Supporting information

Efficient hydrosilylation of imines using pre-catalysts based on iridium(III) metallacycles.

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I) General Remarks.

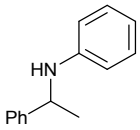
All solvents were dried using standard methods and stored over molecular sieves (4 Å). All silver salts were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere and were repeated at least twice. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV_{254} plates. Flash chromatography was carried out with Macherey silica gel (Kielselgel 60). ^{1}H (300, 600 and 900 MHz), ^{13}C (75 and 126 MHz), ^{19}F (282 MHz) and ^{11}B (128 MHz) spectra were acquired on Bruker Avance I and II spectrometers. Chemical shifts (δ) are reported downfield of Me_4Si in ppm and coupling constants are expressed in Hz. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. HRMS-ESI analyses were performed at CUMA-Pharm. Dept.-University Lille Nord de-France. Ir(III) pre-catalysts[1] and BARF salts[2] were prepared following related procedures. Reagents **4a**,[3] **4b**,[4] **4c**,[5] **4d**,[6] **4e**,[3] **4f**,[3] **4g**,[3] **4h**,[7] **4i**,[3] **4j**,[8] **4k**,[6] **4l**,[3] **6a**,[3] **6b**,[9] **6c**,[9] **6d,**[9] **6e**,[9] **6f**,[10] **6g**,[10] **6h**,[9] **6i**,[9] **6j**,[9] **6k**,[9] **6l**,[10] **6m**[11] were prepared as reported.

II) General Procedure for the catalysis:

In a glovebox, imine reagent (0.15 mmol, 1 eq.), selected iridium(III) catalyst (x mol%) and additive (2x mol%) were introduced in a Schlenk tube. Under nitrogen, solvent (2 mL) was added followed by silane reagent (0.18 mmol, 1.2 eq.). The reaction mixture was then heated at 25°C under stirring. In order to follow the progress of the reaction, aliquots (0.1 mL) were taken at defined times, filtered through Celite with a CH_2Cl_2 wash (3 mL), evaporated under vacuum and analysed by ^{1}H NMR. At the end of the reaction, solvent was evaporated under vacuum and the crude product was directly purified by flash chromatography or by preparative TLC.

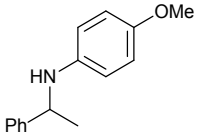
III) Characterization of compounds.

N-(1-phenylethyl)aniline 5a[3]



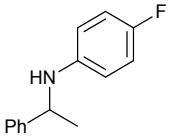
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.51 (d, ^{3}J = 6.3 Hz, 3H, CH_3), 4.10 (1s, 1H, NH), 4.49 (q, ^{3}J= 6.69 Hz, 1H, CH), 6.51 (d, ^{3}J= 8.64 Hz, 2H, H_{Ar}), 6.64 (t, ^{3}J= 7.2 Hz, 1H, H_{Ar}), 7.09 (m, 2H, H_{Ar}), 7.24 (m, 1H, H_{Ar}), 7.34 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.1 (CH_3), 53.7 (CH), 113.5 (2CH), 117.4 (CH), 125.9 (2CH), 127.0 (CH), 128.8 (2CH), 129.2 (2CH), 145.3 (C), 147.4 (C, CN).

4-methoxy-*N*-(1-phenylethyl)aniline 5b[4]



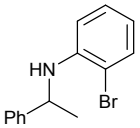
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.50 (d, ^{3}J = 6.7 Hz, 3H, CH_3), 3.70 (1s, 3H, OCH_3), 3.77 (bs, 1H, NH), 4.43 (q, ^{3}J= 6.7 Hz, 1H, CH), 6.48 (d, ^{3}J= 8.9 Hz, 2H, H_{Ar}), 6.70 (d, ^{3}J= 9.0 Hz, 2H, H_{Ar}), 7.21 (m, 1H, H_{Ar}), 7.29 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.2 (CH_3), 54.4 (OMe), 55.9 (CH), 114.7 (2CH), 114.9 (2CH), 126.0 (2CH), 126.9 (CH), 128.7 (2CH), 141.8 (C, CN), 145.7 (C), 152.1 (C, OMe).

4-fluoro-*N*-(1-phenylethyl)aniline 5c[5]



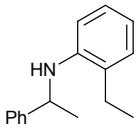
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.50 (d, ^3J= 6.7 Hz, 3H, CH_3), 4.41 (q, ^3J= 6.7 Hz, 1H, CH), 6.44 (m, 2H, H_{Ar}), 6.78 (m, 2H, H_{Ar}), 7.31 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.2 (CH_3), 54.3 (CH), 114.3 (d, $2CH_{meta}$, J_{C-F}= 7.3 Hz), 115.5 (d, $2CH_{ortho}$, J_{C-F}= 22.2 Hz), 125.9 (2CH), 127.1 (CH), 128.8 (2CH), 143.6 (d, C_{para}, J_{C-F}= 1.1 Hz), 145.1 (C, CN), 156.0 (d, C_{ipso}, J_{C-F}= 233.4 Hz).

2-bromo-*N*-(1-phenylethyl)aniline 5d[6]



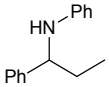
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.57 (d, ^3J = 6.8 Hz, 3H, CH_3), 4.51 (q, ^3J = 6.7 Hz, 1H, CH), 4.74 (bs, 1H, NH), 6.38 (dd, ^3J = 1.5, 8.1 Hz, 1H, H_{Ar}), 6.50 (m, 1H, H_{Ar}), 6.98 (m, 1H, H_{Ar}), 7.22 (m, 1H, H_{Ar}), 7.32 (m, 4H, H_{Ar}), 7.40 (dd, ^3J = 1.5, 7.9 Hz, 1H, H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.3 (CH_3), 53.7 (CH), 109.4 (C), 112.8 (CH), 117.9 (CH), 125.8 (2CH), 127.2 (CH), 128.4 (CH), 128.8 (2CH), 132.3 (CH), 143.9 (C), 144.6 (C).

2-ethyl-*N*-(1-phenylethyl)aniline 5e



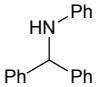
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.37 (s, 3H, $CH_{3\ Et}$), 1.61 (d, J = 6.59 Hz, 3H, CH_3), 2.63 (q, ^3J = 7.54 Hz, 2H, CH_2), 4.0 (bs, 1H, NH), 4.58 (q, ^3J = 6.59 Hz, 1H), 6.44 (dd, ^3J = 1.00 Hz, 1H, H_{Ar}), 6.70 (td, ^3J= 7.39 Hz, 1H, H_{Ar}), 7.0 (m, 1H, H_{Ar}), 7.12 (m, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.38 (m, 4H, H_{Ar}).^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 (CH_3), 24.1 (CH_2), 25.4 (CH_3), 53.4 (CH), 111.5 (CH), 117.1 (CH), 125.9 (2CH), 126.9 (2CH), 127.3 (C), 127.8 (CH), 128.7 (2CH), 144.5 (C), 145.4 (C). HRMS (EI): calculated for $C_{16}H_{20}N$ (M+), 226.3407; found, 226.15903.

***N*-(1-phenylpropyl)aniline 5f[3]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.96 (t, ^3J= 7.4 Hz, 3H, CH_3), 1.83 (m, 2H, CH_2), 4.06 (bs, 1H, NH), 4.23 (t, ^3J= 6.7 Hz, 1H, CH), 6.52 (d, ^3J= 7.7 Hz, 2H, H_{Ar}), 6.63 (t, ^3J= 7.3 Hz, 1H, H_{Ar}), 7.08 (t, ^3J= 7.9 Hz, 2H, H_{Ar}), 7.21 (m, 1H, H_{Ar}), 7.31 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 10.9 (CH_3), 31.8 (CH_2), 59.9 (CH), 113.4 (2CH), 117.3 (CH), 126.6 (2CH), 127.1 (CH), 128.6 (2CH), 129.2 (2CH), 144.0 (C), 147.6 (C, CN).

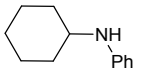
***N*-benzhydrylaniline 5g[3]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 5.50 (s, 1H, CH), 6.57 (d, ^3J= 7.7 Hz, 2H, H_{Ar}), 6.71 (t, ^3J=7.3 Hz, 1H, H_{Ar}), 7.12 (t, ^3J= 7.5 Hz, 2H, H_{Ar}), 7.29 (m, 10H, H_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ= 63.2 (CH), 113.7 (2CH), 117.9 (CH), 127.5 (2CH), 127.7 (4CH), 128.9 (4CH), 129.3 (2CH), 143.1 (2C), 147.6 (C, CN).

_N_-cyclohexylaniline 5h[12]

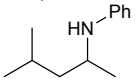


^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.25 (m, 6H), 1.75 (m, 2H), 2.06 (m, 2H), 3.25 (non, ^3J= 3.7 Hz, 1H), 6.59 (d, ^3J= 7.6 Hz, 2H_{Ar}), 6.67 (t, ^3J= 7.3 Hz, 1H_{Ar}), 7.16 (t, ^3J= 7.9 Hz, 2H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.2 (2CH_2), 26.1 (CH_2), 33.5 (2CH_2), 51.9 (CH), 113.4 (2CH), 117.1 (CH), 129.5 (2CH), 147.4 (C).

_N_-benzyl-1-phenylethanamine 5i[3]

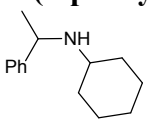
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.27 (d, ^3J= 6.3 Hz, 3H, CH_3), 1.78 (bs, 1H, NH), 3.51 (dd, ^3J= 13.2 Hz, 2H, CH_2), 3.71 (q, ^3J= 6.6 Hz, 1H, CH), 7.17 (m, 10H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 24.5 (CH_3), 51.7 (CH_2), 57.6 (CH), 126.9 (2CH), 127.0 (1CH), 127.1 (1CH), 128.3 (2CH), 128.5 (2CH), 128.6 (2CH), 140.5 (C), 145.5 (C).

_N_-(4-methylpentan-2-yl)aniline 5j[8]



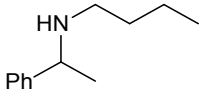
^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.94 (d+d, ^3J= 6.9 Hz, 6H), 1.16 (d, ^3J= 6.5 Hz, 3H), 1.27 (pent, d, ^3J= 7.1 Hz, 1H), 1.48 (hex, ^3J= 7.1 Hz, 1H), 1.76 (hept, ^3J= 6.8 Hz, 1H), 3.54 (hex, ^3J= 6.5 Hz, 1H, CH), 6.59 (d, ^3J= 7.7 Hz, 2H, H_{Ar}), 6.66 (t, ^3J= 7.3 Hz, 1H, H_{Ar}), 7.16 (t, ^3J= 7.8 Hz, 2H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 21.2 (CH_3), 22.7 (CH_3), 23.1 (CH_3), 25.3 (CH), 46.7 (CH_2), 47.1 (CH), 113.3 (2CH), 116.9 (CH), 129.4 (2CH), 147.8 (C).

_N_-(1-phenylethyl)cyclohexanamine 5k[13]



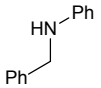
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.21 (m, 5H), 1.29 (d, ^3J= 6.6 Hz, 3H, CH_3), 1.49 (m, 1H), 1.64 (m, 3H), 1.93 (m, 1H), 2.24 (m, 1H), 3.92 (q, ^3J= 6.6 Hz, 1H, CH), 7.28 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 25.0 (CH_3), 25.1 (CH_2), 25.4 (CH_2), 26.3 (CH_2), 33.3 (CH_2), 34.6 (CH_2), 53.8 (CH), 54.6 (CH), 126.6 (2CH), 126.8 (CH), 128.5 (2CH), 146.3 (C).

_N_-Benzylbutan-1-amine 5l[4]



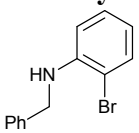
^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.87 (t, ^3J = 1.0 Hz, 3H, CH_3 $_{n\text{-Bu}}$), 1.29 (m, 2H, CH_2), 1.37 (d, ^3J = 6.6 Hz, 3H, CH_3), 1.46 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 3.76 (q, ^3J = 6.6 Hz, 1H, CH), 7.23 (m, 2H, H_{Ar}), 7.33 (m, 3H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 14.1 (CH_3), 20.6 (CH_2), 24.4 (CH_3), 32.4(CH_2), 47.5(CH_2), 58.6 (CH), 126.7 (2CH), 127.0 (CH), 128.5 (2CH), 145.4(C).

***N*-benzylaniline 7a[3]**



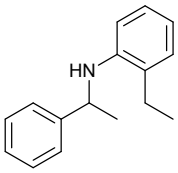
^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.03 (bs, 1H, NH), 4.35 (s, 2H, CH_2), 6.65 (d, ^3J= 8.2 Hz, 2H, H_{Ar}), 6.75 (t, ^3J= 7.3 Hz, 1H, H_{Ar}), 7.17 (t, ^3J= 7.4 Hz, 2H, H_{Ar}), 7.35 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 48.4 (CH_2), 112.9 (2CH), 117.7 (1CH), 127.3 (1CH), 127.6 (2CH), 128.7 (2CH), 129.3 (2CH), 139.5 (C), 148.3 (C, CN).

***N*-benzyl-2-bromoaniline 7b[14]**



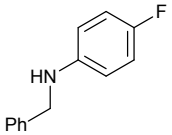
^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.42 (s, 2H, CH_2), 4.86 (bs, 1H, NH), 6.61 (m, 2H, H_{Ar}), 7.14 (m, 1H, H_{Ar}), 7.34 (m, 5H, H_{Ar}), 7.46 (dd, ^3J=1.41, 7.82 Hz, 1H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 48.2 (CH_2), 109.9 (C), 111.9 (CH), 118.2 (CH), 127.4 (2CH), 127.5 (CH), 128.6 (CH), 128.9 (2CH), 132.5 (CH), 138.7 (C), 144.8 (C).

2-ethyl-N-(1-phenylethyl)aniline 7c



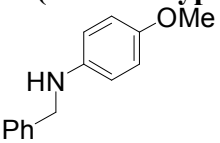
^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.37 (s, 3H, $CH_{3\ Et}$), 1.61 (d, J = 6.59 Hz, 3H, CH_3), 2.63 (q, ^3J = 7.54 Hz, 2H, CH_2), 4.0 (bs, 1H, NH), 4.58 (q, ^3J = 6.59 Hz, 1H), 6.44 (dd, ^3J = 1.00 Hz, 1H, H_{Ar}), 6.70 (td, ^3J= 7.39 Hz, 1H, H_{Ar}), 7.0 (m, 1H, H_{Ar}), 7.12 (m, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.38 (m, 4H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 (CH_3), 24.1 (CH_2), 25.4 (CH_3), 53.4 (CH), 111.5 (CH), 117.1 (CH), 125.9 (2CH), 126.9 (2CH), 127.3 (C), 127.8 (CH), 128.7 (2CH), 144.5 (C), 145.4 (C).
HRMS (EI): calculated for $C_{16}H_{20}N$ (M+), 226.3407; found, 226.15903.

***N*-(4-Fluorophenyl)benzenemethanamine 7d[15]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (br s, 1H, NH), 4.31 (s, 2H, CH_2), 6.66 (m, 2H, H_{Ar}), 6.89 (m, 2H, H_{Ar}), 7.33 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 49.1 (CH_2), 113.8 (d, $2CH_{meta}$, $J_{C\text{-}F}$= 7.5 Hz), 115.8 (d, $2CH_{ortho}$, $J_{C\text{-}F}$= 22.5 Hz), 127.5 (CH), 127.6 (2CH), 128.8 (2CH), 139.3(C, CN), 144.5 (d, C_{para}, $J_{C\text{-}F}$= 2.3 Hz), 156.0 (d, C_{ipso}, $J_{C\text{-}F}$= 234.0 Hz).

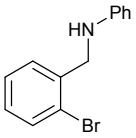
***N*-(4-Methoxyphenyl)benzenemethanamine 7e[15]**



^{1}H NMR (300 MHz, $CDCl_3$): δ= 3,47 (bs, 1H, NH), 3.76 (s, 3H, OCH_3), 4.30 (s, 2H, CH_2), 6.63 (m, 2H, H_{Ar}), 6.80 (m, 2H, H_{Ar}), 7.34 (m, 5H, H_{Ar}).

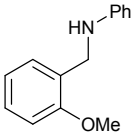
^{13}C NMR (75 MHz, $CDCl_3$): δ= 49.4 (CH_2), 55.9 (OCH_3), 114.3 (2CH), 115.1 (2CH), 127.3 (CH), 127.7 (2CH), 128.7 (2CH), 139.8 (C), 142.6 (C), 152.4 (C).

_N_-(2-bromobenzyl)aniline 7f[16]



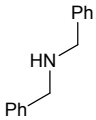
^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.24 (bs, 1H, NH), 4.43 (s, 2H, CH_2), 6.64 (m, 2H, H_{Ar}), 6.75 (tt, ^{3}J= 7.3 Hz, 1H, H_{Ar}), 7.17 (m, 3H, H_{Ar}), 7.27 (q, ^{3}J= 1.0 Hz, 1H, H_{Ar}), 7.43 (m, 1H, H_{Ar}), 7.58 (dd, ^{3}J= 7.9 Hz, 1H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 48.6 (CH_2), 113.2 (2CH), 118.1 (CH), 123.4 (C), 127.7 (CH), 128.8 (CH), 129.4 (CH), 129.5 (2CH), 132.9 (CH), 138.2 (C), 147.7 (C).

_N_-(2-methoxybenzyl)aniline 7g[16]



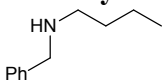
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.88 (s, 3H, OCH_3), 4.36 (s, 2H, CH_2), 6.71 (m, 3H, H_{Ar}), 6.93 (m, 2H, H_{Ar}), 7.19 (m, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.33 (dd, ^{3}J= 7.3 Hz, 1H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 43.7 (CH_2), 55.4 (OCH_3), 110.4 (CH), 113.4 (2CH), 117.6 (CH), 120.7 (CH), 127.4 (C), 128.5 (CH), 129.1 (CH), 129.3 (2CH), 148.4 (C), 157.6 (C).

Dibenzylamine 7h[17]



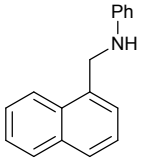
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (s, 4H, CH_2), 7.31 (m, 10H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 53.3 ($2CH_2$), 127.1(2CH), 128.3 (2CH), 128.5 (2CH), 140.5 (2C).

_N_-Benzyl-butyl-amine 7i[18]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.94 (t, ^{3}J= 7.3 Hz, 3H, CH_3), 1.36 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 2.66 (t, ^{3}J= 7.2 Hz, 2H, CH_2), 3.82 (s, 2H, N-CH_2), 7.31 (m, 5H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 14.1 (CH_3), 20.6 (CH_2), 32.2 (CH_2), 49.3 (CH_2), 54.1 (CH_2), 127.0 (CH), 128.3 (2CH), 128.5 (2CH), 140.5 (C).

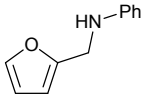
_N_-(naphthalen-1-ylmethyl)aniline 7j[14]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 4.03 (bs, 1H, NH), 4.75 (s, 2H, CH_2), 6.70 (m, 2H, H_{Ar}), 6.77 (m, 1H, H_{Ar}), 7.21 (m, 2H, H_{Ar}), 7.21 (m, 2H, H_{Ar}), 7.44 (m, 1H, H_{Ar}), 7.54 (m, 3H, H_{Ar}), 7.82 (d, ^{3}J= 8.10 Hz, 1H, H_{Ar}), 7.91 (m, 1H, H_{Ar}), 8.09 (m, 1H, H_{Ar}).

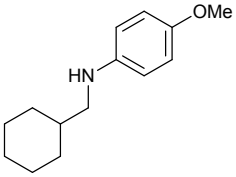
^{13}C NMR (75 MHz, $CDCl_3$): δ= 46.7 (CH_2), 112.9 (2CH), 117.8 (CH), 123.7(CH), 125.7(CH), 126.0 (CH), 126.2 (CH), 126.5 (CH), 128.3 (CH), 128.9 (CH), 129.5 (2CH), 131.7 (C), 134.1 (C), 134.5 (C), 148.4 (C).

_N_-(furan-2-ylmethyl)aniline 7k[14]



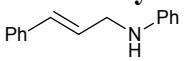
^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (bs, 1H), 4.34 (d, ^3J = 0.8 Hz, 2H, CH_2), 6.26 (qd, ^3J =3.2 Hz, 1H, H_{fur}), 6.34 (dd, ^3J= 3.3 Hz, 1 H, H_{fur}), 6.70 (m, 2H, H_{Ar}), 6.78 (m, 1H, H_{Ar}), 7.21 (m, 2H, H_{Ar}), 7.39 (dd, ^3J= 1.9 Hz, 1H, H_{fur}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 41.5 (CH_2), 107.1 (CH), 110.5 (CH), 113.3 (2CH), 118.2 (CH), 129.4 (2CH), 142.1 (CH), 147.6 (C), 152.8 (C).

_N_-(cyclohexylmethyl)-4-methoxyaniline 7l[19]



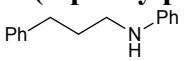
^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.98 (m, 2H, H_{Cy}), 1.24 (m, 3H, H_{cy}), 1.55 (m, 1H, H_{cy}), 1.77 (m, 5H, CH_{cy}), 2.91 (d, ^3J= 6.6 Hz, 2H, N-CH_2), 3.75 (s, 3H, OCH_3), 6.57 (m, 2H, H_{Ar}), 6.77 (m, 2H, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 26.0 ($2CH_2$), 26.8 (CH_2), 31.4 ($2CH_2$), 37.8 (CH), 51.8 (CH_2), 56.0 (OCH_3), 114.1 (2CH), 115.1 (2CH), 142.9 (C), 151.8 (C).

_N_-cinnamylaniline 7m$_1$[20]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.83 (bs, 1H), 3.94 (dd, ^3J= 4.1 Hz, 2H), 6.30 (t+t, ^3J= 5.8 Hz, 1H), 6.69 (m, 4H), 7.22 (m, 3H), 7.35 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 46.4 (CH_2), 113.2 (2CH), 117.8 (CH), 126.5 (2CH), 127.2 (CH), 127.7 (CH), 128.7 (2CH), 129.4 (2CH), 131.7 (CH), 137.0 (C), 148.2 (C).

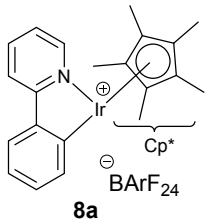
_N_-(3-phenylpropyl)aniline 7m$_2$[21]



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.96 (pent, ^3J= 7.7 Hz, 2H), 2.74 (t, ^3J= 6.8 Hz, 2H), 3.15 (d, ^3J= 7.1 Hz, 2H), 3.62 (bs, 1H), 6.59 (d, ^3J= 8.6 Hz, 2H), 6.69 (t, ^3J= 7.3 Hz, 1H), 7.19 (m, 5H), 7.29 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 31.2 (CH_2), 33.6 (CH_2), 43.6 (CH_2), 112.9 (2CH), 117.4 (CH), 126.1 (CH), 128.5 (2CH), 128.6 (2CH), 129.4 (2CH), 141.9 (C), 148.5 (C).

IV) Synthesis and characterization of complexes 8a-b and 9a-b.

Synthesis of complex 8a:

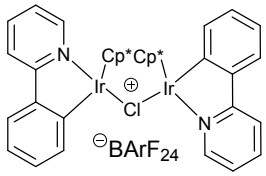


8a

In a glovebox, iridium(III) complex **1** (40 mg, $7.7.10^{-5}$ mmol, 1 eq.) and $NaBArF_{24}$ (1 eq) were introduced in a Schlenk tube. Under nitrogen, degassed CH_2Cl_2 (1 mL) was added. The reaction mixture was stirred during 30 minutes at room temperature and then filtered through dry Celite which was further washed with CH_2Cl_2. Solvent was removed under reduced pressure to afford complex **8a** as a red powder (quantitative).

Elemental analysis: calculated for $C_{53}H_{35}BF_{24}IrN$ + 0.5 CH_2Cl_2 C, 46.31; H, 2.59; N, 1.01; measured C, 46.47; H, 2.99; N, 0.90. HMRS-ESI (m/z): $[M]^+$ calcd for $C_{21}H_{23}IrN$: 482.14489, found: 482.14543 (100%); $[M]^-$ m/z calcd for $C_{32}H_{12}BF_{24}$: 863.06543 [M], measured: 863.06150 (100%).

Synthesis of complex 8b:



8b

A mixture of iridium(III) complex **1** (50 mg, 0.097 mmol) and $NaBArF_{24}$ (43 mg, 0.048 mmol) was stirred at room temperature for two hours in freshly distilled acetone (1 mL) and CH_2Cl_2 (1 mL) resulting in a marked change in color from deep orange to lemon yellow. Upon concentration of the solvent, the residue was washed with cold pentane to afford a red powder after removal of the solvents under reduced pressure. The remaining solid was recrystallized using CH_2Cl_2/pentane (46.6 mg, 52%).

^{1}H NMR (600 MHz, 253 K, $CDCl_3$) δ 8.44 (m, 2H, *H*-C=N), 7.77 (m, 2H, H_{Ar}), 7.74-7.71 (m, 9H, H_{Ar}+H_{BArF24}), 7.69-7.63 (m, 5H, H_{BArF24}), 7.55 (d, 1H, H_{Ar}), 7.52 (m, 4H, H_{Ar}), 7.30 (t, 1H, H_{Ar}), 7.24 (t, 1H, H_{Ar}), 7.17-7.08 (m, 3H, H_{Ar}), 1.08-1.04 (m, 30H, Cp-Me_5).

^{13}C (126 MHz, 293 K, $CDCl_3$) δ 167.0, 162.0 (q, 4C, $^1J_{B\text{-}C}$ = 50.0, BArF), 151.8, 144.9, 138.9, 138.4, 134.9 (bs, 8CH_{ortho} BArF), 131.2, 129.0 (q, 8*C*-CF_3, $^2J_{C\text{-}F}$ = 31.8 Hz), 125.0 (q, 8CF_3, $^1J_{C\text{-}F}$= 272.2 Hz), 123.8, 123.6, 123.0, 121.4, 118.8, 117.6 (bs, 4CH_{para} BArF), 89.6 (*Cp*-Me_5), 8.4 (Cp-Me_5).

^{19}F (282 MHz, 298 K, $CDCl_3$) δ -65.28. ^{11}B (128 MHz, 298 K, $CDCl_3$) δ -6.62.

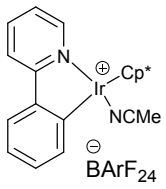
HRMS-ESI (*m/z*): $[M]^+$ calcd for $C_{42}H_{46}ClIr_2N_2$, 999.2593; found, 999.2580; $[M]^-$ calcd for $C_{32}H_{12}BF_{24}$, 863.0649; found, 863.0670.

Elemental analysis: calculated for $C_{74}H_{58}BClF_{24}Ir_2N_2$ + 2 CH_2Cl_2 C, 44.93; H, 3.08; N, 1.38; measured C, 45.00; H, 2.90; N, 1.20.

Synthesis of complexes 9a-d:

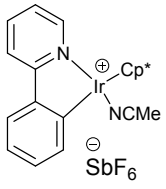
In a glovebox, iridium(III) complex **1** (40 mg, $7.7.10^{-5}$ mmol, 1 eq.) was added to $NaBArF_{24}$ (1 eq) (or $AgBF_4$ or $AgPF_6$ or $AgSbF_6$) in a Schlenk tube. Under nitrogen, degassed CH_2Cl_2 (1 mL) was added. The reaction mixture was stirred during 30 minutes at room temperature. Then, CH_3CN (7 µL, 1,5 eq.) was added. After 30 minutes, the reaction mixture was filtered through dry Celite which was further washed with CH_2Cl_2. After all, solvent was removed under reduced pressure. The complex obtained was recristallized twice with acetone/*n*-Hexane for **9a**, CH_2Cl_2/*n*-Hexane for **9c** or **9d** and CH_2Cl_2/cyclohexane for **9b**, to give a solid: pale yellow powder (**9a**, 85% yield), yellow powder (**9b**, 83% yield), yellow powder (**9c**, 77% yield), orange powder (**9d,** 70% yield).

Complex 9a



^{1}H NMR (300 MHz, CD_2Cl_2) : δ= 1.66 (s, 15H, CH_3-Cp*), 2.23 (s, 2H, CH_3-CN), 7.20 (m, 2H, H_{Ar}), 7.25 - 7.33 (m, 1H, H_{Ar}), 7.57 (s, 4H, H_{Ar} BArF *para*), 7.74 (m, 10H, $2H_{Ar}$ + $8H_{Ar}$ BArF *meta*), 7.83 (m, 1H, H_{Ar}), 7.92 (m, 1H, H_{Ar}), 8.61 (d, 1H, J = 6 Hz, H_{Ar}).
^{13}C NMR (75 MHz, CD_2Cl_2): 4.3 (*CH_3*-CN), 9.1 (5CH_3-Cp*), 92.0 (5C-Cp*), 118.1 (bs, 4CH_{para} BArF), 118.6 (C, Me-*CN*), 120.5 (CH), 124.2 (CH), 124.7 (CH), 125.1 (CH), 125.2 (q, 8CF_3, $^1J_{C\text{-}F}$= 255.0 Hz), 129.4 (q, 8*C*-CF_3, $^2J_{C\text{-}F}$ = 31.5Hz), 130.6 (C), 132.4 (CH), 135.4 (bs, 8CH_{ortho} BArF), 136.3 (CH), 139.9 (CH), 145.3 (C), 152.1 (CH), 156.8 (C), 162.4 (q, 4C, $^1J_{B\text{-}C}$ = 49.5, BArF), 168.3(C).
^{19}F NMR (282 MHz, CD_2Cl_2): -62.9.
Elemental analysis: calculated for $C_{55}H_{38}BF_{24}IrN_2$, C, 47.67; H, 2.76; N, 2.02; measured C, 47.20; H, 3.09; N, 1.52.
HRMS-ESI (*m/z*): $[M]^+$ calcd for $C_{23}H_{26}IrN_2$, 523.17197; found, 523.17141 (100); $[M]^+$ calcd for $C_{21}H_{23}IrN$, 482.14543; found, 482.14523 (32); $[M]^-$ calcd for $C_{32}H_{12}BF_{24}$, 863.06433; found, 863.06599.

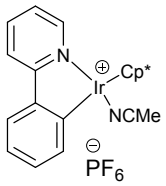
Complex 9b



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.70 (s, 15H, CH_3-Cp*), 2.29 (s, 3H, CH_3-CN), 7.16 (m, 1H, J = 6.0 Hz, H_{Ar}), 7.25 (t, 1H, H_{Ar}), 7.34 (t, 1H, J = 6.0 Hz, H_{Ar}), 7.72 (d+d, 2H, J = 6.0 Hz), 7.88 (m, 2H, H_{Ar}), 8.80 (d, 1H, J = 6.0 Hz, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 3.7 (*CH_3*-CN), 8.8 (5CH_3-Cp*), 91.4 (5C-Cp*), 118.6 (C, Me-*CN*), 119.5 (CH), 124.0 (CH), 124.3 (CH), 124.5 (CH), 131.6 (CH), 135.9 (CH), 139.3 (CH), 145.0 (C), 152.8 (CH), 156.7 (C), 167.0 (C).
^{19}F NMR (282 MHz, CD_3CN): -63.3.
Elemental analysis: calculated for $C_{23}H_{26}SbF_6IrN_2$, C, 36.42; H, 3.46; N, 3.69; measured C, 37.17; H, 3.44; N, 4.02.

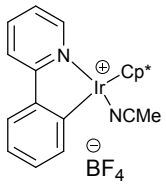
HRMS-ESI (*m/z*): $[M]^+$ calcd for $C_{23}H_{26}IrN_2$, 523.17197; found, 523.17060 (100); $[M]^+$ calcd for $C_{21}H_{23}IrN$, 482.14543; found, 482.14431 (41); $[M]^-$ calcd for SbF_6, 234.89479; found, 234.89442 (100).

Complex 9c



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.62 (s, 15H, CH_3-Cp*), 2.24 (s, 3H, CH_3-CN), 7.15 (t, 1H, J = 6 Hz, H_{Ar}), 7.25 (t, 1H, J = 6 Hz, H_{Ar}), 7.29 (m, 1H, H_{Ar}), 7.65 (d+d, 2H, J = 6 Hz, H_{Ar}), 7.79 (m, 2H, H_{Ar}), 8.76 (d, 1H, J = 6 Hz, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 3.7 (*CH_3*-CN), 8.8 (5CH_3-Cp*), 91.4 (5C-Cp*), 118.8 (C, Me-*CN*), 119.4 (CH), 124.0 (CH), 124.3 (CH), 124.4 (CH), 131.5 (CH), 135.9 (CH), 139.3 (CH), 145.0 (C), 153.0 (CH), 156.7 (C), 167.0 (C).
^{19}F NMR (282 MHz, $CDCl_3$): -73.1 (d, J= 711.3).
^{31}P NMR (121 MHz, $CDCl_3$): -144.3 (hept).
Elemental analysis: calculated for $C_{23}H_{26}PF_6IrN_2$ + ¼ cyclohexane, C, 42.73; H, 4.21; N, 4.07; measured C, 43.05; H, 4.07; N, 2.92.
HRMS-ESI (*m/z*): $[M]^+$ calcd for $C_{23}H_{26}IrN_2$, 523.17197; found, 523.17048 (100); $[M]^+$ calcd for $C_{21}H_{23}IrN$, 482.14543; found, 482.14426 (46); $[M]^-$ calcd for PF_6, 144.96363; found, 144.96364 (100).

Complex 9d



^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.71 (s, 15H, CH_3-Cp*), 2.36 (s, 3H, CH_3-CN), 7.16 (m, 1H, H_{Ar}), 7.26 (m, 1H, H_{Ar}), 7.38 (m, 1H, H_{Ar}), 7.72 (m, 2H), 7.87 (m, 2H, H_{Ar}), 8.9 (d, 1H, J = 6 Hz, H_{Ar}).
^{13}C NMR (75 MHz, $CDCl_3$): δ= 3.9 (*CH_3*-CN), 8.8 (5CH_3-Cp*), 91.4 (5C-Cp*), 119.1 (C, Me-*CN*), 119.3 (CH), 123.9 (CH), 124.3 (CH), 124.4 (CH), 131.4 (CH), 135.8 (CH), 139.2 (CH), 145.1 (C), 153.2 (CH), 156.8 (C), 166.9 (C).
^{19}F NMR (282 MHz, $CDCl_3$): -152.8.
Elemental analysis: calculated for $C_{23}H_{26}BF_4IrN_2$, C, 45.32; H, 4.30; N, 4.60; measured C, 44.76; H, 4.41; N, 2.80.
HRMS-ESI (*m/z*): $[M]^+$ calcd for $C_{23}H_{26}IrN_2$, 523.17197; found, 523.17090 (100); $[M]^+$ calcd for $C_{21}H_{23}IrN$, 482.14543; found, 482.14453 (71); $[M]^-$ calcd for BF_4, 87.00237; found, 87.00202 (100).

V) Structural studies.

The X-ray structure determination of **8b** confirmed the dimeric patern of the complex, two Cp* iridacycle fragments built on 2-phenyl-pyridine ligands were shown to be bonded to a chloride atom. The compound bears a single positive charge and a single $BArF_{24}$ anion. See file CCDC 1031536. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre : www.ccdc.cam.ac.uk/data_request/cif.

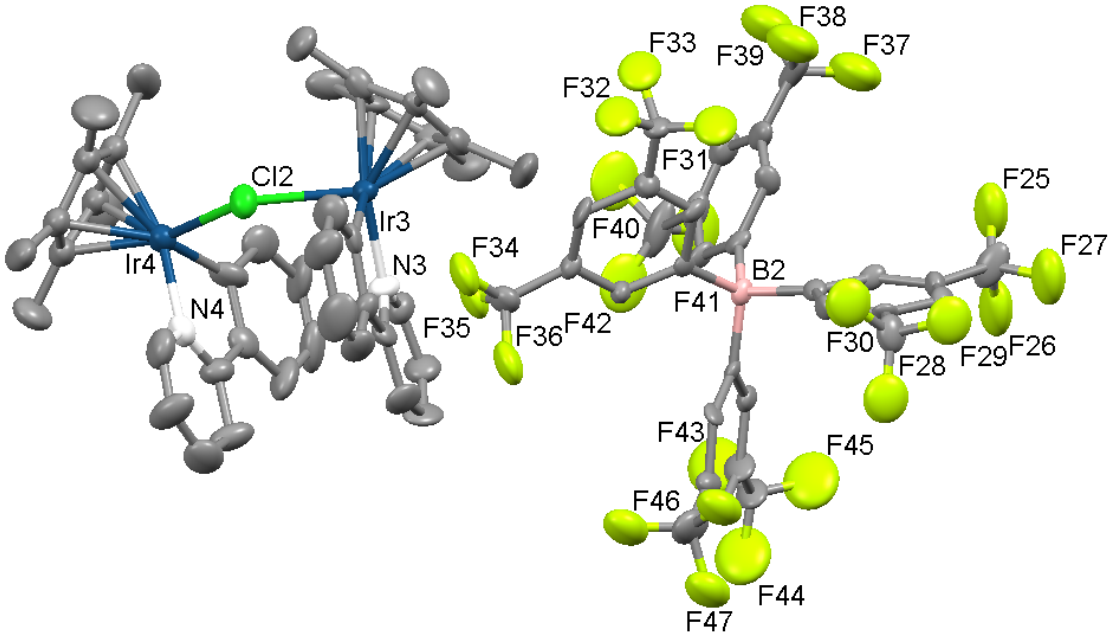


Figure S1. Molecular structure of two chlorobridged iridium complex **8b**. Disorders on some CF_3 groups were deleted for clarity reason. Another complex and its anion as well as one molecule of dichloromethane and all hydrogen atoms were deleted for clarity reason. Selected bond lengths (Å): Ir3-Cl2 2.479 (3), Ir4-Cl2 2.441 (4), Ir3-N3 2.073 (11), Ir4-N4 2.085 (12) and from the two 2-phenyl-pyridine ligands: Ir3-C53 2.043 (13), Ir4-C74 2.019 (16). CCDC 1031536.

Compound **8b** (CCDC 1031536)	
formula	$C_{75}H_{60}BCl_3F_{24}Ir_2N_2$
mol. wt	1946.81
cryst. Syst.	triclinic
Space group	*P*-1
a (Å)	19.0059 (5)
b (Å)	21.9914 (5)
c (Å)	22.0920 (7)
α (deg)	114.0030 (10)
β (deg)	107.6660 (10)
γ (deg)	99.412 (2)
V (Å^3)	7588.0 (4)
Z	4
color	red
crystal dim. (mm)	0.25×0.20×0.10
D_{calc} (gcm^{-3})	1.4353
F_{000}	3800
μ (mm^{-1})	3.712
trans. Min. and max	0.43577/0.64126
T (K)	173 (2)
hkl limits	-24,+22/-28,+28/-28,+28
2θ limits (deg)	1.074/27.504
num. of data meas.	34734
num. of data with $I > 2\ \sigma(I)$	17047
num. of var.	1734
R	0.0985
R_w	0.2244
GOF	1.01

Regarding complex **9a**, the coordination of acetonitrile to the iridium was confimed at the liquid state by several analysis. DOSY ^{1}H NMR experiment showed similar diffusion coefficient D (D of 8.8-9.1) for the 2-phenyl-pyridine ligand, the pentamethylcyclopentadienyl (Cp*) fragment and the acetonitrile (Figure S2, D in 10^{-10} m^2/s not calibrated). As expected, BARF anion was bigger (D of 7.7-7.9) and solvents were much more mobile and free: $CDHCl_2$ (D of 30.0) and acetone solvate (D of 28.4).

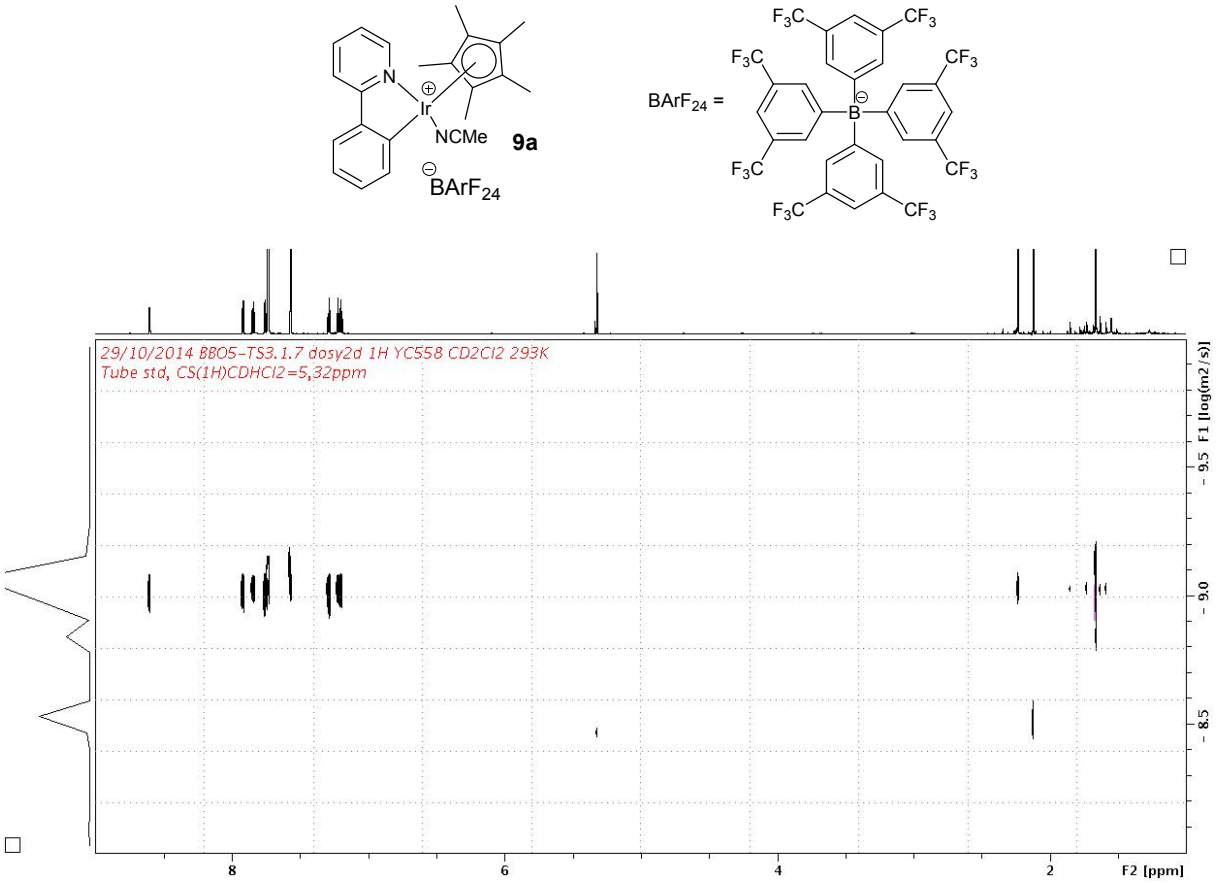


Figure S2. DOSY ^{1}H NMR experiment on complex **9a**.

The coordination of acetonitrile was also confirmed by 2D-^{15}N-HMBC NMR experiment (Figure S3). Chemical shifts were referred to NH_3 liquid at 25°C. If ^{15}N is referred to NH_3 liquid at 25°C (0.0 ppm), the ^{15}N chemical shit in $MeNO_2$ is 380.2 ppm. We observed two ^{15}N atoms at 211 and 147 ppm (-169.2 and -233.2 ppm with $MeNO_2$ as reference).

The chemical shift at 211 ppm correlated with aromatic protons from the 2-phenyl-pyridine ligand (8.60 / 7.91 / 7.22 ppm) and with the aliphatic protons from the pentamethylcyclopentadienyl fragment. Such nitrogen chemical shift is typical of pyridine rings.[22]

The chemical shift at 147 ppm correlated with aliphatic protons from the acetonitrile (at 2.23 ppm) and the pentamethylcyclopentadienyl fragment (at 1.66 ppm). Such nitrogen chemical shift is typical for a coordinated nitrile,[23] free acetonitrile having a chemical shift at 243 ppm.[24]

Moreover, considering the ^{13}C NMR spectrum of **9a** in CD_2Cl_2, chemicals shifts were observed at 4.30 (C_I) and 118.6 (C_{IV}) ppm whereas a free acetonitrile molecule would have carbons shifting at 1.97 (C_I) and 116.90 (C_{IV}) ppm. Finally, the pentamethylcyclopentadienyl fragment and its 15 protons correlated with both nitrogens through 4 bonds.

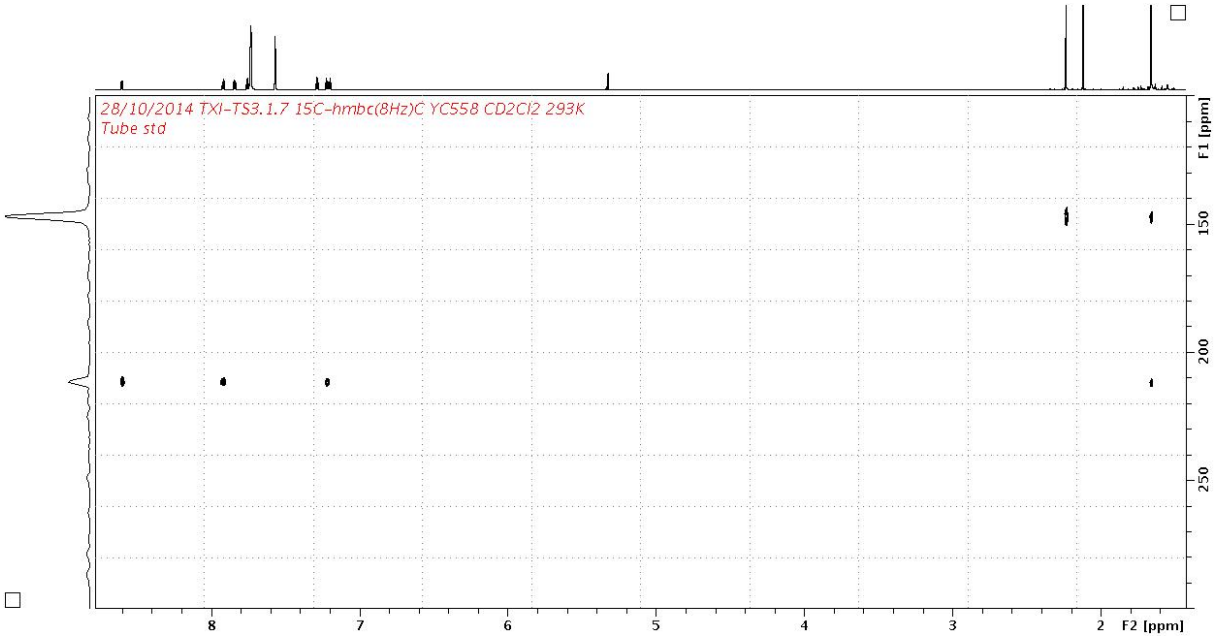
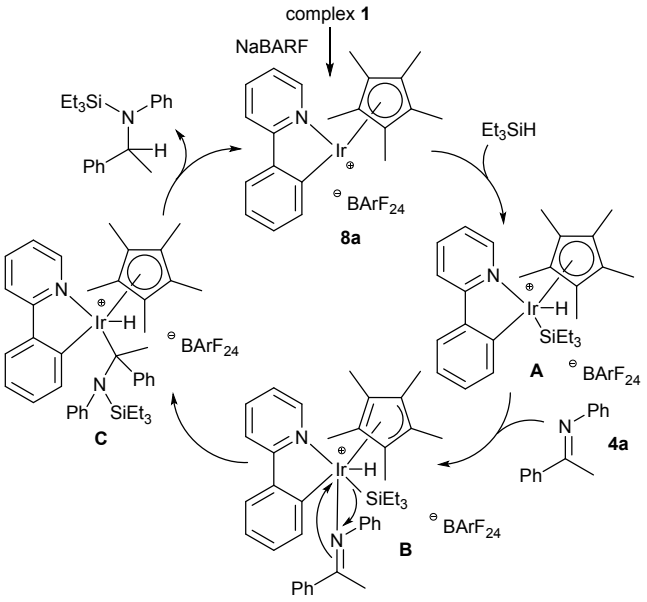


Figure S3. 2D-^{15}N-HMBC NMR experiment on complex **9a**.

