Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ruthenium-Catalyzed Direct C-3 Oxidative Olefination of Imidazo[1,2-a]pyridines

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Longbin Chen,[a] Jingyun Liu,[a] Jinqiang Liao[a] and Hua Cao[a]

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A. General method

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard. Elemental analyses were performed with a Vario EL elemental analyzer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals, Alfa Aesar and Acros Chemical.

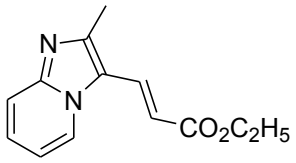
B. General Procedure

Synthesis of 4a according to the following procedure:

2-methylimidazo[1,2-a]pyridine (**1a** 0.5 mmol), ethyl acrylate (**2a** 2.5 mmol), 3 mol%$[RuCl_2(p\text{-cymene})]_2$, $Cu(OAc)_2 \cdot H_2O$ (1.0 mmol), 40 mol% $AgSbF_6$, were added in anhydrous DCE (3 mL) at room temperature. And then the mixture was stirred at 120 ℃ under air 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 **3aa**.

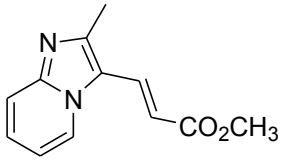
C. Analytical data

(2E)-ethyl 3-(2-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3aa)



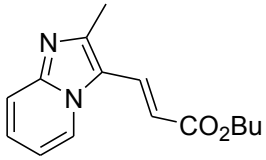
^{1}H NMR (400 MHz, $CDCl_A$): δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 16.1 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.36 – 7.31 (m, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 146.2, 128.9, 126.3, 124.3, 121.1, 117.3, 113.7, 113.0, 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;

(2E)-methyl 3-(2-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ab)



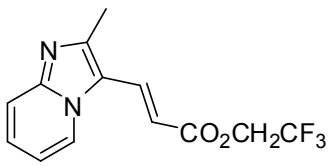
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 16.1 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 3.84 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 148.8, 146.4, 129.1, 126.2, 124.2, 120.3, 117.3, 113.5, 112.2, 51.7, 15.6. 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;

(2E)-butyl 3-(2-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ac)



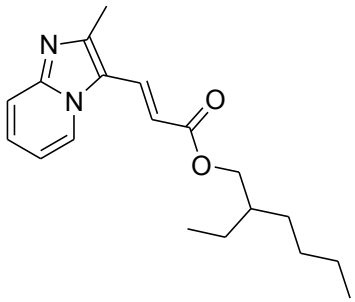
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 16.1 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 9.7 Hz, 1H), 6.96 (s, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 4.25 (s, 2H), 2.63 (s, 3H), 1.76 – 1.67 (m, 2H), 1.51 – 1.42(m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 148.7, 146.4, 128.9, 126.1, 124.2, 117.3, 113.5, 112.7, 64.5, 30.8, 19.2, 15.6, 13.7. 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;

(2E)-2,2,2-trifluoroethyl 3-(2-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ad)



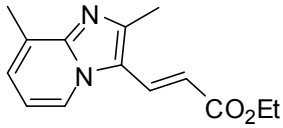
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 2.7 Hz, 1H), 8.03 (d, *J* = 16.0 Hz, 1H), 7.68 (s, 1H), 7.36 (s, 1H), 7.02 (s, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 11.1, 4.5 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 146.9, 131.1, 127.0, 124.5, 117.7, 117.5, 114.0, 109.5, 60.6 (*J* = 41.2 Hz), 15.7. ESI-MS m/z (%) 285 (100) $[M+H]^+$. Calcd for $C_{13}H_{14}F_3N_2O_2$: C, 64.93; H, 3.90; N, 9.86; Found: C, 65.04; H, 3.88; N, 9.81;

(2E)-2-ethylhexyl 3-(2-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ae)



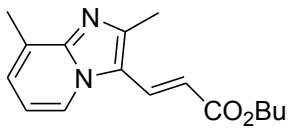
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 16.1 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 6.8 Hz, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 4.21 – 4.12 (m, 2H), 2.63 (s, 3H), 1.71 – 1.65 (m, 1H), 1.44 – 1.30 (m, 8H), 0.97 – 0.90 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 146.4, 129.0, 126.3, 124.3, 117.4, 113.7, 112.9, 67.1, 39.0, 30.5, 29.0, 23.9, 23.0, 14.1, 11.1. MS (EI) m/z (%): 314, 284, 277, 202, 185, 158, 78. Calcd for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.33; N, 8.91; Found: C, 72.04; H, 8.38; N, 8.97;

(2E)-ethyl 3-(2,8-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ba)



^{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 (101 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;

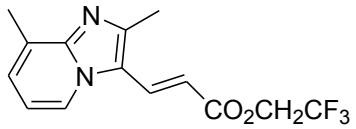
(2E)-butyl 3-(2,8-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3bc)



^{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*

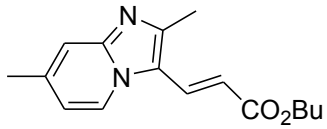
= 6.7 Hz, 2H), 2.62 (d, *J* = 9.8 Hz, 6H), 1.74 – 1.66 (m, 2H), 1.44 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 148.1, 146.7, 129.3, 127.3, 125.4, 122.2, 118.2, 113.5, 112.5, 64.5, 30.9, 19.2, 17.0, 15.6, 13.8. MS (EI) m/z (%): 280, 272, 199, 172, 159, 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;

(2E)-2,2,2-trifluoroethyl 3-(2,8-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3bd)



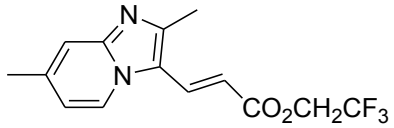
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 16.0 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 6.90 (t, *J* = 6.9 Hz, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 4.61 (q, *J* = 8.5 Hz, 2H), 2.64 (d, *J* = 12.6 Hz, 6H), 2.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 149.7, 147.2, 131.4, 127.5, 126.1, 122.3 (*J* = 140.4 Hz), 118.1, 113.9, 112.6, 109.1, 60.4 (*J* = 16.4 Hz), 17.0, 15.7. MS (EI) m/z (%): 298, 199, 184, 171, 154, 129, 104, 92, 78, 65; ESI-MS m/z (%) 299 (100) $[M+H]^+$. Calcd for $C_{14}H_{13}F_3N_2O_2$: C, 56.38; H, 4.39; N, 9.39; Found: C, 56.49; H, 4.37; N, 9.33;

(2E)-butyl 3-(2,7-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3cc)



^{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 (101 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;

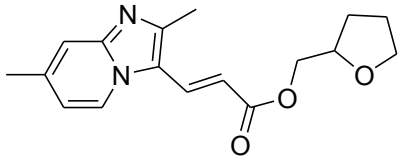
(2E)-2,2,2-trifluoroethyl 3-(2,7-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3cd)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.0 Hz, 1H), 8.03 (s, 1H), 7.42 (s, 1H), 6.85 (d, *J* = 6.9 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.63 (q, *J* = 8.5 Hz, 2H), 2.62 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1, 150.5, 147.5, 138.6, 131.2, 123.9, 117.3 (*J* = 171.0 Hz), 116.5, 108.2, 60.4 (*J* = 23.2 Hz), 21.3, 15.5. MS (EI) m/z (%): 297, 281, 256, 228, 215, 199, 193, 169, 136, 102, 73. ESI-MS m/z (%) 299 (100)

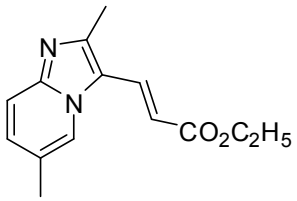
$[M+H]^+$. Calcd for $C_{14}H_{13}F_3N_2O_2$: C, 56.38; H, 4.39; N, 9.39; Found: C, 56.48; H, 4.37; N, 9.34;

(2E)-(tetrahydrofuran-2-yl)methyl 3-(2,7-dimethylH-imidazo[1,2-a]pyridin-3-yl) acrylate (3ce)



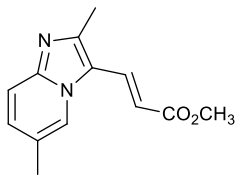
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.0 Hz, 1H), 7.95 (d, *J* = 16.1 Hz, 1H), 7.38 (s, 1H), 6.80 (d, *J* = 6.9 Hz, 1H), 6.25 (d, *J* = 16.1 Hz, 1H), 4.35 (dd, *J* = 11.2, 3.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.96 (q, *J* =6.8 Hz, 1H), 3.90 – 3.84 (m, 1H), 2.60 (s, 3H), 2.45 (s, 3H), 1.99 -1.91 (m, 2H), 1.74 – 1.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 147.0, 137.8, 129.6, 129.5, 123.7, 116.1, 116.0, 110.9, 68.4, 66.5, 28.0, 25.6, 21.2, 15.4. ESI-MS m/z (%)300 (100) $[M+H]^+$. Calcd for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33; Found: C, 68.29; H, 6.67; N, 9.26;

(2E)-ethyl 3-(2,5-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3da)



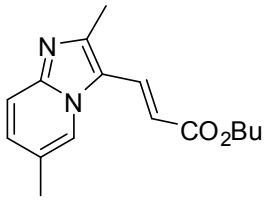
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.89 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 9.1 Hz, 1H), 7.13 (q, *J* = 9.0 Hz, 1H), 6.19 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 2.37 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 148.4, 132.9, 129.2, 129.1, 123.4, 122.2, 116.5, 112.3, 60.5, 18.3, 15.5, 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;

(2E)-methyl 3-(2,5-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3db)



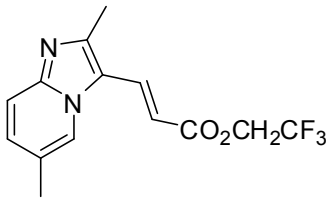
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.90 (d, *J* = 16.1 Hz, 1H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 9.0 Hz, 1H), 6.20 (d, *J* = 16.1 Hz, 1H), 3.82 (s, 3H), 2.57 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 145.1, 132.9, 129.3, 129.2, 123.5, 122.1, 116.4, 115.7, 111.8, 51.6, 18.2, 15.3. 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;

(2E)-butyl 3-(2,5-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3dc)



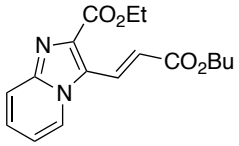
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 6.22 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.59 (s, 3H), 2.39 (s, 3H), 1.76 – 1.69 (m, 2H), 1.51 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 145.0, 129.2, 128.9, 128.8, 123.4, 122.0, 117.3, 116.2, 112.3, 64.2, 30.7, 19.0, 18.1, 15.2, 13.5. 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;

(2E)-2,2,2-trifluoroethyl 3-(2,5-dimethylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3dd)



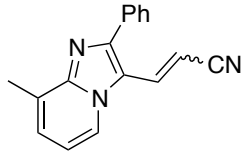
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 8.01 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 4.63 (q, *J* = 8.5 Hz, 2H), 2.62 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.9, 166.1, 150.2, 132.9, 131.2, 129.8, 123.9, 122.5 (*J* = 140.0 Hz), 117.6, 116.8, 108.7, 60.5 (*J* = 36.2 Hz), 29.7, 18.4, 15.7. ESI-MS m/z (%) 299 (100) $[M+H]^+$. Calcd for $C_{14}H_{13}F_3N_2O_2$: C, 56.38; H, 4.39; N, 9.39; Found: C, 56.49; H, 4.37; N, 9.34;

ethyl 3-((E)-2-(butoxycarbonyl)vinyl)H-imidazo[1,2-a]pyridine-2-carboxylate(3de)



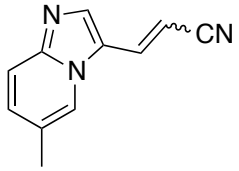
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.37 (m, 2H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.04 (t, *J* = 6.9 Hz, 1H), 6.75 (d, *J* = 16.6 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.48 – 1.41 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 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;

(2Z)-3-(8-methyl-2-phenylH-imidazo [1, 2-a] pyridin-3-yl) acrylonitrile; (2E)-3-(8-methyl-2-phenylH-imidazo [1, 2-a] pyridin-3-yl) acrylonitrile (3dg)



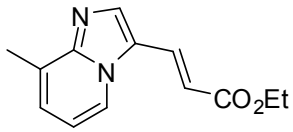
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.18 (m, 1.75H), 7.78 – 7.70 (m, 3.75H), 7.56 – 7.49 (m, 5H), 7.46 – 7.39 (m, 1.75H), 7.22 (q, *J* = 7.0 Hz, 1.75H), 7.02 – 6.96 (m, 1.75H), 5.71 – 5.65 (m, 0.75H), 5.60 – 5.53 (m, 1H), 2.74 – 2.70 (m, 5.27H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.19, 149.14, 136.23, 135.88, 133.78, 132.33, 130.93, 129.51, 129.21, 128.97, 128.86, 128.77, 128.14, 126.32, 125.79, 124.27, 122.52, 114.55, 113.23, 94.90, 90.48, 17.17. ESI-MS m/z (%) 184 (100) $[M+H]^+$. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20; Found: C, 78.47; H, 5.13; N, 16.37;

(2*E*)-3-(6-methyl-imidazo[1,2-a]pyridin-3-yl)acrylonitrile;(2Z)-3-(6-methylH-imidazo[1,2-a]pyridin-3-yl)acrylonitrile(3dh):



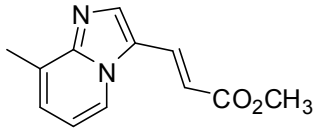
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 0.6H), 8.02 (d, *J* = 7.6 Hz, 2.6H), 7.93 (s, 0.6H), 7.66 (t, *J* = 8.6 Hz, 1.6H), 7.52 (d, *J* = 16.4 Hz, 1H), 7.23 (d, *J* = 10.9 Hz, 1.6H), 5.78 (d, *J* = 16.4 Hz, 1H), 5.31 (d, *J* = 11.9 Hz, 0.6H), 2.41 (d, *J* = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.36, 136.36, 133.92, 133.23, 131.25, 130.09, 124.68, 124.25, 121.61, 120.94, 118.71, 117.83, 91.30, 89.91, 18.44. ESI-MS m/z (%) 184 (100) $[M+H]^+$. Calcd for $C_{11}H_{19}N_3$: C, 72.11; H, 4.95; N, 22.94; Found: C, 71.89; H, 5.01; N, 23.05;

(2E)-ethyl 3-(8-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3ea)



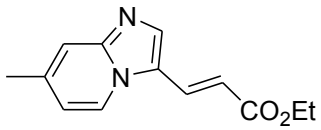
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 6.7 Hz, 1H), 8.02 (s, 1H), 7.87 (d, *J* = 15.9 Hz, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 6.91 (t, *J* = 6.9 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.32 – 4.26 (m, 2H), 2.64 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 149.4, 136.1, 128.7, 128.3, 125.1, 121.9, 114.0, 113.9, 60.5, 16.8, 14.3. 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;

(2E)-methyl 3-(8-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3eb)



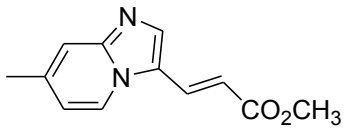
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 6.8 Hz, 1H), 8.07 (s, 1H), 7.87 (d, *J* = 15.9 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 1H), 6.93 (t, *J* = 6.8 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 135.5, 128.8, 128.2, 125.7, 125.6, 122.0, 121.9, 114.1, 114.0, 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;

(2E)-ethyl 3-(7-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3fa)



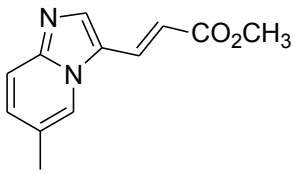
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.98 (s, 1H), 7.88 (d, *J* = 16 Hz, 1H), 7.47 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 16 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3,137.6, 137.3, 128.7, 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;

(2E)-methyl 3-(7-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3fb)



^{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 (101 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;

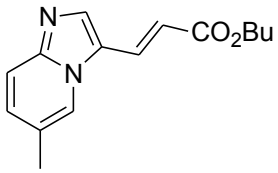
(2E)-methyl 3-(6-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3gb)



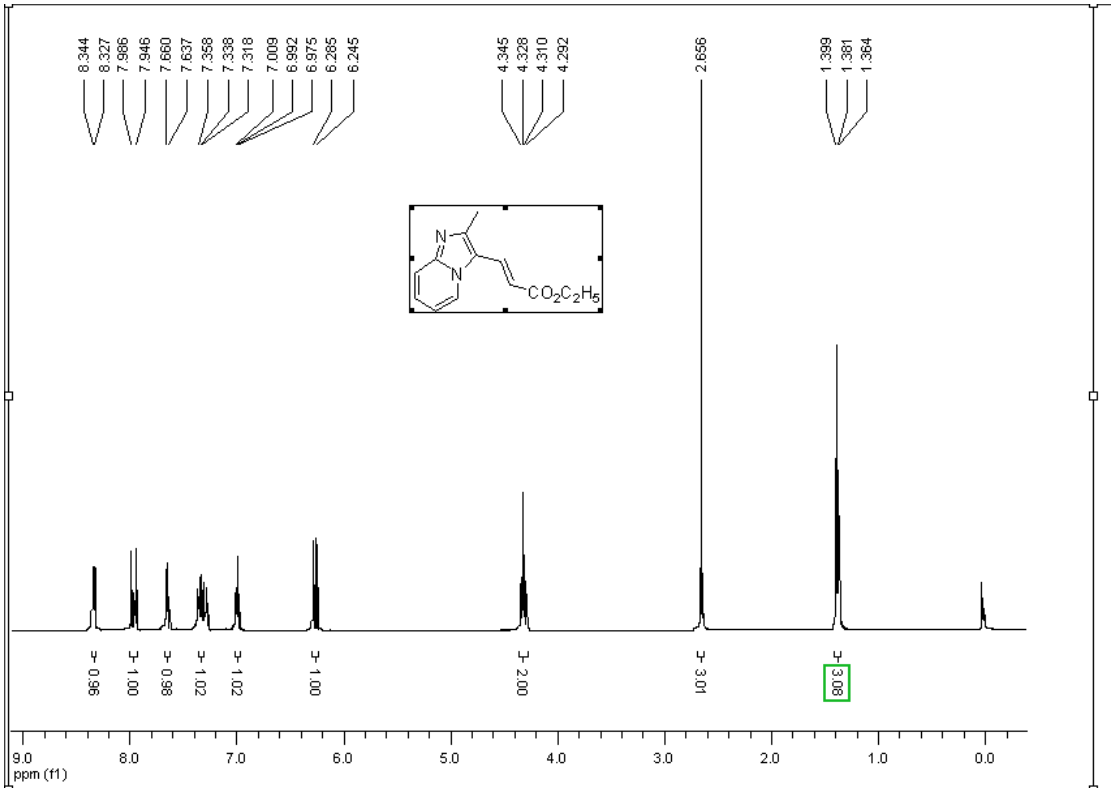
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.02 (s, 1H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 149.6, 136.0, 129.8, 128.7,

