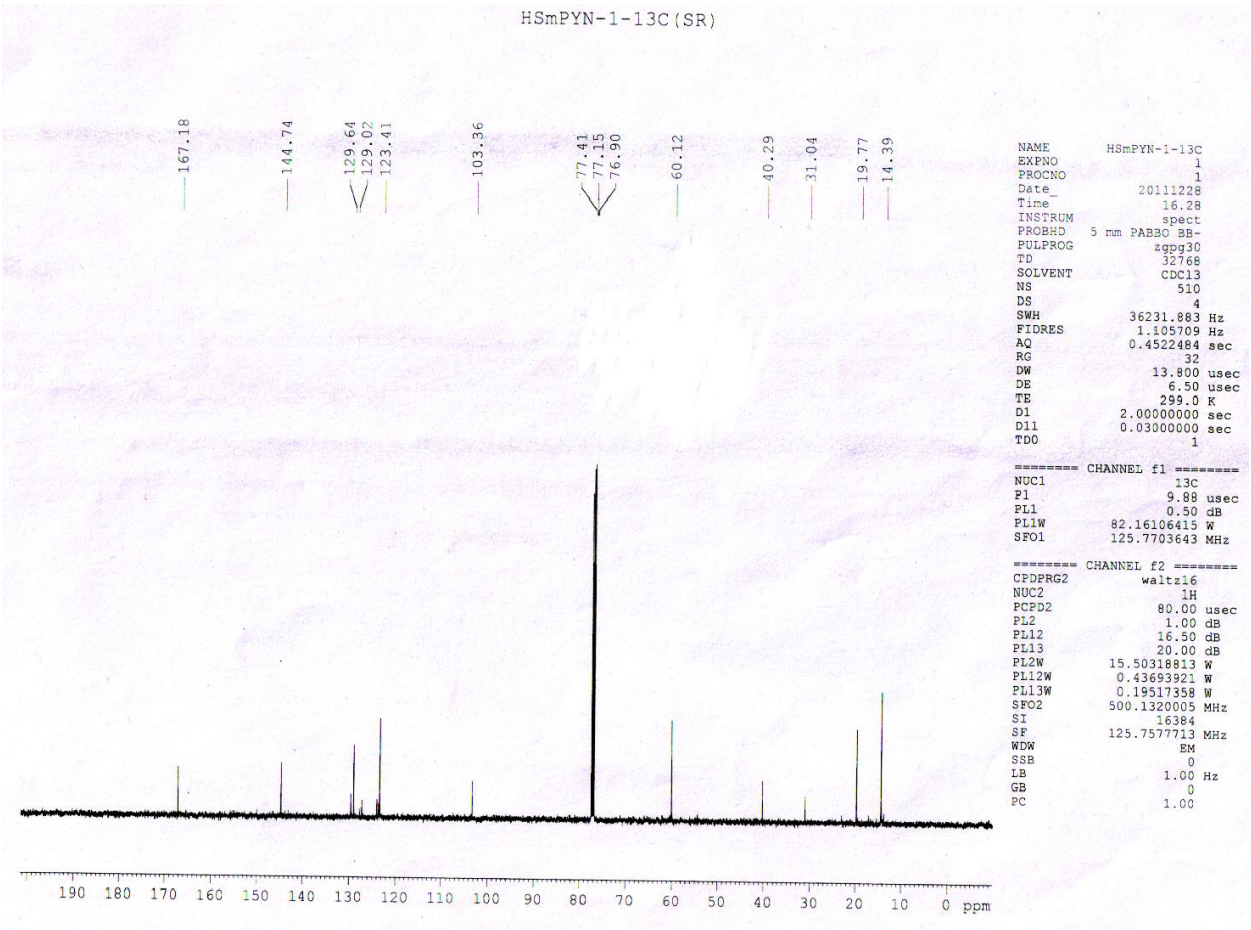
# Diethyl 1,4-dihydro-2,6-dimethyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate




**Entry 7:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 1.31 (t, 6H), 2.26 (s, 6H), 4.07 (q, 4H), 5.08 (s, 1H), 5.79 (b, 1H), 7.43 (d, 2H), 8.06 (d, 2H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : δ (ppm): 14.39, 19.77, 31.04, 40.29, 60.12, 103.36, 123.41, 129.02, 129.64, 144.74, 167.18.

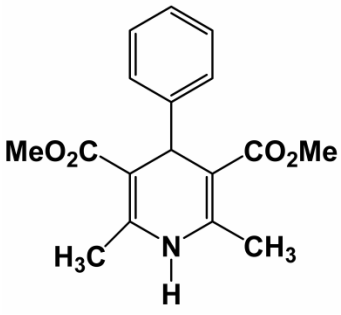



## $^{1}$H NMR

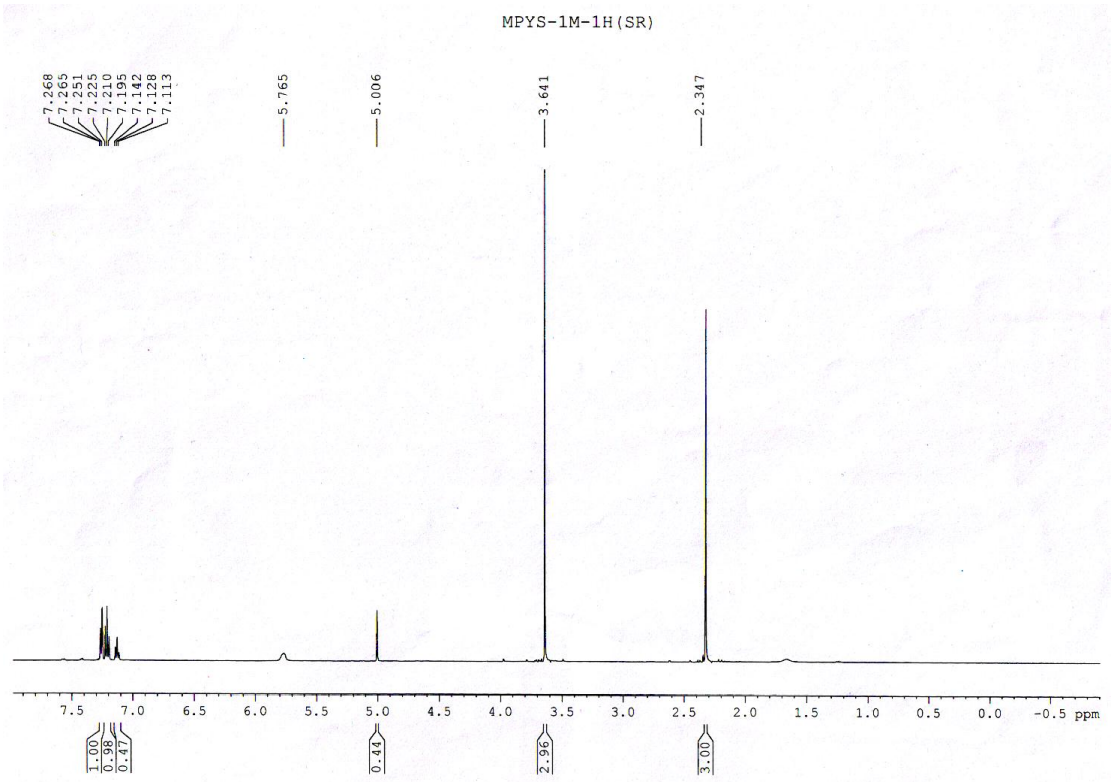



## $^{13}$C NMR

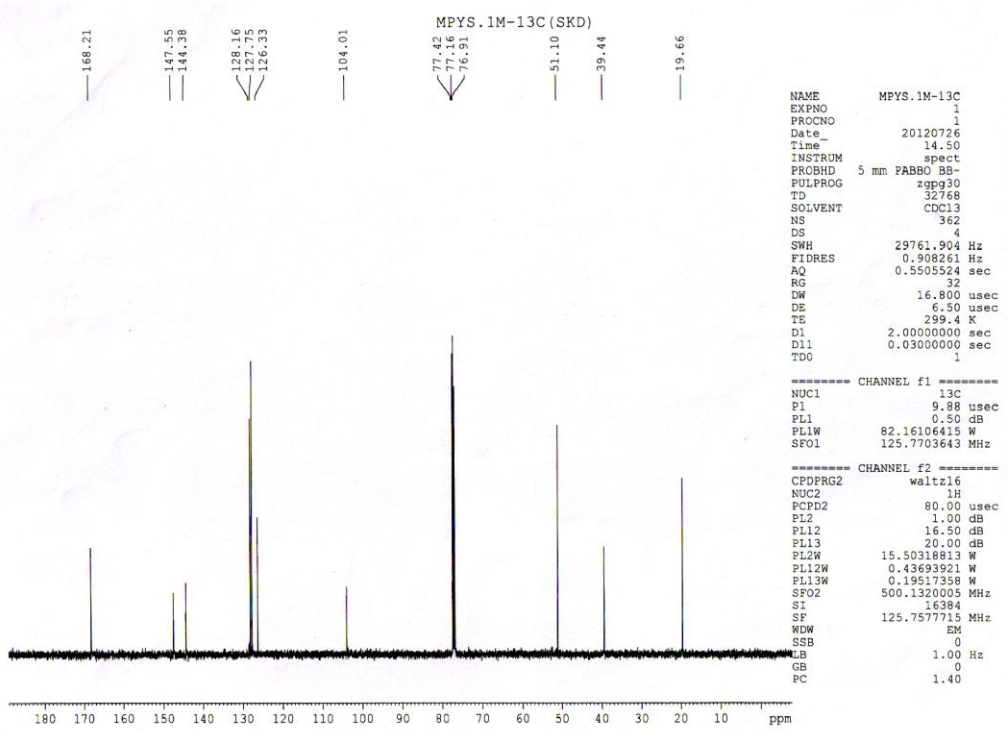
## Dimethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate




**Entry 8:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 2.34 (s, 6H), 3.64 (s, 6H), 5.00 (s, 1H), 5.76 (b, 1H), 7.11-7.26 (m, 4H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : δ (ppm): 19.66, 39.44, 51.10, 104.01, 126.33,127.75, 128.16, 144.38, 147.55, 168.21.

