Supporting Information

Regioselective C–H Functionalization Directed by Removable Carboxyl Group: Palladium-Catalyzed Vinylation at the Unusual Position of Indole and Related Heteroaromatic Rings

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Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, or 270 MHz and 68 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m) on a Shimadzu QP-5050. All starting materials and other reagents are commercially available. The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Indole-3-carboxylic acids **1b**[12] and **1c-d**[13] were prepared according to published procedures. Other starting materials were commercially available.

Experimental Procedures.

Procedure for the Reaction of 1-Methylindole-3-carboxylic Acid (1a) with Butyl Acrylate (2a) (entry 5 in Table 1): To a 20 mL two-necked flask were added 1-methylindole-3-carboxylic acid (**1a**) (0.4 mmol, 70 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 2 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3a** (73 mg, 71%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-Methylindole-3-carboxylic Acid (1a) with Cyclohexyl Acrylate (2c) (entry 2 in Table 2): To a 20 mL two-necked flask were added 1-methylindole-3-carboxylic acid (**1a**) (0.4 mmol, 70 mg), cyclohexyl acrylate (**2c**) (1.2 mmol, 185 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 4 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3c** (70 mg, 62%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-Methylindole-3-carboxylic Acid (1a) with *t*-Butyl Acrylate (2d) (entry 3 in Table 2): To a 20 mL two-necked flask were added 1-methylindole-3-carboxylic acid (**1a**) (0.4 mmol, 70 mg), *t*-butyl acrylate (**2d**) (1.2

mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 8 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3d** (56 mg, 54%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-(Methoxymethyl)indole-3-carboxylic Acid (1b) with Butyl Acrylate (2a) (entry 5 in Table 2): To a 20 mL two-necked flask were added 1-(methoxymethyl)indole-3-carboxylic acid (**1b**) (0.4 mmol, 82 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 8 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3f** (57 mg, 50%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-Phenylindole-3-carboxylic Acid (1c) with Butyl Acrylate (2a) (entry 6 in Table 2): To a 20 mL two-necked flask were added 1-phenylindole-3-carboxylic acid (**1c**) (0.4 mmol, 95 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 8 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3g** (54 mg, 43%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-(4-Methylphenyl)indole-3-carboxylic Acid (1d) with Butyl Acrylate (2a) (entry 7 in Table 2): To a 20 mL two-necked flask were added 1-(4-methylphenyl)indole-3-carboxylic acid (**1d**) (0.4 mmol, 100 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 4 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3h** (52 mg, 39%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of 1-Methylpyrrole-2-carboxylic Acid (6b) with Butyl Acrylate (2a) (entry 2 in Table 3): To a 20 mL two-necked flask were added 1-methylpyrrole-2-carboxylic acid (**6b**) (0.4 mmol, 50 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 1 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **7b** (52 mg, 62%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of Benzo[*b*]furan-2-carboxylic Acid (6c) with Butyl Acrylate (2a) (entry 3 in Table 3): To a 20 mL two-necked flask were added benzo[*b*]furan-2-carboxylic acid (**6c**) (0.4 mmol, 65 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 °C for 4 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. **7c** (36 mg, 37%) was obtained as a mixture of C3- and C2-vinylated products (C3:C2 > 95:5) by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of Benzo[*b*]thiophene-2-carboxylic Acid (6d) with Butyl Acrylate (2a) (entry 4 in Table 3): To a 20 mL two-necked flask were added benzo[*b*]thiophene-2-carboxylic acid (**6d**) (0.4 mmol, 71 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 120 °C for 4 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. **7d** (35 mg, 34%) was obtained as a mixture of C3- and C2-vinylated products (C3:C2 = 7:1) by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Procedure for the Reaction of Furan-2-carboxylic Acid (6e) with Butyl Acrylate (2a) (entry 5 in Table 3): To a 20 mL two-necked flask were added furan-2-carboxylic acid (**6e**) (0.4 mmol, 45 mg), butyl acrylate (**2a**) (1.2 mmol, 154 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), $Cu(OAc)_2$•H_2O (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), MS4A (400mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (10 mL). The resulting mixture was stirred under N_2 at 140 ºC for 5 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. **7e** (23 mg, 30%) was obtained as a mixture of C3- and C2-vinylated products (C3:C2 = ~1:1) by thin-layer chromatography on silica gel using hexane-ethyl acetate (95:5, v/v).

Characterization Data of Products.

Butyl (*E*)-3-(1-Methylindol-2-yl)-2-propenoate (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.39-1.49 (m, 2H), 1.66-1.73 (m, 2H), 3.75 (s, 3H), 4.22 (t, *J* = 6.5 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.92 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.21-7.27 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.3, 30.0, 30.9, 64.5, 103.7, 109.6, 118.2, 120.5, 121.4, 123.6, 127.5, 132.6, 135.0, 139.1, 167.2; HRMS m/z (M^+) Calcd for $C_{16}H_{19}NO_2$: 257.1416. Found 257.1413.

Ethyl (*E*)-3-(1-Methylindol-2-yl)-2-propenoate (3b): mp 84-87 ºC (lit.[14] 119 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.0 Hz, 3H), 3.80 (s, 3H), 4.28 (q, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.94 (s, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 7.23-7.31 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 30.0, 60.5, 103.7, 109.6, 118.2, 120.4, 121.3, 123.5, 127.4, 132.6, 134.9, 139.0, 167.0; HRMS m/z (M^+) Calcd for $C_{14}H_{15}NO_2$: 229.1103. Found 229.1100.

Cyclohexyl (*E*)-3-(1-Methylindol-2-yl)-2-propenoate (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.60 (m, 6H), 1.77-1.80 (m, 2H), 1.92-1.96 (m, 2H), 3.83 (s, 3H), 4.87-4.94 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.95 (s, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 7.26 (dd, *J* = 8.1, 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 25.4, 30.1, 31.8, 72.8, 103.6, 109.6, 118.9, 120.4, 121.3, 123.5, 127.5, 132.4, 135.0, 139.0, 166.5; HRMS m/z (M^+) Calcd for $C_{18}H_{21}NO_2$: 283.1572. Found 283.1590.

***t*-Butyl (*E*)-3-(1-Methylindol-2-yl)-2-propenoate (3d)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 9H), 3.79 (s, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.92 (s, 1H), 7.08-7.12 (m, 1H), 7.22-7.31 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 30.0, 80.6, 103.3, 109.6, 120.3, 120.4, 121.3, 123.4, 127.5, 131.7, 135.2, 139.0, 166.40; HRMS m/z (M^+) Calcd for $C_{16}H_{19}NO_2$: 257.1416. Found 257.1413.

(*E*)-1-Methyl-3-(2-phenylethenyl)indole (3e): mp 114-118 ºC (lit.[15] 119 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.80 (s, 1H), 7.07-7.12 (m, 1H), 7.16-7.30 (m, 5H), 7.35-7.39 (m, 2H), 7.51-7.53 (m, 2H), 7.58 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.9, 99.0, 109.1, 117.0, 119.9, 120.4, 121.7, 126.4, 127.8, 128.8, 130.1, 130.9, 137.1, 138.1, 138.4; HRMS m/z (M^+) Calcd for $C_{17}H_{15}N$: 233.1204. Found 233.1202.

Butyl (*E*)-3-[1-(Methoxymethyl)indol-2-yl]-2-propenoate (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.40-1.49 (m, 2H), 1.66-1.74 (m, 2H), 3.27 (s, 3H), 4.22 (t, *J* = 6.6 Hz, 2H), 5.54 (s, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.99 (s, 1H), 7.13-7.17 (m, 1H), 7.26-7.30 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.2, 30.8, 55.9, 64.6, 73.8, 105.9, 109.8, 119.2, 121.2, 121.5, 124.2, 127.8, 132.4, 135.2, 139.3, 167.0; HRMS m/z (M^+) Calcd for $C_{17}H_{21}NO_3$: 287.1521. Found 287.1516.

Butyl (*E*)-3-(1-Phenylindol-2-yl)-2-propenoate (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.33-1.43 (m, 2H), 1.59-1.66 (m, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 7.09 (s, 1H), 7.13-7.21 (m, 3H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.47-7.57 (m, 4H), 7.66 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.2, 30.8, 64.4, 105.1, 110.8, 118.2, 121.2, 121.3, 124.1, 127.6, 128.3, 128.4, 129.8, 133.4, 135.3, 136.9, 139.8, 167.0; HRMS m/z (M^+) Calcd for $C_{21}H_{21}NO_2$: 319.1572. Found 319.1568.

Butyl (*E*)-3-[1-(4-Methylphenyl)indol-2-yl]-2-propenoate (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.34-1.43 (m, 2H), 1.58-1.67 (m, 2H), 2.46 (s, 3H), 4.14 (t, *J* = 6.6 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 7.07 (s, 1H), 7.11-7.24 (m, 5H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 15.8 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 21.2, 30.7, 64.3, 104.7, 110.8, 118.1, 121.0, 121.2, 123.9, 127.5, 128.0, 130.3, 133.5, 134.2, 135.4, 138.4, 139.8, 167.0; HRMS m/z (M^+) Calcd for $C_{22}H_{23}NO_2$: 333.1729. Found 333.1737.

Butyl (*E*)-3-(1-Methylindol-3-yl)-2-propenoate (5 = 7a):[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.41-1.50 (m, 2H), 1.66-1.73 (m, 2H), 3.75 (s, 3H), 4.21 (t, *J* = 6.5 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 7.22-7.32 (m, 4H), 7.85-7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.3, 31.0, 33.1, 64.0, 109.9, 112.1, 112.6, 120.6, 121.3, 122.9, 126.1, 133.1, 137.9, 138.1, 168.5; HRMS m/z (M^+) Calcd for $C_{16}H_{19}NO_2$: 257.1416. Found 257.1418.

Butyl (*E*)-3-(1-Methylpyrrol-3-yl)-2-propenoate (7b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.38-1.47 (m, 2H), 1.63-1.70 (m, 2H), 3.67 (s, 3H), 4.16 (t, *J* = 6.6 Hz, 2H), 6.07 (d, *J* = 15.8 Hz, 1H), 6.36-6.37 (m, 1H), 6.57 (t, *J* = 2.6 Hz, 1H), 6.83 (t, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.9, 36.3, 63.8, 106.9, 112.8, 120.8, 123.8, 124.9, 138.7, 168.2; HRMS m/z (M^+) Calcd for $C_{12}H_{17}NO_2$: 207.1259. Found 207.1263.

Butyl (*E*)-3-(Benzo[*b*]furan-3-yl)-2-propenoate (7c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3H), 1.41-1.50 (m, 2H), 1.67-1.74 (m, 2H), 4.23 (t, *J* = 6.5 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 7.32-7.40 (m, 2H), 7.52-7.54 (m, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.84-7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.8, 64.5, 112.0, 117.9, 118.5, 121.0, 123.7, 124.8, 125.4, 134.4, 147.7, 156.1, 167.2; HRMS m/z (M^+) Calcd for $C_{15}H_{16}O_3$: 244.1099. Found 244.1102.

Butyl (*E*)-3-(Benzo[*b*]thien-3-yl)-2-propenoate (7d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3H), 1.41-1.51 (m, 2H), 1.68-1.75 (m, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 7.39-7.48 (m, 2H), 7.75 (s, 1H), 7.88 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 15.8 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.8, 64.5, 118.7, 122.1, 123.0, 124.9, 125.0, 128.0, 131.7, 136.3, 137.1, 140.5, 167.2; HRMS m/z (M^+) Calcd for $C_{15}H_{16}O_2S$: 260.0871. Found 260.0867.

