Supporting Information

CuCl-Catalyzed Direct C-H Alkenylation of Benzoxazoles with Allyl Halides

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CONTENTS

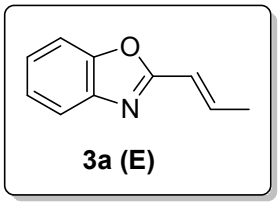
1. General information

All commercially available reagents were used directly without purification unless otherwise stated. All solvents were purified following standard procedures. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard when $CDCl_3$ was used as solvent. IR spectra were recorded on a FT-IR instrument. The HRMS analysis was obtained on a QTOF mass spectrometer. Melting points were determined with melting points apparatus and are uncorrected.

2.General procedure for the CuCl-catalyzed alkenylation of benzoxazoles with allyl halides

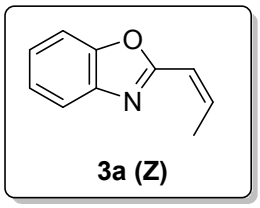
To a solution of benzoxazole (1.0 mmol), allyl halide (1.5 mmol) and ^{t}BuOLi (3.0 mmol) in toluenene (3.0 mL) was added CuCl (0.1 mmol) under a N_2 atmosphere. The resulting mixture was heated at 110 °C for the indicated time. After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (Petroleum ether/EtOAc = 50:1) to provide the desired products **3**.

3. Spectral data of C2-alkenylbenzoxazole products 3

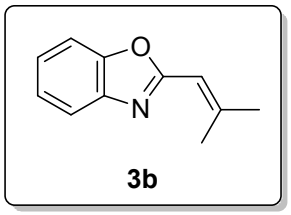


3a (E)

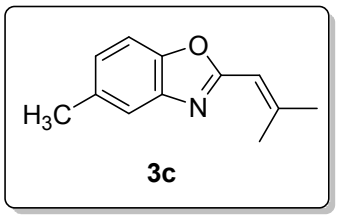
(E)-2-(Prop-1-en-1-yl)benzo[d]oxazole (3a) (E). Pale yellow oil ; 111 mg, 70% yield; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3738, 3673, 2929, 2855, 2372, 1512, 1015, 821 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98 (dd, J_1 = 1.5 Hz, J_2 = 7.0 Hz, 3H), 6.44 (dd, J_1 = 1.5 Hz, J_2 = 15.5 Hz, 1H), 6.97-7.04 (m, 1H), 7.26-7.29 (m, 2H), 7.44-7.45 (m, 1H), 7.65-7.67(m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.7, 110.2, 118.2, 119.8, 124.3, 124.8, 139.0, 141.9, 150.3, 162.4; HRMS (ESI) calcd for $C_{10}H_{10}NO$ $[M+H]^+$ 160.0757, found 160.0762.



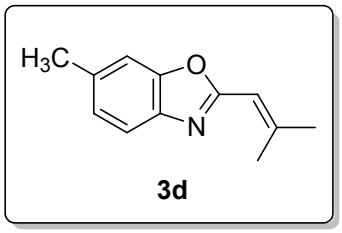
(Z)-2-(Prop-1-en-1-yl)benzo[d]oxazole (3a) (Z). Pale yellow oil; 31 mg, 20% yield; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3740, 3663, 2926, 2852, 2367, 1512, 1265, 1021, 809, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (dd, J_1 = 1.5 Hz, J_2 = 7.0 Hz, 3H), 6.34-6.39 (m, 1H), 6.43 (dd, J_1 = 1.0 Hz, J_2 = 11.5 Hz, 1H), 7.31-7.33 (m, 2H), 7.50-7.52 (m, 1H), 7.72-7.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.1, 110.4, 116.2, 119.9, 124.4, 125.0, 139.6, 141.7, 149.9, 162.6.



2-(2-Methylprop-1-en-1-yl)benzo[d]oxazole (3b) [1]. White solid; 156 mg, 90% yield; m.p: 42-45 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3440, 3055, 2923, 1639, 1536, 1454, 1242, 1006, 968, 924, 850, 744, 615cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.33 (s, 3H), 6.22 (s, 1H), 7.26-7.29 (m, 2H), 7.46-7.47 (m, 1H), 7.68-7.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 27.6, 110.1, 111.9, 119.6, 124.1, 124.4, 142.0, 149.7, 150.5, 162.8.

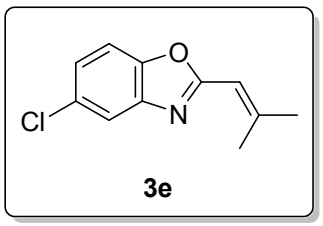


5-Methyl-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3c). Pale yellow solid; 159 mg, 84% yield; m.p: 50-53 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3438, 2920, 1648, 1533, 1451, 1348, 1242, 1006, 965, 850, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.32 (s, 3H), 2.42 (s, 3H), 6.21 (s, 1H), 7.05 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 27.6, 110.1, 111.6, 119.9, 124.1, 124.4, 124.5, 142.0, 149.7, 150.5, 162.8; HRMS (ESI) calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1070, found 188.1067. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.77; H, 7.13; N, 7.30.



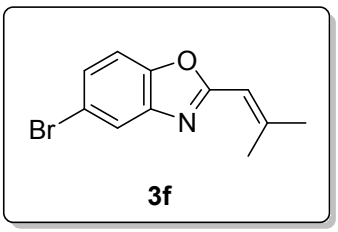
3d

6-Methyl-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3d). Pale yellow solid; 167 mg, 89% yield; m.p: 54-56 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3435, 3055, 2931, 1645, 1536, 1454, 1345, 1242, 1006, 965, 853, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.33 (s, 3H), 2.44 (s, 3H), 6.22 (s, 1H), 7.08 (d, J = 8.5 Hz, 1H), 7.25 (s, 1H), 7.54 (d, J = 8.0 Hz,1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 21.7, 27.6, 110.38, 112.0, 118.9, 125.3, 134.8, 139.8, 149.8, 150.0, 162.4; HRMS (ESI) calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1070, found 188.1065. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.77; H, 7.27; N, 7.35.



3e

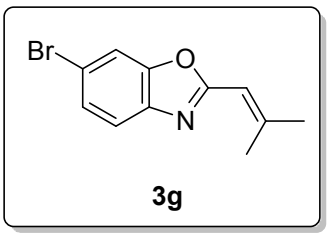
5-Chloro-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3e). Pale yellow solid; 162 mg, 78% yield; m.p: 59-63 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3432, 3055, 2914, 1645, 1536, 1451, 1345, 1242, 1000, 965, 856, 747, 624 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.01(s, 3H), 2.32 (s, 3H), 6.19 (s, 1H), 7.20 (dd, J_1 = 2.0 Hz, J_2 = 8.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 27.7, 110.8, 111.5, 119.4, 124.6, 129.5, 143.1, 148.2, 151.9, 164.0; HRMS (ESI) calcd for $C_{11}H_{11}ClNO$ $[M+H]^+$ 208.0524, found 208.0526. Anal. Calcd for $C_{11}H_{10}ClNO$: C, 63.62; H, 4.85; N, 6.75. Found: C, 63.66; H, 5.09; N, 6.41.



3f

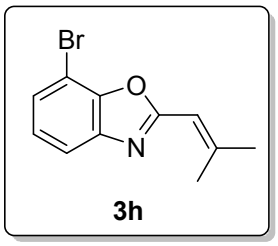
5-Bromo-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3f). Pale yellow solid; 201 mg, 80% yield; m.p: 62-65 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3090, 1804, 1657, 1539, 1452, 1249, 1141, 1045, 953 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.04 (d, J = 1.0 Hz, 3H), 2.34 (s, 1H), 6.21 (t, J = 1.0 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.37 (dd, J_1 = 2.0 Hz, J_2 = 8.5 Hz, 1H), 7.80 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1,

27.8, 111.4, 111.5, 116.8, 122.5, 127.4, 143.6, 148.7, 152.1, 163.9; HRMS (ESI) calcd for $C_{11}H_{10}BrNONa$ $[M+Na]^+$ 273.9837, found 273.9828.



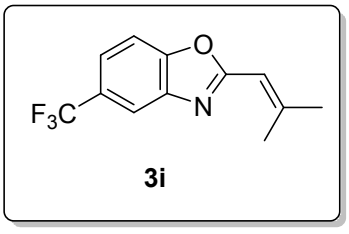
3g

6-Bromo-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3g). Pale yellow solid; 218 mg, 87% yield; m.p: 77-79 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3099, 2979, 2911, 1884, 1654, 1539, 1427, 1257, 1133, 1045, 945, 906, 839, 806, 676, 588, 424 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.32 (s, 3H), 6.19 (s, 1H), 7.39 (dd, J_1 = 1.5 Hz, J_2 = 8.5, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 27.7, 111.5, 113.7, 117.2, 120.5, 127.5, 141.2, 150.2, 151.8, 163.2; HRMS (ESI) calcd for $C_{11}H_{11}BrNO$ $[M+H]^+$ 252.0019, found 252.0016.



3h

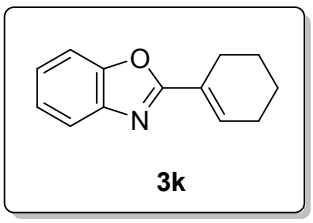
7-Bromo-2-(2-methylprop-1-en-1-yl)benzo[d]oxazole (3h). Pale yellow solid; 193 mg, 77% yield; m.p: 57-59 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3079, 2917, 1919, 1654, 1548, 1421, 1348, 1262, 1215, 1127, 1068, 959, 836, 786, 736, 624 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.36 (s, 3H), 6.27 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 27.8, 102.1, 111.4, 118.6, 125.3, 127.5, 142.7, 147.9, 152.3, 162.9; HRMS (ESI) calcd for $C_{11}H_{11}BrNO$ $[M+H]^+$ 252.0019, found 252.0024. Anal. Calcd for $C_{11}H_{10}BrNO$: C, 52.41; H, 4.00; N, 5.56. Found: C, 52.56; H, 4.18; N, 5.40.



3i

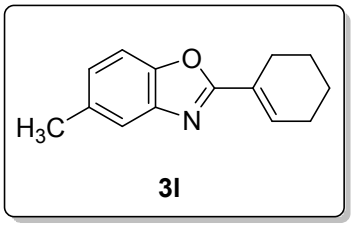
2-(2-Methylprop-1-en-1-yl)-5-(trifluoromethyl)benzo[d]oxazole (3i). Pale yellow solid; 176 mg, 73% yield; m.p: 56-58 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3058, 2920, 1657, 1524, 1442, 1321, 1168, 1124, 1045, 933, 812, 656cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (d, *J* = 1.0 Hz, 3H), 2.36 (d, *J* = 0.5 Hz, 3H), 6.24-6.25 (m, 1H), 7.53 (t, *J* = 0.8 Hz, 2H), 7.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 27.7, 110.5, 111.3, 117.1, 117.1, 121.6, 121.6, 142.2, 151.4, 152.9, 164.4; HRMS (ESI) calcd for $C_{12}H_{11}F_3NO$ $[M+H]^+$ 242.0787, found 242.0785.



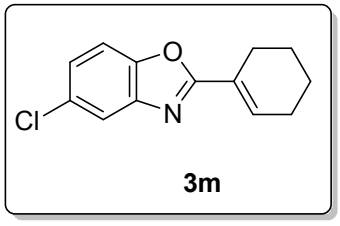
3k

2-(Cyclohex-1-en-1-yl)benzo[d]oxazole (3k). Pale yellow solid; 159 mg, 80% yield; m.p: 29-31 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3432, 3055, 2923, 1639, 1533, 1454, 1242, 1006, 955, 847, 747, 623 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67-1.70 (m, 2H), 1.77-1.80 (m, 2H), 2.28 (dd, J_1 = 2.5Hz, J_2 = 6.5 Hz, 2H), 2.59 (t, *J* = 3.0 Hz, 2H), 7.05-7.06 (m, 1H), 7.26-7.28 (m, 2H), 7.44-7.46 (m, 1H), 7.68-7.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 22.1, 24.7, 25.8, 110.1, 120.0, 124.0, 124.1, 124.7, 135.4, 142.0, 150.3, 164.1; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1069, found 200.1076.



3l

2-(Cyclohex-1-en-1-yl)-5-methylbenzo[d]oxazole (3l). White solid; 149 mg, 70% yield; m.p: 50-53 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3426, 2923, 1651, 1542, 1460, 1345, 1236, 1101, 1003, 968, 850, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67-1.71 (m, 2H), 1.76-1.80 (m, 2H), 2.28-2.30 (m, 2H), 2.43 (s, 3H), 2.59 (dd, J_1 = 5.5 Hz, J_2 = 7.5 Hz, 2H), 7.02-7.07 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 21.9, 22.1, 24.7, 25.8, 109.5, 119.7, 125.7, 126.4, 133.8, 135.0, 142.1, 148.5, 164.3; HRMS (ESI) calcd for $C_{14}H_{16}NO$ $[M+H]^+$ 214.1226, found 214.1231.



3m

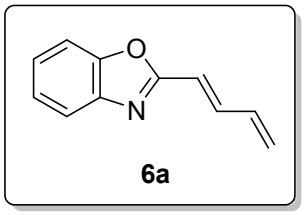
5-Chloro-2-(cyclohex-1-en-1-yl)benzo[d]oxazole (3m). White solid; 175 mg, 75% yield; m.p: 60-62 ℃;

(recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3435, 3061, 2923, 1539, 1448, 1236, 1003, 968, 855, 736, 618cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67-1.70 (m, 2H), 1.77-1.80 (m, 2H), 2.28 (dd, J_1 = 2.5 Hz, J_2 = 6.5 Hz, 2H), 2.59 (t, J = 3.0 Hz, 2H), 7.05-7.06 (t, J = 1.8 Hz, 1H), 7.25-7.28 (m, 1H), 7.44-7.46 (m, 1H), 7.68-7.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 22.0, 24.6, 25.9, 110.9, 119.7, 124.9, 126.1, 129.5, 136.5, 143.1, 148.9, 165.4; HRMS (ESI) calcd for $C_{13}H_{13}NOCl$ $[M+H]^+$ 234.0680, found 234.0678.

4. General procedure for the synthesis of 1,3-diene containing benzoxazoles

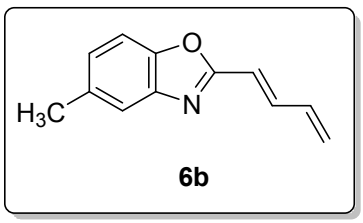
To a solution of benzoxazole (1.5 mmol), 1,4-dibromobut-2-ene (1.0 mmol) and ^{t}BuOLi (3.0 mmol) in toluenene (3.0 mL) was added CuCl (0.1 mmol) under a N_2 atmosphere. The resulting mixture was heated at 50 °C for the indicated time. After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (Petroleum ether/EtOAc = 50:1) to provide the desired products **6**.

5. Spectral data of 1,3-diene containing benzoxazoles 6



6a

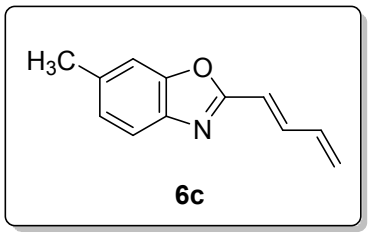
(E)-2-(Buta-1,3-dien-1-yl)benzo[d]oxazole (6a). White solid ; 128 mg, 75% yield; m.p: 32-34℃; (recrystallized from petroleum ether and ethyl acetate at room temperature) IR (KBr) 2926, 1527, 1451, 1242, 1000, 912, 850, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (d, J = 10.0 Hz, 1H), 5.60 (d, J = 16.5 Hz, 1H), 6.52-6.60 (m, 2H), 7.29-7.31 (m, 2H), 7.39 (dd, J_1 = 11.0 Hz, J_2 = 15.5 Hz, 1H), 7.46-7.50 (m, 1H), 7.68-7.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.3, 117.9, 120.0, 123.8, 124.5, 125.2, 135.5, 140.0, 142.2, 150.4, 162.5; HRMS (ESI) calcd for $C_{11}H_{10}NO$ $[M+H]^+$ 172.0757, found 172.0752.



6b

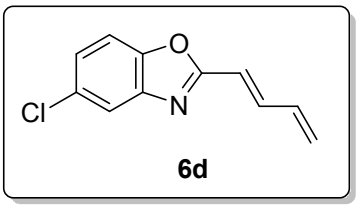
(E)-2-(buta-1,3-dien-1-yl)-5-methylbenzo[d]oxazole (6b).

White solid; 139 mg, 75% yield; m.p: 60-62 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3014, 1845, 1595, 1519, 1257, 1186, 1003, 924, 856, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 5.46 (d, J = 10.0 Hz, 1H), 5.61 (d, J = 17.0 Hz, 1H), 6.51-6.61 (m, 2H), 7.12 (dd, J_1 = 1.0 Hz, J_2 = 8.5 Hz, 1H), 7.35-7.40 (m, 2H), 7.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 109.7, 118.0, 119.8, 123.6, 126.4, 134.3, 135.6, 139.6, 142.3, 148.6, 162.6; HRMS (ESI) calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0913, found 186.0912.



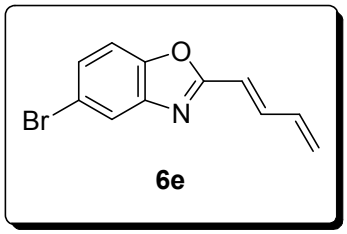
6c

(E)-2-(Buta-1,3-dien-1-yl)-6-methylbenzo[d]oxazole (6c). White solid; 135 mg, 73% yield; m.p: 59-62 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3431, 2917, 1610, 1486, 1239, 1112, 965, 812, 594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3H), 5.45 (d, J = 10.0 Hz, 1H), 5.60 (d, J = 17.0 Hz, 1H), 6.51-6.61 (m, 2H), 7.13 (d, J = 8.5 Hz, 1H), 7.29 (s, 1H), 7.36 (dd, J_1 = 11.0 Hz, J_2 = 16.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 21.8, 110.5, 118.0, 119.2, 123.4, 125.7, 135.6, 135.8, 139.4, 140.0, 150.7, 164.9; HRMS (ESI) calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0913, found 186.0900.