VI) Preliminary study of the reaction mechanism.

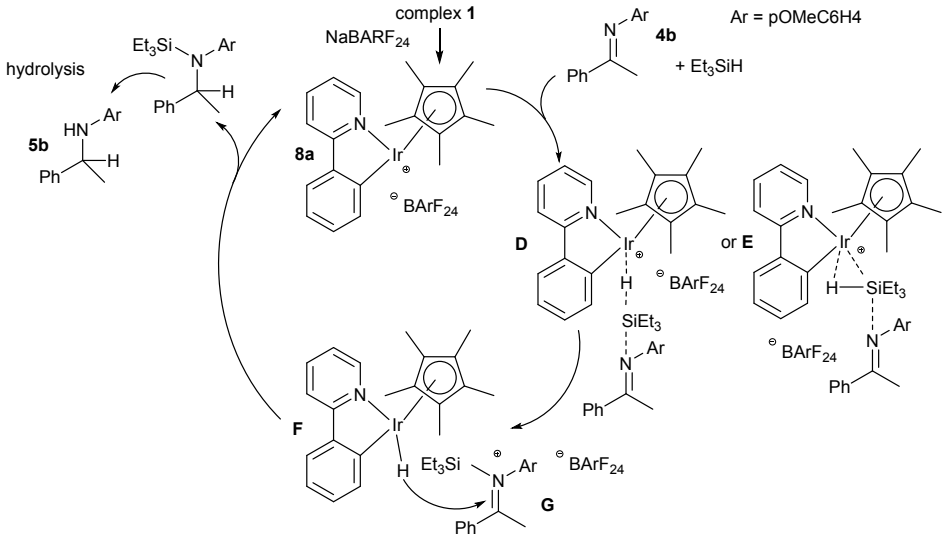
Regarding the reaction mechanism, two pathways may be considered for the hydrosilylation of imines catalysed by Ir(III) pre-catalyst **1**.

A first one would be based on the Chalk-Harrod mechanism.[25] It may start by the activation of the complex **1** by $NaBArF_{24}$ salt which displaces the chloride ligand and affords the cationic catalyst **8** (Scheme S1). The latter may activate the triethylsilane by oxidative addition to afford intermediate **A** according to previous calculations.[26a] In the past, Ir–hydrido intermediate **3** (Scheme 1) was also isolated and may be a key species for the transfer of the hydritic H atom to the electrophilic imine substrate. In the next step, species **A** may further coordinate the imine reagent **4b**[27] thanks to the ring-slippage of Cp* ligand and leads to intermediate **B** (Scheme S1). Such catalyst activation by shifting from a η^5 to η^3 coordination mode of the Ir(III) to the Cp* was already calculated for the hydrosilylation of terminal alkynes by Ir(III) catalyst.[26a] In addition, Crabtree et al. proposed recently the activation of an Ir(III) catalyst by loss of a cyclopentadienyl ligand.[26b] From intermediate **B**, the insertion of the imine C=N bond into the Ir-Si bond shall allow the formation of intermediate **C** (Scheme S1). Finally, a reductive elimination step can afford the reaction product and releases catalytic intermediate **8**.



Scheme S1. Proposed reaction pathway 1 for the hydrosilylation of imines using Ir(III) catalyst **1**.

On the basis of a possible activating role of the silane,[28] a second reaction pathway can be considered (Scheme S2). Starting from complex **8**, the triethylsilane may coordinate the iridium through a single Ir-$HSiEt_3$ sigma bond[28a,b] like in intermediate **D**, or through a three-center, two-electron "agostic" bond as displayed in intermediate **E**.[29] In the meantime, imine reagent **4b** would be activated by the electrophilic silicium to lead to the cleavage of Si-H bond and afford silyliminium ion **G** along with neutral iridium hydride **F**. We noticed a "push-pull" intermediate like **D** was recently highlighted for the hydrosilylation of ketones with another Ir(III) catalyst[28a,b] and species **I** was very similar to previously observed Ir-hydrido intermediate **3** (Scheme 1). Finally, the reaction of hydride species **F** with silyliminium **G** would afford the corresponding silylamine and cationic complex **8**.



Scheme S2. Proposed reaction pathway 2 for the hydrosilylation of imines using Ir(III) catalyst **1**.

By performing an ESI-MS analysis of the reaction mixture issued from the hydrosilylation of ketimine **4b**, we could characterized complex **8a** along with the hydrolysed reaction product **5b** (see manuscript, Figure 1).
When $BArF_{24}$ complex **8a** (or a BF_4 counterpart) was prepared in-situ and allowed to react with a stoechiometric amount of triethylsilane, the ^1H NMR analysis of the resulting sample showed a mixture of several mono and dihydride species whose ratios evolved within 14 hours (Figures S4 and S5). A chemical shift around 4.6 ppm could have been attributed to the presence of hydrogen but T1 (^1H) measurements clearly stated no hydrogen was coordinated to the iridium.[30]

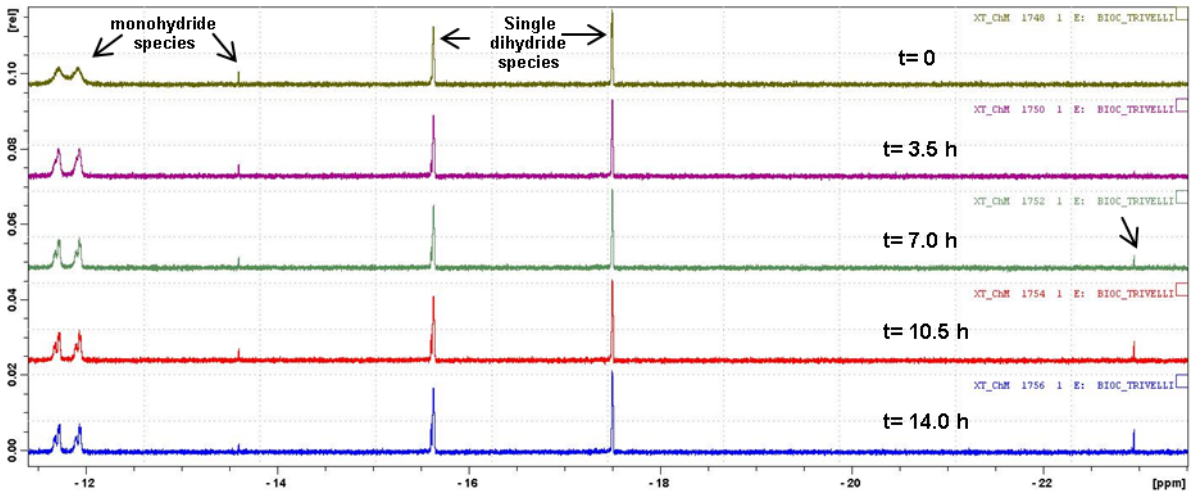


Figure S4. ^1H NMR spectra along time at 300 K of a stoichiometric mixture of complex **8a** and Et_3SiH.

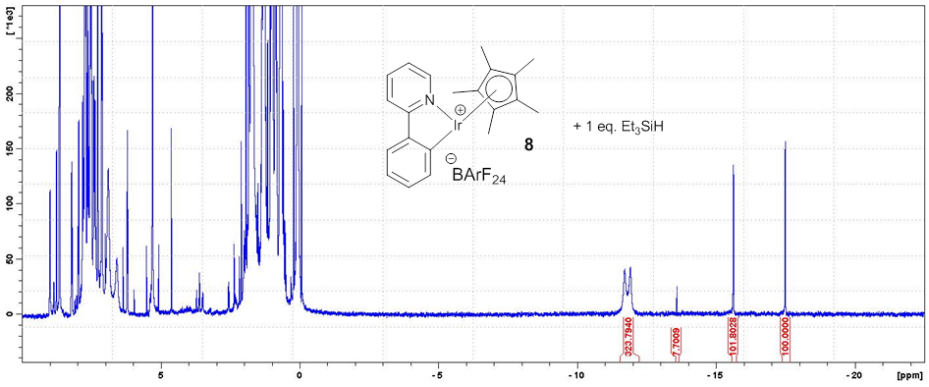


Figure S5. ^{1}H NMR spectra at 300 K of a stoichiometric mixture of complex **8a** and Et_3SiH.

^{29}Si experiments (INEPT et DEPT45) showed a single silicon species at -22 ppm coupling with 6 protons (Figures S6 and S7).
To summarize, we didn‘t see any triethylsilane oxidative addition to the iridium, nor Si–$H_{bridged}$–Ir species.[25a] At this stage, further investigations on the reaction mechanism proved to be difficult.

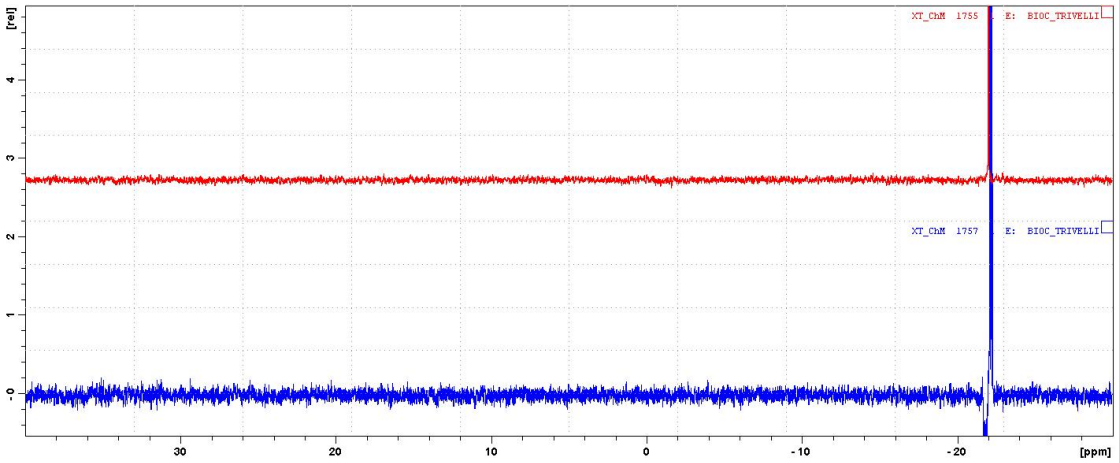


Figure S6. ^{29}Si DEPT45 experiment at 300 K of a stoichiometric mixture of complex **8** and Et_3SiH.

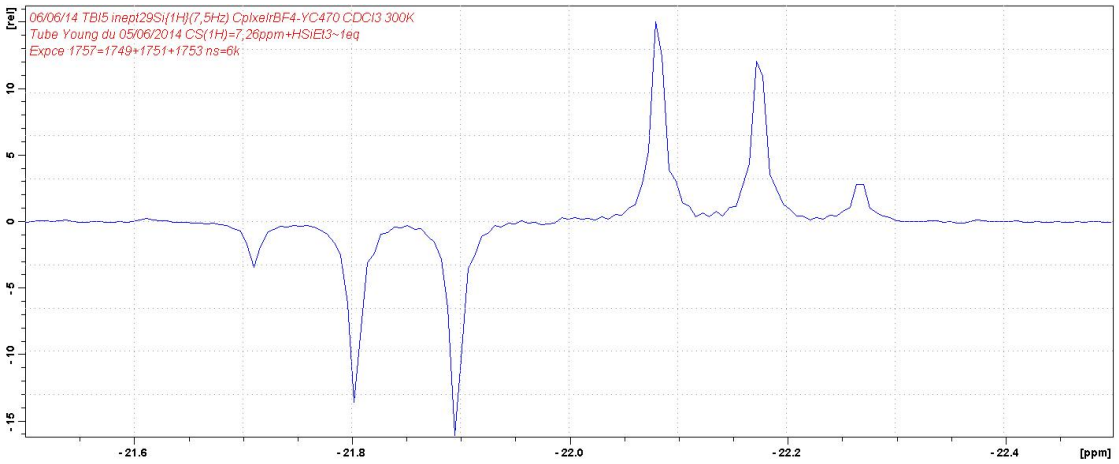


Figure S7. ^{29}Si INEPT experiment at 300 K of a stoichiometric mixture of complex **8** and Et_3SiH.

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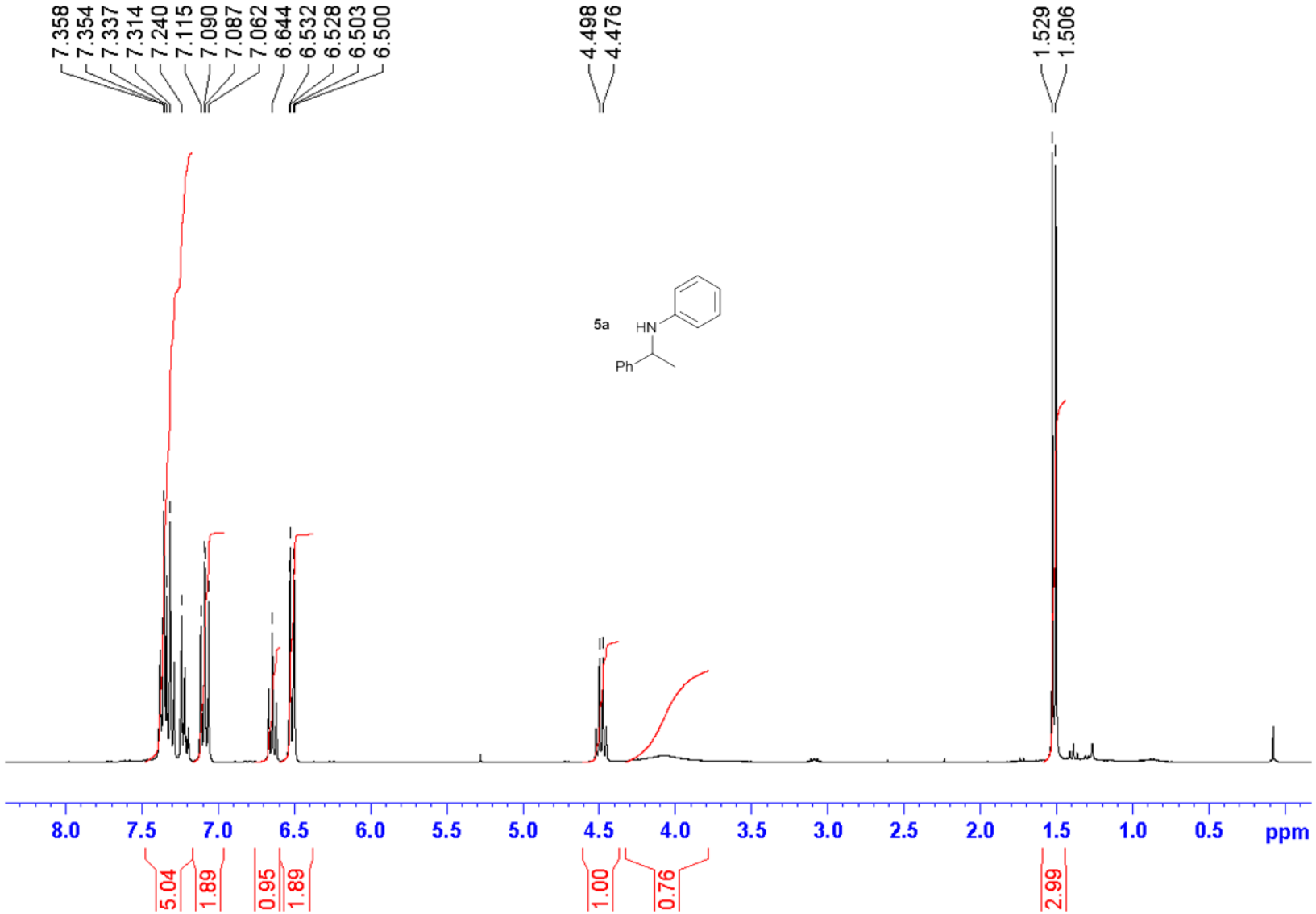
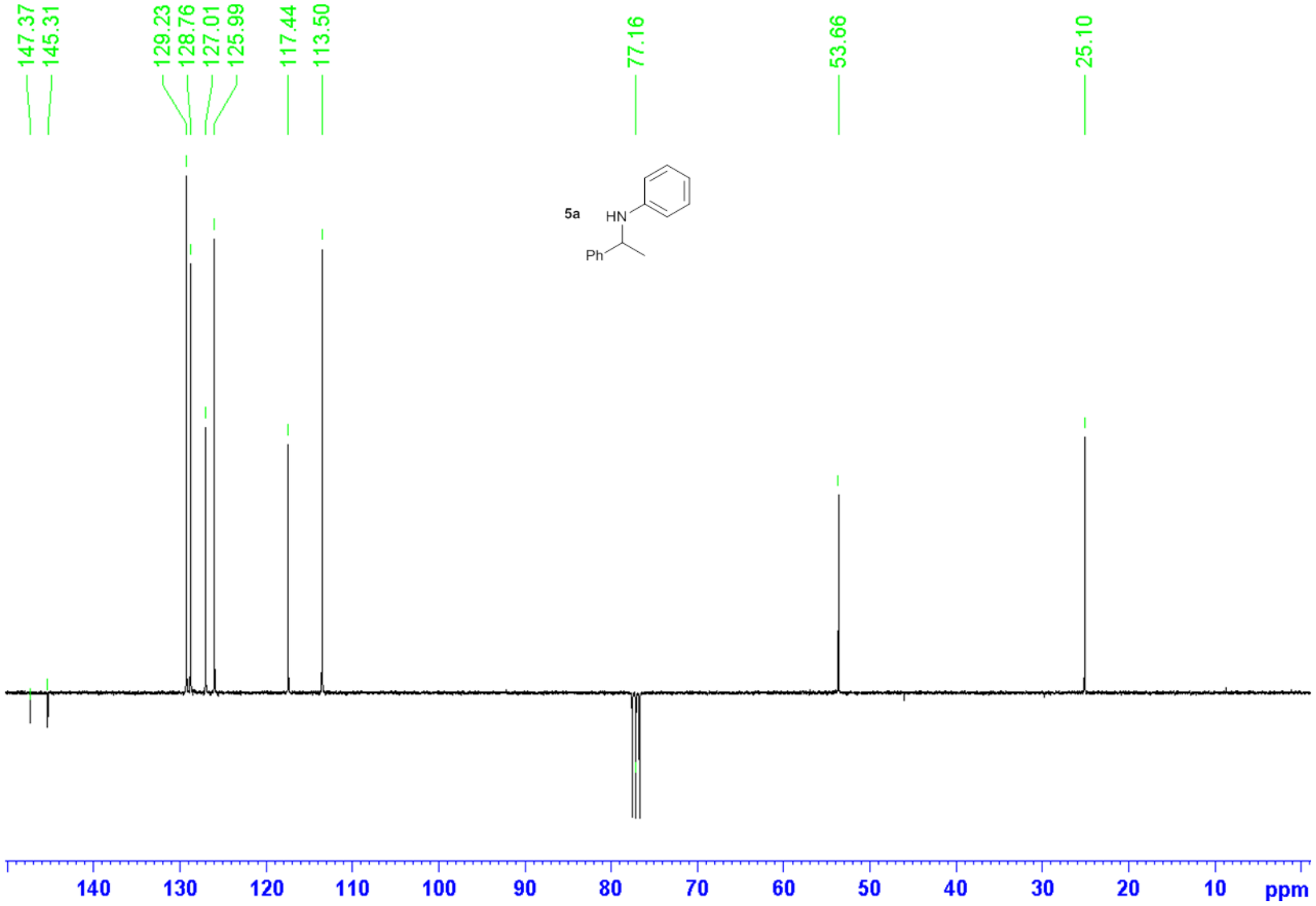
VIII) ^{1}H, ^{13}C NMR spectra of isolated compounds.

