Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Regioselective C−H Alkenylation of Imidazoles and its Application to the Synthesis of Unsymmetrically Substituted Benzimidazoles

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I. General Information

Flash column chromatography was performed on silica gel (40-63 μm) using the indicated solvent system. NMR spectra were recorded in $CDCl_3$ at 300 K on a 300 MHz Fourier transform NMR spectrometer. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$, δ 77.16). Crude yields were determined by ^1H NMR using either of the following internal NMR standards [trichloroethylene (1H, 6.45 ppm) or 1,3,5-trimethoxybenzene (1H, 6.08 ppm)], which were added to reaction mixtures after cooling to 25 °C. Gas chromatography (GC) analyses were also performed to determine crude yields using *n*-dodecane as an internal standard. Infrared (IR) spectra are reported as absorption wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were acquired on high-resolution mass spectrometers: Q-TOF (ionization mode: ESI).

II. Experimental Procedures

II.A. General Procedure for the *N*-protection of Imidazoles.

To a stirred solution of imidazole (1.00 equiv) in DMF (and/or THF) at 0 °C under an argon atmosphere was added sodium hydride (1.10 equiv). After stirring for 20 min at 0 °C, a protecting reagent (1.05 equiv) was added dropwise, and the resulting mixture was stirred for 12 h at 25 °C. The reaction mixture was treated with water (50 mL) and EtOAc (50 mL) and transferred to a 125 mL separatory funnel. The organic layer was collected, and the aqueous layer was extracted with EtOAc (50 mL×2). The combined organic layers were washed with brine (50 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired imidazole.

II.B. General Procedure for C5-Alkenylation of C2-Unsubstituted Imidazoles.

A 40 mL-glass vial was evacuated and potassium pivalate (295 mg, 2.0 mmol) and DMA (3.00 mL, 0.33 M) were added under an oxygen atmosphere. Imidazole substrate (1.0 mmol), alkene (2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were then added to this solution. The vial was evacuated and filled with oxygen three times. After stirring for 24 h at 120 °C under 1 atm of oxygen (balloon), the reaction mixture was cooled to 25 °C. The reaction mixture was treated with water (20 mL) and EtOAc (20 mL) and transferred to a 125 mL separatory funnel. The organic layer was collected, and the aqueous layer was extracted with EtOAc (20 mL×2). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated, and

the residue was purified by flash column chromatography to afford the desired imidazole.

II.C. General Procedure for the C5-Alkenylation of C2-Substituted Imidazoles.

To a solution of imidazole substrate (0.50 mmol) and 1,4-dioxane (1.50 mL, 0.33 M) in an 8 mL-glass vial were added alkene (1.5 mmol), $Cu(OAc)_2$ (182 mg, 1.0 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol). The reaction mixture was stirred at 100 °C for 15 h, and then cooled to 25 °C. The reaction mixture was treated with ammonium hydroxide solution (15% NH_3 in H_2O, 25 mL) and EtOAc (25 mL) and transferred to a 125 mL separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with brine (15 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated, and the resulting residue was purified by flash column chromatography to afford the desired imidazole.

II.D. General Procedure for SEM-switch of Imidazoles.[1]

To a stirred solution of alkenyl imidazole (1.0 equiv) in CH_3CN (0.10 M) was added (2-(chloromethoxy)ethyl)trimethylsilane (SEM-Cl) (0.050 equiv) at 100 °C for 24 h. The reaction mixture was concentrated, and the residue was purified by flash column chromatography to afford the desired C4-substituted imidazole.

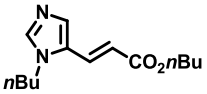
II.E. General Procedure for Electrocyclization/Oxidation of Di-alkenyl Imidazoles.

A 40 mL-glass vial was evacuated and di-alkenylated imidazole substrate (0.30 mmol), DDQ (7.0 mg, 0.030 mmol), $NaNO_2$ (2.0 mg, 0.030 mmol), and Ph_2O (3.0 mL, 0.10 M) were added under an oxygen atmosphere. The vial was evacuated and filled with oxygen three times. After stirring for 36 h at 180 °C under 1 atm of oxygen (balloon), the reaction mixture was cooled to 25 °C and concentrated. The residue was purified by flash column chromatography to afford the desired benzimidazole.

[1] J. M. Joo, B. B. Touré, D. Sames, *J. Org. Chem.* **2010**, *75*, 4911.

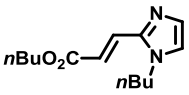
III. Product Characterization Data

(*E*)-Butyl 3-(1-butyl-1*H*-imidazol-5-yl)acrylate (1b)



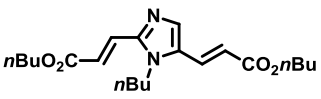
Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *n*-butyl acrylate (287 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:4) provided imidazole **1b** as a yellow oil (161 mg, 64% yield). IR (film) 2957, 2931, 2871, 1701, 1629, 1455, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H) 7.50 (d, *J* = 16.2 Hz, 1H), 7.47 (s, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 7.2 Hz, 2H), 1.79-1.66 (m, 4H), 1.51-1.39 (m, 2H), 1.38-1.27 (m, 2H), 1.05-0.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 140.1, 131.8, 129.5, 128.0, 116.4, 64.5, 45.2, 32.9, 30.8, 19.7, 19.2, 13.7, 13.5; HRMS (ESI) calcd for $C_{14}H_{23}N_2O_2$ $[M+H]^+$ 251.1754, found 251.1755.

(*E*)-Butyl 3-(1-butyl-1*H*-imidazol-2-yl)acrylate (1b-c2)



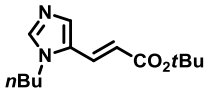
^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.49 (d, *J* = 15.8 Hz, 1H), 7.47 (s, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 7.1 Hz, 2H), 1.79-1.70 (m, 2H), 1.70-1.61 (m, 2H), 1.49-1.38 (m, 2H), 1.37-1.27 (m, 2H), 1.01-0.88 (m, 6H).

(2*E*, 2*E'*)-Dibutyl 3,3'-(1-butyl-1*H*-imidazole-2,5-yl)diacrylate (1b-di)



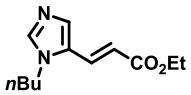
^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.47 (d, *J* = 15.4 Hz, 2H), 6.93 (d, *J* = 15.6 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.24-4.19 (m, 4H), 4.09 (t, *J* = 7.5 Hz, 2H), 1.72-1.64 (m, 6H), 1.47-1.39 (m, 4H), 1.37-1.32 (m, 2H), 0.95 (t, *J* = 7.1 Hz, 9H).

(*E*)-*tert*-Butyl 3-(1-butyl-1*H*-imidazol-5-yl)acrylate (1c)



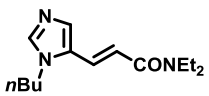
Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *t*-butyl acrylate (300 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 10:1) provided imidazole **1c** as a brown oil (143 mg, 57% yield). IR (film) 2961, 2872, 1699, 1630, 1455, 1148 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45 (s, 1H), 7.41 (d, *J* = 16.1 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 3.99 (t, *J* = 7.2 Hz, 2H), 1.79-1.68 (m, 2H), 1.52 (s, 9H), 1.38-1.29 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 139.9, 131.5, 128.6, 128.1, 118.4, 80.6, 45.2, 32.9, 28.2, 19.8, 13.5; HRMS (ESI) calcd for $C_{14}H_{23}N_2O_2$ $[M+H]^+$ 251.1754, found 251.1748.

(*E*)-Ethyl 3-(1-butyl-1*H*-imidazol-5-yl)acrylate (1d)



Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), ethyl acrylate (300 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 97:3) provided imidazole **1d** as an orange oil (129 mg, 58% yield). IR (film) 2960, 2933, 2873, 1704, 1632, 1177 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.50 (d, *J* = 16.0 Hz, 1H), 7.47 (s, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.00 (t, *J* = 7.2 Hz, 2H), 1.77-1.69 (m, 2H), 1.38-1.28 (m, 5H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 140.0, 131.7, 129.4, 127.8, 116.1, 60.4, 45.0, 32.7, 19.5, 14.1, 13.3; HRMS (ESI) calcd for $C_{12}H_{19}N_2O_2$ $[M+H]^+$ 223.1447, found 223.1445.

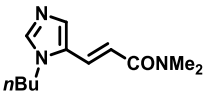
(*E*)-*O*-(3-(1-butyl-1*H*-imidazol-5-yl)acryloyl)-*N*,*N*-diethylhydroxylamine (1e)



Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *N*,*N*-diethyl acrylamide (279 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used.

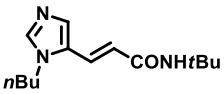
Flash column chromatography (DCM/MeOH = 96:4) provided imidazole **1e** as a yellow oil (188 mg, 75% yield). IR (film) 3102, 2963, 2932, 2872, 1644, 1601 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.55 (d, *J* = 14.8 Hz, 1H), 7.45 (s, 1H), 6.72 (d, *J* = 15.2 Hz, 1H), 4.00 (t, *J* = 7.3 Hz, 2H), 3.53-3.42 (m, 4H), 1.79-1.70 (m, 2H), 1.40-1.30 (m, 2H), 1.28-1.24 (m, 3H), 1.19 (t, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 139.2, 129.7, 128.9, 127.3, 116.2, 45.0, 42.1, 41.1, 32.9, 19.7, 15.0, 13.4, 13.1; HRMS (ESI) calcd for $C_{14}H_{24}N_3O_2$ $[M+H]^+$ 266.1863, found 266.1870.

(*E*)-*O*-(3-(1-butyl-1*H*-imidazol-5-yl)acryloyl)-*N*,*N*-dimethylhydroxylamine (1f)



Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *N*,*N*-dimethyl acrylamide (206 μL, 2.00 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 98:2) provided imidazole **1f** as an orange oil (121 mg, 54% yield). IR (film) 3102, 2963, 2932, 2872, 1644, 1601 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.45 (s, 1H), 6.77 (d, *J* = 15.2 Hz, 1H), 3.99 (t, *J* = 7.2 Hz, 2H), 3.16 (s, 3H), 3.07 (s, 3H), 1.77-1.68 (m, 2H), 1.36-1.26 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 139.4, 130.0, 129.0, 127.6, 115.9, 45.1, 37.4, 36.0, 33.1, 19.8, 13.6; HRMS (ESI) calcd for $C_{12}H_{20}N_3O$ $[M+H]^+$ 222.1606, found 222.1600.

(*E*)-*N*-(*tert*-butyl)-3-(1-butyl-1*H*-imidazol-5-yl)acrylamide (1g)

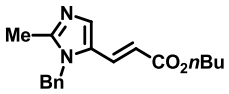


Following the general procedure B, *n*-butyl imidazole (**1a**) (132 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *t*-butyl acrylate (300 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 10:1) provided imidazole **1g** as a brown oil (171 mg, 69% yield). IR (film) 2961, 2872, 1657, 1549, 1330, 1223, 1122 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.41 (d, *J* = 15.6 Hz, 1H), 7.37 (s, 1H), 6.24 (d, *J* = 15.3 Hz, 1H), 5.60 (s, 1H), 3.96 (t, *J* = 7.2 Hz, 2H), 1.77-1.67 (m, 2H), 1.42 (s, 9H), 1.33-1.27 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 139.0, 129.2, 128.7, 124.9, 121.4, 51.6, 45.1, 33.0, 28.9, 27.4, 19.8, 13.6; HRMS (ESI) calcd for $C_{14}H_{24}N_3O_1$ $[M+H]^+$ 250.1919, found 250.1912.

1-Benzyl-2-methyl-1*H*-imidazole (2a)

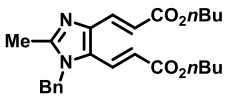
A commercial bottle was distilled prior to use. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.29 (m, 3H), 7.05 (d, *J* = 6.9 Hz, 2H), 6.96 (s, 1H), 6.85 (s, 1H), 5.05 (s, 2H), 2.33 (s, 3H).

(*E*)-Butyl 3-(1-benzyl-2-methyl-1*H*-imidazol-5-yl)acrylate (2b)



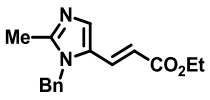
Following the general procedure C, **2a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (EtOAc only) provided imidazole **2b** as a yellow solid (110 mg, 74% yield). mp 56-60 °C; IR (film) 2960, 2873, 1701, 1630, 1304, 1158 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.39 (d, *J* = 15.9 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 3H), 6.96 (d, *J* = 6.7 Hz, 2H), 6.20 (d, *J* = 15.8 Hz, 1H), 5.17 (s, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 1.67-1.58 (m, 2H), 1.43-1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 148.5, 135.4, 130.3, 129.7, 128.9, 128.6, 127.8, 125.6, 115.4, 64.1, 47.0, 30.5, 19.0, 13.6, 13.4; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ 299.1754, found 299.1750.

(2*E*, 2'*E*)-Dibutyl 3,3'-(1-benzyl-2-methyl-1*H*-imidazol-4,5-diyl)diacrylate (2b-di)



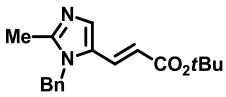
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 16.1 Hz, 1H), 7.38-7.29 (m, 3H), 6.98 (d, *J* = 6.6 Hz, 2H), 6.78 (d, *J* = 15.3 Hz, 1H), 6.12 (d, *J* = 16.1 Hz, 1H), 5.17 (s, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.69-1.63 (m, 4H), 1.45-1.35 (m, 4H), 0.97-0.90 (m, 6H).

(*E*)-Ethyl 3-(1-benzyl-2-methyl-1*H*-imidazol-5-yl)acrylate (2c)



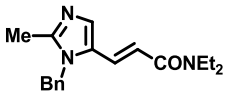
Following the general procedure C, **2a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), ethyl acrylate (163 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (EtOAc only) provided imidazole **2c** as a brown solid (95.0 mg, 70% yield). mp 77-80 °C; IR (film) 2981, 1701, 1629, 1413, 1309, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.41 (d, *J* = 15.9 Hz, 1H), 7.36-7.28 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.20 (d, *J* = 16.6 Hz, 1H), 5.17 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 148.7, 135.4, 130.5, 129.8, 129.0, 128.7, 127.9, 125.7, 115.4, 60.3, 47.0, 14.2, 13.5; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2$ $[M+H]^+$ 271.1441, found 271.1439.

(*E*)-tert-Butyl 3-(1-benzyl-2-methyl-1*H*-imidazol-5-yl)acrylate (2d)



Following the general procedure C, **2a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *t*-butyl acrylate (220 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:2) provided imidazole **2d** as a yellow solid (111 mg, 74% yield). mp 162-167 °C; IR (film) 3062, 2973, 2926, 1691, 1621, 1315 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.33 (s, 1H), 7.31-7.28 (m, 3H), 6.96 (d, *J* = 6.6 Hz, 2H), 6.15 (d, *J* = 15.7 Hz, 1H), 5.16 (s, 2H), 2.37 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 148.2, 135.4, 129.8, 128.9, 128.7, 127.7, 125.6, 117.3, 80.1, 46.8, 28.0, 13.5; HRMS (ESI) calcd for $C_{19}H_{23}N_2O_2$ $[M+H]^+$ 299.1754, found 299.1753.

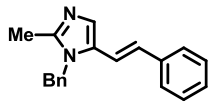
(*E*)-3-(1-Benzyl-2-methyl-1*H*-imidazol-5-yl)-*N*,*N*-diethylacrylamide (2e)



Following the general procedure C, **2a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0

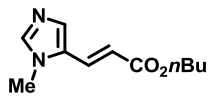
mmol), *N*,*N*-diethyl acrylamide (207 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (DCM/MeOH = 97:3) provided imidazole **2e** as a yellow solid (90.0 mg, 61% yield). mp 120-125 °C; IR (film) 2973, 2930, 1641, 1593, 1426, 1357 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 15.3 Hz, 1H), 7.40 (s, 1H), 7.35-7.30 (m, 3H), 6.97 (d, *J* = 7.1 Hz, 2H), 6.55 (d, *J* = 15.3 Hz, 1H), 5.19 (s, 2H), 3.42 (q, *J* = 7.0 Hz, 2H), 3.30 (q, *J* =7.0 Hz, 2H), 2.38 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 147.8, 135.4, 129.3, 129.1, 128.7, 127.6, 127.5, 125.3, 114.9, 46.7, 41.8, 40.7, 14.7, 13.2, 12.9; HRMS (ESI) calcd for $C_{18}H_{24}N_3O$ $[M+H]^+$ 298.1914, found 298.1916.

(*E*)-1-Benzyl-2-methyl-5-styryl-1*H*-imidazole (2f)



Following the general procedure C, **2a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), styrene (172 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:4) provided imidazole **2f** as a yellow solid (63.0 mg, 46% yield). mp 109-113 °C; IR (film) 3059, 2924, 1715, 1670, 1492, 1156 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.29 (m, 7H), 7.23-7.20 (m, 2H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 16.2 Hz, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 5.16 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 136.9, 136.1, 131.2, 129.0, 128.6, 128.5, 127.7, 127.5, 126.0, 125.8, 125.3, 114.4, 46.9, 13.5; HRMS (ESI) calcd for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1543, found 275.1548.

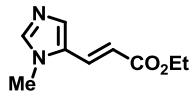
(*E*)-Butyl 3-(1-methyl-1*H*-imidazol-5-yl)acrylate (3b)



Following the general procedure B, 1-methyl imidazole (**3a**) (80.0 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *n*-butyl acrylate (287 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (DCM/MeOH = 98:2) provided imidazole **3b** as a yellow oil (134 mg, 64% yield). IR (film) 3107, 2979, 1699, 1630, 1280, 1123 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.51 (d, *J* = 15.7 Hz, 1H), 7.49 (s, 1H), 6.30 (d, *J* = 16.1 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 1.74-1.62 (m, 2H), 1.50-1.36 (m, 2H),

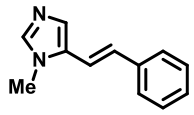
0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 141.0, 132.4, 129.6, 128.8, 116.4, 64.6, 32.4, 30.8, 19.3, 13.8; HRMS (ESI) calcd for $C_{11}H_{17}N_2O_2$ $[M+H]^+$ 209.1285, found 209.1285.

(*E*)-Ethyl 3-(1-methyl-1*H*-imidazol-5-yl)acrylate (3c)[2]



Following the general procedure B, 1-methyl imidazole (**3a**) (80.0 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), ethyl acrylate (218 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (DCM/MeOH = 97:3) provided imidazole **3c** as a white solid (122 mg, 68% yield). mp 45-47 °C; IR (film) 3107, 2979, 2113, 1799, 1650, 1491 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (d, J = 16.1 Hz, 1H), 7.47 (s, 1H), 6.28 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 141.0, 132.4, 129.5, 128.8, 116.4, 60.6, 32.4, 14.4; HRMS (ESI) calcd for $C_9H_{13}N_2O_2$ $[M+H]^+$ 181.0972, found 181.0969.

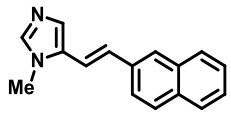
(*E*)-1-Methyl -5-styryl-1*H*-imidazole (3d)



Following the general procedure B, 1-methyl imidazole (**3a**) (80.0 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), styrere (230 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 97:3) provided imidazole **3d** as a yellow solid (67.0 mg, 37% yield). mp 102-105 °C; IR (film) 3110, 2955, 2927, 1723, 1494, 1278 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.42 (m, 3H), 7.39-7.28 (m, 4H), 6.97 (d, J = 16.3 Hz, 1H), 6.85 (d, J = 16.3 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 136.9, 131.3, 129.0, 128.8, 127.8, 127.4, 126.3, 114.0, 32.0; HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M+H]^+$ 185.1079, found 185.1073.

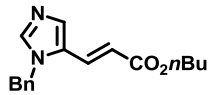
[2] M. A. Jinks, H. Sun, C. A. Hunter, *Org. Biomol. Chem.* **2014**, *12*, 1440.

(*E*)-1-Methyl -5-(2-naphthalen-2-yl)-1*H*-imidazole (3e)



Following the general procedure B, 1-methyl imidazole (**3a**) (80.0 μL, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), 2-vinylnaphthalene (318 mg, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (EtOAc/MeOH = 97:3) provided imidazole **3e** as a yellow solid (108 mg, 46% yield). mp 100-102 °C; IR (film) 3091, 3051, 2953, 1625, 1496, 1114 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86-7.79 (m, 4H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.51-7.43 (m, 3H), 7.37 (s, 1H), 7.14 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.4, 133.7, 133.1, 131.4, 129.1, 128.5, 128.1, 127.8, 127.5, 126.6, 126.5, 126.1, 123.1, 114.3, 32.0; HRMS (ESI) calcd for $C_{16}H_{15}N_2$ $[M+H]^+$ 235.1235, found 235.1232.

(*E*)-Butyl 3-(1-benzyl-1*H*-imidazol-5-yl)acrylate (4b)



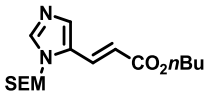
Following the general procedure B, 1-benzyl imidazole (**4a**) (163 mg, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *n*-butyl acrylate (287 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:4) provided imidazole **4b** as a yellow solid (160 mg, 55% yield). mp 46-49 °C; IR (film) 3107, 2956, 2870, 1700, 1630, 1290 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.55 (s, 1H), 7.44 (d, *J* = 16.0 Hz, 1H), 7.40-7.30 (m, 3H), 7.12 (d, *J* = 5.9 Hz, 2H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.24 (s, 2H), 4.15 (t, *J* = 6.6 Hz, 2H), 1.69-1.58 (m, 2H), 1.46-1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 140.6, 135.4, 132.1, 129.3, 129.2, 128.6, 128.4, 126.7, 117.0, 64.4, 49.0, 30.7, 19.2, 13.7; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_2$ $[M+H]^+$ 285.1598, found 285.1602.

1-((2-(Trimethylsilyl)ethoxy)methyl-1*H*-imidazole (5a)[1]

Following the general procedure A, 1*H*-imidazole (2.00 g, 29.38 mmol), NaH (775 mg, 32.31 mmol), SEM-Cl (5.70 ml, 30.85 mmol), THF (15.0 ml), DMF (15.0 ml) were used. Flash column chromatography (EtOAc only)

provided imidazole **5a** as a yellow liquid (2.50 g, 42% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.10 (s, 1H), 7.04 (s, 1H), 5.27 (s, 2H), 3.46 (t, *J* = 8.1 Hz, 2H), 0.89 (t, *J* = 8.1 Hz, 2H), 0.03 (s, 9H).

(*E*)-Butyl 3-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-5-yl)acrylate (5b)



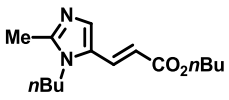
Following the general procedure B, **5a** (198 mg, 1.0 mmol), DMA (3.00 mL), KOPiv (295 mg, 2.0 mmol), *n*-butyl acrylate (287 μL, 2.0 mmol), and $Pd(OAc)_2$ (22.5 mg, 0.10 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:3) provided imidazole **5b** as a yellow oil (186 mg, 63% yield). IR (film) 3107, 2954, 2873, 1703, 1632, 1169 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.60 (d, *J* = 16.1 Hz, 1H), 7.48 (s, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 5.38 (s, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.52 (t, *J* = 8.1 Hz, 2H), 1.73-1.63 (m, 2H), 1.50-1.36 (m, 2H), 0.99-0.88 (m, 5H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 140.6, 132.8, 129.3, 128.4, 117.2, 74.2, 66.1, 64.2, 30.6, 19.0, 17.4, 13.5, -1.6; HRMS (ESI) calcd for $C_{16}H_{29}N_2O_3Si$ $[M+H]^+$ 325.1942, found 325.1948.

1-Butyl-2-methyl-1*H*-imidazole (6a)[3]

Following the general procedure A, 2-methyl-1*H*-imidazole (1.00 g, 12.18 mmol), DMF (5.00 mL), potassium tert-butoxide (1.64 g, 14.62 mmol), and 1-bromobutane (1.88 mL, 17.54 mmol) were used. Flash column chromatography (EtOAc only) provided imidazole **6a** as a pale yellow oil (1.40 g, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.80 (s, 1H), 3.81 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.75-1.62 (m, 2H), 1.40-1.26 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

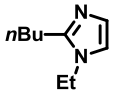
[3] M. Smiglak, C. C. Hines, W. M. Reichert, A. S. Vincek, A. R. Katritzky, J. S. Thrasher, L. Sun, P. D. MacCrary, P. A. Beasley, S. P. Kelley, R. D. Rogers, *New J. Chem.* **2012**, *36*, 702.

(*E*)-Butyl 3-(1-butyl-2-methyl-1*H*-imidazol-5-yl)acrylate (6b)



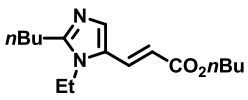
Following the general procedure C, **6a** (69.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:4) provided imidazole **6b** as a brown oil (93.0 mg, 70% yield). IR (film) 2957, 2931, 2872, 1702, 1626, 1542, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 15.9 Hz, 1H), 7.38 (s, 1H), 6.23 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.91 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.72-1.59 (m, 4H), 1.46-1.32 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 147.8, 129.9, 127.9, 114.7, 64.2, 43.6, 32.6, 30.6, 19.7, 19.0, 13.6, 13.5, 13.4; HRMS (ESI) calcd for $C_{15}H_{25}N_2O_2$ $[M+H]^+$ 265.1911, found 265.1906.

2-Butyl-1-ethyl-1*H*-imidazole (7a)



Following the general procedure A, 2-(*n*-butyl)-1*H*-imidazole (500 mg, 3.90 mmol), THF (4.00 mL), sodium hydride 60% in oil (172 mg, 4.30 mmol), and 1-bromoethane (327 μL, 4.30 mmol) were used. Flash column chromatography (EtOAc only) provided imidazole **7a** as a pale yellow oil (553 mg, 93% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.82 (s, 1H), 3.88 (q, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.81-1.68 (m, 2H), 1.49-1.40 (m, 2H), 1.38 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 124.3, 115.4, 37.6, 27.6, 23.7, 19.9, 13.6, 11.3.

(*E*)-Butyl 3-(2-butyl-1-ethyl-1*H*-imidazol-5-yl)acrylate (7b)



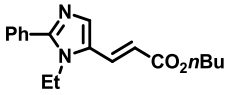
Following the general procedure C, **7a** (76.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0

mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexane/EtOAc = 1:1) provided imidazole **7b** as a brown oil (111 mg, 80% yield). IR (film) 2932, 2956, 2870, 1701, 1626, 1539, 1153 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 15.6 Hz, 1H), 7.41 (s, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 1.79-1.64 (m, 4H), 1.49-1.36 (m, 4H), 1.33 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 151.3, 130.6, 129.9, 127.4, 114.6, 64.2, 38.3, 30.6, 29.8, 26.7, 22.4, 19.1, 16.2, 13.74, 13.65; HRMS (ESI) calcd for $C_{16}H_{27}N_2O_2$ $[M+H]^+$ 279.2067, found 279.2061.

1-Ethyl-2-phenyl-1*H*-imidazole (8a)[4]

Following the general procedure A, 2-pheyl-1*H*-imidazole (1.00 g, 6.8 mmol), THF (7.00 mL), sodium hydride 60% in oil (300 mg, 7.5 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:2) to give **8a** as a yellow oil (1.24 g, quantitative yield). ^1H NMR (300 MHz, $CDCl_3$) δ 7.66-7.52 (m, 2H), 7.51-7.37 (m, 3H), 7.14 (s, 1H), 7.04 (s, 1H), 4.06 (q, *J* = 7.3 Hz, 2H), 1.41 (t, *J* = 7.3 Hz, 3H).

(*E*)-Butyl 3-(1-ethyl-2-phenyl-1*H*-imidazol-5-yl)acrylate (8b)



Following the general procedure C, **8a** (86.1 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 3:1) provided imidazole **8b** as a yellow oil (104 mg, 70% yield). IR (film) 3062, 2957, 2871, 1701, 1625, 1430 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.54 (s, 1H), 7.51-7.43 (m, 3H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.74-1.66 (m, 2H), 1.49-1.42 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 150.4,

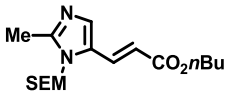
[4] O. S. Kim, J. H. Jang, H. T. Kim, S. J. Han, G. C. Tsui, J. M. Joo, *Org. Lett.* **2017**, *19*, 1450.

131.5, 130.2, 129.9, 129.2, 128.9, 128.7, 128.6, 115.8, 64.3, 39.5, 30.6, 19.1, 16.6, 13.7; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ 299.1754, found 299.1752.

2-Methyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazole (9a)[5]

Following the general procedure A, 2-methyl-1*H*-imidazole (1.00 g, 12.18 mmol), DMF (7.00 mL), sodium hydride 60% in oil (512 mg, 12.79 mmol), and SEM-Cl (2.52 mL, 12.79 mmol) were used. Flash column chromatography (EtOAc only) provided imidazole **9a.** Also, it was purified as a colorless oil (1.72 g, 66% yield) by distillation. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H), 5.19 (s, 2H), 3.47 (t, *J* = 8.3 Hz, 2H), 2.44 (s, 3H), 0.89 (t, *J* = 8.1 Hz, 2H), -0.02 (s, 9H).

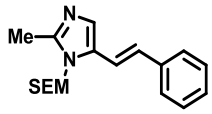
(*E*)-Butyl 3-(2-methyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-5-yl)acrylate (9b)



Following the general procedure C, **9a** (106 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:2) provided imidazole **9b** as a yellow solid (124 mg, 75% yield). mp 36-38 °C; IR (film) 2953, 1699, 1627, 1543, 1476, 1411, 1149 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.9 Hz, 1H), 7.36 (s, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 5.27 (s, 2H), 4.18 (t, *J* = 6.8 Hz, 2H), 3.52 (t, *J* = 8.1 Hz, 2H), 2.49 (s, 3H), 1.71-1.63 (m, 2H), 1.48-1.35 (m, 2H), 0.98-0.88 (m, 5H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 140.8, 133.1, 129.6, 128.7, 117.6, 74.5, 66.4, 64.6, 30.8, 19.3, 17.6, 13.8, 13.8, -1.4; HRMS (ESI) calcd for $C_{17}H_{31}N_2O_3Si$ $[M+H]^+$ 339.2098, found 339.2096.

[5] M. D. Markey, T. R. Kelly, *J. Org. Chem.* **2008**, *73*, 7441.

(*E*)-2-Methyl-5-styryl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazole (9c)

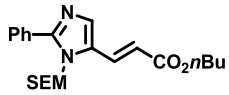


Following the general procedure C, **9a** (106 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), styrene (172 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:3) provided imidazole **9c** as a brown oil (90.0 mg, 57% yield). IR (film) 3376, 2956, 2870, 1491, 1456, 1276cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26-7.18 (m, 2H), 6.97 (d, *J* = 16.8 Hz, 1H), 6.92 (d, *J* = 16.8 Hz, 1H), 5.28 (s, 2H), 3.54 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 3H), 0.93 (t, *J* = 8.0 Hz, 2H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 136.6, 131.0, 128.3, 127.2, 125.8, 124.9, 114.1, 71.9, 65.4, 17.3, 13.1, -1.8; HRMS (ESI) calcd for $C_{18}H_{27}N_2OSi$ $[M+H]^+$ 315.1887, found 315.1886.

2-Phenyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazole (10a)[1]

Following the general procedure A, 2-phenylimidazole (2.00 g, 13.87 mmol), THF (40.0 mL), DMF (4.00 mL), NaH (610 mg, 15.26 mmol), SEM-Cl (2.90 mL, 14.57 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:1) provided imidazole **10a** as a yellow oil (2.60 g, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.2 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 3H), 7.15 (s, 1H), 7.12 (s, 1H), 5.28 (s, 2H), 3.57 (t, *J* = 8.2 Hz, 2H), 0.93 (t, *J* = 8.2 Hz, 2H), 0.01 (s, 9H).

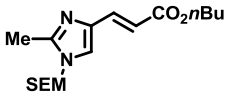
(*E*)-Butyl 3-(2-phenyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-5-yl)acrylate (10b)



Following the general procedure C, **10a** (686 mg, 2.50 mmol), 1,4-dioxane (6.00 mL), $Cu(OAc)_2$ (907 mg, 5.00 mmol), *n*-butyl acrylate (1.08 mL, 7.50 mmol), and $Pd(OAc)_2$ (56.1 mg, 0.250 mmol) were used. Flash column chromatography (hexanes/EtOAc = 3:1) provided imidazole **10b** as a yellow oil (733 mg, 73% yield). IR (film)

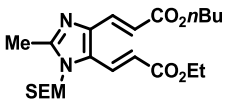
2954, 2895, 2872, 1705, 1628, 1539, 1160 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78-7.69 (m, 2H), 7.64 (d, *J* = 15.9 Hz, 1H), 7.57 (s, 1H), 7.53-7.43 (m, 3H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.30 (s, 2H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.53 (t, *J* = 8.3 Hz, 2H), 1.75-1.63 (m, 2H), 1.51-1.37 (m, 2H), 1.02-0.89 (m, 5H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 151.9, 131.7, 130.1, 130.0, 129.64, 129.57, 129.1, 128.7, 116.9, 73.0, 66.0, 64.4, 30.7, 19.2, 17.7, 13.8, -1.5; HRMS (ESI) calcd for $C_{22}H_{33}N_2O_3Si$ $[M+H]^+$ 401.2255, found 401.2252.

(*E*)-Butyl 3-(2-methyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-4-yl)acrylate (11a)



Following the general procedure D, **9b** (342 mg, 1.0 mmol), SEM-Cl (9.90 μL, 0.051 mmol), and CH_3CN (1.70 mL) were used. Flash column chromatography (hexanes/EtOAc = 3:1) provided imidazole **11a** as a brown solid (311 mg, 91% yield). mp 57-58 °C; IR (film) 2953, 2897, 1700, 1628, 1530, 1472, 1160 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 15.6 Hz, 1H), 7.09 (s, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 5.18 (s, 2H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.69-1.63 (m, 2H), 1.46-1.36 (m, 2H), 0.96-0.87 (m, 5H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 147.1, 136.1, 135.7, 122.4, 115.8, 75.2, 66.3, 64.0, 30.7, 19.1, 17.6, 13.7, 13.0, -1.5; HRMS (ESI) calcd for $C_{17}H_{31}N_2O_3Si$ $[M+H]^+$ 339.2104, found 339.2098.

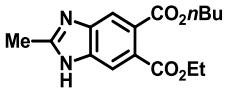
(*E*)-Butyl 3-(5-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-methyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-4-yl)acrylate (11b)



Following the general procedure C, **11a** (169 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), ethyl acrylate (164 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 2:1) provided imidazole **11b** as a yellow oil (203 mg, 85% yield). IR (film) 2955, 2873, 1704, 1626, 1524, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75-7.62 (m, 2H), 6.73 (d, *J* = 15.3 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 5.25 (s, 2H), 4.31-4.23 (m, 2H), 4.22-4.16 (m, 2H), 3.55 (t, *J* = 8.1 Hz, 2H), 2.51 (s, 3H), 1.71-1.65 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.31 (m, 3H), 0.98-0.91 (m, 5H), -0.01 (s, 9H); ^{13}C NMR (75

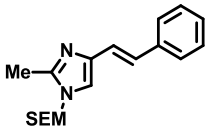
MHz, $CDCl_3$) δ 167.5, 166.6, 149.7, 138.9, 133.4, 129.3, 128.7, 120.5, 119.4, 73.1, 66.5, 64.4, 60.9, 30.9, 19.3, 17.9, 14.4, 13.84, 13.81, -1.3; HRMS (ESI) calcd for $C_{22}H_{37}N_2O_5Si$ $[M+H]^+$ 437.2466, found 437.2460.

