Palladium(II)-Catalyzed Intermolecular Oxidative C-3 Alkenylations of Imidazo[1,2-a] pyridines by Substrate-Contolled Regioselective C-H Functionalization

Hua Cao,* Sai Lei, Jinqiang Liao, Jianping Huang, HuifangQiu, Qinlin Chen，Shuxian Qiu and Yaoyi Chen

[a]*School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou 510006, P.R. of China;*

[b] *BASF Catalyst, 23800 mercantile road, beachwood, ohio, 44124*

E-mail: caohua@gdpu.edu.cn,

Supporting Information

List of Contents

A. General method

All reactions were performed for synthesis of products at 120 ℃ in a round bottom flask equipped with magnetic stir bar. All the chemicals were purchased from Alfa Aesar and Acros Chemical, and used without further purification. NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 M Hz for carbon) and respectively referenced to 7.26 and 77.0 ppm for chloroform-d solvent with TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS–QP5050A at an ionization voltage of 70eV equipped with a DB–WAX capillary column (internal diameter = 0.25 mm, length = 30 m). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

B. General Procedure

Synthesis of 3a according to the following procedure:

2-methylimidazo[1,2-a]pyridine (**1a** 0.5 mmol), styrene (**2a** 2.5 mmol), 5 mol% $Pd(OAc)_2$, 5 mol% $AgCO_3$, AcOH (0.5 mol) and Ac_2O (0.5 mol) were added in dioxane (3 mL) at room temperature. And then the mixture was stirred at 120 ℃under oxygen atmosphere (with oxygen balloon 500 mL) for 24 h . After completion of the reaction, water (8 mL) was added. The aqueous solution was extracted with diethyl ether (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the crude product was separated by column hromatography (eluted with petroleum ether : ethyl acetate=2:1) to give a pure sample of **4a**.

General procedure for the synthesis of 4a:

2-methylimidazo[1,2-a]pyridine (**1a** 0.5 mmol), butyl acrylate (**2a** 2.5 mmol), 5 mol% $Pd(OAc)_2$, 5 mol% $AgCO_3$, AcOH (0.5 mol) and Ac_2O (0.5 mol) were added in dioxane (3 mL) at room temperature. And then the mixture was stirred at 120 ℃ under oxygen atmosphere (with

oxygen balloon 500 mL) for 24 h . After completion of the reaction, water (8 mL) was added. The aqueous solution was extracted with diethyl ether (3×15 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the crude product was separated by column hromatography (eluted with petroleum ether: ethyl acetate=2:1) to give a pure sample of **3a**.

C. Analytical data

3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.28-7.36 (m, *5*H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 5.77 (s, 1H),5.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 137.2, 133.5, 128.9, 128.7, 127.0, 125.1, 117.7, 117.6, 112.5. ESI-MS m/z (%) 201 (100) $[M+H]^+$. Anal. Calcd for $C_{15}H_{12}N_2$:C, 69.74; H, 7.02; N, 12.72; Found: C, 81.66; H, 5.45; N, 12.81;

7-methyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3b): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.28-7.35 (m, *5*H), 6.51 (t, *J* = 6.8 Hz, 1H), 5.72 (s, 1H), 5.58 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 138.3, 137.3, 133.0, 128.8, 128.6, 127.0, 124.3, 117.0, 116.6, 115.2, 21.2. ESI-MS m/z (%) 235 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{14}N_2$:C, 82.02; H, 6.02; N, 11.96; Found: C, 82.10; H, 6.00; N, 11.91;

8-methyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3c): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.49 (d, *J* = 6.8 Hz, 1H), 7.28-7.35 (m, *5*H), 6.96 (d, *J* = 6.8 Hz, 1H), 6.57 (d, *J* = 6.8 Hz, 1H), 5.74 (s, 1H), 5.59 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.7, 133.4, 128.8, 128.6, 128.5, 127.6, 127.0, 123.1, 122.9, 117.7, 112.2, 17.0. ESI-MS m/z (%) 235 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{14}N_2$:C, 82.02; H, 6.02; N, 11.96; Found: C, 82.12; H, 5.99; N, 11.69;

6-methyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3d): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.42 (s, 1H), 7.29-7.36 (m, *5*H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.77 (s, 1H), 5.59 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.3, 133.1, 128.8, 128.6, 128.1, 127.0, 122.7, 117.7, 117.0, 18.3. ESI-MS m/z (%) 235 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{14}N_2$:C, 82.02; H, 6.02; N, 11.96; Found: C, 82.09; H, 6.05; N, 11.92;

3-(1-(4-fluorophenyl)vinyl)imidazo[1,2-a]pyridine(3e): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.18-7.31 (m, 4H), 7.02-7.06 (m, 2H), 6.72 (t, *J* = 6.8 Hz, 1H), 5.72 (s, 1H), 5.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (*J* = 247.1 Hz), 148.8, 136.2, 134.3, 131.2, 129.5, 128.8, 128.7, 125.0, 117.7 (*J* = 49.1 Hz), 116.0, 115.6(*J* = 43.6 Hz), 112.7. ESI-MS m/z (%) 239 (100) $[M+H]^+$. Anal. Calcd for $C_{15}H_{11}FN_2$:C, 75.62; H, 4.65; N, 11.76; Found: C, 75.53; H, 4.67; N, 11.71;

3-(1-(4-fluorophenyl)vinyl)-7-methylimidazo[1,2-a]pyridine(3f): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.41 (s, 1H), 7.28-7.31 (m, 2H), 7.01-7.06 (m, 2H), 6.51 (d, *J* = 7.2 Hz, 1H), 5.64 (s, 1H), 5.55 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (*J* = 246.9

Hz), 136.5, 135.5, 134.7, 133.9, 129.9, 129.8, 128.9, 128.8, 124.1, 116.3, 115.8, 115.0, 21.2. ESI-MS m/z (%) 253 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{13}FN_2$:C, 76.17; H, 5.19; N, 11.10; Found: C, 76.29; H, 5.16; N, 11.05;

3-(1-(4-fluorophenyl)vinyl)-8-methylimidazo[1,2-a]pyridine(3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.25-7.28 (m, 2H), 6.96-7.04 (m, 3H), 6.60 (t, *J* = 7.2 Hz, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (*J* = 246.7 Hz), 146.7, 136.6, 133.5, 129.9, 128.8, 128.7, 127.7, 123.2, 122.8, 116.7, 115.8, 112.3, 17.0. ESI-MS m/z (%) 253 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{13}FN_2$:C, 76.17; H, 5.19; N, 11.10; Found: C, 76.26; H, 5.21; N, 11.06;

3-(1-(4-fluorophenyl)vinyl)-6-methylimidazo[1,2-a]pyridine(3h): ^{1}H NMR (400 MHz, $CDCl_3$): δ7.60 (d, *J* = 6.8 Hz, 1H), 7.56 (s, 1H), 7.44 (s, 1H), 7.27-7.30 (m, 2H), 7.01-7.05 (m, 3H), 5.69 (s, 1H), 5.56 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (*J* = 246.7 Hz), 145.4, 136.5, 134.7, 133.9, 131.2, 128.8, 128.7, 127.7, 124.4, 122.5, 122.0, 117.2, 116.6, 115.8, 18.3. ESI-MS m/z (%) 253 (100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{13}FN_2$:C, 76.17; H, 5.19; N, 11.10; Found: C, 76.29; H, 5.17; N, 11.05;

3-(1-(4-tert-butylphenyl)vinyl)imidazo[1,2-a]pyridine(3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.71 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.16-7.24 (m, 3H), 6.70 (t, *J* = 6.8 Hz, 1H), 5.77(s, 1H), 5.56(s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 137.0, 135.2, 128.6, 126.6, 125.7, 125.2, 117.7, 116.7, 112.3, 34.6, 31.29. ESI-MS m/z (%) 277 (100) $[M+H]^+$. Anal. Calcd for $C_{19}H_{20}N_2$:C, 82.57; H, 7.29; N, 10.14; Found: C, 82.46; H, 7.32; N, 10.20;

3-(1-(4-tert-butylphenyl)vinyl)-7-methylimidazo[1,2-a]pyridine(3j): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.42 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 6.8 Hz, 1H), 5.70 (s, 1H), 5.52 (s, 1H),2.37 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ151.8, 137.2, 135.5, 135.3, 133.6, 126.7, 125.7, 124.3, 116.2, 116.0, 114.8, 34.6, 31.3, 21.2. ESI-MS m/z (%) 291 (100) $[M+H]^+$. Anal. Calcd for $C_{20}H_{22}N_2$:C, 82.72; H, 7.64; N, 9.65; Found: C, 82.61; H, 7.67; N, 9.71;

3-(1-(4-tert-butylphenyl)vinyl)-5-methylimidazo[1,2-a]pyridine(4k): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 6.8 Hz, 1H), 5.73 (s, 1H), 5.53 (s, 1H), 2.64 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 137.3, 135.5, 133.4, 127.6, 126.7, 125.7, 123.0, 116.4, 112.1, 34.6, 31.3, 17.0. ESI-MS m/z (%) 291 (100) $[M+H]^+$. Anal. Calcd for $C_{20}H_{22}N_2$:C, 82.72; H, 7.64; N, 9.65; Found: C, 82.63; H, 7.62; N, 9.70;

3-(1-(4-chlorophenyl)vinyl)imidazo[1,2-a]pyridine(3l): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.15-7.25 (m, 4H), 6.69 (t, *J* = 6.8 Hz, 1H), 5.73 (s, 1H), 5.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 136.9, 136.4, 134.3, 129.4, 129.0, 128.8, 128.3, 124.8, 124.4, 118.0, 117.4, 112.4. ESI-MS m/z (%) 255 (100) $[M+H]^+$. Anal. Calcd for $C_{15}H_{11}ClN_2$:C, 70.73; H, 4.35; N, 11.00; Found: C, 70.64; H, 4.37; N, 11.06;

3-(1-(4-chlorophenyl)vinyl)-8-methylimidazo[1,2-a]pyridine(3m): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 5.73 (s, 1H), 5.60 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 146.7, 137.0, 136.6, 134.5, 133.5, 129.0, 128.3, 127.7, 123.3, 122.7, 117.4, 112.4, 17.0. ESI-MS m/z (%) 269(100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{13}ClN_2$:C, 71.51; H, 4.88; N, 10.42; Found: C, 71.59; H, 4.90; N, 10.35;

3-(1-(4-chlorophenyl)vinyl)-7-methylimidazo[1,2-a]pyridine(3n): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 6.8 Hz, 1H), 5.70 (s, 1H), 5.59 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 136.9, 136.2, 134.6, 133.4, 129.4, 129.0, 128.8, 128.3, 124.1, 116.2, 115.4, 21.2. ESI-MS m/z (%) 269(100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{13}ClN_2$:C, 71.51; H, 4.88; N, 10.42; Found: C, 71.60; H, 4.85; N, 10.37;

2-methyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3o): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.24-7.33 (m, 5H), 7.12 (t, *J* = 6.8 Hz, 1H), 6.59 (t, *J* = 6.8 Hz, 1H), 5.98 (s, 1H), 5.49 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 144.2, 138.3, 137.2, 128.9, 128.5, 126.5, 124.5, 124.1, 119.0, 116.6, 111.6, 14.0. ESI-MS m/z (%) 235(100) $[M+H]^+$. Anal. Calcd for $C_{16}H_{14}N_2$:C, 82.02; H, 6.02; N, 11.96; Found: C, 82.15; H, 5.99; N, 11.90;

2,7-dimethyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3p): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.37 (m, 7H), 6.41 (t, *J* = 6.8 Hz, 1H), 5.94 (s, 1H), 5.47 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 144.2, 138.5, 137.3, 135.2, 128.8, 128.5, 126.6, 123.8, 118.6, 115.1, 114.3, 21.2, 13.9. ESI-MS m/z (%) 249 (100) $[M+H]^+$. Anal. Calcd for $C_{17}H_{16}N_2$:C, 82.22; H, 6.49; N, 11.28; Found: C, 82.10; H, 5.96; N, 11.37;

2,8-dimethyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3q): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.39 (m, 6H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.50 (t, *J* = 6.8 Hz, 1H), 5.98 (s, 1H), 5.48 (s, 1H), 2.62 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 141.7, 138.4, 137.5, 128.8, 128.4, 126.5, 126.3, 123.1, 122.5, 119.0, 111.6, 17.1, 14.0. ESI-MS m/z (%) 249 (100) $[M+H]^+$. Anal. Calcd for $C_{17}H_{16}N_2$:C, 82.22; H, 6.49; N, 11.28; Found: C, 82.15; H, 5.99; N, 11.32;

2-phenyl-3-(1-phenylvinyl)imidazo[1,2-a]pyridine(3r): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.95 (m, 2H), 7.63-7.70 (m, 2H), 7.31-7.39 (m, 7H), 7.12-7.19 (m, 2H), 6.67 (d, *J* = 6.8 Hz, 1H), 6.16 (s, 1H), 5.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 132.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 127.6, 127.2, 126.2, 124.7, 121.4, 117.3, 112.2. ESI-MS m/z (%) 249 (100) $[M+H]^+$. Anal. Calcd for $C_{21}H_{16}N_2$:C, 85.11; H, 6.44; N, 9.45; Found: C, 85.00; H, 6.47; N, 9.51;

(2*E*)-butyl 3-(2-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 16.1 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 9.7 Hz, 1H), 6.96 (s, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 4.25 (s, 2H), 2.63 (s, 3H), 1.76 – 1.67 (m, 2H), 1.51 – 1.42(m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 146.4, 129.0, 126.2, 124.3, 117.4, 113.5, 112.8, 64.5, 39.9, 19.2, 15.6, 13.8. ESI-MS m/z (%) 259 (100) $[M+H]^+$. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84; Found: C, 69.63; H, 7.05; N, 10.90;

(2*E*)-methyl 3-(2-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4b): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 16.1 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 3.84 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 146.2, 129.2, 126.3, 124.3, 117.4, 113.6, 112.3, 51.8, 15.7. ESI-MS m/z (%) 217 (100) $[M+H]^+$. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.56; H, 5.56; N, 13.04;

(2*E*)-ethyl 3-(2-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4c): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 16.1 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.36 – 7.31 (m, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 146.3, 129.0, 126.4, 124.3, 117.4, 113.7, 113.1, 60.6, 15.6, 14.4. MS (EI) m/z (%): 230, 185, 158, 78, 51; ESI-MS m/z (%) 231 (100) $[M+H]^+$. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.95; H, 5.52; N, 12.97;

(2*E*)-butyl 3-(2,5-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4d): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 6.22 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.59 (s, 3H), 2.39 (s, 3H), 1.76 – 1.69 (m, 2H), 1.51 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 129.4, 129.0, 123.6, 122.2, 116.4, 112.5, 76.8, 64.4, 30.8, 19.2, 18.3, 15.3, 13.7. ESI-MS m/z (%) 273 (100) $[M+H]^+$. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29; Found: C, 70.42; H, 7.44; N, 10.35;

(2*E*)-methyl 3-(2,5-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4e): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.90 (d, *J* = 16.1 Hz, 1H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 9.0 Hz, 1H), 6.20 (d, *J* = 16.1 Hz, 1H), 3.82 (s, 3H), 2.57 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 145.3, 129.5, 129.3, 123.6, 122.2, 116.5, 112.0, 77.4, 77.1, 76.8, 51.7, 18.4, 15.4. ESI-MS m/z (%) 231 (100) $[M+H]^+$. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.70; H, 6.16; N, 12.24;

(2*E*)-ethyl 3-(2,5-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.89 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 9.1 Hz, 1H), 7.13 (q, *J* = 9.0 Hz, 1H), 6.19 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 2.37 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 129.3, 129.1, 123.5, 122.3, 116.5, 112.3, 60.5 (*J* = 36.4), 18.4, 15.6, 14.4. ESI-MS m/z (%) 245 (100) $[M+H]^+$. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47; Found: C, 68.70; H, 6.64; N, 11.54;

(2*E*)-butyl 3-(2,8-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4g): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 6.8 Hz, 1H), 7.92 (d, *J* = 16.1 Hz, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.85 (t, *J* = 6.9 Hz, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.62 (d, *J* = 9.8 Hz, 6H), 1.74 – 1.66 (m, 2H), 1.44 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 148.1, 146.7, 129.3, 127.3, 125.4, 122.2, 118.2, 113.5, 112.5, 64.5, 30.9, 19.2, 17.0, 15.6, 13.8. MS (EI) m/z (%): 280, 272, 199, 172, 159, 146, 103, 92, 63. ESI-MS m/z (%) 273 (100) $[M+H]^+$. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.04; N, 10.29; Found: C, 70.42; H, 7.07; N, 10.36;

(2*E*)-ethyl 3-(2,8-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4h): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 16.1 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 6.86 (t, *J* = 6.9 Hz, 1H), 6.22 (d, *J* = 16.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.62 (d, *J* = 10.2 Hz, 6H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 148.0, 146.6, 129.3, 127.3, 125.4, 122.1, 118.1, 113.5, 112.6, 60.5, 17.0, 15.6, 14.4. MS (EI) m/z (%): 244, 213, 207, 199, 197, 172, 169, 146, 102, 92, 85, 63; ESI-MS m/z (%) 245 (100) $[M+H]^+$. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47; Found: C, 68.72; H, 6.62; N, 11.54;

(2*E*)-butyl 3-(2,7-dimethyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4i):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.37 (s, 1H), 6.79 (d, *J* = 7.0 Hz, 1H), 6.18 (d, *J* = 16.1 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.60 (s, 3H), 2.44 (s, 3H), 1.71 (dt, *J* = 14.6, 6.8 Hz, 2H), 1.46 (q, *J* = 7.5 Hz, 2H), 0.98 (q, *J* =5.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 149.0, 146.9, 137.7, 129.1, 123.7, 116.1, 116.0, 111.6, 64.4, 30.9, 21.3, 19.2, 15.4, 13.8. ESI-MS m/z (%) 273 (100) $[M+H]^+$. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29; Found: C, 70.42; H, 7.43; N, 10.36;

Ethyl 3-((*E*)-2-(butoxycarbonyl)vinyl)-imidazo[1,2-a]pyridine-2-carboxylate(4j): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.37 (m, 2H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.04 (t, *J* = 6.9 Hz, 1H), 6.75 (d, *J* = 16.6 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.48 – 1.41 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 163.1, 146.0, 137.3, 129.1, 127.4, 125.3, 119.6, 119.4, 118.1, 64.8, 61.6, 30.7, 19.1, 14.3, 13.7. ESI-MS m/z (%) 317 (100) $[M+H]^+$. Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86; Found: C, 64.67; H, 6.39; N, 8.80;

(2*E*)-methyl 3-(7-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4k):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.99 (s, 1H), 7.89 (d, *J* = 16 Hz, 1H), 7.48 (s, 1H), 6.86 (d, *J* = 6.8 Hz, 1H), 6.38 (d, *J* = 16 Hz, 1H), 3.84 (s, 3H), 2.47 (s, 3H),. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6,137.7, 137.2, 128.9, 123.4, 117.1, 116.6, 112.8, 51.8, 21.3. ESI-MS m/z (%) 217 (100) $[M+H]^+$. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.54; H, 5.62; N, 13.02;

(2*E*)-ethyl 3-(7-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate (4l): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.98 (s, 1H), 7.88 (d, *J* = 16 Hz, 1H), 7.47 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 16 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3,137.6, 137.3, 128.7, 123.5, 117.0, 116.6, 113.2, 60.6, 21.3, 14.4. ESI-MS m/z (%) 231 (100) $[M+H]^+$. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.70; H, 6.16; N, 12.23;

(2*E*)-methyl 3-(8-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4m): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 6.8 Hz, 1H), 8.07 (s, 1H), 7.87 (d, *J* = 15.9 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 1H), 6.93 (t, *J* = 6.8 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 135.6, 128.8, 128.3, 125.7, 121.9, 114.2, 114.1, 51.8, 20.9, 16.9. ESI-MS m/z (%) 217 (100) $[M+H]^+$. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.52; H, 5.61; N, 13.04;

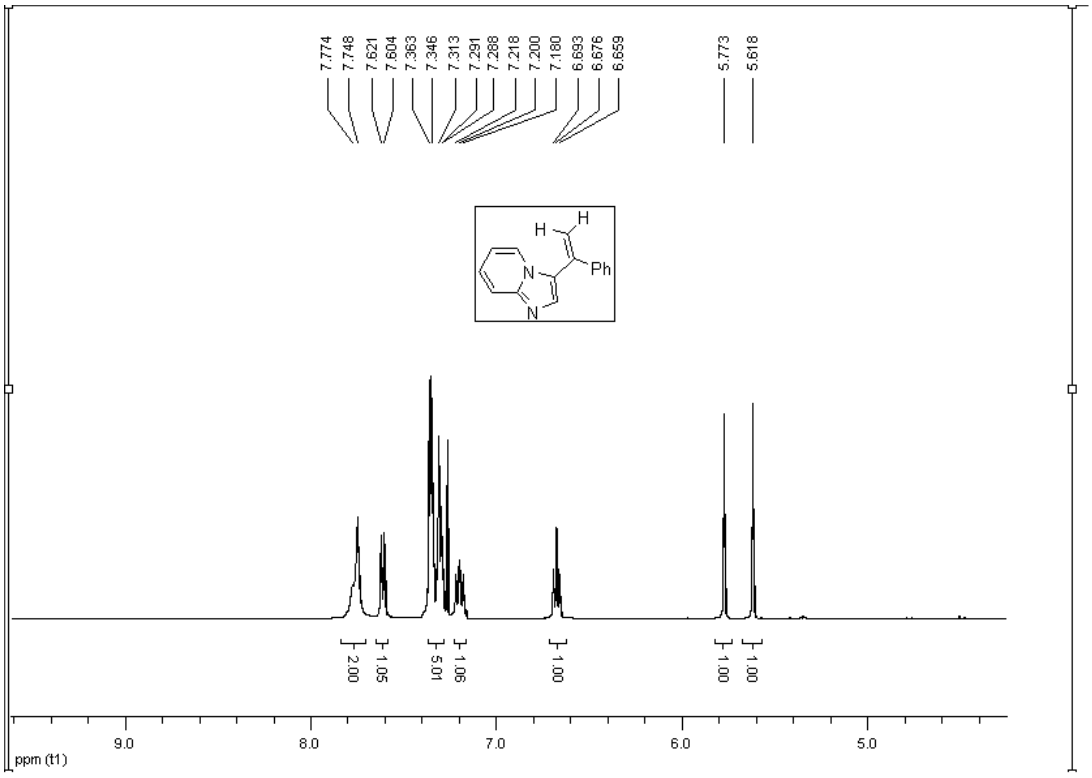
(2*E*)-ethyl 3-(8-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4l): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 6.7 Hz, 1H), 8.02 (s, 1H), 7.87 (d, *J* = 15.9 Hz, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 6.91 (t, *J* = 6.9 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.32 – 4.26 (m, 2H), 2.64 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 136.2, 128.8, 128.4, 125.2, 122.0, 114.7, 114.0, 60.6, 16.9, 14.4. ESI-MS m/z (%) 231 (100) $[M+H]^+$. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.68; H, 6.17; N, 12.26;

