Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

Bis(imidazoline-2-thione)–copper(I) catalyzed regioselective boron addition to internal alkynes

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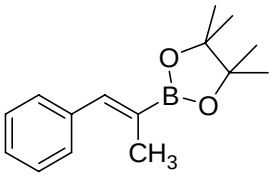
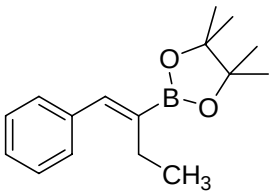
Genaral Methods. All reactions were performed in oven-dried Schlenk tubes under a nitrogen atmostphere. THF was distilled using sodium benzophenone ketyl as drying agent under nitrogen. CuCl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased and used as received. Flash chromatography was performed on silica gel from Merck (70-230 mesh). All ^{1}H NMR spectra were obtained on Varian Mercury 300 systems and reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra were reported in ppm referenced to deuteriochloroform (77.16 ppm). GC analysis was performed on a Younglin Acme 9000 series. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, Korea). Alkynes that are not commercially unavailable were prepared by Negishi coupling and sonogashira coupling reaction according to reported procedures.[1]

General procedure for the regioselective boron addition to internal alkynes catalyzed by bis(1,3-dimetylimidazoline-2-thione)copper chloride (Table 2): To a oven dried schlenk tube equipped with a stir bar were added CuCl (2.5 mg, 0.025 mmol), NaO*t*-Bu (9.6 mg, 0.10 mmol), 1,3-dimetylimidazoline-2-thione (6.4 mg, 0.050 mmol) and THF (0.40 mL) under nitrogen. After the mixture was stirred at room temperature for 30 min, bis(pinacolato)diboron (140 mg, 0.55 mmol) in THF (0.30 mL) was added. The reaction mixture was stirred for 10 min. Then, internal alkyne (0.50 mmol) was added, followed by MeOH (0.04 mL, 1 mmol). The reaction was washed with THF (0.30 mL), sealed, and stirred for 24 h. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

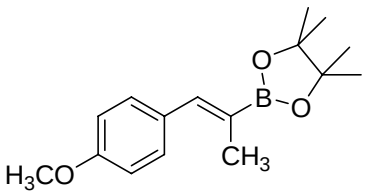
Characterization data of new compounds



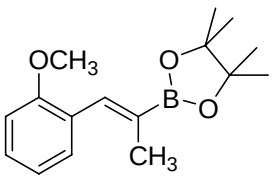
(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 1). Using the general procedure, the title compound was prepared as a colorless oil (103.8 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 5H), 7.24 (br s, 1H), 2.00 (d, *J* = 1.8 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 138.0, 129.5, 128.2, 127.2, 83.6, 25.0, 16.1; HRMS (EI) calcd for $C_{15}H_{21}BO_2$: 244.1635; found 244.1641.



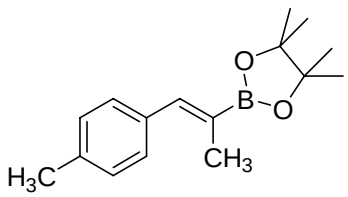
(Z)-4,4,5,5-tetramethyl-2-(1-phenylbut-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 2). Using the general procedure, the title compound was prepared as colorless oil (194 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 5H), 7.20 (br s, 1H), 2.39 (q, *J* = 7.5 Hz, 2H), 1.32 (s, 12H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5, 138.0, 129.1, 128.2, 127.1, 83.5, 25.0, 22.8, 14.8; HRMS (EI) calcd for $C_{16}H_{23}BO_2$: 258.1791; found 258.1790.



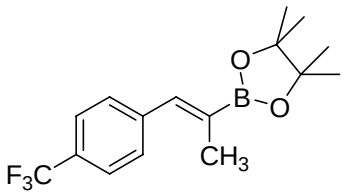
(Z)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 4). Using the general procedure, the title compound was prepared as colorless oil (165 mg, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.8 Hz, 2H), 7.18 (br s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 142.1, 131.1, 130.8, 113.6, 83.5, 55.3, 25.0, 16.1; HRMS (EI) calcd for $C_{16}H_{23}BO_3$: 274.1740; found 274.1738.



