

Experimental Section

Materials and Methods. All chemicals were purchased from the Aldrich Chemical Company and used without further purification DCM was distilled over CaH₂ prior to use. Analytical thin-layer chromatography (TLC) was performed using general purpose 60-Å silica gel on glass (Aldrich). Flash chromatography columns were prepared with Kieselgel 60-Å silica gel 230-400 mesh (Merck). ¹H, and ¹³C NMR spectra were acquired with Bruker AC-250, Bruker AC-300 and Bruker AC-500 spectrometers.

Compound 3: 2-amino-4-iodomethyl benzoate (20.0g, 0.0722 mol), 4-bromobenzeneboronic acid (16.0g, 0.0800 mol), K₂CO₃ (22.5g, 0.163 mol), and tetrakis(triphenylphosphine) (1.99g, 1.72 mmol) were dissolved in anhydrous MeOH (300 mL). The reaction was purged with nitrogen and heated to 60 °C overnight. The mixture was filtered through a pad of celite and concentrated under reduced pressure. Both H₂O (200 mL) and EtOAc (200 mL) was added and the layers separated. The aqueous phase was extracted with EtOAc (3 x 200 mL), combined, dried with MgSO₄ and the solvent removed under reduced pressure. The residual was dissolved in DCM and passed through a silica filter. Removal of the solvent followed by trituration with hexanes and filtration afforded 19.8g (89.7 %) of a light yellow solid.

Compound 4: To a solution of **3** (3.02g, 9.90 mmol) and I₂ (1.51g, 5.94 mmol) in anhydrous benzene (100 mL) was added t-butyl nitrite (90 %, 1.40 mL, 10.60 mmol) at 0 °C. The reaction was warmed to room temperature overnight and then heated to 60 °C for 10 minutes. H₂O was added (100 mL) and the layers separated. The aqueous phase was extracted with EtOAc (3 x 100 mL), combined, dried with MgSO₄, and the solvent removed under reduced pressure. The residual was coevaporated with hexanes, triturated in hexanes, and filtered to afford 3.18g (77.9 %) of a brown solid.

Compound 6: Compound **3** (3.02g, 9.86 mmol), bis(pinacolato)diboron (2.81g, 11.1 mmol), KOAc (3.24g, 33.0 mmol), and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.163g, 0.290 mmol) were dissolved in anhydrous DMF (100 mL). The reaction was heated to 60 °C overnight, cooled, and filtered through a pad of celite. The solvent was removed *in vacuo* followed by addition of both H₂O (100 mL) and DCM (100 mL). The aqueous phase was extracted with DCM (3 X 100 mL), combined, dried with MgSO₄, and concentrated. The residue was dissolved into DCM and passed through a silica filter. Removal of the solvent and trituration in hexanes afforded 3.17g (91.5 %) of a white solid.

Compound 7: Compound **6** (2.80g, 7.93 mmol), compound **4** (3.00g, 7.19 mmol), K₂CO₃ (2.09g, 15.1 mmol), and tetrakis(triphenylphosphine) (0.249g, 0.216 mmol) were dissolved in 4:1 DMF/H₂O (100 mL) solution and heated to 60 °C overnight. Both the H₂O and DMF were removed *under vacuum*, followed by addition of DMF (100 mL) and filtered through a celite pad. The DMF was again removed *under vacuum* and both H₂O (100 mL) and DCM (100 mL) was added. The phases were separated and the aqueous phase extracted with DCM (3 x 100 mL). The combined organic layers were

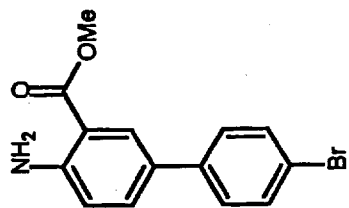
dried with MgSO_4 , concentrated, and passed through a silica plug. Removal of the solvent yielded 1.44g (38.8 %) of a white solid.

Compound 8: To a solution of compound 7 (0.300g, 0.582 mmol) and I_2 (0.0920g, 0.362 mmol) in anhydrous benzene (50 mL) was added t-butyl nitrite (90 %, 0.1 mL, 0.76 mmol) at 0 °C. The reaction was warmed to room temperature overnight and then heated to 60 °C for 10 minutes. H_2O was added (50 mL) and the layers separated. The aqueous phase was extracted with EtOAc (3 x 100 mL), combined, dried with MgSO_4 , and the solvent removed under reduced pressure. The residual was coevaporated with hexanes, triturated in hexanes, and filtered to afford 0.364g (89.3 %) of a brown solid.