Butyl (*E*)-3-(Furanyl)-2-propenoate (7e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.3 Hz, 6H), 1.38-1.47 (m, 4H), 1.64-1.71 (m, 4H), 4.17-4.21 (m, 4H), 6.16 (d, *J* = 15.8 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.46 (dd, *J* = 1.8, 1.8 Hz, 1H), 6.59-6.61 (m, 2H), 7.40-7.44 (m, 2H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.57 (d, *J* = 15.8 Hz, 1H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.7, 64.3, 64.3, 107.4, 112.2, 114.5, 116.0, 118.0, 122.6, 130.9, 134.5, 144.3, 144.4, 144.6, 150.9, 167.06, 167.13; HRMS m/z (M^+) Calcd for $C_{11}H_{14}O_3$: 194.0943. Found 194.0945.

Butyl (*E*)-3-(Thien-3-yl)-2-propenoate (7f):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.72 (m, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 6.27 (d, *J* = 15.8 Hz, 1H), 7.29-7.37 (m, 2H), 7.49-7.50 (m, 1H), 7.66 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.8, 64.3, 117.9, 125.1, 126.9, 127.9, 137.6, 138.0, 167.3; HRMS m/z (M^+) Calcd for $C_{11}H_{14}O_2S$: 210.0715. Found 210.0724.

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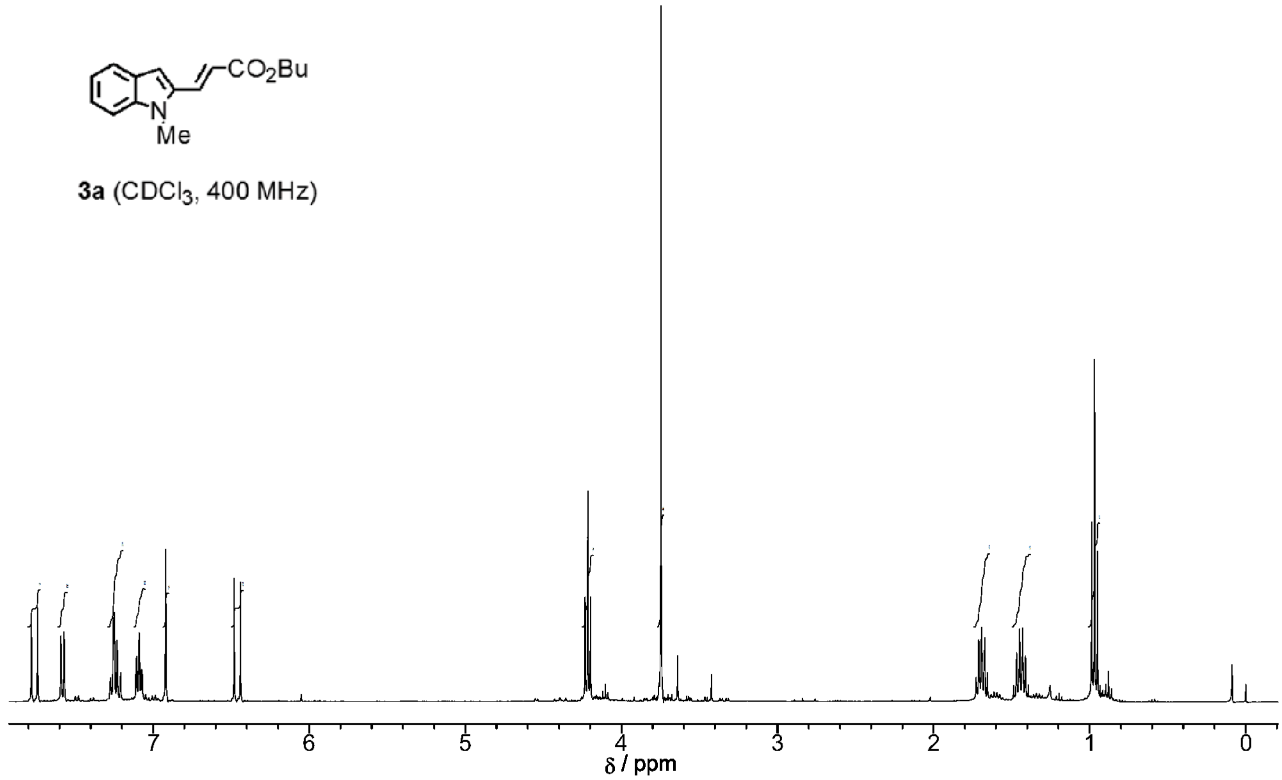
3a ($CDCl_3$, 400 MHz)



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6	123.59	12301.9	54.06
7	121.40	12083.5	82.54
8	120.45	11989.2	67.11
9	118.23	11768.5	82.60
10	109.64	10913.0	87.02
11	103.72	10324.0	55.55
12	77.44	7708.3	41.29
13	77.12	7676.4	44.02
14	76.80	7644.4	43.36
15	64.51	6420.6	70.50
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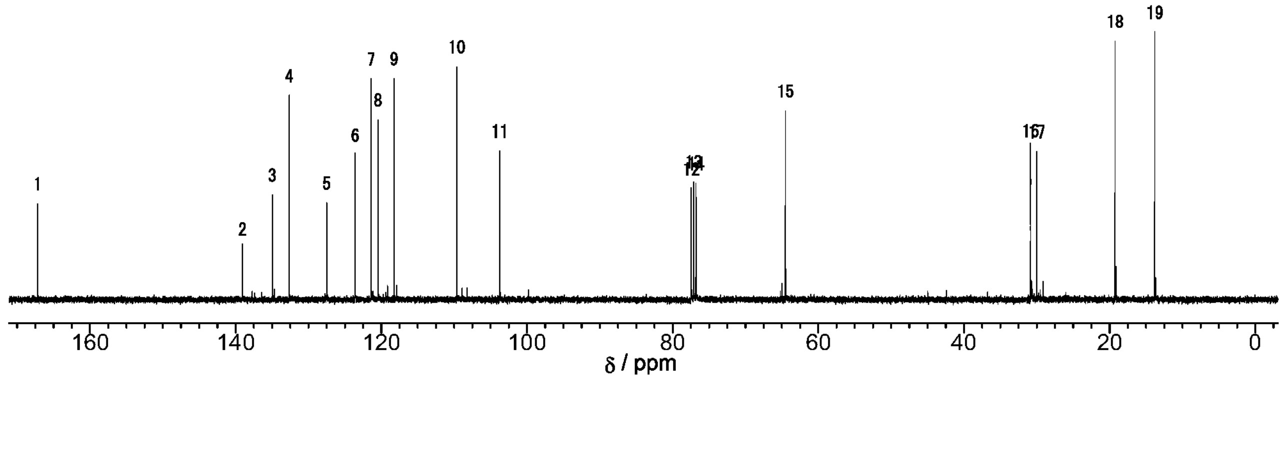
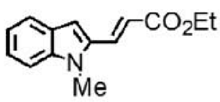
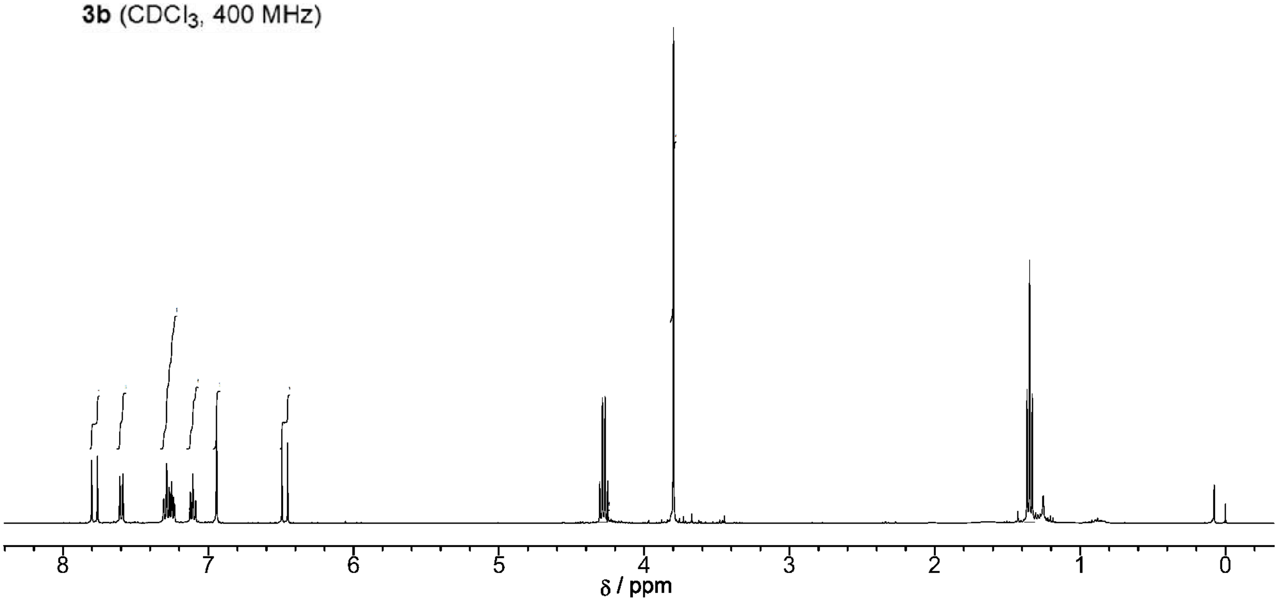
19	13.80	1373.4	100

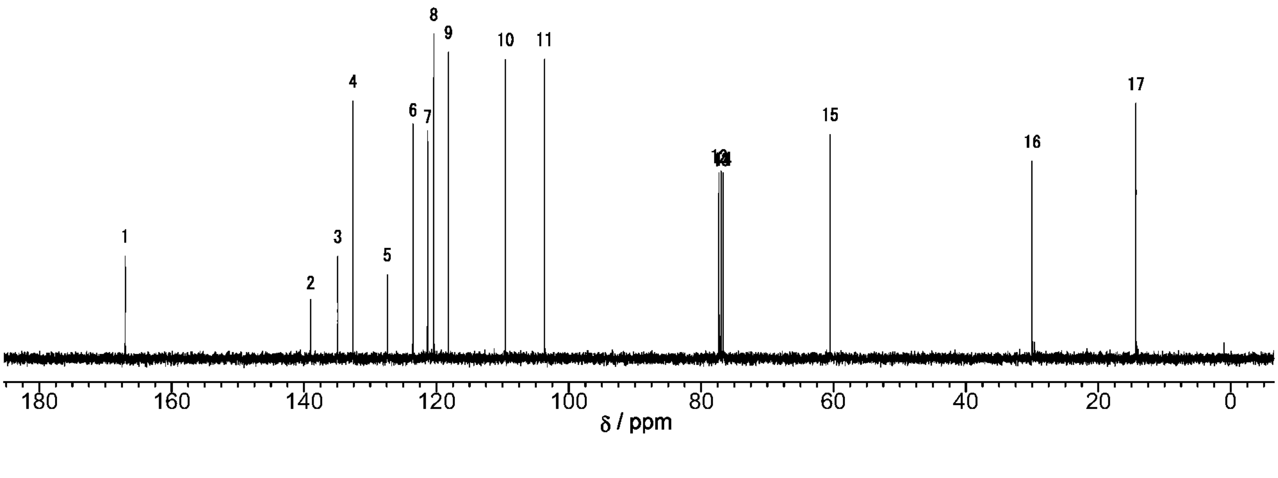


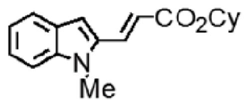


3b ($CDCl_3$, 400 MHz)