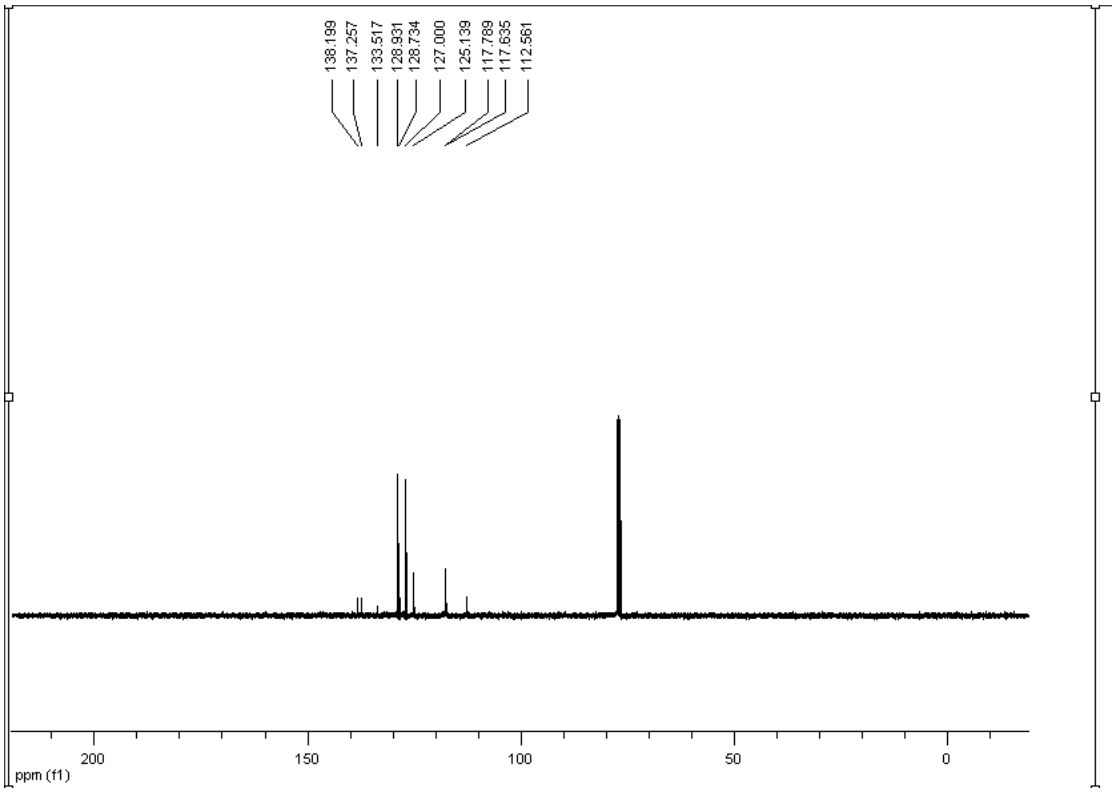
(2*E*)-butyl 3-(6-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4o): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.14 (d, *J* = 9.1 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 1.72 – 1.65 (m, 2H), 1.43 (q, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.45, 136.86, 129.21, 128.65, 123.86, 122.02, 117.70, 113.69, 64.53, 30.84, 19.22, 18.40, 13.77. MS (EI) m/z (%): 258, 202, 185, 158, 145, 92, 77, 51; ESI-MS m/z (%) 259 (100) $[M+H]^+$. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84;

Found: C, 69.62; H, 7.02; N, 10.91;

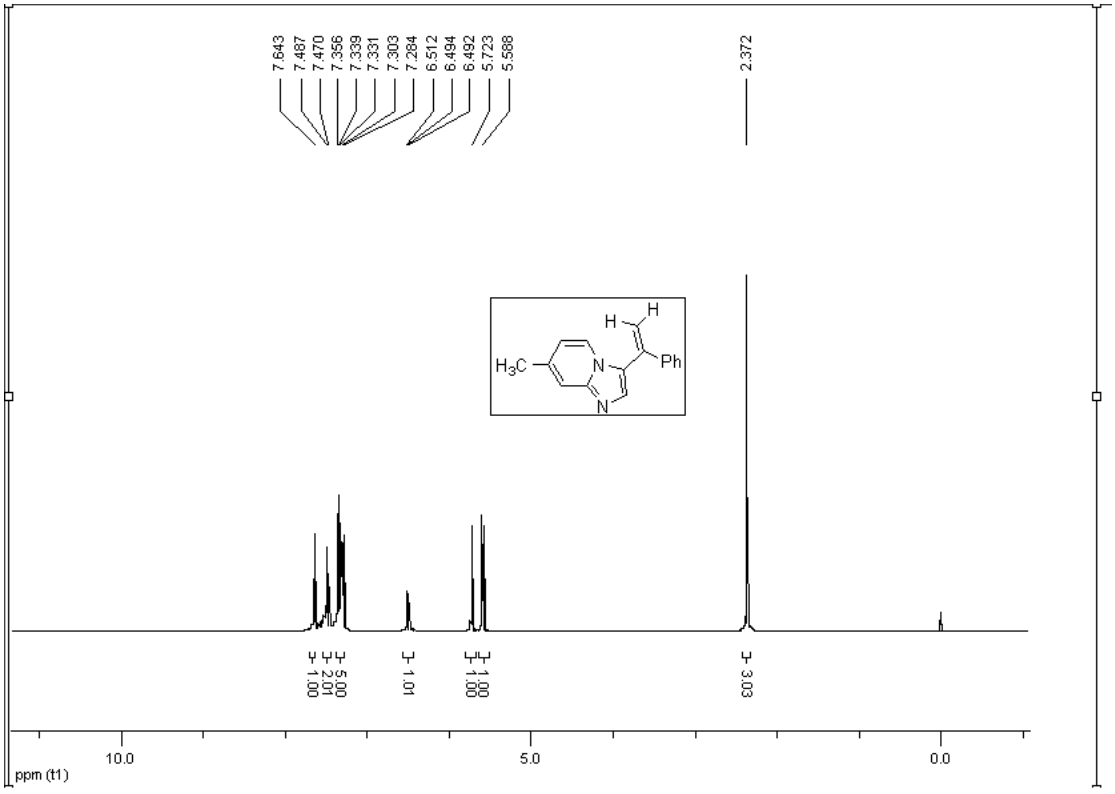
(2*E*)-methyl 3-(6-methyl-imidazo[1,2-a]pyridin-3-yl)acrylate(4p): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.02 (s, 1H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 136.0, 129.8, 128.7, 124.3, 122.0, 117.5, 113.8, 51.9, 18.4. ESI-MS m/z (%) 217 (100) $[M+H]^+$. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.74; H, 5.55; N, 12.88;

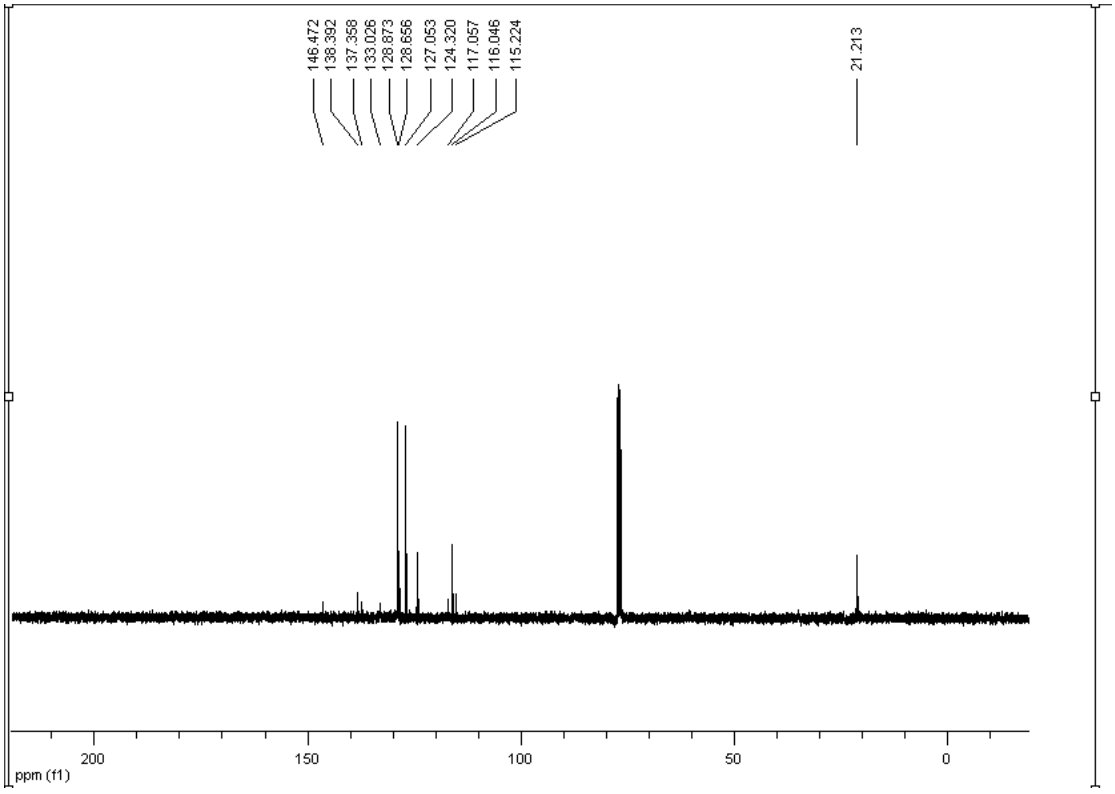
3a


7.774
7.748
7.621
7.604
7.363
7.346
7.313
7.291
7.288
7.218
7.200
7.180
6.693
6.676
6.659
5.773
5.618
H
H
Ph
N
N
2.00
1.05
5.01
1.06
1.00
1.00
1.00
9.0
8.0
7.0
6.0
5.0
ppm (t1)

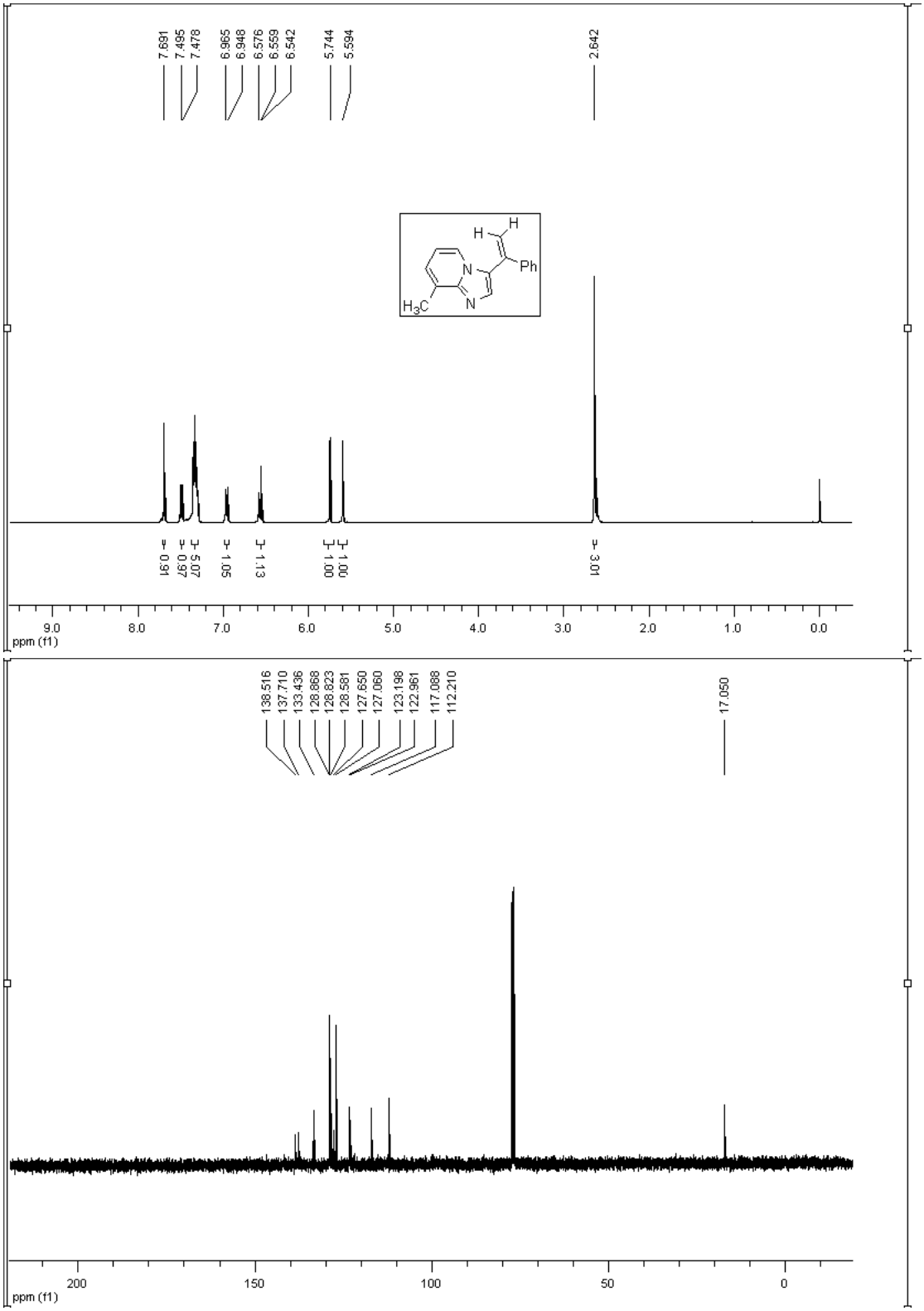

138.199
137.257
133.517
128.931
128.734
127.000
125.139
117.789
117.635
112.561
200
150
100
50
0
ppm (f1)

3b

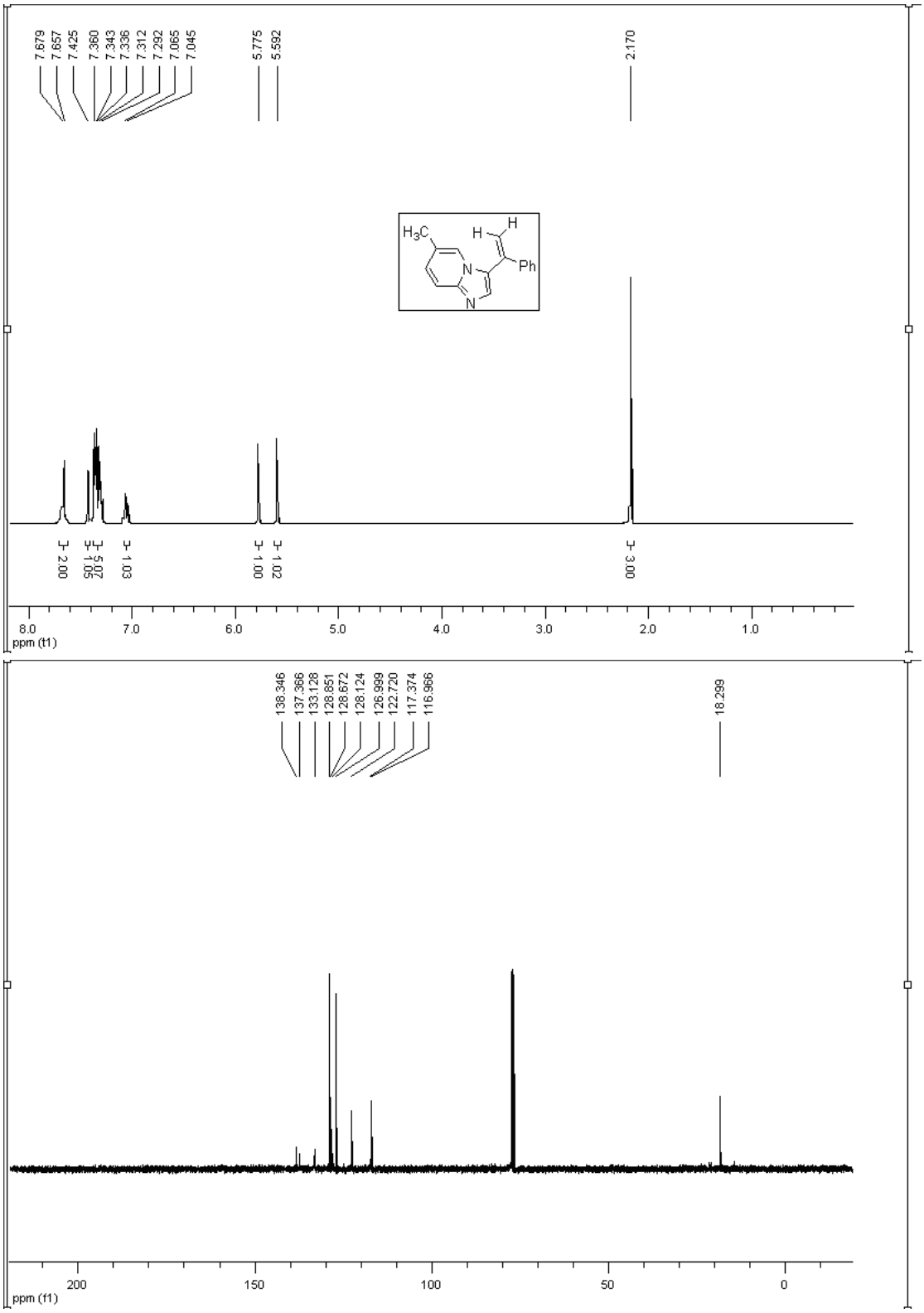

7.643
7.487
7.470
7.356
7.339
7.331
7.303
7.264
6.512
6.494
6.492
5.723
5.588
2.372
H
H
Ph
H3C
N
N
1.00
2.01
5.00
1.01
1.00
1.00
3.03
10.0
5.0
0.0
ppm (t1)


146.472
138.392
137.358
133.026
128.873
128.656
127.053
124.320
117.057
116.046
115.224
21.213
200
150
100
50
0
ppm (f1)

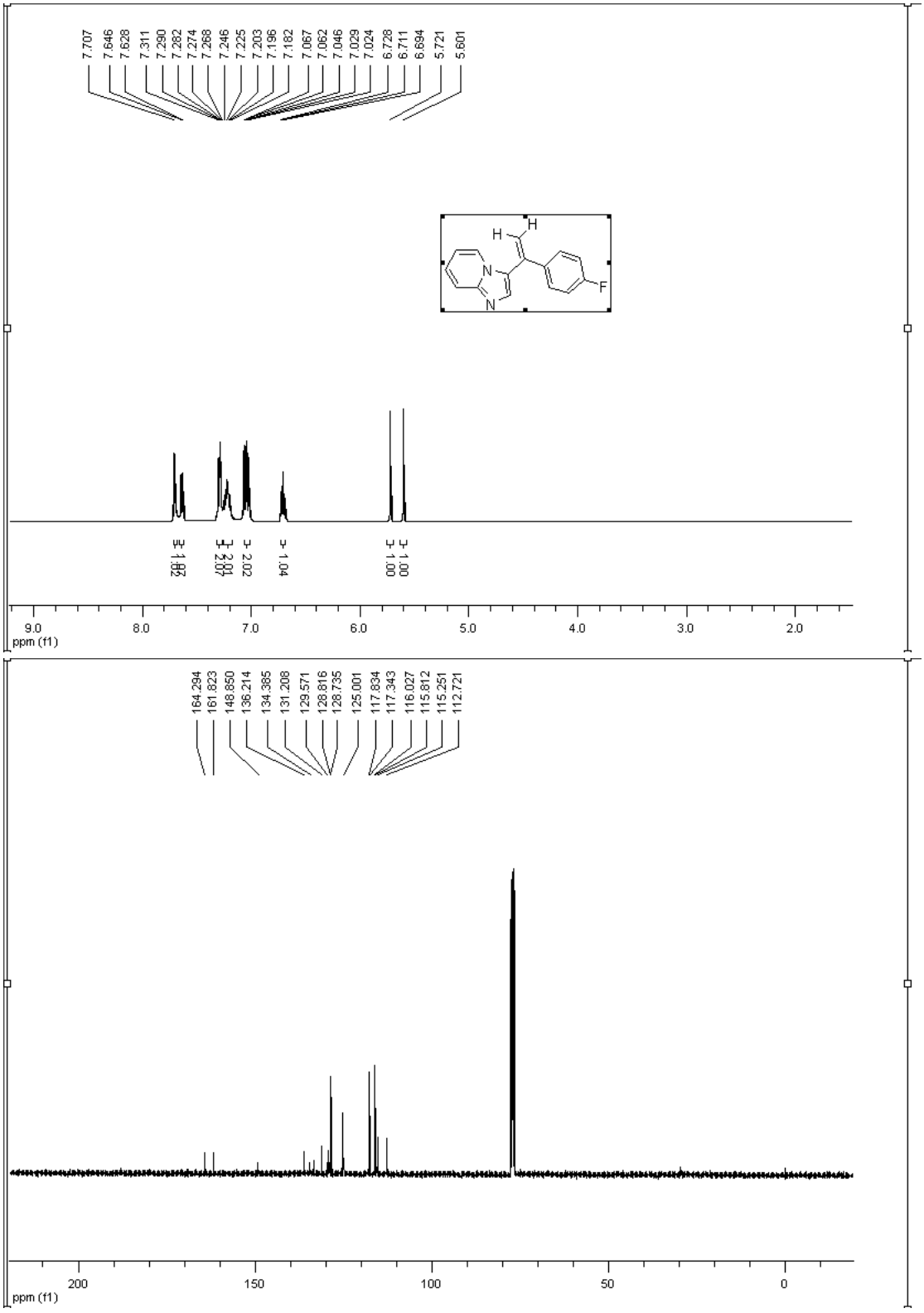
3c


7.691
7.495
7.478
6.965
6.948
6.576
6.559
6.542
5.744
5.594
2.642
H
H
Ph
N
N
H3C
0.91
0.97
5.07
1.05
1.13
1.00
1.00
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
138.516
137.710
133.436
128.868
128.823
128.581
127.650
127.060
123.198
122.961
117.088
112.210
17.050
200
150
100
50
0
ppm (f1)

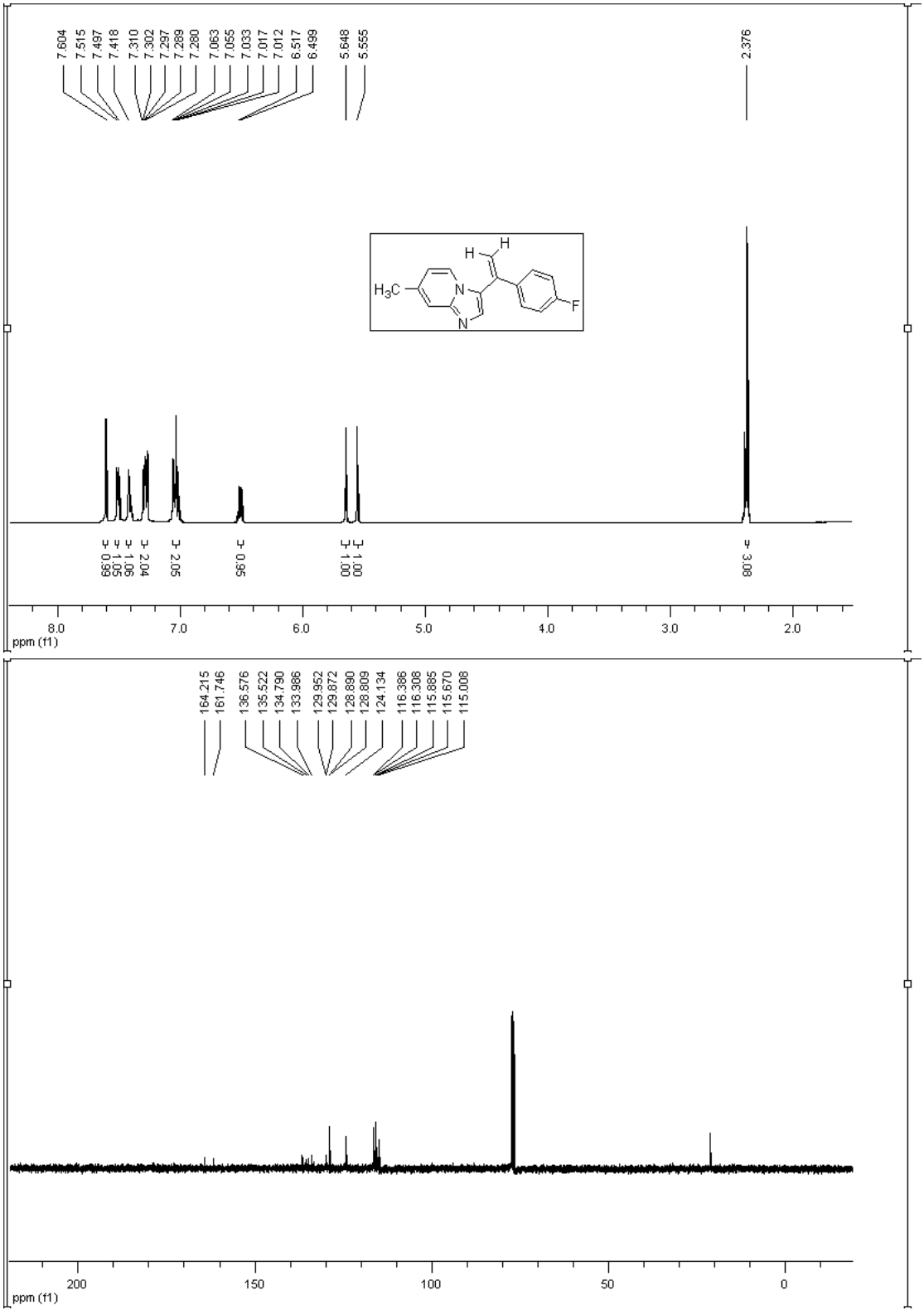
3d


7.679
7.657
7.425
7.360
7.343
7.336
7.312
7.292
7.065
7.045
5.775
5.592
2.170
H3C
H
H
Ph
N
N
2.00
5.07
1.05
1.03
1.00
1.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
138.346
137.366
133.128
128.851
128.672
128.124
126.999
122.720
117.374
116.966
18.299
200
150
100
50
0
ppm (f1)