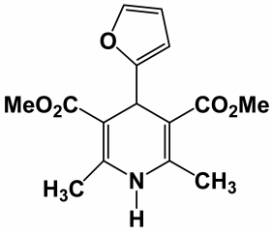



**$^{1}$H NMR**

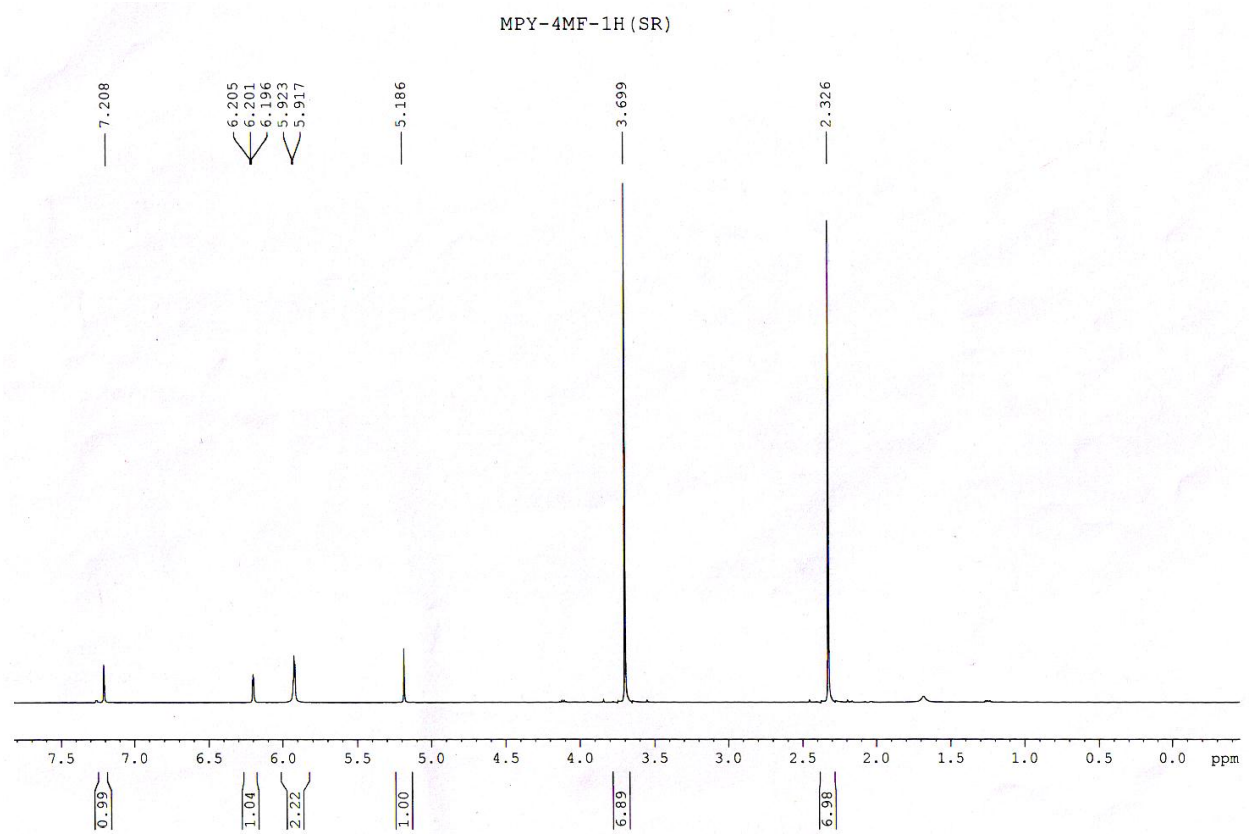



**$^{13}$C NMR**

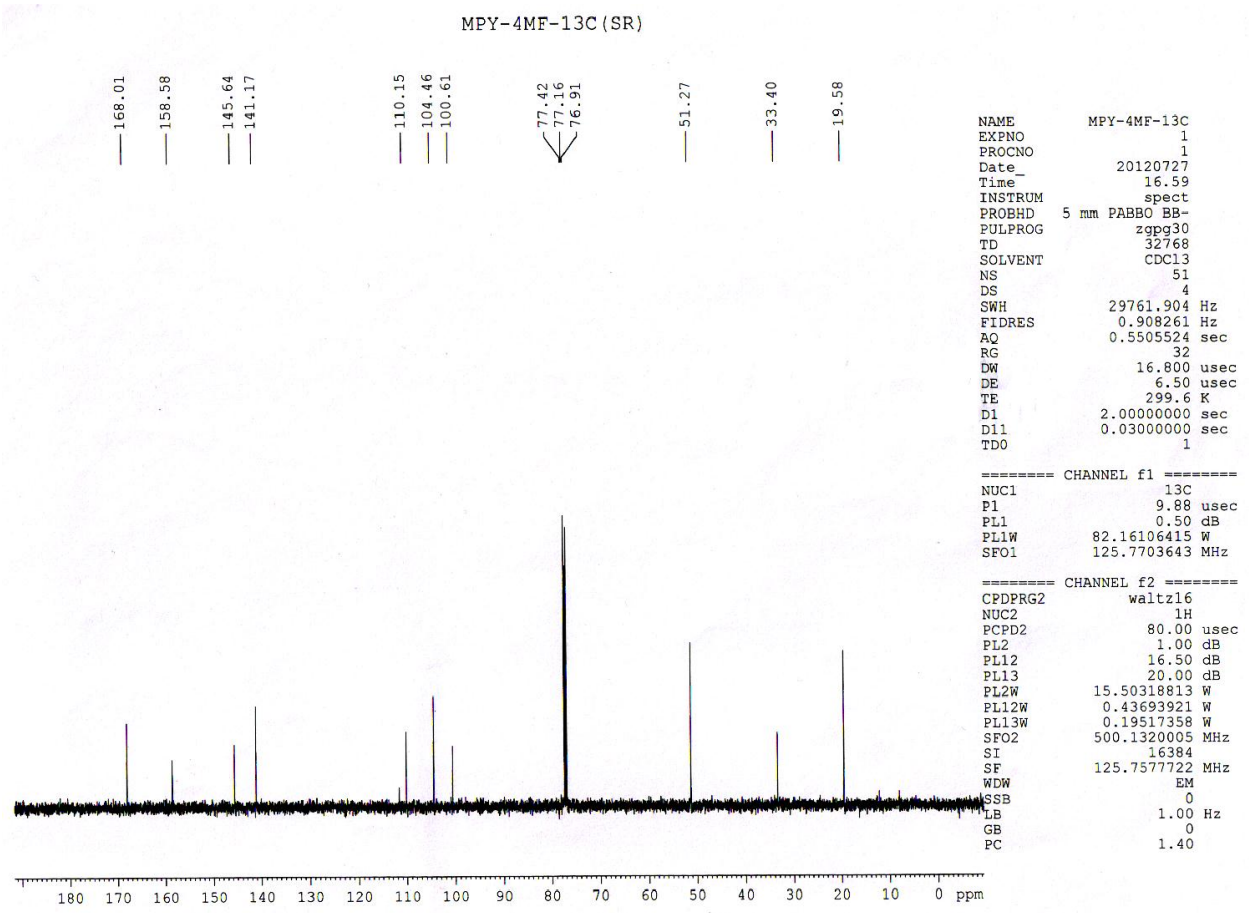
## Dimethyl 4-(furan-2-yl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 9:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 2.32 (s, 6H), 3.69 (s, 6H), 5.18 (s, 1H), 5.91 (1H), 5.923 (1H), 6.19-6.20 (t, 1H), 7.20 (s, 1H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : δ (ppm): 19.58, 33.40, 51.27, 100.61, 104.46, 110.15, 141.17, 145.64, 158.58, 168.01.