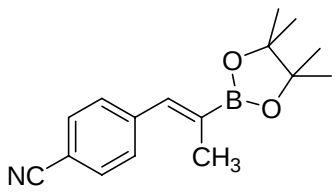
(Z)-2-(1-(2-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 5). Using the general procedure, the title compound was prepared as colorless oil (165 mg, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (br s, 1H), 7.31–7.06 (m, 2H), 6.91 (dd, *J* = 8.2, 6.9 Hz, 2H), 3.83 (s, 3H), 1.92 (d, *J* = 1.8 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 138.1, 130.5, 128.7, 126.8, 119.9, 110.4, 83.5, 55.4, 25.0, 16.1; HRMS (EI) calcd for $C_{16}H_{23}BO_3$: 274.1740; found 274.1742.



(Z)-4,4,5,5-tetramethyl-2-(1-p-tolylprop-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 6). Using the general procedure, the title compound was prepared as colorless oil (194 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 2H), 7.21 (br s, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H), 2.00 (d, *J* = 1.6 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 137.0, 135.2, 129.5, 128.9, 83.5, 24.9, 21.3, 16.0; HRMS (EI) calcd for $C_{16}H_{23}BO_2$: 258.1791; found 258.1794.



(Z)-4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (Table 2, entry 7). Using the general procedure, the title compound was prepared as colorless oil (250 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.23 (br s, 1H), 1.98 (d, *J* = 1.6 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4, 140.8, 129.2, 128.7, 126.1, 125.1, 83.9, 25.0, 12.0; HRMS (EI) calcd for $C_{16}H_{20}BF_3O_2$: 312.1508; found 312.1506.



(Z)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl) Benzonitrile (Table 2, entry 8). Using the general procedure, the title compound was prepared as white crystal (234 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.20 (br s, 1H), 1.98 (d, *J* = 1.8 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 140.3, 132.0, 129.9, 119.1, 110.5, 83.9, 25.0, 16.1; HRMS (EI) calcd for $C_{16}H_{20}BNO_2$: 269.1587; found 269.1584.

IMO[2], **IMSE**[3], **IMS**[4], **IMS-Bu**[5] and **IMS-Octyl**[5] were prepared by literature methods.

IMS-Dodecyl: 1,3-dodecylmethylimidazolium iodide (6.9 mmol) and potassium carbonate (34 mmol) were added to methanol (50 mL). The reaction mixture was stirred for 30 min. Excess sulfur (21 mmol) was added and the solution was stirred for 12 h at room temperature. Excess potassium carbonate and sulfur were filtered off, and the filtrate was concentrated. The remaining residue was diluted with dichloromethane and washed with aqueous $NaHCO_3$. The organic layer was separated, dried over magnesium sulfate and concentrated to a solid. The pure product was isolated via column chromatography

with hexanes and ether (4:1) as eluant. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.70 (s, 2H), 4.02 (t, *J* = 7.5 Hz, 2H), 3.61 (s, 3H), 1.76 (t, *J* = 6.9 Hz, 2H), 1.32–1.19 (m, 18H), 0.88 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR(75 MHz, $CDCl_3$): δ = 161.9, 117.6, 116.5, 48.1, 35.0, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 26.5, 22.6, 14.1; Elemental Analysis for $C_{16}H_{30}N_2S$, Calc. C; 68.03, H; 10.70, N; 9.92, S; 11.35, Obs. C; 67.94, H;10.85, N; 9.95, S;11.94.

IMS-Hexadecyl: 1,3-Hexadecylmethylimidazolium iodide (6.9 mmol) was used instead of 1,3-dodecylmethylimidazolium iodide. ^{1}H NMR (300MHz, $CDCl_3$): δ = 6.67 (s, 2H), 4.02 (t, *J* = 7.5 Hz, 2H), 3.61 (s, 3H), 1.76 (t, *J* = 7.4 Hz, 2H), 1.33–1.21 (m, 26H), 0.88 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR(75 MHz, $CDCl_3$): δ = 162.1, 117.6, 116.6, 48.2, 35.1, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 26.6, 22.8, 14.2; Elemental Analysis for $C_{20}H_{38}N_2S$, Calc. C; 70.95, H; 11.31, N; 8.27, S; 9.47, Obs. C; 71.07, H; 11.49, N; 8.27, S; 9.22.

References

1. (*a*) E.-I. Negishi, M. Kotora and C. Xu, *J. Org. Chem*., 1997, **62**, 8957; (*b*) F. Y. Kwong, Y. M. Li, W. H. Lam, L. Qiu, H. W. Lee, C. H. Yeung, K. S. Chan and A.S. C. Chan, *Chem. Eur. J.,* 2005, **11**, 3872.
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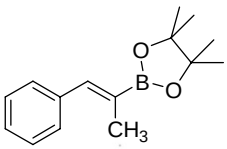
5. A. J. Arduengo III, *U.S. Pat. Appl*., 2008-171883, 5.



