# A Versatile Cyclodehydration Reaction for the Synthesis of Isoquinoline and β-Carboline Derivatives.

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**Contents:**



## Supporting Information

**General Procedures.** All reactions were performed in oven-dried or flame-dried round bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

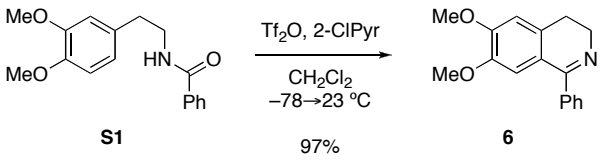
**Materials.** Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T.

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

Baker (Cycletainer$^{TM}$) and were purified by the method of Grubbs et al. under positive argon pressure.[2] 2-chloropyridine was distilled from calcium hydride and stored sealed under an argon atmosphere. The starting amides were prepared by acylation of the corresponding phenethylamine or tryptamine derivatives[3] or via previously reported copper–catalyzed C–N bond–forming reactions.[4,5]

**Instrumentation.** All reaction conducted at 140 ºC were performed in a CEM Discover Lab Mate microwave reactor. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, $C_6HD_5$: δ 7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), integration, coupling constant(s) in Hertz, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.2, benzene-$d_6$: δ 128.0, DMSO: δ 39.5). Fluorine-19 nuclear magnetic resonance spectra were recorded with a Varian 300 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the fluorine resonances of trifluoroacetic acid ($CDCl_3$: δ –76.6). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption ($cm^{-1}$), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Chiral HPLC analysis was performed on an Agilent 1100 Series HPLC with a Chiralpak OD-H column. We thank Dr. Li Li at the Massachusetts Institute of Technology Department of Chemistry instrumentation facility for obtaining mass spectrometric data.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
[3] For a general procedure, see: DeRuiter, J.; Swearingen, B. E,; Wandrekar, V.; Mayfield, C. A. *J. Med. Chem.* **1989**, *32*, 1033–1038.
[4] For the general procedure used for the synthesis of all *N*-vinyl amides, see: Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667–3669.
[5] For related reports, see: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805–818. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (c) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131–209. (d) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337–2364. (e) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973–986.

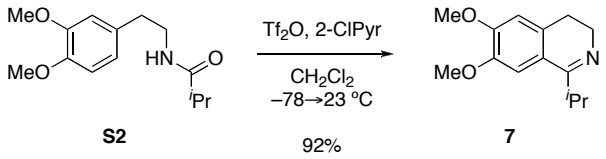



**6,7-Dimethoxy-1-phenyl-3,4-dihydroisoquinoline (6, Figure 1):**

Trifluoromethanesulfonic anhydride (64 μL, 0.39 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1** (100 mg, 0.350 mmol, 1 equiv) and 2-chloropyridine (36 μL, 0.39 mmol, 1.1 equiv) in dichloromethane (1.8 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, aqueous sodium hydroxide solution (0.5 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 30% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **6**[6] as a pale yellow solid (90 mg, 97%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.62–7.59 (m, 2H, Ar**H**), 7.46–7.41 (m, 3H, Ar**H**), 6.80 (s, 1H, Ar**H**), 6.79 (s, 1H, Ar**H**), 3.96 (s, 3H, OC**H**$_3$), 3.84–3.80 (m, 2H, $CH_2C\mathbf{H}_2N$), 3.74 (s, 3H, OC**H**$_3$), 2.77–2.72 (m, 2H, C**H**$_2CH_2N$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 166.8, 151.0, 147.2, 139.4, 132.7, 129.4, 128.9, 128.3, 121.7, 111.6, 110.4, 56.3, 56.2, 47.9, 26.2. |
| FTIR (neat) cm$^{-1}$: | 3058 (w), 2999 (w), 2936 (m), 2833 (m), 1605 (m), 1562 (m), 1513 (s), 1464 (m), 1355 (s), 1277 (s), 1116 (s). |
| HRMS (ESI): | calc'd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1334. |
| TLC (10% EtOAc in hexanes), $R_f$: | 0.31 (UV). |

[6] For a prior report on the synthesis of **6**, see Georgiev, V. S.; Carlson, R. P.; Van Inwegen, R. G.; Khandwala, A. *J. Med. Chem.* **1979**, *22*, 348–352.

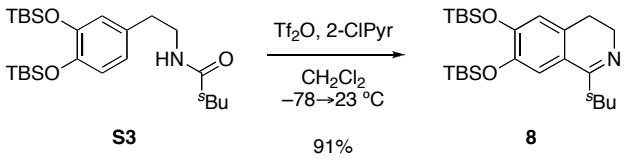



**S2** 92% **7**

**1-Isopropyl-6,7-dimethoxy-3,4-dihydroisoquinoline (7, Figure 1):**

Trifluoromethanesulfonic anhydride (72 μL, 0.44 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S2** (100 mg, 0.398 mmol, 1 equiv) and 2-chloropyridine (45 μL, 0.48 mmol, 1.1 equiv) in dichloromethane (2.0 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, aqueous sodium hydroxide solution (0.5 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5→40% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **7** as a pale yellow oil (85 mg, 92%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.04 (s, 1H, Ar**H**), 6.70 (s, 1H, Ar**H**), 3.92 (s, 3H, OC**H**$_3$), 3.91 (s, 3H, OC**H**$_3$), 3.66–3.61 (m, 2H, $CH_2C\mathbf{H}_2N$), 3.20 (septet, 1H, $J$ = 6.7 Hz, C**H**$(CH_3)_2$), 2.61–2.56 (m, 2H, C**H**$_2CH_2N$), 1.21 (d, 6H, $J$ = 6.7 Hz, $CH(C\mathbf{H}_3)_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 170.9, 150.6, 147.5, 132.2, 121.8, 110.5, 108.7, 56.4, 56.1, 47.1, 32.0, 26.2, 21.0. |
| FTIR (neat) cm$^{-1}$: | 3386 (w), 2963 (s), 2935 (s), 2868 (m), 2835 (m), 2068 (w), 1624 (s), 1605 (s), 1572 (s), 1515 (s), 1465 (s), 1367 (m), 1358 (m), 1279 (s), 1209 (s), 1136 (s). |
| HRMS (ESI): | calc'd for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1489, found: 234.1441. |
| TLC (15% EtOAc in hexanes), $R_f$: | 0.28 (UV). |




**S3** 91% **8**

**1-*sec*-Butyl-6,7-bis(*tert*-butyldimethylsilyloxy)-3,4-dihydroisoquinoline (8, Figure 1):**

Trifluoromethanesulfonic anhydride (78 μL, 0.47 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S3** (200 mg, 0.429 mmol, 1 equiv) and 2-chloropyridine (49 μL, 0.52 mmol, 1.1 equiv) in dichloromethane (1.4 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give 3,4-dihydroisoquinoline derivative **8** as a pale yellow oil (175 mg, 91%).

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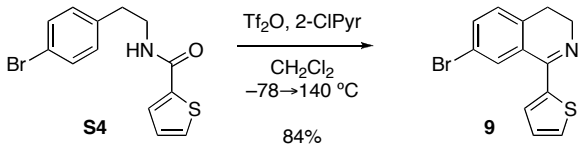
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.02 (s, 1H, Ar**H**), 6.62 (s, 1H, Ar**H**), 3.72–3.64 (m, 1H, $CH_2C\mathbf{H}_2N$), 3.61–3.53 (m, 1H, $CH_2C\mathbf{H}_2N$), 2.91–2.82 (m, 1H, $C\mathbf{H}(CH_3)CH_2CH_3$), 2.54–2.49 (m, 2H, $C\mathbf{H}_2CH_2N$), 1.83–1.73 (m, 1H, $CH(CH_3)C\mathbf{H}_2CH_3$), 1.50–1.39 (m, 1H, $CH(CH_3)C\mathbf{H}_2CH_3$), 1.19 (d, 3H, $J$ = 6.8 Hz, $CH(C\mathbf{H}_3)CH_2CH_3$), 1.03–0.99 (m, 18H, $OSi(C(C\mathbf{H}_3)_3)(CH_3)_2$), 0.93 (t, 3H, $J$ = 7.4 Hz, $CH(CH_3)CH_2C\mathbf{H}_3$), 0.24–0.21 (m, 12H, $OSi(C(CH_3)_3)(C\mathbf{H}_3)_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 170.3, 148.6, 145.2, 132.0, 123.1, 119.9, 118.1, 47.2, 38.9, 28.3, 26.1, 26.0, 26.0, 18.6, 18.6, 18.3, 12.2, –3.9, –3.9, –3.9, –3.9. |
| FTIR (neat) $cm^{-1}$: | 2932 (s), 2896 (s), 2859 (s), 1623 (m), 1603 (m), 1560 (s), 1508 (s), 1473 (s), 1463 (s), 1429 (m), 1410 (s), 1322 (s), 1255 (s), 1195 (s), 1138 (s), 1055 (w), 1004 (m). |
| HRMS (ESI): | calc'd for $C_{25}H_{46}NO_2Si_2$ $[M+H]^+$: 448.3062, found: 448.3050. |
| TLC (10% EtOAc in hexanes), $R_f$: | 0.45 (UV). |




**7-Bromo-1-(thiophen-2-yl)-3,4-dihydroisoquinoline (9, Figure 1):**

Trifluoromethanesulfonic anhydride (59 μL, 0.36 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S4** (100 mg, 0.322 mmol, 1 equiv) and 2-chloropyridine (37 μL, 0.39 mmol, 1.2 equiv) in dichloromethane (1.1 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C for 5 min before the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **9** as a pale yellow oil (79 mg, 84%).

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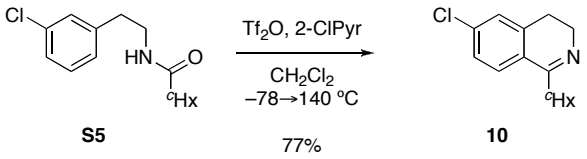
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.83 (d, 1H, *J* = 2.0 Hz, Ar**H**), 7.56 (dd, 1H, *J* = 8.0, 2.0 Hz, Ar**H**), 7.46 (d, 1H, *J* = 5.1 Hz, Ar**H**), 7.37 (d, 1H, *J* = 3.6 Hz, Ar**H**), 7.19 (d, 1H, *J* = 8.0 Hz, Ar**H**), 7.14 (dd, 1H, *J* = 5.1, 3.7 Hz, Ar**H**), 3.82–3.77 (m, 2H, $CH_2C\mathbf{H}_2N$), 2.74–2.70 (m, 2H, $C\mathbf{H}_2CH_2N$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 159.9, 142.8, 138.0, 133.7, 130.3, 129.8, 129.3, 129.1, 128.6, 127.5, 120.3, 47.3, 26.1. |
| FTIR (neat) $cm^{-1}$: | 3069 (w), 2943 (m), 2893 (w), 2838 (w), 1588 (s), 1552 (s), 1477 (m), 1430 (s), 1299 (s), 1221 (m), 1107 (m). |
| HRMS (ESI): | calc'd for $C_{13}H_{11}BrNS$ $[M+H]^+$: 291.9790, found: 291.9779. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.63 (UV). |




**S5** 77% **10**

**6-Chloro-1-cyclohexyl-3,4-dihydroisoquinoline (10, Figure 1):**

Trifluoromethanesulfonic anhydride (68 μL, 0.41 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S5** (100 mg, 0.376 mmol, 1 equiv) and 2-chloropyridine (43 μL, 0.45 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **10** as a pale yellow oil (72 mg, 77%).

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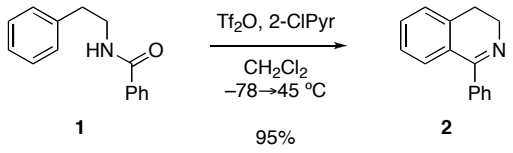
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.44 (d, 1H, *J* = 8.3 Hz, Ar**H**), 7.28–7.25 (m, 1H, Ar**H**), 7.19–7.18 (m, 1H, Ar**H**), 3.68–3.63 (m, 2H, $CH_2C\mathbf{H}_2N$), 2.88–2.81 (m, 1H, $^cC_6\mathbf{H}_{11}$), 2.65–2.60 (m, 2H, $C\mathbf{H}_2CH_2N$), 1.90–1.82 (m, 4H, $^cC_6\mathbf{H}_{11}$), 1.78–1.72 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.48–1.32 (m, 4H, $^cC_6\mathbf{H}_{11}$), 1.32–1.22 (m, 1H, $^cC_6\mathbf{H}_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 170.1, 140.4, 135.8, 127.9, 127.3, 127.1, 126.2, 46.7, 42.3, 31.4, 26.7, 26.4, 26.4. |
| FTIR (neat) $cm^{-1}$: | 2930 (s), 2851 (s), 2668 (w), 1623 (s), 1594 (m), 1561 (m), 1482 (w), 1449 (m), 1199 (m), 1017 (m). |
| HRMS (ESI): | calc'd for $C_{15}H_{19}ClN$ $[M+H]^+$: 248.1201, found: 248.1201. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.67 (UV). |




**1-Phenyl-3,4-dihydroisoquinoline (2, Figure 1):**

Trifluoromethanesulfonic anhydride (61 μL, 0.37 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1** (75 mg, 0.33 mmol, 1 equiv) and 2-chloropyridine (38 μL, 0.40 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a preheated oil bath at 45 ºC and maintained at that temperature. After 2 h, the mixture was allowed to cool to 23 °C and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 7.5→70% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **2**[7] as a pale yellow oil (66 mg, 95%).

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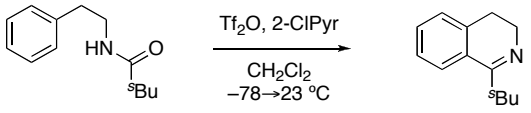
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.64–7.61 (m, 2H, Ar**H**), 7.47–7.39 (m, 4H, Ar**H**), 7.31–7.25 (m, 3H, Ar**H**), 3.90–3.85 (m, 2H, $CH_2C\mathbf{H}_2N$), 2.85–2.80 (m, 2H, $C\mathbf{H}_2CH_2N$). |
| $^{13}$C NMR (125 MHz, DMSO, 20 °C) δ: | 165.7, 138.6, 138.6, 130.7, 129.3, 128.5, 128.1, 128.0, 127.6, 127.1, 126.7, 47.1, 25.6. |
| FTIR (neat) $cm^{-1}$: | 3059 (w), 3026 (w), 2939 (m), 2893 (w), 2839 (w), 1956 (w), 1608 (s), 1565 (m), 1445 (m), 1318 (s), 1307 (s), 1020 (m). |
| HRMS (ESI): | calc'd for $C_{15}H_{14}N$ $[M+H]^+$: 208.1121, found: 208.1125. |
| TLC (15% EtOAc in hexanes), $R_f$: | 0.37 (UV). |

[7] For a prior report on the synthesis of **2**, see Parham, W. E.; Bradsher, C. K.; Hunt, D. A. *J. Org. Chem.* **1978**, *43*, 1606–1607.

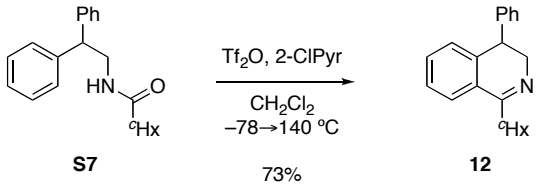



**S6** 77% **11**

**1-*sec*-Butyl-3,4-dihydroisoquinoline (11, Figure 1):**

Trifluoromethanesulfonic anhydride (88 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S6** (100 mg, 0.487 mmol, 1 equiv) and 2-chloropyridine (55 μL, 0.58 mmol, 1.2 equiv) in dichloromethane (1.6 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **11** as a colorless oil (70 mg, 77%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.54–7.52 (m, 1H, Ar**H**), 7.37–7.29 (m, 2H, Ar**H**), 7.23–7.19 (m, 1H, Ar**H**), 3.78–3.70 (m, 1H, $CH_2CH_2N$), 3.64–3.57 (m, 1H, $CH_2CH_2N$), 3.10–3.02 (m, 1H, $CH(CH_3)CH_2CH_3$), 2.68–2.64 (m, 2H, $CH_2CH_2N$), 1.84–1.75 (m, 1H, $CH(CH_3)CH_2CH_3$), 1.53–1.44 (m, 1H, $CH(CH_3)CH_2CH_3$), 1.21 (d, 3H, $J$ = 7.0 Hz, $CH(CH_3)CH_2CH_3$), 0.92 (t, 3H, $J$ = 7.5 Hz, $CH(CH_3)CH_2CH_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 171.0, 138.4, 130.2, 129.4, 127.7, 127.0, 124.8, 47.0, 38.6, 28.2, 26.6, 18.5, 12.1. |
| FTIR (neat) $cm^{-1}$: | 3061 (w), 3023 (w), 2962 (s), 2934 (s), 2873 (s), 2845 (m), 1919 (w), 1809 (w), 1624 (s), 1572 (m), 1486 (w), 1453 (s), 1426 (m), 1377 (m), 1236 (m), 1019 (m). |
| HRMS (ESI): | calc'd for $C_{13}H_{18}N$ $[M+H]^+$: 188.1439,<br>found: 188.1438. |
| TLC (10% EtOAc in hexanes), $R_f$: | 0.80 (UV). |

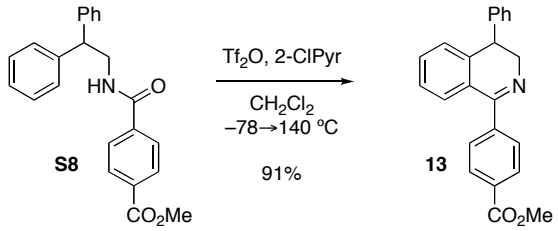



**S7** 73% **12**

**1-Cyclohexyl-4-phenyl-3,4-dihydroisoquinoline (12, Figure 1):**

Trifluoromethanesulfonic anhydride (71 μL, 0.43 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S7** (120 mg, 0.390 mmol, 1 equiv) and 2-chloropyridine (44 μL, 0.47 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **12** as a pale yellow oil (83 mg, 73%).

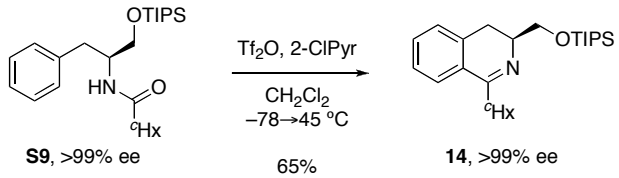
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.62–7.59 (m, 1H, Ar**H**), 7.36–7.30 (m, 4H, Ar**H**), 7.29–7.24 (m, 1H, Ar**H**), 7.21–7.17 (m, 2H, Ar**H**), 6.96–6.93 (m, 1H, Ar**H**), 4.04–3.81 (m, 3H, C**H**C**H**$_2$N), 3.02–2.95 (m, 1H, $^c$C$_6$**H**$_{11}$), 2.01–1.72 (m, 5H, $^c$C$_6$**H**$_{11}$), 1.54–1.35 (m, 4H, $^c$C$_6$**H**$_{11}$), 1.35 (m, 1H, $^c$C$_6$**H**$_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 171.1, 141.6, 141.0, 130.6, 128.8, 128.7, 128.6, 127.7, 127.2, 127.0, 124.8, 54.0, 42.5, 42.2, 31.5, 31.4, 26.8, 26.7, 26.4. |
| FTIR (neat) cm$^{-1}$: | 3061 (w), 3027 (w), 2929 (s), 2851 (s), 1951 (w), 1625 (s), 1602 (w), 1571 (w), 1494 (m), 1450 (m), 1256 (w), 1003(w). |
| HRMS (ESI): | calc'd for $C_{21}H_{24}N$ $[M+H]^+$: 290.1903,<br>found: 290.1907. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.38 (UV). |




**Methyl 4-(4-phenyl-3,4-dihydroisoquinolin-1-yl)benzoate (13, Figure 1):**

Trifluoromethanesulfonic anhydride (51 μL, 0.31 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S8** (100 mg, 0.278 mmol, 1 equiv) and 2-chloropyridine (32 μL, 0.33 mmol, 1.2 equiv) in dichloromethane (900 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the reaction mixture. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5→10% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **13** as a pale yellow oil (86 mg, 91%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.14–8.11 (m, 2H, Ar**H**), 7.73–7.70 (m, 2H, Ar**H**), 7.41–7.35 (m, 3H, Ar**H**), 7.32–7.26 (m, 5H, Ar**H**), 7.02 (d, 1H, *J* = 7.5 Hz, Ar**H**), 4.25 (dd, 1H, *J* = 15.2, 5.6 Hz, CHC**H**$_2$N), 4.17 (dd, 1H, *J* = 11.1, 5.6 Hz, C**H**CH$_2$N), 4.04 (dd, 1H, *J* = 15.2, 11.1 Hz, CHC**H**$_2$N), 3.96 (s, 3H, OC**H**$_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 167.1, 167.0, 143.4, 141.6, 140.9, 131.5, 131.0, 129.7, 129.0, 129.0, 128.9, 128.3, 127.9, 127.6, 127.3, 127.1, 54.8, 52.5, 42.5. |
| FTIR (neat) cm$^{-1}$: | 3061 (w), 3028 (w), 2950 (w), 2888 (w), 2842 (w), 1942 (w), 1723 (s), 1611 (m), 1569 (w), 1436 (m), 1311 (s), 1278 (s), 1115 (m), 1103 (m). |
| HRMS (ESI): | calc'd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1489,<br>found: 342.1495. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.41 (UV). |

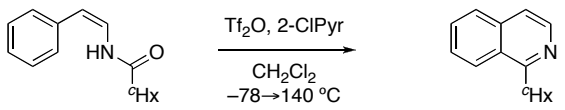



**S9**, >99% ee 65% **14**, >99% ee

**(*S*)-1-Cyclohexyl-3-((triisopropylsilyloxy)methyl)-3,4-dihydroisoquinoline (14, Figure 1):**

Trifluoromethanesulfonic anhydride (65 μL, 0.40 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S9** (150 mg, 0.359 mmol, 1 equiv) and 2-chloropyridine (41 μL, 0.43 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a preheated oil bath at 45 ºC and maintained at that temperature. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0.5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **14** as a colorless oil (94 mg, 65%). The enantiomeric excess of 3,4-dihydroisoquinoline **14** was determined to be >99% ee by chiral HPLC analysis [Chiralpak OD-H; 0.5 mL/min; 5% $^i$PrOH in hexanes; $t_R$(minor) = 14.5 min, $t_R$ (major) = 17.7 min].

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.50 (d, 1H, *J* = 7.2 Hz, Ar**H**), 7.34–7.30 (m, 1H, Ar**H**), 7.30–7.26 (m, 1H, Ar**H**), 7.22 (d, 1H, *J* = 7.3 Hz, Ar**H**), 4.12–4.06 (m, 1H, $CH_2CHC\mathbf{H}_2O$), 3.64–3.56 (m, 2H, $CH_2C\mathbf{H}C\mathbf{H}_2O$), 2.94–2.85 (m, 2H, $C\mathbf{H}_2CHCH_2O$, $^cC_6\mathbf{H}_{11}$), 2.59 (dd, 1H, *J* = 15.7, 9.9 Hz, $C\mathbf{H}_2CHCH_2O$), 1.95–1.70 (m, 5H, $^cC_6\mathbf{H}_{11}$), 1.56–1.48 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.44–1.04 (m, 25H, $^cC_6\mathbf{H}_{11}$, $OSi(C\mathbf{H}(C\mathbf{H}_3)_2)_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 170.5, 137.9, 130.2, 129.3, 128.4, 126.8, 124.6, 66.7, 58.3, 42.3, 31.8, 31.1, 29.1, 26.8, 26.7, 26.5, 18.2, 12.2. |
| FTIR (neat) $cm^{-1}$: | 2930 (s), 2865 (s), 1623 (m), 1571 (w), 1463 (m), 1381 (w), 1257 (w), 1124 (m). |
| HRMS (ESI): | calc'd for $C_{25}H_{42}NOSi$ $[M+H]^+$: 400.3030, found: 400.3014. |
| TLC (10% EtOAc in hexanes), $R_f$: | 0.83 (UV). |



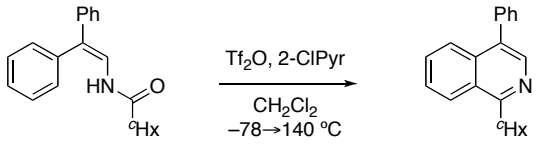

**S10** 66% **15**

**1-Cyclohexylisoquinoline (15, Figure 1):**

Trifluoromethanesulfonic anhydride (30 μL, 0.18 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S10** (38 mg, 0.17 mmol, 1 equiv) and 2-chloropyridine (19 μL, 0.20 mmol, 1.2 equiv) in dichloromethane (550 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the isoquinoline derivative **15**[8] as a white solid (23 mg, 66%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.48 (d, 1H, *J* = 5.7 Hz, Ar**H**), 8.23 (d, 1H, *J* = 8.3 Hz, Ar**H**), 7.82 (d, 1H, *J* = 8.1 Hz, Ar**H**), 7.66 (ddd, 1H, *J* = 8.0, 6.8, 1.2 Hz, Ar**H**), 7.59 (ddd, 1H, *J* = 8.3, 6.9, 1.4 Hz, Ar**H**), 7.49 (d, 1H, *J* = 5.7 Hz, Ar**H**), 3.57 (tt, 1H, *J* = 11.6, 3.2 Hz, $^c$C$_6$**H**$_{11}$), 2.04–1.91 (m, 4H, $^c$C$_6$**H**$_{11}$), 1.88–1.75 (m, 3H, $^c$C$_6$**H**$_{11}$), 1.54 (qt, 2H, *J* = 12.5, 3.1 Hz, $^c$C$_6$**H**$_{11}$), 1.40 (qt, 1H, *J* = 12.7, 3.4 Hz, $^c$C$_6$**H**$_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 165.9, 142.1, 136.6, 129.7, 127.7, 127.0, 126.5, 124.9, 119.1, 41.7, 32.8, 27.1, 26.4. |
| FTIR (neat) cm$^{-1}$: | 3051 (w), 2927 (s), 2852 (m), 1683 (w), 1622 (w), 1586 (w), 1562 (m), 1501 (w), 1449 (m), 1391 (w), 1194 (w). |
| HRMS (ESI): | calc'd for $C_{15}H_{18}N$ $[M+H]^+$: 212.1434,<br>found: 212.1438. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.57 (UV). |

[8] For a prior report on the synthesis of **15**, see Minisci, F.; Vismara, E.; Fontana, F. *J. Org. Chem.* **1989**, *54*, 5224–5227.