5-Butyl 6-ethyl 2-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (11c)



Following the general procedure E, the electrocyclization/oxidation reaction was carried out with **11b** (131 mg, 0.30 mmol), DDQ (7.10 mg, 0.030 mmol), $NaNO_2$ (2.00 mg, 0.030 mmol), and Ph_2O (3.00 mL, 0.10 M) under an oxygen atmosphere (1.00 atm, balloon). Then, the crude mixture was filtered through a pad of silica gel and the solvent was removed under reduced pressure. The residue was treated with a solution of 3 N HCl (1.00 mL) and H_2O (4.00 mL). After stirring for 3 h at 80 °C, the reaction mixture was treated with aqueous saturated $NaHCO_3$ solution (25 mL) and EtOAc (25 mL) and transferred to a 125 mL-separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated and then purified by flash column chromatography (DCM/MeOH = 96:4) to provide (NH)-free benzimidazole **11c** as a yellow oil (63.0 mg, 69% yield). IR (film) 3053, 2960, 1712, 1629, 1541, 1311 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.85 (s, 1H), 4.43-4.26 (m, 4H), 2.62 (s, 3H), 1.77-1.66 (m, 2H), 1.50-1.40 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 166.9, 148.8, 138.4, 134.0, 129.2, 128.6, 119.6, 118.7, 64.9, 60.5, 44.6, 32.5, 30.8, 20.0, 19.3, 14.5, 13.8; HRMS (ESI) calcd for $C_{16}H_{21}N_2O_4$ $[M+H]^+$ 305.1496, found 305.1494.

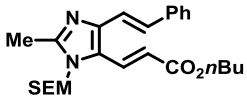
(*E*)-2-Methyl-4-styryl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazole (12a)



Following the general procedure D, **9c** (360 mg, 1.14 mmol), SEM-Cl (11.0 μL, 0.0570 mmol), and CH_3CN (1.10 mL) were used. Flash column chromatography (hexanes/EtOAc = 2:1) provided **12a** as a yellow solid (335 mg, 93% yield). mp 58-60 °C; IR (film) 2952, 2892, 1637, 1358, 1249, 1084 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.44 (m, 2H), 7.36-7.28 (m, 2H), 7.25-7.16 (m, 2H), 6.98-6.90 (m, 2H), 5.18 (s, 2H), 3.51 (t, *J* = 8.3 Hz, 2H),

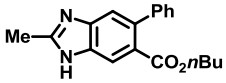
2.48 (s, 3H), 0.51 (t, J = 8.3 Hz, 2H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 137.9, 137.4, 128.3, 126.7, 126.1, 125.8, 119.7, 118.2, 74.7, 65.8, 17.4, 12.8, -1.6; HRMS (ESI) calcd for $C_{18}H_{27}N_2OSi$ $[M+H]^+$ 315.1887, found 315.1884.

(*E*)-Butyl 3-(2-methyl-4-((*E*)-styryl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-5-yl)acrylate (12b)



Following the general procedure C, **12a** (157 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), *n*-butyl acrylate (215 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:1) provided imidazole **12b** as a yellow oil (210 mg, 88% yield). IR (film) 3025, 2956, 1707, 1619, 1176, 1085 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 16.1 Hz, 1H), 7.56-7.54 (m, 2H), 7.51-7.38 (m, 2H), 7.36-7.28 (m, 2H), 7.15 (d, J = 15.6 Hz, 1H), 6.30 (d, J = 16.1 Hz, 1H), 5.27 (s, 2H), 4.23 (t, J = 6.7 Hz, 2H), 3.59 (t, J = 8.1 Hz, 2H), 2.54 (s, 3H), 1.74-1.67 (m, 2H), 1.49-1.39 (m, 2H), 1.00-0.92 (m, 5H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 149.5, 142.3, 137.3, 130.7, 129.5, 128.8, 127.9, 126.9, 125.8, 118.0, 117.0, 73.1, 66.3, 64.6, 30.9, 19.4, 17.9, 13.9, -1.3; HRMS (ESI) calcd for $C_{25}H_{37}N_2O_3Si$ $[M+H]^+$ 440.2495, found 441.2564.

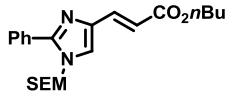
***n*-Butyl 2-methyl-5-phenyl-1H-benzo[*d*]imidazole-6-carboxylate (12c)**



Following the general procedure E, the electrocyclization/oxidation reaction was carried out with **12b** (132 mg, 0.30 mmol), DDQ (7.10 mg, 0.030 mmol), $NaNO_2$ (2.00 mg, 0.030 mmol), and Ph_2O (3.00 mL, 0.10 M) under an oxygen atmosphere (1.00 atm, balloon). Then, the crude mixture was filtered through a pad of silica gel and the solvent was removed under reduced pressure. The residue was treated with a solution of 3 N HCl (1.00 mL) and H_2O (4.00 mL). After stirring for 3 h at 80 °C, the reaction mixture was treated with aqueous saturated $NaHCO_3$ solution (25 mL) and EtOAc (25 mL) and transferred to a 125 mL-separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated and then purified by flash column chromatography (DCM/MeOH = 96:4) to provide (NH)-free benzimidazole **12c** as a yellow oil (59.0 mg,

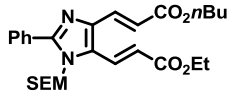
64% yield). IR (film) 3055, 2957, 2870, 1701, 1461, 1249 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.42 (s, 1H), 7.38-7.27 (m, 5H), 4.04 (t, *J* = 6.5 Hz, 2H), 2.63 (s, 3H), 1.39-1.29 (m, 2H), 1.17-1.06 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 153.9, 142.5, 140.6, 137.7, 128.8, 128.1, 126.9, 125.9, 117.1, 116.4, 65.1, 30.4, 19.1, 15.2, 13.8; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$ 309.1598, found 309.1594.

(*E*)-Butyl 3-(2-phenyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazol-4-yl)acrylate (13a)



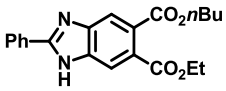
Following the general procedure D, **10b** (400 mg, 1.0 mmol), SEM-Cl (9.80 μL, 0.050 mmol), and CH_3CN (2.00 mL) were used. Flash column chromatography (hexanes/EtOAc = 4:1) provided imidazole **13a** as a yellow solid (324 mg, 81% yield). mp 52-53 °C; IR (film) 2954, 2892, 1695, 1640, 1477, 1366, 1169 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82-7.73 (m, 2H), 7.59 (d, *J* = 15.6 Hz, 1H), 7.51-7.43 (m, 3H), 7.30 (s, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 5.26 (s, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.56 (t, *J* = 8.3 Hz, 2H), 1.69-1.64 (m, 2H) 1.47-1.36 (m, 2H), 0.97-0.89 (m, 5H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 149.5, 136.9, 135.5, 129.2, 129.1, 128.7, 128.3, 123.7, 116.3, 75.2, 66.2, 63.7, 30.5, 18.9, 17.4, 13.5, -1.7; HRMS (ESI) calcd for $C_{22}H_{33}N_2O_3Si$ $[M+H]^+$ 401.2255, found 401.2258.

(*E*)-Butyl 3-(5-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-2-phenyl-1-((2-(trimethylsilyl)etho-xy)methyl)-1*H*-imidazol-4-yl)acrylate (13b)



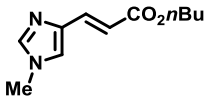
Following the general procedure C, **13a** (200 mg, 0.50 mmol), 1,4-dioxane (1.50 mL), $Cu(OAc)_2$ (182 mg, 1.0 mmol), ethyl acrylate (164 μL, 1.5 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were used. Flash column chromatography (hexanes/EtOAc = 4:1) provided imidazole **13b** as a white solid (214 mg, 86% yield). mp 71-73 °C; IR (film) 2952, 2873, 2928, 2900, 1698, 1623, 1163 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82-7.71 (m, 4H), 7.54-7.48 (m, 3H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 16.2 Hz, 1H), 5.22 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 8.3 Hz, 2H), 1.73-1.64 (m, 2H), 1.48-1.39 (m, 2H), 1.38-1.32 (m, 3H), 0.99-0.92 (m, 5H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 166.6, 152.7, 139.7, 133.3, 130.2, 129.4, 129.2, 128.9, 128.8, 120.7, 120.1, 73.7, 66.1, 64.4, 60.9, 30.8, 19.3, 17.9, 14.4, 13.9, -1.4; HRMS (ESI) calcd for $C_{27}H_{39}N_2O_5Si$ $[M+H]^+$ 499.2623, found 499.2620.

5-Butyl 6-ethyl 2-phenyl-1H-benzo[d]imidazole-5,6-dicarboxylate (13c)



Following the general procedure E, the electrocyclization/oxidation reaction was carried out with **13b** (150 mg, 0.30 mmol), DDQ (7.10 mg, 0.030 mmol), $NaNO_2$ (2.00 mg, 0.030 mmol), and Ph_2O (3.00 mL, 0.10 M) under an atmosphere of oxygen (1 atm, balloon). Then, the crude mixture was filtered through a pad of silica gel and the solvent was removed under reduced pressure. The residue was treated with a solution of 3 N HCl (1.00 mL) and H_2O (4.00 mL). After stirring for 3 h at 80 ºC, the reaction mixture was treated with aqueous saturated $NaHCO_3$ solution (25 mL) and EtOAc (25 mL) and transferred to a 125 mL-separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated and then purified by flash column chromatography (hexanes/EtOAc = 1:3) to provide (NH)-free benzimidazole **13c** as a brown oil (75.0 mg, 68% yield). IR (film) 3285, 2960, 1717, 1628,1463, 1320 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 (s, 1H), 7.86 (d, *J* = 9.2 Hz, 2H), 7.43-7.27 (m, 3H), 4.40-4.27 (m, 2H), 4.27-4.17 (m, 2H), 1.73-1.56 (m, 2H), 1.44-1.22 (m, 5H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 156.0, 130.9, 129.1, 128.9, 127.1, 127.03, 126.98, 65.7, 61.8, 30.5, 19.1, 14.1, 13.7; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_4$ $[M+H]^+$ 367.1652, found 367.1654.

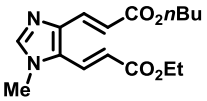
(*E*)-Butyl 3-(1-methyl-1*H*-imidazol-4-yl)acrylate (14a)



To a stirred solution of **5b** (300 mg, 0.92 mmol) in anhydrous DCM (10.0 mL, 0.10 M) was added Me_3OBF_4 (164 mg, 1.1 mmol) at room temperature for 1 h under an argon atomesphere. The residue was treated with a solution of TFA (8.00 mL) and DCM (8.00 mL). After stirring for 16 h at room temperature, the reaction mixture was treated with aqueous saturated $NaHCO_3$ solution (25 mL) and EtOAc (25 mL) and transferred to a 125 mL-separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (15 mL × 2). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. The filtrate was concentrated and then purified by flash column chromatography (EtOAc/MeOH = 10:1) to provide imidazole **14a** as a brown oil (57.0 mg, 89% yield). IR (film) 2959, 2873, 1701, 1639, 1272, 1160 cm^{-1}; ^1H NMR (300 MHz,

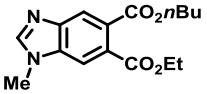
$CDCl_3$) δ 7.63 (s, 1H), 7.52 (d, *J* = 15.7 Hz, 1H), 7.09 (s, 1H), 6.59 (d, *J* = 15.7 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.73 (s, 3H), 1.71-1.61 (m, 2H), 1.45-1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 139.1, 138.3, 135.9, 122.5, 115.9, 64.1, 33.6, 30.7, 19.2, 13.7; HRMS (ESI) calcd for $C_{11}H_{17}N_2O_2$ $[M+H]^+$ 209.2649, found 209.1279.

(*E*)-Butyl 3-(5-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-1-methyl-*1H*-imidazol-4-yl)acrylate (14b)



Following the general procedure B, **14a** (53 mg, 0.26 mmol), DMA (0.75 mL), KOPiv (72 mg, 0.51 mmol), ethyl acrylate (55 μL, 0.51 mmol), and $Pd(OAc)_2$ (5.8 mg, 0.030 mmol) were used. Flash column chromatography (hexanes/EtOAc = 1:6) provided imidazole **14b** as a brown oil (30 mg, 39% yield). IR (film) 2959, 1707, 1632, 1299, 1259, 1178 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.62 (m, 2H), 7.58 (s, 1H), 6.77 (d, *J* = 15.4 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 1.73-1.64 (m, 2H), 1.49-1.39 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 166.4, 141.7, 140.5, 133.4, 128.54, 128.49, 119.5, 119.3, 64.3, 60.9, 33.5, 30.7, 19.2, 14.3, 13.8; HRMS (ESI) calcd for $C_{16}H_{23}N_2O_4$ $[M+H]^+$ 307.1658, found 307.1647.

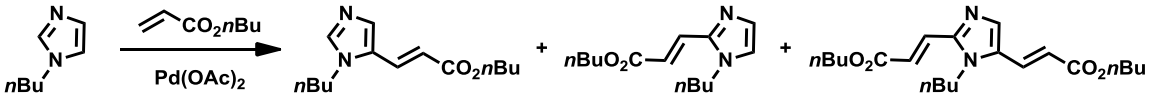
5-Butyl 6-ehtyl 1-methyl-*1H*-benzo[*d*]imidazole-5,6-dicarboxylate (14c)



Following the general procedure E, the electrocyclization/oxidation reaction was carried out with **14b** (95 mg, 0.31 mmol), DDQ (7.0 mg, 0.031 mmol), $NaNO_2$ (2.0 mg, 0.031 mmol), and Ph_2O (6.0 mL, 0.050 M) under an atmosphere of oxygen (1.0 atm, balloon). Flash column chromatography (EtOAc/MeOH = 10:1) provided benzimidazole **14c** as a dark brown oil (74 mg, 78% yield). IR (film) 2959, 2873, 1335, 1279, 1188, 1101 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.03 (s, 1H), 7.79 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.91 (s, 3H), 1.79-1.69 (m, 2H), 1.53-1.37 (m, 5H), 0.96 (t, *J* = 7.3 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 168.0, 146.8, 144.5, 135.4, 127.4, 126.5, 121.6, 111.0, 65.4, 61.7, 31.4, 30.5, 19.2, 14.1, 13.8; HRMS (ESI) calcd for $C_{16}H_{21}N_2O_4$ $[M+H]^+$ 305.1501, found 305.1492.

IV. Optimization Studies

Table S1. Alkenylation of 1-(*n*-Butyl)imidazole[a]

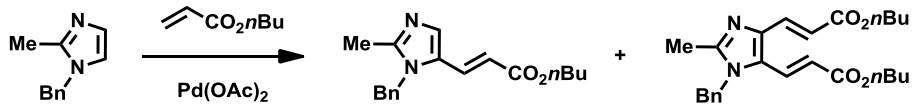


1a 1b 1b-c2 1b-di

entry	additive	oxidant	solvent	temp. (°C)	yield (%)[b]			
					1a	1b	1b-c2	1b-di
1[c]	1,10-phenanthroline (10 mol%)	AgTFA	toluene	130	37	1	33	< 1
2	−	AgTFA	1,4-dioxane	100	71	3	25	< 1
3	−	$Cu(OAc)_2 \cdot H_2O$	1,4-dioxane	100	9	20	36	7
4	−	$Cu(OAc)_2$	1,4-dioxane	100	8	12	38	< 1
5	pyridine (20 mol%)	$Cu(OAc)_2$	1,4-dioxane	100	7	14	35	< 1
6	−	$Cu(OAc)_2$	1,4-dioxane	120	6	6	42	16
7	−	O_2 (1 atm)	1,4-dioxane	120	88	11	< 1	< 1
8	−	O_2 (1 atm)	DMA	120	61	32	< 1	2
9	KOAc	O_2 (1 atm)	DMA	120	36	57	< 1	3
10	**KOPiv**	**O_2 (1 atm)**	**DMA**	**120**	**20**	**67**	**< 1**	**2**
11	CsOPiv	O_2 (1 atm)	DMA	120	25	64	< 1	2
12[d]	K_2CO_3/PivOH	O_2 (1 atm)	DMA	120	37	54	< 1	< 1
13	KOPiv	air	DMA	120	42	52	< 1	< 2

[a] Reaction conditions: imidazole (1.0 mmol), *n*-butyl acrylate (2.0 mmol), $Pd(OAc)_2$ (0.10 mmol), additive (2.0 mmol), oxidant (2.0 mmol or O_2 balloon), solvent (0.33 M), 24 h. [b] GC yield. [c] Imidazole (1.0 mmol), *n*-butyl acrylate (5.0 mmol), $Pd(TFA)_2$ (0.10 mmol), 1,10-phenanthroline (0.15 mmol), AgTFA (2.0 mmol), toluene (0.50 M). [d] PivOH (0.5 mmol) was used.

Table S2. Alkenylation of 1-Benzyl-2-methylimidazole[a]



2a 2b 2b-di

entry	additive	oxidant	solvent	temp. (°C)	yield (%)[b]		
					2a	2b	2b-di
1[c]	1,10-phenanthroline	AgTFA	toluene	130	97	< 1	< 1
2	–	AgTFA	1,4-dioxane	100	98	< 1	< 1
3	–	$Cu(OAc)_2 \cdot H_2O$	1,4-dioxane	100	0	68	8
4	**–**	**$Cu(OAc)_2$**	**1,4-dioxane**	**100**	**0**	**76**	**12**
5	pyridine (20 mol%)	$Cu(OAc)_2$	1,4-dioxane	100	0	72	15
6	–	$Cu(OAc)_2$	1,4-dioxane	120	0	62	15
7	–	O_2 (1 atm)	1,4-dioxane	120	89	7	< 1
8	–	O_2 (1 atm)	DMA	120	41	50	< 1
9	KOAc	O_2 (1 atm)	DMA	120	33	61	< 1
10	KOPiv	O_2 (1 atm)	DMA	120	30	67	< 1
11	CsOPiv	O_2 (1 atm)	DMA	120	35	64	< 1
12[d]	K_2CO_3/PivOH	O_2 (1 atm)	DMA	120	55	40	< 1
13	KOPiv	air	DMA	120	48	50	< 1

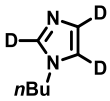
[a]Reaction conditions: imidazole (0.50 mmol), *n*-butyl acrylate (1.5 mmol), $Pd(OAc)_2$ (0.050 mmol), additive (1.0 mmol), oxidant (1.0 mmol or O_2 balloon), solvent (0.33 M), 15 h. [b] ^1H NMR yield. [c] Imidazole (0.5 mmol), *n*-butyl acrylate (2.5 mmol), $Pd(TFA)_2$ (0.050 mmol), 1,10-phenanthroline (0.075 mmol), AgTFA (1.0 mmol), toluene (0.50 M). [d] PivOH (0.25 mmol) was used.

V. Mechanistic Studies

V.A. Preparation of Deuterated Imidazoles

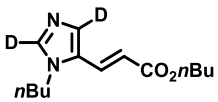
Imidazole-d_4 was purchased from Cambridge Isotope Laboratories. A mixture of imidazole-d_4 (1.00 g, 13.87 mmol), *n*-butyl iodide (1.58 mL, 13.87 mmol), and K_2CO_3 (3.83 g, 27.74 mmol) in acetone (26.0 mL) was refluxed at 50 °C for 16 h. Upon filtration and removal of the solvent, the residue was subjected to flash chromatography using ethyl acetate as an eluent, affording **1a**-d_3 (606 mg, 34% yield).

(*E*)-Butyl 3-(1-butyl-1*H*-2,4,5-D-imidazol-5-yl)acrylate (1a-d_3)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 0.03H), 7.04 (s, 0.01H), 6.91 (s, 0.01H), 3.92 (t, *J* = 7.1 Hz, 2H), 1.75 (quintet, *J* = 7.3 Hz, 2H), 1.32 (sextet, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

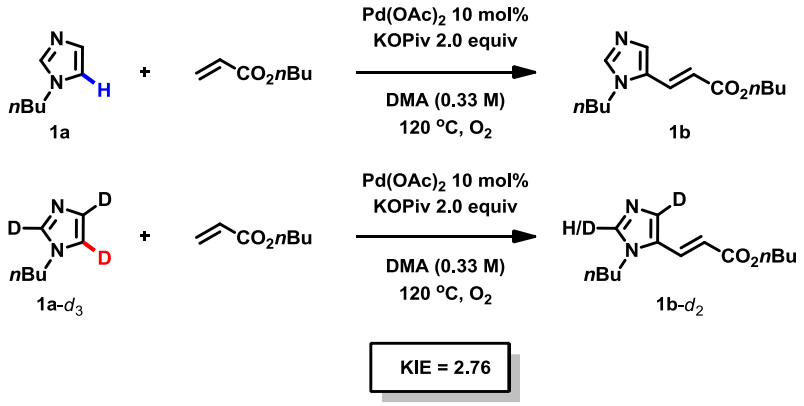
(*E*)-Butyl 3-(1-butyl-1*H*-2,4-D-imidazol-5-yl)acrylate (1b-d_2)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (s, 0.65H, C2-D was lost during the alkenylation reaction), 7.49 (d, *J* = 16.2 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 7.2 Hz, 2H), 1.79-1.64 (m, 4H), 1.47-1.31 (m, 4H), 1.00-0.91 (m, 6H).

V.B. Kinetic Isotope Effects of the Pd-catalyzed C5-alkenylation Reaction

A 40 mL-glass vial was evacuated and potassium pivalate (140 mg, 1.0 mmol) and DMA (1.50 mL, 0.33 M) were added under oxygen atmosphere. **1a** (66 μL, 0.5 mmol) [or **1a**-d_3 (64 mg, 0.5 mmol)], *n*-butyl acrylate (117 μL, 1.0 mmol), and $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) were then added to this solution. The reaction mixture was stirred at 120 °C under 1 atm of oxygen (balloon). For each desired time point, 10 μL of the reaction mixture was taken out from the 40 mL-glass vial and GC yield was determined by GC analysis versus *n*-dodecane as the internal standard. The initial reaction rate was obtained by plotting the six points to obtain ***KIE*** value to be **2.76**.



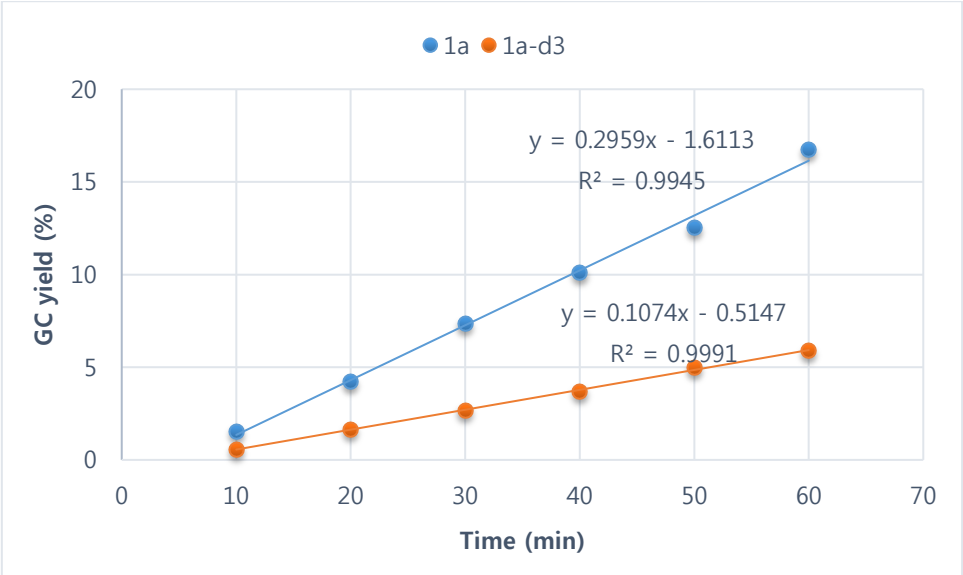
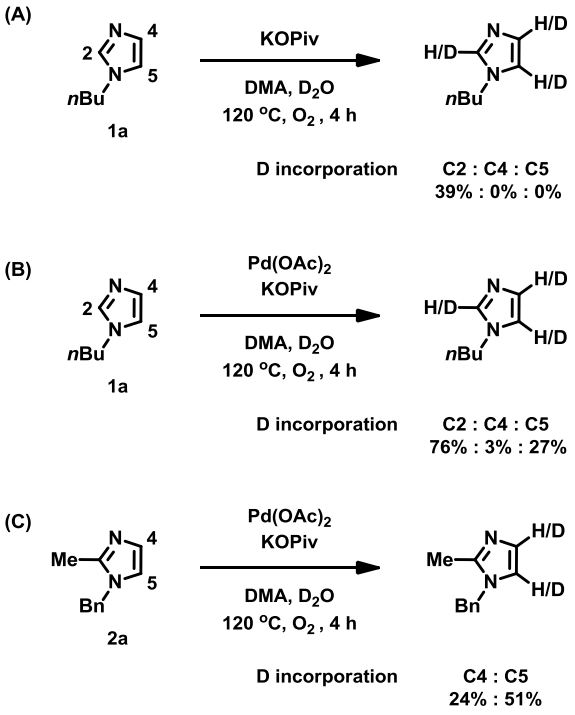


Figure S1. Initial rates of 1-butylimidazole **1a** and 1-butyl-2,4,5-D-imidazole **1a**-d_3

V.C. H/D Exchange Experiments

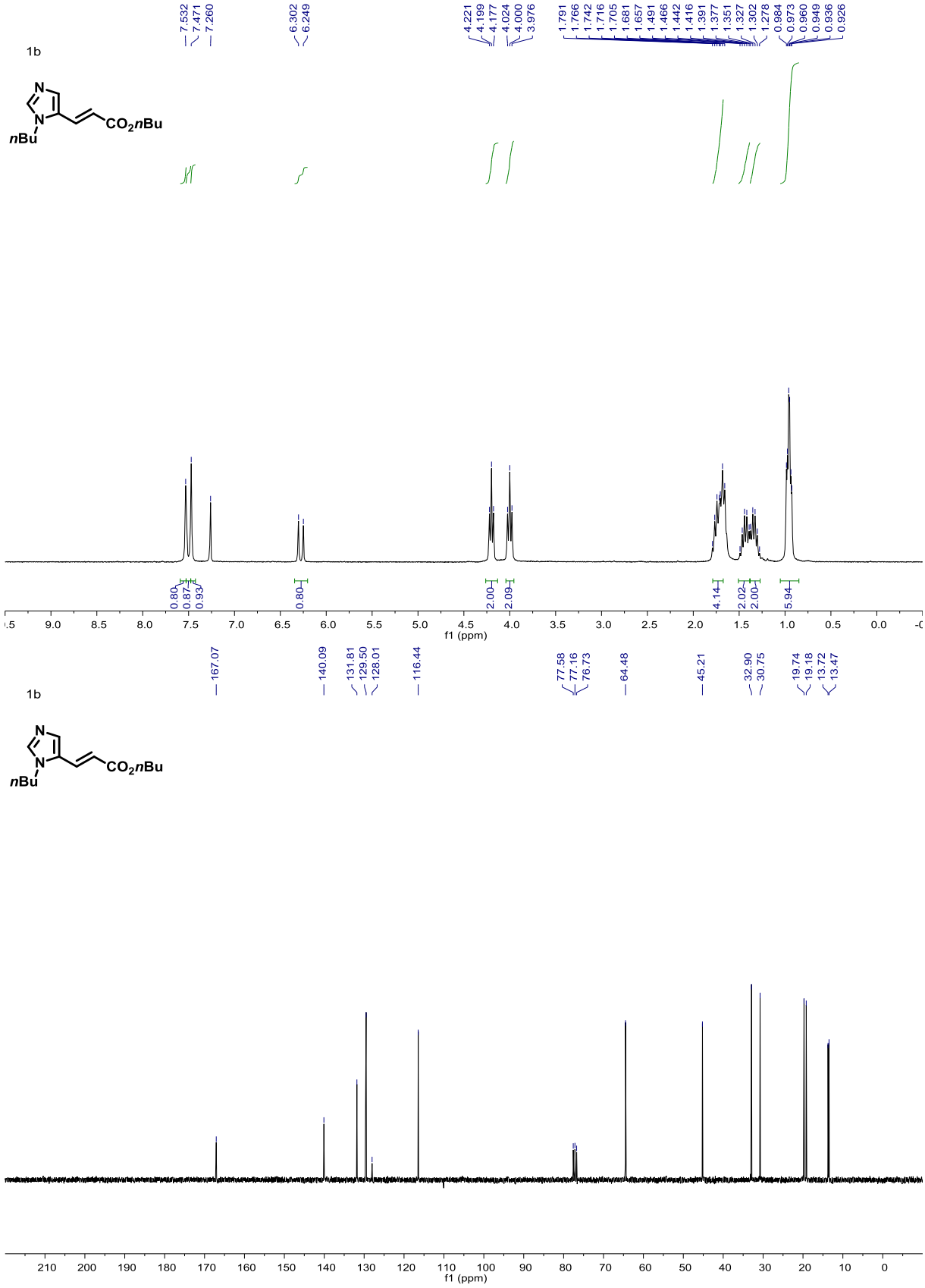
The H/D isotope exchange experiments were conducted in the presence of D_2O (Scheme S1). In the absence of $Pd(OAc)_2$, deuterium incorporation was observed only at the C2 position (Scheme S1A).[6] Under the palladium conditions, both the C2 and C5 positions of C2-unsubstituted imidazole **1a** were labeled, indicating the critical role of the palladium complex in the deuteration of the C5 position (Scheme S1B). In addition, C2-substituted imidazole **2a** was labeled at both the C4 and C5 positions with a slight preference for the C5 position (Scheme S1C).



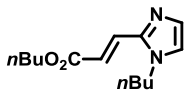
Scheme S1. H/D exchange experiments of imidazoles

[6] For C2-deuteration of imidazoles by base, see: (a) J. D. Vaughan, Z. Mughrabi, E. C. Wu, *J. Org. Chem.* **1970**, *35*, 1141; (b) T. L. Amyes, S. T. Diver, J. P. Richard, F. M. Rivas, K. Toth, *J. Am. Chem. Soc.* **2004**, *126*, 4366.

