Enantioselective Synthesis of Quaternary Carbon Stereogenic Centers through Cu-Catalyzed Conjugate Additions of Aryl – and Alkylaluminum Reagents to Acyclic Trisubstituted Enones

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SUPPORTING INFORMATION

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General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, bs = broad singlet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS or JEOL AccuTOF-DART (positive mode) at the Mass Spectrometry Facility at Boston College. Enantiomer ratios were determined by HPLC analysis (Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), OJ-H (4.6 x 250 mm), or GC analysis (Chiraldex B-DM 30 m x 0.25 mm), Chiraldex GTA 30 mx 0.25 mm, Betadex 30 m x 0.25 mm), in comparison with authentic racemic materials. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Specific rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard dry box or vacuum-line techniques. Solvents were purified under a positive pressure of dry argon by a modified Innovative Technologies purification system: toluene, benzene and hexanes were purified through a copper oxide and alumina column; CH_2Cl_2 and Et_2O were purged with Ar and purified by passage through two alumina columns. Tetrahydrofuran (Aldrich) was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher) in air.

■ Solvents, Reagents & Catalysts:

Acetic acid was purchased from Fisher and used as received.

Racemic-2,2'-bis(diphenylphosphino)-1,1'-binapthyl (*rac*-binap) was purchased from Strem and used as received.

4-Bromoanisole was purchased from Aldrich and distilled from CaH_2 prior to use.

Bromobenzene was purchased from Aldrich and distilled from CaH_2 prior to use.

4-Bromobenzotrifluoride was purchased from Aldrich and distilled from CaH_2 prior to use.

3-Bromofuran was purchased from Aldrich and distilled from CaH_2 prior to use.

1-Bromo-2-isopropylbenzene was purchased from Alfa Aesar and distilled from CaH_2 prior to use.

3-Bromothiophene was purchased from Aldrich and distilled from CaH_2 prior to use.

2-Bromotoluene was purchased from Aldrich and distilled from CaH_2 prior to use.

***n*-Butyllithium** was purchased from Strem (15% in hexanes) and titrated before use.

Copper (II) trifluoromethanesulfonate (99%) was purchased from Aldrich and used as received.

Dimethylaluminum chloride (neat) was purchased from Aldrich and used as received.

Furan was purchased from Aldrich and distilled from Na(0) prior to use.

***Iso*butyl-2-bromobenzenesulfonate** was prepared as previously reported.[2]

***N*-Methyl-*N*-methylideneiminium iodide (Eschenmoser's salt)** was purchased from Aldrich and used as received.

Ozone was generated by passing O_2 (Airgas) through a Pacific Instrument ozonolysis machine.

Palladium II acetate was purchased from Strem and used as received.

Silver oxide was freshly prepared as previously reported.[1]

Sodium *tert*-butoxide (98%) was purchased from Strem and used as received.

Sodium hypochlorite (10–15%) was purchased from Aldrich and used as received.

2,2,6,6-Tetramethylpiperidine was purchased from Aldrich and distilled over CaH_2 prior to use.

Thiophene was purchased from Aldrich and distilled from Na(0) prior to use.

Triethylaluminum (neat) was purchased from Strem and used as received.

Trimethylaluminum (neat) was purchased from Strem and used as received. We have found that old bottles (>1 year) of Me_3Al were not as effective for the ECA reactions (conversions suffered, enantioselectivities remained the same).

Trimethylsilyl trifluoromethanesulfonate was purchased from Aldrich and distilled prior to use.

NHC–Ag complexes III,[1] **IIa and IIb,**[2] **Ib**[3] were prepared according to published procedures.

NHC–Ag complexes IVa-c, Va-b were prepared according to the procedure below from NHCs prepared previously. [4]

- **Experimental Procedures for the Synthesis of Enone Substrates:**

Enones **2b**, **2h**, **2i** were synthesized according to literature procedure.[5]

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[1] J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici, A. H. Hoveyda, *J. Am. Chem. Soc.* **2005**, *127*, 6877–6882.

[2] a) Y. Lee, K. Akiyama, D. G. Gillingham, M. K. Brown, A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, *130*, 446–447; b) T. L. May, M. K. Brown, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2008**, *47*, 7358–7362; c) K. Akiyama, F. Gao, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2010**, *49*, 419–423.

[3] a) M. K. Brown, T. L. May, C. A. Baxter, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2007**, *46*, 1097–1100; b) Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 3160–3161.

[4] K-s. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2010**, *132*, 2898–2900.

[5] D. Monguchi, C. Beemelmanns, D. Hashizume, Y. Hamashima, M. Sodeoka, *J. Organometallic Chem.* **2008**, *693*, 867–873.

Other enone substrates were synthesized according to a modified reported precedence[6] for Zr-catalyzed carboalumination: To a flame-dried round bottom flask equipped with a stir bar was added Cp_2ZrCl_2 (643 mg, 2.20 mmol) and CH_2Cl_2 (50 mL) under N_2 after which Me_3Al (2.9 mL, 30 mmol, USE CAUTION, PYROPHORIC) was added by syringe. The resulting mixture was allowed to cool to –23 ºC (dry ice/acetone bath) and H_2O (0.27 ml, 15 mmol) was added by syringe dropwise (reaction is extremely vigorous). After allowing the mixture to stir for 10 min, phenylacetylene (1.1 ml, 10 mmol) was added by syringe. The solution was allowed to stir for an additional 10 minutes, after which, acetyl chloride (0.85 ml, 12 mmol) was added. The mixture was allowed to stir for 10 min at –23 ºC and then warm to 22 ºC and stir an additional 10 min. The reaction was quenched upon dropwise addition of a saturated aqueous solution of K_2CO_3 (1 mL, reaction is vigorous, use of a vent needle is recommended) until evolution of gas ceases. The mixture was transferred to a seperatory funnel, Rochelle's salt was added (20 mL) and the layers separated. The aqueous layer was washed with Et_2O (2 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by silica gel chromatography (100% hexanes –> 20:1 Hexanes/Et_2O) as a light yellow solid (1.3 g, 8.0 mmol, 80%).

Characterization data for previously undisclosed substrates:

(*E*)-4-(Thiophen-3-yl)pent-3-en-2-one (2a): IR (neat): 3105 (w), 2999 (w), 2953 (w), 2917 (w), 1676 (m), 1586 (s), 1514 (w), 1420 (w), 1367 (w), 1353 (m), 1332 (w), 1260 (w), 1208 (w), 1173 (s), 1096 (w), 1015 (w), 963 (m), 918 (w), 880 (w), 850 (w), 780 (s), 699 (w), 640 (w), 580 (w), 529 (m), 505 (w), 464 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52–7.51 (1H, m), 7.32–7.31 (2H, m), 6.60 (1H, s), 2.53 (3H, s), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.2, 147.3, 143.8, 126.4, 125.4, 125.0, 122.8, 32.5, 17.8; HRMS (ESI^+): Calcd for $C_9H_{11}O_1S_1$ $[M+H]^+$: 167.0531; Found: 167.0531.

(*E*)-4-(Thiophen-2-yl)pent-3-en-2-one (2c): IR (neat): 3107 (w), 3004 (w), 2954 (w), 1673 (m), 1582 (s), 1516 (w), 1424 (w), 1384 (w), 1361 (w), 1259 (w), 1220 (w), 1183 (m), 1053 (w), 1015 (w), 975 (w), 955 (w), 853 (w), 706 (w), 635 (w), 530 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.33 (2H, m), 7.07–7.05 (1H, m), 6.63 (1H, s), 2.57 (3H, d, J = 1.2 Hz), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.1, 146.6, 146.3, 128.5, 127.8, 127.7, 121.8, 32.2, 17.4; HRMS (ESI^+): Calcd for $C_9H_{11}O_1S_1$ $[M+H]^+$: 167.0531; Found: 167.0524.

(*E*)-4-(4-(Trifluoromethyl)phenyl)pent-3-en-2-one (2e): IR (neat): 1686 (m), 1606 (m), 1573 (w), 1411 (w), 1357 (w), 1325 (s), 1267 (w), 1168 (m), 1119 (m), 1083 (w), 1066 (w), 1015 (w), 963 (w), 831 (w), 665 (w), 607 (w), 552 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (2H, d, J = 8.4 Hz), 7.56 (2H, d, J = 8.8 Hz), 6.50 (1H, d, J = 1.2 Hz), 2.53 (3H, d, J = 1.6 Hz), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 152.2, 146.3, 131.0 (q, $J_{C–F}$ = 32.2 Hz), 127.0, 125.7, 125.5, 124.1 (q, $J_{C–F}$ = 272.3 Hz), 32.3, 18.4; HRMS (ESI^+): Calcd for $C_{12}H_{12}O_1F_3$ $[M+H]^+$: 229.0840; Found: 229.0849.

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[6] P. Wipf, S. Lim, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1068–1071.

(*E*)-4-(4-Methoxyphenyl)pent-3-en-2-one (2f): IR (neat): 2958 (w), 2838 (w), 1676 (m), 1590 (s), 1570 (m), 1511 (m), 1460 (w), 1437 (w), 1420 (w), 1377 (w), 1356 (w), 1291 (w), 1252 (m), 1178 (s), 1129 (w), 1081 (w), 1030 (w), 926 (w), 826 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (2H, dd, *J* = 6.8, 2.4 Hz), 6.90 (2H, dd, *J* = 6.8, 2.4 Hz), 6.50 (1H, d, *J* = 1.2 Hz), 3.84 (3H, s), 2.53 (3H, d, *J* = 1.6) 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.9, 160.7, 153.5, 134.7, 128.0, 123.0, 114.1, 55.5, 32.4, 18.2; HRMS (ESI+) Calcd for $C_{12}H_{15}O_2$ $[M+H^+]$: 191.1072. Found: 191.1076.

(*E*)-4-cyclohexylpent-3-en-2-one (2g): IR (neat): 2961 (m), 2924 (s), 2880 (w), 2852 (m), 1708 (s), 1449 (m), 1417 (w), 1378 (w), 1355 (m), 1270 (w), 1183 (w), 1148 (w), 1036 (w), 1007 (w), 965 (w), 933 (w), 894 (w), 848 (w), 795 (w), 774 (w), 641 (w), 572 (w), 535 (w), 504 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.05 (1H, s), 2.17 (3H, s), 2.10 (3H, s), 1.97–1.92 (1H, m), 1.81–1.69 (5H, m), 1.34–1.14 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.5, 163.6, 122.0, 49.1, 32.1, 31.5, 26.6, 26.3, 18.0; HRMS (ESI^+): Calcd for $C_{11}H_{19}O_1$ $[M+H]^+$: 167.1436; Found: 167.1436.

(*E*)-4-(3-fluorophenyl)pent-3-en-2-one (2j): IR (neat): 3069 (w), 3003 (w), 2953 (w), 1682 (s), 1603 (s), 1581 (s), 1485 (w), 1431 (w), 1378 (w), 1356 (m), 1283 (w), 1268 (w), 1196 (s), 1088 (w), 1016 (w), 964 (w), 919 (w), 876 (w), 850 (w), 784 (m), 738 (w), 690 (w), 648 (w), 524 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.31 (1H, m), 7.27–7.25 (1H, m), 7.18–7.15 (1H, m), 7.06–7.06 (1H, m), 6.50 (1H, s), 2.50 (3H, d, *J* = 1.4 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 162.9 (d, $J_{C–F}$ = 244.8 Hz), 152.2, 144.9 (d, $J_{C–F}$ = 7.5 Hz), 130.2 (d, $J_{C–F}$ = 8.2 Hz), 125.2, 122.3 (d, $J_{C–F}$ = 3.0 Hz), 115.9 (d, $J_{C–F}$ = 20.8 Hz), 113.6 (d, $J_{C–F}$ = 22.3 Hz), 32.3, 18.3; HRMS (ESI^+): Calcd for $C_{11}H_{12}O_1F_1$ $[M+H]^+$: 179.0872; Found: 179.0880.

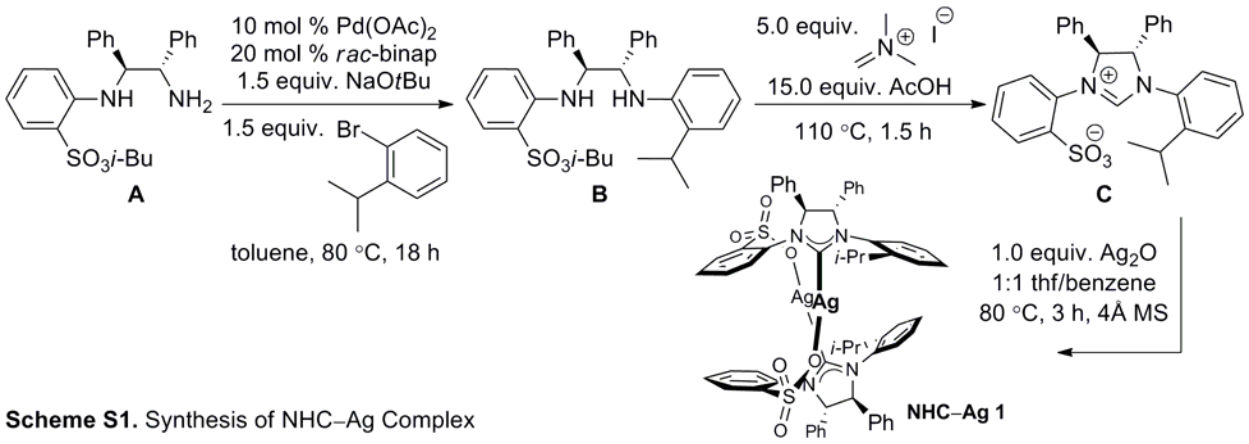
(*E*)-*tert*-Butyl-2-methyl-4-oxopent-2-enoate (Substrate for 6c): IR (neat): 2979 (w), 2932 (w), 1714 (s), 1693 (s), 1620 (w), 1478 (w), 1458 (w), 1425 (w), 1392 (w), 1368 (m), 1275 (s), 1257 (s), 1190 (m), 1169 (s), 1124 (s), 1017 (w), 966 (w), 899 (w), 848 (w), 760 (w), 741 (w), 944 (w), 568 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.99 (1H, app d, *J* = 1.2 Hz), 2.23 (3H, s), 2.17 (3H, d, *J* = 1.6 Hz), 1.51 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.8, 166.9, 142.7, 131.8, 82.0, 32.3, 28.1, 14.5; HRMS (ESI^+): Calcd for $C_{10}H_{17}O_3$ $[M+H]^+$: 185.1178; Found: 185.1173.

(*E*)-4-Methyl-5-phenylpent-3-en-2-one (Substrate for 6a): IR (neat): 3062 (w), 3028 (w), 2913 (w), 1687 (s), 1618 (s), 1495 (w), 1454 (w), 1424 (w), 1388 (w), 1359 (w), 1212 (w), 1178 (w), 1160 (w), 1077 (w), 1029 (w), 1016 (w), 965 (w), 858 (w), 792 (w), 745 (m), 701 (m), 647 (w), 598 (w), 494 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.25 (3H, m), 7.18–7.16 (2H, m), 6.07 (1H, d, *J* = 1.2 Hz), 3.42 (2H, s), 2.18 (3H, s), 2.09 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.4, 156.9, 137.9, 129.3, 128.7, 126.8, 125.1, 47.9, 31.4, 18.7; HRMS (ESI^+): Calcd for $C_{12}H_{15}O_1$ $[M+H]^+$: 175.1123; Found: 175.1124.

(*E*)-4-(4-Methoxyphenyl)hex-3-en-2-one (SM for *S*-5d): IR (neat): 3073 (w), 2966 (w), 2936 (w), 2874 (w), 2838 (w), 1678 (m), 1589 (m), 1511 (s), 1463 (w), 1442 (w), 1418 (w), 1356 (w), 1287 (w), 1254 (m), 1176 (s), 1102 (w), 1064 (w), 1034 (w), 971 (w), 920 (w), 828 (m), 764 (w), 718 (w), 610 (w), 589 (w), 519 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44 (2H, dd, *J* = 6.4, 2.0 Hz), 6.91 (2H, dd, *J* = 6.8, 2.0 Hz), 6.39 (1H, s), 3.84 (3H, s), 3.04 (2H, q, *J* = 7.2 Hz), 2.27

(3H, s), 1.07 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.4, 160.6, 160.1, 133.4, 128.3, 122.7, 114.1, 55.5, 32.5, 24.3, 13.9; HRMS (ESI^+): Calcd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1229; Found: 205.1247.

■ **Experimental Procedures for the Synthesis of NHC–Ag Complex:**



Scheme S1. Synthesis of NHC–Ag Complex

Isobutyl-2-(((1*S*,2*S*)-2-((2-isopropylphenyl)amino)-1,2-diphenylethyl)amino)benzene-sulfonate (B): To a flame-dried round bottom flask in a N_2-filled glove box were added 1-bromo-2-*iso*propylbenzene (810. g, 4.07 mmol), $Pd(OAc)_2$ (56.5 mg, 0.271 mmol), NaO*t*Bu (391 mg, 4.07 mmol) and *rac*-binap (338 mg, 0.543 mmol). The flask was fitted with a reflux condenser capped with a septum and removed from the glove box. A solution of diamine **A** (1.15 g, 2.71 mmol) in toluene (20.0 mL) was added through a syringe and the resulting red solution that was allowed to stir at 80 °C (oil bath) for 18 h. The mixture was allowed to cool to 22 °C and the mixture was concentrated under reduced pressure to afford a red oil, which was dissolved in toluene, loaded on top of a column containing silica gel, and purified by silica gel chromatography (100% petroleum ether (to elute toluene)→90% petroleum ether/Et_2O) to afford **B** (841 mg, 1.85 mmol, 68.1%) as a yellow solid. Melting point: 54–56°C. IR (neat): 3417 (w), 3363 (w), 3035 (w), 2959 (w), 2872 (w), 1598 (w), 1575 (w), 1502 (m), 1465 (m), 1449 (m), 1395 (w), 1353 (w), 1332 (m), 1301 (m), 1264 (w), 1242 (w), 1192 (w), 1164 (s), 1113 (w), 1103 (w), 1067 (w), 1042 (w), 977 (w), 941 (w), 911 (w), 891 (s), 846 (w), 818 (m), 776 (w), 748 (s), 739 (s), 728 (w), 701 (s), 675 (w), 613 (s), 589 (m), 577 (w), 569 (w), 550 (w), 523 (m), 510 (w), 443 (w) cm^{-1}; (We have found that 1H NMR peaks of this compound can be concentration dependent and can shift +/- 0.2 ppm.) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72–7.70 (1H, m), 7.38–7.36 (2H, m), 7.33–7.23 (8H, m), 7.21–7.17 (1H, m), 7.12 (1H, d, J = 7.6 Hz), 6.91 (1H, d, J = 6.0 Hz), 6.87 (1H, dt, J = 7.8, 1.6 Hz), 6.67 (2H, dt, J = 7.2, 0.8 Hz), 6.41 (1H, d, J = 8.4 Hz), 6.28 (1H, d, J = 8.4 Hz), 4.94–4.92 (1H, m), 4.80 (1H, br s), 4.41 (1H, br s), 3.73–3.63 (2H, m), 3.01–2.95 (1H, m), 1.96–1.86 (1H, m), 1.31 (3H, d, J = 6.2 Hz), 1.17 (3H, d, J = 6.4 Hz), 0.91–0.85 (6H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 143.3, 139.6, 139.0, 135.2, 133.9, 130.9, 129.0, 128.7, 128.2, 127.8, 127.5, 127.2, 126.4, 125.0, 118.4, 117.4, 116.0, 113.8,

112.8, 76.4, 63.4, 62.9, 28.2, 27.4, 22.7, 22.5, 18.79, 18.76; HRMS (EI+): Calcd for $C_{33}H_{39}N_2O_3S_1$ $[M+H]^+$: 543.2681, Found: 543.2678; specific rotation: $[\alpha]_D^{20}$ –99.9 (*c* = 0.506, $CHCl_3$).

Imdizolinium Salt C: Diamine **B** (552 mg, 1.02 mmol) and *N*-methyl-*N*-methylideneiminium iodide (944 mg, 5.10 mmol) were weighed out into a 75 mL heavy wall sealed tube. Acetic acid (0.884 mL, 15.3 mmol) was added, the vessel sealed, and the mixture allowed to stir at 110 °C (the yellow heterogeneous mixture becomes black and homogeneous upon heating). After 1.5 h, the mixture was allowed to cool to 22 °C and diluted with Et_2O (5 mL) and water (5 mL). The resulting mixture was basified by the *slow* addition of a saturated aqueous solution of K_2CO_3 until gas evolution ceased. Dichloromethane (10 mL) was added and the aqueous layer separated. The aqueous layer was washed further with CH_2Cl_2 (2 x 10 mL) and the combined organic layers dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a yellow solid. The yellow solid was purified by silica gel column chromatography (100% EtOAc →2% MeOH/EtOAc →5% MeOH/EtOAc) to afford imidazolinium salt **C** (400. mg, 0.804 mmol, 78.7%) as a white solid. (Note: Separation of a yellow impurity by silica gel column chromatography can often be tedious. This solid can be obtained in white crystalline form by recrystallization from CH_2Cl_2:Et_2O, but such a procedure is not required for effective formation of Ag complex **1**.) IR (neat): 3063 (w), 2967 (w), 2928 (w), 1869 (w), 2242 (w), 1618 (s), 1587 (m), 1576 (m), 1497 (w), 1481 (w), 1457 (w), 1365 (w), 1273 (w), 1229 (s), 1204 (s), 1140 (w), 1088 (m), 1022 (m), 1005 (w), 909 (m), 884 (w), 759 (m), 725 (s), 701 (s), 664 (w), 646 (w), 612 (s), 564 (m), 534 (m), 484 (w), 448 (w) cm^{-1}; (We have found that ^1H NMR peaks of this compound can be concentration dependent and can shift +/- 0.2 ppm.) ^1H NMR ($CDCl_3$, 400 MHz**):** δ 8.83 (1H, s), 8.26 (1H, dd, *J* = 7.6, 1.6 Hz), 7.70–7.67 (2 H, m), 7.50–7.44 (6H, m), 7.36–7.28 (6H, m), 7.19–7.14 (1H, m), 7.11–7.07 (1H, m), 6.67 (1H, dd, *J* = 8.0 , 1.2 Hz), 6.28 (1H, d, *J* = 10.8 Hz), 5.58 (1H, d, *J* = 10.8 Hz), 3.33 (1H, septet, *J* = 6.4 Hz), 1.28 (3H, d, *J* = 6.8 Hz), 1.07 (3H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 153.2, 148.3, 146.2, 143.6, 135.2, 132.7, 131.4, 130.9, 130.8, 130.4, 130.4, 130.1, 130.1, 129.94, 129.90, 129.5, 128.9, 128.4, 127.5, 127.4, 78.3, 76.4, 28.4, 24.6, 24.3; HRMS (ESI+): Calcd for $C_{30}H_{28}N_2O_3S_1Na_1$ $[M+Na]^+$: 519.1718, Found: 519.1712; specific rotation: $[\alpha]_D^{20}$ +91.8 (*c* = 0.146, $CHCl_3$).

NHC–Ag complex: Imidazolinium salt **C** (170. mg, 0.526 mmol), Ag_2O (244. mg, 1.05 mmol) and oven-dried <5 micron 4Å molecular sieves (ca. 50 mg) were weighed out into an oven-dried 10 mL round bottom flask fitted with a reflux condenser, and wrapped with aluminum foil. Tetrahydrofuran (2.0 mL) followed immediately by benzene (2.0 mL) were added through a syringe resulting in a black heterogeneous mixture, which was allowed to stir at 80 °C. After 3 h, the mixture was allowed to cool to 22 °C and filtered through a short plug of Celite 545 (4 x 1 cm) eluted with thf (ca. 20 mL). The volatiles were removed in vacuo to afford 182. mg (0.301 mmol, 57.3%) of Ag complex as a white solid, which was stored under low light conditions. The silver complex exists as a mixture of rotamers of dimer and monomer in solution. All characterization is reported on this mixture. IR (neat): 3470 (br), 3064 (w), 3033 (w), 2960 (w),

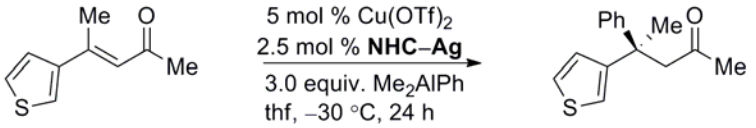
2925 (w), 2868 (w), 1626 (w), 1604 (w), 1590 (w), 1481 (m), 1456 (m), 1349 (w), 1280 (w), 1231 (m), 1204 (m), 1139 (w), 1091 (w), 1023 (w), 1104 (w), 920 (w), 898 (w), 764 (w), 724 (w), 701 (m), 665 (w), 651 (w), 614 (w), 560 (w), 543 (w) cm^{-1}; (We have found that ^1H NMR peaks of this compound can be concentration dependent and can shift +/- 0.2 ppm.) ^1H NMR ($CDCl_3$, 400 MHz): δ 8.18–8.12 (1H, m), 7.59–7.51 (2H, m), 7.42–6.99 (11H, m), 6.80–6.65 (2H, m), 6.48–6.40 (0.5H, m), 6.36–6.29 (1H, m), 6.24–6.06 (0.5H, m), 5.25–5.02 (1H, m), 4.41 (0.05 H, t, J = 7.2 Hz), 3.33–3.12 (1H, m), 2.72 (2H, s), 2.57–2.53 (0.07 H, m), 2.34–2.30 (0.07 H, m), 2.17 (0.11 H, br s), 1.46–1.24 (5H, m), 1.13 (0.16 H, d, J = 6.8 Hz), 0.95–0.89 (0.44 H, m), 0.73 (0.23H, br s), 0.55 (0.59H, br s), 0.30 (1H, d, J = 6.0 Hz), 0.13 (0.45H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.4, 205.3, 144.8, 143.1, 138.6, 137.5, 136.9, 136.5, 135.5, 131.3, 131.0, 130.7, 130.1, 129.8, 129.6, 128.9, 128.8, 128.7, 128.6, 128.4, 127.1, 126.9, 126.7, 125.8, 125.6, 80.1, 79.1, 76.4, 68.7, 68.1, 66.0, 64.5, 38.2, 35.4, 30.7, 29.8, 28.3, 27.9, 26.9, 25.7, 25.2, 24.5, 23.8, 22.7, 22.3, 21.7, 19.2; HRMS (EI+): Calcd for $C_{25}H_{25}N_2O_3NaSAg$ $[M+Na]^+$: 563.0535, Found: 563.0536; specific rotation: $[\alpha]_D^{20}$ –44. (c = 0.25, $CHCl_3$).

■ **Representative Procedure for the Preparation of Arylaluminum Reagents:** To a flame-dried 10 mL round bottom flask equipped with a stir bar was added bromobenzene (0.42 mL, 4.00 mmol) and thf (2 mL). The mixture was allowed to cool to –78 ˚C before *n*BuLi (2.52 mL, 4.00 mmol) was added dropwise by syringe addition and the solution was allowed to stir at –78 ˚C for 1 h. At this point Me_2AlCl (0.37 mL, 4.0 mmol) was added dropwise by syringe and the solution was allowed to warm to 22 °C and stir for 12 h. Pentanes (2 mL) was added and the solution was allowed to stir for 1 h. The solution was allowed to stand for >1 h before using the top pentane layer in reactions. (The lower thf layer contains LiCl salts, which are detrimental to the enantioselectivity of the reaction).

■ **Representative Procedure for Catalytic Enantioselective Addition of Arylaluminum Reagents to Acyclic Enones:** An oven-dried 1 dram vial, equipped with a stir bar was charged with chiral NHC–Ag complex **1** (3.0 mg, 5.0 μmol) and $Cu(OTf)_2$ (1.6 mg, 5.0 μmol), weighed out under a N_2 atmosphere in a glove box. The vial was sealed with a septum cap and removed from the glovebox. Tetrahydrofuran (1.0 mL) was added to the vial and the resulting solution was allowed to stir for five minutes prior to cooling to –30 ˚C. Dimethylphenylaluminum (0.581M, 200 μL, 0.200 mmol) was added, resulting in a brown solution to which a solution of the enone substrate (*E*)-4-(thiophen-3-yl)pent-3-en-2-one (0.2M, 0.5 ml, 100 μmol) was added. The septum cap was exchanged for a solid cap and the vial was transferred to a cryocool (–30 ˚C) for 1 hour. The reaction was quenched with a saturated solution of sodium potassium tartrate (1.0 mL). After the mixture was allowed to warm to 22 ˚C, the solution was diluted with Et_2O and the layers were separated. The aqueous layer was washed with Et_2O (3 x 1 mL). The combined organic layers were passed through a short plug of silica gel (4 cm x 1 cm) eluting with Et_2O (10.0 mL). The organic layer was concentrated to a yellow oil and purified by silica gel chromatography (10:1 hexanes/Et_2O) to afford 17.1 mg of (*R*)-4-phenyl-4-(thiophen-3-yl)pentan-2-one as a clear, yellow oil (0.087 mmol, 87% yield).

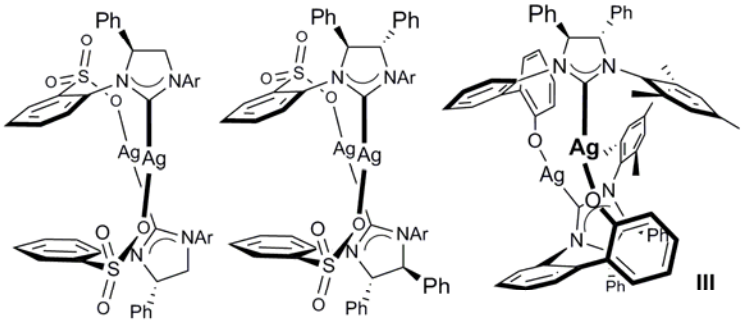
■ Catalyst Screen for Aryl Addition:

Table S1: Catalyst Screen for Aryl Addition to Acyclic Enones[a]



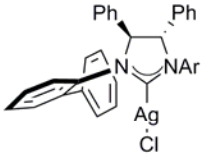
entry	NHC–Ag	conv. [%][b]	yield [%][c]	er[d]
1	**Ia**	70	65	89:11
2	**Ib**	65	55	52:48
3	**Ic**	5	nd	nd
4	**IIa**	70	61	85:15
5	**IIb**	>98	85	97.5:2.5
6	**IIc**	98	71	99:1
7	**III**	90	70	54:46
8	**IVa**	>98	81	94:6
9	**IVb**	>98	76	94.5:5.5
10	**IVc**	>98	73	93:7
11	**Va**	>98	73	69:31
12	**Vb**	>98	79	82:18

[a] Reactions were performed under a N_2 atmosphere. [b] Determined by analysis of 400 MHz ^{1}H NMR of unpurified mixtures. [c] Yields of isolated products after purification (±5%). [d] Determined by GC analysis. nd = not determined.