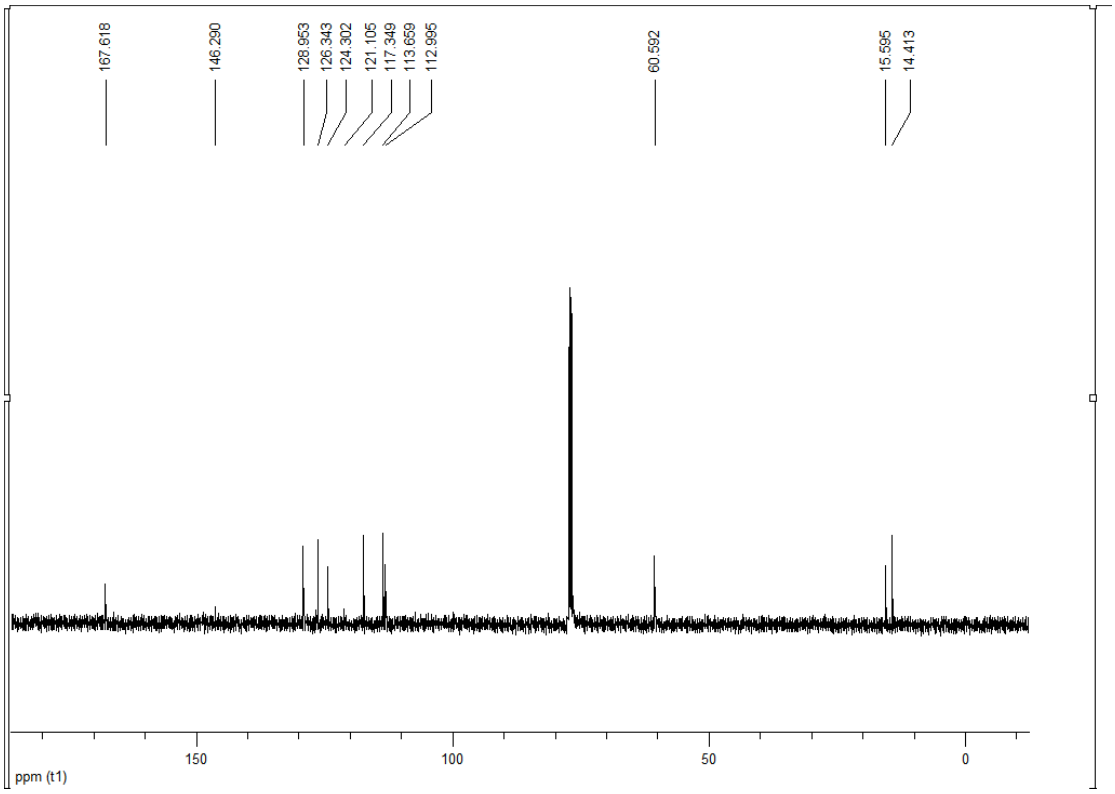
124.3, 122.0, 117.5, 113.8, 51.9, 18.4. ESI-MS m/z (%) 217 (100) $[M+H]^+$. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.74; H, 5.55; N, 12.88;

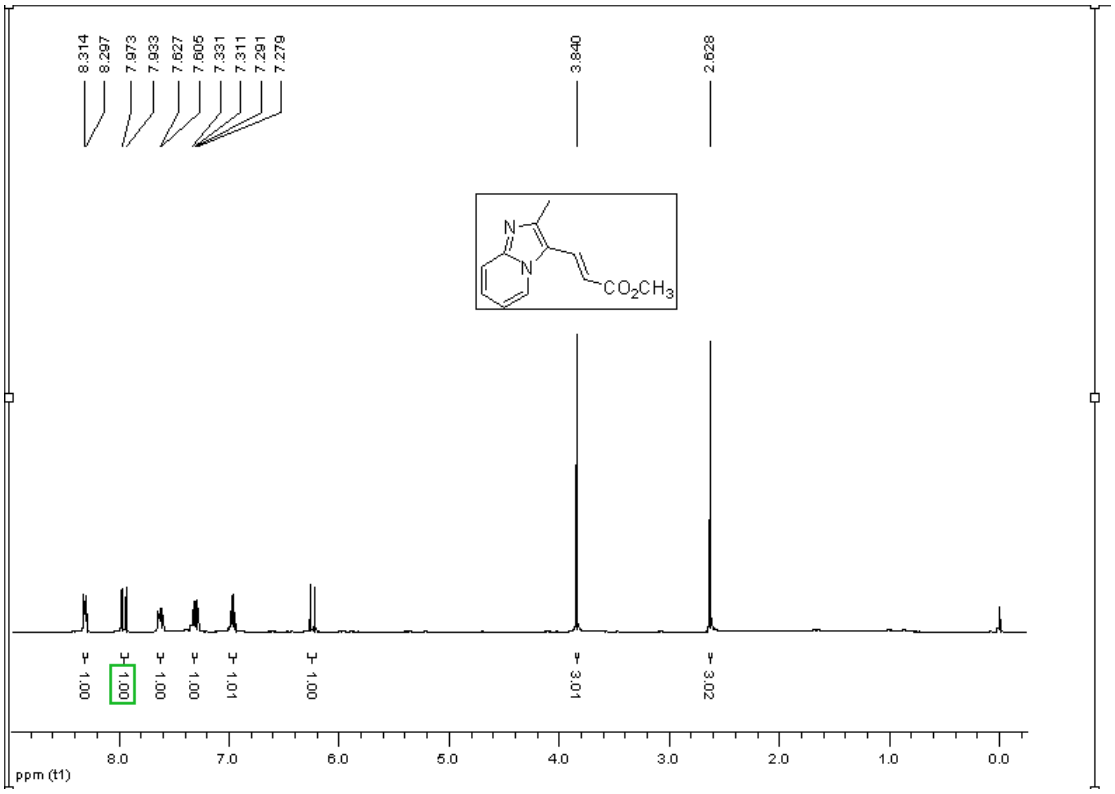
(2E)-butyl 3-(6-methylH-imidazo[1,2-a]pyridin-3-yl)acrylate (3gc)

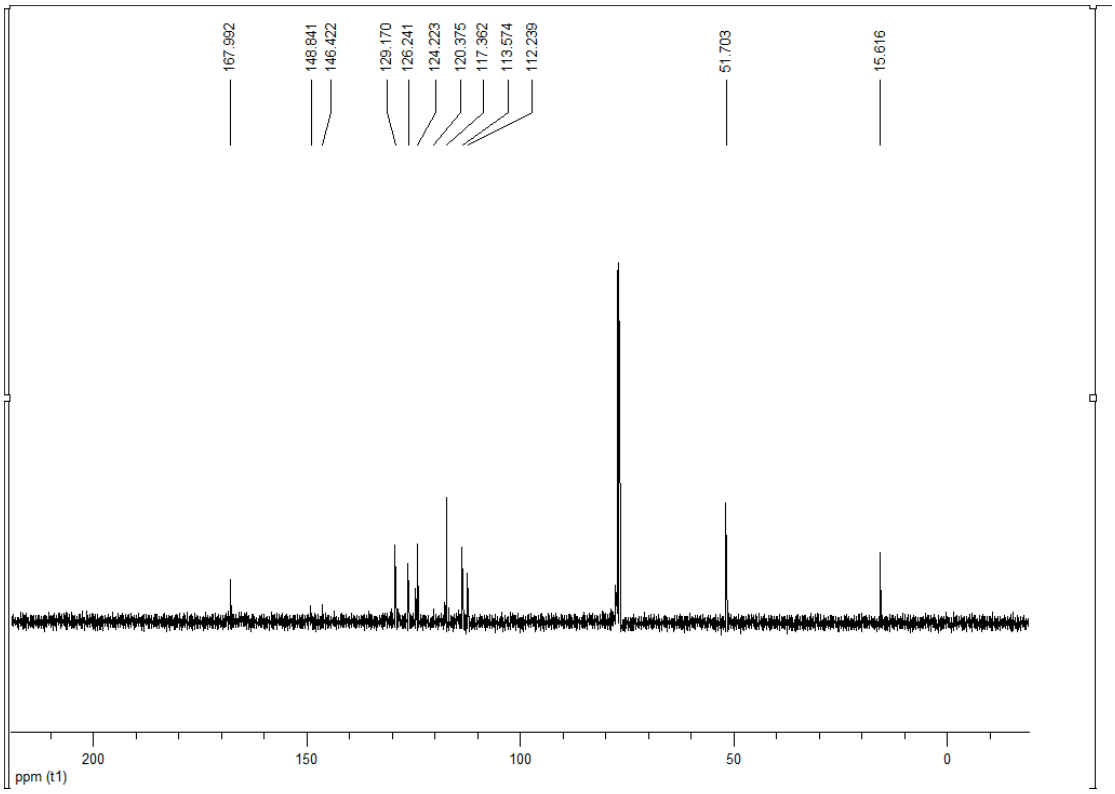


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.57 (d, *J* = 9.1 Hz, 1H), 7.14 (d, *J* = 9.1 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 1.72 – 1.65 (m, 2H), 1.43 (q, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 146.9, 136.7, 129.1, 128.5, 123.7, 121.9, 121.3, 117.6, 113.6, 64.4, 30.7, 19.1, 18.3, 13.7. 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;




167.618
146.290
128.953
126.343
124.302
121.105
117.349
113.659
112.995
60.592
15.595
14.413
150
100
50
0
ppm (t1)


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 (t1)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148.841
146.422
129.170
126.241
124.223
120.375
117.362
113.574
112.239
51.703
15.616
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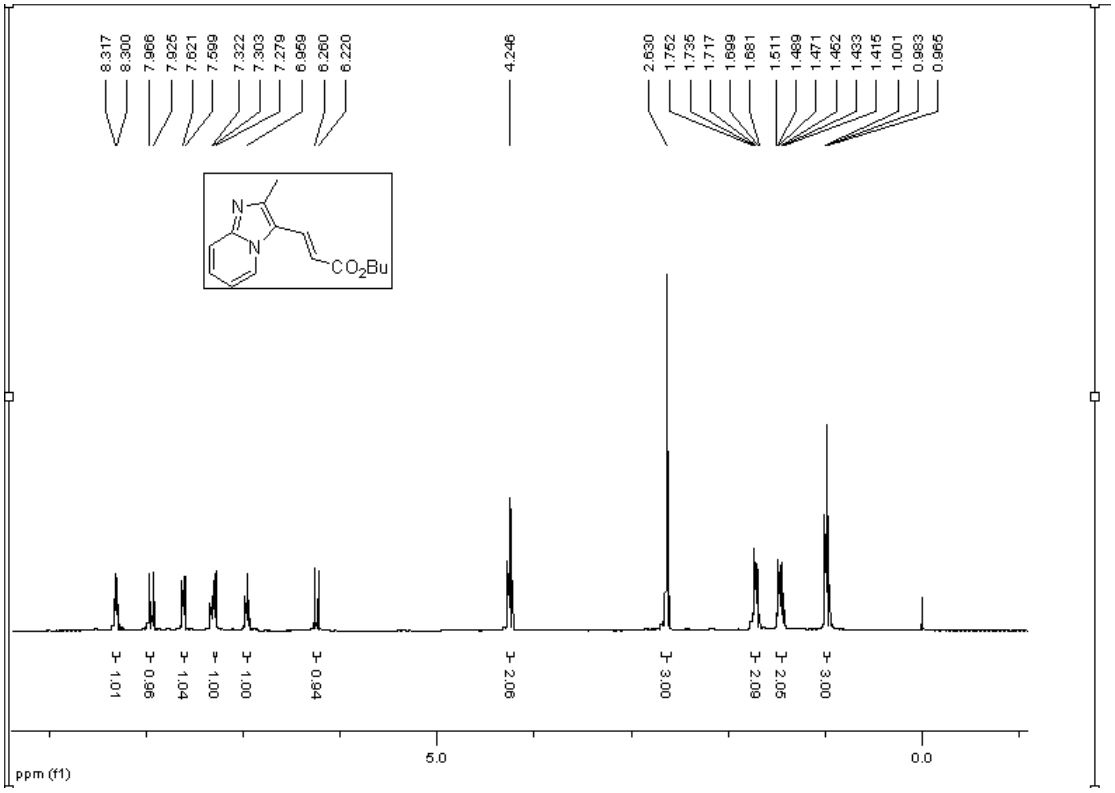
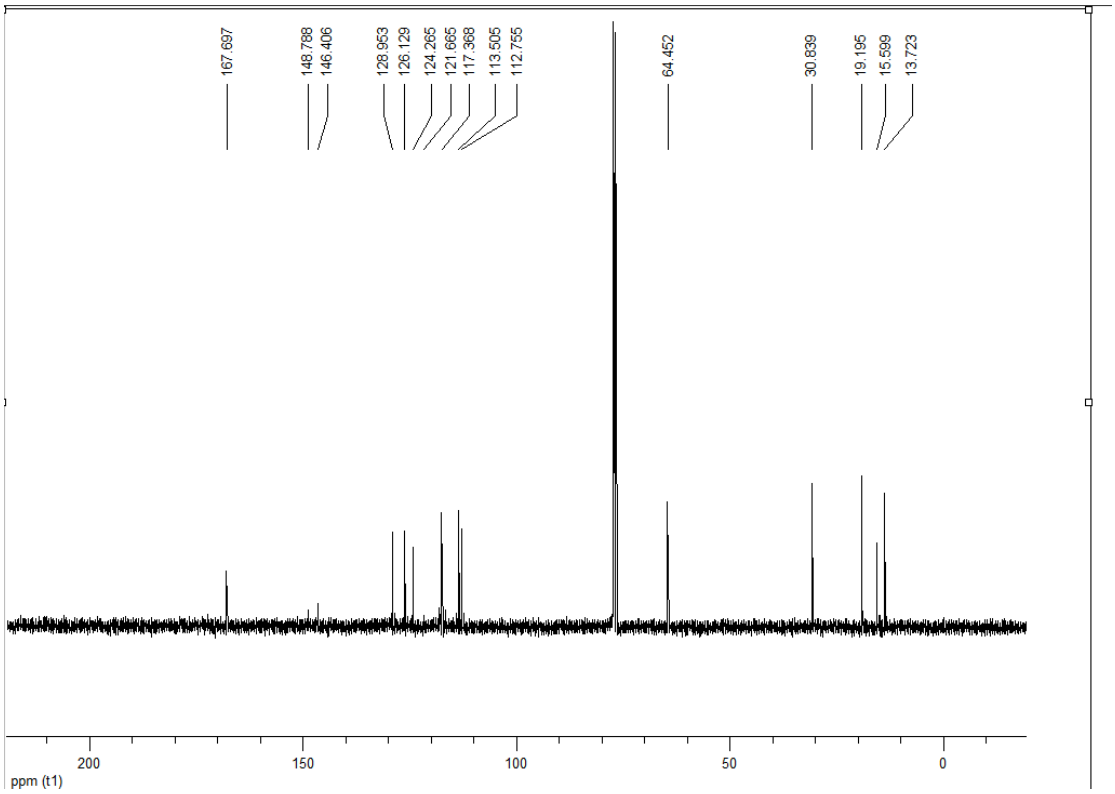
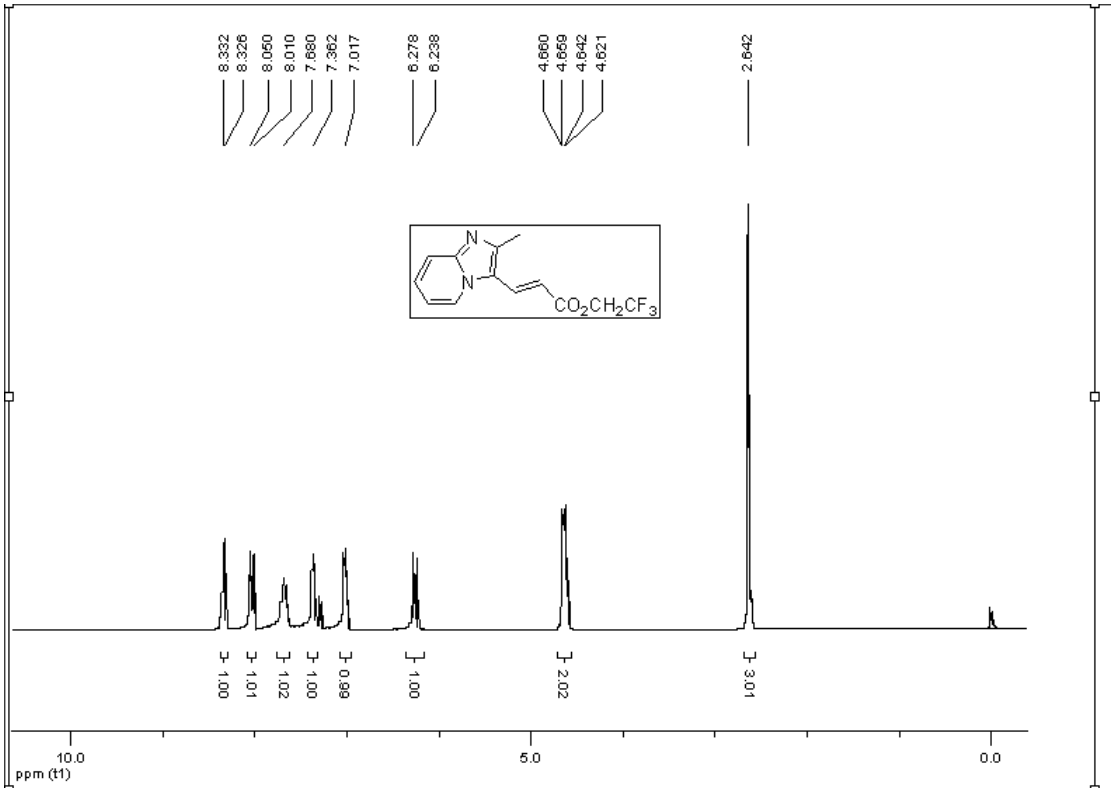
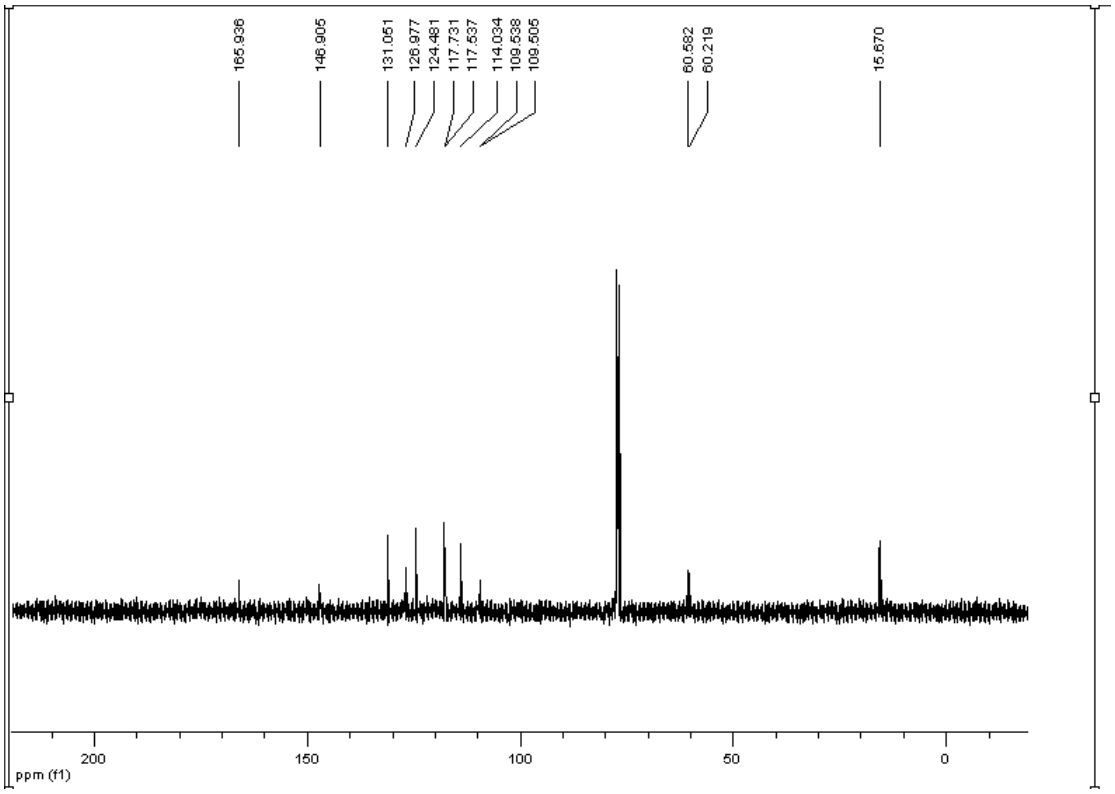
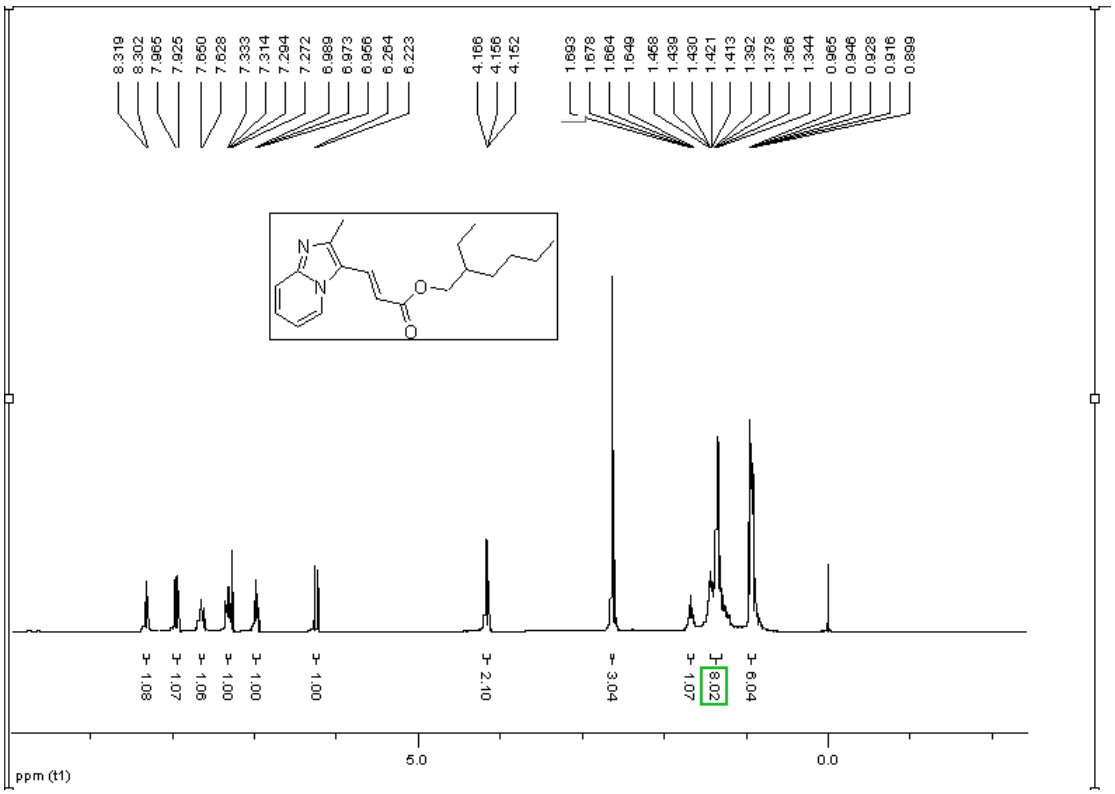
150
100
50
0
ppm (t1)