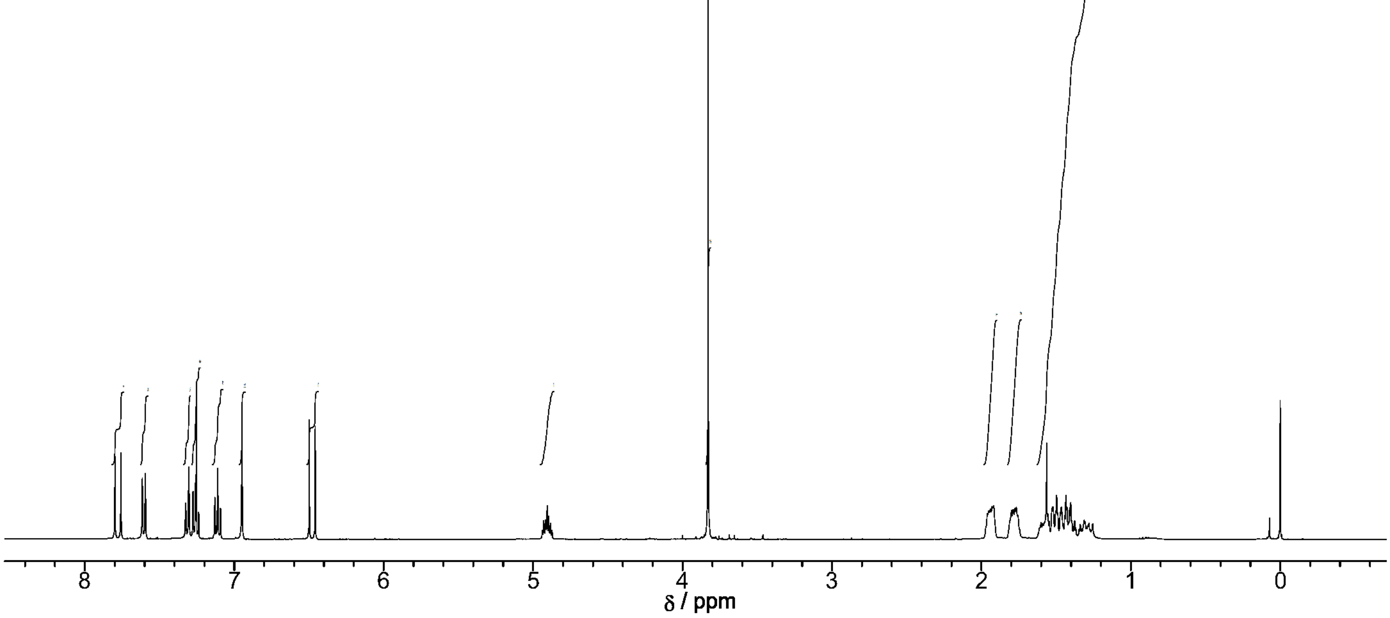


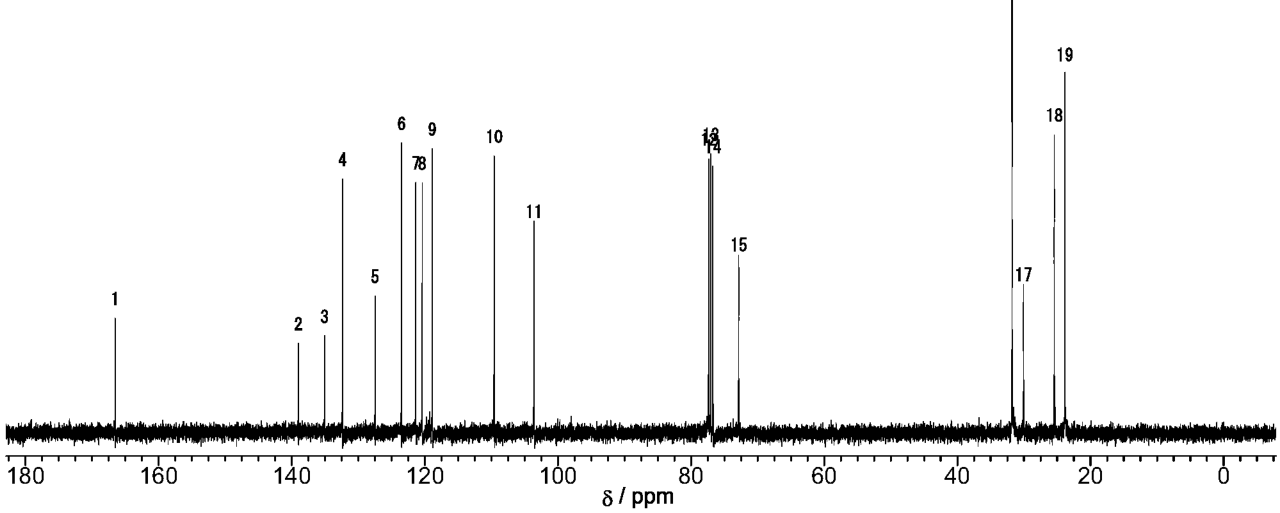
No.	ppm	Hz	Height
1	167.01	16788.9	31.62
2	138.99	13972.1	17.25
3	134.90	13560.9	31.47
4	132.60	13329.7	79.42
5	127.40	12807.1	25.84
6	123.54	12418.8	70.58
7	121.33	12196.8	68.48
8	120.39	12102.2	100
9	118.17	11879.4	94.45
10	109.57	11015.0	92.23
11	103.66	10420.7	92.30
12	77.32	7772.5	56.24
13	77.00	7740.5	55.21
14	76.69	7709.2	55.45
15	60.53	6084.9	69.12
16	30.01	3016.3	60.78
17	14.33	1440.1	78.68





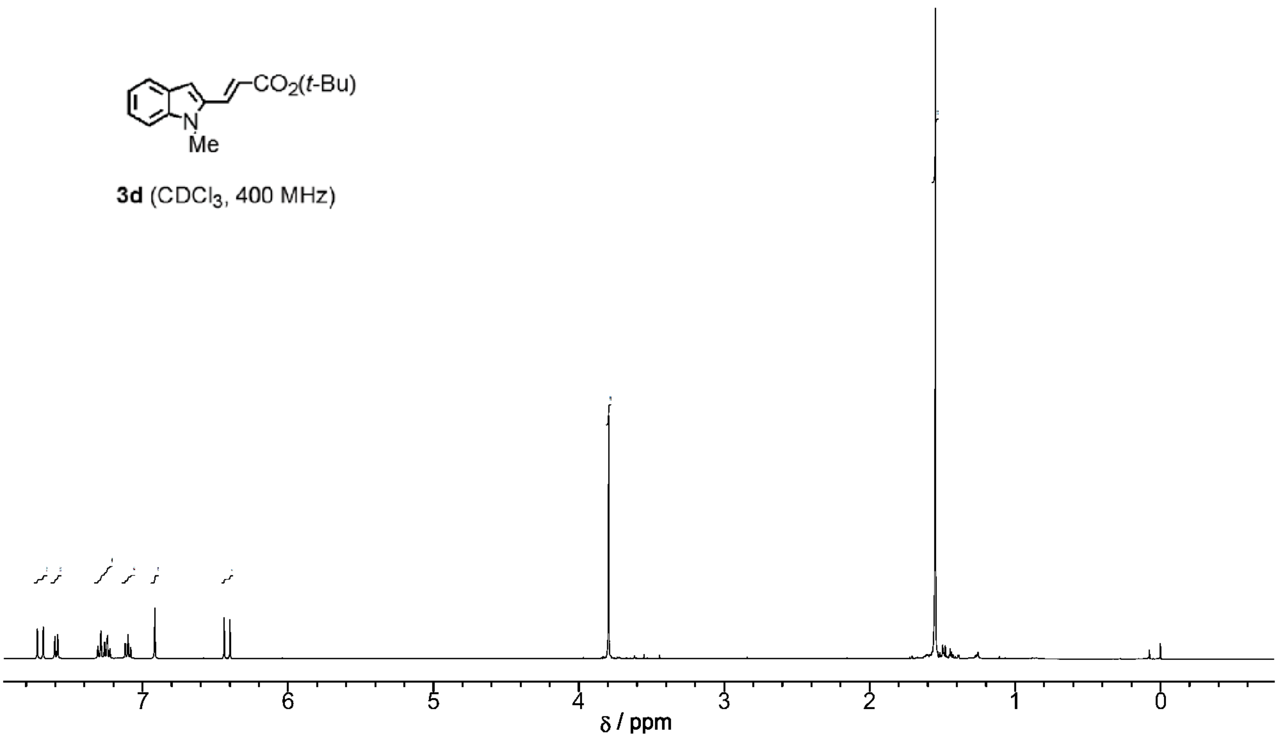
3c (CDCl$_3$, 400 MHz)



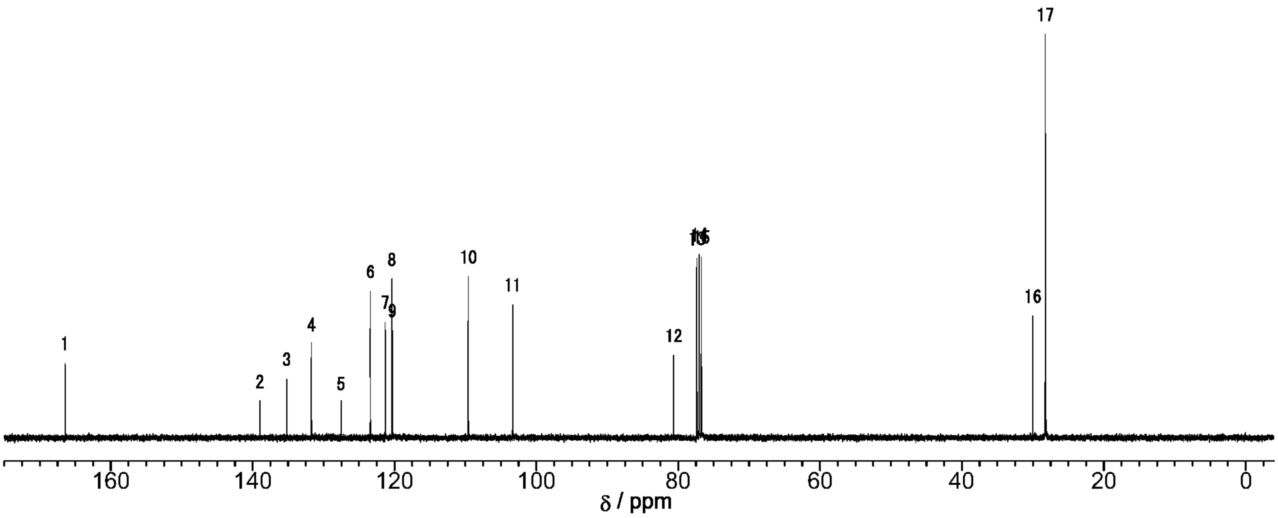


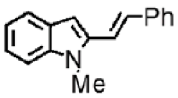
No.	ppm	Hz	Height
1	166.50	16737.8	21.30
2	138.99	13972.1	16.58
3	135.04	13575.4	17.99
4	132.36	13305.3	47.21
5	127.46	12812.5	25.38
6	123.49	12414.2	53.91
7	121.35	12198.3	46.58
8	120.38	12101.4	46.48
9	118.86	11948.8	52.87
10	109.59	11016.5	51.50
11	103.59	10413.8	37.50
12	77.36	7776.3	50.93
13	77.04	7744.3	51.86
14	76.72	7712.2	49.60
15	72.85	7323.1	31.34
16	31.78	3194.9	100
17	30.06	3021.7	25.76
18	25.44	2557.0	55.47
19	23.85	2397.6	66.76

3d ($CDCl_3$, 400 MHz)