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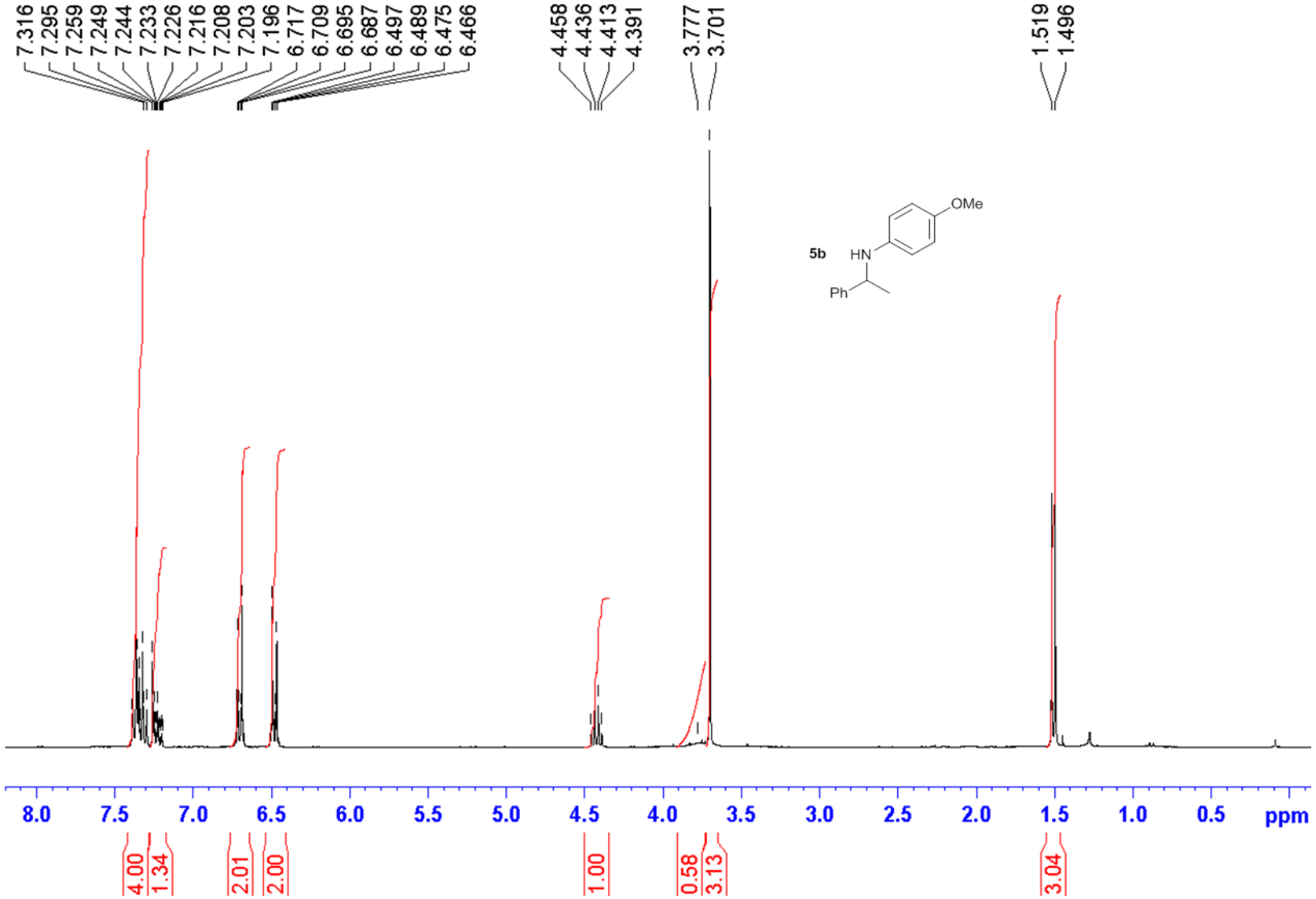
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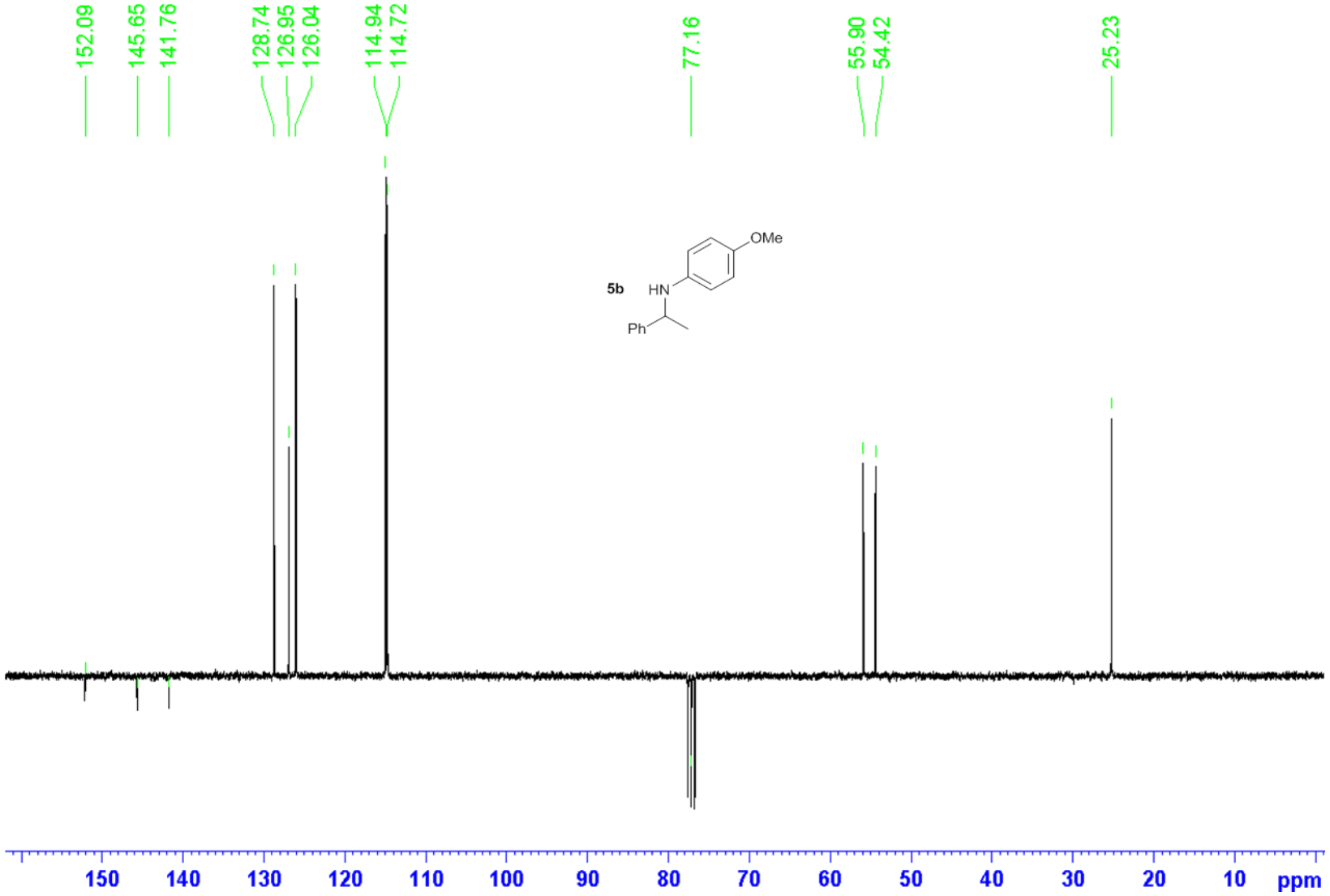
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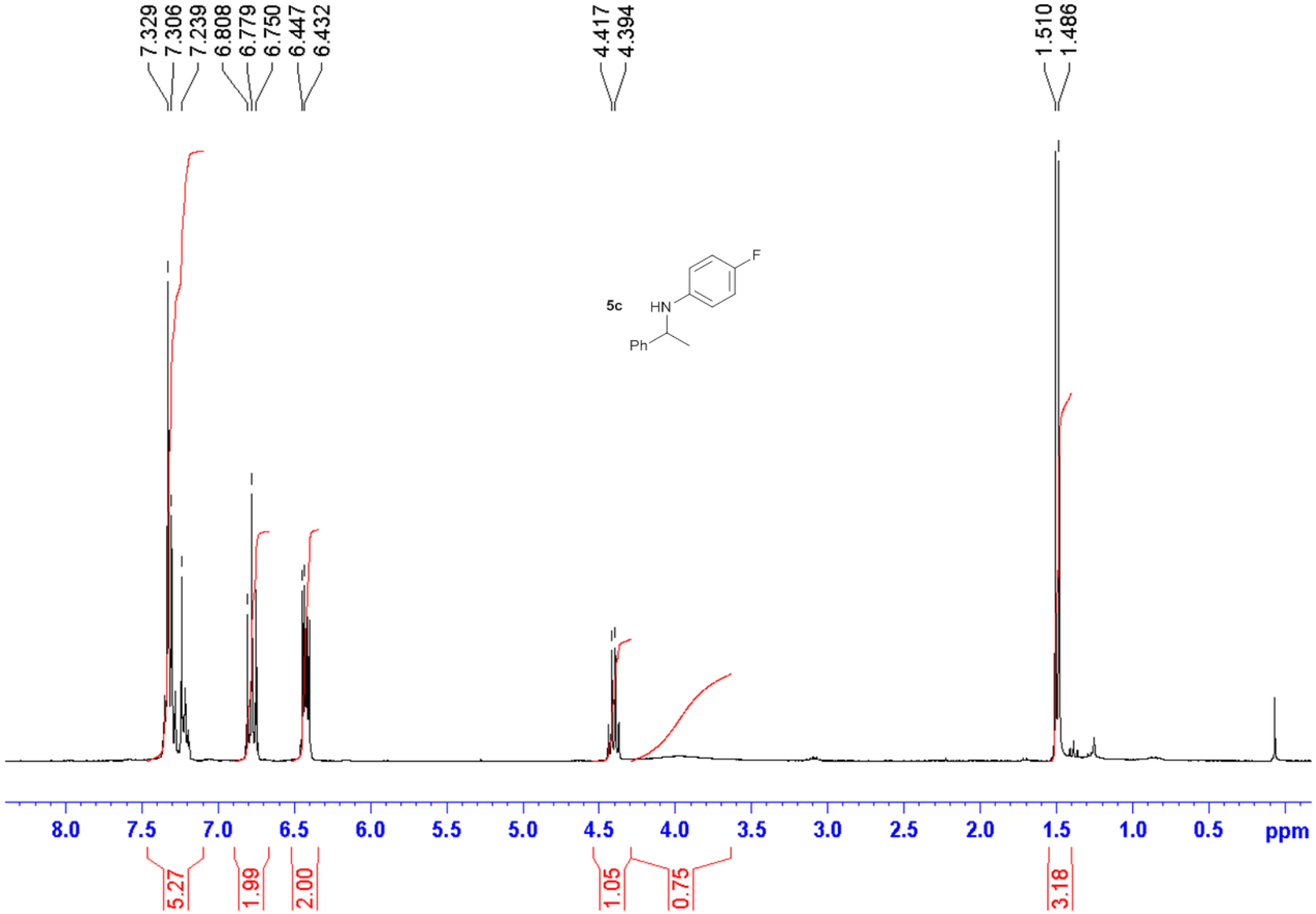
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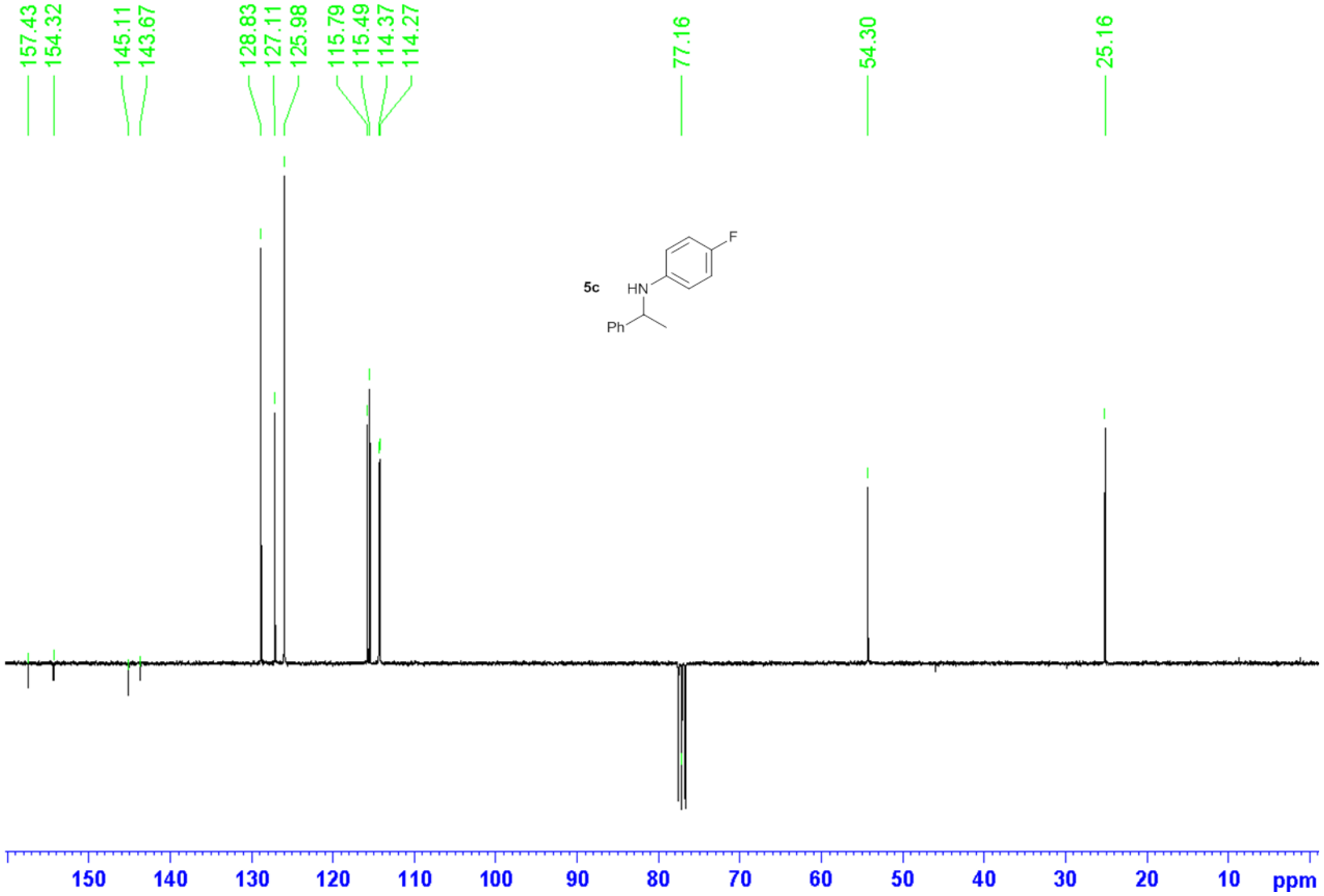
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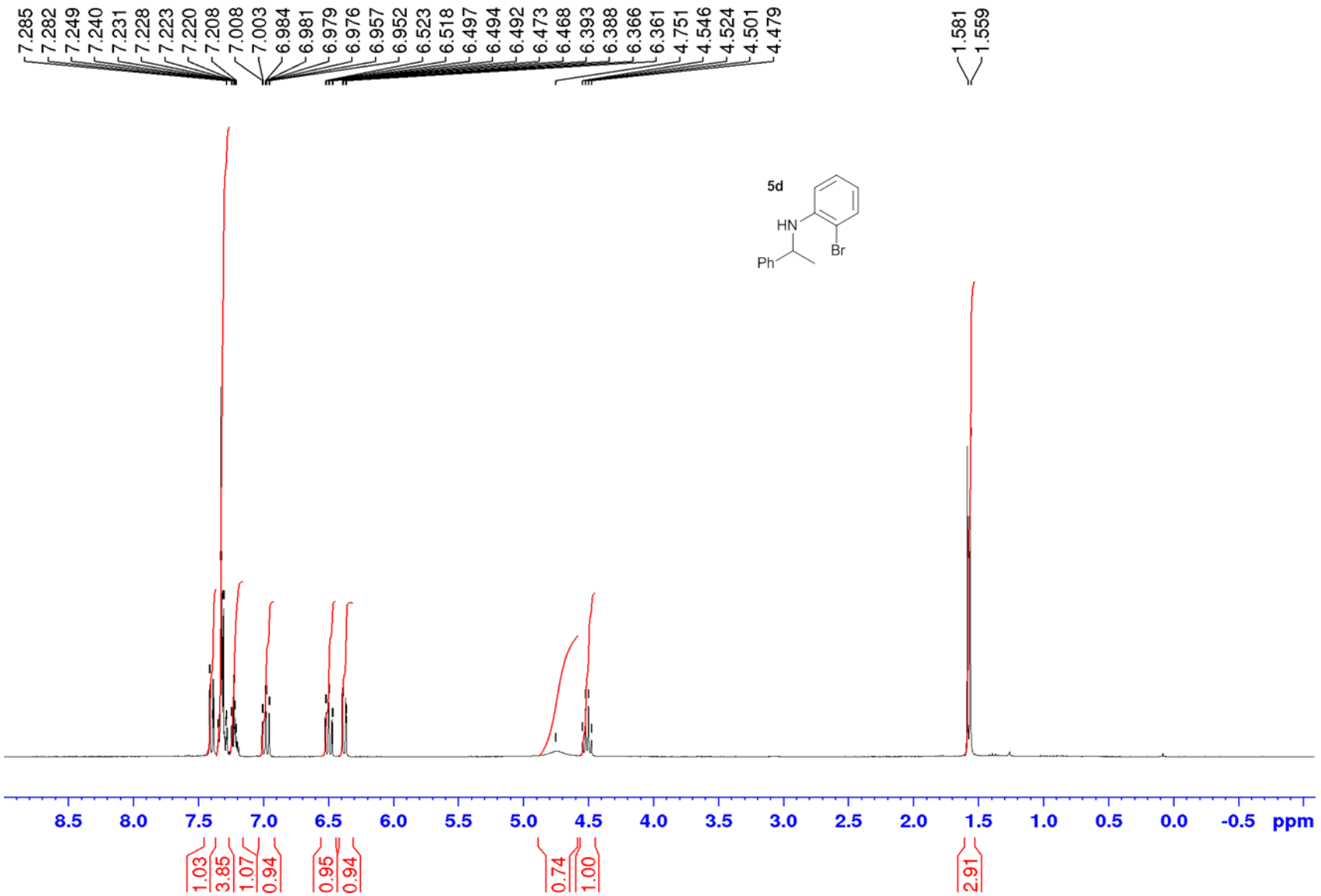
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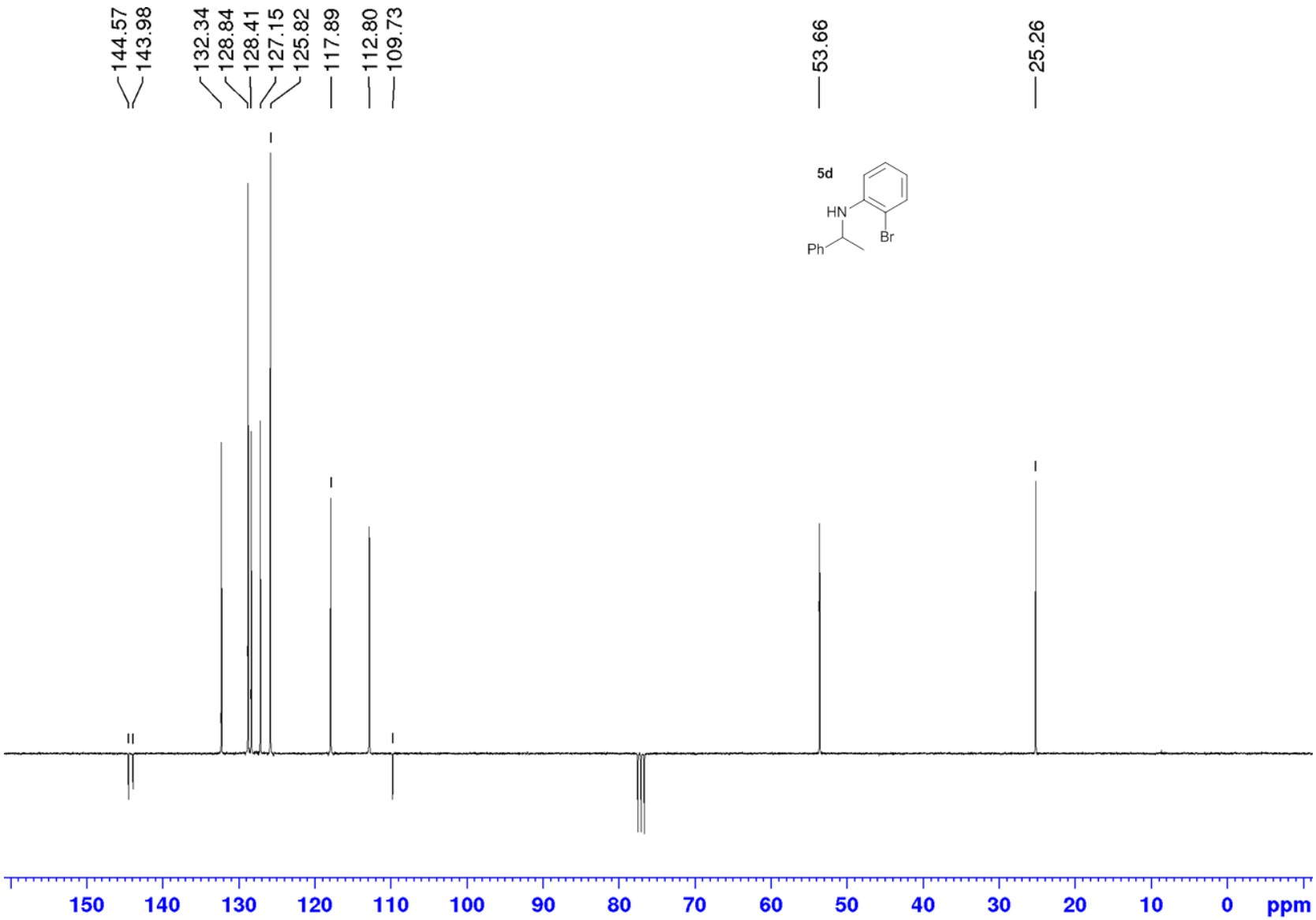
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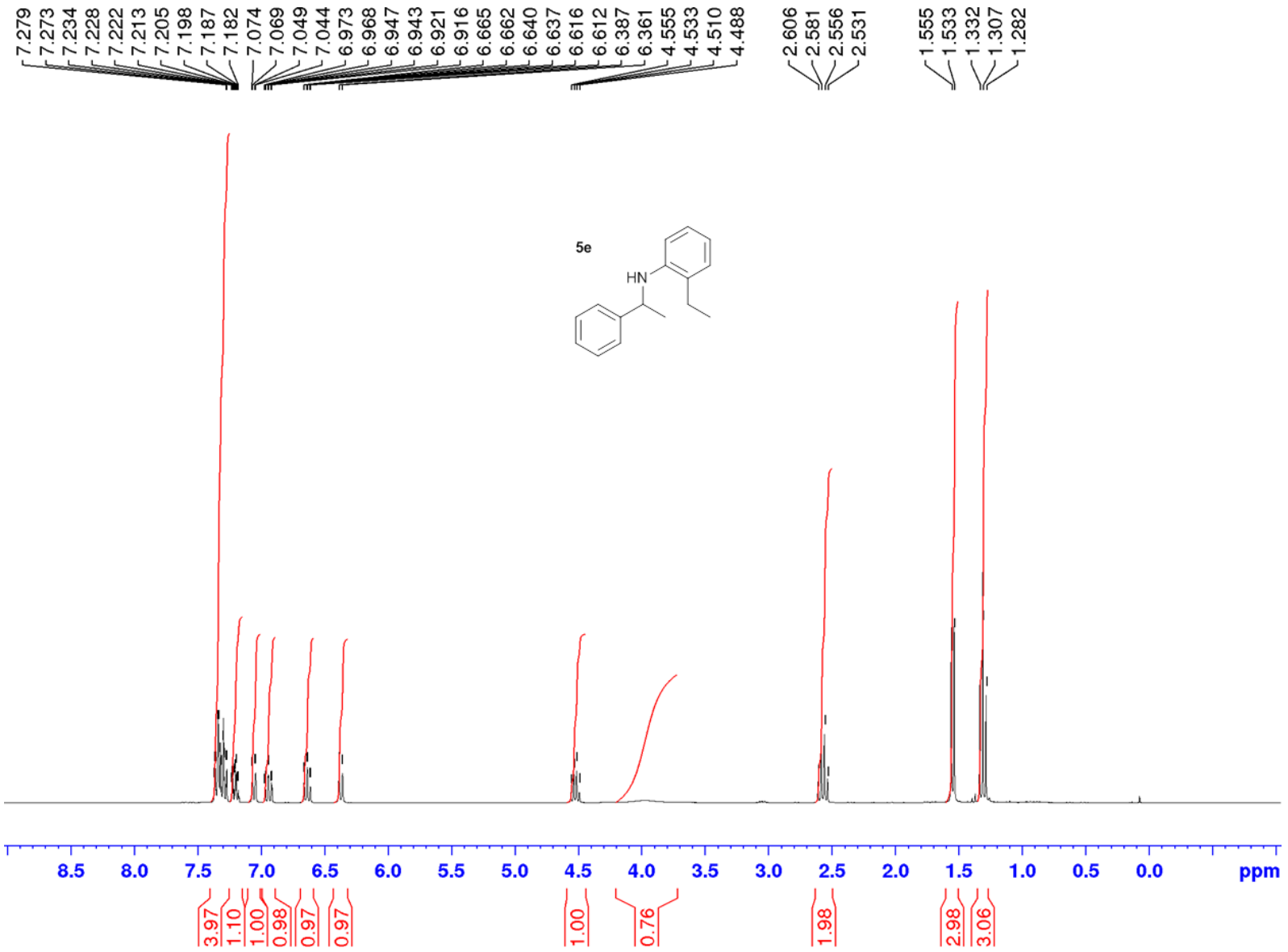
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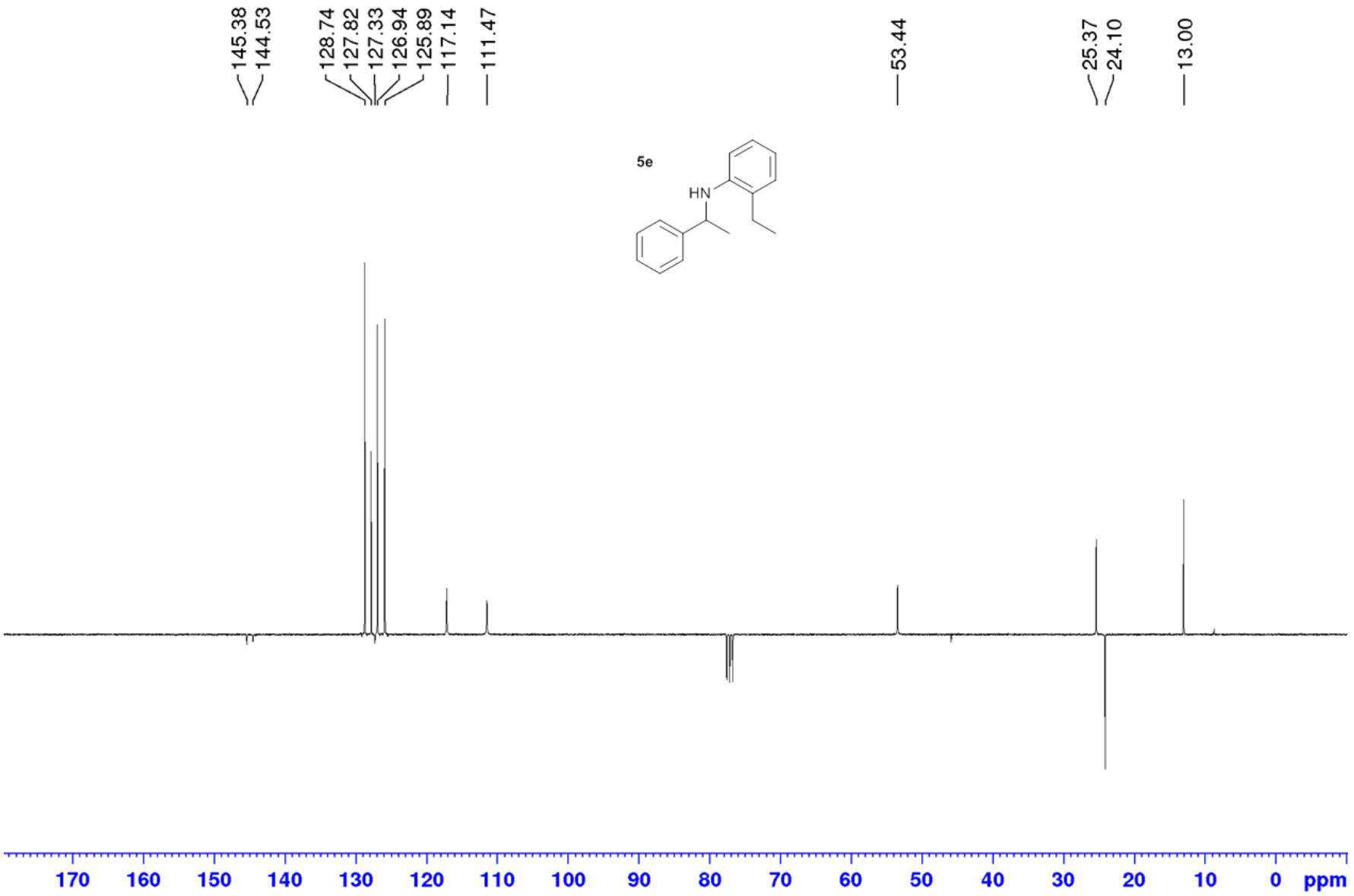
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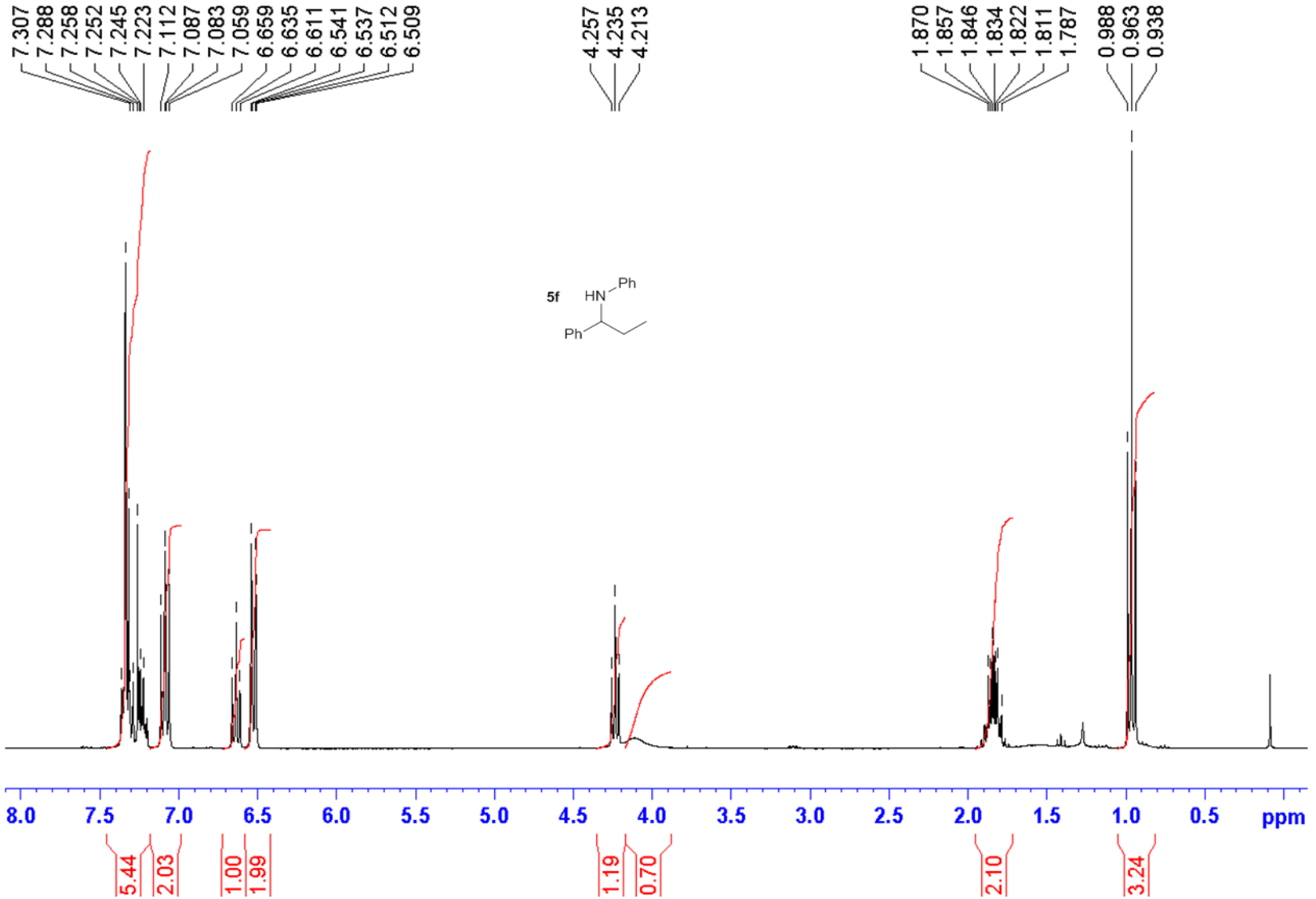
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6.541
6.537
6.512
6.509
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4.235
4.213
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1.834
1.822
1.811
1.787
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0.963
0.938
5f
HN
Ph
Ph
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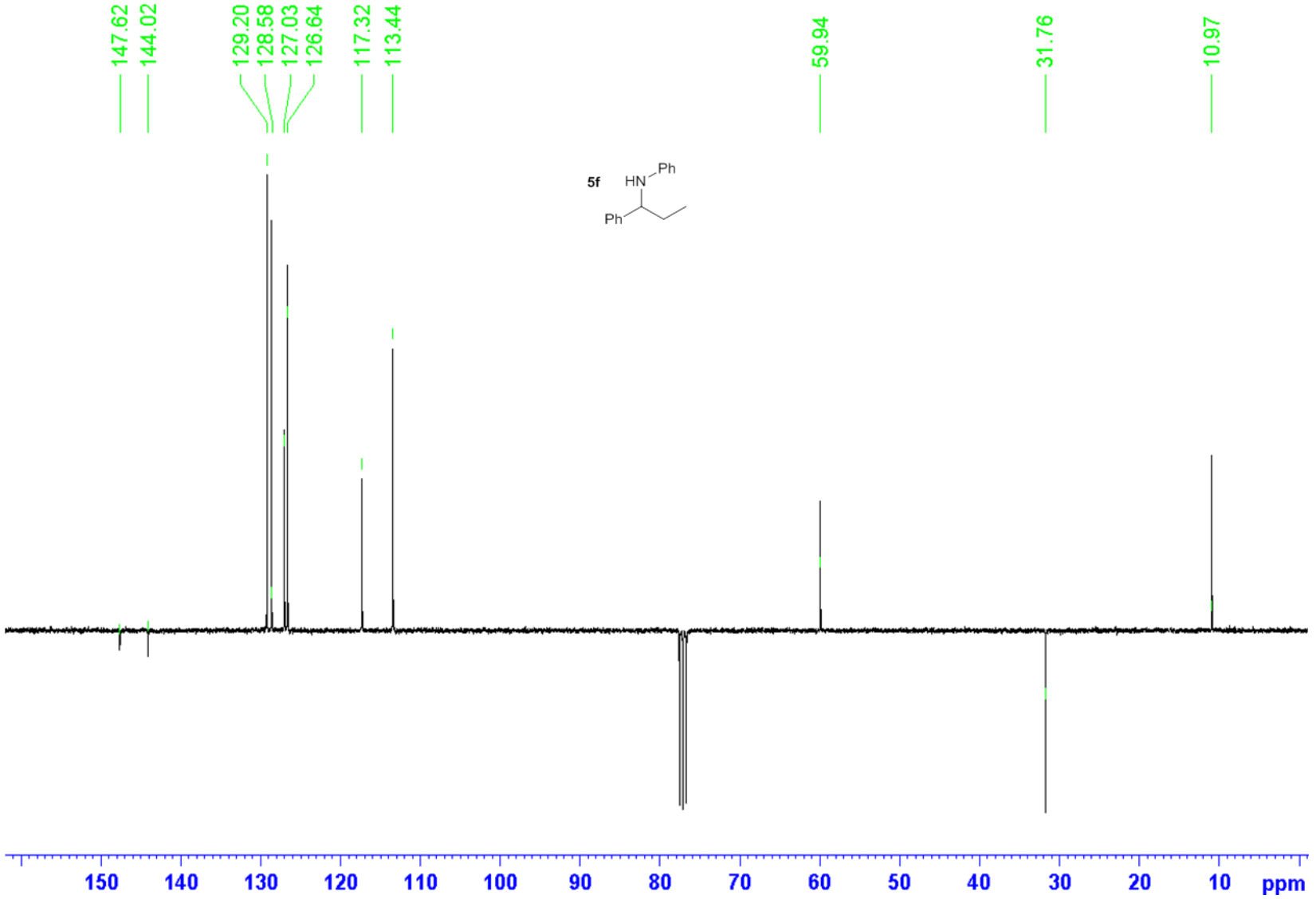
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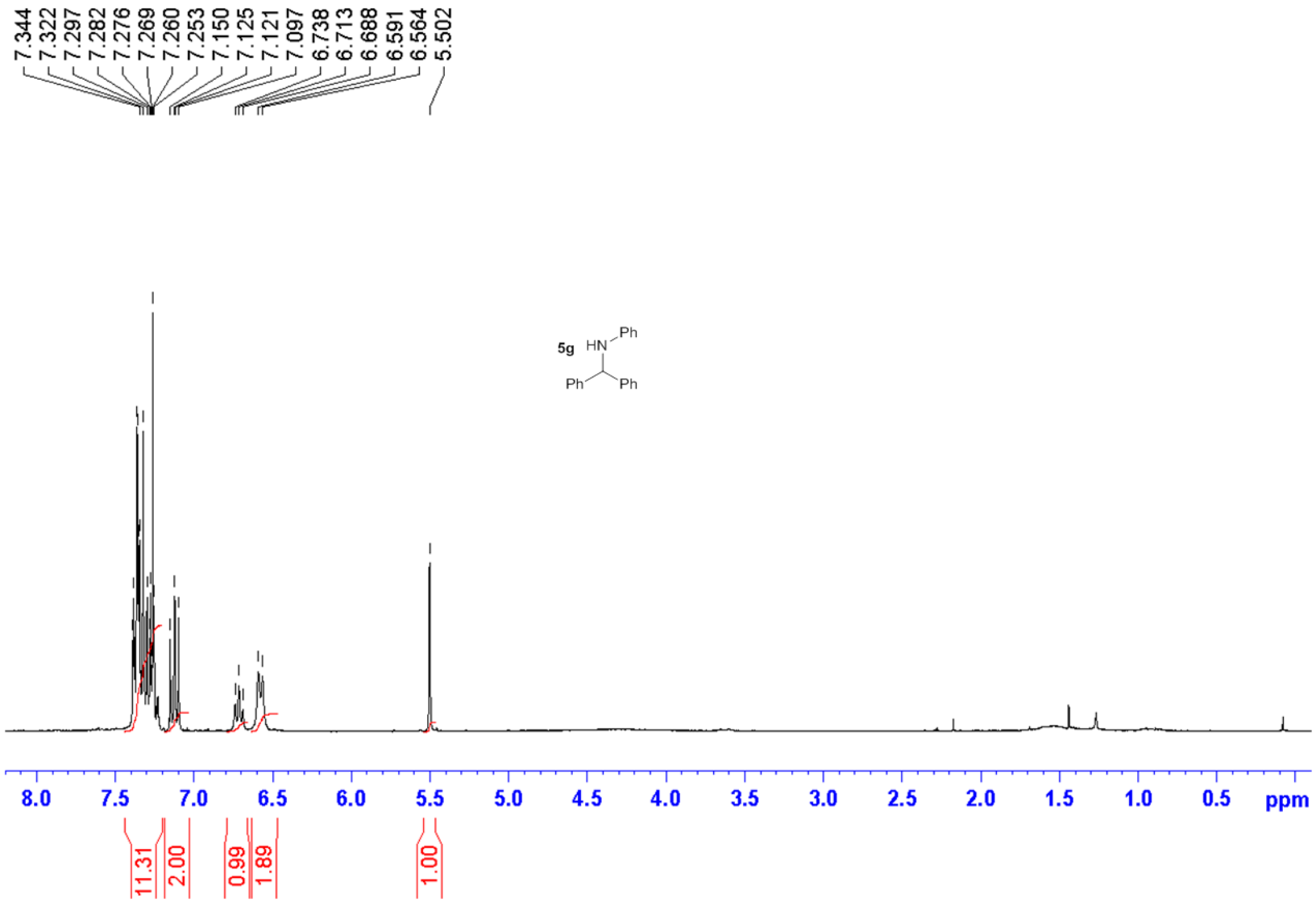
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6.688
6.591
6.564
5.502
5g
HN
Ph
Ph
Ph
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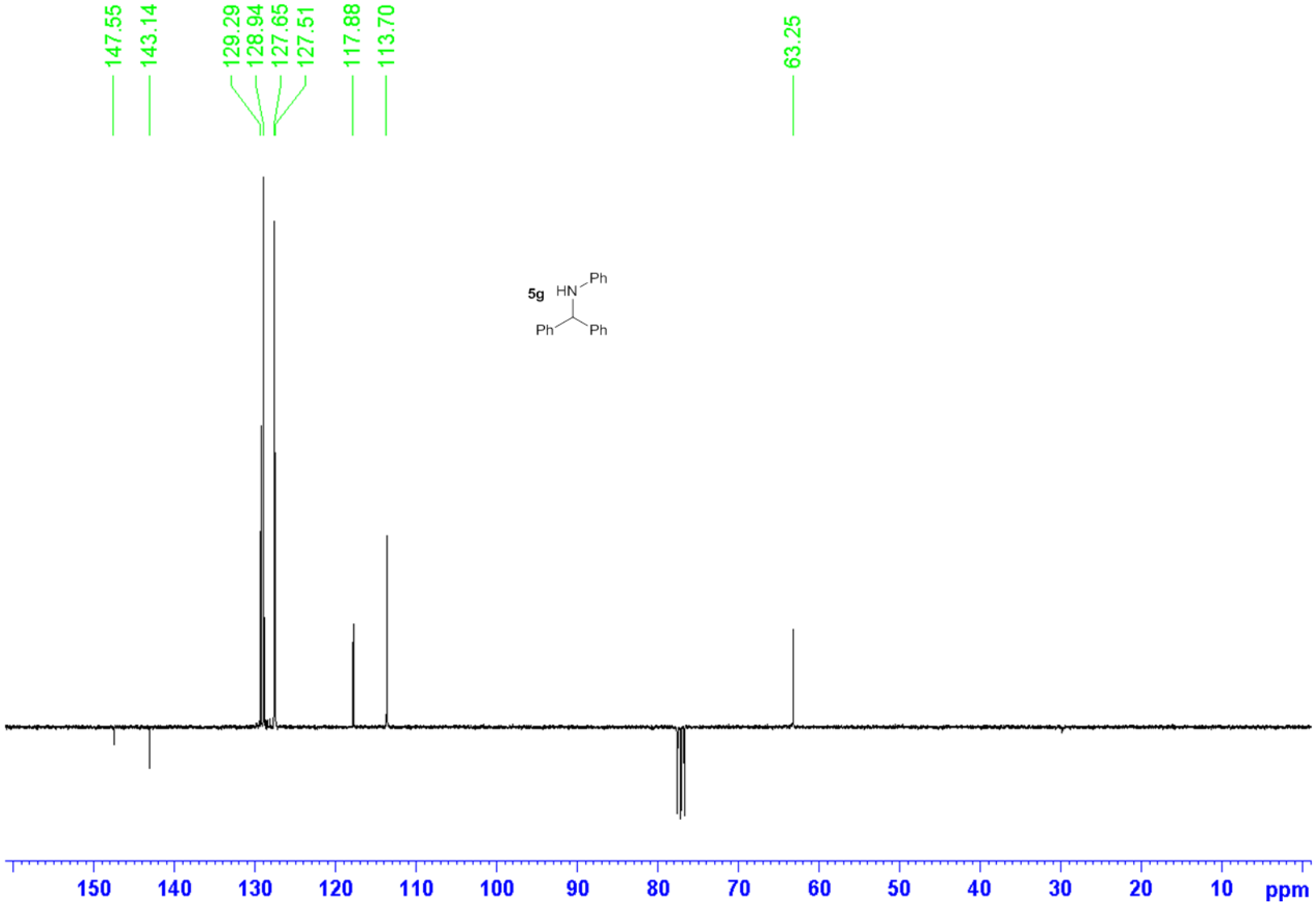
1.00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5g
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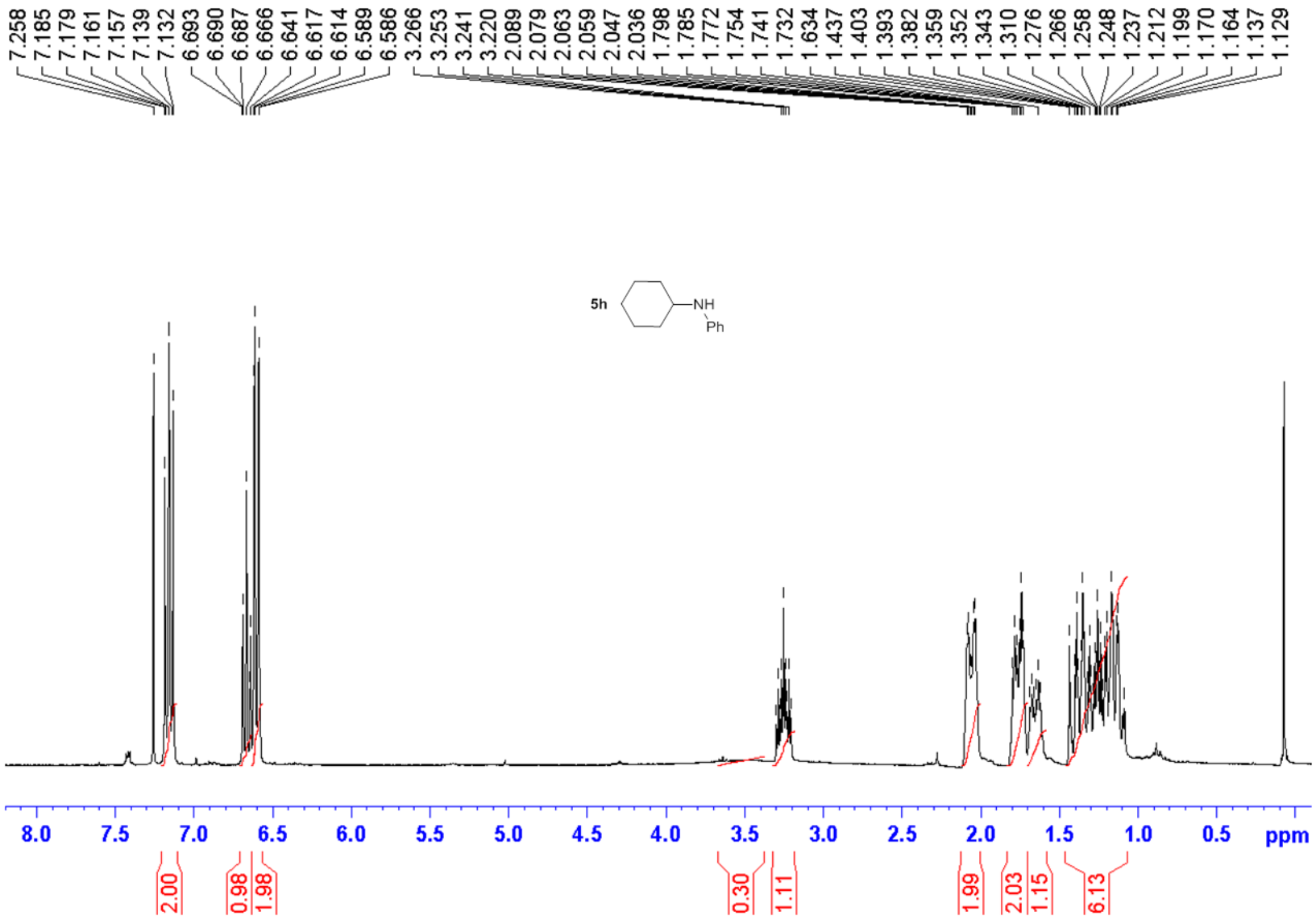
ppm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6.614
6.589
6.586
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3.220
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2.059
2.047
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1.754
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1.248
1.237
1.212
1.199
1.170
1.164
1.137
1.129
5h
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4.0
3.5
3.0
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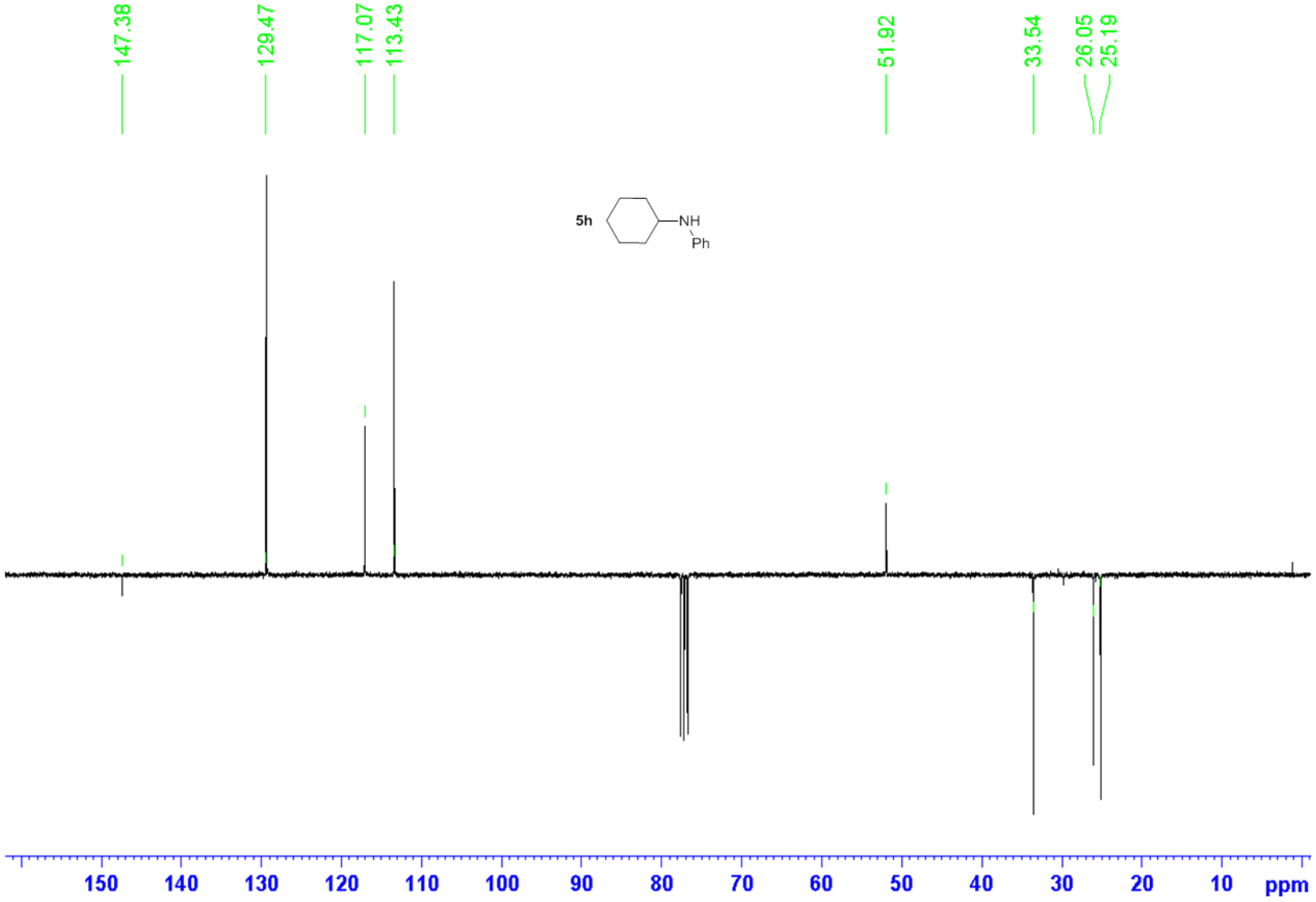
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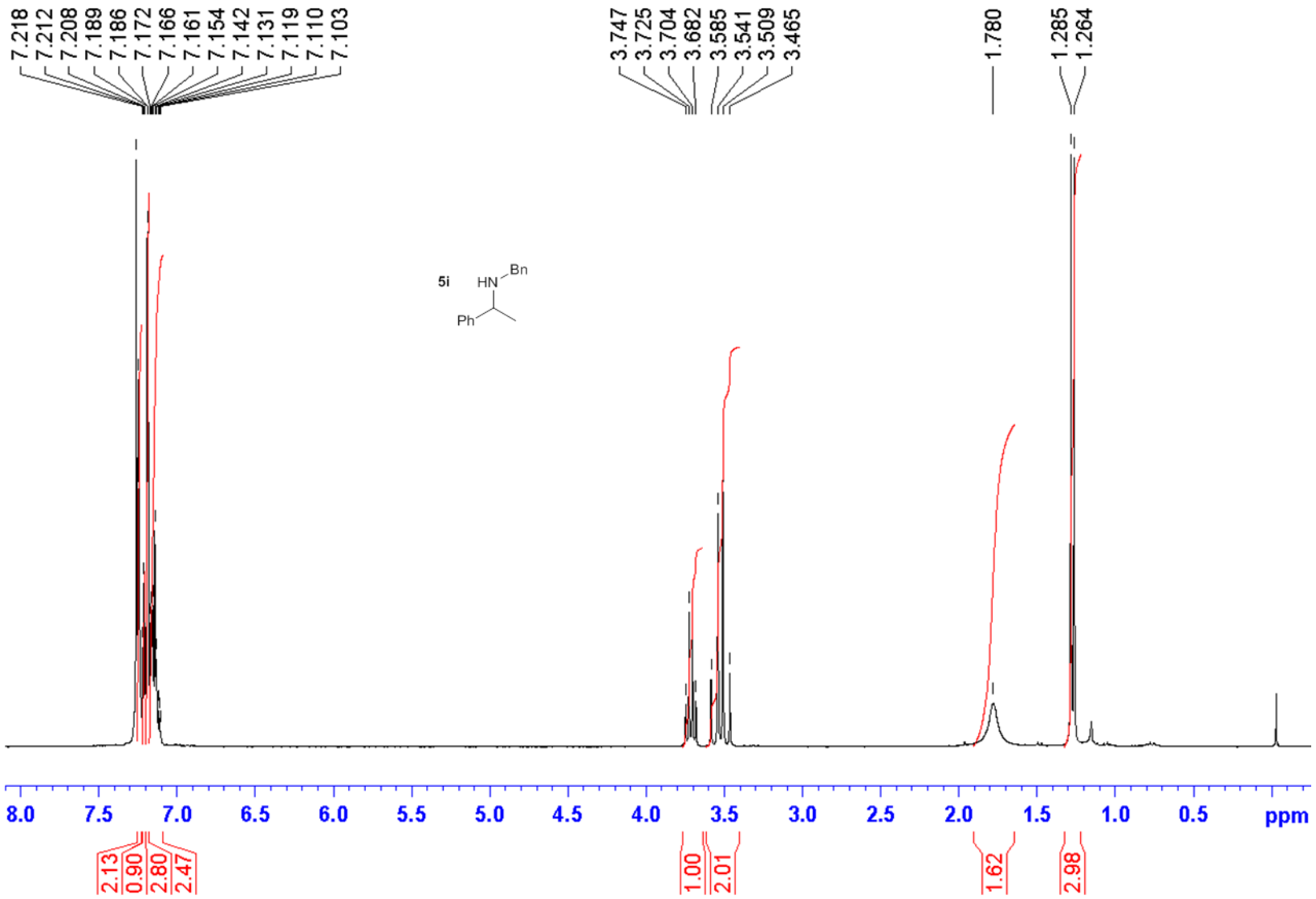
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7.110
7.103
3.747
3.725
3.704
3.682
3.585
3.541
3.509
3.465
1.780
1.285
1.264
5i
HN
Bn
Ph
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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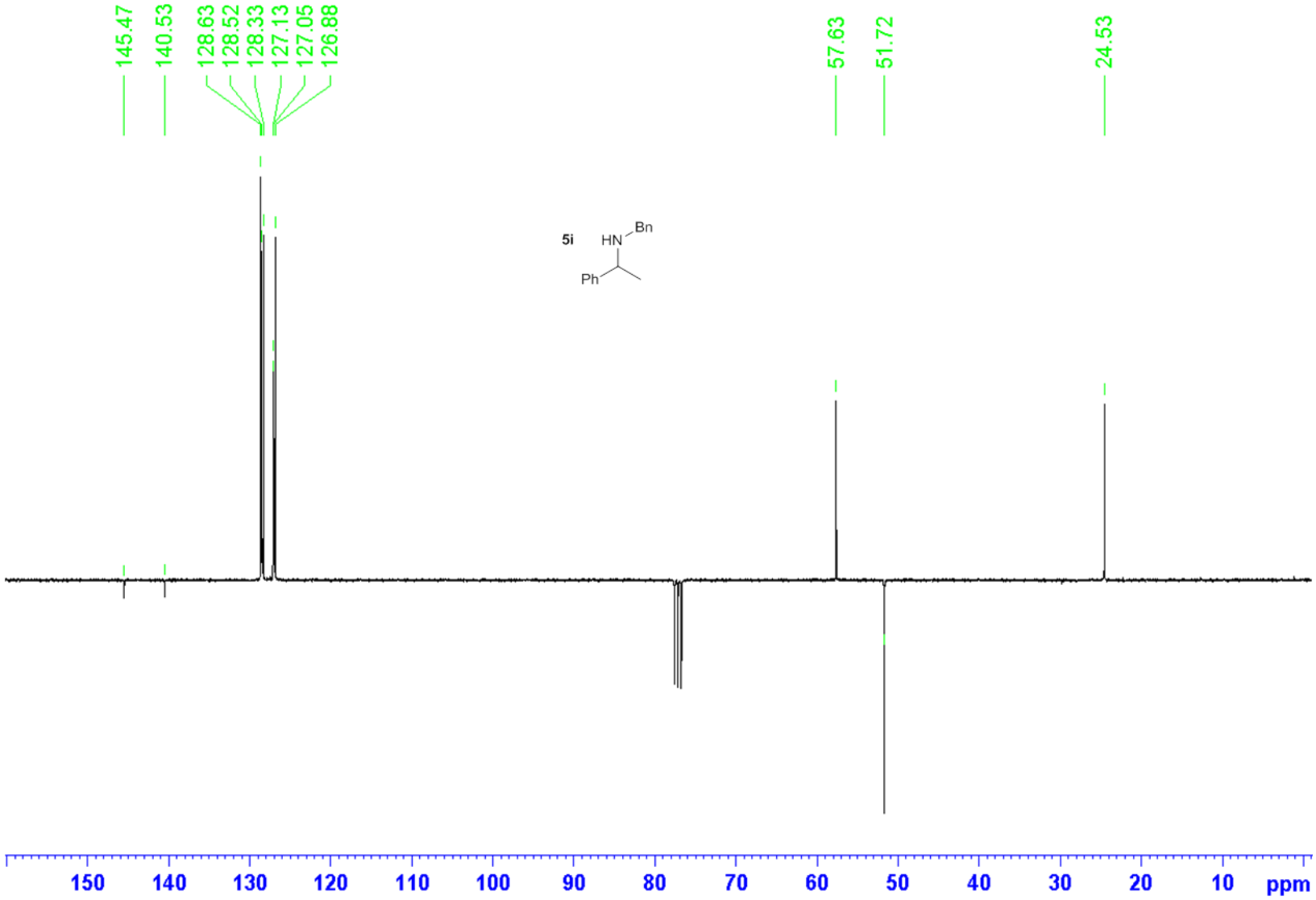
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24.53
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Bn
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140
130
120
110
100
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70
60
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30
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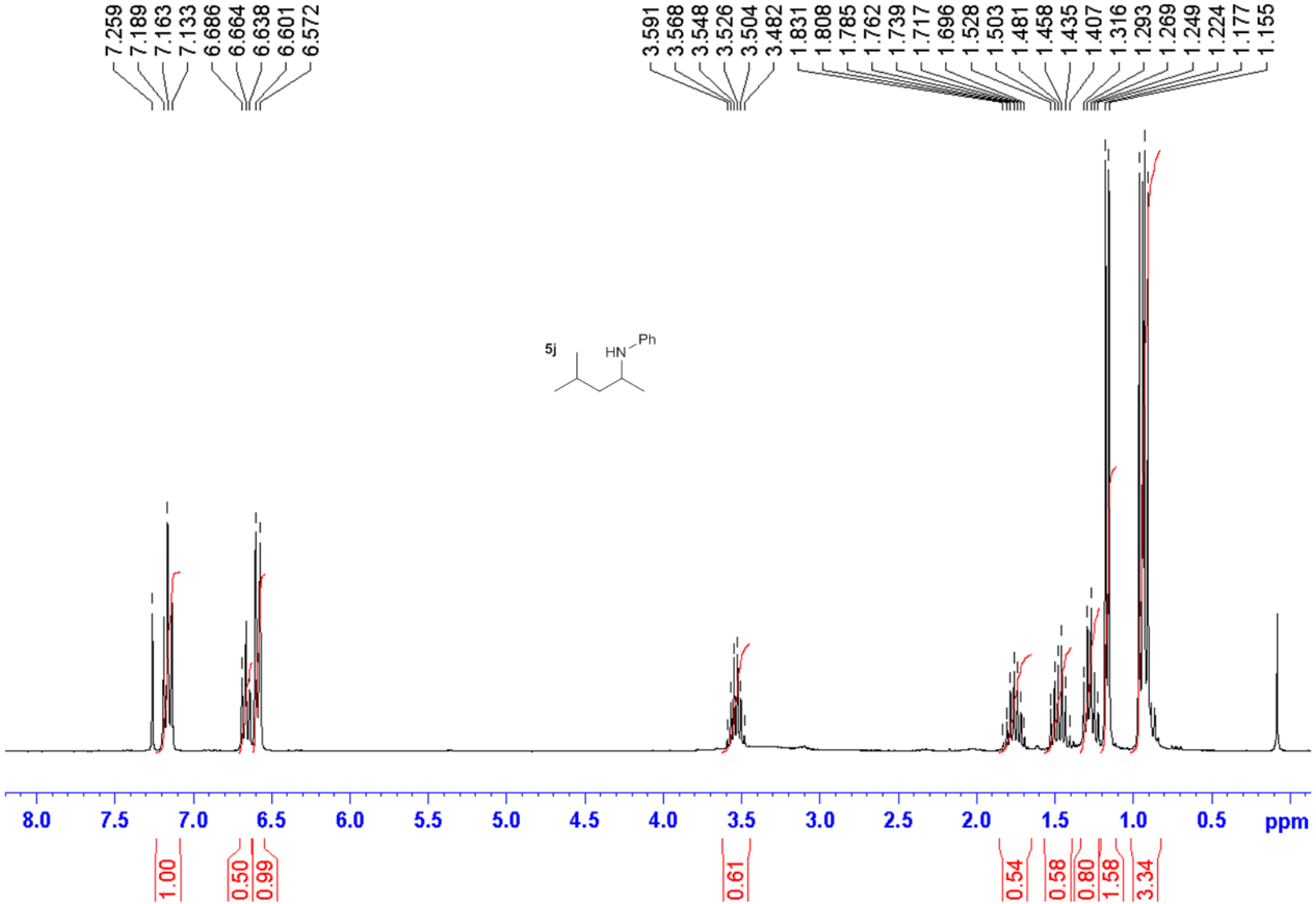
10
ppm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1.808
1.785
1.762
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1.407
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1.293
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1.155
5j
HN
Ph
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6.0
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2.0
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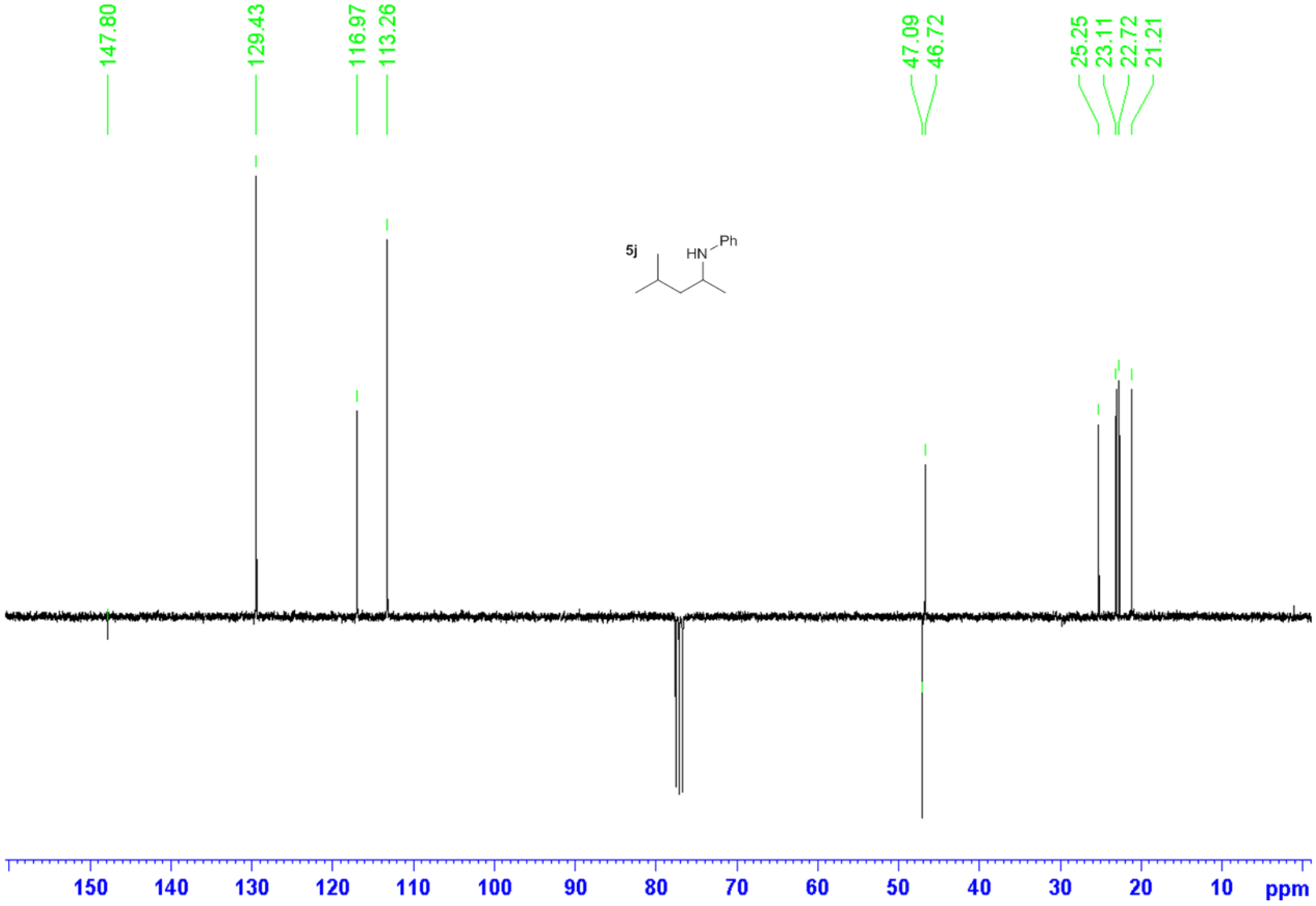
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22.72
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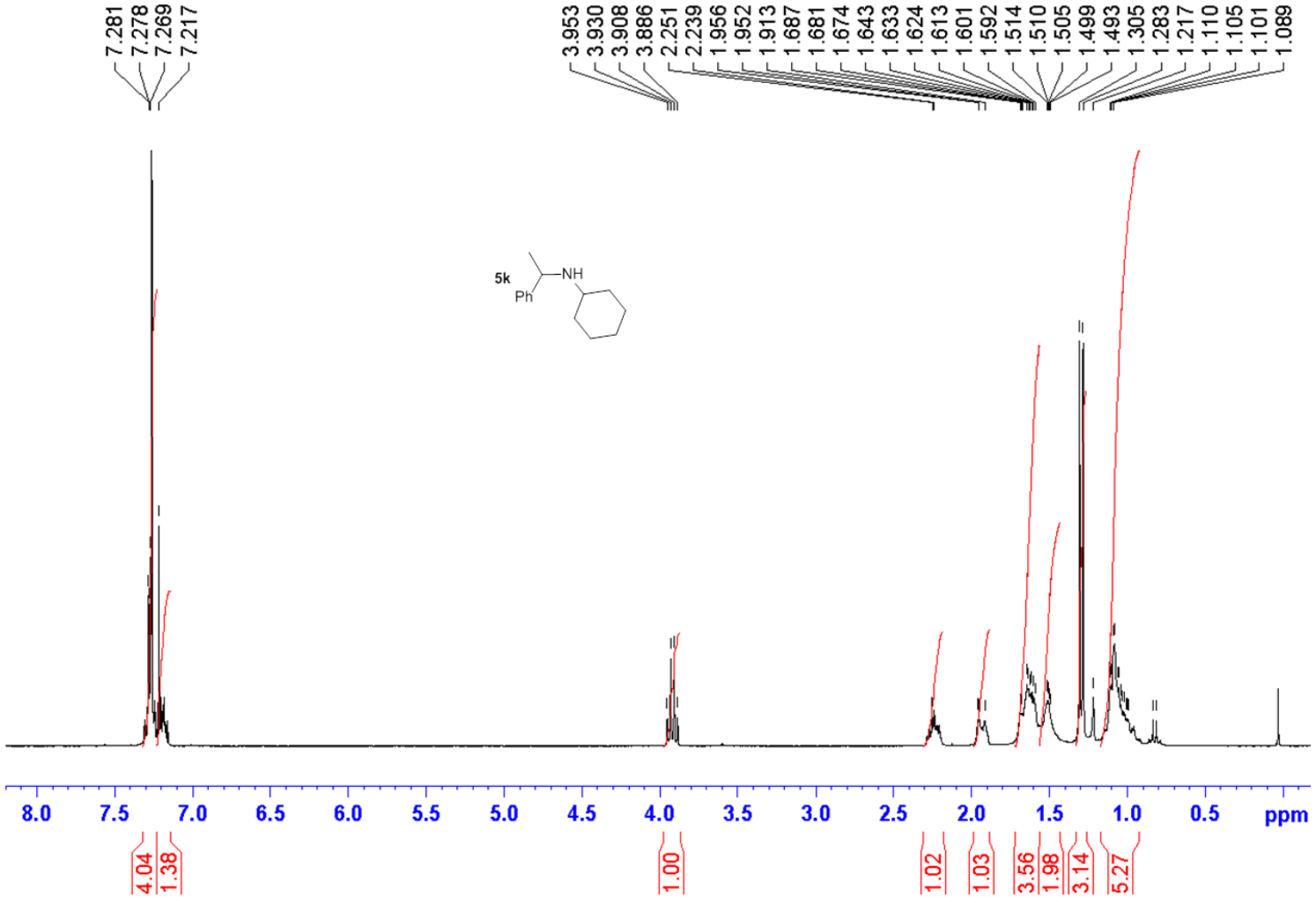
30
20
10
ppm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1.624
1.613
1.601
1.592
1.514
1.510
1.505
1.499
1.493
1.305
1.283
1.217
1.110
1.105
1.101
1.089
5k
Ph
NH
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6.0
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3.0
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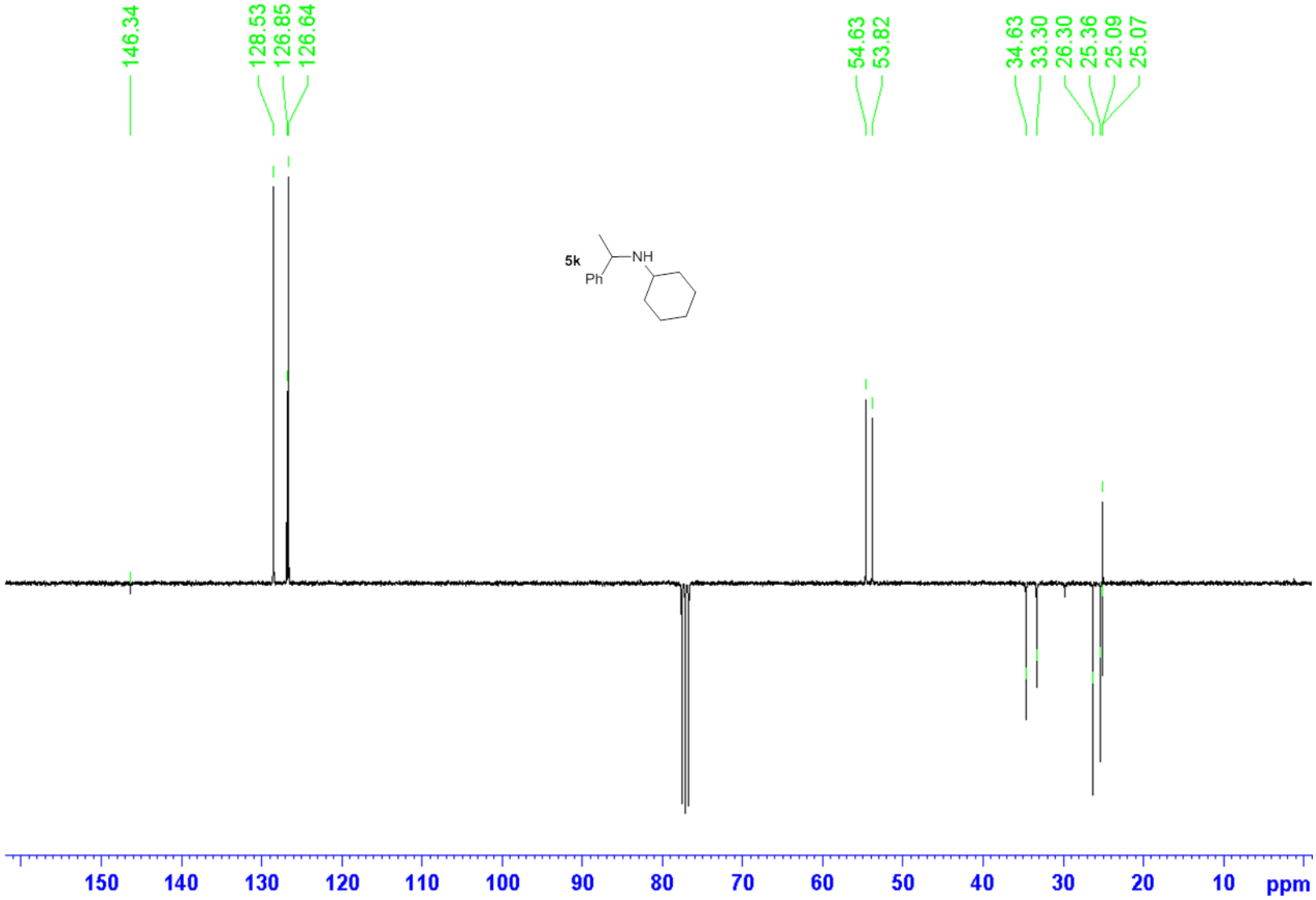
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25.09
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130
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70
60
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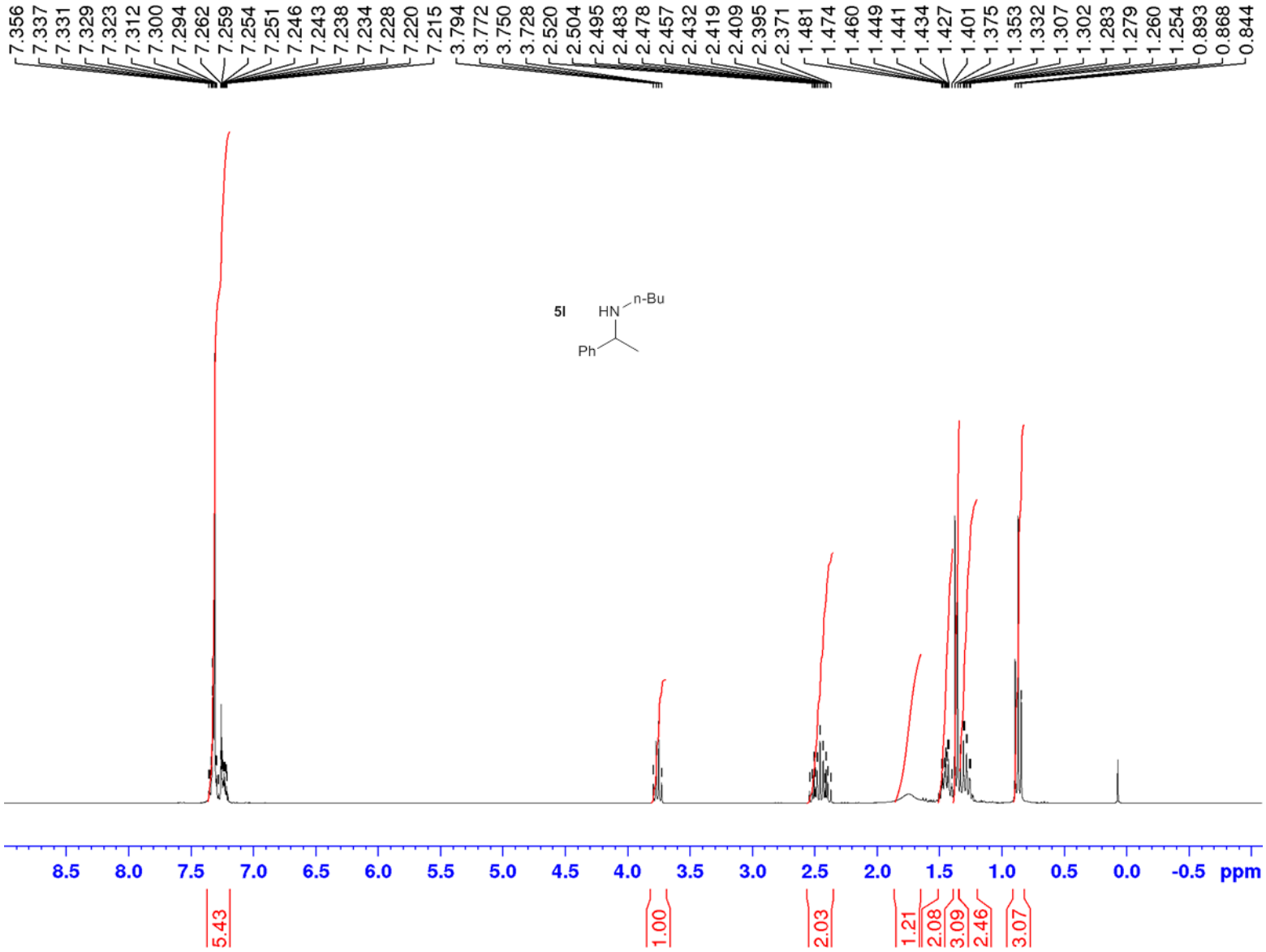
40
30
20
10
ppm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7.243
7.238
7.234
7.228
7.220
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3.750
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1.460
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1.302
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1.279
1.260
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0.844
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HN
n-Bu
Ph
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4.0
3.5
3.0
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2.0
1.5
1.0
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ppm
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1.21
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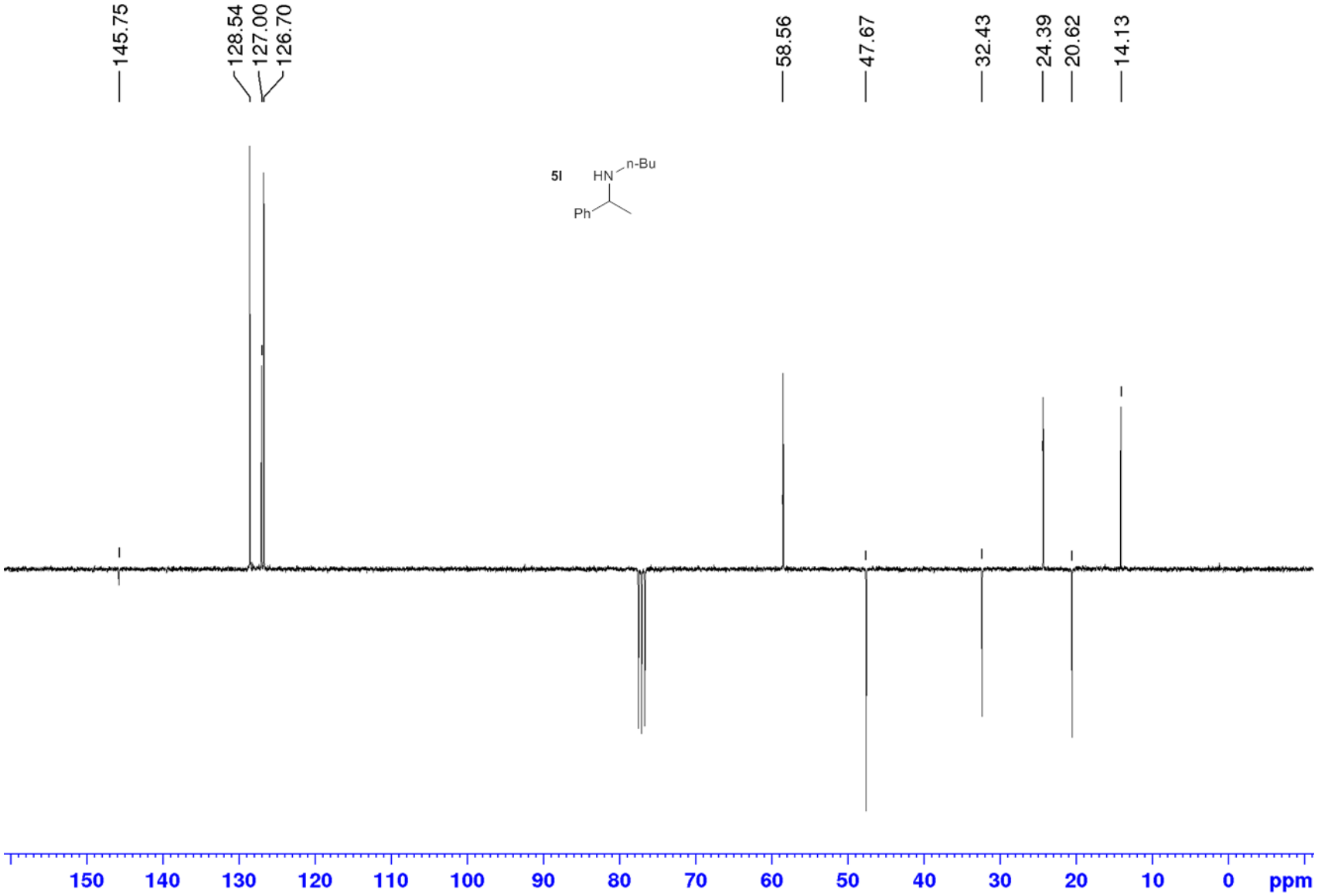
2.46
3.07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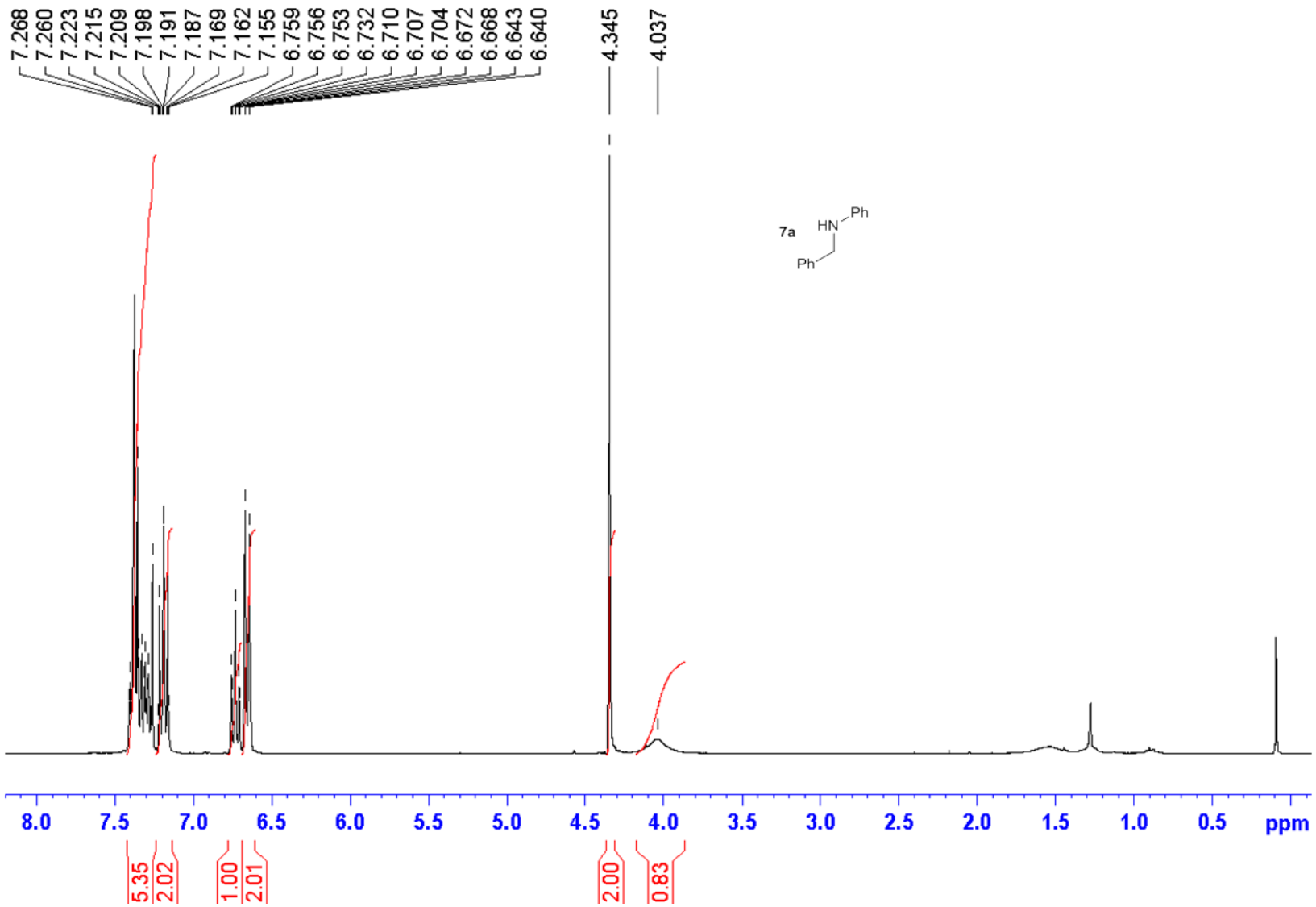
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Ph
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6.0
5.5
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4.0
3.5
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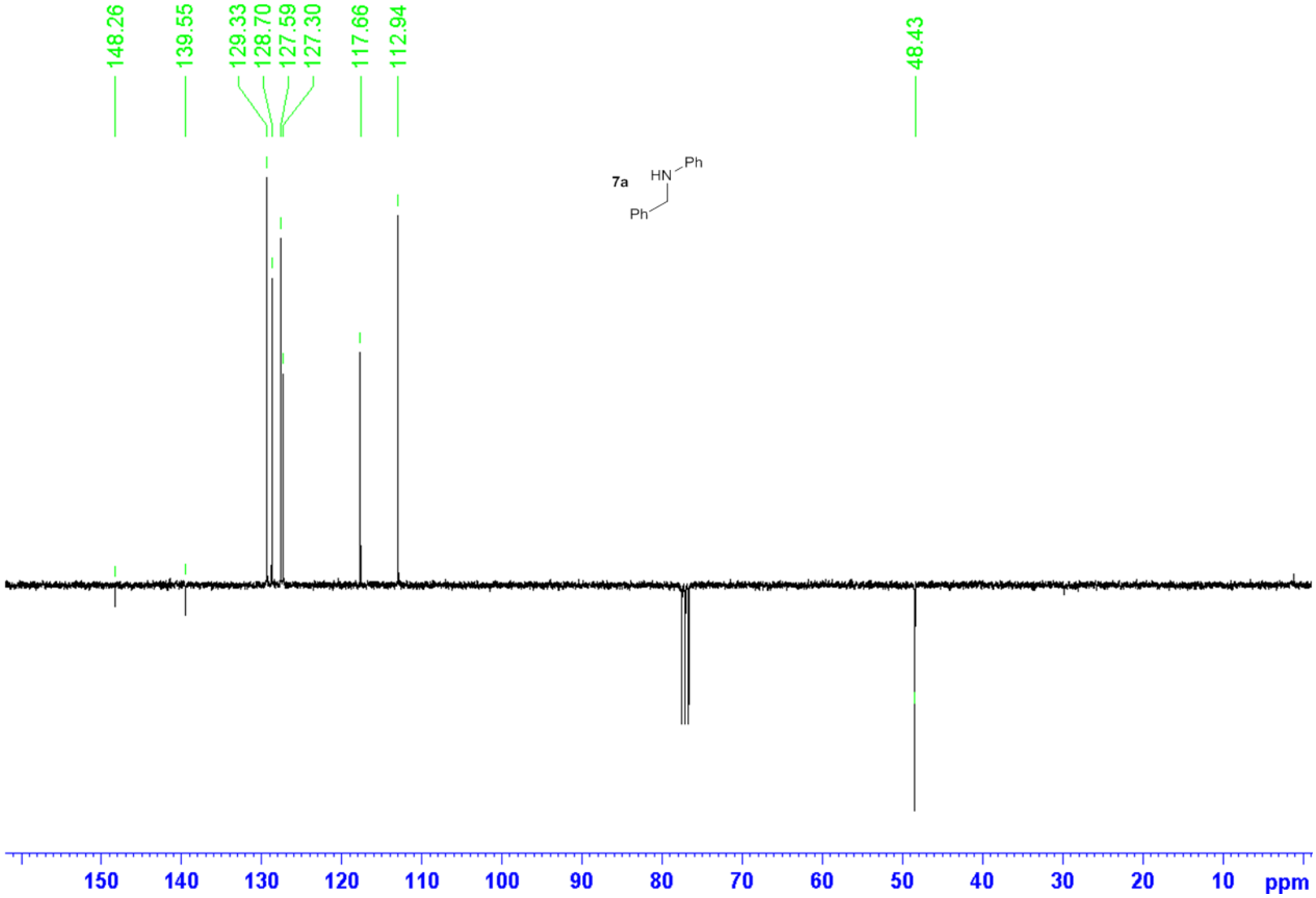
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127.30
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112.94
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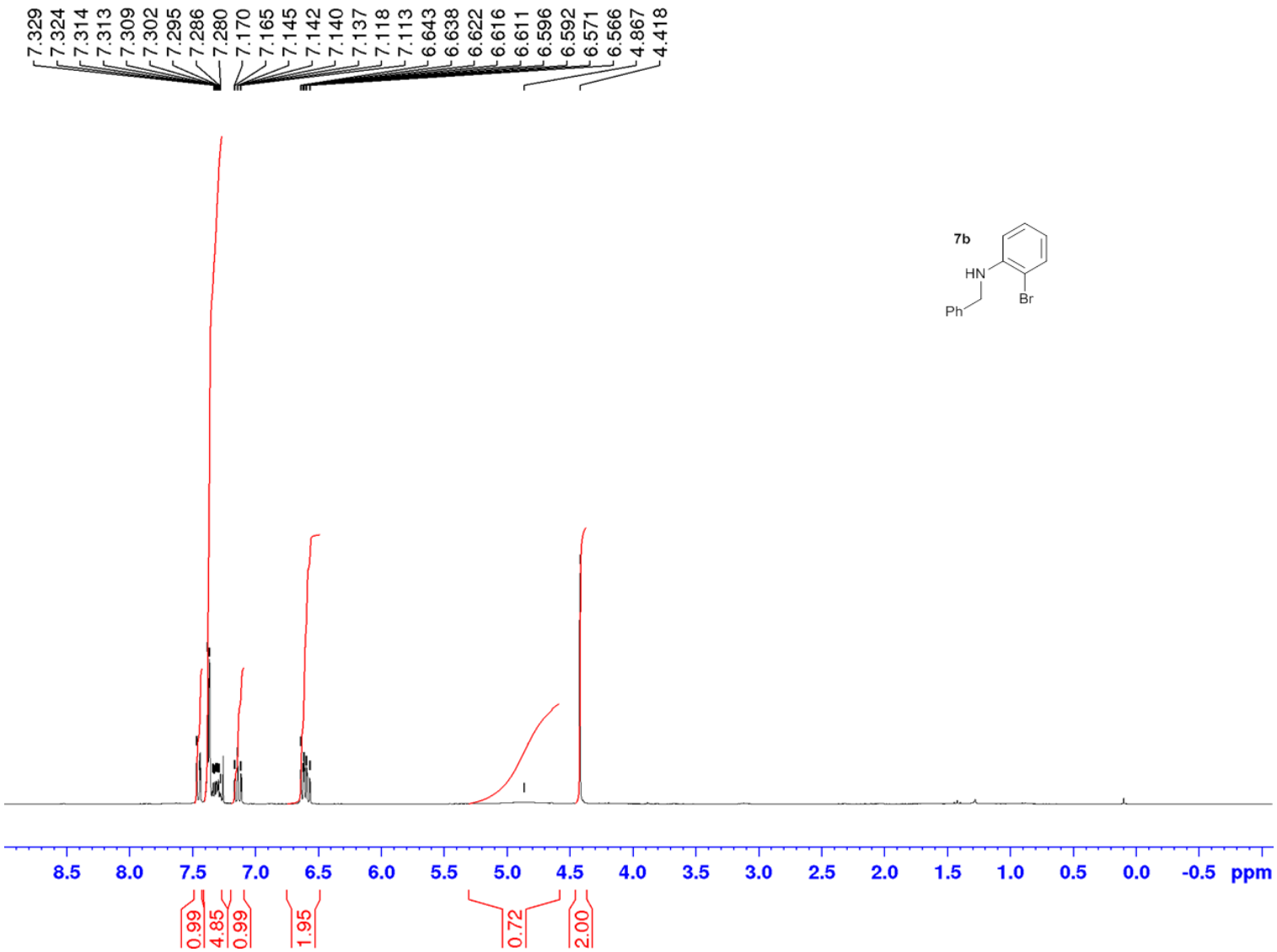
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7.140
7.137
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7.113
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6.622
6.616
6.611
6.596
6.592
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Ph
Br
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3.5
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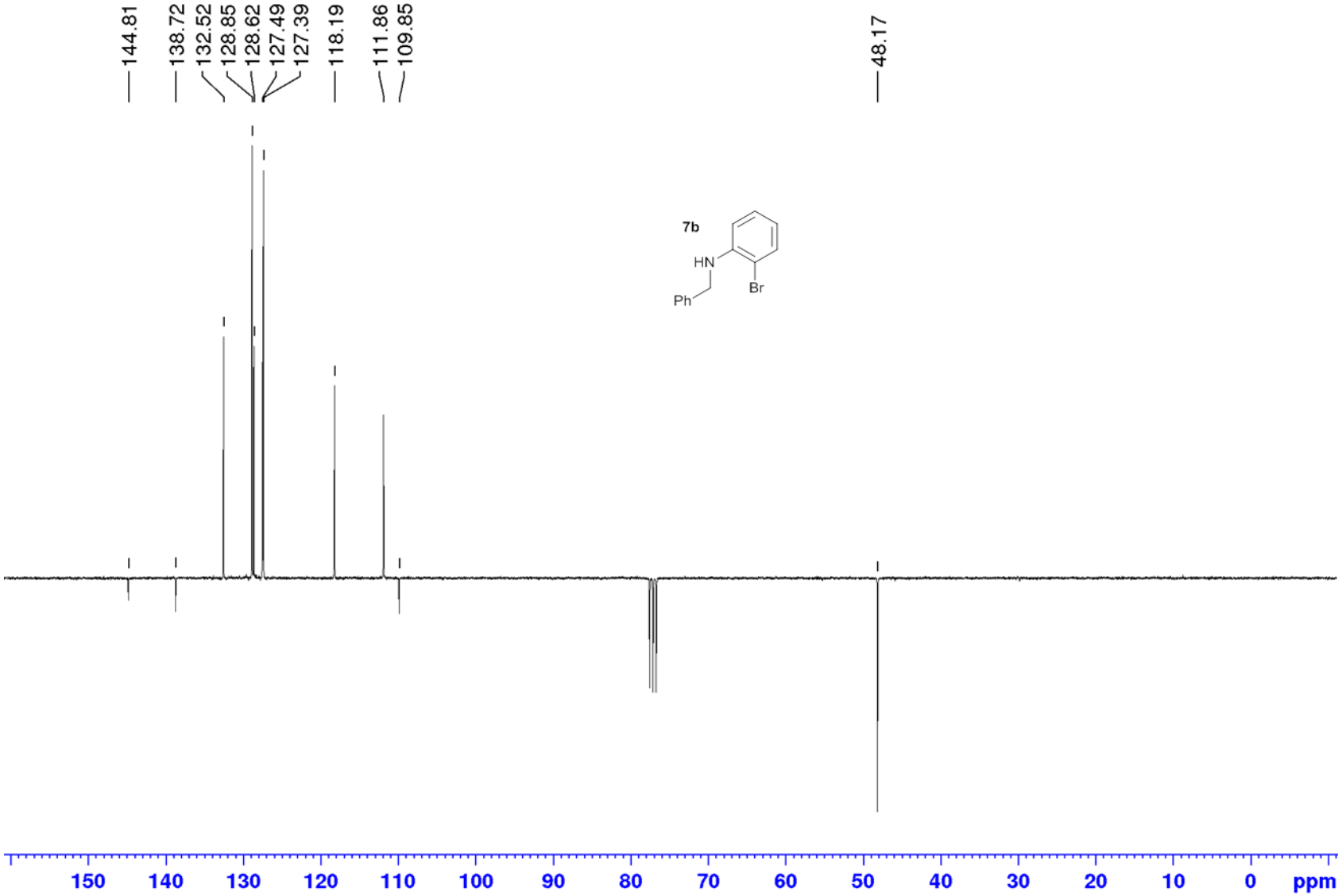
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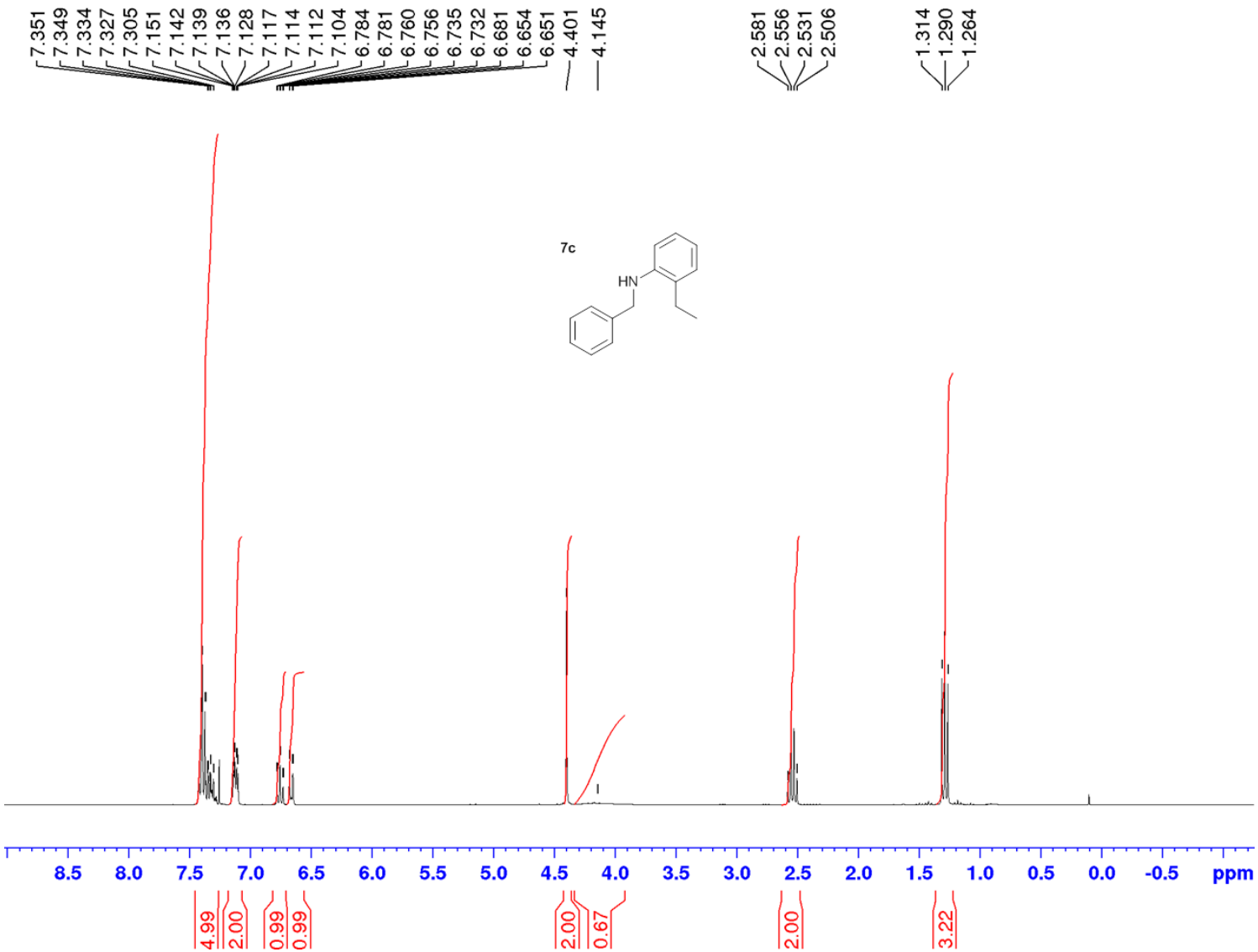
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6.781
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6.732
6.681
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2.556
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2.506
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1.264
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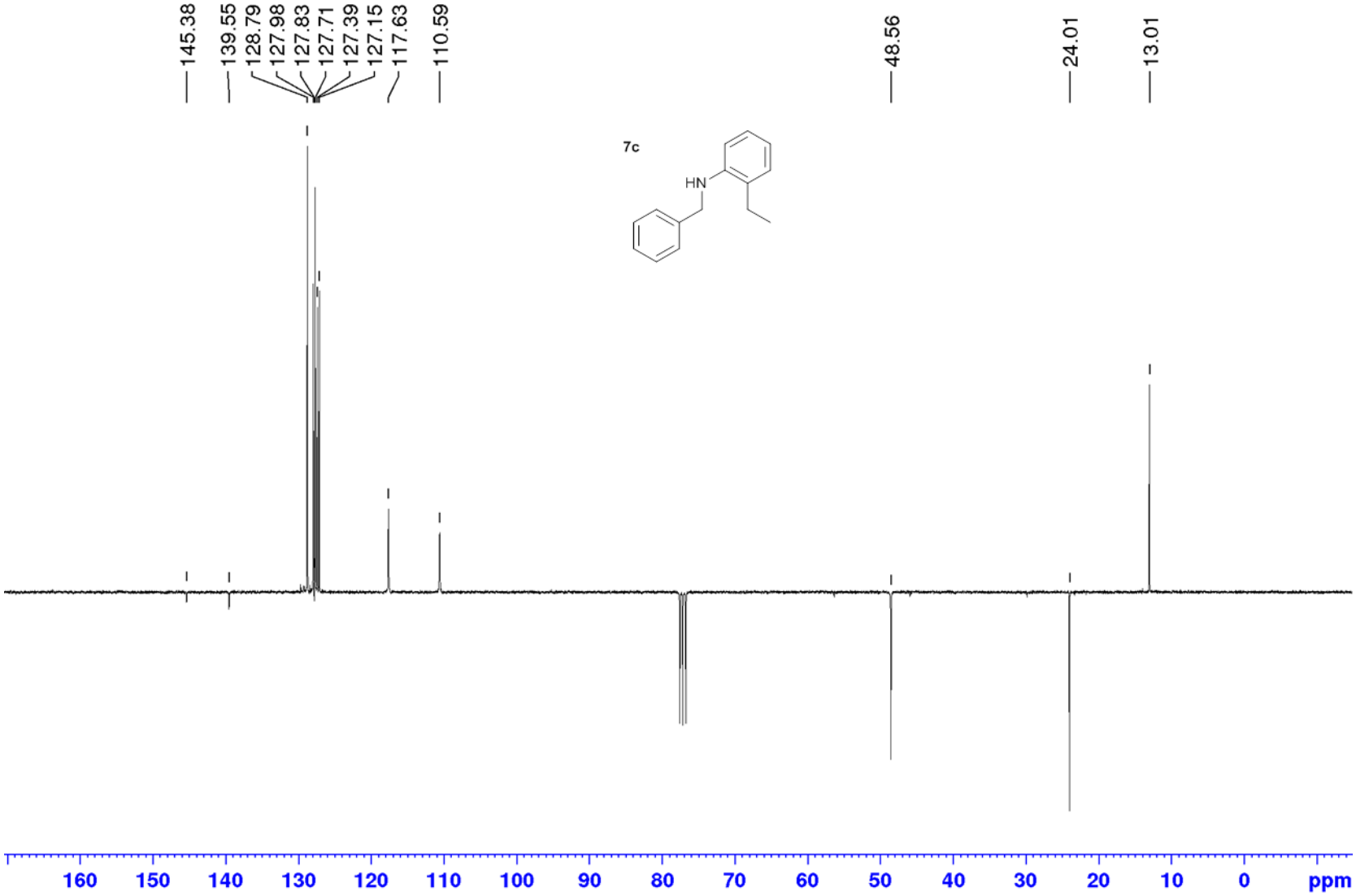
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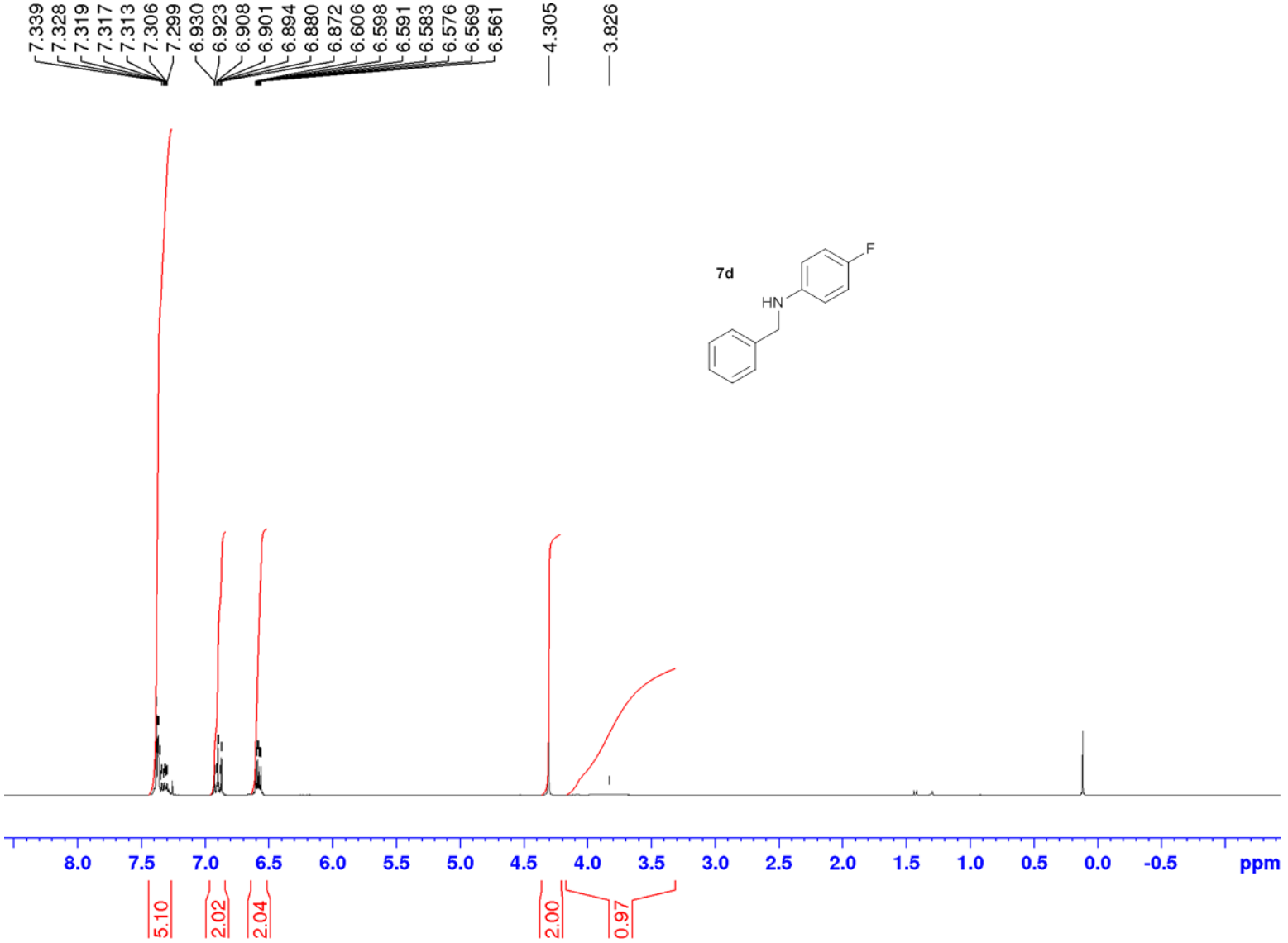
0
ppm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6.872
