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Manuscript Title:

Synthesis and Applications of 1-Iodo-4-MgCl-1,3-dienes and 1-Iodovinyl Phenylmagnesium Chlorides

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1) Experimental Details and Characterization Data

General Methods: All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glove box. ^{n}BuLi and ^{t}BuLi were obtained from Acros and J&K. 1,4-Diiodo-1,3-dienes **1** were prepared according to the references.[1] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or a Bruker-500 spectrometer (FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization).

General procedure for I/Mg exchange reaction of 1,4-diiodo-1,3-dienes 1a and *o*-iodo-2-(2-iodovinyl)benzenes 1b with Knochel reagent. 1,4-diiodo-1,3-dienes **1a** (0.8 mmol) in 4 mL of THF was treated with ^{i}PrMgCl•LiCl (1.6 mmol for **1b**) and the reaction mixture was stirred at room temperature for 6 h (3 h for **1b**). After quenched with aq. HCl or allyl bromide at 0 ºC and stirring at room temperature for 4 h, purification by column chromatography (petroleum ether) gave **2a1-5a2** as pure products. Quenched with isopropoxyboronic acid pinacol ester at room temperature overnight, purification by column chromatography (petroleum ether: ethyl acetate = 20 : 1) gave **6a-6b2** as pure products. Quenched with a CO_2 ballon at room temperature for 30 minutes, purification by column chromatography (petroleum ether: ethyl acetate = 10 : 1) gave **7a** and **7b** as pure products.

2a1[2]: colorless oil, isolated yield 75% (175 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.94 (t, 3H, *J* = 7.5 Hz, CH_3), 0.97-1.04 (m, 6H, CH_3), 1.09 (t, 3H, *J* = 7.3 Hz, CH_3), 2.03-2.25 (m, 6H, CH_2), 2.58 (q, 2H, *J* = 7.3 Hz, CH_2), 5.06 (t, 1H, *J* = 7.3 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.86, 13.44, 14.02, 14.82, 21.08, 22.39, 24.30, 35.01, 106.59, 131.49, 143.98, 149.41 ppm. HRMS: *m/z*: calcd for $C_{12}H_{22}I$ $[M+H]^+$: 293.0761, found 293.0759

2a2[2]: colorless oil, isolated yield 78% (217 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.85-0.97 (m, 12H, CH_3), 1.33-1.47 (m, 6H, CH_2), 1.56-1.61 (m, 2H, CH_2), 2.02-2.18 (m, 6H, CH_2), 2.53 (t, 2H, *J* = 7.3 Hz, CH_2), 5.10 (t, 1H, *J* = 7.2 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.10, 13.97, 14.23, 14.96, 21.63, 21.88, 22.76, 23.04, 30.00, 31.97, 33.43, 43.11, 105.18, 130.64, 143.97, 149.16 ppm. HRMS: *m/z*: calcd for $C_{16}H_{30}I$ $[M+H]^+$: 349.1387, found 349.1384

2b: colorless oil, isolated yield 77% (176 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.93 (t, 3H, *J* = 7.5 Hz, CH_3), 1.16 (t, 3H, *J* = 7.3 Hz, CH_3), 2.47 (q, 2H, *J* = 7.5 Hz, CH_2), 2.71 (q, 2H, *J* = 7.3 Hz, CH_2), 7.06-7.08 (m, 2H, CH), 7.28-7.35 (m, 2H, CH), 7.41-7.60 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.23, 14.88, 27.72, 35.12, 107.35, 126.99, 127.27, 128.18, 128.39, 128.86, 147.33, 148.08 ppm. HRMS: *m/z*: calcd for $C_{12}H_{16}I$ $[M+H]^+$: 287.0291, found 287.0288

4a1: colorless oil, isolated yield 72% (191 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.94-1.12 (m, 12H, CH_3), 2.00-2.09 (m, 3H, CH_2), 2.15-2.20 (m, 1H, CH_2), 2.28-2.34 (m, 1H, CH_2), 2.41-2.46 (m, 1H, CH_2), 2.58-2.64 (m, 2H, CH_2), 2.80-2.84 (m, 2H, CH_2), 4.98-5.05 (m, 2H, CH_2), 5.76-5.86 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.52, 13.22, 13.32, 14.71, 22.91, 24.21, 25.26, 35.00, 37.80, 108.71, 115.86, 134.03, 137.66, 139.92, 146.81 ppm. HRMS: *m/z*: calcd for $C_{15}H_{26}I$ $[M+H]^+$: 333.1074, found 333.1067 403.1847 403.1856

4a2: colorless oil, isolated yield 77% (239 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.88-0.96 (m, 12H, CH_3), 1.42-1.62 (m, 8H, CH_2), 1.94-2.37 (m, 6H, CH_2), 2.52-2.56 (m, 2H, CH_2), 2.78-2.83 (m, 2H, CH_2), 4.98-5.04 (m, 2H, CH_2), 5.75-5.85 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.24, 14.63, 14.70, 15.17, 21.23, 22.00, 22.04, 23.19, 32.24, 34.24, 35.13, 38.17, 43.02, 107.41, 115.81, 133.00, 137.71, 140.11, 147.14 ppm. HRMS: *m/z*: calcd for $C_{19}H_{34}I$ $[M+H]^+$: 389.1700, found 389.1698

4a3: colorless oil, isolated yield 85% (226 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.87-0.92 (m, 6H, CH_3), 1.33-1.44 (m, 8H, CH_2), 2.09 (br, 2H, CH_2), 2.19 (t, 2H, *J* = 7.2 Hz, CH_2), 2.71 (br, 2H, CH_2), 4.95-5.06 (m, 2H, CH_2), 5.30 (t, 1H, *J* = 7.2 Hz, CH), 5.79-5.89 (m, 1H, CH), 6.10 (br, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 14.01, 14.13, 22.57, 22.89, 29.87, 30.01, 33.95, 35.30, 37.81, 75.97, 114.96, 124.26, 137.40, 141.45, 152.90 ppm. HRMS: *m/z*: calcd for $C_{15}H_{26}I$ $[M+H]^+$: 333.1074, found 333.1069

4b: colorless oil, isolated yield 93% (243 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.97 (t, 3H, *J* = 7.6 Hz, CH_3), 1.18 (t, 3H, *J* = 7.6 Hz, CH_3), 2.18-2.27 (m, 1H, CH_2), 2.58-2.78 (m, 3H, CH_2), 3.23-3.36 (m, 2H, CH_2), 5.07-5.13 (m, 2H, CH_2), 5.93-6.03 (m, 1H, CH), 6.91-6.93 (m, 1H, CH), 7.18-7.25 (m, 3H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.11, 14.85, 27.41, 34.74, 36.96, 109.32, 116.24, 126.07, 127.33, 128.91, 129.28, 136.48, 137.41, 146.42, 147.08 ppm. HRMS: *m/z*: calcd for $C_{15}H_{20}I$ $[M+H]^+$: 327.0604, found 327.0598

5a1: colorless oil, isolated yield 74% (205 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.98-1.12 (m, 12H, CH_3), 1.66 (s, 3H, CH_3), 1.91-1.96 (m, 1H, CH_2), 2.12-2.23 (m, 3H, CH_2), 2.28-2.34 (m, 2H, CH_2), 2.59 (q, 2H, *J* = 7.2 Hz, CH_2), 2.71-2.84 (m, 2H, CH_2), 4.67 (s, 1H, CH_2), 4.77 (s, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.62, 13.31, 13.60, 14.78, 23.09,

23.43, 24.55, 25.91, 34.95, 40.81, 109.00, 111.75, 133.48, 141.77, 144.84, 146.78 ppm. HRMS: *m/z*: calcd for $C_{16}H_{28}I$ $[M+H]^+$: 347.1230, found 347.1225

5a2: colorless oil, isolated yield 92% (255 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.86-0.93 (m, 6H, CH_3), 1.30-1.43 (m, 8H, CH_2), 1.74 (s, 3H, CH_3), 2.11-2.20 (m, 4H, CH_2), 2.66 (br, 2H, CH_2), 4.71-4.72 (m, 2H, CH_2), 5.36 (t, 1H, *J* = 7.2 Hz, CH), 6.08 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.99, 14.14, 22.59, 22.89, 23.27, 29.92, 29.94, 35.34, 37.55, 37.84, 75.83, 110.34, 124.27, 141.83, 145.28, 152.94 ppm. HRMS: *m/z*: calcd for $C_{16}H_{28}I$ $[M+H]^+$: 347.1230, found 347.1228

5b1: colorless oil, isolated yield 93% (253 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.97 (t, 3H, *J* = 7.4 Hz, CH_3), 1.17 (t, 3H, *J* = 7.6 Hz, CH_3), 1.72 (s, 3H, CH_3), 2.10-2.19 (m, 1H, CH_2), 2.65-2.77 (m, 3H, CH_2), 3.254 (d, 2H, *J* = 3.2 Hz, CH_2), 4.73 (s, 1H, CH_2), 4.88 (s, 1H, CH_2), 6.93 (d, 1H, *J* = 7.3 Hz, CH), 7.18-7.25 (m, 3H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.18, 14.84, 22.89, 27.17, 34.75, 40.97, 109.11, 113.20, 125.99, 127.22, 129.16, 129.30, 135.81, 144.54, 146.86, 147.22 ppm. HRMS: *m/z*: calcd for $C_{16}H_{22}I$ $[M+H]^+$: 341.0761, found 341.0758

5b2: colorless oil, isolated yield 67% (198 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.37 (s, 9H, CH_3), 1.71 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.20-3.32 (m, 2H, CH_2), 4.71 (s, 1H, CH_2), 4.86 (s, 1H, CH_2), 6.88-6.92 (m, 1H, CH), 7.22-7.25 (m, 3H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.96, 22.85, 24.87, 41.17, 108.50, 113.00, 126.65, 126.68, 127.14, 129.69, 134.28, 144.57, 150.41, 156.83 ppm. HRMS: *m/z*: calcd for $C_{16}H_{24}ISi$ $[M+H]^+$: 371.0686, found 371.0681

6a: colorless oil, isolated yield 70% (234 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.98-1.03 (m, 6H, CH_3), 1.05 (t, 2H, *J* = 7.0 Hz, CH_3), 1.10 (t, 2H, *J* = 7.3 Hz, CH_3), 1.22 (s, 12H, CH_3), 2.06-2.24 (m, 4H, CH_2), 2.36-2.46 (m, 2H, CH_2), 2.57 (q, 2H, *J* = 7.3 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.78, 13.27, 14.00, 14.49, 23.69, 24.78, 25.02, 25.11, 25.47, 34.99, 82.66, 106.11, 148.36, 157.71 ppm. HRMS: *m/z*: calcd for $C_{18}H_{33}BIO_2$ $[M+H]^+$: 419.1613, found 419.1614

6b1: colorless oil, isolated yield 80% (262 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.95 (t, 3H, *J* = 7.6 Hz, CH_3), 1.18 (t, 3H, *J* = 7.6 Hz, CH_3), 1.30 (s, 12H, CH_3), 2.32-2.41 (m, 1H, CH_2), 2.53-2.69 (m, 2H, CH_2), 2.77-2.86 (m, 1H, CH_2), 6.95-6.97 (m, 1H, CH), 7.24-7.29 (m, 1H, CH), 7.39-7.43 (m, 1H, CH) 7.83-7.85 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.95, 13.99, 24.98, 25.05, 27.94, 34.87, 83.44, 106.50, 126.19, 128.44, 130.64, 135.87, 148.87, 153.73 ppm. HRMS: *m/z*: calcd for $C_{18}H_{27}BIO_2$ $[M+H]^+$: 413.1143, found 413.1135

6b2: colorless oil, isolated yield 92% (273 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.31 (s, 12H, CH_3), 2.22 (s, 3H, CH_3), 6.14 (s, 1H, CH), 7.01-7.03 (m, 1H, CH), 7.28-7.32 (m, 1H, CH), 7.44-7.47 (m, 1H, CH), 7.80-7.82 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 24.95, 27.10, 75.98, 83.66, 126.73, 127.12, 131.12, 135.61, 150.64, 151.54 ppm. HRMS: *m/z*: calcd for $C_{15}H_{21}BIO_2$ $[M+H]^+$: 371.0674, found 371.0671

7a: colorless oil, isolated yield 45% (121 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.03-1.15 (m, 12H, CH_3), 2.25-2.69 (m, 8H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.32, 13.29, 13.34, 13.65, 22.43, 26.01, 26.41, 34.68, 104.77, 130.64, 146.63, 156.63, 173.49 ppm. HRMS: *m/z*: calcd for $C_{13}H_{22}IO_2$ $[M+H]^+$: 337.0659, found 337.0660

7b: colorless solid, isolated yield 85% (224 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.97 (t, 3H, *J* = 7.6 Hz, CH_3), 1.16 (t, 3H, *J* = 7.4 Hz, CH_3), 2.26-2.35 (m, 1H, CH_2), 2.55-2.64 (m, 1H, CH_2), 2.73-2.86 (m, 2H, CH_2), 7.08-7.10 (m, 1H, CH), 7.38-7.42 (m, 1H, CH), 7.55-7.59 (m, 1H, CH), 8.12-8.14 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 13.11, 13.98, 27.34, 34.64, 106.11, 127.37, 128.87, 130.97, 131.64, 133.07, 147.77, 149.37, 172.05 ppm. HRMS: *m/z*: calcd for $C_{13}H_{16}IO_2$ $[M+H]^+$: 331.0189, found 331.0192

General procedure for intramolecular Heck reactions of 1-iodo-1,3-dienes analogues. 1-Iodo-1,3-dienes analogues (0.4 mmol) in 4 mL of toluene was treated with $Pd(OAc)_2$ (0.04 mmol), Et_3N (1.2 mmol) and PPh_3 (0.08 mmol). The reaction mixture was stirred at 100 ºC for 12 h based on the structures. Generally a longer reaction time has little effect on the Heck reaction. After purification by column chromatography, the corresponding products were given as pure compounds.

8a1: colorless oil, isolated yield 94% (77 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.12-1.24 (m, 12H, CH_3), 2.29 (s, 3H, CH_3), 2.60-2.68 (m, 8H, CH_2), 6.86 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 14.74, 15.77, 15.81, 16.12, 19.85, 21.85, 22.15, 22.59, 25.71, 128.67, 133.71, 137.63, 138.23, 139.49, 139.89 ppm. HRMS: *m/z*: calcd for $C_{15}H_{25}$ $[M+H]^+$: 205.1951, found 205.1949

8a2: colorless oil, isolated yield 99% (103 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.98-1.06 (m, 12H, CH_3), 1.47-1.52 (m, 6H, CH_2), 1.56-1.62 (m, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.48-2.56 (m, 8H, CH_2), 6.82 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 14.71, 15.11, 15.16, 15.24, 20.00, 23.85, 24.93, 24.98, 25.22, 31.70, 32.11, 32.31, 35.38, 129.30, 133.56, 136.61, 137.08, 138.22, 138.99 ppm. HRMS: *m/z*: calcd for $C_{19}H_{33}$ $[M+H]^+$: 261.2577, found 261.2573

8b: colorless oil, isolated yield 95% (76 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.99 (t, 3H, *J* = 7.6 Hz, CH_3), 1.29 (t, 3H, *J* = 7.6 Hz, CH_3), 2.48 (s, 3H, CH_3), 2.82 (q, 2H, *J* = 7.6 Hz, CH_2), 3.11 (q, 2H, *J* = 7.6 Hz, CH_2), 7.33-7.42 (m, 2H, CH), 7.48

(s, 1H, CH), 7.69 (d, 1H, *J* = 7.8 Hz, CH), 7.97 (d, 1H, *J* = 8.3 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 14.86, 15.66, 20.76, 21.61, 22.92, 123.96, 124.72, 125.07, 127.02, 127.99, 130.96, 132.74, 134.87, 136.94, 138.51 ppm. HRMS: *m/z*: calcd for $C_{15}H_{19}$ $[M+H]^+$: 199.1481, found 199.1479

9a1: colorless oil, isolated yield 80% (70 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.72 (t, 3H, *J* = 7.4 Hz, CH_3), 0.99 (t, 3H, *J* = 7.4 Hz, CH_3), 1.03-1.11 (m, 6H, CH_3), 1.14-1.19 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 2.04-2.23 (m, 6H, CH_2), 2.60 (t, 1H, *J* = 8.4 Hz, CH) 5.70 (s, 1H, CH), 6.02 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 12.44, 13.01, 13.77, 15.44, 19.93, 25.01, 27.19, 29.74, 33.05, 50.20, 121.60, 129.02, 132.16, 133.69, 134.88, 143.20 ppm. HRMS: *m/z*: calcd for $C_{16}H_{27}$ $[M+H]^+$: 219.2107, found 219.2105

9a2: colorless oil, isolated yield 74% (64 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.83-0.90 (m, 6H, CH_3), 1.17-1.37 (m, 8H, CH_2), 1.94 (s, 3H, CH_3), 2.15-2.18 (m, 4H, CH_2), 2.32 (t, 2H, *J* = 7.2 Hz, CH_2), 5.23 (t, 1H, *J* = 7.2 Hz, CH), 5.73 (d, 1H, *J* = 5.2 Hz, CH), 6.22 (d, 1H, *J* = 5.4 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 14.13, 14.14, 22.58, 22.61, 23.87, 32.03, 32.96, 33.43, 33.59, 36.24, 119.11, 121.07, 128.13, 135.33, 138.81, 143.65 ppm. HRMS: *m/z*: calcd for $C_{16}H_{27}$ $[M+H]^+$: 219.2107, found 219.2106

9b1: colorless oil, isolated yield 55% (46 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.15 (d, 1H, *J* = 4.3 Hz, CH_2), 0.46 (d, 1H, *J* = 4.0 Hz, CH_2), 1.02-1.05 (m, 4H, CH_3+CH_2), 1.08-1.14 (m, 1H, CH_2), 1.30 (s, 3H, CH_3), 1.88 (d, 3H, *J* = 7.1 Hz, CH_3), 2.70 (d, 1H, *J* = 15.4 Hz, CH_2), 2.87 (d, 1H, *J* = 15.3 Hz, CH_2), 5.61 (q, 1H, *J* = 7.0 Hz, CH), 7.03-7.06 (m, 1H, CH), 7.12-7.17 (m, 2H, CH), 7.21-7.23 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 11.77, 16.18, 20.90, 21.99, 23.73, 23.77, 32.28, 39.17, 118.04, 125.37, 126.70, 127.82, 128.94, 135.78, 137.33, 138.90 ppm. HRMS: *m/z*: calcd for $C_{16}H_{21}$ $[M+H]^+$: 213.1638, found 213.1635

9b2: colorless oil, isolated yield 70% (67 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.12 (s, 9H, CH_3), 0.75 (d, 1H, *J* = 4.2 Hz, CH_2), 0.84 (d, 1H, *J* = 4.2 Hz, CH_2), 1.32 (s, 3H, CH_3), 2.58 (d, 1H, *J* = 15.3 Hz, CH_2), 2.82 (d, 1H, *J* = 15.3 Hz, CH_2), 5.11 (s, 1H, CH) 5.24 (s, 1H, CH), 7.02-7.04 (m, 1H, CH), 7.16-7.18 (m, 2H, CH), 7.24-7.26 (m, 1H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 0.94, 21.29, 22.82, 24.44, 25.03, 40.13, 112.75, 125.30, 126.60, 127.02, 127.26, 136.96, 140.03, 150.26 ppm. HRMS: *m/z*: calcd for $C_{16}H_{23}Si$ $[M+H]^+$: 243.1564, found 243.1563

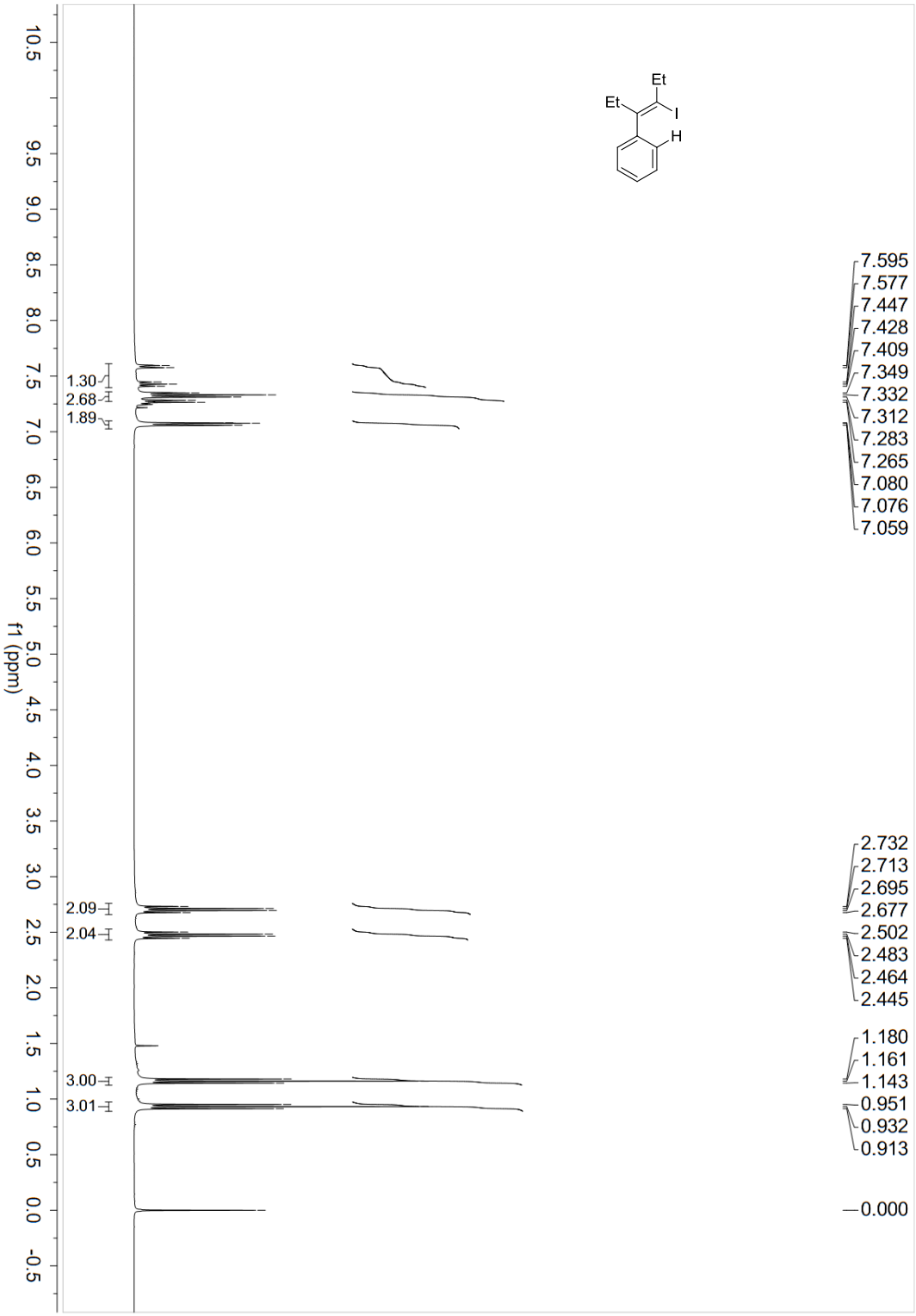
Procedure for synthesis of 10. Compound **6b2** (0.4 mmol) in 4 mL of toluene was treated with $PdCl_2(PPh_3)_2$ (0.02 mmol), Et_3N (1.6 mmol) and Ph_2PH (0.5 mmol, 10 wt.% in hexane). The reaction mixture was stirred at 100 ºC for 12 h. After purification by column chromatography, **10** was obtained.