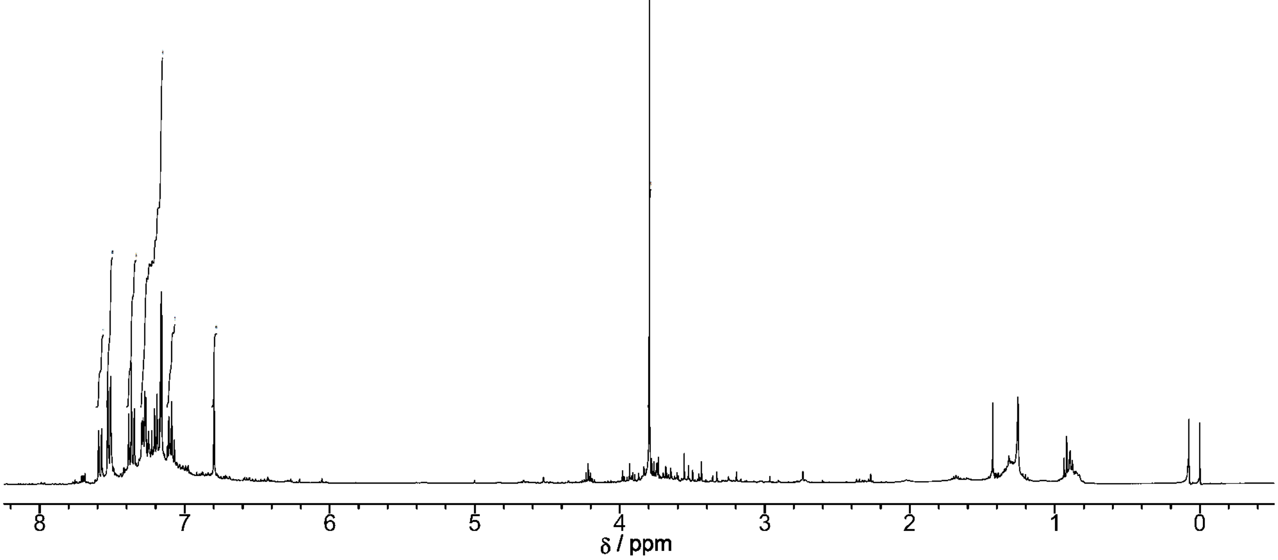


No.	ppm	Hz	Height
1	166.44	16566.3	18.40
2	138.97	13832.6	9.03
3	135.18	13455.1	14.47
4	131.70	13108.9	23.14
5	127.53	12693.3	8.48
6	123.40	12282.4	36.22
7	121.31	12074.6	28.62
8	120.36	11980.2	39.29
9	120.29	11972.6	26.55
10	109.59	10907.9	39.89
11	103.34	10286.2	32.88
12	80.63	8025.9	20.36
13	77.37	7700.9	44.47
14	77.05	7669.0	45.40
15	76.73	7637.0	44.79
16	30.01	2987.1	30.13
17	28.25	2812.0	100

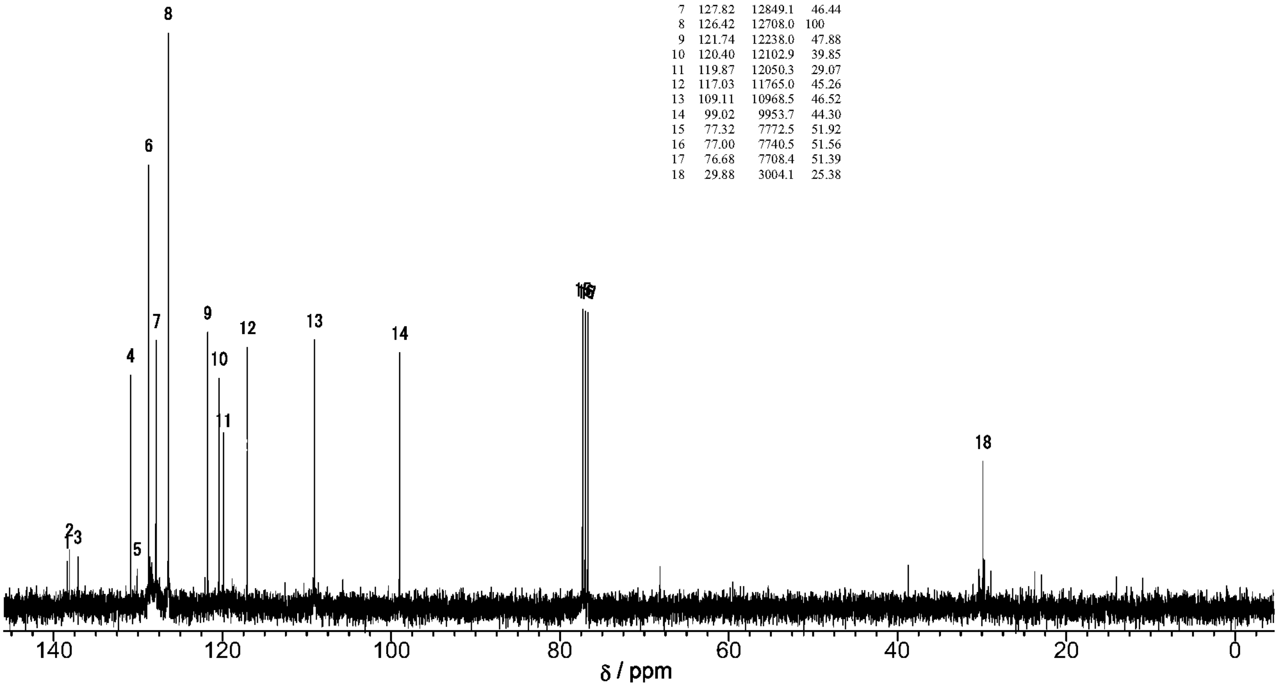


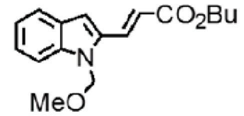


3e ($CDCl_3$, 400 MHz)

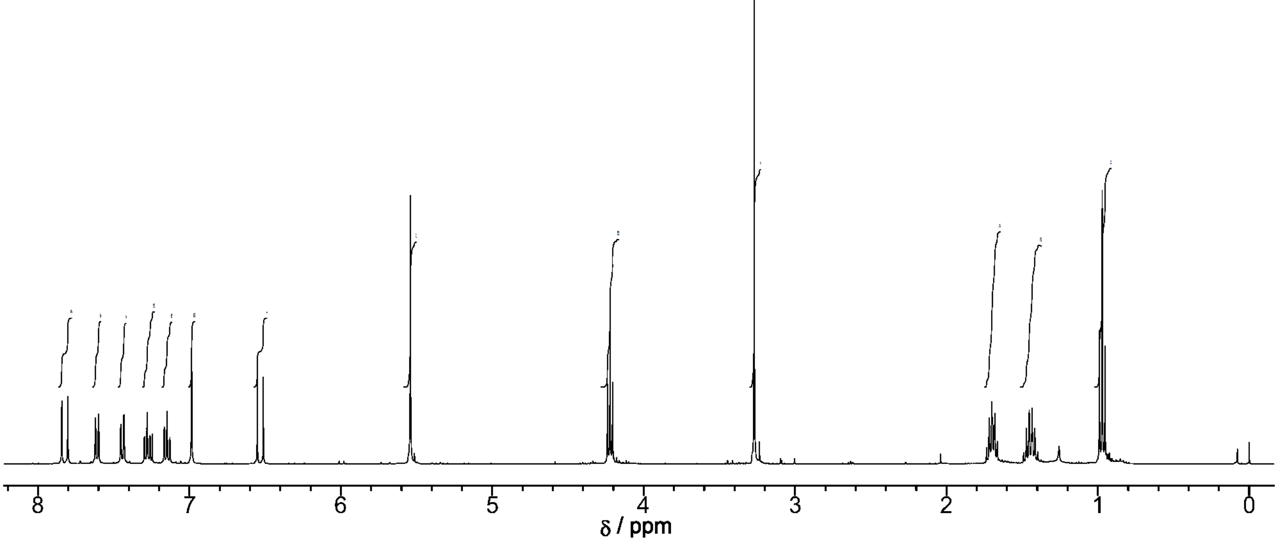


No.	ppm	Hz	Height
1	138.38	13911.1	7.99
2	138.13	13885.2	10.02
3	137.13	13785.2	8.76
4	130.89	13157.3	40.42
5	130.09	13077.2	6.67
6	128.75	12942.2	77.00
7	127.82	12849.1	46.44
8	126.42	12708.0	100
9	121.74	12238.0	47.88
10	120.40	12102.9	39.85
11	119.87	12050.3	29.07
12	117.03	11765.0	45.26
13	109.11	10968.5	46.52
14	99.02	9953.7	44.30
15	77.32	7772.5	51.92
16	77.00	7740.5	51.56
17	76.68	7708.4	51.39
18	29.88	3004.1	25.38

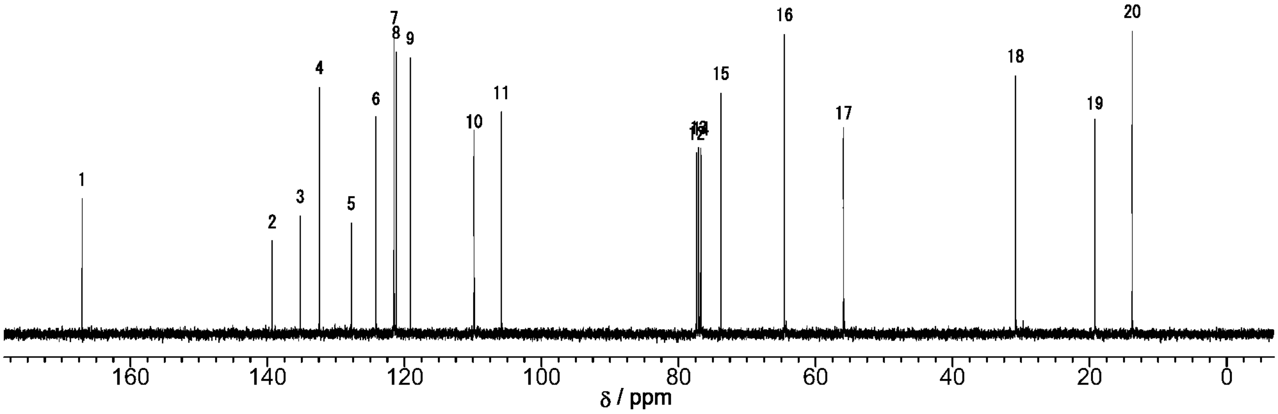


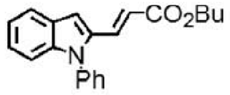


3f ($CDCl_3$, 400 MHz)