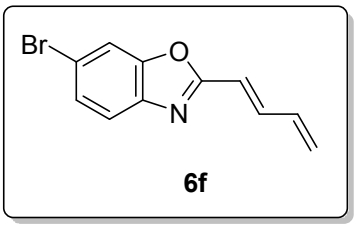
6d

(E)-2-(Buta-1,3-dien-1-yl)-5-chlorobenzo[d]oxazole (6d). White solid; 164 mg, 80% yield; m.p: 58-60 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3014, 1586, 1524, 1445, 1257, 1012, 915, 906, 853, 792, 697, 591 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.49 (d, J = 10.0 Hz, 1H), 5.62 (d, J = 17.0 Hz, 1H), 6.47-6.60 (m, 2H), 7.25-7.28 (m, 1H), 7.35-7.40 (m, 2H), 7.64 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.0, 117.4, 119.8, 124.4, 125.4, 129.9, 135.4, 140.7, 143.3, 148.9, 163.7; HRMS (ESI) calcd for $C_{11}H_9ClNO$ $[M+H]^+$ 206.0211, found 206.0216.



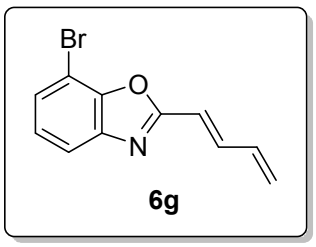
6e

(E)-2-(Buta-1, 3-dien-2-yl)-5-bromobenzo[d]oxazole (6e). White solid; 174 mg, 70% yield; m.p: 71-73 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3087, 1845, 1583, 1519, 1445, 1251, 1165, 1000, 927, 862, 797, 680, 583 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.49 (d, J = 10.0 Hz, 1H), 5.62 (d, J = 17.0 Hz, 1H), 6.48-6.60 (m, 2H), 7.32-7.41 (m, 3H), 7.79 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.5, 117.2, 117.3, 122.8, 124.5, 128.1, 135.4, 140.8, 143.7, 149.4, 163.5; HRMS (ESI) calcd for $C_{11}H_9NOBr$ $[M+H]^+$ 249.9862, found 249.9867.



6f

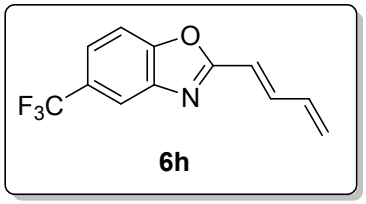
(E)-6-Bromo-2-(buta-1,3-dien-1-yl)benzo[d]oxazole (6f). Pale yellow solid; 189mg, 76% yield; m.p: 70-72 ℃; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 3017, 1604, 1457, 1262, 1000, 918, 800, 580 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.51 (d, J = 10.0 Hz, 1H), 5.64 (d, J = 17.0 Hz, 1H), 6.52 (d, J = 15.5 Hz, 1H), 6.55-6.62 (m, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.44 (dd, J_1 = 1.5 Hz, J_2 = 8.5 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.9, 117.4, 118.1, 120.8, 124.4, 128.0, 135.4, 140.6, 141.4, 151.0, 163.0; HRMS (ESI) calcd for $C_{11}H_9BrNO$ $[M+H]^+$ 249.9862, found 249.9869.



6g

(E)-7-Bromo-2-(buta-1,3-dien-1-yl)benzo[d]oxazole (6g). Pale yellow oil; 199 mg, 80% yield; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2923, 1607, 1524, 1474, 1416, 1265, 1218, 1071, 1006, 909, 776, 733, 730, 621, 456 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.52 (d, J = 10.0 Hz, 1H), 5.68 (d, J = 16.5 Hz, 1H), 6.54-6.63 (m, 2H), 7.21 (t, J = 7.75 Hz, 1H), 7.46-7.51 (m, 2H), 7.62 (dd, J_1 = 0.5 Hz, J_2 = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.3, 117.2, 118.9, 124.6, 125.7, 128.3, 135.4,

141.1, 142.9, 148.6, 162.6; HRMS (ESI) calcd for $C_{11}H_8BrNONa$ $[M+Na]^+$ 271.9681, found 271.9705.



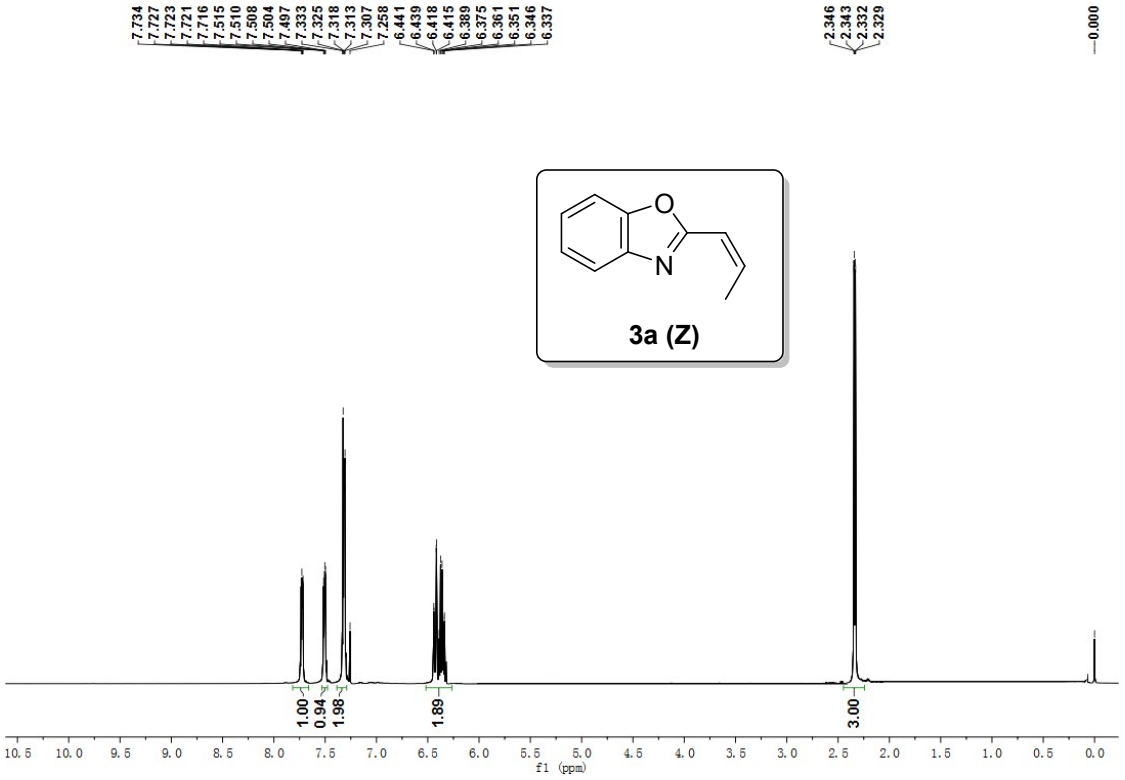
6h

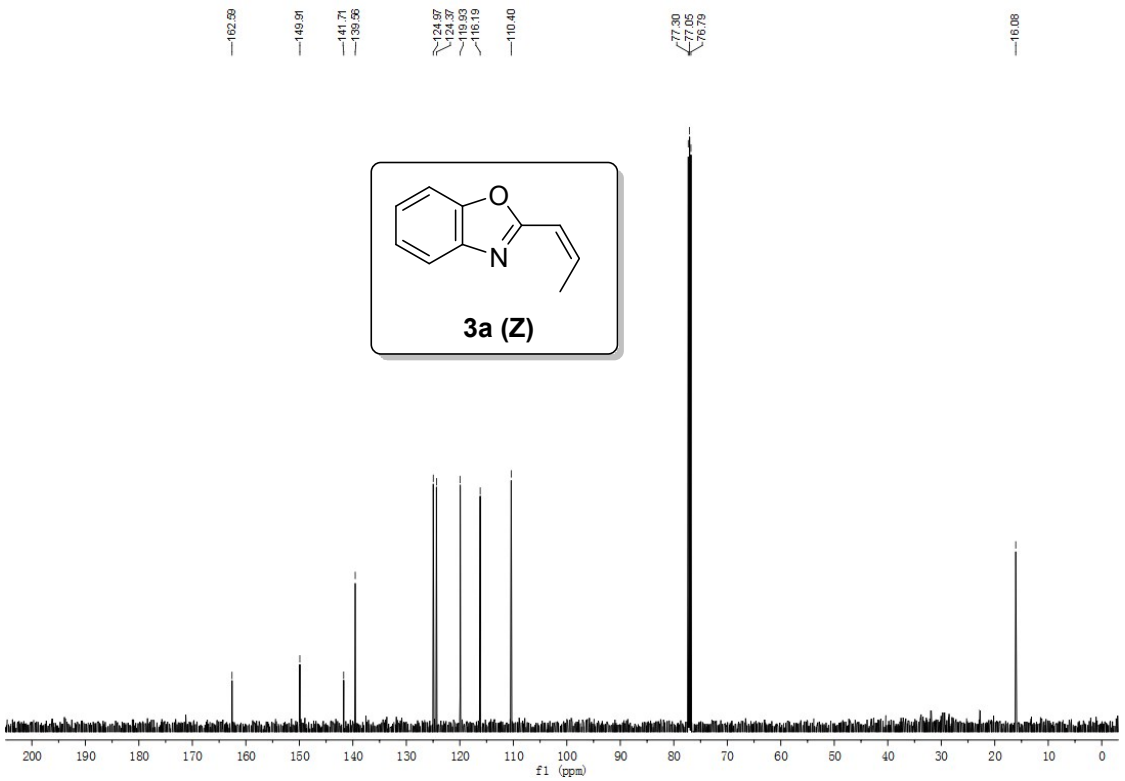
(E)-2-(Buta-1,3-dien-1-yl)-5-(trifluoromethyl)benzo[d]oxazole (6h). Colorless oil; 96 mg, 40% yield; (recrystallized from petroleum ether and ethyl acetate at room temperature); IR (KBr) 2958, 2926, 2855, 1725, 1460, 1380, 1324, 1257, 1124, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.52-5.54 (d, J = 10.0 Hz, 1H), 5.65-5.68 (d, J = 17.0 Hz, 1H), 6.54-6.64 (m, 2H), 7.42-7.48 (dd, J_1 = 11.0 Hz, J_2 = 15.5 Hz, 1H), 7.57-7.61 (m, 2H), 7.96 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.7, 117.2, 117.5, 117.6, 122.4 (q, J_{C-F} = 265 Hz), 124.8, 127.8, 135.3, 141.3, 142.3, 152.1, 164.1; HRMS (ESI) calcd for $C_{12}H_9F_3NO$ $[M+H]^+$ 240.0631, found 240.0636.

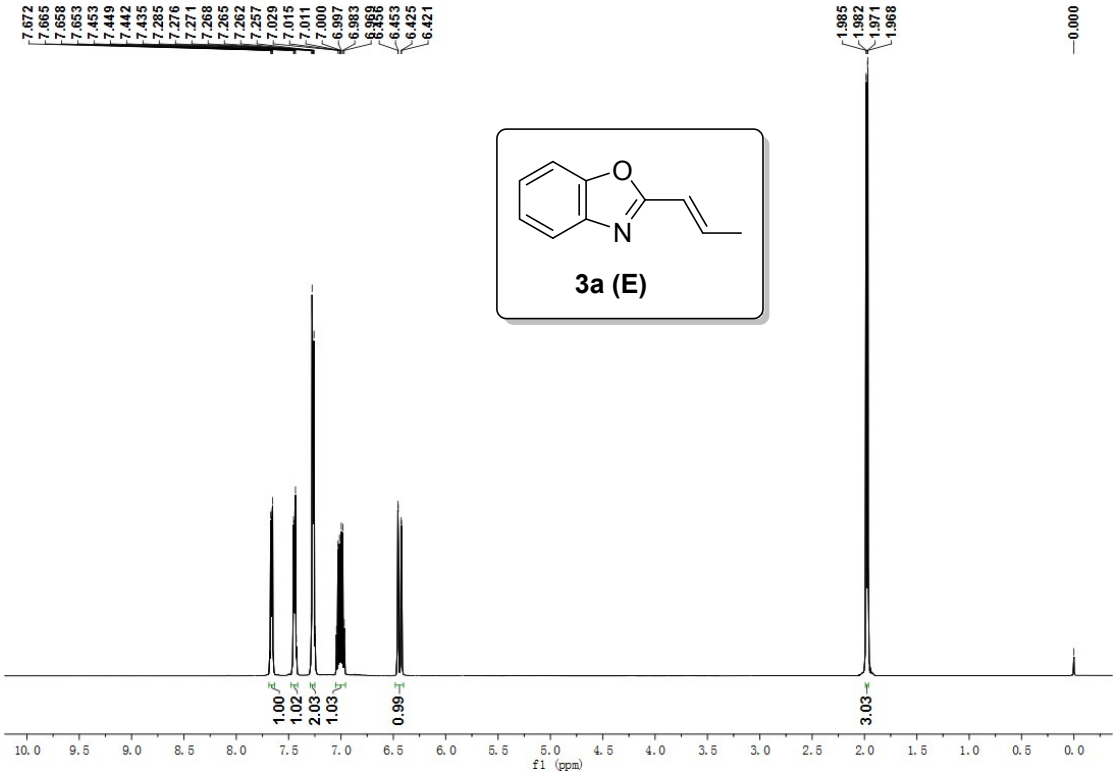
6. Reference

(1) Xie, W.; Chang, S. *Angew. Chem., Int. Ed*. **2016**, *55*, 1876.

