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Supporting Information

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On the Origin of the Haouamine Alkaloids

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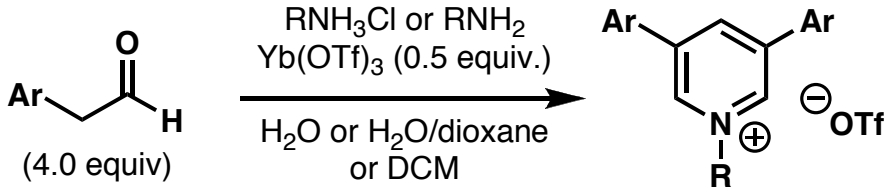
General Procedures. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), triethylamine (TEA), dichloromethane (DCM), methanol (MeOH), dimethylformamide (DMF), and benzene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and *p*-anisaldehyde in ethanol/aqueous H_2SO_4/CH_3CO_2H and heat as developing agents. NMR spectra were recorded on either a Bruker DRX 600, DRX 500 or an AMX 400 and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, b = broad. IR spectra were recorded on a Perkin-Elmer Spetrum BX spectrometer. High resolution mass spectra (HRMS)

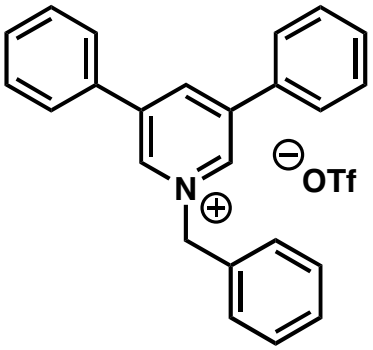
were recorded on an Agilent Mass spectrometer (at Scripps) using ESI-TOF (electrospray ionization-time of flight) or a ThermoFinnigan Mass spectrometer (at UCSD) using FAB (fast atom bombardment), or EI (electron impact). Low resolution mass spectra (LRMS) were recorded on an Agilent (at Scripps) or ThermoFinnigan Mass spectrometer (at UCSD) GC-MS. Melting points (m.p.) are uncorrected and were recorded on a Fisher-Johns 12-144 melting point apparatus. Circular dichroism measurements were obtained on an AVIV model 62DS spectrophotometer.

General procedure for the abnormal Chichibabin pyridine synthesis:



A solution of an arylacetaldehyde (2.0 mmol) and an alkylamine (0.5 mmol, as either the hydrochloride salt or free base) in a solvent of water, water/1,4-dioxane, or DCM (0.1 – 0.5 M) is treated with ytterbium triflate (0.25 mmol), and the reaction mixture is stirred vigorously for 24 h. The reaction mixture is diluted with water (20 mL), extracted with EtOAc (2 × 20 mL), dried over $MgSO_4$, filtered, and concentrated. Purification by flash column chromatography (silica gel, 99:1 → 95:5 DCM/MeOH) affords the product 3,5-diarylpyridinium.

Phenyl pyridinium 7:



The general procedure with phenylacetaldehyde and benzylammonium chloride on 0.21 mmol scale in water (0.5 M) afforded the title pyridinium as a white solid (66 mg, 66%);

m.p. = 159 – 160 ˚C;

$\mathbf{R_f}$ = 0.30 (silica gel, 9:1 DCM/MeOH);

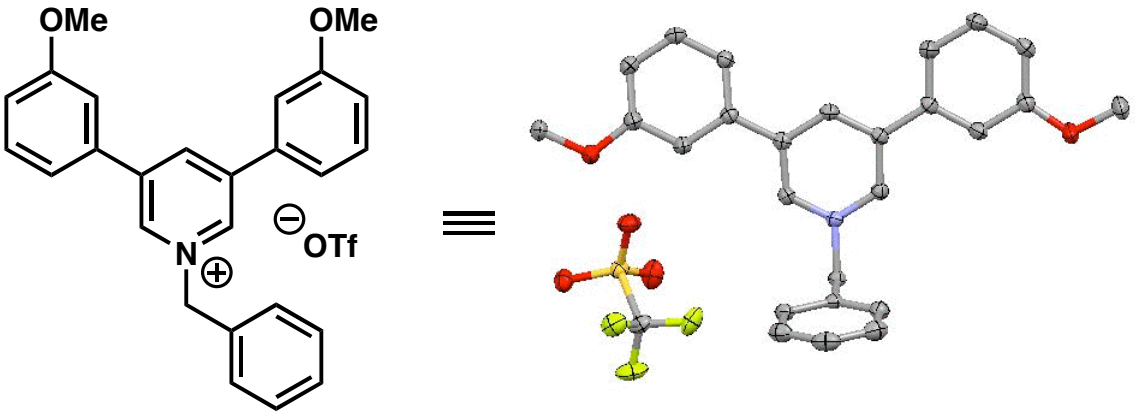
IR (film) $\boldsymbol{\nu_{max}}$ 3063, 1252 (s), 1156, 1027 (s), 901, 758, 695, 636 (s) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 2 H), 8.52 (s, 1 H), 7.74 (d, *J* = 7.0 Hz, 4 H), 7.60 – 7.59 (m, 2 H), 7.53 – 7.48 (m, 6 H), 7.34 – 7.32 (m, 3 H), 6.08 (s, 2 H);

^{13}C-APT NMR (125 MHz, $CDCl_3$) δ 141.9, 140.4, 139.9, 132.8, 132.7, 130.6, 130.0, 129.8, 129.6, 129.5, 127.6, 65.1;

HRMS (ESI) calcd. for $C_{24}H_{20}N$ $[M^+]$ 322.1596, found 322.1596.

***meta*-Methoxyphenyl pyridinium 9:**



The general procedure with *m*-methoxyphenylacetaldehyde and benzylammonium chloride on a 0.12 mmol scale in 1:1 water/1,4-dioxane (0.5 M) afforded the product as clear needles (43 mg, 68%);

m.p. = 139 – 140 °C;

$\mathbf{R_f}$ = 0.28 (silica gel, 9:1 DCM/MeOH);

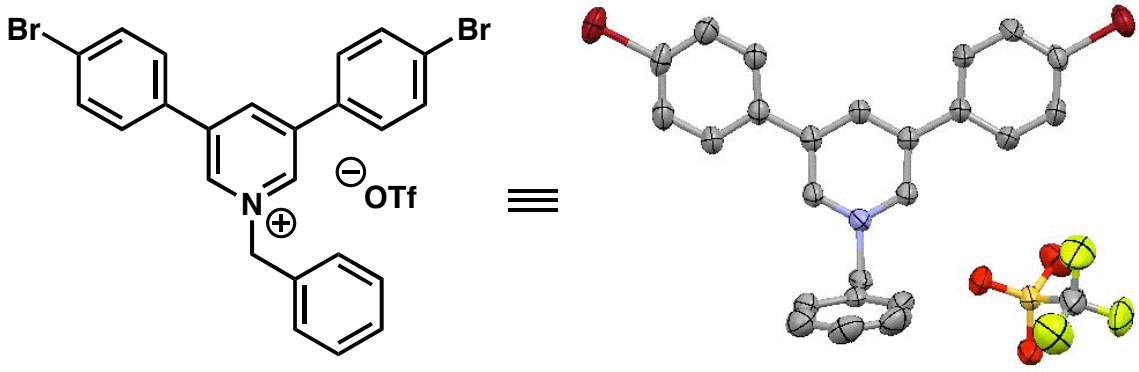
IR (film) $\boldsymbol{\nu_{max}}$ 1587, 1480, 1255 (s), 1159, 1027 (s), 909, 783, 754, 728, 691, 636 (s) cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17 (s, 2 H), 8.49 (s, 1 H), 7.59 (dd, *J* = 3.1, 5.9 Hz, 2 H), 7.41 (t, *J* = 7.9 Hz, 2 H), 7.32 (m, 3 H), 7.28 – 7.26 (m, 4 H), 7.01 (dd, *J* = 2.3, 8.3 Hz, 2H), 6.11 (s, 2 H), 3.88 (s, 6 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 160.6, 141.8, 140.5, 140.1, 134.1, 132.9, 130.9, 129.9, 129.6, 129.4, 119.8, 116.7, 112.6, 65.0, 55.7;

HRMS (ESI) calcd. for $C_{26}H_{24}NO_2$ $[M^+]$ 382.1807, found 382.1803.

***para*-Bromophenyl pyridinium 10**:



The general procedure with *p*-bromophenylacetaldehyde and benzylammonium chloride on 0.098 mmol scale in 2:1 1,4-dioxane/water (0.3 M) yielded the title pyridinium as colorless cubes (40.3 mg, 65%);

m.p. = 241 –242 ˚C;

R_f = 0.38 (silica gel, 9:1 DCM/MeOH);

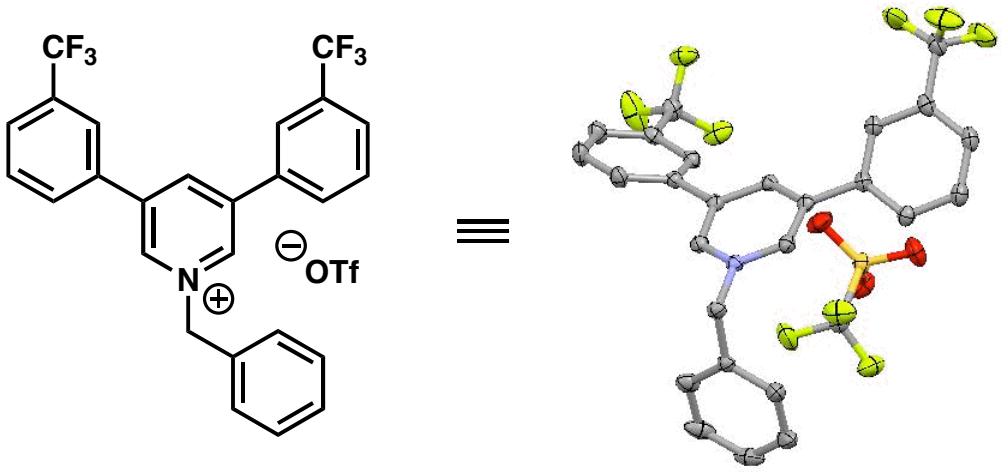
IR (film) ν_{max} 1594, 1476, 1252 (s), 1222, 1159, 1027, 1005, 817, 710, 636 cm^{-1};

^{1}H NMR (600 MHz, CD_3CN) δ 8.99 (d, *J* = 1.6 Hz, 2 H), 8.87 (t, *J* = 1.6 Hz, 1 H), 7.79 (d, *J* = 8.6 Hz, 4 H), 7.73 (d, *J* = 8.6 Hz, 4 H), 7.56 (m, 2 H), 7.49 – 7.47 (m, 3 H), 5.84 (s, 2 H);

^{13}C-APT NMR (150 MHz, CD_3CN) δ 142.4, 141.8, 141.5, 133.8, 133.6, 133.3, 130.8, 130.6, 130.3, 130.0, 125.6, 65.9;

HRMS (ESI) calcd. for $C_{24}H_{18}Br_2N$ [M^+] 477.9806, found 477.9805.

***meta*-Trifluoromethylpyridinium 11**:



The general procedure with *m*-trifluoromethylphenylacetaldehyde and benzylammonium chloride on a 0.17 mmol scale in 1:1 water/1,4-dioxane (0.4 M) yielded the title pyridinium as clear needles (55.6 mg, 54%);

m.p. = 58 – 60˚C;

R_f = 0.40 (silica gel, 9:1 DCM/MeOH);

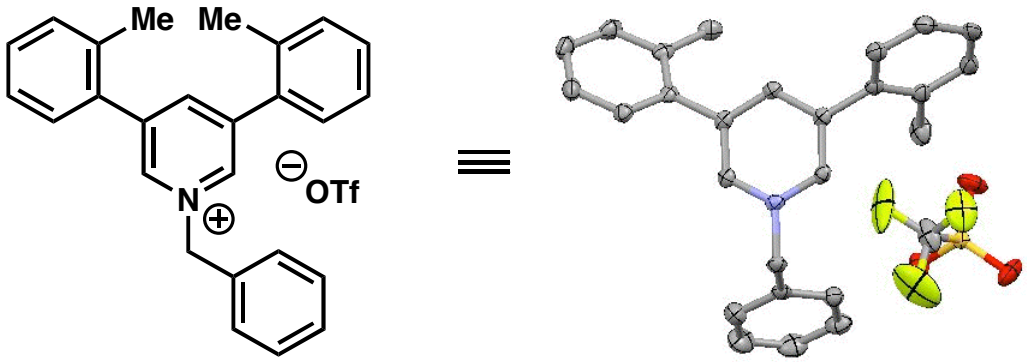
IR film ν_{max} 2354, 1329, 1252 (s), 1159, 1123 (s), 1071, 1027 (s), 802, 699, 636 cm^{-1};

^{1}H NMR (600 MHz, CD_2Cl_2) 9.22 (s, 2 H), 8.68 (s, 1 H), 8.05 (d, *J* = 7.8 Hz, 2 H), 7.98 (s, 2 H), 7.82 (d, *J* = 7.9 Hz, 2 H), 7.74 (t, *J* = 7.9 Hz, 2 H), 7.60 – 7.59 (m, 2 H), 7.42 – 7.40 (m, 3 H), 6.11 (s, 2 H);

^{13}C-APT NMR (150 MHz, CD_2Cl_2) 142.1, 141.7, 141.5, 134.3, 132.8, 132.5 (d, *J* = 32.8 Hz), 132.1, 131.2, 130.8, 130.3, 130.1, 127.9, 125.0, 124.2 (q, *J* = 272.7 Hz), 66.2;

HRMS (ESI) calcd. for $C_{26}H_{18}F_6N$ [M^+] 458.1343, found 458.1339.

***o*-Methylphenyl pyridinium 12**:



The general procedure with *o*-methylphenylacetaldehyde and benzylammonium chloride on a 0.2 mmol scale in 1:1 water/1,4-dioxane (0.5 M) yielded the title pyridinium as clear needles (62 mg, 62%);

m.p. = 164 – 167°;

R_f = 0.4 (silica gel, 9:1 DCM/MeOH);

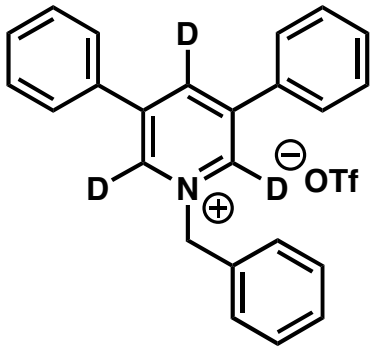
IR (film) ν_{max} 1476, 1454, 1255 (s), 1222, 1152, 1027 (s), 761, 635 (s) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 1.6 Hz, 2 H), 8.20 (t, *J* = 1.4 Hz, 1 H), 7.57 – 7.55 (m, 2 H), 7.43 – 7.41 (m, 3 H), 7.39 – 7.35 (m, 4 H), 7.32 – 7.30 (m, 4 H), 6.06 (s, 2H), 2.29 (s, 6 H);

^{13}C-APT NMR (500 MHz, $CDCl_3$) δ 145.4, 142.0, 141.9, 135.5, 133.1, 132.3, 131.2, 130.22, 130.17 (2 C), 129.9, 129.8, 127.0, 65.3, 20.1;

HRMS (ESI) calcd. for $C_{26}H_{24}N$ [M^+] 350.1909, found 350.1908.

Trideuteropyridinium 13 :



The general procedure with phenylacetaldehyde-*d* and benzylammonium chloride in water (0.5 M) yielded the title pyridinium as a white solid.

m.p. = 159 – 160 °C;

R_f = 0.33 (silica gel, 9:1 DCM/MeOH)

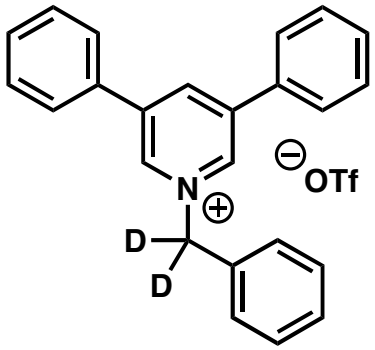
IR (film) ν_{max} 2354, 2332, 1554, 1418, 1252, 1152, 1027, 750, 695, 636, 514 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 4 H), 7.61 – 7.59 (m, 2 H), 7.52 – 7.44 (m, 6 H), 7.32 (t, *J* = 3.2 Hz, 3 H), 6.05 (s, 2 H);

^{13}C-APT NMR (125 MHz, $CDCl_3$): δ 141.7, 132.8, 132.6, 130.6, 130.0, 129.8, 129.6, 129.5, 127.6, 64.9.

HRMS (ESI) calcd. for $C_{24}H_{17}D_3N$ [M^+] 325.1781, found 325.1775.

Dideuteropyridine 14:



The general procedure with phenylacetaldehyde and benzylammonium chloride-d_2 yielded the title pyridinium as a white solid.

m.p. = 154 – 155 ˚C;

R_f = 0.24 (silica gel, 9:1 DCM/MeOH);

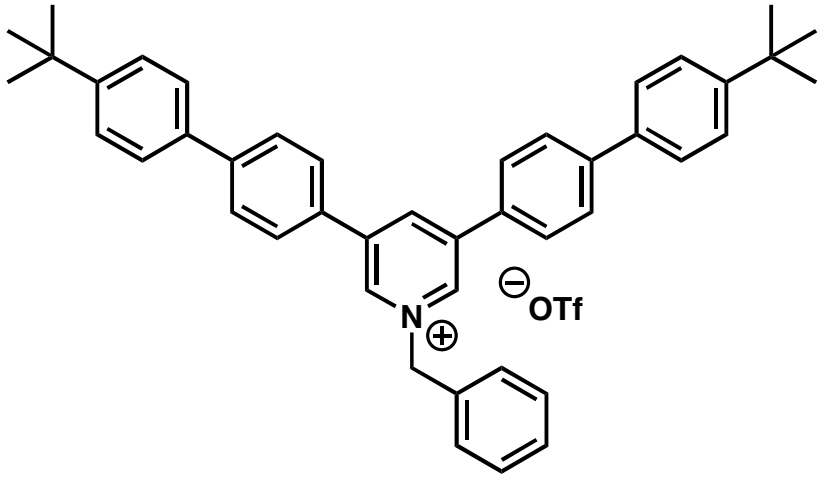
IR (film) ν_{max} 3067, 1595, 1498, 1475, 1442, 1257 (s), 1225, 1157, 1029 (s), 759, 696 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, *J* = 1.7 Hz, 2 H), 8.52 (t, *J* = 1.7 Hz, 1 H), 7.75 – 7.73 (m, 4 H), 7.61 – 7.59 (m, 2 H), 7.54 – 7.47 (m, 6 H), 7.34 (t, *J* = 3.1 Hz, 3 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$): δ 141.9, 140.3, 139.9, 132.68, 132.65, 130.6, 130.0, 129.8, 129.6, 129.4, 127.5;

HRMS (ESI) calcd. for $C_{24}H_{18}D_2N$ [M^+] 324.1719, found 324.1717.

4-(4-*tert*-butylphenyl)-phenyl pyridinium 18:



The general procedure with 4-(*tert*-butylphenyl)-phenylacetaldehyde and benzylamine on a 0.054 mmol scale in DCM (0.1 M) yielded the known 4-(*tert*-butylphenyl)-benzaldehyde[1] (6 mg, 0.7 equiv based on isolated product) and the title pyridinium as a white solid (26 mg, 65%);

m.p. > 300 ˚C;

$\mathbf{R_f}$ = 0.39 (silica gel, 9:1 DCM/MeOH);

IR (film) ν_{max} 3067, 2923, 1595, 1498, 1475, 1452, 1442, 1412, 1341, 1254 (s), 1224, 1155, 1029, 758, 695 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 2 H), 8.45 (s, 1 H), 7.79 (d, *J* = 8.4 Hz, 4 H), 7.73 (d, *J* = 8.4 Hz, 4 H), 7.62 – 7.6- (m, 2 H), 7.52 (d, *J* = 8.4 Hz, 4 H), 7.47 (d, *J* = 8.4 Hz, 4 H), 7.40 – 7.36 (m, 3 H), 6.16 (s, 2 H), 1.36 (s, 18 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 151.4, 143.1, 141.2, 139.9, 138.9, 136.2, 132.9, 131.0, 130.0, 129.7, 129.4, 128.0, 127.9, 126.6, 126.0, 65.3, 34.6, 31.3;

HRMS (ESI) calcd. for [M^+] 586.3474 found 586.3469.

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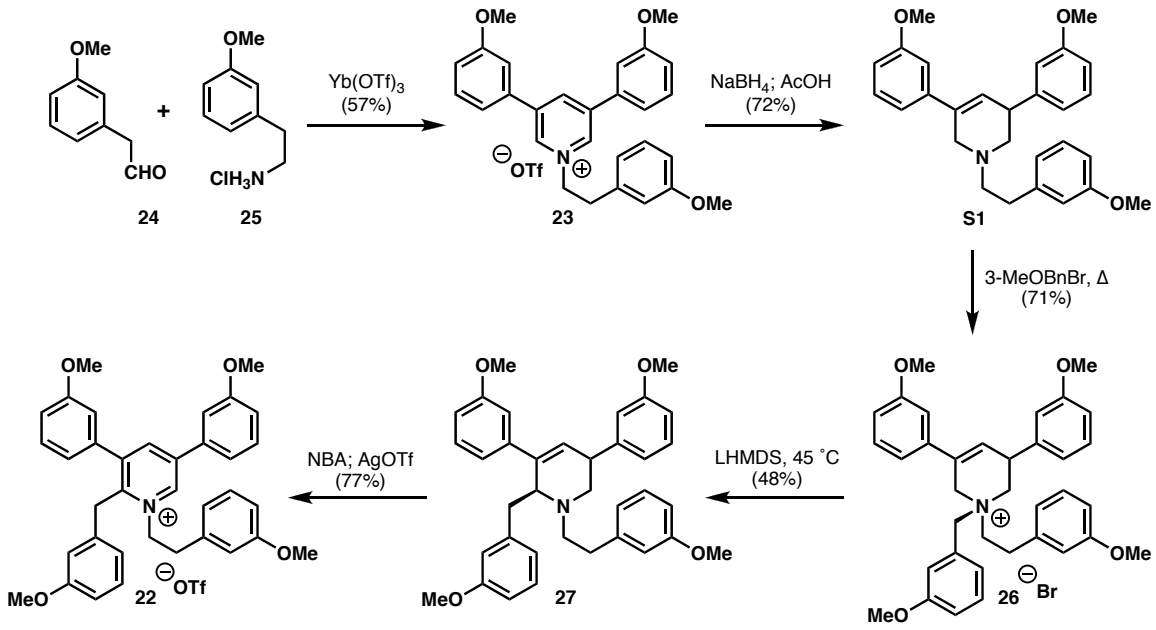
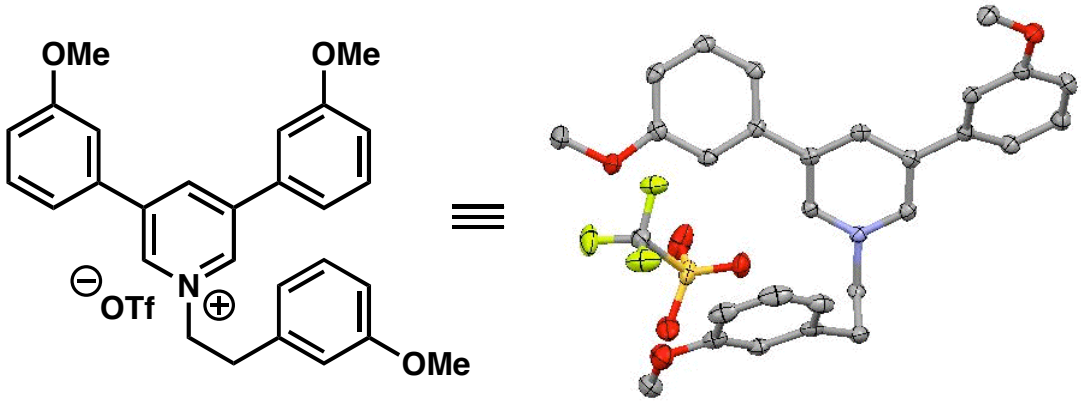
[1] Yang, J.; Gabriele, B.; Belvedere, S.; Huang, Y.; Breslow, R. *J. Org. Chem.* **2002**, *67*, 5057 – 5067.

Scheme S1.



Pyridinium 23:



The general procedure with *m*-methoxyphenylacetaldehyde **24** and 2-(*meta*-methoxyphenyl)-ethylamine hydrochloride **25** on a 0.54 mmol scale in water (0.5 M) yielded the title pyridinium as a white solid (131 mg, 57%);[2]

[2] Poupon and coworkers (Gravel, E.; Poupon, E.; Hocquemiller, R. *Chem. Commun.* **2007**, 719 – 721) conducted this reaction in DCM with the free amine. Identical results are obtained regardless of the procedure (*vide infra*).

m.p. = 158 – 160 ˚C;

R_f = 0.22 (silica gel, 9:1 DCM/MeOH);

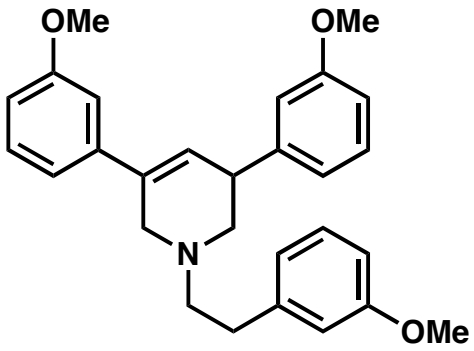
IR (film) ν_{max} 2937, 1735, 1594, 1583, 1488, 1454, 1255 (s), 1152, 1027, 783, 691, 636 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 1.6 Hz, 2 H), 8.50 (t, *J* = 1.6 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 2 H), 7.17 – 7.14 (m, 3 H), 7.10 (t, *J* = 2.0 Hz, 2 H), 7.03 (dd, *J* = 2.4, 8.3 Hz, 2 H), 6.74 (dd, *J* = 2.4, 8.2 Hz, 1 H), 6.68 (t, *J* = 2.1 Hz, 1 H), 6.63 (d, *J* = 7.7 Hz, 1 H), 5.15 (t, *J* = 6.5 Hz, 2 H), 3.89 (s, 6 H), 3.72 (s, 3 H), 3.30 (t, *J* = 6.5 Hz, 2 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 160.7, 141.4, 140.5, 139.9, 136.9, 134.0, 130.8, 130.2, 121.1, 119.6, 116.7, 114.2, 113.5, 112.4, 63.6, 55.7, 55.3, 37.9;

HRMS (ESI) calcd. for $C_{28}H_{28}NO_3$ [M^+] 426.2069, found 426.2062.

Tetrahydropyridine S1:



To a solution of pyridinium **23** (316 mg, 0.74 mmol) in methanol (3.7 mL) and DCM (3.7 mL) at 0 ˚C was added cerium trichloride (276 mg, 0.74 mmol, 1.0 equiv). Sodium borohydride was added CAUTIOUSLY (560 mg, 14.8 mmol, 20.0 equiv). A distinct bright color is observed upon addition. The reaction mixture was stirred for 20 min, and acetic acid (3.7 mL) was then added CAUTIOUSLY dropwise. A disappearance in color

signified the completion of the reaction (more sodium borohydride was added if complete decoloration did not occur within 30 min). The reaction mixture was then diluted with 1.0 M NaOH (40 mL), and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 5:1 hexanes/EtOAc) afforded the product as a clear oil (229 mg, 72%).

R_f = 0.29 (silica gel, 3:1 hexanes/EtOAc)

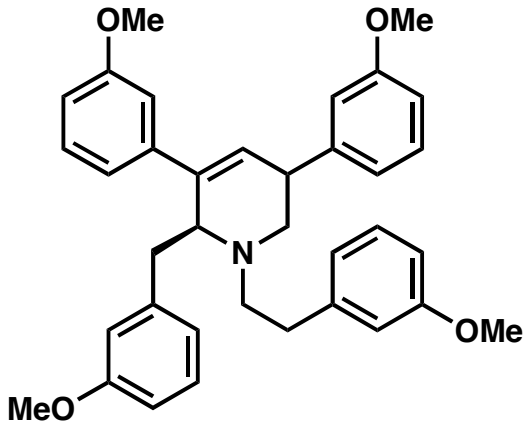
IR (film) ν_{max} 2930, 2827, 1598, 1580, 1484, 1462, 1451, 1429, 1285, 1259, 1148, 1045, 780, 691 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 7.8 Hz, 1 H), 7.02 (d, *J* = 7.7 Hz, 1 H), 6.96 (s, 1 H), 6.90 (d, *J* = 7.5 Hz, 1 H), 6.86 – 6.75 (m, 6 H), 6.19 (s, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.79 (m, 1 H), 3.68 (d, *J* = 15.8 Hz, 1 H), 3.37 (dt, *J* = 2.5, 15.6 Hz, 1 H), 3.16 (dd, *J* = 5.5, 11.2 Hz, 1 H), 2.88 (dd, *J* = 11.3, 9.4 Hz, 2 H), 2.81 (dd, *J* = 9.7, 10.9 Hz, 2 H), 2.43 (dd, *J* = 9.0, 11.1 Hz, 1 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 159.7, 159.6 (2C), 145.2, 141.9, 141.3, 136.1, 129.42, 129.35, 129.34, 126.2, 121.1, 120.5, 117.7, 114.5, 114.0, 112.5, 111.8, 111.3, 111.2, 59.8, 58.3, 55.23, 55.19, 55.1, 54.6, 43.2, 33.9;

HRMS (ESI) calcd. for $C_{28}H_{31}NO_3$ [M + H^+] 430.2377, found 430.2370.

2-Benzyltetrahydropyridine 27:



To a solution of tetrahydropyridine **S1** (51.8 mg, 0.12 mmol) in acetone (600 μL) was added 3-methoxylbenzylbromide (167 μL, 1.2 mmol, 10.0 equiv), and the reaction mixture was heated in a 60 ˚C oil bath overnight. Concentration and flash column chromatography (silica gel, 95:5 DCM/MeOH) afforded the quaternary ammonium salt as a white solid (75 mg, 99%). This salt was dissolved in THF (4.0 mL) and placed in a 45 ˚C oil bath. LHMDS (720 μL, 0.5 M, 0.36 mmol, 3.0 equiv) was added at once, and after 5 min the reaction was cooled and quenched with water (10 mL). The organic layer was extracted twice with EtOAc (20 mL), dried over $MgSO_4$, filtered, and concentrated. Flash column chromatography (silica gel, 99:1 to 95:5 benzene/EtOAc) afforded the product (as a 7:3 mixture of diastereomers) that appeared as a slightly yellow oil (32 mg, 48%).