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
1.462
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)


167.697
148.788
146.406
128.953
126.129
124.265
121.665
117.368
113.505
112.755
64.452
30.839
19.195
15.599
13.723
200
150
100
50
0
ppm (t1)


8.332
8.326
8.050
8.010
7.680
7.362
7.017
6.278
6.238
4.860
4.859
4.842
4.821
2.842
N
N
CO2CH2CF3
1.00
1.01
1.02
1.00
0.99
1.00
2.02
3.01
10.0
5.0
0.0
ppm (t1)


165.936
146.905
131.051
126.977
124.481
117.731
117.537
114.034
109.538
109.505
60.582
60.219
15.670
200
150
100
50
0
ppm (f1)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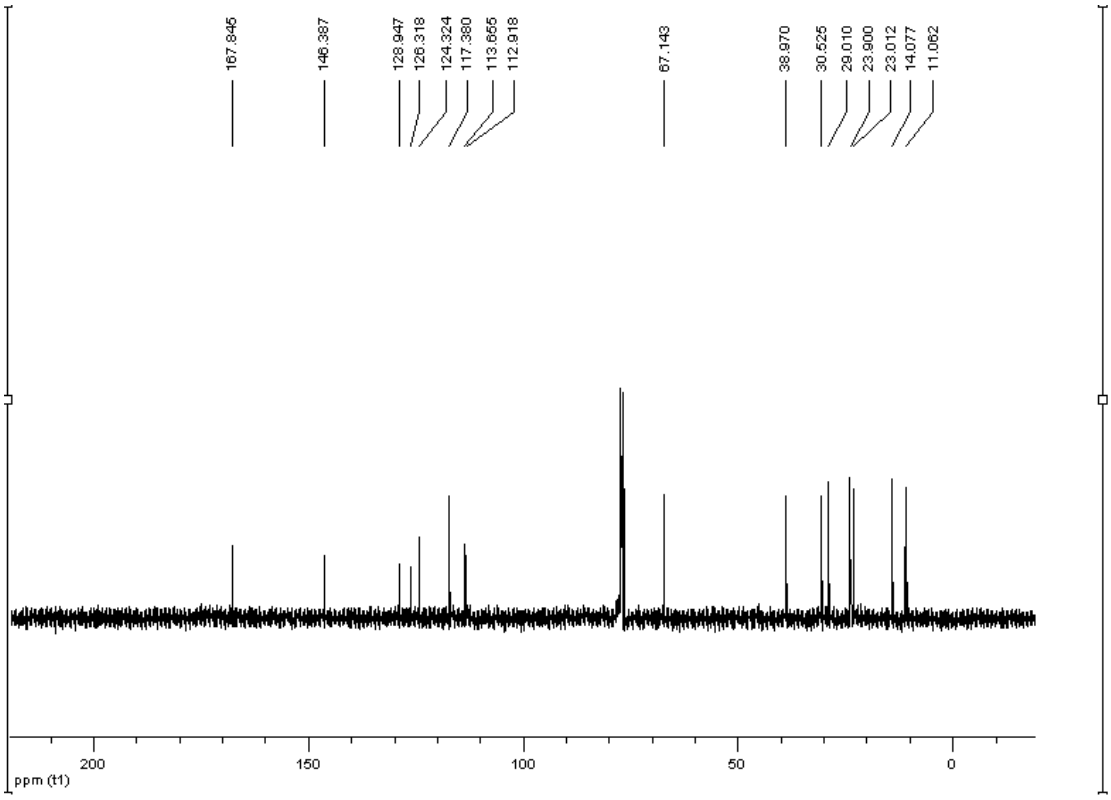
8.302
7.965
7.925
7.650
7.628
7.333
7.314
7.294
7.272
6.989
6.973
6.956
6.264
6.223
4.166
4.156
4.152
1.893
1.878
1.864
1.649
1.468
1.439
1.430
1.421
1.413
1.392
1.378
1.366
1.344
0.965
0.946
0.928
0.916
0.899
N
N
O
O
1.08
1.07
0.96
1.00
1.00
1.00
2.10
3.04
1.07
8.02
6.04
5.0
0.0
ppm (f1)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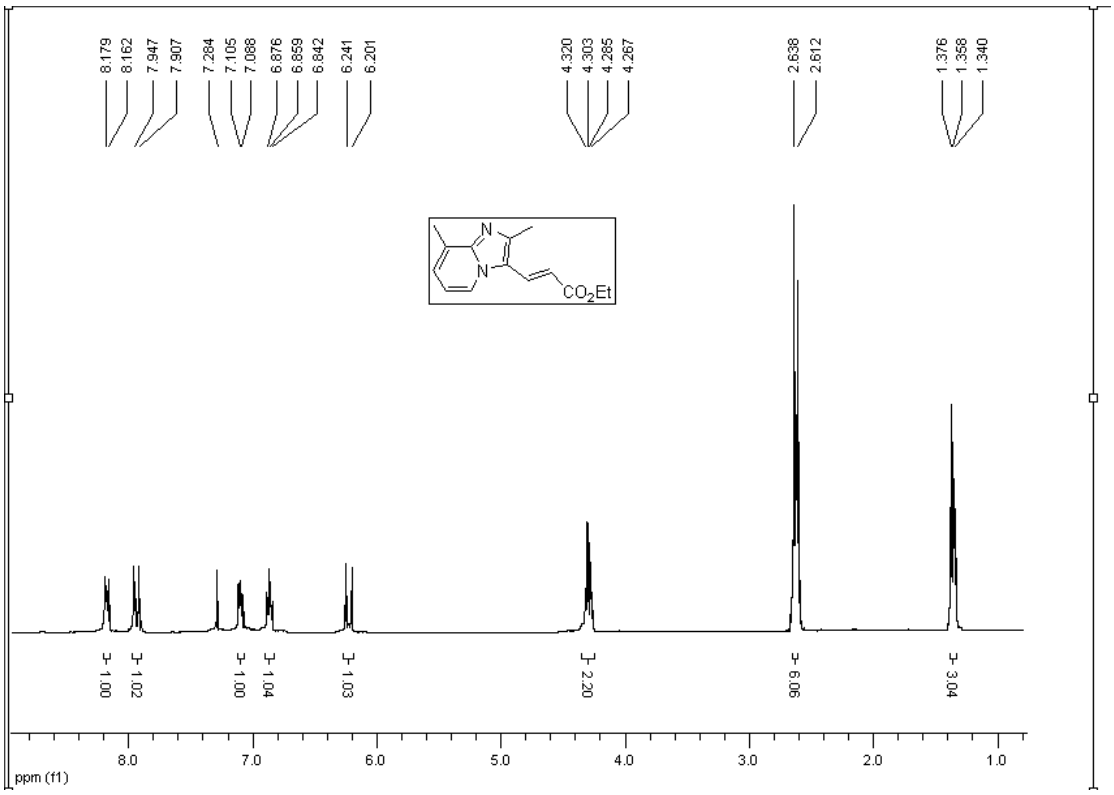
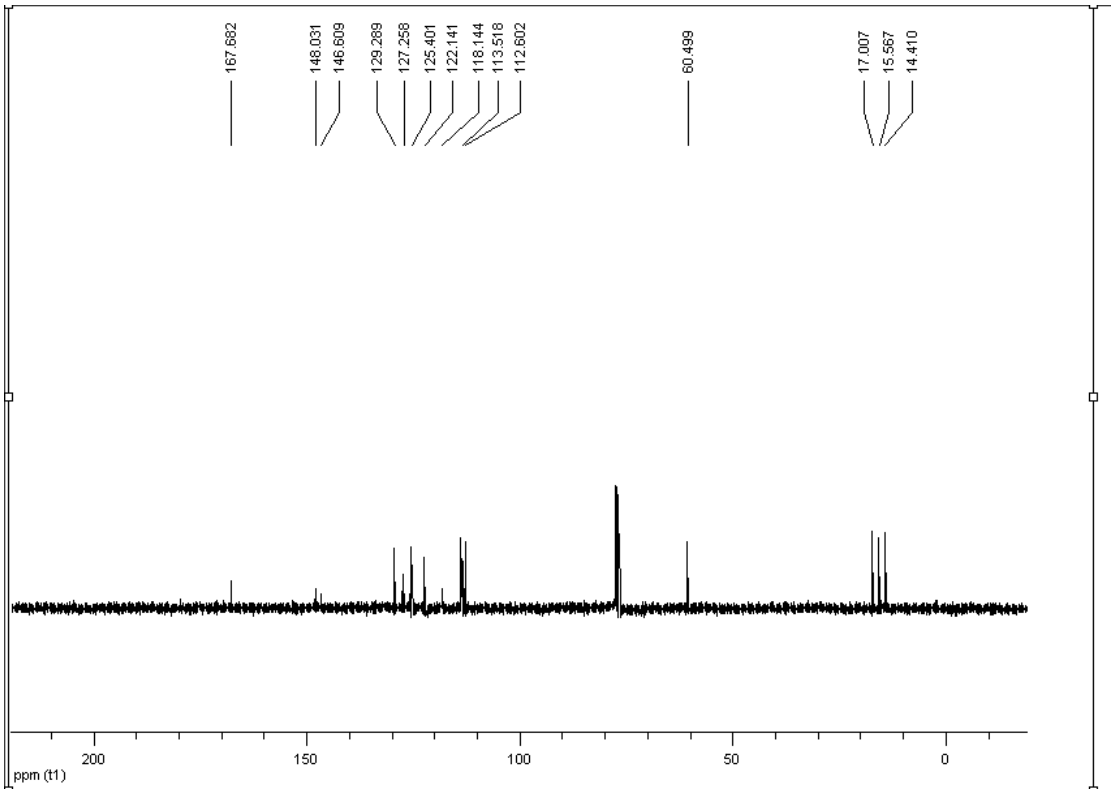
146.387
128.947
126.318
124.324
117.380
113.655
112.918
67.143
38.970
30.525
29.010
23.900
23.012
14.077
11.062
200
150
100
50
0
ppm (f1)


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)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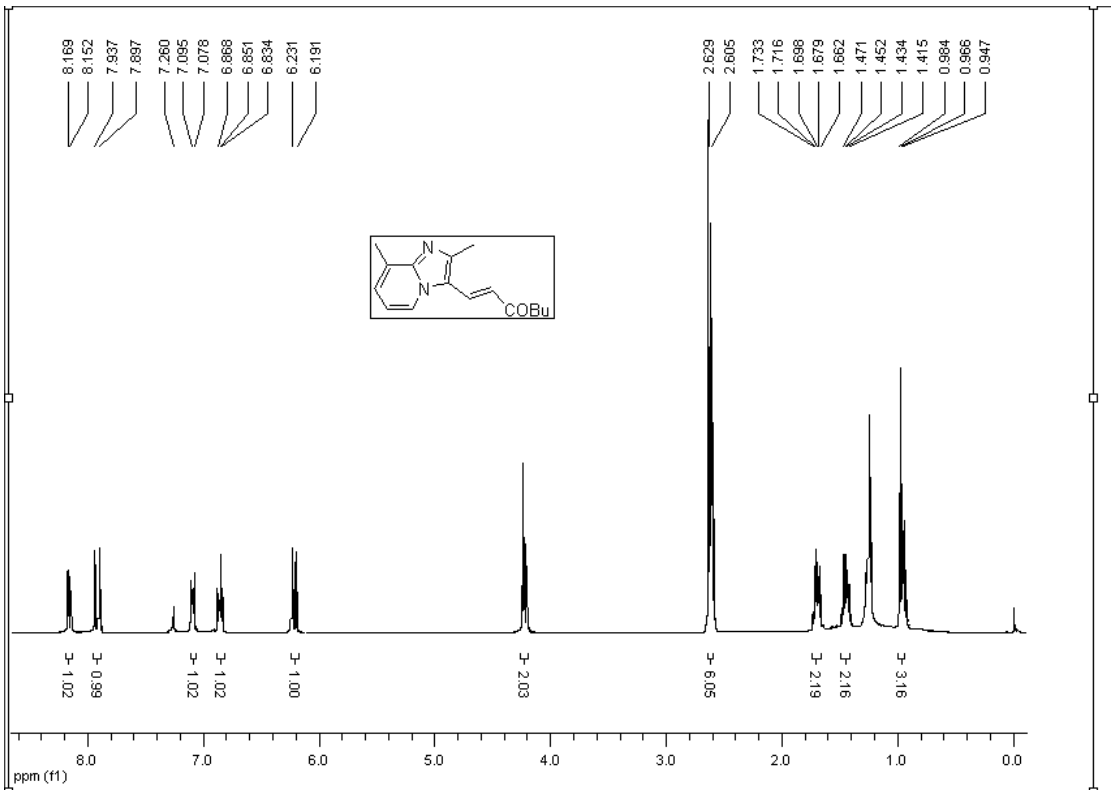
148.031
146.609
129.289
127.258
125.401
122.141
118.144
113.518
112.602
60.499
17.007
15.567
14.410
200
150
100
50
0
ppm (t1)