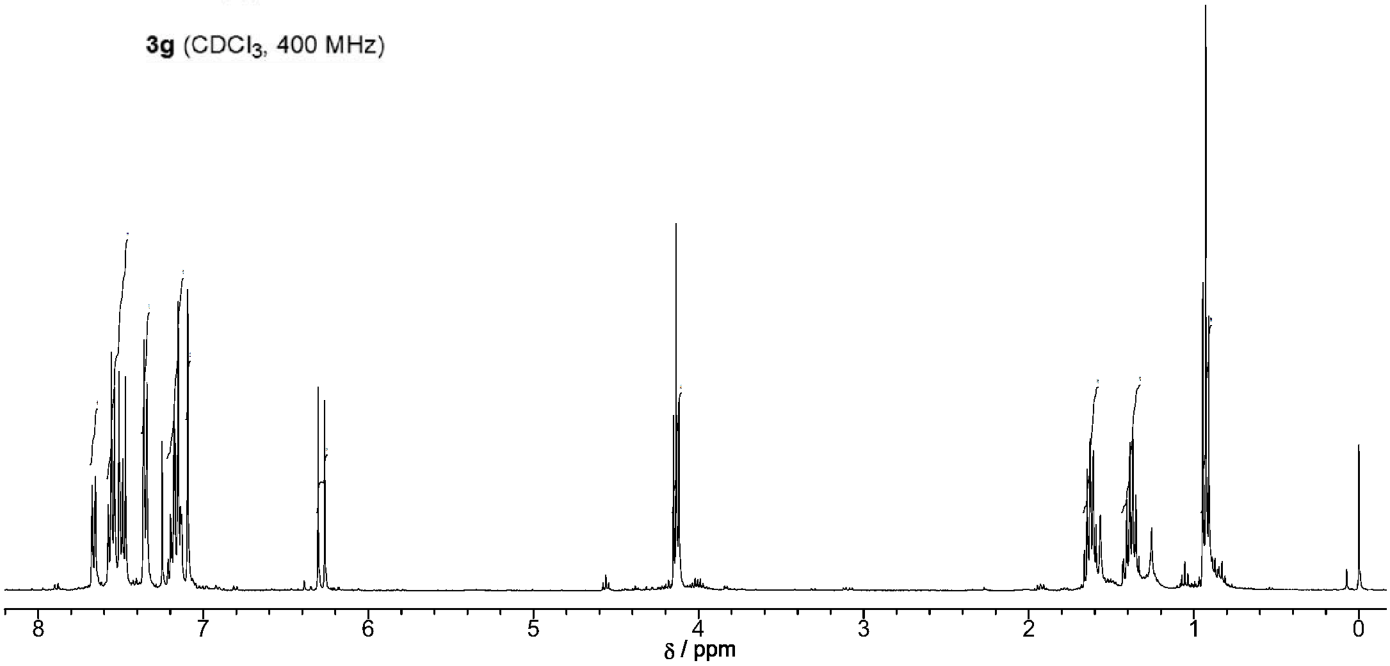


No.	ppm	Hz	Height
1	167.03	16790.8	44.48
2	139.29	14002.2	30.62
3	135.19	13590.2	38.83
4	132.42	13311.8	81.43
5	127.76	12843.3	36.56
6	124.18	12483.2	71.15
7	121.52	12215.4	97.93
8	121.20	12184.1	93.02
9	119.15	11977.4	91.10
10	109.84	11042.0	63.60
11	105.85	10640.7	73.22
12	77.39	7779.7	59.79
13	77.07	7747.7	61.58
14	76.75	7715.6	61.25
15	73.84	7422.6	79.51
16	64.55	6488.8	98.88
17	55.93	5622.1	66.43
18	30.82	3098.3	85.21
19	19.23	1933.3	69.69
20	13.78	1385.5	100

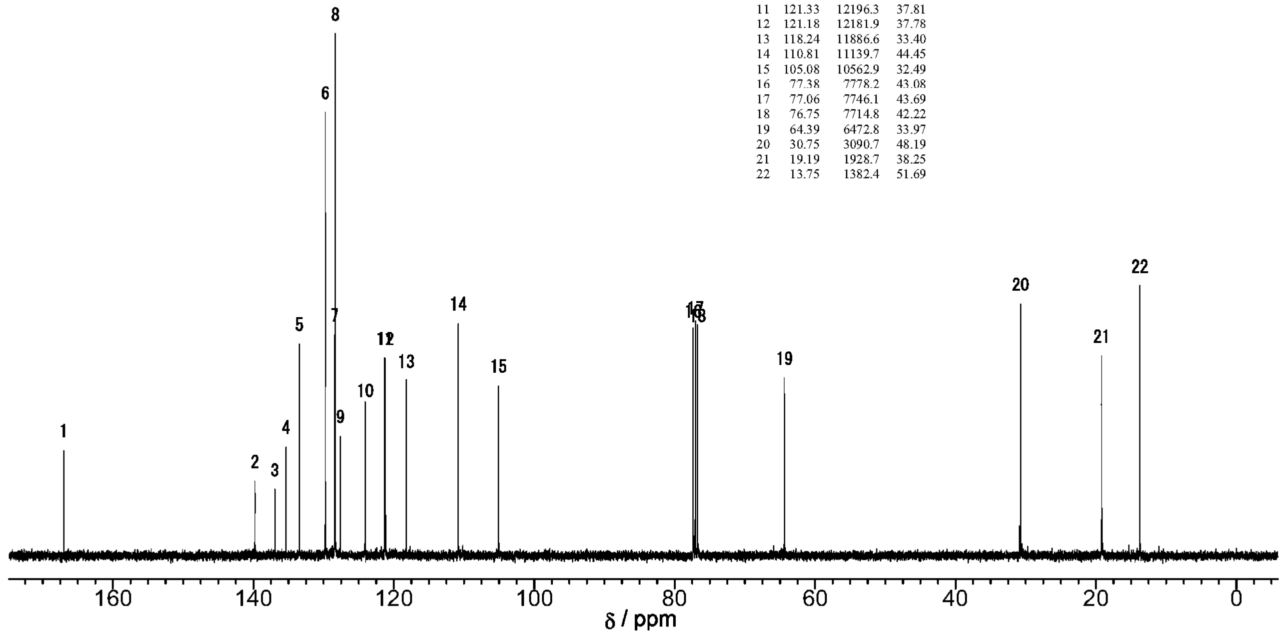


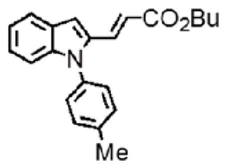


3g ($CDCl_3$, 400 MHz)

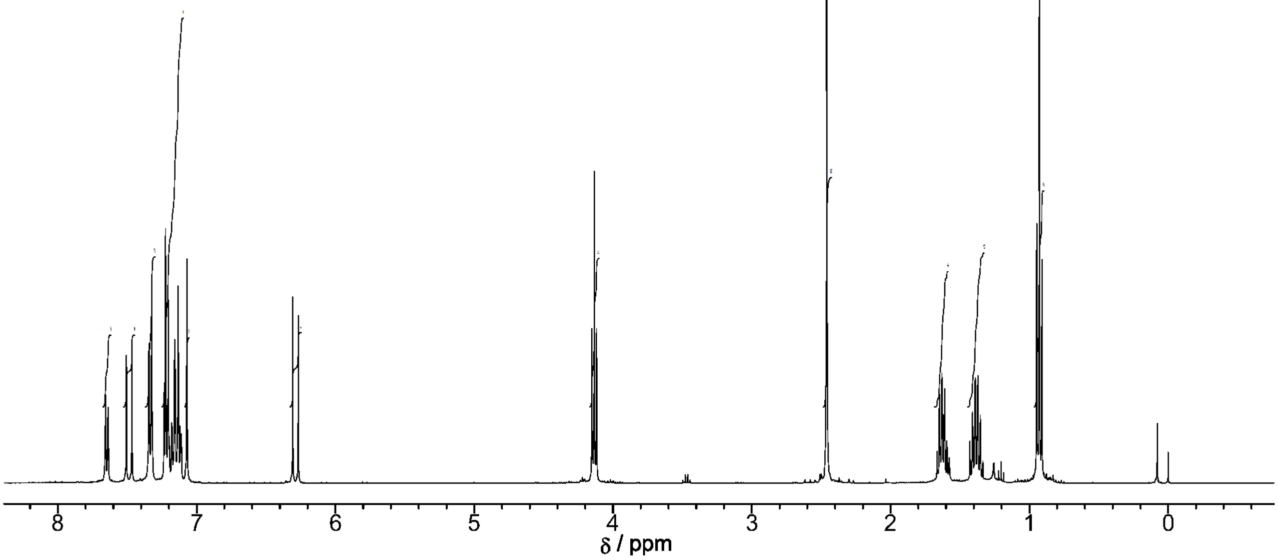


No.	ppm	Hz	Height
1	167.00	16787.7	20.13
2	139.78	14051.1	14.23
3	136.93	13765.0	12.60
4	135.34	13605.5	20.77
5	133.44	13414.0	40.52
6	129.75	13043.2	84.92
7	128.41	12908.9	42.31
8	128.31	12898.3	100
9	127.59	12825.8	22.80
10	124.08	12473.3	27.86
11	121.33	12196.3	37.81
12	121.18	12181.9	37.78
13	118.24	11886.6	33.40
14	110.81	11139.7	44.45
15	105.08	10562.9	32.49
16	77.38	7778.2	43.08
17	77.06	7746.1	43.69
18	76.75	7714.8	42.22
19	64.39	6472.8	33.97
20	30.75	3090.7	48.19
21	19.19	1928.7	38.25
22	13.75	1382.4	51.69

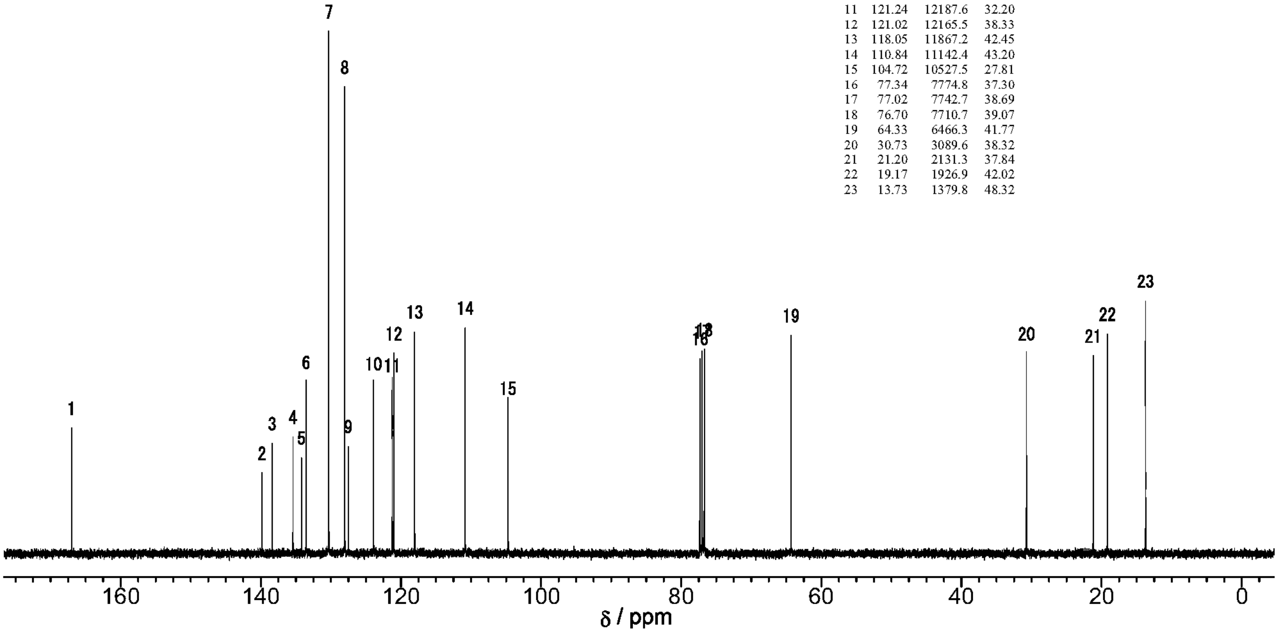


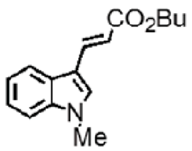


3h ($CDCl_3$, 400 MHz)

