Revised

Supporting Information for the Letter Entitled

"A Novel Synthesis of 2-Aryl-2*H*-indazoles via a Palladium-Catalyzed Intramolecular Amination Reaction"

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Modified literature procedures[18] for the preparation of the *N*-aryl-*N*-benzyl hydrazines: [***N*-(2-bromo-5-fluorobenzyl)-*N*-(*p*-tolyl) hydrazine (1h)**] To a solution of NaHMDS (34 mL, 1.0 M/THF, 34 mmol) at 0 °C under Ar was added *p*-tolylhydrazine hydrochloride (2.7 g, 17 mmol). After 15 min, the cooling bath was removed and the reaction mixture was stirred at rt for 1 h. The reaction mixture was re-cooled to 0°C and then the 2-bromo-5-fluorobenzylbromide was added (4.5 g, 17 mmol). Then the reaction mixture was stirred at rt for 1 h and quenched with water. The mixture was extracted with methylene chloride three times and the combined organics were dried over $MgSO_4$. Filtration and concentration afforded an oil which was purified by chromatography (5% ether/hexanes) to give the desired product (3.3 g, 63%). Other substrates (**1a-1g, 1i** and **1j**) were prepared similarly in 50-70% yield.

1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.92 Hz, 1H), 7.29 (m, 2H), 7.15 (ddd, J = 1.86, 7.7, 7.7 Hz, 1H), 7.08 (d, J = 8.25 Hz, 2H), 6.93 (d, J = 8.61 Hz, 2H), 4.64 (s, 2H), 3.71 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 136.9, 133.0, 129.7, 129.0, 128.7, 127.9, 127.5, 123.6, 113.3, 61.2, 20.3.

1b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.12 Hz, 1H), 7.28 (m, 4H), 7.16 (m, 1H), 7.01 (d, J = 8.60 Hz, 2H), 6.82 (dd, J = 7.20 Hz, 1H), 4.70 (s, 2H), 3.75 (s, 2H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 151.4, 136.7, 133.0, 129.1, 128.8, 128.7, 127.6, 123.5, 118.4, 112.9, 60.7.

1c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.93 Hz, 1H), 7.35 (d, J = 6.11 Hz, 1H), 7.29 (d, J = 6.32 Hz, 1H), 7.15 (dd, J = 7.74, 7.74 Hz, 1H), 7.02 (d, J = 9.10 Hz, 2H), 6.85 (d, J = 9.10 Hz, 2H), 4.56 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 146.1, 136.8, 133.0, 129.5, 128.8, 127.5, 123.8, 115.5, 114.5, 62.3, 55.7.

1d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.14, 7.85 Hz, 1H), 7.39 (s, 1H), 7.30 (m, 2H), 7.19 (m, 2H), 7.09 (dd, J = 2.40, 8.36 Hz, 1H), 7.02 (d, J = 8.35 Hz, 1H), 4.73 (s, 2H), 3.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 135.6, 133.3, 131.5 (q, $J_{C\text{-}F}$ = 33.0 Hz), 129.5, 129.1, 128.6, 127.8, 124.5 (q, $J_{C\text{-}F}$ = 220.1 Hz), 123.7, 115.6, 114.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 109.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 60.2.

1e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.18, 7.93 Hz, 1H), 7.30-7.15 (m, 5H), 6.95 (m, 2H), 4.66 (s, 2H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 136.0, 133.2, 128.9, 128.8, 128.7, 127.6, 123.6, 123.2, 114.2, 60.6.

1f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.29, 7.88 Hz, 1H), 7.47 (d, J = 11.6 Hz, 2H), 7.28 (t, J = 7.46 Hz, 1H), 7.19 (t, J = 7.82 Hz, 1H), 7.09 (d, J = 7.57 Hz, 1H), 7.02 (d, J = 9.00 Hz, 2H), 4.79 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 134.7, 133.5, 133.4, 129.3, 128.0, 127.9, 123.4, 120.3, 111.9, 99.4, 59.1.

1g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 5.27, 8.77 Hz, 1H), 7.14 (dd, J = 3.05, 9.42 Hz, 1H), 6.96 (d, J = 12.58 Hz, 2H), 6.90-6.84 (m, 3H), 4.52 (s, 2H), 3.78 (s, 3H), 3.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 245.0 Hz), 153.5, 146.0, 139.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 134.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 117.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 116.3 (d, $J_{C\text{-}F}$ = 23.8 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 115.4, 114.6.