6.606
6.598
6.591
6.583
6.576
6.569
6.561
4.305
3.826
7d
HN
F
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6.5
6.0
5.5
5.0
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3.5
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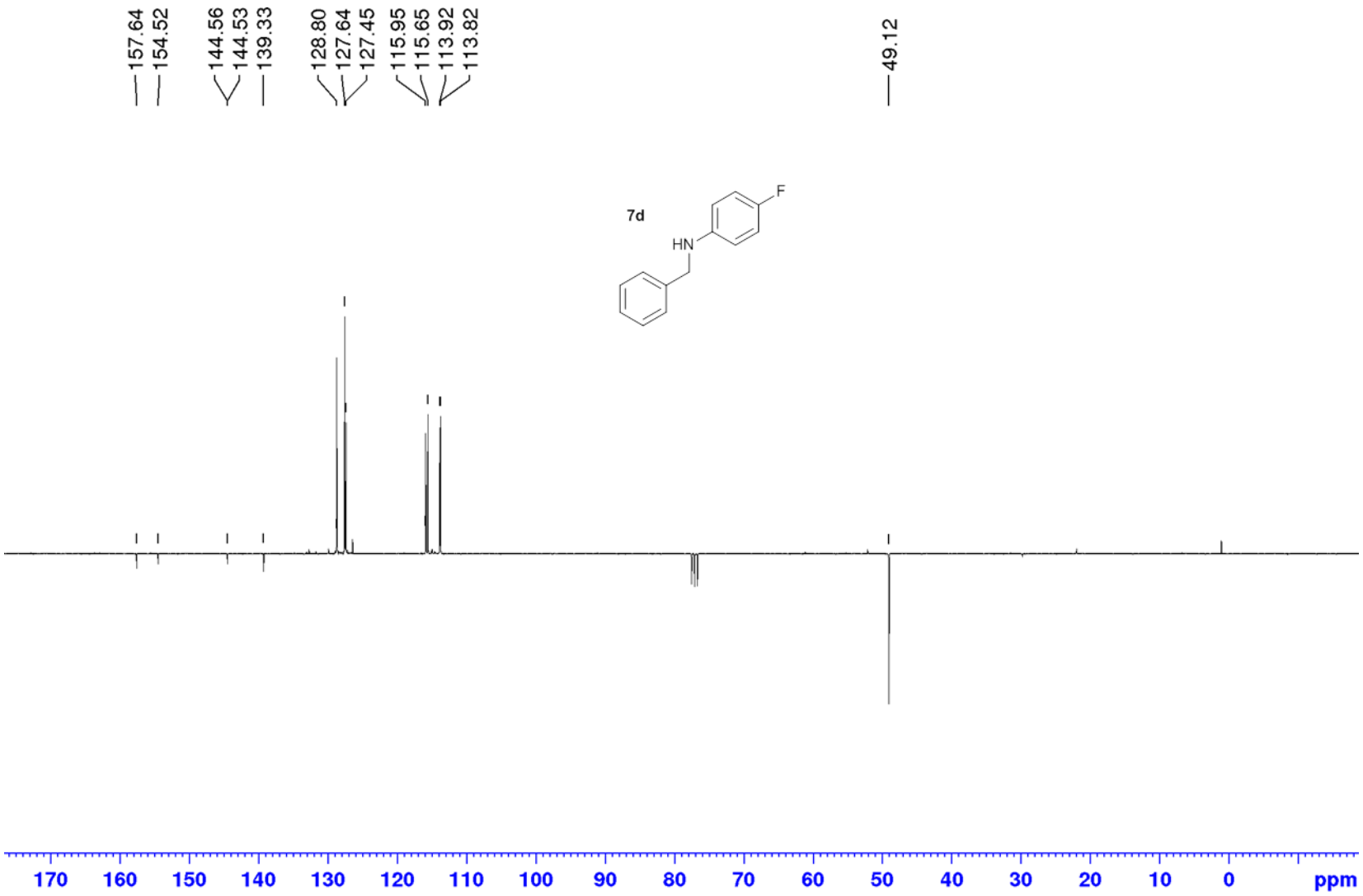
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7d
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F
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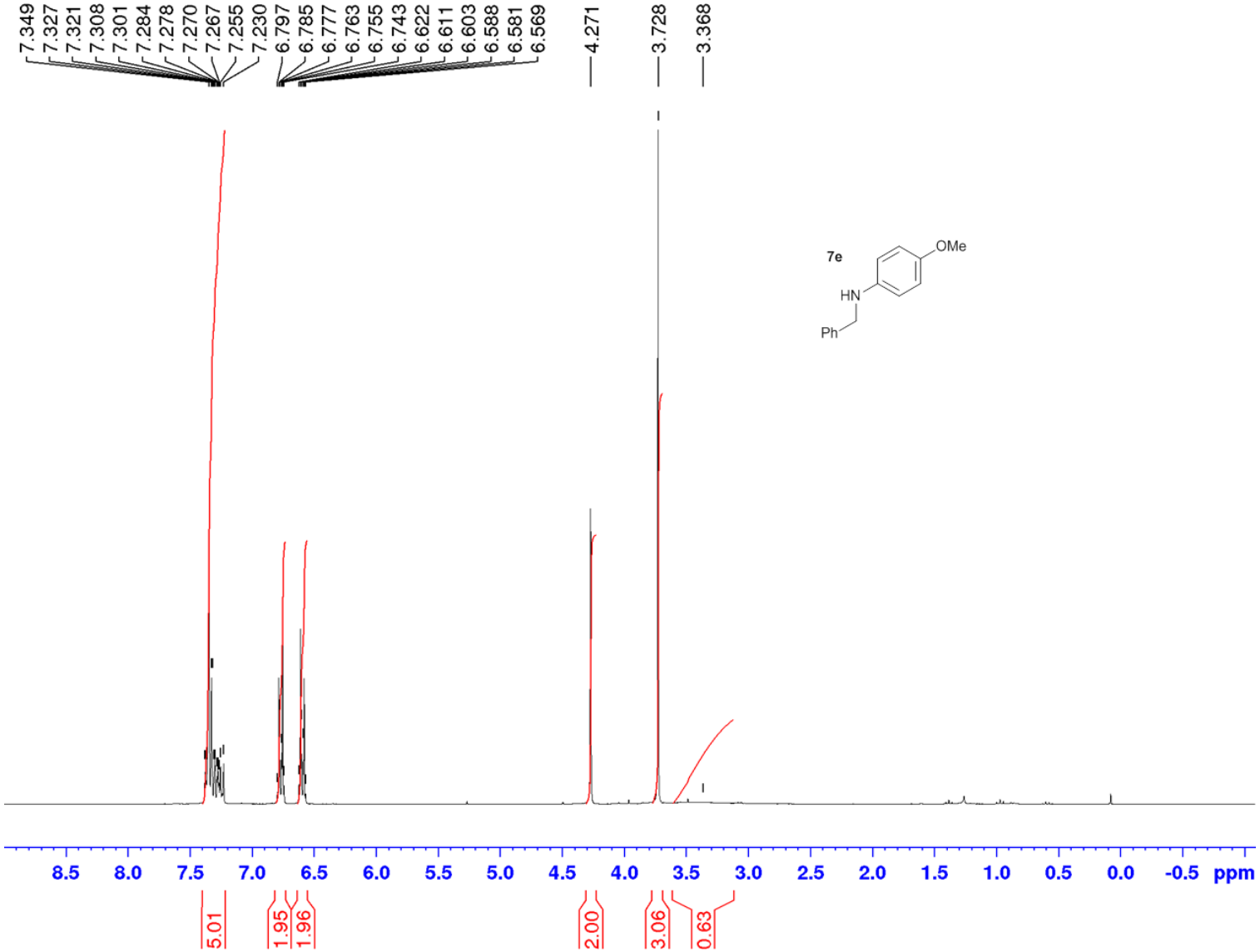
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6.785
6.777
6.763
6.755
6.743
6.622
6.611
6.603
6.588
6.581
6.569
4.271
3.728
3.368
7e
OMe
HN
Ph
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4.5
4.0
3.5
3.0
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2.0
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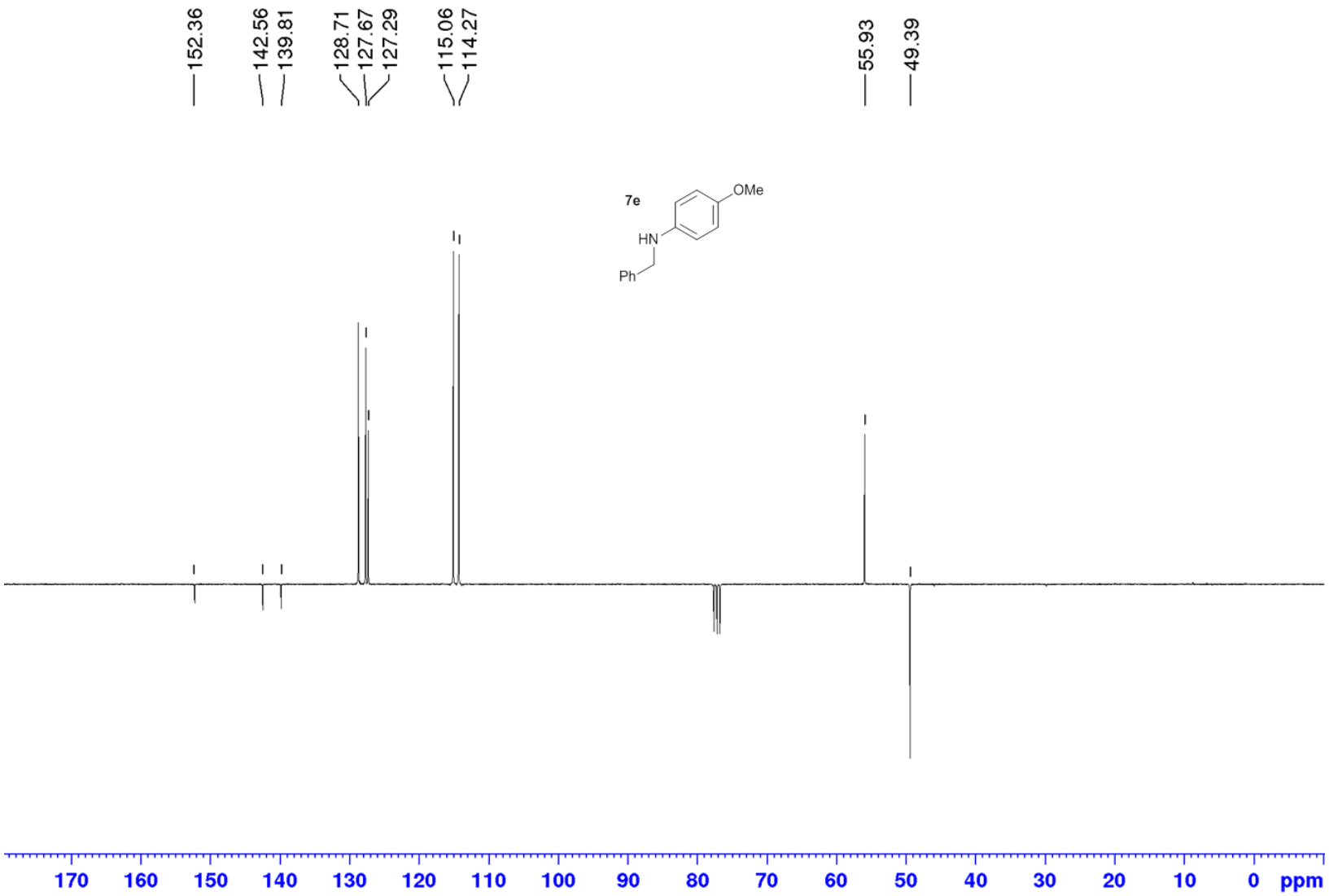
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49.39
7e
OMe
HN
Ph
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160
150
140
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120
110
100
90
80
70
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50
40
30
20
10
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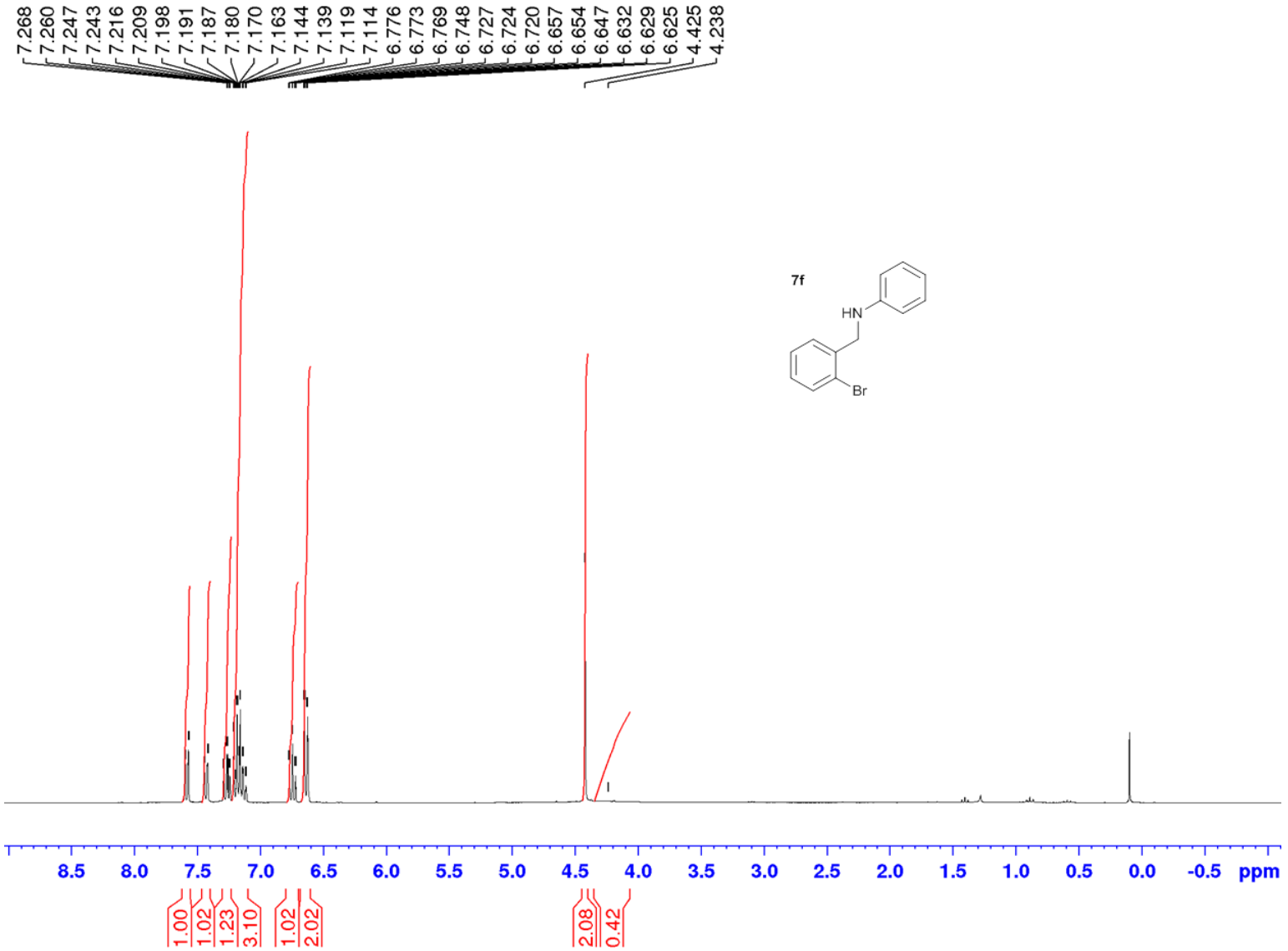
ppm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7.243
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7.170
7.163
7.144
7.139
7.119
7.114
6.776
6.773
6.769
6.748
6.727
6.724
6.720
6.657
6.654
6.647
6.632
6.629
6.625
4.425
4.238
7f
HN
Br
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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2.02
2.08
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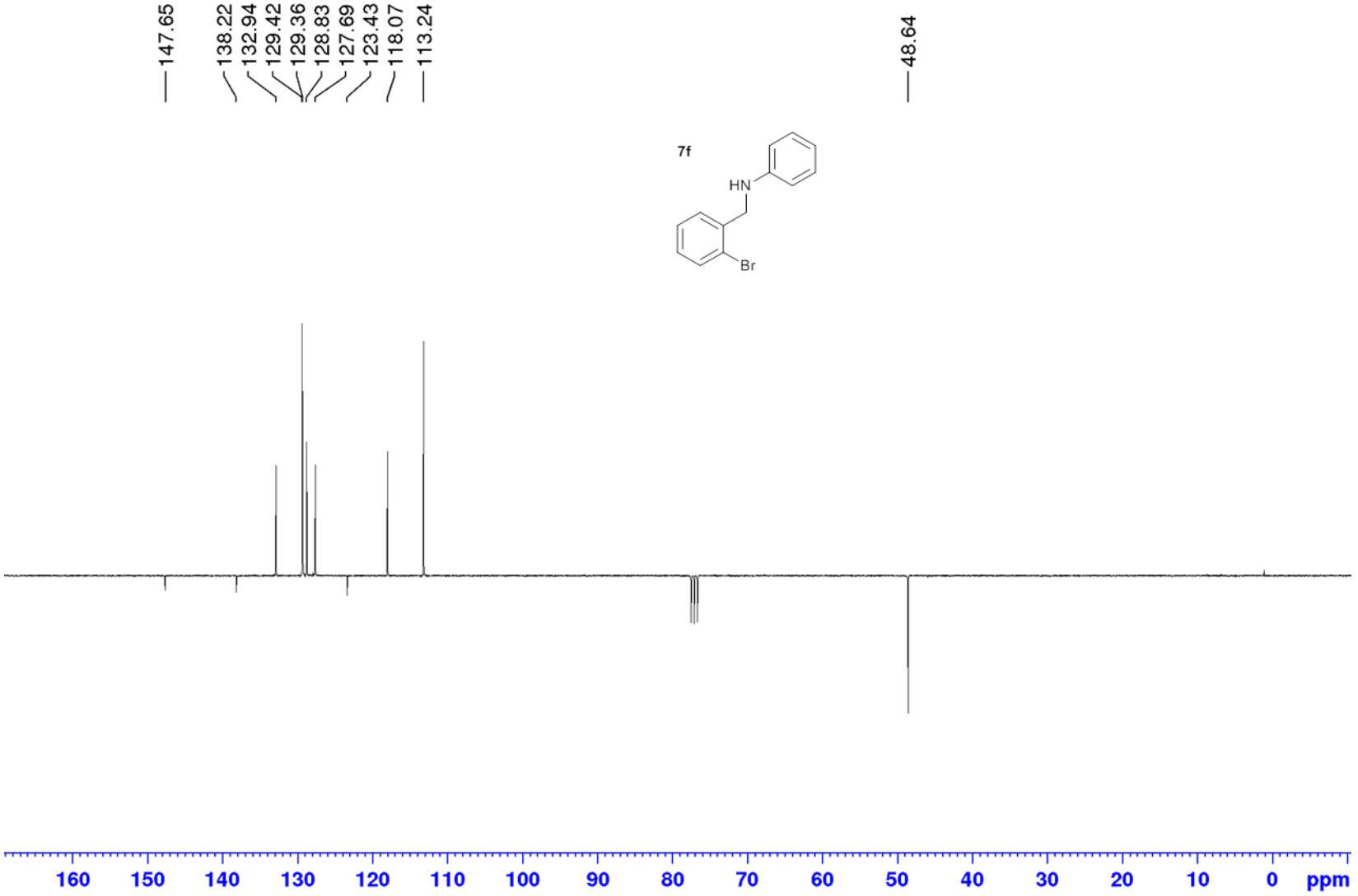
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132.94
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129.36
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127.69
123.43
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113.24
48.64
7f
HN
Br
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140
130
120
110
100
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60
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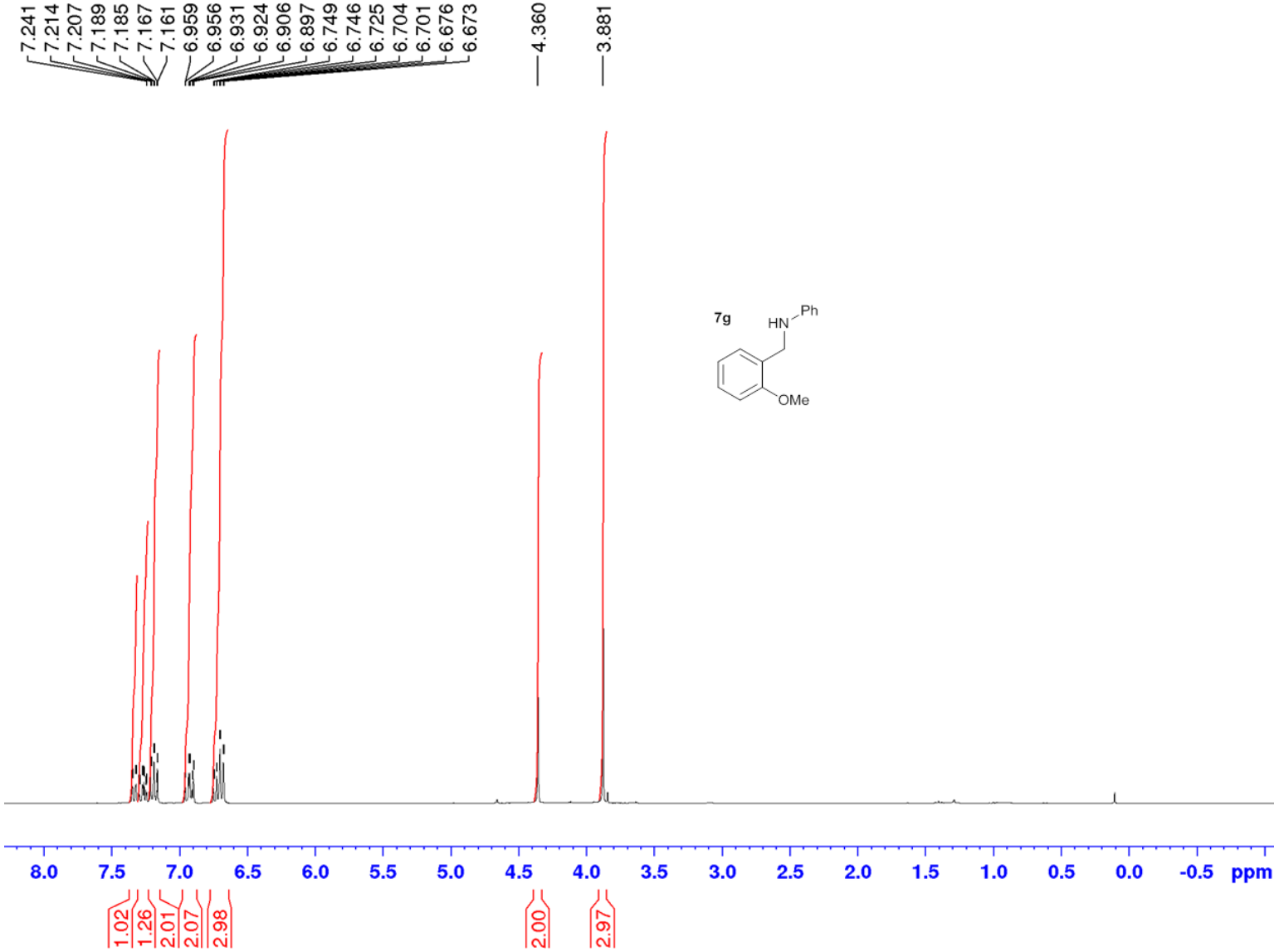
20
10
0
ppm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6.924
6.906
6.897
6.749
6.746
6.725
6.704
6.701
6.676
6.673
4.360
3.881
7g
HN
Ph
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.0
-0.5
ppm
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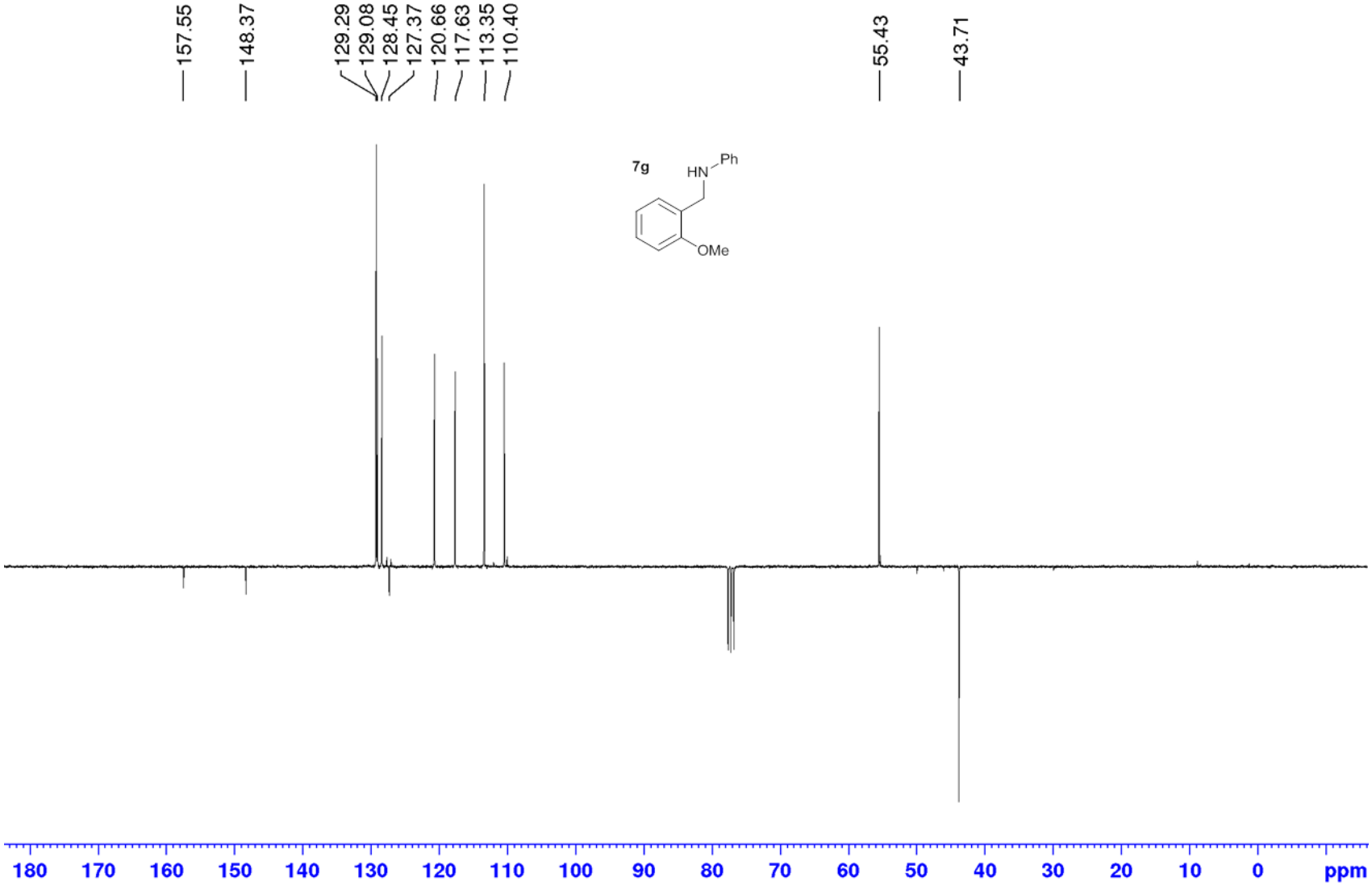
2.00
2.97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129.29
129.08
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127.37
120.66
117.63
113.35
110.40
55.43
43.71
7g
HN
Ph
OMe
180
170
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140
130
120
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100
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60
50
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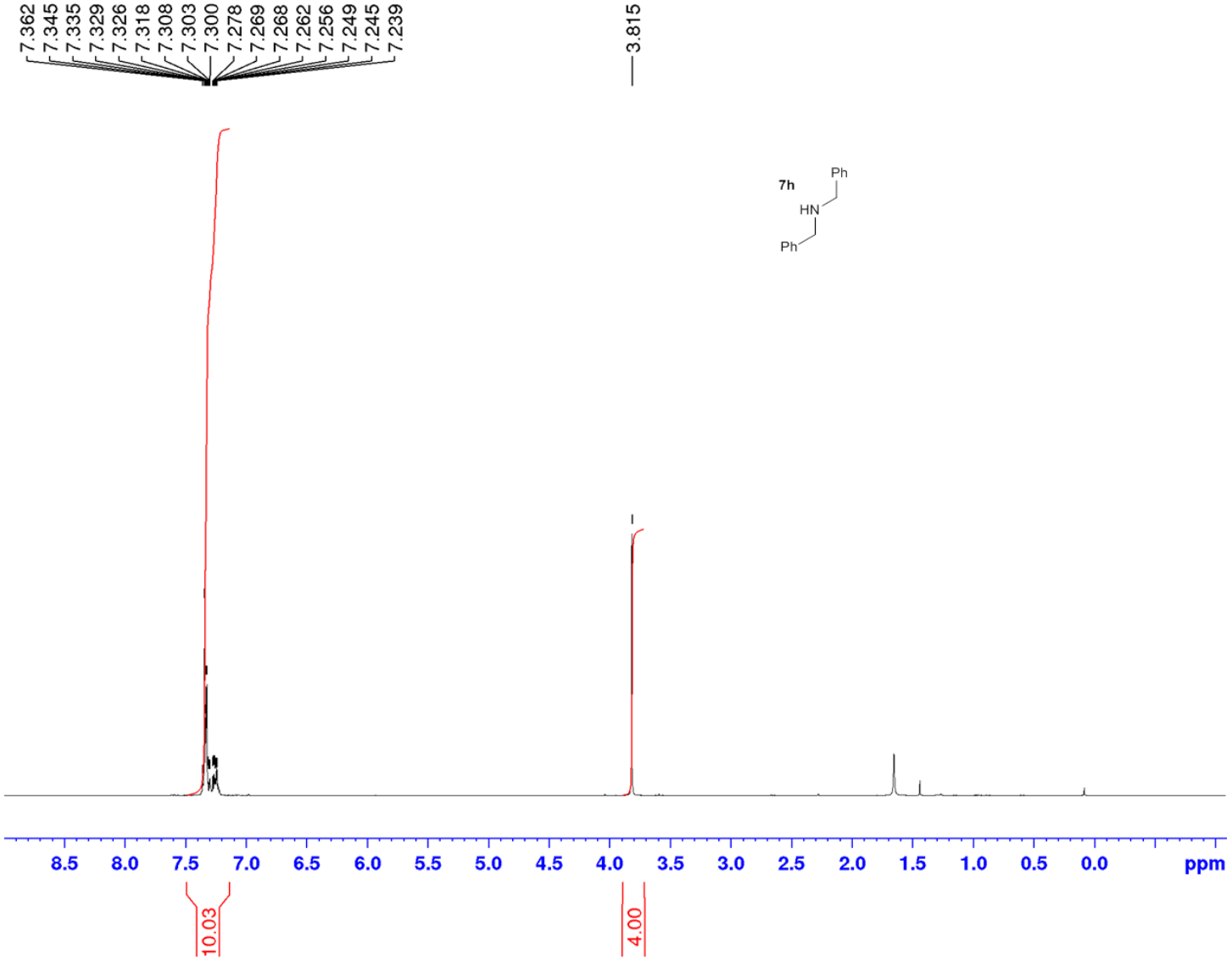
30
20
10
0
ppm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7.335
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7.303
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7.278
7.269
7.268
7.262
7.256
7.249
7.245
7.239
3.815
7h
Ph
HN
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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0.5
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ppm
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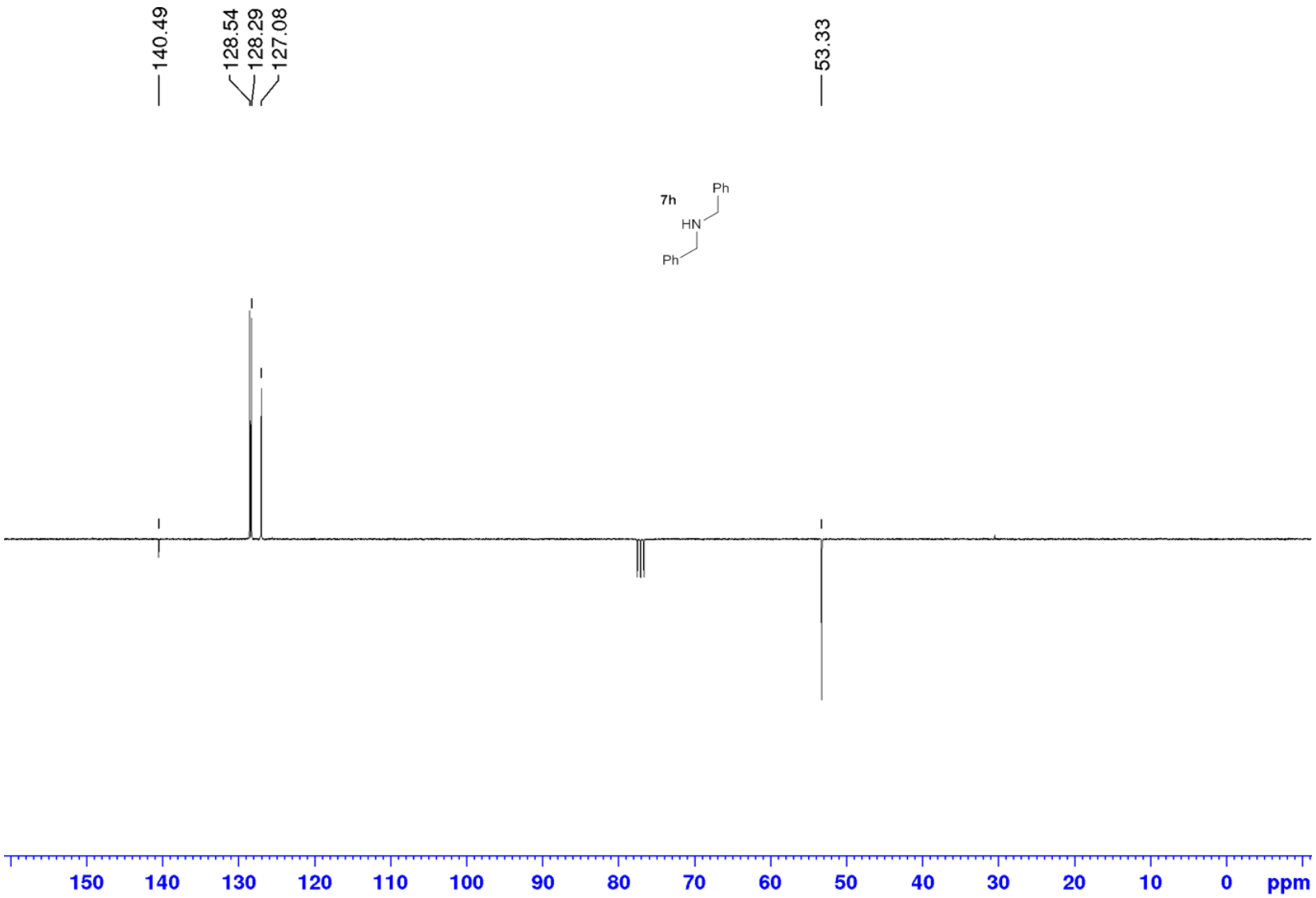
4.00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128.29
127.08
53.33
7h
Ph
HN
Ph
150
140
130
120
110
100
90
80
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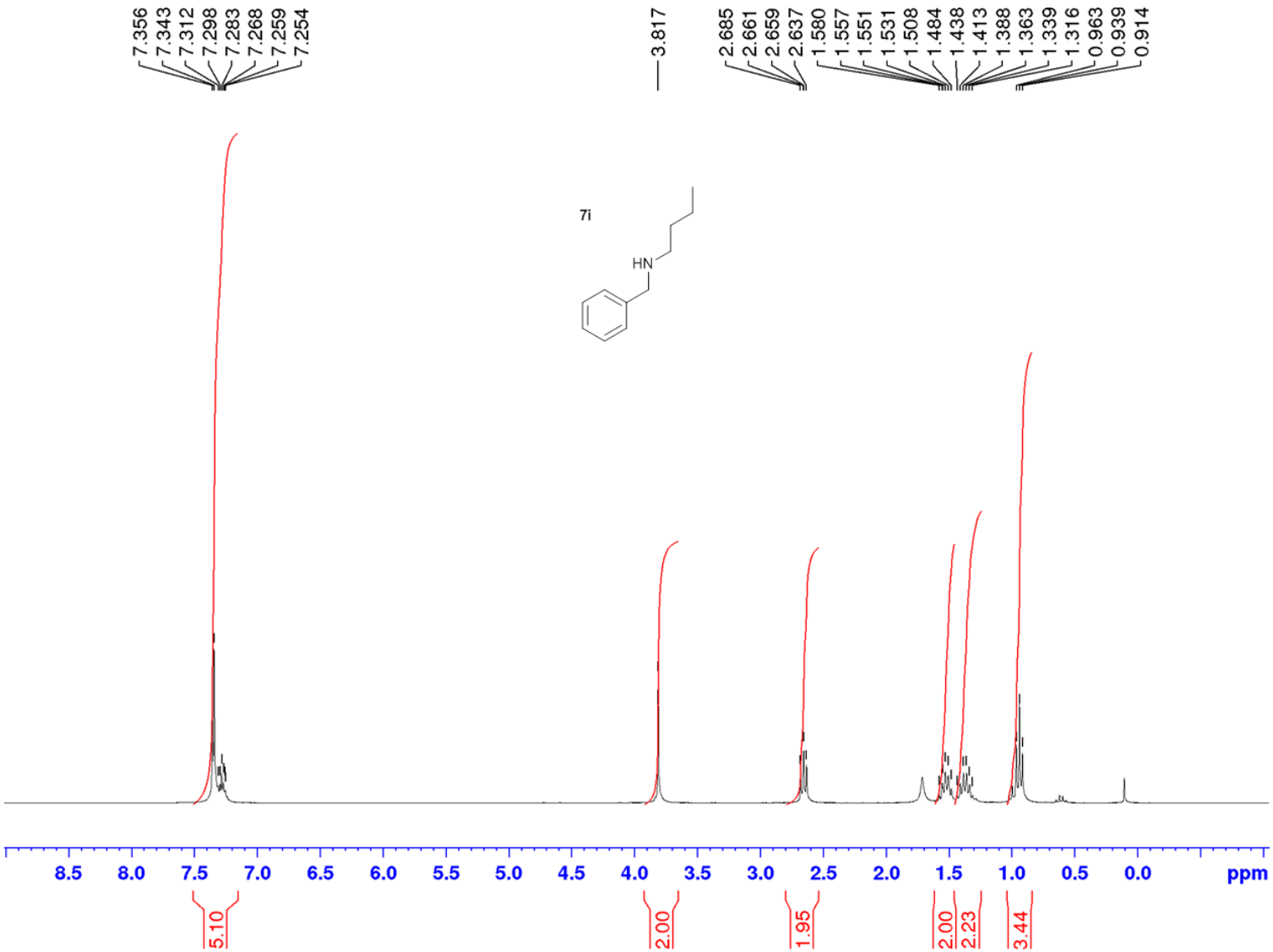
60
50
40
30
20
10
0
ppm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2.659
2.637
1.580
1.557
1.551
1.531
1.508
1.484
1.438
1.413
1.388
1.363
1.339
1.316
0.963
0.939
0.914
7i
HN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
0.0
ppm
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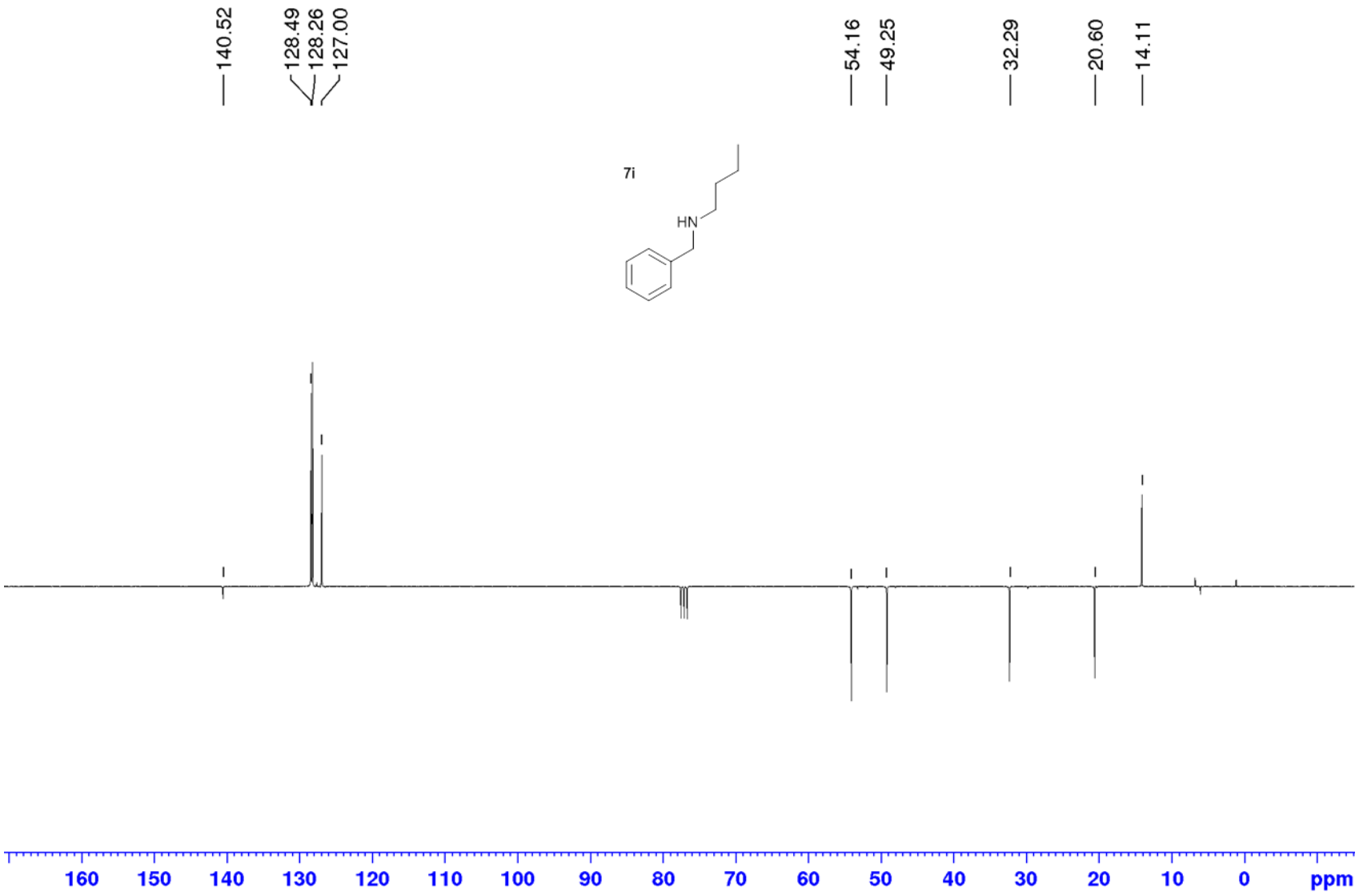
2.00
1.95
2.00
2.23
3.44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128.49
128.26
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54.16
49.25
32.29
20.60
14.11
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HN
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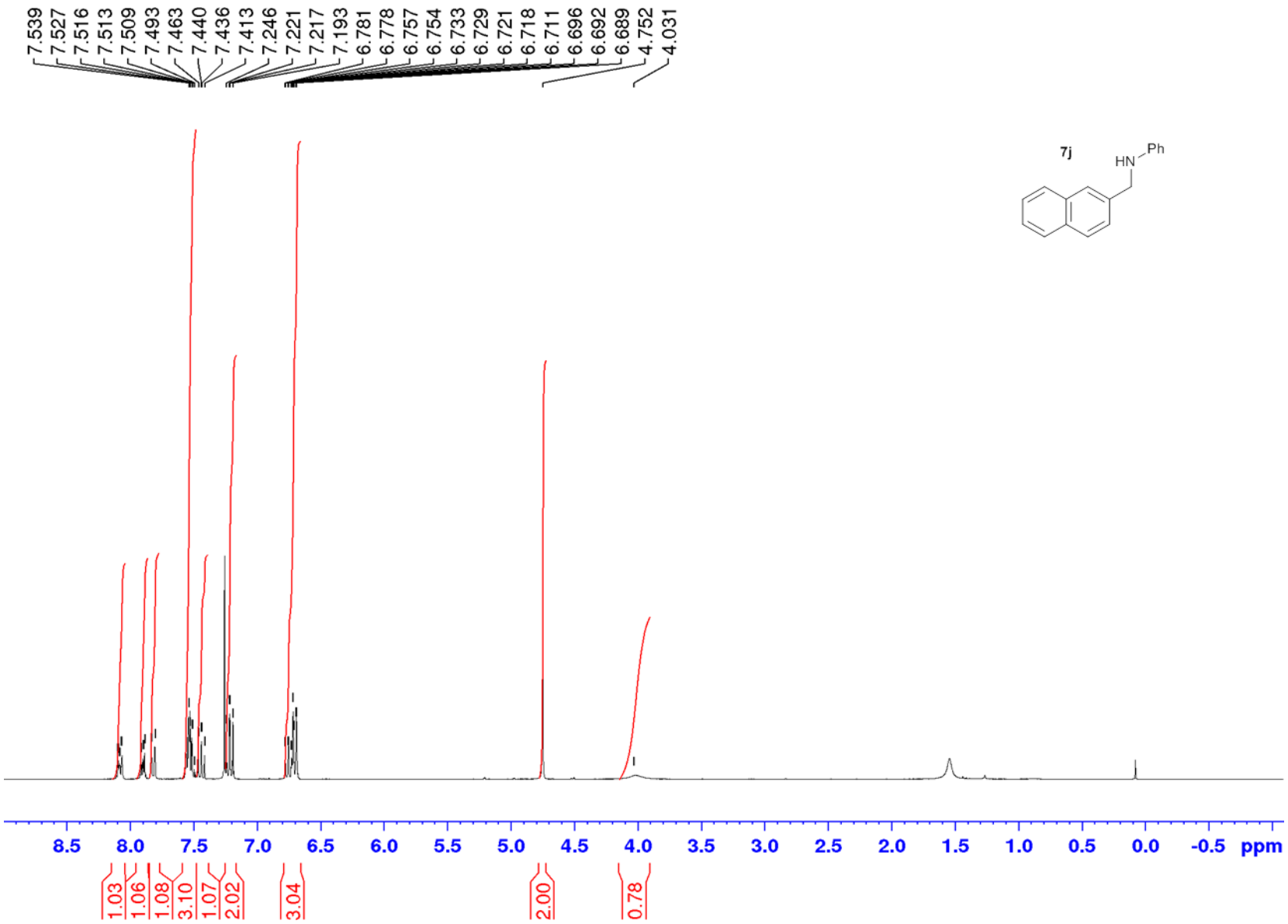
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.513
7.509
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7.463
7.440
7.436
7.413
7.246
7.221
7.217
7.193
6.781
6.778
6.757
6.754
6.733
6.729
6.721
6.718
6.711
6.696
6.692
6.689
4.752
4.031
7j
HN
Ph
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
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ppm
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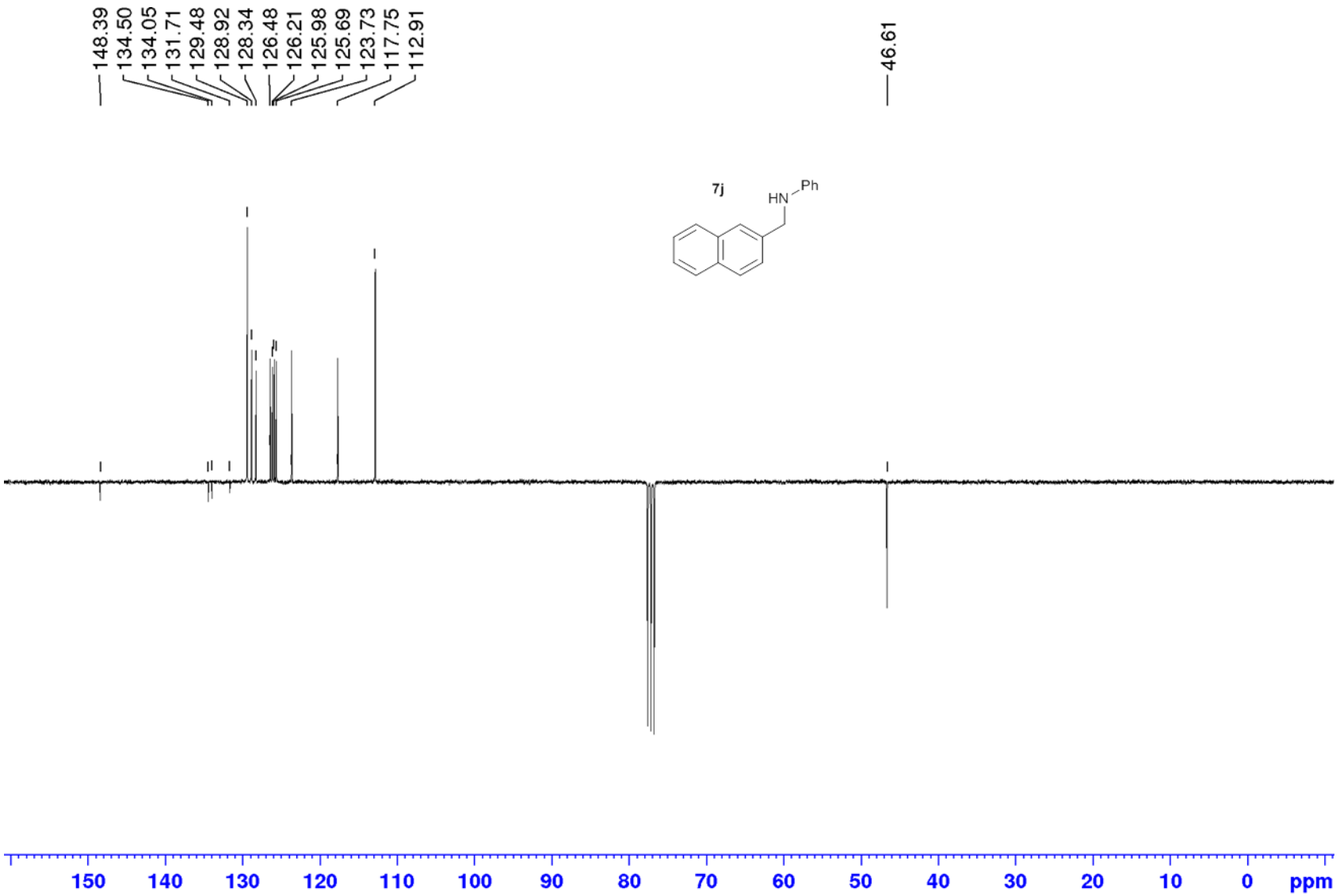
1.06
1.08
3.10
1.07
2.02
3.04
2.00
0.78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128.92
128.34
126.48
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125.69
123.73
117.75
112.91
46.61
7j
HN
Ph
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140
130
120
110
100
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60
50
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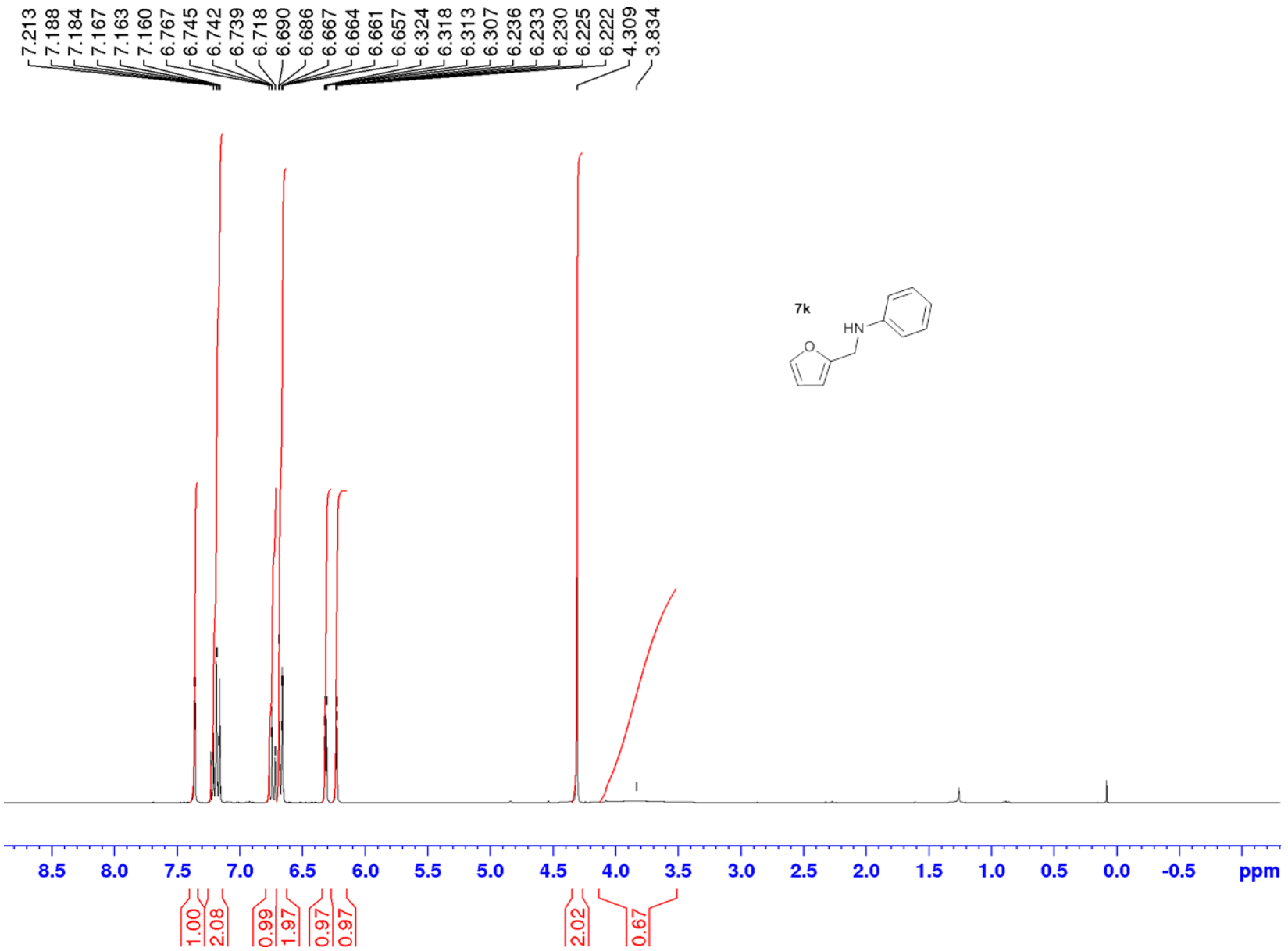
30
20
10
0
ppm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6.739
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6.690
6.686
6.667
6.664
6.661
6.657
6.324
6.318
6.313
6.307
6.236
6.233
6.230
6.225
6.222
4.309
3.834
7k
HN
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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-0.5
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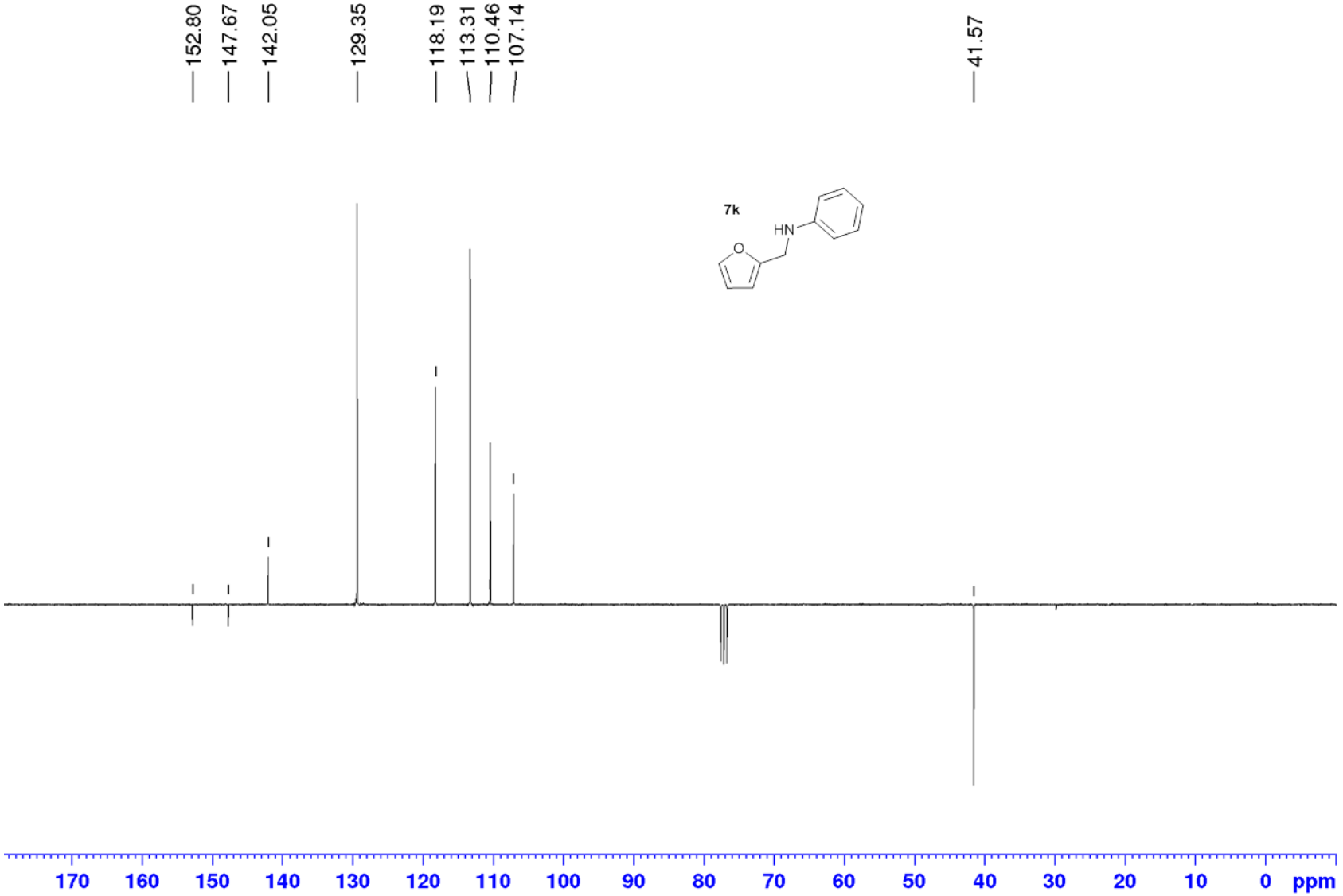
1.97
0.97
0.97
2.02
0.67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142.05
129.35
118.19
113.31
110.46
107.14
41.57
7k
HN
O
170
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150
140
130
120
110
100
90
80
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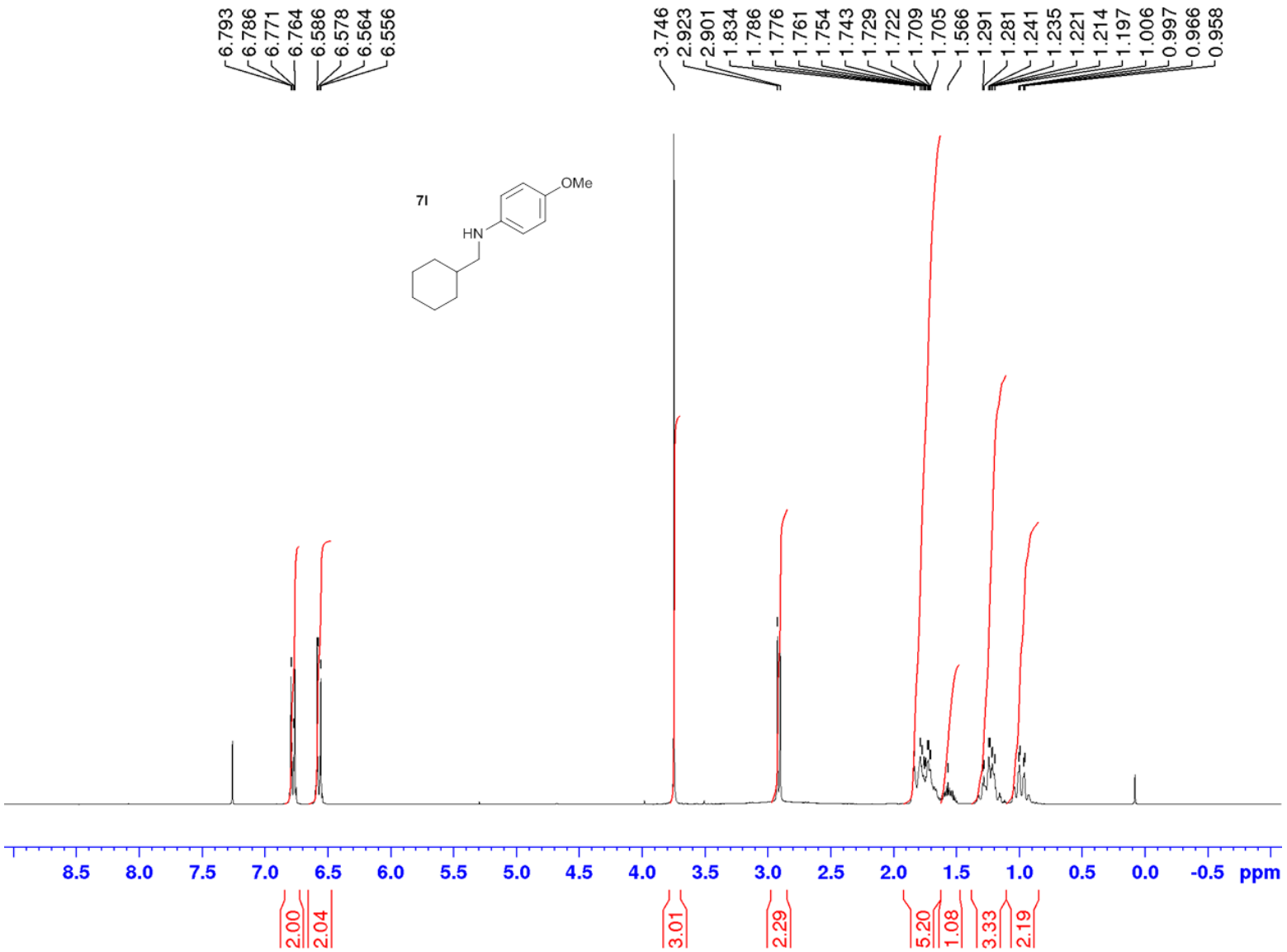
60
50
40
30
20
10
0
ppm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6.556
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2.901
1.834
1.786
1.776
1.761
1.754
1.743
1.729
1.722
1.709
1.705
1.566
1.291
1.281
1.241
1.235
1.221
1.214
1.197
1.006
0.997
0.966
0.958
7l
HN
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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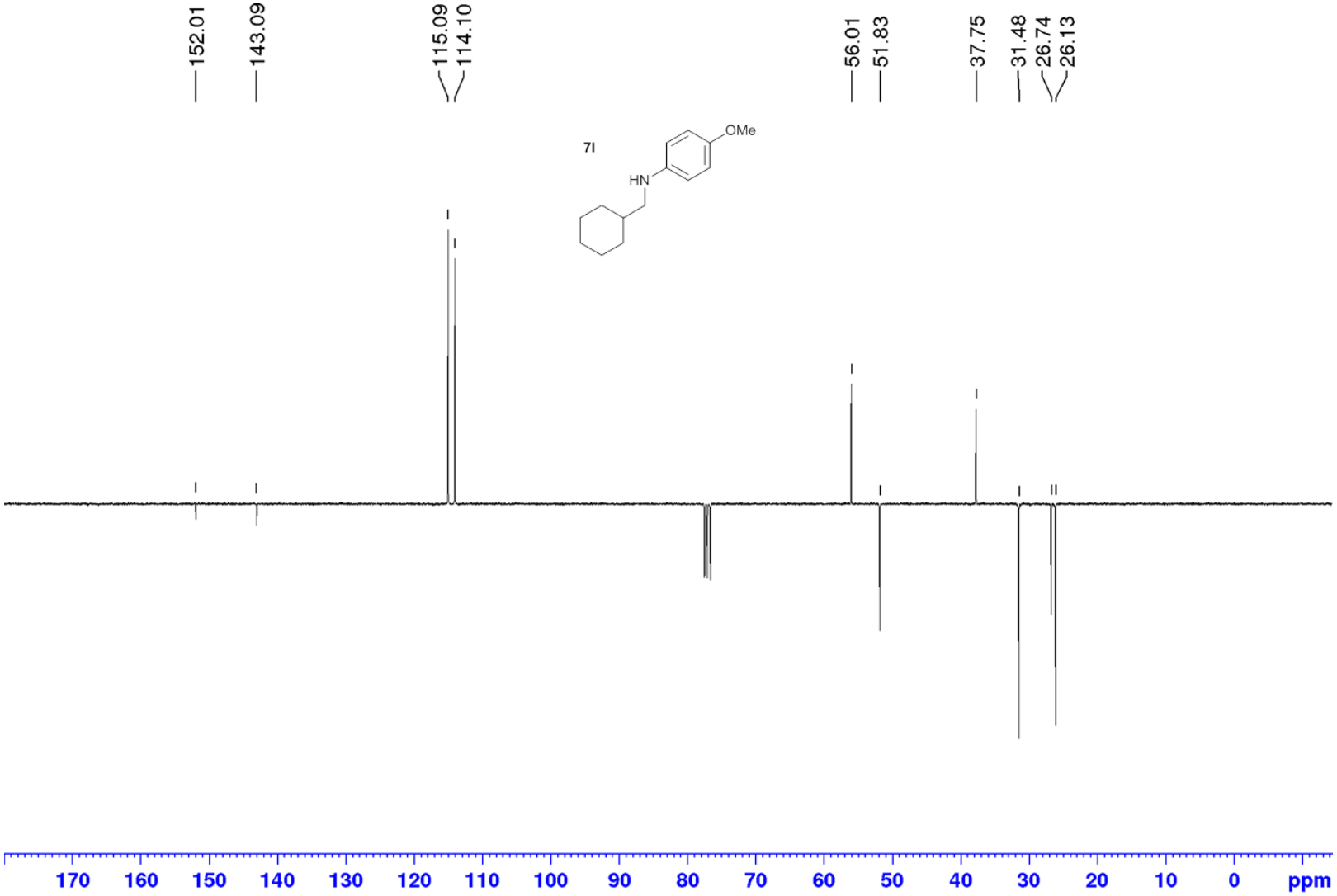
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143.09
115.09
114.10
56.01
51.83
37.75
31.48
26.74
26.13
7l
OMe
HN
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140
130
120
110
100
90
80
