



Supporting Information

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On the Origin of the Haouamine Alkaloids

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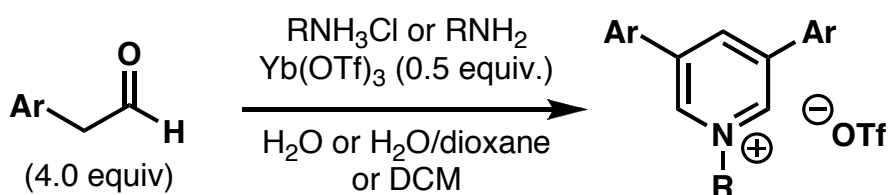
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General Procedures. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), triethylamine (TEA), dichloromethane (DCM), methanol (MeOH), dimethylformamide (DMF), and benzene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H 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 $\text{H}_2\text{SO}_4/\text{CH}_3\text{CO}_2\text{H}$ 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 Spectrum BX spectrometer. High resolution mass spectra (HRMS)

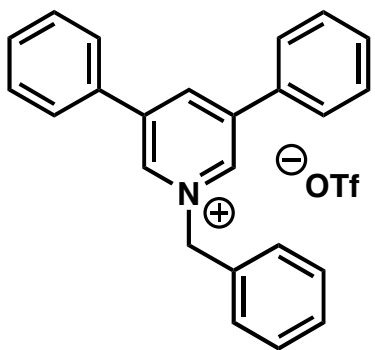
were recorded on an Agilent Mass spectrometer (at Scripps) using ESI-TOF (electrospray ionization-time of flight) or a ThermoFinnigan Mass spectrometer (at UCSD) using FAB (fast atom bombardment), or EI (electron impact). Low resolution mass spectra (LRMS) were recorded on an Agilent (at Scripps) or 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 arylaldehyde (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 MgSO₄, 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;

R_f = 0.30 (silica gel, 9:1 DCM/MeOH);

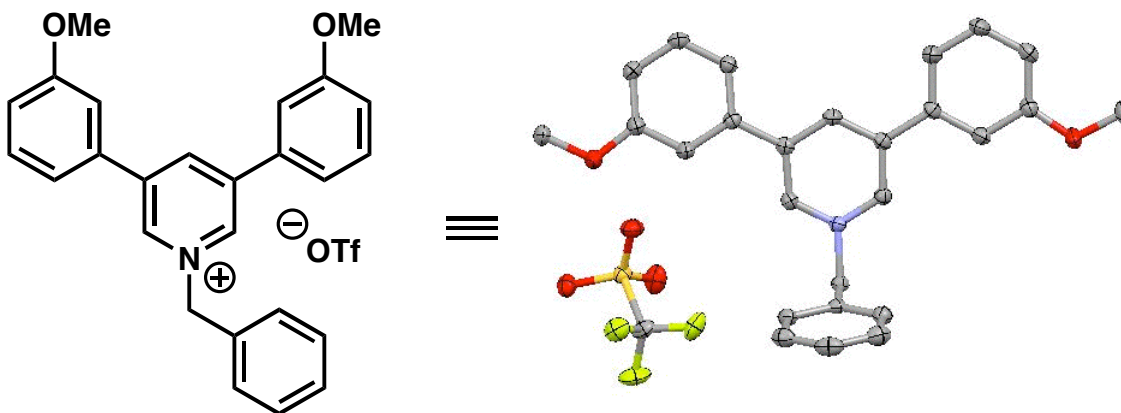
IR (film) ν_{max} 3063, 1252 (s), 1156, 1027 (s), 901, 758, 695, 636 (s) cm^{-1} ;

¹H NMR (500 MHz, CDCl₃) 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);

¹³C-APT NMR (125 MHz, CDCl₃) 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 C₂₄H₂₀N [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;

R_f = 0.28 (silica gel, 9:1 DCM/MeOH);

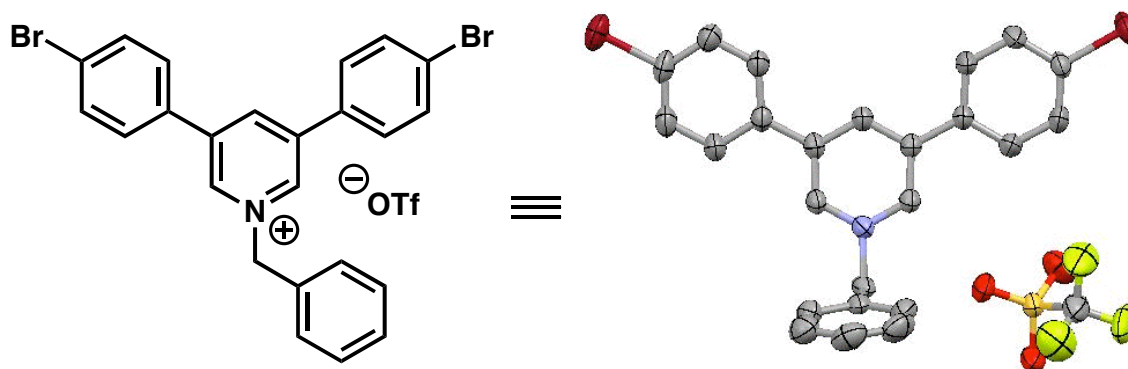
IR (film) ν_{max} 1587, 1480, 1255 (s), 1159, 1027 (s), 909, 783, 754, 728, 691, 636 (s) cm⁻¹;

¹H NMR (600 MHz, CDCl₃) 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);

¹³C-APT NMR (150 MHz, CDCl₃) 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 C₂₆H₂₄NO₂ [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);

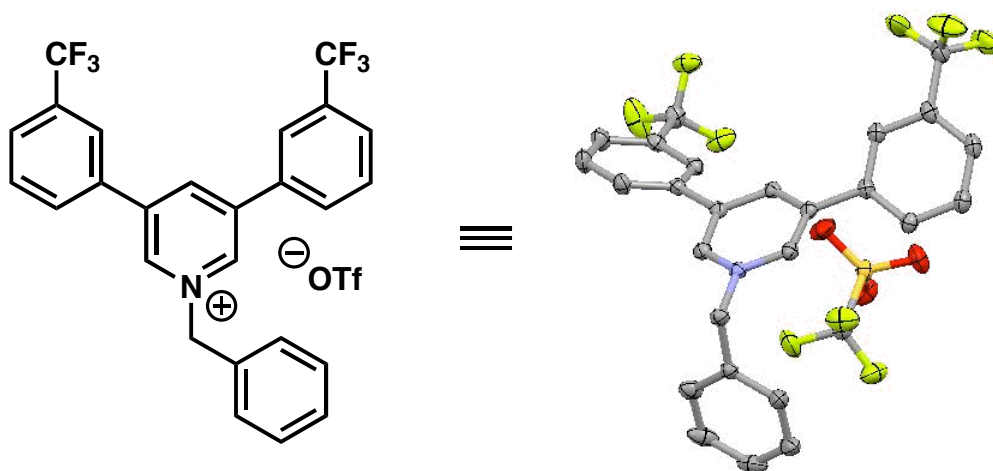
IR (film) ν_{max} 1594, 1476, 1252 (s), 1222, 1159, 1027, 1005, 817, 710, 636 cm⁻¹;

¹H NMR (600 MHz, CD₃CN) 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);

¹³C-APT NMR (150 MHz, CD₃CN) 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 C₂₄H₁₈Br₂N [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);

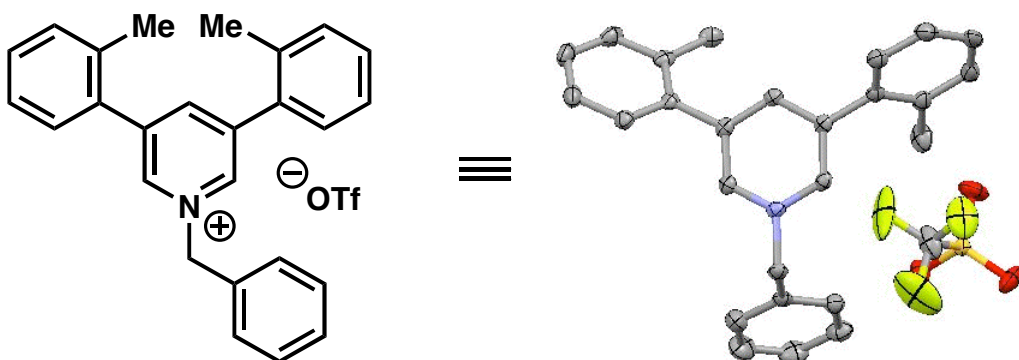
IR film $\nu_{\max}$ 2354, 1329, 1252 (s), 1159, 1123 (s), 1071, 1027 (s), 802, 699, 636 cm^{-1} ;

^1H 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 $\text{C}_{26}\text{H}_{18}\text{F}_6\text{N}$ [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);

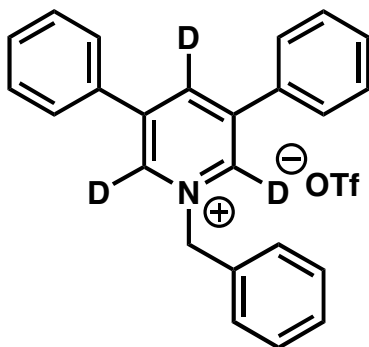
IR (film) $\nu_{\max}$ 1476, 1454, 1255 (s), 1222, 1152, 1027 (s), 761, 635 cm^{-1} ;

^1H 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 $\text{C}_{26}\text{H}_{24}\text{N}$ [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)

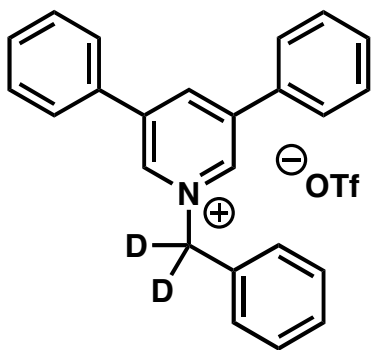
IR (film) ν_{max} 2354, 2332, 1554, 1418, 1252, 1152, 1027, 750, 695, 636, 514 cm^{-1} ;

^1H 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 $\text{C}_{24}\text{H}_{17}\text{D}_3\text{N}$ [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);

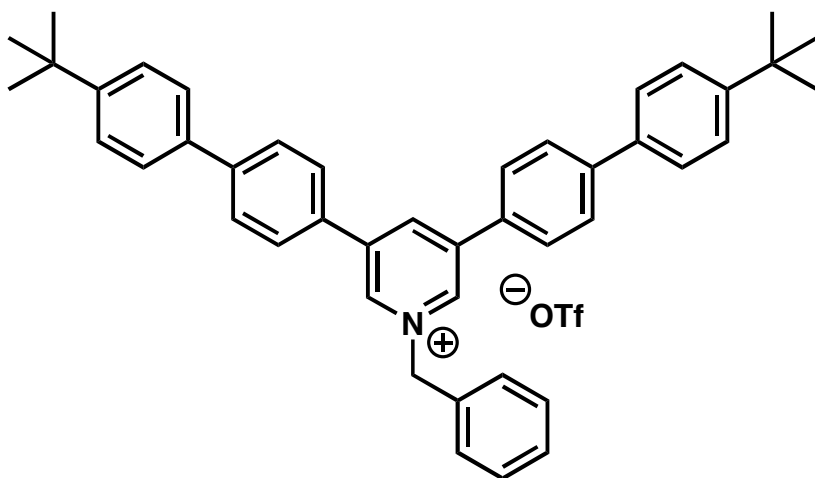
IR (film) ν_{max} 3067, 1595, 1498, 1475, 1442, 1257 (s), 1225, 1157, 1029 (s), 759, 696 cm^{-1} ;

¹H NMR (500 MHz, CDCl₃) 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);

¹³C-APT NMR (150 MHz, CDCl₃): 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 C₂₄H₁₈D₂N [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)-benzaldehyde¹ (6 mg, 0.7 equiv based on isolated product) and the title pyridinium as a white solid (26 mg, 65%);

m.p. > 300 °C;

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;

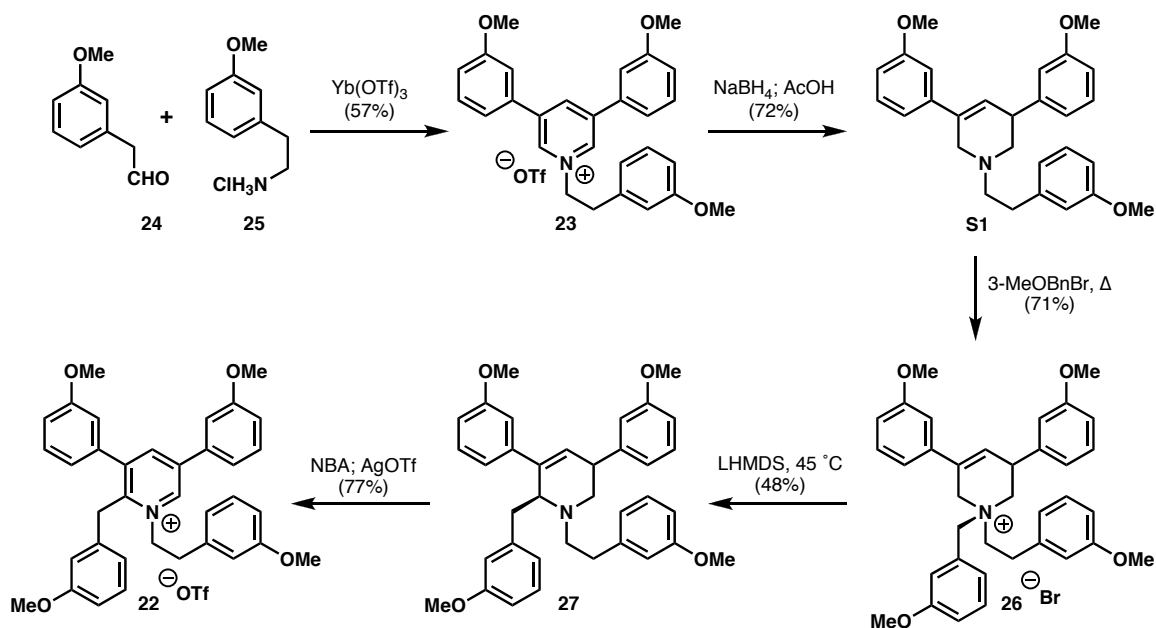
¹H NMR (500 MHz, CDCl₃) δ 9.18 (s, 2 H), 8.45 (s, 1 H), 7.79 (d, *J* = 8.4 Hz, 4 H), 7.73 (d, *J* = 8.4 Hz, 4 H), 7.62 – 7.6- (m, 2 H), 7.52 (d, *J* = 8.4 Hz, 4 H), 7.47 (d, *J* = 8.4 Hz, 4 H), 7.40 – 7.36 (m, 3 H), 6.16 (s, 2 H), 1.36 (s, 18 H);

¹³C-APT NMR (150 MHz, CDCl₃) 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;

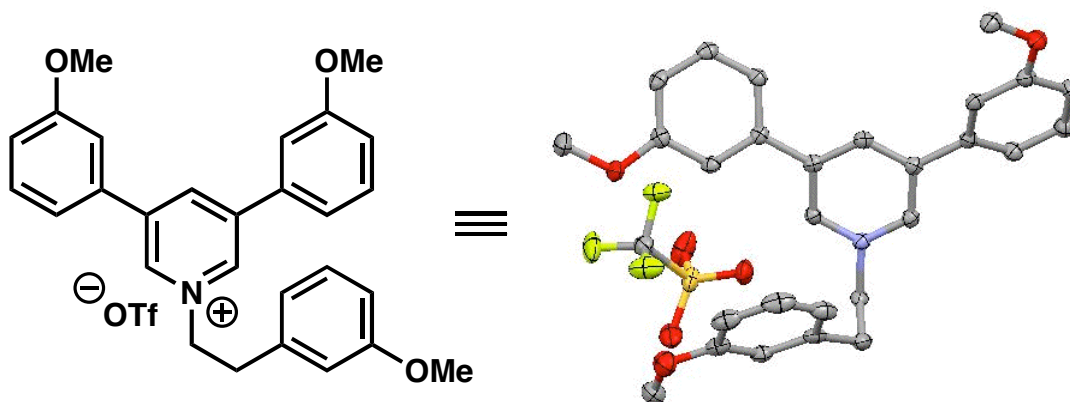
HRMS (ESI) calcd. for [M⁺] 586.3474 found 586.3469.

