Palladium-catalyzed Enantioselective α-arylation and α-vinylation of Oxindoles Facilitated by an Axially Chiral P-Stereogenic Ligand

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77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Supporting Information

Further reports of the enantioselective α-arylation and α-vinylation of ketone enolates:
(a) Hamada, T.; Chieffi, A.; Åhman, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1261.
(b) Chieffi, A.; Kamikawa, K.; Åhman, J.; Fox, J. M.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 1897.
(c) Åhman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 1918.

Further reports of the enantioselective formation of 3,3-disubstituted oxindoles with quaternary carbon centers:
(a) Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4590.
(b) Trost, B. M.; Brennan, M. K. *Org. Lett.* **2006**, *8*, 2027.
(c) Arao, T.; Kondo, K.; Aoyama, T. *Chem. Pharm. Bull.* **2006**, *54*, 1743.
(d) Arao, T.; Sato, K.; Kondo, K.; Aoyama, T. *Chem. Pharm Bull.* **2006**, *54*, 1576.
(e) Arao, T.; Kondo, K.; Aoyama, T. *Tet. Lett.* **2006**, *47*, 1417.
(e) Trost, B. M.; Frederiksen, M. U. *Angew. Chem., Int. Ed.* **2005**, *44*, 308.
(f) Hills, I. D.; Fu, G. C. *Angew. Chem., Int. Ed.* **2003**, *41*, 3921.
(g) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704.
(h) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402.

Further reports of the enantioselective formation of 3,3-disubstituted oxindoles bearing heteroatoms:
(a) Ishimaru, T.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T.; Kanemasa, S. *J. Am. Chem. Soc.* **2006**, *128*, 16488.
(b) Hamashima, Y.; Suzuki, T.; Takano, H.; Shimura, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2005**, *127*, 10164.
(c) Shibata, N.; Ishimaru, T.; Suzuki, E.; Kirk, K. L. *J. Org. Chem.* **2003**, *68*, 2494.

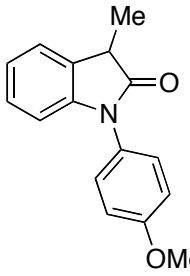
General Reagent Information
3-methyloxindole was purchased from Aldrich and used as delivered. 1,3-dimethyloxindole, 3-benzyl-1-methyloxindole, and 5-methoxy-1,3-dimethyloxindole were prepared as previously described.[1,2,3] 1-(4-methoxyphenyl)-3-methyloxindole was prepared as described below. TMEDA•$PdMe_2$ was prepared as previously described[4] and stored at 4 °C. NaO^{t}Bu was purchased from Aldrich Chemical Co. and stored in a N_2 glovebox. Small portions (~1 g) were removed from the glove box in glass vials, weighed in the air, and stored in a desiccator filled with anhydrous calcium sulfate. Ligand **1** was synthesized as previously described.[5] All reagents were weighed in air with no use of a glove box. All other reagents, including aryl and vinyl bromides, were purchased from Aldrich Chemical Co., Alfa Aesar, or TCI America and used as received, with the exception of β-bromostyrene, which was passed through silica gel before use, and 2,5-dimethylaniline, which was distilled before use. Cyclohexane was purchased from Aldrich Chemical Co. in a Sure-Seal bottle and degassed by sparging with Argon prior to use.

General Analytical Information
All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, melting point (where applicable), optical rotation (where applicable), HPLC, GC, and elemental analysis. Gas chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatograph with an FID detector and a 25m x 0.20 mm capillary

[1] Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. *J. Am. Chem. Soc.* **2006**, *128*, 925.
[2] Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4590.
[3] Angelovski, G.; Keränen, M. D.; Linnepe, P.; Grudzielanek, S.; Eilbracht, P. *Adv. Synth. Catal.* **2006**, *348*, 1193.
[4] Biscoe, M. R.; Fors. B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 6686.
[5] Hamada, T.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 999.

column with cross-linked methyl siloxane as the stationary phase. ^{1}H NMR and ^{13}C NMR spectra are included for all compounds and were recorded on a Bruker 400 MHz or a Varian 500 MHz instrument. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were referenced to the signal for $CHCl_3$ (7.26 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.0 ppm) and were obtained with ^{1}H decoupling. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using KBr plates (thin film). Optical rotations were measured on a Jasco P-1010 polarimeter using a Na lamp (589 nm) at 21-22 °C. (The concentration of the samples is given in g 100 mL^{-1}.) HPLC analyses were carried out on an Agilent 1100 Series system with Daicel Chiralcel®, Chiralpak®, or Regis Technologies, Inc. WHELK columns (4.6 mm x 250 mm) in hexanes/^{i}PrOH mixtures. The HPLC spectra of all compounds were compared to those of corresponding authentic racemic compounds. Representative HPLC traces are included for several compounds from these studies. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were obtained on a Mel-Temp capillary melting point apparatus. The yields reported in table 1 and figure 2 refer to isolated yields and represent an average of two independent runs. Reported compounds are estimated to be >95% pure as determined by ^{1}H NMR and GC analysis and/or combustion analysis.

Synthesis of starting material



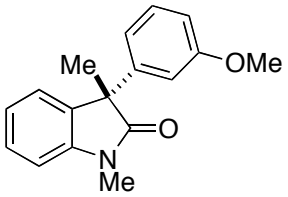
1-(4-methoxyphenyl)-3-methyloxindole (Table 2) A Schlenk tube was charged with 3-methyloxindole (2.94 g, 20 mmol, 1 equiv), 4-iodoanisole (5.62 g, 24 mmol, 1.2 equiv), CuI (191 mg, 1 mmol, 0.05 equiv), K_2CO_3 (5.53 g, 40 mmol, 2 equiv), and a stirbar before being sealed with a rubber septum. The vessel was evacuated and purged with argon (this sequence was repeated two additional times) before the addition of *N*,*N*-dimethylcyclohexane-1,2-diamine (315 μL, 2 mmol, 0.1 equiv) and 1,4-dioxane (20 mL, [oxindole] = 1 M). The rubber septum was replaced with a glass stopper under positive argon pressure, and the mixture was stirred at 110 °C for 20 h. Following cooling, the mixture was diluted with EtOAc, filtered through a pad of silica gel, and concentrated *in vacuo*. The residue was purified by column chromatography with a Biotage. The title compound was isolated as a white solid (3.21 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (m, 3H), 7.22 (t, J = 7.68 Hz, 1H), 7.10 (t, J = 7.36 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 7.76 Hz, 1H), 3.85 (s, 3H), 3.64 (q, J = 7.6, 15.16 Hz, 1H), 1.60 (d, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.1, 158.9, 144.2, 130.3, 127.8, 127.6, 127.0, 127.6, 127.6, 123.6, 122.6, 114.8, 109.0, 55.4, 40.6, 15.6 ppm. IR (neat, cm^{-1}): 3053.2, 2971.0, 2933.9, 2837.9, 1718.8, 1611.5, 1586.3, 1514.1, 1484.6, 1464.7, 1375.8, 1329.3, 1298.8, 1249.9, 1209.1, 1173.9, 1102.1, 1061.8, 1032.0. Anal. Calc. for $C_{16}H_{14}NO_2$: C, 75.87; H, 5.97. Found: C, 75.98; H, 5.95. M. P.: 80 °C.

Experimental procedures for examples described in *Figure 1*, *Table 1*, and *Figure 2*

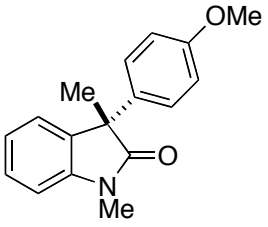
General procedure: All reactions were conducted in disposable resealable glass vials fitted with Teflon-lined screw caps. One of these tubes, equipped with a magnetic stir bar, was charged with the oxindole (0.75 mmol, 1.5 equiv), TMEDA•$PdMe_2$ (5.1 mg, 0.02 mmol, 4 mol%), ligand **1** (9.2 mg, 0.02 mmol, 4 mol%), $NaO^{t}Bu$ (96 mg, 1.0 mmol, 2 equiv) and, when applicable, solid aryl bromide (0.5 mmol, 1.0 equiv) before being sealed with the teflon-lined screw cap. The vessel was evacuated and backfilled with argon (this sequence was repeated two additional times) before the aryl bromide or vinyl bromide was added via syringe through the septum (when applicable). Cyclohexane (1 mL, [aryl halide] = 0.5 M) was added immediately via syringe through the septum, and the reaction was stirred in an oil bath at the temperature described for 24 h. The reaction vessel was then cooled to room temperature, and dodecane (100 μL) was added as an internal standard. The crude reaction was diluted with EtOAc (~1 mL), filtered through a Si-gel plug, eluted with EtOAc (~3 mL), and analyzed by GC.[6] Following concentration *in vacuo*, the

[6] Note: Under the reaction conditions, the oxindole substrates were deprotonated and were not in solution. Following workup, a small amount (~ 5%) of the neutral starting material oxindole was observed in the filtrate (GC,

mixture was purified with a Biotage SP4 (silica-packed SNAP-10g, SNAP-25g, or 25+M columns; EtOAc/hexanes) to provide the product described.



3-(3-methoxyphenyl)-1,3-dimethylindolin-2-one (Figure 1) The reaction was conducted according to the general procedure to afford the title compound as a clear oil (103 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (dt, *J* = 1.3, 7.7, 7.7 Hz, 1H), 7.22 (m, 2H), 7.12 (dt, *J* = 1, 7.6, 7.6 Hz, 1H), 6.91 (m, 3H), 6.8 (ddd, *J* = 0.8, 2.5, 8.2 Hz, 1H), 3.76 (s, 3H), 3.24 (s, 3H), 1.79 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.1, 159.5, 143.0, 142.3, 134.6, 129.4, 128.0, 124.0, 122.7, 118.9, 113.1, 111.9, 108.2, 55.0, 52.0, 26.3, 23.6 ppm. IR (neat, cm^{-1}): 2968.0, 2934.7, 2834.8, 1715.5, 1611.6, 1582.3, 1492.5, 1470.6, 1432.5, 1373.6, 1344.8, 1292.3, 1256.6, 1160.0, 1102.6, 1043.1, 1024.1. Enantiomeric excess: 97%, Chiralcel OD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 9.738 min, t_{major}= 8.356 min; $[\alpha]_D^{22}$ -110.5 ° (c 0.35, $CHCl_3$).



3-(4-methoxyphenyl)-1,3-dimethylindolin-2-one (**2**, Table 1, entry 1)[7] The reaction was conducted according to the general procedure to yield the title compound as an oil that turned into an off-white solid on sitting (114 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (td, *J* = 1.4, 7.7, 7.7 Hz, 1H), 7.26 (dt, *J* = 3.4, 3.4, 10.2 Hz, 2H), 7.21 (dq, *J* = 0.5, 1.3, 7.4 Hz, 1H), 7.13 (td, *J* = 1, 7.5, 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.85 (dt, *J* = 3.2, 3.2, 9.9 Hz, 2H), 3.76 (s, 3H), 3.24 (s, 3H), 1.78 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.5, 158.6, 143.1, 134.8, 132.7.127.9, 127.6, 124.0, 122.6, 113.7, 108.2, 55.1, 51.3, 26.3, 23.8 ppm. IR (neat, cm^{-1}): 2932.9, 1714.5, 1610.8, 1511.4, 1492.9, 1470.0, 1384.1, 1373.4, 1344.0, 1303.8, 1251.0, 1181.8, 1147.0, 1096.7, 1030.5. Enantiomeric excess: 95%, Chiralpak AD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 11.324 min, t_{major}= 8.960 min; $[\alpha]_D^{21}$ -122.6 ° (c 0.34, $CHCl_3$). M. P.: 144 °C.

NMR). In most cases, this oxindole was readily separated from the desired product by chromatography. When the two were not separable, however, the remaining starting material oxindole was oxidized *in situ* during the workup by opening the reaction vessel and stirring the crude mixture in air for 30 minutes before filtration through silica gel. The oxidized starting material was then no longer observed in the crude filtrate, which was otherwise treated as described above.

[7] Arao, T.; Sato, K.; Kondo, K.; Aoyama, T. *Chem. Pharm Bull.* **2006**, *54*, 1576.

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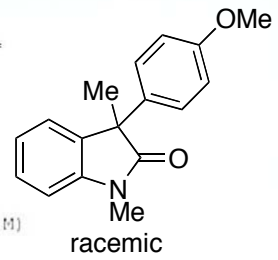

racemic

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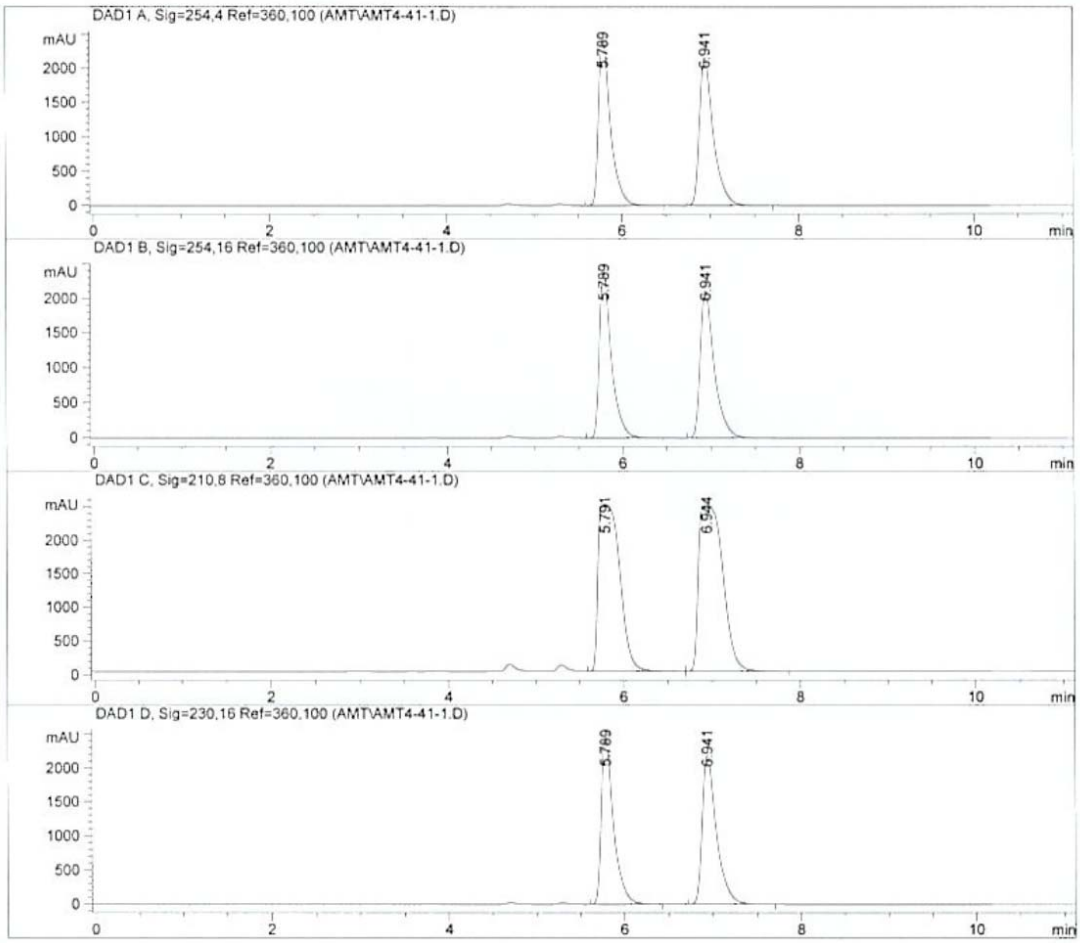

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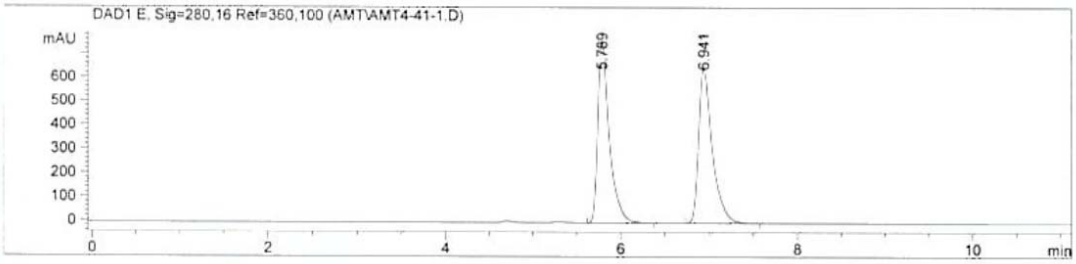

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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1	5.789	VB	0.1430	2.31518e4	2433.19312	49.4850
2	6.941	BB	0.1636	2.36338e4	2161.04834	50.5150
Totals :				4.67856e4	4594.24146	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.789	VB	0.1423	2.25958e4	2390.47144	49.5407
2	6.941	BB	0.1632	2.30148e4	2111.41211	50.4593
Totals :				4.56106e4	4501.88354	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.791	VV	0.2756	4.21172e4	2486.60913	47.4948
2	6.944	VB	0.3058	4.65602e4	2470.89551	52.5052
Totals :				8.86774e4	4957.50464	

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Signal 4: DAD1 D, Sig=230,16 Ref=360,100

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1	5.789	BB	0.1443	2.36273e4	2455.05786	49.4025
2	6.941	BB	0.1652	2.41988e4	2185.16113	50.5975
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Signal 5: DAD1 E, Sig=280,16 Ref=360,100

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1	5.789	BB	0.1337	6908.16895	762.62616	49.9366
2	6.941	BB	0.1586	6925.70947	648.27563	50.0634
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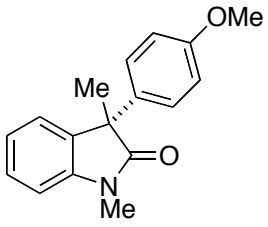

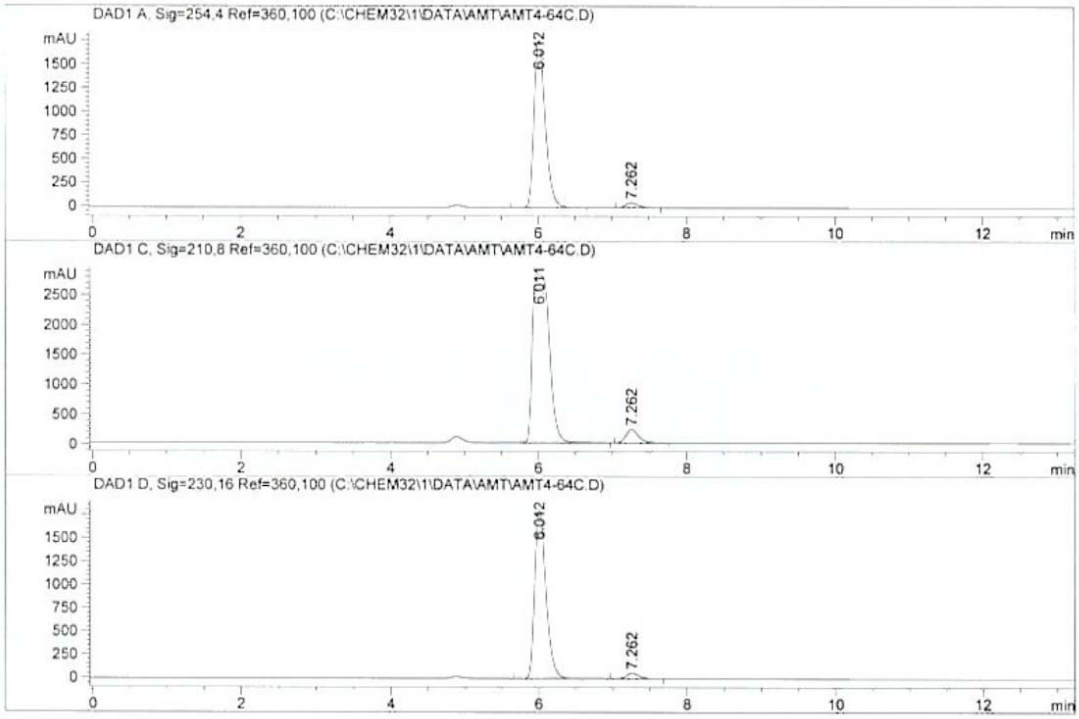


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Instrument 1 6/17/2009 7:31:55 PM jACLYN Page 1 of 2

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Totals :				1.93830e4	1827.32149	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

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Signal 3: DAD1 D, Sig=230,16 Ref=360,100

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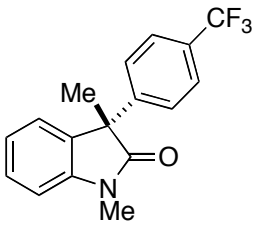

3-(4-trifluoromethylphenyl)-1,3-dimethylindolin-2-one (Table 1, entry 2)[2] The reaction was conducted according to the general procedure to yield the title compound as a white solid (100 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (dt, *J* = 0.6, 0.6, 8.3 Hz, 2H), 7.46 (dd, *J* = 0.6, 8.8 Hz, 2H), 7.39 (dt, *J* = 1.4, 7.8, 7.8, 2H), 7.21 (ddd, *J* = 0.5, 1.4, 7.4 Hz, 1H), 7.15 (dt, *J* = 1, 7.5, 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.26 (s, 3H), 1.82 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.6, 144.7, 143.1, 133.8, 129.5, 129.2, 128.5, 127.1, 125.4 (q, *J* = 14.6, 29.4 Hz), 124.1, 122.9, 122.6, 108.5, 52.0, 26.5, 23.7 ppm. ^{19}F NMR (400 MHz, $CDCl_3$) δ: 62.9 ppm. IR (neat, cm^{-1}): 2974.1, 2935.9, 1718.1, 1612.3, 1493.7, 1472.2, 1410.4, 1375.7, 1347.0, 1328.2, 1166.8, 1123.0, 1096.34, 1075.9, 1016.8. Enantiomeric excess: 95%, Chiralpak AD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 6.856 min, t_{major}= 5.749 min; $[\alpha]_D^{22}$ -1.35 ° (c 0.316, $CHCl_3$). Anal. Calc. for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62. Found: C, 66.93; H, 4.65. M. P.: 84 °C.

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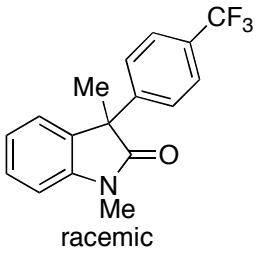
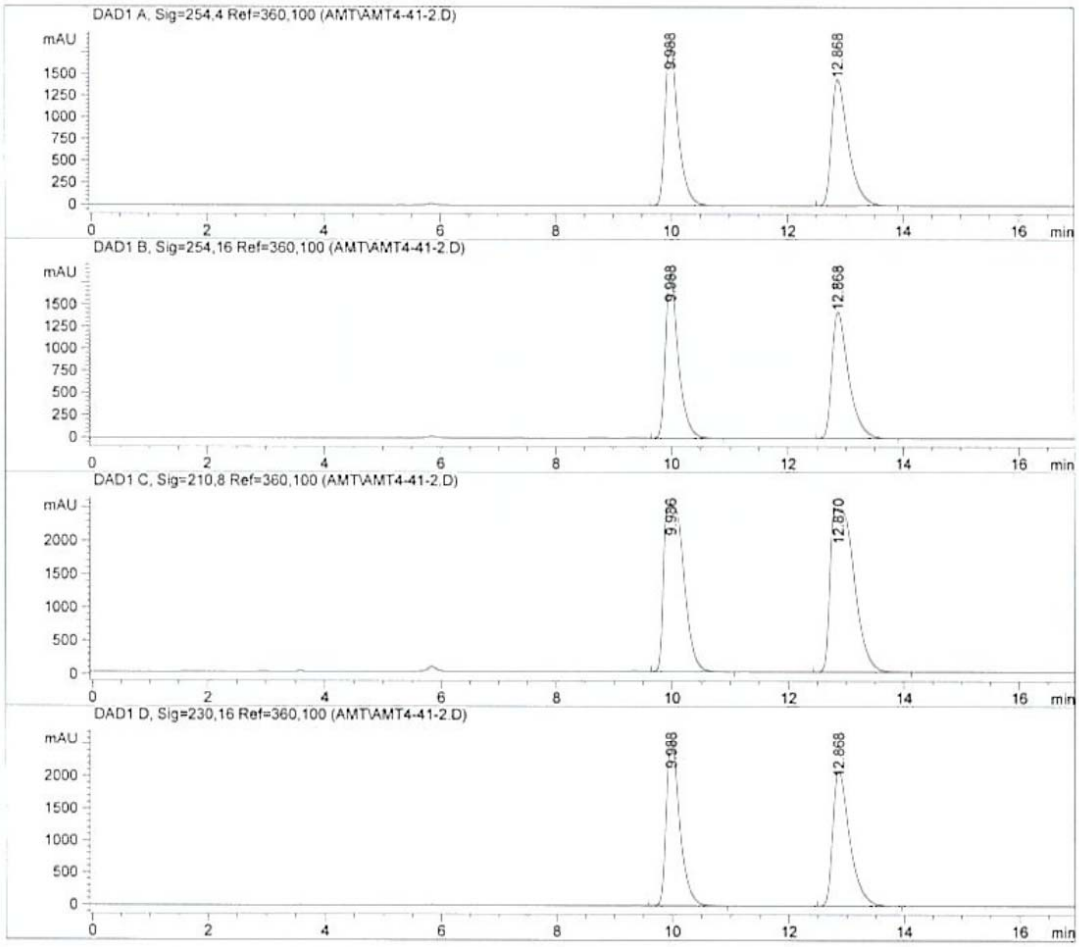


racemic



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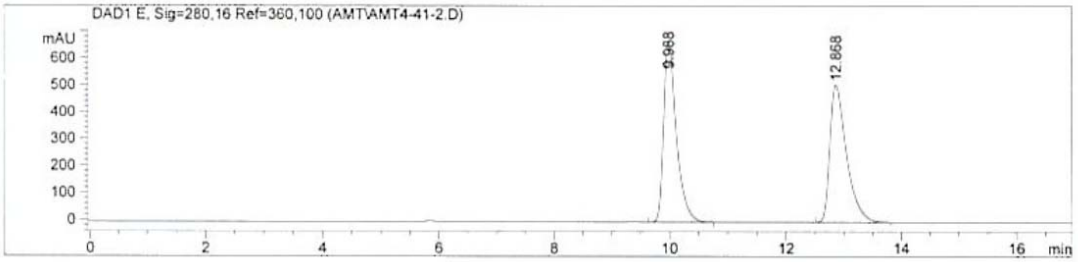

Area Percent Report

Sorted By : Signal
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Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	VB	0.2276	2.88810e4	1896.94104	49.8181
2	12.868	BB	0.3017	2.90919e4	1452.16882	50.1819
Totals :				5.79728e4	3349.10986	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	VB	0.2275	2.83379e4	1863.01538	49.8305
2	12.868	BB	0.3017	2.85306e4	1424.43042	50.1695
Totals :				5.68685e4	3287.44580	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.986	VB	0.3317	5.98217e4	2477.47412	45.9483
2	12.870	BB	0.4558	7.03719e4	2445.18311	54.0517
Totals :				1.30194e5	4922.65723	

Data File C:\CHEM32\2\DATA\AMT\AMT4-41-2.D
Sample Name: AMT4-41-2

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

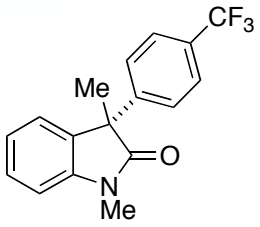
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	VB	0.2426	4.13541e4	2586.09985	49.2967
2	12.868	BB	0.3072	4.25342e4	2092.38477	50.7033
Totals :				8.38883e4	4678.48462	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	VB	0.2253	1.01391e4	674.62262	49.9725
2	12.868	BB	0.3009	1.01503e4	508.46445	50.0275
Totals :				2.02894e4	1183.08707	

*** End of Report ***

Data File C:\CHEM32\1\DATA\AMT\AMT4-64A-2.D
Sample Name: AMT4-64A-2

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Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 4/29/2009 5:15:55 PM
                                                  Inj Volume : 0.5 ul
Acq. Method      : C:\CHEM32\1\METHODS\AMH.M
Last changed     : 4/29/2009 5:07:40 PM by AMT
                   (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\AMT\AMT4-64A-2.D\DA.M (AMH.M)
Last changed     : 4/29/2009 5:30:57 PM by AMT
Sample Info      : OD-H 20% IPA 1ML/MIN
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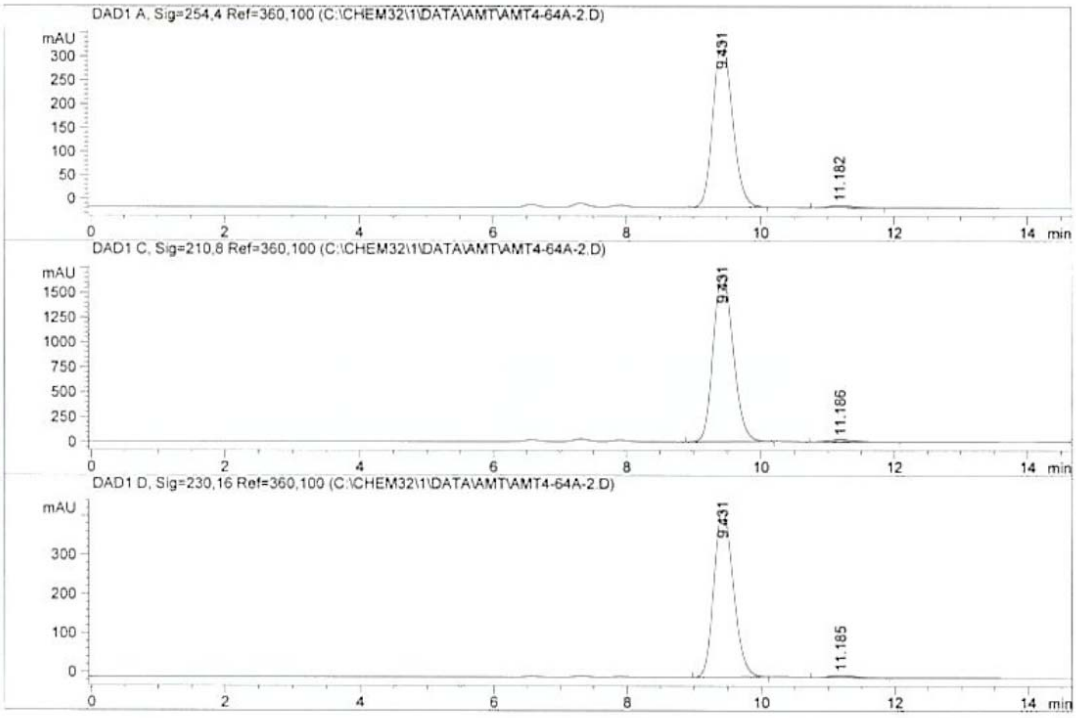


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
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Data File C:\CHEM32\1\DATA\AMT\AMT4-64A-2.D
Sample Name: AMT4-64A-2

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.431	BB	0.3126	7102.49219	353.20538	98.4334
2	11.182	BB	0.3935	113.03805	4.43260	1.5666
Totals :				7215.53024	357.63798	

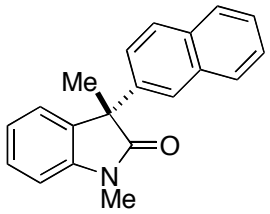
Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.431	BB	0.3226	3.47120e4	1683.12036	98.3534
2	11.186	BB	0.4016	581.15155	22.63275	1.6466
Totals :				3.52932e4	1705.75311	

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

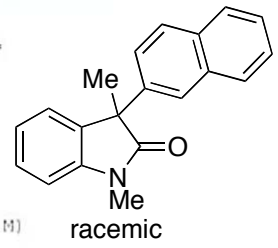
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.431	BB	0.3109	8578.76465	429.71759	98.4012
2	11.185	BB	0.3977	139.38789	5.46328	1.5988
Totals :				8718.15254	435.18087	

*** End of Report ***



1,3-dimethyl-3-(naphthalen-2-yl)indolin-2-one (Table 1, entry 3) The reaction was conducted according to the general procedure to afford the title compound as a clear oil (117 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (m, 4H), 7.53 (m, 2H), 7.45 (dd, *J* = 2.0, 8.6 Hz, 1H), 7.42 (td, *J* = 1.2, 7.7, 7.7 Hz, 1H), 7.28 (d, *J* = 6.7 Hz, 1H), 7.19 (td, *J* = 0.8, 7.5, 7.5 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.32 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.3, 143.1, 138.0, 134.7, 133.1, 132.3, 128.1, 127.9, 127.3, 126.0, 125.9, 125.2, 124.8, 124.1, 122.7, 108.3, 52.2, 26.4, 23.5 ppm. IR (neat, cm^{-1}): 3055.0, 2969.7, 2932.3, 1714.1, 1506.5, 1493.2, 1470.6, 1419.0, 1373.5, 1343.1, 1302.6, 1259.5, 1157.9, 1144.3, 1128.4, 1114.2, 1100.5, 1053.2, 1024.1, 1053.2, 1024.1. Enantiomeric excess: 96%, Chiralpak AD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 16.561 min, t_{major}= 11.831 min; $[\alpha]_D^{22}$ -90.3 ° (c 0.558, $CHCl_3$).