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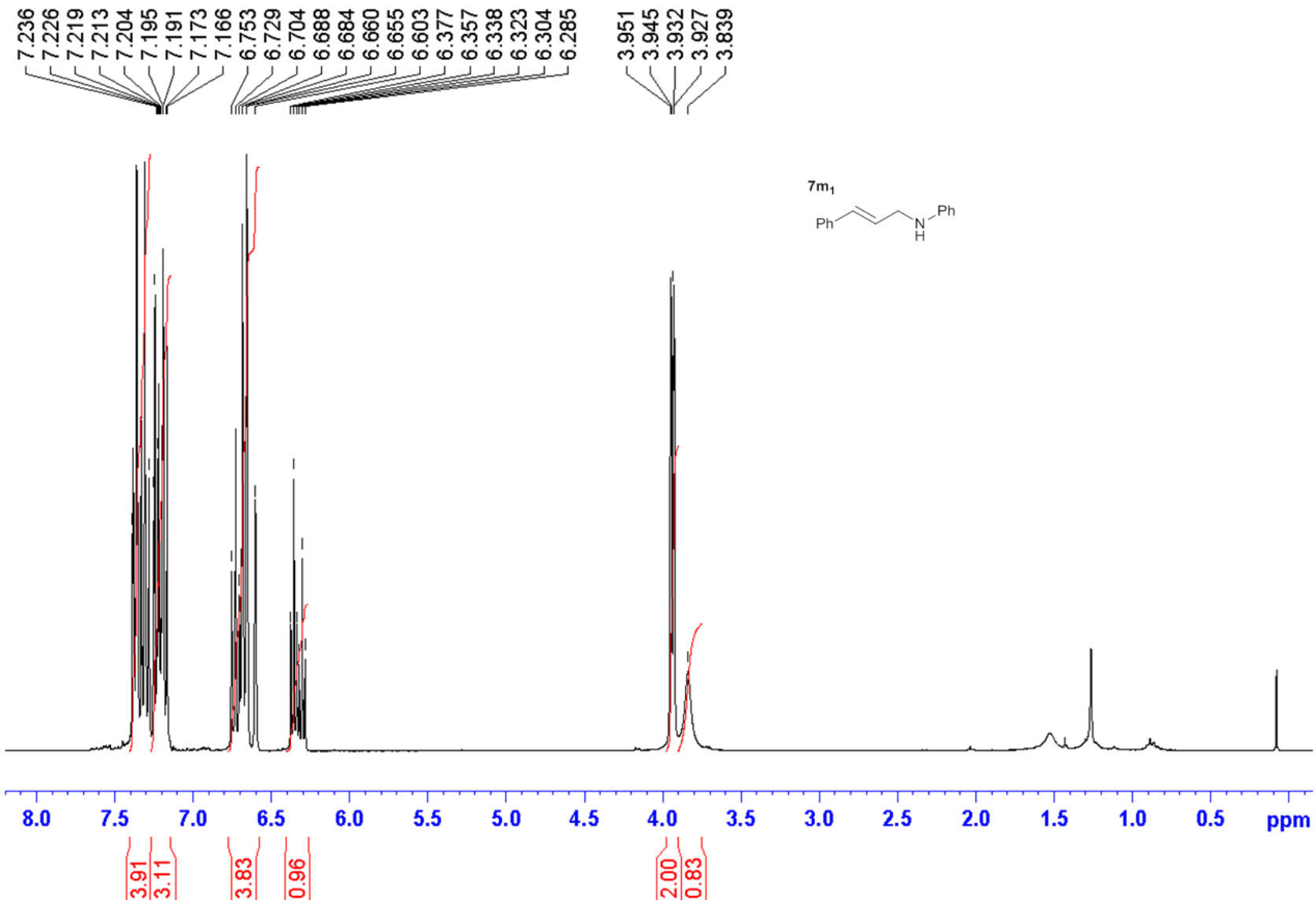
60
50
40
30
20
10
0
ppm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6.684
6.660
6.655
6.603
6.377
6.357
6.338
6.323
6.304
6.285
3.951
3.945
3.932
3.927
3.839
7m1
Ph
N
H
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
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3.11
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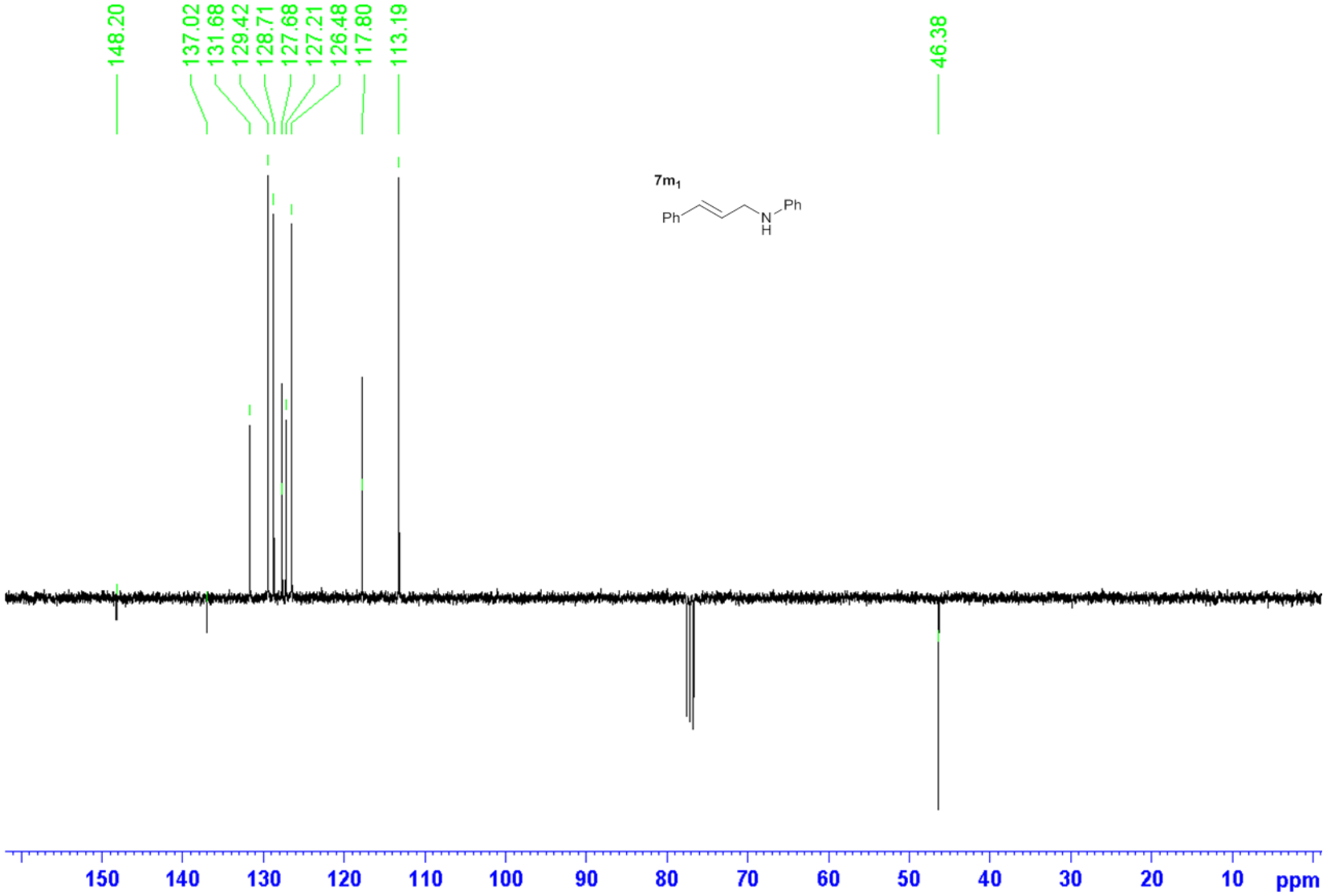
0.83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137.02
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129.42
128.71
127.68
127.21
126.48
117.80
113.19
46.38
7m1
Ph
N
H
Ph
150
140
130
120
110
100
90
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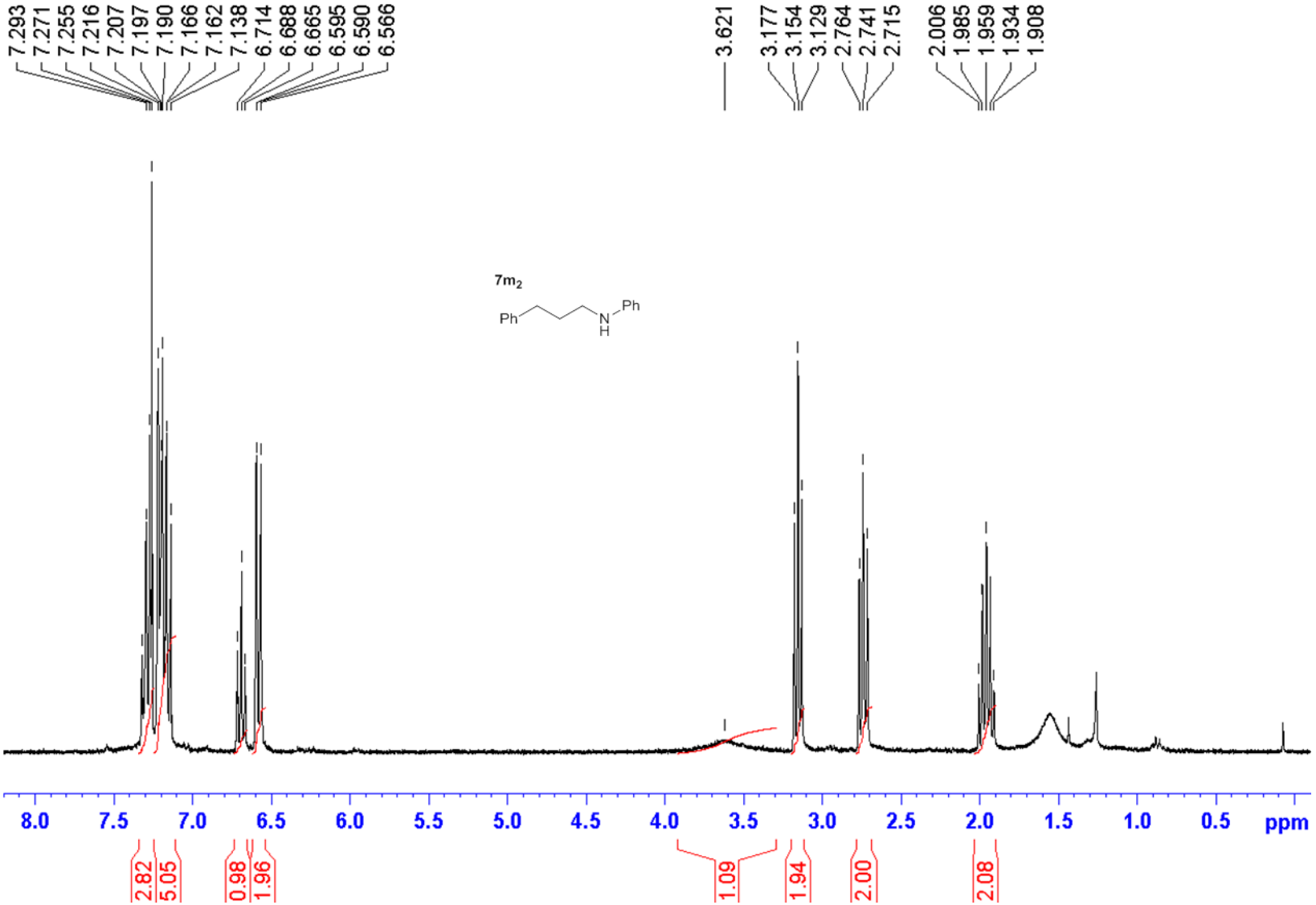
70
60
50
40
30
20
10
ppm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7.197
7.190
7.166
7.162
7.138
6.714
6.688
6.665
6.595
6.590
6.566
3.621
3.177
3.154
3.129
2.764
2.741
2.715
2.006
1.985
1.959
1.934
1.908
7m2
Ph
N
H
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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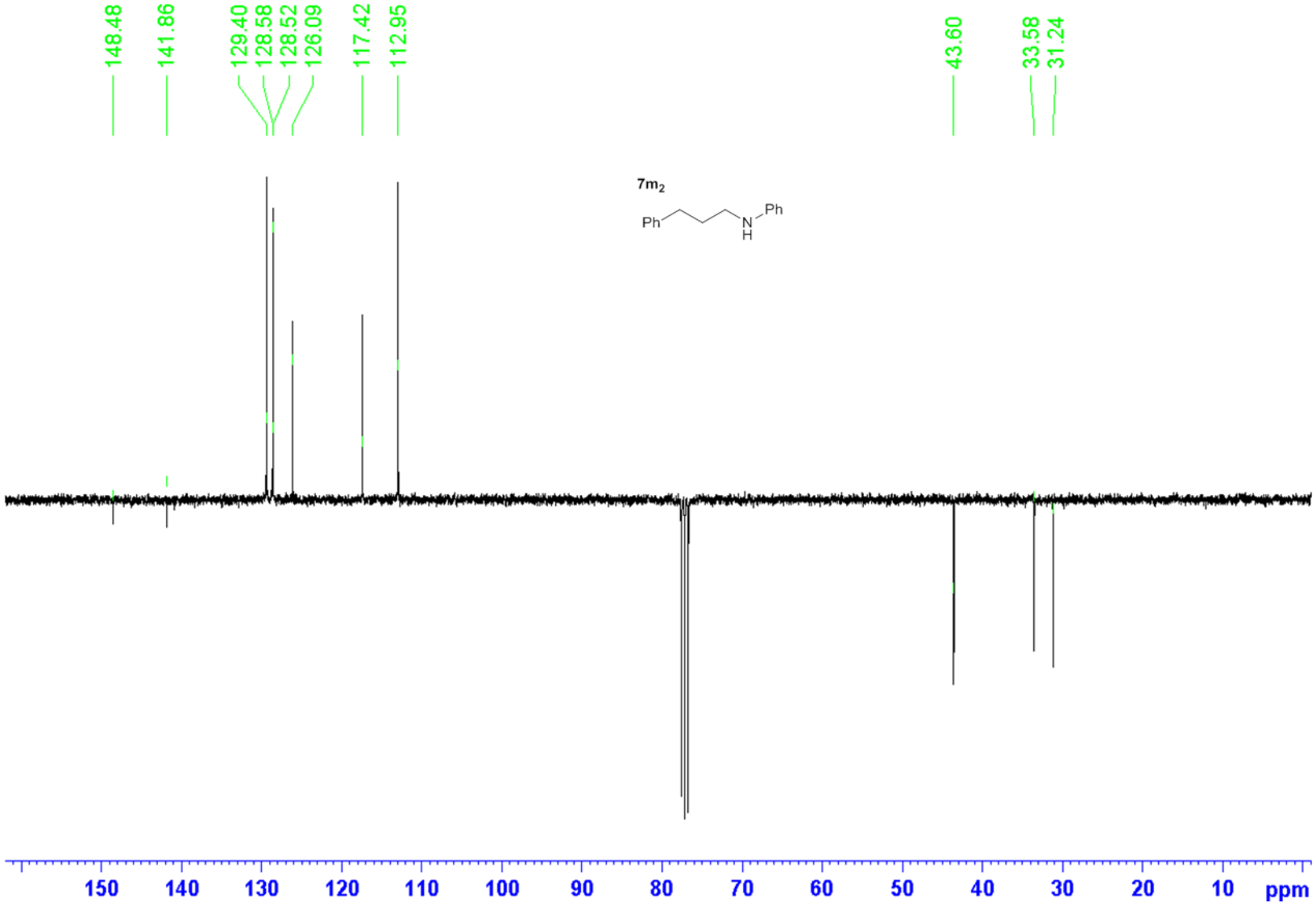
2.08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126.09
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112.95
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33.58
31.24
7m2
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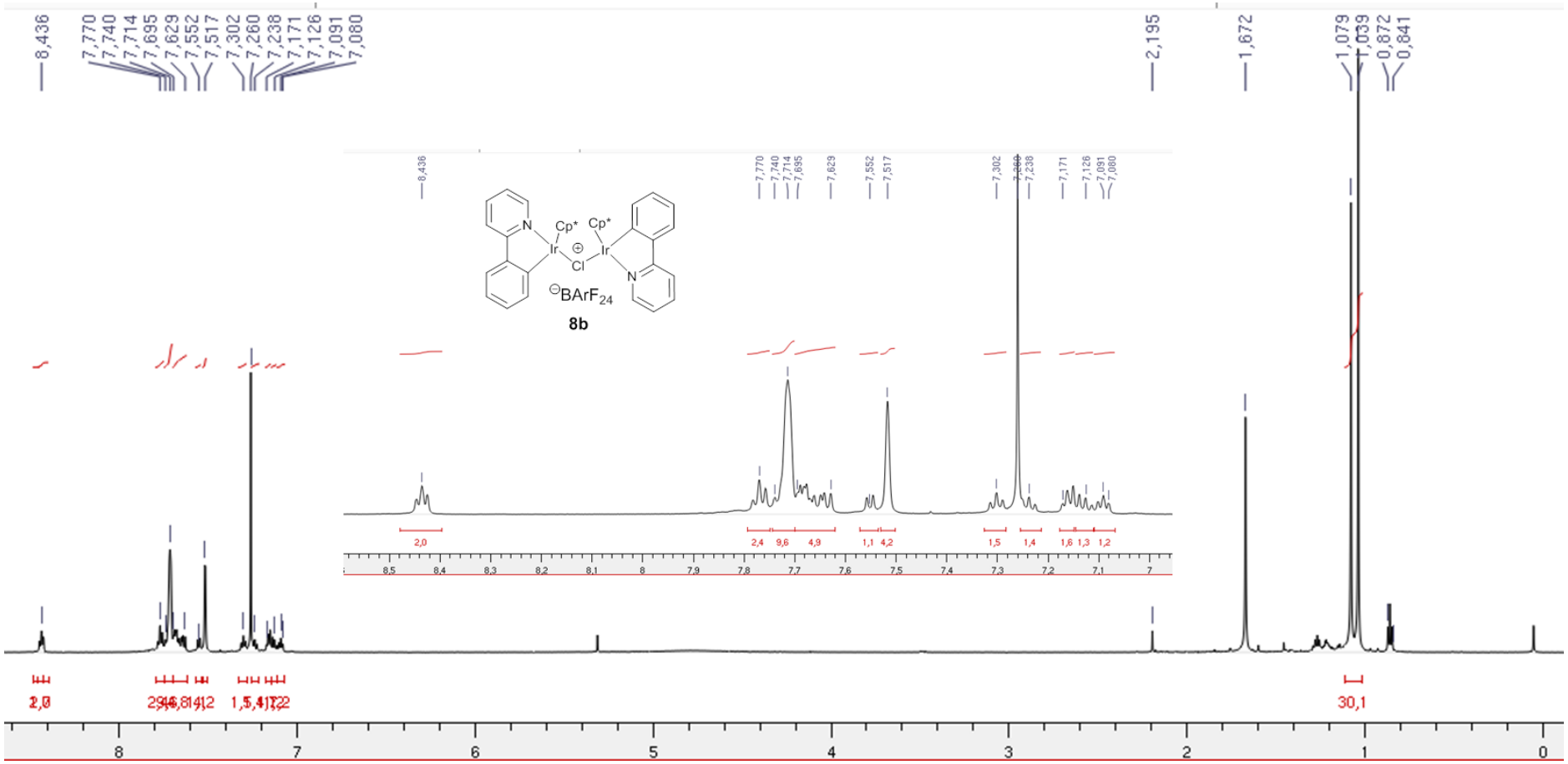
10
ppm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7,126
7,091
7,080
2,195
1,672
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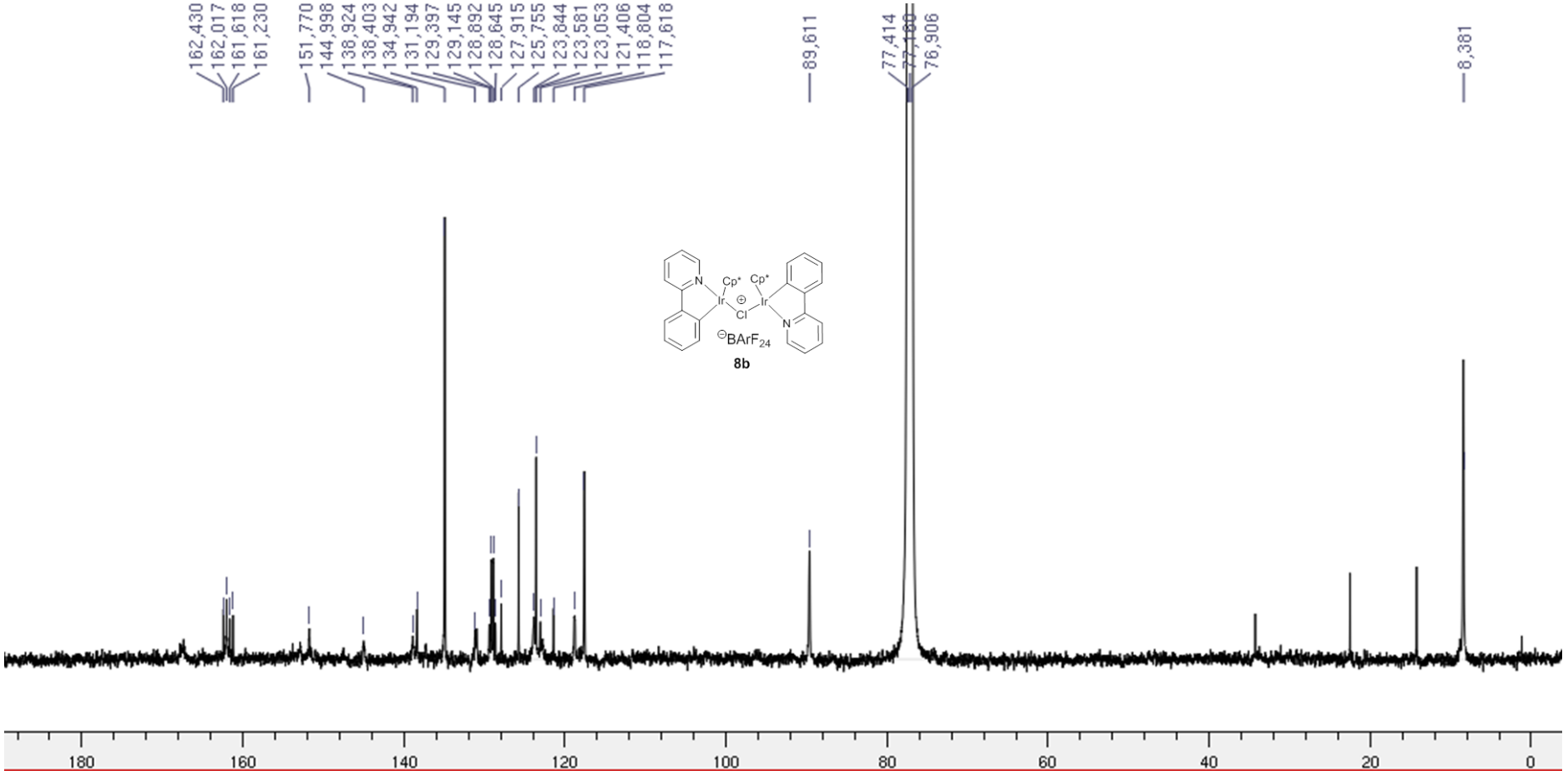
Cp*
Cp*
Ir
Ir
N
N
Cl
BArF24
8b
30,1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129,397
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128,892
128,645
127,915
125,755
123,844
123,581
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121,406
118,804
117,618
89,611
77,414
77,100
76,906
8,381
Cp*
Cp*
Ir
Ir
Cl
N
N
⊖BArF24
8b
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140
120
100
80
60
40
20
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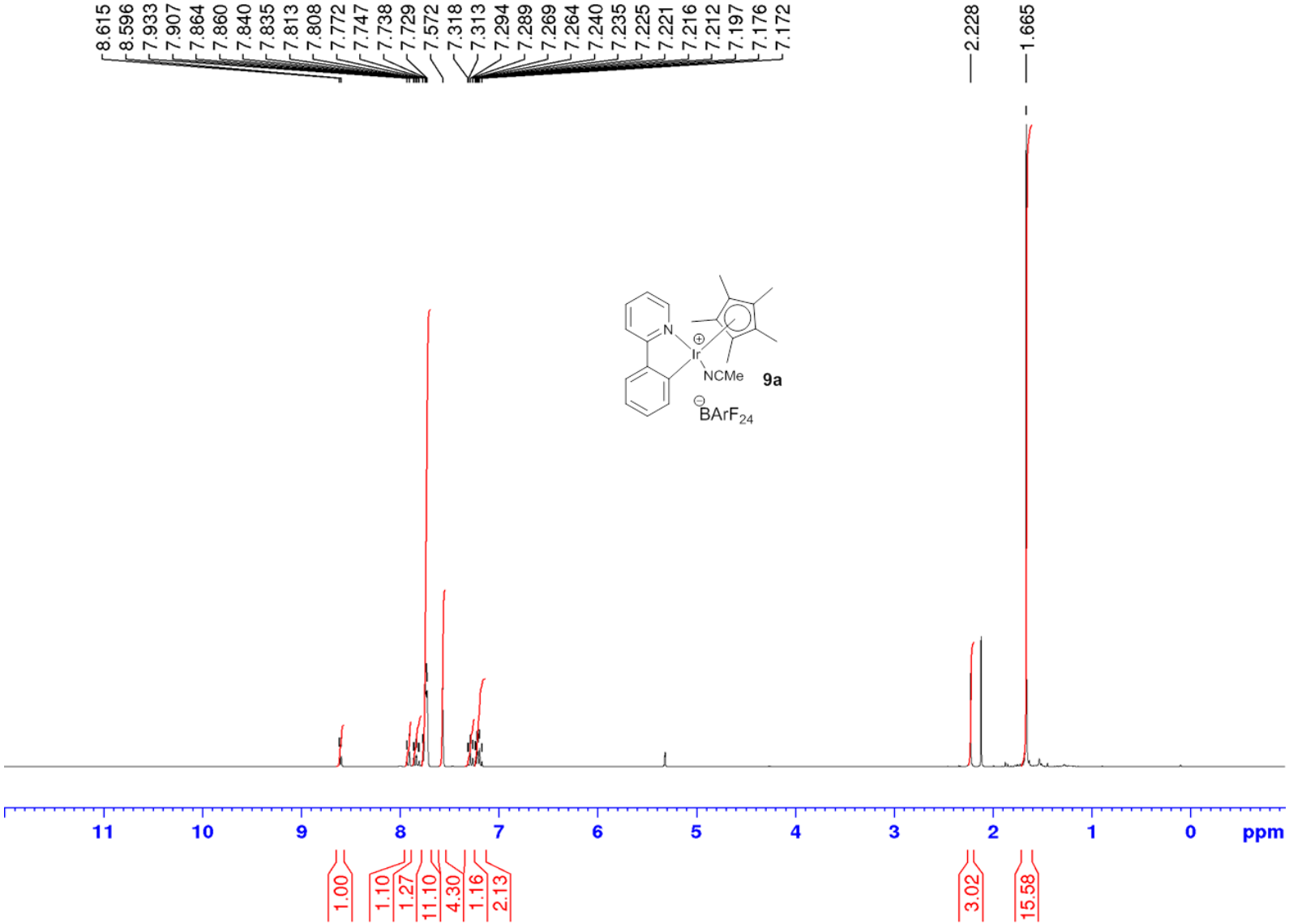
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7.808
7.772
7.747
7.738
7.729
7.572
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7.313
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7.264
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7.235
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7.221
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7.197
7.176
7.172
2.228
1.665
N
Ir
NCMe
9a
BArF24
11
10
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8
7
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5
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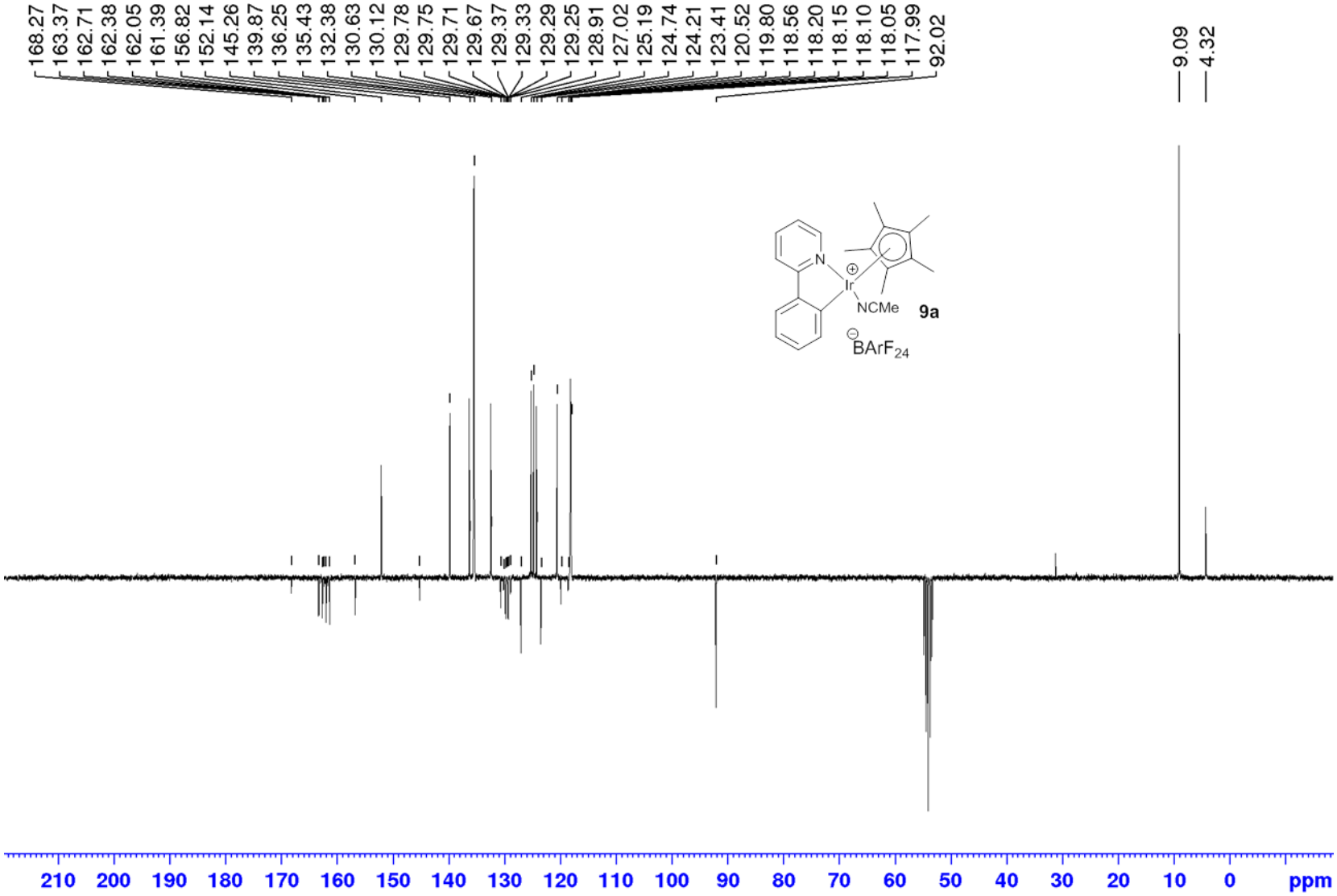
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130.12
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129.37
129.33
129.29
129.25
128.91
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125.19
124.74
124.21
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120.52
119.80
118.56
118.20
118.15
118.10
118.05
117.99
92.02
9.09
4.32
N
Ir
NCMe
9a
BArF24
210
200
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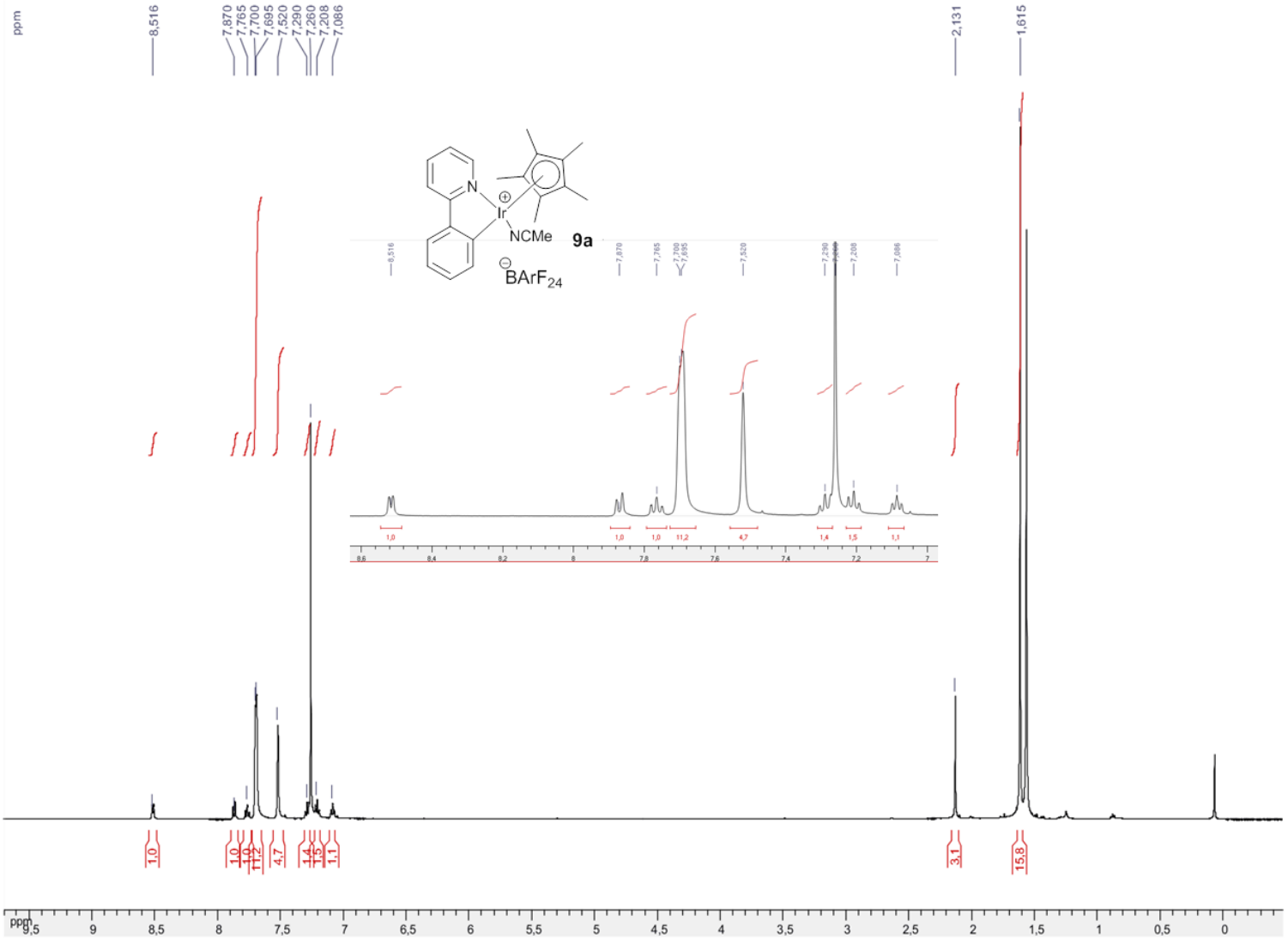
ppm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Ir
NCMe
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BArF24
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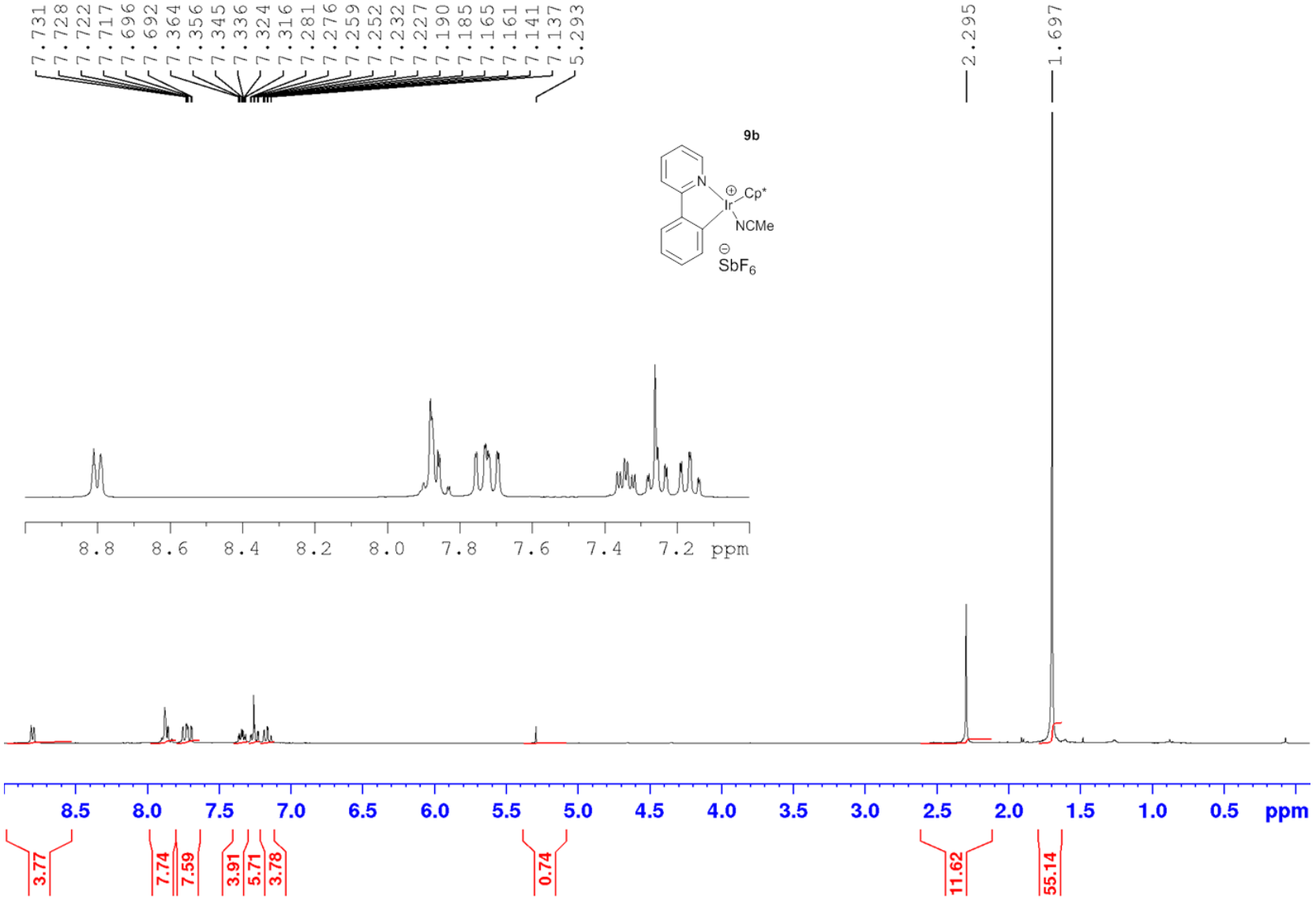
1,0
1,0
11,2
4,7
1,4
1,5
1,1
3,1
15,8
ppm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7.276
7.259
7.252
7.232
7.227
7.190
7.185
7.165
7.161
7.141
7.137
5.293
2.295
1.697
9b
N
Ir
Cp*
NCMe
SbF6
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8.4
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7.4
7.2
ppm
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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ppm
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7.74
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3.91
5.71
3.78
0.74
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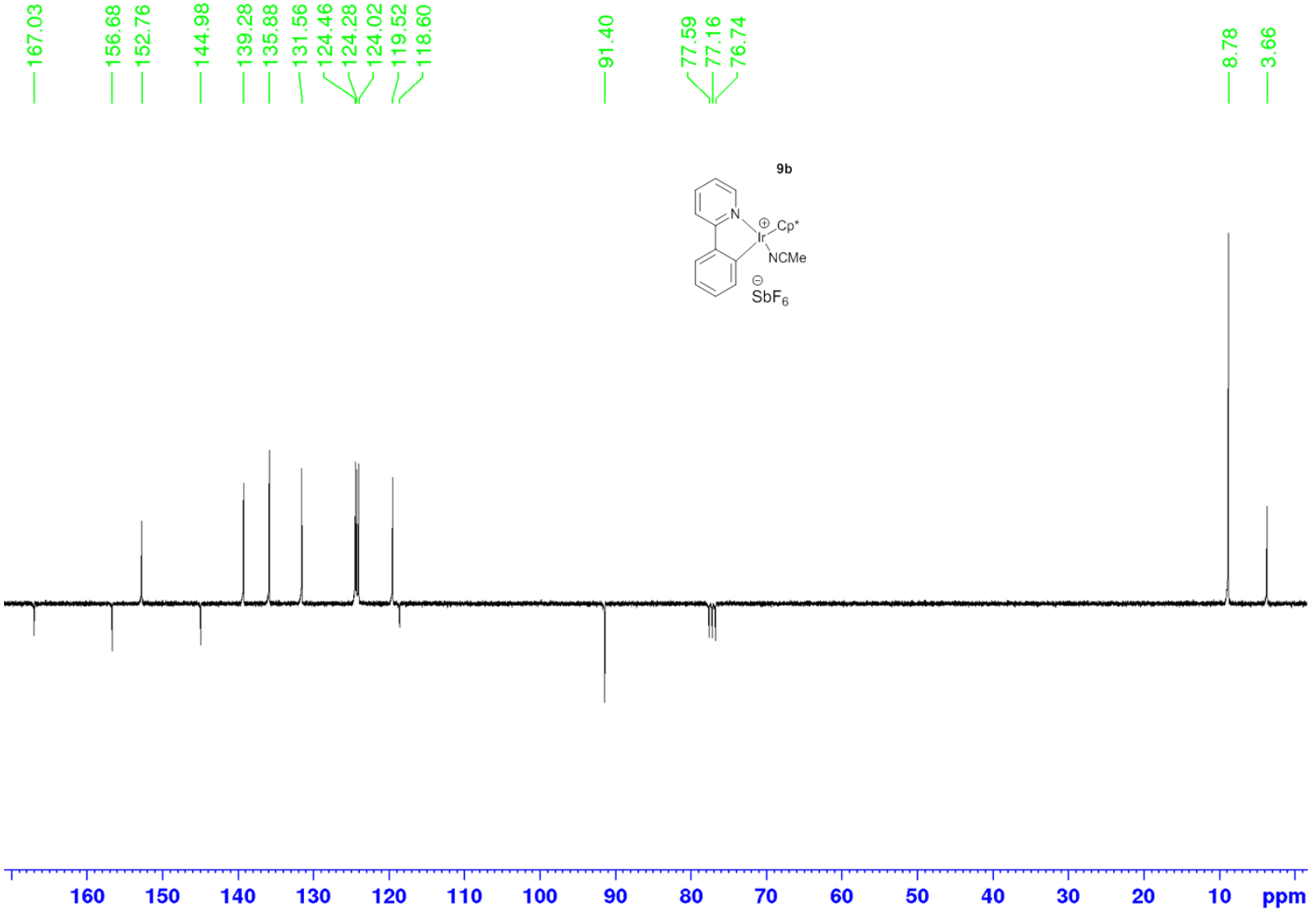
55.14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135.88
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124.02
119.52
118.60
91.40
77.59
77.16
76.74
8.78
3.66
9b
N
Ir
Cp*
NCMe
SbF6
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150
140
130
120
110
100
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70
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30
20
10
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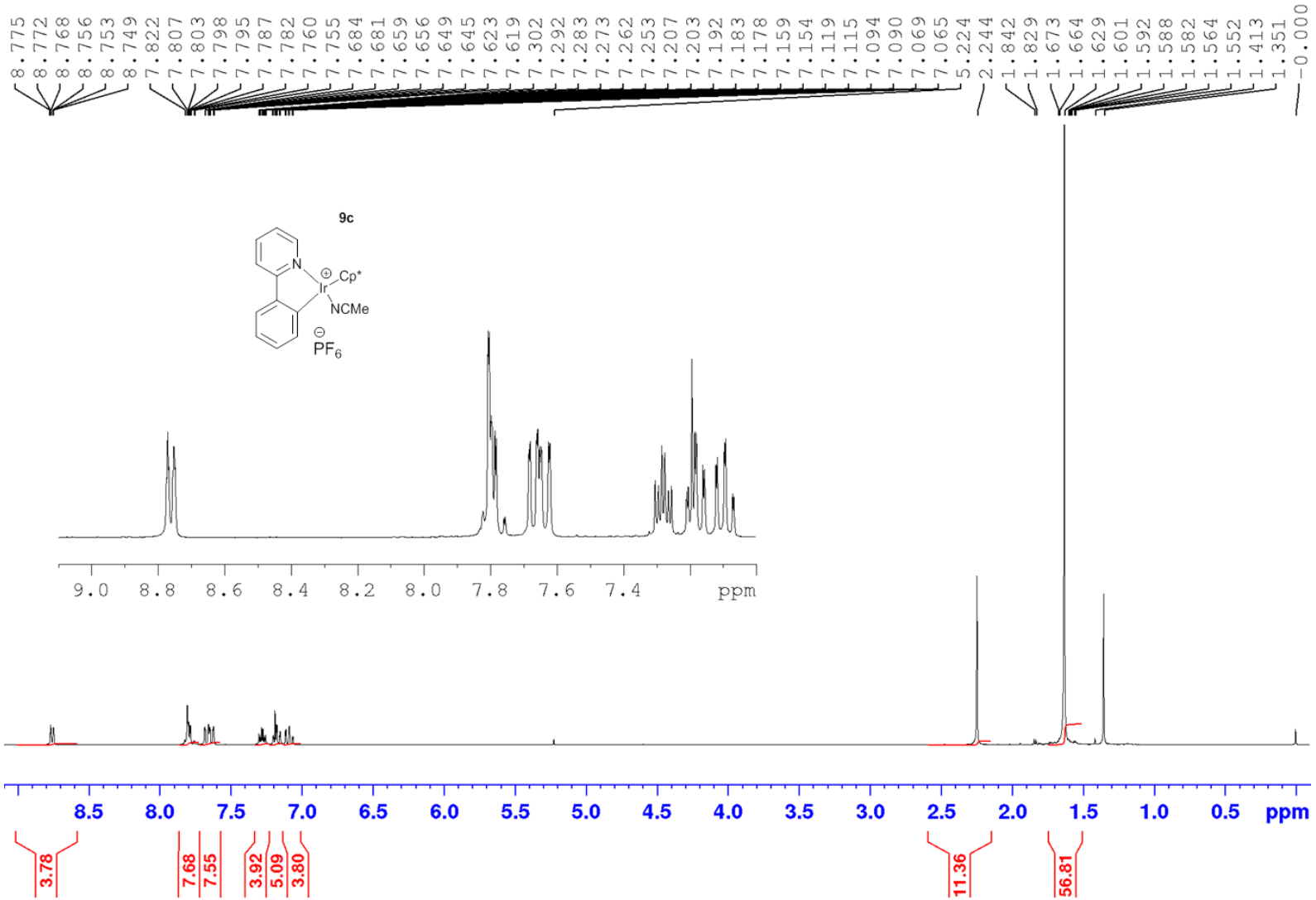
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7.659
7.656
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7.645
7.623
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7.292
7.283
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7.253
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7.183
7.178
7.159
7.154
7.119
7.115
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7.090
7.069
7.065
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2.244
1.842
1.829
1.673
1.664
1.629
1.601
1.592
1.588
1.582
1.564
1.552
1.413
1.351
0.000
9c
N
Ir
Cp*
NCMe
PF6
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8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
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7.0
6.5
6.0
5.5
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3.5
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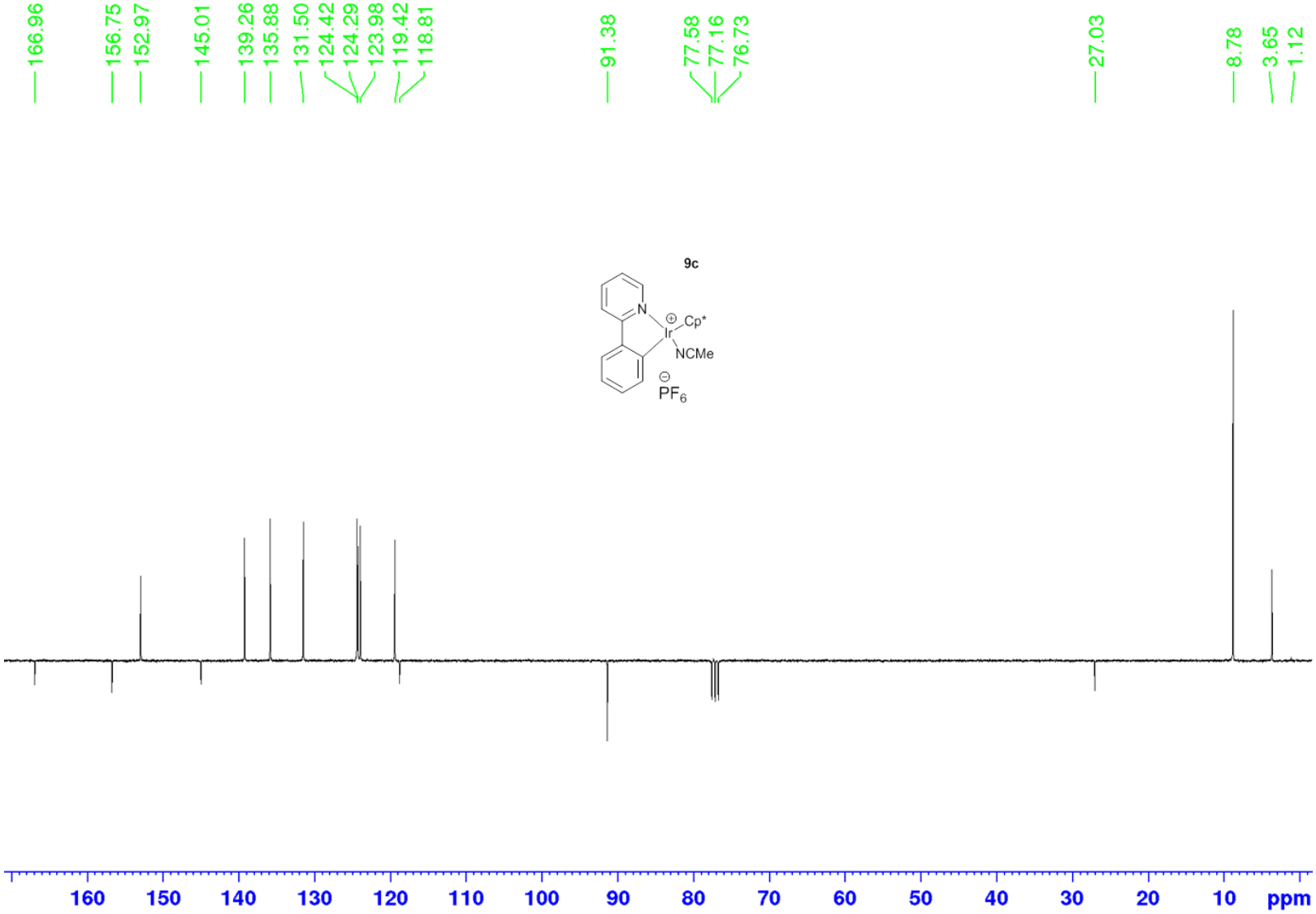
56.81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91.38
77.58
77.16
76.73
27.03
8.78
3.65
1.12
9c
N
Ir
Cp*
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PF6
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150
140
130
120
110
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80
70
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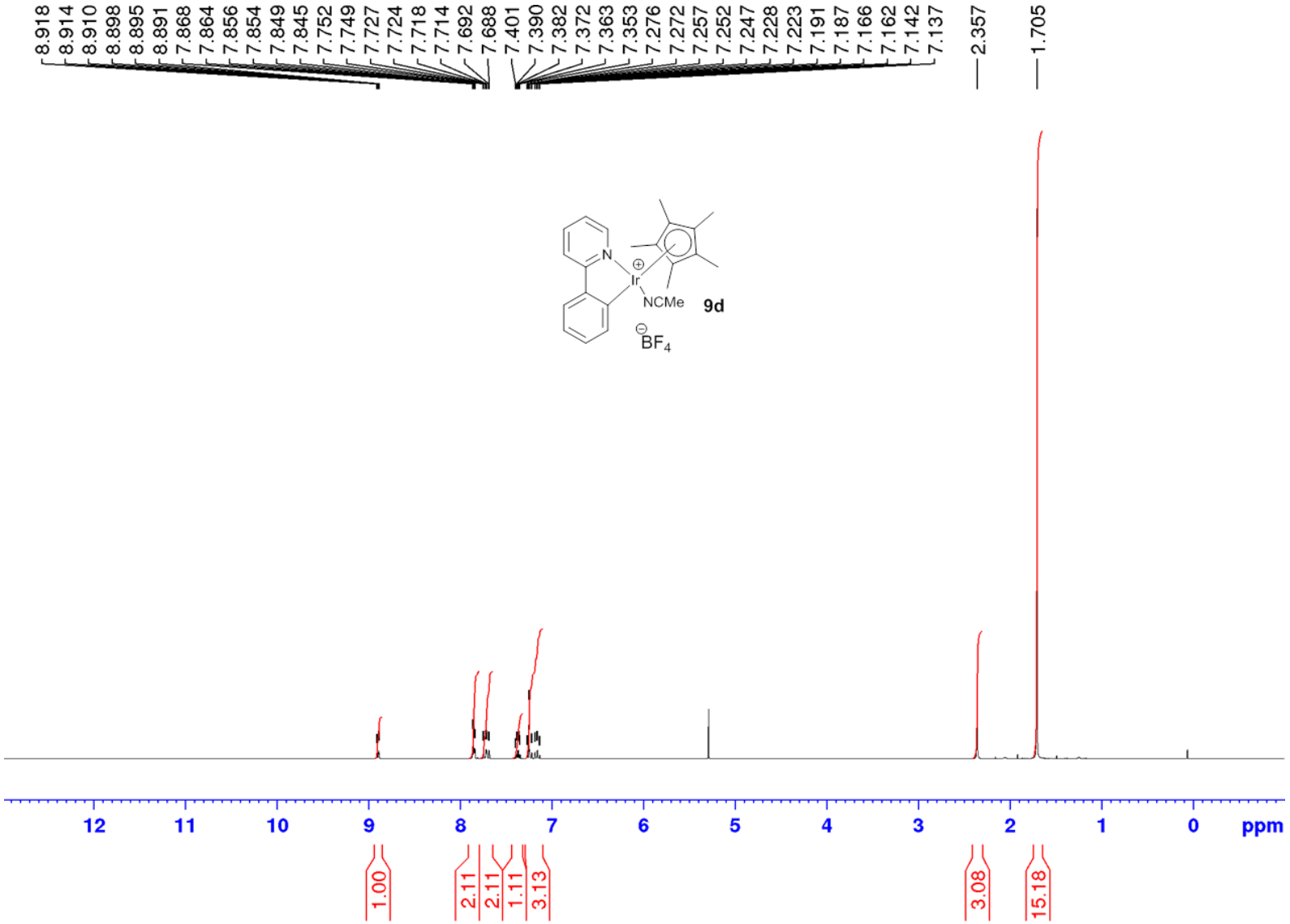
10
ppm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7.854
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7.845
7.752
7.749
7.727
7.724
7.718
7.714
7.692
7.688
7.401
7.390
7.382
7.372
7.363
7.353
7.276
7.272
7.257
7.252
7.247
7.228
7.223
7.191
7.187
7.166
7.162
7.142
7.137
2.357
1.705
N
Ir
NCMe
9d
BF4
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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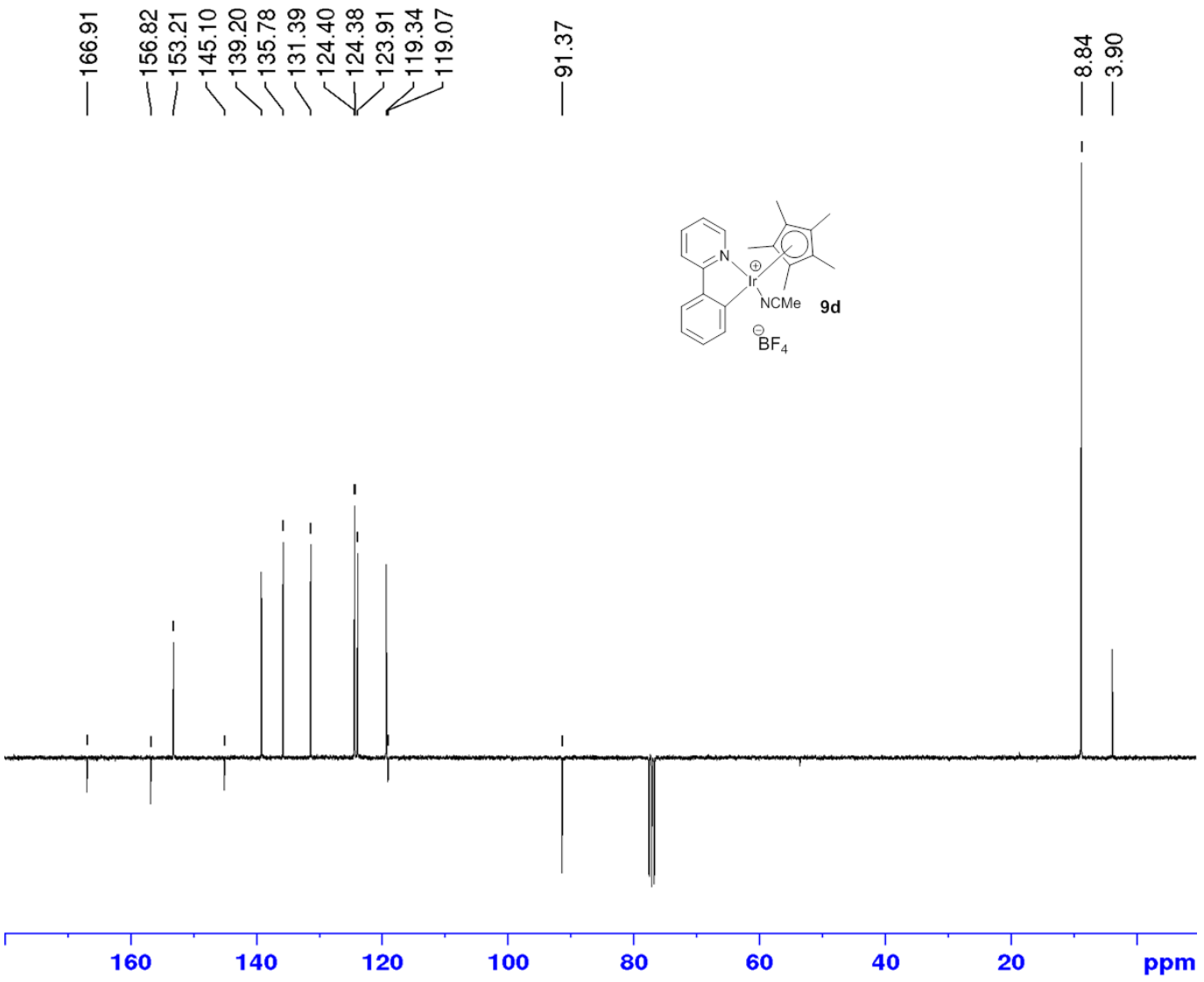
2.11
2.11
1.11
3.13
3.08
15.18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131.39
124.40
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123.91
119.34
119.07
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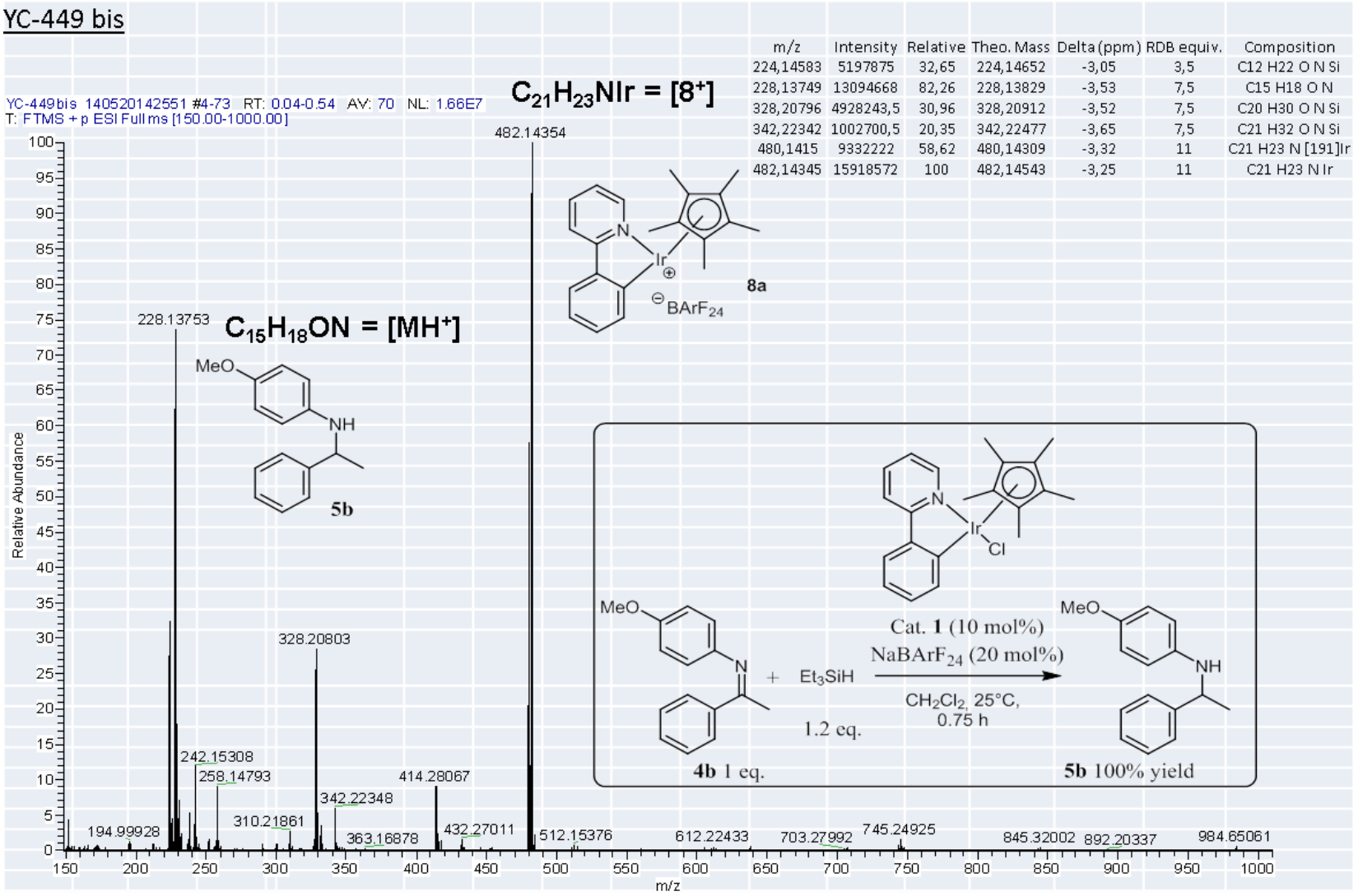
8.84
3.90
N
Ir
NCMe
9d
BF4
160
140
120
100
80
60
40
20
ppm

