Electronic Supplementary Material (ESI) for Chemical Communications

TBAI-Catalyzed oxidative coupling of aminopyridines with β-keto esters and 1,3-diones—Synthesis of imidazo[1,2-*a*]pyridines

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The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz spectrometer with TMS as the internal standard in $CDCl_3$. The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out with silica gel (300-350 mesh).

1. Optimization of the reaction conditions

Table 1 Screening of the conditions for the TBAI-catalyzed reaction between **1a** and **2a** [a]

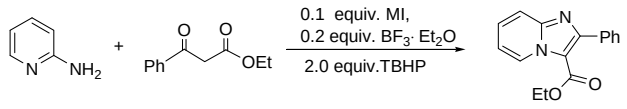
Entry	**1a**/**2a**	Equiv. of TBAI	Oxidant	Acid (equiv.)	Solvent	Reaction temp. (°C)	Reaction time (hrs)	Yield (%) [b]
1	1:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	50	16	17
2	1:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	DMF	50	16	39
3	1:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	DCE	50	16	8
4	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	DCE	50	16	5
5	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	50	16	17

6	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	DMF	50	16	31
7	1:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	16	47
8	1:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	DMF	80	16	21
9	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	16	53
10	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	DMF	80	16	42
11	1:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	EtOAc	80	16	35
12	1:1	0	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	16	0
13	1:1.5	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	12	30
14	**1.5:1**	**0.1**	**TBHP**	**$BF_3{\cdot}Et_2O$ (0.2)**	**CH_3CN**	**80**	**12**	**81**
15	1.5:1	0.1	TBHP	none	CH_3CN	80	12	48
16	1.5:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (1.0)	CH_3CN	80	12	44
17	1.5:1	1.0	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	16	10
18	1.5:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	DMF	80	12	58
19	1.5:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	EtOAc	80	12	41
20	1.5:1	0.1	TBHP	$BF_3{\cdot}Et_2O$ (0.2)	DCE	80	30	68
21	1.5:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	CH_3CN	80	35	64
22	1.5:1	0.1	30% H_2O_2	$BF_3{\cdot}Et_2O$ (0.2)	DMF	80	12	33
23	1.5:1	0.1	TBHP	CF_3OOH (0.2)	CH_3CN	80	12	51
24	1.5:1	0.1	TBHP	$BiCl_3$ (0.2)	CH_3CN	80	12	28
25	1.5:1	0.1	TBHP	$InCl_3$ (0.2)	CH_3CN	80	12	26

[a] The reaction was performed with 2 equiv. of oxidant; 5 mL solvent was used. [b] Isolated yield based on the

compound used in fewer amount.

Table 2 The reaction of **1a** and **2a** with NaI or KI as the catalyst [a]



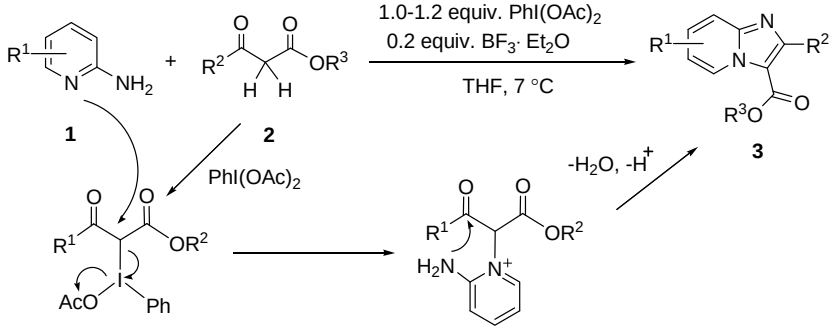
1a **2a** **3a**

Entry	MI	**1a**/**2a**	Solvent	Reaction time (hours)	Conversion (%) [b]	Yield of **3a** (%) [b]
1	NaI	1.0	CH_3CN	16	86	55
2	NaI	1.5	CH_3CN	12	100	73
3	NaI	1.5	DMF	12	100	62
4	NaI	1.5	EtOAc	12	62	38
5	KI	1.0	CH_3CN	16	95	55
6	KI	1.5	CH_3CN	12	96	66
7	KI	1.5	DMF	12	98	46
8	KI	1.5	EtOAc	12	46	23

[a] The reaction was carried out at 80 °C. [b] Based on **2a**.

2. Mechanistic discussions

We have demonstrated that the direct oxidative coupling of 2-aminopyridines (**1**) with 1,3-dicarbonyl compounds (**2**) can be effected by using $PhI(OAc)_2$ as oxidant and $BF_3{\cdot}Et_2O$ as catalyst. The reaction is believed to proceed following the mechanism depicted in Scheme 1.[1] To see if the current TBAI-catalyzed reaction follows a similar reaction pathway (Scheme 2), control experiments were conducted, and the results are listed in Table 3.



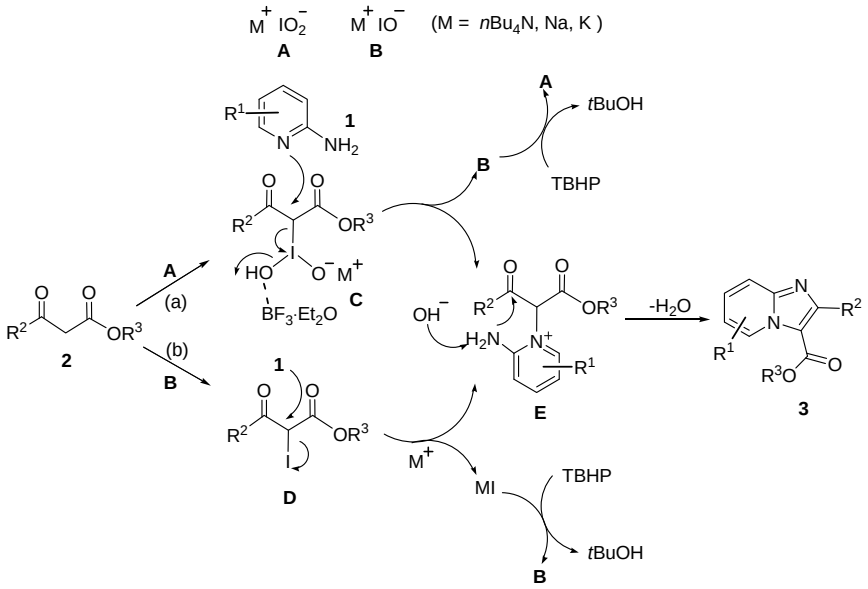
Scheme 1

Table 3 The reaction of **1a** and **2a** under various conditions[a]

Entry	Reagent(s) (equiv.)	Equiv. of $BF_3{\cdot}Et_2O$	Reaction time (hours)	Conversion (%)	Yield of **3a** (%) [b]
1	$NaIO_4$ (1.0)	0.2	16	87 %	63
2	$NaIO_4$ (1.0)	0.2	14	no reaction [c]	--
3	$NaIO_4$ (0.25)	0.2	14	19	16
4	$NaIO_4$ (0.25), TBAI (0.1)	0.2	14	42	32
5	I_2 (1.0)	0.2	16	25	17
6	I_2 (1.0), Bu_4NOH (2.0)	0.2	16	complex mixtures	3
7	NIS (1.0)	0.2	16	51	28
8	Bu_4NBr (0.1), TBHP (2.0)	none	16	no reaction	--
9	Bu_4NBr (0.1), TBHP (2.0)	0.2	16	20	13

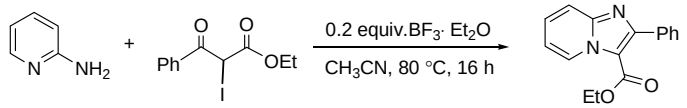
[a] The reaction was performed with 1 mmol of **1a** and **2a** in acetonitrile at 80 °C unless otherwise specified. [b] Isolated yield. [c] The reaction was performed at room temperature.

As shown in Table 3, the reaction took place at 80 °C when $NaIO_4$ was used as the oxidant (Table 3, entries 1 and 3). The reaction was promoted by TBAI (Table 3, entry 4). These results are consistent with those obtained by Ishihara et al.,[2] suggesting that iodine species (+1 or +3) possibly act as the active oxidizing species. Based on these results and the works of Ishihara et al,[2] a mechanism is proposed as shown in Scheme 2.



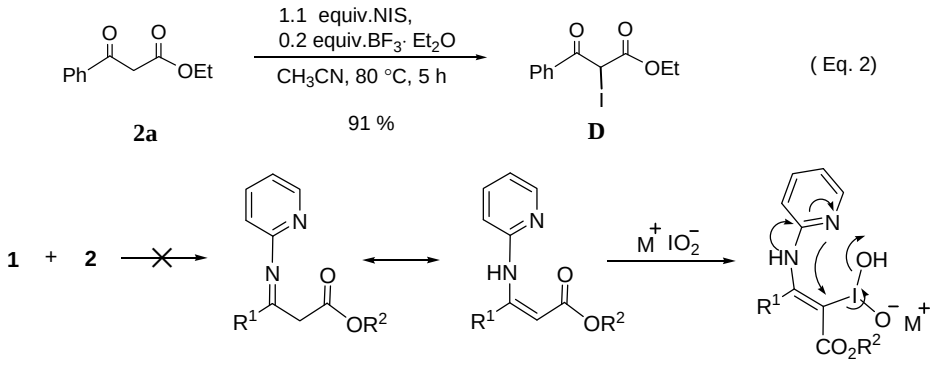
Scheme 2

While both path a and b are possible for the formation of **3** from **1** and **2**, further experiments showed that the reaction of **1a** with ethyl 2-iodo-3-oxo-3-phenylpropanoate (**D**) only afforded **3a** in low yield (Eq. 1). Besides, we did not obtain **D** when **2a** was treated with 1.0 equiv. of TBAI, 1.5 equiv. of TBHP and 0.2 equiv. of $BF_3{\cdot}Et_2O$. Therefore, Path b shown in Scheme 1 seems less likely the working mechanism.



1a **D** 27 % **3a**

3a was also generated when 1.0 equiv. of I_2 or NIS was used (Table 3, entries 5 and 7). But the yield was much lower than that of using TBAI/TBHP. We believe that the function of NIS or I_2 in the reaction is to react with **2a** to generate *in situ* compound **D**, which then react with **1** to afford **E** (Scheme 2, path b). This assumption is supported by the control experiment (Eq. 2). Another alternative mechanism, which involves firstly the condensation between **1** and **2**, and then the oxidation of thus formed enamine ester, can be ruled out because the condensation of **1a** and **2a** can not take place in refluxing acetonitrile (Scheme 3)



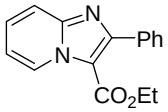
Scheme 3

Recently, Nagano et al reported that bromide ion could catalyze the α-acetoxylation of ketones.[3] As a comparison, we examined the catalytic behavior of tetrabutyl ammonium iodide (TBAB) in the present reaction. Our results (Table 3, entries 8 and 9) show that the performance of TBAB is poor compared with TBAI.

General procedure for the synthesis of substituted imidazo[1,2-*a*]pyridines (3) from 2-aminopyridines (1) and β-keto esters and acetylacetone (2)

A mixture of 1.0 mmol of **2**, 1.5 mmol of **1**, 0.1 mmol of TBAI, 2.0 mmol of TBHP (70% in water) and 26 μL of $BF_3 \cdot Et_2O$ (0.2 mmol) in 5 mL of CH_3CN was stirred in a 15 mL Pyrex screw-cap pressure tube at 80 °C for the indicated period of time shown in Table 2 of the manuscript. After the reaction finished as indicated by TLC, the reaction mixture was cooled to the room temperature, and then poured into 15 mL saturated Na_2SO_3 solution. The product was extracted with EtOAc (20 mL×3). The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residual was treated with silica gel chromatography to give product **3**. For the synthesis of **3x** and **3y**, 1.0 mmol of **1** and 1.1 mmol of **2** were used for the convenience of product purification.

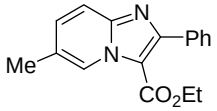
Spectroscopic data for the products 3[1]



Ethyl 2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3a)

White solid, mp: 66-67 °C

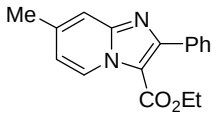
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.21 (t, 3H, J = 7.2 Hz), 4.30 (q, 2H, J = 7.2 Hz), 7.02 (t, 1H, J = 6.8 Hz), 7.40-7.45 (m, 4H), 7.72-7.78 (m, 3H), 9.41 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 60.4, 111.8, 114.0, 117.4, 127.5, 127.8, 128.2, 128.6, 130.1, 134.4, 147.0, 153.5, 161.0; EI-MS *m*/*z* (rel. int., %): 266 (M^+, 63), 194 (100), 78 (11).



Ethyl 6-methyl-2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3b)

White solid, mp: 72-74 °C

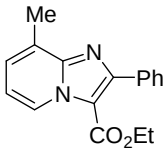
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.21 (t, 3H, J = 7.2 Hz), 2.42 (s, 3H), 4.30 (q, 2H, J = 7.2 Hz), 7.29 (dd, 1H, J = 9.2 Hz, J = 1.6 Hz), 7.40-7.45 (m, 3H), 7.64 (d, 1H, J = 8.8 Hz), 7.74-7.76 (m, 2H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 18.5, 60.4, 111.6, 116.6, 124.1, 126.1, 127.5, 128.6, 130.1, 131.0, 134.3, 146.0, 153.2, 161.2; EI-MS *m*/*z* (rel. int., %): 280 (M^+, 51), 208 (100).



Ethyl 7-methyl-2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3c)

White solid, mp: 90-91 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.21 (t, 3H, J = 7.2 Hz), 2.46 (s, 3H), 4.29 (q, 2H, J = 7.2 Hz), 6.86 (dd, 1H, J = 6.8 Hz, J = 1.6 Hz), 7.40-7.44 (m, 3H), 7.48 (s, 1H), 7.75-7.77 (m, 2H), 9.27 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 21.3, 60.2, 111.4, 116.0, 116.5, 127.3, 127.4, 128.5, 130.1, 134.5, 139.2, 147.5, 153.6, 161.1; EI-MS *m*/*z* (rel. int., %): 280 (M^+, 54), 208 (100); HRMS (ESI): calcd for C_{17} H_{16} N_2O_2 + H = 281.1285, found: 281.1282.

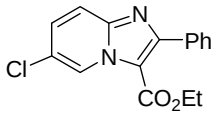


Ethyl 8-methyl-2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3d)

White solid, mp: 113-114 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.19 (t, 3H, J = 7.2 Hz), 2.68 (s, 3H), 4.28 (q,

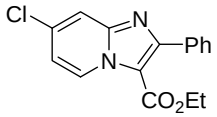
2H, *J* = 7.2 Hz), 6.94 (t, 1H, *J* = 7.0 Hz), 7.22 (dd, 1H, *J* = 6.8 Hz, *J* = 1.2 Hz) 7.40-7.45 (m, 3H), 7.74-7.76 (m, 2H), 9.27 (d, 1H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 17.1, 60.3, 112.3, 114.0, 126.0. 126.7, 127.4, 127.5, 128.4, 130.2, 134.9, 147.3, 153.2, 161.2; EI-MS *m*/*z* (rel. int., %): 280 (M^+, 53), 208 (100); HRMS (ESI): calcd for $C_{17}H_{16}N_2O_2$ + H = 281.1285, found: 281.1286.



Ethyl 6-chloro-2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3e)

White solid, mp: 117-119 °C

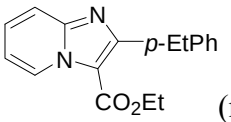
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.23 (t, 3H, *J* = 7.2 Hz), 4.32 (q, 2H, *J* = 7.2 Hz), 7.40-7.46 (m, 4H), 7.68 (d, 1H, *J* = 9.2 Hz), 7.74-7.76 (m, 2H), 9.52 (d, 1H, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 60.7, 112.3, 117.7, 122.4, 126.3, 127.6, 128.9, 129.2, 130.1, 134.0, 145.3, 154.0, 160.9; EI-MS *m*/*z* (rel. int., %): 302 (17), 300 (M^+, 54), 230 (28), 228 (100), 174 (42), 159 (66), 149 (36).



Ethyl 7-chlorol-2-phenylimidazo[1,2-*a*]pyridine-3-carboxylate (3f)

White solid, mp: 116-118 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.22 (t, 3H, *J* = 7.2 Hz), 4.31 (q, 2H, *J* = 7.2 Hz), 7.02 (d, 1H, *J* = 7.6 Hz), 7.43-7.47 (m, 3H), 7.72-7.76 (m, 3H), 9.36 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 60.6, 112.0, 115.5, 116.4, 127.6, 128.6, 128.9, 130.1, 133.9, 134.5, 146.9, 154.2, 160.8; EI-MS *m*/*z* (rel. int., %): 302 (20), 300 (M^+, 50), 230 (32), 228 (100), 149 (42), 57 (35); HRMS (ESI): calcd for $C_{16}H_{13}ClN_2O_2$ + H = 301.0738, found: 301.0736.



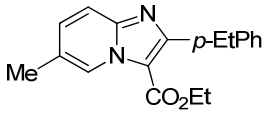
(new compound)

Ethyl 2-(4-ethyl-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3g)

White solid, mp: 48-49 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.25 (t, 3H, *J* = 7.2 Hz), 1.28 (t, 3H, *J* = 7.6 Hz), 2.72 (q, 2H, *J* = 7.6 Hz), 4.32 (q, 2H, *J* = 7.2 Hz), 7.01 (t, 1H, *J* = 6.8 Hz), 7.27 (d,

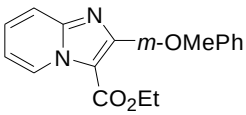
2H, J = 8.0 Hz), 7.41 (ddd, 1H, J = 8.8 Hz, J = 6.8 Hz, J = 0.8 Hz), 7.70-7.73 (m, 3H), 9.40 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.0, 15.5, 28.7, 60.3, 111.8, 113.9, 117.4, 127.0, 127.7, 128.3, 130.1, 131.7, 144.9, 147.0, 153.7, 161.2; EI-MS *m*/*z* (rel. int., %): 294 (M^+, 77), 222 (100), 207 (55); HRMS (ESI): calcd for $C_{18}H_{18}N_2O_2$ + H = 295.1441, found: 295.1450.



Ethyl 6-methyl-2-(4-ethyl-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3h)

White solid, mp: 60-62 °C

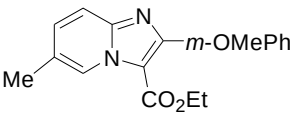
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.24 (t, 3H, J = 7.2 Hz), 1.27 (t, 3H, J = 7.6 Hz), 2.41 (s, 3H), 2.71 (q, 2H, J = 7.6 Hz), 4.31 (q, 2H, J = 7.2 Hz), 7.26 (d, 3H, J = 8.4 Hz), 7.62 (d, 1H, J = 8.8 Hz), 7.69 (d, 2H, J = 8.0 Hz), 9.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.0, 15.5, 18.4, 28.7, 60.2, 111.4, 116.6, 123.7, 126.2, 127.0, 130.1, 130.7, 131.8, 144.7, 146.1, 153.5, 161.3; EI-MS *m*/*z* (rel. int., %) 308 (M^+, 71), 236 (100), 221 (47); HRMS (ESI): calcd for $C_{19}H_{20}N_2O_2$ + H = 309.1598, found: 309.1591.



Ethyl 2-(3-methoxyl-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3i)[4]

White solid, mp: 70-71 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.22 (t, 3H, J = 7.2 Hz), 3.85 (s, 3H), 4.30 (q, 2H, J = 7.2 Hz), 6.95-6.98 (m, 1H), 7.01 (t, 1H, J = 6.8 Hz), 7.32-7.35 (m, 3H), 7.41 (dd, 1H, J = 8.6 Hz, J = 7.4 Hz), 7.72 (d, 1H, J = 9.2 Hz), 9.40 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 55.2, 60.3, 111.9, 114.0, 114.6, 115.4, 117.4, 122.7, 127.8, 128.2, 128.4, 135.7, 146.9, 153.3, 158.9, 161.0; EI-MS *m*/*z* (rel. int., %): 296 (M^+, 100), 267 (34), 224 (70), 223 (62), 194 (40).

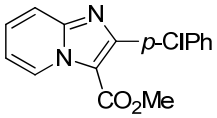


(new compound)

White solid, mp: 93-94 °C

Ethyl 6-methyl-2-(3-methoxyl-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3j)

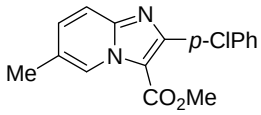
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.22 (t, 3H, *J* = 7.2 Hz), 2.41 (s, 3H), 3.86 (s, 3H), 4.30 (q, 2H, *J* = 7.2 Hz), 6.95-6.99 (m, 1H), 7.27 (dd, 1H, *J* = 9.2 Hz, *J* = 1.6 Hz), 7.31-7.34 (m, 3H), 7.62 (d, 1H, *J* = 9.2 Hz), 9.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 13.9, 18.4, 55.2, 60.2, 111.6, 114.5, 115.3, 116.6, 122.7, 123.9, 126.1, 128.4, 130.7, 135.9, 146.0, 153.1, 158.9, 161.1; EI-MS *m*/*z* (rel. int., %): 310 (M^+, 100), 281 (33), 238 (85), 237 (70), 208 (40); HRMS (ESI): calcd for $C_{18}H_{18}N_2O_3$ + H = 311.1390, found: 311.1401.



Methyl 2-(4-chloro-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3k)

White solid, mp: 130-132°C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 3.81 (s, 3H), 7.02 (dt, 1H, *J* = 6.8 Hz, *J* = 1.2 Hz), 7.39-7.44 (m, 3H), 7.70 (d, 3H, *J* = 8.4 Hz), 9.37 (dd, 1H, *J* = 6.8 Hz, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 51.2, 111.6, 114.2, 117.4, 127.8, 128.1, 128.3, 131.3, 132.8, 134.7, 147.1, 152.3, 161.1; EI-MS *m*/*z* (rel. int., %): 288 (37), 286 (M^+, 100), 273 (17), 271 (60), 242 (18), 240 (42), 230 (23), 228 (73), 149 (59); HRMS (ESI): calcd for $C_{15}H_{11}ClN_2O_2$ + H = 287.0582, found: 287.0579.

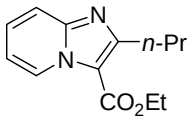


(new compound)

White solid, mp: 153-154 °C

Methyl 6-methyl-2-(4-chloro-phenyl)imidazo[1,2-*a*]pyridine-3-carboxylate (3l)

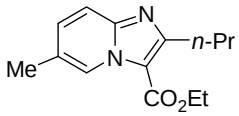
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.42 (s, 3H), 3.82 (s, 3H), 7.30 (dd, 1H, *J* = 9.2 Hz, *J* = 1.6 Hz,), 7.39-7.43 (m, 2H), 7.62 (d, 1H, *J* = 9.2 Hz), 7.68-7.72 (m, 2H), 9.20 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 18.5, 51.2, 111.4, 116.7, 124.2, 126.2, 127.9, 131.1, 131.4, 133.1, 134.7, 146.2, 152.2, 161.4; EI-MS *m*/*z* (rel. int., %): 302 (35), 300 (M^+, 100), 287 (17), 285 (40), 244 (23), 242 (79), 179 (37), 57 (32); HRMS (ESI): calcd for $C_{16}H_{13}ClN_2O_2$ + H = 301.0738, found: 301.0746.