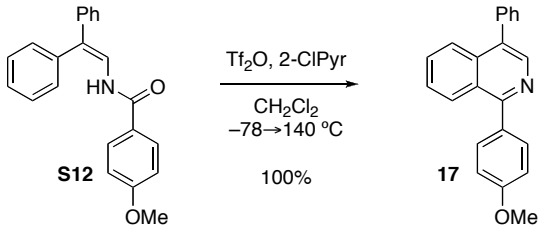

**S11** 100% **16**

**1-Cyclohexyl-4-phenylisoquinoline (16, Figure 1):**

Trifluoromethanesulfonic anhydride (77 μL, 0.47 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S11** (130 mg, 0.426 mmol, 1 equiv) and 2-chloropyridine (48 μL, 0.51 mmol, 1.2 equiv) in dichloromethane (1.4 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the isoquinoline derivative **16**[9] as a pale yellow oil (122 mg, 100%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.44 (s, 1H, Ar**H**), 8.33–8.29 (m, 1H, Ar**H**), 7.94–7.90 (m, 1H, Ar**H**), 7.63–7.59 (m, 2H, Ar**H**), 7.55–7.49 (m, 4H, Ar**H**), 7.49–7.44 (m, 1H, Ar**H**), 3.66 (tt, 1H, $J$ = 11.7, 3.3 Hz, $^c$C$_6$**H**$_{11}$), 2.08–2.01 (m, 2H, $^c$C$_6$**H**$_{11}$), 2.01–1.94 (m, 2H, $^c$C$_6$**H**$_{11}$), 1.93–1.82 (m, 3H, $^c$C$_6$**H**$_{11}$), 1.57 (qt, 2H, $J$ = 12.9, 3.5 Hz, $^c$C$_6$**H**$_{11}$), 1.42 (qt, 1H, $J$ = 12.8, 3.5 Hz, $^c$C$_6$**H**$_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 165.2, 141.9, 137.8, 134.9, 131.5, 130.4, 129.8, 128.7, 127.8, 126.8, 126.0, 125.9, 125.1, 41.7, 32.8, 27.1, 26.5. |
| FTIR (neat) cm$^{-1}$: | 3059 (w), 3030 (w), 2926 (s), 2851 (m), 1602 (w), 1615 (w), 1554 (m), 1508 (m), 1445 (m), 1393 (m), 1359 (w), 1350 (w). |
| HRMS (ESI): | calc'd for $C_{21}H_{22}N$ $[M+H]^+$: 288.1752,<br>found: 288.1755. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.68 (UV). |

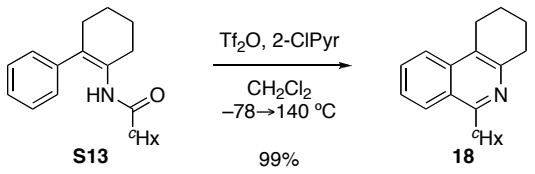
[9] For a prior report on the synthesis of **16**, see Kobayashi, K.; Hayashi, K.; Miyamoto, K.; Morikawa, O.; Konishi, H. *Synthesis* **2006**, 2934–2938.




**1-(4-Methoxyphenyl)-4-phenylisoquinoline (17, Figure 1):**

Trifluoromethanesulfonic anhydride (72 μL, 0.44 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S12** (130 mg, 0.395 mmol, 1 equiv) and 2-chloropyridine (45 μL, 0.47 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the isoquinoline derivative **17** as a pale yellow oil (123 mg, 100%).

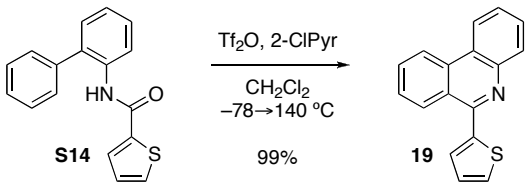
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.55 (s, 1H, Ar**H**), 8.22 (d, 1H, *J* = 8.5 Hz, Ar**H**), 7.98 (d, 1H, *J* = 8.5 HZ, Ar**H**), 7.74–7.70 (m, 2H, Ar**H**), 7.68–7.64 (app. t, 1H, *J* = 7.7 Hz, Ar**H**), 7.59–7.54 (m, 5H, Ar**H**), 7.52–7.48 (m, 1H, Ar**H**), 7.12–7.08 (m, 2H, Ar**H**), 3.93 (s, 3H, OC**H**$_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.2, 160.0, 142.2, 137.4, 135.4, 132.3, 132.2, 131.5, 130.4, 130.2, 128.8, 128.1, 128.0, 127.0, 126.6, 125.4, 114.0, 55.6. |
| FTIR (neat) cm$^{-1}$: | 3002 (w), 3033 (w), 2956 (w), 2933 (w), 2836 (w), 2044 (w), 1609 (s), 1578 (w), 1542 (w), 1514 (s), 1452 (w), 1385 (s), 1301 (w), 1250 (s), 1176 (m), 1032 (m). |
| HRMS (ESI): | calc'd for $C_{22}H_{18}NO$ $[M+H]^+$: 312.1388,<br>found: 312.1386. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.38 (UV). |




**6-Cyclohexyl-1,2,3,4-tetrahydrophenanthridine (18, Figure 1):**

Trifluoromethanesulfonic anhydride (64 μL, 0.39 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S13** (100 mg, 0.353 mmol, 1 equiv) and 2-chloropyridine (40 μL, 0.42 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the isoquinoline derivative **18** as a colorless oil (93 mg, 99%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.20 (d, 1H, *J* = 8.5 Hz, Ar**H**), 7.91 (d, 1H, *J* = 8.4 Hz, Ar**H**), 7.64 (ddd, 1H, *J* = 8.1, 6.9, 1.1 Hz, Ar**H**), 7.50 (ddd, 1H, *J* = 8.1, 6.8, 1.0 Hz, Ar**H**), 3.51 (tt, 1H, *J* = 11.5, 3.1 Hz, $^c$C$_6$**H**$_{11}$), 3.08–3.02 (m, 4H, C**H**$_2$CH$_2$CH$_2$C**H**$_2$), 1.99–1.78 (m, 11H, CH$_2$C**H**$_2$C**H**$_2$CH$_2$, $^c$C$_6$**H**$_{11}$), 1.53 (tt, 2H, *J* = 13.2, 4.1 Hz, $^c$C$_6$**H**$_{11}$), 1.40 (tt, 1H, *J* = 12.7, 3.3 Hz, $^c$C$_6$**H**$_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 162.9, 149.1, 136.0, 129.3, 125.3, 125.3, 124.6, 122.8, 122.2, 41.5, 33.3, 32.7, 27.1, 26.4, 25.0, 23.4, 23.1. |
| FTIR (neat) cm$^{-1}$: | 3069 (w), 2927 (s), 2852 (m), 1616 (w), 1581 (w), 1566 (m), 1505 (w), 1449 (m), 1390 (w), 1335 (w), 1263 (w). |
| HRMS (ESI): | calc'd for $C_{19}H_{24}N$ $[M+H]^+$: 266.1903,<br>found: 266.1897. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.68 (UV). |

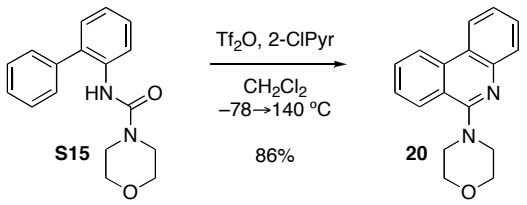



**6-(Thiophen-2-yl)phenanthridine (19, Figure 1):**

Trifluoromethanesulfonic anhydride (65 μL, 0.39 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S14** (100 mg, 0.358 mmol, 1 equiv) and 2-chloropyridine (41 μL, 0.43 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the phenanthridine derivative **19**[10] as a pale yellow oil (93 mg, 99%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.71 (d, 1H, *J* = 8.3 Hz, Ar**H**), 8.59 (dd, 2H, *J* = 7.9, 4.6 Hz, Ar**H**), 8.22 (d, 1H, *J* = 8.2 Hz, Ar**H**), 7.89 (t, 1H, *J* = 7.5 Hz, Ar**H**), 7.78–7.65 (m, 4H, Ar**H**), 7.58 (dd, 1H, *J* = 5.1, 1.0 Hz, Ar**H**), 7.25 (dd, 1H, *J* = 5.2, 3.6 Hz, Ar**H**). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 154.2, 143.9, 142.7, 133.8, 130.8, 130.4, 129.5, 129.1, 128.3, 128.1, 127.6, 127.6, 127.2, 124.9, 123.7, 122.5, 122.1. |
| FTIR (neat) $cm^{-1}$: | 3070 (m), 1956 (w), 1812 (w), 1734 (w), 1610 (m), 1577 (m), 1562 (s), 1519 (m), 1484 (s), 1458 (s), 1430 (s). |
| HRMS (EI): | calc'd for $C_{17}H_{12}NS$ $[M+H]^+$: 262.0685,<br>found: 262.0683. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.51 (UV, $KMnO_4$). |

[10] For formation of **19** as the product of a competing pathway in our intermolecular condensation reaction for synthesis of pyridines, see Movassaghi, M.; Hill, M. D.; Ahmad. O. K. *J. Am. Chem. Soc.* **2007**, *129*, 10096–10097.

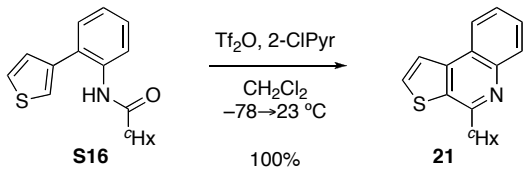



**4-(Phenanthridin-6-yl)morpholine (20, Figure 1):**

Trifluoromethanesulfonic anhydride (64 μL, 0.39 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S15** (100 mg, 0.354 mmol, 1 equiv) and 2-chloropyridine (40 μL, 0.43 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 20% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the phenanthridine derivative **20**[11] as a pale yellow oil (81 mg, 86%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.58 (d, 1H, *J* = 8.3 Hz, Ar**H**), 8.44 (d, 1H, *J* = 8.1 Hz, Ar**H**), 8.22 (d, 1H, *J* = 8.2 Hz, Ar**H**), 7.85 (d, 1H, *J* = 8.1 Hz, Ar**H**), 7.82–7.76 (m, 1H, Ar**H**), 7.68–7.60 (m, 2H, Ar**H**), 7.54–7.48 (m, 1H, Ar**H**), 4.05–4.00 (m, 4H, $N(CH_2C\mathbf{H}_2)_2O$), 3.55–3.49 (m, 4H, $N(C\mathbf{H}_2CH_2)_2O$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 159.9, 143.7, 135.0, 130.2, 128.8, 128.6, 126.8, 126.4, 125.0, 122.8, 122.7, 121.9, 121.3, 67.1, 51.8. |
| FTIR (neat) $cm^{-1}$: | 3070 (w), 2958 (m), 2890 (w), 2849 (m), 1946 (w), 1611 (m), 1582 (s), 1569 (s), 1524 (m), 1485 (m), 1454 (m), 1382 (s), 1363 (s), 1223 (s), 1117 (s), 1021 (m). |
| HRMS (ESI): | calc'd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335,<br>found: 265.1326. |
| TLC (40% EtOAc in hexanes), $R_f$: | 0.64 (UV). |

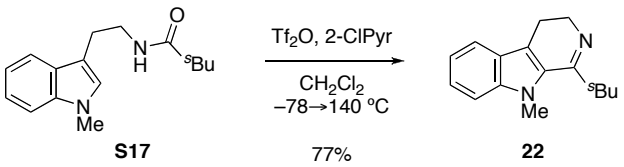
[11] For a prior report on the synthesis of **20**, see Mikhailovskii, A. G.; Vakhrin, M. I. *Khim. Geterotsikl. Soedin.*, **1991**, 1361–1364.




**4-Cyclohexyl thieno[2,3-c]quinoline (21, Figure 1):**

Trifluoromethanesulfonic anhydride (57 μL, 0.35 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S16** (90 mg, 0.32 mmol, 1 equiv) and 2-chloropyridine (36 μL, 0.38 mmol, 1.2 equiv) in dichloromethane (1.1 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc and 1% $Et_3N$ in hexanes; $SiO_2$: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **21** as a pale yellow oil (84 mg, 100%).

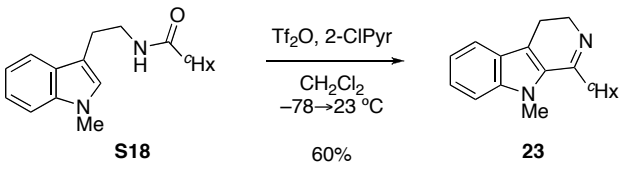
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.25 (dd, 1H, *J* = 8.1, 1.4 Hz, Ar**H**), 8.19 (dd, 1H, *J* = 8.3, 1.2 Hz, Ar**H**), 7.99 (d, 1H, *J* = 5.3 Hz, Ar**H**), 7.79 (d, 1H, *J* = 5.3 Hz, Ar**H**), 7.68 (ddd, 1H, *J* = 8.4, 7.0, 1.5 Hz, Ar**H**), 7.58 (ddd, 1H, *J* = 8.1, 6.9, 1.2 Hz), 3.17 (tt, 1H, *J* = 11.6, 3.5 Hz, $^c$C$_6$**H**$_{11}$), 2.15–2.08 (m, 2H, $^c$C$_6$**H**$_{11}$), 2.04–1.93 (m, 4H, $^c$C$_6$**H**$_{11}$), 1.86–1.80 (m, 1H, $^c$C$_6$**H**$_{11}$), 1.58–1.39 (m, 3H, $^c$C$_6$**H**$_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.9, 145.2, 142.0, 132.7, 130.2, 129.7, 128.0, 126.0, 123.6, 123.3, 122.3, 47.0, 31.7, 26.8, 26.2. |
| FTIR (neat) cm$^{-1}$: | 3063 (m), 2927 (s), 2852 (s), 2667 (w), 1615 (w), 1557 (s), 1497 (s), 1464 (w), 1449 (s), 1367 (m), 1341 (m), 1282 (m), 1211 (m), 1160 (m). |
| HRMS (ESI): | calc'd for $C_{17}H_{18}NS$ $[M+H]^+$: 268.1154,<br>found: 268.1149. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.59 (UV). |




***N*-Methyl-1-*sec*-butyl-3,4-dihydro-β-carboline (22, Figure 1):**

Trifluoromethanesulfonic anhydride (70 μL, 0.43 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S17** (100 mg, 0.387 mmol, 1 equiv) and 2-chloropyridine (44 μL, 0.46 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **22** as a pale yellow oil (71 mg, 77%).

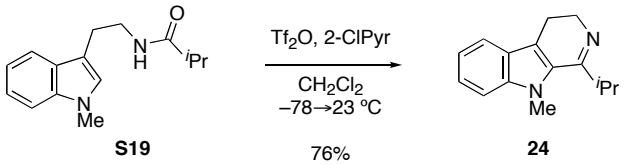
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.60 (app. dt, 1H, *J* = 7.9, 1.0 Hz, Ar**H**), 7.36–7.30 (m, 2H, Ar**H**), 7.15 (ddd, 1H, *J* = 7.9, 6.3, 1.6 Hz, Ar**H**), 3.92 (s, 3H, NC**H**$_3$), 3.91–3.84 (m, 1H, $CH_2C\mathbf{H}_2N$), 3.66–3.59 (m, 1H, $CH_2C\mathbf{H}_2N$), 3.12–3.04 (m, 1H, C**H**($CH_3$)$CH_2CH_3$), 2.83–2.68 (m, 2H, C**H**$_2CH_2N$), 1.88–1.80 (m, 1H, $CH(CH_3)C\mathbf{H}_2CH_3$), 1.54–1.44 (1H, m, $CH(CH_3)C\mathbf{H}_2CH_3$), 1.26 (d, 3H, *J* = 6.7 Hz, $CH(C\mathbf{H}_3)CH_2CH_3$), 0.93 (t, 3H, *J* = 7.5 Hz, $CH(CH_3)CH_2C\mathbf{H}_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 165.2, 138.9, 131.7, 124.7, 124.3, 120.0, 120.0, 119.1, 110.2, 48.2, 40.0, 32.7, 28.0, 19.9, 17.9, 11.9. |
| FTIR (neat) cm$^{-1}$: | 3054 (w), 2962 (s), 2933 (s), 2872 (m), 2832 (m), 1596 (m), 1527 (s), 1460 (s), 1416 (m), 1370 (s), 1253 (m), 1232 (m), 1216 (m). |
| HRMS (ESI): | calc'd for $C_{16}H_{21}N_2$ $[M+H]^+$: 241.1699,<br>found: 241.1690. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.69 (UV). |




**_N_-Benzyl-1-cyclohexyl-3,4-dihydro-β-carboline (23, Figure 1):**

Trifluoromethanesulfonic anhydride (64 μL, 0.39 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S18** (100 mg, 0.350 mmol, 1 equiv) and 2-chloropyridine (40 μL, 0.42 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **23** as a colorless oil (58 mg, 60%).

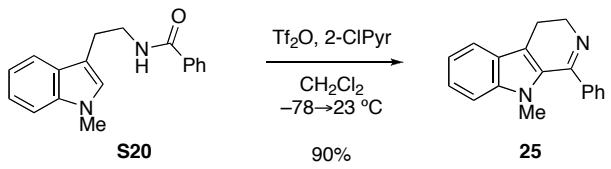
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.60 (ddd, 1H, *J* = 7.9, 0.9, 0.9 Hz, Ar**H**), 7.36–7.30 (m, 2H, Ar**H**), 7.14 (ddd, 1H, *J* = 7.9, 6.3, 1.5 Hz, Ar**H**), 3.92 (s, 3H, NC**H**$_3$), 3.77–3.72 (m, 2H, $CH_2C\mathbf{H}_2N$), 2.91 (tt, 1H, *J* = 11.2, 3.0 Hz, $^c C_6\mathbf{H}_{11}$), 2.78–2.73 (m, 2H, $C\mathbf{H}_2CH_2N$), 1.99–1.85 (m, 4H, $^c C_6\mathbf{H}_{11}$), 1.79–1.72 (m, 1H, $^c C_6\mathbf{H}_{11}$), 1.55–1.45 (m, 2H, $^c C_6\mathbf{H}_{11}$), 1.44–1.25 (m, 3H, $^c C_6\mathbf{H}_{11}$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 165.2, 138.9, 131.2, 124.7, 124.3, 120.0, 120.0, 119.2, 110.2, 48.1, 43.8, 32.5, 31.2, 26.8, 26.4, 19.9. |
| FTIR (neat) cm$^{-1}$: | 3054 (w), 2930 (s), 2850 (m), 1596 (w), 1527 (m), 1459 (m), 1416 (w), 1372 (m), 1306 (w), 1246 (w), 1211 (w). |
| HRMS (ESI): | calc'd for $C_{18}H_{23}N_2$ $[M+H]^+$: 267.1856, found: 267.1847. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.55 (UV). |




***N*-Benzyl-1-*iso*-butyl-3,4-dihydro-β-carboline (24, Figure 1):**

Trifluoromethanesulfonic anhydride (74 μL, 0.45 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S19** (100 mg, 0.409 mmol, 1 equiv) and 2-chloropyridine (46 μL, 0.49 mmol, 1.2 equiv) in dichloromethane (1.4 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **24** as a colorless solid (70 mg, 76%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.61 (d, 1H, $J$ = 7.9 Hz, Ar**H**), 7.37–7.31 (m, 2H, Ar**H**), 7.15 (ddd, 1H, $J$ = 7.9, 6.3, 1.5 Hz, Ar**H**), 3.94 (s, 3H, NC**H**$_3$), 3.78–3.73 (m, 2H, $CH_2$C**H**$_2$N), 3.29 (septet, 1H, $J$ = 6.7 Hz, C**H**($CH_3$)$_2$), 2.79–2.74 (m, 2H, C**H**$_2$$CH_2$N), 1.26 (d, 6H, $J$ = 6.7 Hz, CH(C**H**$_3$)$_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 165.8, 138.9, 131.2, 124.7, 124.3, 120.1, 120.0, 119.2, 110.2, 48.1, 33.4, 32.6, 20.7, 19.9. |
| FTIR (neat) cm$^{-1}$: | 3054 (w), 2965 (s), 2932 (s), 2832 (m), 1596 (m), 1528 (s), 1460 (s), 1417 (w), 1370 (s), 1328 (m), 1236 (m), 1219 (m), 1064 (m). |
| HRMS (ESI): | calc'd for $C_{15}H_{19}N_2$ $[M+H]^+$: 227.1543, found: 227.1547. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.54 (UV). |

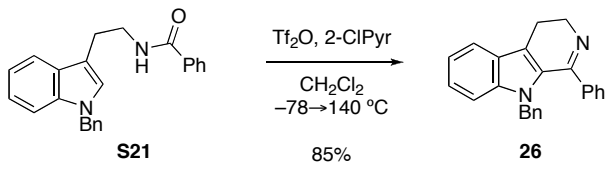



**S20** 90% **25**

***N*-Methyl-1-phenyl-3,4-dihydro-β-carboline (25, Figure 1):**

Trifluoromethanesulfonic anhydride (69 μL, 0.42 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S20** (106 mg, 0.381 mmol, 1 equiv) and 2-chloropyridine (43 μL, 0.46 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **25** as a pale yellow oil (90 mg, 90%).

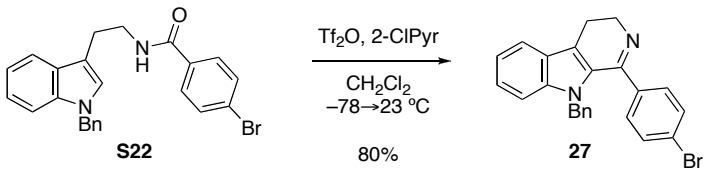
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.68 (app. dt, 1H, *J* = 8.0, 1.0, Hz, Ar**H**), 7.62–7.58 (m, 2H, Ar**H**), 7.49–7.44 (m, 3H, Ar**H**), 7.37–7.31 (m, 2H, Ar**H**), 7.20, (ddd, 1H, *J* = 7.9, 6.4, 1.5 Hz, Ar**H**), 3.97–3.93 (m, 2H, $CH_2C\mathbf{H}_2N$), 3.34 (s, 3H, $NC\mathbf{H}_3$), 2.96–2.91 (m, 2H, $C\mathbf{H}_2CH_2N$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.3, 139.5, 139.3, 131.0, 129.7, 128.7, 128.1, 124.8, 124.5, 120.2, 120.2, 119.6, 110.5, 49.0, 33.0, 20.0. |
| FTIR (neat) $cm^{-1}$: | 3055 (w), 2940 (w), 2830 (w), 1587 (w), 1527 (s), 1460 (m), 1418 (m), 1374 (s), 1295 (m), 1254 (w), 1175 (w). |
| HRMS (ESI): | calc'd for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.1386,<br>found: 261.1380. |
| TLC (30% EtOAc in hexanes), $R_f$: | 0.54 (UV). |




***N*-Benzyl-1-phenyl-3,4-dihydro-β-carboline (26, Figure 1):**

Trifluoromethanesulfonic anhydride (51 μL, 0.31 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S21** (100 mg, 0.282 mmol, 1 equiv) and 2-chloropyridine (32 μL, 0.34 mmol, 1.2 equiv) in dichloromethane (940 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→10% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **26** as a colorless oil (81 mg, 85%).

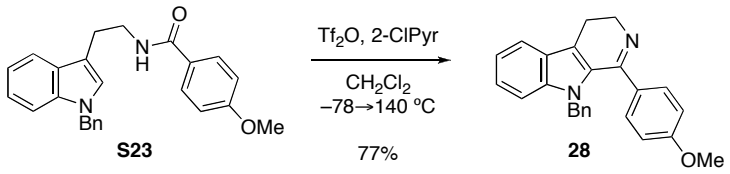
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.71–7.68 (m, 1H, Ar**H**), 7.48–7.45 (m, 2H, Ar**H**), 7.42–7.37 (m, 1H, Ar**H**), 7.35–7.30 (m, 2H, Ar**H**), 7.29–7.27 (m, 2H, Ar**H**), 7.21–7.18 (m, 1H, Ar**H**), 7.15–7.09 (m, 3H, Ar**H**), 6.60–6.58 (m, 2H, Ar**H**), 4.99 (s, 2H, NC**H**$_2$), 3.96–3.91 (m, 2H, $CH_2C$**H**$_2$N), 2.98–2.93 (m, 2H, C**H**$_2CH_2$N). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.5, 139.3, 139.1, 137.7, 130.6, 129.7, 128.6, 128.5, 128.1, 127.3, 126.1, 125.4, 124.8, 121.0, 120.6, 120.4, 111.5, 48.9, 48.6, 20.1. |
| FTIR (neat) cm$^{-1}$: | 3057 (w), 2939 (w), 2885 (w), 2831 (w), 1588 (w), 1573 (w), 1526 (s), 1495 (w), 1451 (s), 1425 (m), 1373 (m), 1347 (m), 1297 (s), 1204 (w), 1171 (w). |
| HRMS (ESI): | calc'd for $C_{24}H_{21}N_2$ $[M+H]^+$: 337.1699,<br>found: 337.1695. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.32 (UV). |




***N*-Benzyl-1-(4-bromophenyl)- 3,4-dihydro-β-carboline (27, Figure 1):**

Trifluoromethanesulfonic anhydride (57 μL, 0.35 mmol, 1.0 equiv) was added via syringe over 1 min to a stirred mixture of amide **S22** (150 mg, 0.346 mmol, 1 equiv) and 2-chloropyridine (39 μL, 0.42 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 1% $Et_3N$ in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **27** as a pale yellow solid (114 mg, 80%).

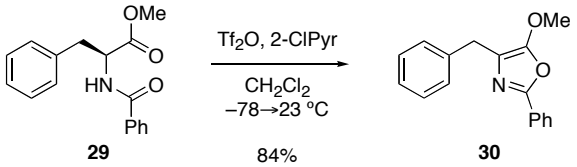
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.70 (d, 1H, *J* = 7.9 Hz, Ar**H**), 7.44 (d, 2H, *J* = 8.4 Hz, Ar**H**), 7.35–7.31 (m, 2H, Ar**H**), 7.31–7.28 (m, 2H, Ar**H**), 7.23–7.19 (m, 1H, Ar**H**), 7.18–7.11 (m, 3H, Ar**H**), 6.59 (d, 2H, *J* = 7.1 Hz, Ar**H**), 5.00 (s, 2H, NC**H**$_2$), 3.94–3.88 (m, 2H, $CH_2C\mathbf{H}_2N$), 2.97–2.92 (m, 2H, $C\mathbf{H}_2CH_2N$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 159.5, 139.4, 138.1, 137.5, 131.7, 130.3, 129.7, 128.6, 127.5, 126.1, 125.3, 125.1, 124.0, 121.3, 120.8, 120.4, 111.5, 49.0, 48.8, 20.1. |
| FTIR (neat) cm$^{-1}$: | 3030 (w), 2940 (w), 2886 (w), 2831 (w), 1589 (m), 1527 (s), 1489 (m), 1451 (s), 1425 (m), 1373 (m), 1347 (m), 1301 (s), 1291 (s), 1172 (w). |
| HRMS (ESI): | calc'd for $C_{24}H_{20}BrN_2$ $[M+H]^+$: 415.0804, found: 415.0817. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.45 (UV). |




***N*-Benzyl-1-(4-methoxyphenyl)-3,4-dihydro-β-carboline (28, Figure 1):**

Trifluoromethanesulfonic anhydride (64 μL, 0.39 mmol, 1.0 equiv) was added via syringe over 1 min to a stirred mixture of amide **S23** (150 mg, 0.390 mmol, 1 equiv) and 2-chloropyridine (44 μL, 0.47 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→10% EtOAc and 1% $Et_3N$ in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydro-β-carboline derivative **28** as a pale yellow solid (110 mg, 77%).