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);

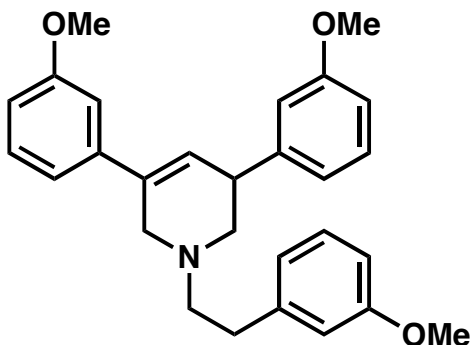
IR (film) ν_{max} 2937, 1735, 1594, 1583, 1488, 1454, 1255 (s), 1152, 1027, 783, 691, 636 cm^{-1} ;

¹H NMR (500 MHz, CDCl₃) 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);

¹³C-APT NMR (150 MHz, CDCl₃) 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 C₂₈H₂₈NO₃ [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 MgSO₄, 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)

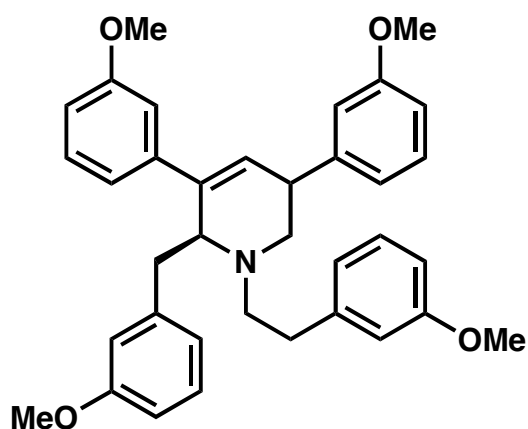
IR (film) ν_{max} 2930, 2827, 1598, 1580, 1484, 1462, 1451, 1429, 1285, 1259, 1148, 1045, 780, 691 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) 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);

¹³C-APT NMR (150 MHz, CDCl₃) 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 C₂₈H₃₁NO₃ [*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 μ L) was added 3-methoxybenzylbromide (167 μ L, 1.2 mmol, 10.0 equiv), and the reaction mixture was heated in a 60 $^{\circ}$ 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 $^{\circ}$ C oil bath. LHMDS (720 μ L, 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} ;

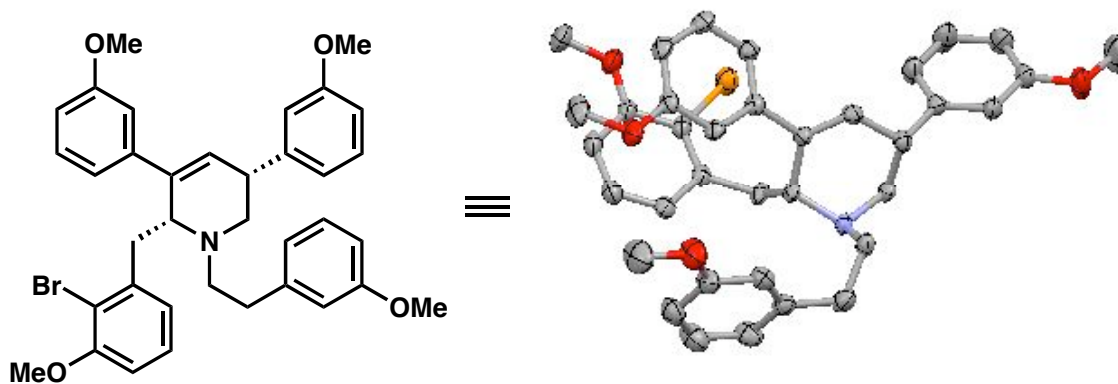
^1H NMR (600 MHz, CDCl_3) δ 7.31 (dt, J = 2.9, 8.0 Hz, 1.3 H), 7.25 – 7.20 (m, 0.7 H), 7.19 – 7.15 (m, 1.7 H), 7.10 (t, J = 7.8 Hz, 0.3 H), 7.01 (d, J = 7.7 Hz, 0.7 H), 6.95 – 6.92 (m, 1 H), 6.87 – 6.61 (m, 10.3 H), 6.12 (s, 0.7 H), 6.05 (s, 0.3 H), 4.05 (s, 0.3 H), 3.90 (d,

$J = 8.8$ 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);

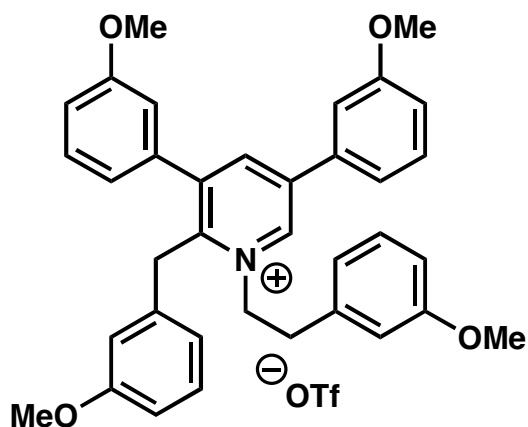
^{13}C -APT NMR (150 MHz, CDCl_3) δ 159.72, 159.67, 159.51, 159.45, 159.44, 159.4, 159.1, 158.8, 145.9, 145.2, 142.5, 142.4, 142.3, 142.2, 142.0, 141.39, 141.37, 140.4, 129.6, 129.5, 129.3, 129.2, 128.84, 128.79, 128.4, 127.4, 122.2, 121.6, 121.1, 121.0, 120.4, 120.3, 119.1, 118.7, 115.3, 115.0, 114.3, 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 $\text{C}_{36}\text{H}_{40}\text{NO}_4$ $[\text{M} + \text{H}^+]$ 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. $\text{Na}_2\text{S}_2\text{O}_4$ (10 mL). The organic layer was extracted with EtOAc (2 $\times$ 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} ;

^1H 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),

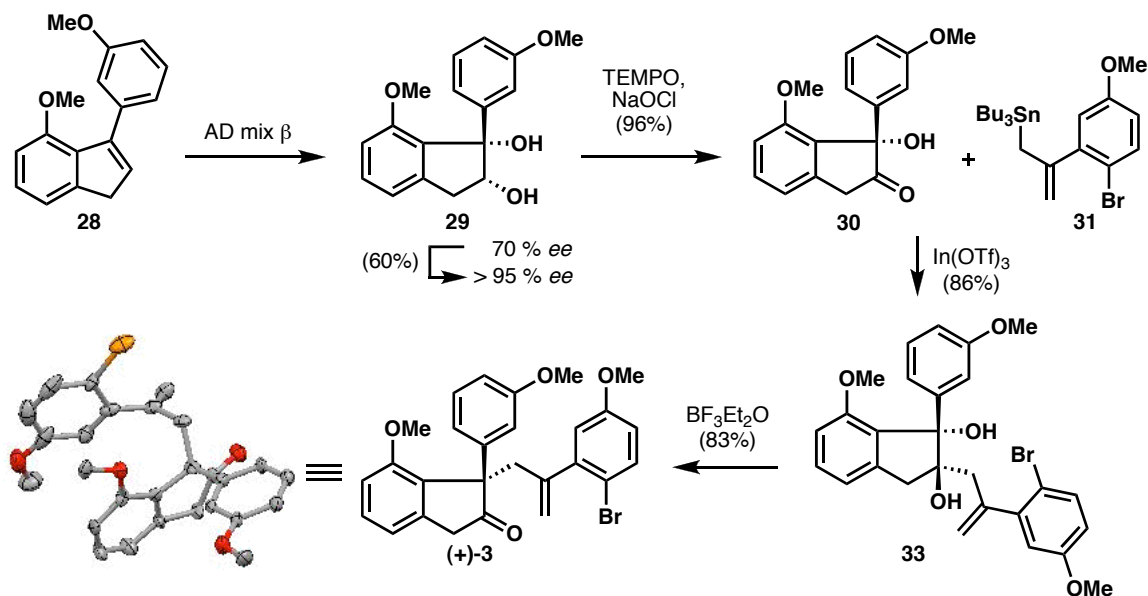
5.00 (t, $J = 7.0$ Hz, 2 H), 4.29 (s, 2 H), 3.91 (s, 3 H), 3.761 (s, 3 H), 3.760 (s, 3 H), 3.75 (s, 3 H), 3.02 (t, $J = 7.0$ Hz, 2 H);

^{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.

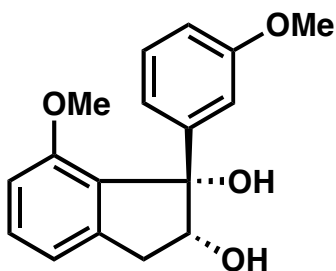
^{13}C -APT NMR (150 MHz, CD_2Cl_2): δ 161.3, 161.1, 160.9, 160.6, 152.6, 144.8, 144.4, 144.3, 139.6, 137.4, 137.1, 136.8, 134.2, 131.4, 131.3, 131.0, 130.9, 121.7, 121.3, 120.3, 120.1, 117.0, 116.0, 115.2, 114.8, 114.6, 113.8, 113.5, 113.1, 60.8, 56.3, 55.95, 55.88, 55.8, 37.7, 36.1.

HRMS (ESI) calcd. for $\text{C}_{36}\text{H}_{36}\text{NO}_4$ [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 described³) 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), K₂CO₃ (4.56 g, 33.0 mmol, 3.0 equiv), and H₂O (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 Na₂S₂O₃ (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 MgSO₄, 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%).

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);

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

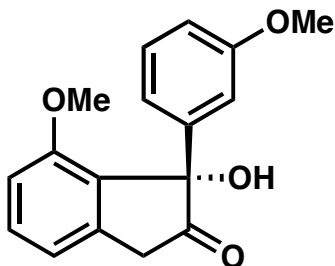
IR (film) ν_{max} 3447 (br), 2937, 2835, 1589, 1480 (s), 1262 (s), 1078 (s), 1044 (s) cm^{-1} ;

^1H 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 $\text{C}_{17}\text{H}_{18}\text{O}_4$ $[\text{M} + \text{Na}^+]$ 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 $\times$ 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 °C;

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

[α]_D = +37.9° (CH_2Cl_2 , *c* 0.43);

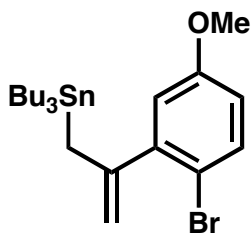
IR (film) ν_{max} 3467 (br) 3011, 1744 (s), 1587 (s), 1484 (s), 1291 (s), 1053 (s) cm^{-1} ;

¹H 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);

¹³C 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 $\text{C}_{17}\text{H}_{16}\text{O}_4$ [$\text{M} + \text{Na}^+$] 307.0941, found 307.0929.

Allyl stannane 31:



The corresponding allyl iodide (1.41 g, 3.99 mmol, synthesized as previously described³) was dissolved in dry THF (20 mL) and treated with bis(tributyltin) (2.0 mL, 3.99 mmol, 1.0 equiv) followed by $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (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.

NaHCO₃ (50 mL) was added and the mixture was extracted with Et₂O (2 × 100 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL) and dried over MgSO₄, 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%).

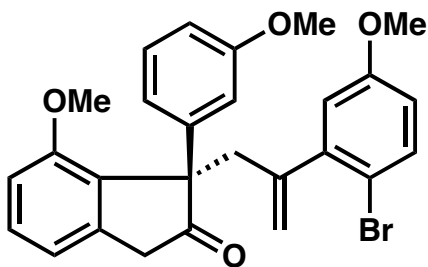
R_f = 0.15 (silica gel, hexanes);

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

¹H NMR (600 MHz, CDCl₃) 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);

¹³C NMR (150 MHz, CDCl₃) 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 $\rightarrow$ 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 trifluoride 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 $\rightarrow$ 6:1 hexanes/EtOAc) afforded the title ketone as a white solid (603 mg, 83%).

m.p. = 88 – 90 °C;

R_f = 0.39 (silica gel, 1:1 hexanes/ Et_2O);

$[\alpha]_D$ = +6.8° (CH_2Cl_2 , c 0.5);

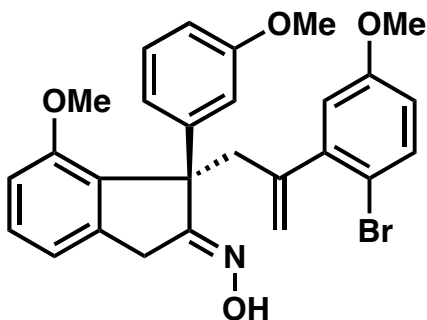
IR (film) ν_{max} 1749 (s), 1586 (s), 1482 (s), 1463 (s), 1289 (s), 1264 (s), 1050 (s), 1016 cm^{-1} ;

^1H 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);

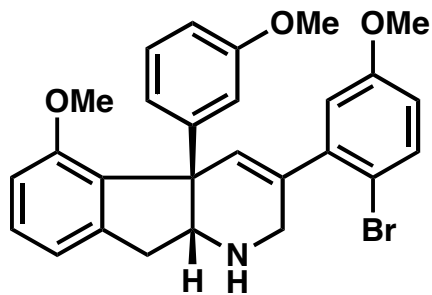
^{13}C NMR (150 MHz, CDCl_3) δ 215.2, 159.6, 158.0, 157.3, 147.5, 143.7, 142.4, 138.5, 132.7, 130.3, 129.6, 129.3, 120.4, 119.2, 116.8, 115.6, 114.6, 113.2, 112.7, 111.8, 109.2, 63.4, 55.3, 55.2, 54.6, 42.9, 41.3;

HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{25}\text{BrO}_4$ $[\text{M} + \text{H}^+]$ 493.1014, found 493.0988.

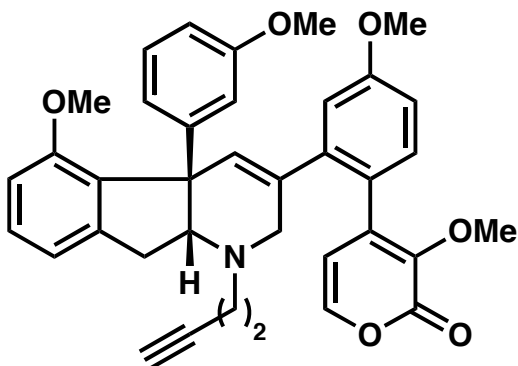
The following compounds were spectroscopically identical to those we reported previously¹ except for optical rotation data given below:



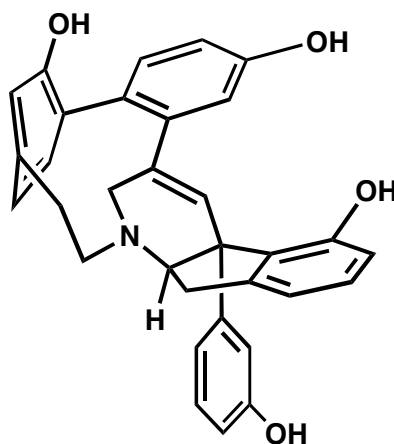
$[\alpha]_D = -13.5^\circ$ (CH_2Cl_2 , c 0.45)



$[\alpha]_D = +18.8^\circ$ (2:1 MeOH/ CH_2Cl_2 , c 0.47)

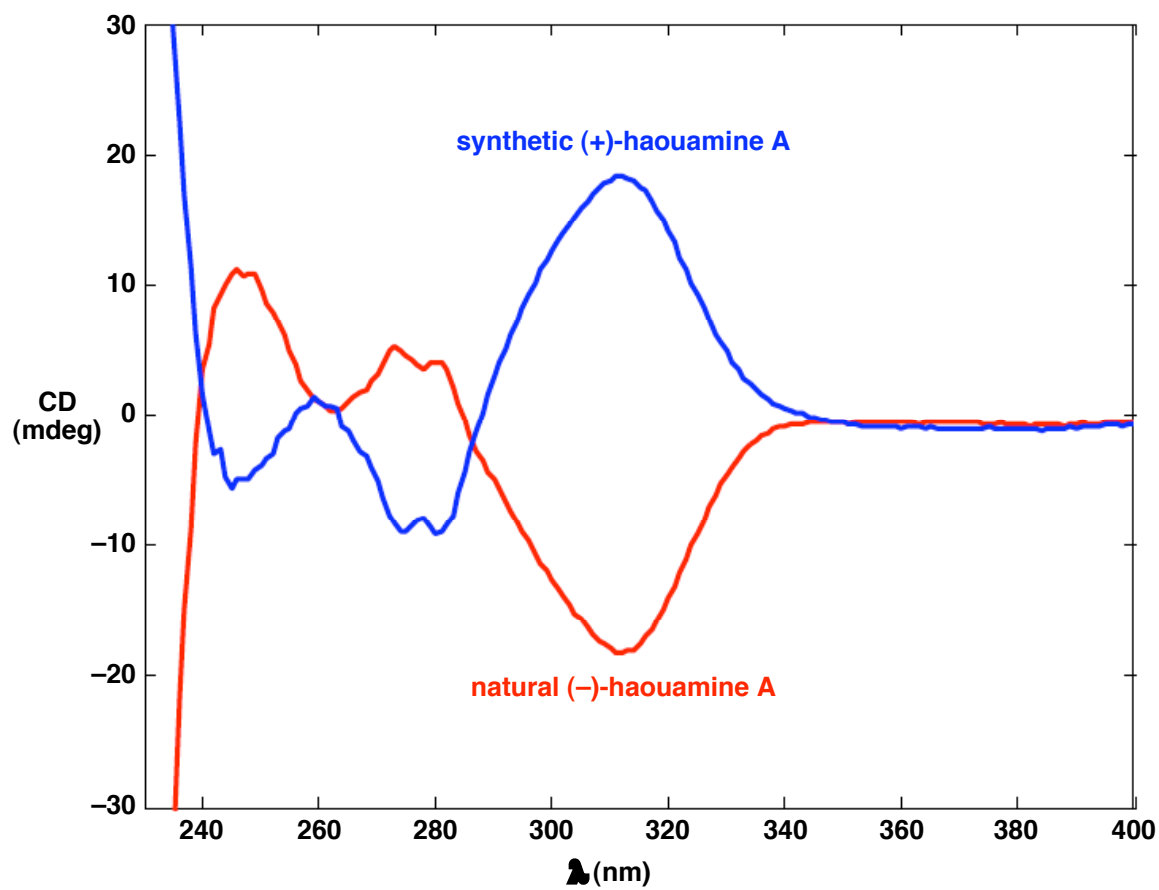


$[\alpha]_D = +66.3^\circ$ (CH_2Cl_2 , c 0.40)