Compound 9: Compound 7 (0.603g, 1.17 mmol), bis(pinacolato)diboron (0.370g, 1.45 mmol), KOAc (0.478g, 4.87 mmol), and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.037g, 0.067 mmol) were dissolved in anhydrous DMF (100 mL). The reaction was heated to 60 °C overnight, cooled, and filtered through a pad of celite. The solvent was removed *in vacuo* followed by addition of both H_2O (50 mL) and DCM (50 mL). The aqueous phase was extracted with DCM (3 x 50 mL), combined, dried with MgSO_4 and concentrated. The residual was dissolved into DCM and passed through a silica filter. Removal of the solvent followed by trituration in hexanes afforded 0.702g (97.4 %) of a brown gum.

Lauryl amide of compound 9: To a solution of the above (0.477g, 0.847 mmol) and 2,6-ditert-butyl pyridine (0.25 mL, 1.25 mmol) in anhydrous DCM (50 mL) was added lauroyl chloride (0.26 mL, 1.12 mmol) at 0 °C. The reaction was allowed to warm to room temperature overnight followed by the addition of H_2O (50 mL). The phases were separated and the aqueous phase extracted with DCM (3 x 50 mL). The combined organic layers were dried with MgSO_4 and concentrated to afford 0.62g (98.4 %) of a light yellow solid (mixture of two compounds). A small sample was separated by chromatography (hexanes, 5%, 10%, then 15% EtOAc/hexanes) for analytical analysis. mp: 104 - 106 °C. ^1H NMR (CDCl_3): δ : 0.81 (t, $J = 6.85$ Hz, 3H), 1.19 (m, 16H), 1.31 (s, 12H), 1.71 (p, $J = 7.33$ Hz, 2H), 2.40 (t, $J = 7.36$ Hz, 2H), 3.66 (s, 3H), 3.91 (s, 3H), 7.35 - 7.45 (m, 3H), 7.57 (d, $J = 7.02$ Hz, 2H), 7.61 (d, $J = 6.97$ Hz, 2H), 7.73 (dd, $J = 1.87, 8.06$ Hz, 1H), 7.78 (dd, $J = 2.06, 8.80$ Hz, 1H), 7.85 (d, $J = 8.05$ Hz, 2H), 8.04 (d, $J = 1.87$ Hz, 1H), 8.27 (d, $J = 2.22$ Hz, 1H), 8.77 (d, $J = 8.80$ Hz, 1H), 11.0 (bs, 1H). ^{13}C NMR (CDCl_3): δ : 14.1, 22.7, 24.8, 25.5, 29.3, 29.5, 29.6, 31.9, 38.7, 52.2, 52.4, 115.1, 120.8, 126.3, 126.4, 128.6, 128.9, 129.1, 129.9, 131.1, 131.3, 133.0, 135.4, 138.5, 140.0, 140.9, 141.0, 142.2, 168.7, 168.9, 172.4. HRMS m/z Calcd for $\text{C}_{46}\text{H}_{56}\text{BNO}_7$: 745.4150, found 745.4166.

Compound 10: The lauryl amide of compound 9 (0.589g, 0.790 mmol), compound 8 (0.408g, 0.650 mmol), K_2CO_3 (0.226g, 1.64 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.032g, 0.0278 mmol) were dissolved in 50 mL anhydrous DMF and heated to 60 °C overnight. The resulting precipitate was filtered, washed with H_2O followed by MeOH. The residual solid was dissolved into 10 % MeOH/DCM and passed through a silica filter with the same solvent. Removal of the solvent afforded 0.309g (42.5 %) of a white solid