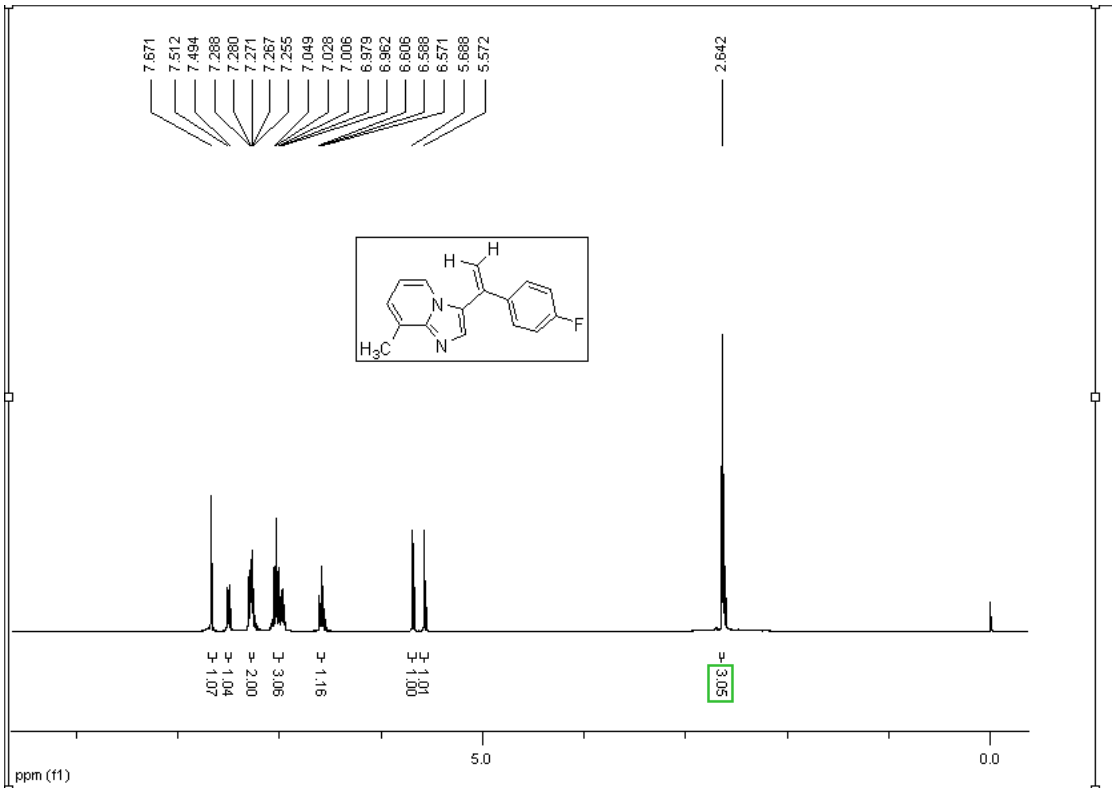
3e

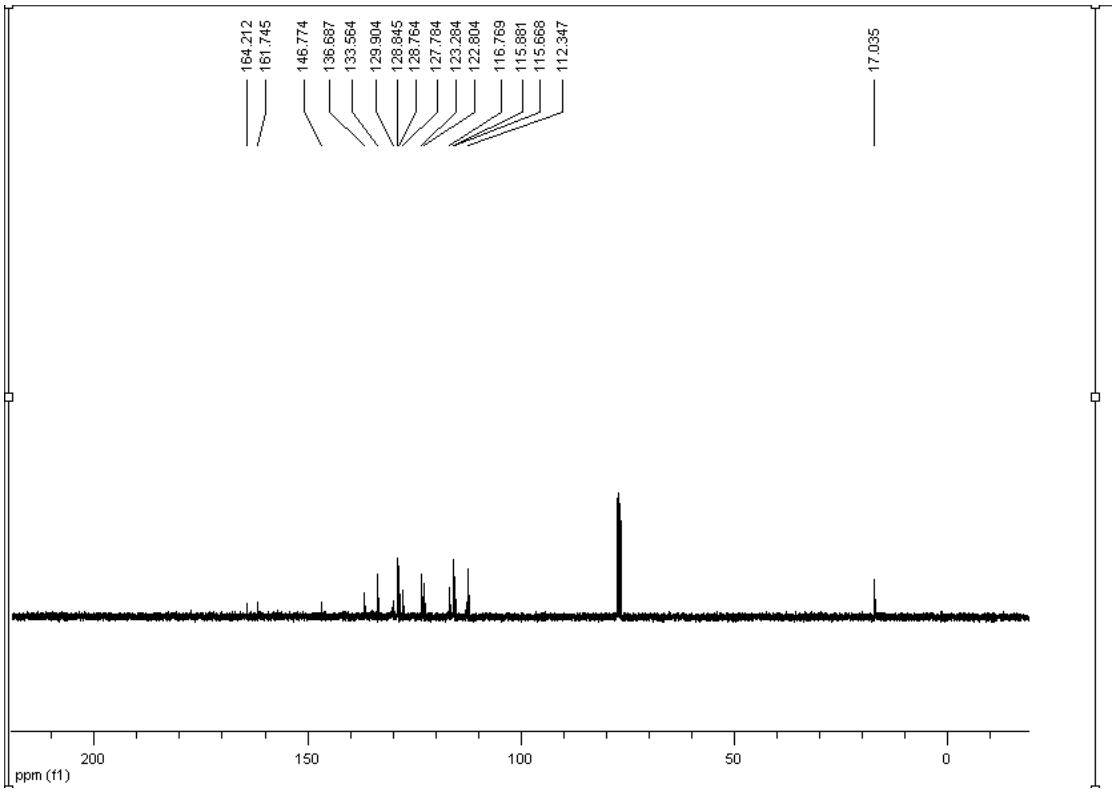

7.707
7.646
7.628
7.311
7.290
7.282
7.274
7.268
7.246
7.225
7.203
7.196
7.182
7.067
7.062
7.046
7.029
7.024
6.728
6.711
6.694
5.721
5.601
H
H
N
N
F
1.82
2.07
2.02
1.04
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)
164.294
161.823
148.850
136.214
134.385
131.208
129.571
128.816
128.735
125.001
117.834
117.343
116.027
115.812
115.251
112.721
200
150
100
50
0
ppm (f1)

3f

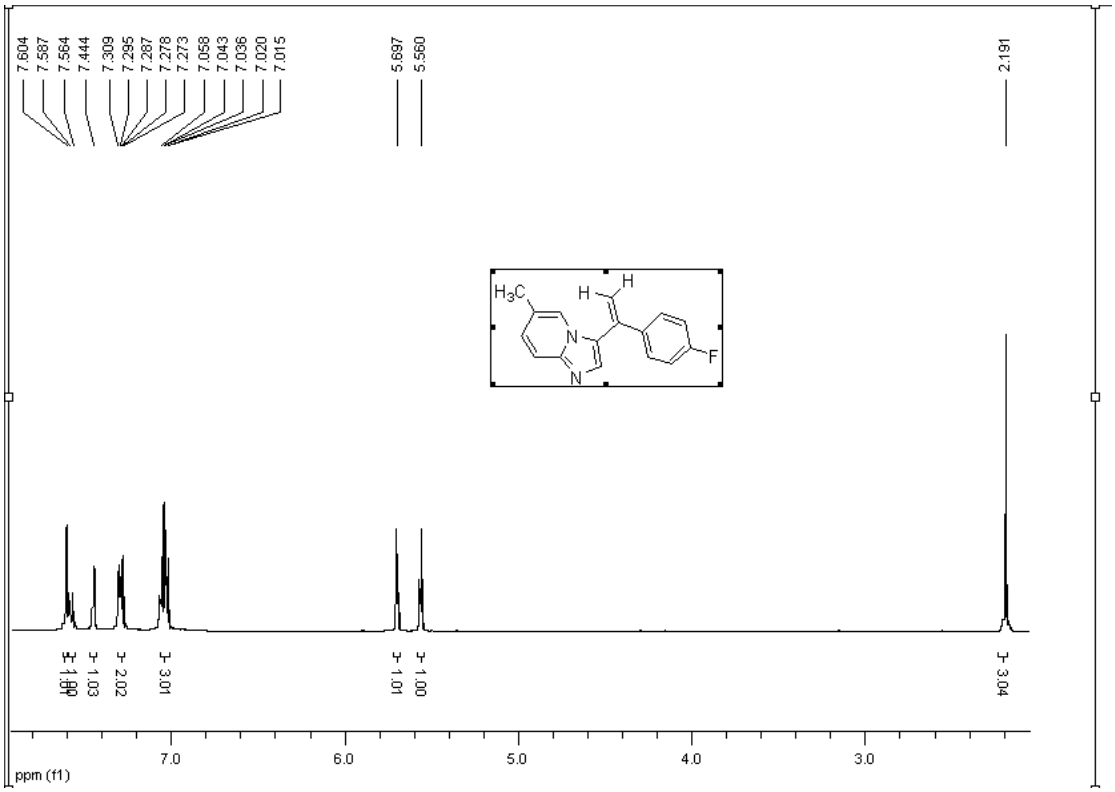

7.604
7.515
7.497
7.418
7.310
7.302
7.297
7.289
7.280
7.063
7.055
7.033
7.017
7.012
6.517
6.499
5.648
5.555
2.376
H
H
H3C
N
N
F
0.99
1.05
1.06
2.04
2.05
0.95
1.00
1.00
3.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)
164.215
161.746
136.576
135.522
134.790
133.986
129.952
129.872
128.890
128.809
124.134
116.386
116.308
115.885
115.670
115.008
200
150
100
50
0
ppm (f1)

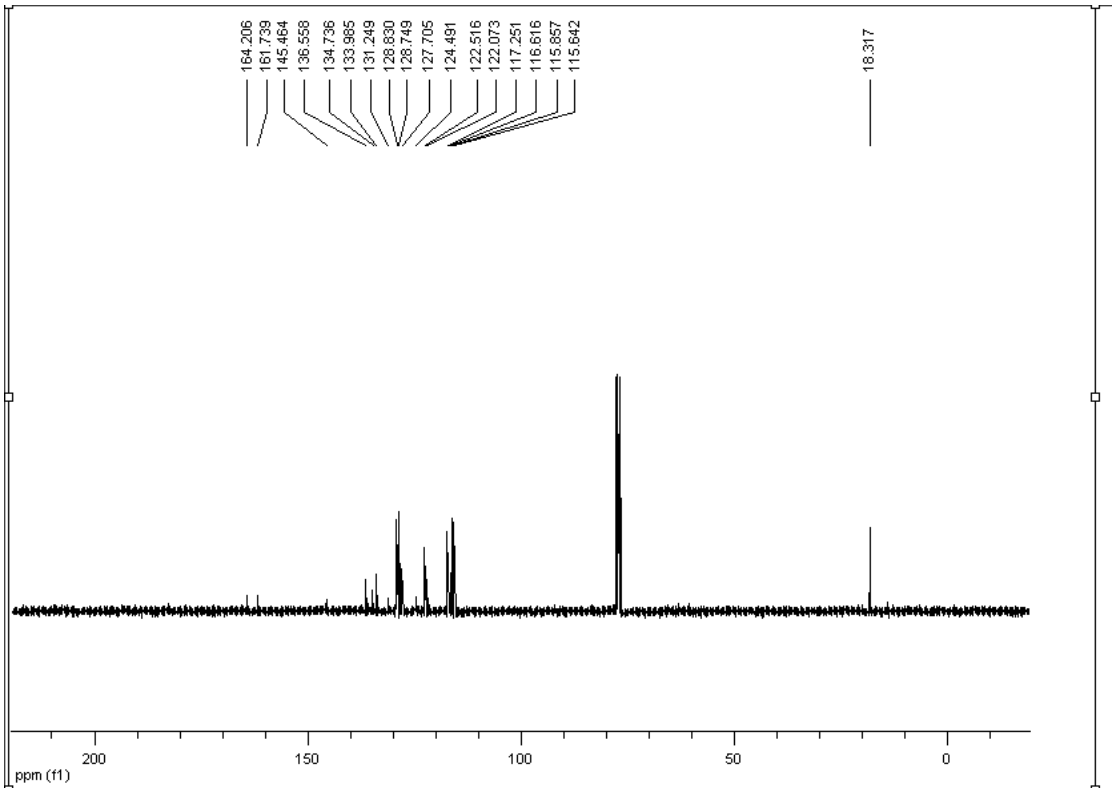
3g


7.671
7.512
7.494
7.288
7.280
7.271
7.267
7.255
7.049
7.028
7.006
6.979
6.962
6.606
6.588
6.571
5.688
5.572
2.642
H
H
N
N
F
H3C
1.07
1.04
2.00
3.06
1.16
1.00
1.01
3.05
5.0
0.0
ppm (f1)

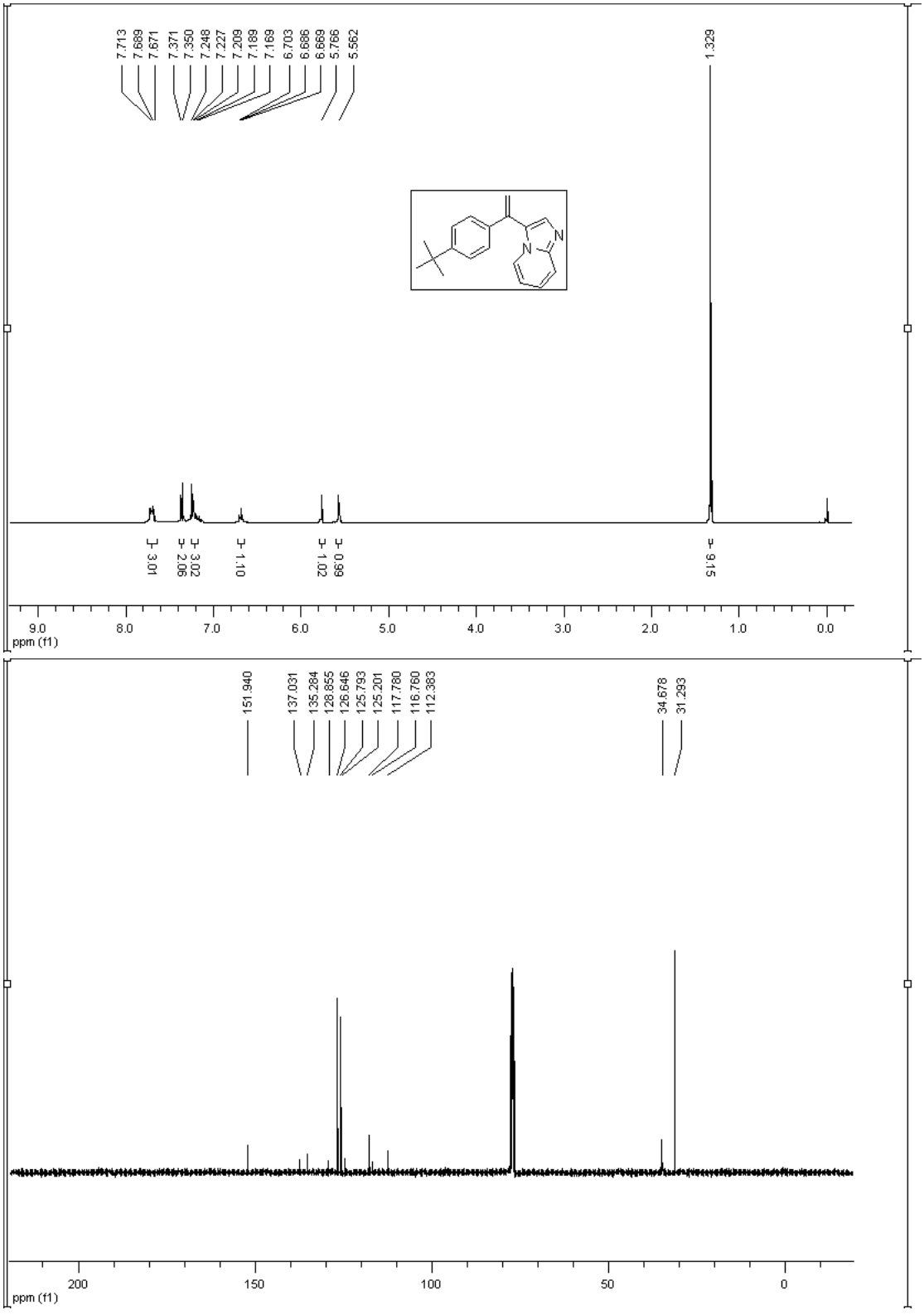

164.212
161.745
146.774
136.687
133.564
129.904
128.845
128.764
127.784
123.284
122.804
116.769
115.881
115.668
112.347
17.035
200
150
100
50
0
ppm (f1)

3h

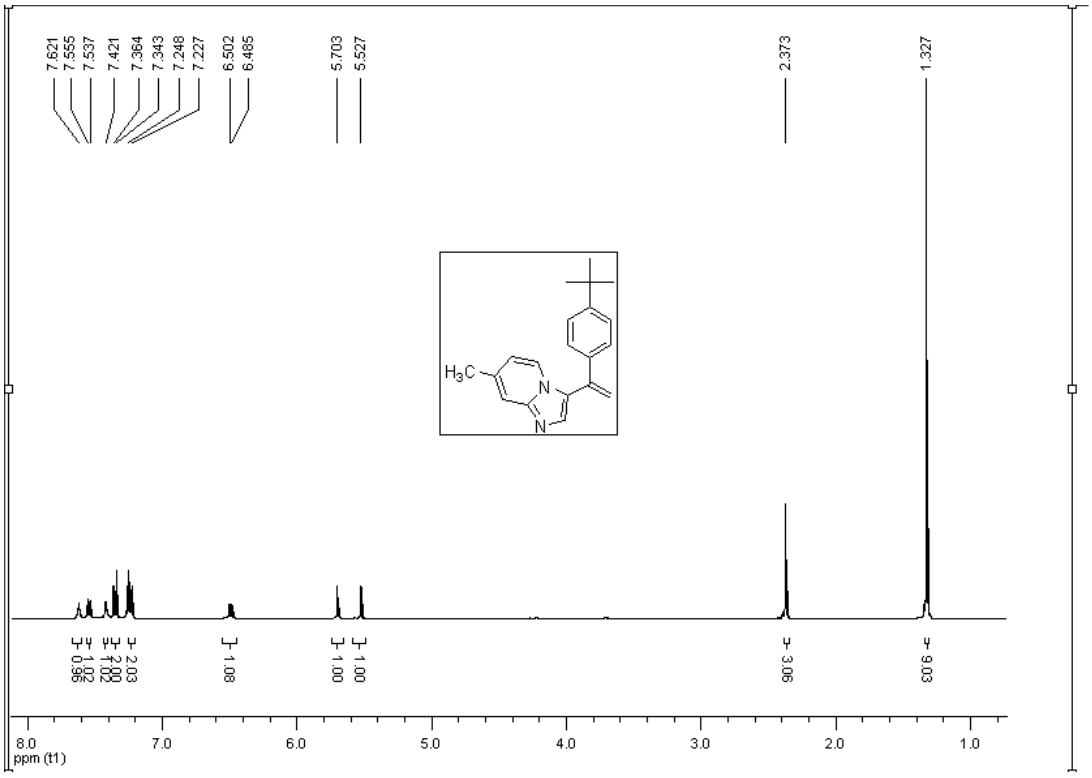

7.604
7.587
7.564
7.444
7.309
7.295
7.287
7.278
7.273
7.058
7.043
7.036
7.020
7.015
5.697
5.560
2.191
H3C
H
H
N
N
F
1.00
1.03
2.02
3.01
1.01
1.00
3.04
7.0
6.0
5.0
4.0
3.0
ppm (f1)

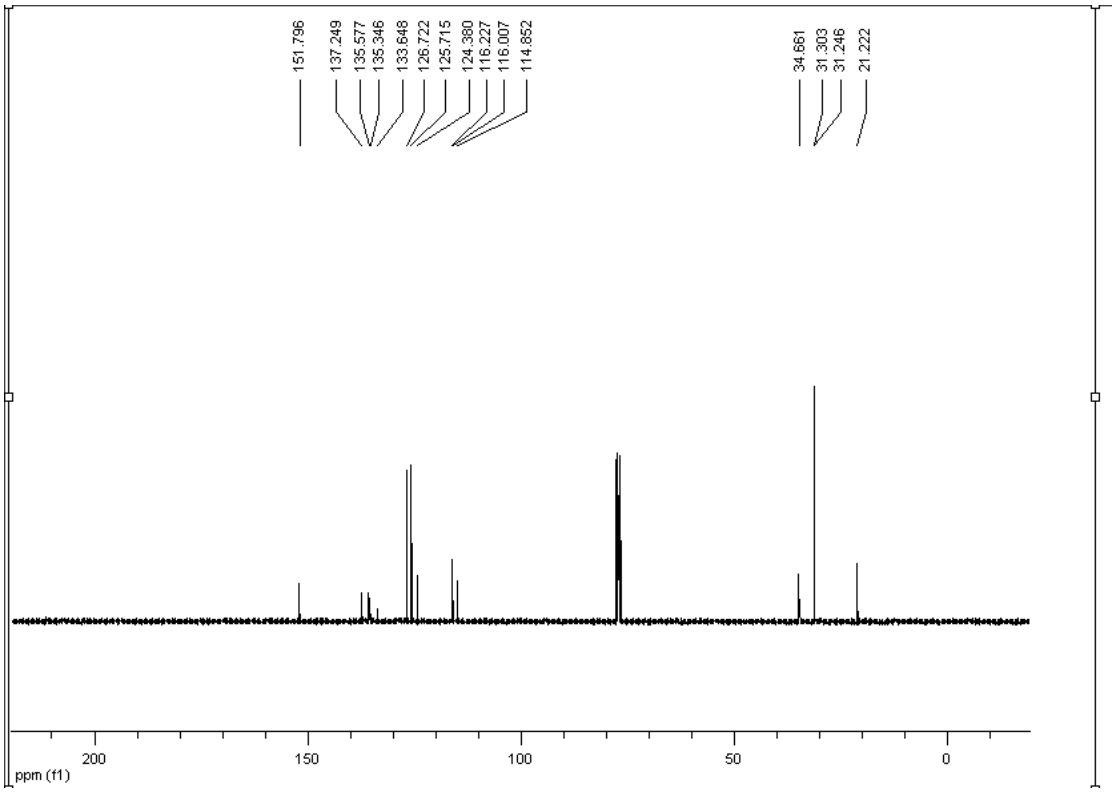

164.206
161.739
145.464
136.558
134.736
133.985
131.249
128.830
128.749
127.705
124.491
122.516
122.073
117.251
116.616
115.857
115.642
18.317
200
150
100
50
0
ppm (f1)