VI. ^{1}H NMR and ^{13}C NMR Spectra



1b-c2



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6.245
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4.190
4.168
4.019
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1.758
1.733
1.707
1.699
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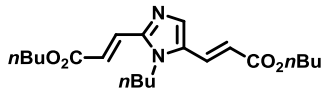
1.341
1.316
1.292
1.266
0.976
0.964
0.951
0.941
0.89
0.86
0.81
0.89
2.00
2.13
2.08
2.03
2.03
2.11
6.02
f1 (ppm)

1b-di



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6.903
6.393
6.340
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4.228
4.214
4.208
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4.110
4.085
4.060
1.704
1.682
1.658
1.635
1.458
1.436
1.413
1.388
1.362
1.337
1.313
0.977
0.953
0.929
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0.80
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4.13
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6.04
4.08
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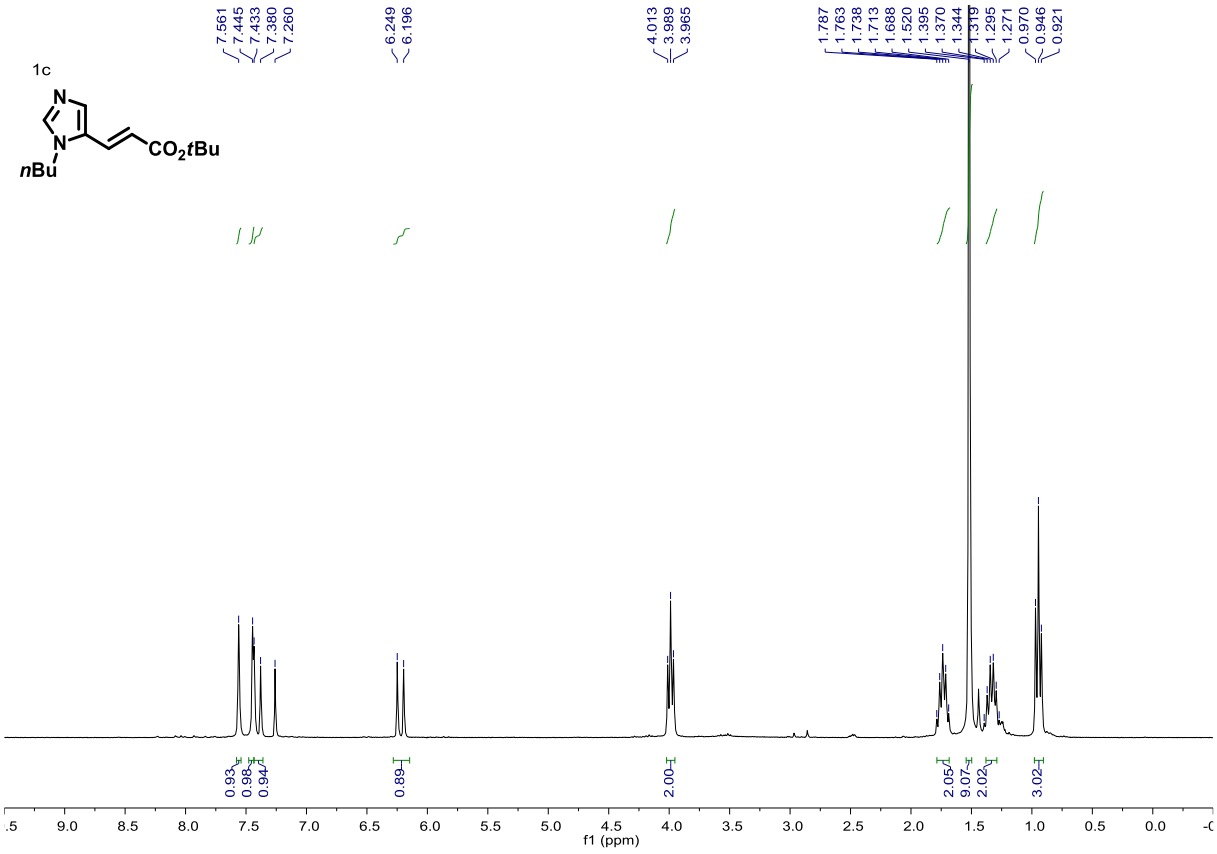
9.29
f1 (ppm)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1.713
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1.520
1.395
1.370
1.344
1.319
1.295
1.271
0.970
0.946
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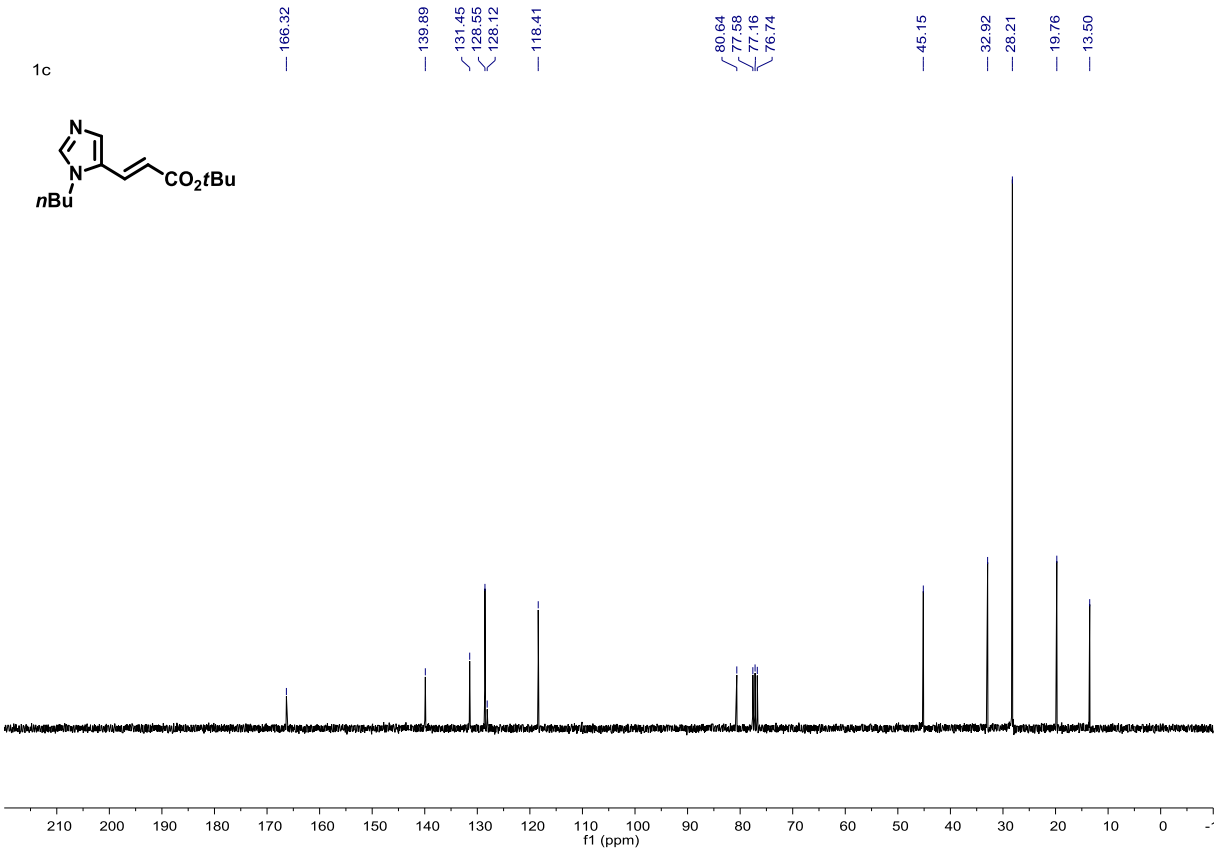
0.89
2.00
2.05
9.07
2.02
3.02
f1 (ppm)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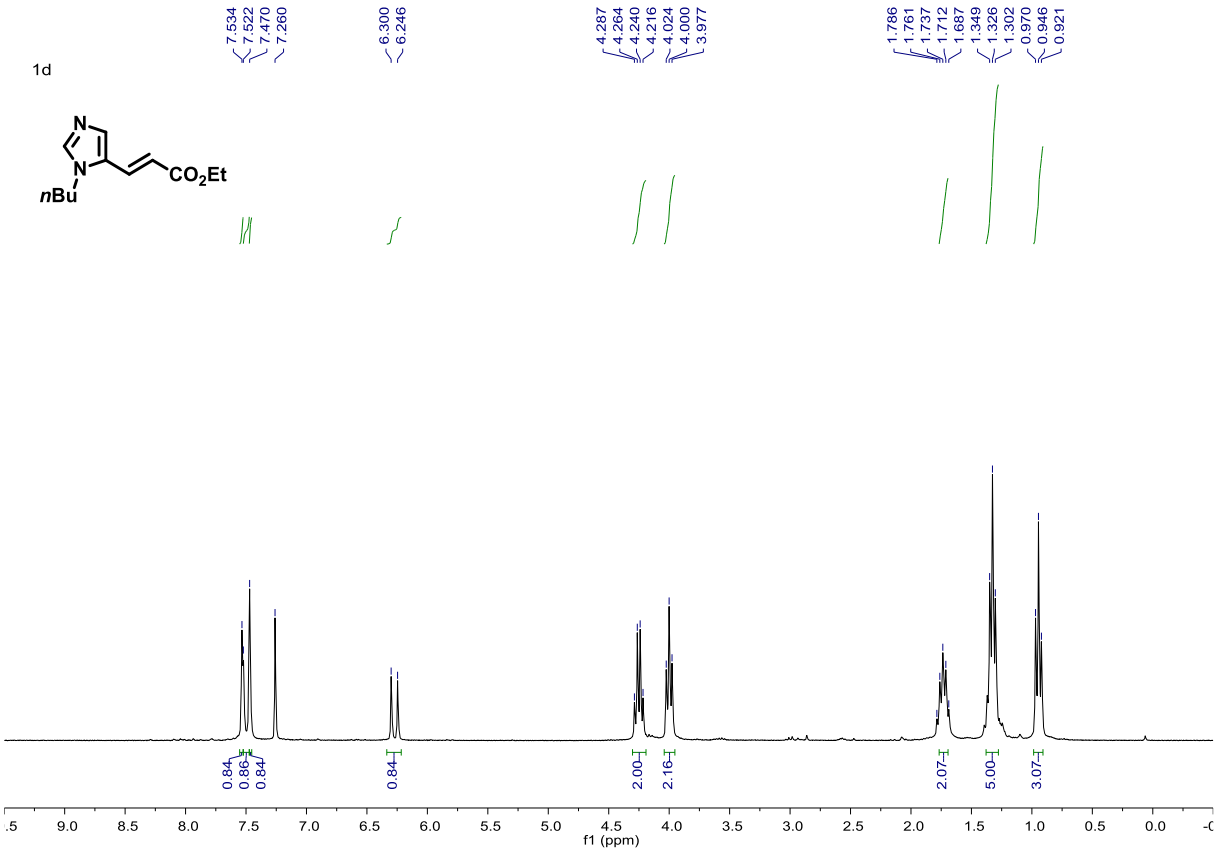
19.76
13.50
f1 (ppm)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4.264
4.240
4.216
4.024
4.000
3.977
1.786
1.761
1.737
1.712
1.687
1.349
1.326
1.302
0.970
0.946
0.921
N
N
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0.86
0.84
0.84
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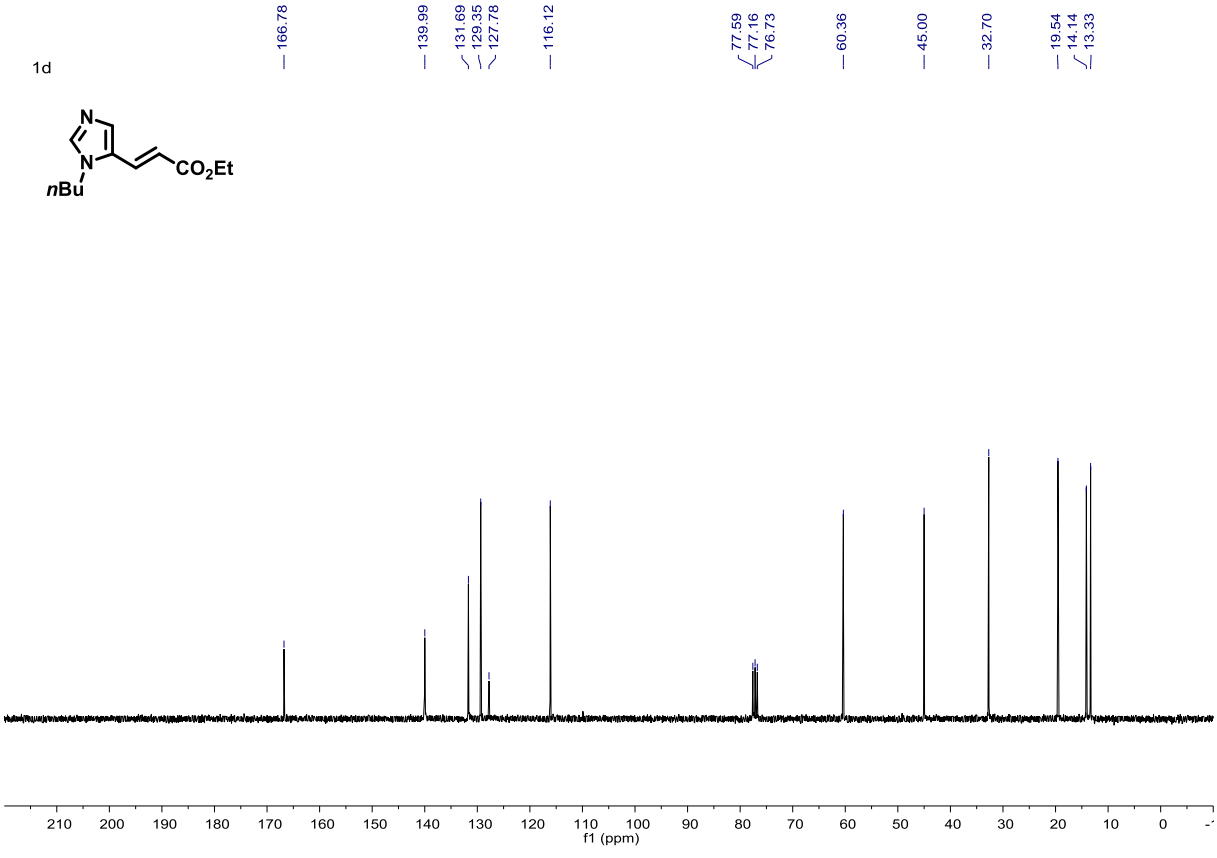
2.07
5.00
3.07
f1 (ppm)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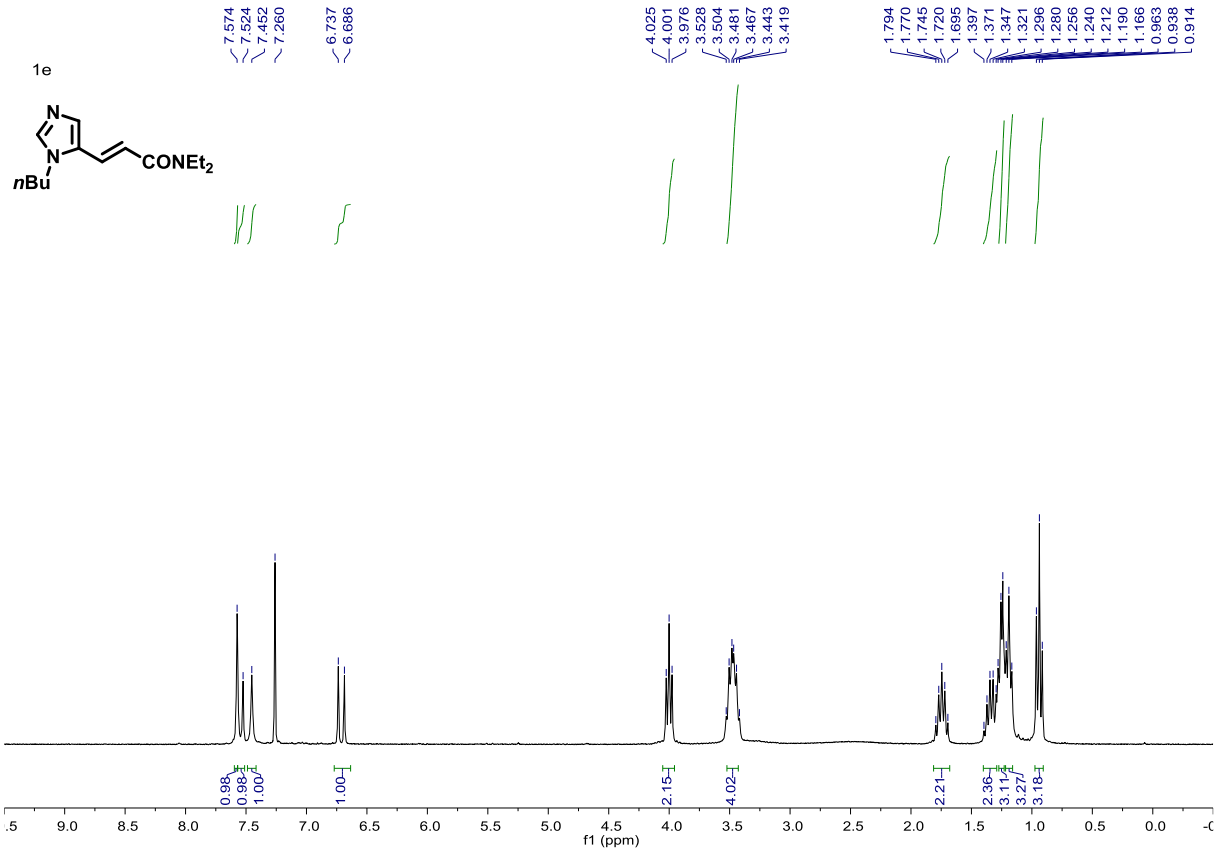
N
N
nBu
CO2Et
f1 (ppm)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1.745
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1.296
1.280
1.256
1.240
1.212
1.190
1.166
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0.938
0.914
CONEt2
nBu
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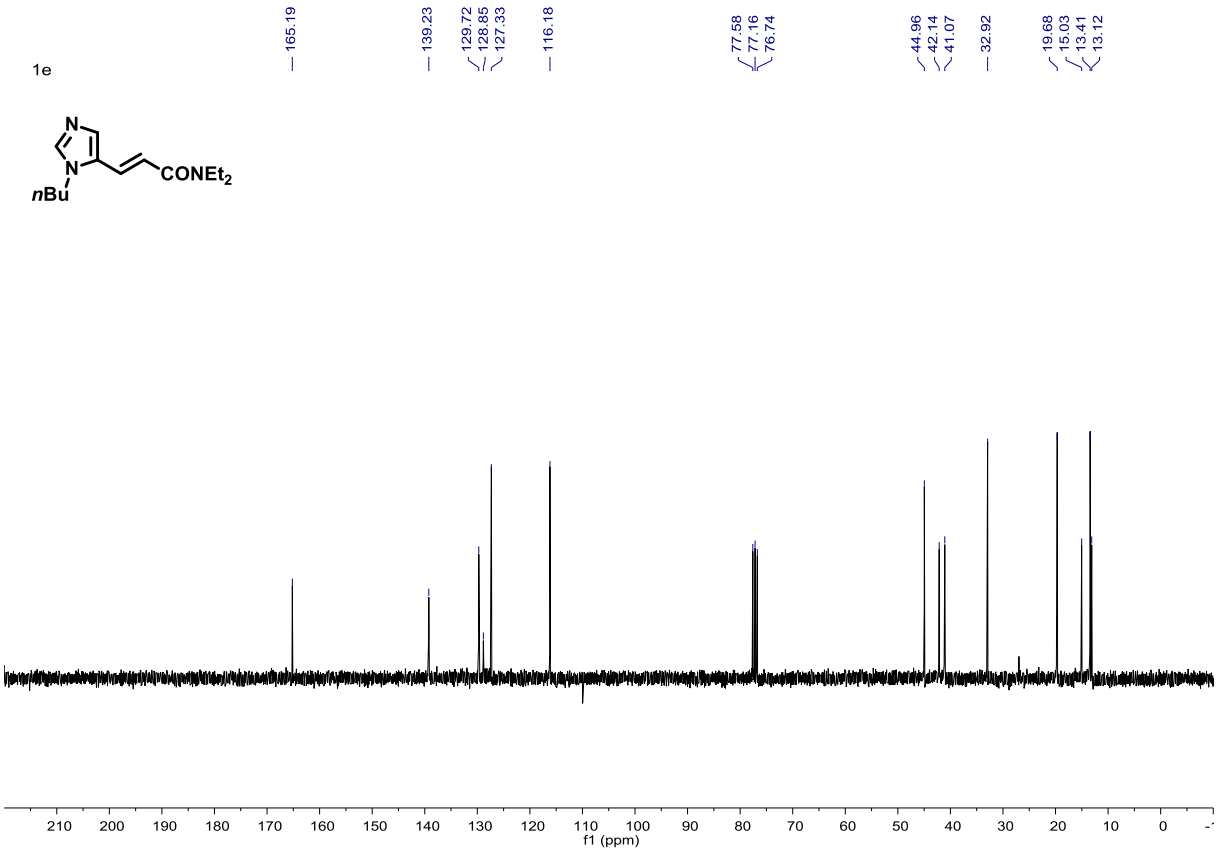
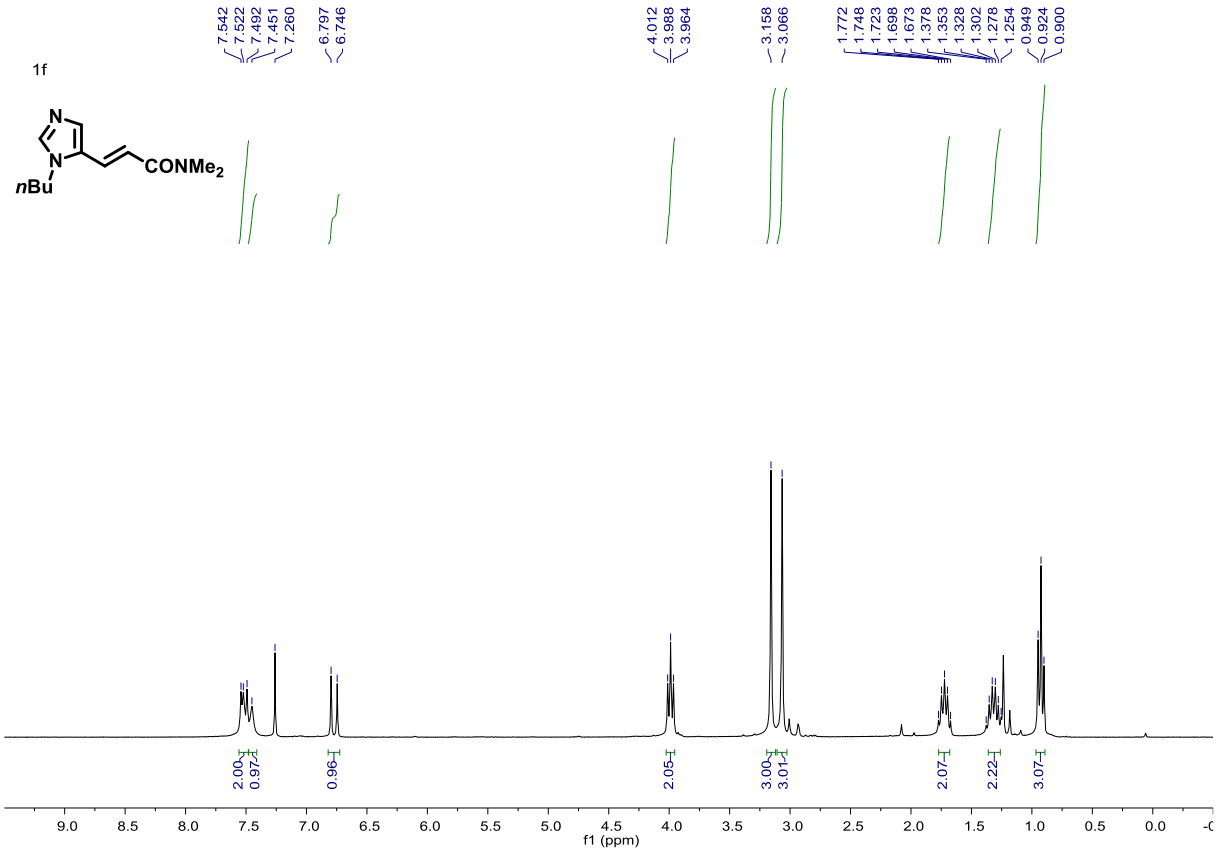
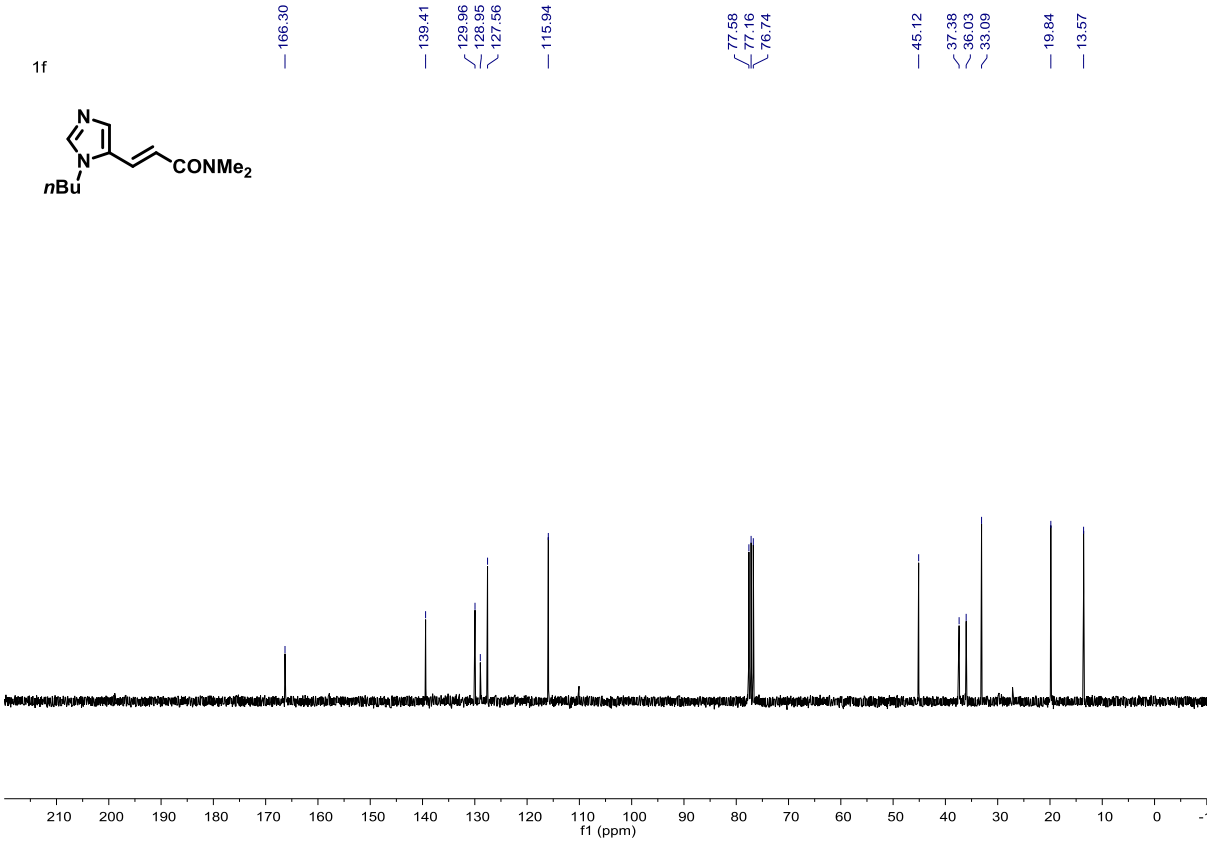
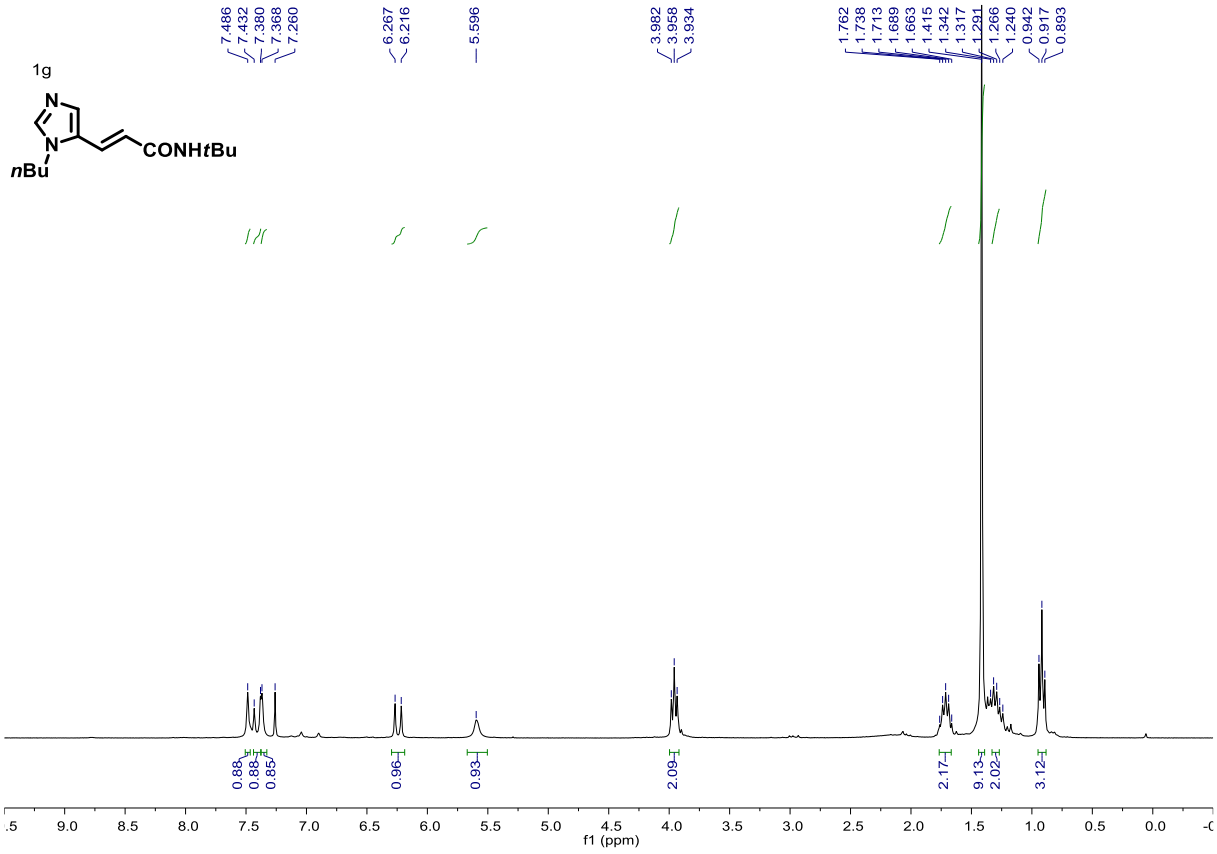
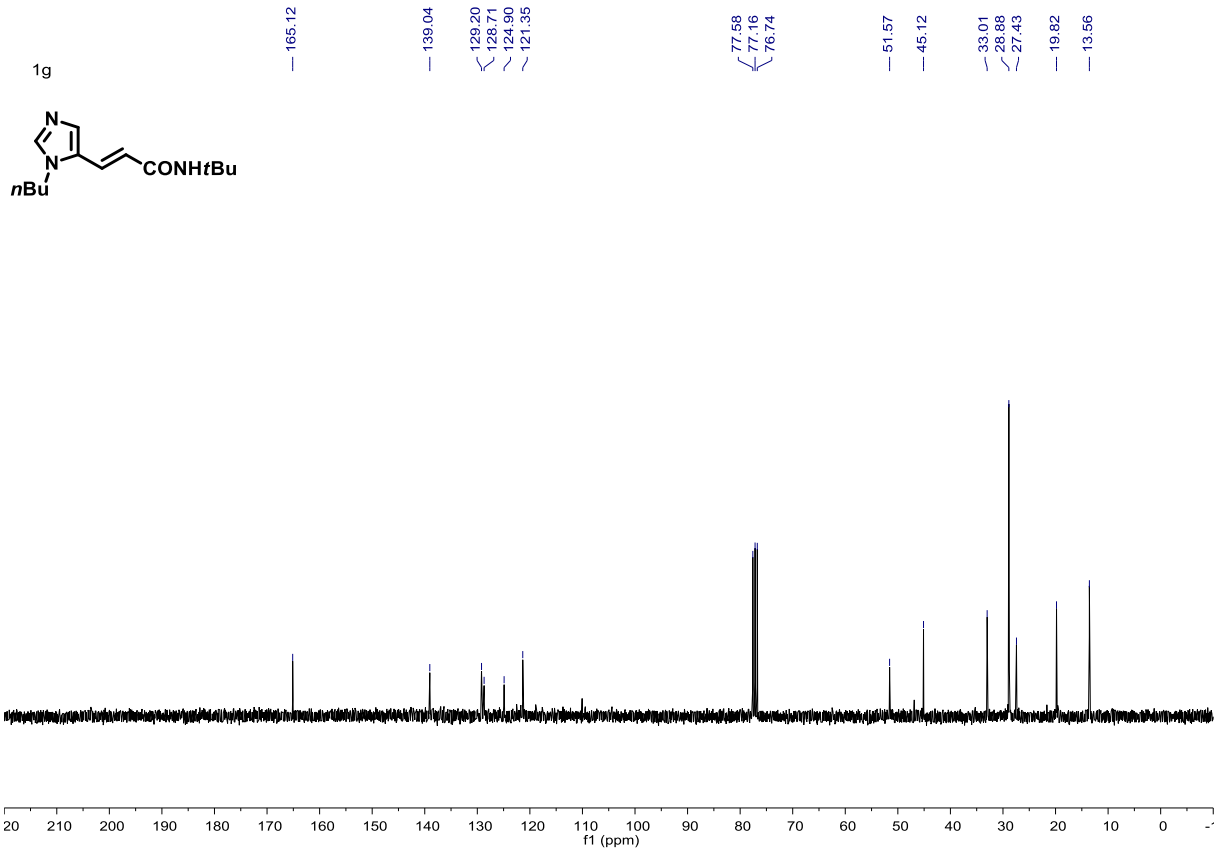
0.98
1.00
1.00
2.15
4.02
2.21
2.36
3.11
3.27
3.18
f1 (ppm)

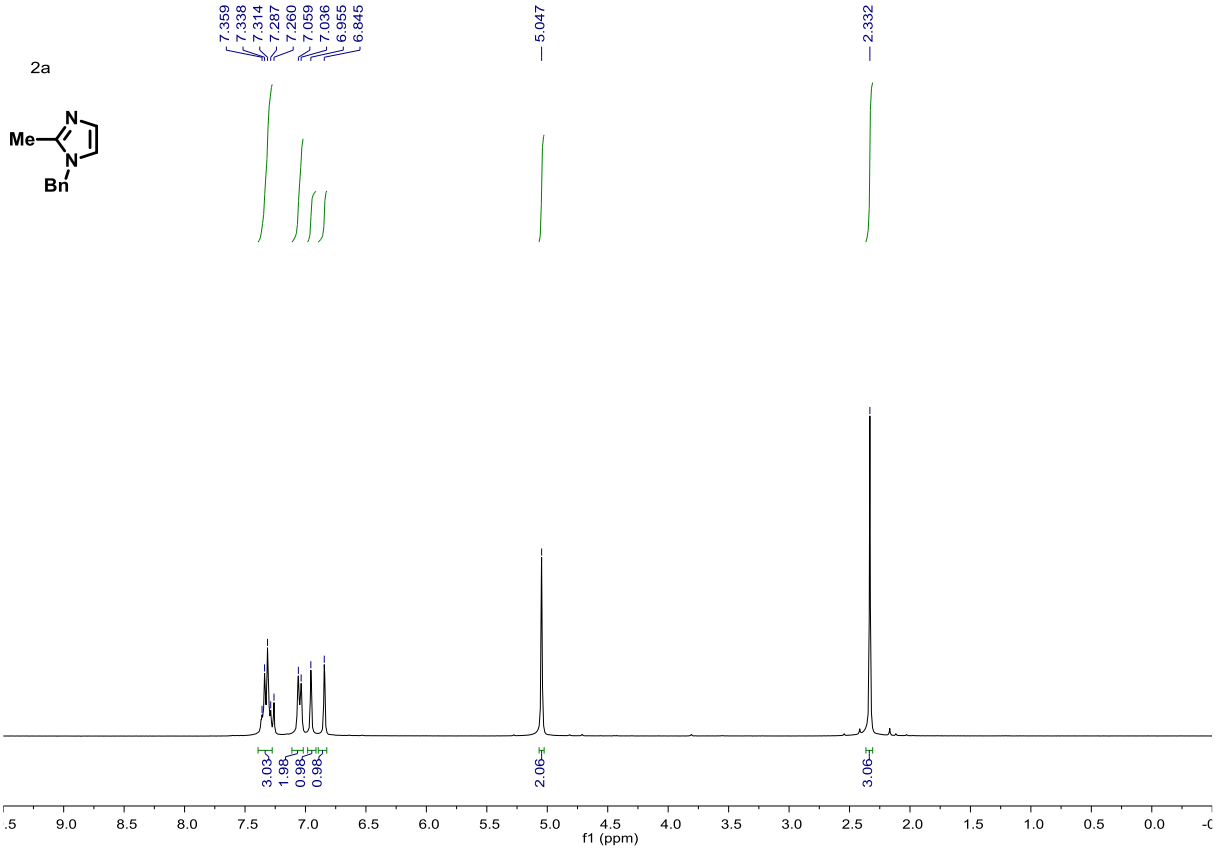

1e
165.19
139.23
129.72
128.85
127.33
116.18
77.58
77.16
76.74
44.96
42.14
41.07
32.92
19.68
15.03
13.41
13.12
CONEt2
nBu
f1 (ppm)