7. ^{1}H and ^{13}C NMR spectra



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6.421
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1.971
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O
N
3a (E)
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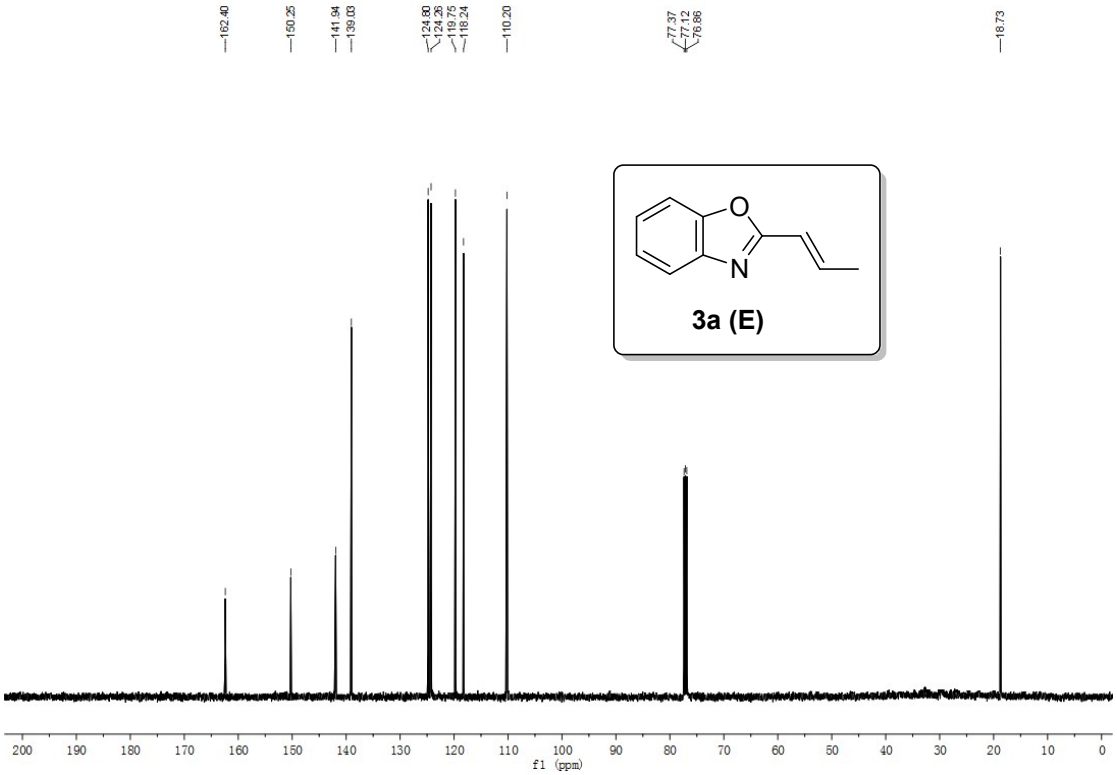
1.02
2.03
1.03
0.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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O
N
3a (E)
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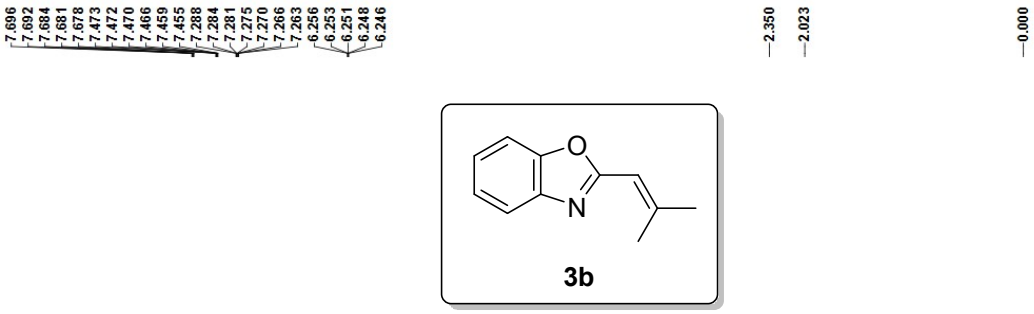
f1 (ppm)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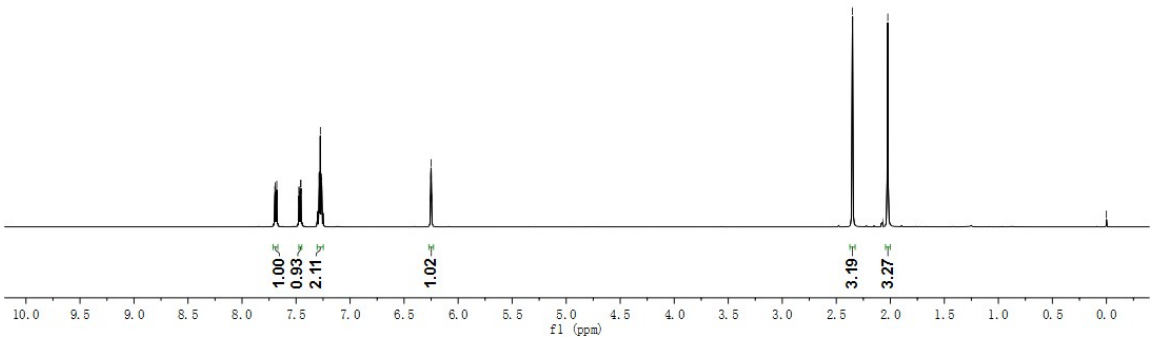
3b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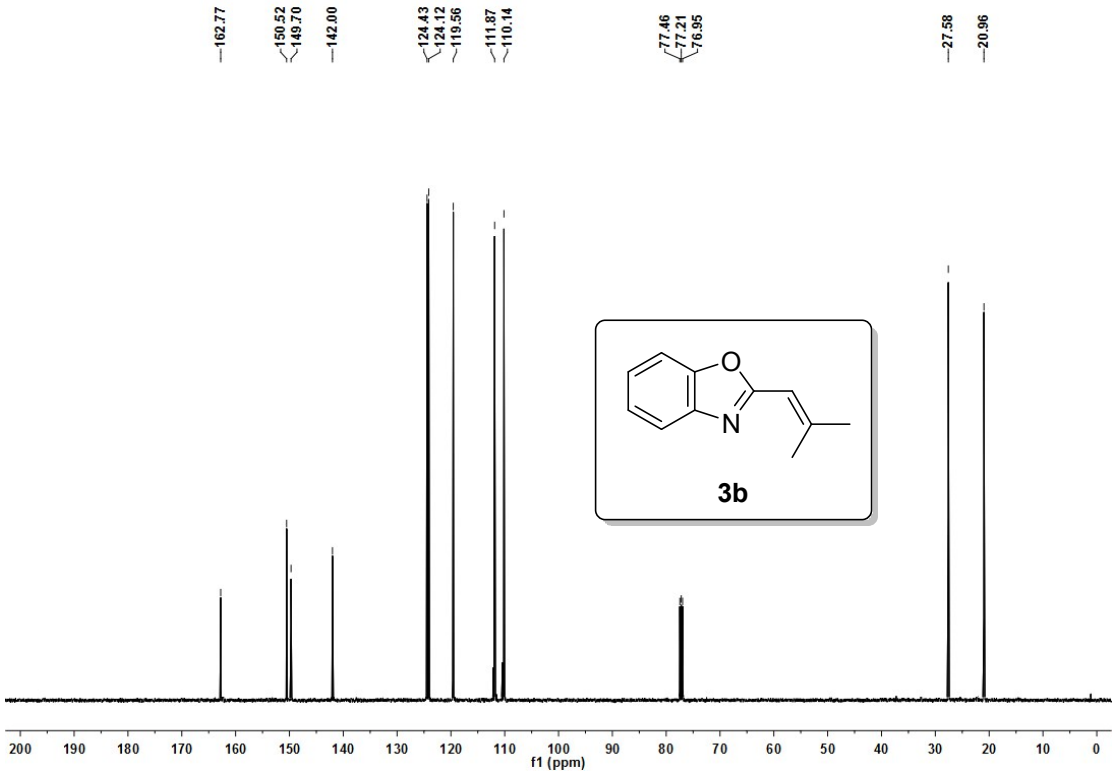
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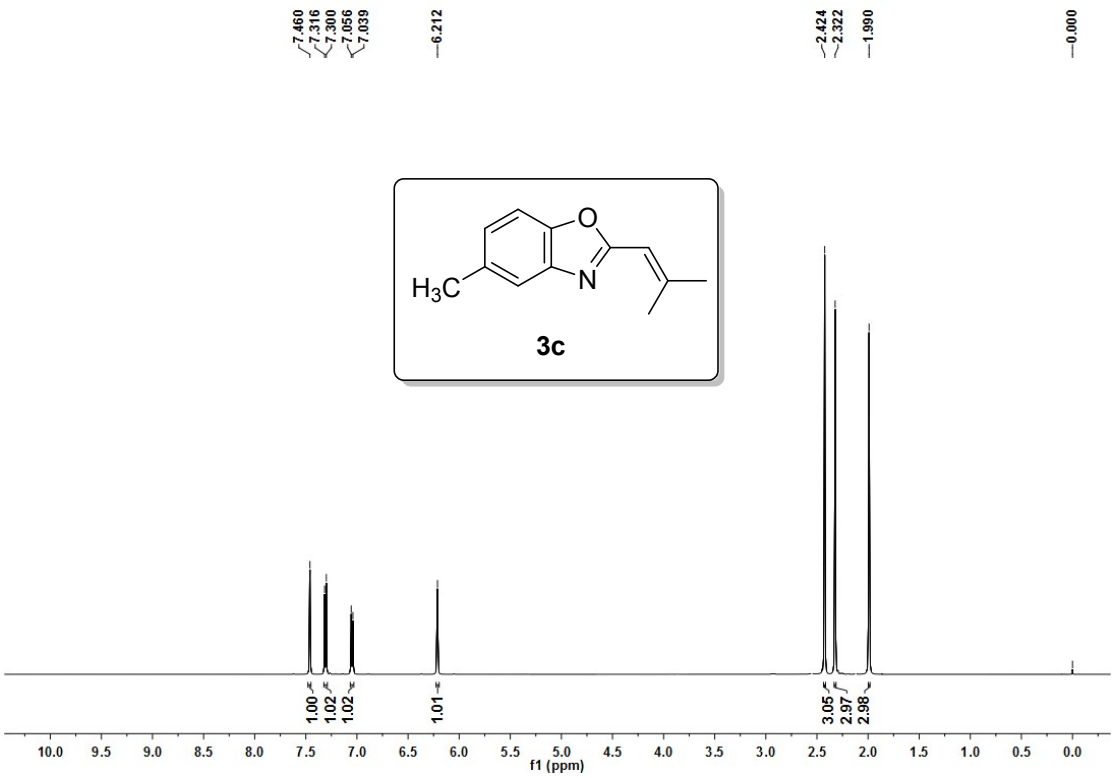
3b
f1 (ppm)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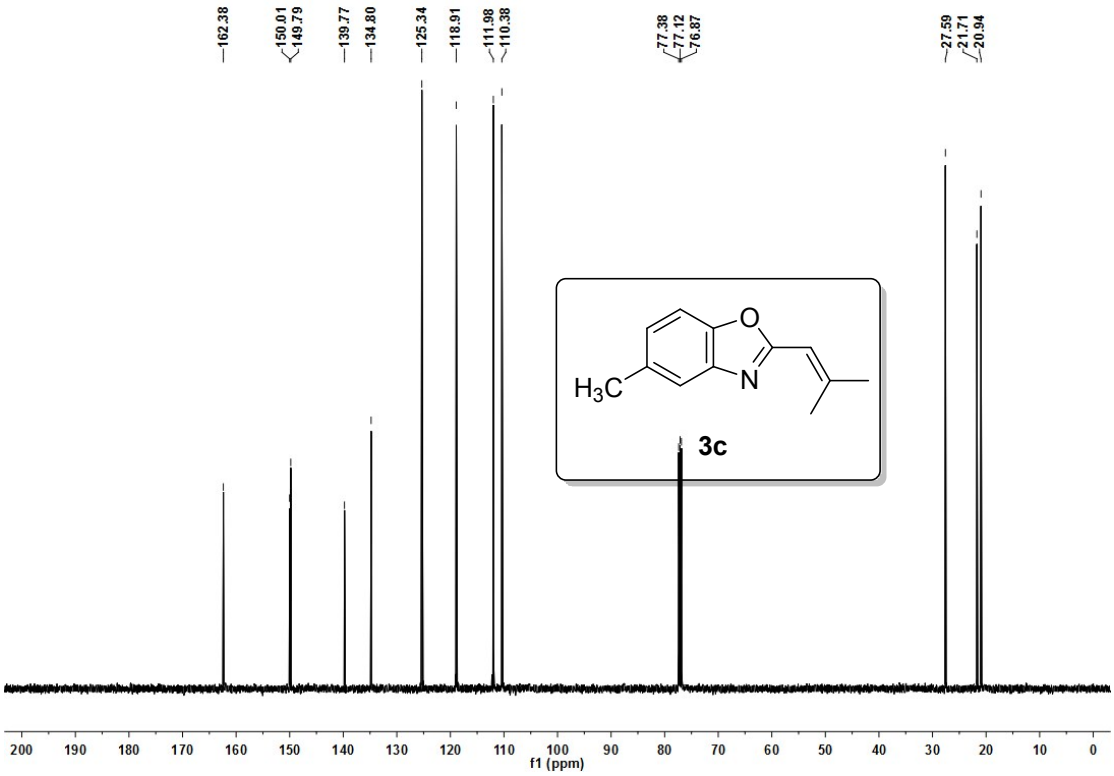
f1 (ppm)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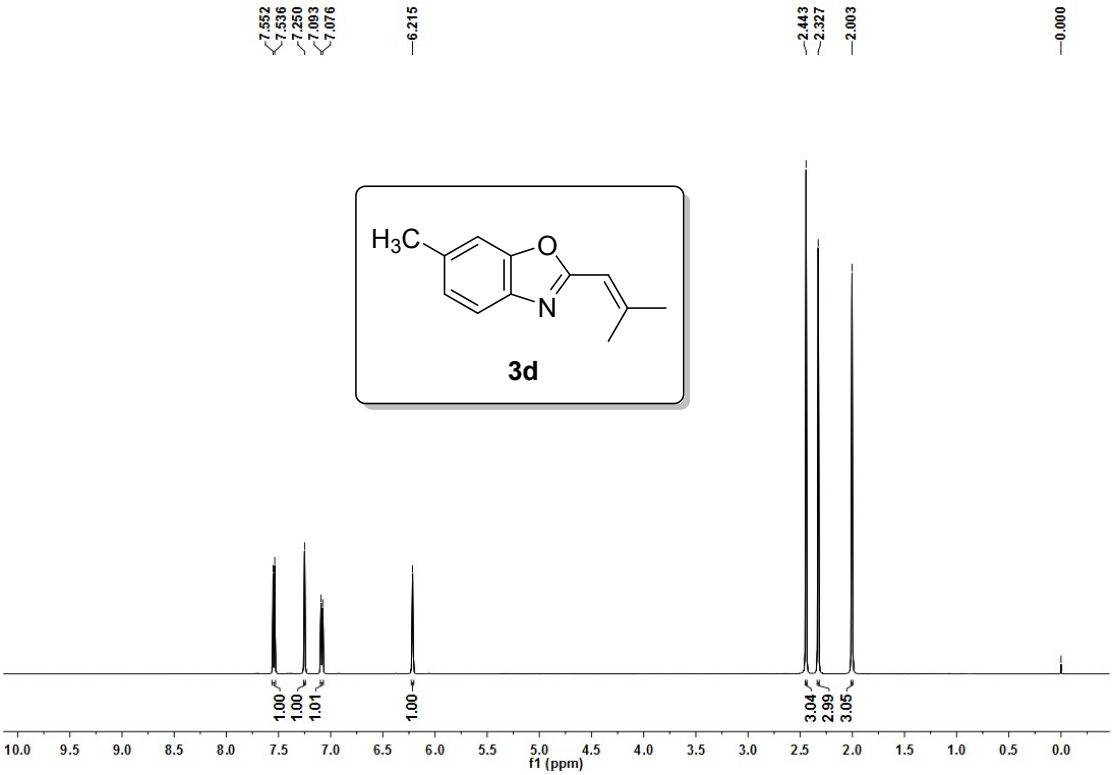
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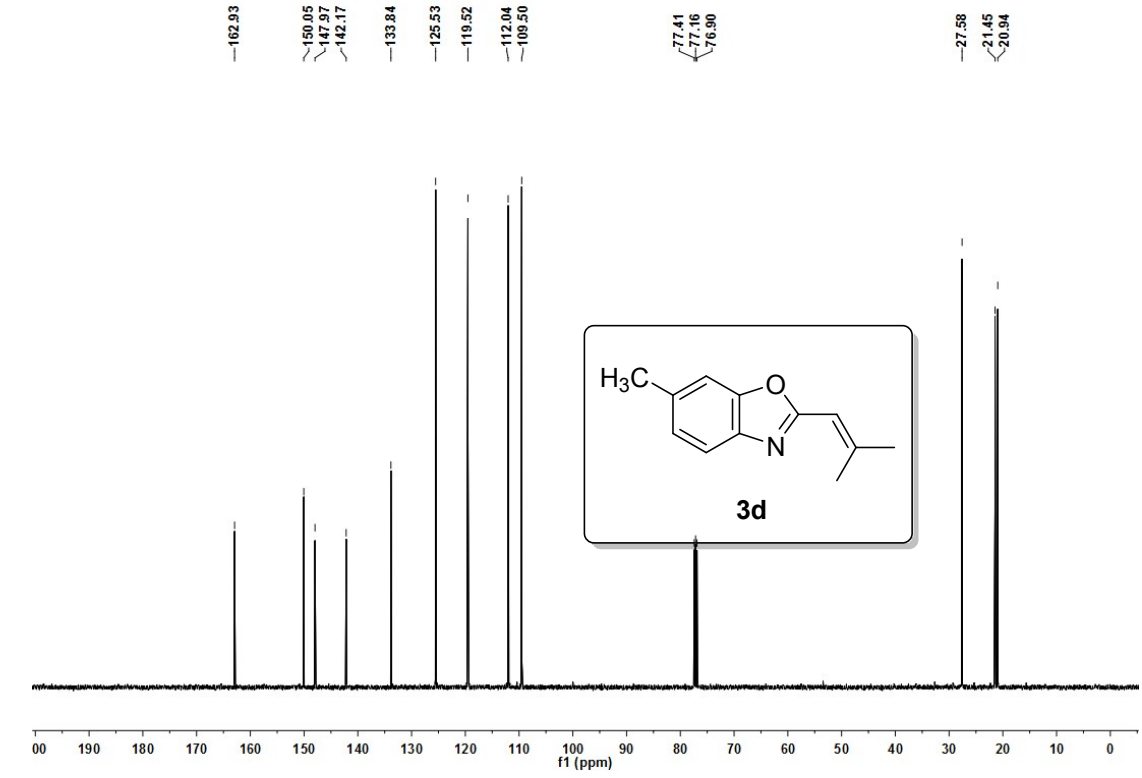