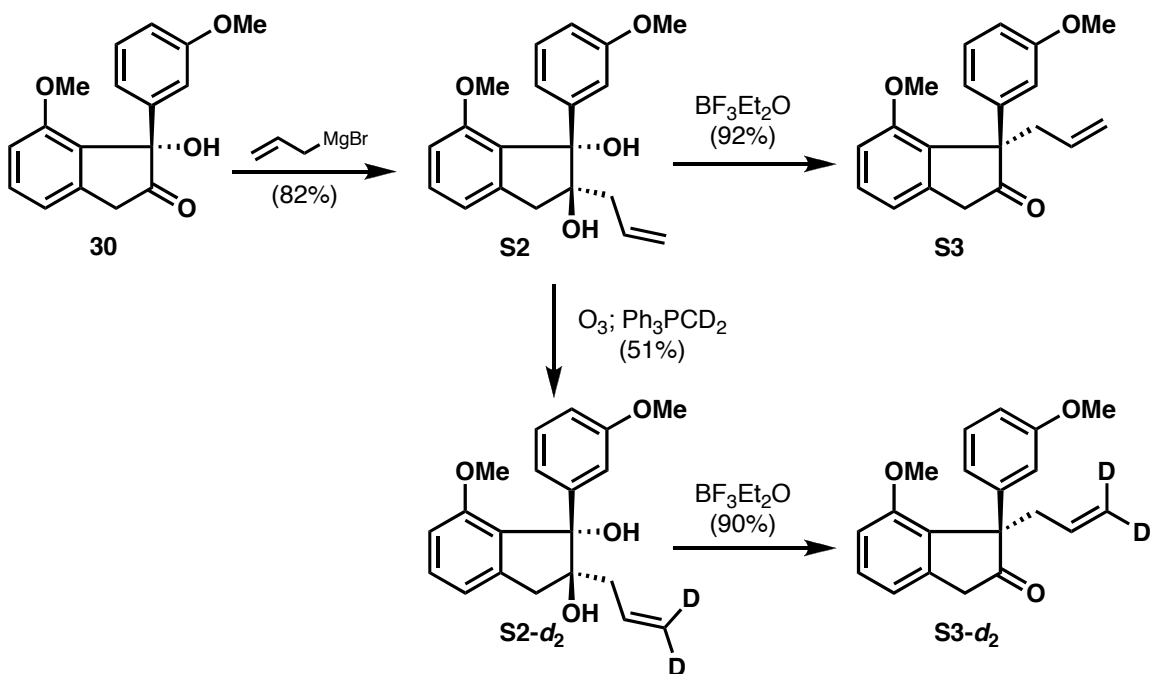


(+)-Haouamine A: $[\alpha]_D = +45.8^\circ$ (MeOH, c 0.05)

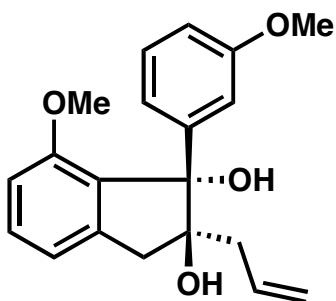
Figure S1. Circular dichroism spectrum of natural-(–)- and synthetic-(+)-haouamine A.



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 μ L, 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. NH₄Cl (5 mL). This mixture was extracted with EtOAc (2 $\times$ 20 mL), and the combined organic layers were dried over MgSO₄, 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/Et₂O);

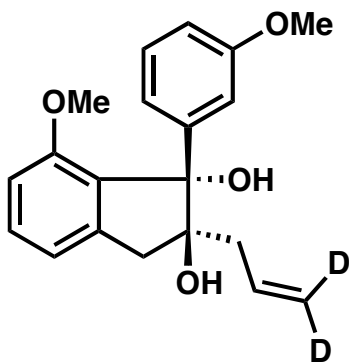
IR (film) $\nu_{\max}$ 3509 (br), 2937, 2834, 1592, 1480 (s), 1260 (s), 1085, 1039 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) 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);

¹³C NMR (150 MHz, CDCl₃) 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 C₂₀H₂₂O₄ [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 CH₂Cl₂ (1 mL) and cooled to -78°. Ozone was bubbled through the solution for 5 min, and the reaction mixture was then quenched with Me₂S (2 mL) and warmed to room temperature. Et₂O (20 mL) and 5 % NaHCO₃ (3 mL) were added and the organic phase was washed with H₂O (10 mL) and brine (10 mL), dried over MgSO₄, filtered, and concentrated. The

crude aldehyde was dissolved in dry THF (3 mL) and a solution of $\text{Ph}_3\text{P}=\text{CD}_2$ (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;

R_f = 0.67 (silica gel, 1:1 hexanes/ EtOAc);

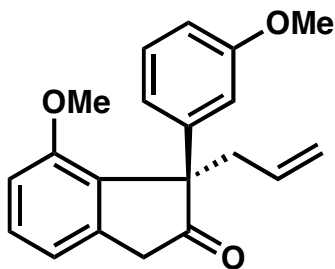
IR (film) ν_{max} 3509 (br), 1592, 1480 (s), 1261 (s), 1083, 1042 (s) cm^{-1} ;

^1H 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, 6.3 Hz, 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 $\text{C}_{20}\text{H}_{20}\text{D}_2\text{O}_4$ [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 trifluoride diethyl etherate (17 μ L, 0.13 mmol, 1.1 equiv) dropwise. After stirring for 10 min at 0°, sat. aq. NaHCO₃ (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 MgSO₄, filtered and concentrated. Flash column chromatography (silica gel, 9:1 hexanes/Et₂O) afforded the title ketone as a clear oil (34 mg, 92%).

R_f = 0.35 (silica gel, 4:1 hexanes/Et₂O);

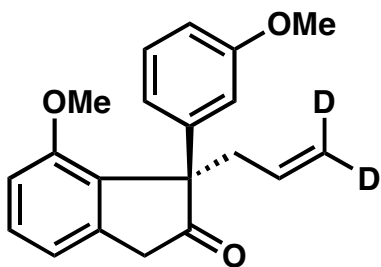
IR (film) ν_{max} 2915, 2841, 1746 (s), 1583, 1480, 1292, 1248 (s), 1053, 769, 695 cm⁻¹;

¹H NMR (500 MHz, CDCl₃) 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);

¹³C NMR (150 MHz, CDCl₃) 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 C₂₀H₂₁O₃ [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 trifluoride diethyl etherate (11 µL, 0.084 mmol, 1.1 eq) dropwise. After stirring for 10 min at 0 °C, sat. aq. NaHCO₃ (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 MgSO₄, filtered and concentrated. Flash column chromatography (silica gel, 2:1 hexanes/Et₂O) afforded the title ketone as a white film (21.2 mg, 90%).

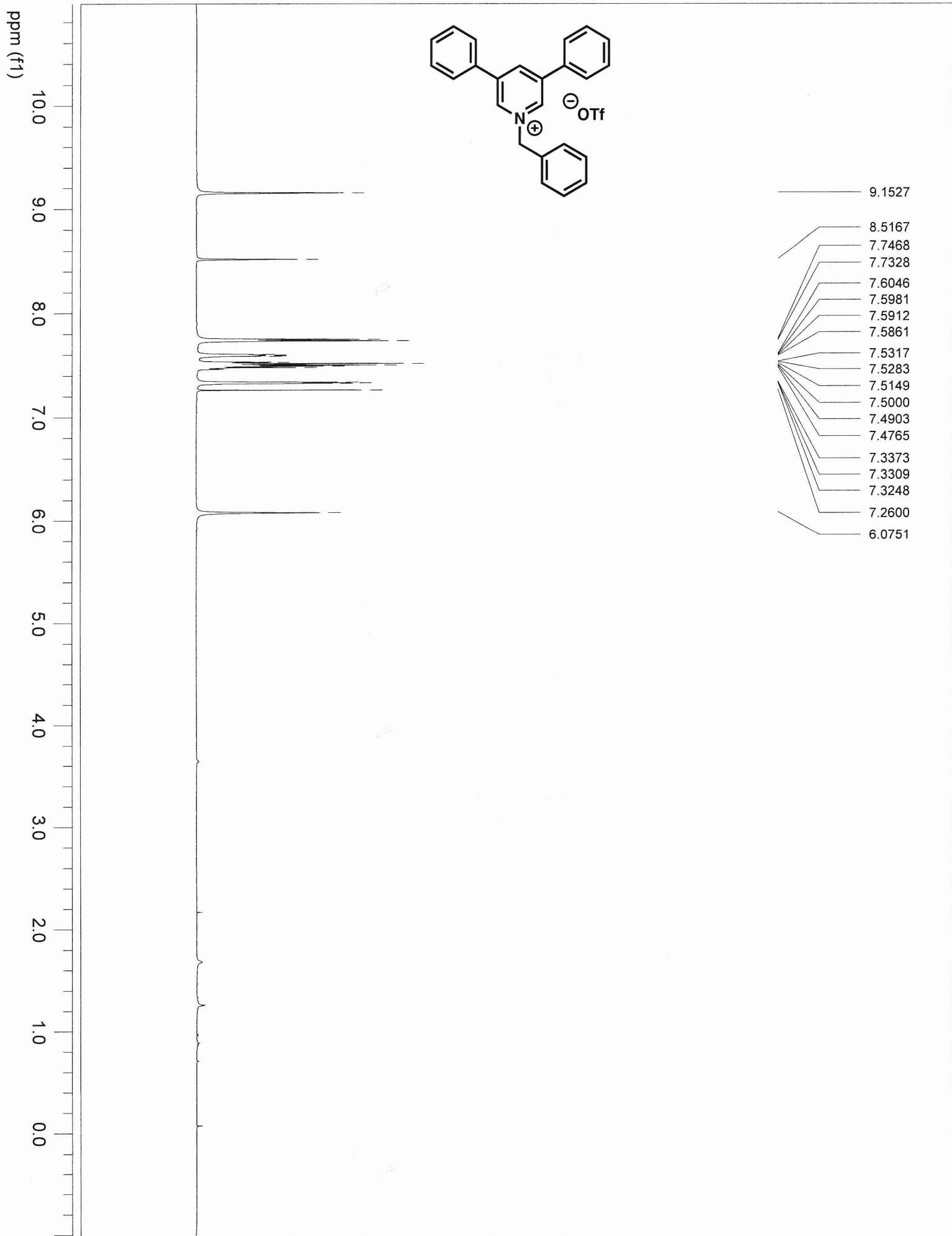
R_f = 0.58 (silica gel, 1:1 hexanes/Et₂O);

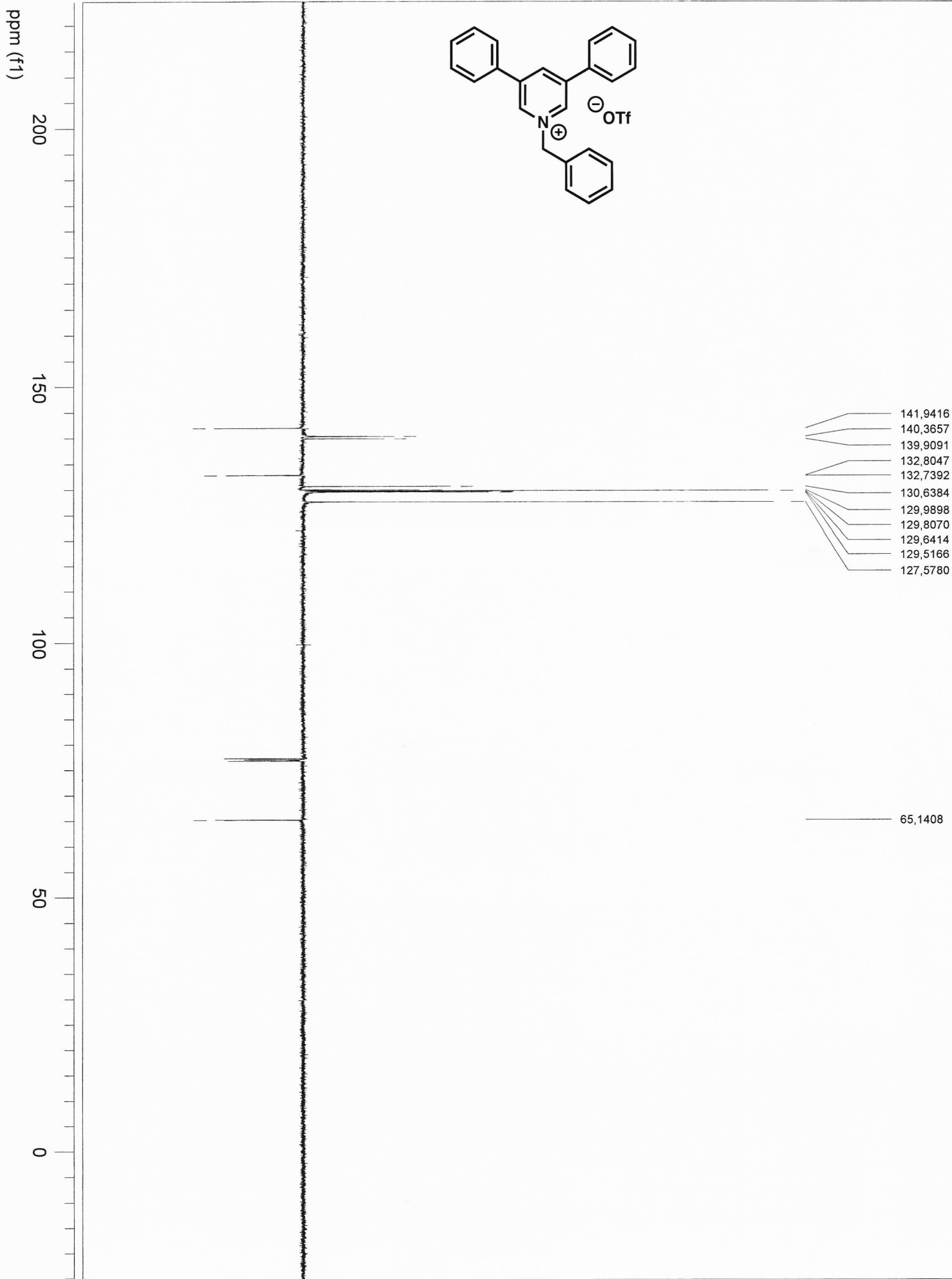
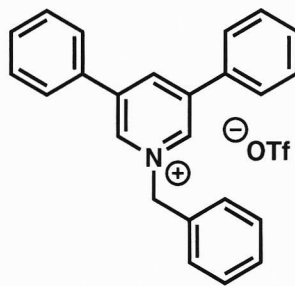
IR (film) ν_{max} 2936, 1749 (s), 1584 (s), 1482 (s), 1289 (s), 1252 (s), 1143, 1053 cm⁻¹;

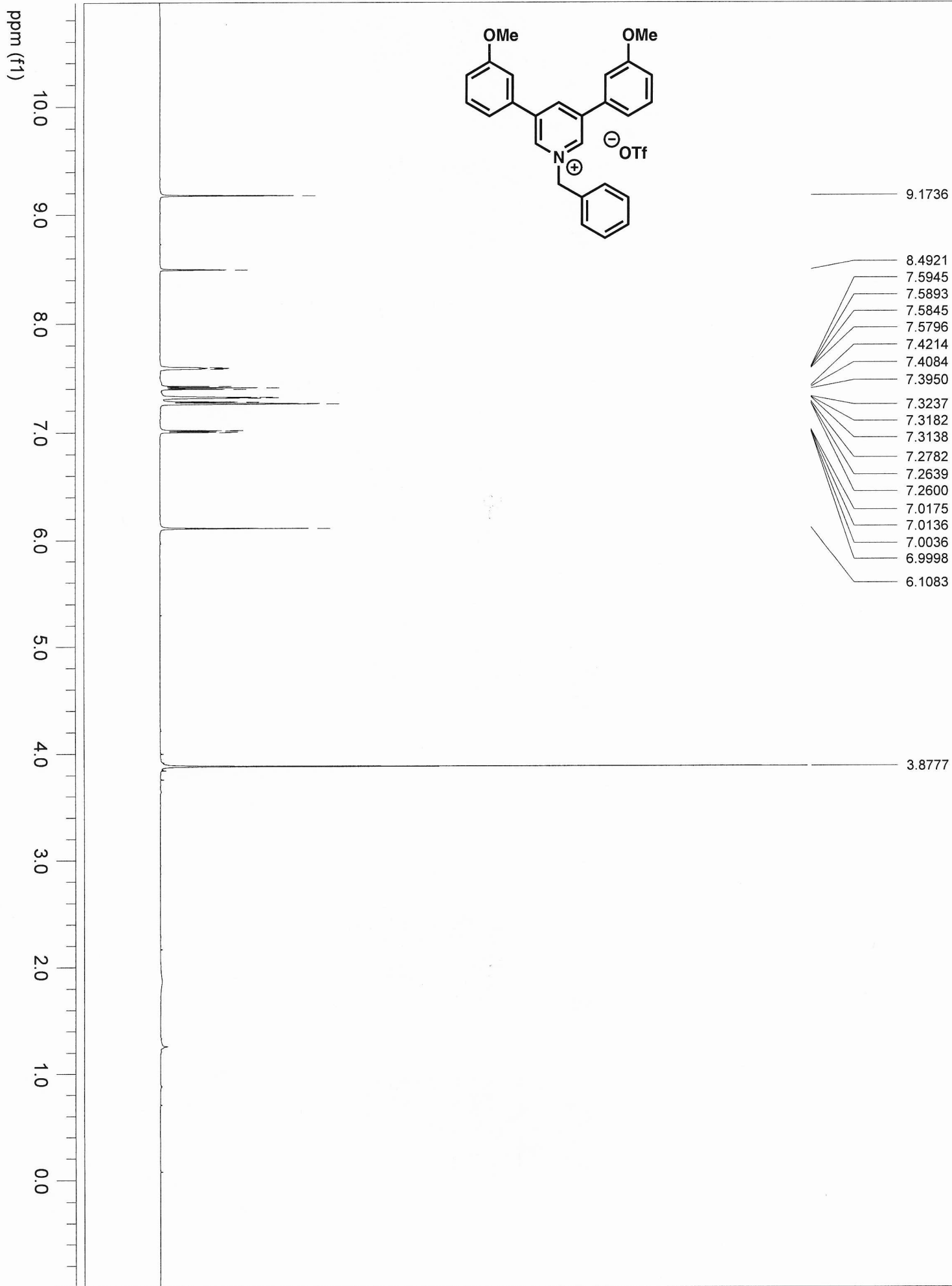
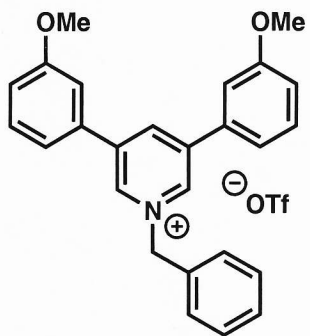
¹H NMR (600 MHz, CDCl₃) δ 7.33 (t, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 8.2 Hz, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 8.3 Hz, 1 H), 6.76 (m, 1 H), 5.34 (m, 1 H), 5.00 (m, 0.2 H [80% D]), 4.82 (m, 0.2 H [80% D]), 3.75 (s, 6 H), 3.59 (d, *J* = 22.4 Hz, 1 H), 3.36 (d, *J* = 22.4 Hz, 1 H), 3.26 (dd, *J* = 13.0, 7.7 Hz, 1 H), 3.18 (dd, *J* = 12.9, 6.8 Hz, 1 H);