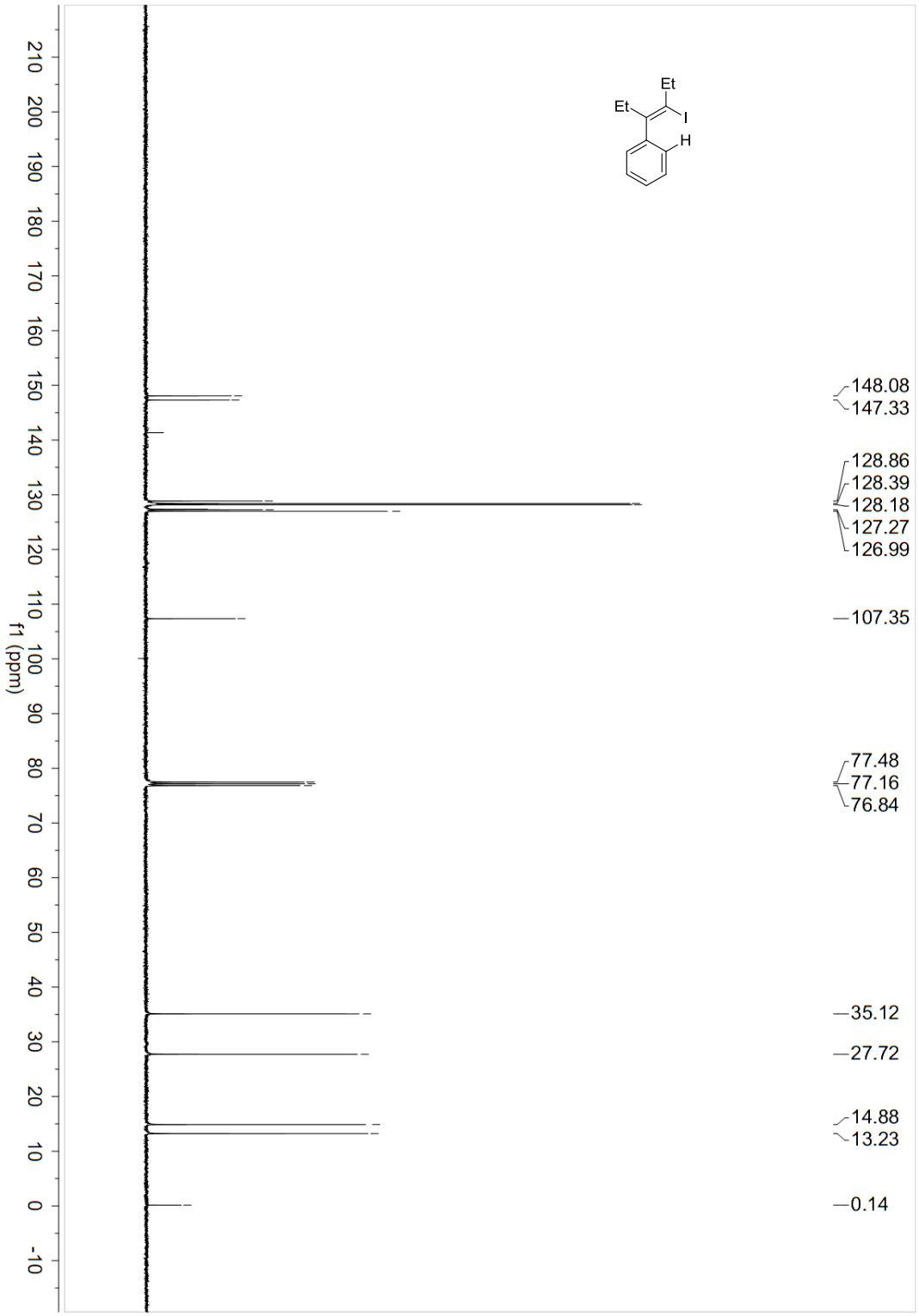
10: colorless solid, isolated yield 73% (125 mg). ^{1}H NMR (400MHz, $CDCl_3$, 25 ℃, TMS): δ = 1.25 (s, 12H, CH_3), 2.26 (s, 3H, CH_3), 6.22 (br, 1H, CH), 7.02 (d, 1H, *J* = 7.5 Hz, CH), 7.27-7.39 (m, 12H, CH), 7.84 (d, 1H, *J* = 7.3 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ℃, TMS): δ = 24.92, 29.44 (d, *J* = 6.7 Hz), 83.58, 124.82 (d, *J* = 5.6 Hz), 126.48, 127.90, 128.21 (d, *J* = 6.2 Hz), 128.58, 128.64 (d, *J* = 2.8 Hz), 128.83, 130.59, 132.71 (d, *J* = 18.4 Hz), 133.86 (d, *J* = 19.5 Hz), 135.90, 140.80 (d, *J* = 10.7 Hz), 149.46 (d, *J* = 8.8 Hz), 158.28 (d, *J* = 29.8 Hz) ppm. HRMS: *m/z*: calcd for $C_{27}H_{31}BO_2P$ $[M+H]^+$: 429.2149, found 429.2150

X-ray crystallographic studies: The single crystals of **10** suitable for X-ray analysis were grown as shown in were grown in mixed solvent of hexane and ethanol for 1 day. Data collections for **10** was performed at 180 K on a SuperNova diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved with the shelxs-97[3] and refined with the XL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compound **10** are summarized in Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1011067 (**10**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2) Copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds

2b

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Et
I
H
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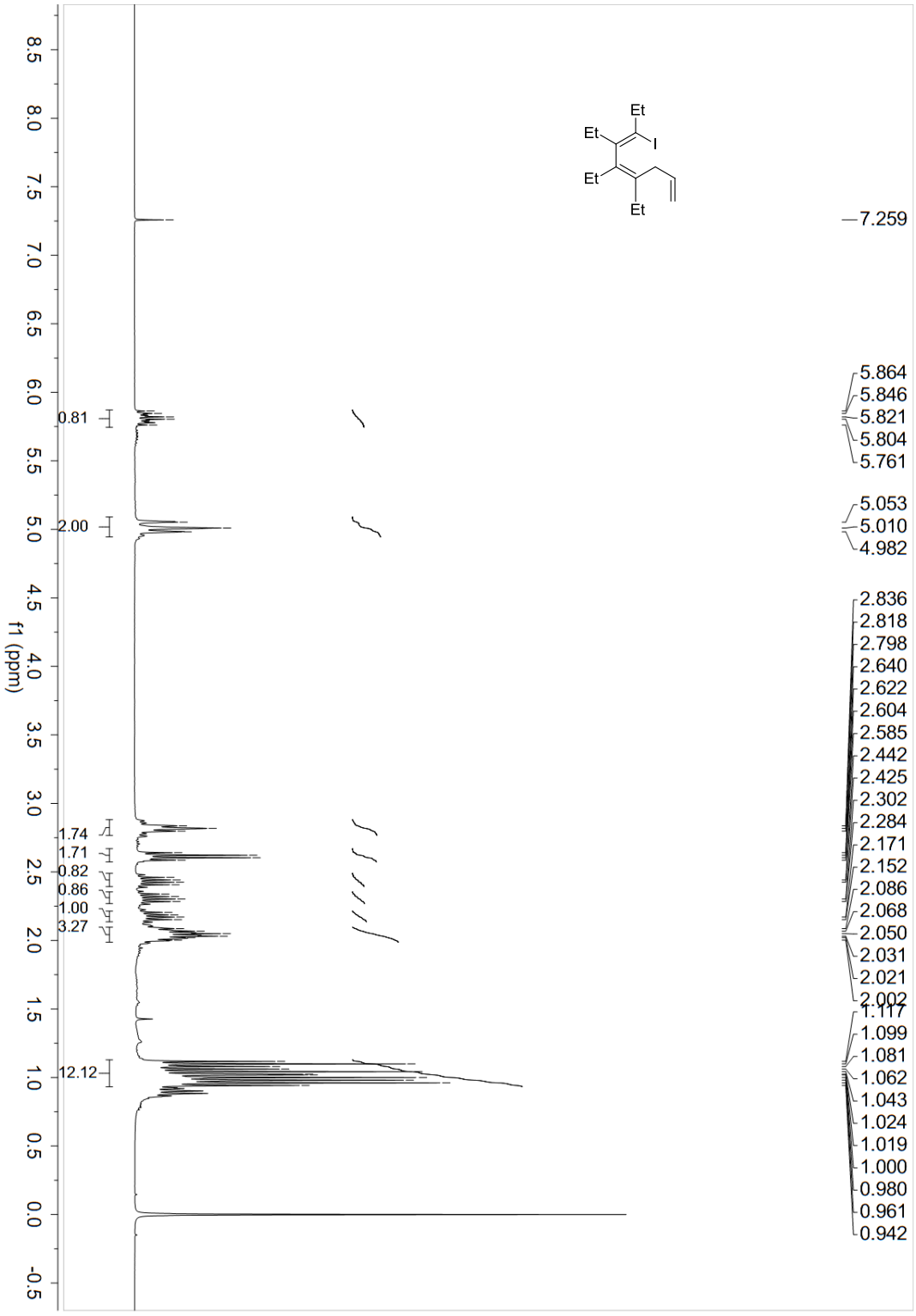
128.39
128.18
127.27
126.99
107.35
77.48
77.16
76.84
35.12
27.72
14.88
13.23
0.14
f1 (ppm)

4a1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Et
I
Et
Et
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5.053
5.010
4.982
2.836
2.818
2.798
2.640
2.622
2.604
2.585
2.442
2.425
2.302
2.284
2.171
2.152
2.086
2.068
2.050
2.031
2.021
2.002
1.117
1.099
1.081
1.062
1.043
1.024
1.019
1.000
0.980
0.961
0.942
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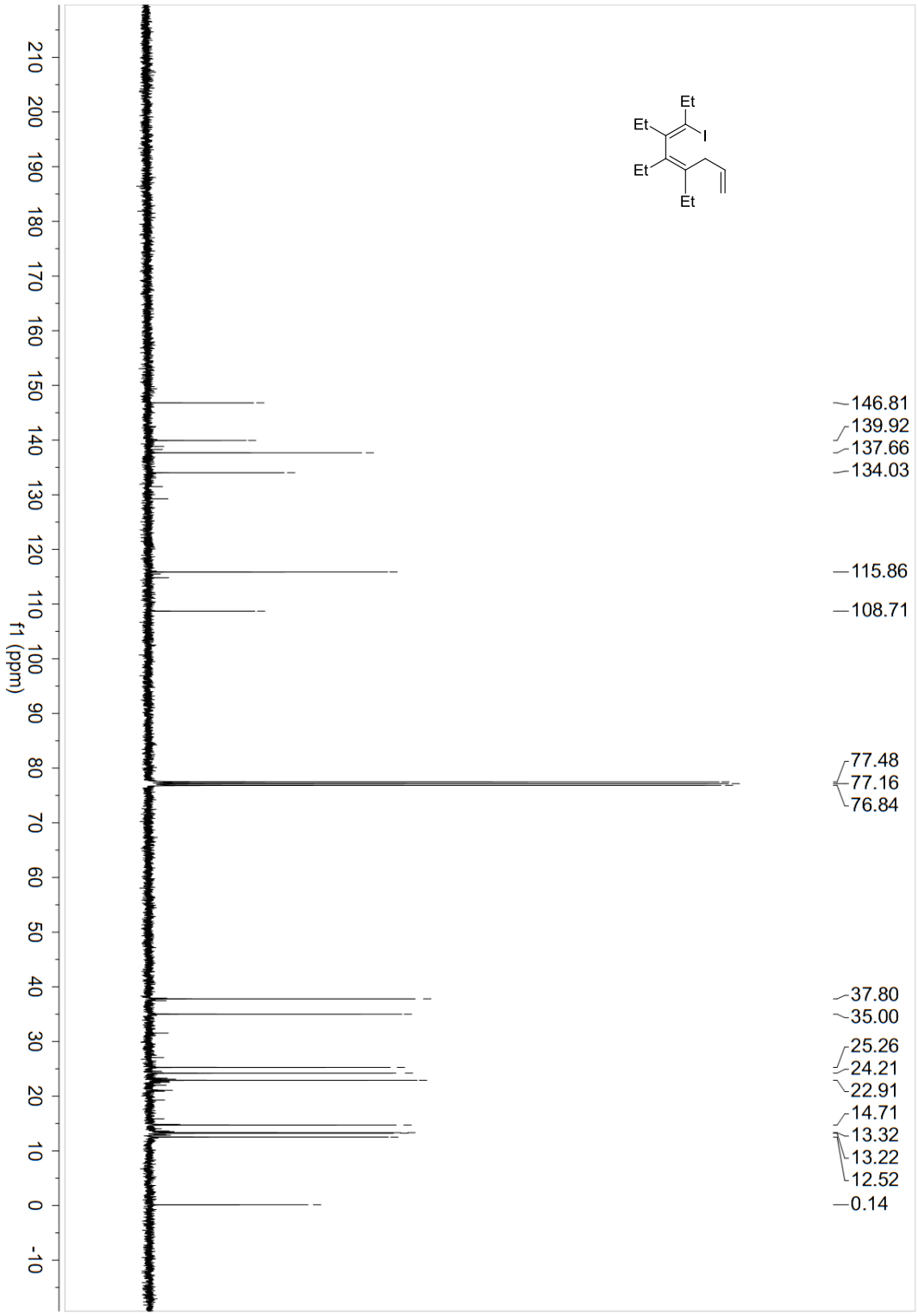
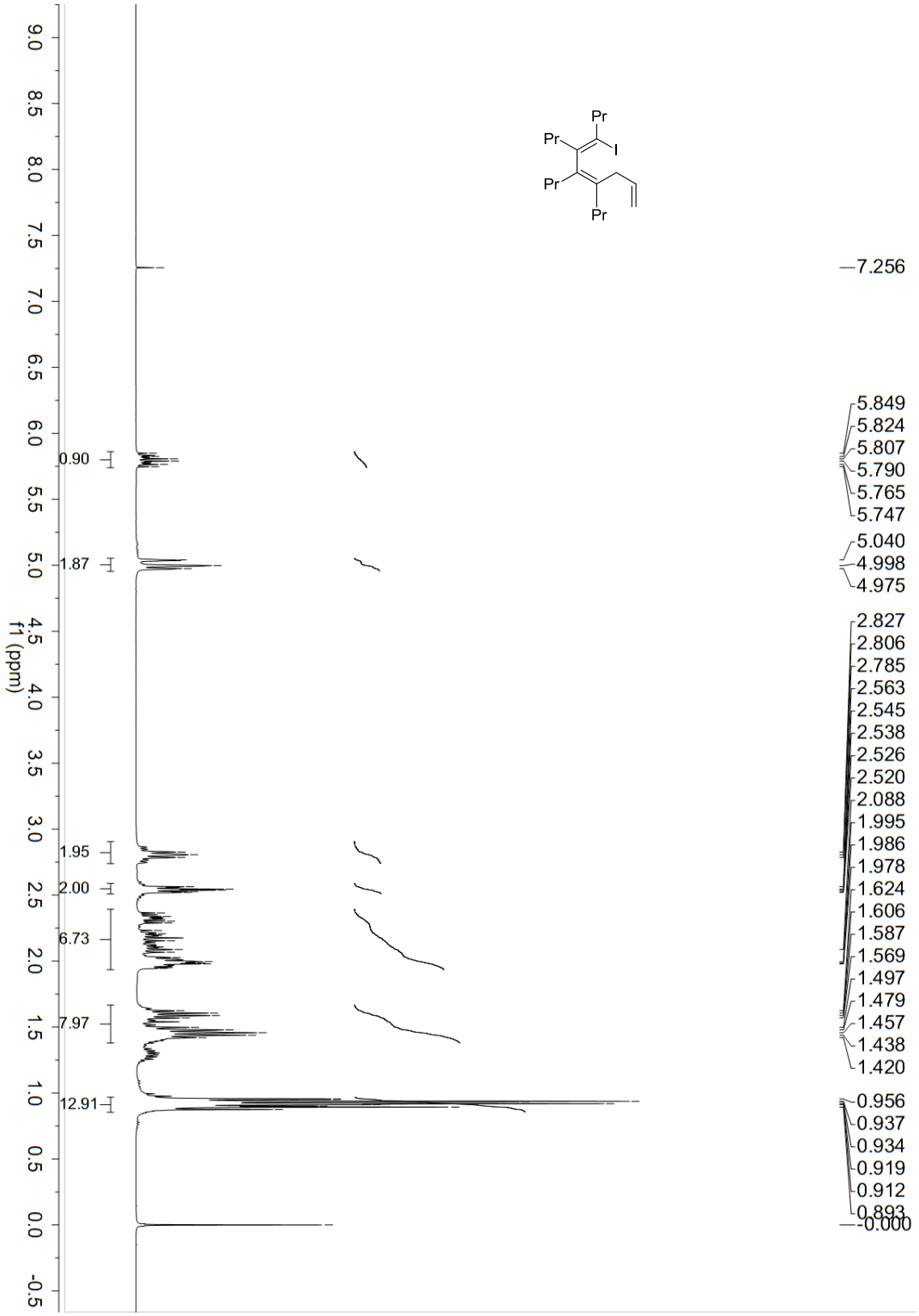
2.00
1.74
1.71
0.82
0.86
1.00
3.27
12.12
f1 (ppm)


Et
Et
I
Et
Et
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
146.81
139.92
137.66
134.03
115.86
108.71
77.48
77.16
76.84
37.80
35.00
25.26
24.21
22.91
14.71
13.32
13.22
12.52
0.14

4a2


Pr
Pr
I
Pr
Pr
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7.97
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5.849
5.824
5.807
5.790
5.765
5.747
5.040
4.998
4.975
2.827
2.806
2.785
2.563
2.545
2.538
2.526
2.520
2.088
1.995
1.986
1.978
1.624
1.606
1.587
1.569
1.497
1.479
1.457
1.438
1.420
0.956
0.937
0.934
0.919
0.912
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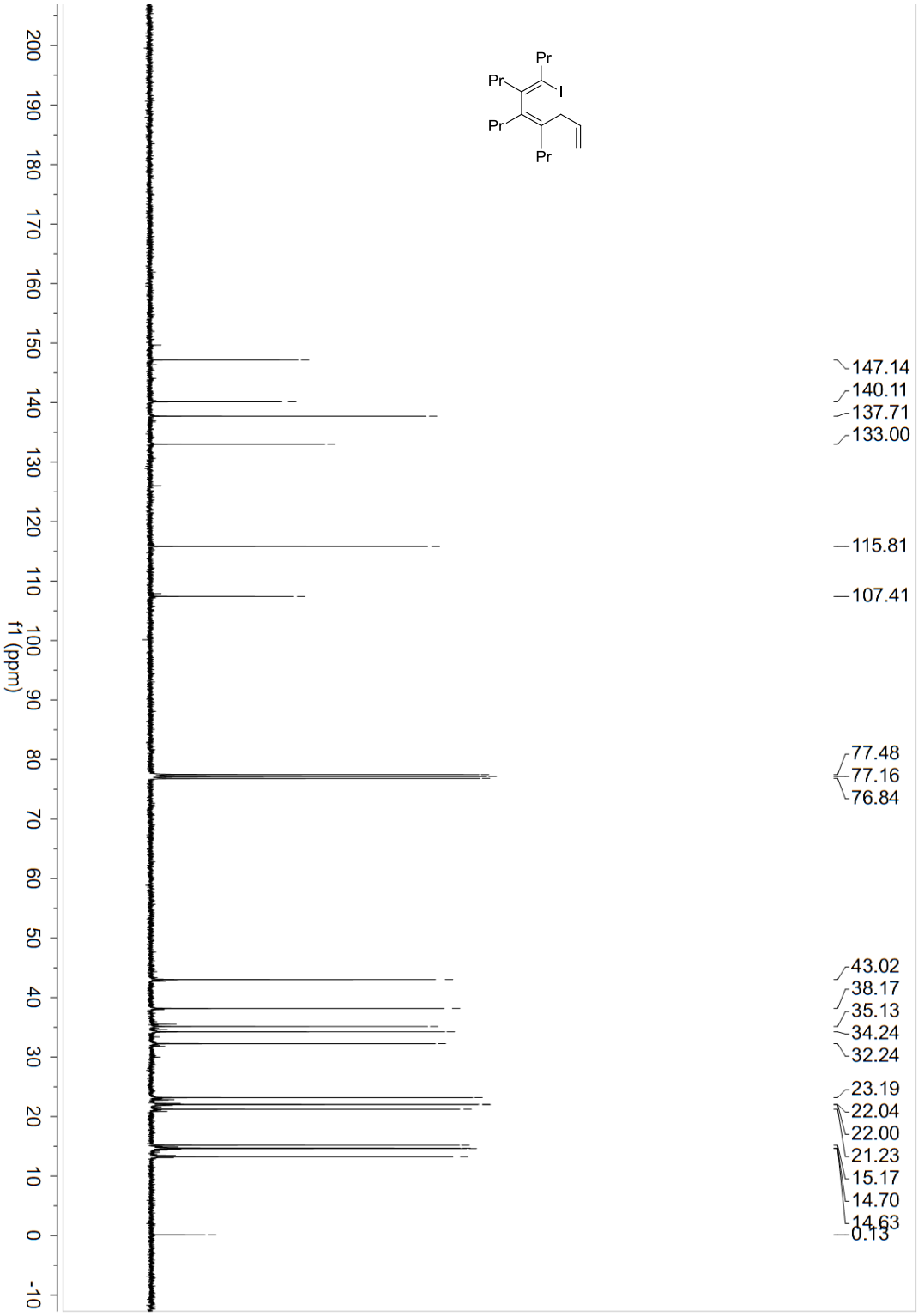
Pr
Pr
I
Pr
Pr
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
147.14
140.11
137.71
133.00
115.81
107.41
77.48
77.16
76.84
43.02
38.17
35.13
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23.19
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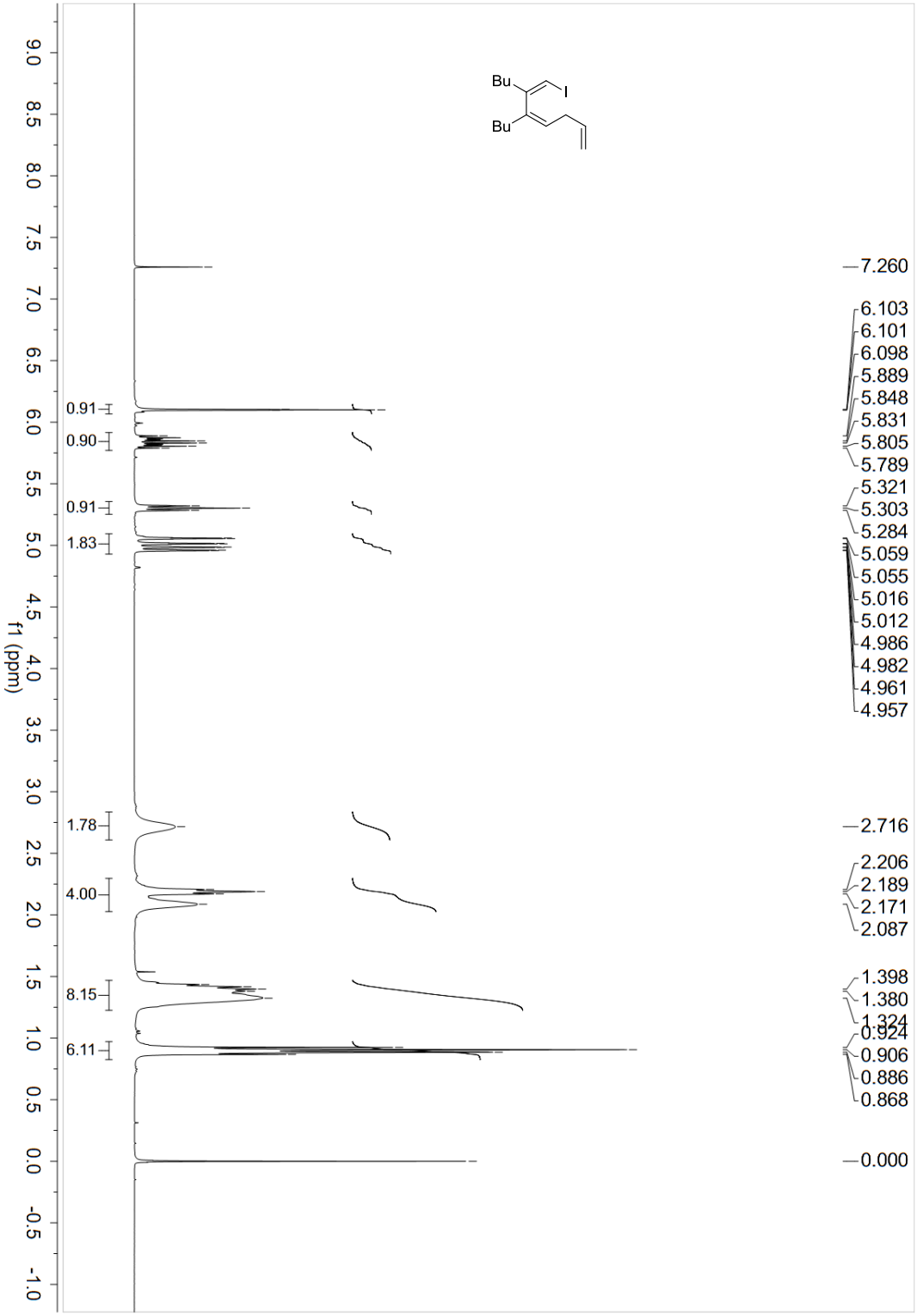
22.00
21.23
15.17
14.70
14.63
0.13