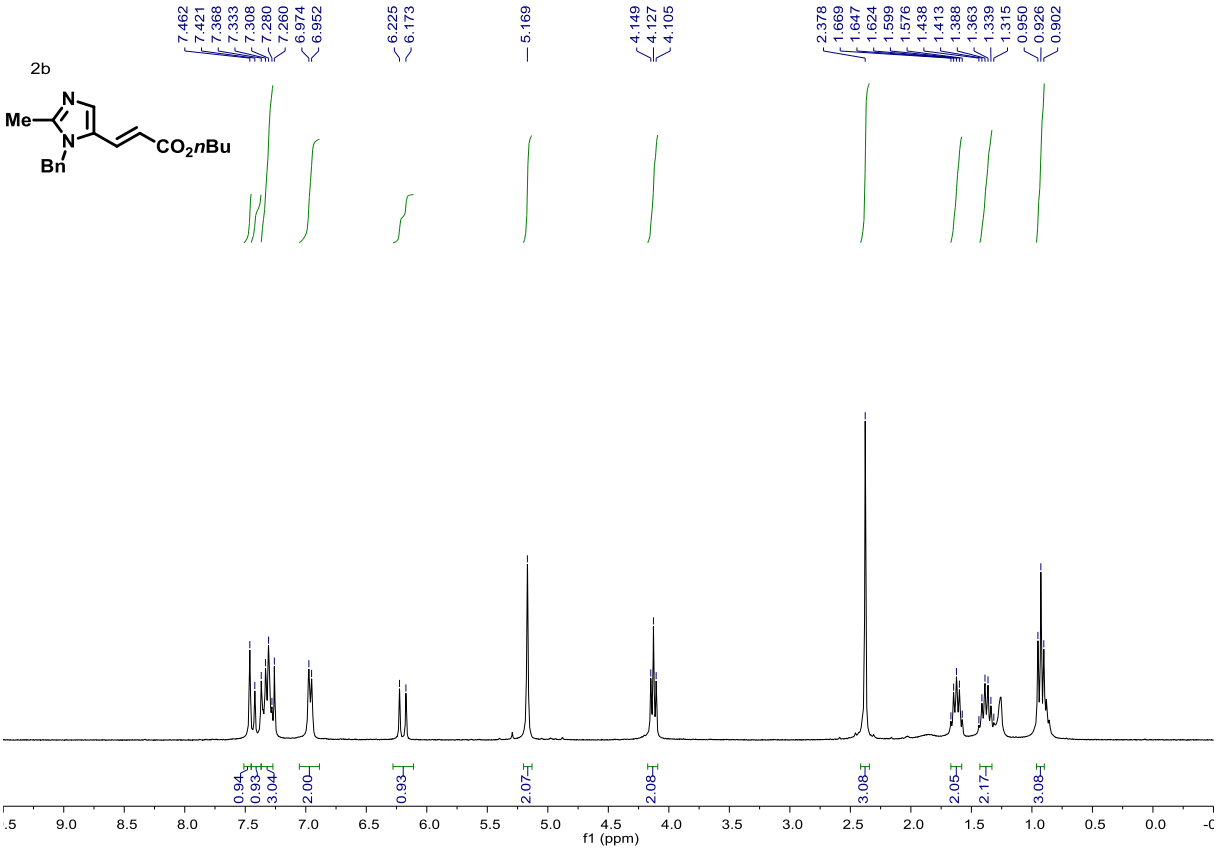

1f
7.542
7.522
7.492
7.451
7.260
6.797
6.746
4.012
3.988
3.964
3.158
3.066
1.772
1.748
1.723
1.698
1.673
1.378
1.353
1.328
1.302
1.278
1.254
0.949
0.924
0.900
CONMe2
nBu
2.00
0.97
0.96
2.05
3.00
3.01
2.07
2.22
3.07
f1 (ppm)


1f
166.30
139.41
129.96
128.95
127.56
115.94
77.58
77.16
76.74
45.12
37.38
36.03
33.09
19.84
13.57
CONMe2
nBu
f1 (ppm)

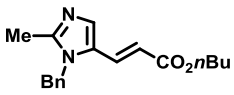

1g
CONHtBu
nBu
7.486
7.432
7.380
7.368
7.260
6.267
6.216
5.596
3.982
3.958
3.934
1.762
1.738
1.713
1.689
1.663
1.415
1.342
1.317
1.291
1.266
1.240
0.942
0.917
0.893
0.88
0.88
0.85
0.96
0.93
2.09
2.17
9.13
2.02
3.12
f1 (ppm)


1g
CONHtBu
nBu
165.12
139.04
129.20
128.71
124.90
121.35
77.58
77.16
76.74
51.57
45.12
33.01
28.88
27.43
19.82
13.56
f1 (ppm)

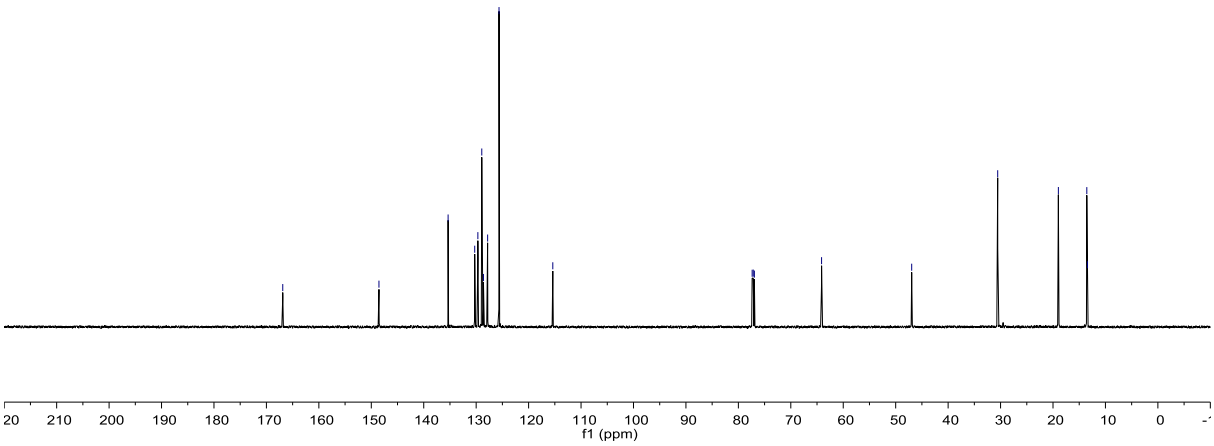

2a
Me
N
N
Bn
7.359
7.338
7.314
7.287
7.260
7.059
7.036
6.955
6.845
5.047
2.332
3.03
1.98
0.98
0.98
2.06
3.06
f1 (ppm)


2b
Me
N
N
Bn
CO2nBu
7.462
7.421
7.368
7.333
7.308
7.280
7.260
6.974
6.952
6.225
6.173
5.169
4.149
4.127
4.105
2.378
1.669
1.647
1.624
1.599
1.576
1.438
1.413
1.388
1.363
1.339
1.315
0.950
0.926
0.902
0.94
0.93
3.04
2.00
0.93
2.07
2.08
3.08
2.05
2.17
3.08
f1 (ppm)

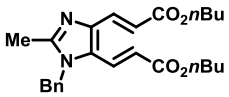
2b



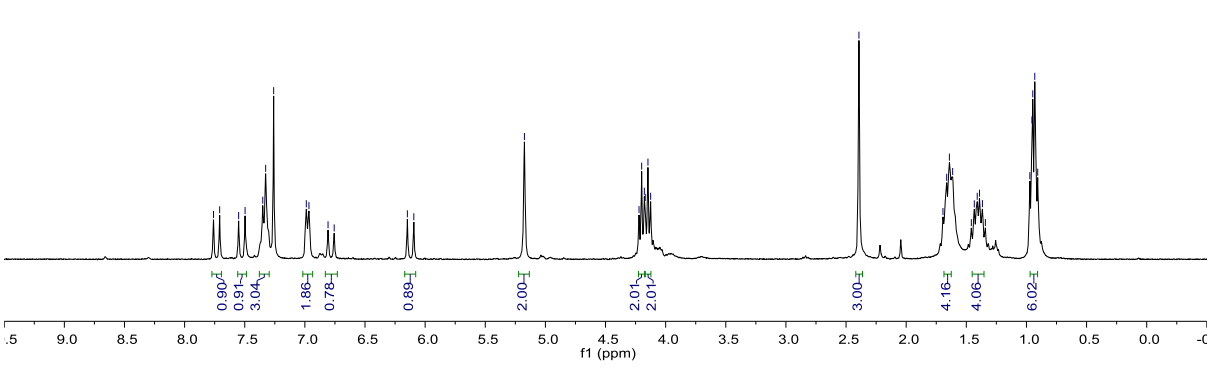
166.88
148.54
135.35
130.28
129.68
128.93
128.61
127.82
125.64
115.39
77.37
77.16
76.95
64.13
46.95
30.54
18.98
13.55
13.42

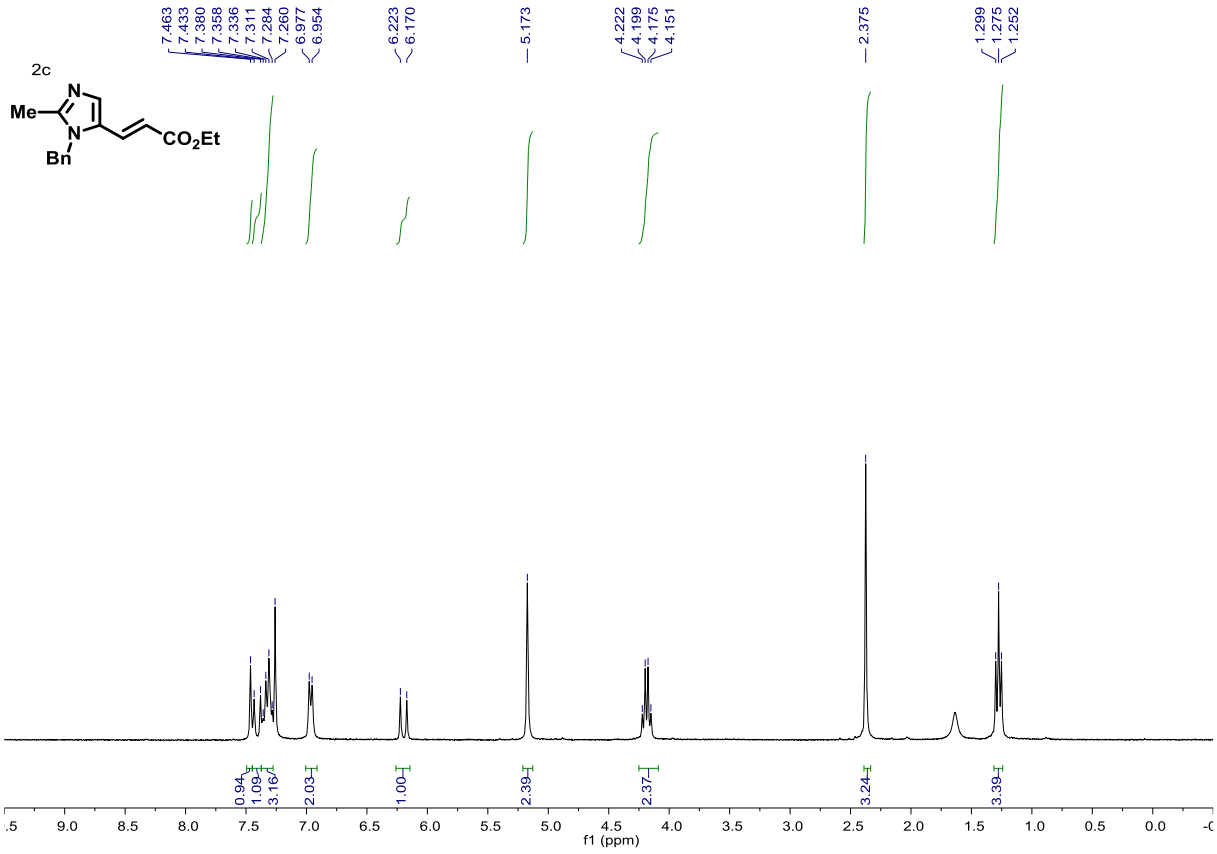


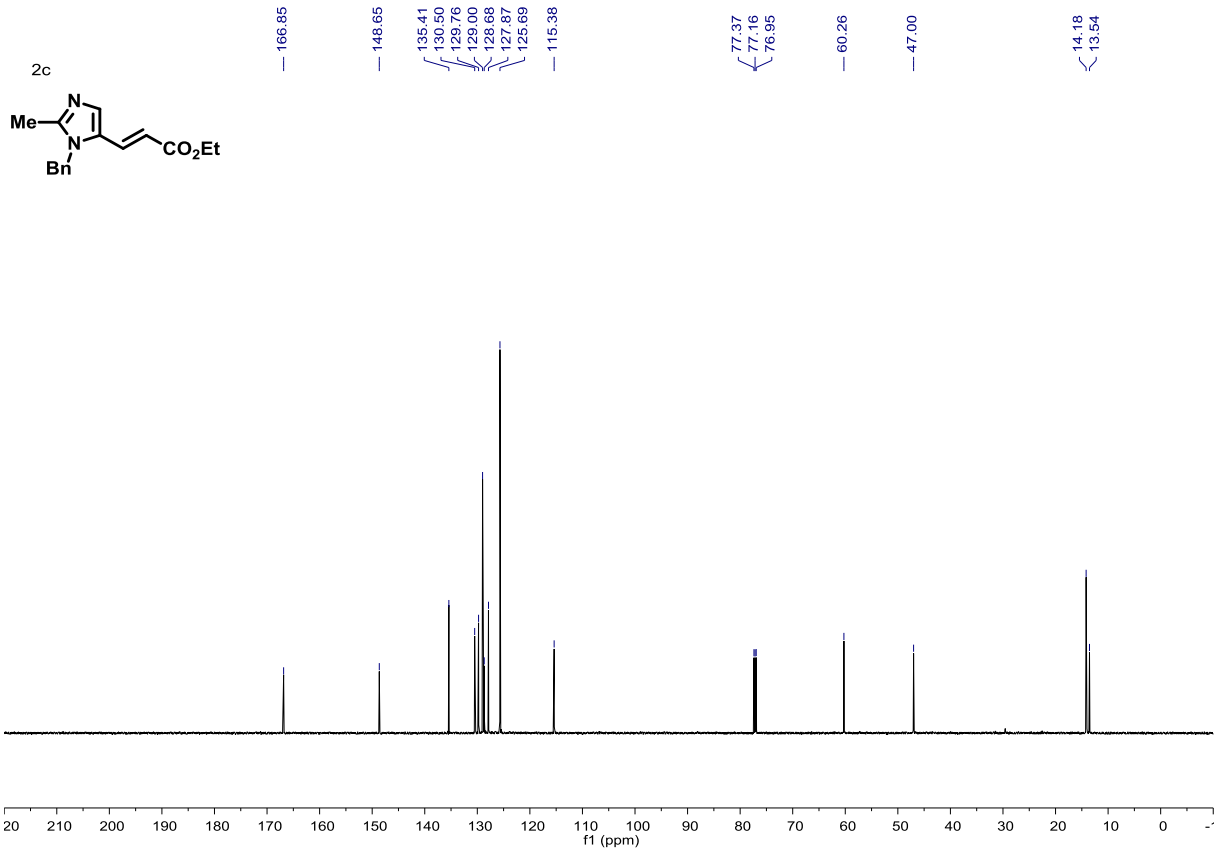
2b-di

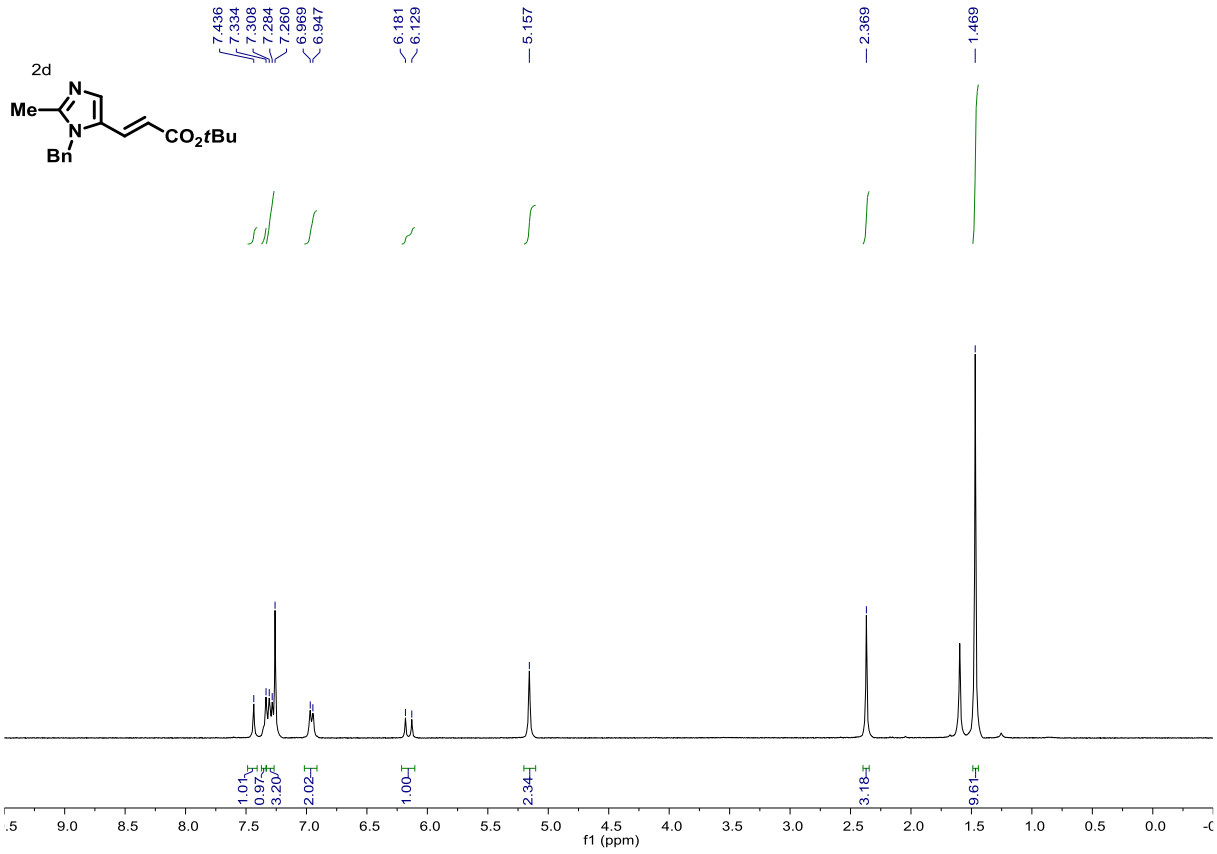


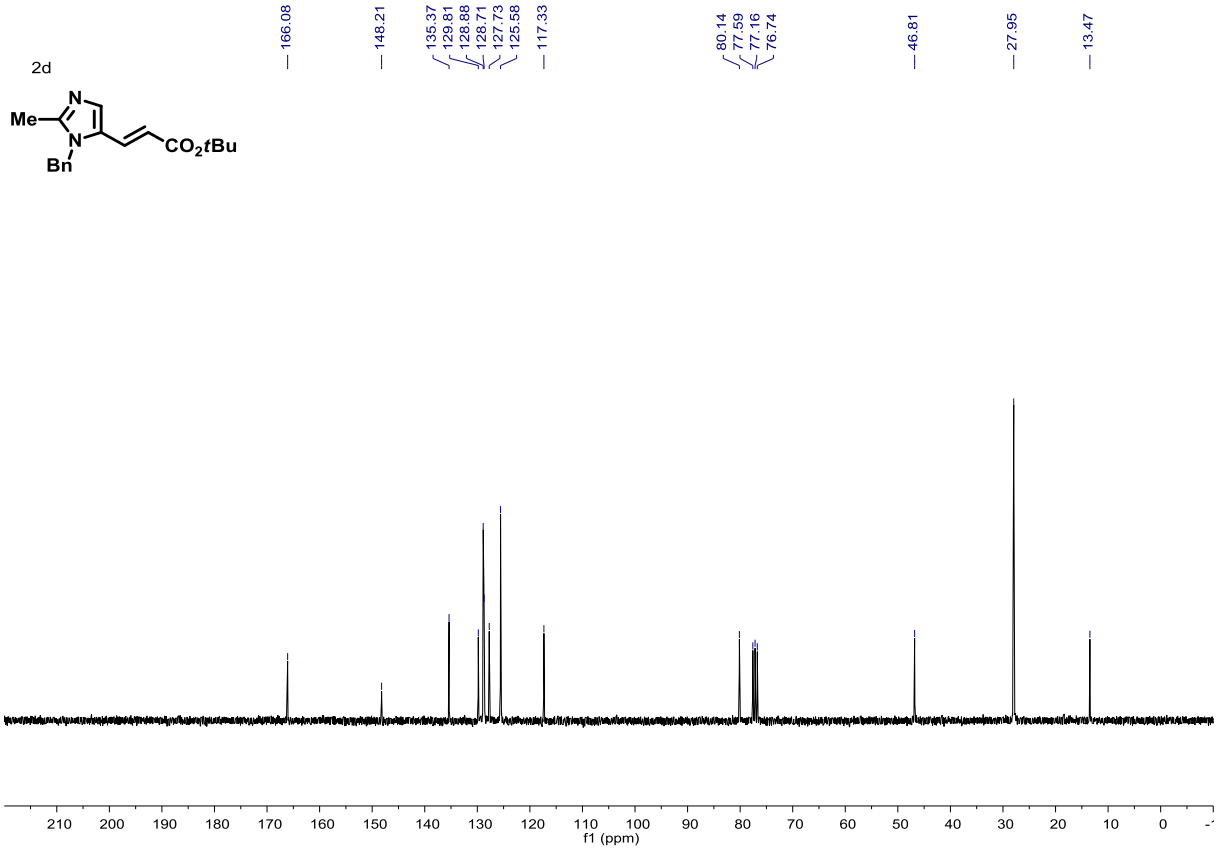
7.760
7.708
7.551
7.497
7.350
7.326
7.260
6.988
6.966
6.807
6.756
6.148
6.094
5.174
4.221
4.200
4.177
4.170
4.147
4.125
2.393
1.694
1.663
1.641
1.614
1.458
1.434
1.409
1.391
1.366
1.342
0.972
0.955
0.948
0.931
0.906

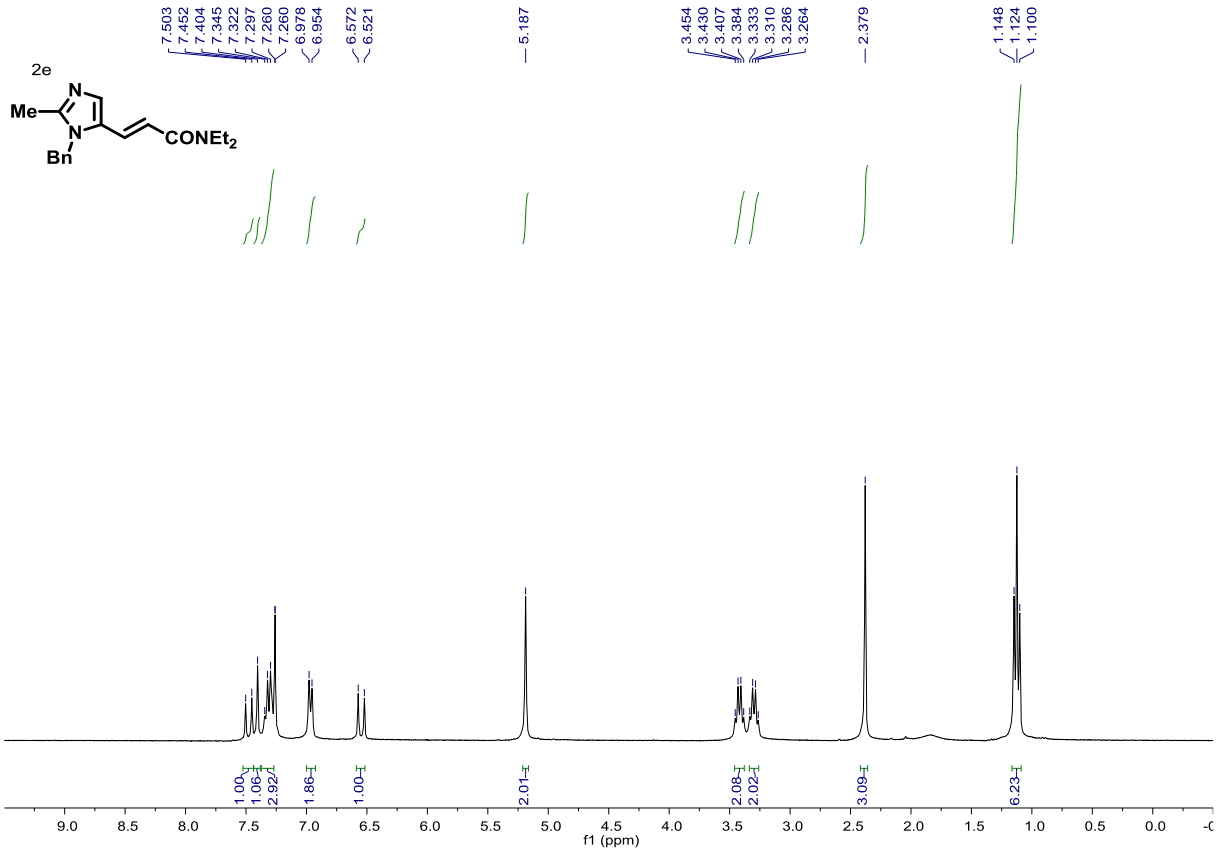


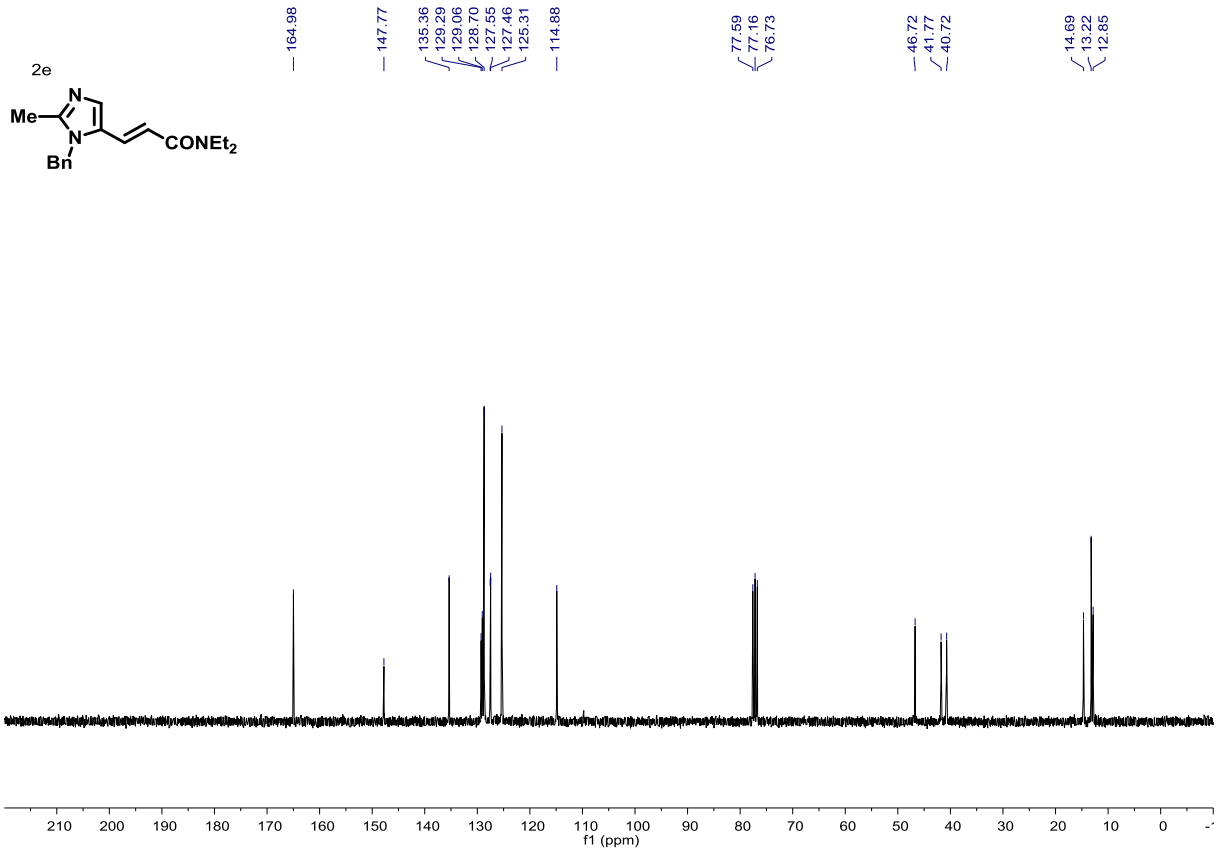

7.463
7.433
7.380
7.358
7.336
7.311
7.284
7.260
6.977
6.954
6.223
6.170
5.173
4.222
4.199
4.175
4.151
2.375
1.299
1.275
1.252
2c
Me
N
N
Bn
CO2Et
0.94
1.09
3.16
2.03
1.00
2.39
2.37
3.24
3.39
f1 (ppm)

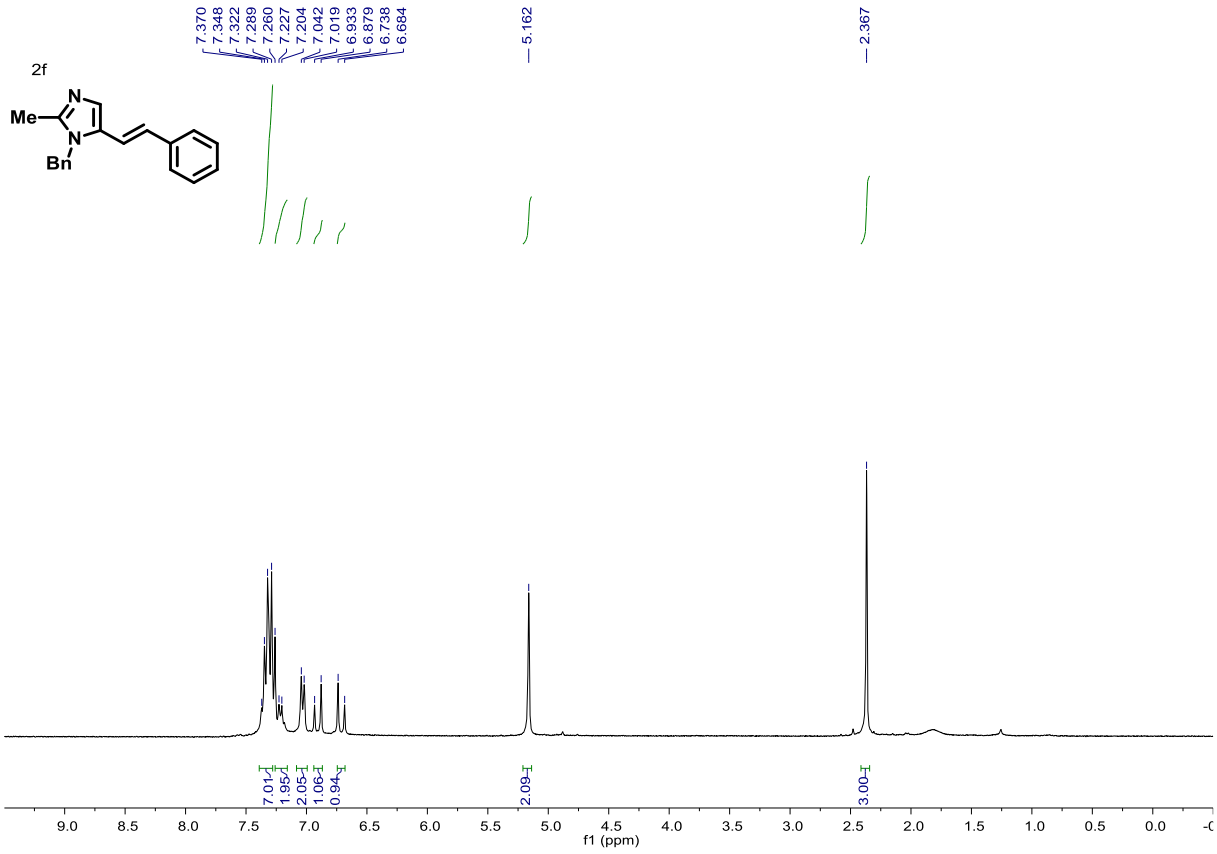

166.85
148.65
135.41
130.50
129.76
129.00
128.68
127.87
125.69
115.38
77.37
77.16
76.95
60.26
47.00
14.18
13.54
2c
Me
N
N
Bn
CO2Et
f1 (ppm)

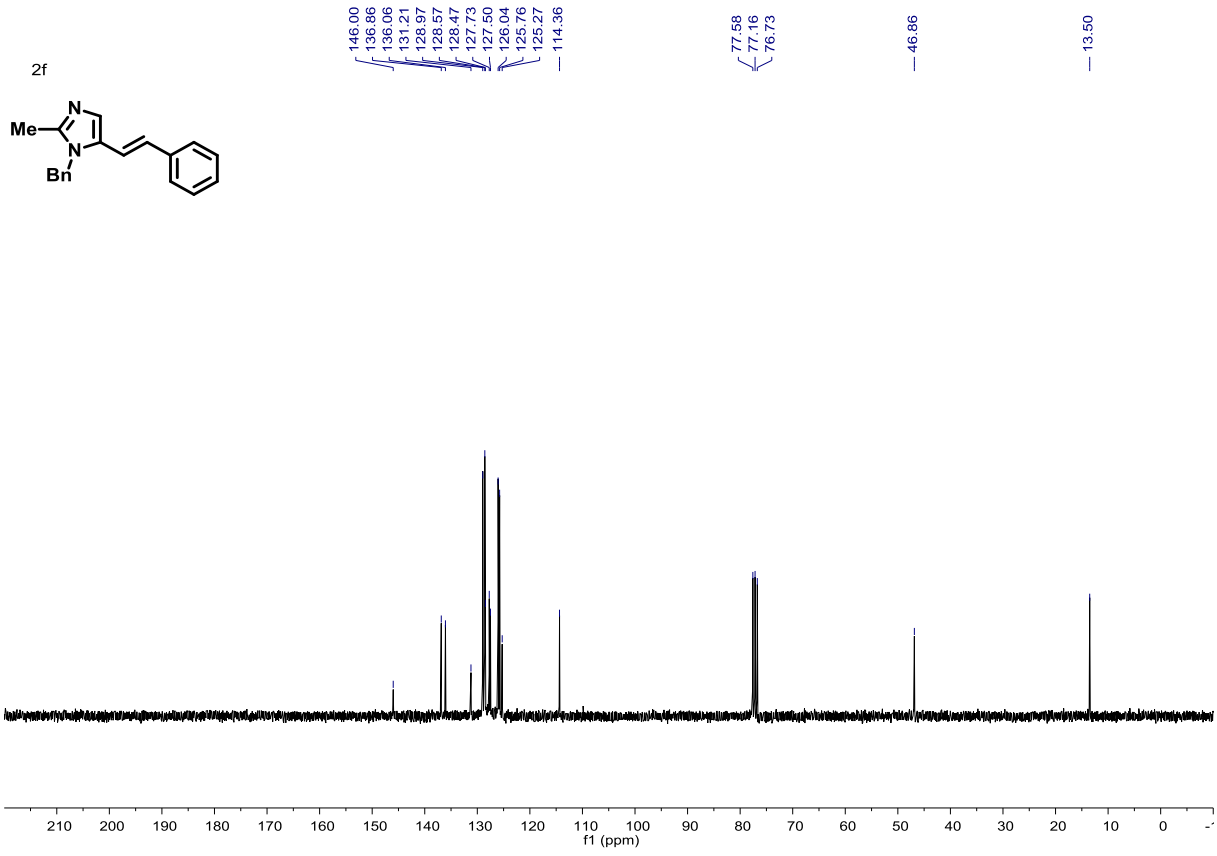

2d
Me
N
N
Bn
CO2tBu
7.436
7.334
7.308
7.284
7.260
6.969
6.947
6.181
6.129
5.157
2.369
1.469
1.01
0.97
3.20
2.02
1.00
2.34
3.18
9.61
f1 (ppm)

