Supporting Information

Copper-Catalyzed Trans-Hydroboration of Terminal Aryl Alkynes: Stereodivergent Synthesis of Alkenylboron Compounds

Won Jun Jang, Woo Lim Lee, Jong Hun Moon, Jin Yong Lee,* and Jaesook Yun*

Department of Chemistry and Institute of Basic Science

Sungkyunkwan University, Suwon 440-746, Korea

Fax: (+82)-31-290-7075; e-mail: jaesook@skku.edu.

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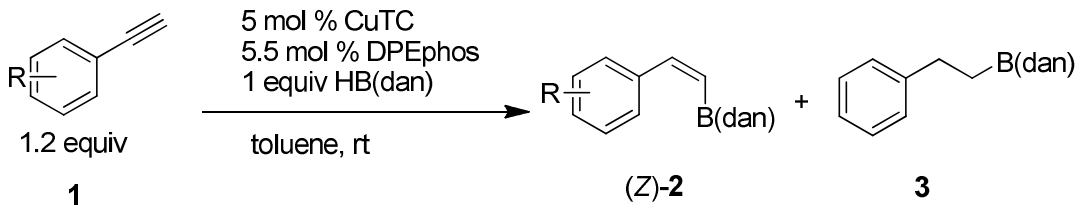
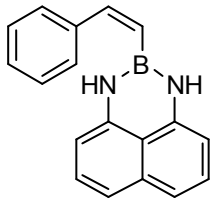
General methods: CuTC, DPEphos, NaO*t*-Bu, terminal alkynes and other commercial reagents were purchased from Aldrich and used as received. Toluene was distilled from sodium under nitrogen. 1,8-naphthalenediaminatoborane(HB(dan))[1] and SIPr·CuCl complex[2] were prepared by following literature procedures. Reactions with oxygen- and moisture-sensitive materials were carried out with standard Schlenk technique. Flash chromatography was performed on silica gel from Merck (70–230 mesh). Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and are recorded in cm^{-1}. All ^{1}H NMR spectra were obtained on Varian Mercury 300 systems or Bruker at 500 systems and reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra are reported in ppm referenced to deuteriochloroform (77.16 ppm). High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, Korea) and reported in the form of *m/z* (intensity relative to peak = 100).

General procedure for the copper-catalyzed (*Z*)-selective hydroboration of terminal alkynes with 1,8-Naphthalenediaminatoborane (HB(dan)) (General procedure A)



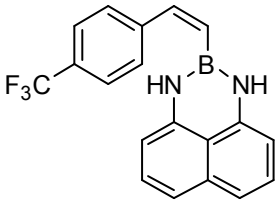
Mixture of CuTC (5 mol %, 0.025 mmol), DPEphos (5.5 mol %, 0.0275 mmol) and HB(dan) (0.5 mmol) in anhydrous toluene (3 mL) were stirred for 15 min in a Schlenk tube under an atmosphere of nitrogen. A terminal alkyne (**1**) (0.6 mmol) was added to the reaction mixture with the use of toluene (3 mL) and reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography using hexane/CH_2Cl_2 (2% NEt_3) as the eluent.

Characterization of (*Z*)-vinyl B(dan) Products ((*Z*)-2)



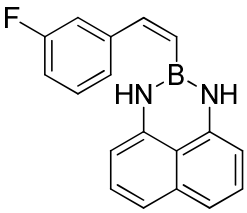
(*Z*)-**2a**

(*Z*)-2-styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2a) (Table 1, entry 7) : According to the general procedure A, (*Z*)-**2a** was obtained along with **3a** (yellow viscous oil, 82%, ratio = 90:10, 110.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.46–7.43 (m, 2H), 7.36–7.28 (m, 3H), 7.23–7.18 (m, 1H), 7.09–6.98 (m, 4H), 6.17 (d, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 14.7 Hz, 1H), 5.58 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.8, 117.6, 127.6, 128.0, 128.2, 128.5, 136.3, 138.7, 141.0, 145.2;); ^{11}B NMR (160 MHz, $CDCl_3$) : δ 28.7; IR(neat) : 3405, 3053, 1628, 1598, 1504, 1417, 1139, 1038; HRMS (EI) calcd for $C_{18}H_{15}BN_2$: 270.1328, found : 270.1327.



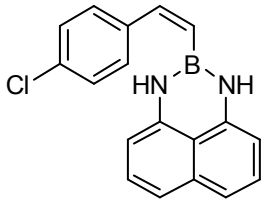
(*Z*)-**2b**

(*Z*)-2-(4-(trifluoromethyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]-diazaborinine ((*Z*)-2b) (Table 2, entry 1) According to the general procedure A, (*Z*)-**2b** was obtained along with **3b** (yellow solid, 87%, ratio = 88:12, 147.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.62–7.53 (m, 4H), 7.19–7.14 (m, 1H), 7.11–7.00 (m, 4H), 6.21 (d, *J* = 7.2 Hz, 2H), 5.92 (d, *J* = 14.7 Hz, 1H), 5.56 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 106.0, 117.9, 119.8, 124.1 (q, *J* = 270 Hz), 125.5 (q, *J* = 3.7 Hz), 126.9, 127.6, 128.4, 129.8 (q, *J* = 32.2 Hz), 140.6, 143.1; IR(neat) : 3397, 3052, 1628, 1599, 1503, 1408, 1165, 1114, 1065; HRMS (EI) calcd for $C_{19}H_{14}BF_3N_2$: 338.1202, found: 338.1200.



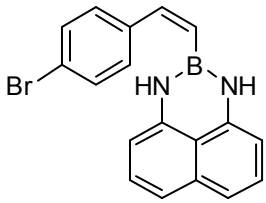
(*Z*)-**2c**

(*Z*)-2-(3-fluorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine [(*Z*)-2c] (Table 2, entry 2) According to the general procedure A, (*Z*)-**2c** was obtained along with **3c** (yellow solid, 81%, ratio = 89:11, 116.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.31–7.27 (m, 2H), 7.15–6.99 (m, 7H), 6.20 (d, *J* = 6.9 Hz, 2H), 5.82 (d, *J* = 14.7 Hz, 1H), 5.58 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 114.8 (d, *J* = 21 Hz), 115.0 (d, *J* = 21 Hz), 117.7, 123.7 (d, *J* = 2.9 Hz), 127.6, 130.0 (d, *J* = 8.4 Hz), 136.3, 140.8, 143.6 (d, *J* = 2.1 Hz), 162.8 (d, *J* = 245 Hz); IR(neat) : 3402, 3051, 1628, 1599, 1504, 1412, 1253, 1143; HRMS (EI) calcd for $C_{18}H_{14}BFN_2$: 288.1234, found: 288.1237.



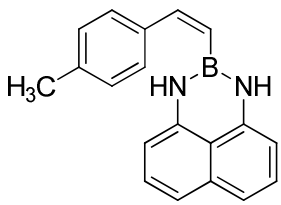
(*Z*)-**2d**

(*Z*)-2-(4-chlorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2d) (Table 2, entry 3) : According to the general procedure A, (*Z*)-**2d** was obtained along with **3d** (yellow solid, 88%, ratio = 86:14, 134.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.40–7.36 (m, 2H), 7.30–7.27 (m, 2H), 7.11–7.06 (m, 3H), 7.03–7.00 (m, 2H), 6.21 (d, *J* = 7.2 Hz, 2H), 5.80 (d, *J* = 14.7 Hz, 1H), 5.57 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 117.8, 119.7, 127.6, 128.7, 129.5, 133.8, 136.3, 137.0, 140.8, 143.5; IR(neat) : 3424, 3057, 1627, 1598, 1503, 1419, 1140, 1088; HRMS (EI) calcd for $C_{18}H_{14}BClN_2$: 304.0939, found: 304.0937.



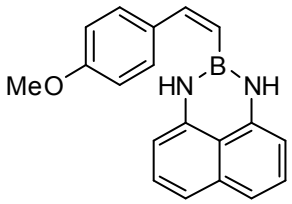
(*Z*)-**2e**

(*Z*)-2-(4-bromostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2e) (Table 2, entry 4) : According to the general procedure A, (*Z*)-**2e** was obtained along with **3e** (yellow solid, 77%, ratio = 89:11, 134.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.46–7.40 (m, 2H), 7.34–7.31 (m, 2H), 7.12–7.06 (m, 3H), 7.04–7.01 (m, 2H), 6.22 (d, *J* = 7.2 Hz, 2H), 5.81 (d, *J* = 14.7 Hz, 1H), 5.58 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 117.8, 119.7, 122.0, 127.6, 129.8, 131.6, 136.3, 137.5, 140.8, 143.5; ^{11}B NMR (160 MHz, $CDCl_3$) : δ 28.7; IR(neat) : 3411, 3050, 1629, 1596, 1504, 1142, 1050; HRMS (EI) calcd for $C_{18}H_{14}BBrN_2$: 348.0434, found: 348.0434.



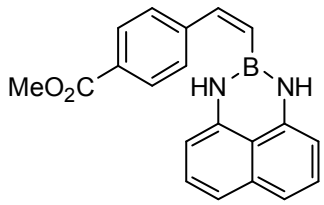
(*Z*)-**2f**

(*Z*)-2-(4-methylstyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2f) (Table 2, Entry 5) : According to the general procedure A, (*Z*)-**2f** was obtained along with **3f** (yellow solid, 68%, ratio = 92:8, 96.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.34–7.31 (m, 2H), 7.12–7.08 (m, 3H), 7.06–7.03 (m, 2H), 7.00–6.97 (m, 2H), 6.15 (d, *J* = 7.2 Hz, 2H), 5.67 (d, *J* = 14.7 Hz, 1H), 5.58 (brs, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 21.3, 105.7, 117.5, 119.7, 127.6, 128.1, 129.2, 135.8, 136.3, 137.9, 141.1, 145.1; IR(neat) : 3402, 2924, 1627, 1600, 1504, 1413, 1374, 1139, 1035; HRMS (EI) calcd for $C_{19}H_{17}BN_2$: 284.1485, found: 284.1485.



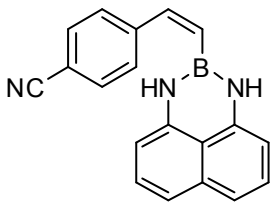
(*Z*)-**2g**

(*Z*)-2-(4-methoxystyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2g) (Table 2, entry 6) : According to the general procedure A, (*Z*)-**2g** was obtained along with **3g** (pale yellow solid, 55%, ratio = 89:11, 82.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.14–7.06 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.20 (d, *J* = 7.3 Hz, 2H), 5.64 (d, *J* = 14.6 Hz, 1H), 5.62 (brs, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 55.3, 105.7, 113.9, 117.5, 119.7, 127.6, 129.5, 131.3, 136.3, 141.1, 144.6, 159.4; ^{11}B NMR (160 MHz, $CDCl_3$) : δ 28.7; IR(neat) : 3389, 1628, 1595, 1508, 1414, 1385, 1245, 1175, 1140, 1025; HRMS (EI) calcd for $C_{19}H_{17}BN_2O$: 300.1434, found: 300.1431.



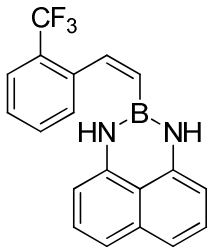
(*Z*)-**2h**

(*Z*)-methyl 4-(2-1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-vinyl)benzoate ((*Z*)-2h) (Table 2, entry 7) : According to the general procedure A, (*Z*)-**2h** was obtained along with **3h** (yellow solid, 79%, ratio = 80:20, 129.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.12–7.09 (m, 1H), 7.08–7.05 (m, 2H), 7.03–6.99 (m, 2H), 6.20 (d, *J* = 7.2 Hz, 2H), 5.90 (d, *J* = 14.7 Hz, 1H), 5.58 (brs, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 52.2, 105.9, 117.8, 119.7, 127.6, 128.1, 129.8, 136.3, 140.7, 143.7, 168.8; ^{11}B NMR (160 MHz, $CDCl_3$) : δ 28.6; IR(neat) : 3386, 2924, 1704, 1627, 1596, 1513, 1408, 1242, 1143, 1108; HRMS (EI) calcd for $C_{20}H_{17}BN_2O_2$: 328.1383, found: 328.1380.



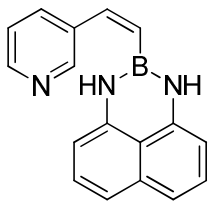
(*Z*)-**2i**

(*Z*)-4-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)vinyl)-benzonitrile ((*Z*)-2i) (Table 2, entry 8) : According to the general procedure A, compound (*Z*)-**2i** was obtained along with **3i** (yellow solid, 72%, ratio = 84:16, 106.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.56–7.52 (m, 4H), 7.12–7.07 (m, 3H), 7.04–7.00 (m, 2H), 6.21 (d, *J* = 7.2 Hz, 2H), 5.97 (d, *J* = 14.7 Hz, 1H), 5.56 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 106.1, 111.3, 118.1, 118.8, 119.8, 127.6, 128.7, 132.3, 136.3, 140.5, 142.4, 143.0; IR(neat) : 3395, 2225, 1628, 1596, 1509, 1419, 1143, 1042; HRMS (EI) calcd for $C_{19}H_{14}BN_3$: 295.1281, found: 295.1283.



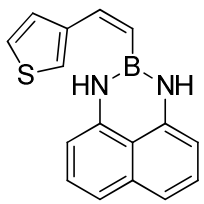
(*Z*)-**2j**

(*Z*)-2-(2-(trifluoromethyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2j) (Table 2, entry 9) : According to the general procedure A, compound (*Z*)-**2j** was obtained along with **3j** (yellow solid, 53%, ratio = 83:17, 90.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.56–7.48 (m, 3H), 7.46–7.43 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.12 (d, *J* = 7.3 Hz, 2H), 5.94 (d, *J* = 14.5 Hz, 1H), 5.38 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.8, 117.7, 119.7, 124.2 (q, *J* = 272 Hz), 125.9 (q, *J* = 5.4 Hz), 127.6, 128.0, 128.1 (q, *J* = 29.8 Hz), 130.6, 131.8, 136.3, 137.9, 140.8, 142.3; IR(neat) : 3395, 1629, 1598, 1505, 1416, 1166, 1118, 1035; HRMS (EI) calcd for $C_{19}H_{14}BF_3N_2$: 338.1202, found: 338.1201.



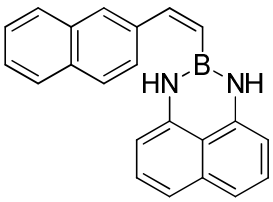
(*Z*)-**2k**

(*Z*)-2-(2-(pyridin-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2k) (Table 2, entry 10) : According to the general procedure A, (*Z*)-**2k** was obtained in 68% yield (pale yellow solid, 92.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 8.61 (s, 1H), 8.48 (d, *J* = 4.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.22–7.18 (m, 1H), 7.10–7.05 (m, 3H), 7.03–7.01 (m, 2H), 6.21 (d, *J* = 7.3 Hz, 2H), 5.93 (d, *J* = 14.7 Hz, 1H), 5.65 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 106.0, 111.6, 117.9, 119.8, 123.3, 126.2, 127.6, 134.2, 134.8, 136.3, 140.6, 140.7, 148.9, 149.7; ^{11}B NMR (160 MHz, $CDCl_3$) : δ 28.8; IR(neat) : 3419, 3045, 1628, 1601, 1516, 1408, 1146, 1027; HRMS (EI) calcd for $C_{17}H_{14}BN_3$: 271.1281, found: 271.1282.



(*Z*)-**2l**

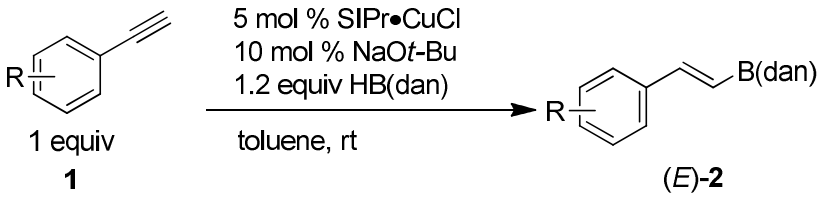
(*Z*)-2-(2-(thiophen-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*Z*)-2l) (Table 2, entry 11) : According to the general procedure A, (*Z*)-**2l** was obtained along with **3l** (yellow viscous oil, 61%, ratio = 78:22, 84.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.28–7.26 (m, 2H), 7.23–7.21 (m, 1H), 7.09–7.05 (m, 3H), 7.01–6.98 (m, 2H), 6.20 (d, *J* = 7.2 Hz, 2H), 5.67 (d, *J* = 14.7 Hz, 1H), 5.64 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 117.2, 119.8, 124.2, 125.7, 126.3, 127.4, 127.7, 128.0, 136.4, 138.2, 140.8, 141.0, 144.4; IR(neat) : 3403, 3045, 1628, 1598, 1516, 1408, 1321, 1146, 1027; HRMS (EI) calcd for $C_{16}H_{13}BN_2S$: 276.0893, found: 276.0893.



(*Z*)-**2m**

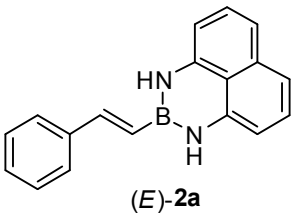
(*Z*)-2-(2-(naphrhalen-2-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]-diazaborinine ((*Z*)-2m) (Table 2, entry 12) : According to the general procedure A, (*Z*)-**2m** was obtained along with **3m** (yellow viscous oil, 76%, ratio = 85:15, 120.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.84(s, 1H), 7.82–7.75 (m, 3H), 7.66–7.23 (m, 1H), 7.47–7.44 (m, 2H), 7.35–7.32 (m, 1H), 7.08–7.04 (m, 2H), 7.01–6.99 (m, 2H), 6.14 (d, *J* = 7.2 Hz, 2H), 5.83 (d, *J* = 14.7 Hz, 1H), 5.64 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.8, 117.6, 119.7, 125.8, 126.3, 126.4, 127.6, 127.7, 128.1, 133.0, 133.3, 136.1, 136.3, 140.9, 145.1; IR(neat) : 3408, 3052, 1628, 1598, 1504, 1416, 1139, 1037; HRMS (EI) calcd for $C_{22}H_{17}BN_2$: 320.1485, found: 320.1487.

General procedure for the SIPr-Cu catalyzed hydroboration of terminal alkynes with 1,8-naphthalenediaminatoborane (HB(dan)) (General procedure B)



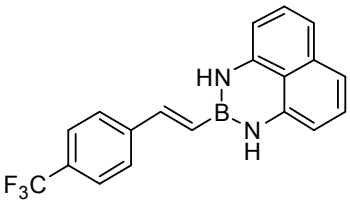
Mixture of SIPr•CuCl complex (5 mol %, 0.025 mmol), NaO*t*-Bu (10 mol %, 0.05 mmol) and HB(dan) (1.2 equiv, 0.6 mmol) in anhydrous toluene (3 mL) were stirred for 15 min in a Schlenk tube under an atmosphere of nitrogen A terminal alkyne (**1**) (0.5 mmol) was added to the reaction mixture with the use of toluene (3 mL) and reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography using hexane/CH_2Cl_2 (2% NEt_3) as the eluent.

Characterization of (*E*)-vinyl B(dan) Products ((*E*)-2)



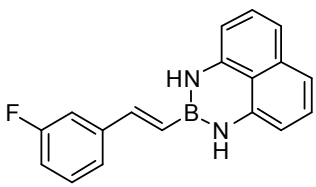
(*E*)-**2a**

(*E*)-2-styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine ((*E*)-2b)[3] (Table 1, entry 10) : According to the general procedure B, (*E*)-**2a** was obtained in 76% yield (yellow solid, 102.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28–7.31 (m, 1H), 7.09–7.13 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 6.28 (d, *J* = 18.6 Hz, 1H), 5.80 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.8, 117.6, 119.9, 126.8, 127.6, 128.7, 136.4, 137.6, 141.1, 143.7.



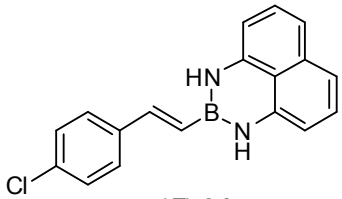
(*E*)-**2b**

(*E*)-2-(4-(trifluoromethyl)styryl)-2,3-dihydro-1H-naphtho-[1,8-de][1,3,2]diaza-borinine ((*E*)-2b) (Scheme 2) : According to the general procedure B, (*E*)-**2b** was obtained in 84% yield (yellow solid, 141.9 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.65–7.58 (m, 4H), δ 7.10–7.20 (m, 3H), δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 18.6 Hz, 1H), 6.38 (d, *J* = 7.2 Hz, 2H), 5.86 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 106.0, 117.9, 120.0, 124.2 (q, *J* = 271 Hz), 125.7 (q, *J* = 3.7 Hz), 126.9, 127.6, 128.4, 129.8 (q, *J* = 32.2 Hz), 140.6, 143.1; HRMS (EI) calcd for $C_{16}H_{21}BF_3N_2$: 338.1202, found: 338.1201.



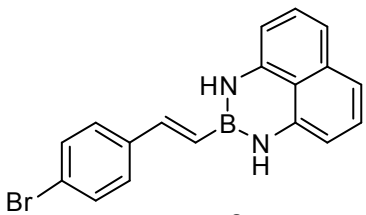
(*E*)-**2c**

(*E*)-2-(3-fluorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]-diaza-borinine ((*E*)-2c) (Scheme 2) : According to the general procedure B, (*E*)-**2c** was obtained in 76% yield (yellow solid, 109.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.61–7.55 (m, 1H), 7.35–7.23 (m, 2H), 7.16–7.05 (m, 4H), 7.03–7.00 (m, 2H), 6.35 (d, *J* = 18.6 Hz, 1H), 6.35 (d, *J* = 7.2 Hz, 2H), 5.84 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 113.0 (d, *J* = 21 Hz), 115.5 (d, *J* = 21 Hz), 117.8, 119.9, 122.8, 127.6, 130.0 (d, *J* = 7.4 Hz), 136.4, 140.0 (d, *J* = 7.4 Hz), 141.0, 142.3 (d, *J* = 2.5 Hz), 163.2 (d, *J* = 244 Hz).