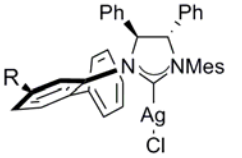


Ia Ar = 2,4,6MeC$_6$H$_2$
Ib Ar = 3,5MeC$_6$H$_3$
Ic Ar = 2,6*i*PrC$_6$H$_3$

IIa Ar = 2,4,6MeC$_6$H$_2$
IIb Ar = 2,6EtC$_6$H$_3$
IIc Ar = 2*i*PrC$_6$H$_4$



IVa Ar = 2,4,6MeC$_6$H$_2$
IVb Ar = 2,6EtC$_6$H$_3$
IVc Ar = 2(C$_6$H$_5$)C$_6$H$_4$



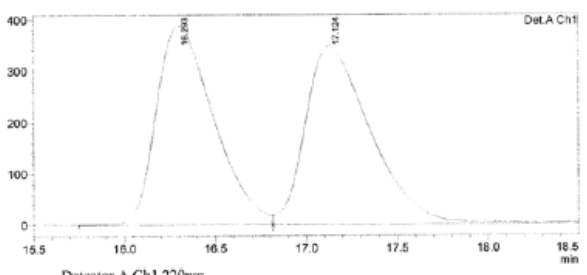
Mes = 2,4,6MeC$_6$H$_2$
Va R = *i*-Pr
Vb R = *t*-Bu

entry	Cu source	conv. [%][b]	er[d]
1	$CuBr_2$	60	93:7
2	$CuCl_2$	61	92:8
3	$CuCl_2•2H_2O$	64	93:7
4	CuCl	83	94:6
5	$CuOTf_2$	>98	99:1

2.5 mol % **IIc**, 5 mol % ***Cu Source***
3.0 equiv. Me_2AlPh, thf, 24 h, –30 °C

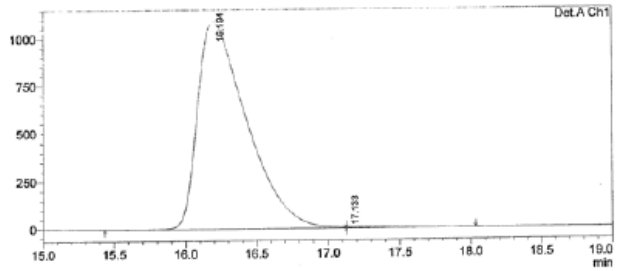
■ Analytical Data of Aryl Addition Products:

(*S*)-4-Phenyl-4-(thiophen-3-yl)pentan-2-one (*S*-3a): IR (neat): 3109 (w), 3085 (w), 3057 (w), 3026 (w), 2970 (w), 2933 (w), 2887 (w), 1719 (s), 1599 (w), 1494 (w), 1445 (w), 1414 (w), 1356 (m), 1305 (w), 1272 (w), 1228 (w), 1201 (w), 1156 (w), 1085 (w), 1030 (w), 971 (w), 932 (w), 910 (w), 865 (w), 787 (m), 769 (m), 701 (s), 676 (w), 661 (w), 612 (w), 550 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.13 (6H, m), 6.97–6.96 (1H, m), 6.75–6.73 (1H, m), 3.15 (2H, ABq, $\Delta\delta_{AB}$ = 0.05, J_{AB} = 13.6 Hz), 1.74 (3H, s), 1.70 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.9, 150.0, 147.8, 128.4, 127.7, 126.9, 126.5, 125.8, 120.2, 54.9, 43.8, 32.0, 27.8; HRMS (ESI$^+$): Calcd for $C_{15}H_{20}N_1O_1S_1[M+NH_4]^+$: 262.1266; Found: 262.1270; specific rotation: $[\alpha]_D^{20}$ +1.09 (*c* = 1.13 $CHCl_3$) for an enantiomerically enriched sample of 99.6:0.4 er. Enantiomeric purity (99.6:0.4er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 0.8 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.293	8535564	387936	49.085
2	17.124	8853662	348350	50.915
Total		17389226	736286	100.000

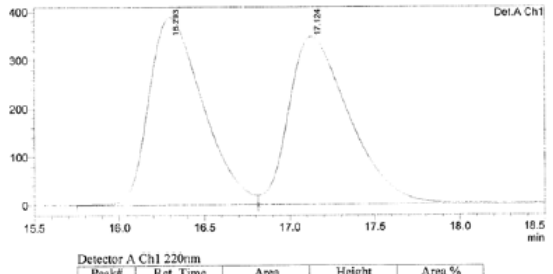


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.194	26274348	1092593	99.630
2	17.133	97474	4387	0.370
Total		26371822	1096980	100.000

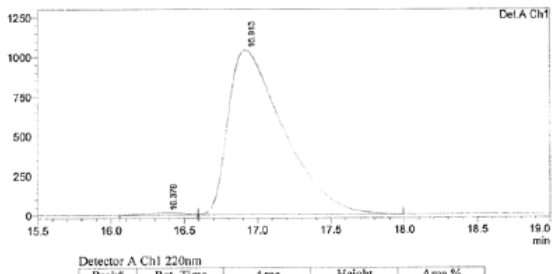
Retention Time	Area	Area %	Retention Time	Area	Area %
16.293	8535564	49.085	16.194	26274348	99.630
17.124	8853662	50.915	17.133	97474	0.370

(*R*)-4-Phenyl-4-(thiophen-3-yl)pentan-2-one (*R*-3a): IR (neat): 3109 (w), 3085 (w), 3057 (w), 3026 (w), 2970 (w), 2933 (w), 2887 (w), 1719 (s), 1599 (w), 1494 (w), 1445 (w), 1414 (w), 1356 (m), 1305 (w), 1272 (w), 1228 (w), 1201 (w), 1156 (w), 1085 (w), 1030 (w), 971 (w), 932 (w), 910 (w), 865 (w), 787 (m), 769 (m), 701 (s), 676 (w), 661 (w), 612 (w), 550 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.13 (6H, m), 6.97–6.96 (1H, m), 6.75–6.73 (1H, m), 3.15 (2H, ABq, $\Delta\delta_{AB} = 0.05$, $J_{AB} = 13.6$ Hz), 1.74 (3H, s), 1.70 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.9, 150.0, 147.8, 128.4, 127.7, 126.9, 126.5, 125.8, 120.2, 54.9, 43.8, 32.0, 27.8; HRMS (ESI^+): Calcd for $C_{15}H_{20}N_1O_1S_1[M+NH_4]^+$: 262.1266; Found: 262.1262; specific rotation: $[\alpha]_D^{20}$ –4.2 (*c* = 0.35 $CHCl_3$) for an enantiomerically enriched sample of 92:8 er. Enantiomeric purity (99:1 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 0.8 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.293	8535564	387936	49.085
2	17.124	8853662	348350	50.915
Total		17389226	736286	100.000



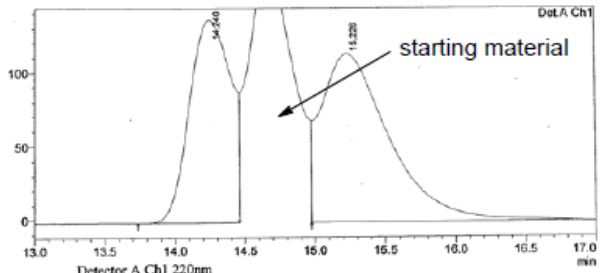
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	16.378	281652	15861	1.015
2	16.913	27463380	1041516	98.985
Total		27745033	1057377	100.000

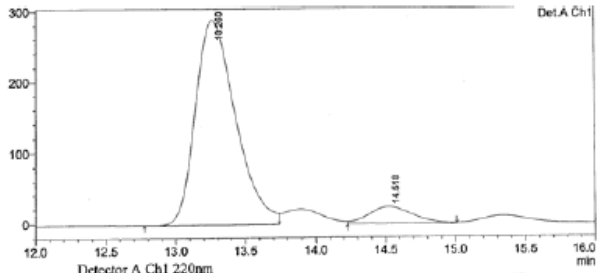
Retention Time	Area	Area %	Retention Time	Area	Area %
16.293	8535564	49.085	16.378	281652	1.015
17.124	8853662	50.915	16.913	27463380	98.985

(*R*)-4-Phenyl-4-(thiophen-2-yl)pentan-2-one (3b): IR (neat): 3107 (w), 3087 (w), 3060 (w), 3024 (w), 2996 (w), 1971 (w), 1932 (w), 1851 (w), 1720 (m), 1705 (m), 1582 (w), 1494 (w), 1445 (w), 1357 (m), 1308 (w), 1236 (w), 1157 (w), 1081 (w), 1054 (w), 1031 (w), 968 (w), 921 (w), 851 (w), 830 (w), 765 (w), 698 (s), 597 (w), 545 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.27 (4H, m), 7.24–7.19 (1H, m), 7.16 (1H, dd, *J* = 4.8, 1.2 Hz), 6.92 (1H, dd, *J* = 5.2, 3.6 Hz), 6.80 (1H, dd, *J* = 3.6, 1.2 Hz), (2H, ABq, $\Delta\delta_{AB} = 0.11$, $J_{AB} = 14.8$ Hz), 1.90 (3H, s), 1.83

(3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.0, 128.4, 126.7, 126.54, 126.49, 124.01, 124.02, 55.9, 44.1, 28.9; HRMS (ESI^+): Calcd for $C_{15}H_{17}O_1S_1[M+H]^+$: 245.1000; Found: 245.0992; specific rotation: $[\alpha]_D^{20}$ –4.2 (*c* = 0.35 $CHCl_3$) for an enantiomerically enriched sample of 92:8 er. Enantiomeric purity (92:8 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.8% hexanes, 0.2% *i*-PrOH, 0.8 mL/min, 220 nm.



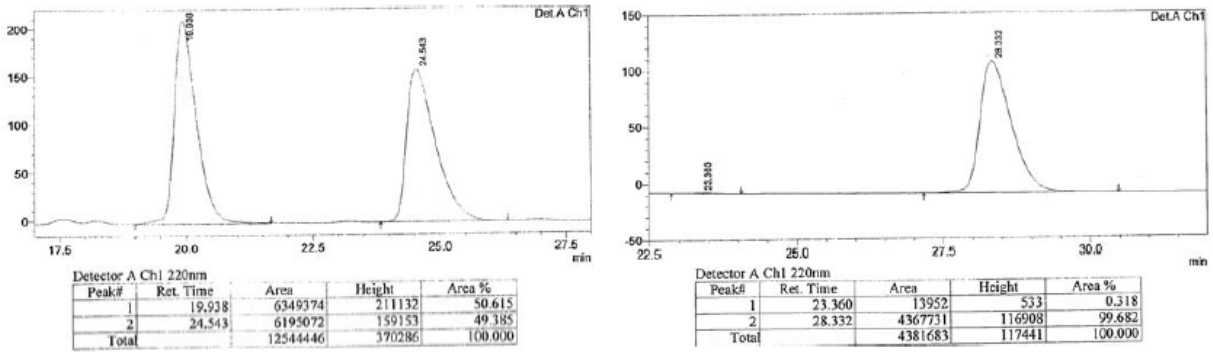
Peak#	Ret. Time	Area	Height	Area %
1	14.240	2841616	137407	42.590
2	15.226	3830386	113954	57.410
Total		6672002	251361	100.000



Peak#	Ret. Time	Area	Height	Area %
1	13.260	5828505	289043	91.730
2	14.518	525475	24162	8.270
Total		6353980	313205	100.000

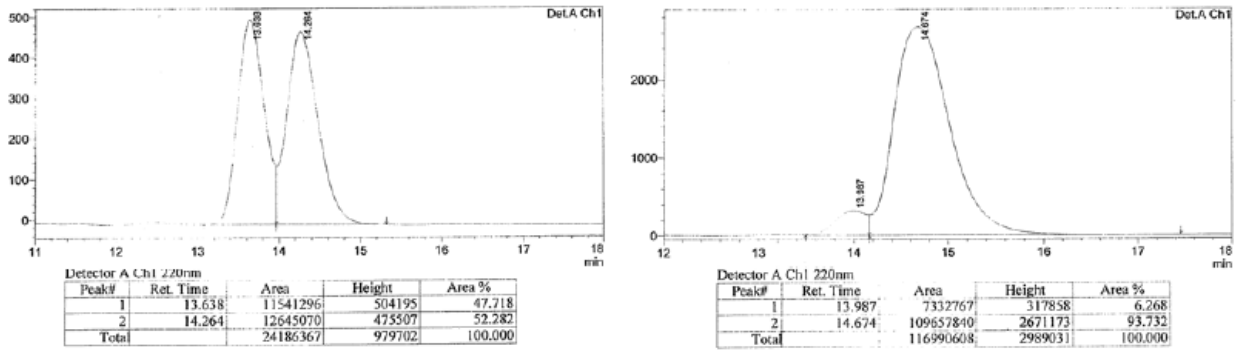
Retention Time	Area	Area %	Retention Time	Area	Area %
14.240	2841616	42.590	13.260	528505	91.730
15.226	3830386	57.410	14.518	525475	8.270

(*R*)-4-(2-Fluorophenyl)-4-phenylpentan-2-one (3c): (All data are reported on an inseparable mixture of 1:1.3 product: 1,4-Me addition) IR (neat): 3085 (w), 3061 (w), 3032 (w), 2966 (w), 2928 (w), 2883 (w), 2855 (w), 1718 (s), 1612 (w), 1602 (w), 1578 (w), 1488 (s), 1446 (m), 1421 (w), 1358 (m), 1309 (w), 1280 (w), 1210 (m), 1162 (w), 1135 (w), 1113 (w), 1085 (w), 1031 (w), 970 (w), 942 (w), 813 (w), 757 (s), 700 (m), 597 (w) 557 (w), 528 (w), 500 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41–7.37 (1H, m), 7.33–7.13 (8H, m), 7.12–7.06 (2H, m), 7.02–6.91 (2H, m), 3.36 (2H, ABq, $\Delta\delta_{AB}$ = 0.38, J_{AB} = 14.4 Hz), 2.95 (3H, s), 1.89 (4H, s), 1.82 (3H, s), 1.81 (3H, s), 1.46 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.0, 207.7, 161.6 (d, J_{CF} = 244.8 Hz), 161.1 (d, J_{CF} = 247.0 Hz), 148.6, 134.4, 134.3, 129.0, 128.8 (d, J_{CF} = 4.5 Hz), 128.7 (d, J_{CF} = 8.2 Hz), 128.2 (d, J_{CF} = 5.7 Hz), 128.1 (d, J_{CF} = 8.9 Hz), 127.8, 126.2, 125.84, 125.83, 124.2 (d, J_{CF} = 3.0 Hz), 124.0 (d, J_{CF} = 3.0 Hz), 116.5 (d, J_{CF} = 23.1 Hz), 116.3 (d, J_{CF} = 24.6 Hz), 54.3 (d, J_{CF} = 5.2 Hz), 52.6 9 d, J_{CF} = 3.7 Hz), 44.0 (d, J_{CF} = 1.5 Hz), 36.5 (d, J_{CF} = 3.0 Hz), 32.0, 31.5, 29.9, 28.6 (d, J_{CF} = 2.2 Hz), 27.9; HRMS (ESI^+): Calcd for $C_{17}H_{18}F_1O_1[M+H]^+$: 257.1342; Found: 257.1349. specific rotation: $[\alpha]_D^{20}$ +32. (*c* = 0.38 $CHCl_3$) for an enantiomerically enriched sample of 99.7:0.3 er. Enantiomeric purity (99.7:0.3 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.8 mL/min, 220 nm.



Retention Time	Area	Area %	Retention Time	Area	Area %
19.938	6349374	50.615	23.360	13952	0.318
24.543	6195072	49.385	28.332	4367731	99.682

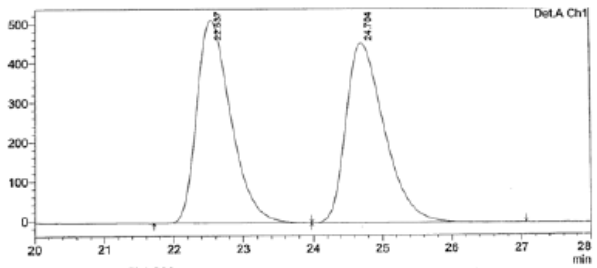
(*R*)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one (3d): (Carbon spectra was recorded as an inseparable 92:8 mixture of product and Me addition product). IR (neat): 3060 (w), 2971 (w), 2922 (w), 2851 (w), 1720 (m), 1617 (w), 1495 (w), 1409 (w), 1358 (w), 1324 (s), 1162 (m), 1113 (s), 1071 (m), 1030 (w), 1015 (m), 840 (w), 769 (w), 746 (w), 700 (m), 611 (w), 553 (w), 539 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54–7.52 (2H, m), 7.32–7.18 (5H, m) 7.17–7.15 (2H, m), 3.27 (2H, ABq, $\Delta\delta_{AB} = 0.03$, $J_{AB} = 14.9$ Hz), 1.83 (3H, s), 1.79 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.1, 152.9, 147.8, 129.2, 128.7, 128.5, 127.6, 127.1, 126.6, 126.4, 126.0, 125.3 (q, $J_{CF} = 3.7$ Hz), 125.2 (q, $J_{CF} = 3.8$ Hz), 124.3 (q, $J_{CF} = 270.8$ Hz), 56.4, 54.3, 45.8, 32.1, 31.7, 29.1, 27.8, 22.8, 14.3; HRMS (ESI^+): Calcd for $C_{18}H_{21}F_3N_1O_1[M+NH_4]^+$: 324.1575; Found: 324.1577; specific rotation: $[\alpha]_D^{20}$ –1.8 (*c* = 0.43 $CHCl_3$) for an enantiomerically enriched sample of 94:6 er. Enantiomeric purity (94:6 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.5 ml/min, 220nm.



Retention Time	Area	Area %	Retention Time	Area	Area %
13.638	11541296	47.718	13.987	7332767	6.268
14.264	12645070	52.282	14.674	109657840	93.732

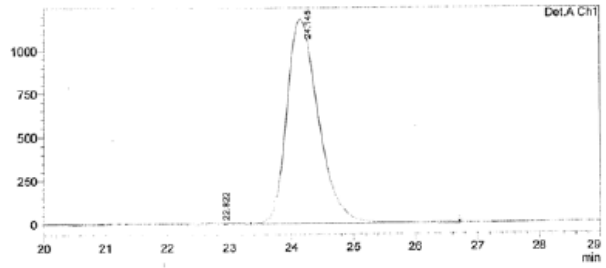
(*R*)-4-(4-Methoxyphenyl)-4-phenylpentan-2-one (3e): IR (neat): 3057 (w), 2964 (w), 2935 (w), 2836 (w), 1703 (m), 1609 (w), 1581 (w), 1511 (s), 1495 (w), 1464 (w), 1444 (w), 1415 (w), 1356

(w), 1297 (s), 1250 (m), 1183 (w), 1158 (w), 1113 (w), 1076 (w), 1031 (m), 830 (m), 804 (w), 777 (w), 766 (w), 701 (m), 551 (m), cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.27 (3H, m), 7.20–7.17 (2H, m) 7.12–7.09 (2H, m), 6.83–6.81 (2H, m), 3.79 (3H, s), 3.20 (2H, ABq, $\Delta\delta_{AB} = 0$, J_{AB} = 14.4 Hz), 1.78 (3H, s), 1.70 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.4, 157.9, 149.1, 140.7, 128.3, 128.0, 127.1, 126.2, 113.6, 55.3, 54.8, 45.1, 32.2, 28.1; HRMS (ESI^+): Calcd for $C_{18}H_{20}O_2[M+H]^+$: 268.1463; Found: 268.1472; specific rotation: $[\alpha]_D^{20}$ +13. (*c* = 0.29 $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Enantiomeric purity (98:2 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.5 ml/min, 220nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	22.537	17628066	514822	50.068
2	24.704	17580052	456085	49.932
Total		35208118	970907	100.000

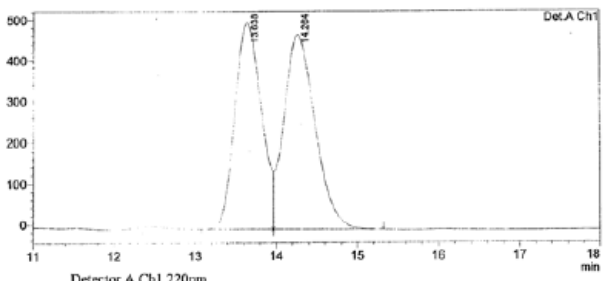


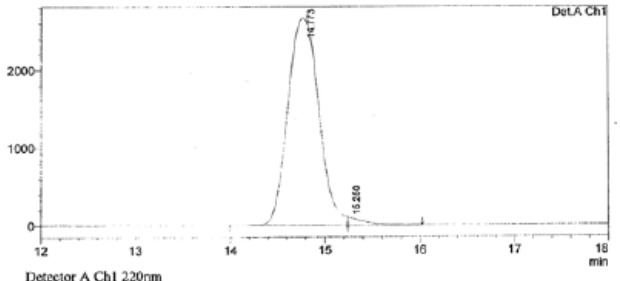
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	22.822	86349	2805	0.208
2	24.145	41446667	1178824	99.792
Total		41533016	1181629	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
22.537	17628066	50.068	22.609	52935217	98.394
24.704	17580052	49.932	23.971	864133	1.606

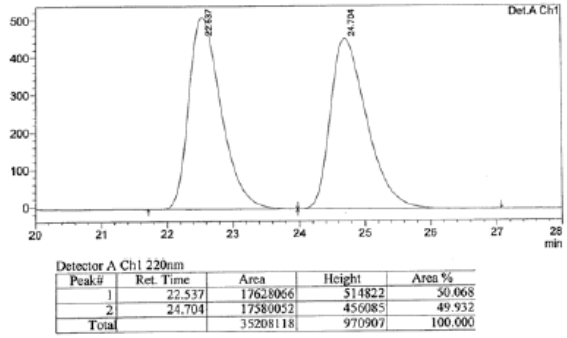
(*S*)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one (3f): (Carbon spectra was recorded as an inseparable 92:8 mixture of product and Me addition product). IR (neat): 3060 (w), 2971 (w), 2922 (w), 2851 (w), 1720 (m), 1617 (w), 1495 (w), 1409 (w), 1358 (w), 1324 (s), 1162 (m), 1113 (s), 1071 (m), 1030 (w), 1015 (m), 840 (w), 769 (w), 746 (w), 700 (m), 611 (w), 553 (w), 539 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54–7.52 (2H, m), 7.32–7.18 (5H, m) 7.17–7.15 (2H, m), 3.27 (2H, ABq, $\Delta\delta_{AB}$ = 0.03, J_{AB} = 14.9 Hz), 1.83 (3H, s), 1.79 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.1, 152.9, 147.8, 129.2, 128.7, 128.5, 127.6, 127.1, 126.6, 126.4, 126.0, 125.3 (q, J_{CF} = 3.7 Hz), 125.2 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 270.8 Hz), 56.4, 54.3, 45.8, 32.1, 31.7, 29.1, 27.8, 22.8, 14.3; HRMS (ESI^+): Calcd for $C_{18}H_{21}F_3N_1O_1[M+NH_4]^+$: 324.1575; Found: 324.1588; specific rotation: $[\alpha]_D^{20}$ +16.3 (*c* = 1.53 $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Enantiomeric purity (98:2 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.5 ml/min, 220nm.

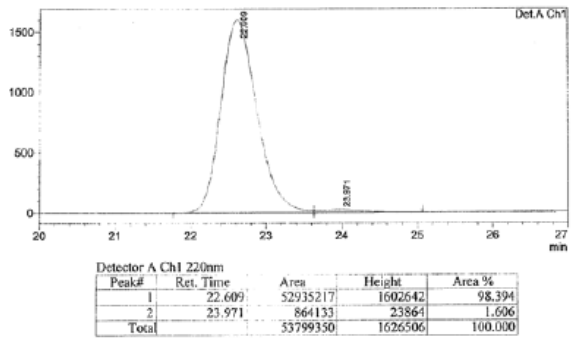




Retention Time	Area	Area %	Retention Time	Area	Area %
13.638	11541296	47.718	14.773	2666923	98.262
14.264	12645070	52.282	15.250	1067308	1.738

(*S*)-4-(4-Methoxyphenyl)-4-phenylpentan-2-one (3g): IR (neat): 3057 (w), 2964 (w), 2935 (w), 2836 (w), 1703 (m), 1609 (w), 1581 (w), 1511 (s), 1495 (w), 1464 (w), 1444 (w), 1415 (w), 1356 (w), 1297 (s), 1250 (m), 1183 (w), 1158 (w), 1113 (w), 1076 (w), 1031 (m), 830 (m), 804 (w), 777 (w), 766 (w), 701 (m), 551 (m), cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.27 (3H, m), 7.20–7.17 (2H, m) 7.12–7.09 (2H, m), 6.83–6.81 (2H, m), 3.79 (3H, s), 3.20 (2H, ABq, $\Delta\delta_{AB} = 0$, J_{AB} = 14.4 Hz), 1.78 (3H, s), 1.70 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.4, 157.9, 149.1, 140.7, 128.3, 128.0, 127.1, 126.2, 113.6, 55.3, 54.8, 45.1, 32.2, 28.1; HRMS (ESI^+): Calcd for $C_{18}H_{24}N_1O_2[M+NH_4]^+$: 286.1807; Found: 286.1802; specific rotation: $[\alpha]_D^{20}$ –13.4 (*c* = 1.38 $CHCl_3$) for an enantiomerically enriched sample of 99.8:0.2 er. Enantiomeric purity (99.8:0.2 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.5 ml/min, 220nm.

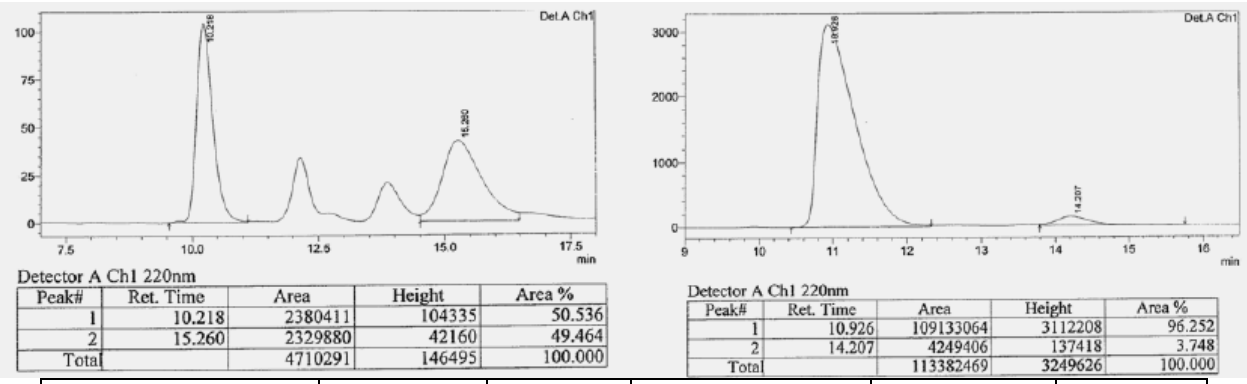




Retention Time	Area	Area %	Retention Time	Area	Area %
22.537	17628066	50.068	22.822	86349	0.208
24.704	17580052	49.932	24.145	41446667	99.792

(*R*)-4-(Thiophen-3-yl)-4-(4-(trifluoromethyl)phenyl)pentan-2-one (3h): IR (neat): 3107 (w), 2972 (w), 2936 (w), 1720 (m), 1618 (w), 1460 (w), 1411 (w), 1358 (w), 1327 (s), 1164 (m), 1122 (s), 1079 (m), 1064 (w), 1015 (w), 932 (w), 841 (w), 783 (w), 748 (w), 728 (w), 682 (w), 659 (w), 625 (w), 608 (w), 541 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.54 (2H, d, *J* = 8.0 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.26 (1H, s), 7.01 (1H, app s), 6.75 (1H, d, *J* = 4.4 Hz), 3.23 (2H, ABq, $\Delta\delta_{AB} = 0$, J_{AB} = 16.8 Hz), 1.84 (3H, s), 1.82 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ

206.8, 151.9, 149.1, 128.6 (q, J_{CF} = 32.2 Hz), 127.4, 127.1, 126.2, 125.3 (q, J_{CF} = 3.7 Hz), 124.4 (q, J_{CF} = 288.7 Hz), 120.5, 54.4, 43.7, 31.6, 27.8; HRMS (ESI^+): Calcd for $C_{16}H_{19}F_3N_1O_1S_1[M+NH_4]^+$: 330.1139; Found: 330.1143; specific rotation: $[\alpha]_D^{20}$ +10.2 (*c* = 1.03 $CHCl_3$) for an enantiomerically enriched sample of 96:4 er. Enantiomeric purity (96:4 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AS(H), 99.5% hexanes, 0.5% *i*-PrOH, 1.0 ml/min, 220nm.



Detector A Ch1 220nm

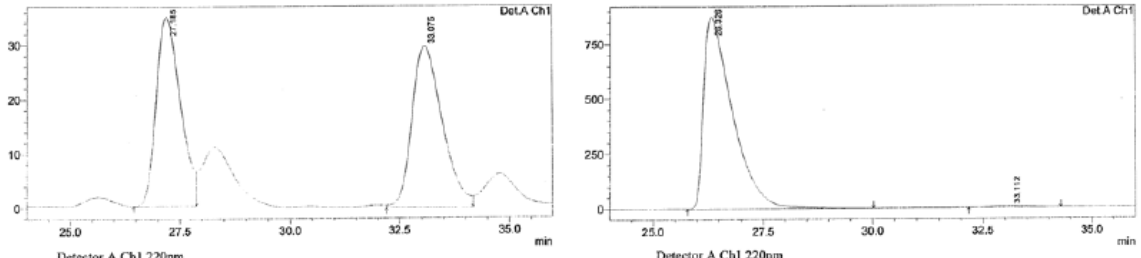
Peak#	Ret. Time	Area	Height	Area %
1	10.218	2380411	104335	50.536
2	15.260	2329880	42160	49.464
Total		4710291	146495	100.000

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	10.926	109133064	3112208	96.252
2	14.207	4249406	137418	3.748
Total		113382469	3249626	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
10.218	2380411	50.536	10.926	109133064	96.252
15.260	2329880	49.464	14.207	4249406	3.748

(*R*)-4-(4-Methoxyphenyl)-4-(thiophen-3-yl)pentan-2-one (3i): IR (neat): 3106 (w), 3038 (w), 2961 (w), 2834 (w), 1702 (m), 1609 (w), 1581 (w), 1510 (s), 1462 (w), 1441 (w), 1414 (w), 1355 (w), 1294 (w), 1248 (s), 1182 (m), 1156 (w), 1108 (w), 1085 (w), 1032 (m), 866 (w), 829 (m), 785 (m), 669 (w), 649 9w), 552 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.22 (1H, m), 7.14–7.11 (2H, m), 7.00–6.99 (1H, m), 6.83–6.81 (2H, m), 6.80–6.78 (1H, m), 3.79 (3H, s), 3.16 (2H, ABq, $\Delta\delta_{AB}$ = 0.06, J_{AB} = 13.6 Hz), 1.76 (3H, s), 1.74 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.1, 158.0, 150.4, 139.8, 127.7, 127.6, 125.7, 120.0, 113.6, 55.3, 55.1, 43.2, 32.1, 27.9; HRMS (ESI^+): Calcd for $C_{16}H_{22}N_1O_1S_1[M+NH_4]^+$: 292.1371; Found: 292.1377; specific rotation: $[\alpha]_D^{20}$ –9.9 (*c* = 0.66 $CHCl_3$) for an enantiomerically enriched sample of 99.5:0.5 er. Enantiomeric purity (99.5:0.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.8 mL/min, 220 nm.