1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 5.20, 8.71 Hz, 1H), 7.08 (m, 3H), 6.86 (m, 3H), 4.59 (s, 2H), 3.77 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 245.0 Hz), 149.3, 139.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 134.0 (d, $J_{C\text{-}F}$ = 7.8 Hz), 129.7, 128.3, 117.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 116.0 (d, $J_{C\text{-}F}$ = 23.9 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.6 Hz).

1i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.74 Hz, 1H), 7.26 (t, J = 9.32 Hz, 2H), 7.01 (d, J = 7.90 Hz, 2H), 6.87 (d, J = 3.00 Hz, 1H), 6.82 (t, J = 7.30 Hz, 1H), 6.70 (dd, J = 3.06, 9.80 Hz, 1H), 4.64 (s, 2H), 3.74 (s, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 151.5, 137.8, 133.6, 129.1, 118.6, 114.6, 114.2, 113.7, 113.1, 61.0, 55.4.

1j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.67 Hz, 1H), 7.19 (d, J = 9.18 Hz, 2H), 6.96 (d, J = 9.18 Hz, 2H), 6.80 (d, J = 3.03 Hz, 1H), 6.71 (dd, J = 3.09, 8.81 Hz, 1H), 4.62 (s, 2H), 3.72 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 149.9, 137.1, 133.7, 128.9, 123.3, 114.6, 114.3, 114.2, 113.7, 60.9, 55.4.

Synthesis of 2-aryl-2*H*-indazoles: See the reference 21 in the text for the representative procedures.

2a (light yellow crystals, 55%): m.p. 96.5-97.6 °C (reported 92-94 °C).

2b (white crystals, 58%): m.p. 80.8-81.6°C (reported 80-82 °C).

2c (light tan crystals, 54%): m.p. 130.1-130.6 °C (reported 130-131 °C).

2d (white crystals, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.23 (s, 1H), 8.12 (m, 1H), 7.78 (d, J = 9.12 Hz, 1H), 7.72 (d, J = 8.47 Hz, 1H), 7.67 (m, 2H), 7.35 (t, J = 8.62 Hz, 1H), 7.14 (dd, J = 6.59, 8.44 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 140.9, 132.1 (q, $J_{C\text{-}F}$ = 32.9 Hz), 130.2, 127.4, 124.3 (q, $J_{C\text{-}F}$ = 3.5 Hz), 123.7, 123.6 (q,

$J_{C\text{-}F}$ = 218.3 Hz), 120.4, 120.3, 118.0, 117.8 (q, $J_{C\text{-}F}$ = 3.8 Hz). m.p. 76.7-77.4 °C. HRMS calcd for the $[M+1]^+$: 263.0796, found: 263.0803.

2e (white crystals, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 0.56 Hz, 1H), 7.85 (d, J = 11.7 Hz, 2H), 7.77 (dd, J = 0.78, 8.72 Hz, 1H), 7.70 (d, J = 8.51 Hz, 1H), 7.49 (d, J = 11.7 Hz, 2H), 7.33 (ddd, J = 0.98, 6.58, 8.75 Hz, 1H), 7.12 (dd, J = 6.68, 8.53 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.0, 133.6, 129.7, 127.1, 122.9, 122.7, 122.0, 120.4, 120.3, 117.9. m.p. 134.8-135.9 °C (reported 133 °C).

2f (light yellow crystals, 52%): m.p. 160.5-161.5 °C (reported 159-161°C).