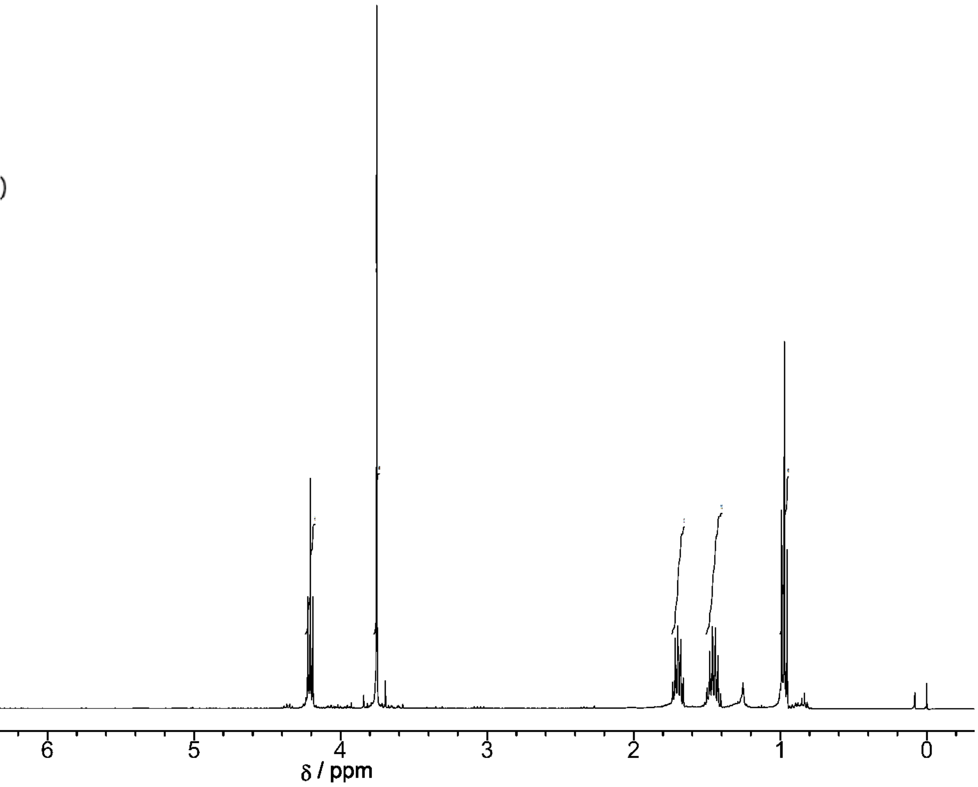


No.	ppm	Hz	Height
1	167.01	16788.9	24.00
2	139.83	14056.1	15.40
3	138.36	13908.8	21.03
4	135.40	13611.3	22.28
5	134.19	13489.2	18.31
6	133.54	13424.4	32.76
7	130.31	13099.3	100
8	128.02	12869.7	89.33
9	127.50	12817.1	20.46
10	123.93	12457.7	32.48
11	121.24	12187.6	32.20
12	121.02	12165.5	38.33
13	118.05	11867.2	42.45
14	110.84	11142.4	43.20
15	104.72	10527.5	27.81
16	77.34	7774.8	37.30
17	77.02	7742.7	38.69
18	76.70	7710.7	39.07
19	64.33	6466.3	41.77
20	30.73	3089.6	38.32
21	21.20	2131.3	37.84
22	19.17	1926.9	42.02
23	13.73	1379.8	48.32

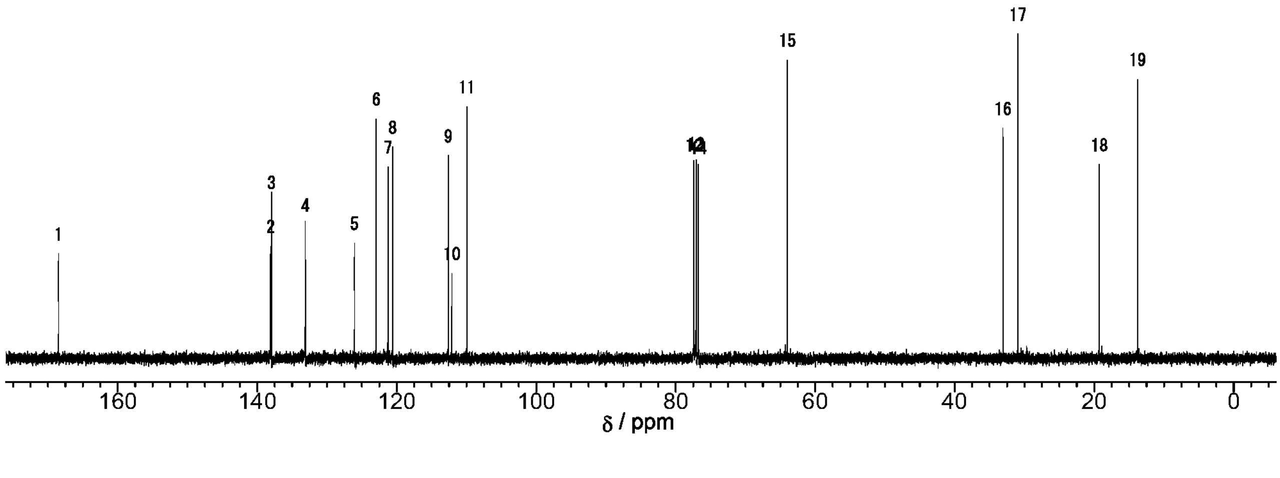


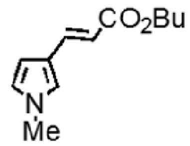


7a ($CDCl_3$, 400 MHz)

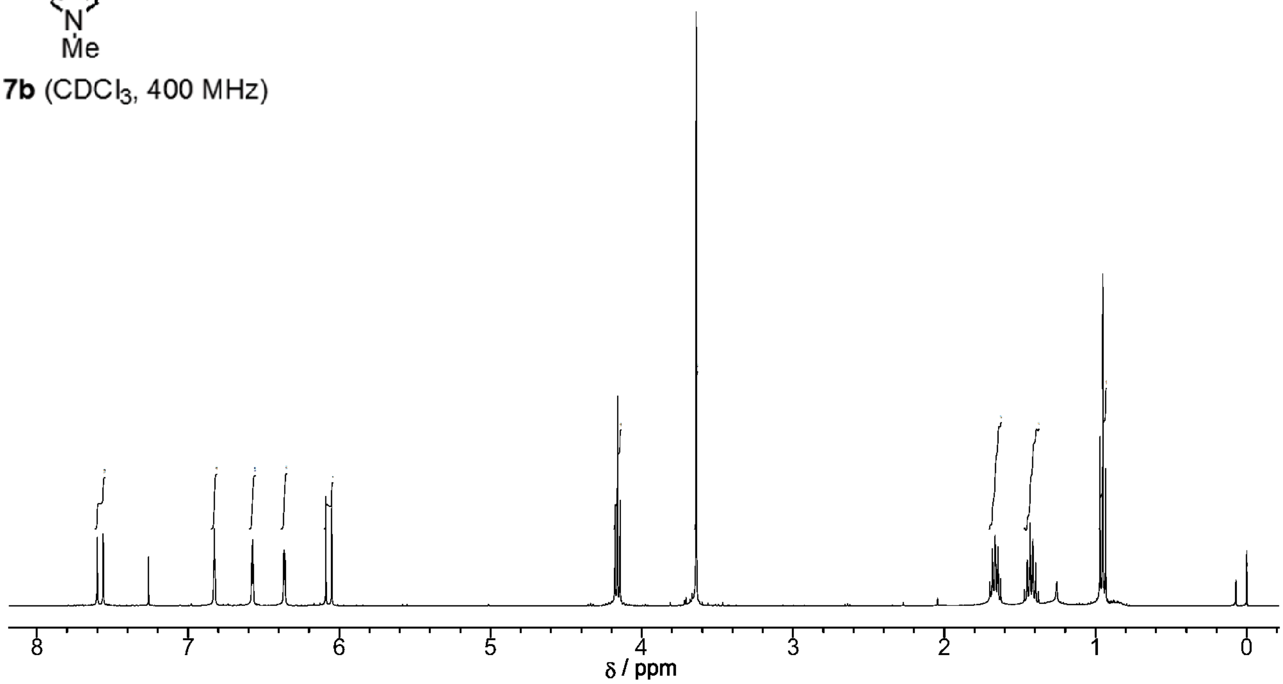


No.	ppm	Hz	Height
1	168.47	16768.5	32.26
2	138.08	13743.3	34.60
3	137.94	13729.6	48.17
4	133.11	13248.7	41.17
5	126.05	12546.2	35.49
6	122.94	12236.5	73.86
7	121.25	12068.3	59.01
8	120.58	12002.1	65.22
9	112.61	11208.3	62.54
10	112.09	11156.6	26.26
11	109.94	10942.7	77.63
12	77.39	7703.0	59.74
13	77.07	7671.0	60.16
14	76.75	7639.1	58.81
15	63.98	6368.1	91.98
16	33.10	3294.3	70.93
17	30.96	3081.2	100
18	19.27	1918.4	59.77
19	13.80	1373.4	86.14

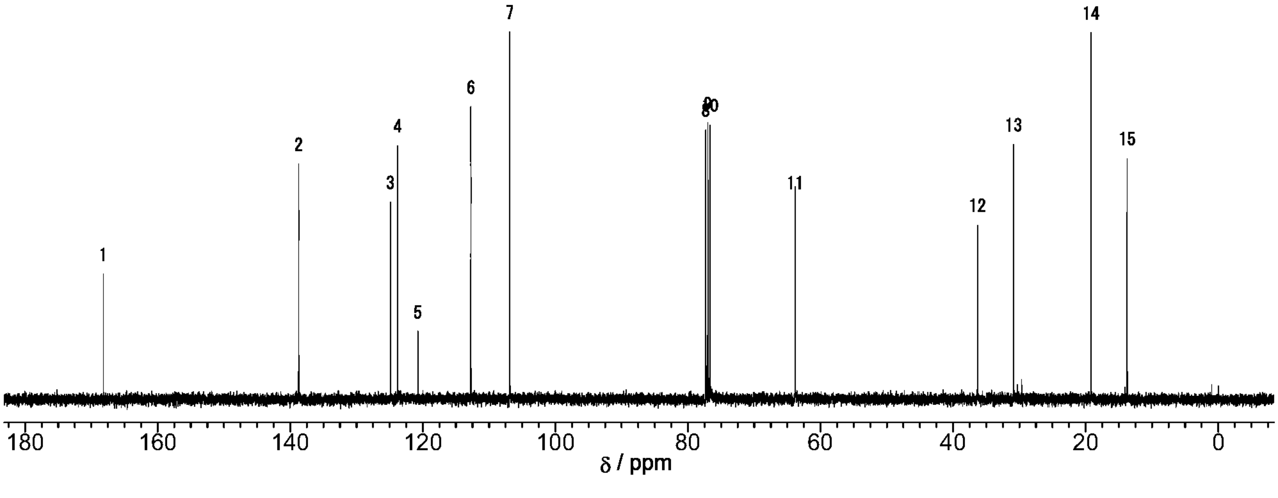


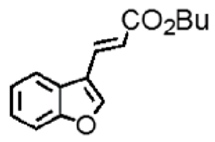


7b ($CDCl_3$, 400 MHz)