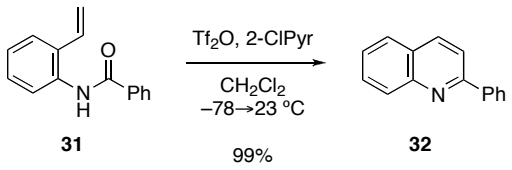
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.71–7.68 (m, 1H, Ar**H**), 7.47–7.43 (m, 2H, Ar**H**), 7.29–7.27 (m, 2H, Ar**H**), 7.21–7.17 (m, 1H, Ar**H**), 7.15–7.10 (m, 3H, Ar**H**), 6.87–6.83 (m, 2H, Ar**H**), 6.64–6.60 (m, 2H, Ar**H**), 5.05 (s, 2H, NC$\mathbf{H}_2$), 3.92–3.86 (m, 2H, $CH_2C\mathbf{H}_2N$), 3.84 (s, 3H, OC$\mathbf{H}_3$), 2.96–2.91 (m, 2H, C$\mathbf{H}_2CH_2N$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.9, 160.0, 139.4, 137.7, 131.5, 130.8, 129.6, 128.5, 127.3, 126.2, 125.5, 124.8, 121.2, 120.6, 120.3, 113.9, 111.6, 55.5, 48.7, 48.7, 20.1. |
| FTIR (neat) cm$^{-1}$: | 3059 (w), 3030 (w), 2936 (m), 2835 (m), 2195 (w), 1672 (w), 1608 (s), 1587 (m), 1526 (m), 1512 (s), 1496 (m), 1452 (m), 1372 (m), 1346 (w), 1302 (s), 1251 (s), 1173 (s). |
| HRMS (ESI): | calc'd for $C_{25}H_{23}N_2O$ $[M+H]^+$: 367.1805,<br>found: 367.1793. |
| TLC (40% EtOAc in hexanes), $R_f$: | 0.55 (UV). |




**4-Benzyl-2-phenyl-5-methoxyoxazole (30, Equation 1):**

Trifluoromethanesulfonic anhydride (77 μL, 0.47 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **29** (120 mg, 0.424 mmol, 1 equiv) and 2-chloropyridine (48 μL, 0.51 mmol, 1.2 equiv) in dichloromethane (1.4 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 15 min, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0→5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the oxazole derivative **30** as a colorless oil (94 mg, 84%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.95–7.91 (m, 2H, Ar**H**), 7.44–7.36 (m, 3H, Ar**H**), 7.35–7.28 (m, 4H, Ar**H**), 7.23–7.19 (m, 1H, Ar**H**), 3.95 (s, 3H, OC**H**$_3$), 3.85 (s, 2H, CC**H**$_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 155.4, 152.3, 139.5, 129.6, 128.7, 128.7, 128.5, 127.9, 126.3, 125.5, 116.6, 61.2, 31.2. |
| FTIR (neat) cm$^{-1}$: | 3062 (w), 3028 (w), 2943 (w), 2850 (w), 1743 (w), 1657 (s), 1604 (m), 1553 (w), 1494 (m), 1451 (m), 1363 (m), 1319 (w), 1257 (m), 1118 (w). |
| HRMS (ESI): | calc'd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found: 266.1182. |
| TLC (10% EtOAc in hexanes), $R_f$: | 0.50 (UV, $KMnO_4$). |



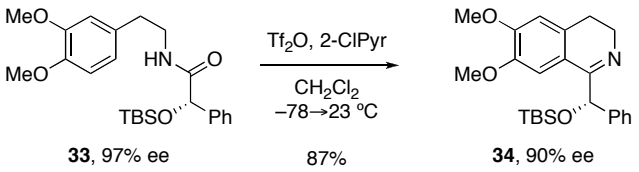

**31** **32**

**2-Phenylquinoline (32, Equation 2):**

Trifluoromethanesulfonic anhydride (45 μL, 0.27 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **31** (55 mg, 0.25 mmol, 1 equiv) and 2-chloropyridine (28 μL, 0.30 mmol, 1.2 equiv) in dichloromethane (820 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $SiO_2$: 15 × 1.5 cm) on silica gel to give the quinoline derivative **32**[12] as a white solid (50 mg, 99%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.25 (d, 1H, *J* = 8.5 Hz, Ar**H**), 8.21–8.16 (m, 3H, Ar**H**), 7.90 (d, 1H, *J* = 8.5 Hz, Ar**H**), 7.85 (d, 1H, *J* = 8.2 Hz, Ar**H**), 7.75 (ddd, 1H, *J* = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.57–7.52 (m, 3H, Ar**H**), 7.48 (tt, 1H, *J* = 7.3, 1.2 Hz, Ar**H**). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 157.5, 148.4, 139.8, 137.0, 129.9, 129.9, 129.5, 129.0, 127.8, 127.7, 127.3, 126.5, 119.2. |
| FTIR (neat) $cm^{-1}$: | 3189 (s), 3055 (w), 2091 (s), 1617 (w), 1597 (s), 1491 (m), 1447 (s). |
| HRMS (EI): | calc'd for $C_{15}H_{11}N$ $[M]^+$: 205.0886,<br>found: 205.0885. |
| Analysis | calc'd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82,<br>found: C, 87.55; H, 5.37; N, 6.84. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.51 (UV, CAM). |

[12] For an alternative condensation approach for the synthesis of **32**, see Movassaghi, M.; Hill, M. D.; Ahmad. O. K. *J. Am. Chem. Soc.* **2007**, *129*, 10096–10097.



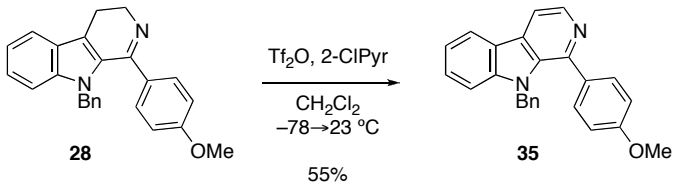

**33**, 97% ee 87% **34**, 90% ee

**(*S*)-1-(*tert*-Butyldimethylsilyloxy)(phenyl)methyl)-6,7-dimethoxy-3,4-dihydroisoquinoline (34, Equation 3):**

Trifluoromethanesulfonic anhydride (42 μL, 0.26 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **33**[13] (100 mg, 0.233 mmol, 1 equiv) and 2-chloropyridine (26 μL, 0.28 mmol, 1.2 equiv) in dichloromethane (800 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 1 h, triethylamine (75 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the 3,4-dihydroisoquinoline derivative **34** as a colorless oil (84 mg, 87%). The enantiomeric excess of 3,4-dihydroisoquinoline **34** was determined to be 90% ee by chiral HPLC analysis [Chiralpak OD-H; 1.0 mL/min; 1% $^i$PrOH in hexanes; $t_R$ (minor) = 9.1 min, $t_R$ (major) = 18.5 min].

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 7.58–7.55 (m, 2H, Ar**H**), 7.33–7.29 (m, 3H, Ar**H**), 7.23–7.19 (m, 1H, Ar**H**), 6.60 (s, 1H, Ar**H**), 5.70 (s, 1H, C**H**(OTBS)Ph), 3.86 (s, 3H, OC**H**$_3$), 3.82–3.70 (m, 2H, $CH_2$C**H**$_2$N), 3.68 (s, 3H, OC**H**$_3$), 2.68–2.58 (m, 2H, C**H**$_2$$CH_2$N), 0.94 (s, 9H, OSi(C(C**H**$_3$)$_3$)($CH_3$)$_2$), 0.18 (s, 3H, OSi(C($CH_3$)$_3$)(C**H**$_3$)$_2$), –0.01 (s, 3H, OSi(C($CH_3$)$_3$)(C**H**$_3$)$_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 167.3, 150.3, 146.5, 142.3, 132.4, 128.4, 127.1, 124.9, 119.7, 111.3, 109.8, 80.5, 55.9, 55.8, 47.5, 26.1, 25.8, 18.4, –4.4, –5.1. |
| FTIR (neat) cm$^{-1}$: | 2952 (s), 2934 (s), 2894 (w), 2856 (m), 1622 (w), 1606 (w), 1571 (m), 1516 (s), 1493 (w), 1464 (m), 1406 (w), 1357 (m), 1321 (m), 1269 (s), 1212 (s), 1156 (m), 1097 (m). |
| HRMS (ESI): | calc'd for $C_{24}H_{34}NO_3Si$ $[M+H]^+$: 412.2302, found: 412.2307. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.53 (UV). |

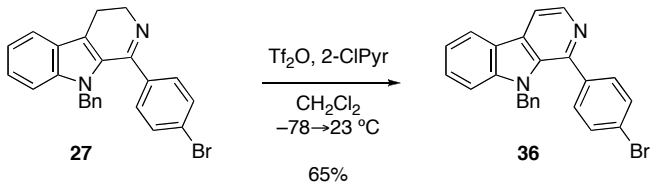
[13] (*S*)-2-(*Tert*-butyldimethylsilyloxy)-*N*-(3,4-dimethoxyphenethyl)-2-phenylethanamide (**33**) was prepared by an 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) promoted coupling of 2-(3,4-dimethoxyphenyl)ethanamine with (*S*)-2-(*tert*-butyldimethylsilyloxy)-2-phenylethanoic acid (Bremner, J. B.; Perkins, D. F. *Tetrahedron* **2005**, *61*, 2659). The enantiomeric excess of amide **33** was determined to be 97% ee by chiral HPLC analysis [Chiralpak AD-H; 1.0 mL/min; 7% $^i$PrOH in hexanes; $t_R$ (minor) = 8.8 min, $t_R$ (major) = 22.2 min].




***N*-Benzyl-1-(4-methoxyphenyl)-β-carboline (35, Figure 2):**

Trifluoromethanesulfonic anhydride (48 μL, 0.29 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of 3,4-dihydro-β-carboline **28** (96 mg, 0.26 mmol, 1 equiv) and 2-chloropyridine (30 μL, 0.31 mmol, 1.2 equiv) in dichloromethane (870 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 20% → 40% EtOAc and 1% $Et_3N$ in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the β-carboline derivative **35** as a pale yellow solid (53 mg, 55%).

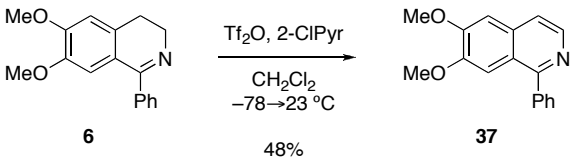
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.54 (d, 1H, *J* = 5.2 Hz, Ar**H**), 8.23 (d, 1H, *J* = 8.2 Hz, Ar**H**), 8.01 (d, 1H, *J* = 5.1 Hz, Ar**H**), 7.56–7.52 (m, 1H, Ar**H**), 7.36–7.31 (m, 4H, Ar**H**), 7.18–7.11 (m, 3H, Ar**H**), 6.85–6.81 (m, 2H, Ar**H**), 6.64 (d, 2H, *J* = 6.5 Hz, Ar**H**), 5.28 (s, 2H, NC**H**$_2$), 3.84 (s, 3H, OC**H**$_3$). |
| $^{13}$C NMR (125 MHz, $C_6D_6$, 20 °C) δ: | 160.0, 145.1, 143.0, 139.5, 137.6, 135.2, 133.0, 131.1, 130.7, 128.5, 128.5, 128.3, 127.0, 125.9, 122.2, 121.7, 120.3, 113.5, 111.1, 54.7, 48.2. |
| FTIR (neat) cm$^{-1}$: | 3032 (w), 2932 (w), 2836 (w), 1890 (w), 1620 (m), 1609 (m), 1560 (w), 1513 (s), 1496 (m), 1449 (s), 1418 (m), 1316 (m), 1247 (s), 1203 (m), 1174 (m). |
| HRMS (ESI): | calc'd for $C_{25}H_{21}N_2O$ $[M+H]^+$: 365.1648,<br>found: 365.1651. |
| TLC (40% EtOAc in hexanes), $R_f$: | 0.55 (UV). |




***N*-Benzyl-1-(4-bromophenyl)-β-carboline (36, Figure 2):**

Trifluoromethanesulfonic anhydride (51 μL, 0.31 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of 3,4-dihydro-β-carboline **27** (117 mg, 0.281 mmol, 1 equiv) and 2-chloropyridine (32 μL, 0.34 mmol, 1.2 equiv) in dichloromethane (940 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the β-carboline derivative **36** as a pale yellow solid (75 mg, 65%) and recovered starting material **27** (12 mg, 10%).

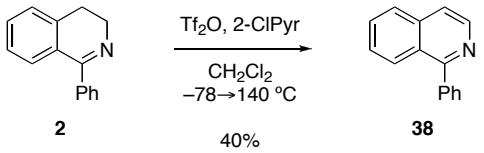
| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.54 (d, 1H, *J* = 5.1 Hz, Ar**H**), 8.24 (ddd, 1H, *J* = 8.1, 1.2, 0.6 Hz, Ar**H**), 8.05 (d, 1H, *J* = 5.1 Hz, Ar**H**), 7.57 (ddd, 1H, *J* = 8.3, 7.2, 1.3 Hz, Ar**H**), 7.43–7.40 (m, 2H, Ar**H**), 7.38–7.34 (m, 2H, Ar**H**), 7.26–7.23 (m, 2H, Ar**H**), 7.20–7.13 (m, 3H, Ar**H**), 6.62–6.58 (m, 2H, Ar**H**), 5.25 (s, 2H, NC**H**$_2$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 143.4, 142.9, 139.0, 138.7, 136.9, 134.6, 131.3, 131.1, 130.9, 129.0, 128.7, 127.4, 125.7, 122.8, 121.8, 121.6, 120.6, 114.2, 110.7, 48.4. |
| FTIR (neat) cm$^{-1}$: | 3059 (w), 3031 (w), 2921 (w), 2851 (w), 2207 (w), 1896 (w), 1621 (m), 1593 (w), 1559 (m), 1494 (m), 1448 (s), 1414 (s), 1330 (m), 1203 (s), 1128 (m). |
| HRMS (ESI): | calc'd for $C_{24}H_{18}BrN_2$ $[M+H]^+$: 413.0648,<br>found: 413.0645. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.35 (UV). |




**6,7-Dimethoxy-1-phenylisoquinoline (37, Figure 2):**

Trifluoromethanesulfonic anhydride (31 μL, 0.19 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of 3,4-dihydroisoquinoline **6** (45 mg, 0.17 mmol, 1 equiv) and 2-chloropyridine (19 μL, 0.20 mmol, 1.2 equiv) in dichloromethane (560 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 2 h, triethylamine (50 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 10%→20% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the isoquinoline derivative **37** as a pale yellow solid (25 mg, 48%) and recovered starting material **6** (14 mg, 30%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.50 (d, 1H, *J* = 5.6 Hz, Ar**H**), 7.74–7.70 (m, 2H, Ar**H**), 7.57–7.47 (m, 4H, Ar**H**), 7.39 (s, 1H, Ar**H**), 7.15 (s, 1H, Ar**H**), 4.07 (s, 3H, OC**H**$_3$), 3.88 (s, 3H, OC**H**$_3$). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 158.5, 152.8, 150.2, 141.6, 140.2, 133.9, 129.8, 128.6, 128.6, 122.7, 118.9, 105.7, 105.2, 56.3, 56.1. |
| FTIR (neat) cm$^{-1}$: | 3005 (w), 2935 (w), 2835 (w), 1622 (w), 1559 (m), 1507 (s), 1478 (s), 1434 (m), 1419 (s), 1351 (w), 1310 (w), 1265 (s), 1236 (s), 1221 (s), 1163 (m), 1121 (s). |
| HRMS (ESI): | calc'd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found: 266.1174. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.20 (UV). |




**1-Phenylisoquinoline (38, Figure 2):**

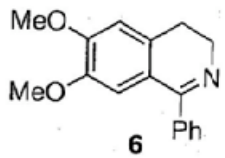
Trifluoromethanesulfonic anhydride (84 μL, 0.51 mmol, 2.1 equiv) was added via syringe over 1 min to a stirred mixture of 3,4-dihydroisoquinoline **2** (50 mg, 0.24 mmol, 1 equiv) and 2-chloropyridine (50 μL, 0.53 mmol, 2.2 equiv) in dichloromethane (800 μL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC. After 5 min, the resulting solution was allowed to warm to 23 °C. After 5 min, the reaction vessel was placed into a microwave reactor and heated to 140 ºC. After 5 min, the reaction vessel was removed from the microwave reactor and allowed to cool to 23 °C before triethylamine (50 μL) was introduced to neutralize the trifluoromethanesulfonate salts. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; $Al_2O_3$: 15 × 1.5 cm) on alumina gel to give the isoquinoline derivative **38**[14] as a pale yellow solid (20 mg, 40%) and recovered starting material **2** (4 mg, 8%).

| | |
|---|---|
| $^1$H NMR (500 MHz, $CDCl_3$, 20 °C) δ: | 8.63 (d, 1H, *J* = 5.6 Hz, Ar**H**), 8.12 (d, 1H, *J* = 8.5 Hz, Ar**H**), 7.90 (d, 1H, *J* = 8.3 Hz, Ar**H**), 7.73–7.69 (m, 3H, Ar**H**), 7.67 (d, 1H, *J* = 5.7 Hz, Ar**H**), 7.58–7.49 (m, 4H, Ar**H**). |
| $^{13}$C NMR (125 MHz, $CDCl_3$, 20 °C) δ: | 160.9, 142.4, 139.8, 137.1, 130.2, 130.1, 128.8, 128.6, 127.8, 127.4, 127.2, 126.9, 120.1. |
| FTIR (neat) $cm^{-1}$: | 3053 (w), 2918 (w), 2849 (w), 1915 (w), 1618 (w), 1582 (w), 1553 (s), 1500 (w), 1491 (w), 1441 (m), 1381 (m), 1353 (m), 1319 (m). |
| HRMS (ESI): | calc'd for $C_{15}H_{12}N$ $[M+H]^+$: 206.0970, found: 206.0959. |
| TLC (20% EtOAc in hexanes), $R_f$: | 0.48 (UV). |

[14] For a prior report on the synthesis of **38**, see the SI in Larivée, A.; Mousseau, J. J.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 52–54.

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

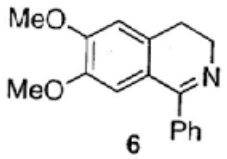
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7446545 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



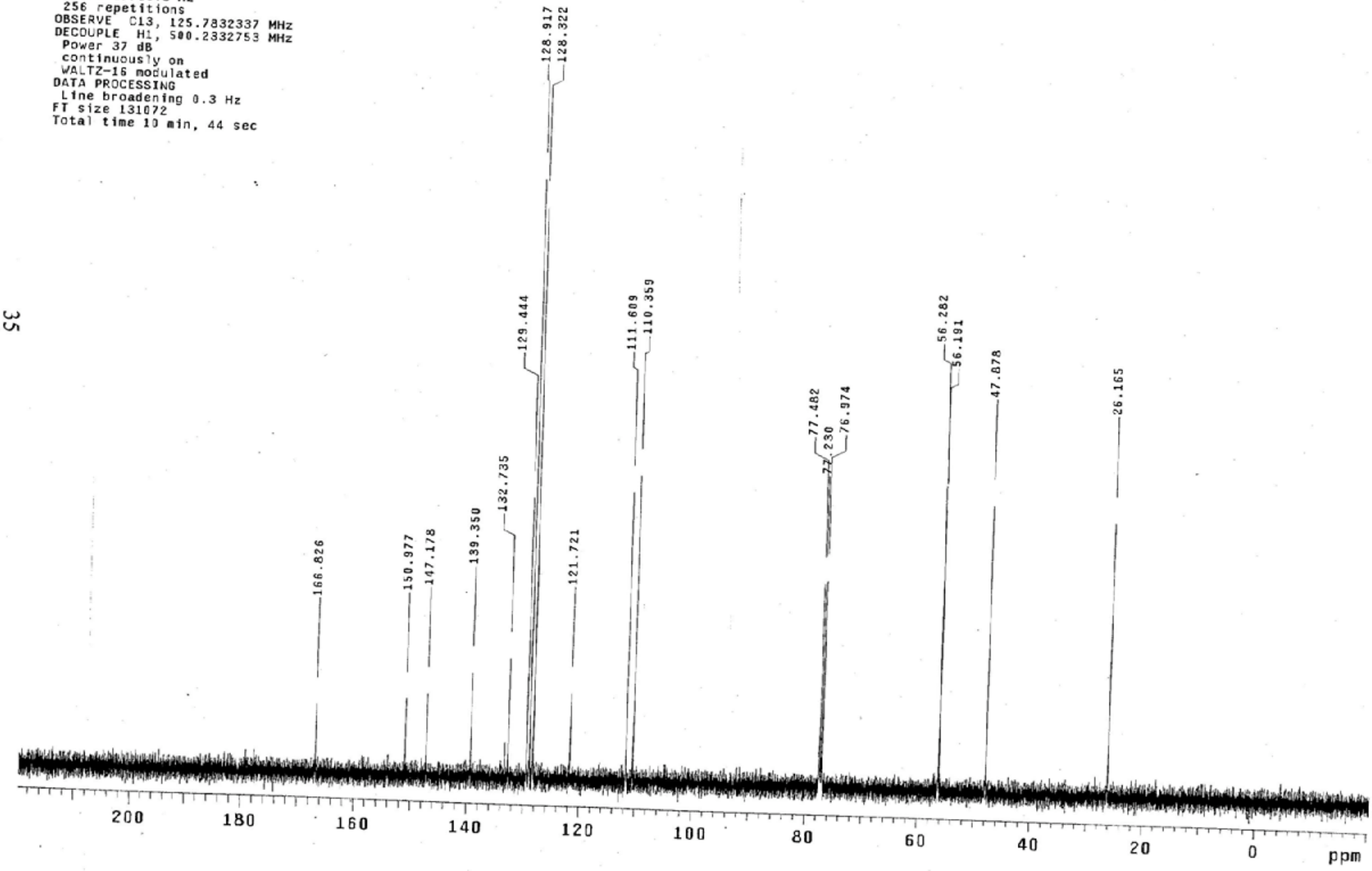

6

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-IV-187carbon
INOVA-500 "zippy"

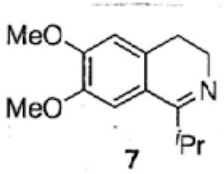
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
256 repetitions
OBSERVE C13, 125.7832337 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 10 min, 44 sec




6



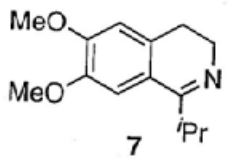
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-IV-208fr3-10
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
3 repetitions
OBSERVE H1, 499.7446548 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec




7

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

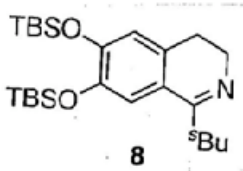
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
96 repetitions
OBSERVE C13, 125.7832291 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes




7

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-VIII-28
INOVA-500 "casper"

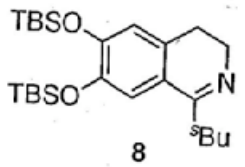
Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
4 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec




**8**

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

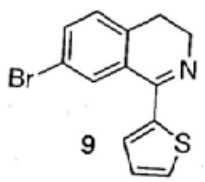
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
1000000 repetitions
OBSERVE C13, 125.7822125 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 694.2 hours