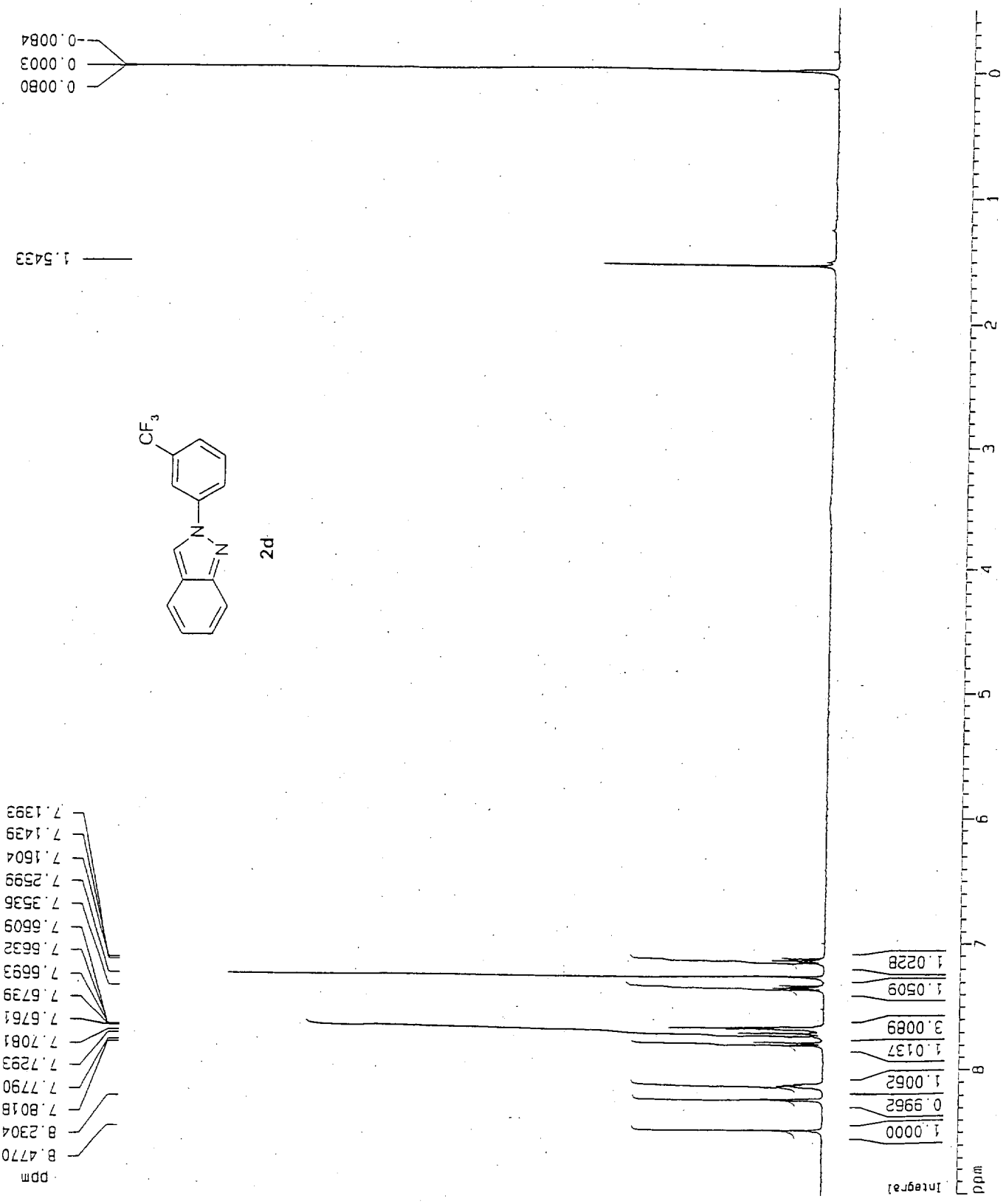
2g (light yellow crystals, 51%): See the reference 21 in the text for characterization data for this compound.

2h (white crystals, 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 0.70 Hz, 1H), 7.76 (m, 3H), 7.32 (d, J = 8.02 Hz, 2H), 7.27 (dd, J = 2.26, 9.52 Hz, 1H), 7.12 (dt, J = 2.49, 9.26 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, $J_{C\text{-}F}$ = 254.0 Hz), 147.0, 138.1 (d, $J_{C\text{-}F}$ = 6.40 Hz), 130.1, 121.9 (d, $J_{C\text{-}F}$ = 11.7 Hz), 120.7, 120.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 120.0 (d, $J_{C\text{-}F}$ = 9.7 Hz), 118.2 (d, $J_{C\text{-}F}$ = 28.8 Hz), 102.6 (d, $J_{C\text{-}F}$ = 24.2 Hz). m.p. 139.6-140.5 °C. HRMS calcd for the $[M+1]^+$: 227.0985, found: 227.0986.