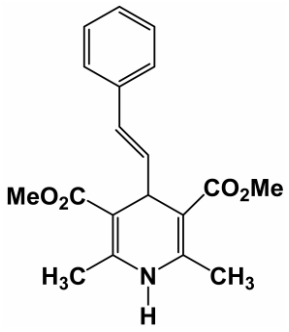



**$^{1}$H NMR**

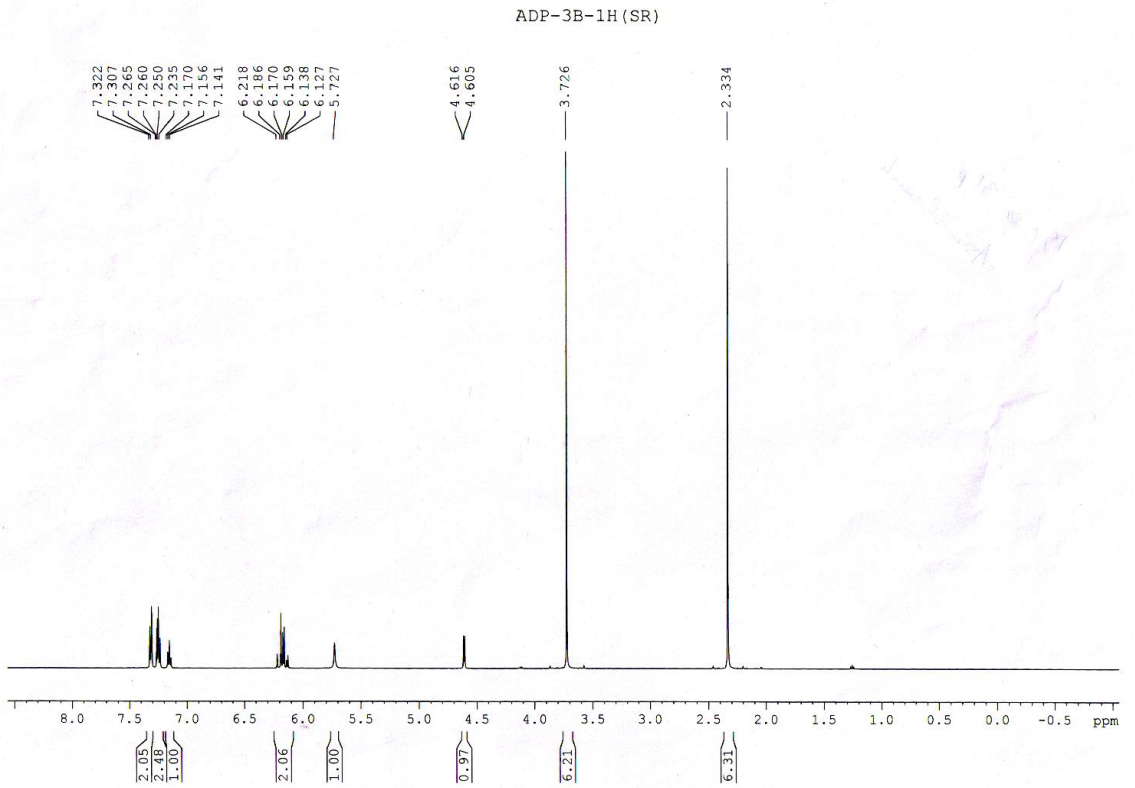



## $^{13}$C NMR

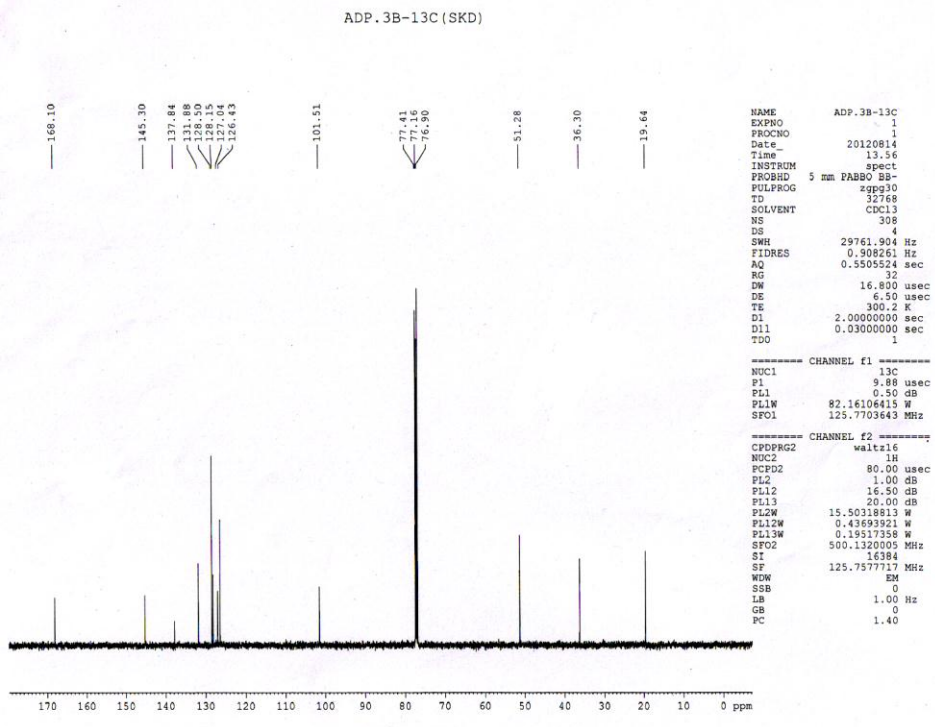
## Dimethyl 1,4-dihydro-2,6-dimethyl-4-styrylpyridine-3,5-dicarboxylate




**Entry 10:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 2.334 (s, 6H), 3.726 (s, 6H), 4.605-4.616 (d, 1H), 5.727 (s, 1H), 6.127-6.218 (m, 2H), 7.141-7.170 (t, 1H), 7.235-7.265 (m, 2H), 7.307- 7.322 (d, 1H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : 19.64, 36.30, 51.28, 101.51, 126.43, 127.04, 128.15, 128.50, 131.88, 137.84, 145.30, 168.10.

