General Methods. All reactions involving air-sensitive reagents were performed under nitrogen using syringe-septum cap techniques. All glassware was dried with heat gun under vacuum prior to use. Flash chromatography (FC)[1] was performed using silica gel Merck 60 (70-230 mesh). TLC was performed using Merck silica gel 60 F_{254} aluminium sheets. The sheets were visualised under UV-light (254 nm). Melting points are uncorrected. All new compounds were colorless, unless otherwise stated. NMR spectra were recorded on a 300 MHz Bruker spectrometer with tetramethylsilane as internal standard.

Materials. All solvents and reagents were commercially available and used without further purification except THF which was distilled from Na/benzophenone under nitrogen and DMF which was sequentially dried with and stored over 3Å molecular sieves.[2] *n*-Butyllithium was titrated prior to use.[3] A 1.0 M solution of $ZnCl_2$ was prepared by flame drying $ZnCl_2$ *in vacuo* and dissolving it in dry THF. A 0.85 M solution of isopropylmagnesium bromide (*i*-PrMgBr) in THF was prepared as previously described,[4] and titrated prior to use.[5] $Pd(PPh_3)_4$ was prepared as previously described.[6]

5-(2-Aminophenyl)-1-benzyloxy-4-iodopyrazole (11a). 1.6 M LDA in THF (1.3 ml, 2.0 mmol) was added to **7**[8] (0.30 g, 1.0 mmol) in THF (8 mL) at – 78 °C under N_2. After 5 min at –78 °C, 1M $ZnCl_2$ in Et_2O (2.0 mL, 2.0 mmol) was added, the mixture was allowed to warm to rt, and stirred for 1 h before $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) and 2-iodoaniline (0.44 g, 2.0 mmol) in DMF (16 mL) were added, and the mixture was heated to 80 °C for 2 h. Further standard work up and FC (heptane/EtOAc 1:0→2:1) gave 0.17 g (43 %) of **11a** as a yellow oil. R_f (EtOAc-heptane, 1:2) 0.39. $\delta_H(CDCl_3)$ 7.46 (s, 1H), 7.30-7.17 (m, 4H), 7.10-7.00 (m, 2H), 6.86-6.72 (m, 3H), 5.11 (s, 2H), 3.62 (br s, 2H). $\delta_C(CDCl_3)$ 145.10, 138.45, 135.65, 132.98, 131.74, 130.94, 129.81, 129.20, 128,51, 118.14, 115.89, 112.34, 80.92, 58.11.

1-Benzyloxy-5-(2-N-pivaloyl-aminophenyl)-4-iodopyrazole (11b). To a mixture of **10a**[7] (1.80 g, 6.8 mmol) and triethylamine (1.05 mL, 7.5 mmol) in dry dichloromethane (20 mL) at 0 °C under N_2 was added pivaloyl chloride (0.92 mL, 7.5 mmol). The mixture was stirred at 0 °C for 30 min, poured into H_2O (50 mL) extracted with CH_2Cl_2 (3 x 20 mL), $MgSO_4$ dried and evaporated to dryness to give crude **10c**, which was iodinated the same way as **1**. FC (heptane/EtOAc 3:1) gave 3.22 g (100 %) of **11b** as pale yellow crystals, mp 63-65 °C (EtOAc-heptane). R_f (EtOAc-heptane, 1:2) 0.38. $\delta_H(CDCl_3)$ 8.20 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.50-7.42 (m, 1H), 7.32-6.90 (m, 8H), 5.13 (s, 2H), 1.11 (s, 9H). $\delta_C(CDCl_3)$: 176.04, 138.74, 135.94, 134.12, 132.21, 130.85, 130.32, 129.37, 129.04, 128.21, 123.67, 122.23, 117.73, 80.54, 58.21, 39.28, 26.96. Anal. Calcd for $C_{21}H_{22}IN_3O_2$: C, 53.06; H, 4.67; N, 8.84. Found: C, 52.90; H, 4.70; N, 8.67.