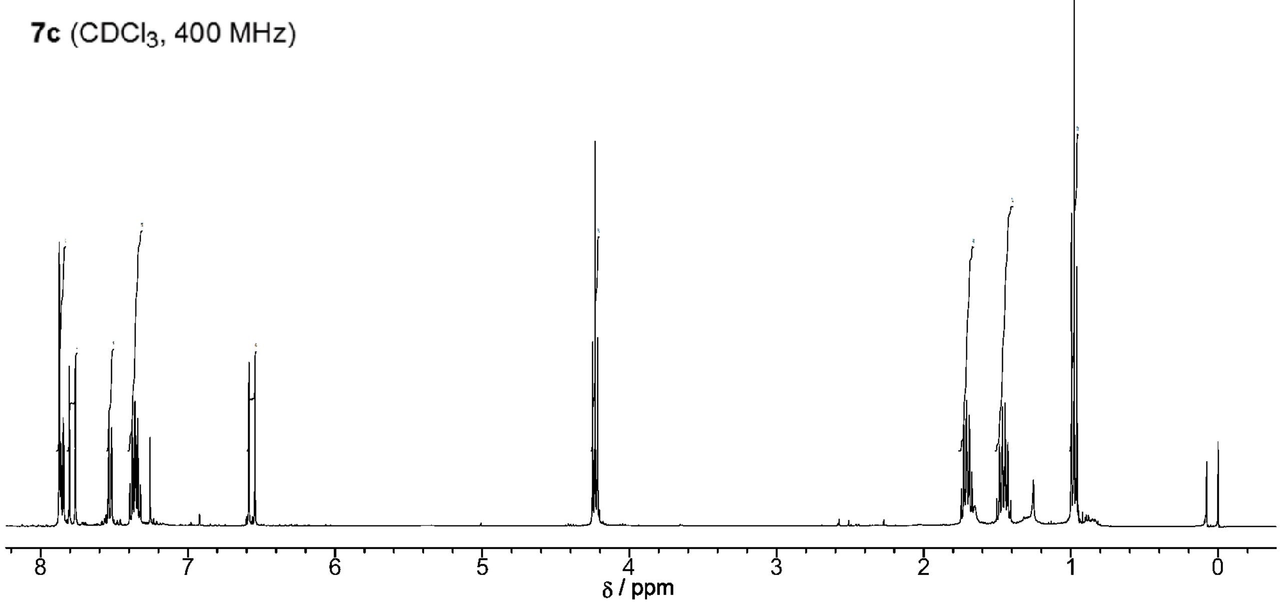


No.	ppm	Hz	Height
1	168.19	16907.2	33.98
2	138.73	13946.2	64.04
3	124.88	12553.8	53.57
4	123.80	12444.7	68.99
5	120.75	12138.8	18.25
6	112.75	11334.7	79.60
7	106.90	10745.7	100
8	77.32	7772.5	73.27
9	77.00	7740.5	75.17
10	76.68	7708.4	74.59
11	63.82	6416.0	53.50
12	36.33	3651.9	47.38
13	30.86	3102.5	69.30
14	19.20	1929.9	99.82
15	13.74	1381.4	65.54

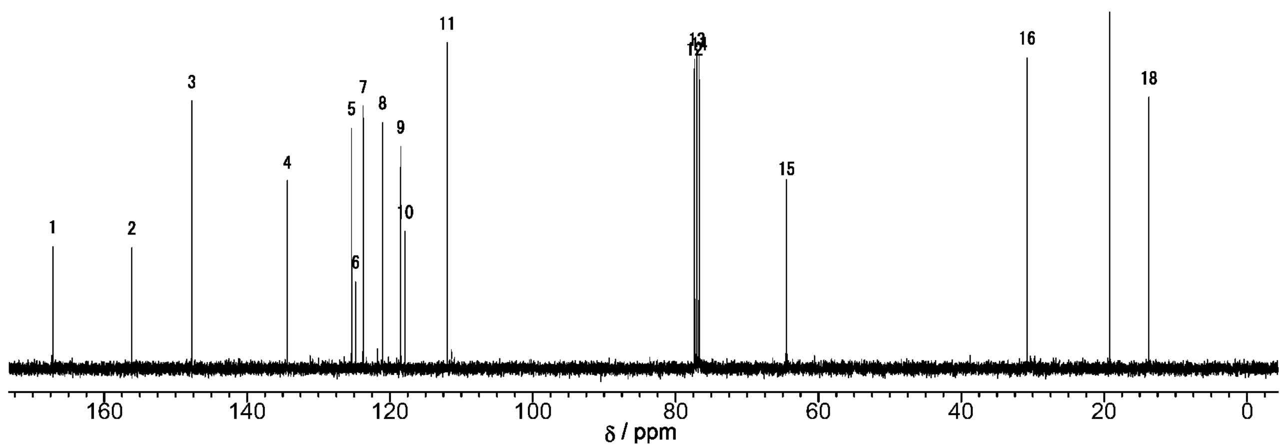


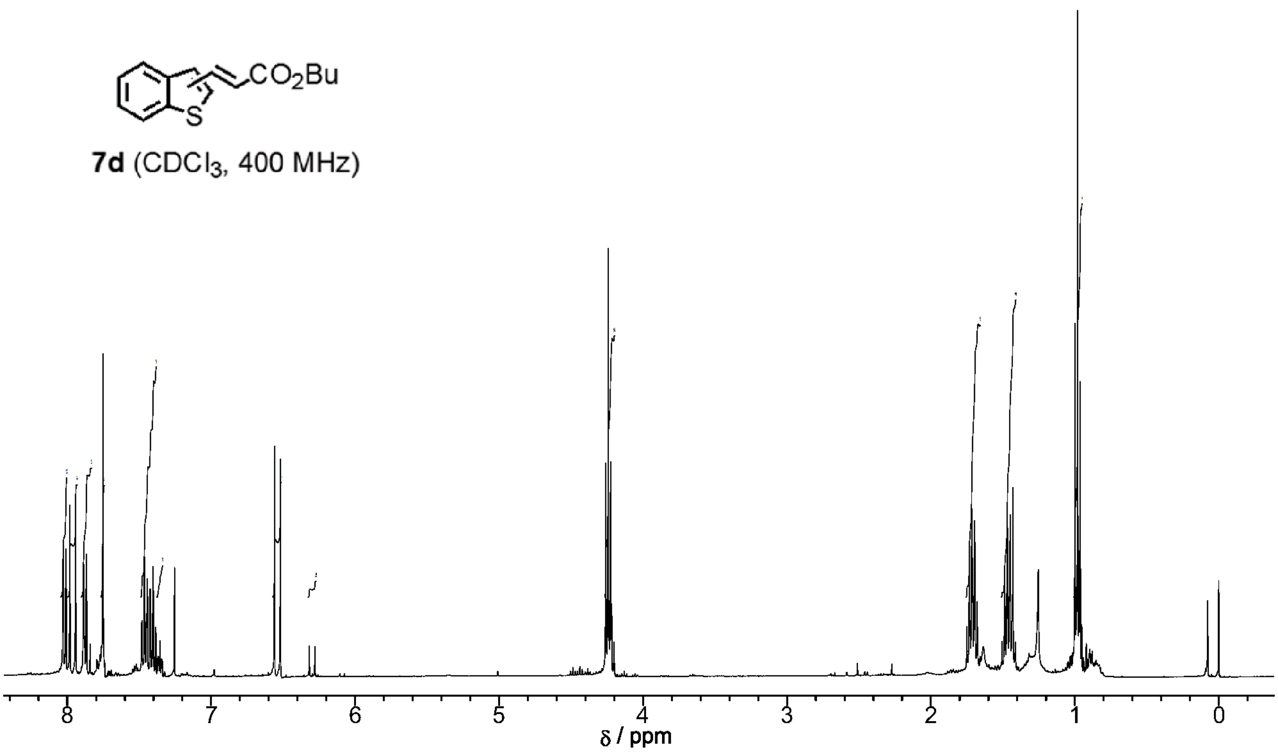


7c ($CDCl_3$, 400 MHz)



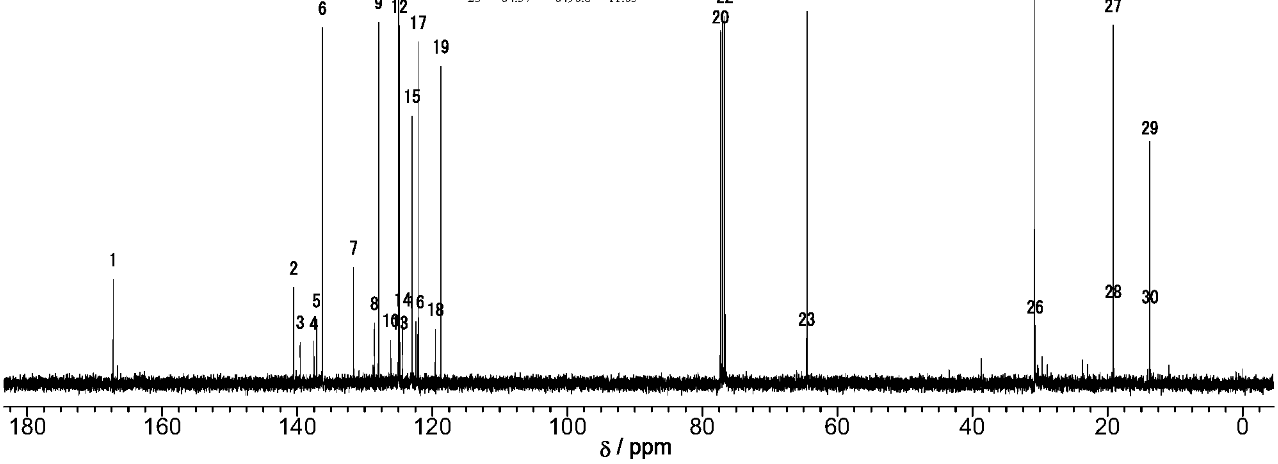
No.	ppm	Hz	Height
1	167.19	16641.4	34.14
2	156.12	15539.4	33.80
3	147.72	14703.0	74.94
4	134.35	13372.7	52.24
5	125.36	12477.7	67.25
6	124.80	12422.2	24.31
7	123.74	12316.4	73.48
8	121.02	12045.5	68.88
9	118.47	11792.0	62.17
10	117.89	11734.2	38.38
11	111.98	11145.9	91.26
12	77.34	7698.4	84.04
13	77.02	7666.5	86.78
14	76.70	7634.5	85.44
15	64.45	6415.3	50.45
16	30.80	3066.0	87.11
17	19.20	1911.5	100
18	13.74	1367.4	76.00



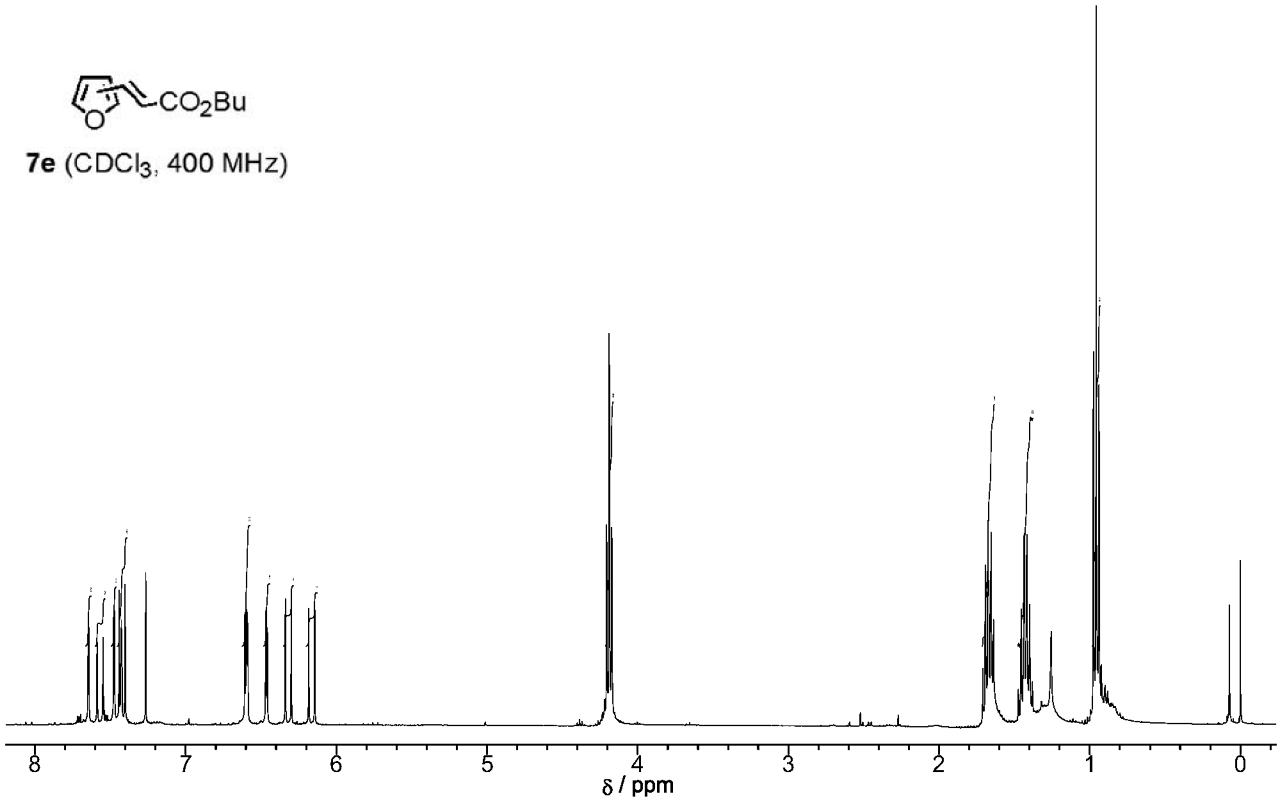


7d ($CDCl_3$, 400 MHz)

