Suzuki-Miyaura Cross-Coupling Reactions of Aryl Tellurides with Potassium Aryltrifluoroborate Salts

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Experimental Section

General: Palladium catalyst and silver (I) oxide were obtained from a commercial sources. The triethylamine was distilled from potassium hydroxide and the methanol was distilled from sodium methoxide and kept over molecular sieves. THF was distilled from sodium benzophenone.

Mass Spectrometric Experiments. Typically, aliquots of 40 μL were taken from the reaction mixture and diluted in 960 μL of methanol containing 10 μL of formic acid for acid quenching.10 μL of sample was analyzed in the spectrometer with a capillary voltage of 3.1 kV, cone voltage of 20 to 75 V. The collision induced dissociation (CID) for MS/MS experiments were performed with collision energy ranged from 10 to 40 eV with argon as collision gas

Potassium Organotrifluoroborate synthesis

Potassium phenyltrifluoroborate (**2a**), potassium 4-methoxyphenyltrifluoroborate (**2b**), potassium 4-chlorophenylborate (**2c**), potassium 2-furyltrifluoroborate (**2d**) and potassium 3-methoxyphenyltrifluoroborate (**2e**) were prepared from boronic acids according to the reported procedures.[1]

Butyl(aryl)tellanes synthesis.

Method A:[2] To a solution of arylmagnesium bromide (20 mmol) in THF (25 mL) was added elemental tellurium (2.55 g, 20 mmol), in one portion, at room temperature (rt). The resulting suspension was stirred for 2 h at the same temperature. The mixture was then cooled to -20ºC and *n*-bromobutane (2.88 g, 21 mmol) was added dropwise. After stirring at rt for 2 h, the reaction was diluted with ethyl acetate (50 mL) and then washed with brine (3 x 20 mL). The organic layer was dried

over $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography to afford the respective aryl butyl telluride.

Method B:[3] The 4-hidroxiphenyl tellurium trichoride (3.27 g, 10 mmol) was dissolved in THF (40 mL) and *n*-bromobutane (1.64g, 12 mmol) was added. The mixture was cooled to 0ºC and a solution of sodium borohydride (0.75 g, 20mmol) in water (20 mL) was added dropwise. The reaction was stirred for further 20 min at room temperature and quenched with saturated solution of NH_4Cl (30 mL). The mixture was extracted with ethyl acetate (3x 20 mL) and washed with brine (2 x 20 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography (eluting with hexane:ethyl acetate 8:2) to yield butyl(4-hidroxyphenyl)tellane (**1f**) (1.94g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.64 (d, *J* 8.6 Hz, 2H), 6.72 (d, *J* 8.2 Hz, 2H), 5.40 (br s, 1H), 2.82 (t, *J* 7.5 Hz, 2H), 1.75 (qn, *J* 7.3 Hz, 2H), 1.37 (sex, *J* 7.3 Hz, 2H), 0.90 (t, *J* 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 155.6, 141.0, 116.5, 100.6, 33.8, 24.9, 13.3, 8.8. MS: m/z (%) 280 (13); 278 (12); 220 (8); 94 (100); 57 (28).

Method C:[4] An aqueous solution of sodium nitrite (1.73g, 25 mmol in 10 mL of water) was added dropwise to a solution of appropriated aniline (17 mmol), hydrochloric acid concentrate (5 mL) in water (5 mL) at 0 ºC and stirred for 5 minutes. After the reaction mixture was treated with a saturated solution of $NaHCO_3$ and then was added a solution of *n*-butyl ditelluride (1.98g, 5 mmol) in dichloromethane (15 mL) at 0 ºC. The reaction was stirred for further 30 minutes at room temperature and quenched with brine (15 mL). The mixture was extracted with dichloromethane (2 x 15 mL) and washed with brine (2 x 20 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography to afford the respective aryl butyl telluride.

Method D:[5] *n*-Buthyllithium (5 mmol, 1.6M in hexane, 1.87 mL) was added to a solution of the appropriated heterocycle (5 mmol) in THF (5 mL) at 75 ºC and stirred for 45 min. After this time was added elemental tellurium (0.638 g, 5 mmol), in one portion, at room temperature (rt). The resulting suspension was stirred for 2 h at the same temperature. The mixture was then cooled to -20 ºC and *n*-

bromobutane (0.82 g, 6 mmol) was added dropwise. After stirring at rt for 2 h, the reaction was diluted with ethyl acetate (50 mL) and then washed with brine (3 x 20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by silica gel chromatography to afford the respective heteroaryl butyl telluride.

Butyl(4-methoxyphenyl)tellane (**1a**).[3] This product was obtained as a yellow oil in 80% yield from 4-methoxybromobenzene, elemental tellurium and *n*-bromobutane by method **A**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9.5:0.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.62 (d, *J* 8.73 Hz, 2H), 6.7 (d, *J* 8.7 Hz, 2H), 3.73 (s, 3H), 2.77 (t, *J* 7.7 Hz, 2H), 1.68 (qn, *J* 7.2 Hz, 2H), 1.32 (sex, *J* 7.3 Hz, 2H), 0.83 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.8, 141.1, 115.3, 100.8, 55.3, 34.1, 25.2, 13.6, 8.9. MS: m/z (%) 294 (48); 292 (50); 234 (33); 108 (100); 77 (38).

Butyl(4-nitrophenyl)tellane (**1b**). This product was obtained as a yellow oil in 60% yield from 4-nitroaniline and *n*-butyl ditelluride by method **C**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9:1).^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.00 (d, *J* 8.9 Hz, 2H), 7.74 (d, *J* 8.7 Hz, 2H), 3.03 (t, *J* 7.5 Hz, 2H), 1.84 (qn, *J* 7.5 Hz, 2H), 1.43 (sex, *J* 7.5 Hz, 2H), 0.93 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 146.9, 136.2, 124.3, 123.4, 33.4, 25.0, 13.3, 9.2. MS: m/z (%) 308 (7); 306 (6); 249 (2); 203 (4); 76 (28); 57 (100).

Butyl(4-methylphenyl)tellane (**1c**).[3] This product was obtained as a yellow oil in 69% yield from 4-methylphenyl tellurium trichloride and *n*-bromobutane by method **B**, after purification by chromatography on silica gel (eluting with hexane).^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* 7.9 Hz, 2H), 7.00 (d, *J* 7.9 Hz, 2H), 2.85 (t, *J* 7.6 Hz, 2H), 2.32 (s, 3H), 1.75 (qn, *J* 7.3 Hz, 2H), 1.37 (sex, *J* 7.4 Hz, 2H), 0.88 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 138.8, 137.6, 130.2, 107.7, 34.1, 25.2, 21.4, 13.6, 8.6. MS: m/z (%) 278 (17); 276 (16); 219 (8); 91 (100); 57 (38).

Butyl(2-methylphenyl)tellane (**1d**). This product was obtained as a yellow oil in 65% yield from 2-bromotoluene, elemental tellurium and *n*-bromobutane by method **A**, after purification by

chromatography on silica gel (eluting with hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.56 (d, *J* 7.59 Hz, 1H), 7.18-7.0 (m, 2H), 6.95 (t, *J* 7.46 Hz, 1H), 2.83 (t, *J* 7.5 Hz, 2H), 2.37 (s, 3H), 1.73 (qn, *J* 7.2 Hz, 2H), 1.36 (sex, *J* 7.3 Hz, 2H), 0.86 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 142.5, 136.8, 129.2, 127.7, 126.6, 116.7, 33.8, 26.6, 25.4, 13.6, 7.7. MS: m/z (%) 278 (30); 276 (30); 219 (14); 91 (100); 57 (36). Anal. Calcd. For $C_{11}H_{16}Te$: C, 47.9; H, 5.85. Found: C, 48.24; H, 6.19.

Butyl(naphthalene-1-yl)tellane (**1e**).[6] This product was obtained as a yellow oil in 86% yield from 1-bromonaphthalene, elemental tellurium and *n*-bromobutane by method **A**, after purification by chromatography on silica gel (eluting with hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.22 (d, *J* 8.1 Hz, 1H), 8.02 (d, *J* 7.0 Hz, 1H), 7.76-7.72 (m, 2H), 7.53-7.422 (m, 2H), 7.24 (t, *J* 8.1 Hz, 1H), 2.88 (t, *J* 7.6 Hz, 2H), 1.70 (qn, *J* 7.3 Hz, 2H), 1.34 (sex, *J* 7.4 Hz, 2H), 0.80 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 138.2, 136.3, 133.4, 132.1, 128.8, 128.7, 126.6, 126.1, 126.0, 115.5, 33.7, 25.0, 13.3, 8.6. MS: m/z (%) 314 (23); 312 (22); 255 (12); 128 (100); 57 (32).

1-(4-(butyltellanyl)phenyl)ethanone (**1g**). This product was obtained as a yellow oil in 65% yield from 1-(4-aminophenil)ethanone and *n*-butyl ditelluride by method **C**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.67-7.61 (m, 4H), 2.88 (t, *J* 7.2 Hz, 2H), 2.48 (s, 3H), 1.73 (qn, *J* 8.1 Hz, 2H), 1.33 (sex, *J* 7.6 Hz, 2H), 0.83 (t, *J* 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 197.7, 136.7, 135.9, 128.6, 121.0, 33.8, 26.7, 25.2, 13.5, 8.8. MS: m/z (%) 306 (15); 304 (14); 247 (3); 232 (9); 204 (7); 76 (25); 57 (58); 43 (100). Anal. Calcd. For $C_{12}H_{16}OTe$: C, 47.43; H, 5.31. Found: C, 47.28; H, 5.28.

Methyl 4-(butyltellanyl)benzoate (**1h**). This product was obtained as a yellow oil in 59% yield from methyl 4-aminobenzoate and *n*-butyl ditelluride by method **C**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* 8.3 Hz, 2H), 7.62 (d, *J* 8.3 Hz, 2H), 3.85 (s, 3H), 2.89 (t, *J* 7.4 Hz, 2H), 1.73 (qn, *J* 7.2 Hz, 2H), 1.33 (sex, *J* 7.5 Hz, 2H), 0.83 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 167.2, 136.8, 130.0, 129.1, 120.4, 52.3, 33.9, 25.3, 13.6, 8.8. MS: m/z (%) 322 (26); 320 (25); 289 (2); 263 (7); 232 (16); 204

(10); 135 (6); 105 (100); 76 (42); 57 (95). Anal. Calcd. For $C_{12}H_{16}O_2Te$: C, 45.06; H, 5.04. Found: C, 45.23; H, 4.87.

2-(Butyltellanyl)thiophene (**1i**).[7] This product was obtained as a yellow oil in 83% yield from 2-bromothiophene, elemental tellurium and *n*-bromobutane by method **D**, after purification by chromatography on silica gel (eluting with hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.35 (d, *J* 4.6 Hz, 1H), 7.29 (d, *J* 3.4, 1H), 6.86 (dd, *J* 5.1;3.6 Hz, 1H), 2.72 (t, *J* 7.6 Hz, 2H), 1.67 (qn, *J* 7.7, 2H), 1.30 (sex, *J* 7.3 Hz, 2H), 0.81 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 141.4, 134.2, 128.9, 97.5, 33.8, 25, 13.6, 11.5 MS: m/z (%) 270 (54); 268 (53); 210 (28); 83 (100); 57 (85).