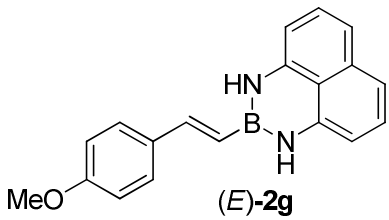
(*E*)-**2d**

(*E*)-2-(4-chlorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]-diazaborinine ((*E*)-2d) (Scheme 2) : According to the general procedure B, (*E*)-**2d** was obtained in 71% yield (yellow solid, 108.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.13–7.02 (m, 5H), 6.34 (d, *J* = 7.3 Hz, 2H), 6.26 (d, *J* = 18.6 Hz, 1H), 5.80 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 117.8, 119.9, 127.6, 128.0, 128.9, 134.4, 136.1, 136.4, 141.1, 142.3.



(*E*)-**2e**

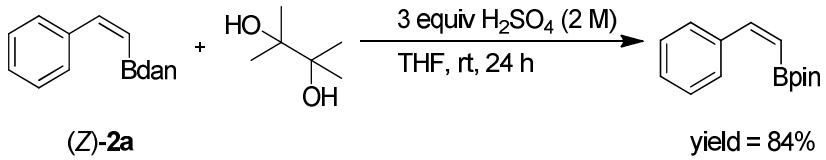
(*E*)-2-(4-bromostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]-diazaborinine ((*E*)-2e)[3] **(Scheme 2) :** According to the general procedure B, (*E*)-**2e** was obtained in 70% yield (yellow solid, 121.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.13–7.09 (m, 2H), 7.06–7.02 (m, 3H), 6.34 (d, *J* = 7.3 Hz, 2H), 6.27 (d, *J* = 18.6 Hz, 1H), 5.80 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 105.9, 117.8, 119.9, 122.6, 127.6, 128.3, 131.9, 136.4, 136.5, 141.0, 142.3.



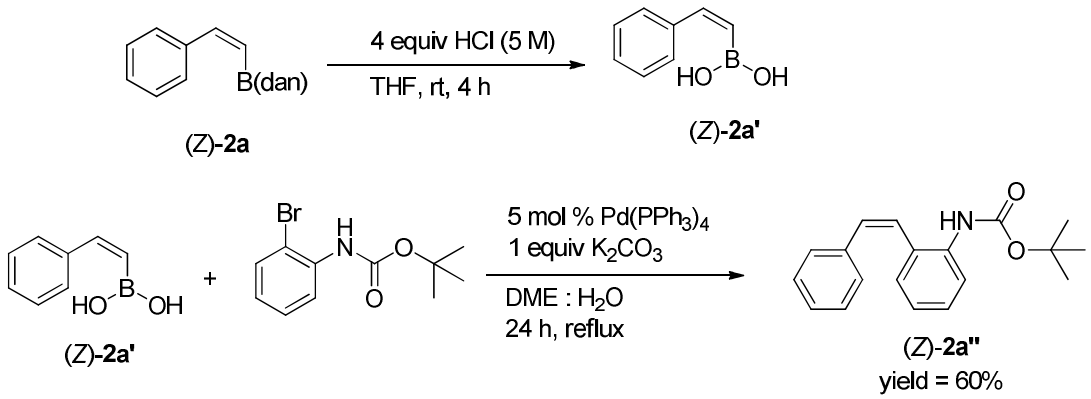
(*E*)-**2g**

(*E*)-2-(4-methoxystyryl)-2,3-dihydro-1H-naphtho[1,8-de]-[1,3,2]diazaborinine ((*E*)-2g)[3] **(Scheme 2) :** According to the general procedure B, (*E*)-**2g** was obtained in 79% yield (pale yellow solid, 119.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.47–7.44 (m, 2H), 7.07–7.14 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.93–6.88 (m, 2H), 6.36 (d, *J* = 7.2 Hz, 2H), 6.17 (d, *J* = 18.6 Hz, 1H), 5.83 (brs, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 55.4, 105.7, 114.1, 117.5, 119.8, 127.6, 128.1, 130.5, 136.4, 141.2, 143.2, 160.2.

Determination of the stereochemistry of (*Z*)-2a



(*Z*)-**2a** was prepared according to general procedure A. H_2SO_4 (2 M, 1.5 mmol) and pinacol (2.5 mmol) were sequentially added to a stirred solution of (*Z*)-**2a** (0.5 mmol) in THF (5 mL). The reaction was stirred for 24 h at room temperature and quenched by water (5 mL). The mixture was extracted by diethyl ether, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.52 (m, 2H), 7.28–7.34 (m, 3H), 7.18–7.23 (m, 1H), 5.59 (d, *J* =14.7 Hz, 1H), 1.29 (s, 12H). ^{1}H NMR spectra are consistent with previously reported data.[4]

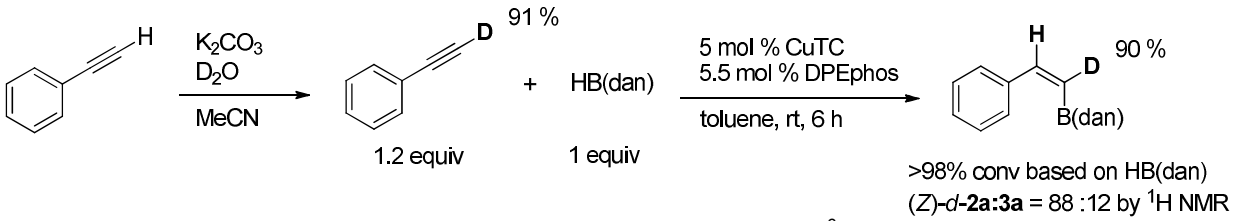


(*Z*)-**2a** was prepared by following general procedure A. To a solution of (*Z*)-**2a** (0.45 mmol) in THF was added HCl (5 M, 1.8 mmol) at room temperature. The mixture was stirred at room temperature for 4 h, leading to the formation of precipitation. The suspension was filtered through a pad of Celite and the solution was dried over Na_2SO_4. Filtration and evaporation of the volatile material under vacuum gave (*Z*)-**2a'**. A portion of the material was used for the cross coupling reaction without further purification.

A solution of tetrakis(triphenyl phosphine) palladium (0.015 mmol) and *N*-(*tert*-butoxycarbonyl)-2-bromoaniline (0.3 mmol) in DME (10 mL) was stirred under nitrogen, in the dark for 30 min. (*Z*)-**2a'** (0.45 mmol), K_2CO_3 (0.3 mmol), and water (5 mL) were added and the mixture was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and DME was removed under reduced pressure. The aqueous layer was extracted with CH_2Cl_2, the combined organic layers were dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel. ^{1}H NMR (300 MHz,

$CDCl_3$): δ 8.02–7.99 (m, 1H), 7.29–7.24 (m, 1H), 7.19–7.11 (m, 6H), 6.99–6.94 (m, 1H), 6.75 (d, *J* = 12.1 Hz, 1H), 6.52 (s, 1H), 6.52 (d, *J* = 12.1 Hz, 1H), 1.42 (s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$) : δ 28.2, 80.2, 119.5, 122.9, 125.4, 126.8, 127.9, 128.3, 128.8, 129.2, 133.4, 135.5, 136.0, 152.7. ^{1}H and ^{13}C NMR spectra are consistent with previously reported data.[5]

Deuterium labeling experiments (Scheme 3 (1))



Phenylacetylene-*d* was prepared by following the literature procedure.[6]

A mixture of CuTC (5 mol %, 0.025 mmol), DPEphos (5.5 mol %, 0.0275 mmol) and HB(dan) (0.5 mmol) in anhydrous toluene (3 mL) was stirred for 15 min in a Schlenk tube under an atmosphere of nitrogen. Phenylacetylene-*d* (0.6 mmol) was added to the reaction mixture with the use of toluene (3 mL). The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

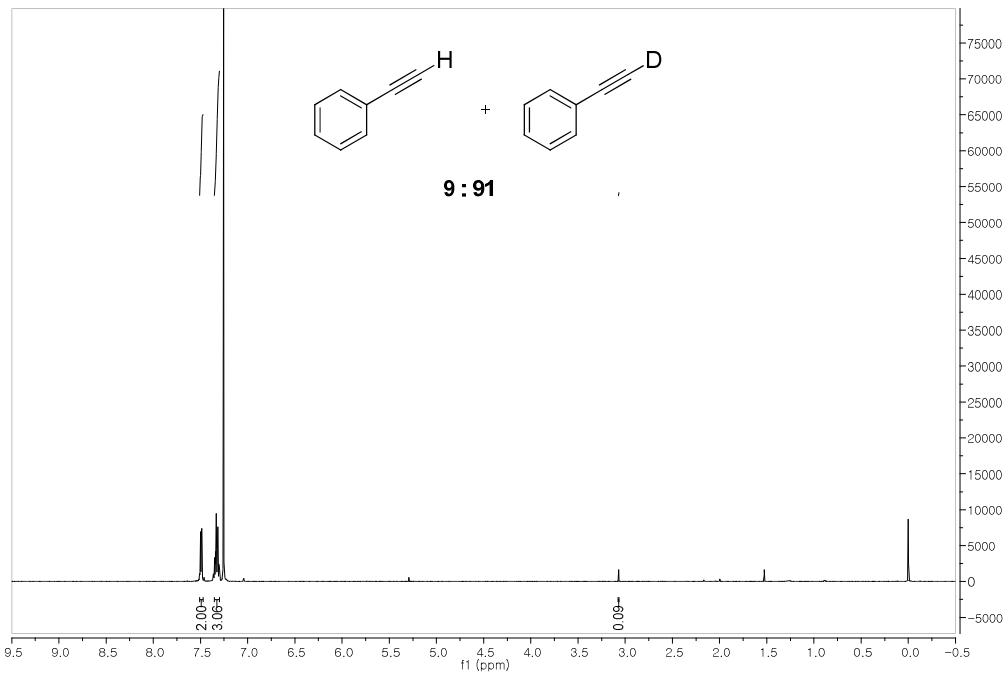


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of phenylacetylene-*d*

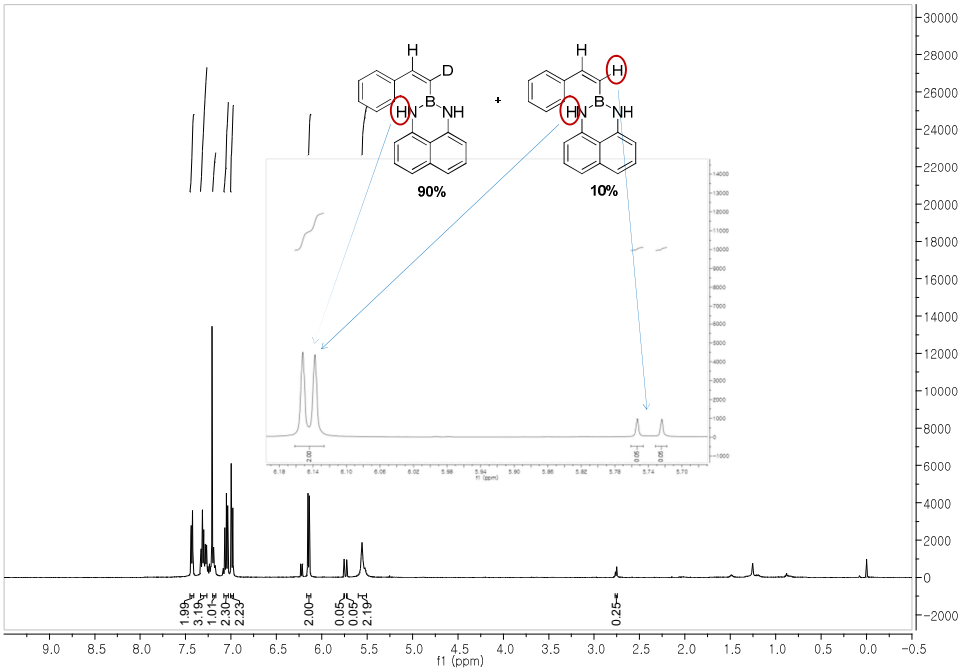
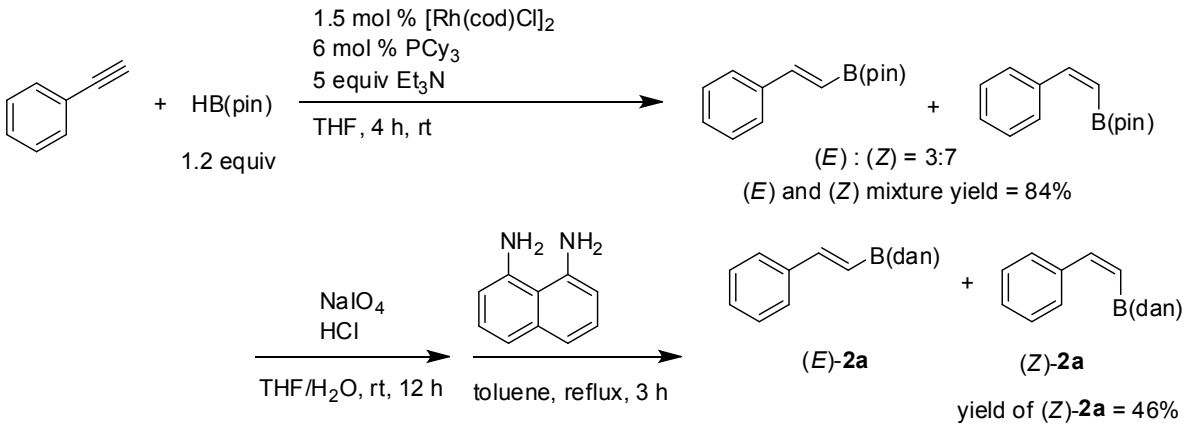


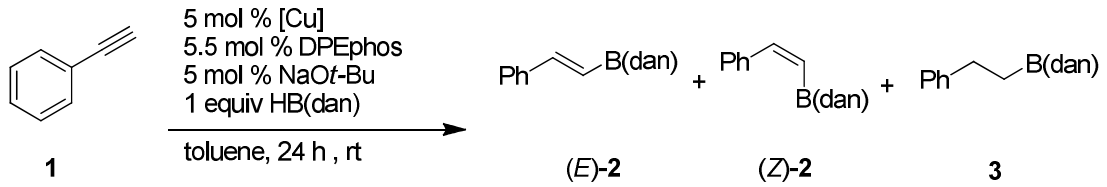
Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (*Z*)-*d*-**2a** : **3a**

Preparation of (*Z*)-2a (Scheme 3)

Pure (*Z*)-**2a** was prepared by the Rh-catalyzed hydroboration[7] and subsequent protection with 1,8-diaminonaphthalene[8] and used for isomerization studies in Scheme 3.



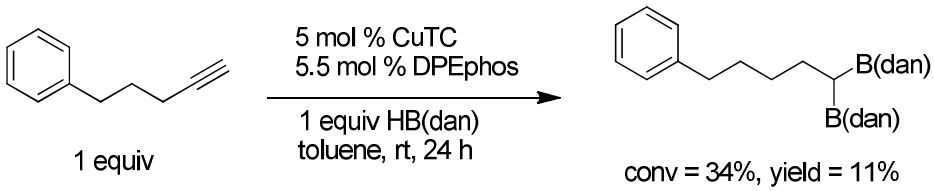
Hydroboration of alkynes with other copper precursors



entry	[Cu]	conv (%)[a]	product ratio (*E*)-**2** (*Z*)-**2**:**3**[a]	yield (%)[b]
1	CuOAc	77	-:74:26	54[c]
2	$Cu(OAc)_2$	79	-:79:21	-
3	$[Cu(CH_3CN)_4]PF_6$	55	36:43:21	-
4	$[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Cu$	67	-:75:25	-

[a] Determined by ^{1}H NMR. [b] Yield of coeluted (*Z*)-**2** and **3**. [c] (*Z*)-**2** and **3** = 85 : 15.

Hydroboration of alkyl-substituted alkynes (Ref.15 in the main text)

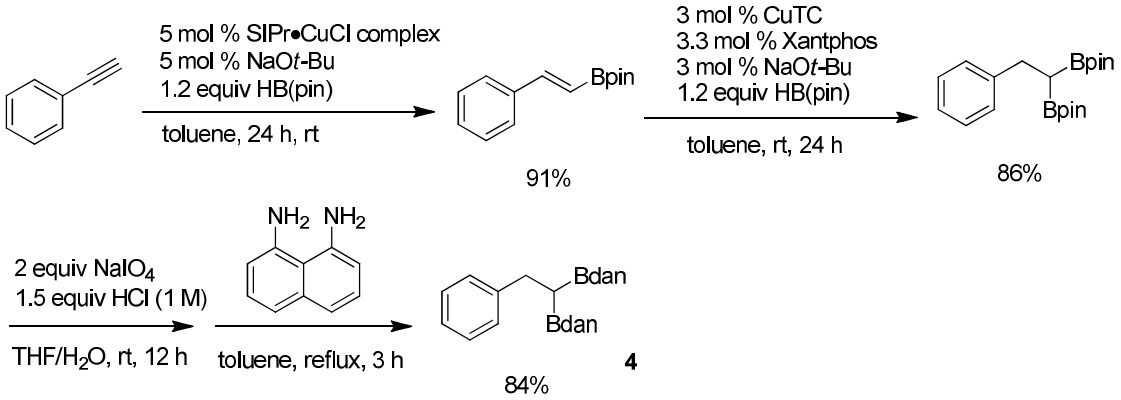


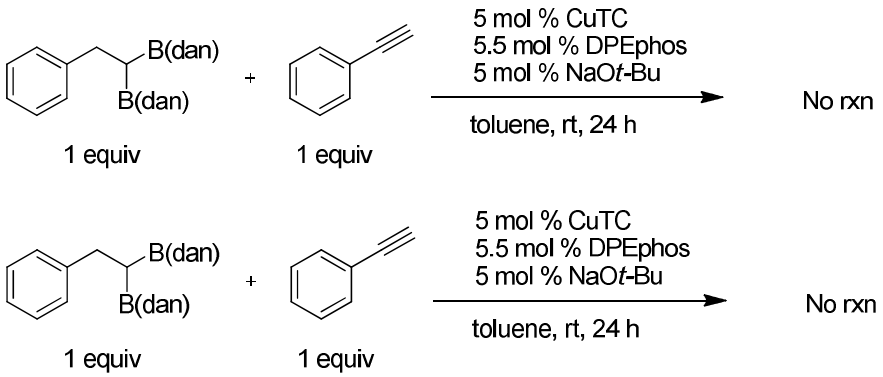
Hydroboration of 5-phenyl-1-pentyne resulted in the formation of 1,1-diborylalkane product with low conversion and low yield under the standard hydroboration conditions.

Preparation of 1,1-diborylalkane (4)

1,1-Diborylalkane(**4**) was prepared by the hydroboration of (*E*)-2-phenylvinylboronic acid pinacol ester and subsequent exchange of the B(pin) moiety to the corresponding 1,8-diaminonapthyl derivatives as shown below.[8,9] The compound was used for deborylation experiments.

^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.29–7.27 (m, 1H), 7.24–7.15 (m, 3H), 7.11–6.99 (m, 9H), 6.28 (d, *J* = 7.2 Hz, 4H), 5.61 (s, 4H), 2.96 (d, *J* = 8.1 Hz, 2H), 1.09 (t, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 28.9, 32.9, 105.8, 117.1, 117.7, 119.5, 126.2, 127.1, 127.5, 128.0, 128.6, 136.2, 140.8, 142.9.