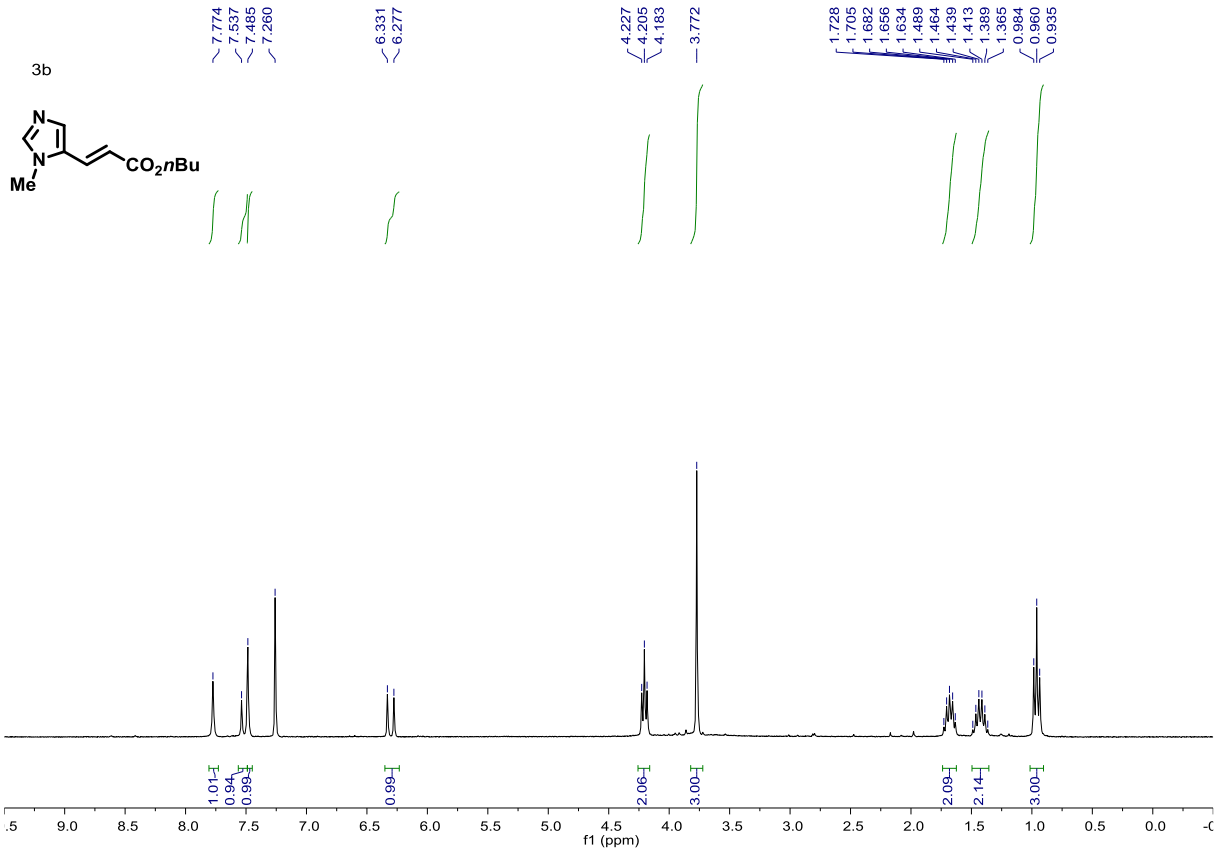

2d
Me
N
N
Bn
CO2tBu
166.08
148.21
135.37
129.81
128.88
128.71
127.73
125.58
117.33
80.14
77.59
77.16
76.74
46.81
27.95
13.47
f1 (ppm)

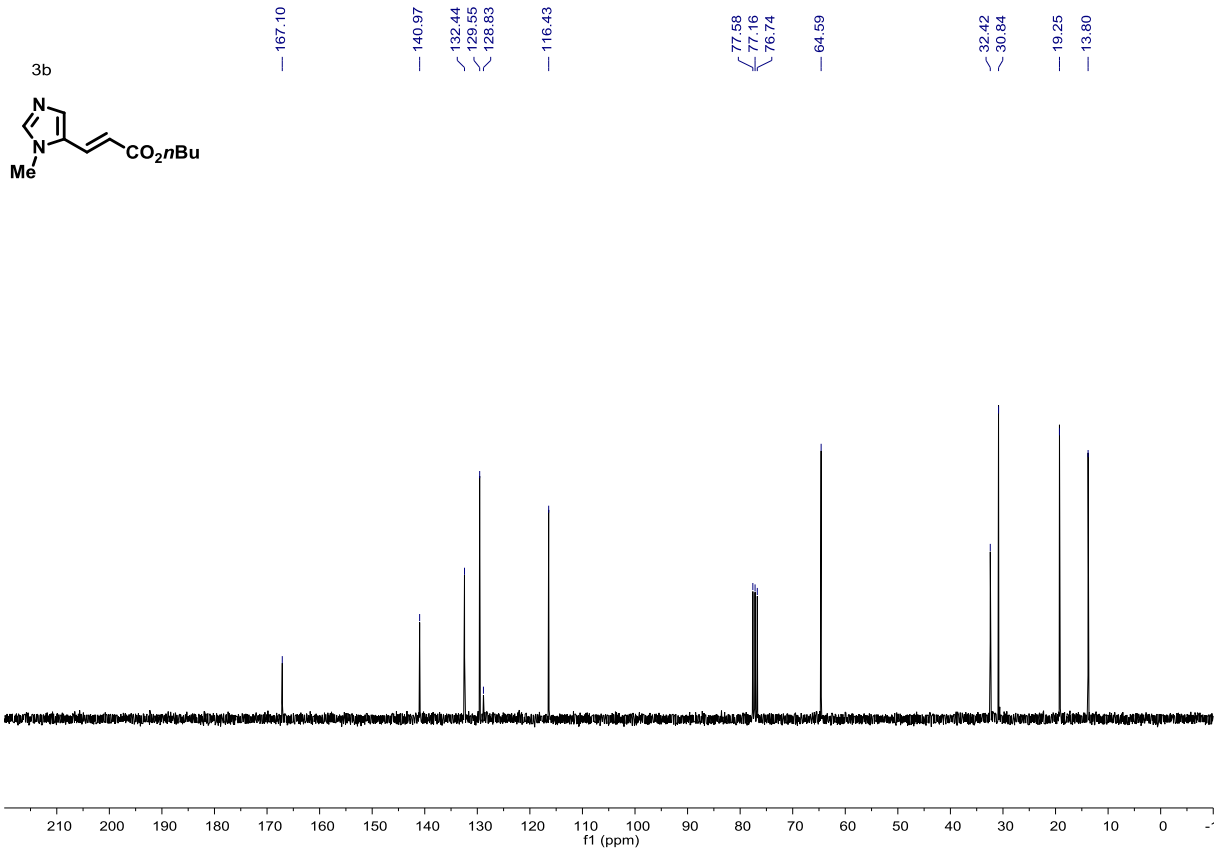

2e
Me
N
N
Bn
CONEt2
7.503
7.452
7.404
7.345
7.322
7.297
7.260
7.260
6.978
6.954
6.572
6.521
5.187
3.454
3.430
3.407
3.384
3.333
3.310
3.286
3.264
2.379
1.148
1.124
1.100
1.00
1.06
2.92
1.86
1.00
2.01
2.08
2.02
3.09
6.23
f1 (ppm)

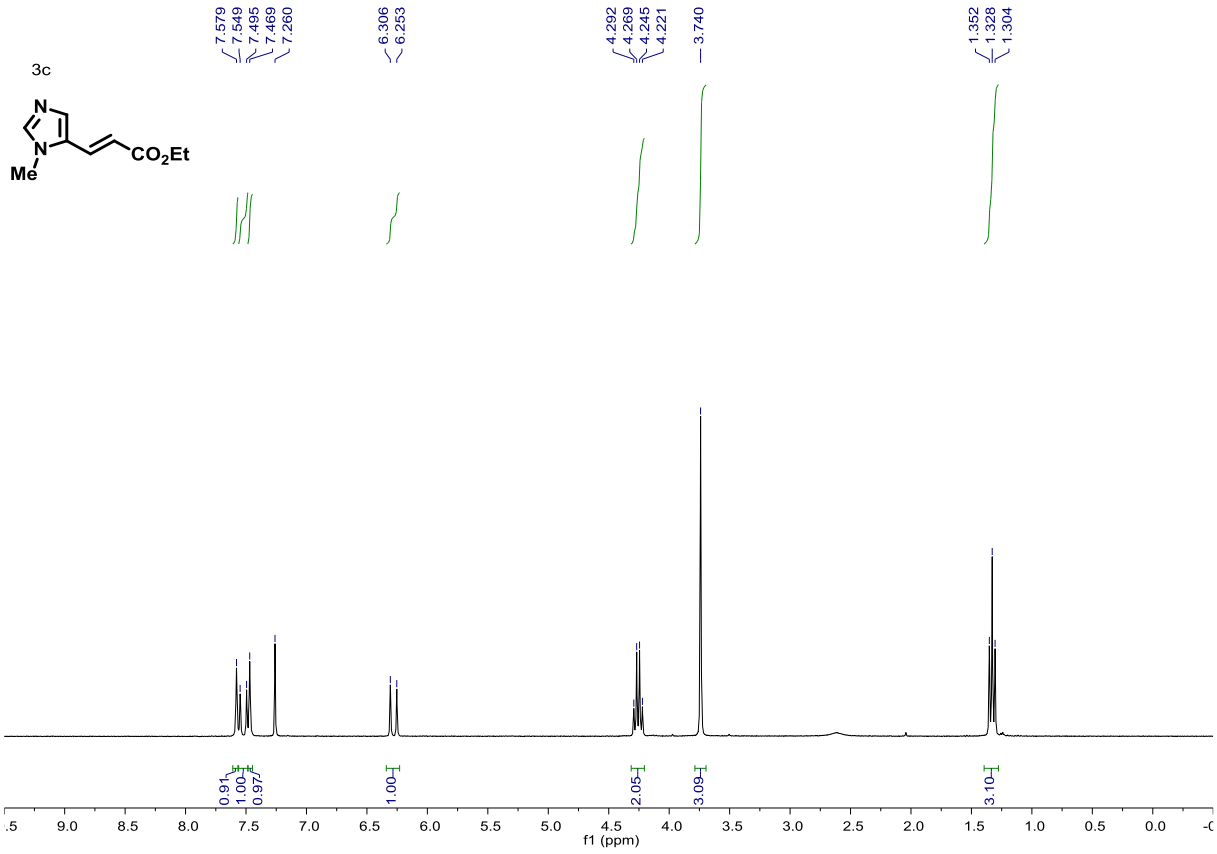

2e
Me
N
N
Bn
CONEt2
164.98
147.77
135.36
129.29
129.06
128.70
127.55
127.46
125.31
114.88
77.59
77.16
76.73
46.72
41.77
40.72
14.69
13.22
12.85
f1 (ppm)

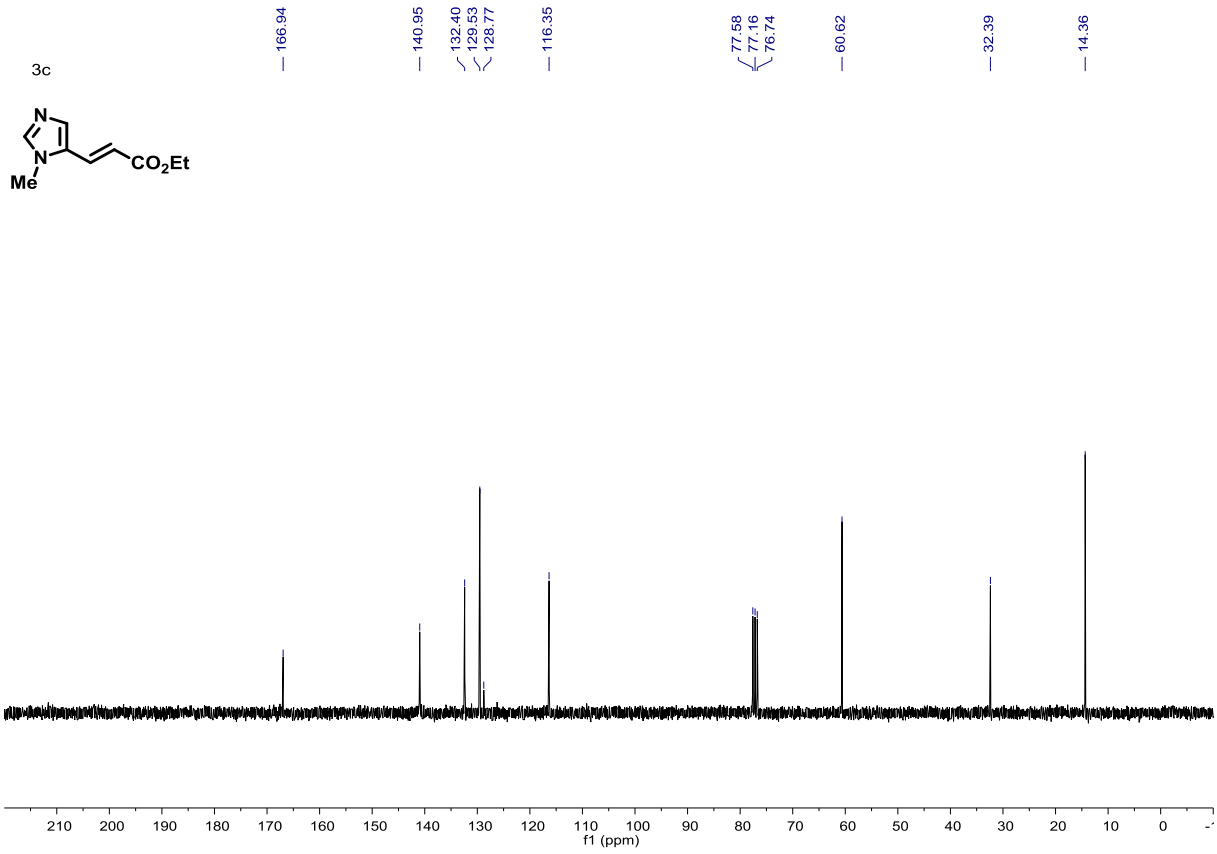

2f
Me
N
N
Bn
7.370
7.348
7.322
7.289
7.260
7.227
7.204
7.042
7.019
6.933
6.879
6.738
6.684
5.162
2.367
7.01
1.95
2.05
1.06
0.94
2.09
3.00
f1 (ppm)

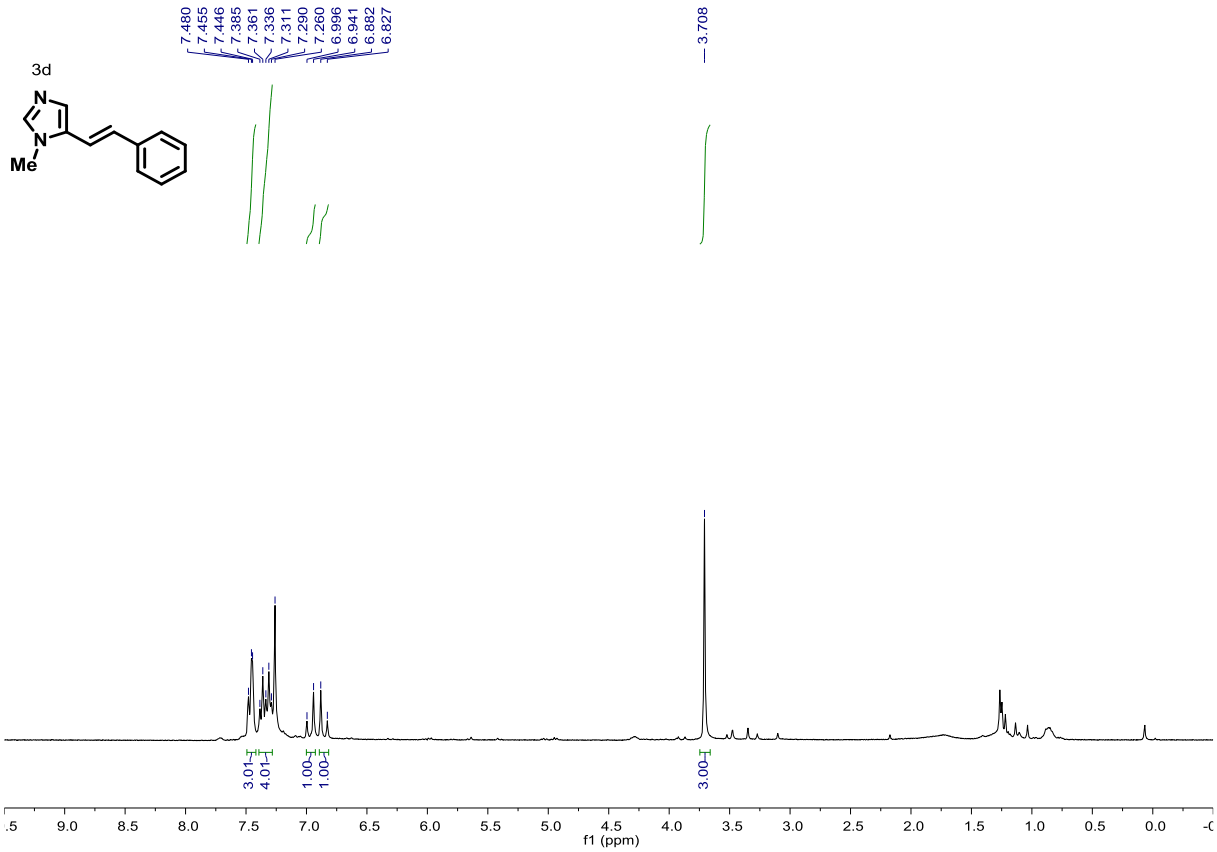

2f
Me
N
N
Bn
146.00
136.86
136.06
131.21
128.97
128.57
128.47
127.73
127.50
126.04
125.76
125.27
114.36
77.58
77.16
76.73
46.86
13.50
f1 (ppm)

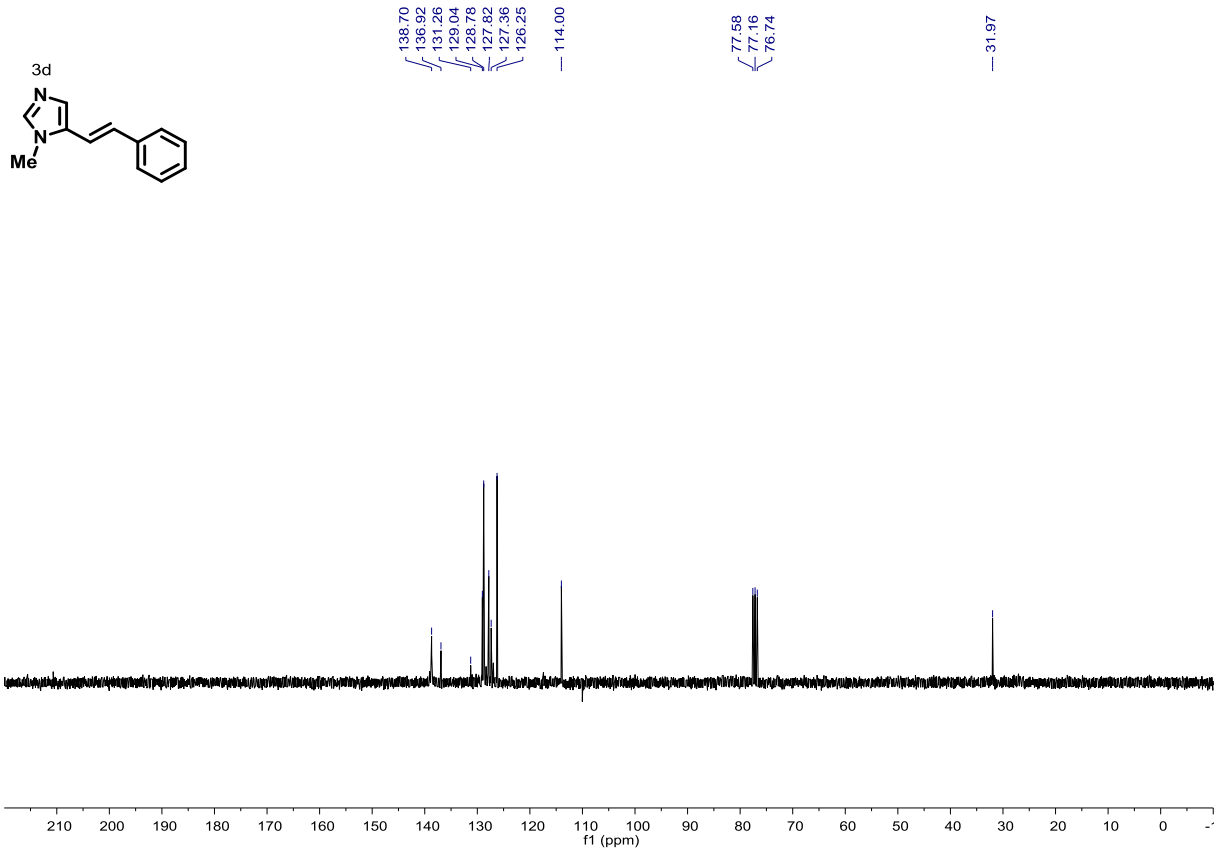

3b
7.774
7.537
7.485
7.260
6.331
6.277
4.227
4.205
4.183
3.772
1.728
1.705
1.682
1.656
1.634
1.489
1.464
1.439
1.413
1.389
1.365
0.984
0.960
0.935
1.01
0.94
0.99
0.99
2.06
3.00
2.09
2.14
3.00
f1 (ppm)

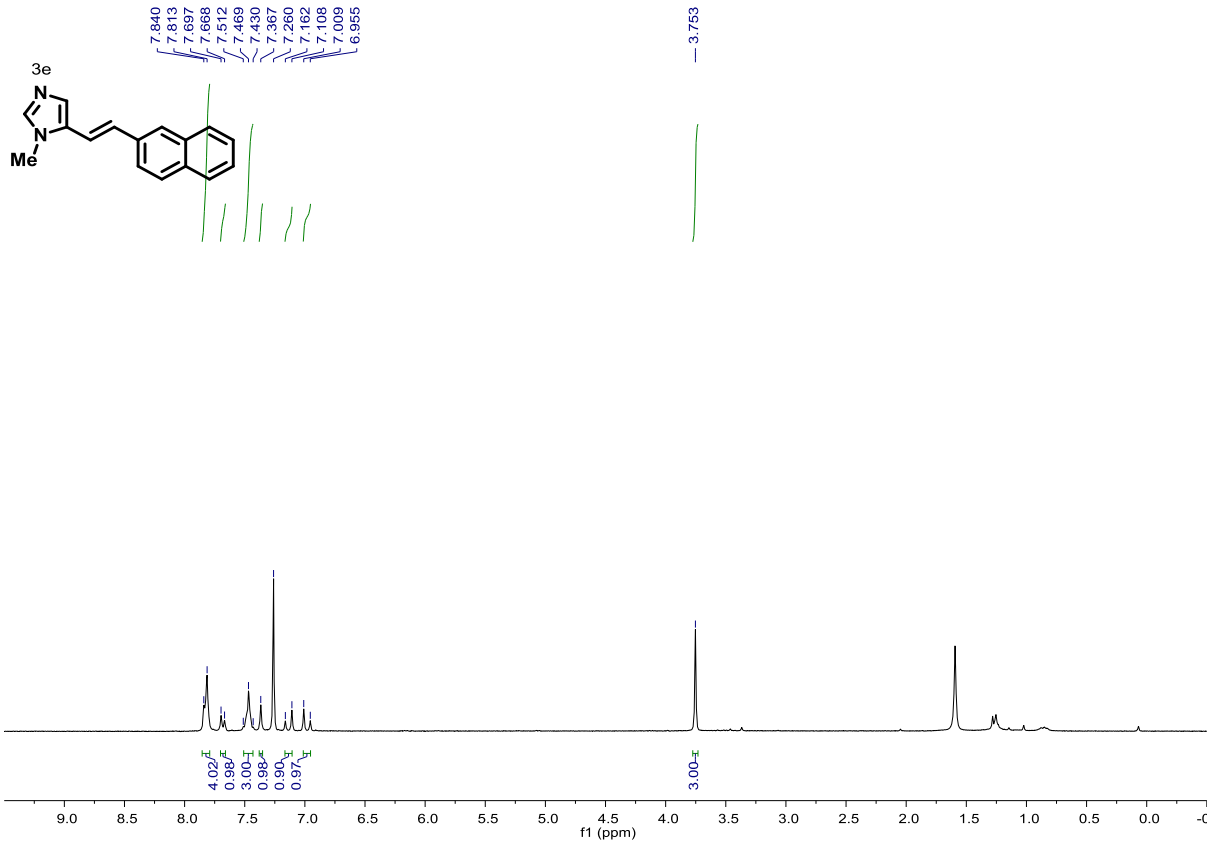

3b
167.10
140.97
132.44
129.55
128.83
116.43
77.58
77.16
76.74
64.59
32.42
30.84
19.25
13.80
f1 (ppm)


3c
7.579
7.549
7.495
7.469
7.260
6.306
6.253
4.292
4.269
4.245
4.221
3.740
1.352
1.328
1.304
0.91
1.00
0.97
1.00
2.05
3.09
3.10
f1 (ppm)


3c
166.94
140.95
132.40
129.53
128.77
116.35
77.58
77.16
76.74
60.62
32.39
14.36
f1 (ppm)


7.480
7.455
7.446
7.385
7.361
7.336
7.311
7.290
7.260
6.996
6.941
6.882
6.827
3.708
3d
N
N
Me
3.01
4.01
1.00
1.00
3.00
f1 (ppm)


138.70
136.92
131.26
129.04
128.78
127.82
127.36
126.25
114.00
77.58
77.16
76.74
31.97
3d
N
N
Me
f1 (ppm)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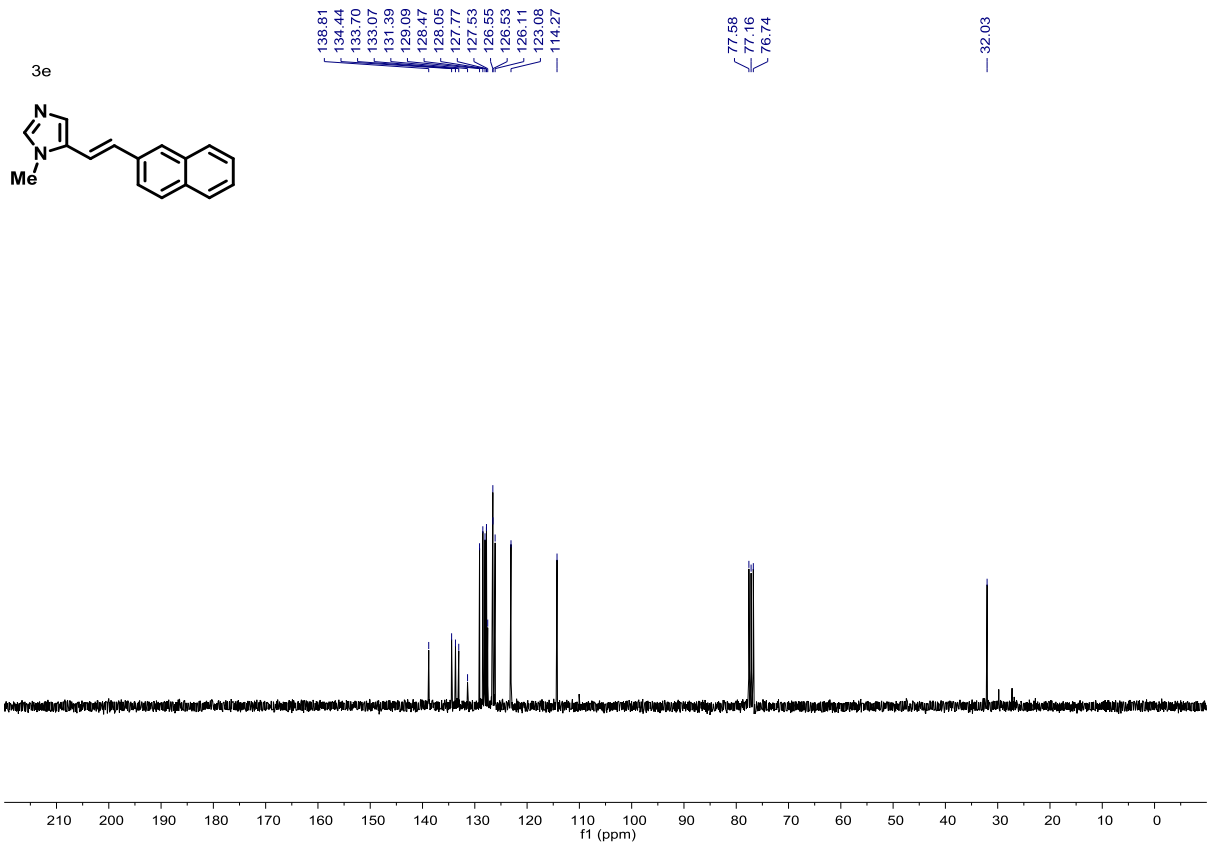
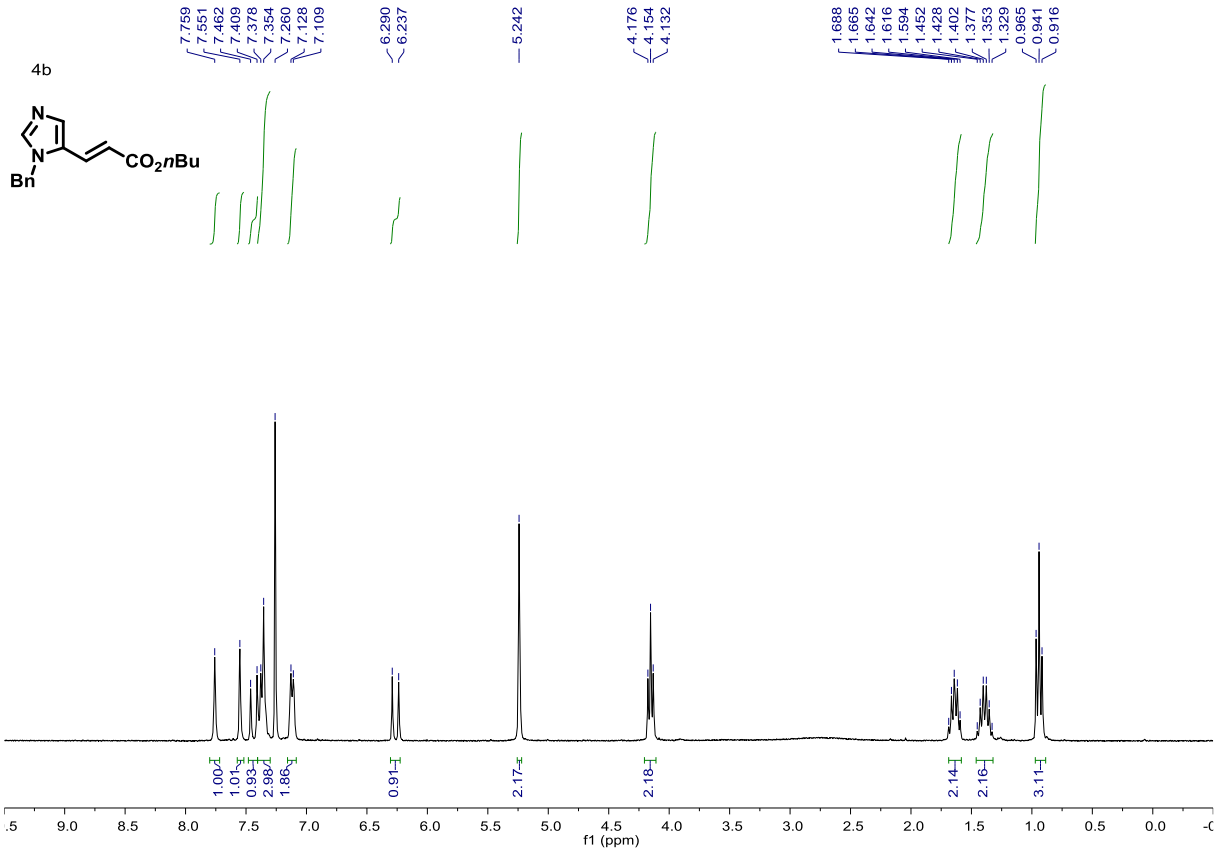
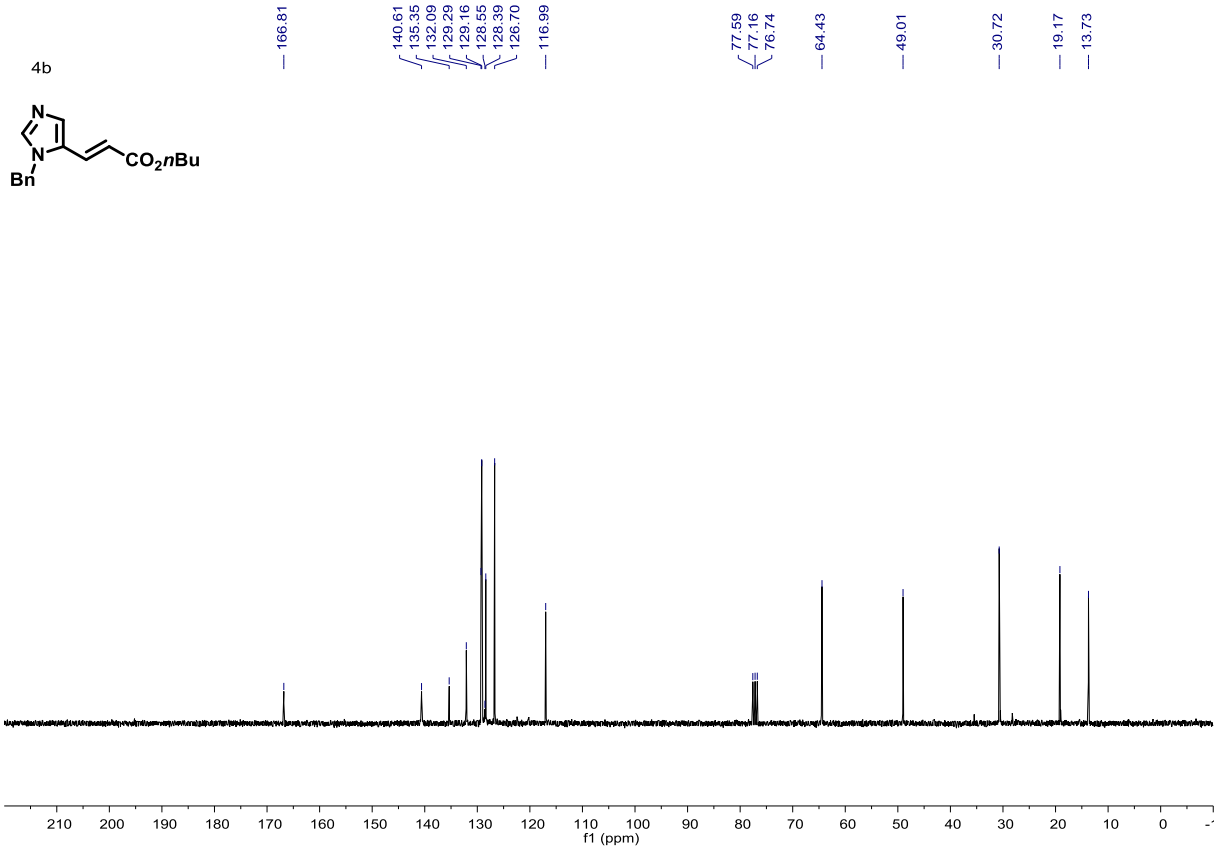
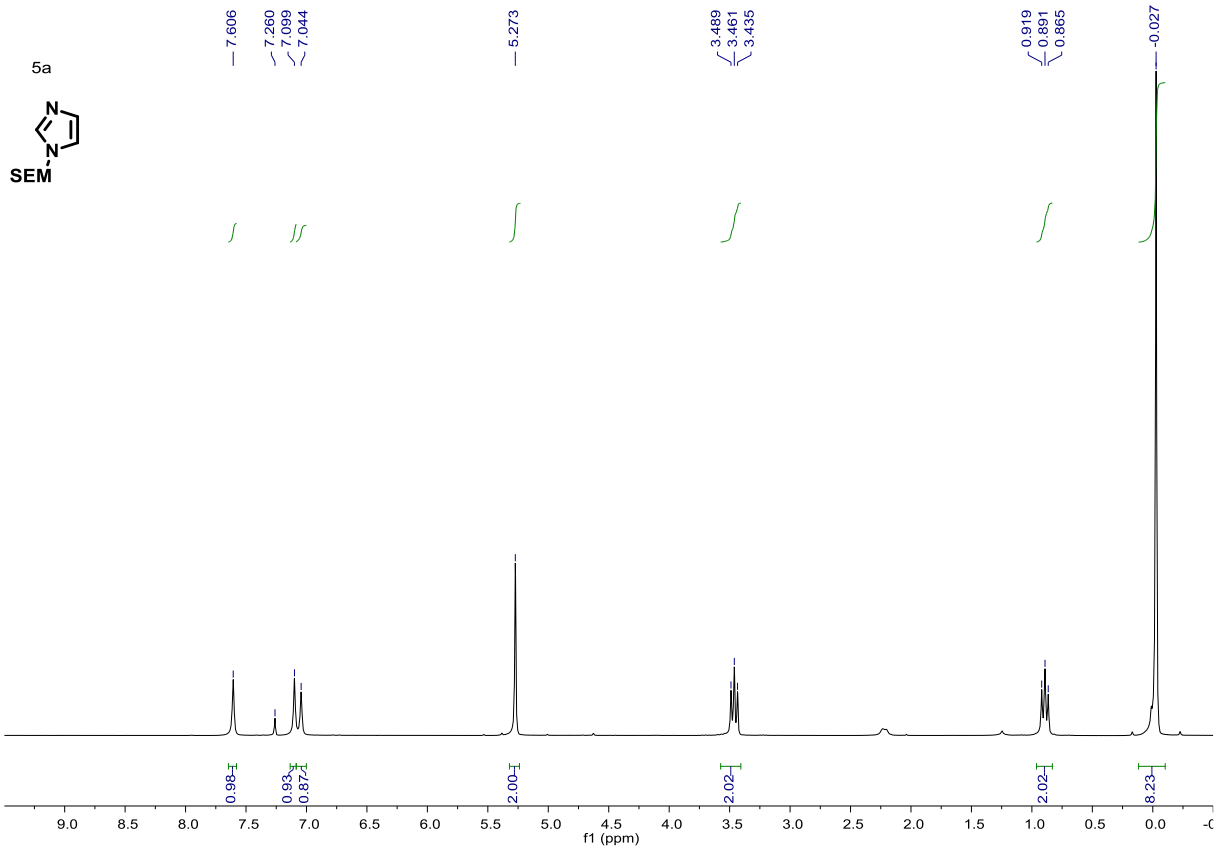
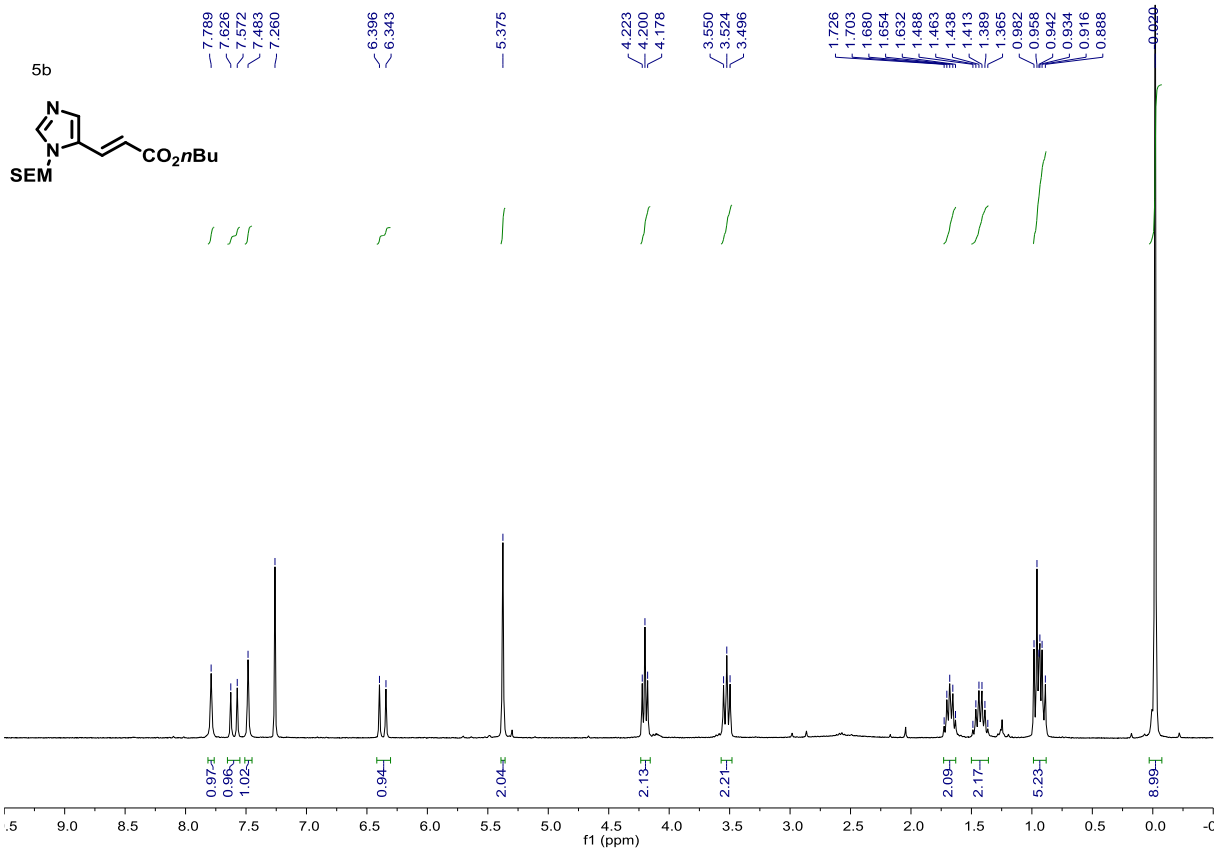
7.813
7.697
7.668
7.512
7.469
7.430
7.367
7.260
7.162
7.108
7.009
6.955
3.753
3e
N
N
Me
4.02
0.98
3.00
0.98
0.90
0.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.81
134.44
133.70
133.07
131.39
129.09
128.47
128.05
127.77
127.53
126.55
126.53
126.11
123.08
114.27
77.58
77.16
76.74
32.03
3e
N
N
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