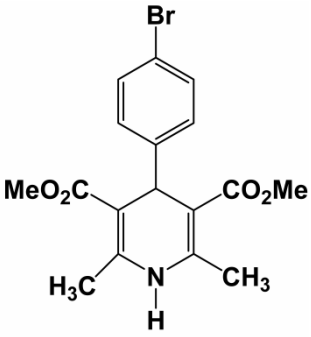



**$^{1}$H NMR**

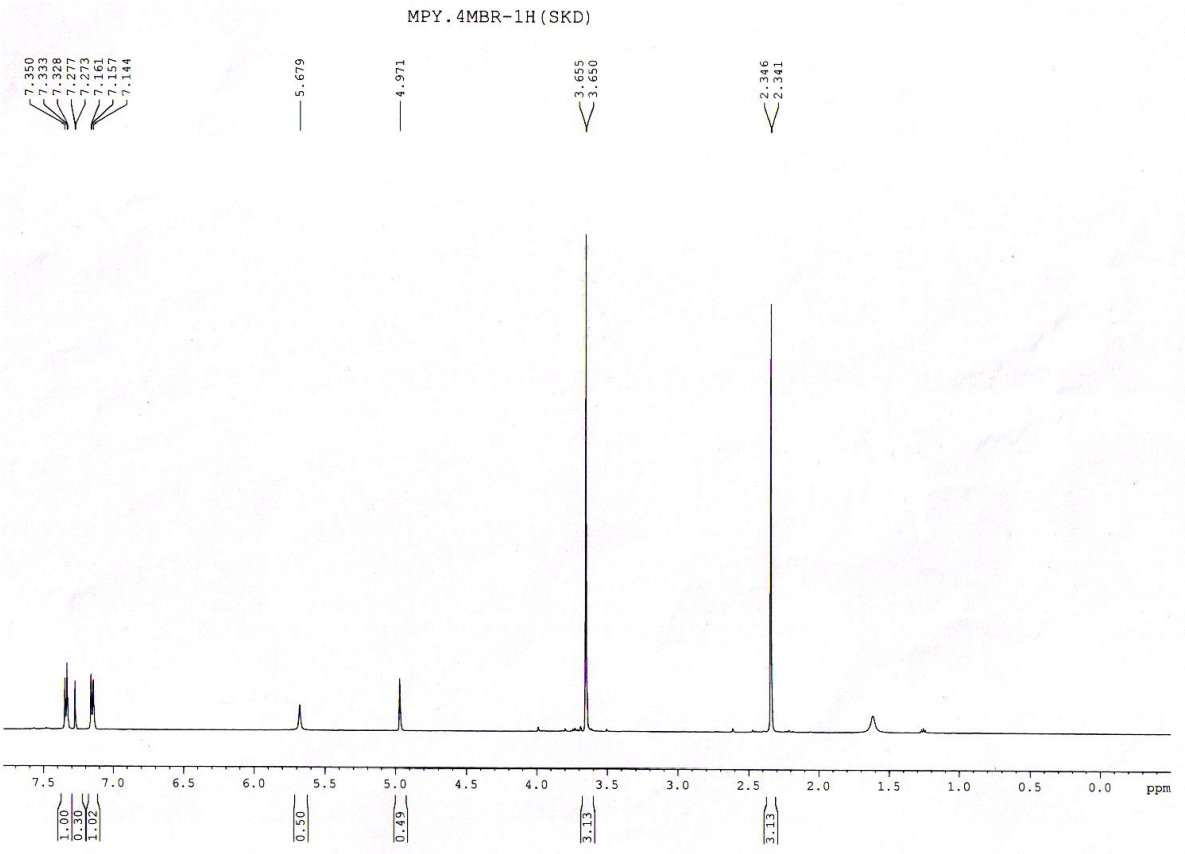



**$^{13}$C NMR**

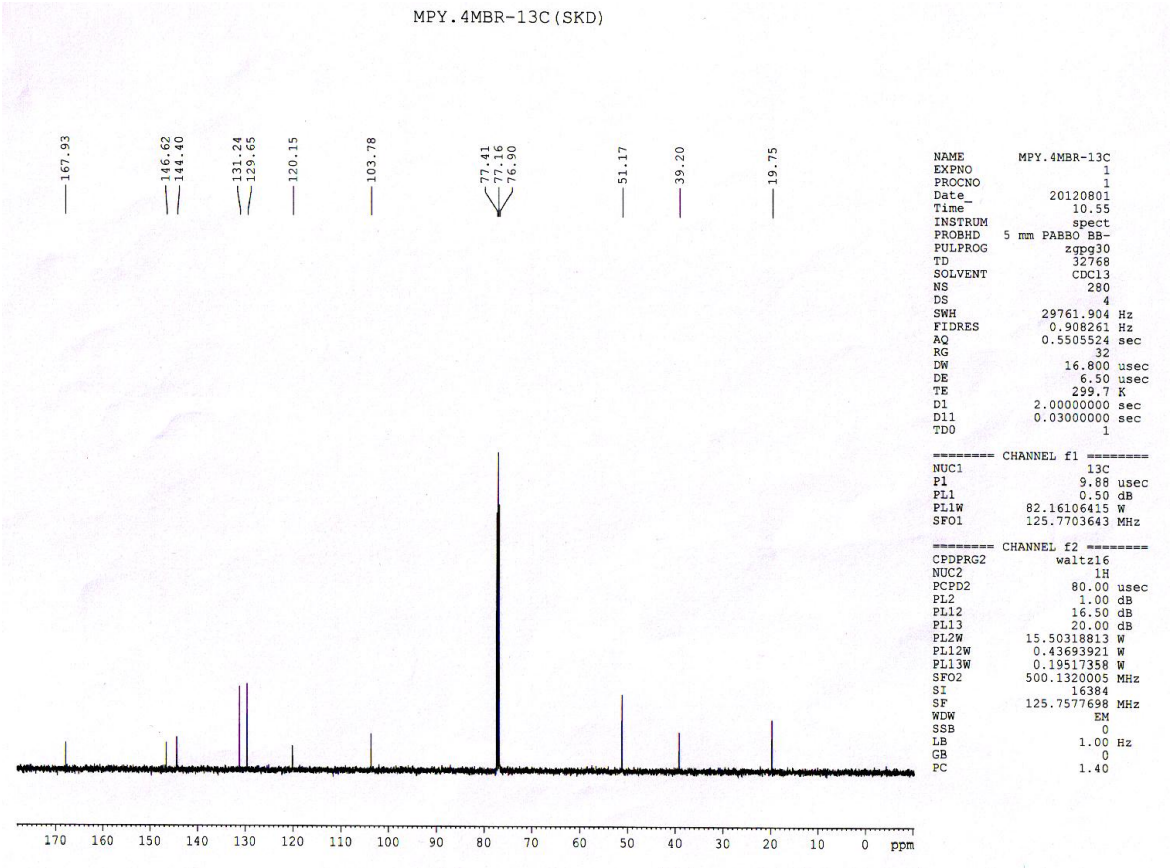
# Dimethyl 4-(4-bromophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 11:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 2.341 (s, 6H), 3.65 (s, 6H), 4.97 (s, 1H), 5.67 (b, 1H), 7.14-7.16 (t, 2H), 7.32-7.35 (t, 2H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : 19.75, 39.20, 51.17, 103.78, 120.15, 129.65, 131.24, 144.40, 146.62, 167.93.

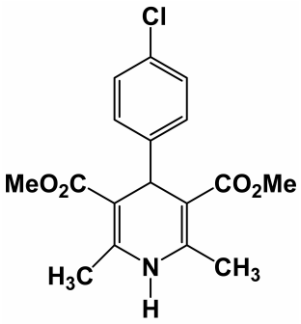



**$^{1}$H NMR**

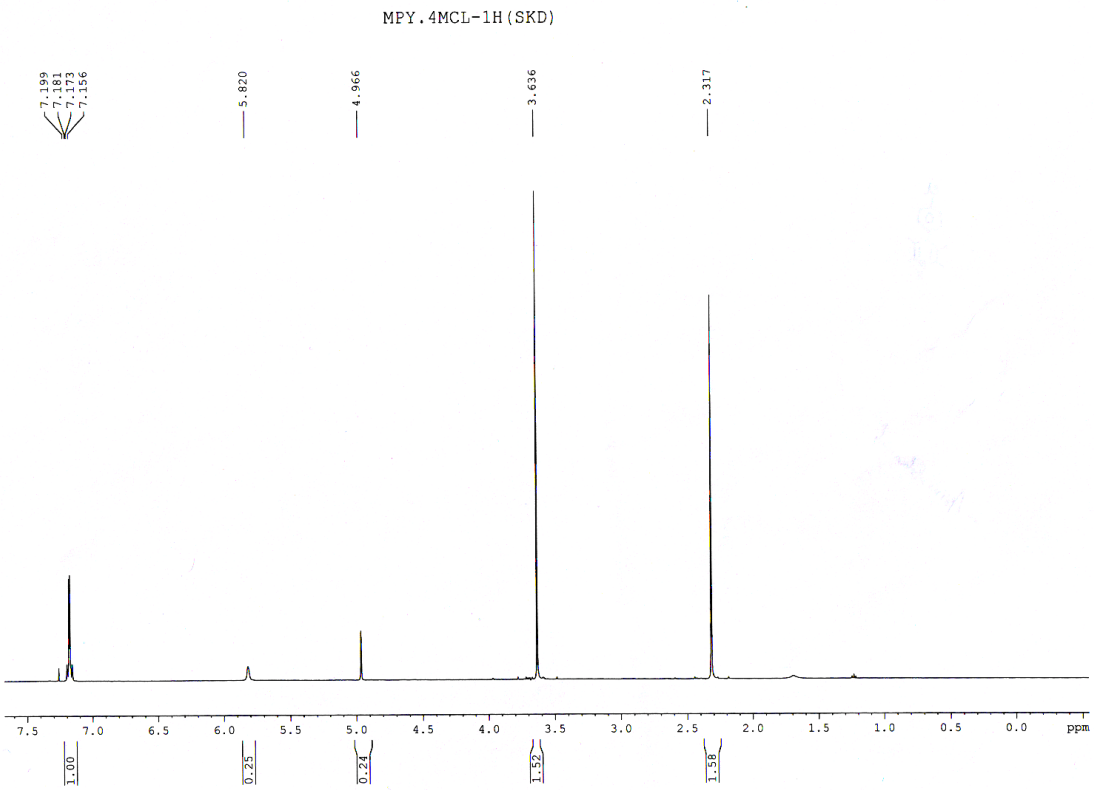



## $^{13}$C NMR

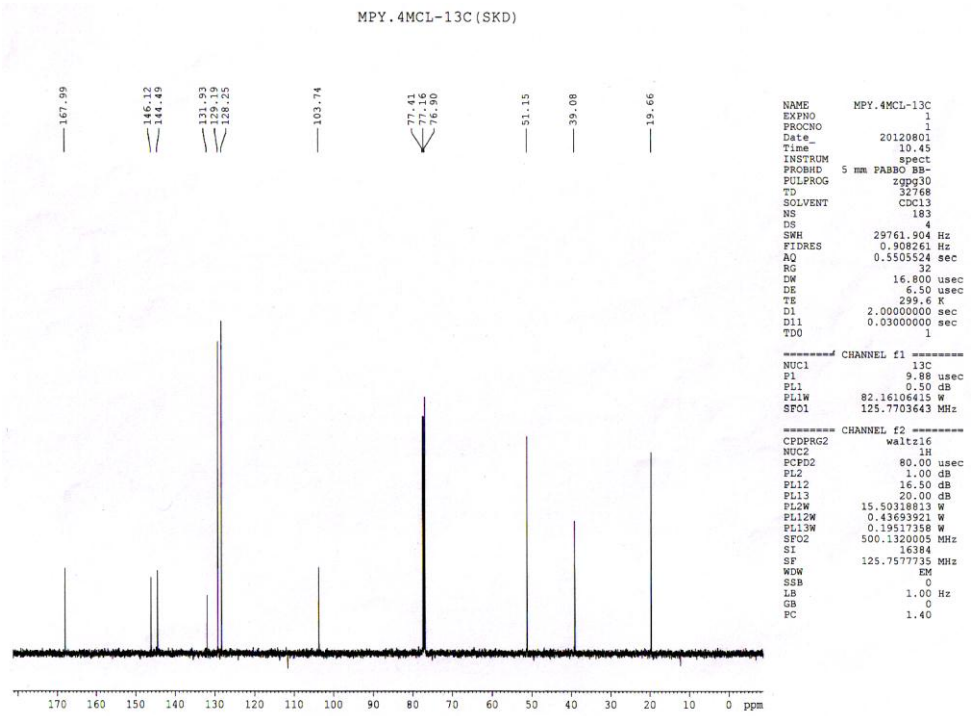
## Dimethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 12:** $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm): 2.317 (s, 6H), 3.63 (s, 6H), 4.96 (s, 1H), 5.82 (s, 1H), 7.156-7.199 (m, 4H); $^{13}$C NMR ($CDCl_3$, 500 MHz) :19.66, 39.08, 51.15, 103.74, 128.25, 129.19, 131.93, 144.49, 146.12, 167.99.