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
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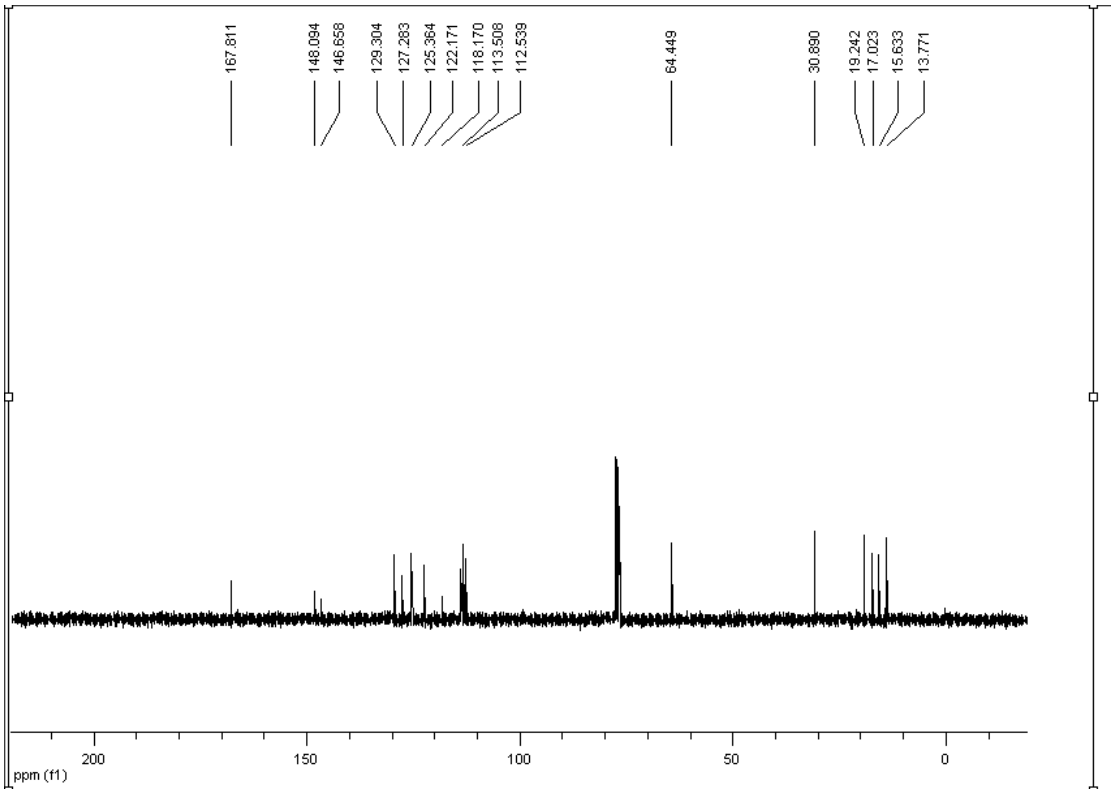
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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146.658
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127.283
125.364
122.171
118.170
113.508
112.539
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30.890
19.242
17.023
15.633
13.771
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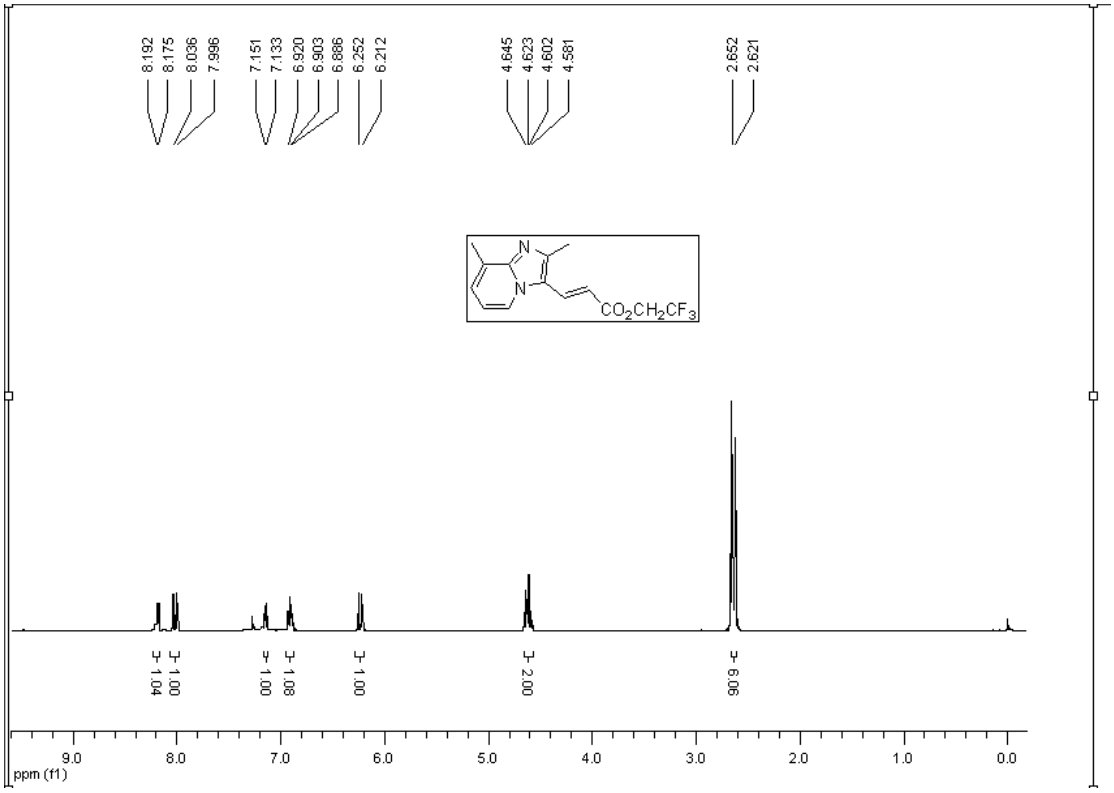
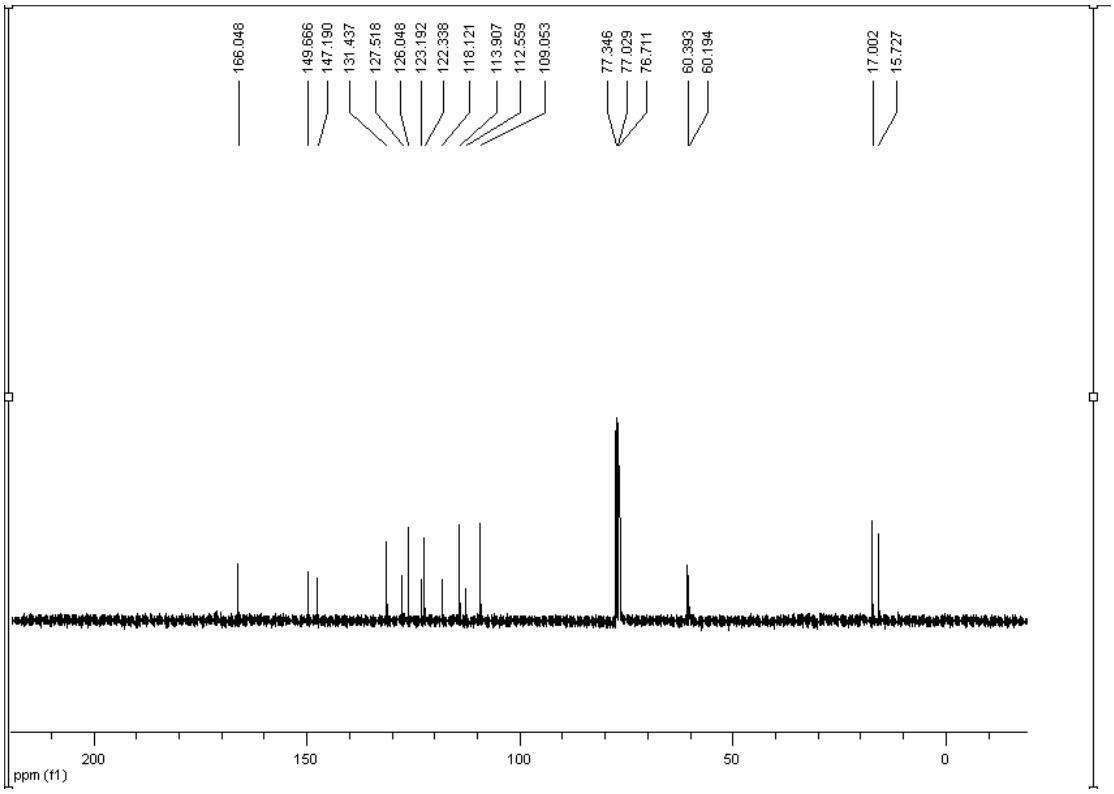
150
100
50
0
ppm (f1)


8.192
8.175
8.036
7.996
7.151
7.133
6.920
6.903
6.886
6.252
6.212
4.645
4.623
4.602
4.581
2.652
2.621
N
N
CO2CH2CF3
1.04
1.00
1.08
1.00
1.00
2.00
6.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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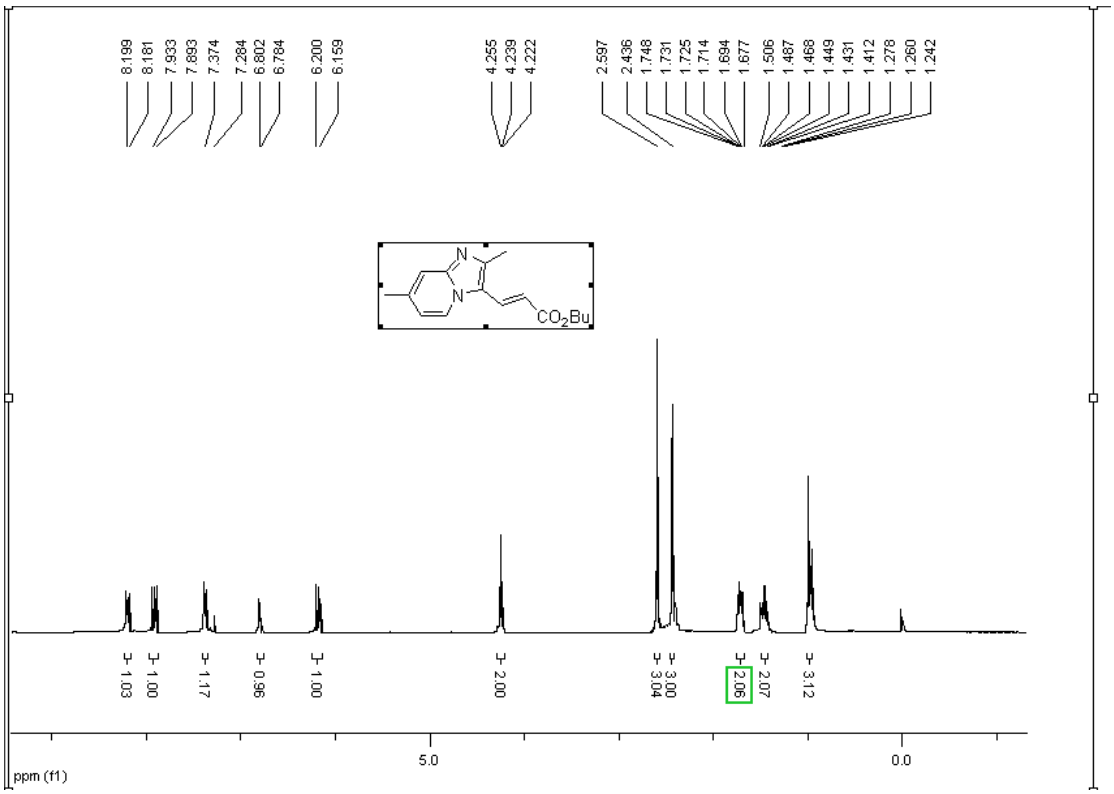
149.666
147.190
131.437
127.518
126.048
123.192
122.338
118.121
113.907
112.559
109.053
77.346
77.029
76.711
60.393
60.194
17.002
15.727
200
150
100
50
0
ppm (f1)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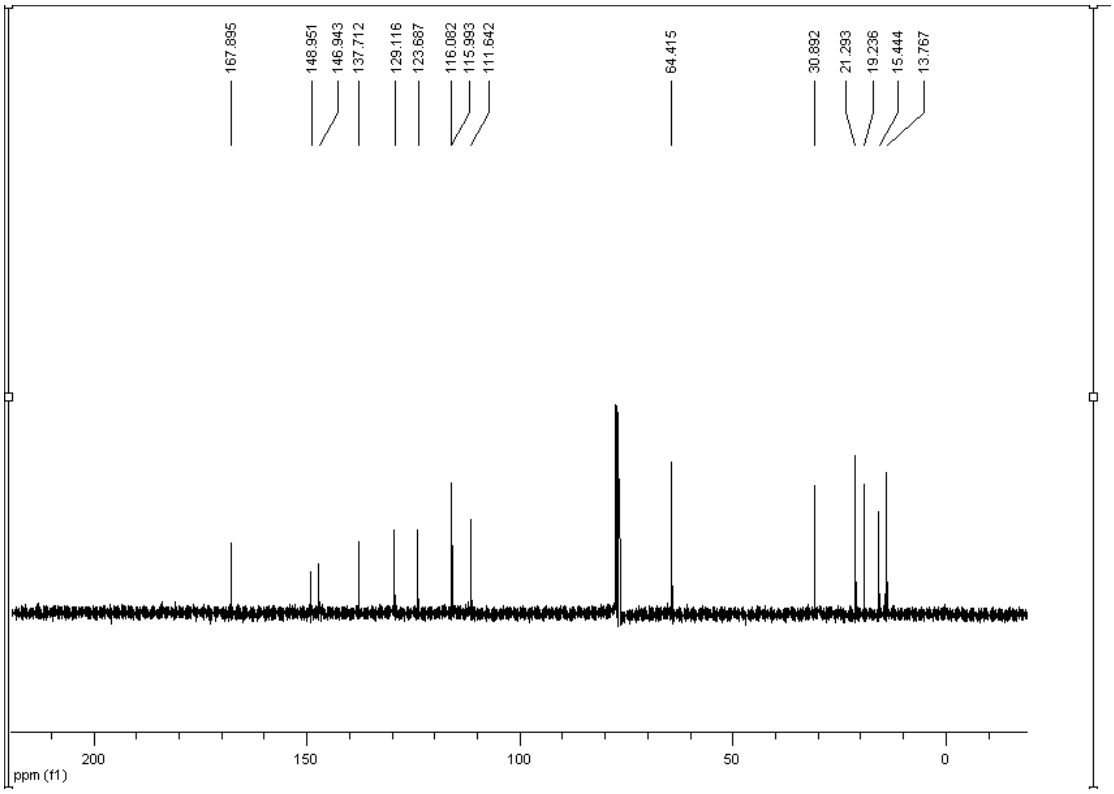
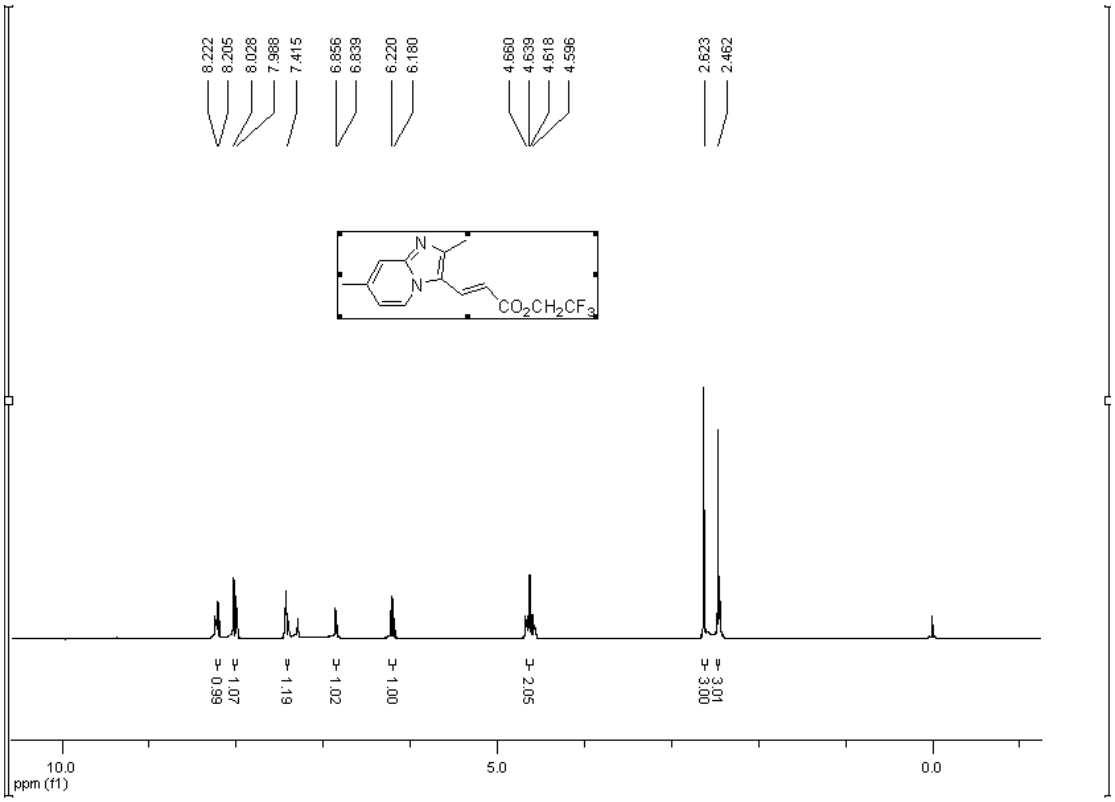
8.181
7.933
7.893
7.374
7.284
6.802
6.784
6.200
6.159
4.255
4.239
4.222
2.597
2.436
1.748
1.731
1.725
1.714
1.694
1.677
1.506
1.487
1.468
1.449
1.431
1.412
1.278
1.260
1.242
N
N
CO2Bu
1.03
1.00
1.17
0.96
1.00
2.00
3.04
3.00
2.06
2.07
3.12
5.0
0.0
ppm (f1)