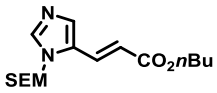

4b
Bn
CO2nBu
7.759
7.551
7.462
7.409
7.378
7.354
7.260
7.128
7.109
6.290
6.237
5.242
4.176
4.154
4.132
1.688
1.665
1.642
1.616
1.594
1.452
1.428
1.402
1.377
1.353
1.329
0.965
0.941
0.916
1.00
1.01
0.93
2.98
1.86
0.91
2.17
2.18
2.14
2.16
3.11
f1 (ppm)


4b
Bn
CO2nBu
166.81
140.61
135.35
132.09
129.29
129.16
128.55
128.39
126.70
116.99
77.59
77.16
76.74
64.43
49.01
30.72
19.17
13.73
f1 (ppm)


5a
SEM
7.606
7.260
7.099
7.044
5.273
3.489
3.461
3.435
0.919
0.891
0.865
-0.027
0.98
0.93
0.87
2.00
2.02
2.02
8.23
f1 (ppm)


5b
SEM
CO2nBu
7.789
7.626
7.572
7.483
7.260
6.396
6.343
5.375
4.223
4.200
4.178
3.550
3.524
3.496
1.726
1.703
1.680
1.654
1.632
1.488
1.463
1.438
1.413
1.389
1.365
0.982
0.958
0.942
0.934
0.916
0.888
0.020
0.97
0.96
1.02
0.94
2.04
2.13
2.21
2.09
2.17
5.23
8.99
f1 (ppm)

5b

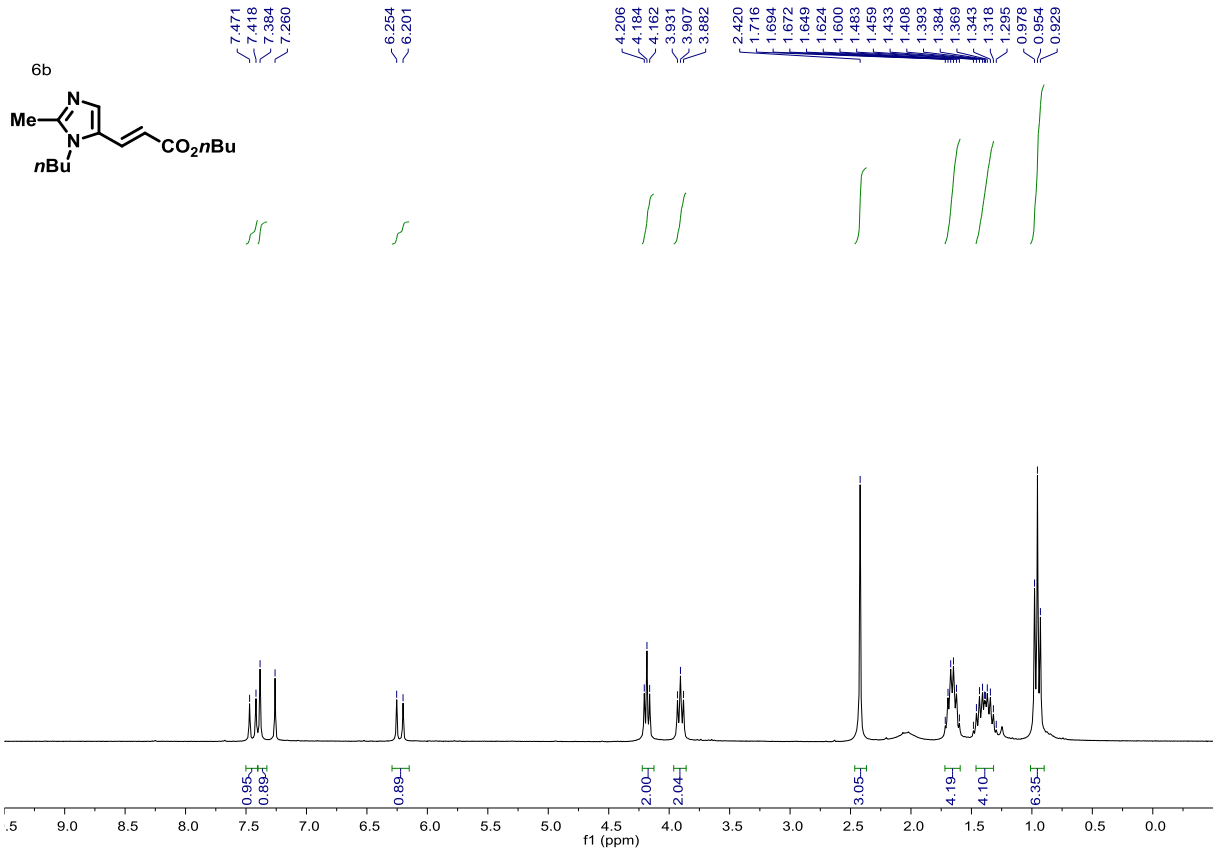

N
N
SEM
CO2nBu

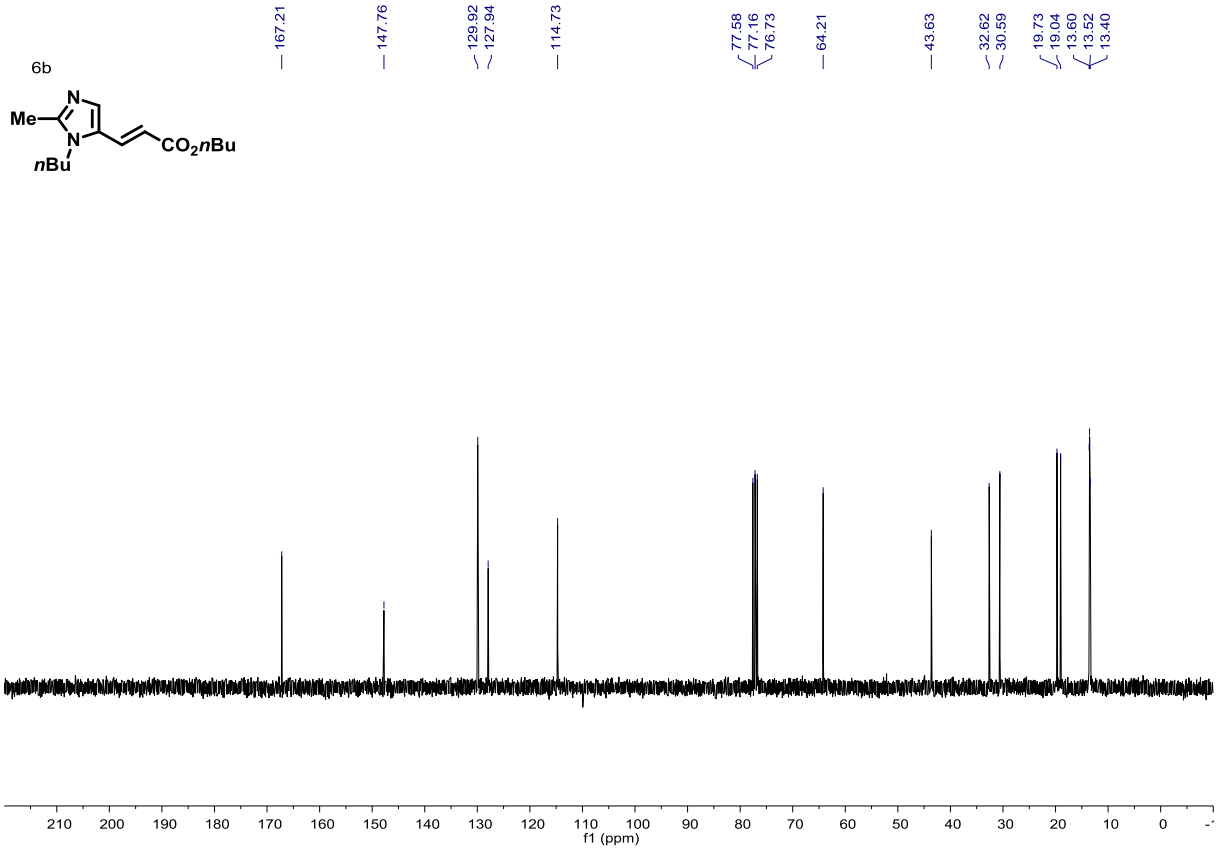
166.64
140.60
132.83
129.34
128.36
117.20
77.60
77.16
76.74
74.21
66.08
64.17
30.56
18.97
17.35
13.53
-1.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

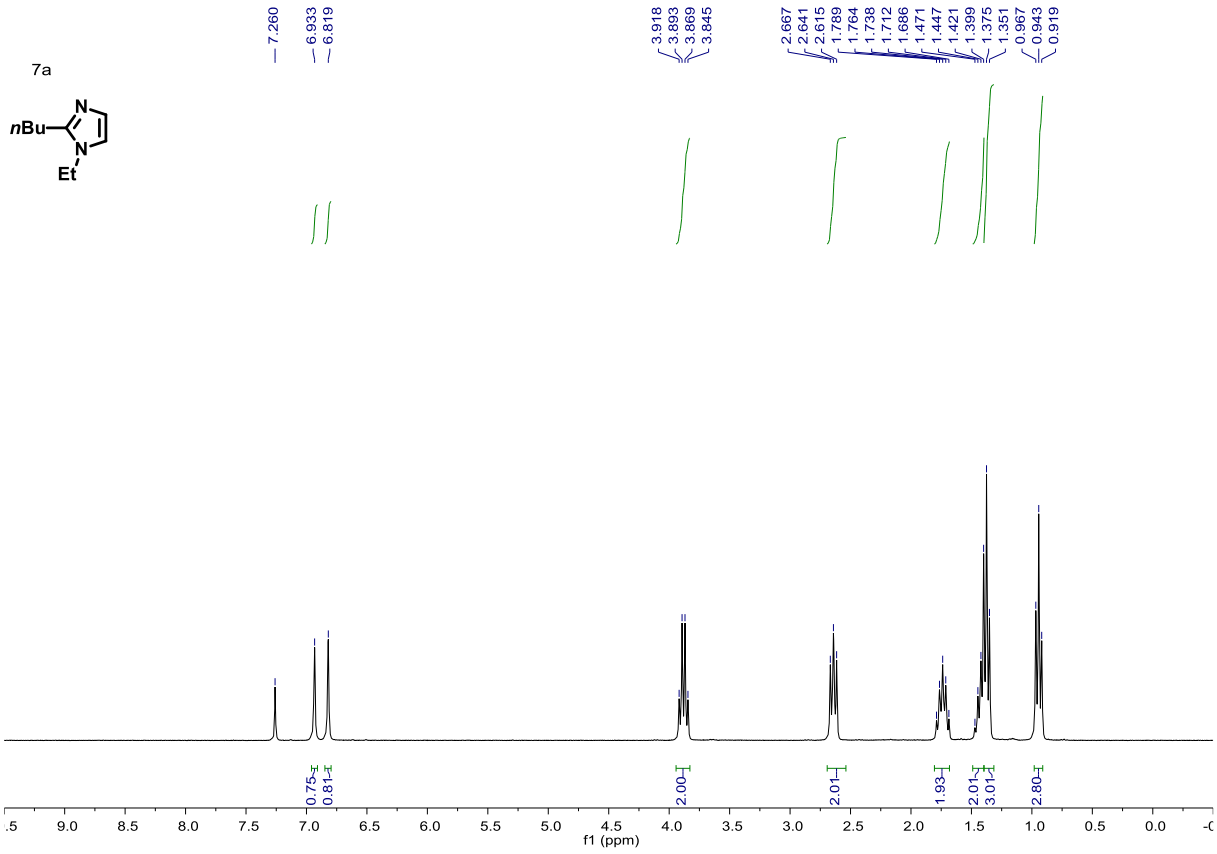
6a

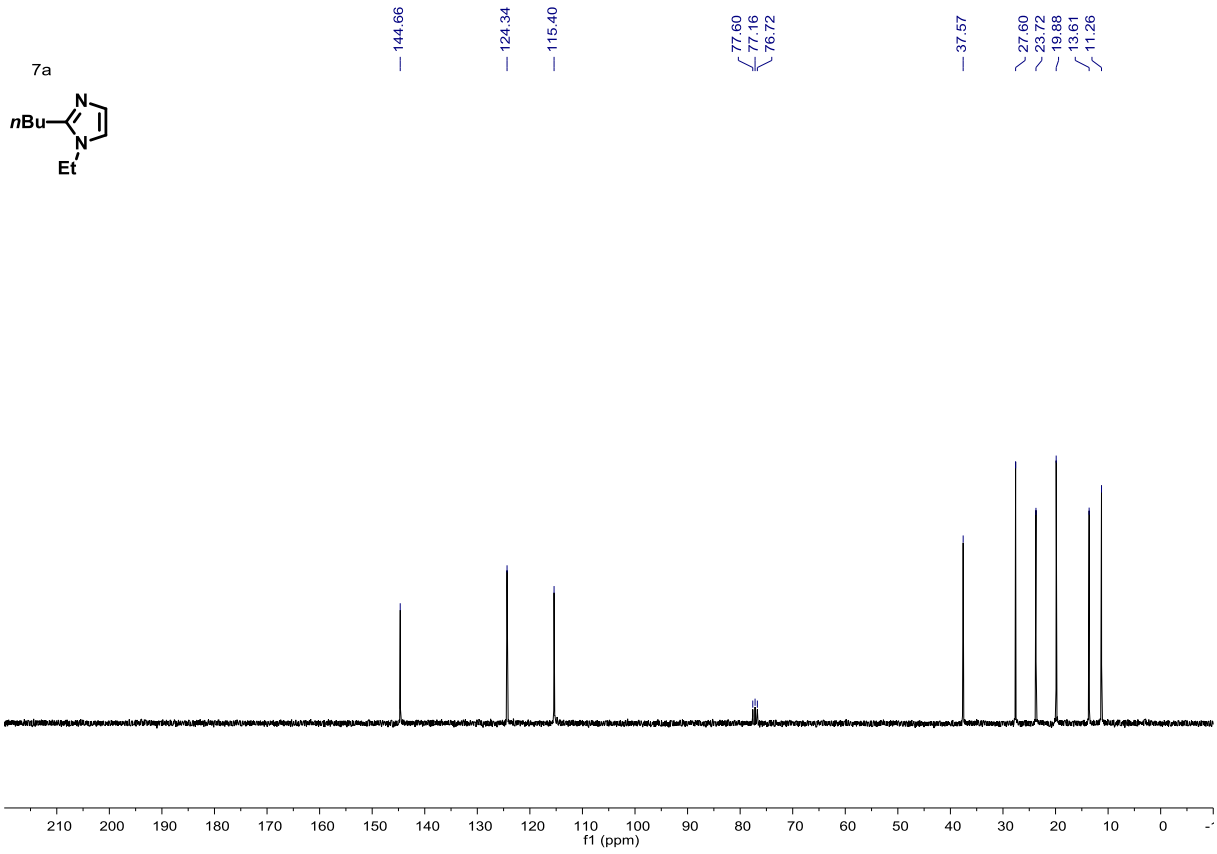

N
Me
N
nBu

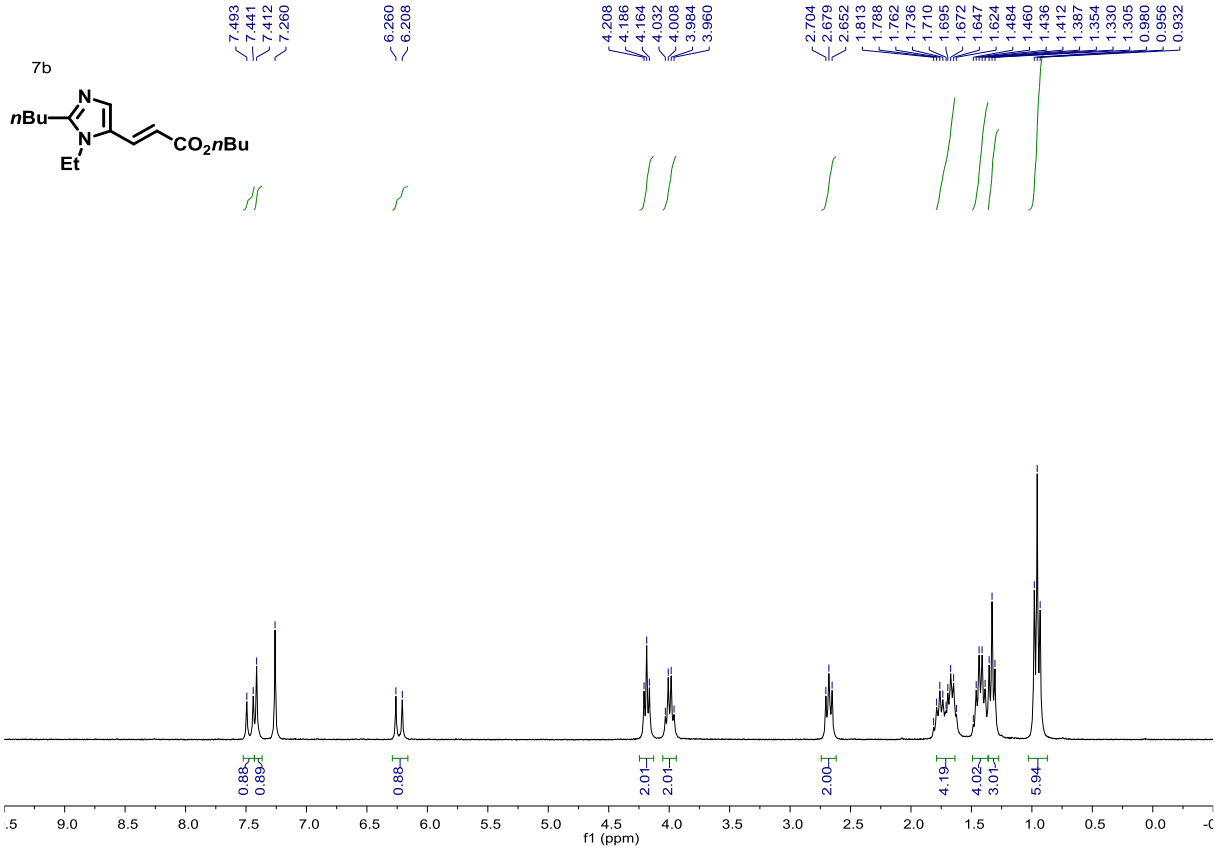
7.260
6.892
6.804
3.833
3.809
3.784
2.369
1.738
1.714
1.689
1.664
1.639
1.391
1.366
1.341
1.316
1.291
1.267
0.958
0.933
0.909
1.00
0.96
2.04
3.05
2.15
2.16
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

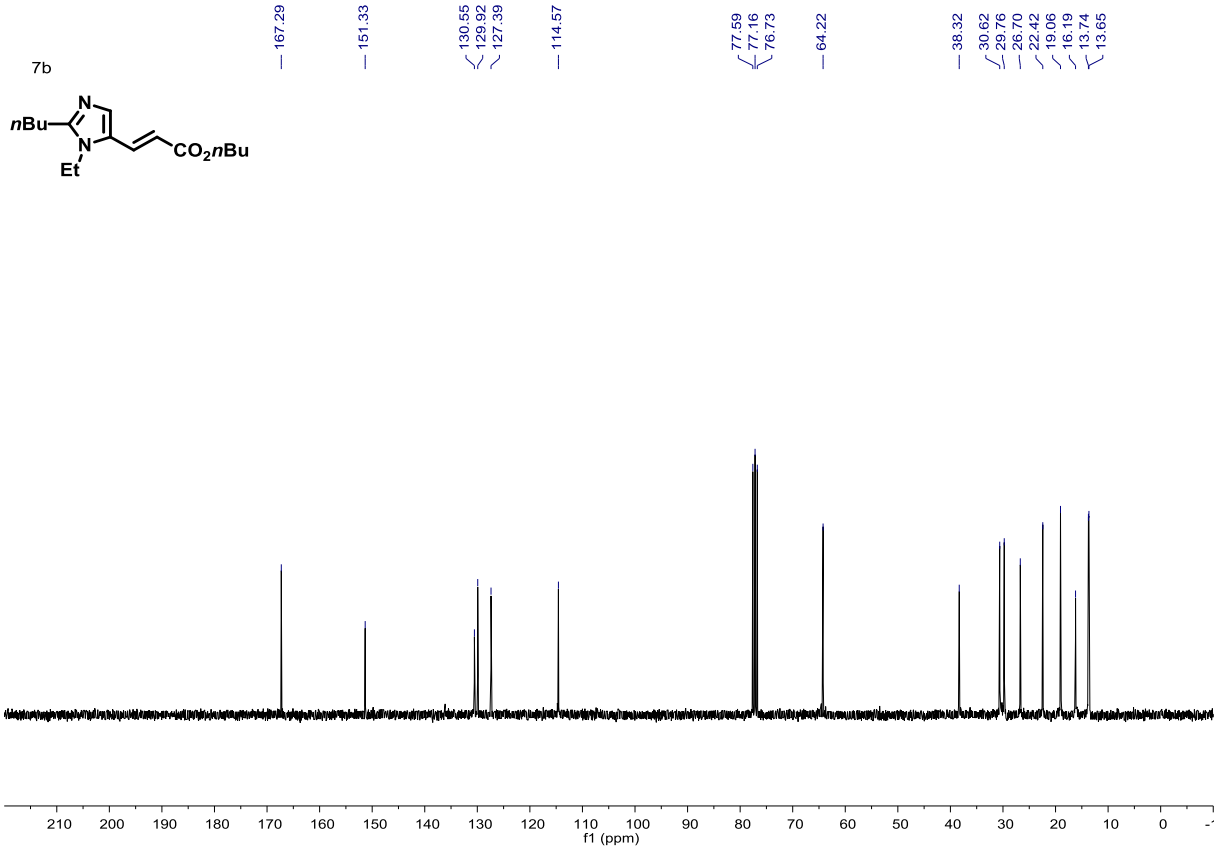

6b
Me
N
N
nBu
CO2nBu
7.471
7.418
7.384
7.260
6.254
6.201
4.206
4.184
4.162
3.931
3.907
3.882
2.420
1.716
1.694
1.672
1.649
1.624
1.600
1.483
1.459
1.433
1.408
1.393
1.384
1.369
1.343
1.318
1.295
0.978
0.954
0.929
0.95
0.89
0.89
2.00
2.04
3.05
4.19
4.10
6.35
f1 (ppm)

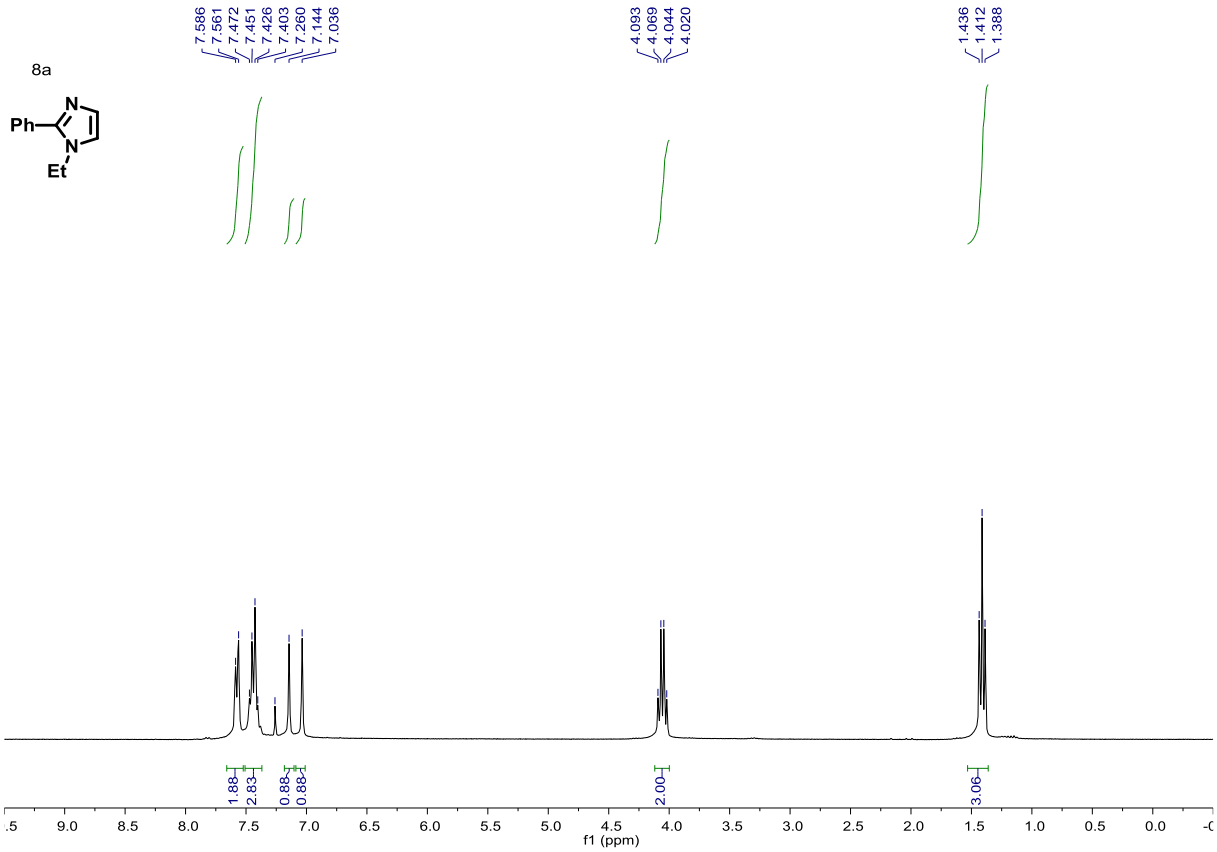

6b
Me
N
N
nBu
CO2nBu
167.21
147.76
129.92
127.94
114.73
77.58
77.16
76.73
64.21
43.63
32.62
30.59
19.73
19.04
13.60
13.52
13.40
f1 (ppm)