5 mol % SIPr•CuCl complex
5 mol % NaO*t*-Bu
1.2 equiv HB(pin)
toluene, 24 h, rt
Bpin
91%
3 mol % CuTC
3.3 mol % Xantphos
3 mol % NaO*t*-Bu
1.2 equiv HB(pin)
toluene, rt, 24 h
Bpin
Bpin
86%
2 equiv $NaIO_4$
1.5 equiv HCl (1 M)
THF/H_2O, rt, 12 h
NH_2 NH_2
toluene, reflux, 3 h
Bdan
Bdan
84%
4


B(dan)
B(dan)
1 equiv
+
1 equiv
5 mol % CuTC
5.5 mol % DPEphos
5 mol % NaO*t*-Bu
toluene, rt, 24 h
No rxn
B(dan)
B(dan)
1 equiv
+
1 equiv
5 mol % CuTC
5.5 mol % DPEphos
5 mol % NaO*t*-Bu
toluene, rt, 24 h
No rxn

^{1}H-NMR studies of LCu–H

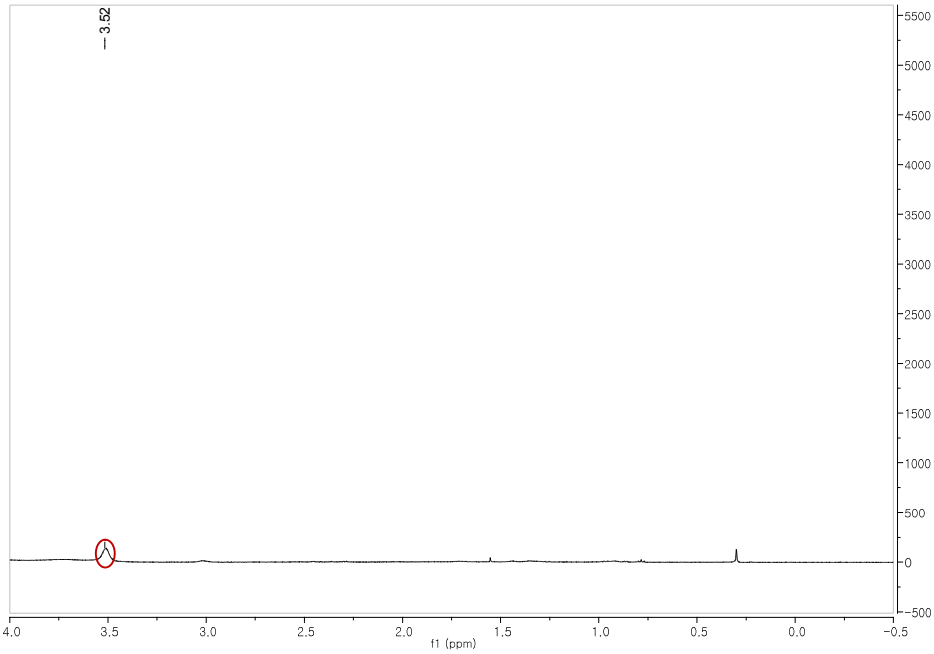


Figure S3. ^{1}H NMR (500 MHz, C_6D_6) spectrum of $[(PPh_3)CuH]_6$ obtained from a mixture of CuTC, PPh_3, and HB(dan)

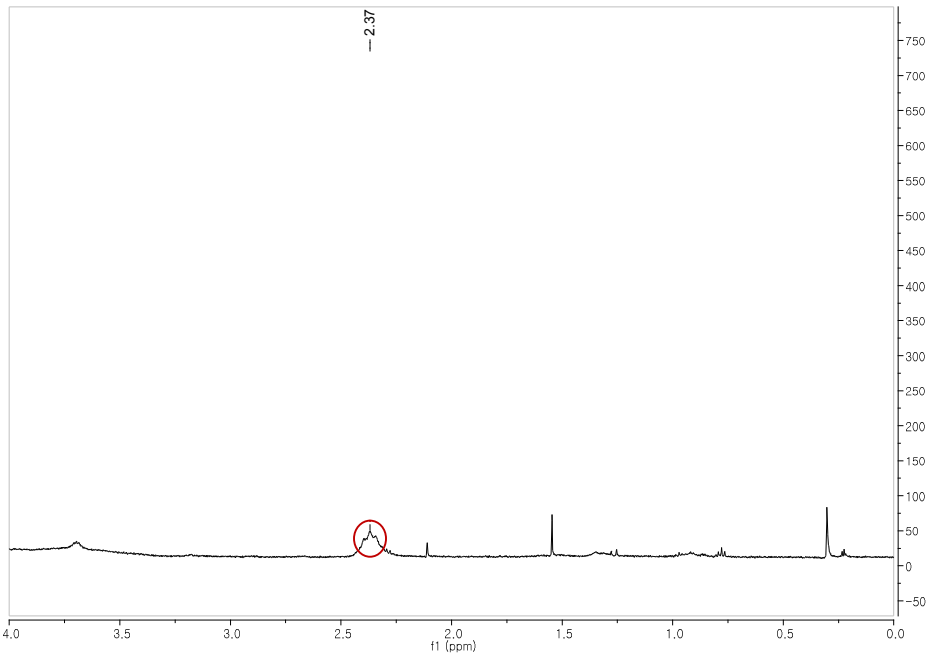
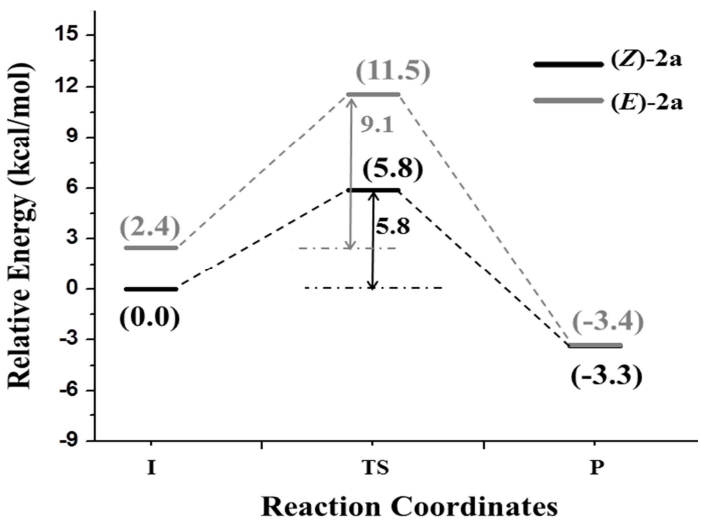


Figure S4. ^{1}H NMR (500 MHz, C_6D_6) spectrum of (DPEphos)CuH obtained from a mixture of CuTC, DPEphos, and HB(dan)

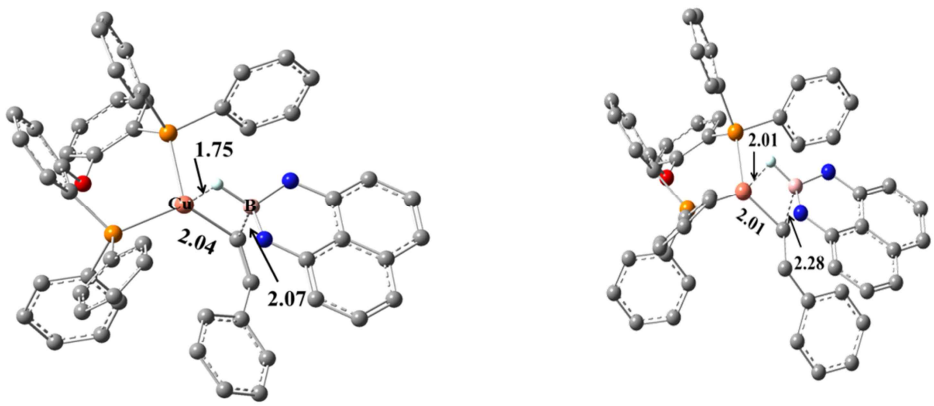
DFT calculations of (*Z*)-2a formation with DPEphos catalyst

The structure of probe **I**, **TS** and **P** were optimized by density functional theory (DFT) with M06-2X functional and 6-31G* basis sets using a suite of Gaussian 09 programs: Frisch, M. J. et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. The transition states (**TS**) were confirmed from the one imaginary frequency and its normal mode vibration, whereas the intermediates (**I**) and products (**P**) were confirmed to be local minima from the all-positive frequencies.

(a)



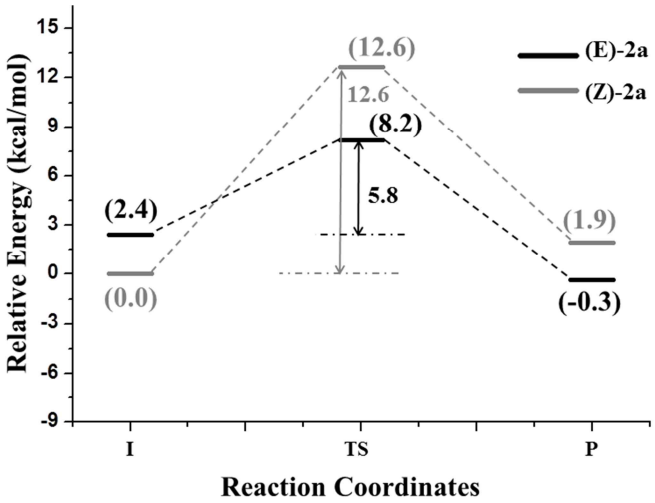
(b)



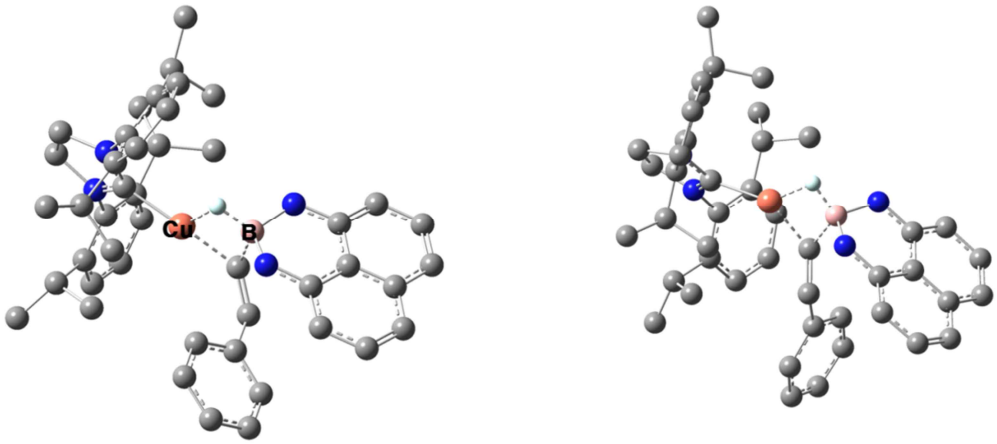
(*Z*)-TS **(*E*)-TS**

Figure S5. Calculated energy profile (a) and structures of transition states (b) with DPEphos

(a)



(b)



(*Z*)-TS (*E*)-TS

Figure S6. Calculated energy profile (a) and structures of transition states (b) with SIPr-CuCl complex

References

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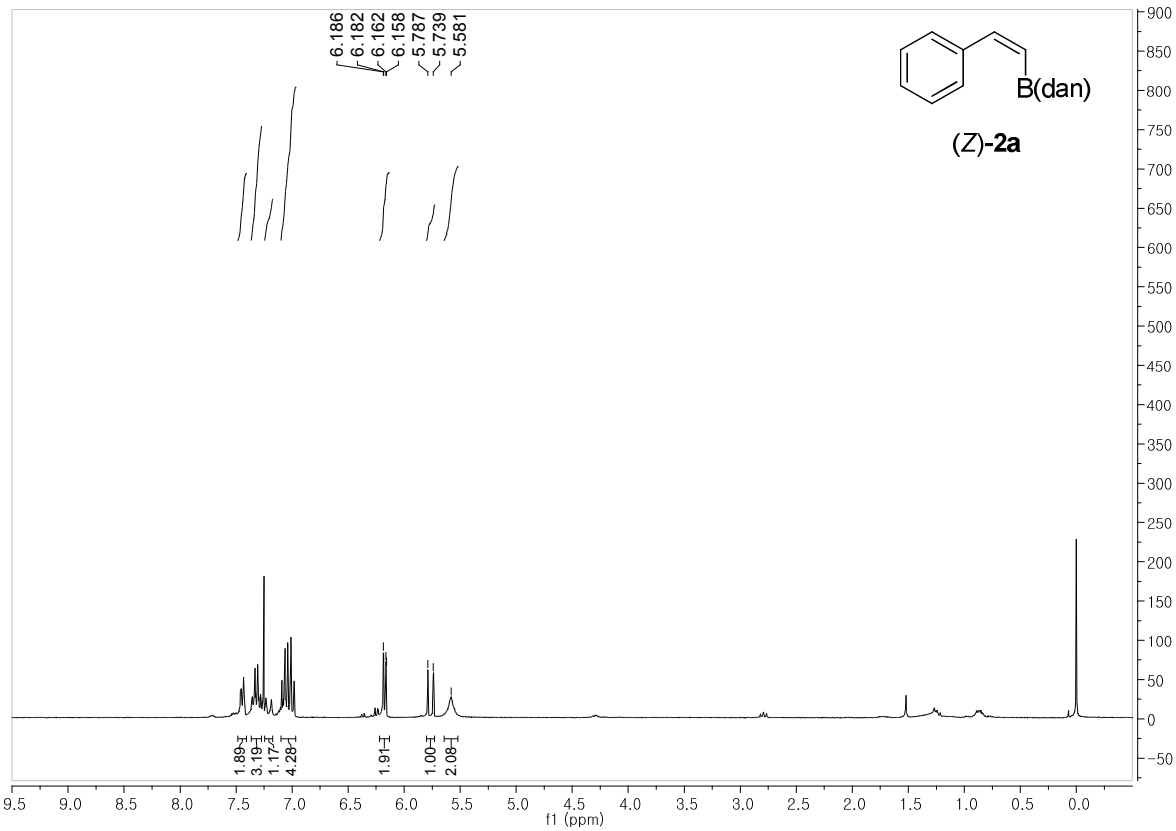
(7) Cid, J.; Carbó, J. J.; Fernández, E. *Chem. –Eur. J.* **2012**, *18*, 1512–1521.

(8) Sun, C.; Potter, B.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 6534–6537.

(9) Lee, S.; Li, D.; Yun, J. *Asian J.* **2014**, *9*, 2440–2443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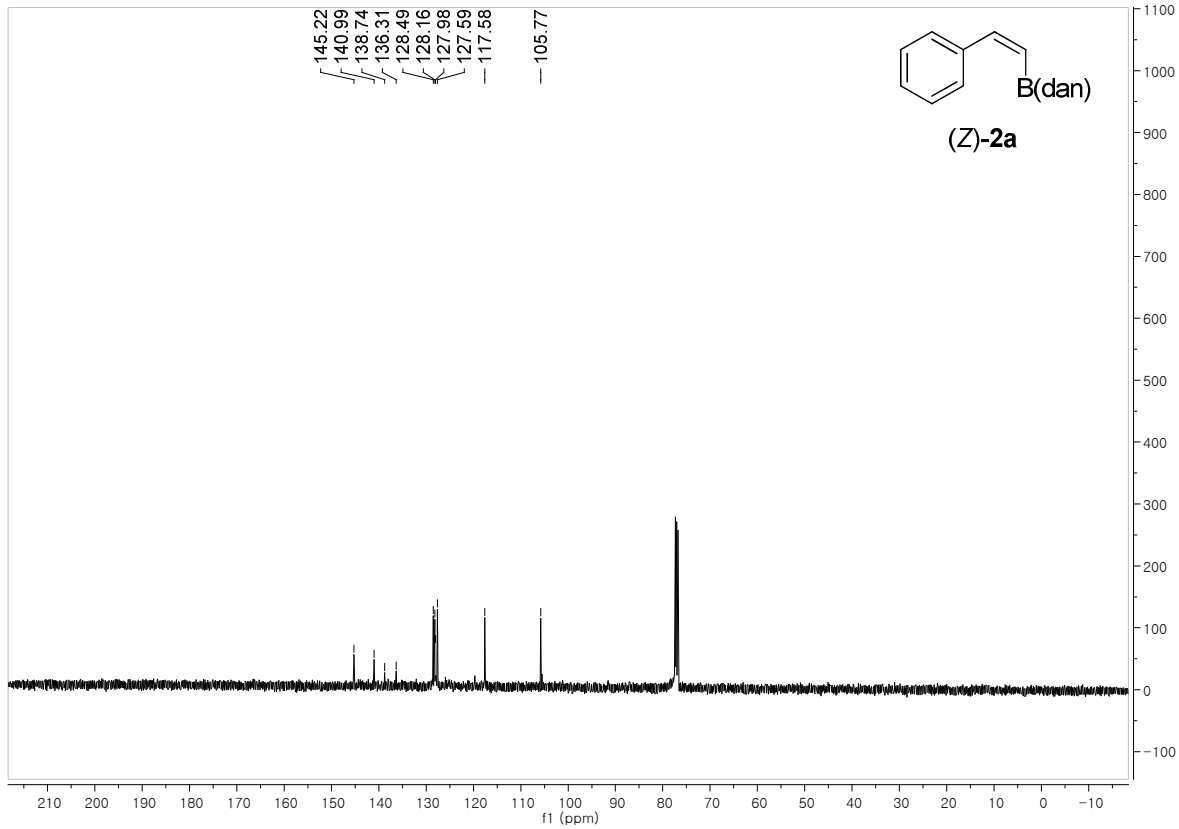
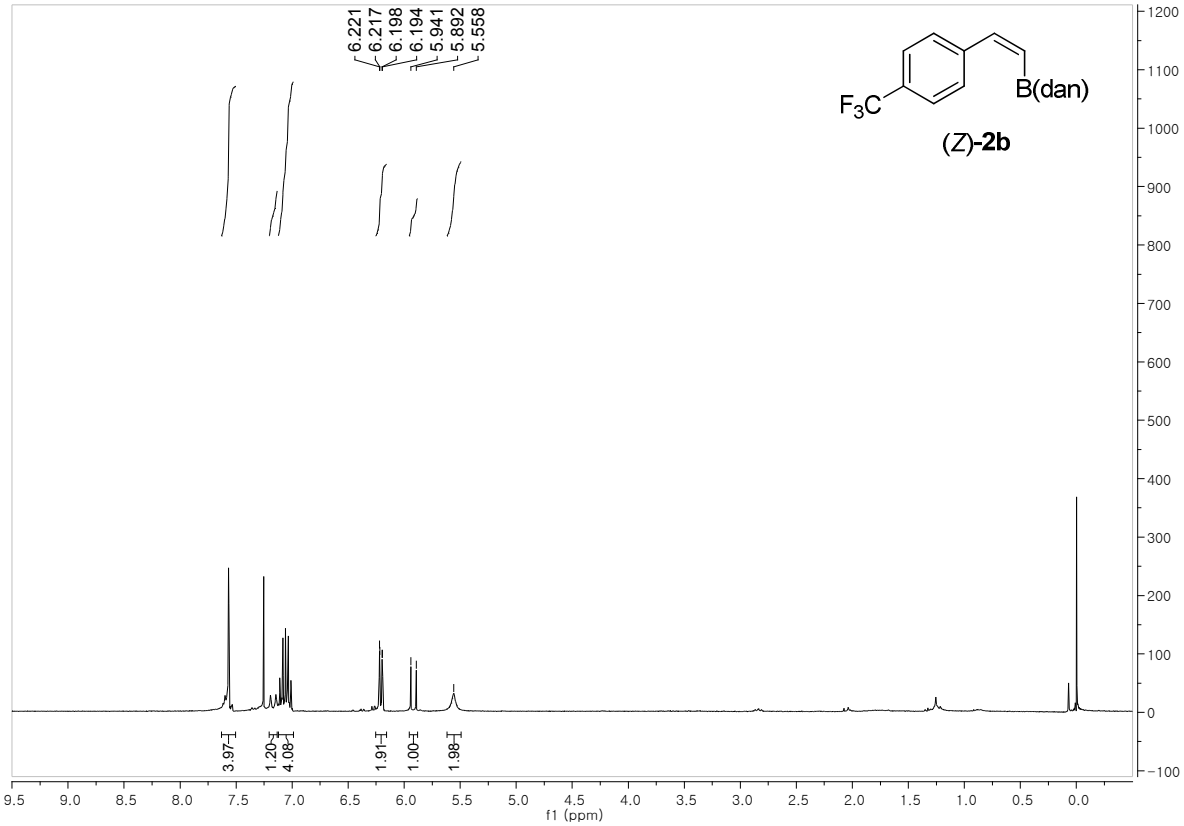
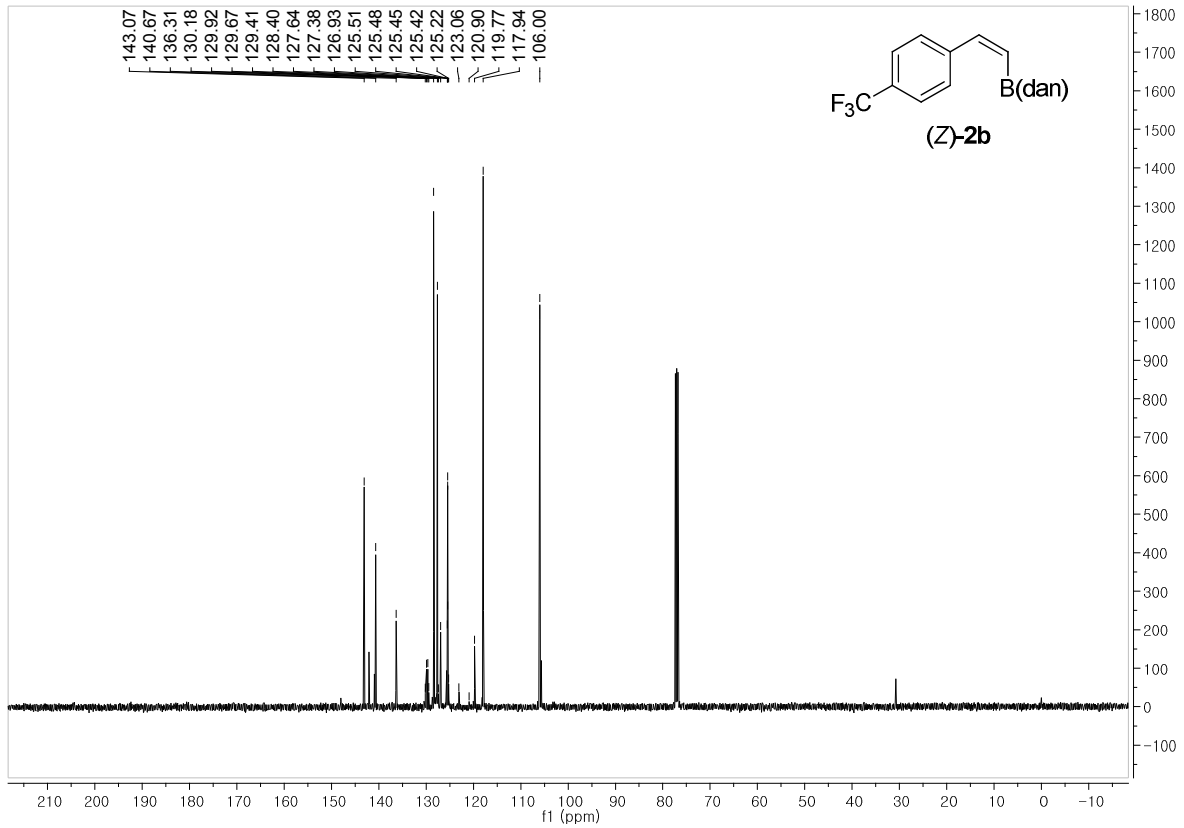
6.182
6.162
6.158
5.787
5.739
5.581
B(dan)
(Z)-2a
1.89
3.19
1.17
4.28
1.91
1.00
2.08
f1 (ppm)


145.22
140.99
138.74
136.31
128.49
128.16
127.98
127.59
117.58
105.77
B(dan)
(Z)-2a
f1 (ppm)