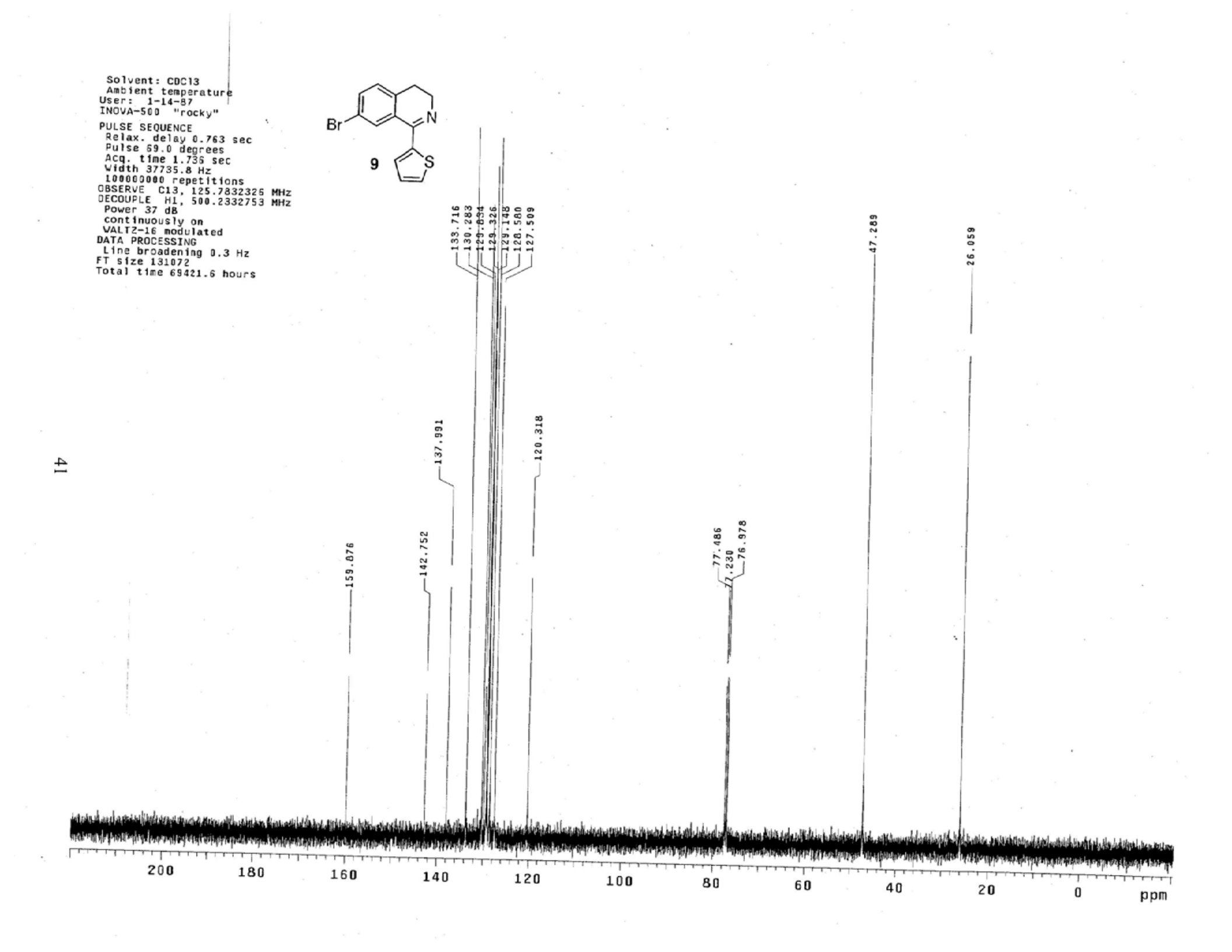
8

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

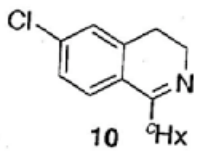


9

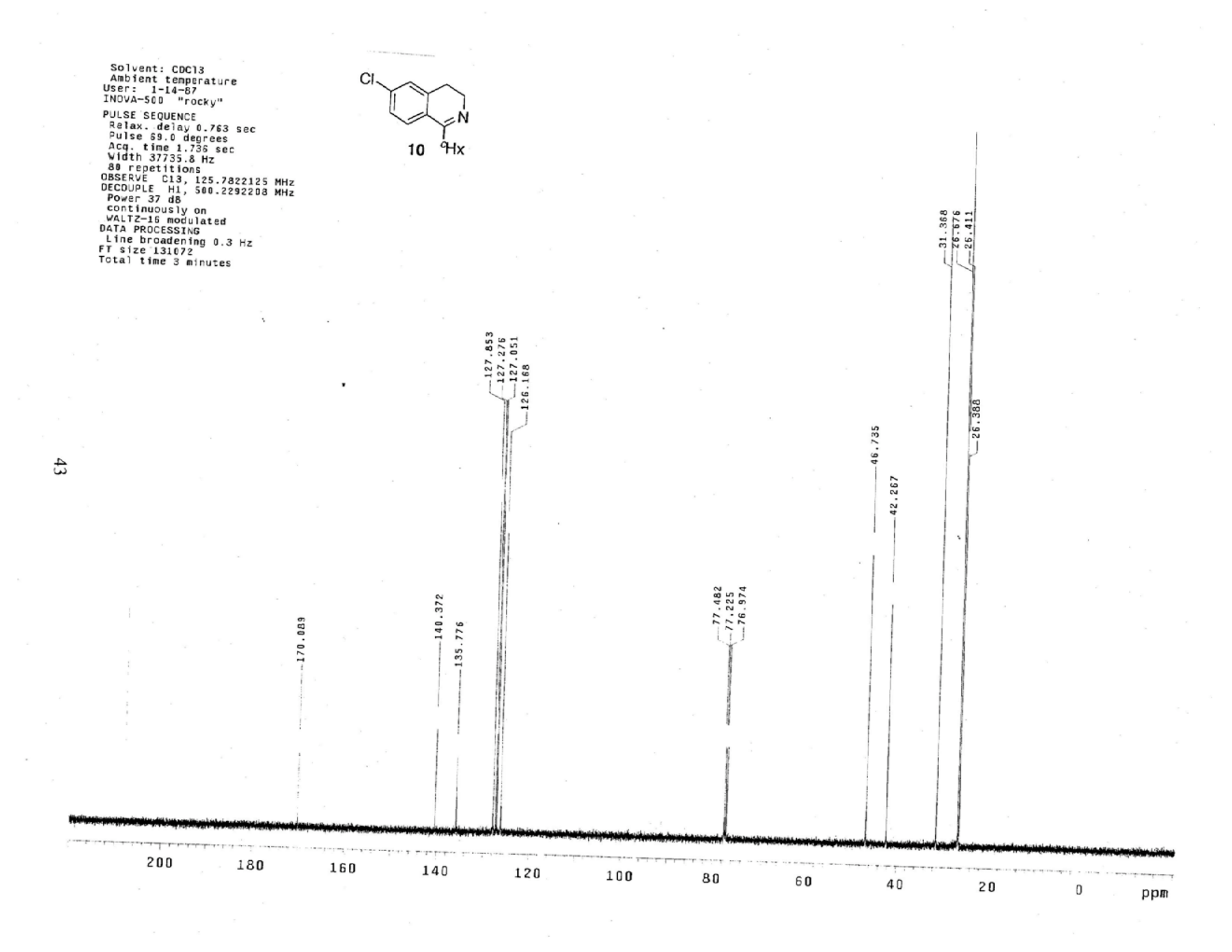

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
100000000 repetitions
OBSERVE C13, 125.7832325 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 69421.6 hours
Br
N
S
9
133.716
130.283
129.634
129.326
129.148
128.580
127.509
159.676
142.752
137.991
120.318
77.486
77.230
76.978
47.289
26.059
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7417205 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

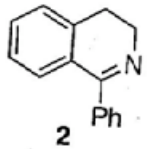



10 $^{9}$Hx

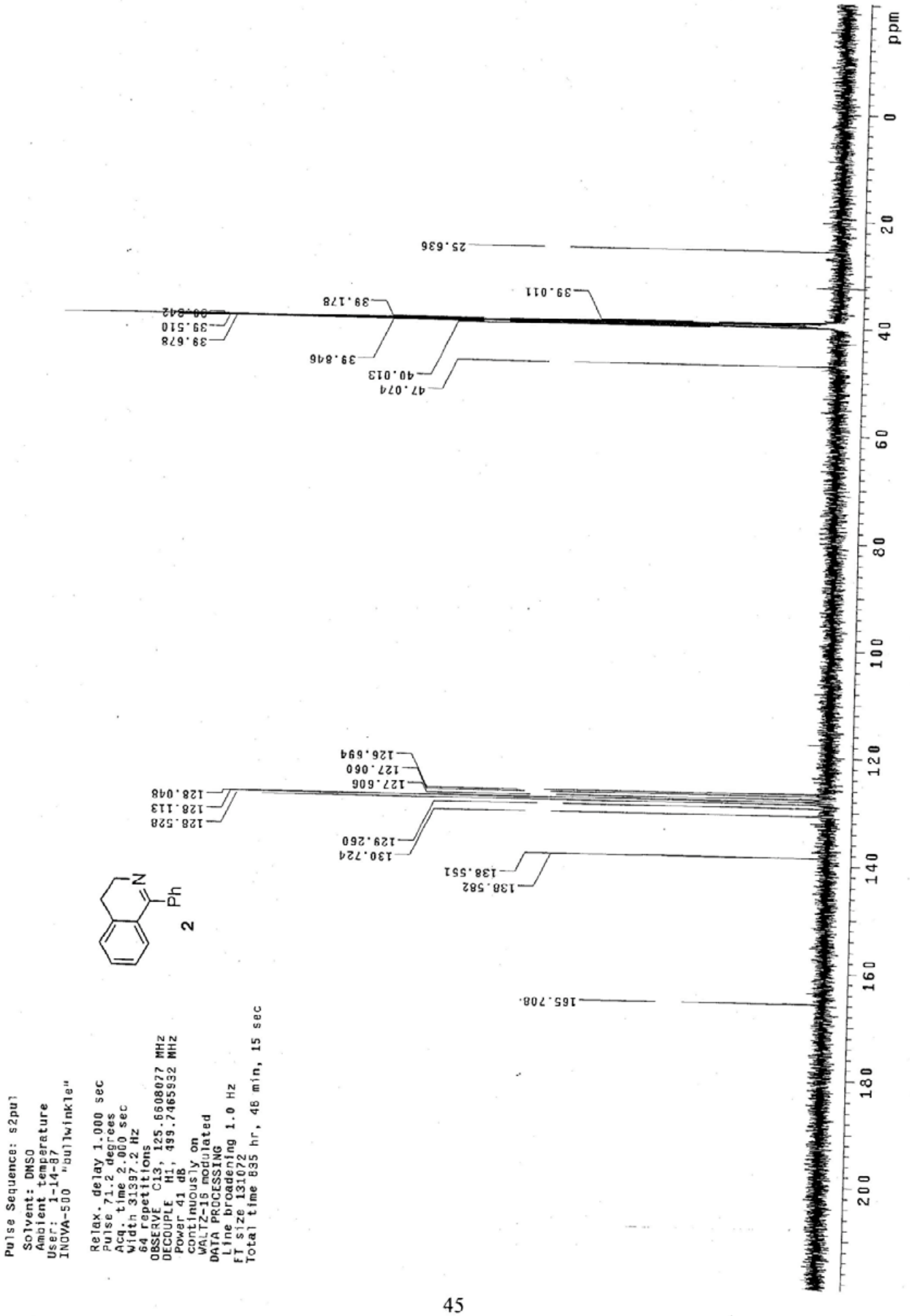

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
80 repetitions
OBSERVE C13, 125.7822125 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes
Cl
N
9Hx
10
170.089
140.372
135.776
127.853
127.276
127.051
126.168
77.482
77.225
76.974
46.735
42.267
31.368
26.676
26.411
26.388
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
4 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec

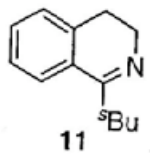



2

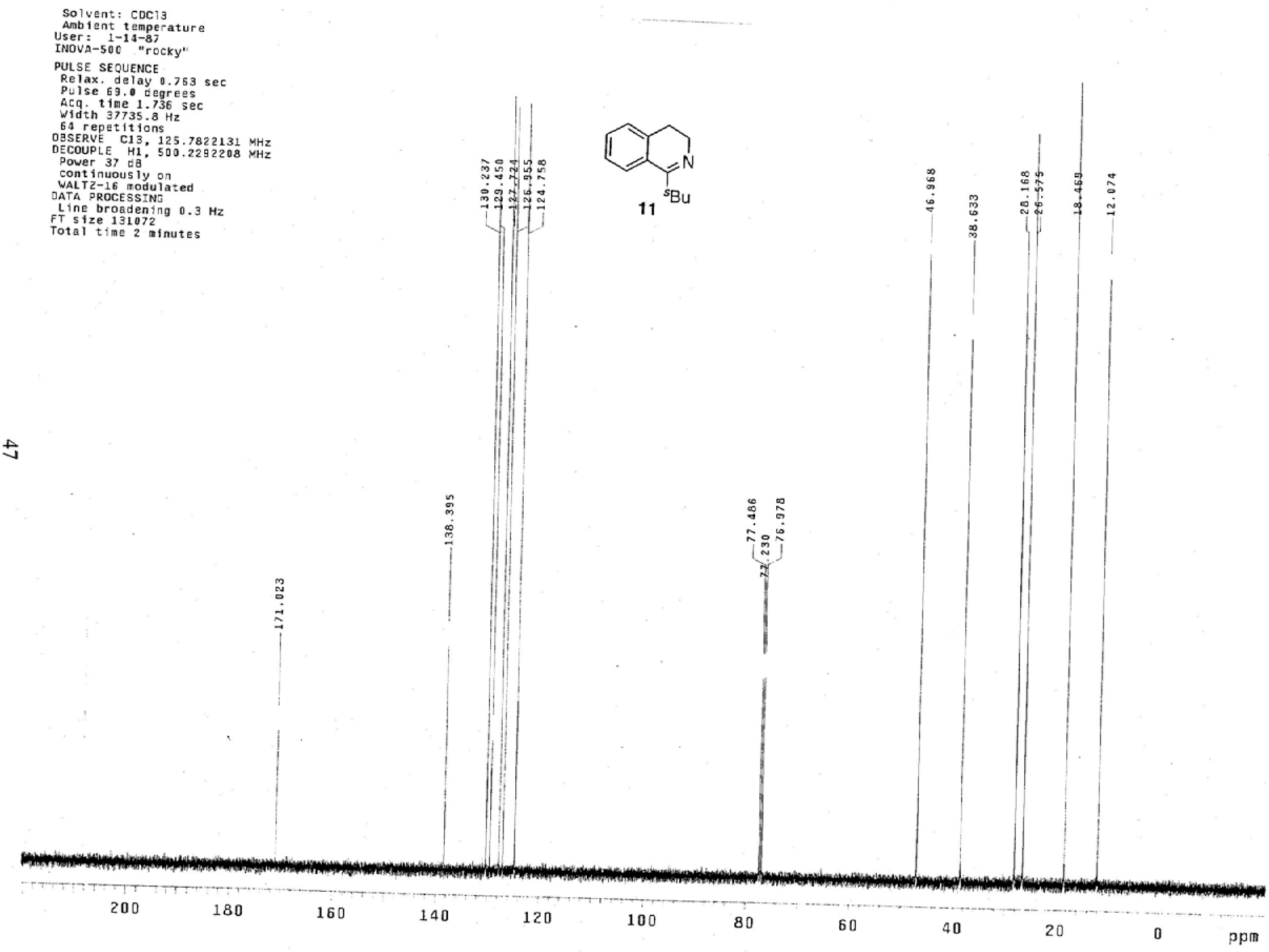

Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 1.000 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
64 repetitions
OBSERVE C13, 125.6608077 MHz
DECOUPLE H1, 499.7465932 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 835 hr, 46 min, 15 sec
N
Ph
2
165.708
138.582
138.551
130.724
129.260
128.528
128.113
128.048
127.606
127.060
126.694
47.074
40.013
39.846
39.678
39.510
39.342
39.178
39.011
25.636
ppm
200
180
160
140
120
100
80
60
40
20
0

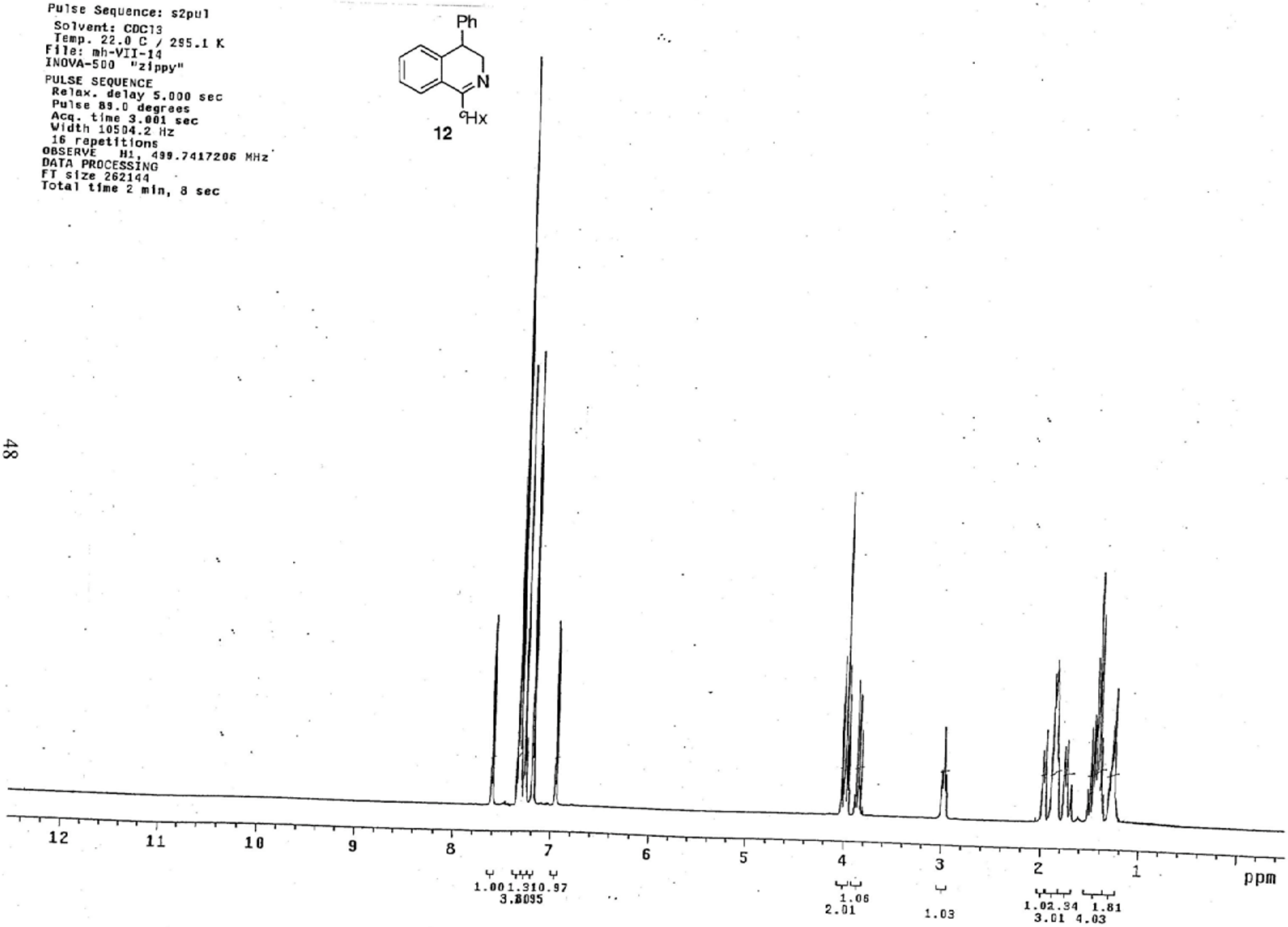
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

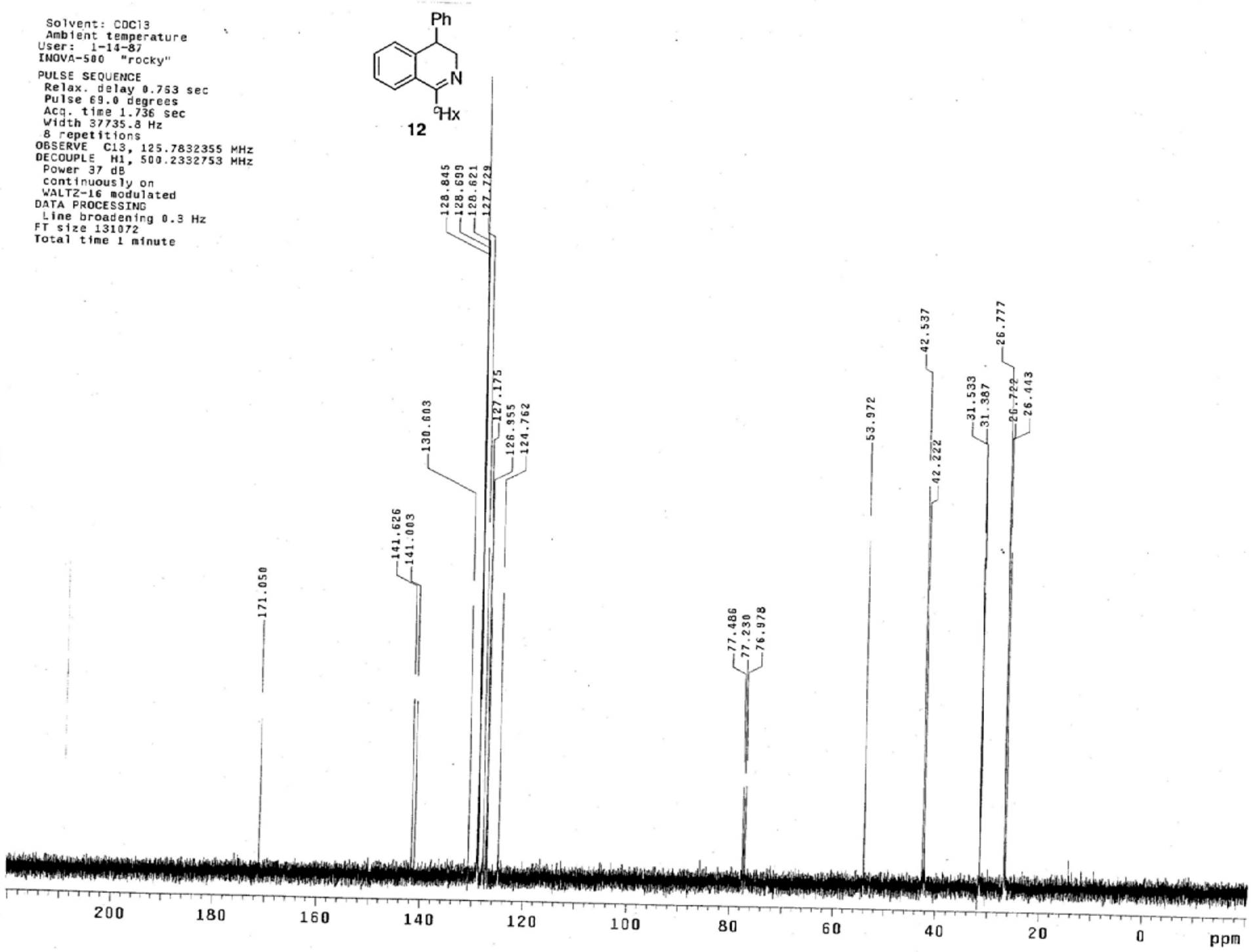
Relax. delay 2.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
13 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec



11

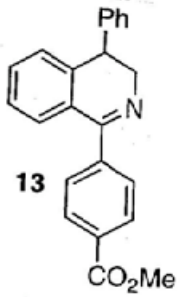

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
64 repetitions
OBSERVE C13, 125.7822131 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2 minutes
N
sBu
11
171.023
138.395
130.237
129.450
127.724
126.955
124.758
77.486
77.230
76.978
46.968
38.633
28.168
26.575
18.469
12.074
200
180
160
140
120
100
80
60
40
20
0
ppm

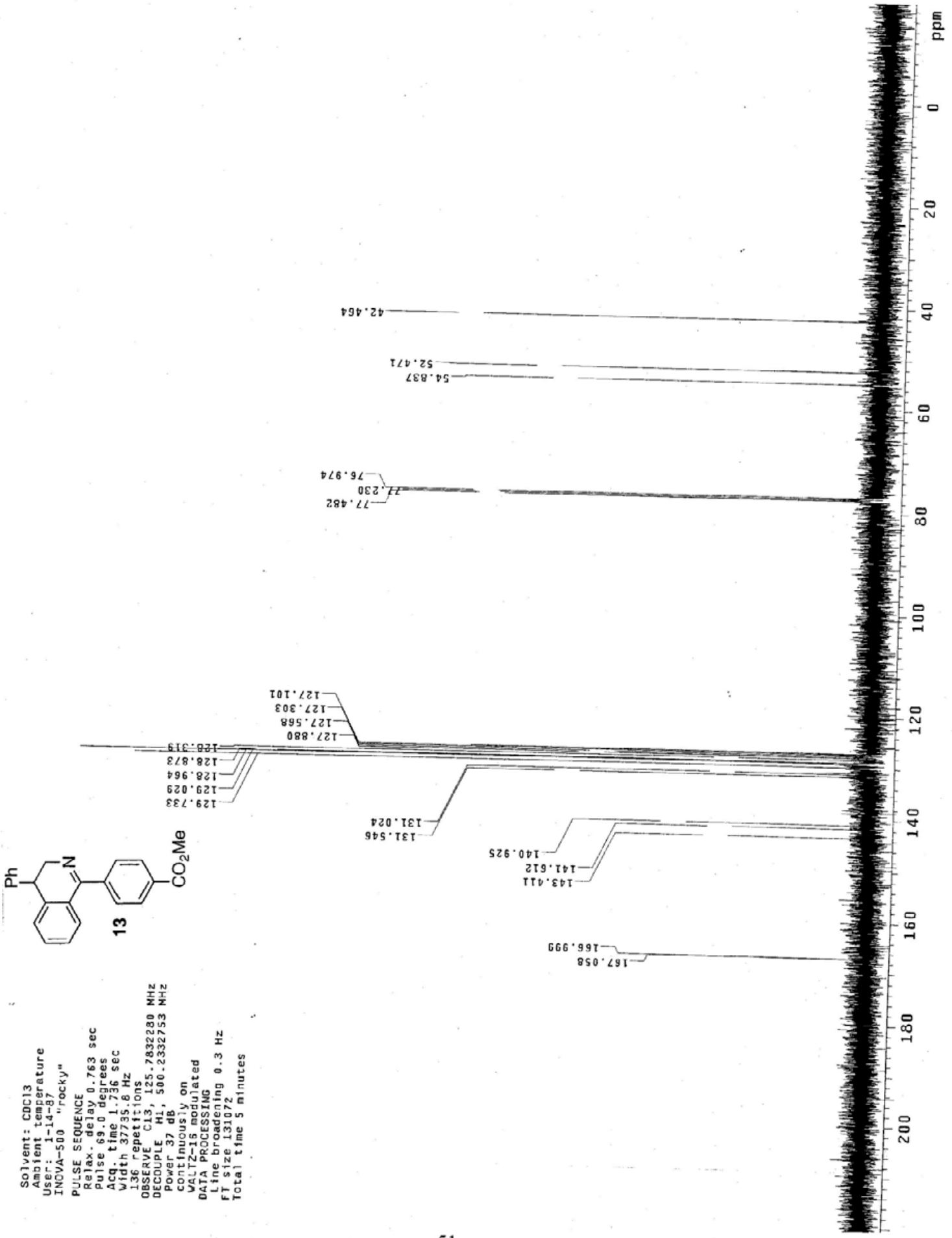

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: mh-VII-14
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec
Ph
N
cHx
12
1.00 1.31 0.97
3.8095
1.06
2.01
1.03
1.02 3.34 1.81
3.01 4.03
12
11
10
9
8
7
6
5
4
3
2
1
ppm


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
8 repetitions
OBSERVE C13, 125.7832355 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
Ph
N
9Hx
12
128.845
128.699
128.621
127.729
127.175
126.955
124.762
130.603
141.626
141.003
171.050
77.486
77.230
76.978
53.972
42.537
42.222
31.533
31.387
26.777
26.722
26.443
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

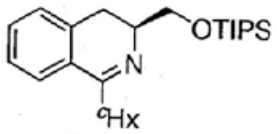
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
136 repetitions
OBSERVE C13, 125.7832280 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 5 minutes
Ph
N
CO2Me
13
167.058
166.999
143.411
141.612
140.925
131.546
131.024
129.733
129.029
128.964
128.873
128.319
127.880
127.568
127.303
127.101
77.482
77.230
76.974
54.837
52.471
42.464
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

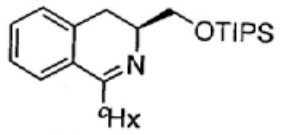
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
8 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




14

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-VII-152
INOVA-500 "zippy"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
176 repetitions
OBSERVE C13, 125.7822113 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 131072
Total time 696 hr, 41 min, 12 sec

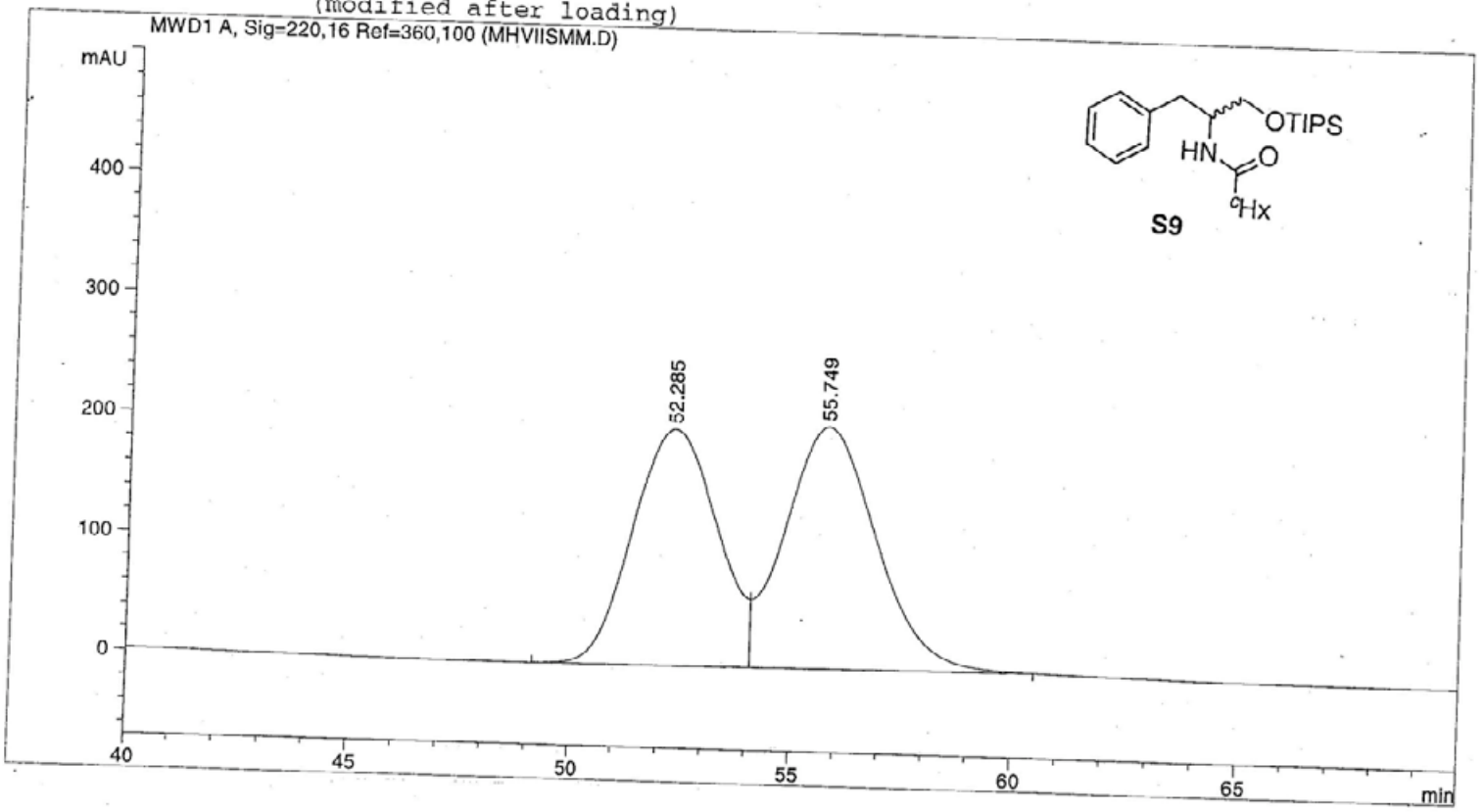



14

Injection Date : 1/10/2008 4:51:15 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 20
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 1/10/2008 4:50:20 PM
Analysis Method : C:\HPCHEM\2\METHODS\JUSTIN.M
Last changed : 1/10/2008 6:04:34 PM
(modified after loading)




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 52.285 | BV | 1.8294 | 2.62919e4 | 197.72366 | 47.3324 |
| 2 | 55.749 | VB | 1.9654 | 2.92555e4 | 202.50642 | 52.6676 |
| Totals : | | | | 5.55474e4 | 400.23009 | |

Results obtained with enhanced integrator!