R_f = 0.38 (silica gel, 4:1 hexanes/EtOAc)

IR (film) ν_{max} 2998, 2938, 1833, 1598, 1583, 1486, 1464, 1453, 1433, 1286, 1260 (s), 1151. 1047, 777, 696 cm^{-1};

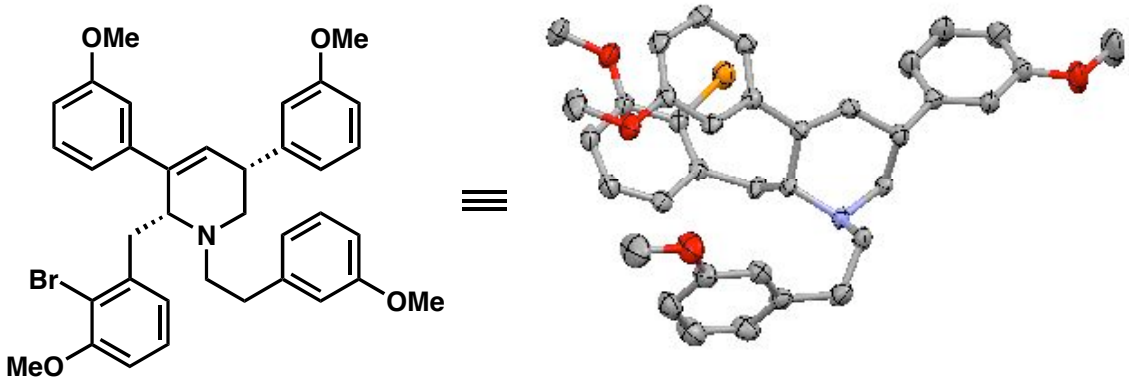
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 2.9, 8.0 Hz, 1.3 H), 7.25 – 7.20 (m, 0.7 H), 7.19 – 7.15 (m, 1.7 H), 7.10 (t, *J* = 7.8 Hz, 0.3 H), 7.01 (d, *J* = 7.7 Hz, 0.7 H), 6.95 – 6.92 (m, 1 H), 6.87 – 6.61 (m, 10.3 H), 6.12 (s, 0.7 H), 6.05 (s, 0.3 H), 4.05 (s, 0.3 H), 3.90 (d,

J = 8.8 Hz, 0.7 H), 3.85 – 3.74 (m, 12.7 H), 3.67 (t, *J* = 8.1 Hz, 0.7 H), 3.46 (s, 0.3 H), 3.33 (dd, *J* = 11.4, 5.0 Hz, 0.3 H), 3.10 – 3.02 (m, 1 H), 2.98 – 2.90 (m, 2 H), 2.85 – 2.73 (m, 2 H), 2.69 – 2.58 (m, 2 H);

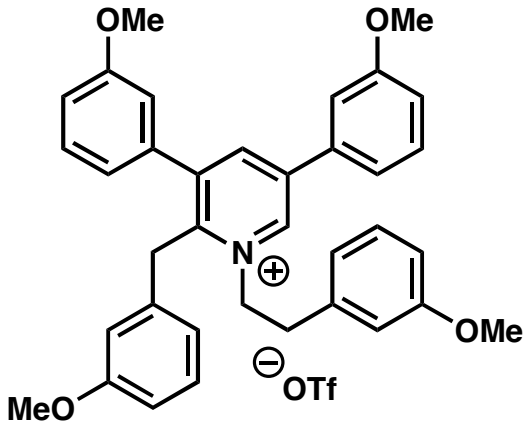
^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 159.72, 159.67, 159.51, 159.45, 159.44, 159.4, 159.1, 158.8, 145.9, 145.2, 142.5, 142.4, 142.3, 142.2, 142.0, 141.39, 141.37, 140.4, 129.6, 129.5, 129.3, 129.2, 128.84, 128.79, 128.4, 127.4, 122.2, 121.6, 121.1, 121.0, 120.4, 120.3, 119.1, 118.7, 115.3, 115.0, 114.3, 114.2, 113.9, 113.8, 112.5, 112.4, 112.2, 111.5, 111.3, 111.24, 111.19, 111.1, 111.0, 61.7, 61.0, 59.0, 56.9, 55.8, 55.24, 55.18, 55.14, 55.09, 55.01, 54.97, 54.5, 52.2, 41.9, 38.8, 37.3, 35.3, 33.8;

HRMS (ESI) calcd. for $C_{36}H_{40}NO_4$ [M + H^+] 550.2957, found 550.2945.

Note- The following compound was synthesized in an analogous manner (substituting 2-bromo-3-methoxybenzyl bromide for 3-methoxybenzyl bromide) and its structure proven by x-ray crystallographic analysis:



2-Benzylpyridinium 22:



To a solution of **27** (100 mg, 0.18 mmol) in DCM (1.8 mL) was added N-bromoacetamide (55 mg, 0.40 mmol, 2.2 equiv) at room temperature. The reaction mixture was stirred for 1.5 h and quenched with sat. aq. $Na_2S_2O_4$ (10 mL). The organic layer was extracted with EtOAc (2 × 20 mL), dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (99:1 to 95:5 DCM/MeOH) afforded the pyridinium bromide as a yellowish solid (90 mg, 79%). This compound was dissolved in DCM (1.0 mL), and treated with silver triflate (40.6 mg, 0.16 mmol, 1.1 equiv). The reaction mixture was stirred for 1 h and quenched with water (10 mL). The aqueous layer was extracted twice with EtOAc (20 mL), dried over $MgSO_4$, filtered, and concentrated. Flash column chromatography (silica gel, 99:5 DCM/MeOH) afforded the pyridinium triflate as a yellowish semisolid (97 mg, 97%).

R_f = 0.32 (silica gel, 9:1 DCM/MeOH);

IR (film) ν_{max} 2926, 1600, 1584, 1490, 1468, 1258 (s), 1224, 1153, 1030, 787, 698 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 2.0 Hz, 1 H), 8.36 (d, *J* = 2.0 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 7.9 Hz, 1 H), 7.26 (t, *J* = 7.9 Hz, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 7.16 – 7.14 (m, 2 H), 7.04 (ddd, *J* = 8.3, 2.4, 0.7 Hz, 1 H), 7.01 (ddd, *J* = 8.4, 2.5, 0.7 Hz, 1 H), 6.93 (ddd, *J* = 7.5, 1.4, 0.8 Hz, 1 H), 6.89 (m, 1 H), 6.83 – 6.79 (m, 2 H),

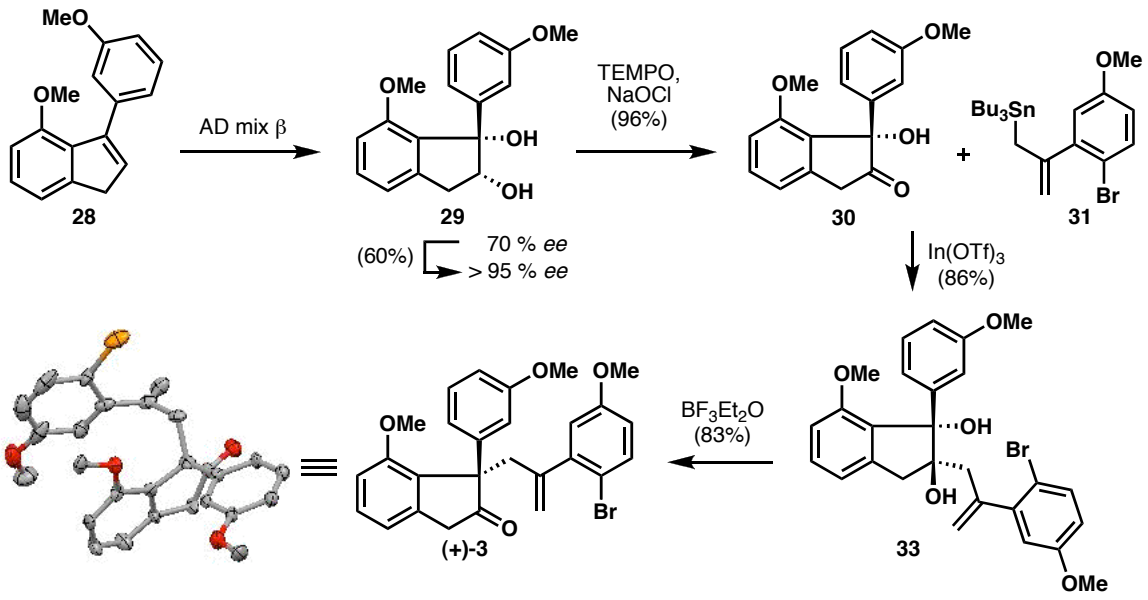
5.00 (t, *J* = 7.0 Hz, 2 H), 4.29 (s, 2 H), 3.91 (s, 3 H), 3.761 (s, 3 H), 3.760 (s, 3 H), 3.75 (s, 3 H), 3.02 (t, *J* = 7.0 Hz, 2 H0;

^{13}C-APT NMR (150 MHz, $CDCl_3$): δ 160.7, 160.5, 160.2, 159.9, 152.1, 144.0, 143.2, 139.0, 136.8, 136.7, 136.4, 133.5, 130.8, 130.7, 130.4, 130.3, 121.1, 120.7, 119.8, 119.6, 116.9, 115.7, 114.6, 114.1, 114.0, 113.4, 112.9, 112.3, 60.1, 55.8, 55.4, 55.33, 55.32, 37.1, 35.6.

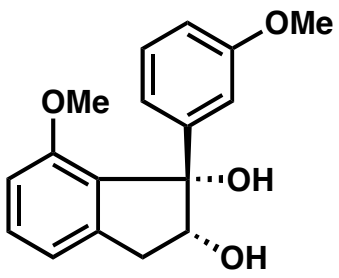
^{13}C-APT NMR (150 MHz, CD_2Cl_2): δ 161.3, 161.1, 160.9, 160.6, 152.6, 144.8, 144.4, 144.3, 139.6, 137.4, 137.1, 136.8, 134.2, 131.4, 131.3, 131.0, 130.9, 121.7, 121.3, 120.3, 120.1, 117.0, 116.0, 115.2, 114.8, 114.6, 113.8, 113.5, 113.1, 60.8, 56.3, 55.95, 55.88, 55.8, 37.7, 36.1.

HRMS (ESI) calcd. for $C_{36}H_{36}NO_4$ [M^+] 546.2644, found 546.2635.

Scheme S2.



Diol 29:



To a solution of unstable (gradually decomposes upon exposure to air/moisture, as such it is stored in a frozen benzene solution) indene **28** (2.78 g, 11.0 mmol, synthesized as previously described[3]) in *t*-BuOH (55 mL) was added sequentially: methanesulfonamide (5.2 g, 55.0 mmol, 5.0 equiv), $(DHQD)_2PHAL$ (428.0 mg, 0.55 mmol, 0.05 equiv), K_2CO_3 (4.56 g, 33.0 mmol, 3.0 equiv), and H_2O (55.0 mL). This solution was cooled to 0 ˚C and treated with potassium ferricyanide (10.9 g, 33.0 mmol, 3.0 equiv) followed by osmium tetroxide (2.5% in *t*-BuOH; 1.38 mL, 0.11 mmol, 0.01 equiv). The reaction flask was placed in a 5 ˚C cold room and stirred for 44 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ (100 mL), removed from the cold room, and allowed to warm to room temperature and stir for 1 h. The aqueous layer was then extracted with EtOAc (3 ×150 mL), dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 4:1 → 3:1 hexanes/EtOAc) afforded the diol as a brown semisolid (3.10 g, 98%). To the resulting diol mixture was added hexanes (40 mL) and EtOAc (10 mL), followed by heating to a brief reflux with a heat gun in order to assure complete dissolution. The hot solution was then seeded with a sample of crystalline racemic diol and allowed to cool to room temperature. Clear needles of racemic diol crystallized, and the supernatant was then removed and concentrated to afford the enantiomerically pure title diol as a thick oil (1.89 g, 60%).

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[3] P. S. Baran, N. Z. Burns, *J. Am. Chem. Soc.* **2006**, *128*, 3908 – 3909.

R_f = 0.24 (silica gel, 2:1 hexanes/EtOAc);

$[\alpha]_D$ = +43.4° ($CHCl_3$, *c* 0.53);

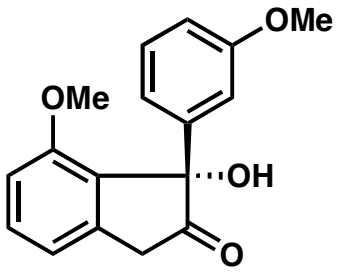
IR (film) ν_{max} 3447 (br), 2937, 2835, 1589, 1480 (s), 1262 (s), 1078 (s), 1044 (s) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.1 Hz, 1 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 6.95 (d, *J* = 7.5 Hz, 1 H), 6.83 – 6.78 (m, 3 H), 6.70 – 6.68 (m, 1 H), 4.29 (d, *J* = 4.6 Hz, 1 H), 4.15 (s, 1 H, D_2O exchangeable), 3.77 (s, 3 H), 3.75 (s, 3 H), 3.48 (s, 1 H, D_2O exchangeable), 3.02 (dd, *J* = 16.5, 4.5 Hz, 1 H), 2.90 (d, *J* = 16.4 Hz, 1 H);

^{13}C-APT NMR (150 MHz, $CDCl_3$) δ 159.6, 156.7, 145.8, 143.6, 130.5, 130.0, 129.1, 118.3, 118.2, 112.5, 111.8, 109.1, 85.8, 80.5, 55.3, 55.1, 38.1;

HRMS (ESI) calcd. for $C_{17}H_{18}O_4$ [M + Na^+] 309.1097, found 309.1092.

α-Hydroxy ketone 30:



To a solution of diol **29** (599 mg, 2.09 mmol) in DCM (10.5 mL) at 0 °C was added sequentially: saturated aqueous $NaHCO_3$ (4.2 mL), potassium bromide (12.0 mg, 0.10 mmol, 0.05 equiv), TEMPO (16.0 mg, 0.10 mmol, 0.05 equiv), and aqueous sodium hypochlorite (6.2 mL, 4.18 mmol, 2.0 equiv). The reaction mixture was stirred at 0 °C for 30 min then quenched with saturated aqueous $NaHSO_4$ (10 mL). The ice bath was removed and the reaction mixture was allowed to warm to room temperature. The aqueous layer was extracted with EtOAc (3 × 30 mL), and the combined organic layers

were washed once with brine (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 3:1 hexanes/EtOAc) afforded the title ketone as an off-white solid (570 mg, 96%).

m.p. = 117 – 119 ºC;

$\mathbf{R_f}$ = 0.24 (silica gel, 2:1 hexanes/EtOAc);

$\mathbf{[\alpha]_D}$ = +37.9° (CH_2Cl_2, *c* 0.43);

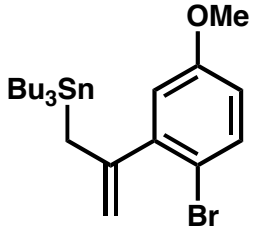
IR (film) $\mathbf{\nu_{max}}$ 3467 (br) 3011, 1744 (s), 1587 (s), 1484 (s), 1291 (s), 1053 (s) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.9 Hz, 1 H), 7.19 (t, *J* = 7.9 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 6.97 (m, 1 H), 6.89 (d, *J* = 8.3 Hz, 1 H), 6.82 (m, 1 H), 6.77 (m, 1 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.67 (d, *J* = 21.6 Hz, 1 H), 3.57 (s, 1 H), 3.49 (d, *J* = 21.6 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 210.4, 160.0, 156.8, 141.5, 137.5, 130.8, 129.6, 129.5, 117.9, 117.4, 113.7, 111.3, 110.0, 82.2, 55.5, 55.2, 40.2;

HRMS (ESI) calcd. for $C_{17}H_{16}O_4$ [M + Na^+] 307.0941, found 307.0929.

Allyl stannane 31:



The corresponding allyl iodide (1.41 g, 3.99 mmol, synthesized as previously described[3]) was dissolved in dry THF (20 mL) and treated with bis(tributyltin) (2.0 mL, 3.99 mmol, 1.0 equiv) followed by Pd_2dba_3•$CHCl_3$ (207 mg, 0.20 mmol, 0.05 equiv). Argon was bubbled through the solution for 25 min and it was then heated to 55° for 3 h. Sat. aq.

$NaHCO_3$ (50 mL) was added and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL) and dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (triethylamine neutralized silica gel, 100% hexanes) afforded the title allyl stannane as a clear oil (1.78 g, 86%).

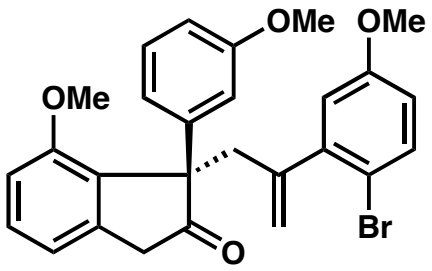
R_f = 0.15 (silica gel, hexanes);

IR (film) ν_{max} 2953 (s), 1560, 1462 (s), 1300, 1231 (s), 1016 (s) cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 1 H), 6.74 (d, *J* = 3.1 Hz, 1 H), 6.66 (dd, *J* = 8.7, 3.1 Hz, 1 H,), 4.99 (m, 1 H), 4.71 (m, 1 H), 3.78 (s, 3 H), 2.23 (s, 2 H), 1.35 (m, 6 H), 1.23 (qd, *J* = 14.6, 7.3, 6 H), 0.84 (t, *J* = 7.3 Hz, 9 H), 0.76 (m, 6 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 150.4, 146.3, 133.7, 115.8, 114.1, 112.4, 110.9, 55.6, 29.1, 27.5, 20.1, 13.8, 9.8.

Ketone 3:



To a solution of α-hydroxy ketone **30** (490 mg, 1.72 mmol) and allyl stannane **31** (1.78 g, 3.45 mmol, 2.0 equiv) in THF (11.5 mL) at 0 °C was added indium(III) trifluoromethanesulfonate (1.16 g, 2.06 mmol, 1.2 equiv). After complete dissolution, the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. Saturated aqueous sodium potassium tartrate (20 mL) and EtOAc (50 mL) were added,

and the organic layer was washed with brine (20 mL). The combined aqueous layers were extracted with EtOAc (50 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash column chromatography (silica gel, 6:1 → 4:1 hexanes/EtOAc) afforded the homoallylic diol as a clear oil (755 mg, 86%). To a solution of this diol (755 mg, 1.48 mmol) in DCM (14.8 mL) at 0 ˚C was added boron triflouride diethyl etherate (204 μL, 1.62 mmol, 1.1 equiv) dropwise. After stirring for 10 min at 0 ˚C, sat. aq. $NaHCO_3$ (20 mL) and EtOAc (20 mL) were added. The organic layer was washed with brine (20 mL), and the combined aqueous layers were extracted with EtOAc (20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 9:1 → 6:1 hexanes/EtOAc) afforded the title ketone as a white solid (603 mg, 83%).

m.p. = 88 – 90 ºC;

$\mathbf{R_f}$ = 0.39 (silica gel, 1:1 hexanes/Et_2O);

$\mathbf{[\alpha]_D}$ = +6.8˚ (CH_2Cl_2, *c* 0.5);

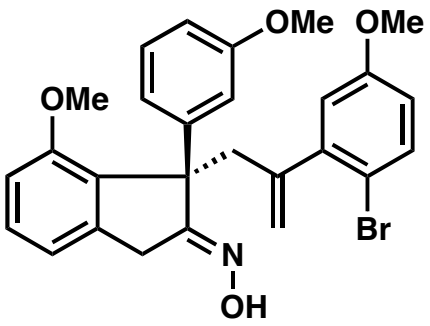
IR (film) $\mathbf{\nu_{max}}$ 1749 (s), 1586 (s), 1482 (s), 1463 (s), 1289 (s), 1264 (s), 1050 (s), 1016 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.0 Hz, 1 H), 7.23 (t, *J* = 7.9 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 7.2 Hz, 1 H), 6.79 (d, *J* = 7.9 Hz, 1 H), 6.76 (dd, *J* = 8.4, 6.3 Hz, 1 H), 6.74 (dd, *J* = 8.1, 1.9 Hz, 1 H), 6.53 (dd, *J* = 8.8, 3.1 Hz, 1 H), 6.51 (d, *J* = 10.0 Hz, 1 H), 5.63 (d, *J* = 3.1 Hz, 1 H), 5.24 (s, 1 H), 4.88 (d, *J* = 1.4 Hz, 1 H), 3.91 (d, *J* = 13.2 Hz, 1 H), 3.74 (s, 3 H), 3.72 (d, *J* = 13.1 Hz, 1 H), 3.57 (s, 3 H), 3.48 (d, *J* = 22.5 Hz, 1 H), 3.42 (m, 3 H), 3.11 (d, *J* = 22.5 Hz, 1 H);

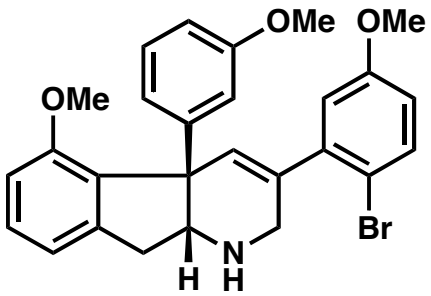
^{13}C NMR (150 MHz, $CDCl_3$) δ 215.2, 159.6, 158.0, 157.3, 147.5, 143.7, 142.4, 138.5, 132.7, 130.3, 129.6, 129.3, 120.4, 119.2, 116.8, 115.6, 114.6, 113.2, 112.7, 111.8, 109.2, 63.4, 55.3, 55.2, 54.6, 42.9, 41.3;

HRMS (ESI) calcd. for $C_{27}H_{25}BrO_4$ [M + H^+] 493.1014, found 493.0988.

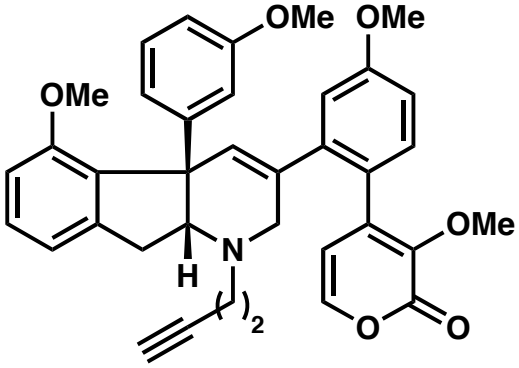
The following compounds were spectroscopically identical to those we reported previously[1] except for optical rotation data given below:



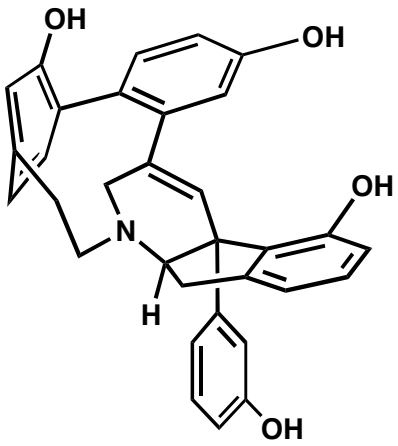
[α]$_D$ = –13.5° (CH_2Cl_2, *c* 0.45)



[α]$_D$ = +18.8° (2:1 MeOH/CH_2Cl_2, *c* 0.47)

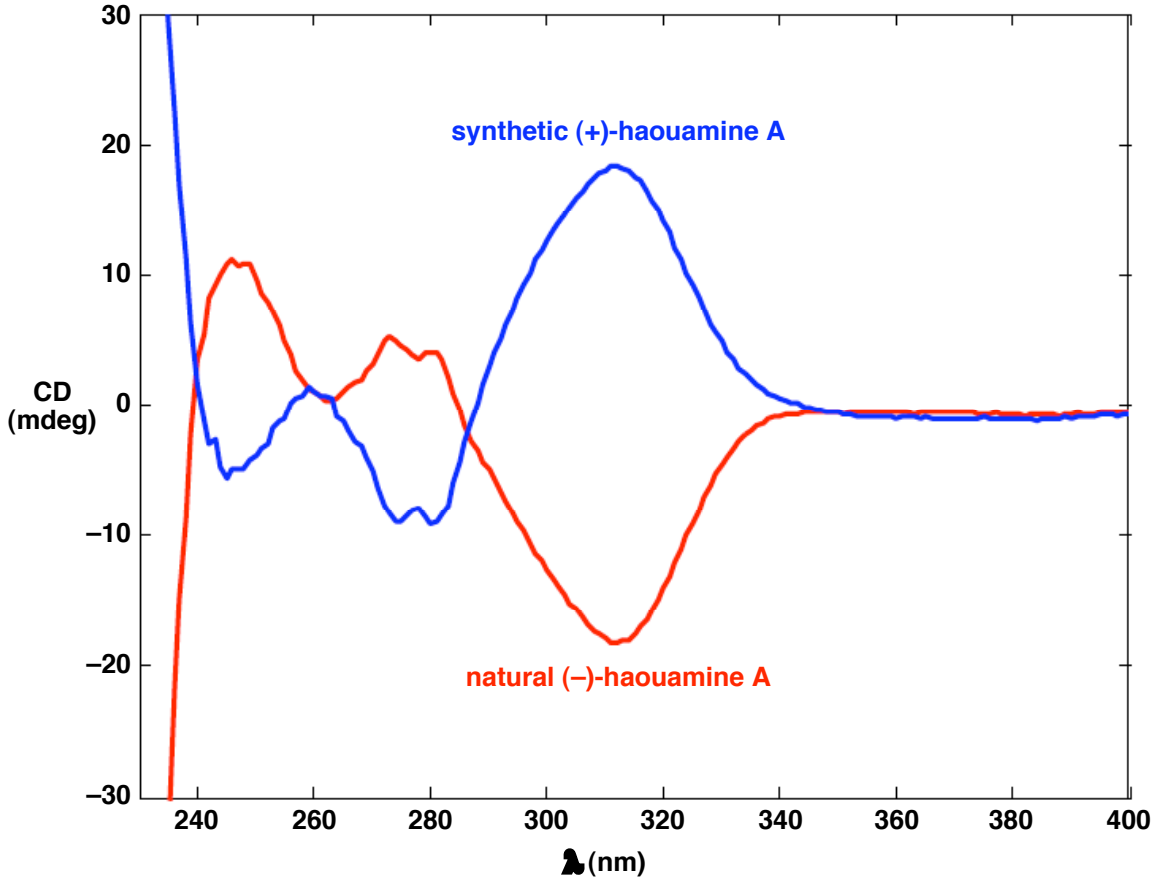


[α]$_D$ = +66.3° (CH_2Cl_2, *c* 0.40)

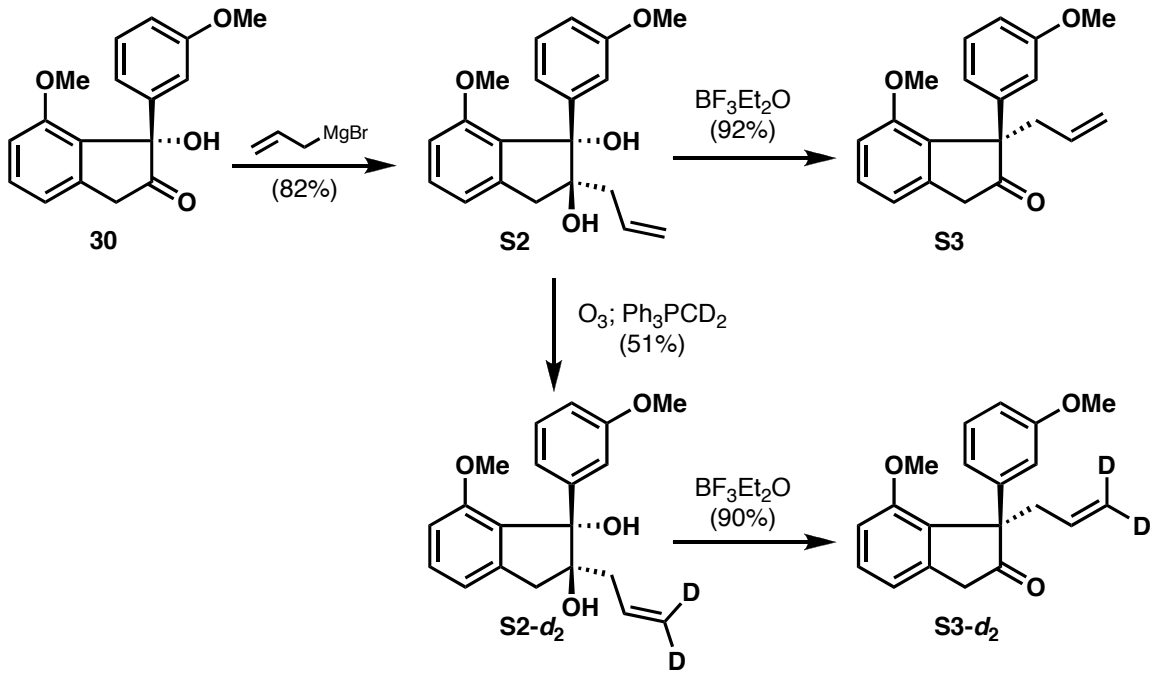


(+)-Haouamine A: **[α]$_D$** = +45.8° (MeOH, *c* 0.05)

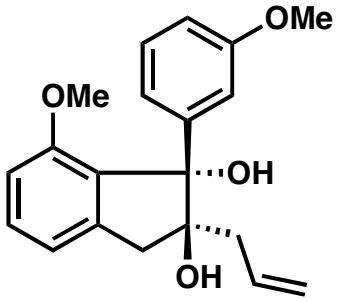
Figure S1. Circular dichroism spectrum of natural-(–)- and synthetic-(+)-haouamine A.



Scheme S3.



Homoallylic diol S2:



To a solution of racemic α-hydroxy ketone **30** (50 mg, 0.18 mmol) in toluene (3.6 mL) at –78° was added allylmagnesium bromide (880 μL, 1.0 M, 0.88 mmol, 5.0 equiv). The reaction mixture was allowed to stir at –78° for 20 min and then warmed to room temperature before being quenched with sat. aq. NH_4Cl (5 mL). This mixture was extracted with EtOAc (2 × 20 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash column chromatography (silica gel, 8:1 hexanes/EtOAc) afforded the title diol as a clear oil (47 mg, 82%).