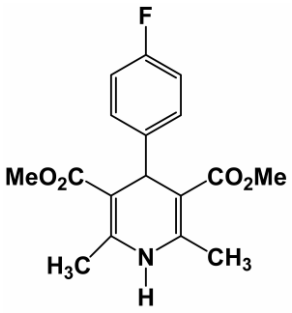



**$^{1}$H NMR**

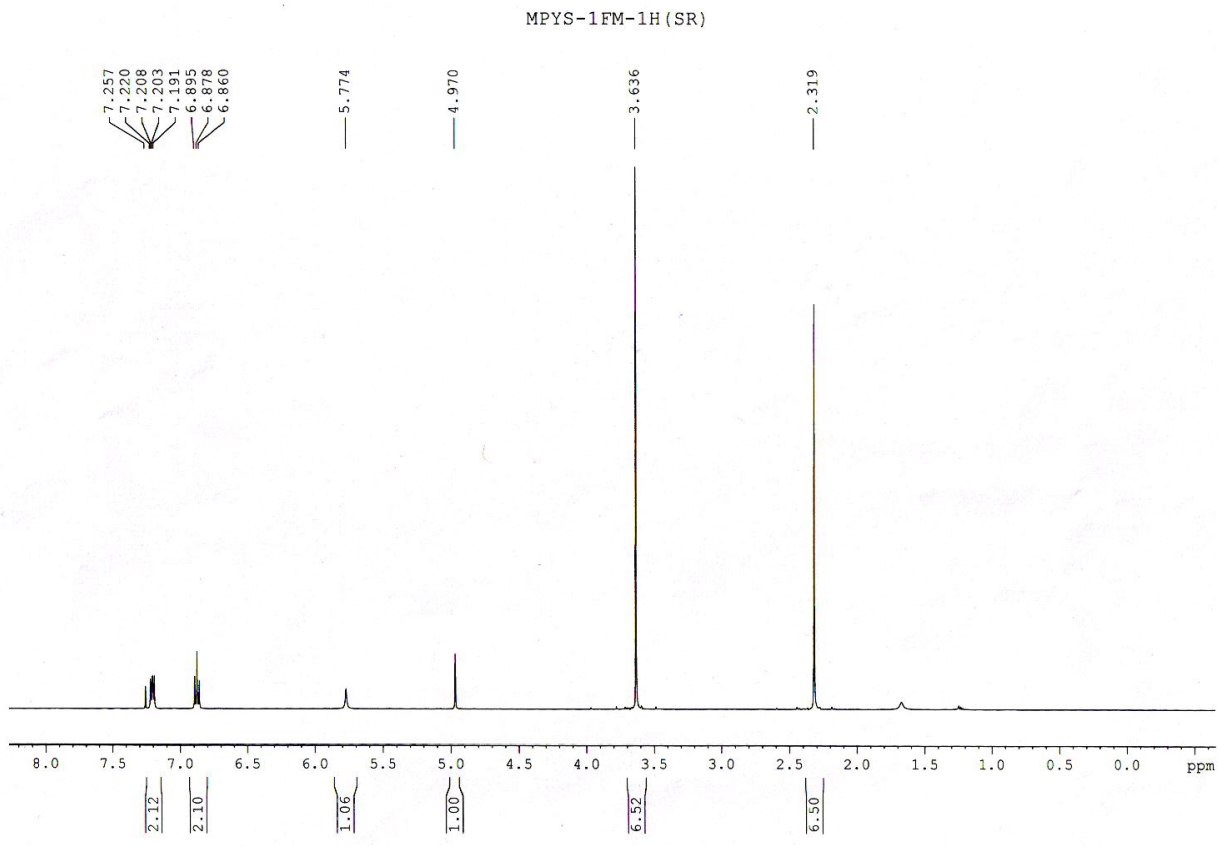



**$^{13}$C NMR**

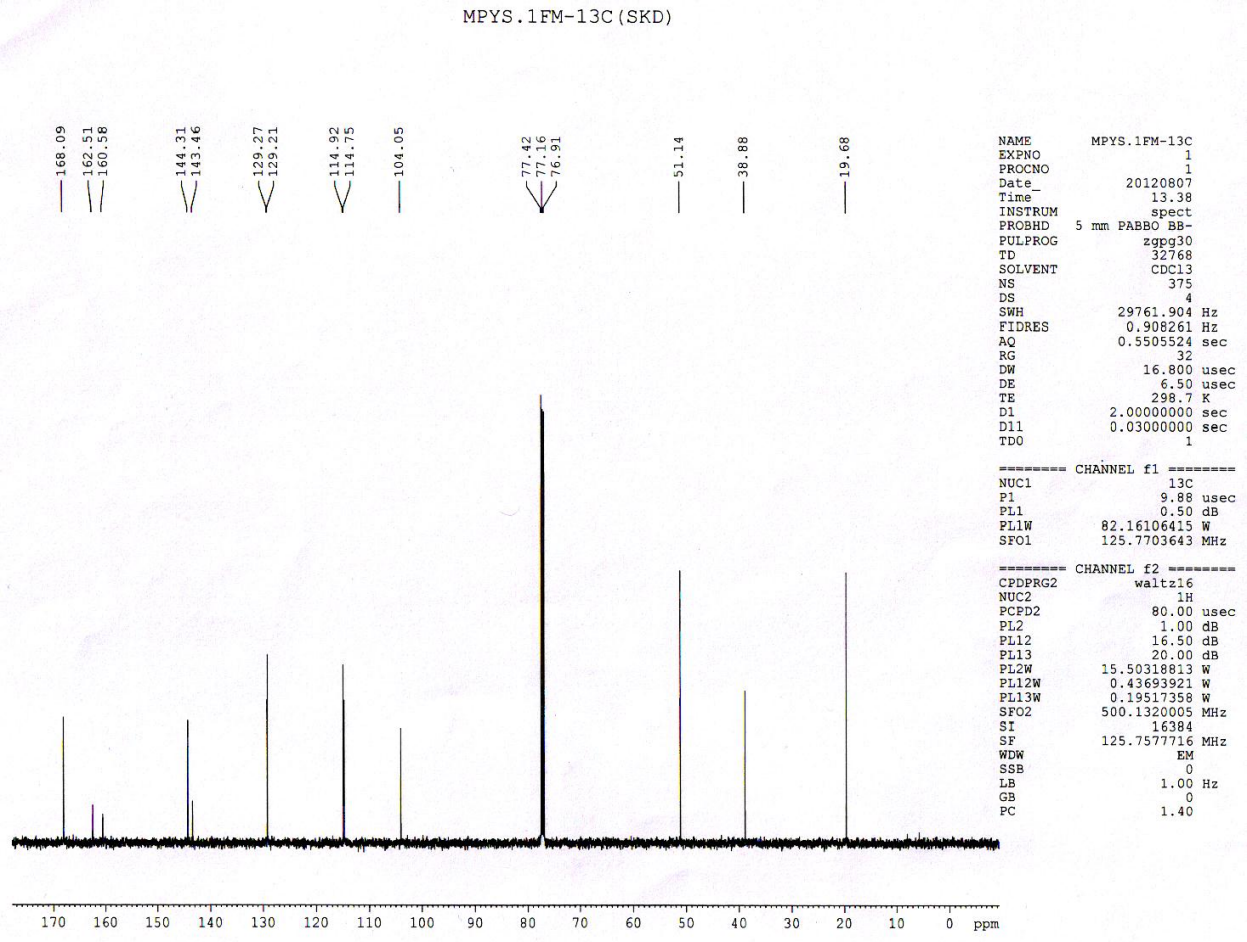
# Dimethyl 4-(4-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate




**Entry 13:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 2.31 (s, 6H), 3.63 (s, 6H), 4.97 (s, 1H), 5.77 (b, 1H), 6.86-6.89 (t, 2H), 7.19-7.22 (t, 2H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : 19.68, 38.88, 51.14, 104.05, 114.75, 114.92, 129.21, 129.27, 143.46, 144.31, 160.58, 162.51, 168.09.