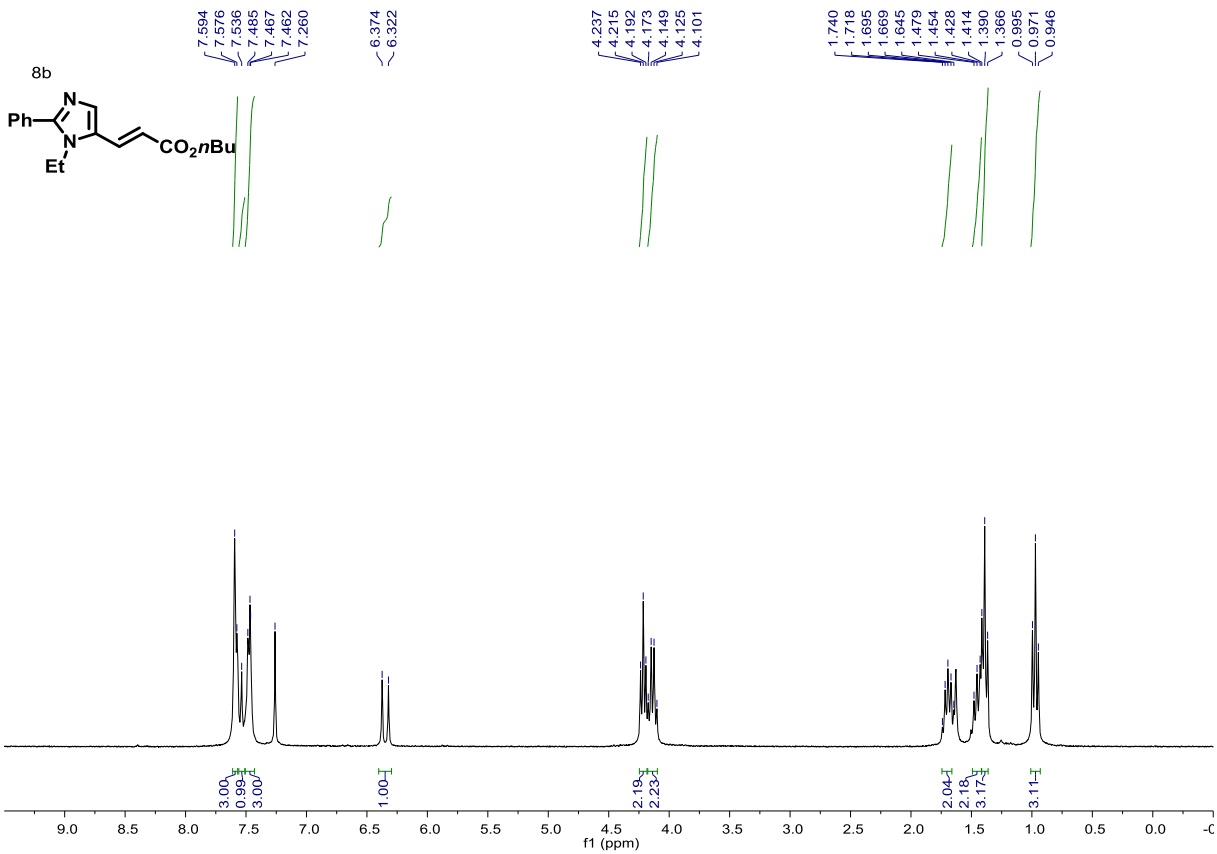

7a
nBu
N
N
Et
7.260
6.933
6.819
3.918
3.893
3.869
3.845
2.667
2.641
2.615
1.789
1.764
1.738
1.712
1.686
1.471
1.447
1.421
1.399
1.375
1.351
0.967
0.943
0.919
0.75
0.81
2.00
2.01
1.93
2.01
3.01
2.80
f1 (ppm)


7a
nBu
N
N
Et
144.66
124.34
115.40
77.60
77.16
76.72
37.57
27.60
23.72
19.88
13.61
11.26
f1 (ppm)

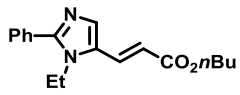

7b
nBu
N
N
Et
CO2nBu
7.493
7.441
7.412
7.260
6.260
6.208
4.208
4.186
4.164
4.032
4.008
3.984
3.960
2.704
2.679
2.652
1.813
1.788
1.762
1.736
1.710
1.695
1.672
1.647
1.624
1.484
1.460
1.436
1.412
1.387
1.354
1.330
1.305
0.980
0.956
0.932
0.88
0.89
0.88
2.01
2.01
2.00
4.19
4.02
3.01
5.94
f1 (ppm)


7b
nBu
N
N
Et
CO2nBu
167.29
151.33
130.55
129.92
127.39
114.57
77.59
77.16
76.73
64.22
38.32
30.62
29.76
26.70
22.42
19.06
16.19
13.74
13.65
f1 (ppm)

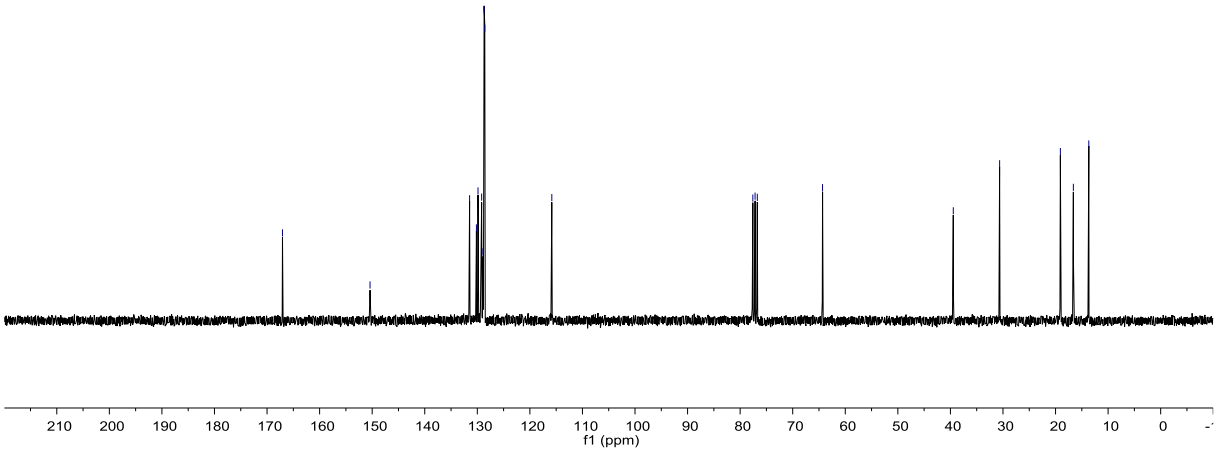

8a
Ph
N
N
Et
7.586
7.561
7.472
7.451
7.426
7.403
7.260
7.144
7.036
4.093
4.069
4.044
4.020
1.436
1.412
1.388
1.88
2.83
0.88
0.88
2.00
3.06
f1 (ppm)


8b
Ph
N
N
Et
CO2nBu
7.594
7.576
7.536
7.485
7.467
7.462
7.260
6.374
6.322
4.237
4.215
4.192
4.173
4.149
4.125
4.101
1.740
1.718
1.695
1.669
1.645
1.479
1.454
1.428
1.414
1.390
1.366
0.995
0.971
0.946
3.00
0.99
3.00
1.00
2.19
2.23
2.04
2.18
3.17
3.11
f1 (ppm)

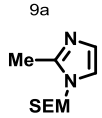
8b



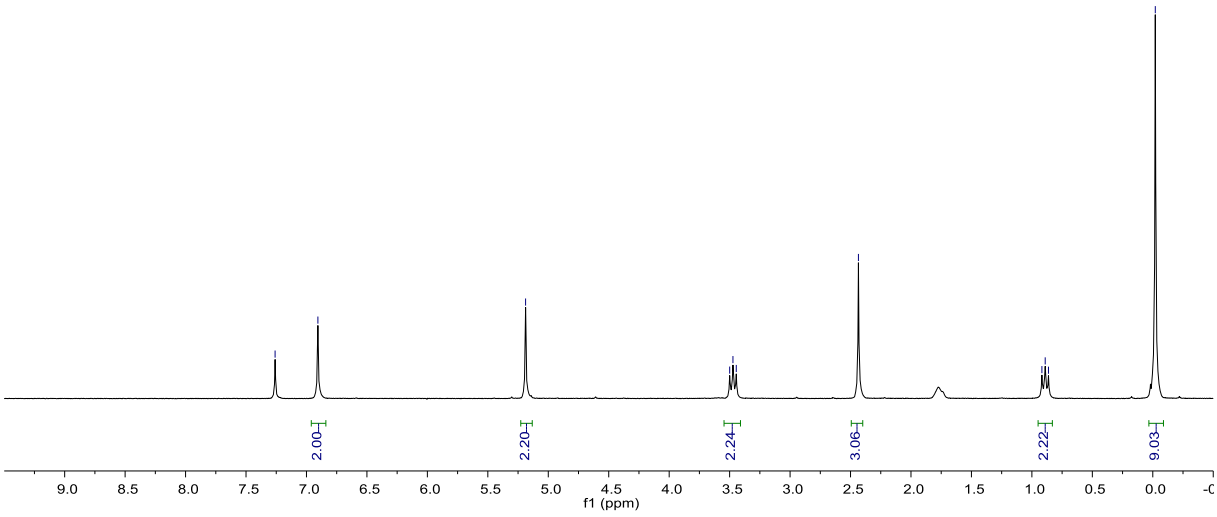
167.07 150.41 131.47 130.17 129.87 129.18 128.92 128.70 128.58 115.83 77.58 77.16 76.73 64.32 39.45 30.64 19.08 16.61 13.67

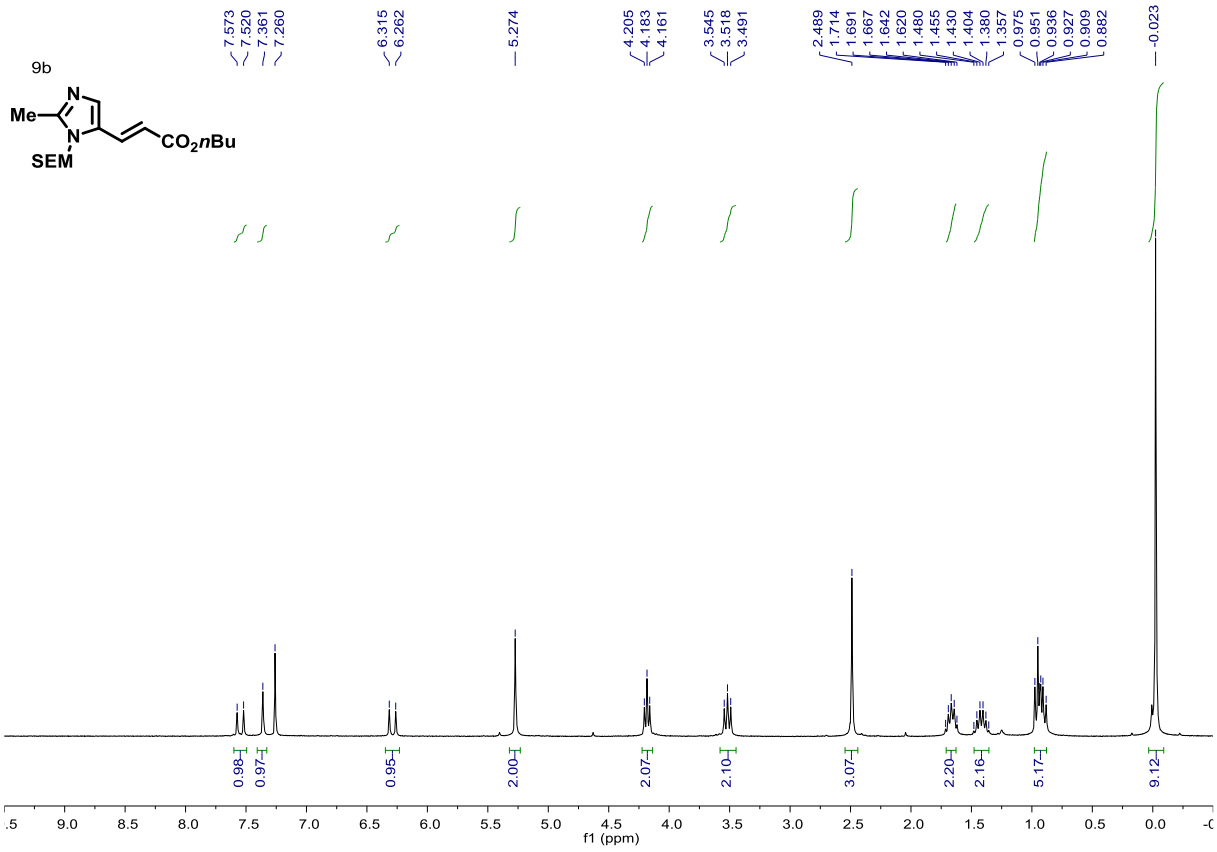


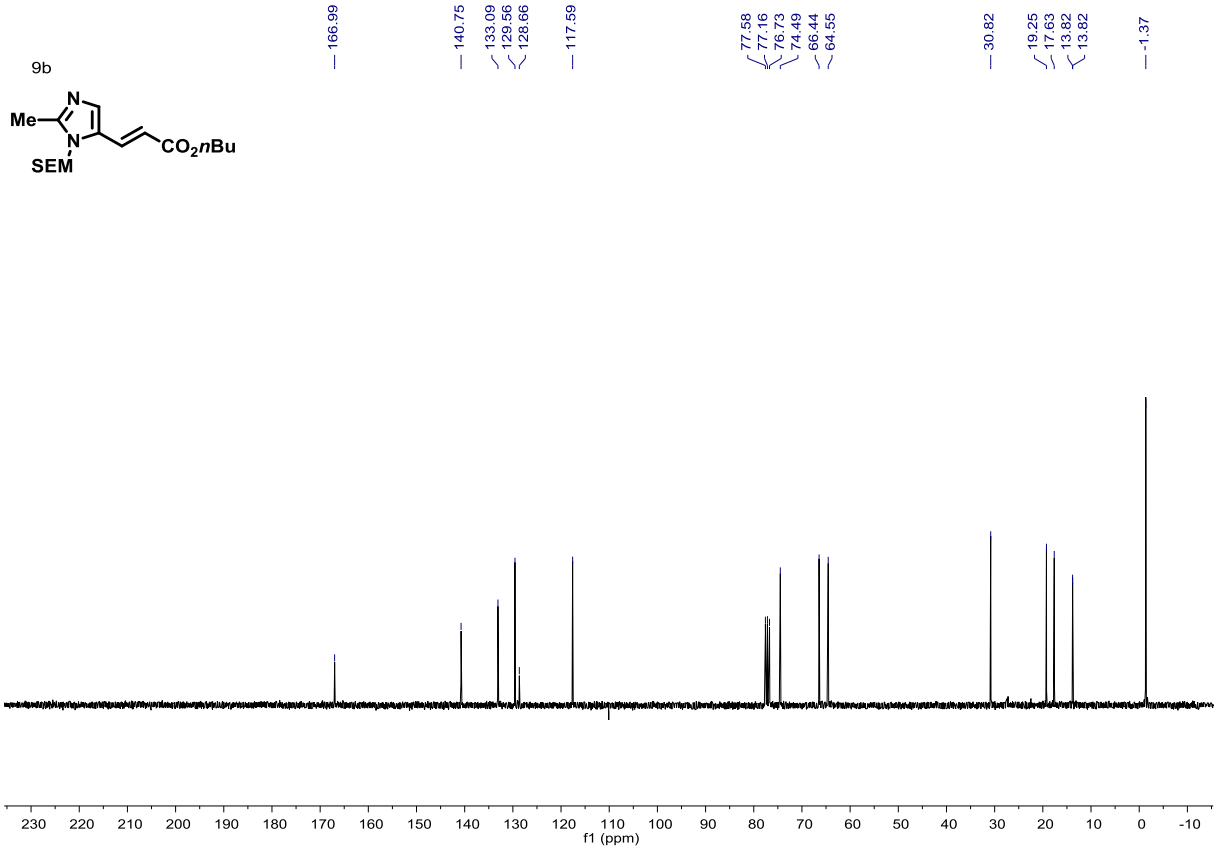
9a

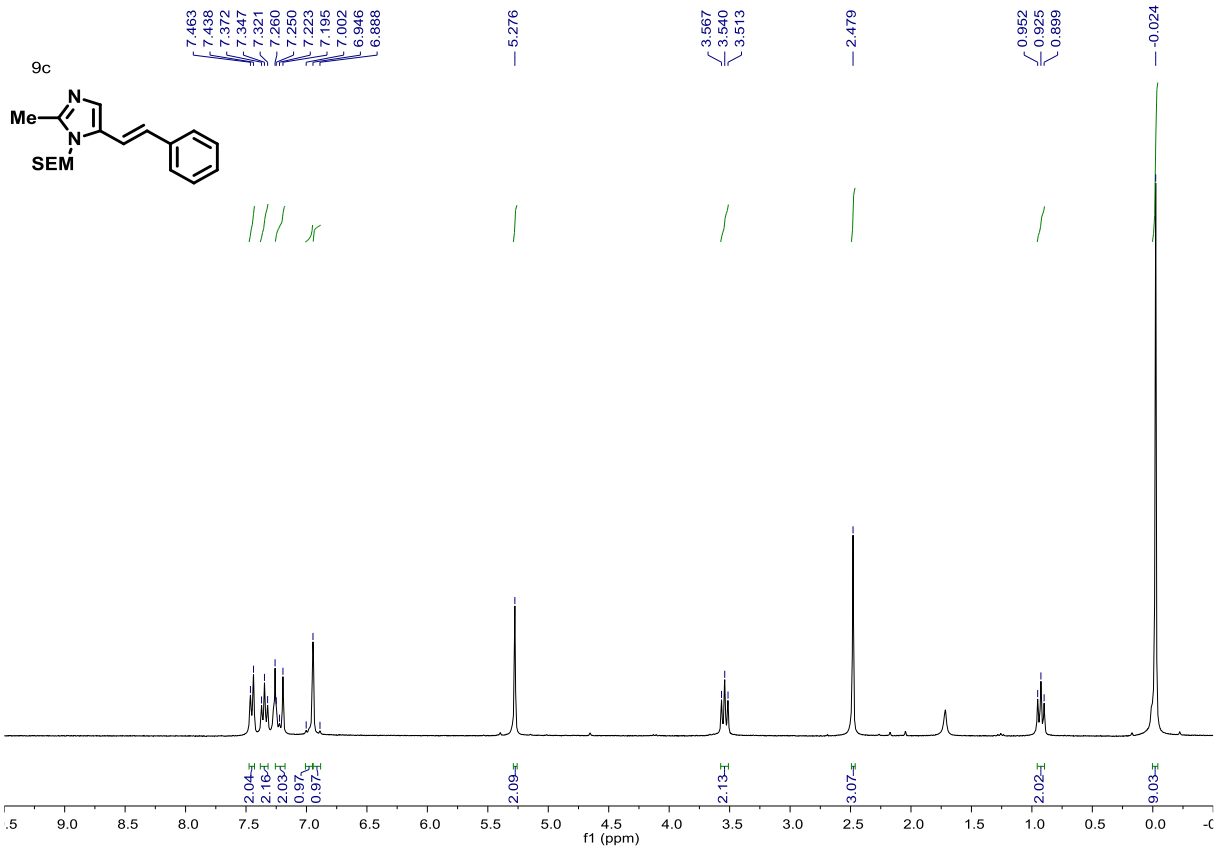


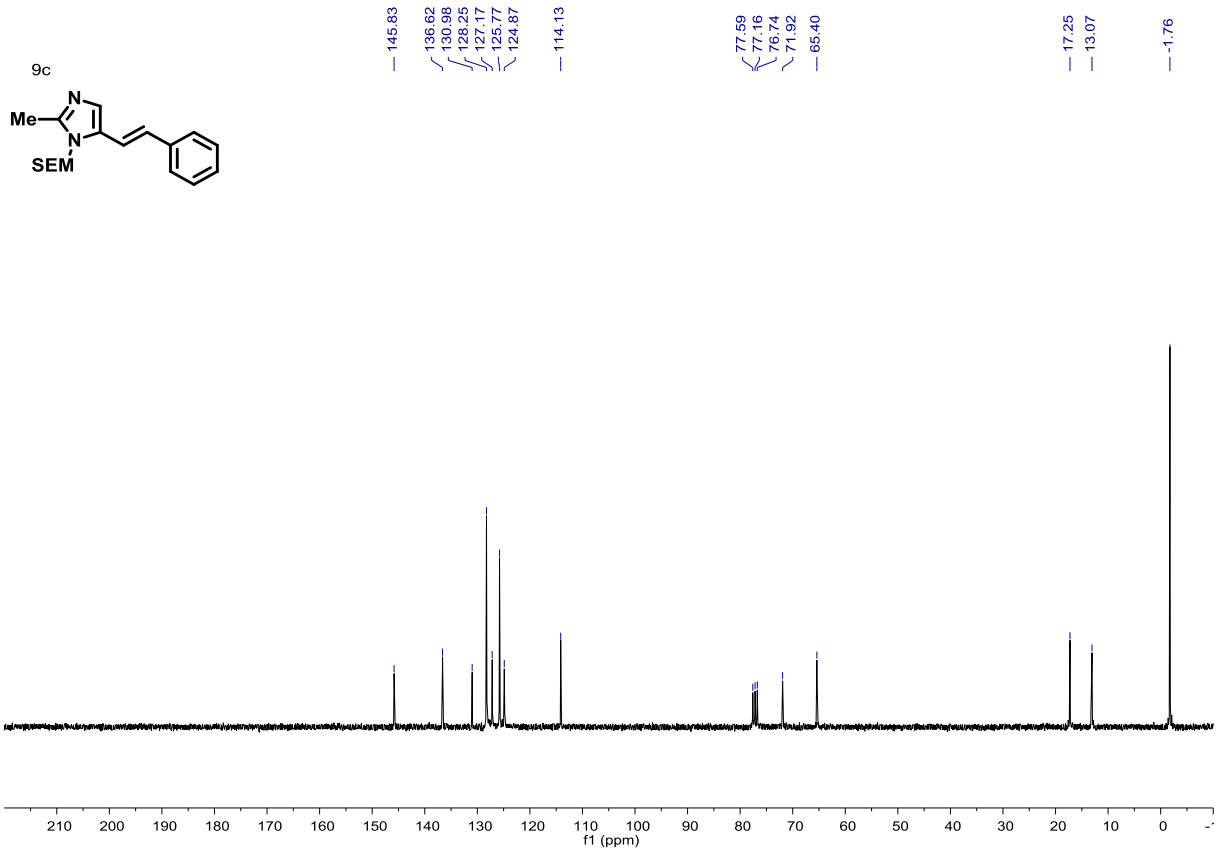
7.260 6.905 5.188 3.500 3.473 3.445 2.435 0.917 0.890 0.863 -0.021

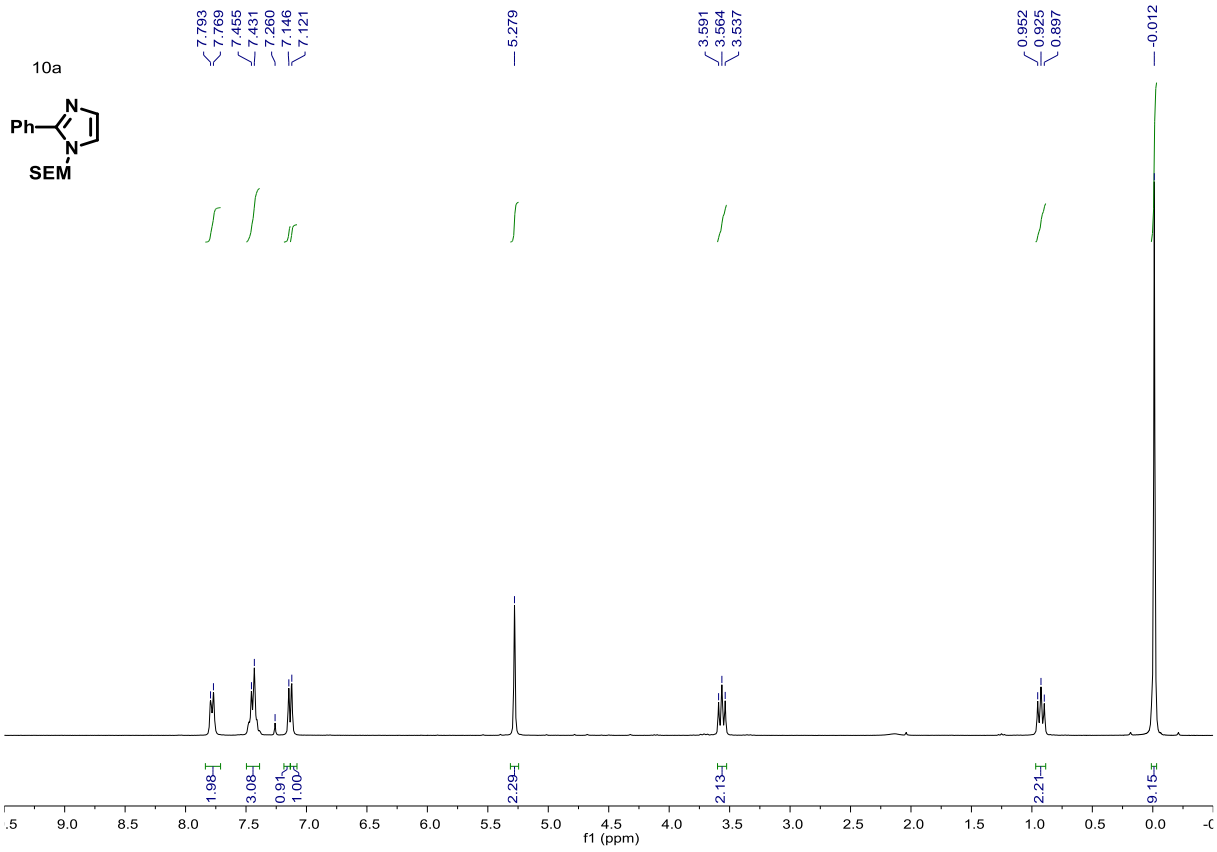


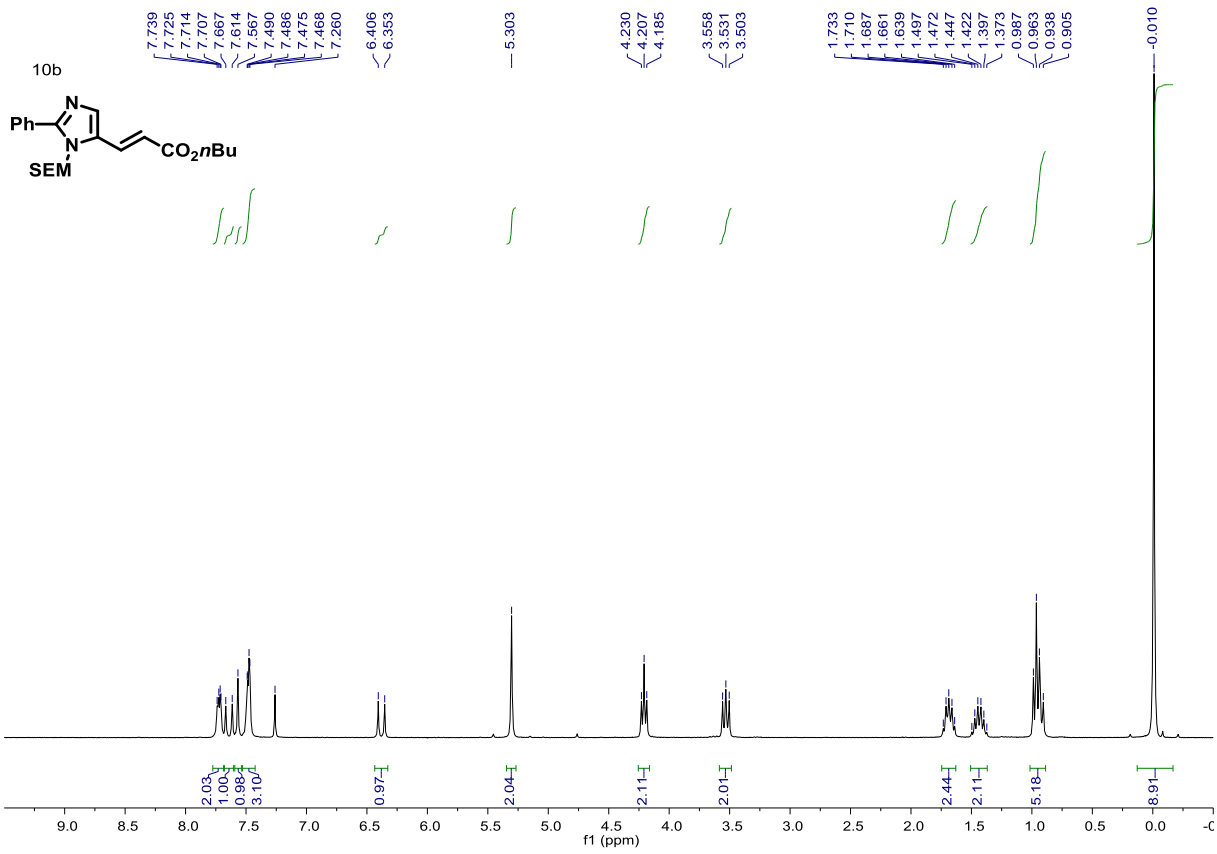

9b
Me
N
N
SEM
CO2nBu
7.573
7.520
7.361
7.260
6.315
6.262
5.274
4.205
4.183
4.161
3.545
3.518
3.491
2.489
1.714
1.691
1.667
1.642
1.620
1.480
1.455
1.430
1.404
1.380
1.357
0.975
0.951
0.936
0.927
0.909
0.882
-0.023
0.98
0.97
0.95
2.00
2.07
2.10
3.07
2.20
2.16
5.17
9.12
f1 (ppm)

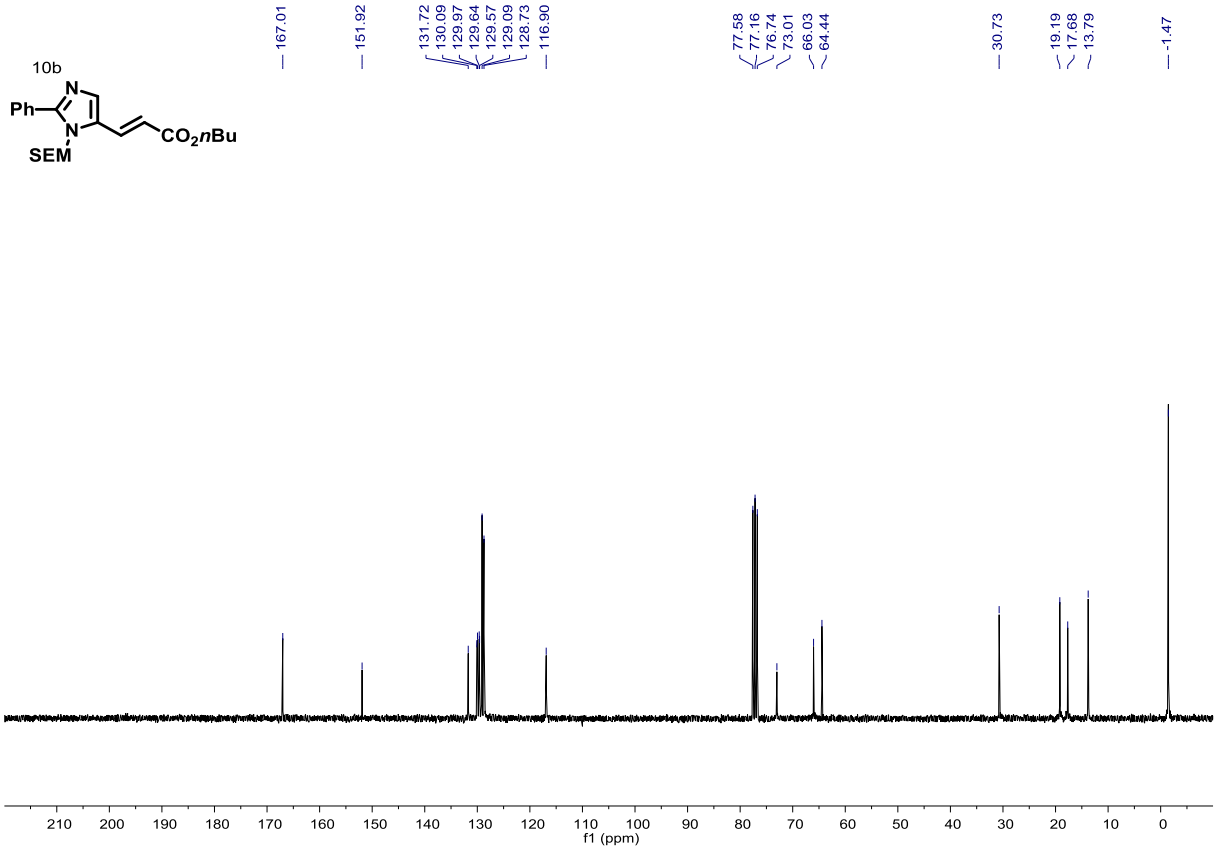

9b
Me
N
N
SEM
CO2nBu
166.99
140.75
133.09
129.56
128.66
117.59
77.58
77.16
76.73
74.49
66.44
64.55
30.82
19.25
17.63
13.82
13.82
-1.37
f1 (ppm)

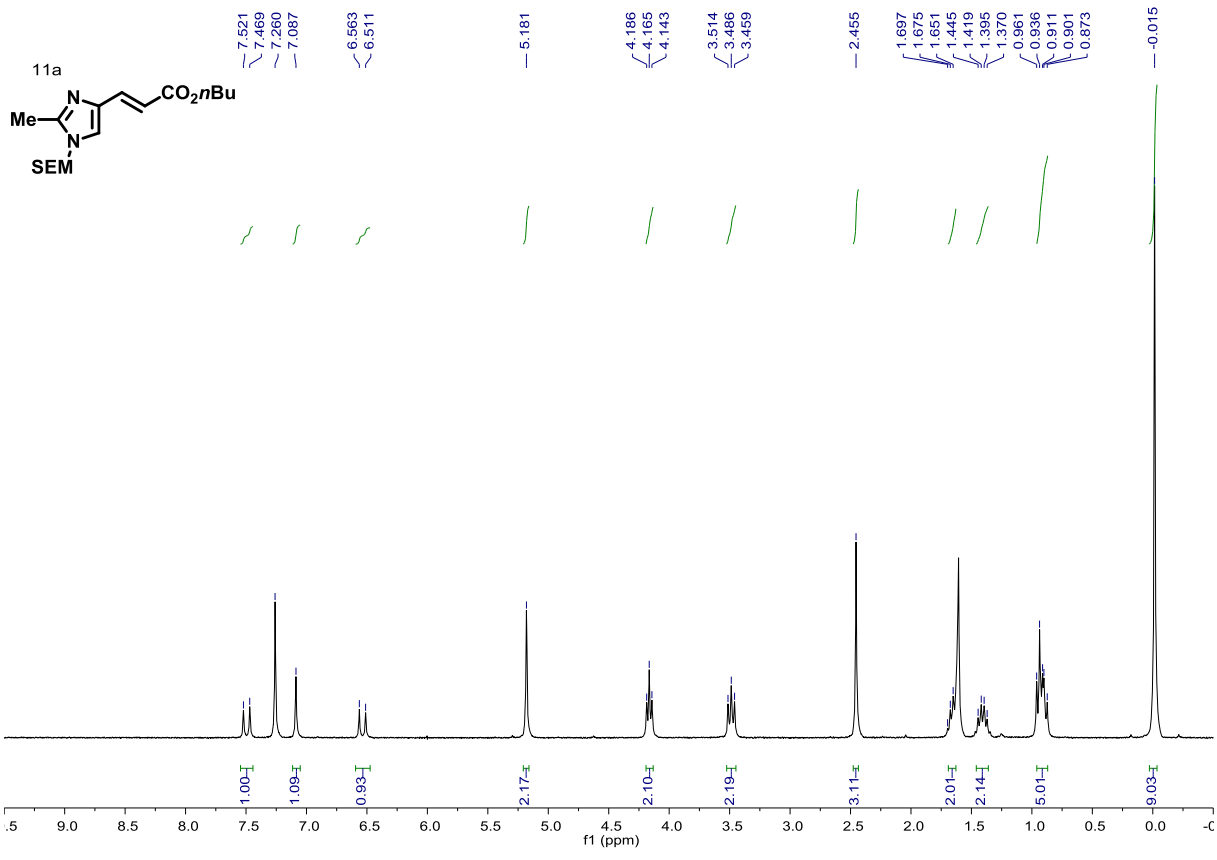

9c
Me
N
N
SEM
7.463
7.438
7.372
7.347
7.321
7.260
7.250
7.223
7.195
7.002
6.946
6.888
5.276
3.567
3.540
3.513
2.479
0.952
0.925
0.899
-0.024
2.04
2.16
2.03
0.97
0.97
2.09
2.13
3.07
2.02
9.03
f1 (ppm)