R_f = 0.32 (silica gel, 1:1 hexanes/Et_2O);

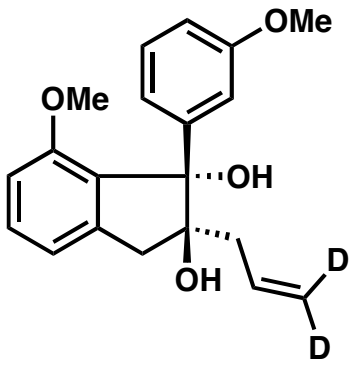
IR (film) ν_{max} 3509 (br), 2937, 2834, 1592, 1480 (s), 1260 (s), 1085, 1039 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 7.9 Hz, 1 H), 6.93 (d, *J* = 7.5 Hz, 1 H), 6.85 (m, 1 H), 6.78 (dd, *J* = 8.2, 1.9 Hz, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.65 (m, 1 H), 5.93 (m, 1 H), 5.04 (dd, *J* = 9.2, 0.9 Hz, 1 H), 4.96 (dd, *J* = 17.1, 0.6 Hz, 1 H), 4.25 (s, 1 H), 3.77 (s, 3 H), 3.71 (s, 3 H), 3.63 (s, 1 H), 2.97 (d, *J* = 16.2 Hz, 1 H), 2.91 (d, *J* = 16.2 Hz, 1 H), 2.19 (dd, *J* = 14.1, 6.3 Hz, 1 H), 1.65 (dd, *J* = 14.1, 7.9 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 156.3, 144.6, 142.7, 134.7, 132.7, 130.3, 129.2, 118.5, 118.3, 117.6, 112.3, 112.2, 109.4, 87.7, 84.5, 55.5, 55.3, 42.7, 41.6;

HRMS (ESI) calcd. for $C_{20}H_{22}O_4$ [M + Na^+] 349.1416, found 349.1399.

Homoallylic diol S2-*d_2*:



Diol **S2** (66 mg, 0.20 mmol) was dissolved in MeOH (3 mL) and CH_2Cl_2 (1 mL) and cooled to -78°. Ozone was bubbled through the solution for 5 min, and the reaction mixture was then quenched with Me_2S (2 mL) and warmed to room temperature. Et_2O (20 mL) and 5 % $NaHCO_3$ (3 mL) were added and the organic phase was washed with H_2O (10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The

crude aldehyde was dissolved in dry THF (3 mL) and a solution of $Ph_3P{=}CD_2$ (2.0 mmol, 10 equiv) in dry THF (4.4 mL) was added at RT. The resulting solution was stirred for 1.5 hours and then quenched with sat. aq. NH_4Cl (5 mL) and H_2O (20 mL) and diluted with Et_2O (20 mL). The organic phase was washed with brine (20 mL) and the aqueous phase was extracted with Et_2O (20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Flash column chromatography (silica gel, 3:1 hexanes/EtOAc) afforded the title diol as colorless/white needles (34 mg, 51%).

m.p. = 124 °C;

$\mathbf{R_f}$ = 0.67 (silica gel, 1:1 hexanes/EtOAc);

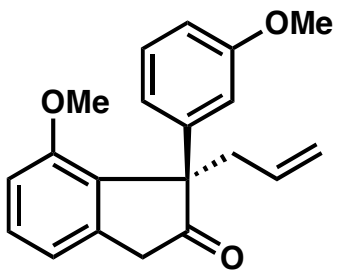
IR (film) $\boldsymbol{\nu_{max}}$ 3509 (br), 1592, 1480 (s), 1261 (s), 1083, 1042 (s) cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 1 H), 7.17 (t, *J* = 7.9 Hz, 1 H), 6.94 (d, *J* = 7.5 Hz, 1 H), 6.86 (m, 1 H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.63 (m, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 5.94 (m, 1 H), 5.04 (m, 0.2 H [80% D]), 4.96 (m, 0.2 H [80% D]), 4.27 (s, 1 H), 3.77 (s, 3 H), 3.70 (s, 3 H), 3.66 (s, 1 H), 2.98 (d, *J* = 16.2 Hz, 1 H), 2.92 (d, *J* = 16.2 Hz, 1 H), 2.20 (dd, *J* = 14.1, 6.3Hz, 1 H), 1.66 (dd, *J* = 14.1, 7.9 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 156.1, 144.4, 142.5, 134.3, 132.5, 130.1, 129.0, 118.3, 118.06, 118.05, 112.1, 112.0, 109.2, 87.4, 84.3, 55.3, 55.1, 42.5, 41.3;

GC/MS calcd. for $C_{20}H_{20}D_2O_4$ [M^+] 328, found 328.

Ketone S3:



To a solution of diol **S2** (40.0 mg, 12 mmol) in DCM (1.2 mL) at 0˚ was added boron triflouride diethyl etherate (17 μL, 0.13 mmol, 1.1 equiv) dropwise. After stirring for 10 min at 0˚, sat. aq. $NaHCO_3$ (5 mL) and EtOAc (20 mL) were added. The organic layer was washed with brine (10 mL), and the combined aqueous layers were extracted with EtOAc (20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 9:1 hexanes/Et_2O) afforded the title ketone as a clear oil (34 mg, 92%).

R_f = 0.35 (silica gel, 4:1 hexanes/Et_2O);

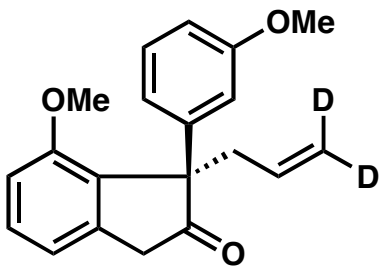
IR (film) ν_{max} 2915, 2841, 1746 (s), 1583, 1480, 1292, 1248 (s), 1053, 769, 695 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 6.97 (d, *J* = 7.5 Hz, 1 H), 6.86 (d, *J* = 8.3 Hz, 1 H), 6.77 – 6.74 (m, 3 H), 5.39 – 5.30 (m, 1 H), 5.01 (dd, *J* = 17.0, 1.7 Hz, 1 H), 4.82 (dd, *J* = 10.1, 1.8 Hz, 1 H), 3.75 (s, 3 H), 3.59 (d, *J* = 22.4 Hz, 1 H), 3.35 (d, *J* = 22.4 Hz, 1 H), 3.26 (dd, *J* = 13.0, 7.7 Hz, 1 H), 3.18 (dd, *J* = 13.0, 6.9 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 215.4, 159.5, 157.0, 142.0, 138.0, 134.1, 130.3, 129.3, 129.2, 119.0, 117.8, 117.1, 113.0, 111.8, 109.6, 63.3, 55.2, 55.1, 42.9, 39.4;

HRMS (ESI) calcd. for $C_{20}H_{21}O_3$ [M + H^+] 309.1491, found 309.1485.

Ketone S3-*d_2*:



To a solution of **S2-*d*$_2$** (25 mg, 0.076 mmol) in DCM (1.0 mL) at 0 ˚C was added boron triflouride diethyl etherate (11 μL, 0.084 mmol, 1.1 eq) dropwise. After stirring for 10 min at 0 ˚C, sat. aq. $NaHCO_3$ (5 mL) and EtOAc (10 mL) were added. The organic layer was washed with brine (10 mL), and the combined aqueous layers were extracted with EtOAc (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (silica gel, 2:1 hexanes/Et_2O) afforded the title ketone as a white film (21.2 mg, 90%).

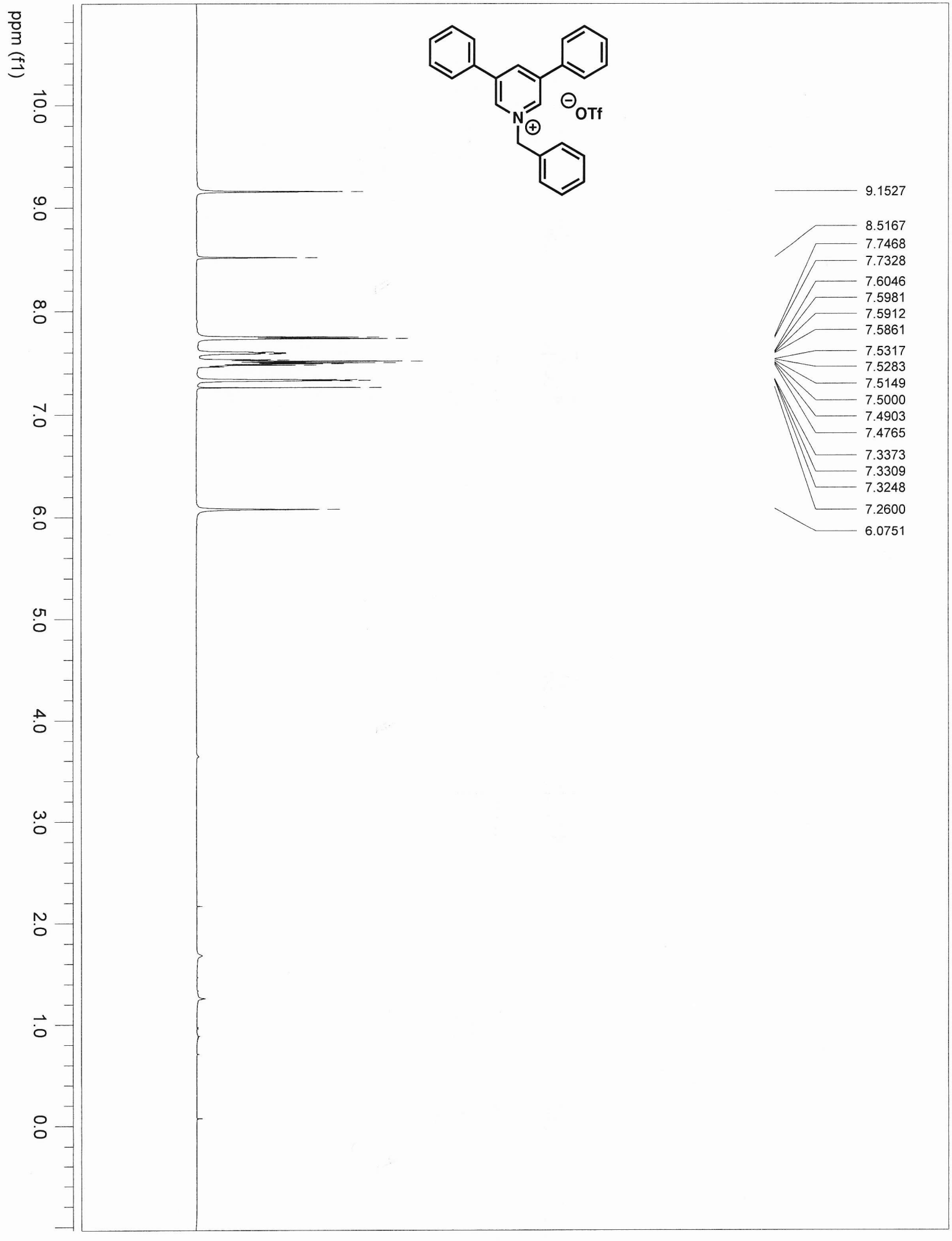
R_f = 0.58 (silica gel, 1:1 hexanes/Et_2O);

IR (film) ν_{max} 2936, 1749 (s), 1584 (s), 1482 (s), 1289 (s), 1252 (s), 1143, 1053 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 8.2 Hz, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 8.3 Hz, 1 H), 6.76 (m, 1 H), 5.34 (m, 1 H), 5.00 (m, 0.2 H [80% D]), 4.82 (m, 0.2 H [80% D]), 3.75 (s, 6 H), 3.59 (d, *J* = 22.4 Hz, 1 H), 3.36 (d, *J* = 22.4 Hz, 1 H), 3.26 (dd, *J* = 13.0, 7.7Hz, 1 H), 3.18 (dd, *J* = 12.9, 6.8 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 215.4, 159.5, 157.0, 142.0, 138.0, 134.0, 133.9, 130.3, 129.3, 129.2, 119.0, 117.0, 113.0, 111.8, 109.6, 63.3, 55.2, 55.1, 42.9, 39.3;