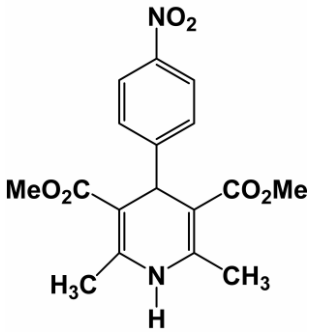



**$^{1}$H NMR**

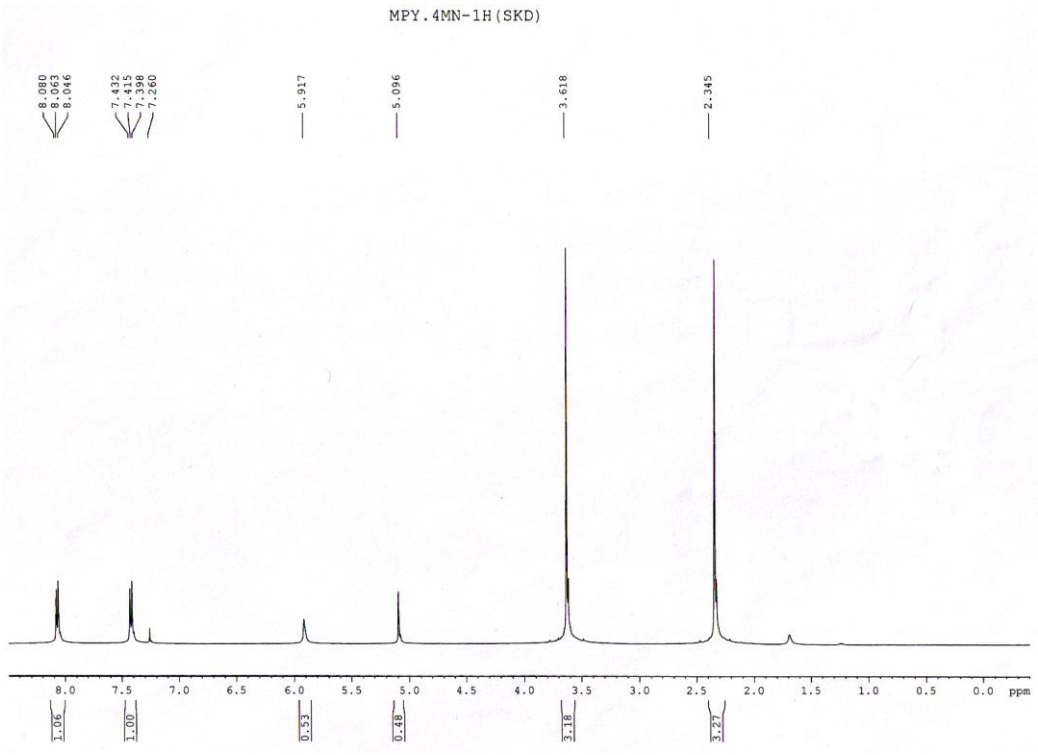



## $^{13}$C NMR

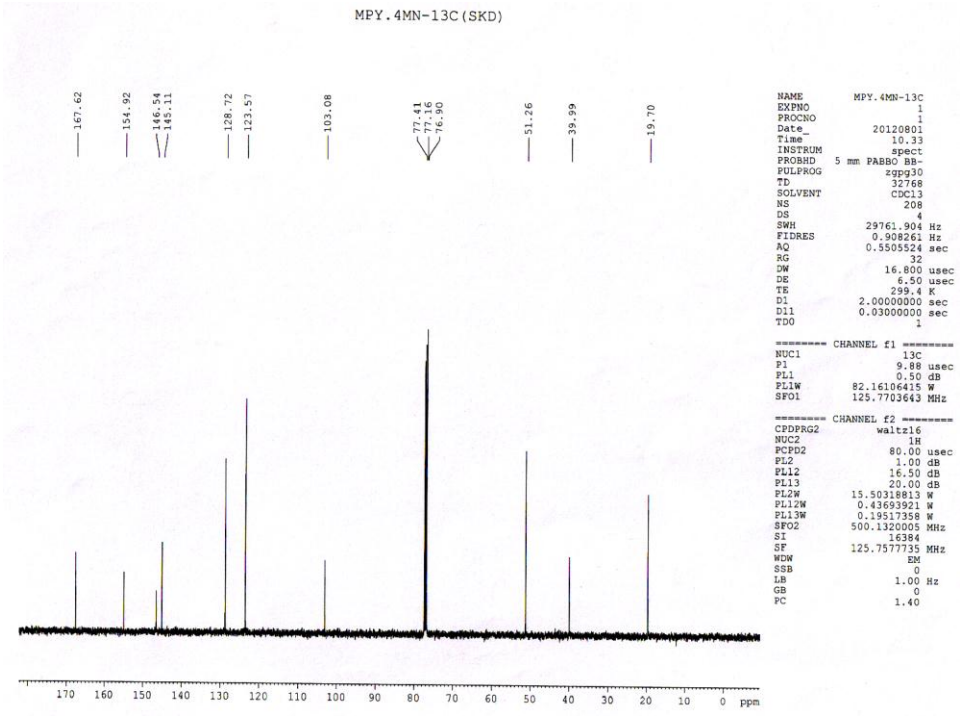
## Dimethyl 1,4-dihydro-2,6-dimethyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate




**Entry 14:** $^{1}$H NMR ($CDCl_3$, 500 MHz) : δ (ppm): 3.24 ( s, 6H), 3.61 (s, 6H), 5.09 (s, 1H), 5.91 (b, 1H), 7.3-7.432 (t, 2H), 8.04-8.08 (t, 2H); $^{13}$C NMR ($CDCl_3$, 500 MHz) : 19.70, 39.99, 51.26, 103.08, 123.57, 128.72, 145.11, 146.54, 154.92, 167.62.




**$^{1}$H NMR**

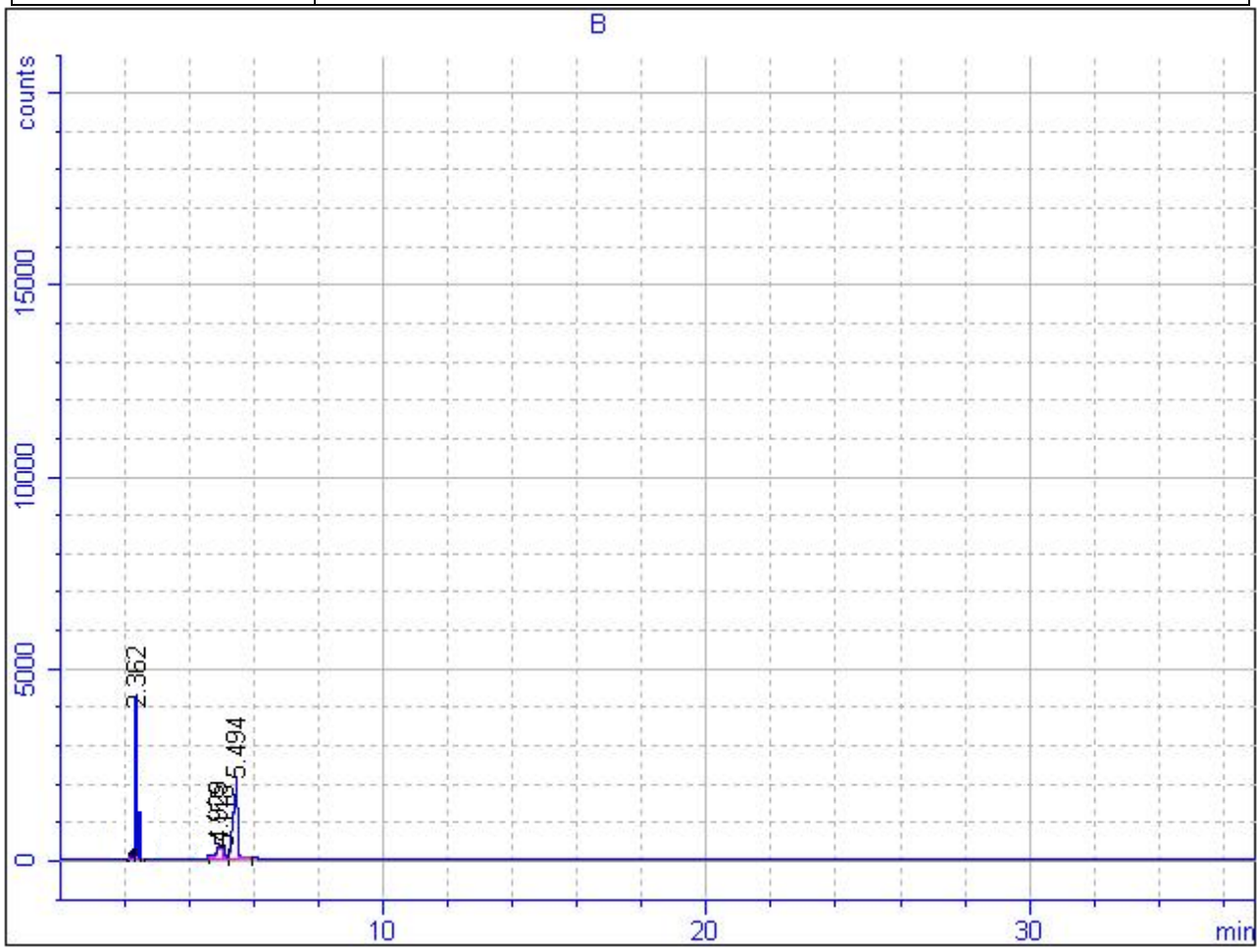



**$^{13}$C NMR**

**GC Analysis of Table 4 reaction mixtures**

**(1) GC analysis of the blank reaction mixture**

| | |
|---|---|
| Sample name: | Benzaldehyde-EAA-$CHCl_3$ |
| Sample note: | Benzaldehyde-EAA-$CHCl_3$ |
| Submission time: | Monday, February 04, 2013 12:53:56 PM |
| Injection date: | Monday, February 04, 2013 1:32:43 PM |
| GC Description: | Gas Chromatograph |
| Signal description: | OOS1 A, B |
| Method: | 80-4-5-250 |



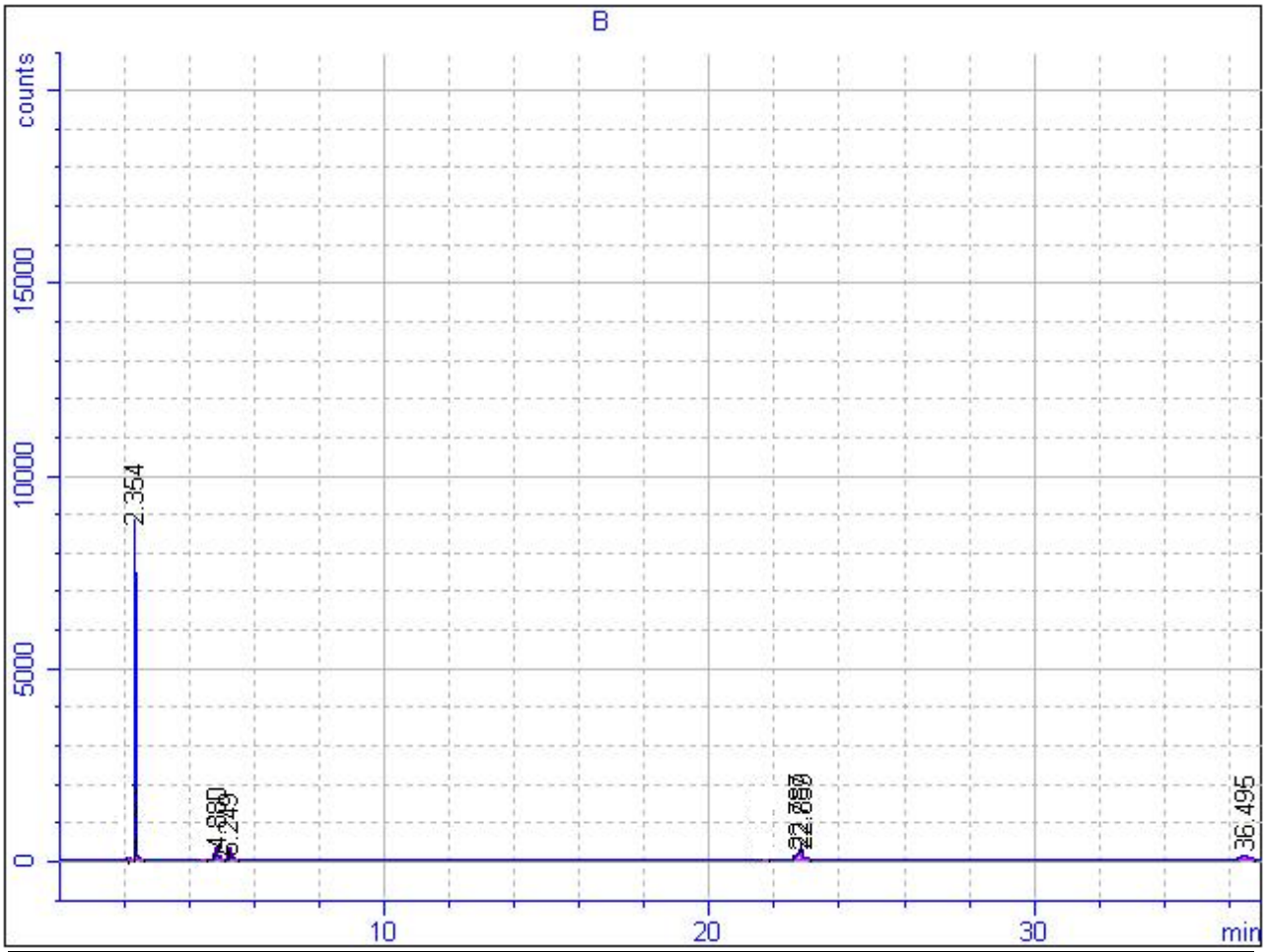

| | |
|---|---|
| Multiplier: | 1.0000 |
| Dilution: | 1.0000 |

| | |
|---|---|
| Sample amount: | 0.0000 Microlitres |
| Sample type: | Sample |
| Sampling source: | Manual |