2-(Butyltellanyl)furan (**1j**).[5] This product was obtained as a yellow oil in 87% yield from 2-bromofuran, elemental tellurium and *n*-bromobutane by method **D**, after purification by chromatography on silica gel (eluting with hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.55 (d, *J* 4.6 Hz, 1H), 6.72 (d, *J* 4.0, 1H), 6.31 (dd, *J* 4.9; 3.1 Hz, 1H), 2.75 (t, *J* 7.3 Hz, 2H), 1.72 (qn, *J* 7.9, 2H), 1.36 (sex, *J* 7.3 Hz, 2H), 0.87 (t, *J* 6.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 148.5, 125.8, 118.6, 111.8, 34.0, 24.8, 13.5, 10.0. MS: m/z (%) 254 (65); 252 (64); 194 (18); 67 (85); 57 (90); 41 (100).

3-(Butyltellanyl)pyridine (**1k**). This product was obtained as a yellow oil in 75% yield from 3-bromopyridine, elemental tellurium and *n*-bromobutane by method **D**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.86 (d, *J* 1.0 Hz, 1H), 8.47 (d, *J* 4.8 Hz, 1H), 7.99 (dt, *J* 7.8; 1.7 Hz, 1H), 7.11 (dd, *J* 7.73; 4.8 Hz, 1H), 2.88 (t, *J* 7.4 Hz, 2H), 1.74 (qn, *J* 7.4, 2H), 1.36 (sex, *J* 7.4 Hz, 2H), 0.86 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 157.9, 148.6, 145.9, 124.5, 109.4, 34.0, 25.1, 13.54, 9.1. MS: m/z (%) 265 (43); 263 (43); 205 (39); 78 (100); 57 (67). Anal. Calcd. For $C_9H_{13}NTe$: C, 41.13; H, 4.99; N, 5.33. Found: C, 40.73; H, 4.91; N, 5.71.

Butyl(4-chlorophenyl)tellane (**1l**). This product was obtained as a yellow oil in 80% yield from 4-bromochlorobenzene, elemental tellurium and *n*-bromobutane by method **A**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9.5:0.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ

ppm 7.60 (d, *J* 8.4 Hz, 2H), 7.14 (d, *J* 8.4 Hz, 2H), 2.87 (t, *J* 7.5 Hz, 2H), 1.75 (qn, *J* 7.3 Hz, 2H), 1.37 (sex, *J* 7.2 Hz, 2H), 0.89 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 139.6, 133.9, 129.2, 109.3, 33.8, 25.0, 13.4, 8.9. MS: m/z (%) 298 (46); 296 (41); 294 (24); 239 (34); 203 (3); 111 (53); 76 (41); 57 (100). Anal. Calcd. For $C_{10}H_{13}ClTe$: C, 40.54; H, 4.42. Found: C, 40.91; H, 4.31.

Butyl(4-bromophenyl)tellane (**1m**). This product was obtained as a yellow oil in 51% yield from 4-bromoaniline and *n*-butyl ditelluride by method **C**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9.5:0.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.48 (d, *J* 8.2 Hz, 2H), 7.23 (d, *J* 8.2 Hz, 2H), 2.81 (t, *J* 7.4 Hz, 2H), 1.69 (qn, *J* 7.2 Hz, 2H), 1.31 (sex, *J* 7.3 Hz, 2H), 0.82 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 140.2, 132.4, 122.4, 110.2, 34.0, 25.2, 13.6, 9.1. MS: m/z (%) 341 (20); 284 (12); 204 (10); 156 (15); 76 (44); 57 (100).

Butyl(4-iodophenyl)tellane (**1n**). This product was obtained as a yellow oil in 48% yield from 4-iodoaniline and *n*-butyl ditelluride by method **C**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9.5:0.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.47 (d, *J* 8.2 Hz, 2H), 7.39 (d, *J* 8.1 Hz, 2H), 2.85 (t, *J* 7.5 Hz, 2H), 1.75 (qn, *J* 7.2 Hz, 2H), 1.37 (sex, *J* 7.4 Hz, 2H), 0.88 (t, *J* 7.3 Hz, 3H).. ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 139.8, 138.0, 111.1, 93.8, 33.5, 24.9, 13.4, 8.8. MS: m/z (%) 390 (8); 388 (8); 330 (3); 204 (6); 76 (42); 57 (100). Anal. Calcd. For $C_{10}H_{13}ITe$: C, 30.98; H, 3.38. Found: C, 31.28; H, 3.51.

Butyl(Phenyl)tellane (**1o**).[2] This product was obtained as a yellow oil in 85% yield from bromobenzene, elemental tellurium and *n*-bromobutane by method **A**, after purification by chromatography on silica gel (eluting with hexane:ethyl acetate 9.5:0.5).^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* 8.0 Hz, 2H), 7.18-7.04 (m, 3H), 2.79 (t, *J* 7.4 Hz, 2H), 1.67 (qn, *J* 7.2 Hz, 2H), 1.29 (sex, *J* 7.5 Hz, 2H), 0.79 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 138.3, 129.2, 127.5, 112.0, 34.0, 25.2, 13.5, 8.6. MS: m/z (%) 264 (34); 262 (34); 204 (24); 77 (100); 57 (53).

Representative Procedure of Suzuki-Miyaura Cross-Coupling Reaction. To a suspension of butyl(4-methoxyphenyl)tellane (**1a**) (0.146 g, 0.5 mmol), potassium phenyltrifluoroborate (**2a**) (0.110 g, 0.6 mmol), $Pd(Ph_3P)_4$ (0.058 g, 0.05mmol) and silver (I) oxide (0.232 g, 1 mmol) in 3 mL of methanol was added triethylamine (0.2 g, 2 mmol), and the reaction mixture was stirred and heated at reflux for 90 minutes, then cooled to room temperature and diluted with ethyl acetate (30 mL). The organic layer was washed with saturated solution of NH_4Cl (2 x 10 mL) and water (2 x 10 mL), dried over $MgSO_4$ and concentrated under vacuum. Purification by silica gel chromatography (eluting with hexane:ethyl acetate 9.5:0.5) yielded **4-Methoxy-biphenyl** (**3a**)[1] (0.076g, 83%). This product was obtained as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.52 (t, *J* 8.6 Hz, 4H), 7.39 (t, *J* 7.8 Hz, 2H), 7.28 (t, *J* 7.2 Hz, 1H), 6.95 (d, *J* 8.7 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. MS: m/z (%) 185 (10); 184 (100); 169 (67); 152 (21); 76 (61).

4-Nitro-biphenyl (**3b**)**.**[2] This product was obtained as a white solid in 89% yield from **1b** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.26 (d, *J* 8.7 Hz, 2H), 7.70 (d, *J* 8.7 Hz, 2H), 7.60 (t, *J* 7.5 Hz, 2H), 7.51-7.40 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 147.6, 147.0, 138.7, 129.1, 128.9, 127.7, 127.4, 124.1. MS: m/z (%) 200 (14); 199 (86); 152 (100); 77 (25); 76 (48).

4-Methyl-biphenyl (**3c**)**.**[8] This product was obtained as a white solid in 80% yield from **1c** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.49 (m, 2H), 7.39 (m, 2H), 7.33 (m, 2H), 7.24 (m, 1H), 7.14 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 141.2. 138.4, 136.9, 129.4, 128.7, 127.0, 126.9, 21. MS: m/z (%) 169 (14); 168 (100); 153 (20); 91 (10); 77 (8); 76 (9).

2-Methyl-biphenyl (**3d**)**.**[9] This product was obtained as a colorless liquid in 74% yield from **1d** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.32-7.27 (m, 3H), 7.22-7.20 (m, 3H), 7.15-7.12 (m, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 142.3, 135.6, 130.6, 130.1, 129.5, 129.0, 128.4, 127.6, 127.5, 127.1, 126.1, 20.8. MS: m/z (%) 169 (6); 168 (32); 153 (100); 91 (6); 77 (38); 76 (72).

1-Phenylnaphtalene (**3e**)**.**[1] This product was obtained as a colorless liquid in 79% yield from **1e** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.89-7.82 (m, 3H), 7.47-7.40 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 140.7, 140.2, 133.7, 131.6, 130.0, 128.7, 128.2, 127.6, 127.2, 127.1, 126.9, 126.0, 125.7, 125.4. δ ppm MS: m/z (%) 205 (20); 204 (29); 203 (100); 76 (18).

4-Hidroxy-biphenyl (**3f**)**.**[1] This product was obtained as a white solid in 92% yield from **1f** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.50 (d, *J* 8.9 Hz, 2H), 7.42 (d, *J* 7.2 Hz, 2H), 7.35-7.20 (m, 5H), 1.15 (broad, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 141.9, 139.5, 129.2, 128.3, 127.4, 121.8, 121.1, 116.9. MS: m/z (%) 170 (23); 169 (100); 76 (6).

1-(biphenyl-4-yl)ethanone (**3g**)**.**[9] This product was obtained as a white solid in 80% yield from **1g** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* 8.4 Hz, 2H), 7.58-7.50 (m, 4H), 7.38-7.26 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 197.8, 145.9, 139.9, 135.9, 129.1, 129.0, 128.4, 127.4, 127.3, 26.8. MS: m/z (%) 197 (8); 196 (47); 181 (100); 153 (36); 76 (46); 43 (41).

Methyl biphenyl-4-carboxylate (**3h**)**.**[10] This product was obtained as a white solid in 83% yield from **1h** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.14 (d, *J* 8.3 Hz, 2H), 7.66 (t, *J* 8.4 Hz, 4H), 7.51-7.41 (m, 3H), 3.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 167.2, 145.8, 140.2, 130.3, 129.1, 128.3, 127.5, 127.2, 52.3. MS: m/z (%) 213 (9); 212 (55); 181 (100); 153 (32); 76 (84); 59 (2).

2-Phenylthiophene (**3i**)**.**[11] This product was obtained as a colorless liquid in 46% yield from **1i** and **2a** by the general method. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* 6.9 Hz, 1H); 7.37-7.16 (m, 5H), 7.02-6.99 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm 137.4, 134.4, 128.8, 127.7, 125.9, 124.8, 124.3, 123.1. MS: m/z (%) 161 (19); 160 (100); 82 (4); 77 (13).

2-Phenylfuran (**3j**)**.**[11] This product was obtained as a colorless liquid in 63% yield from **1j** and **2a** by the general method. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.68 (t, *J* 8.3, 2H), 7.44 (d, *J* 8.9, 1H), 7.39-

7.24 (m, 3H), 6.64 (d, *J* 3.4, 1H), 6.45 (dd, *J* 3.34; 1.8, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.7, 131.5, 129.9, 128.6, 127.3, 126.8, 123.8, 122.5 MS: m/z (%) 145 (39); 144 (88); 115 (100); 77 (23); 65 (37).

3-Phenylpyridine (**3k**).[10] This product was obtained as a yellow liquid in 65% yield from **1k** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.72 (d, *J* 2.3 Hz, 1H), 8.46 (dd, *J* 4.8; 1.1 Hz, 1H), 7.75 (dt, *J* 8.0; 1.6 Hz, 1H), 7.46 (d, *J* 7.0 Hz, 2H), 7.36 (t, *J* 7.0 Hz, 1H), 7.30-7.21 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 148.5, 148.3, 137.9, 136.7, 134.4, 129.2, 128.2, 127.2, 123.6. MS: m/z (%) 156 (20); 155 (100); 78 (10); 77 (47).