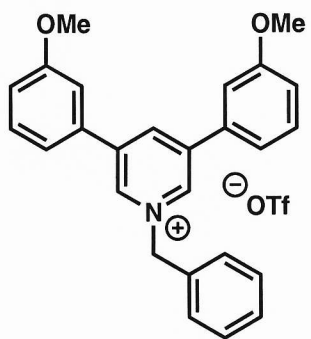
¹³C NMR (150 MHz, CDCl₃) δ 215.4, 159.5, 157.0, 142.0, 138.0, 134.0, 133.9, 130.3, 129.3, 129.2, 119.0, 117.0, 113.0, 111.8, 109.6, 63.3, 55.2, 55.1, 42.9, 39.3;

HRMS (ESI) calcd. for C₂₀H₁₈D₂O₃ [M + H⁺] 311.1616, found 311.1609.









ppm (f1)

200

150

100

50

0

160.615

141.783

140.520

140.108

134.094

132.860

130.859

129.920

129.586

129.426

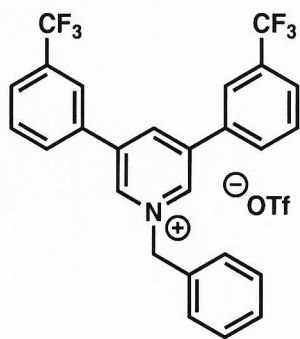
119.786

116.686

112.584

65.020

55.691



ppm (f1)

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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

9.2225

8.6802

8.0575

8.0445

7.9809

7.8310

7.8179

7.7539

7.7408

7.7278

7.6001

7.5970

7.5911

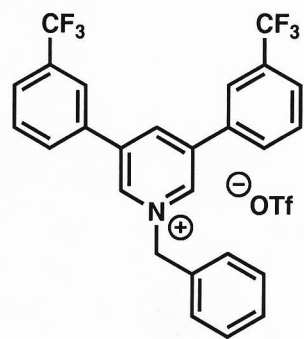
7.5850

7.4129

7.4096

7.4034

6.1075



ppm (f1)

200

150

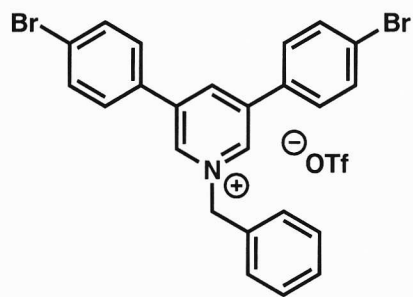
100

50

0

142.1361
141.7096
141.5217
134.2813
132.8360
132.6138
132.3968
132.1240
131.2389
130.8253
130.3027
130.0916
127.9464
126.9399
125.1328
124.9877
123.3260
121.5198

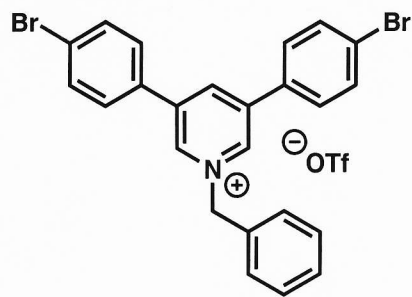
66.2000



ppm (f1)

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

8.9947
8.9920
8.8733
8.8705
8.8678
7.7927
7.7894
7.7817
7.7784
7.7380
7.7341
7.7306
7.7229
7.7198
7.5711
7.5642
7.5585
7.5552
7.4805
7.4771
7.4721
7.4686
5.8369



ppm (f1)

200

150

100

50

0

142,3737

141,8028

141,4518

133,8488

133,5766

133,2627

130,7824

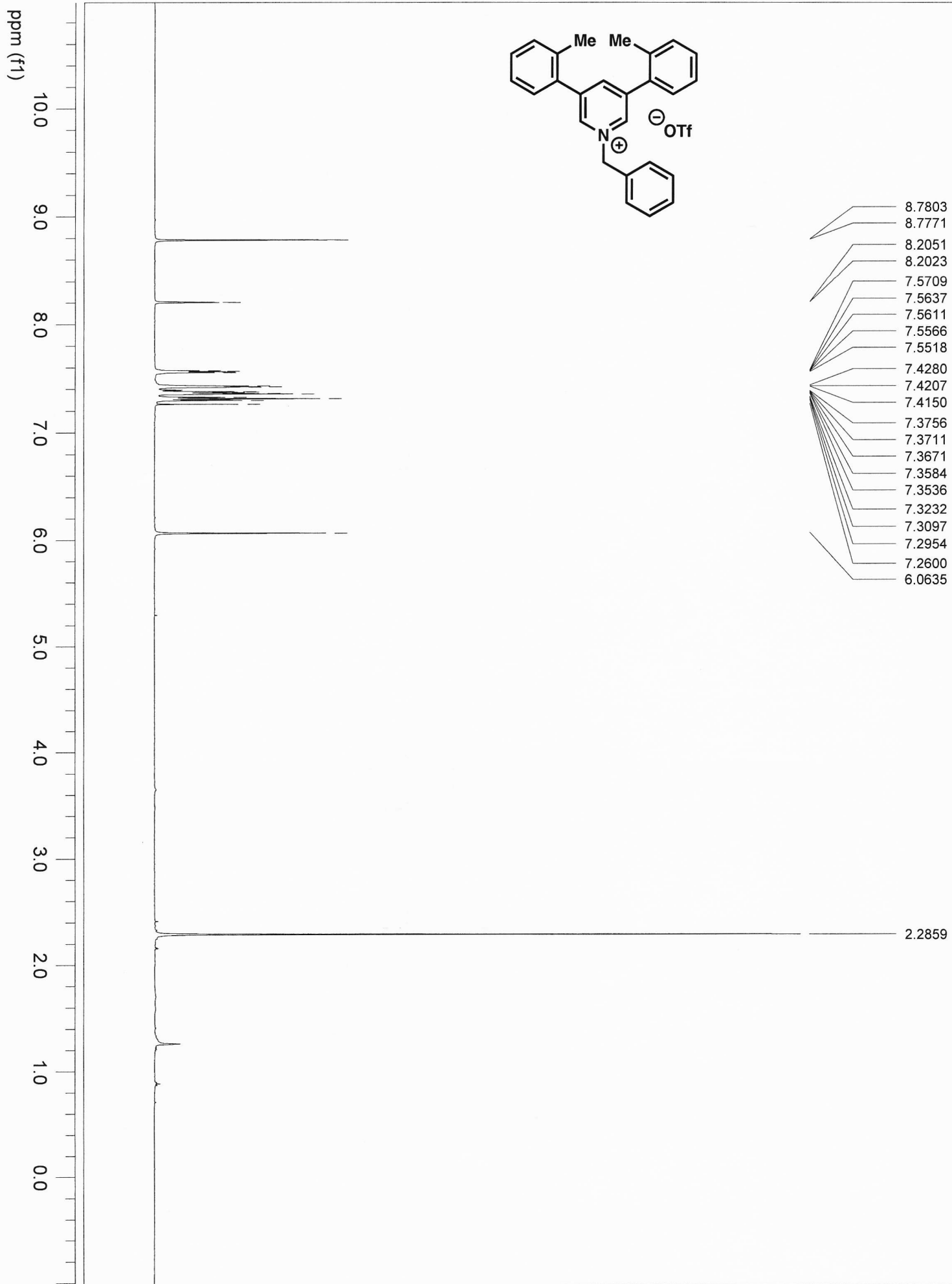
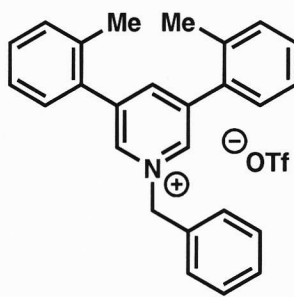
130,5834

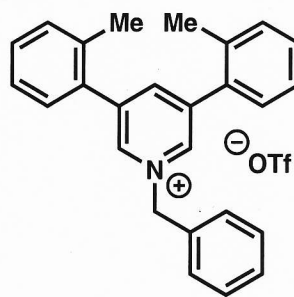
130,3481

130,0066

125,6289

65,9273





ppm (f1)

200

150

100

50

0

145,4334

141,9993

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135,4639

133,0984

132,2677

131,2482

130,2249

130,1660

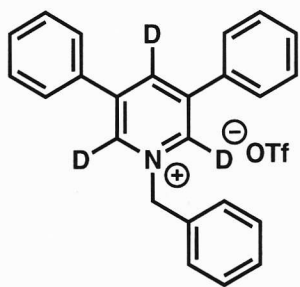
129,8537

129,8007

127,0010

65,3045

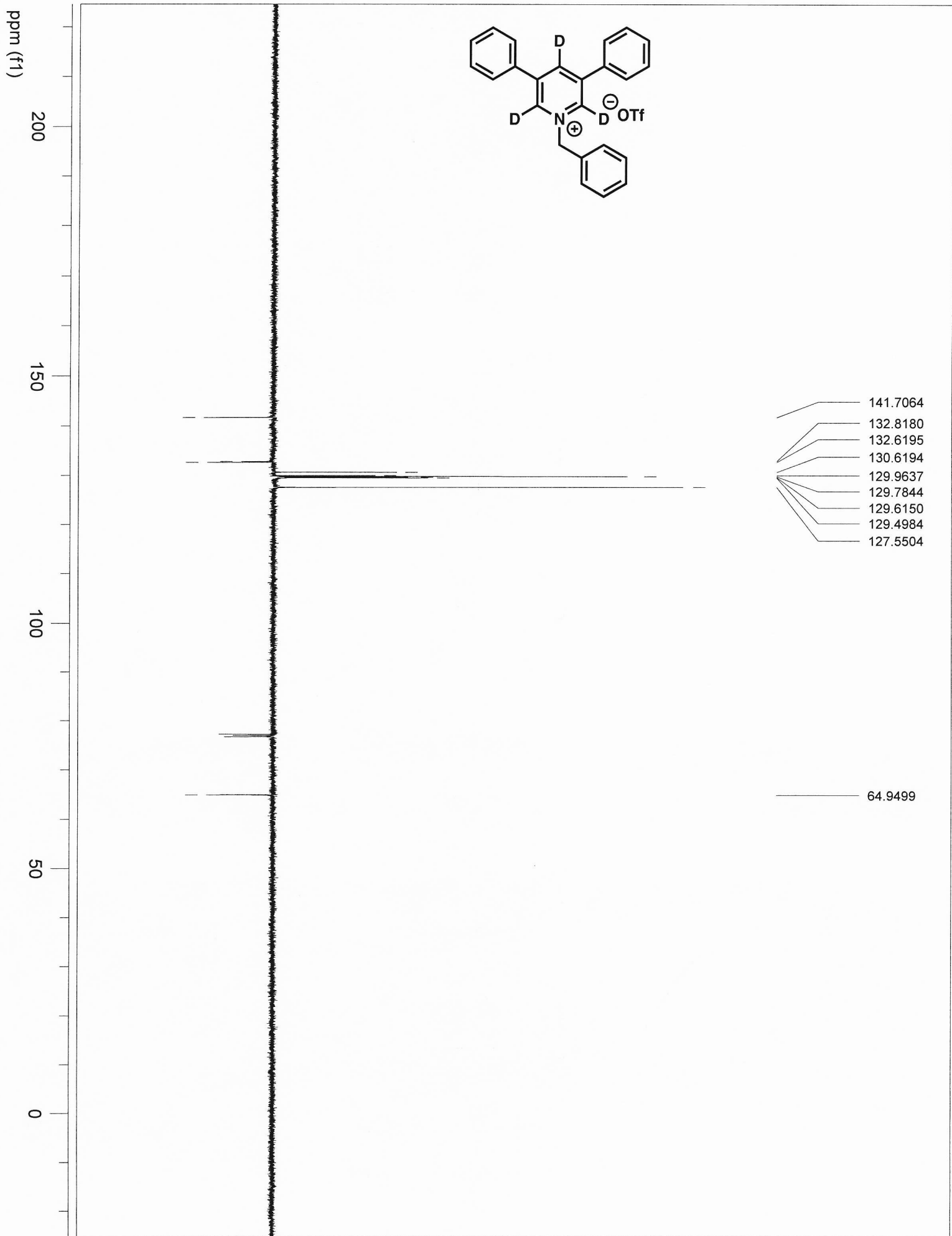
20,0586

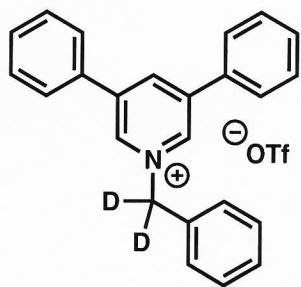


ppm (f1)

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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

7.7481
7.7452
7.7348
7.7314
7.7293
7.6109
7.6054
7.6025
7.5995
7.5944
7.5918
7.5157
7.5124
7.4984
7.4951
7.4836
7.4719
7.4580
7.4513
7.4455
7.4431
7.4407
7.3213
7.3150
7.3085
7.2600
6.0503





ppm (f1)

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

9.1570
9.1536
8.5229
8.5195
8.5161
7.7499
7.7468
7.7428
7.7333
7.7258
7.6075
7.5999
7.5969
7.5938
7.5884
7.5374
7.5334
7.5299
7.5200
7.5051
7.4992
7.4961
7.4934
7.4875
7.4821
7.4674
7.3419
7.3354
7.3292
7.2600

ppm (f1)

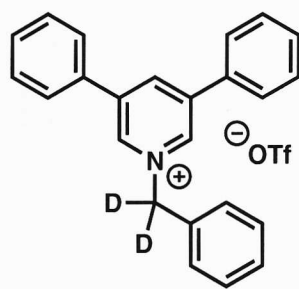
200

150

100

50

0



141.8987

140.2633

139.8678

132.6768

132.6543

130.6382

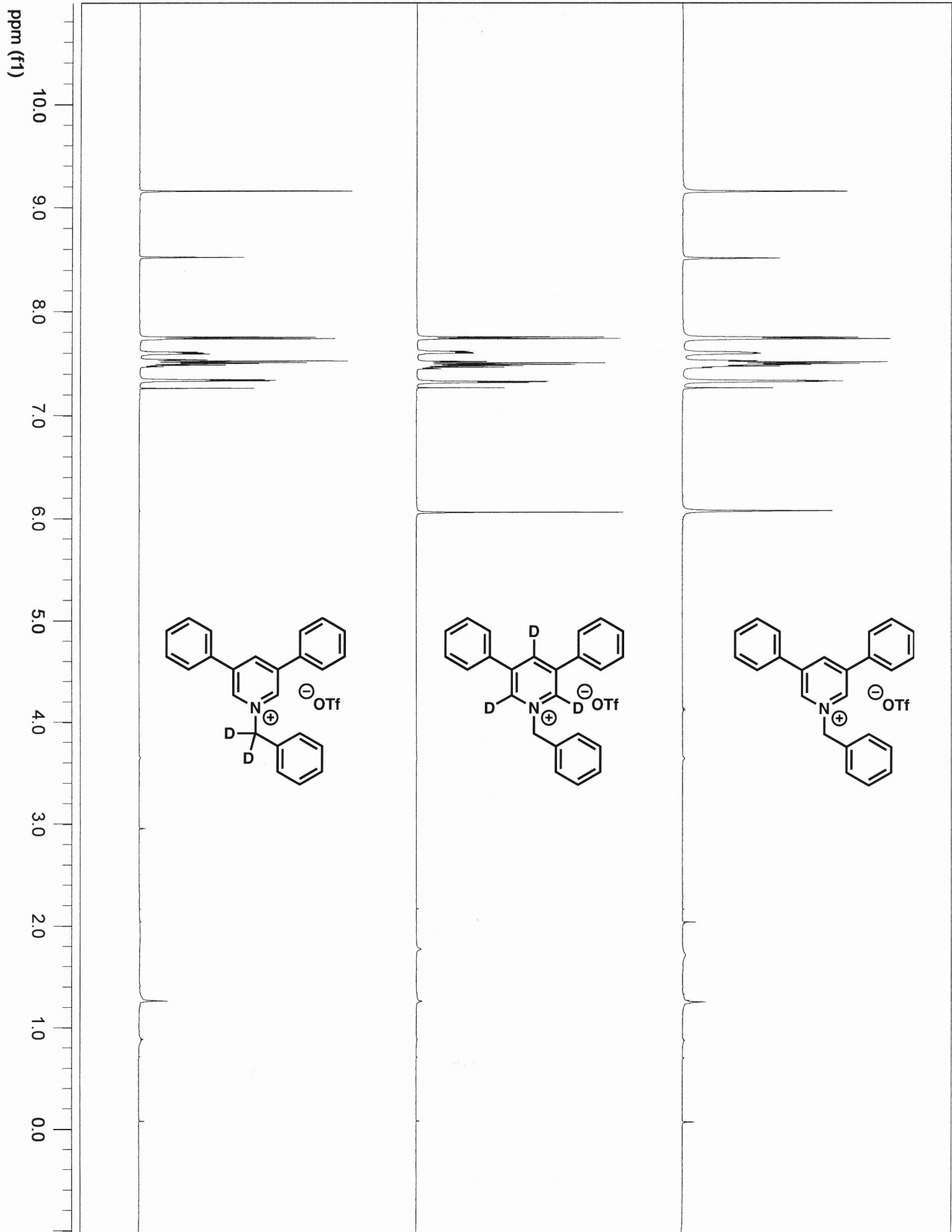
129.9858

129.8012

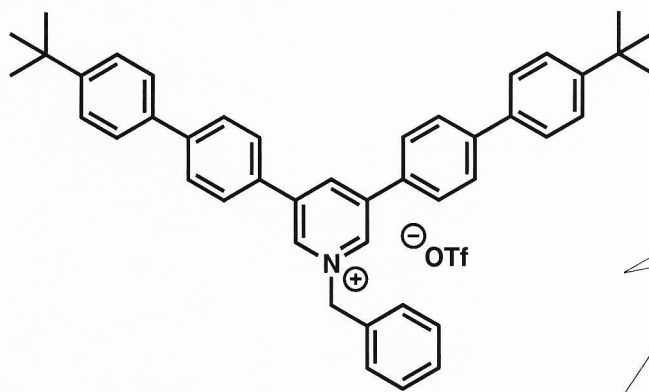
129.6194

129.4464

127.5349



ppm (f1)