Ethyl 2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3m)

White solid, mp: 24-26 °C

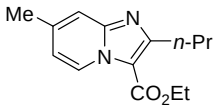
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.00 (t, 3H, *J* = 7.2 Hz), 1.42 (t, 3H, *J* = 7.0 Hz), 1.75-1.84 (m, 2H), 3.06 (t, 2H, *J* = 7.6 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 6.95 (t, 1H, *J* = 6.8 Hz), 7.35 (t, 1H, *J* = 8.4 Hz), 7.62 (d, 1H, *J* = 9.2 Hz), 9.31 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.1, 14.3, 22.9, 32.2, 60.2, 112.2, 113.5, 116.8, 127.4, 128.0, 146.9, 156.9. 161.4; EI-MS *m*/*z* (rel. int., %): 232 (M^+, 21), 204 (67), 132 (100), 78 (20); HRMS (ESI): calcd for $C_{13}H_{16}N_2O_2$ + H = 233.1285, found: 233.1280.



Ethyl 6-methyl-2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3n)

Pale yellow solid, mp: 31-33 °C

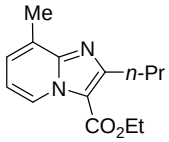
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.01 (t, 3H, *J* = 7.2 Hz), 1.44 (t, 3H, *J* = 7.0 Hz), 1.74-1.84 (m, 2H), 2.38 (s, 3H), 3.05 (t, 2H, *J* = 7.6 Hz), 4.42 (q, 2H, *J* = 7.2 Hz), 7.23 (dd, 1H, *J* = 9.2 Hz, *J* = 1.6 Hz), 7.54 (d, 1H, *J* = 9.2 Hz), 9.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.1, 14.4, 18.4, 22.9, 32.2, 60.1, 111.9, 116.0, 123.4, 126.0, 130.4, 145.9, 156.6, 161.5; EI-MS *m*/*z* (rel. int., %): 246 (M^+, 20), 218 (61), 146 (100), 92 (14); HRMS (ESI): calcd for $C_{14}H_{18}N_2O_2$ + H = 247.1441, found: 247.1449.



Ethyl 7-methyl-2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3o)

White solid, mp: 52-54 °C

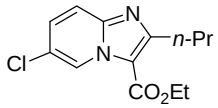
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 0.94 (t, 3H, *J* = 7.2 Hz), 1.36 (t, 3H, *J* = 7.2 Hz), 1.68-1.77 (m, 2H), 2.34 (s, 3H), 2.98 (t, 2H, *J* = 7.8 Hz), 4.34 (q, 2H, *J* = 7.2 Hz), 6.70 (d, 1H, *J* = 7.2 Hz), 7.30 (s, 1H), 9.09 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.0, 14.2, 21.1, 22.8, 32.0, 59.9, 111.6, 115.3, 115.8, 127.0, 138.6, 147.2, 156.8, 161.2; EI-MS *m*/*z* (rel. int., %): 246 (M^+, 21), 218 (61), 146 (100), 92 (16); HRMS (ESI): calcd for $C_{14}H_{18}N_2O_2$ + H = 247.1441, found: 247.1436.



Ethyl 8-methyl-2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3p)

White solid, mp: 60-62 °C

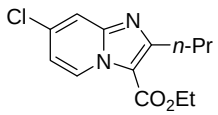
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.03 (t, 3H, J = 7.2 Hz), 1.44 (t, 3H, J = 7.2 Hz), 1.74-1.83 (m, 2H), 2.64 (s, 3H), 3.09 (t, 2H, J = 7.8 Hz), 4.42 (q, 2H, J = 7.2 Hz), 6.88 (t, 1H, J = 6.8 Hz), 7.17 (d, 1H, J = 6.8 Hz), 9.20 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.2, 14.4, 17.1, 23.5, 32.4, 60.1, 112.5, 113.5, 125.8, 126.5, 126.6, 147.2, 156.5, 161.6; EI-MS m/z (rel. int., %): 246 (M^+, 19), 218 (60), 146 (100), 92 (15); HRMS (ESI): calcd for $C_{14}H_{18}N_2O_2$ + H = 247.1441, found: 247.1446.



Ethyl 6-chloro-2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3q)

Orange solid, mp: 91-93 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.00 (t, 3H, J = 7.2 Hz), 1.44 (t, 3H, J = 7.2 Hz), 1.76-1.81 (m, 2H), 3.05 (t, 2H, J = 7.8 Hz), 4.43 (q, 2H, J = 7.2 Hz), 7.33 (dd, 1H, J = 9.2 Hz, J = 2.0 Hz), 7.56 (dd, 1H, J = 9.2 Hz, J = 2.4 Hz), 9.41 (d, 1H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 14.1, 14.3, 22.8, 32.1, 60.5, 112.7, 117.0, 121.8, 126.0, 128.7, 145.2, 157.3, 161.2; EI-MS m/z (rel. int., %): 268 (6), 266 (M^+, 17), 240 (21), 238 (72), 168 (32), 166 (100); HRMS (ESI): calcd for $C_{13}H_{15}ClN_2O_2$ + H = 267.0895, found: 267.0900.

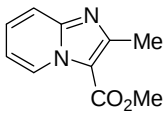


Ethyl 7-chloro-2-propylimidazo[1,2-*a*]pyridine-3-carboxylate (3r)

White solid, mp: 61-63 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.00 (t, 3H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.0 Hz), 1.73-1.82 (m, 2H), 3.04 (t, 2H, J = 7.8 Hz), 4.41 (q, 2H, J = 7.2 Hz), 6.94 (dd, 1H, J = 7.2 Hz, J = 2.0 Hz), 7.60 (d, 1H, J = 2.0 Hz), 9.25 (d, 1H, J = 7.2 Hz); ^{13}C NMR

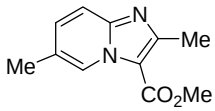
($CDCl_3$, 100 MHz, δ ppm): 14.1, 14.3, 22.8, 32.1, 60.4, 112.4, 114.9, 115.8, 128.2, 134.1, 146.8, 157.6, 161.2; EI-MS *m*/*z* (rel. int., %): 268 (6), 266 (M^+, 19), 240 (22), 238 (69), 168(33), 166 (100); HRMS (ESI): calcd for $C_{13}H_{15}ClN_2O_2$ + H = 267.0895, found: 267.0893.



Methyl 2-methylimidazo[1,2-*a*]pyridine-3-carboxylate (3s)

Pale yellow solid, mp: 103-105 °C

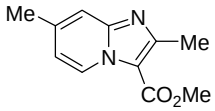
^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.72 (s, 3H), 3.97 (s, 3H), 6.99 (t, 1H, *J* = 6.8 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 7.63 (d, 1H, *J* = 9.2 Hz), 9.31 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 16.5, 51.3, 112.4, 113.7, 116.6, 127.7, 127.9, 146.9, 152.8, 161.8; EI-MS *m*/*z* (rel. int., %): 190 (M^+, 100), 159 (83), 132 (68), 131 (24), 90 (28); HRMS (ESI): calcd for $C_{10}H_{10}N_2O_2$ + H = 191.0815, found: 191.0817.



Methyl 2,6-dimethylimidazo[1,2-*a*]pyridine-3-carboxylate (3t)

Pale yellow solid, mp: 47-49 °C

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.37 (s, 3H), 2.67 (s, 3H), 3.94 (s, 3H), 7.21 (d, 1H, *J* = 8.8 Hz), 7.49 (d, 1H, *J* = 8.8 Hz), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 16.6, 18.3, 51.2, 112.1, 115.8, 123.4, 125.9, 130.5, 145.9, 152.6, 161.9; EI-MS *m*/*z* (rel. int., %): 204 (M^+, 100), 173 (73), 146 (68), 145 (21), 104 (13); HRMS (ESI): calcd for $C_{11}H_{12}N_2O_2$ + H = 205.0972, found: 205.0974.

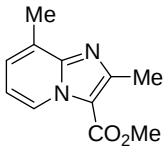


Methyl 2,7-dimethylimidazo[1,2-*a*]pyridine-3-carboxylate (3u)

White solid, mp: 36-38 °C

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.40 (s, 3H), 2.65 (s, 3H), 3.92 (s, 3H), 6.77 (dd, 1H, *J* = 6.8 Hz, *J* = 1.2 Hz), 7.32 (s, 1H), 9.11 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 16.5, 21.3, 51.1, 111.9, 115.3, 116.0, 127.0, 139.0, 147.3, 152.9, 161.8; EI-MS *m*/*z* (rel. int., %): 204 (M^+, 100), 173 (71), 146 (76), 145 (33), 104 (13);

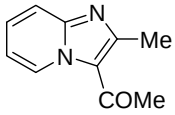
HRMS (ESI): calcd for $C_{11}H_{12}N_2O_2$ + H = 205.0972, found: 205.0979.



Methyl 2,8-dimethylimidazo[1,2-*a*]pyridine-3-carboxylate (3v)

White solid, mp: 99-100 °C

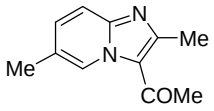
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.62 (s, 3H), 2.72 (s, 3H), 3.95 (s, 3H), 6.87 (t, 1H, *J* = 7.0 Hz), 7.16 (d, 1H, *J* = 6.8 Hz), 9.15 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 16.5, 17.0, 51.2, 112.8, 113.6, 125.7, 126.4, 126.8, 147.0, 152.1, 161.9; EI-MS *m*/*z* (rel. int., %): 204 (M^+, 100), 173 (65), 146 (65), 145 (20); HRMS (ESI): calcd for $C_{11}H_{12}N_2O_2$ + H = 205.0972, found: 205.0976.



1-(2-Methyl*H*-imidazo[1,2-*a*]pyridin-3-yl)ethanone (3w)

White solid, mp: 105-106 °C

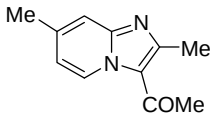
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.55 (s, 3H), 2.72 (s, 3H), 6.94 (t, 1H, *J* = 7.2 Hz), 7.38 (t, 1H, *J* = 7.6 Hz), 7.56 (d, 1H, *J* = 8.0 Hz), 9.65 (dd, 1H, *J* = 7.2 Hz, *J* = 0.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 18.2, 30.1, 114.3. 116.2, 121.6, 128.8, 128.9, 146.7, 152.6, 187.4; EI-MS *m*/*z* (rel. int., %): 174 (M^+, 69), 159 (100), 131 (17), 90 (33).



1-(2,6-Dimethyl*H*-imidazo[1,2-*a*]pyridin-3-yl)ethanone (3x)

Pale yellow solid, mp: 101-103 °C

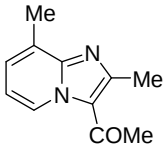
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.40 (s, 3H), 2.61 (s, 3H), 2.78 (s, 3H), 7.31 (d, 1H, *J* = 9.2 Hz), 7.53 (d, 1H, *J* = 9.2 Hz), 9.55 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 18.3, 30.2, 115.5, 121.6, 124.3, 127.0, 131.8, 145.7, 152.5, 187.5; EI-MS *m*/*z* (rel. int., %): 188 (M^+, 55), 173 (100), 104 (14); HRMS (ESI): calcd for $C_{11}H_{12}N_2O_1$ + H = 189.1022, found: 189.1026.



1-(2,7-Dimethyl*H*-imidazo[1,2-*a*]pyridin-3-yl)ethanone (3y)

White solid, mp: 137-138 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.43 (s, 3H), 2.57 (s, 3H), 2.74 (s, 3H), 6.82 (dd, 1H, J = 6.8 Hz, J = 1.2 Hz), 7.36 (s, 1H), 9.56 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 18.3, 21.4, 30.0, 115.1, 116.8, 121.5, 128.2, 140.6, 147.2, 152.9, 187.2; EI-MS *m*/*z* (rel. int., %): 188 (M^+, 67), 173 (100), 145 (17); HRMS (ESI): calcd for $C_{11}H_{12}N_2O_1$ + H = 189.1022, found: 189.1026.



1-(2,8-Dimethyl*H*-imidazo[1,2-*a*]pyridin-3-yl)ethanone (3z)

White solid, mp: 156-157 °C

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.60 (s, 3H), 2.62 (s, 3H), 2.79 (s, 3H), 6.90 (t, 1H, J = 7.2 Hz), 7.23 (d, 1H, J = 7.2 Hz), 9.58 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 16.9, 18.4, 30.3, 114.4, 122.1, 126.1, 126.8, 128.1, 146.9, 152.1, 187.6; EI-MS *m*/*z* (rel. int., %): 188 (M^+, 63), 173 (100), 104 (13); HRMS (ESI): calcd for $C_{11}H_{12}N_2O_1$ + H = 189.1022, found: 189.1024.