Data File C:\CHEM32\2\DATA\AMT\AMT4-41-3.D
Sample Name: AMT4-41-3



racemic

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==========================================================================
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Acq. Instrument : Instrument 2                    Location : Vial 3
Injection Date  : 4/7/2009 3:31:57 PM
                                                  Inj Volume : 1 µl
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Last changed    : 4/7/2009 3:31:14 PM by AMT
                  (modified after loading)
Analysis Method : C:\CHEM32\2\DATA\AMT\AMT4-41-3.D\DA.M (AMTSTANDARD.M)
Last changed    : 4/7/2009 4:11:13 PM by AMT
Sample Info     : AD-H 10% IPA IN HEXANES 1.0 ML/MIN
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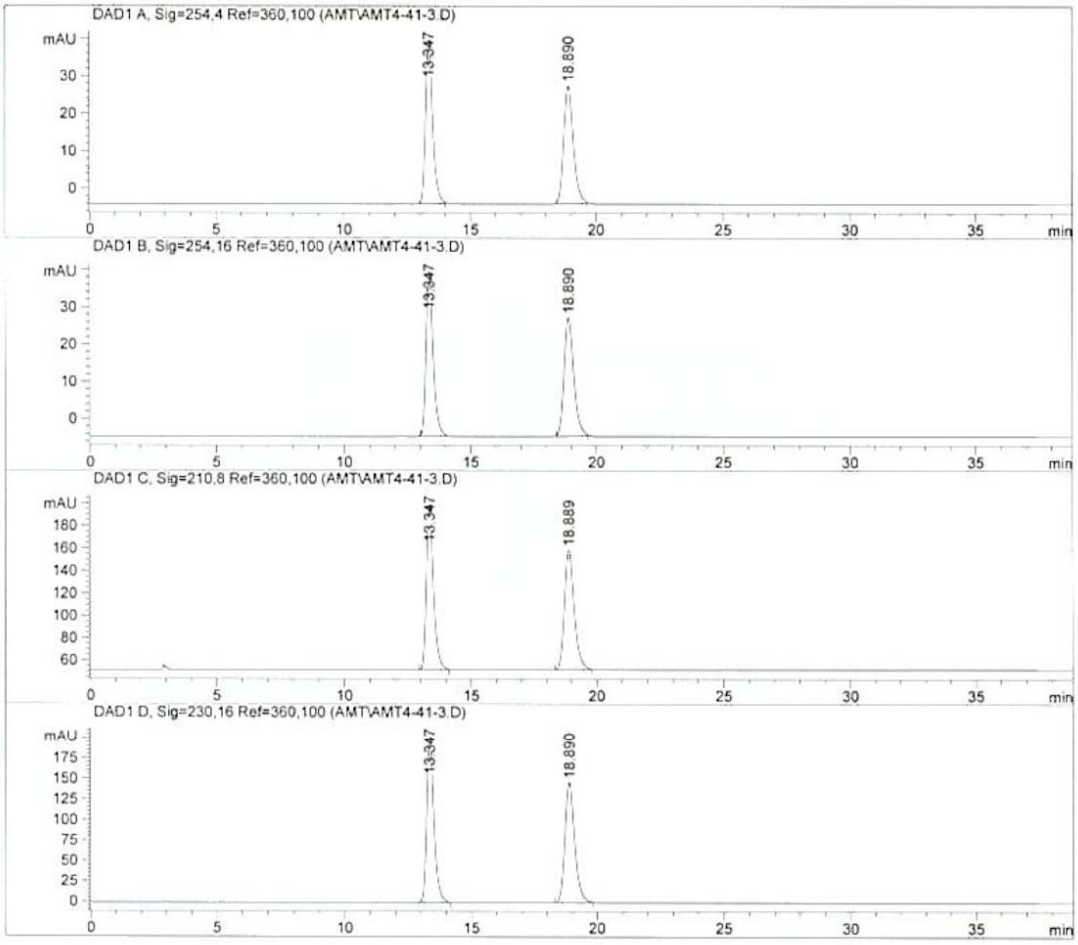
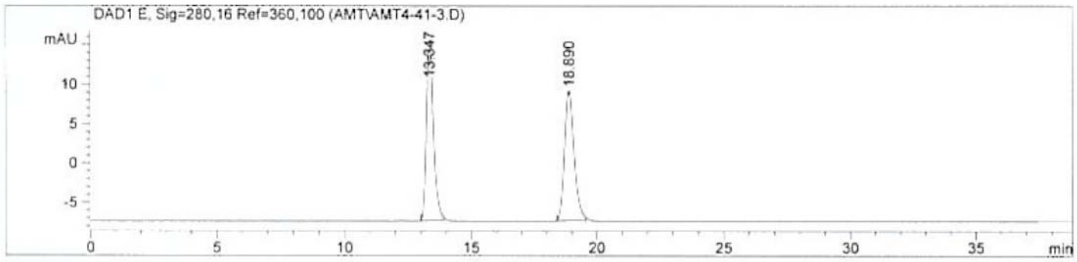


Data File C:\CHEM32\2\DATA\AMT\AMT4-41-3.D
Sample Name: AMT4-41-3



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.2944	846.07355	43.60836	50.2405
2	18.890	BB	0.4069	837.97266	31.44374	49.7595
Totals :				1684.04620	75.05210	

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.2946	856.91003	44.12596	50.2575
2	18.890	BB	0.4070	848.12775	31.81866	49.7425
Totals :				1705.03778	75.94463	

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.2957	2887.28345	147.94829	50.0503
2	18.889	BB	0.4104	2881.48096	106.91277	49.9497
Totals :				5768.76440	254.86106	

Data File C:\CHEM32\2\DATA\AMT\AMT4-41-3.D
Sample Name: AMT4-41-3

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.2963	3968.54932	202.79507	50.0531
2	18.890	BB	0.4108	3960.12939	146.76143	49.9469
Totals :				7928.67871	349.55650	

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.2928	440.29120	22.84582	50.2520
2	18.890	BB	0.4029	435.87531	16.46381	49.7480
Totals :				876.16650	39.30963	

*** End of Report ***

Data File C:\CHEM32\1\DATA\AMT\AMT4-64D.D
Sample Name: AMT4-64D

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==========================================================================
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Acq. Instrument : Instrument 1                    Location : Vial 1
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                                                  Inj Volume : 1 µl
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Last changed     : 4/28/2009 11:35:58 AM by AMT
                   (modified after loading)
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Last changed     : 4/28/2009 12:00:27 PM by AMT
Sample Info      : AD-H, 10% IPA 1 ML/MIN
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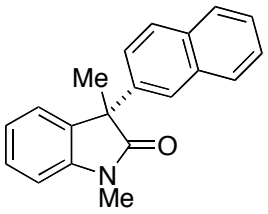

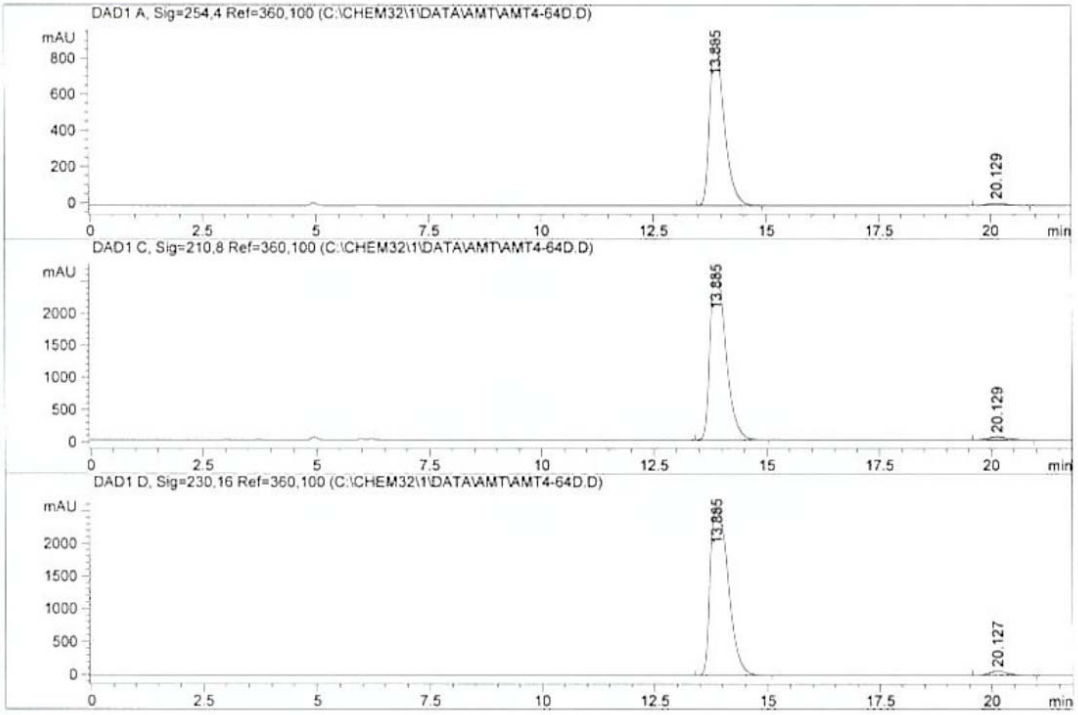


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
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Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
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Data File C:\CHEM32\1\DATA\AMT\AMT4-64D.D
Sample Name: AMT4-64D

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.885	BB	0.3335	2.03936e4	931.11536	98.1642
2	20.129	BB	0.4360	381.39459	13.32124	1.8358
Totals :				2.07750e4	944.43660	

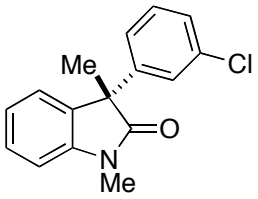
Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.885	BB	0.3803	6.36561e4	2611.97803	97.9878
2	20.129	BB	0.4366	1307.15881	45.30059	2.0122
Totals :				6.49632e4	2657.27862	

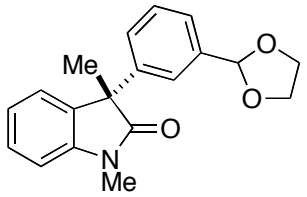
Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.885	BB	0.4431	7.08319e4	2573.75708	97.5325
2	20.127	BB	0.4407	1791.97412	62.08633	2.4675
Totals :				7.26238e4	2635.84341	

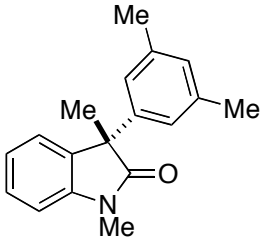
*** End of Report ***



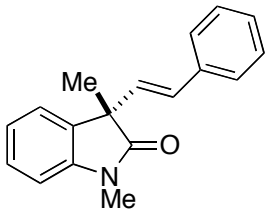
3-(3-chlorophenyl)-1,3-dimethylindolin-2-one (**3**, Table 1, entry 4) The reaction was conducted according to the general procedure for 18 h to afford the title compound as an off-white solid (86 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (td, *J* = 1.4, 7.7, 7.7 Hz, 1H), 7.29 (m, 1H), 7.22 (m, 3H), 7.19 (ddd, *J* = 0.5, 1.4, 7.4 Hz, 1H), 7.13 (td, *J* = 1.0, 7.4, 7.4 Hz, 1H), 6.94 (d, 7.8 Hz, 1H), 3.25 (s, 3H), 1.77 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.7, 143.0, 142.7, 134.3, 133.9, 129.7, 128.3, 127.4, 126.9, 124.9, 124.0, 122.9, 108.4, 51.8, 26.4, 23.7 ppm. IR (neat, cm^{-1}): 1715.6, 1611.9, 1593.7, 1569.8, 1492.7, 1471.1, 1418.0, 1374.3, 1345.3, 1303.6, 1256.7, 1144.8, 1102.9, 1024.2. Enantiomeric excess: 97%, Chiralpak AD-H column, 2% ^{i}PrOH, 98% hexanes; t_{minor}= 15.2 min, t_{major}= 12.8 min; $[\alpha]_D^{21}$ -14.68 ° (c 0.066, $CHCl_3$). Anal. Calc. for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19. Found: C, 70.85; H, 5.15. M. P.: 90 °C.



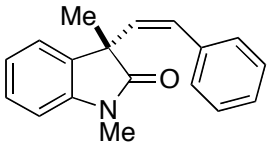
3-[3-(1,3-dioxolan-2-yl)phenyl]-1,3-dimethylindolin-2-one (Table 1, entry 5) The reaction was conducted according to the general procedure to afford the title compound as a clear oil (97 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (m, 1H), 7.38 (m, 1H), 7.31 (m, 3H), 7.20 (dd, *J* = 1.2, 7.4 Hz, 1H), 7.10 (dt, *J* = 0.9, 7.5, 7.5 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.76 (s, 1H), 4.08 (m, 4H), 3.23 (s, 3H), 1.79 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.0, 143.0, 140.8, 138.0, 134.4, 128.5, 128.0, 127.5, 125.1, 124.7, 124.1, 122.6, 108.2, 103.5, 65.1, 65.0, 51.9, 26.3, 23.9 ppm. IR (neat, cm^{-1}): 3054.8, 2970.1, 2887.3, 1715.2, 1611.8, 1492.2, 1471.1, 1420.1, 1374.0, 1345.8, 1304.0, 1255.4, 1221.3, 1174.1, 1143.9, 1102.9, 1083.6, 1024.7. Enantiomeric excess: 96%, Chiralpak AS-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 17.339 min, t_{major}= 15.328 min; $[\alpha]_D^{22}$ -11.65 ° (c 0.086, $CHCl_3$).



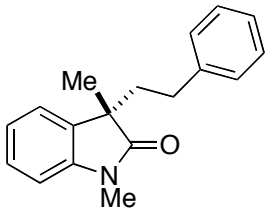
3-(3,5-dimethylphenyl)-1,3-dimethylindolin-2-one (Table 1, entry 6) The reaction was conducted according to the general procedure to afford the title compound as an off-white solid (106 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (dt, *J* = 1.3, 7.7, 7.7 Hz, 1H), 7.22 (m, 1H), 7.14 (m, 1H), 6.94 (m, 4H), 3.28 (s, 3H), 2.30 (s, 6H), 1.80 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.5, 143.0, 140.5, 137.8, 135.1, 128.9, 127.8, 124.2, 124.0, 122.6, 108.1, 51.9, 26.3, 23.5, 21.3 ppm. IR (neat, cm^{-1}): 1716.6, 1611.5, 1492.7, 1470.6, 1372.8, 1342.7, 1303.3, 1256.4, 1102.2, 1026.4. Enantiomeric excess: 96%, Chiralpak AD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 5.240 min, t_{major}= 4.338 min; $[\alpha]_D^{22}$ -112.7 ° (c 0.582, $CHCl_3$). Anal. Calc. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22. Found: C, 81.47; H, 7.31. M. P.: 86 °C.



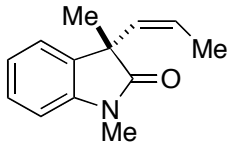
(*E*)-1,3-dimethyl-3-styrylindolin-2-one (Table 1, entry 7 *trans*) The reaction was conducted according to the general procedure at room temperature for 24 h. The title compound was isolated as a white foam (98 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (m, 3H), 7.31 (m, 3H), 7.23 (tt, *J* = 1, 1, 6.5, 6.5 Hz, 1H), 7.17 (td, *J* = 1, 8, 8 Hz, 1H), 3.25 (s, 3H), 1.62 (s, 3H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ: 178.6, 142.9, 136.4, 132.8, 129.9, 129.8, 128.4, 128.1, 127.6, 126.4, 123.9, 122.5, 108.3, 50.6, 26.3, 23.0 ppm. IR (neat, cm^{-1}): 1714.5, 1611.7, 1492.7, 1490.3, 1447.4, 1419.1, 1373.7, 1348.2, 1254.5. Enantiomeric excess: 77%, Chiralpak AD-H column, 5% ^{i}PrOH, 95% hexanes; t_{minor}= 12.100 min, t_{major}= 19.285 min; $[\alpha]_D^{22}$ -91.78 ° (c 1.428, $CHCl_3$). Anal. Calc. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51. Found: C, 82.06; H, 6.51.



(*Z*)-1,3-dimethyl-3-styrylindolin-2-one (Table 1, entry 7 *cis*) The title compound was isolated as a clear oil (14 mg, 11%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (tt, *J* = 0.5, 0.5, 7.5, 7.5 Hz, 1H), 7.13 (dt, *J* = 0.5, 0.5, 7 Hz, 1H), 7.03 (m, 3H), 6.49 (d, *J* = 11.5 Hz, 1H), 6.58 (m, 2H), 5.95 (dd, *J* = 0.5, 11.5 Hz, 1H), 2.81 (d, *J* = 1 Hz, 3H), 1.15 (d, *J* = 0.5 Hz, 3H) ppm. IR (neat, cm^{-1}): 1715.5, 1611.3, 1492.3, 1469.8, 1372.0, 1343.9, 1252.0, 1122.6, 1028.4. Enantiomeric excess: 98% (determined from reduced compound, *vide infra*); $[\alpha]_D^{22}$ -159 ° (c 0.28, $CHCl_3$). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 179.0, 142.5, 136.6, 136.0, 133.2, 133.0, 127.9, 127.6, 127.2, 126.5, 123.0, 122.4, 107.9, 48.7, 26.6, 25.9 ppm.

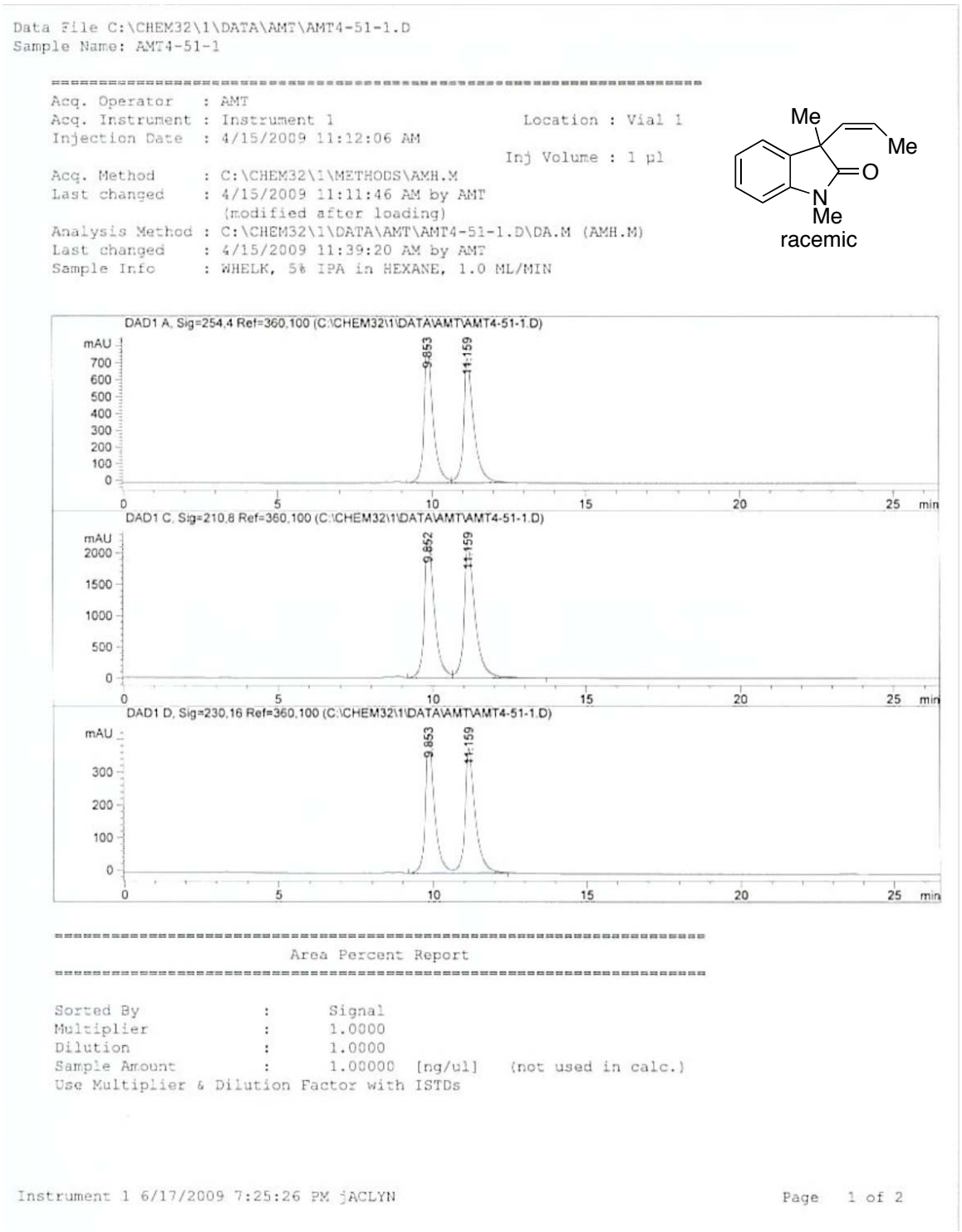


1,3-dimethyl-3-phenethylindolin-2-one (Table 1, entry 7 *cis* reduced) A round-bottomed flask was charged with (*Z*)-1,3-dimethyl-3-styrylindolin-2-one (6.1 mg, 0.023 mmol, 1 equiv), a stirbar, and a small amount of Pd/C before being sealed with a rubber septum. EtOH/ EtOAc (1:1, 4 mL) was added, and the vessel was evacuated and backfilled with H_2 three times. The reaction was stirred vigorously at rt for 2 h before the mixture was filtered though a plug of silica gel and eluted with EtOAc. The filtrate was concentrated *in vacuo* and purified by column chromatography with a Biotage (hexanes/ EtOAc) to yield the title compound as a clear oil (6 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (td, *J* = 1.3, 7.7, 7.7 Hz, 1H), 7.21 (m, 3H), 7.11 (m, 2H), 7.03 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 2.29 (m, 2H), 2.16 (dd, *J* = 2.2, 11.8 Hz, 1H), 2.01 (m, 1H), 1.39 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 180.3, 143.4, 141.4, 133.8, 128.3, 128.2, 127.8, 125.8, 122.6, 122.5, 108.0, 48.4, 40.2, 31.0, 26.1, 23.9 ppm. IR (neat, cm^{-1}): 1711.6, 1612.8, 1383.7. Enantiomeric excess: 98%, Chiralcel OD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 6.11 min, t_{major}= 7.44 min; $[\alpha]_D^{22}$ 0.34 ° (c 0.092, $CHCl_3$).



(*Z*)-1,3-dimethyl-3-(prop-1-enyl)indolin-2-one (Table 1, entry 8) The reaction was conducted according to the general procedure at room temperature for 24 h. The title compound was isolated as a clear oil (81 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (td, *J* = 1.5, 8, 8 Hz, 1H), 7.16 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.05 (td, *J* = 1, 7.5, 7.5

Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 5.62 (dq, J = 1.5, 3, 11 Hz, 1H), 5.56 (m, 1H), 3.23 (s, 3H), 1.50 (s, 3H), 1.07 (dd, J = 1.5, 7 Hz, 3H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ: 179.7, 142.5, 135.4, 131.2, 128.6, 127.5, 122.9, 122.7, 107.9, 48.5, 26.4, 26.2, 13.3 ppm. IR (neat, cm^{-1}): 3019.7, 2969.5, 2926.4, 1717.1, 1611.2, 1492.1, 1470.6, 1451.6, 1420.9, 1400.9, 1372.2, 1343.1, 1303.1, 1252.7, 1158.0, 1124.8, 1053.8, 1024.9. Enantiomeric excess: 94%, Whelk-O1 column, 5% ^{i}PrOH, 95% hexanes; t_{minor}= 10.593 min, t_{major}= 11.827 min; $[\alpha]_D^{22}$ -44.98 ° (c 1.04, $CHCl_3$). Anal. Calc. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.30; H, 7.61.



Data File C:\CHEM32\1\DATA\AMT\AMT4-51-1.D
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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1	9.853	VV	0.2969	1.69955e4	829.83063	49.4578
2	11.159	VB	0.3371	1.73681e4	741.84705	50.5422
Totals :				3.43637e4	1571.67767	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.852	VV	0.3399	5.12177e4	2230.54956	48.6064
2	11.159	VB	0.3773	5.41548e4	2097.07861	51.3936
Totals :				1.05373e5	4327.62817	

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.853	VV	0.2965	8723.73730	426.65952	49.6775
2	11.159	VB	0.3347	8836.99316	380.91174	50.3225
Totals :				1.75607e4	807.57126	

*** End of Report ***

Data File C:\CHEM32\1\DATA\AMT\AMT4-69B.D
Sample Name: AMT4-69B

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Acq. Operator   : AMT
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 5/2/2009 4:15:23 PM
                                                  Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\1\METHODS\AMH.M
Last changed    : 5/2/2009 4:28:51 PM by AMT
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\AMT\AMT4-69B.D\DA.M (AMH.M)
Last changed    : 5/2/2009 4:30:50 PM by AMT
Sample Info     : WHELK-O, 5% IPA 1.0 ML/MIN
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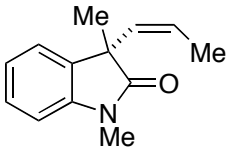

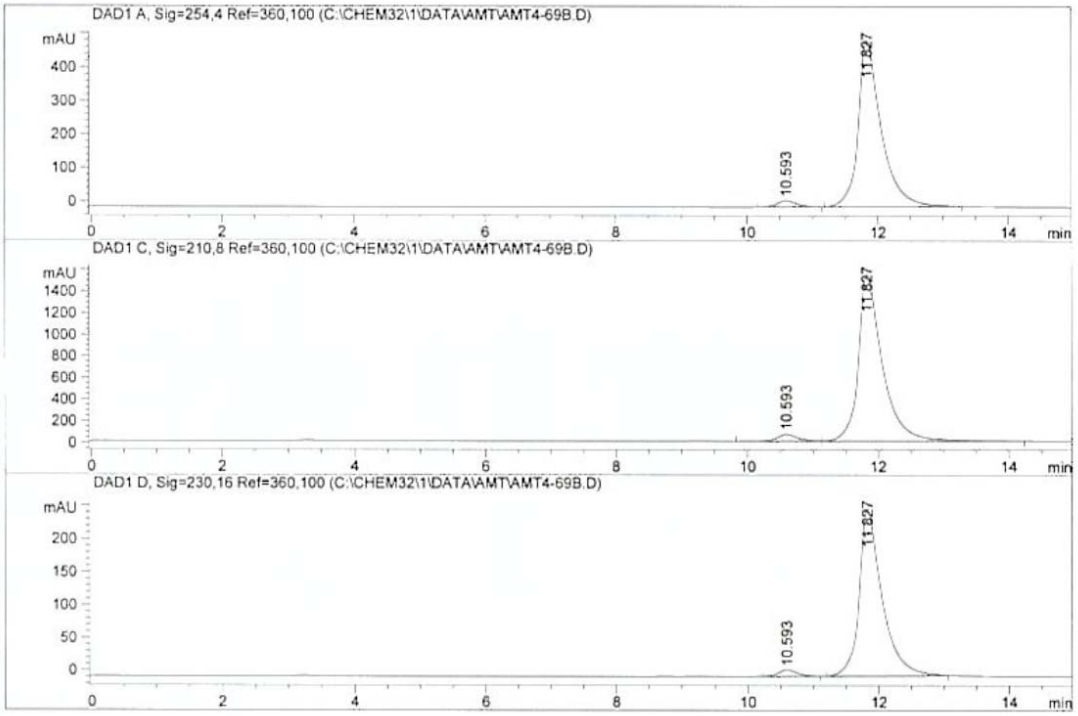


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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
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Data File C:\CHEM32\1\DATA\AMT\AMT4-69B.D
Sample Name: AMT4-69B

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.593	BB	0.3052	384.30042	18.74267	3.0553
2	11.827	BB	0.3540	1.21940e4	493.94867	96.9447
Totals :				1.25783e4	512.69134	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

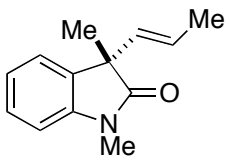
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.593	BV	0.3216	1380.08276	62.99067	3.3643
2	11.827	VB	0.3725	3.96410e4	1539.27563	96.6357
Totals :				4.10211e4	1602.26630	

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.593	BB	0.3003	192.49416	9.58444	3.0021
2	11.827	BB	0.3523	6219.52051	253.46826	96.9979
Totals :				6412.01466	263.05270	

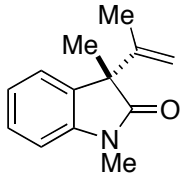
*** End of Report ***

Instrument 1 6/17/2009 7:35:45 PM jACLYN Page 2 of 2

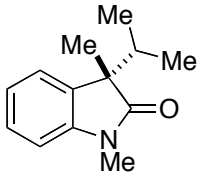


(*E*)-1,3-dimethyl-3-(prop-1-enyl)indolin-2-one (Table 1, entry 9) The reaction was conducted according to the general procedure at room temperature for 24 h. The title compound was isolated as a clear oil (90 mg, 89%). ^{1}H

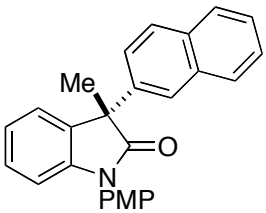
NMR (500 MHz, $CDCl_3$) δ: 7.28 (tt, *J* = 1, 1, 7.5, 7.5 Hz, 1H), 7.18 (dt, *J* = 0.5, 0.5, 7.5 Hz, 1H), 7.08 (tt, *J* = 1, 1, 8, 8 Hz, 1H), 6.85 (dd, *J* = 0.5, 7.5 Hz, 1H), 5.60 (dq, *J* = 1.5, 2.5, 15.5 Hz, 1H), 5.54 (m, 1H), 3.19 (d, *J* = 1 Hz, 3H), 1.65 (dd, *J* = 1, 6 Hz, 3H), 1.45 (d, *J* = 0.5 Hz, 3H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ: 179.1, 142.8, 133.4, 130.9, 127.7, 125.9, 123.6, 122.3, 108.0, 50.3, 26.1, 22.8, 17.8 ppm. IR (neat, cm^{-1}): 2967.2, 2927.0, 1718.8, 1611.7, 1493.2, 1471.0, 1450.0, 1420.0, 1373.8, 1345.6, 1306.0, 1256.2, 1158.8, 1119.7, 1084.8, 1055.0, 1024.5. Enantiomeric excess: 54%, Whelk-O1 column, 5% ^{i}PrOH, 95% hexanes; t_{minor}= 9.863 min, t_{major}= 12.001 min; $[\alpha]_D^{22}$ -0.46 ° (c 0.25, $CHCl_3$). Anal. Calc. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.29; H, 7.59.