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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

9.1855
9.1831
8.4521
7.8006
7.7839
7.7410
7.7242
7.6198
7.6152
7.6042
7.6009
7.5275
7.5238
7.5106
7.4744
7.4706
7.4576
7.3861
7.3742
7.3715
7.2600
6.1561

1.3620

ppm (f1)

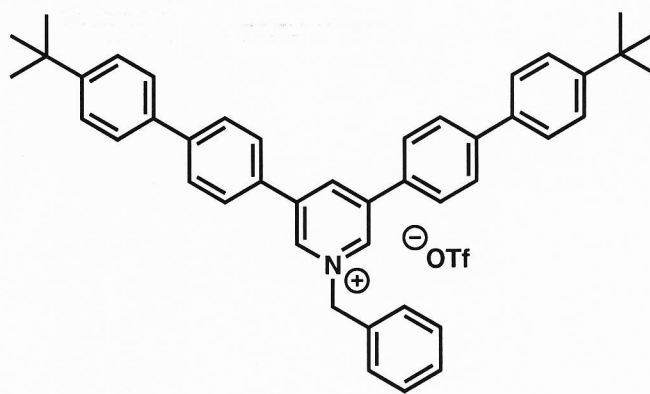
200

150

100

50

0



151.3595

143.0776

141.1608

139.9057

138.8873

136.2315

132.8591

131.0440

129.9721

129.6532

129.4378

128.0297

127.8813

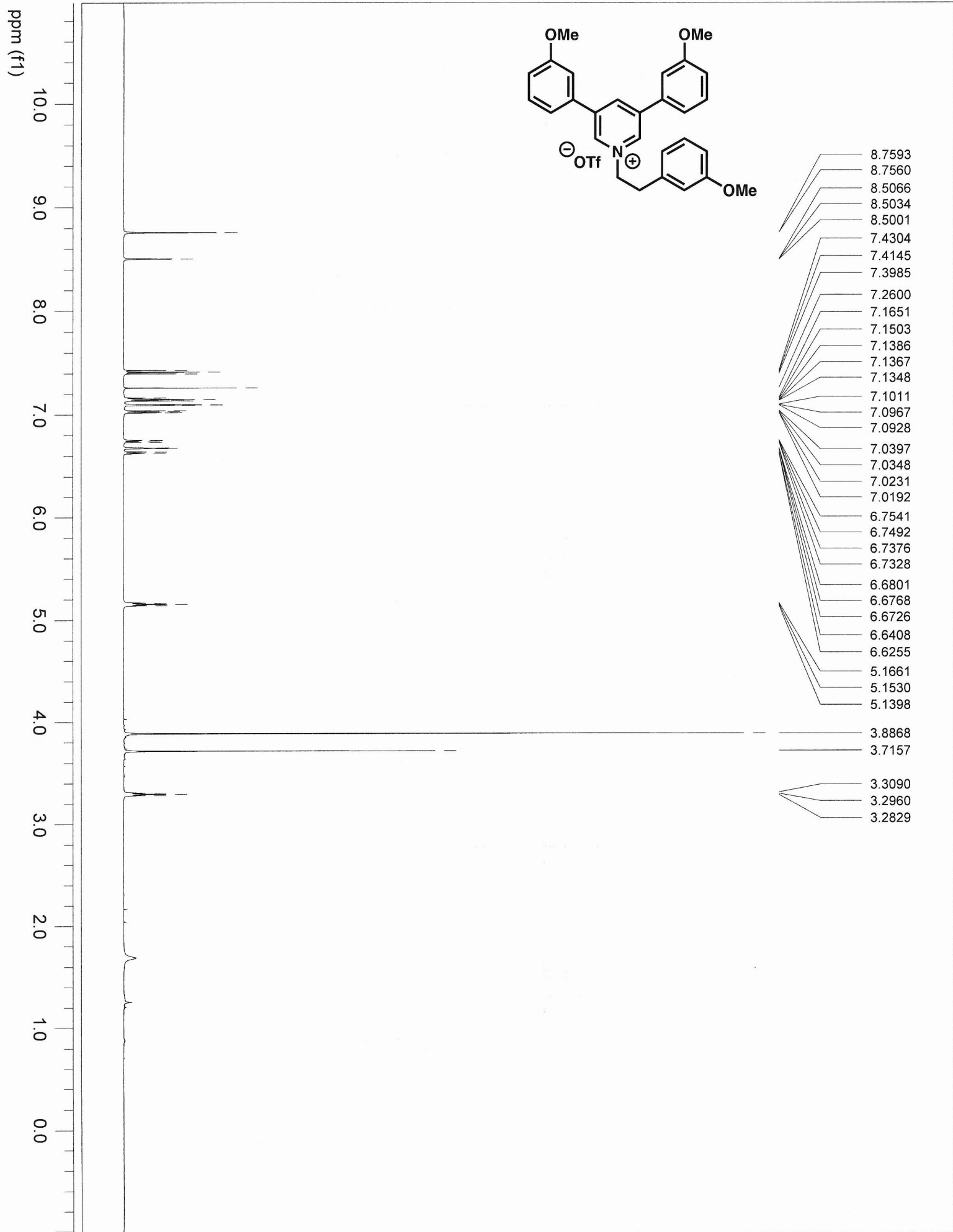
126.6359

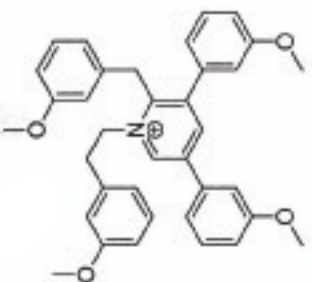
125.9547

65.2593

34.6003

31.2682

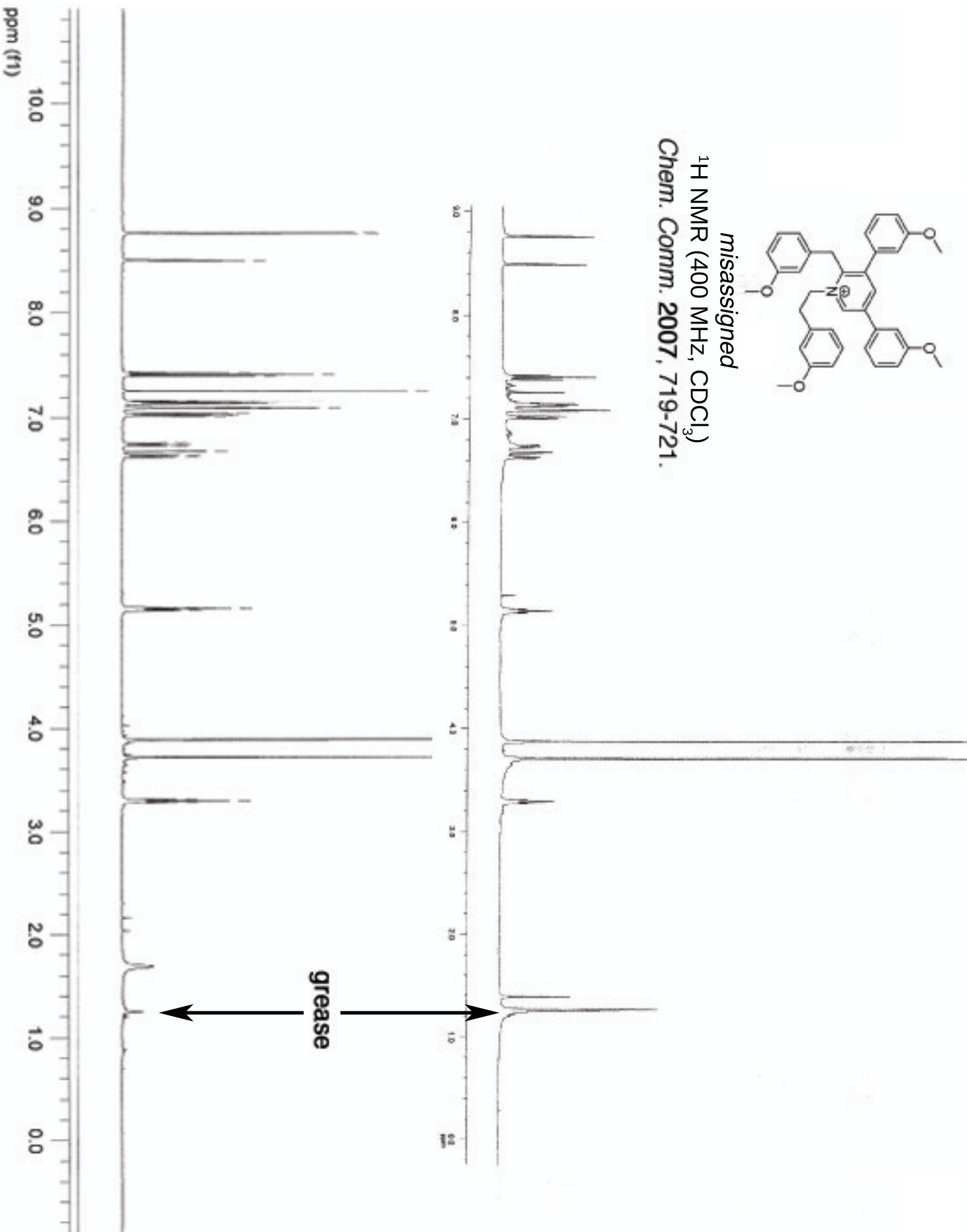




misassigned

^1H NMR (400 MHz, CDCl_3)

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



ppm (f1)

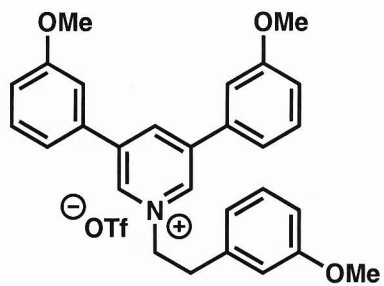
200

150

100

50

0



160.6553
160.2160

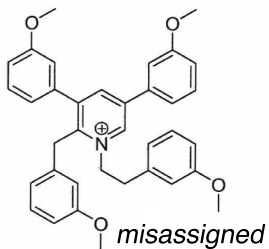
141.3802
140.5478
139.8592
136.8797
133.9987
130.8441
130.2068
121.1449
119.6460
116.7452
114.2373
113.5304
112.4445

63.5854

55.7142
55.2725

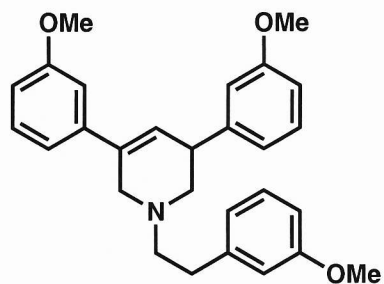
37.8603

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



grease

ppm (f1)

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

7.2815
7.2684
7.2600
7.2550
7.2416
7.2267
7.2138
7.2006
7.0311
7.0183
6.9647
6.9619
6.9058
6.8932
6.8594
6.8459
6.8417
6.8322
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)

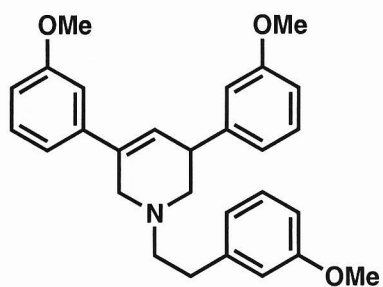
200

150

100

50

0

159.7046
159.6249145.2152
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

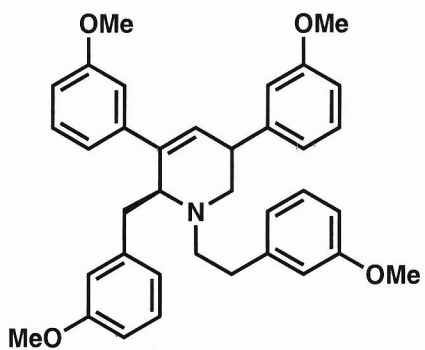
4.0

3.0

2.0

1.0

0.0



7.2949

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

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2.8237

2.8192

2.8074

2.8000

2.7884

2.7844

2.7832

2.7832

ppm (f1)

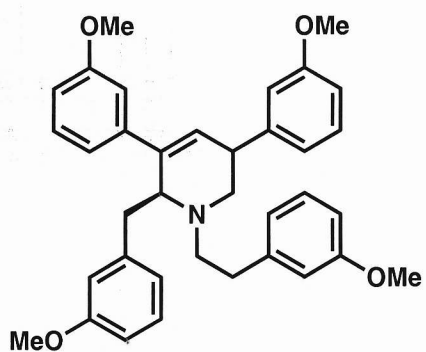
200

150

100

50

0



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

37.3027

ppm (f1)

10.0

9.0

8.0

7.0

6.0

5.0

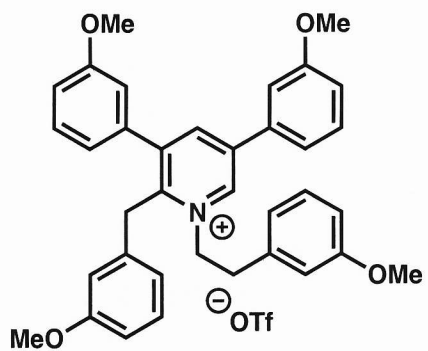
4.0

3.0

2.0

1.0

0.0



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

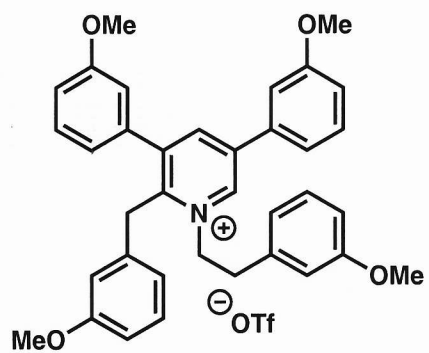
100

75

50

25

0



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

ppm (f1)