f1 (ppm)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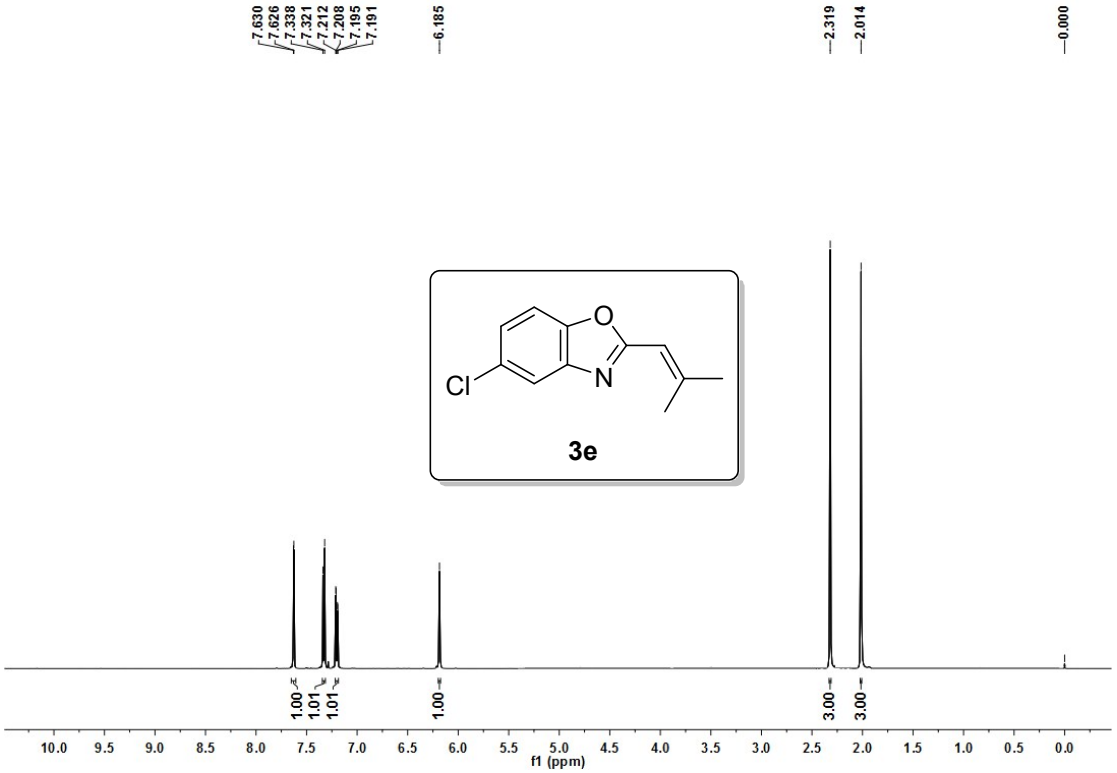
f1 (ppm)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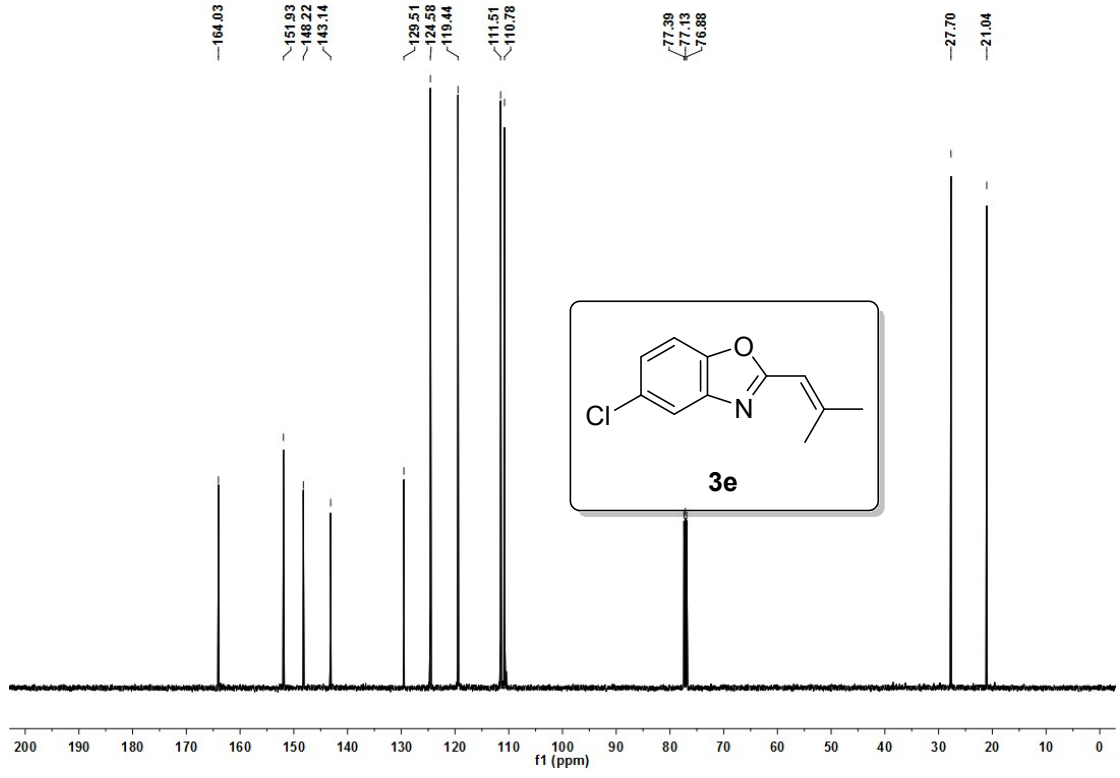
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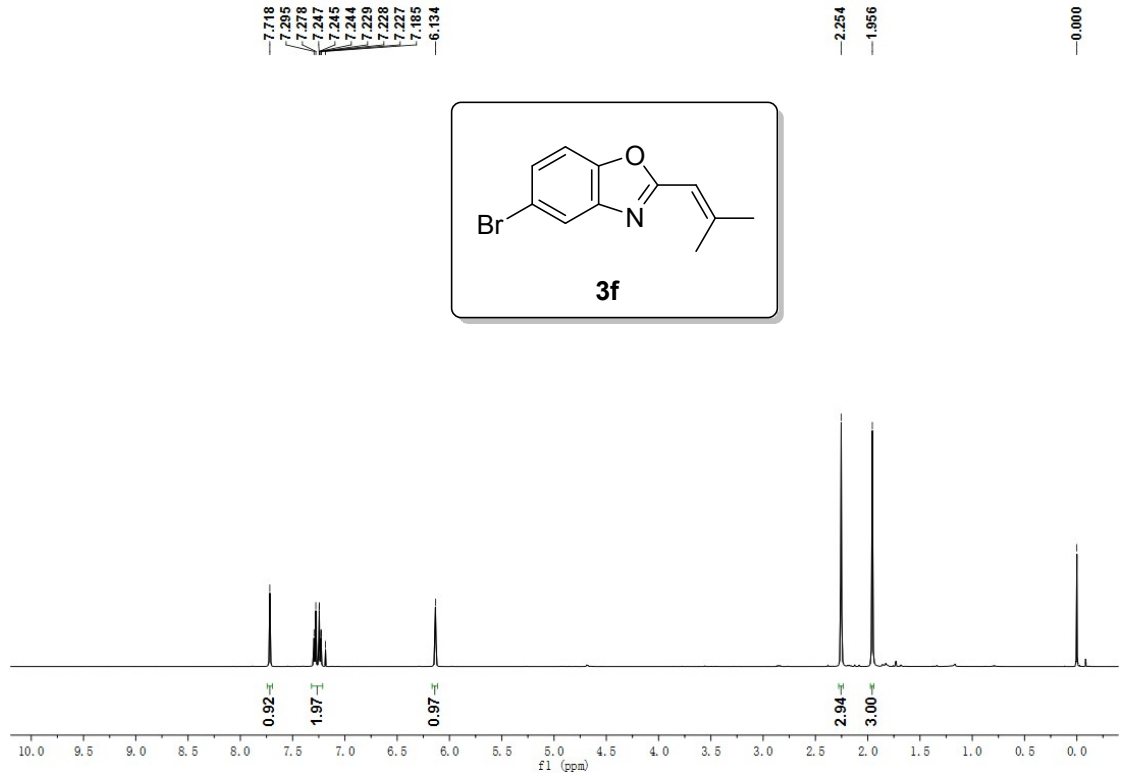
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Br
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0.97
2.94
3.00
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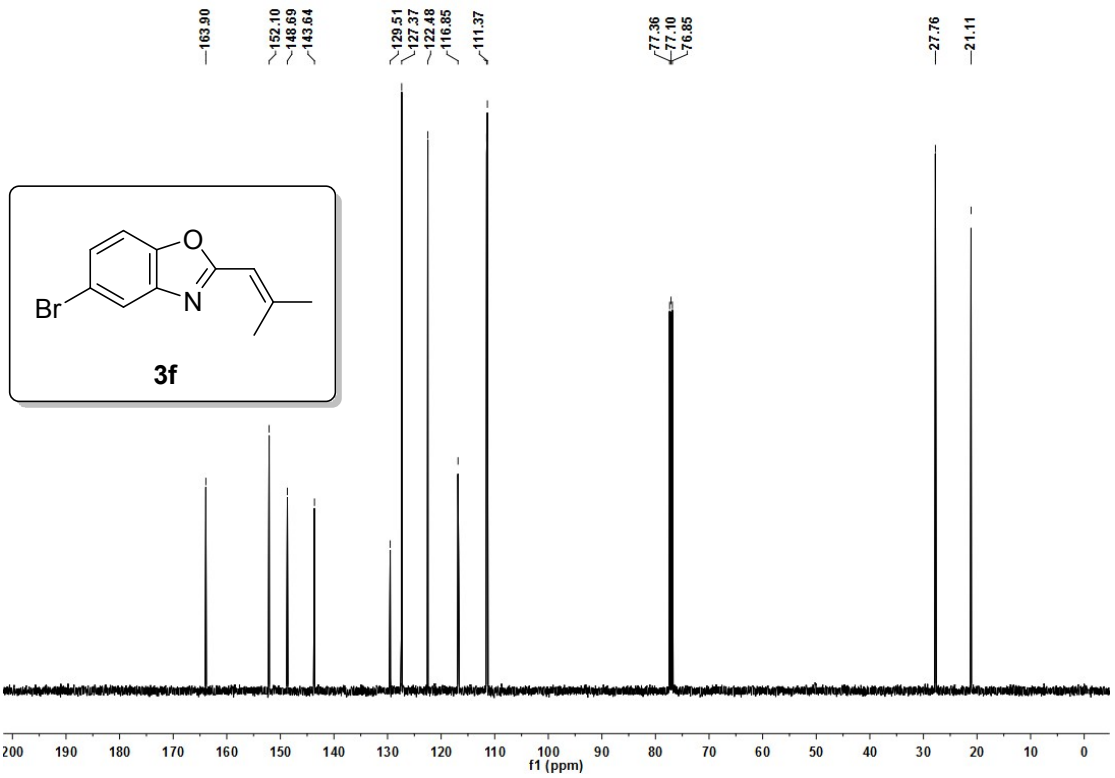
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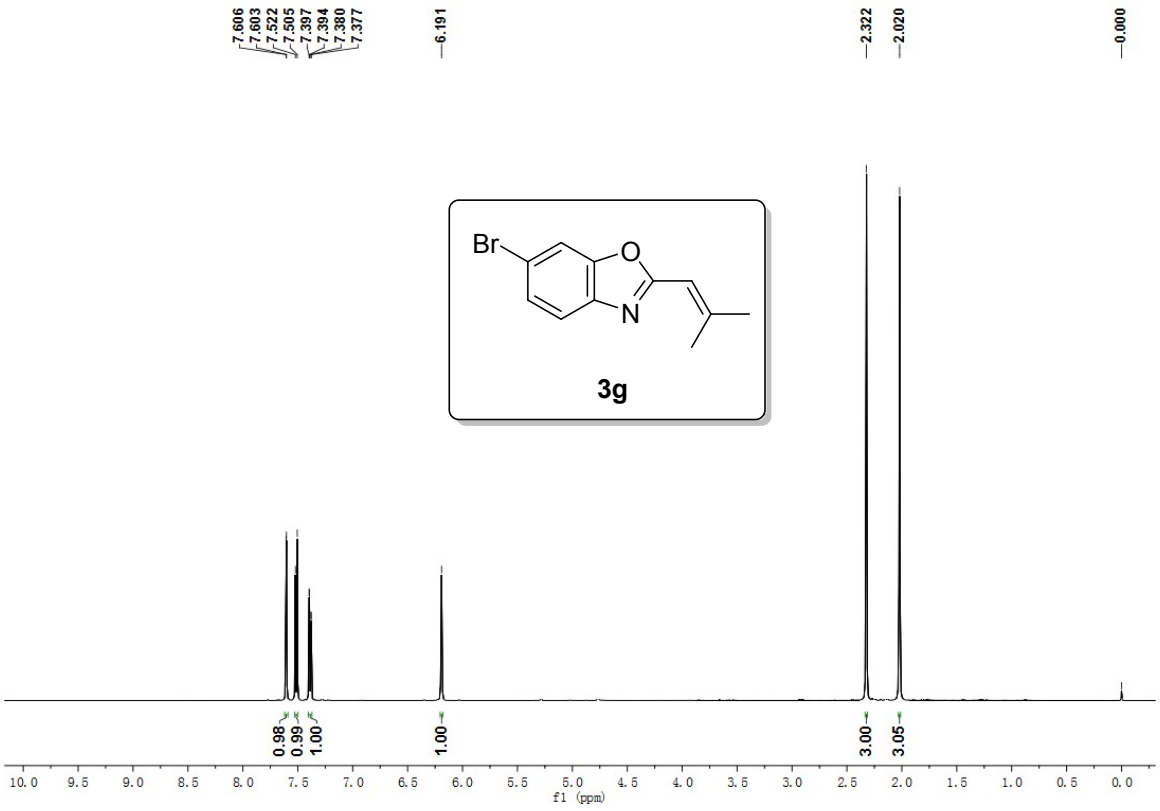
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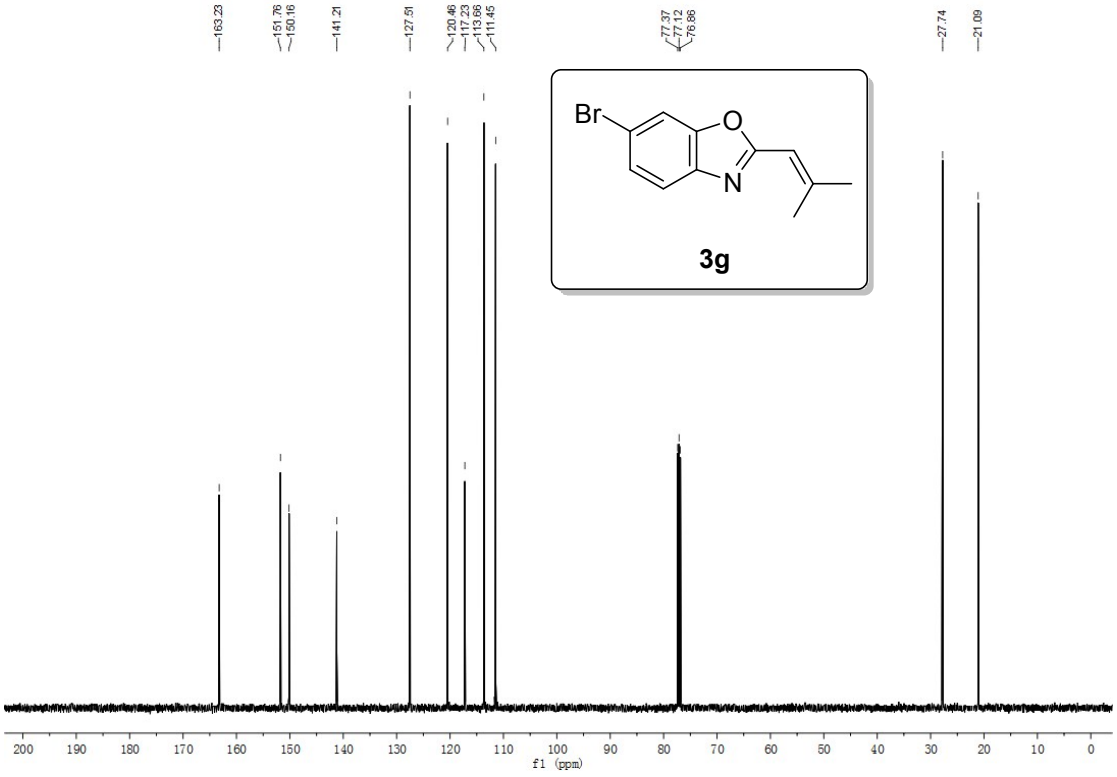
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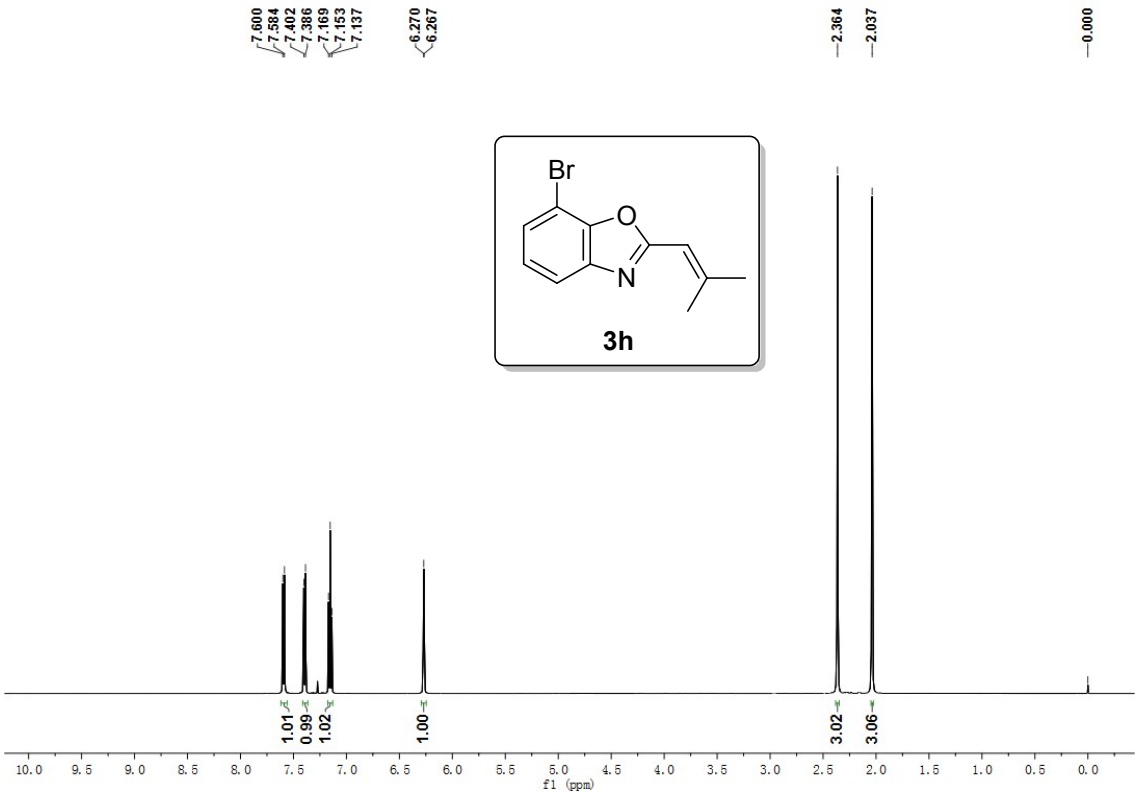
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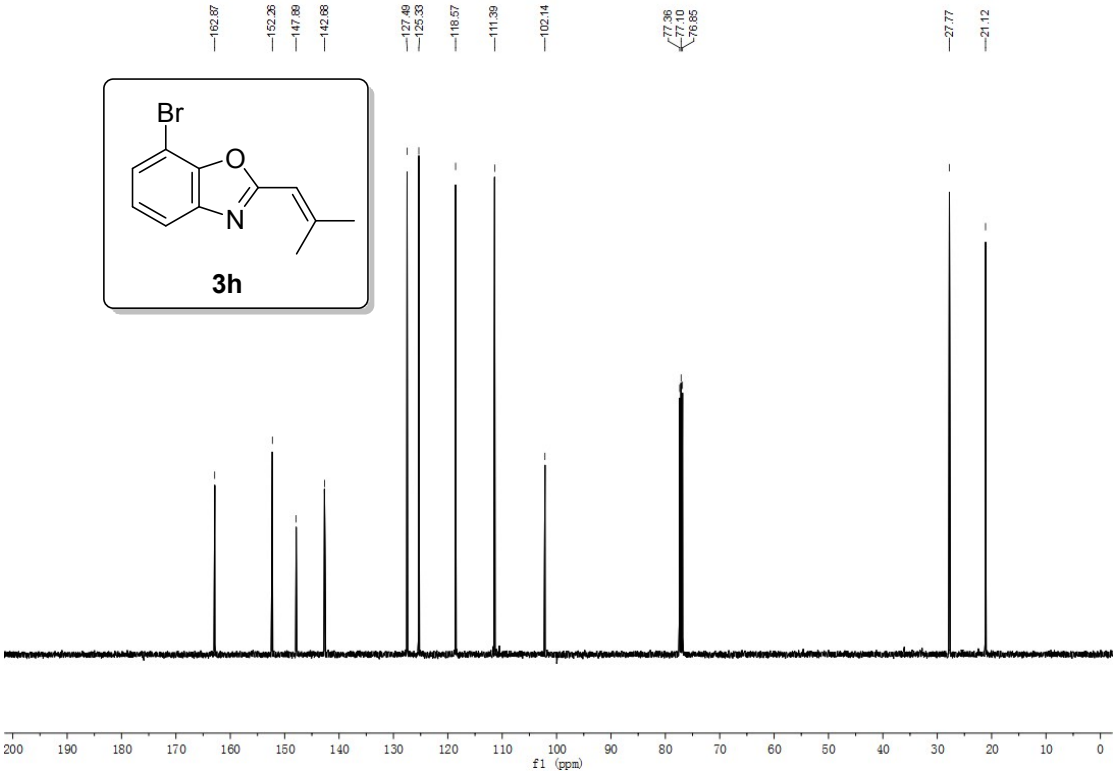
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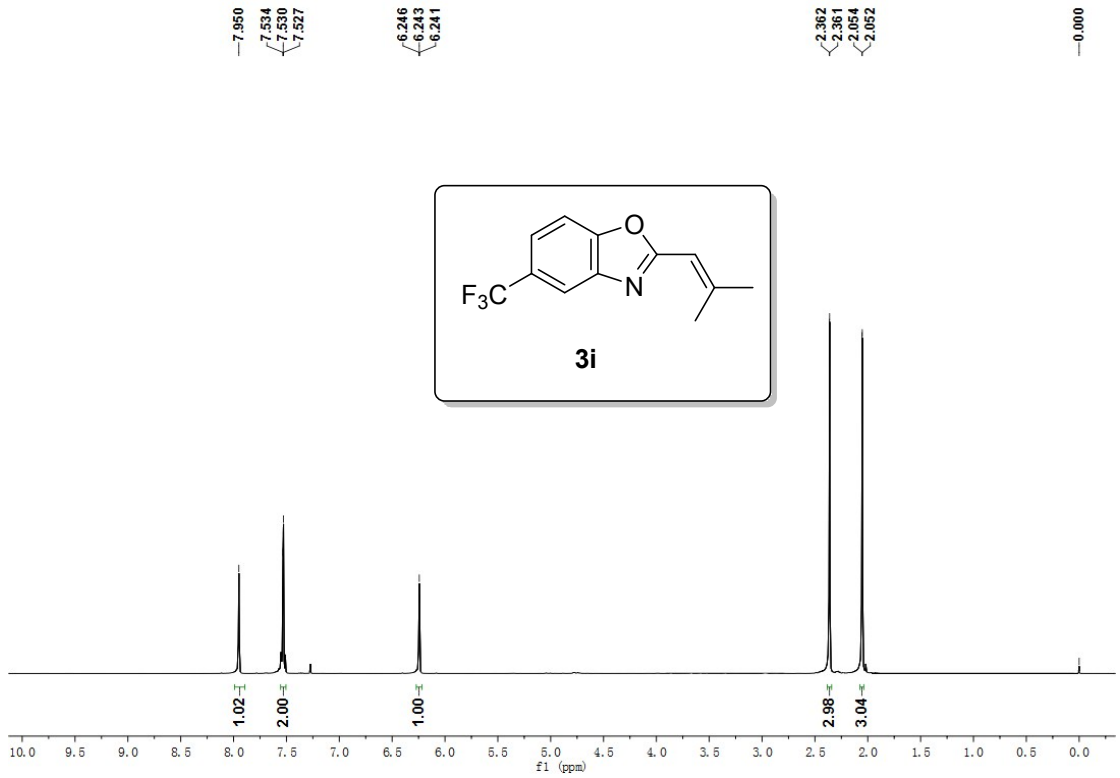
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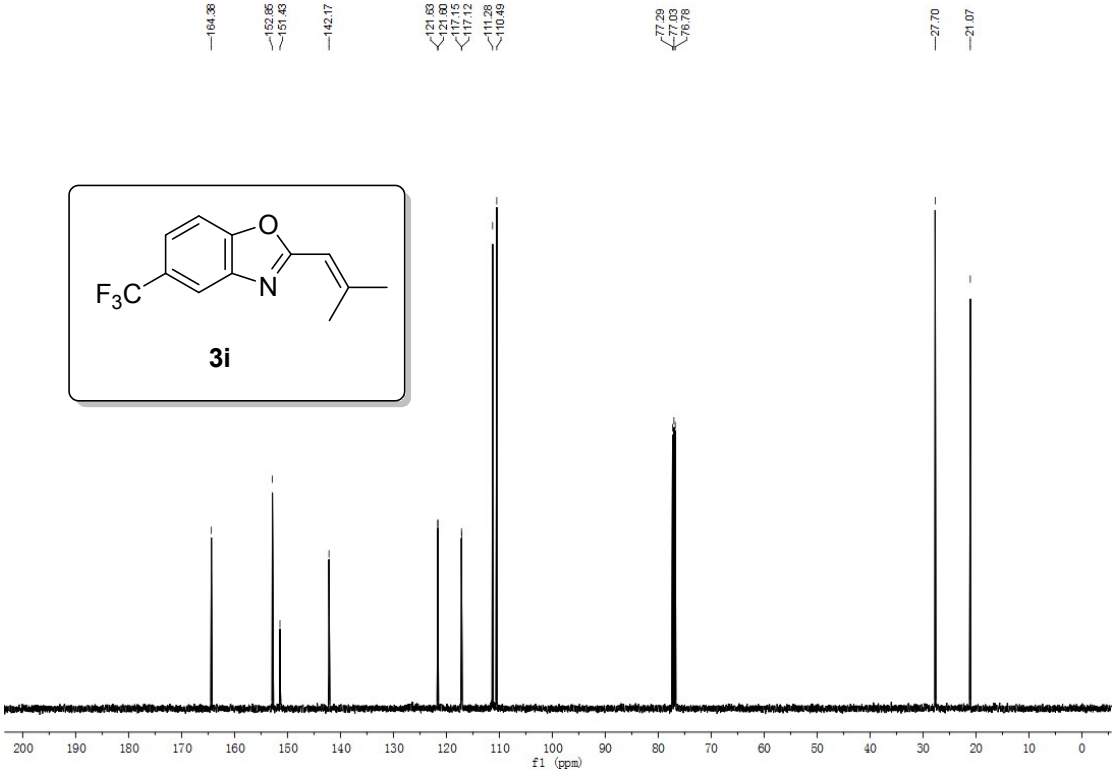
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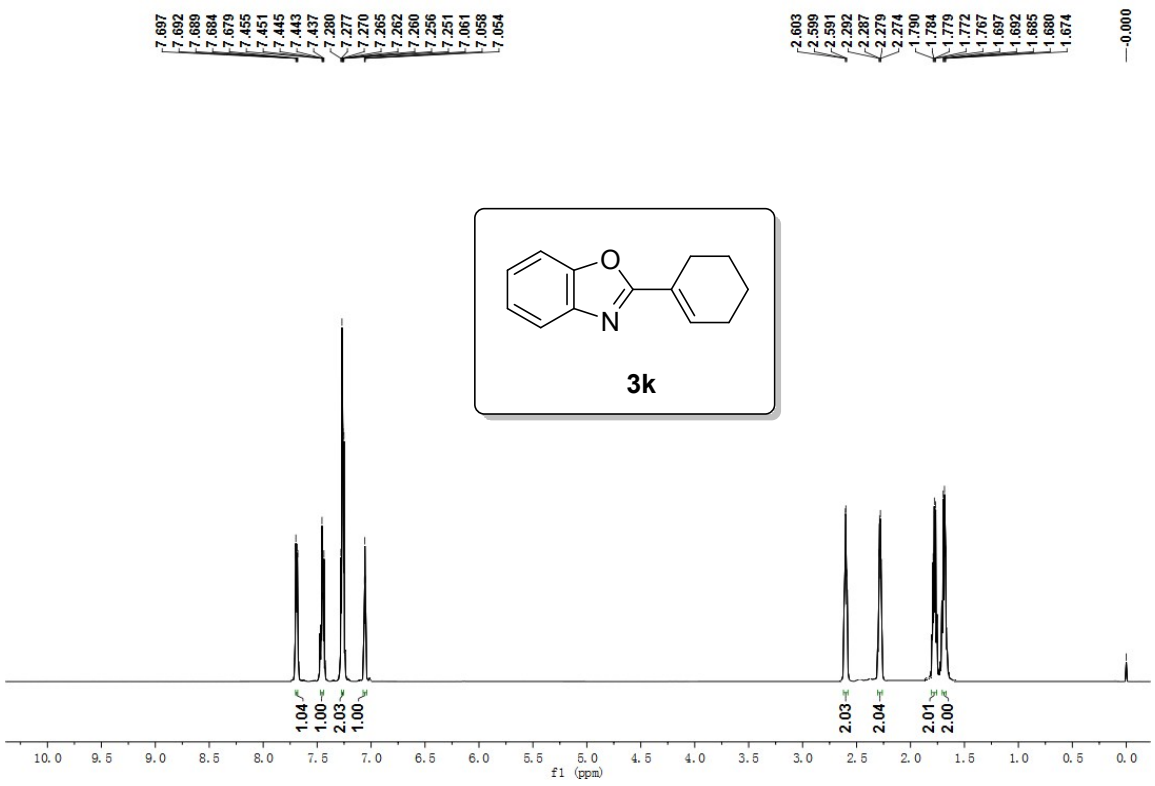