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)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8.205
8.028
7.988
7.415
6.856
6.839
6.220
6.180
4.660
4.639
4.618
4.596
2.623
2.462
N
N
CO2CH2CF3
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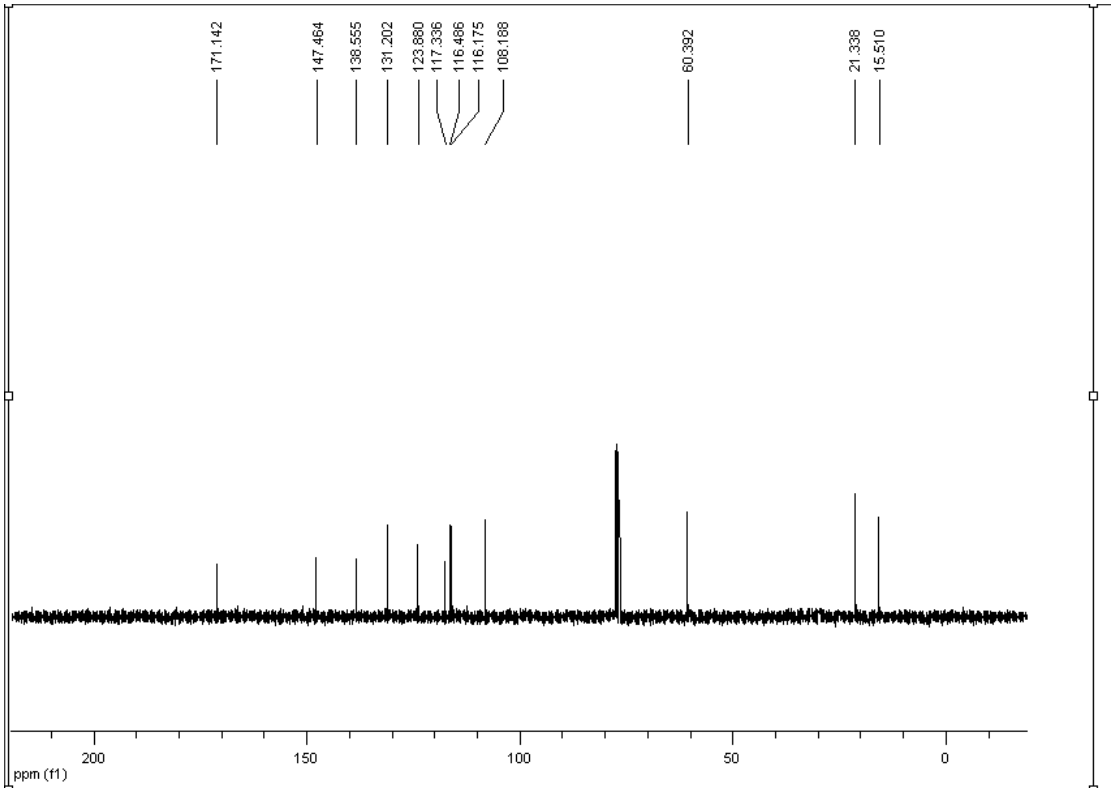
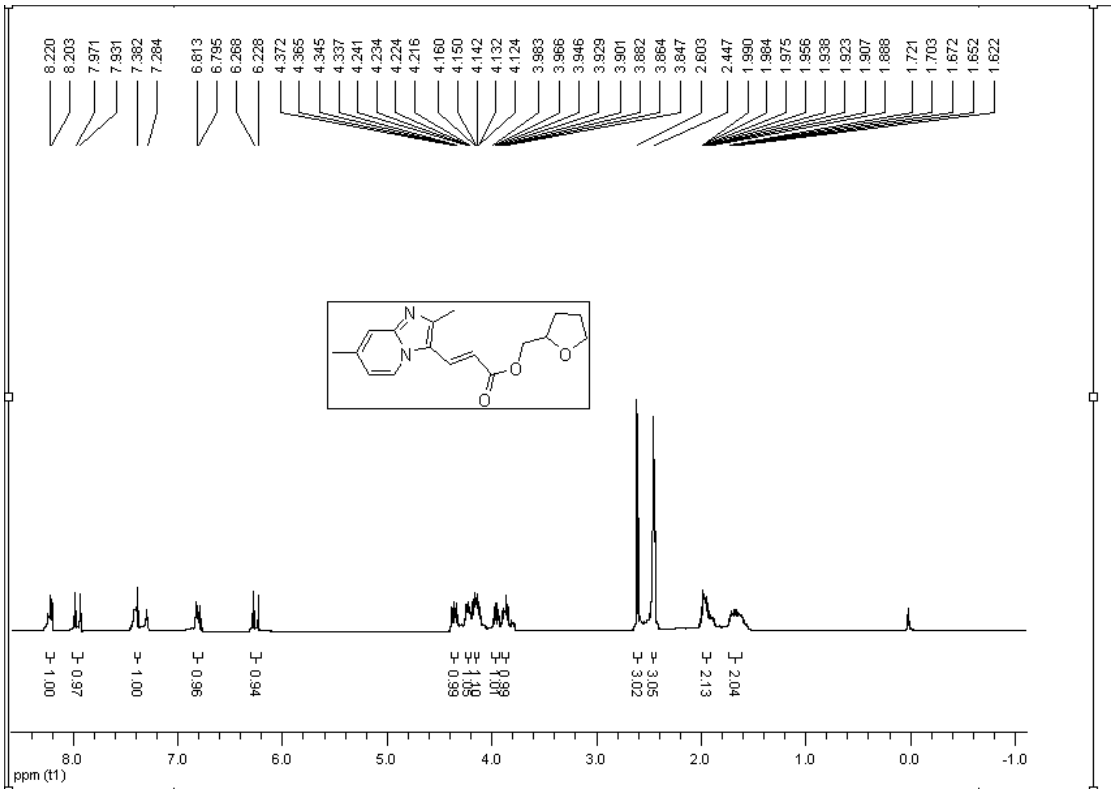
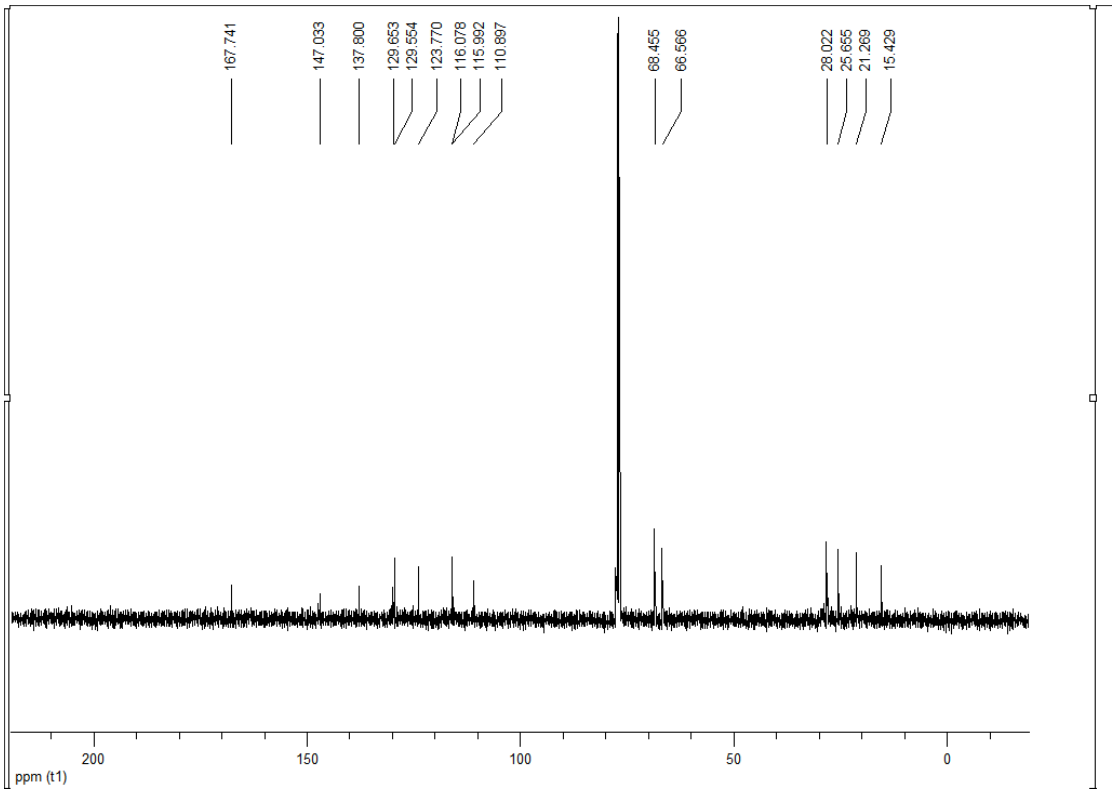
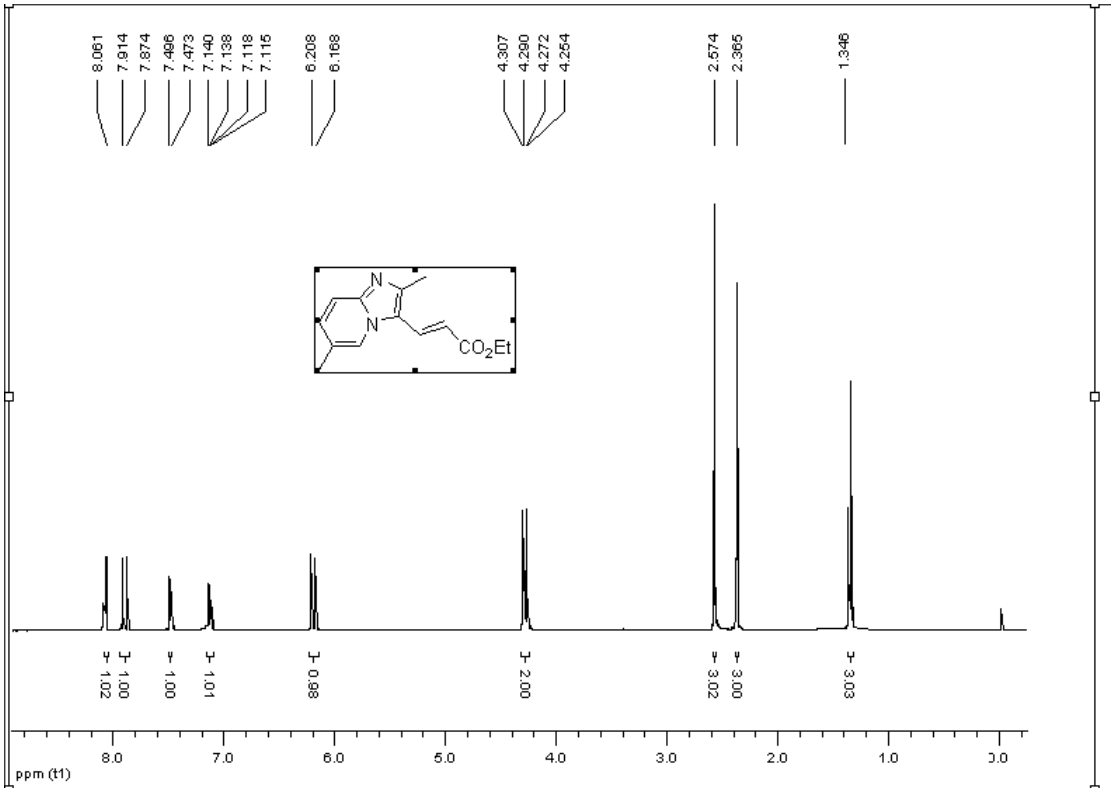
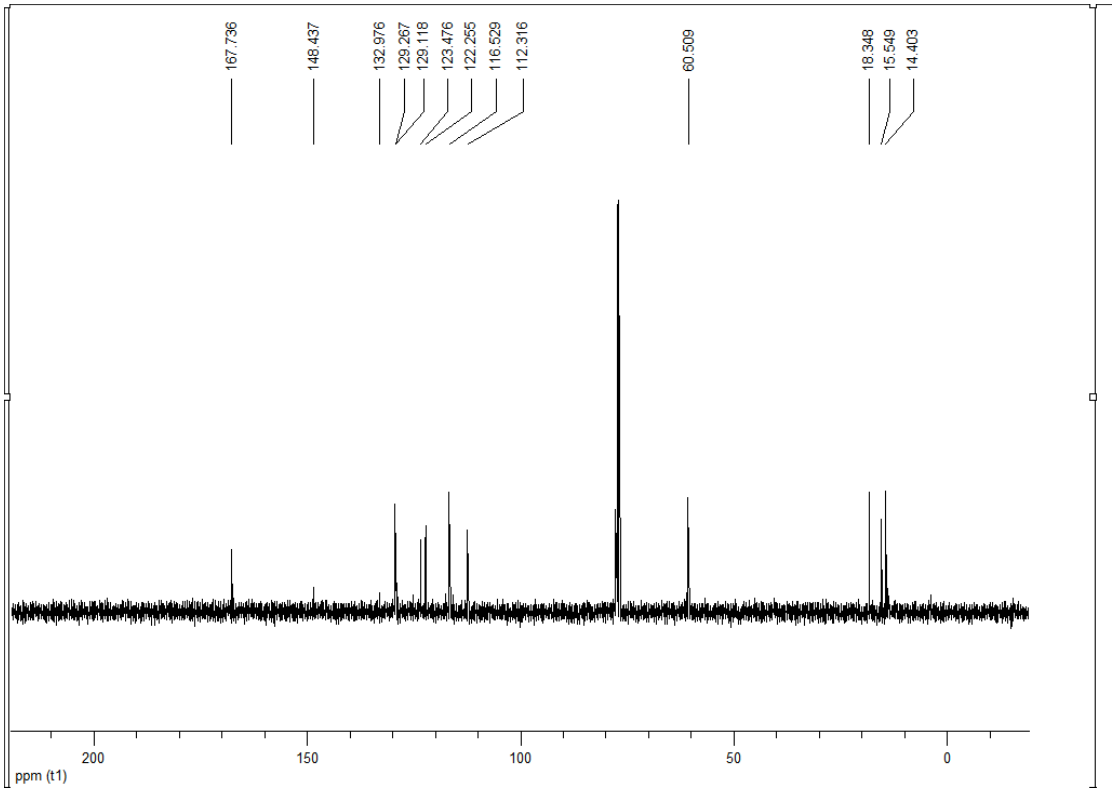
1.19
1.02
1.00
2.05
3.00
3.01
10.0
5.0
0.0
ppm (f1)

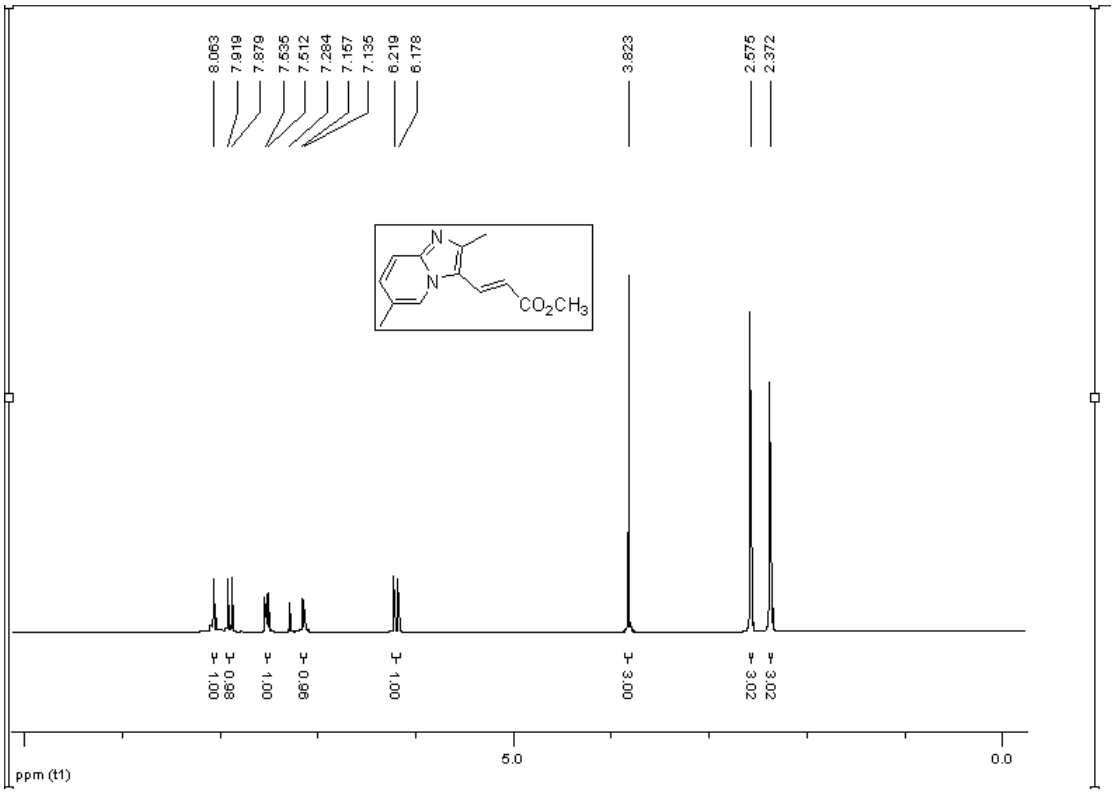

171.142
147.464
138.555
131.202
123.880
117.336
116.486
116.175
108.188
60.392
21.338
15.510
200
150
100
50
0
ppm (f1)

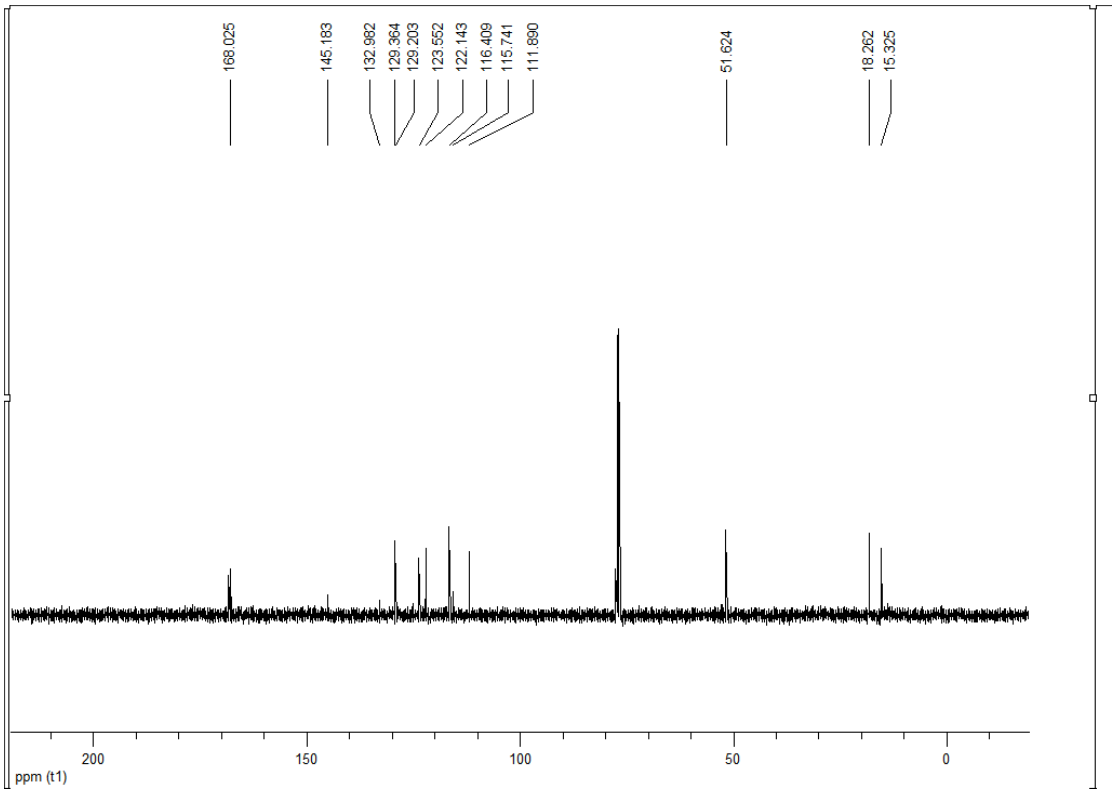

8.220
8.203
7.971
7.931
7.382
7.284
6.813
6.795
6.268
6.228
4.372
4.365
4.345
4.337
4.241
4.234
4.224
4.216
4.160
4.150
4.142
4.132
4.124
3.983
3.966
3.946
3.929
3.901
3.882
3.864
3.847
2.603
2.447
1.990
1.984
1.975
1.956
1.938
1.923
1.907
1.888
1.721
1.703
1.672
1.652
1.622
1.00
0.97
1.00
0.96
0.94
0.98
1.09
0.89
3.02
3.05
2.13
2.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

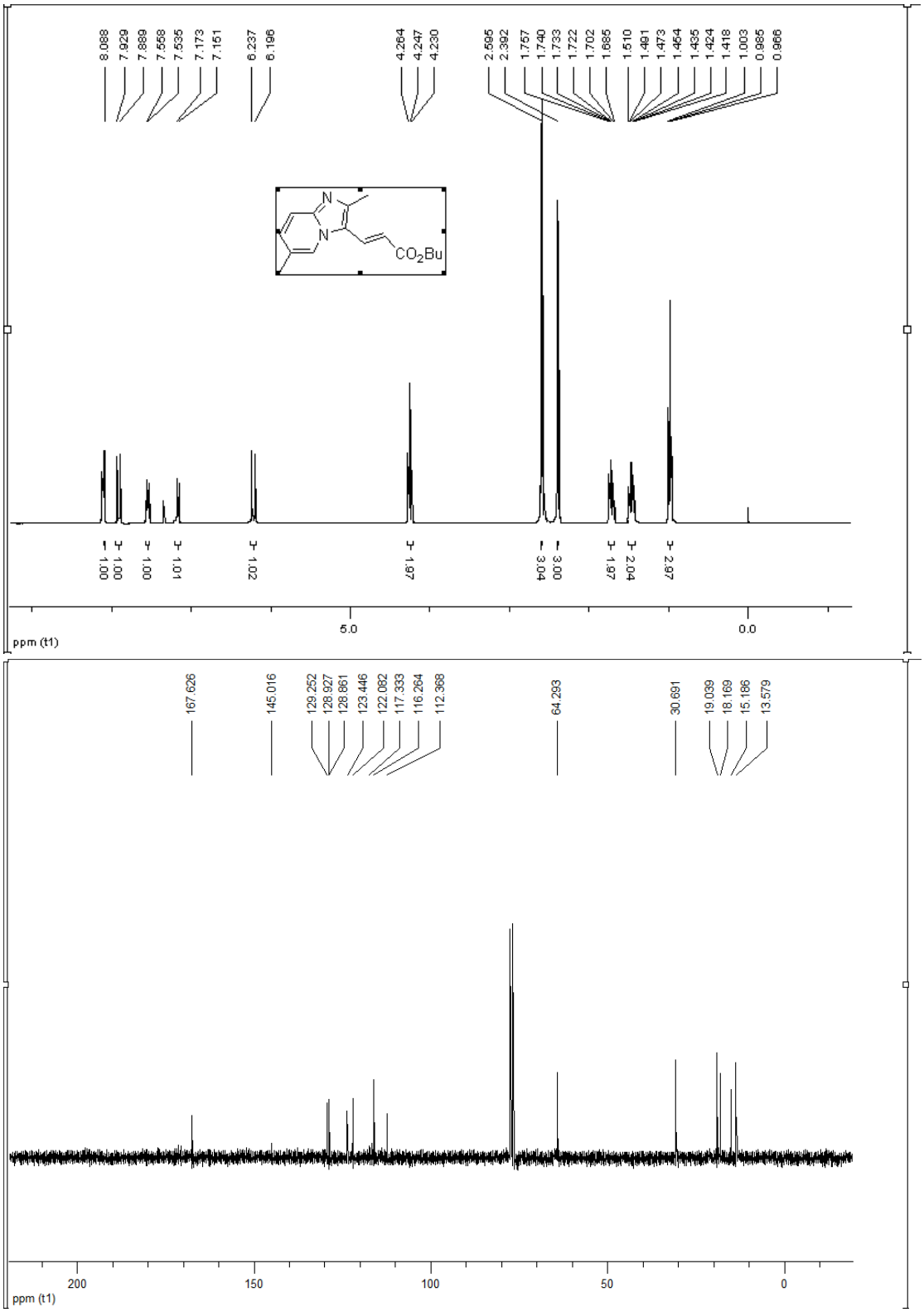

167.741
147.033
137.800
129.653
129.554
123.770
116.078
115.992
110.897
68.455
66.566
28.022
25.655
21.269
15.429
200
150
100
50
0
ppm (t1)