*** End of Report ***

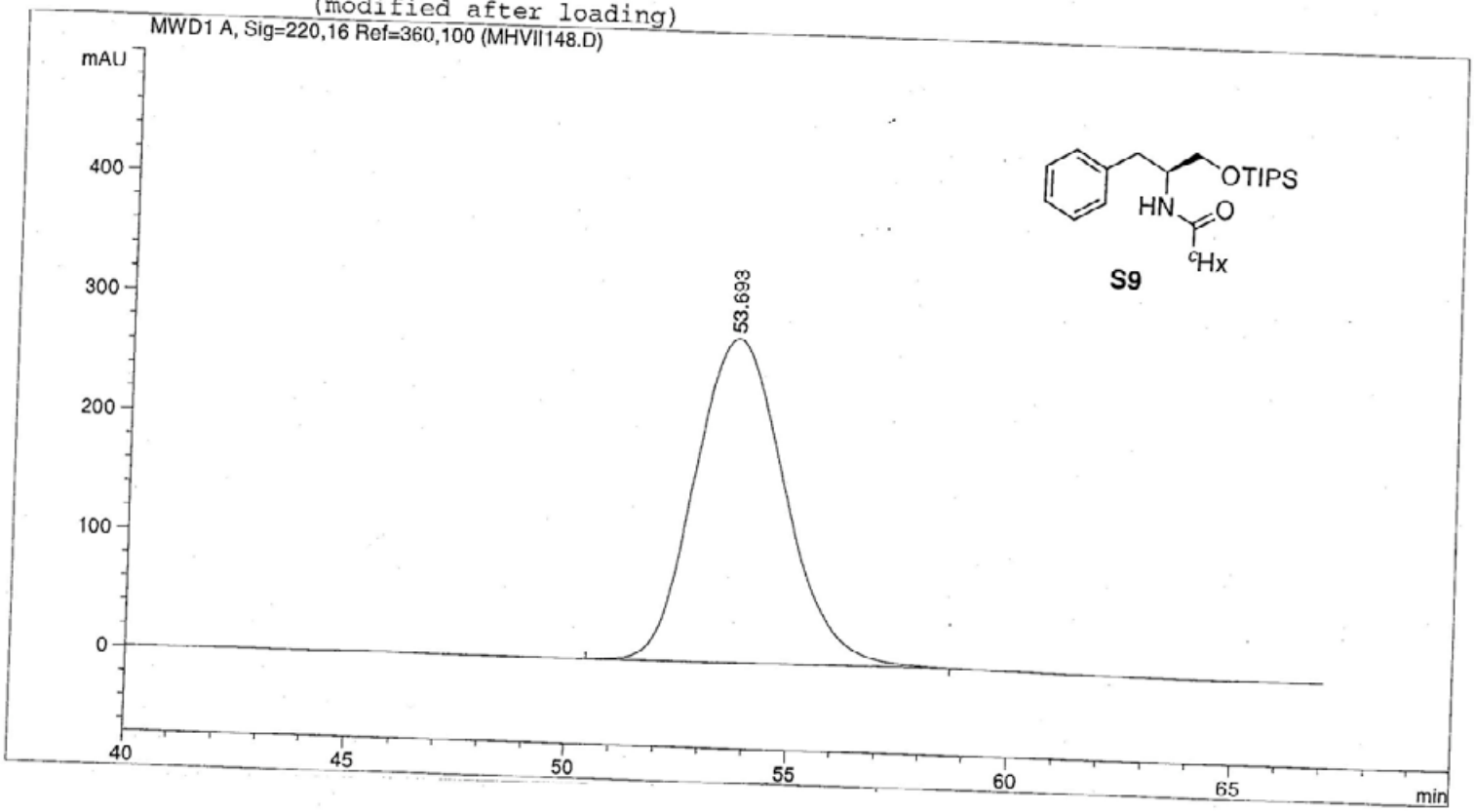


strument 2 1/10/2008 6:04:40 PM

Injection Date : 1/10/2008 6:04:48 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 18
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 1/10/2008 4:50:20 PM
Analysis Method : C:\HPCHEM\2\METHODS\JUSTIN.M
Last changed : 1/10/2008 7:13:16 PM
(modified after loading)




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 53.693 | BB | 1.8004 | 3.84635e4 | 272.55997 | 100.0000 |
| Totals : | | | | 3.84635e4 | 272.55997 | |

Results obtained with enhanced integrator!

*** End of Report ***

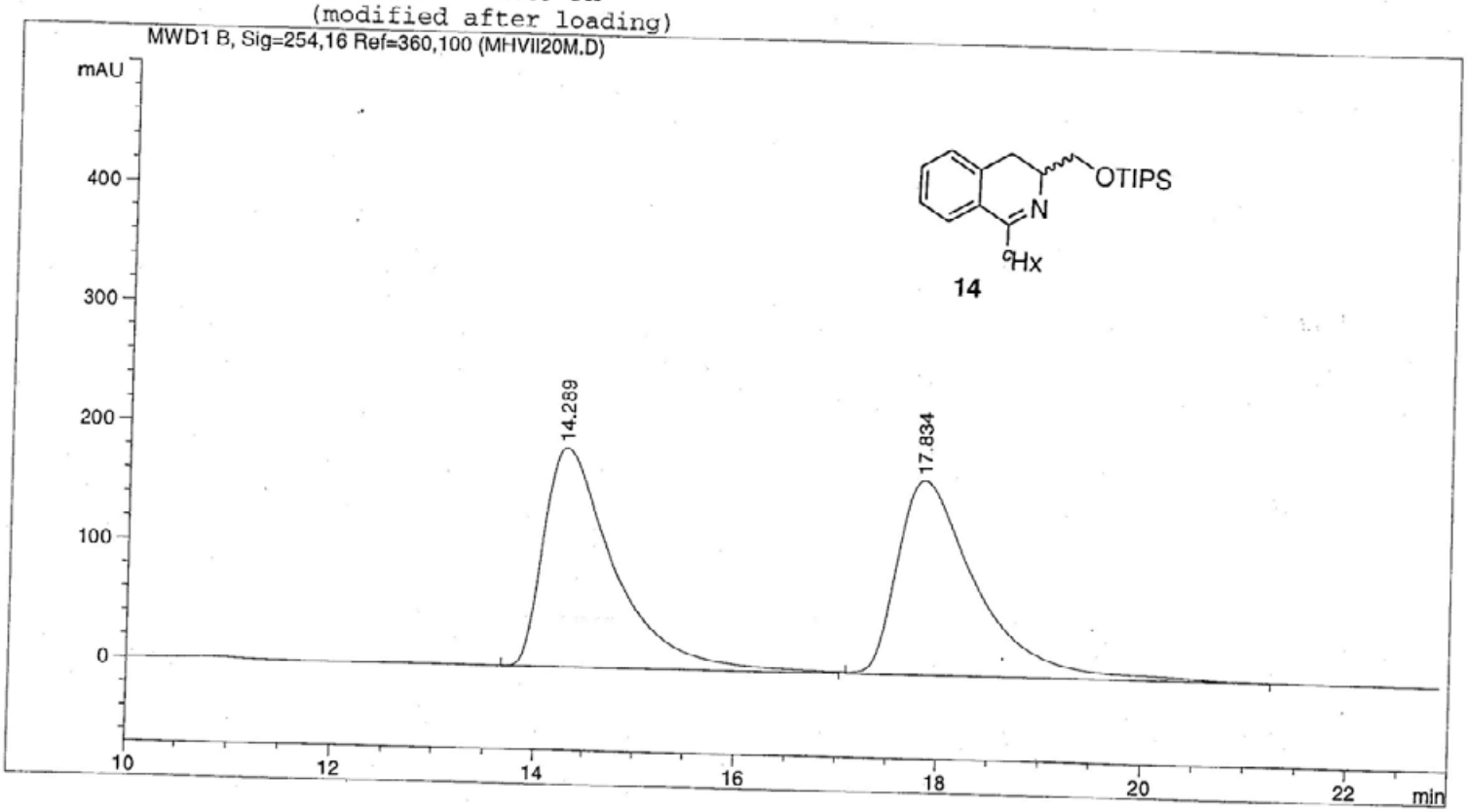


strument 2 1/10/2008 7:13:50 PM

Injection Date : 1/9/2008 3:30:45 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 10
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 1/9/2008 2:50:16 PM
Analysis Method : C:\HPCHEM\2\METHODS\JUSTIN.M
Last changed : 1/9/2008 3:54:59 PM
(modified after loading)




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.289 | BB | 0.7323 | 9075.85254 | 183.74214 | 50.3283 |
| 2 | 17.834 | BB | 0.8213 | 8957.44141 | 162.95314 | 49.6717 |
| Totals : | | | | 1.80333e4 | 346.69528 | |

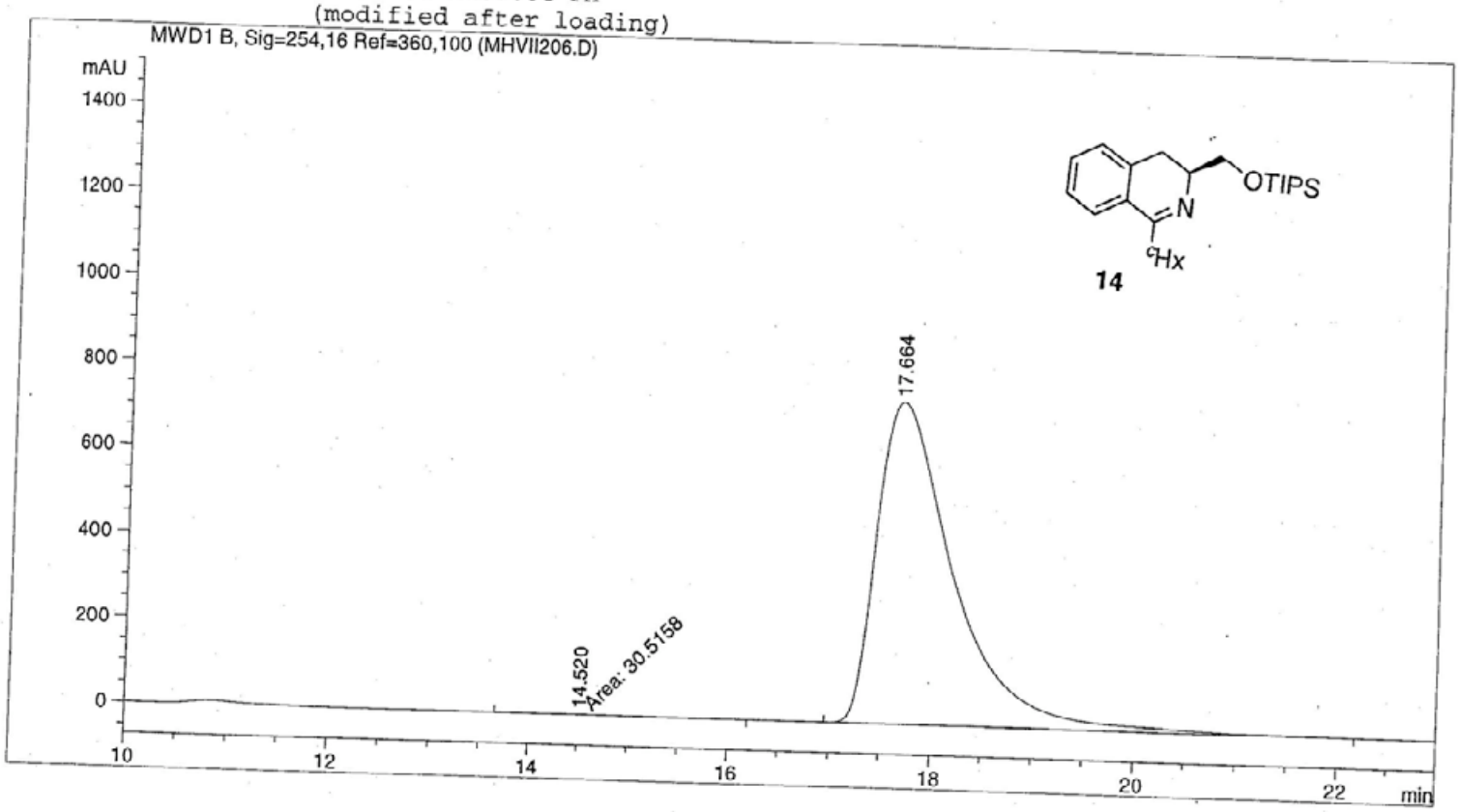
Results obtained with enhanced integrator!

*** End of Report ***

Injection Date : 1/9/2008 2:51:12 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 7
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 1/9/2008 2:50:16 PM
Analysis Method : C:\HPCHEM\2\METHODS\JUSTIN.M
Last changed : 1/9/2008 3:57:04 PM
(modified after loading)




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.520 | MM | 1.0958 | 30.51582 | 4.64142e-1 | 0.0770 |
| 2 | 17.664 | PB | 0.7885 | 3.95936e4 | 749.21863 | 99.9230 |
| Totals : | | | | 3.96241e4 | 749.68277 | |

Results obtained with enhanced integrator!

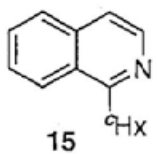
*** End of Report ***



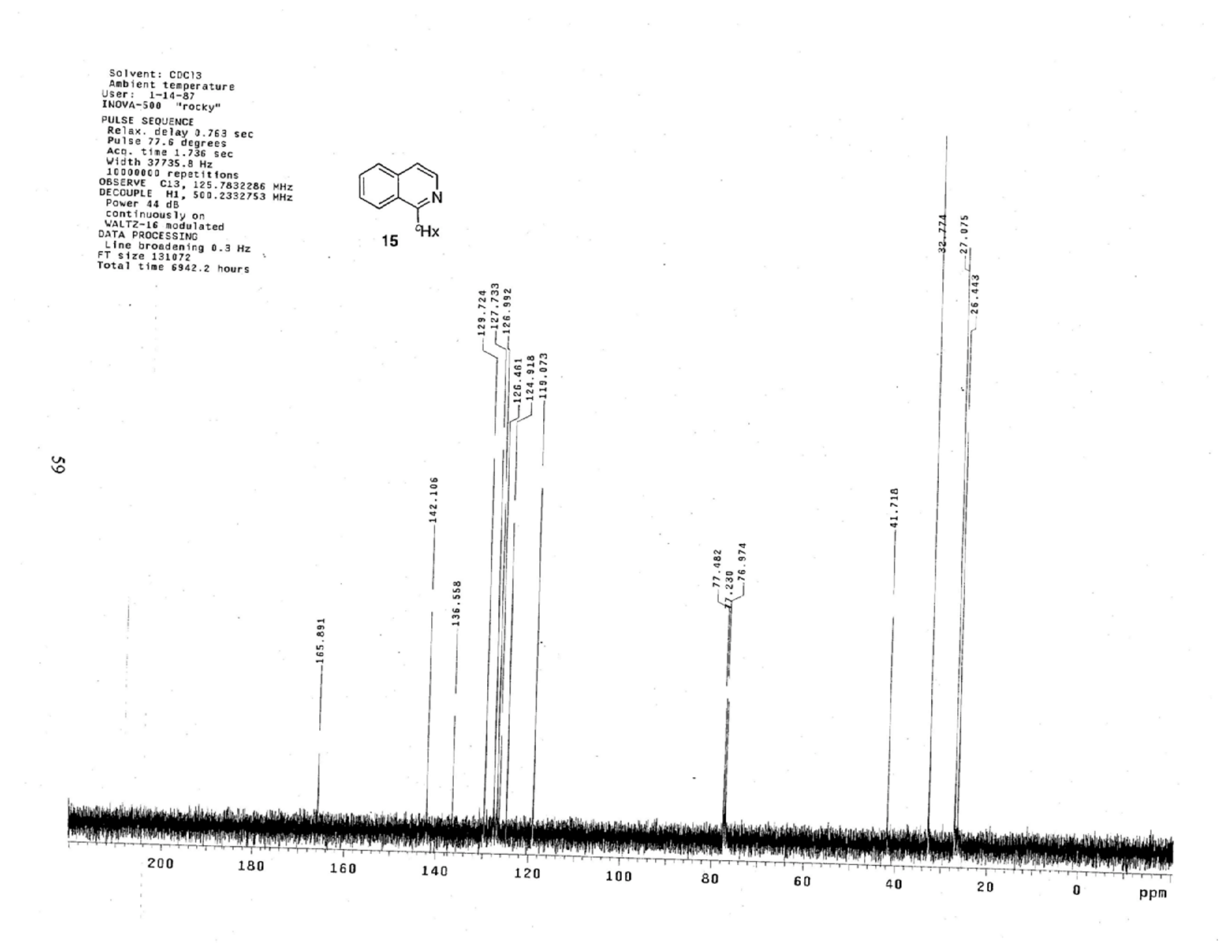
Instrument 2 1/9/2008 3:57:09 PM

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

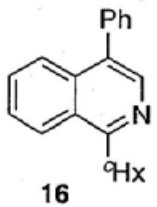



15

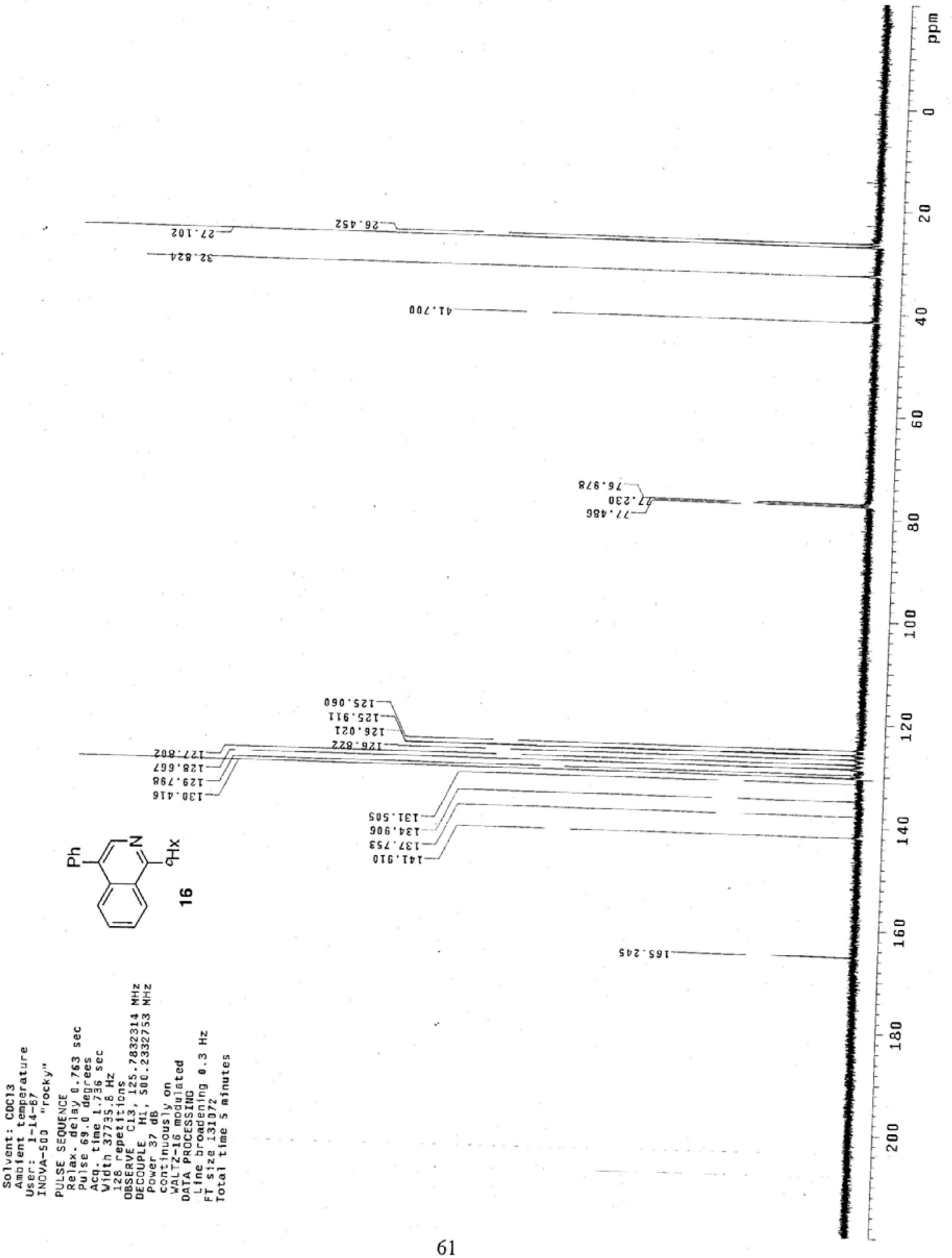

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 77.6 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
10000000 repetitions
OBSERVE C13, 125.7832286 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6942.2 hours
N
9Hx
15
165.891
142.106
136.558
129.724
127.733
126.992
126.461
124.918
119.073
77.482
77.230
76.974
41.718
32.774
27.075
26.443
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

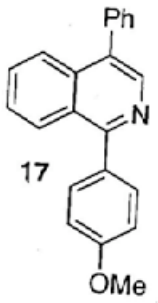


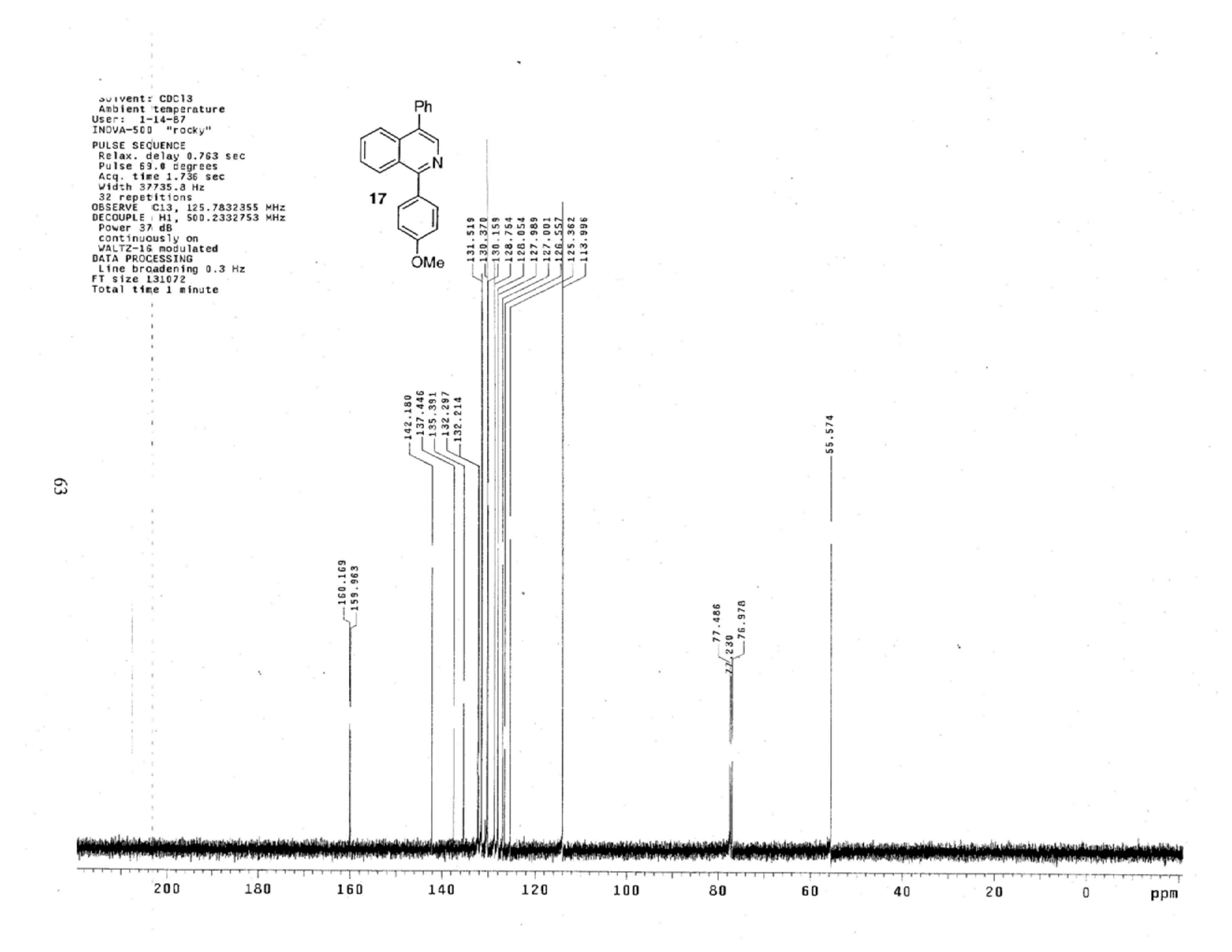

16


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
128 repetitions
OBSERVE C13, 125.7832314 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 5 minutes
Ph
N
Hx
16
165.245
141.910
137.753
134.906
131.505
130.416
129.798
128.667
127.802
126.822
126.021
125.911
125.060
77.486
77.230
76.978
41.700
32.824
27.102
26.452
ppm
0
20
40
60
80
100
120
140
160
180
200