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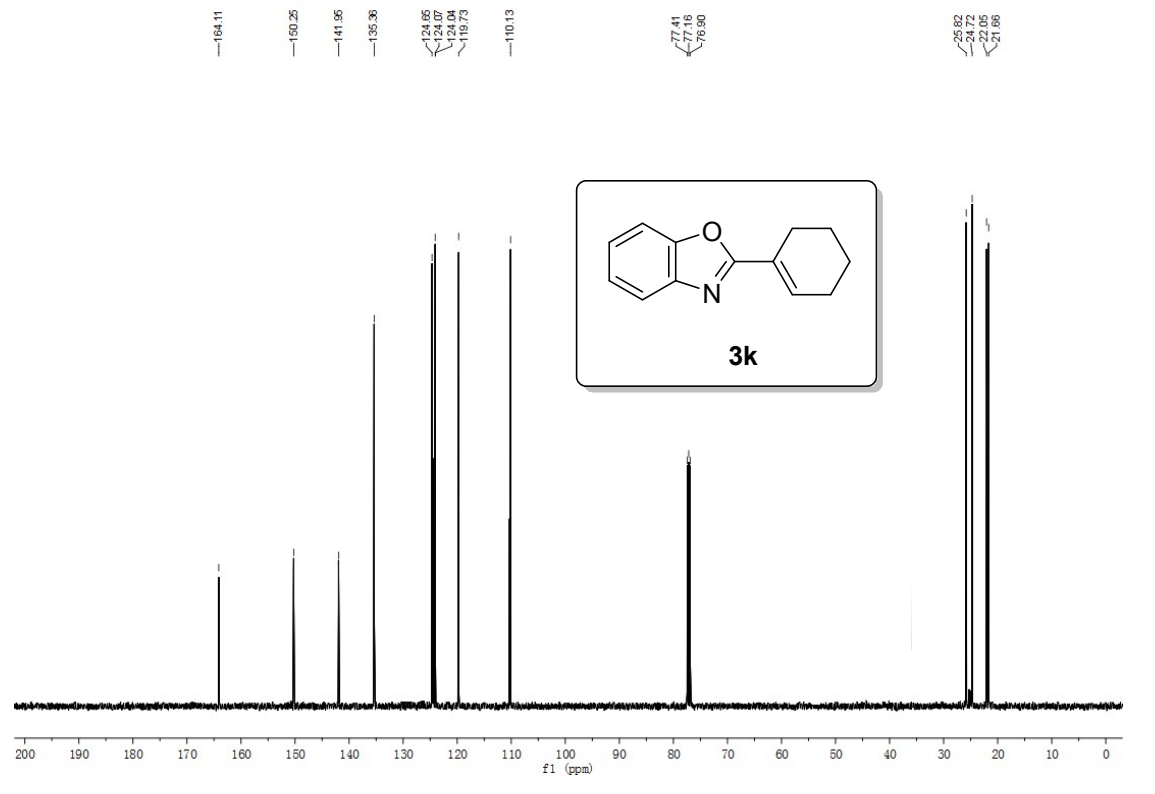
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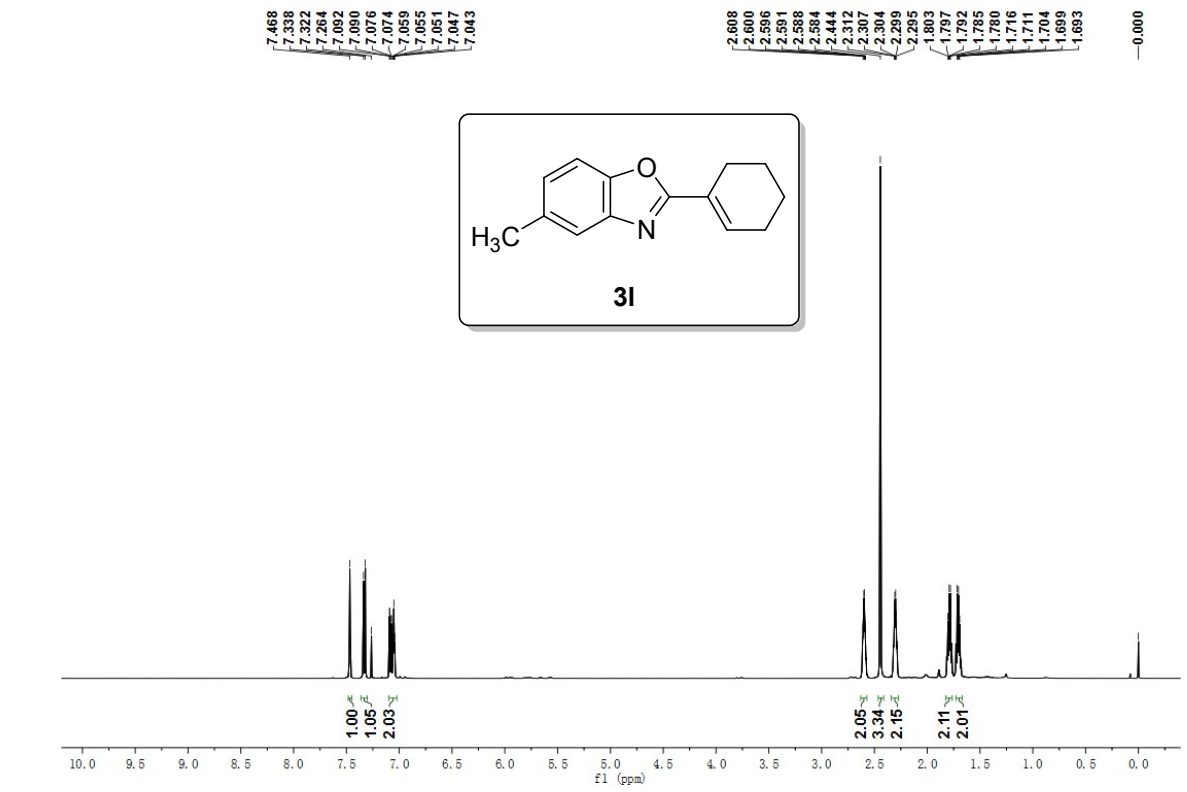
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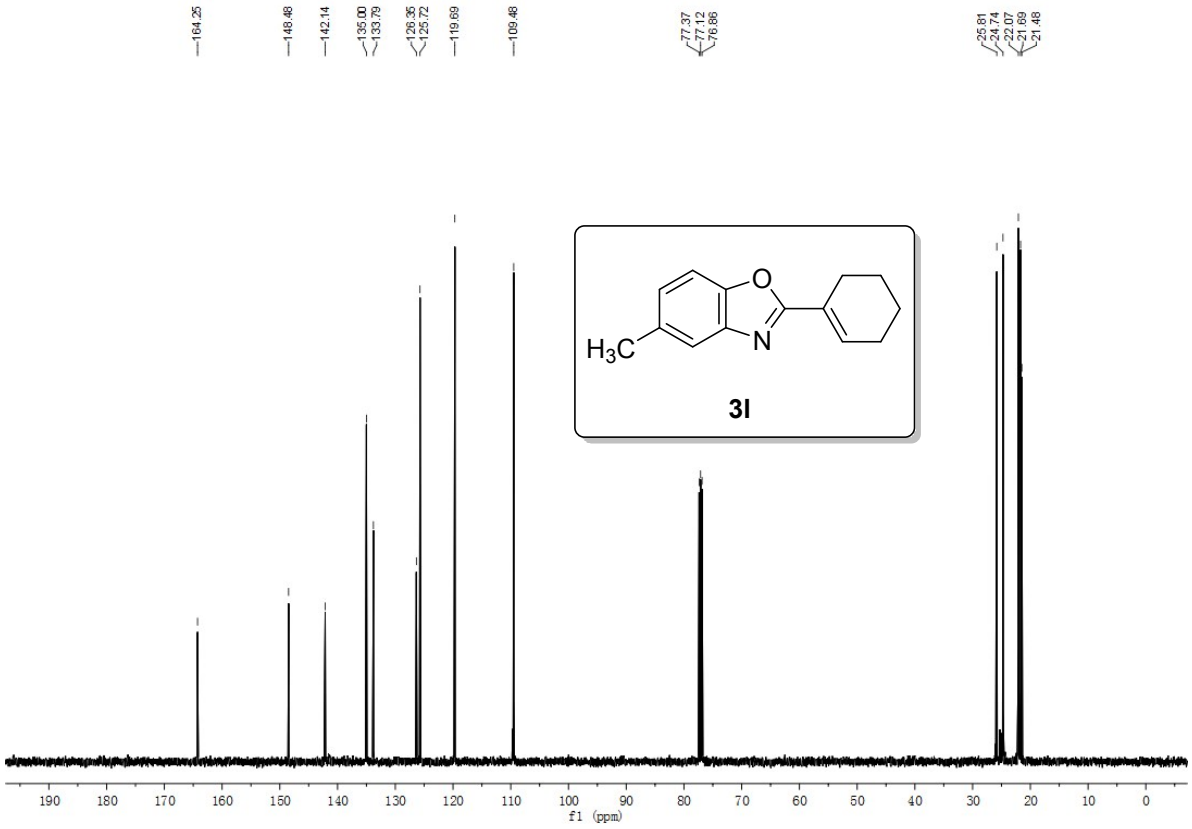
1.780
1.716
1.711
1.704
1.699
1.693
0.000
O
N
H3C
3l
1.00
1.05
2.03
2.05
3.34
2.15
2.11
2.01
f1 (ppm)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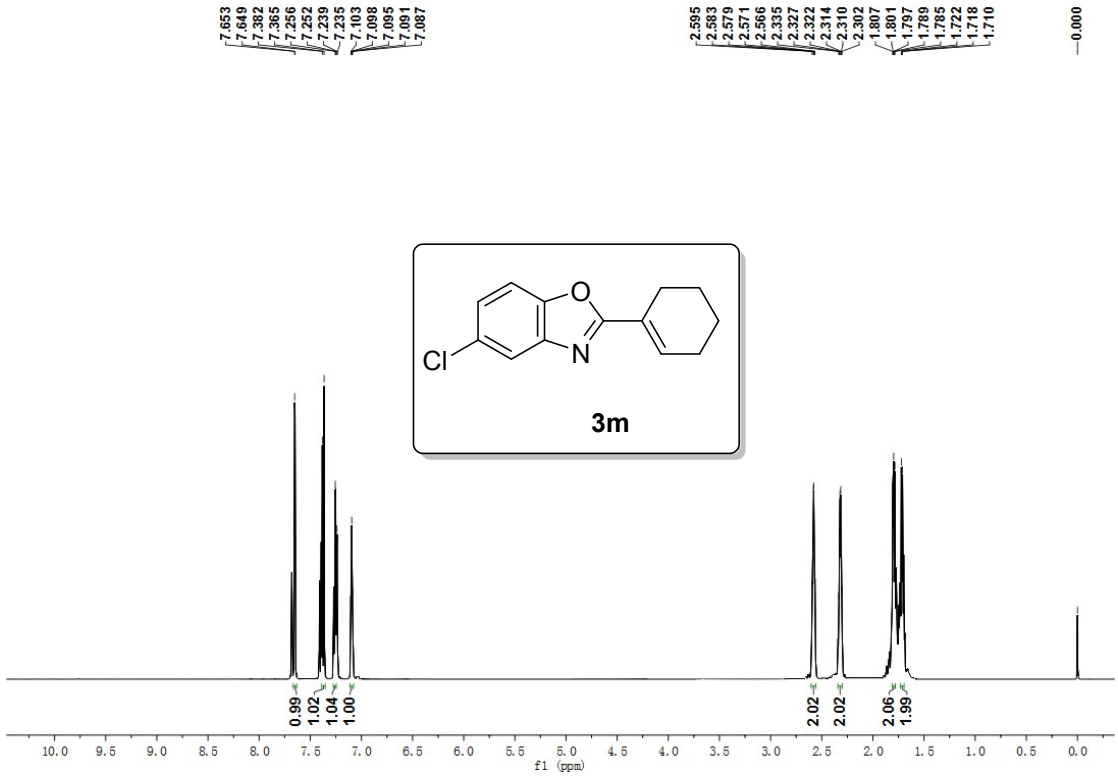
148.48
142.14
135.00
133.79
126.35
125.72
119.69
109.48
77.37
77.12
76.86
25.81
24.74
22.07
21.69
21.48
O
N
H3C
3l
f1 (ppm)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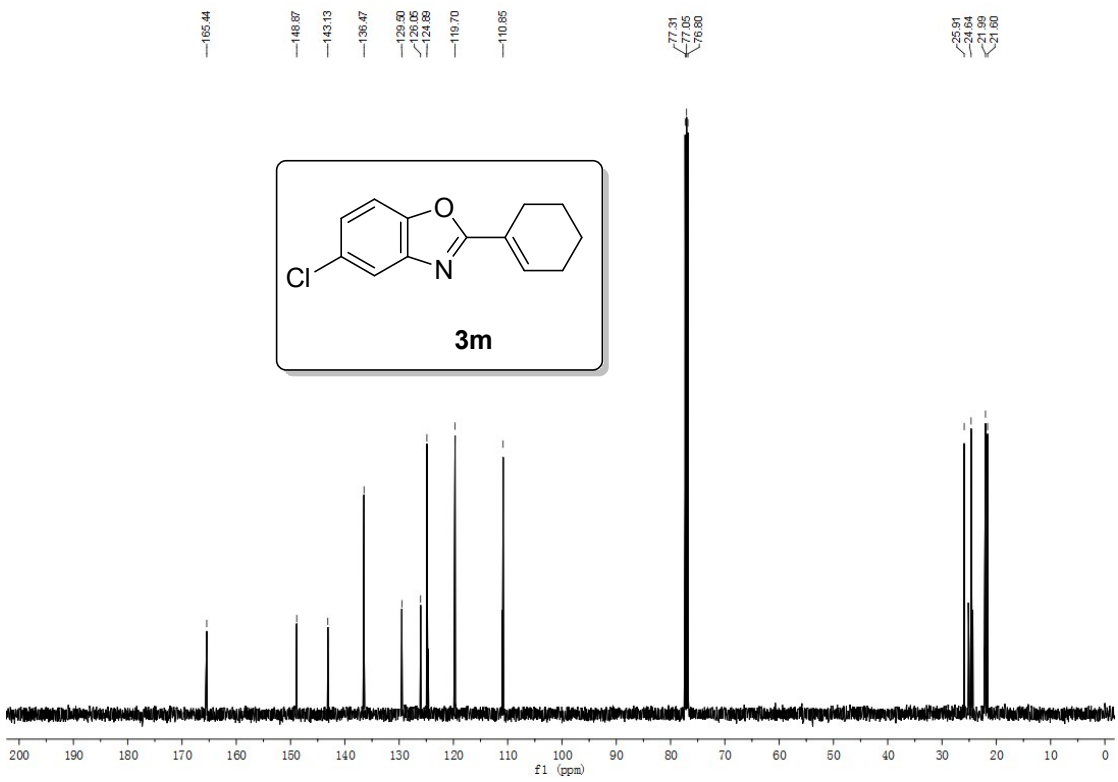
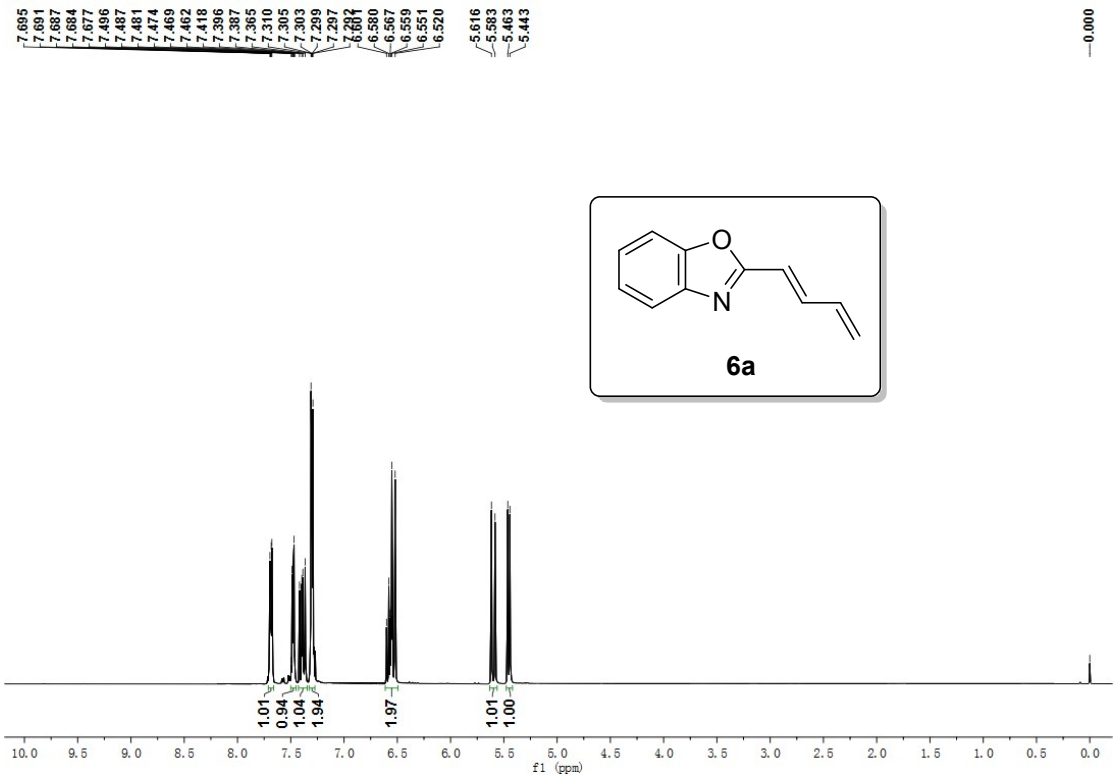
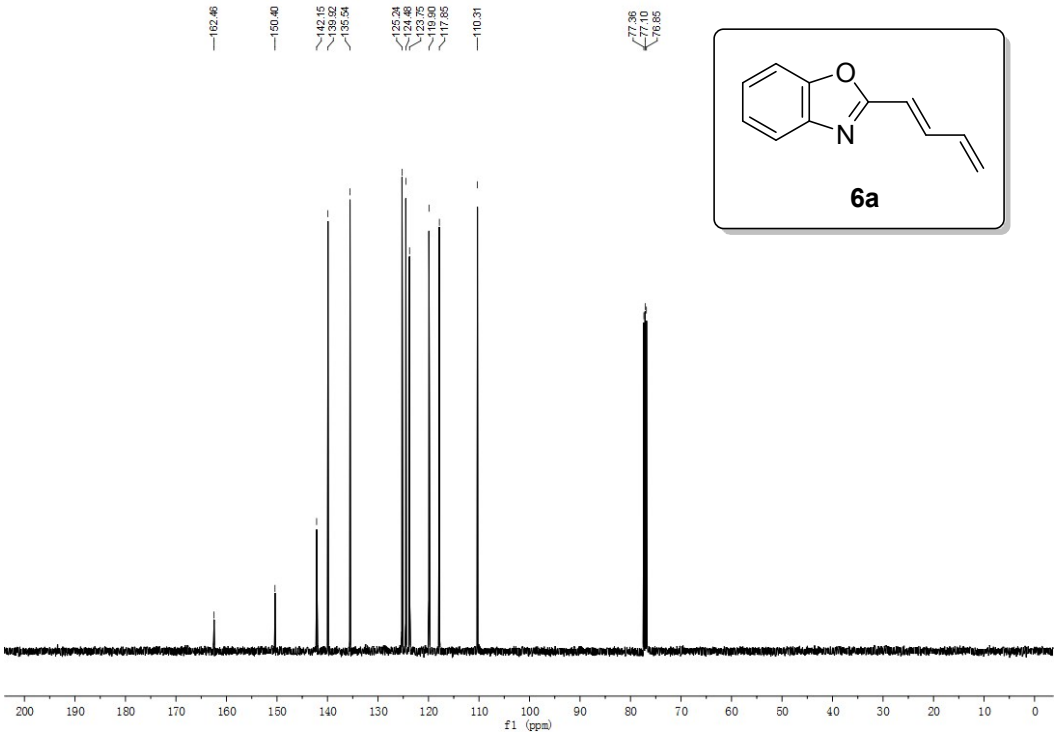
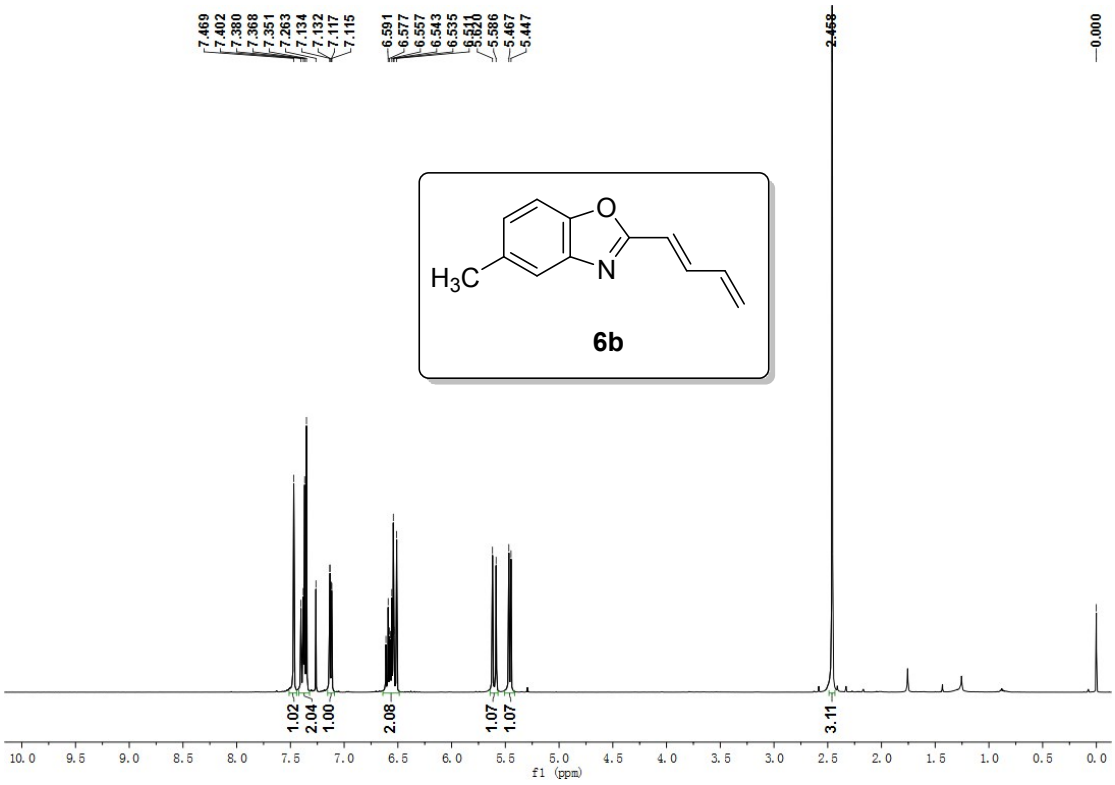
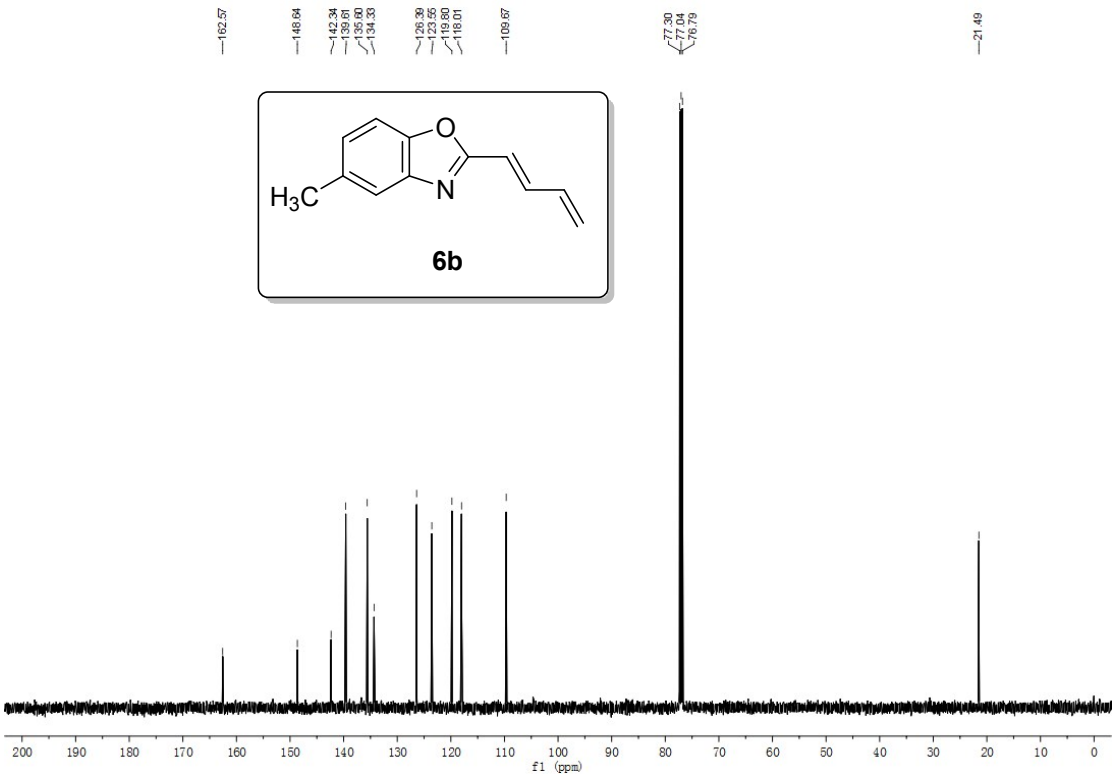
7.649
7.382
7.365
7.256
7.252
7.239
7.235
7.103
7.098
7.095
7.091
7.087
2.595
2.583
2.579
2.571
2.566
2.335
2.327
2.322
2.314
2.310
2.302
1.807
1.801
1.797
1.789
1.785
1.722
1.718
1.710
0.000
Cl
O
N
3m
0.99
1.02
1.04
1.00
2.02
2.02
2.06
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