HRMS (ESI) calcd. for $C_{20}H_{18}D_2O_3$ [M + H^+] 311.1616, found 311.1609.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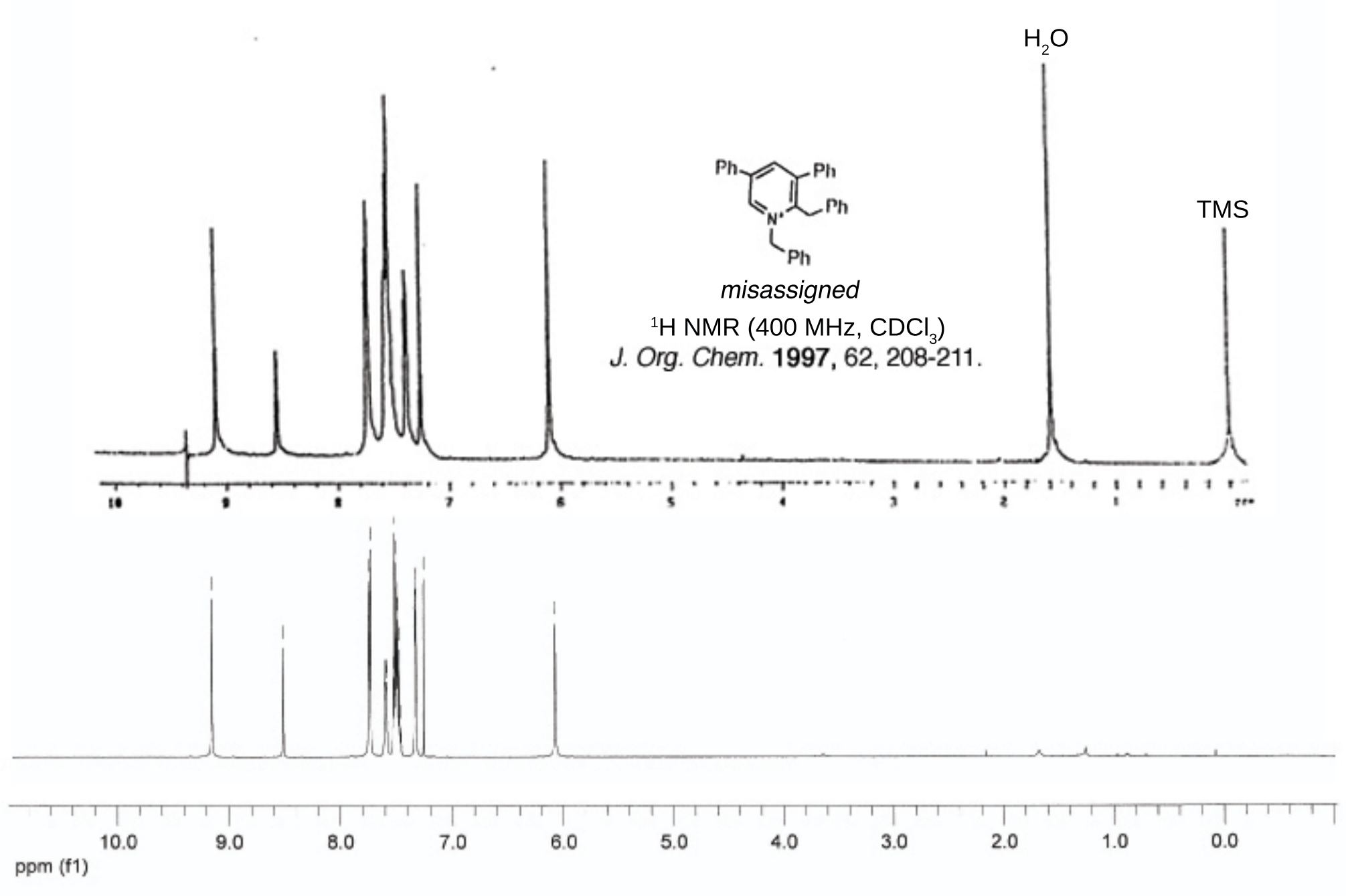
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TMS
Ph
Ph
Ph
N
Ph
misassigned
1H NMR (400 MHz, CDCl3)
J. Org. Chem. 1997, 62, 208-211.
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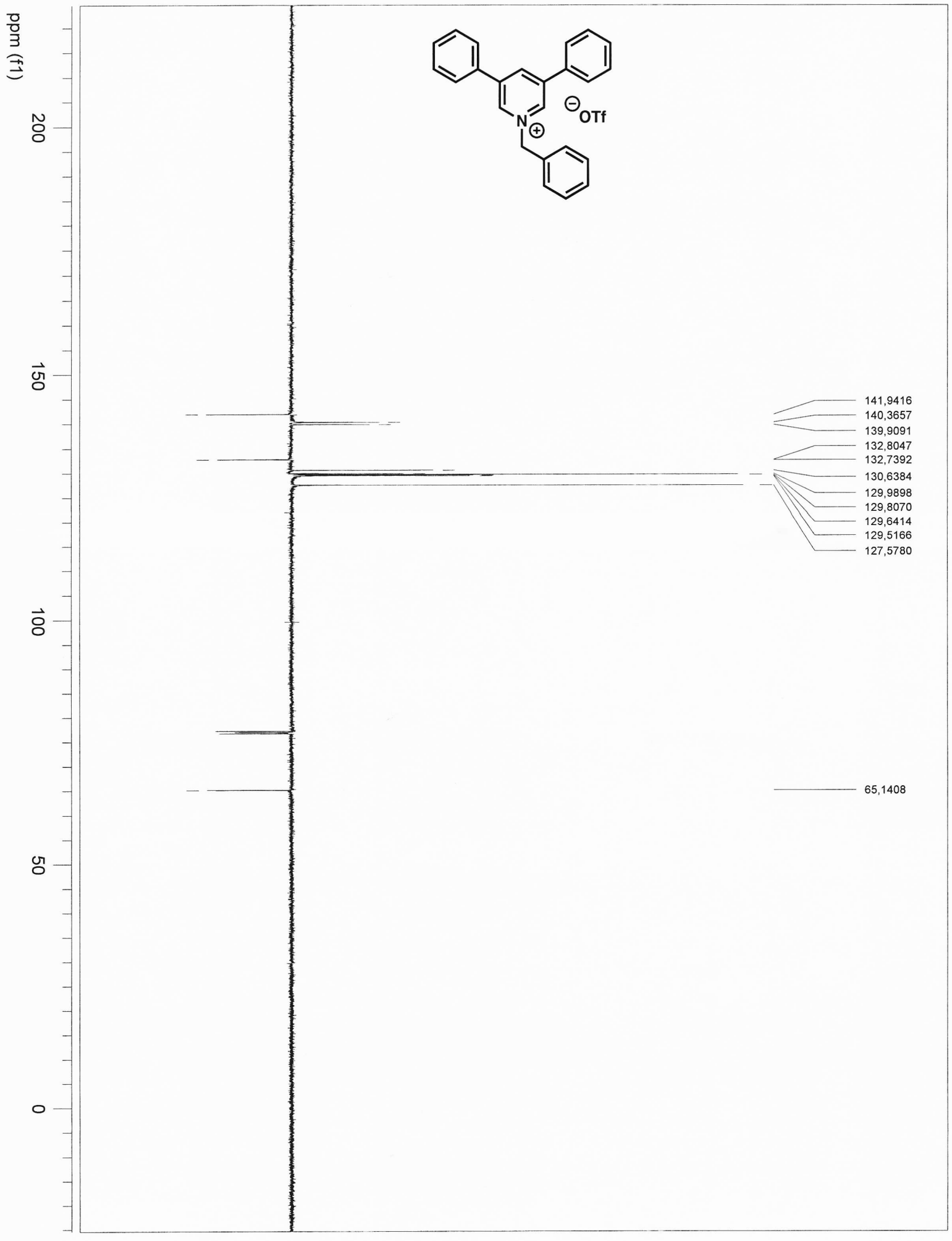
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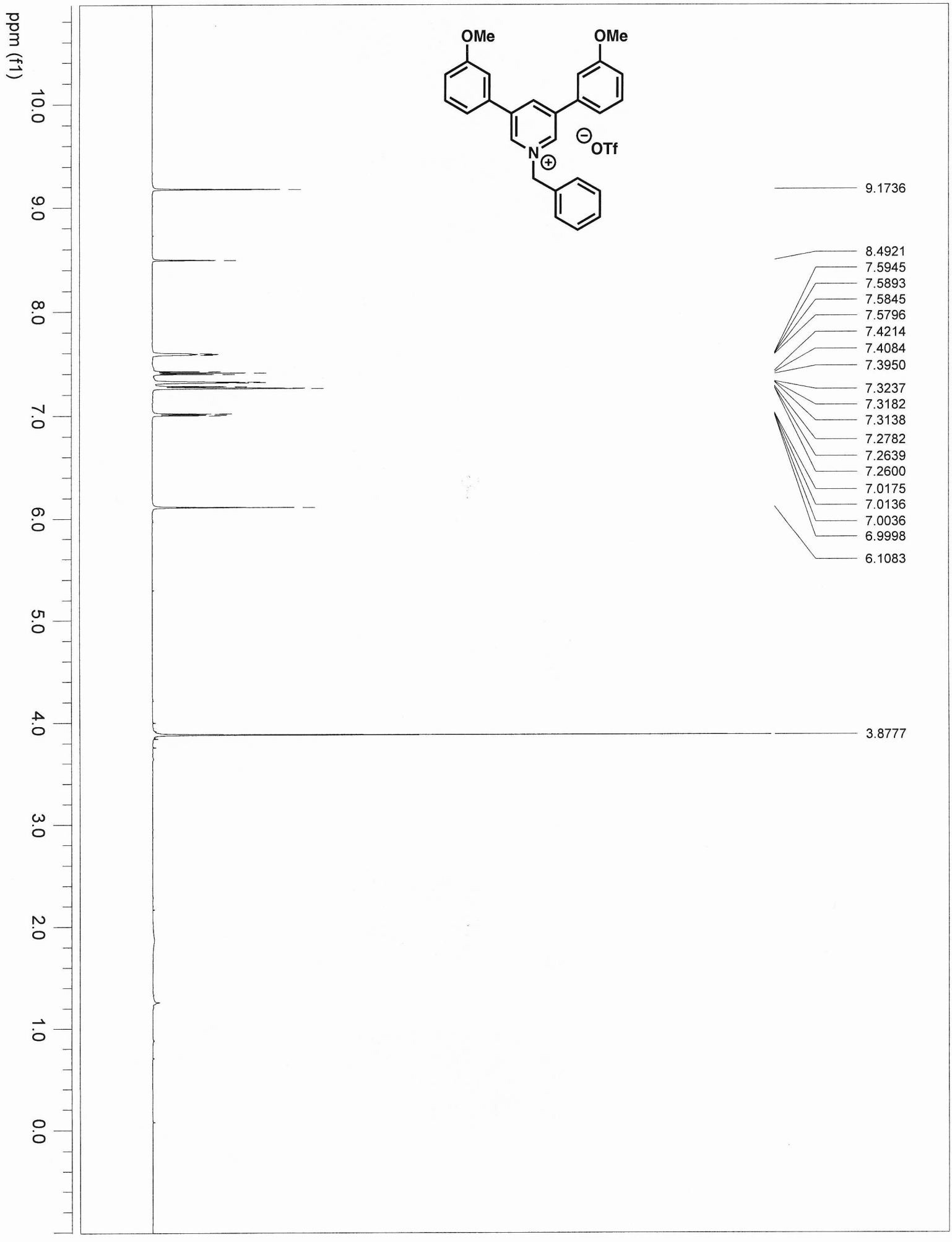
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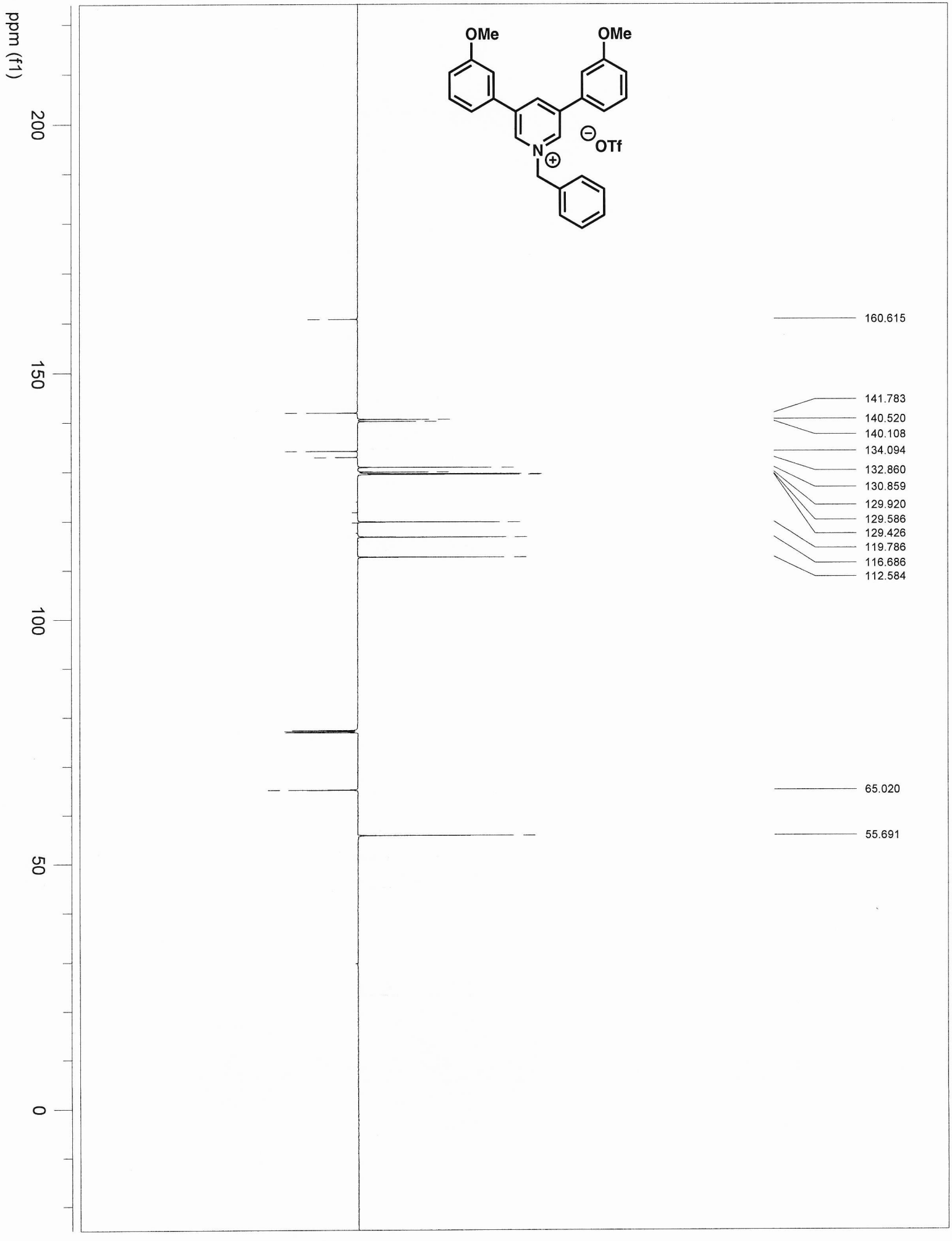
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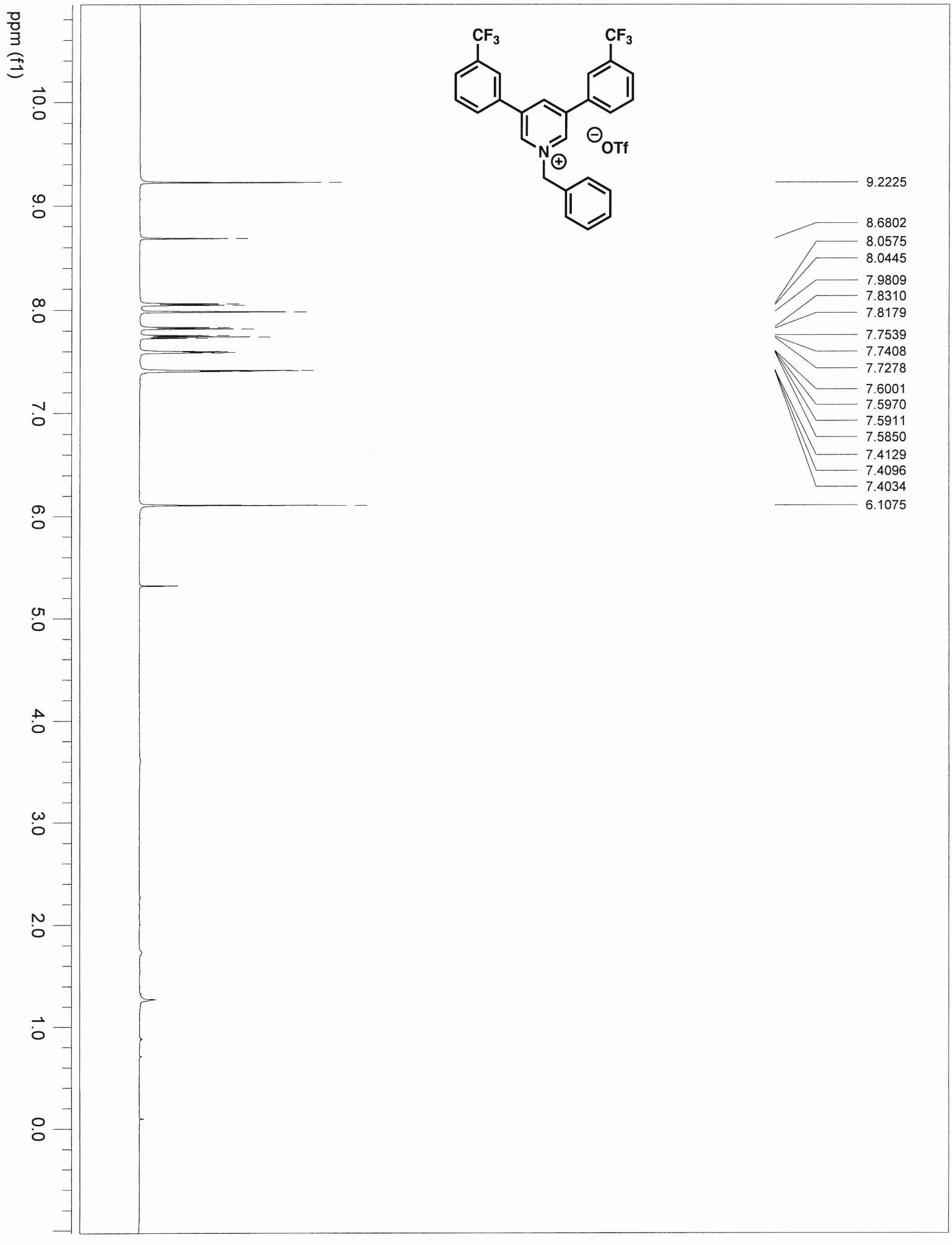
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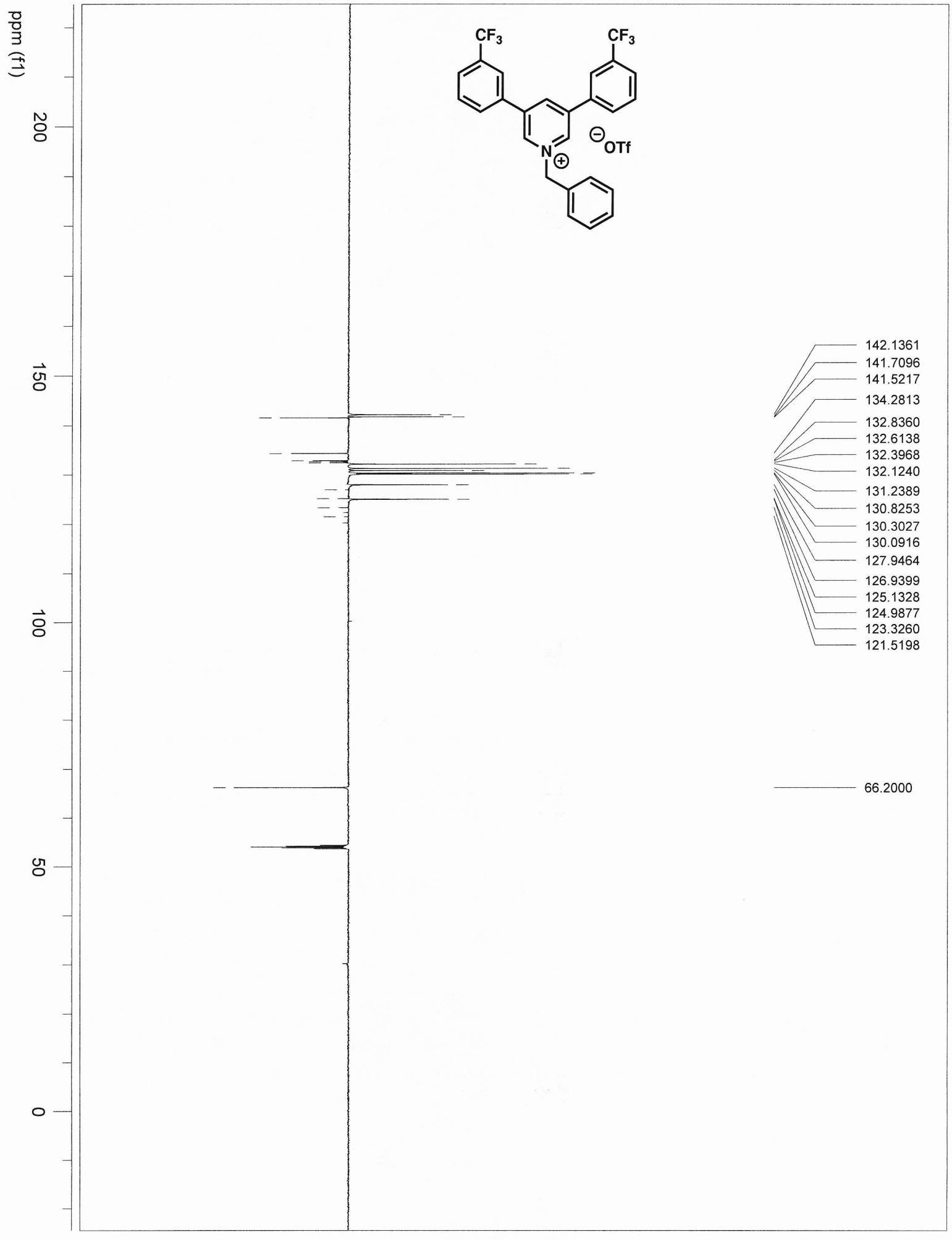
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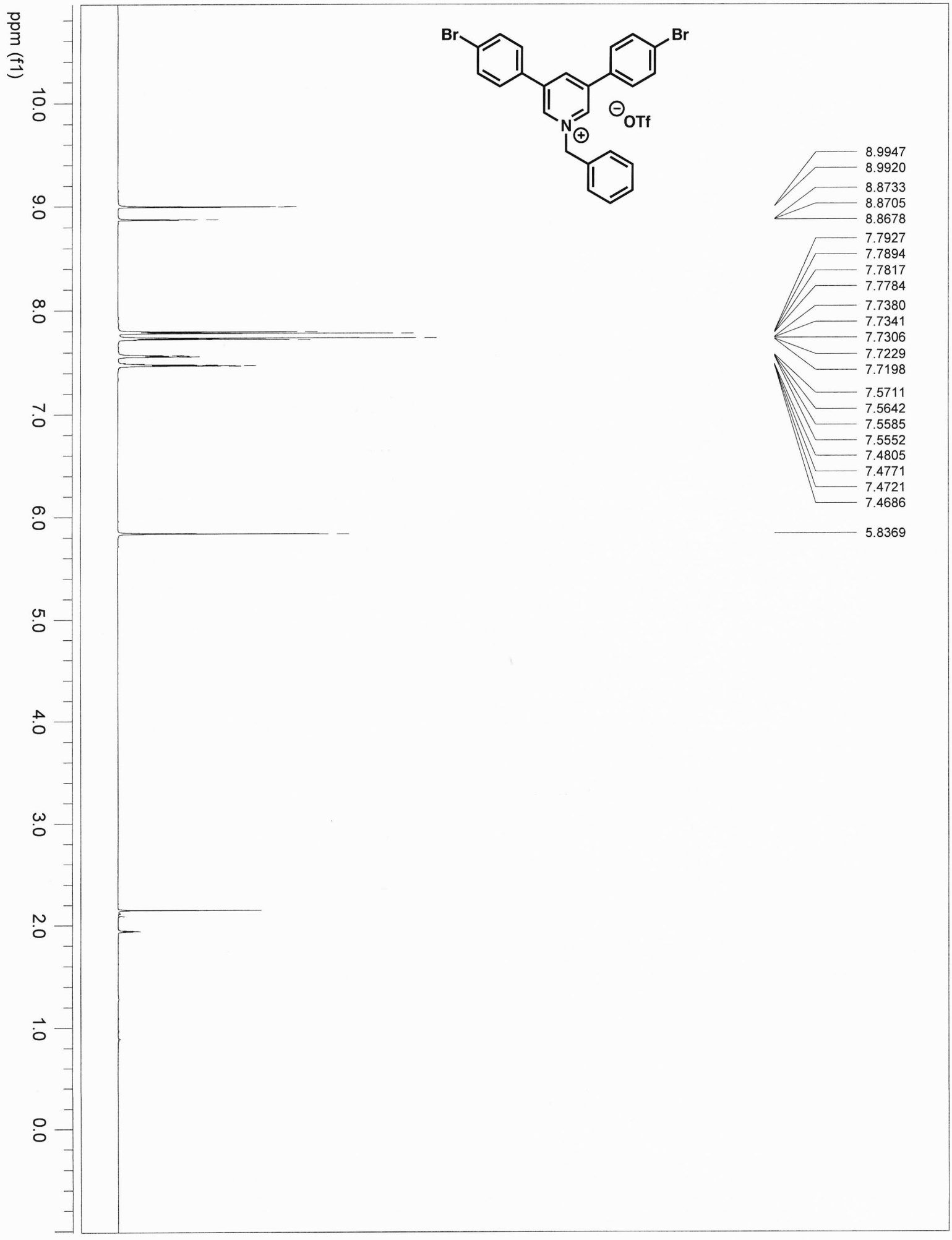
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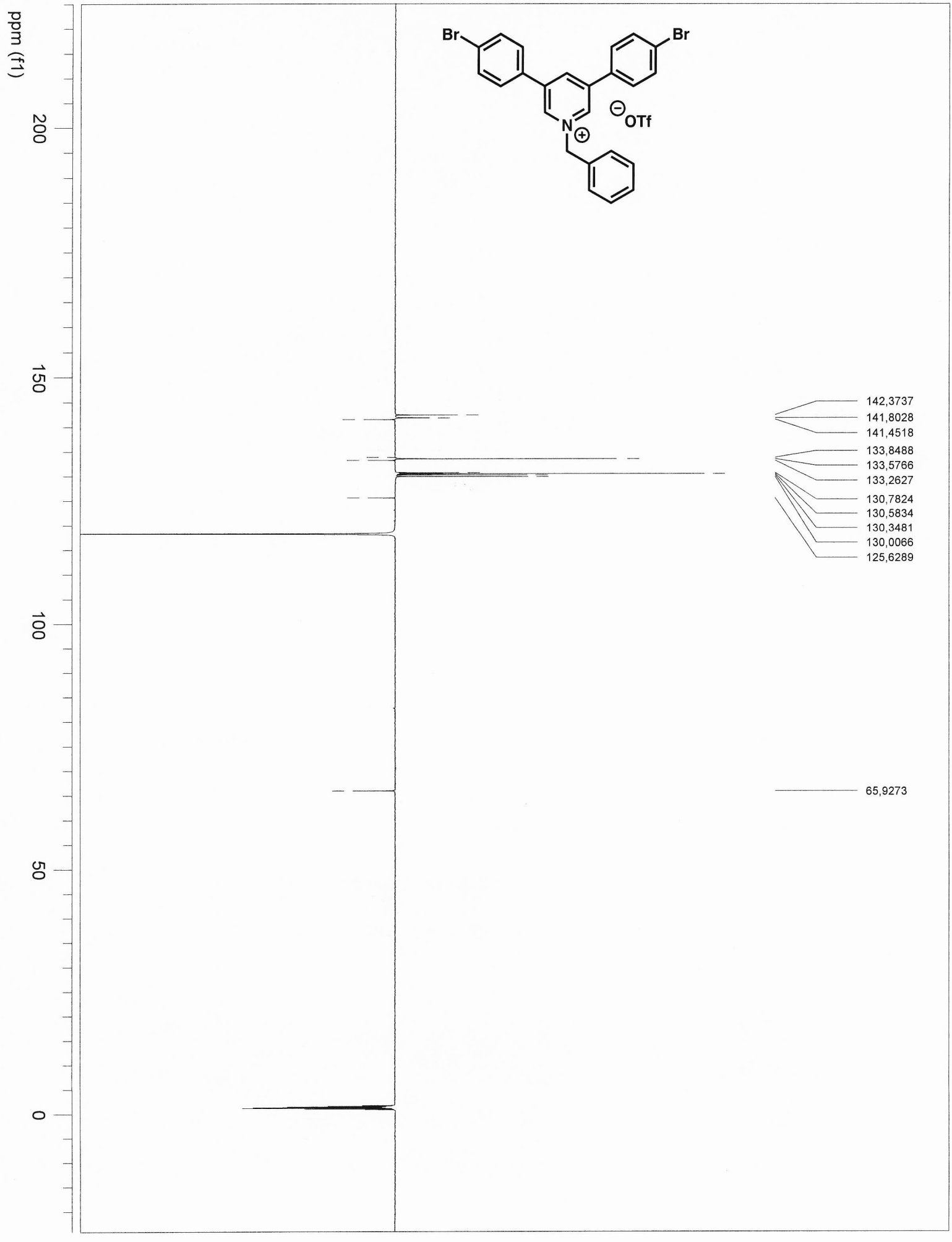
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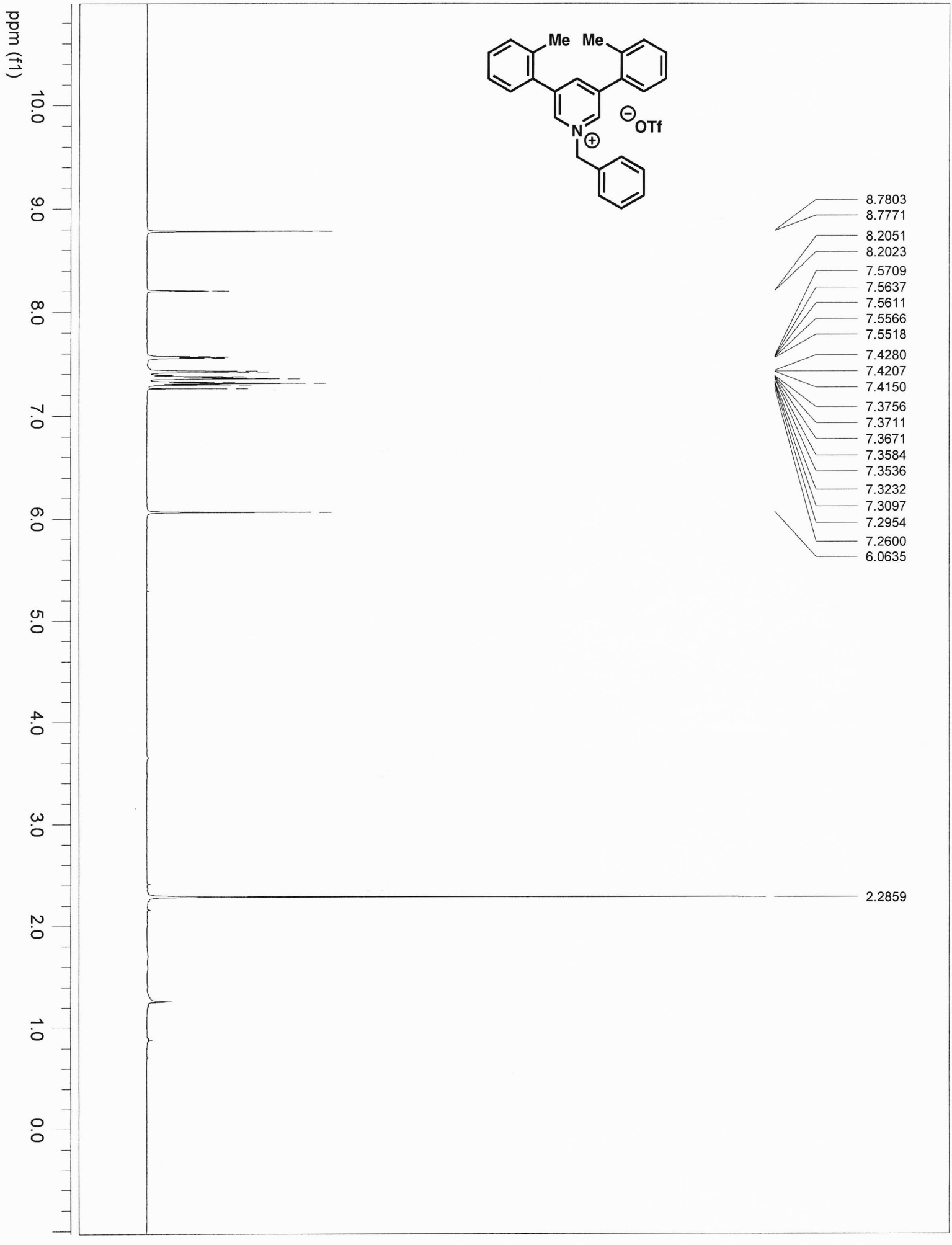
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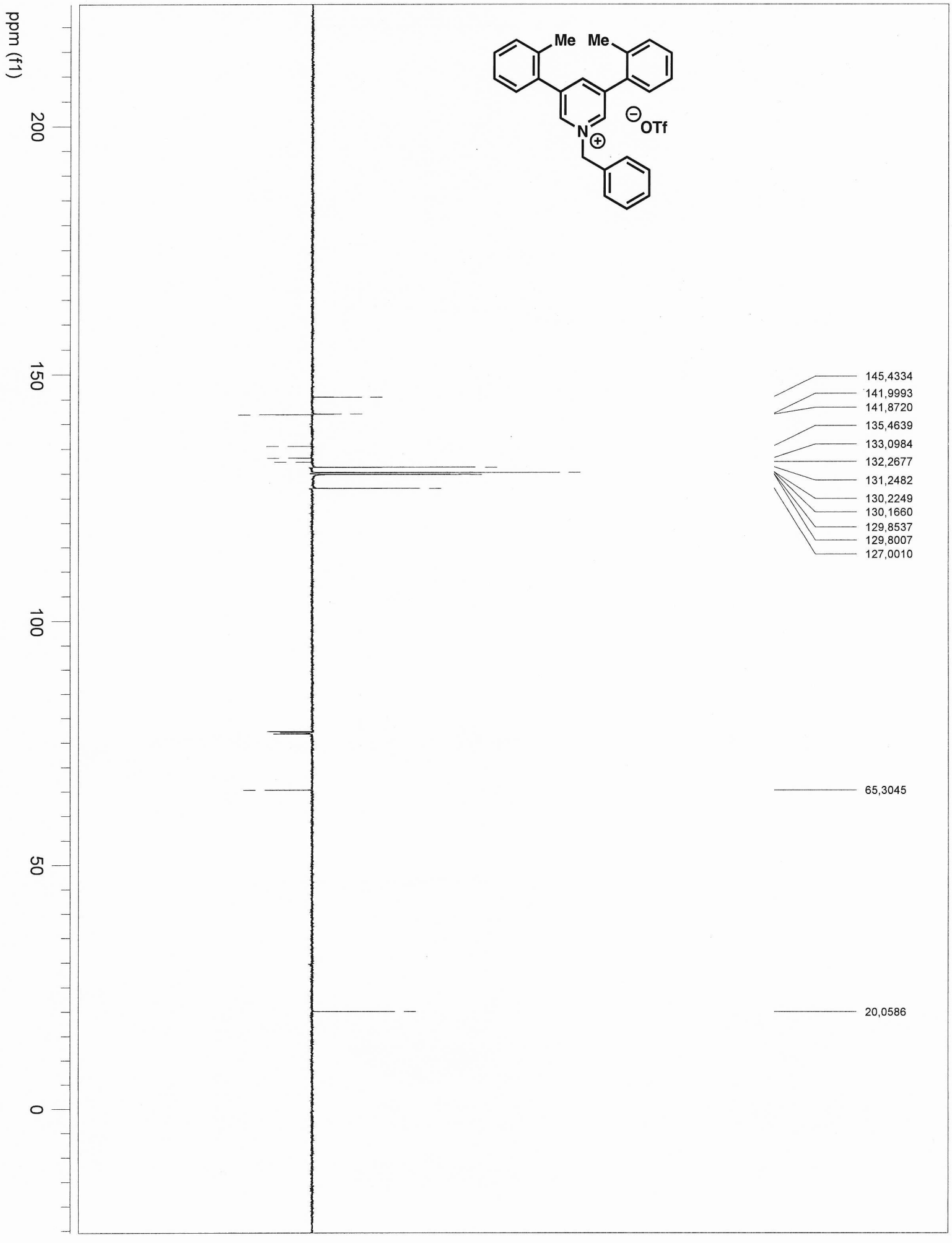
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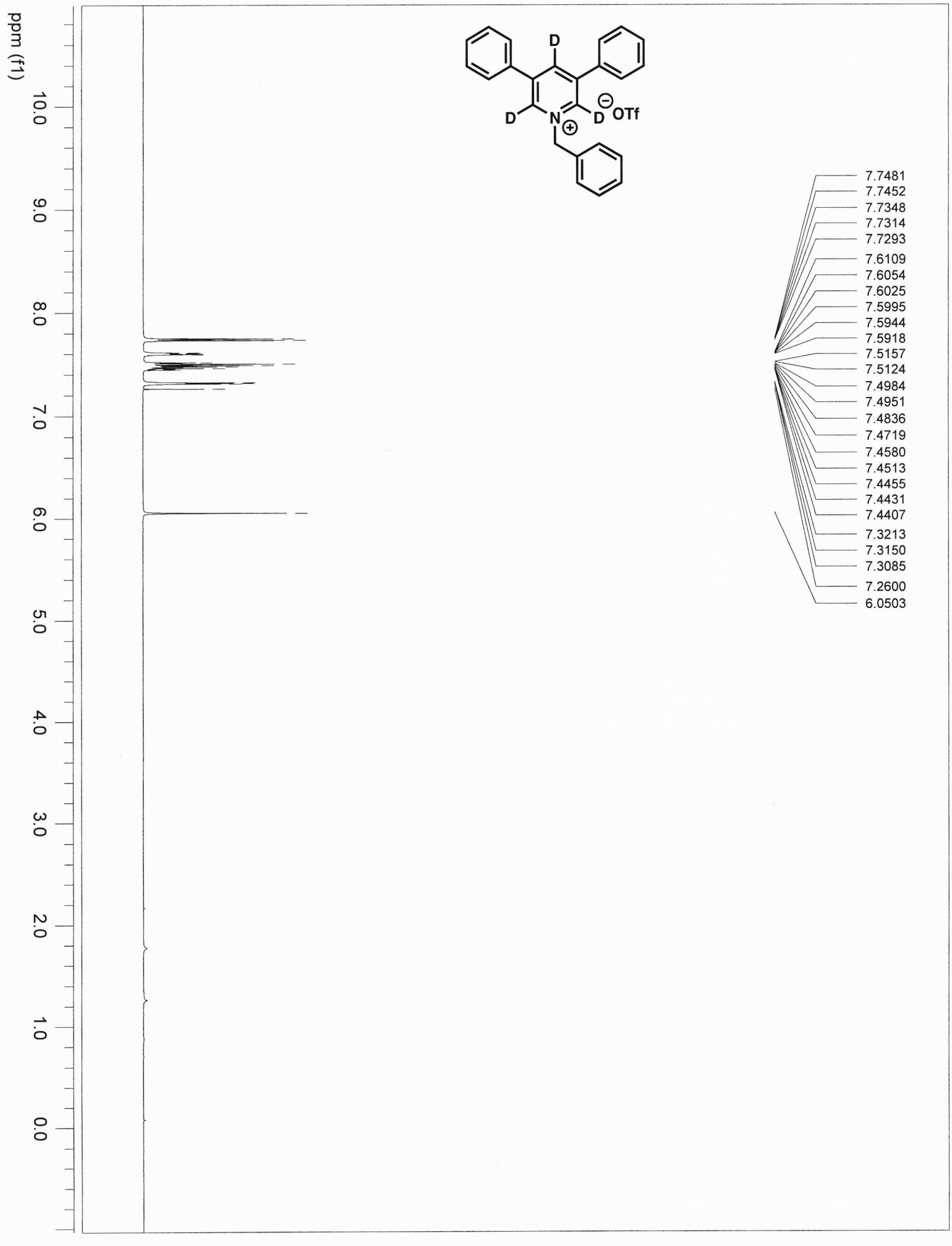
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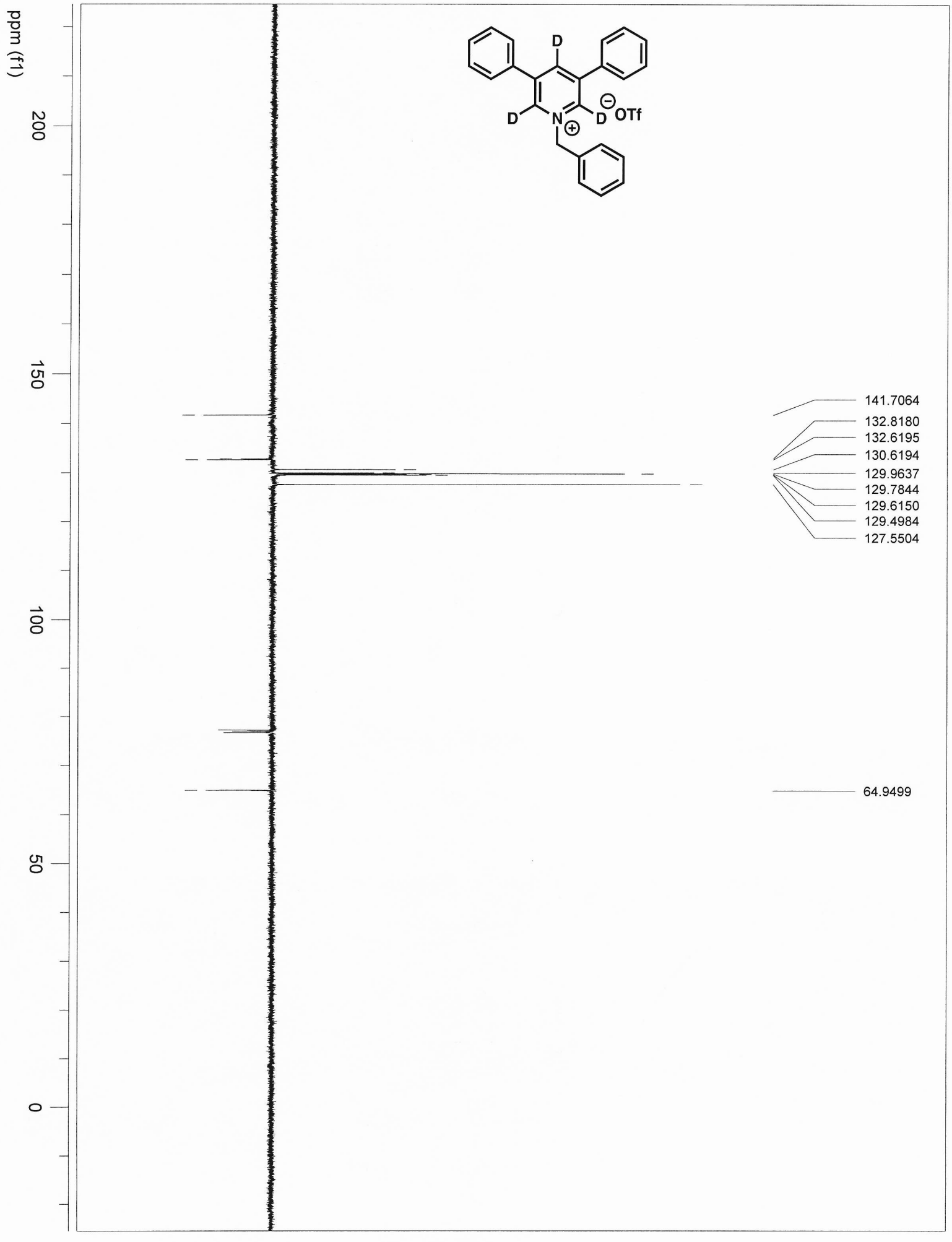
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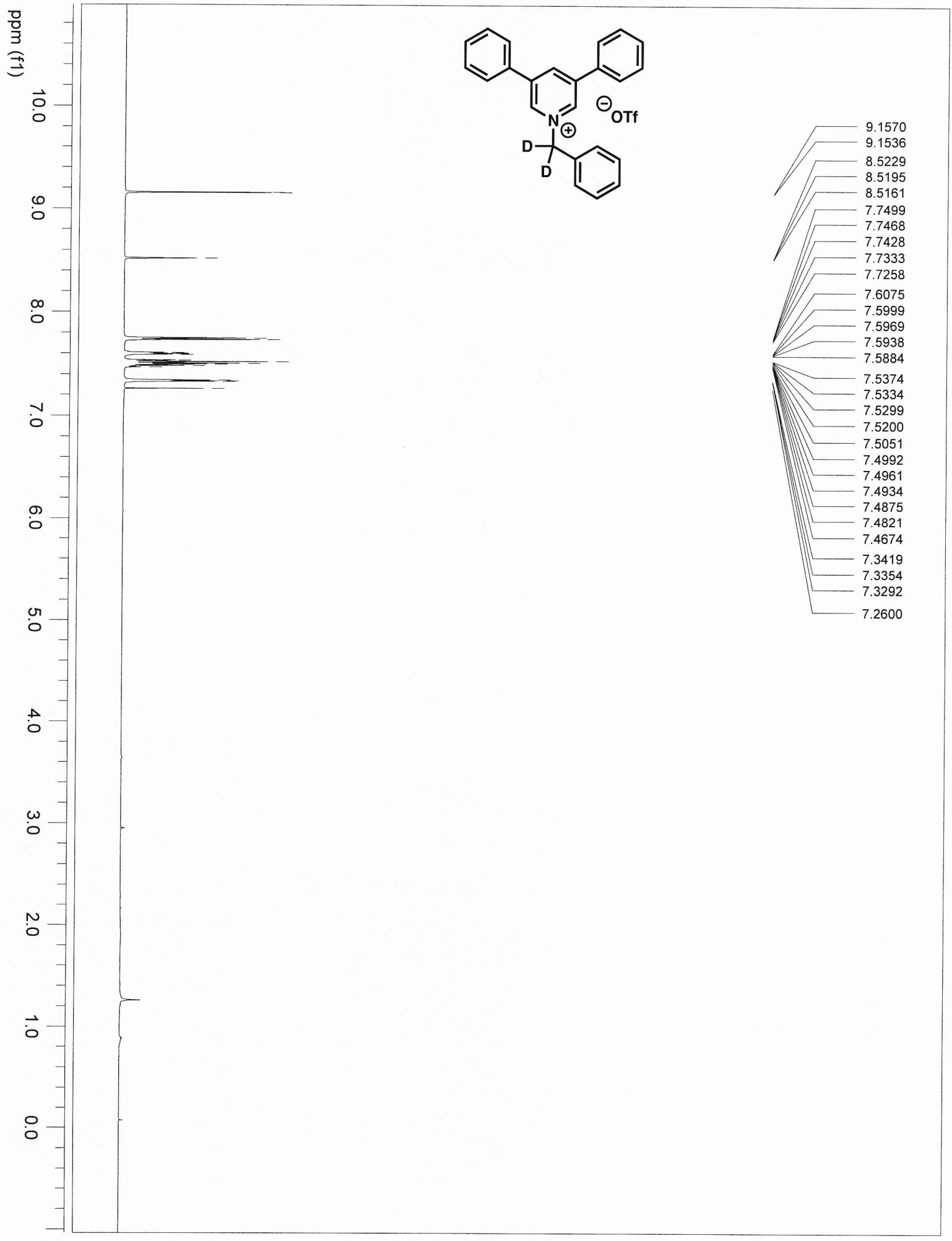
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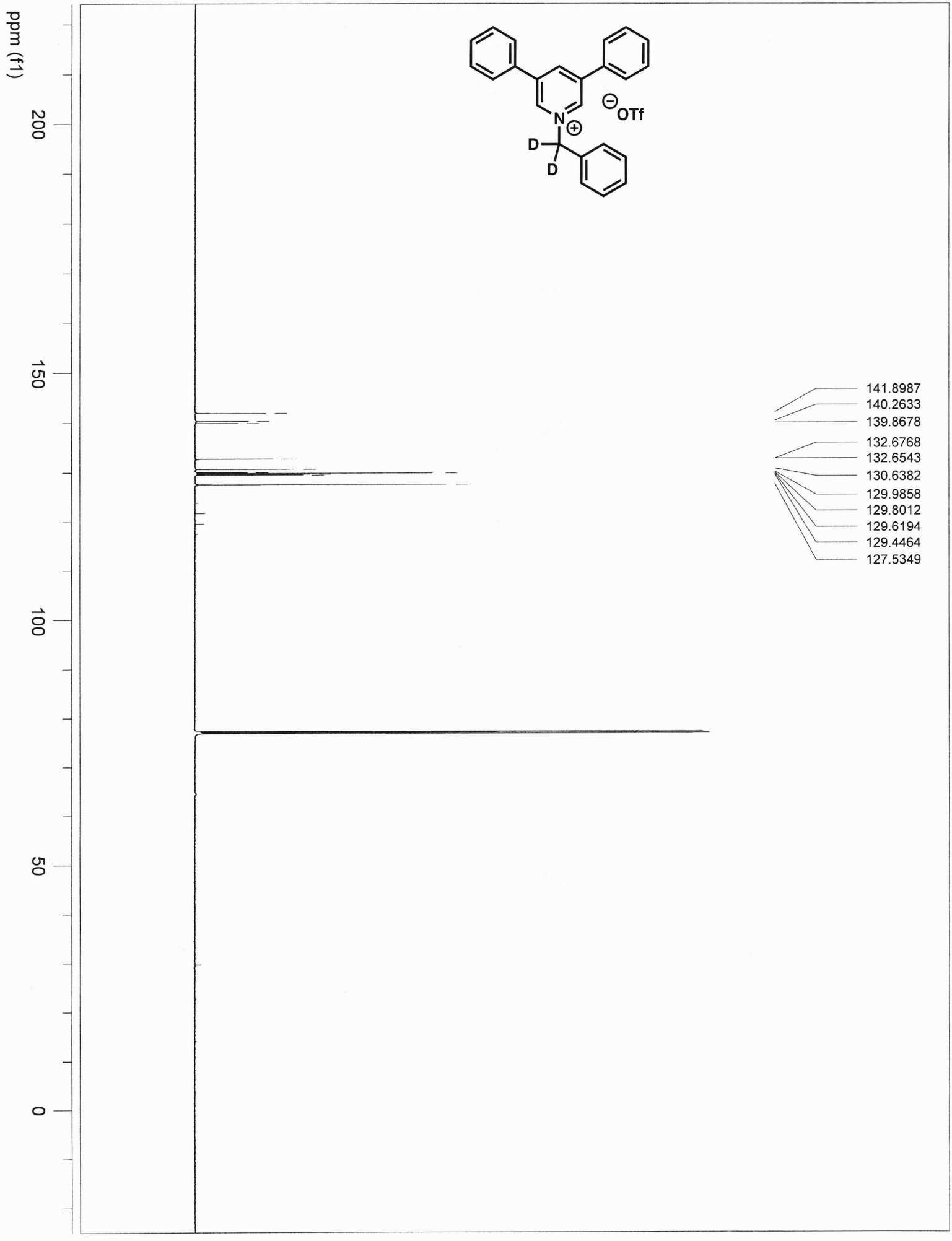
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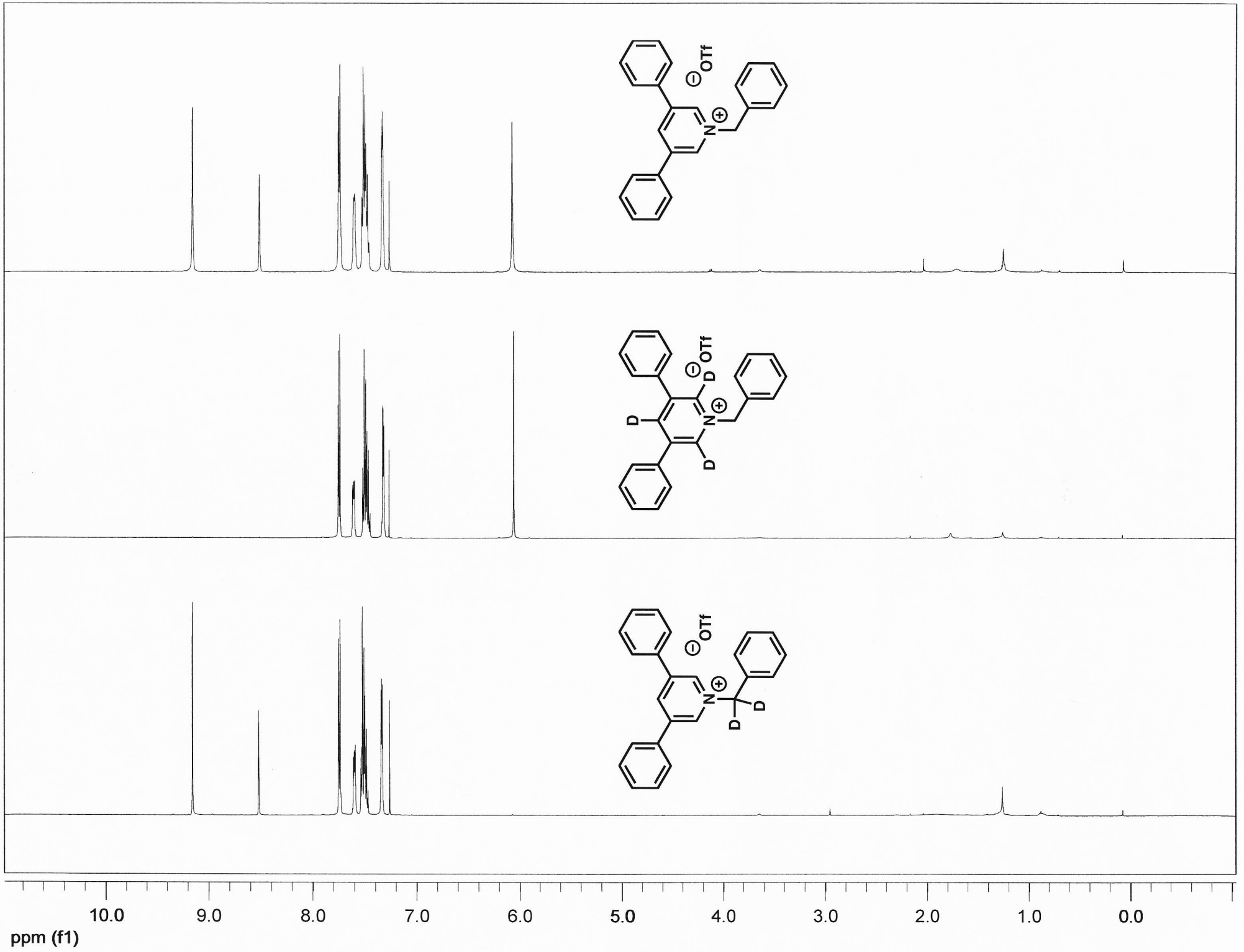