4-Chloro-biphenyl (**3l**).[1] This product was obtained as a white solid in 83% yield from **1l** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.80-7.12 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 139.9, 139.6, 133.3, 128.9, 128.8, 128.4, 127.6, 126.9. MS: m/z (%) 190 (41); 188 (100);153 (27); 152 (68); 76 (58).

4-Bromo-biphenyl (**3m**).[12] This product was obtained as a white solid in 84% yield from **1m** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.49-7.44 (m, 4H), 7.38-7.25 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 140.3, 140.1, 132.0, 129.1, 128.9, 127.8, 127.1, 121.7. MS: m/z (%) 234 (77); 233 (10); 232 (78); 153 (20); 77 (24); 76 (100).

4-Iodo-biphenyl (**3n**).[1b] This product was obtained as a white solid in 42% yield from **1n** and **2a** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.68 (d, *J* 9.0 Hz, 2H), 7.46 (d, *J* 6.0 Hz, 2H), 7.35 (d, *J* 6.0 Hz, 2H), 7.29-7.22 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 140.9, 140.2, 138.0, 129.2, 129.1, 127.9, 127.1, 93.2. MS: m/z (%) 281 (16); 280 (100); 153 (31); 127 (16); 77 (21); 76 (71).

1-(4-Methoxyphenyl)naphtalene (**3o**).[13] This product was obtained as a white solid in 87% yield from **1e** and **2b** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.93-7.78 (m, 3H), 7.49-7.36 (m, 6H), 6.99 (d, *J* 8.6 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.4, 140.4,

134.3, 133.6, 132.3, 131.6, 128.8, 127.8, 127.4, 126.7, 126.6, 126.2, 125.9, 114.2, 55.8. MS: m/z (%) 235 (19); 234 (100); 219 (29); 203 (11).

4-Chloro-4'-methoxybiphenyl (**3p**)**.**[14] This product was obtained as a white solid in 75% yield from **1l** and **2b** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.50-7.43 (m, 4H), 7.35 (d, *J* 8.6 Hz, 2H), 6.95 (d, *J* 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.3, 139.2, 132.6, 132.4, 128.8, 128.0, 127.9, 114.3, 55.3. MS: m/z (%) 220 (33); 218 (100); 203 (48); 152 (10), 76 (16).

1-(4-Chlorophenyl)naphtalene (**3q**)**.**[13] This product was obtained as a white solid in 87% yield from **1e** and **2c** by the general method.^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.76-7.69 (m, 3H), 7.38-7.21 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 139.4, 139.1, 133.5, 131.6, 131.5, 128.7, 128.6, 128.2, 127.1, 126.4, 126.1, 125.8, 125.5. MS: m/z (%) 240 (25); 238 (49); 203 (33); 126 (3), 101 (100), 76 (5).

4-Chloro-4'-chlorobiphenyl (**3r**)**.**[15] This product was obtained as a white solid in 94% yield from **1l** and **2c** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.38-7.35 (m, 4H), 7.33-7.29 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 138.6, 133.9, 129.2, 128.4. MS: m/z (%) 220 (33); 218 (100); 203 (48); 152 (10), 76 (16).

2-(4-Chlorophenyl)furan (**3s**)**.**[16] This product was obtained as a red solid in 52% yield from **1l** and **2d** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.50 (d, *J* 6.8 Hz, 2H), 7.37 (d, *J* 1.6 Hz, 1H), 7.24 (d, *J* 6.8 Hz, 2H), 7.50 (d, *J* 6.8 Hz, 2H), 6.54 (d, *J* 3.3 Hz, 2H), 6.38 (dd, *J* 3.3; 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 142.5, 133.1, 129.6, 129.2, 129.0, 125.2, 111.9, 105.6. MS: m/z (%) 180 (40); 178 (93); 143 (2); 115 (100); 76 (4).

1-(3-Methoxyphenyl)naphthalene (**3t**)**.**[17] This product was obtained as a colorless liquid in 79% yield from **1e** and **2e** by the general method.^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.93-7.83 (m, 3H), 7.53-7.31 (m, 6H); 7.11-6.95 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.7, 142.4, 140.3, 134.0, 131.8, 129.9, 129.4, 128.5, 127.9, 127.0, 126.3, 126.0, 125.5, 122.8, 119.9, 115.8, 113.1, 55.5. MS: m/z (%) 235 (31); 234 (100); 219 (23); 203 (69); 76 (7).

4'-Chloro-3-methoxybiphenyl (**3u**)**.**[18] This product was obtained as a colorless liquid in 80% yield from **1l** and **2e** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.48 (d, *J* 6.7, 2H), 7.38-7.29 (m, 3H); 7.20-7.05 (m, 2H), 6.87 (d, *J* 8.2, 1H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 160.3, 141.7, 139.7, 133.7, 130.1, 129.1, 128.6, 119.9, 119.7, 113.1, 55.5. MS: m/z (%) 220 (65); 218 (100); 203 (2); 188 (45); 152 (50); 111 (4); 76 (63).

3-Methoxy-biphenyl (**3v**)**.**[19] This product was obtained as a colorless liquid in 78% yield from **1o** and **2e** by the general method. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.47 (d, *J* 7.1, 2H), 7.31 (t, *J* 7.0 Hz, 2H); 7.25-7.20 (m, 2H), 7.08-7.02 (m, 2H), 6.78 (dd, *J* 8.2; 2.4 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 160.2, 142.8, 141.3, 129.9, 128.9, 127.6, 127.4, 119.8, 113.0, 112.9, 55.4. MS: m/z (%) 185 (27); 184 (100); 169 (8); 153 (49); 77 (24); 76 (45).

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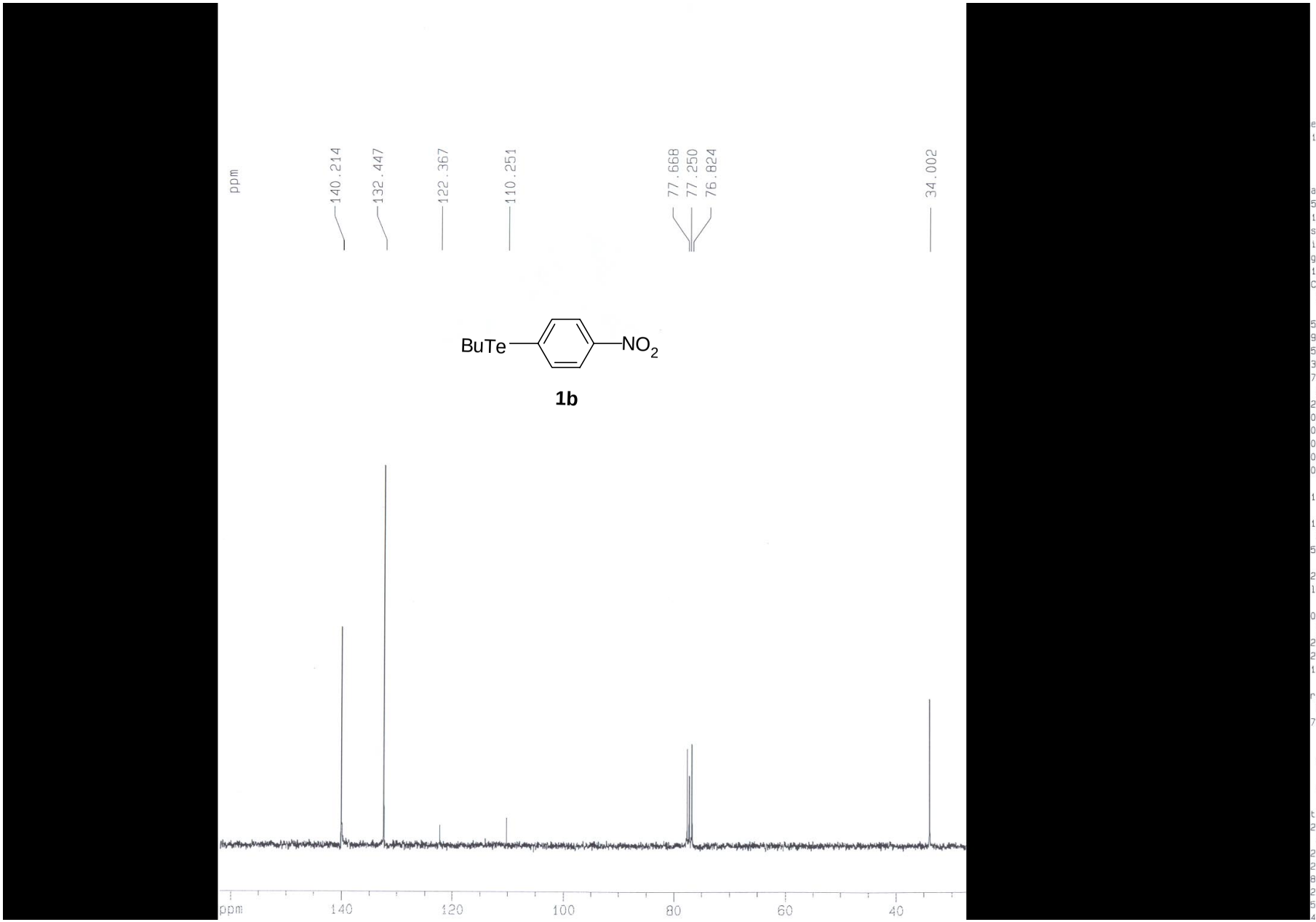
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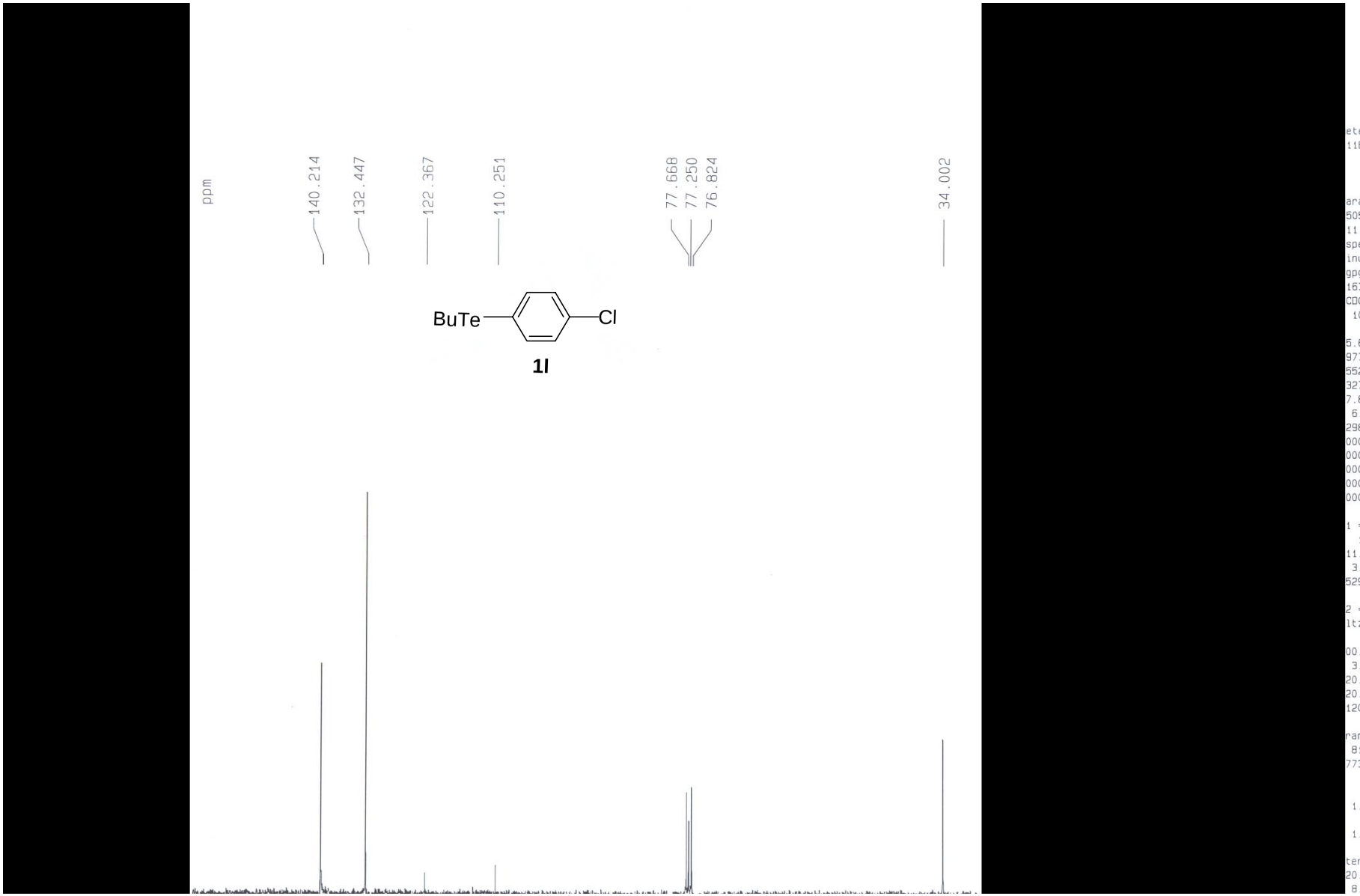
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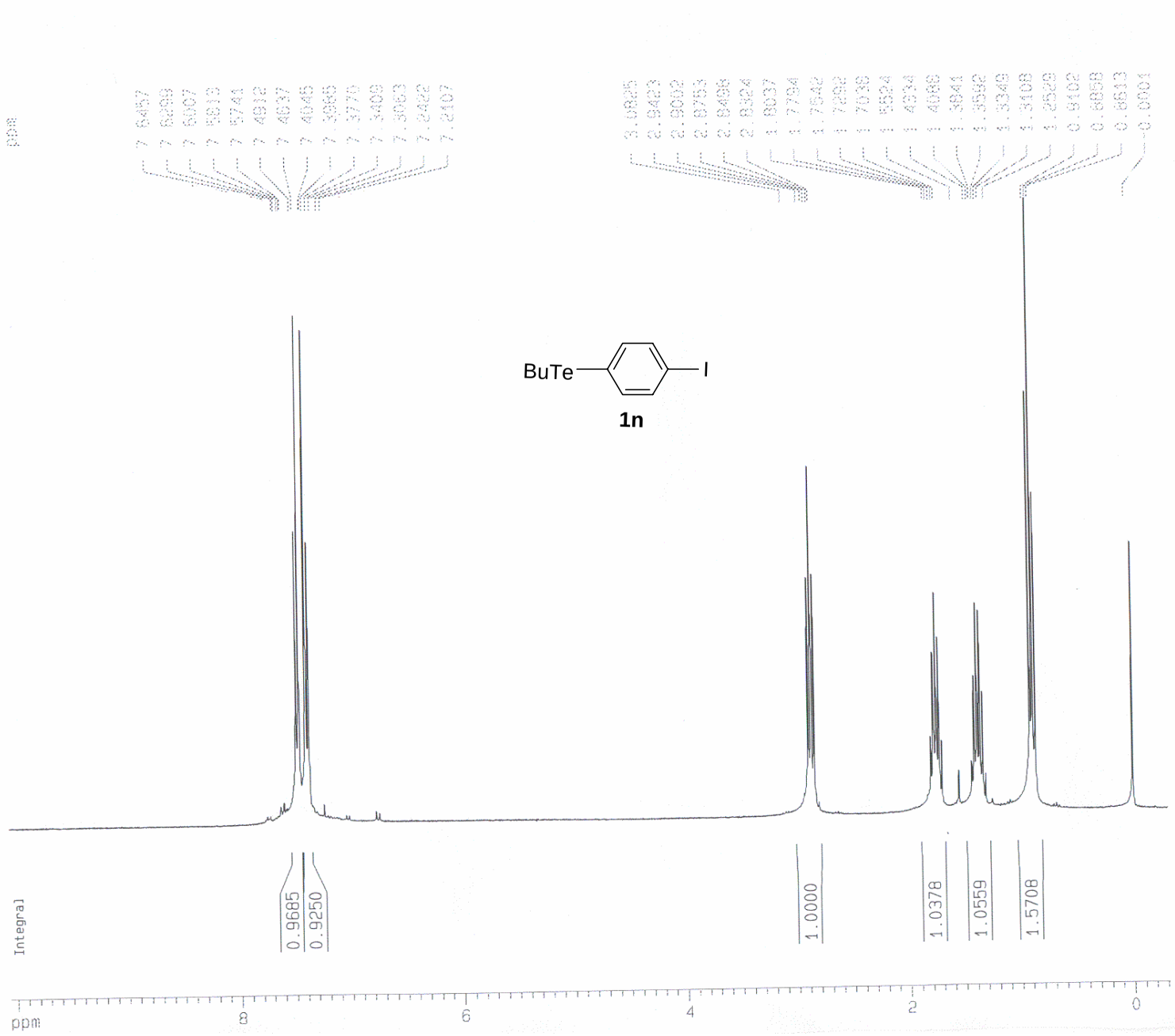