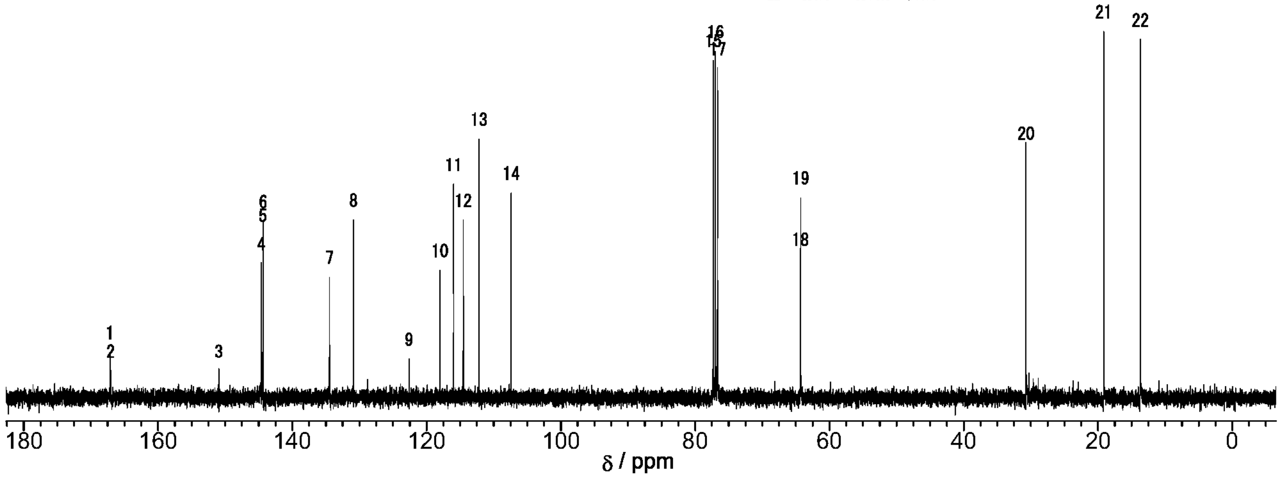
No.	ppm	Hz	Height	No.	ppm	Hz	Height
1	167.22	16810.3	25.77	24	64.49	6483.1	92.21
2	140.50	14124.0	23.71	25	30.79	3094.9	100
3	139.54	14027.1	10.23	26	30.74	3090.3	14.05
4	137.53	13825.7	10.03	27	19.21	1930.7	88.79
5	137.12	13784.5	15.56	28	19.18	1927.6	17.81
6	136.27	13698.2	88.14	29	13.74	1381.4	58.50
7	131.66	13235.1	28.71	30	13.72	1379.1	16.51
8	128.54	12921.6	14.91				
9	127.95	12862.1	89.58				
10	126.16	12682.0	10.65				
11	125.01	12566.8	97.33				
12	124.91	12556.9	88.59				
13	124.81	12547.0	10.16				
14	124.37	12502.7	15.86				
15	122.98	12363.1	66.22				
16	122.43	12307.4	15.27				
17	122.09	12273.1	84.57				
18	119.53	12016.0	13.40				
19	118.74	11936.6	78.58				
20	77.33	7773.3	85.97				
21	77.01	7741.2	92.11				
22	76.69	7709.2	91.03				
23	64.57	6490.8	11.03				

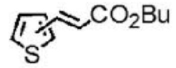


7e ($CDCl_3$, 400 MHz)

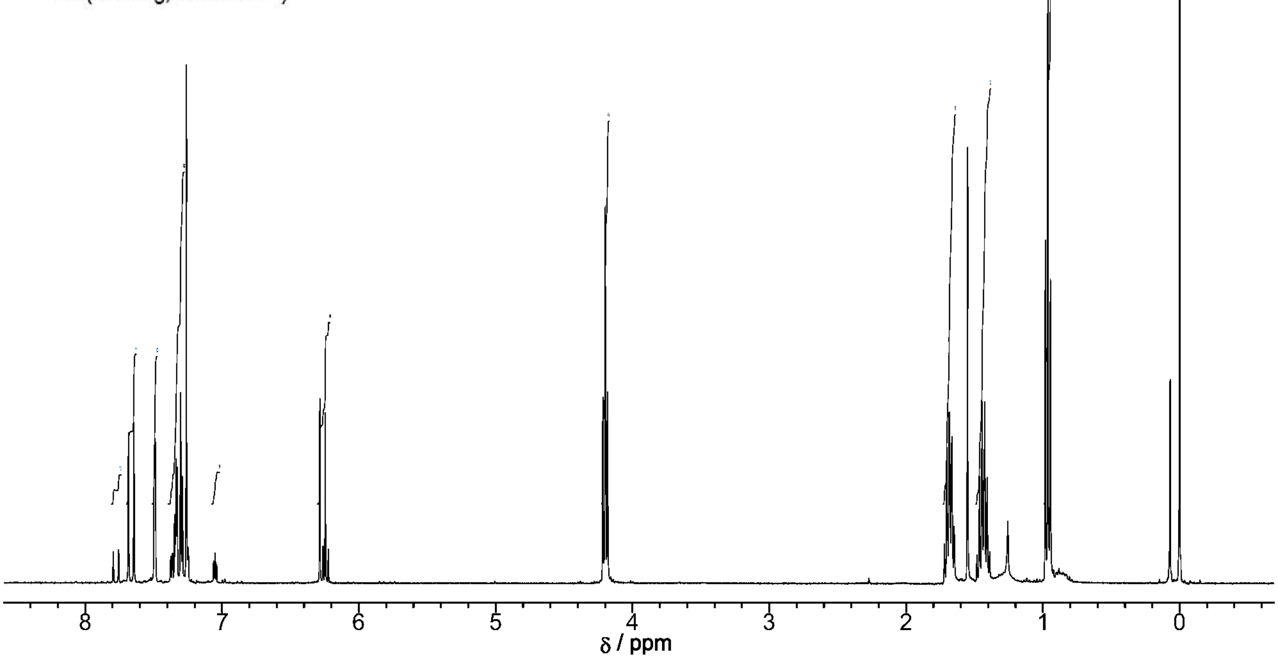


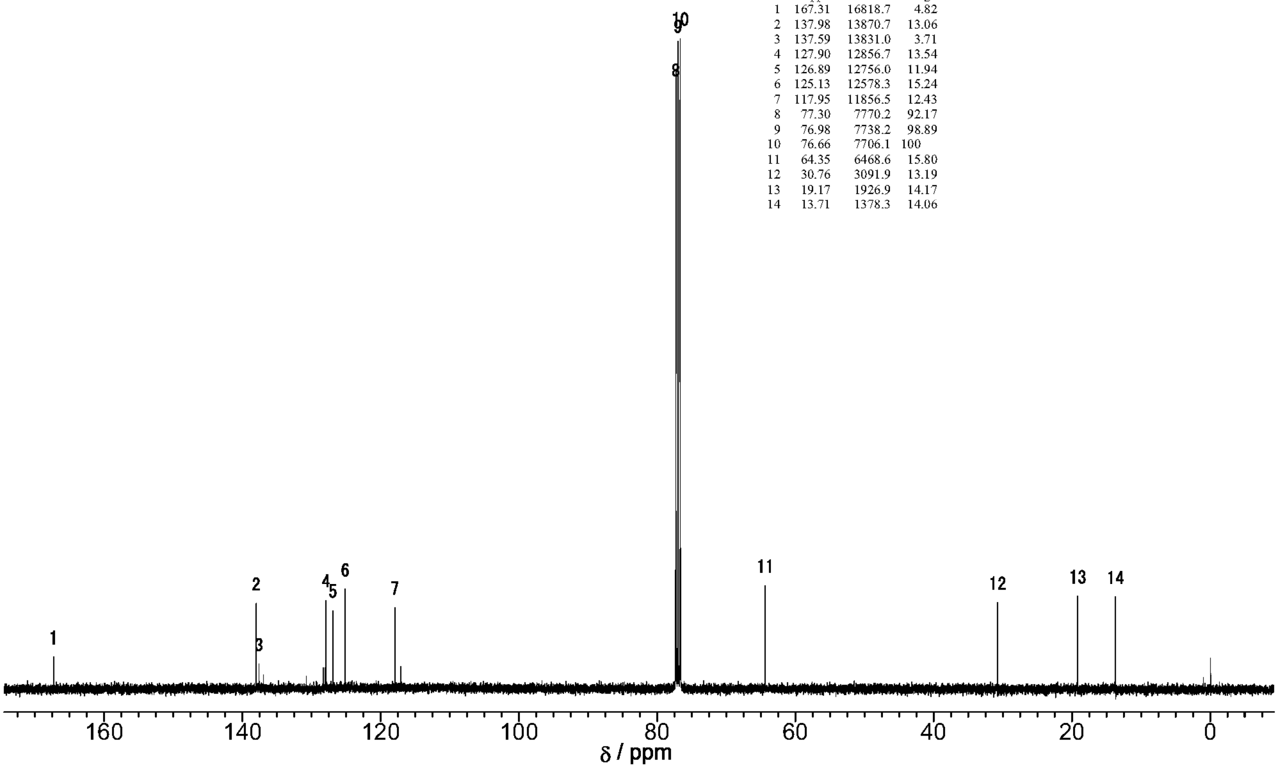
No.	ppm	Hz	Height
1	167.13	16800.4	12.40
2	167.06	16793.5	7.32
3	150.94	15173.8	7.30
4	144.62	14537.5	36.57
5	144.38	14513.8	44.43
6	144.34	14510.0	48.15
7	134.46	13516.7	32.86
8	130.89	13157.3	48.53
9	122.61	12325.0	10.56
10	118.03	11864.9	34.74
11	115.97	11658.1	58.26
12	114.53	11513.2	48.48
13	112.19	11278.2	70.55
14	107.40	10796.8	55.83
15	77.30	7771.0	92.02
16	76.98	7738.9	94.52
17	76.67	7706.9	89.81
18	64.33	6467.1	37.78
19	64.28	6461.8	54.54
20	30.73	3089.6	66.80
21	19.15	1925.3	100
22	13.70	1376.8	97.76





7f ($CDCl_3$, 400 MHz)





No.	ppm	Hz	Height
1	167.31	16818.7	4.82
2	137.98	13870.7	13.06
3	137.59	13831.0	3.71
4	127.90	12856.7	13.54
5	126.89	12756.0	11.94
6	125.13	12578.3	15.24
7	117.95	11856.5	12.43
8	77.30	7770.2	92.17
9	76.98	7738.2	98.89
10	76.66	7706.1	100
11	64.35	6468.6	15.80
12	30.76	3091.9	13.19
13	19.17	1926.9	14.17
14	13.71	1378.3	14.06