4a3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I
Bu
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8.0
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7.0
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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
-0.5
-1.0
0.91
0.90
0.91
1.83
1.78
4.00
8.15
6.11
7.260
6.103
6.101
6.098
5.889
5.848
5.831
5.805
5.789
5.321
5.303
5.284
5.059
5.055
5.016
5.012
4.986
4.982
4.961
4.957
2.716
2.206
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1.398
1.380
1.324
0.924
0.906
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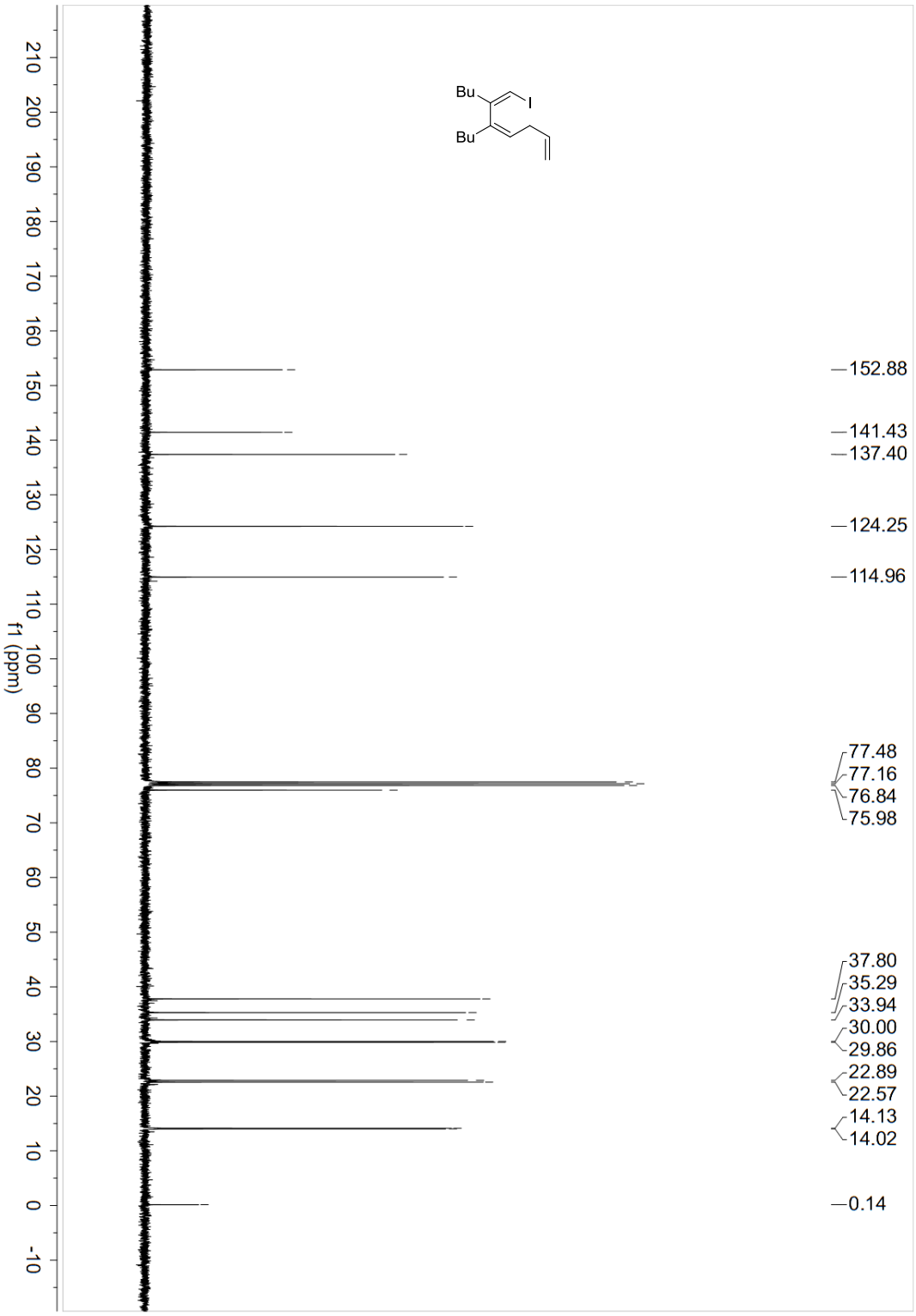
0.868
0.000


Bu
I
Bu
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
152.88
141.43
137.40
124.25
114.96
77.48
77.16
76.84
75.98
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33.94
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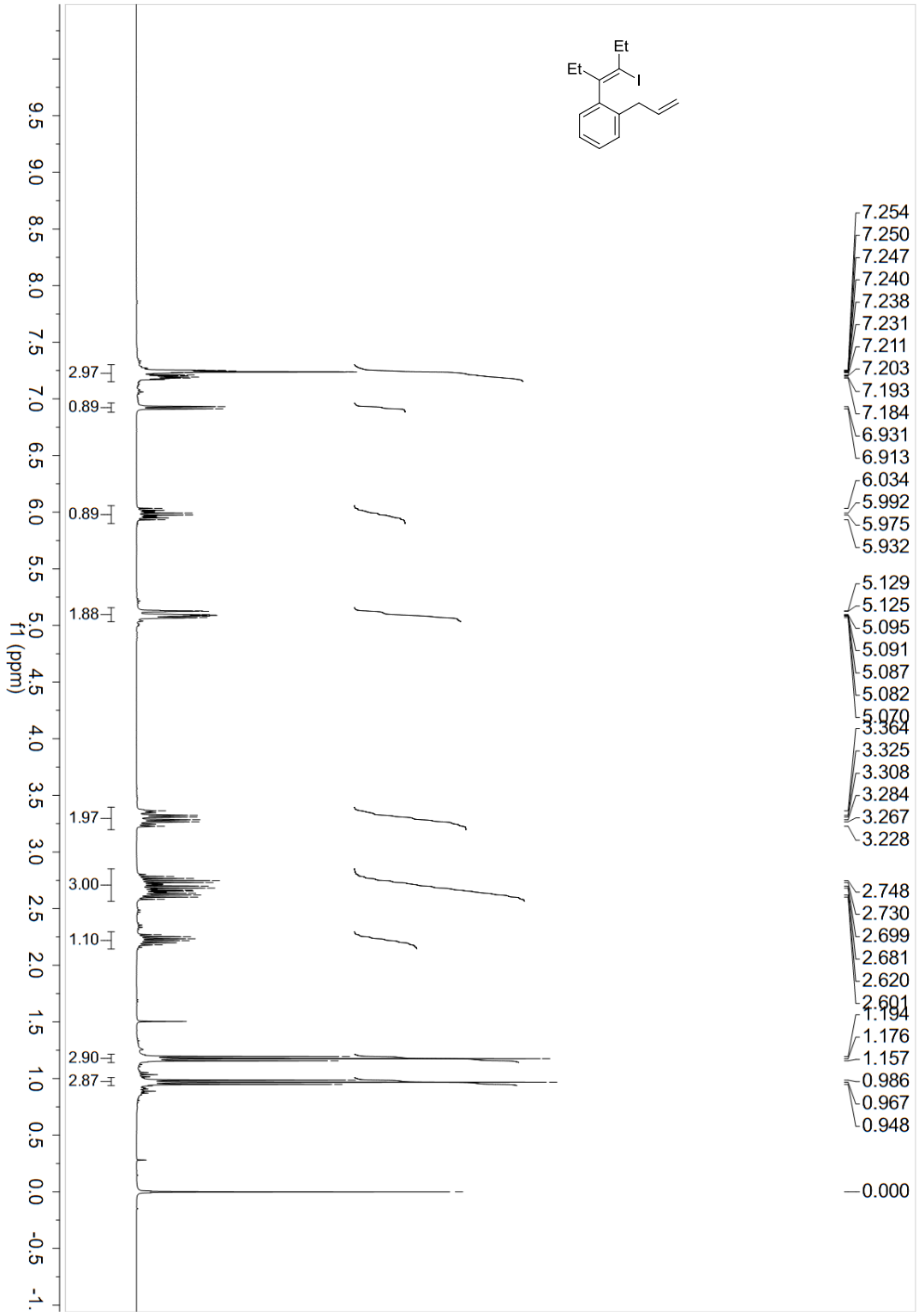
22.57
14.13
14.02
0.14

4b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7.240
7.238
7.231
7.211
7.203
7.193
7.184
6.931
6.913
6.034
5.992
5.975
5.932
5.129
5.125
5.095
5.091
5.087
5.082
5.070
3.364
3.325
3.308
3.284
3.267
3.228
2.748
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0.948
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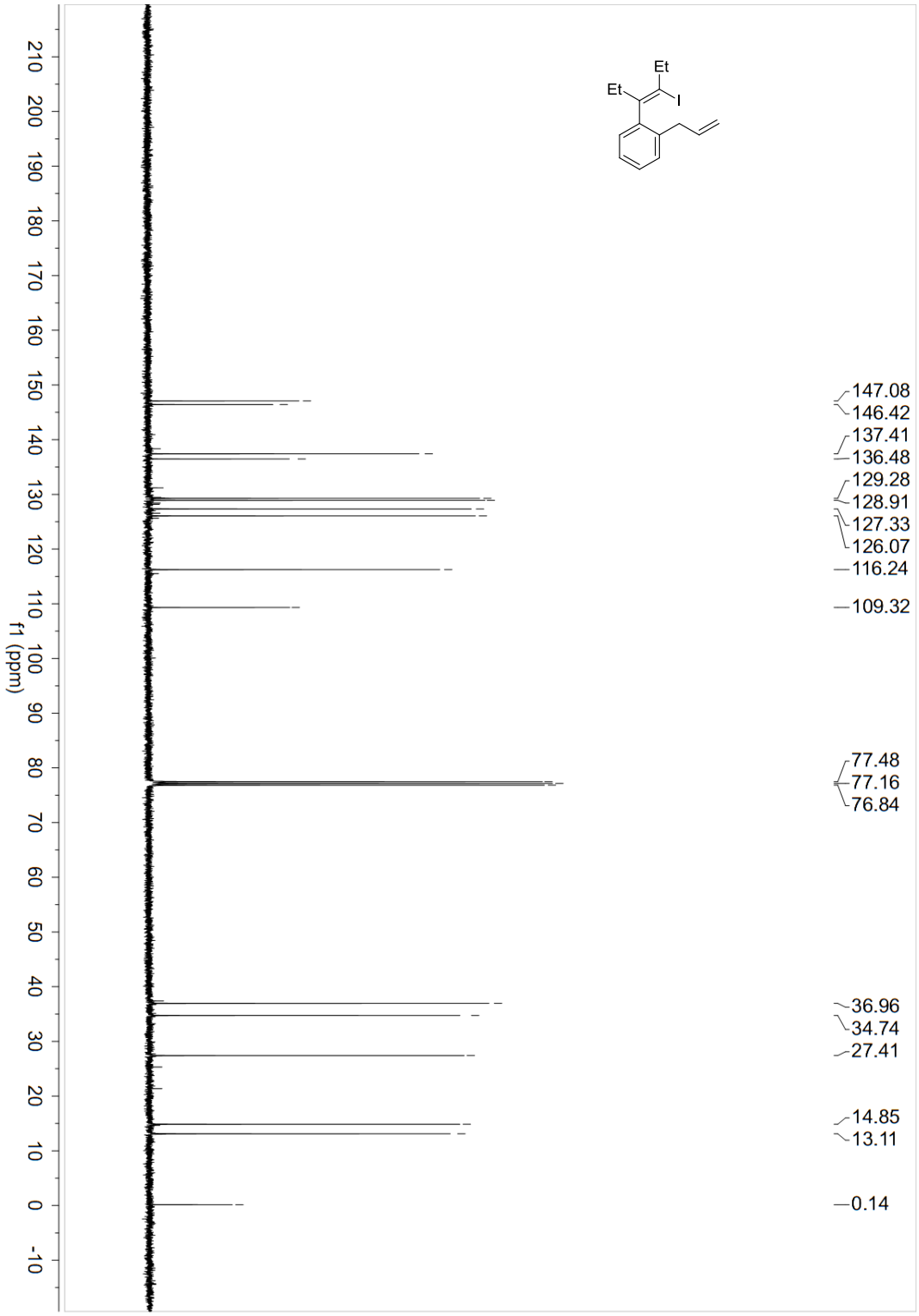
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Et
I
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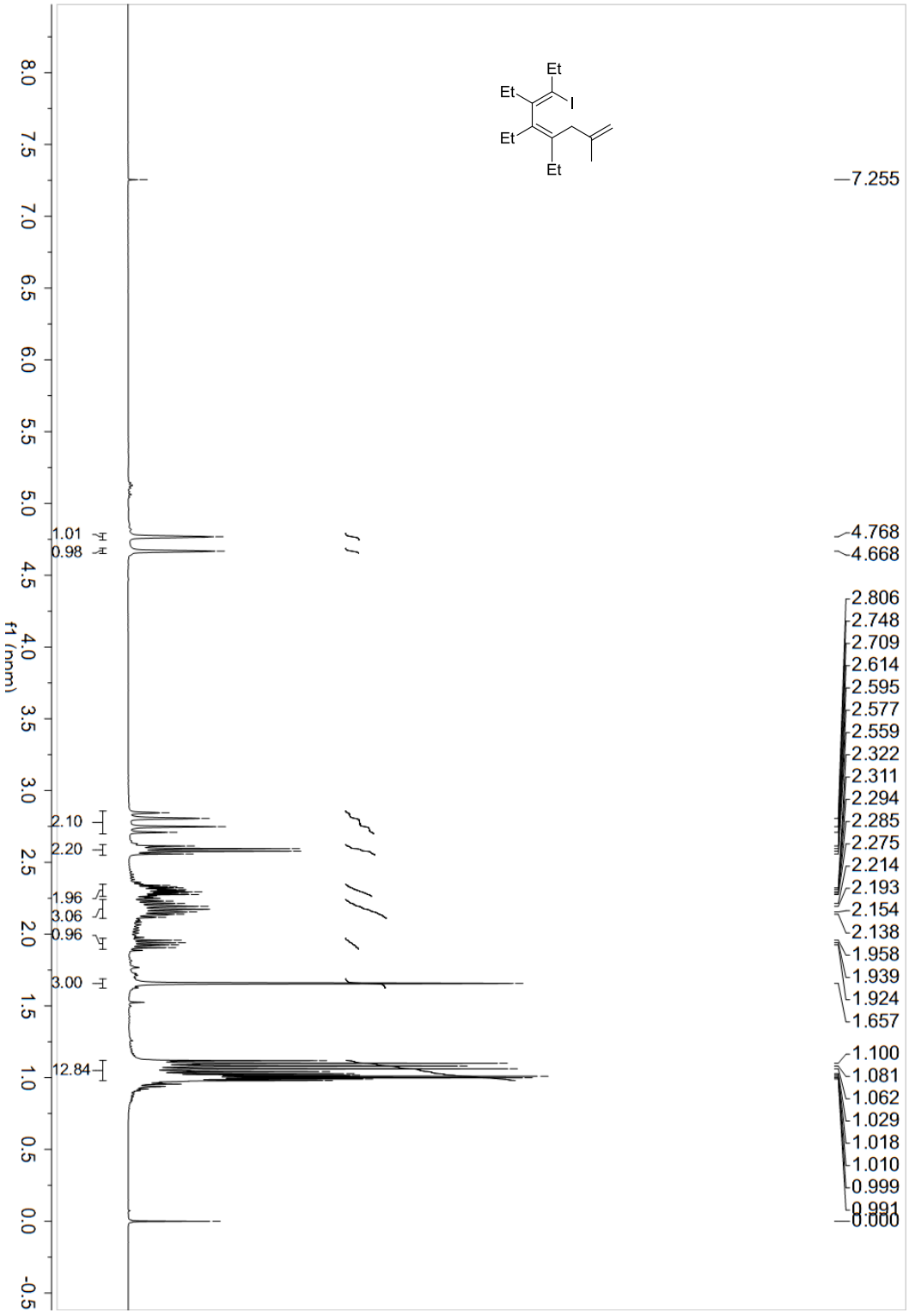
137.41
136.48
129.28
128.91
127.33
126.07
116.24
109.32
77.48
77.16
76.84
36.96
34.74
27.41
14.85
13.11
0.14
f1 (ppm)

5a1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Et
I
Et
Et
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4.668
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2.748
2.709
2.614
2.595
2.577
2.559
2.322
2.311
2.294
2.285
2.275
2.214
2.193
2.154
2.138
1.958
1.939
1.924
1.657
1.100
1.081
1.062
1.029
1.018
1.010
0.999
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0.000
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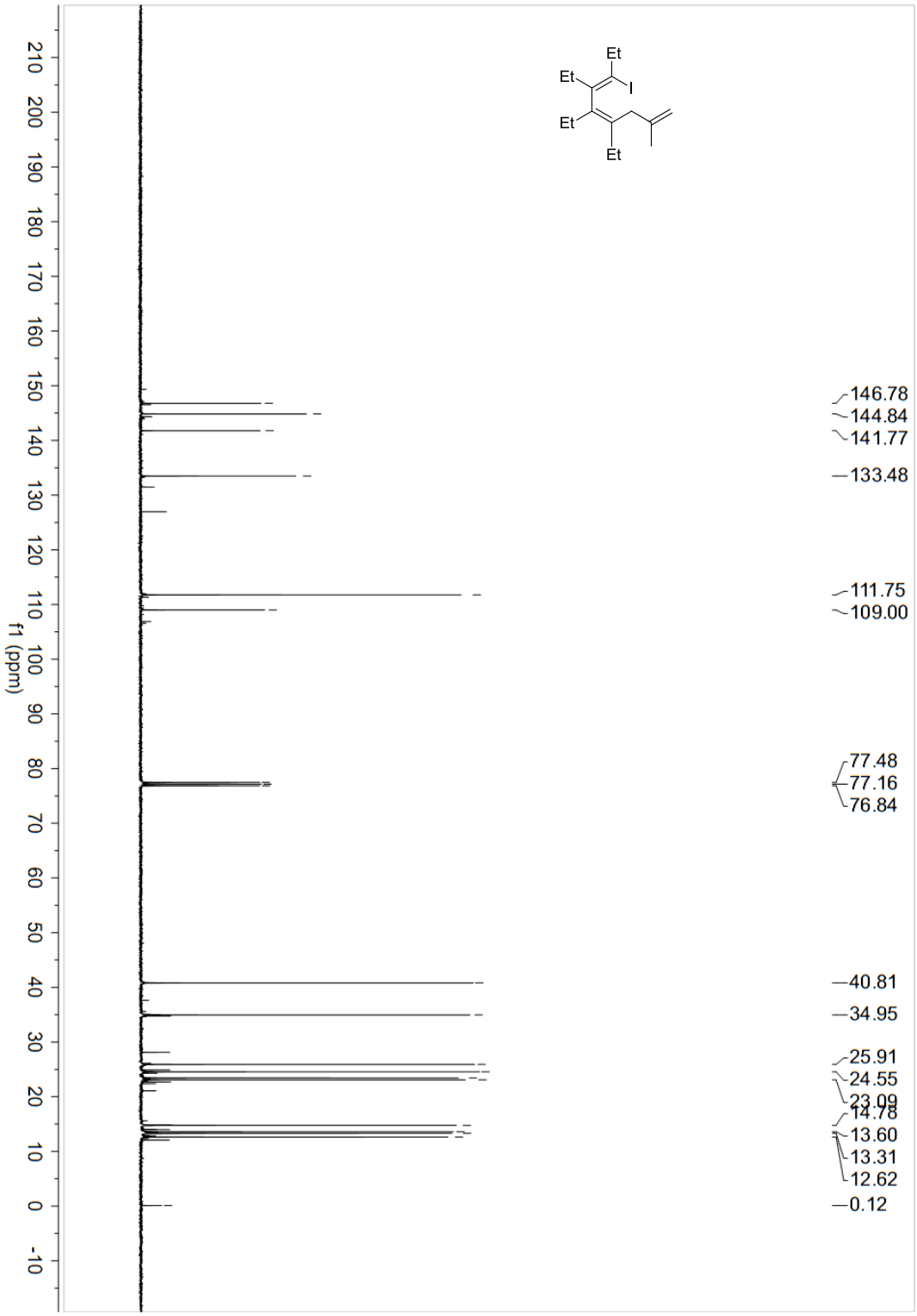
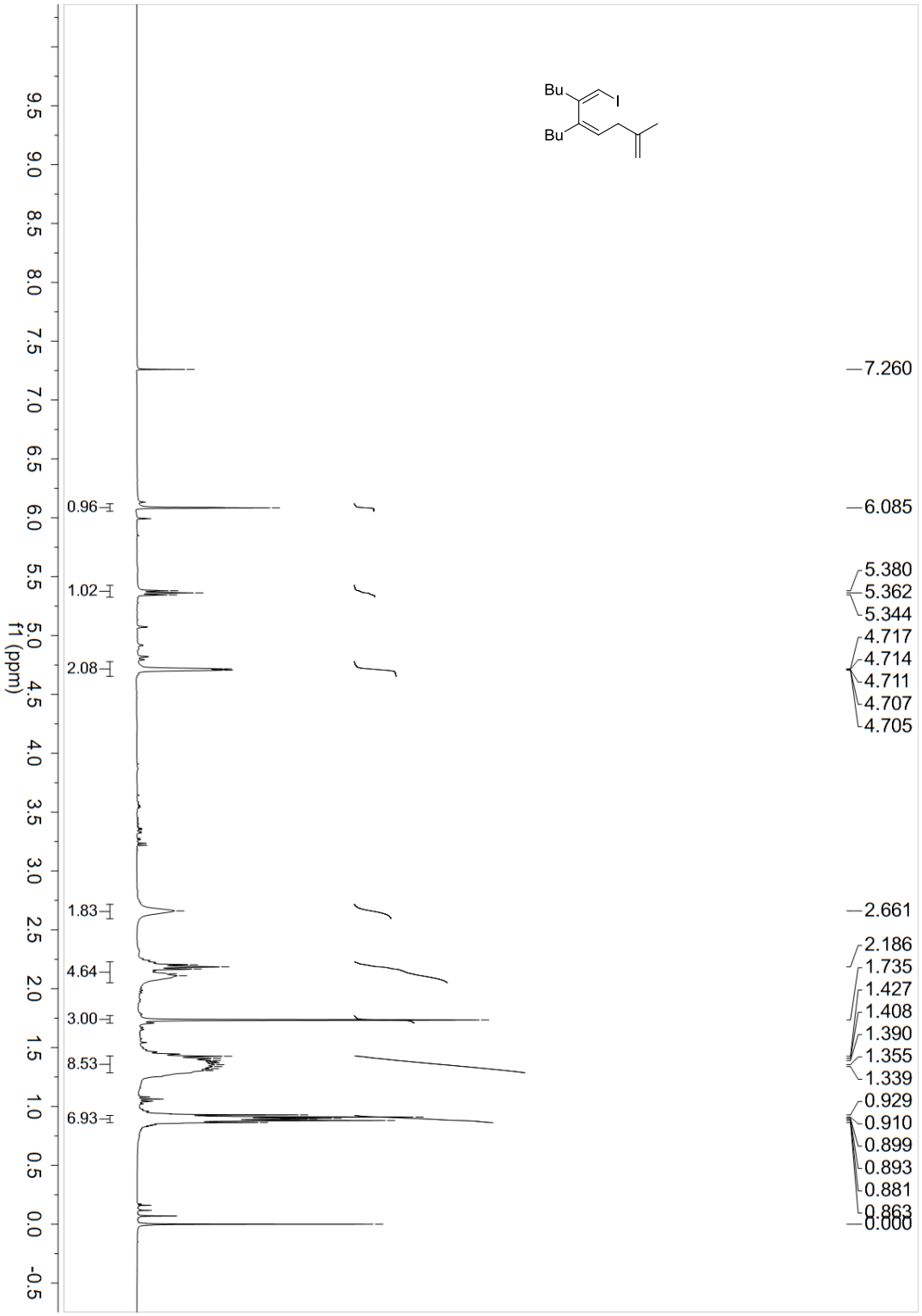
2.20
1.96
3.06
0.96
3.00
12.84
f1 (ppm)


Et
Et
I
Et
Et
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
146.78
144.84
141.77
133.48
111.75
109.00
77.48
77.16
76.84
40.81
34.95
25.91
24.55
23.09
14.78
13.60
13.31
12.62
0.12