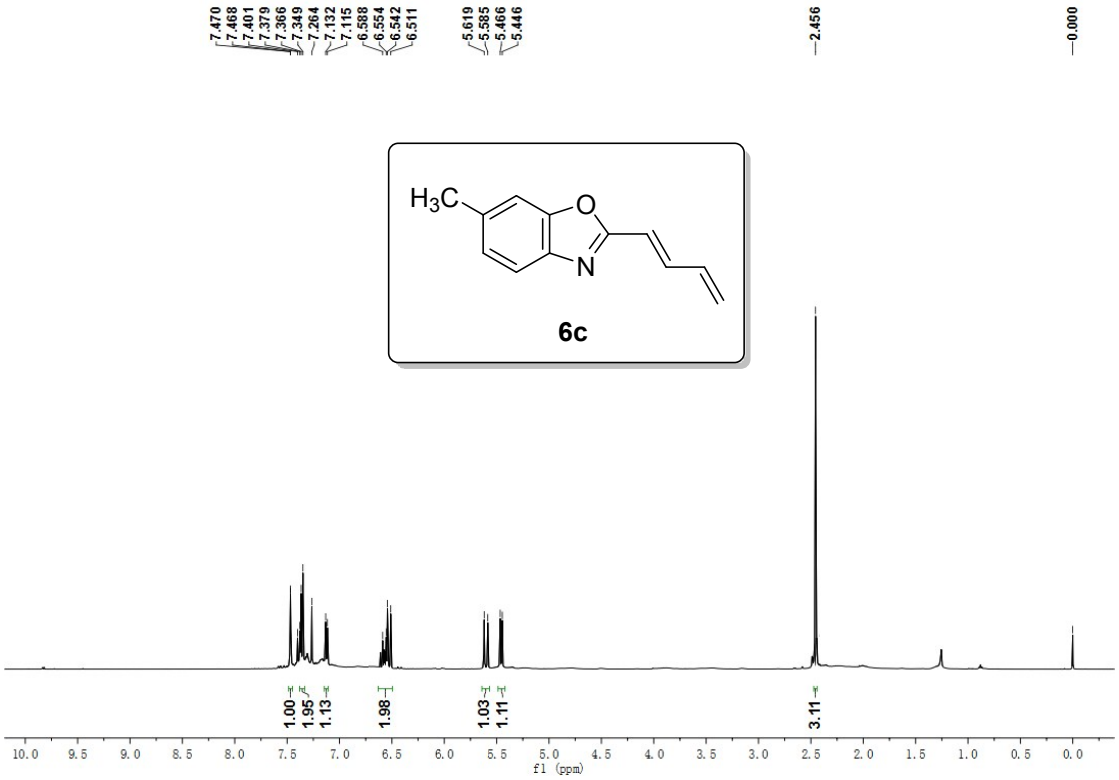

165.44
148.87
143.13
136.47
129.90
126.85
124.88
119.70
110.85
77.31
77.05
76.80
25.91
24.64
21.99
21.60
Cl
O
N
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