Detector A Ch1 220nm

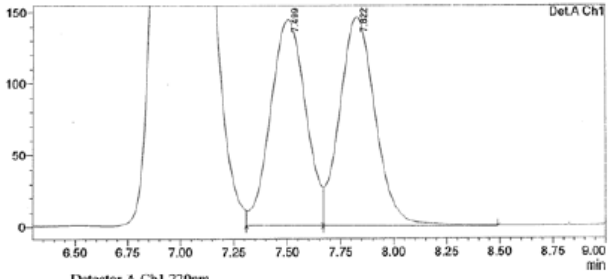
Peak#	Ret. Time	Area	Height	Area %
1	27.185	1336592	34773	48.490
2	33.075	1419824	29717	51.510
Total		2756416	64490	100.000

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	26.326	39389571	873113	99.450
2	33.112	217691	4754	0.550
Total		39607263	877866	100.000

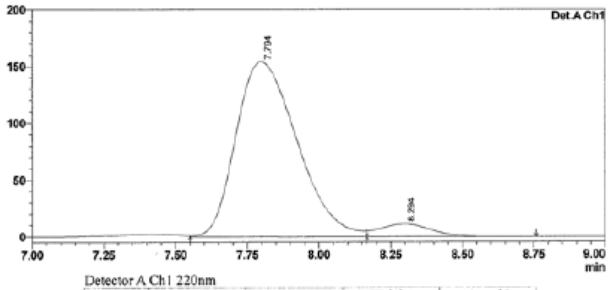
Retention Time	Area	Area %	Retention Time	Area	Area %
27.185	1336592	48.490	26.326	873113	99.450
33.075	1419824	51.510	33.112	4754	0.550

(*S*)-4-Cyclohexyl-4-phenylpentan-2-one (3j): IR (neat): 3108 (w), 3088 (w), 3056 (w), 3023 (w), 2927 (s), 2852 (m), 1702 (m), 1601 (w), 1496 (w), 1446 (w), 1420 (w), 1377 (w), 1356 (w), 1298 (w), 1271 (w), 1243 (w), 1182 (w), 1167 (w), 1135 (w), 1072 (w), 1031 (w), 970 (w), 933 (w), 894 (w), 844 (w), 780 (w), 761 (w), 700 (m), 549 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.28 (4H, m), 7.20–7.15 (1H, m), 2.81 (2H, ABq, $\Delta\delta_{AB} = 0.32$, $J_{AB} = 14.4$ Hz), 1.81–1.72 (1H, m), 1.71 (3H, s), 1.63–1.55 (2 H, m), 1.37 (3H, s), 1.31–1.18 (4H, m), 1.10–1.00 (2H, m), 0.98–0.83 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.0, 146.6, 128.2, 126.6, 125.9, 53.9, 49.4, 43.6, 32.2, 31.7, 28.0, 27.6, 27.3, 27.2, 26.8; HRMS (ESI^+): Calcd for $C_{17}H_{28}N_1O_1$ $[M+NH_4]^+$: 262.2171; Found: 262.2172; specific rotation: $[\alpha]_D^{20}$ –51. (c = 0.43 $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity (97.5:2.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel AD(H), 99.5% hexanes, 0.5% *i*-PrOH, 0.8 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	7.499	1643301	144368	48.840
2	7.822	1721330	146377	51.160
Total		3364632	290745	100.000



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	7.794	2283874	154048	94.441
2	8.294	134442	11046	5.559
Total		2418316	165094	100.000

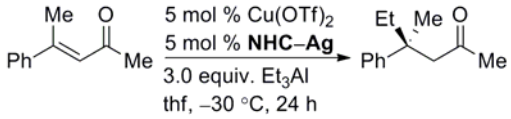
Retention Time	Area	Area %	Retention Time	Area	Area %
7.499	1643301	48.840	7.794	2283874	94.441
7.822	1721330	51.160	8.294	134442	5.559

■ **Representative Procedure for Catalytic Enantioselective Addition of Alkylaluminum Reagents to Acyclic Enones:** An oven-dried 1 dram vial, equipped with a stir bar was charged with chiral NHC–Ag complex **1** (0.3 mg, 0.5 μmol) and $Cu(OTf)_2$ (0.16 mg, 0.50 μmol), weighed out under a N_2 atmosphere in a glove box. The vial was sealed with a septum cap and removed from the glove box. Tetrahydrofuran (0.5 mL) was added to the vial and the resulting solution was allowed to stir for five minutes prior to cooling to –30 ˚C. Triethylaluminum (34.2 μL, 0.250 mmol) was added, resulting in a brown solution to which a solution of the enone substrate (*E*)-4-methyl-5-phenylpent-3-en-2-one (0.2M, 0.5 ml, 100 μmol) was added. The septum cap was exchanged for a solid cap and the vial was transferred to a cryocool (–30 ˚C) for 1 hour. The reaction was quenched with a saturated solution of sodium potassium tartrate (1.0 mL). After the mixture was allowed to warm to 22 ˚C, the solution was diluted with Et_2O and the layers were separated. The aqueous layer was washed with Et_2O (3 x 1 mL). The combined organic layers were passed through a short plug of silica (4 cm x 1 cm) eluting with Et_2O (10.0 mL). The organic layer was concentrated to a yellow oil and purified by silica gel

chromatography (10:1 hexanes/Et_2O) to afford 17.1 mg of (*S*)-4-methyl-4-(thiophen-2-yl)hexan-2-one as a clear, yellow oil (0.087 mmol, 87% yield).

■ Catalyst Screen for Alkyl Additions:

Table S2: Catalyst Screen for Aryl Addition to Acyclic Enones[a]

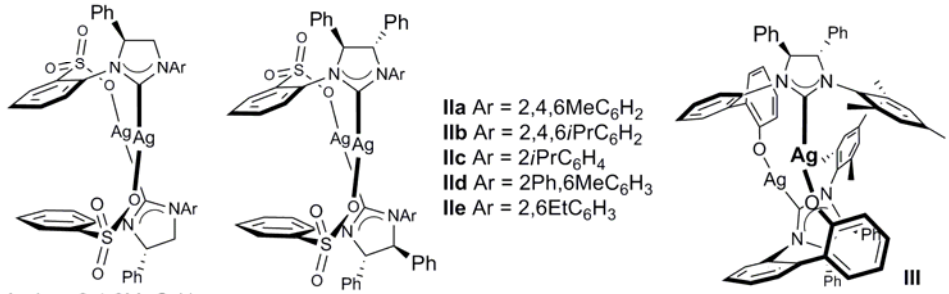


entry	NHC–Ag	conv. [%][b]	yield [%][c]	er[d]
1	**Ia**	>98	79	83:17
2	**Ib**	>98	60	76.5:23.5
3	**IIa**	>98	65	87.5:12.5
4	**IIb**	>98	73	90:10
5	**IIc**	>98	80	98:2
6	**IId**	12	nd	92:8
7	**IIe**	>98	60	76.5:23.5
8	**III**	>98	78	84:16

[a]-[d] See Table S1.

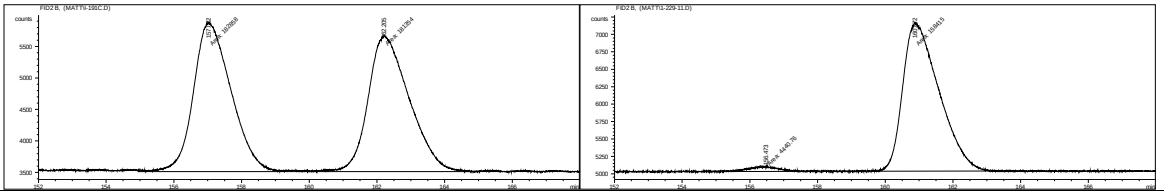
2.5 mol % **IIc**, 5 mol % ***Cu Source***
3.0 equiv. Et_3Al, thf, 30 min, –30 °C

entry	Cu source	conv. [%][b]	er[d]
1	$CuBr_2$	35	80:20
2	$CuCl_2$	88	93:7
3	$CuCl_2 \bullet 2H_2O$	5	95:5
4	$CuOTf_2$	>98	99:1



■ Analytical Data of Alkyl Addition Products:

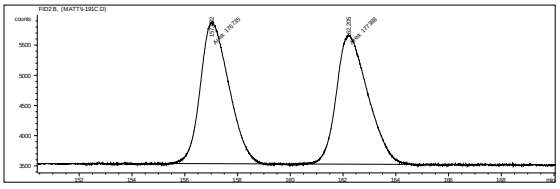
(*S*)-4-Methyl-4-phenylhexan-2-one (5a): IR (neat): 3089 (w), 3058 (w), 3026 (w), 2967 (m), 2932 (m), 2880 (m), 1703 (s), 1601 (w), 1496 (m), 1460 (m), 1446 (m), 1419 (m), 1378 (m), 1357 (s), 1250 (w), 1199 (m), 1168 (w), 1134 (w), 1108 (w), 1081 (w), 1053 (w), 1031 (w), 1007 (w), 965 (w), 922 (w), 760 (m), 699 (s), 549 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.28 (3H, m), 7.20–7.16 (2H, m), 2.73 (2H, ABq, $\Delta\delta_{AB} = 0.29$, $J_{AB} = 14.3$ Hz), 1.88–1.83 (1H, m), 1.76 (3H, s), 1.68 (1H, m), 1.40 (3H, s), 0.68 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 146.4, 128.4, 126.3, 126.0, 56.2, 40.9, 35.6, 32.1, 23.3, 8.6; HRMS (ESI^+): Calcd for $C_{13}H_{19}O_1$ $[M+H]^+$: 191.1439; Found: 191.1436; specific rotation: $[\alpha]_D^{20}$ +54.5 (*c* = 0.600 $CHCl_3$) for an enantiomerically enriched sample of 97:3 er. Enantiomeric purity (97:3 er) was determined by GC analysis in comparison with authentic racemic material; **β**-dex column, 100 ˚C, 15 psi.

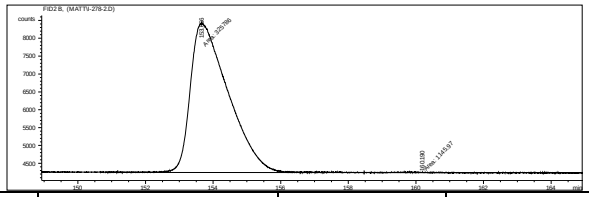


Retention Time	Area	Area %	Retention Time	Area	Area %

157.022	182858.2	50.207	156.473	4440.8	2.727
162.205	181353.8	49.793	160.872	158415.2	97.273

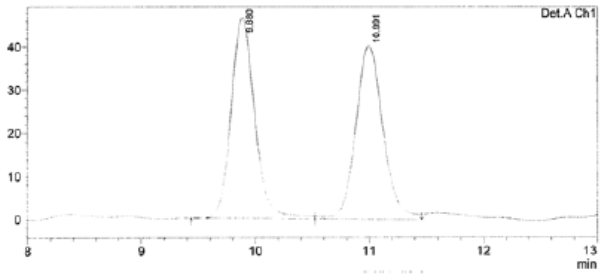
(*R*)-4-Methyl-4-phenylhexan-2-one (*R*-5a): IR (neat): 3089 (w), 3058 (w), 3026 (w), 2967 (m), 2932 (m), 2880 (m), 1703 (s), 1601 (w), 1496 (m), 1460 (m), 1446 (m), 1419 (m), 1378 (m), 1357 (s), 1250 (w), 1199 (m), 1168 (w), 1134 (w), 1108 (w), 1081 (w), 1053 (w), 1031 (w), 1007 (w), 965 (w), 922 (w), 760 (m), 699 (s), 549 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.28 (3H, m), 7.20–7.16 (2H, m), 2.73 (2H, ABq, $\Delta\delta_{AB} = 0.29$, $J_{AB} = 14.3$ Hz), 1.88–1.83 (1H, m), 1.76 (3H, s), 1.68 (1H, m), 1.40 (3H, s), 0.68 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 146.4, 128.4, 126.3, 126.0, 56.2, 40.9, 35.6, 32.1, 23.3, 8.6; HRMS (ESI^+): Calcd for $C_{13}H_{19}O_1$ $[M+H]^+$: 191.1439; Found: 191.1436; specific rotation: $[\alpha]_D^{20}$ –0.7 (*c* = 0.04 $CHCl_3$) for an enantiomerically enriched sample of >99:1 er. Enantiomeric purity (>99:1 er) was determined by GC analysis in comparison with authentic racemic material; **β**-dex column, 100 ˚C, 15 psi.

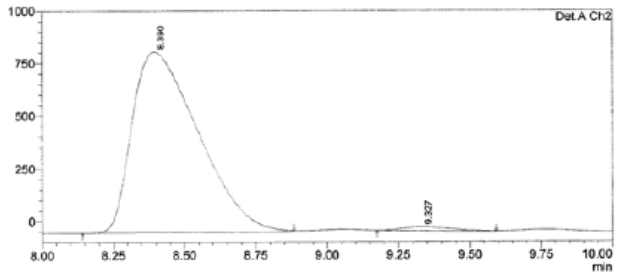




Retention Time	Area	Area %	Retention Time	Area	Area %
157.022	182858.2	50.207	153.656	325785.8	99.649
162.205	181353.8	49.793	160.19	1146	0.351

(*R*)-4-Methyl-4-(thiophen-2-yl)hexan-2-one (5b): IR (neat): 2967 (m), 2922 (w), 2879 (w), 1703 (s), 1460 (m), 1378 (m), 1356 (m), 1237 (m), 1156 (m), 1132 (w), 1087 (w), 1054 (w), 1025 (w), 1006 (w), 962 (w), 918 (w), 851 (m), 827 (m), 796 (w), 692 (s), 605 (w), 584 (w), 527 (m), 413 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (1H, dd, *J* = 5.1, 1.2 Hz), 6.92 (1H, dd, *J* = 5.1, 3.5 Hz), 6.80 (1H, dd, *J* = 3.7, 1.2 Hz), 2.73 (2H, ABq, $\Delta\delta_{AB} = 0.17$, $J_{AB} = 14.3$ Hz), 1.86 (3H, s), 1.80 (2H, m), 1.45 (3H, s), 0.79 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 153.7, 127.1, 123.9, 123.7, 56.6, 40.5, 36.6, 32.0, 24.7, 8.5; HRMS (ESI^+): Calcd for $C_{11}H_{17}OS$ $[M+H]^+$: 197.1000; Found: 197.0996; specific rotation $[\alpha]_D^{20}$ +57.5 (c = 1.07 in $CHCl_3$) for an enantiomerically enriched sample of 98.5:1.5 er. Enantiomeric purity (98.5:1.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.





Detector A Ch1 220nm

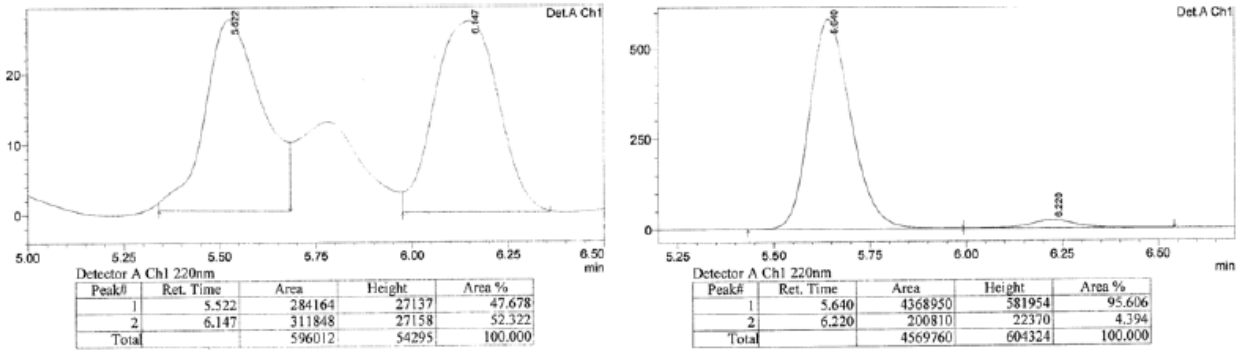
Peak#	Ret. Time	Area	Height	Area %
1	9.880	672431	46478	49.963
2	10.991	673433	40333	50.037
Total		1345864	86811	100.000

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.390	13807125	855664	98.451
2	9.327	217302	17254	1.549
Total		14024428	872918	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
9.880	672431	49.963	8.390	13807125	98.451
10.991	673433	50.037	9.327	217302	1.549

(*S*)-4-Methyl-4-(4-(trifluoromethyl)phenyl)hexan-2-one (5c): IR (neat): 2970 (w), 1936 (w), 2884 (w), 1720 (w), 1619 (w), 1462 (w), 1411 (w), 1379 (w), 1359 (w), 1327 (s), 1165 (m), 1116 (s), 1069 (m), 1016 (w), 965 (w), 921 (w), 839 (w), 709 (w), 604 (w), 540 (w), 401 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (2H, d, J = 8.2 Hz), 7.41 (2H, d, J = 8.2 Hz), 2.80 (2H, ABq, $\Delta\delta_{AB}$ = 0.27, J_{AB} = 15.5 Hz), 1.84 (3H, s), 1.83–1.62 (2H, m), 1.42 (3H, s), 0.63 (3H, t, J = 10.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.0, 150.8, 128.2 (q, J_{C-F} = 32.0 Hz), 126.5, 125.1, 124.2 (q, J_{C-F} = 270.9 Hz), 55.2, 40.7, 35.6, 31.8, 23.2, 8.3; HRMS (ESI^+): Calcd for $C_{14}H_{18}F_3O$ $[M+H]^+$: 259.1310; Found: 259.1310; specific rotation: $[\alpha]_D^{20}$ +17.6 (*c* = 1.36, $CHCl_3$) for an enantiomerically enriched sample of 95.5:4.5 er. Enantiomeric purity (95.5:4.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.

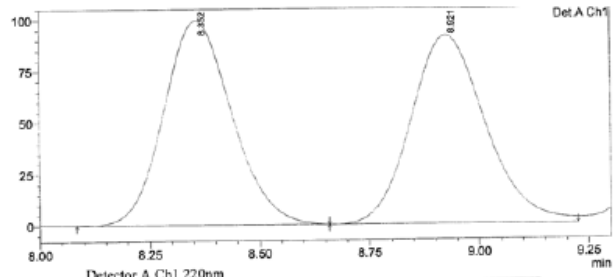


Peak#	Ret. Time	Area	Height	Area %
1	5.522	284164	27137	47.678
2	6.147	311848	27158	52.322
Total		596012	54295	100.000

Peak#	Ret. Time	Area	Height	Area %
1	5.640	4368950	581954	95.606
2	6.220	200810	22370	4.394
Total		4569760	604324	100.000

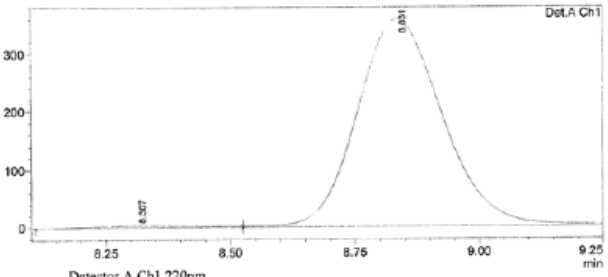
Retention Time	Area	Area %	Retention Time	Area	Area %
5.522	284164	47.678	5.640	4368950	95.606
6.147	311848	52.322	6.220	200810	4.394

(*S*)-4-(4-Methoxyphenyl)-4-methylhexan-2-one (*S*-5d): IR (neat): 3061 (w), 3037 (w), 2965 (w), 2936 (w), 2879 (w), 2836 (w), 1702 (m), 1611 (w), 1581 (w), 1513 (s), 1463 (w), 1415 (w), 1377 (w), 1357 (w), 1292 (w), 1250 (s), 1186 (m), 1136 (w), 1116 (w), 1035 (m), 1010 (w), 965 (w), 916 (w), 829 (m), 806 (w), 672 (w), 612 (w), 554 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.21 (2H, m), 6.87–6.85 (2H, m), 3.80 (3H, s), 2.70 (2H, ABq, $\Delta\delta_{AB}$ = 0.28, J_{AB} = 13.9 Hz), 1.86–1.80 (1H, m), 1.76 (3H, s), 1.67–1.54 (1H, m), 1.38 (3H, s), 0.68 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 157.6, 138.2, 127.2, 113.5, 56.2, 55.1, 40.1, 35.6, 32.0, 23.3, 8.4; HRMS (ESI^+): Calcd for $C_{14}H_{20}O_2$ $[M+]^+$: 220.1463; Found: 220.1463; specific rotation: $[\alpha]_D^{20}$ +40.5 (*c* = 0.147, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity (99:1 er) was determined by HPLC analysis in comparison with authentic racemic; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.352	1078908	99494	49.670
2	8.921	1093239	92067	50.330
Total		2172147	191561	100.000

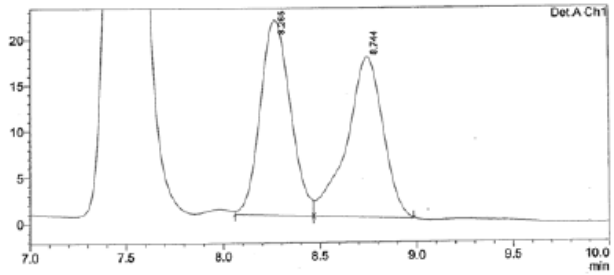


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.307	47579	3188	1.095
2	8.831	4296193	361050	98.905
Total		4343772	364238	100.000

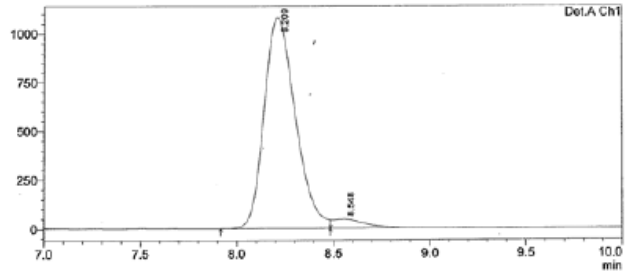
Retention Time	Area	Area %	Retention Time	Area	Area %
8.352	1078908	49.670	8.307	47579	1.095
8.921	1093239	50.330	8.831	4296193	98.905

(*R*)-4-(4-Methoxyphenyl)-4-methylhexan-2-one (5d): IR (neat): 3061 (w), 3037 (w), 2965 (w), 2936 (w), 2879 (w), 2836 (w), 1702 (m), 1611 (w), 1581 (w), 1513 (s), 1463 (w), 1415 (w), 1377 (w), 1357 (w), 1292 (w), 1250 (s), 1186 (m), 1136 (w), 1116 (w), 1035 (m), 1010 (w), 965 (w), 916 (w), 829 (m), 806 (w), 672 (w), 612 (w), 554 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.21 (2H, m), 6.87–6.85 (2H, m), 3.80 (3H, s), 2.70 (2H, ABq, $\Delta\delta_{AB} = 0.28$, $J_{AB} = 13.9$ Hz), 1.86–1.80 (1H, m), 1.76 (3H, s), 1.67–1.54 (1H, m), 1.38 (3H, s), 0.68 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 157.6, 138.2, 127.2, 113.5, 56.2, 55.1, 40.1, 35.6, 32.0, 23.3, 8.4; HRMS (ESI^+): Calcd for $C_{14}H_{24}N_1O_2$ $[M+NH_4]^+$: 238.1807; Found: 23.1804; specific rotation: $[\alpha]_D^{20}$ –44.7 (*c* = 1.11, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er. Enantiomeric purity (97:3 er) was determined by HPLC analysis in comparison with authentic racemic; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.265	231854	21271	50.574
2	8.744	226594	17449	49.426
Total		458448	38720	100.000



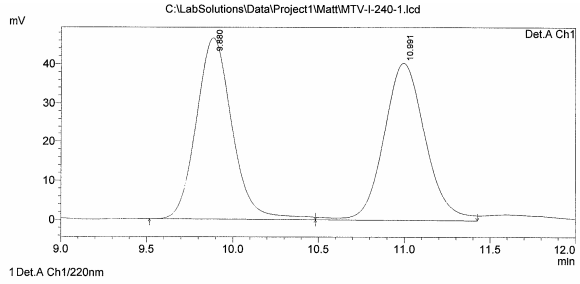
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.209	12184383	1080163	96.832
2	8.548	398634	46135	3.168
Total		12583017	1126298	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
8.265	231854	50.574	8.209	1080163	96.832
8.744	226594	49.426	8.548	46135	3.168

(*R*)-4-Methyl-4-(naphthlen-2-yl)hexan-2-one (5e): IR (neat): 3056 (w), 2966 (m), 2932 (w), 2878 (w), 1703 (s), 1632 (w), 1599 (w), 1505 (w), 1461 (w), 1418 (w), 1378 (w), 1356 (m), 1275 (w), 1246 (w), 1198 (w), 1168 (w), 1132 (w), 1055 (w), 1018 (w), 964 (w), 949 (w), 895 (w), 855 (w), 818 (m), 747 (m), 549 (w), 477 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.80 (3H,

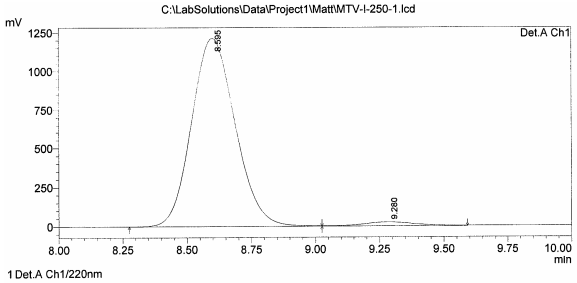
m), 7.70 (1H, m), 7.53–7.44 (3H, m), 2.84 (2H, ABq, $\Delta\delta_{AB}$ = 0.31, J_{AB} = 14.1 Hz), 1.98–1.94 (1H, m), 1.76 (3H, s), 1.79–1.73 (1H, m), 1.53 (3H, s), 0.69 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.2, 143.7, 131.8, 128.0, 127.9, 127.3, 125.9, 125.5, 124.9, 124.6, 55.9, 40.9, 35.4, 32.0, 23.2, 8.5; HRMS (ESI$^+$): Calcd for $C_{17}H_{24}O_1N_1$ [M+NH_4]$^+$: 258.1858; Found: 258.1857; specific rotation: $[\alpha]_D^{20}$ +63.5 (*c* = 1.14, $CHCl_3$) for an enantiomerically enriched sample of 97.5:2.5 er. Enantiomeric purity (97.5:2.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	9.880	671622	46491	49.957
2	10.991	672785	40340	50.043
Total		1344406	86831	100.000



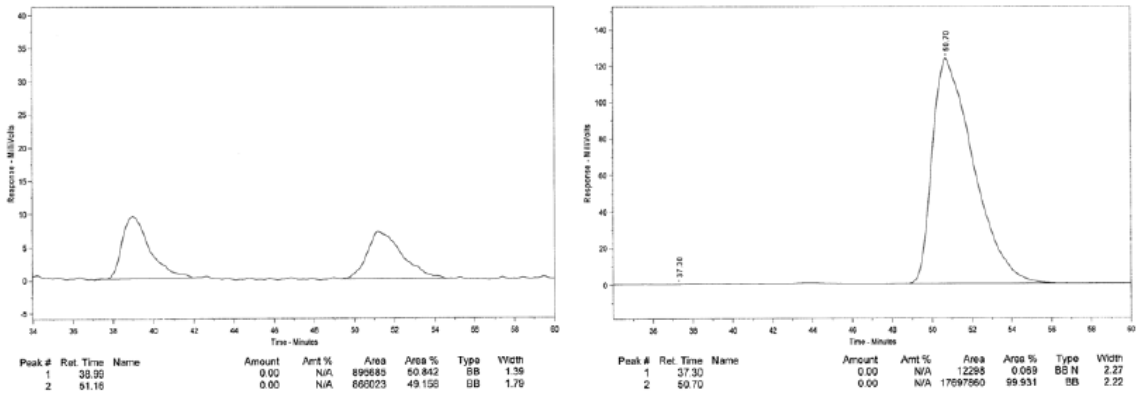
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	8.595	14217226	1214418	97.421
2	9.280	376430	25821	2.579
Total		14593656	1240239	100.000

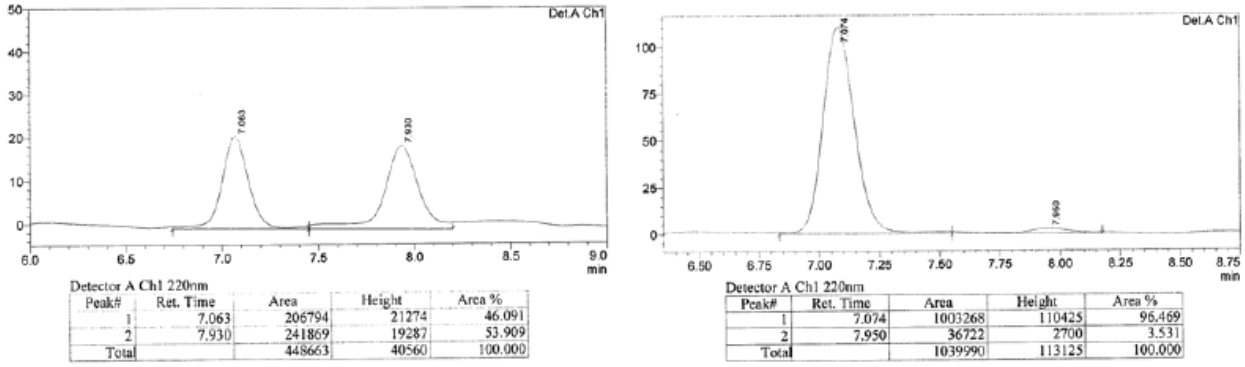
Retention Time	Area	Area %	Retention Time	Area	Area %
9.880	671622	49.957	8.595	14217226	97.421
10.991	672785	50.043	9.280	376430	2.579

(*S*)-4-(2-Bromophenyl)-4-methylhexan-2-one (5f): IR (neat): 3059 (w), 2964 (s), 2928 (s), 2880 (w), 2856 (w), 2194 (w), 1717 (s), 1616 (w), 1589 (w), 1465 (m), 1425 (w), 1378 (w), 1356 (m), 1315 (w), 1296 (w), 1261 (w), 1201 (w), 1165 (w), 1134 (w), 1109 (w), 1045 (w), 1016 (m), 961 (w), 787 (w), 754 (s), 727 (w), 703 (w), 649 (w), 552 (w), 412 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58–7.55 (1H, m), 7.39–7.38 (1H, m), 7.26–7.16 (1H, m), 7.07–7.03 (1H, m), 3.86 (1H, d, *J* = 15.7 Hz), 2.64 (1H, d, *J* = 15.7 Hz), 2.53 (1H, sextet, *J* = 6.8 Hz), 1.87 (3H, s), 1.62–1.55 (1H, m), 1.52 (3H, s), 0.63 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.8, 143.2, 135.5, 130.7, 127.8, 127.2, 121.8, 52.5, 42.4, 32.0, 31.2, 25.5, 8.5; HRMS (ESI$^+$): Calcd for $C_{13}H_{17}Br_1O_1$ [M+H]$^+$: 269.0541; Found: 269.0539; specific rotation: $[\alpha]_D^{20}$ +7.9 (*c* = 0.46, $CHCl_3$) for an enantiomerically enriched sample of 99.9:0.1 er. Enantiomeric purity (99.9:0.1 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD, 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



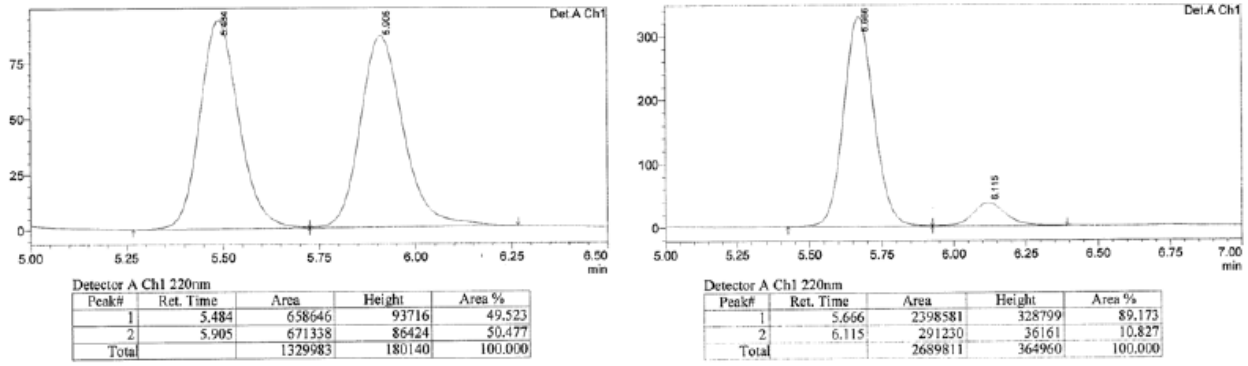
Retention Time	Area	Area %	Retention Time	Area	Area %
38.99	895685	50.842	37.30	12298	0.069
51.16	866023	49.158	50.70	17697860	99.931

(*S*)-4-(3-Fluorophenyl)-4-methylhexan-2-one (5g): IR (neat): 3072 (w), 2968 (s), 2931 (w), 2881 (w), 1717 (s), 1703 (s), 1614 (m), 1585 (s), 1489 (m), 1460 (m), 1434 (m), 1378 (m), 1357 (s), 1324 (w), 1273 (m), 1223 (m), 1193 (m), 1165 (m), 1133 (w), 1105 (w), 1073 (w), 1052 (w), 967 (w), 924 (m), 911 (m), 889 (w), 867 (w), 780 (s), 701 (s), 526 (w), 447 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.25 (1H, m), 7.09–7.06 (1H, m), 7.02–6.98 (1H, m) 6.91–6.86 (1H, m), 2.74 (2H, ABq, $\Delta\delta_{AB} = 0.27$, $J_{AB} = 14.9$ Hz), 1.84 (3H, s), 1.84–1.76 (1H, m), 1.71–1.63 (1H, m), 1.40 (3H, s), 0.67 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.5, 163.0 (J_{C-F} = 245.3 Hz), 149.4 (J_{C-F} = 0.07 Hz), 129.5 (J_{C-F} = 0.08 Hz), 121.8 (J_{C-F} = 0.02 Hz), 113.4 (J_{C-F} = 0.20 Hz), 112.7 (J_{C-F} = 0.20 Hz), 55.5, 40.7, 35.5, 31.9, 23.1, 8.3; HRMS (ESI^+): Calcd for $C_{13}H_{17}F_1O_1$ $[M+H]^+$: 209.1342; Found: 209.1345; specific rotation: $[\alpha]_D^{20}$ +40.2 (*c* = 0.500, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 er. Enantiomeric purity (96.5:3.5 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD-H, 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



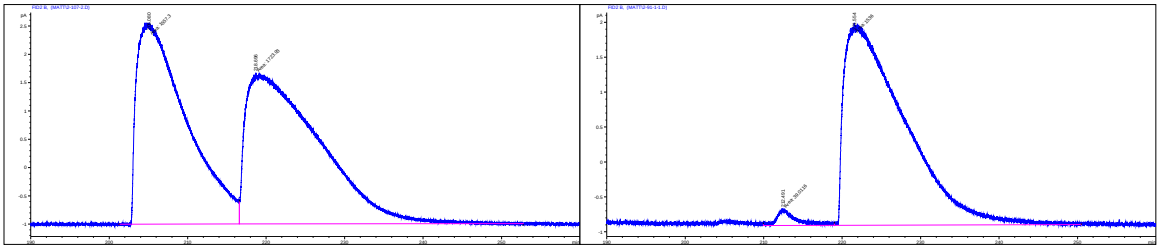
Retention Time	Area	Area %	Retention Time	Area	Area %
7.063	206794	46.091	7.074	10003268	96.469
7.930	241869	53.909	7.950	36722	3.532

(*R*)-4-Benzyl-4-methylhexan-2-one (6a): IR (neat): 3084 (w), 3061 (w), 3028 (w), 2963 (m), 2929 (m), 2880 (m), 1714 (s), 1602 (w), 1495 (w), 1454 (m), 1404 (w), 1359 (m), 1196 (w), 1153 (w), 1076 (w), 1053 (w), 1032 (w), 1009 (w), 974 (w), 914 (w), 759 (w), 723 (m), 703 (s), 630 (w), 598 (w), 535 (w), 509 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.20 (2.5H, m), 7.13–7.11 (2.5H, m), 2.71 (2H, ABq, $\Delta\delta_{AB} = 0.097$, $J_{AB} = 13.1$ Hz), 2.27–2.25 (2H, m), 2.11 (3H, s), 1.51–1.36 (2H, m), 0.95 (3H, s), 0.89 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.0, 138.8, 130.6, 127.8, 125.9, 50.1, 44.7, 37.2, 32.3, 31.5, 24.3, 8.3; HRMS (ESI^+): Calcd for $C_{14}H_{21}O_1$ $[M+H]^+$: 205.1592; Found: 205.1600; specific rotation: $[\alpha]_D^{20}$ –7.70 (*c* =1.35, $CHCl_3$) for an enantiomerically enriched sample of 89:11 er. Enantiomeric purity (89:11 er) was determined by HPLC analysis in comparison with authentic racemic material; Chiracel OD(H), 99% hexanes, 1% *i*-PrOH, 1.0 mL/min, 220 nm.