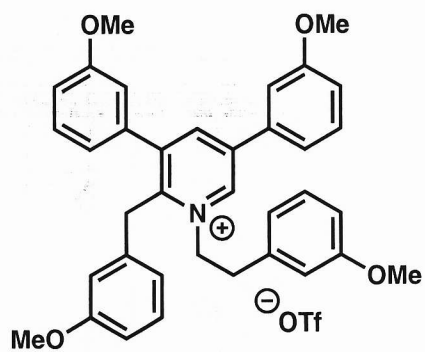
200

150

100

50

0

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

161.2987

161.1293

160.8961

160.5672

152.5819

144.7693

144.3800

144.2994

139.6292

137.3618

137.1425

136.8335

134.2154

131.3974

131.2994

131.0045

130.8731

121.6501

121.3298

120.3237

120.1235

117.0184

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115.2342

114.8245

114.5968

113.8098

113.4564

113.1390

60.8341

56.2728

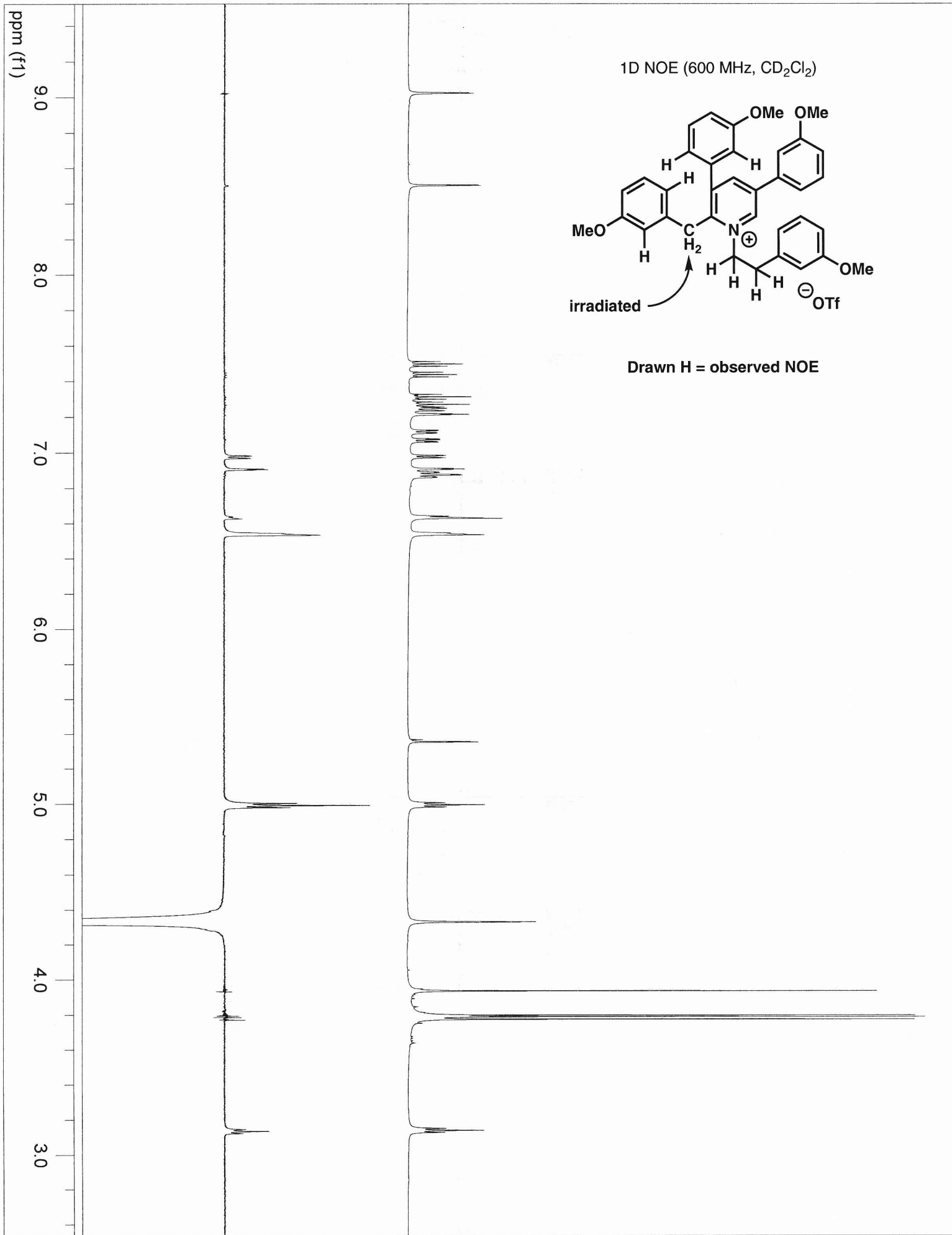
55.9481

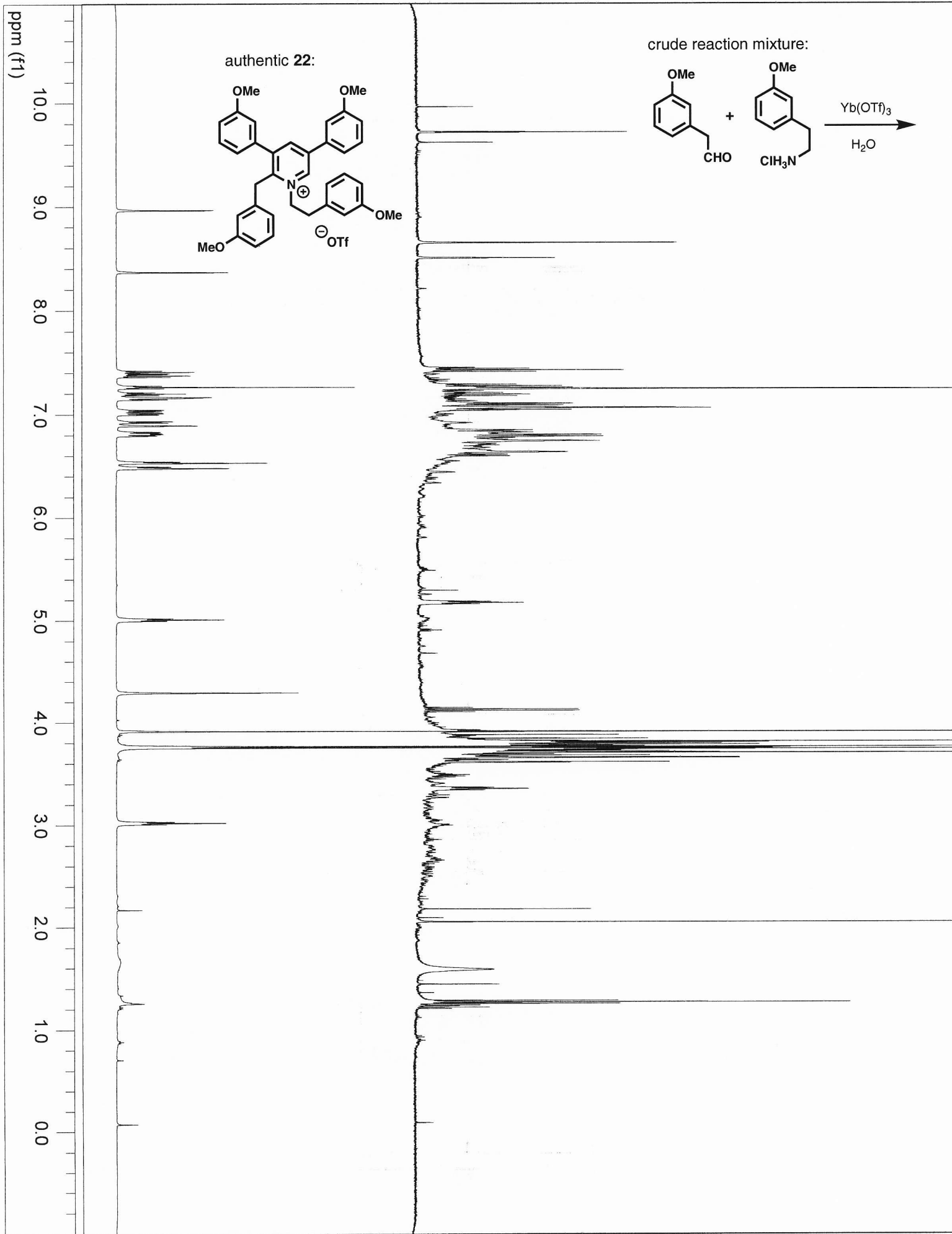
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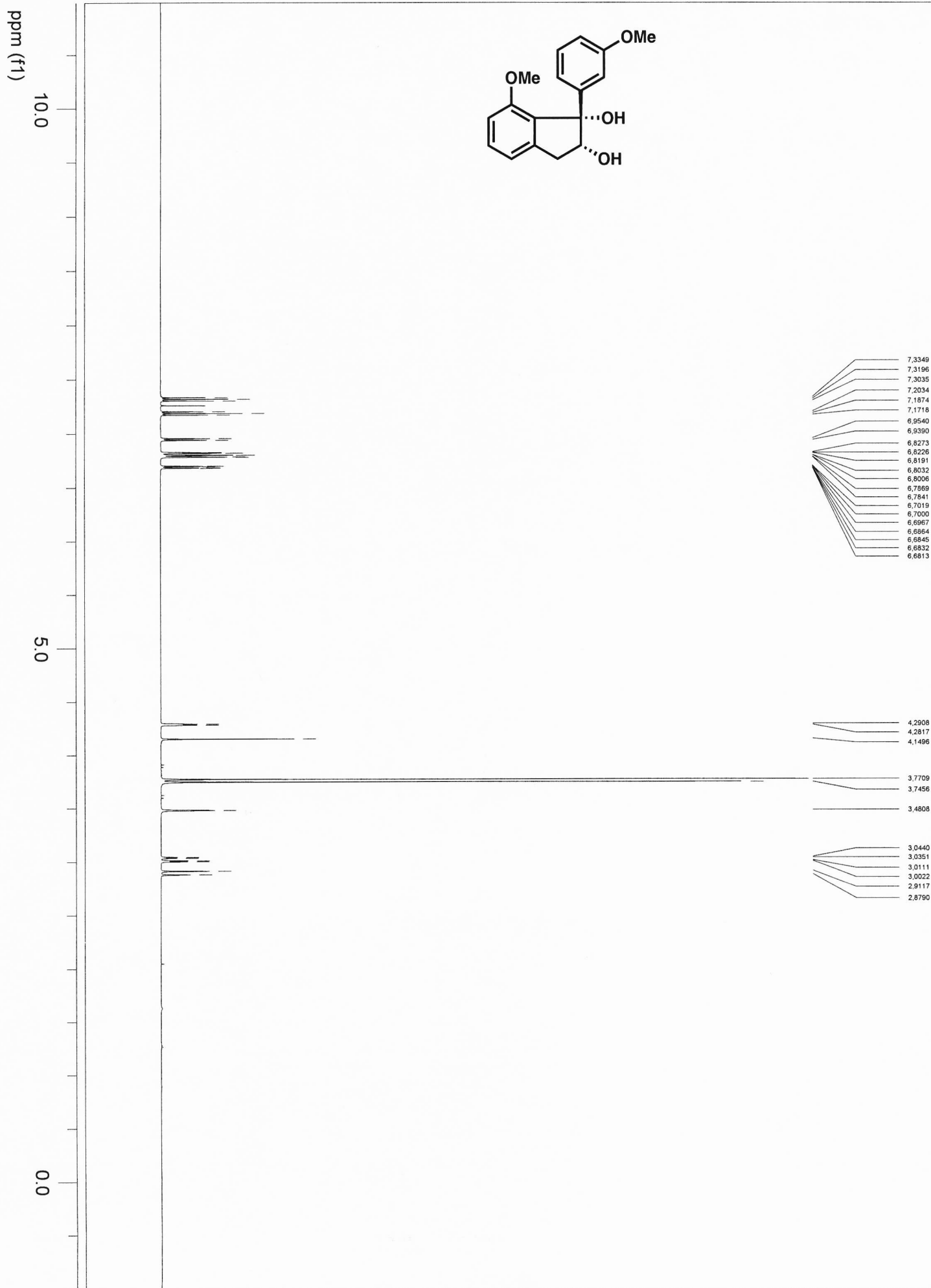
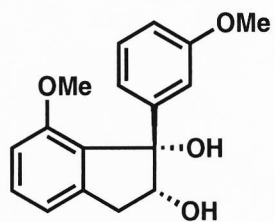
55.8496

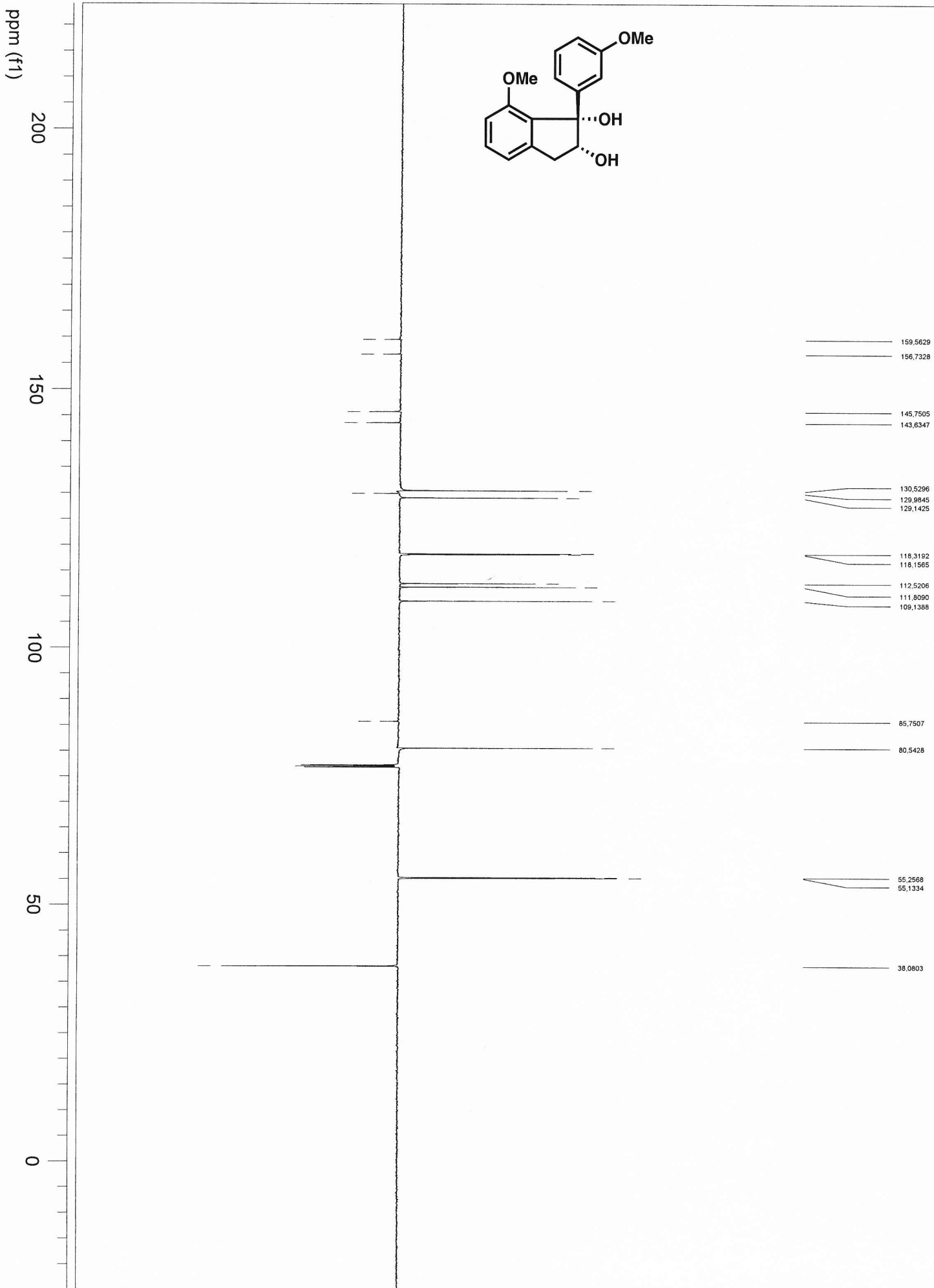
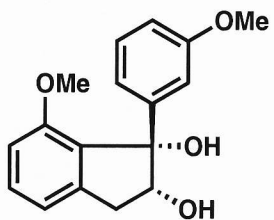
37.6634

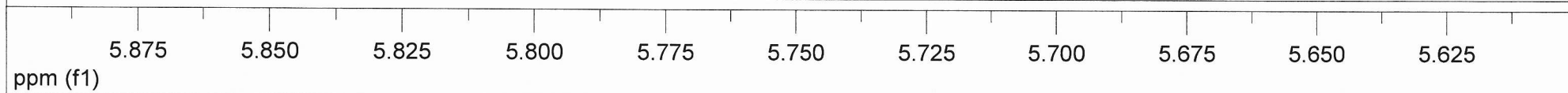
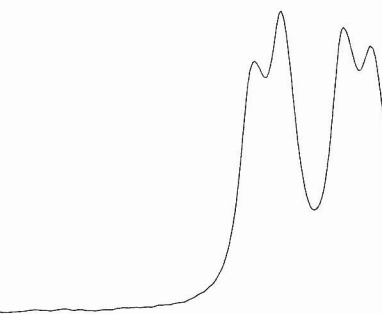
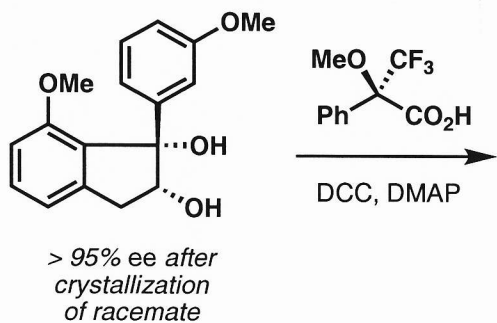
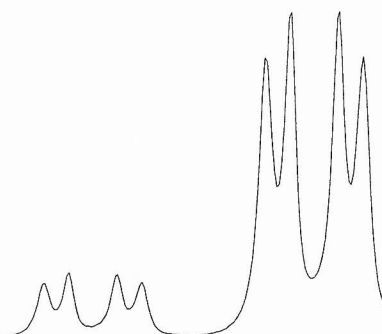
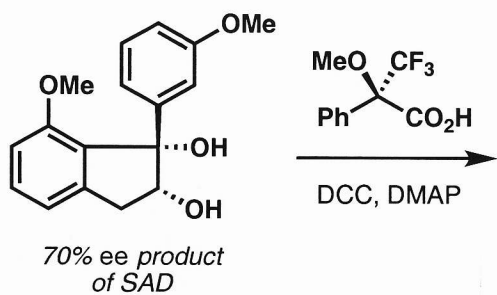
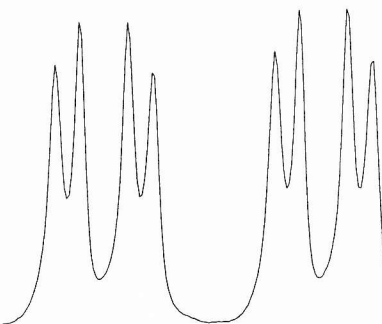
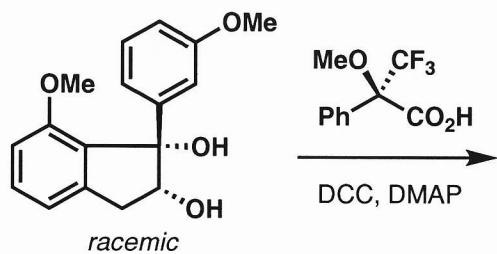
36.1002