3i

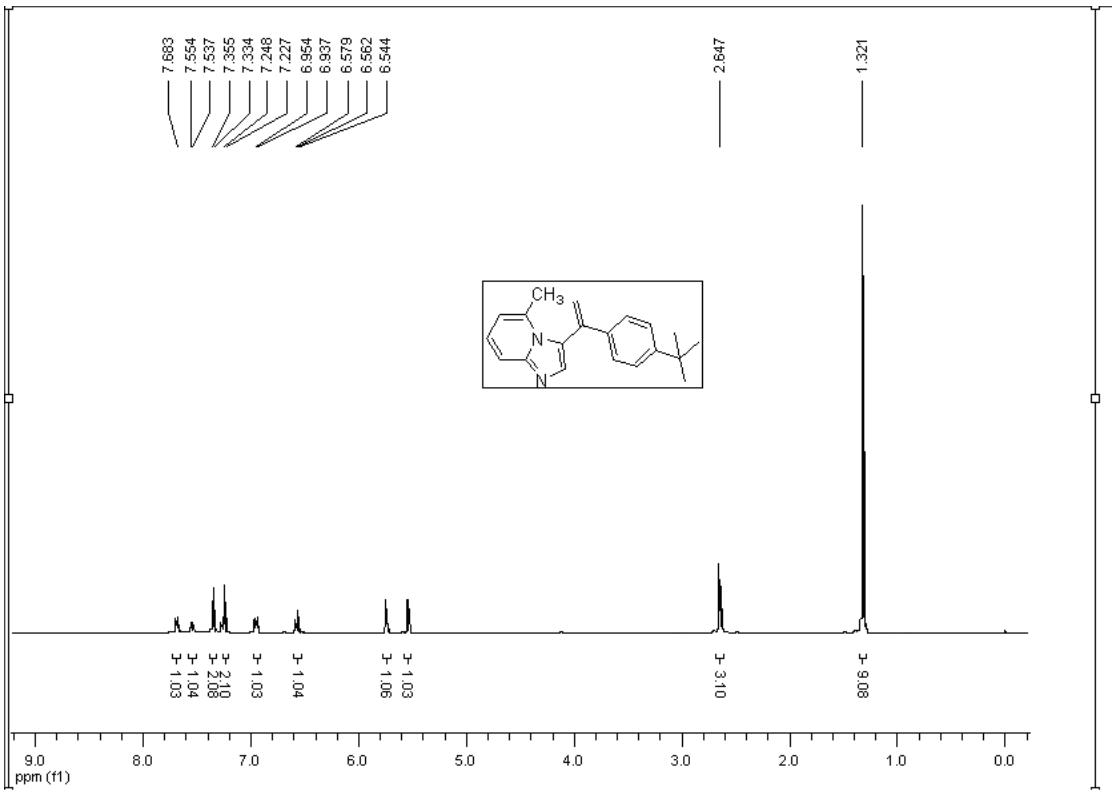

7.713
7.689
7.671
7.371
7.350
7.248
7.227
7.209
7.189
7.169
6.703
6.686
6.669
5.766
5.562
1.329
3.01
2.06
3.02
1.10
1.02
0.99
9.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
151.940
137.031
135.284
128.855
126.646
125.793
125.201
117.780
116.760
112.383
34.678
31.293
200
150
100
50
0
ppm (f1)

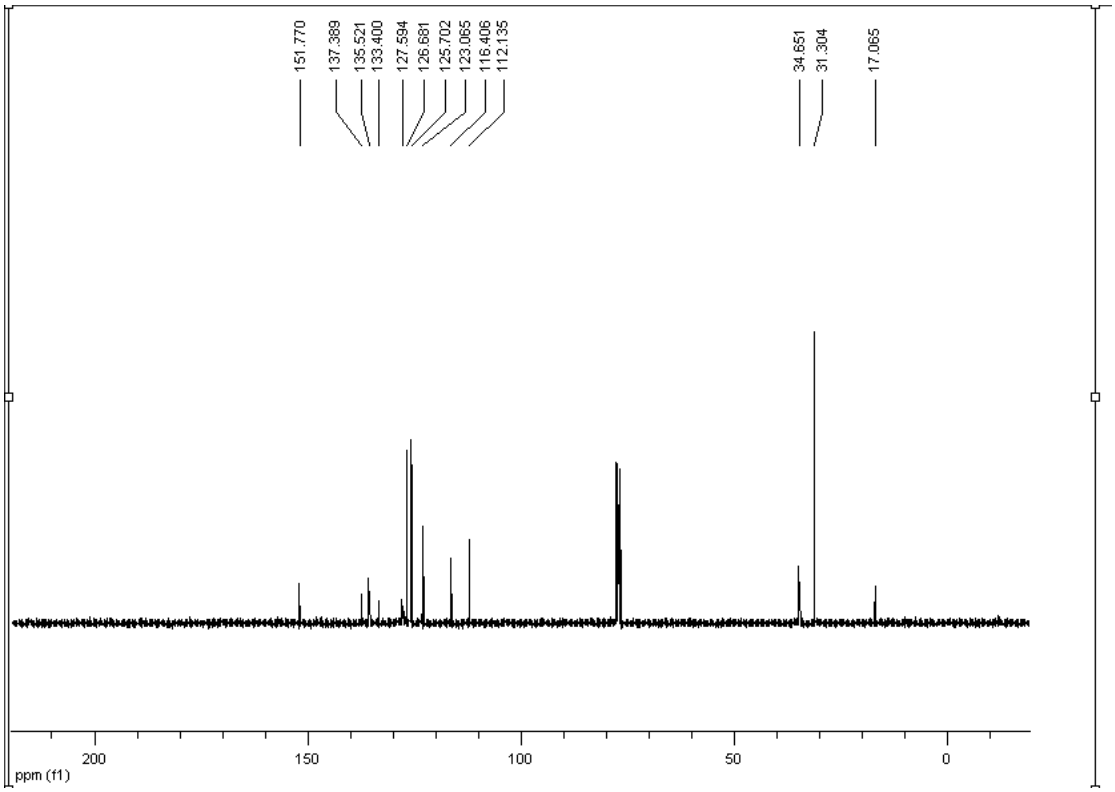
3j


7.621
7.555
7.537
7.421
7.364
7.343
7.248
7.227
6.502
6.485
5.703
5.527
2.373
1.327
H3C
N
N
0.96
1.02
2.04
2.00
2.03
1.08
1.00
1.00
3.06
9.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

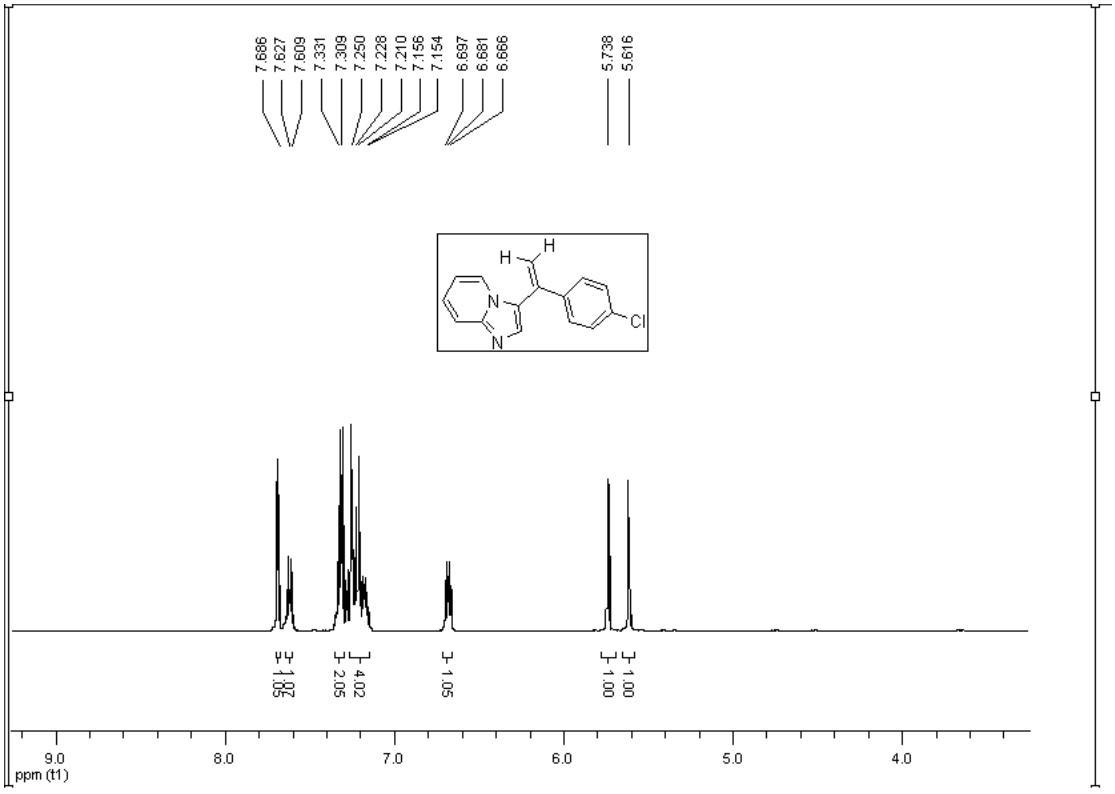

151.796
137.249
135.577
135.346
133.648
126.722
125.715
124.380
116.227
116.007
114.852
34.661
31.303
31.246
21.222
200
150
100
50
0
ppm (f1)

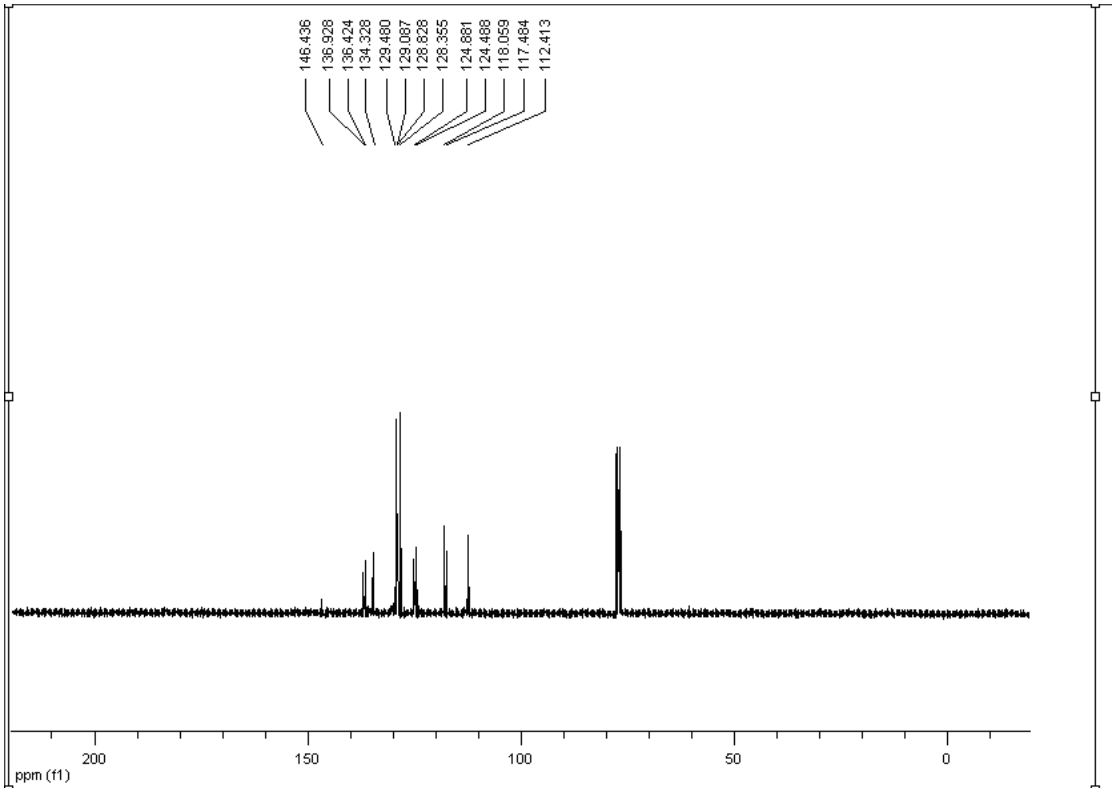
3k


7.683
7.554
7.537
7.355
7.334
7.248
7.227
6.954
6.937
6.579
6.562
6.544
2.647
1.321
CH3
N
N
1.03
1.04
2.08
1.03
1.04
1.06
1.03
3.10
9.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

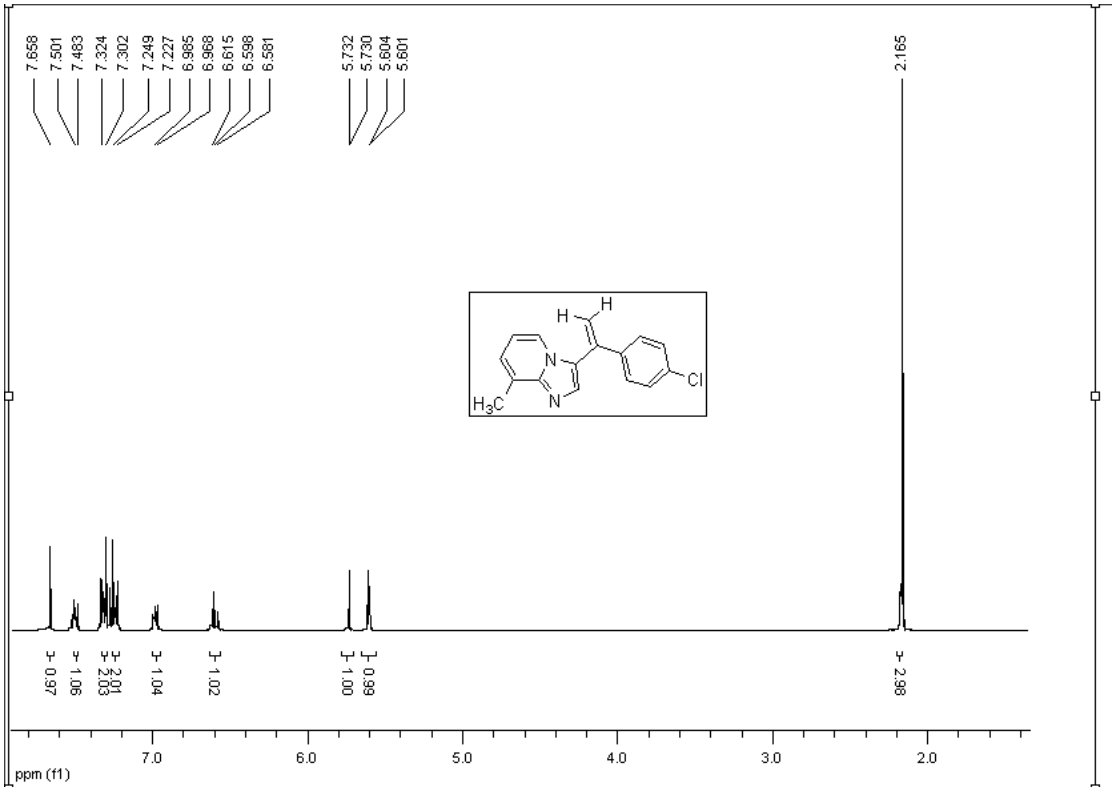

151.770
137.389
135.521
133.400
127.594
126.681
125.702
123.065
116.406
112.135
34.651
31.304
17.065
200
150
100
50
0
ppm (f1)

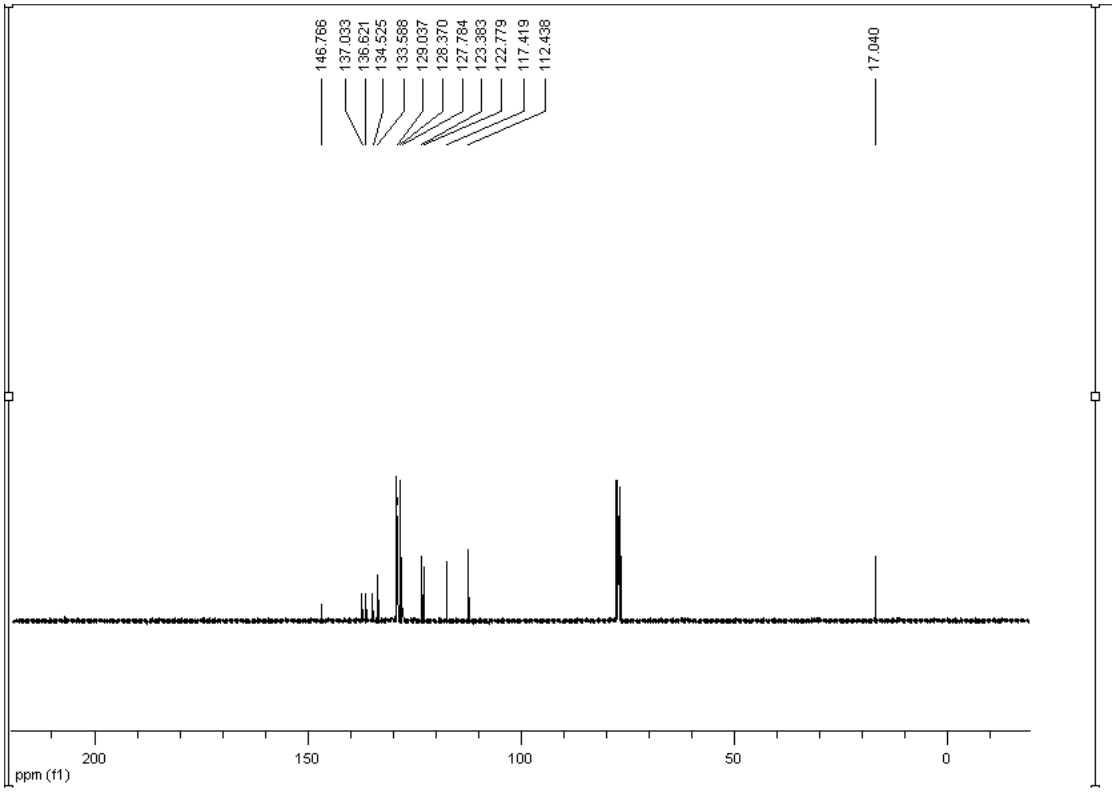
3l


7.686
7.627
7.609
7.331
7.309
7.250
7.228
7.210
7.156
7.154
6.697
6.681
6.666
5.738
5.616
H
H
N
N
Cl
1.05
2.05
4.02
1.05
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
ppm (t1)

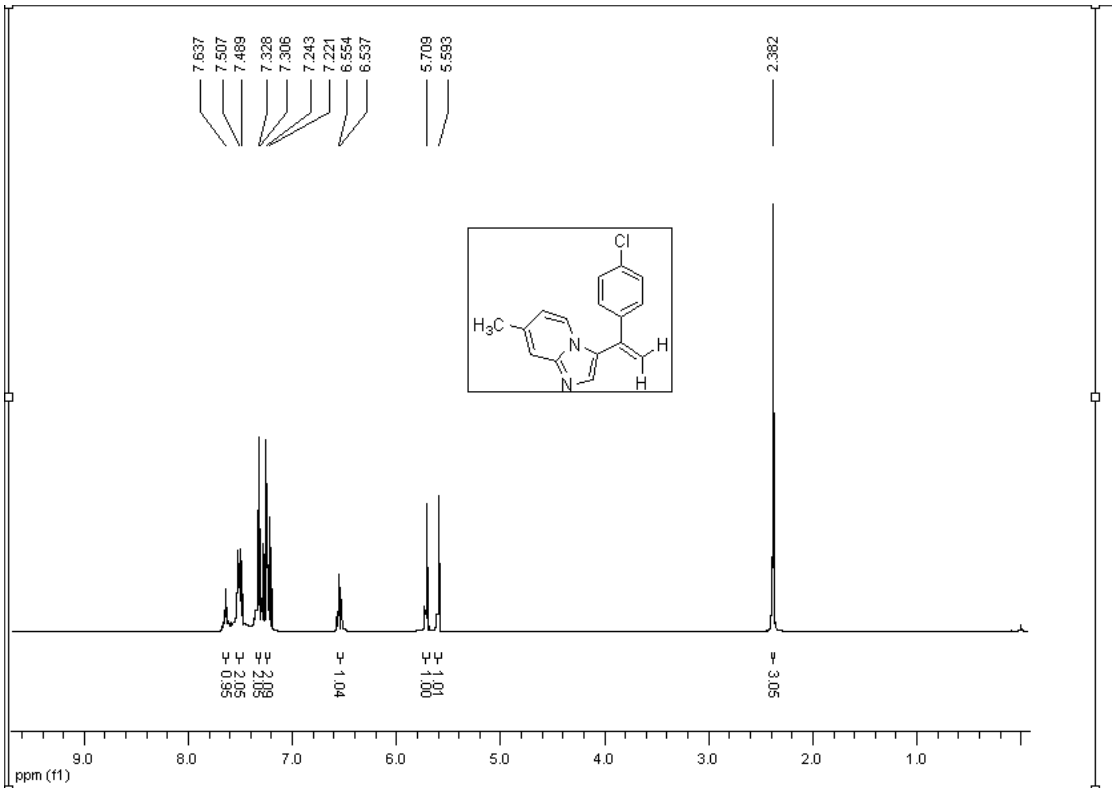

146.436
136.928
136.424
134.328
129.480
129.087
128.828
128.355
124.881
124.488
118.059
117.484
112.413
200
150
100
50
0
ppm (f1)

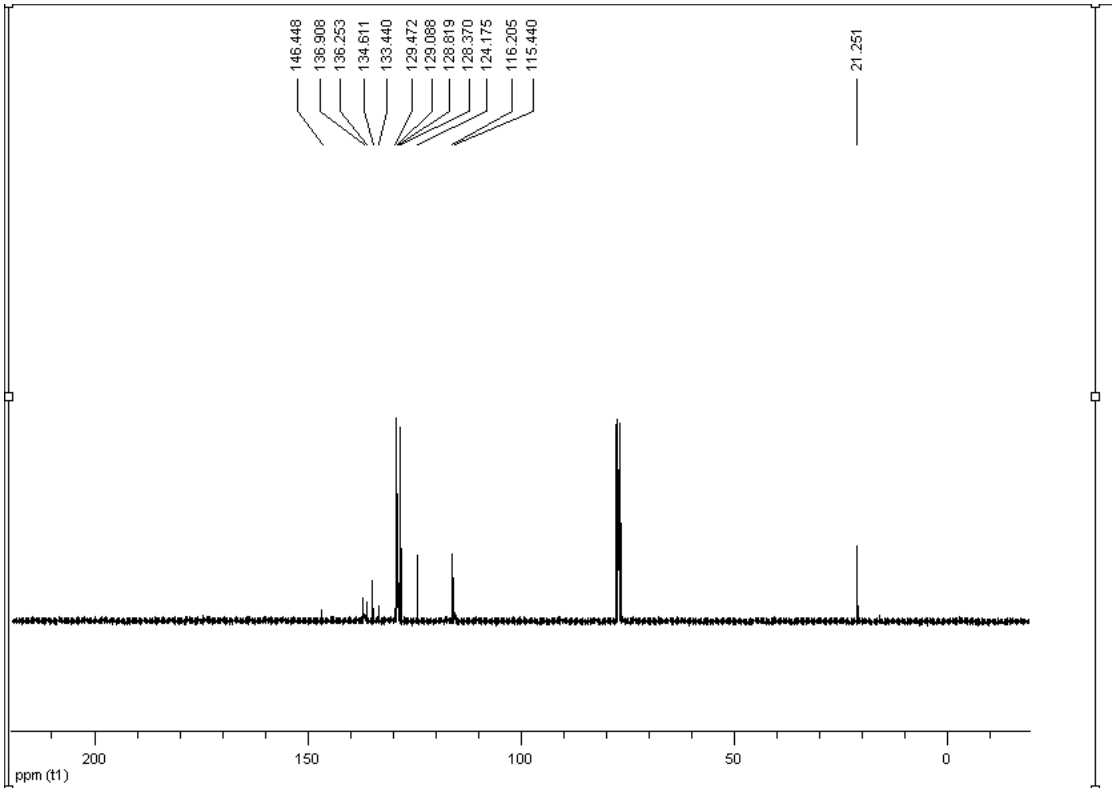
3m


7.658
7.501
7.483
7.324
7.302
7.249
7.227
6.985
6.968
6.615
6.598
6.581
5.732
5.730
5.604
5.601
2.165
H
H
N
N
Cl
H3C
0.97
1.06
2.03
1.04
1.02
1.00
0.99
2.98
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