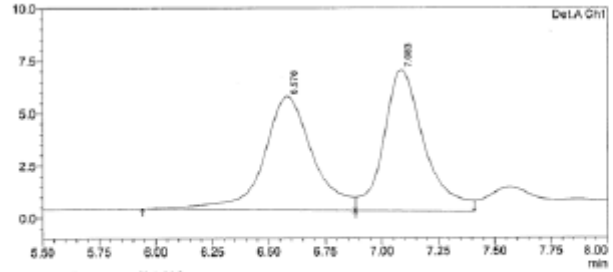
Retention Time	Area	Area %	Retention Time	Area	Area %
5.484	658646	49.523	5.666	328799	89.173
5.905	671338	50.477	6.115	36161	10.827

(*S*)-4-Cyclohexyl-4-methylhexan-2-one (6b): IR (neat): 2960 (m), 2924 (s), 2880 (w), 1708 (s), 1449 (m), 1417 (w), 1378 (w), 1355 (m), 1270 (w), 1207 (w), 1183 (w), 1148 (w), 1036 (w), 1007 (w), 965 (w), 933 (w), 894 (w), 847 (w), 795 (w), 773 (w), 641 (w), 572 (w), 535 (w), 504 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.35 (2H, ABq, $\Delta\delta_{AB} = 0.17$, $J_{AB} = 14.7$ Hz), 2.12 (3H, s), 1.77–1.64 (5H, m), 1.43 (2H, q, J = 7.6 Hz), 1.36–0.88 (9H, m), 0.78 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.8, 49.1, 44.2, 38.6, 32.7, 29.1, 27.2, 27.1, 26.9, 21.9, 8.1; HRMS (ESI^+): Calcd for $C_{13}H_{25}O_1$ $[M+H]^+$: 197.1905; Found: 197.1896 specific rotation: $[\alpha]_D^{20}$ –2.0 (c = 0.37, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity (97.5:2.5 er) was determined by GC analysis in comparison with authentic racemic material; Chiraldex GTA column, 80 °C, 15 psi.



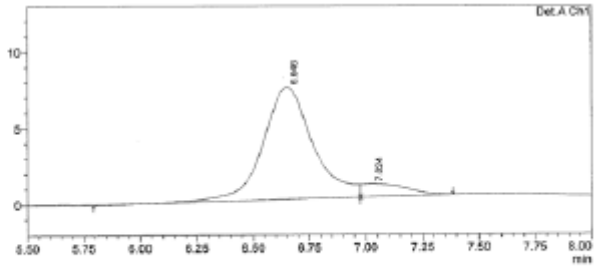
Retention Time	Area	Area %	Retention Time	Area	Area %
205.08	1557.3	47.461	212.491	39	2.477
218.696	1723.9	52.539	221.554	1536	97.523

(*S*)-*tert*-Butyl-2-ethyl-methyl-4-oxopentanoate (6c): IR (neat): 2974 (w), 2933 (w), 2882 (w), 1718 (s), 1459 (w), 1392 (w), 1366 (m), 1291 (w), 1252 (w), 1221 (s), 1162 (m), 1146 (m), 1134 (m), 1059 (w), 1040 (w), 1010 (w), 938 (w), 852 (w), 746 (w), 518 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.65 (2H, ABq, $\Delta\delta_{AB} = 0.41$, $J_{AB} = 17.6$ Hz), 2.11 (3H, s), 1.61–1.47 (2H, m), 1.42 (9H, s), 1.16 (3H, s), 0.84 (3H, t, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 206.5, 175.6, 80.0, 51.4, 44.3, 32.6, 30.6, 27.9, 21.0, 8.5; HRMS (ESI^+): Calcd for $C_{12}H_{23}O_3$ $[M+H]^+$: 215.1647; Found: 215.1647; specific rotation: $[\alpha]_D^{20}$ +22 (c = 0.06, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er. Enantiomeric purity (91:9 er) was determined by HPLC analysis in comparison with authentic racemic; Chiracel AD(H), 99.8% hexanes, 0.2% *i*-PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	6.578	82432	5428	49.413
2	7.083	84392	6763	50.587
Total		166825	12192	100.000

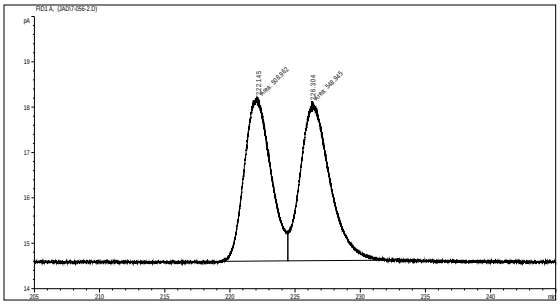


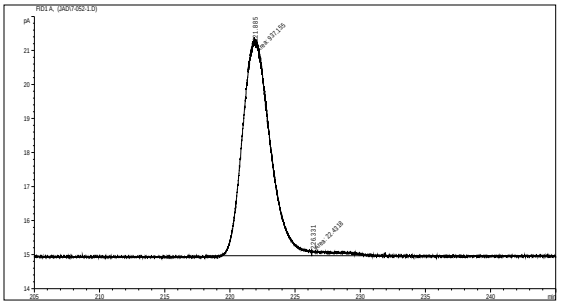
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %
1	6.646	114802	7371	91.040
2	7.024	11299	862	8.960
Total		126101	8233	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
6.578	82432	49.413	6.646	114802	91.040
7.083	84392	50.587	7.024	11299	8.960

(*S*)-4,6-Dimethyl-4-phenylheptan-2-one (7): IR (neat): 3088 (w), 3058 (w), 3026 (w), 2953 (m), 2926 (w), 2869 (w), 1703 (s), 1601 (w), 1581 (w), 1497 (w), 1466 (w), 1446 (w), 1383 (w), 1356 (m), 1306 (w), 1201 (w), 1166 (w), 1134 (w), 1118 (w), 1073 (w), 1031 (w), 966 (w), 925 (w), 841 (w), 765 (m), 700 (s), 638 (w), 571 (w), 552 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.28 (4H, m), 7.21–7.16 (1H, m), 2.72 (2H, ABq, $\Delta\delta_{AB} = 0.35$, $J_{AB} = 14.0$ Hz), 1.75 (3H, s), 1.69 (2H, ABX, $\Delta\delta_{AB} = 0.19$, $J_{AB} = 13.6$ Hz, $J_{AX} = 5.6$ Hz,), 1.58–1.44 (1H, m), 1.48 (3H, s), 0.83 (3H, d, $J = 6.8$ Hz), 0.58 (3H, d, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 208.3, 146.8, 128.3, 126.4, 126.1, 57.3, 52.2, 41.0, 32.2, 25.3, 24.7, 23.6, 23.8; HRMS (ESI^+): Calcd for $C_{15}H_{26}O_1N_1$ $[M+NH_4]^+$: 236.2014; Found: 236.2012; specific rotation: $[\alpha]_D^{20}$ +83.5 (c = 1.10, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Enantiomeric purity (98:2 er) was determined by GC analysis in comparison with authentic racemic; Chiraldex B/DM, 85 °C, 15 psi.





Retention Time	Area	Area %	Retention Time	Area	Area%
222.145	509.0	48.11	221.885	937.2	97.662
226.304	548.9	51.890	226.331	22.4	2.338

■ **Proof of Absolute Stereochemistry:** ***Aryl Additions***

■ **Representative Procedure for Oxidation of Methyl Ketone to Carboxylic Acid-2 step:** A flame-dried 4 mL vial equipped with stirbar was charged with 2,2,6,6-tetramethyl piperidine (17.2 μL, 0.101 mmol) and thf (0.22 mL) by syringe under N_2. The vial was allowed to cool to –78°C and a solution of *n*BuLi (54.5 μL, 0.0872 mmol, 1.6 M), was added. The resulting mixture was allowed to warm to 22 °C and stir for 5 minutes, and cooled again to –78°C. (*R*)-4-Phenyl-4-(thiophen-3-yl)pentan-2-one (14.2 mg, 0.0581 mmol) dissolved in thf (0.2 mL) was added to the mixture, which was allowed to sitr for 30 min and –78°C. Trimethylsilyltriflate (31.9 μL, 0.176 mmol) was added by syringe and the mixture was allowed to stir for an additional 15 minutes at –78°C. A saturated solution of $NaHCO_3$ (1.0 mL) was added and the mixture was allowed to slowly warm to 22°C, at which time the solution was diluted with H_2O (1 mL) and Et_2O (1 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 1 mL) and the combined organic layers were dried by Na_2SO_4, filtered, and concentrated in a 20 mL vial to yield a clear oil. The oil was dissolved in CH_2Cl_2 (2.5 mL) and the solution was allowed to cool to –78°C, then ozone was bubbled through by a pipet until the reaction turned blue (~10 s, longer reaction times afford products from ozonolysis of the thiophene ring) at which time the pipet was removed and a stirbar was added to the vial. Dimethylsulfide (90 μL) was added by syringe and the solution was allowed to stir and slowly warm to 22°C over 30 min. The mixture was filtered through a sodium sulfate plug and concentrated to afford a yellow oily solid which was purified by column chromatography (100% CH_2Cl_2 to 15:1 CH_2Cl_2/EtOAc) to obtain (*R*)-3-Phenyl-3-(thiophen-3-yl)butanoic acid as a white solid (13.5 mg, 0.0552 mmol, 95% yield). **(*R*)-3-Phenyl-3-(thiophen-3-yl)butanoic acid (4):** IR (neat): 3104 (w), 3085 (w), 3058 (w), 3057 (br), 3024 (w), 2972 (w), 2934 (w), 2554 (br), 1781 (w), 1707 (s), 1600 (w), 1536 (w), 1495 (w) 1445 (w), 1412 (w), 1374 (w), 1310 (w), 1247 (w), 1218 (m), 1150 (m), 1085 (w), 1030 (w), 939 (w), 910 (w), 864 (w), 835 (w), 777 (m), 700 (s), 663 (m), 601 (w), 555 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.73 (1H, br s), 7.39–7.33 (1H, m), 7.30–7.27 (1H, m), 7.24–7.17 (4H, m), 7.04–7.03 (1H, m), 6.79 (1H, dd, J = 5.2, 1.2 Hz), 3.12 (2H, ABq, $\Delta\delta_{AB}$ = 0.05, J_{AB} = 14.4 Hz), 1.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.1, 149.3, 147.4, 128.3, 127.6, 126.6, 126.5, 125.7, 120.3,

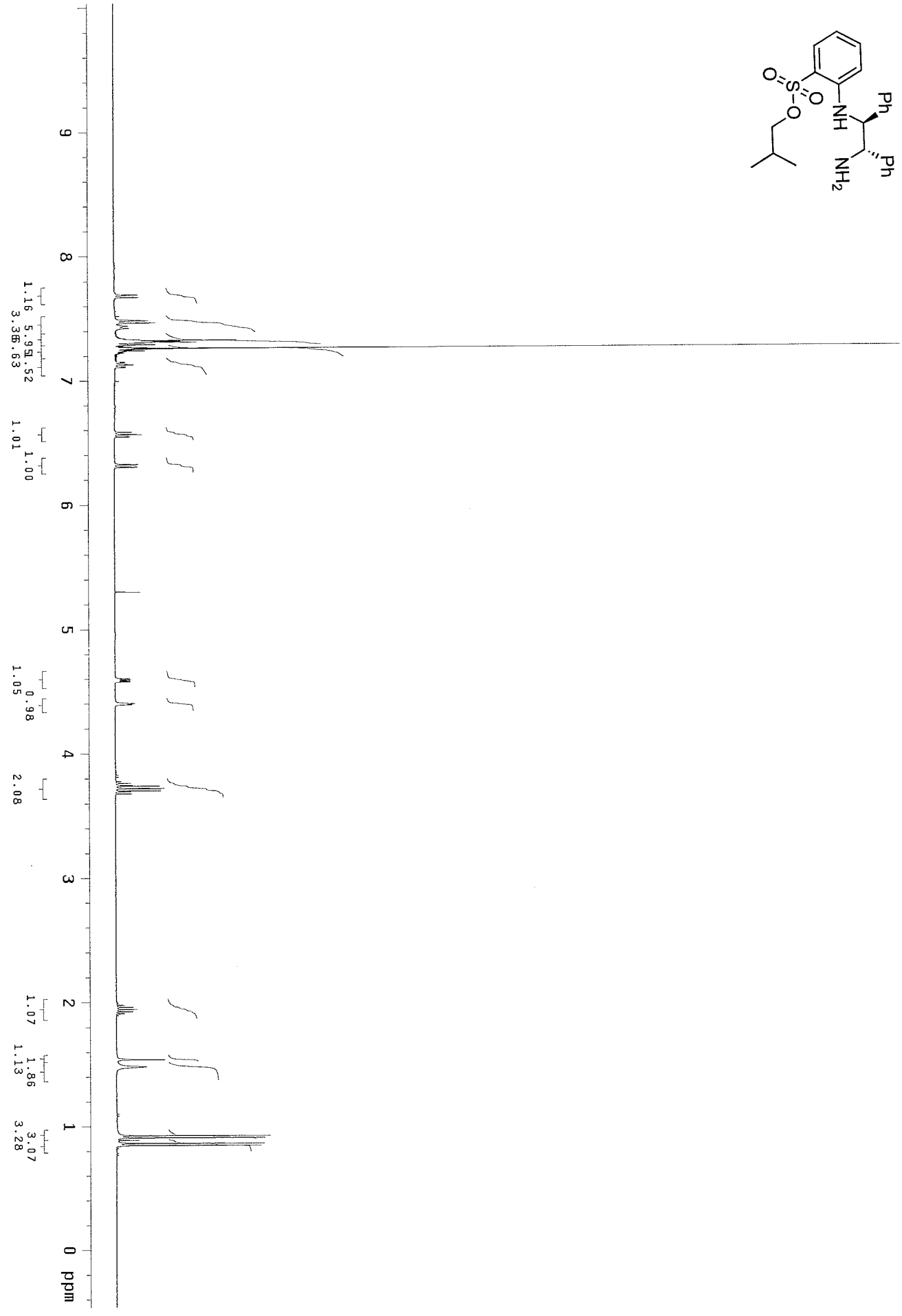
46.4, 43.5, 28.0; HRMS (ESI^+): Calcd for $C_{14}H_{15}O_2S_1$ $[M+H]^+$: 247.0793; Found: 247.0801; specific rotation: $[\alpha]_D^{20}$ +3.0 (c = 0.43) for an enantiomerically enriched sample of 99:1 er. All other products were assigned by analogy.

■ **Proof of Absolute Stereochemistry: *Alkyl Additions***

■ **Representative Procedure for Oxidation of Methyl Ketone to Carboxylic Acid-1 step:** A 20 mL vial equipped with stirbar was charged with (*S*)-4-methyl-4-phenylhexan-2-one (9.5 mg, 0.50 mmol). NaOCl (1.7 mL, 0.25 mmol) and NaOH (aq, 2M, 20. μL, 0.055 mmol) were added by syringe at 22°C. The resulting solution was allowed to stir and warm to 70 °C (oil bath) and stir for 12 hours. The reaction was allowed to cool to 22 °C and acetone (0.1 mL) was added by syringe (additional acetone was added until the reaction tested negative for peroxides by starch paper). The reaction was allowed to cool to 0 °C and 12M HCl was added dropwise until the solution was strongly acidic by litmus paper test. CH_2Cl_2 (2 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated to yield a yellow oil (62% conv.) which was purified by column chromatography (100% CH_2Cl_2) to afford (*S*)-3-methyl-3-phenylpentanoic acid as a white solid (5.8 mg, 0.030 mmol, 60% yield). **(*S*)-3-Methyl-3-phenylpentanoic acid (8):** The analytical data are fully consistent with those reported previously.[7] IR (neat): 3090 (w), 3059 (w), 3028 (w), 2968 (w), 2927 (w), 2880 (w), 2567 (br), 1704 (s), 1602 (w), 1497 (w), 1446 (w), 1409 (w), 1382 (w), 1288 (w), 1234 (w), 1132 (w), 1107 (w), 1032 (w), 1007 (w), 934 (w), 761 (w), 699 (w), 632 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.30 (4H, m), 7.21–7.18 (1H, m), 2.67 (2H, ABq, $\Delta\delta_{AB}$ = 0.11, J_{AB} = 14.4 Hz), 1.78 (2H, ABX_3, $\Delta\delta_{AB}$ = 0.094, $\Delta\delta_{AX}$ = 2.46, J_{AB} = 14.4, J_{AX} = 7.2 Hz), 1.47 (3H, s), 0.68 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.1, 149.3, 147.4, 128.3, 127.6, 126.6, 126.5, 125.7, 120.3, 46.4, 43.5, 28.0; HRMS (ESI^+): Calcd for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1229; Found: 193.1226; specific rotation: $[\alpha]_D^{20}$ +5.1 (c = 0.38 $CHCl_3$) for an enantiomerically enriched sample of >99:1 er. **Literature Precedence:** *R*-isomer $[\alpha]_D^{20}$ –8.8 (c = 0.24 $CHCl_3$) for an enantiomerically enriched sample of >99:1 er. Other products were assigned by inference.

■ **^1H NMR Spectra of New Compounds:**

[7] E. Fillion, A. Wilsily, *J. Am. Chem. Soc.* **2006**, *128*, 2774–2775.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1.52
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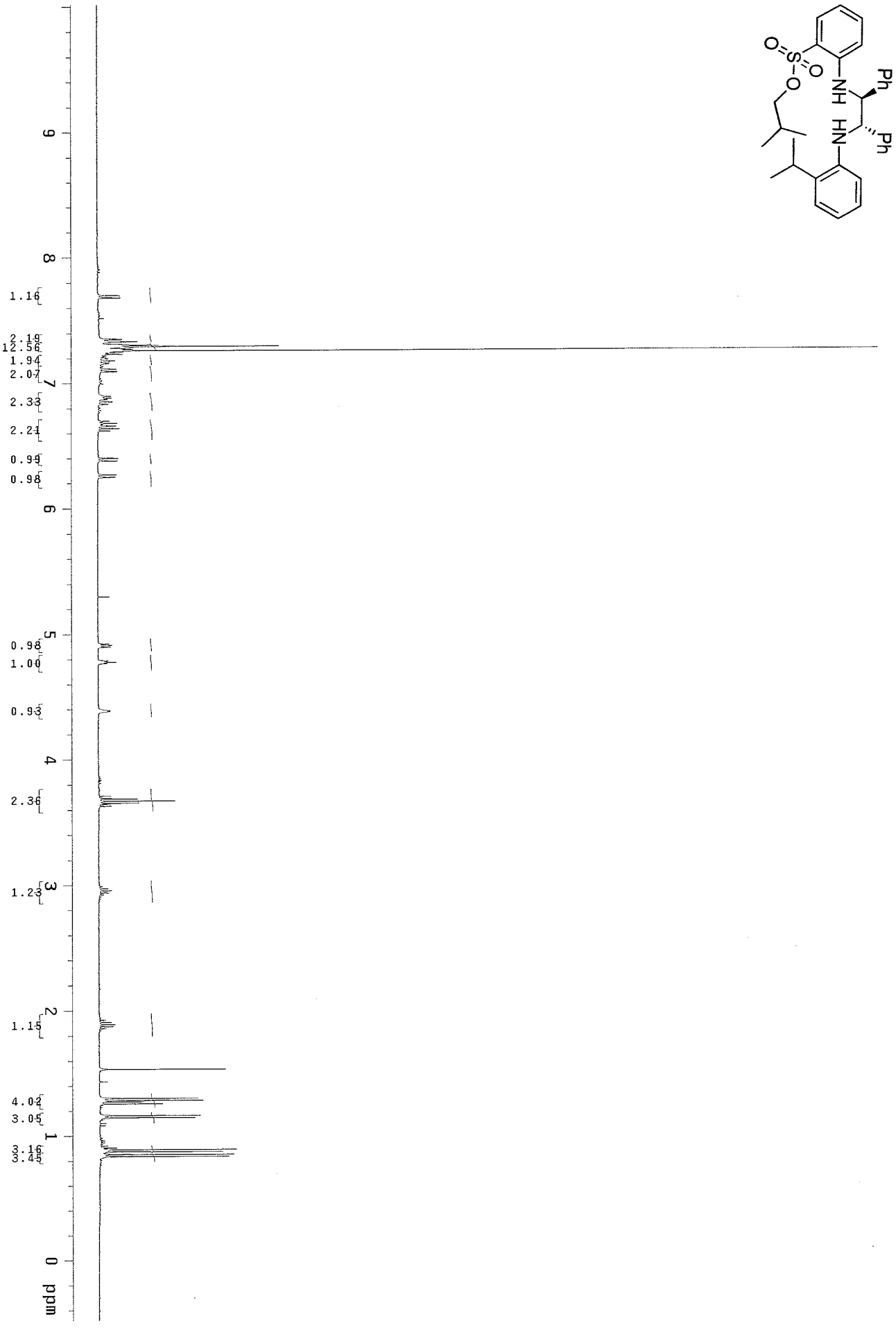
1.07
1.86
1.13
3.07
3.28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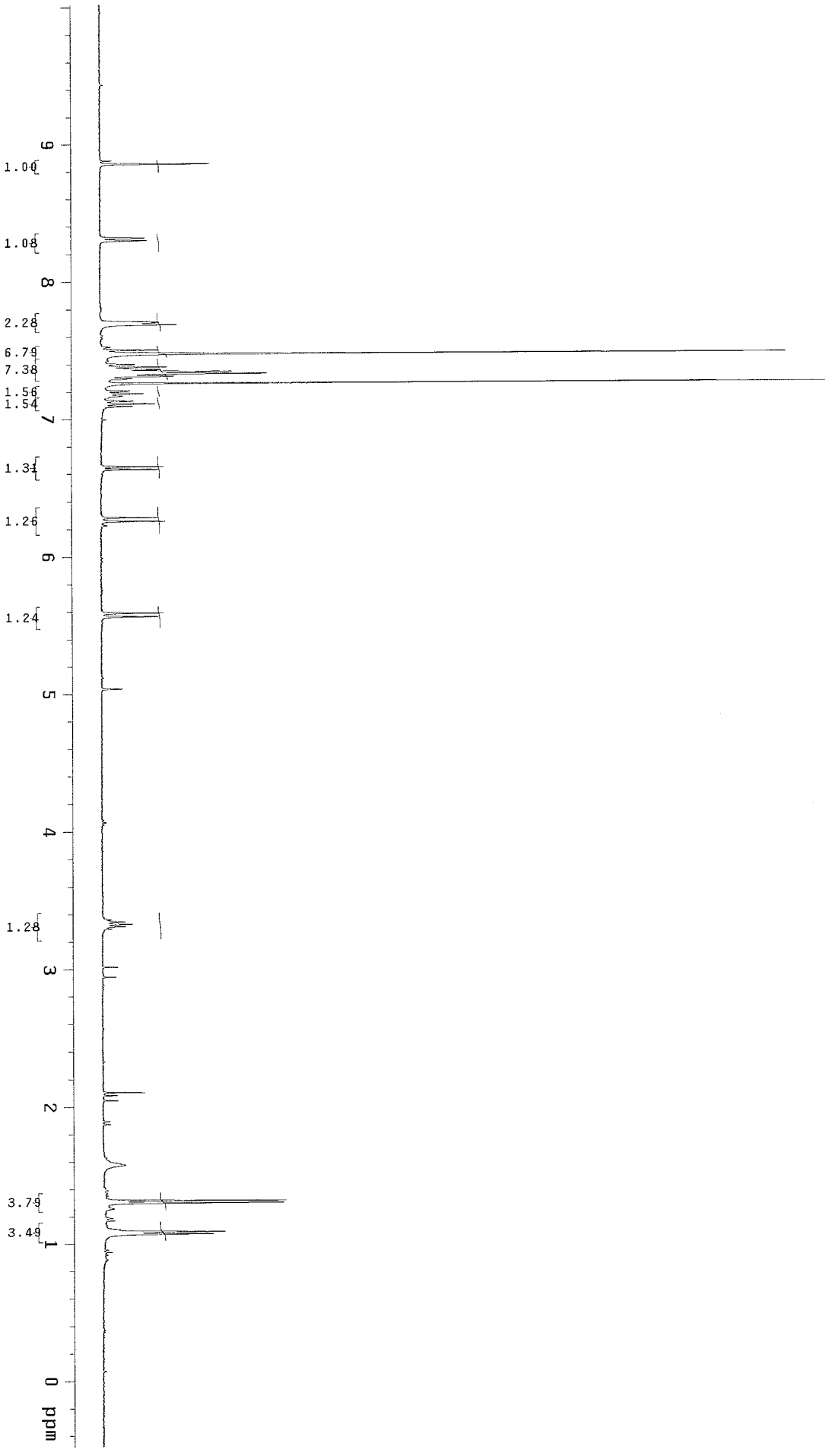
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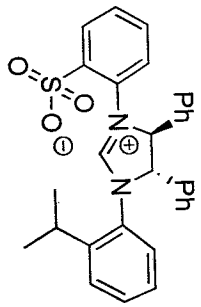
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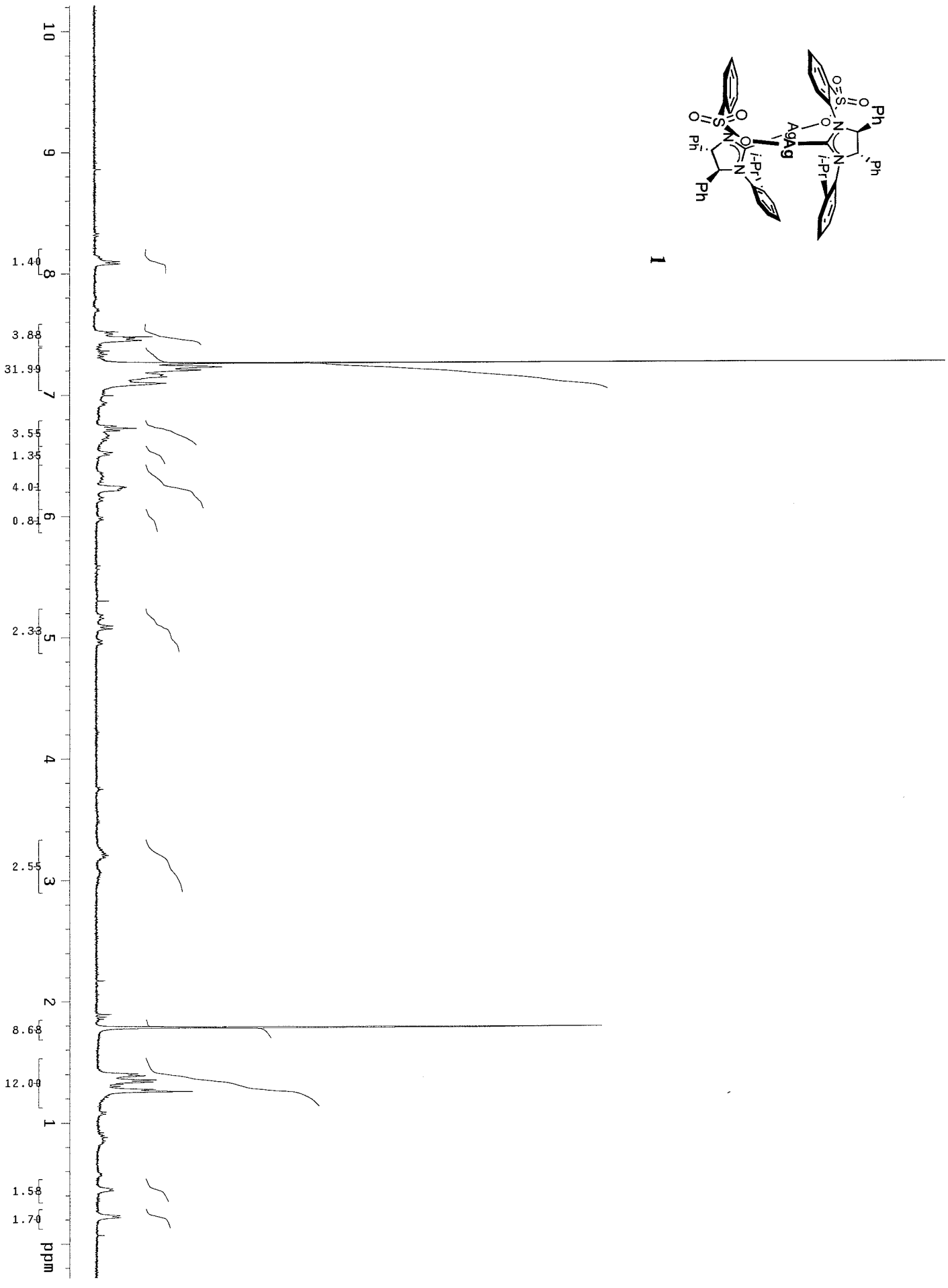
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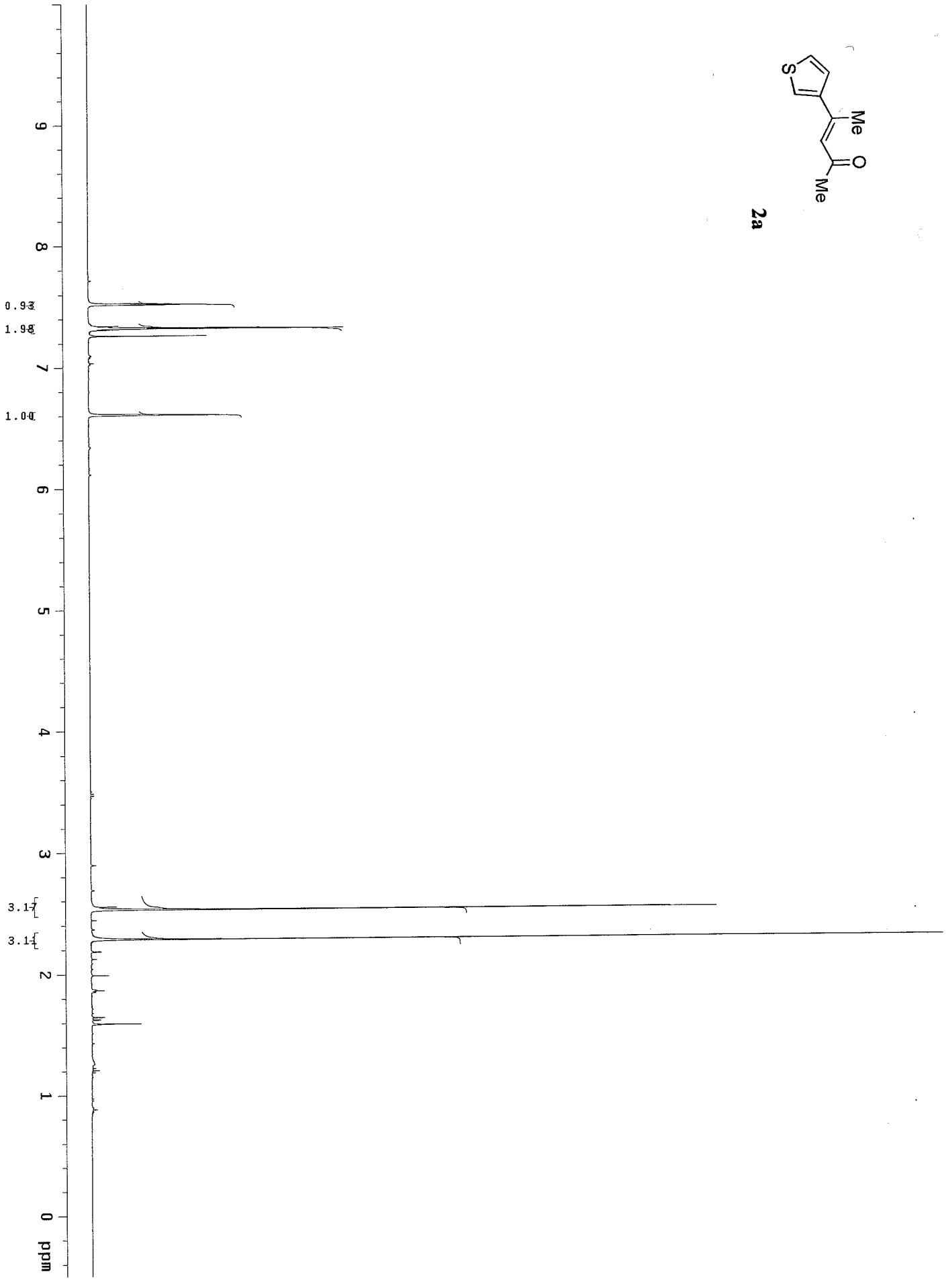
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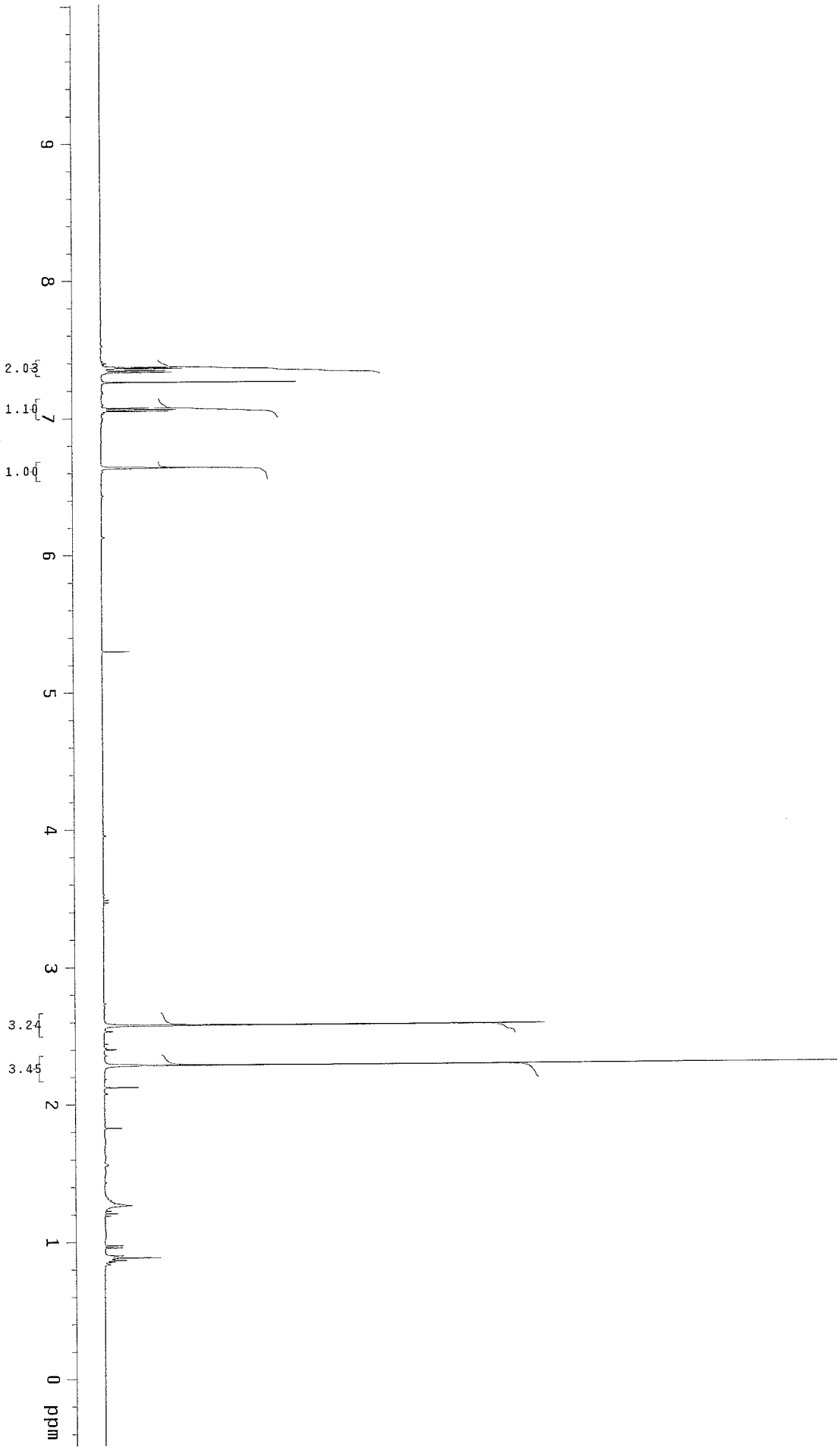