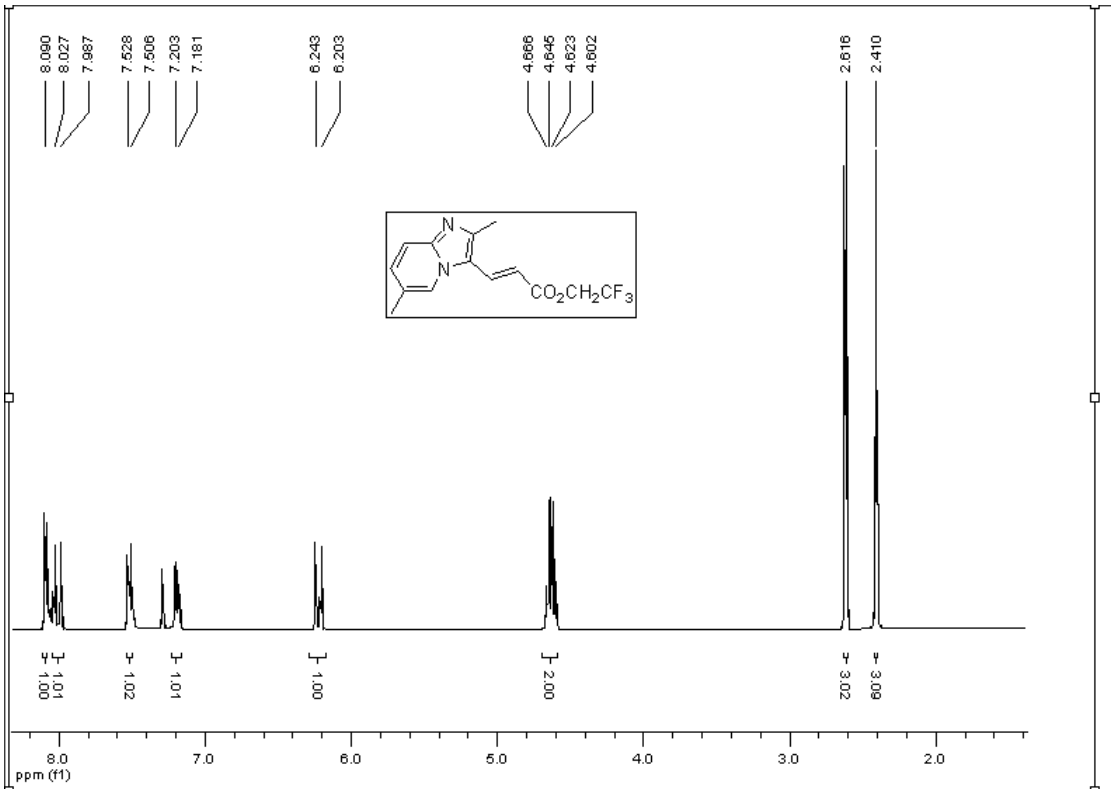

8.061
7.914
7.874
7.496
7.473
7.140
7.138
7.118
7.115
6.208
6.168
4.307
4.290
4.272
4.254
2.574
2.365
1.346
N
N
CO2Et
1.02
1.00
1.00
1.01
0.98
2.00
3.02
3.00
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

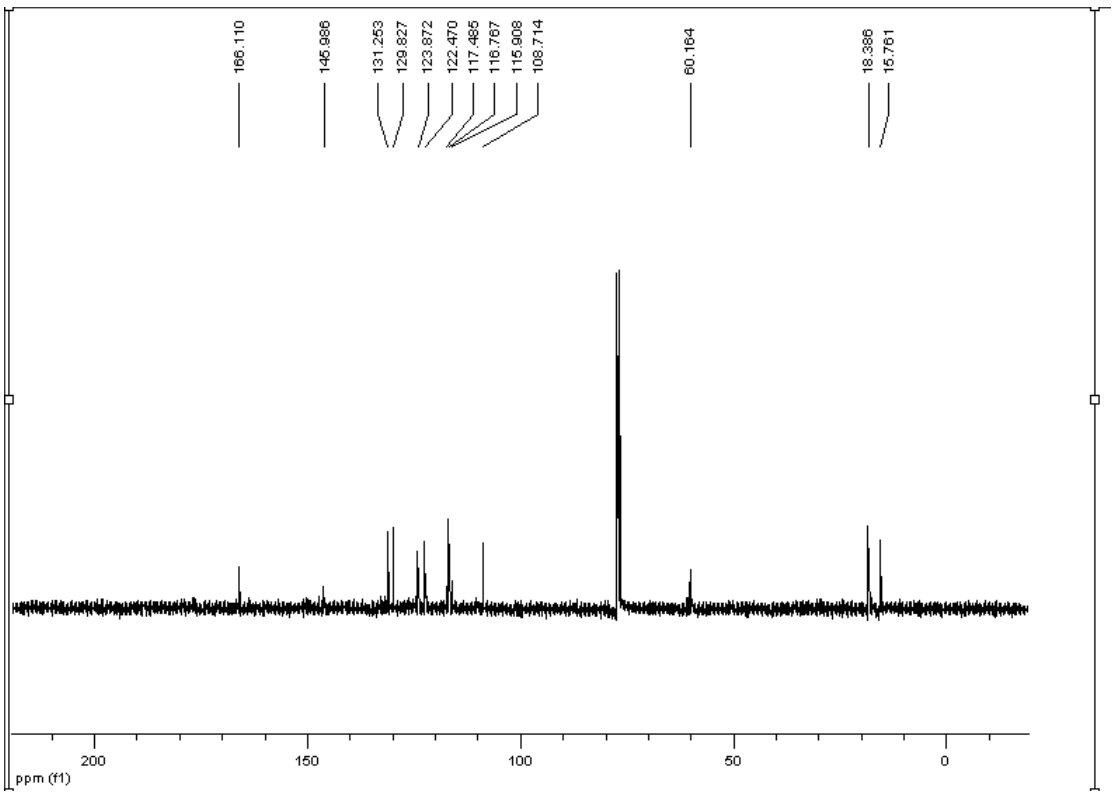

167.736
148.437
132.976
129.267
129.118
123.476
122.255
116.529
112.316
60.509
18.348
15.549
14.403
200
150
100
50
0
ppm (t1)


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)


168.025
145.183
132.982
129.364
129.203
123.552
122.143
116.409
115.741
111.890
51.624
18.262
15.325
200
150
100
50
0
ppm (t1)


8.088
7.929
7.889
7.558
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)
167.626
145.016
129.252
128.927
128.861
123.446
122.082
117.333
116.264
112.368
64.293
30.691
19.039
18.169
15.186
13.579
200
150
100
50
0
ppm (t1)


8.090
8.027
7.987
7.528
7.506
7.203
7.181
6.243
6.203
4.666
4.645
4.623
4.602
2.616
2.410
N
N
CO2CH2CF3
1.01
1.00
1.02
1.01
1.00
2.00
3.02
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)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145.986
131.253
129.827
123.872
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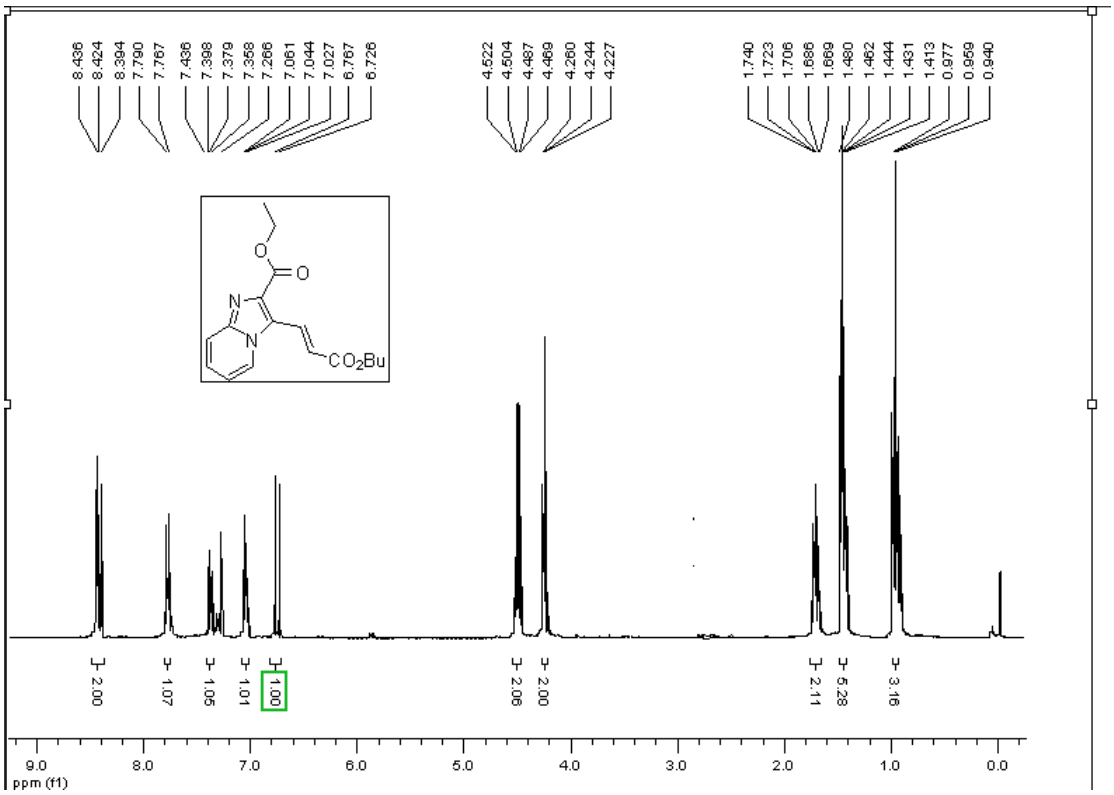
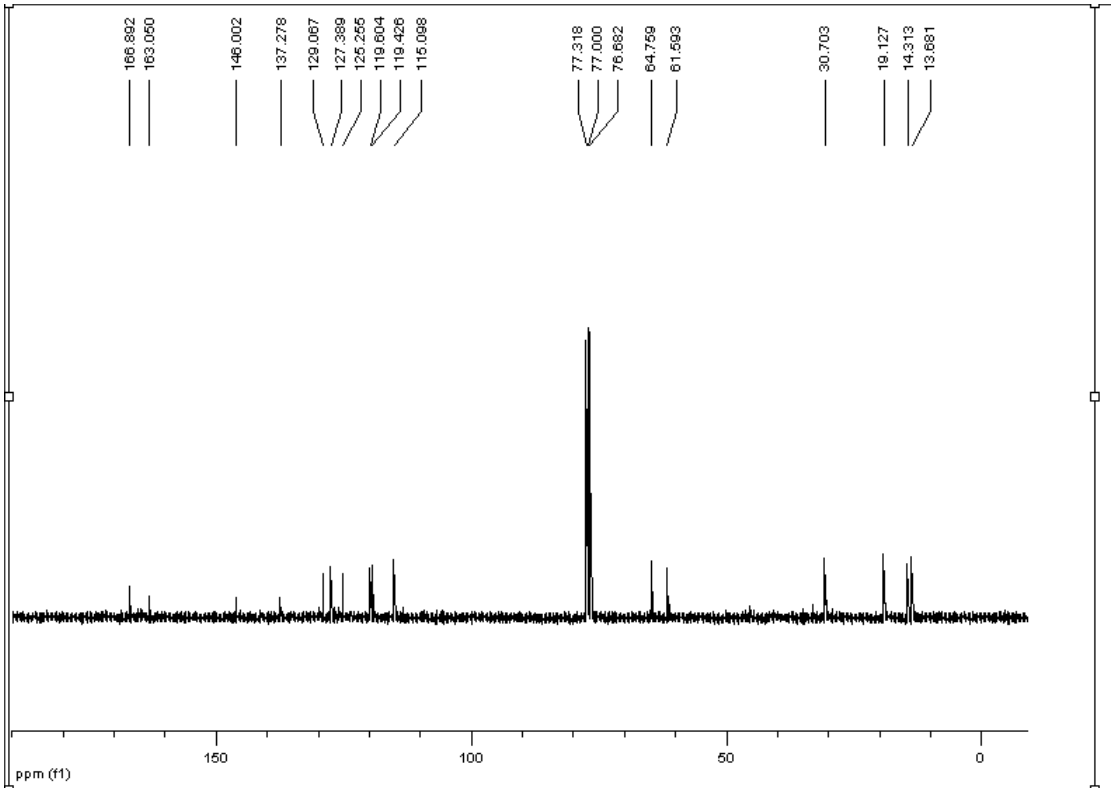
117.485
116.767
115.908
108.714
60.164
18.386
15.761
200
150
100
50
0
ppm (f1)


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
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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137.278
129.067
127.389
125.255
119.604
119.426
115.098
77.318
77.000
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64.759
61.593
30.703
19.127
14.313
13.681
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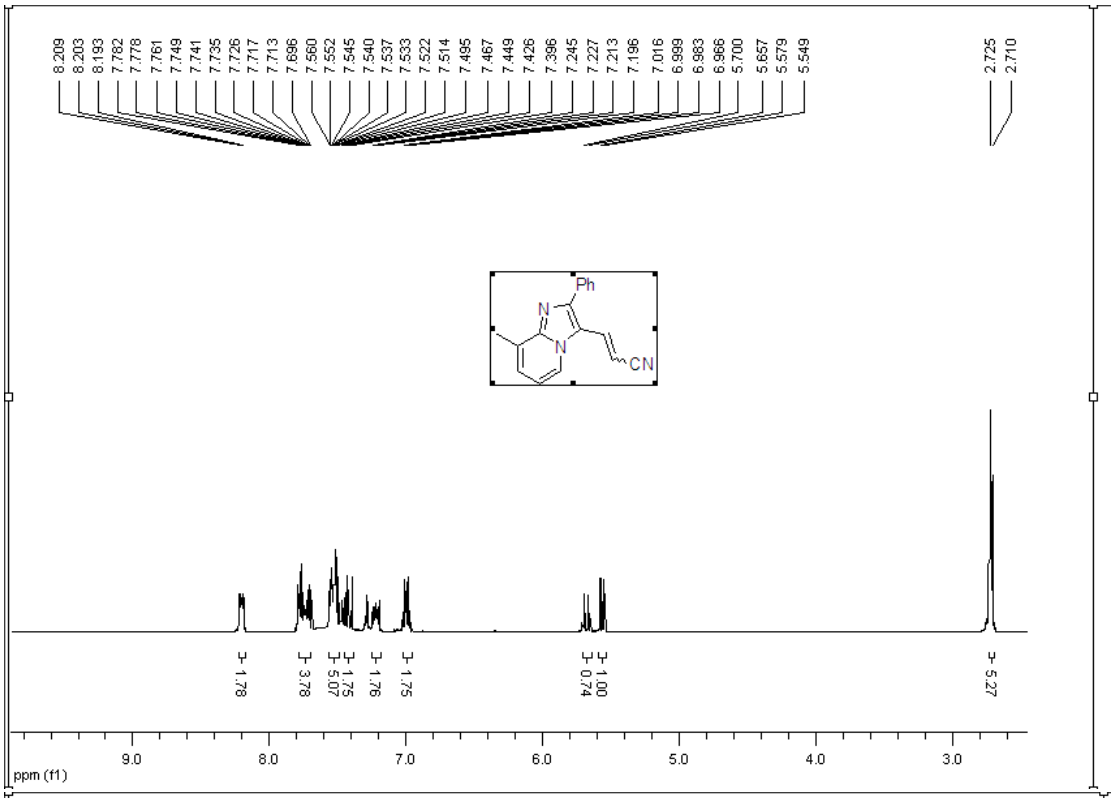
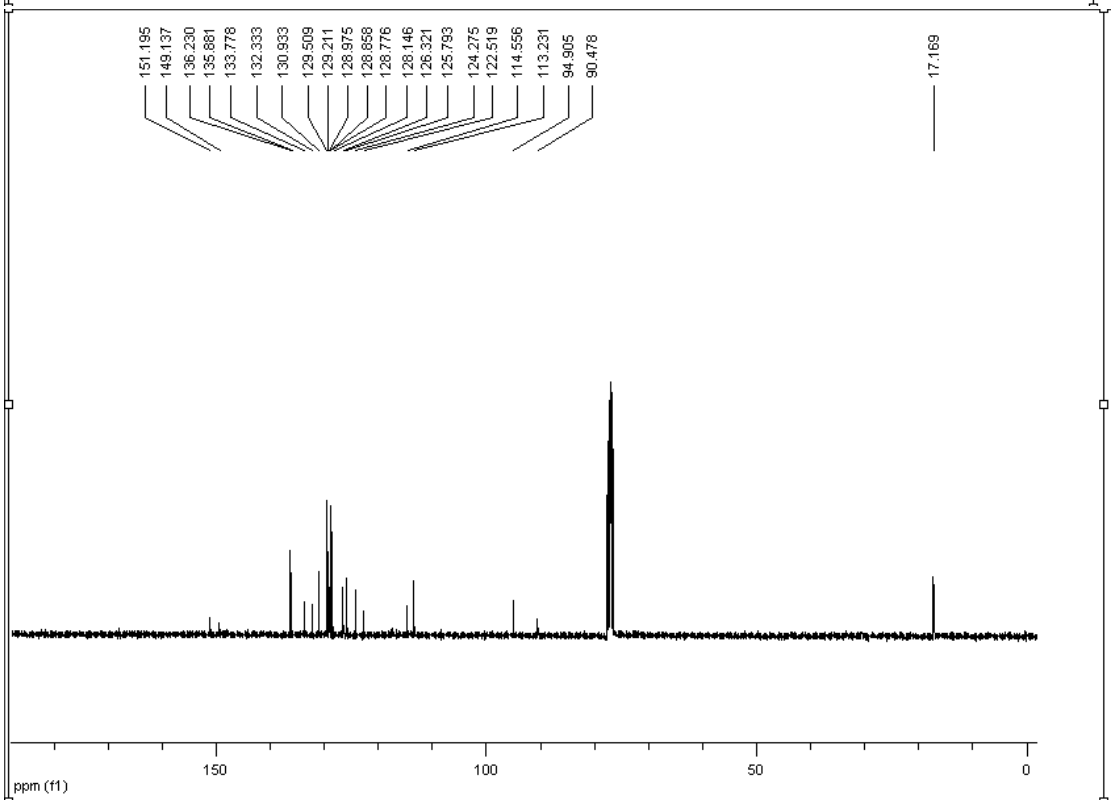
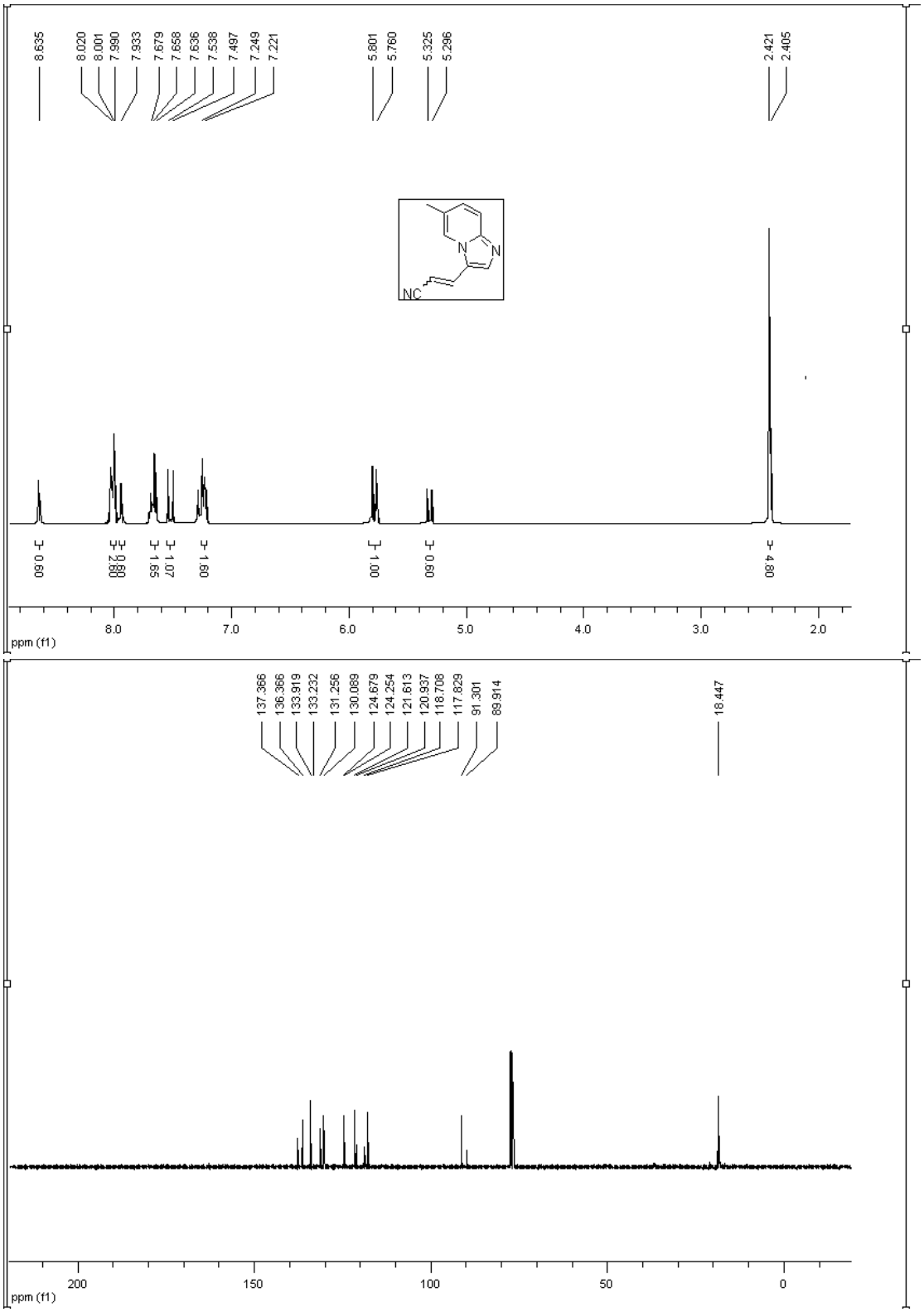
100
50
0
ppm (f1)