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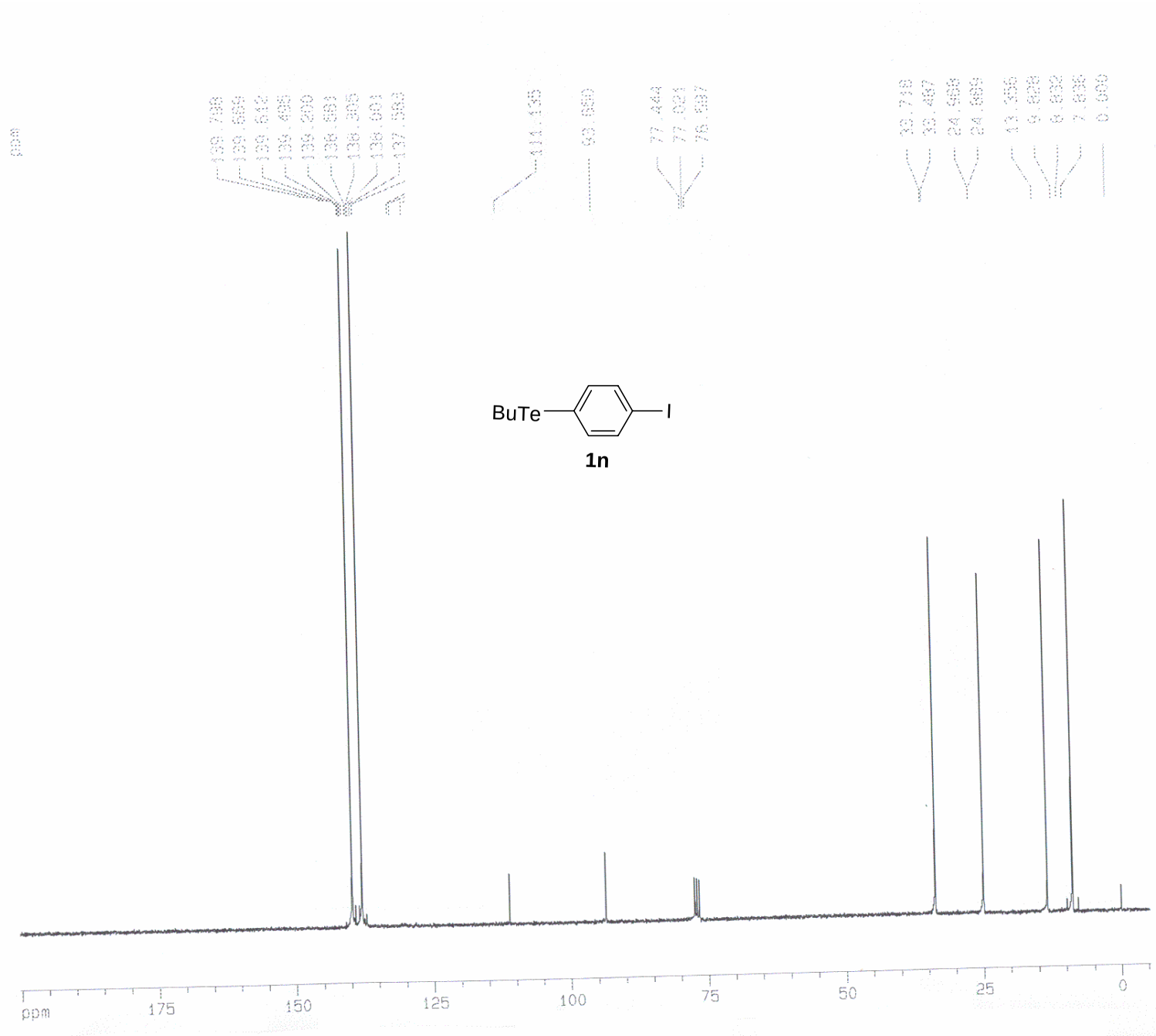