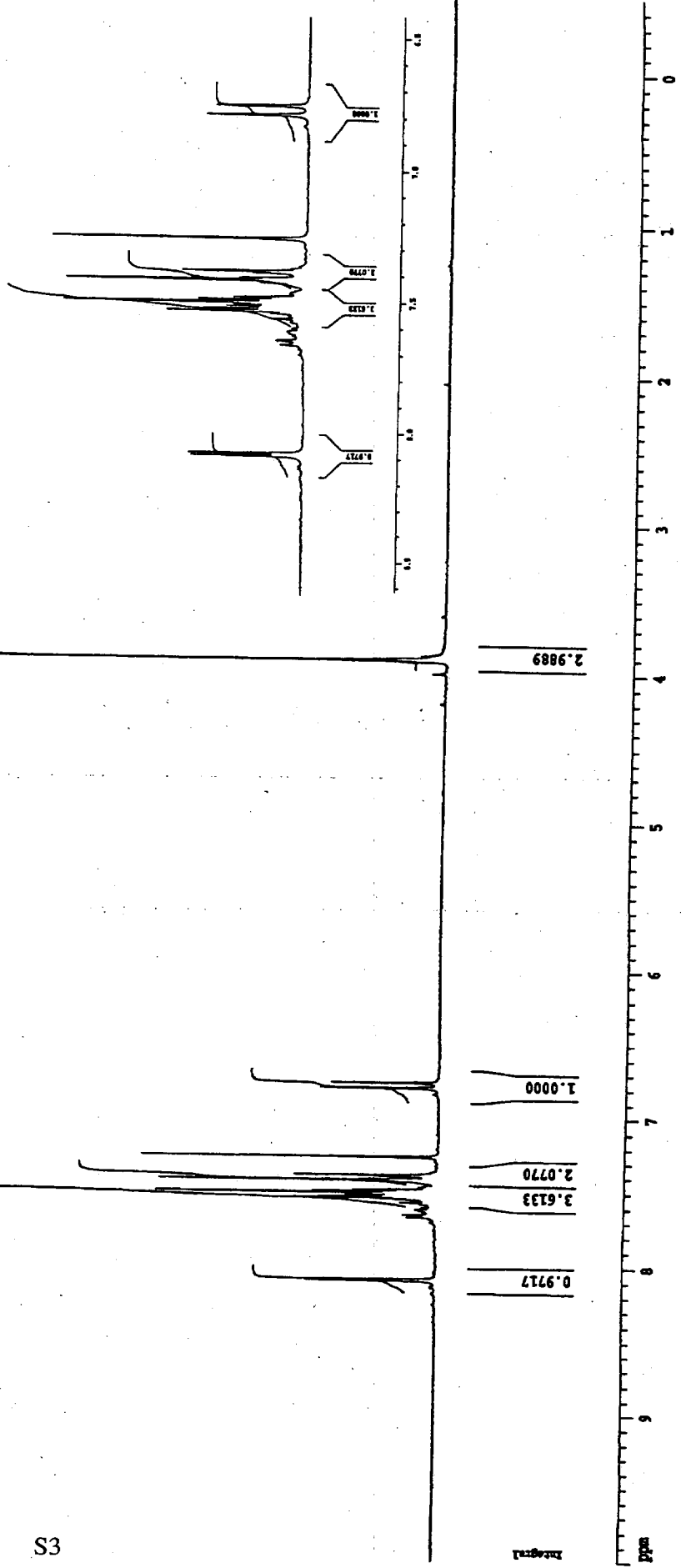


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- 7.41292
- 7.42133
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- 7.52878
- 7.53790
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- 8.09142