8.209
8.203
8.193
7.782
7.778
7.761
7.749
7.741
7.735
7.726
7.717
7.713
7.696
7.560
7.552
7.545
7.540
7.537
7.533
7.522
7.514
7.495
7.467
7.449
7.426
7.396
7.245
7.227
7.213
7.196
7.016
6.999
6.983
6.966
5.700
5.657
5.579
5.549
2.725
2.710
Ph
N
N
CN
1.78
3.78
5.07
1.75
1.76
1.75
0.74
1.00
5.27
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)


151.195
149.137
136.230
135.881
133.778
132.333
130.933
129.509
129.211
128.975
128.858
128.776
128.146
126.321
125.793
124.275
122.519
114.556
113.231
94.905
90.478
17.169
150
100
50
0
ppm (f1)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7.933
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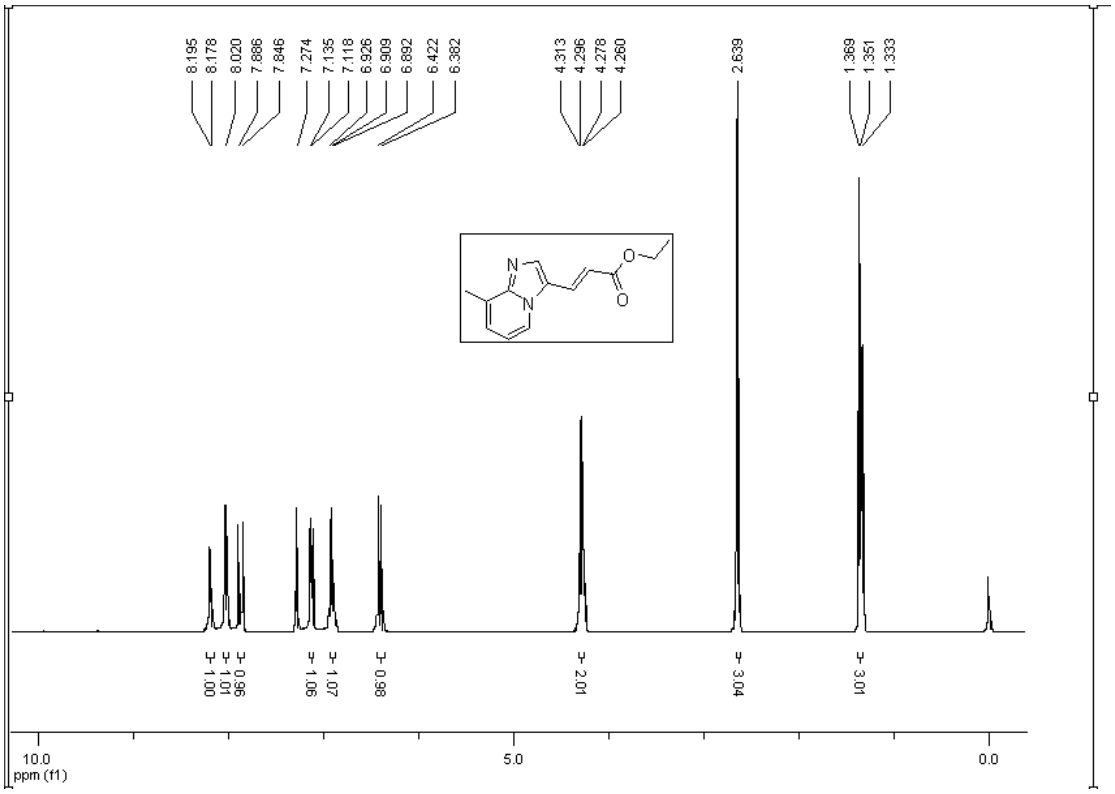
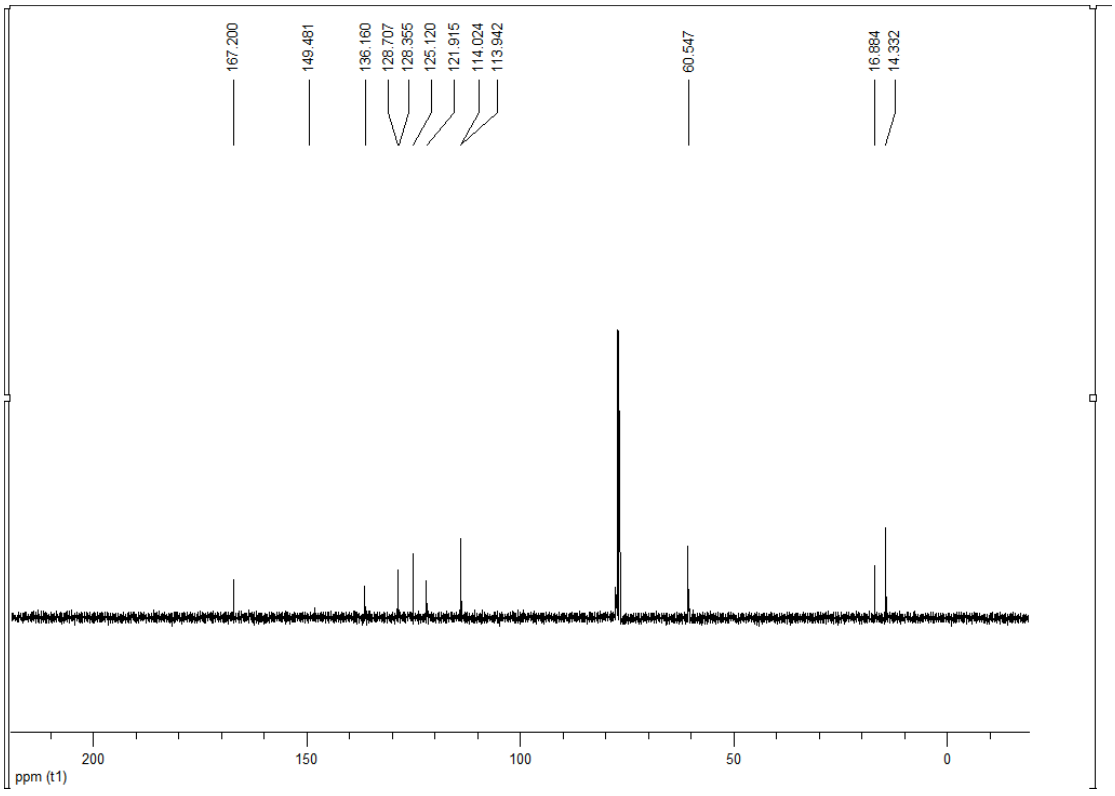
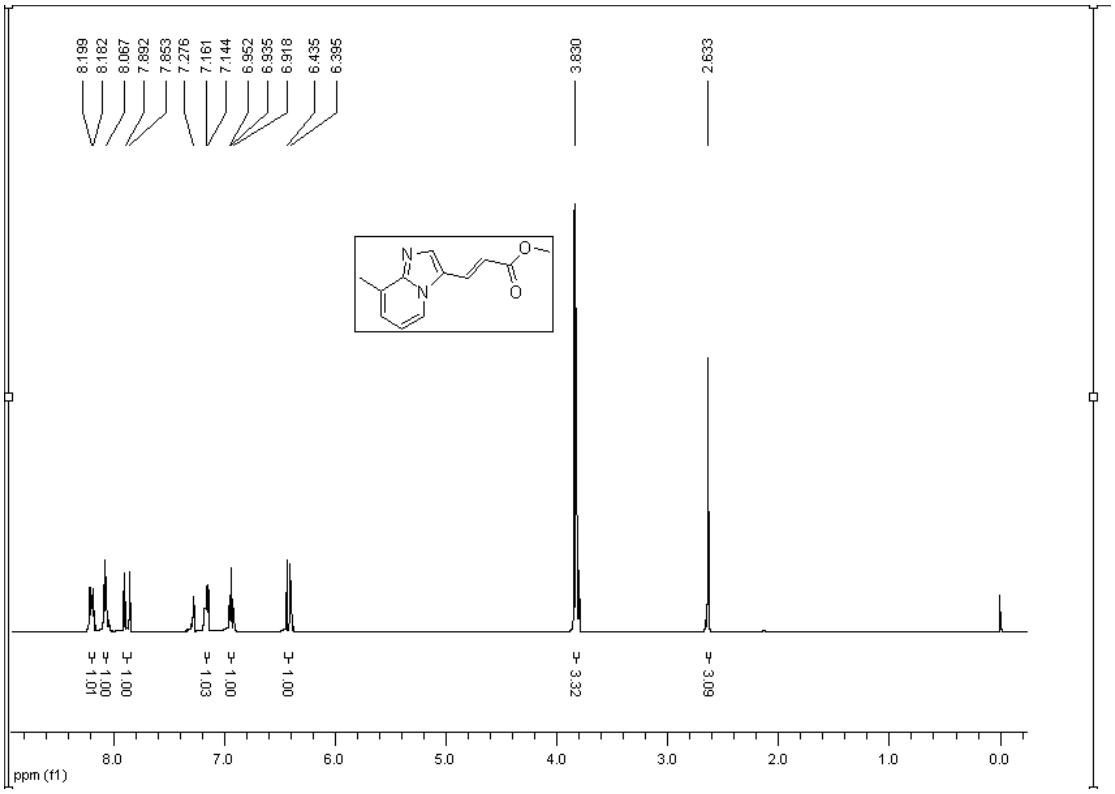
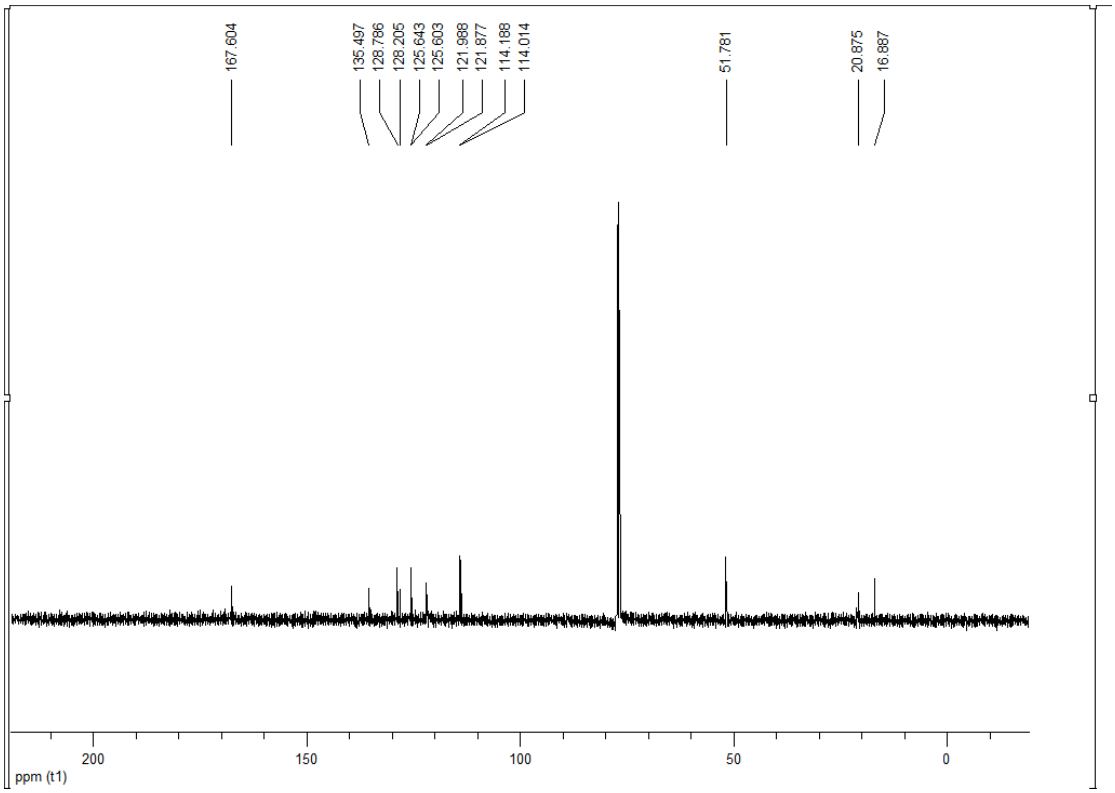
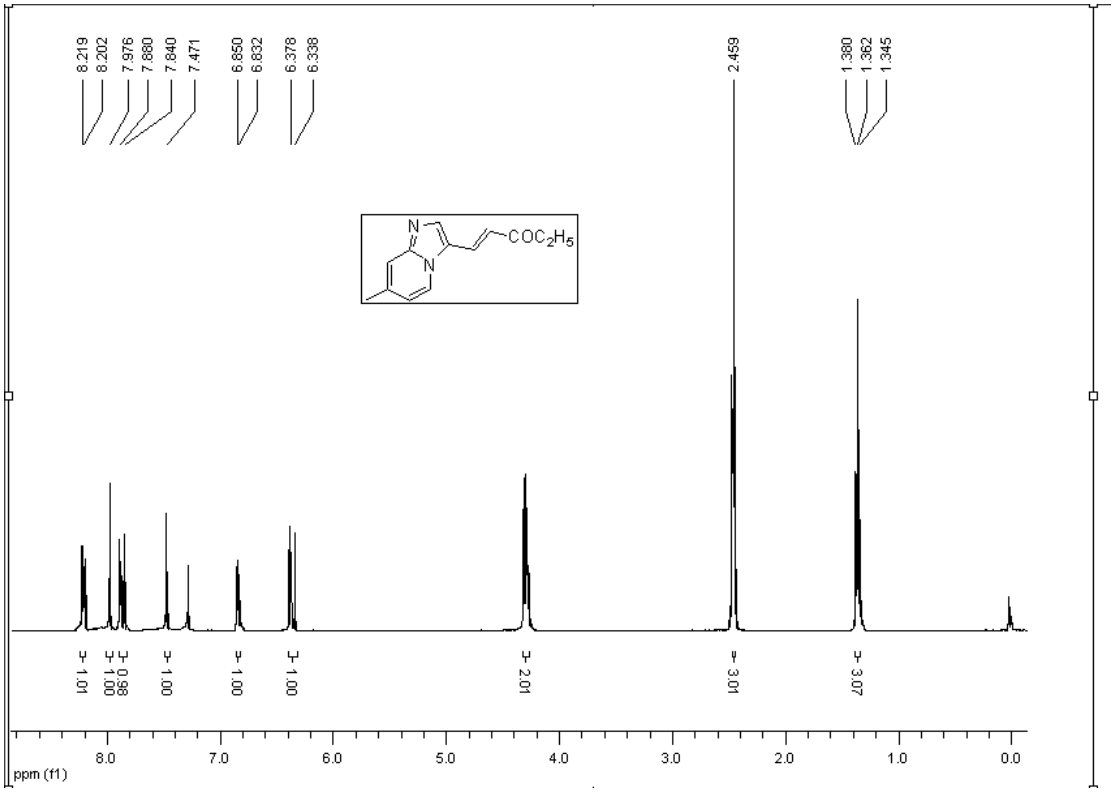
7.658
7.636
7.538
7.497
7.249
7.221
5.801
5.760
5.325
5.296
2.421
2.405
N
N
NC
0.60
2.80
1.65
1.07
1.60
1.00
0.60
4.80
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)
137.366
136.366
133.919
133.232
131.256
130.089
124.679
124.254
121.613
120.937
118.708
117.829
91.301
89.914
18.447
200
150
100
50
0
ppm (f1)