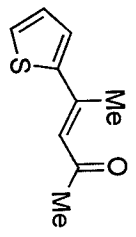

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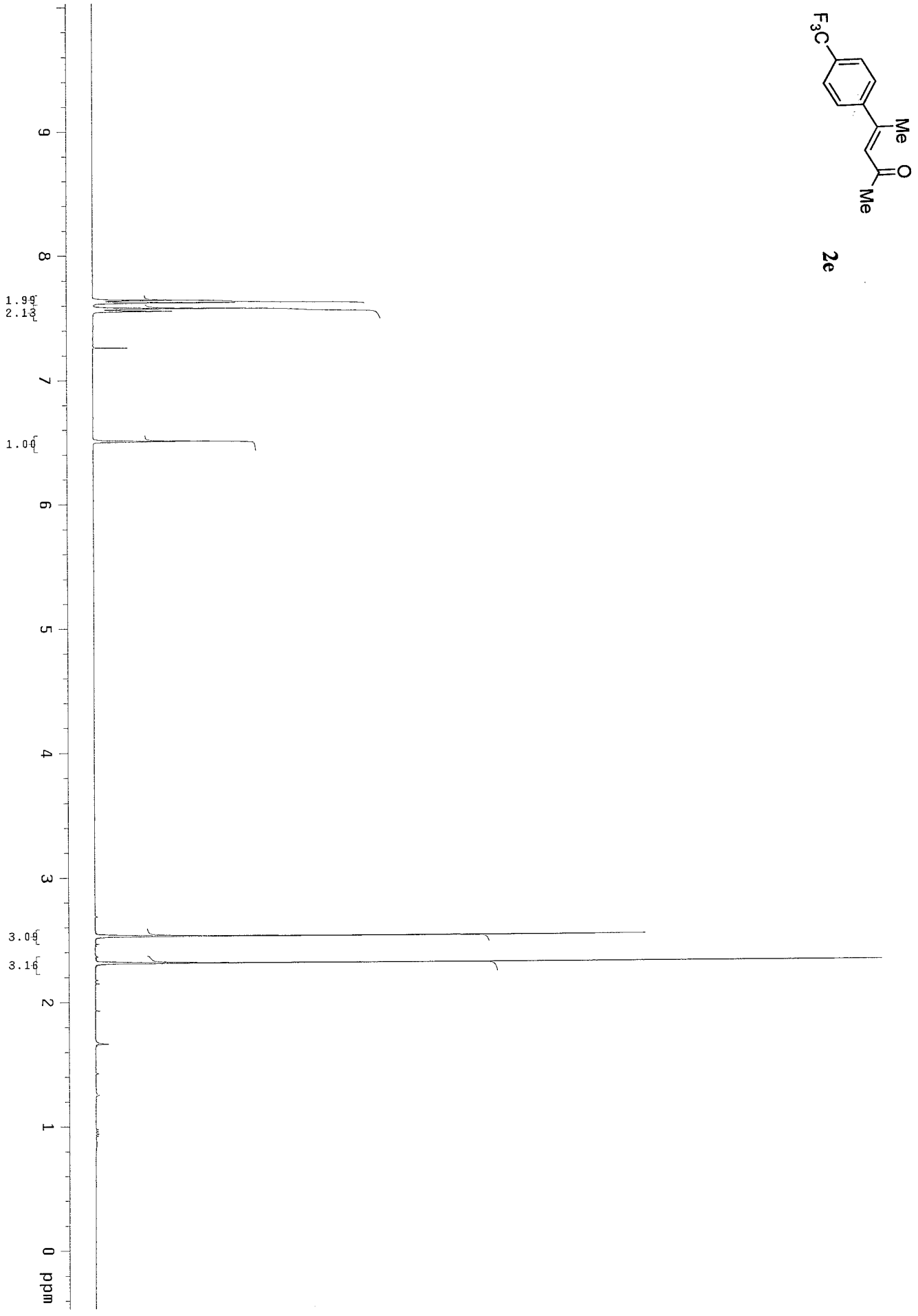
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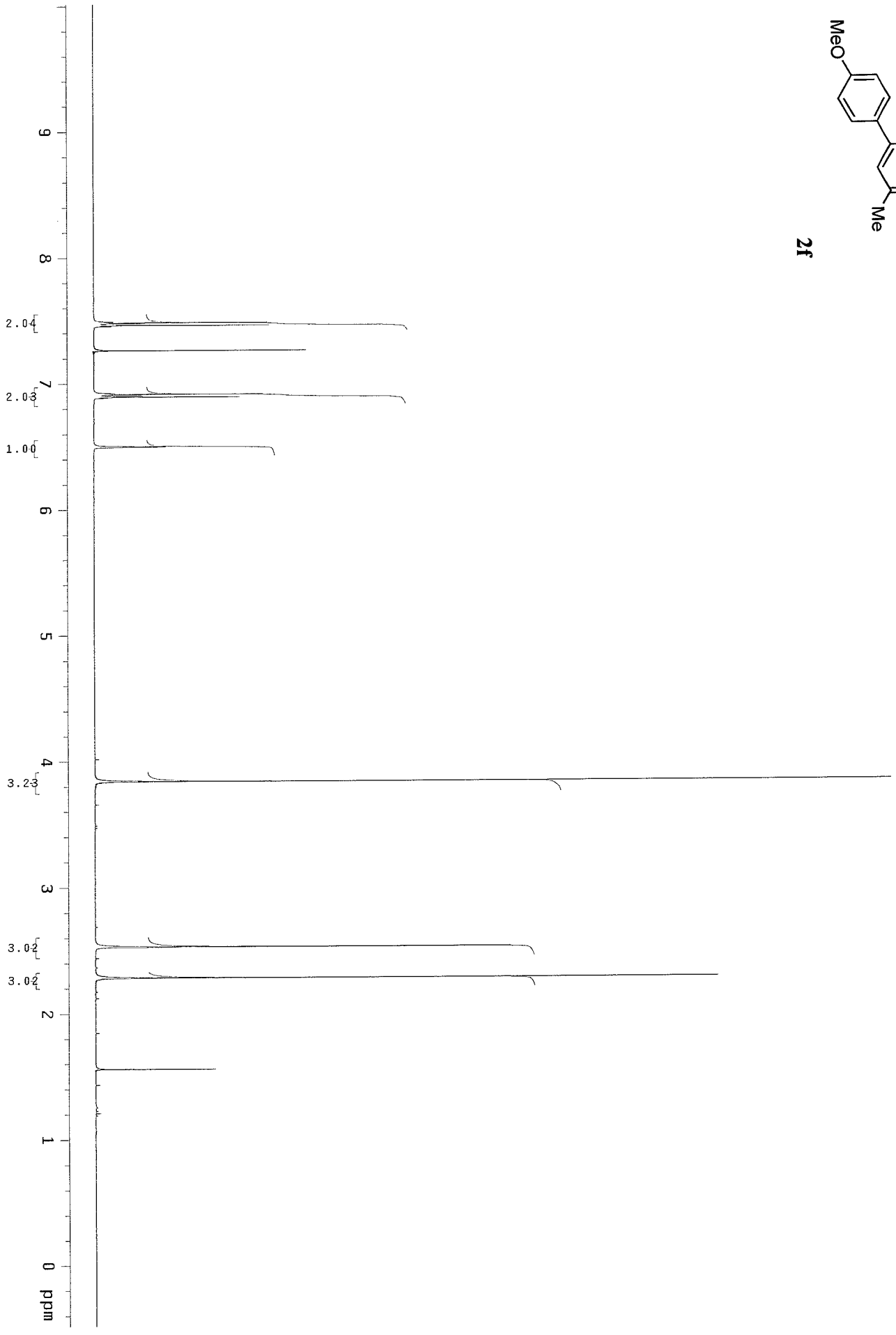
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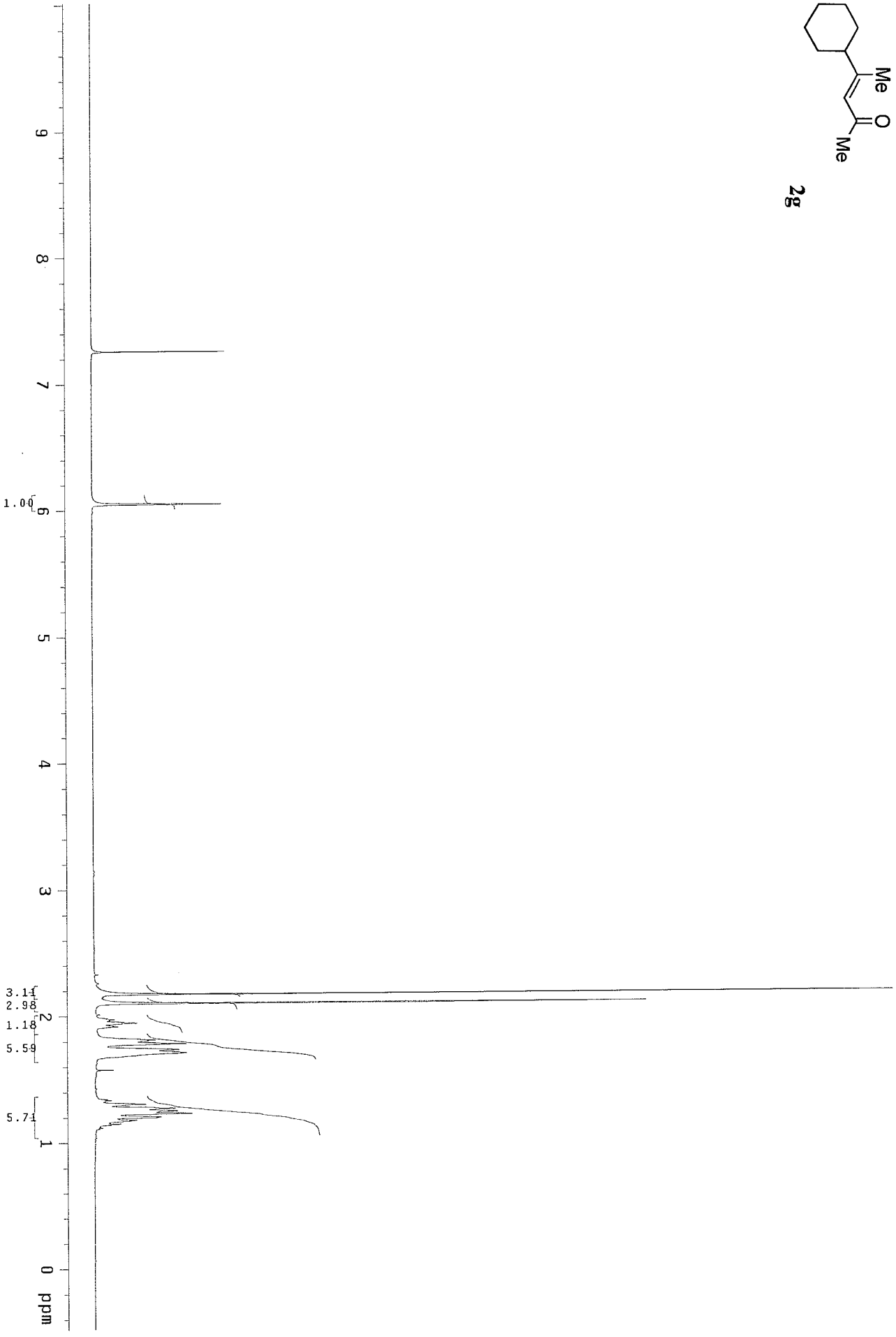
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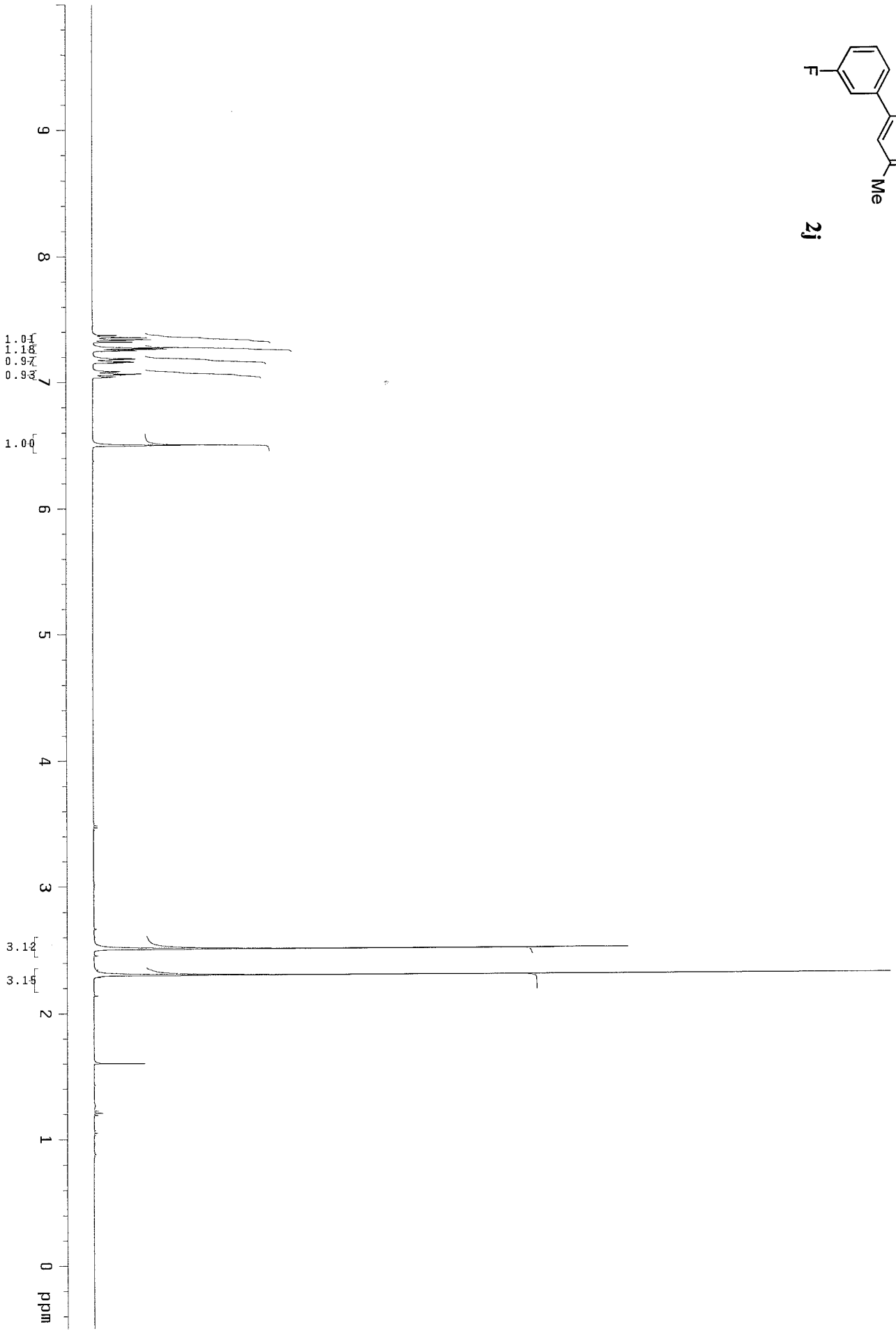
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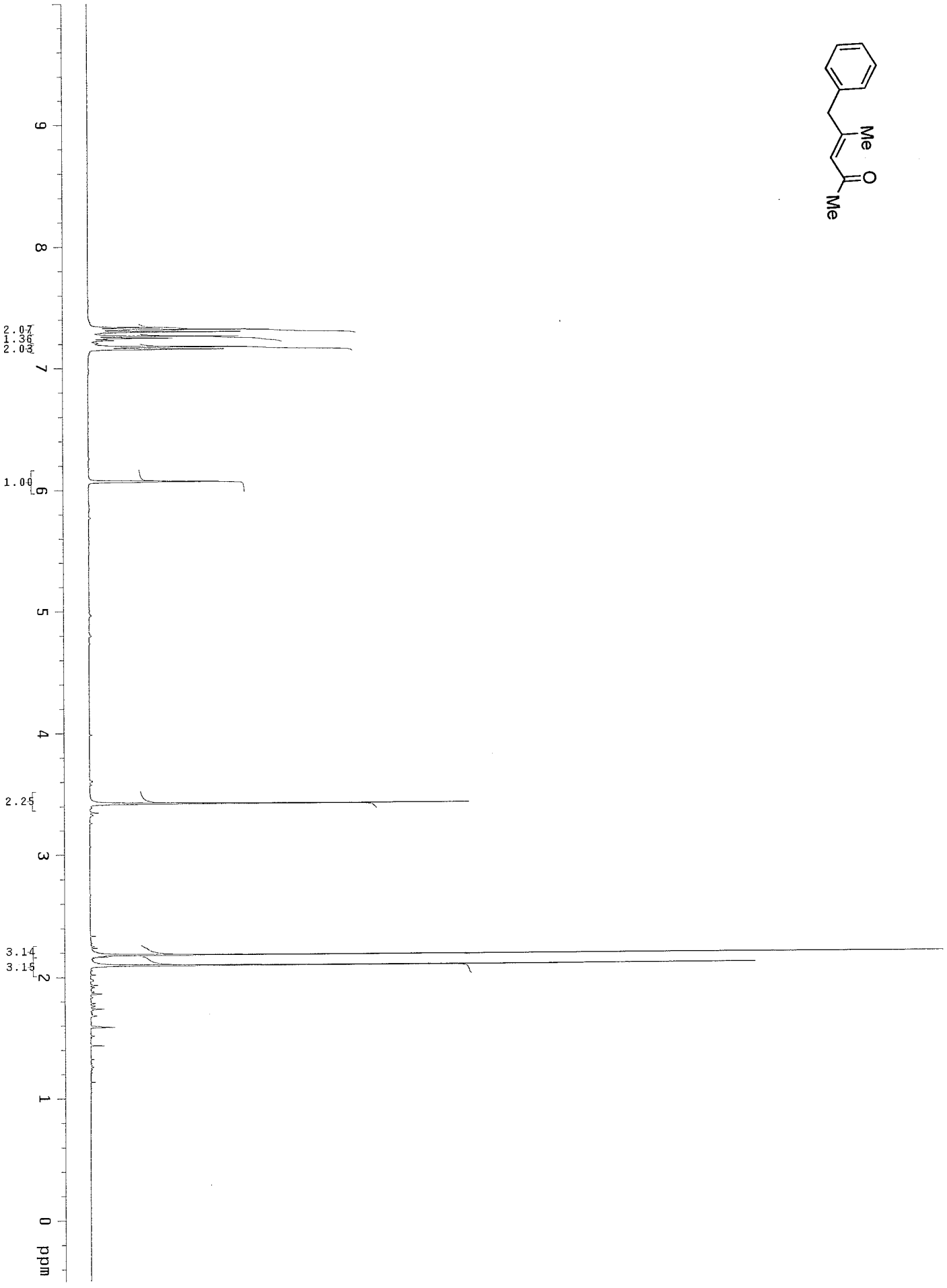
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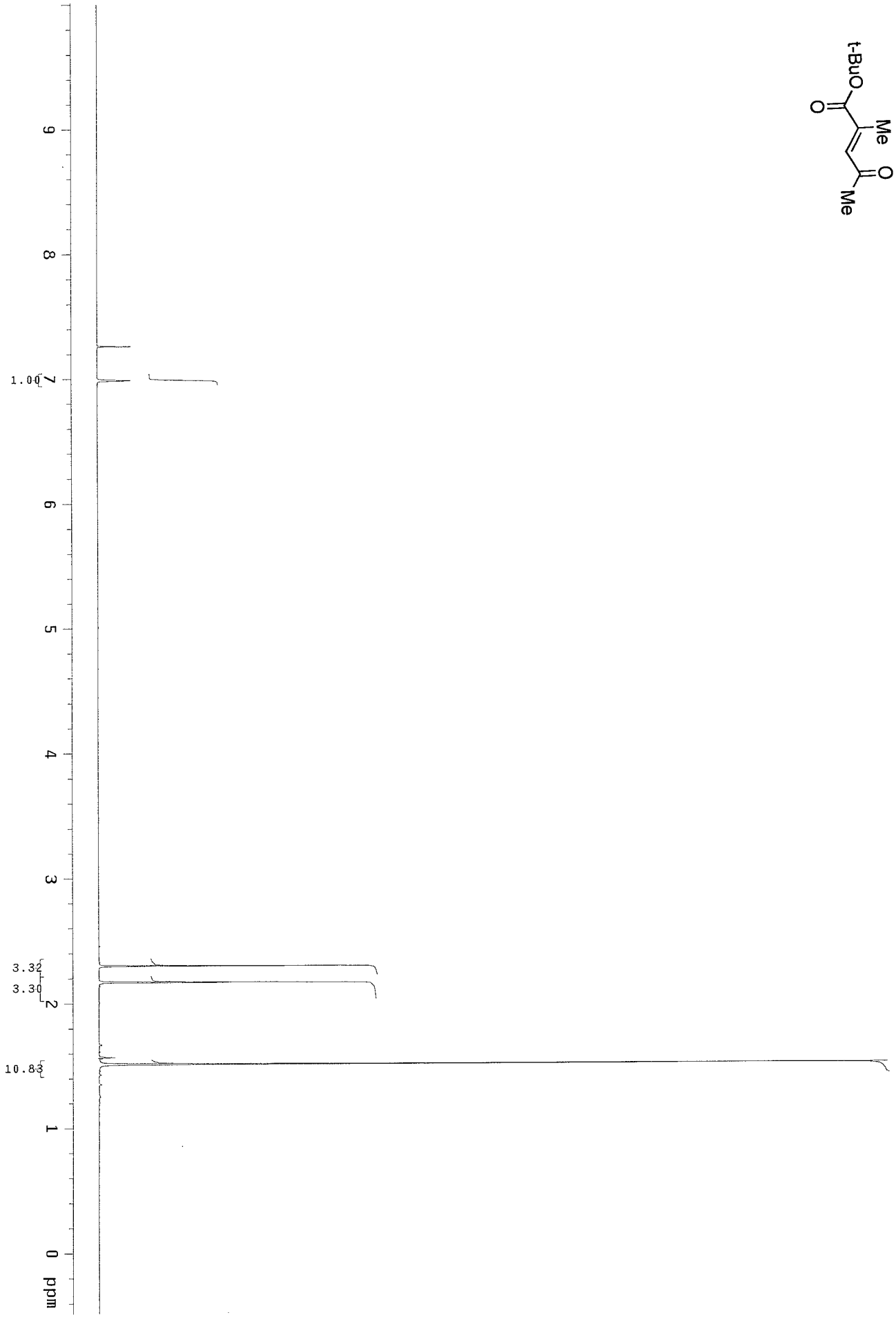
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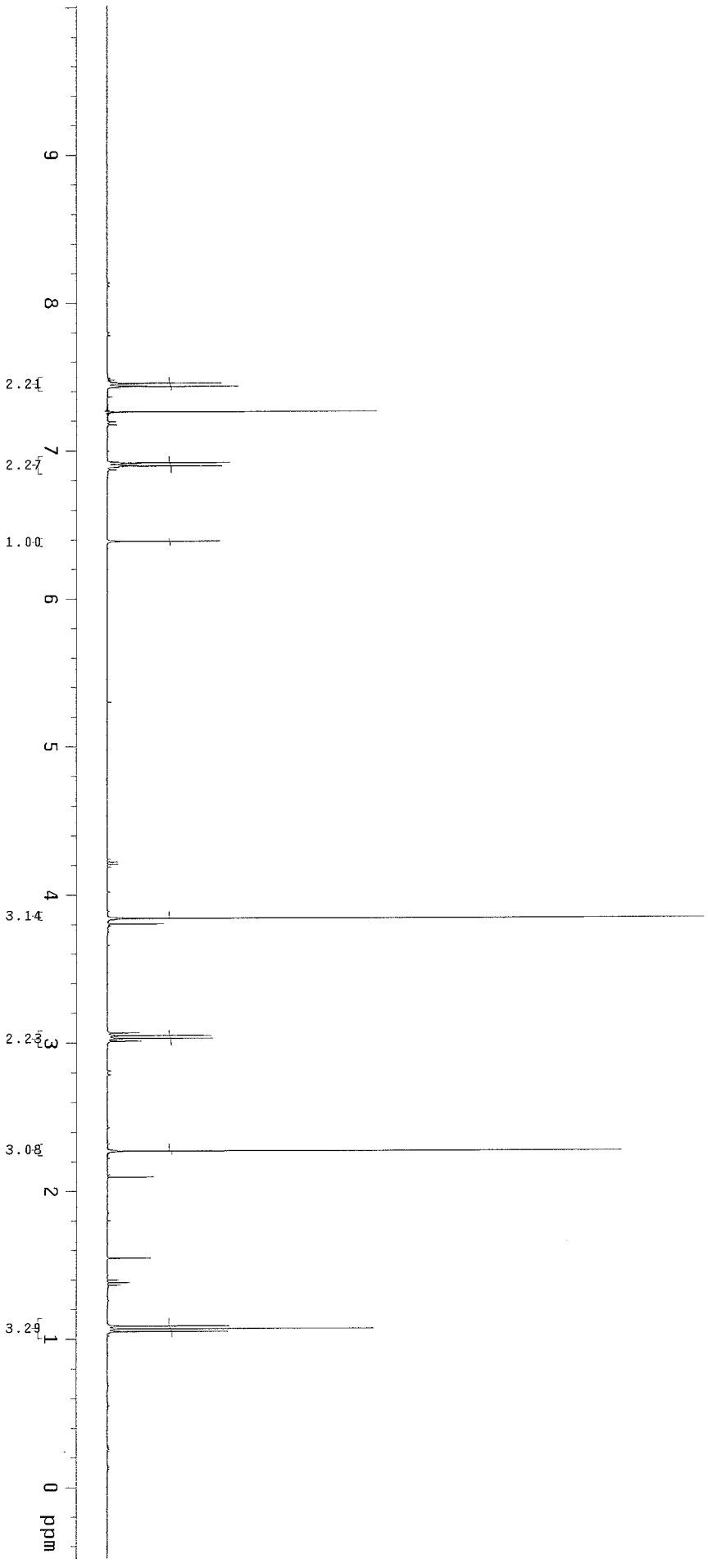
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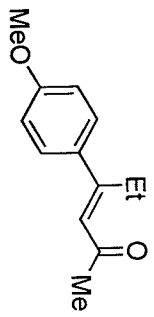
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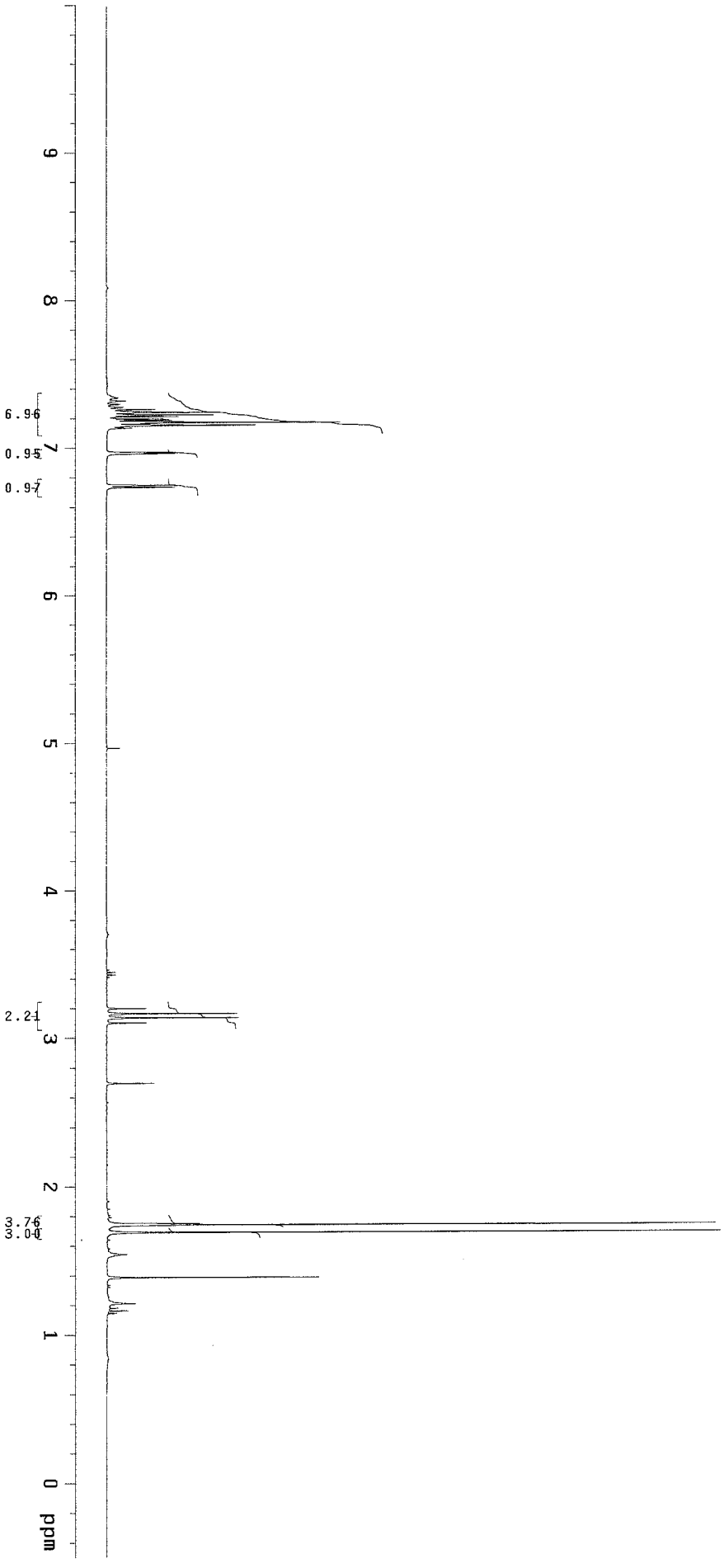
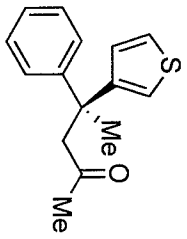
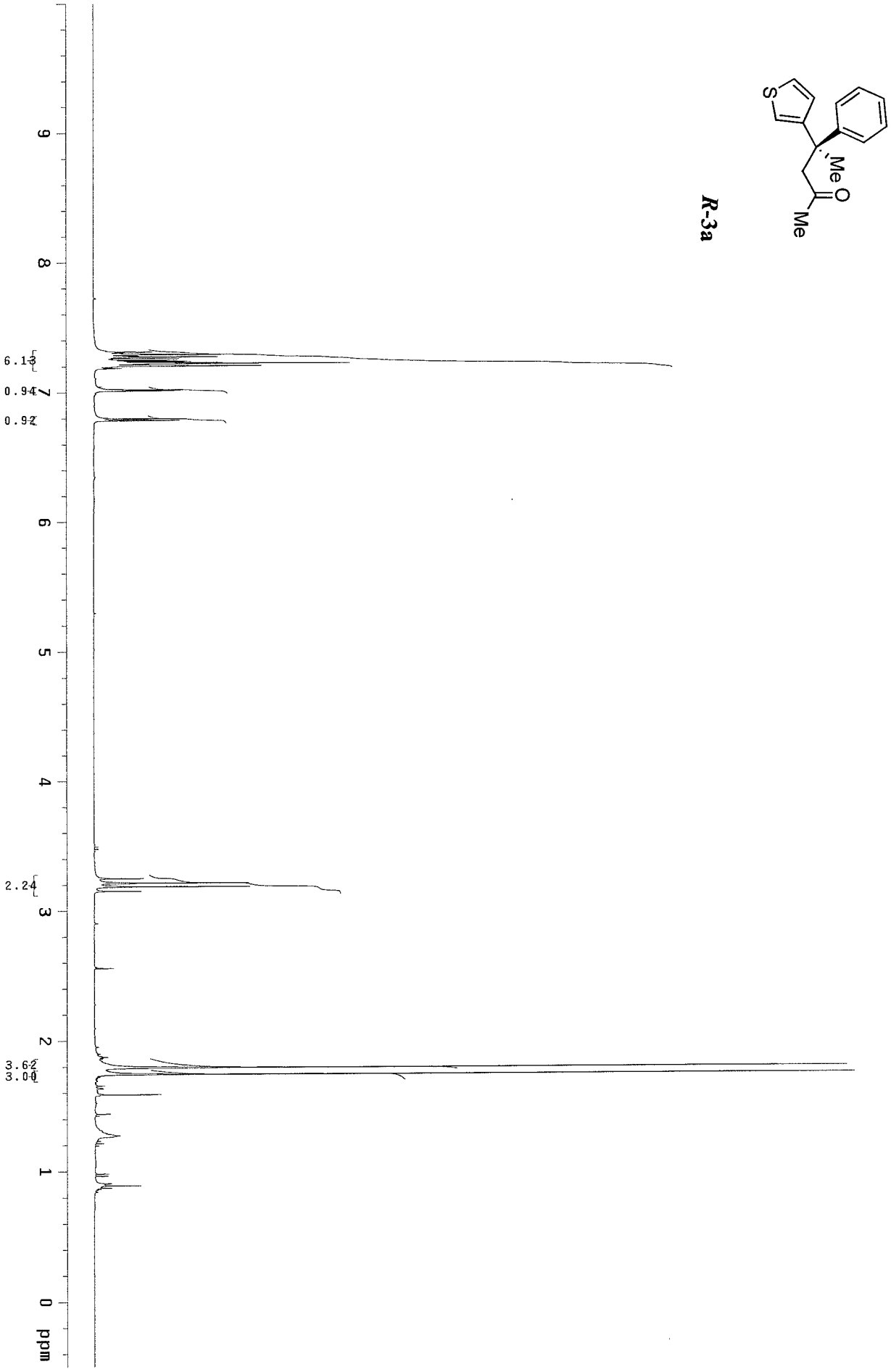
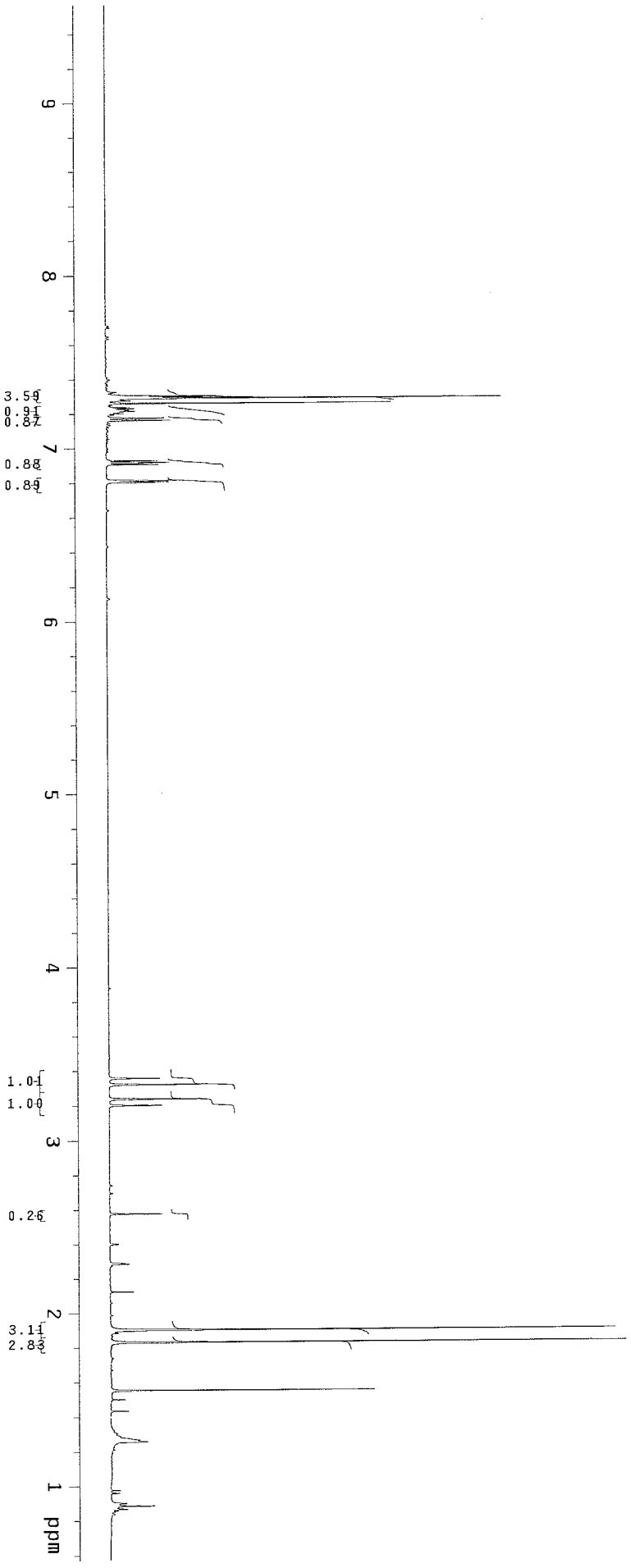