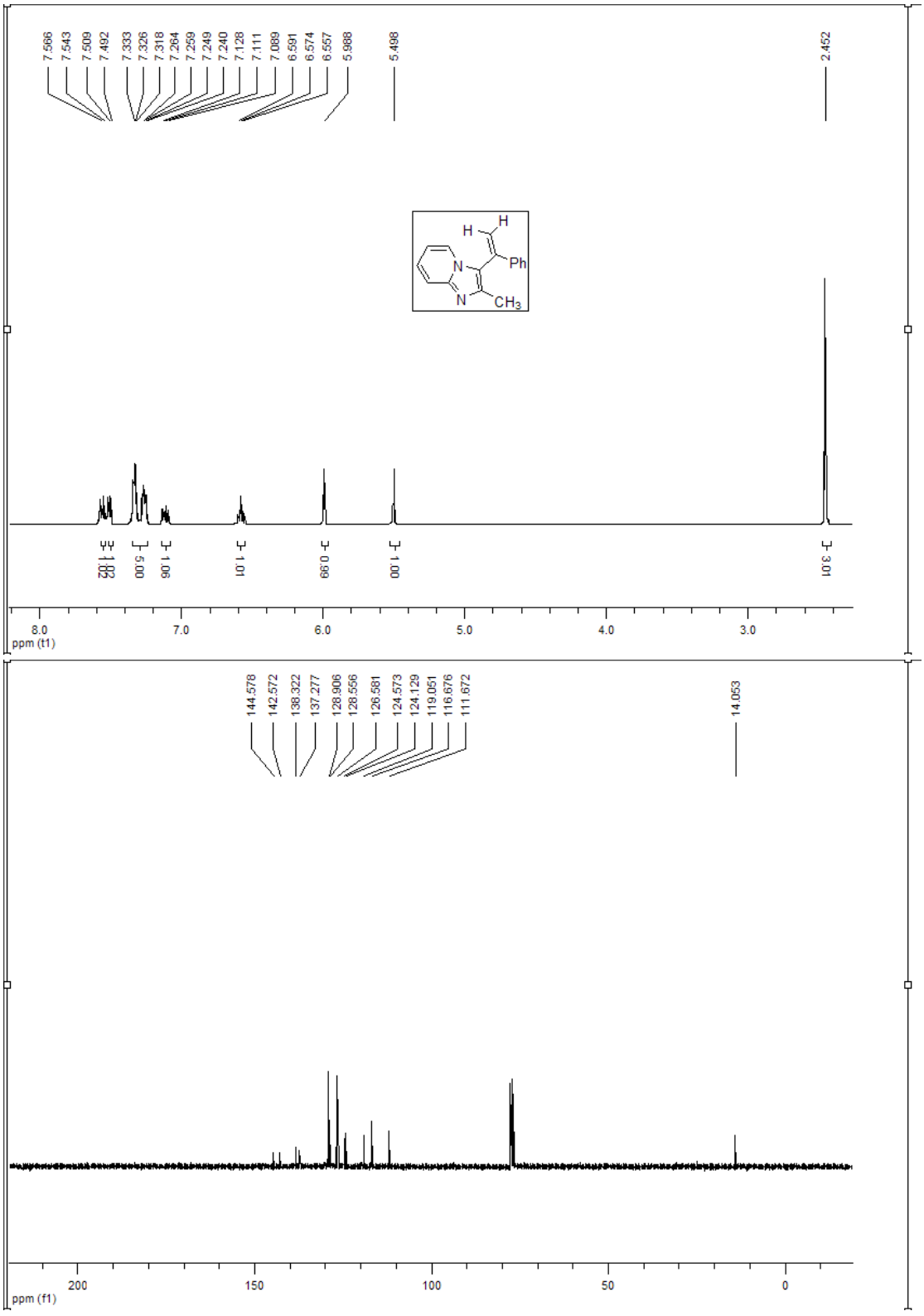

146.766
137.033
136.621
134.525
133.588
129.037
128.370
127.784
123.383
122.779
117.419
112.438
17.040
200
150
100
50
0
ppm (f1)

3n

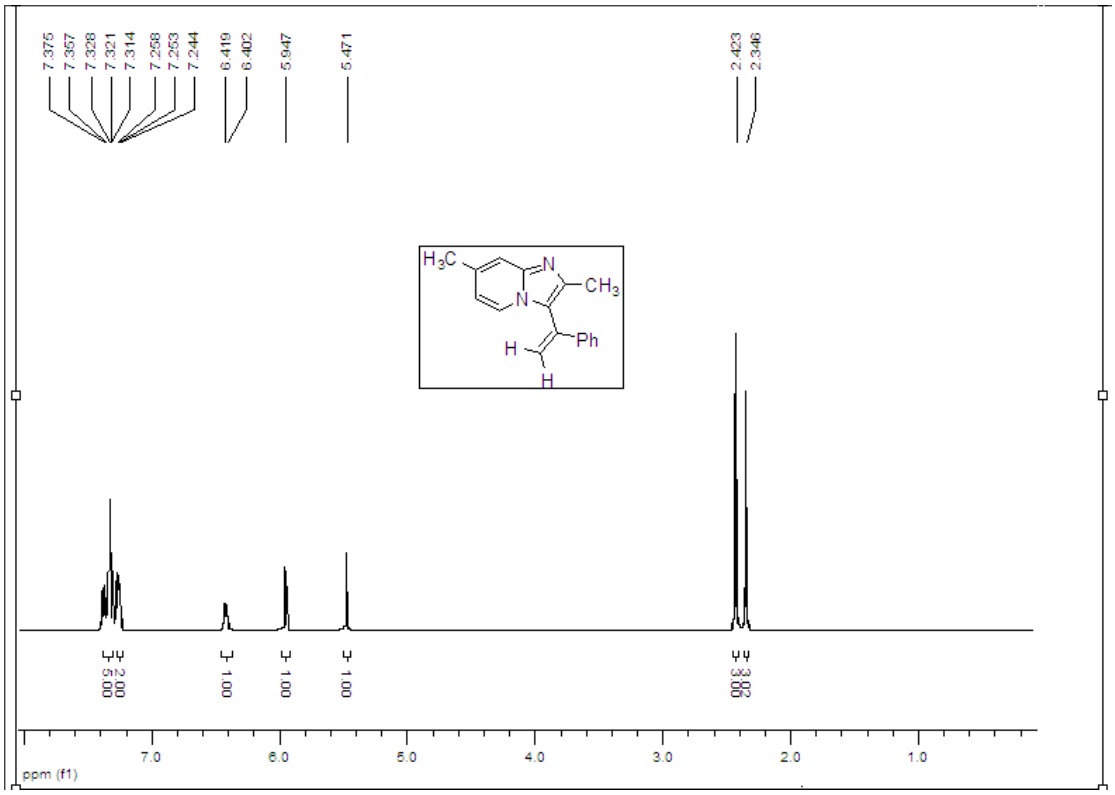

7.637
7.507
7.489
7.328
7.306
7.243
7.221
6.554
6.537
5.709
5.593
2.382
Cl
H3C
N
N
H
H
0.95
2.05
2.08
1.04
1.00
1.01
3.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

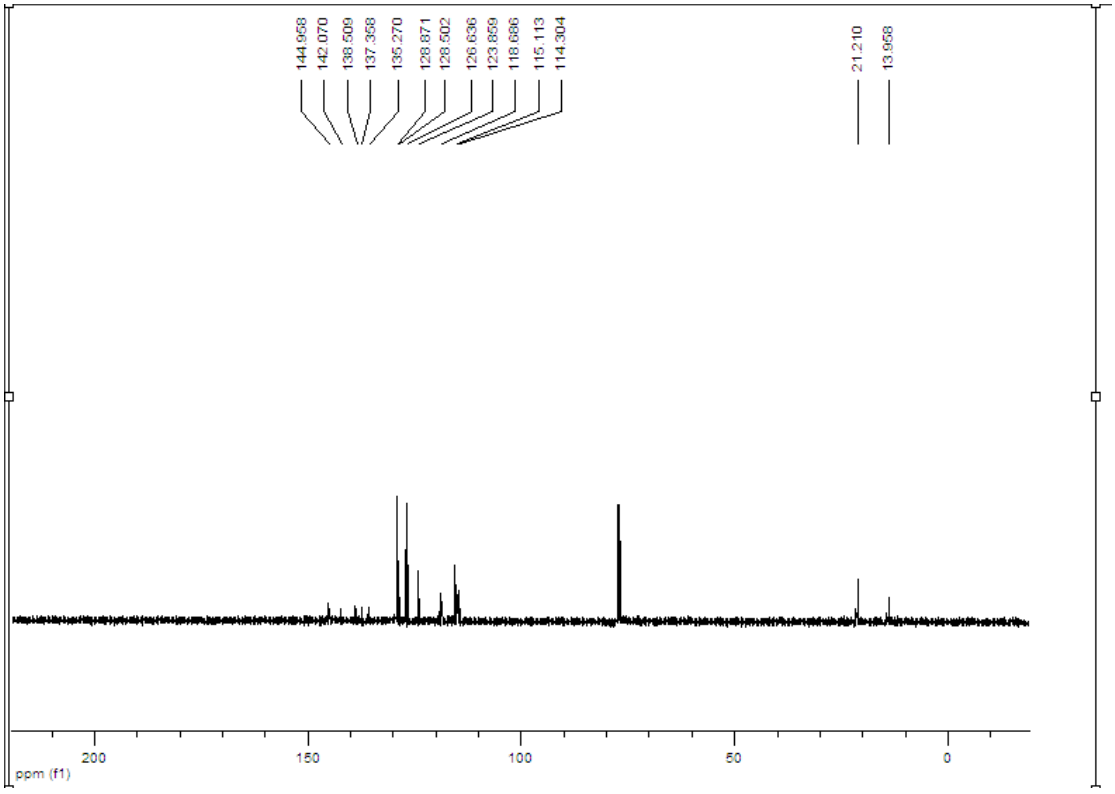

146.448
136.908
136.253
134.611
133.440
129.472
129.088
128.819
128.370
124.175
116.205
115.440
21.251
200
150
100
50
0
ppm (f1)

3o

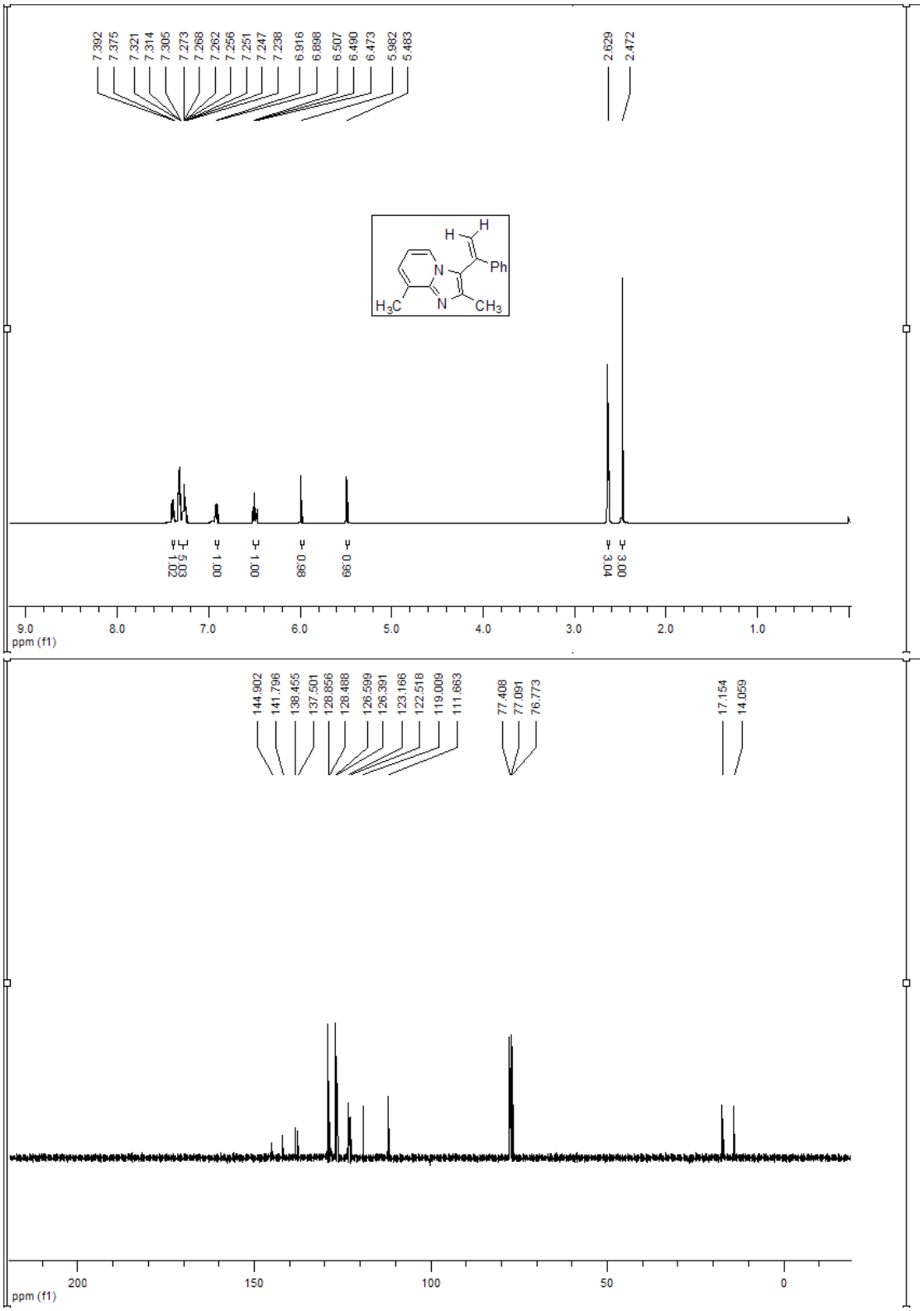

7.566
7.543
7.509
7.492
7.333
7.326
7.318
7.264
7.259
7.249
7.240
7.128
7.111
7.089
6.591
6.574
6.557
5.988
5.498
2.452
H
H
Ph
N
N
CH3
1.02
5.00
1.06
1.01
0.99
1.00
3.01
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)
144.578
142.572
138.322
137.277
128.906
128.556
126.581
124.573
124.129
119.051
116.676
111.672
14.053
200
150
100
50
0
ppm (f1)

3p

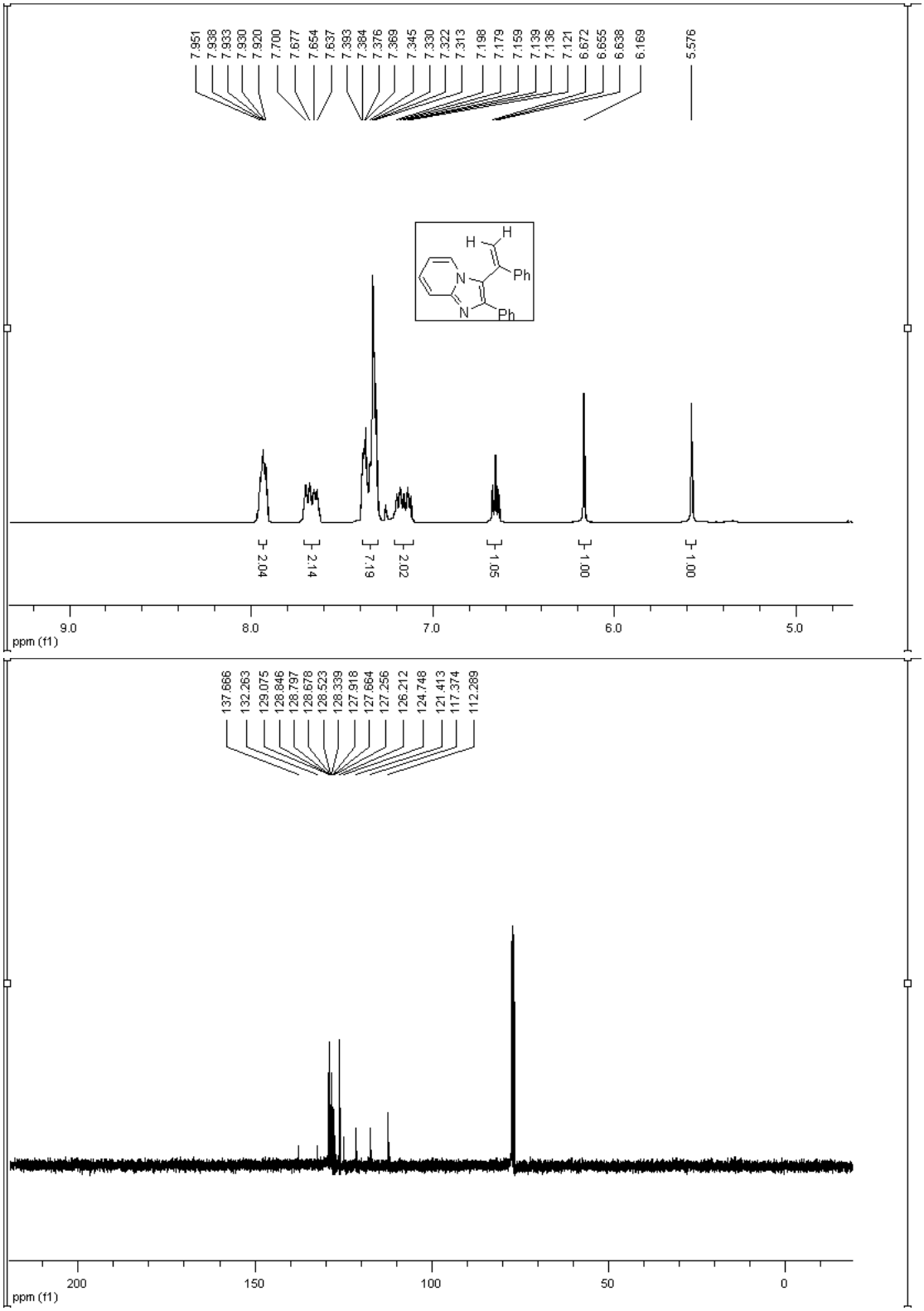

7.375
7.357
7.328
7.321
7.314
7.258
7.253
7.244
6.419
6.402
5.947
5.471
2.423
2.346
H3C
N
CH3
N
Ph
H
H
2.00
1.00
1.00
1.00
3.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


144.958
142.070
138.509
137.358
135.270
128.871
128.502
126.636
123.859
118.686
115.113
114.304
21.210
13.958
200
150
100
50
0
ppm (f1)

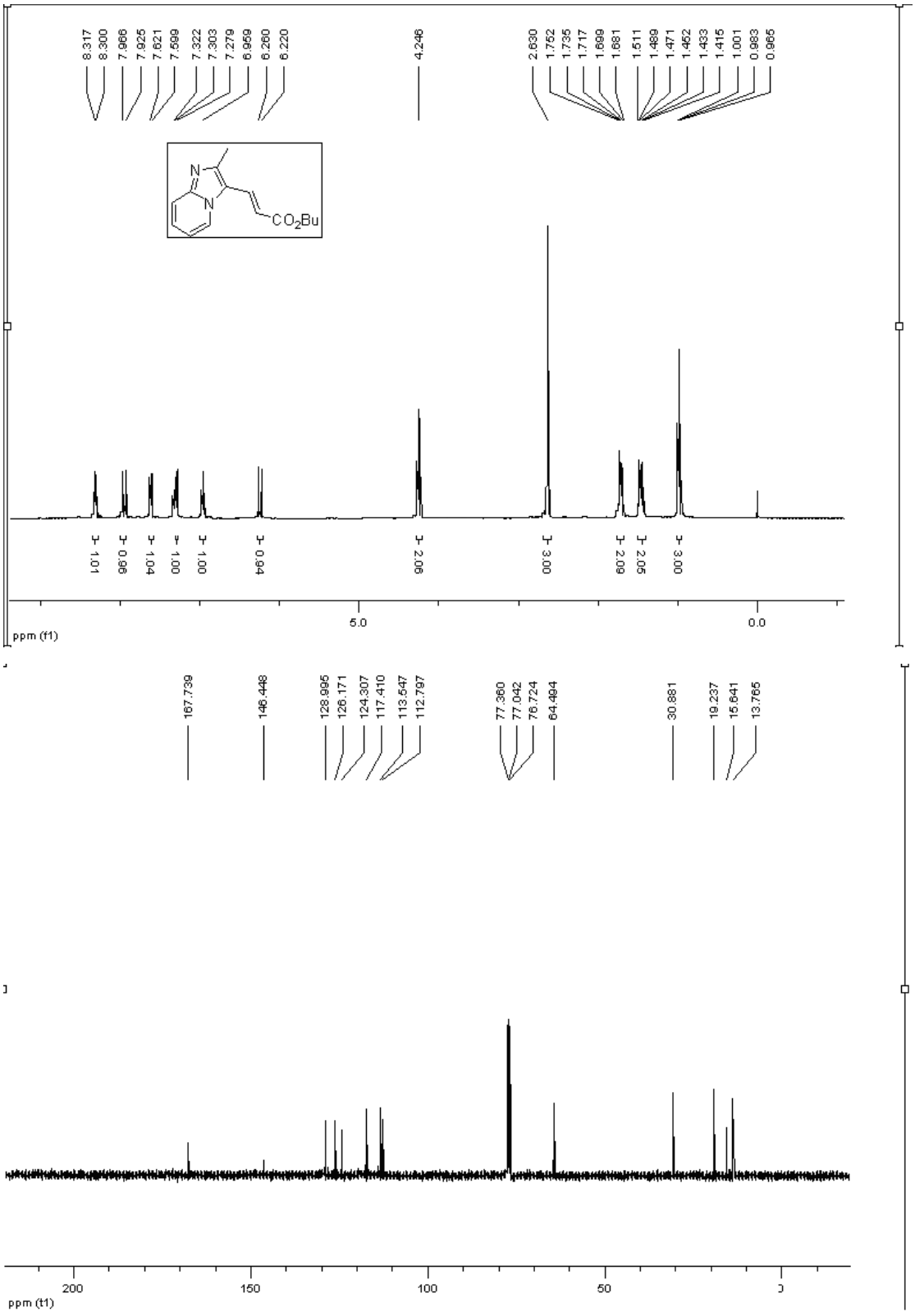
3q


7.392
7.375
7.321
7.314
7.305
7.273
7.268
7.262
7.256
7.251
7.247
7.238
6.916
6.898
6.507
6.490
6.473
5.982
5.483
2.629
2.472
H
H
Ph
N
N
H3C
CH3
5.03
1.02
1.00
1.00
0.98
0.99
3.04
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
144.902
141.796
138.455
137.501
128.856
128.488
126.599
126.391
123.166
122.518
119.009
111.663
77.408
77.091
76.773
17.154
14.059
200
150
100
50
0
ppm (f1)