6.221
6.217
6.198
6.194
5.941
5.892
5.558
F3C
B(dan)
(Z)-2b
3.97
1.20
4.08
1.91
1.00
1.98
f1 (ppm)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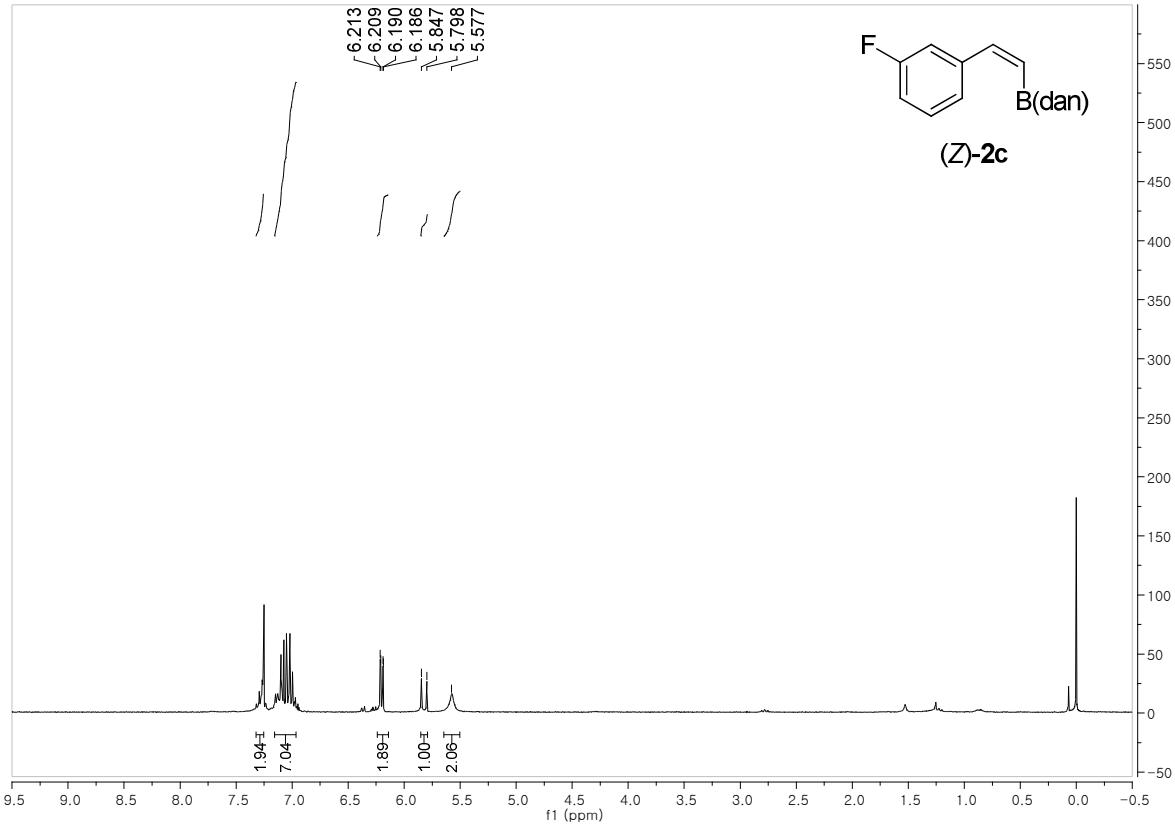
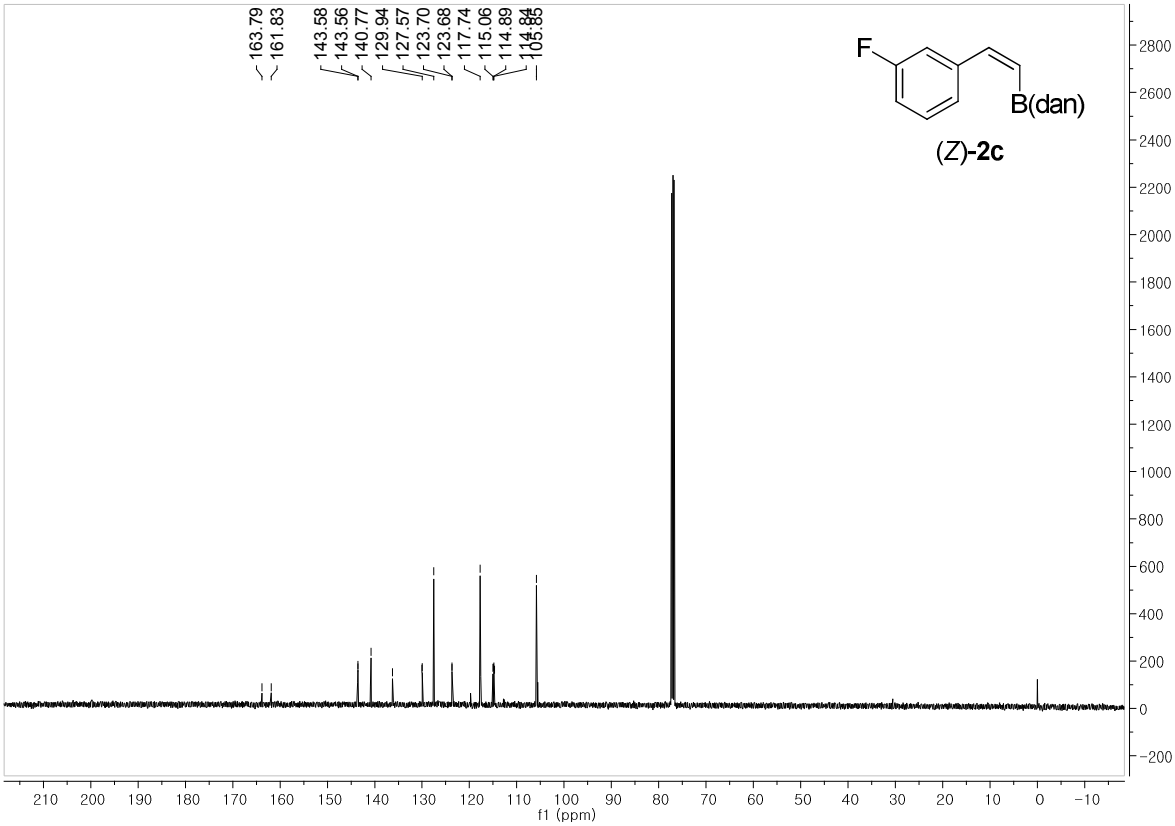
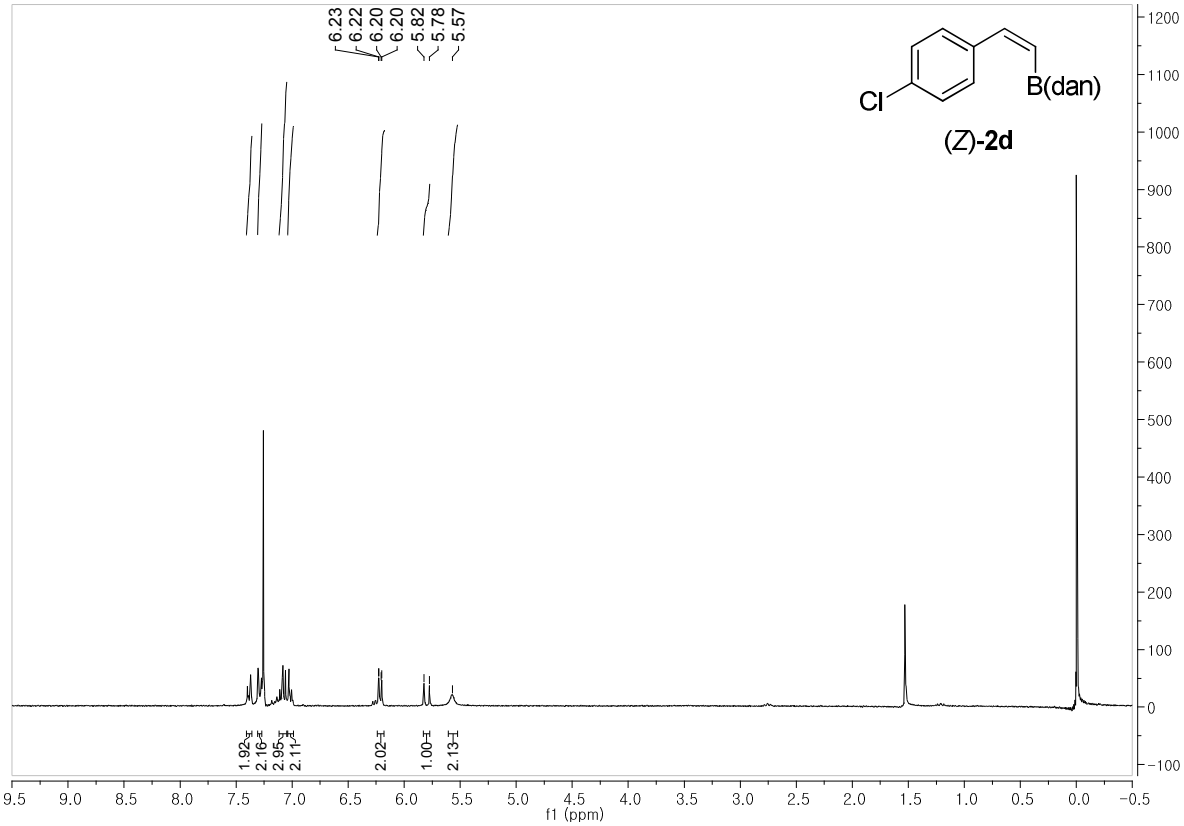
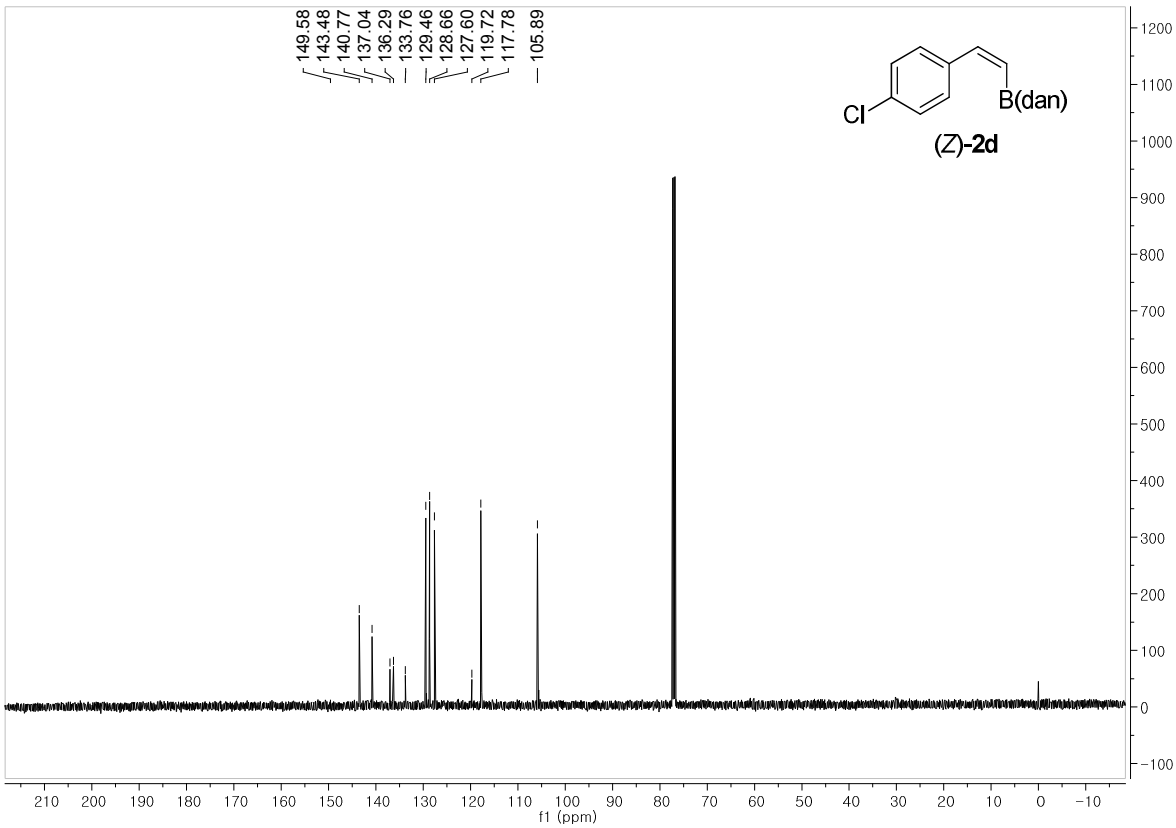
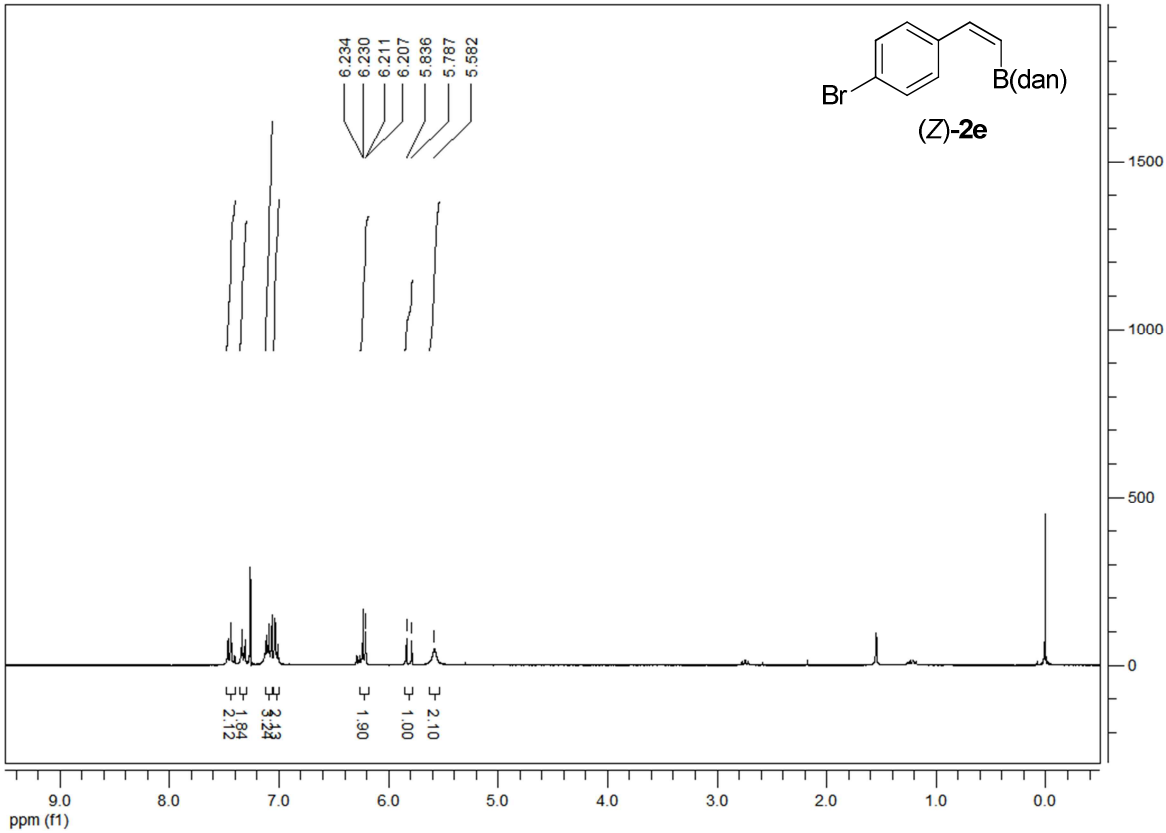
140.67
136.31
130.18
129.92
129.67
129.41
128.40
127.64
127.38
126.93
125.51
125.48
125.45
125.42
125.22
123.06
120.90
119.77
117.94
106.00
F3C
B(dan)
(Z)-2b
f1 (ppm)

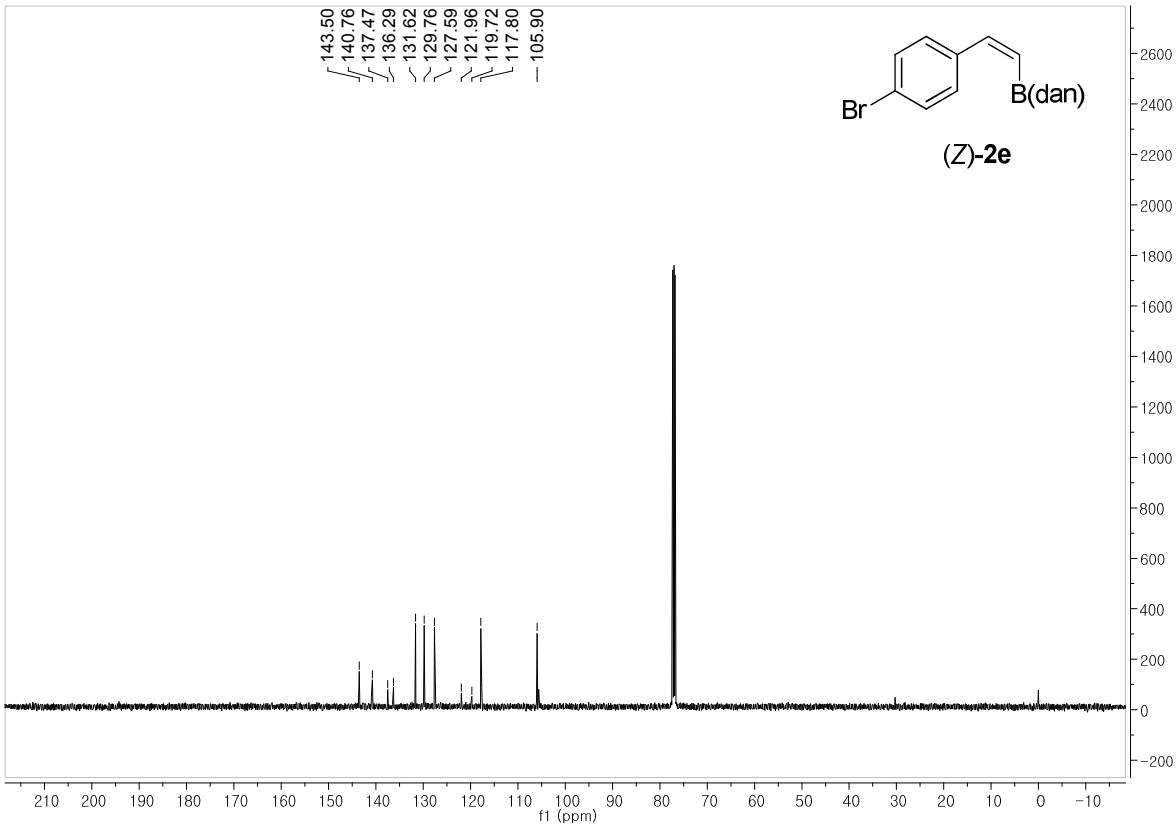

6.213
6.209
6.190
6.186
5.847
5.798
5.577
F
B(dan)
(Z)-2c
1.94
7.04
1.89
1.00
2.06
f1 (ppm)

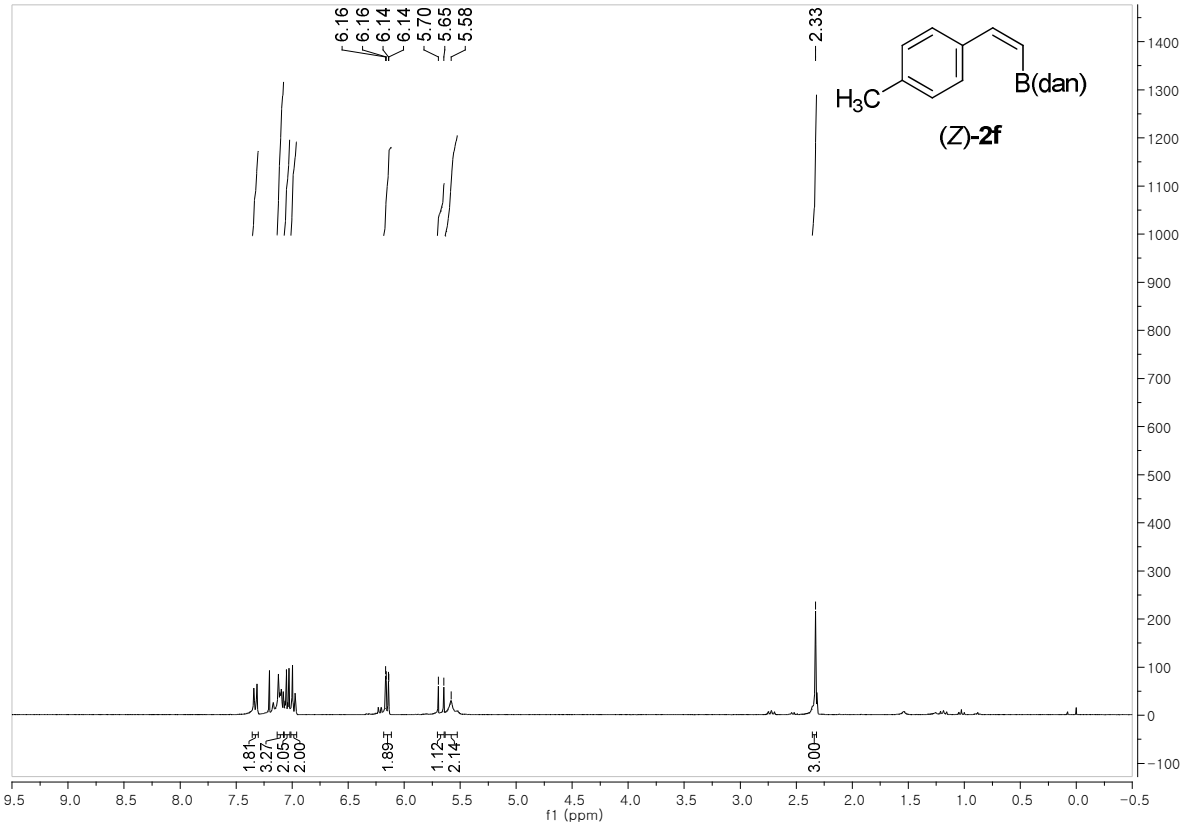

163.79
161.83
143.58
143.56
140.77
129.94
127.57
123.70
123.68
117.74
115.06
114.89
114.84
105.85
F
B(dan)
(Z)-2c
f1 (ppm)