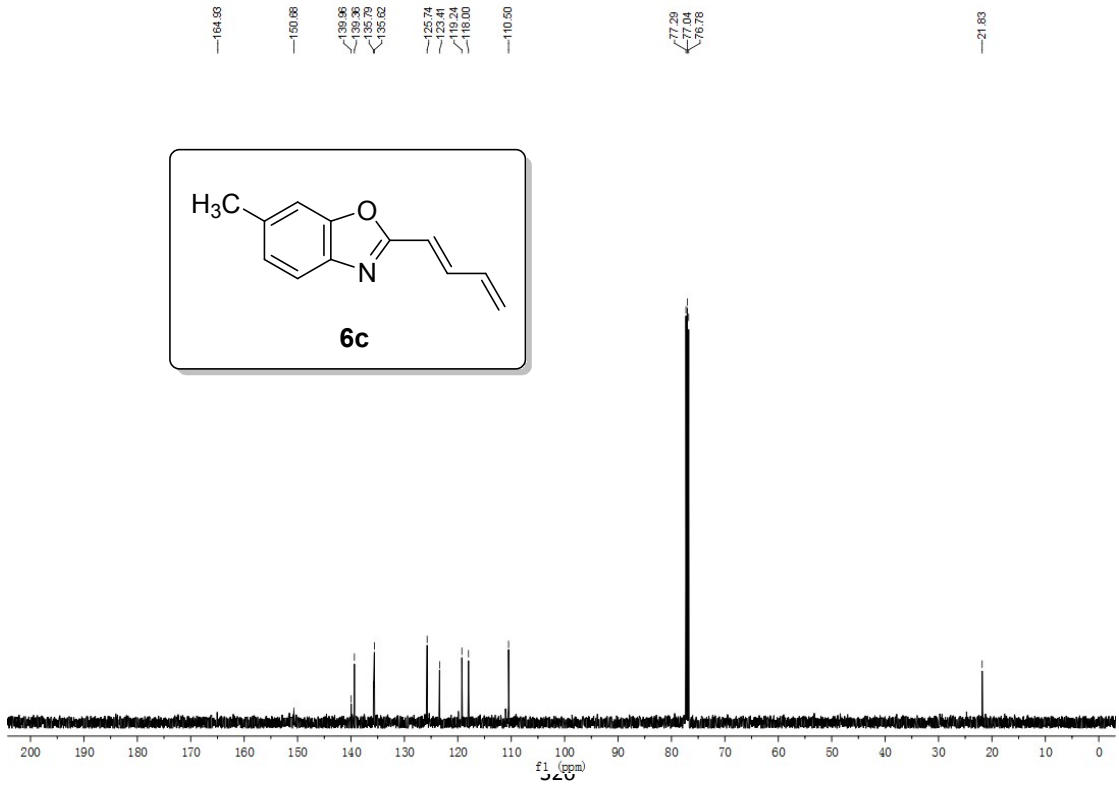

7.695
7.691
7.687
7.684
7.677
7.496
7.487
7.481
7.474
7.469
7.462
7.418
7.396
7.387
7.365
7.310
7.305
7.303
7.299
7.297
6.580
6.567
6.559
6.551
6.520
5.616
5.583
5.463
5.443
0.000
O
N
6a
1.01
0.94
1.04
1.94
1.97
1.01
1.00
f1 (ppm)


162.46
150.40
142.15
139.92
135.54
125.24
124.48
123.75
119.90
117.85
110.31
77.36
77.10
76.85
O
N
6a
f1 (ppm)


7.469
7.402
7.380
7.368
7.351
7.263
7.134
7.132
7.117
7.115
6.591
6.577
6.557
6.543
6.535
5.520
5.386
5.467
5.447
2.468
0.000
6b
1.02
2.04
1.00
2.08
1.07
1.07
3.11
f1 (ppm)


162.57
148.64
142.34
139.61
135.60
134.33
126.39
123.55
119.80
118.01
108.67
77.30
77.04
76.79
21.49
6b
f1 (ppm)


7.470
7.468
7.401
7.379
7.366
7.349
7.264
7.132
7.115
6.588
6.554
6.542
6.511
5.619
5.585
5.466
5.446
2.456
0.000
H3C
O
N
6c
1.00
1.95
1.13
1.98
1.03
1.11
3.11
f1 (ppm)


164.93
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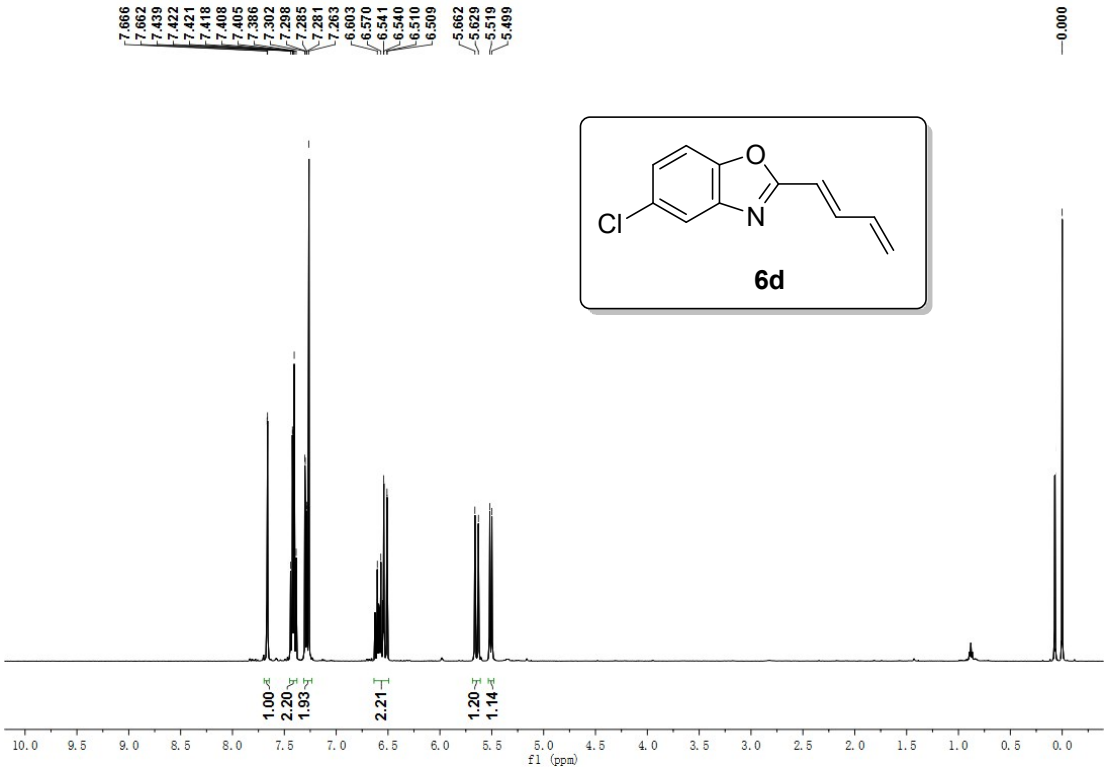
139.96
139.36
135.79
135.62
125.74
123.41
119.24
118.00
110.50
77.29
77.04
76.78
21.83
H3C
O
N
6c
f1 (ppm)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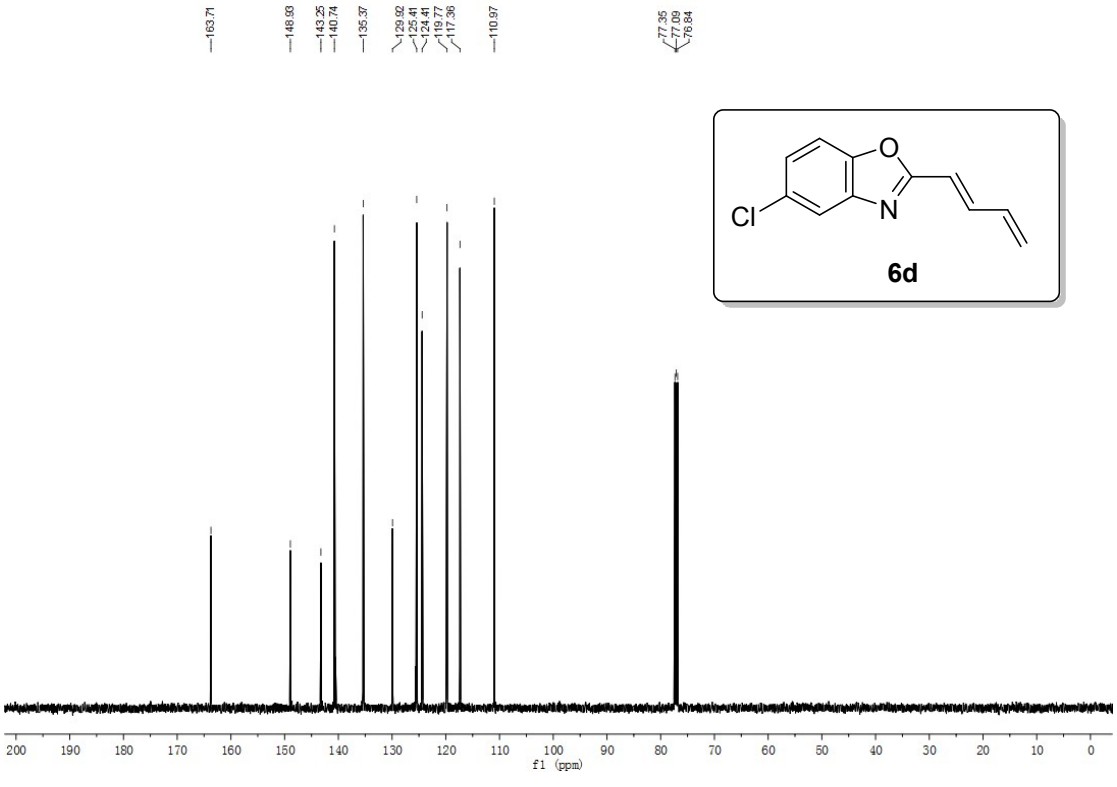
7.662
7.439
7.422
7.421
7.418
7.408
7.405
7.386
7.302
7.298
7.285
7.281
7.263
6.603
6.570
6.541
6.540
6.510
6.509
5.662
5.629
5.519
5.499
0.000
Cl
O
N
6d
1.00
2.20
1.93
2.21
1.20
1.14
f1 (ppm)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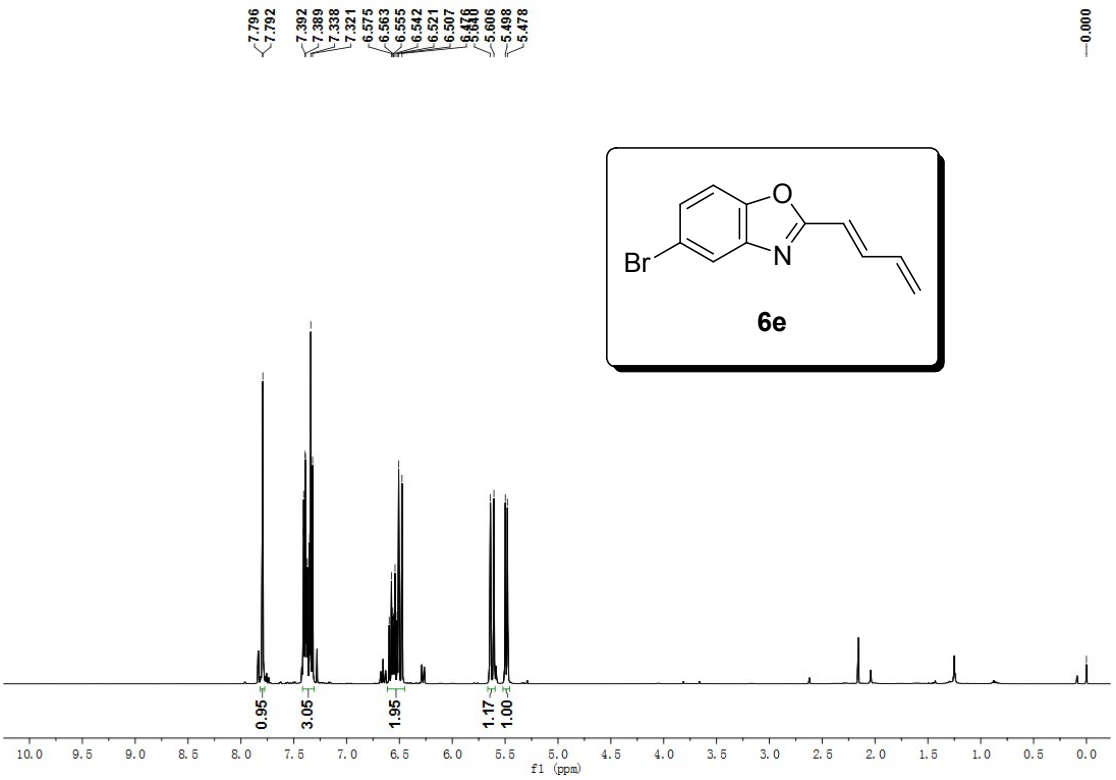
148.93
143.25
140.74
135.37
129.92
125.41
124.41
119.77
117.36
110.97
77.35
77.09
76.84
Cl
O
N
6d
f1 (ppm)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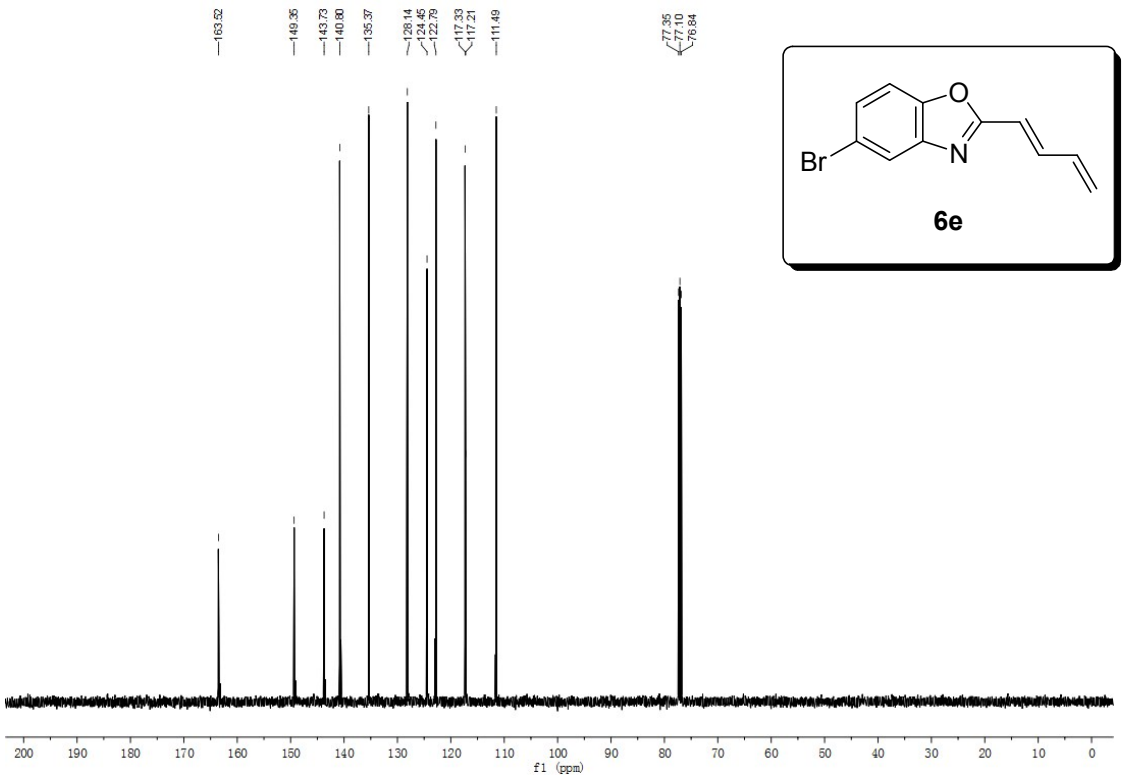
7.792
7.392
7.389
7.338
7.321
6.575
6.563
6.555
6.542
6.521
6.507
5.606
5.498
5.478
0.000
Br
O
N
6e
0.95
3.05
1.95
1.17
1.00
f1 (ppm)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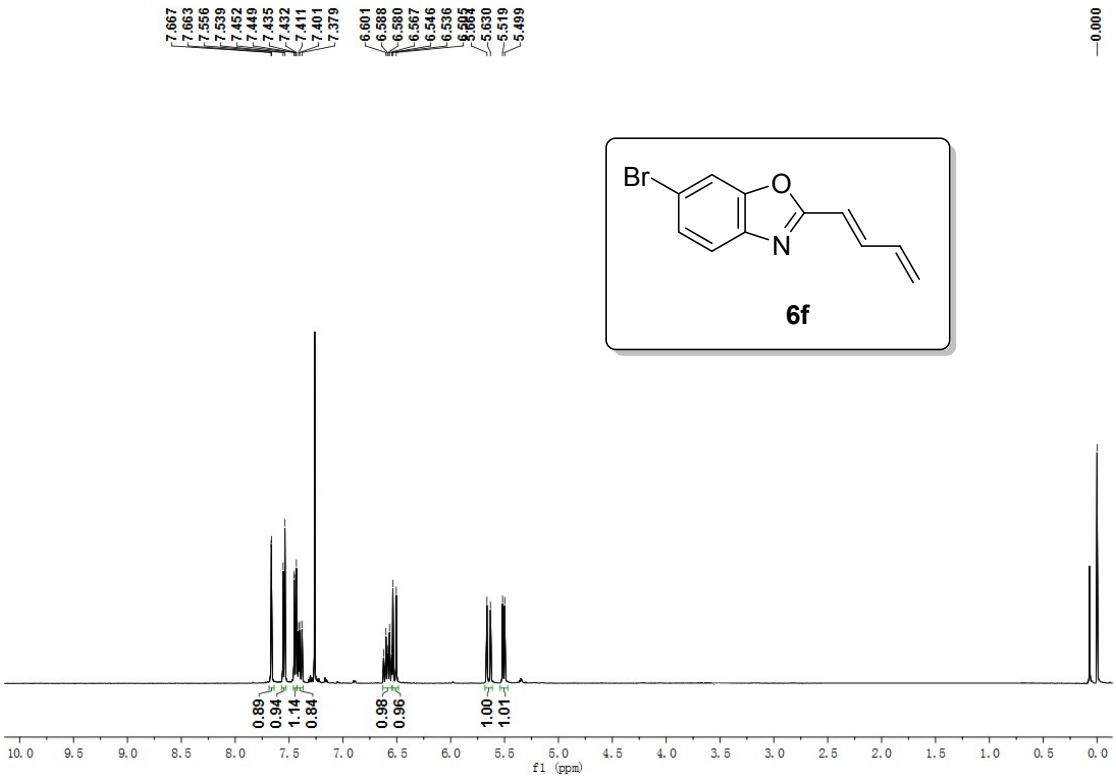
149.35
143.73
140.80
135.37
128.14
124.45
122.79
117.33
117.21
111.49
77.35
77.10
76.84
Br
O
N
6e
f1 (ppm)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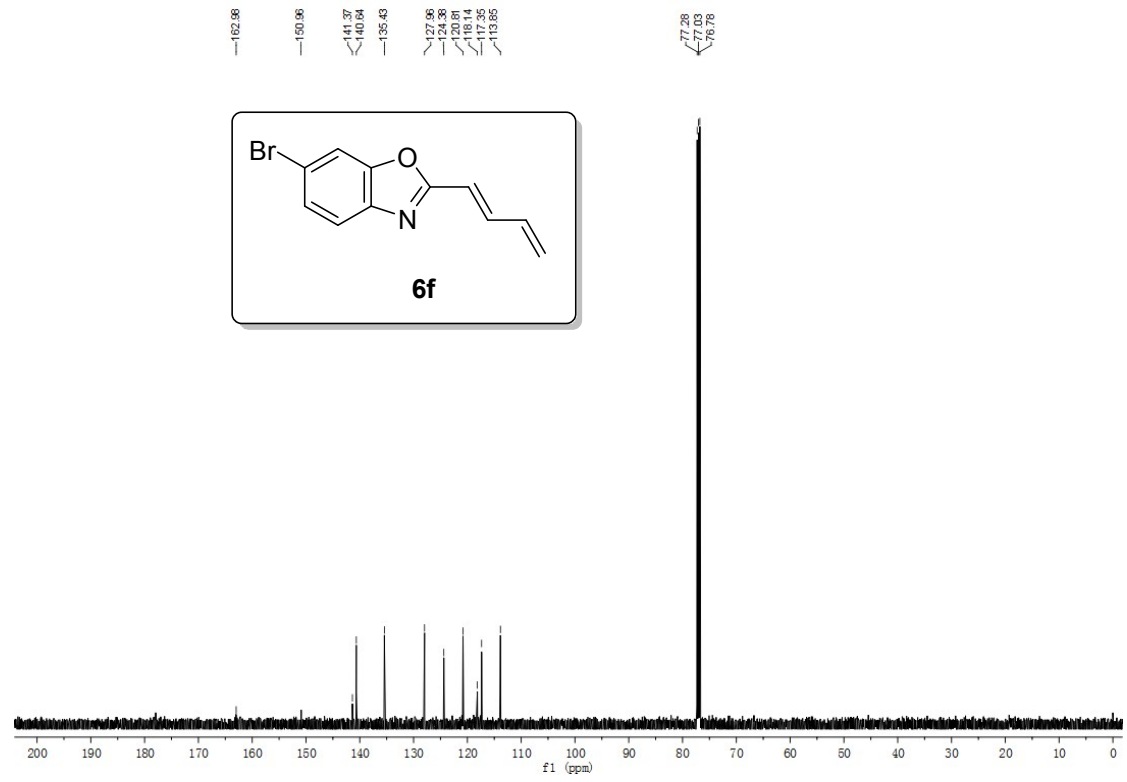
7.452
7.449
7.435
7.432
7.411
7.401
7.379
6.601
6.588
6.580
6.567
6.546
6.536
5.630
5.519
5.499
0.000
Br
O
N
6f
0.89
0.94
1.14
0.84
0.98
0.96
1.00
1.01
f1 (ppm)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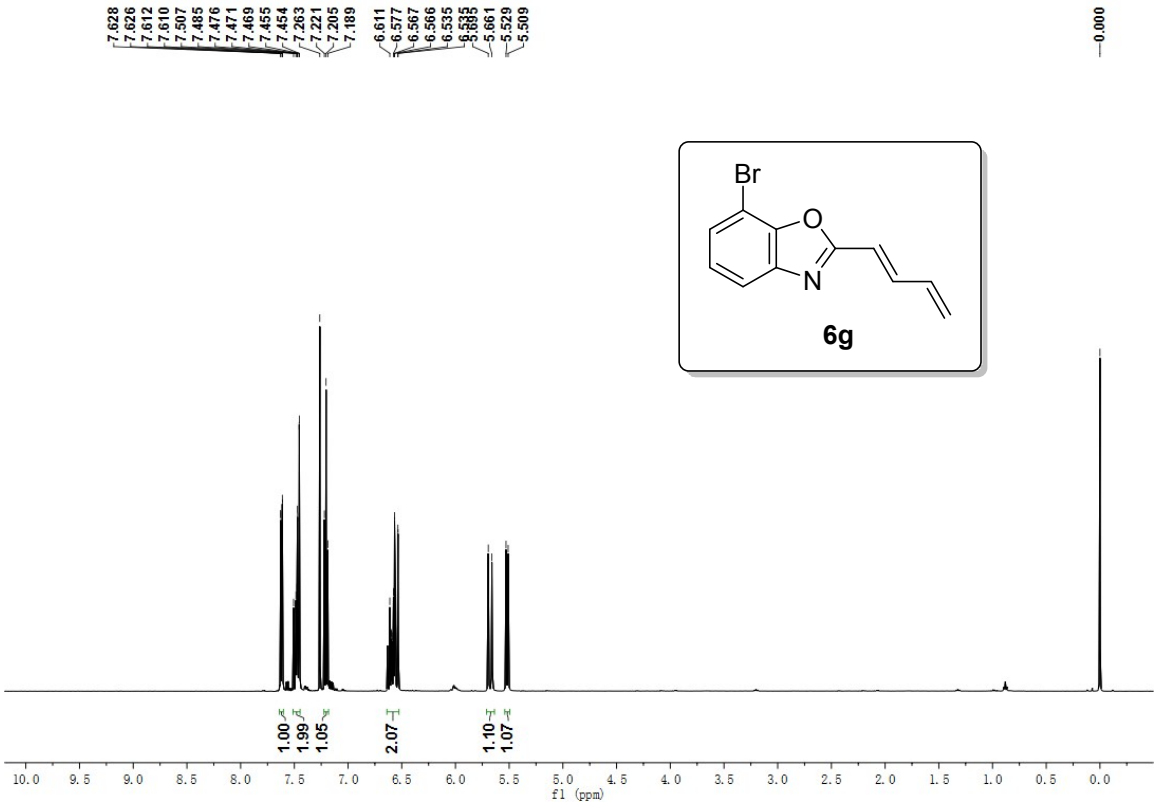
141.37
140.64
135.43
127.96
124.38
120.81
118.14
117.35
113.85
77.28
77.03
76.78
Br
O
N
6f
f1 (ppm)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7.626
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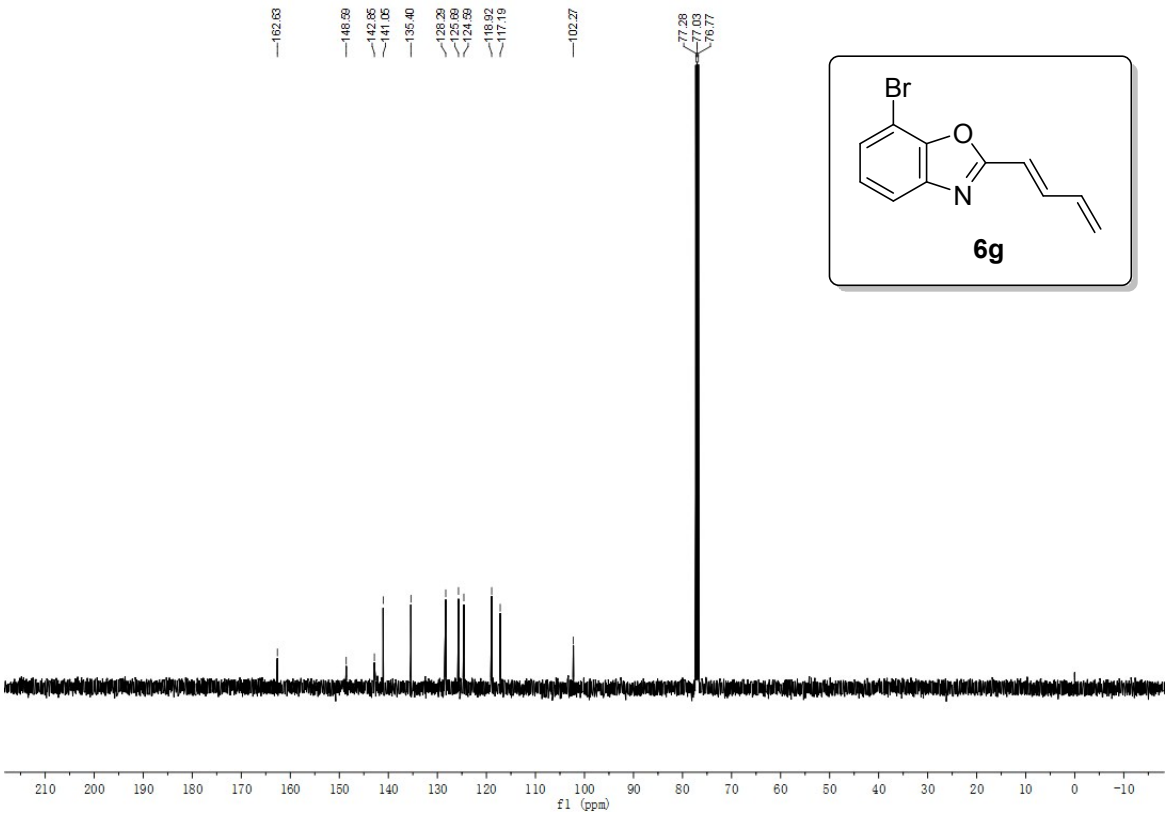
7.610
7.507
7.485
7.476
7.471
7.469
7.455
7.454
7.263
7.221
7.205
7.189
6.611
6.577
6.567
6.566
6.535
5.661
5.529
5.509
0.000
Br
O
N
6g
1.00
1.99
1.05
2.07
1.10
1.07
f1 (ppm)