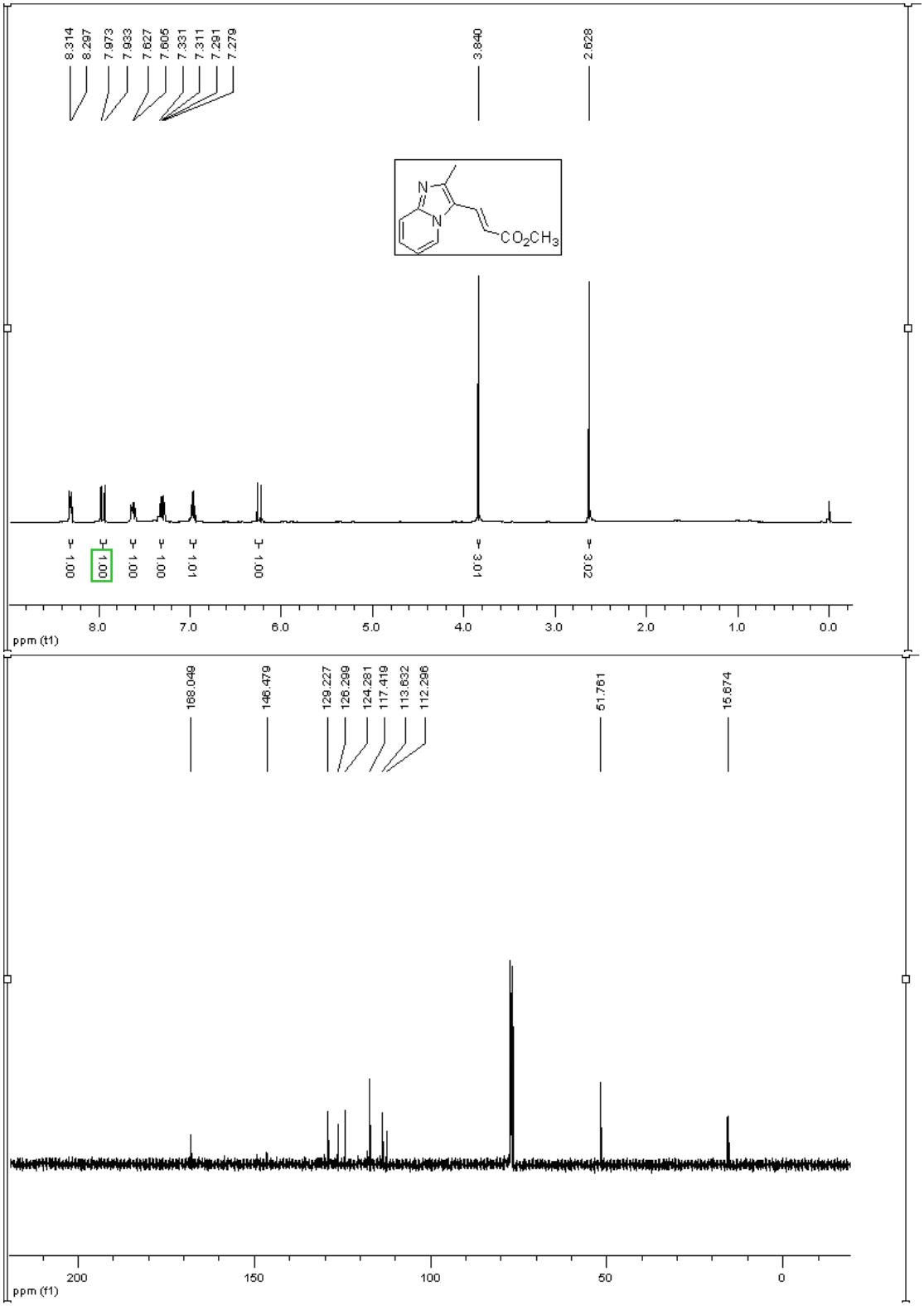
3r


7.951
7.938
7.933
7.930
7.920
7.700
7.677
7.654
7.637
7.393
7.384
7.376
7.369
7.345
7.330
7.322
7.313
7.198
7.179
7.159
7.139
7.136
7.121
6.672
6.655
6.638
6.169
5.576
H
H
Ph
N
N
Ph
2.04
2.14
7.19
2.02
1.05
1.00
1.00
9.0
8.0
7.0
6.0
5.0
ppm (f1)
137.666
132.263
129.075
128.846
128.797
128.678
128.523
128.339
127.918
127.664
127.256
126.212
124.748
121.413
117.374
112.289
200
150
100
50
0
ppm (f1)

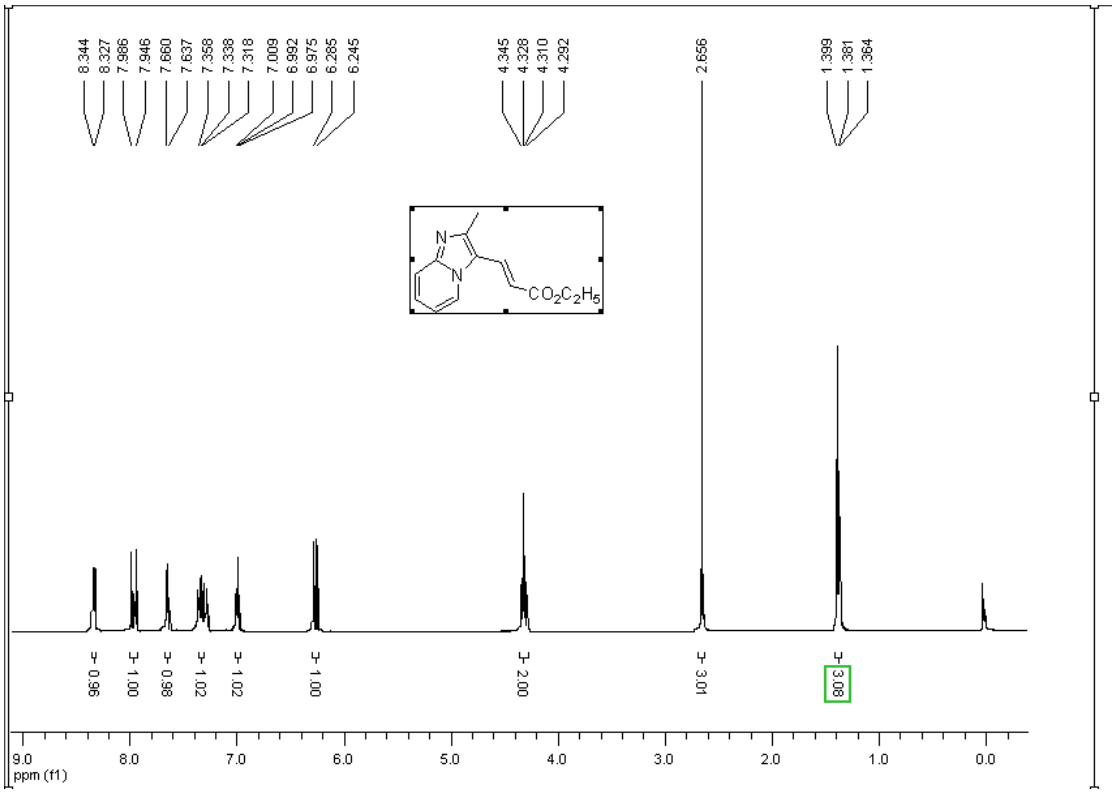
4a

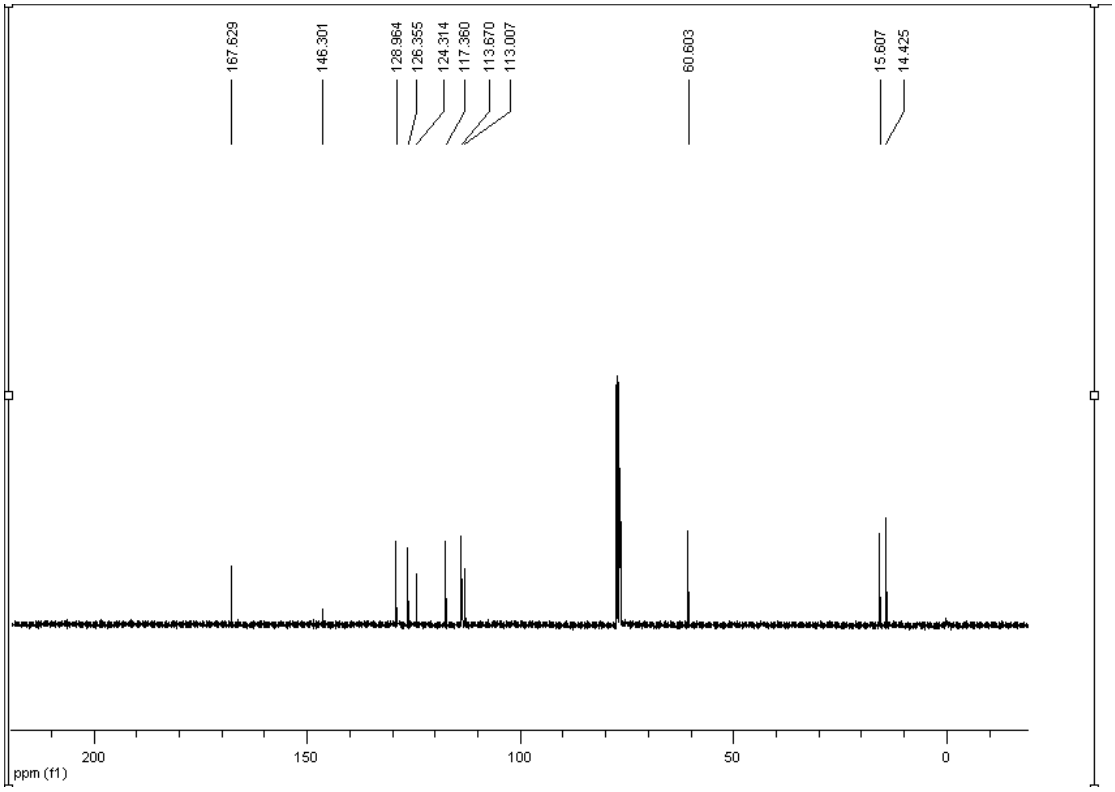

8.317
8.300
7.966
7.925
7.621
7.599
7.322
7.303
7.279
6.959
6.260
6.220
4.246
2.630
1.752
1.735
1.717
1.699
1.681
1.511
1.489
1.471
1.452
1.433
1.415
1.001
0.983
0.965
N
N
CO2Bu
1.01
0.96
1.04
1.00
1.00
0.94
2.06
3.00
2.09
2.05
3.00
5.0
0.0
ppm (f1)
167.739
146.448
128.995
126.171
124.307
117.410
113.547
112.797
77.360
77.042
76.724
64.494
30.881
19.237
15.641
13.765
200
150
100
50
ppm (t1)

4b

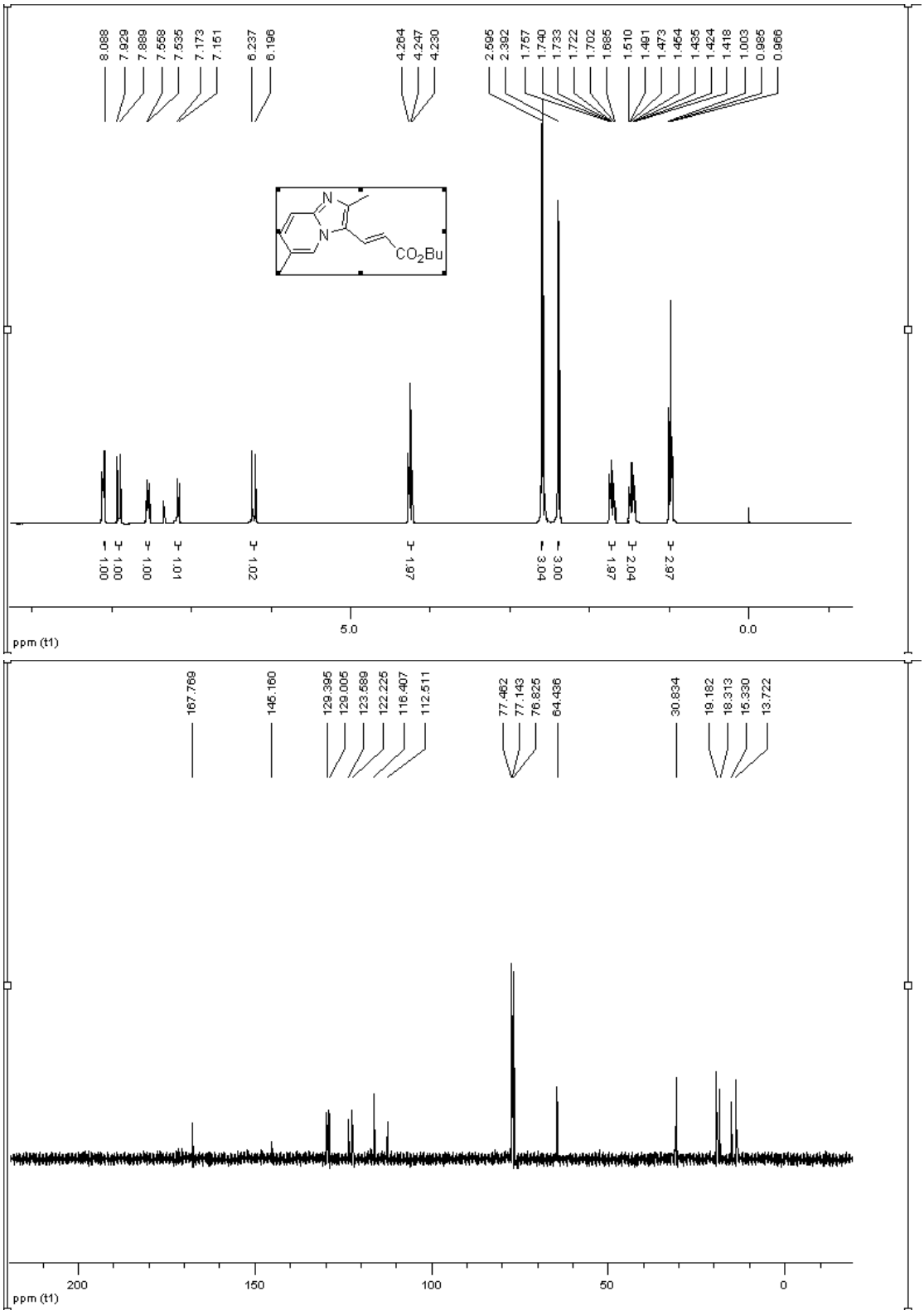

8.314
8.297
7.973
7.933
7.627
7.605
7.331
7.311
7.291
7.279
3.840
2.628
N
N
CO2CH3
1.00
1.00
1.00
1.00
1.01
1.00
3.01
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
168.049
146.479
129.227
126.299
124.281
117.419
113.632
112.296
51.761
15.674
200
150
100
50
0
ppm (f1)

4c

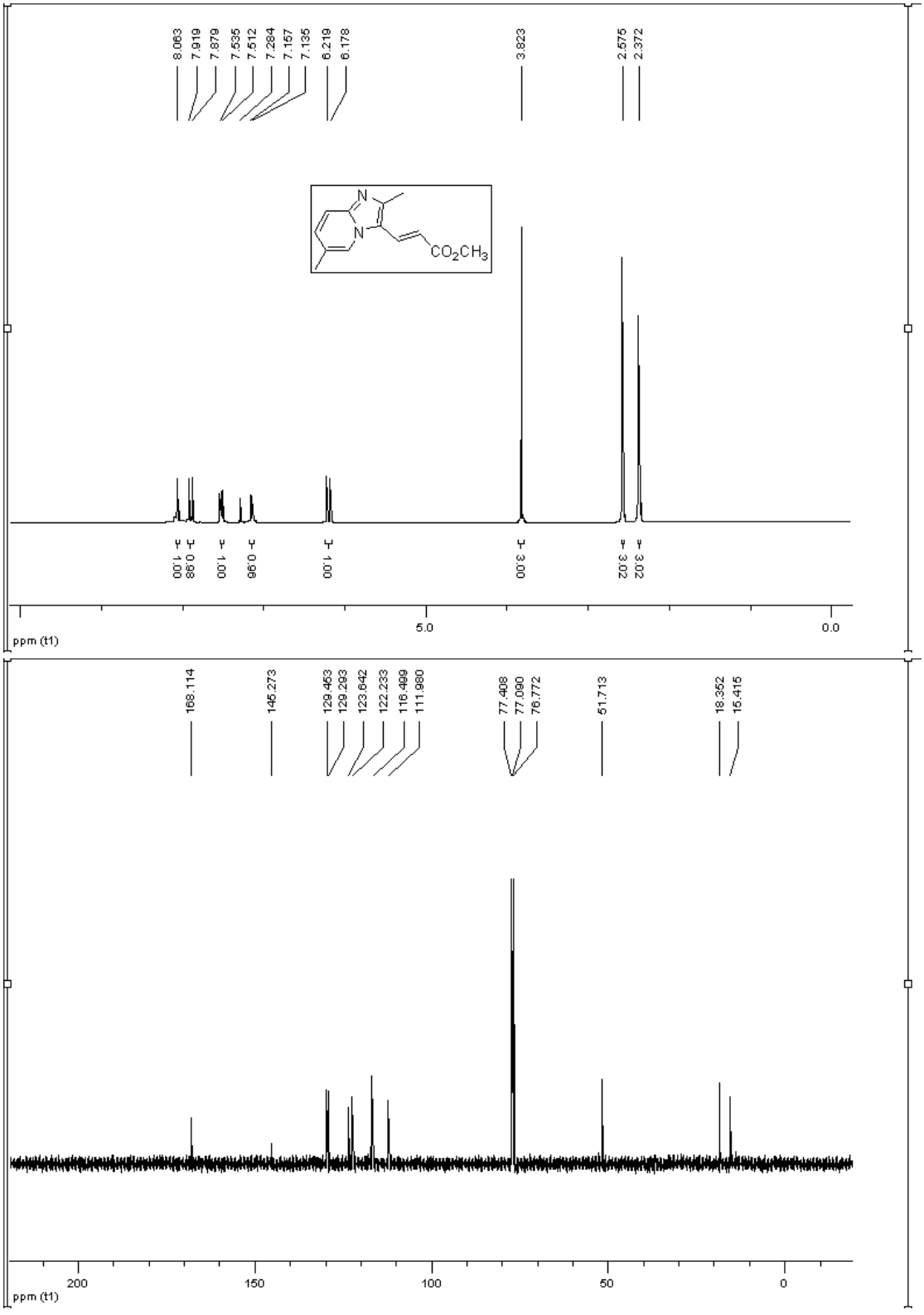

8.344
8.327
7.986
7.946
7.660
7.637
7.358
7.338
7.318
7.009
6.992
6.975
6.285
6.245
4.345
4.328
4.310
4.292
2.656
1.399
1.381
1.364
N
N
CO2C2H5
0.96
1.00
0.98
1.02
1.02
1.00
2.00
3.01
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


167.629
146.301
128.964
126.355
124.314
117.360
113.670
113.007
60.603
15.607
14.425
200
150
100
50
0
ppm (f1)

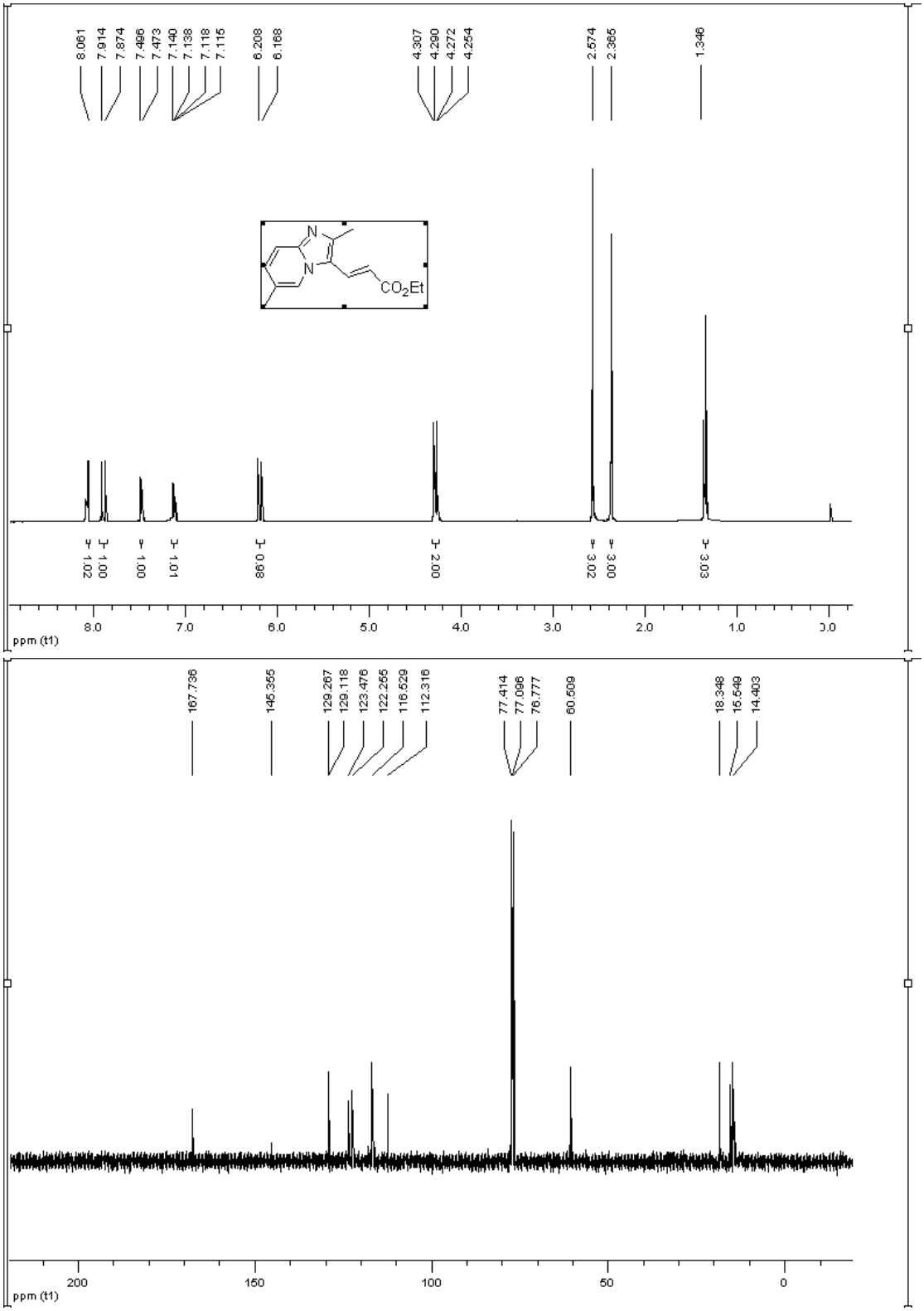
4d


8.088
7.929
7.889
7.568
7.535
7.173
7.151
6.237
6.196
4.264
4.247
4.230
2.595
2.392
1.757
1.740
1.733
1.722
1.702
1.685
1.510
1.491
1.473
1.464
1.435
1.424
1.418
1.003
0.985
0.966
N
N
CO2Bu
1.00
1.00
1.00
1.01
1.02
1.97
3.04
3.00
1.97
2.04
2.97
5.0
0.0
ppm (t1)
167.769
146.160
129.395
129.005
123.589
122.225
116.407
112.511
77.462
77.143
76.825
64.436
30.834
19.182
18.313
15.330
13.722
200
150
100
50
0
ppm (t1)