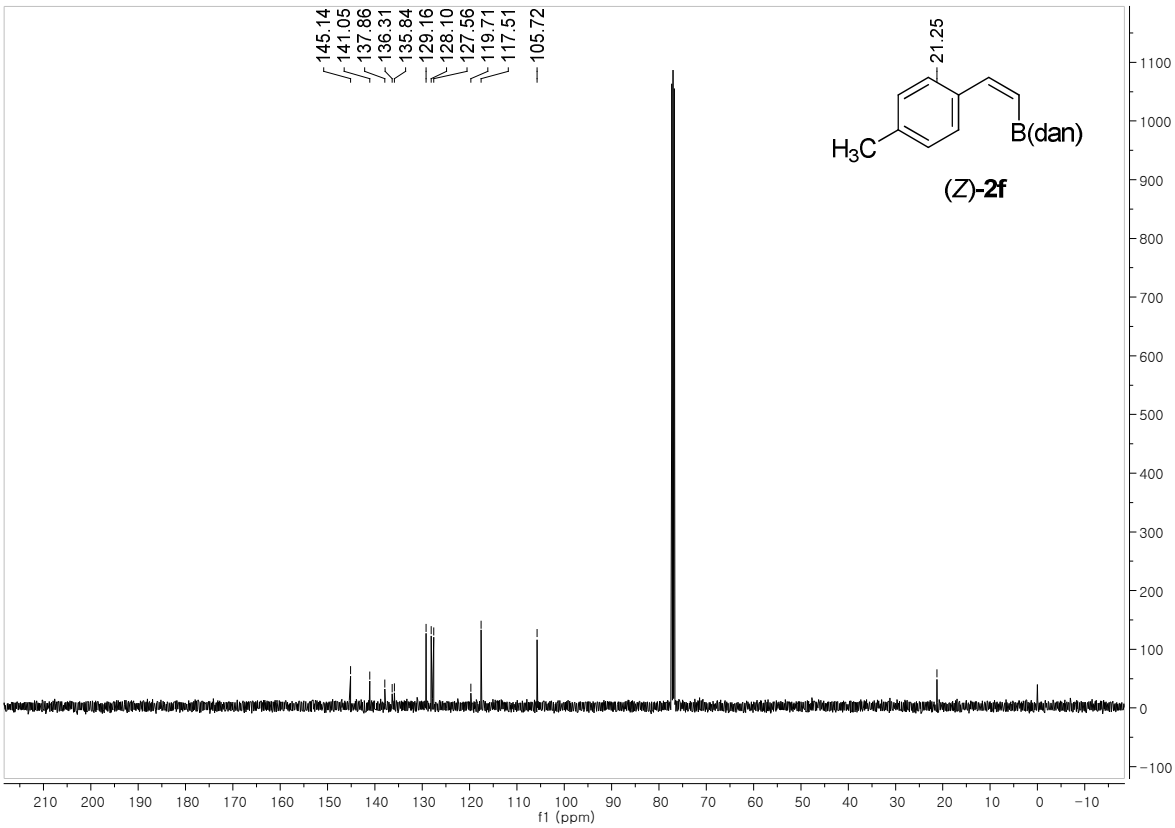

6.23
6.22
6.20
6.20
5.82
5.78
5.57
Cl
B(dan)
(Z)-2d
1.92
2.16
2.95
2.11
2.02
1.00
2.13
f1 (ppm)

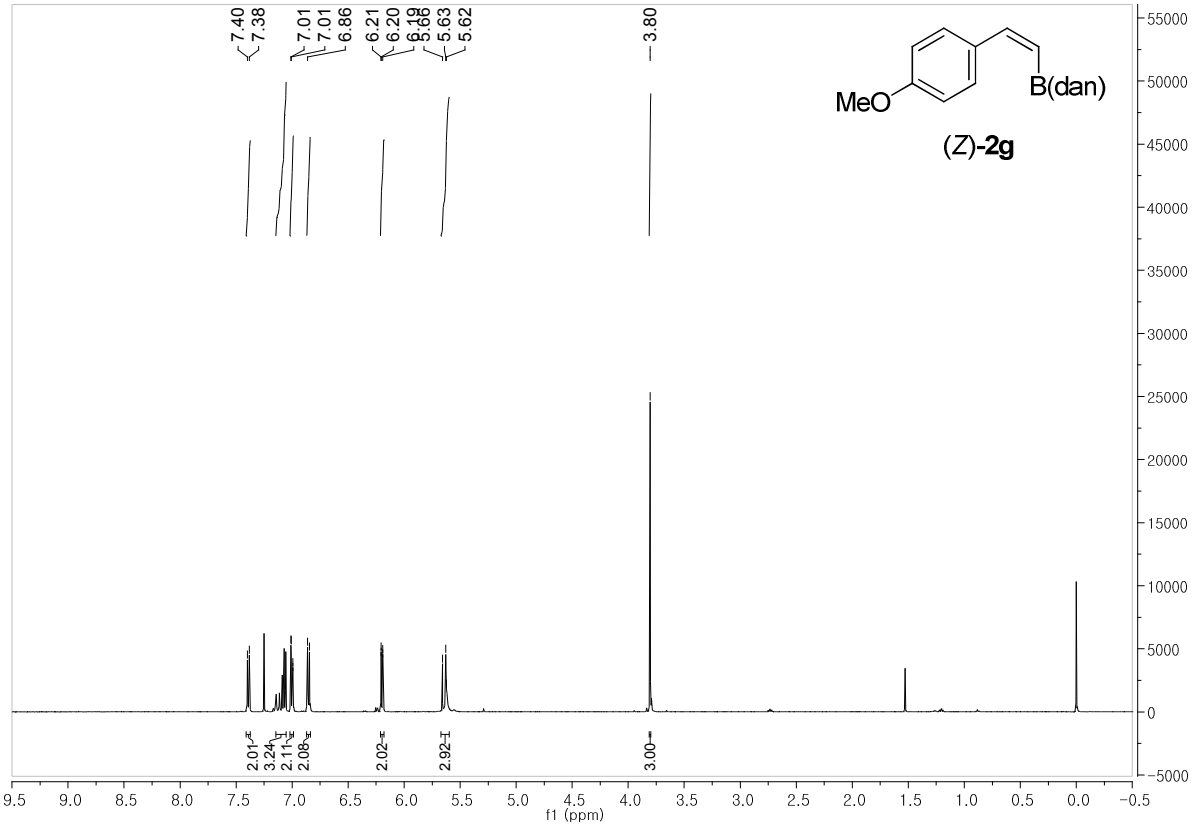

149.58
143.48
140.77
137.04
136.29
133.76
129.46
128.66
127.60
119.72
117.78
105.89
Cl
B(dan)
(Z)-2d
f1 (ppm)

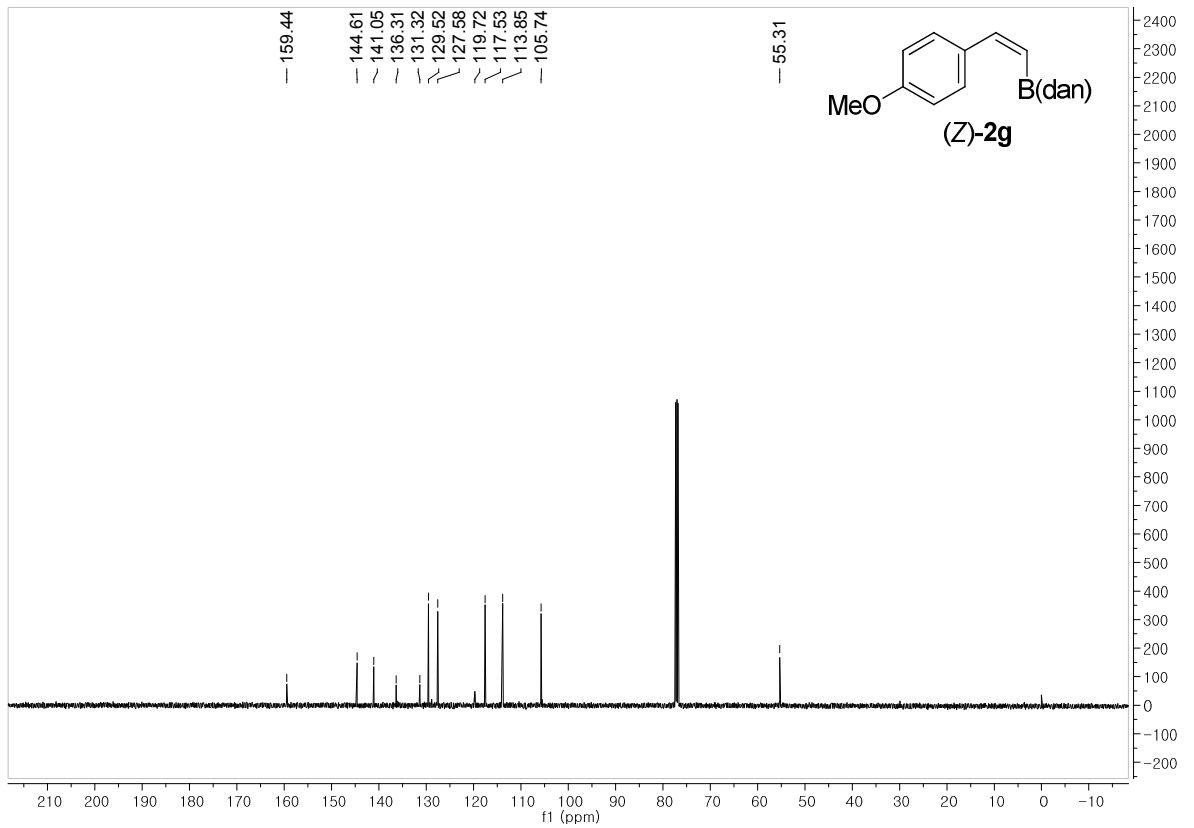

6.234
6.230
6.211
6.207
5.836
5.787
5.582
Br
B(dan)
(Z)-2e
1.84
2.12
1.90
1.00
2.10
ppm (f1)


143.50
140.76
137.47
136.29
131.62
129.76
127.59
121.96
119.72
117.80
105.90
Br
B(dan)
(Z)-2e
f1 (ppm)


6.16
6.16
6.14
6.14
5.70
5.65
5.58
2.33
H3C
B(dan)
(Z)-2f
1.81
3.27
2.05
2.00
1.89
1.12
2.14
3.00
f1 (ppm)


145.14
141.05
137.86
136.31
135.84
129.16
128.10
127.56
119.71
117.51
105.72
21.25
H3C
B(dan)
(Z)-2f
f1 (ppm)


7.40
7.38
7.01
7.01
6.86
6.21
6.20
6.19
5.66
5.63
5.62
3.80
MeO
B(dan)
(Z)-2g
2.01
3.24
2.11
2.08
2.02
2.92
3.00
f1 (ppm)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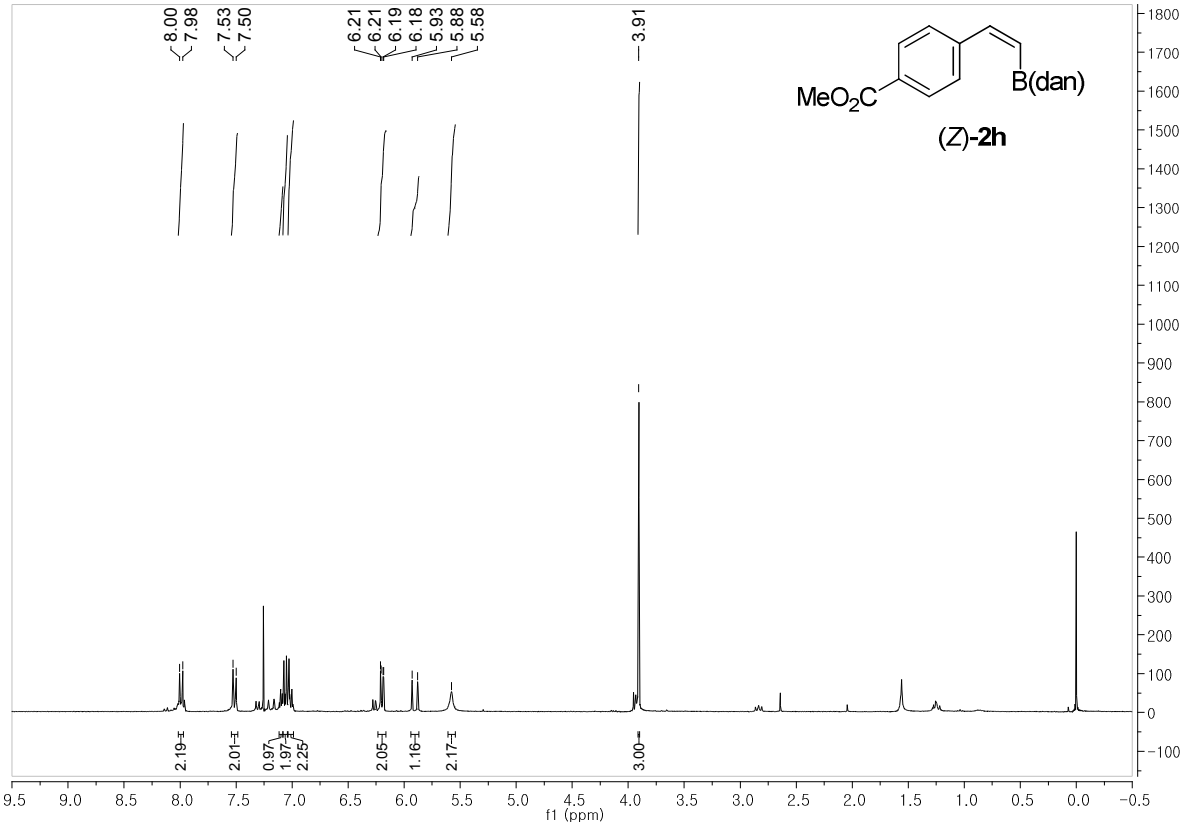
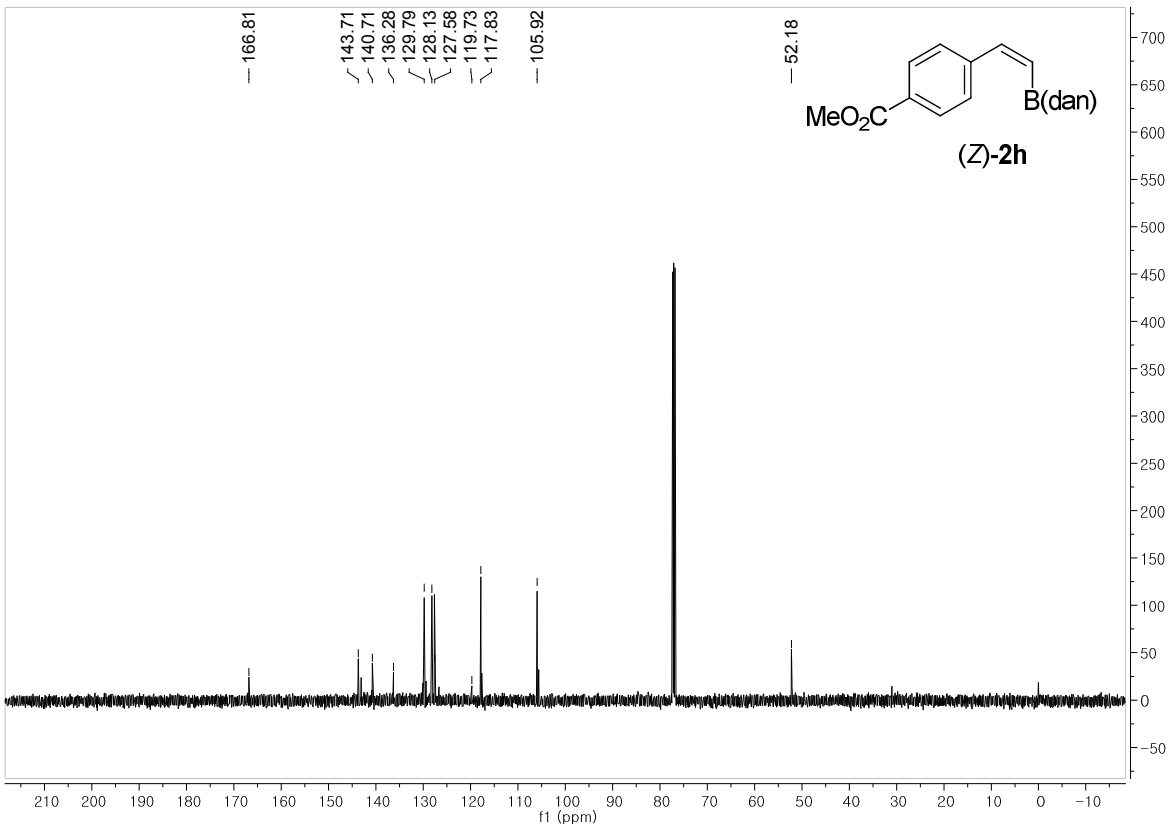
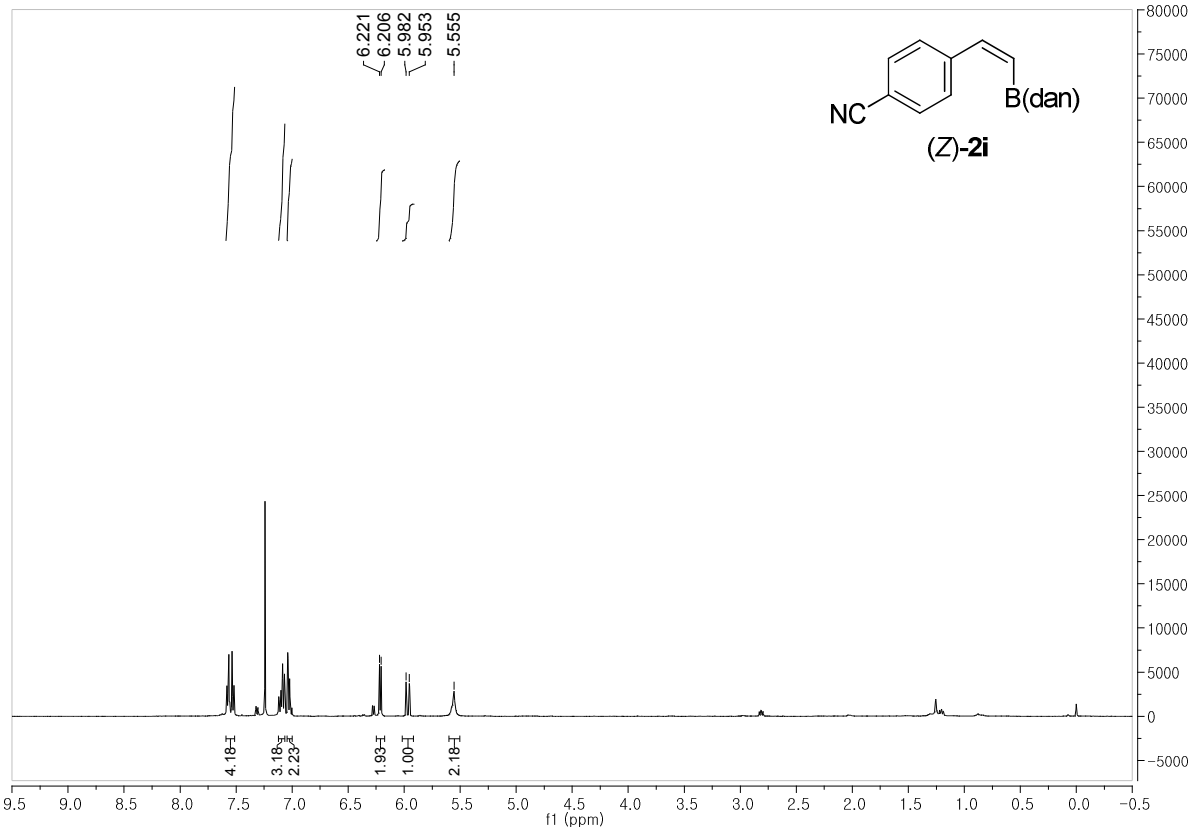
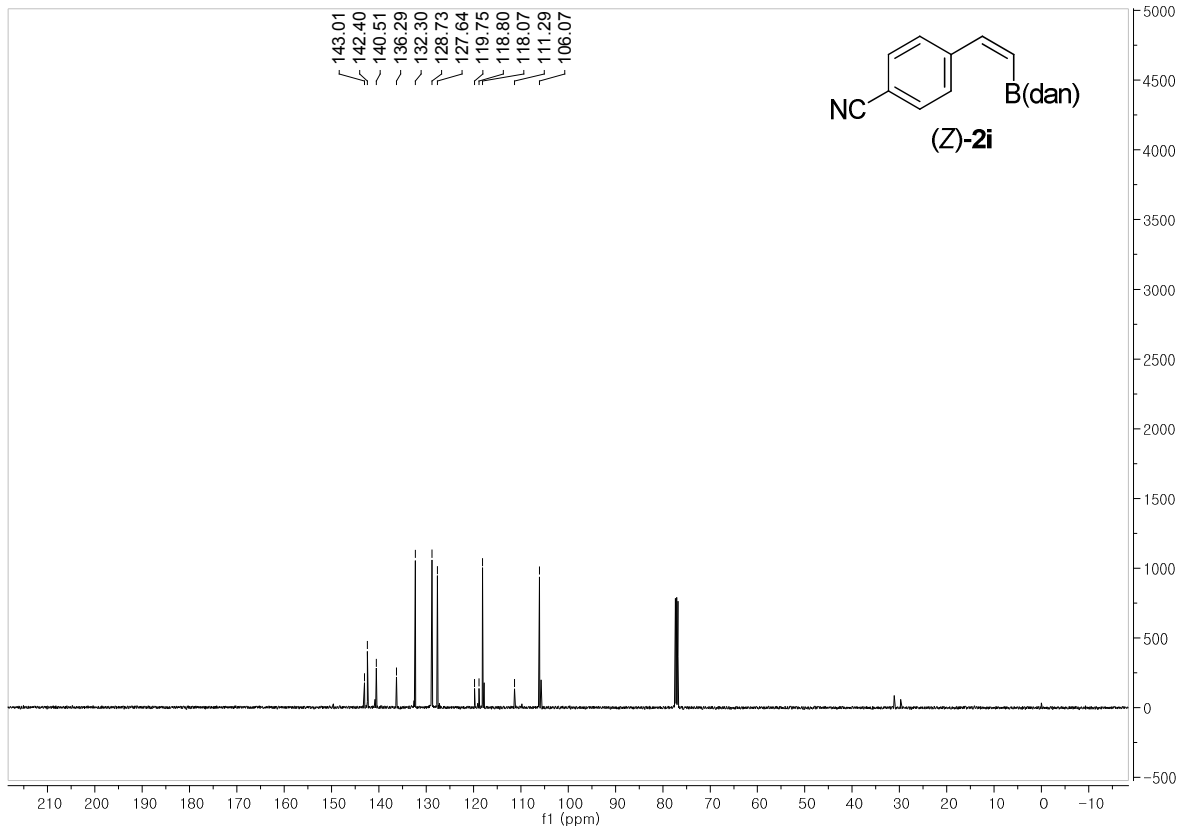
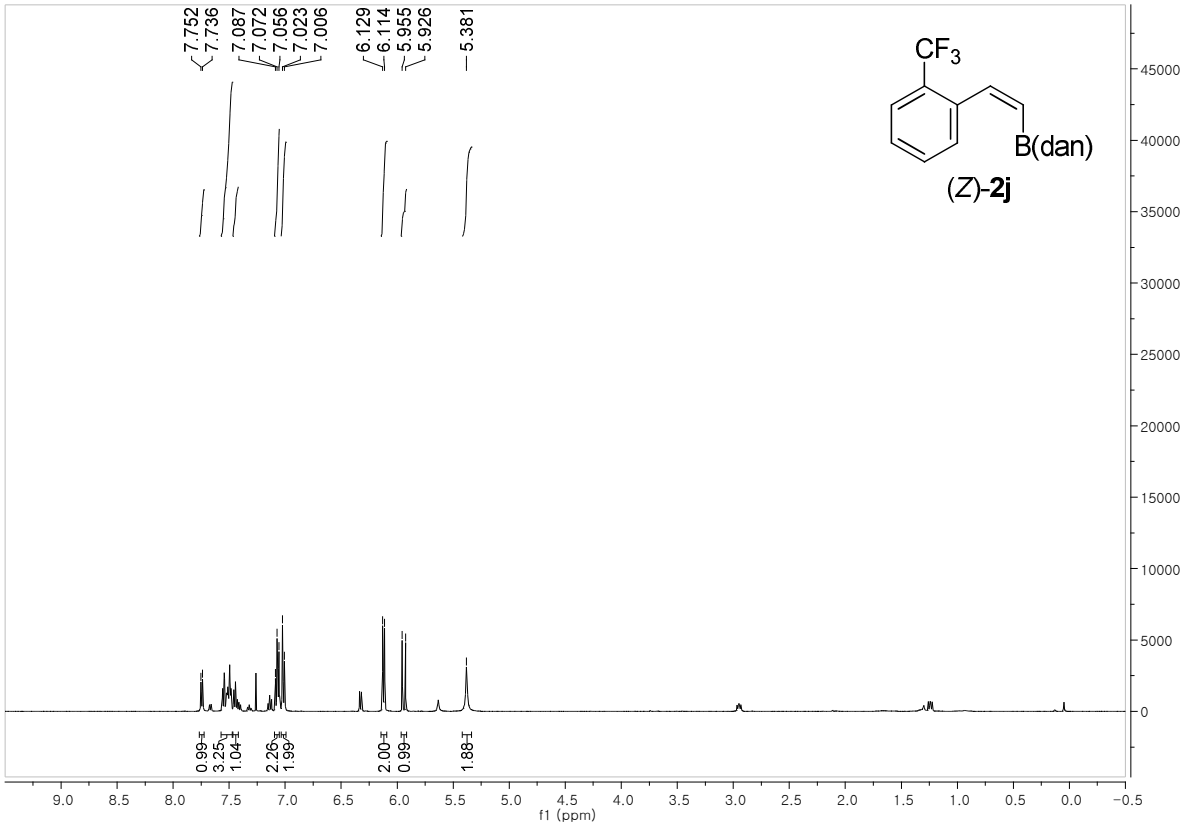
144.61
141.05
136.31
131.32
129.52
127.58
119.72
117.53
113.85
105.74
55.31
MeO
B(dan)
(Z)-2g
f1 (ppm)