5a2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I
Bu
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6.085
5.380
5.362
5.344
4.717
4.714
4.711
4.707
4.705
2.661
2.186
1.735
1.427
1.408
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1.355
1.339
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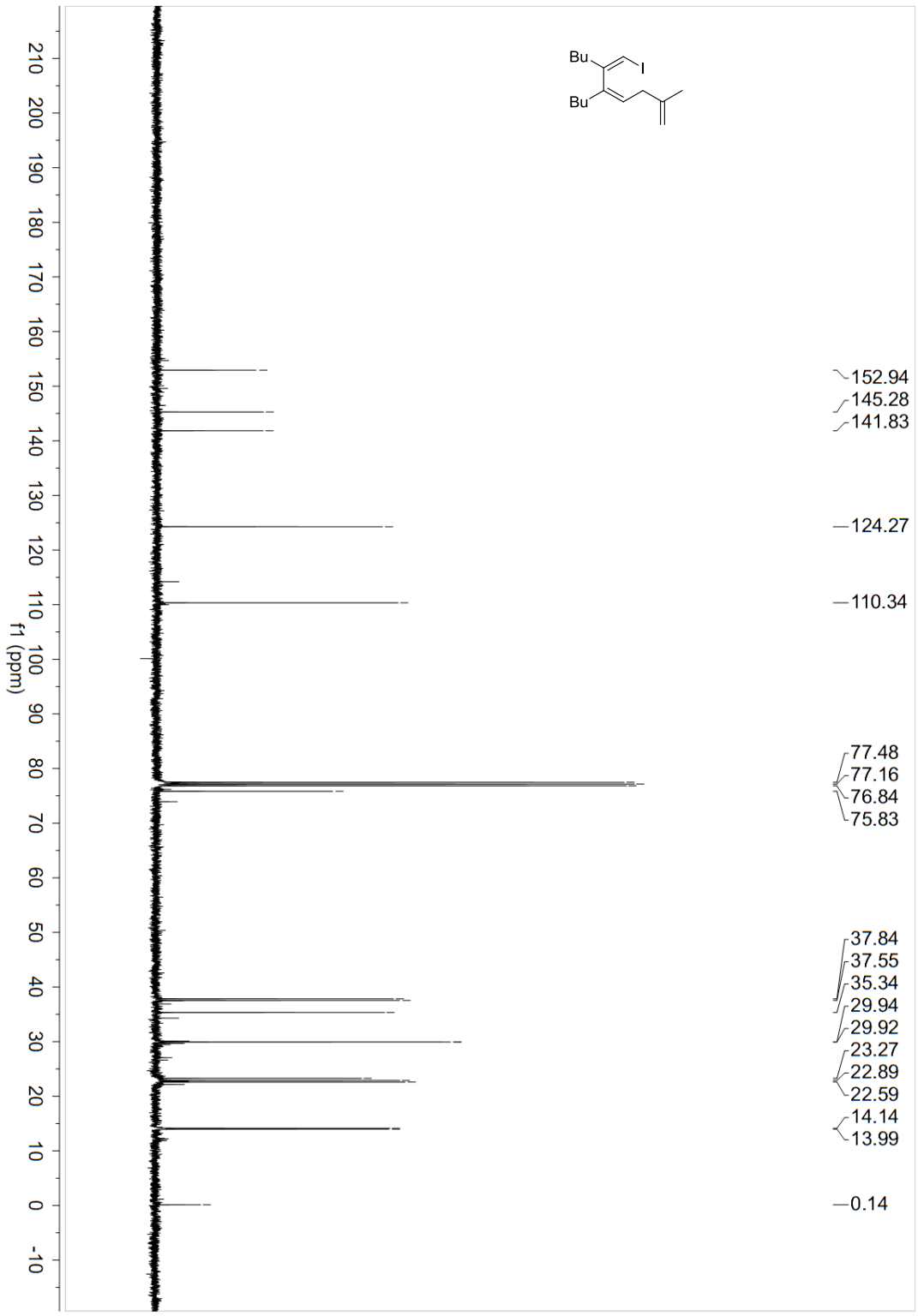
0.863
0.000


Bu
I
Bu
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
152.94
145.28
141.83
124.27
110.34
77.48
77.16
76.84
75.83
37.84
37.55
35.34
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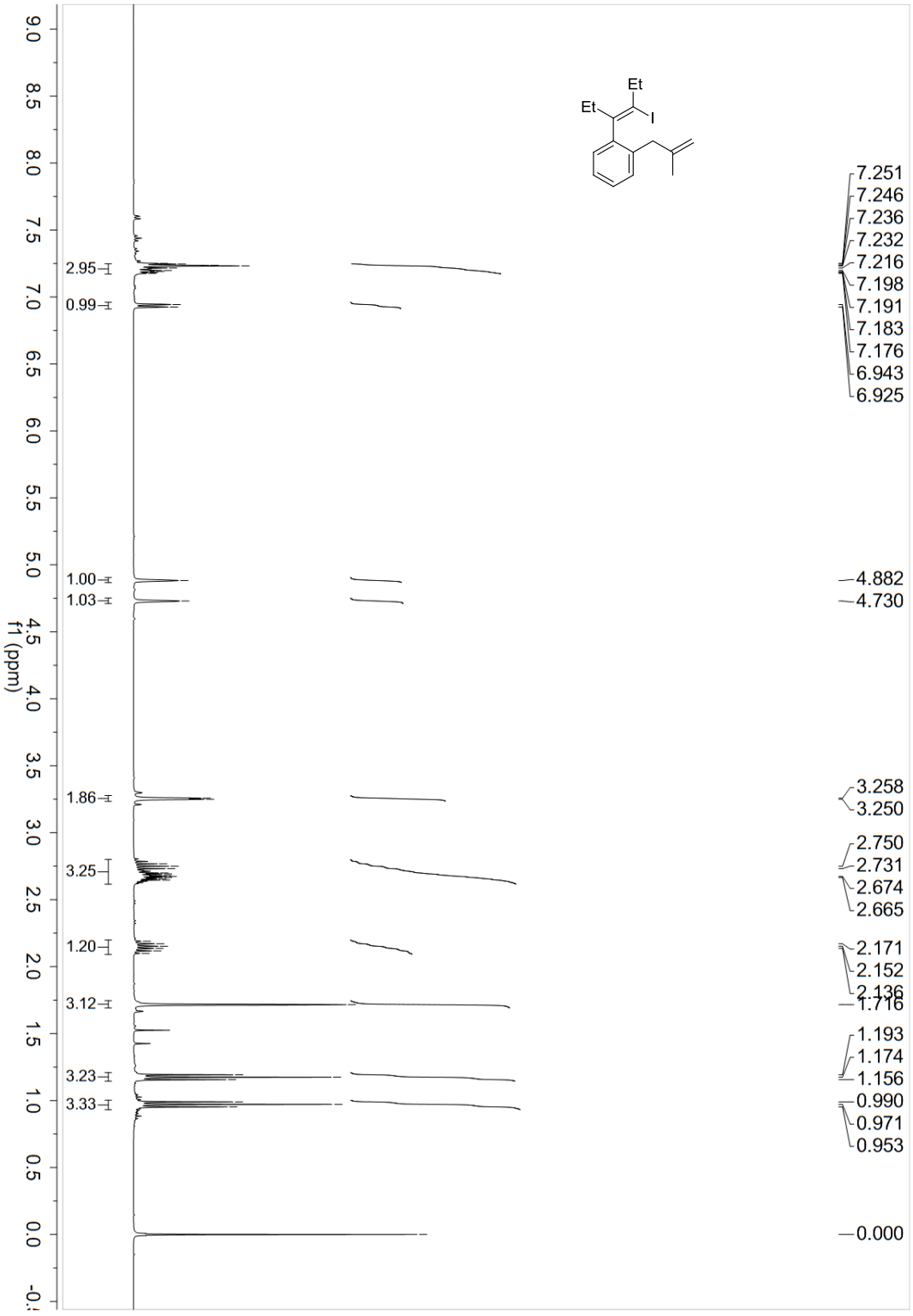
23.27
22.89
22.59
14.14
13.99
0.14

5b1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I
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7.232
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7.191
7.183
7.176
6.943
6.925
4.882
4.730
3.258
3.250
2.750
2.731
2.674
2.665
2.171
2.152
1.716
1.193
1.174
1.156
0.990
0.971
0.953
0.000
2.95
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1.00
1.03
1.86
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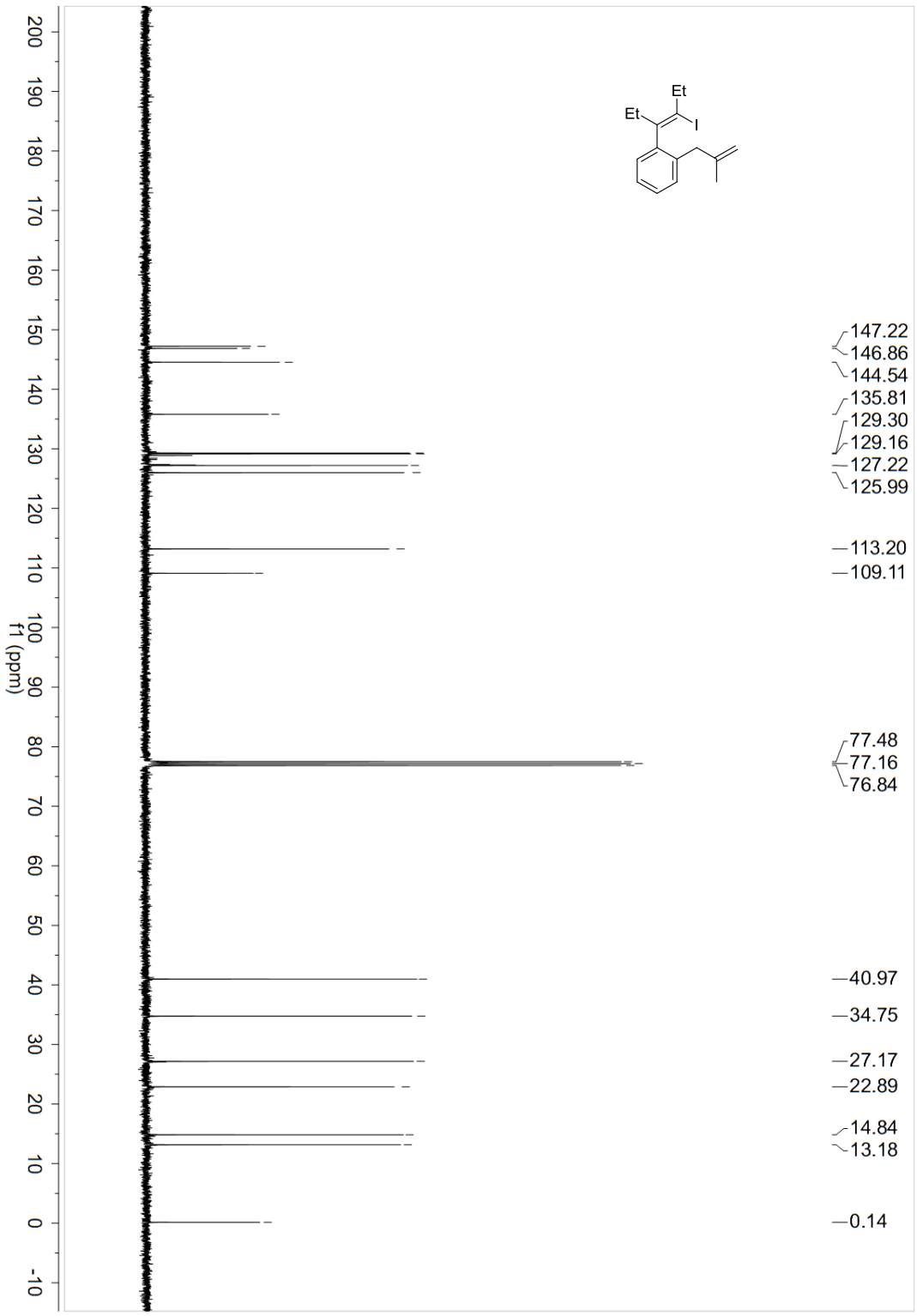
1.20
3.12
3.23
3.33
f1 (ppm)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129.16
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113.20
109.11
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77.16
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40.97
34.75
27.17
22.89
14.84
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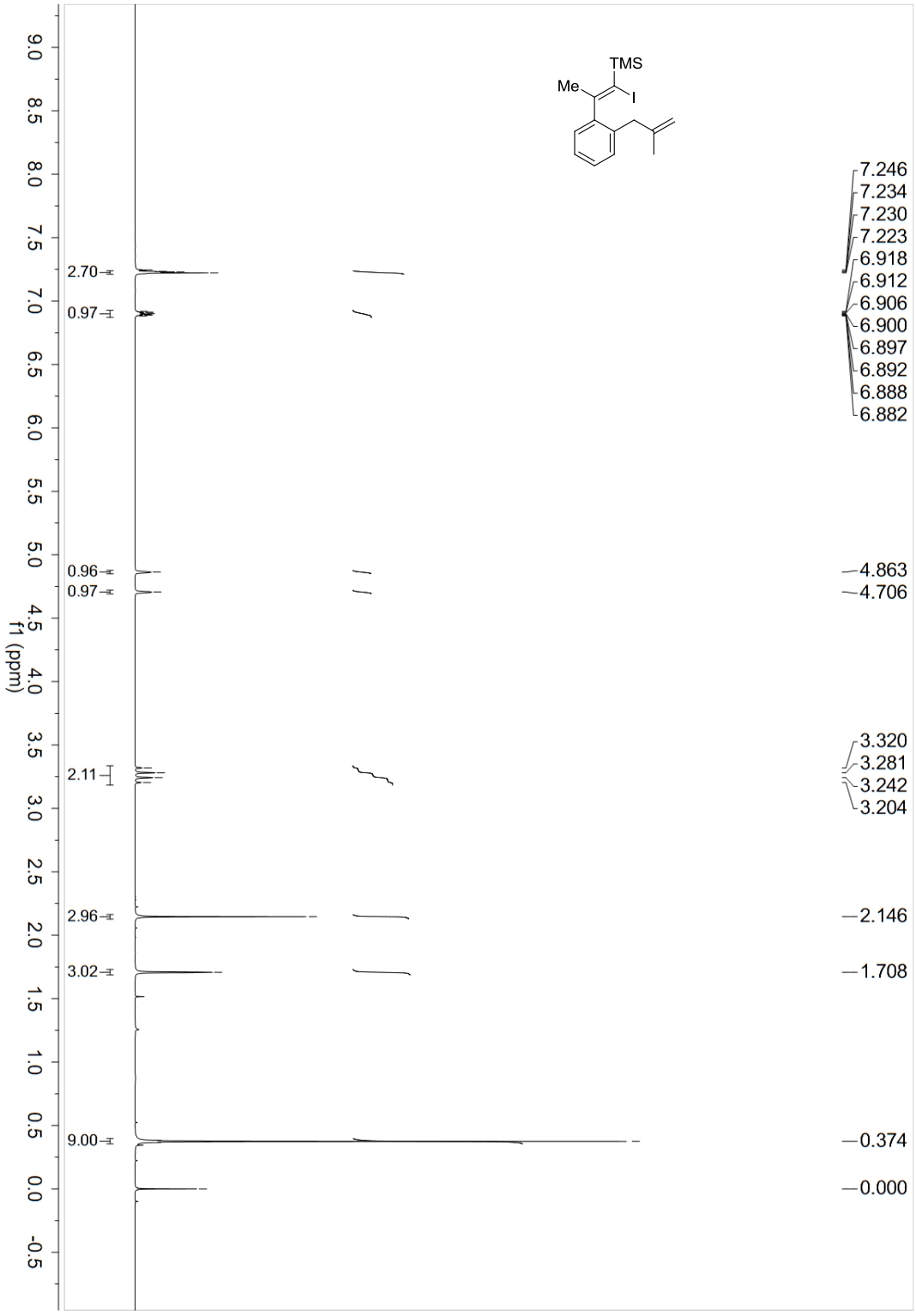
f1 (ppm)

5b2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6.900
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4.706
3.320
3.281
3.242
3.204
2.146
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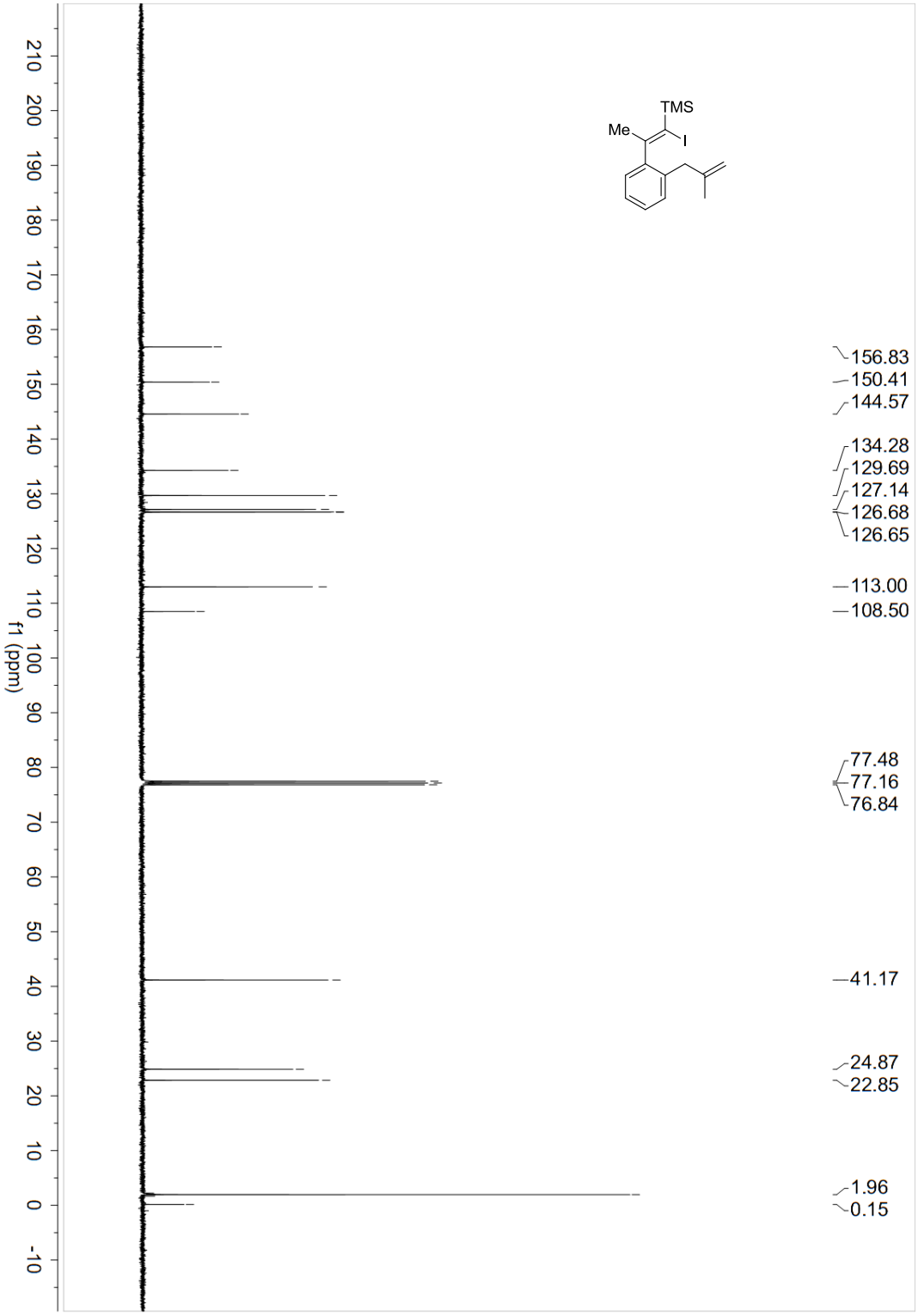
9.00
f1 (ppm)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127.14
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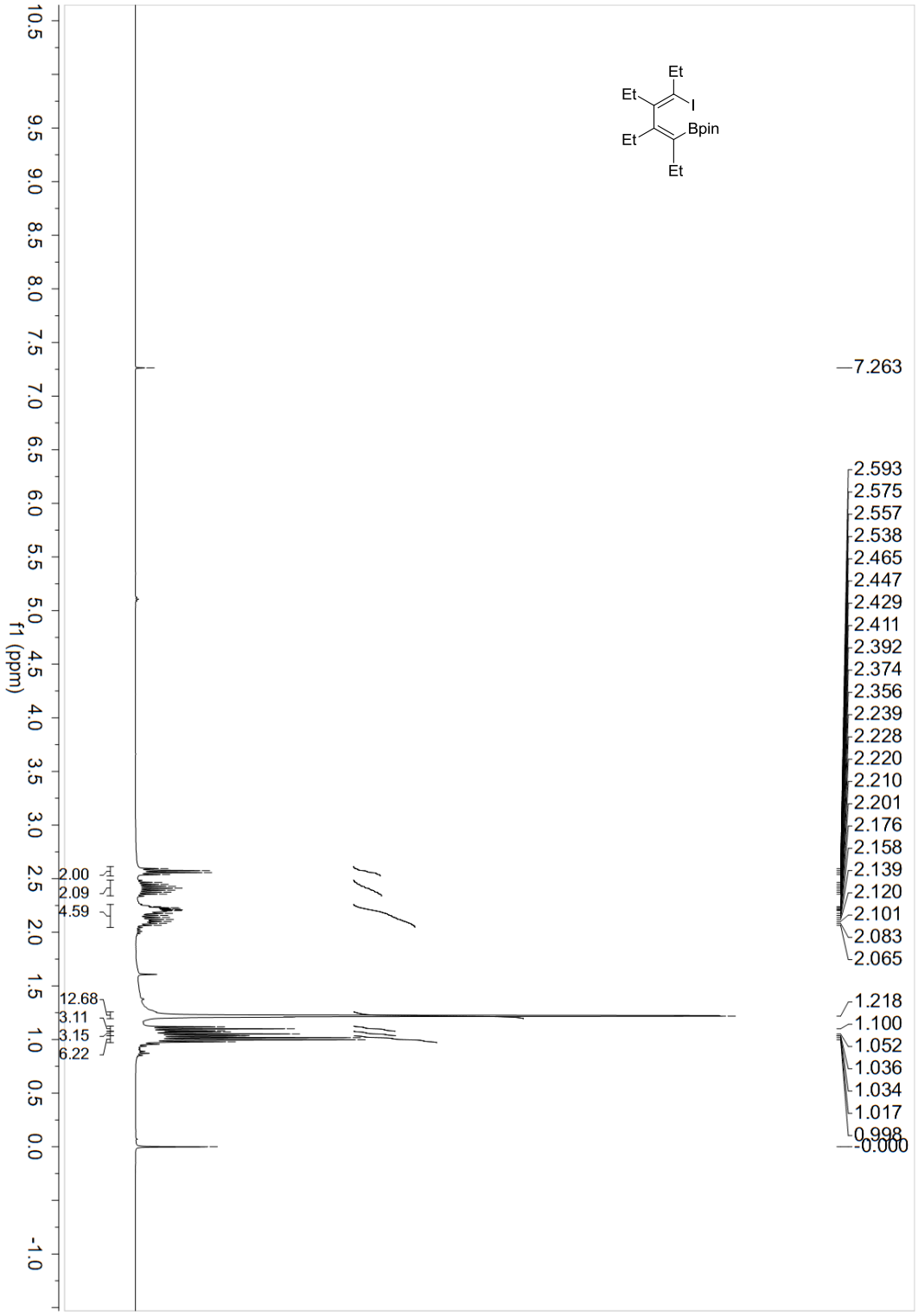
77.16
76.84
41.17
24.87
22.85
1.96
0.15
f1 (ppm)