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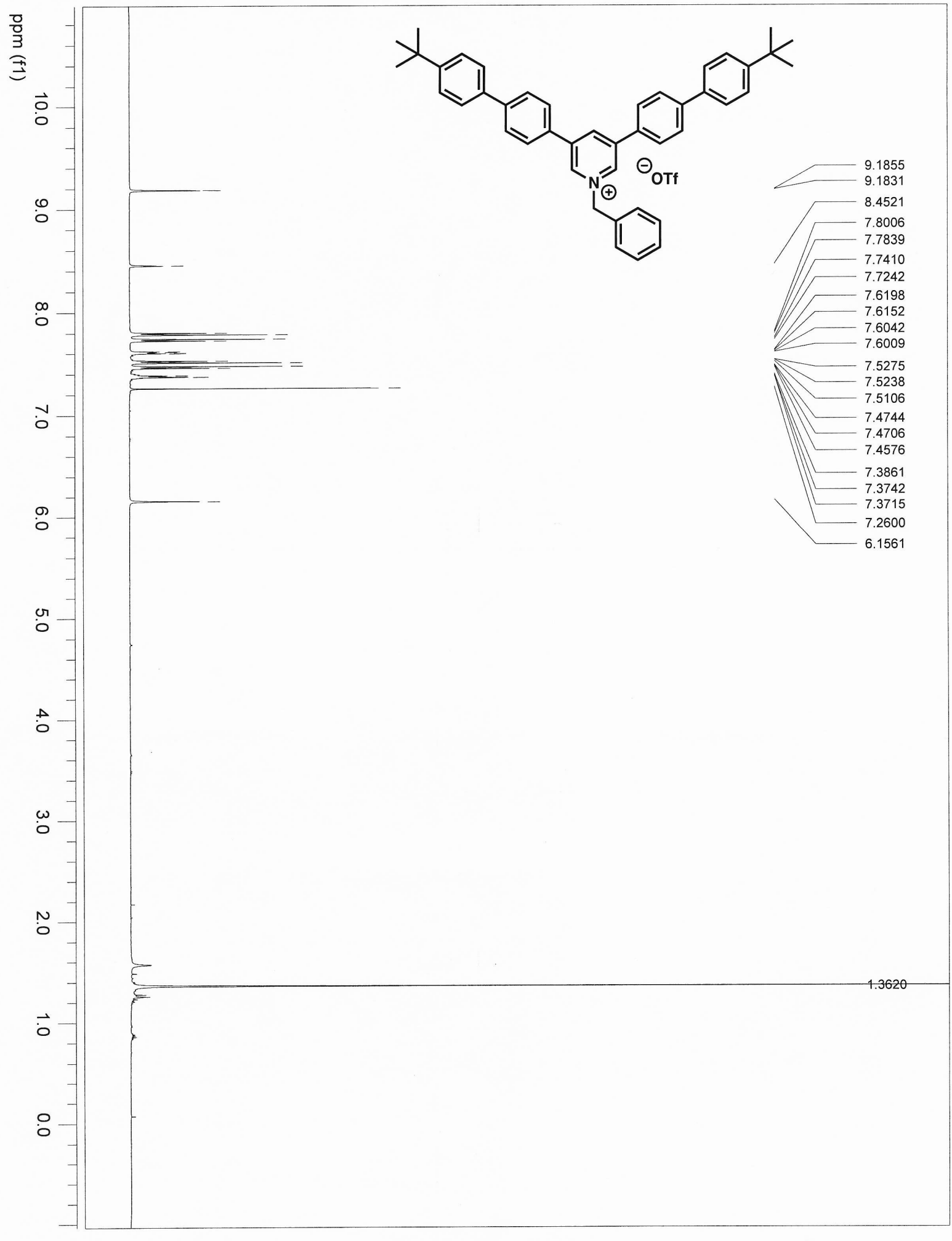
ppm (f1)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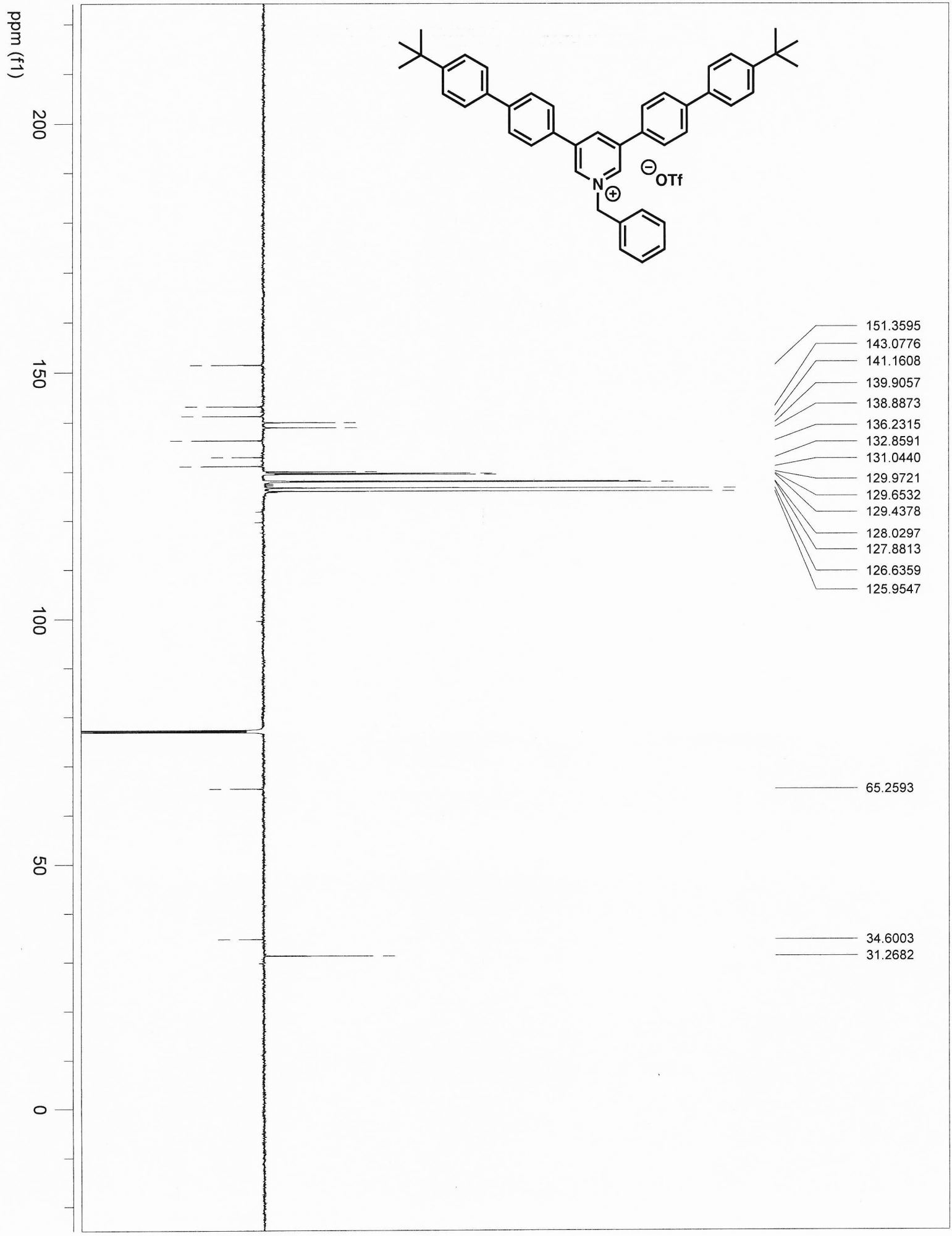
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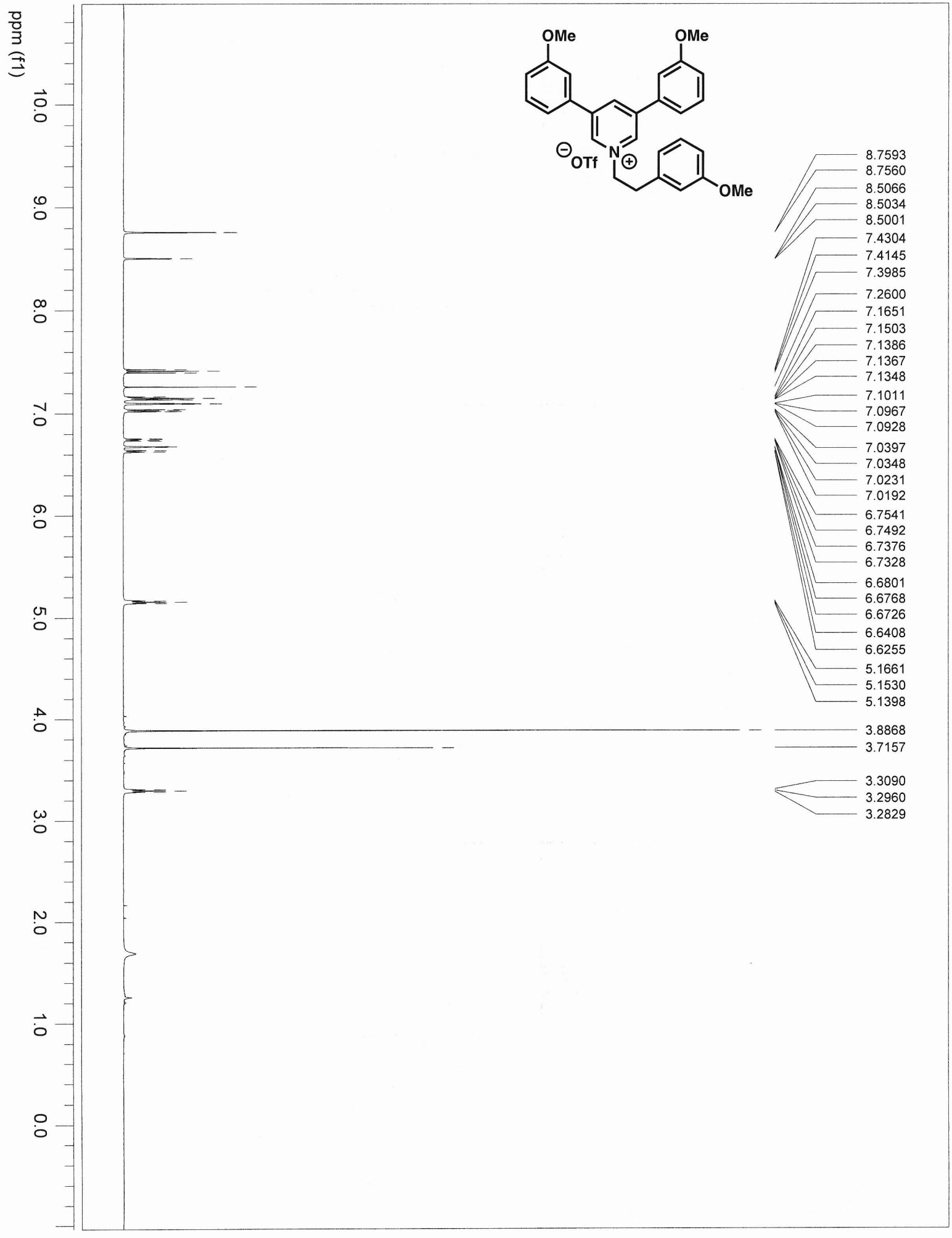
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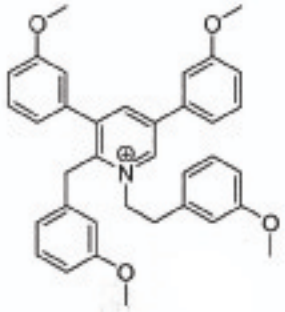

misassigned

^{1}H NMR (400 MHz, $CDCl_3$)

Chem. Comm. **2007**, 719-721.

grease

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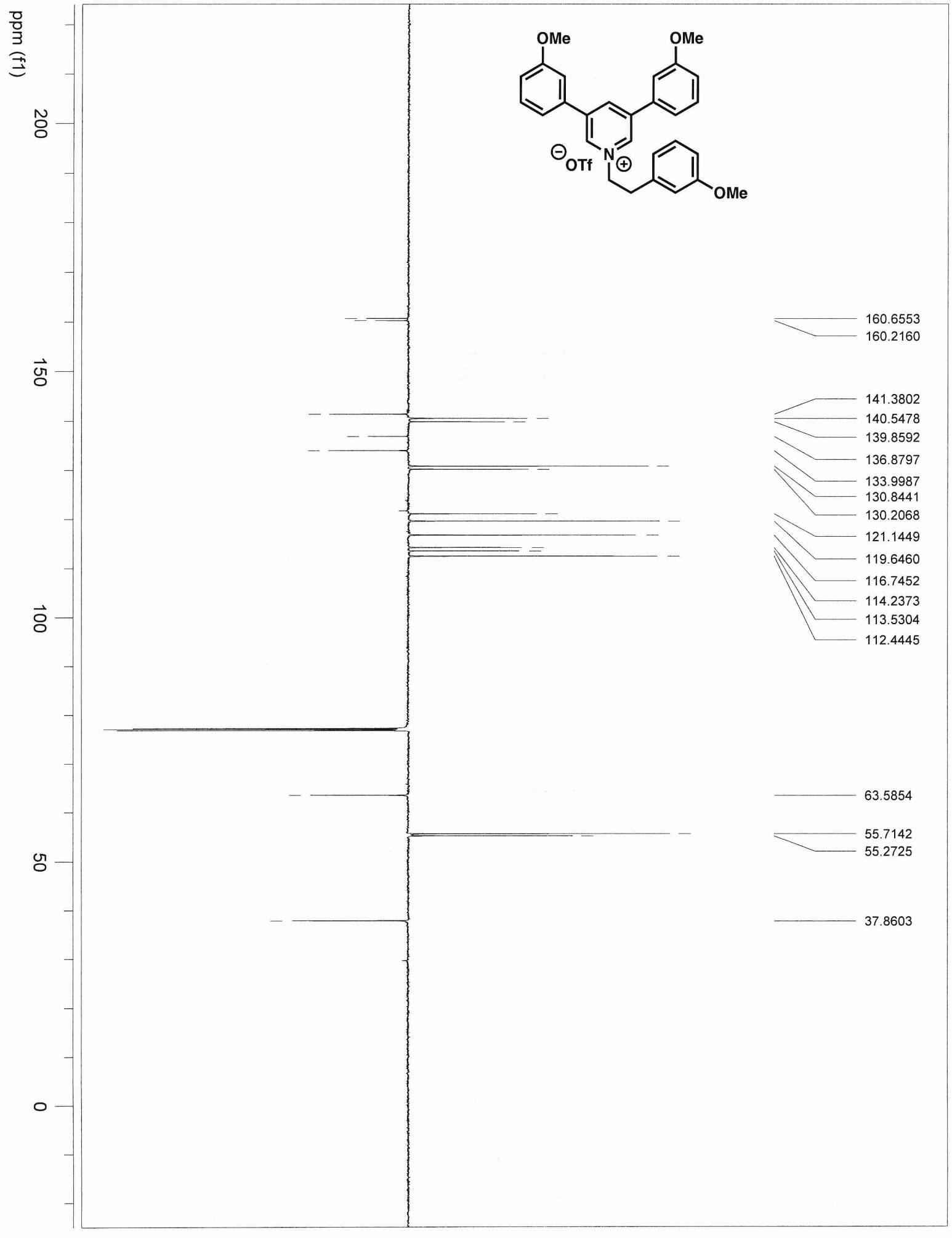
ppm (f1)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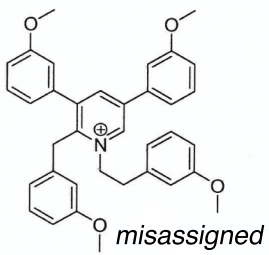
^{13}C-APT NMR (400 MHz, $CDCl_3$)
Chem. Comm. **2007**, 719-721.