1,3-dimethyl-3-(prop-1-en-2-yl)indolin-2-one (**4**, Table 1, entry 10) The reaction was conducted according to the general procedure at 50 °C for 24 h. The title compound was isolated as a white crystalline solid (64 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (td, *J* = 1.5, 7.5, 7.5 Hz, 1H), 7.09 (ddd, *J* = 0.5, 1.5, 7.5 Hz, 1H), 7.05 (dt, *J* = 1, 1, 8.5 Hz, 1H), 6.85 (d, *J* = 8 Hz, 1H), 5.09 (d, *J* = 1 H, 1H), 5.03 (p, *J* = 1.5, 1.5, 2.5 Hz, 1H), 3.22 (s, 3H), 1.48 (m, 6H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ: 179.0, 143.5, 143.3, 133.7, 127.9, 123.0, 122.6, 112.9, 108.0, 53.8, 26.3, 21.3, 19.4 ppm. IR (neat, cm^{-1}): 2979.0, 2935.7, 2880.2, 1720.4, 1645.4, 1610.9, 1493.1, 1474.0, 1445.2, 1418.4, 1373.0, 1345.0, 1300.9, 1258.7, 1228.5, 1118.4, 1102.9, 1060.2, 1032.9, 1001.9. Enantiomeric excess: (determined from reduced compound, *vide infra*); $[\alpha]_D^{21}$ +28.4 (c 0.38, $CHCl_3$). Anal. Calc. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.42; H, 7.59. M. P.: 60 °C.

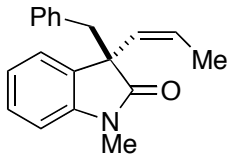


3-isopropyl-1,3-dimethylindolin-2-one (**5**, Scheme 1) A round bottomed flask was charged with 1,3-dimethyl-3-(prop-1-en-2-yl)indolin-2-one (**2**, 28 mg, 0.138 mmol), Pd/C (small spatula tip, ~10 mg), and a stirbar. EtOH/ EtOAc (1:1, 4 mL) was added, and the mixture was evacuated and purged with H_2 three times before the mixture was stirred at room temperature for 2 h. The mixture was filtered through a plug of silica gel, concentrated, and purified with a Biotage on silica gel with hexanes and ethyl acetate to yield the title compound was isolated as a white solid (25 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (td, *J* = 1.3, 7.7, 7.7 Hz, 1H), 7.20 (dd, *J* = 0.5, 7.6, 7.6 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.20 (s, 3H), 2.18 (sept, *J* = 6.9, 6.9, 13.8, 13.8 Hz, 1H), 1.36 (s, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.71 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 180.9, 143.5, 133.0, 127.5, 123.4, 122.1, 107.7, 51.5, 35.4, 25.9, 21.4, 17.4, 17.1 ppm. IR (neat, cm^{-1}): 2964.4, 1708.3, 1611.8, 1493.1 1469.3, 1376.0, 1348.8, 1300.9, 1259.9, 1125.1, 1074.4, 1020.8. Enantiomeric excess: 96%, Chiralcel OC column, 2% ^{i}PrOH, 98% hexanes; t_{minor}= 25.17 min, t_{major}= 22.64 min; $[\alpha]_D^{21}$ +53.94 °(c = 0.404, $CHCl_3$). M. P.: 54 °C.

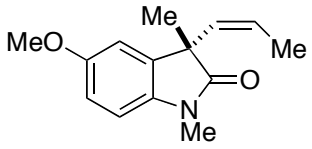


1-(4-methoxyphenyl)-3-methyl-3-(naphthalen-2-yl)indolin-2-one (Figure 2) The reaction was conducted according to the general procedure at 50 °C for 24 h. The title compound was isolated as a white solid (139 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 1.6 Hz, 1H), 7.85, (m, 3H), 7.55 (m, 3H), 7.44 (dt, *J* = 3.3, 3.3, 10.1 Hz, 2H), 7.31 (m, 2H), 7.19 (td, *J* = 0.7, 7.5, 7.5 Hz, 1H), 7.10 (dt, *J* = 3.3, 3.3, 10.1 Hz, 2H), 6.97 (m, 1H), 3.89 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.8, 159.0, 143.5, 138.2, 134.5, 133.1, 132.4, 128.3, 18.0, 127.9, 127.3, 127.0, 126.0, 125.9, 125.3, 124.8, 124.4, 123.1, 114.7, 109.5, 55.4, 52.2, 23.7 ppm. IR

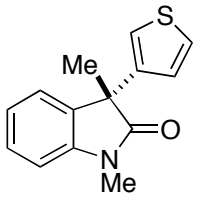
(neat, cm^{-1}): 3054.7, 2969.4, 2933.5, 2837.4, 22467.0, 2047.0, 1719.8, 1632.2, 1586.7, 1513.9, 1483.4, 1463.8, 1375.5, 1324.8, 1298.9, 1249.5, 1210.3, 1180.8, 1167.0, 1129.0, 1106.7, 1059.7, 1031.6. Enantiomeric excess: >99%, Chiralpak AD-H column, 30% ^{i}PrOH, 70% hexanes; t_{minor}= 49.348 min, t_{major}= 14.142 min; $[\alpha]_D^{21}$ +29.8 ° (c = 2.56, $CHCl_3$). Anal. Calc. for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58. Found: C, 82.30; H, 5.64. M. P.: 144 °C.



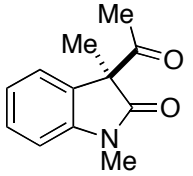
(*Z*)-3-benzyl-1-methyl-3-(prop-1-enyl)indolin-2-one (Figure 2) The reaction was conducted according to the general procedure at 50 °C for 24 h. The title compound was isolated as a yellow solid (104 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (m, 2H), 7.01 (m, 4H), 6.78 (m, 2H), 6.53 (m, 1H), 5.80 (dq, *J* = 1.6, 3.3, 10.9 Hz, 1H), 5.65 (m, 1H), 3.33 (d, *J* = 12.6 Hz, 2H), 3.18 (d, *J* = 12.6 Hz, 1H), 2.90 (s, 3H), 1.09 (dd, *J* = 1.7, 7.04 Hz, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.0, 143.1, 134.8, 132.5, 130.1, 129.8, 129.2, 127.6, 127.1, 126.4, 123.8, 122.2, 107.5, 54.4, 45.8, 25.7, 13.9 ppm. IR (neat, cm^{-1}): 3028.5, 1712.2, 1610.3, 1492.5, 1469.8, 1373.1, 1350.1, 1254.1, 1118.4, 1088.1, 1021.4. Enantiomeric excess: 86%, Chiralpak AD-H column, 2% ^{i}PrOH, 1.0 mL/ min, 98% hexanes; t_{minor}= 14.64 min, t_{major}= 12.71 min; $[\alpha]_D^{22}$ +3.48 ° (c = 0.168, $CHCl_3$). M. P.: 74 °C.



(Z)-5-methoxy-1,3-dimethyl-3-(prop-1-enyl)indolin-2-one (Figure 2) The reaction was conducted according to the general procedure at 50 °C for 24 h. The title compound was isolated as a clear oil (91 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.74 (m, 3H), 5.55 (m, 2H), 3.75 (s, 3H), 3.19 (s, 3H), 1.46 (s, 3H), 1.07 (dt, *J* = 1.3, 1.3, 6.7 Hz, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.4, 156.1, 136.8, 136.0, 131.1, 128.8, 111.6, 110.3, 108.1, 55.6, 48.9, 26.5, 26.2, 13.3 ppm. IR (neat, cm^{-1}): 3018.5, 2967.6, 2834.6, 1710.7, 1600.3, 1494.9, 1469.3, 1434.5, 1401.1, 1348.3, 1287.4, 1234.1, 1206.2, 1179.8, 1156.1, 1117.7, 1035.5. Enantiomeric excess: 71%, Chiralpak AS-H column, 2% ^{i}PrOH, 90% hexanes; t_{minor}= 18.10 min, t_{major}= 20.50 min; $[\alpha]_D^{22}$ -70.73 ° (c = 1.186, $CHCl_3$).

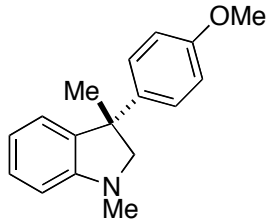


1,3-dimethyl-3-(thiophen-3-yl)indolin-2-one (Figure 2) The reaction was conducted according to the general procedure at 50 °C for 24 h. The title compound was isolated as a clear oil (50 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (dd, *J* = 1.1, 7.6 Hz, 1H), 7.30 (m, 1H), 7.27 (dd, *J* = 3.2, 5.0), 7.14 (td, *J* = 0.7, 7.4, 7.4 Hz, 1H), 7.07 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 1.76 (s, 3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.6, 142.9, 141.5, 134.1, 128.2, 126.4, 126.0, 123.8, 122.7, 121.4, 108.3, 49.9, 26.4, 24.4 ppm. IR (neat, cm^{-1}): 3105.1, 3054.3, 2970.3, 2929.7, 1715.8, 1612.0, 1493.4, 1470.9, 1451.9, 1419.5, 1373.5, 1346.5, 1303.2, 1246.2, 1203.5, 1157.8, 1143.7, 1114.2, 1057.5, 1024.5. Enantiomeric excess: 95%, Chiralpak AD-H column, 10% ^{i}PrOH, 90% hexanes; t_{minor}= 6.80 min, t_{major}= 7.96 min; $[\alpha]_D^{22}$ -164.0 ° (c = 0.56, $CHCl_3$).

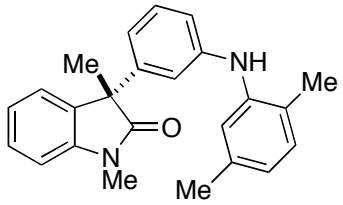


3-acetyl-1,3-dimethylindolin-2-one (**6**, Scheme 1) A round bottomed flask was charged with 1,3-dimethyl-3-(prop-1-en-2-yl)indolin-2-one (**2**, 18 mg, 0.089 mmol, 1 equiv) and a stirbar. Methylene chloride (10 mL) was added, and

the reaction was cooled to -78 °C. A Welsbach ozonator was used to generate ozone at a rate of about 0.9 mmol/ min, and O_3 was bubbled through the solution until a blue color persisted. Argon was then bubbled through the solution until the blue color disappeared. PPh_3 (47 mg, 0.18 mg, 2 equiv) was added, and the solution was warmed to room temperature and stirred for 2 h before being concentrated. Silica gel chromatography with a Biotage yielded the title compound was isolated as a white film (12 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (td, *J* = 1.4, 7.8, 7.8 Hz, 1H), 7.16 (ddd, *J* = 0.6, 1.4, 7.4 Hz, 1H), 7.11 (td, *J* = 1.0, 7.4, 7.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.30 (s, 3H), 1.96 (s, 3H), 1.57 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 201.0, 175.9, 143.7, 129.4, 129.1, 123.5, 123.2, 108.6, 62.0, 26.6, 25.9, 18.9 ppm. IR (neat, cm^{-1}): 1725.5, 1704.9, 1609.4, 1492.6, 1470.5, 1373.8, 1345.8, 1196.5, 1103.7, 1029.7. Enantiomeric excess: 96%, Chiralcel OC column, 2% ^{i}PrOH, 98% hexanes; t_{minor}= 62.30 min, t_{major}= 53.69 min; $[\alpha]_D^{22}$ +211.13 ° (c = 0.124, $CHCl_3$).



3-(4-methoxyphenyl)-1,3-dimethylindoline (**7**, Scheme 1) A round-bottomed flask was charged with **2** (43 mg, 0.161 mmol, 1 equiv) and a stirbar before being evacuated and purged with argon three times. Et_2O (0.8 mL, [**2**] = 0.1 M) was added, and the solution was cooled to 0 °C before the addition of a solution of $LiAlH_4$ (1.0 M in Et_2O, 800 μL, 0.805 mmol, 5 equiv). The solution was stirred at 0 °C for five minutes before being warmed to room temperature and stirred for 2 h. The reaction was quenched with H_2O, extracted with EtOAc, dried with magnesium sulfate, and concentrated *in vacuo*. Silica gel chromatography with a Biotage yielded the title compound as a red oil (25 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28 (m, 2H), 7.21 (td, *J* = 1.5, 7.5, 7.5 Hz, 1H), 7.00 (ddd, *J* = 0.5, 1, 7 Hz, 1H), 6.87 (m, 2H), 6.78 (td, *J* = 1, 7.5, 7.5 Hz, 1H), 6.62 (d, *J* = 8 Hz, 1H), 3.81 (s, 3H), 3.52 (d, *J* = 9 Hz, 1H), 3.33 (d, *J* = 9 Hz, 1H), 2.81 (s, 3H), 1.72 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 157.8, 152.5, 139.6, 137.9, 127.8, 127.6, 123.6, 118.1, 113.4, 107.7, 72.2, 55.2, 47.6, 36.0, 26.3 ppm. IR (neat, cm^{-1}): 3045.4, 2960.0, 2853.8, 2833.9, 2806.4, 1605.5, 1580.4, 1510.7, 1489.6, 1462.5, 1422.3, 1378.1, 1324.3, 1296.3, 1249.2, 1182.4, 1156.1, 1115.7, 1097.7, 1083.8, 1034.5, 1021.7. Enantiomeric excess: 96%, OJ column, 0.5% ^{i}PrOH, 99.5% hexanes; t_{minor}= 75.48 min, t_{major}= 51.62 min; $[\alpha]_D^{22}$ -27.42 ° (c = 0.5, $CHCl_3$).



3-(3-(2,5-dimethylphenylamino)phenyl)-1,3-dimethylindolin-2-one (**8**, Scheme 1) For more details about the method that was used, see the recent publication regarding BrettPhos.[8] A round-bottomed flask was charged with 3-(3-chlorophenyl)-1,3-dimethylindolin-2-one (35.7 mg, 0.13 mmol, 1 equiv) before being evacuated and purged with Argon three times. 2,5-dimethylaniline (20 μL, 0.158 mmol, 1.2 equiv) was added, followed by dibutyl ether (1 mL). The solution was added to a disposable tube containing BrettPhos precatalyst (1.05 mg, 0.0013 mmol, 0.01 equiv) and NaO^{t}Bu (15.2 mg, 0.158, 1.2 equiv), which had been previously evacuated and purged with Argon three times. The mixture was stirred at 110 °C for 2 h before being cooled, diluted with ethyl acetate, washed with water and brine, dried with magnesium sulfate, filtered, and concentrated. Silica gel chromatography with a Biotage (hexanes: ethyl acetate) yielded the title compound as a white solid (41 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (td, *J* = 1.3, 7.7, 7.7 Hz, 1H), 7.25 (ddd, *J* = 0.6, 1.3, 7.4 Hz, 1H), 7.20 (t, *J* = 8, 8, Hz, 1H), 7.06 (td, *J* = 1, 7.6, 7.6 Hz, 1H), 7.02 (s, 1H), 6.91 (m, 2H), 6.87 (dd, *J* = 1.9, 7.7 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.37 (s, 1H), 3.25 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 1.79 (s, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ: 179.4, 143.8, 143.1, 141.9, 140.8, 136.3, 134.9, 130.6, 129.3, 128.0, 124.5, 124.1, 122.7, 122.3, 118.6, 118.5, 116.2, 116.1, 108.2, 52.1, 26.4, 23.5, 21.1, 17.4 ppm. IR (neat, cm^{-1}): 1707.0, 1611.6, 1471.2, 1373.3, 1346.3, 1102.8. Enantiomeric excess: 97%,

[8] Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 13552.

Chiralcel OD-H column, 5% ^{i}PrOH, 95% hexanes; t_{minor}= 18.23 min, t_{major}= 14.22 min; $[\alpha]_D^{21}$ -68.7 ° (c = 0.736, $CHCl_3$). M. P.: 48 °C

X-ray crystallographic information for ent-**4**

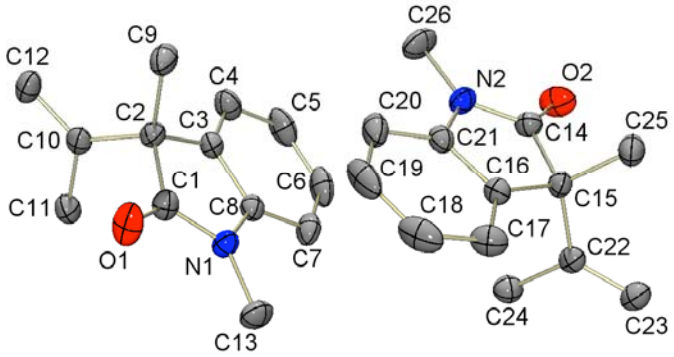


Table 1. Crystal data and structure refinement for **amt 4-3-4**.

Empirical formula	$C_{13}H_{15}NO$	
Formula weight	201.26	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.3945(3) Å	α= 90°
	b = 17.4160(6) Å	β= 90.9340(10)°
	c = 8.8582(3) Å	γ = 90°
Volume	1140.63(7) $Å^3$	
Z	4	
Density (calculated)	1.172 Mg/m^3	
Absorption coefficient	0.581 mm^{-1}	
F(000)	432	
Crystal size	0.48 x 0.36 x 0.18 mm^3	
Theta range for data collection	4.99 to 68.59°.	
Index ranges	-8<=h<=8, -20<=k<=21, -10<=l<=10	
Reflections collected	15919	
Independent reflections	3991 [R(int) = 0.0168]	
Completeness to theta = 68.59°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9027 and 0.7680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3991 / 1 / 271	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0848	
R indices (all data)	R1 = 0.0307, wR2 = 0.0848	
Absolute structure parameter	-0.03(19)	
Largest diff. peak and hole	0.162 and -0.264 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **amt 4-3-4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9740(2)	1327(1)	2357(1)	25(1)
O(1)	9268(2)	73(1)	1644(1)	39(1)
C(1)	9447(2)	750(1)	1337(2)	26(1)
N(2)	4981(2)	3388(1)	2657(1)	27(1)
O(2)	4793(2)	4670(1)	3250(1)	38(1)
C(2)	9341(2)	1109(1)	-266(2)	24(1)
C(3)	9689(2)	1949(1)	82(2)	24(1)
C(4)	9818(2)	2578(1)	-856(2)	32(1)
C(5)	10138(2)	3300(1)	-214(2)	40(1)
C(6)	10311(2)	3383(1)	1337(2)	39(1)
C(7)	10190(2)	2753(1)	2299(2)	32(1)
C(8)	9889(2)	2042(1)	1639(2)	24(1)
C(9)	7419(2)	978(1)	-891(2)	35(1)
C(10)	10819(2)	765(1)	-1239(2)	24(1)
C(11)	12722(2)	879(1)	-659(2)	30(1)
C(12)	10468(2)	396(1)	-2522(2)	31(1)
C(13)	9870(2)	1212(1)	3981(2)	34(1)
C(14)	4788(2)	3996(1)	3615(2)	25(1)
C(15)	4518(2)	3680(1)	5225(2)	23(1)
C(16)	4673(2)	2820(1)	4963(2)	23(1)
C(17)	4586(2)	2211(1)	5963(2)	33(1)
C(18)	4744(2)	1467(1)	5399(2)	43(1)
C(19)	4969(2)	1343(1)	3877(2)	44(1)
C(20)	5059(2)	1952(1)	2850(2)	36(1)
C(21)	4918(2)	2686(1)	3432(2)	24(1)
C(22)	6023(2)	3974(1)	6278(2)	24(1)
C(23)	5692(2)	4331(1)	7569(2)	31(1)
C(24)	7916(2)	3824(1)	5766(2)	30(1)
C(25)	2615(2)	3908(1)	5720(2)	33(1)
C(26)	5209(2)	3460(1)	1034(2)	40(1)

Table 3. Bond lengths [Å] and angles [°] for **amt 4-3-4**.

N(1)-C(1)	1.3662(19)
N(1)-C(8)	1.4033(19)
N(1)-C(13)	1.4536(18)
O(1)-C(1)	1.2184(18)
C(1)-C(2)	1.5516(19)
N(2)-C(14)	1.3647(18)
N(2)-C(21)	1.4046(19)
N(2)-C(26)	1.4558(17)
O(2)-C(14)	1.2173(18)
C(2)-C(3)	1.5170(19)
C(2)-C(10)	1.526(2)
C(2)-C(9)	1.534(2)
C(3)-C(4)	1.379(2)
C(3)-C(8)	1.3944(19)
C(4)-C(5)	1.398(2)
C(5)-C(6)	1.386(3)
C(6)-C(7)	1.392(2)
C(7)-C(8)	1.386(2)
C(10)-C(12)	1.326(2)
C(10)-C(11)	1.504(2)
C(14)-C(15)	1.5448(18)
C(15)-C(16)	1.5206(19)
C(15)-C(22)	1.5287(19)
C(15)-C(25)	1.532(2)
C(16)-C(17)	1.384(2)
C(16)-C(21)	1.391(2)
C(17)-C(18)	1.395(2)
C(18)-C(19)	1.378(3)
C(19)-C(20)	1.400(3)
C(20)-C(21)	1.382(2)
C(22)-C(23)	1.327(2)
C(22)-C(24)	1.501(2)

C(1)-N(1)-C(8)	111.40(11)
C(1)-N(1)-C(13)	124.12(13)
C(8)-N(1)-C(13)	124.48(12)
O(1)-C(1)-N(1)	125.46(13)
O(1)-C(1)-C(2)	126.16(13)
N(1)-C(1)-C(2)	108.36(12)
C(14)-N(2)-C(21)	111.53(11)
C(14)-N(2)-C(26)	124.24(14)
C(21)-N(2)-C(26)	124.22(14)
C(3)-C(2)-C(10)	111.91(11)
C(3)-C(2)-C(9)	111.69(12)
C(10)-C(2)-C(9)	113.96(12)
C(3)-C(2)-C(1)	101.32(11)
C(10)-C(2)-C(1)	109.44(11)
C(9)-C(2)-C(1)	107.66(12)
C(4)-C(3)-C(8)	119.76(14)
C(4)-C(3)-C(2)	131.12(13)
C(8)-C(3)-C(2)	109.12(12)
C(3)-C(4)-C(5)	118.84(15)
C(6)-C(5)-C(4)	120.62(15)
C(5)-C(6)-C(7)	121.27(15)
C(8)-C(7)-C(6)	117.20(14)
C(7)-C(8)-C(3)	122.31(14)

C(7)-C(8)-N(1)	127.94(13)
C(3)-C(8)-N(1)	109.75(12)
C(12)-C(10)-C(11)	121.68(14)
C(12)-C(10)-C(2)	122.83(13)
C(11)-C(10)-C(2)	115.49(12)
O(2)-C(14)-N(2)	125.55(13)
O(2)-C(14)-C(15)	126.08(13)
N(2)-C(14)-C(15)	108.35(11)
C(16)-C(15)-C(22)	111.53(11)
C(16)-C(15)-C(25)	111.75(12)
C(22)-C(15)-C(25)	113.69(12)
C(16)-C(15)-C(14)	101.41(11)
C(22)-C(15)-C(14)	109.90(11)
C(25)-C(15)-C(14)	107.77(12)
C(17)-C(16)-C(21)	120.18(14)
C(17)-C(16)-C(15)	130.75(13)
C(21)-C(16)-C(15)	109.06(12)
C(16)-C(17)-C(18)	118.56(16)
C(19)-C(18)-C(17)	120.59(16)
C(18)-C(19)-C(20)	121.60(15)
C(21)-C(20)-C(19)	116.95(15)
C(20)-C(21)-C(16)	122.12(14)
C(20)-C(21)-N(2)	128.29(14)
C(16)-C(21)-N(2)	109.60(12)
C(23)-C(22)-C(24)	121.86(13)
C(23)-C(22)-C(15)	122.63(14)
C(24)-C(22)-C(15)	115.51(12)

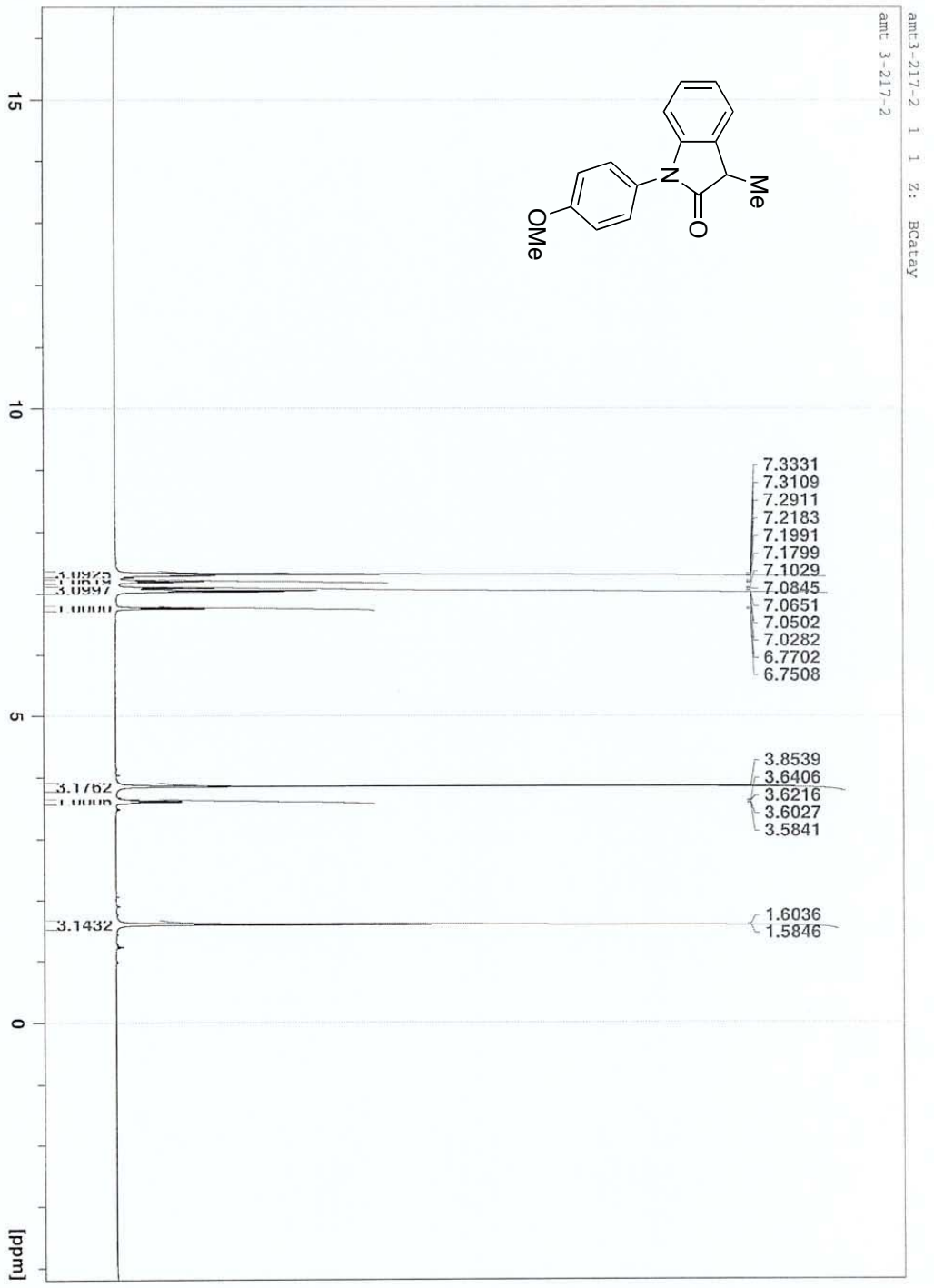
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **amt 4-3-4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	30(1)	25(1)	20(1)	1(1)	0(1)	-1(1)
O(1)	59(1)	23(1)	36(1)	4(1)	14(1)	-4(1)
C(1)	29(1)	25(1)	25(1)	1(1)	4(1)	-1(1)
N(2)	28(1)	33(1)	19(1)	1(1)	1(1)	-1(1)
O(2)	55(1)	23(1)	38(1)	10(1)	-10(1)	-2(1)
C(2)	26(1)	22(1)	22(1)	-1(1)	-1(1)	-2(1)
C(3)	23(1)	24(1)	25(1)	-1(1)	0(1)	3(1)
C(4)	36(1)	28(1)	32(1)	7(1)	4(1)	6(1)
C(5)	39(1)	23(1)	57(1)	10(1)	10(1)	5(1)
C(6)	35(1)	22(1)	61(1)	-11(1)	9(1)	-1(1)
C(7)	29(1)	30(1)	36(1)	-12(1)	1(1)	-3(1)
C(8)	20(1)	25(1)	26(1)	-2(1)	0(1)	0(1)
C(9)	25(1)	44(1)	36(1)	-15(1)	-1(1)	0(1)
C(10)	30(1)	20(1)	23(1)	4(1)	1(1)	1(1)
C(11)	27(1)	31(1)	33(1)	-1(1)	2(1)	4(1)
C(12)	41(1)	27(1)	25(1)	-2(1)	4(1)	0(1)
C(13)	38(1)	45(1)	20(1)	3(1)	-1(1)	0(1)
C(14)	27(1)	24(1)	23(1)	2(1)	-3(1)	-1(1)
C(15)	26(1)	21(1)	21(1)	-1(1)	1(1)	1(1)
C(16)	23(1)	21(1)	26(1)	0(1)	-2(1)	-1(1)
C(17)	33(1)	30(1)	36(1)	8(1)	-5(1)	-6(1)
C(18)	40(1)	25(1)	64(1)	12(1)	-17(1)	-7(1)
C(19)	34(1)	19(1)	77(1)	-10(1)	-15(1)	2(1)
C(20)	29(1)	35(1)	43(1)	-17(1)	-4(1)	4(1)
C(21)	20(1)	24(1)	29(1)	-2(1)	-1(1)	1(1)
C(22)	30(1)	19(1)	23(1)	2(1)	-1(1)	-1(1)
C(23)	40(1)	29(1)	25(1)	-1(1)	-3(1)	-2(1)
C(24)	27(1)	33(1)	30(1)	1(1)	-2(1)	-3(1)
C(25)	26(1)	40(1)	34(1)	-12(1)	0(1)	3(1)
C(26)	39(1)	62(1)	19(1)	-1(1)	3(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **amt 4-3-4**.