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4	2213.258	7.380	8.0
5	2211.644	7.374	6.8
6	2210.030	7.369	6.6
7	2202.694	7.345	6.0
8	2200.934	7.339	2.2
9	2194.771	7.318	2.3
10	2177.459	7.260	4.7
11	2171.443	7.240	4.8
12	599.054	1.997	16.6
13	597.294	1.992	15.7
14	475.977	1.584	2.8
15	394.674	1.316	151.2
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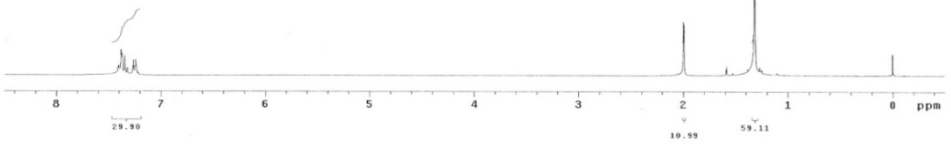

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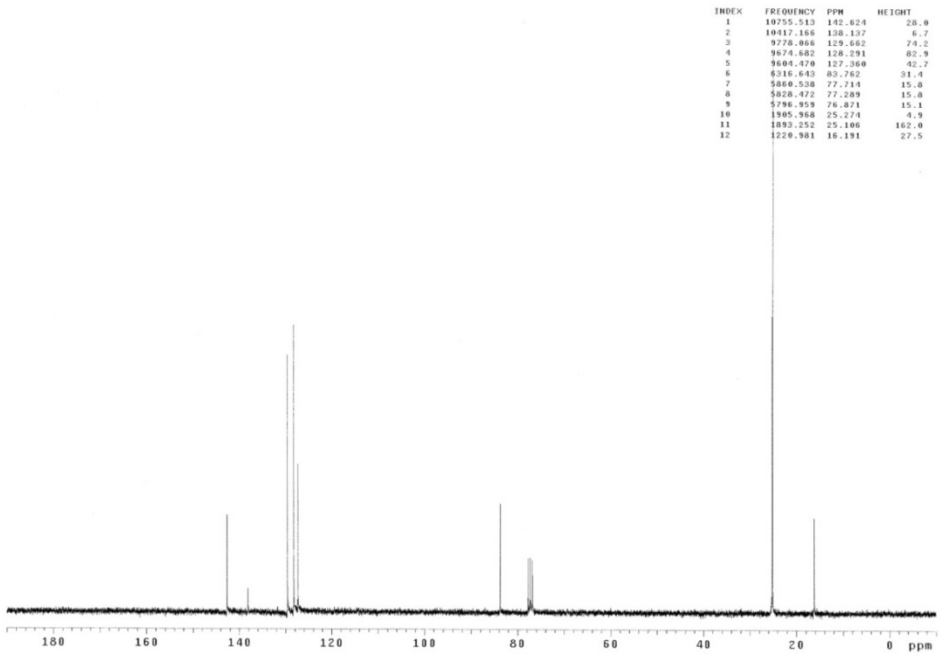
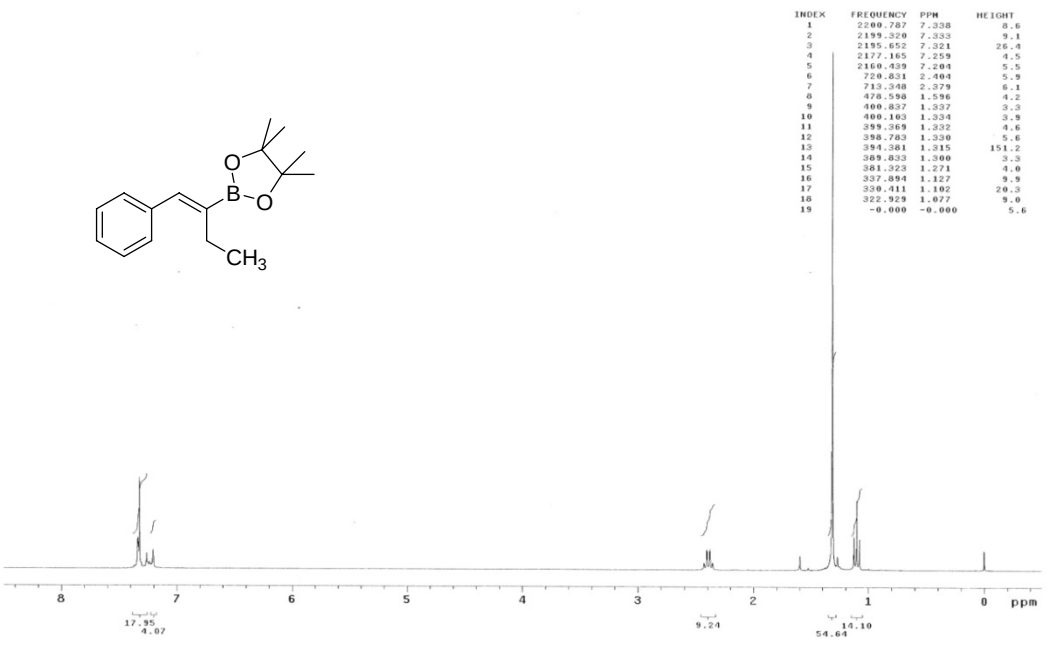
4	9674.682	128.291	82.9
5	9604.470	127.360	42.7
6	6316.643	83.762	31.4
7	5860.538	77.714	15.8
8	5828.472	77.289	15.8
9	5796.959	76.871	15.1
10	1905.968	25.274	4.9
11	1893.252	25.106	162.0
12	1220.981	16.191	27.5