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

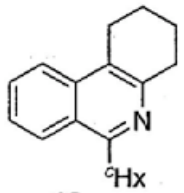
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



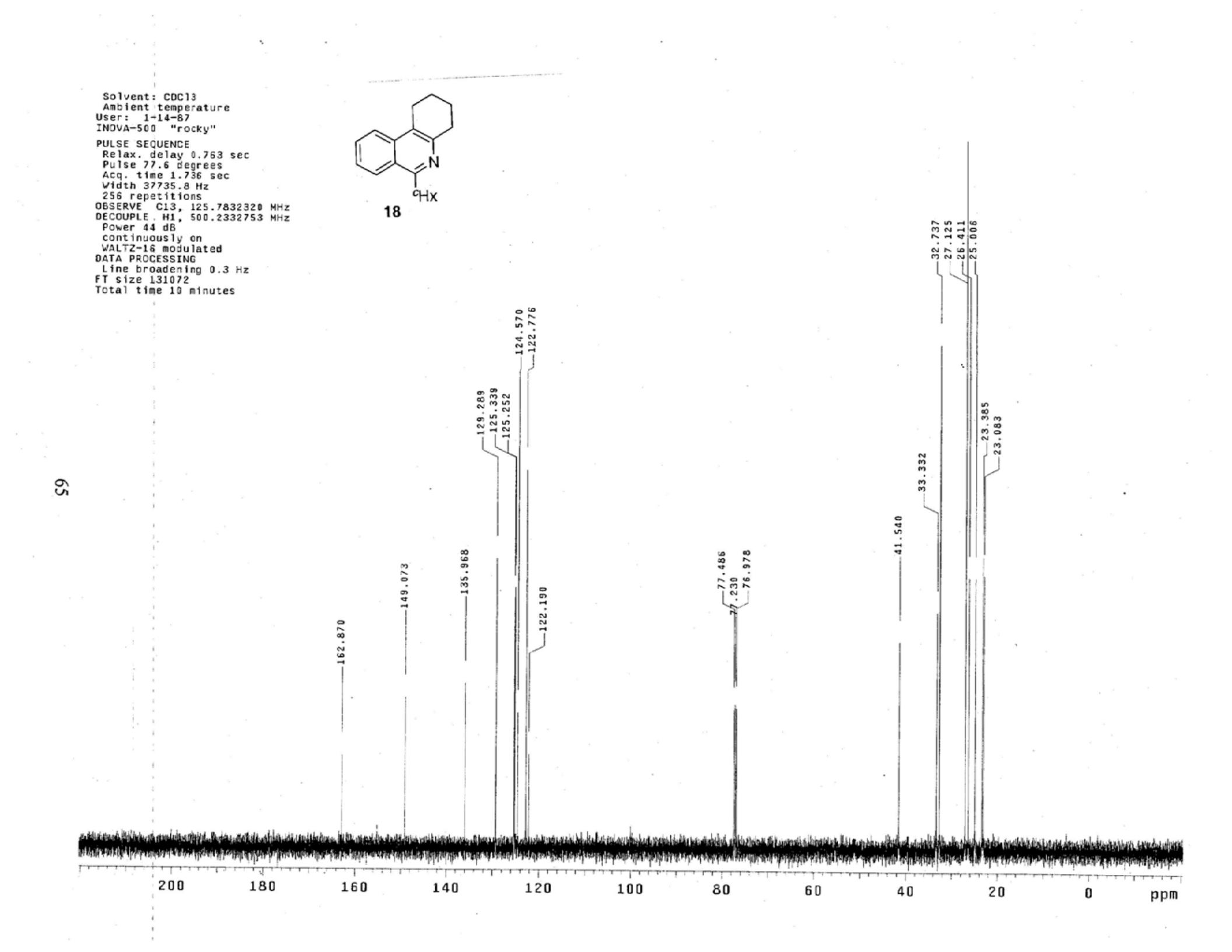

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
32 repetitions
OBSERVE C13, 125.7832355 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
Ph
N
17
OMe
131.519
130.370
130.159
128.754
128.054
127.989
127.001
126.557
125.362
113.996
142.180
137.446
135.391
132.297
132.214
160.169
159.963
77.486
77.230
76.978
55.574
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

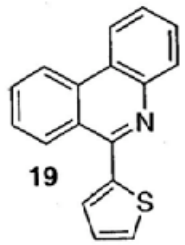



18

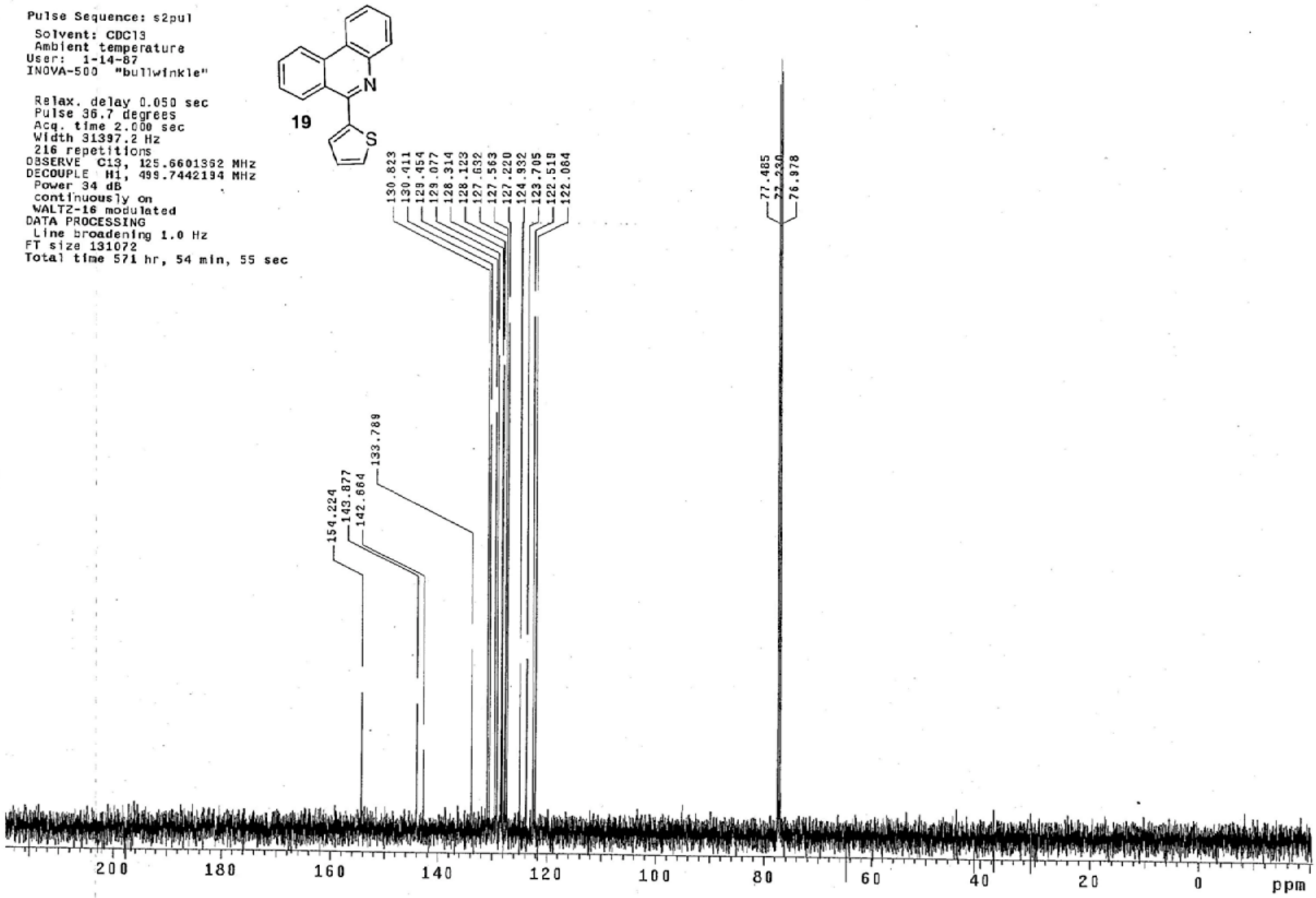

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 77.6 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
256 repetitions
OBSERVE C13, 125.7832320 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 10 minutes
N
cHx
18
162.870
149.073
135.968
129.289
125.339
125.252
124.570
122.776
122.190
77.486
77.230
76.978
41.540
33.332
32.737
27.125
26.411
25.006
23.385
23.083
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

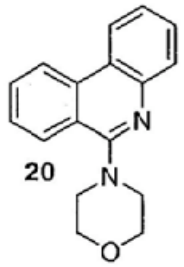


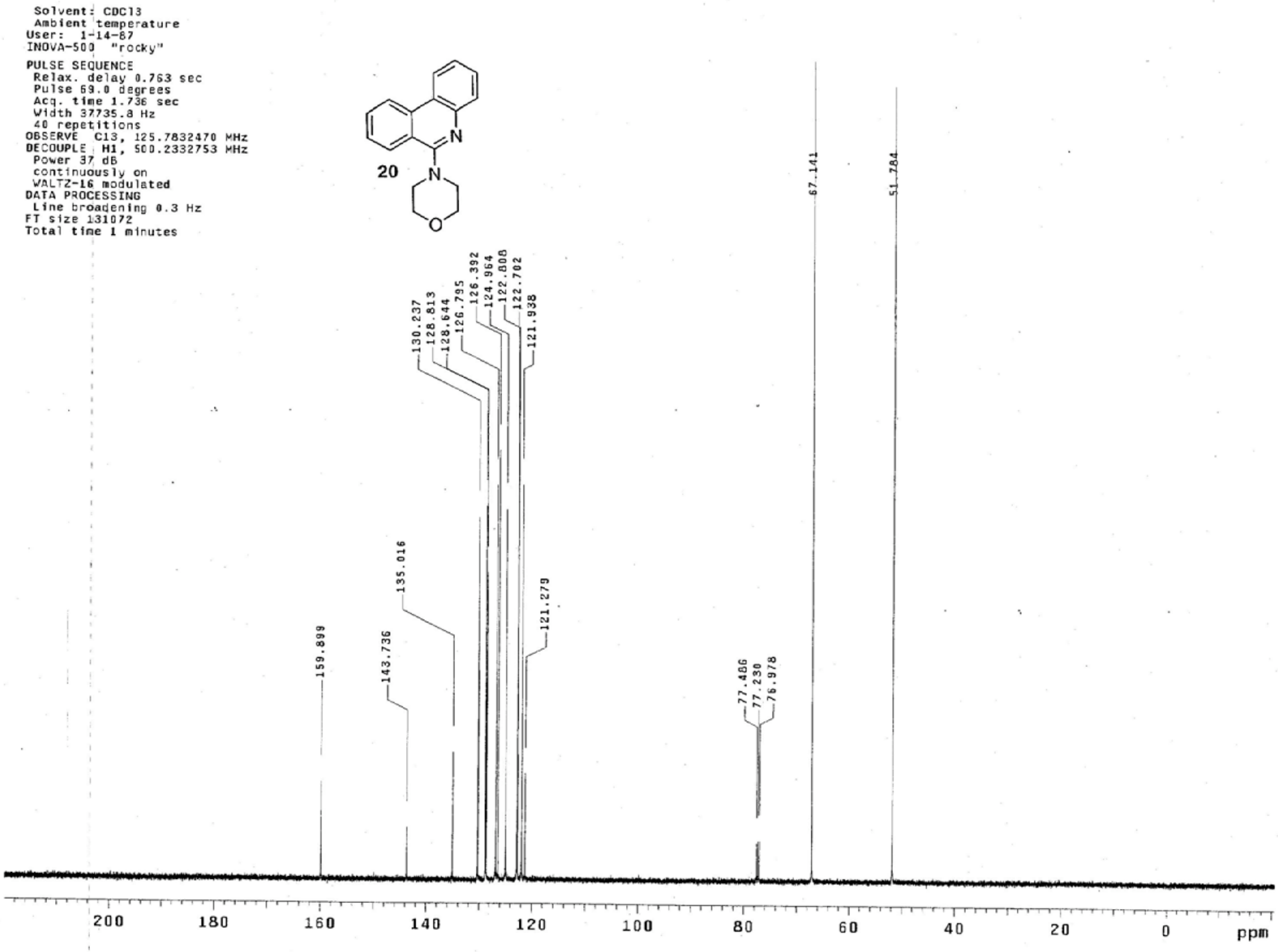

19

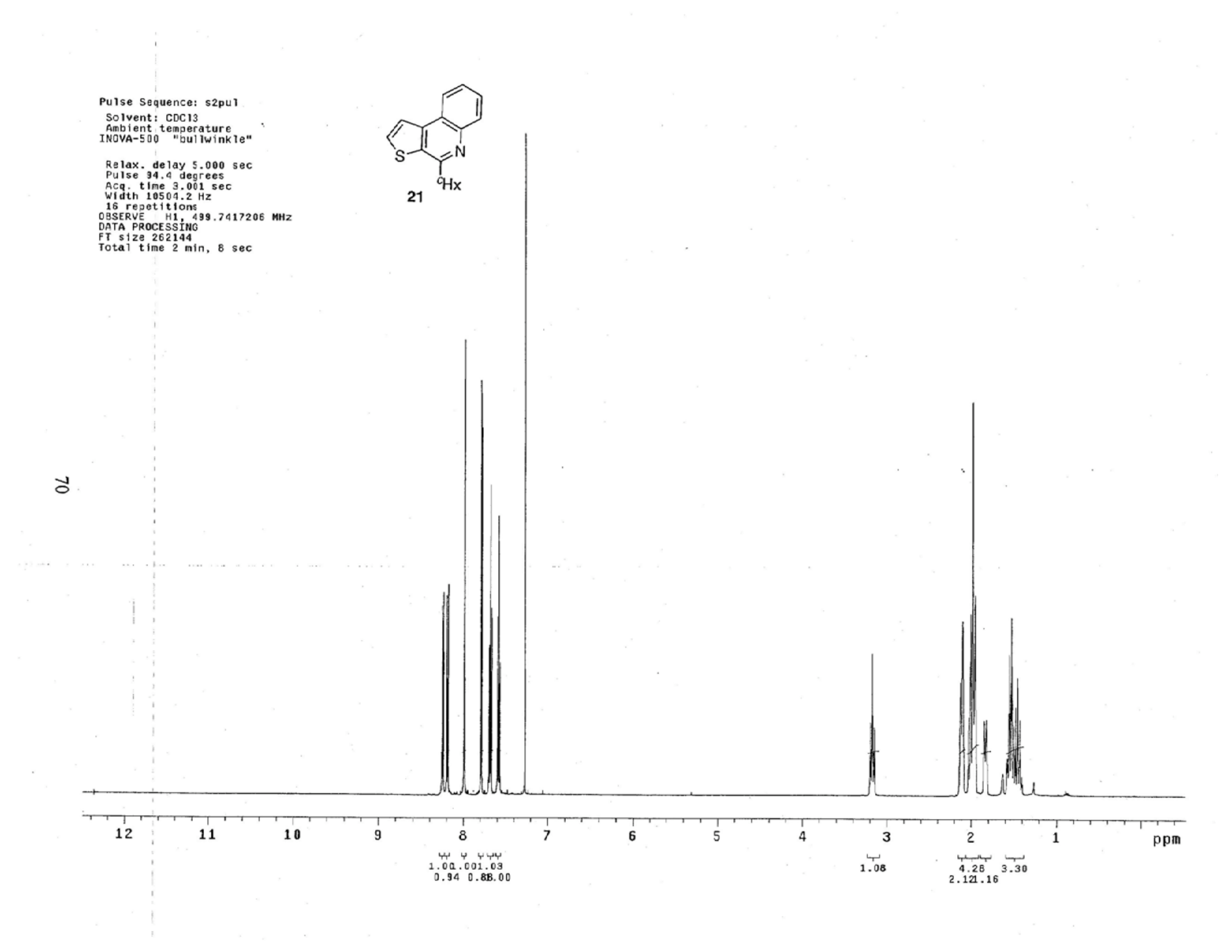

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.050 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
216 repetitions
OBSERVE C13, 125.6601352 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 571 hr, 54 min, 55 sec
19
N
S
130.823
130.411
129.454
129.077
128.314
128.123
127.632
127.563
127.220
124.932
123.705
122.519
122.084
154.224
143.877
142.664
133.789
77.485
77.230
76.978
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

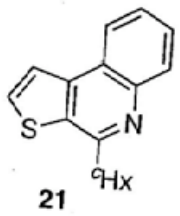



Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
40 repetitions
OBSERVE C13, 125.7832470 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes
20
N
N
O
67.141
51.784
130.237
128.813
128.644
126.795
126.392
124.964
122.808
122.702
121.938
121.279
159.899
143.736
135.016
77.486
77.230
76.978
200
180
160
140
120
100
80
60
40
20
0
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec
S
N
9Hx
21
70
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.03
0.94
0.88
3.00
1.08
4.28
3.30
2.12
1.16

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

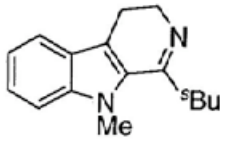
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 77.6 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
88 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes



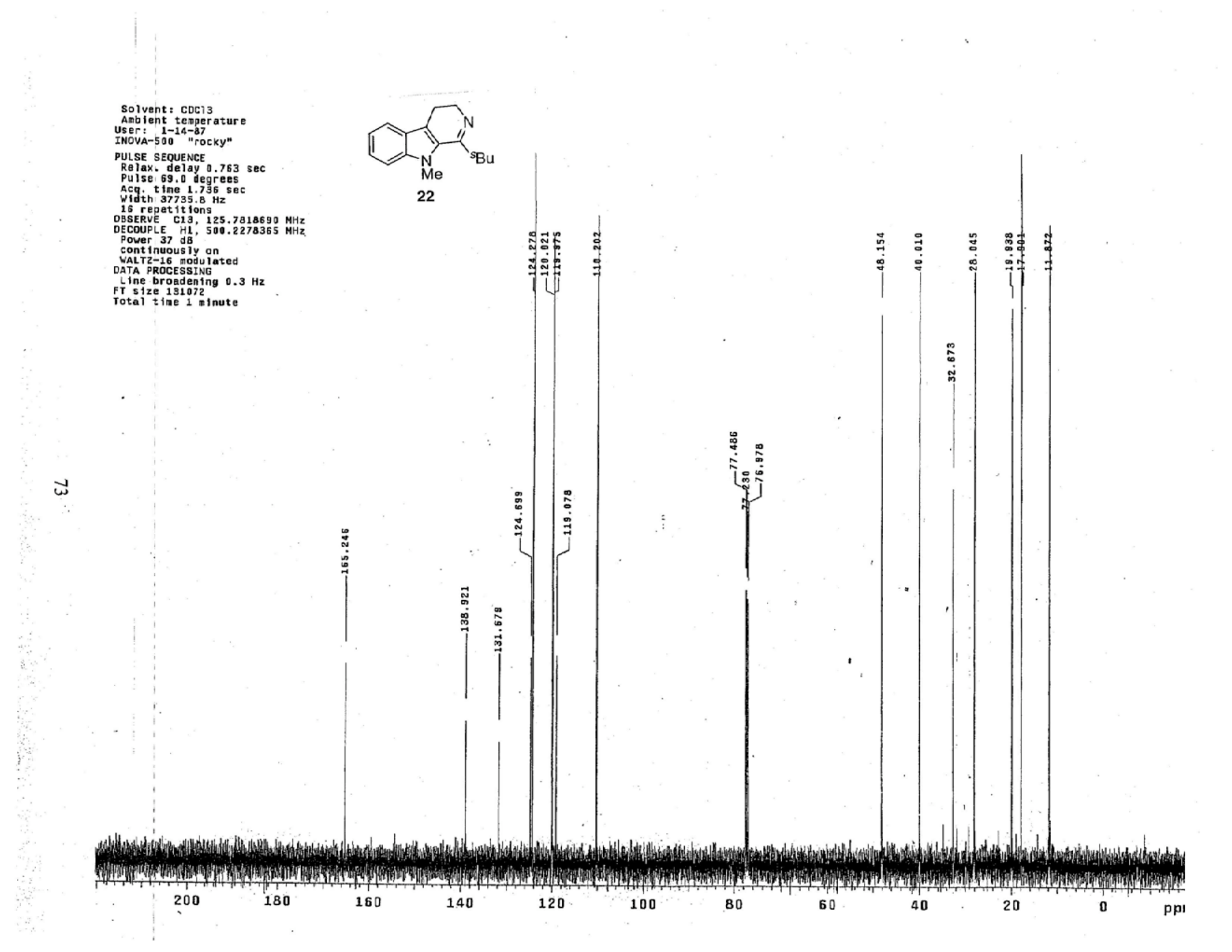

21

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

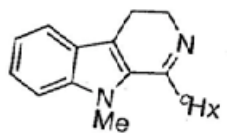



22


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
16 repetitions
OBSERVE C13, 125.7818690 MHz
DECOUPLE H1, 500.2278365 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
N
sBu
N
Me
22
165.245
138.921
131.679
124.699
124.278
120.021
119.078
110.202
77.486
77.230
76.978
48.154
40.010
32.673
28.045
19.938
17.001
11.872
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

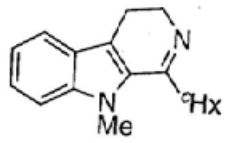
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




**23**

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

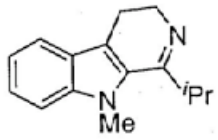
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 59.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
88 repetitions
OBSERVE C13, 125.7822125 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes




23

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

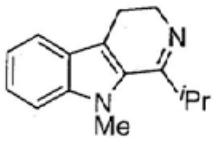
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




**24**

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

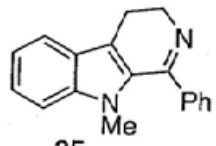
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
120 repetitions
OBSERVE C13, 125.7822131 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 5 minutes



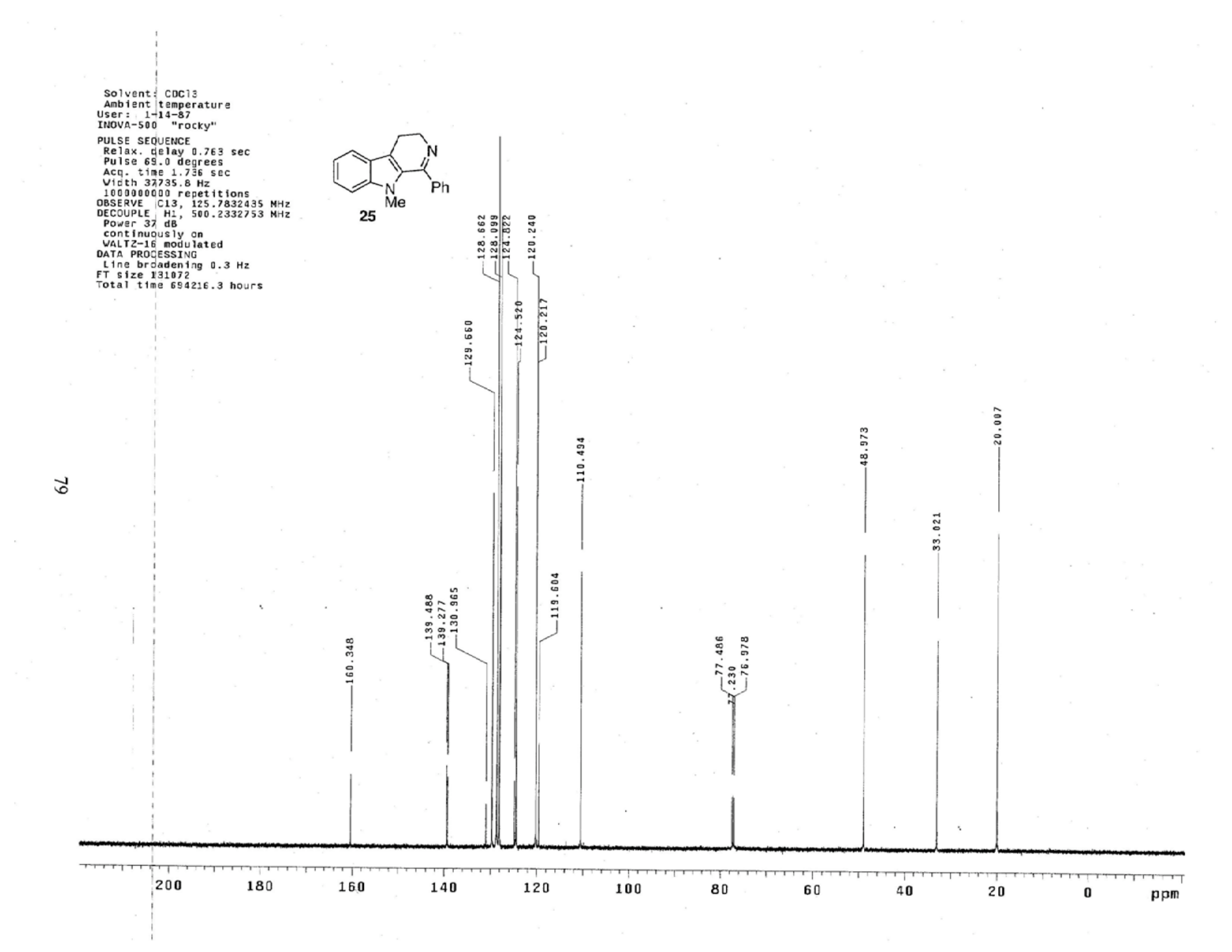

24

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
8 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