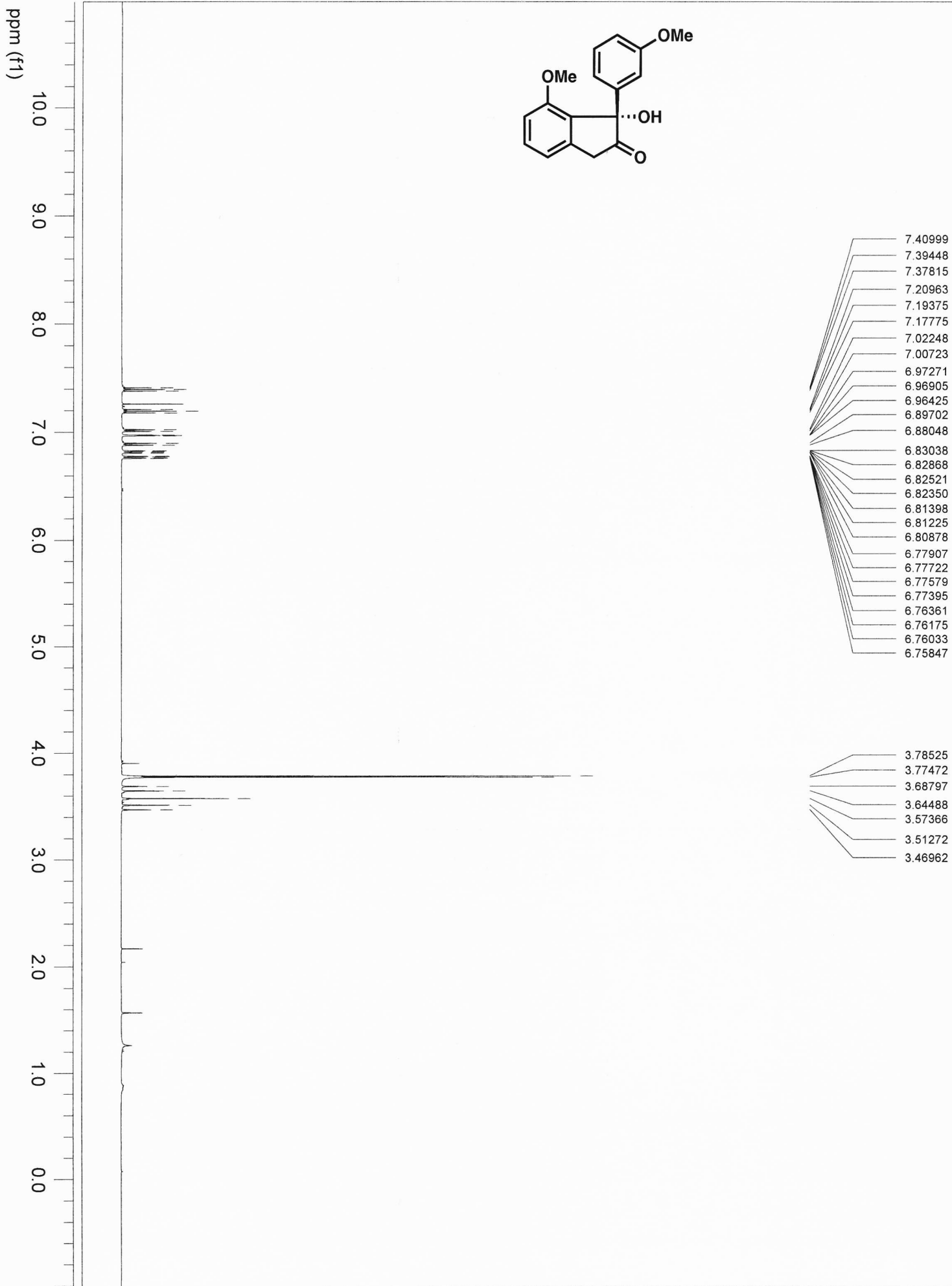


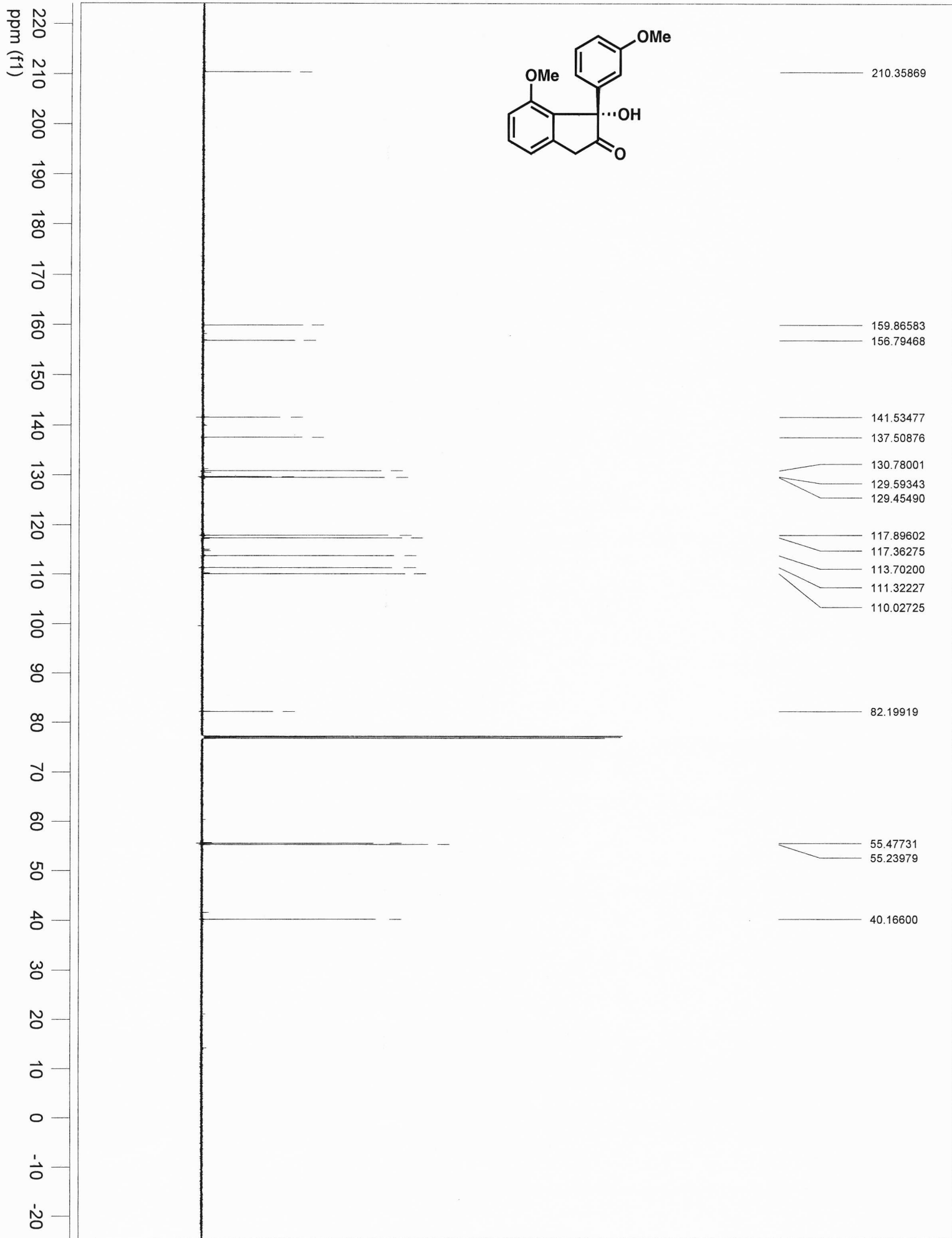






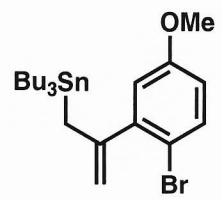




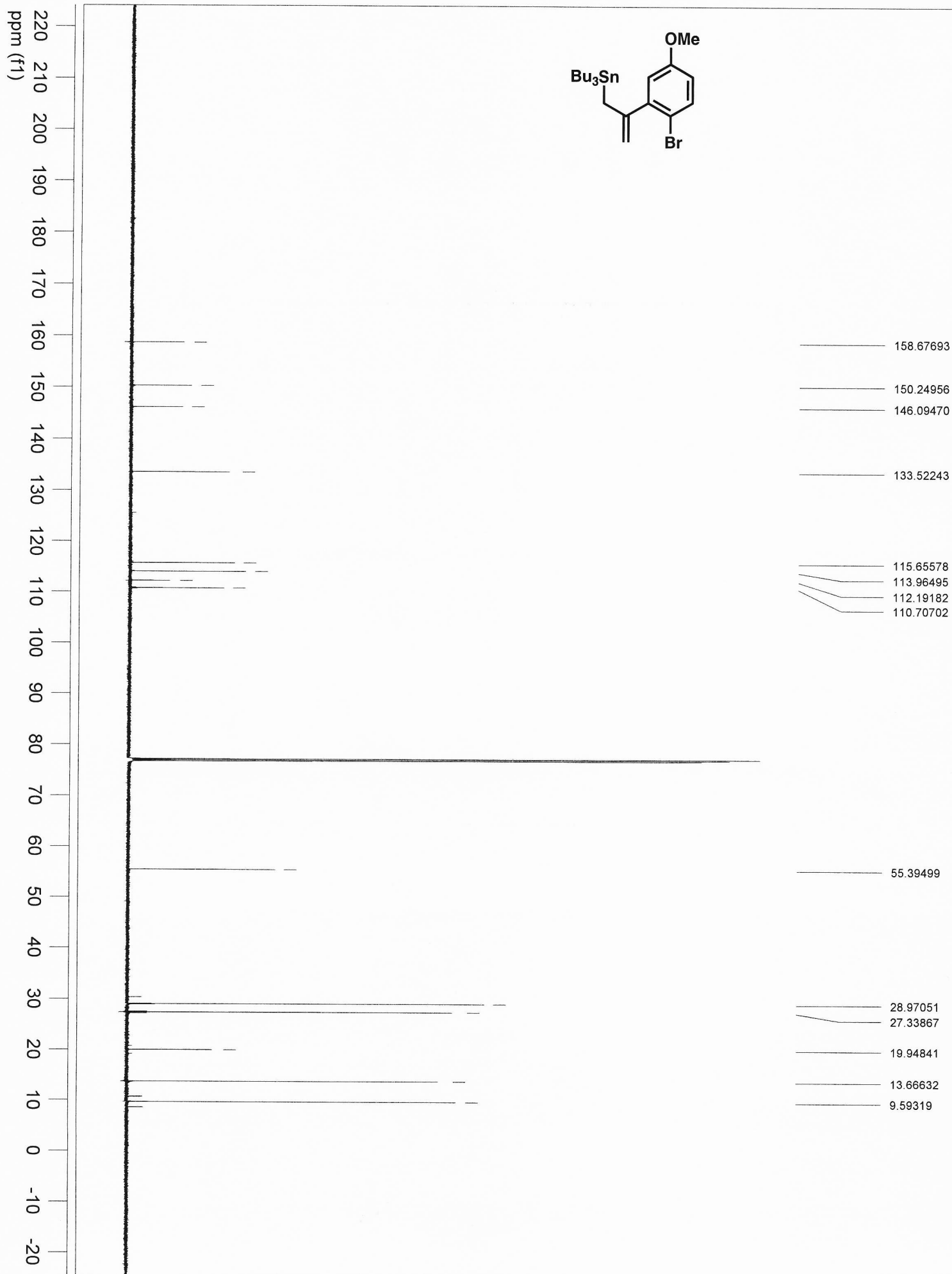
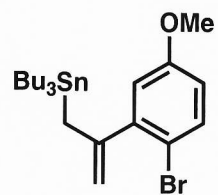


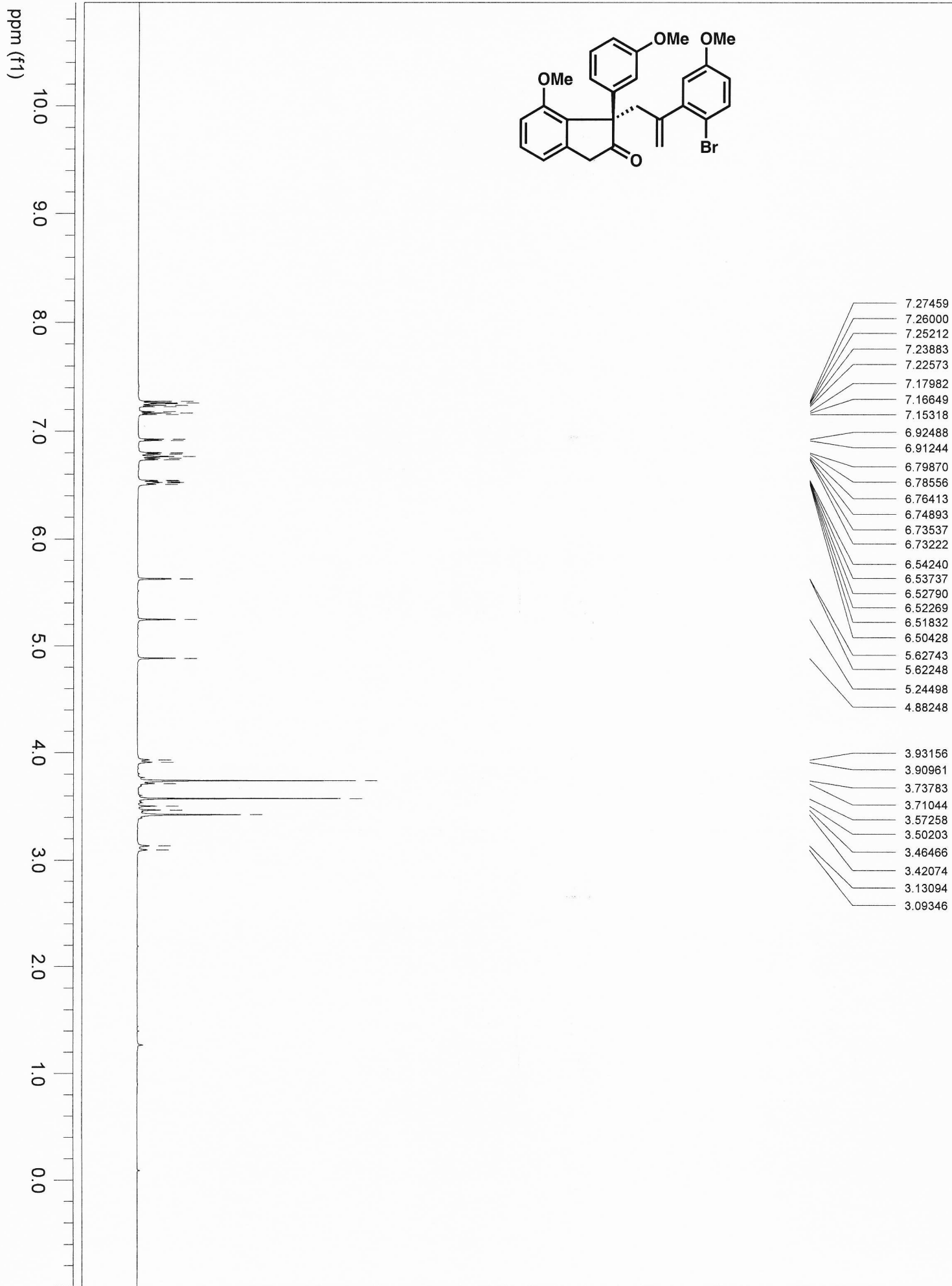
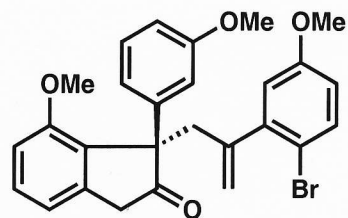
ppm (f1)

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



- 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





ppm (t1)