6a


Et
Et
I
Et
Bpin
Et
f1 (ppm)
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9.0
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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
-1.0
2.00
2.09
4.59
12.68
3.11
3.15
6.22
7.263
2.593
2.575
2.557
2.538
2.465
2.447
2.429
2.411
2.392
2.374
2.356
2.239
2.228
2.220
2.210
2.201
2.176
2.158
2.139
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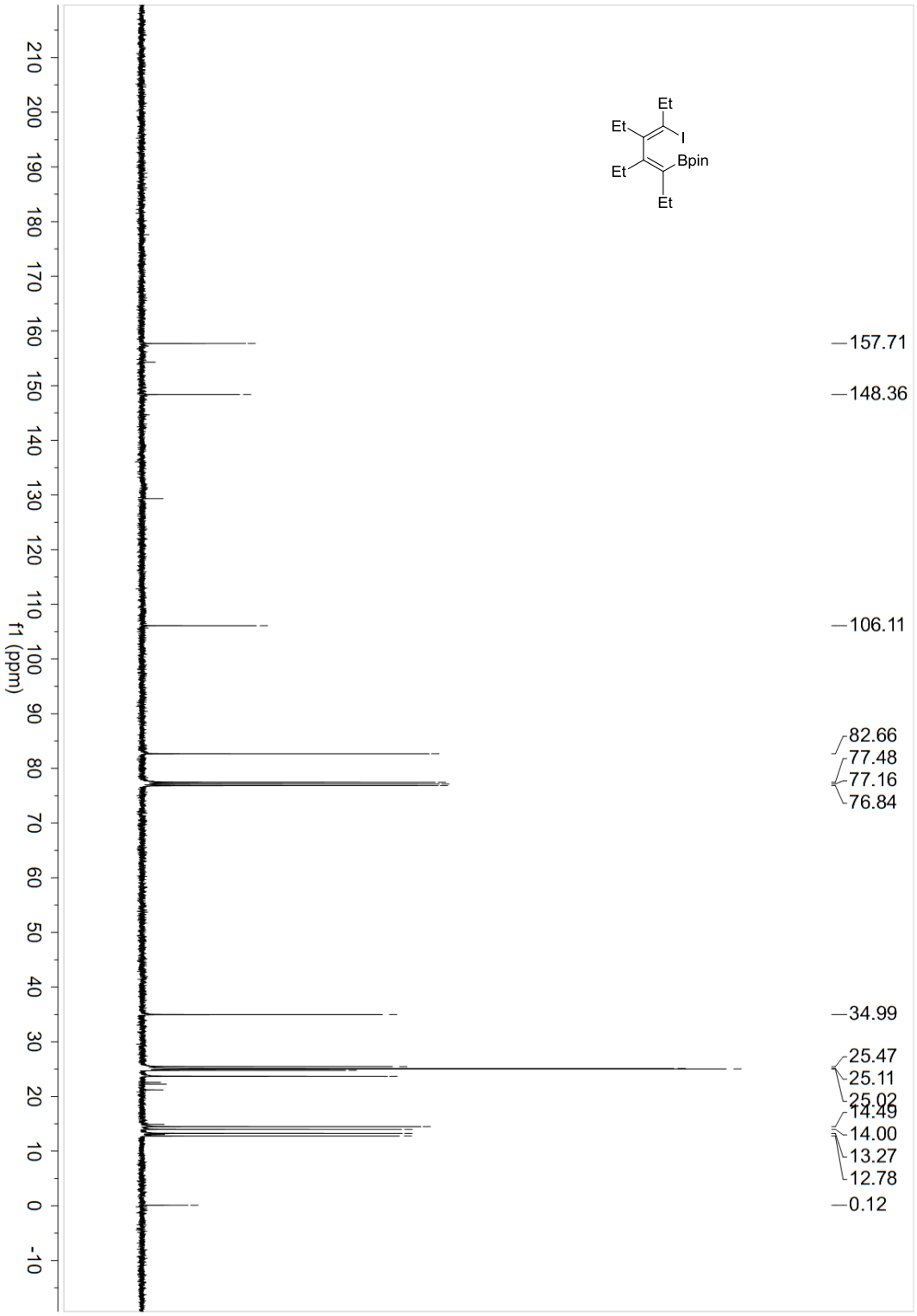
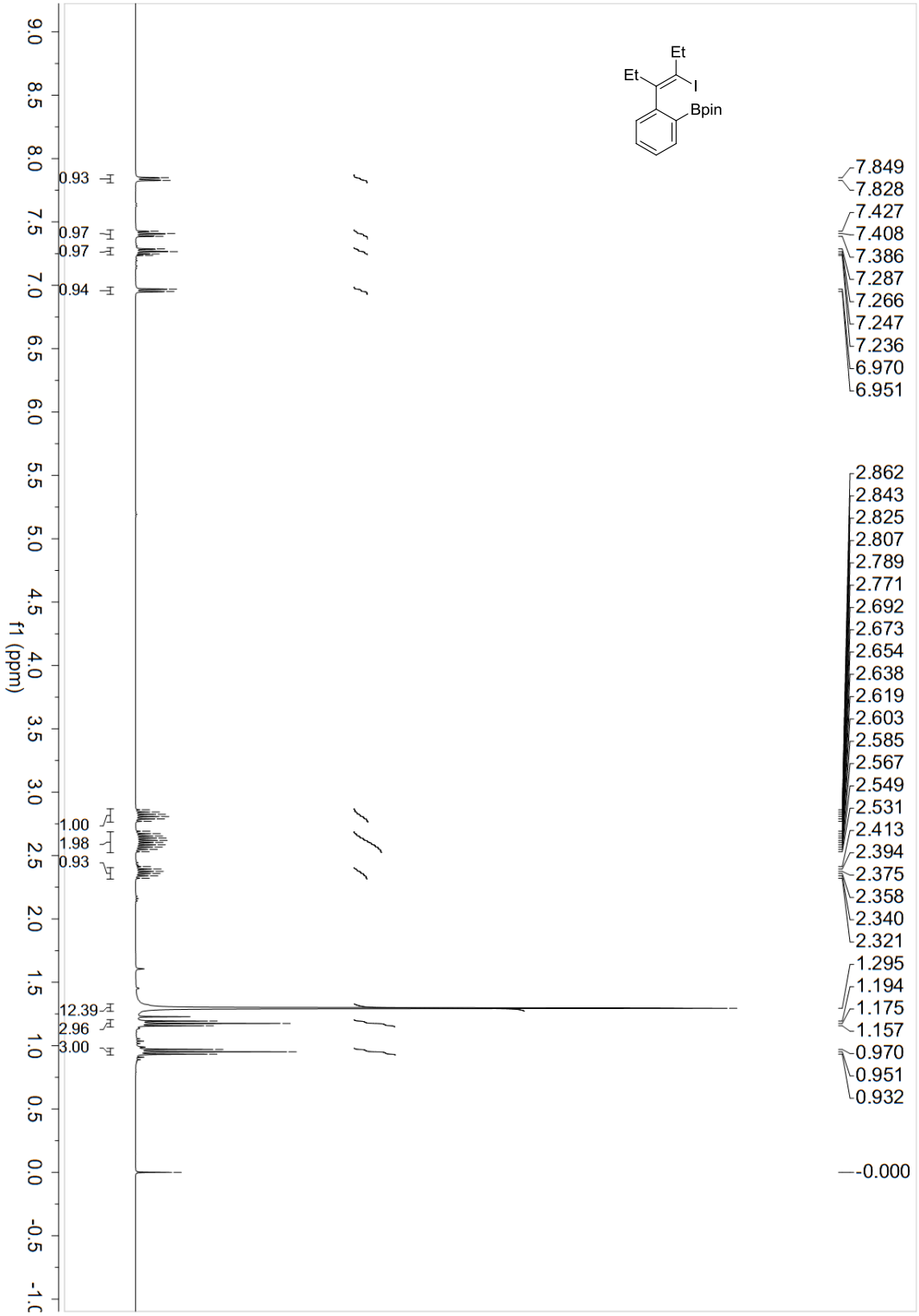

Et
Et
I
Bpin
Et
Et
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
157.71
148.36
106.11
82.66
77.48
77.16
76.84
34.99
25.47
25.11
25.02
14.49
14.00
13.27
12.78
0.12

6b1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Et
I
Bpin
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0.97
0.97
0.94
1.00
1.98
0.93
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2.96
3.00
7.849
7.828
7.427
7.408
7.386
7.287
7.266
7.247
7.236
6.970
6.951
2.862
2.843
2.825
2.807
2.789
2.771
2.692
2.673
2.654
2.638
2.619
2.603
2.585
2.567
2.549
2.531
2.413
2.394
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2.358
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2.321
1.295
1.194
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0.970
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0.932
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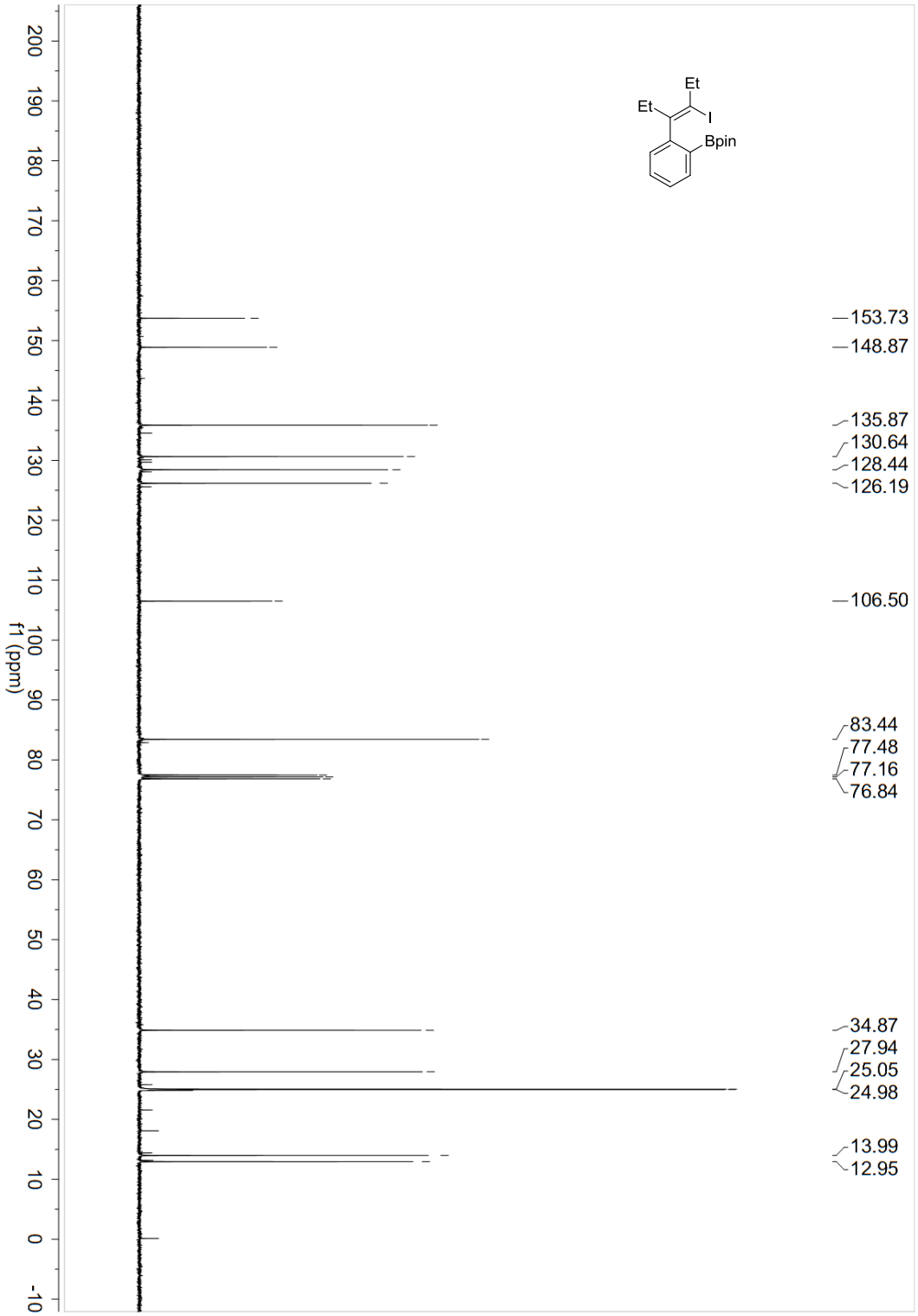
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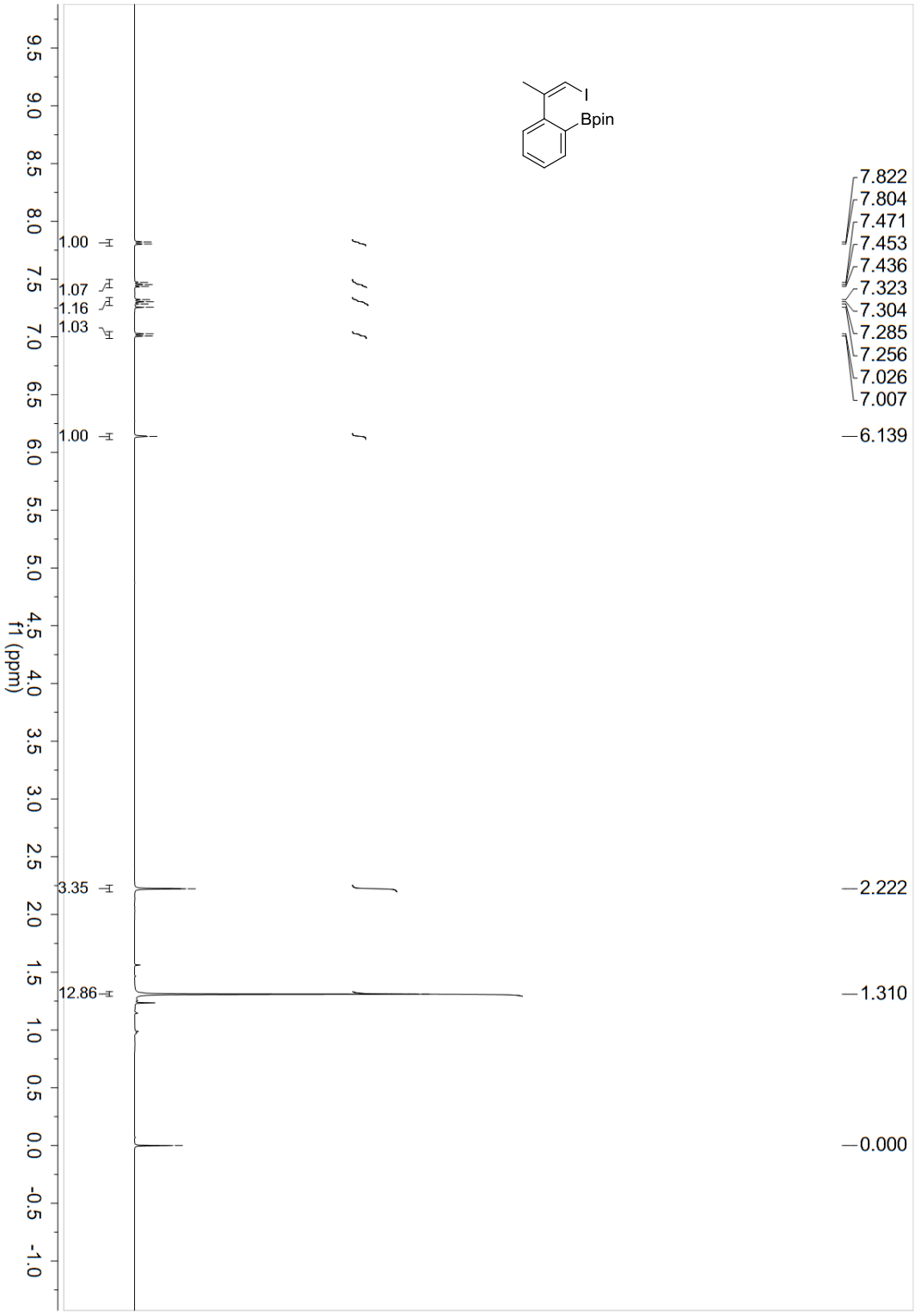
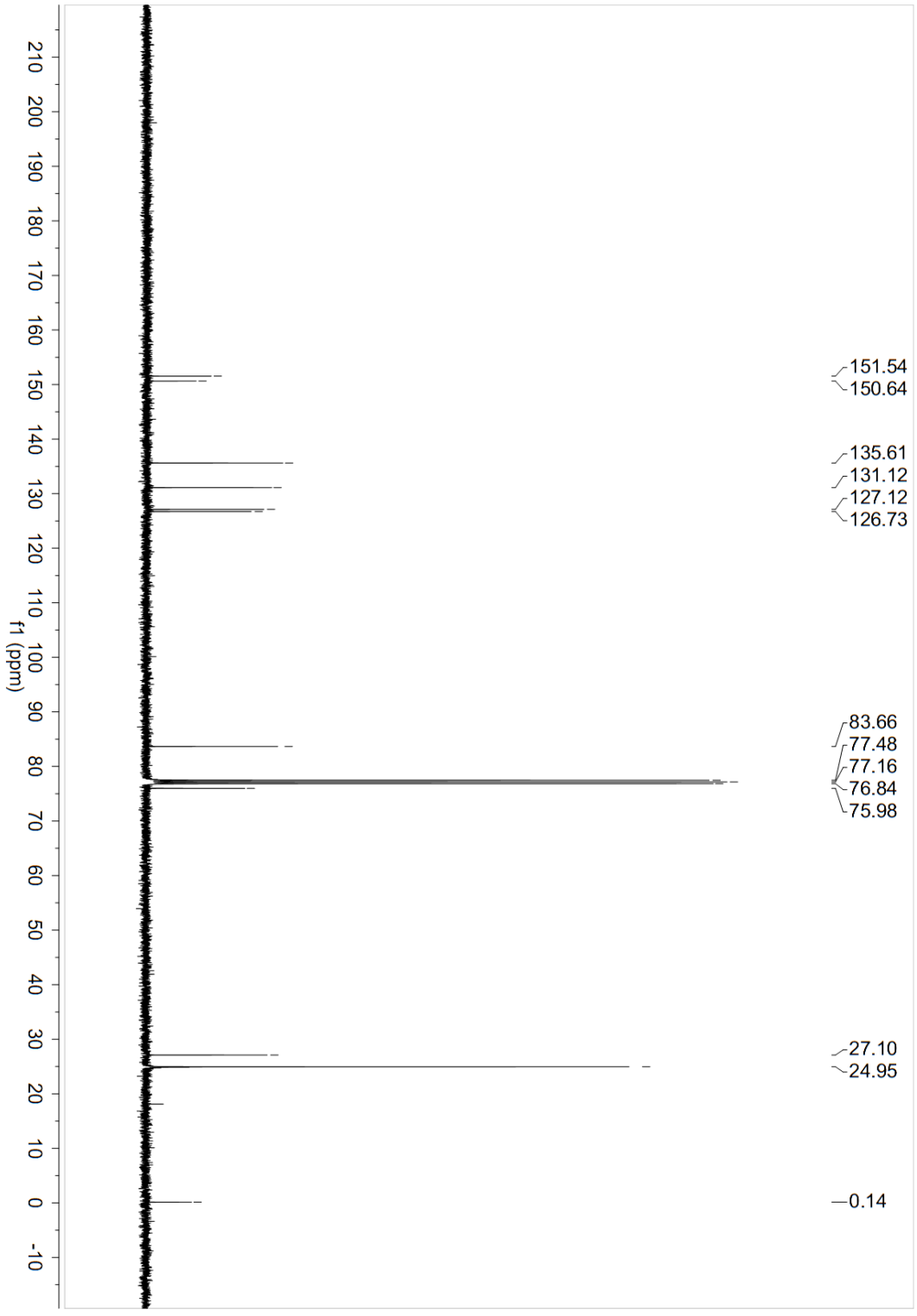
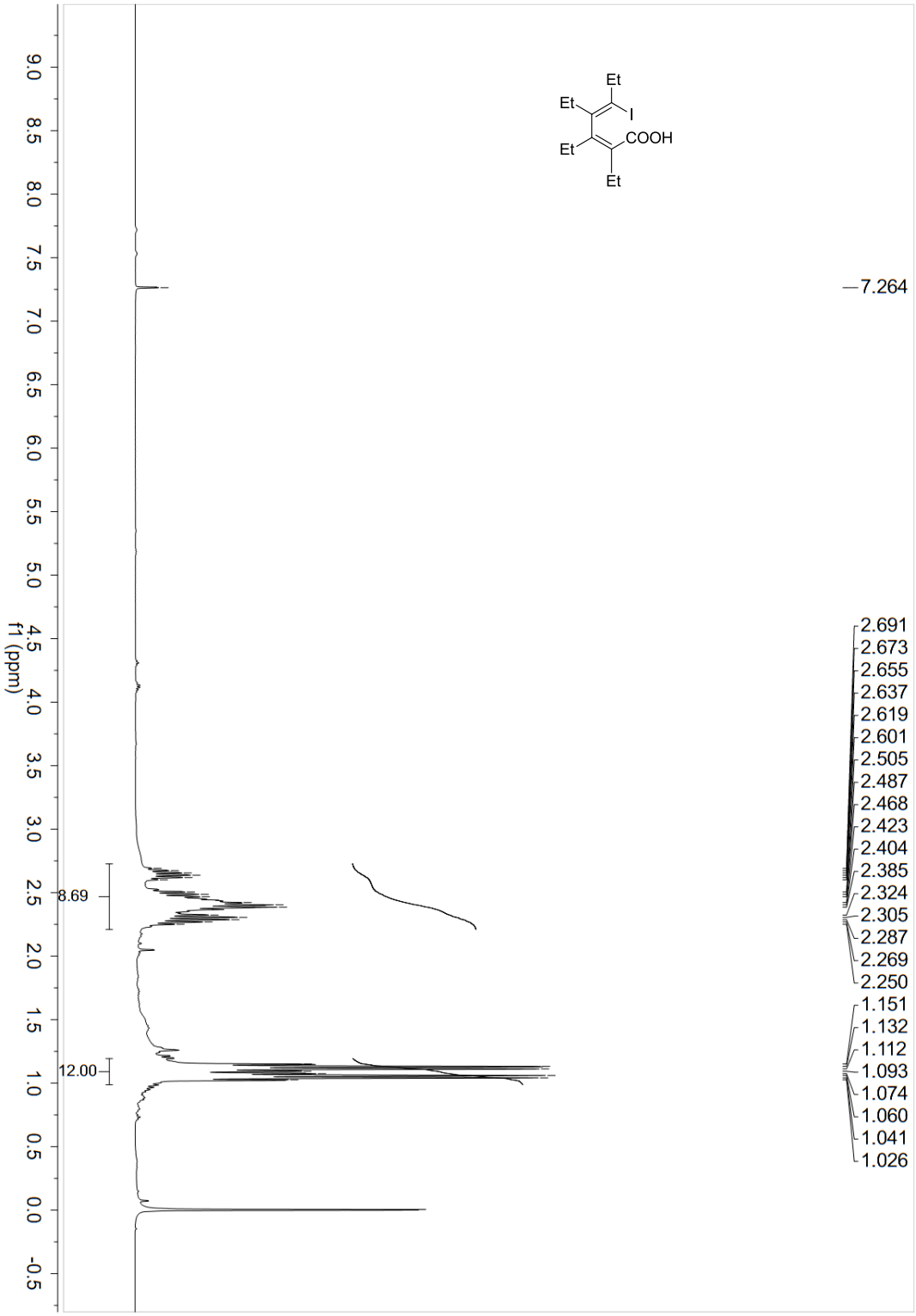
76.84
34.87
27.94
25.05
24.98
13.99
12.95
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

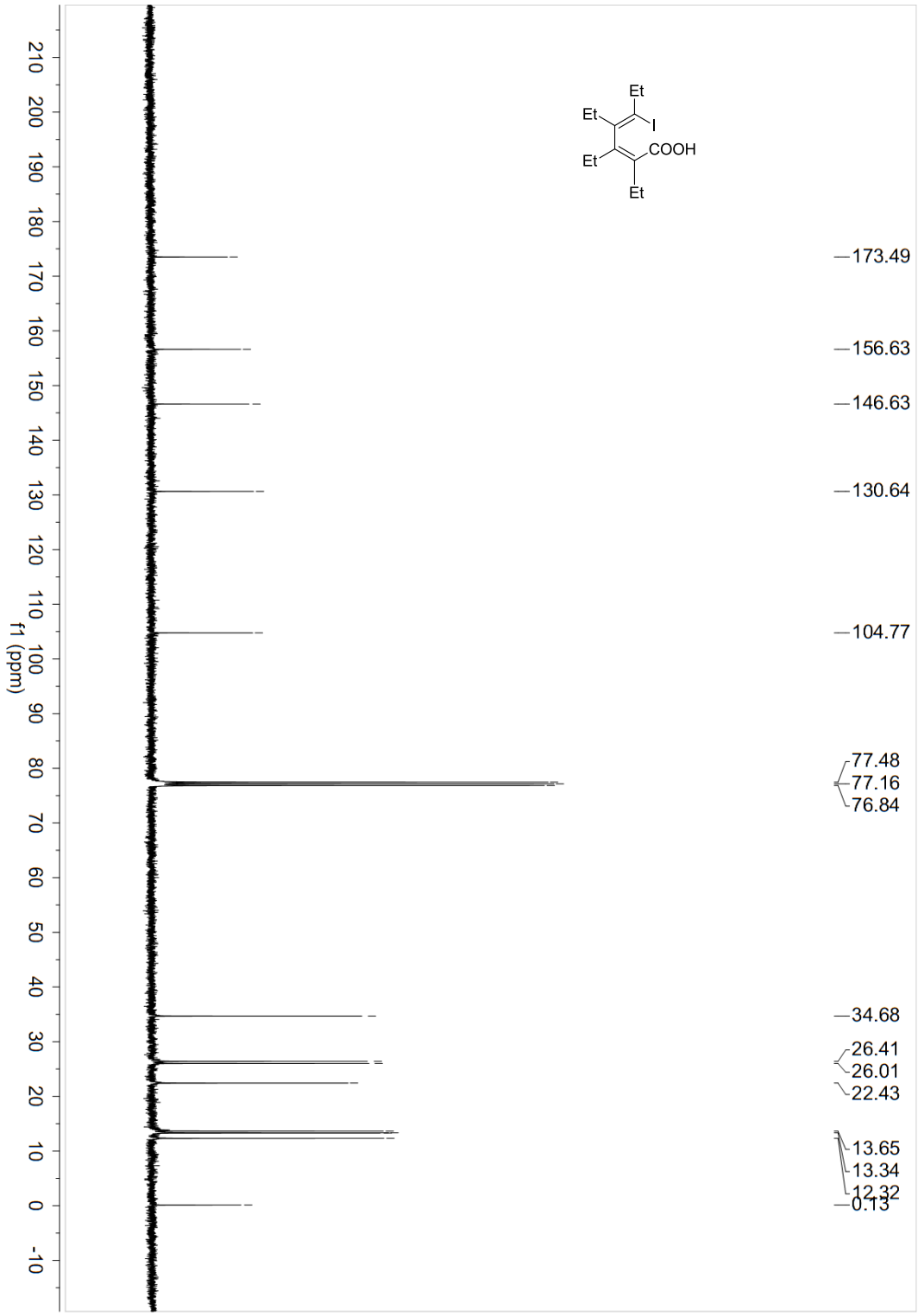
6b2


I
Bpin
7.822
7.804
7.471
7.453
7.436
7.323
7.304
7.285
7.256
7.026
7.007
6.139
2.222
1.310
0.000
1.00
1.07
1.16
1.03
1.00
3.35
12.86
f1 (ppm)