1-Benzyloxy-5-(2-nitrophenyl)-4-iodopyrazole (11c). 10d[7] (0.15 g, 0.5 mmol) was iodinated the same way as **1**. FC (heptane/EtOAc 5:3) gave 0.21 g (98 %) of **11c** as yellow crystals, mp 108-109 °C (EtOAc-heptane). R_f (EtOAc-heptane, 3:5) 0.57. $\delta_H(CDCl_3)$ 8.11 (d, J = 7.8 Hz, 1H), 7.60-7.45 (m, 2H), 7.49 (s, 1H), 7.30-6.80 (m, 6H), 5.22 (d, J = 10.3 Hz, 1H), 4.99 (d, J = 10.3 Hz, 1H). $\delta_C(CDCl_3)$: 148.33, 138.46, 133.76, 133.10, 132.90, 130.18, 129.71, 129.21, 128.50, 125.90, 124.75, 122.15, 80.29, 56.53.

(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(2) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.

(3) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.

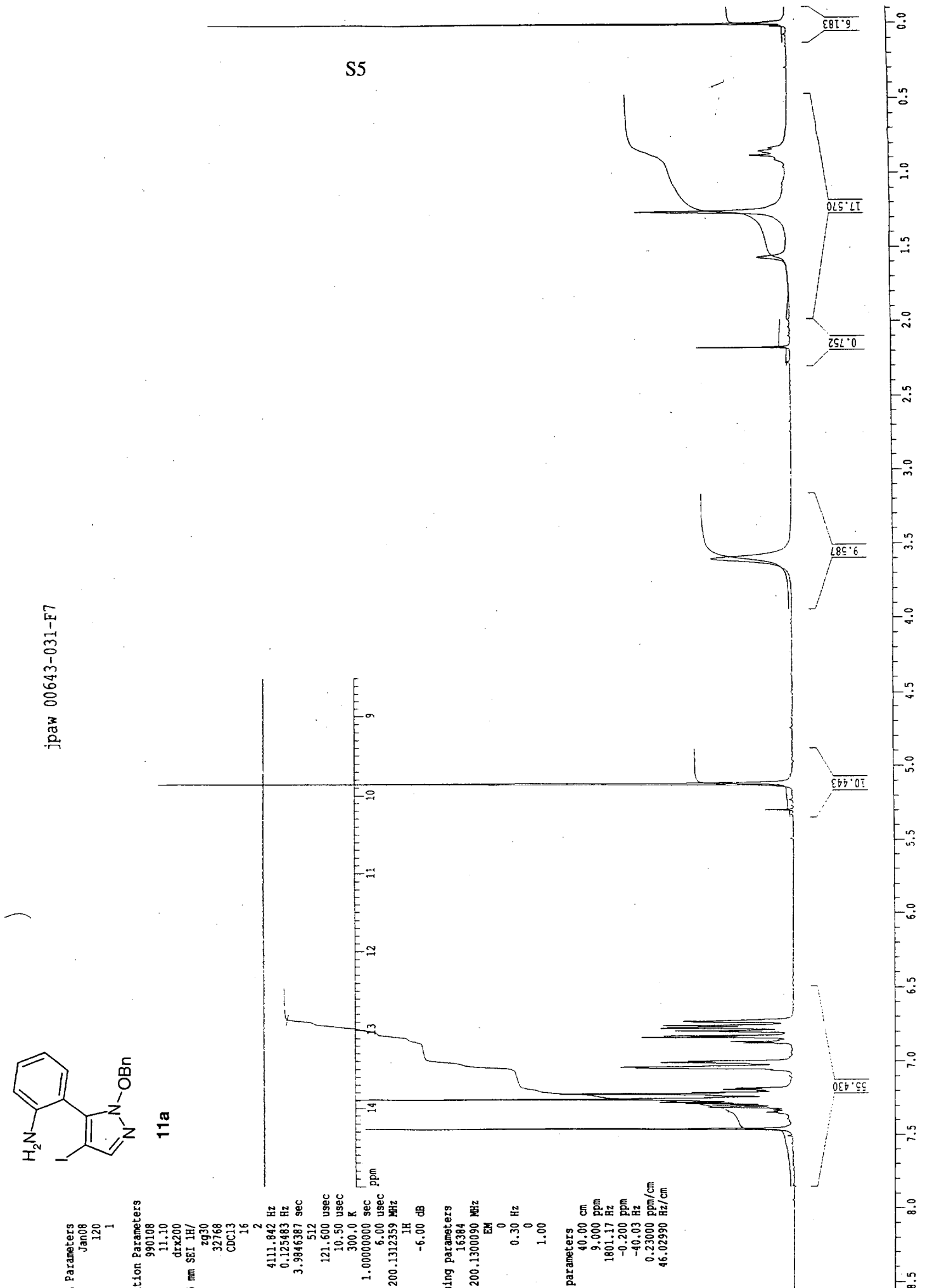
(4) Drake, N. L.; Cooke, G. B. *Org. Synth. Coll. Voll II* **1943**, 406.