2i (white crystals, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 0.82 Hz, 1H), 7.86 (d, J = 7.76 Hz, 2H), 7.68 (d, J = 9.34 Hz, 1H), 7.51 (m, 2H), 7.38 (t, J = 7.42 Hz, 1H), 7.03 (dd, J = 2.36, 9.35 Hz, 1H), 6.90 (d, J = 2.22 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 146.8, 140.6, 129.5, 127.5, 122.8, 122.0, 120.6, 119.3, 119.2, 96.3, 55.3. m.p. 143.1-143.9 °C.

2j (light tan crystals, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 0.82 Hz, 1H), 7.82 (d, J = 12.0 Hz, 2H), 7.66 (d, J = 9.36 Hz, 1H), 7.48 (d, J = 12.0 Hz, 2H), 7.03 (dd, J =

2.36, 9.37 Hz, 1H), 6.88 (d, J = 2.27 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 146.9, 139.1, 133.1, 129.6, 122.9, 122.4, 121.5, 119.3, 119.1, 96.1, 55.3. m.p. 160.2-160.5 °C. HRMS calcd for the $[M+1]^+$: 259.0638, found: 259.0645.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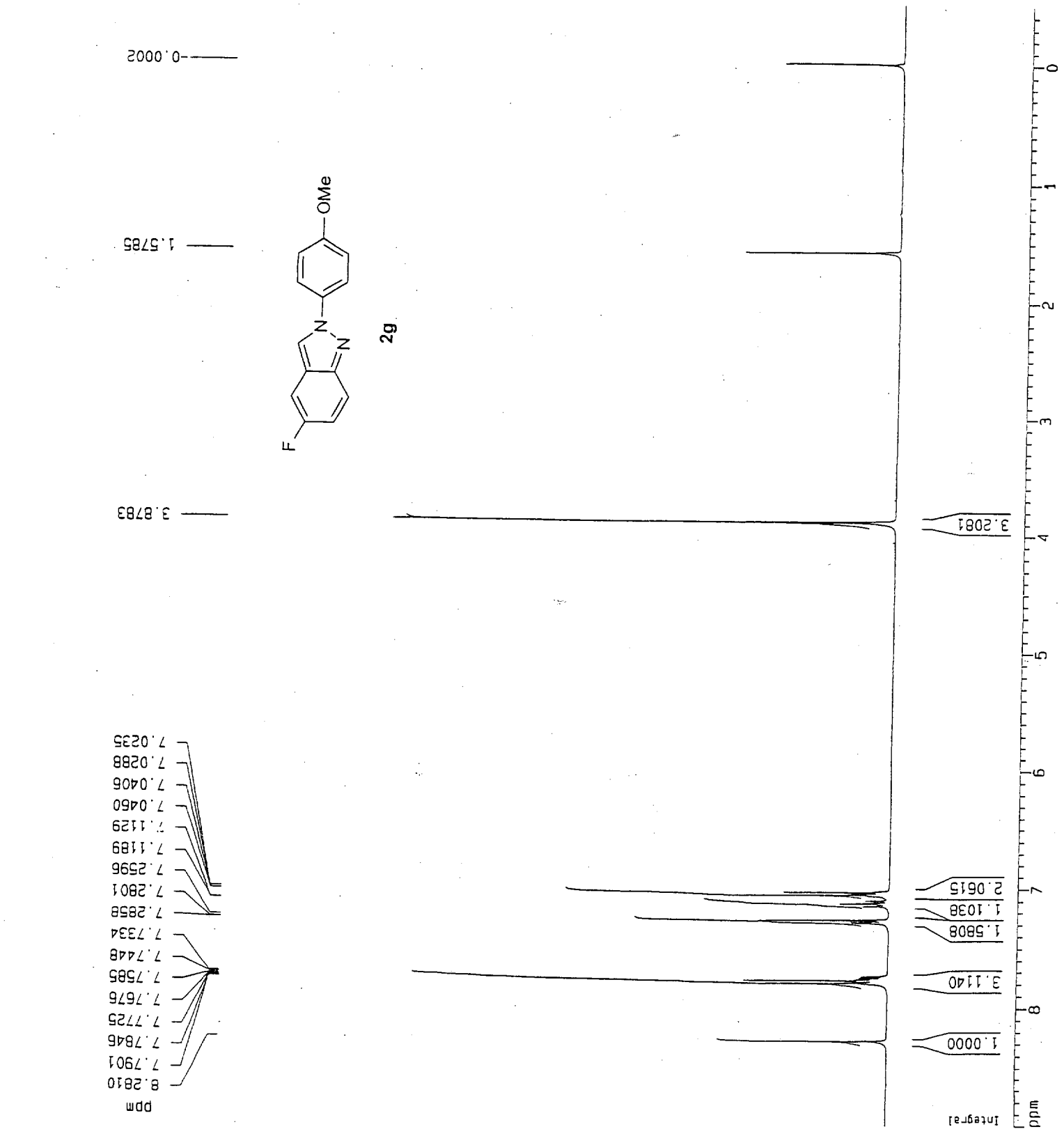
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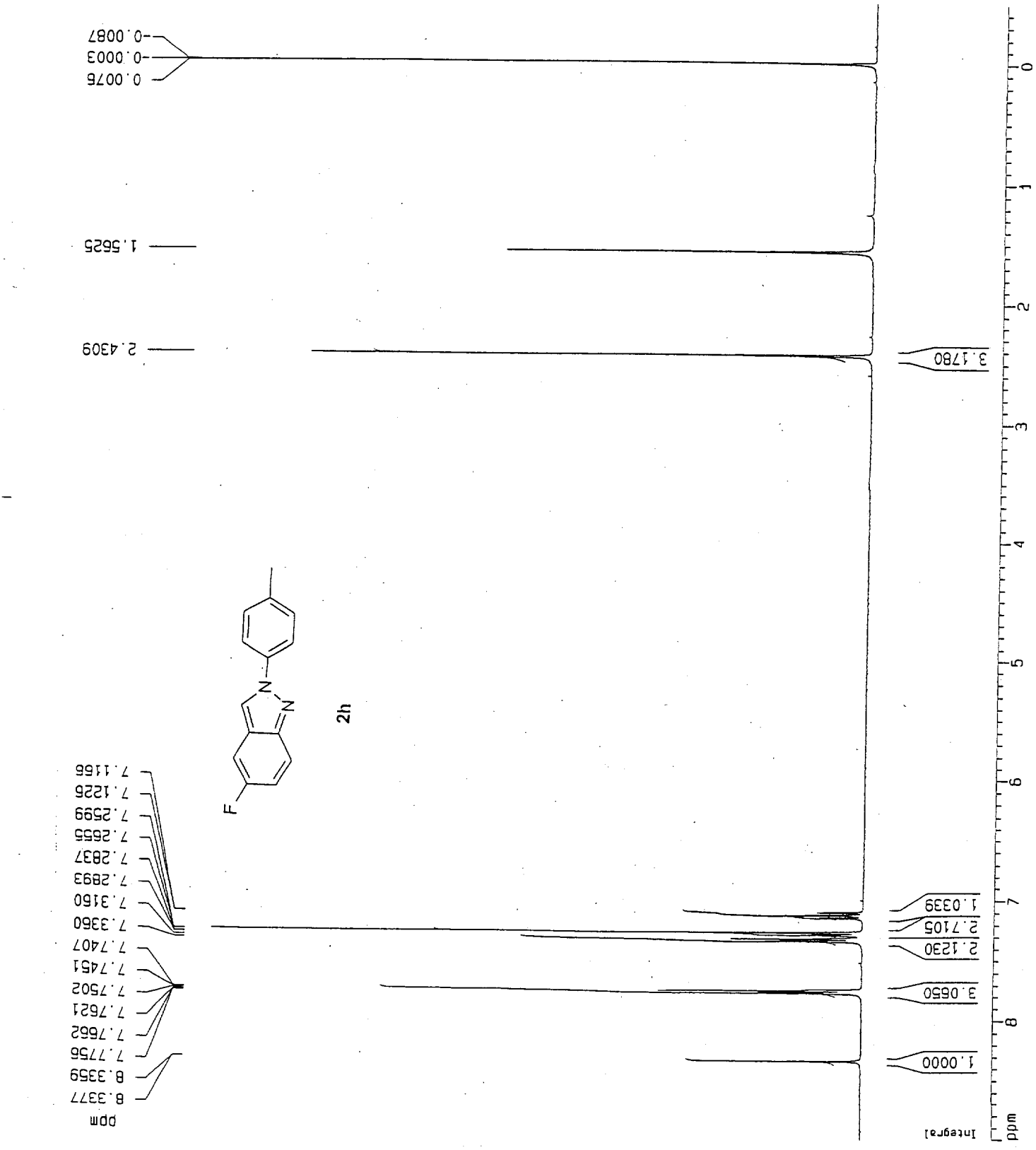
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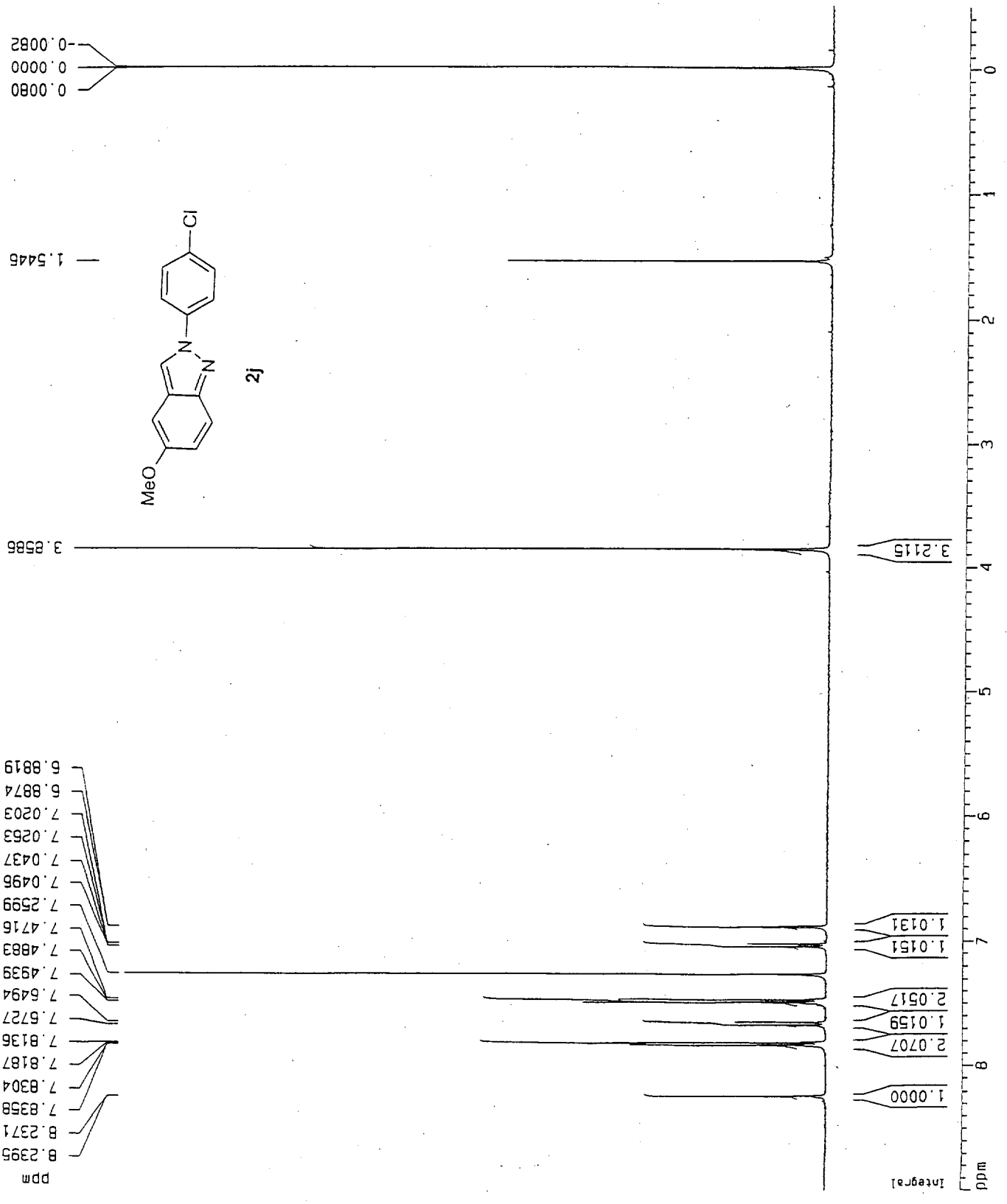
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