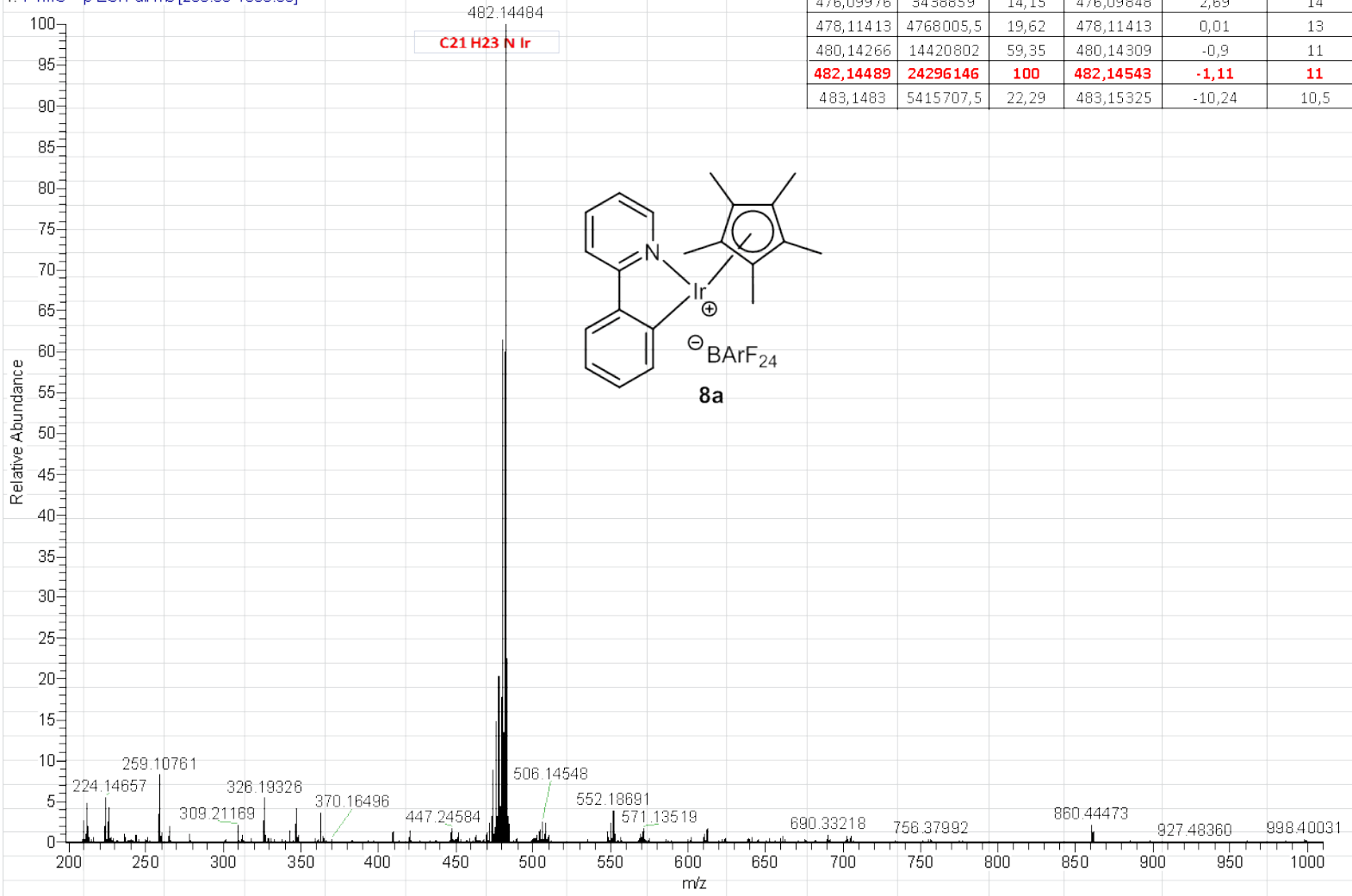
IX) HRMS spectra.