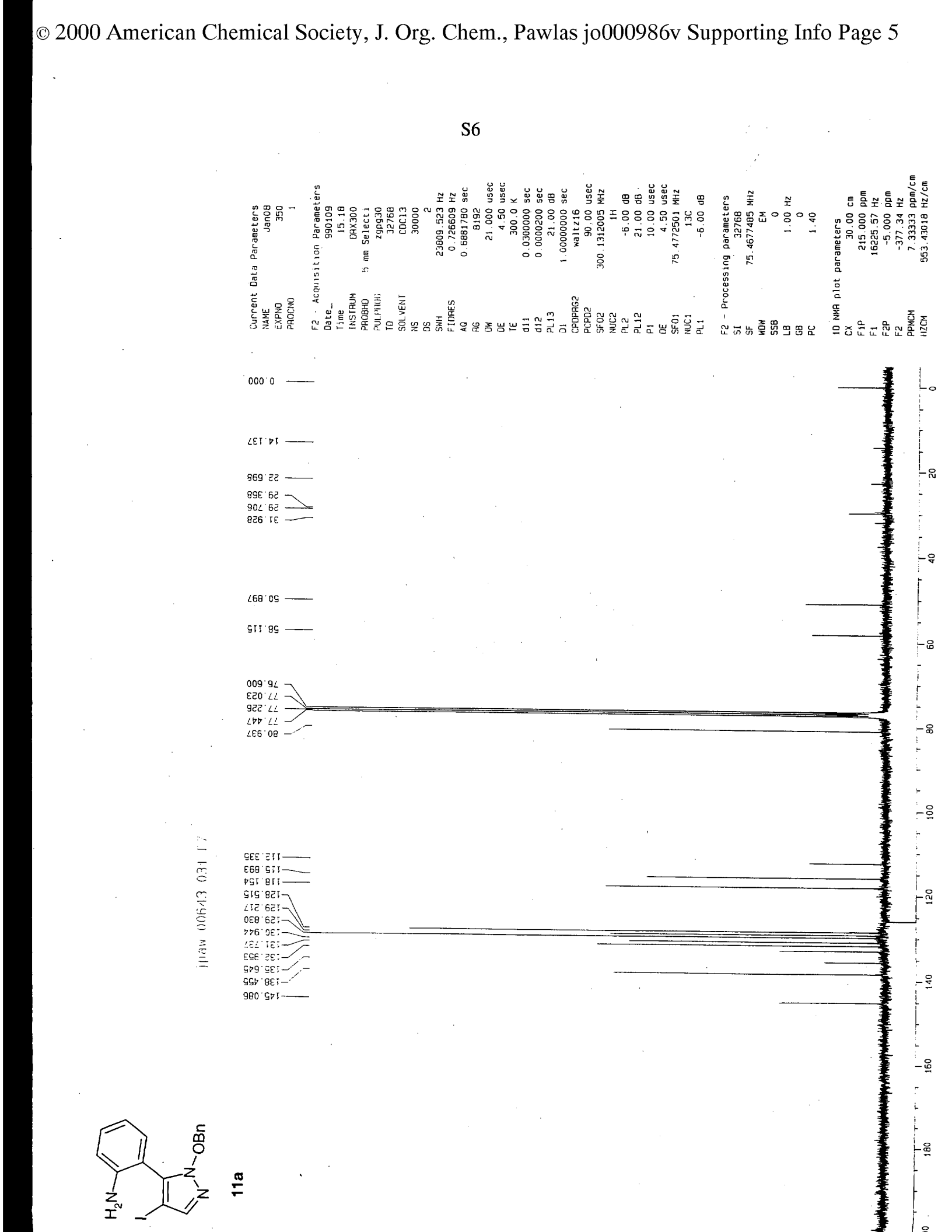
(5) Lin, H.-S.; Paquette, L. A. *Synth. Comm.* **1994**, *24*, 2503.