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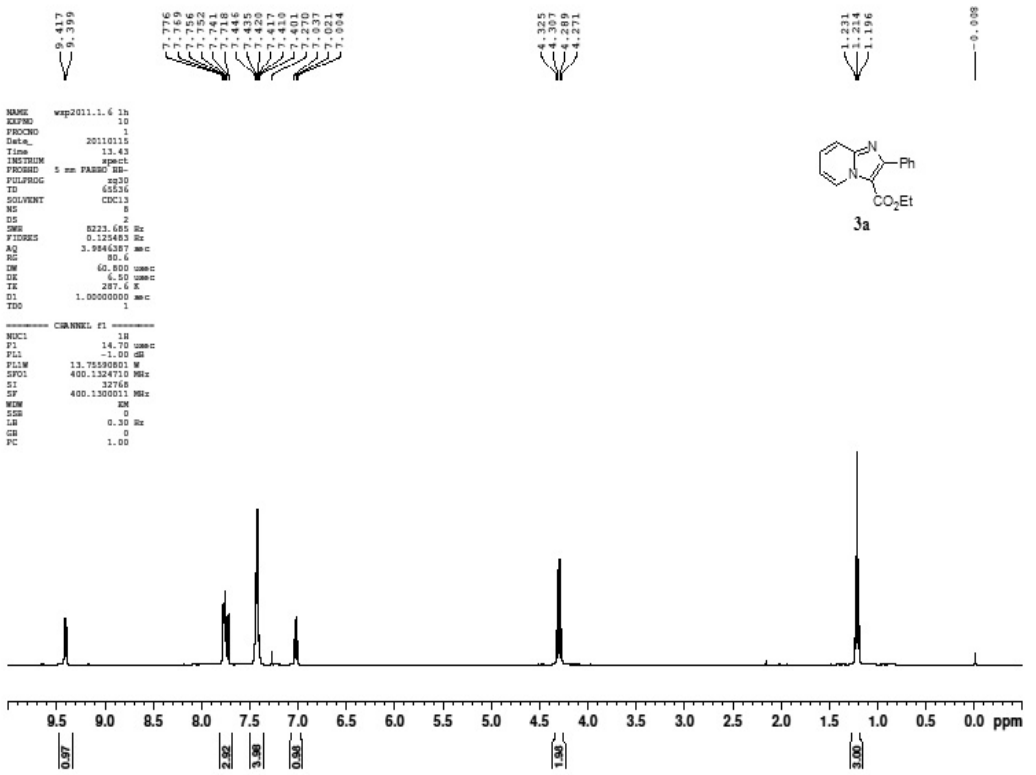
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7.401
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7.021
7.004
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4.289
4.271
1.231
1.214
1.196
-0.098
Ph
CO2Et
3a
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9.0
8.5
8.0
7.5
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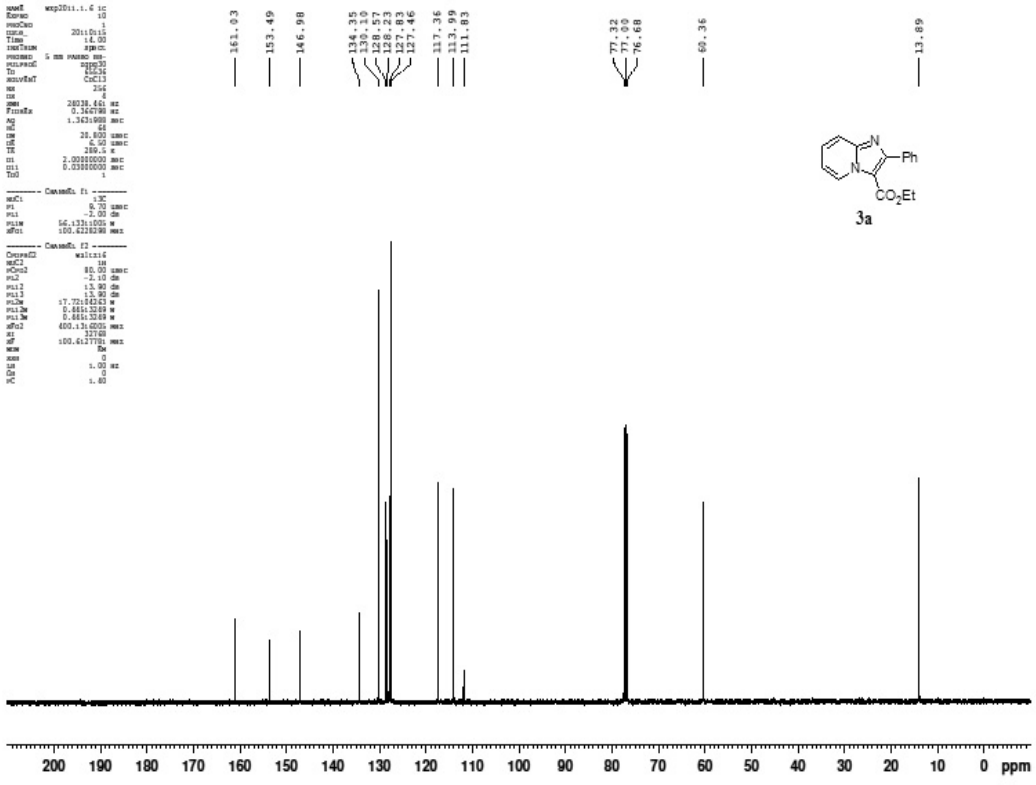
1.00
3.00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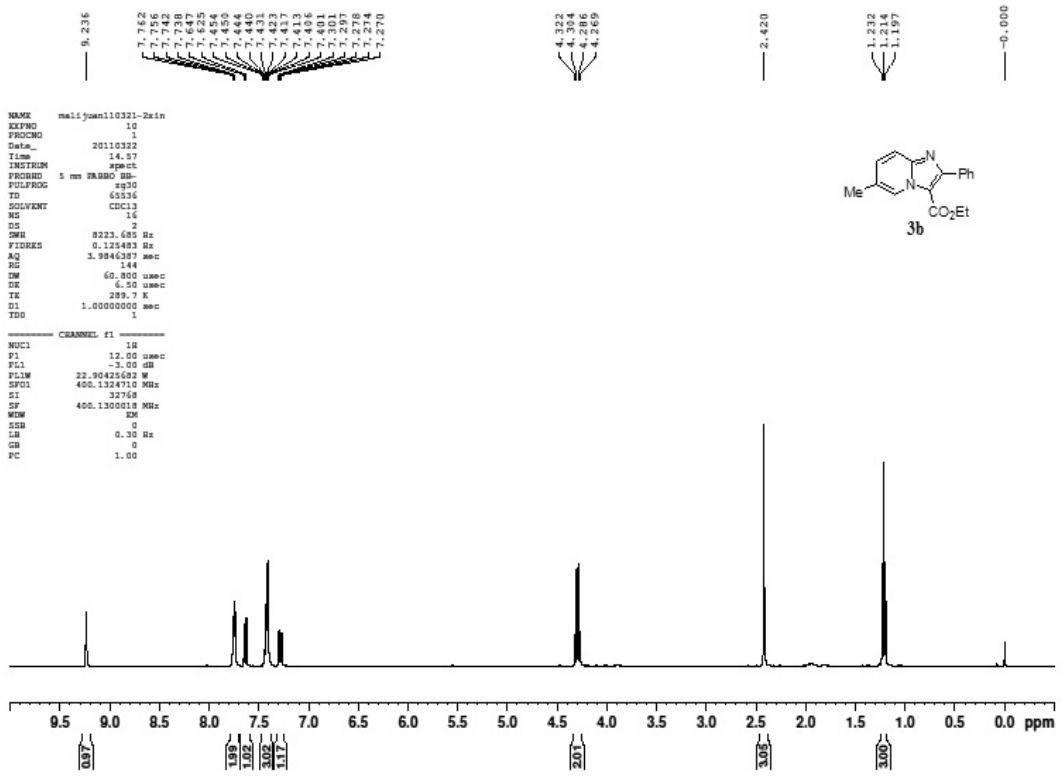
153.49
146.98
134.35
130.10
128.57
128.23
127.83
127.46
117.36
113.99
111.83
77.32
77.00
76.68
60.36
13.89
Ph
CO2Et
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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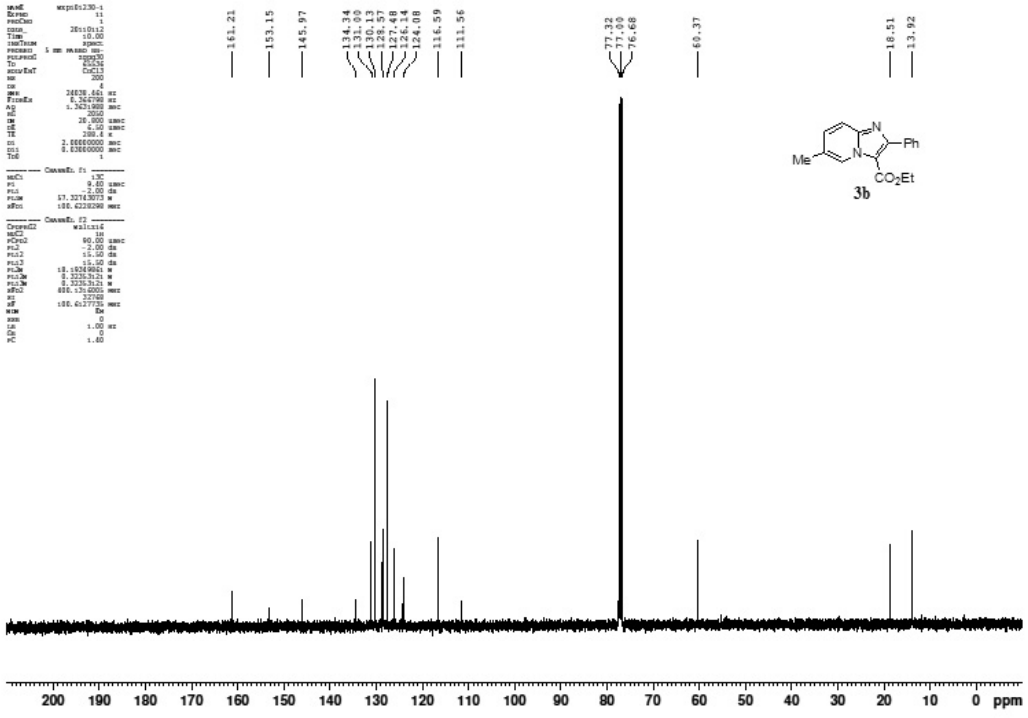
7.762
7.756
7.742
7.738
7.647
7.625
7.454
7.450
7.444
7.440
7.431
7.423
7.417
7.413
7.406
7.401
7.301
7.297
7.278
7.274
7.270
4.322
4.304
4.286
4.269
2.420
1.232
1.214
1.197
-0.000
Me
Ph
N
CO2Et
3b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
1.99
1.02
3.02
1.17
2.01
3.05
3.00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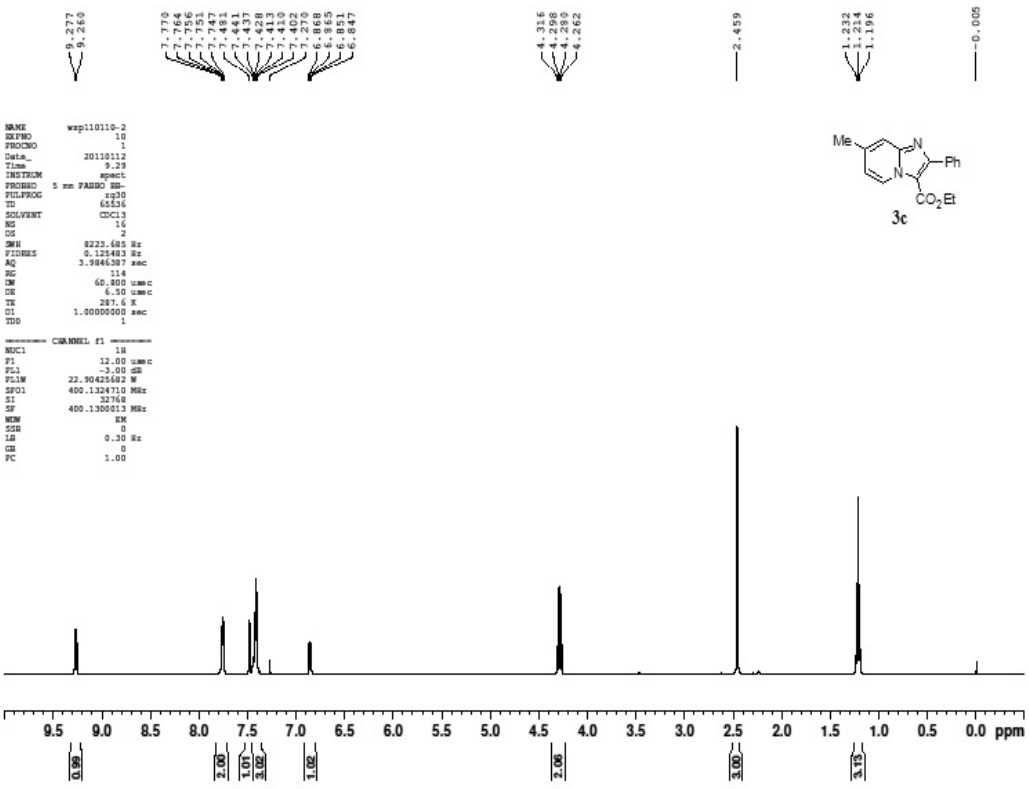
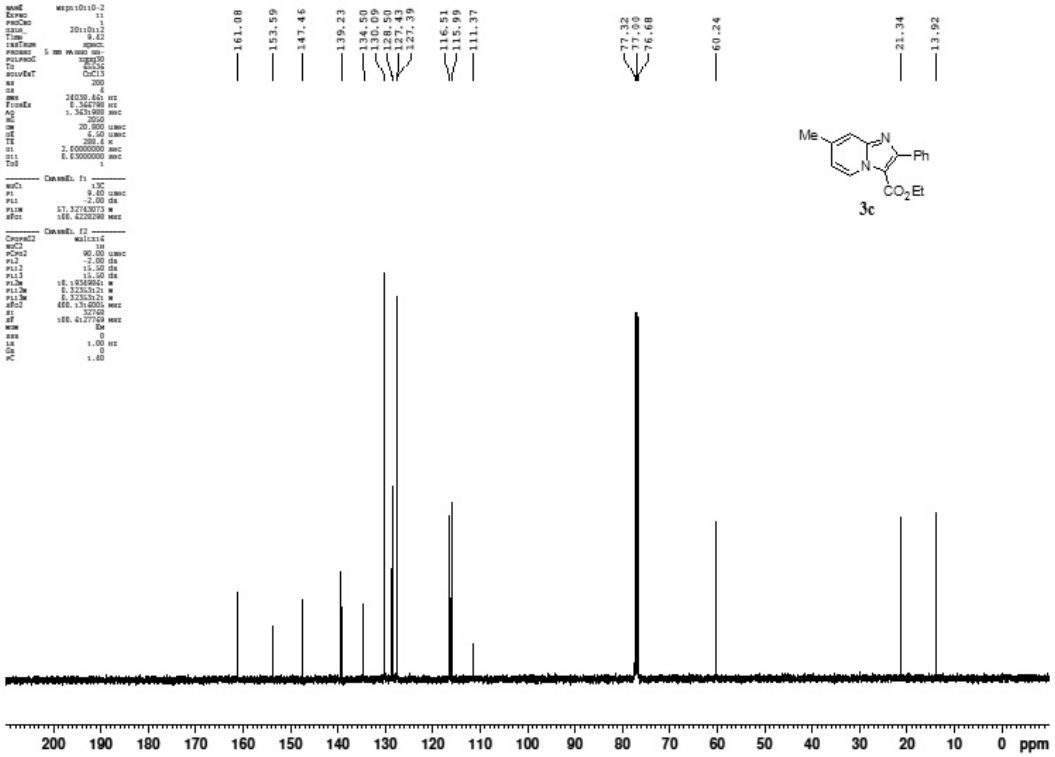
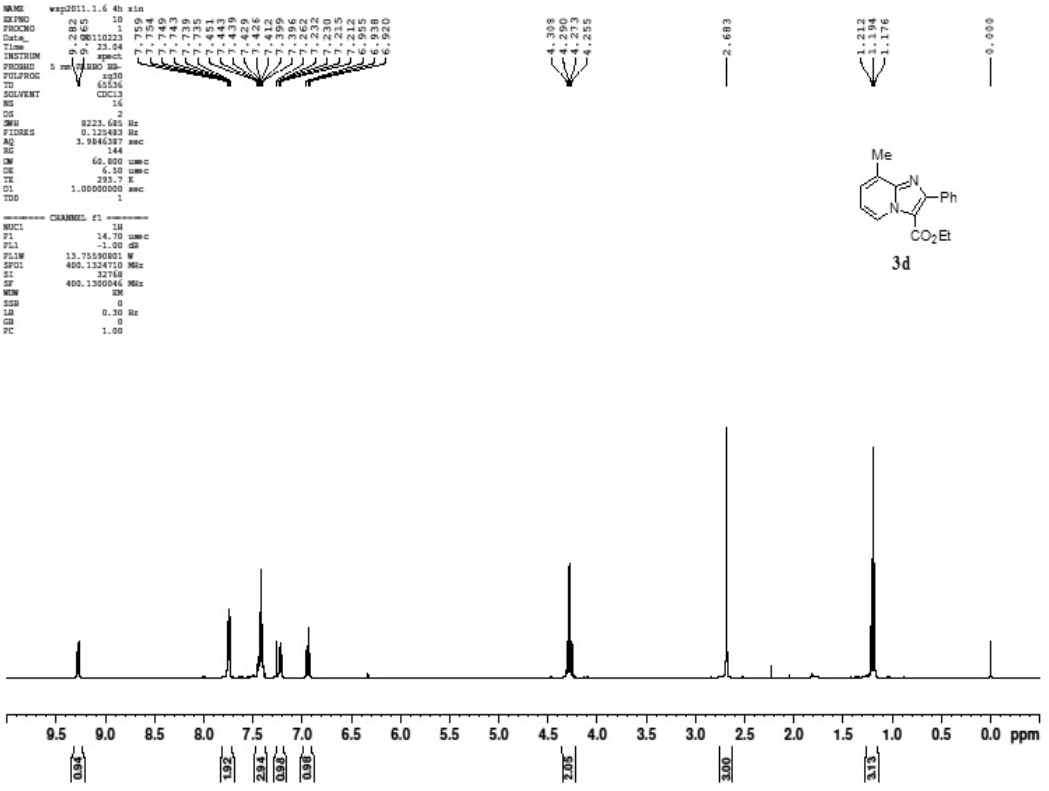
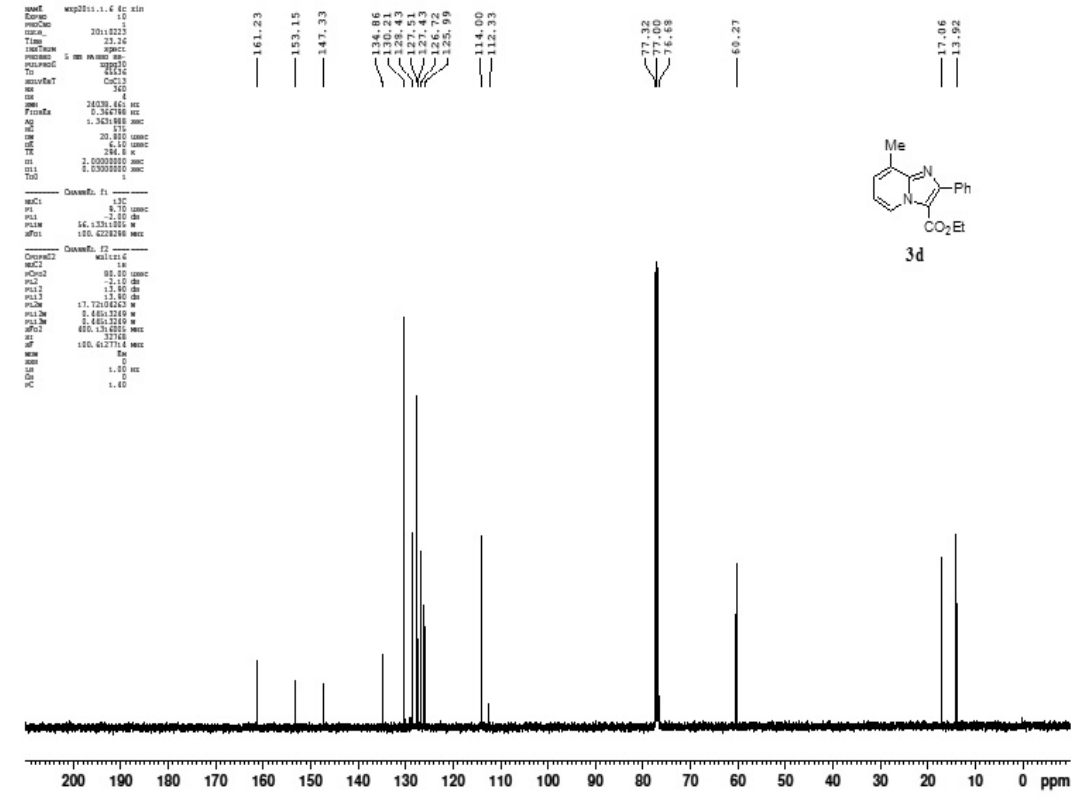
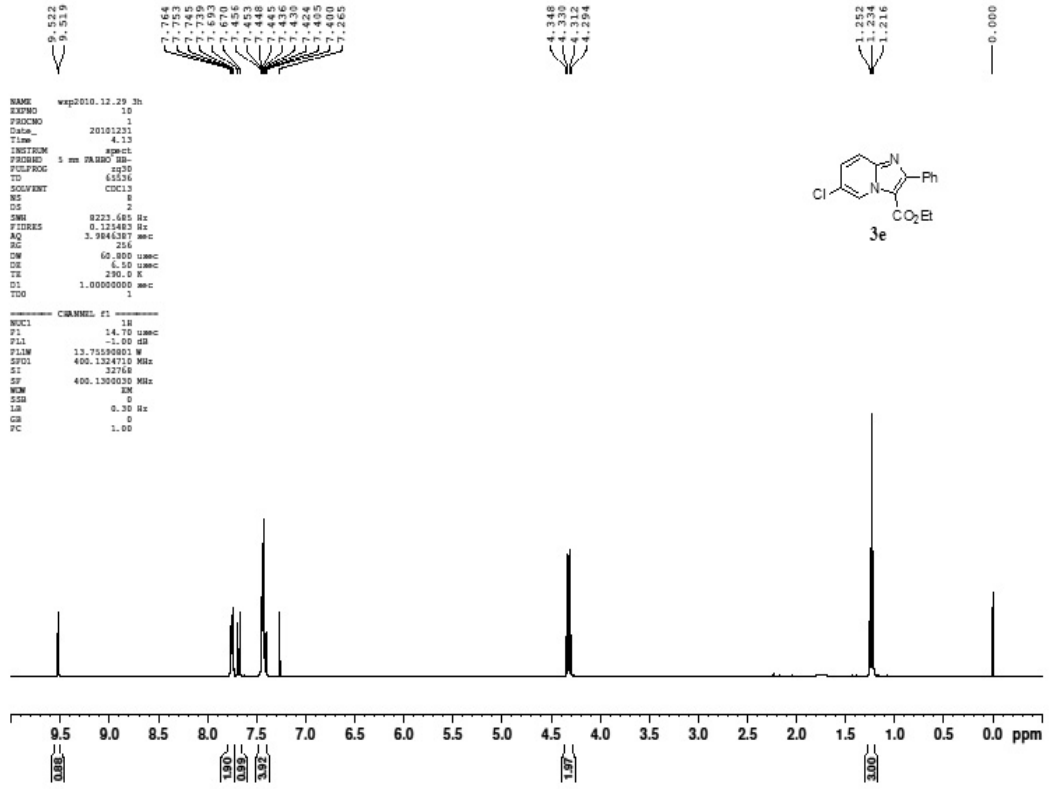
153.15
145.97
134.34
131.60
130.13
128.57
127.48
126.14
124.08
116.59
111.56
77.32
77.00
76.68
69.37
18.51
13.92
Me
Ph
N
CO2Et
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

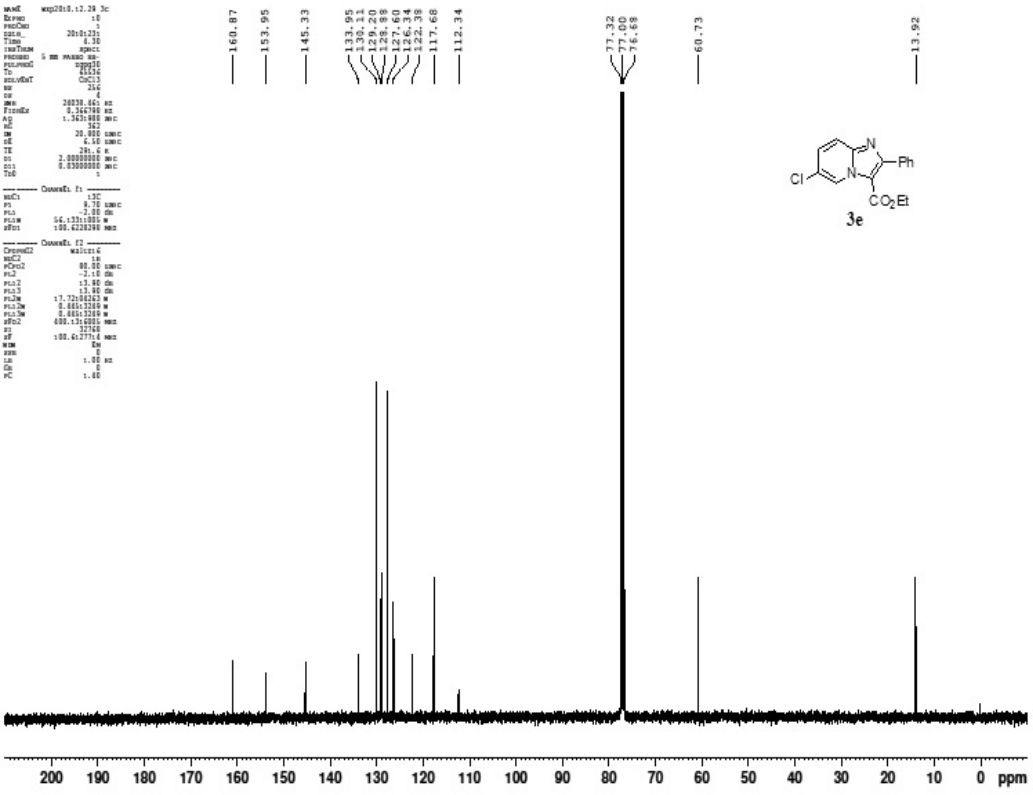

9.277
9.260
7.770
7.764
7.756
7.751
7.747
7.481
7.441
7.437
7.428
7.413
7.410
7.402
7.279
6.868
6.865
6.851
6.847
4.316
4.298
4.280
4.262
2.459
1.232
1.214
1.196
0.005
Me
N
Ph
N
CO2Et
3c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.99
2.00
1.01
3.00
1.02
2.06
3.00
3.13

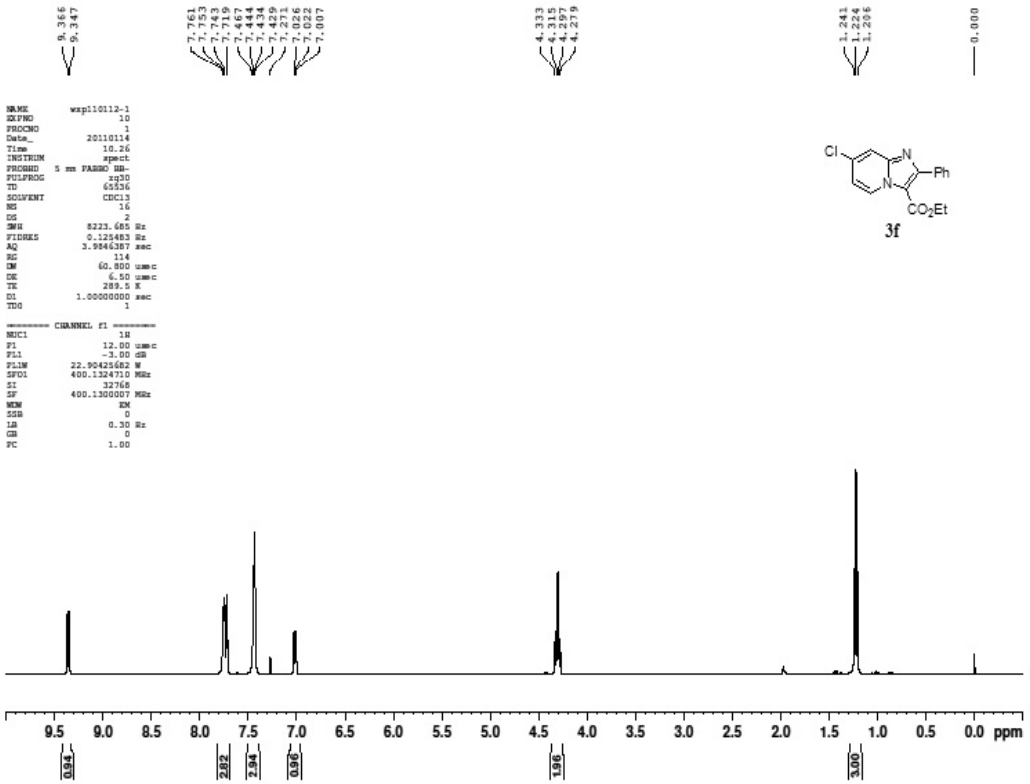

161.08
153.59
147.46
139.23
134.50
130.09
128.50
127.43
127.39
116.51
115.99
111.37
77.32
77.00
76.68
60.24
21.34
13.92
Me
N
Ph
N
CO2Et
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

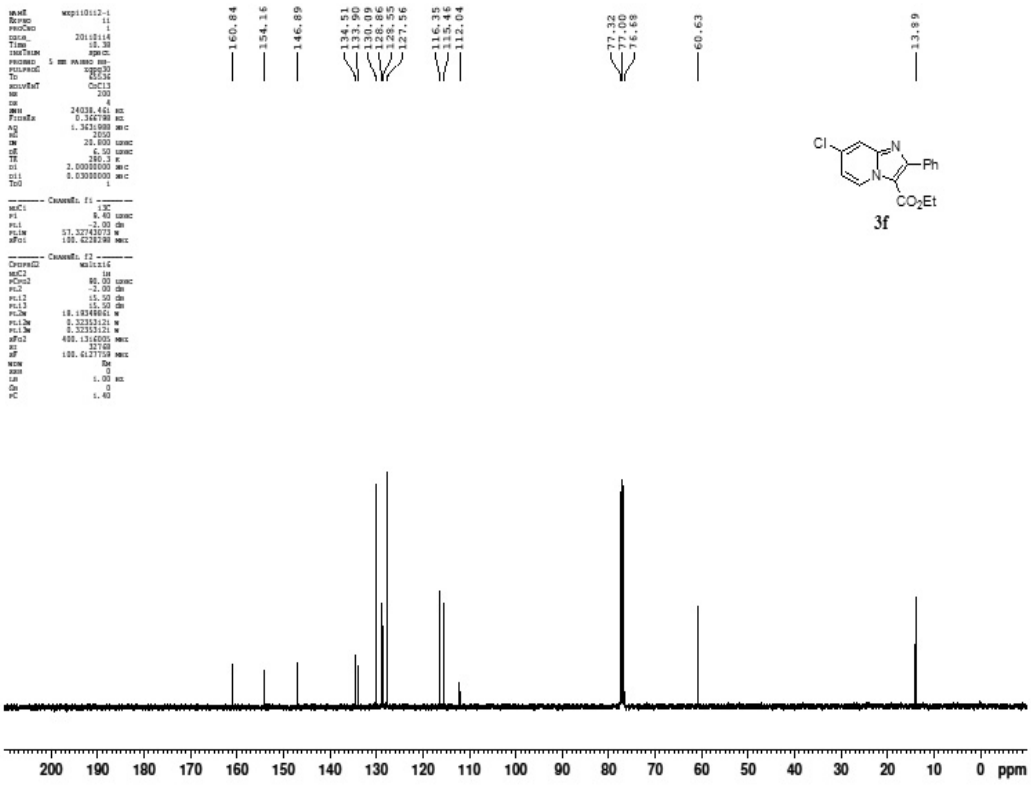

9.282
7.759
7.754
7.749
7.743
7.739
7.735
7.451
7.443
7.439
7.429
7.426
7.412
7.399
7.396
7.262
7.222
7.220
7.215
7.212
6.955
6.938
6.920
4.308
4.290
4.273
4.255
2.683
1.212
1.194
1.176
0.000
Me
N
Ph
N
CO2Et
3d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.94
1.92
2.94
0.98
0.98
2.05
3.00
3.13