	x	y	z	U(eq)
H(4A)	9691	2522	-1919	38
H(5A)	10238	3737	-847	48
H(6A)	10516	3879	1753	47
H(7A)	10309	2809	3363	38
H(9A)	7306	1206	-1899	53
H(9B)	6545	1219	-219	53
H(9C)	7177	426	-953	53
H(11A)	13569	632	-1348	45
H(11B)	12851	649	347	45
H(11C)	12988	1429	-598	45
H(12A)	11432	196	-3099	37
H(12B)	9253	332	-2863	37
H(13A)	9727	666	4210	51
H(13B)	8917	1506	4475	51
H(13C)	11055	1388	4352	51
H(17A)	4423	2298	7010	40
H(18A)	4696	1042	6069	52
H(19A)	5066	831	3516	52
H(20A)	5210	1865	1801	43
H(23A)	6667	4498	8198	37
H(23B)	4480	4418	7864	37
H(24A)	8780	4034	6508	45
H(24B)	8097	4071	4786	45
H(24C)	8105	3269	5670	45
H(25A)	2408	3715	6742	50
H(25B)	1717	3686	5022	50
H(25C)	2503	4469	5712	50
H(26A)	5224	4004	755	60
H(26B)	4204	3203	506	60
H(26C)	6353	3220	748	60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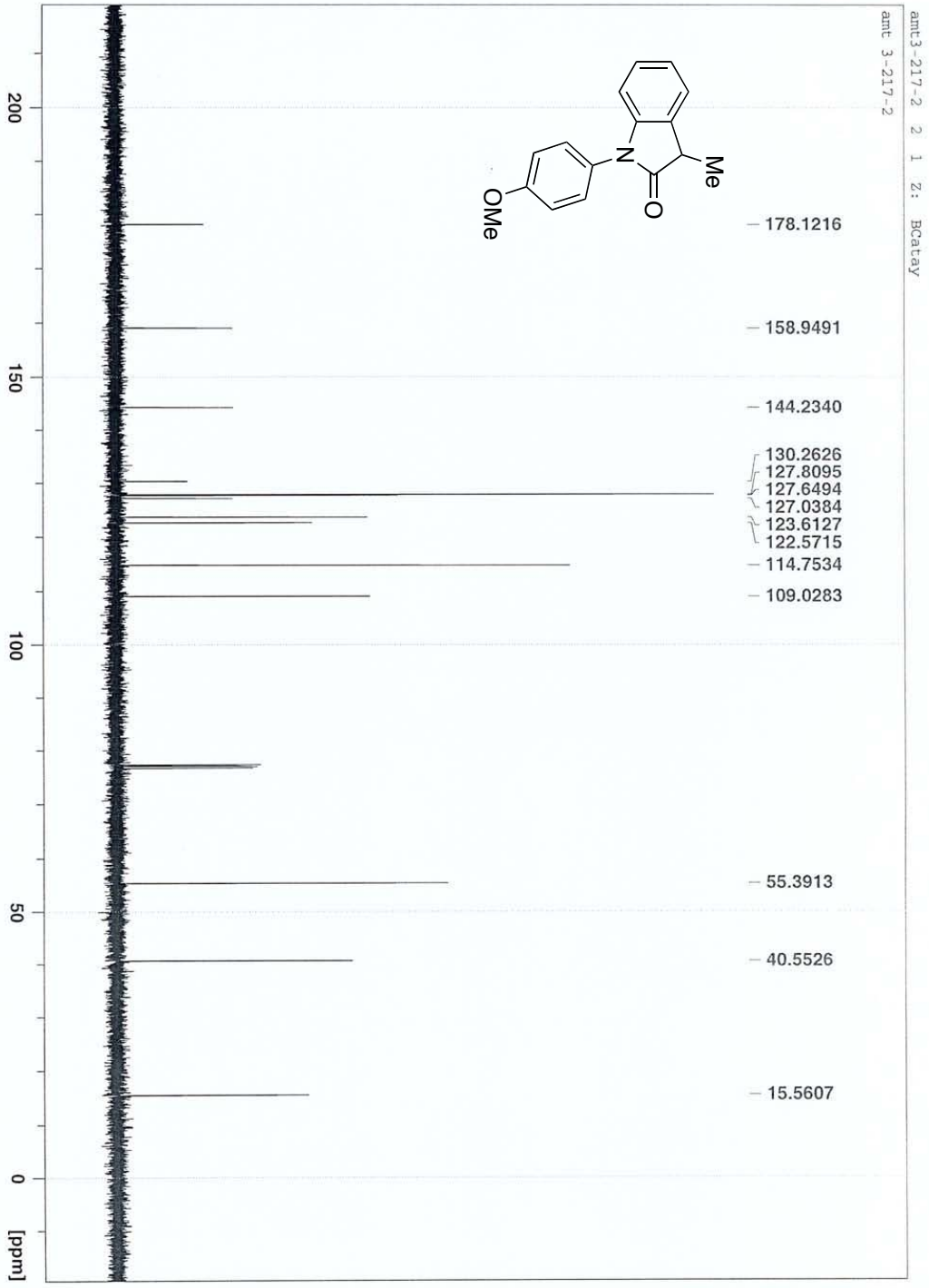
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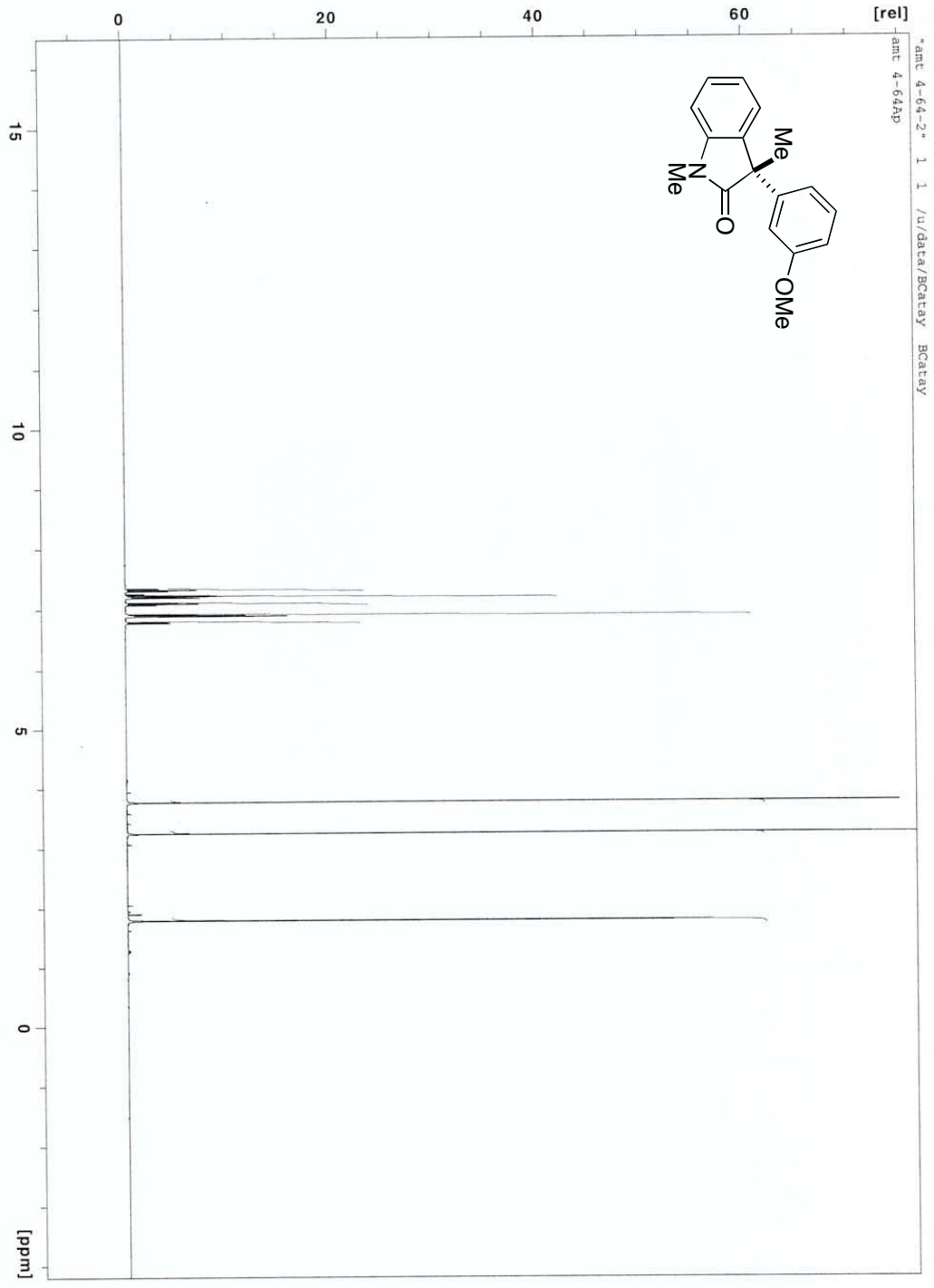
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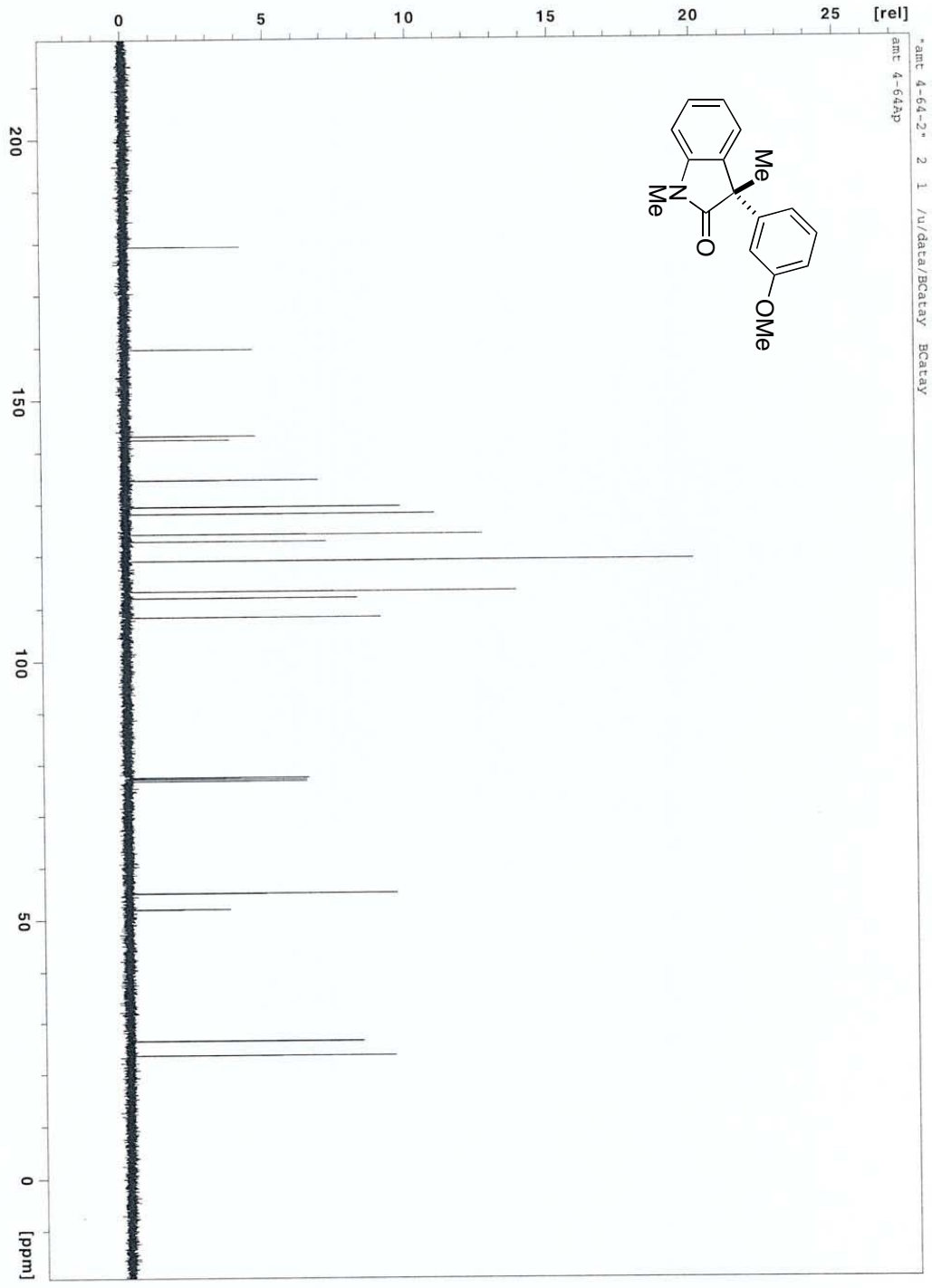
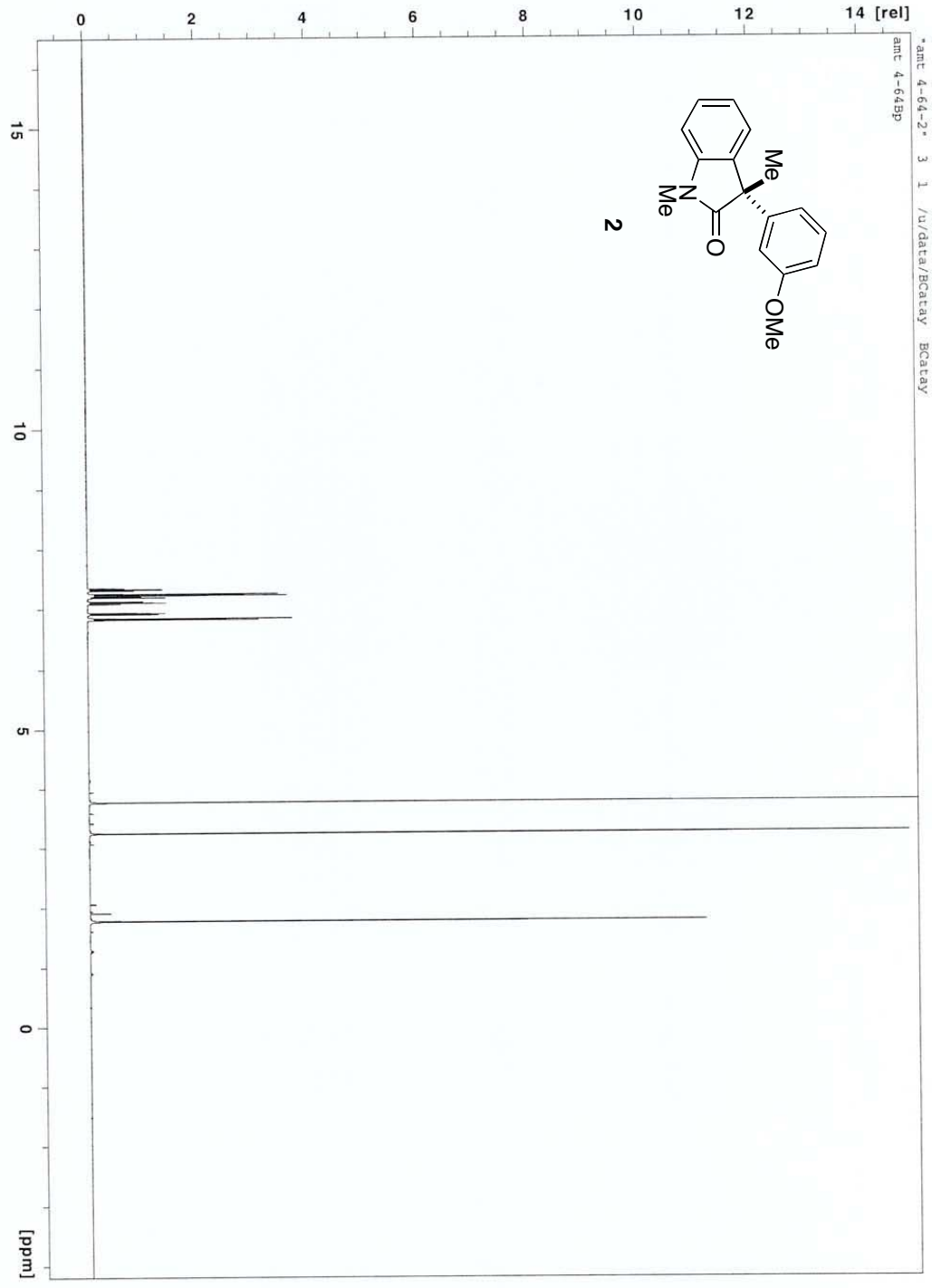
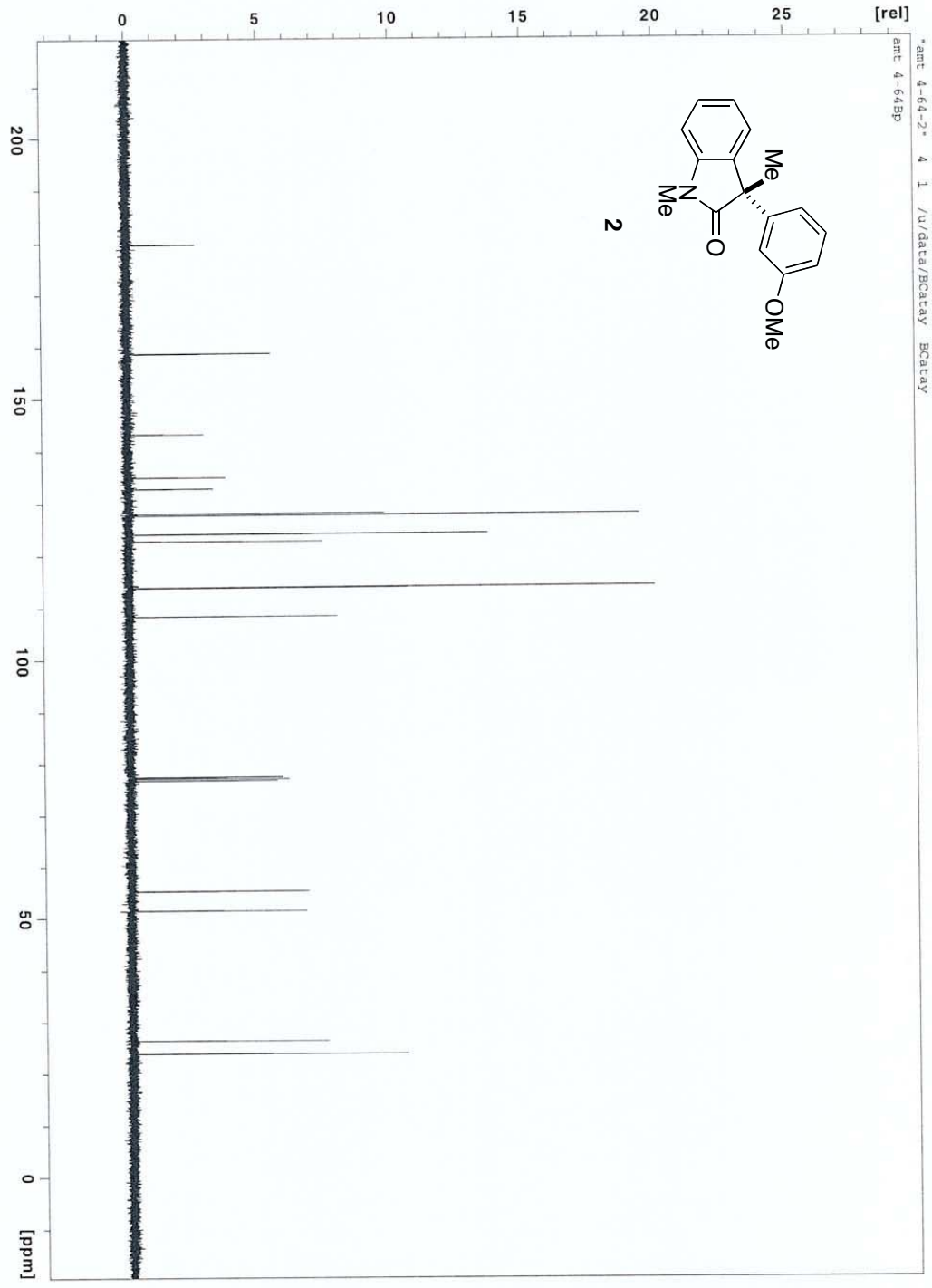
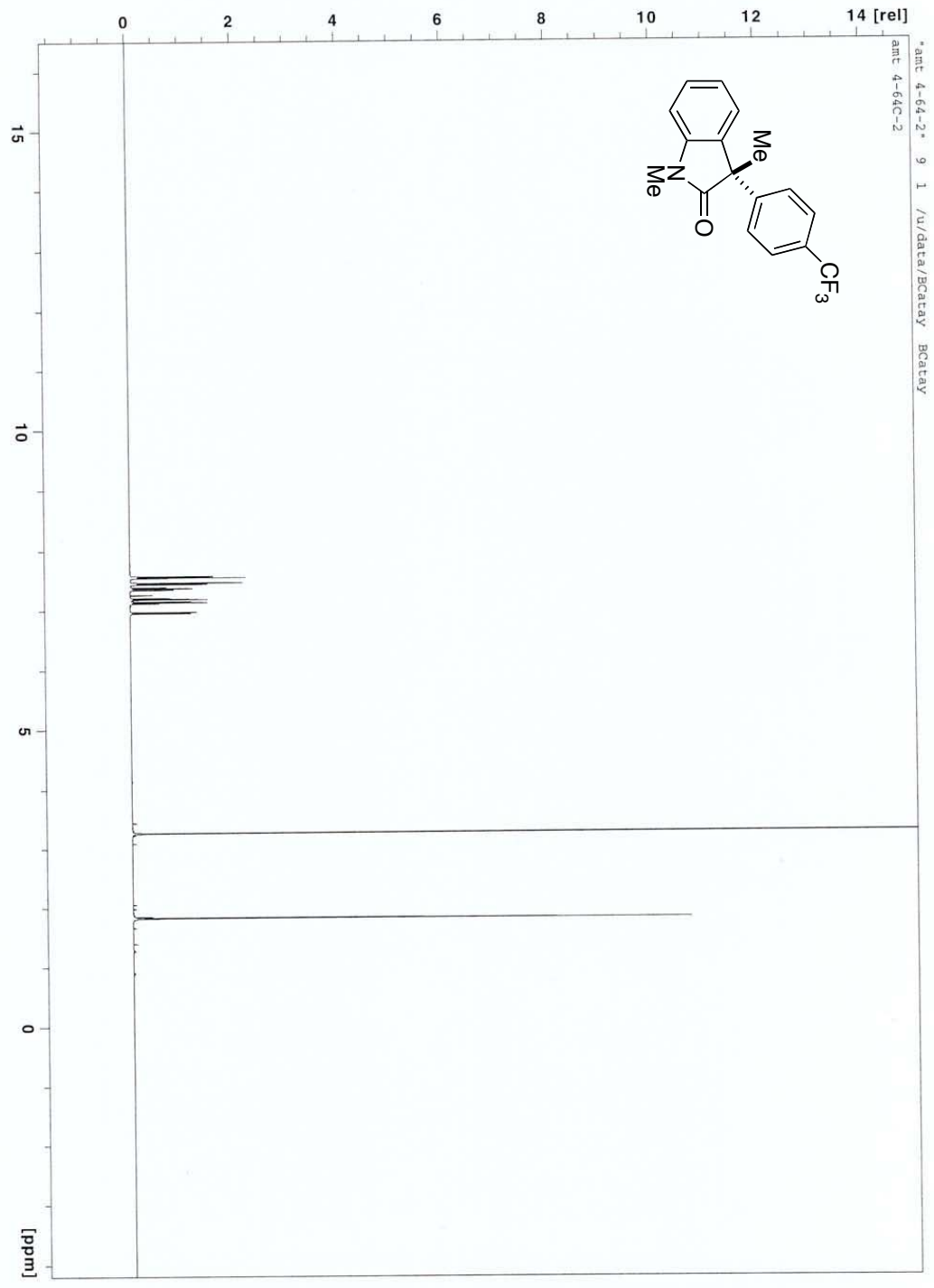
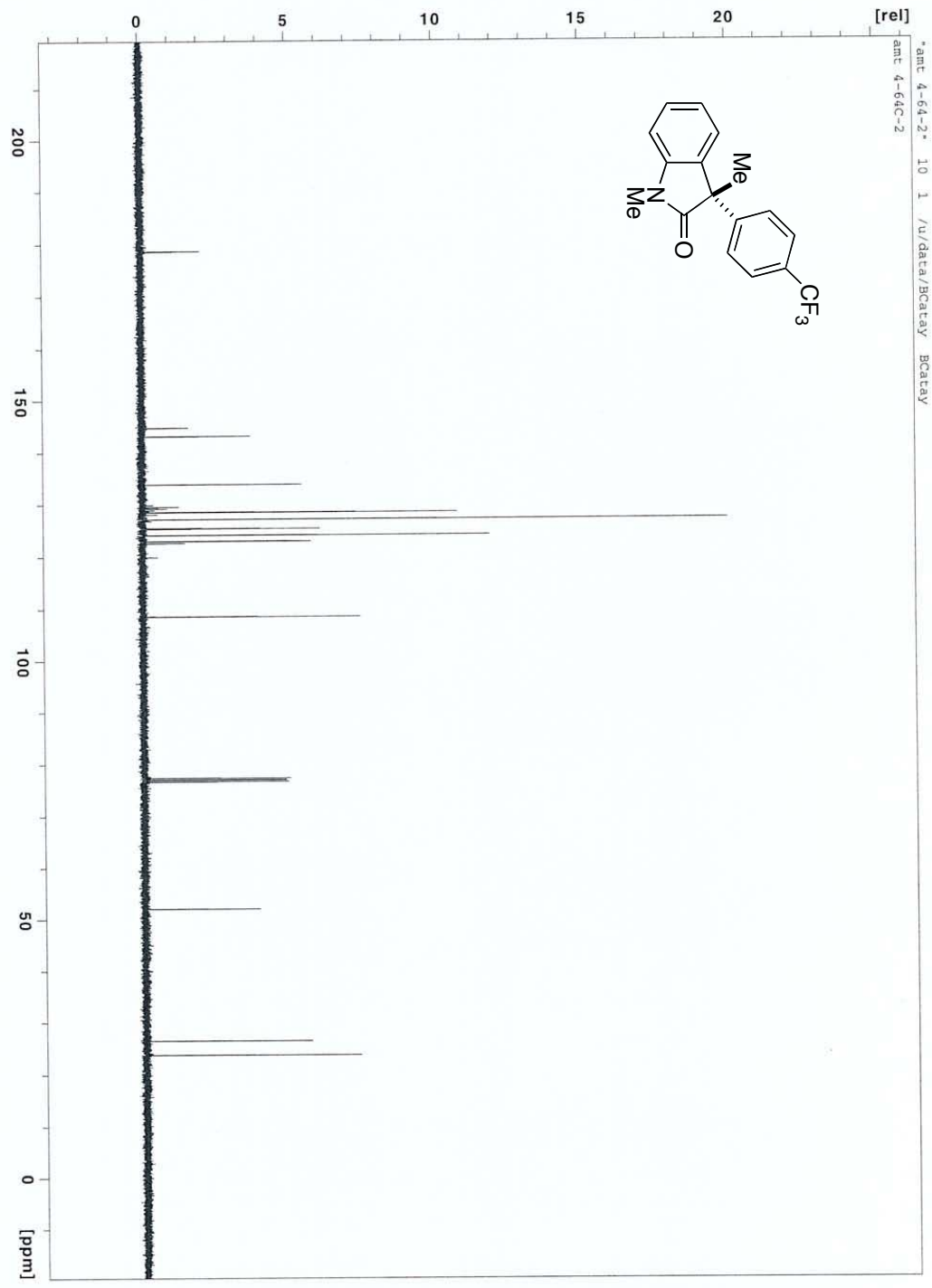
"amt 4-64-2" 1 1 /u/data/BCatay BCatay
amt 4-64Ap
Me
N
Me
O
OMe
15
10
5
0
[ppm]

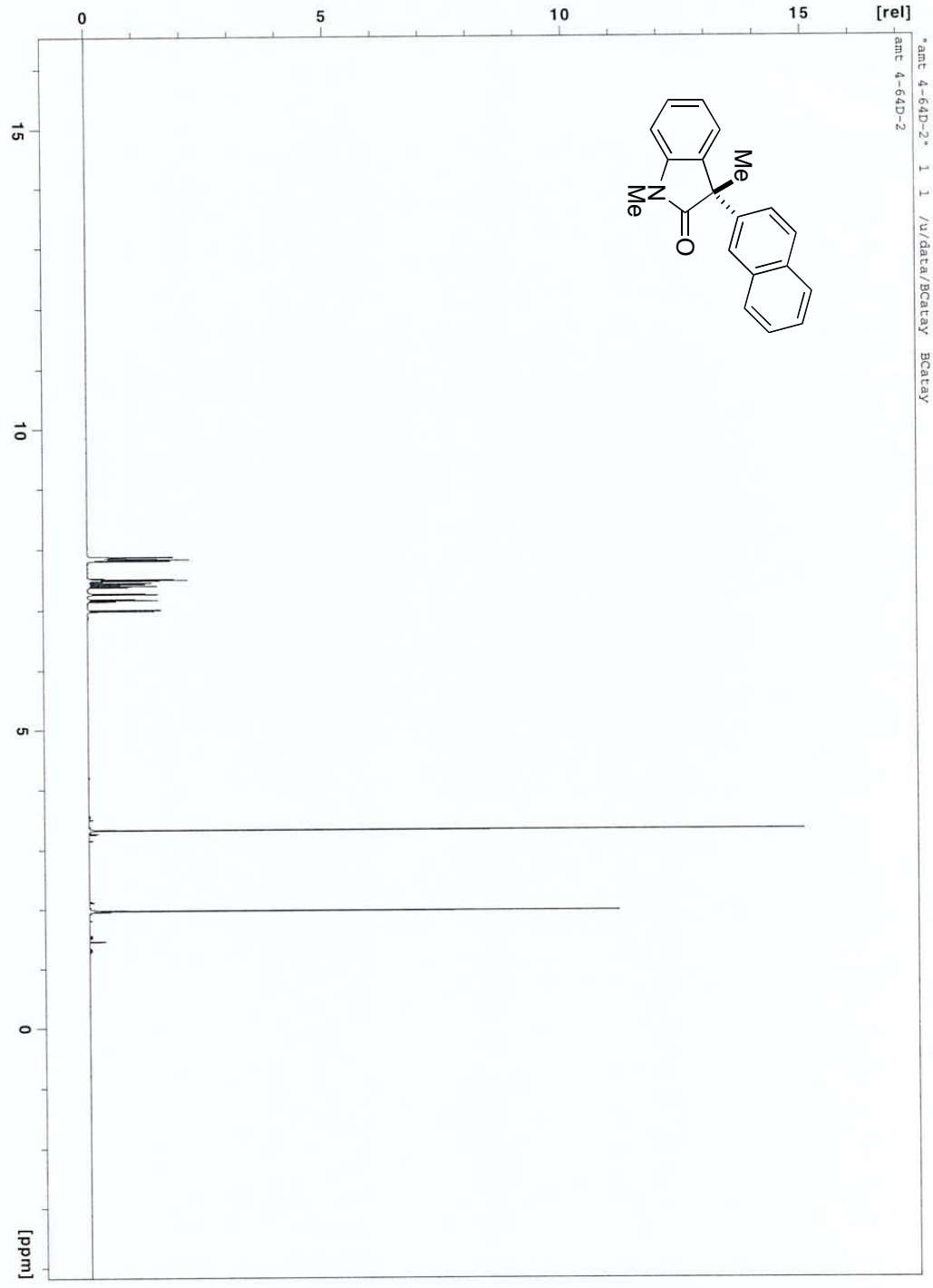

0
5
10
15
20
25
[rel]
"amt 4-64-2" 2 1 /u/data/BCatay BCatay
amt 4-64Ap
Me
N
Me
O
OMe
200
150
100
50
0
[ppm]