(6) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

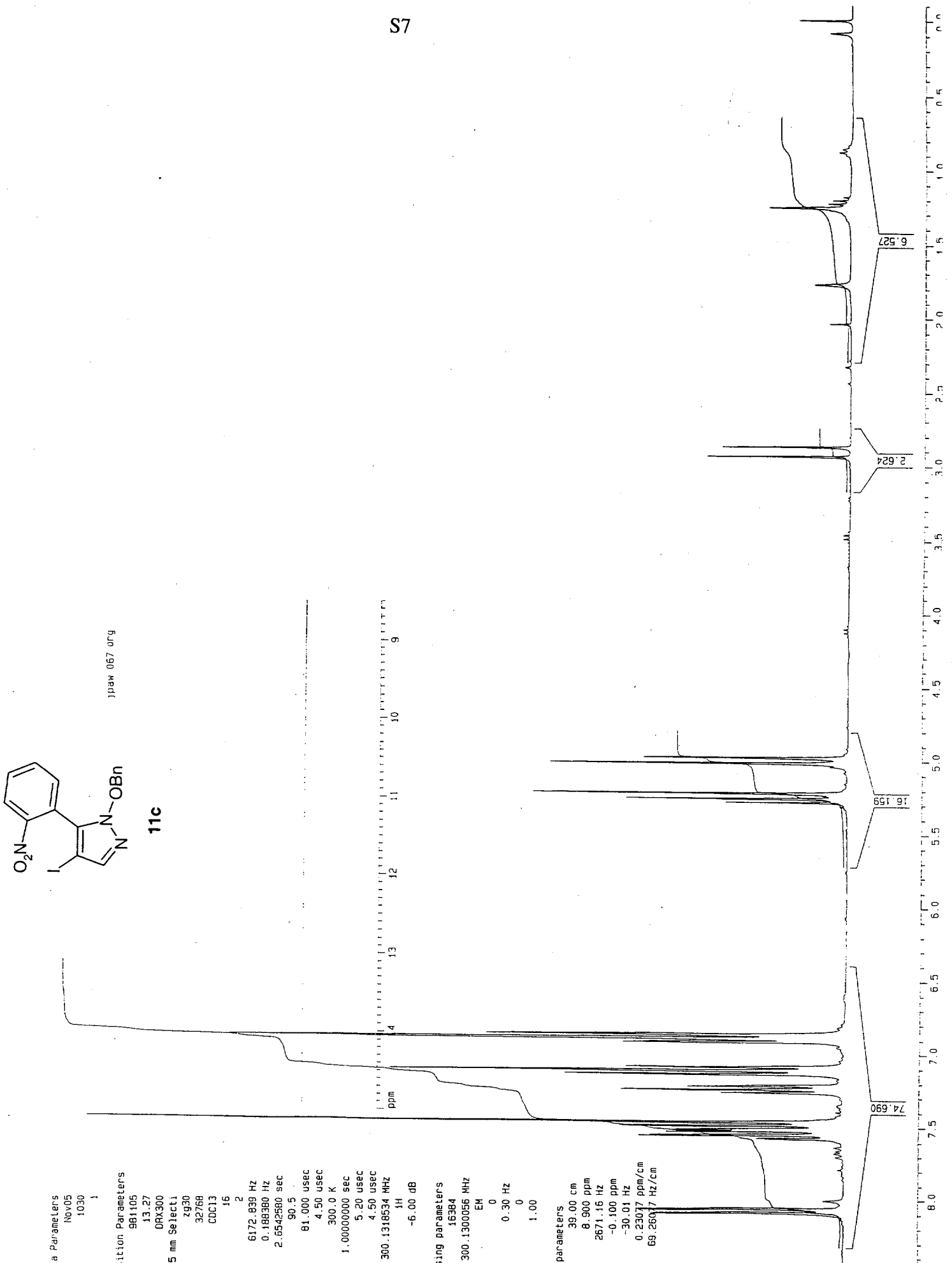
(7) Kristensen, J.; Begtrup, M.; Vedsø, P. *Synthesis* **1998**, 1604.