ppm

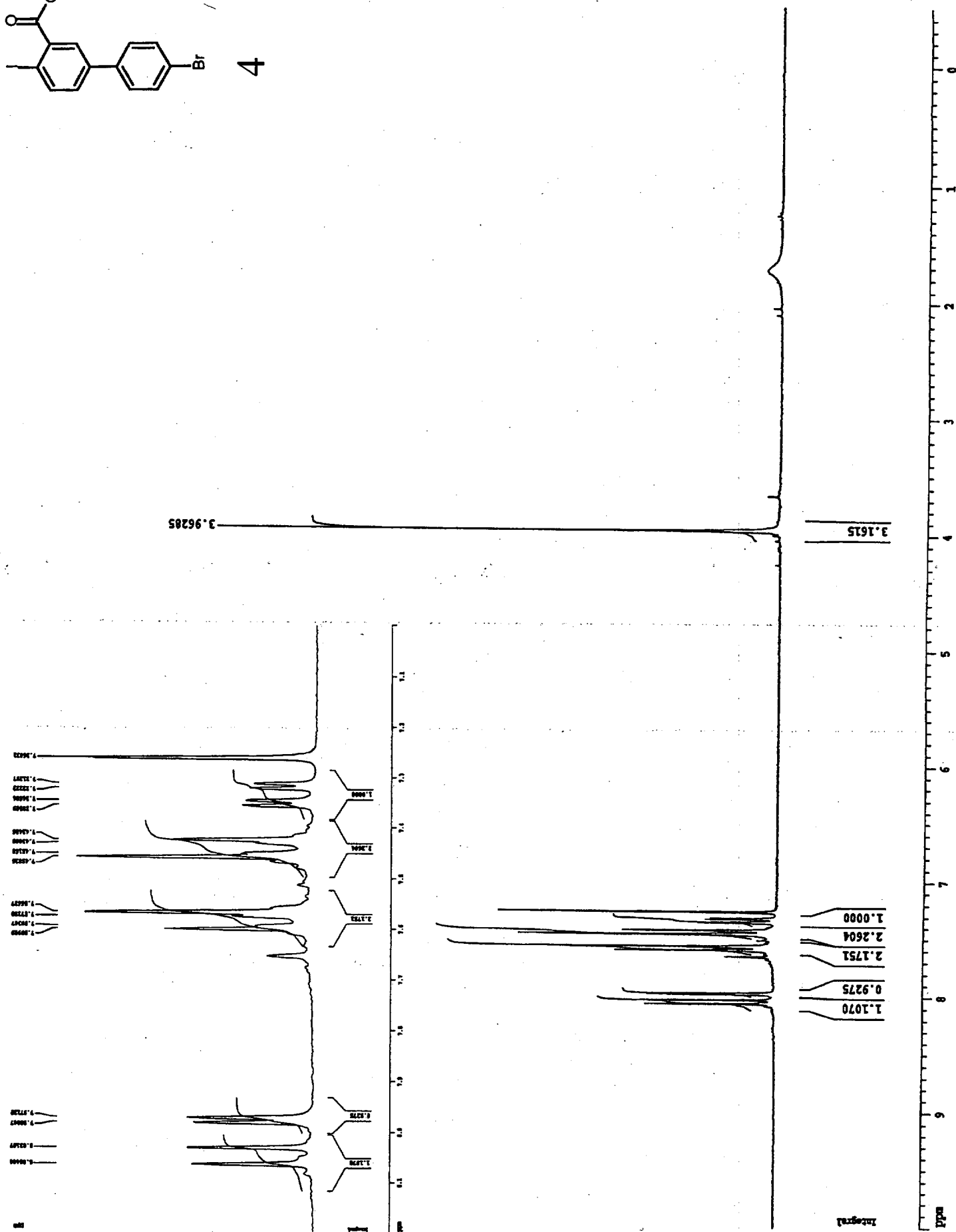
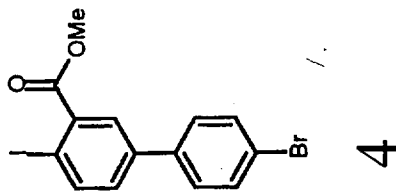
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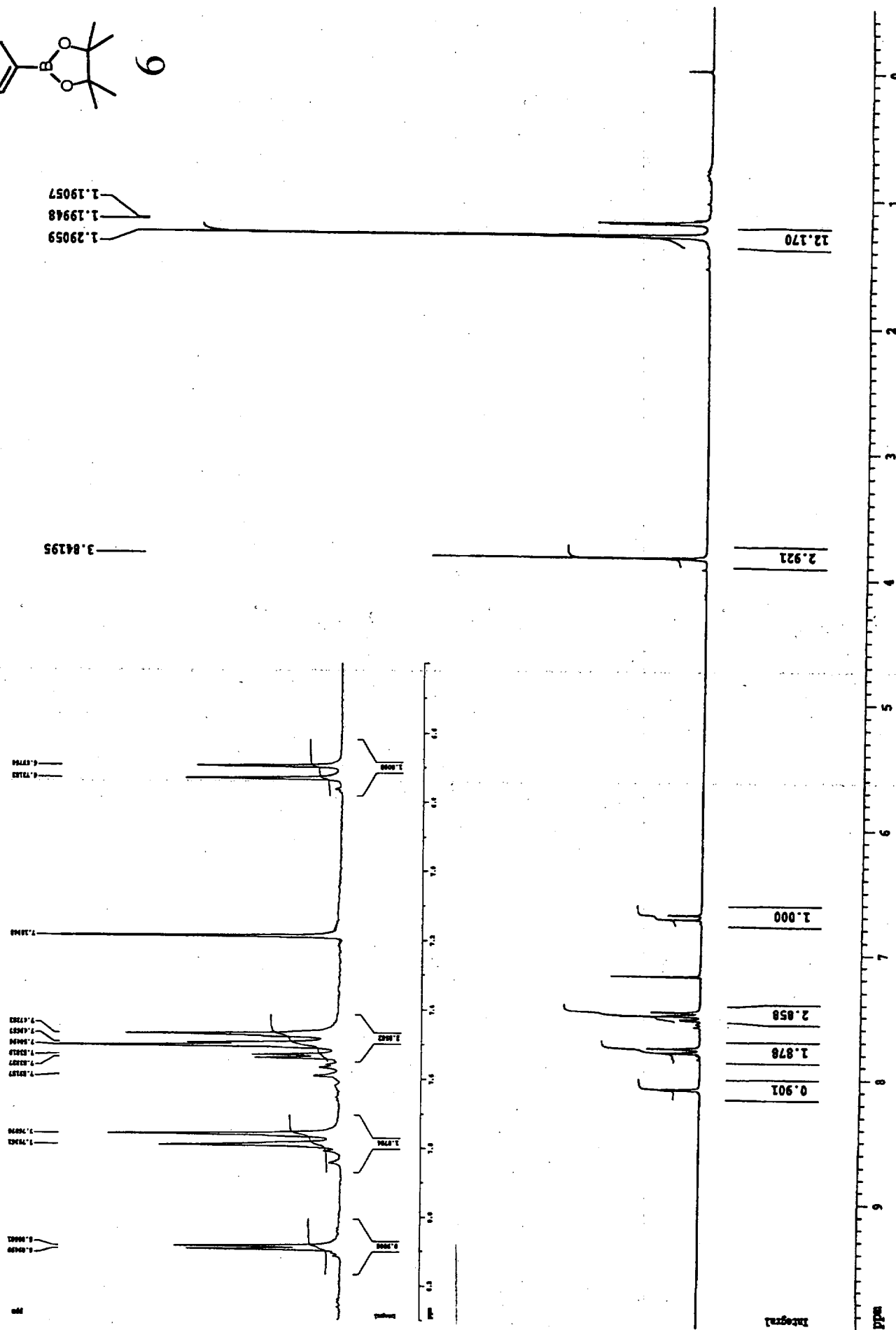
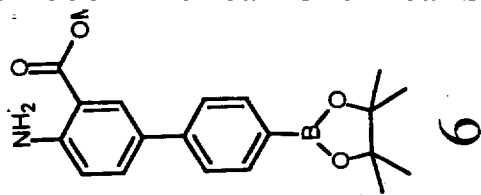