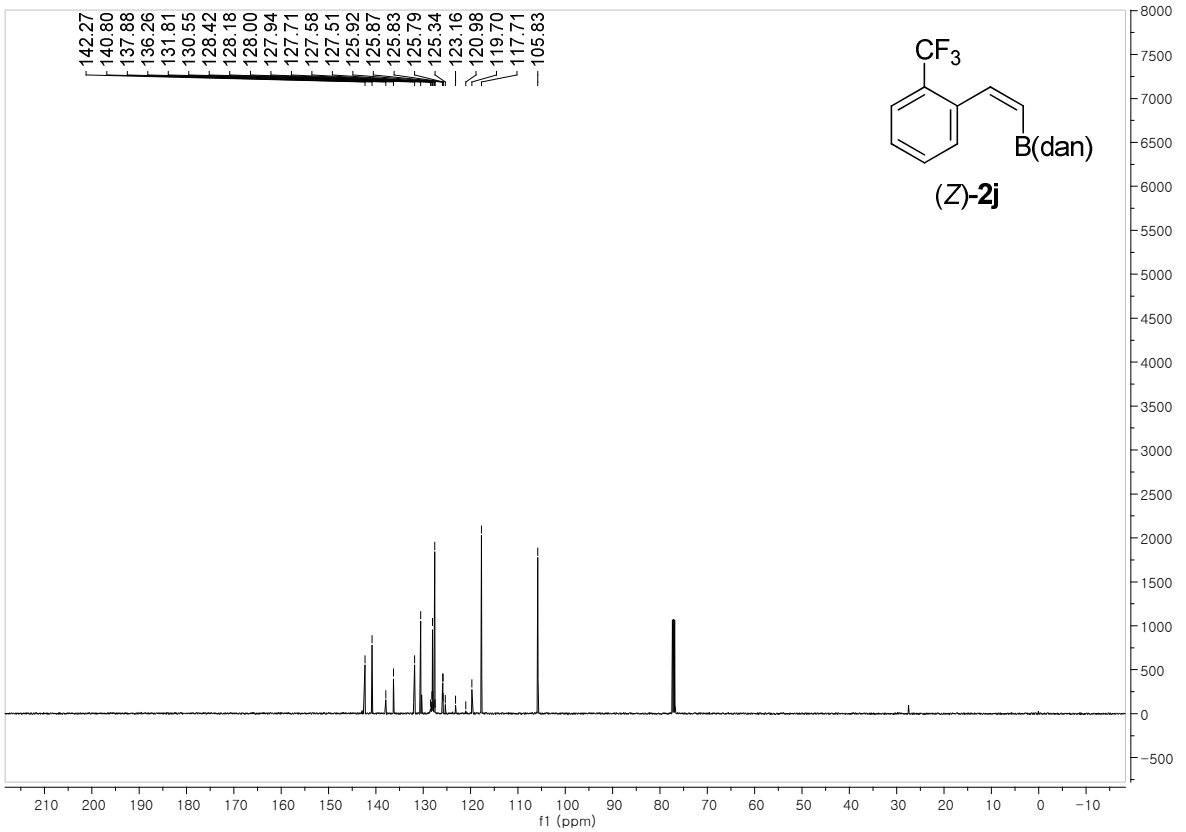

8.00
7.98
7.53
7.50
6.21
6.21
6.19
6.18
5.93
5.88
5.58
3.91
MeO2C
B(dan)
(Z)-2h
2.19
2.01
0.97
1.97
2.25
2.05
1.16
2.17
3.00
f1 (ppm)

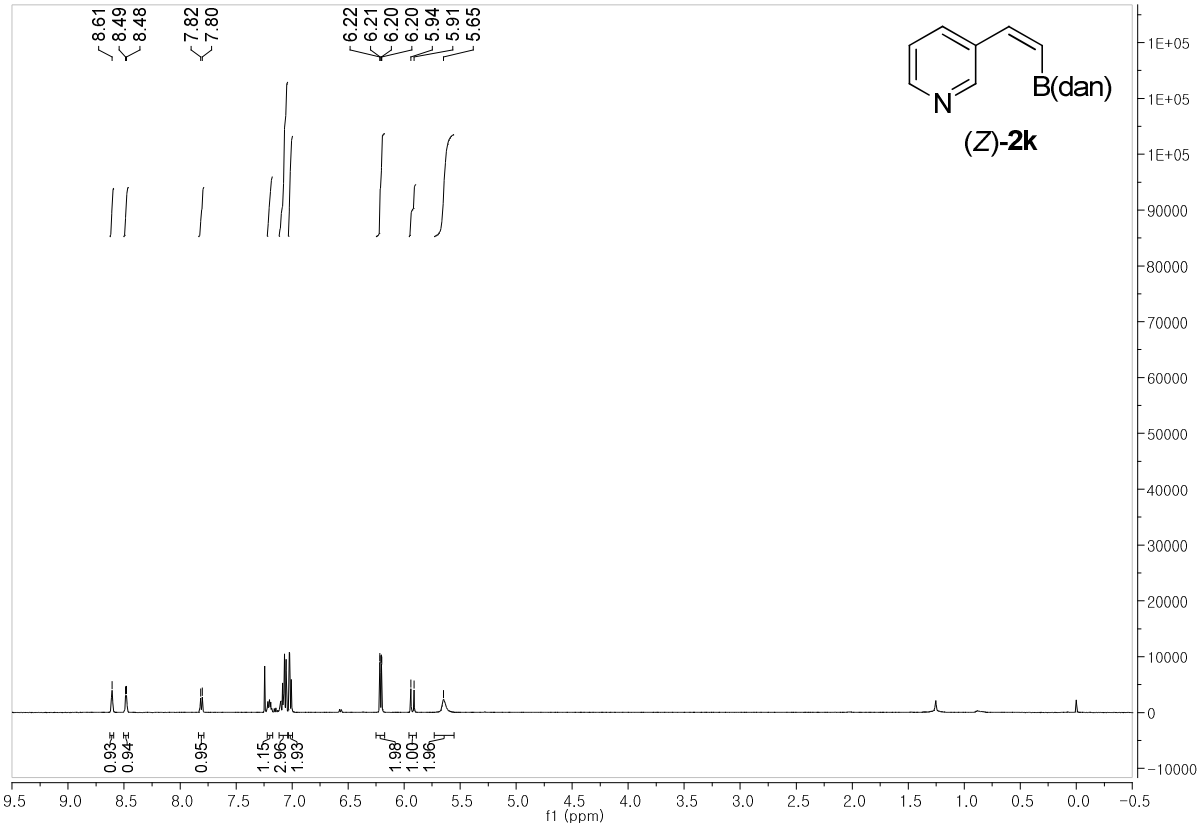

166.81
143.71
140.71
136.28
129.79
128.13
127.58
119.73
117.83
105.92
52.18
MeO2C
B(dan)
(Z)-2h
f1 (ppm)

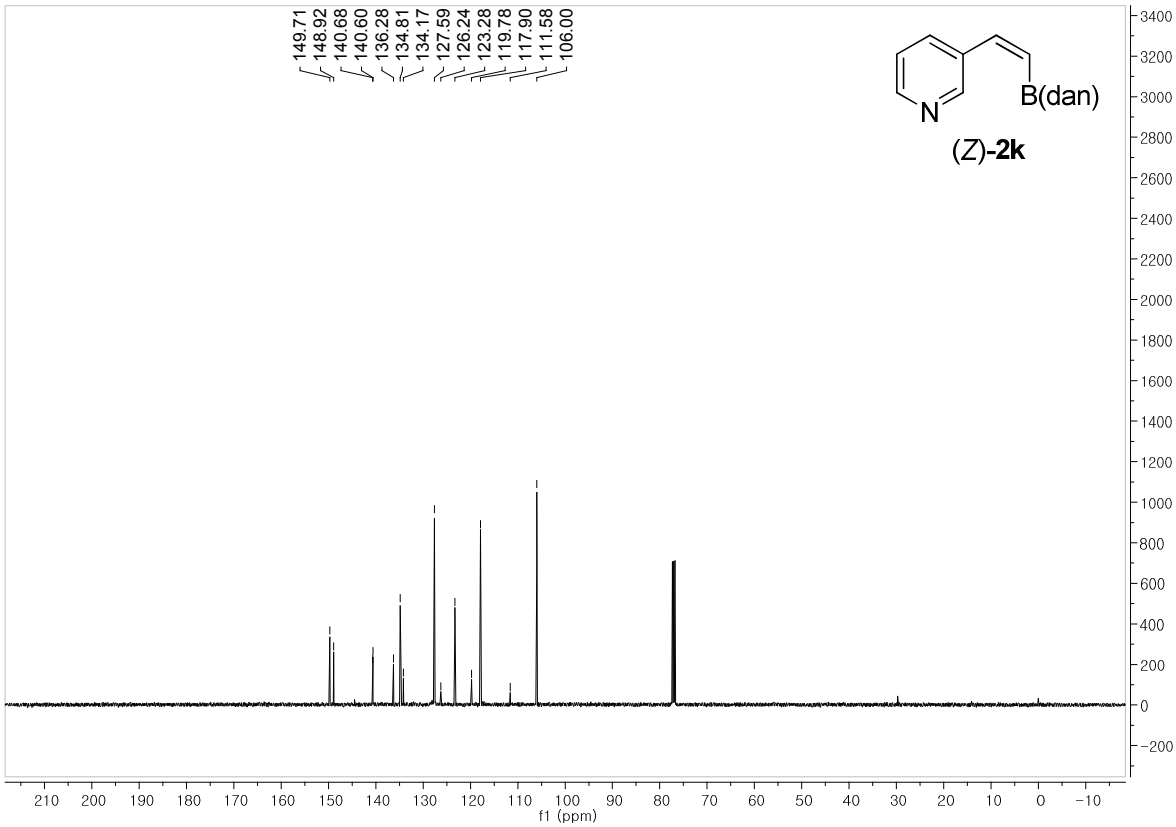

6.221
6.206
5.982
5.953
5.555
NC
B(dan)
(Z)-2i
4.18
3.18
2.23
1.93
1.00
2.18
f1 (ppm)

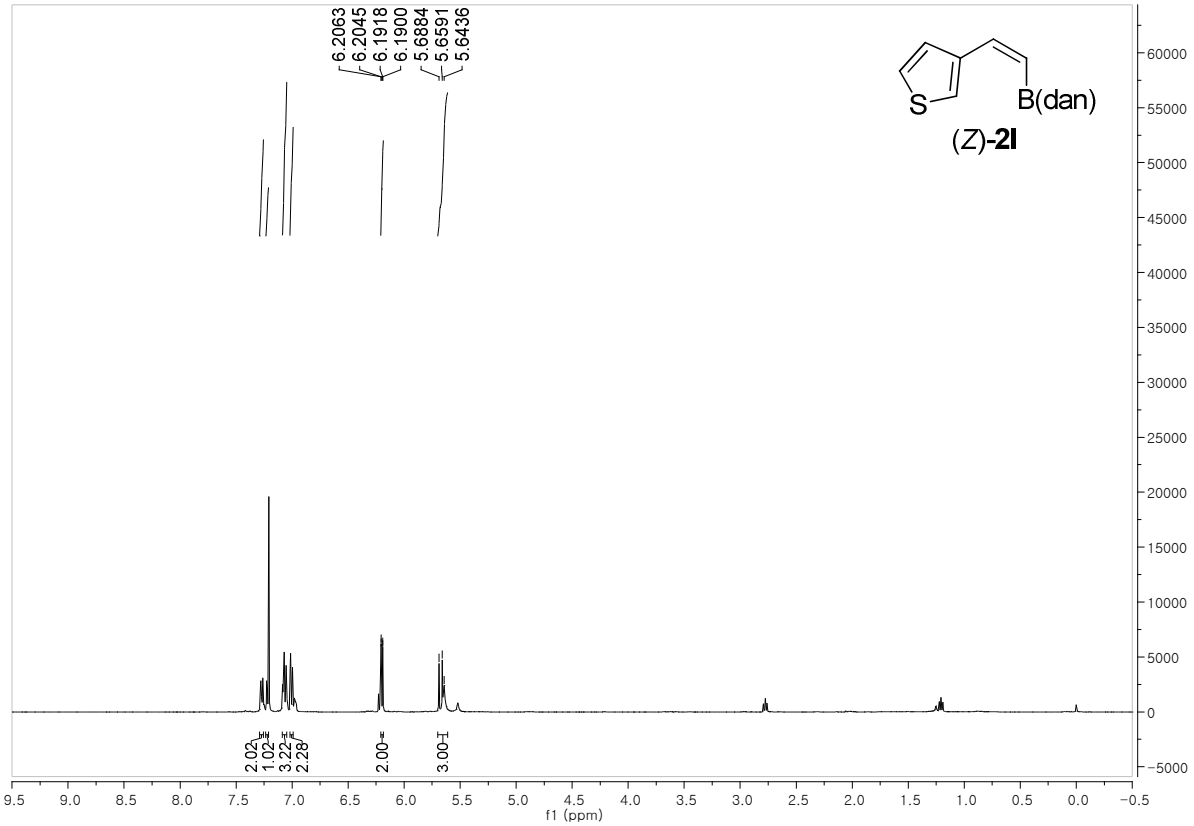

143.01
142.40
140.51
136.29
132.30
128.73
127.64
119.75
118.80
118.07
111.29
106.07
NC
B(dan)
(Z)-2i
f1 (ppm)

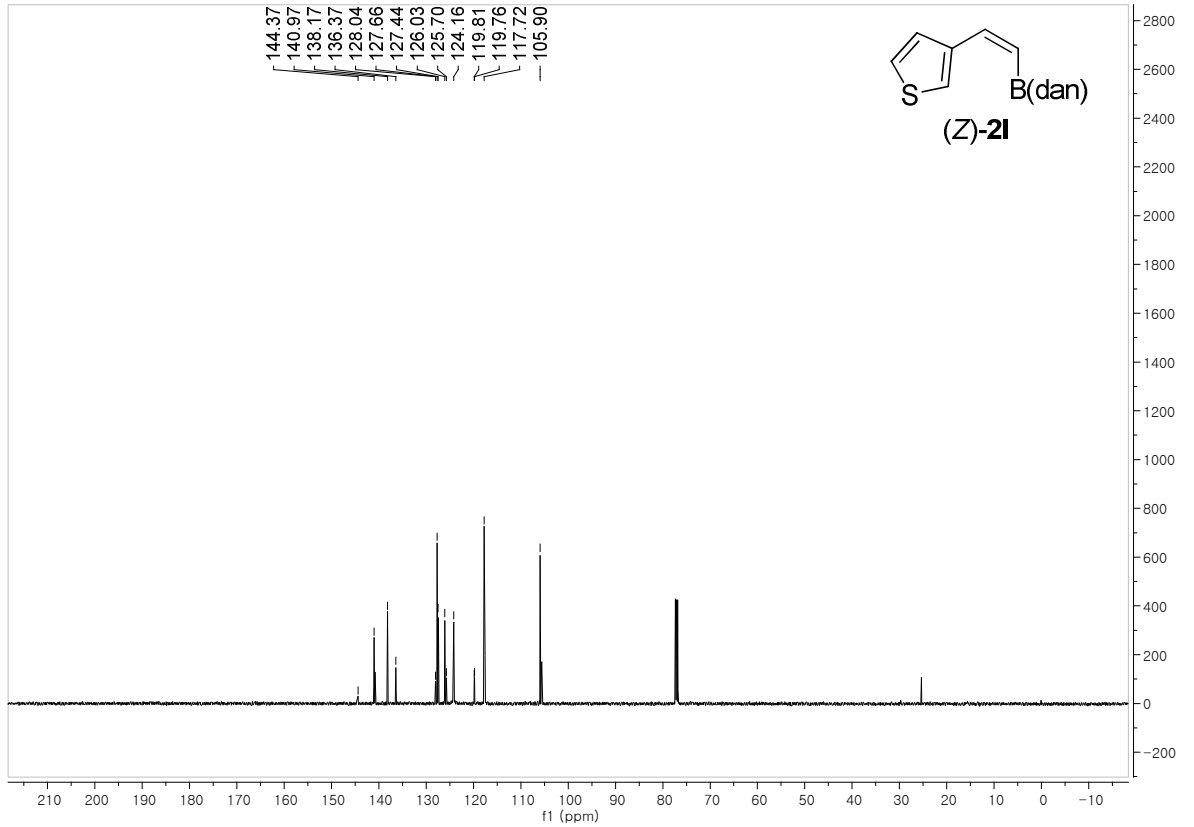

7.752
7.736
7.087
7.072
7.056
7.023
7.006
6.129
6.114
5.955
5.926
5.381
CF3
B(dan)
(Z)-2j
0.99
3.25
1.04
2.26
1.99
2.00
0.99
1.88
f1 (ppm)


142.27
140.80
137.88
136.26
131.81
130.55
128.42
128.18
128.00
127.94
127.71
127.58
127.51
125.92
125.87
125.83
125.79
125.34
123.16
120.98
119.70
117.71
105.83
CF3
B(dan)
(Z)-2j
f1 (ppm)


8.61
8.49
8.48
7.82
7.80
6.22
6.21
6.20
6.20
5.94
5.91
5.65
N
B(dan)
(Z)-2k
0.93
0.94
0.95
1.15
2.96
1.93
1.98
1.00
1.96
f1 (ppm)


149.71
148.92
140.68
140.60
136.28
134.81
134.17
127.59
126.24
123.28
119.78
117.90
111.58
106.00
N
B(dan)
(Z)-2k
f1 (ppm)