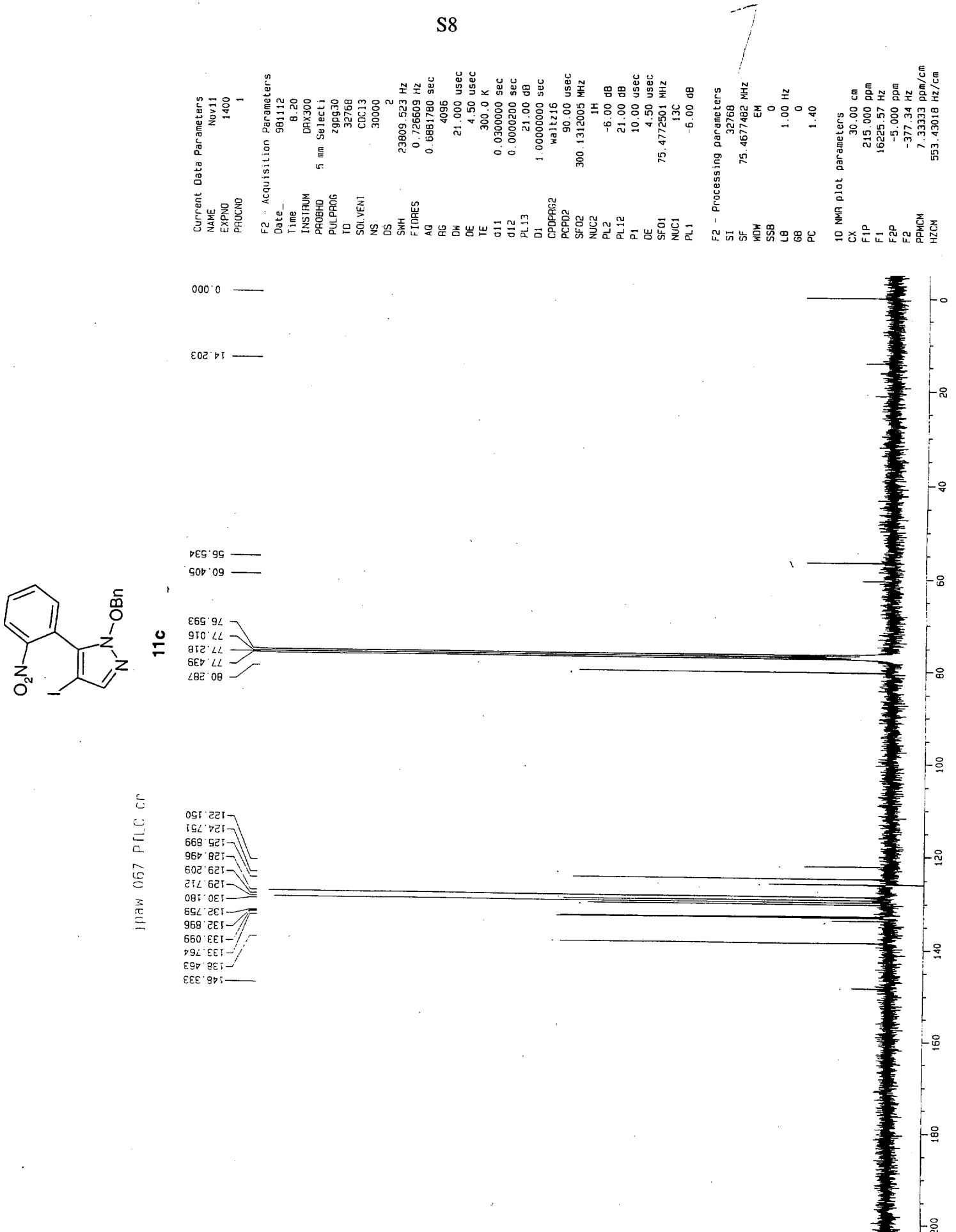
(8) Felding, J.; Kristensen, J.; Bjerregaard, T.; Sander, L.; Vedsø, P.; Begtrup, M. *J. Org. Chem.* **1999**, *64*, 4196.

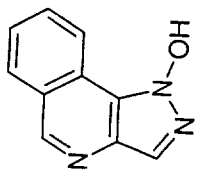




11a







19