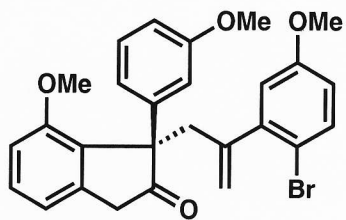
200

150

100

50

0



215.0105

159.4211
157.8169
157.0883

147.2715
143.5099
142.1630
138.2398

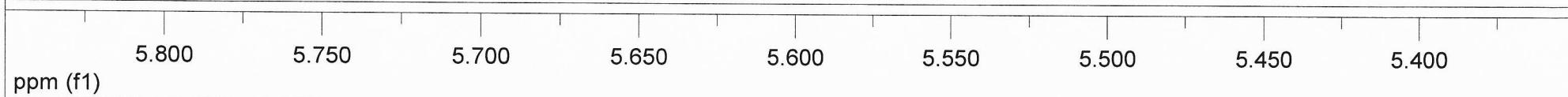
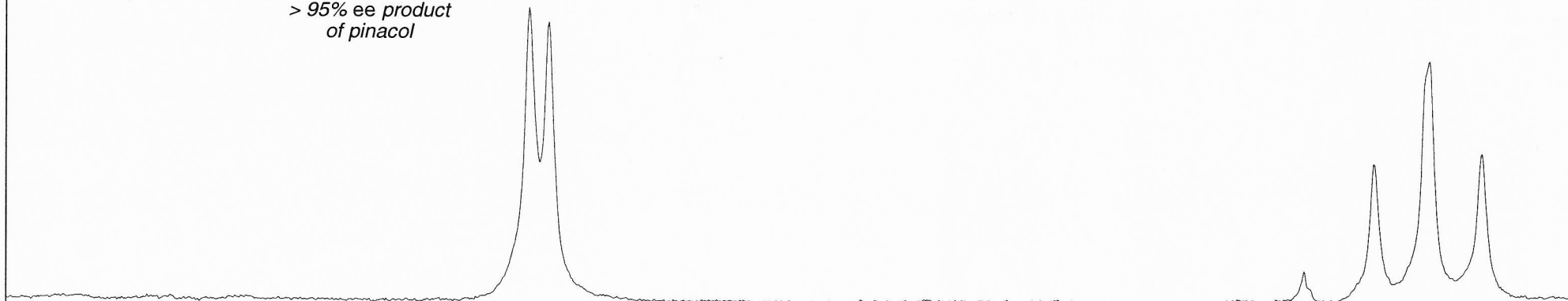
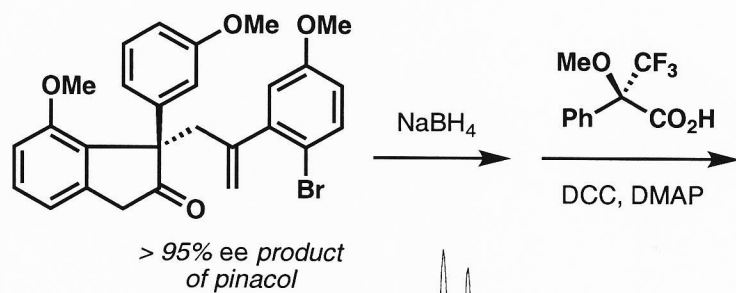
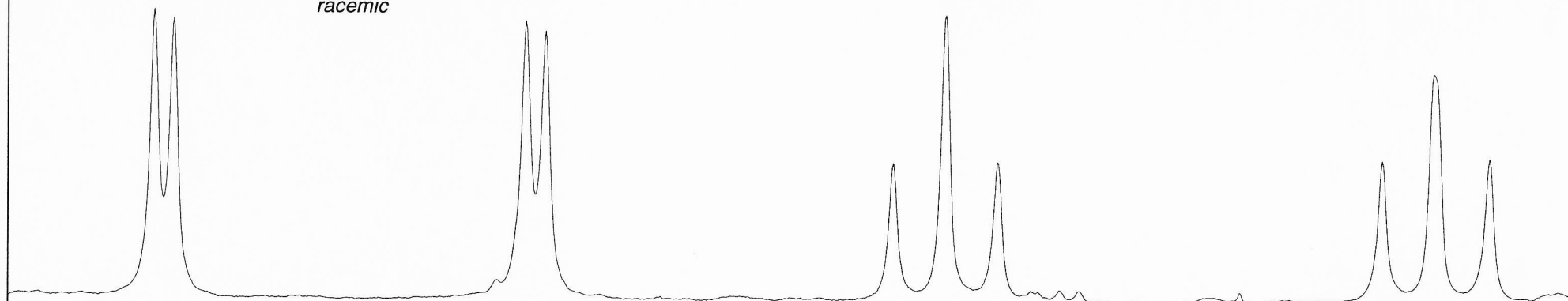
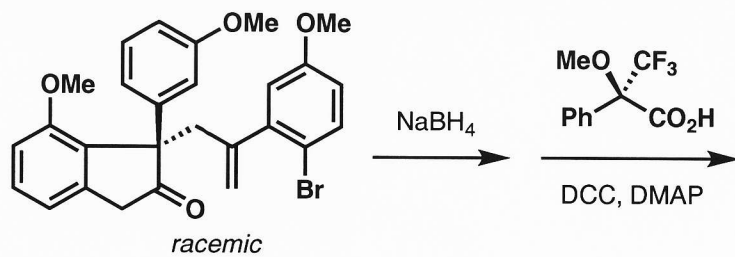
132.5391
130.0714
129.4046
129.1025

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



ppm (f1)

10.0

9.0

8.0

7.0

6.0

5.0

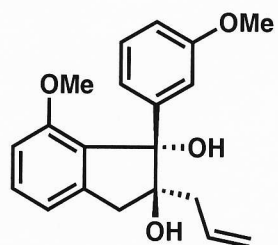
4.0

3.0

2.0

1.0

0.0



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

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2.98638

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2.92677

2.89976

2.20928

2.19882

2.18586

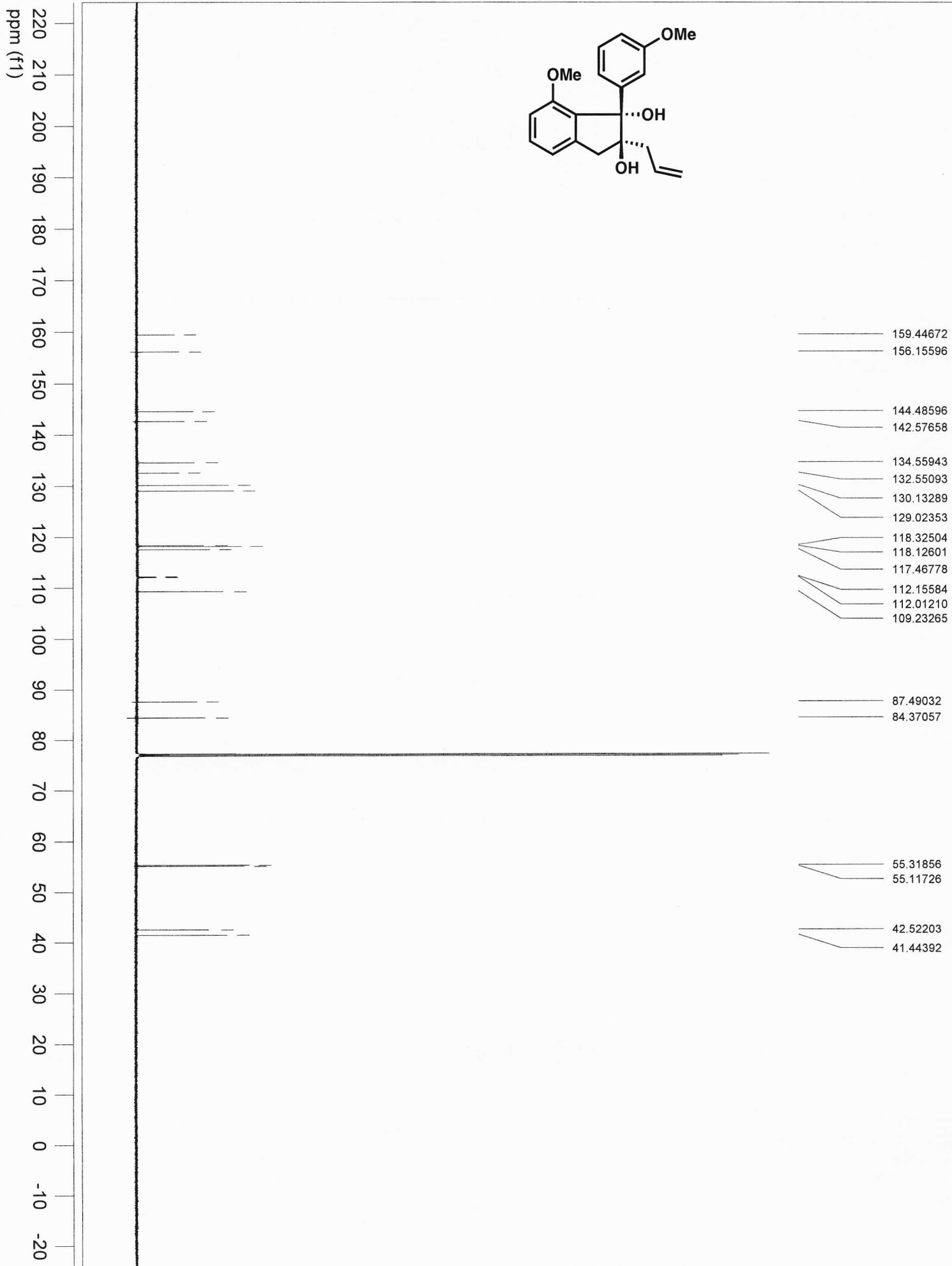
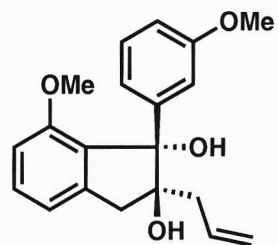
2.17541

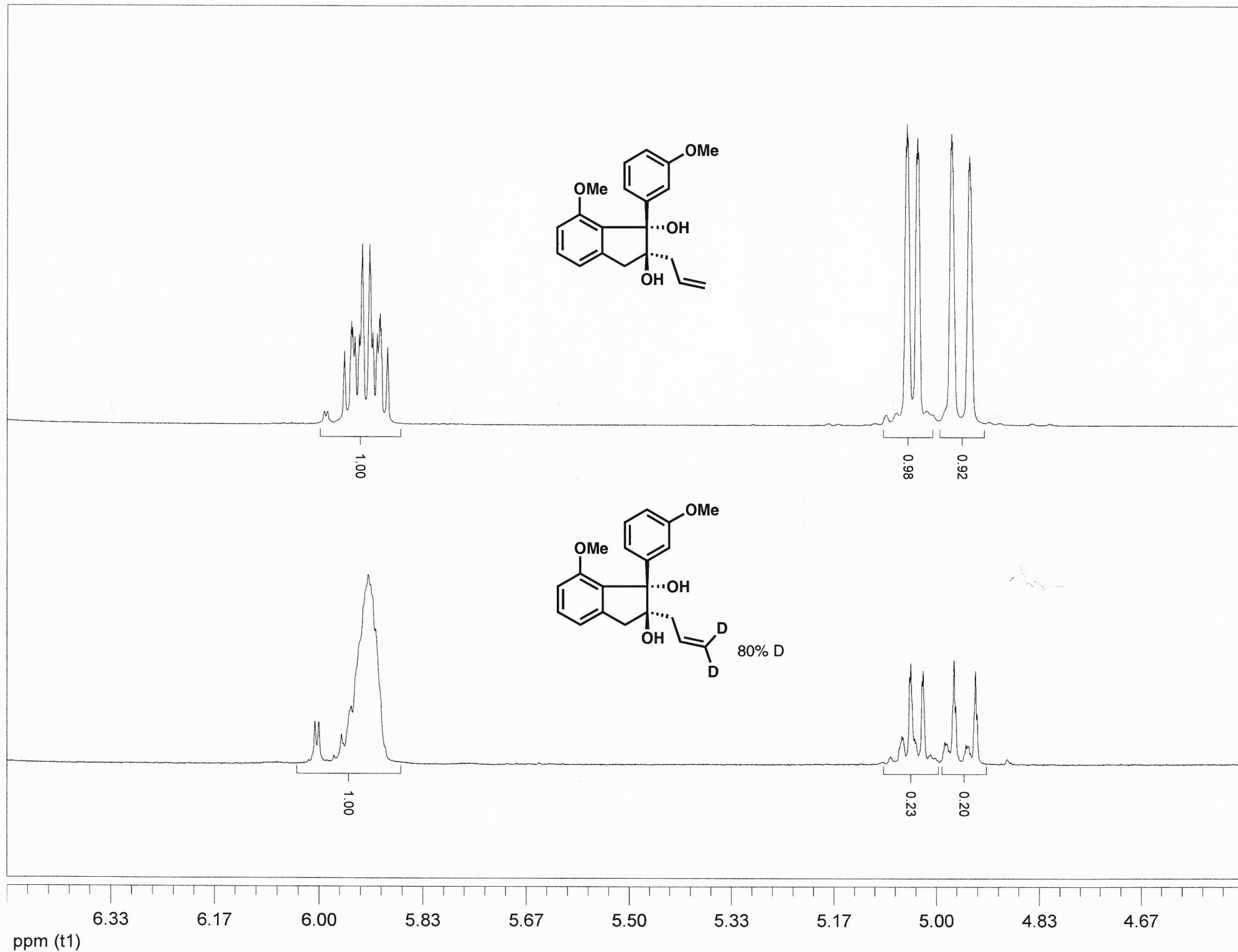
1.67277

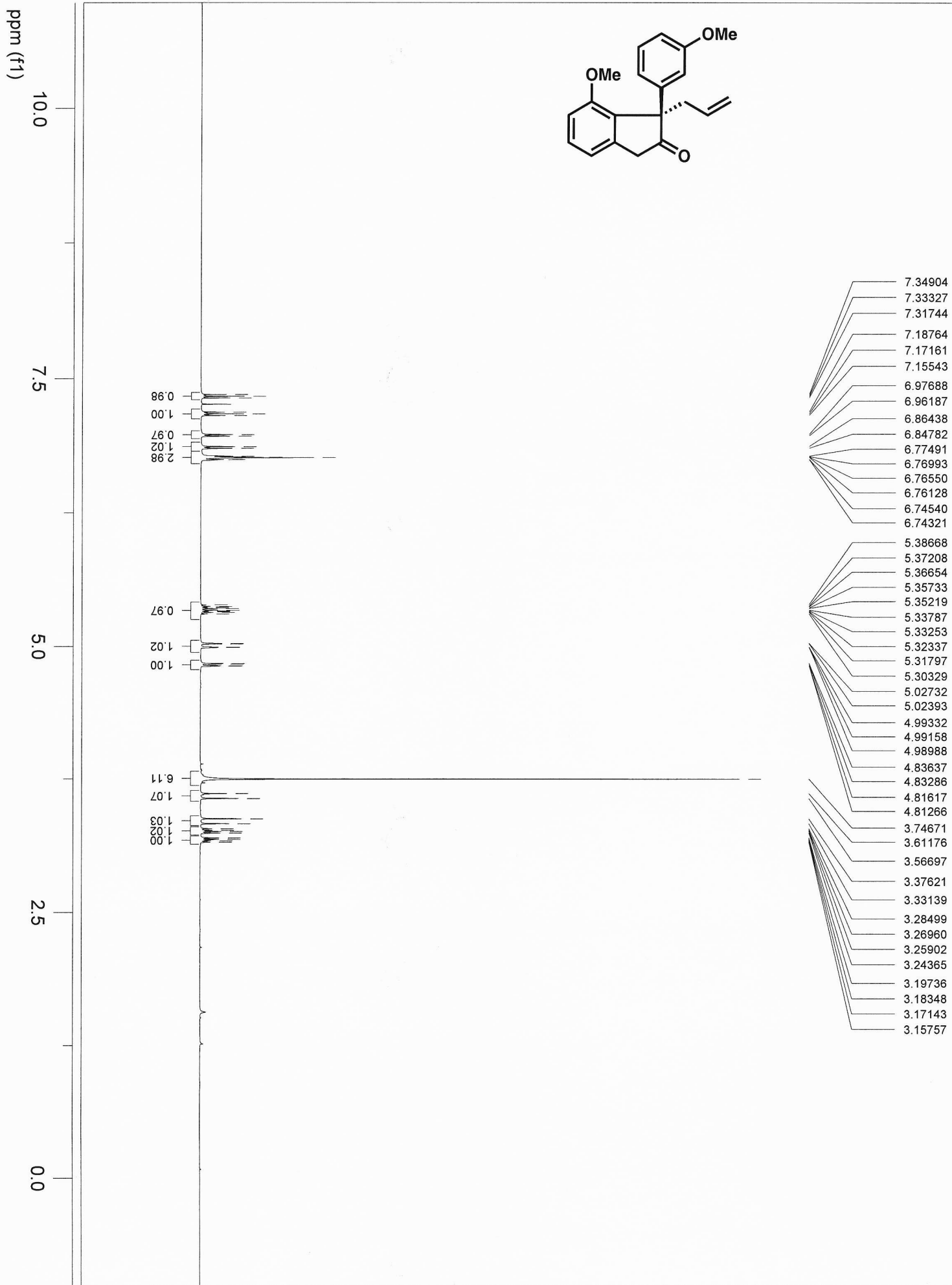
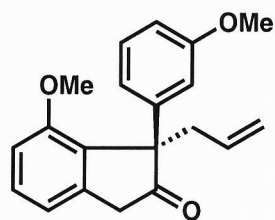
1.65957

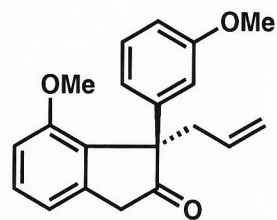
1.64933

1.63613









ppm (f1)

10.0

7.5

5.0

2.5

0.0

7.34904

7.33327

7.31744

7.18764

7.17161

7.15543

6.97688

6.96187

6.86438

6.84782

6.77491

6.76993

6.76550

6.76128

6.74540

6.74321

6.73919

5.38668

5.37208

5.36654

5.35733

5.35219

5.33787

5.33253

5.32337

5.31797

5.30329

5.02732

5.02393

4.99332

4.98988

4.83637

4.83286

4.81617

4.81266

3.74671

3.61176

3.56697

3.37621

3.33139

3.28499

3.26960

3.25902

3.24365

3.19736

3.18348

3.17143

3.15757