162.63
148.59
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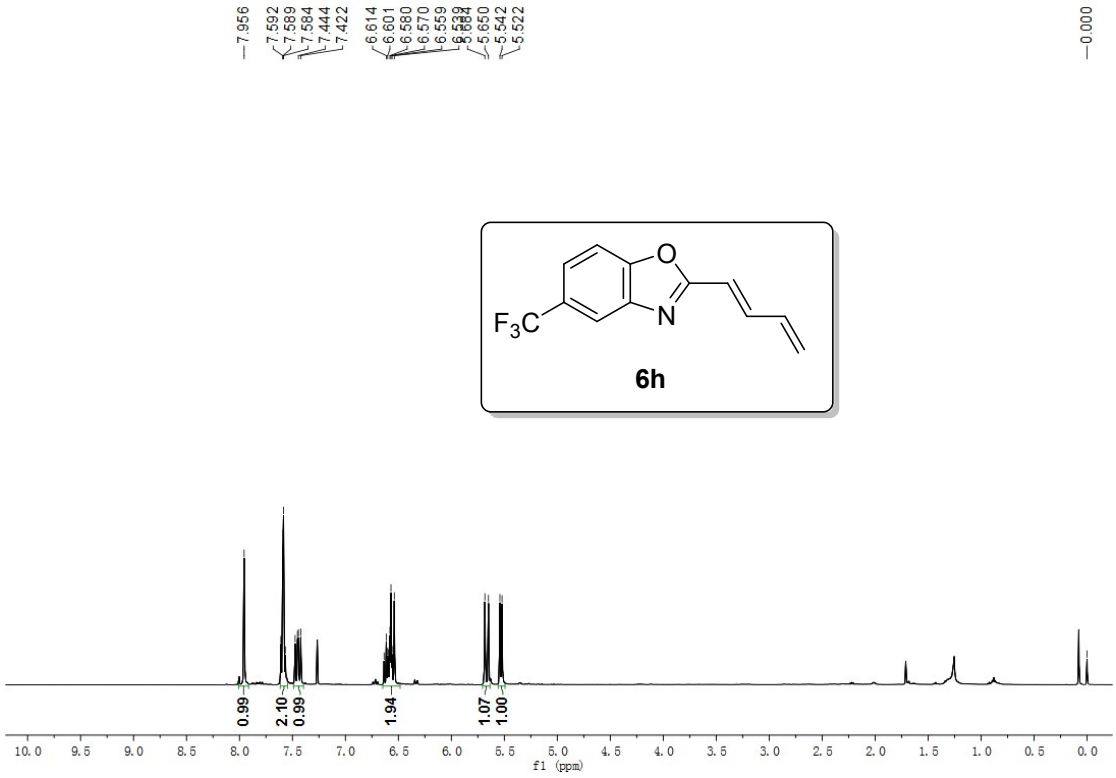
135.40
128.29
125.69
124.59
118.92
117.19
102.27
77.28
77.03
76.77
Br
O
N
6g
f1 (ppm)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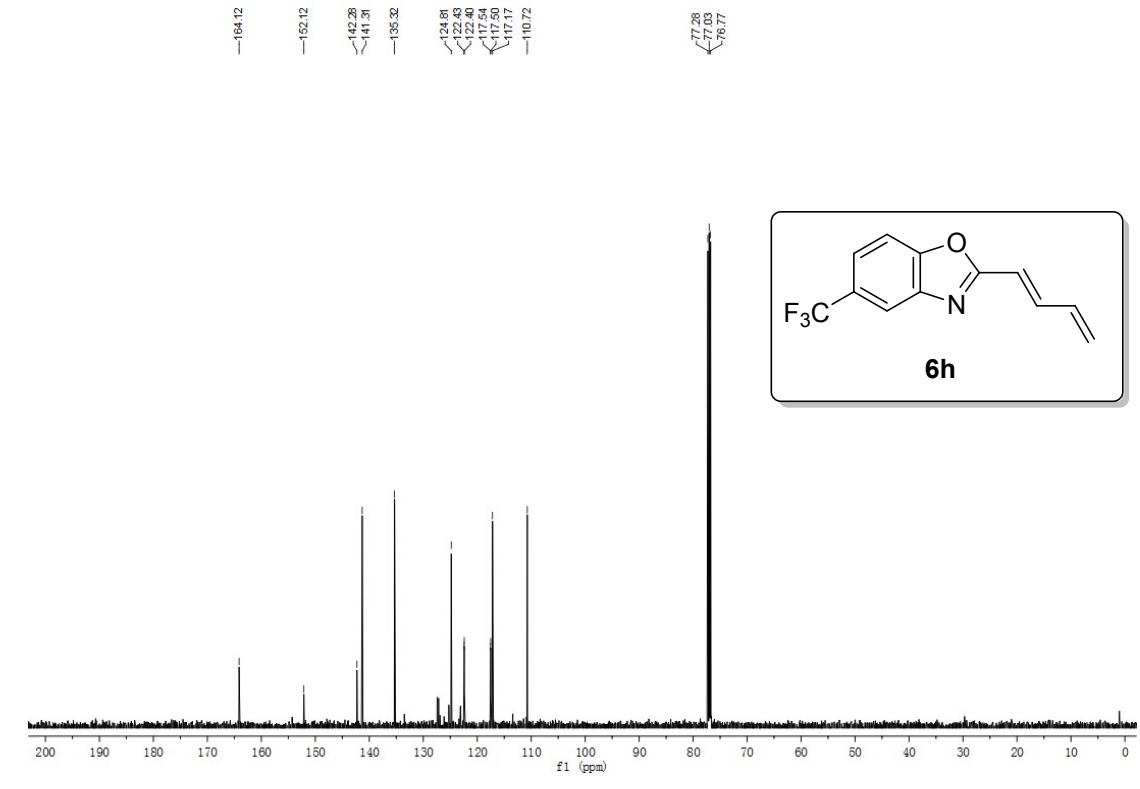
7.584
7.444
7.422
6.614
6.601
6.580
6.570
6.559
5.650
5.542
5.522
0.000
F3C
O
N
6h
0.99
2.10
0.99
1.94
1.07
1.00
f1 (ppm)


164.12
152.12
142.28
141.31
135.32
124.81
122.43
122.40
117.54
117.50
117.17
110.72
77.28
77.03
76.77
F3C
O
N
6h
f1 (ppm)