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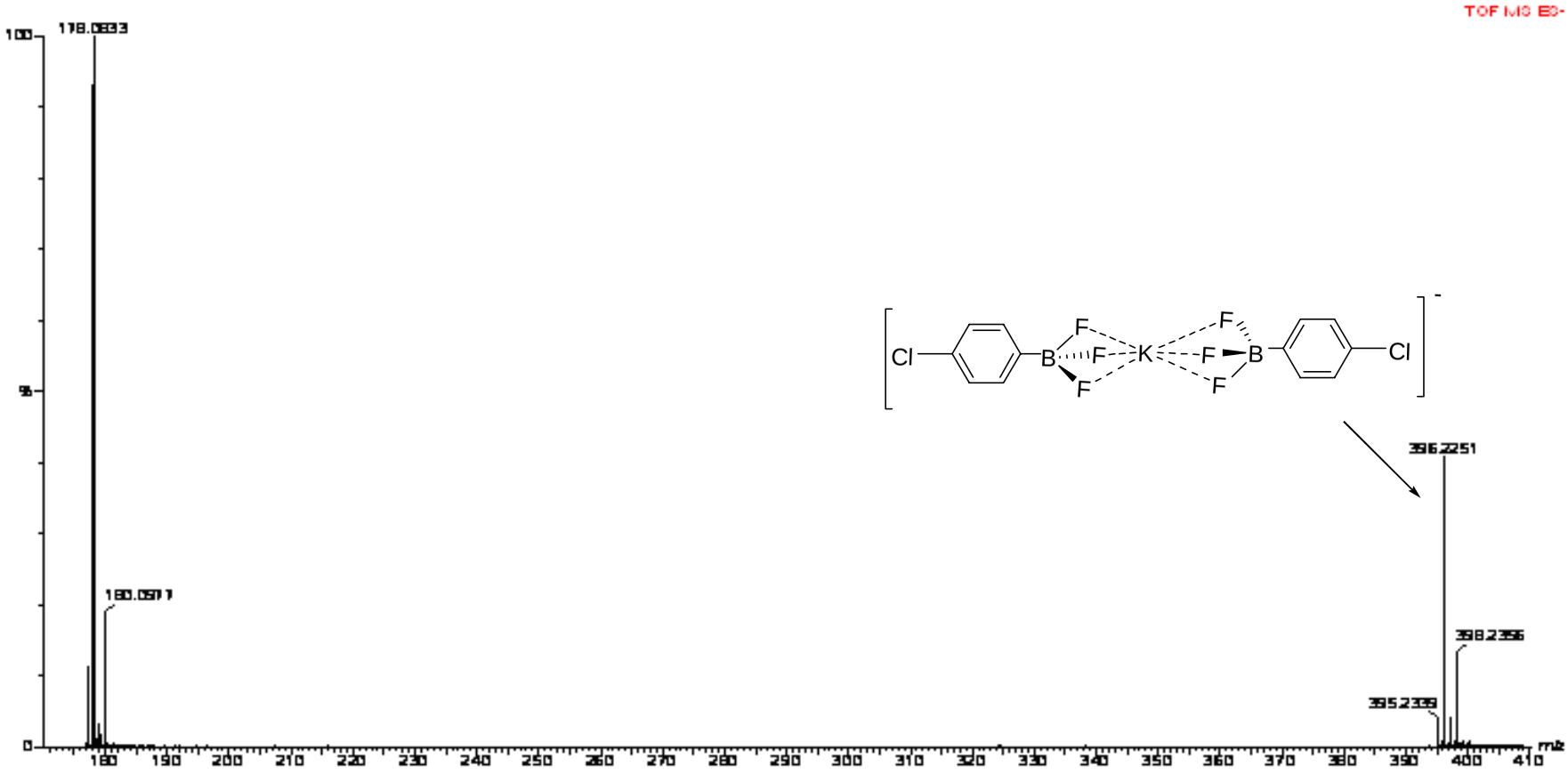
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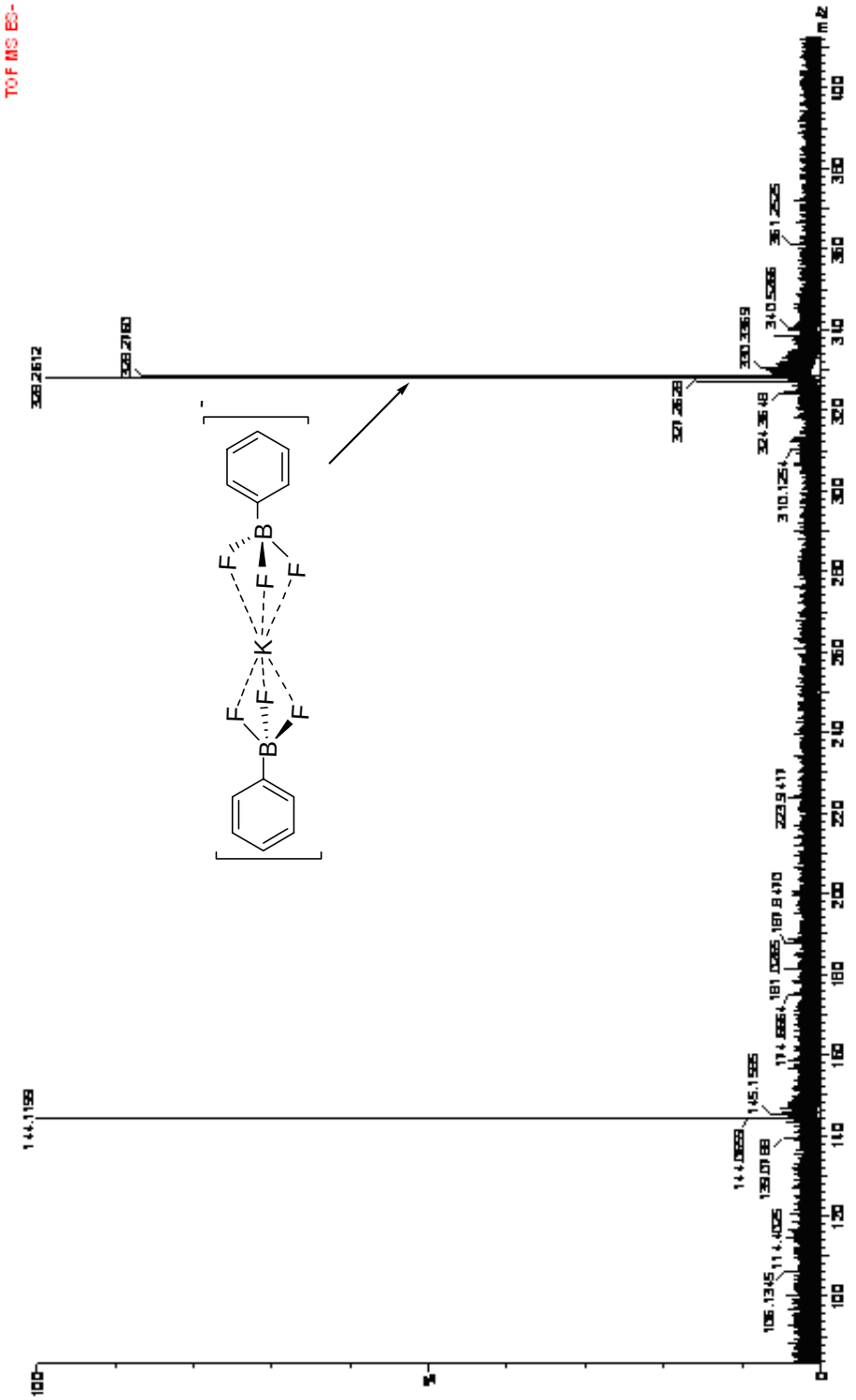
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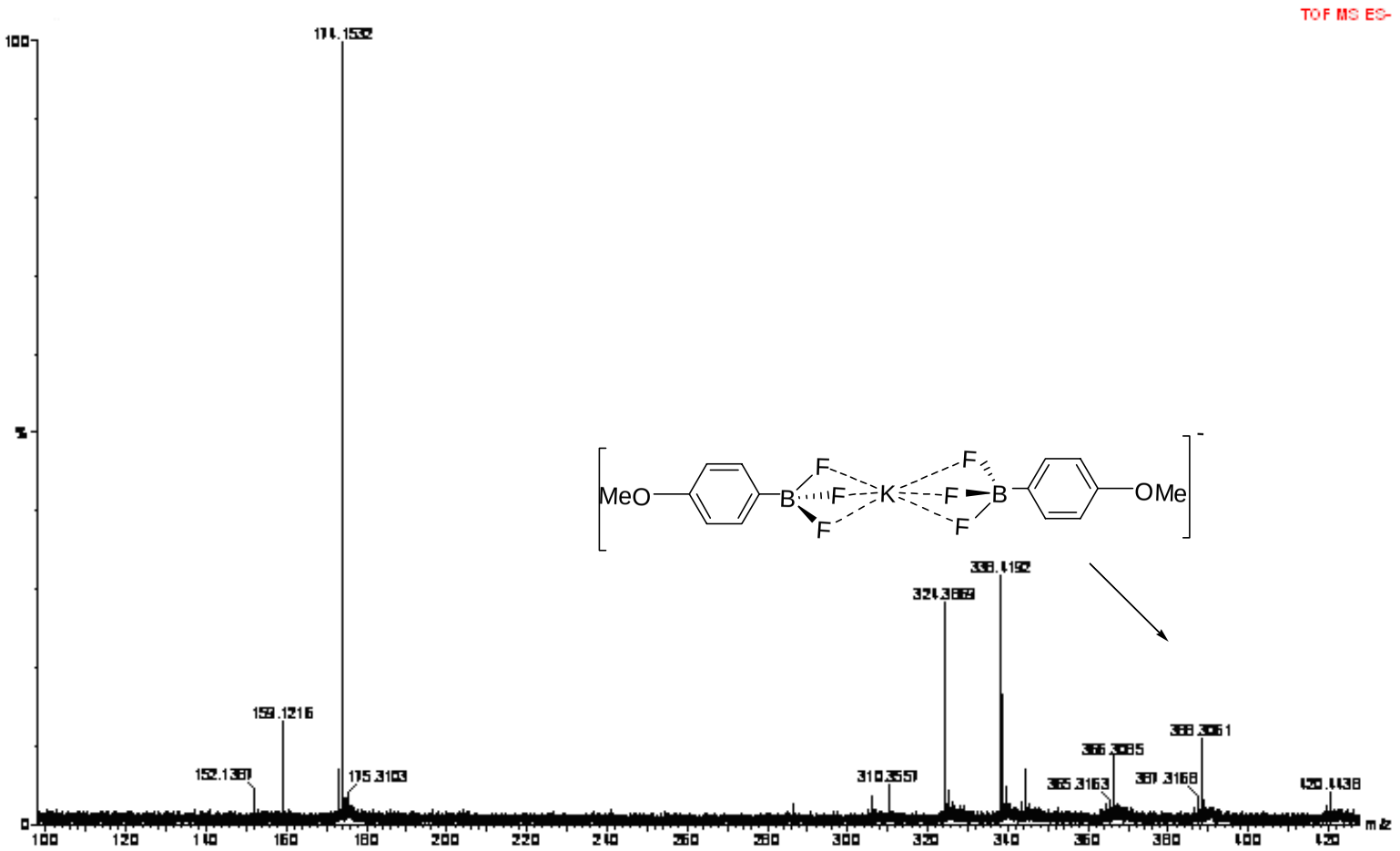