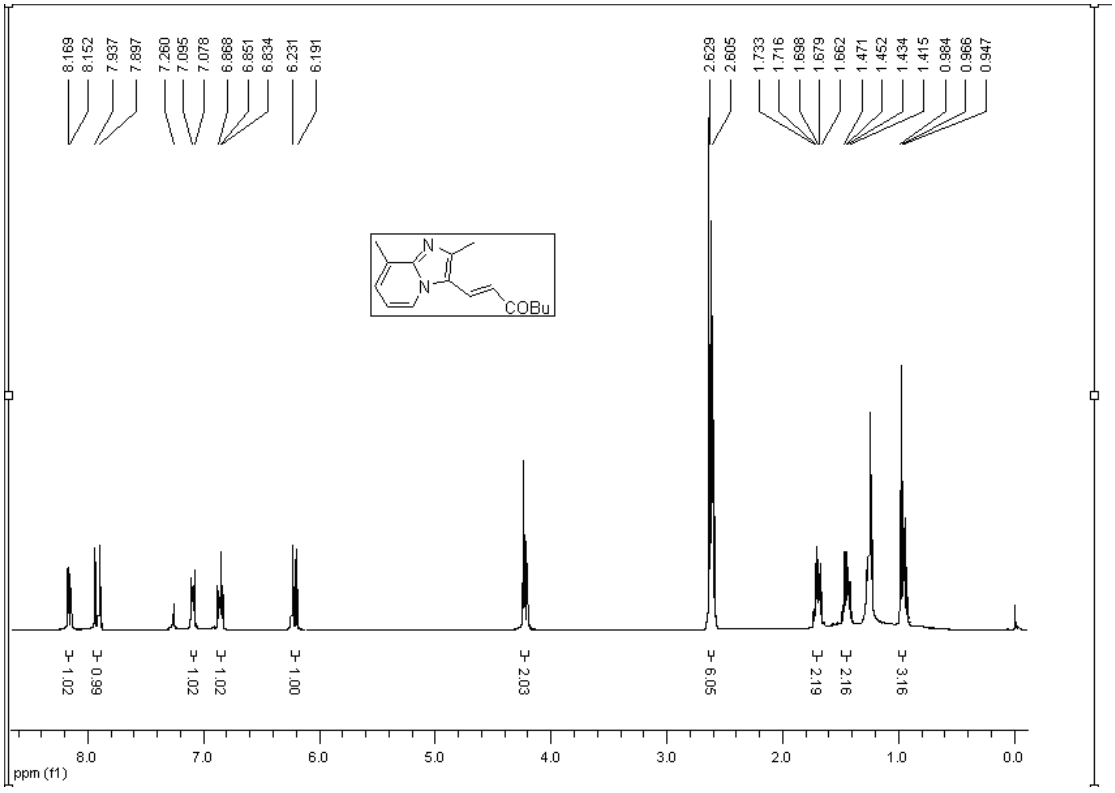
4e

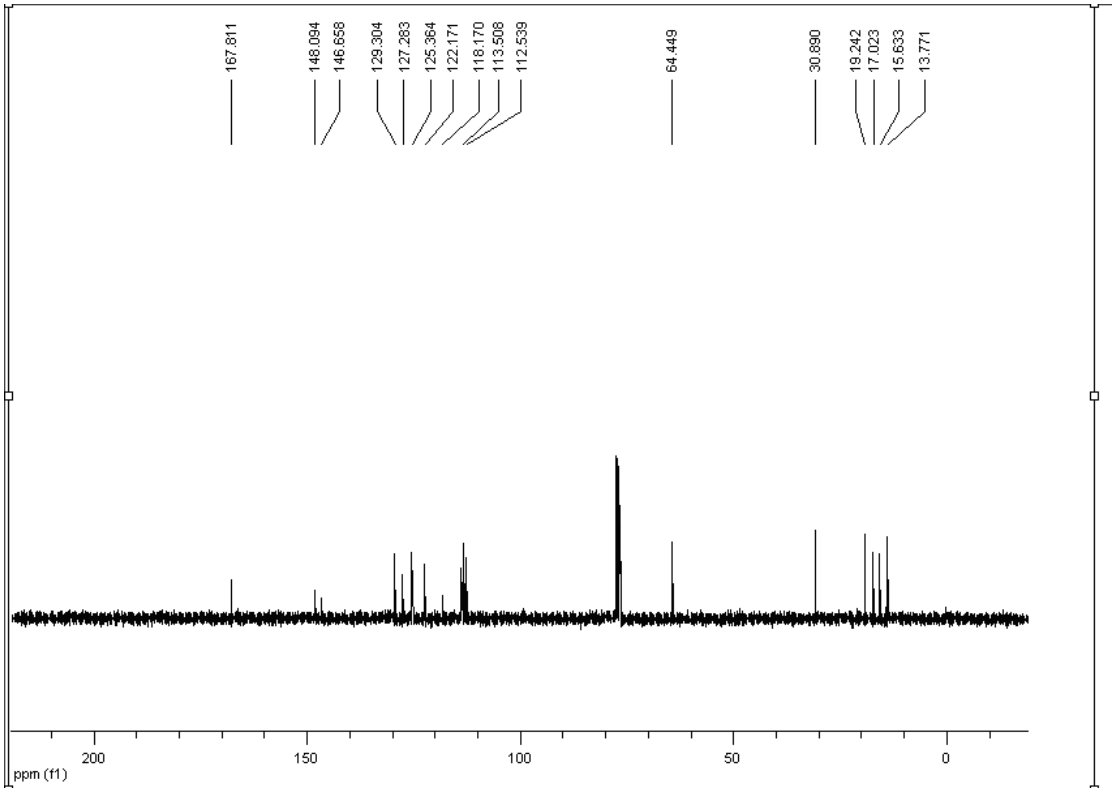

8.063
7.919
7.879
7.535
7.512
7.284
7.157
7.135
6.219
6.178
3.823
2.575
2.372
N
N
CO2CH3
1.00
0.98
1.00
0.96
1.00
3.00
3.02
3.02
5.0
0.0
ppm (t1)
168.114
145.273
129.453
129.293
123.642
122.233
116.499
111.980
77.408
77.090
76.772
51.713
18.352
15.415
200
150
100
50
0
ppm (t1)

4f

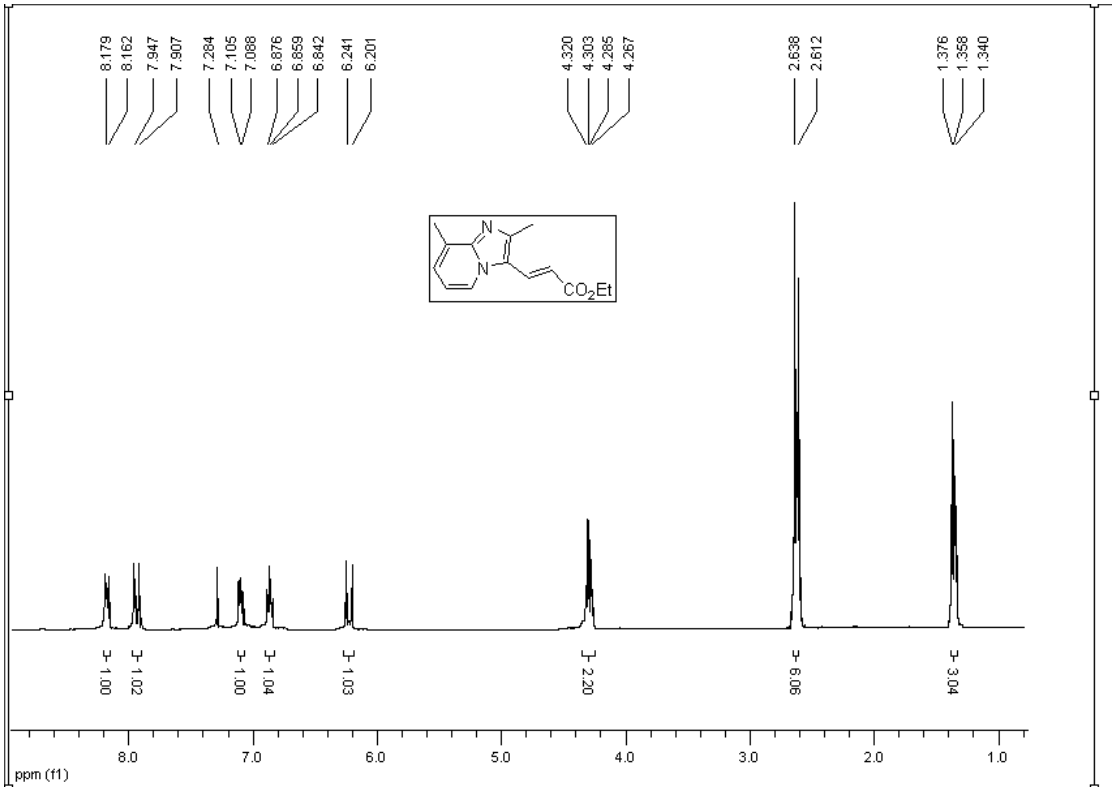

8.061
7.914
7.874
7.496
7.473
7.140
7.138
7.118
7.115
6.208
6.168
4.307
4.290
4.272
4.254
2.574
2.365
1.346
CO2Et
1.02
1.00
1.00
1.01
0.98
2.00
3.02
3.00
3.03
ppm (t1)
167.736
145.355
129.267
129.118
123.476
122.255
116.529
112.316
77.414
77.096
76.777
60.509
18.348
15.549
14.403
ppm (t1)

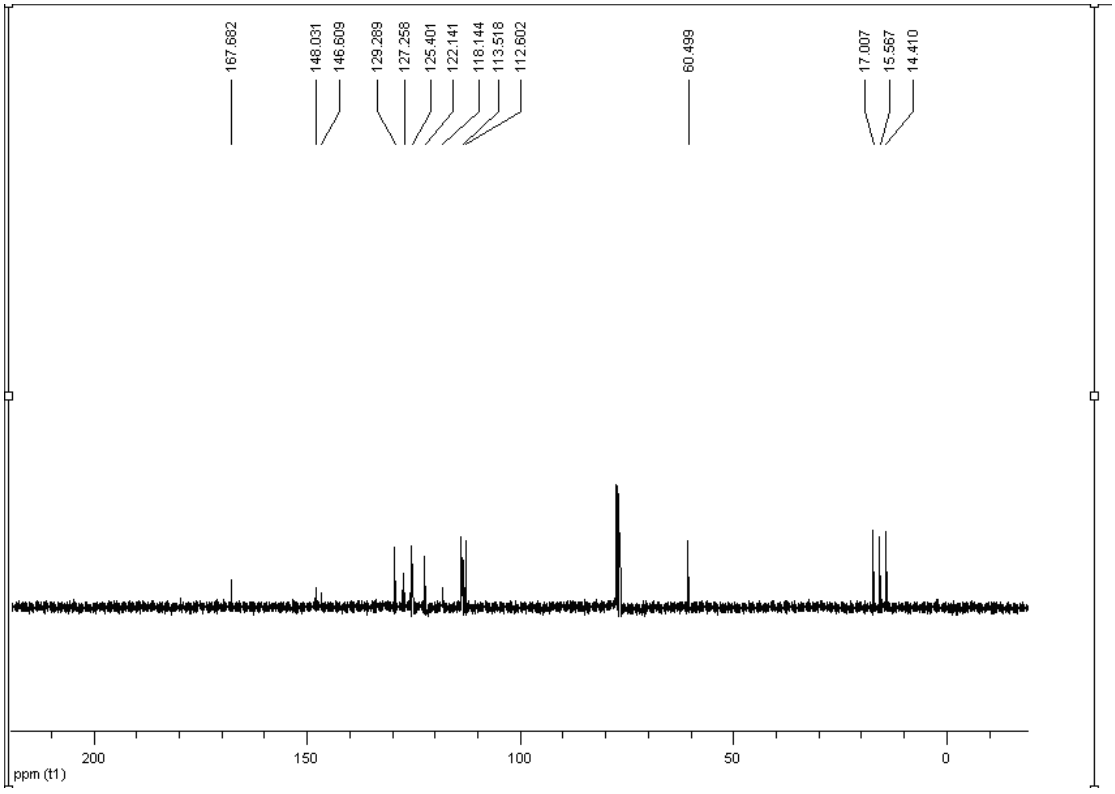
4g


8.169
8.152
7.937
7.897
7.260
7.095
7.078
6.868
6.851
6.834
6.231
6.191
2.629
2.605
1.733
1.716
1.698
1.679
1.662
1.471
1.452
1.434
1.415
0.984
0.966
0.947
N
N
COBu
1.02
0.99
1.02
1.02
1.00
2.03
6.05
2.19
2.16
3.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

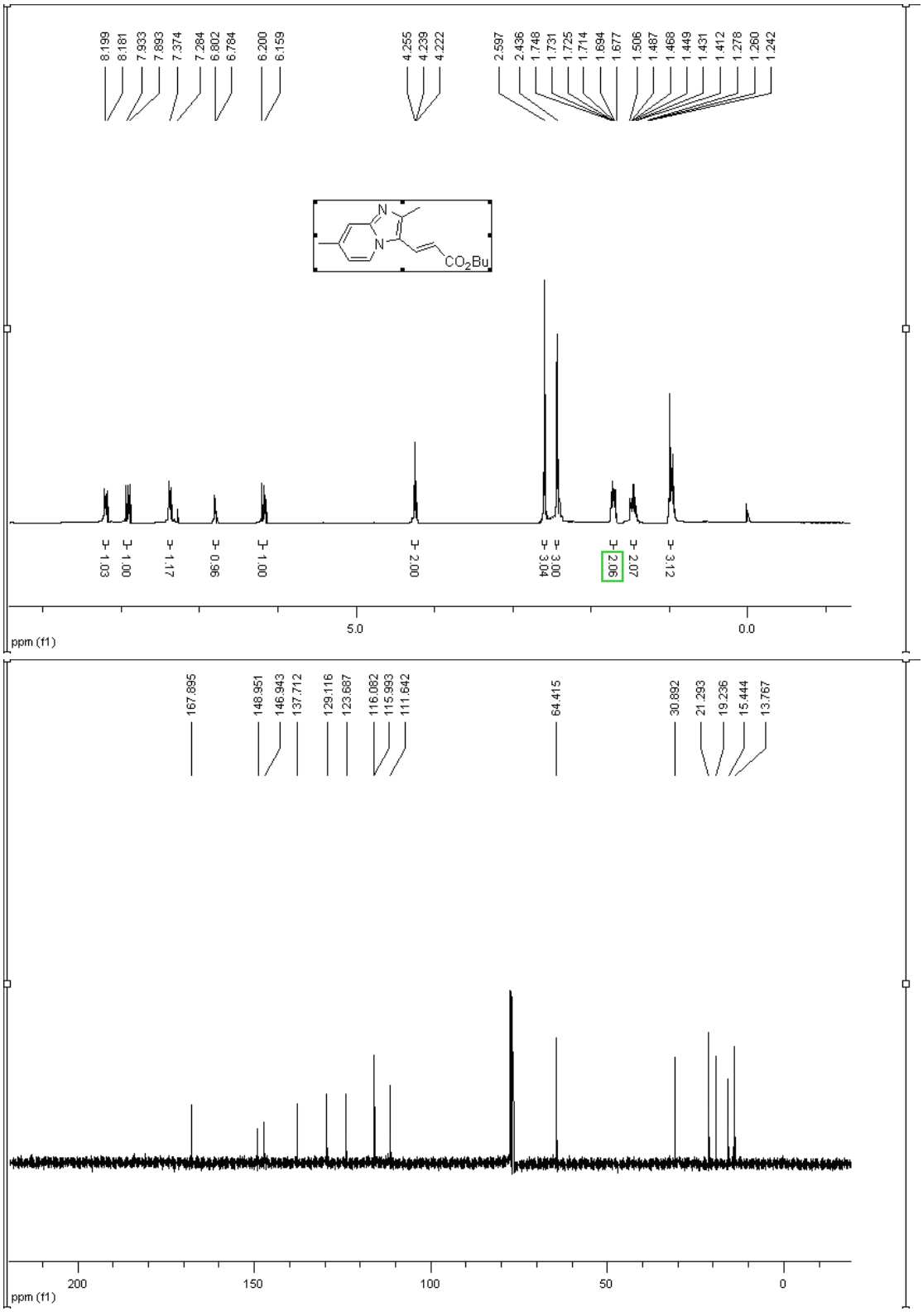

167.811
148.094
146.656
129.304
127.283
125.364
122.171
118.170
113.508
112.539
64.449
30.890
19.242
17.023
15.633
13.771
200
150
100
50
0
ppm (f1)

4h

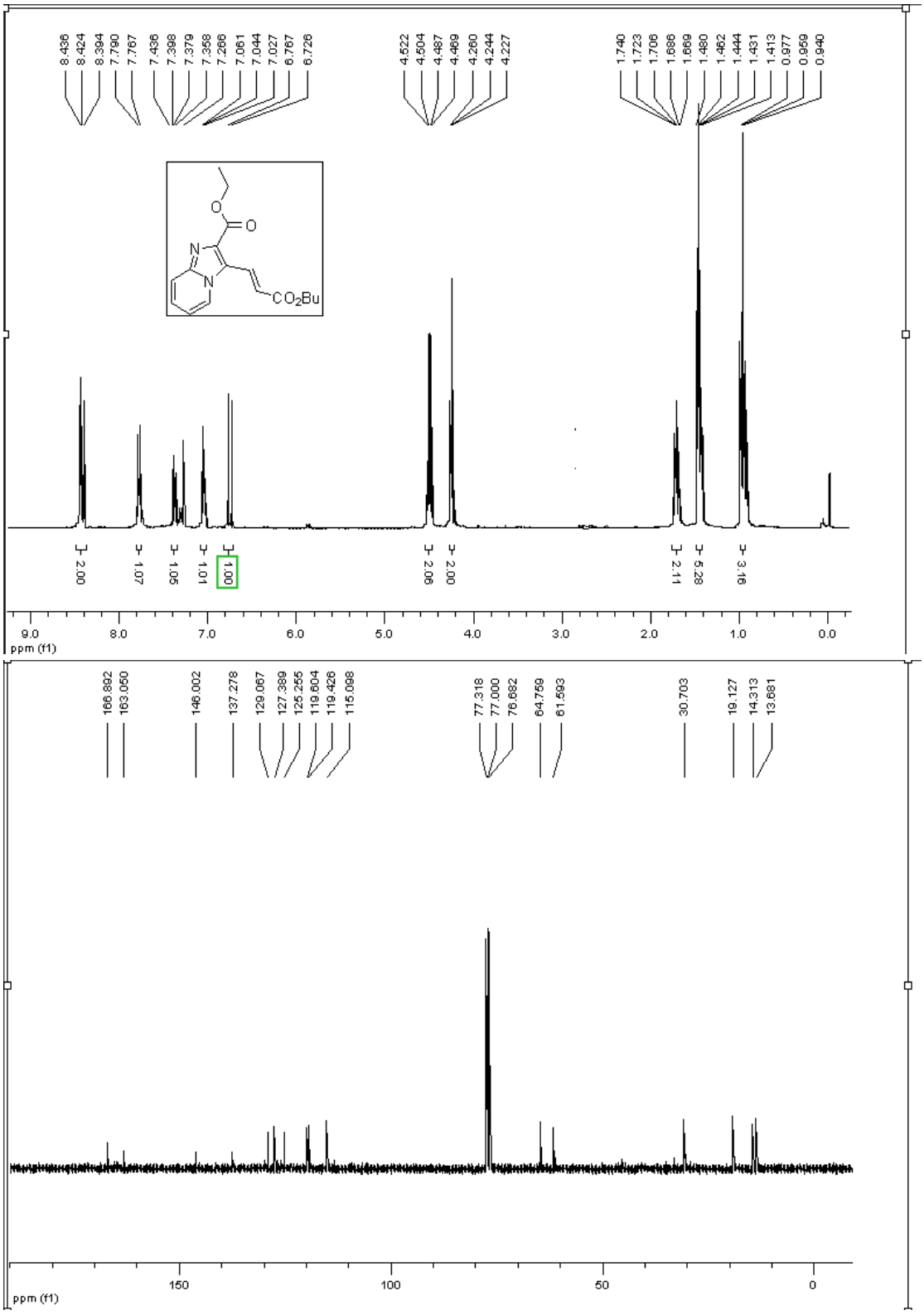

8.179
8.162
7.947
7.907
7.284
7.105
7.088
6.876
6.859
6.842
6.241
6.201
4.320
4.303
4.285
4.267
2.638
2.612
1.376
1.358
1.340
N
N
CO2Et
1.00
1.02
1.00
1.04
1.03
2.20
6.06
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


167.682
148.031
146.609
129.289
127.258
125.401
122.141
118.144
113.518
112.602
60.499
17.007
15.567
14.410
200
150
100
50
0
ppm (f1)

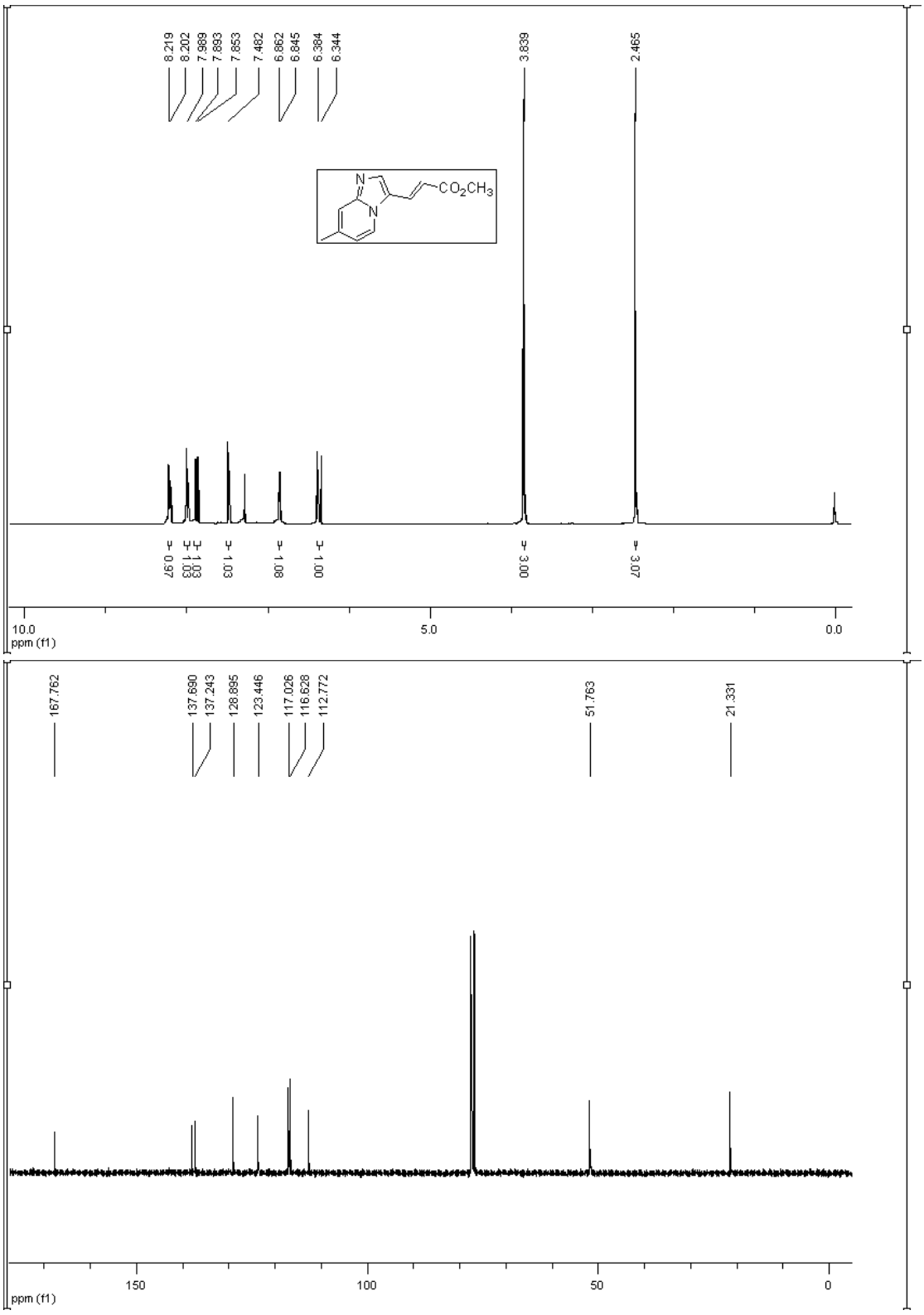
4i


8.199
8.181
7.933
7.893
7.374
7.284
6.802
6.784
6.200
6.159
4.255
4.239
4.222
2.597
2.436
1.748
1.731
1.725
1.714
1.694
1.677
1.506
1.487
1.468
1.449
1.431
1.412
1.278
1.260
1.242
CO2Bu
1.03
1.00
1.17
0.96
1.00
2.00
3.04
3.00
2.06
2.07
3.12
5.0
0.0
ppm (f1)
167.895
148.951
146.943
137.712
129.116
123.687
116.082
115.993
111.642
64.415
30.892
21.293
19.236
15.444
13.767
200
150
100
50
0
ppm (f1)