misassigned

grease

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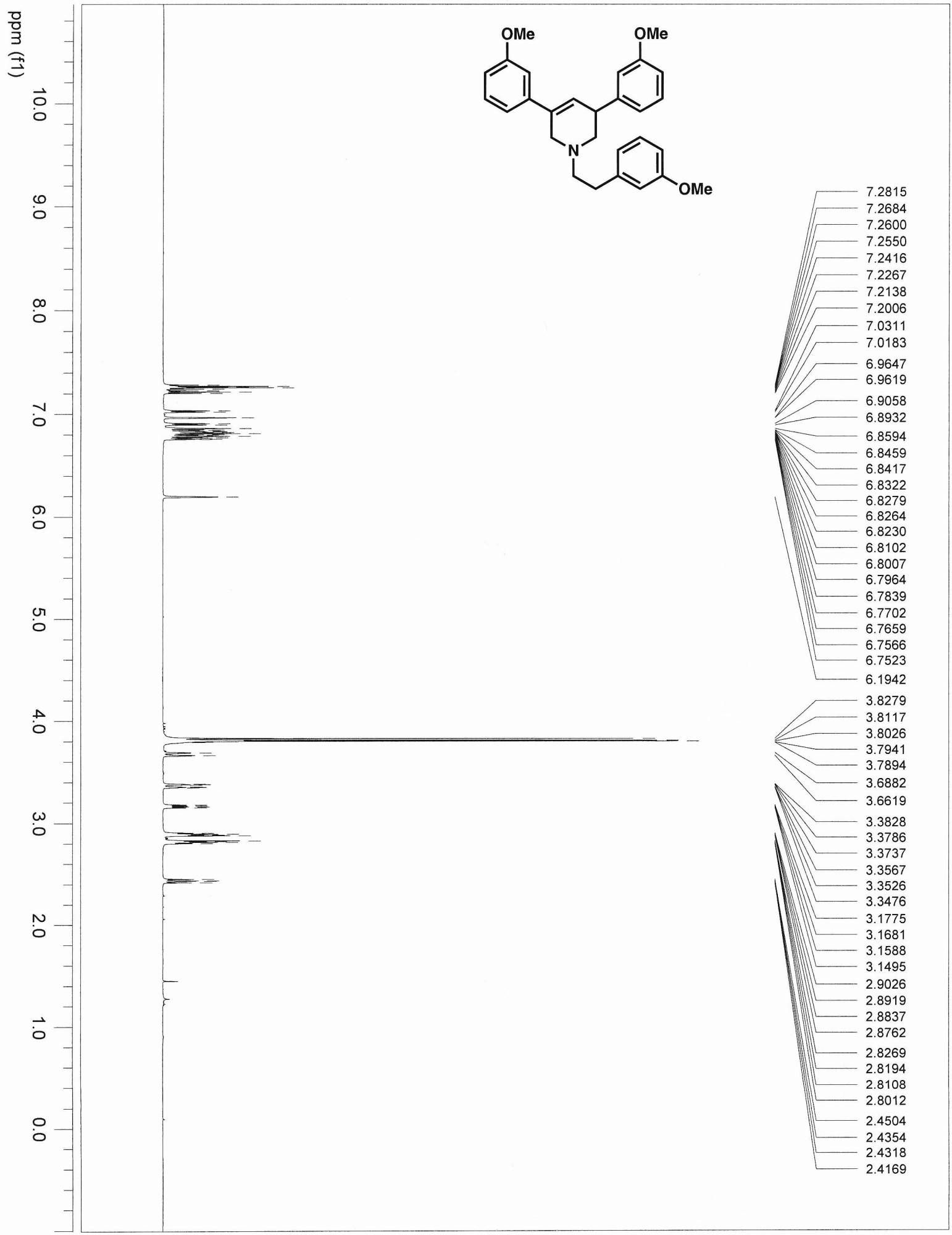
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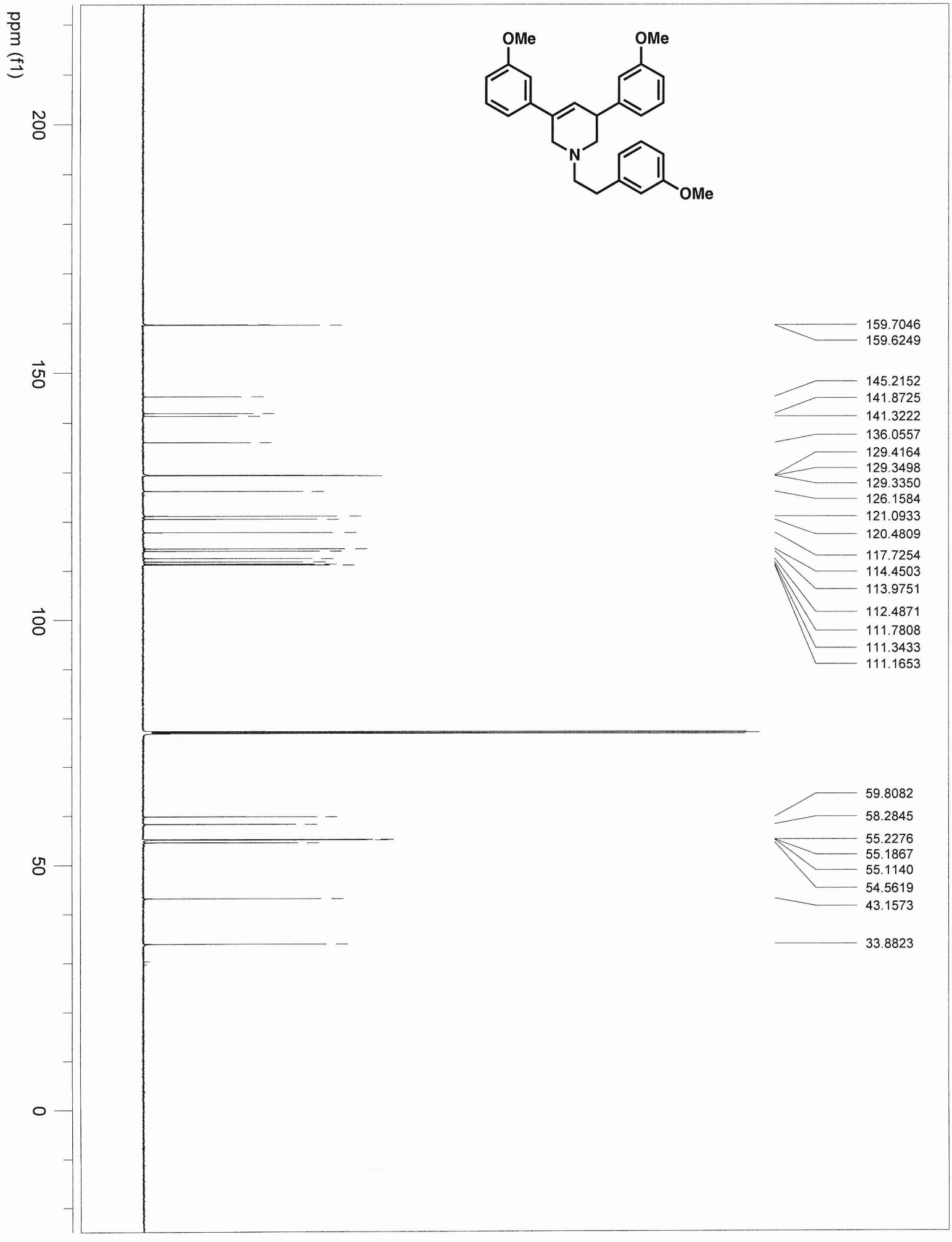
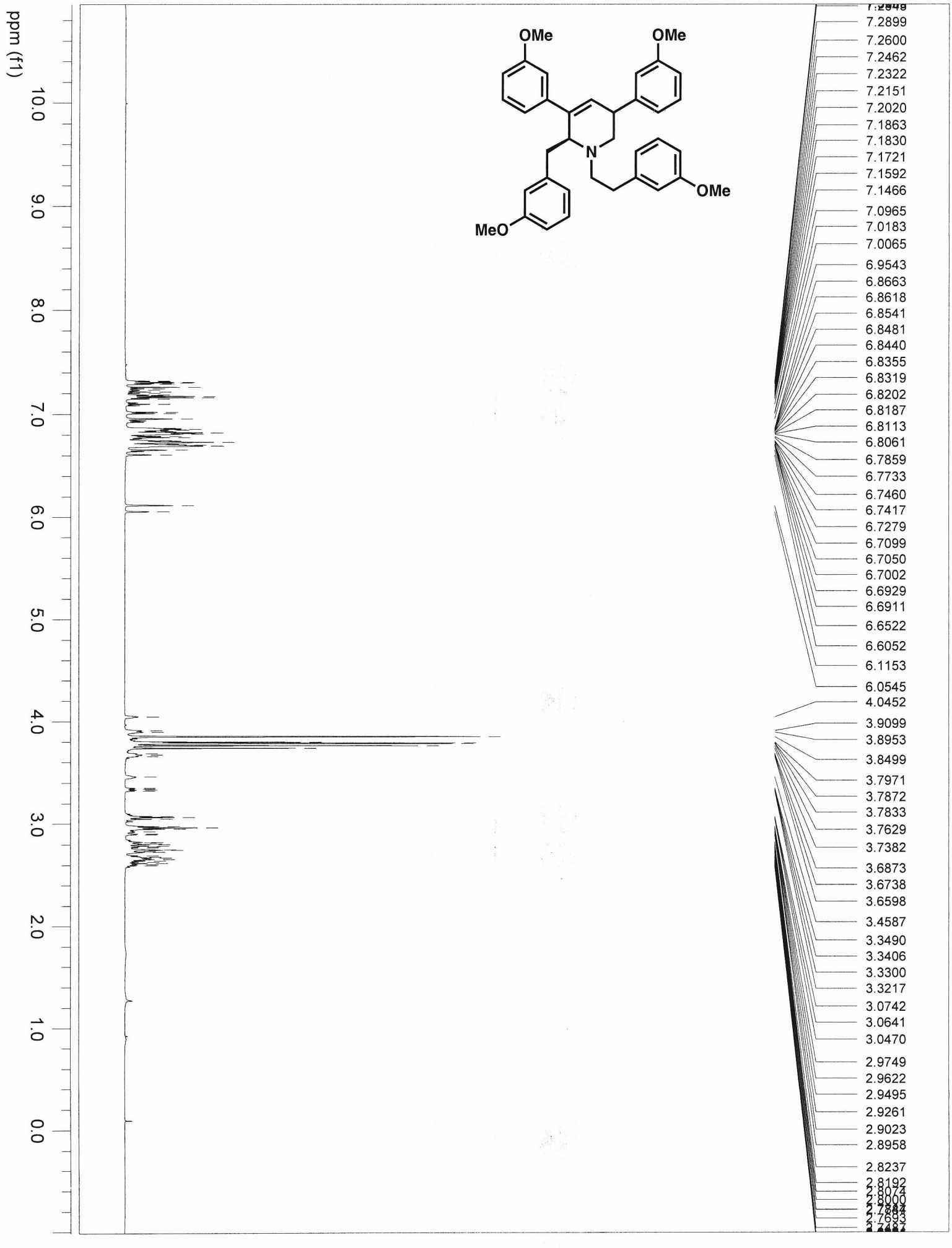
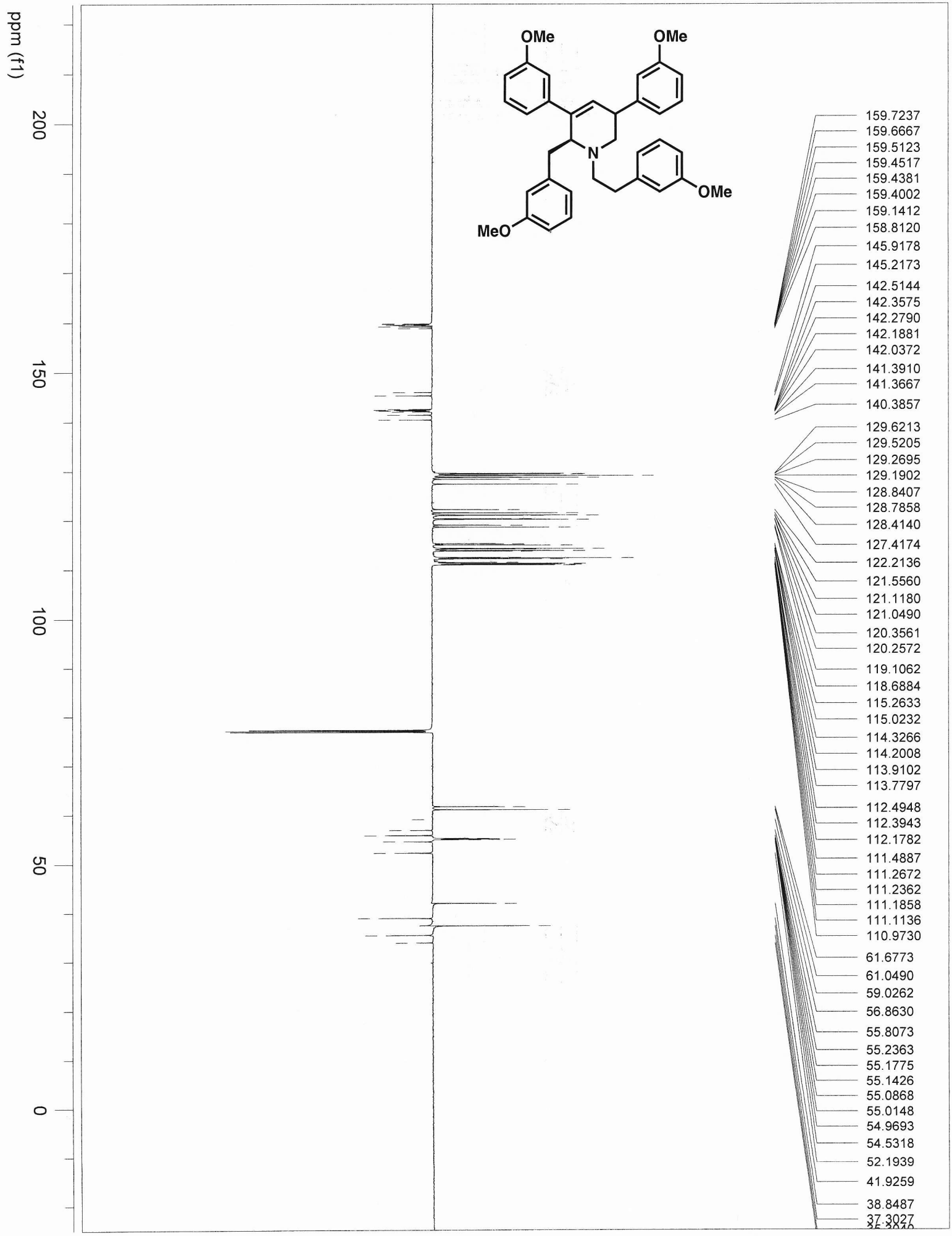
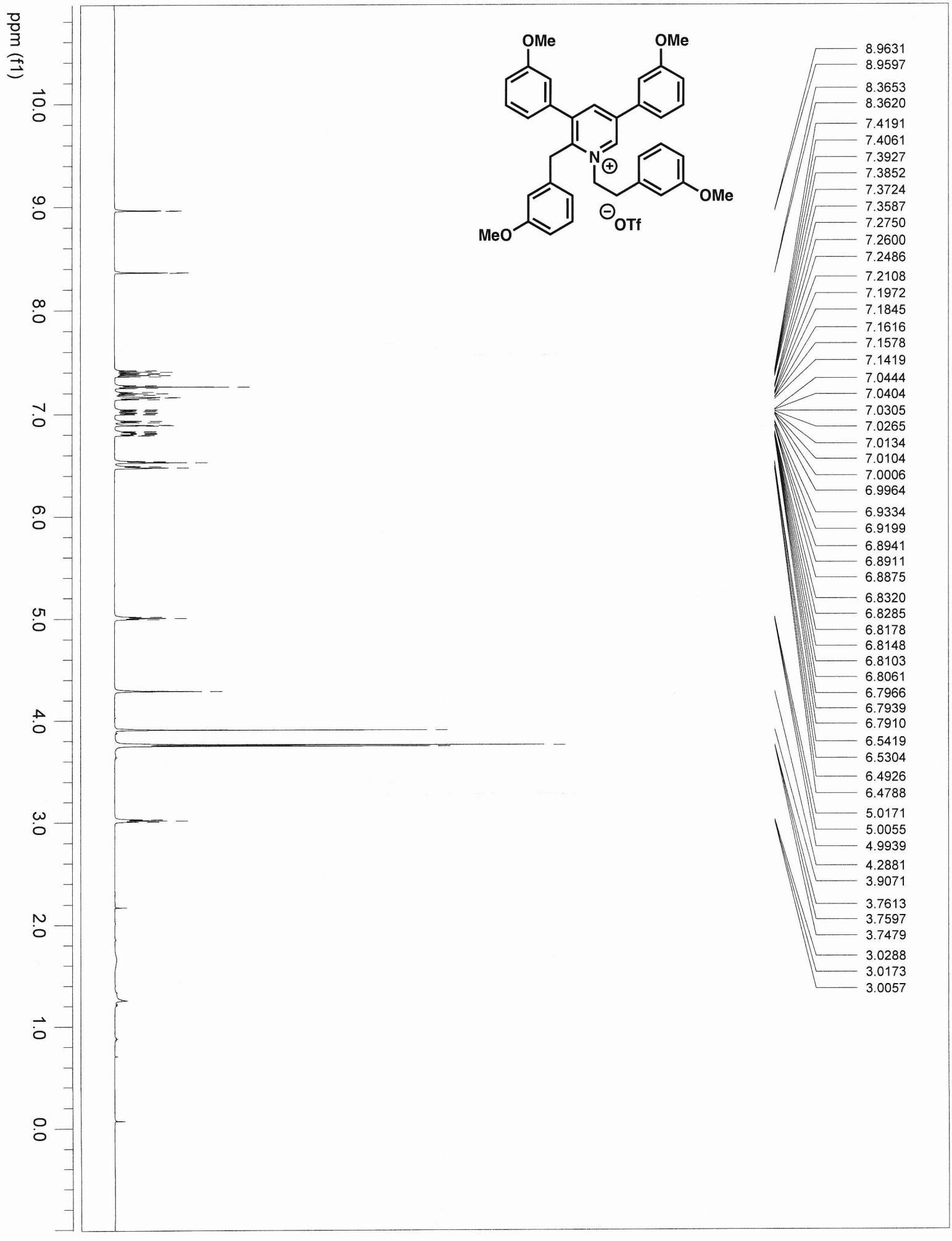
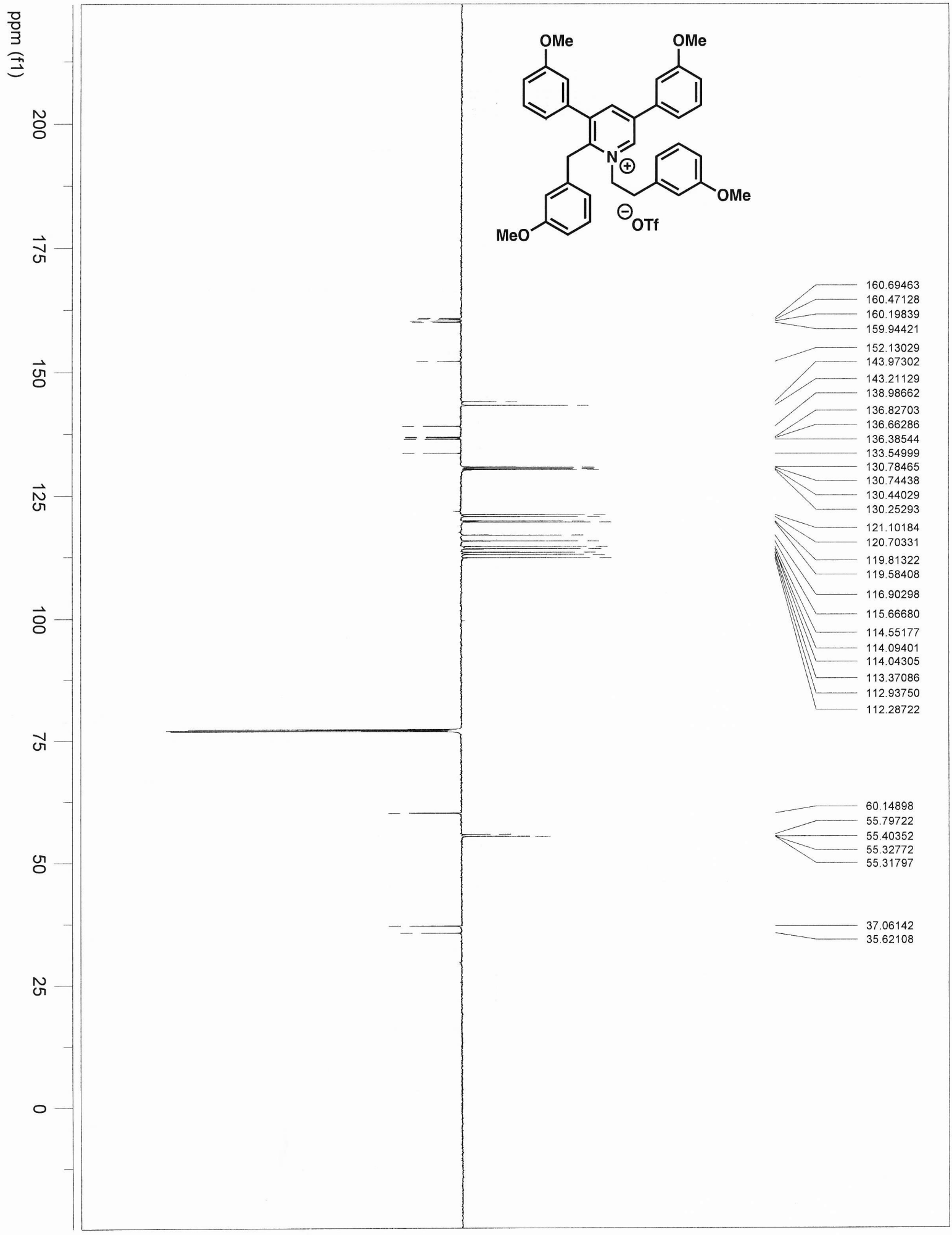
6.8279
6.8264
6.8230
6.8102
6.8007
6.7964
6.7839
6.7702
6.7659
6.7566
6.7523
6.1942
3.8279
3.8117
3.8026
3.7941
3.7894
3.6882
3.6619
3.3828
3.3786
3.3737
3.3567
3.3526
3.3476
3.1775
3.1681
3.1588
3.1495
2.9026
2.8919
2.8837
2.8762
2.8269
2.8194
2.8108
2.8012
2.4504
2.4354
2.4318
2.4169

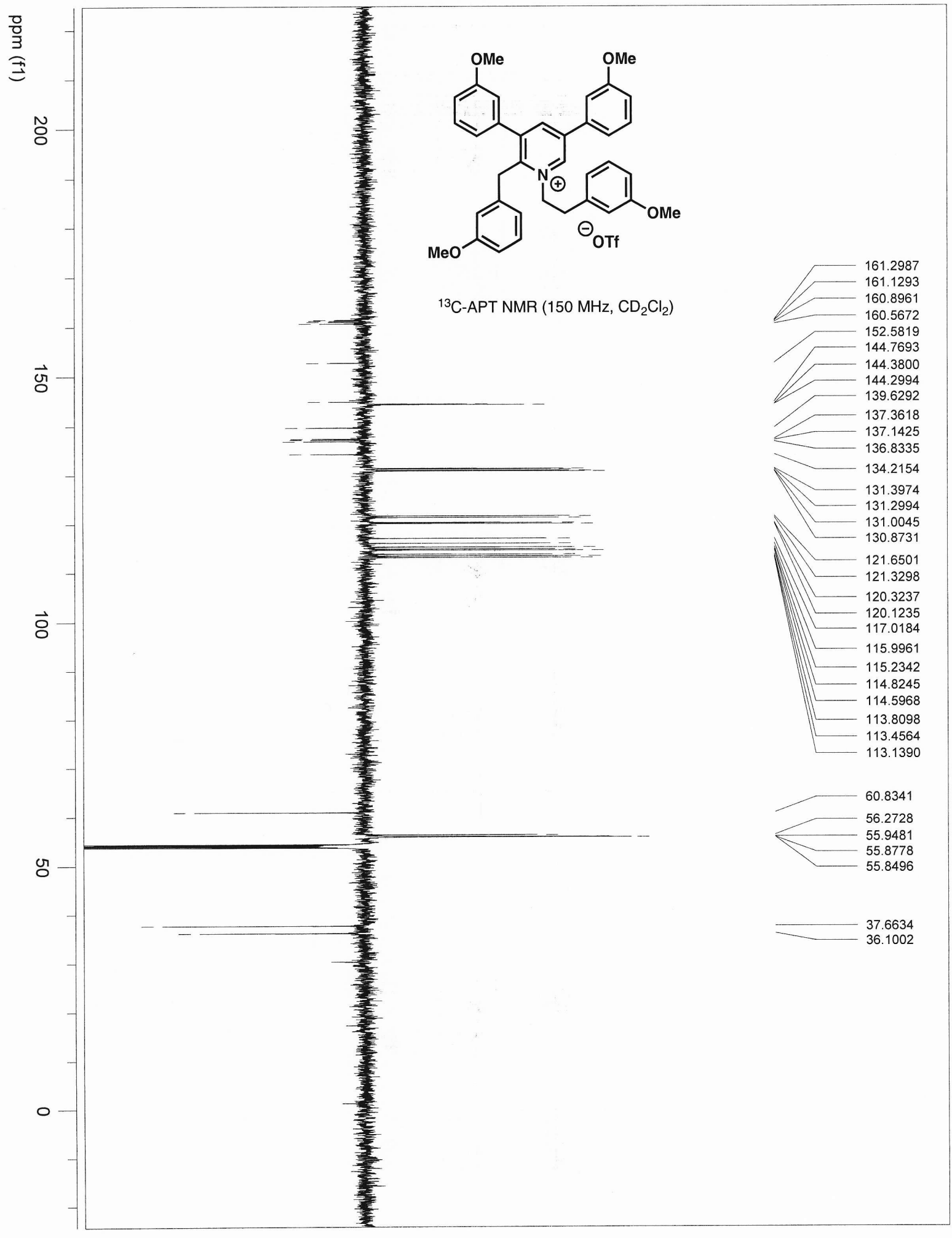

ppm (f1)
200
150
100
50
0
OMe
OMe
OMe
N
159.7046
159.6249
145.2152
141.8725
141.3222
136.0557
129.4164
129.3498
129.3350
126.1584
121.0933
120.4809
117.7254
114.4503
113.9751
112.4871
111.7808
111.3433
111.1653
59.8082
58.2845
55.2276
55.1867
55.1140
54.5619
43.1573
33.8823


ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
OMe
N
OMe
MeO
7.2899
7.2600
7.2462
7.2322
7.2151
7.2020
7.1863
7.1830
7.1721
7.1592
7.1466
7.0965
7.0183
7.0065
6.9543
6.8663
6.8618
6.8541
6.8481
6.8440
6.8355
6.8319
6.8202
6.8187
6.8113
6.8061
6.7859
6.7733
6.7460
6.7417
6.7279
6.7099
6.7050
6.7002
6.6929
6.6911
6.6522
6.6052
6.1153
6.0545
4.0452
3.9099
3.8953
3.8499
3.7971
3.7872
3.7833
3.7629
3.7382
3.6873
3.6738
3.6598
3.4587
3.3490
3.3406
3.3300
3.3217
3.0742
3.0641
3.0470
2.9749
2.9622
2.9495
2.9261
2.9023
2.8958
2.8237
2.8192

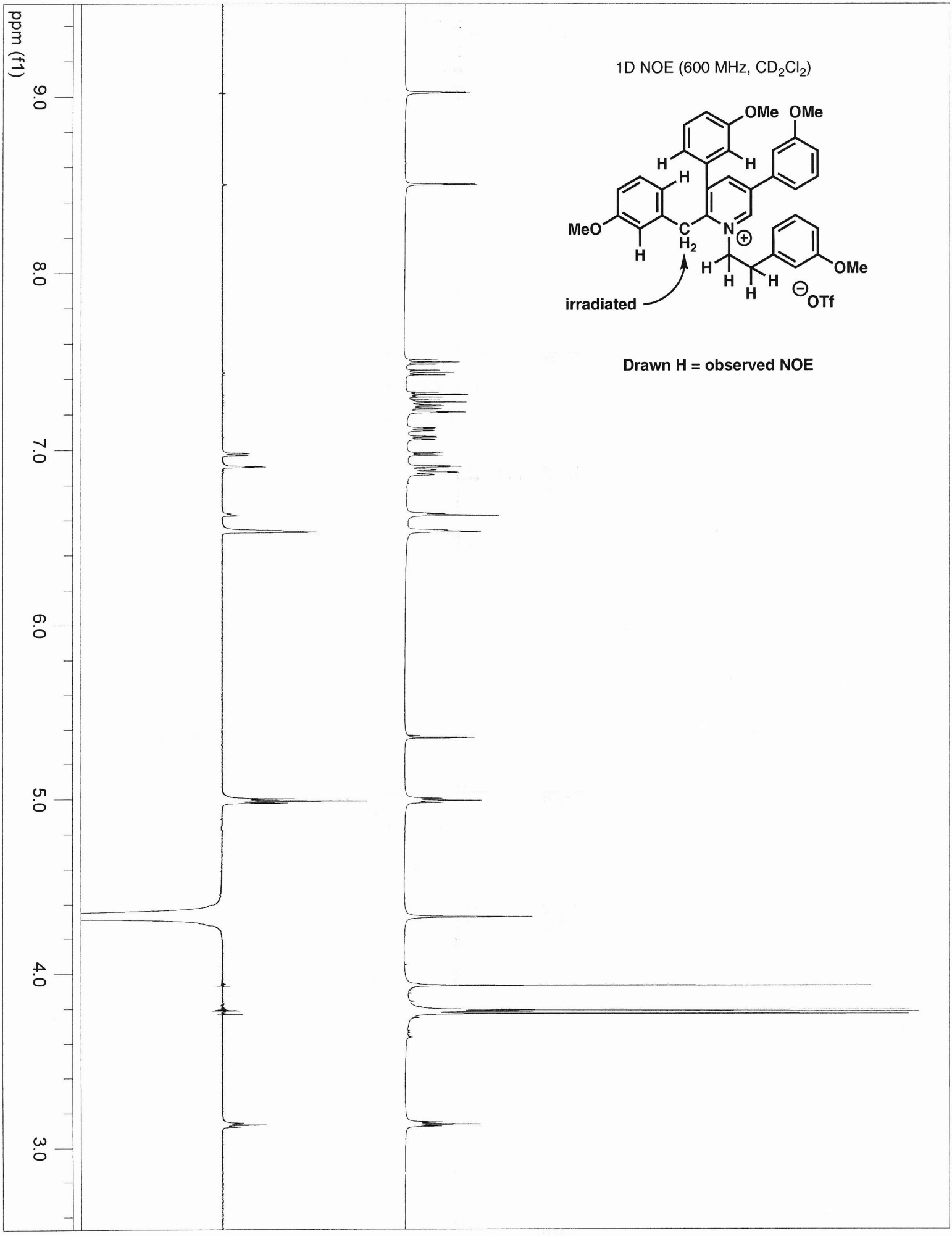

ppm (f1)
200
150
100
50
0
OMe
OMe
N
OMe
MeO
159.7237
159.6667
159.5123
159.4517
159.4381
159.4002
159.1412
158.8120
145.9178
145.2173
142.5144
142.3575
142.2790
142.1881
142.0372
141.3910
141.3667
140.3857
129.6213
129.5205
129.2695
129.1902
128.8407
128.7858
128.4140
127.4174
122.2136
121.5560
121.1180
121.0490
120.3561
120.2572
119.1062
118.6884
115.2633
115.0232
114.3266
114.2008
113.9102
113.7797
112.4948
112.3943
112.1782
111.4887
111.2672
111.2362
111.1858
111.1136
110.9730
61.6773
61.0490
59.0262
56.8630
55.8073
55.2363
55.1775
55.1426
55.0868
55.0148
54.9693
54.5318
52.1939
41.9259
38.8487
37.3027

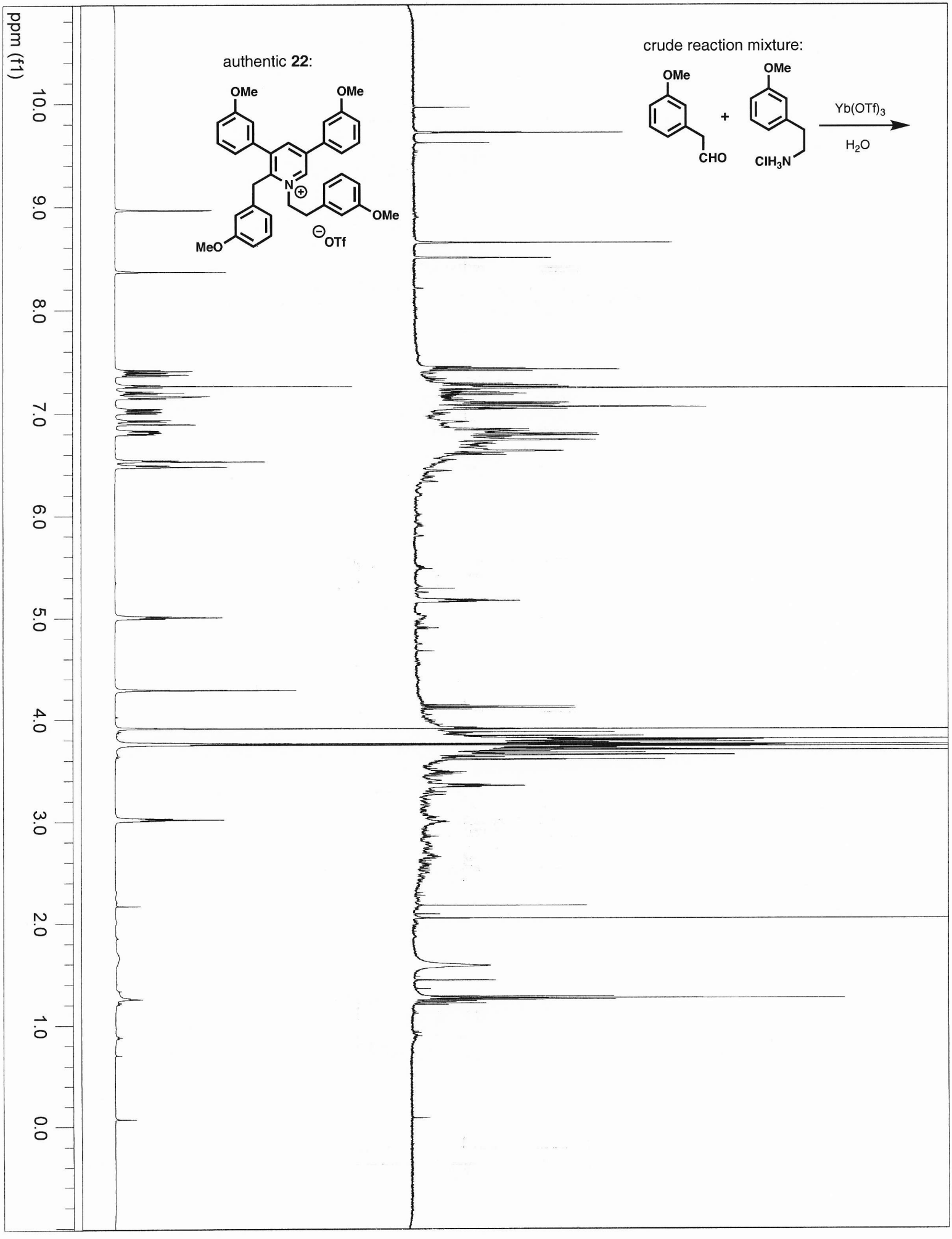

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
OMe
MeO
OMe
OTf
8.9631
8.9597
8.3653
8.3620
7.4191
7.4061
7.3927
7.3852
7.3724
7.3587
7.2750
7.2600
7.2486
7.2108
7.1972
7.1845
7.1616
7.1578
7.1419
7.0444
7.0404
7.0305
7.0265
7.0134
7.0104
7.0006
6.9964
6.9334
6.9199
6.8941
6.8911
6.8875
6.8320
6.8285
6.8178
6.8148
6.8103
6.8061
6.7966
6.7939
6.7910
6.5419
6.5304
6.4926
6.4788
5.0171
5.0055
4.9939
4.2881
3.9071
3.7613
3.7597
3.7479
3.0288
3.0173
3.0057

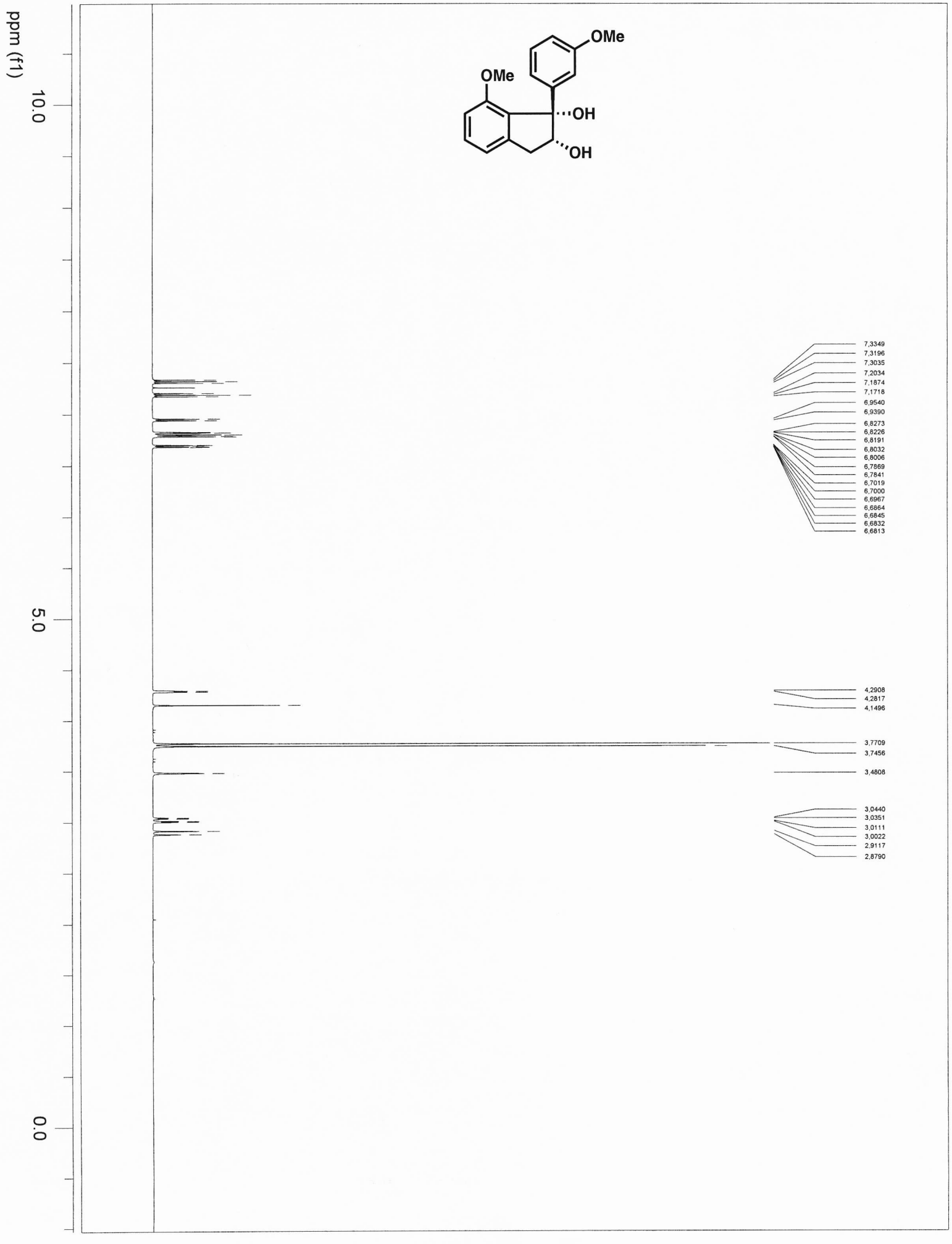

ppm (f1)
200
175
150
125
100
75
50
25
0
OMe
OMe
N
OMe
MeO
OTf
160.69463
160.47128
160.19839
159.94421
152.13029
143.97302
143.21129
138.98662
136.82703
136.66286
136.38544
133.54999
130.78465
130.74438
130.44029
130.25293
121.10184
120.70331
119.81322
119.58408
116.90298
115.66680
114.55177
114.09401
114.04305
113.37086
112.93750
112.28722
60.14898
55.79722
55.40352
55.32772
55.31797
37.06142
35.62108