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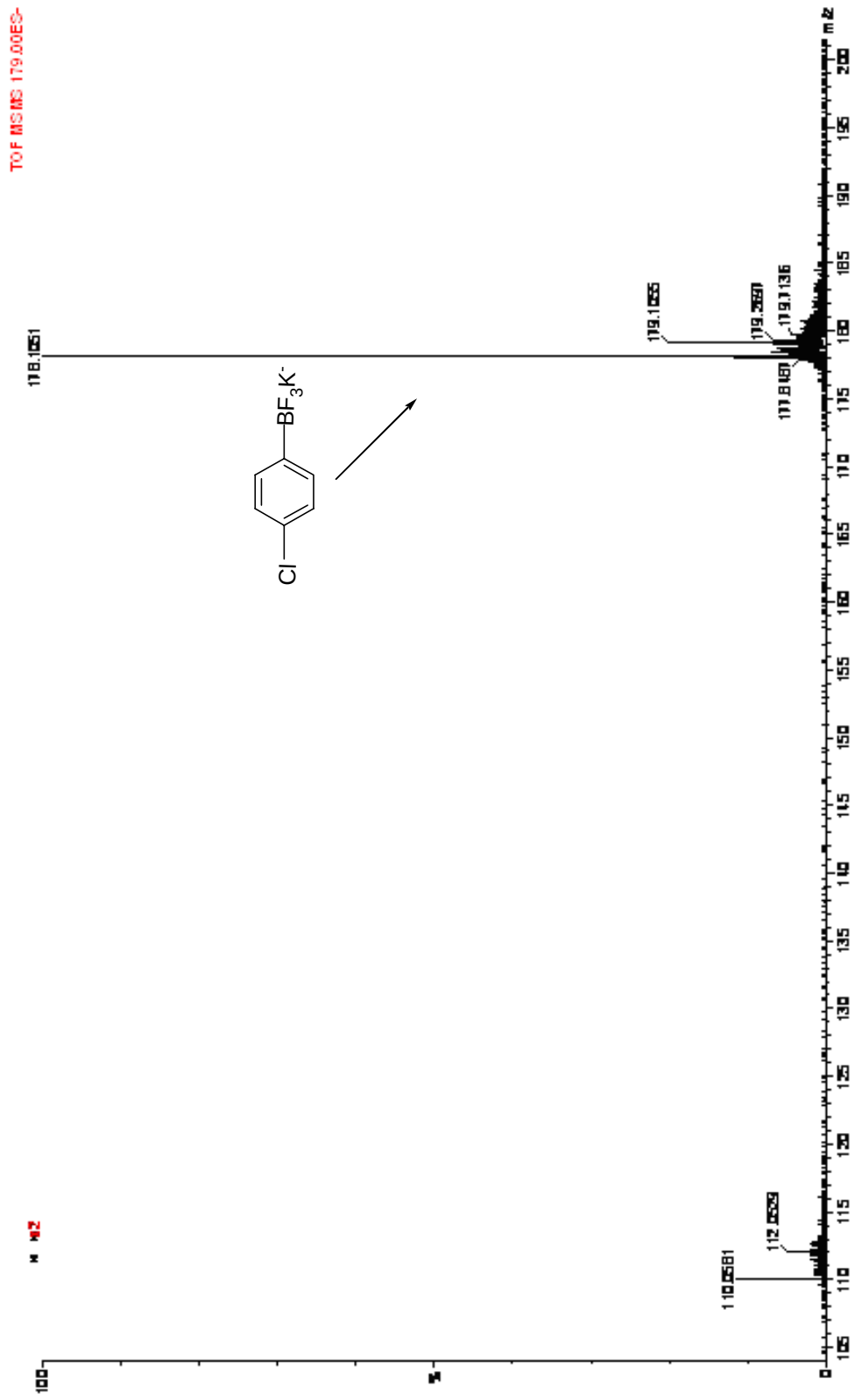
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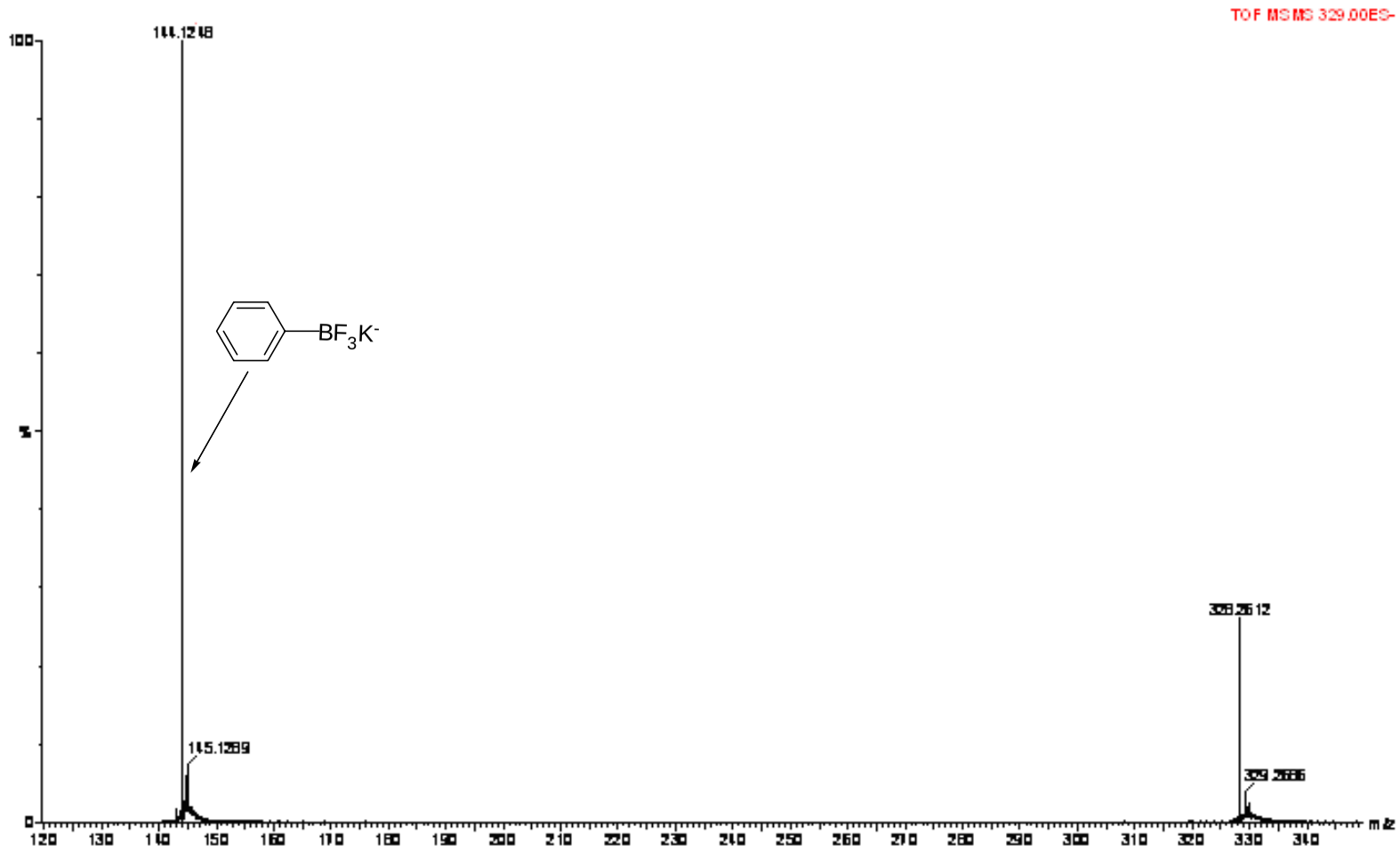
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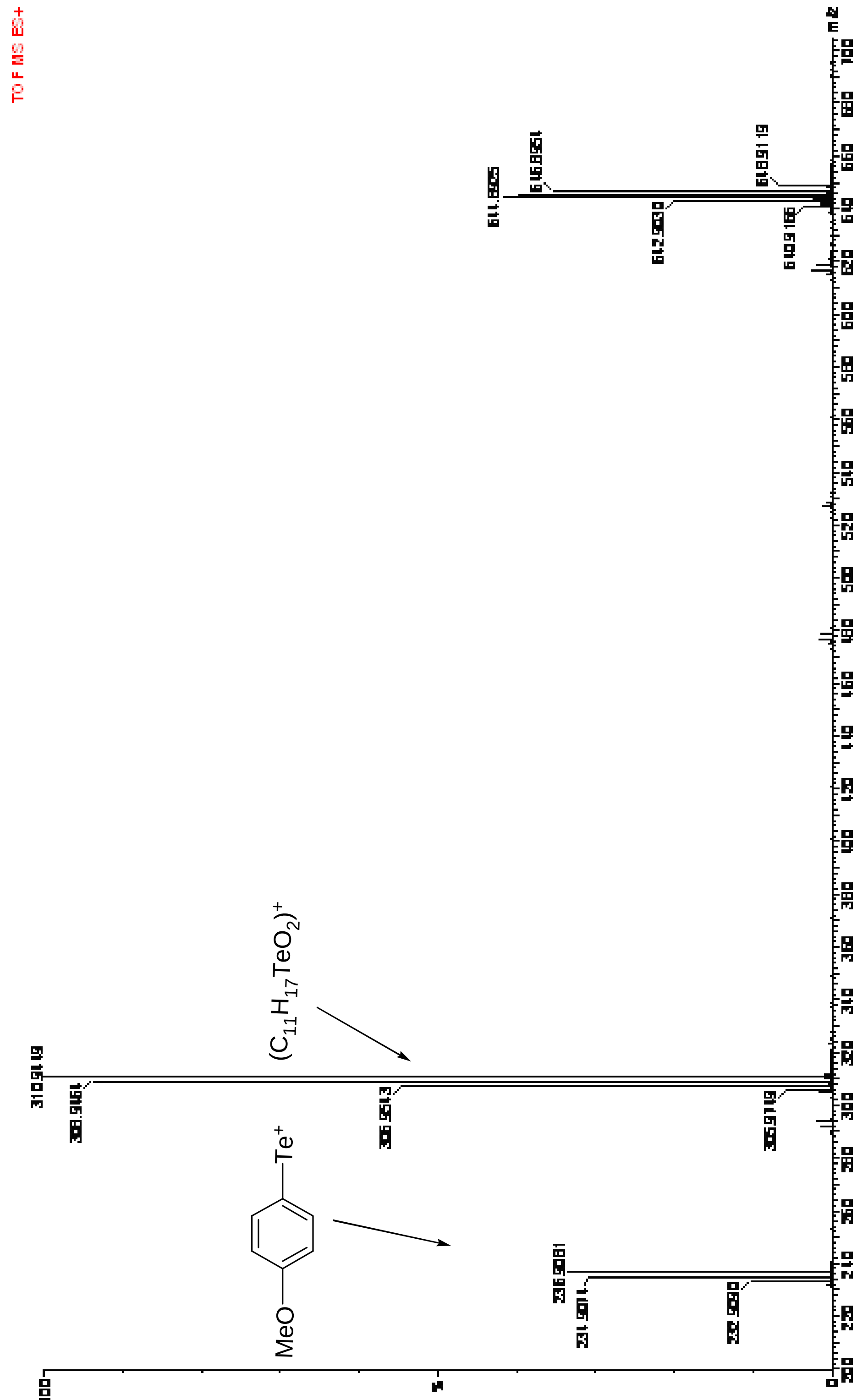