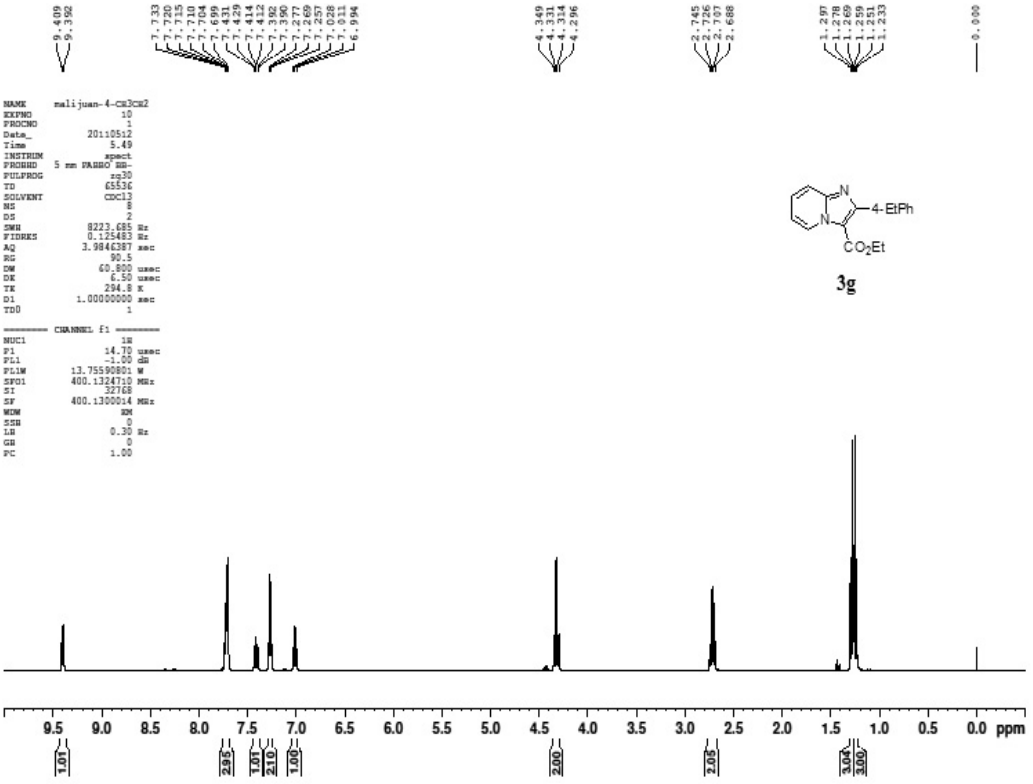

161.23
153.15
147.33
134.86
130.21
130.03
127.51
127.43
126.72
125.99
114.00
112.33
77.32
77.00
76.68
60.27
17.06
13.92
Me
N
Ph
N
CO2Et
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

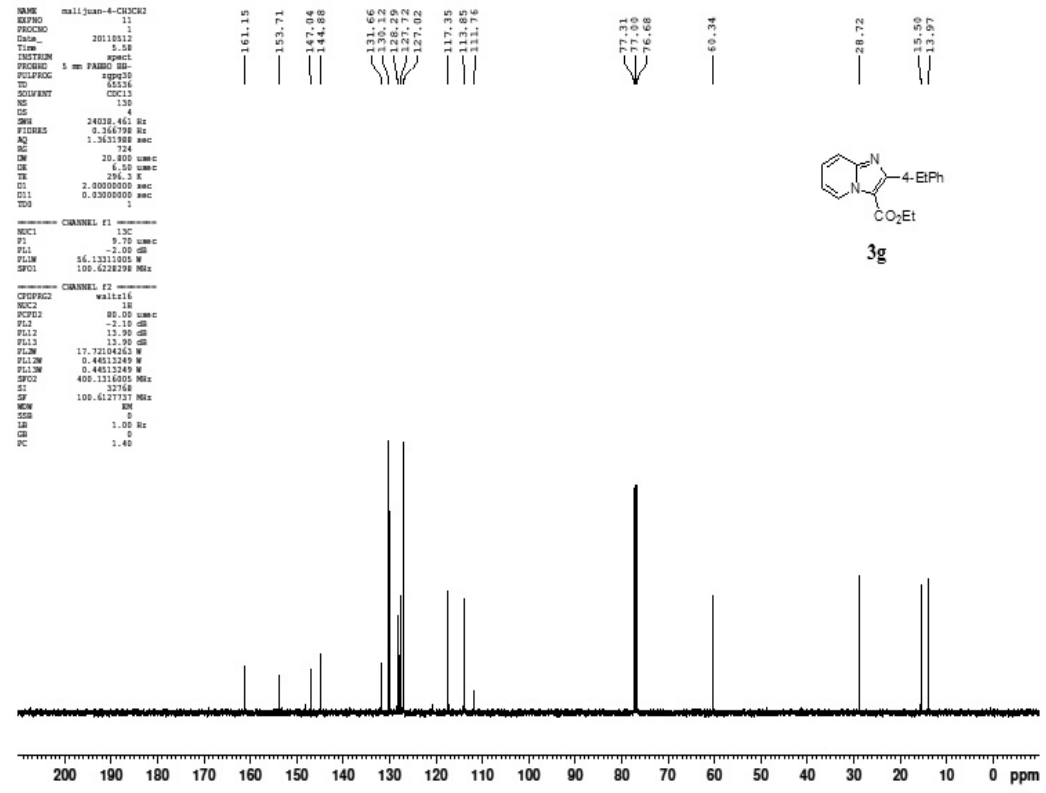

9.522
9.319
7.764
7.753
7.745
7.739
7.693
7.670
7.456
7.453
7.448
7.445
7.436
7.430
7.424
7.405
7.400
7.265
4.348
4.330
4.312
4.294
1.252
1.234
1.216
0.000
Cl
N
Ph
CO2Et
3e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.88
1.90
0.99
3.02
1.97
3.00

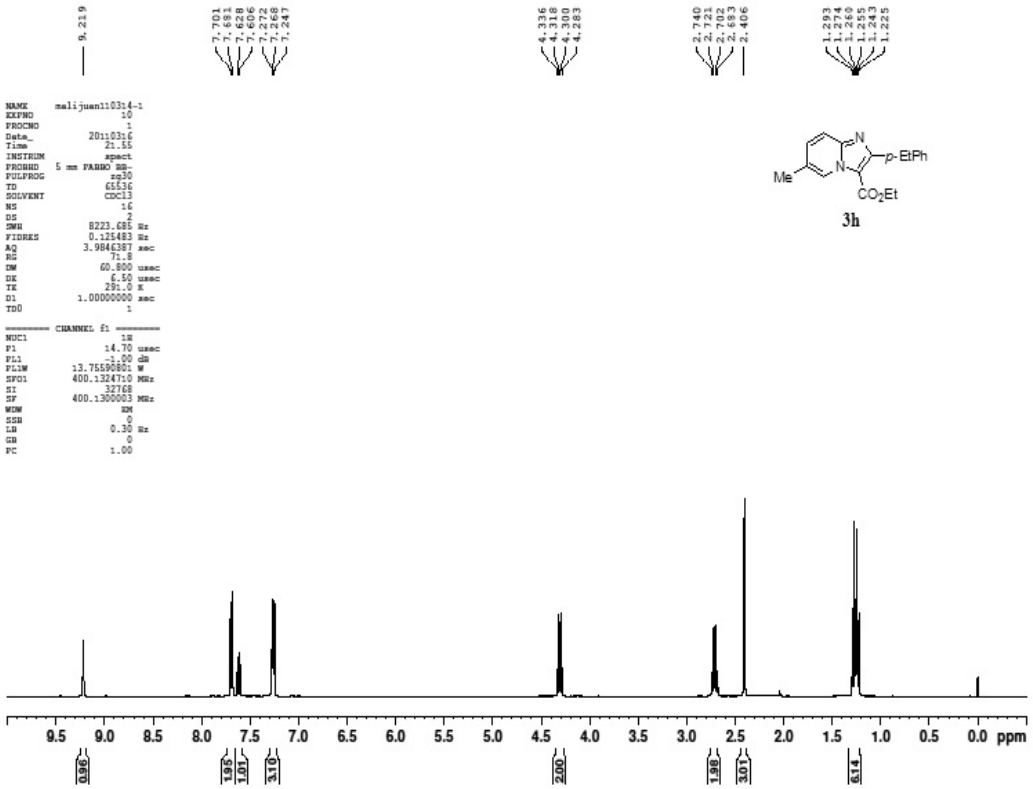

160.87
153.95
145.33
133.95
130.11
129.20
128.86
127.60
126.34
122.38
117.68
112.34
77.32
77.00
76.68
60.73
13.92
Cl
N
Ph
CO2Et
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

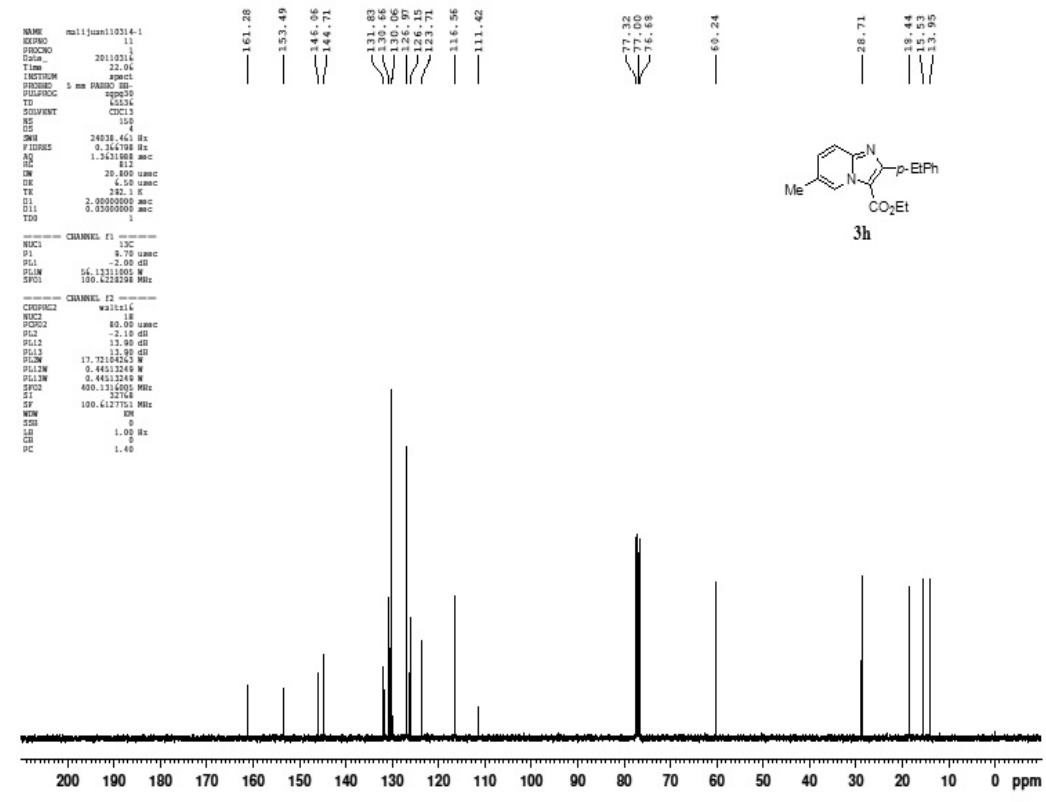

9.366
9.347
7.761
7.753
7.743
7.718
7.467
7.444
7.434
7.429
7.271
7.022
7.007
4.333
4.315
4.297
4.279
1.241
1.224
1.206
0.000
Cl
N
Ph
N
CO2Et
3f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.94
2.82
2.94
0.96
1.96
3.00

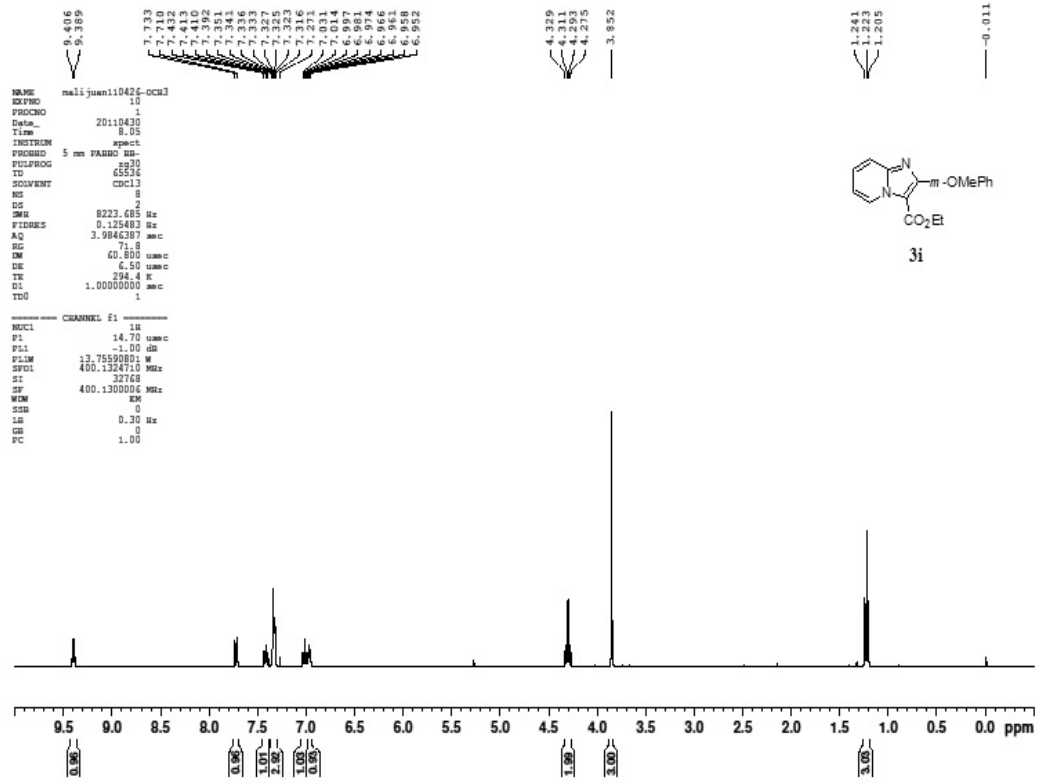

160.84
154.16
146.89
134.51
133.90
130.09
128.86
128.55
127.56
116.35
115.46
112.04
77.32
77.00
76.68
60.63
13.99
Cl
N
Ph
N
CO2Et
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.409
9.392
7.733
7.730
7.715
7.710
7.704
7.699
7.431
7.429
7.414
7.412
7.392
7.390
7.277
7.269
7.257
7.028
7.011
6.994
4.349
4.331
4.314
4.296
2.745
2.726
2.707
2.688
1.297
1.278
1.269
1.259
1.251
1.233
0.000
4-EtPh
CO2Et
3g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
2.95
1.07
2.10
1.00
2.00
2.05
3.04
3.00


161.15
153.71
147.04
144.88
131.66
130.12
128.29
127.72
127.02
117.35
113.85
111.76
77.31
77.00
76.68
60.34
28.72
15.50
13.97
4-EtPh
CO2Et
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.219
7.701
7.688
7.628
7.606
7.272
7.268
7.247
4.336
4.318
4.300
4.283
2.740
2.721
2.702
2.683
2.406
1.293
1.274
1.260
1.255
1.243
1.225
Me
p-EtPh
CO2Et
3h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.96
1.95
1.01
3.10
2.00
1.98
3.01
6.14


161.28
153.49
146.96
144.71
131.83
130.55
130.06
126.97
126.15
123.71
116.56
111.42
77.32
77.00
76.68
60.24
28.71
18.44
15.53
13.95
Me
p-EtPh
CO2Et
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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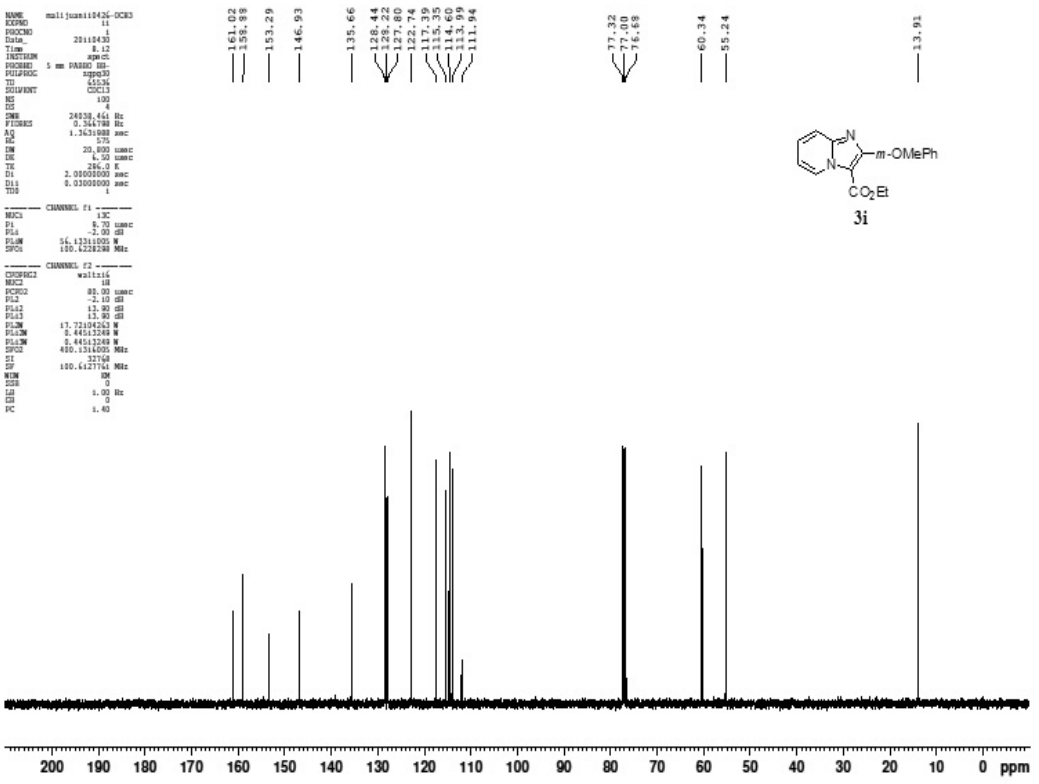
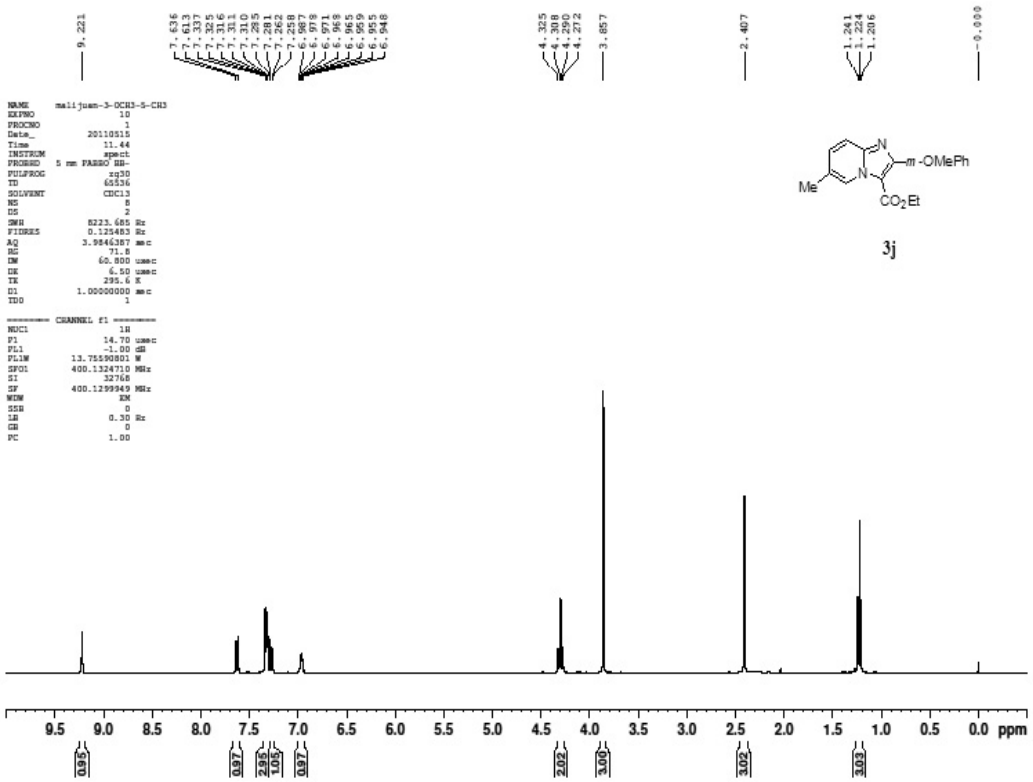
9.389
7.733
7.710
7.432
7.413
7.410
7.392
7.351
7.341
7.336
7.327
7.325
7.323
7.316
7.271
7.031
7.014
6.997
6.981
6.974
6.966
6.961
6.958
6.952
4.329
4.311
4.293
4.275
3.852
1.241
1.223
1.205
-0.011
m-OMePh
CO2Et
3i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