S3

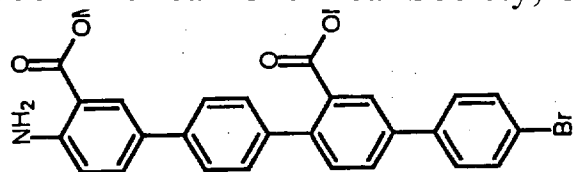
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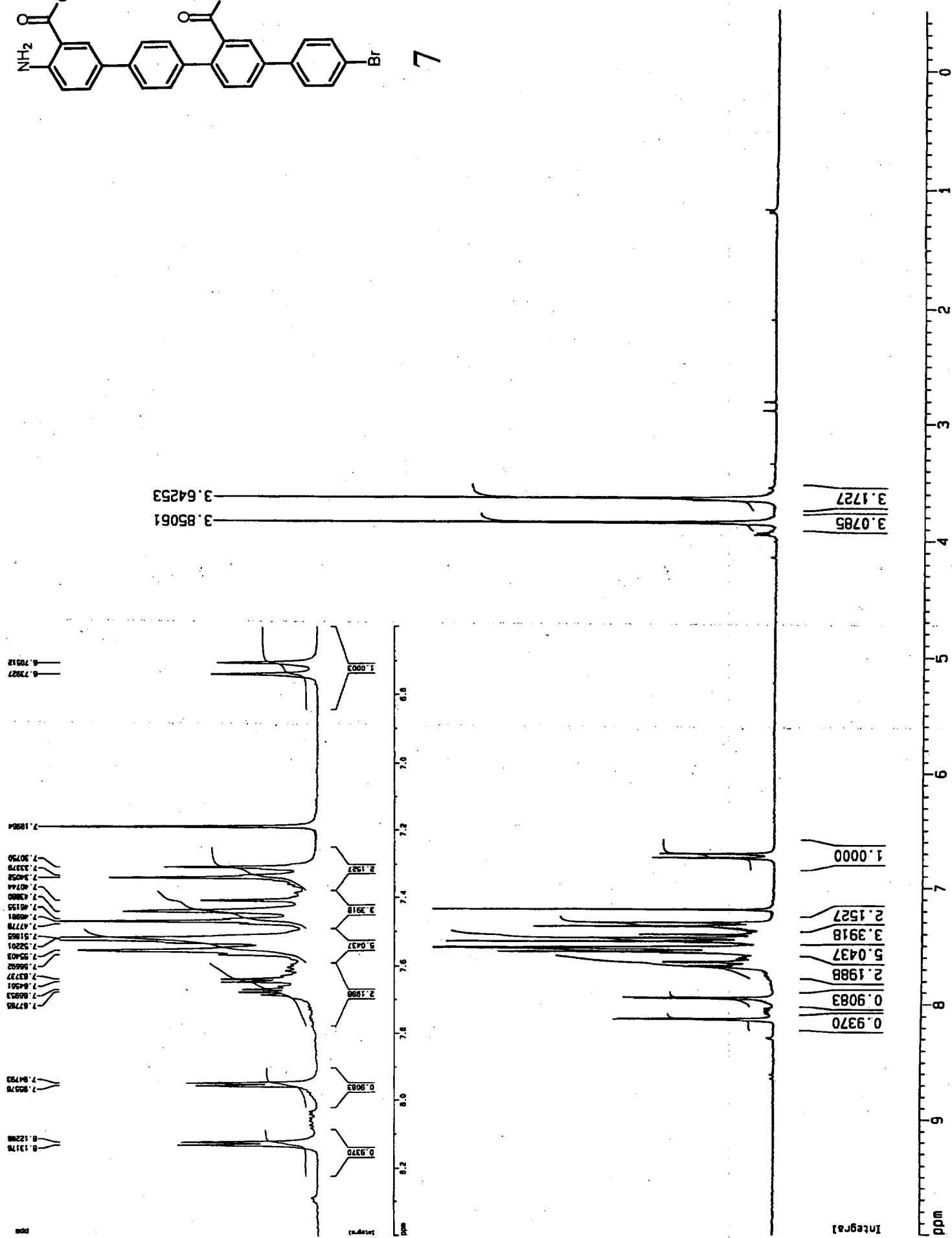