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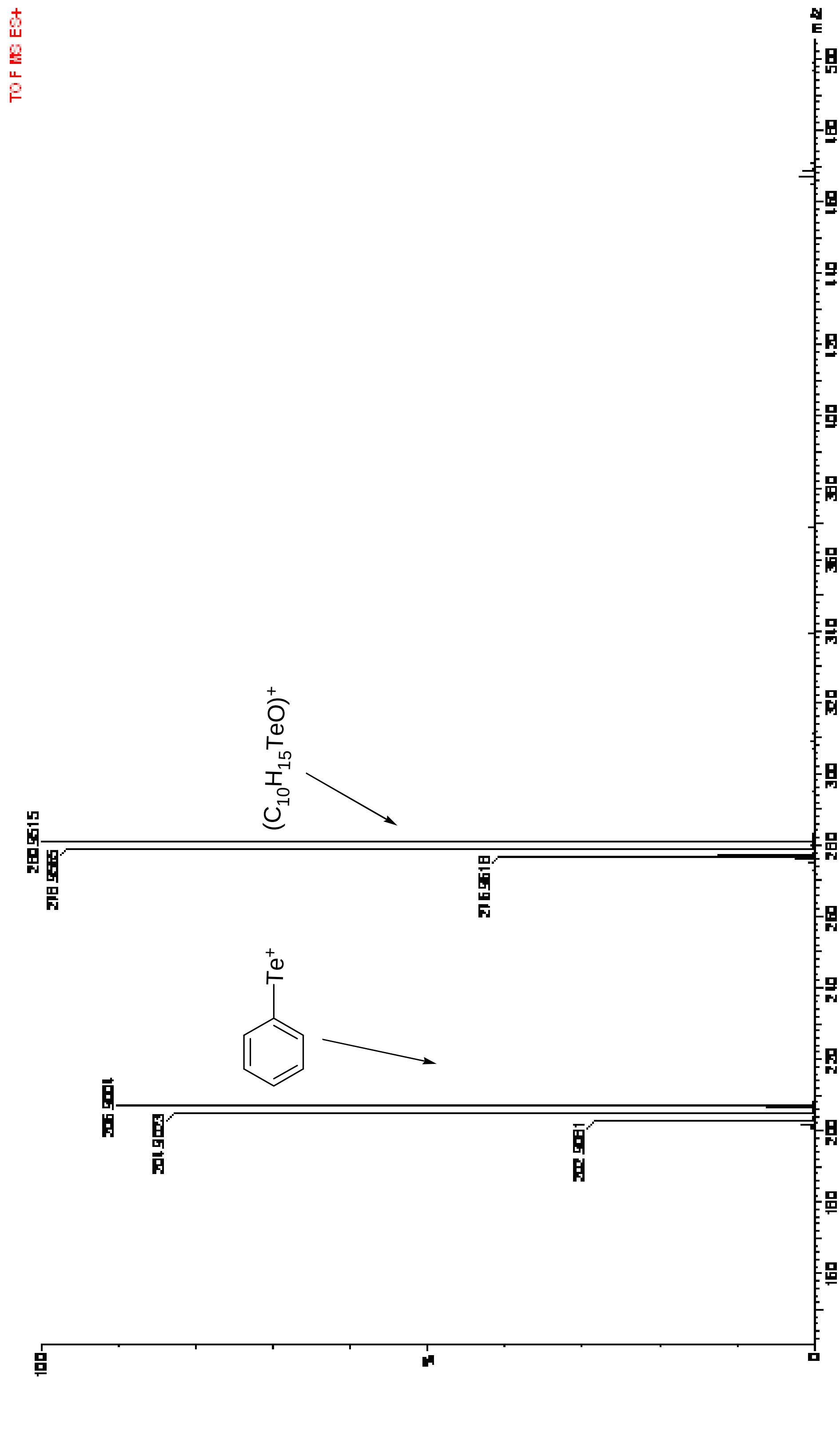
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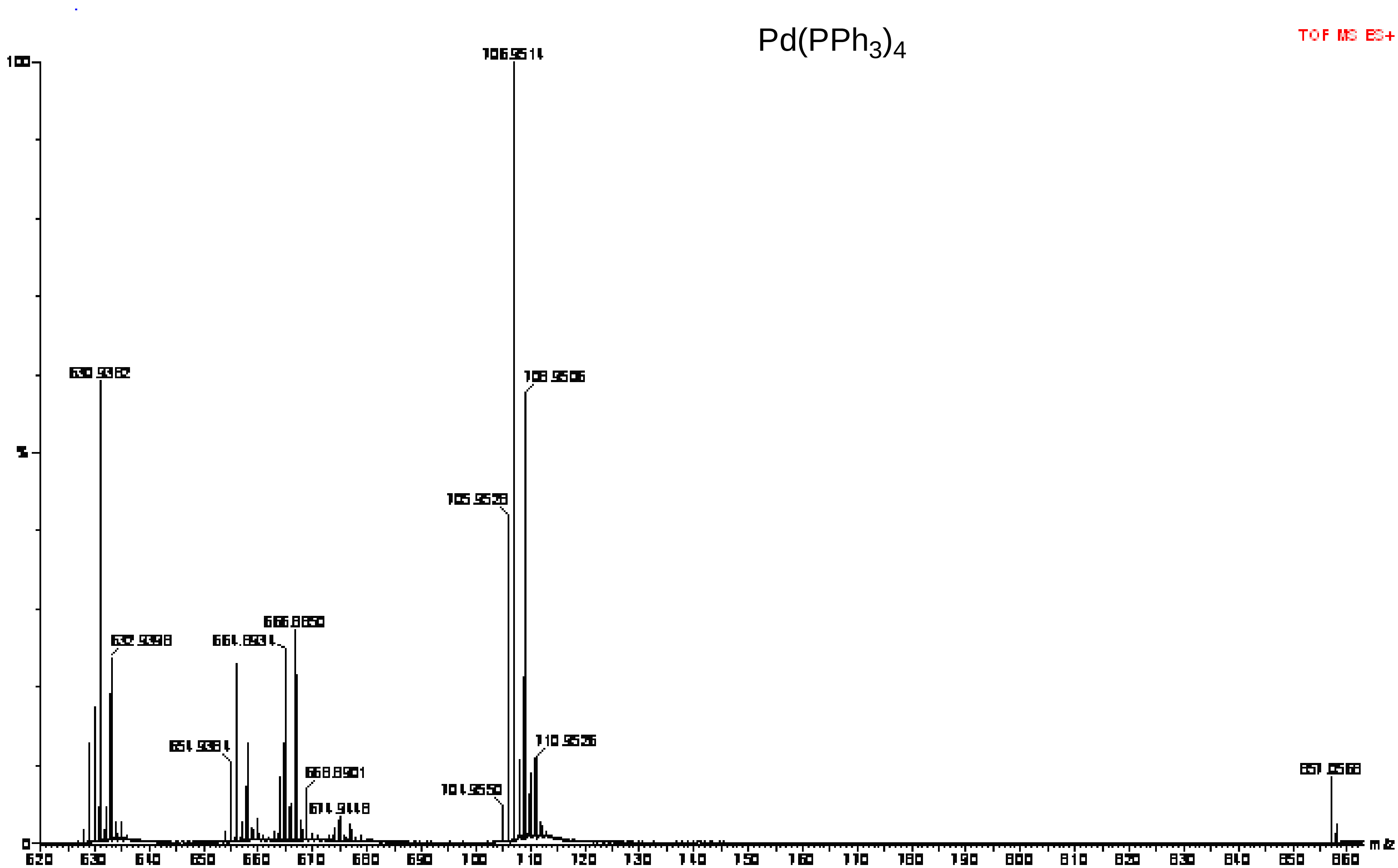
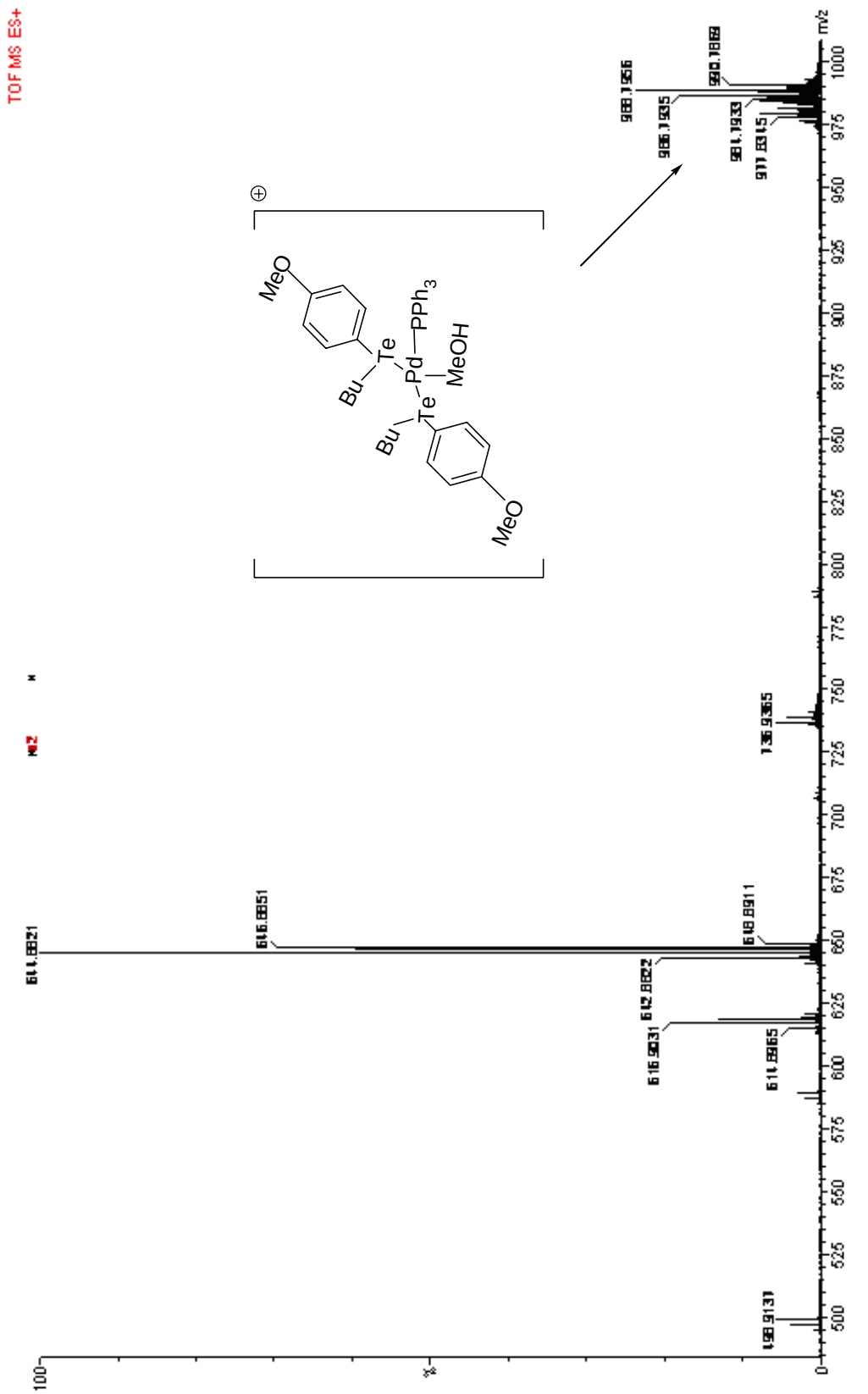
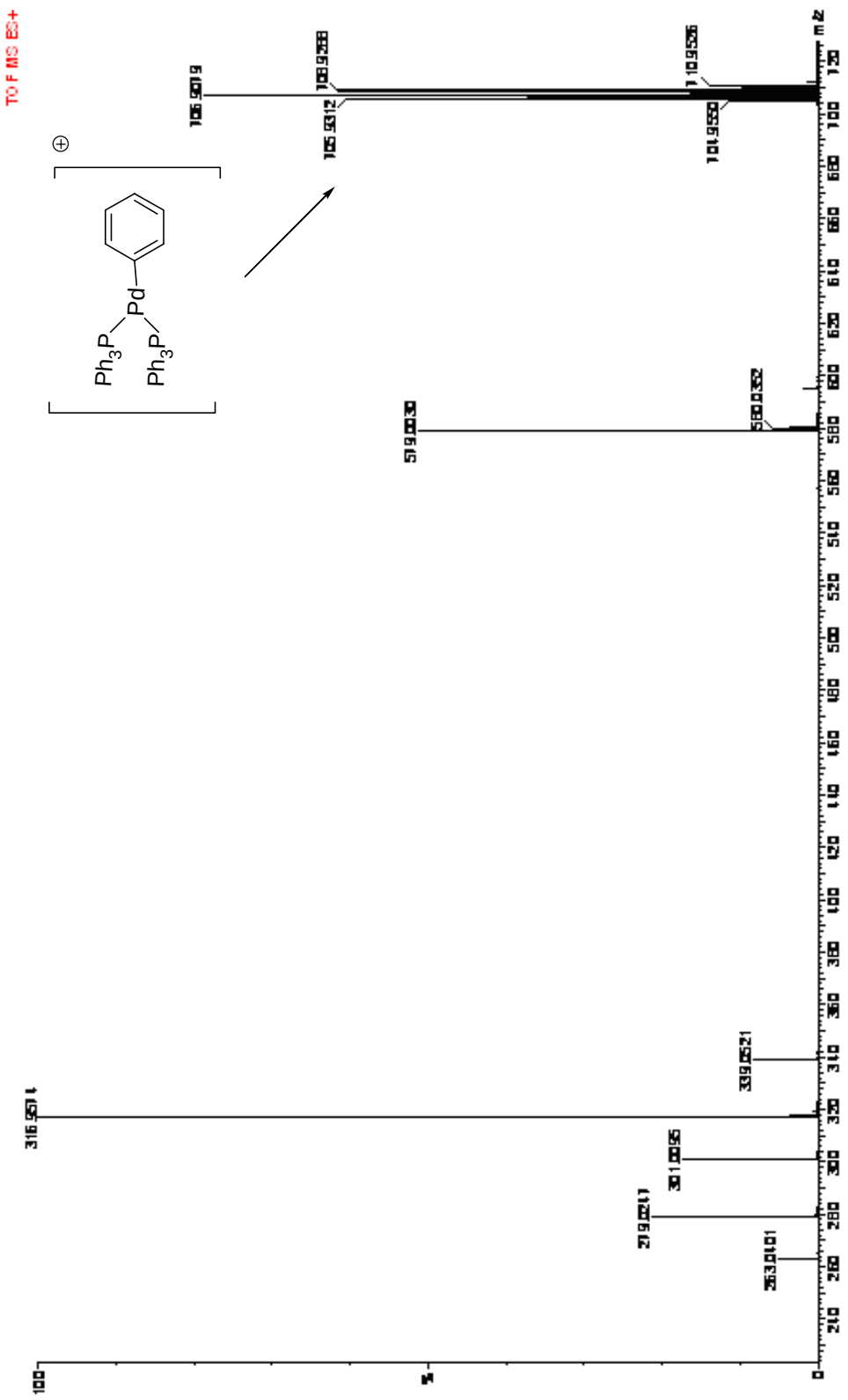
m/z