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8 478.598 1.596 4.2
9 400.837 1.337 3.3
10 400.103 1.334 3.9
11 399.369 1.332 4.6
12 398.783 1.330 5.6
13 394.381 1.315 151.2
14 389.833 1.300 3.3
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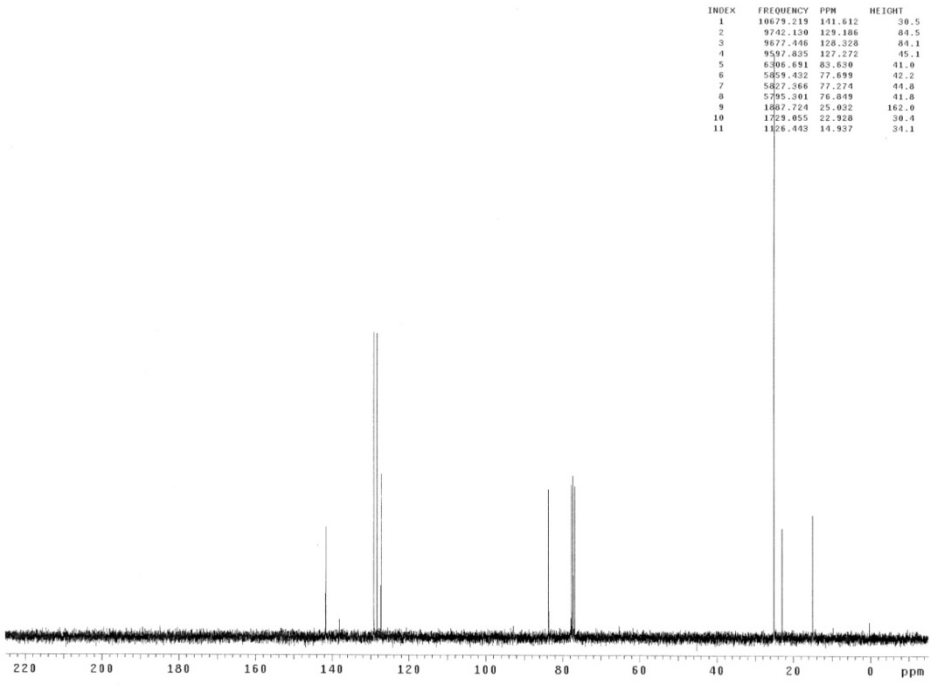
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6 5859.432 77.699 42.2
7 5827.366 77.274 44.8
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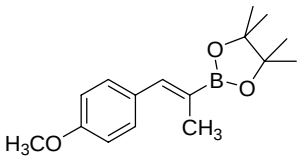