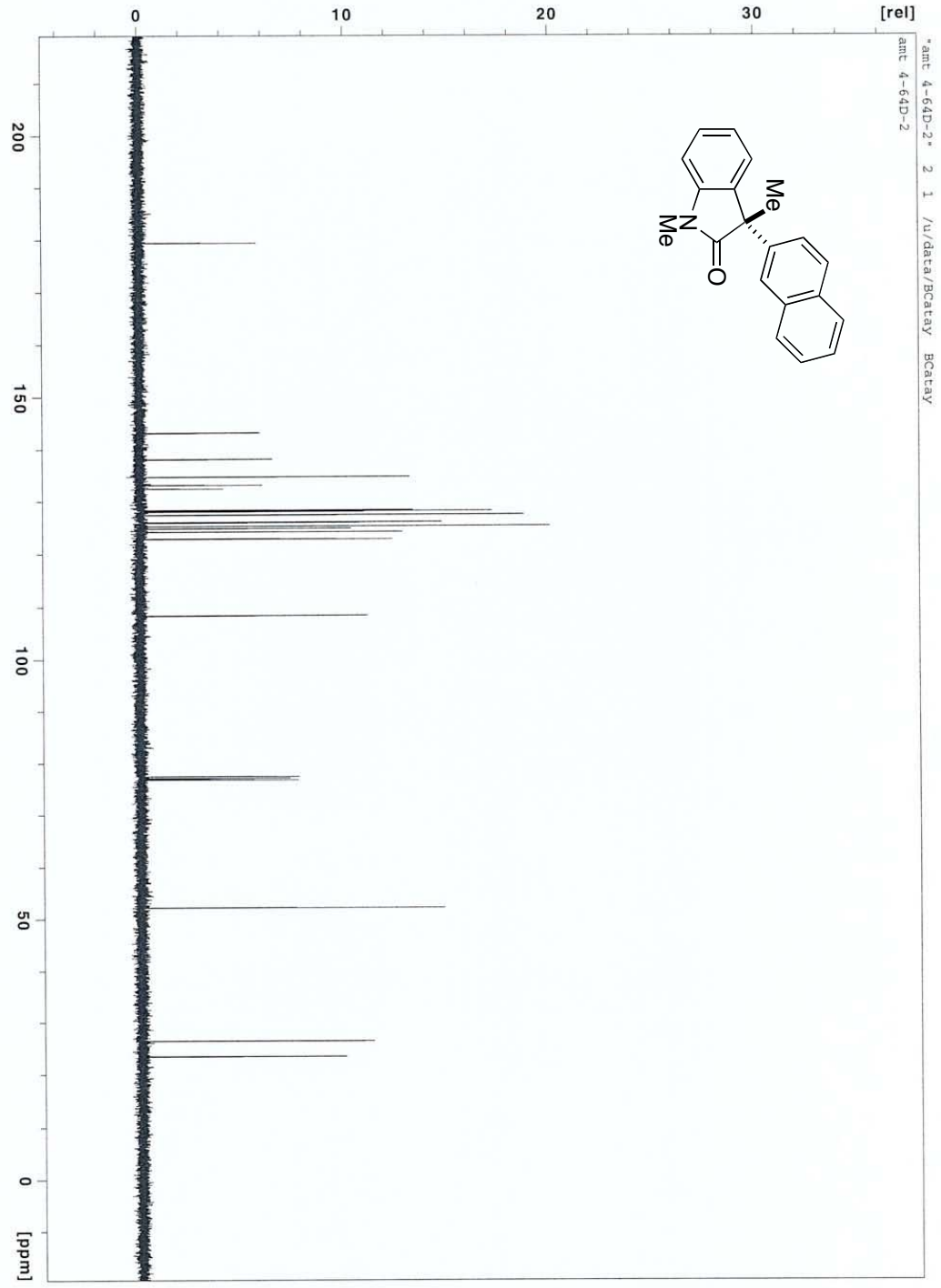

"amt 4-64-2" 3 1 /u/data/BCatay BCatay
amt 4-64Bp
0 2 4 6 8 10 12 14 [rel]
15 10 5 0 [ppm]
Me
N
Me
O
OMe
2

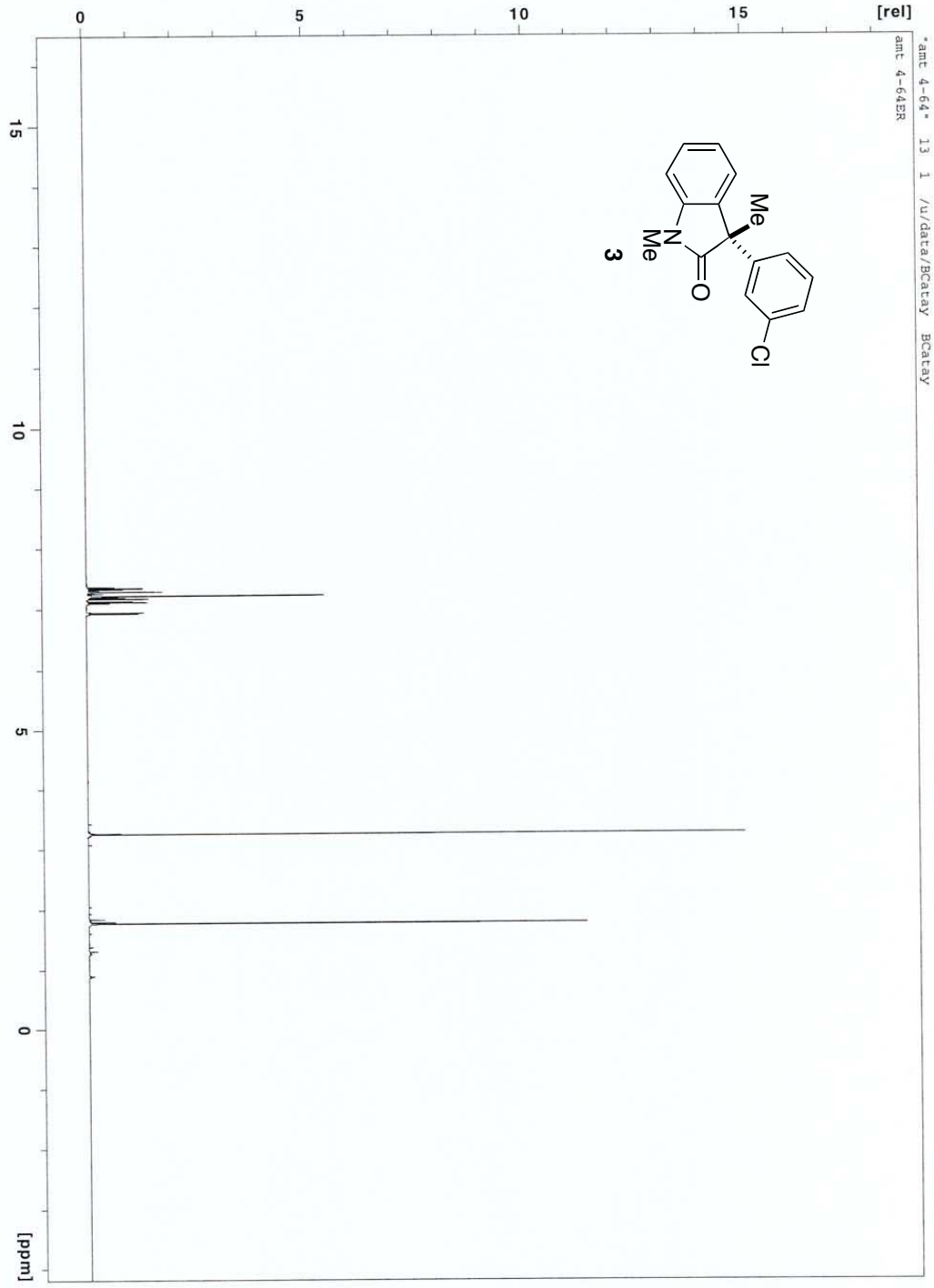

0
5
10
15
20
25
[rel]
"amt 4-64-2" 4 1 /u/data/BCatay BCatay
amt 4-64Bp
200
150
100
50
0
[ppm]
Me
N
Me
O
OMe
2

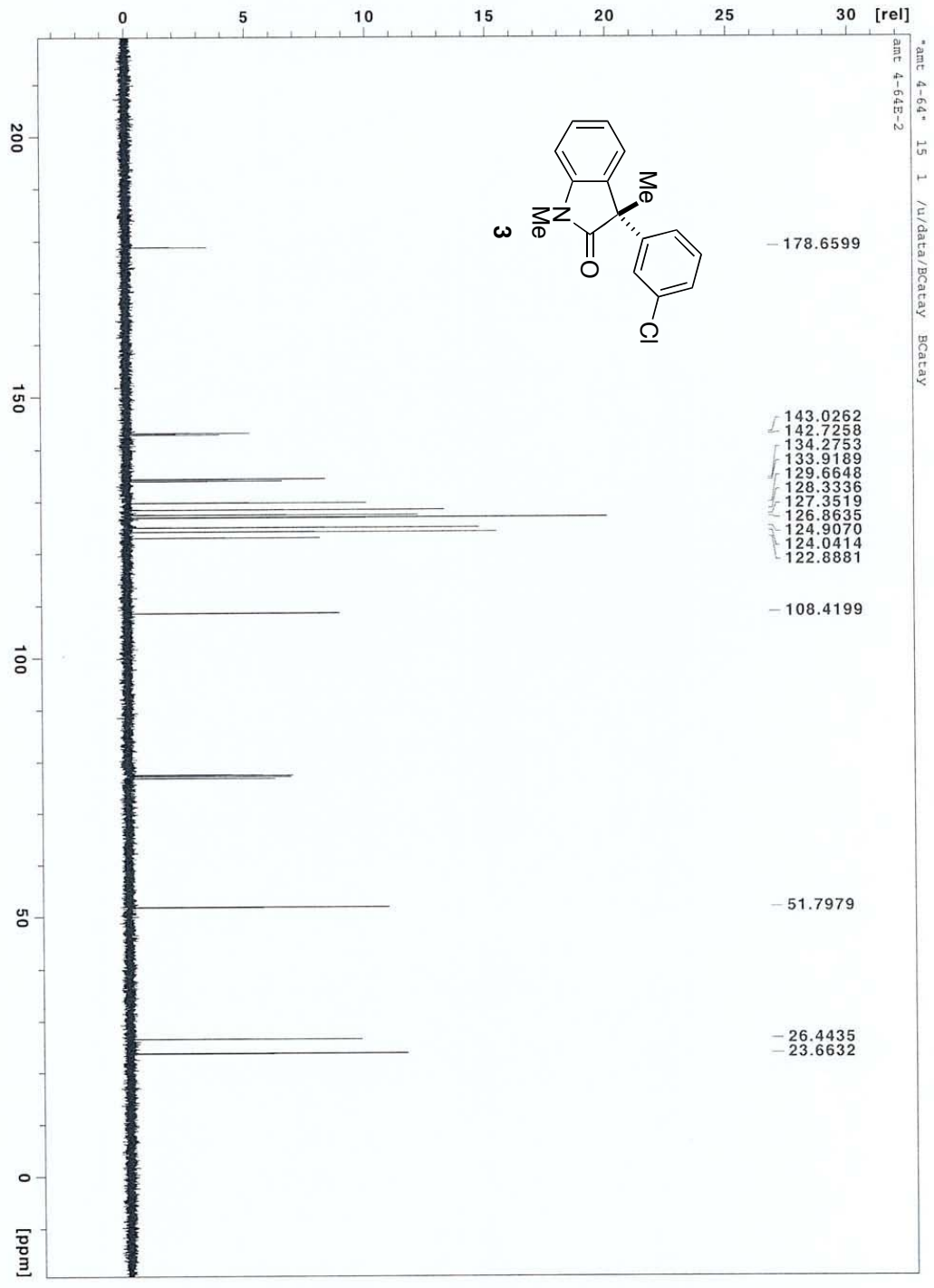

0
2
4
6
8
10
12
14 [rel]
15
10
5
0
[ppm]
Me
N
Me
O
CF3

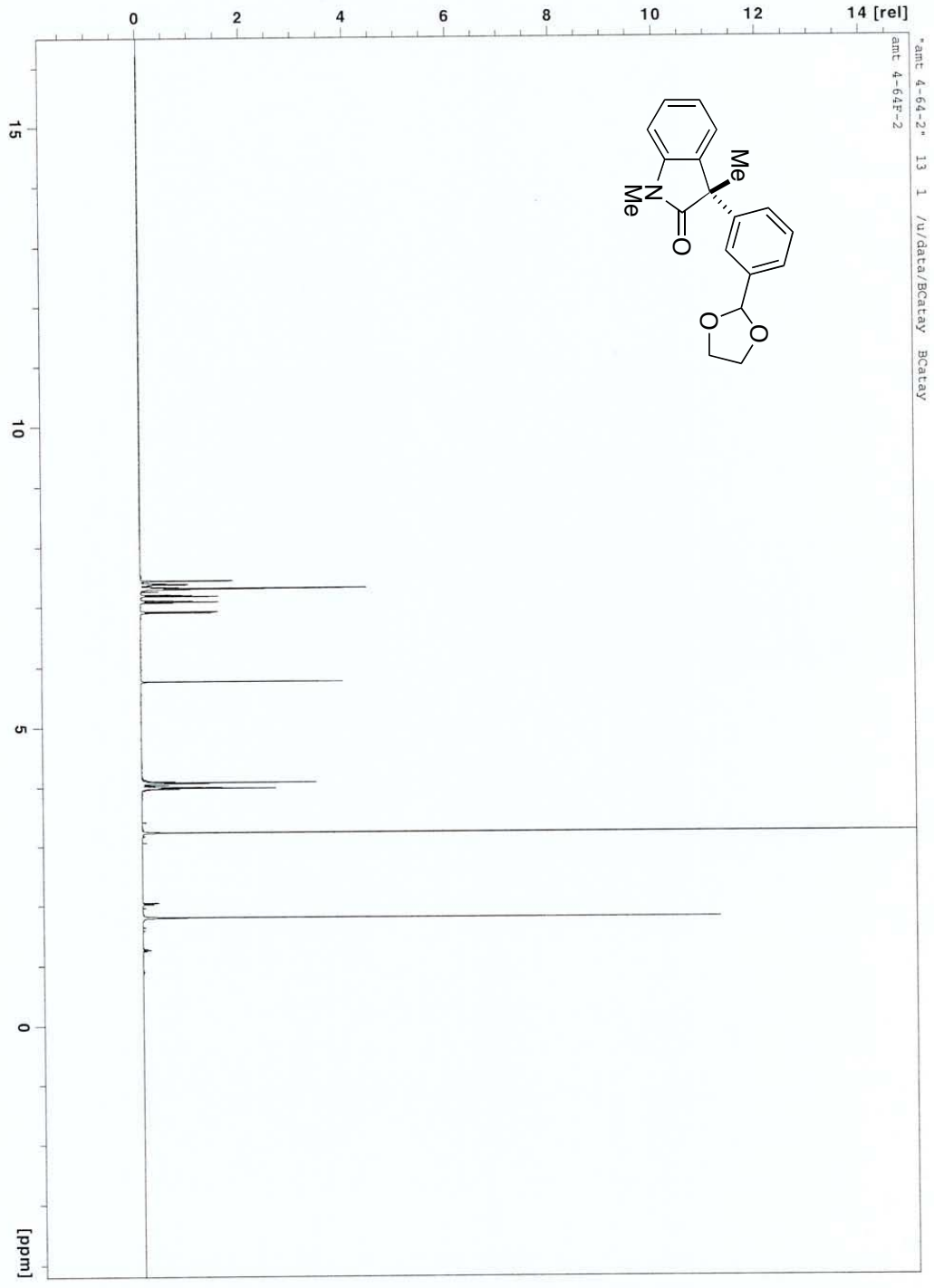

0
5
10
15
20
[rel]
200
150
100
50
0
[ppm]
"amt 4-64-2" 10 1 /u/data/BCatay BCatay
amt 4-64C-2
Me
N
Me
O
CF3

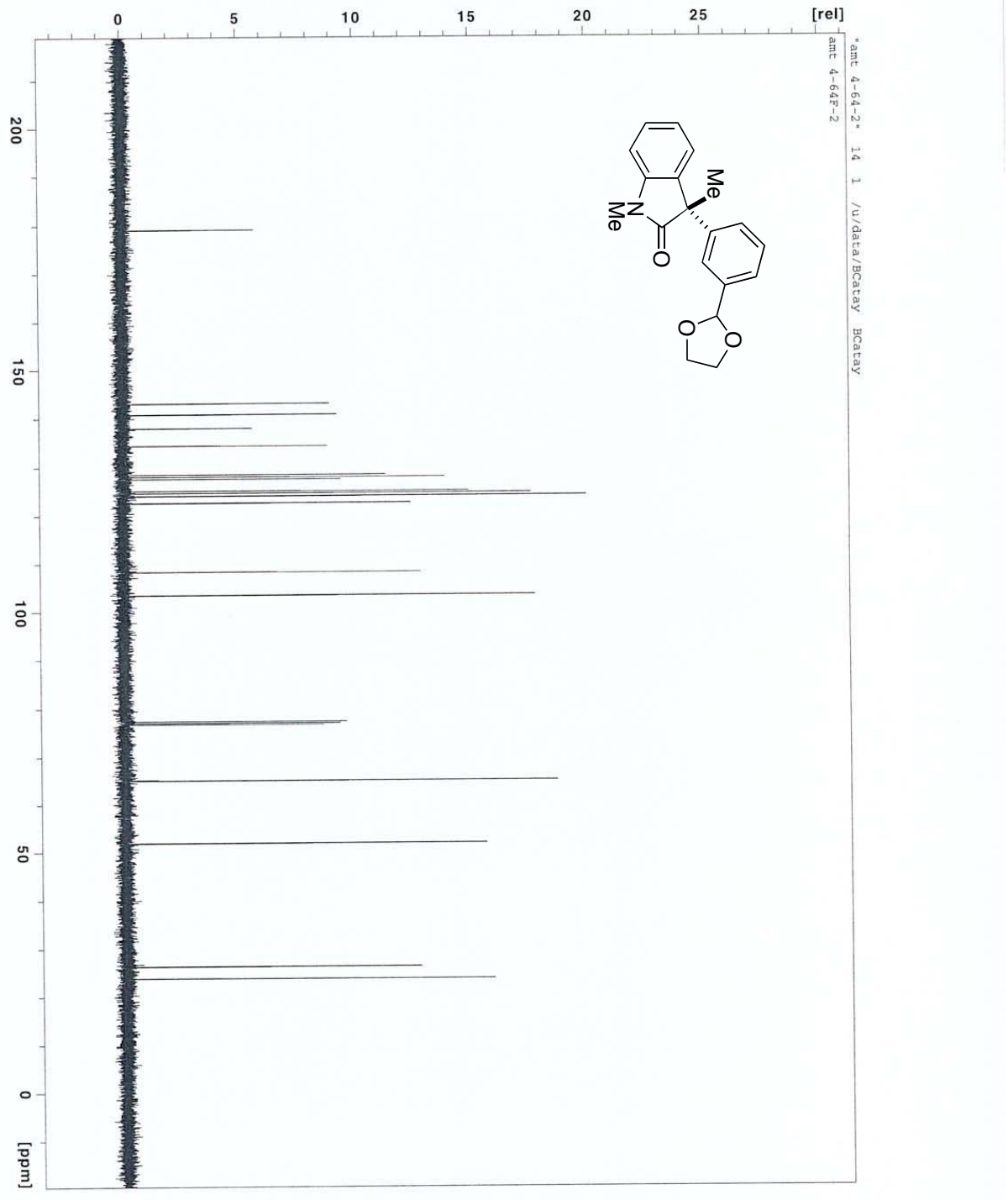

0
5
10
15
[rel]
amt 4-64D-2
"amt 4-64D-2" 1 1 /u/data/BCatay BCatay
Me
N
Me
O
15
10
5
0
[ppm]

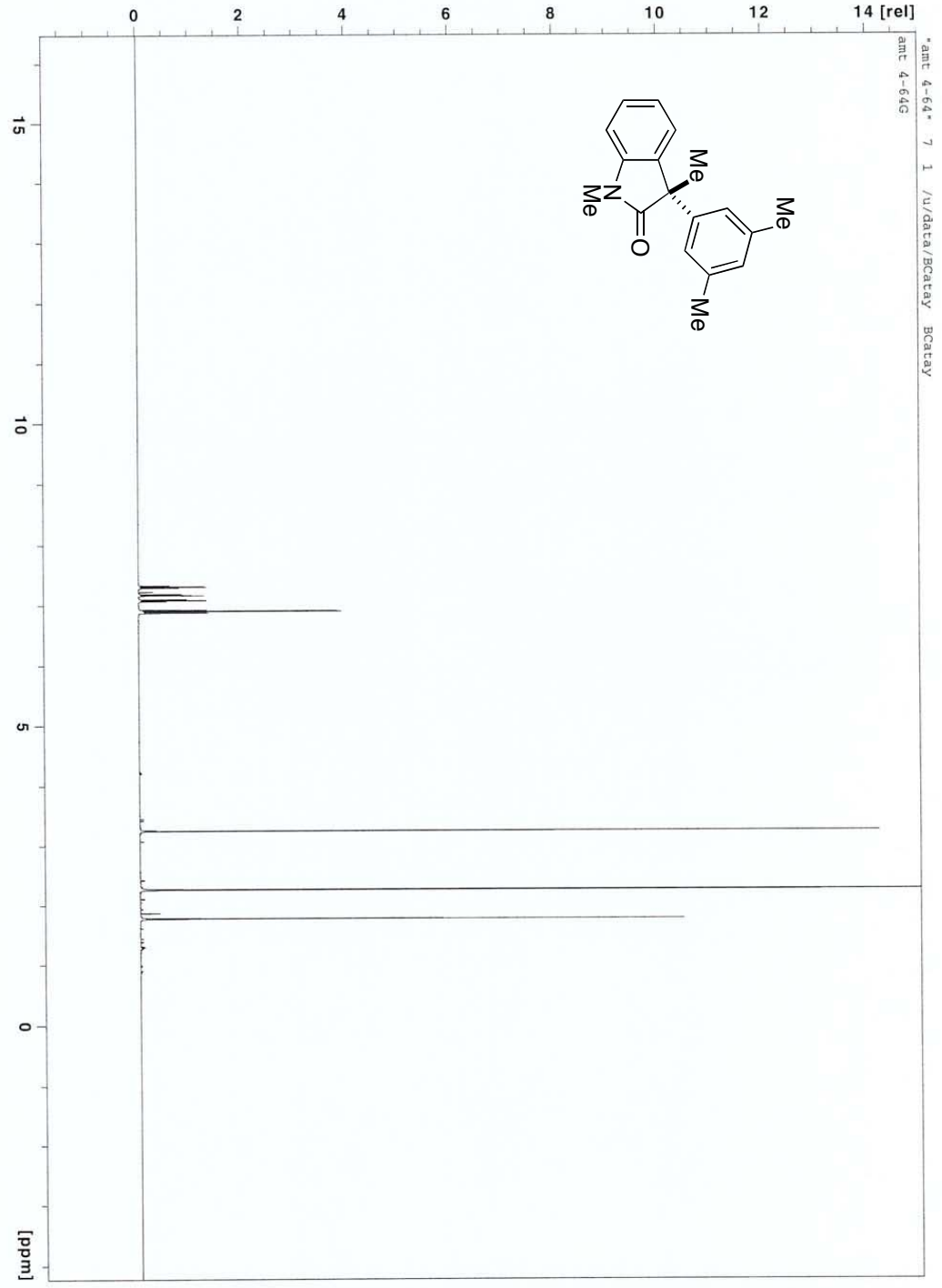

0
10
20
30
[rel]
200
150
100
50
0
[ppm]
amt 4-64D-2
"amt 4-64D-2" 2 1 /u/data/BCatay BCatay
Me
N
Me
O

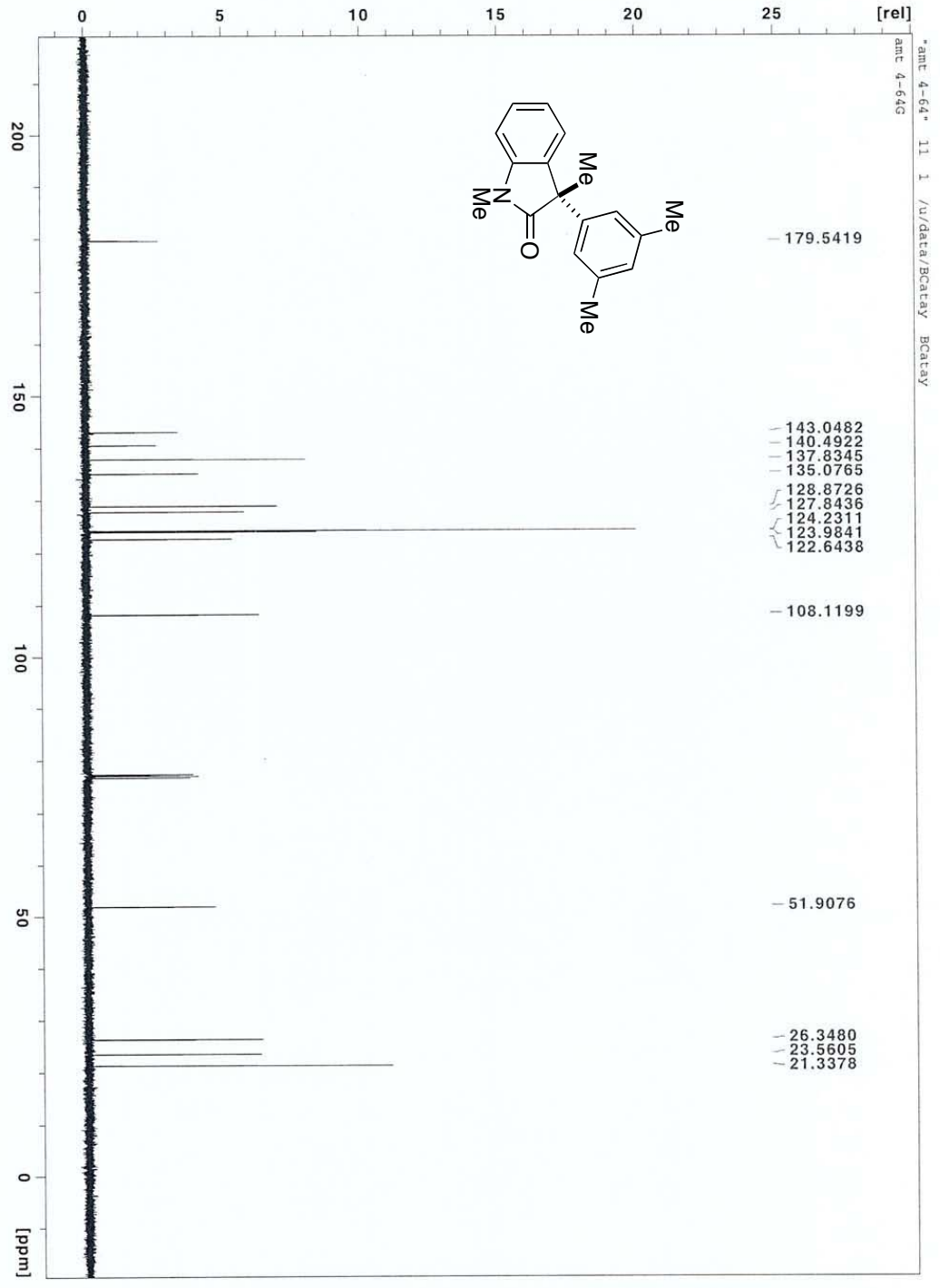

0
5
10
15
[rel]
"amt 4-64" 13 1 /u/data/BCatay BCatay
amt 4-64ER
Me
N
Me
O
Cl
3
15
10
5
0
[ppm]

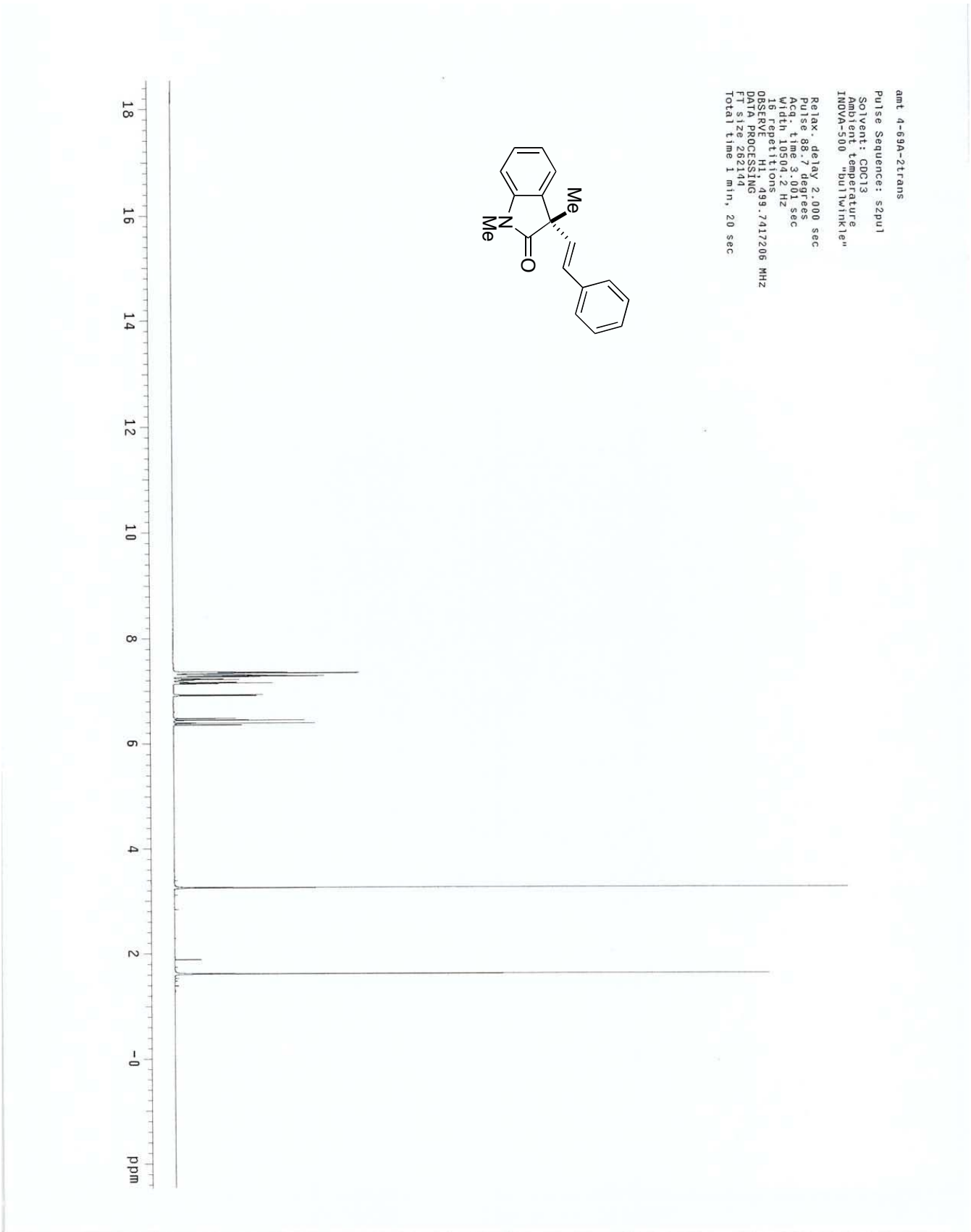

0
5
10
15
20
25
30
[rel]
200
150
100
50
0
[ppm]
Me
N
Me
O
Cl
3
178.6599
143.0262
142.7258
134.2753
133.9189
129.6648
128.3336
127.3519
126.8635
124.9070
124.0414
122.8881
108.4199
51.7979
26.4435
23.6632