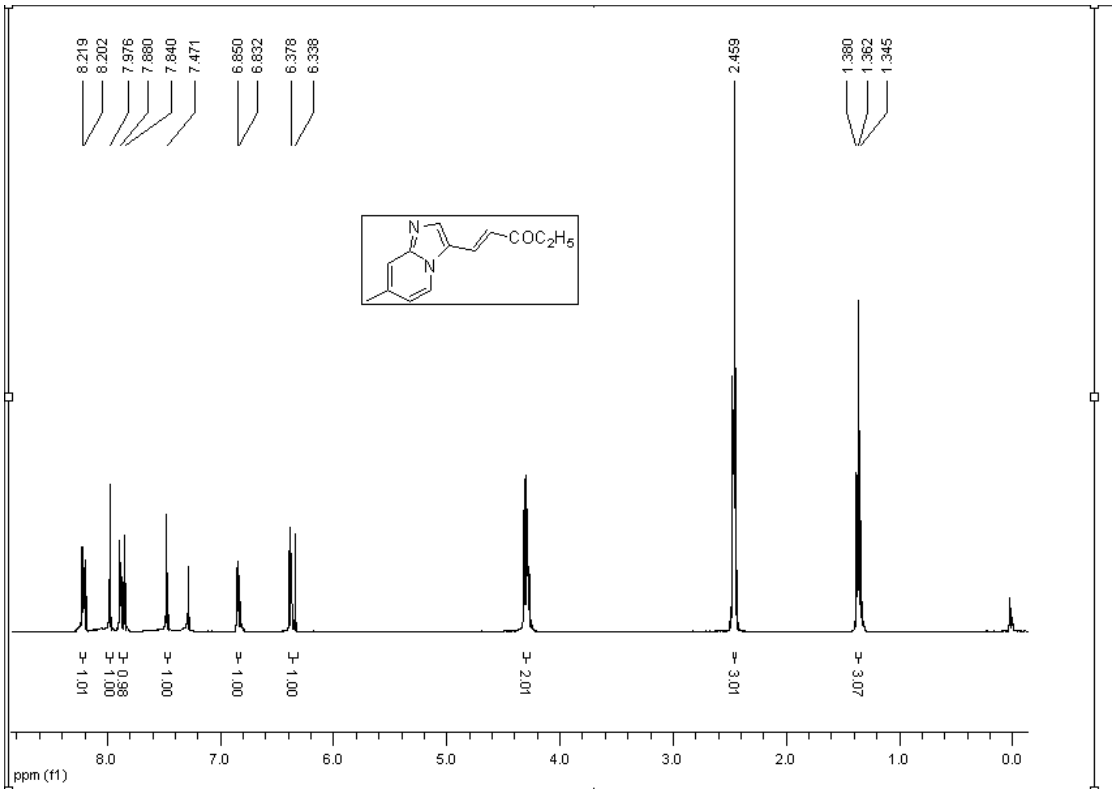
4j

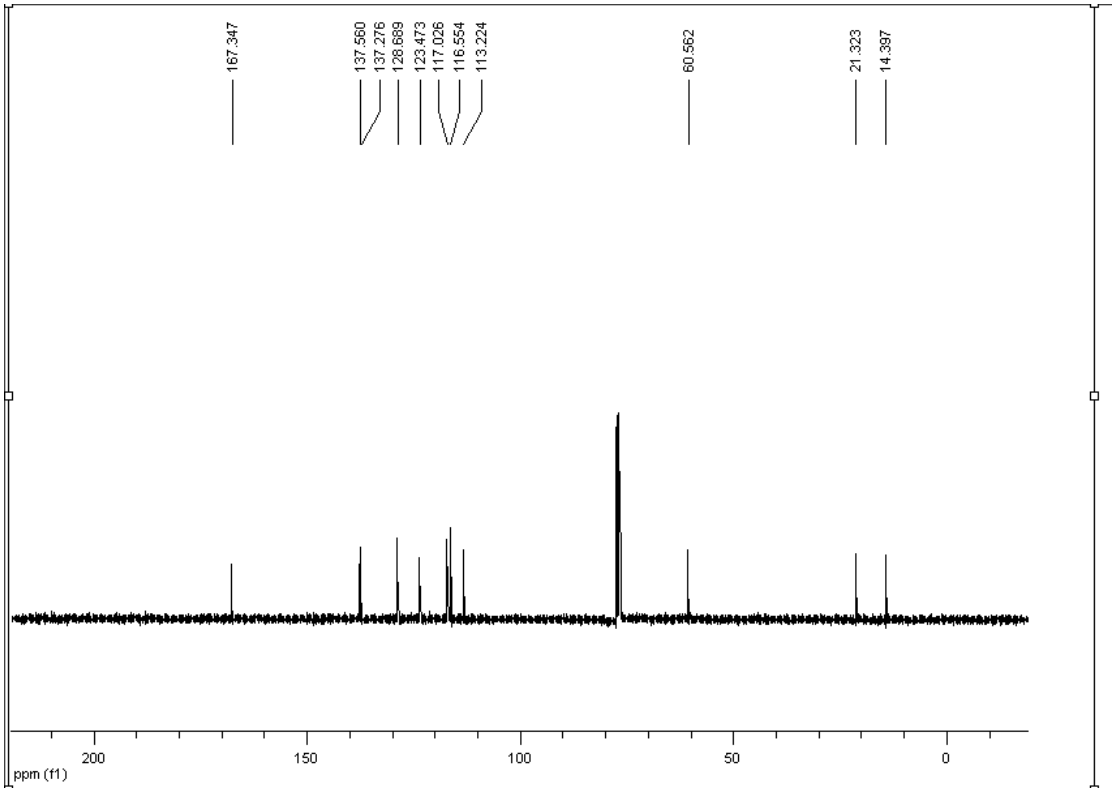

8.436
8.424
8.394
7.790
7.767
7.436
7.398
7.379
7.358
7.266
7.061
7.044
7.027
6.767
6.726
4.522
4.504
4.487
4.469
4.260
4.244
4.227
1.740
1.723
1.706
1.686
1.669
1.480
1.462
1.444
1.431
1.413
0.977
0.959
0.940
O
O
N
N
CO2Bu
2.00
1.07
1.05
1.01
1.00
2.06
2.00
2.11
5.28
9.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
166.892
163.050
146.002
137.278
129.067
127.389
125.255
119.604
119.426
115.098
77.318
77.000
76.682
64.759
61.593
30.703
19.127
14.313
13.681
150
100
50
0
ppm (f1)

4k

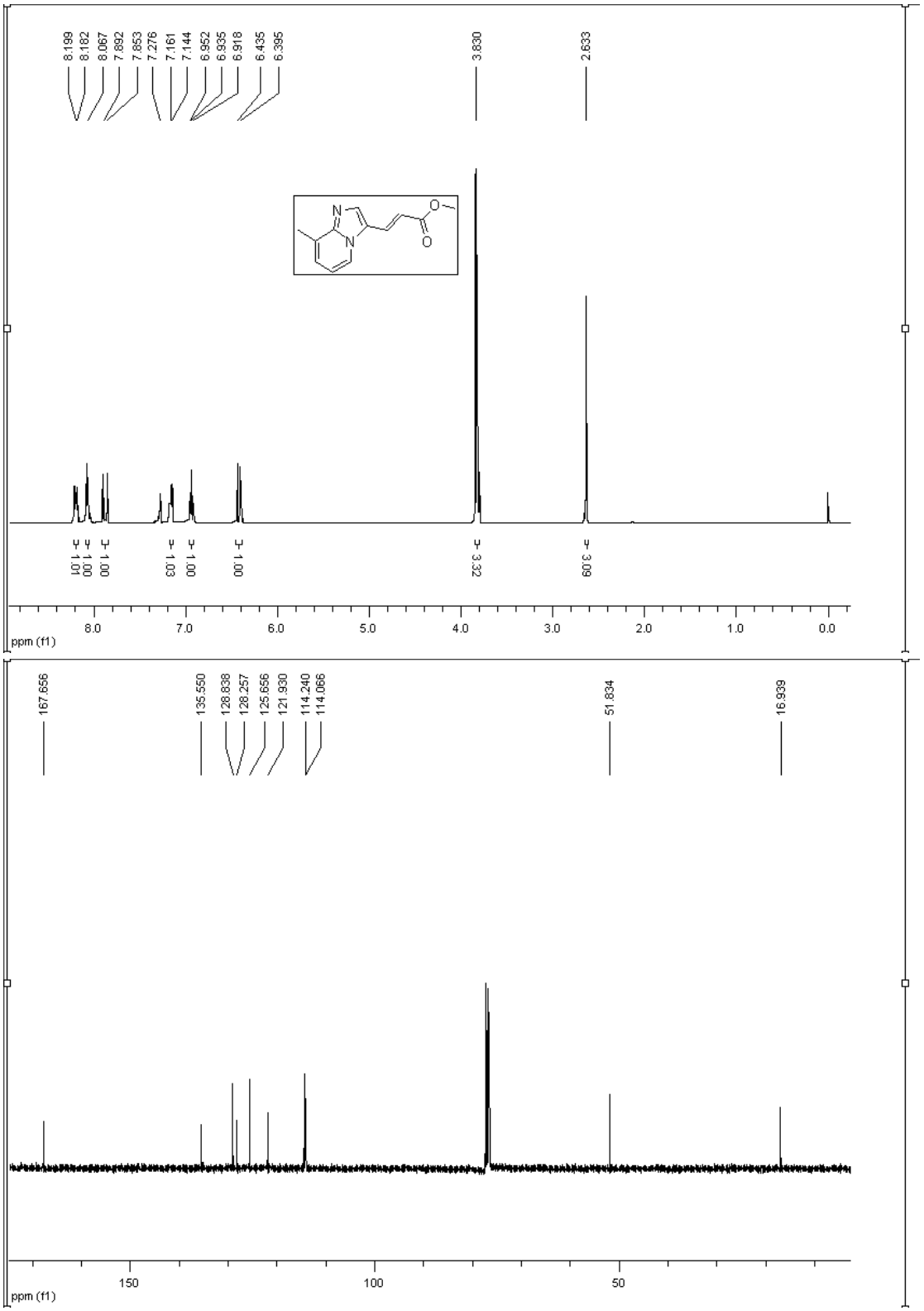

8.219
8.202
7.989
7.893
7.853
7.462
6.862
6.845
6.384
6.344
3.839
2.465
N
N
CO2CH3
0.97
1.03
1.03
1.08
1.00
3.00
3.07
10.0
ppm (f1)
5.0
0.0
167.762
137.690
137.243
128.895
123.446
117.026
116.628
112.772
51.763
21.331
150
100
50
0
ppm (f1)

4l

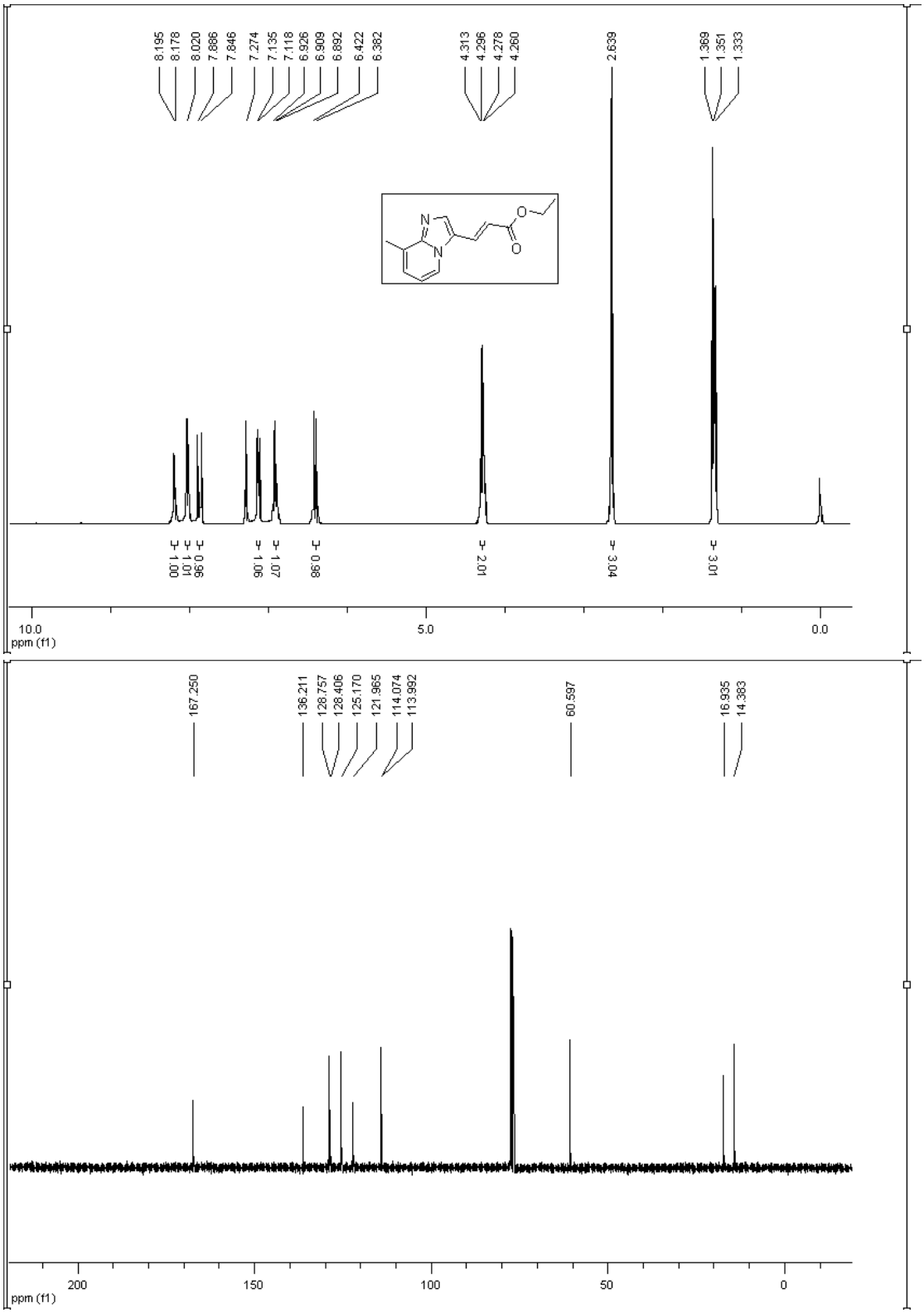

8.219
8.202
7.976
7.880
7.840
7.471
6.850
6.832
6.378
6.338
2.459
1.380
1.362
1.345
N
N
COC2H5
1.01
0.98
1.00
1.00
1.00
2.01
3.01
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


167.347
137.560
137.276
128.689
123.473
117.026
116.554
113.224
60.562
21.323
14.397
200
150
100
50
0
ppm (f1)

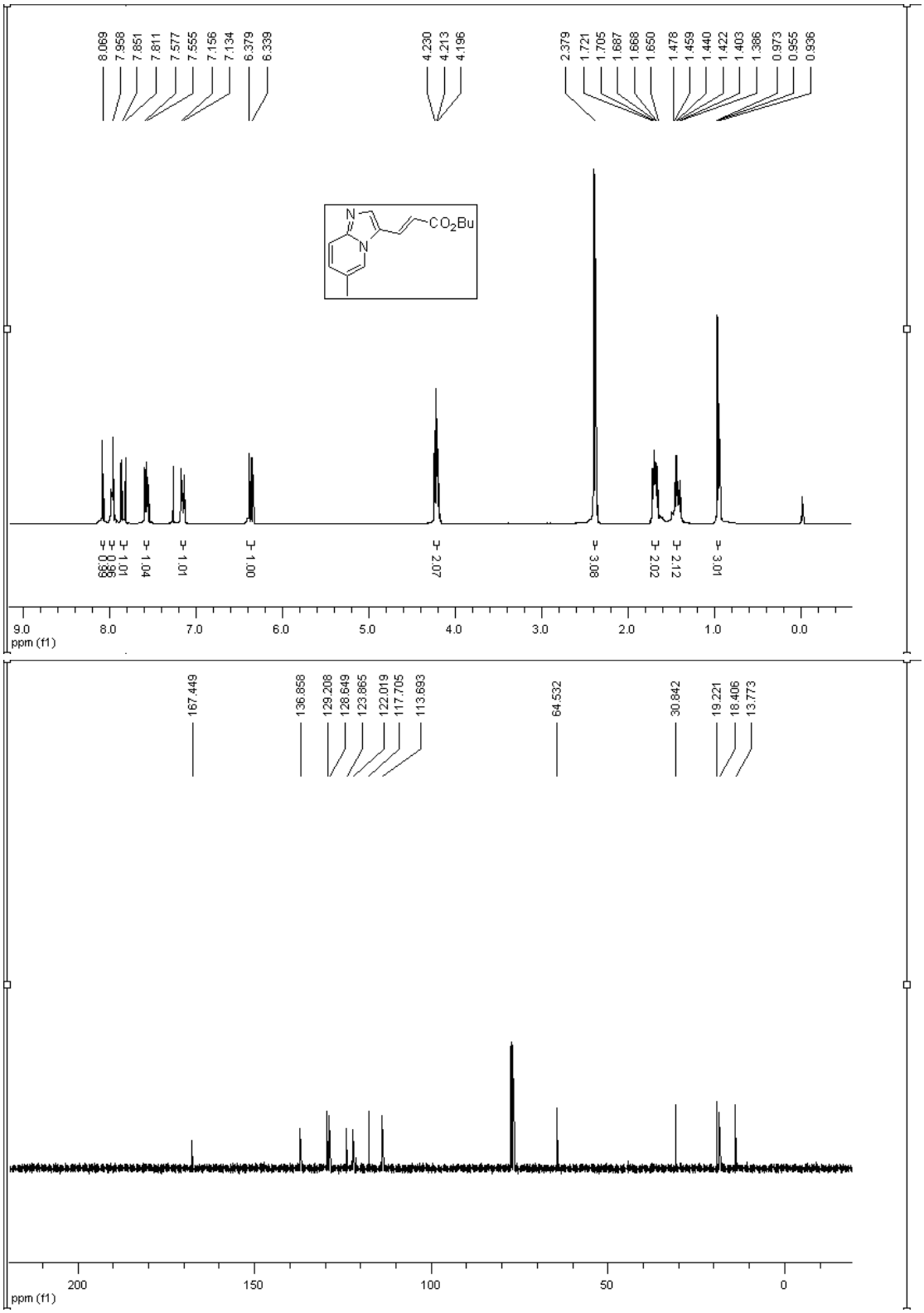
4m


8.199
8.182
8.067
7.892
7.853
7.276
7.161
7.144
6.952
6.935
6.918
6.435
6.395
3.830
2.633
1.01
1.00
1.00
1.03
1.00
1.00
3.32
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
167.656
135.550
128.838
128.257
125.656
121.930
114.240
114.066
51.834
16.939
150
100
50
ppm (f1)

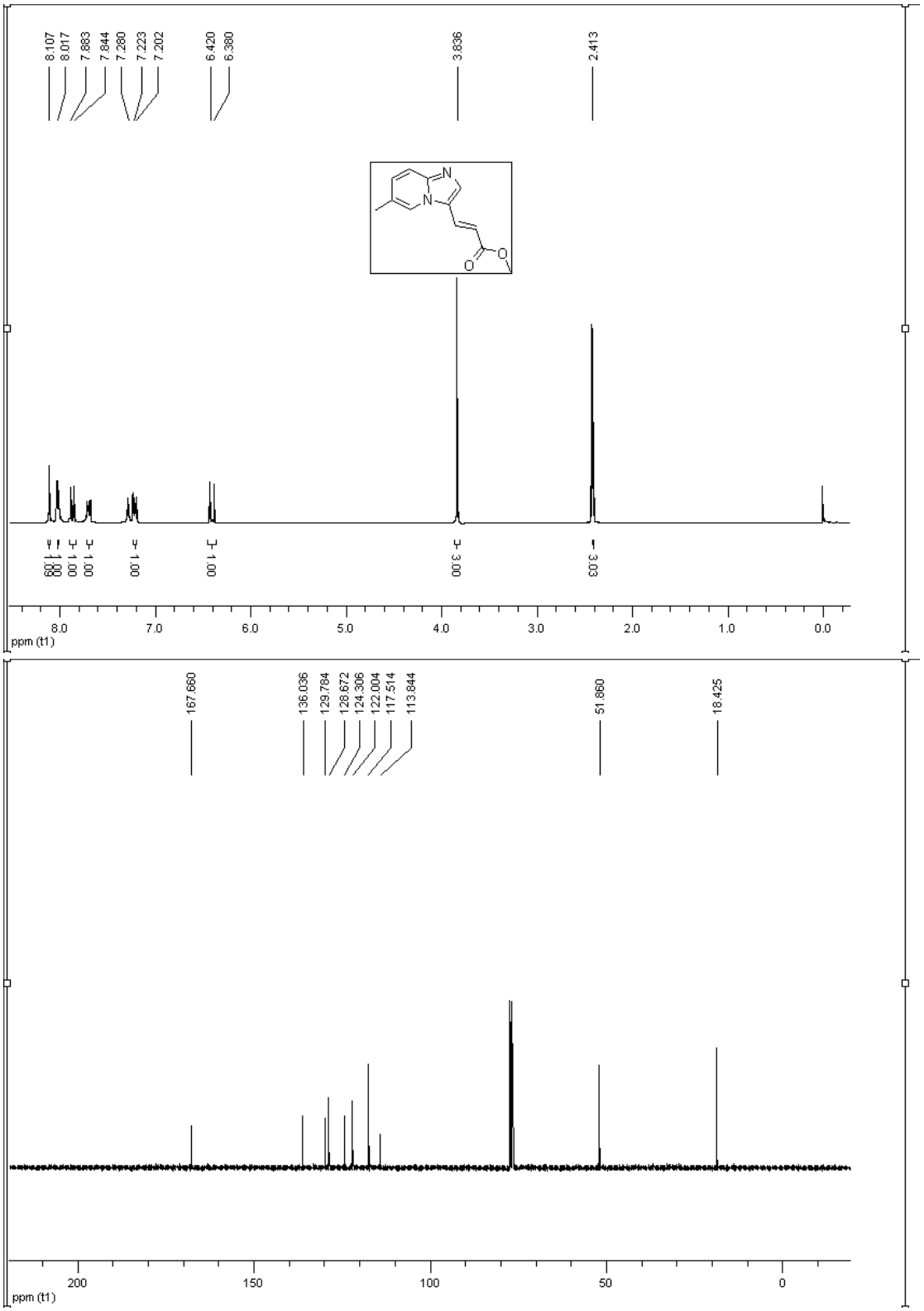
4n


8.195
8.178
8.020
7.886
7.846
7.274
7.135
7.118
6.926
6.909
6.892
6.422
6.382
4.313
4.296
4.278
4.260
2.639
1.369
1.351
1.333
1.00
1.01
0.96
1.06
1.07
0.98
2.01
3.04
3.01
10.0
5.0
0.0
ppm (f1)
167.250
136.211
128.757
128.406
125.170
121.965
114.074
113.992
60.597
16.935
14.383
200
150
100
50
0
ppm (f1)

4o


8.069
7.958
7.851
7.811
7.577
7.555
7.156
7.134
6.379
6.339
4.230
4.213
4.196
2.379
1.721
1.705
1.687
1.668
1.650
1.478
1.459
1.440
1.422
1.403
1.386
0.973
0.955
0.936
CO2Bu
0.98
0.99
1.01
1.04
1.01
1.00
2.07
3.08
2.02
2.12
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
167.449
136.858
129.208
128.649
123.865
122.019
117.705
113.693
64.532
30.842
19.221
18.406
13.773
200
150
100
50
0
ppm (f1)

4p


8.107
8.017
7.883
7.844
7.280
7.223
7.202
6.420
6.380
3.836
2.413
1.00
1.00
1.00
1.00
1.00
3.00
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
167.660
136.036
129.784
128.672
124.306
122.004
117.514
113.844
51.860
18.425
200
150
100
50
0
ppm (t1)