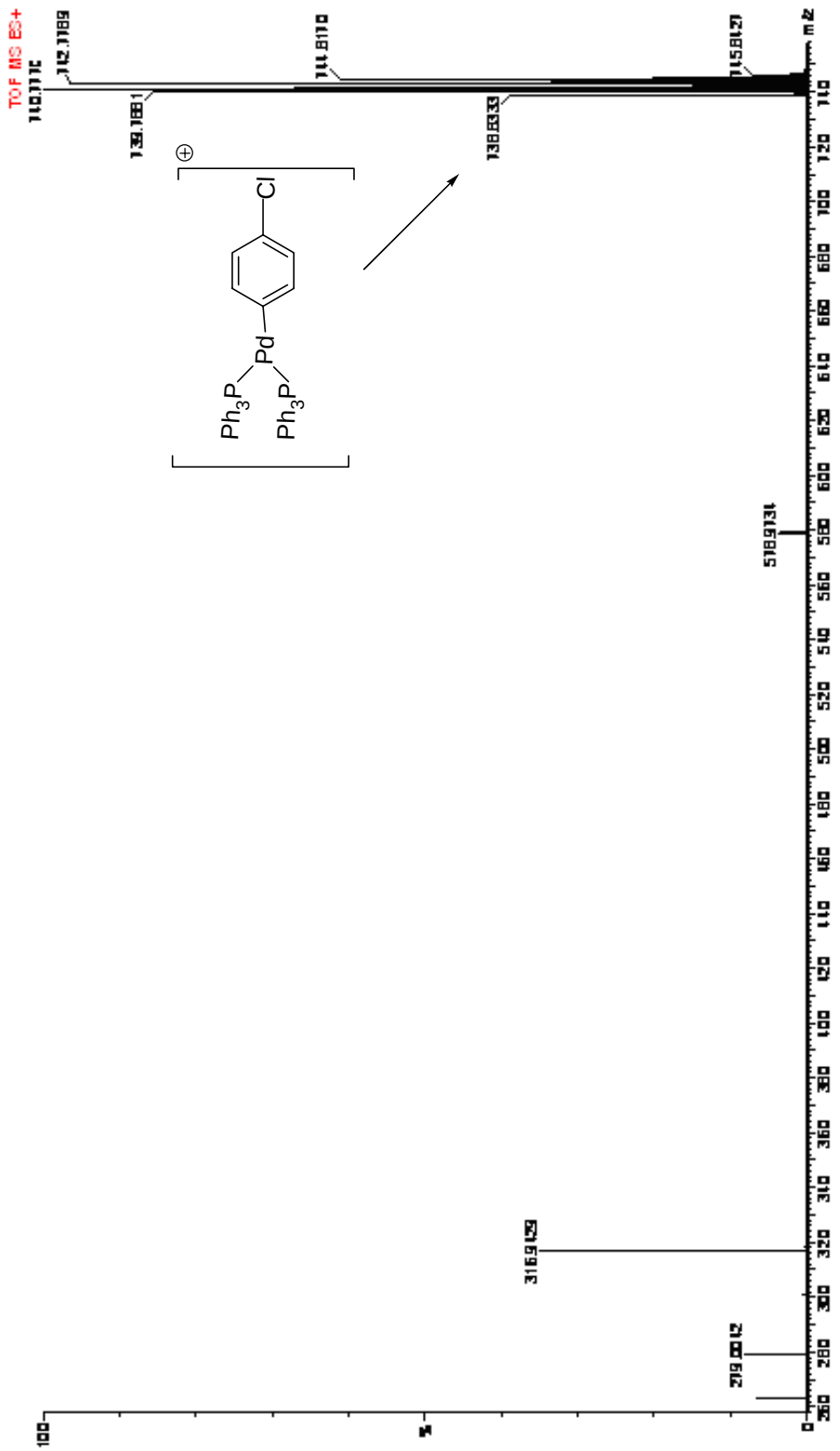
Pd(PPh$_3$)$_4$

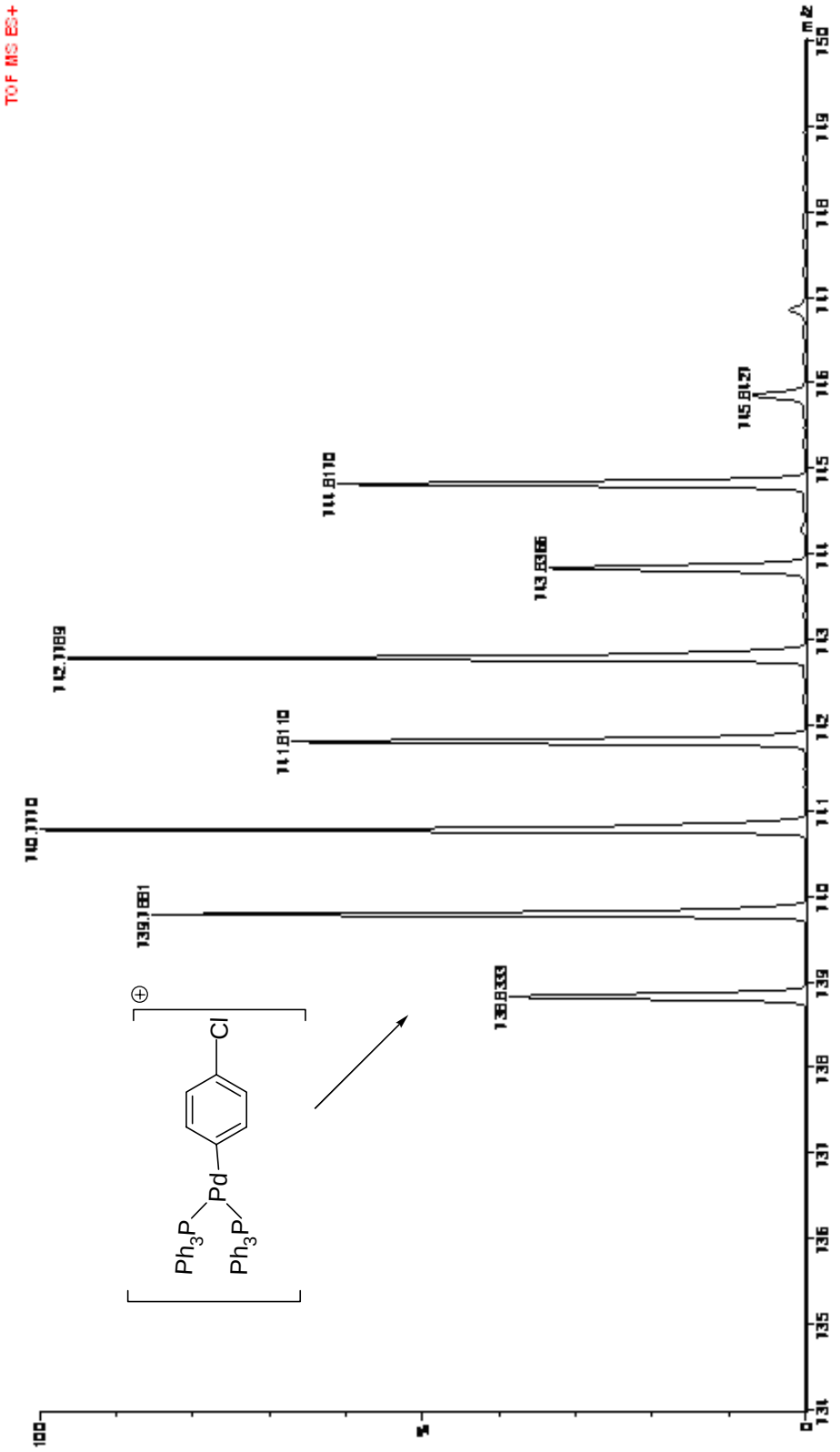


TOF MS ES+
100
%
0
630.9362
632.9398
654.9384
664.8934
666.8850
668.8901
674.9448
704.9550
705.9528
706.9514
708.9506
710.9526
857.0568
620
630
640
650
660
670
680
690
700
710
720
730
740
750
760
770
780
790
800
810
820
830
840
850
860
m/z


TOF MS ES+
100
%
0
614.8821
616.8851
618.8911
612.8822
616.9031
611.8865
588.9137
636.9365
988.1956
986.1935
981.1933
977.8315
990.1888
m/z
500
525
550
575
600
625
650
675
700
725
750
775
800
825
850
875
900
925
950
975
1000
MeO
Bu
Te
Pd
PPh3
MeOH
Bu
Te
MeO


TOF MS ES+
Ph3P
Pd
Ph3P
m/z


TOF MS ES+
112.1189
111.8110
115.8429
139.1881
138.8333
518.9134
316.9129
279.0512
Cl
Pd
Ph3P
Ph3P
m/z
%


TOF MS ES+
100
%
0
m/z
131
135
136
138
139
140
141
142
143
145
146
150
139.1881
140.1910
141.8110
142.1889
143.8366
145.8429
Cl
Pd
Ph_3P
Ph_3P