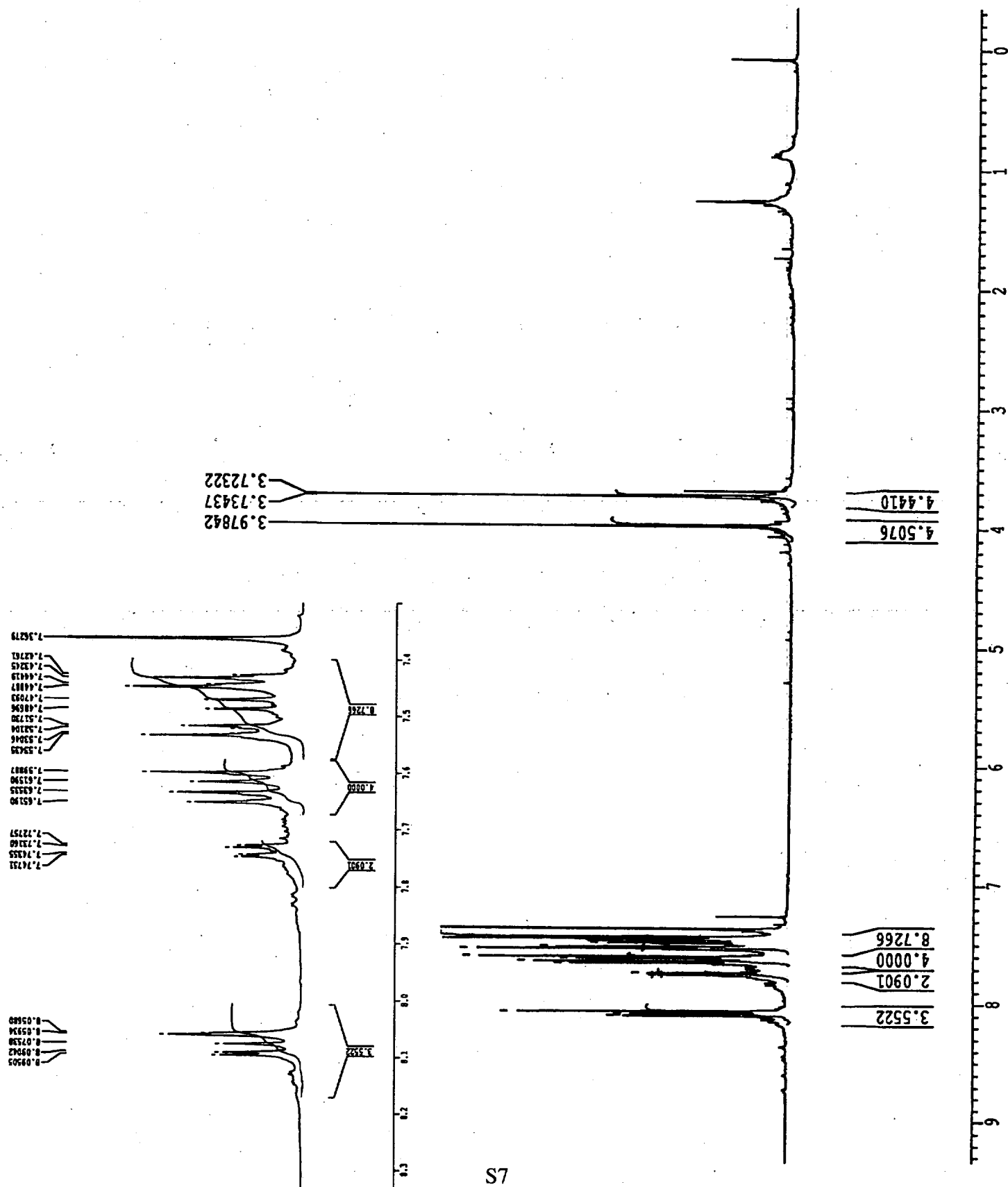
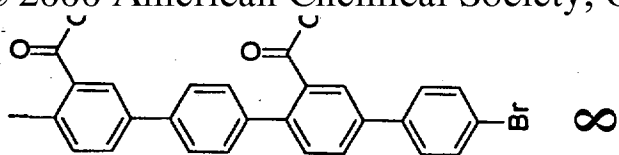