| Signal | Retention Time [min] | Type | Width [min] | Area [counts*s] | Area % |
|---|---|---|---|---|---|
| 1 | 2.362 | VV | 0.020 | 8880.37074 | 26.36282 |
| 1 | 4.466 | PV | 0.105 | 2122.05744 | 6.29967 |
| 1 | 4.929 | VV | 0.152 | 4519.12506 | 13.41575 |
| 1 | 5.494 | VB | 0.109 | 18163.66443 | 53.92176 |

**(2) GC analysis of the reaction mixture using bulk tin phosphonate ($BSnPO_4$) as catalyst.**

| | |
|---|---|
| Sample name: | Benzaldehyde-EAA-$BSnPO_4$-$CHCl_3$ |
| Sample note: | Benzaldehyde-EAA-$BSnPO_4$-$CHCl_3$ |
| Submission time: | Monday, February 04, 2013 12:54:38 PM |
| Injection date: | Monday, February 04, 2013 2:14:55 PM |
| GC Description: | Gas Chromatograph |
| Signal description: | OOS1 A, B |
| Method: | 80-4-5-250 |



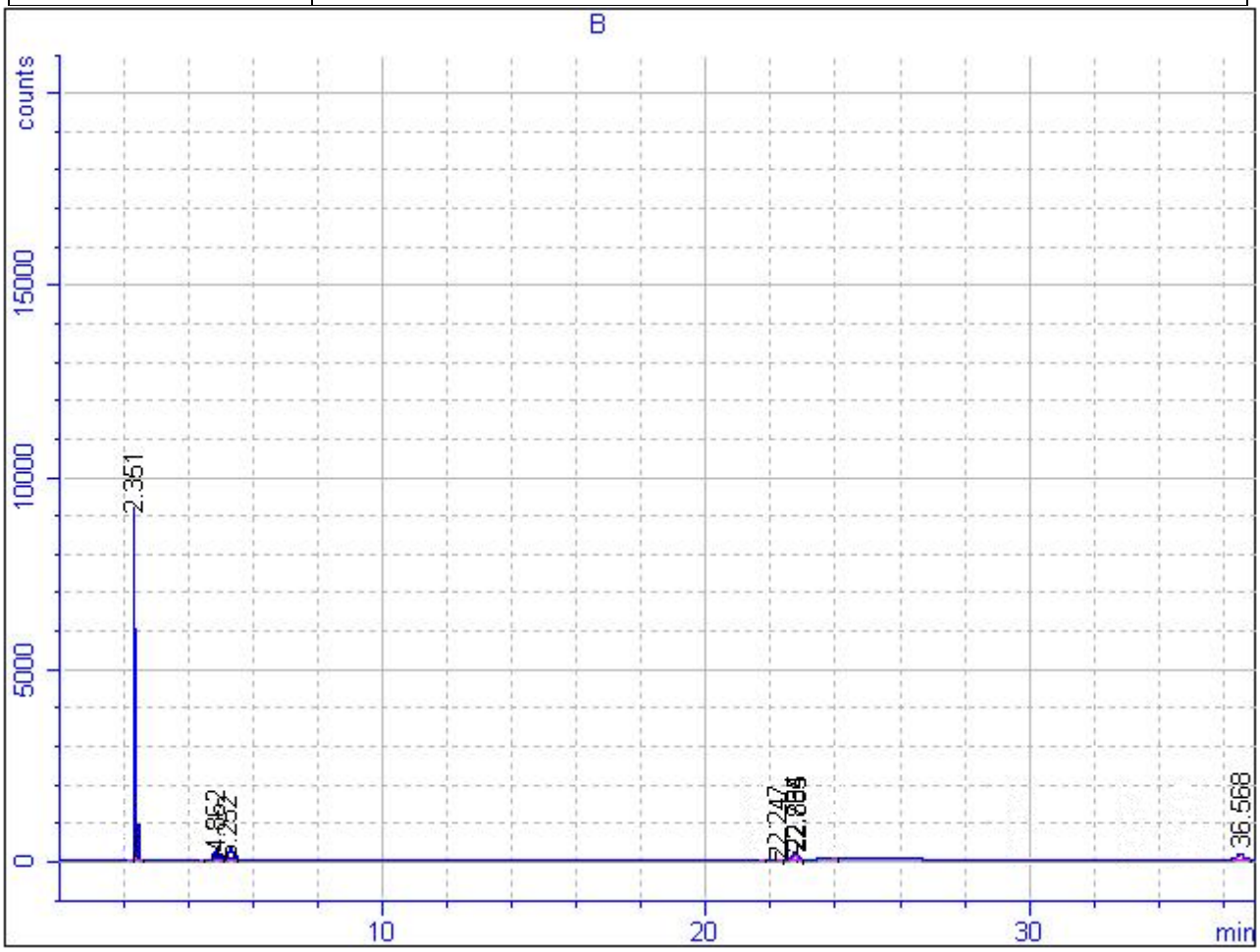

| | |
|---|---|
| Multiplier: | 1.0000 |
| Dilution: | 1.0000 |
| Sample amount: | 0.0000 Microlitres |
| Sample type: | Sample |
| Sampling source: | Manual |

| Signal | Retention Time [min] | Type | Width [min] | Area [counts*s] | Area % |
|---|---|---|---|---|---|
| 1 | 2.354 | VB | 0.024 | 16466.21202 | 72.9099 |
| 1 | 4.880 | BB | 0.054 | 1296.31325 | 5.74291 |
| 1 | 5.249 | PB | 0.079 | 1318.94341 | 5.83730 |
| 1 | 22.787 | PV | 0.095 | 1486.84063 | 6.58419 |
| 1 | 22.859 | VB | 0.055 | 1015.82990 | 4.49793 |

| | | | | | |
|---|---|---|---|---|---|
| 1 | 36.495 | PB | 0.106 | 999.49780 | 4.42769 |

**(3) GC analysis of the reaction mixture using bulk tin oxide (BSnO) as catalyst.**

| | |
|---|---|
| Sample name: | Benzaldehyde-EAA-BSnO-$CHCl_3$ |
| Sample note: | Benzaldehyde-EAA-BSnO-$CHCl_3$ |
| Submission time: | Monday, February 04, 2013 12:55:17 PM |
| Injection date: | Monday, February 04, 2013 2:56:43 PM |
| GC Description: | Gas Chromatograph |
| Signal description: | OOS1 A, B |
| Method: | 80-4-5-250 |