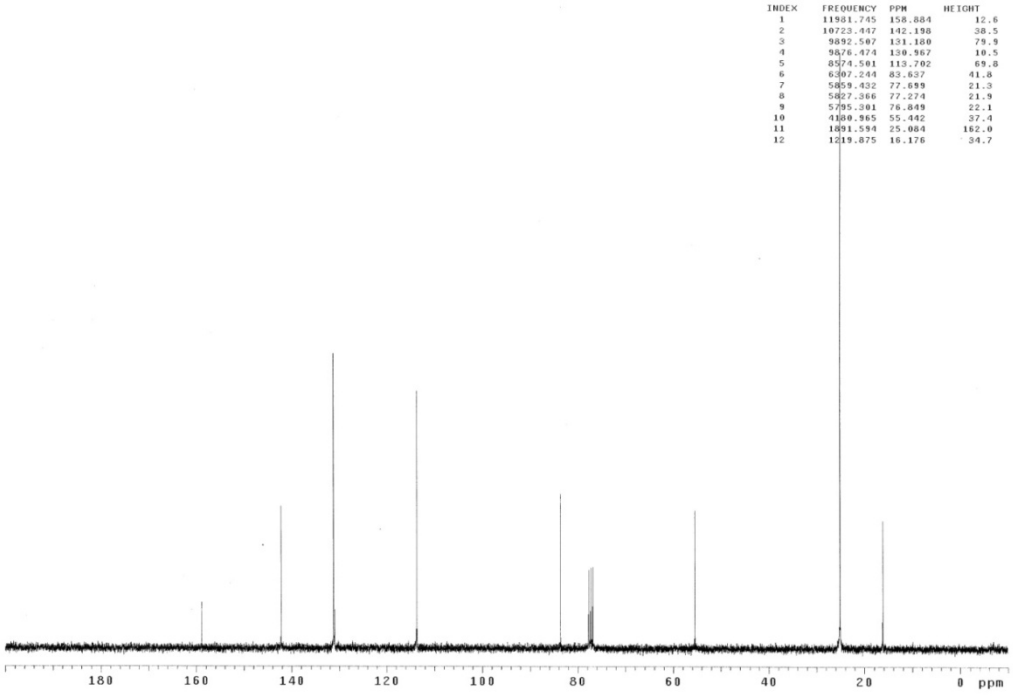

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5	8574.501	113.702	69.8
6	6307.244	83.637	41.8
7	5859.432	77.699	21.3
8	5827.366	77.274	21.9
9	5795.301	76.849	22.1
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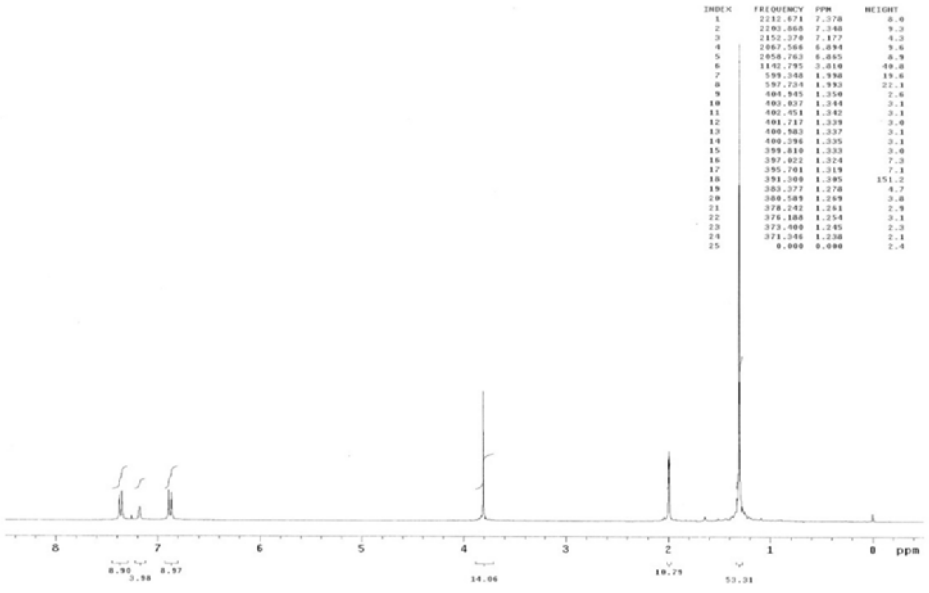

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5	2058.763	6.865	8.9
6	1142.795	3.810	49.8
7	599.348	1.998	19.6
8	597.734	1.993	22.1
9	404.945	1.350	2.6
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11	402.451	1.342	3.1
12	401.717	1.339	3.0
13	400.583	1.337	3.1
14	400.296	1.335	3.1
15	399.810	1.333	3.0
16	397.022	1.324	7.3
17	395.701	1.319	7.1
18	391.300	1.305	151.2
19	383.377	1.278	4.7
20	380.589	1.269	3.8
21	378.242	1.261	2.9
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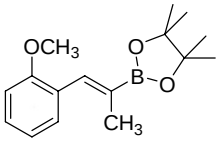