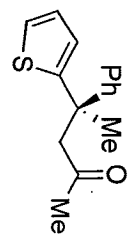


S-3a

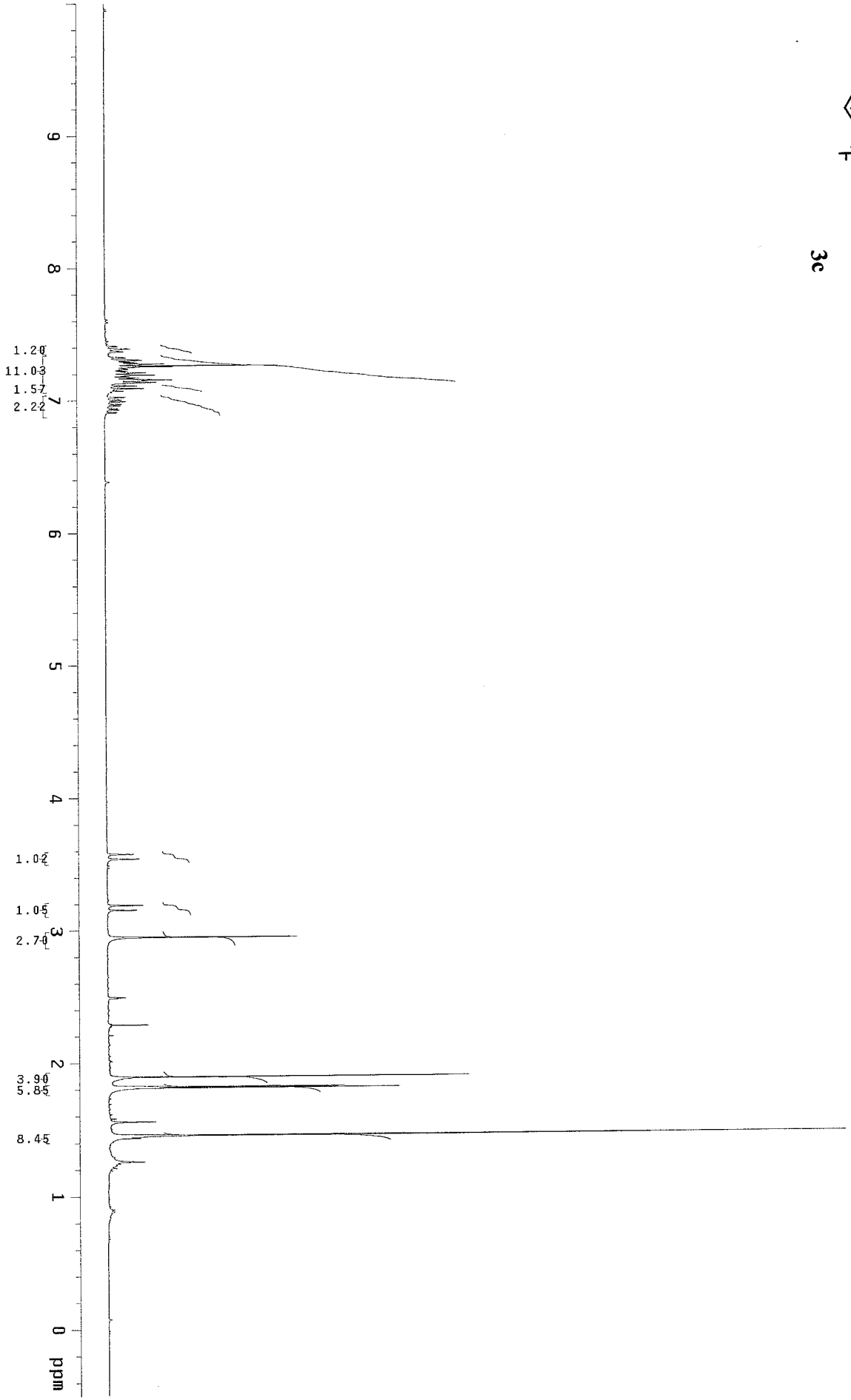


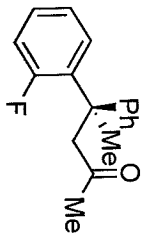
***R*-3a**


3.59
0.91
0.87
0.88
0.89
1.01
1.00
0.26
3.11
2.83
9
8
7
6
5
4
3
2
1
ppm

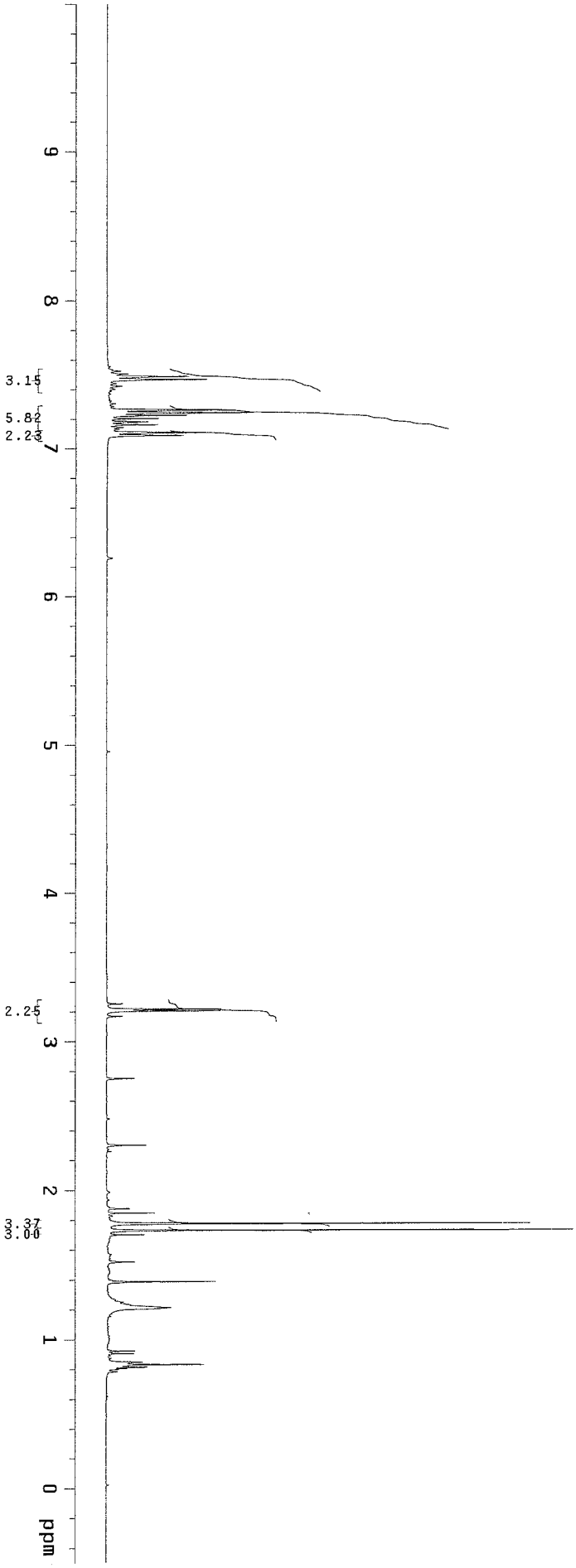

S
Ph
Me
O
Me

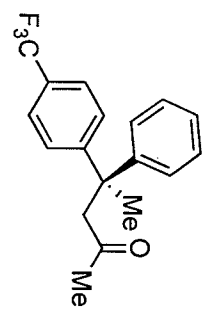
3b



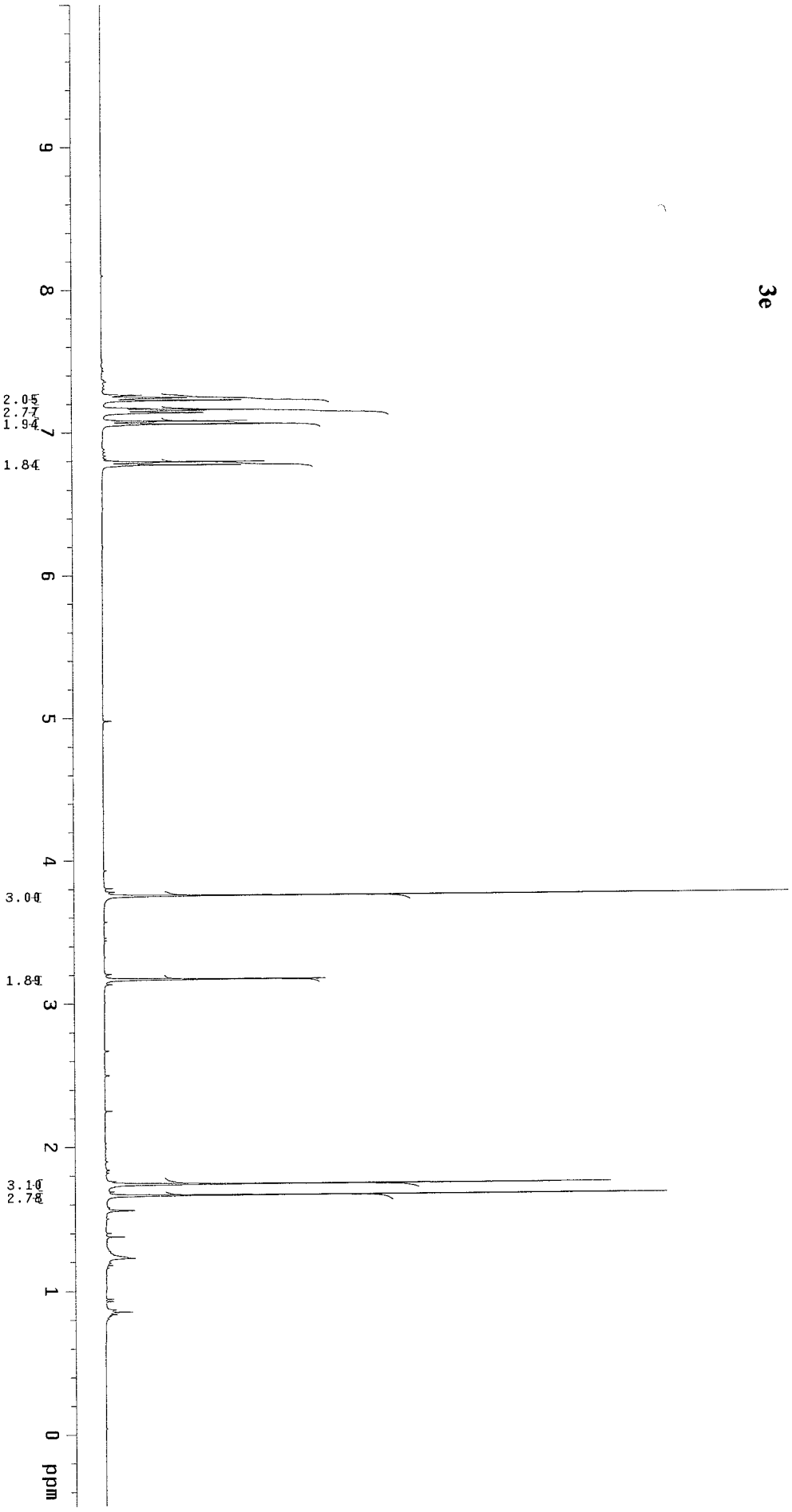


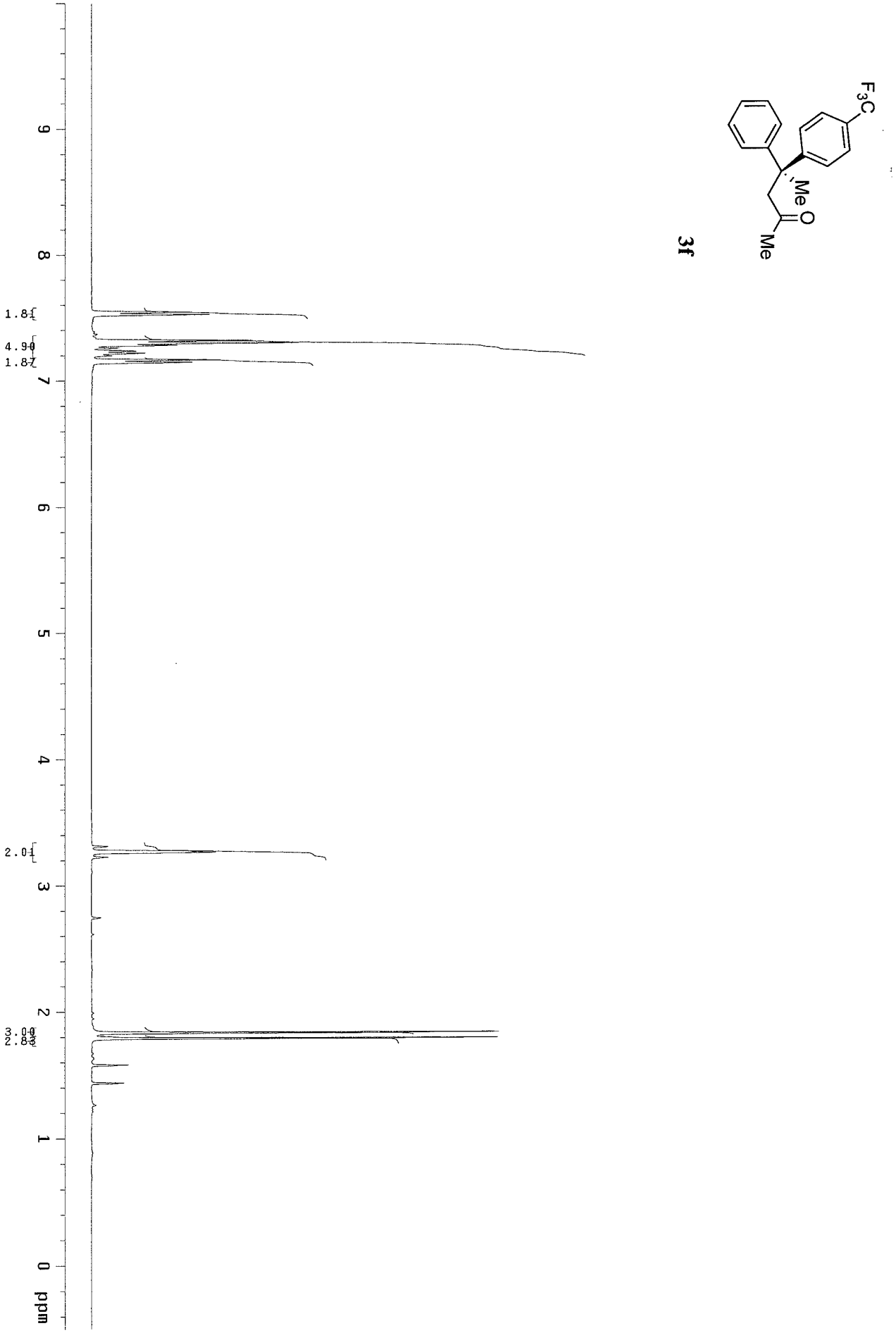
3c



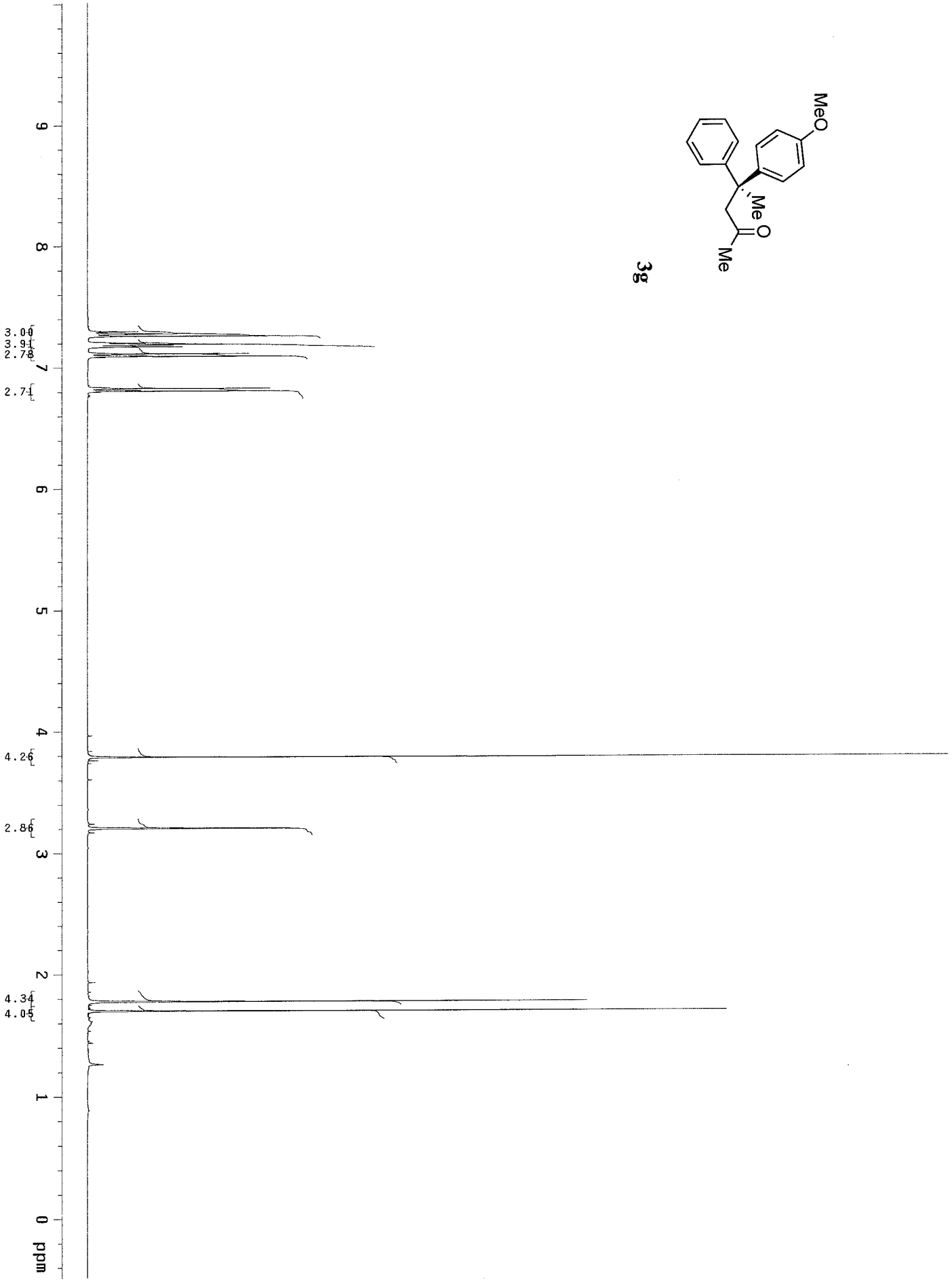


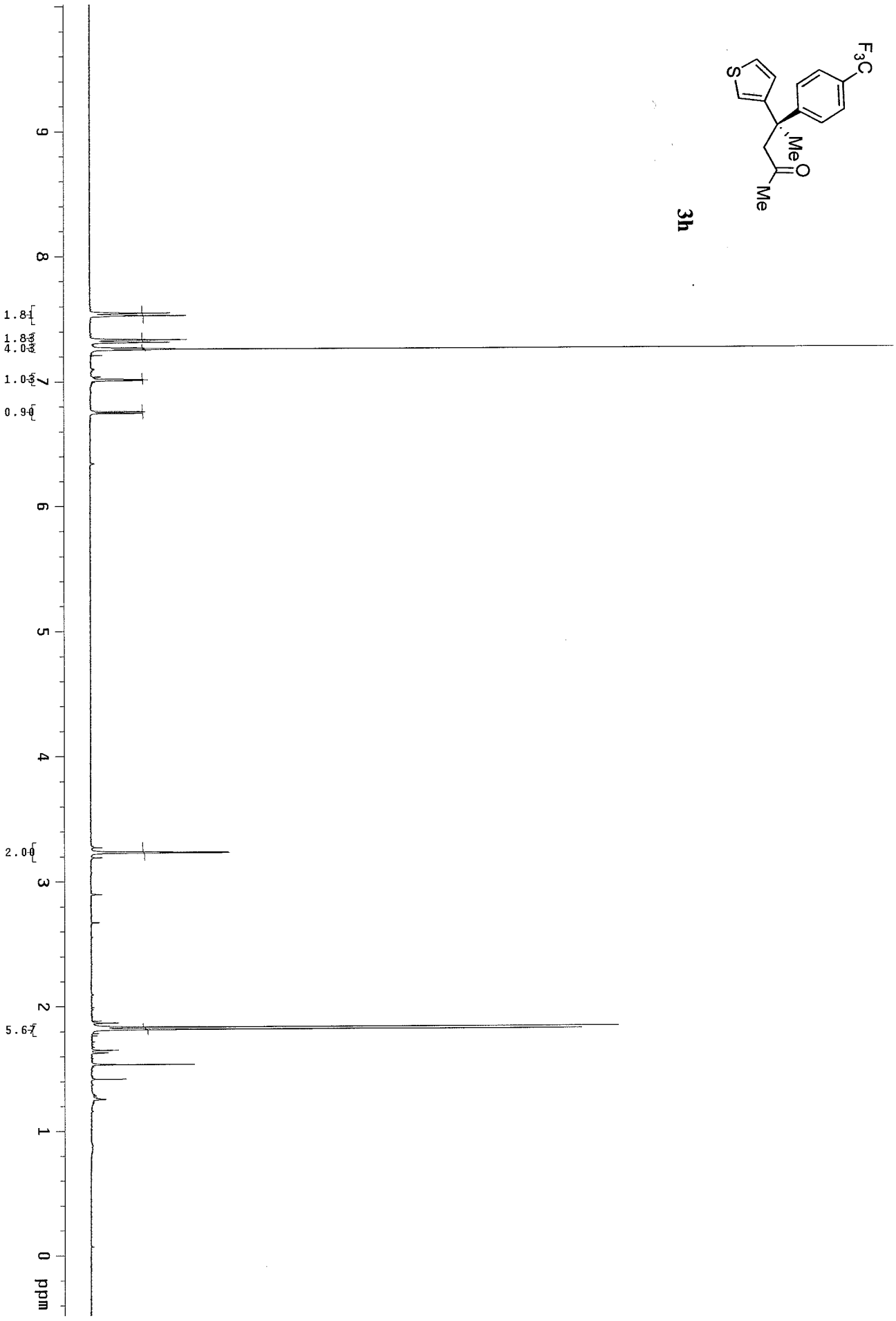
3d

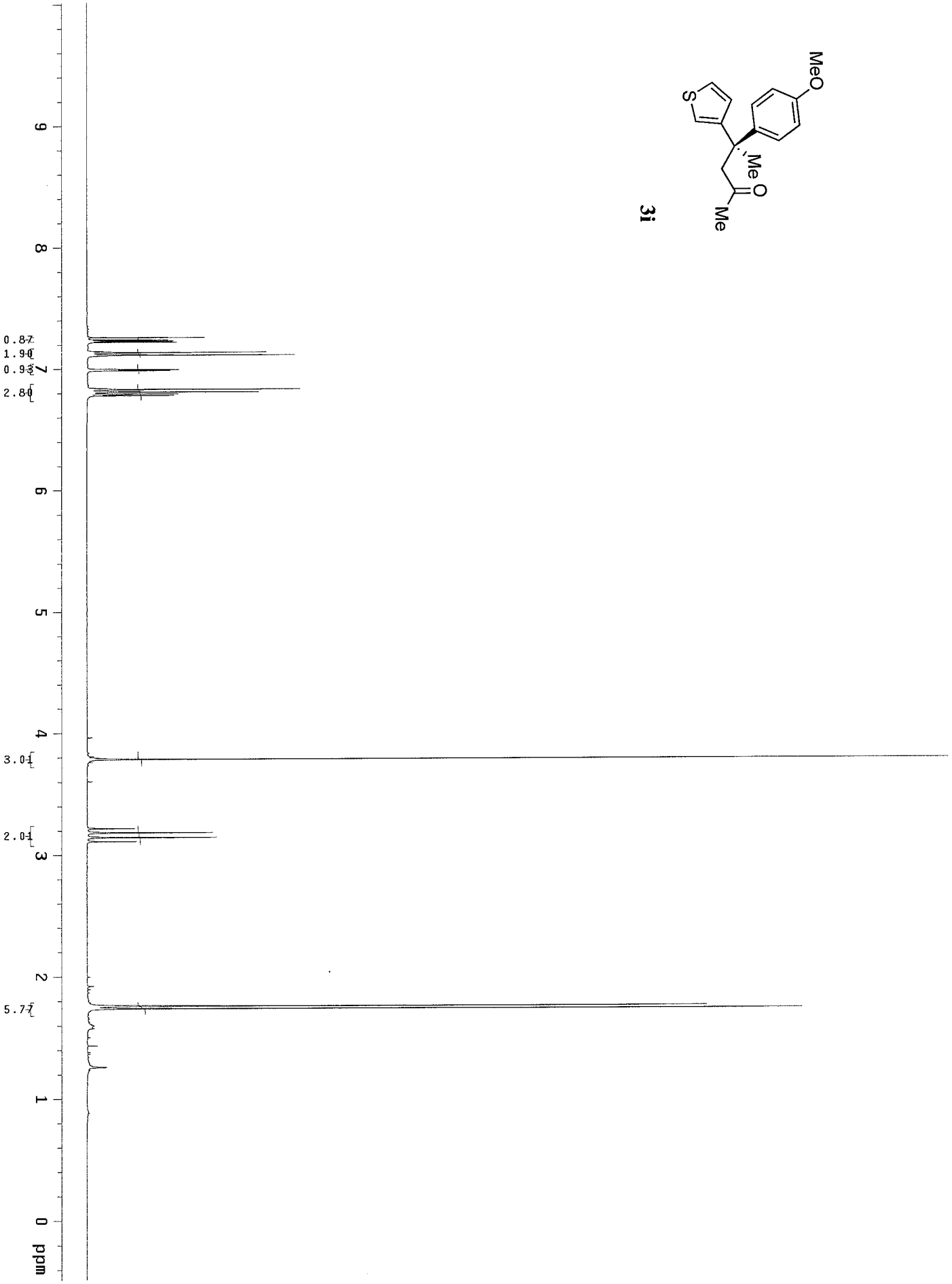

MeO
Me O
Me
3e
2.05
2.77
1.94
1.84
3.04
1.89
3.10
2.78
9
8
7
6
5
4
3
2
1
0
ppm

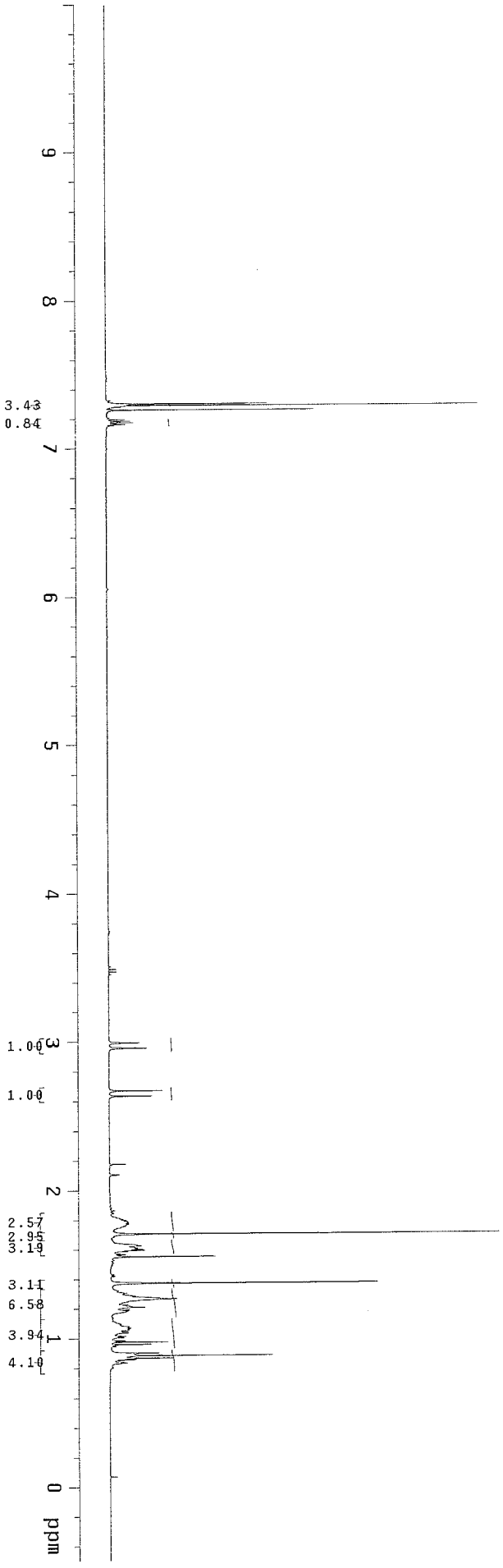


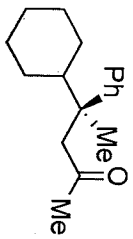
3f


MeO
Me
O
Me
3g
3.00
3.91
2.78
2.71
4.26
2.86
4.34
4.05
ppm

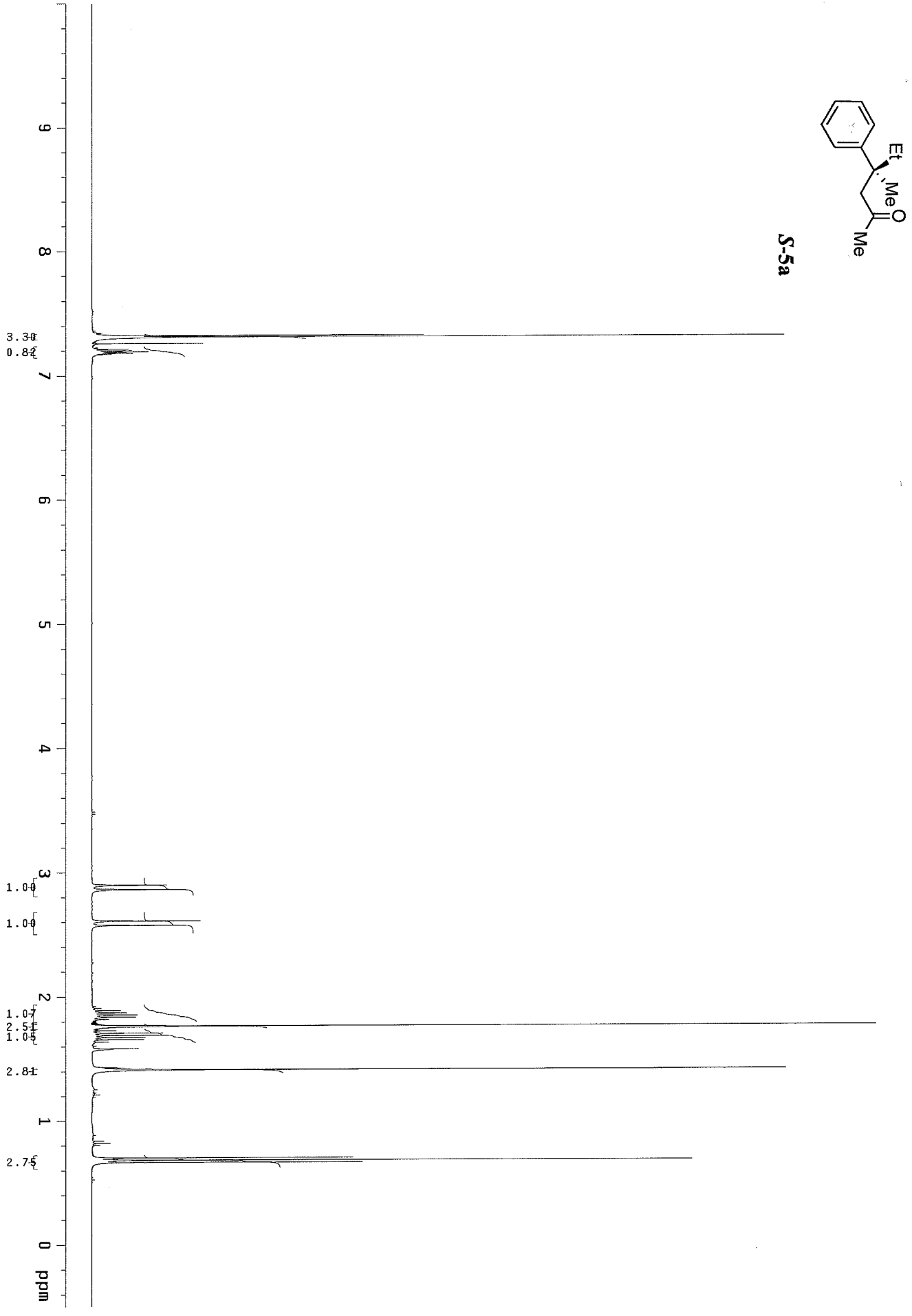

F3C
S
Me
O
Me
3h
1.81
1.83
4.00
1.03
0.90
2.00
5.67
9
8
7
6
5
4
3
2
1