161.02
158.98
153.29
146.93
135.66
128.44
128.22
127.80
122.74
117.39
115.35
114.60
113.99
111.94
77.32
77.00
76.68
60.34
55.24
13.91
m-OMePh
CO2Et
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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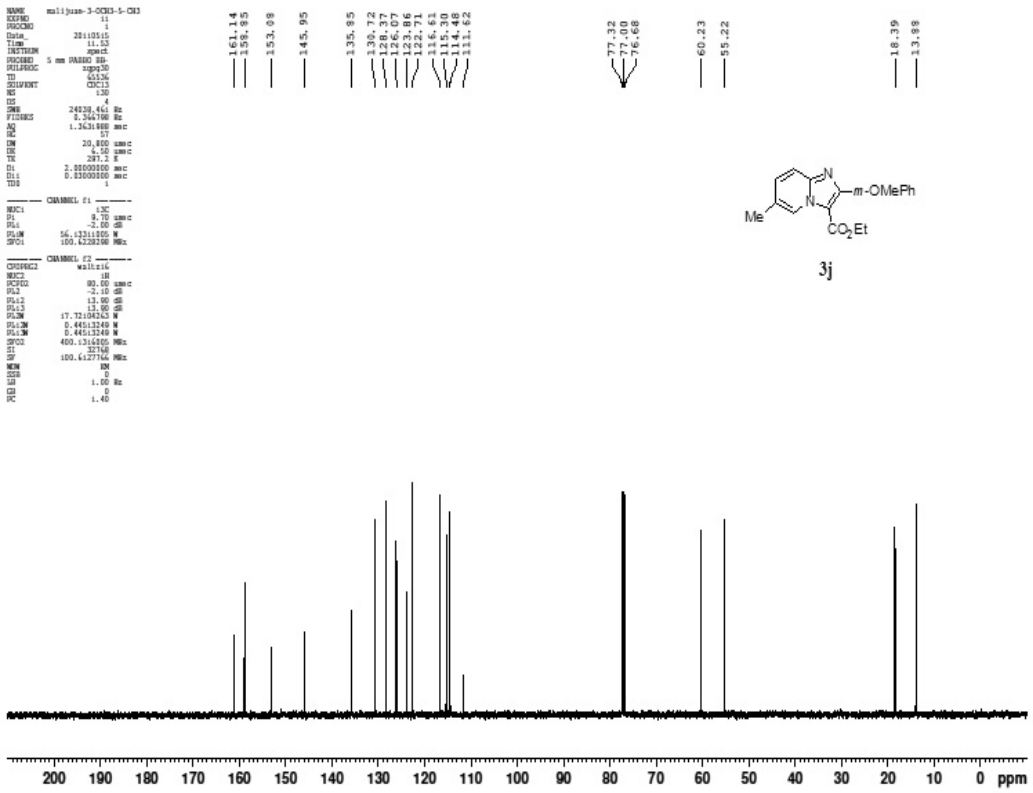
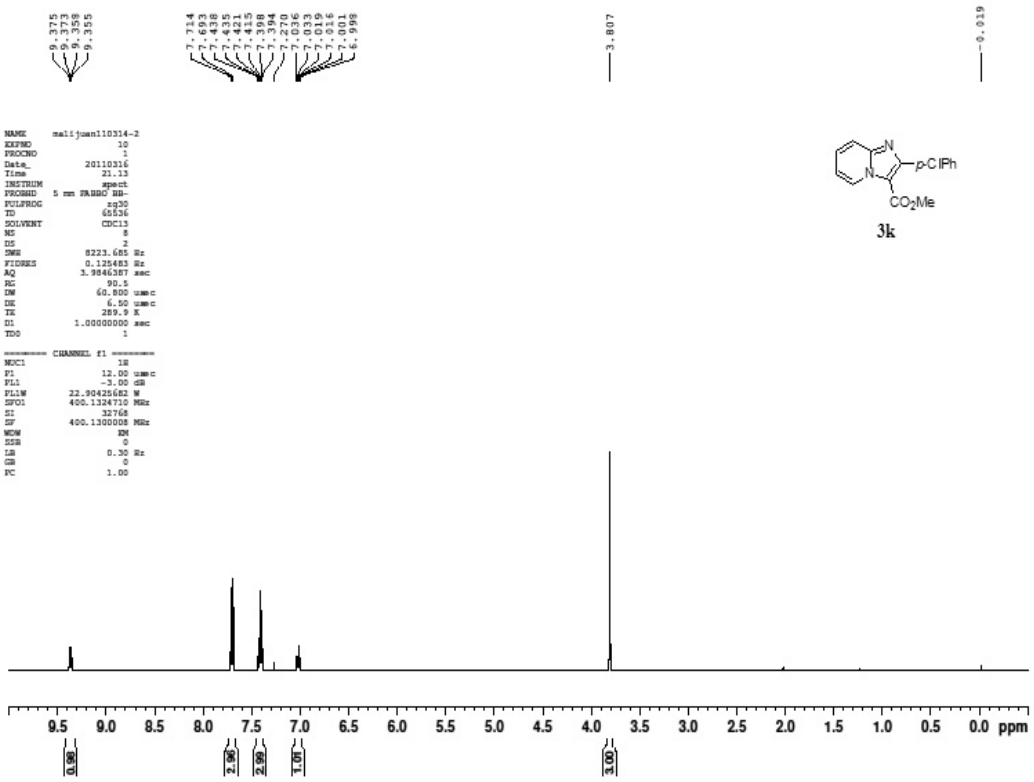
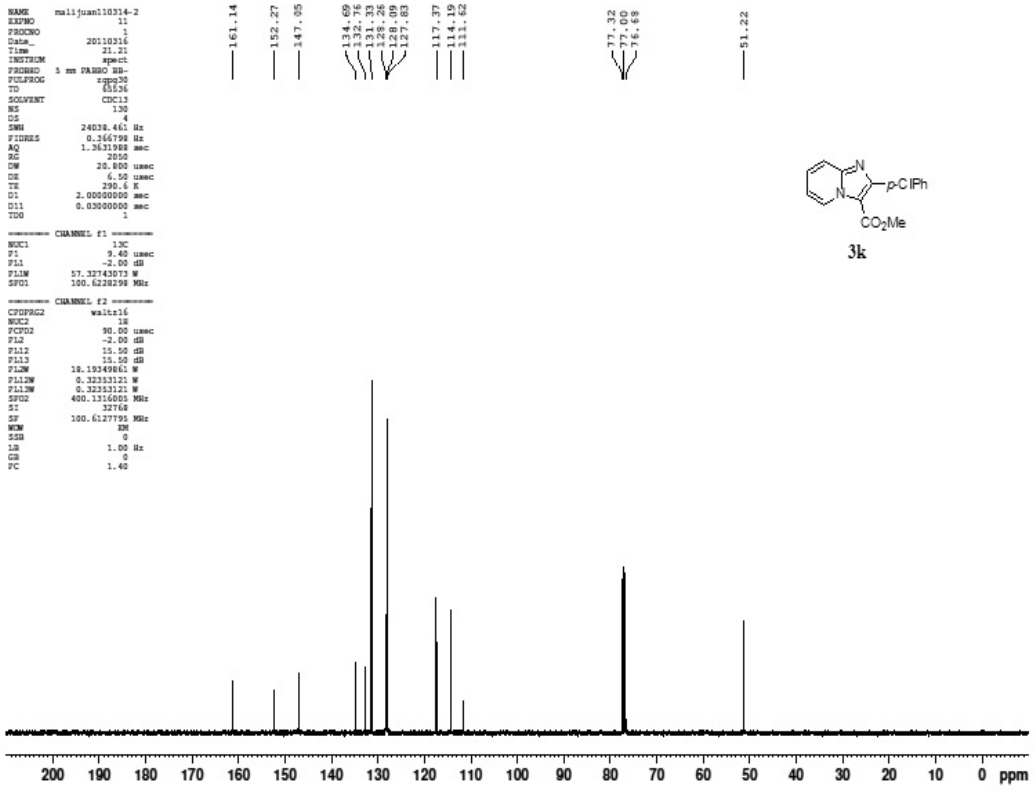
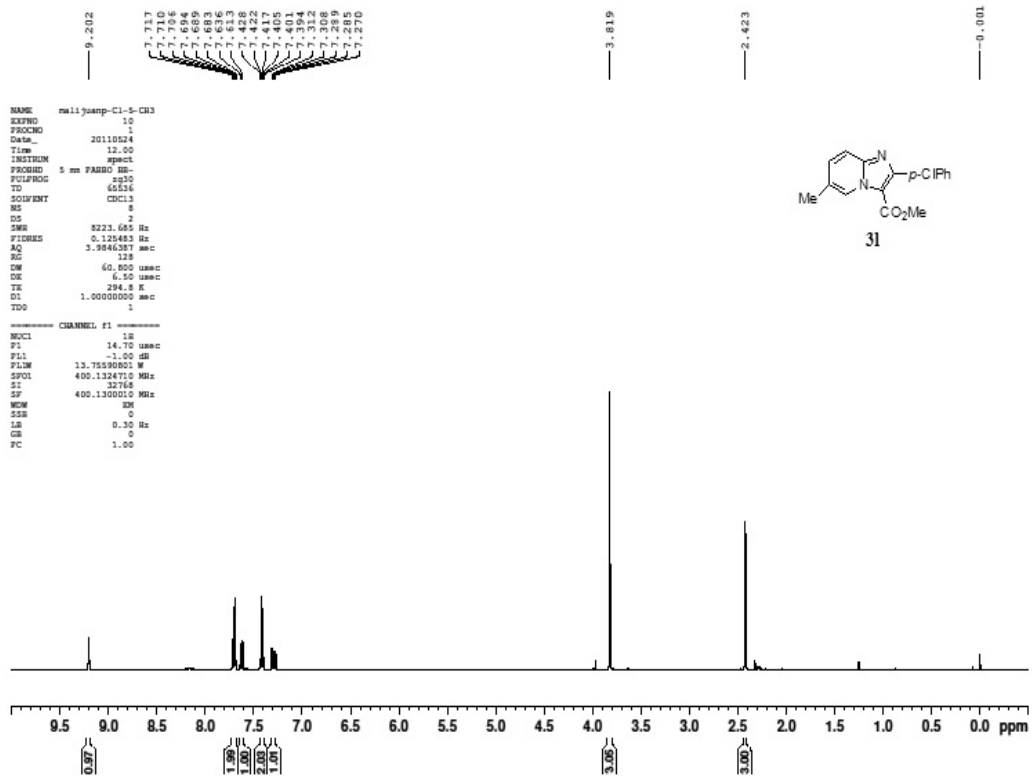
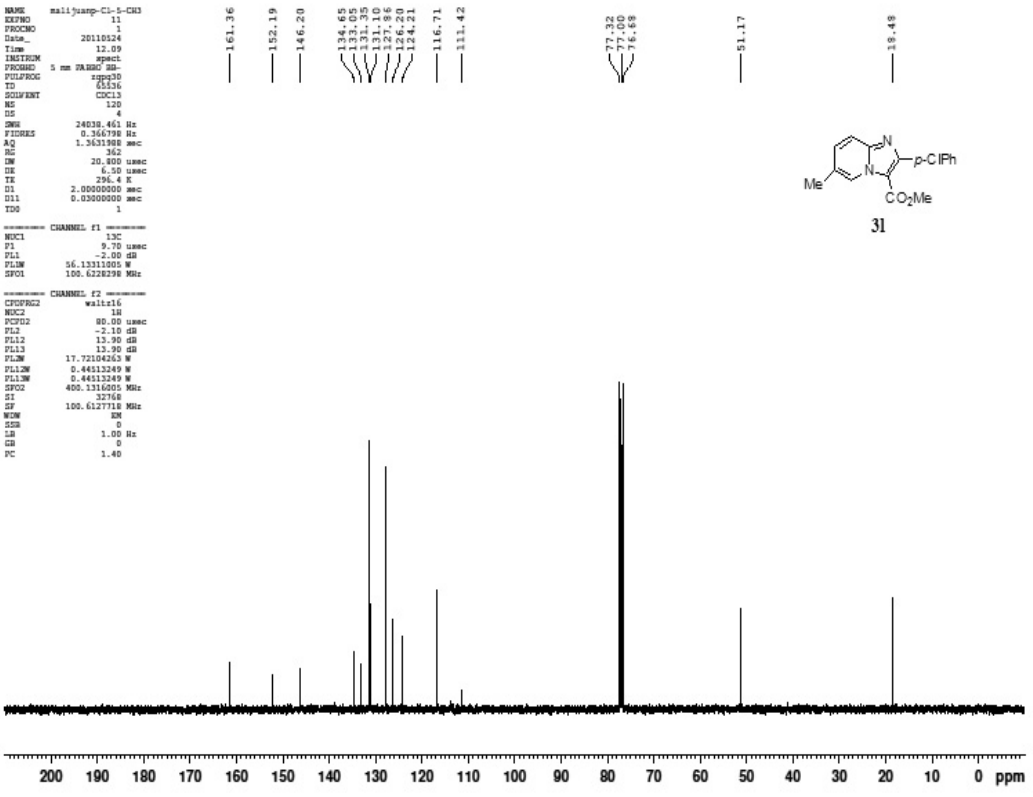
7.636
7.613
7.337
7.325
7.316
7.311
7.310
7.285
7.281
7.262
6.987
6.978
6.971
6.968
6.965
6.959
6.955
6.948
4.325
4.308
4.290
4.272
3.857
2.407
1.241
1.224
1.206
0.000
m-OMePh
Me
CO2Et
3j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
0.97
2.95
1.05
0.97
2.02
3.00
3.02
3.03

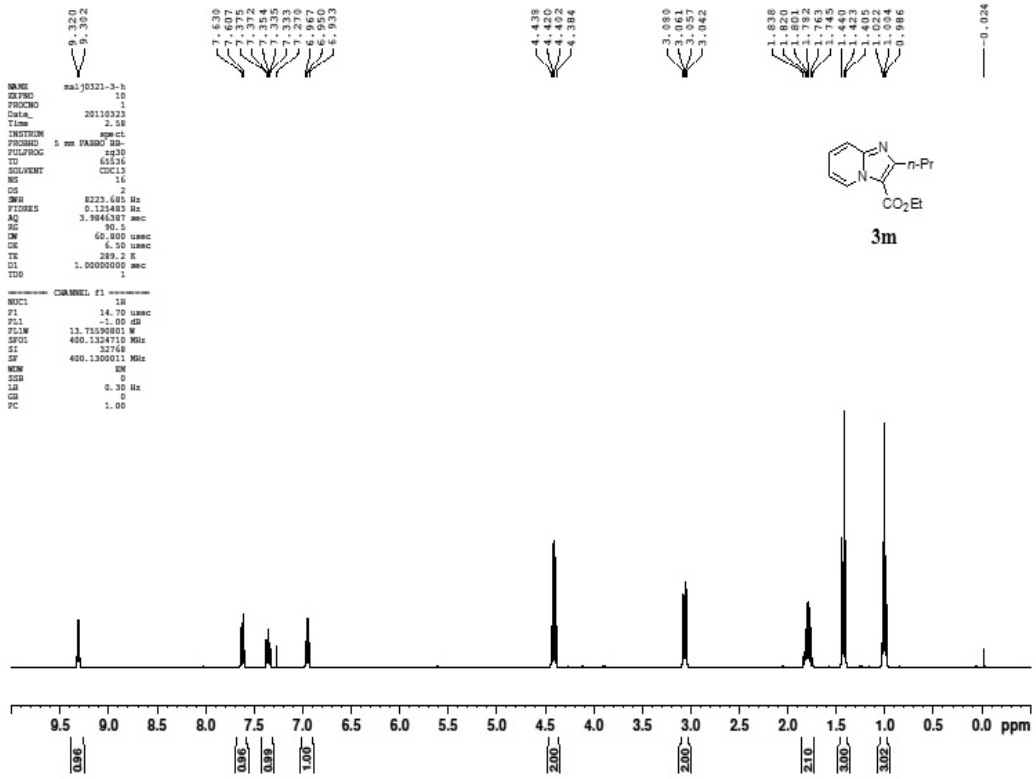

161.14
159.95
153.08
145.95
135.85
130.72
128.37
126.07
123.86
122.71
116.61
115.30
114.48
111.62
77.32
77.08
76.68
60.23
55.22
18.39
13.88
m-OMePh
Me
CO2Et
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

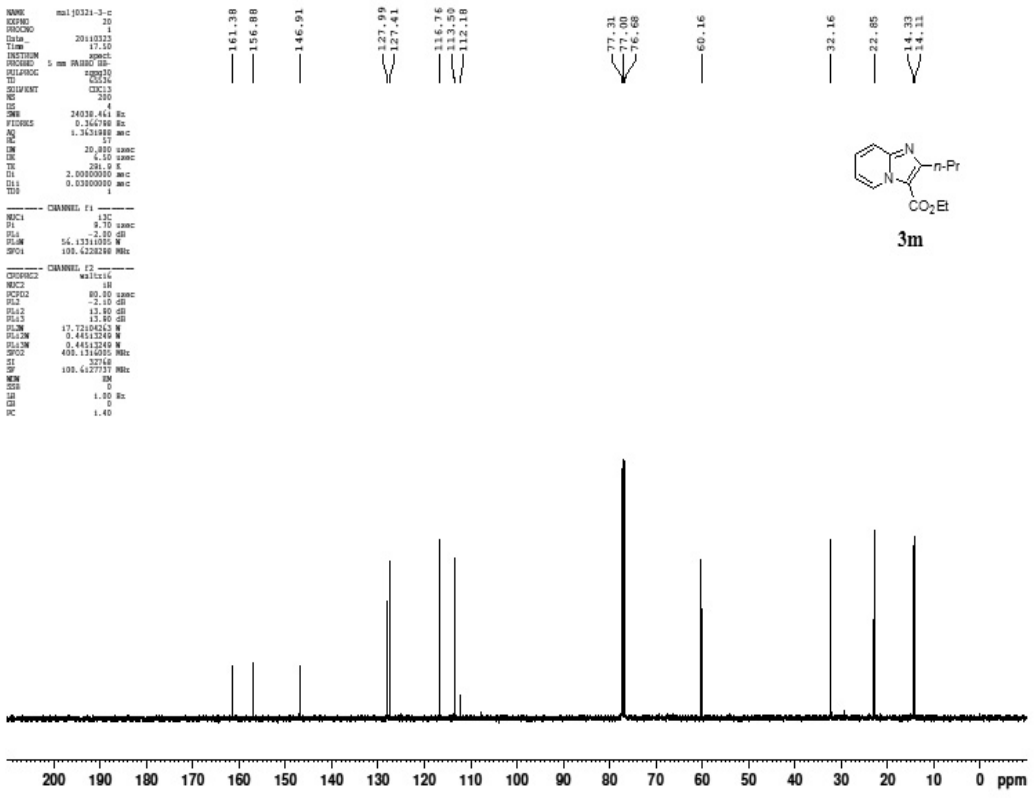

9.375
9.373
9.358
9.355
7.734
7.693
7.438
7.435
7.421
7.415
7.398
7.394
7.373
7.036
7.033
7.019
7.016
7.001
6.998
3.807
0.019
p-ClPh
CO2Me
3k
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
2.96
2.99
1.05
3.00


161.14
152.27
147.05
134.69
132.76
131.33
131.26
128.09
127.83
117.37
114.19
111.62
77.32
77.00
76.68
51.22
p-ClPh
CO2Me
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.202
7.717
7.710
7.706
7.694
7.689
7.683
7.636
7.633
7.428
7.422
7.417
7.405
7.401
7.394
7.312
7.308
7.289
7.285
7.270
3.819
2.423
0.001
p-ClPh
Me
CO2Me
31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