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
224,14583	5197875	32,65	224,14652	-3,05	3,5	C12 H22 O N Si
228,13749	13094668	82,26	228,13829	-3,53	7,5	C15 H18 O N
328,20796	4928243,5	30,96	328,20912	-3,52	7,5	C20 H30 O N Si
342,22342	1002700,5	20,35	342,22477	-3,65	7,5	C21 H32 O N Si
480,1415	9332222	58,62	480,14309	-3,32	11	C21 H23 N [191]Ir
482,14345	15918572	100	482,14543	-3,25	11	C21 H23 N Ir

YC-449

YC-449 #4-136 RT: 0.04-1.00 AV: 133 NL: 2.35E7
T: FTMS + p ESI Full ms [200.00-1000.00]

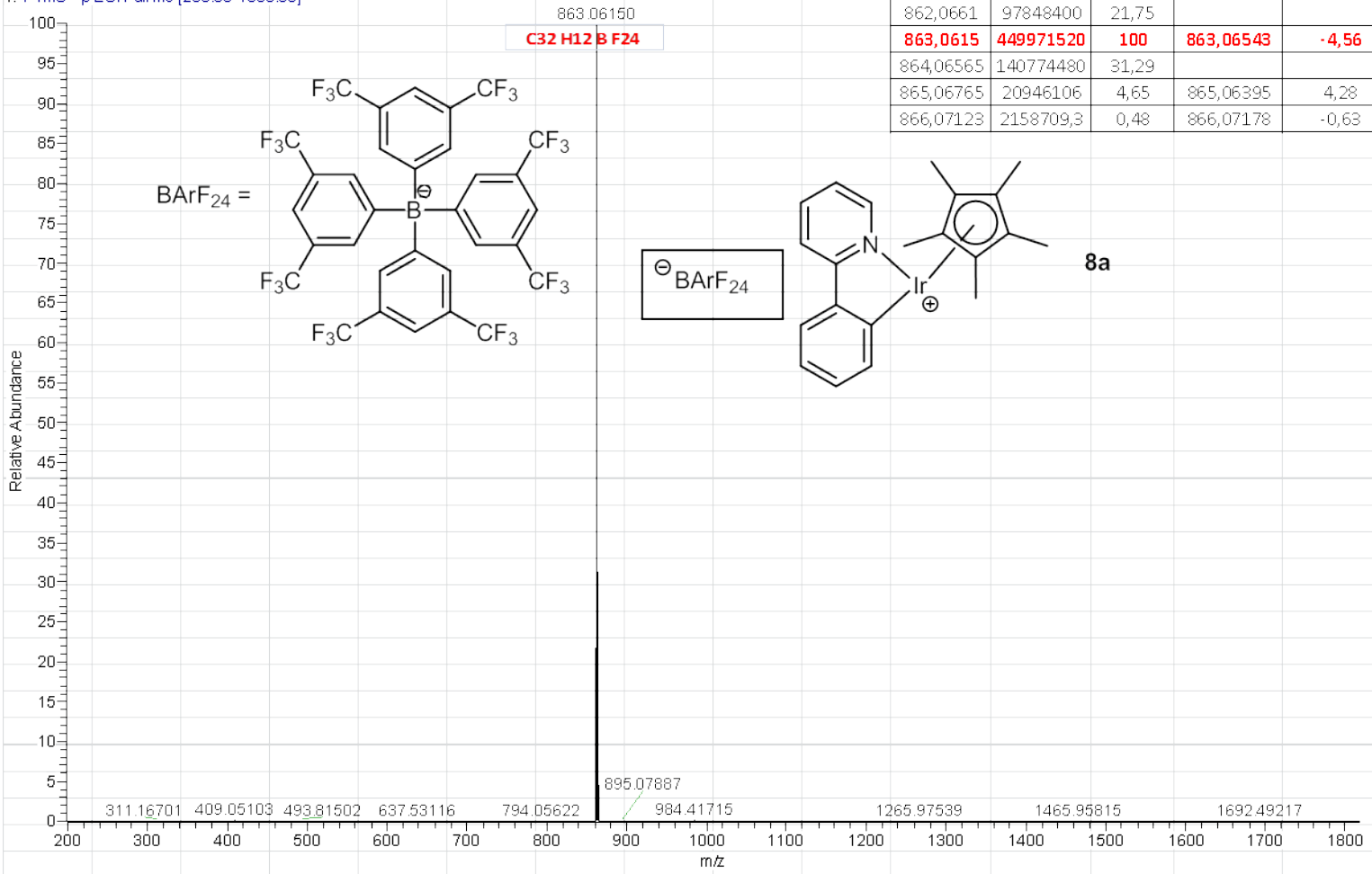


8a

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
476,09976	3438859	14,15	476,09848	2,69	14	C21 H17 N Ir
478,11413	4768005,5	19,62	478,11413	0,01	13	C21 H19 N Ir
480,14266	14420802	59,35	480,14309	-0,9	11	C21 H23 N [191]Ir
482,14489	**24296146**	**100**	**482,14543**	**-1,11**	**11**	**C21 H23 N Ir**
483,1483	5415707,5	22,29	483,15325	-10,24	10,5	C21 H24 N Ir

YC-420 neg

YC-420 neg #2-66 RT: 0.02-0.49 AV: 65 NL: 5.13E8
T: FTMS - p ESI Full ms [200.00-1800.00]



$BArF_{24}$ =

8a

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
862,0661	97848400	21,75				
863,0615	**449971520**	**100**	**863,06543**	**-4,56**	**15,5**	**C32 H12 B F24**
864,06565	140774480	31,29				
865,06765	20946106	4,65	865,06395	4,28	15,5	C33 H13 F24
866,07123	2158709,3	0,48	866,07178	-0,63	15	C33 H14 F24

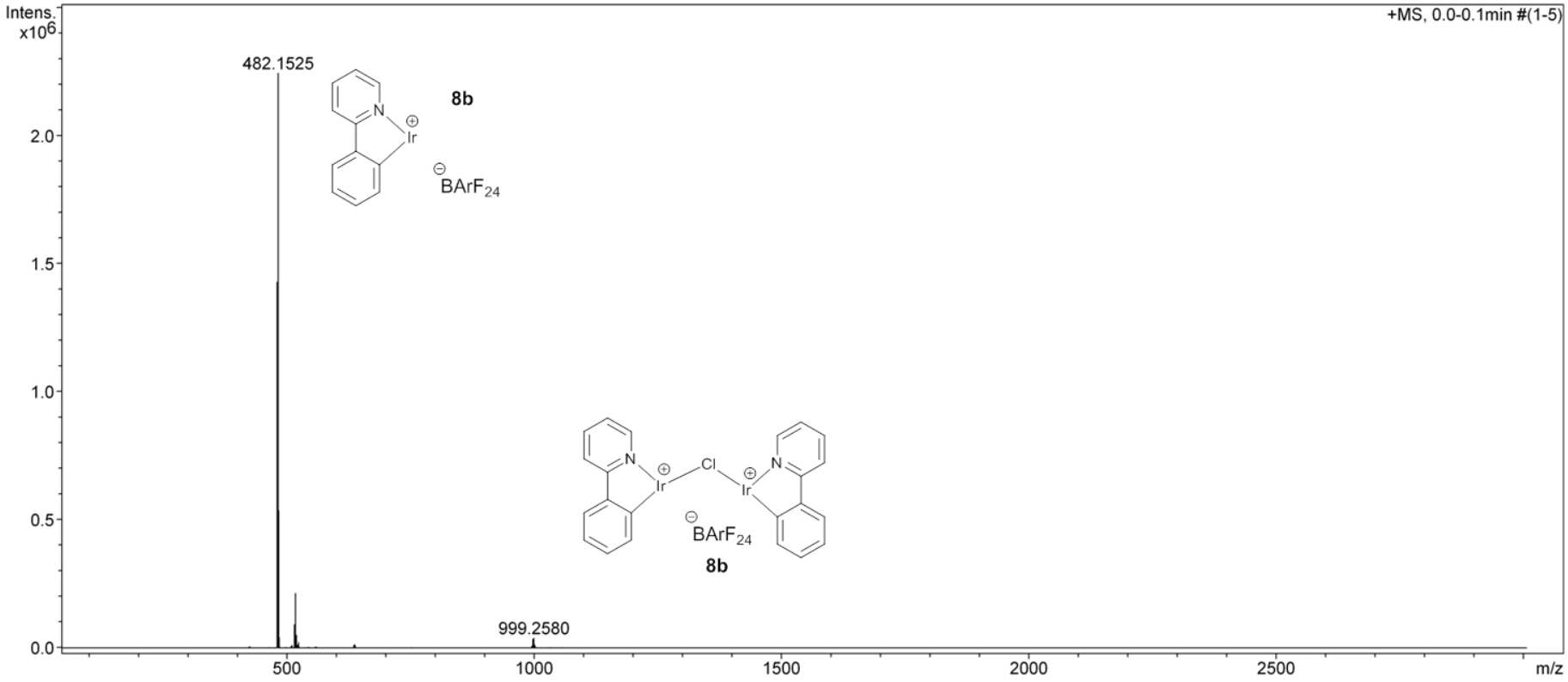
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O31989hn.d	Acquisition Date	10/29/2014 7:58:13 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	MH198	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	80.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C



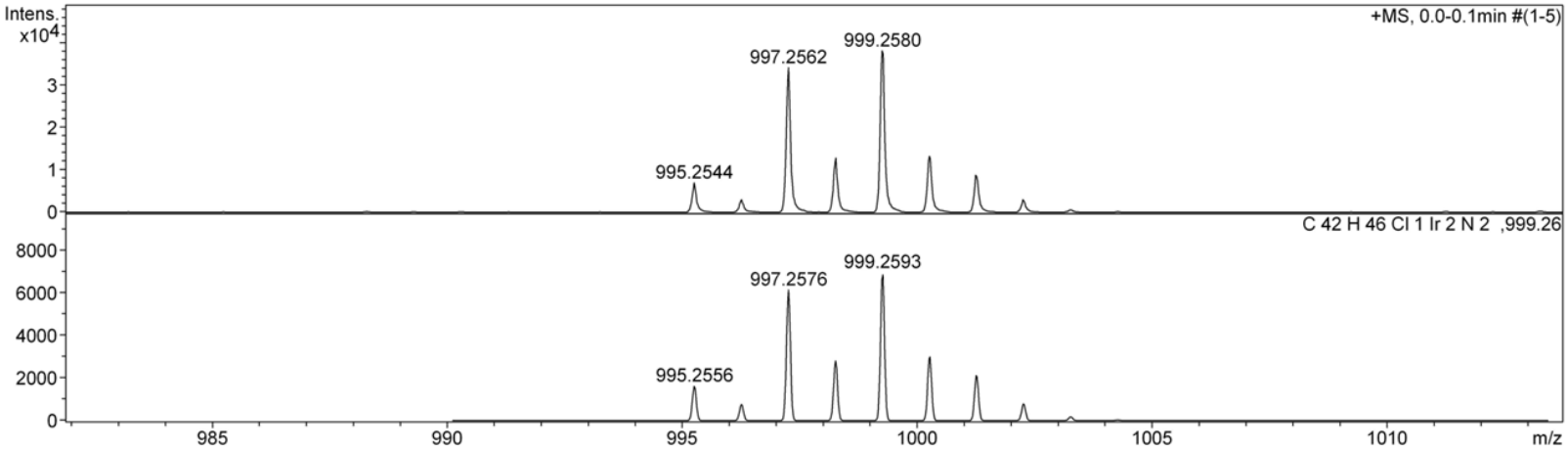
Mass Spectrum Molecular Formula Report

Analysis Info

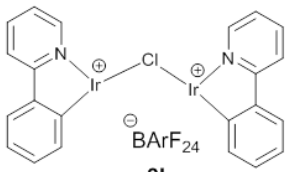
Analysis Name	D:\Data\Service masse à partir du 25 mars 2013\O31989hn.d	Acquisition Date	10/29/2014 7:58:13 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	MH198	Instrument	micrOTOF 66
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	65 V
Scan Range	n/a	Capillary Exit	80.0 V	Set Pulsar Pull	817 V
Scan Begin	50 m/z	Hexapole RF	220.0 V	Set Pulsar Push	817 V
Scan End	3000 m/z	Skimmer 1	50.0 V	Set Reflector	1700 V
		Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2275 V



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 31 H 50 Cl 1 Ir 2 N 2 O 8	0.03	999.2509	-8.28	-8.16	8.50	ok	even
C 35 H 50 Cl 1 Ir 2 N 2 O 5	0.03	999.2661	7.05	6.98	12.50	ok	even
C 28 H 54 Cl 1 Ir 2 N 2 O 10	0.03	999.2720	12.95	12.85	3.50	ok	even
C 38 H 46 Cl 1 Ir 2 N 2 O 3	0.04	999.2450	-14.18	-13.77	17.50	ok	even
C 24 H 54 Cl 1 Ir 2 N 2 O 13	0.05	999.2567	-2.37	-2.41	-0.50	ok	even
C 42 H 46 Cl 1 Ir 2 N 2	0.05	999.2603	1.15	1.25	21.50	ok	even
C 42 H 44 Cl 1 Ir 2 N 2	0.37	997.2446	-12.56	-12.98	22.50	ok	even
C 39 H 48 Cl 1 Ir 2 N 2 O 2	0.37	997.2657	8.66	8.08	17.50	ok	even
C 35 H 48 Cl 1 Ir 2 N 2 O 5	0.37	997.2505	-6.69	-7.32	13.50	ok	even
C 28 H 52 Cl 1 Ir 2 N 2 O 10	0.37	997.2563	-0.81	-1.64	4.50	ok	even
C 21 H 56 Cl 1 Ir 2 N 2 O 15	0.38	997.2622	5.07	4.08	-4.50	ok	even



8b

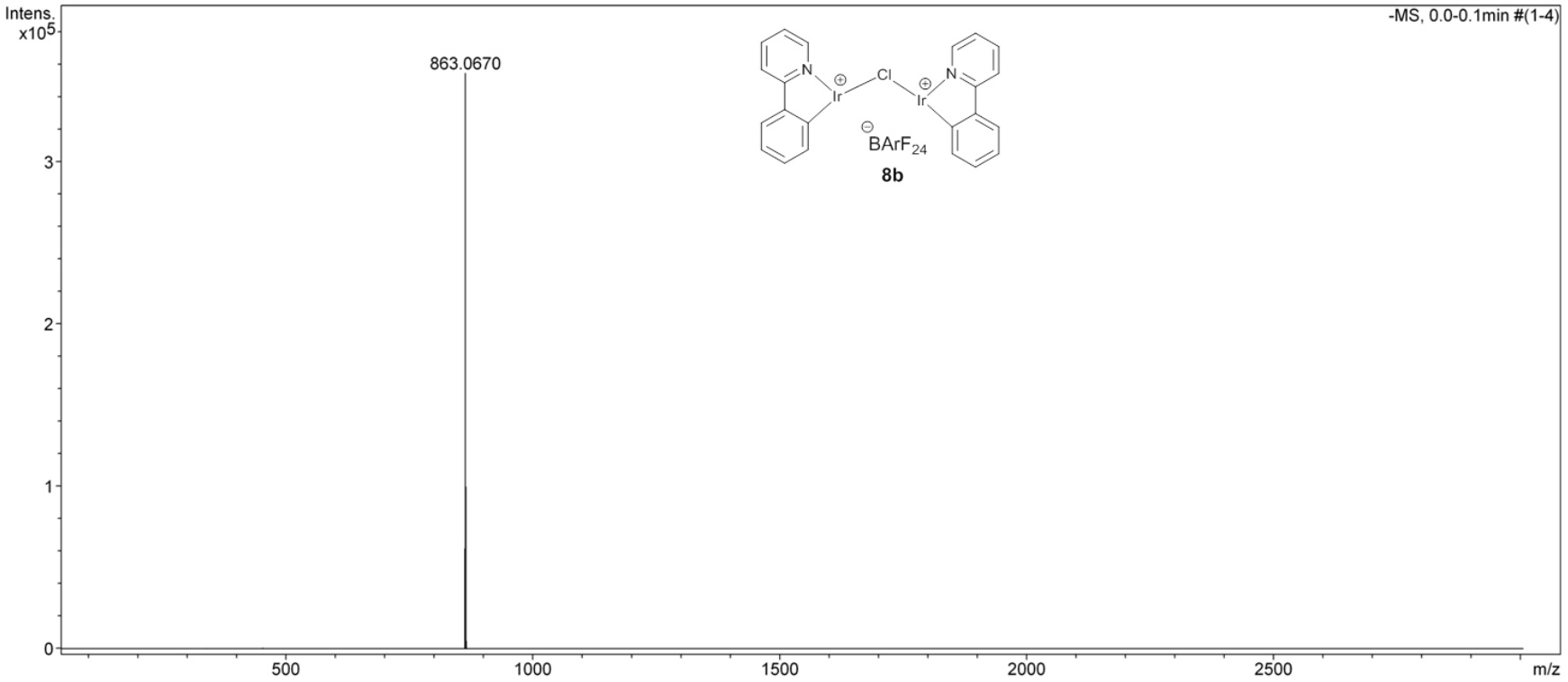
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O31993hn.d	Acquisition Date	10/29/2014 8:39:11 AM
Method	esi low neg.m	Operator	Administrator
Sample Name	MH198 neg	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Negative	Set Capillary Exit	-160.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
Scan Range	n/a	Set Skimmer 1	-50.0 V	Dry Heater	180 °C	APCI Heater	514 °C