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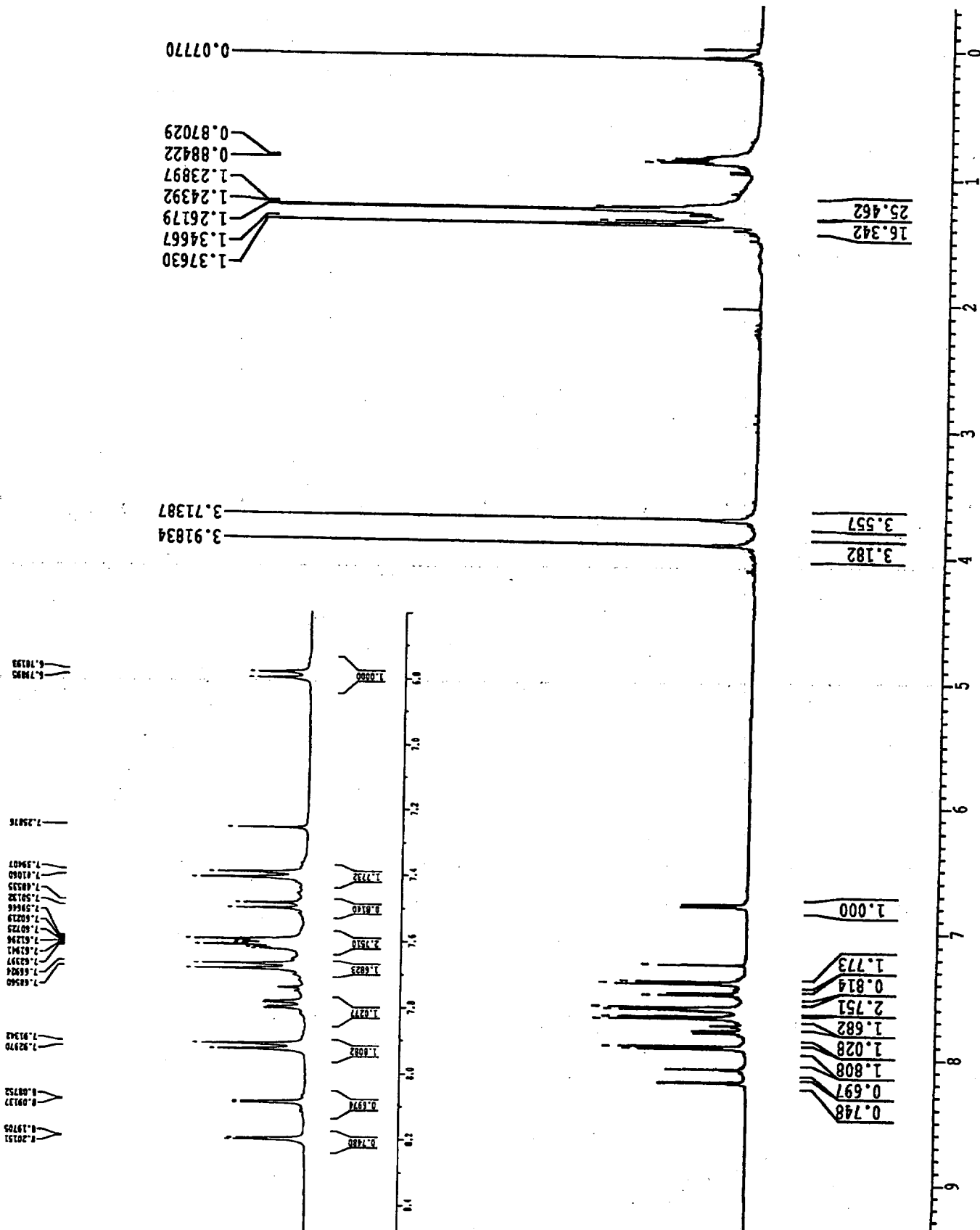
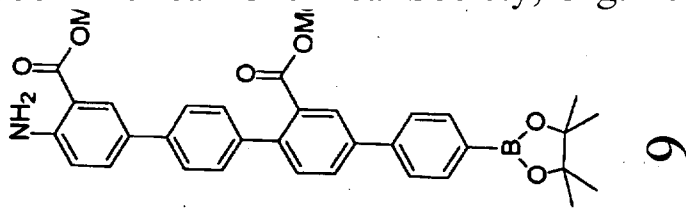