0
ppm


MeO
S
Me
O
Me
3i
0.87
1.90
0.93
2.80
3.01
2.01
5.77
9
8
7
6
5
4
3
2
1
0
ppm

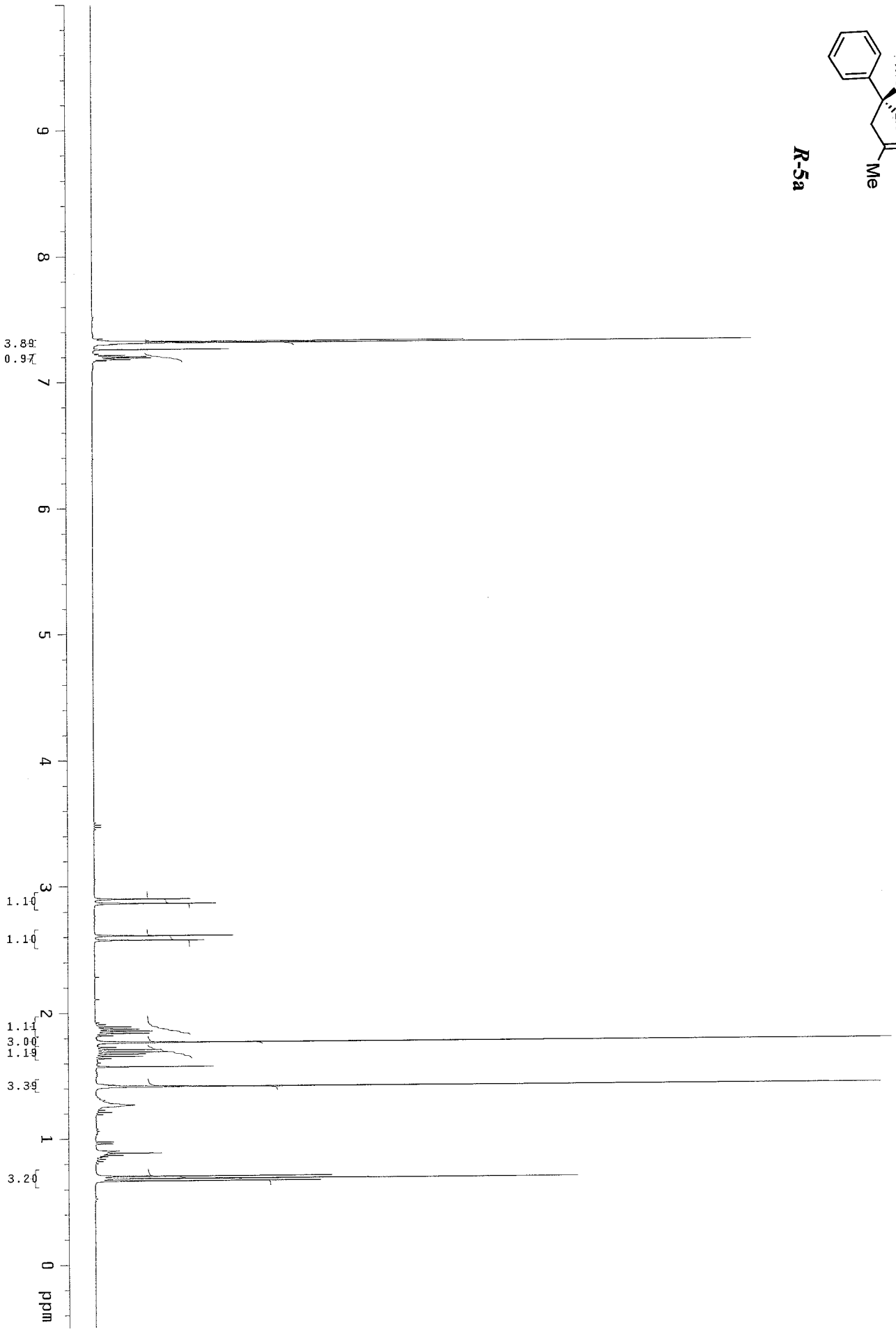

3.43
0.84
1.00
1.00
2.57
2.95
3.19
3.11
6.58
3.94
4.10
9
8
7
6
5
4
3
2
1
0
ppm


Ph
MeO
O
Me

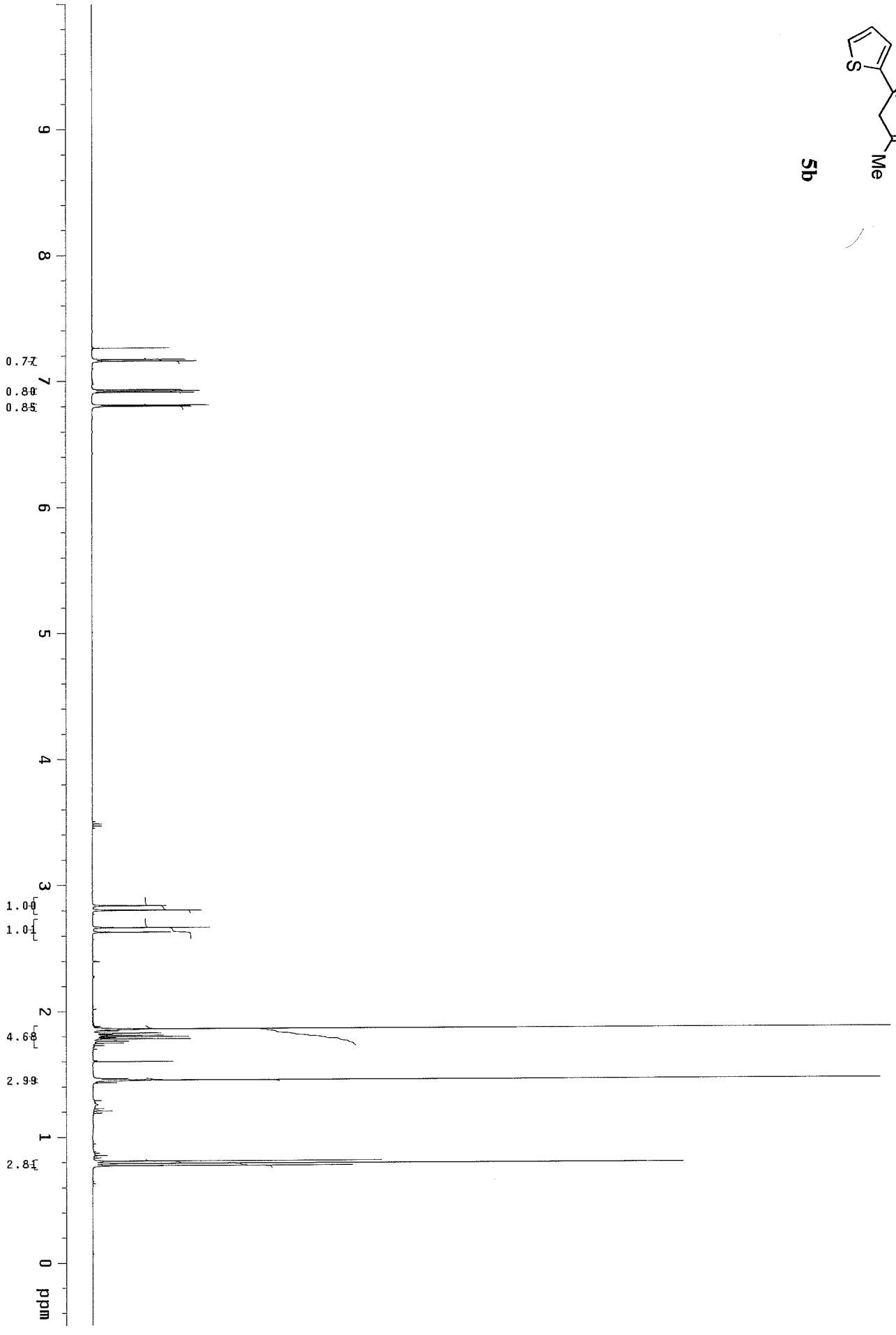
3j

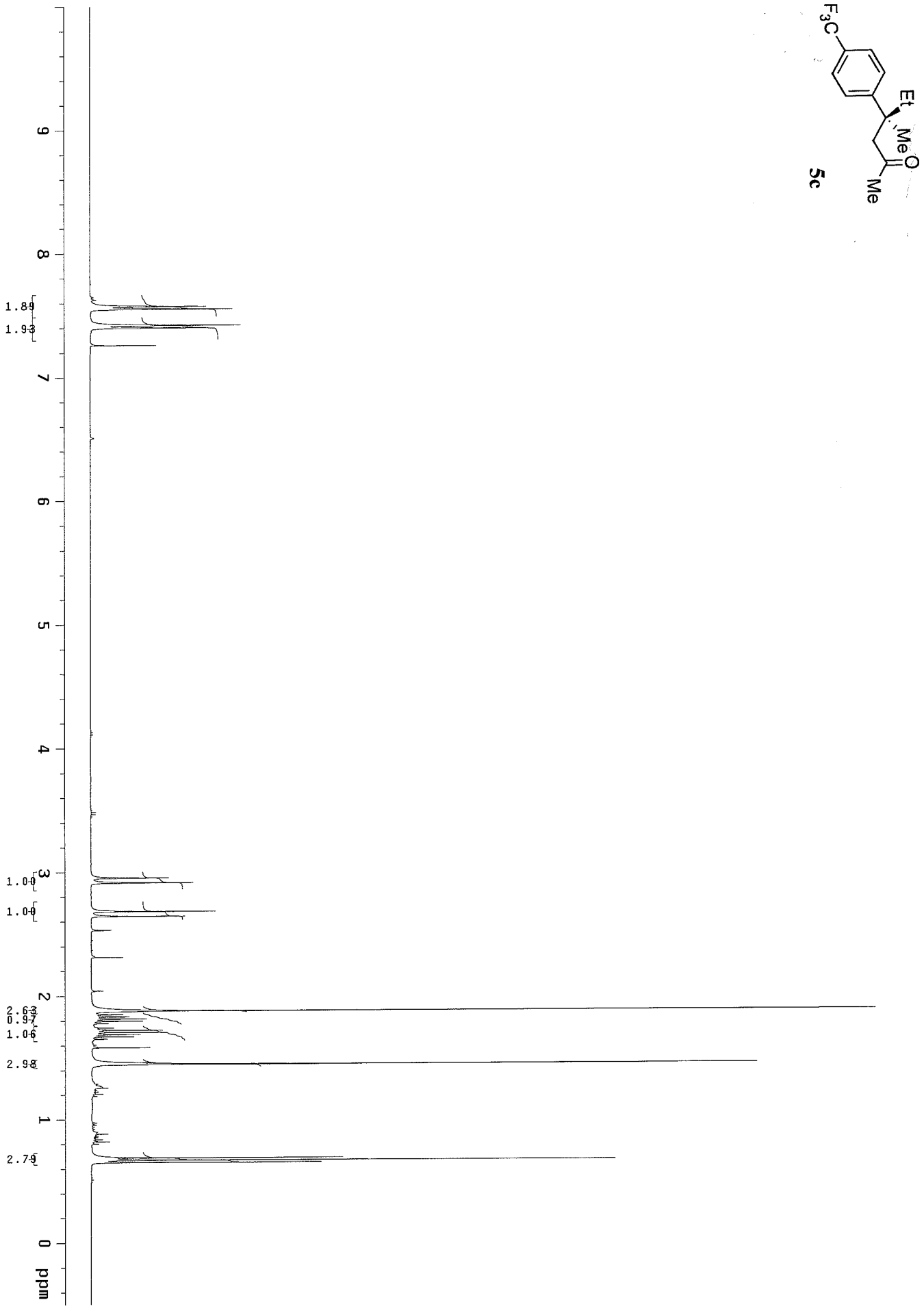


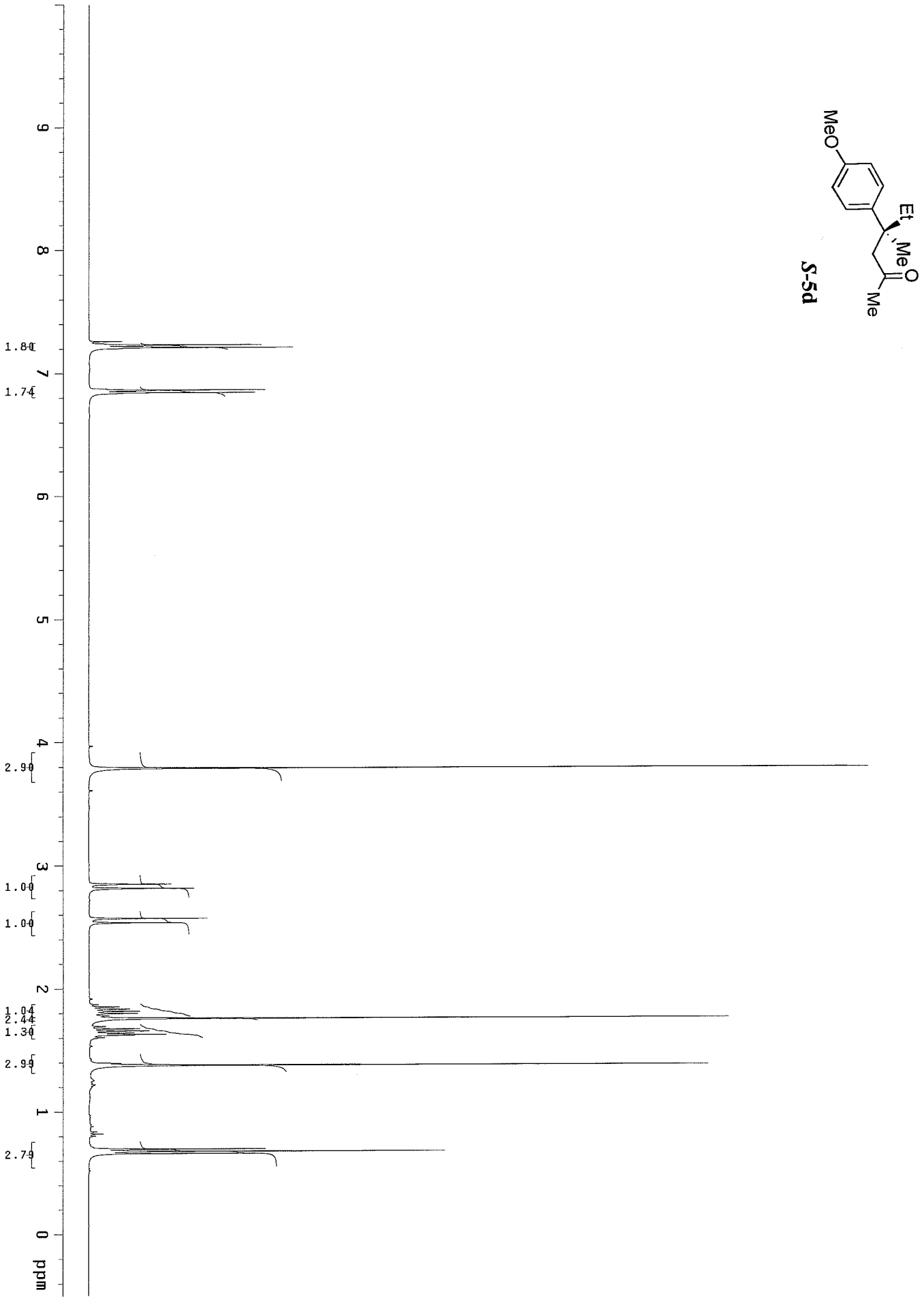
S-5a

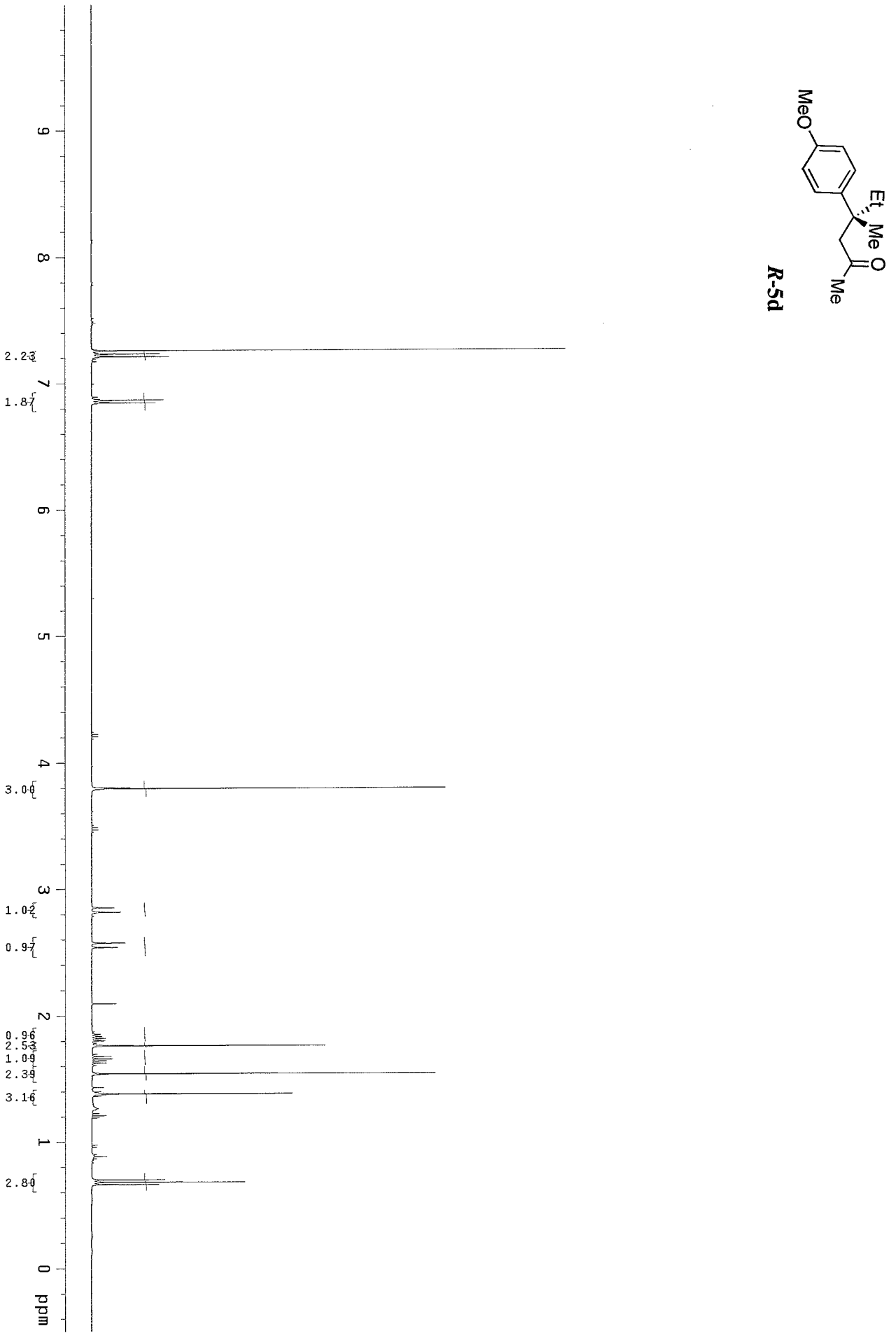


***R*-5a**

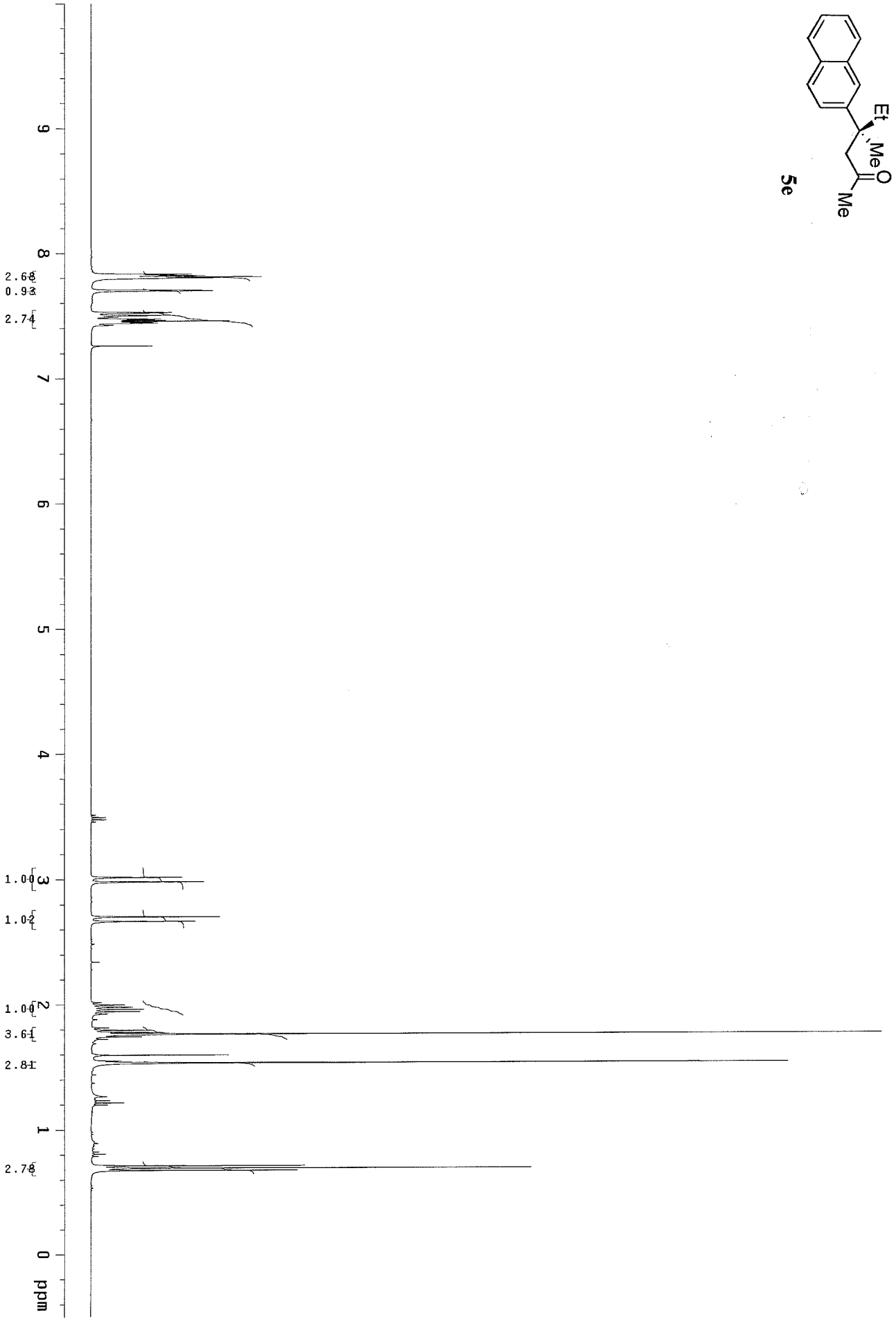

Et
MeO
Me
S
5b
0.77
0.80
0.85
1.00
1.01
4.68
2.99
2.81
9
8
7
6
5
4
3
2
1
0
ppm

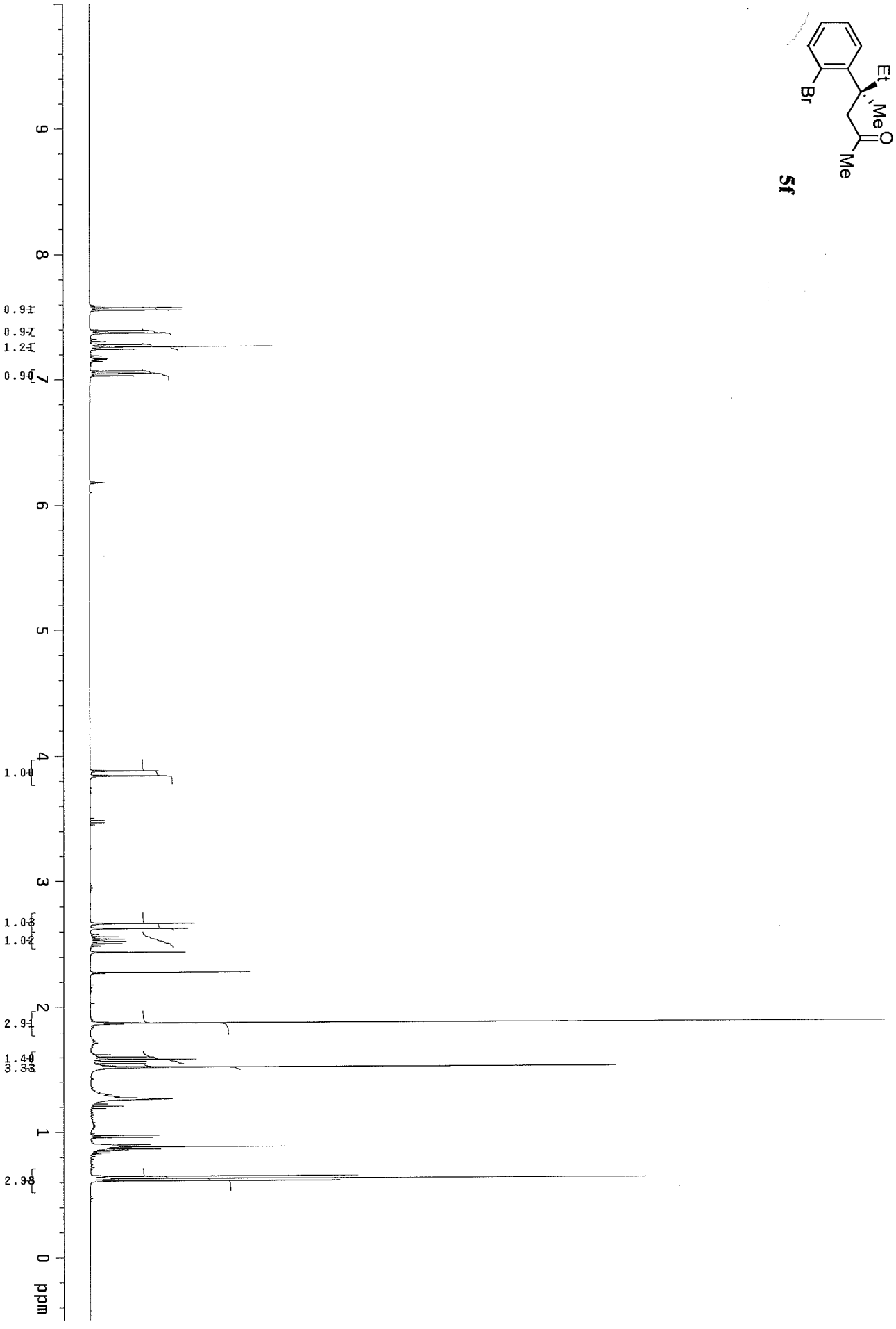

F3C
Et
MeO
Me
5c
1.89
1.93
1.00
1.00
2.63
0.97
1.06
2.98
2.79
ppm

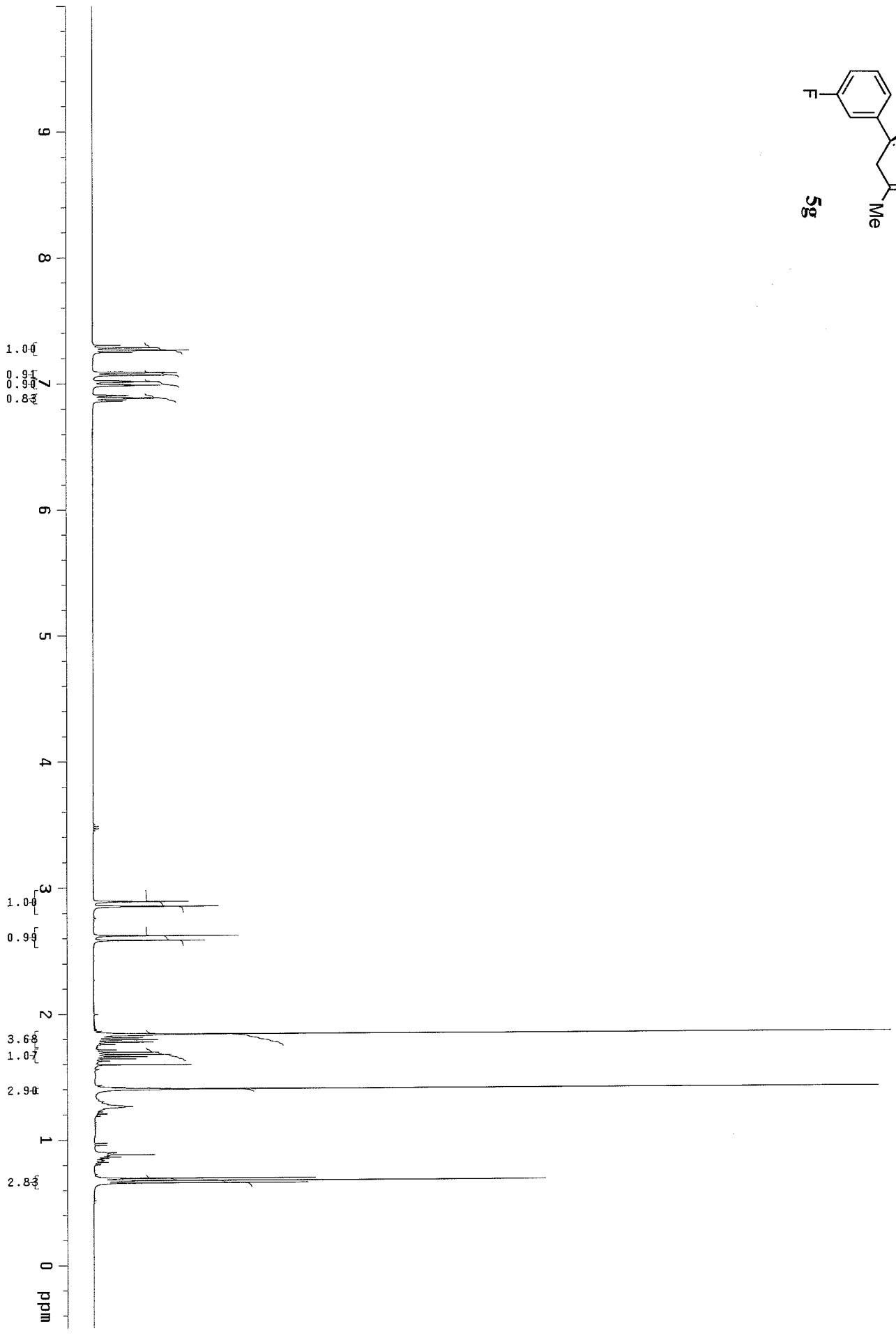

MeO
Et
MeO
Me
S-5d
1.80
1.74
2.90
1.00
1.00
1.04
2.44
1.30
2.99
2.79
9
8
7
6
5
4
3
2
1
0
ppm

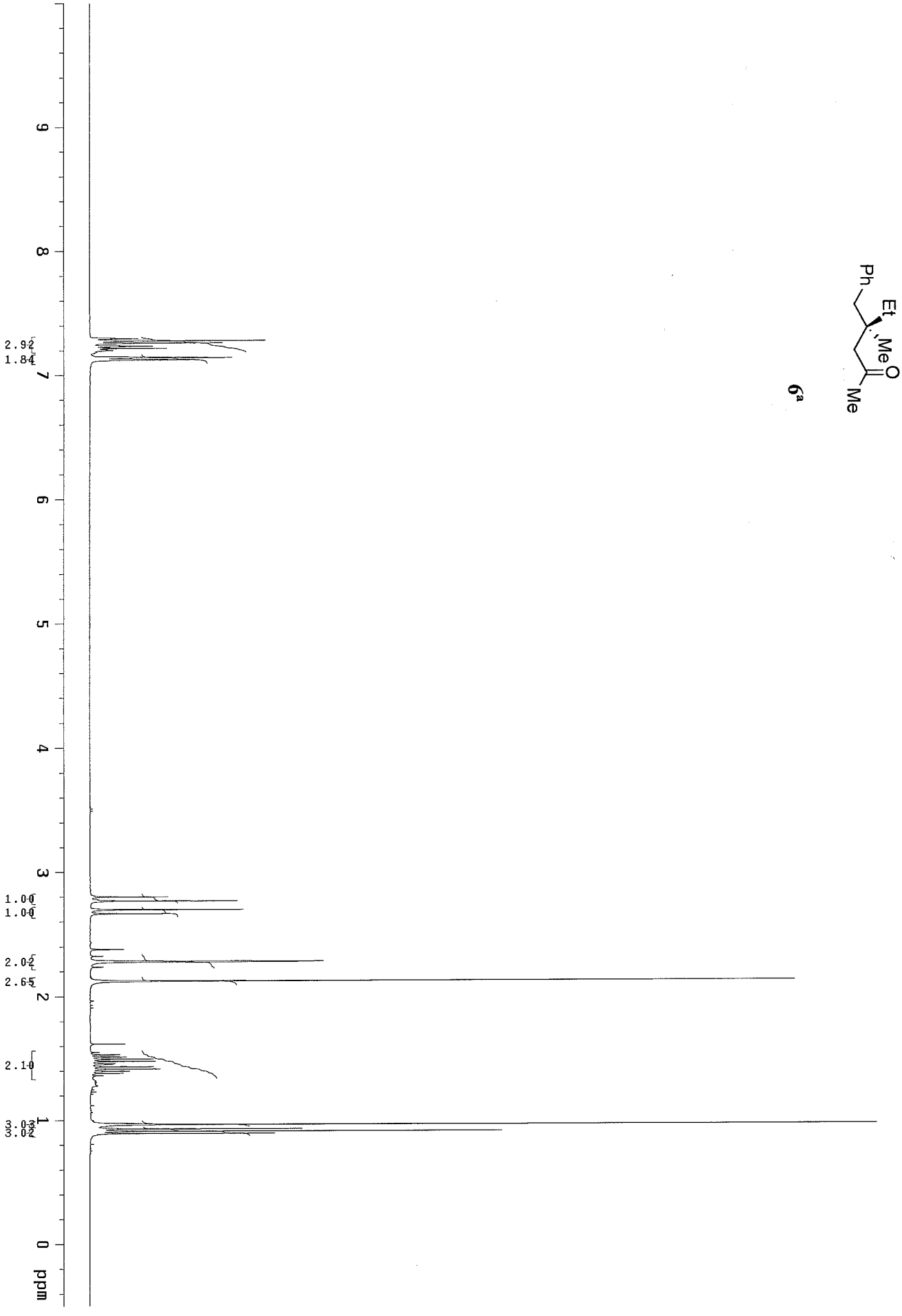

MeO
Et
Me
O
Me
2.23
1.87
3.00
1.02
0.97
0.96
2.58
1.09
2.39
3.16