161.36
152.19
146.20
134.65
133.05
131.35
131.10
127.86
126.20
124.21
116.71
111.42
77.32
77.00
76.68
51.17
18.48
p-ClPh
Me
CO2Me
31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.320
9.302
7.630
7.607
7.375
7.372
7.354
7.335
7.333
7.270
6.967
6.950
6.933
4.438
4.420
4.402
4.384
3.080
3.061
3.057
3.042
1.838
1.820
1.801
1.792
1.763
1.745
1.429
1.420
1.405
1.022
1.004
0.986
0.024
n-Pr
CO2Et
3m
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.96
0.96
0.99
1.00
2.00
2.00
2.10
3.00
3.02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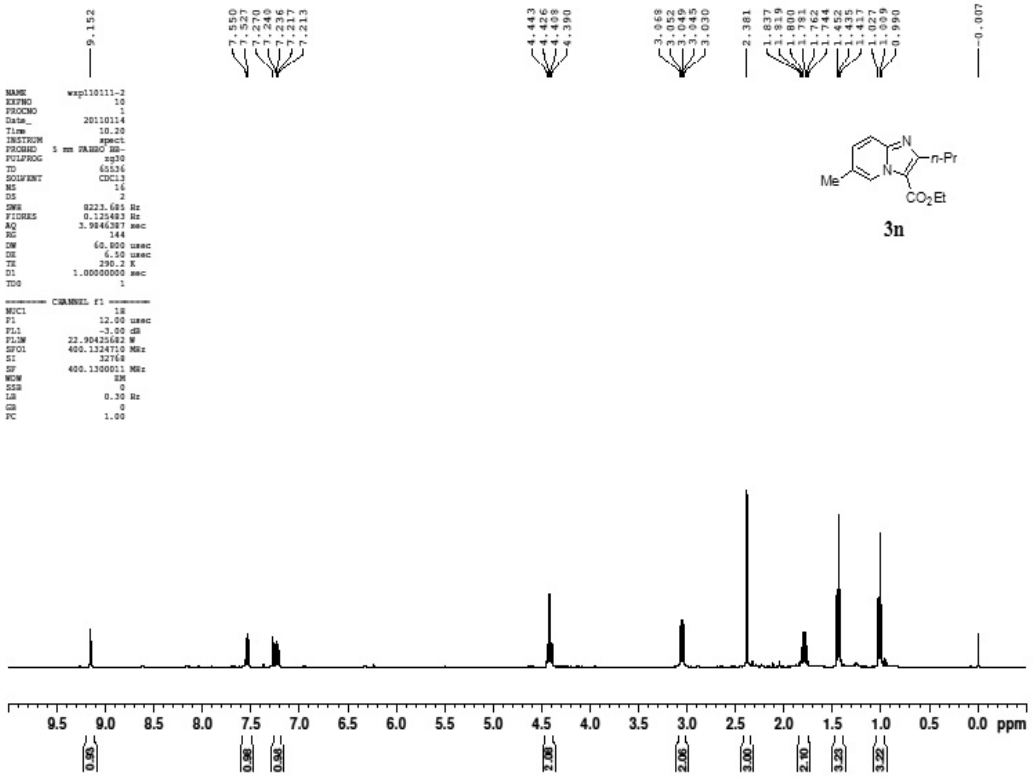
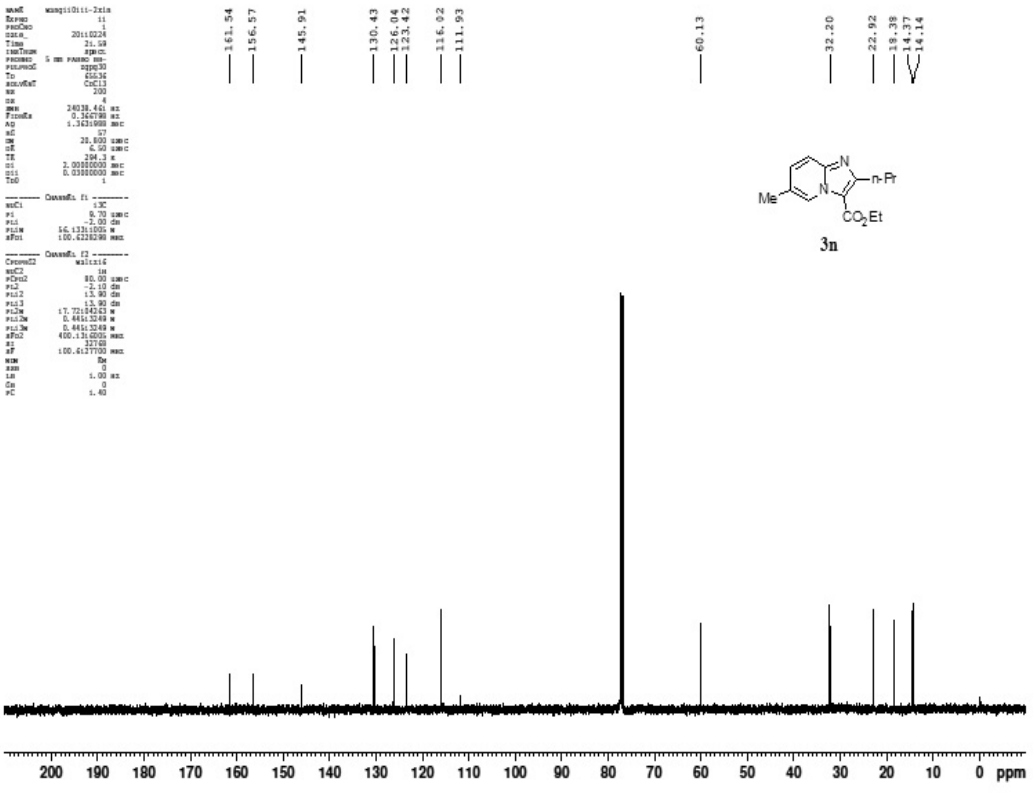
156.88
146.91
127.99
127.41
116.76
113.59
112.18
77.31
77.00
76.68
60.16
32.16
22.85
14.33
14.11
n-Pr
CO2Et
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.152
7.550
7.527
7.520
7.240
7.236
7.217
7.213
4.443
4.426
4.408
4.390
3.068
3.052
3.049
3.045
3.030
2.381
1.837
1.819
1.800
1.781
1.762
1.744
1.452
1.435
1.417
1.029
1.009
0.990
-0.007
n-Pr
Me
CO2Et
3n
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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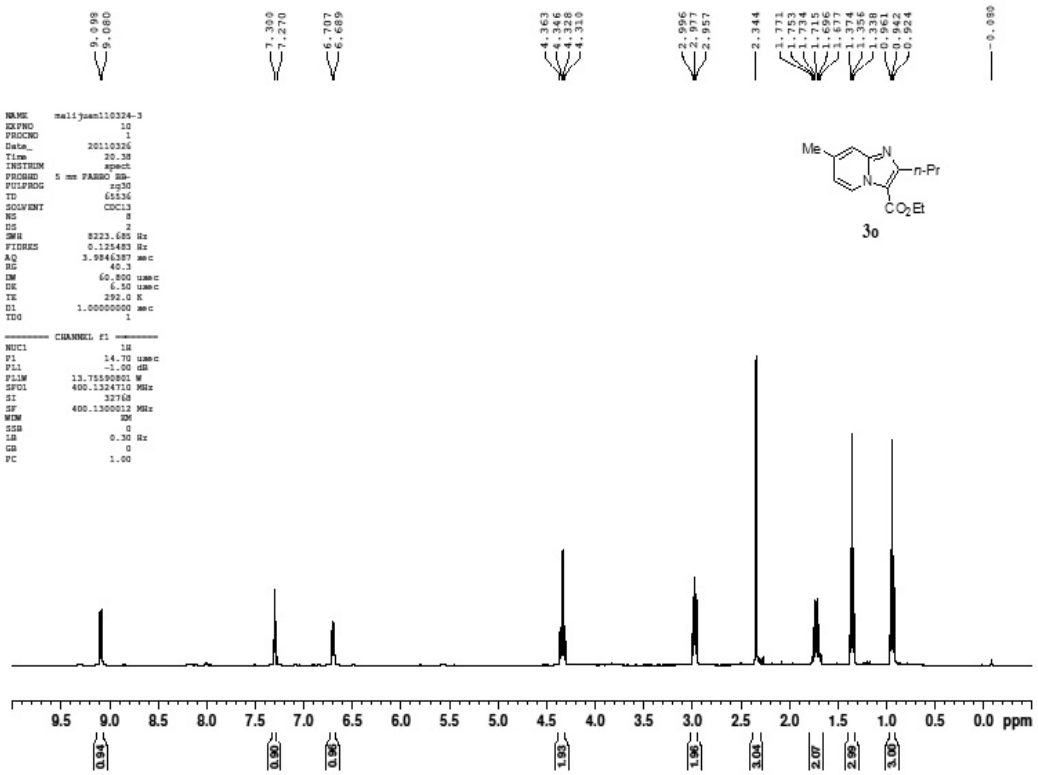
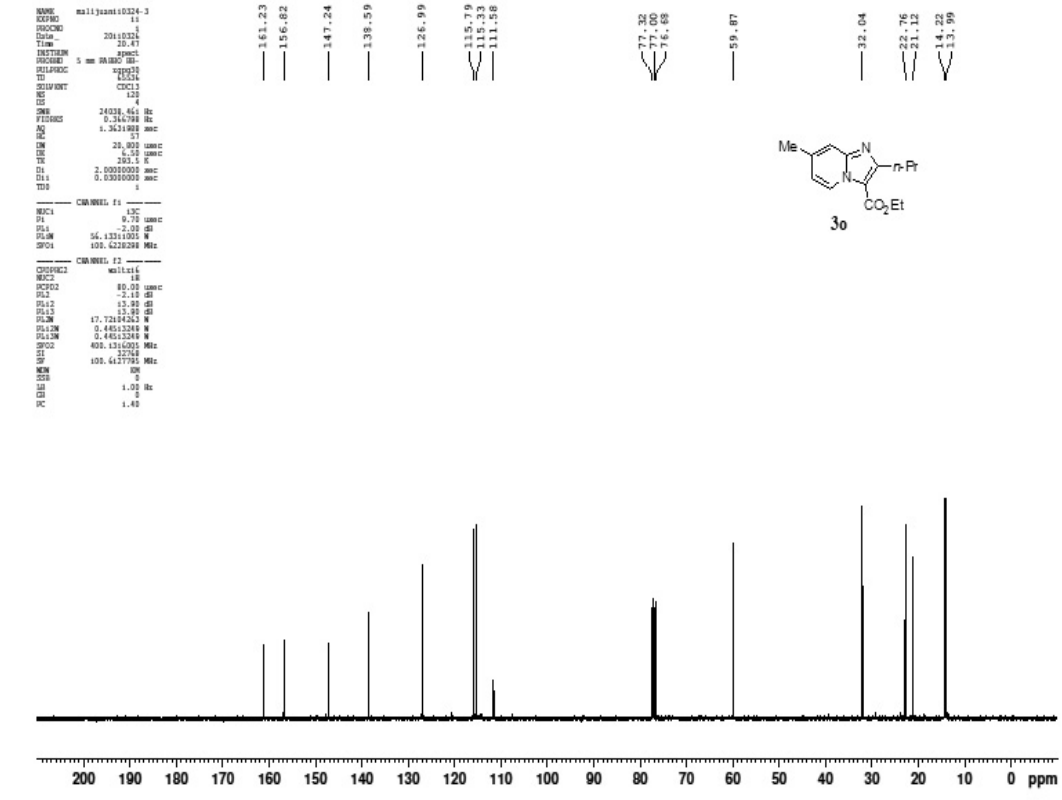
156.57
145.91
130.43
126.04
123.42
116.02
111.93
60.13
32.20
22.92
19.38
14.37
14.14
n-Pr
Me
CO2Et
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.098
9.080
7.300
7.270
6.707
6.689
4.363
4.346
4.328
4.310
2.996
2.977
2.957
2.344
1.771
1.753
1.734
1.715
1.696
1.677
1.374
1.356
1.338
0.961
0.942
0.924
0.000
Me
N
N
n-Pr
CO2Et
3o
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.94
0.90
0.96
1.93
1.96
3.04
2.07
2.00
3.00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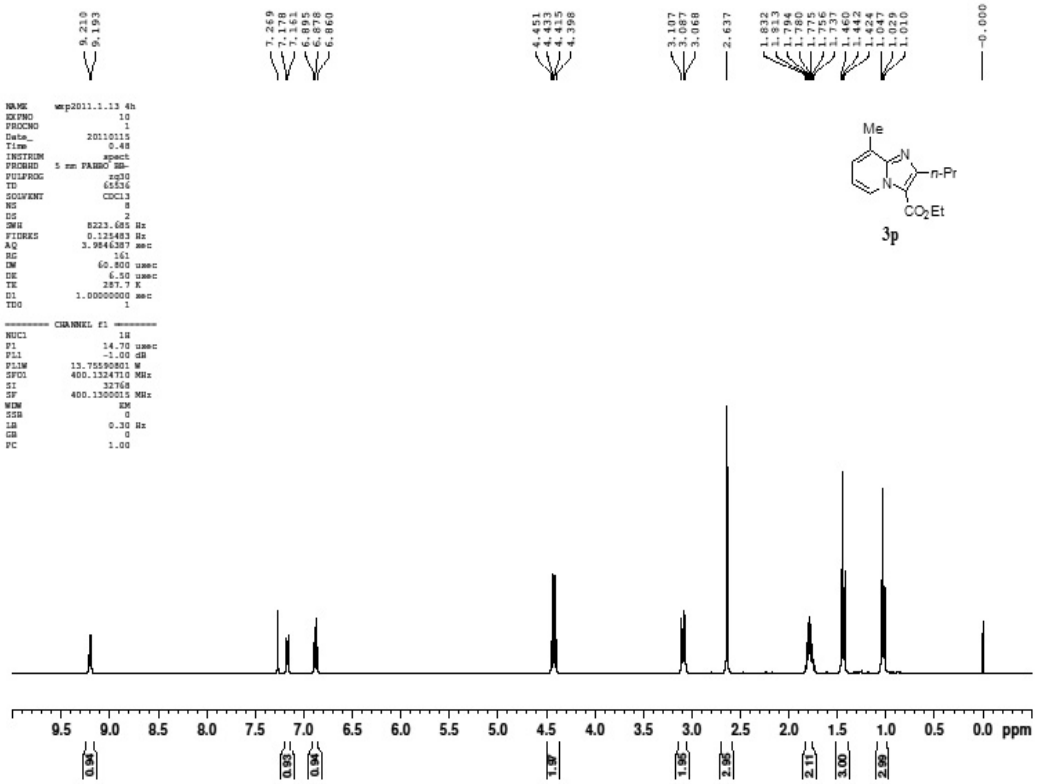
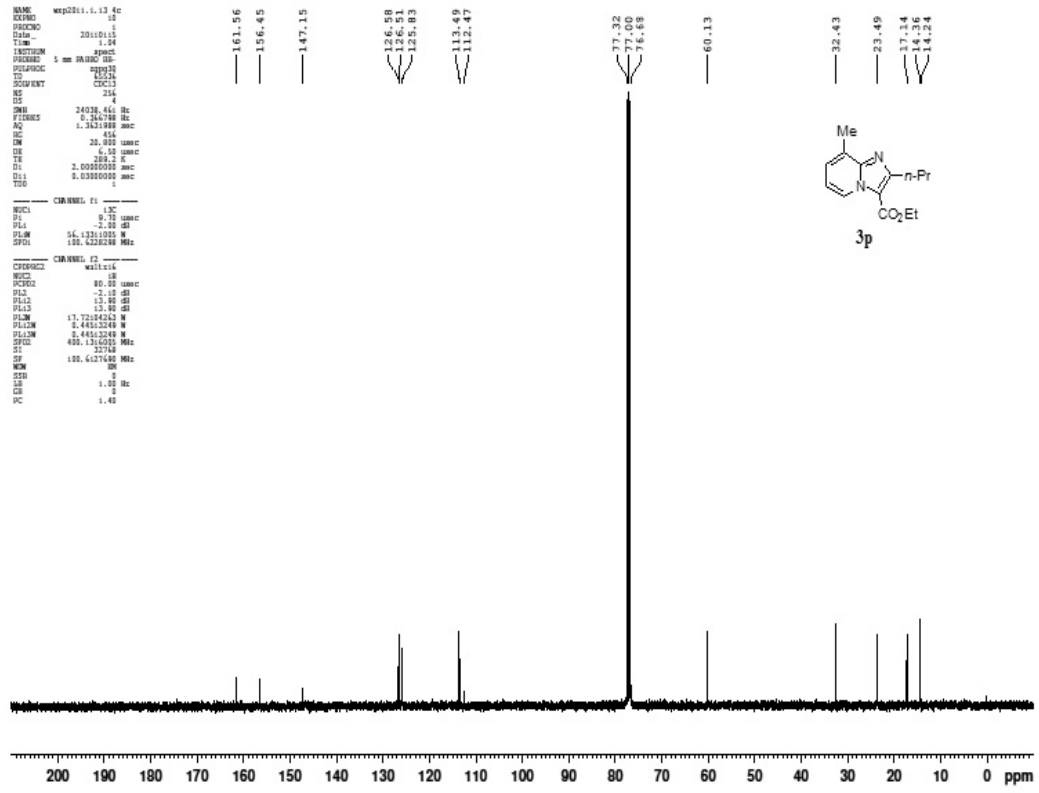
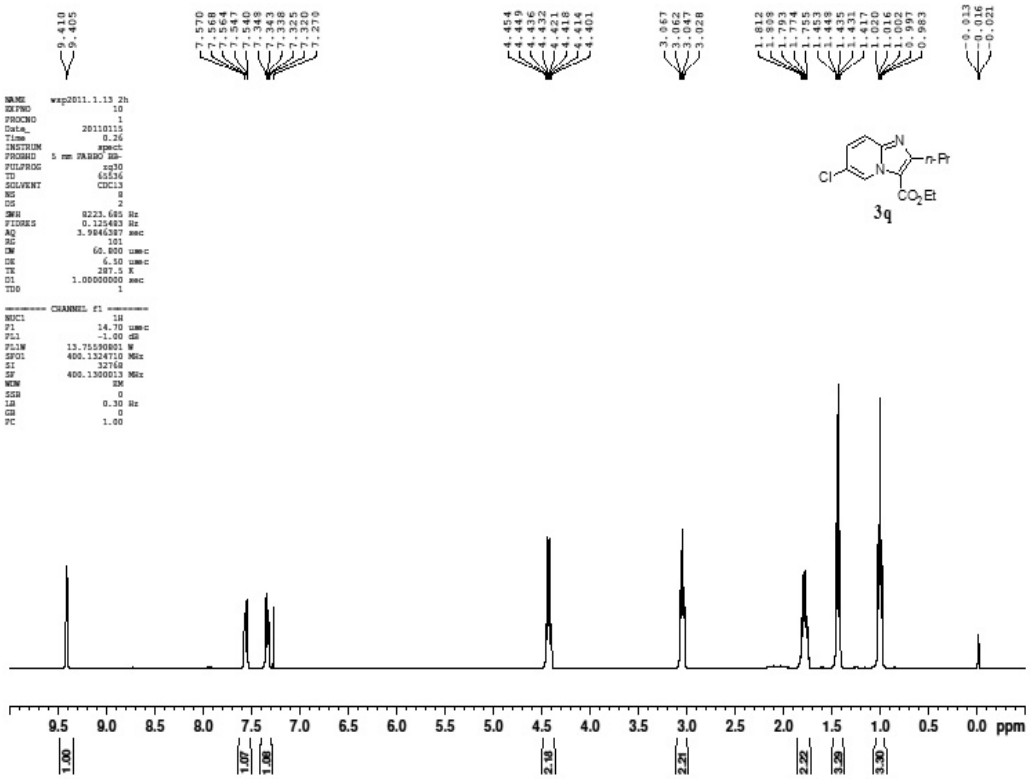
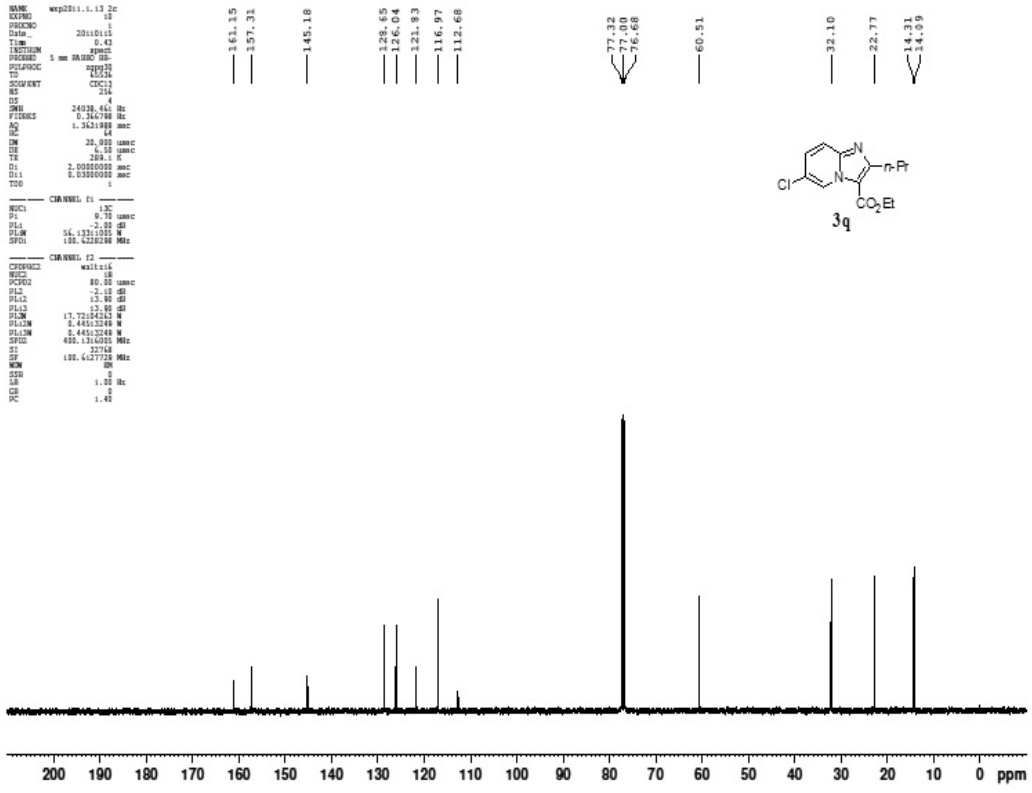
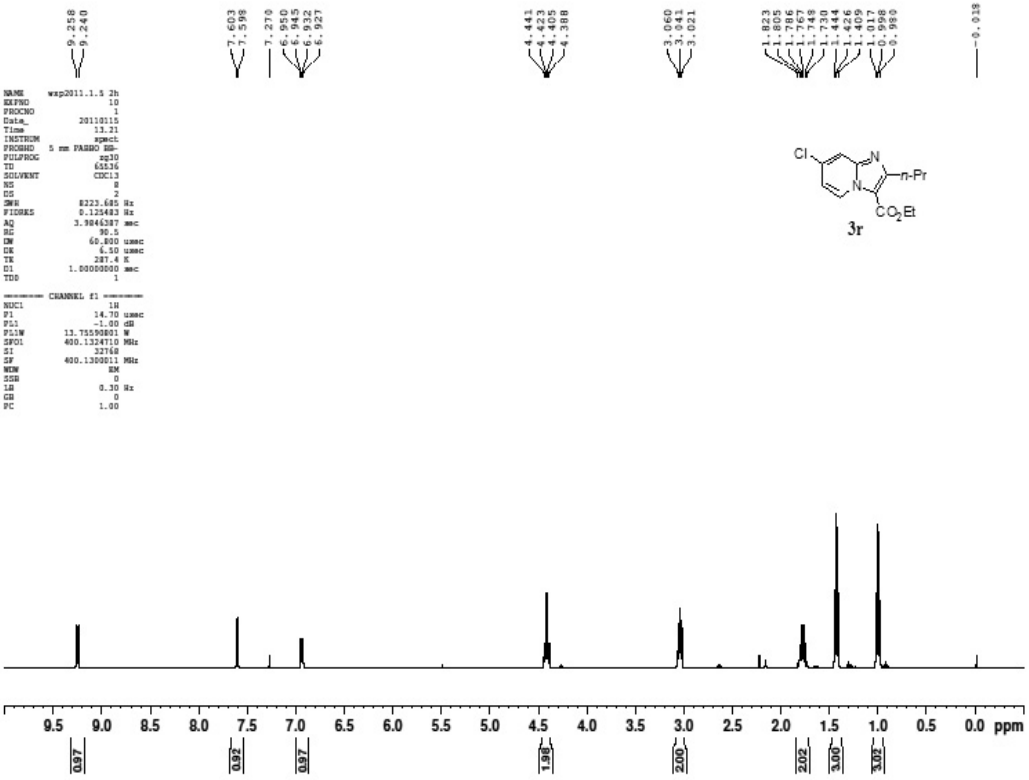
156.82
147.24
138.59
126.99
115.79
113.33
111.58
77.32
77.00
76.68
59.87
32.04
22.76
21.12
14.22
13.99
Me
N
N
n-Pr
CO2Et
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

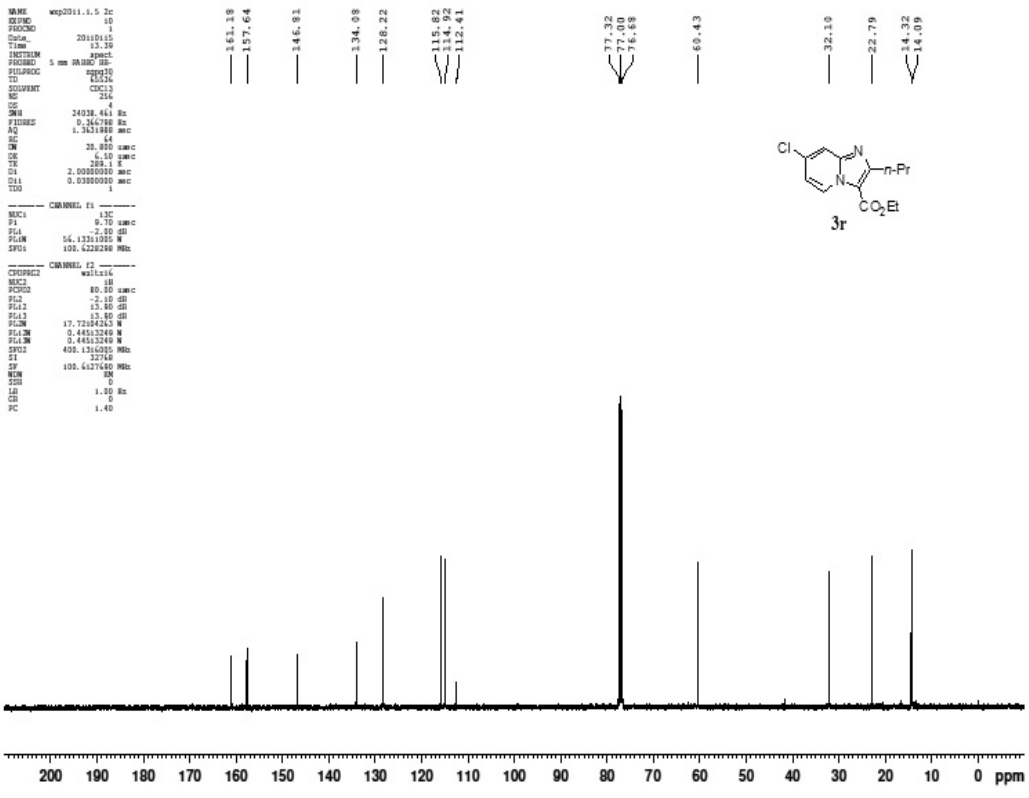

9.210
9.193
7.269
7.178
7.161
6.895
6.878
6.860
4.451
4.433
4.415
4.398
3.107
3.087
3.068
2.637
1.832
1.813
1.794
1.780
1.775
1.756
1.737
1.460
1.442
1.424
1.047
1.029
1.010
-0.000
Me
n-Pr
CO2Et
3p
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.94
0.93
0.94
1.97
1.95
2.95
2.11
3.00
2.99