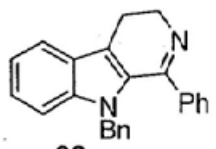



25


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
1000000000 repetitions
OBSERVE C13, 125.7832435 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 694216.3 hours
N
Ph
N
Me
25
128.662
128.099
124.822
120.240
129.660
124.520
120.217
110.494
119.604
139.488
139.277
130.965
160.348
77.486
77.230
76.978
48.973
33.021
20.007
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

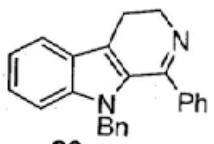
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




26

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

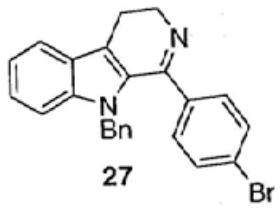
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
80 repetitions
OBSERVE C13, 125.7822125 MHz
DECOUPLE H1, 500.2292208 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes



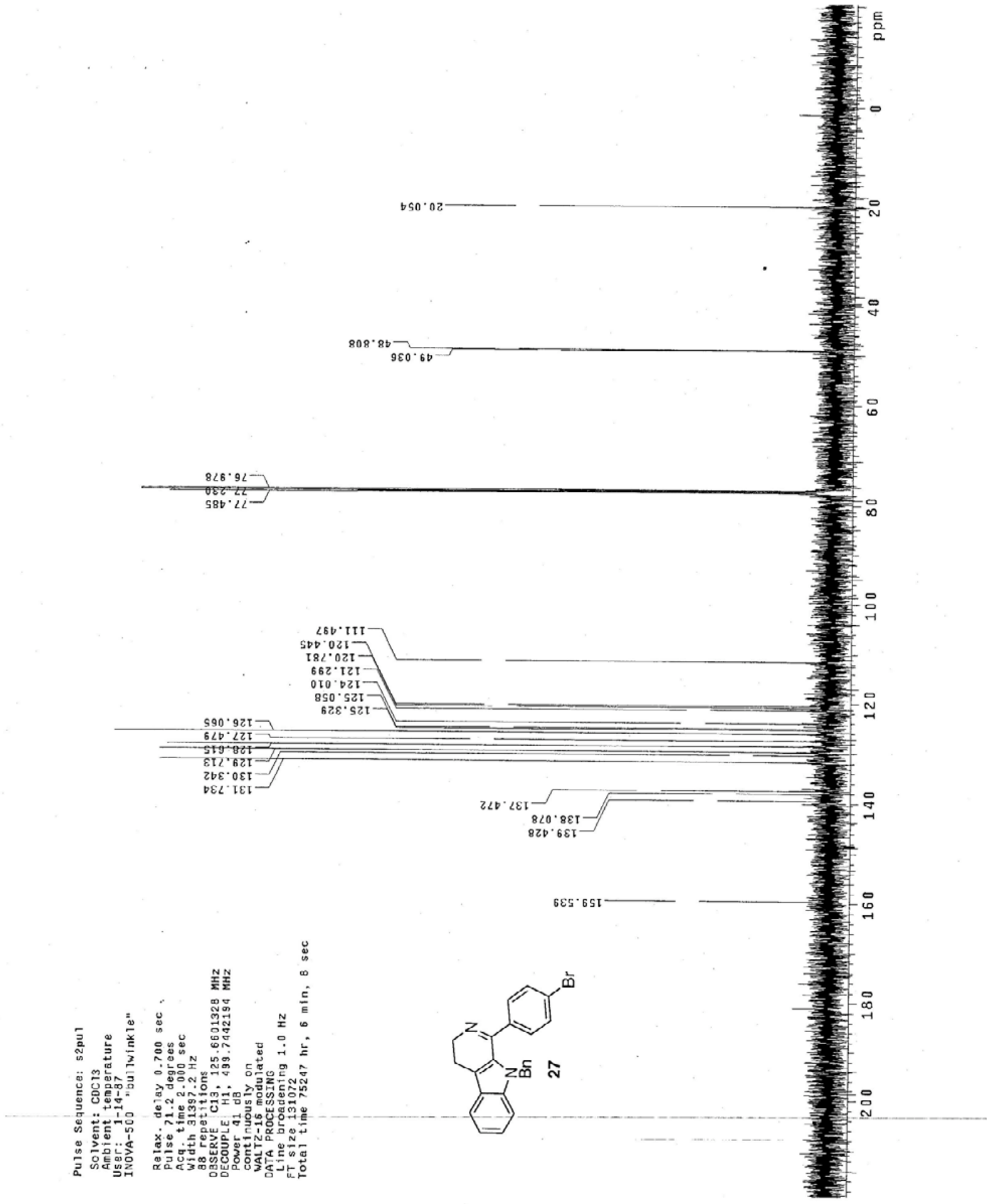

26

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 59.1 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

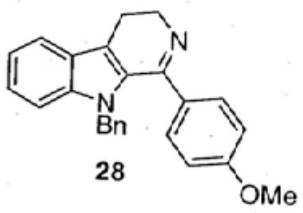


27

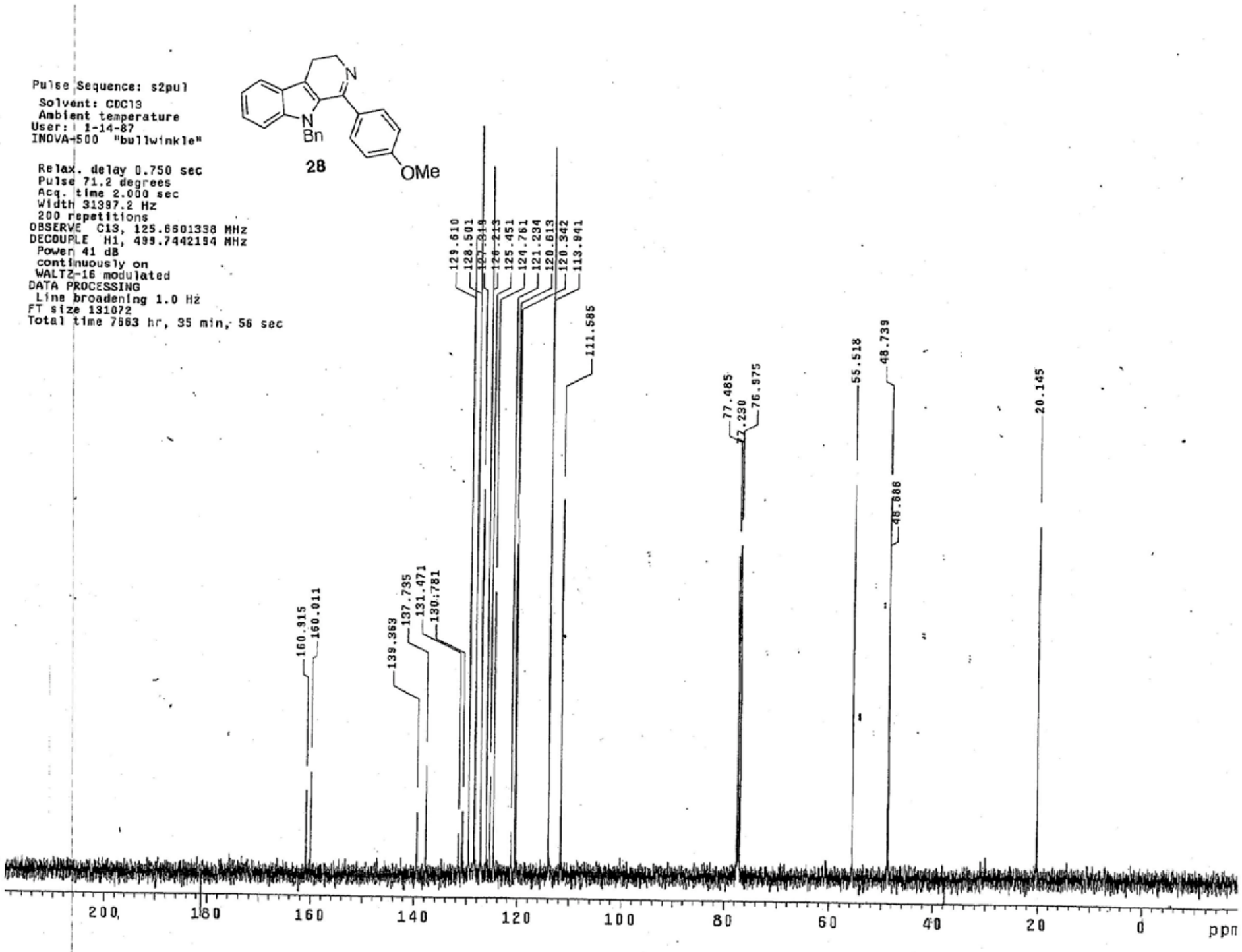

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.700 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
88 repetitions
OBSERVE C13, 125.6601328 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 75247 hr, 6 min, 8 sec
20.054
48.808
49.036
76.878
77.230
77.485
111.497
120.445
120.781
121.299
124.010
125.058
125.329
126.065
127.479
128.615
129.713
130.342
131.734
137.472
138.078
139.428
159.539
Br
N
Bn
N
27
ppm
0
20
40
60
80
100
120
140
160
180
200

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
6 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec

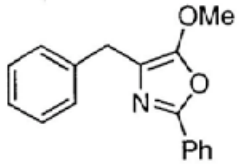



28

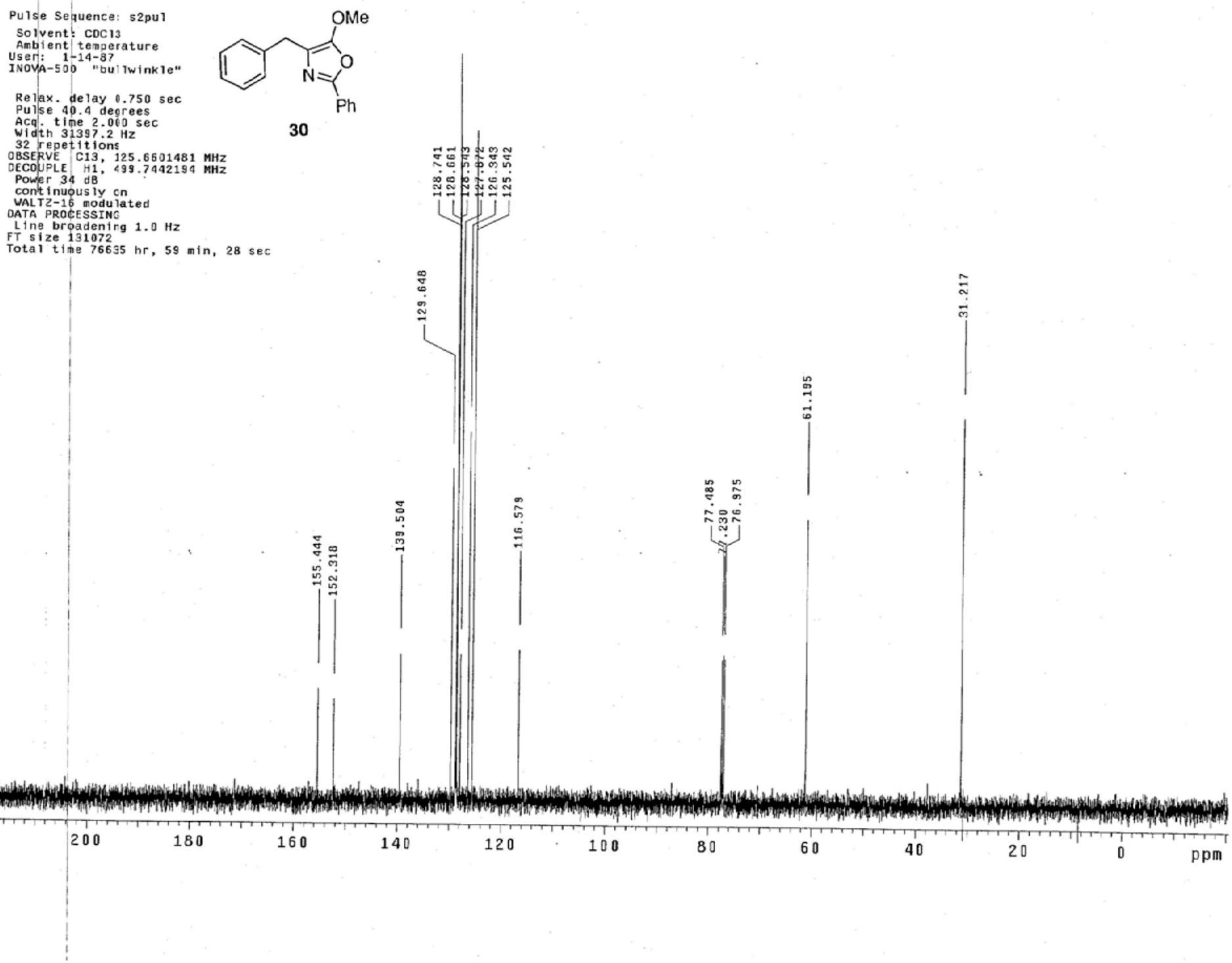

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.750 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31997.2 Hz
200 repetitions
OBSERVE C13, 125.6601338 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 7563 hr, 35 min, 56 sec
N
Bn
28
OMe
129.610
128.501
126.213
125.451
124.761
121.234
120.613
120.342
113.841
111.585
77.485
77.230
76.975
55.518
48.739
48.686
20.145
160.915
160.011
139.363
137.735
131.471
130.781
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

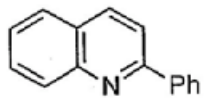
Relax. delay 5.000 sec
Pulse 94.4 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec




**30**

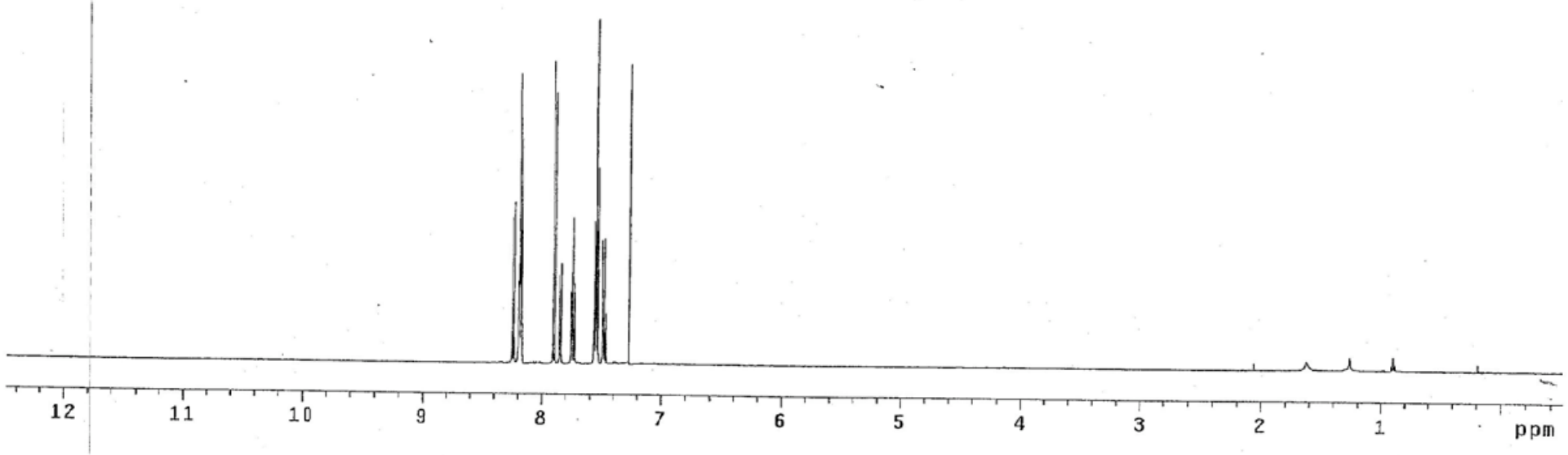

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.750 sec
Pulse 40.4 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
32 repetitions
OBSERVE C13, 125.6501481 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 76635 hr, 59 min, 28 sec
OMe
O
N
Ph
30
128.741
128.661
126.343
125.542
129.648
139.504
116.578
155.444
152.318
77.485
77.230
76.975
61.195
31.217
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537710 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec



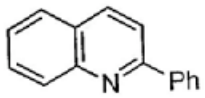

**32**





Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "rocky"

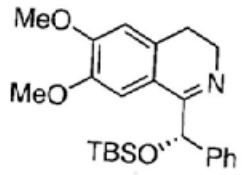
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
100 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes




**32**

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

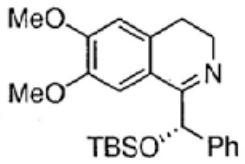
Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
5 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec




34

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1+14-87
INOVA-500 "bullwinkle"

Relax. delay 0.750 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
40 repetitions
OBSERVE C13, 125.6601333 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 7663 hr, 35 min, 56 sec

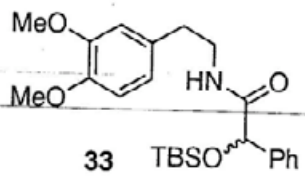



34

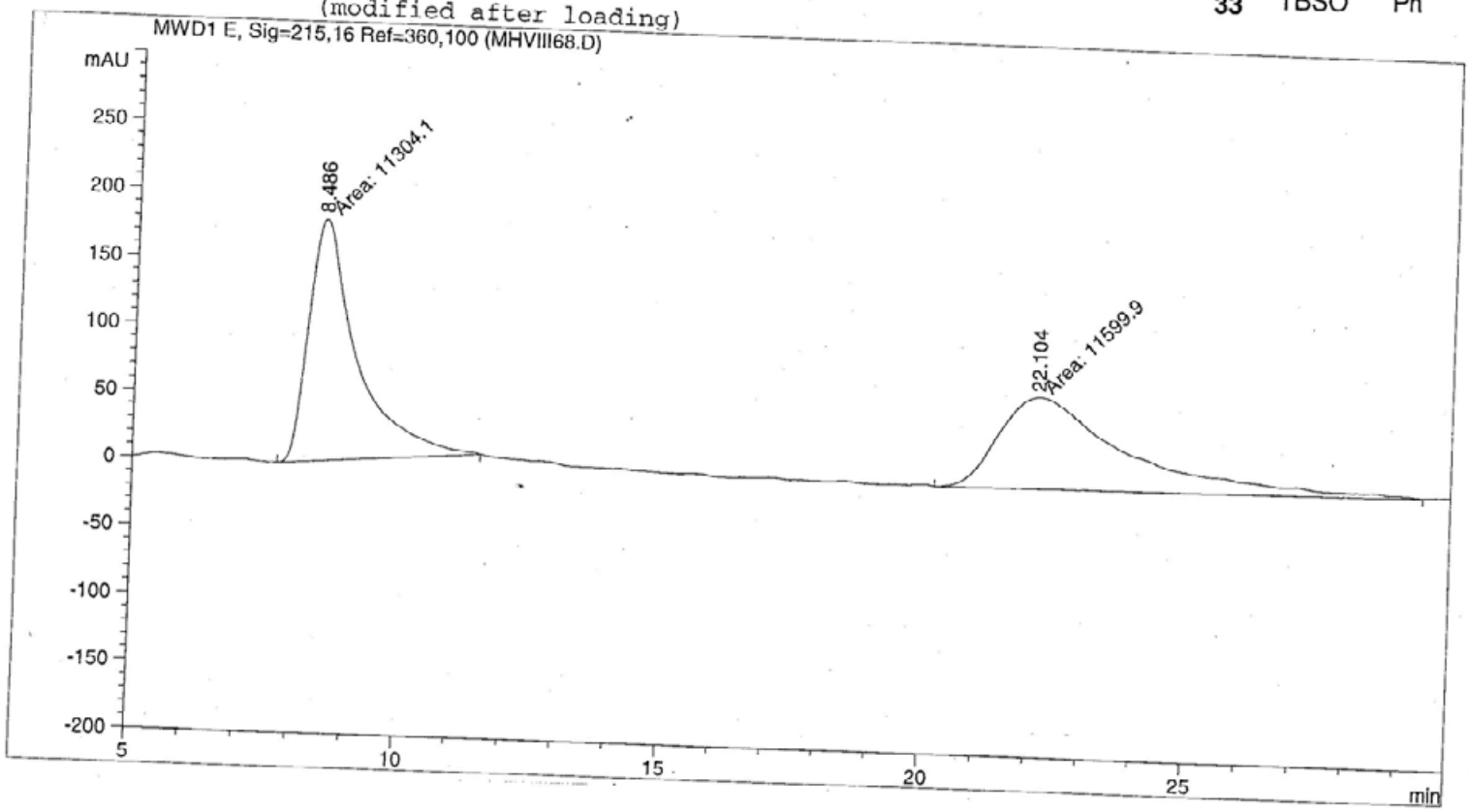
Injection Date : 4/5/2008 6:09:50 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 7
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 4/5/2008 6:08:45 PM
Analysis Method : C:\HPCHEM\2\METHODS\MEDLEY.M
Last changed : 4/5/2008 6:43:57 PM
(modified after loading)




33 TBSO Ph




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 E, Sig=215,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.486 | MM | 1.0498 | 1.13041e4 | 179.47047 | 49.3543 |
| 2 | 22.104 | MM | 2.8252 | 1.15999e4 | 68.42989 | 50.6457 |
| Totals : | | | | 2.29040e4 | 247.90037 | |

Results obtained with enhanced integrator!

*** End of Report ***

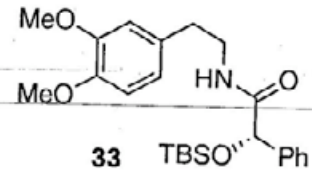


Instrument 2 4/5/2008 6:44:06 PM

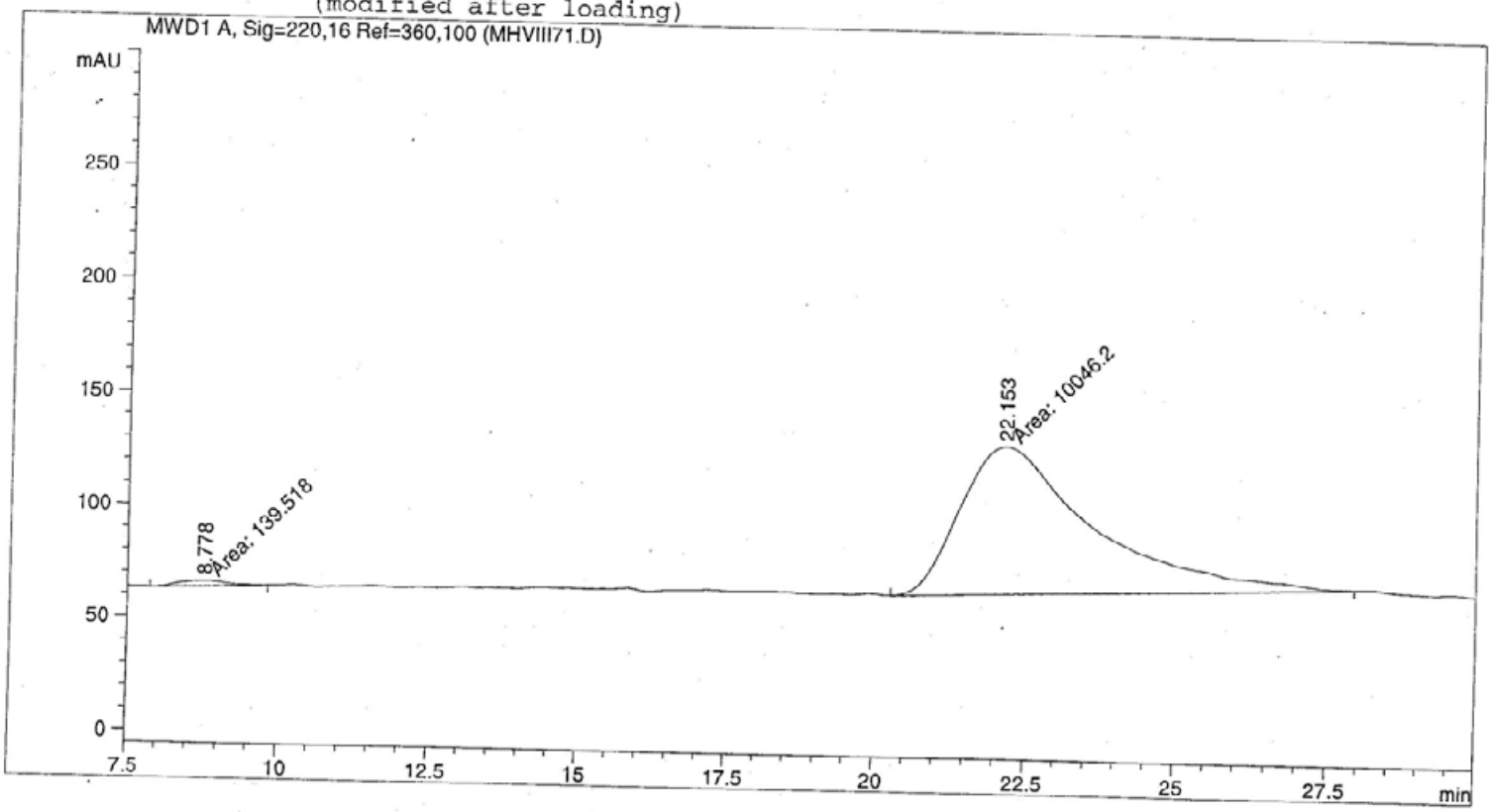
Injection Date : 4/7/2008 2:17:16 PM
Sample Name :
Acq. Operator :

Seq. Line : 1
Location : Vial 6
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 4/5/2008 6:08:45 PM
Analysis Method : C:\HPCHEM\2\METHODS\MEDLEY.M
Last changed : 4/7/2008 2:55:48 PM
(modified after loading)




33




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.778 | MM | 0.9170 | 139.51765 | 2.53569 | 1.3697 |
| 2 | 22.153 | MM | 2.5675 | 1.00462e4 | 65.21315 | 98.6303 |

Totals : 1.01857e4 67.74884

Results obtained with enhanced integrator!