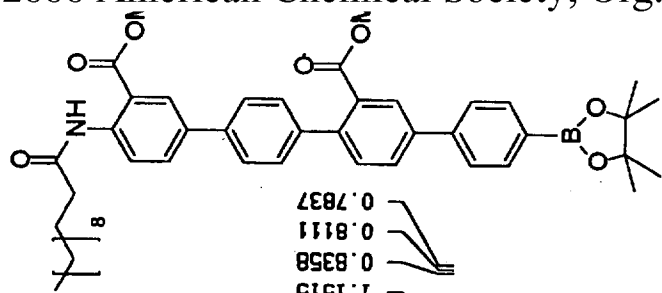
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S7



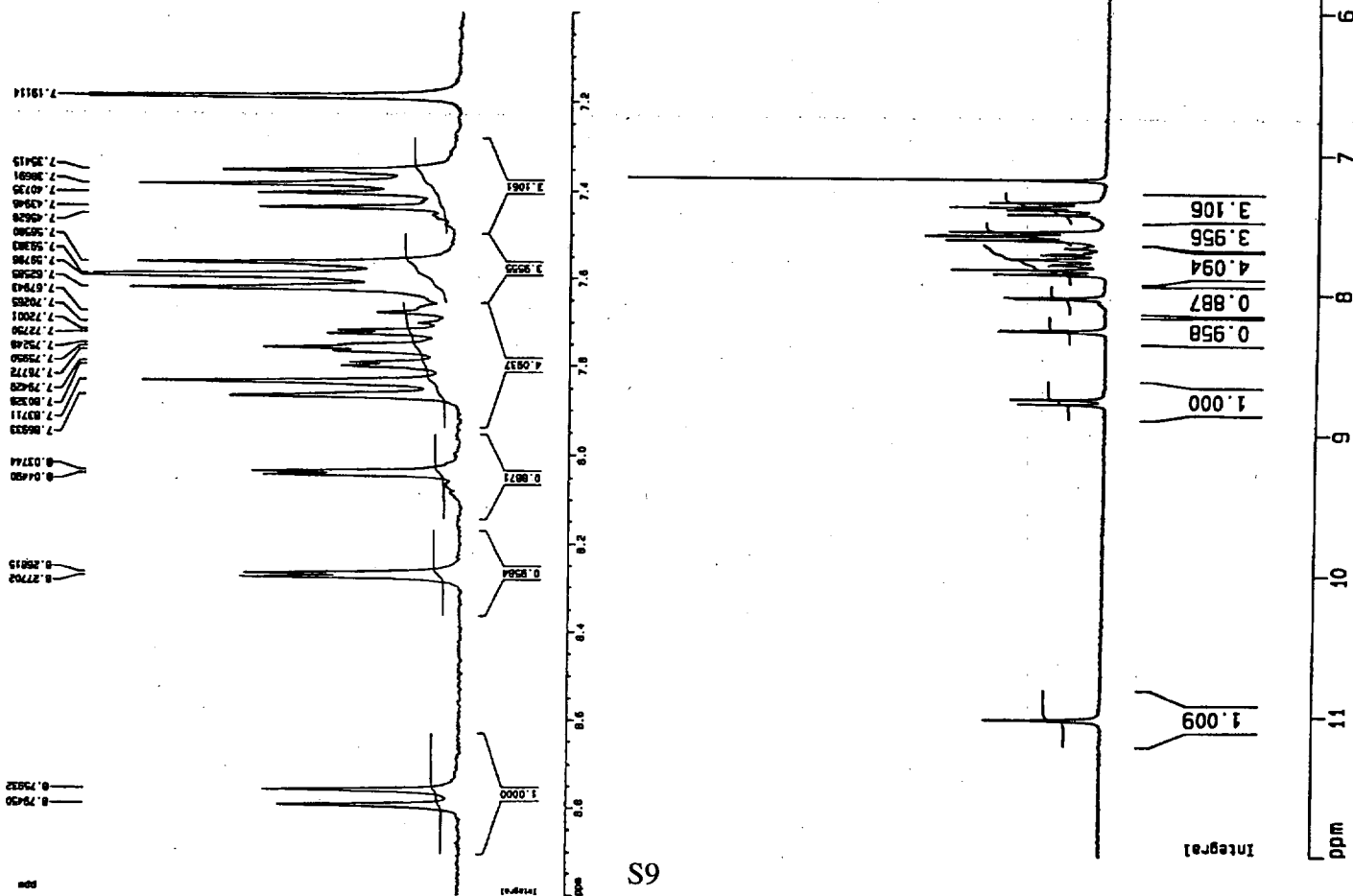


Lauryl Amic
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