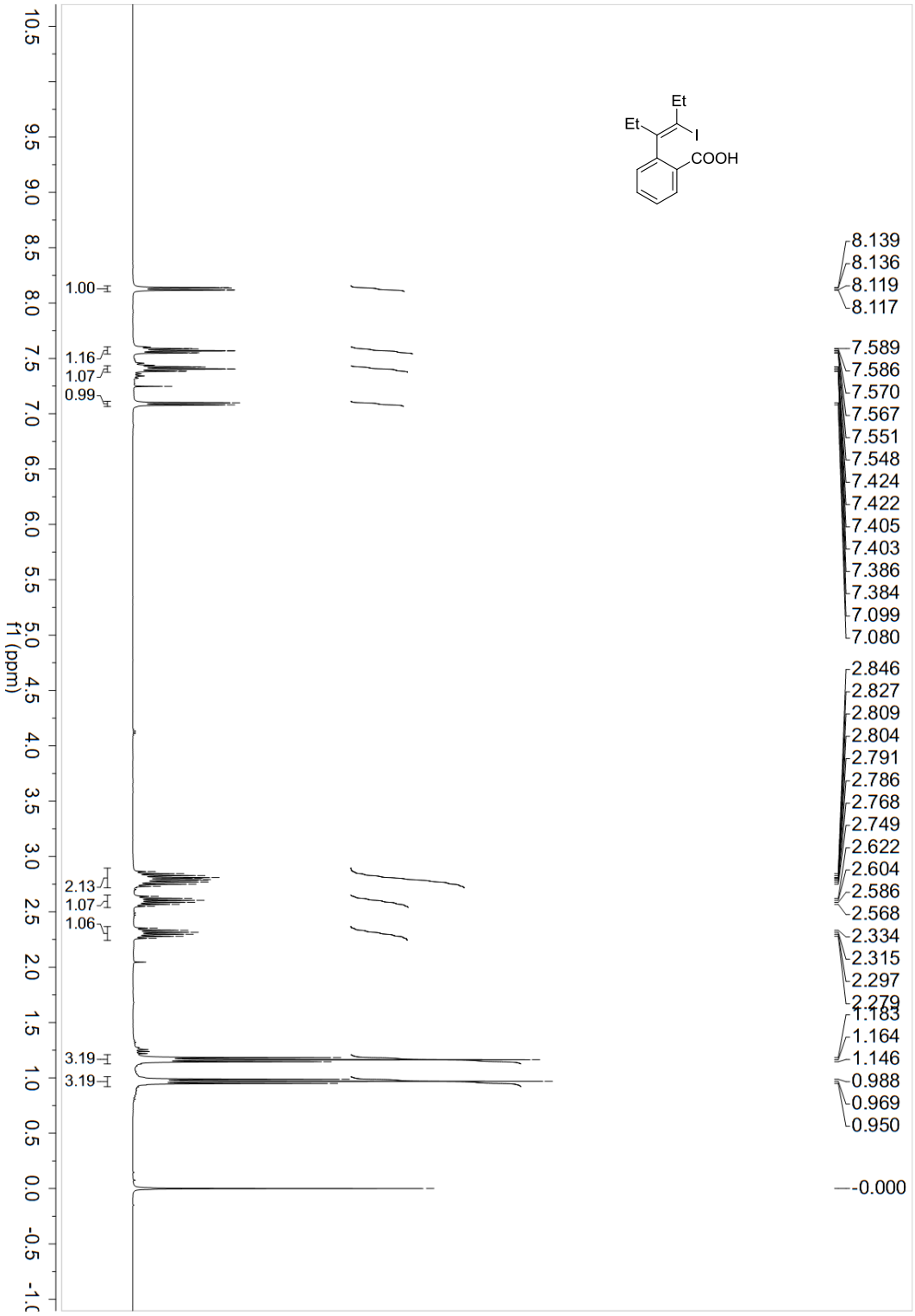

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
151.54
150.64
135.61
131.12
127.12
126.73
83.66
77.48
77.16
76.84
75.98
27.10
24.95
0.14

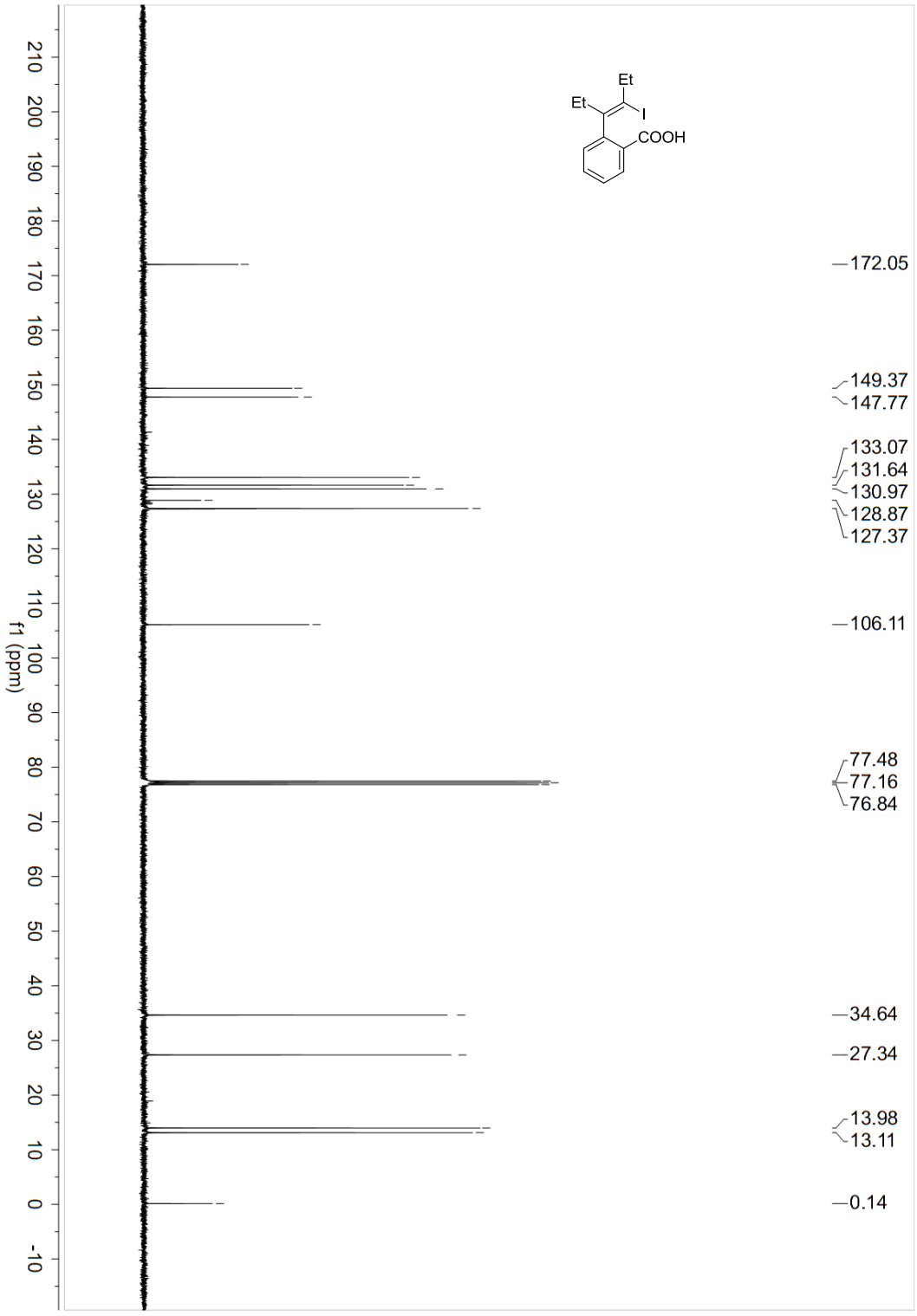
7a


Et
Et
I
Et
COOH
Et
7.264
2.691
2.673
2.655
2.637
2.619
2.601
2.505
2.487
2.468
2.423
2.404
2.385
2.324
2.305
2.287
2.269
2.250
1.151
1.132
1.112
1.093
1.074
1.060
1.041
1.026
8.69
12.00
f1 (ppm)

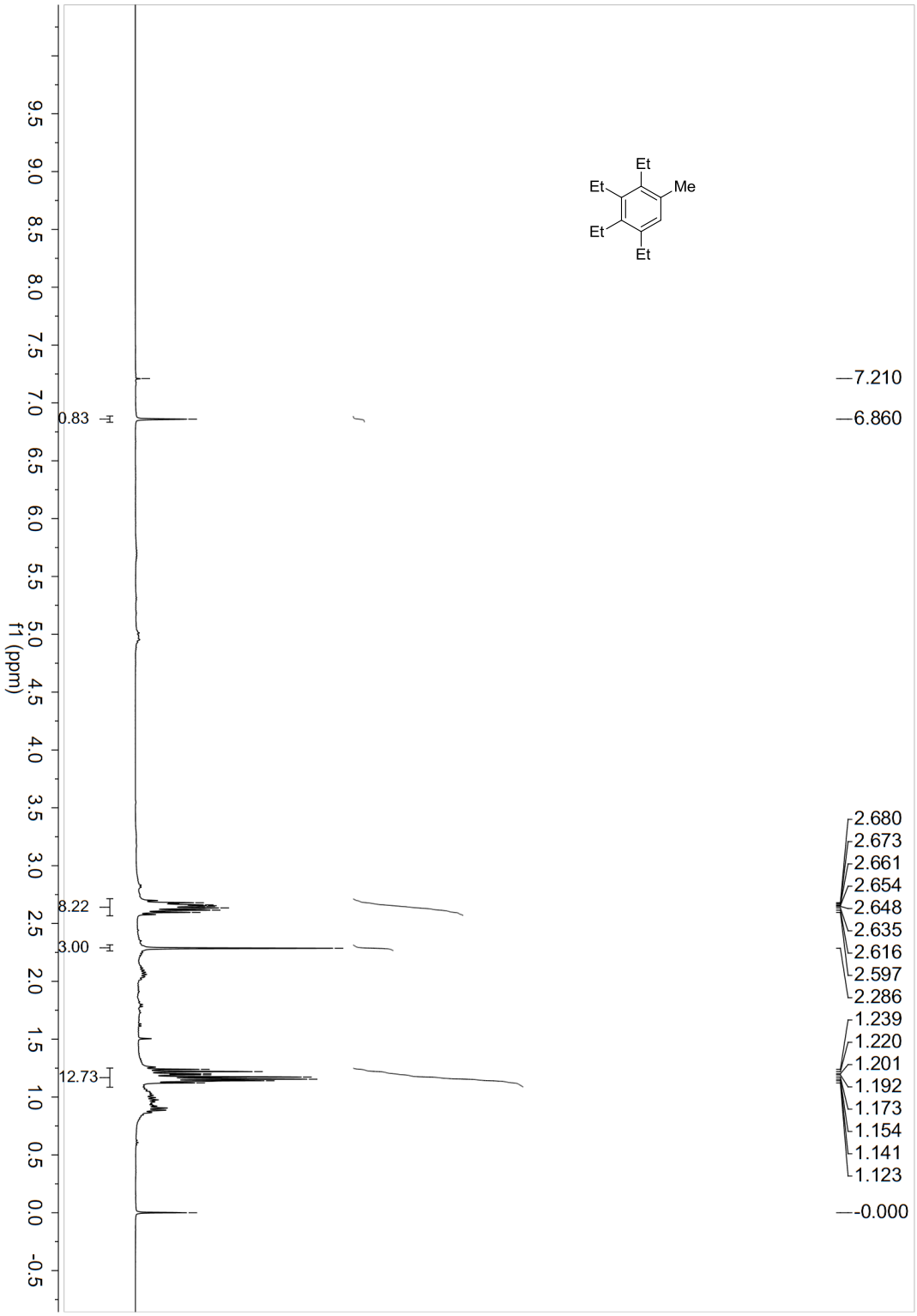

Et
Et
I
COOH
Et
Et
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
173.49
156.63
146.63
130.64
104.77
77.48
77.16
76.84
34.68
26.41
26.01
22.43
13.65
13.34
12.32
0.13

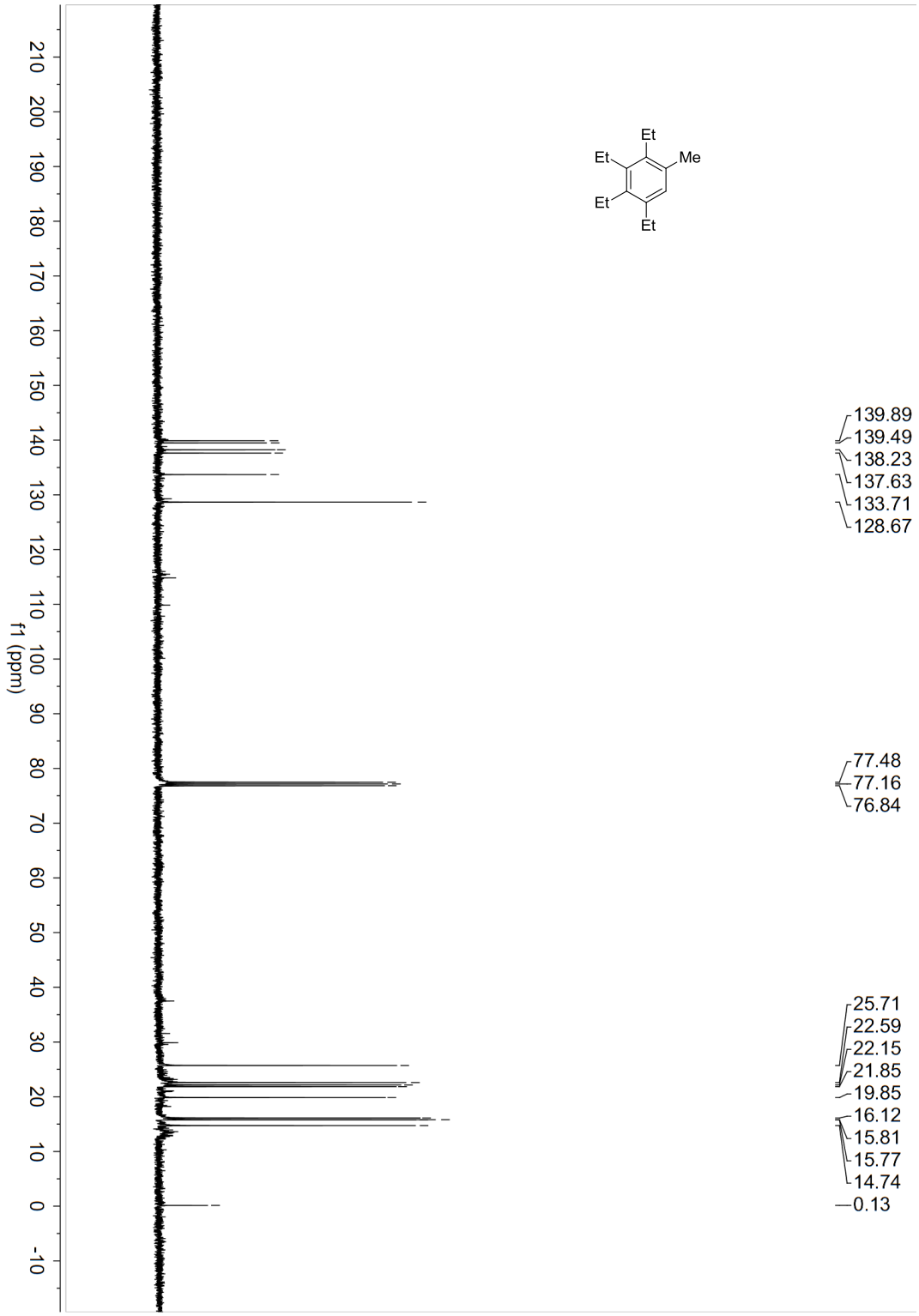
7b


Et
Et
I
COOH
f1 (ppm)
1.00
1.16
1.07
0.99
2.13
1.07
1.06
3.19
3.19
8.139
8.136
8.119
8.117
7.589
7.586
7.570
7.567
7.551
7.548
7.424
7.422
7.405
7.403
7.386
7.384
7.099
7.080
2.846
2.827
2.809
2.804
2.791
2.786
2.768
2.749
2.622
2.604
2.586
2.568
2.334
2.315
2.297
2.279
1.183
1.164
1.146
0.988
0.969
0.950
-0.000

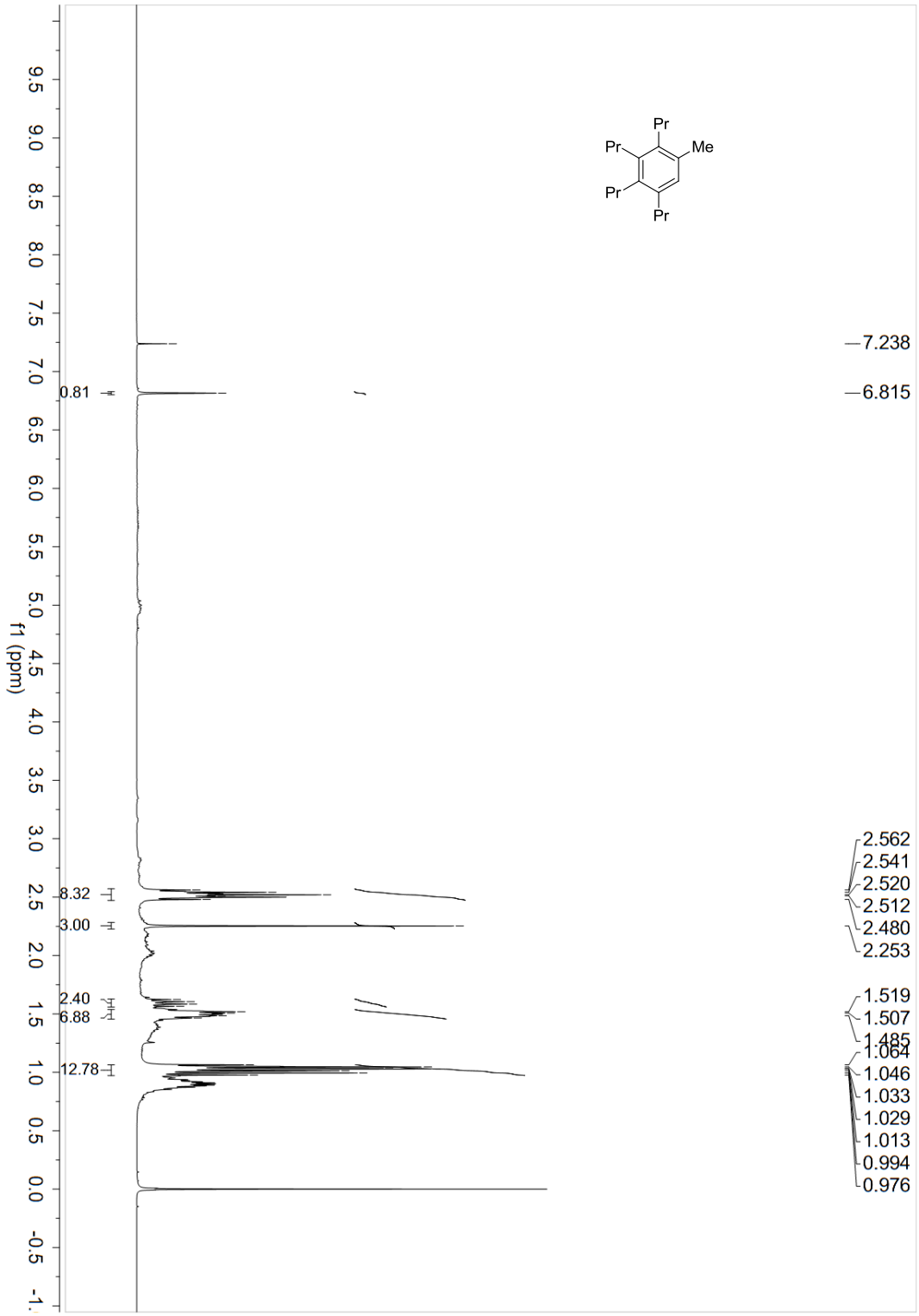

Et
Et
I
COOH
172.05
149.37
147.77
133.07
131.64
130.97
128.87
127.37
106.11
77.48
77.16
76.84
34.64
27.34
13.98
13.11
0.14
f1 (ppm)

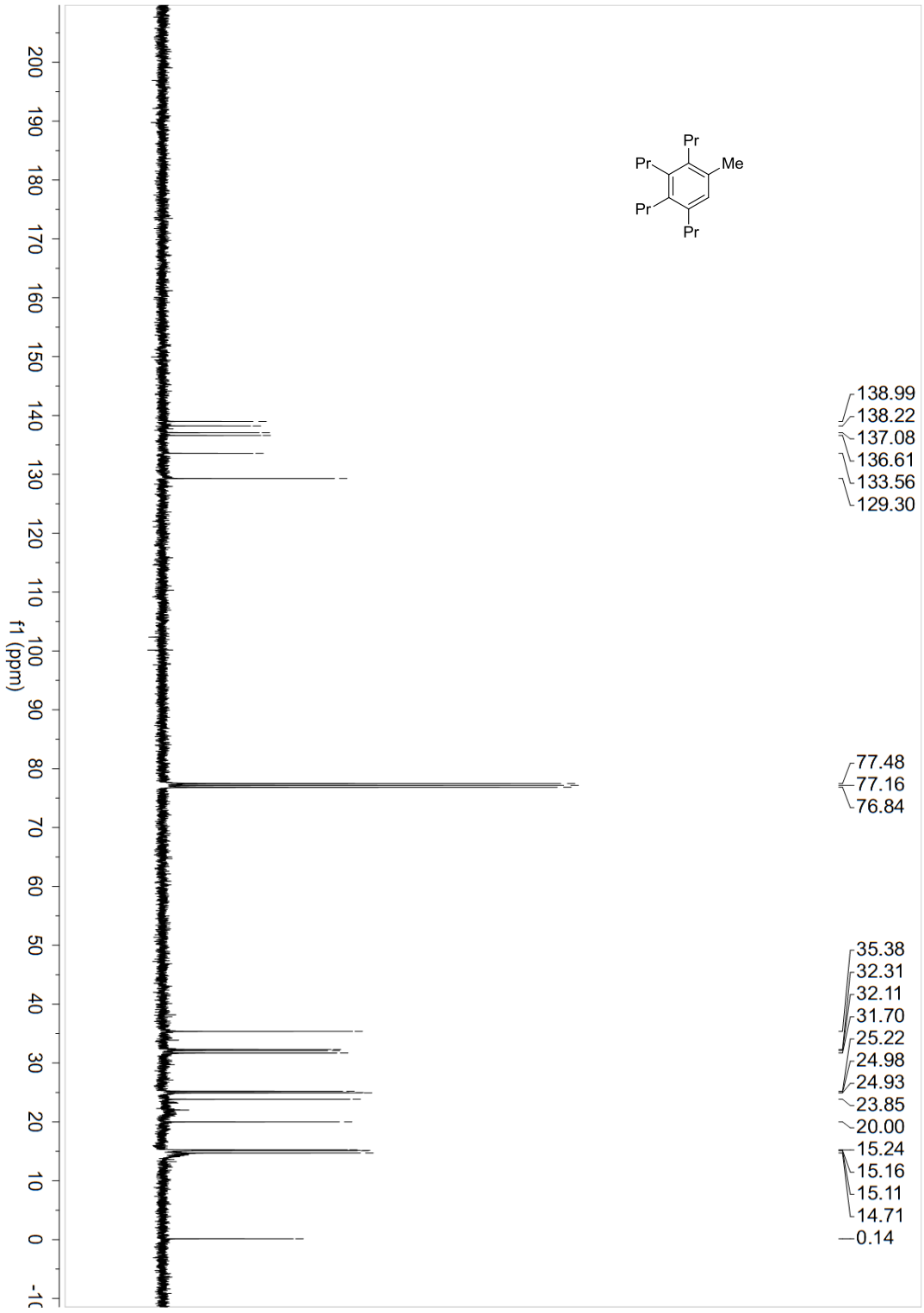
8a1


Et
Et
Me
Et
Et
f1 (ppm)
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
-0.5
0.83
8.22
3.00
12.73
7.210
6.860
2.680
2.673
2.661
2.654
2.648
2.635
2.616
2.597
2.286
1.239
1.220
1.201
1.192
1.173
1.154
1.141
1.123
-0.000