Bruker Daltonics DataAnalysis 3.1 printed: 10/29/2014 8:46:30 AM Page 1 of 1

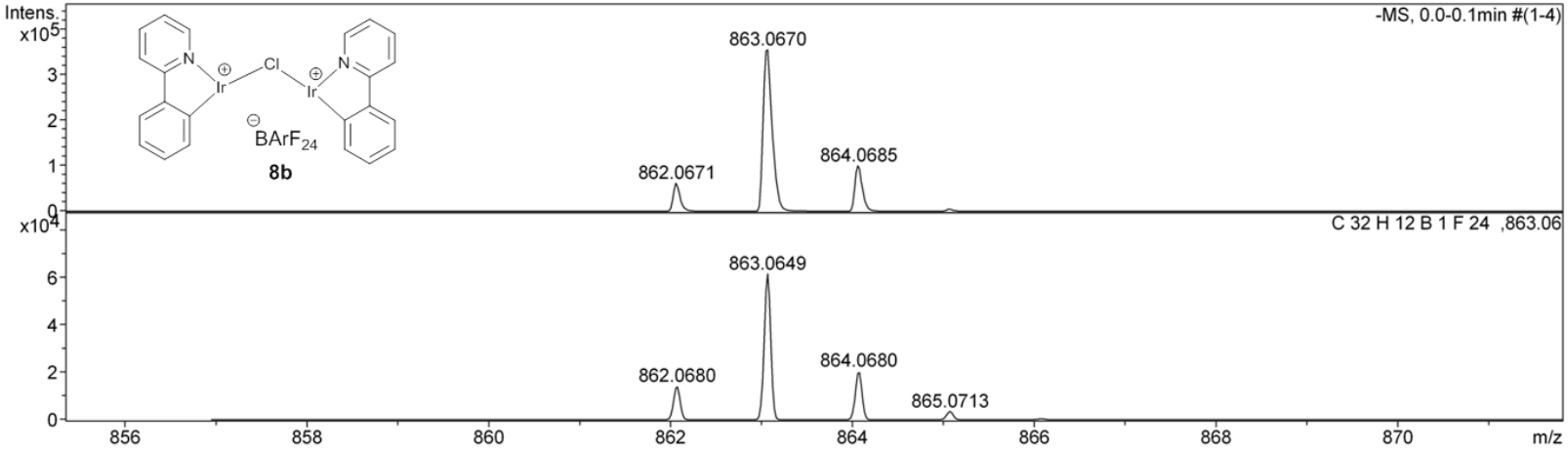
Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\Service masse à partir du 25 mars 2013\O31993hn.d	Acquisition Date	10/29/2014 8:39:11 AM
Method	esi low neg.m	Operator	Administrator
Sample Name	MH198 neg	Instrument	micrOTOF 66
Comment			

Acquisition Parameter

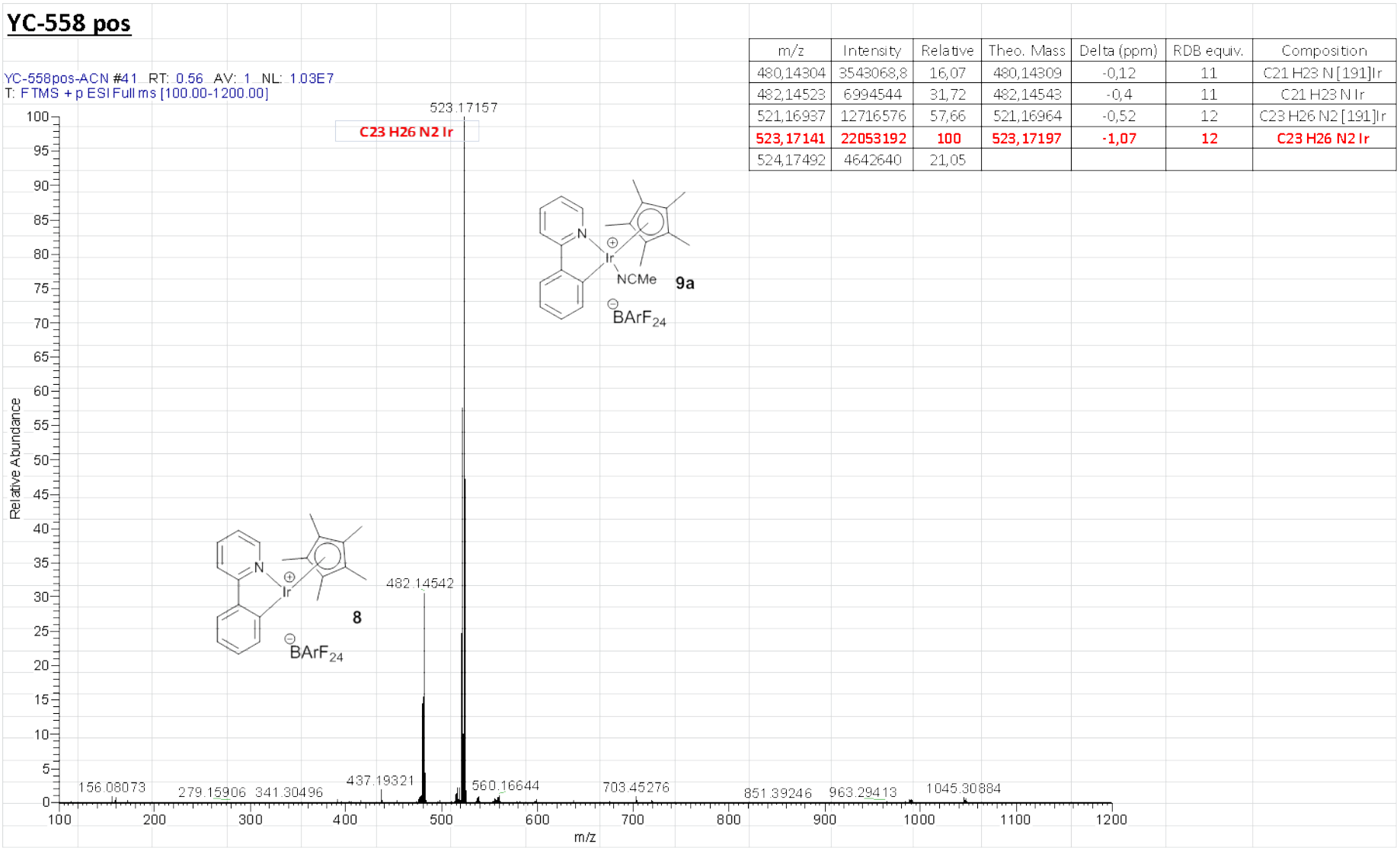
Source Type	ESI	Ion Polarity	Negative	Set Corrector Fill	61 V
Scan Range	n/a	Capillary Exit	-160.0 V	Set Pulsar Pull	801 V
Scan Begin	50 m/z	Hexapole RF	60.0 V	Set Pulsar Push	801 V
Scan End	3000 m/z	Skimmer 1	-50.0 V	Set Reflector	1740 V
		Hexapole 1	-24.0 V	Set Flight Tube	8600 V
				Set Detector TOF	2200 V



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 32 H 12 B 1 F 24	0.04	863.0643	1.05	-1.41	15.50	ok	even
C 32 H 11 B 1 F 24	0.55	862.0565	-12.24	-7.90	16.00	-	odd

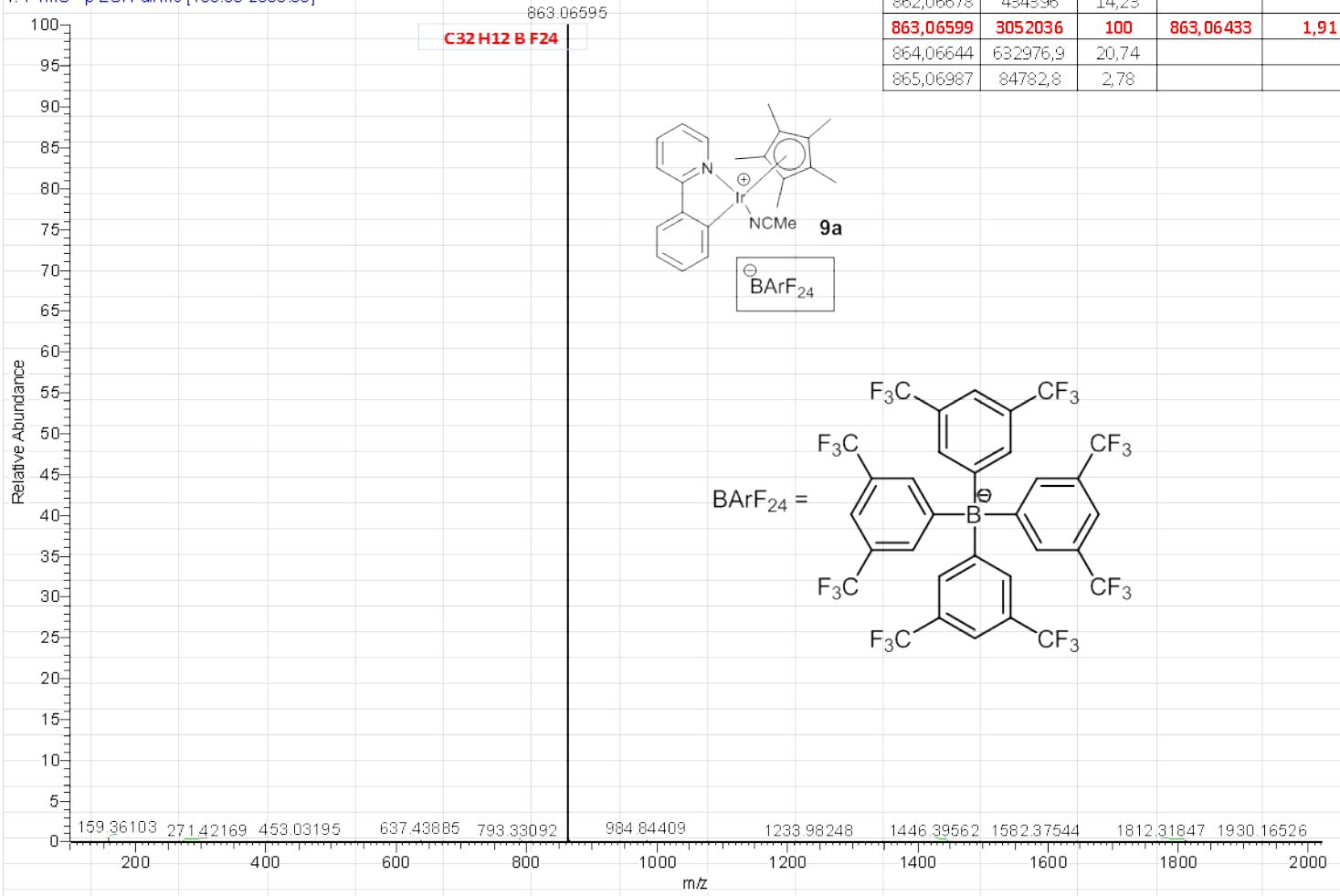
YC-558 pos

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
480,14304	3543068,8	16,07	480,14309	-0,12	11	C21 H23 N [191]Ir
482,14523	6994544	31,72	482,14543	-0,4	11	C21 H23 N Ir
521,16937	12716576	57,66	521,16964	-0,52	12	C23 H26 N2 [191]Ir
523,17141	**22053192**	**100**	**523,17197**	**-1,07**	**12**	**C23 H26 N2 Ir**
524,17492	4642640	21,05				



YC-558 neg

YC-558neg-ACN #17-42 RT: 0.24-0.58 AV: 26 NL: 3.12E6
T: FTMS - p ESI Full ms [100.00-2000.00]



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
159,36066	21285,7	0,7				
862,06678	434396	14,23				
863,06599	**3052036**	**100**	**863,06433**	**1,91**	**15,5**	**C32 H12 B F24**
864,06644	632976,9	20,74				
865,06987	84782,8	2,78				

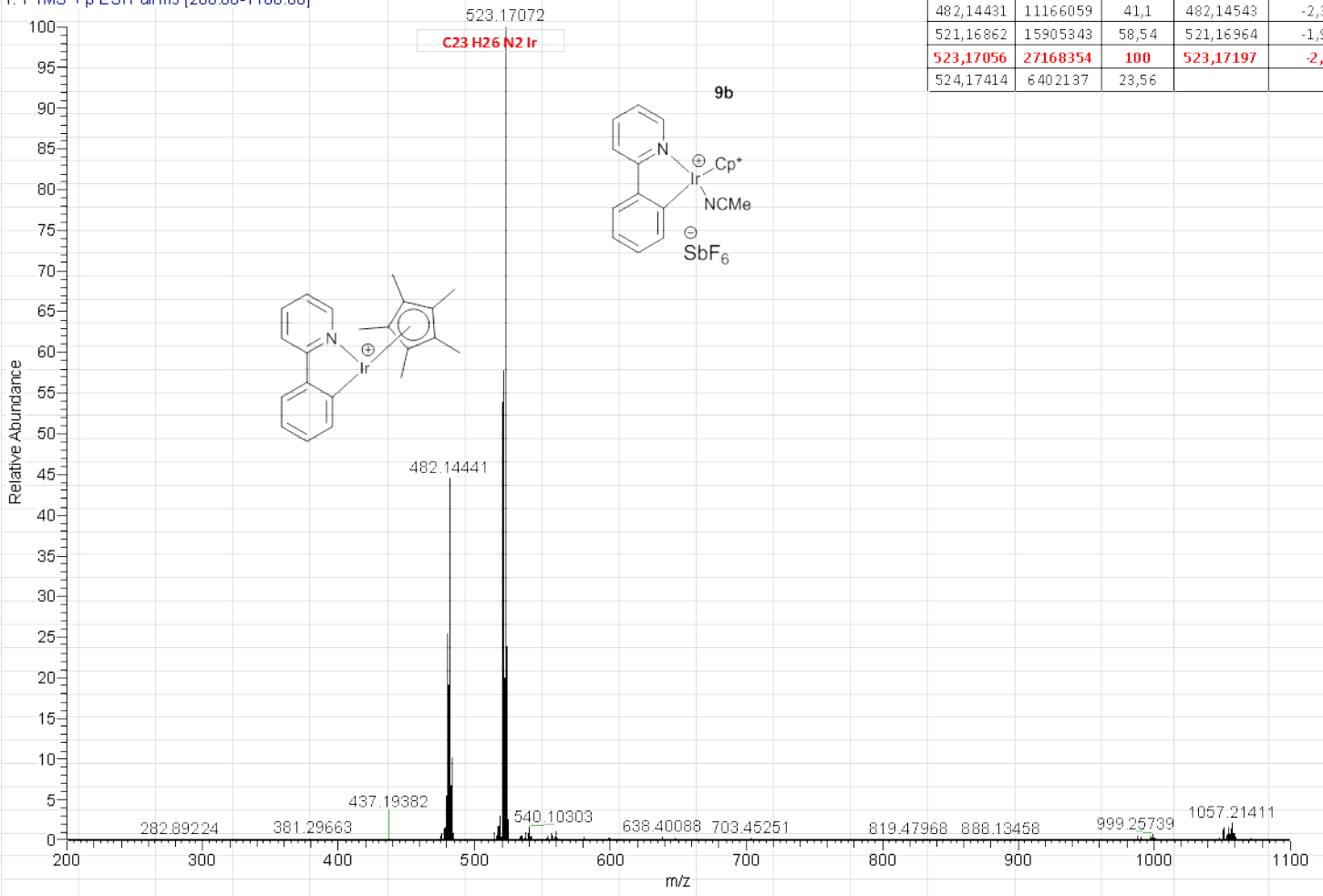
9a

$\ominus BArF_{24}$

$BArF_{24}$ =

YC-575 pos

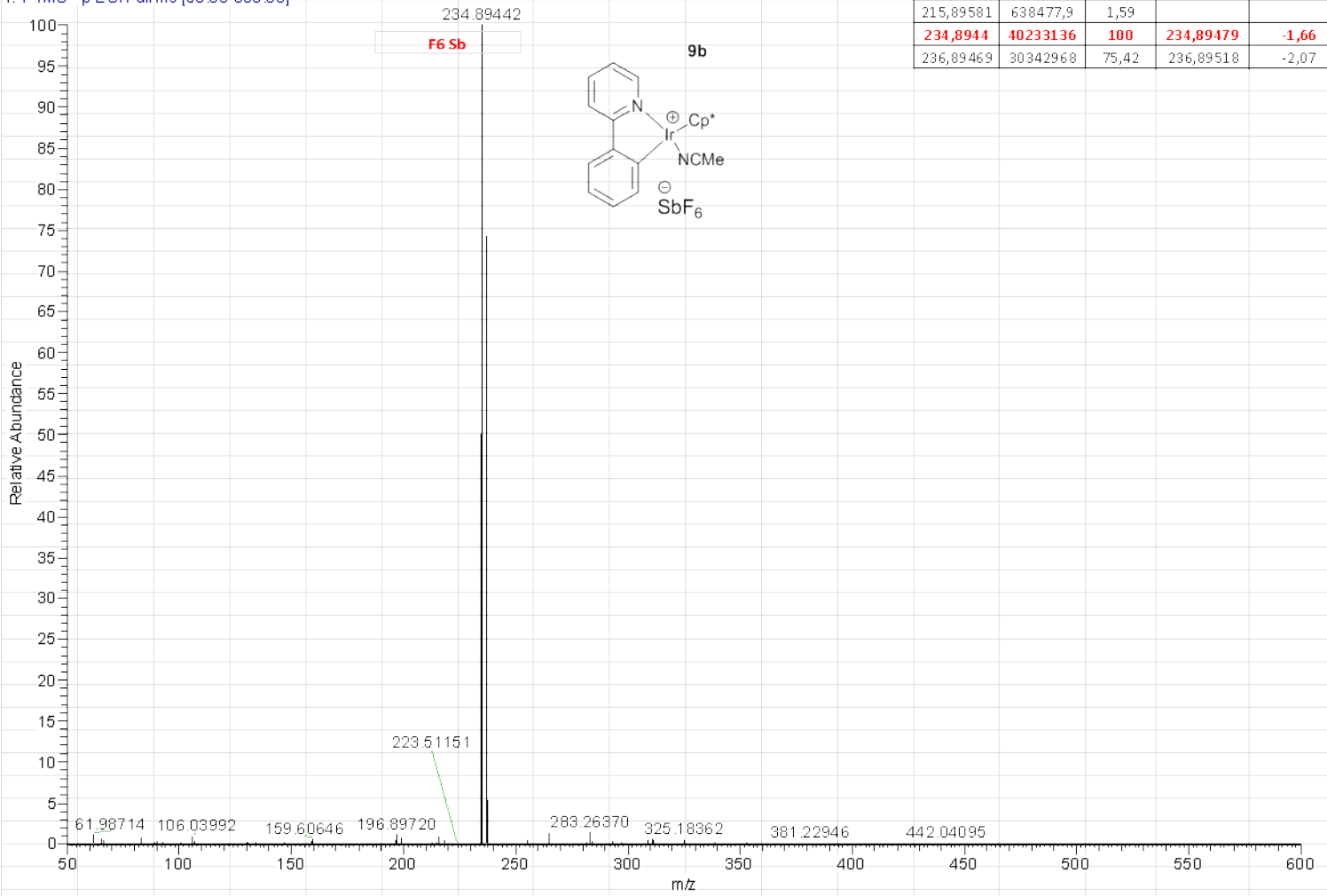
YC-575-pos- #85 RT: 0.63 AV: 1 NL: 2.51E7
T: FTMS + p ESI Full ms [200.00-1100.00]



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
480,14217	6527281,5	24,03	480,14235	-0,39	11,5	C22 H23 Ir
482,14431	11166059	41,1	482,14543	-2,32	11	C21 H23 N Ir
521,16862	15905343	58,54	521,16964	-1,95	12	C23 H26 N2 [191]Ir
523,17056	**27168354**	**100**	**523,17197**	**-2,7**	**12**	**C23 H26 N2 Ir**
524,17414	6402137	23,56				

YC-575 neg

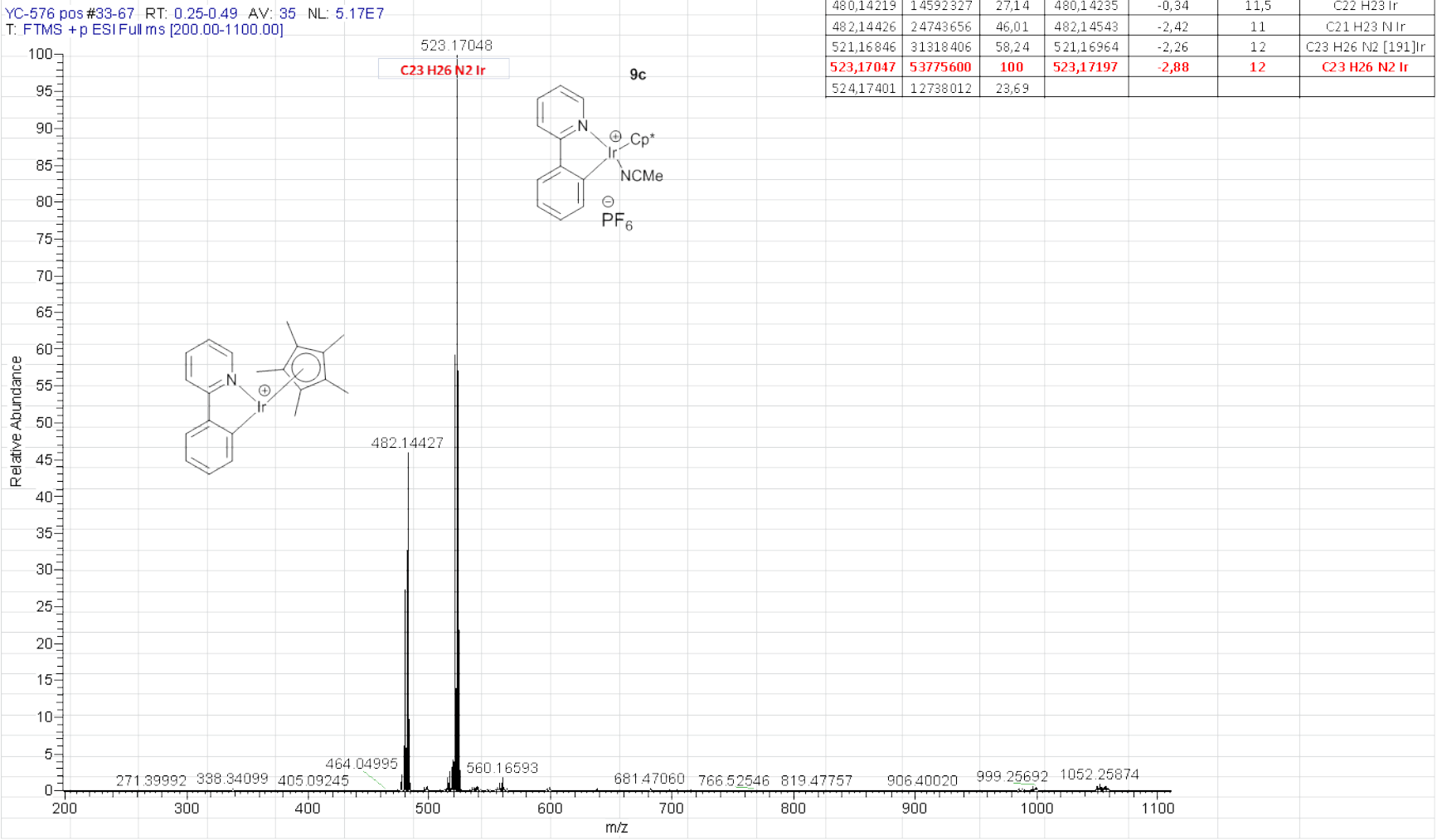
YC-575-neg #75 RT: 0.55 AV: 1 NL: 4.20E7
T: FTMS - p ESI Full ms [50.00-600.00]



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
196,89716	747404,4	1,86				
198,89754	523060,1	1,3				
215,89581	638477,9	1,59				
234,8944	**40233136**	**100**	**234,89479**	**-1,66**	**-1,5**	**F6 Sb**
236,89469	30342968	75,42	236,89518	-2,07	-1,5	F6 [123]Sb

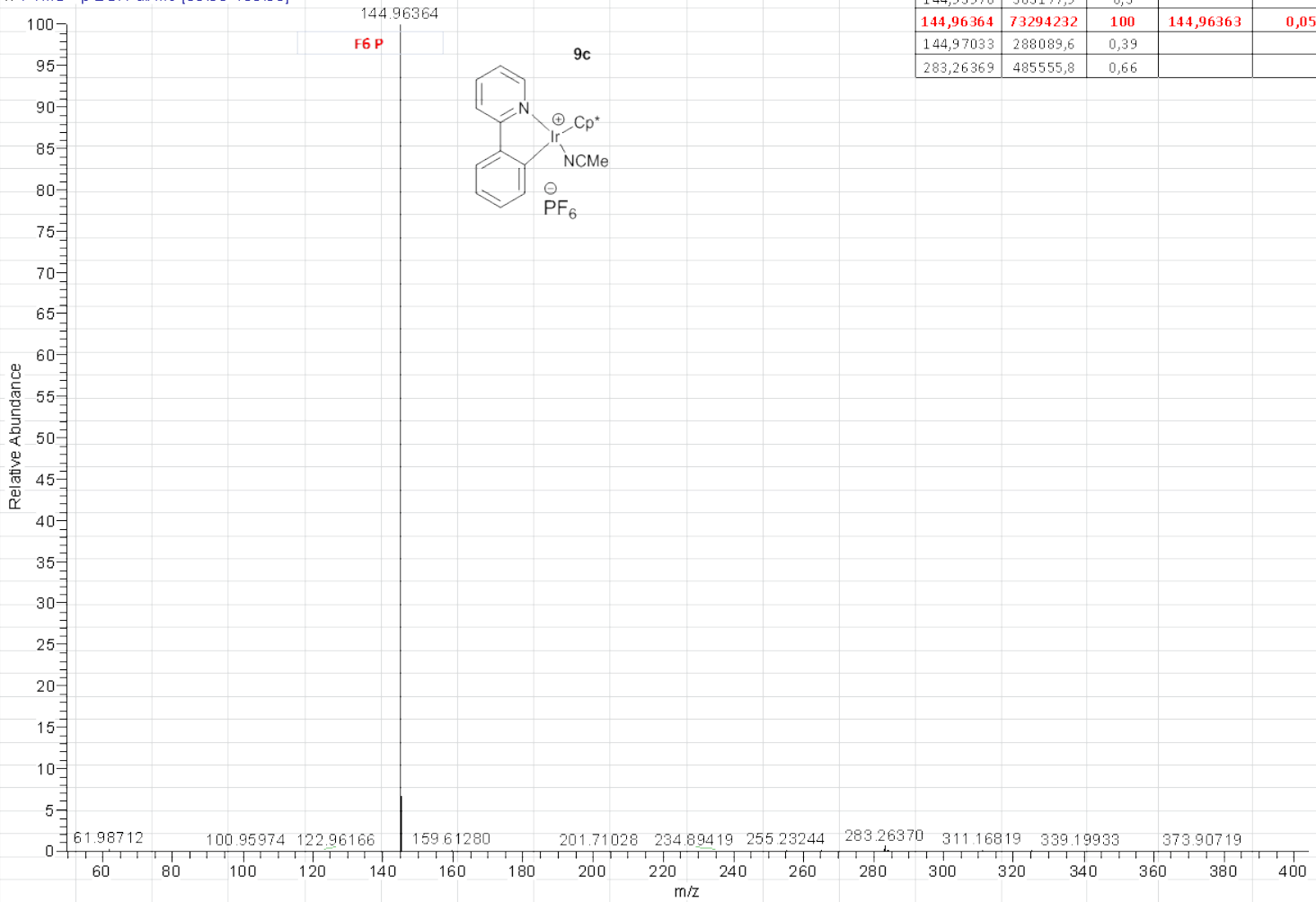
YC-576 pos

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
480,14219	14592327	27,14	480,14235	-0,34	11,5	C22 H23 Ir
482,14426	24743656	46,01	482,14543	-2,42	11	C21 H23 N Ir
521,16846	31318406	58,24	521,16964	-2,26	12	C23 H26 N2 [191]Ir
523,17047	**53775600**	**100**	**523,17197**	**-2,88**	**12**	**C23 H26 N2 Ir**
524,17401	12738012	23,69				



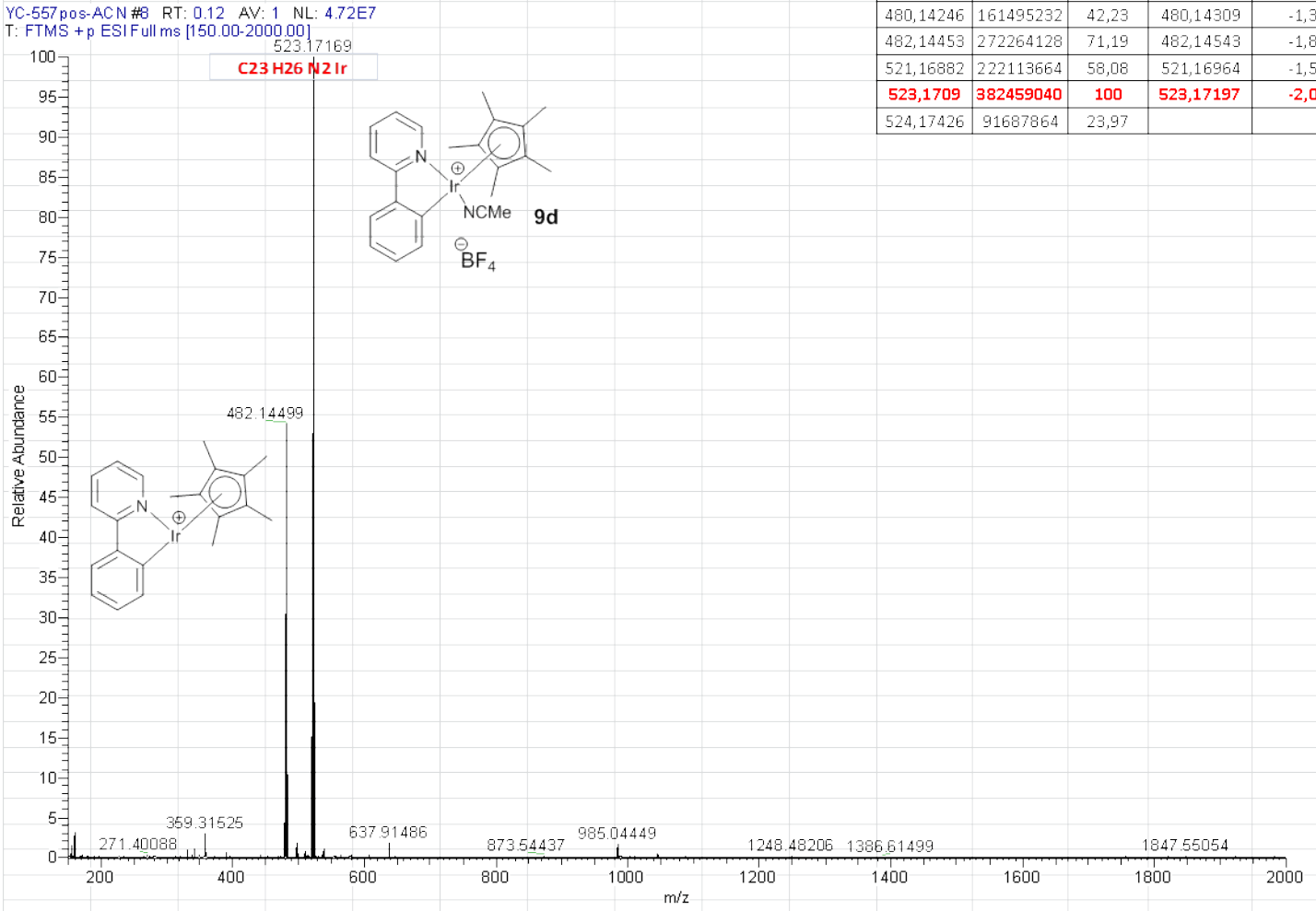
YC-576 neg

YC-576 neg #33-81 RT: 0.25-0.60 AV: 49 NL: 7.15E7
T: FTMS - p ESI Full ms [50.00-400.00]



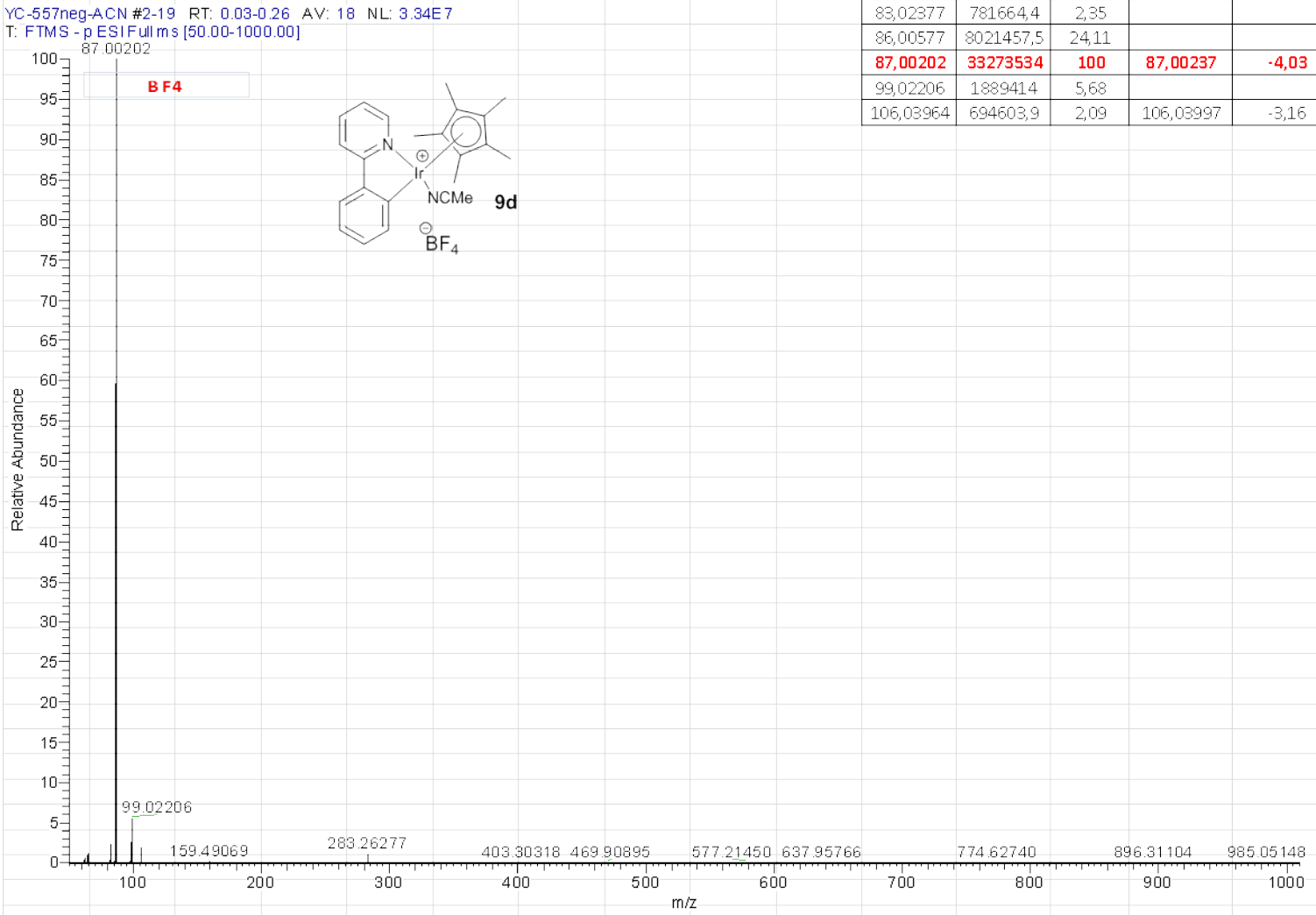
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
61,98712	272244,5	0,37				
144,95976	365177,9	0,5				
144,96364	**73294232**	**100**	**144,96363**	**0,05**	**-1,5**	**F6 P**
144,97033	288089,6	0,39				
283,26369	485555,8	0,66				

YC-557 pos



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
480,14246	161495232	42,23	480,14309	-1,33	11	C21 H23 N [191]Ir
482,14453	272264128	71,19	482,14543	-1,85	11	C21 H23 N Ir
521,16882	222113664	58,08	521,16964	-1,57	12	C23 H26 N2 [191]Ir
523,1709	**382459040**	**100**	**523,17197**	**-2,06**	**12**	**C23 H26 N2 Ir**
524,17426	91687864	23,97				

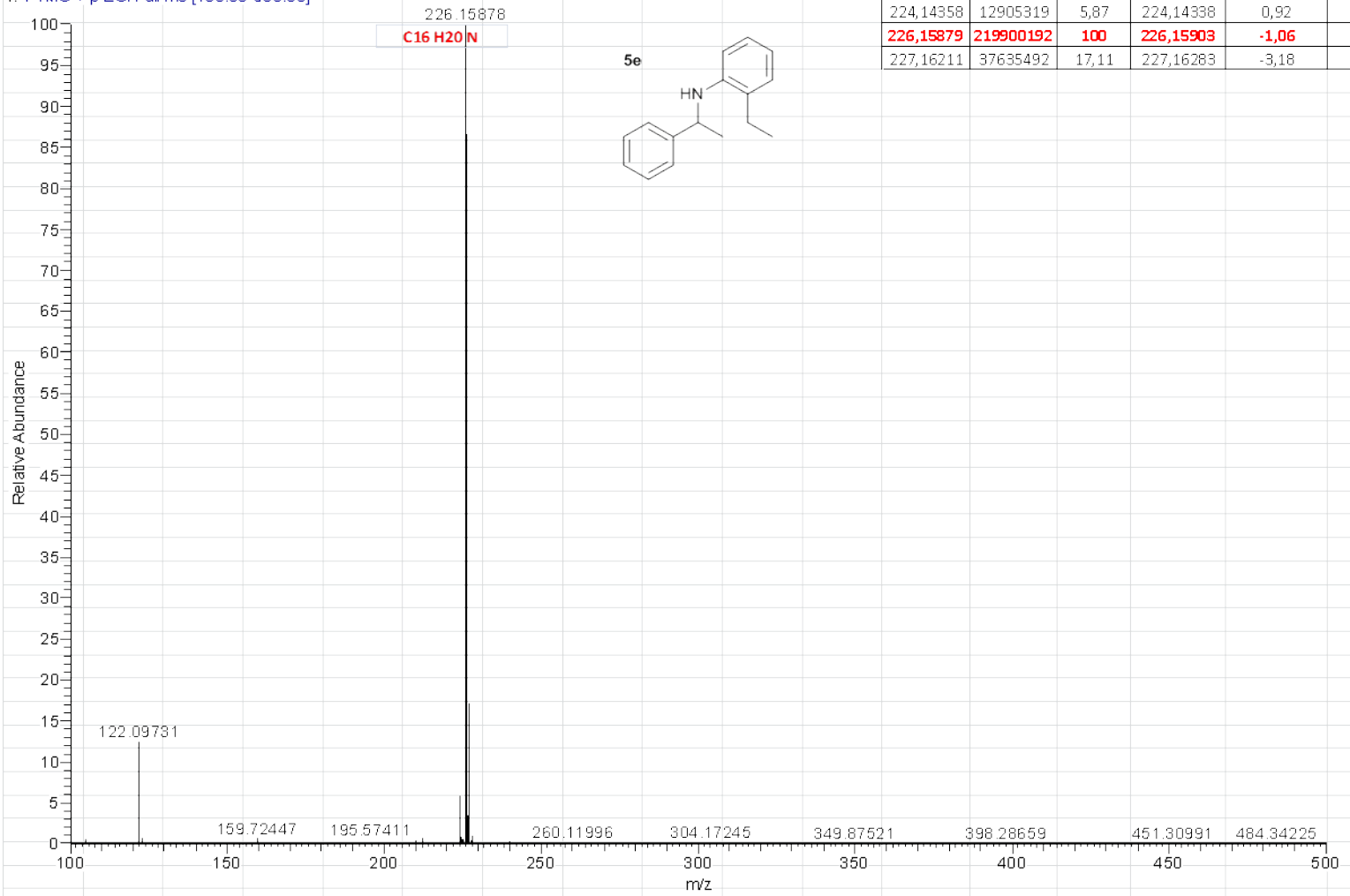
YC-557 neg



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
83,02377	781664,4	2,35				
86,00577	8021457,5	24,11				
87,00202	**33273534**	**100**	**87,00237**	**-4,03**	**-0,5**	**B F4**
99,02206	1889414	5,68				
106,03964	694603,9	2,09	106,03997	-3,16	5,5	C5 H4 N3

YC 510p

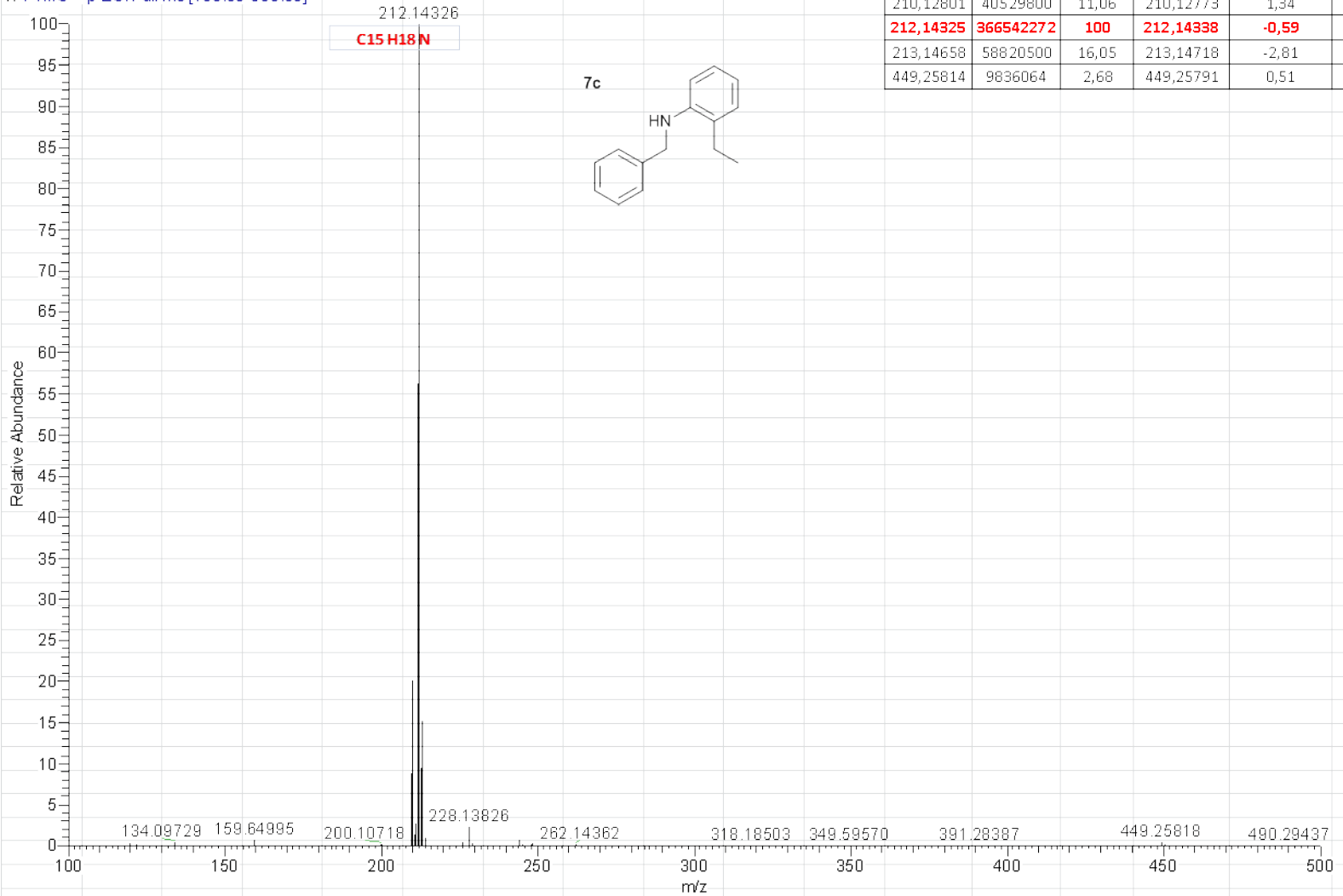
YC-510p #47 RT: 0.64 AV: 1 NL: 2.15E8
T: FTMS + p ESI Full ms [100.00-500.00]



m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
122,09731	25912062	11,78				
212,14334	2389645,3	1,09	212,14338	-0,18	7,5	C15 H18 N
224,14358	12905319	5,87	224,14338	0,92	8,5	C16 H18 N
226,15879	**219900192**	**100**	**226,15903**	**-1,06**	**7,5**	**C16 H20 N**
227,16211	37635492	17,11	227,16283	-3,18	3	C11 H21 O2 N3

YC 502 p

YC-502p #2 RT: 0.03 AV: 1 NL: 5.33E8
T: FTMS + p ESI Full ms [100.00-500.00]



7c

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
134,09733	7551157	2,06				
210,12801	40529800	11,06	210,12773	1,34	8,5	C15 H16 N
212,14325	**366542272**	**100**	**212,14338**	**-0,59**	**7,5**	**C15 H18 N**
213,14658	58820500	16,05	213,14718	-2,81	3	C10 H19 O2 N3
449,25814	9836064	2,68	449,25791	0,51	-1	C16 H39 O11 N3