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
ppm (f1)
5.0
0.0


167.200
149.481
136.160
128.707
128.355
125.120
121.915
114.024
113.942
60.547
16.884
14.332
200
150
100
50
0
ppm (t1)


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)


167.604
135.497
128.786
128.205
125.643
125.603
121.988
121.877
114.188
114.014
51.781
20.875
16.887
200
150
100
50
0
ppm (t1)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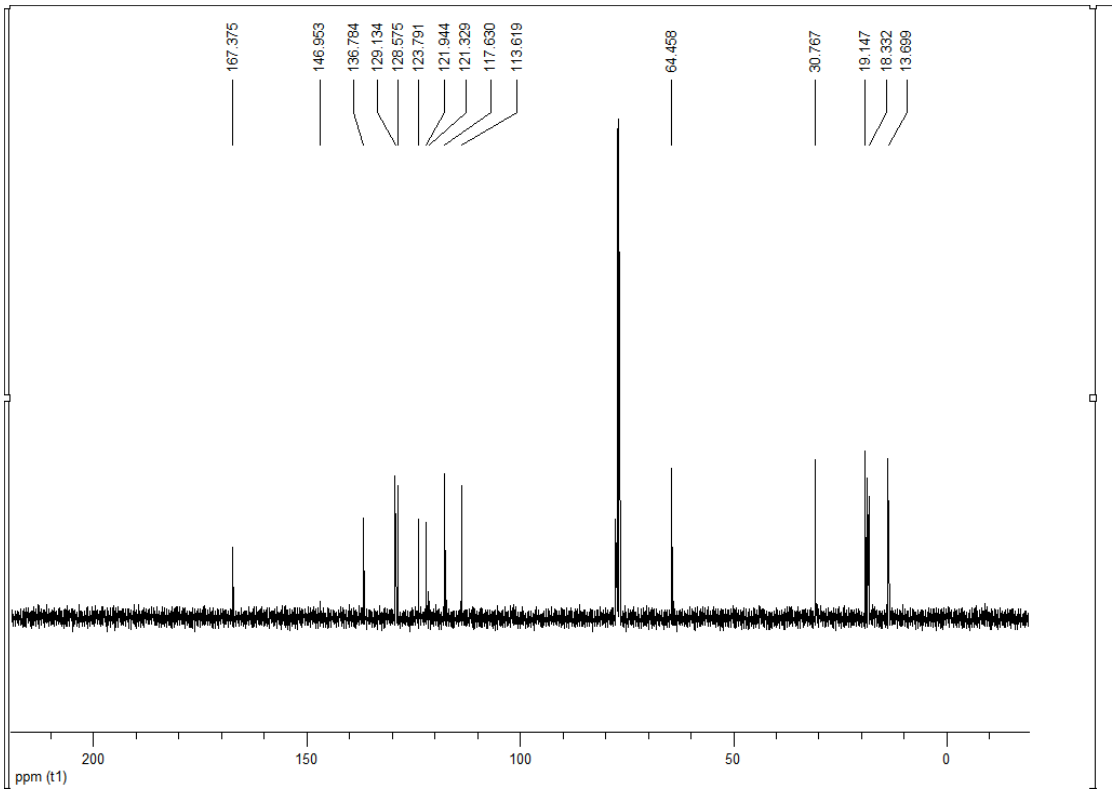
8.202
7.976
7.880
7.840
7.471
6.850
6.832
6.378
6.338
2.459
1.380
1.362
1.345
N
N
COC2H5
1.01
0.98
1.00
1.00
1.00
2.01
3.01
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


167.375
146.953
136.784
129.134
128.575
123.791
121.944
121.329
117.630
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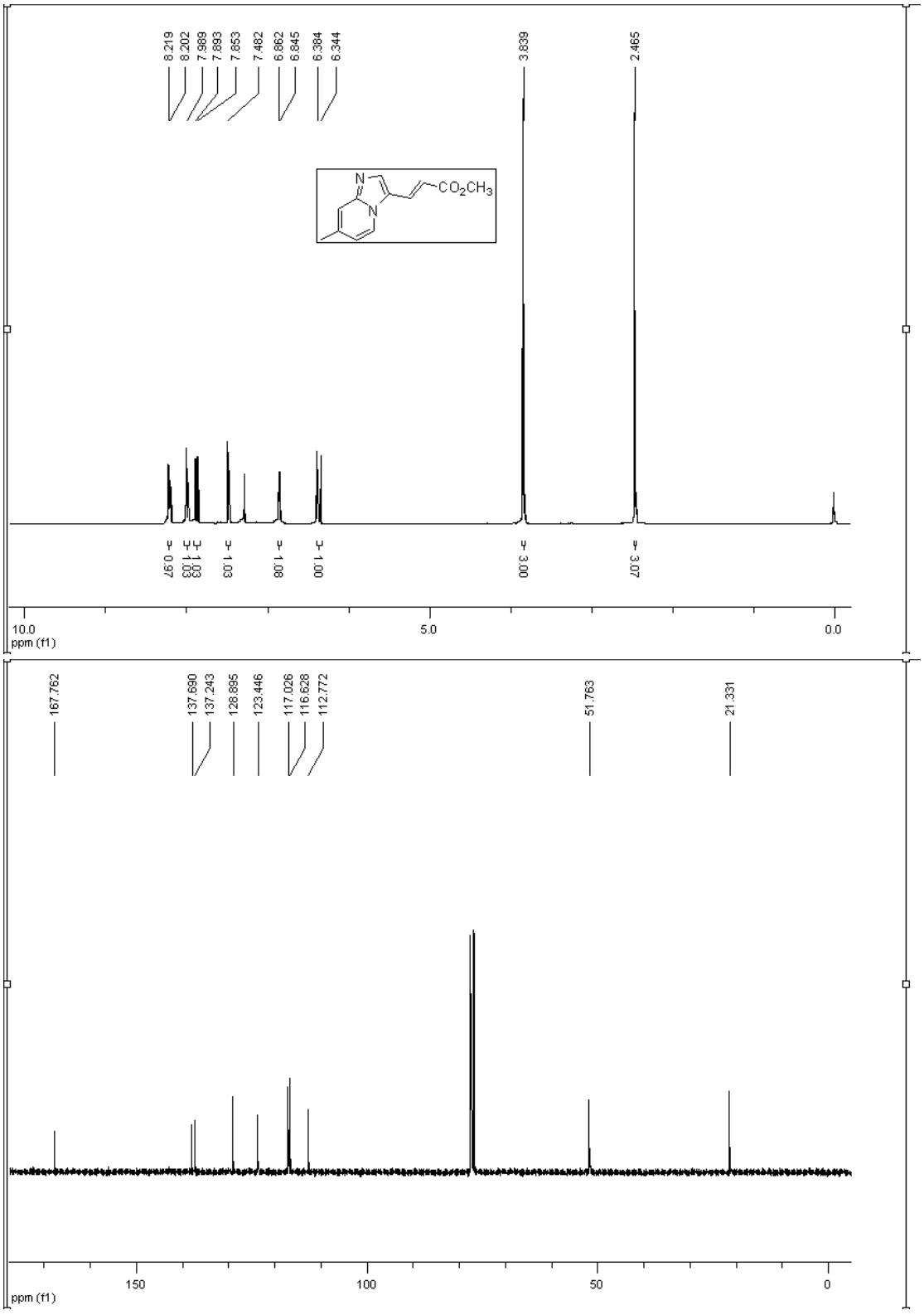
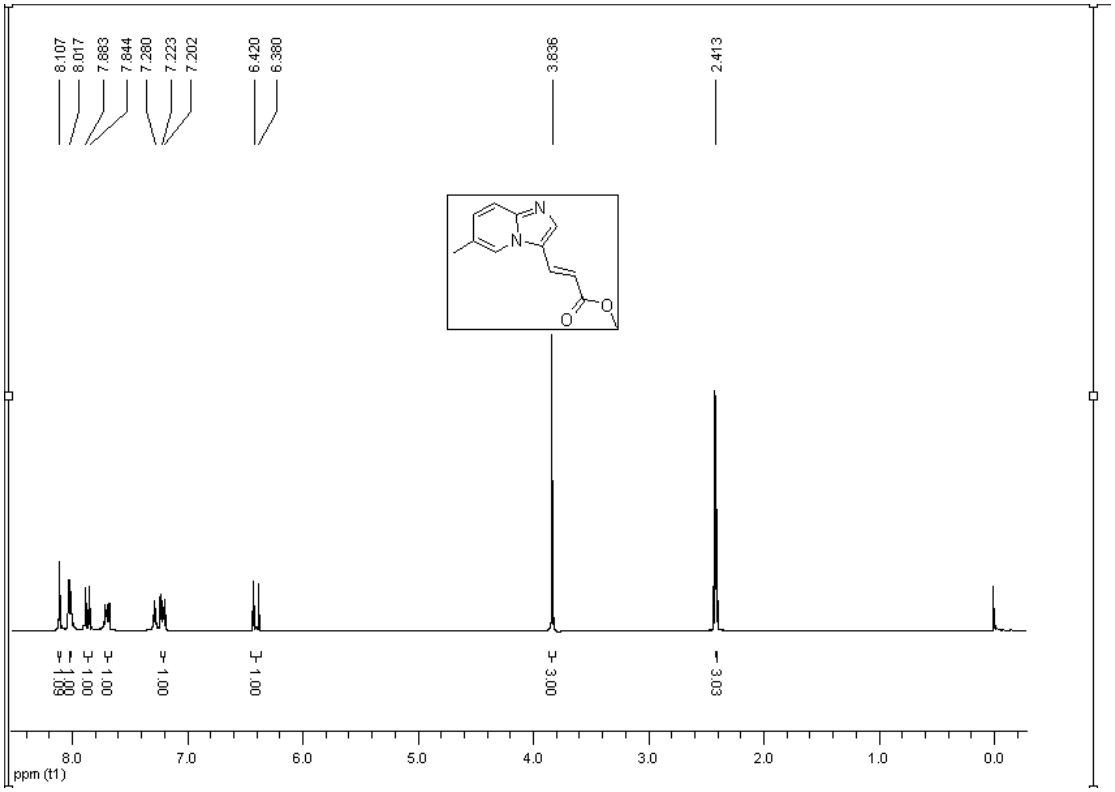
64.458
30.767
19.147
18.332
13.699
200
150
100
50
0
ppm (t1)


8.219
8.202
7.989
7.893
7.853
7.482
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)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8.017
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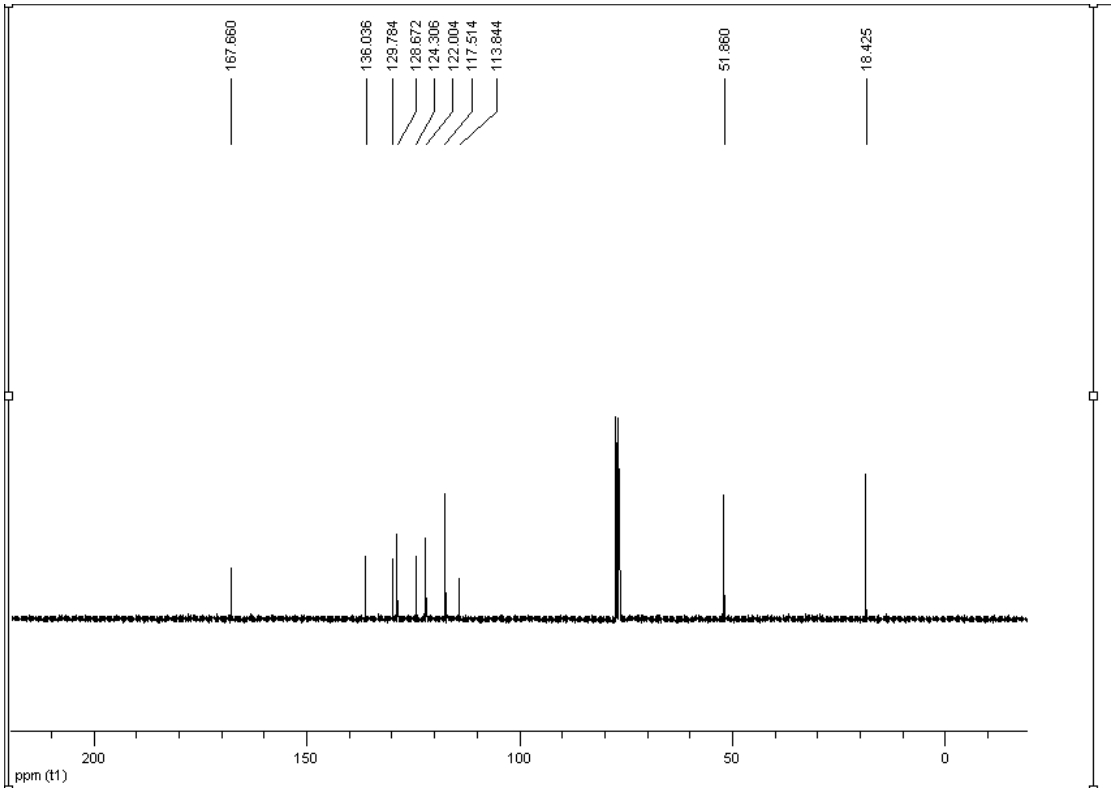
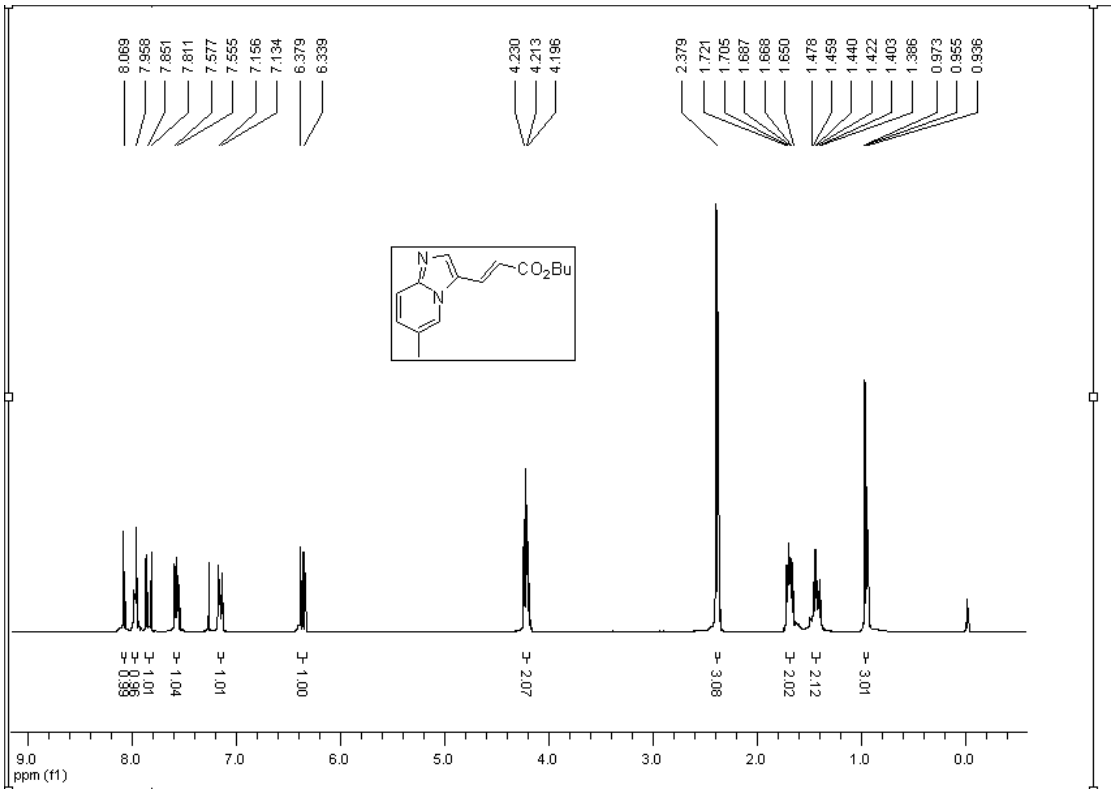
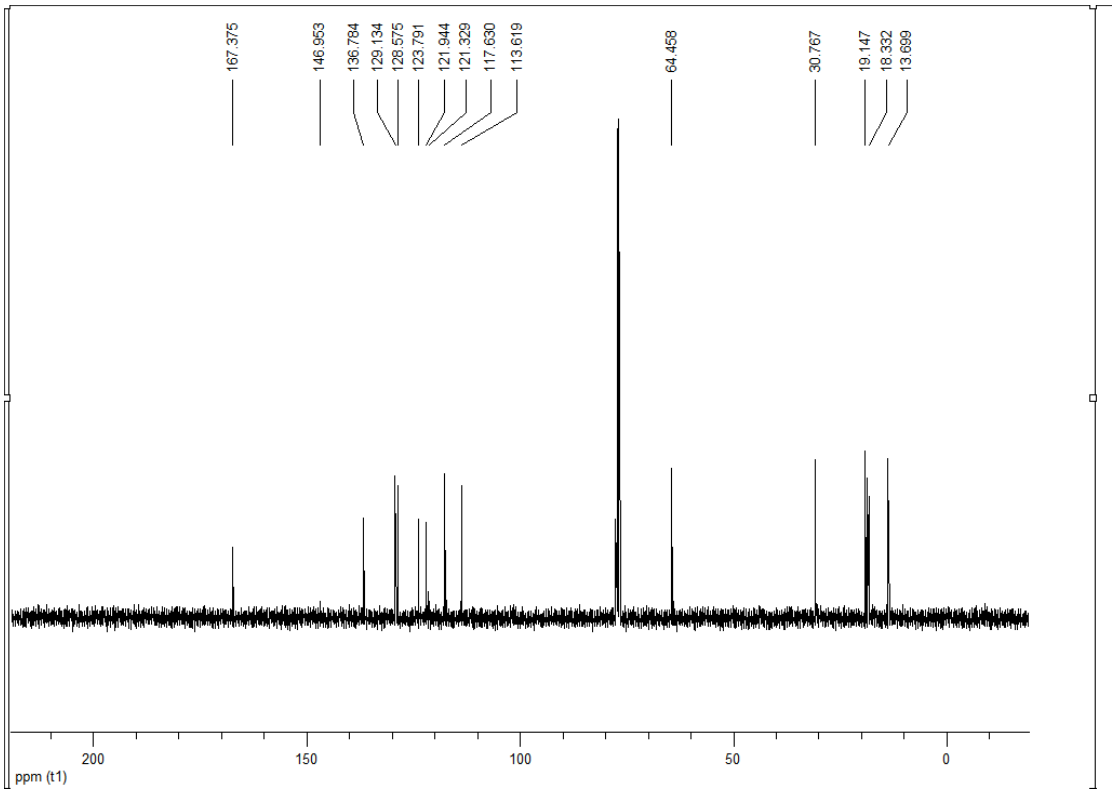
7.844
7.280
7.223
7.202
6.420
6.380
3.836
2.413
1.88
1.00
1.00
1.00
1.00
3.00
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


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)


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
N
N
0.99
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)


167.375
146.953
136.784
129.134
128.575
123.791
121.944
121.329
117.630
113.619
64.458
30.767
19.147
18.332
13.699
200
150
100
50
0
ppm (t1)