6.2063
6.2045
6.1918
6.1900
5.6884
5.6591
5.6436
S
B(dan)
(Z)-2l
2.02
1.02
3.22
2.28
2.00
3.00
f1 (ppm)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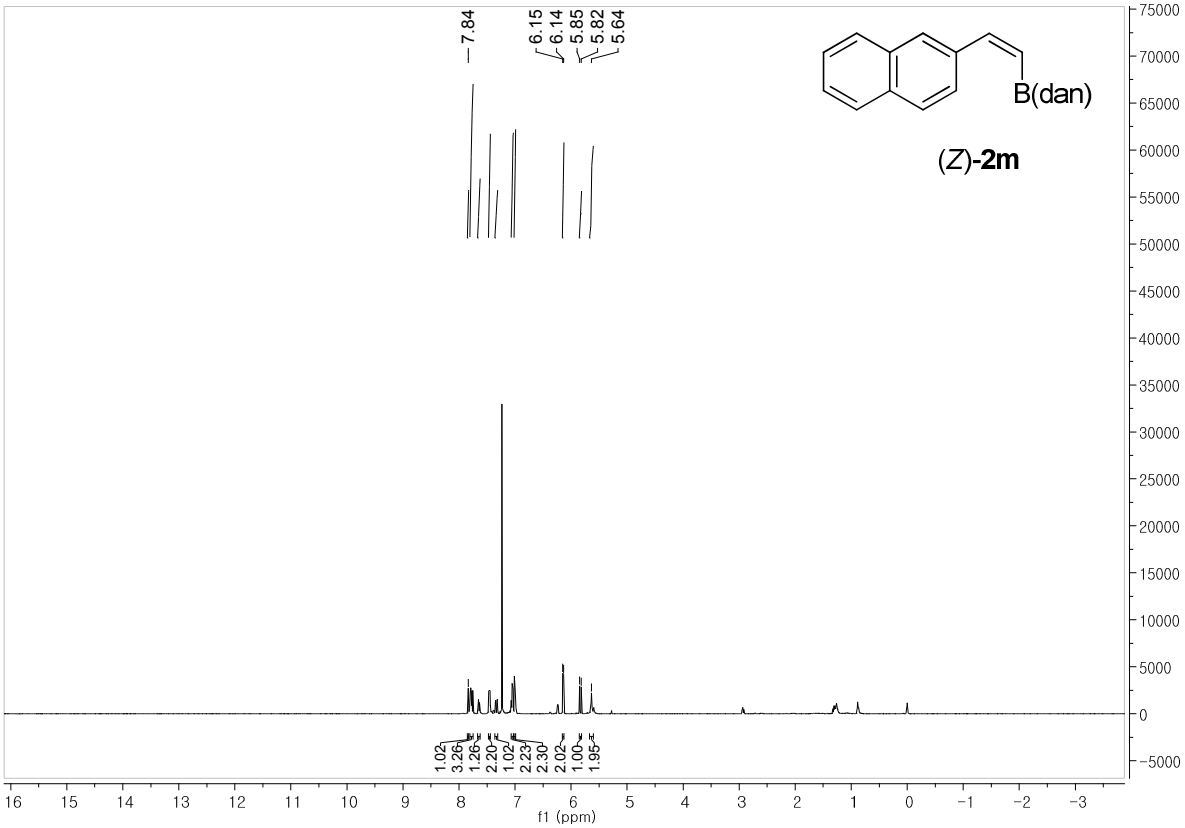
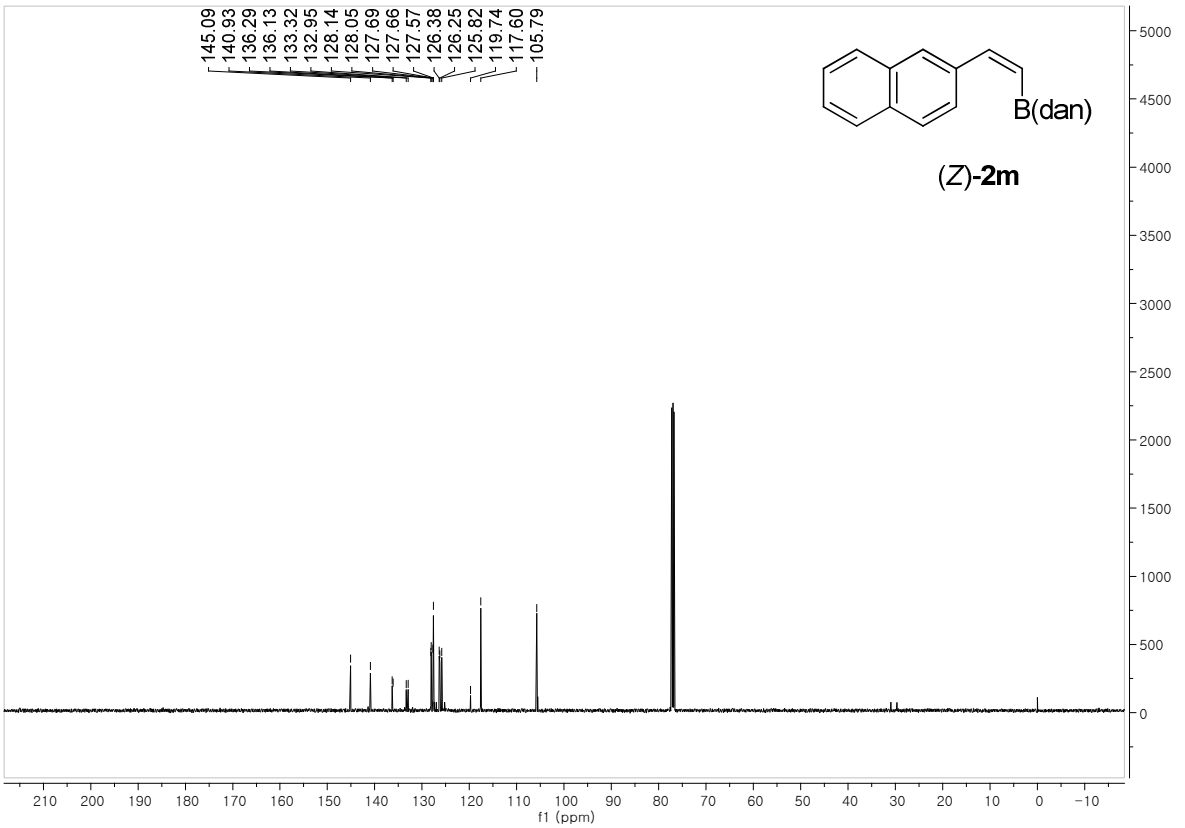
136.37
128.04
127.66
127.44
126.03
125.70
124.16
119.81
119.76
117.72
105.90
S
B(dan)
(Z)-2l
f1 (ppm)


7.84
6.15
6.14
5.85
5.82
5.64
B(dan)
(Z)-2m
1.02
3.26
1.26
2.20
1.02
2.23
2.30
2.02
1.00
1.95
f1 (ppm)


145.09
140.93
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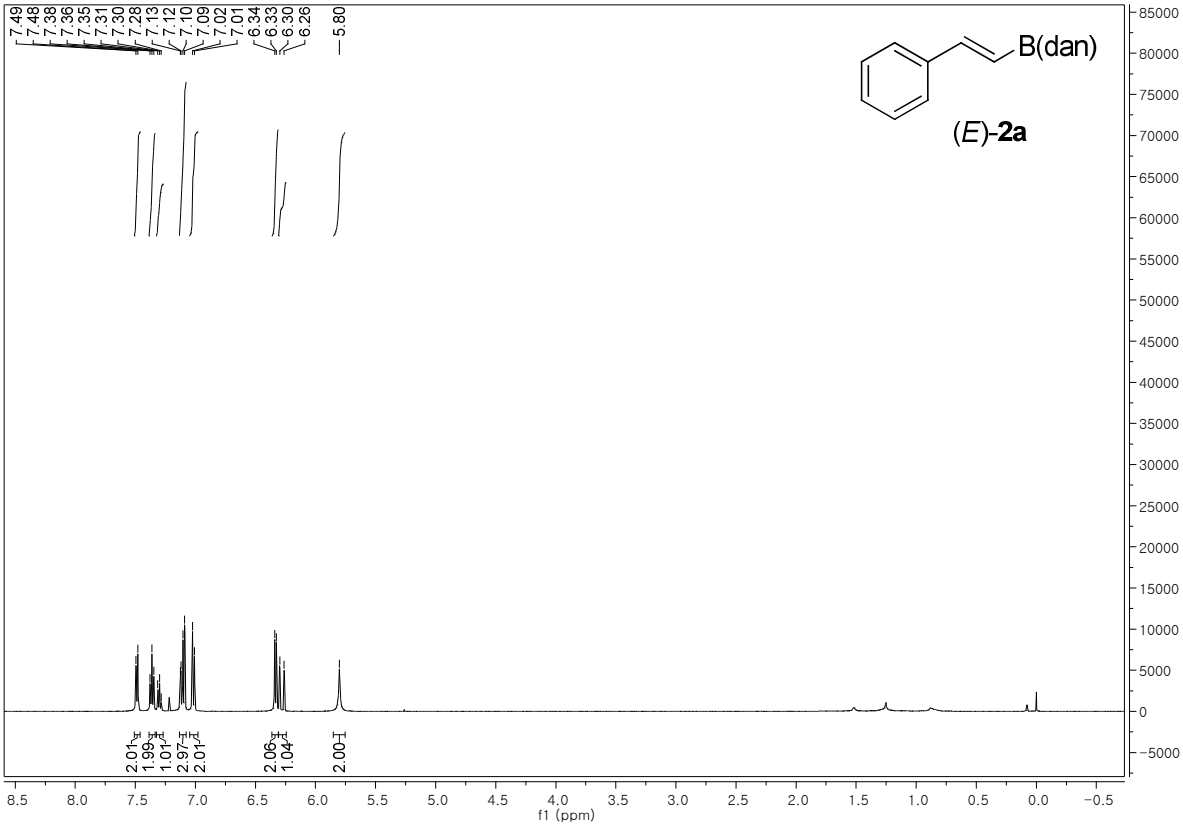
136.13
133.32
132.95
128.14
128.05
127.69
127.66
127.57
126.38
126.25
125.82
119.74
117.60
105.79
B(dan)
(Z)-2m
f1 (ppm)


7.49
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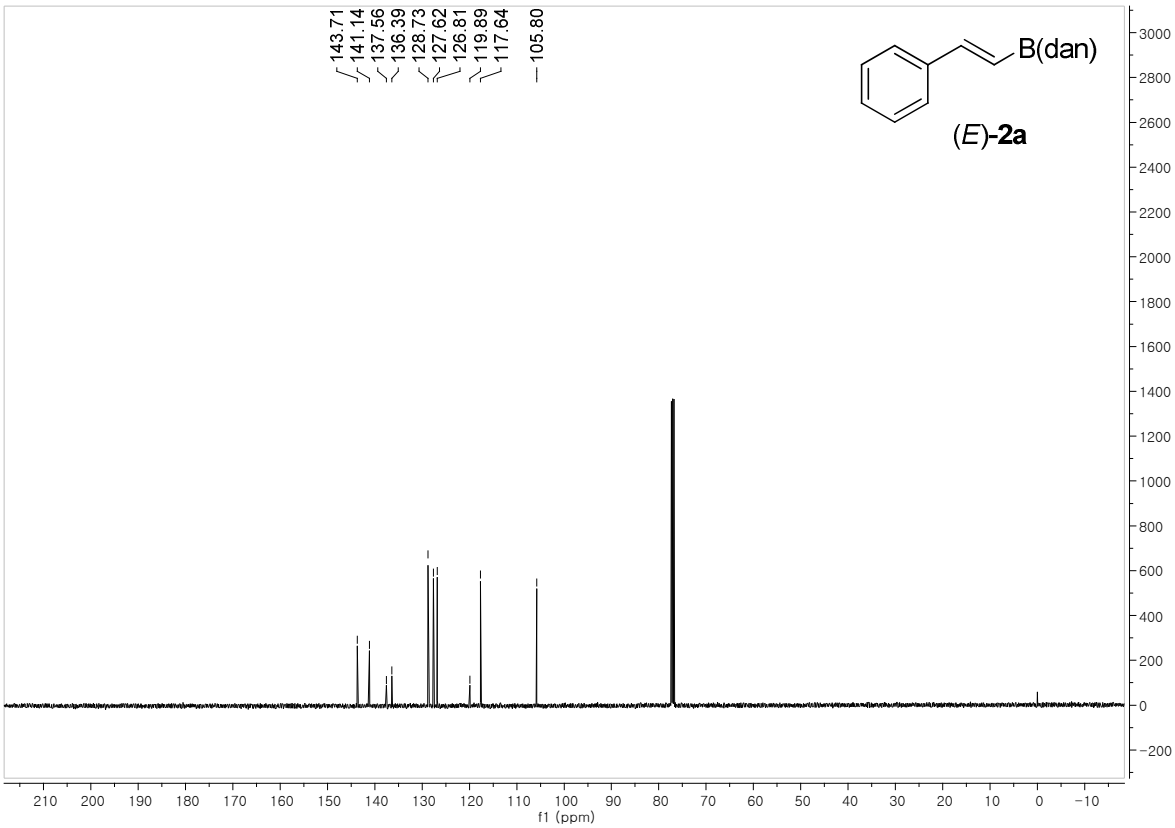
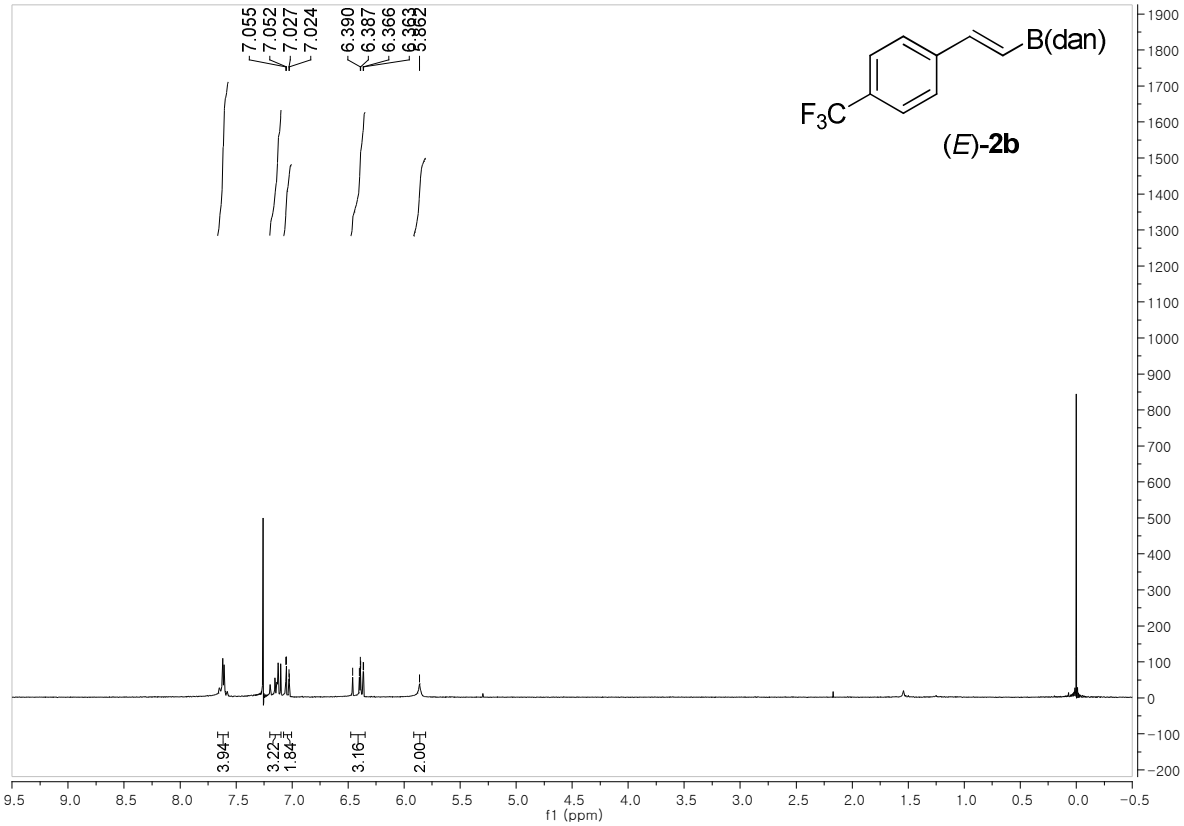
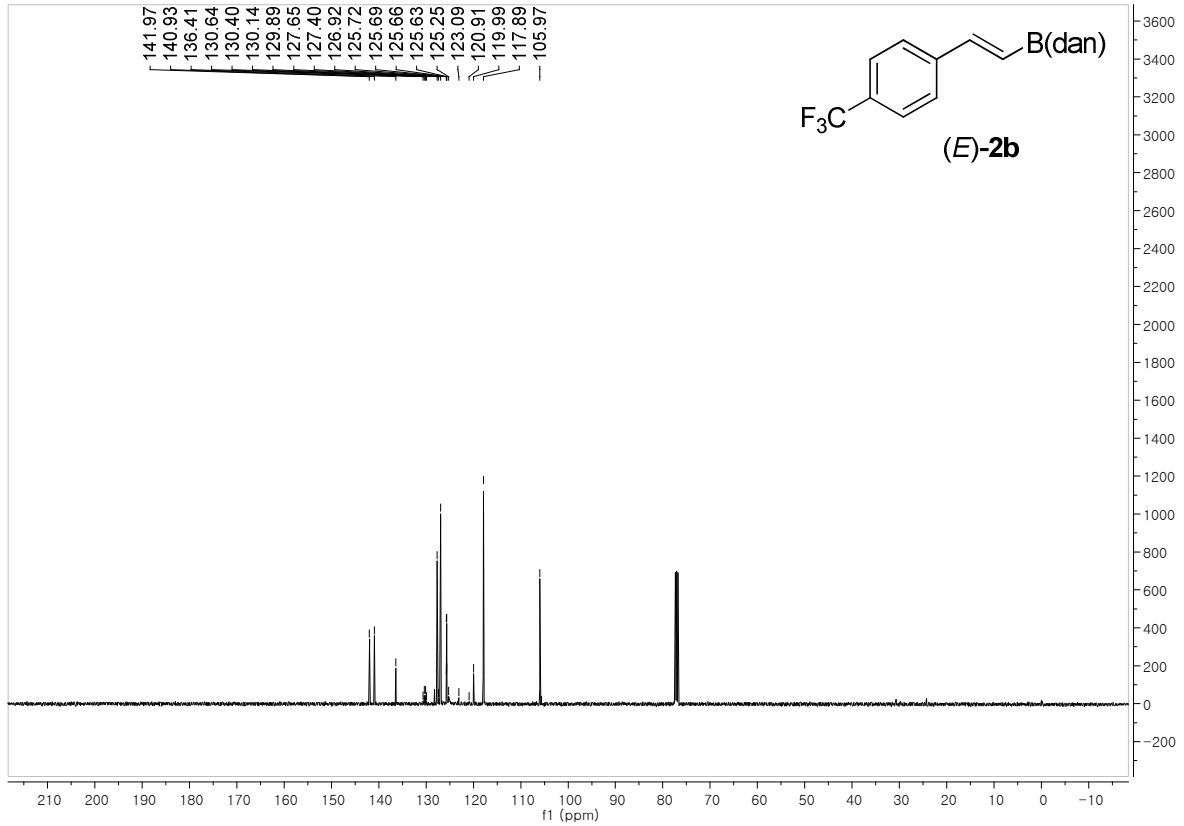
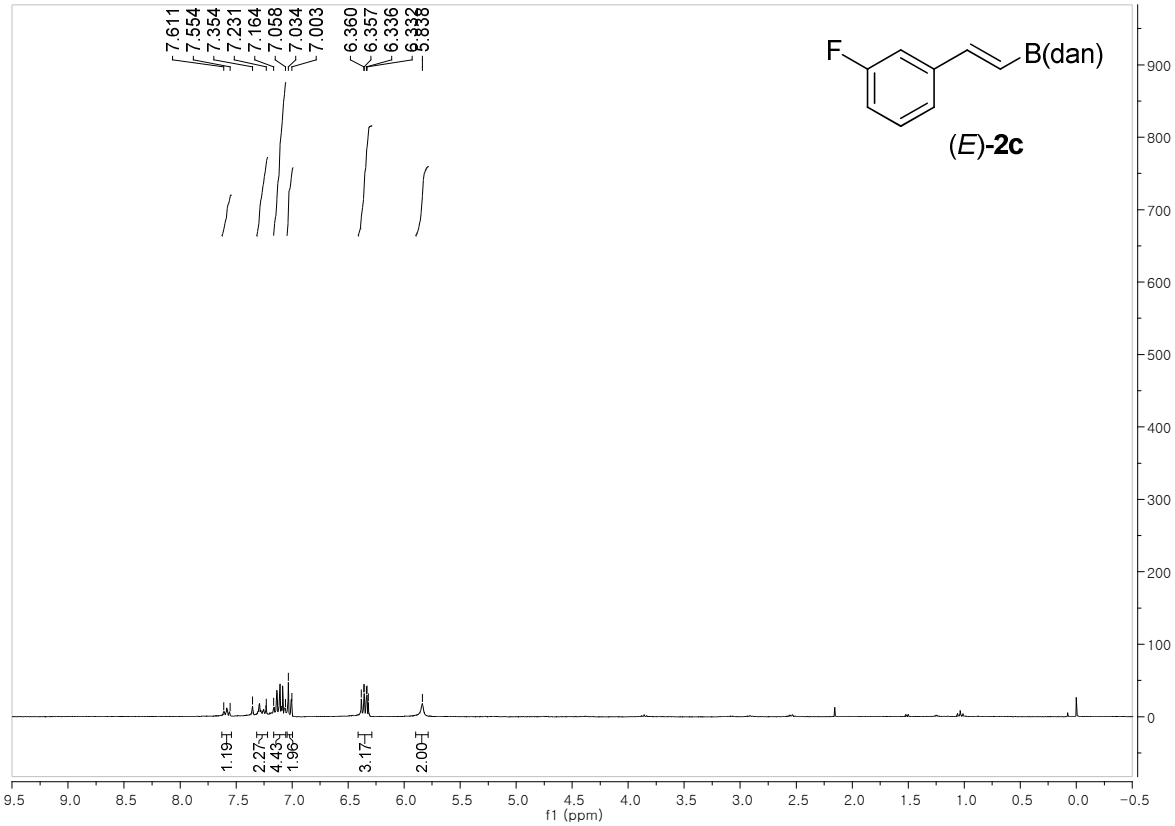
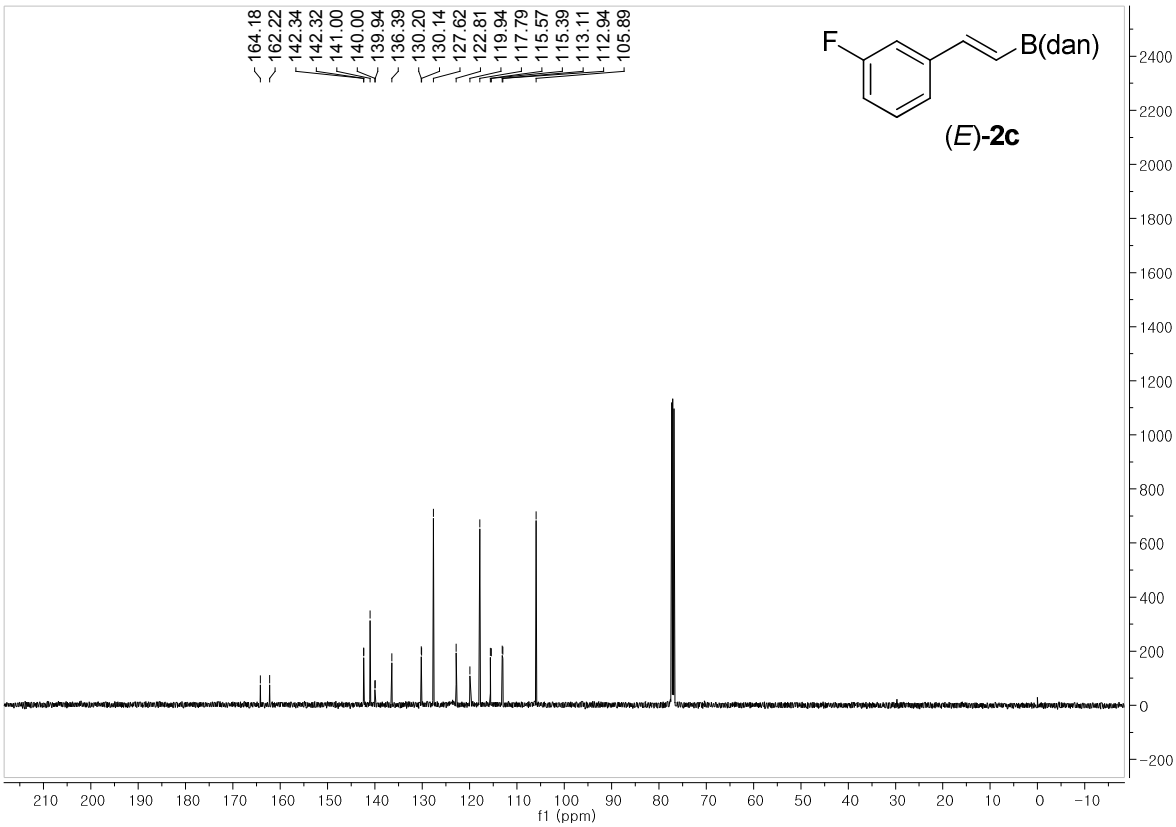
7.36
7.35
7.31
7.30
7.28
7.13
7.12
7.10
7.09
7.02
7.01
6.34
6.33
6.30
6.26
5.80
2.01
1.99
1.01
2.97
2.01
2.06
1.04
2.00
B(dan)
(E)-2a
f1 (ppm)