2.80
9
8
7
6
5
4
3
2
1
0
ppm

***R*-5d**

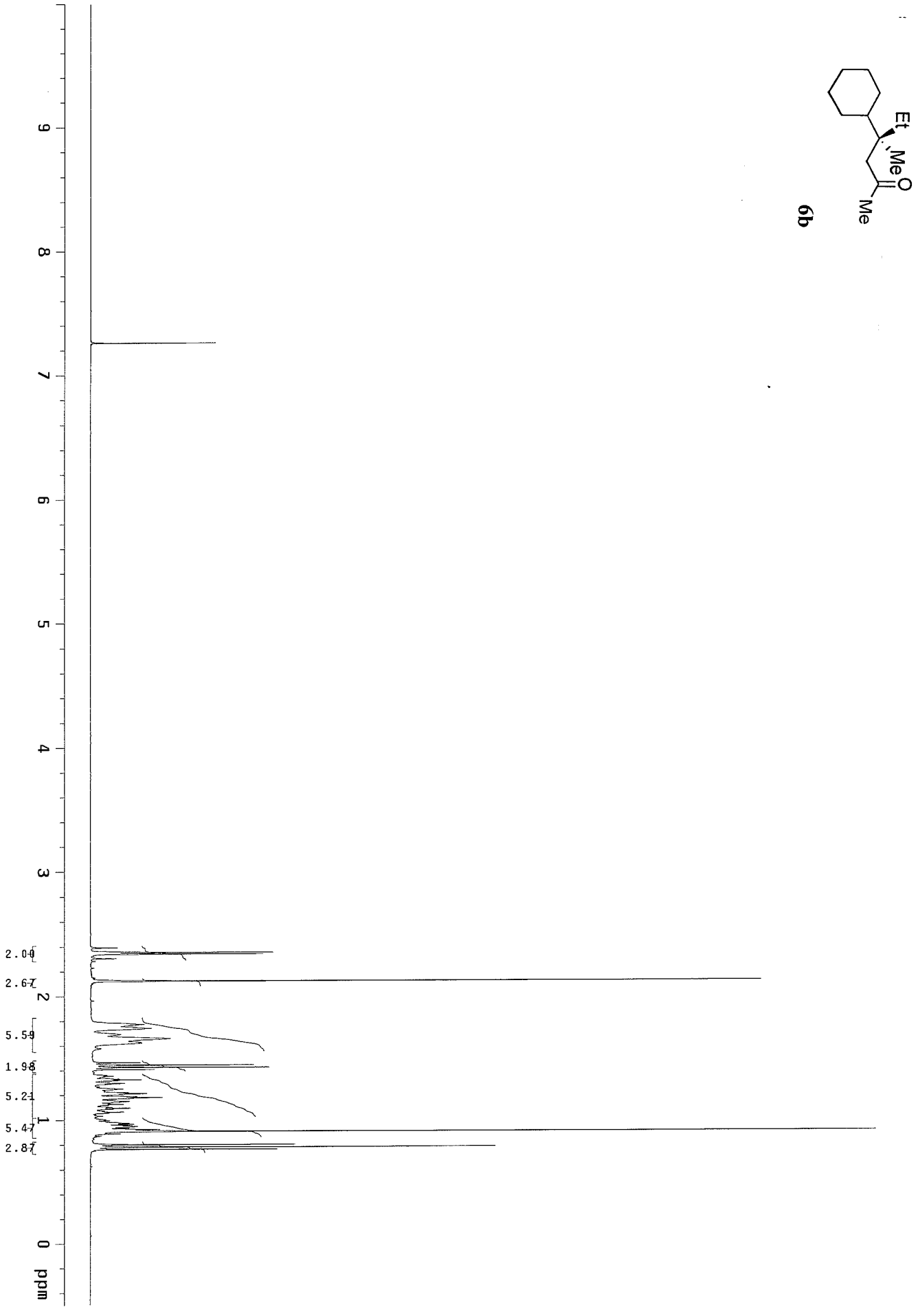

Et
MeO
Me
5e
2.68
0.93
2.74
1.00
1.02
1.00
3.61
2.81
2.78
ppm

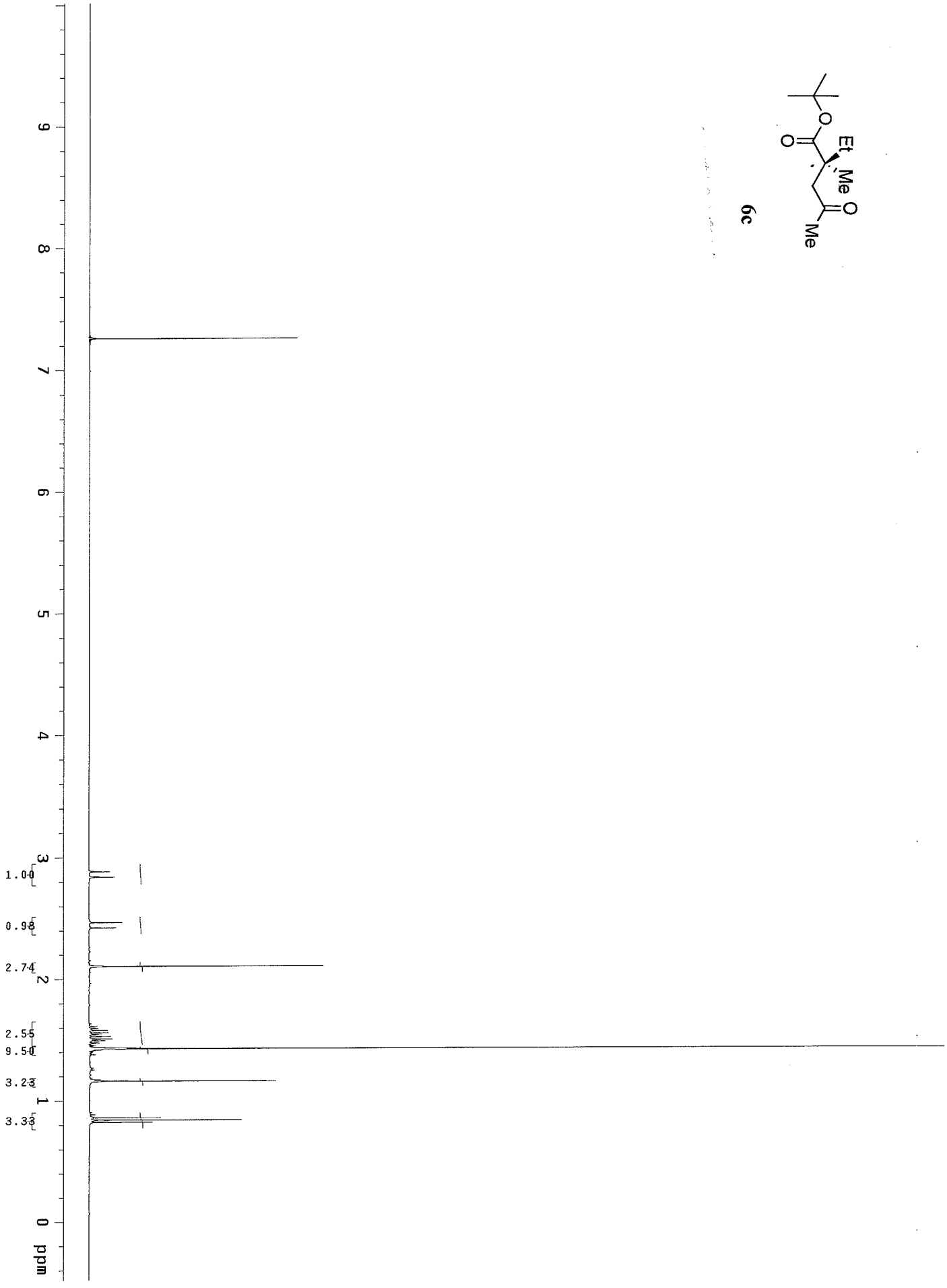

Et
MeO
Me
Br
5f
9
8
7
6
5
4
3
2
1
0
ppm
0.91
0.97
1.21
0.90
1.00
1.03
1.02
2.91
1.40
3.33
2.98


F
Et
Me
O
Me
5g
1.00
0.91
0.90
0.83
1.00
0.99
3.68
1.07
2.90
2.85
9
8
7
6
5
4
3
2
1
0
ppm

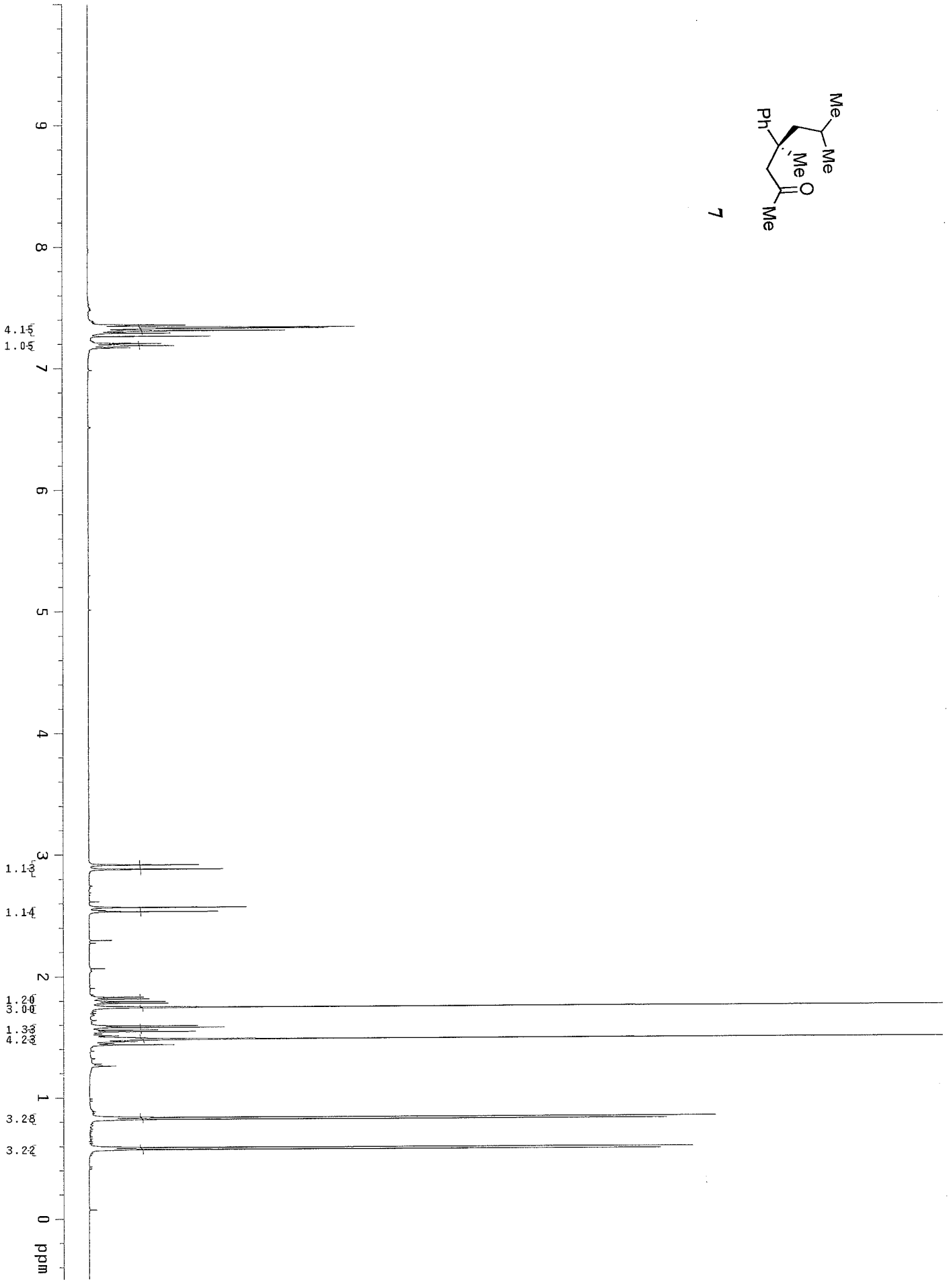


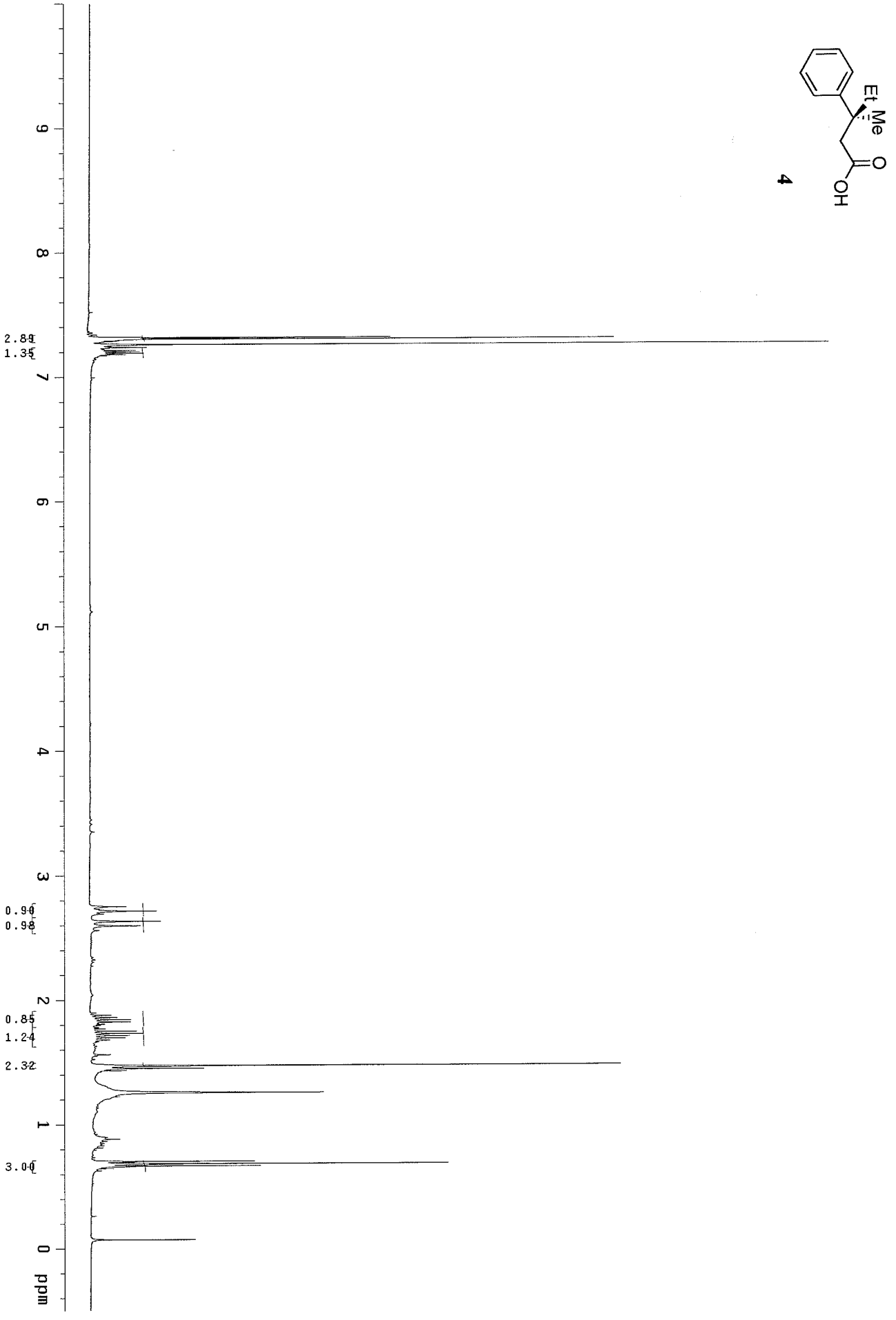
6[a]

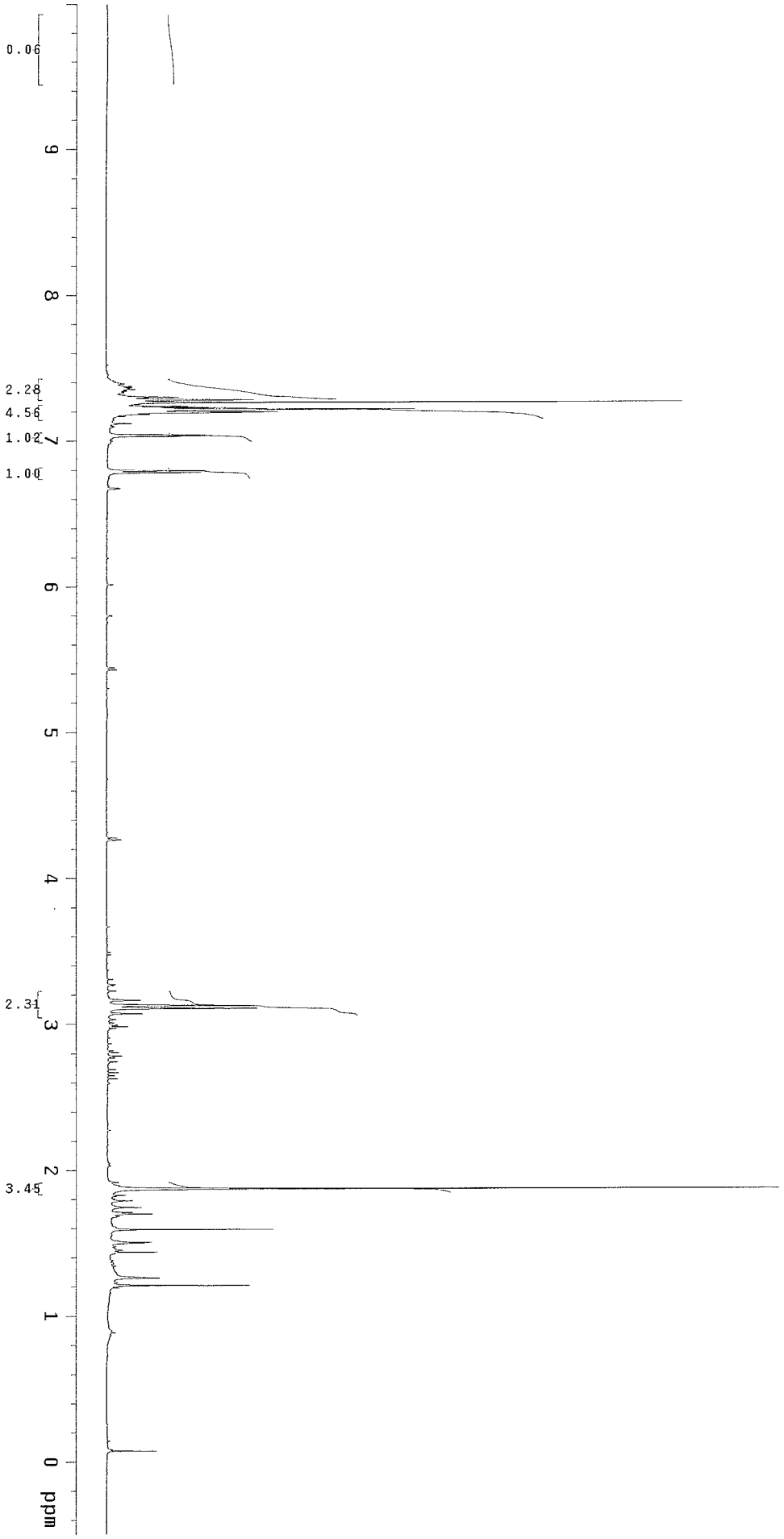

Et
Me
O
Me
6b
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.67
5.59
1.98
5.21
5.47
2.87

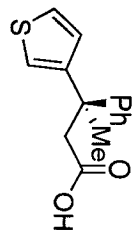


6c


Me
Me
Ph
Me
O
Me
7
4.15
1.05
1.13
1.14
1.20
3.00
1.33
4.23
3.28
3.22
9
8
7
6
5
4
3
2
1
0
ppm


Et
Me
O
OH
4
2.84
1.35
0.90
0.98
0.85
1.24
2.32
3.00
9
8
7
6
5
4
3
2
1
0
ppm





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