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7	2178.192	7.263	2.1				
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12	2077.543	6.927	4.3				
13	2067.566	6.894	4.9				
14	2059.350	6.867	3.9				
15	1155.853	3.854	2.9				
16	1148.811	3.831	39.3				
17	575.286	1.918	21.3				
18	573.525	1.912	19.1				
19	420.497	1.402	2.1				
20	419.030	1.397	2.3				
21	415.949	1.387	2.9				
22	412.427	1.375	3.4				
23	409.787	1.366	4.5				
24	409.200	1.364	4.4				
25	408.466	1.362	4.5				
26	399.223	1.331	13.9				
27	392.474	1.309	151.2				
28	387.485	1.292	6.3				
29	386.752	1.290	6.7				
30	384.698	1.283	4.6				
31	383.524	1.279	4.9				
32	381.470	1.272	4.6				
33	379.416	1.265	3.4				
34	377.948	1.260	5.1				
35	376.921	1.257	4.1				
36	374.134	1.247	2.5				
37	373.547	1.246	2.5				
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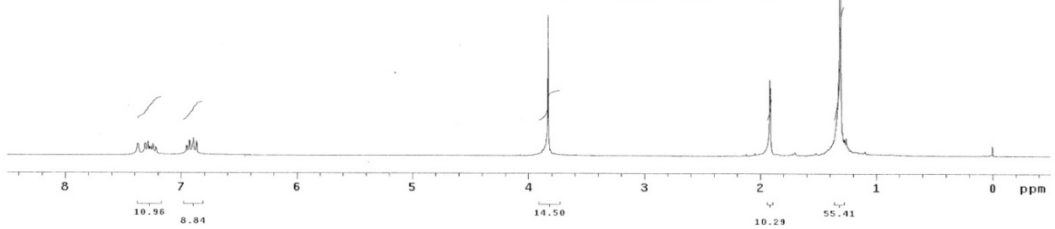

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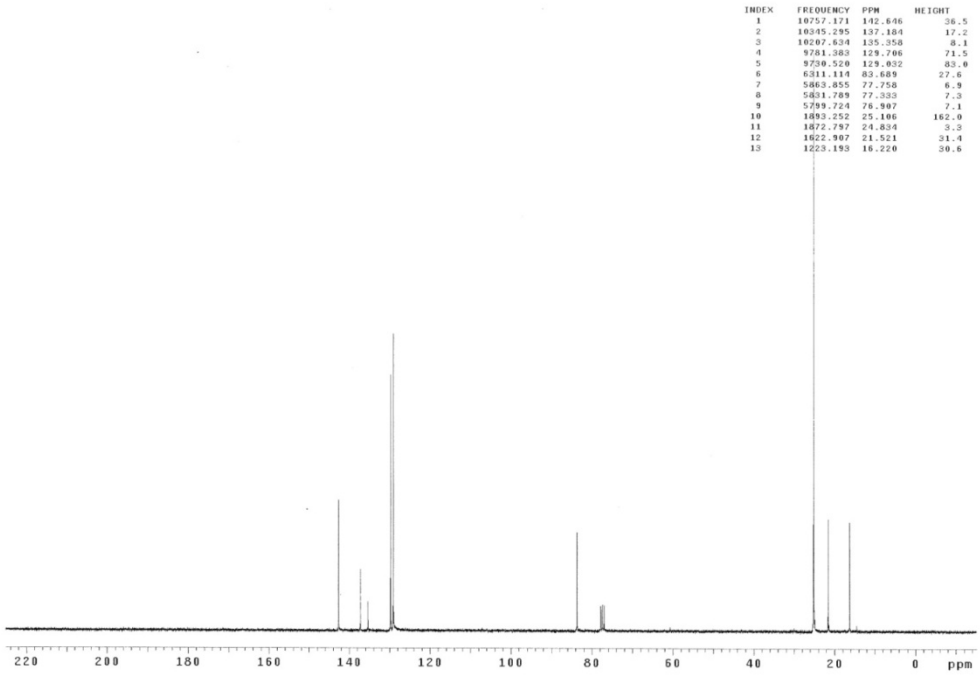
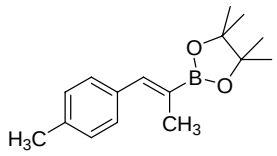
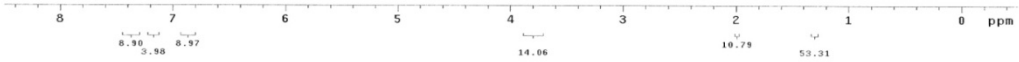
9	5799.724	76.907	7.1
10	1893.252	25.106	162.0
11	1872.797	24.834	3.3
12	1622.907	21.521	31.4
13	1223.193	16.220	30.6