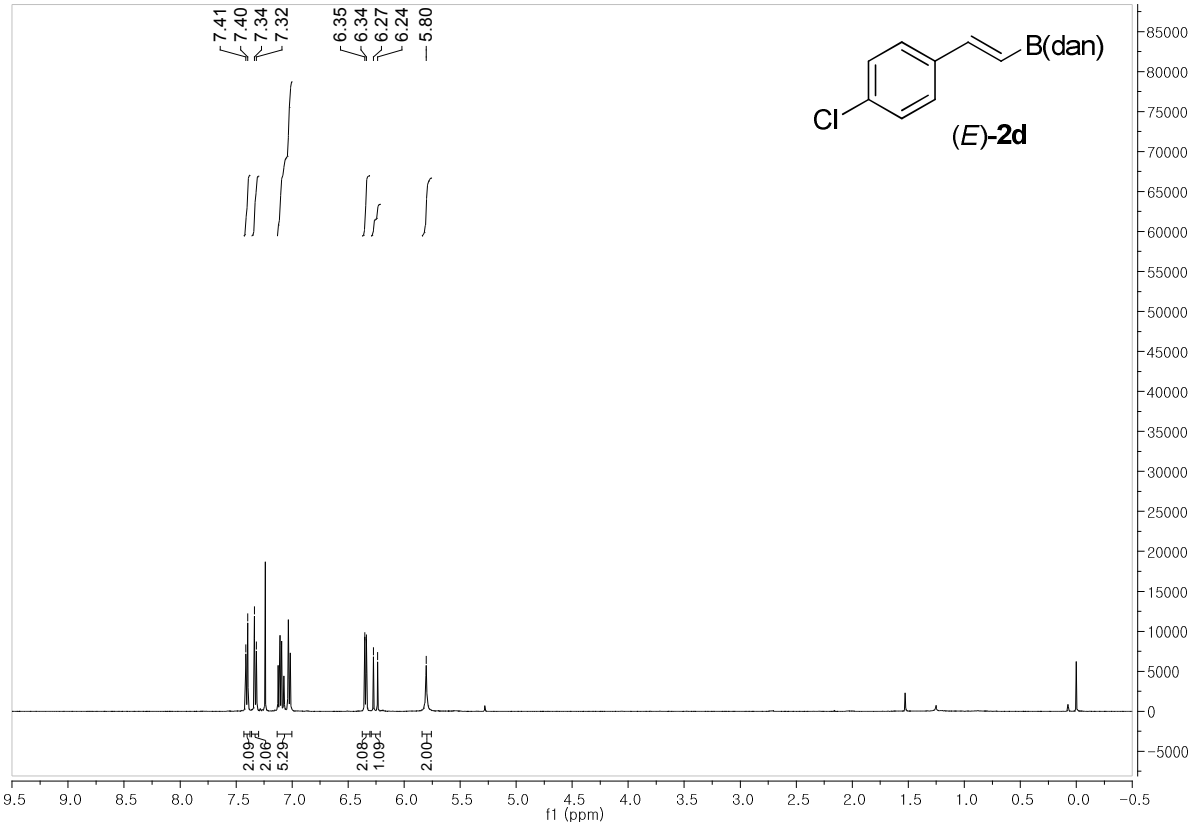

143.71
141.14
137.56
136.39
128.73
127.62
126.81
119.89
117.64
105.80
B(dan)
(E)-2a
f1 (ppm)

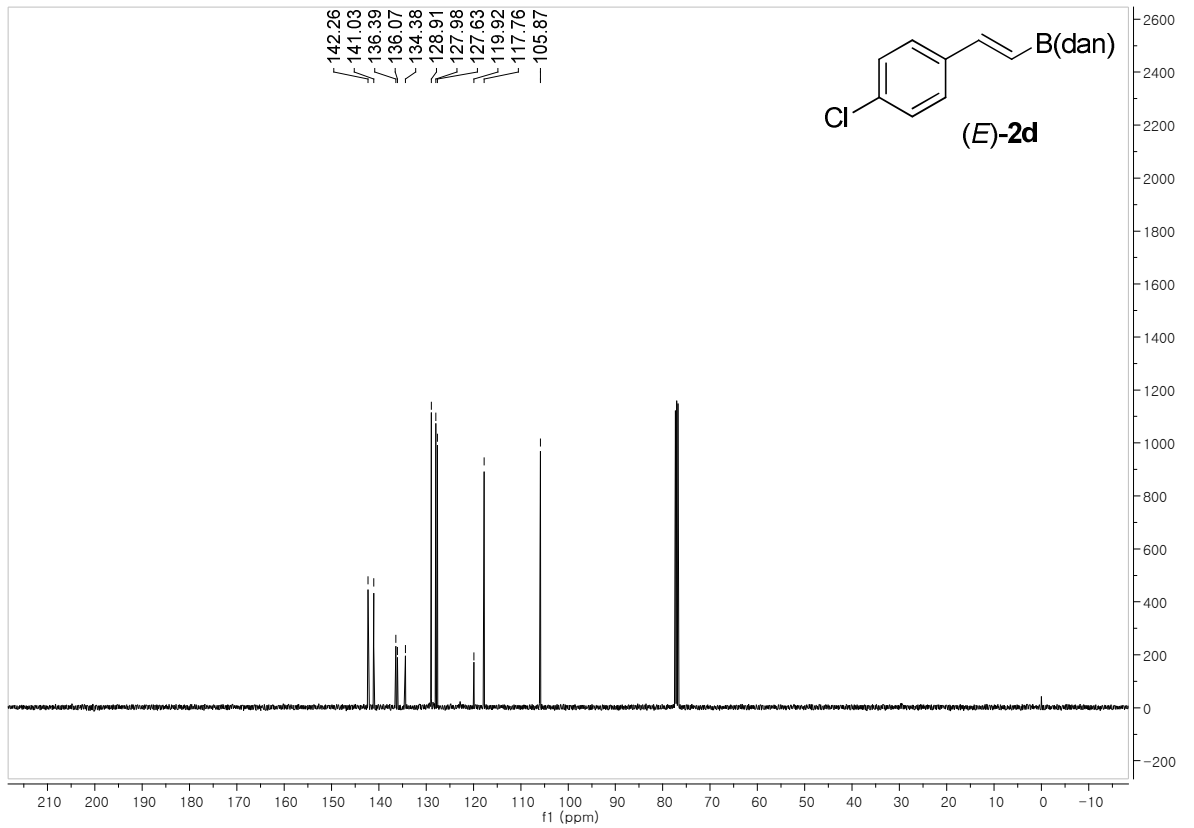

7.055
7.052
7.027
7.024
6.390
6.387
6.366
6.363
5.862
3.94
3.22
1.84
3.16
2.00
B(dan)
F3C
(E)-2b
f1 (ppm)

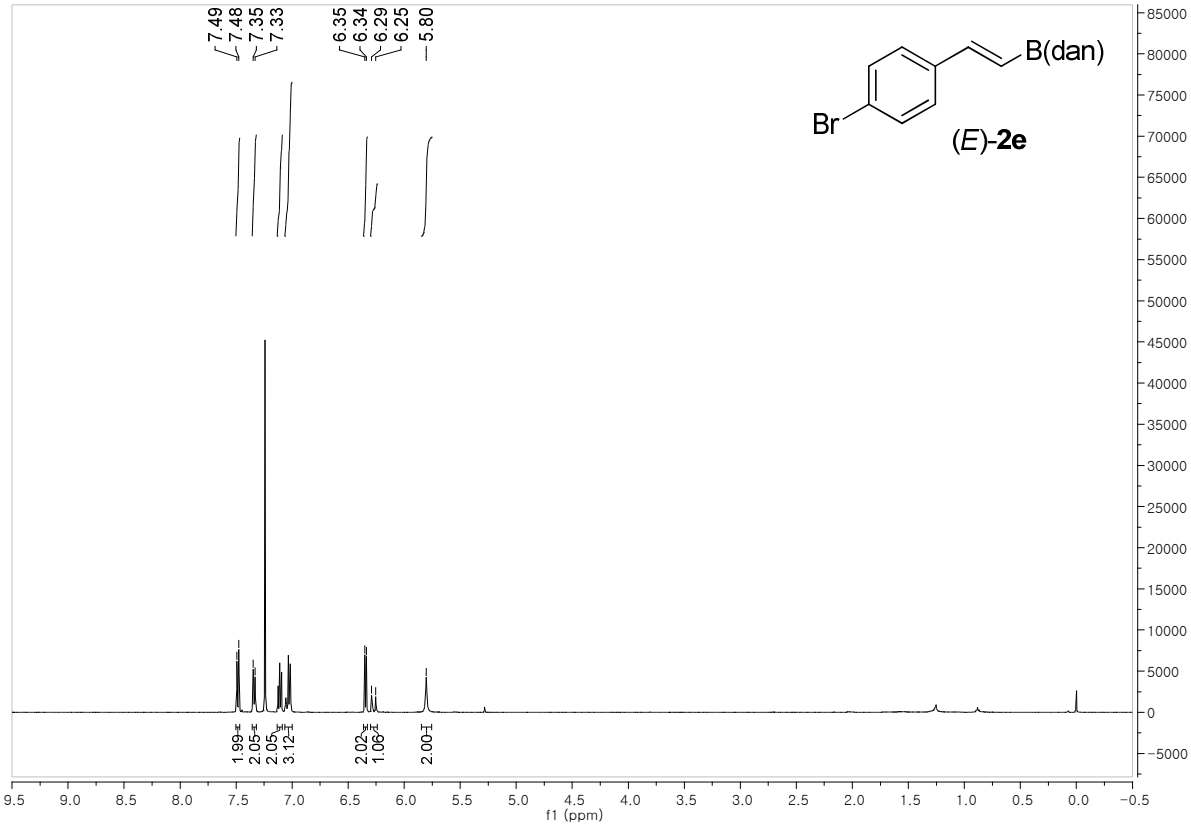

141.97
140.93
136.41
130.64
130.40
130.14
129.89
127.65
127.40
126.92
125.72
125.69
125.66
125.63
125.25
123.09
120.91
119.99
117.89
105.97
B(dan)
F3C
(E)-2b
f1 (ppm)

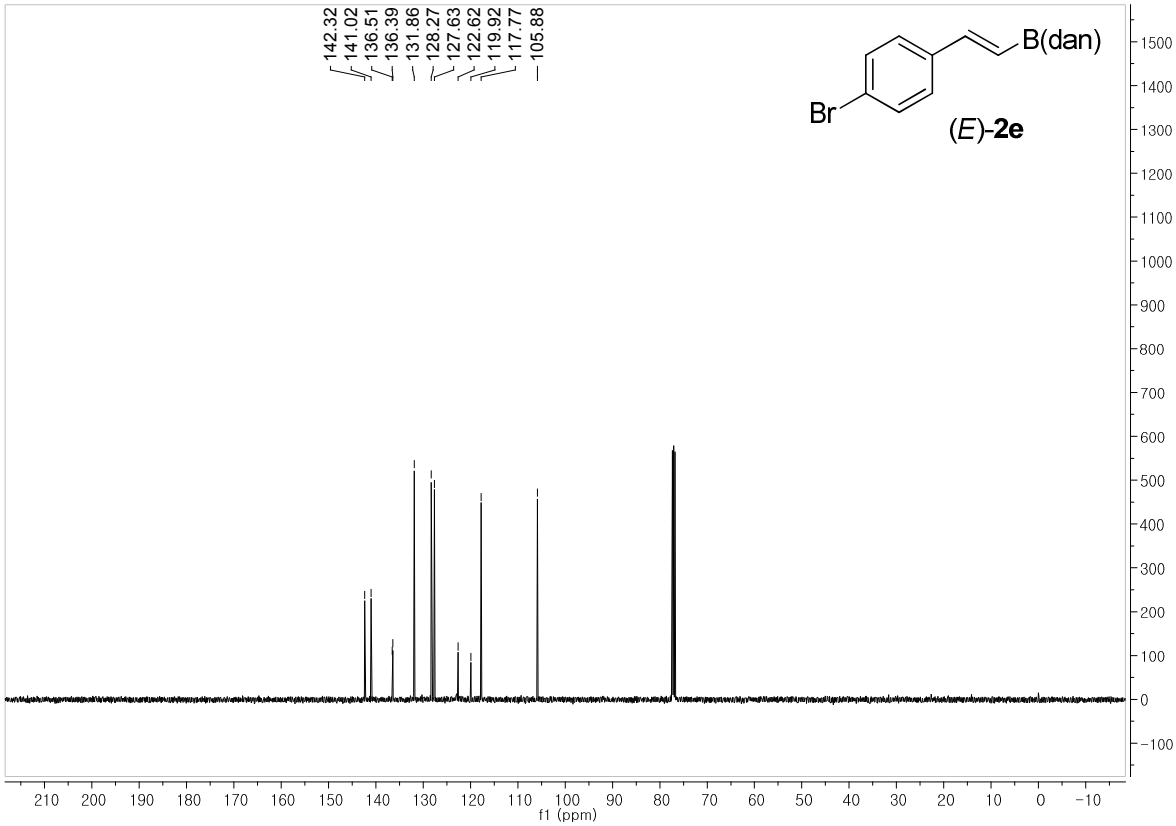

7.611
7.554
7.354
7.231
7.164
7.058
7.034
7.003
6.360
6.357
6.336
5.838
1.19
2.27
4.43
1.96
3.17
2.00
F
B(dan)
(E)-2c
f1 (ppm)

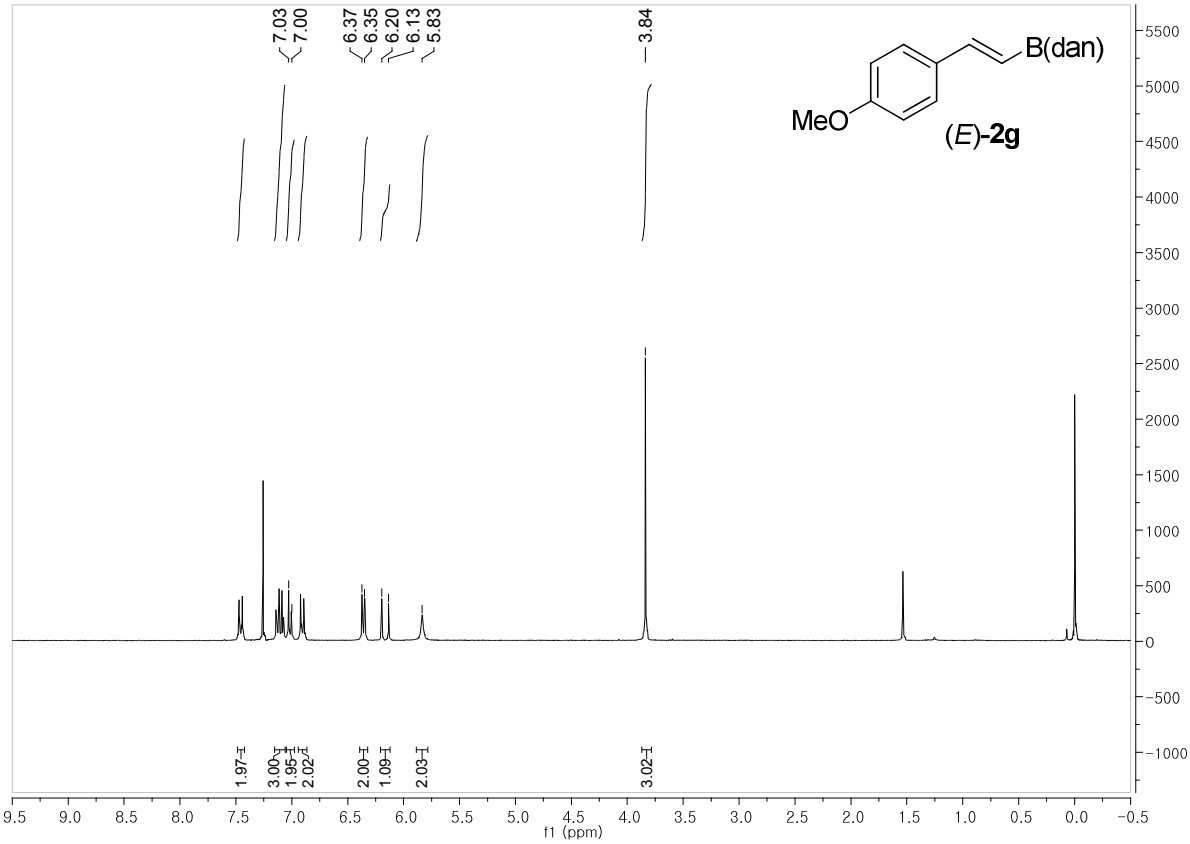

164.18
162.22
142.34
142.32
141.00
140.00
139.94
136.39
130.20
130.14
127.62
122.81
119.94
117.79
115.57
115.39
113.11
112.94
105.89
F
B(dan)
(E)-2c
f1 (ppm)

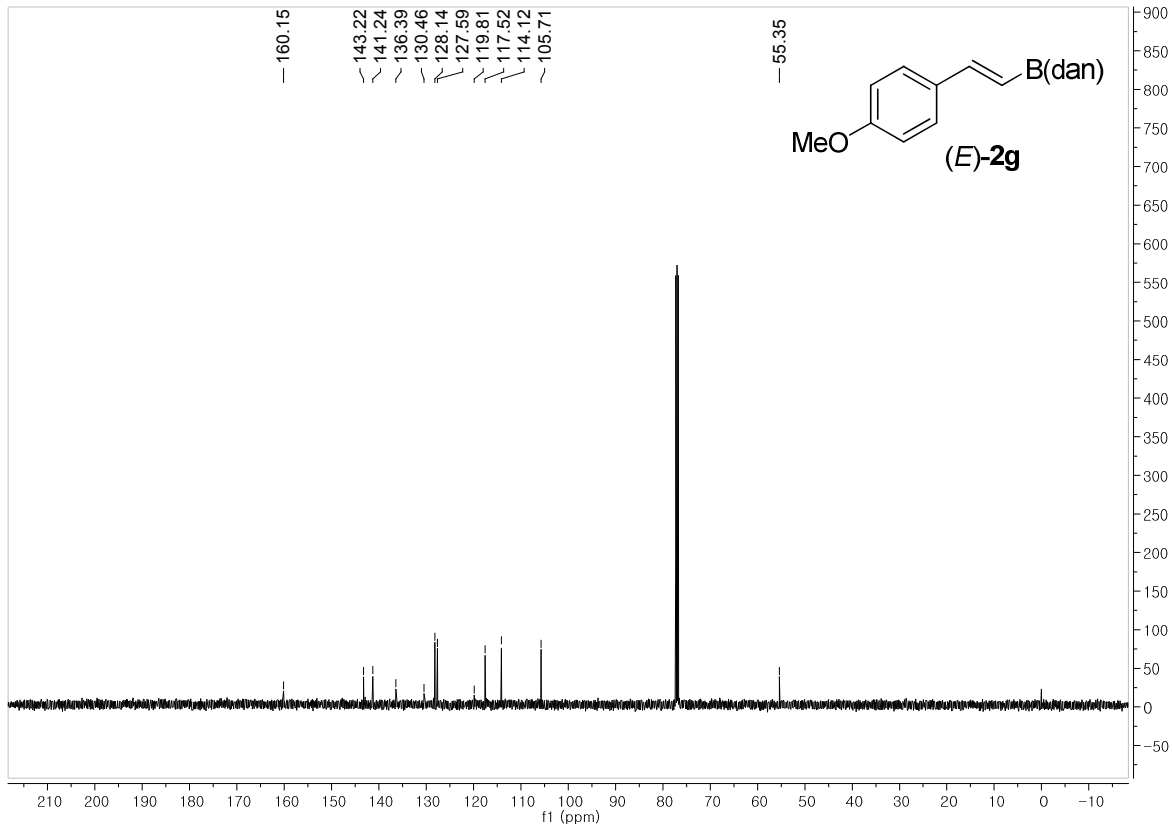

7.41
7.40
7.34
7.32
6.35
6.34
6.27
6.24
5.80
B(dan)
Cl
(E)-2d
2.09
2.06
5.29
2.08
1.09
2.00
f1 (ppm)


142.26
141.03
136.39
136.07
134.38
128.91
127.98
127.63
119.92
117.76
105.87
B(dan)
Cl
(E)-2d
f1 (ppm)


7.49
7.48
7.35
7.33
6.35
6.34
6.29
6.25
5.80
B(dan)
Br
(E)-2e
1.99
2.05
2.05
3.12
2.02
1.06
2.00
f1 (ppm)


142.32
141.02
136.51
136.39
131.86
128.27
127.63
122.62
119.92
117.77
105.88
B(dan)
Br
(E)-2e
f1 (ppm)


7.03
7.00
6.37
6.35
6.20
6.13
5.83
3.84
B(dan)
MeO
(E)-2g
1.97
3.00
1.95
2.02
2.00
1.09
2.03
3.02
f1 (ppm)


160.15
143.22
141.24
136.39
130.46
128.14
127.59
119.81
117.52
114.12
105.71
55.35
B(dan)
MeO
(E)-2g
f1 (ppm)