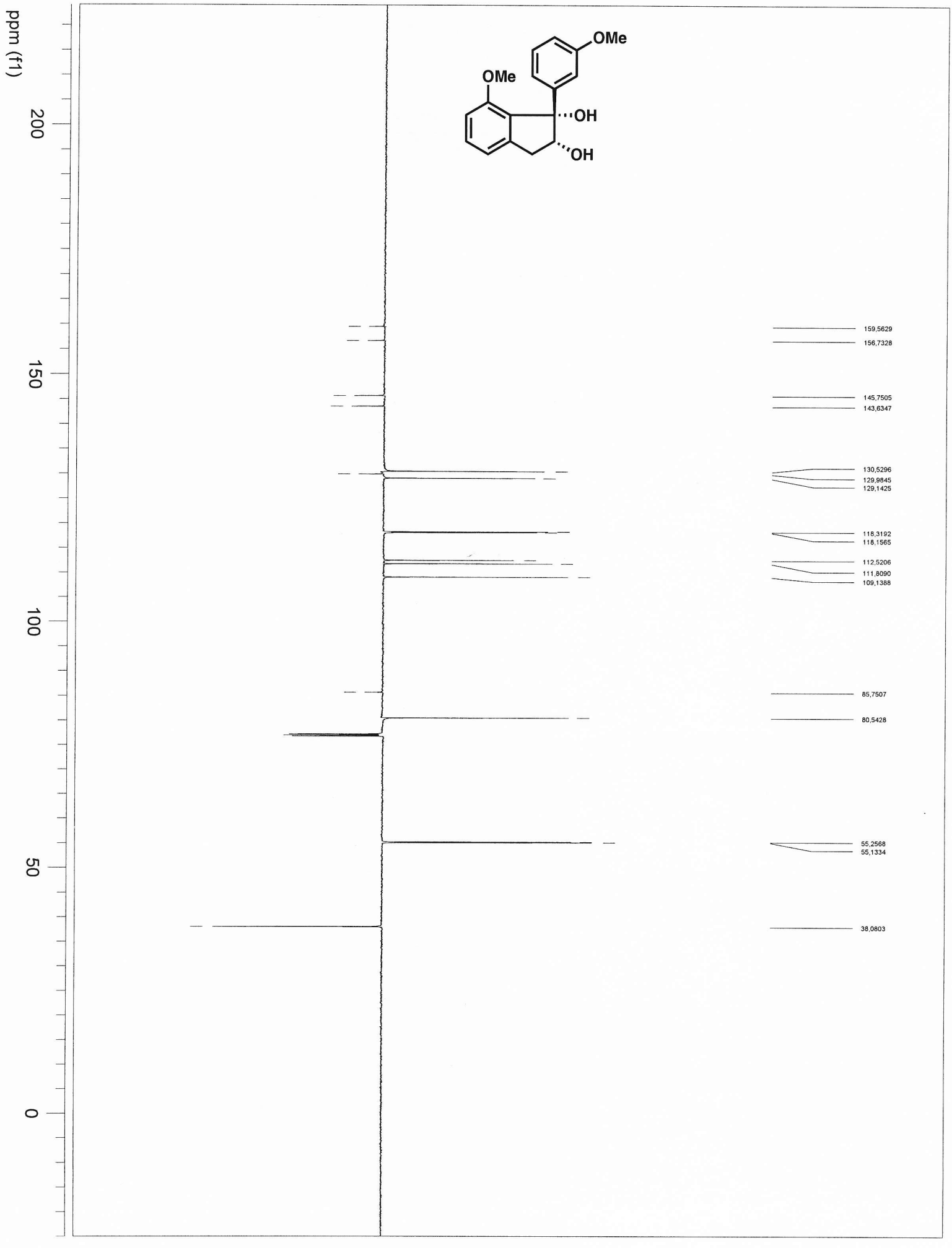


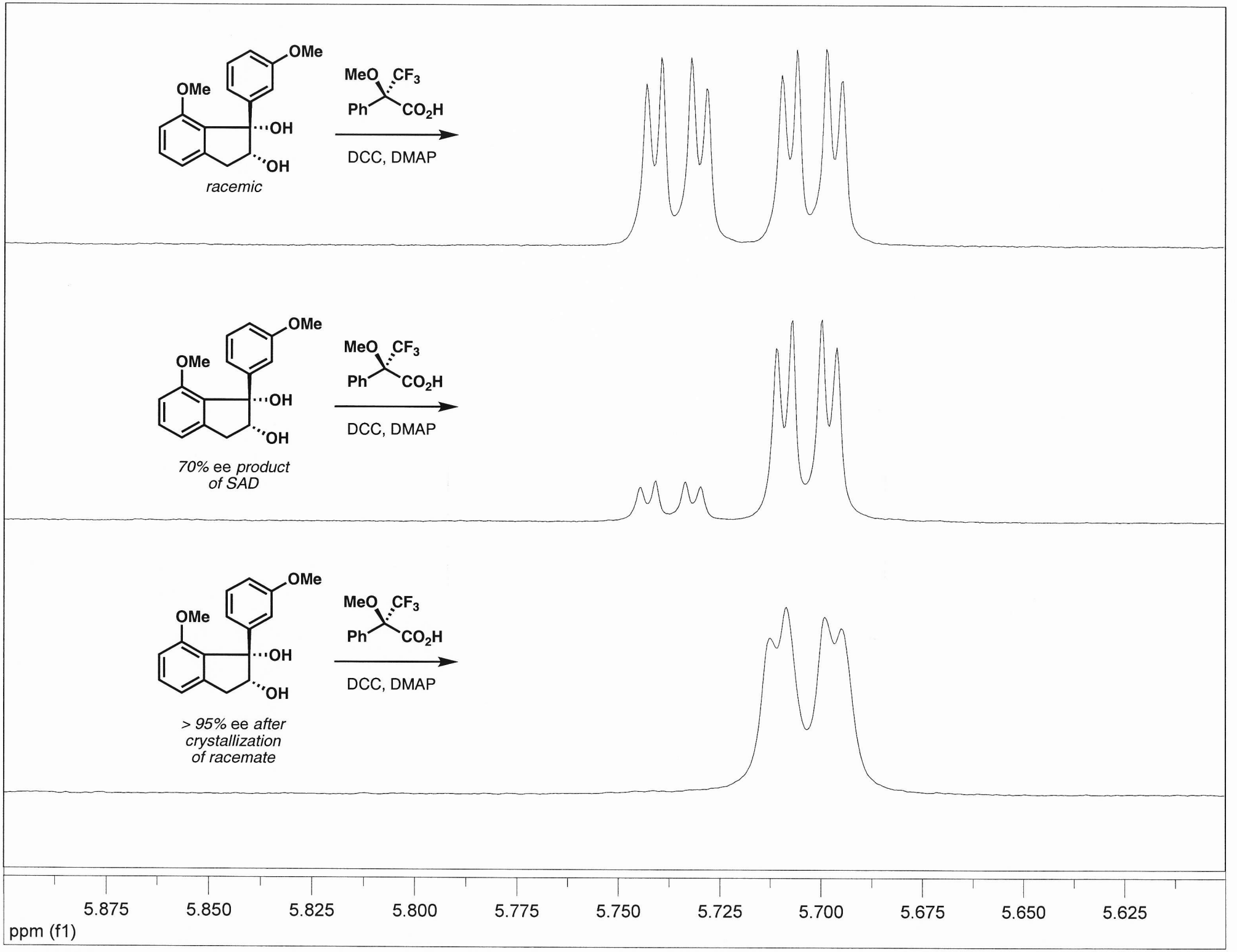
^{13}C-APT NMR (150 MHz, CD_2Cl_2)

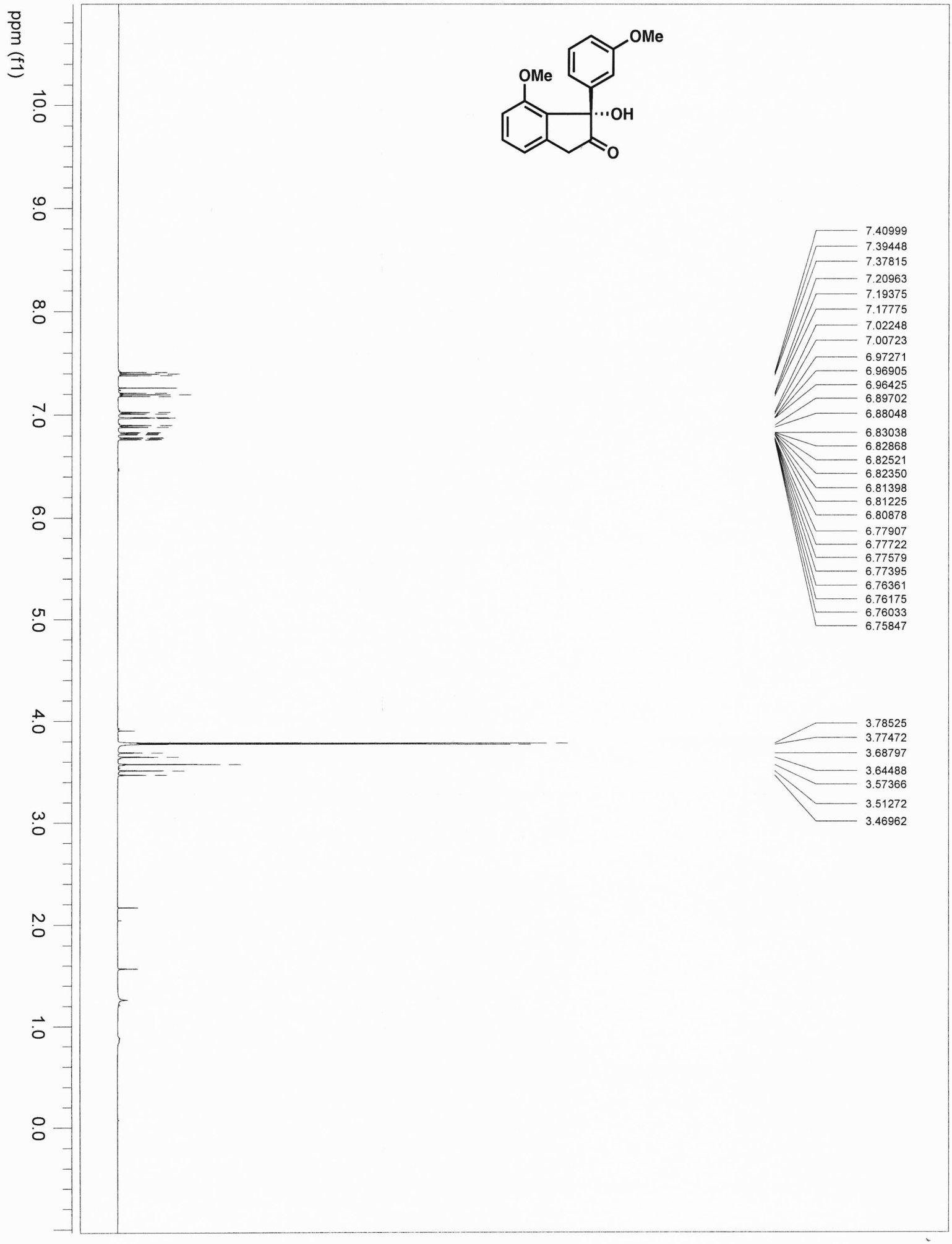

ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
1D NOE (600 MHz, CD_2Cl_2)
OMe
OMe
H
H
H
H
MeO
C
H_2
N
H
H
H
H
H
OMe
OTf
irradiated
Drawn H = observed NOE

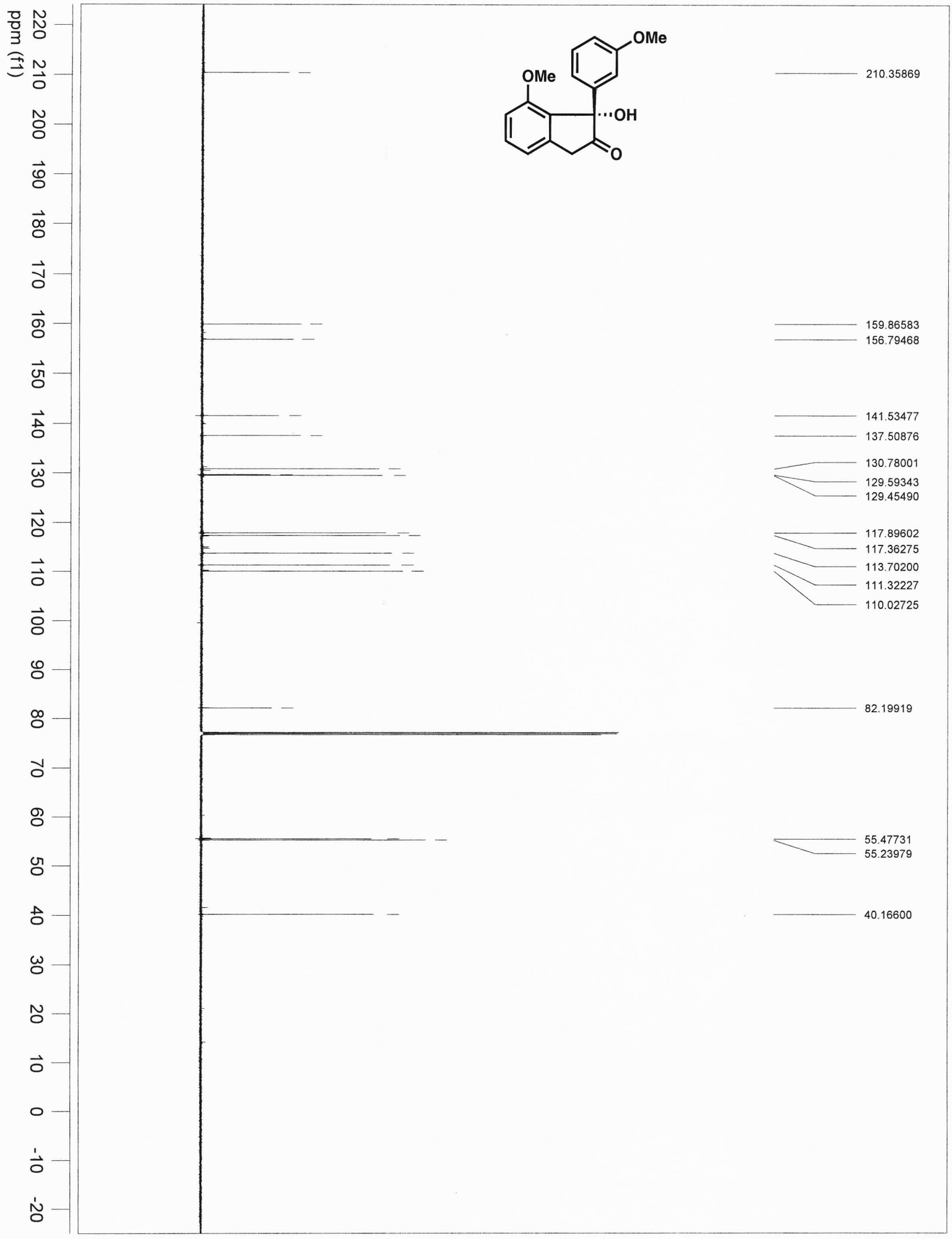

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
authentic 22:
OMe
OMe
OMe
MeO
OTf
crude reaction mixture:
OMe
CHO
+
OMe
ClH3N
Yb(OTf)3
H2O

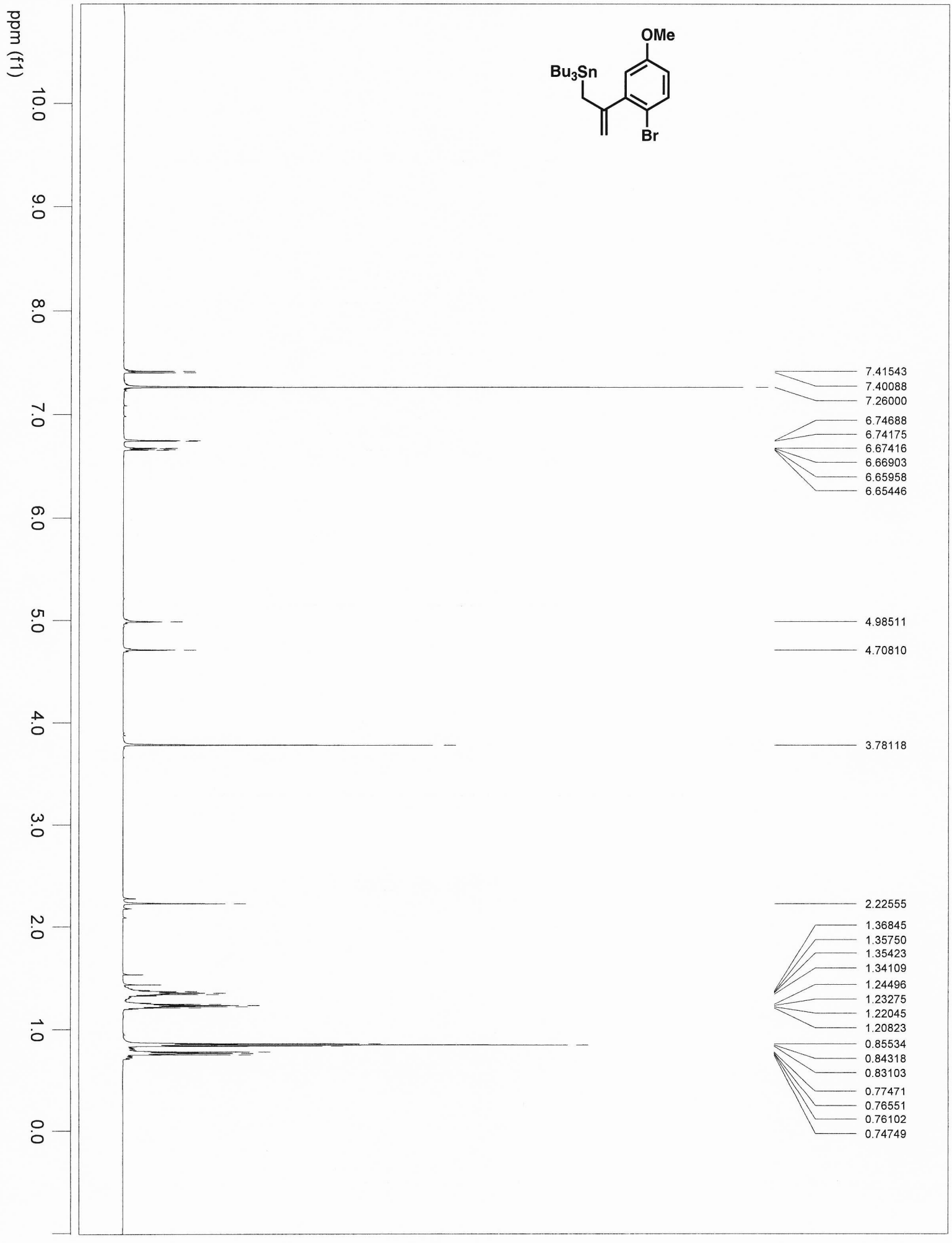

ppm (f1)
10.0
5.0
0.0
OMe
OMe
OH
OH
7,3349
7,3196
7,3035
7,2034
7,1874
7,1718
6,9540
6,9390
6,8273
6,8226
6,8191
6,8032
6,8006
6,7869
6,7841
6,7019
6,7000
6,6967
6,6864
6,6845
6,6832
6,6813
4,2908
4,2817
4,1496
3,7709
3,7456
3,4808
3,0440
3,0351
3,0111
3,0022
2,9117
2,8790

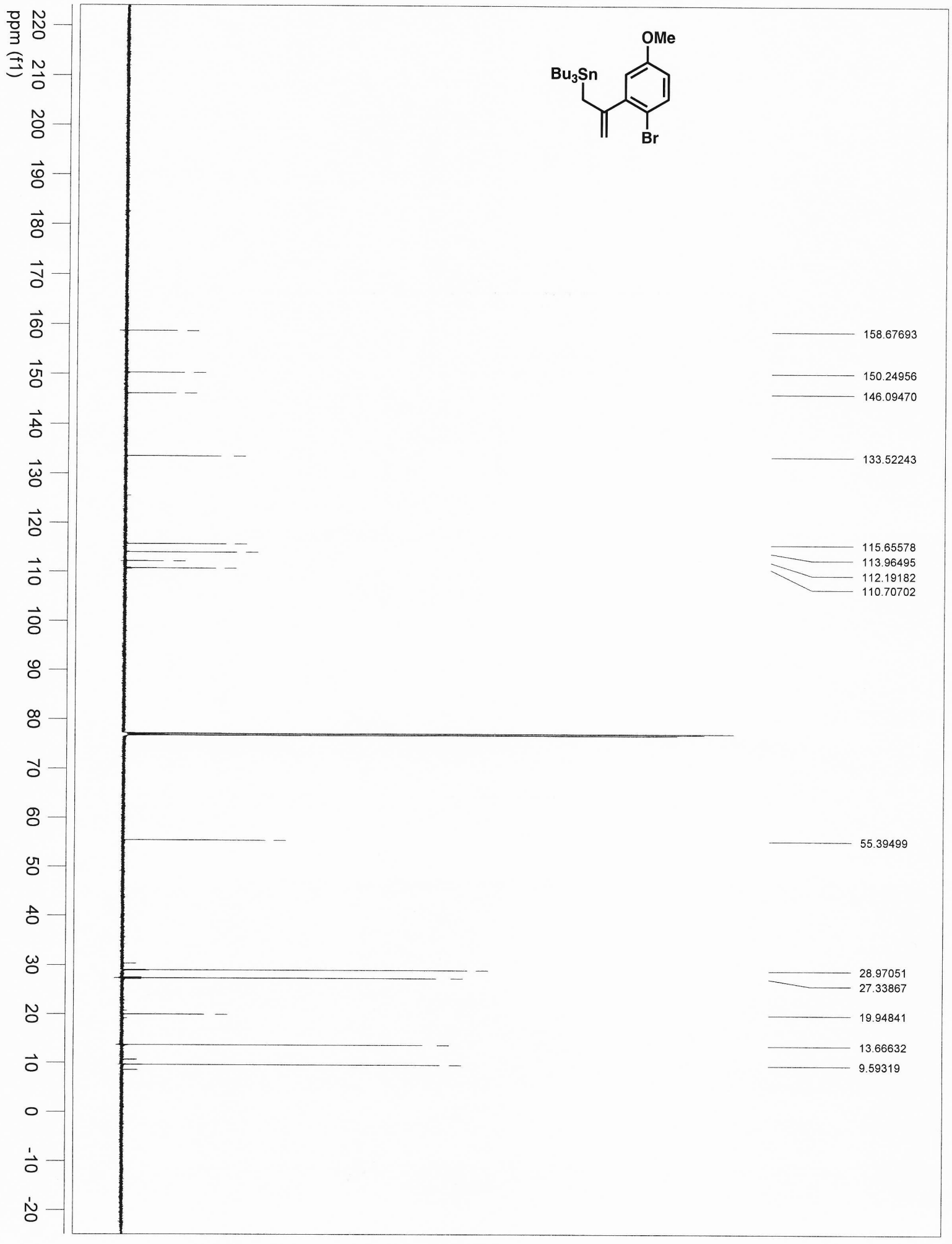

ppm (f1)
200
150
100
50
0
OMe
OMe
OH
OH
159,5629
156,7328
145,7505
143,6347
130,5296
129,9845
129,1425
118,3192
118,1565
112,5206
111,8090
109,1388
85,7507
80,5428
55,2568
55,1334
38,0803

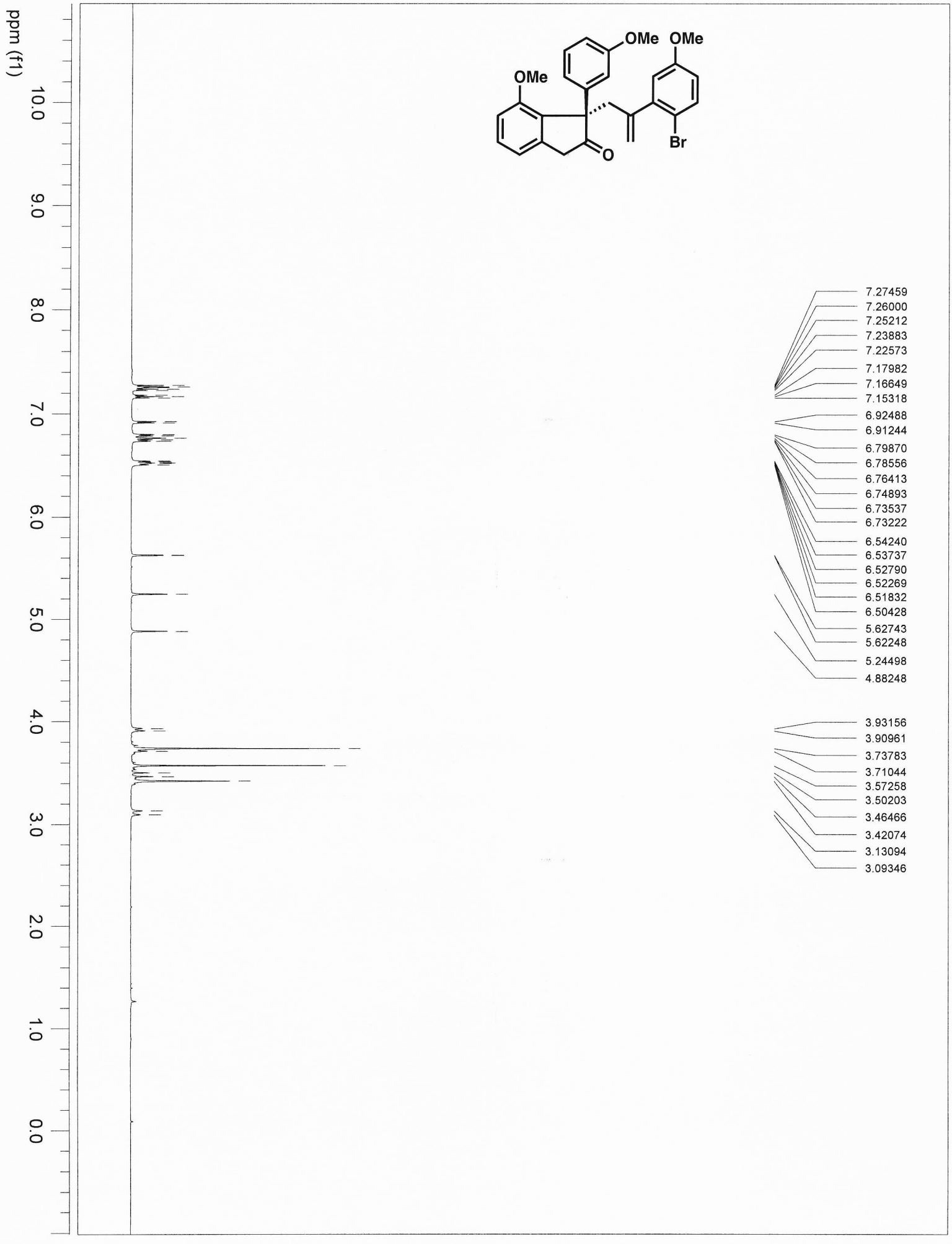

OMe
OMe
OH
OH
racemic
MeO
CF3
Ph
CO2H
DCC, DMAP
70% ee product of SAD
> 95% ee after crystallization of racemate
5.875
5.850
5.825
5.800
5.775
5.750
5.725
5.700
5.675
5.650
5.625
ppm (f1)

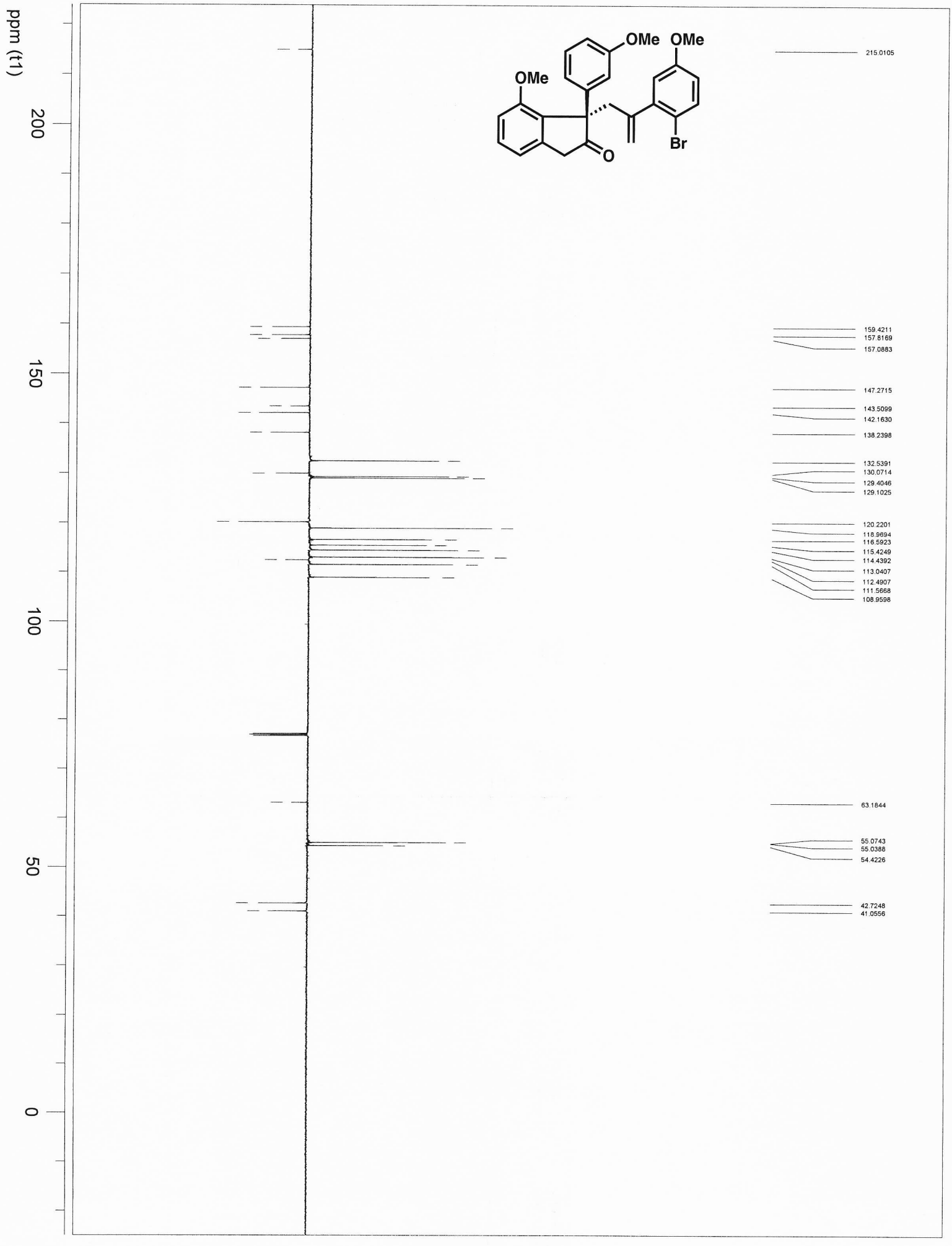

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
OMe
OH
O
7.40999
7.39448
7.37815
7.20963
7.19375
7.17775
7.02248
7.00723
6.97271
6.96905
6.96425
6.89702
6.88048
6.83038
6.82868
6.82521
6.82350
6.81398
6.81225
6.80878
6.77907
6.77722
6.77579
6.77395
6.76361
6.76175
6.76033
6.75847
3.78525
3.77472
3.68797
3.64488
3.57366
3.51272
3.46962