*** End of Report ***

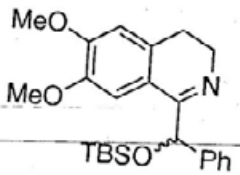


Instrument 2 4/7/2008 2:56:53 PM

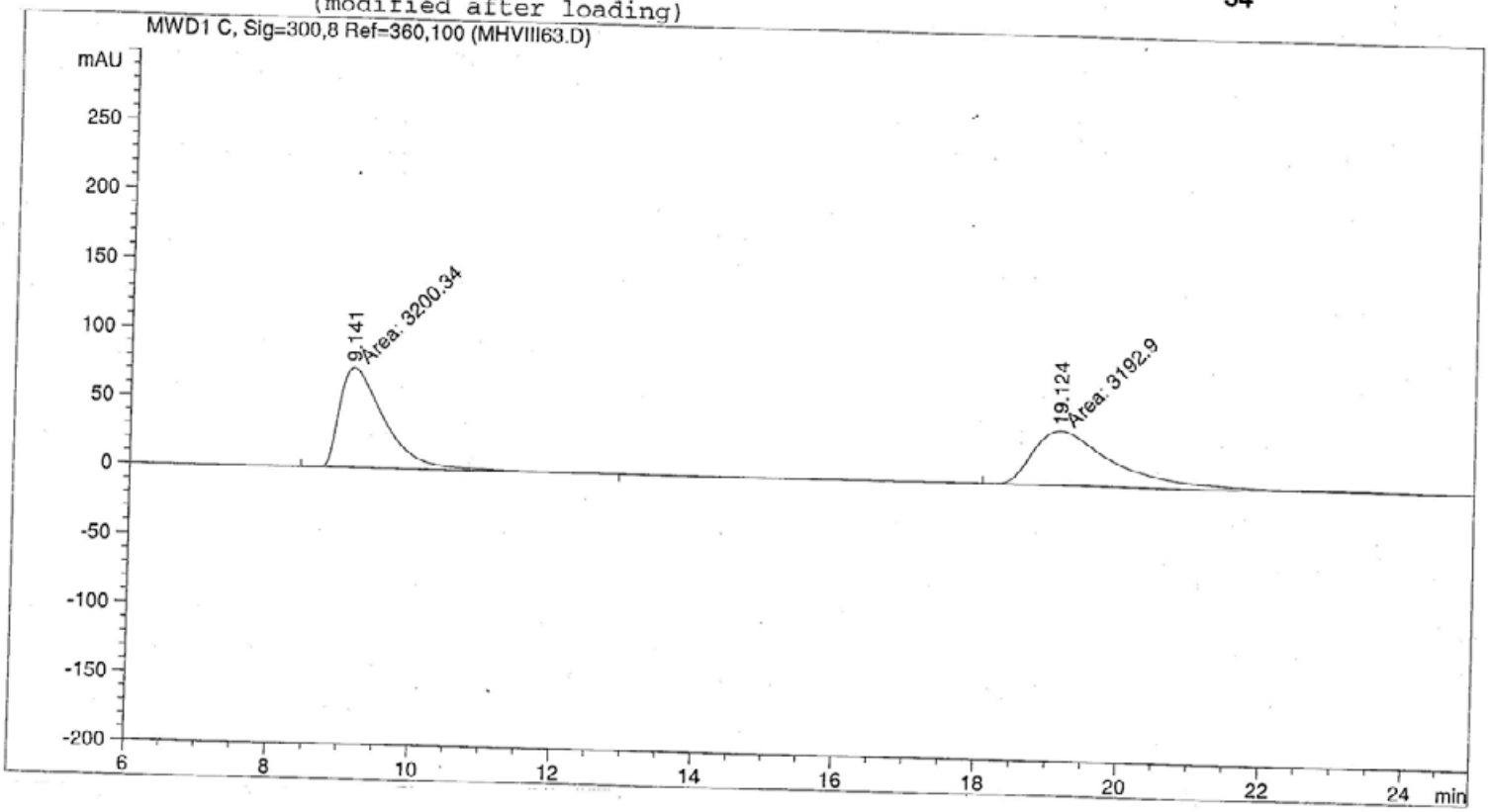
Injection Date : 4/1/2008 6:02:17 PM
Sample Name :
Acq. Operator :

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 4/1/2008 6:00:44 PM
Analysis Method : C:\HPCHEM\2\METHODS\MEDLEY.M
Last changed : 4/1/2008 7:05:25 PM
(modified after loading)

Seq. Line : 1
Location : Vial 10
Inj : 1
Inj Volume : 1 µl




34




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 C, Sig=300,8 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.141 | MM | 0.7312 | 3200.33936 | 72.94856 | 50.0582 |
| 2 | 19.124 | MM | 1.3487 | 3192.89502 | 39.45781 | 49.9418 |

Totals : 6393.23437 112.40637

Results obtained with enhanced integrator!

*** End of Report ***

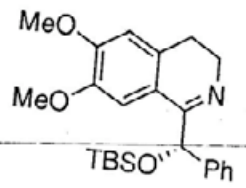


nstrument 2 4/1/2008 7:05:28 PM

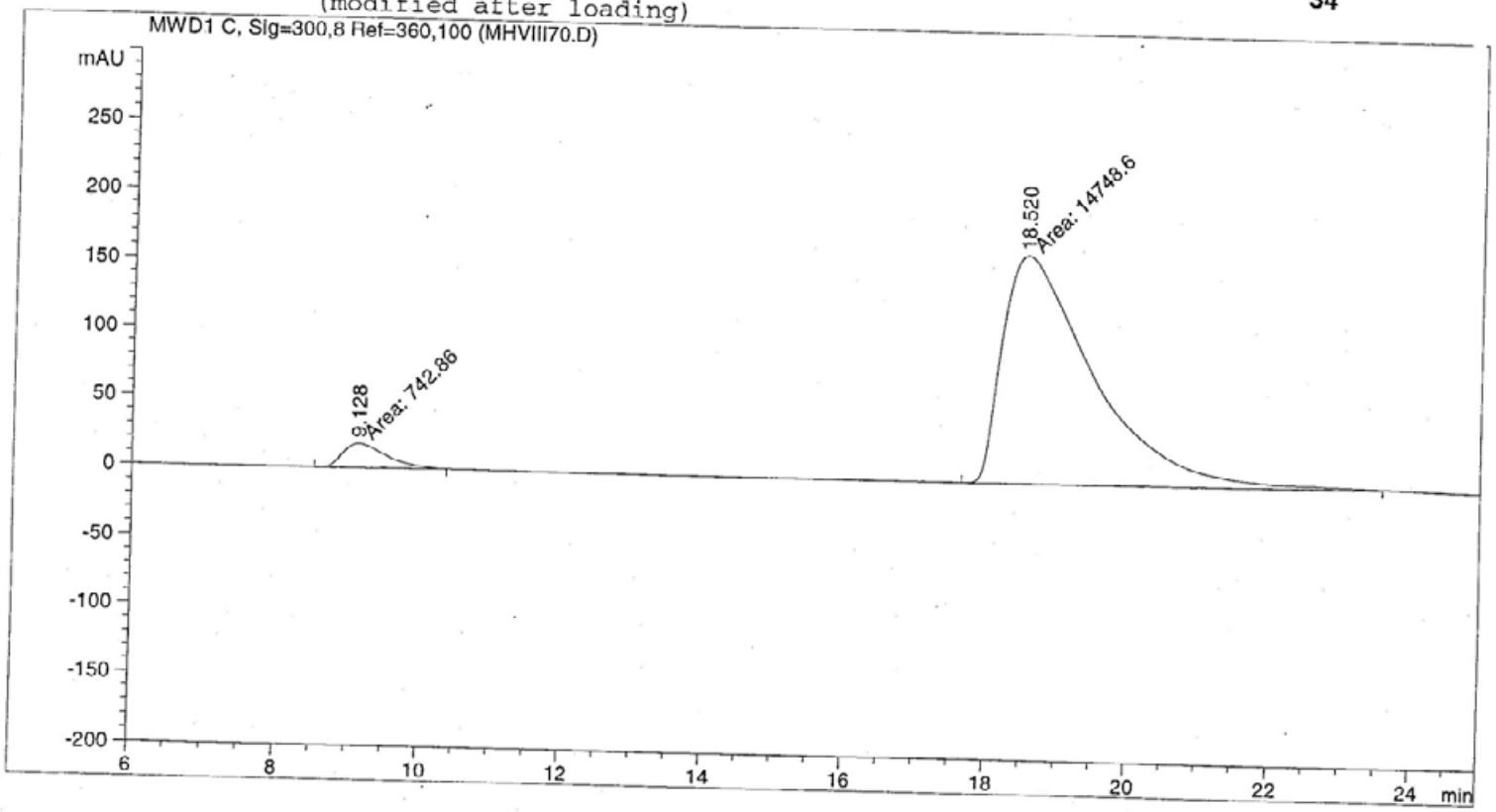
Injection Date : 4/5/2008 5:05:00 PM
Sample Name :
Acq. Operator :

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 4/5/2008 5:03:57 PM
Analysis Method : C:\HPCHEM\2\METHODS\MEDLEY.M
Last changed : 4/5/2008 5:40:43 PM
(modified after loading)

Seq. Line : 1
Location : Vial 6
Inj : 1
Inj Volume : 1 µl




**34**




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 C, Sig=300,8 Ref=360,100

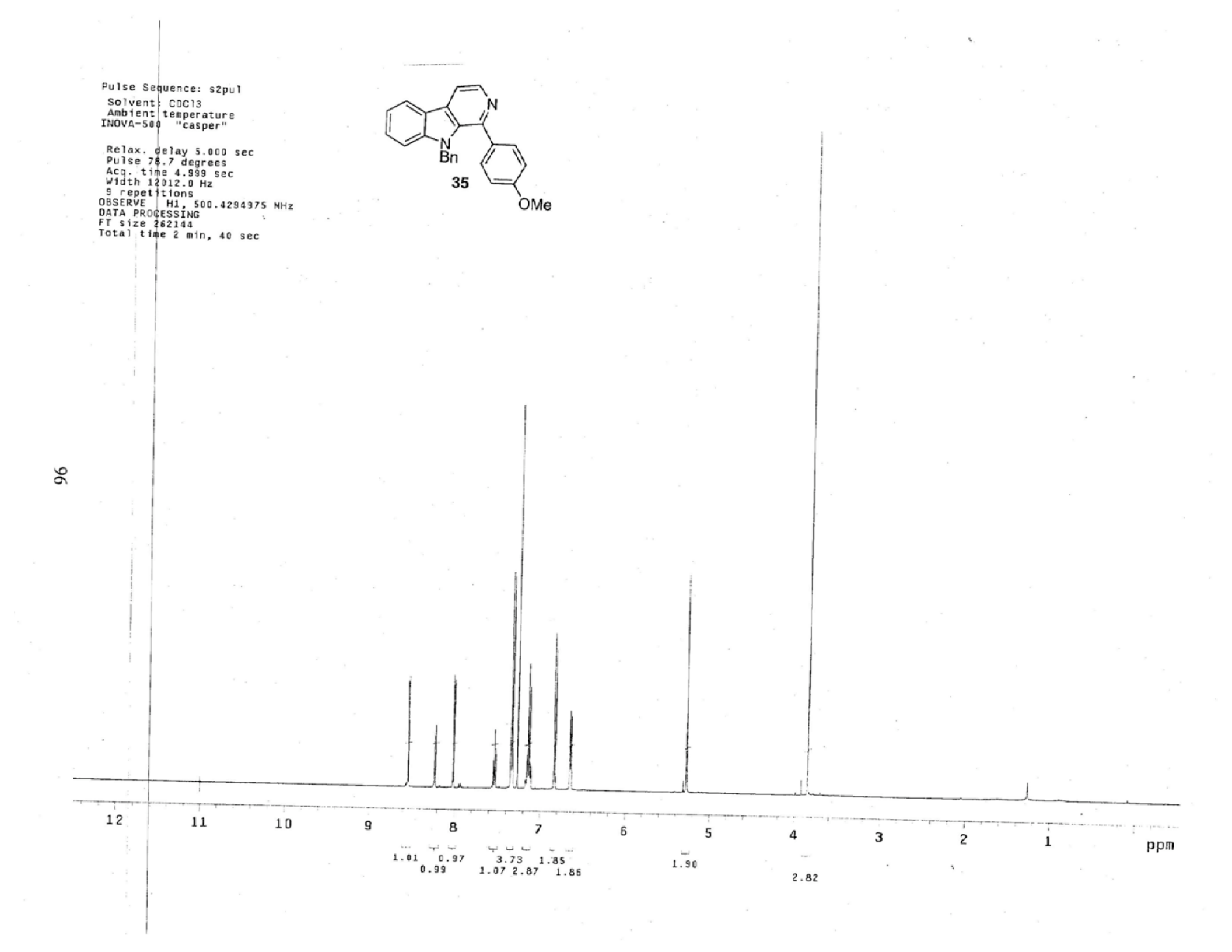
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.128 | MM | 0.7114 | 742.85962 | 17.40329 | 4.7953 |
| 2 | 18.520 | MM | 1.4912 | 1.47486e4 | 164.83789 | 95.2047 |
| Totals : | | | | 1.54914e4 | 182.24118 | |

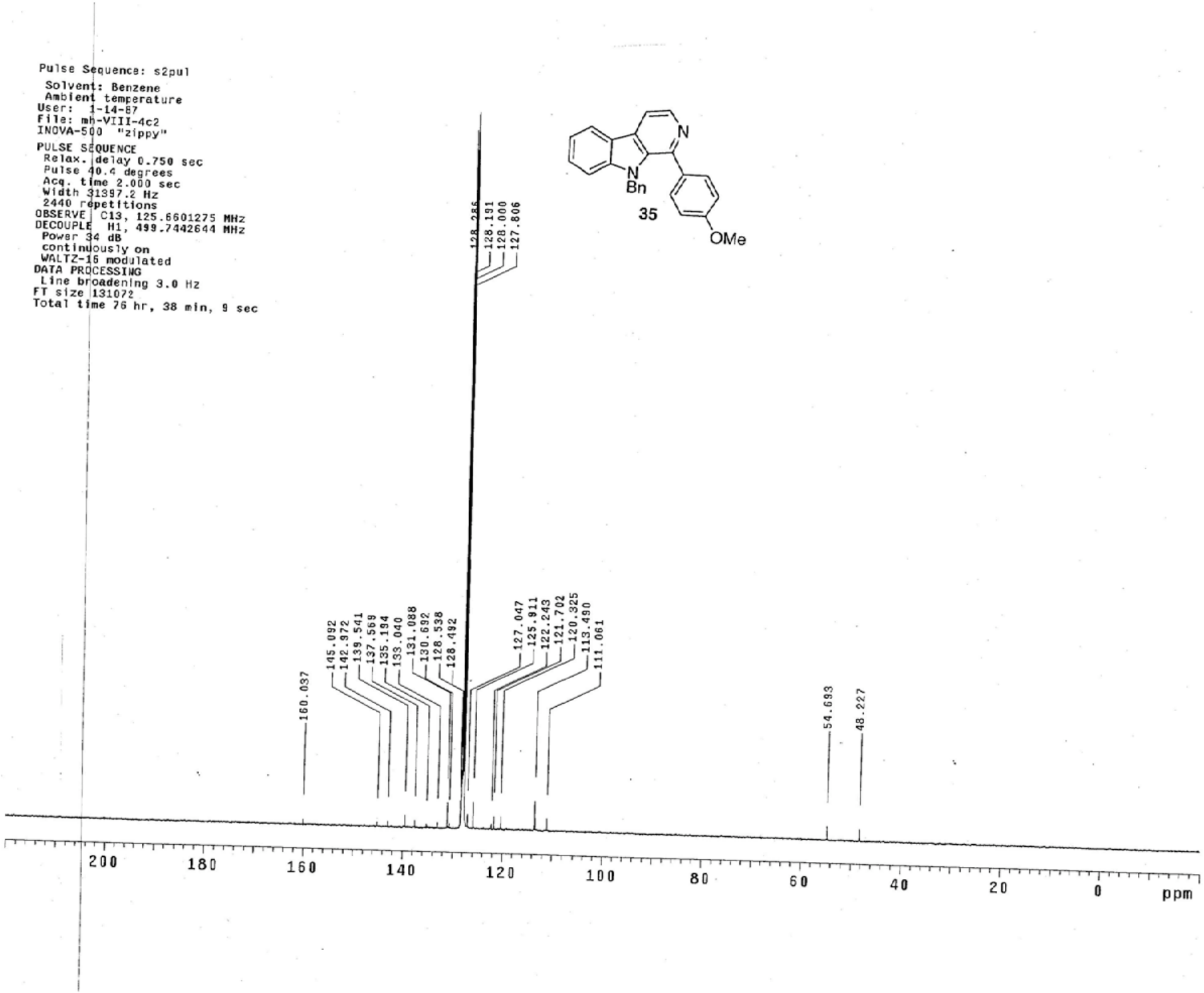
Results obtained with enhanced integrator!

*** End of Report ***



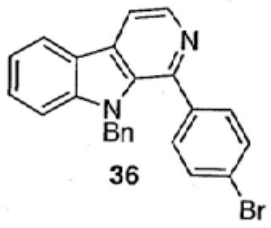
Instrument 2 4/5/2008 5:41:14 PM


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"
Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
8 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec
N
N
Bn
35
OMe
96
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
0.99
0.97
3.73
1.07
2.87
1.85
1.86
1.90
2.82

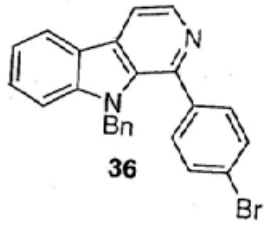

Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
User: 1-14-87
File: mh-VIII-4c2
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 0.750 sec
Pulse 40.4 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
2440 repetitions
OBSERVE C13, 125.6601275 MHz
DECOUPLE H1, 499.7442644 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total time 76 hr, 38 min, 9 sec
N
N
Bn
35
OMe
128.286
128.191
128.000
127.806
160.037
145.092
142.972
139.541
137.569
135.184
133.040
131.088
130.692
128.538
128.492
127.047
125.911
122.243
121.702
120.325
113.490
111.061
54.693
48.227
200
180
160
140
120
100
80
60
40
20
0
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
4 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec




36



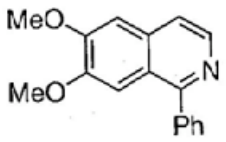

36

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

Relax. delay 0.700 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
248 repetitions
OBSERVE C13, 125.6601314 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 75247 hr, 6 min, 8 sec

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
4 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec

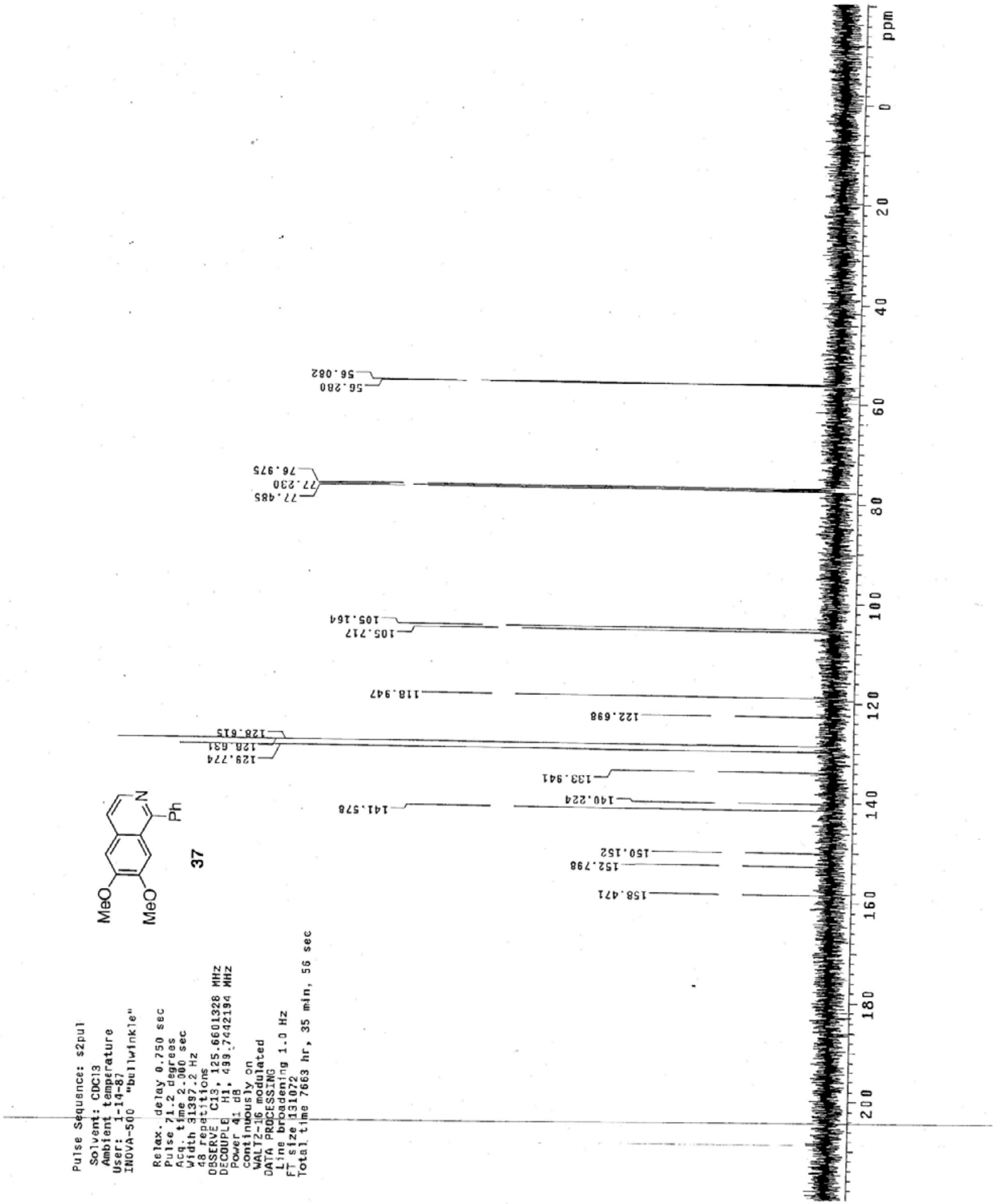



37

100

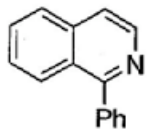
12 11 10 9 8 7 6 5 4 3 2 1 ppm

1.00 4.14 1.03 3.09
2.10 1.06 3.06

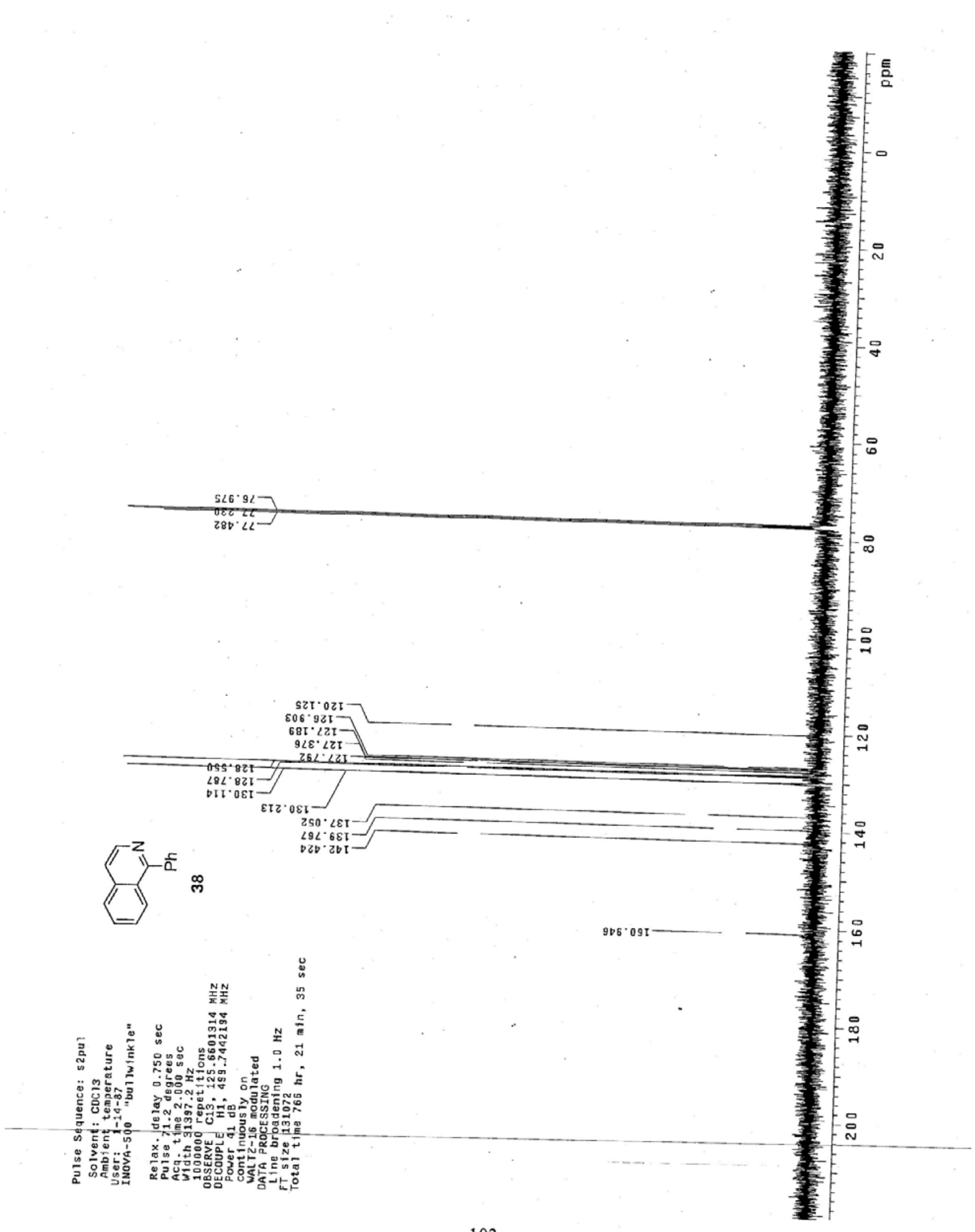

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.750 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
48 repetitions
OBSERVE C13, 125.6601328 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 7663 hr, 35 min, 56 sec
MeO
MeO
N
Ph
37
158.471
152.798
150.152
141.578
140.224
133.941
129.774
128.631
128.615
122.698
118.947
105.717
105.164
77.485
77.230
76.975
56.280
56.082
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "casper"

Relax. delay 5.000 sec
Pulse 78.7 degrees
Acq. time 4.999 sec
Width 12012.0 Hz
5 repetitions
OBSERVE H1, 500.4294975 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 40 sec




38


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.750 sec
Pulse 71.2 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
1000000 repetitions
OBSERVE C13, 125.6601314 MHz
DECOUPLE H1, 499.7442194 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 766 hr, 21 min, 35 sec
N
Ph
38
160.946
142.424
139.767
137.052
130.213
130.114
128.787
128.550
127.792
127.376
127.189
126.903
120.125
77.482
77.230
76.975
ppm
0
20
40
60
80
100
120
140
160
180
200