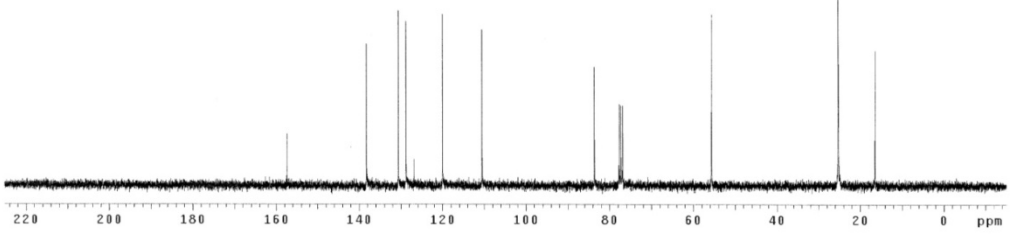


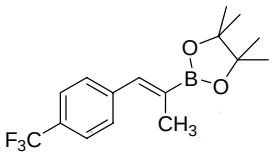


INDEX	FREQUENCY	PPM	HEIGHT
1	2212.671	7.378	8.0
2	2203.868	7.348	9.3
3	2152.370	7.177	4.3
4	2067.566	6.894	9.6
5	2058.763	6.865	8.9
6	1142.795	3.810	40.8
7	599.348	1.998	19.6
8	597.734	1.993	22.1
9	404.945	1.350	2.6
10	403.037	1.344	3.1
11	402.451	1.342	3.1
12	401.717	1.339	3.0
13	400.983	1.337	3.1
14	400.396	1.335	3.1
15	399.810	1.333	3.0
16	397.022	1.324	7.3
17	395.701	1.319	7.1
18	391.300	1.305	151.2
19	383.377	1.278	4.7
20	380.589	1.269	3.8
21	378.242	1.261	2.9
22	376.188	1.254	3.1
23	373.400	1.245	2.3
24	371.346	1.238	2.1
25	0.000	0.000	2.4

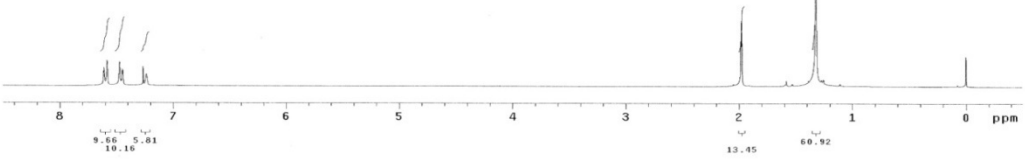


INDEX	FREQUENCY	PPM	HEIGHT
1	11870.621	157.411	13.5
2	10424.353	138.232	36.6
3	9849.384	130.608	45.2
4	9711.723	128.782	42.4
5	9568.534	126.884	6.8
6	9049.403	120.000	44.2
7	8334.562	110.521	40.3
8	6306.139	83.623	30.8
9	5859.985	77.706	21.1
10	5827.919	77.281	20.7
11	5796.406	76.863	20.8
12	4191.469	55.581	44.3
13	1896.017	25.142	162.0
14	1230.380	16.315	34.9