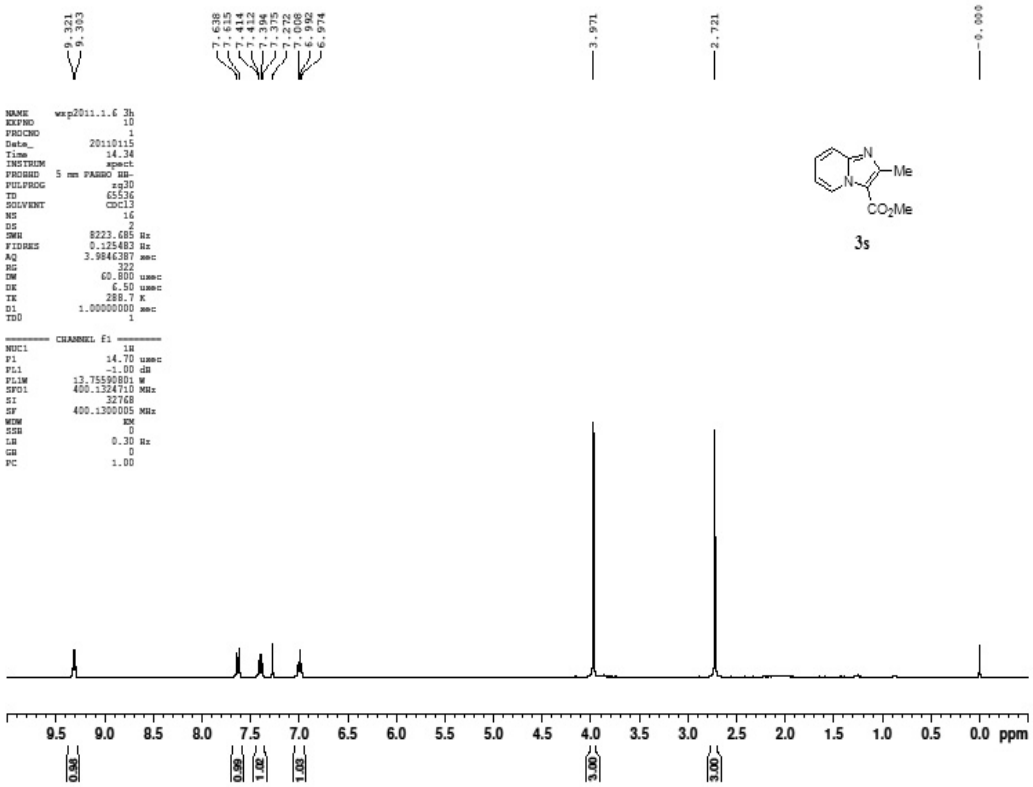

161.56
156.45
147.15
126.58
125.51
125.83
113.49
112.47
77.32
77.00
76.68
60.13
32.43
23.49
17.14
14.36
14.24
Me
n-Pr
CO2Et
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

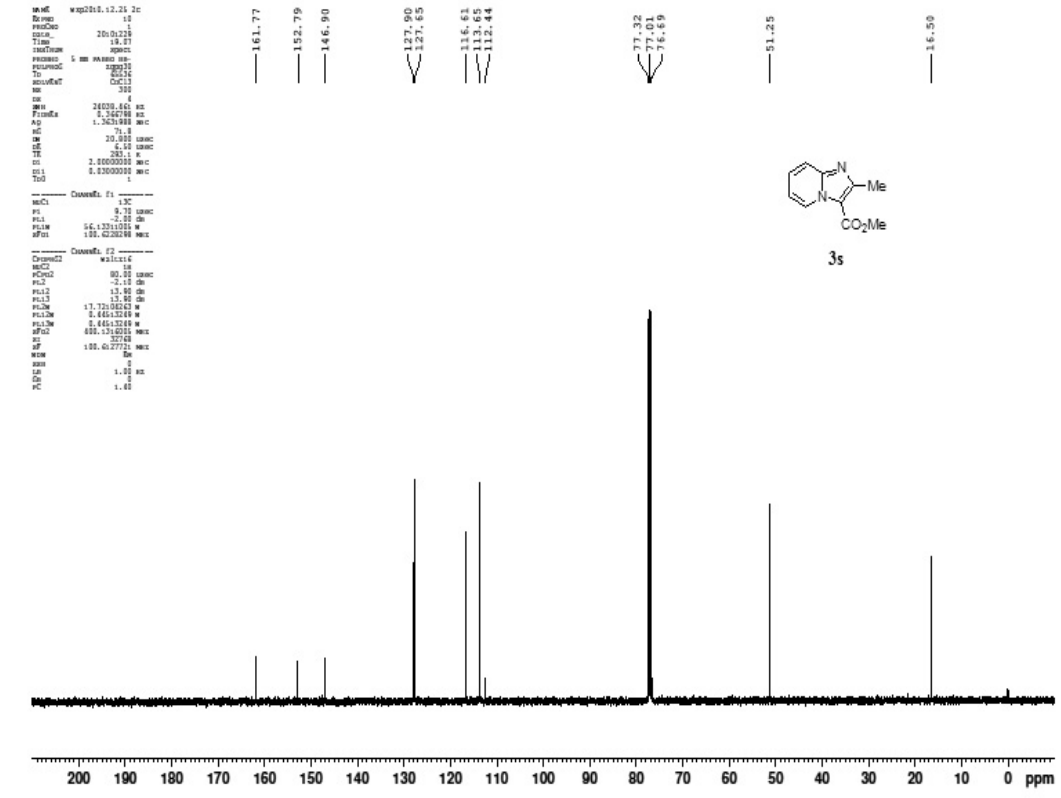

9.410
9.405
7.570
7.568
7.564
7.547
7.540
7.348
7.343
7.338
7.325
7.320
7.270
4.454
4.449
4.436
4.432
4.421
4.418
4.414
4.401
3.067
3.062
3.047
3.028
1.812
1.808
1.793
1.774
1.755
1.453
1.448
1.435
1.431
1.417
1.020
1.016
1.002
0.997
0.983
-0.013
-0.016
-0.021
n-Pr
CO2Et
3q
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.00
1.07
1.00
2.18
2.21
2.22
3.29
3.30

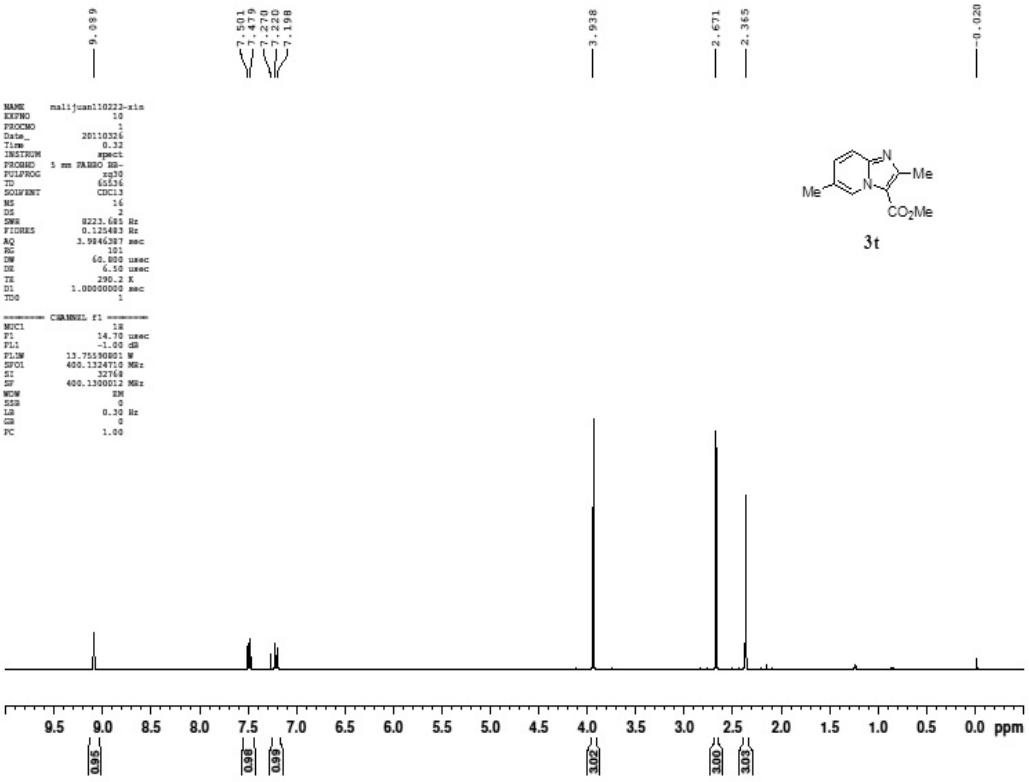

161.15
157.31
145.18
128.65
126.04
121.93
116.97
112.68
77.32
77.00
76.68
60.51
32.10
22.77
14.31
14.09
n-Pr
CO2Et
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

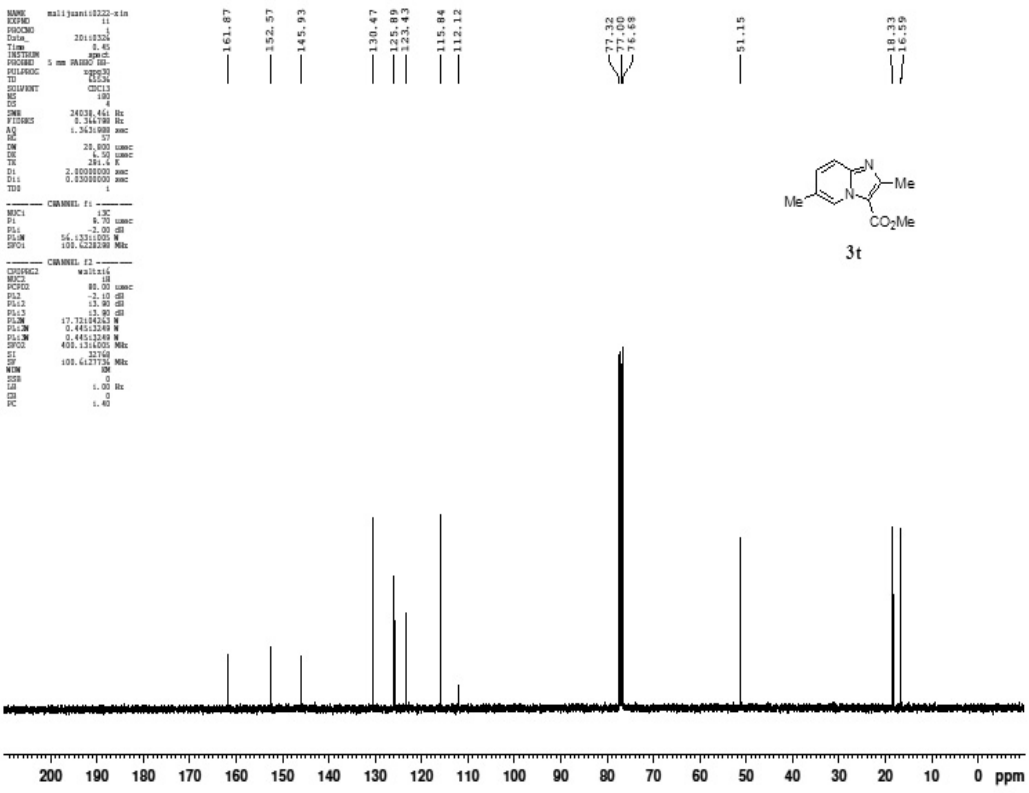

9.258
9.240
7.603
7.598
7.270
6.950
6.945
6.932
6.927
4.441
4.423
4.405
4.388
3.060
3.041
3.021
1.823
1.805
1.786
1.767
1.748
1.730
1.444
1.426
1.409
1.017
0.998
0.980
-0.018
Cl
N
n-Pr
CO2Et
3r
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
0.92
0.97
1.98
2.00
2.02
3.00
3.02

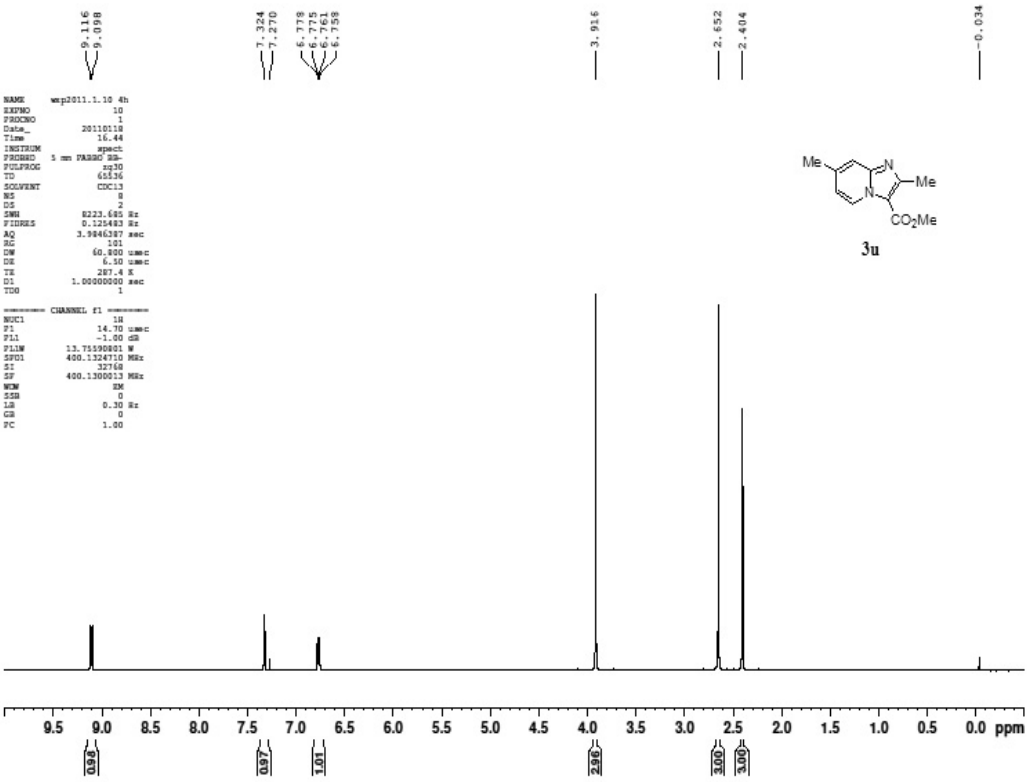

161.18
157.64
146.91
134.09
128.22
115.82
114.52
112.41
77.32
77.00
76.68
60.43
32.10
22.79
14.32
14.09
Cl
N
n-Pr
CO2Et
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

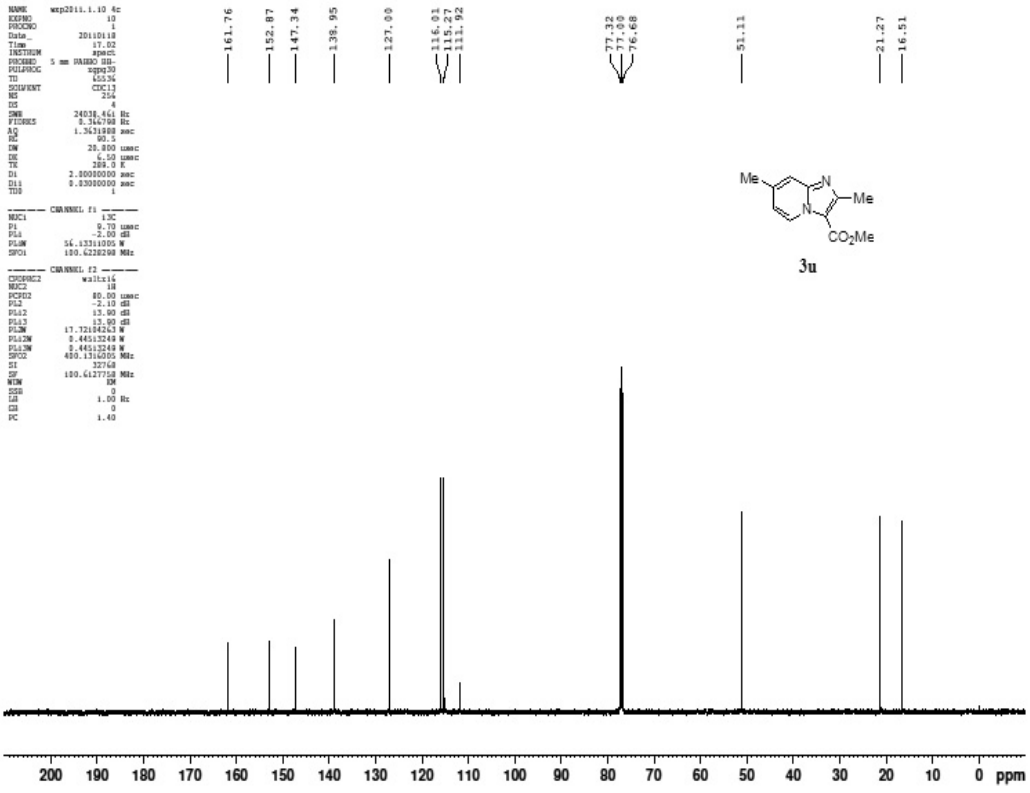

9.321
9.303
7.638
7.635
7.414
7.412
7.394
7.375
7.272
7.008
6.992
6.974
3.971
2.721
0.000
Me
CO2Me
3s
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
0.99
1.02
1.03
3.00
3.00

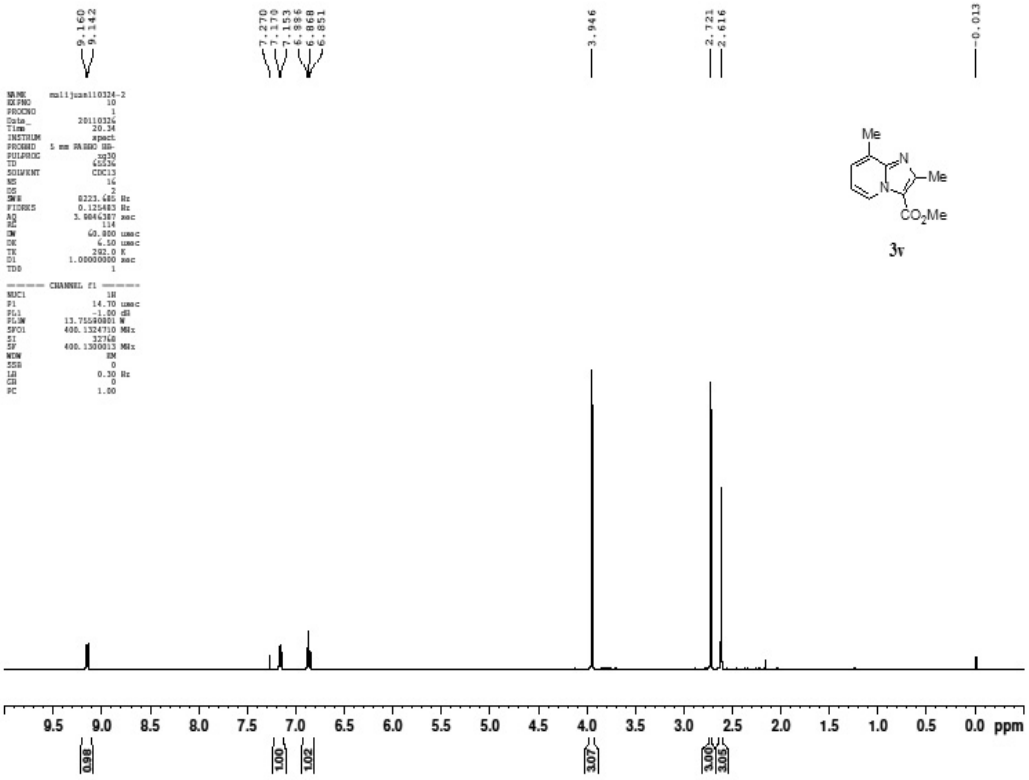

161.77
152.79
146.90
127.90
127.65
116.61
115.45
112.44
77.32
77.01
76.69
51.25
16.59
Me
CO2Me
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

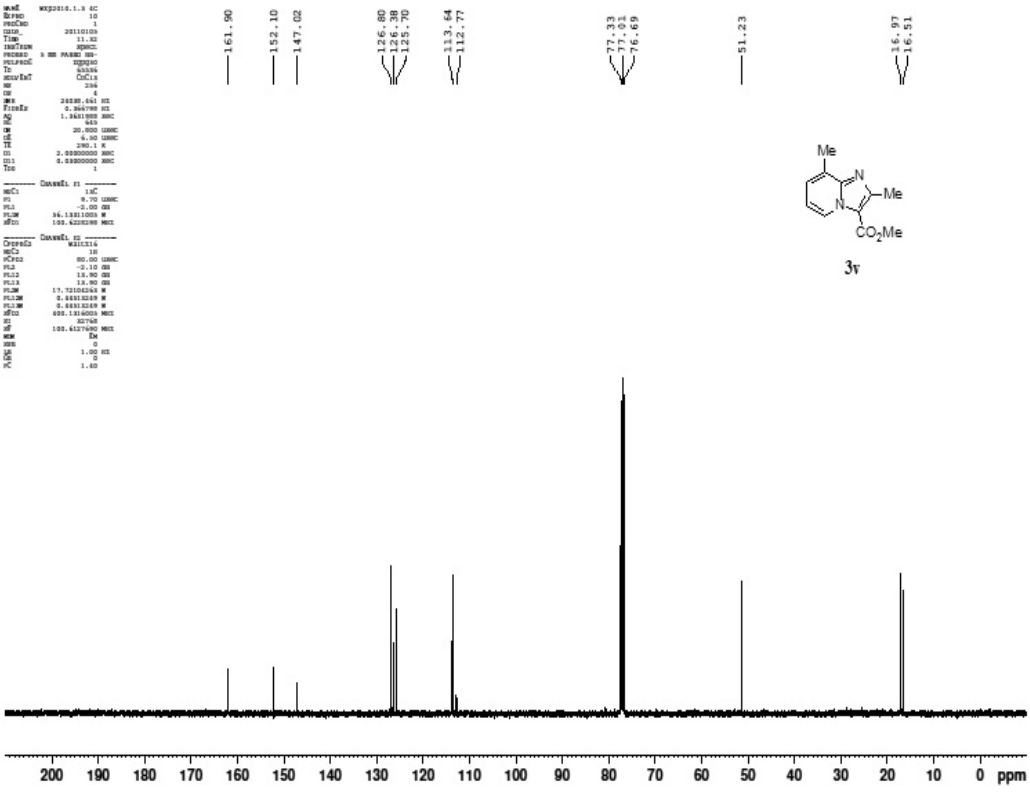

9.069
7.501
7.479
7.270
7.220
7.198
3.938
2.671
2.365
0.020
Me
Me
N
N
CO2Me
3t
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
0.98
0.99
3.02
3.00
3.03