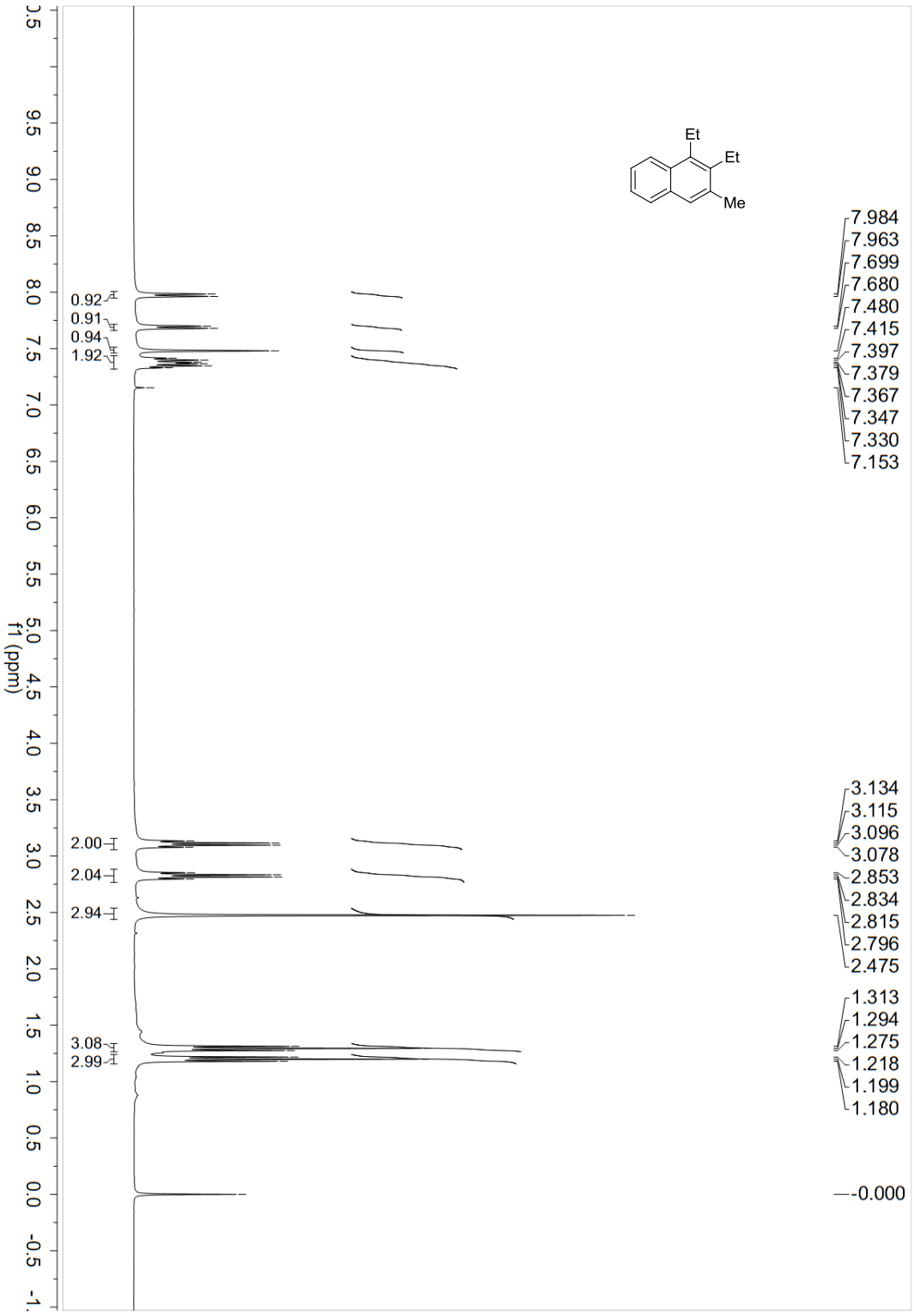

Et
Et
Me
Et
Et
139.89
139.49
138.23
137.63
133.71
128.67
77.48
77.16
76.84
25.71
22.59
22.15
21.85
19.85
16.12
15.81
15.77
14.74
0.13
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

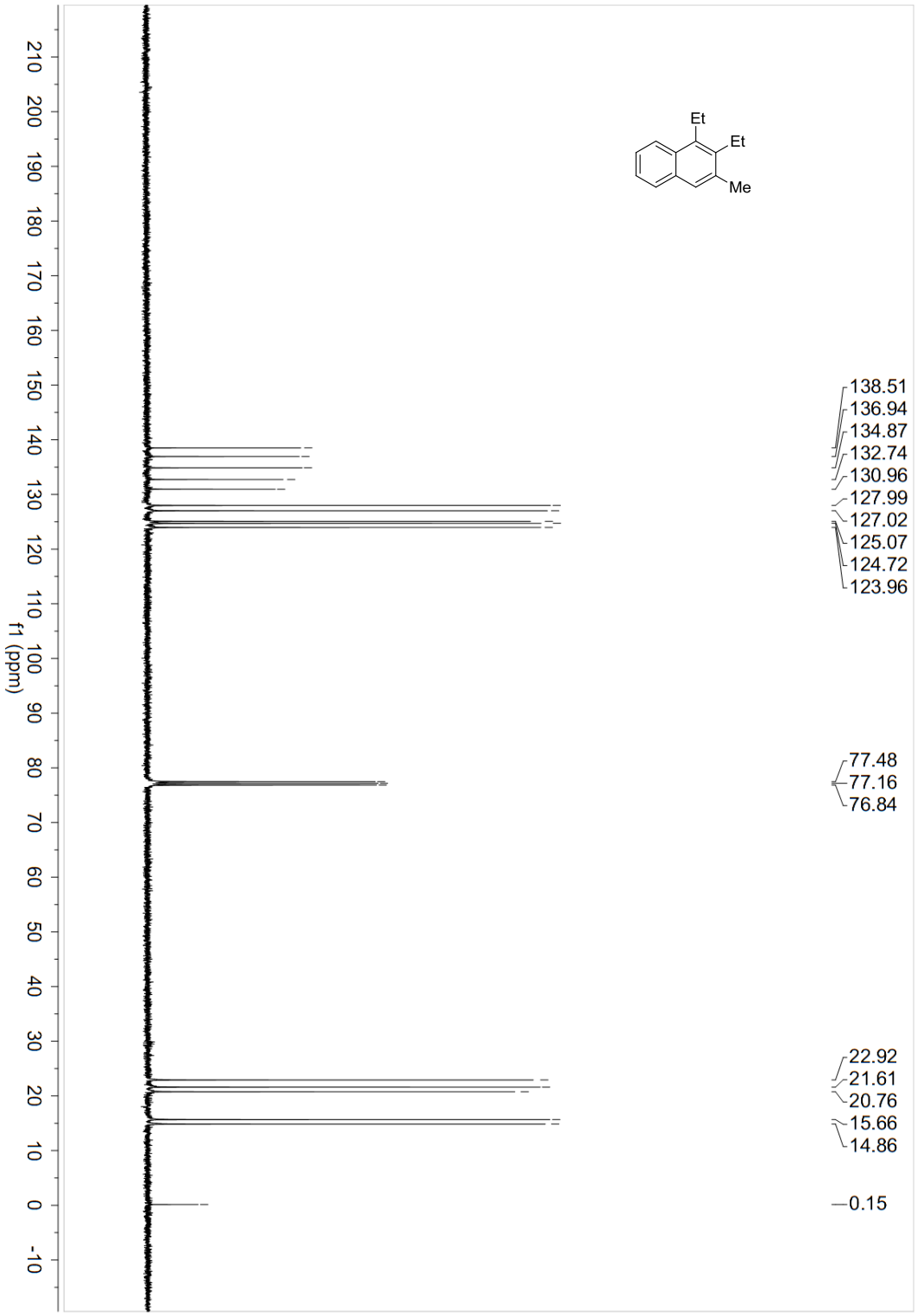
8a2


Pr
Pr
Me
Pr
Pr
f1 (ppm)
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
-0.5
0.81
8.32
3.00
2.40
6.88
12.78
7.238
6.815
2.562
2.541
2.520
2.512
2.480
2.253
1.519
1.507
1.485
1.064
1.046
1.033
1.029
1.013
0.994
0.976

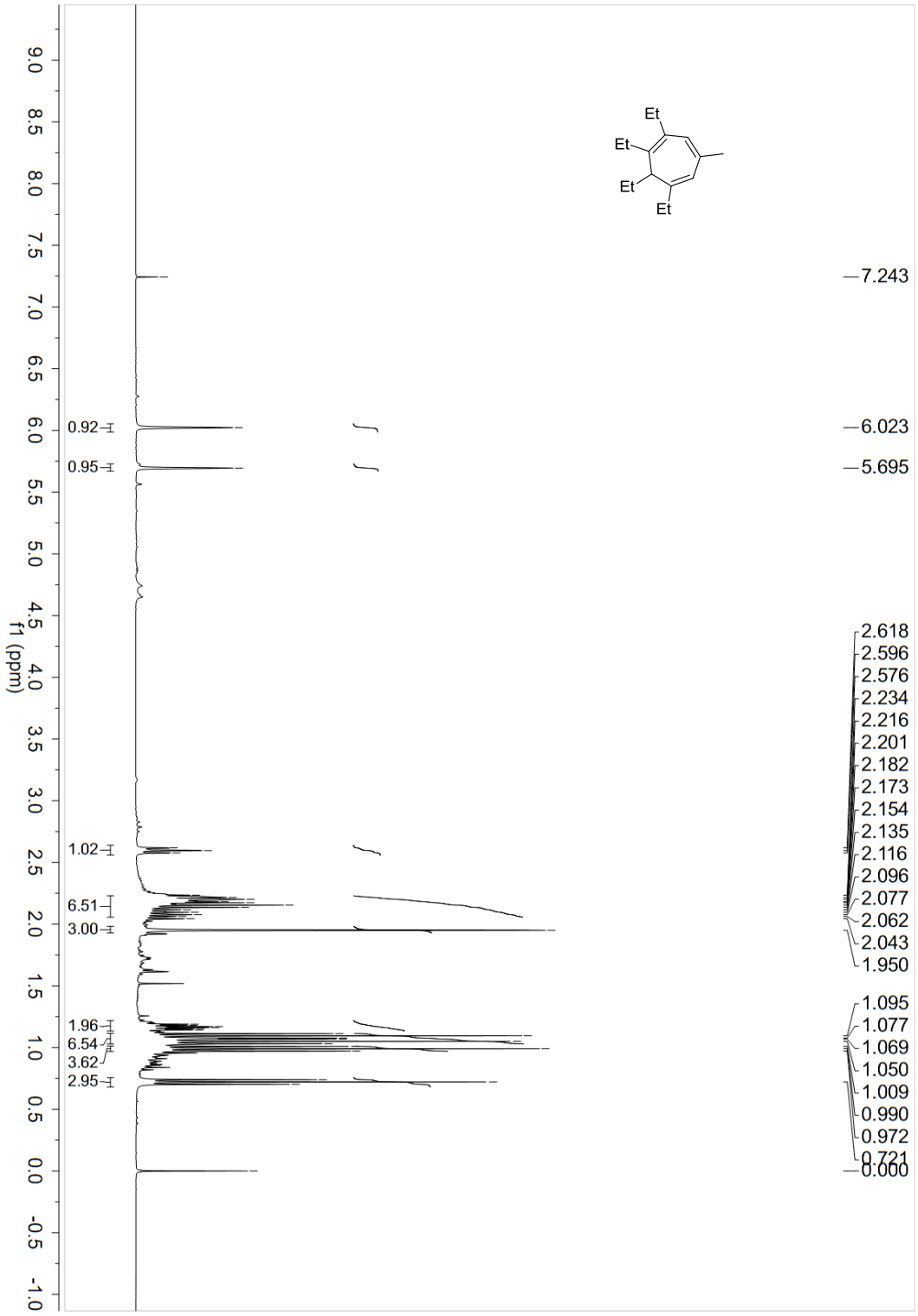

Pr
Pr
Me
Pr
Pr
138.99
138.22
137.08
136.61
133.56
129.30
77.48
77.16
76.84
35.38
32.31
32.11
31.70
25.22
24.98
24.93
23.85
20.00
15.24
15.16
15.11
14.71
0.14
f1 (ppm)

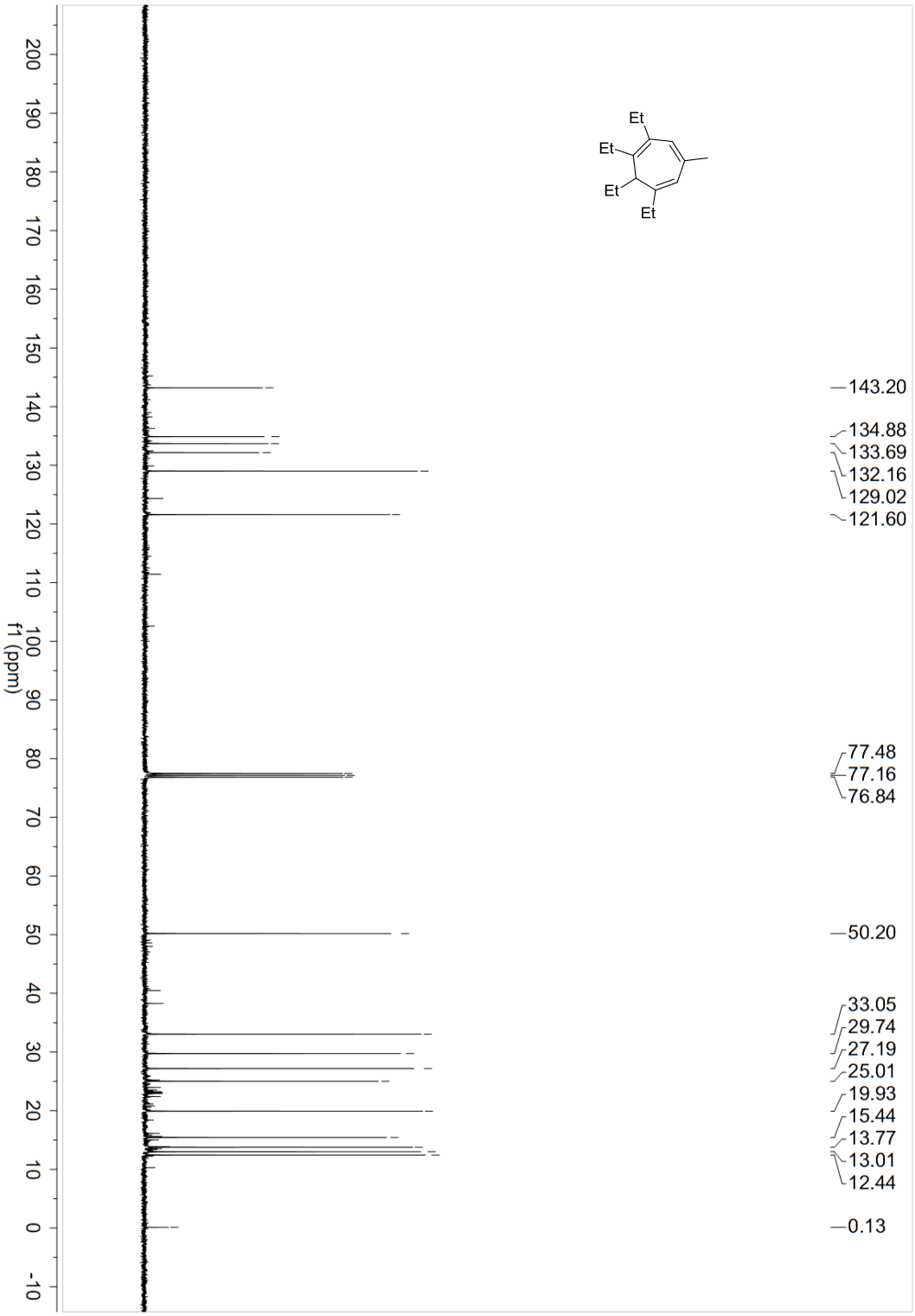
8b


Et
Et
Me
7.984
7.963
7.699
7.680
7.480
7.415
7.397
7.379
7.367
7.347
7.330
7.153
3.134
3.115
3.096
3.078
2.853
2.834
2.815
2.796
2.475
1.313
1.294
1.275
1.218
1.199
1.180
-0.000
0.92
0.91
0.94
1.92
2.00
2.04
2.94
3.08
2.99
f1 (ppm)

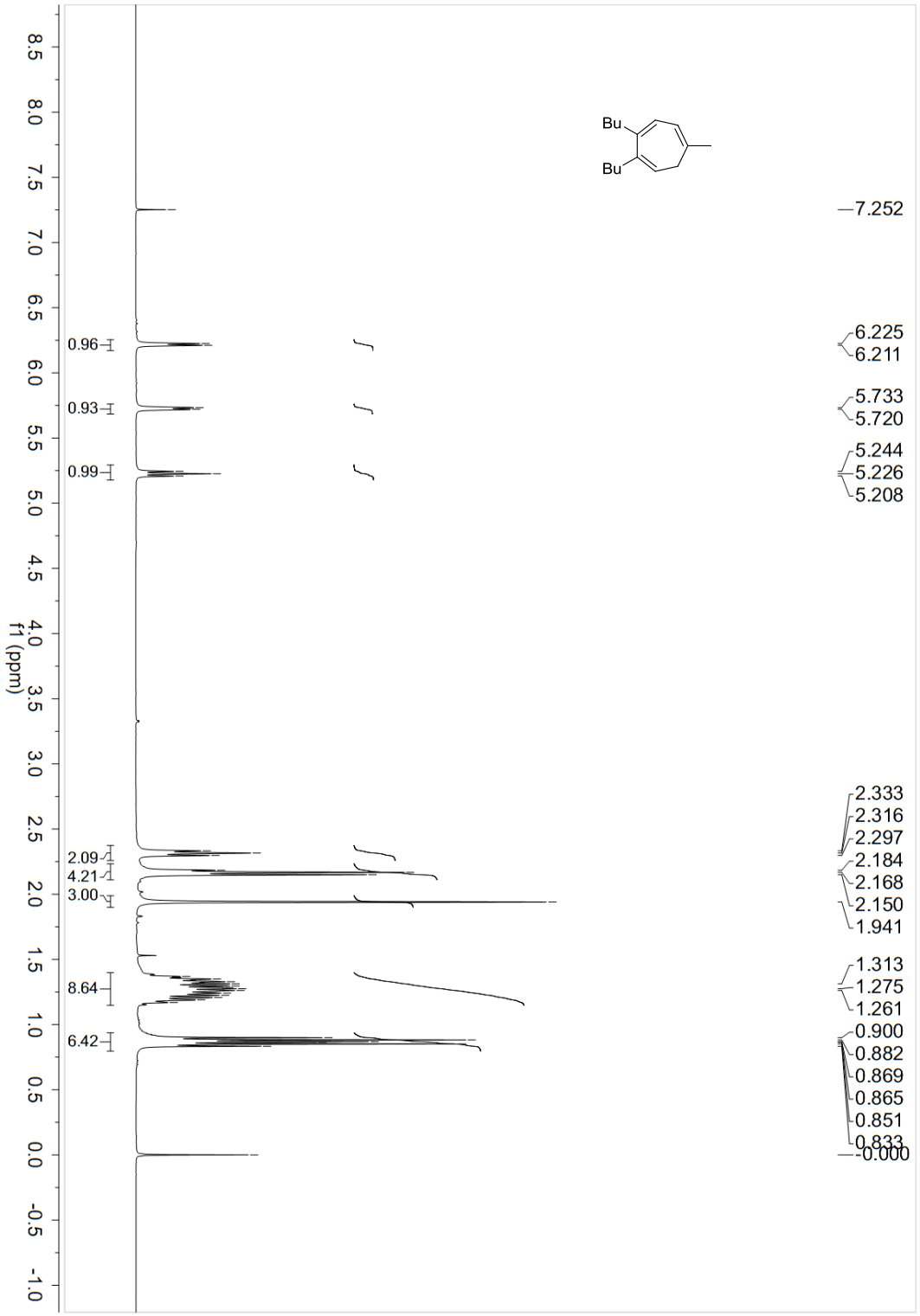

Et
Et
Me
138.51
136.94
134.87
132.74
130.96
127.99
127.02
125.07
124.72
123.96
77.48
77.16
76.84
22.92
21.61
20.76
15.66
14.86
0.15
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

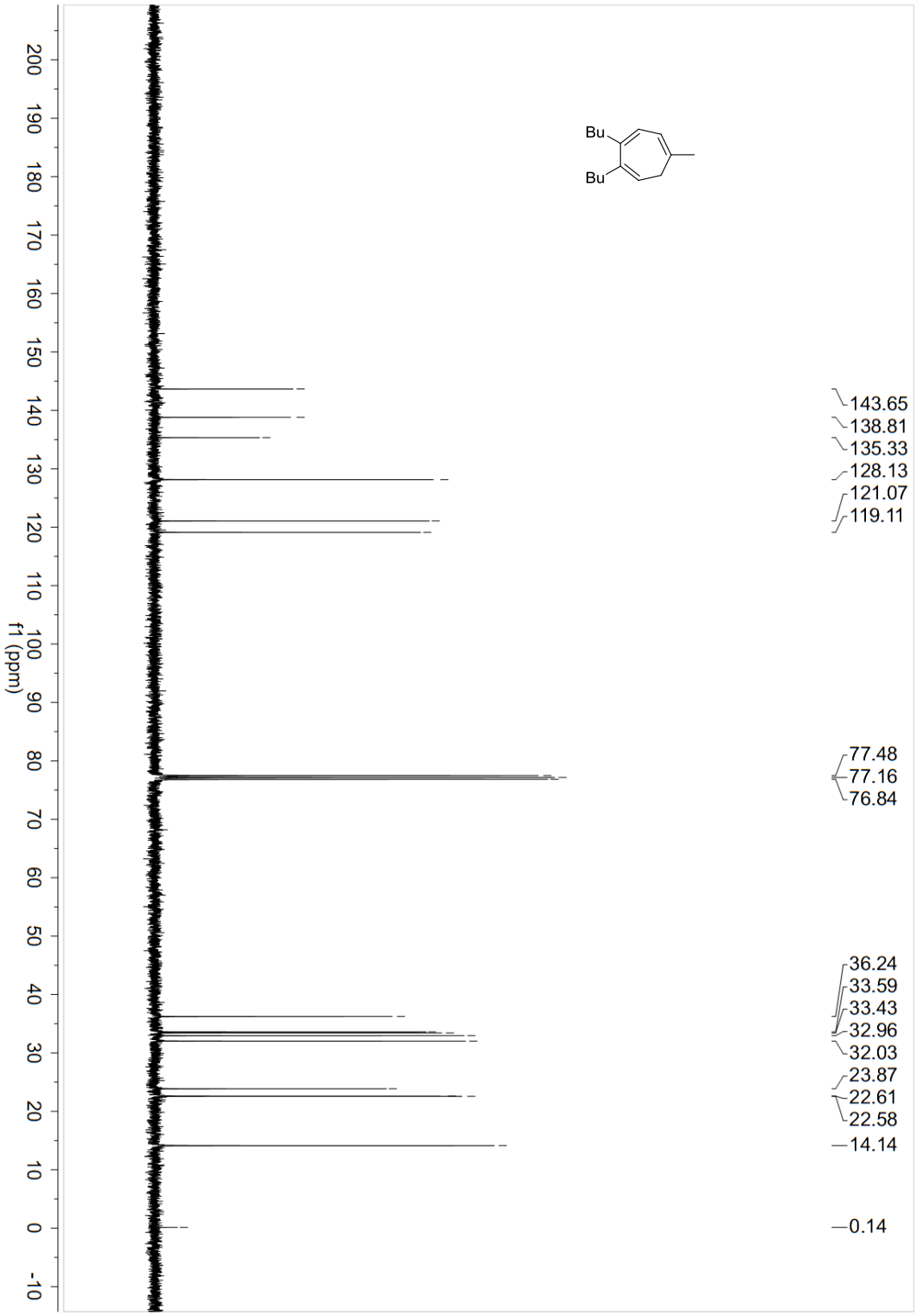
9a1


Et
Et
Et
Et
7.243
6.023
5.695
2.618
2.596
2.576
2.234
2.216
2.201
2.182
2.173
2.154
2.135
2.116
2.096
2.077
2.062
2.043
1.950
1.095
1.077
1.069
1.050
1.009
0.990
0.972
0.721
0.000
0.92
0.95
1.02
6.51
3.00
1.96
6.54
3.62
2.95
f1 (ppm)