0
2
4
6
8
10
12
14 [rel]
15
10
5
0
[ppm]
Me
N
Me
O
O
O
"amt 4-64-2" 13 1 /u/data/BCatay BCatay
amt 4-64F-2


0
5
10
15
20
25
[rel]
200
150
100
50
0
[ppm]
Me
N
Me
O
O
O
"amt 4-64-2" 14 1 /u/data/BCatay BCatay
amt 4-64F-2


0
2
4
6
8
10
12
14 [rel]
15
10
5
0
[ppm]
Me
N
Me
O
Me
Me

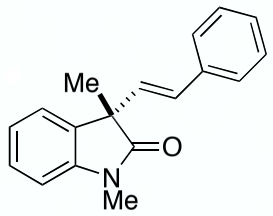

0
5
10
15
20
25
[rel]
200
150
100
50
0
[ppm]
amt 4-64G
"amt 4-64" 11 1 /u/data/BCatay BCatay
Me
N
Me
O
Me
Me
179.5419
143.0482
140.4922
137.8345
135.0765
128.8726
127.8436
124.2311
123.9841
122.6438
108.1199
51.9076
26.3480
23.5605
21.3378

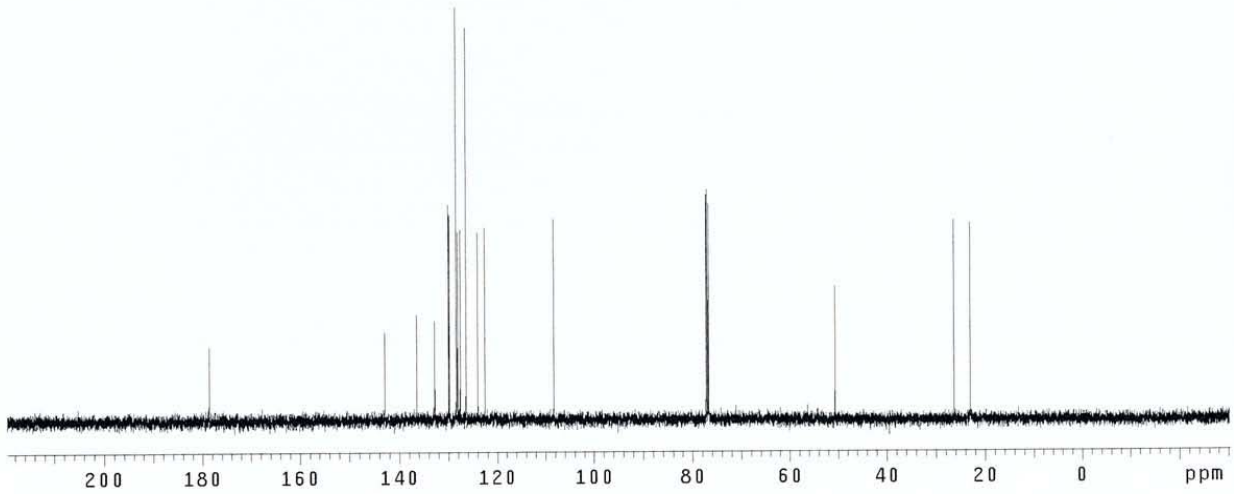

amt 4-69A-2trans
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
Relax. delay 2.000 sec
Pulse 88.7 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec
Me
N
Me
O
18
16
14
12
10
8
6
4
2
-0
ppm

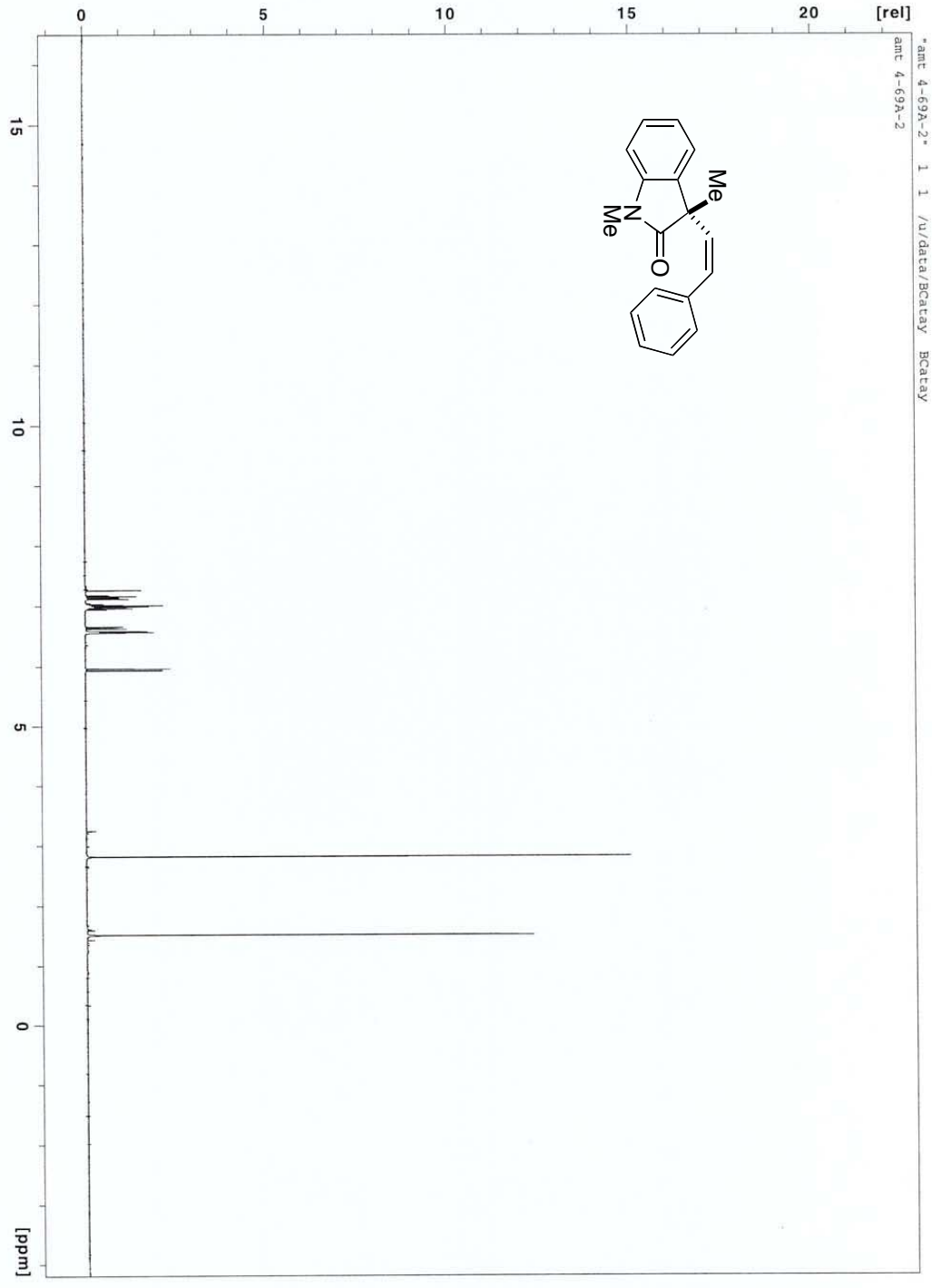
amt 4-69A-2trans

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

 Relax. delay 3.000 sec
 Pulse 33.6 degrees
 Acq. time 2.000 sec
 Width 31397.2 Hz
 64 repetitions
OBSERVE C13, 125.6601718 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 10 min, 41 sec



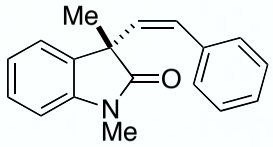


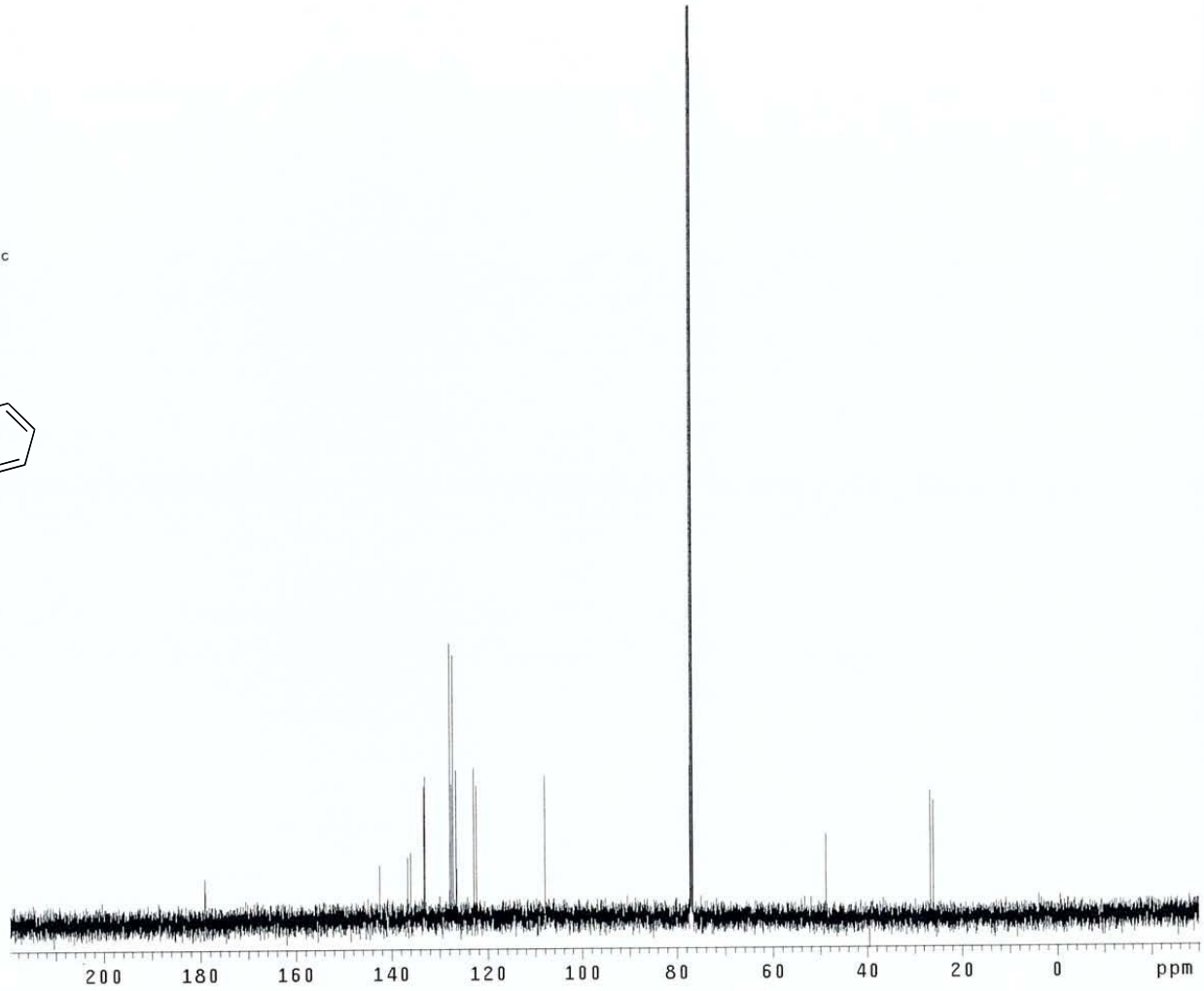

0
5
10
15
20
[rel]
15
10
5
0
[ppm]
"amt 4-69A-2" 1 1 /u/data/BCatay BCatay
amt 4-69A-2
Me
N
Me
O

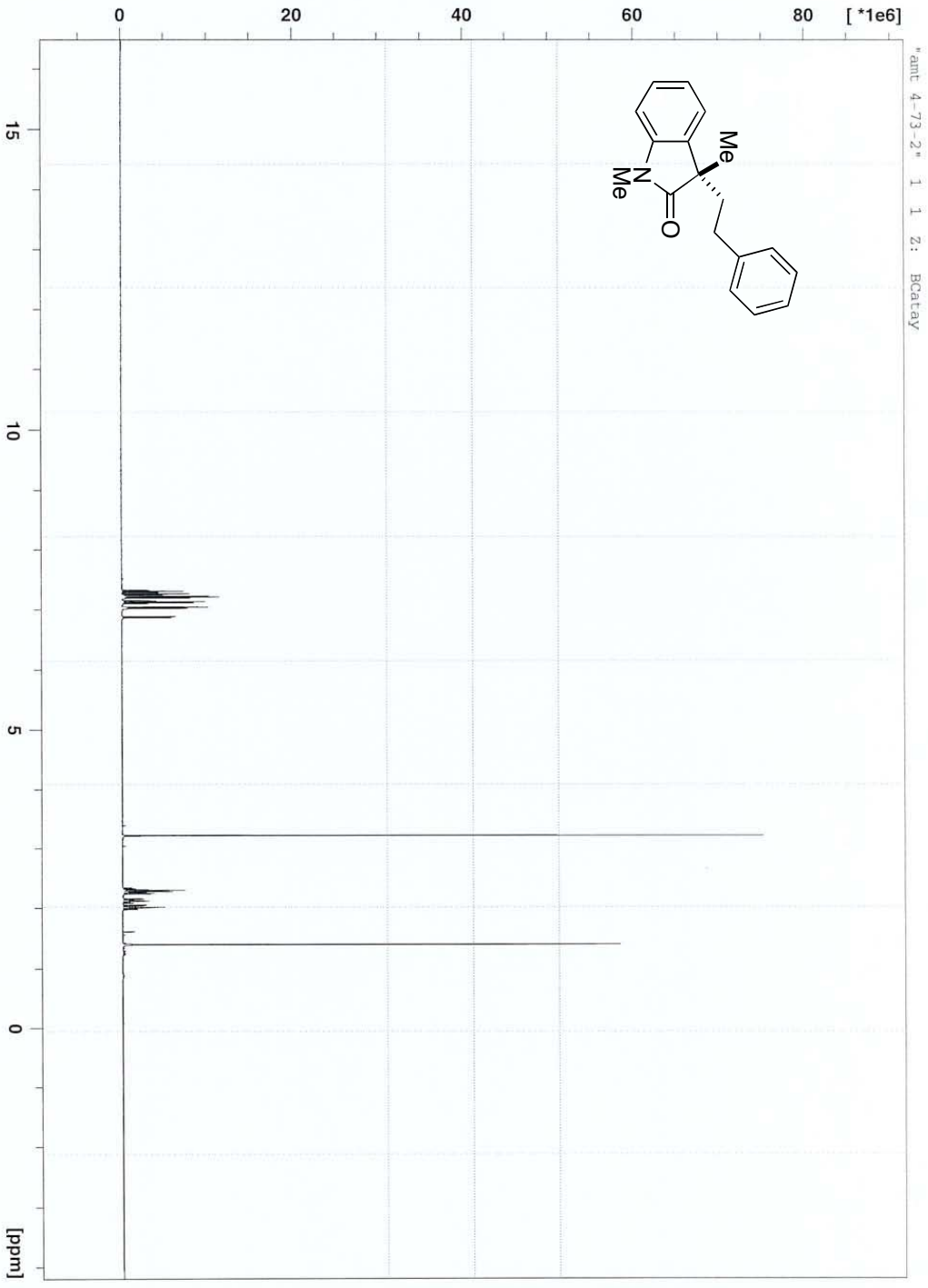
amt 4-69Acis

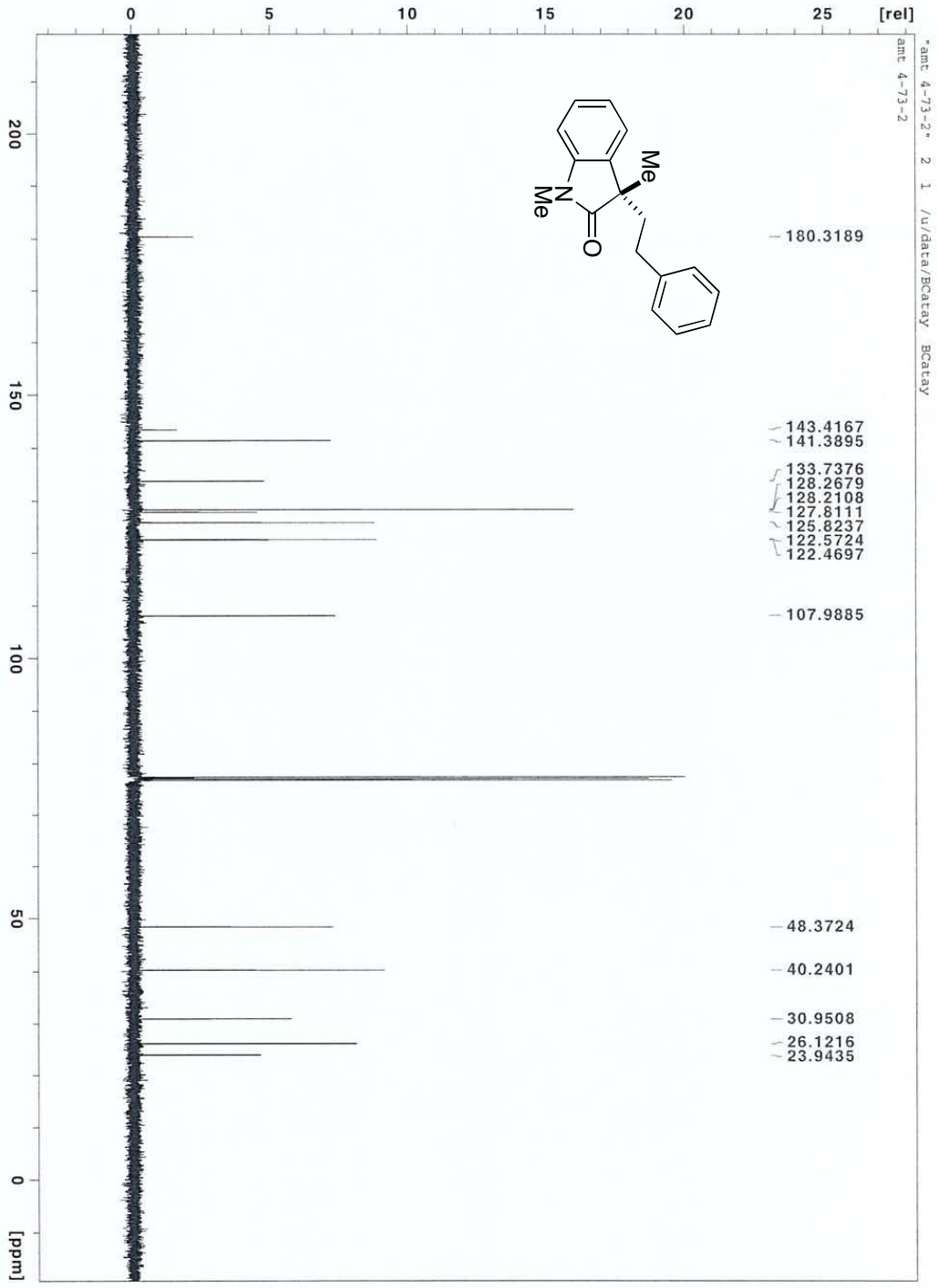
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

 Relax. delay 3.000 sec
 Pulse 33.6 degrees
 Acq. time 2.000 sec
 Width 31397.2 Hz
 312 repetitions
OBSERVE C13, 125.6601593 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 1 hr, 23 min, 28 sec





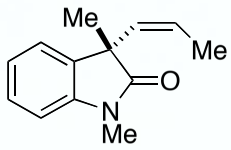

0
20
40
60
80
[*1e6]
15
10
5
0
[ppm]
Me
N
Me
O
"amt 4-73-2" 1 1 Z: BCatay


0
5
10
15
20
25
[rel]
200
150
100
50
0
[ppm]
Me
N
Me
O
180.3189
143.4167
141.3895
133.7376
128.2679
128.2108
127.8111
125.8237
122.5724
122.4697
107.9885
48.3724
40.2401
30.9508
26.1216
23.9435
amt 4-73-2
"amt 4-73-2" 2 1 /u/data/BCatay BCatay

amt 4-69B

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

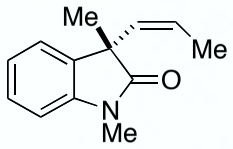
Relax. delay 2.000 sec
Pulse 88.7 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417198 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec

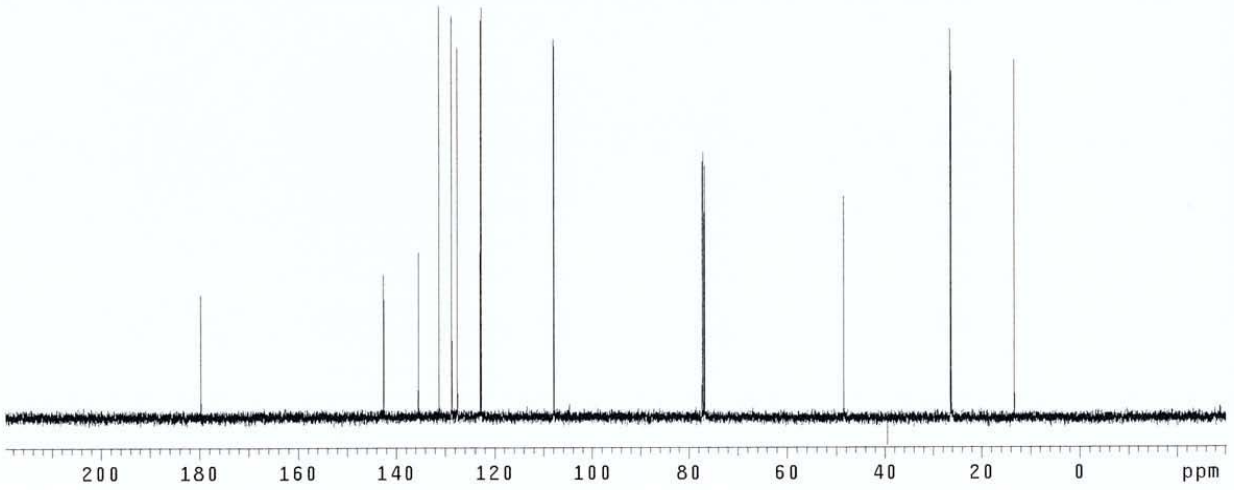


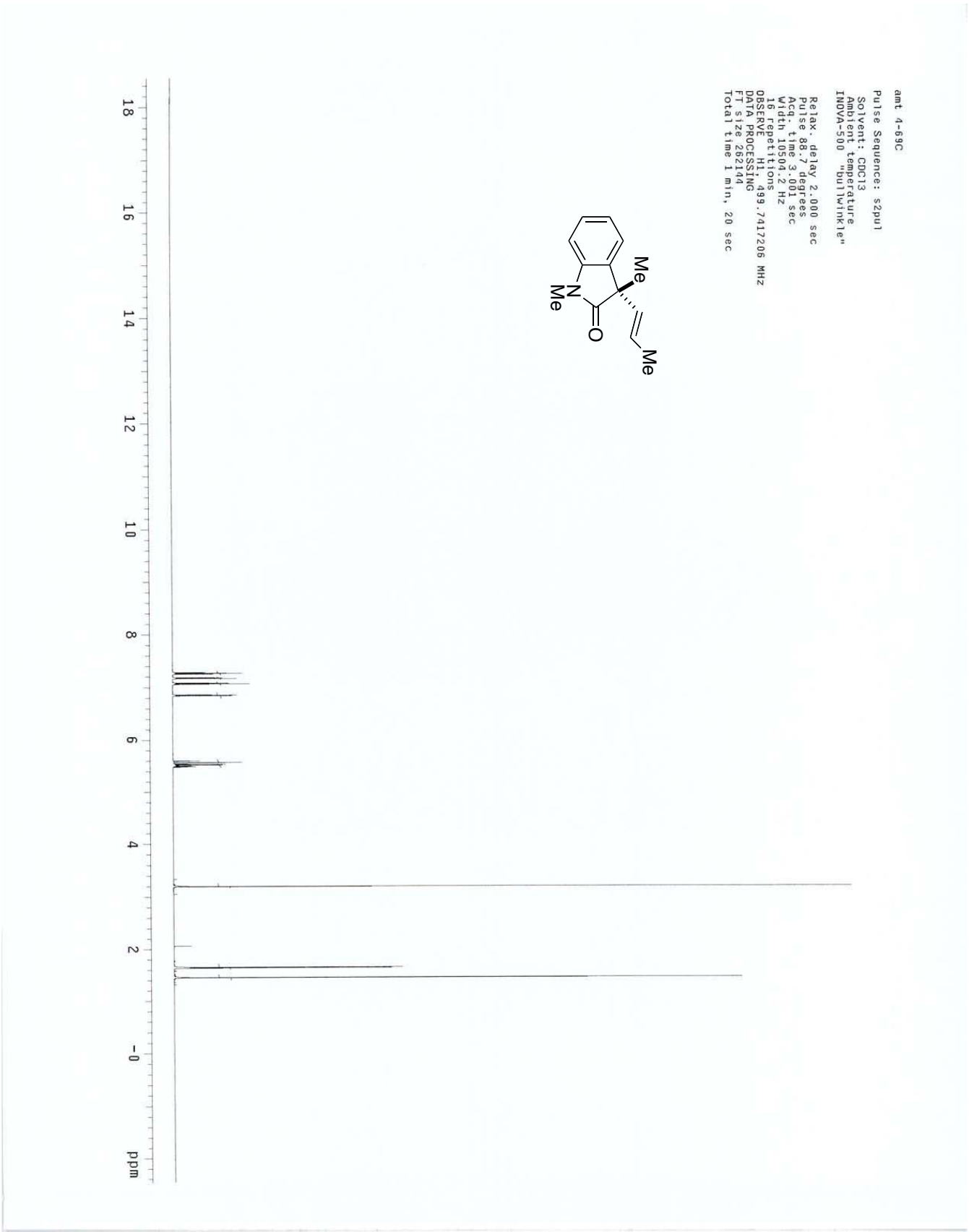
amt 4-69B

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

 Relax. delay 3.000 sec
 Pulse 33.6 degrees
 Acq. time 2.000 sec
 Width 31397.2 Hz
 128 repetitions
OBSERVE C13, 125.6601718 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 10 min, 41 sec



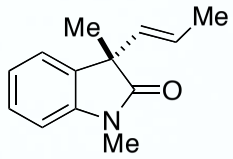


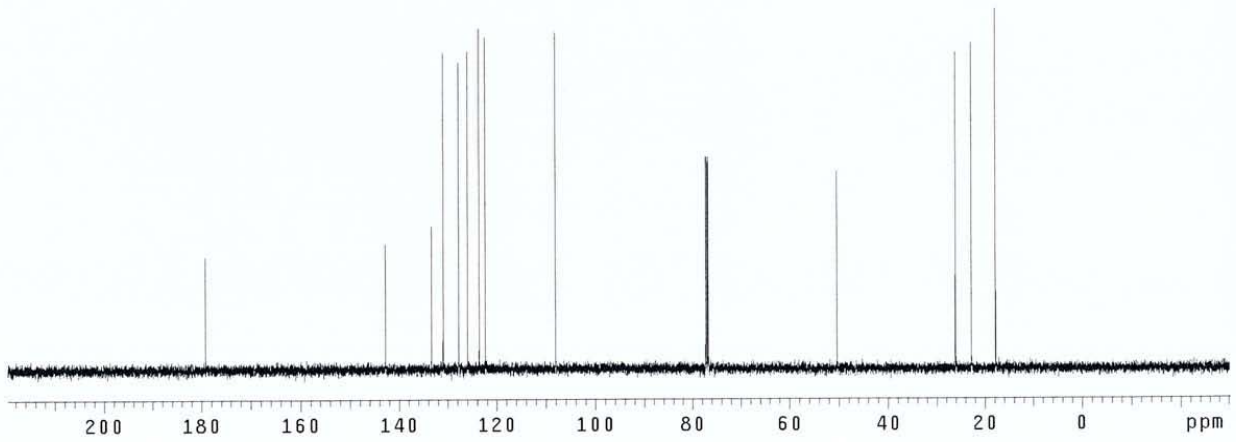

amt 4-69C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
Relax. delay 2.000 sec
Pulse 88.7 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec
Me
N
Me
O
Me
18
16
14
12
10
8
6
4
2
-0
ppm

amt 4-69C

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

 Relax. delay 3.000 sec
 Pulse 33.6 degrees
 Acq. time 2.000 sec
 Width 31397.2 Hz
 80 repetitions
OBSERVE C13, 125.6601723 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 10 min, 41 sec

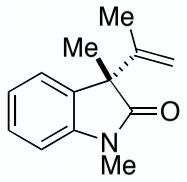




amt 4-69D

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

Relax. delay 2.000 sec
Pulse 88.7 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417227 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec

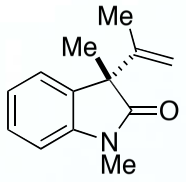


4

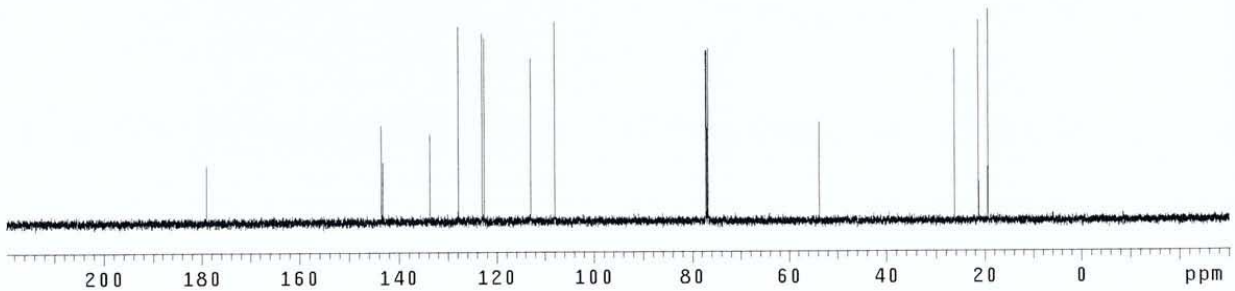
amt 4-69D-2

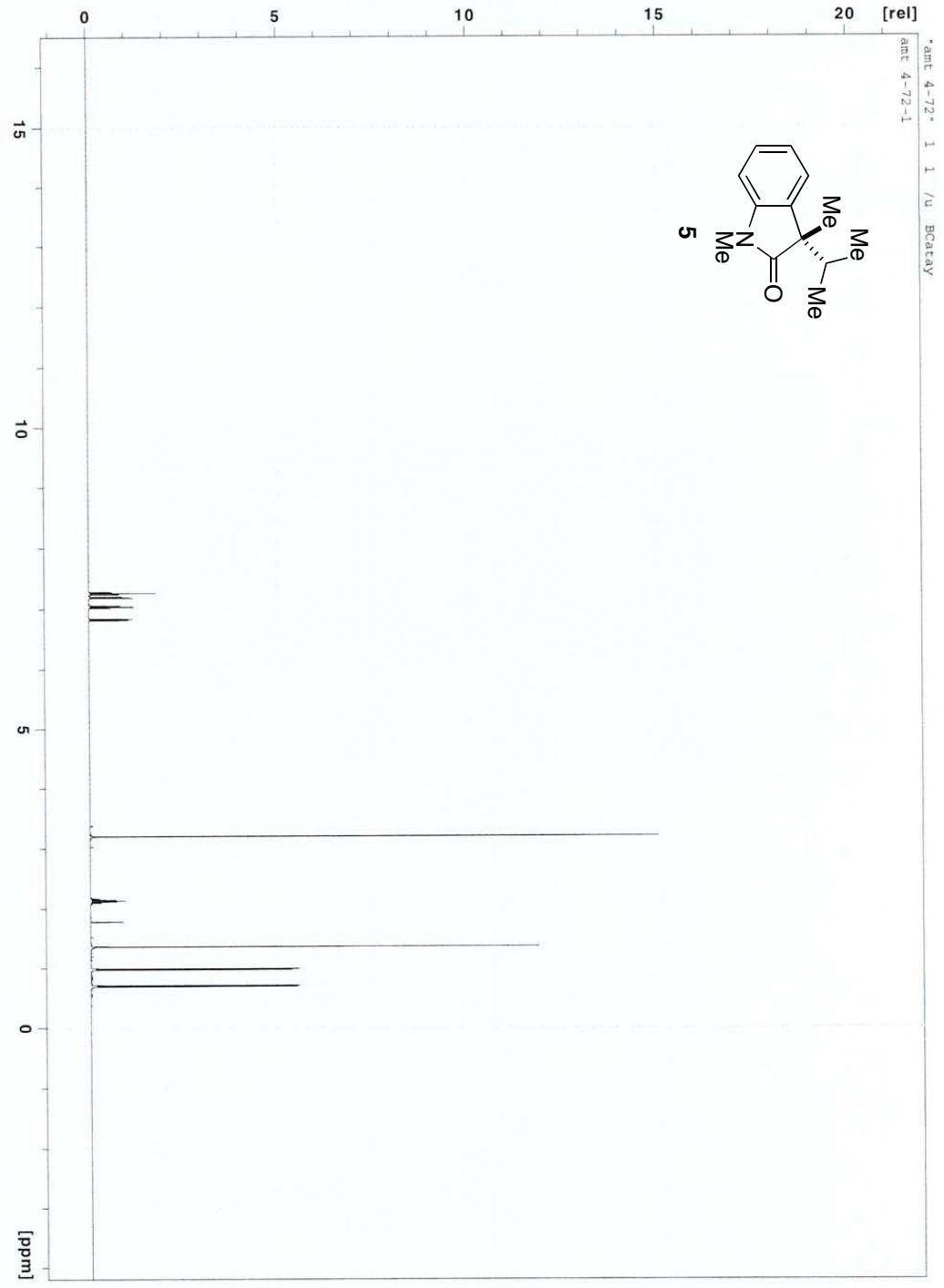
Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

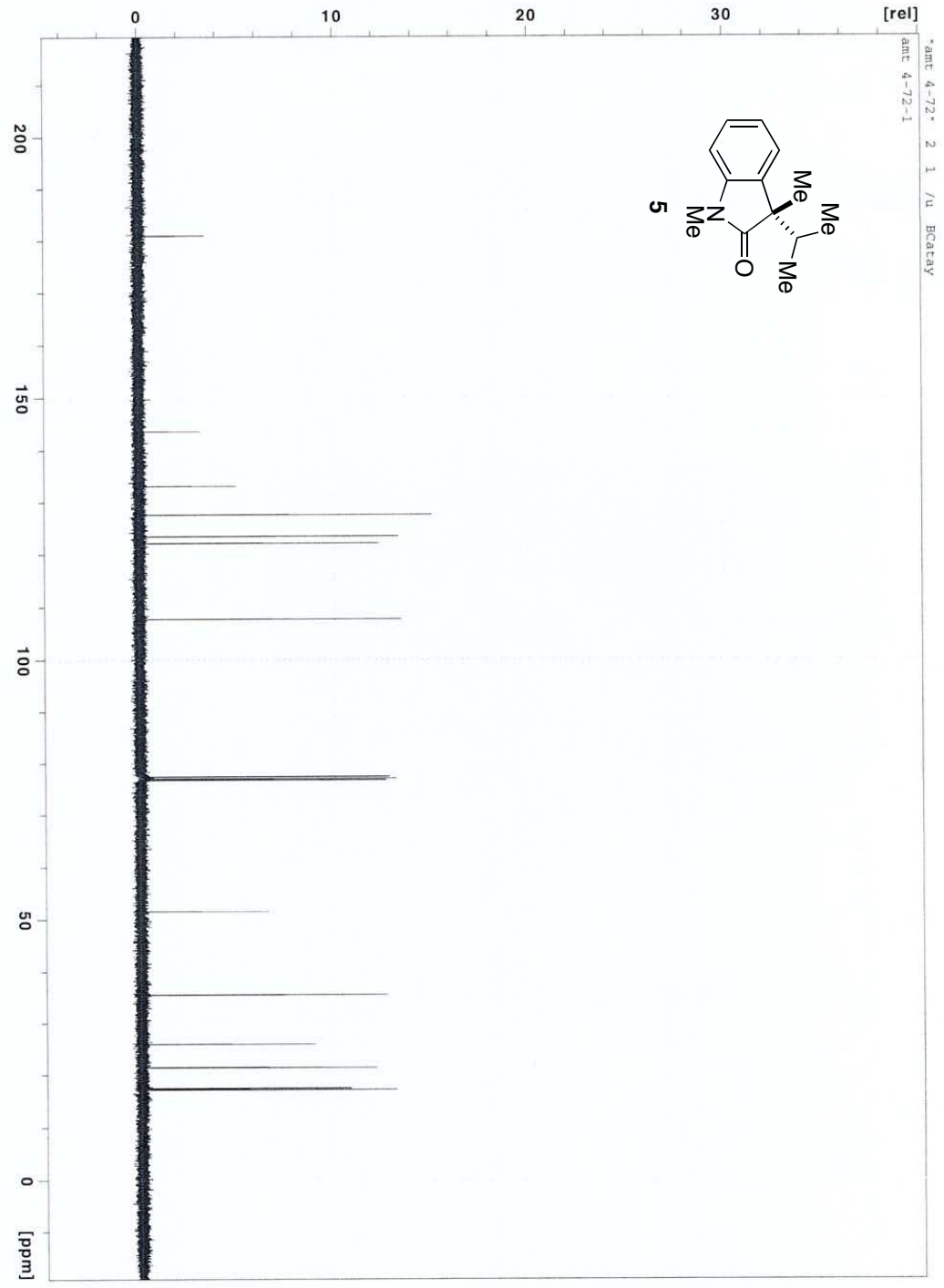
 Relax. delay 3.000 sec
 Pulse 33.6 degrees
 Acq. time 2.000 sec
 Width 31397.2 Hz
 80 repetitions
OBSERVE C13, 125.6601684 MHz
DECOUPLE H1, 499.7442194 MHz
 Power 34 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 10 min, 41 sec

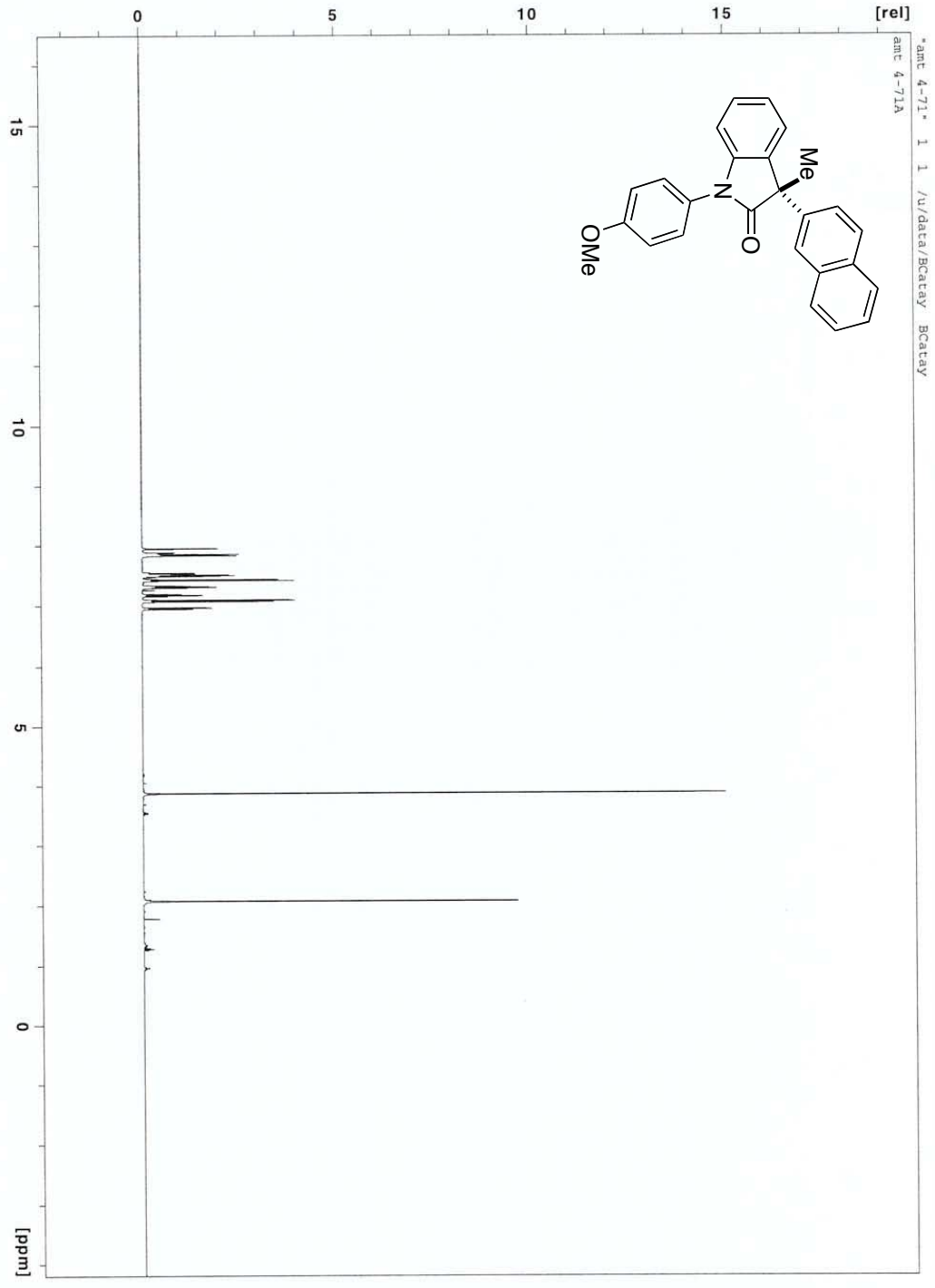


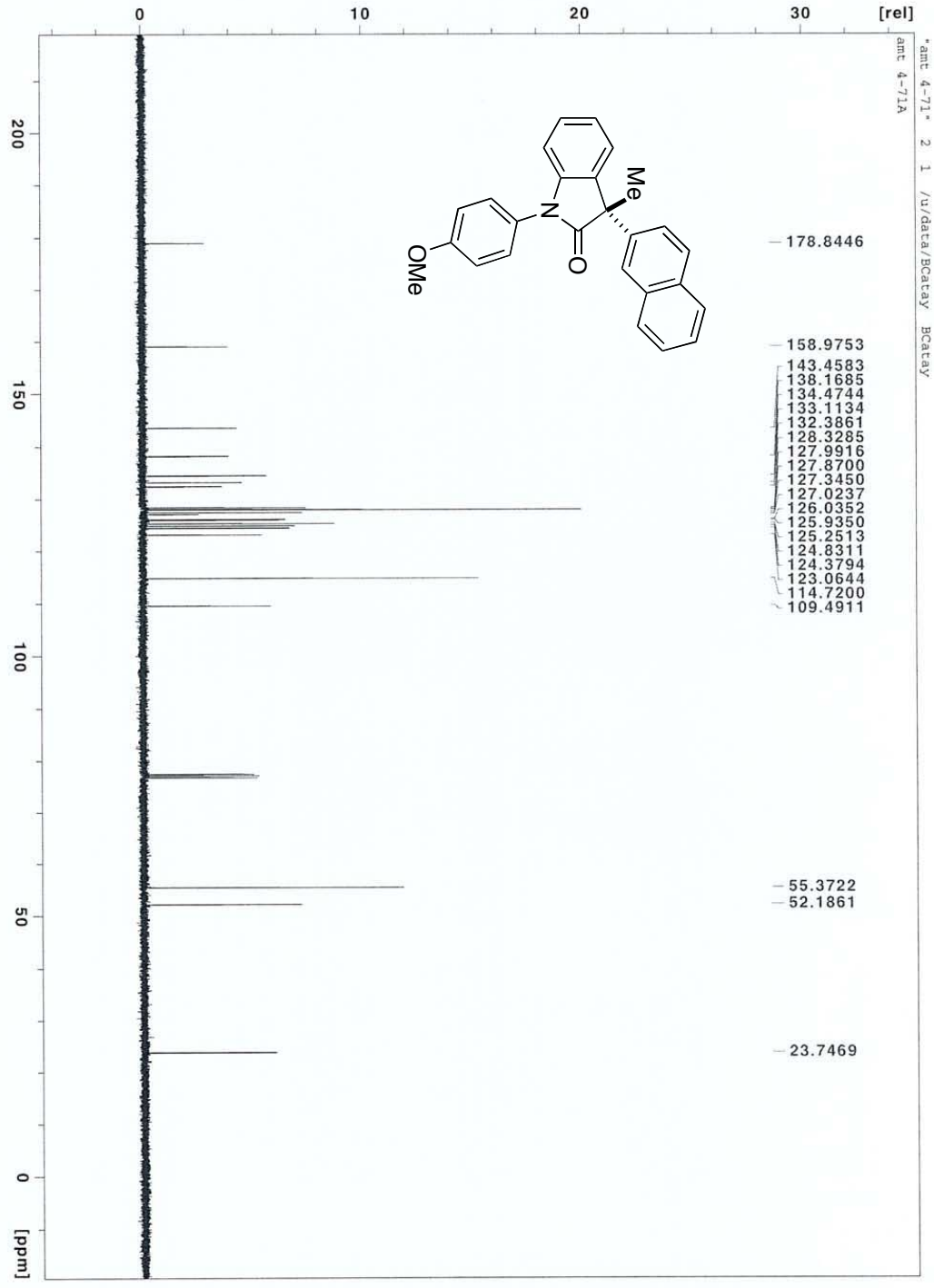
4

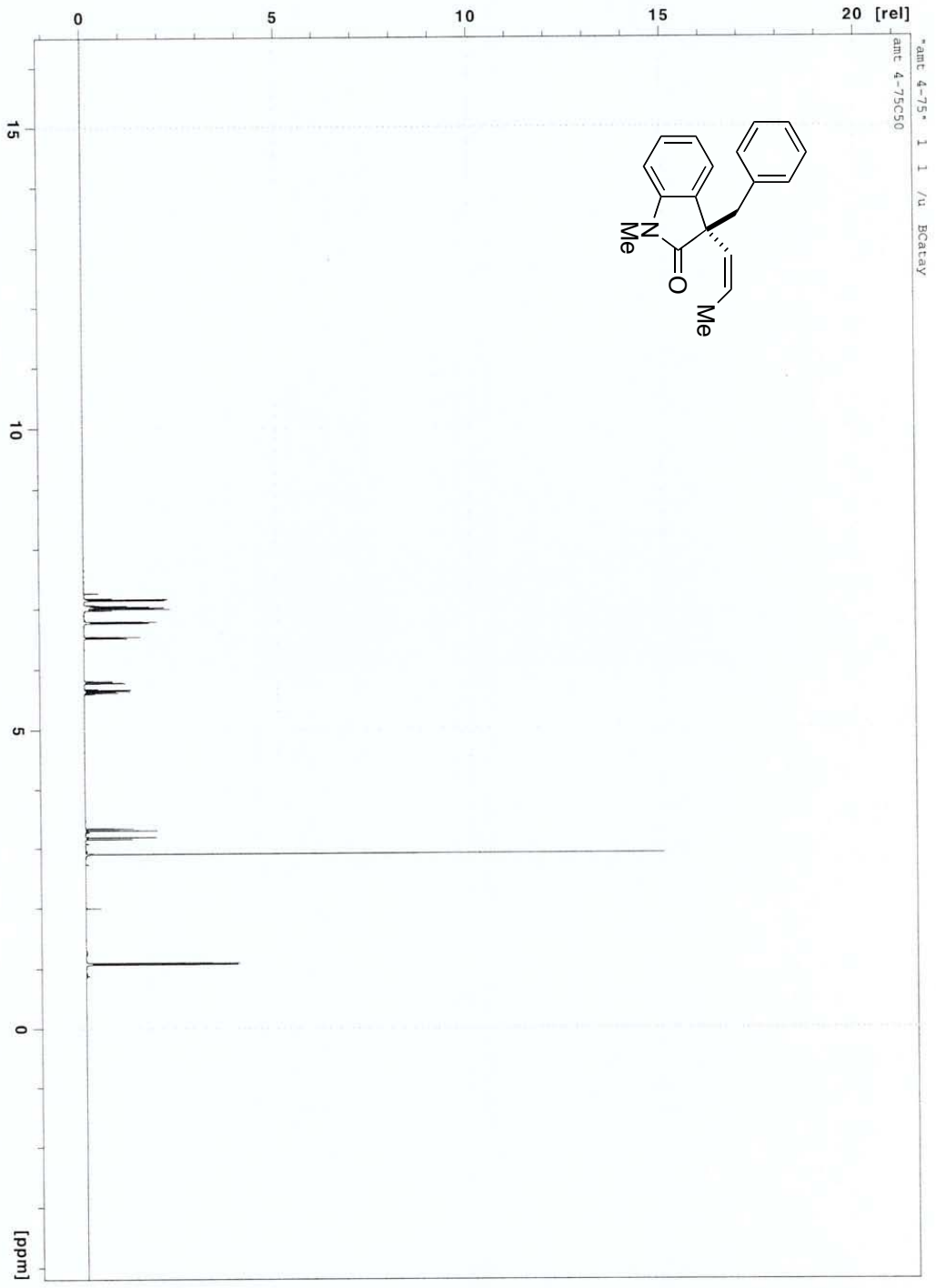


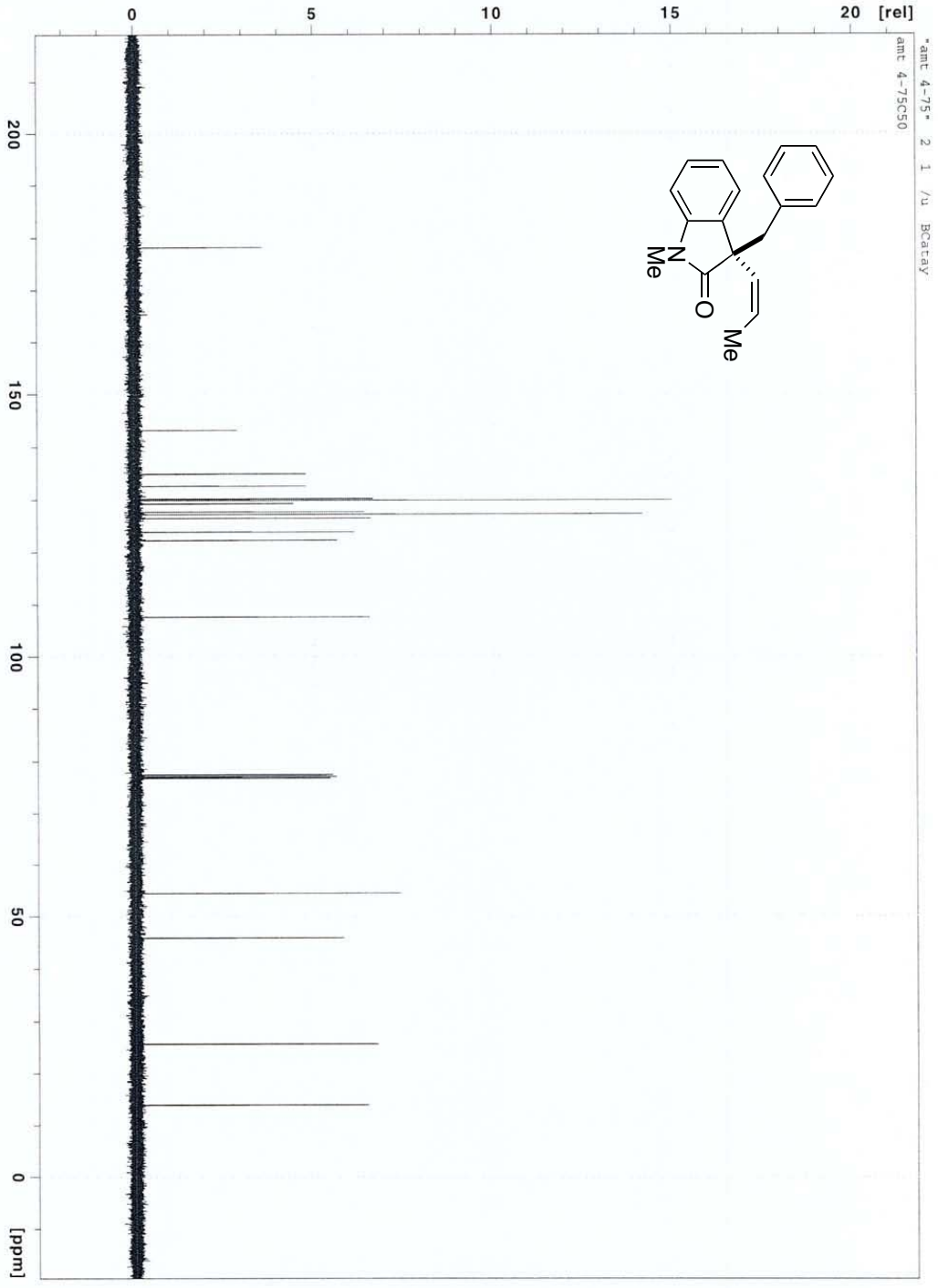

0
5
10
15
20
[rel]
15
10
5
0
[ppm]
amt 4-72-1
amt 4-72 1 1 /u BCatay
Me
N
Me
O
Me
Me
5


0
10
20
30
[rel]
"amt 4-72" 2 1 /u BCatay
amt 4-72-1
200
150
100
50
0
[ppm]
Me
Me
N
Me
Me
O
5


0
5
10
15
[rel]
amt 4-71A
"amt 4-71" 1 1 /u/data/BCatay BCatay
Me
N
O
OMe
15
10
5
0
[ppm]


0
10
20
30
[rel]
200
150
100
50
0
[ppm]
amt 4-71A
amt 4-71 2 1 /u/data/BCatay BCatay
Me
N
O
OMe
178.8446
158.9753
143.4583
138.1685
134.4744
133.1134
132.3861
128.3285
127.9916
127.8700
127.3450
127.0237
126.0352
125.9350
125.2513
124.8311
124.3794
123.0644
114.7200
109.4911
55.3722
52.1861
23.7469