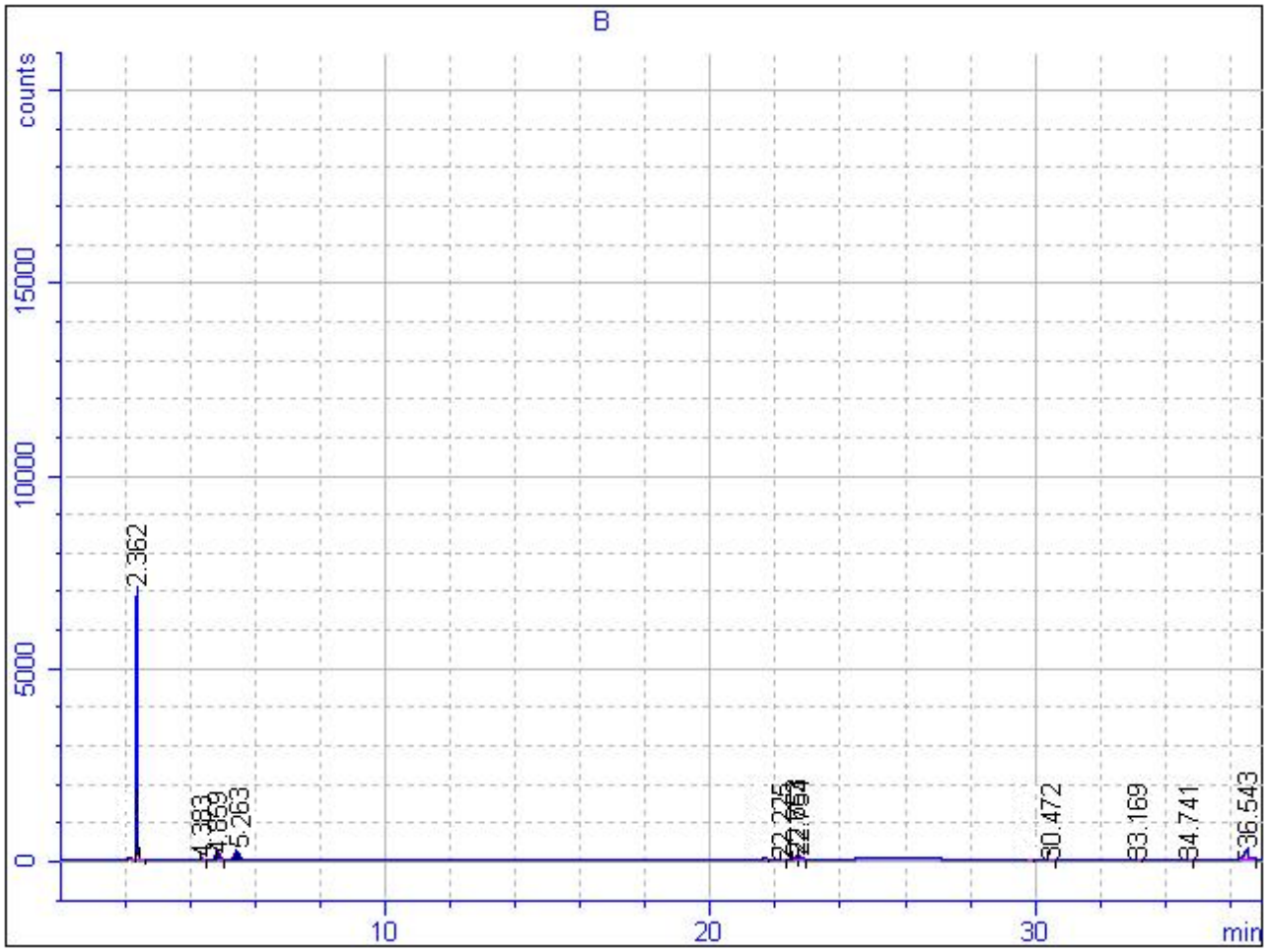


| | |
|---|---|
| Multiplier: | 1.0000 |
| Dilution: | 1.0000 |
| Sample amount: | 0.0000 Microlitres |
| Sample type: | Sample |
| Sampling source: | Manual |

| Signal | Retention Time [min] | Type | Width [min] | Area [counts*s] | Area % |
|---|---|---|---|---|---|
| 1 | 2.351 | VB | 0.023 | 15437.70781 | 72.77116 |
| 1 | 4.862 | BB | 0.051 | 1272.76064 | 5.99686 |
| 1 | 5.252 | PB | 0.092 | 1360.80423 | 6.41322 |
| 1 | 22.764 | PV | 0.088 | 586.45337 | 2.76647 |
| 1 | 22.835 | VB | 0.050 | 735.07140 | 3.46500 |
| 1 | 36.568 | PB | 0.127 | 1821.43479 | 8.58729 |

**(4) GC analysis of the reaction mixture at catalyst free condition.**

| | |
|---|---|
| Sample name: | Benzaldehyde-EAA-CF-$CHCl_3$ |
| Sample note: | Benzaldehyde-EAA-CF-$CHCl_3$ |
| Submission time: | Monday, February 04, 2013 12:55:49 PM |
| Injection date: | Monday, February 04, 2013 3:38:55 PM |
| GC Description: | Gas Chromatograph |
| Signal description: | OOS1 A, B |
| Method: | 80-4-5-250 |



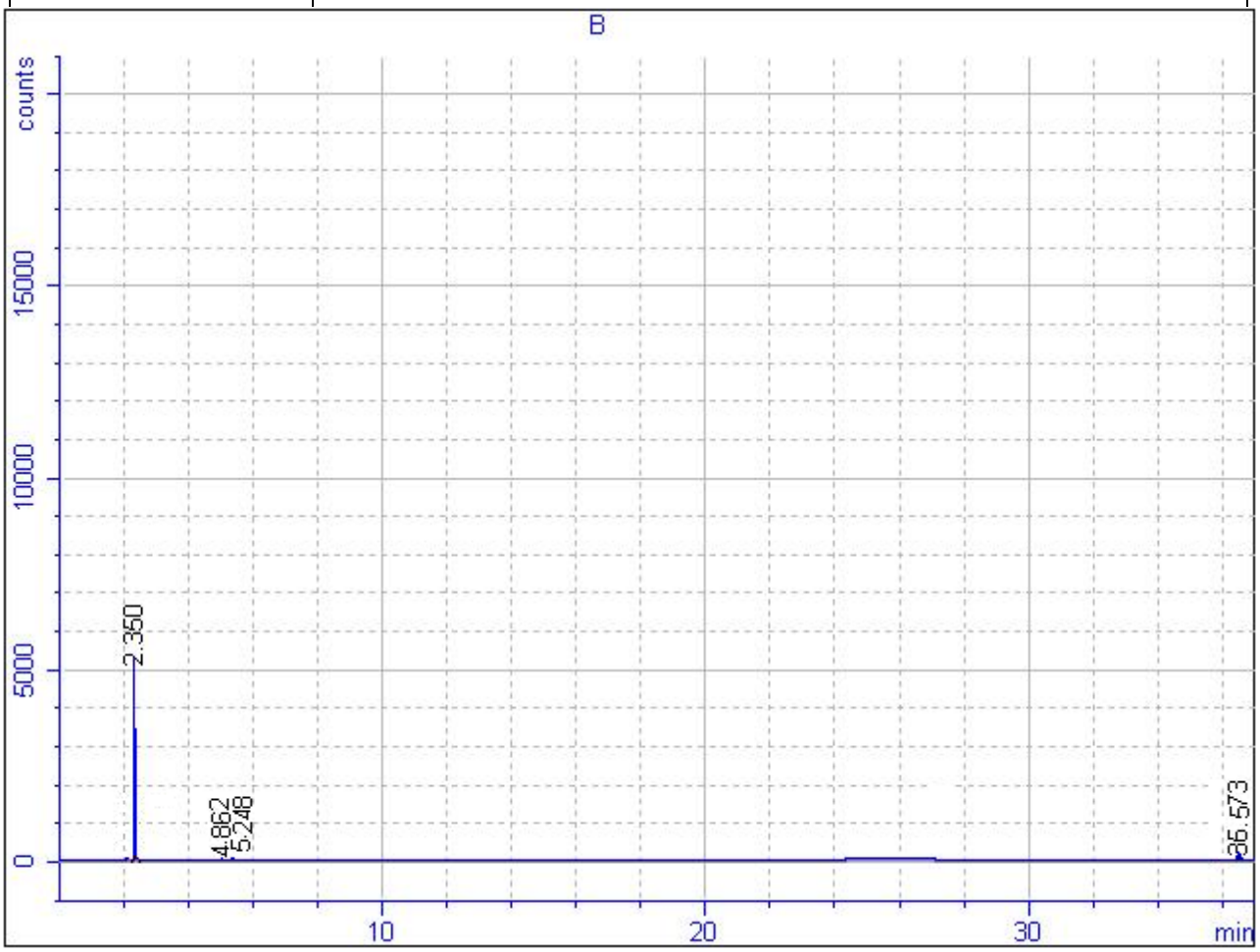

| | |
|---|---|
| Multiplier: | 1.0000 |
| Dilution: | 1.0000 |
| Sample amount: | 0.0000 Microlitres |
| Sample type: | Sample |
| Sampling source: | Manual |

| Signal | Retention Time [min] | Type | Width [min] | Area [counts*s] | Area % |
|---|---|---|---|---|---|
| 1 | 2.362 | VB | 0.032 | 16243.20478 | 79.75476 |
| 1 | 4.383 | PB | 0.044 | 118.75617 | 0.58307 |
| 1 | 4.859 | BB | 0.050 | 1432.32454 | 7.03425 |
| 1 | 5.263 | PB | 0.076 | 1031.74871 | 5.06571 |
| 1 | 22.225 | PB | 0.064 | 21.91495 | 0.10760 |

| | | | | | |
|---|---|---|---|---|---|
| 1 | 22.653 | PV | 0.083 | 475.14483 | 2.33287 |
| 1 | 22.754 | VB | 0.062 | 493.73241 | 2.42413 |
| 1 | 30.472 | PP | 0.074 | 23.17498 | 0.11378 |
| 1 | 33.169 | PP | 0.059 | 11.71430 | 0.05751 |
| 1 | 34.741 | PB | 0.059 | 21.74181 | 0.10675 |
| 1 | 36.543 | PB | 0.114 | 492.54448 | 2.41958 |

**(5) GC analysis of the reaction mixture using HSnP-2 as catalyst.**

| | |
|---|---|
| Sample name: | Benzaldehyde-EAA-HSnP-2-$CHCl_3$ |
| Sample note: | Benzaldehyde-EAA-HSnP-2-$CHCl_3$ |
| Submission time: | Monday, February 04, 2013 12:56:18 PM |
| Injection date: | Monday, February 04, 2013 4:20:12 PM |
| GC Description: | Gas Chromatograph |
| Signal description: | OOS1 A, B |
| Method: | 80-4-5-250 |



| | |
|---|---|
| Multiplier: | 1.0000 |
| Dilution: | 1.0000 |
| Sample amount: | 0.0000 Microlitres |
| Sample type: | Sample |
| Sampling source: | Manual |

| Signal | Retention Time [min] | Type | Width [min] | Area [counts*s] | Area % |
|---|---|---|---|---|---|
| 1 | 2.350 | PB | 0.019 | 6949.34333 | 95.29616 |
| 1 | 4.826 | BB | 0.074 | 4.12851 | 0.05661 |
| 1 | 5.248 | PB | 0.064 | 4.62431 | 0.06341 |
| 1 | 36.573 | BB | 0.082 | 161.64915 | 2.21661 |