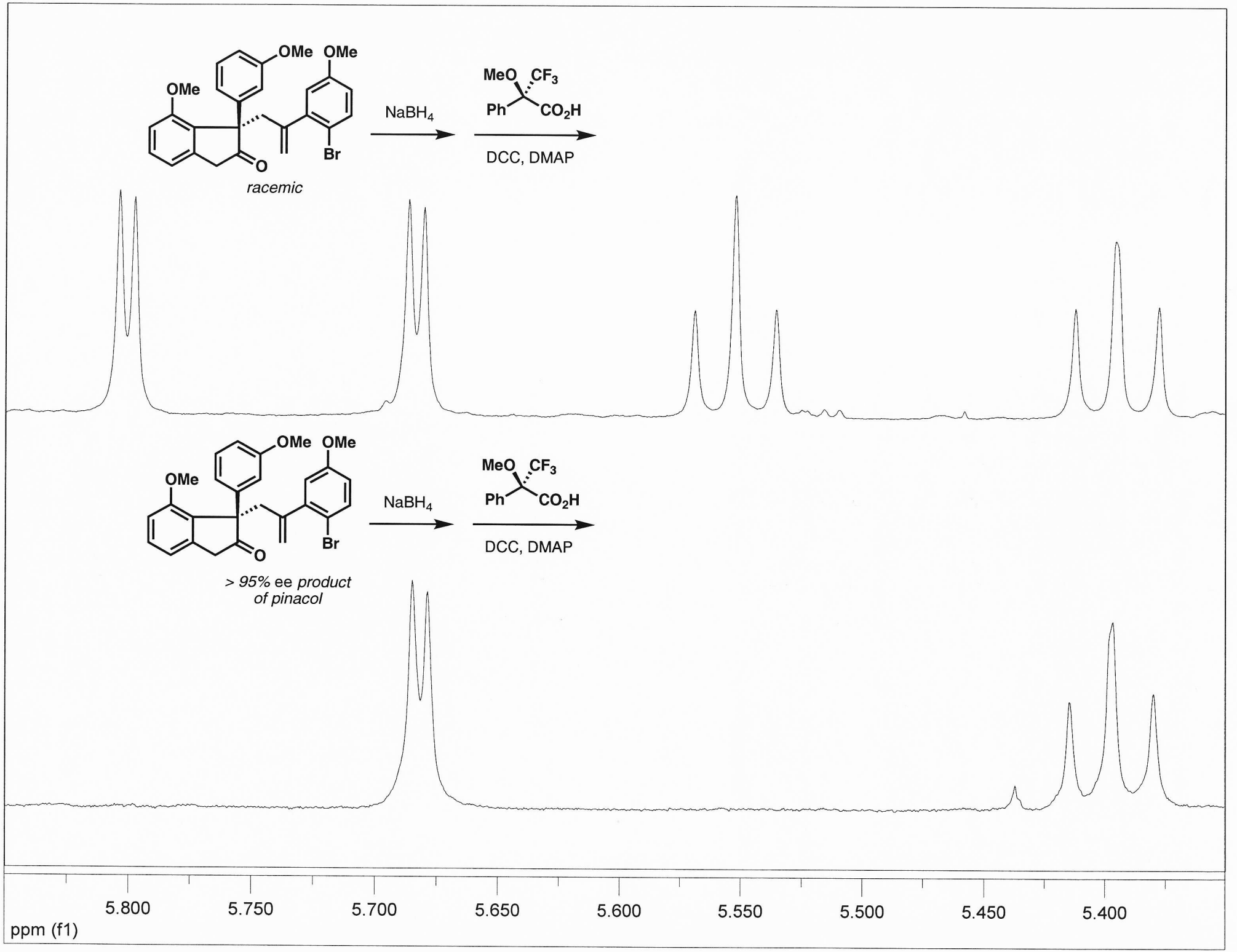

ppm (f1)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
OMe
OMe
OH
O
210.35869
159.86583
156.79468
141.53477
137.50876
130.78001
129.59343
129.45490
117.89602
117.36275
113.70200
111.32227
110.02725
82.19919
55.47731
55.23979
40.16600

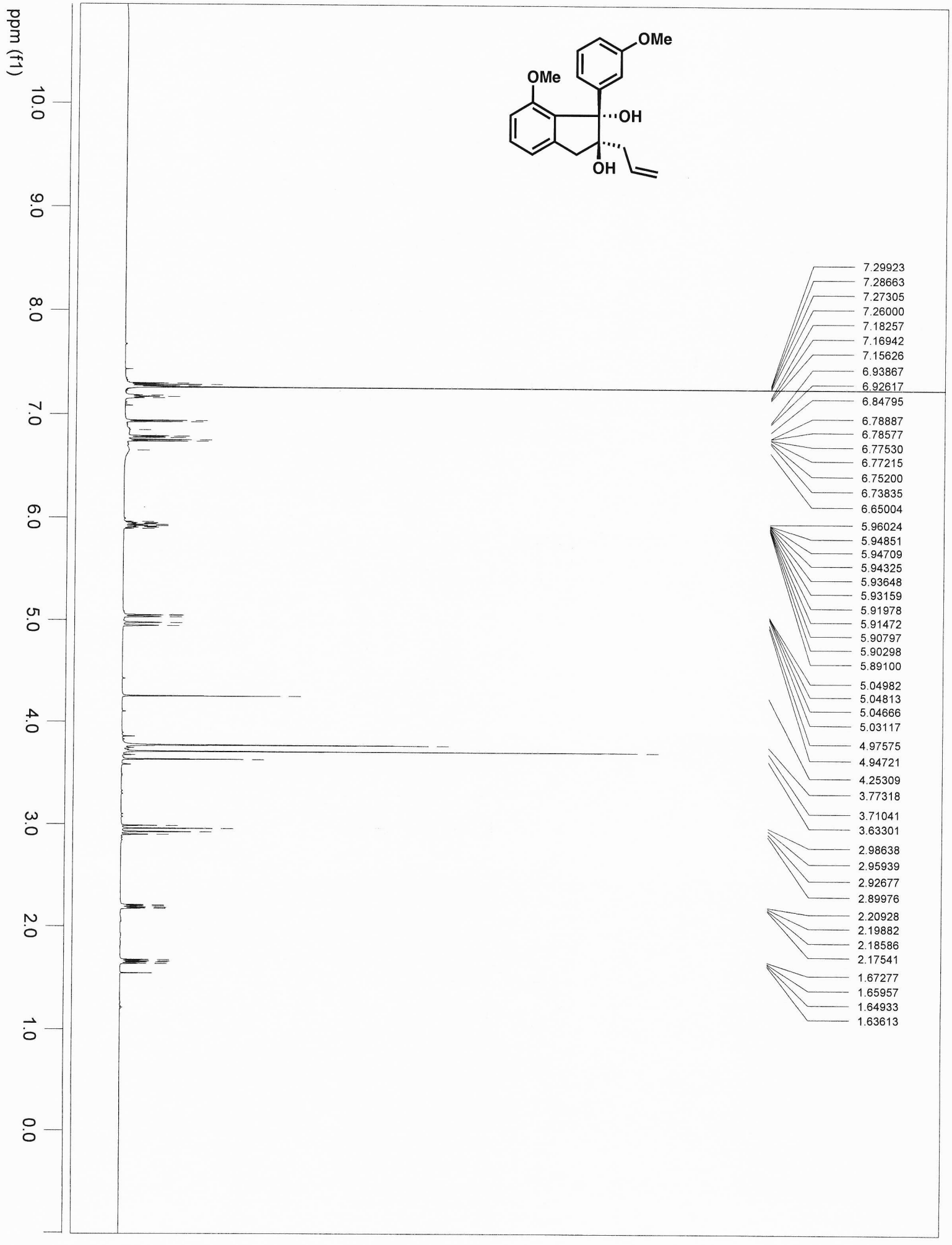

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
Bu3Sn
Br
7.41543
7.40088
7.26000
6.74688
6.74175
6.67416
6.66903
6.65958
6.65446
4.98511
4.70810
3.78118
2.22555
1.36845
1.35750
1.35423
1.34109
1.24496
1.23275
1.22045
1.20823
0.85534
0.84318
0.83103
0.77471
0.76551
0.76102
0.74749

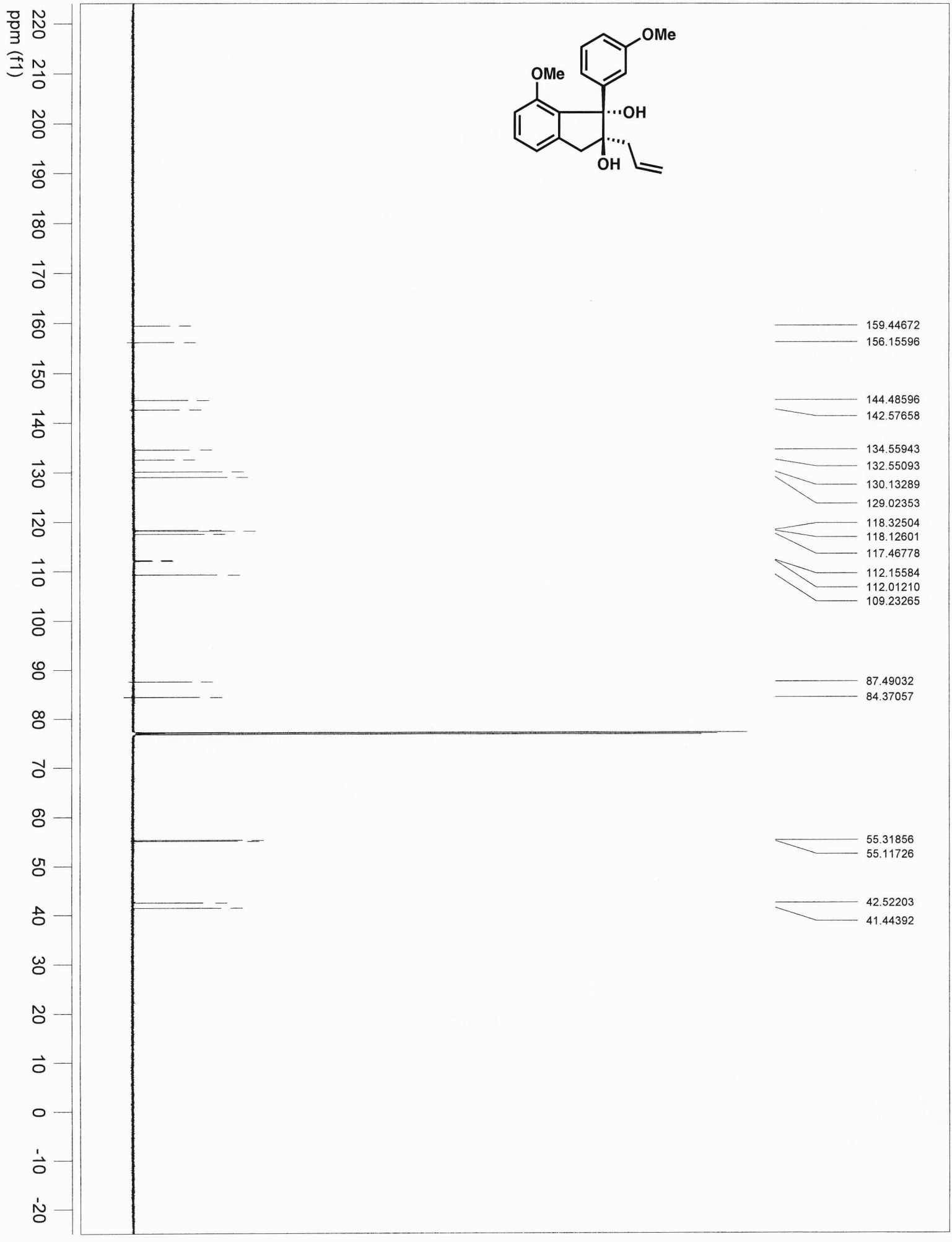

OMe
Bu3Sn
Br
158.67693
150.24956
146.09470
133.52243
115.65578
113.96495
112.19182
110.70702
55.39499
28.97051
27.33867
19.94841
13.66632
9.59319
ppm (f1)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

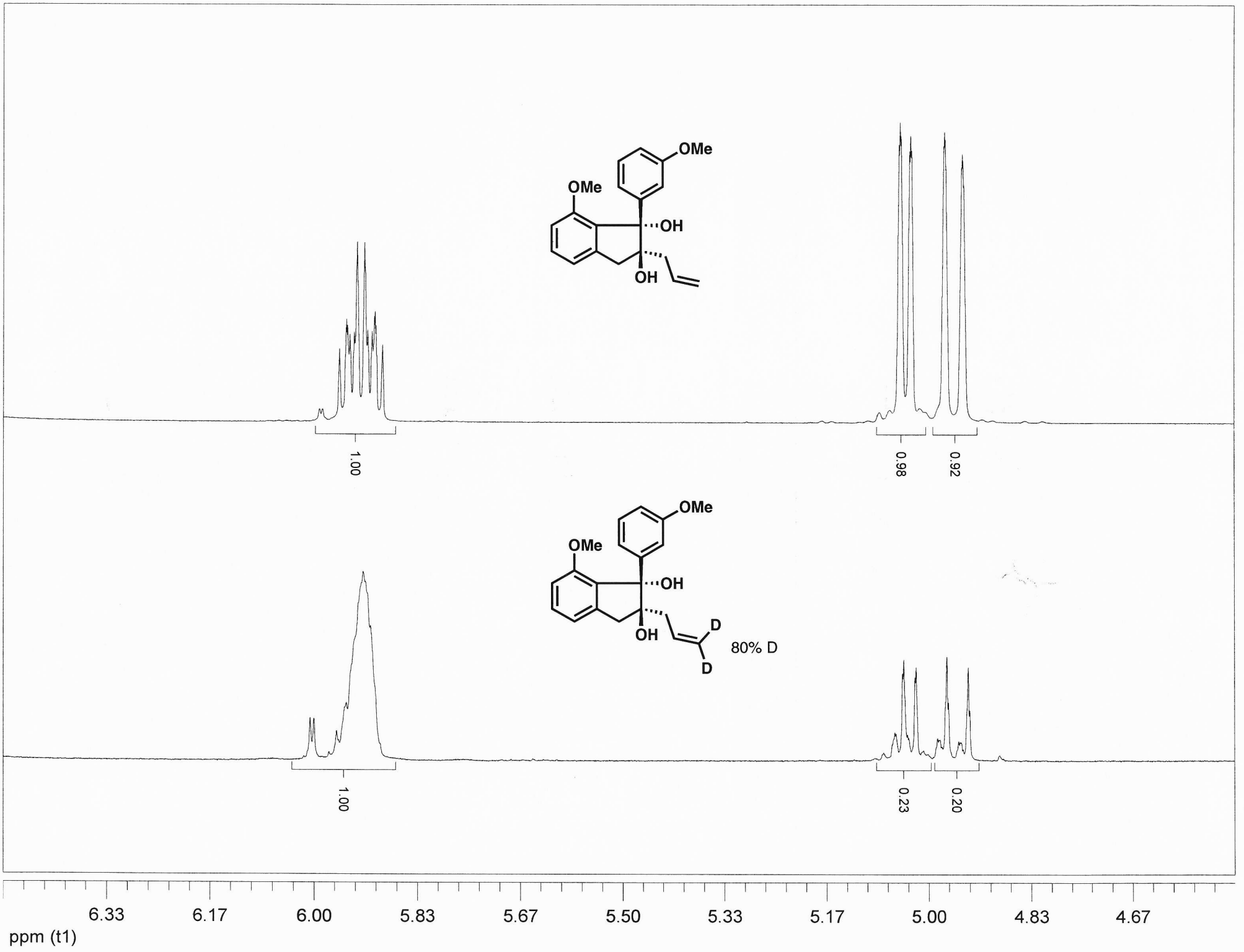

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
OMe
OMe
Br
O
7.27459
7.26000
7.25212
7.23883
7.22573
7.17982
7.16649
7.15318
6.92488
6.91244
6.79870
6.78556
6.76413
6.74893
6.73537
6.73222
6.54240
6.53737
6.52790
6.52269
6.51832
6.50428
5.62743
5.62248
5.24498
4.88248
3.93156
3.90961
3.73783
3.71044
3.57258
3.50203
3.46466
3.42074
3.13094
3.09346

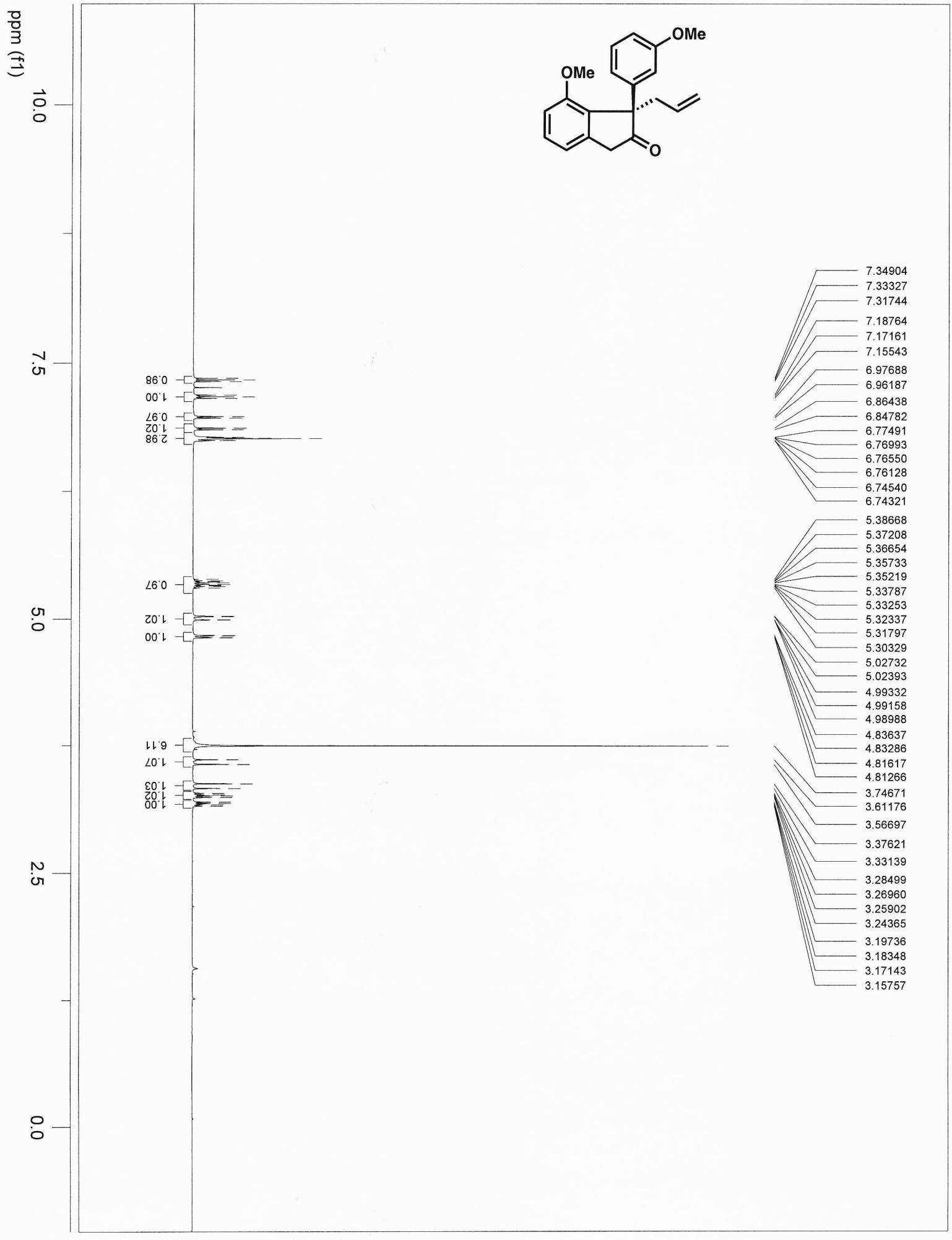

ppm (t1)
200
150
100
50
0
OMe
OMe
OMe
Br
O
215.0105
159.4211
157.8169
157.0883
147.2715
143.5099
142.1630
138.2398
132.5391
130.0714
129.4046
129.1025
120.2201
118.9694
116.5923
115.4249
114.4392
113.0407
112.4907
111.5668
108.9598
63.1844
55.0743
55.0388
54.4226
42.7248
41.0556


OMe
OMe
OMe
Br
O
racemic
NaBH4
MeO
CF3
Ph
CO2H
DCC, DMAP
OMe
OMe
OMe
Br
O
> 95% ee product
of pinacol
NaBH4
MeO
CF3
Ph
CO2H
DCC, DMAP
5.800
5.750
5.700
5.650
5.600
5.550
5.500
5.450
5.400
ppm (f1)


ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
OMe
OMe
OH
OH
7.29923
7.28663
7.27305
7.26000
7.18257
7.16942
7.15626
6.93867
6.92617
6.84795
6.78887
6.78577
6.77530
6.77215
6.75200
6.73835
6.65004
5.96024
5.94851
5.94709
5.94325
5.93648
5.93159
5.91978
5.91472
5.90797
5.90298
5.89100
5.04982
5.04813
5.04666
5.03117
4.97575
4.94721
4.25309
3.77318
3.71041
3.63301
2.98638
2.95939
2.92677
2.89976
2.20928
2.19882
2.18586
2.17541
1.67277
1.65957
1.64933
1.63613


ppm (f1)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
OMe
OMe
OH
OH
159.44672
156.15596
144.48596
142.57658
134.55943
132.55093
130.13289
129.02353
118.32504
118.12601
117.46778
112.15584
112.01210
109.23265
87.49032
84.37057
55.31856
55.11726
42.52203
41.44392


OMe
OMe
OH
OH
1.00
0.98
0.92
OMe
OMe
OH
OH
D
D
80% D
1.00
0.23
0.20
6.33
6.17
6.00
5.83
5.67
5.50
5.33
5.17
5.00
4.83
4.67
ppm (t1)


ppm (f1)
10.0
7.5
5.0
2.5
0.0
OMe
OMe
O
0.98
1.00
0.97
1.02
2.98
0.97
1.02
1.00
6.11
1.07
1.03
1.02
1.00
7.34904
7.33327
7.31744
7.18764
7.17161
7.15543
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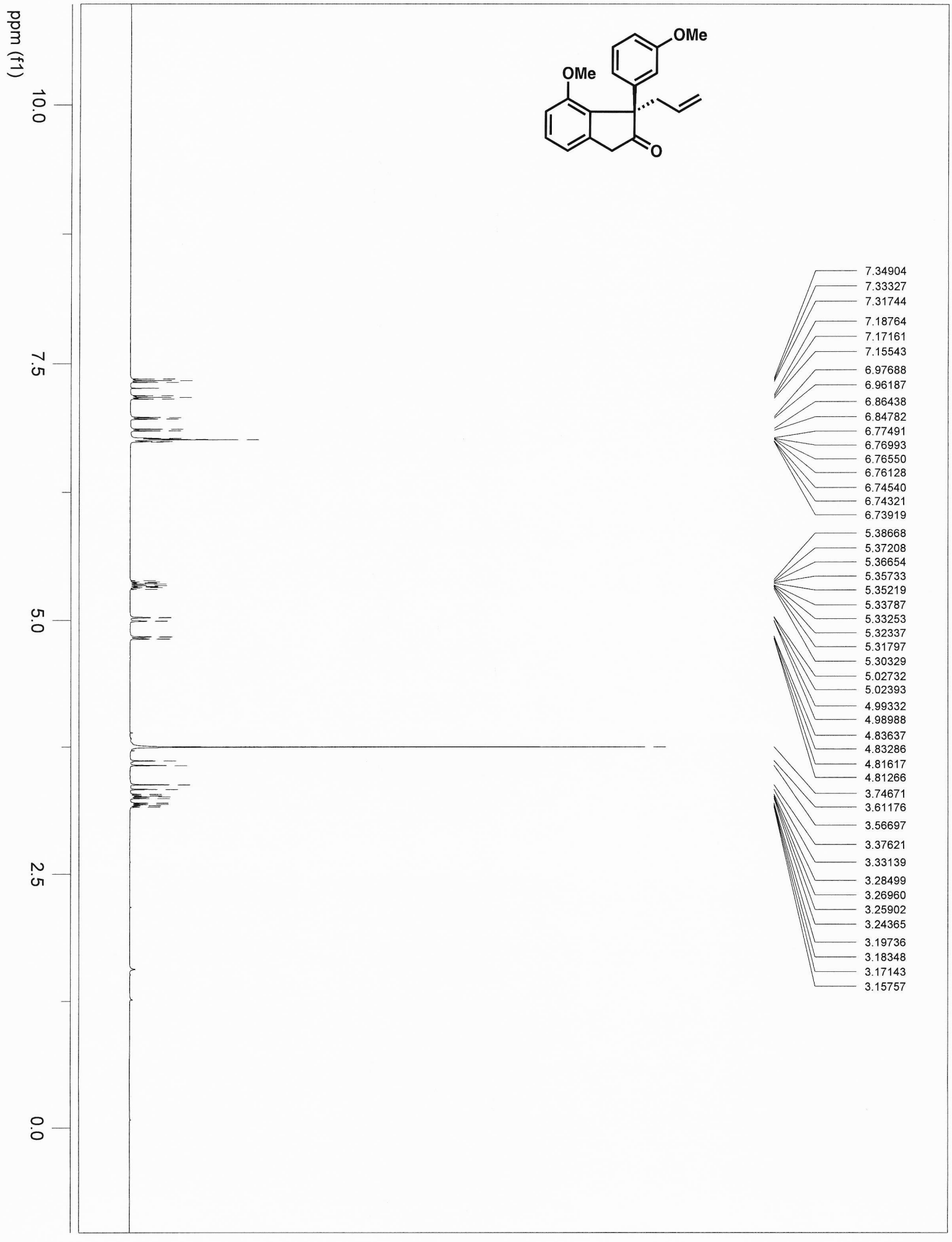
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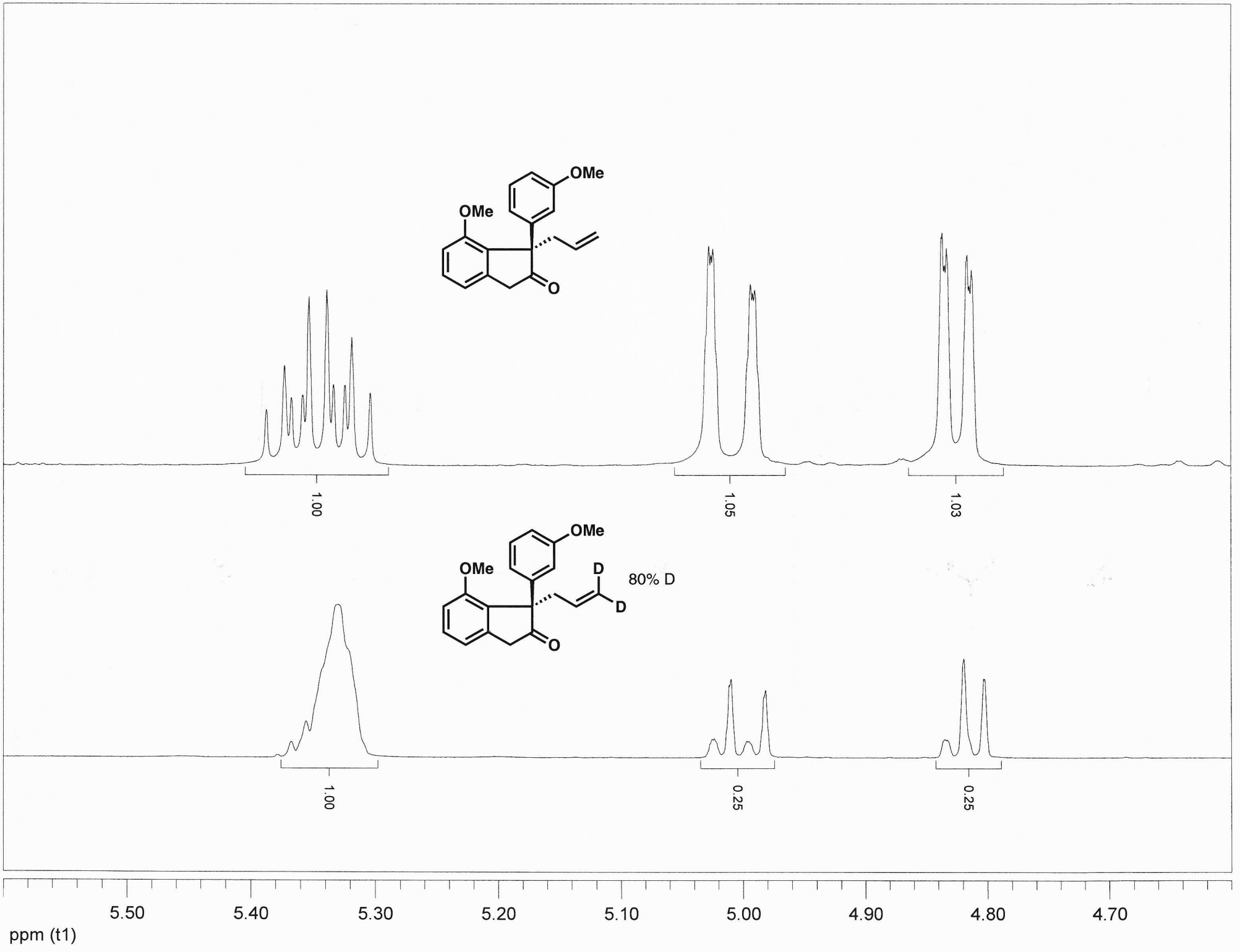
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5.20
5.10
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4.90
4.80
4.70
ppm (t1)