9c
Me
N
N
SEM
145.83
136.62
130.98
128.25
127.17
125.77
124.87
114.13
77.59
77.16
76.74
71.92
65.40
17.25
13.07
-1.76
f1 (ppm)

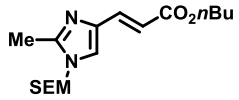

10a
Ph
N
N
SEM
7.793
7.769
7.455
7.431
7.260
7.146
7.121
5.279
3.591
3.564
3.537
0.952
0.925
0.897
-0.012
1.98
3.08
0.91
1.00
2.29
2.13
2.21
9.15
f1 (ppm)


10b
Ph
N
N
SEM
CO2nBu
7.739
7.725
7.714
7.707
7.687
7.614
7.567
7.490
7.486
7.475
7.468
7.260
6.406
6.353
5.303
4.230
4.207
4.185
3.558
3.531
3.503
1.733
1.710
1.687
1.661
1.639
1.497
1.472
1.447
1.422
1.397
1.373
0.987
0.963
0.938
0.905
-0.010
2.03
1.00
0.98
3.10
0.97
2.04
2.11
2.01
2.44
2.11
5.18
8.91
f1 (ppm)


10b
Ph
N
N
SEM
CO2nBu
167.01
151.92
131.72
130.09
129.97
129.64
129.57
129.09
128.73
116.90
77.58
77.16
76.74
73.01
66.03
64.44
30.73
19.19
17.68
13.79
-1.47
f1 (ppm)

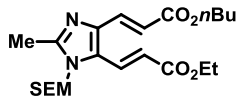

11a
Me
N
N
SEM
CO2nBu
7.521
7.469
7.260
7.087
6.563
6.511
5.181
4.186
4.165
4.143
3.514
3.486
3.459
2.455
1.697
1.675
1.651
1.445
1.419
1.395
1.370
0.961
0.936
0.911
0.901
0.873
-0.015
1.00
1.09
0.93
2.17
2.10
2.19
3.11
2.01
2.14
5.01
9.03
f1 (ppm)

11a


Me
N
N
SEM
CO2nBu

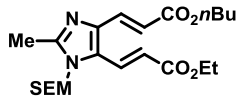
167.72
147.07
136.13
135.68
122.39
115.75
77.59
77.16
76.74
75.19
66.28
63.95
30.73
19.13
17.63
13.72
13.02
-1.46
f1 (ppm)

11b


Me
N
N
SEM
CO2nBu
CO2Et

7.728
7.701
7.676
7.648
7.260
6.765
6.714
6.364
6.310
5.246
4.306
4.282
4.259
4.236
4.216
4.194
4.172
3.591
3.564
3.537
2.508
1.692
1.668
1.642
1.455
1.430
1.405
1.380
1.360
1.337
1.313
0.970
0.946
0.922
-0.009
2.08
1.02
1.00
2.08
2.24
2.19
2.13
3.01
2.25
2.05
3.08
5.12
9.03
f1 (ppm)

11b



167.49
166.64
149.70
138.87
133.42
129.30
128.65
120.48
119.39
77.58
77.16
76.74
73.10
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64.36
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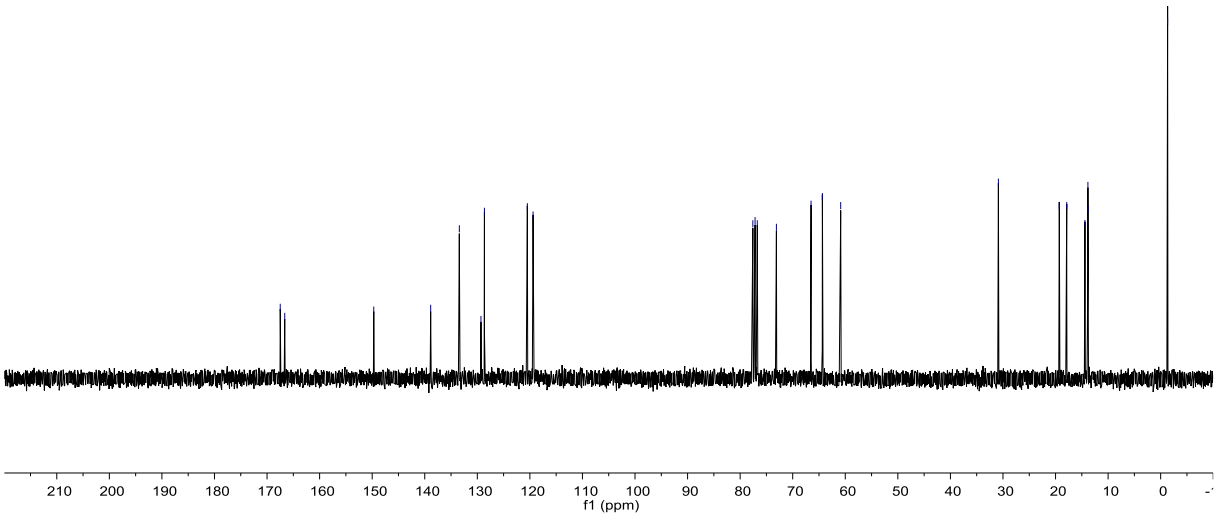
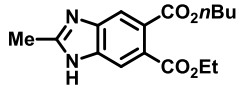
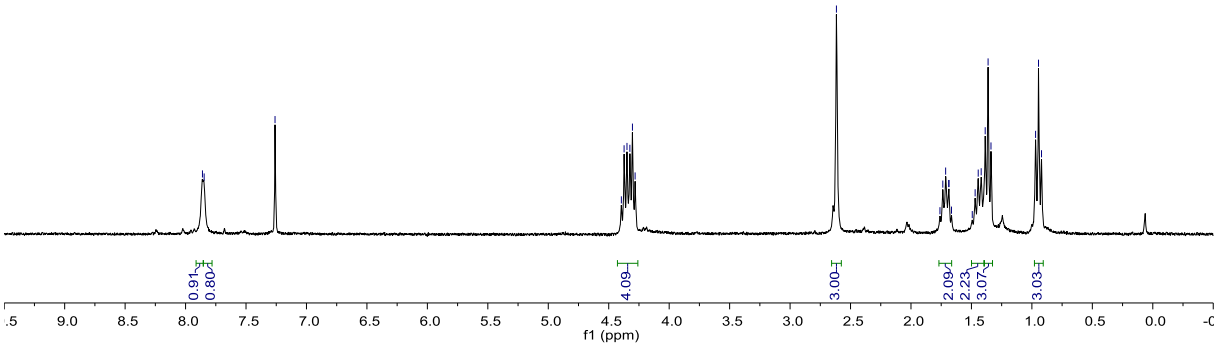
30.87
19.29
17.87
14.41
13.84
13.81
-1.32

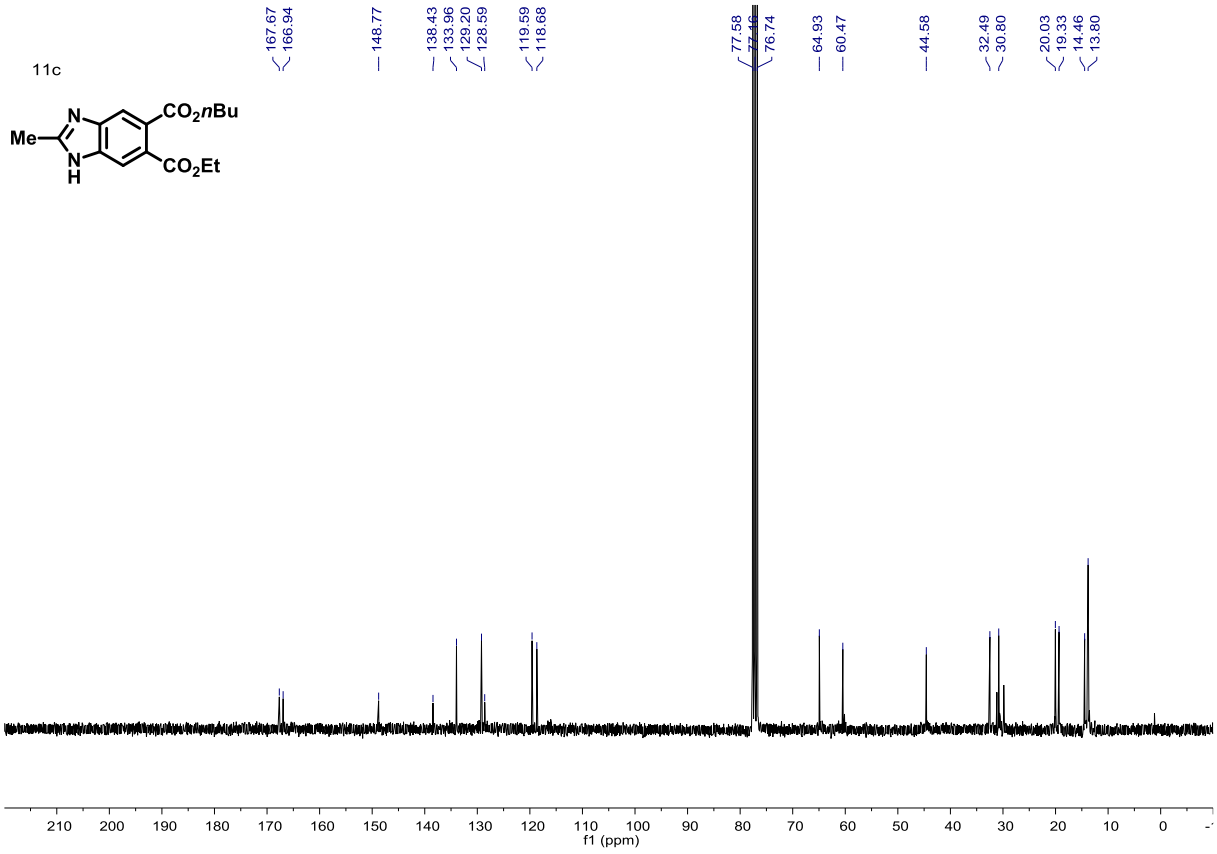


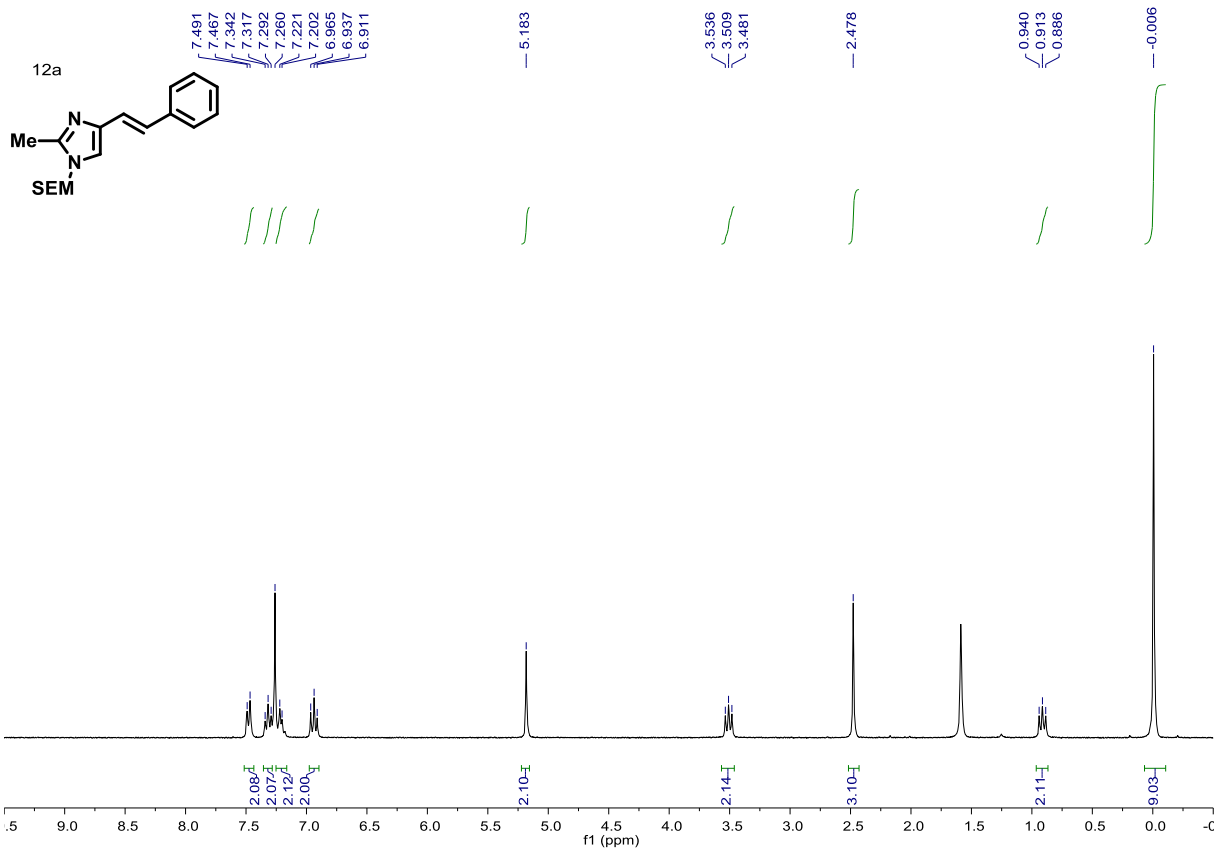
11c



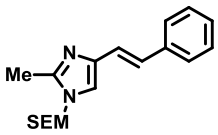
7.860
7.846
7.260
4.395
4.373
4.349
4.325
4.304
4.282
2.617
1.760
1.737
1.713
1.687
1.687
1.665
1.493
1.469
1.444
1.419
1.386
1.362
1.338
0.970
0.945
0.920




11c
Me
N
N
H
CO2nBu
CO2Et
167.67
166.94
148.77
138.43
133.96
129.20
128.59
119.59
118.68
77.58
77.46
76.74
64.93
60.47
44.58
32.49
30.80
20.03
19.33
14.46
13.80
f1 (ppm)

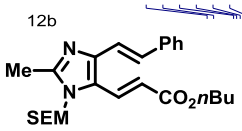

12a
Me
N
N
SEM
7.491
7.467
7.342
7.317
7.292
7.260
7.221
7.202
6.965
6.937
6.911
5.183
3.536
3.509
3.481
2.478
0.940
0.913
0.886
-0.006
2.08
2.07
2.12
2.00
2.10
2.14
3.10
2.11
9.03
f1 (ppm)

12a


Me
N
N
SEM

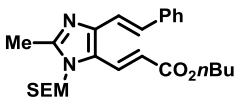
145.77
137.92
137.42
128.27
126.67
126.07
125.84
119.66
118.16
77.59
77.16
76.73
74.69
65.75
17.36
12.78
-1.63
f1 (ppm)

12b

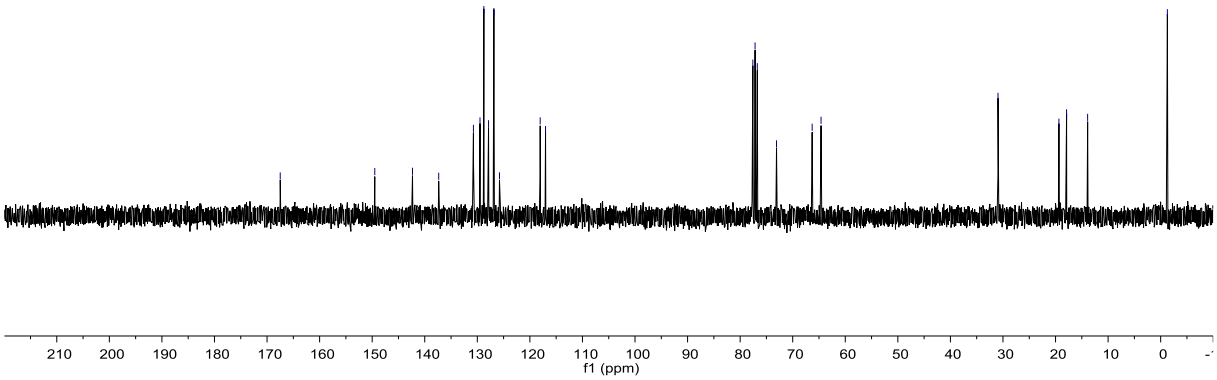

Ph
Me
N
N
CO2nBu
SEM

7.780
7.727
7.562
7.536
7.507
7.455
7.381
7.356
7.331
7.281
7.260
7.183
7.130
6.323
6.270
5.266
4.242
4.220
4.198
3.608
3.580
3.554
2.538
1.721
1.697
1.478
1.452
1.427
1.403
0.993
0.969
0.946
0.923
-0.005
1.00
2.01
2.01
2.01
1.16
1.02
2.06
2.08
2.17
3.13
2.07
2.10
5.27
9.10
f1 (ppm)

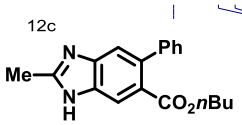
12b



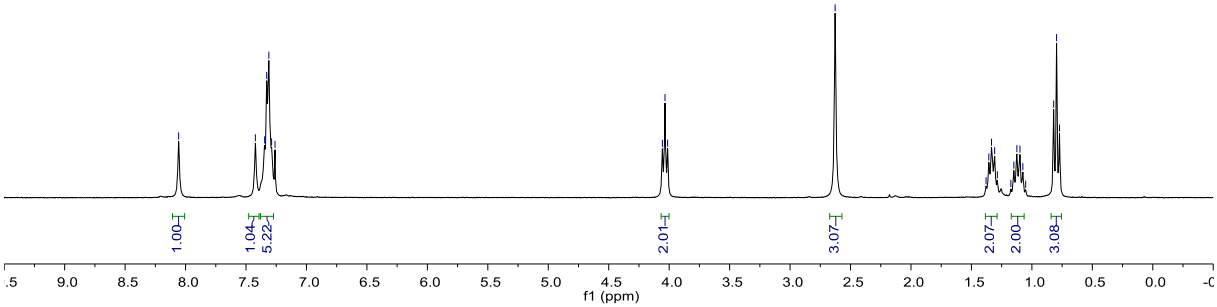
167.49
149.51
142.33
137.34
130.74
129.49
128.76
127.86
126.85
125.78
118.04
117.02
77.58
77.16
76.74
73.08
66.30
64.61
30.94
19.36
17.90
13.90
-1.28



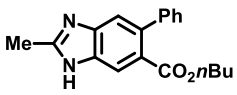
12c



8.057
7.423
7.346
7.329
7.311
7.288
7.260
4.056
4.035
4.013
2.627
1.379
1.356
1.334
1.308
1.286
1.174
1.149
1.124
1.099
1.075
1.052
0.820
0.796
0.772

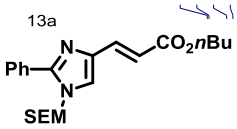


12c


Me
N
H
Ph
CO2nBu

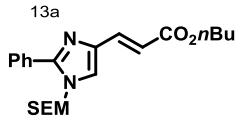
169.64
153.94
142.51
140.61
137.66
128.83
128.06
126.89
125.91
117.08
116.39
77.58
77.16
76.74
65.10
30.42
19.13
15.21
13.78
f1 (ppm)

13a

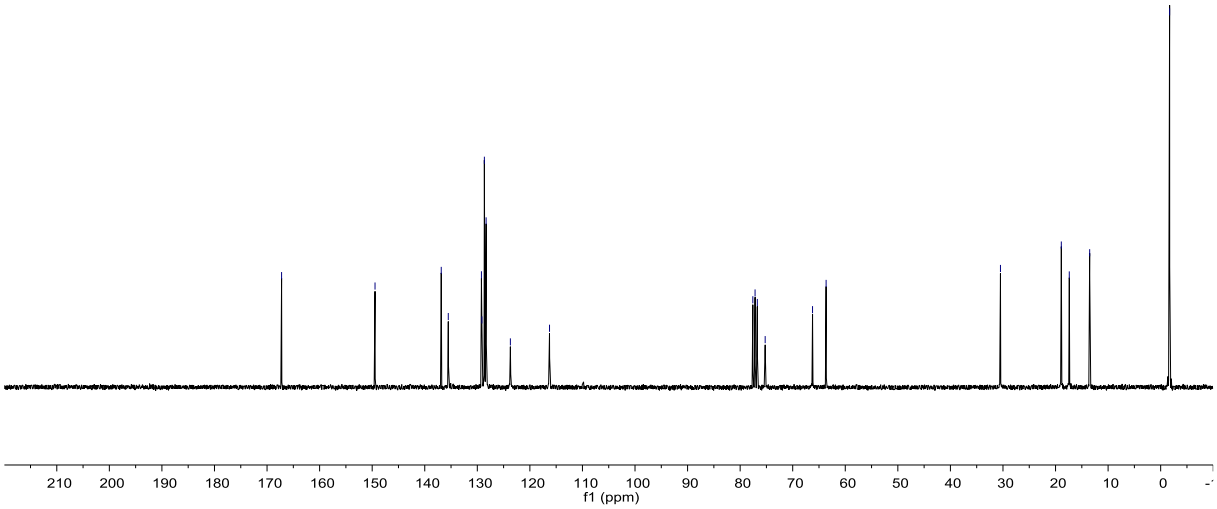

Ph
N
SEM
CO2nBu

7.779
7.765
7.619
7.567
7.476
7.462
7.302
7.260
6.710
6.658
5.262
4.202
4.180
4.159
3.584
3.557
3.529
1.708
1.685
1.663
1.637
1.615
1.479
1.454
1.429
1.404
1.380
1.355
0.966
0.942
0.921
0.898
-0.010
2.10
1.00
3.21
1.07
0.90
2.24
2.13
2.11
2.08
2.07
5.00
9.04
f1 (ppm)

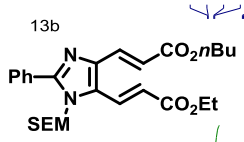
13a



167.23 149.46 136.86 135.52 129.22 129.13 128.66 128.32 123.71 116.26 77.59 77.16 76.73 75.24 66.23 63.65 30.48 18.90 17.39 13.51 -1.70

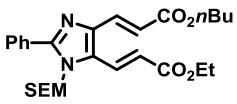


13b

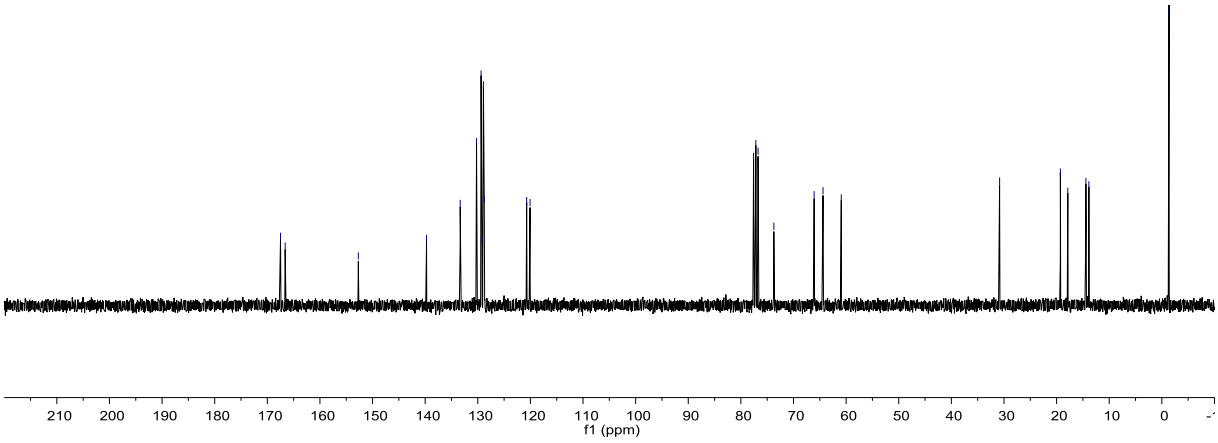


7.801 7.796 7.750 7.743 7.513 7.505 7.260 6.906 6.855 6.441 6.388 5.217 4.327 4.303 4.279 4.255 4.226 4.205 4.183 3.554 3.527 3.499 1.722 1.699 1.675 1.601 1.484 1.459 1.434 1.409 1.377 1.353 1.329 0.986 0.973 0.949 0.931 0.925 0.002

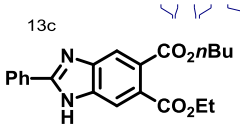
13b



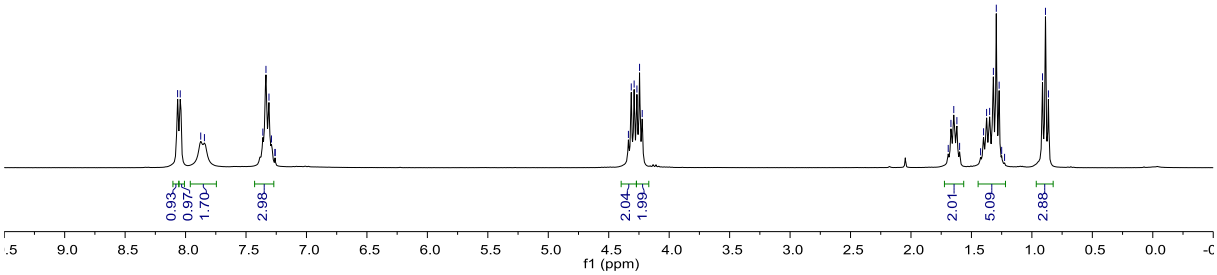
167.49
166.61
152.70
139.74
133.34
130.24
129.37
129.20
128.93
128.77
120.71
120.06
77.59
77.16
76.74
73.73
66.08
64.39
60.92
30.83
19.28
17.87
14.43
13.87
-1.37



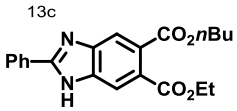
13c



8.066
8.044
7.875
7.844
7.361
7.335
7.310
7.290
7.260
7.260
4.337
4.314
4.290
4.267
4.245
4.223
1.692
1.669
1.646
1.620
1.598
1.424
1.400
1.375
1.349
1.318
1.294
1.271
1.250
1.226
0.912
0.888
0.863

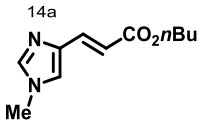


13c


Ph
N
N
H
CO2nBu
CO2Et

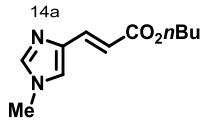
168.68
155.96
130.89
129.05
128.87
127.14
127.03
126.98
77.58
77.16
76.74
65.72
61.80
30.51
19.13
14.05
13.68
f1 (ppm)

14a

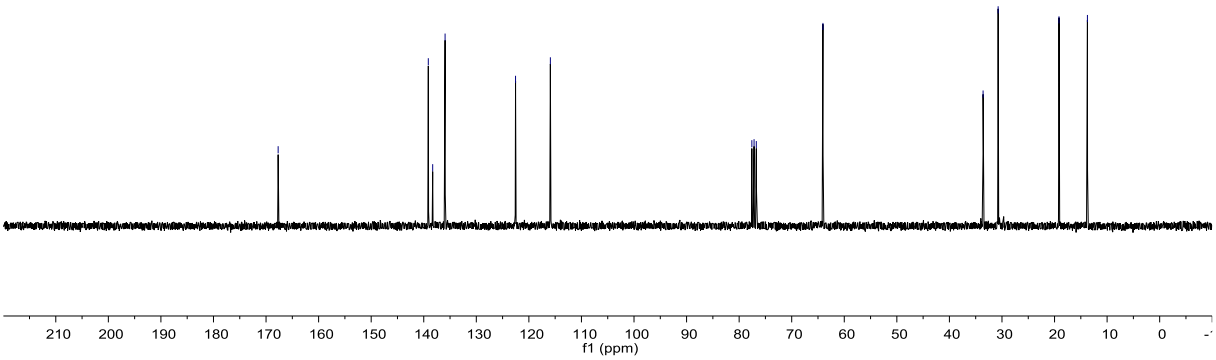

N
N
Me
CO2nBu

7.626
7.543
7.490
7.260
7.090
6.569
6.517
4.192
4.170
4.148
3.728
1.706
1.682
1.673
1.660
1.634
1.612
1.471
1.446
1.420
1.395
1.371
1.347
0.963
0.939
0.914
0.94
0.97
0.89
0.97
2.00
3.00
2.10
2.09
3.01
f1 (ppm)

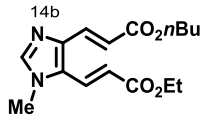
14a



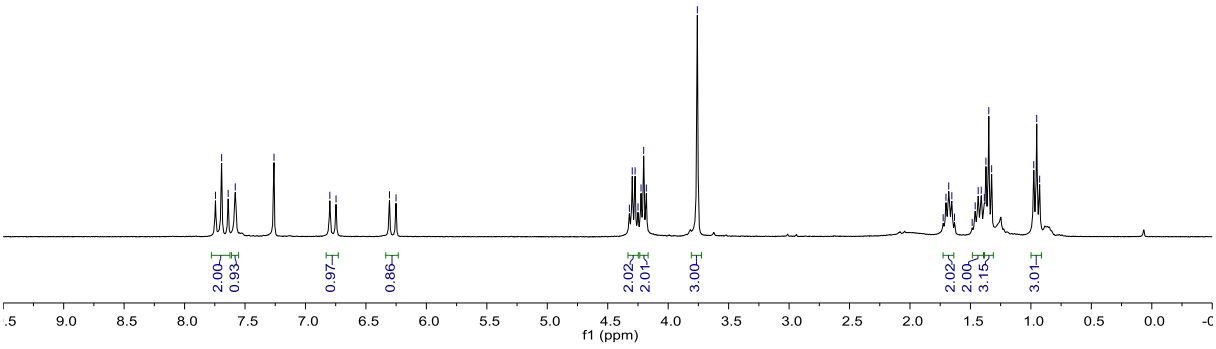
167.70
139.13
138.30
135.94
122.54
115.91
77.58
77.16
76.73
64.06
33.59
30.73
19.15
13.74



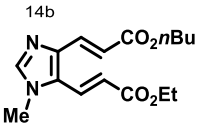
14b



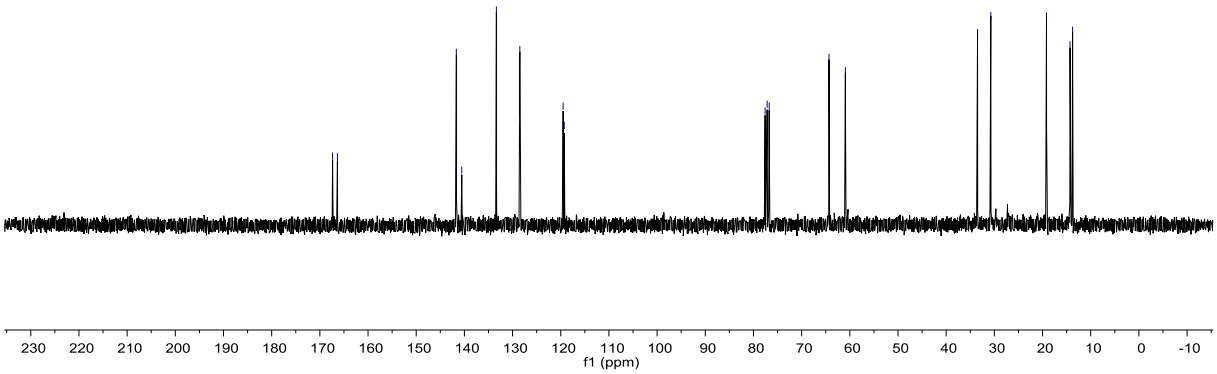
7.745
7.693
7.639
7.581
7.260
6.798
6.747
6.305
6.251
4.321
4.297
4.274
4.250
4.225
4.203
4.181
3.759
1.725
1.703
1.679
1.654
1.632
1.486
1.461
1.436
1.410
1.385
1.372
1.348
1.325
0.976
0.952
0.927



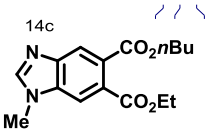
14b



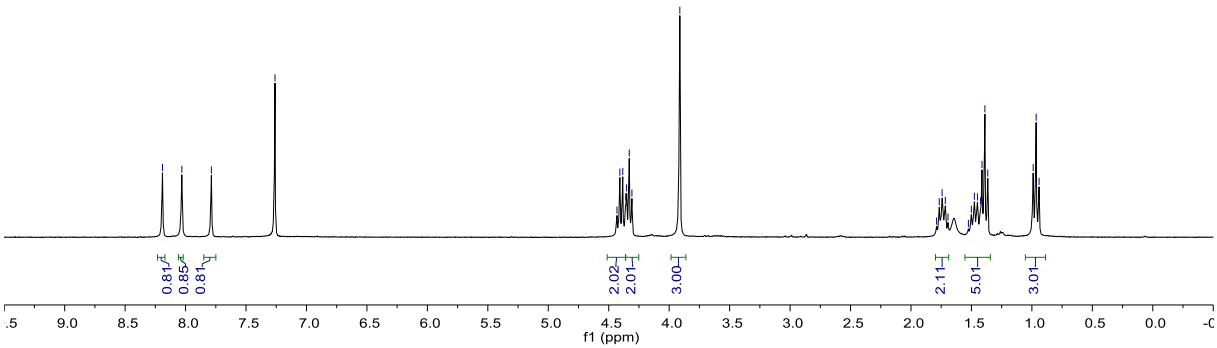
167.36
166.35
141.67
140.54
133.36
128.54
128.49
119.50
119.27
77.59
77.16
76.74
64.32
60.92
33.49
30.74
19.18
14.30
13.76



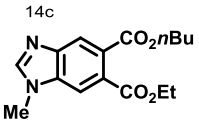
14c



8.191
8.031
7.786
7.260
4.432
4.408
4.384
4.360
4.352
4.330
4.308
3.912
1.788
1.766
1.743
1.716
1.694
1.525
1.501
1.476
1.450
1.424
1.413
1.389
1.365
0.989
0.965
0.940



14c



168.12
168.01
146.76
144.51
135.36
127.43
126.51
121.62
110.95
77.58
77.16
76.73
65.44
61.74
31.41
30.54
19.19
14.12
13.77