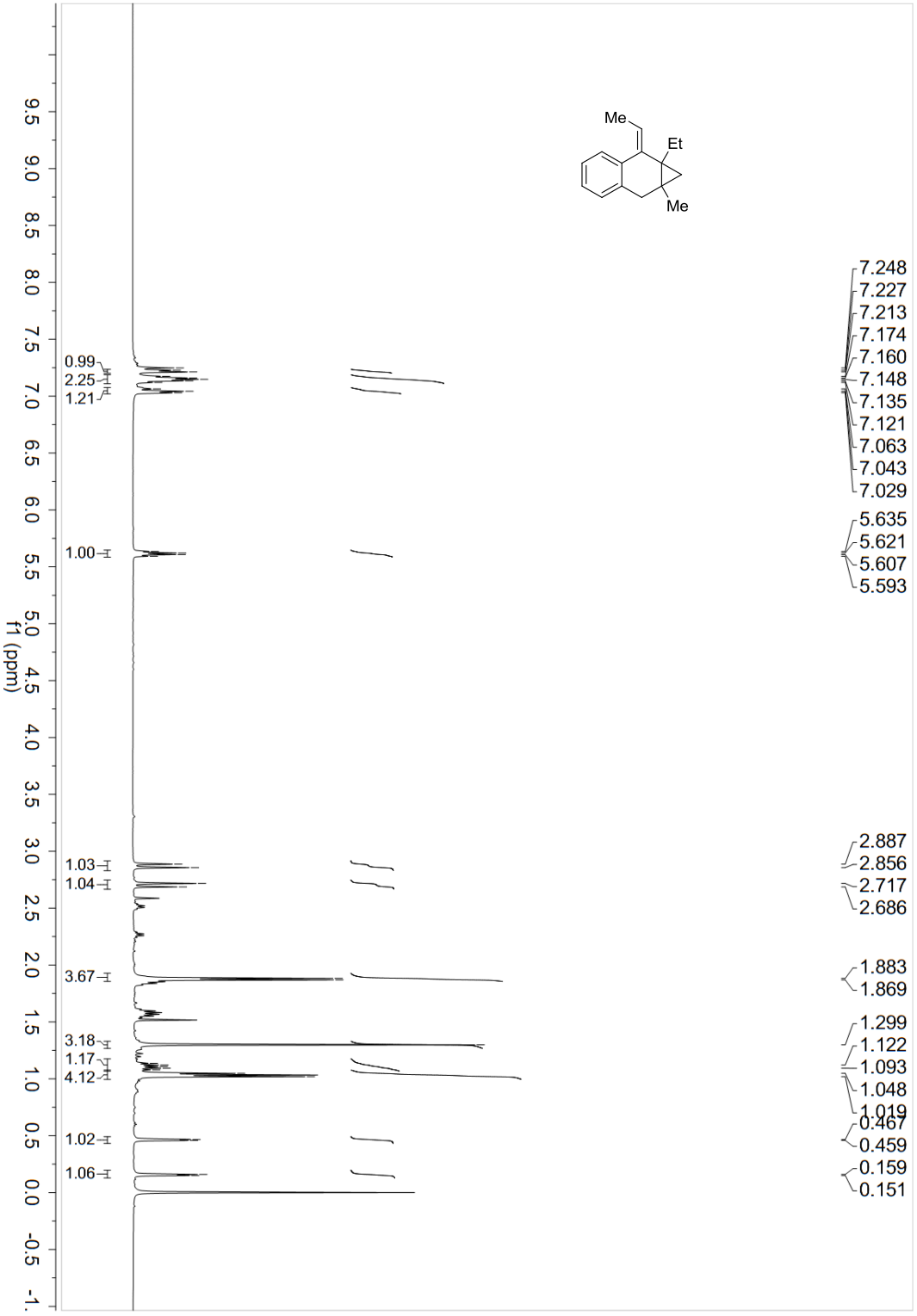

Et
Et
Et
Et
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
143.20
134.88
133.69
132.16
129.02
121.60
77.48
77.16
76.84
50.20
33.05
29.74
27.19
25.01
19.93
15.44
13.77
13.01
12.44
0.13

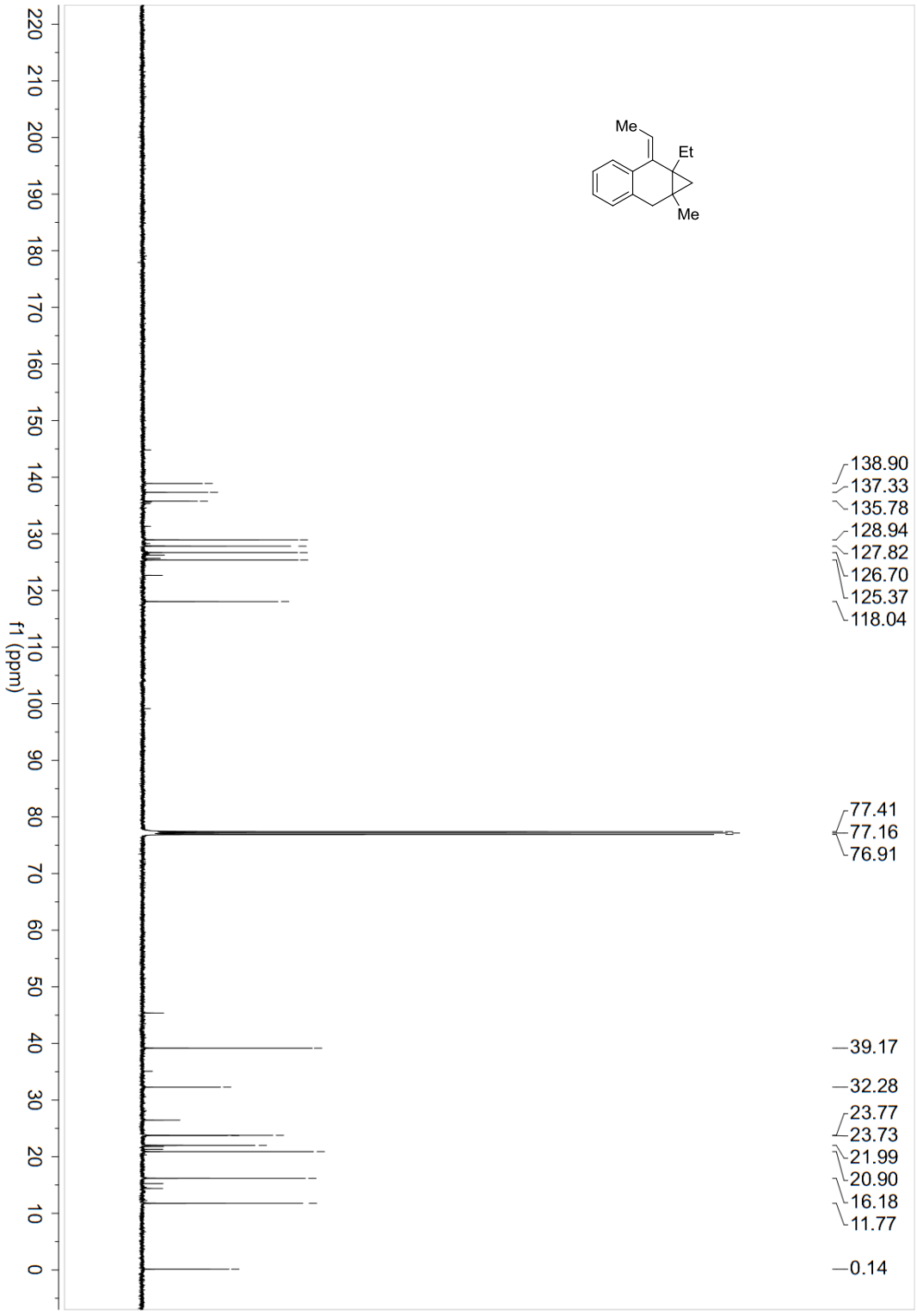
9a2


Bu
Bu
7.252
6.225
6.211
5.733
5.720
5.244
5.226
5.208
2.333
2.316
2.297
2.184
2.168
2.150
1.941
1.313
1.275
1.261
0.900
0.882
0.869
0.865
0.851
0.833
-0.000
0.96
0.93
0.99
2.09
4.21
3.00
8.64
6.42
f1 (ppm)

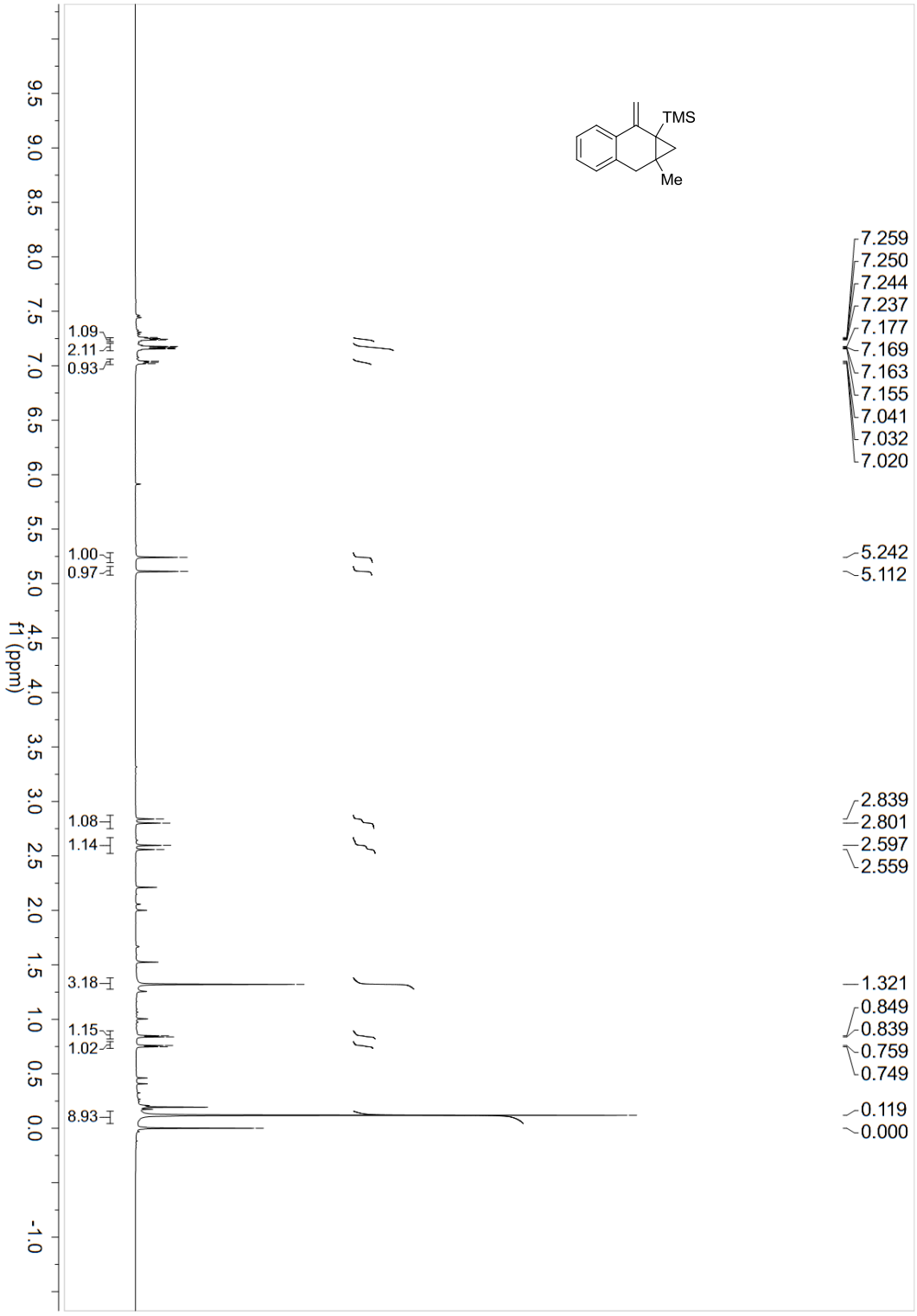

Bu
Bu
143.65
138.81
135.33
128.13
121.07
119.11
77.48
77.16
76.84
36.24
33.59
33.43
32.96
32.03
23.87
22.61
22.58
14.14
0.14
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

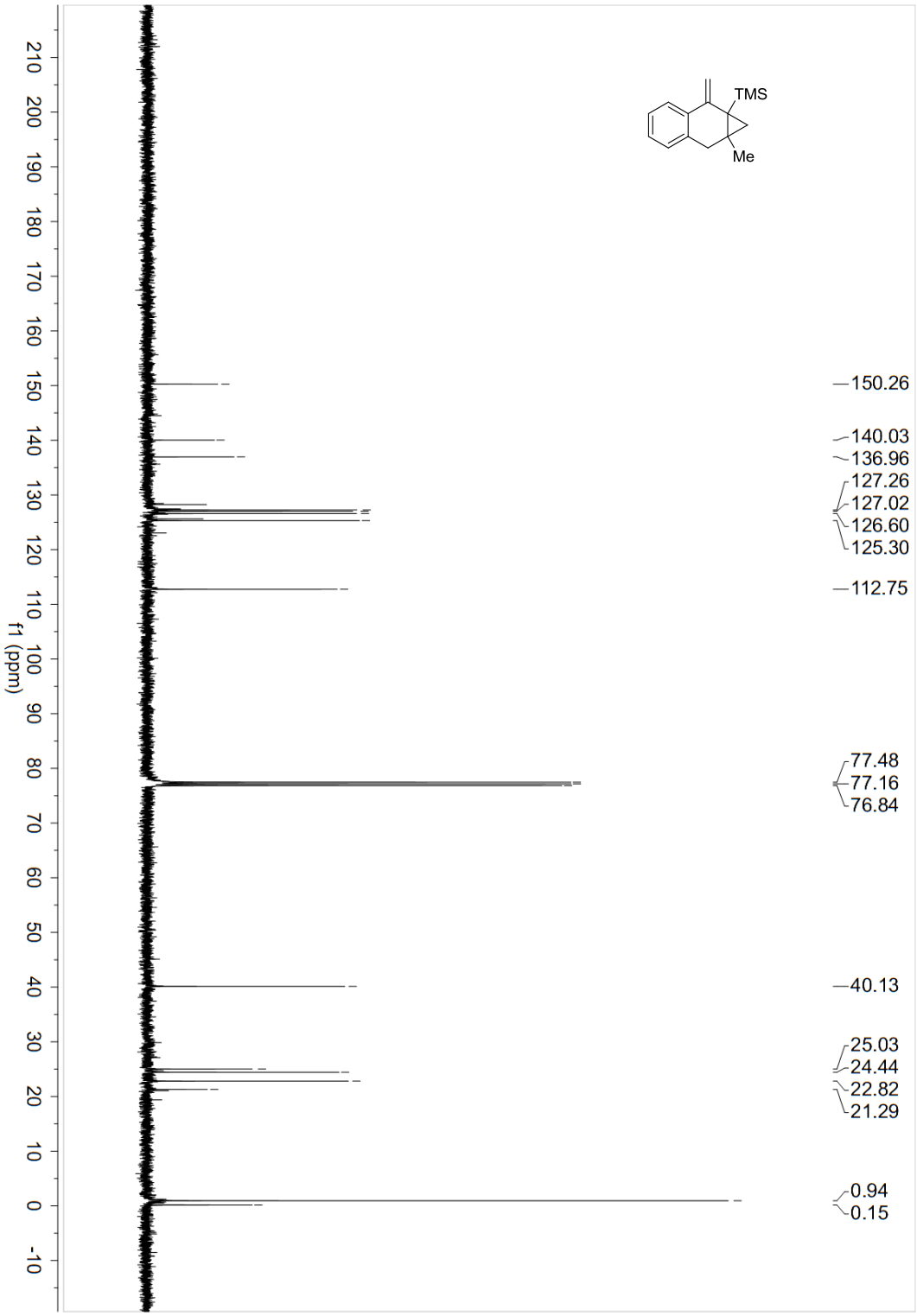
9b1


Me
Et
Me
7.248
7.227
7.213
7.174
7.160
7.148
7.135
7.121
7.063
7.043
7.029
5.635
5.621
5.607
5.593
2.887
2.856
2.717
2.686
1.883
1.869
1.299
1.122
1.093
1.048
1.019
0.467
0.459
0.159
0.151
0.99
2.25
1.21
1.00
1.03
1.04
3.67
3.18
1.17
4.12
1.02
1.06
f1 (ppm)

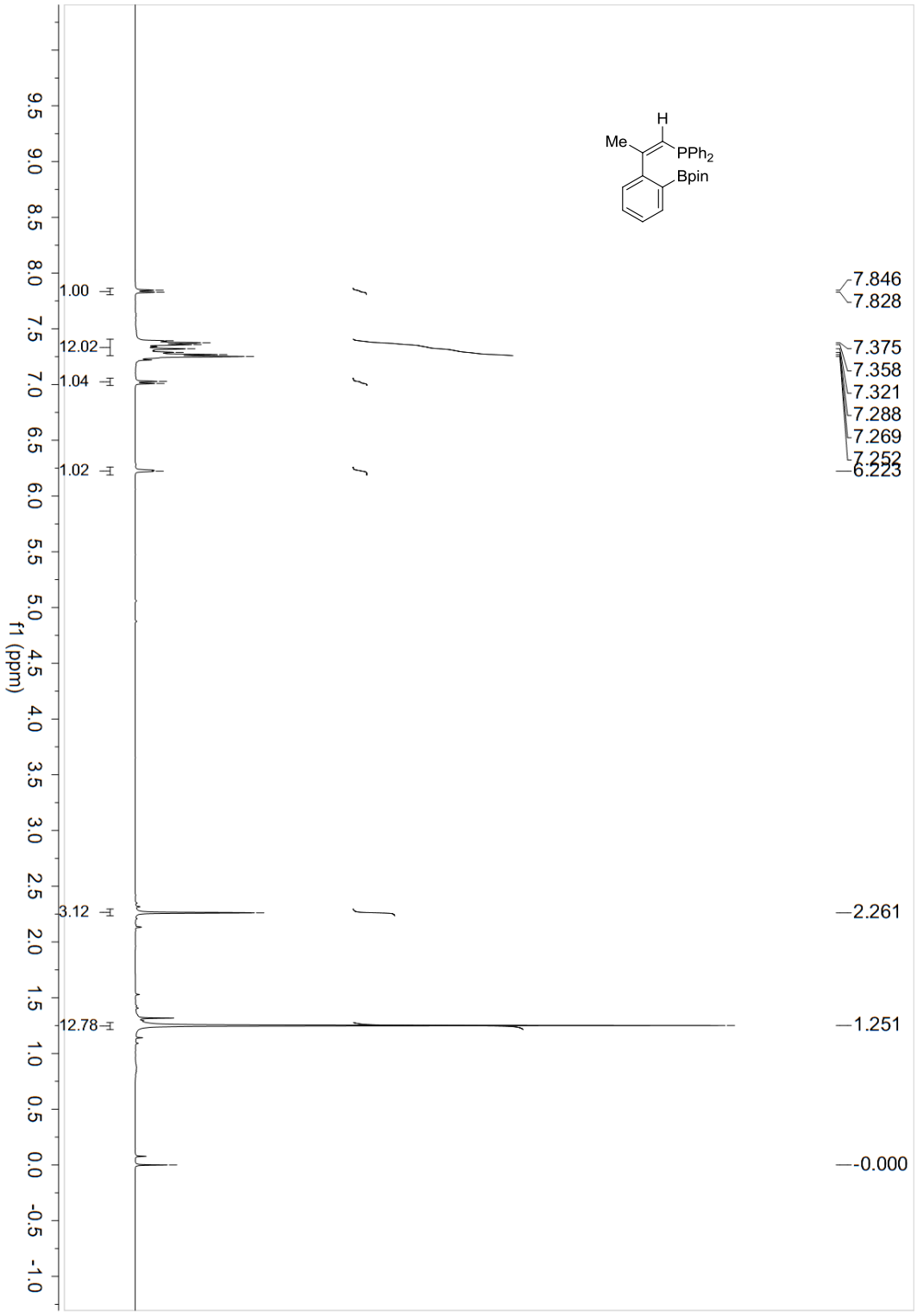

Me
Et
Me
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
138.90
137.33
135.78
128.94
127.82
126.70
125.37
118.04
77.41
77.16
76.91
39.17
32.28
23.77
23.73
21.99
20.90
16.18
11.77
0.14

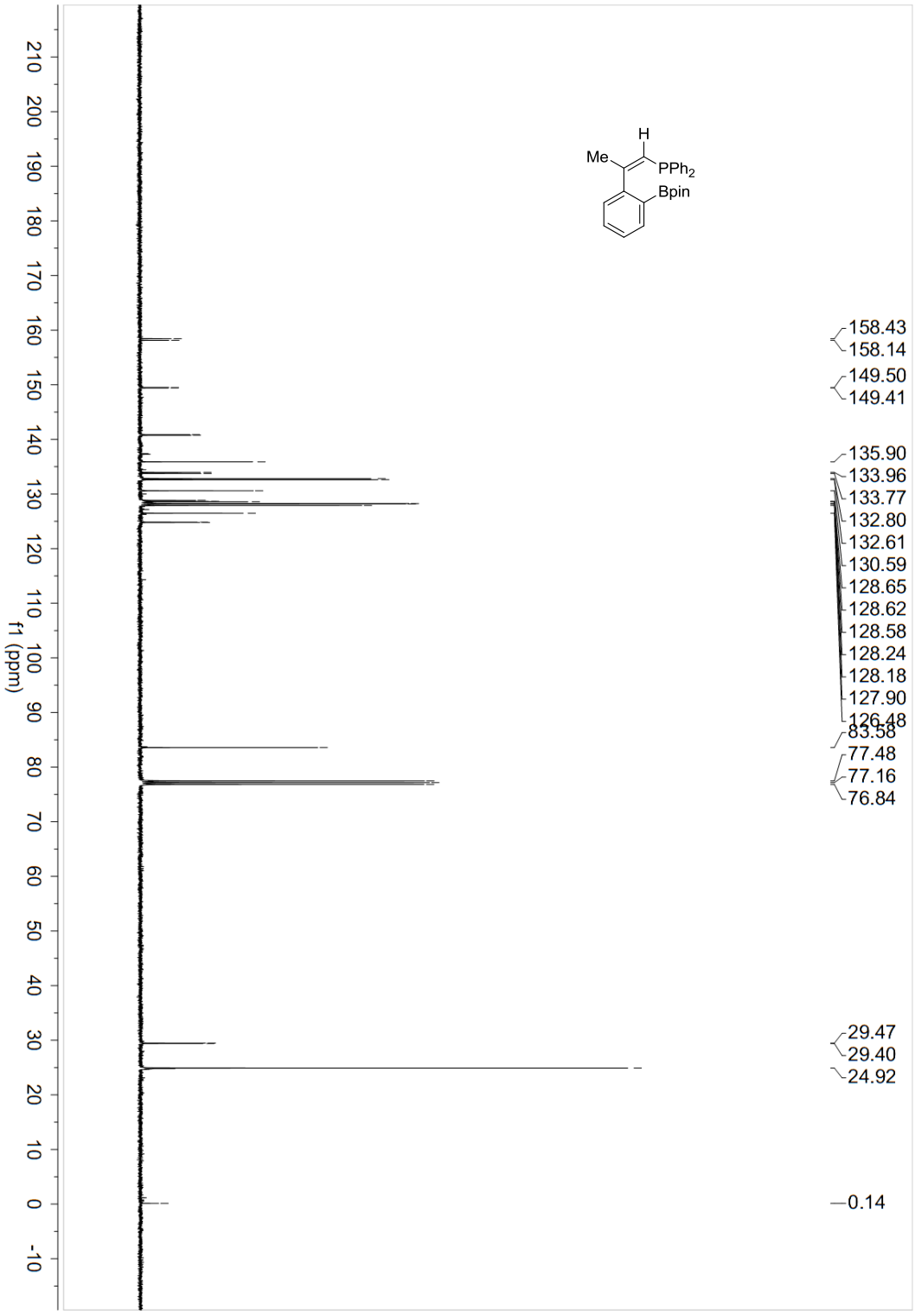
9b2


TMS
Me
f1 (ppm)
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
-1.0
1.09
2.11
0.93
1.00
0.97
1.08
1.14
3.18
1.15
1.02
8.93
7.259
7.250
7.244
7.237
7.177
7.169
7.163
7.155
7.041
7.032
7.020
5.242
5.112
2.839
2.801
2.597
2.559
1.321
0.849
0.839
0.759
0.749
0.119
0.000


TMS
Me
150.26
140.03
136.96
127.26
127.02
126.60
125.30
112.75
77.48
77.16
76.84
40.13
25.03
24.44
22.82
21.29
0.94
0.15
f1 (ppm)

10


H
Me
PPh2
Bpin
1.00
12.02
1.04
1.02
3.12
12.78
7.846
7.828
7.375
7.358
7.321
7.288
7.269
7.252
6.223
2.261
1.251
-0.000
f1 (ppm)


H
Me
PPh2
Bpin
158.43
158.14
149.50
149.41
135.90
133.96
133.77
132.80
132.61
130.59
128.65
128.62
128.58
128.24
128.18
127.90
126.48
83.58
77.48
77.16
76.84
29.47
29.40
24.92
0.14
f1 (ppm)

3) References

[1] For the preparation of 1,3-dienes and diiodo analogues, see: a) S. L. Buchwald, B. T. Watson, J. C. Huffman, *J. Am. Chem. Soc.* **1987**, *109*, 2544-2546; b) T. Takahashi, M. Kageyama, V. Denisov, R. Hara, E. Negishi, *Tetrahedron Lett.* **1993**, *34*, 687-690; c) Z. Xi, R. Hara, T. Takahashi, *J. Org. Chem.* **1995**, *60*, 4444-4448; d) T. Hamada, D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **1999**, *121*, 7342-7344.

[2] For other synthetic methods of **2a1** and **2a2**, see: T. Takahashi, W.-H. Sun, C. Xi, U. Haruka, Z. Xi. *Tetrahedron*, **1998**, *54*, 715-726.

[3] G. M. Sheldrick, SHELXTL 5.10 for Windows NT: *Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, **1997**.