0
5
10
15
20 [rel]
15
10
5
0
[ppm]
N
Me
O
Me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O
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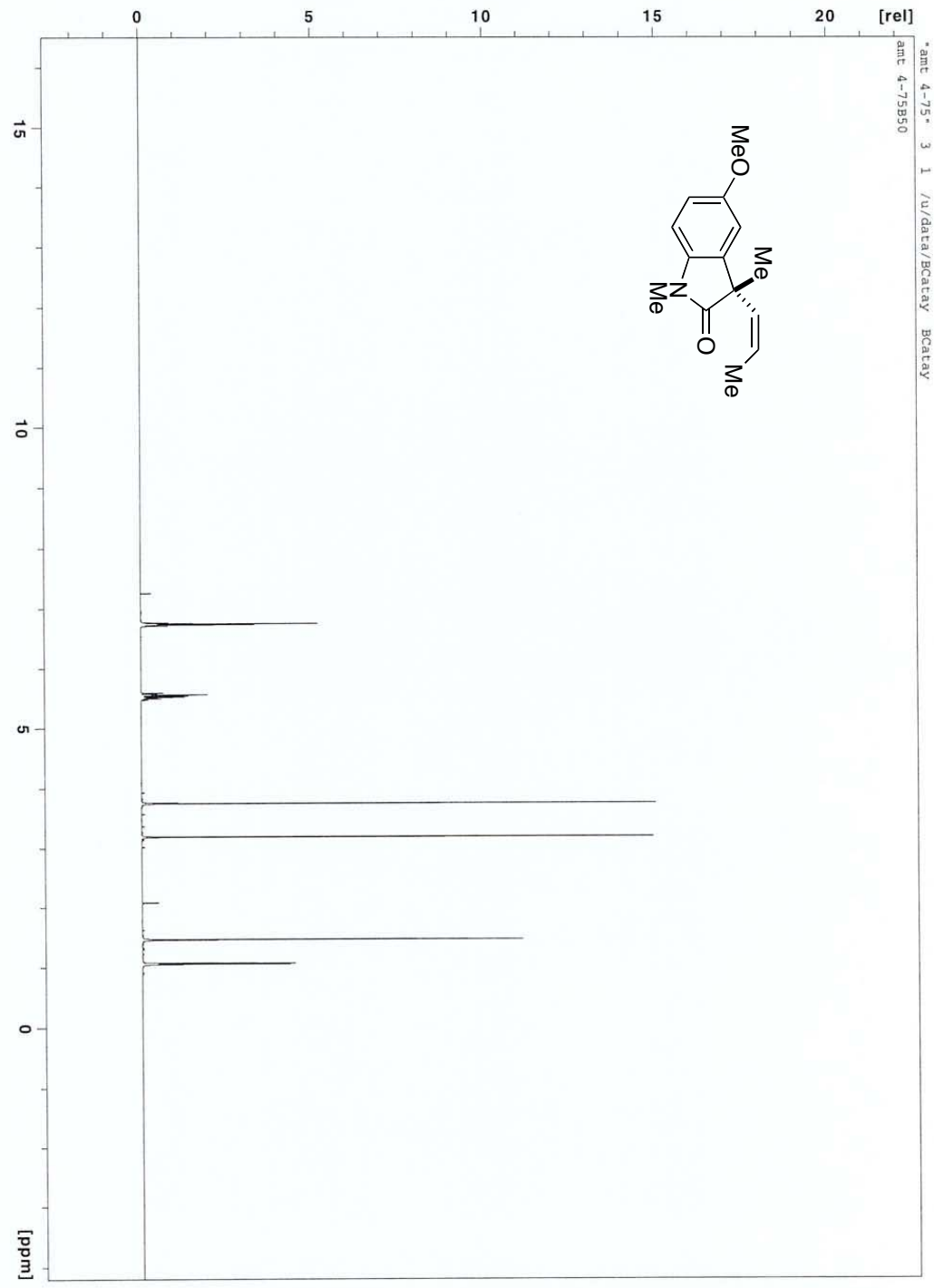
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Me
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Me
O
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15
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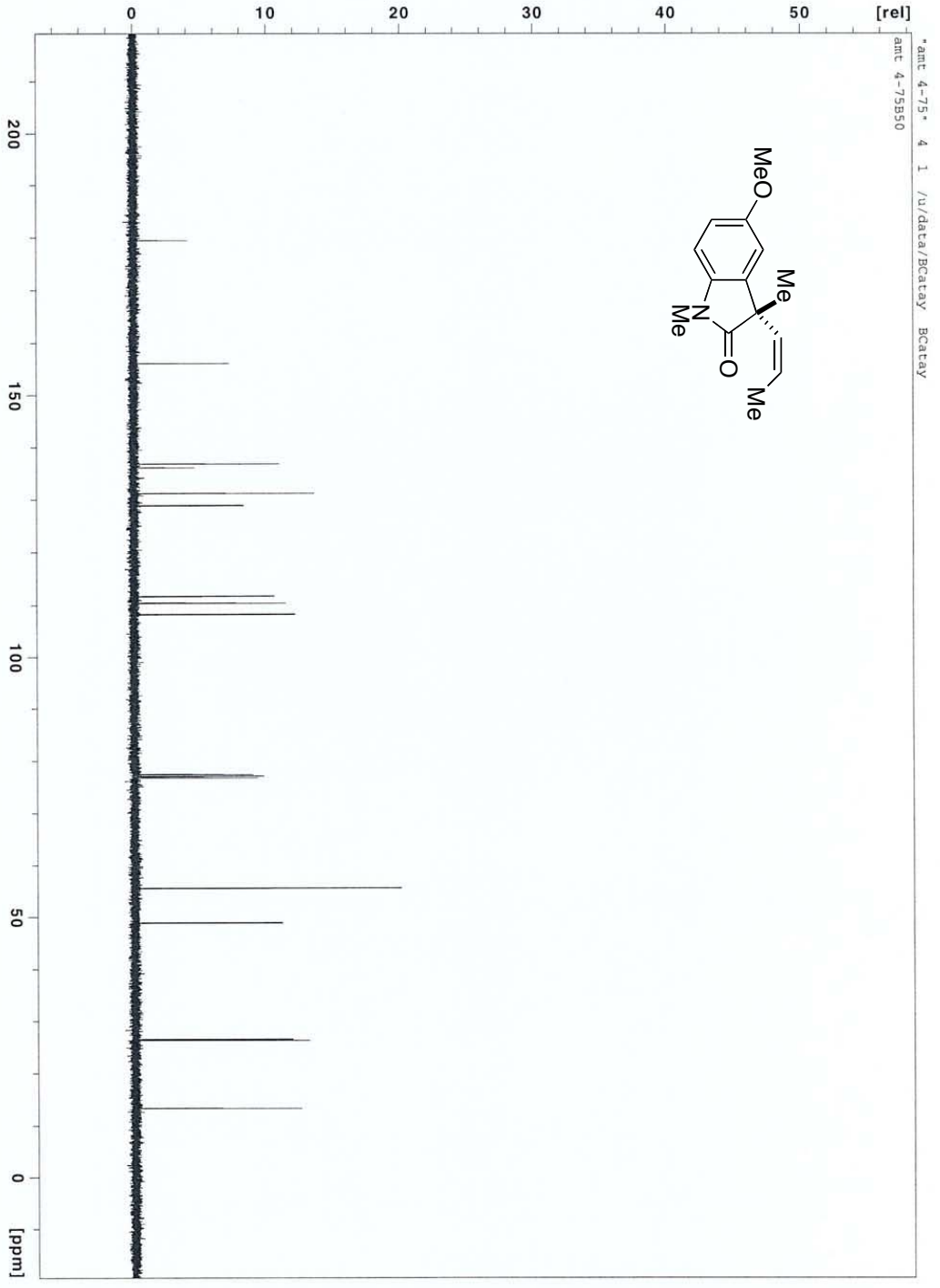
5
0
[ppm]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[ppm]
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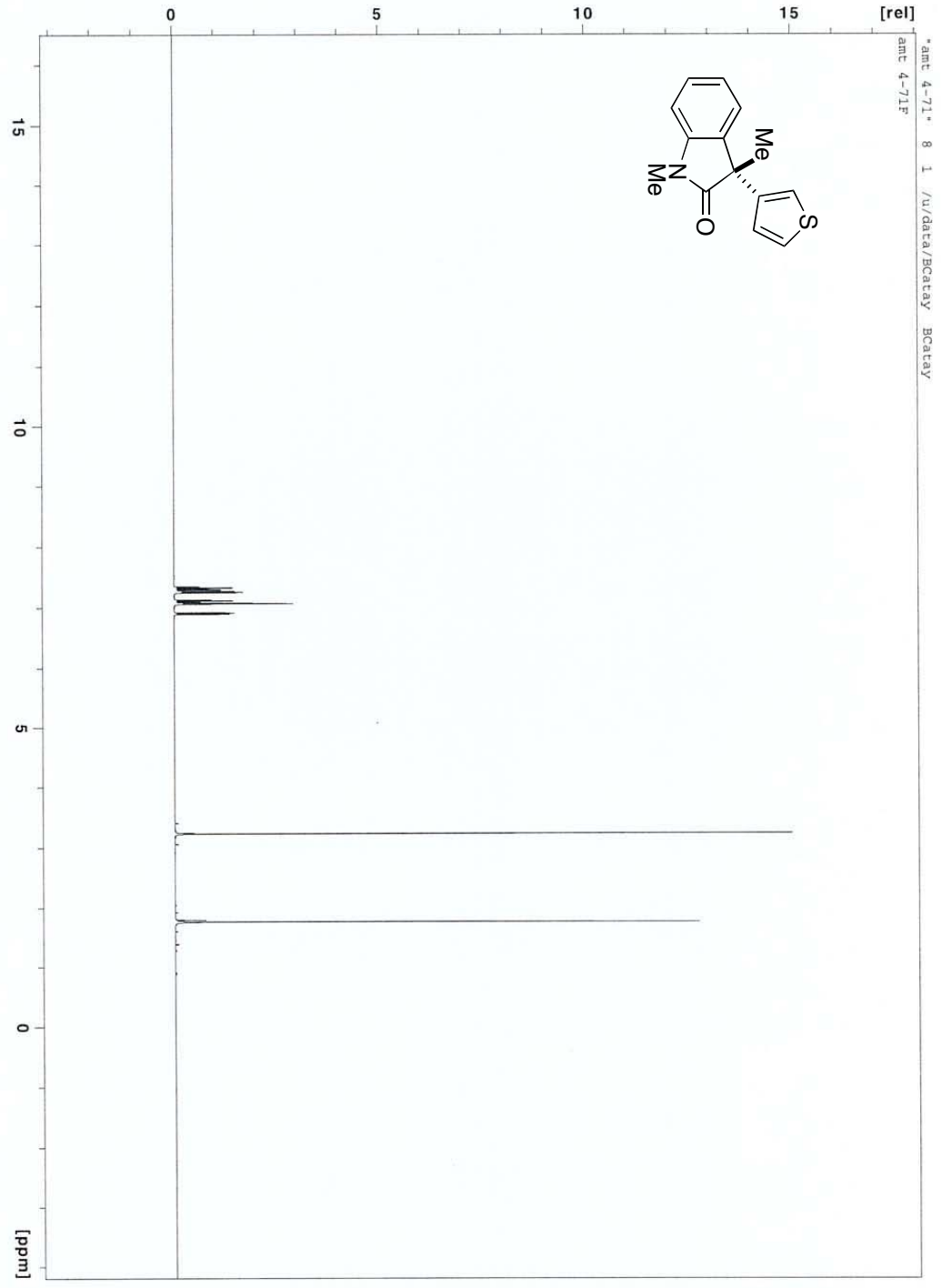
Me
N
Me
O
Me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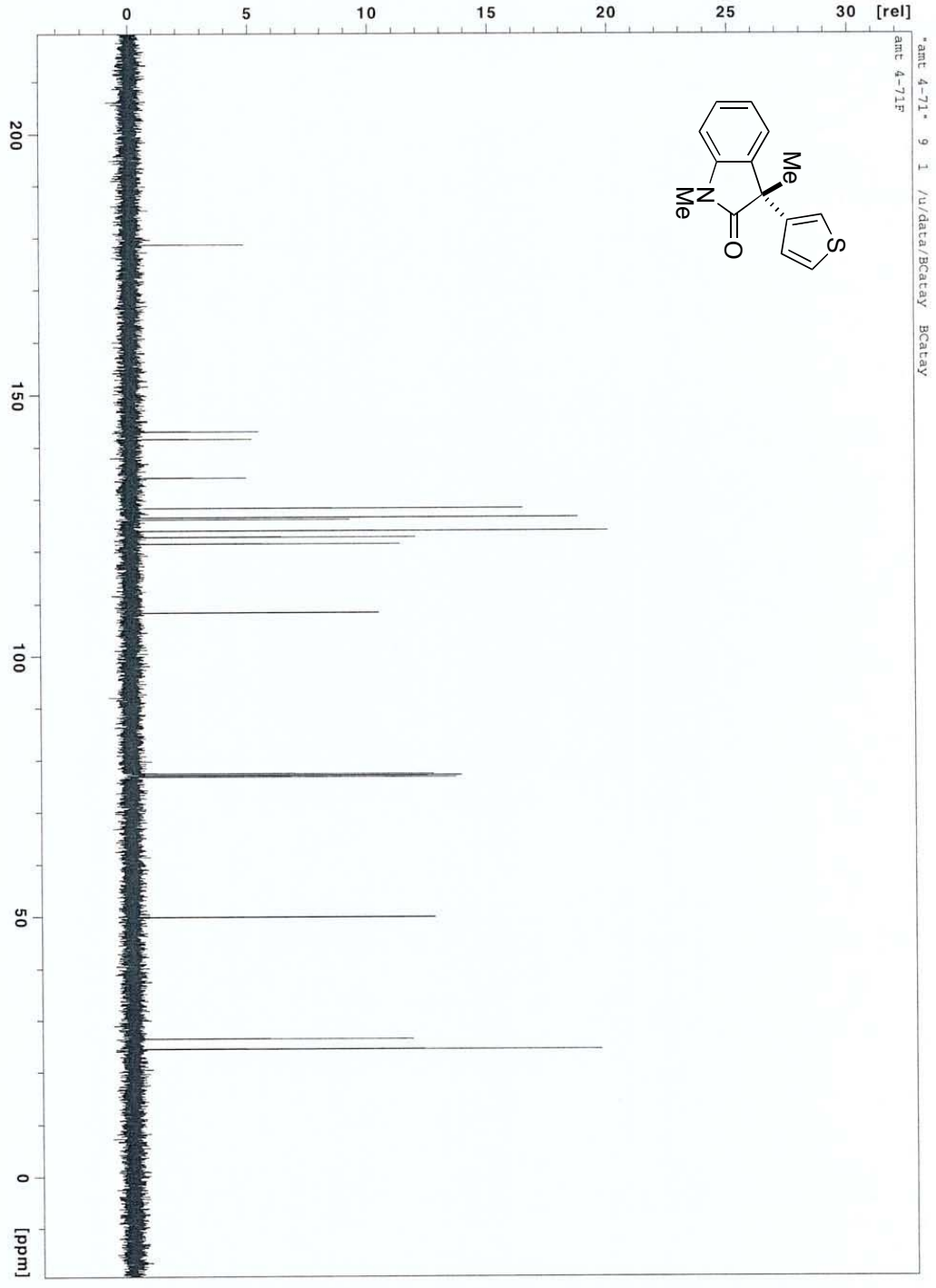
N
Me
O
S
15
10
5
0
[ppm]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Me
N
Me
O
S
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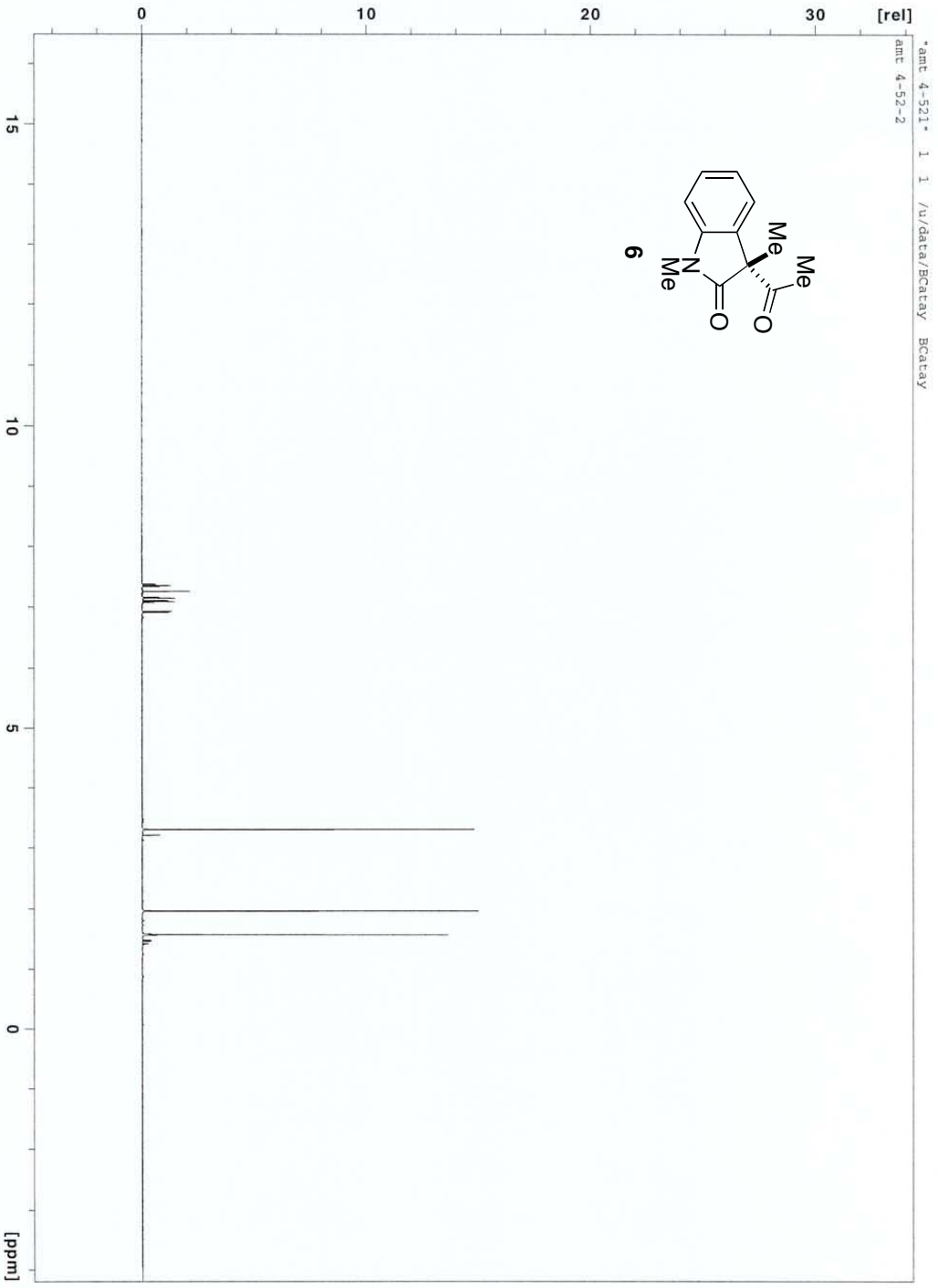
amt 4-71 9 1 /u/data/BCatay BCatay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30
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10
5
0
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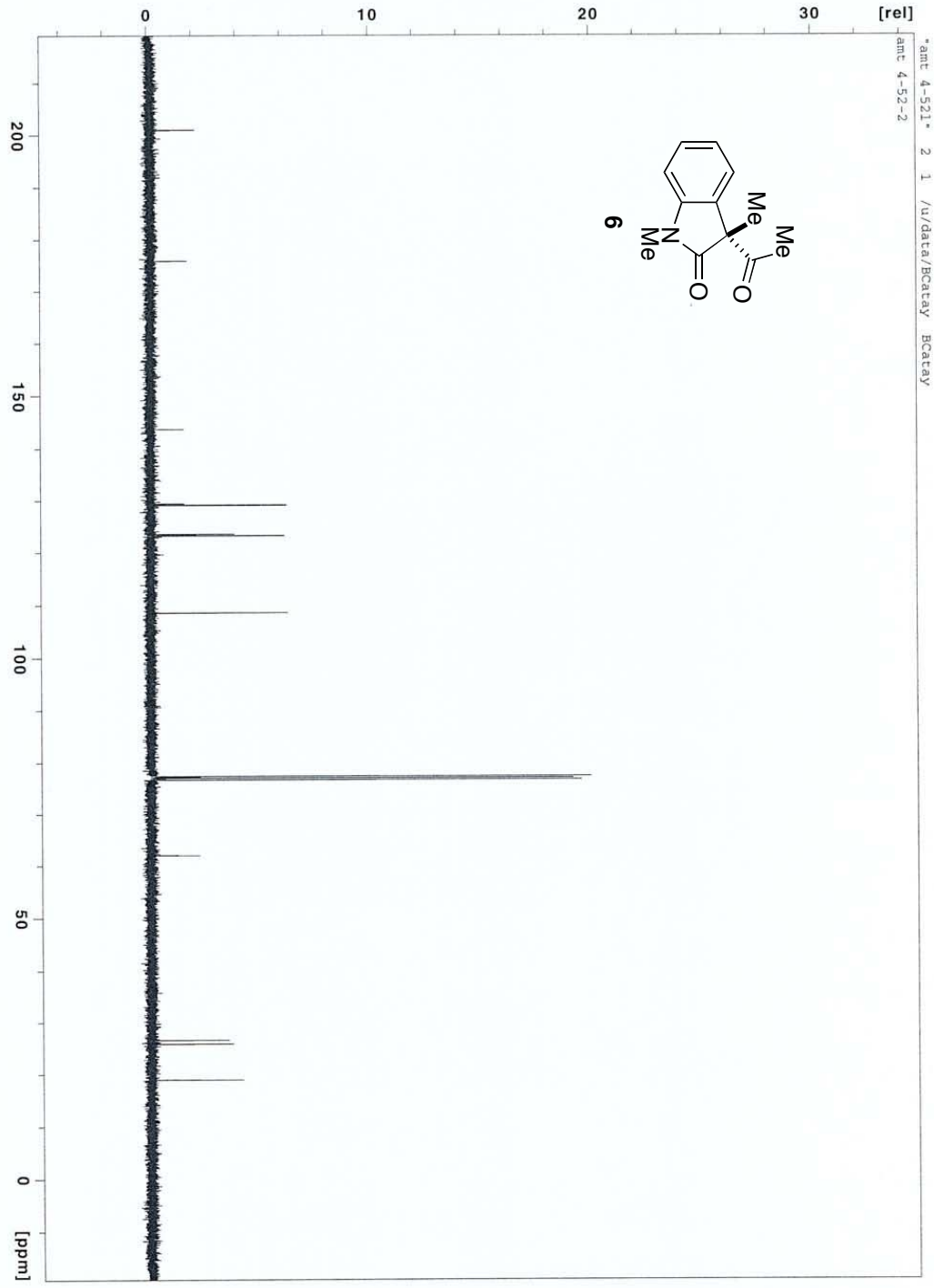
Me
Me
N
Me
O
O
6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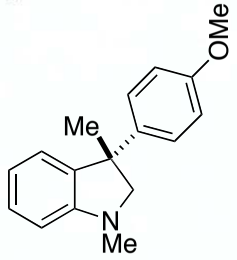
100
50
0
[ppm]
Me
Me
N
Me
O
O
6

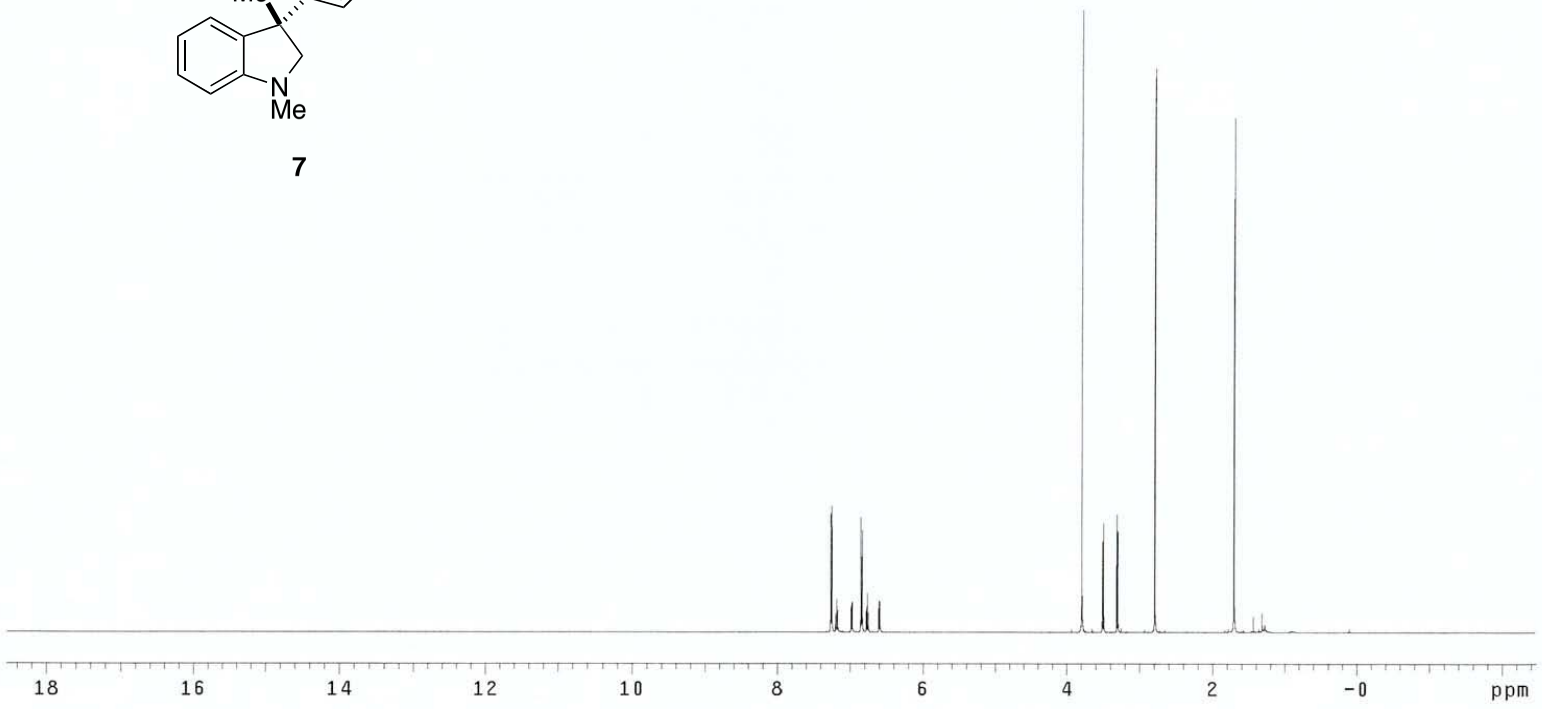
amt 4-63

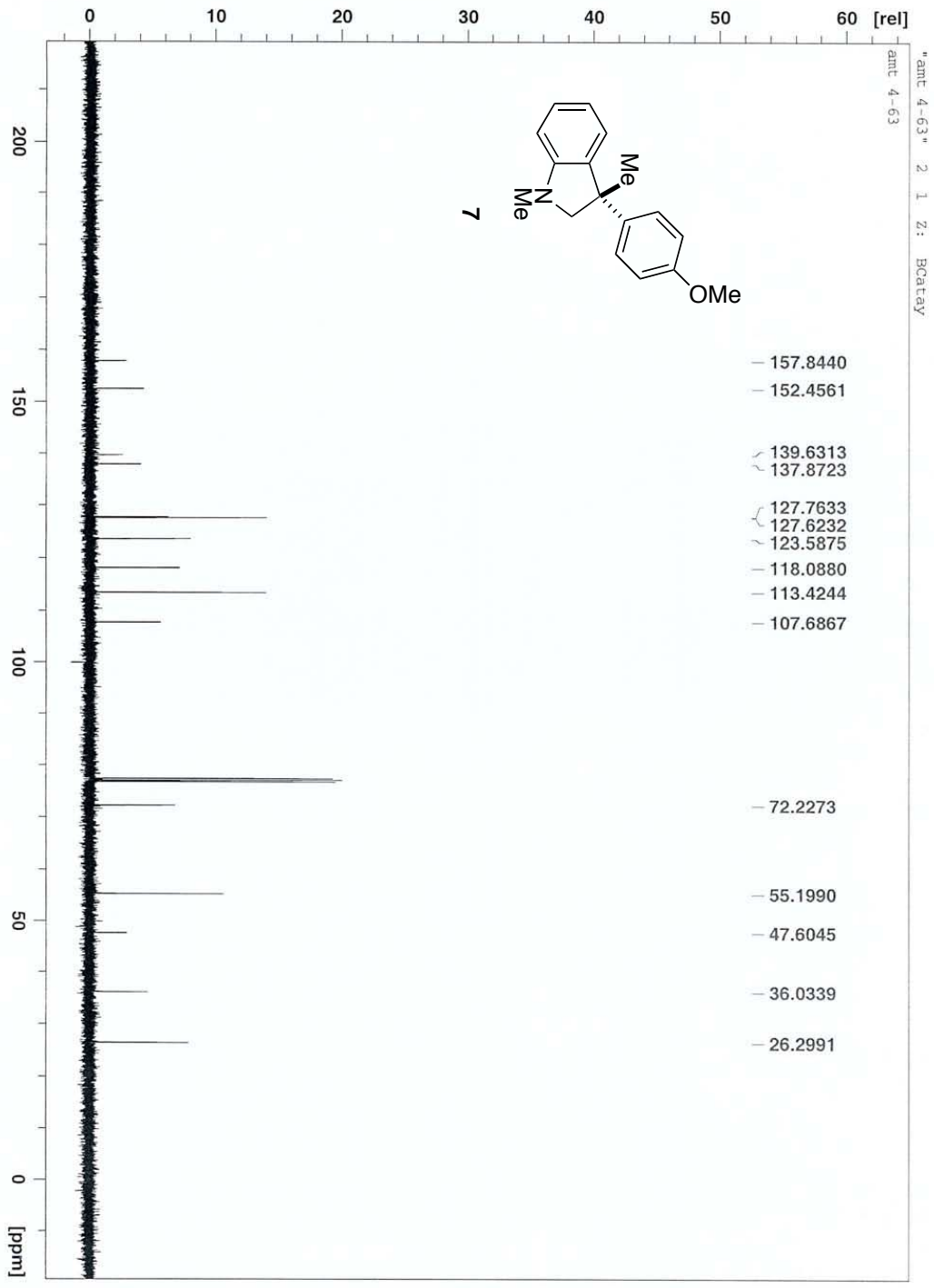
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 2.000 sec
Pulse 88.7 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec



7

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20
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60
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150
100
50
0
[ppm]
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N
Me
OMe
7
157.8440
152.4561
139.6313
137.8723
127.7633
127.6232
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118.0880
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107.6867
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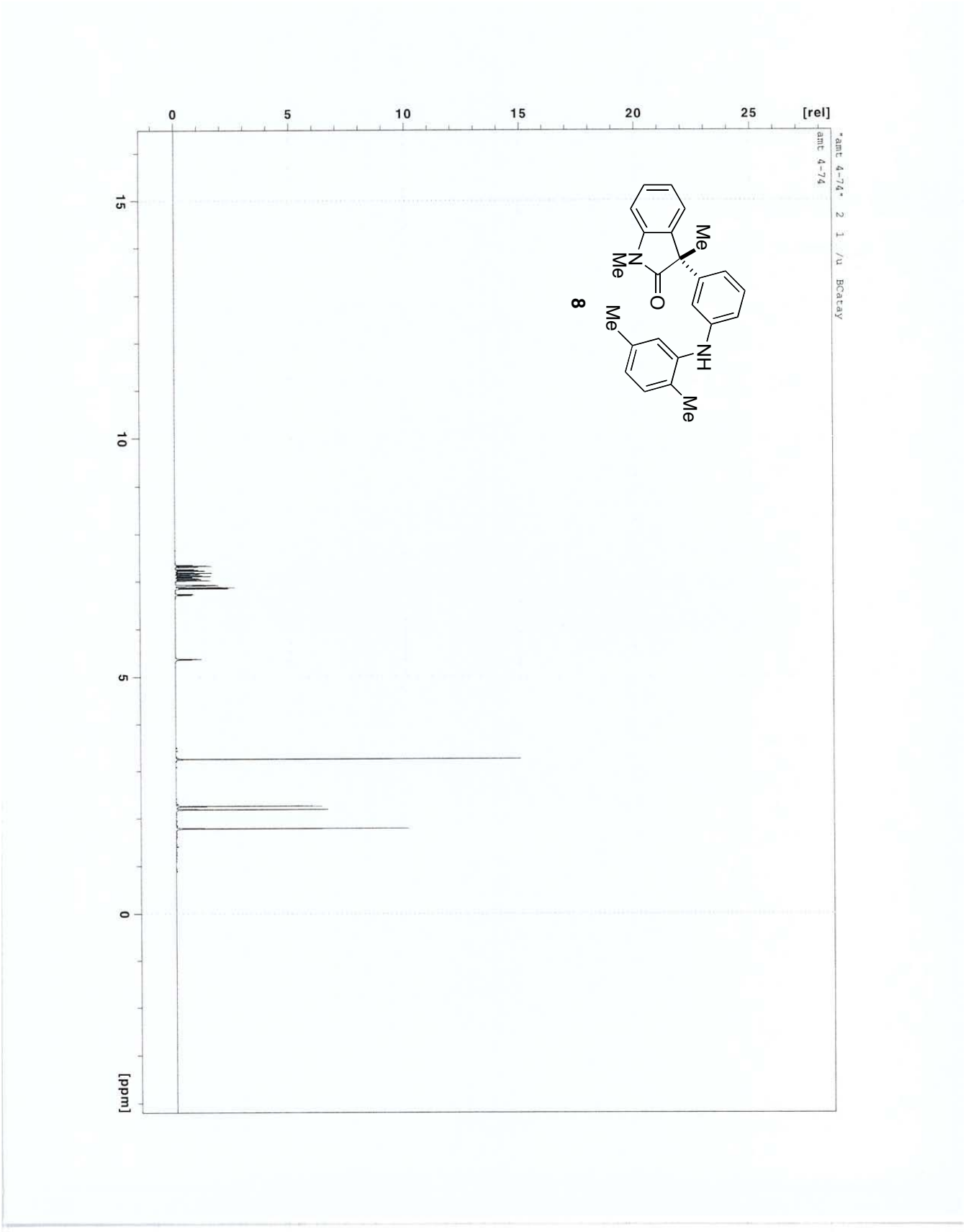
47.6045
36.0339
26.2991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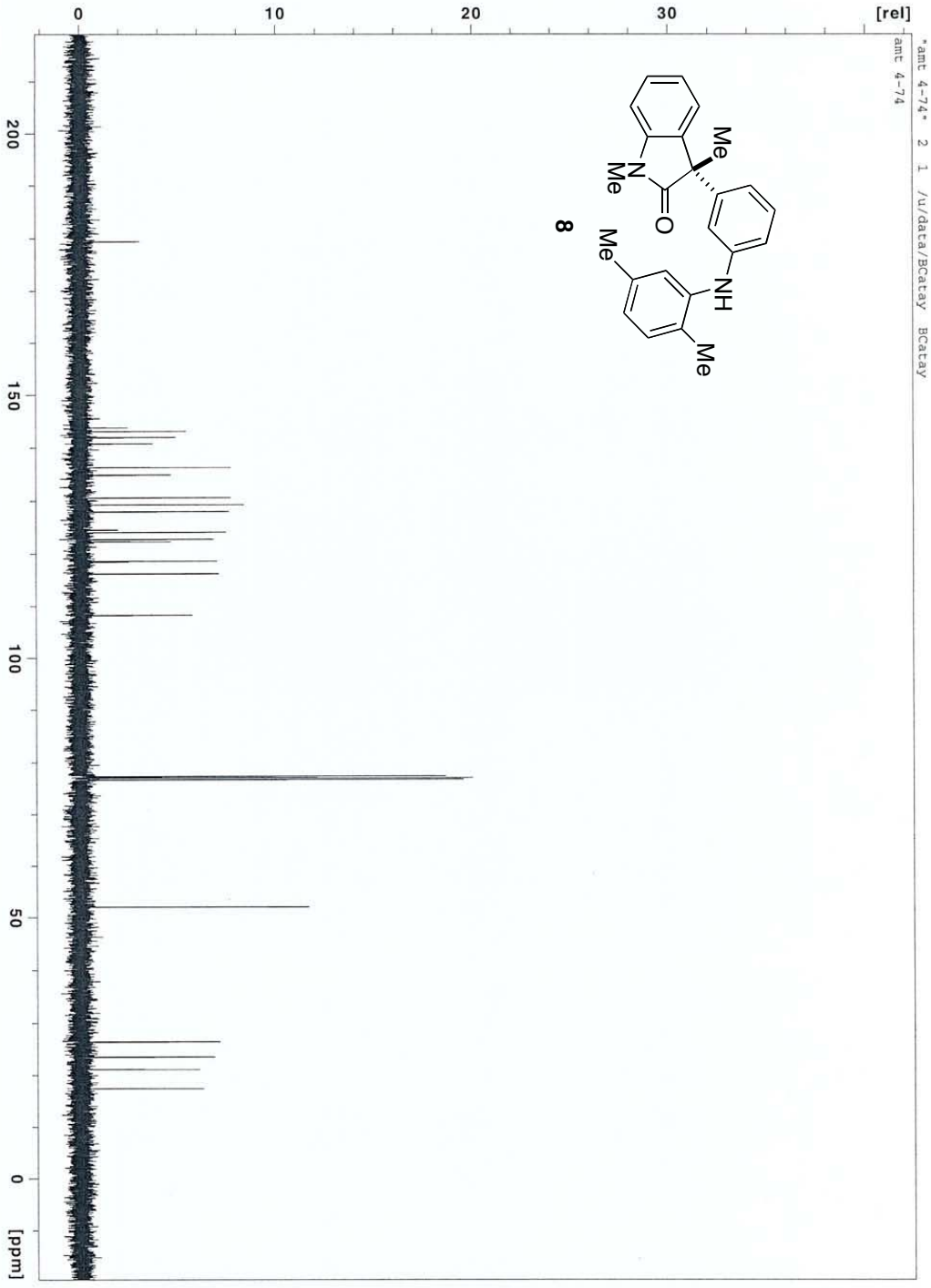
Me
N
Me
O
Me
NH
Me
8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150
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[ppm]
Me
N
Me
O
NH
Me
Me
8