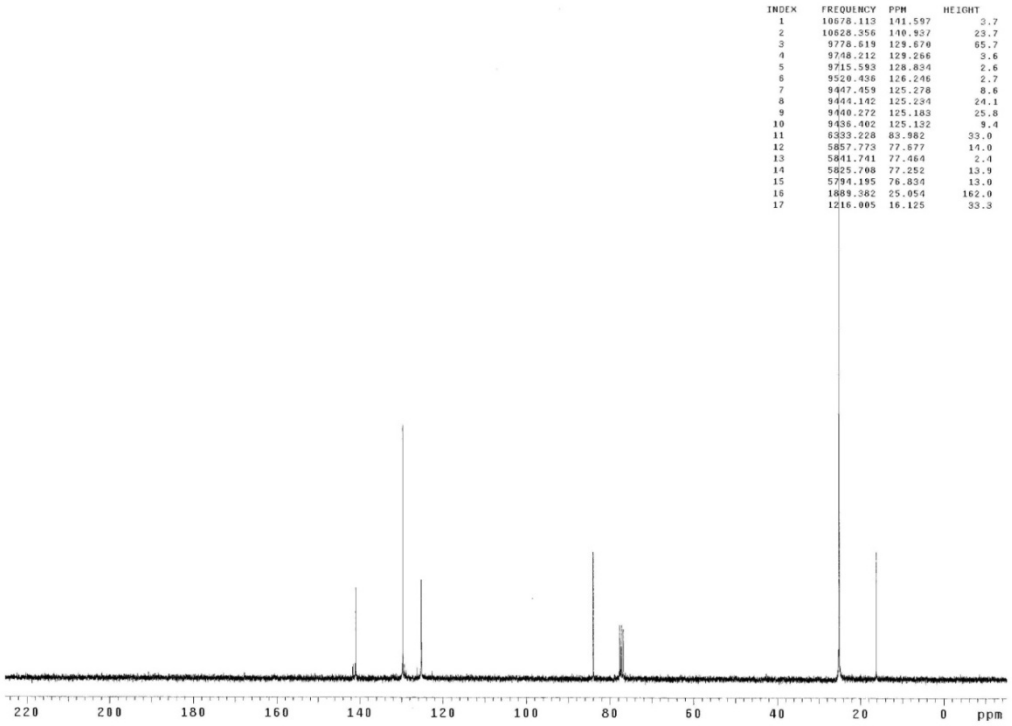


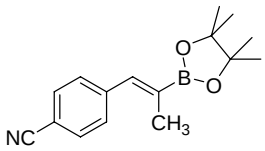


INDEX	FREQUENCY	PPM	HEIGHT
1	2282.069	7.609	5.3
2	2273.706	7.581	7.5
3	2240.841	7.472	7.1
4	2232.625	7.444	4.9
5	2178.339	7.263	5.5
6	2169.976	7.235	3.5
7	594.506	1.982	19.2
8	592.745	1.976	18.7
9	396.288	1.321	151.2
10	376.188	1.254	2.1
11	0.000	0.000	8.8

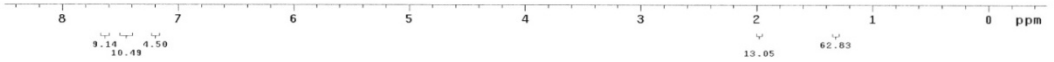


INDEX	FREQUENCY	PPM	HEIGHT
1	10678.113	141.597	3.7
2	10628.356	140.937	23.7
3	9778.619	129.670	65.7
4	9748.212	129.266	3.6
5	9715.593	128.834	2.6
6	9520.436	126.246	2.7
7	9447.459	125.278	8.6
8	9444.142	125.234	24.1
9	9440.272	125.183	25.8
10	9436.402	125.132	9.4
11	6333.228	83.982	33.0
12	5857.773	77.677	14.0
13	5841.741	77.464	2.4
14	5825.708	77.252	13.9
15	5794.195	76.834	13.0
16	1889.382	25.054	162.0
17	1216.005	16.125	33.3





INDEX	FREQUENCY	PPM	HEIGHT
1	2292.486	7.644	5.9
2	2290.726	7.638	2.5
3	2285.884	7.622	2.7
4	2284.123	7.616	8.1
5	2236.880	7.459	7.4
6	2228.664	7.431	5.5
7	2178.779	7.265	11.6
8	2159.852	7.202	2.7
9	2158.385	7.197	2.7
10	593.626	1.979	16.8
11	591.865	1.973	17.0
12	474.196	1.581	10.2
13	402.597	1.342	3.1
14	402.010	1.340	3.3
15	400.543	1.336	4.3
16	399.223	1.331	5.3
17	395.115	1.317	151.2
18	388.952	1.297	3.4
19	388.366	1.295	3.1
20	387.045	1.291	2.6
21	386.311	1.288	2.4
22	385.578	1.286	2.3
23	381.030	1.270	2.1
24	378.242	1.261	2.2
25	377.068	1.257	2.4
26	372.960	1.244	2.3
27	0.000	0.000	15.0



INDEX	FREQUENCY	PPM	HEIGHT
1	10757.724	142.653	9.0
2	10587.998	140.402	32.0
3	9963.825	132.125	68.3
4	9804.603	130.014	69.3
5	8993.565	119.259	11.9
6	8341.749	110.616	11.5
7	6342.074	84.099	26.4
8	5859.985	77.706	22.7
9	5827.919	77.281	22.9
10	5795.854	76.856	20.4
11	1890.488	25.069	162.0
12	1225.957	16.257	28.8