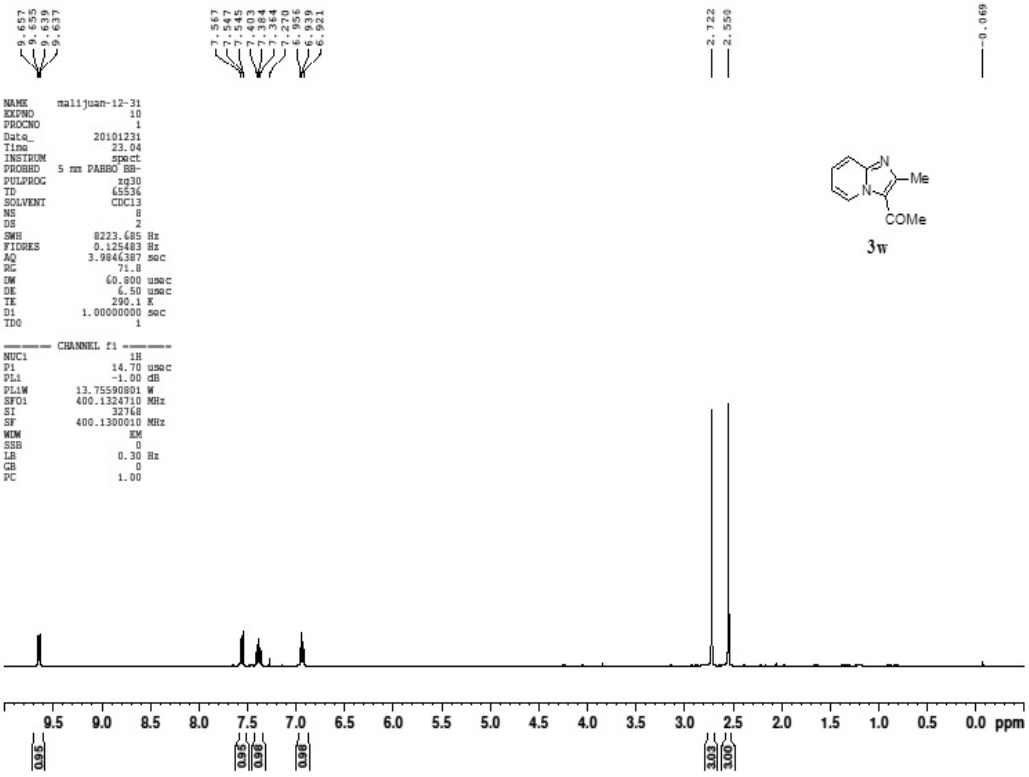

161.87
152.57
145.93
130.47
125.89
123.43
115.84
112.12
77.32
77.00
76.68
51.15
18.33
16.59
Me
Me
N
N
CO2Me
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

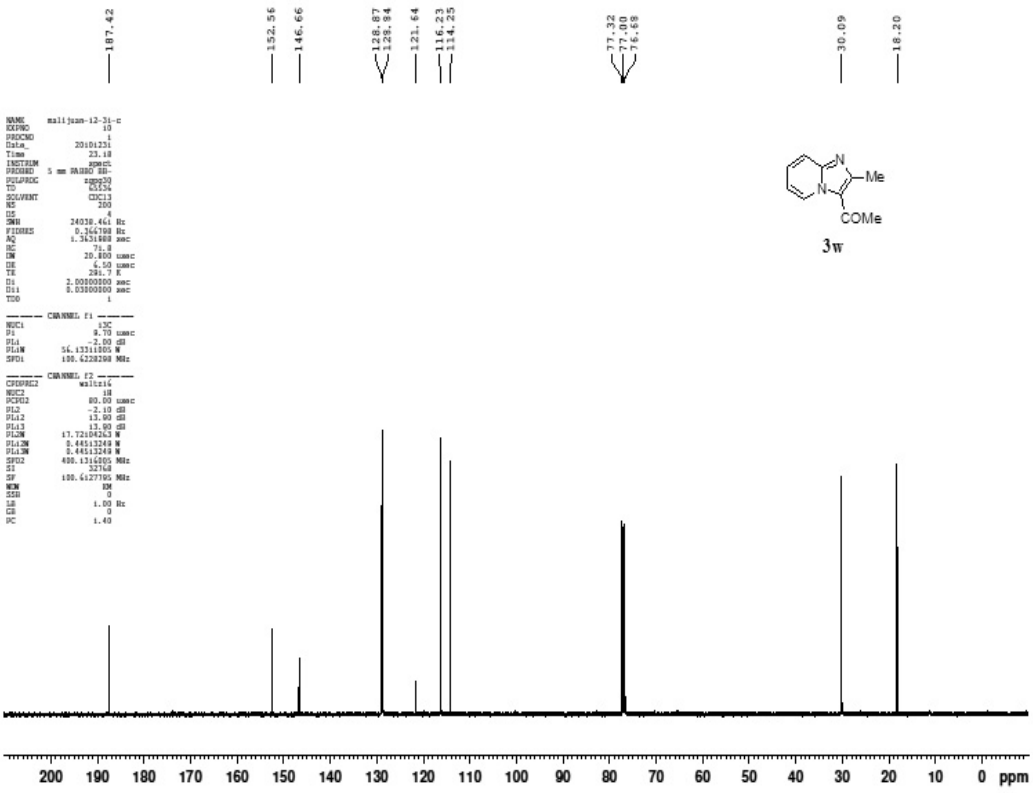

9.116
9.098
7.324
7.270
6.778
6.775
6.761
6.758
3.916
2.652
2.404
-0.034
Me
N
Me
N
CO2Me
3u
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
0.97
1.01
2.96
3.00
3.00

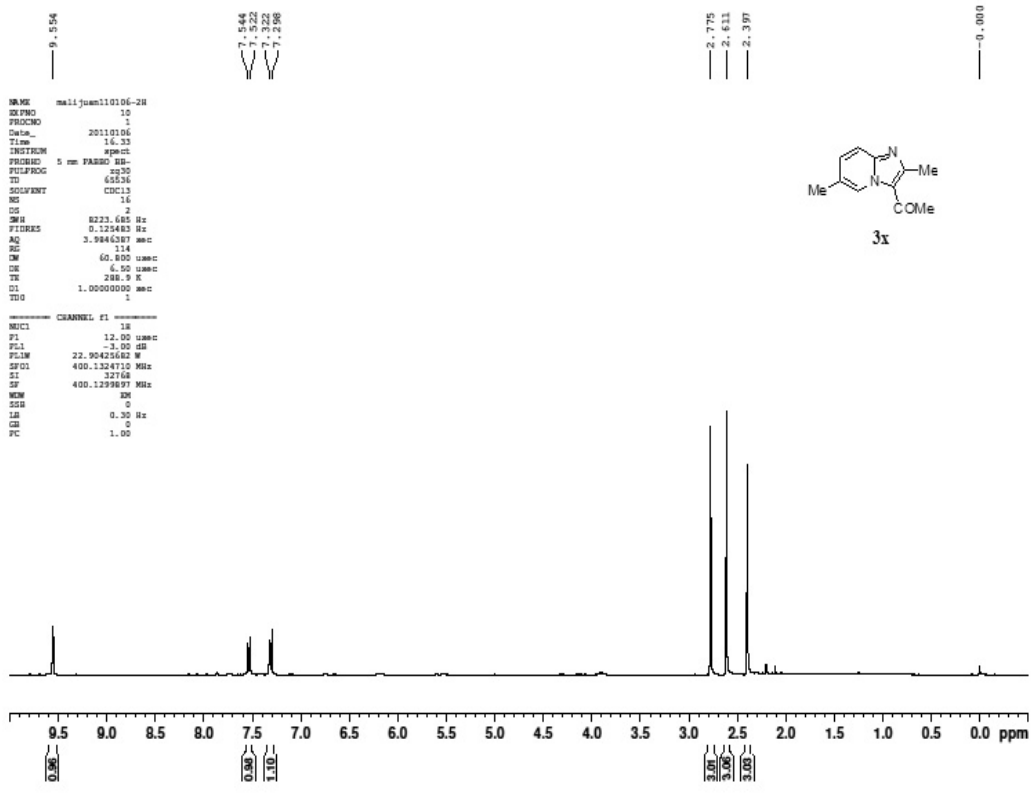

161.76
152.87
147.34
138.95
127.00
116.01
115.27
113.92
77.32
77.00
76.68
51.11
21.27
16.51
Me
N
Me
N
CO2Me
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

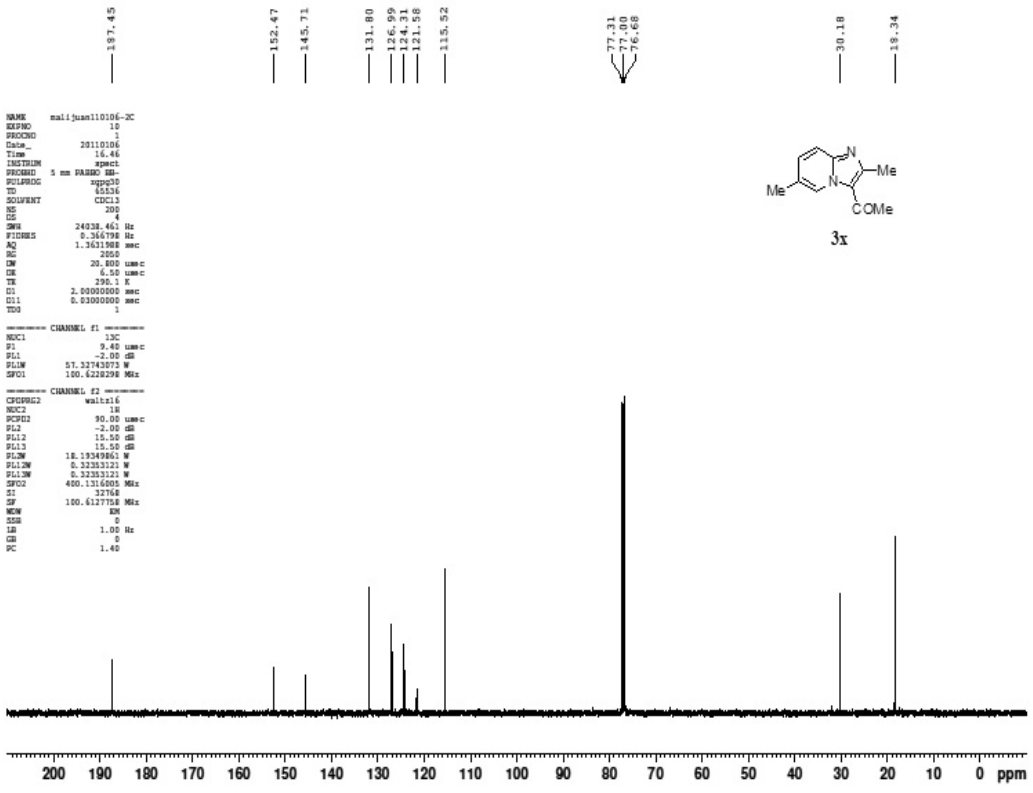

9.160
9.142
7.270
7.170
7.153
6.886
6.868
6.851
3.946
2.721
2.616
0.013
Me
N
Me
N
CO2Me
3v
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
1.00
1.02
3.07
3.00
3.05

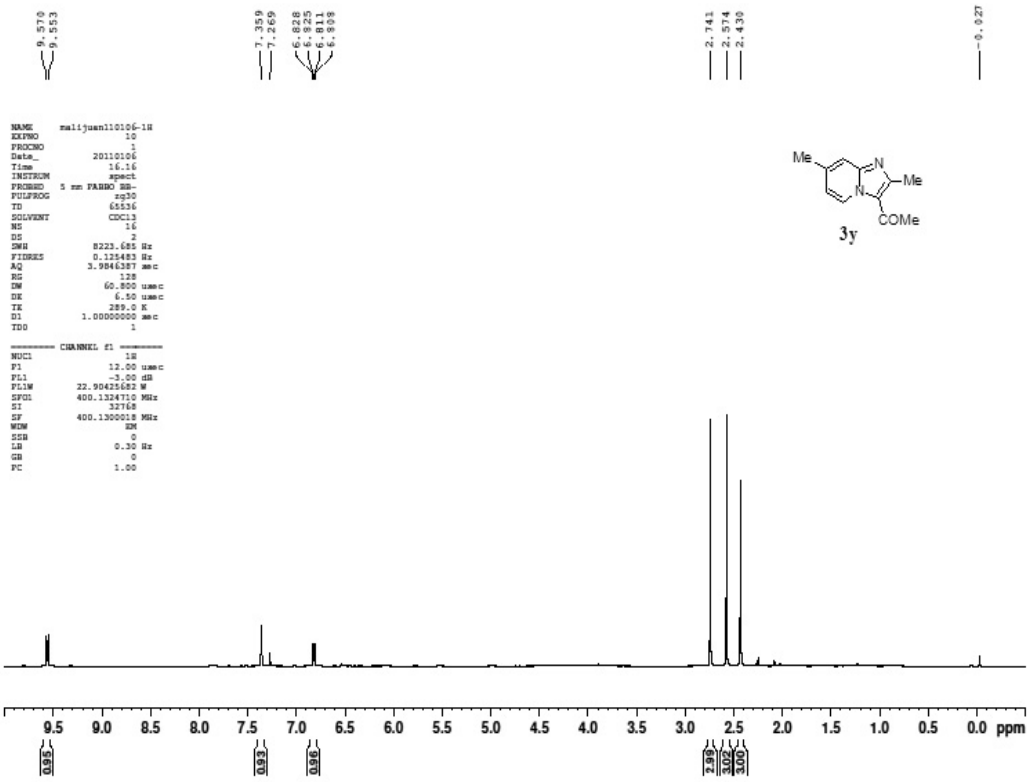

161.90
152.10
147.02
126.80
126.38
125.70
113.64
112.77
77.33
77.01
76.69
51.23
16.97
16.51
Me
N
Me
N
CO2Me
3v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

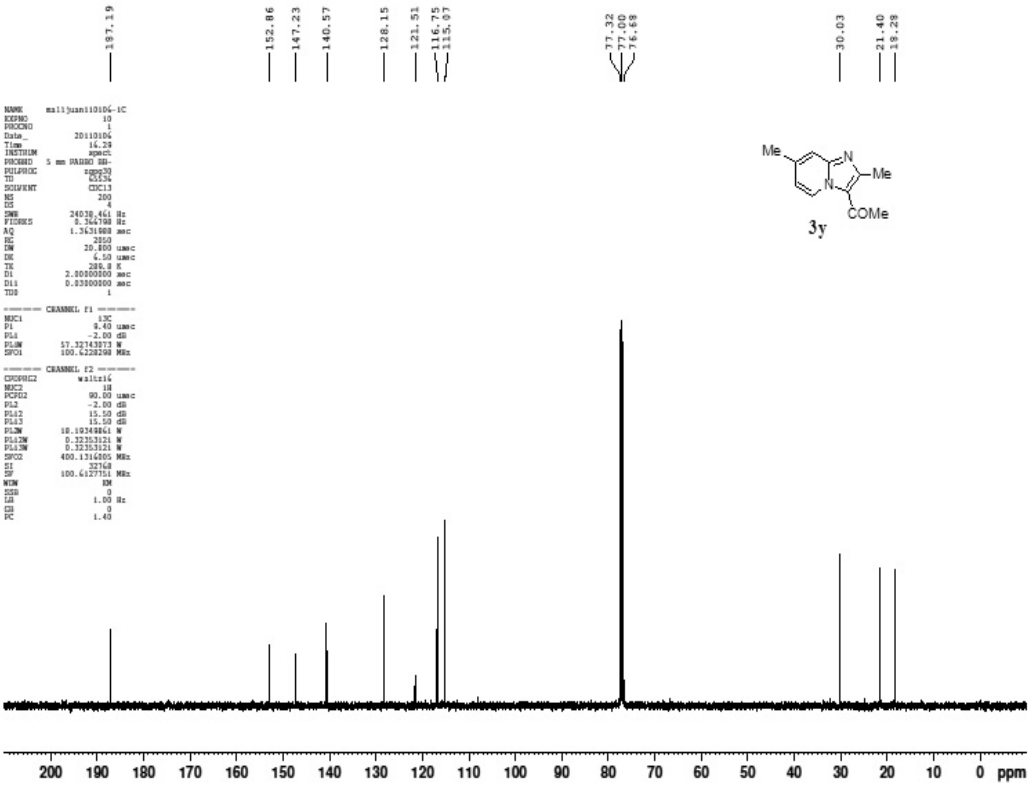

9.657
9.655
9.639
9.637
7.567
7.547
7.445
7.403
7.384
7.364
7.270
6.956
6.939
6.921
2.722
2.550
0.069
Me
COMe
3w
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
0.95
0.98
0.98
3.03
3.00

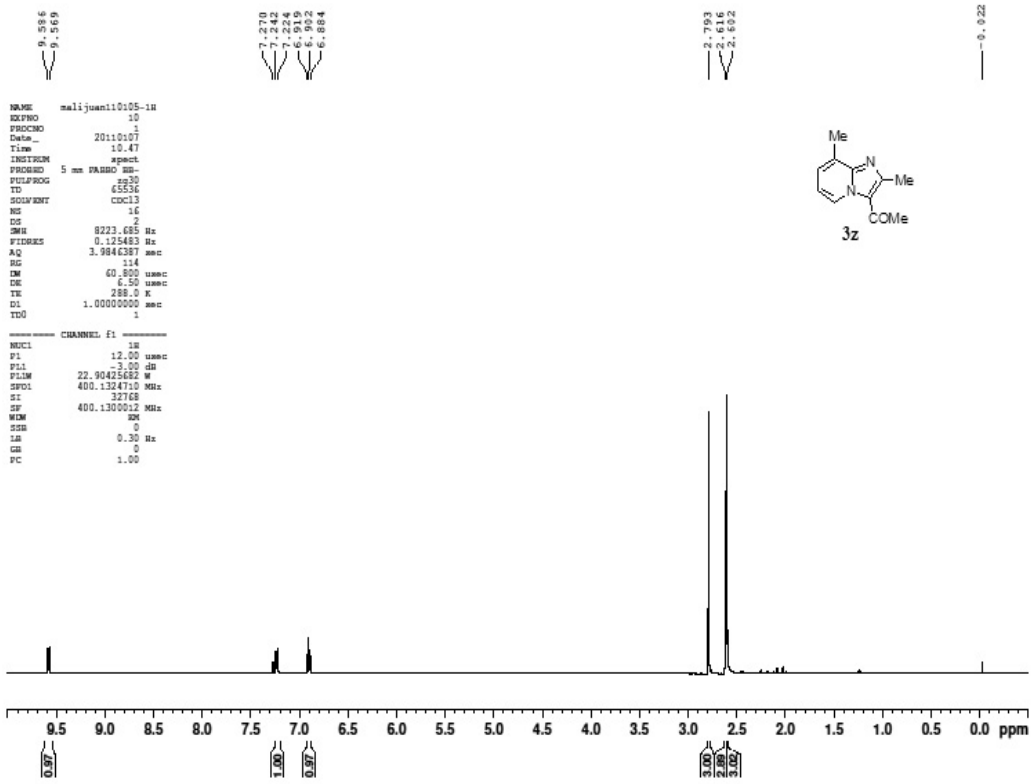

187.42
152.56
146.66
128.87
128.84
121.64
116.23
114.25
77.32
77.00
76.68
30.09
18.20
Me
COMe
3w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

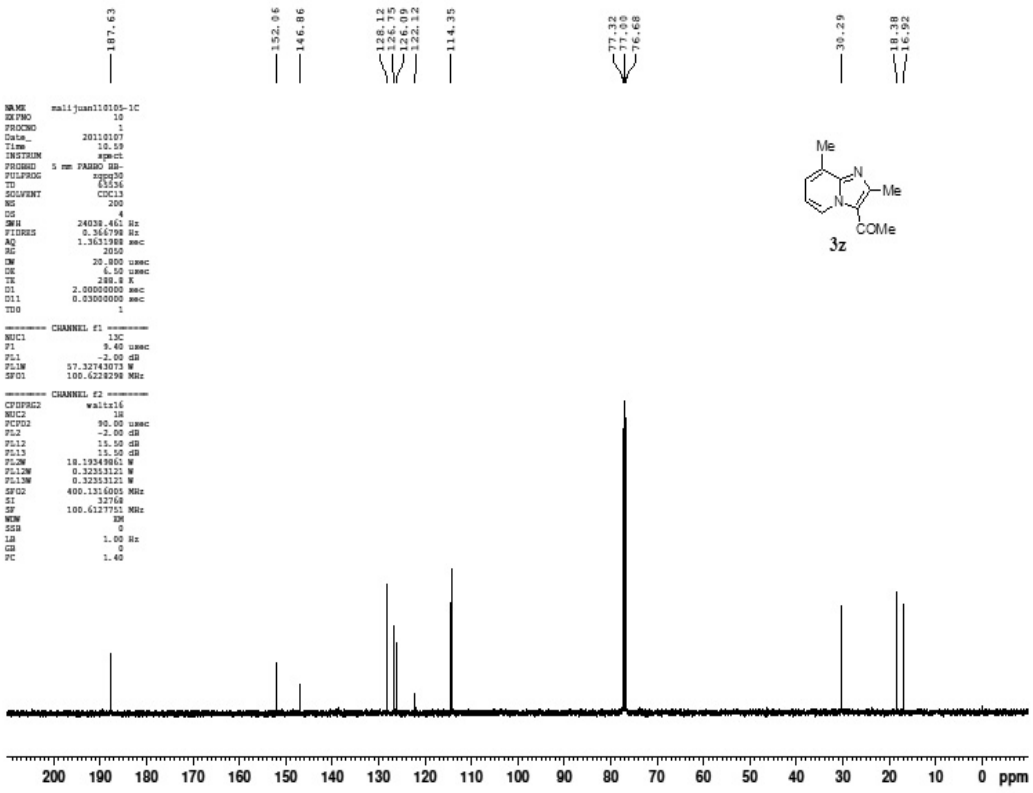

9.554
7.544
7.322
7.298
2.775
2.611
2.397
-0.000
Me
Me
COMe
3x
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.96
0.98
1.10
3.01
3.06
3.03


197.45
152.47
145.71
131.80
126.99
124.31
121.58
115.52
77.31
77.00
76.68
30.18
19.34
Me
Me
COMe
3x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.570
9.553
7.359
7.269
6.828
6.825
6.811
6.808
2.741
2.574
2.430
-0.027
Me
N
Me
N
COMe
3y
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.95
0.93
0.96
2.99
3.02
3.06


197.19
152.86
147.23
140.57
128.15
121.51
116.75
115.07
77.32
77.00
76.68
30.03
21.40
19.28
Me
N
Me
N
COMe
3y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


9.586
9.569
7.270
7.242
7.224
6.919
6.902
6.884
2.793
2.616
2.602
-0.022
Me
N
Me
N
COMe
3z
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.97
1.00
0.97
3.00
2.88
3.02


187.63
152.96
146.86
128.12
126.75
126.09
122.12
114.35
77.32
77.00
76.68
30.29
18.38
16.92
Me
N
Me
N
COMe
3z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm