Supporting Information

Intriguing substituent effect in modified Hoveyda-Grubbs metathesis catalysts incorporating a chelating iodo-benzylidene ligand

Michał Barbasiewicz,* Krzysztof Błocki, Maura Malińska, and Robert Pawłowski

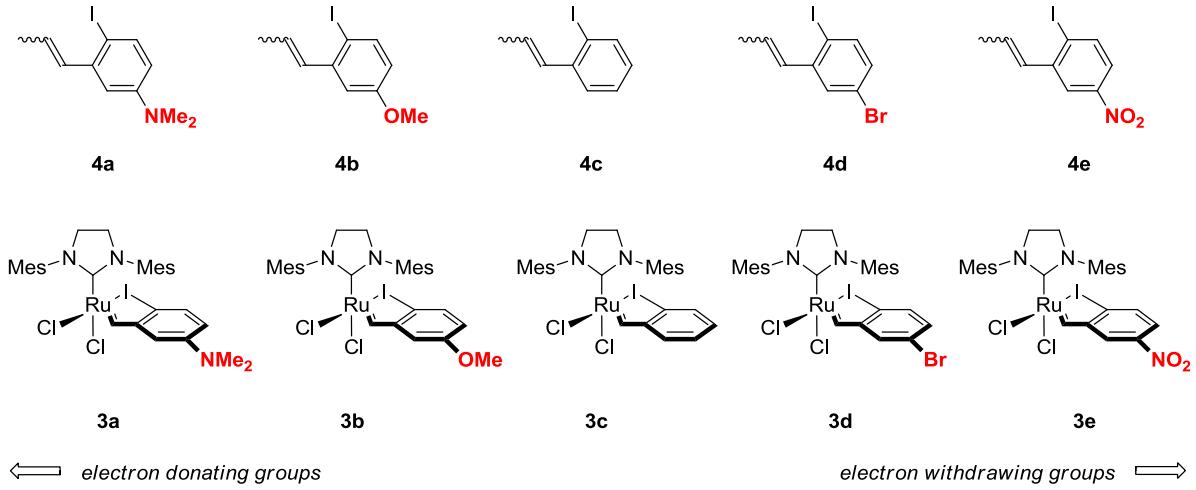
Faculty of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland,
e-mail: barbasiewicz@chem.uw.edu.pl
www.aromaticity.pl

General Informations

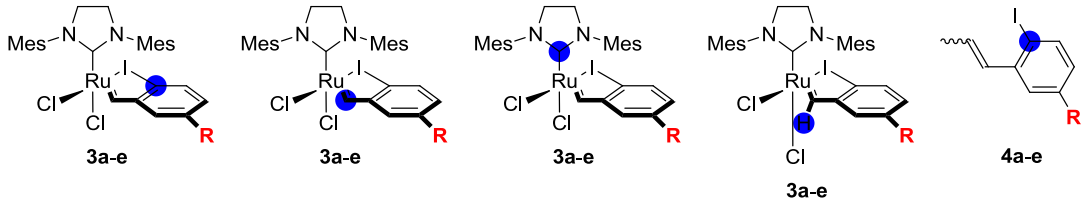
2-Bromo-5-methylbenzoic acid, 3-methoxybenzylalcohol, 2-bromo-5-nitrobenzoic acid, 3-(N,N-dimethylamino)benzoic acid, ethyl 2-iodo-5-bromobenzoate, 2-iodobenzoic acid, and 2-bromo-5-methylbenzoic acid were used from commercial sources and used as received.

[1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(pyridyl) ruthenium(II)(catalyst "M31") was obtained from UMICORE Co & KG.

Iodocomplexes **3a**-**e** and ligands **4a**-**e** described in the manuscript are presented below.



Selected ^{1}H and ^{13}C NMR spectroscopic data of complexes 3 and ligands 4

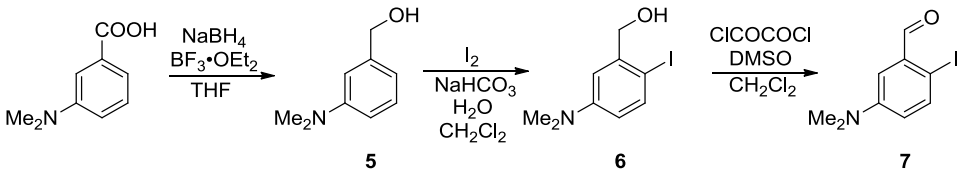


R=	^{13}C NMR C_{ipso}-I	^{13}C NMR Ru=CH	^{13}C NMR Ru-C_{NHC}	^{1}H NMR Ru=CH	^{13}C NMR ligand C_{ipso}-I
NMe_2	83.25	283.7	214.9	18.0	83.1/83.5
OMe	88.82	281.3	214.5	18.0	88.7/88.0
H	100.44	281.5	214.4	18.1	99.2/100.2
Br	98.09	278.5	213.7	18.0	96.9/ -[a]
NO_2	107.57	276.8	212.8	18.1	106.7/108.4

[a] - one predominant isomer of the styrene was isolated after the Wittig reaction

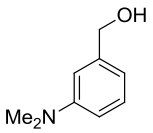
Synthesis of intermediates 5-15

Synthesis of 2-iodo-5-(*N,N*-dimethylamino)benzaldehyde



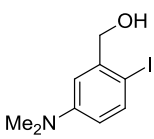
First step of the synthesis - reduction of carboxylic acid - was performed according to modified general procedure described in: S.-D. Cho, Y.-D. Park, J.-J. Kim, J. R. Falck and Y.-J. Yoon, *Bull. Korean Chem. Soc.*, 2004, **25**, 407-409.

A 250 ml round-bottom flask was charged with 3-(*N*,*N*-dimethylamino)benzoic acid (4.961 g; 30.0 mmol) and argonated. THF (100 ml) was added, the flask was placed in a cold-water bath, and to the resulted solution $NaBH_4$ (2.295 g; 60.7 mmol) was added slowly with stirring, while intensive gas evolution was observed. After 15 min $BF_3{\cdot}OEt_2$ (3.7 ml; 30.0 mmol) was added, and mixture was kept at rt for 3.5 h. Then the mixture was was kept at 70 °C for 1 h, cold water bath was applied, and aqueous HCl (5 ml; 1 : 4 *v*/*v*) was added slowly, while intensive gas evolution and white precipitate were observed. To the mixture an aqueous solution of NaOH (0.88 g) in water (15 ml), and brine (50 ml) were added, it was extracted with ethyl acetate (3 × 50 ml), combined organic phases were washed with brine, and dried with $MgSO_4$. The mixture was filtered, evaporated, and residue was placed on a top of chromatographic column (silica gel; cyclohexane : ethyl acetate 1 : 1), eluted, and evaporated to obtain 3-(*N*,*N*-dimethylamino)benzyl alcohol (**5**; 2.864 g; 18.94 mmol; 63%) as a pale-yellow oil.



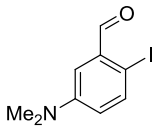
5, oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.23 (dd, *J*=7.7, 7.7 Hz, 1H), 6.76-6.64 (m, 3H), 4.59 (s, 2H), 2.94 (s, 6H), 2.60 (s br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.1, 142.2, 129.4, 115.6, 112.3, 111.5, 65.9, 40.9. The NMR data were consistent with literature: J. Cody and C. J. Fahrni, *Tetrahedron*, 2004, **60**, 11099-11108.

A 100 ml round-bottom flask was charged with 3-(*N*,*N*-dimethylamino)benzyl alcohol (**5**; 2.721 g; 18.0 mmol), CH_2Cl_2 (5.5 ml), solution of $NaHCO_3$ (2.276 g; 26.8 mmol) in water (15 ml), and iodine (4.553 g; 17.94 mmol) was added in two portions with stirring, while intensive gas evolution was observed. The mixture was stirred at rt overnight, and extracted with ethyl acetate (3 × 50 ml). Combined organic phases were washed with brine (50 ml), and dried with $MgSO_4$. The mixture was filtered, evaporated, and residue was dissolved in ethyl acetate (10 ml, slightly warmed) and placed on a top of chromatographic column (silica gel; cyclohexane : ethyl acetate 2 : 1 to 1 : 1), eluted, and evaporated. Residue was crystallized from *n*-heptane (50 ml) to obtain 2-iodo-5-(*N*,*N*-dimethylamino)benzyl alcohol (**6**; 4.007 g; 14.46 mmol; 80%) as a white solid.



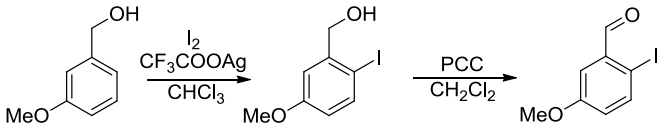
6, mp. 88-92 °C (dec.) (lit. 92-94 °C (dec.): K. R. Roesch, H. Zhang and R. C. Larock, *J. Org. Chem.*, 2001, **66**, 8042-8051). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55 (d, *J*=8.8 Hz, 1H), 6.81 (d, *J*=3.0 Hz, 1H), 6.38 (dd, *J*=8.8, 3.0 Hz, 1H), 4.58 (s, 2H), 2.93 (s, 6H), 2.07 (s br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.8, 142.6, 139.1, 113.7, 112.9, 80.3, 69.6, 40.4.

An argonated 100 ml Schlenk flask was charged with oxalyl chloride (1.869 g; 14.7 mmol), CH_2Cl_2 (15 ml), and cooled to -80 °C. Then a solution of DMSO (2.450 g; 31.4 mmol) in CH_2Cl_2 (15 ml) was added dropwise in 10 min, while temperature slowly risen to -72 °C. After 15 min, while temperature slowly risen to -65 °C a solution of 2-iodo-5-(*N*,*N*-dimethylamino)benzyl alcohol (**6**; 3.327 g; 12.0 mmol) in CH_2Cl_2 (15 ml) was added dropwise in 10 min. In next 15 min the flask was shaken few times to improve stirring, then NEt_3 (7.5 ml) was added, and after 15 min cooling bath was removed, and the mixture was stirred at rt for 30 min. Then water (50 ml), CH_2Cl_2 (100 ml) were added, and the phases were separated. Organic phase was washed with water (5 × 100 ml), brine (100 ml), and dried with $MgSO_4$. The mixture was filtered, evaporated, and residue was placed on a top of chromatographic column (silica gel; cyclohexane : ethyl acetate 3 : 1), eluted, and evaporated to obtain 2-iodo-5-(*N*,*N*-dimethylamino)benzaldehyde (**7**; 3.247 g; 11.80 mmol; 98%) as yellow crystals.



7, mp. 64-65 °C (lit. 65-66.5 °C: K. R. Roesch, H. Zhang and R. C. Larock, *J. Org. Chem.*, 2001, **66**, 8042-8051). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.66 (d, *J*=8.8 Hz, 1H), 7.17 (d, *J*=3.1 Hz, 1H), 6.66 (dd, *J*=8.8, 3.1 Hz, 1H), 2.96 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.5, 150.4, 140.4, 134.7, 119.7, 113.0, 83.7, 40.2.

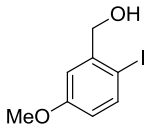
Synthesis of 2-iodo-5-methoxybenzaldehyde



8 **9**

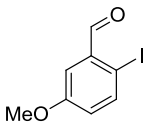
First step of the synthesis - iodination of benzyl alcohol - was performed according to modified procedure described in: J. Ruiz, A. Ardeo, R. Ignacio, N. Sotomayor and E. Lete, *Tetrahedron*, 2005, **61**, 3311-3324.

A 250 ml round-bottom flask was charged with 3-methoxybenzyl alcohol (1.382 g; 10.0 mmol), $CHCl_3$ (30 ml), iodine (2.538 g; 10.0 mmol), and CF_3COOAg (2.200 g; 10.0 mmol) was added. The mixture was stirred for 1 h, and filtered through a pad of silica gel. The solution was evaporated and separated by multiple chromatography (silica gel; cyclohexane : ethyl acetate 3 : 1), eluted, and evaporated to obtain 2-iodo-5-methoxybenzyl alcohol (**8**; 1.254 g ; 4.74 mmol; 47%) as a white solid.



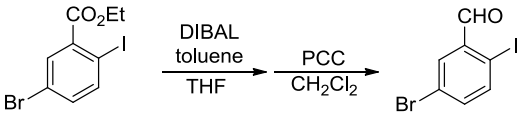
8, mp. 66-67 °C (lit. 64-65 °C: J. Ruiz, A. Ardeo, R. Ignacio, N. Sotomayor and E. Lete, *Tetrahedron*, 2005, **61**, 3311-3324). ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.65 (d, *J*=8.6 Hz, 1H), 7.08 (d, *J*=3.0 Hz, 1H), 6.65 (dd, *J*=8.6, 3.0 Hz, 1H), 5.48 (t, *J*=5.4 Hz, 1H), 4.35 (d, *J*=5.4 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 159.7, 144.9, 139.0, 114.6, 113.6, 84.4, 67.2, 55.2.

A 500 ml round-bottom flask was charged with 2-iodo-5-methoxybenzyl alcohol (**8**; 1.204 g; 4.60 mmol), CH_2Cl_2 (200 ml), and to the resulted solution PCC (1.191 g; 5.52 mmol) was added slowly. The mixture was stirred at rt overnight, and then was directly filtered thought a short chromatographic column (silica gel; CH_2Cl_2), the pad was eluted with CH_2Cl_2, and the eluted solution was evaporated. Residue was dried on a vacuum pump to obtain 2-iodo-5-methoxybenzaldehyde (**9**; 1.165 g; 4.44 mmol; 97%) as a white-yellowish solid.



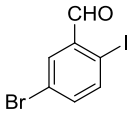
9, mp. 112-113 °C (lit. 114-115 °C: E. Akguen, M. B. Glinski, K. L. Dhawan and T. Durst, *J. Org. Chem.*, 1981, **46**, 2730-2734). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.0 (d, *J*=0.4 Hz, 1H), 7.78 (d, *J*=8.8 Hz, 1H), 7.40 (d, *J*=3.2 Hz, 1H), 6.90 (d, *J*=8.8, 3.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 195.7, 160.2, 141.0, 135.6, 123.5, 113.5, 89.8, 55.6.

Synthesis of 2-iodo-5-bromobenzaldehyde



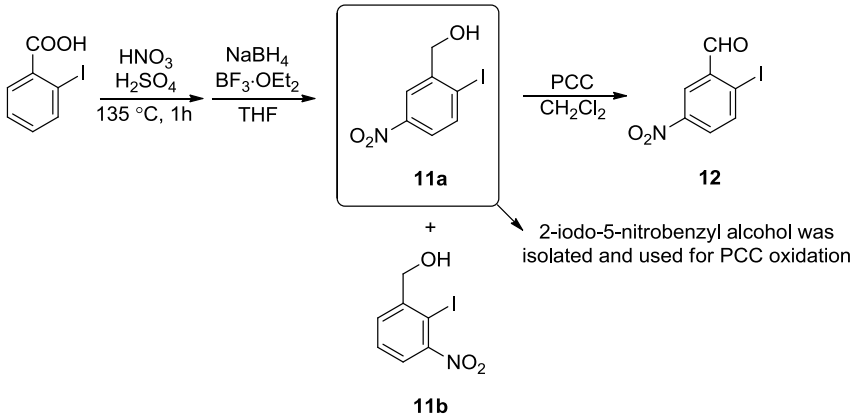
10

A 100 ml round-bottom flask was charged with ethyl 2-iodo-5-bromobenzoate (0.942 g; 2.76 mmol) and argonated. THF (10 ml) was added, the resulted solution was cooled with ice-water bath, and DIBAL (7.0 ml; 7.0 mmol; 1.0M solution in THF) was added slowly with stirring. After 5 min cooling bath was removed, and mixture was kept at rt for 40 min. Ice-water bath was applied, MeOH (5 ml) and an aqueous solution of HCl (30 ml; 1 : 10 *v*/*v*) were consecutively added, and the mixture was extracted with ethyl acetate (3 × 50 ml). Combined organic phases were washed with water (2 × 50 ml), brine (50 ml), and dried with $MgSO_4$. The mixture was filtered, evaporated, and residue was dried on a vacuum pump to obtain a pale-yellow solid (0.836 g). The product was placed in a 250 ml round-bottom flask, dissolved in CH_2Cl_2 (100 ml), and to the resulted solution PCC (0.69 g; 3.2 mmol) was added slowly. The mixture was stirred at rt overnight, and then was directly filtered thought a short chromatographic column (silica gel; CH_2Cl_2), the pad was eluted with CH_2Cl_2, and the eluted solution was evaporated. Residue was dried on a vacuum pump to obtain 2-iodo-5-bromobenzaldehyde (**10**; 0.827 g; 2.66 mmol; 96% from two steps) as a white solid.



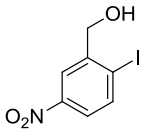
10, mp. 90-92 °C (lit. 89-90 °C: N. Zhou, L. Wang, D. W. Thompson and Y. Zhao, *Org. Lett.*, 2008, **10**, 3001-3004). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.94 (d, *J*=2.6 Hz, 1H), 7.76 (d, *J*=8.4 Hz, 1H), 7.37 (dd, *J*=8.4, 2.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 194.2, 141.7, 138.2, 136.2, 133.0, 123.4, 98.3.

Synthesis of 2-iodo-5-nitrobenzaldehyde

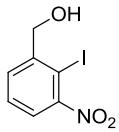


First step of the synthesis - nitration of 2-iodobenzoic acid - was performed according to modified procedure described in: V. Subramanian, V. R. Batchu, D. Barange and M. Pal, *J. Org. Chem.*, 2005, **70**, 4778-4783.

A 250 ml round-bottom flask was charged with 2-iodobenzoic acid (12.4 g; 50.0 mmol), concd H_2SO_4 (56 ml; 98%) and to the resulted mixture concd HNO_3 (19 ml; 65%) was added portionwise with stirring, while exothermic effect was observed. The flask was fitted with reflux condenser and heated at 135 °C for 1 h. The mixture was cooled to rt and poured to a mixture of water (300 ml) and ice (200 g). the resulted suspenson was filtered on a Schott filter, washed with water (200 ml), and dried on air at 70 °C for 10 h. The produced off-white solid (13.98 g) was placed in a 500 ml round-bottom flask, THF (200 ml) was added, and the flask was placed in a cold water bath. To the mixture $NaBH_4$ (5.657 g; 14.95 mmol) was added slowly with stirring, while intensive gas evolution was observed. After 20 min $BF_3{\cdot}OEt_2$ (11 ml; 89 mmol) was added, and mixture was kept at rt for 17 h. Cold water bath was applied, and MeOH (20 ml) was added dropwise, while intensive gas evolution was observed. Most of the solvent was evaporated, and residue was dissolved in ethyl acetate (300 ml). The organic phase was washed with (100 ml), brine (3 × 100 ml), and dried with $MgSO_4$. The mixture was filtered, silica gel (100 ml) was added, and solvent was evaporated. Residue was placed on a top of chromatographic column (silica gel; cyclohexane : ethyl acetate 3 : 1), eluted, evaporated, and dried on a vacuum pump to obtain:

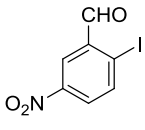


11a, (7.597g; 27.2 mmol; 54%), as a pale-yellow solid, mp. 115-116 °C. ^{1}H NMR (200 MHz, DMSO-d_6): δ 8.19 (d, *J*=2.8 Hz, 1H), 8.09 (d, *J*=8.5 Hz, 1H), 7.82 (dd, *J*=8.5, 2.8 Hz, 1H), 5.85 (t, *J*=5.5 Hz, 1H), 4.46 (d, *J*=5.5 Hz, 2H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 147.8, 146.3, 139.9, 122.8, 121.0, 105.5, 66.8. MS (EI, *m*/*z*, relative intensity): 279 ($M^{+\bullet}$, 100), 262 (7), 250 (7), 233 (64), 215 (24), 203 (27), 152 (35), 150 (24), 124 (12), 122 (8), 105 (37). Elem anal, calcd for $C_7H_6INO_3$: C, 30.13; H, 2.17; N, 5.02; I, 45.48; found: C, 30.12; H, 2.30; N, 4.94; I, 45.32.



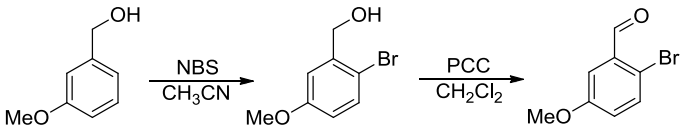
11b, (0.983g; 3.52 mmol; 7%), as a yellow-orange solid, mp. 89-90 °C (*n*-heptane : toluene) (lit. 91-91.5 °C: M. Tercel, M. A. Gieseg, W. A. Denny and W. R. Wilson, *J. Org. Chem.*, 1999, **64**, 5946-5953. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71-7.64 (m, 1H), 7.55 (dd, *J*=8.0, 2.0 Hz, 1H), 7.46 (dd, *J*=8.0, 8.0 Hz, 1H), 4.73 (s, 2H), 2.28 (s br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 146.0, 130.6, 129.1, 123.5, 88.2, 69.7 (one peak was not observed).

An 2 l Erlenmeyer flask was charged with 2-iodo-5-nitrobenzyl alcohol (**11a**; 7.597 g; 27.22 mmol), CH_2Cl_2 (1.5 l), and to the resulted solution PCC (7.063 g; 32.8 mmol) was added slowly. The mixture was stirred at rt for 1 h, second portion of PCC (0.700 g; 3.3 mmol) was added, and it was stirred for 1.5 h. Then the mixture was directly filtered thought a short chromatographic column (silica gel; CH_2Cl_2), the pad was eluted with CH_2Cl_2, and the eluted solution was evaporated. Residue was dried on a vacuum pump to obtain 2-iodo-5-nitrobenzaldehyde (**12**; 7.326 g; 26.5 mmol; 97%) as a pale yellow solid.



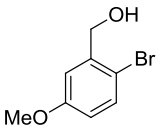
12, mp. 112-113.5 °C (cyclohexane : $CHCl_3$) (lit. 111-112 °C (benzene : hexane): P. W. Jeffs, J. F. Hansen, G. A. Brine, *J. Org. Chem.* **1975**, *40*, 2883-2890). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.63 (d, *J*=2.6 Hz, 1H), 8.18 (d, *J*=8.6 Hz, 1H), 8.10 (dd, *J*=8.6, 2.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 193.3, 142.0, 136.1, 128.6, 124.6, 107.3 (one peak was not observed).

Synthesis of 2-bromo-5-methoxybenzaldehyde



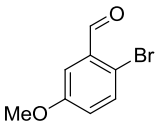
13 **14**

A 250 ml round-bottom flask was charged with 3-methoxybenzyl alcohol (4.84 g; 35.0 mmol), CH_3CN (80 ml), and to the resulted solution NBS (6.59 g; 37 mmol) was added slowly, while exothermic effect was observed. The mixture was stirred at rt overnight, then most of the solvent was evaporated, and residue was placed on a top of large chromatographic column (silica gel; cyclohexane : ethyl acetate 4 : 1), eluted, and evaporated to obtain 2-bromo-5-methoxybenzylalcohol (**13**; 7.17 g; 33.0 mmol; 94%) as a yellowish-orange oil.



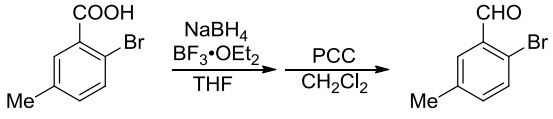
13, oil (lit. mp. 41 °C: A. Speicher, M. Groh, M. Hennrich and A.-M. Huynh, *Eur. J. Org. Chem.*, 2010, 6760-6778). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.35 (d, *J*=8.6 Hz, 1H), 7.00 (d, *J*=3.0 Hz, 1H), 6.65 (dd, *J*=8.6, 3.0 Hz, 1H), 4.63 (s br, 2H), 3.74 (s, 3H), 2.78 (s br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 159.1, 140.6, 133.0, 114.6, 114.0, 112.3, 64.7, 55.4. The NMR data were consistent with literature cited above.

A 1l round bottom flask was charged with 2-bromo-5-methoxybenzyl alcohol (**13**; 6.515g; 30.0 mmol), CH_2Cl_2 (500 ml), and to the resulted solution PCC (6.90 g; 32.0 mmol) was added slowly. The mixture was stirred at rt overnight, and then was directly filtered thought a short chromatographic column (silica gel; CH_2Cl_2), the pad was eluted with CH_2Cl_2, and the eluted solution was evaporated. Residue was dried on a vacuum pump to obtain 2-bromo-5-methoxybenzaldehyde (**14**; 6.385 g; 29.7 mmol; 99%) as an off-white solid.



14, mp. (EtOH) 74.5-75.5 °C (lit. 76 °C: A. Speicher, M. Groh, M. Hennrich and A.-M. Huynh, *Eur. J. Org. Chem.*, 2010, 6760-6778). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.51 (d, *J*=8.8 Hz, 1H), 7.40 (d, *J*=3.4 Hz, 1H), 7.01 (dd, *J*=8.8, 3.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.8, 159.2, 134.6, 133.9, 123.1, 118.0, 112.6, 55.7.

Synthesis of 2-bromo-5-methylbenzaldehyde

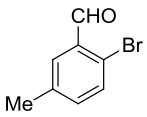


15

First step of the synthesis - reduction of 2-bromo-5-methylbenzoic acid - was performed according to modified general procedure described in: S.-D. Cho, Y.-D. Park, J.-J. Kim, J. R. Falck, and Y.-J. Yoon, *Bull. Korean Chem. Soc.*, 2004, **25**, 407-409.

A 100 ml round-bottom flask was charged with 2-bromo-5-methylbenzoic acid (1.820 g; 8.46 mmol) and argonated. THF (30 ml) was added, and to the resulted solution $NaBH_4$ (0.638 g; 16.9 mmol) was added slowly with stirring, while intensive gas evolution was observed. After 15 min $BF_3{\cdot}OEt_2$ (1.0 ml; 8.1 mmol) was added, and mixture was kept at 60 °C for 1 h. Cold water bath was applied, and MeOH (5 ml) was added

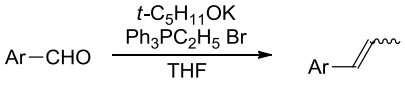
dropwise, while intensive gas evolution and white precipitate were observed. The mixture was left at rt overnight, most of the solvent was evaporated, and residue was placed on a top of chromatographic column (silica gel; cyclohexane : ethyl acetate 3 : 1 to 1 : 1), eluted, and evaporated to obtain a white solid (1.627 g). The product was placed in a 500 ml round-bottom flask, dissolved in CH_2Cl_2 (250 ml), and to the resulted solution PCC (2.093 g; 9.71 mmol) was added slowly. The mixture was stirred at rt overnight, and then was directly filtered thought a short chromatographic column (silica gel; CH_2Cl_2), the pad was eluted with CH_2Cl_2, and the eluted solution was evaporated. Residue was dried on a vacuum pump to obtain 2-bromo-5-methylbenzaldehyde (**15**; 1.574 g; 7.91 mmol; 93% from two steps) as a white-yellowish solid.



15, mp. 41.5-42.5 °C (lit. 42.5-43 °C: J. M. Wurst, G. Liu and D. S. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 7916-7925). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.30 (s, 1H), 7.69 (d, *J*=2.3 Hz, 1H), 7.49 (d, *J*=8.2 Hz, 1H), 7.24 (dd, *J*=8.2, 2.3 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 192.1, 138.1, 136.2, 133.6, 133.1, 130.1, 123.9, 20.7.

Synthesis of ligands 4a-h

Representative procedure of synthesis of propenylarene derivatives 4a-h

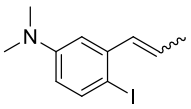


Ar =	
2-I-5-$N(CH_3)_2$-C_4H_6	**4a**, 99%
2-I-5-OCH_3-C_4H_6	**4b**, 98%
2-I-5-Br-C_4H_6	**4d**, 92%
2-I-5-NO_2-C_4H_6	**4e**, 67%*
2-Br-5-OCH_3-C_4H_6	**4g**, 97%
2-Br-5-CH_3-C_4H_6	**4h**, 91%

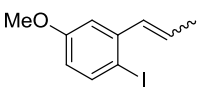
* - Product isolated after chromatography contained small amounts of triphenylphosphine. To remove the contamination it was dissolved in a small volume of ethyl acetate, 3-4 equivalents (large excess) of CuCl were added, and the mixture was stirred at rt overnight under air. Then the mixture was placed on a top of chromatographic column and eluted with cyclohexane : ethyl acetate mixture to obtain product of high purity.

A 100 ml round bottom flask was charged with ethyltriphenylphosphonium bromide (2.67 g; 7.2 mmol) and argonated. THF (20 ml) was added and to the resulted suspension a solution of potassium *tert*-amylate (*t*-PeOK, 5.0 ml; 8.5 mmol; 1.7 M solution in toluene) was added dropwise with stirring. After 10 min the mixture was cooled with ice-water bath and a solution of 2-bromo-5-methylbenzaldehyde (1.197 g; 6.0 mmol) in THF (10 ml) was added dropwise. Cooling bath was removed and the mixture was stirred at rt for 30 min. When TLC analysis (cyclohexane : ethyl acetate 6 : 1) indicated consumption of the substrate (product less polar then aldehyde was formed) an aqueous solution of NH_4Cl (25 ml; 10% *w*/*w*) and brine (50 ml) were added. The mixture was extracted with ethyl acetate (3 × 50 ml), combined organic phases were washed with brine (100 ml), and dried with $MgSO_4$. The mixture was separated with column chromatography (silica gel; cyclohexane : ethyl acetate 10 : 1) to obtain 2-bromo-5-methylpropenylbenzene (**4h**, 1.15 g; 5.45 mmol; 91%) as a yellowish oil.

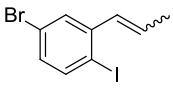
Characterization data



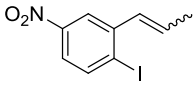
4a, yellow oil, (as a 1 : 1.05 mixture of *E*/*Z* isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.64 (d, *J*=8.8 Hz, 1H), 7.58 (d, *J*=8.8 Hz, 1H), 6.80 (d, *J*=3.0 Hz, 1H), 6.67 (d, *J*=3.2 Hz, 1H), 6.64-6.51 (m, *J*=15.4 Hz, 1H), 6.44-6.32 (m, 3H), 6.20-6.01 (m, 1H), 5.92-5.74 (m, 1H), 2.94 (s, 6H), 2.93 (s, 6H), 1.94 (dd, *J*=6.6, 1.6 Hz, 3H), 1.81 (dd, *J*=7.0, 2.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.5, 150.0, 140.8, 140.7, 139.0, 138.7, 135.3, 134.3, 128.0, 127.0, 114.2, 113.7, 113.1, 110.3, 83.5, 83.2, 40.4 (ovl), 18.4, 14.3. MS (EI, *m*/*z*, relative intensity): 287 ($M^{+\bullet}$, 59), 160 (100), 1444 (19), 115 (25). HRMS (EI), calcd for $C_{11}H_{14}IN$: 287.01710; found: 287.01682. The compound was very unstable, and no satisfactory elemental analysis was obtained.



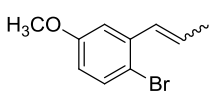
4b, pale yellow oil, (as a 7 : 1 mixture of *E*/*Z* isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (d, *J*=8.6 Hz, 1H), 7.65 (d, *J*=8.6 Hz, 1H), 6.98 (d, *J*=3.0 Hz, 1H), 6.52 (dd, *J*=8.6, 3.0 Hz, 1H), 6.60-6.45 (m, 2H), 6.38-6.28 (m, *J*=11.4 Hz, 1H), 6.20-6.00 (m, 1H), 5.92-5.74 (m, 1H), 3.77 (2s, 6H), 1.91 (dd, *J*=6.6, 1.8 Hz, 3H), 1.76 (dd, *J*=7.1, 1.7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): 159.9, 159.3, 141.7, 139.7 (ovl), 139.3, 134.6, 133.6, 129.0, 127.8, 115.9, 114.8, 114.2, 111.9, 88.7, 88.0, 18.5, 14.3. MS (EI, *m*/*z*, relative intensity): 274 ($M^{+\bullet}$, 100), 147 (12), 132 (11), 115 (19). HRMS (EI), calcd for $C_{10}H_{11}IO$: 273.98547; found: 273.98591. No satisfactory elemental analysis was obtained.



4d, pale yellow oil, (as a 20 : 1 mixture of *E*/*Z* isomers). Only data of predominant isomer was listed. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (d, *J*=8.2 Hz, 1H), 7.52 (d, *J*=2.4 Hz, 1H), 6.99 (dd, *J*=8.2, 2.4 Hz, 1H), 6.54-6.41 (m, *J*=15.8 Hz, 1H), 6.20-6.01 (m, 1H), 1.91 (dd, *J*=6.6, 1.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): 142.7, 140.4, 133.6, 131.1, 130.4, 129.1, 122.6, 96.9, 18.5. MS (EI, *m*/*z*, relative intensity): 324 ($M^{+\bullet}$, 55), 322 ($M^{+\bullet}$, 57), 198 (4), 196 (4), 116 (100). HRMS (EI), calcd for $C_9H_8I^{79}Br$: 321.88541; found: 321.88599. No satisfactory elemental analysis was obtained.

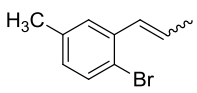


4e, yellow brownish solid, (as a 1.2 : 1 mixture of *E*/*Z* isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.20 (d, *J*=2.6 Hz, 1H), 8.05 (d, *J*=2.6 Hz, 1H), 8.03 (d, *J*=8.6 Hz, 1H), 7.97 (d, *J*=8.8 Hz, 1H), 7.74 (dd, *J*=8.8, 2.6 Hz, 1H), 7.69 (dd, *J*=8.6, 2.8 Hz, 1H), 6.64-6.51 (m, *J*=15.6 Hz, 1H), 6.42-6.18 (m, 2H), 6.08-5.88 (m, 1H), 1.96 (dd, *J*=6.6, 1.6 Hz, 3H), 1.78 (dd, *J*=7.0, 2.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): 142.7, 142.6, 140.3, 140.0, 133.9, 133.5, 133.2, 132.4, 132.0, 130.3, 123.8, 122.4, 122.0, 120.5, 108.4, 106.7, 18.6, 14.2. MS (EI, *m*/*z*, relative intensity): 289 ($M^{+\bullet}$, 96), 243 (4), 145 (5), 132 (4), 115 (100). Elem anal, calcd for $C_9H_8INO_2$: C, 37.39; H, 2.79; N, 4.85; I, 43.90 found: C, 37.48; H, 2.94; N, 4.93; I, 43.65.



4g, colorless oil (as a 1 : 1.5 mixture of *E*/*Z* isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44 (d, *J*=8.8 Hz, 1H), 7.38 (d, *J*=8.8 Hz, 1H), 6.99 (d, *J*=3.0 Hz, 1H), 6.84 (d, *J*=3.2 Hz, 1H), 6.74-6.58 (m, 3H), 6.49-6.38 (m, *J*=11.6 Hz, 1H), 6.26-6.06 (m, 1H), 5.96-5.78 (m, 1H), 3.78 (2s ovl, 6H), 1.91 (dd, *J*=6.6, 1.8 Hz, 3H), 1.78 (dd, *J*=7.0, 2.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ158.9, 158.3, 138.4, 138.1, 133.3, 133.0, 129.9, 129.4, 128.9, 128.2, 116.3, 114.5, 114.3, 113.79, 113.72, 111.9, 55.4 (ovl), 18.6, 14.4. MS (EI, *m*/*z*, relative intensity): 228 ($M^{+\bullet}$, 100), 226 ($M^{+\bullet}$, 100), 147 (50), 132 (30), 115 (45). Elem anal, calcd for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88; Br, 35.18; found: C, 52.76; H, 4.81; Br, 35.16. *Z* isomer of the compound was mentioned in: a) D. A. Bianchi, M. A. Cipulli and T. S. Kaufman, *Eur. J. Org. Chem.*, 2003, **24**, 4731-4736; b) D. A. Bianchi, F. Rúa, T. S. Kaufman, *Tetrahedron*

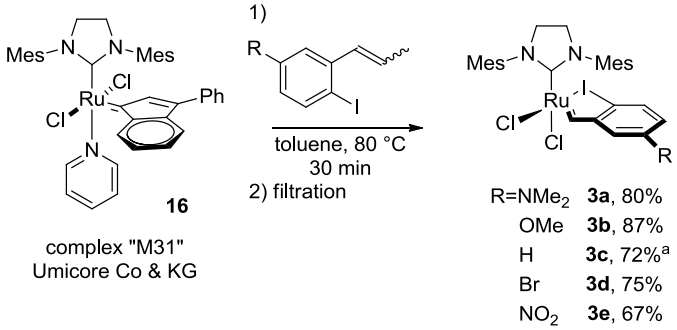
Lett., 2004, **45**, 411-415.



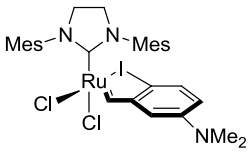
4h, yellowish oil (as a 1 : 1.4 mixture of *E*/*Z* isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45 (d, *J*=8.0 Hz, 1H), 7.39 (d, *J*=8.0 Hz, 1H), 7.3-7.27 (m, 1H), 7.14-7.10 (m, 1H), 6.95-6.83 (m, 2H), 6.78-6.65 (m, *J*=15.6 Hz, 1H), 6.52-6.41 (m, *J*=11.4 Hz, 1H), 6.27-6.08 (m, 1H), 5.96-5.78 (m, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 1.90 (dd, *J*=6.6, 1.7 Hz, 3H), 1.77 (dd, *J*=7.1, 2.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.2, 137.0, 136.9, 136.5, 132.4, 132.2, 131.2, 129.9, 129.4, 129.0, 128.9, 128.4, 127.8, 127.4, 120.6, 119.7, 20.9 (ovl), 18.6, 14.4. MS (EI, *m*/*z*, relative intensity): 212 ($M^{+\bullet}$, 100), 210 ($M^{+\bullet}$, 100), 183 (34), 178 (20), 167 (4), 165 (4), 152 (6), 149 (8), 131 (71), 129 (21), 115 (40). Elem anal, calcd for $C_{10}H_{11}Br$: C, 56.90; H, 5.25; found: C, 56.75; H, 5.16.

Synthesis of iodocomplexes 3a-e

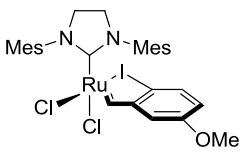
Synthesis of complexes **3a**-**e** was accomplished according to the procedure described in: M. Barbasiewicz, M. Michalak and K. Grela, *Chem. Eur. J.*, 2012, **18**, chem.201202817. [a] - data taken from the literature.



Characterization data

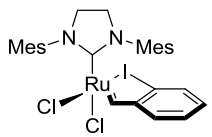


3a, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 18.00 (d, J=1.0 Hz, Ru=CH, 1H), 7.40 (dd, J=1.0, 8.5 Hz, 1H), 7.17 (s, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 6.76 (dd, J=3.0, 8.5 Hz, 1H), 6.37 (d, J=3.0 Hz, 1H), 6.20 (s, 1H), 4.25-4.17 (m, 1H), 4.09-3.96 (m, 1H), 3.92-3.82 (m, 1H), 2.98 (s, 6H), 2.74 (s, 3H), 2.52 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 2.17 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 283.7, 214.9, 158.5, 151.4, 140.6, 140.2, 138.4, 137.9, 136.3, 136.2, 135.6, 133.7, 132.1, 131.1, 130.1, 129.8, 129.3, 114.7, 112.9, 83.2, 52.0, 51.5, 40.7, 21.3, 20.9, 20.3, 20.0, 18.9, 18.0. HRMS (ESI, *m*/*z*), calcd for $C_{30}H_{36}ClIN_3Ru$: 702.0686; found: 702.0702 (M-$Cl^{+\bullet}$). IR (KBr, cm^{-1}): 3469, 2902, 1607, 1574, 1484, 1441, 1403, 1352, 1291, 1265, 1222, 1156, 1031, 908, 855, 807, 575, 419. Elem anal, calcd for $C_{30}H_{36}Cl_2IN_3Ru$: C, 48.86; H, 4.92; N, 5.70; found: C, 49.40; H, 5.21; N, 5.57.

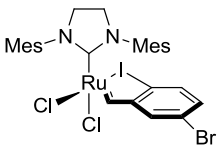


3b, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 18.03 (d, J=0.9 Hz, Ru=CH, 1H), 7.44 (dd, J=0.9, 8.6 Hz, 1H), 7.18 (s, 1H), 7.05 (s, 1H), 6.97 (s, 1H), 6.97 (dd, J=3.0, 8.5 Hz, 1H), 6.51 (d, J=2.9 Hz, 1H), 6.16 (s, 1H), 4.26-4.19 (m, 1H), 4.11-3.97 (m, 1H), 3.92-3.85 (m, 1H), 3.81 (s, OCH_3, 3H), 2.72 (s, 6H), 2.51 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.20 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 281.3, 214.5, 161.4, 158.8, 140.8, 140.3, 138.8, 138.0, 136.3, 136.1, 135.5, 134.1, 131.9, 131.2, 130.1, 129.8, 129.2, 116.9, 113.1, 88.8, 56.0, 52.0, 51.5, 21.3, 20.9, 20.3, 20.1, 18.8, 18.0. HRMS (ESI, *m*/*z*), calcd for $C_{29}H_{33}ClIN_2ORu$: 689.0370; found:

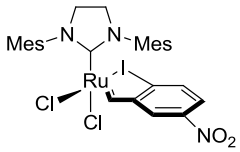
689.0353 (M-Cl$^{+\bullet}$). IR (KBr, *cm^{-1}*): 2902, 1606, 1562, 1484, 1457, 1438, 1269, 1246, 1143, 1040, 1005, 944, 871, 851, 814, 577, 420. Elem anal, calcd for $3C_{29}H_{33}Cl_2IN_2ORu{\cdot}C_6H_5CH_3$: C, 49.83; H, 4.76; N, 3.71; found: C, 49.06; H, 4.81; N, 3.72.



3c. NMR data of the complex was consistent with those described in: M. Barbasiewicz, M. Michalak and K. Grela, *Chem. Eur. J.*, 2012, **18**, chem.201202817.



3d, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 17.99 (d, J=0.6 Hz, Ru=CH, 1H), 7.50 (dd, J=2.2, 8.2 Hz, 1H), 7.45 (dd, *J*=0.7, 8.3 Hz, 1H), 7.18 (s, 1H), 7.06 (d, *J*=2.1 Hz, 1H), 7.05 (s, 1H), 7.01 (s, 1H), 6.21 (s, 1H), 4.26-4.19 (m, 1H), 4.11-3.97 (m, 1H), 3.93-3.85 (m, 1H), 2.71 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 278.6, 213.7, 158.8, 140.9, 140.3, 139.6, 138.2, 136.2, 136.0, 135.4, 135.1, 132.6, 131.6, 131.2, 130.2, 130.1, 130.0, 129.2, 124.0, 98.1, 52.0, 51.6, 21.4, 21.3, 20.3, 20.1, 18.9, 18.0. HRMS (ESI, *m/z*), calcd for $C_{28}H_{30}ClBrIN_2ORu$: 736.9369; found: 736.9356 (M-Cl$^{+\bullet}$). IR (KBr, *cm^{-1}*): 2907, 1605, 1485, 1437, 1291, 1268, 1223, 1068, 1011, 853, 823, 731, 574, 419. Elem anal, calcd for $2C_{29}H_{33}Cl_2IN_2ORu{\cdot}C_6H_5CH_3$: C, 46.17; H, 4.18; N, 3.42; found: C, 46.75; H, 4.22; N, 3.40.

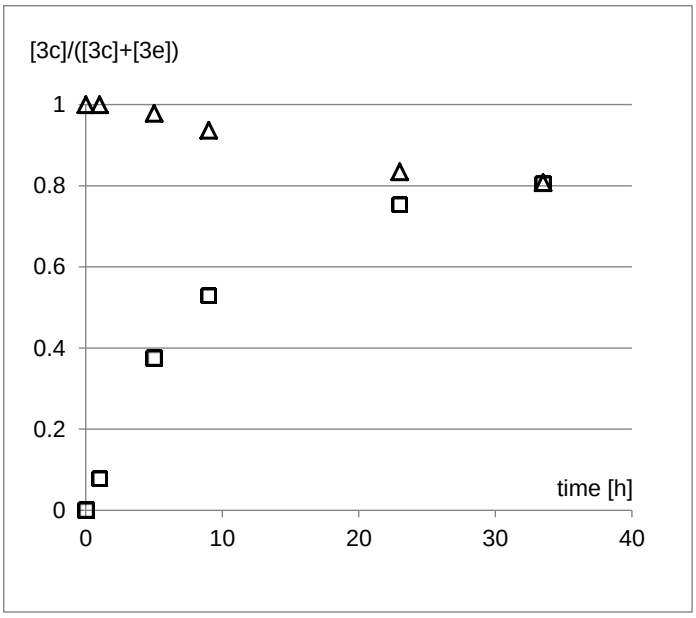


3e, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 18.13 (d, J=0.7 Hz, Ru=CH, 1H), 8.19 (dd, J=2.5, 8.4 Hz, 1H), 7.81 (dd, *J*=0.8, 8.5 Hz, 1H), 7.73 (d, *J*=2.5 Hz, 1H), 7.18 (s, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 6.06 (s, 1H), 4.28-4.21 (m, 1H), 4.13-3.99 (m, 1H), 3.94-3.86 (m, 1H), 2.70 (s, 3H), 2.52 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 2.10 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 276.8, 212.8, 157.6, 149.4, 141.1, 140.4, 139.7, 138.4, 136.1, 135.8, 135.5, 134.7, 131.3, 130.2, 128.9, 123.5, 120.8, 107.6, 52.0, 51.7, 21.3, 20.7, 20.3, 20.1, 18.8, 18.1. HRMS (ESI, *m/z*), calcd for $C_{28}H_{30}ClIN_3O_2Ru$: 704.0115; found: 704.0128 (M-Cl$^{+\bullet}$). IR (KBr, *cm^{-1}*): 2914, 1593, 1525, 1483, 1432, 1344, 1267, 1013, 852, 833, 735, 695, 576, 465, 421. No satisfactory analysis was obtained.

Ligand exchange experiments

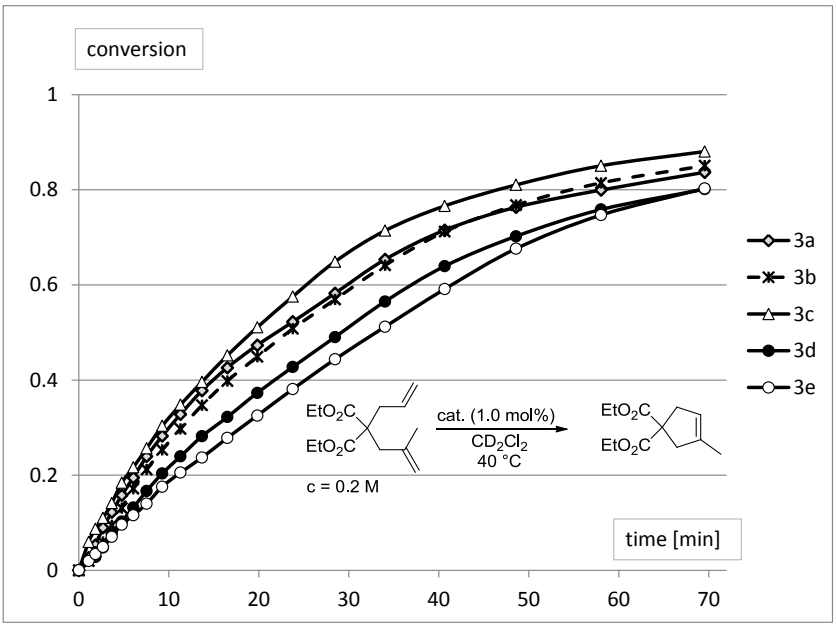
Ligand exchange experiments were performed according to the procedure described below:

A 20 ml Schlenk flask was charged with catalyst **3c** (0.103 g; 0.15 mmol), 2-iodo-5-nitropropenylbenzene (0.0435 g; 0.15 mmol), CD_2Cl_2 (4 ml), and the mixture argonated with three freeze-pump-thaw cycles. Ca 0.7 ml of the solution was transferred into Wilmad Young tube under argon and sealed. The tube was kept at 23 °C and ^{1}H NMR spectra (0-20 ppm range) were recorded in time intervals. Benzylidene proton resonances (δ=18.06 ppm for **3c**, and δ=18.11 ppm for **3e**) were integrated and sum of the integrals was normalized to the number of 100. After ca. 33 h the both mixtures reached an equilibrium state.



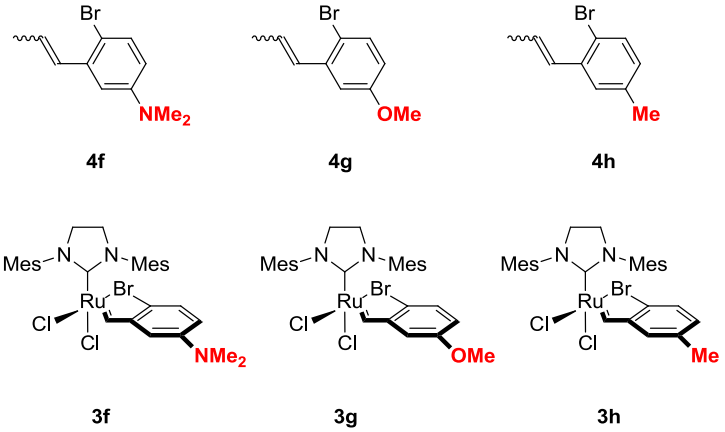
Activity studies of iodocoordinated catalysts 3a-e

Iodocoordinated complexes **3a**-**e** were tested in model RCM reaction of diethyl allylmethallylmalonate in CD_2Cl_2 with 1 mol% of catalyst at 40 °C and followed with ^1H NMR. The data is presented on Figure below.

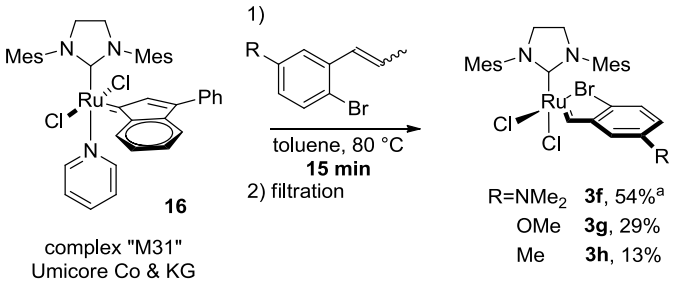


Measurements of activity profiles of complexes **3a**-**e** in model RCM reactions were performed according to general procedure described in: K. Grudzień, M. Malinska and M. Barbasiewicz, *Organometallics*, 2012, **31**, 3636-3646.

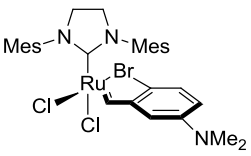
Synthesis of bromocomplexes 3f-h



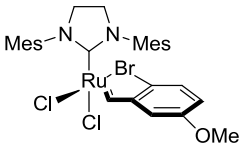
Synthesis of complexes **3f-h** was accomplished according to procedure described in: M. Barbasiewicz, M. Michalak and K. Grela, *Chem. Eur. J.*, 2012, **18**, chem.201202817. [a] - data taken from the literature.



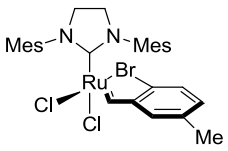
Characterization data



3f. NMR data of the complex was consistent with those described in: M. Barbasiewicz, M. Michalak and K. Grela, *Chem. Eur. J.*, 2012, **18**, chem.201202817.



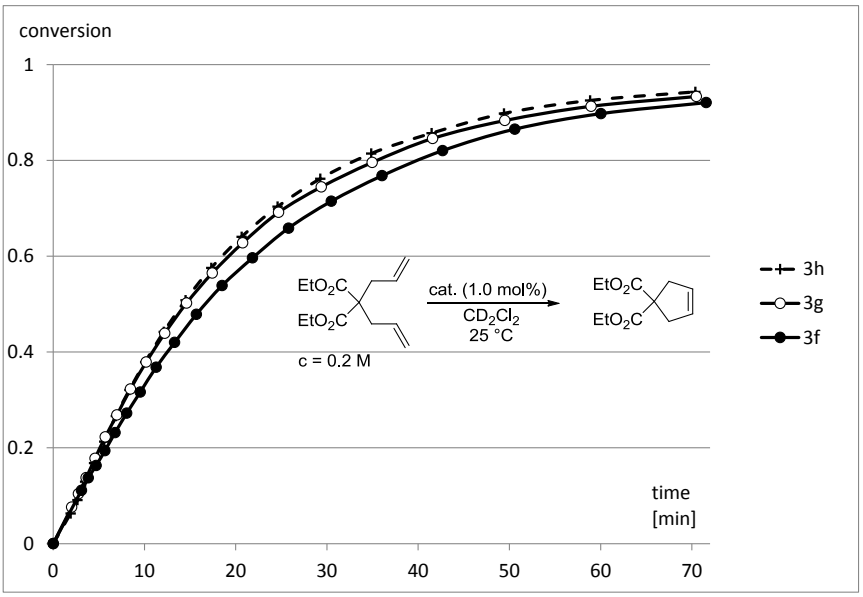
3g, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 17.76 (d, J=1.0 Hz, Ru=CH, 1H), 7.40 (dd, J=1.0, 6.7 Hz, 1H), 7.16 (s, 1H), 7.12 (s, 1H), 7.06 (dd, J=3.0, 8.6 Hz, 1H), 6.96 (s, 1H), 6.60 (d, J=3.0 Hz, 1H), 6.15 (s, 1H), 4.25-4.15 (m, 1H), 4.11-4.04 (m, 1H), 4.01-3.94 (m, 1H), 3.90-3.83 (m, 1H), 3.81 (s, OCH_3, 3H), 2.61 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 278.2, 214.3, 160.9, 152.7, 140.8, 140.3, 138.9, 137.9, 136.8, 136.0, 135.4, 131.6, 131.0, 130.1, 129.7, 129.2, 129.0, 116.2, 116.0, 111.5, 56.2, 51.9, 51.6, 21.3, 20.9, 20.2, 19.1, 18.5, 17.3. HRMS (ESI, *m/z*), calcd for $C_{29}H_{33}ClBrN_2ORu$: 641.0508; found: 641.0535 (M-Cl$^{+\bullet}$). IR (KBr, cm^{-1}): 2908, 1607, 1567, 1486, 1457, 1439, 1270, 1245, 1143, 1042, 1010, 870, 852, 812, 577, 420. No satisfactory analysis was obtained.



3h, light green powder. ^{1}H NMR (500 MHz, CD_2Cl_2): 17.75 (d, *J*=1.0 Hz, Ru=CH, 1H), 7.40 (d, *J*=8.0 Hz, 1H), 7.32 (dd, *J*=0.5, 8.0Hz, 1H), 7.16 (s, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 6.86 (d, *J*=0.5 Hz, 1H), 6.11 (s, 1H), 4.24-4.15 (m, 1H), 4.11-4.02 (m, 1H), 4.01-3.92 (m, 1H), 3.90-3.82 (m, 1H), 2.62 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.22 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2): 279.0, 214.5, 151.8, 140.8, 140.3, 139.8, 138.9, 138.0, 136.9, 136.1, 135.5, 131.7, 131.2, 131.0, 130.1, 129.7, 129.2, 128.5, 127.3, 123.0, 51.9, 51.6, 21.4, 21.2, 20.9, 20.2, 19.2, 18.6, 17.2. HRMS (ESI, *m/z*), calcd for $C_{29}H_{33}ClBrN_2Ru$: 625.0559; found: 625.0572 (M-Cl$^{+\bullet}$). IR (KBr, *cm^{-1}*): 2908, 1607, 1484, 1437, 1293, 1267, 1021, 852, 828, 576, 419. Elem anal, calcd for $C_{29}H_{33}Cl_2BrN_2Ru$: C, 52.66; H, 5.03; N, 4.24; found: C, 52.43; H, 4.86; N, 3.99.

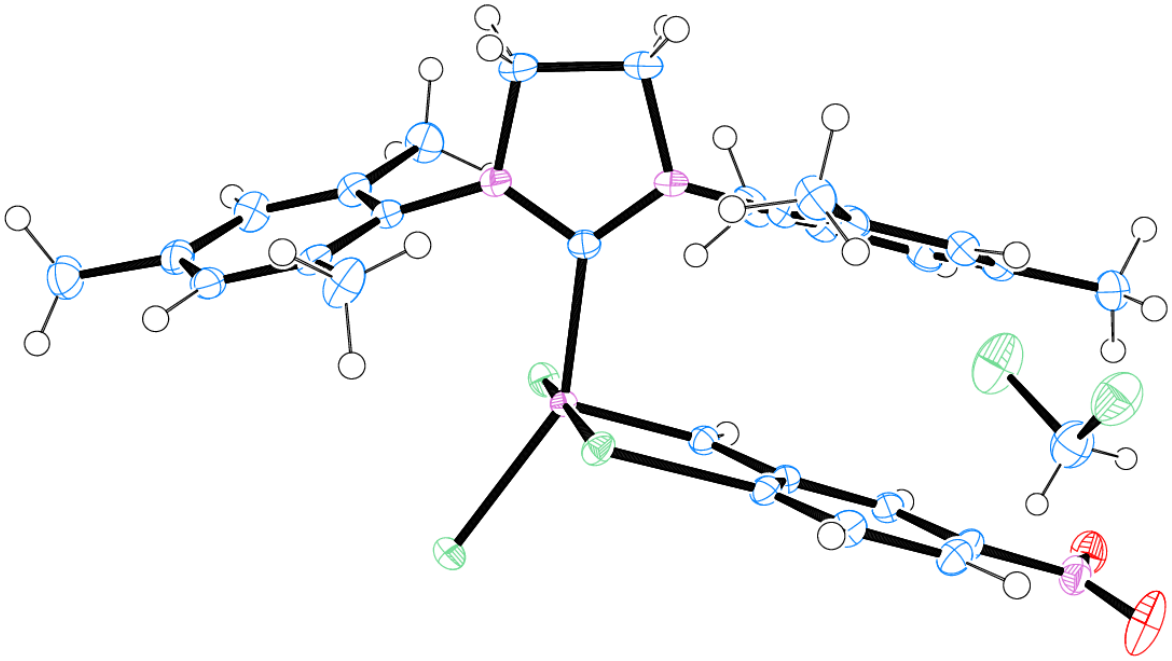
Activity studies of bromo-coordinated catalysts 3g-h

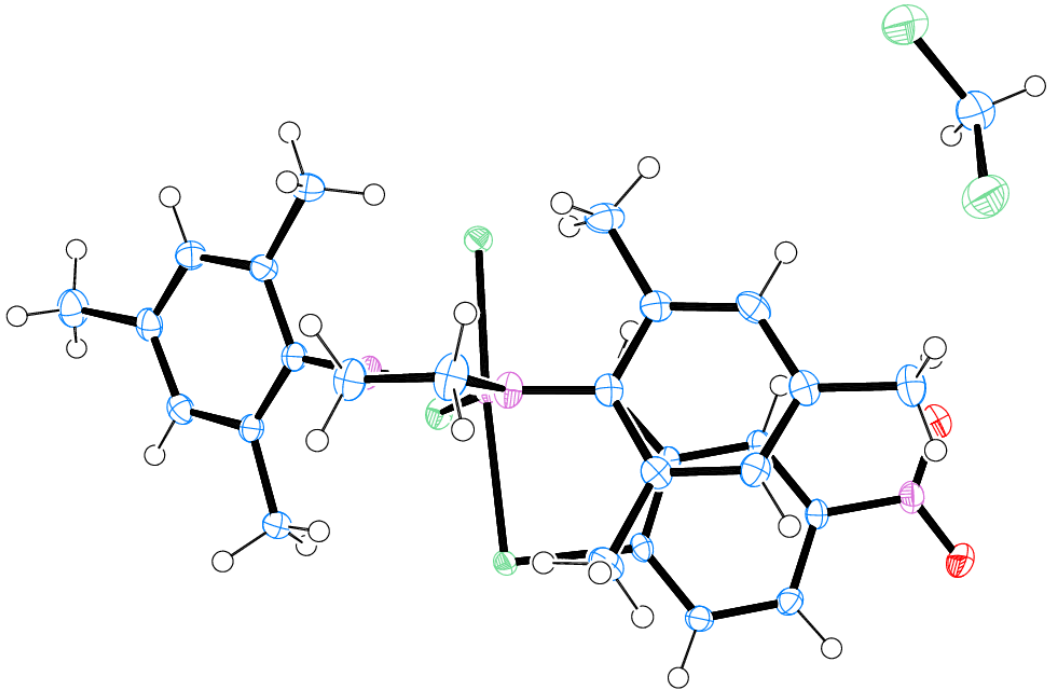
Bromocoordinated complexes **3g**,**h** were tested in model RCM reaction of diethyl diallylmalonate in CD_2Cl_2 with 1 mol% of catalyst at 25 °C and followed with ^{1}H NMR. The results were compared with activity data of complex **3f** taken from: M. Barbasiewicz, M. Michalak and K. Grela, *Chem. Eur. J.*, 2012, **18**, chem.201202817. The data is presented on Figure below.



Measurements of activity profiles of complexes **3g**-**h** in model RCM reactions were performed according to general procedure described in: K. Grudzień, M. Malinska and M. Barbasiewicz, *Organometallics*, 2012, **31**, 3636-3646.

Crystallographic Information Data of Complex 3e (CCDC 902057)





Experimental

The data were collected using the BRUKER KAPPA APEXII ULTRA controlled by APEXII software [1], equipped with MoKα rotating anode X-ray source (λ = 0.71073 Å, 50.0 kV, 22.0 mA) monochromatized by multi-layer optics and APEX-II CCD detector. The experiments were carried out at 100K using the Oxford Cryostream cooling device. The crystal was mounted on Mounted CryoLoop with a droplet of Pantone-N oil and immediately cooled. Indexing, integration and initial scaling were performed with *SAINT* [2] and *SADABS* [3] software (Bruker, 2007). The data collection and processing statistics are reported in tables for according structures.

The crystal was positioned at 50 mm from the CCD camera. 872 frames were measured at 0.5° intervals with a counting time of 10-15 sec.

The structures were solved by direct methods approach using the SHELXS-97 [4] program and refined with the SHELXL-97 [5]. Multi-scan absorption correction have been applied in the scaling procedure.

The refinement was based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on F^2, whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was applied only for R factors calculation was not relevant to the choice of reflections for the refinement. The R factors based on F^2 are for all structures about twice as large as those based on F. The hydrogen atoms were located in idealized geometrical positions, except hydrogen in solvent molecule. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C [6].

Identification code	complex **3e** · CH_2Cl_2
Empirical formula	$C_{29}H_{32}Cl_4IN_3O_2Ru$
Formula weight	824.35
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 17.0543(17) A alpha = 90 deg.
	b = 15.1828(16) A beta = 90 deg.
	c = 23.843(3) A gamma = 90 deg.
Volume	6173.7(11) A^3
Z, Calculated density	8, 1.774 Mg/m^3
Absorption coefficient	1.887 mm^{-1}
F(000)	3264
Crystal size	0.22 x 0.21 x 0.16 mm
Theta range for data collection	1.71 to 30.51 deg.
Limiting indices	-21<=h<=24, -19<=k<=21, -31<=l<=34
Reflections collected / unique	59144 / 9378 [R(int) = 0.0311]
Completeness to theta = 29.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7472 and 0.6784

[1] APEXII-2008v1.0 Bruker Nonius 2007

[2] SAINT V7.34A Bruker Nonius 2007

[3] SADABS-2004/1 Bruker Nonius area detector scaling and absorption correction, 2007

[4] Sheldrick, G. M. Acta Crystallogr. 1990, **A46**, 467-473.

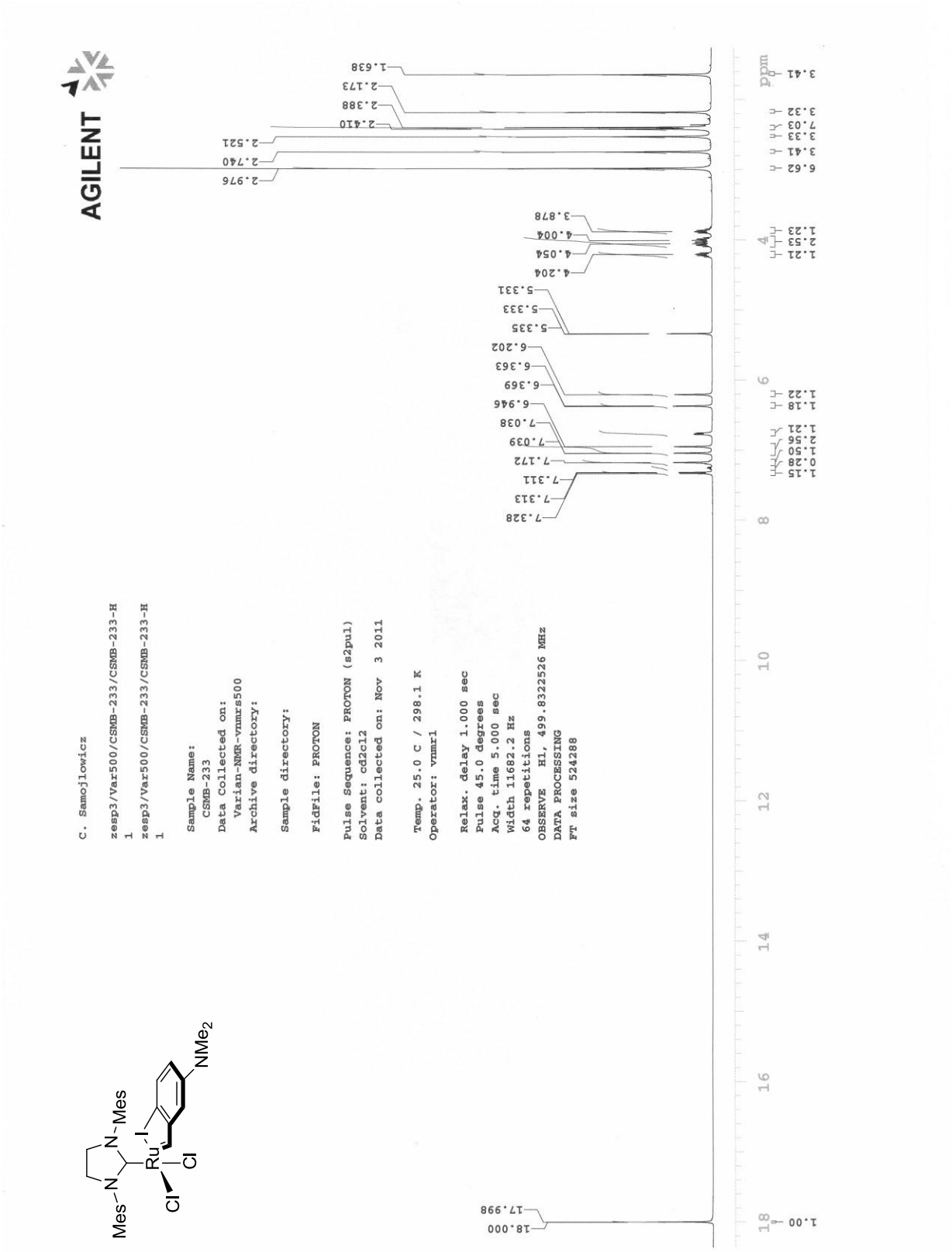
[5] Sheldrick, G. M. *Acta Crystallogr.* 2008, **A64**, 112.

[6] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.

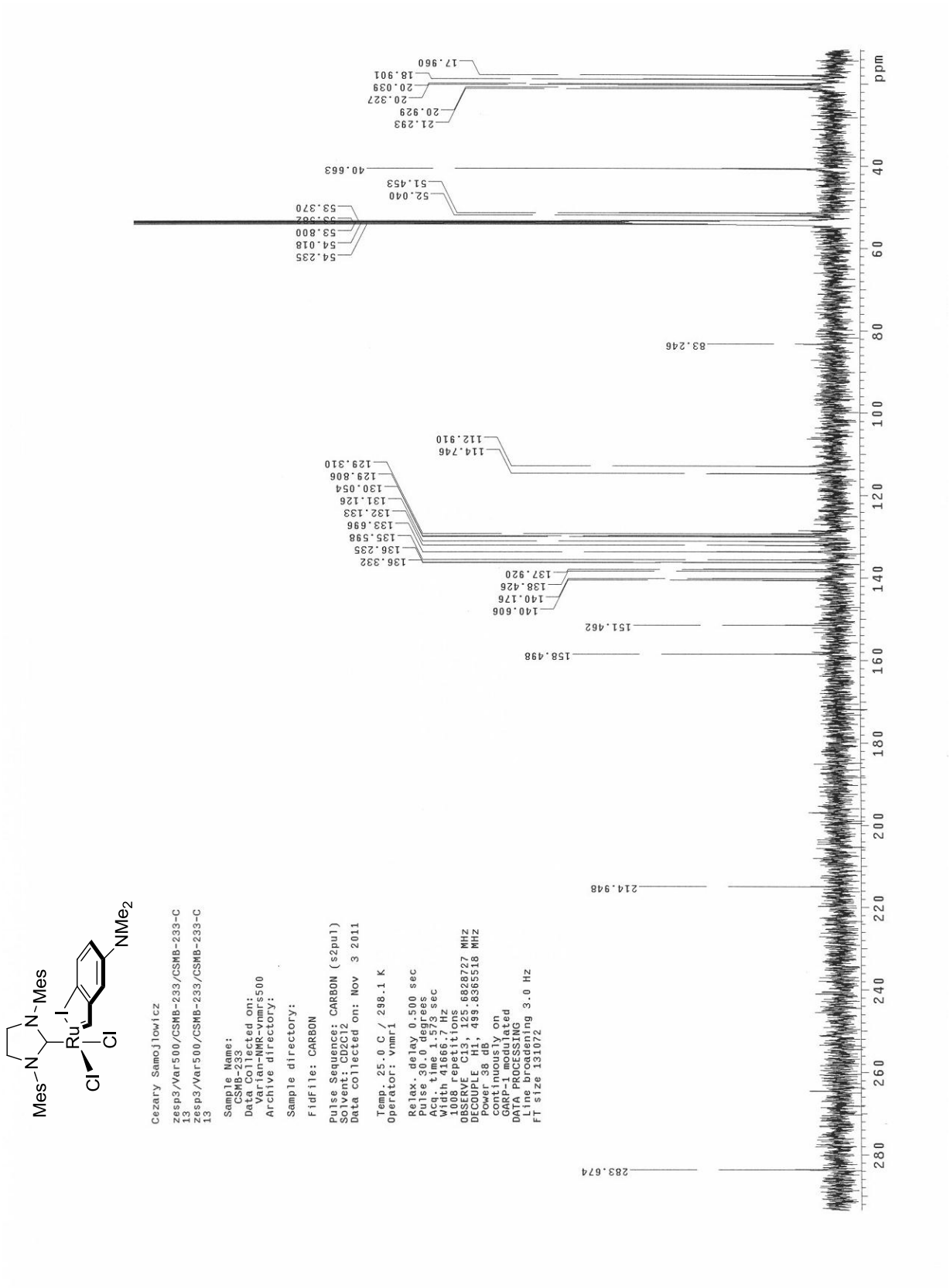
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9378 / 0 / 367
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0866
R indices (all data)	R1 = 0.0391, wR2 = 0.0928
Largest diff. peak and hole	2.396 and -1.881 $e.A^{-3}$

Spectra reproductions

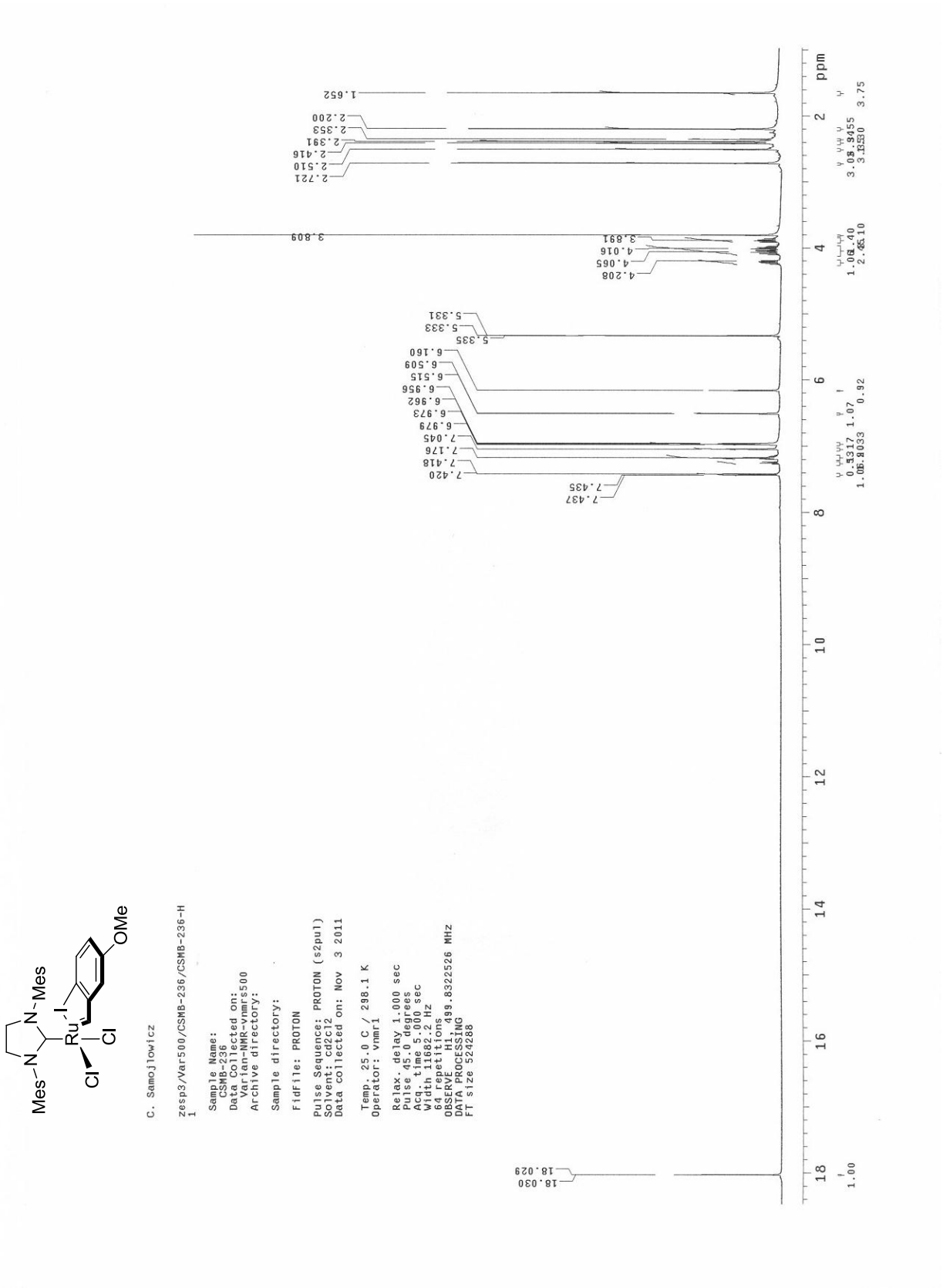
Reproduction of ^{1}H NMR spectrum of complex **3a**.



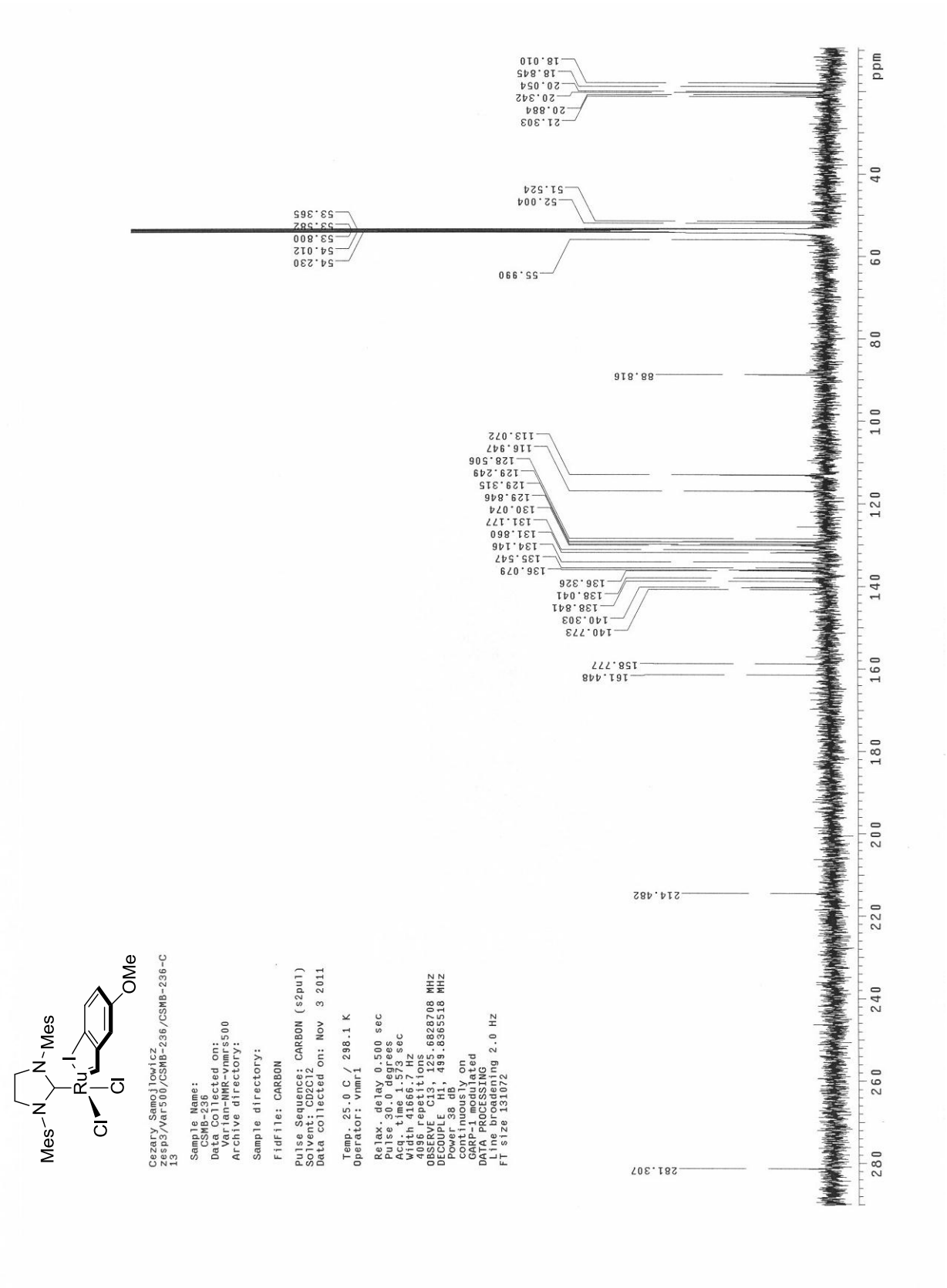
Reproduction of ^{13}C NMR spectrum of complex **3a**.



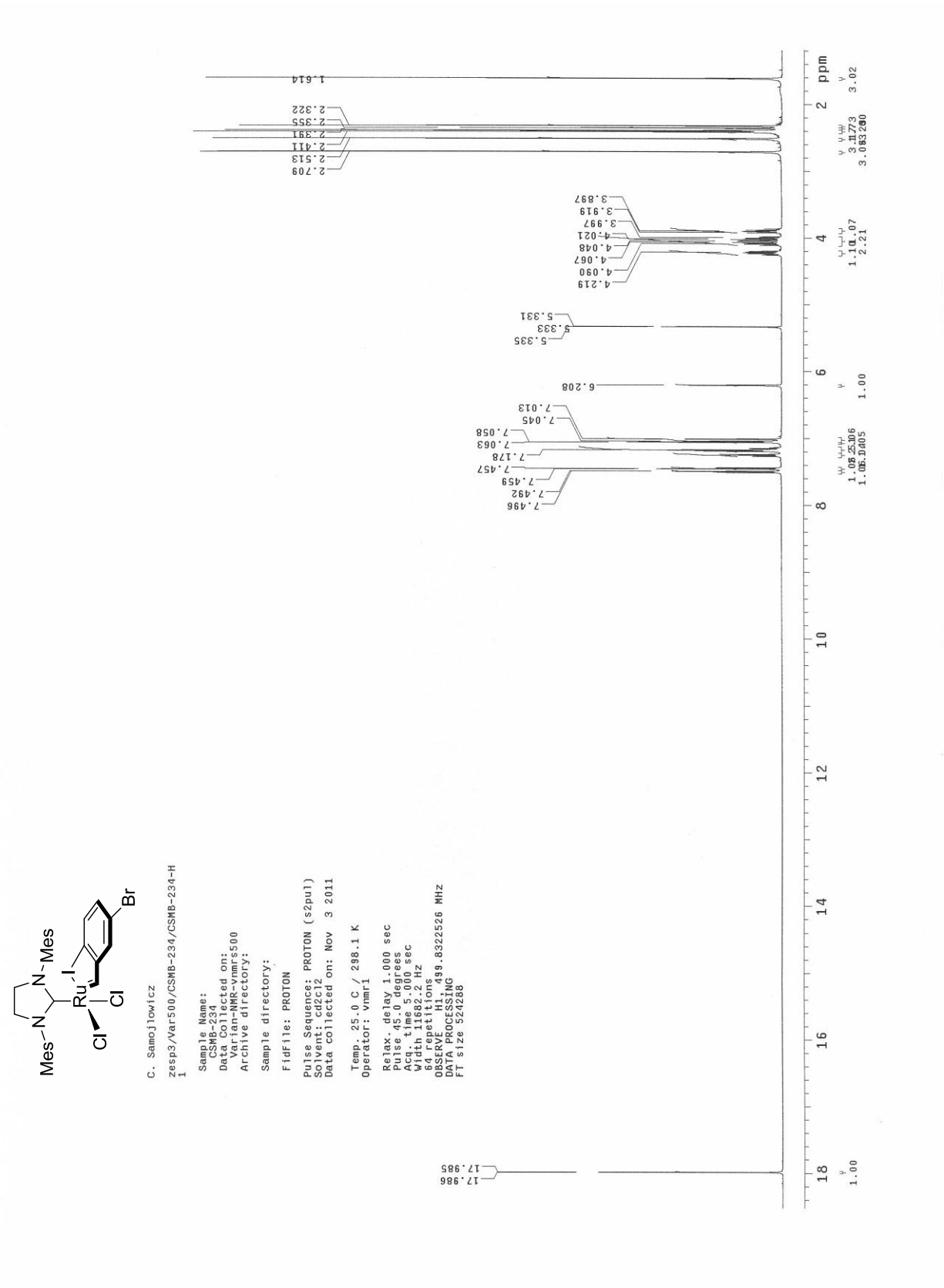
Reproduction of ^{1}H NMR spectrum of complex **3b**.



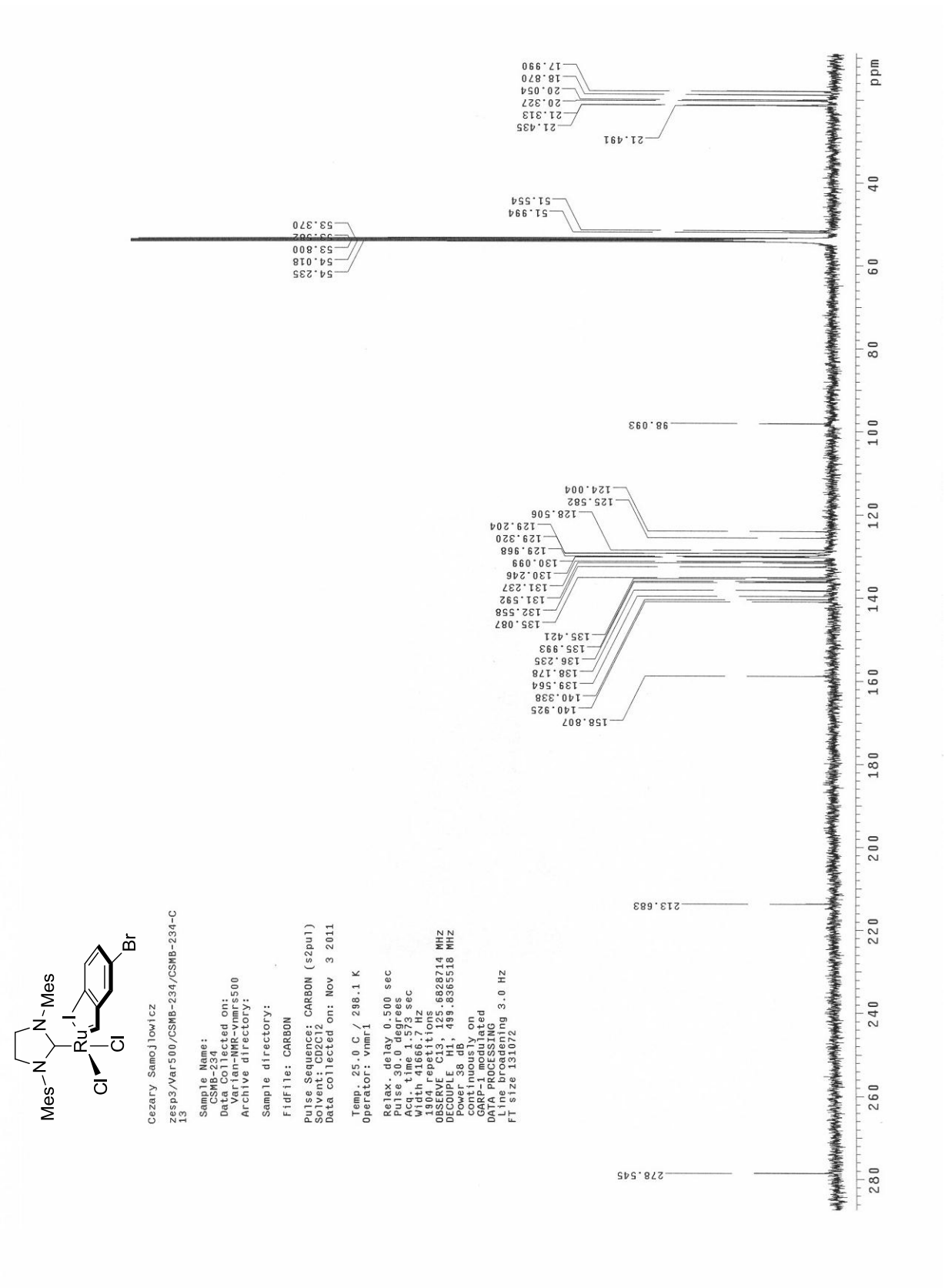
Reproduction of ^{13}C NMR spectrum of complex **3b**.



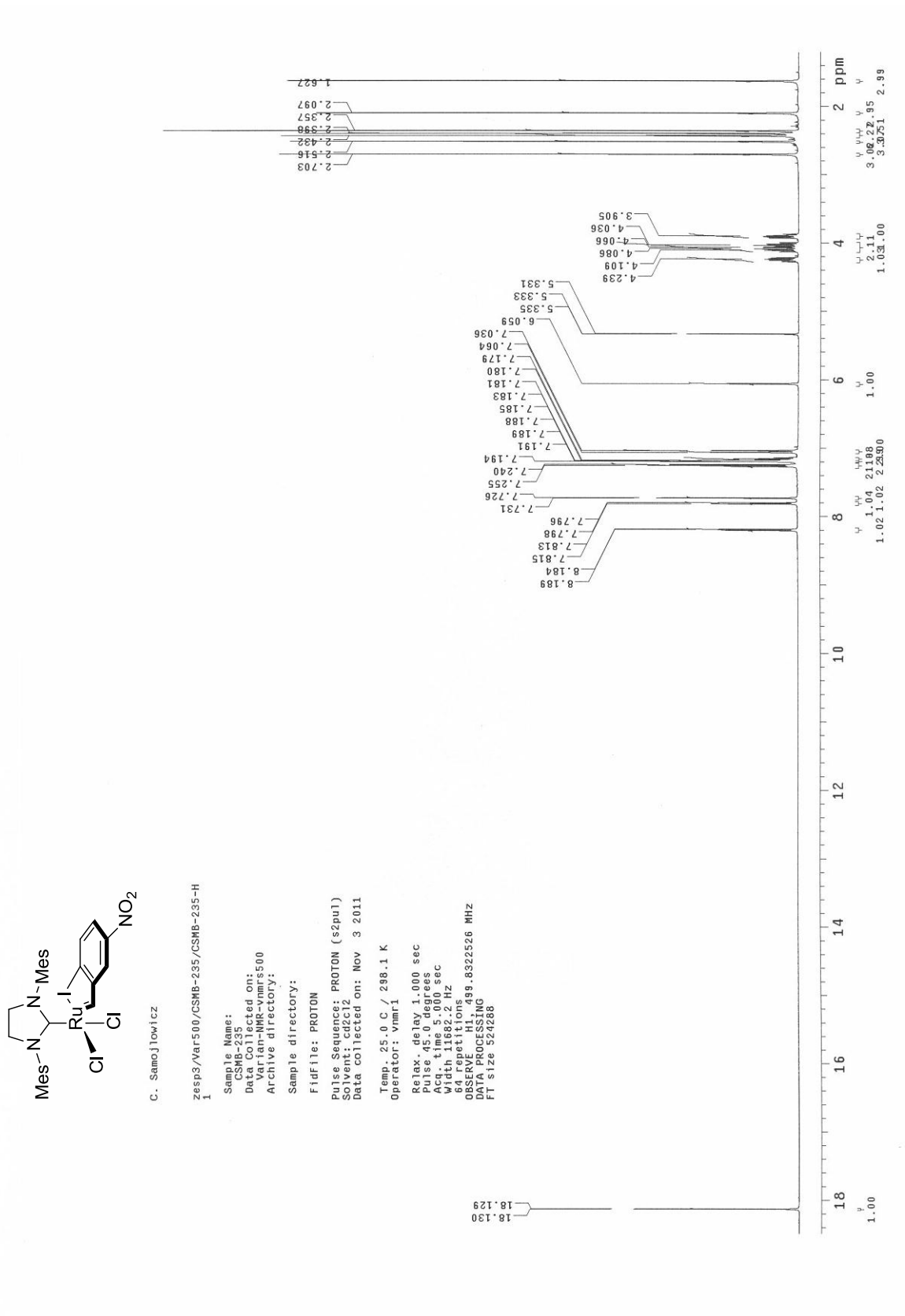
Reproduction of ^{1}H NMR spectrum of complex **3d**.



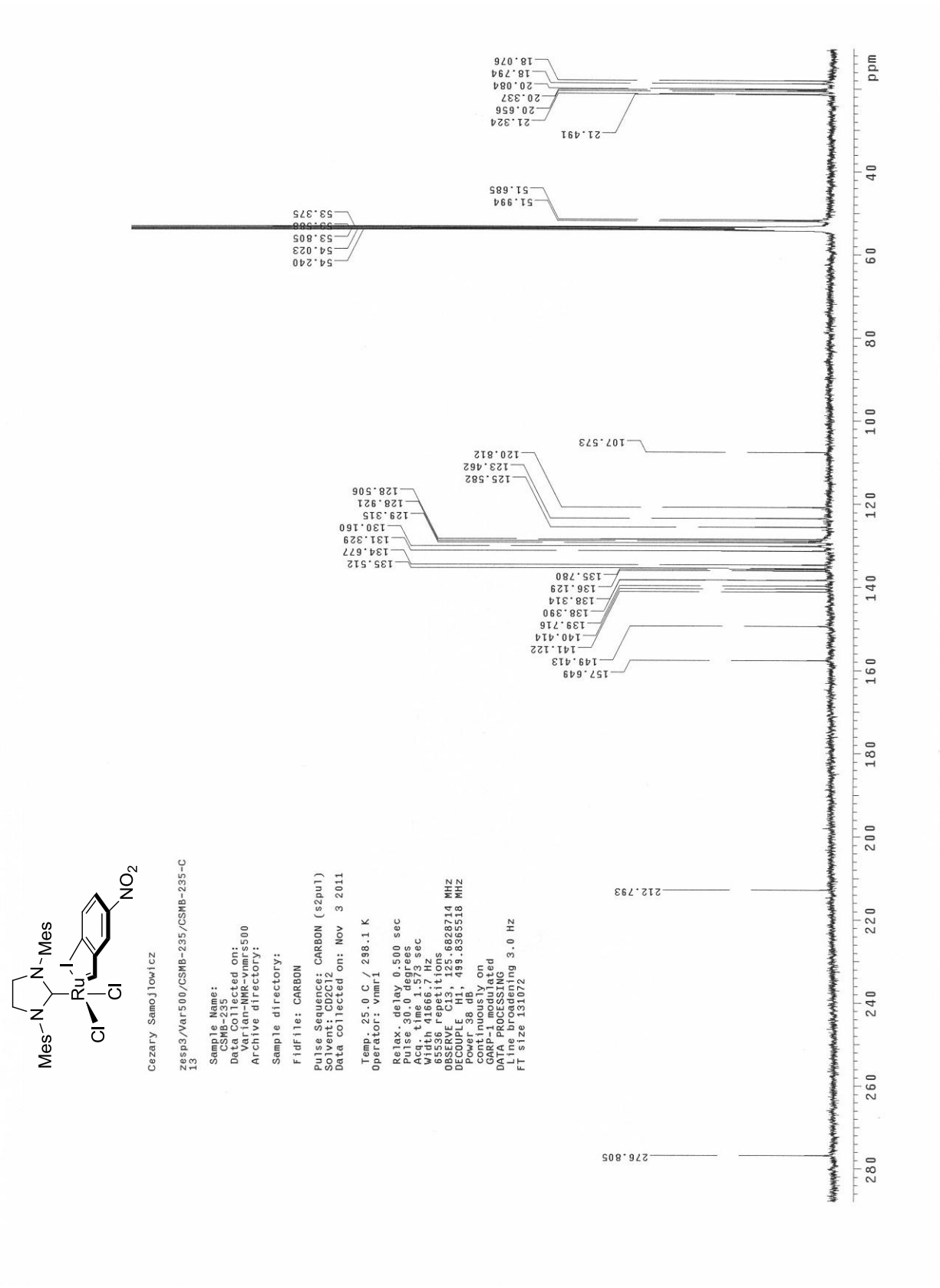
Reproduction of ^{13}C NMR spectrum of complex **3d**.



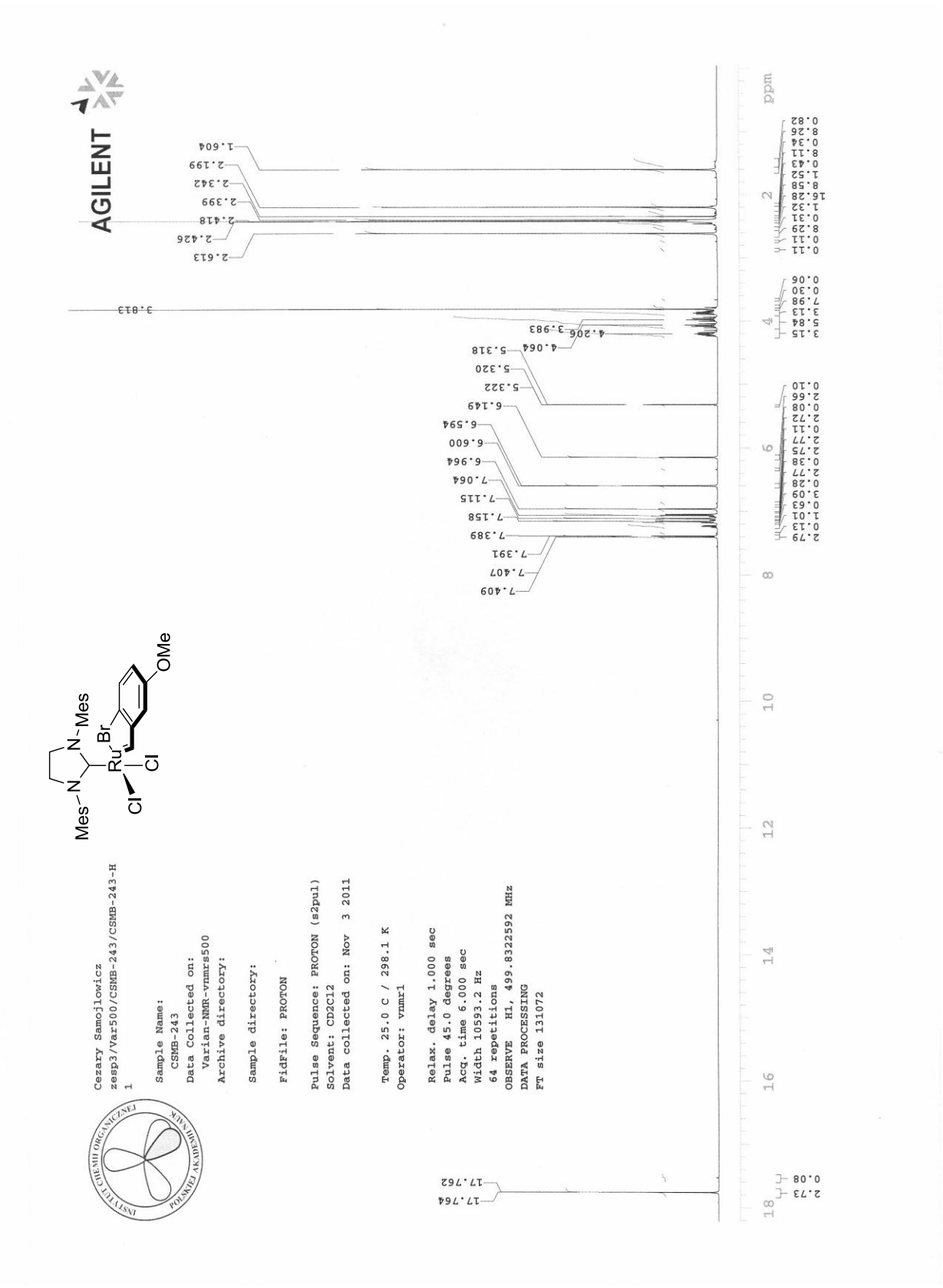
Reproduction of ^{1}H NMR spectrum of complex **3e**.



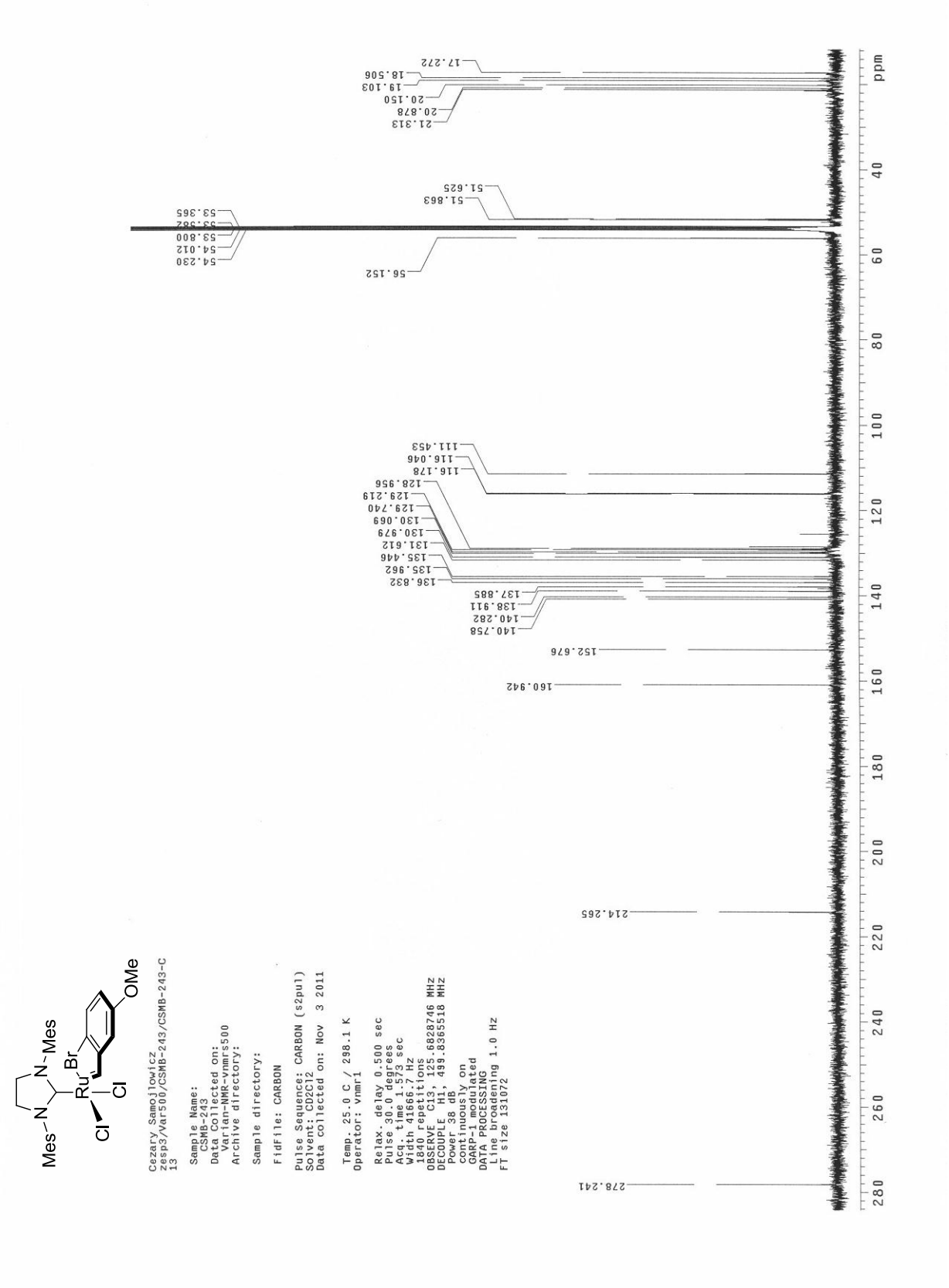
Reproduction of ^{13}C NMR spectrum of complex **3e**.



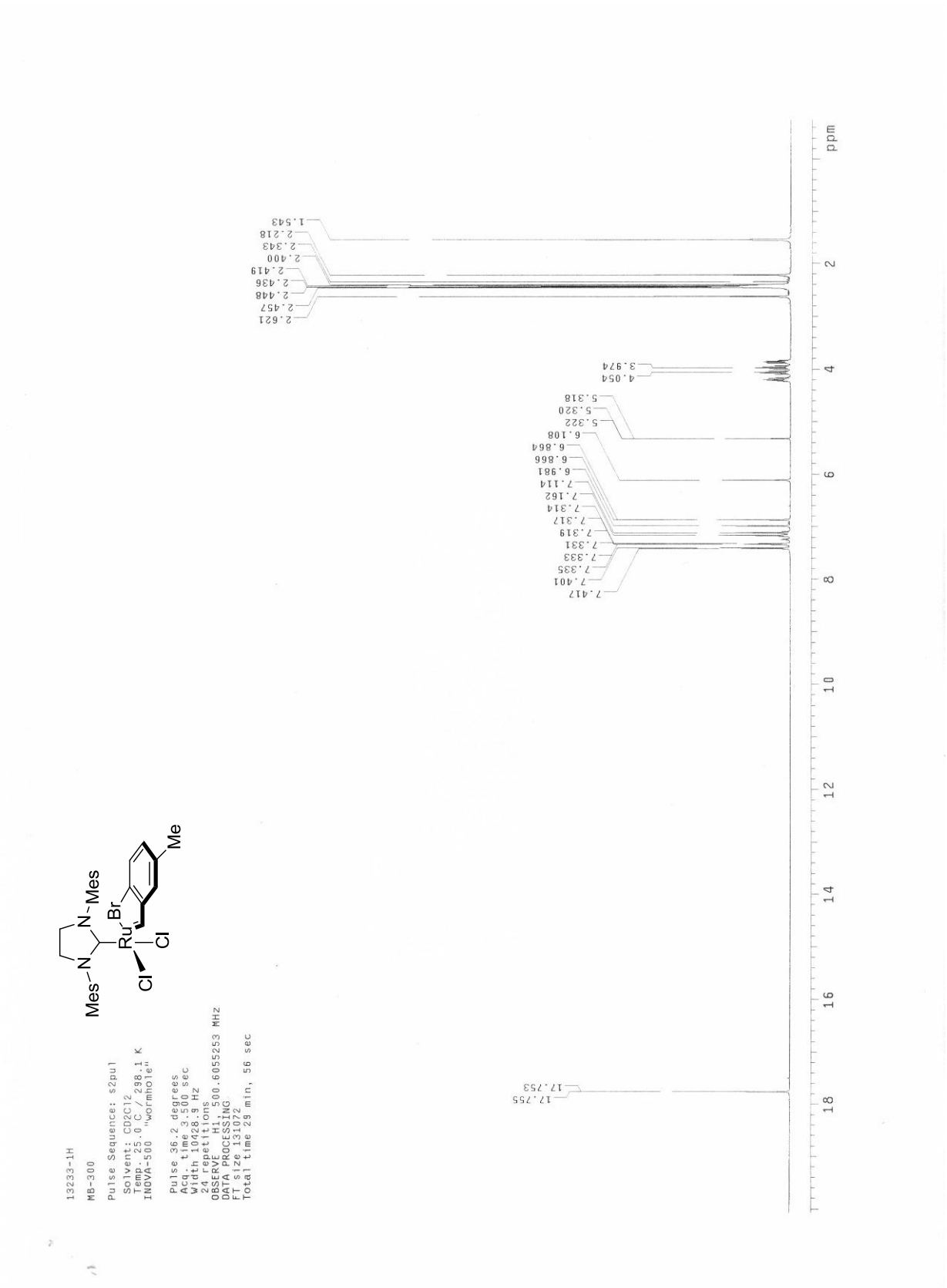
Reproduction of ^{1}H NMR spectrum of complex **3g**.



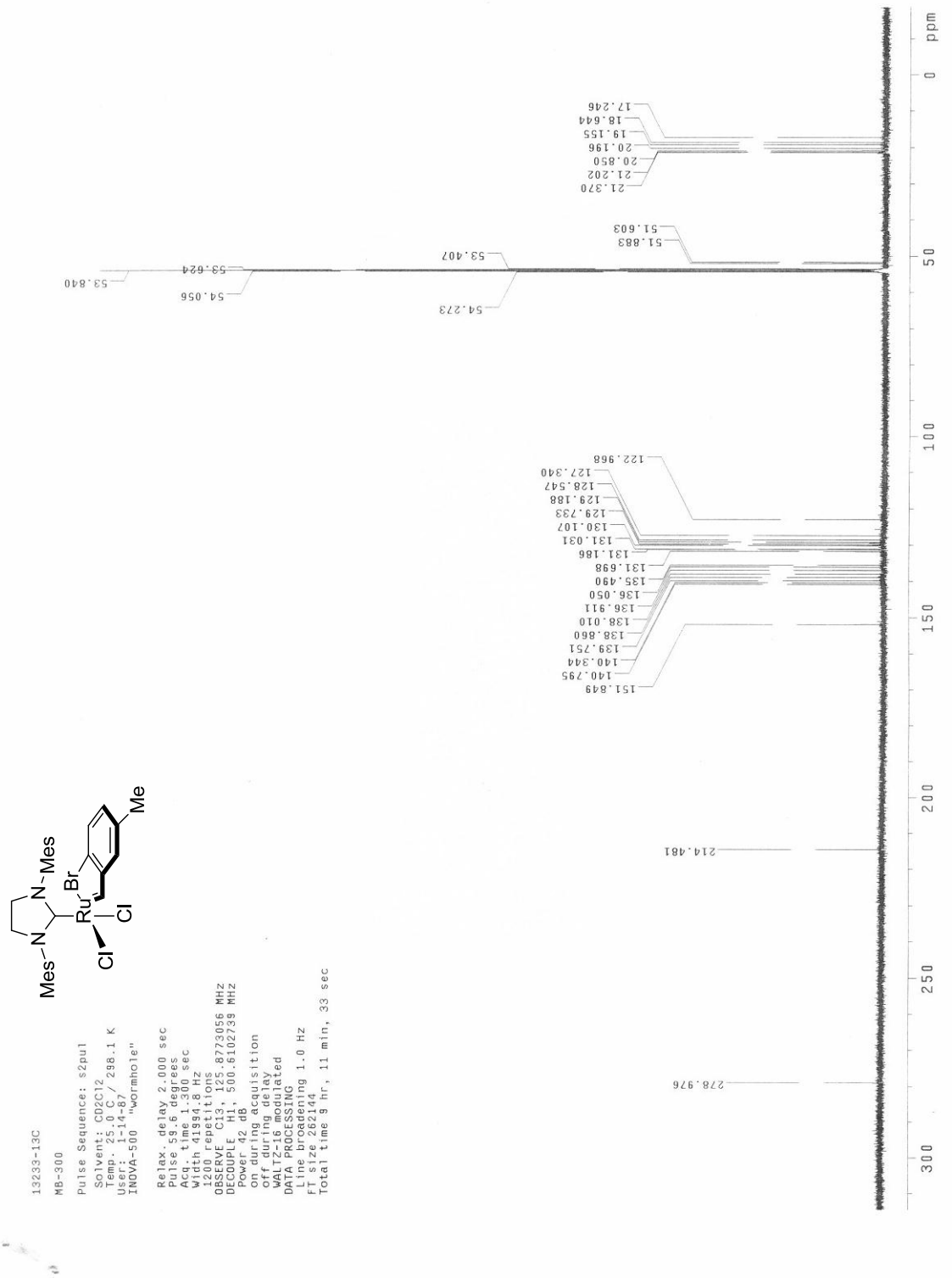
Reproduction of ^{13}C NMR spectrum of complex **3g**.



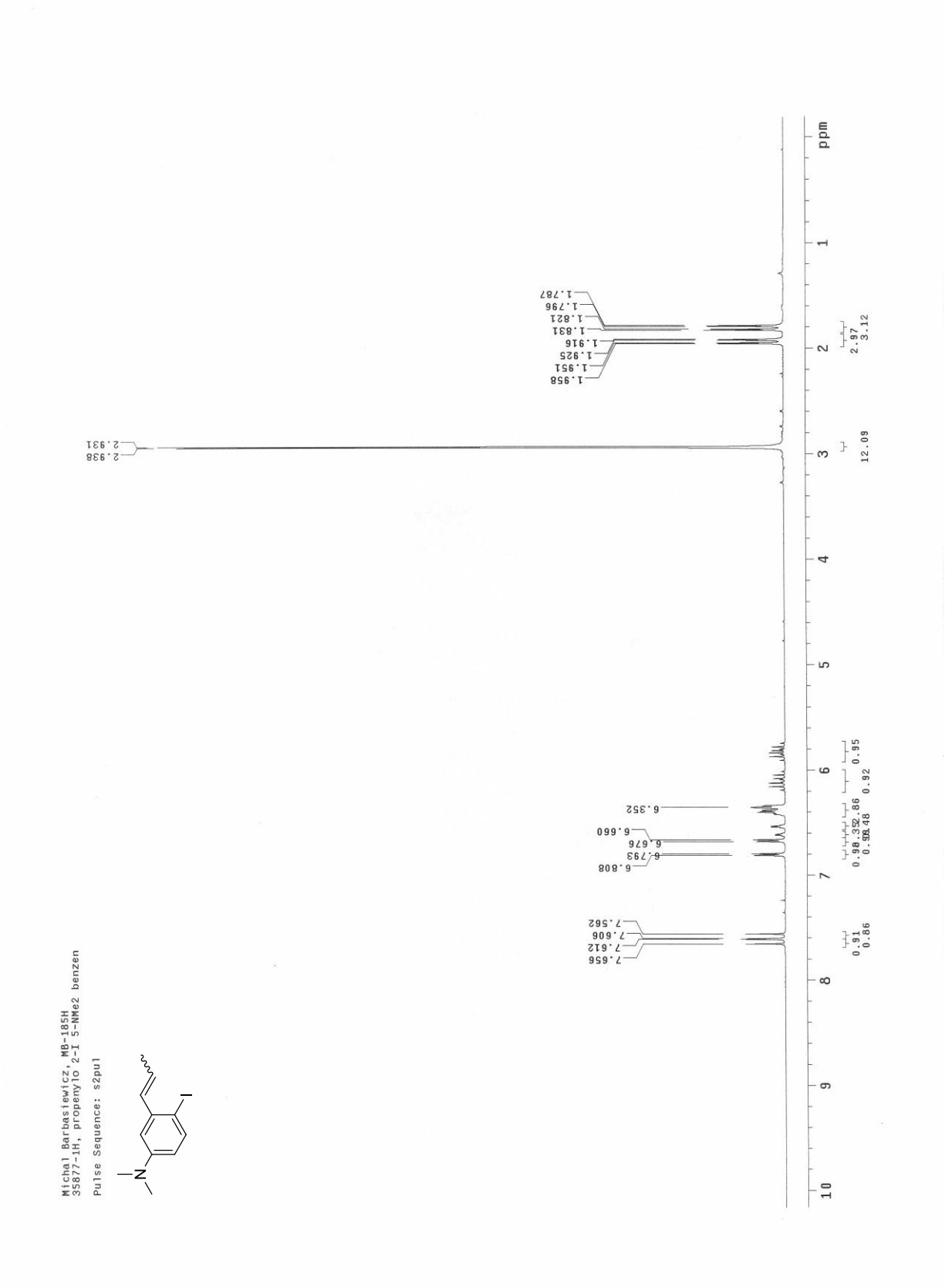
Reproduction of ^{1}H NMR spectrum of complex **3h**.



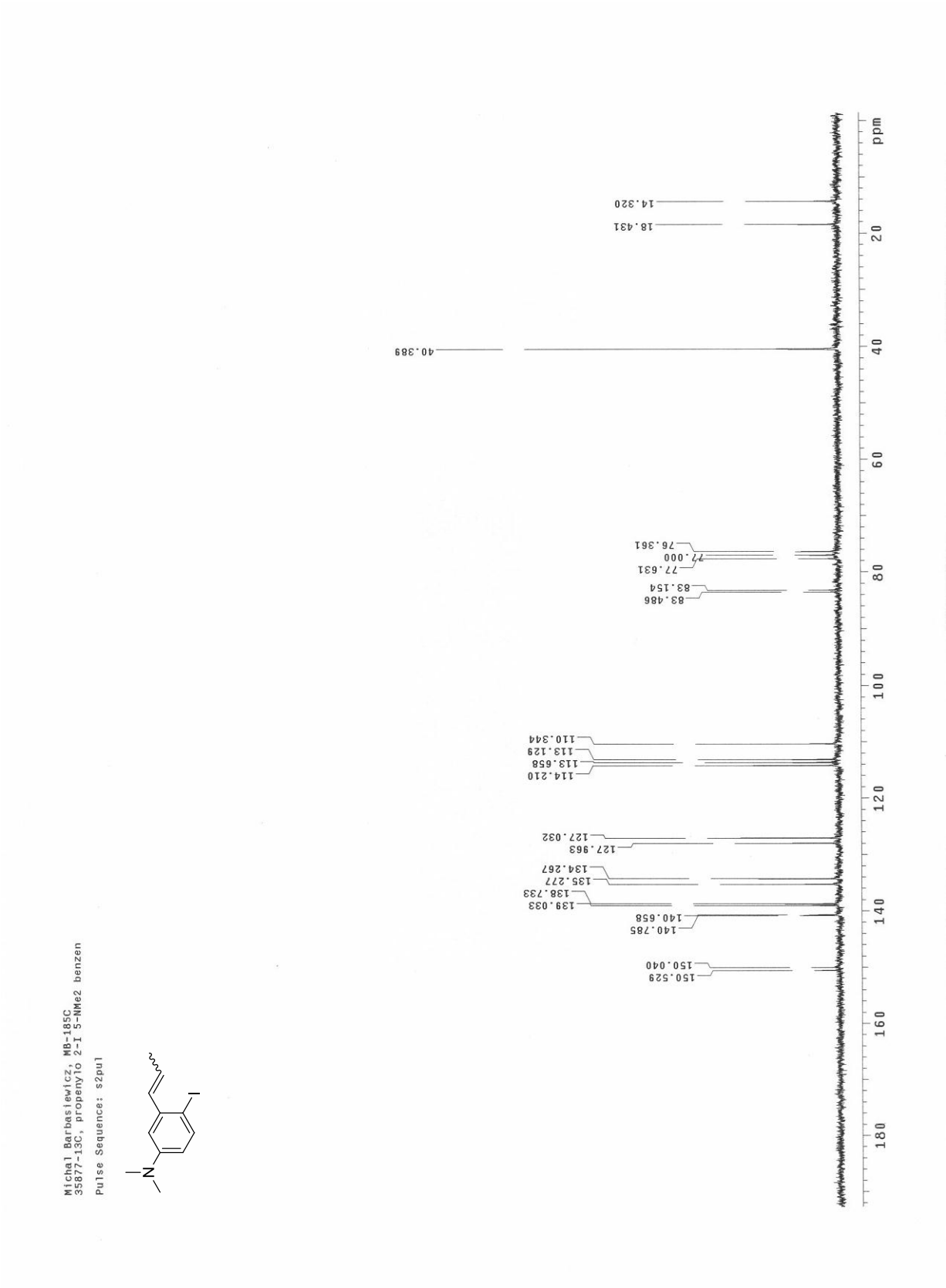
Reproduction of ^{13}C NMR spectrum of complex **3h**.



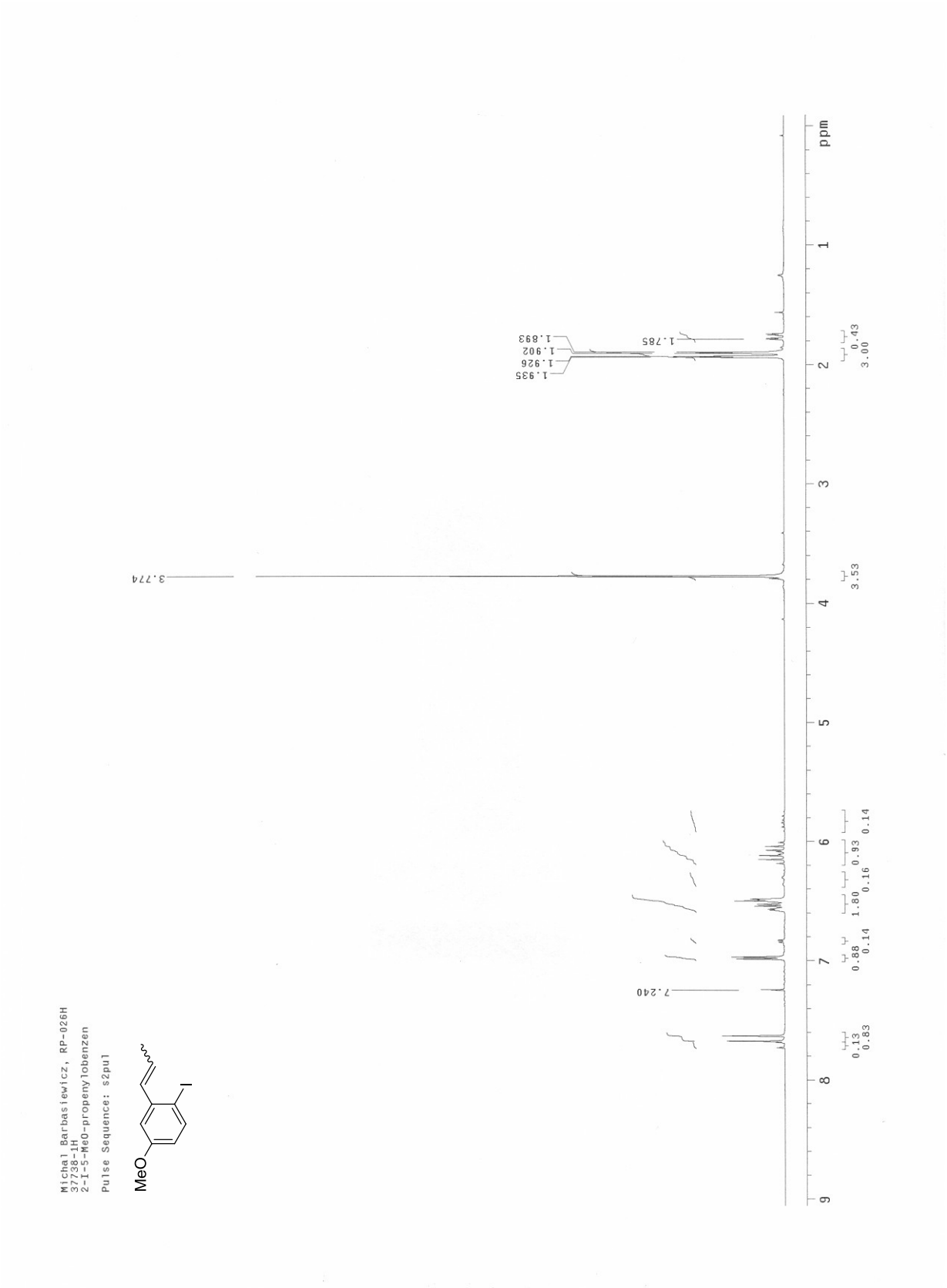
Reproduction of ^{1}H NMR spectrum of compound **4a**.



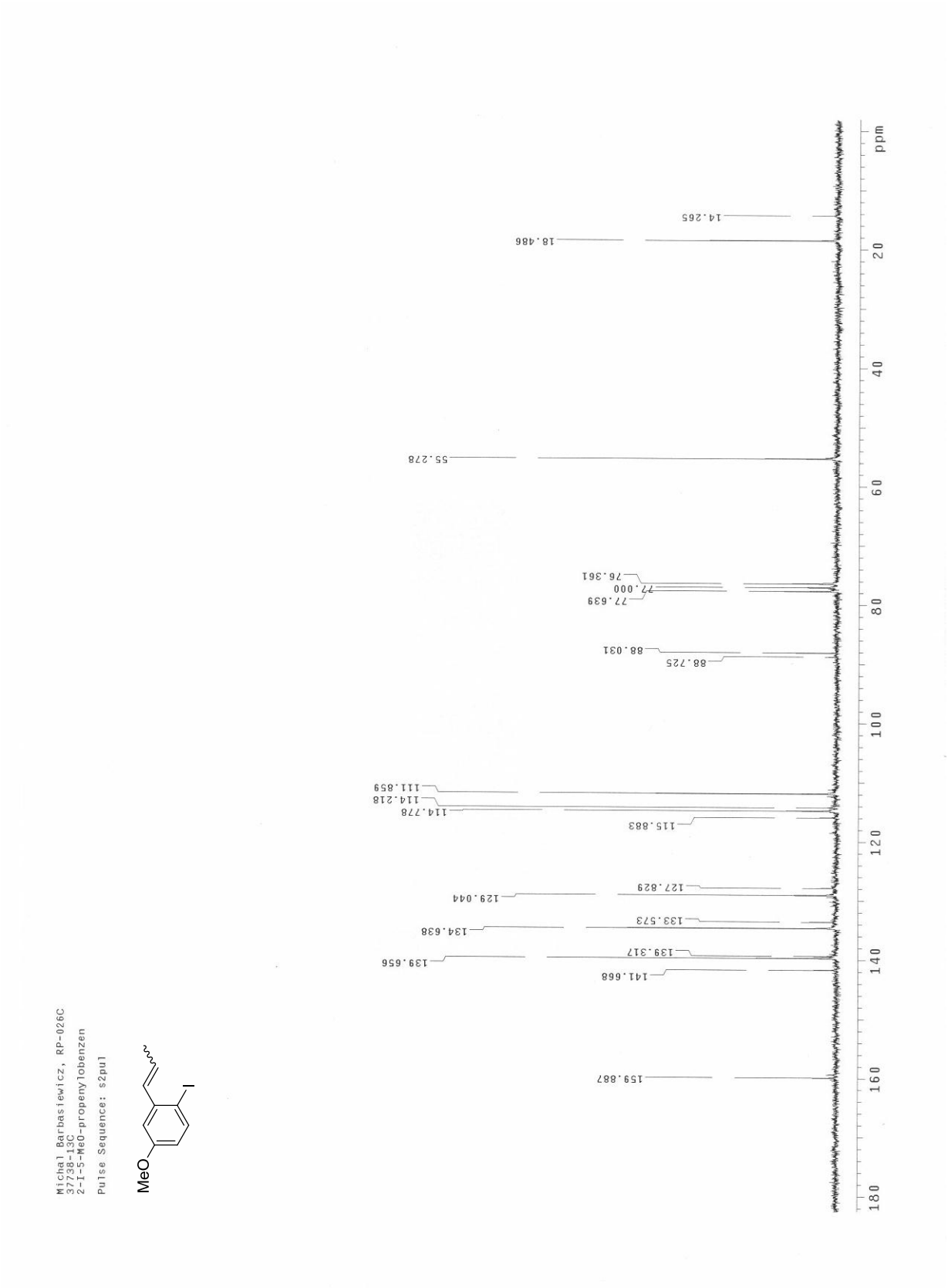
Reproduction of ^{13}C NMR spectrum of compound **4a**.



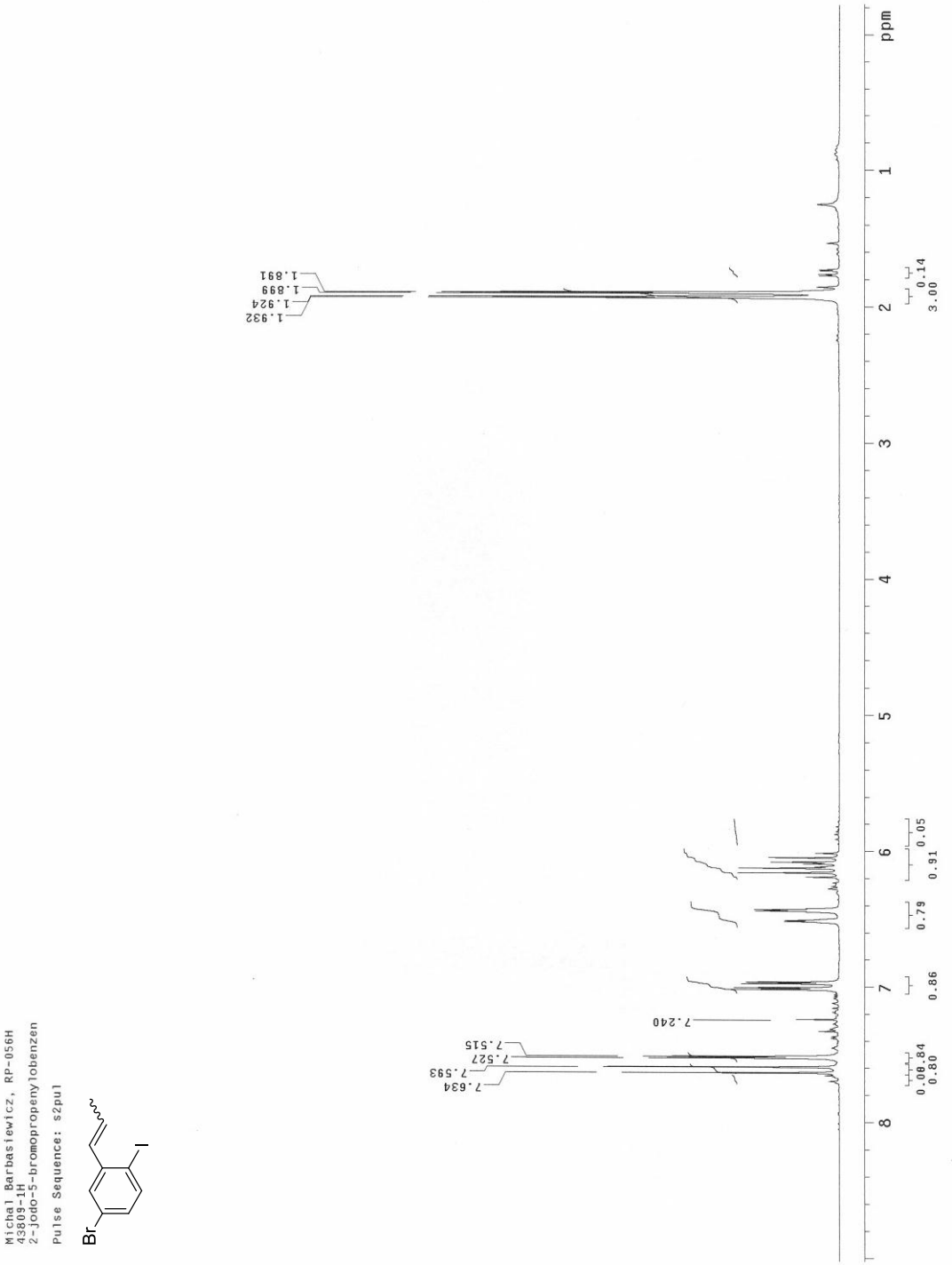
Reproduction of ^{1}H NMR spectrum of compound **4b**.



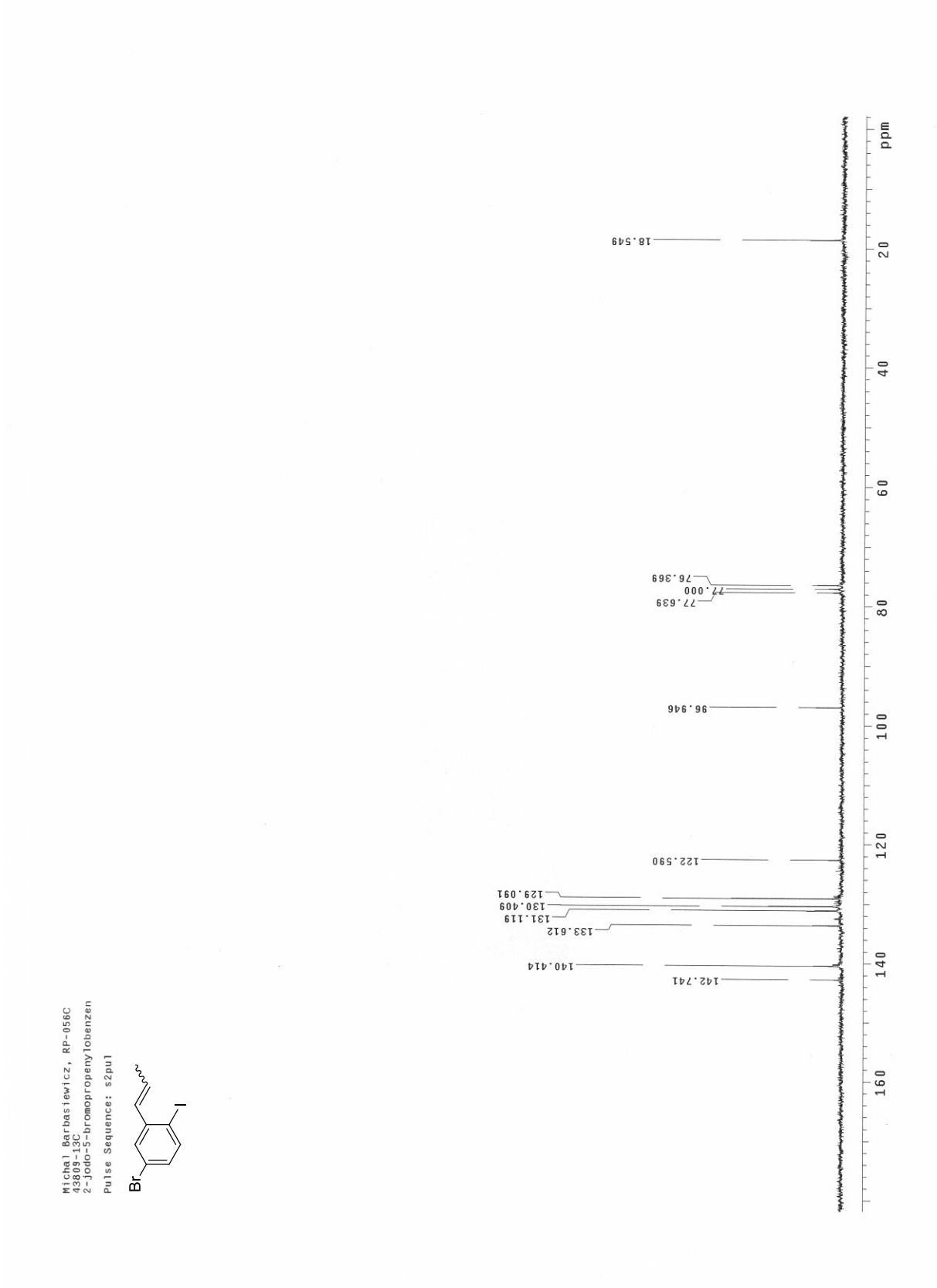
Reproduction of ^{13}C NMR spectrum of compound **4b**.



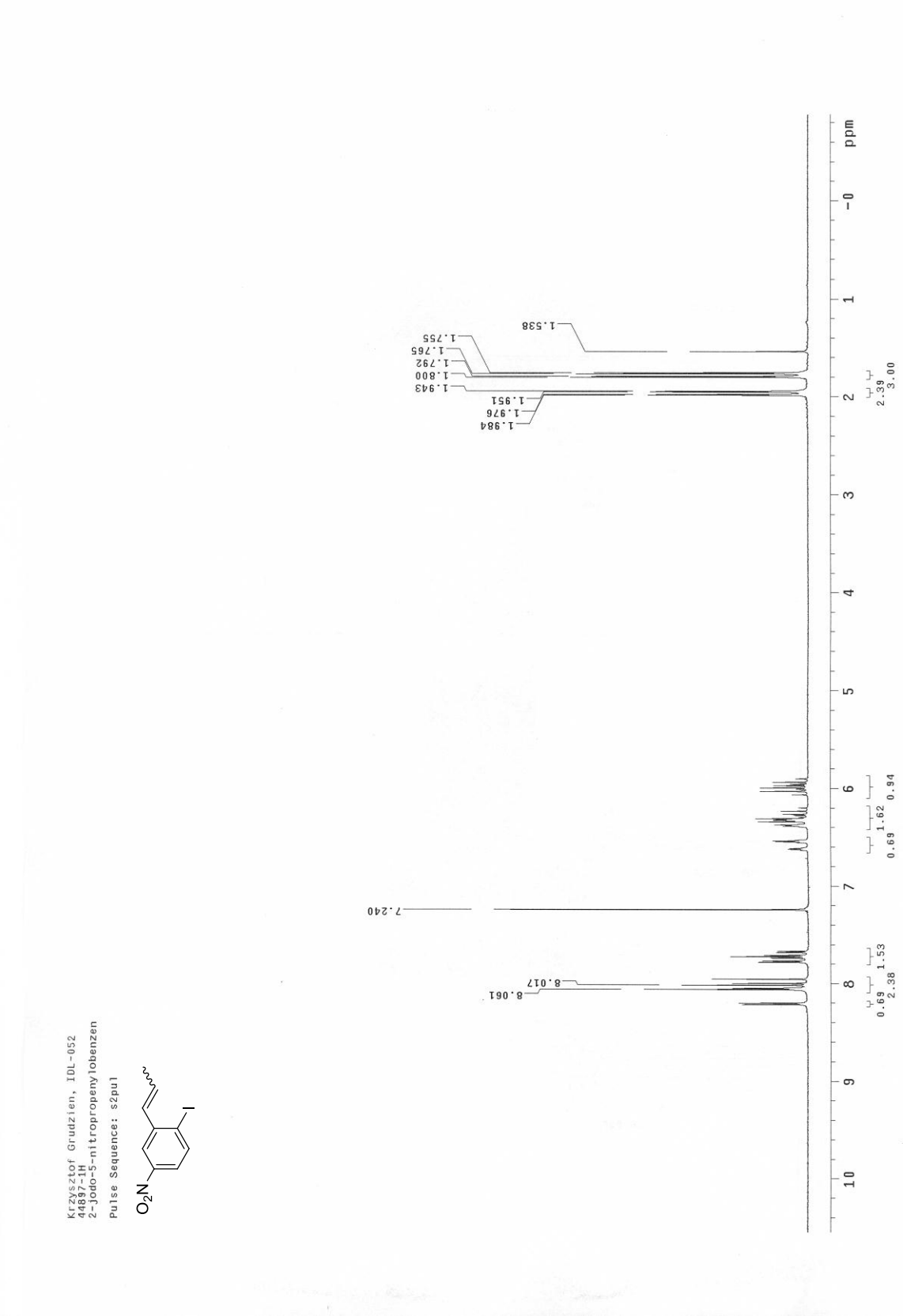
Reproduction of ^{1}H NMR spectrum of compound **4d**.



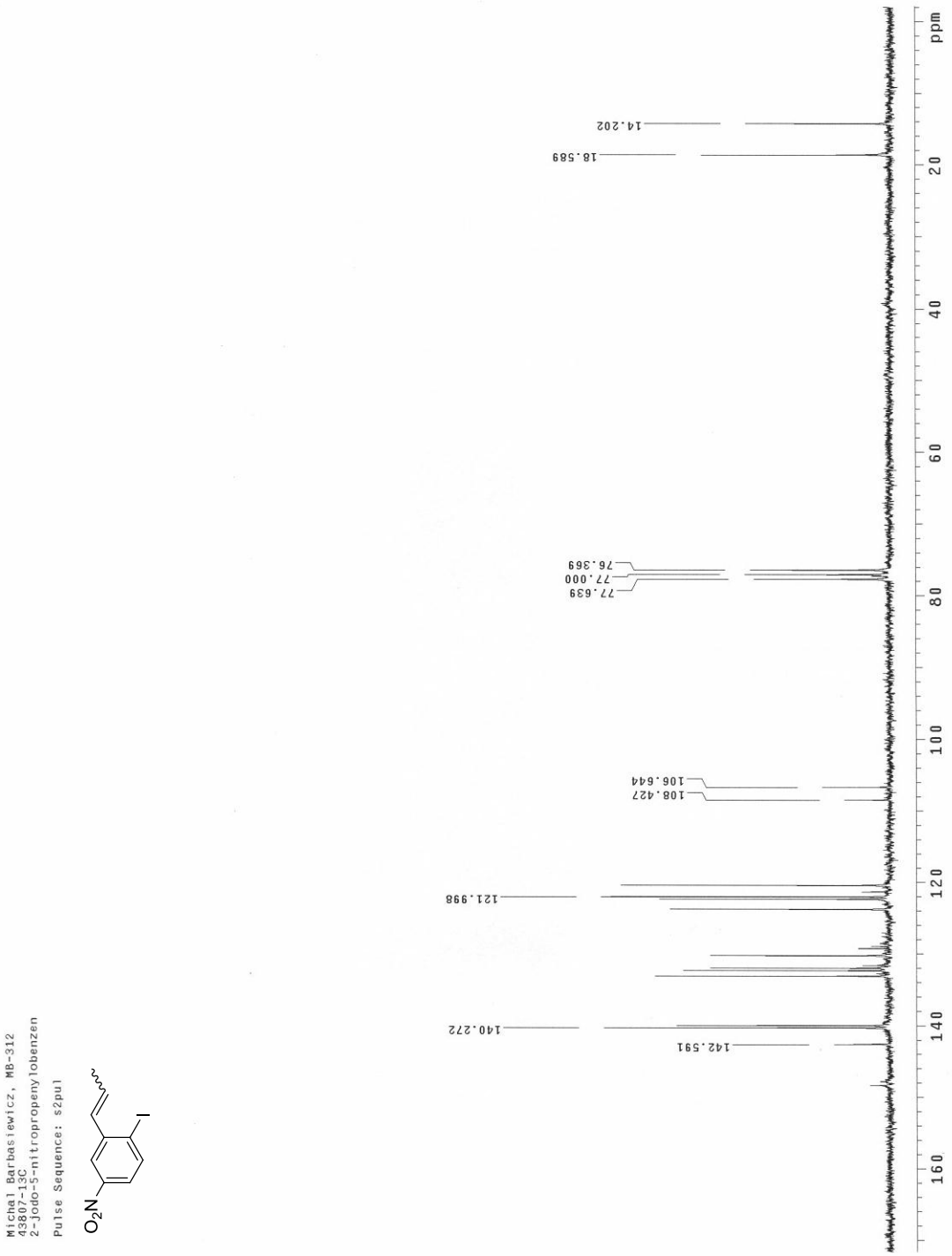
Reproduction of ^{13}C NMR spectrum of compound **4d**.



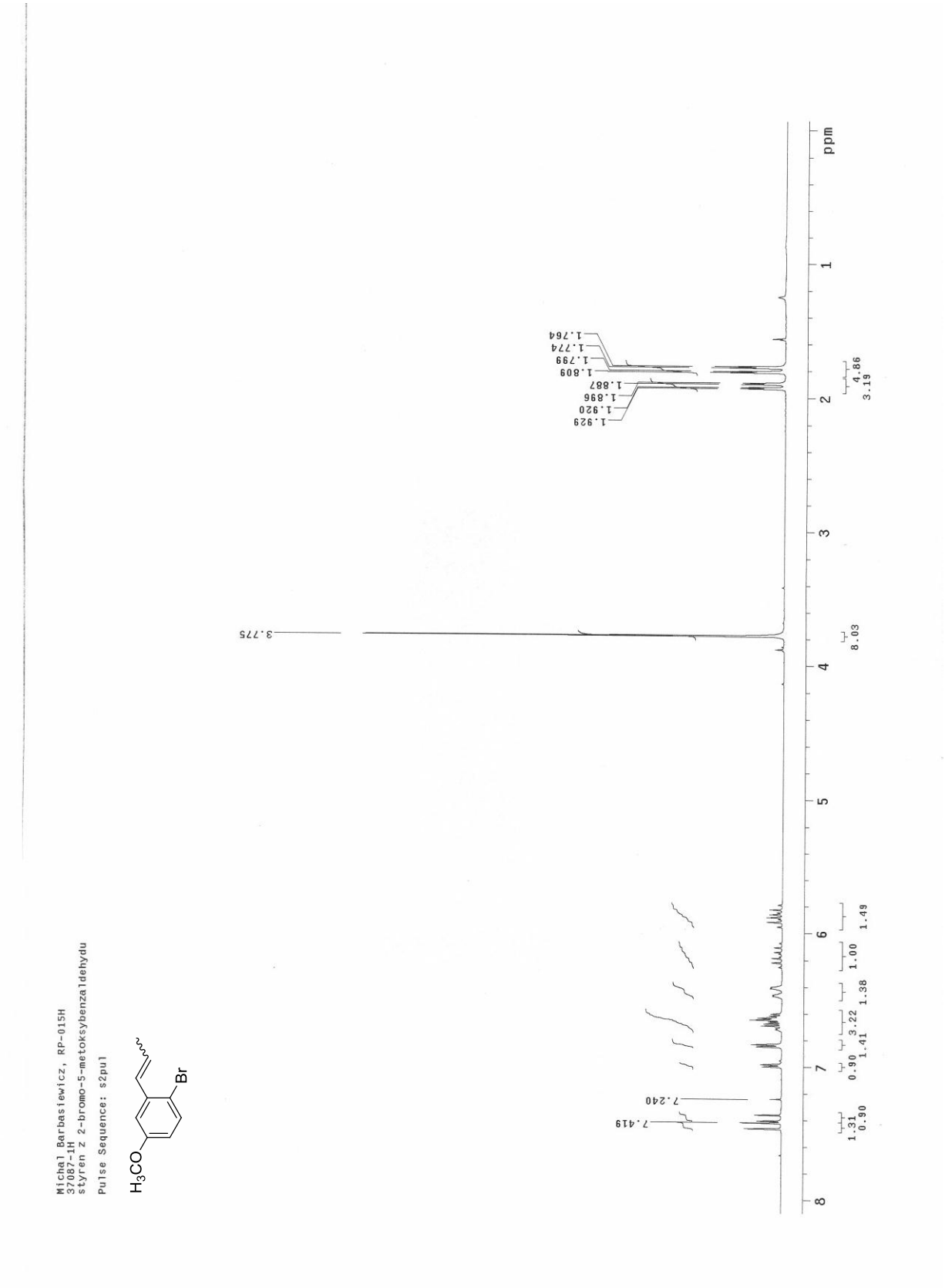
Reproduction of ^{1}H NMR spectrum of compound **4e**.



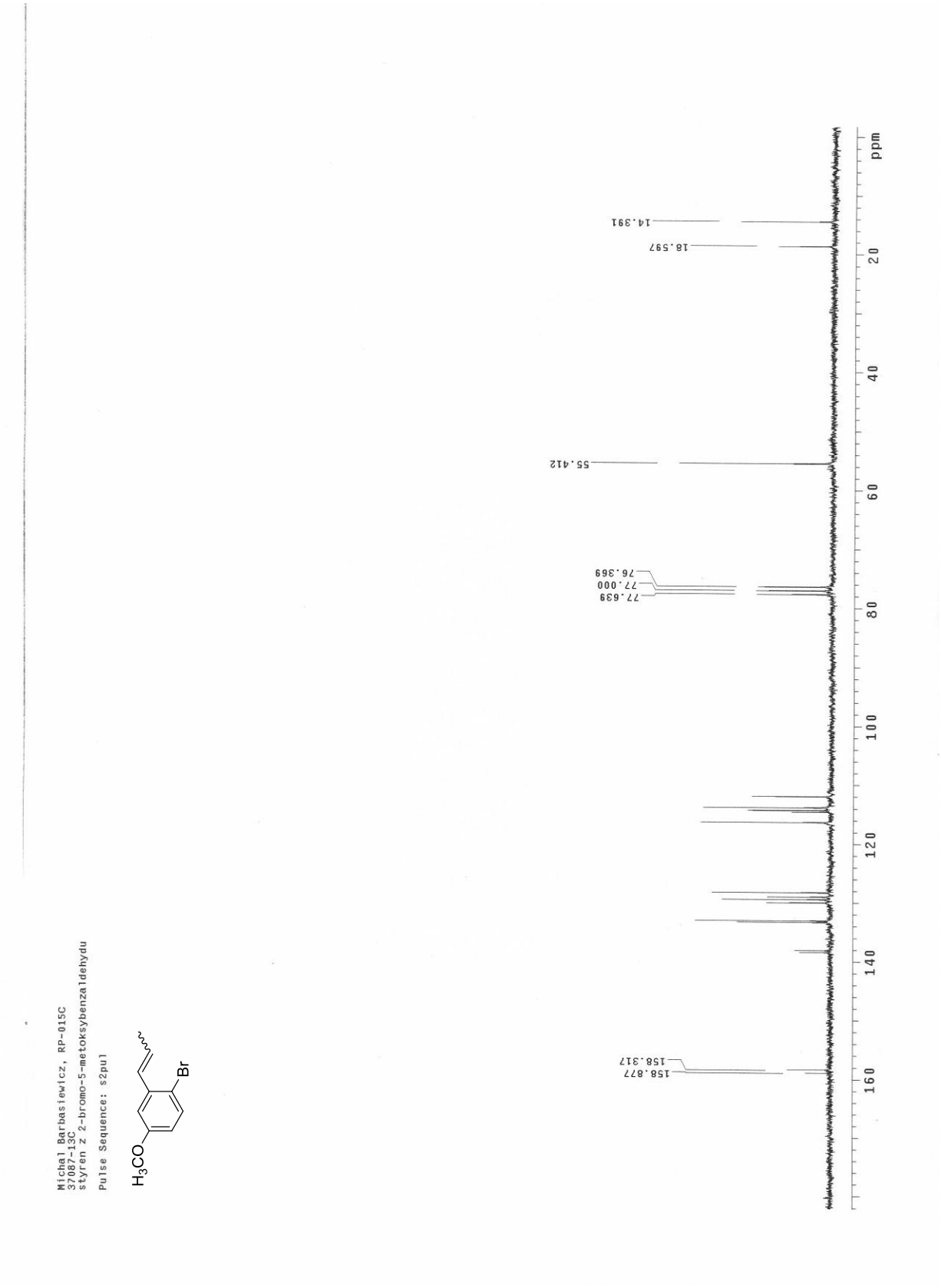
Reproduction of ^{13}C NMR spectrum of compound **4e**.



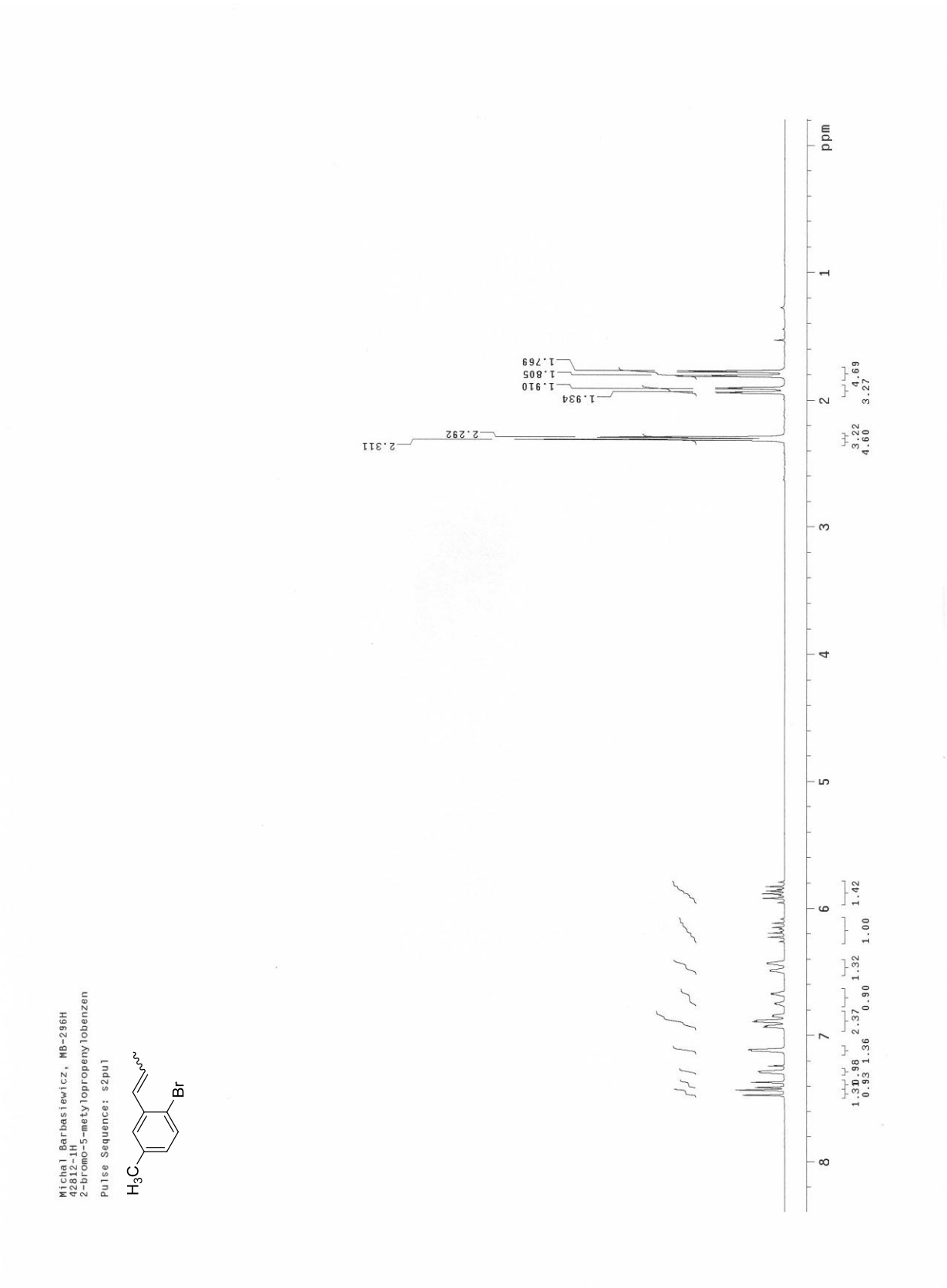
Reproduction of ^{1}H NMR spectrum of compound **4g**.



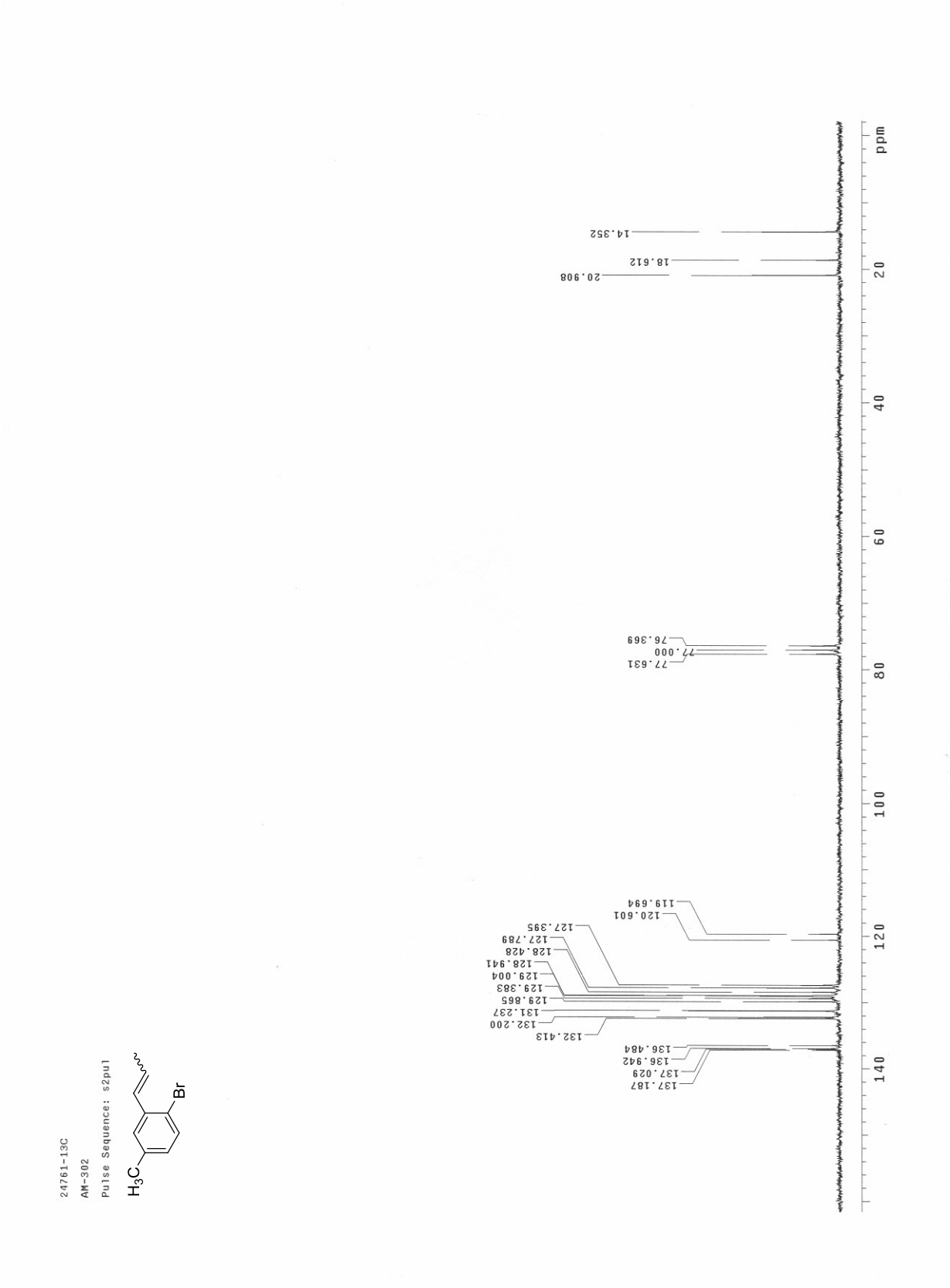
Reproduction of ^{13}C NMR spectrum of compound **4g**.



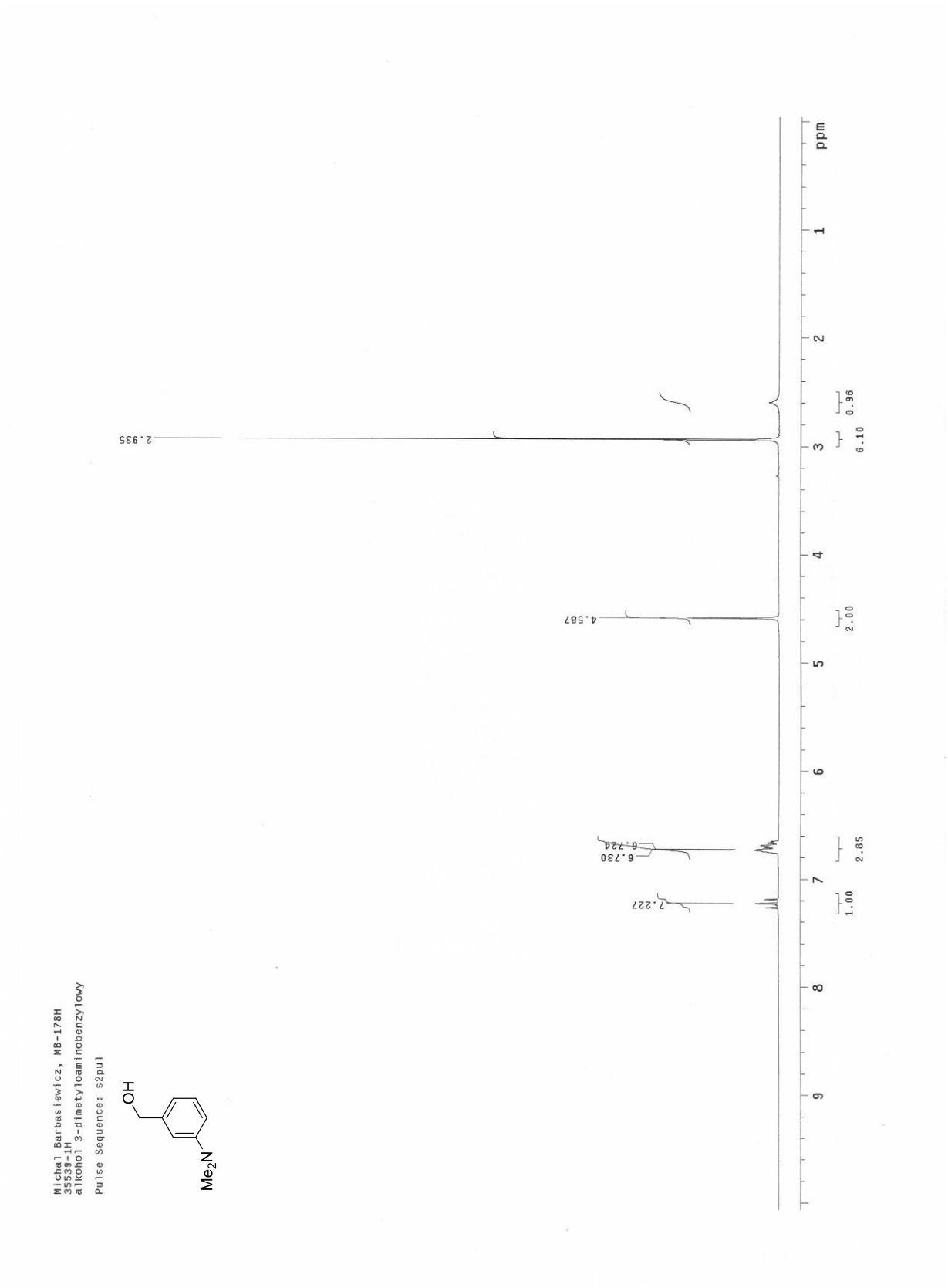
Reproduction of ^{1}H NMR spectrum of compound **4h**.



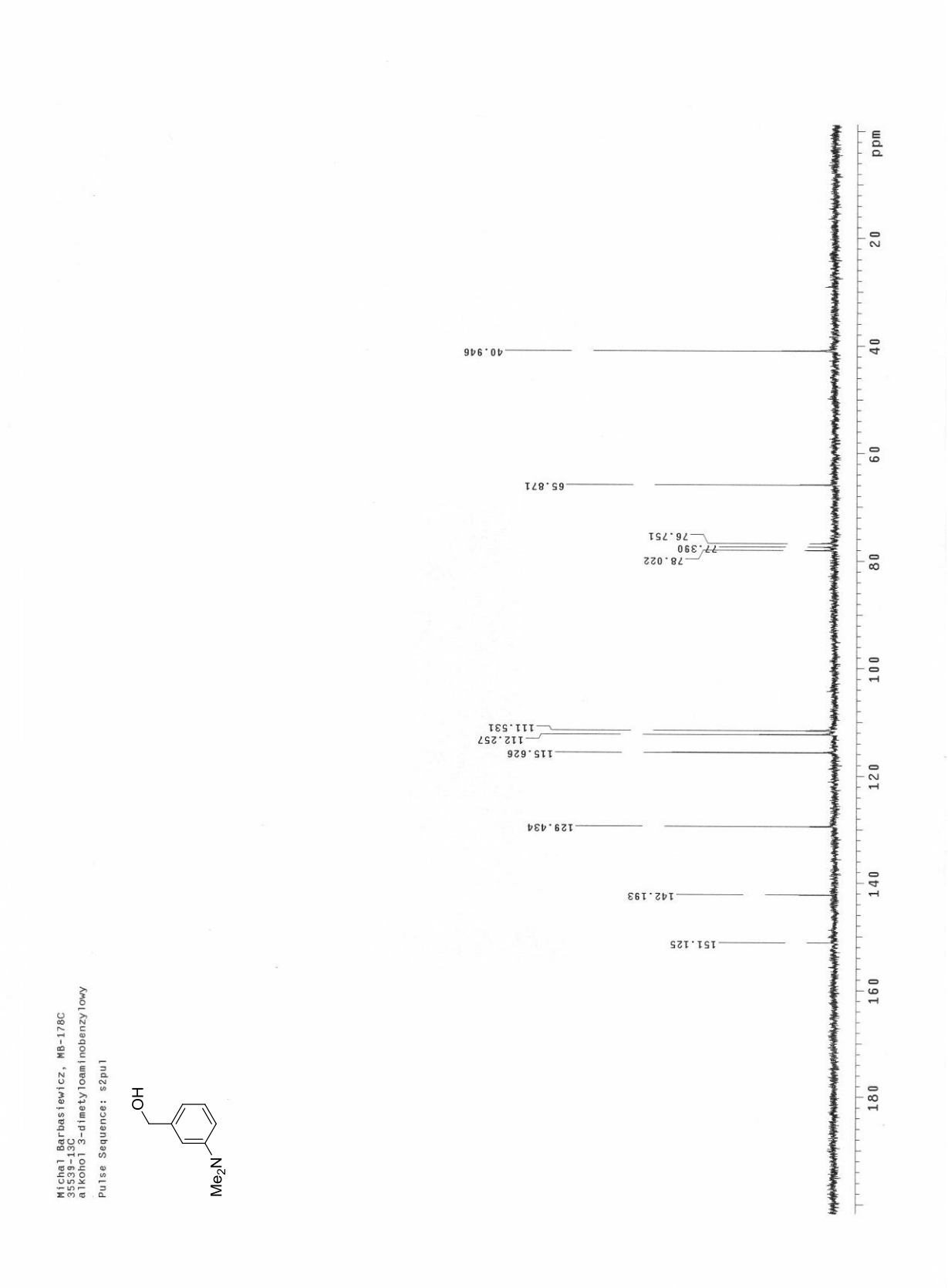
Reproduction of ^{13}C NMR spectrum of compound **4h**.



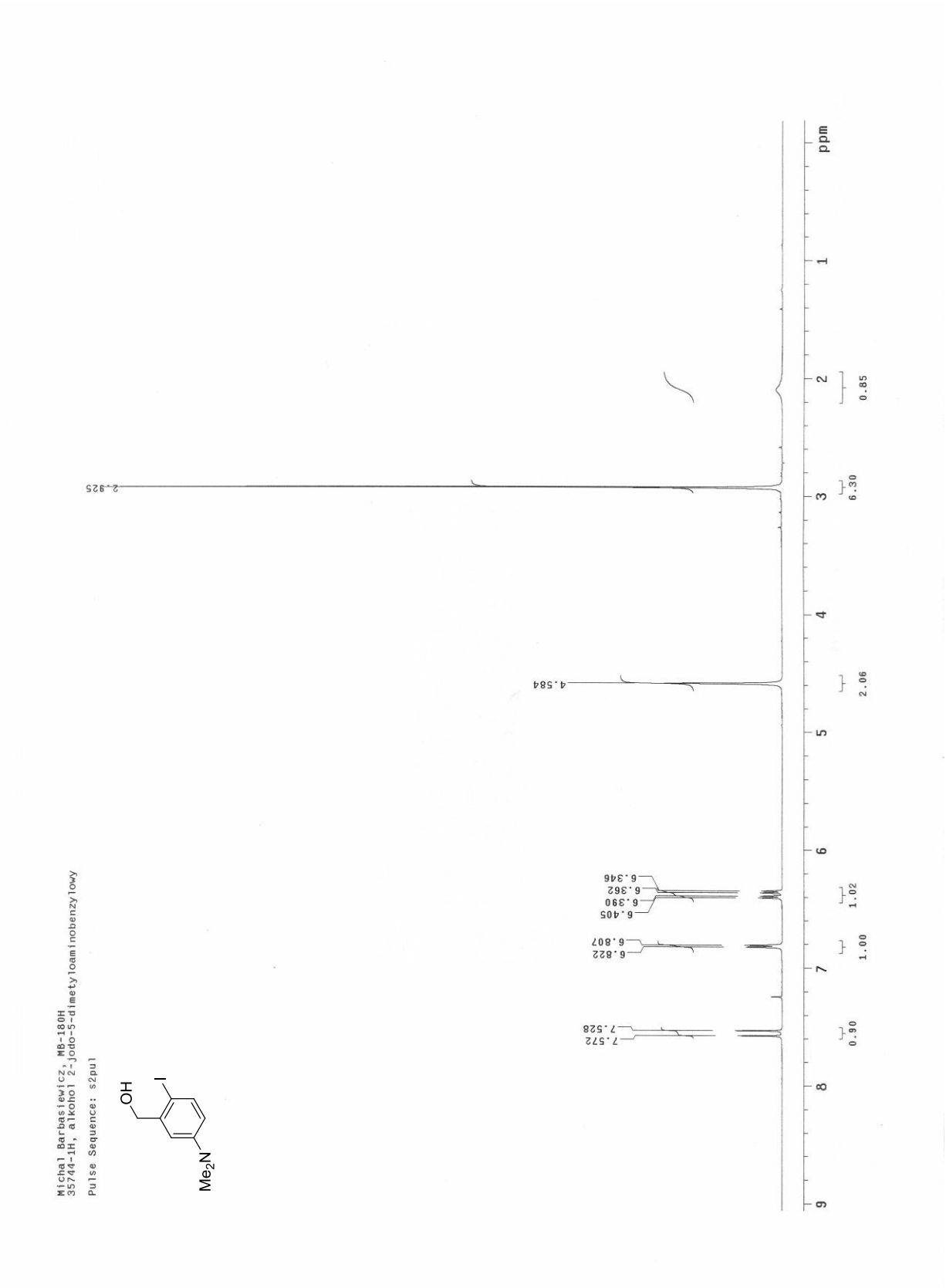
Reproduction of ^{1}H NMR spectrum of compound **5**.



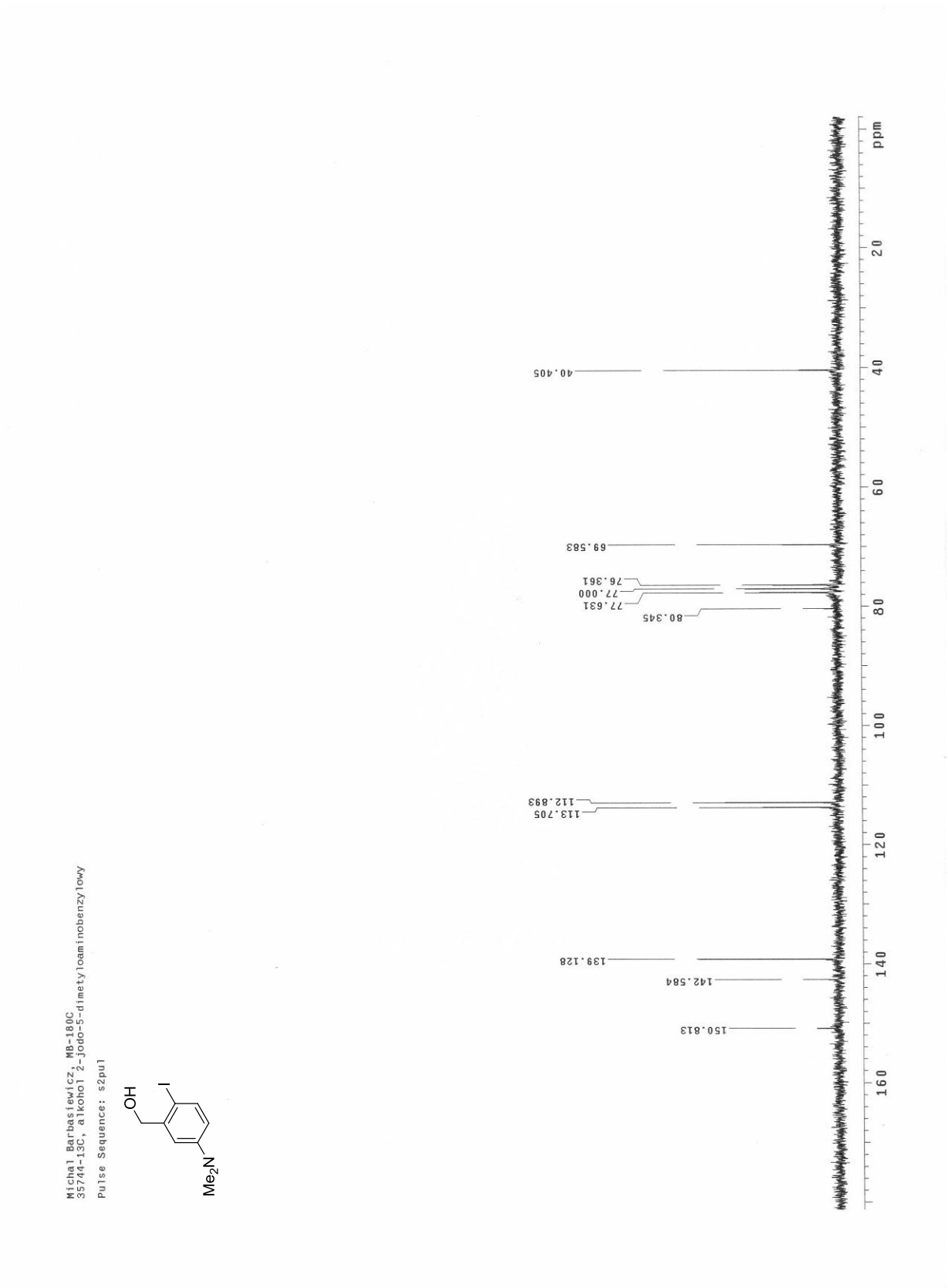
Reproduction of ^{13}C NMR spectrum of compound **5**.



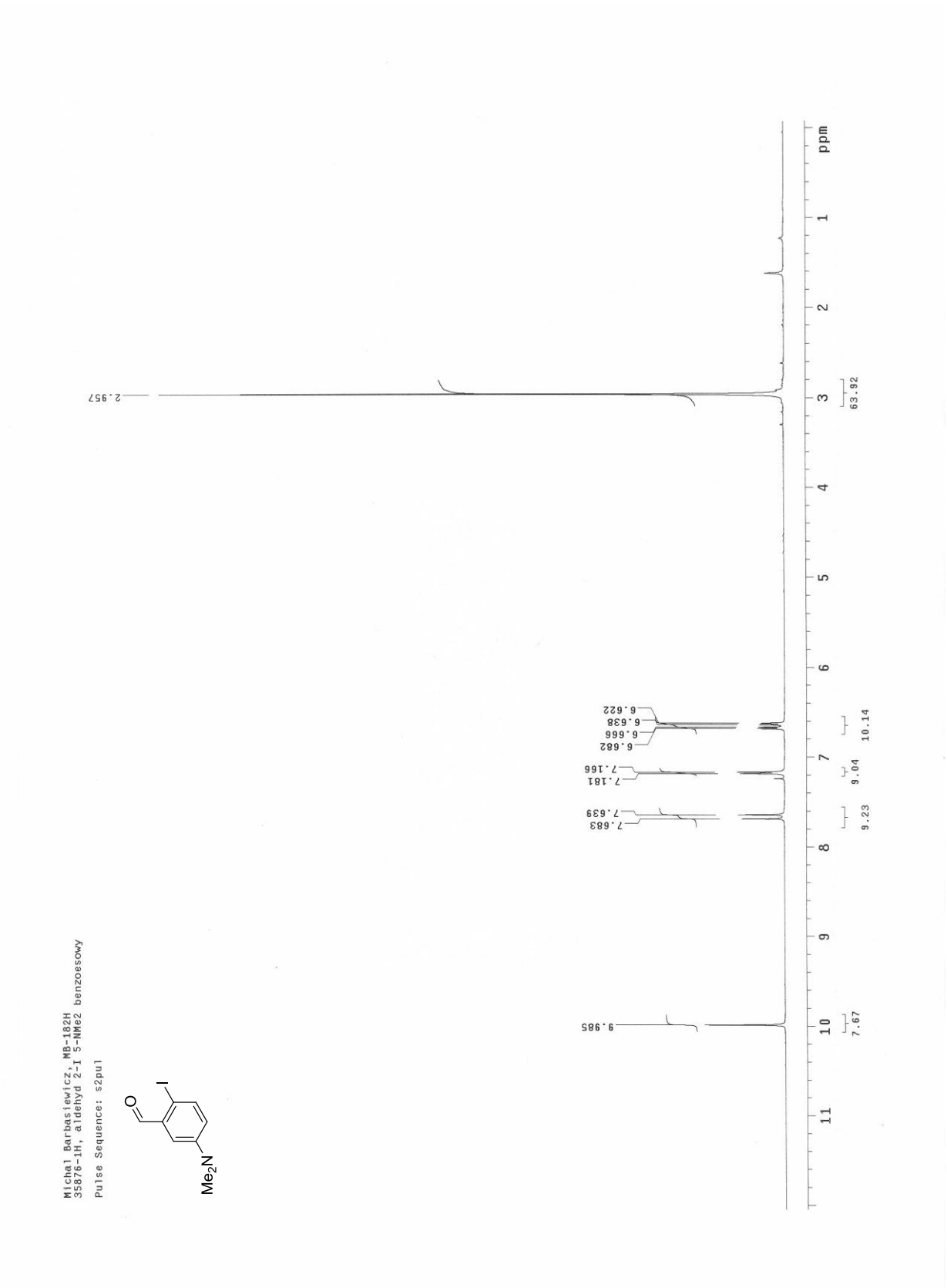
Reproduction of ^{1}H NMR spectrum of compound **6**.



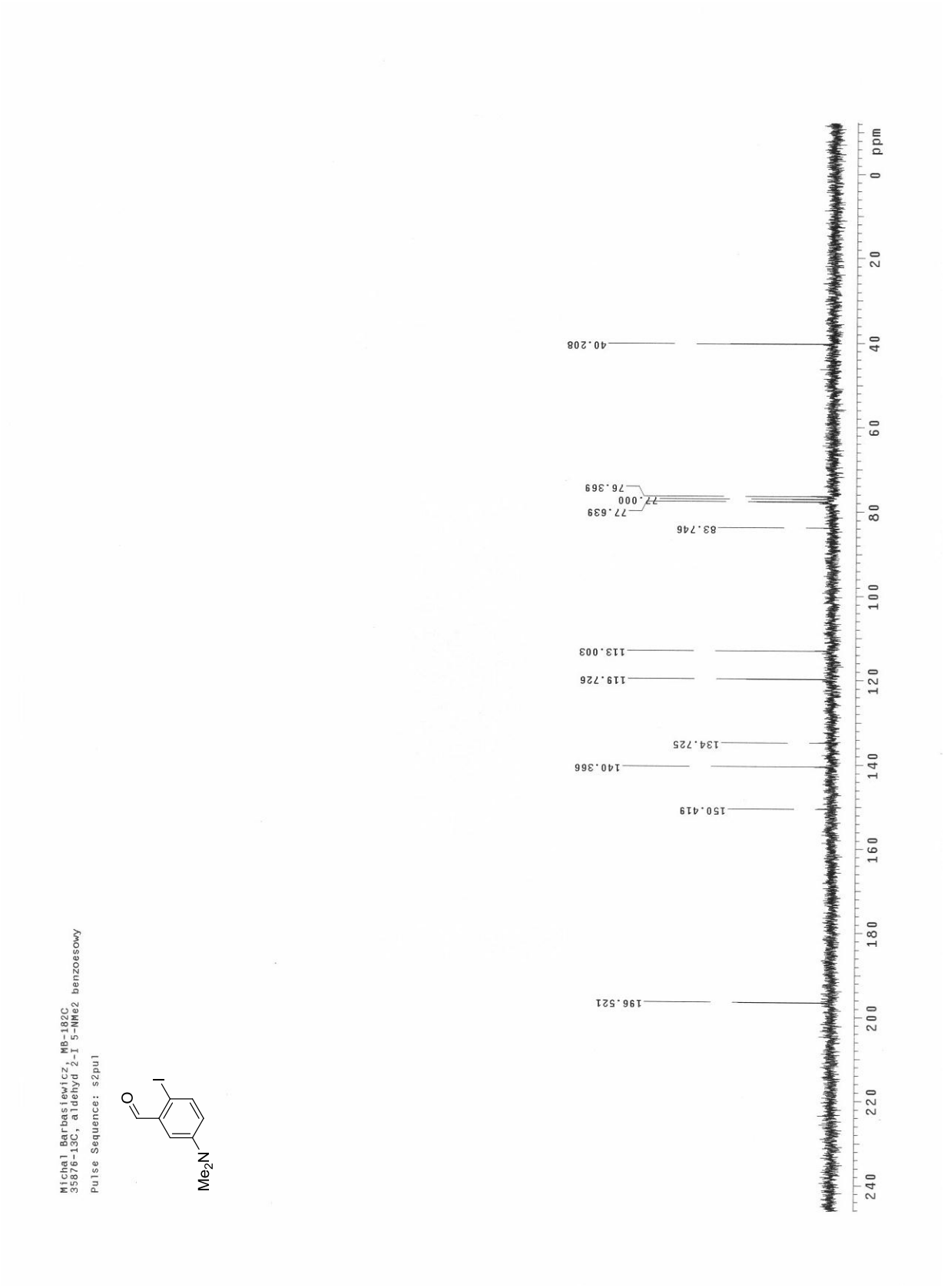
Reproduction of ^{13}C NMR spectrum of compound **6**.



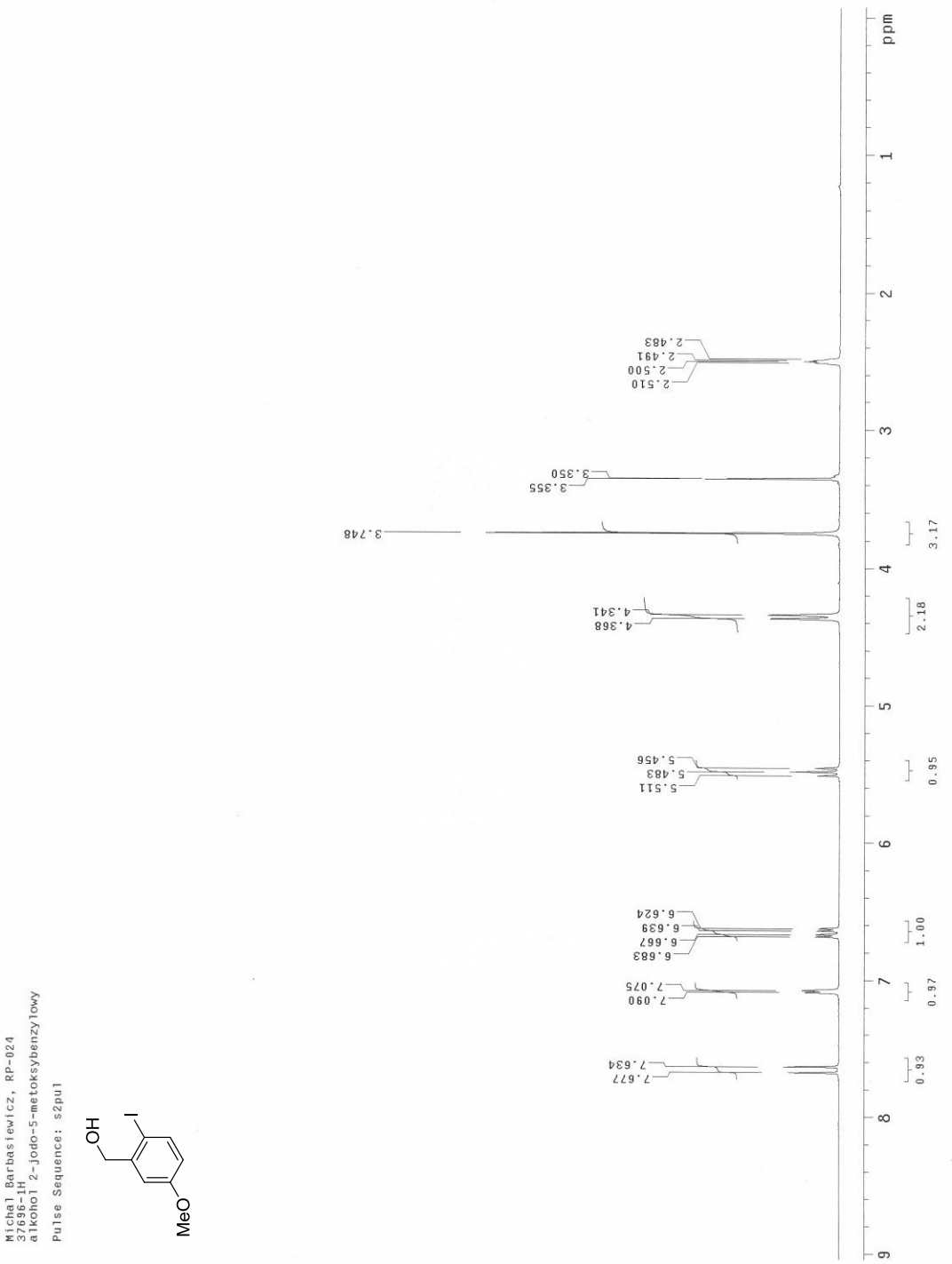
Reproduction of ^{1}H NMR spectrum of compound **7**.



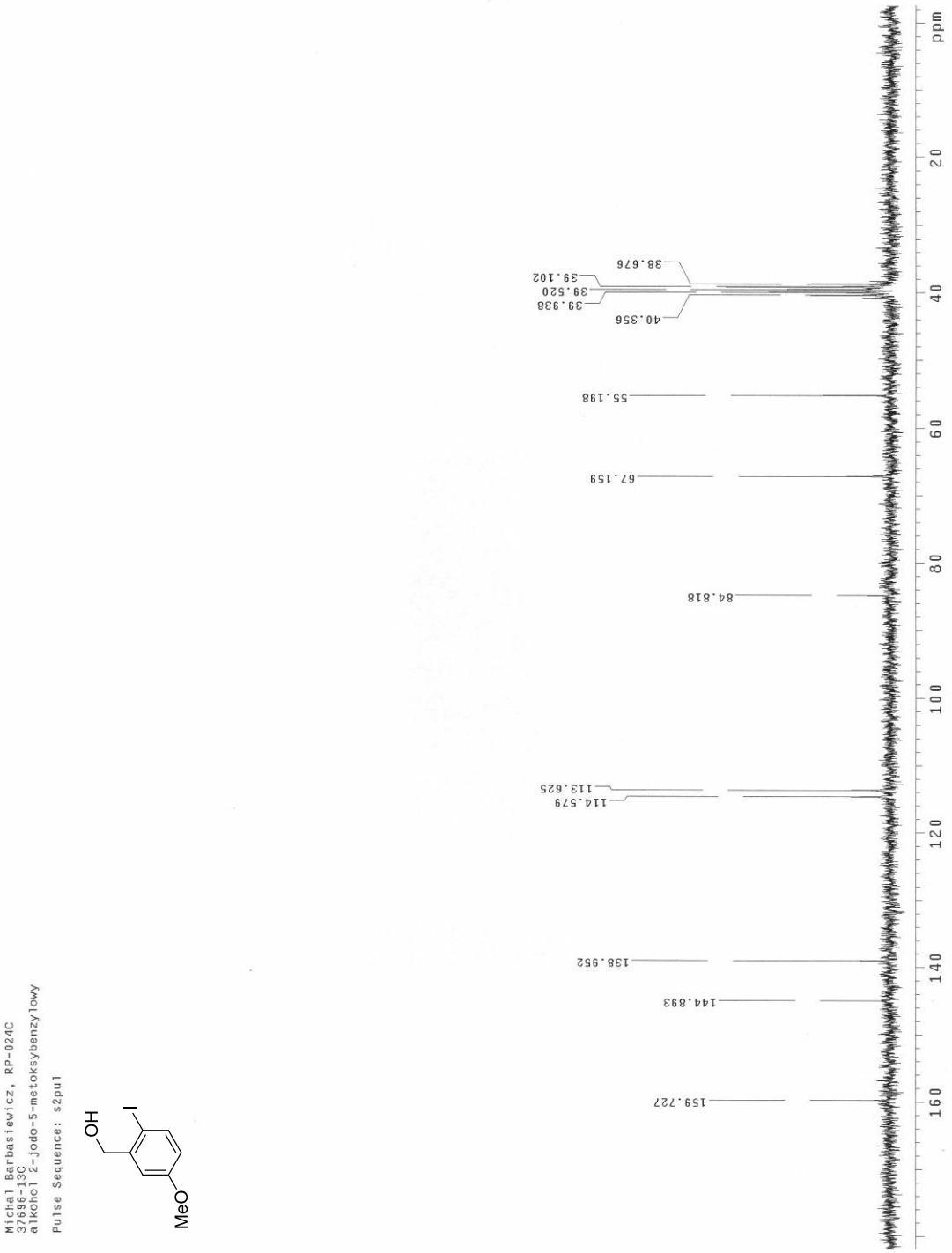
Reproduction of ^{13}C NMR spectrum of compound **7**.



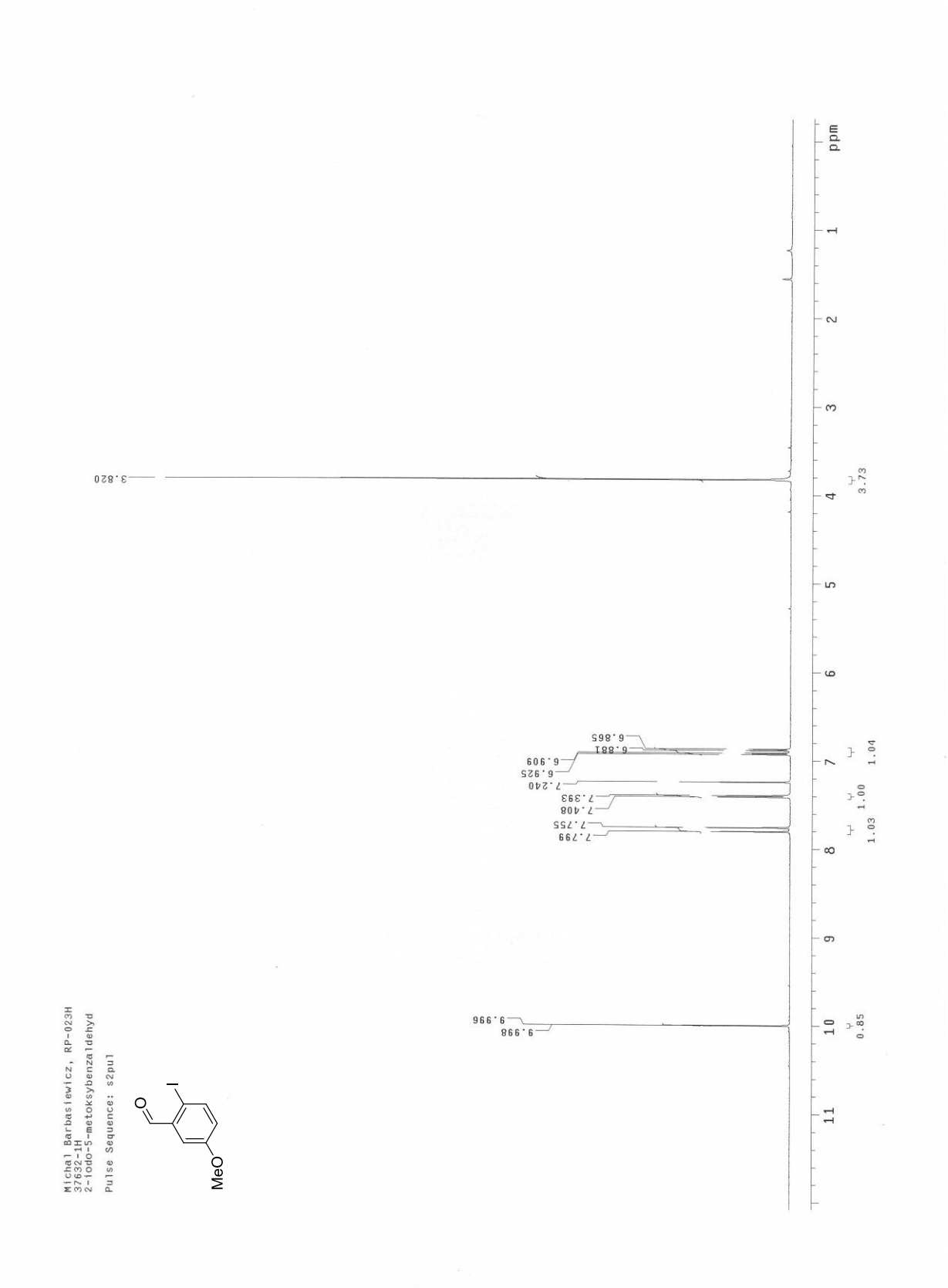
Reproduction of ^{1}H NMR spectrum of compound **8**.



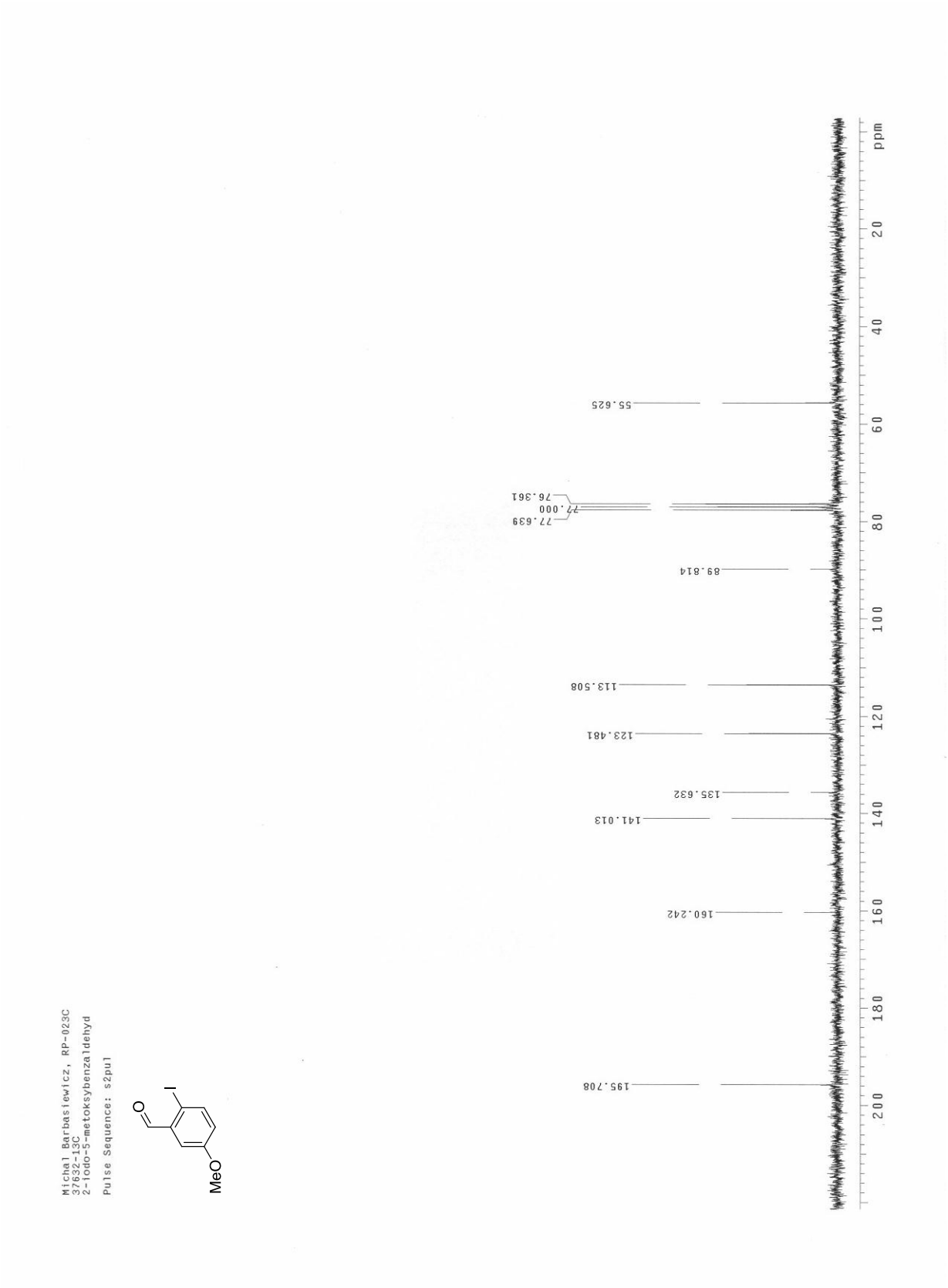
Reproduction of ^{13}C NMR spectrum of compound **8**.



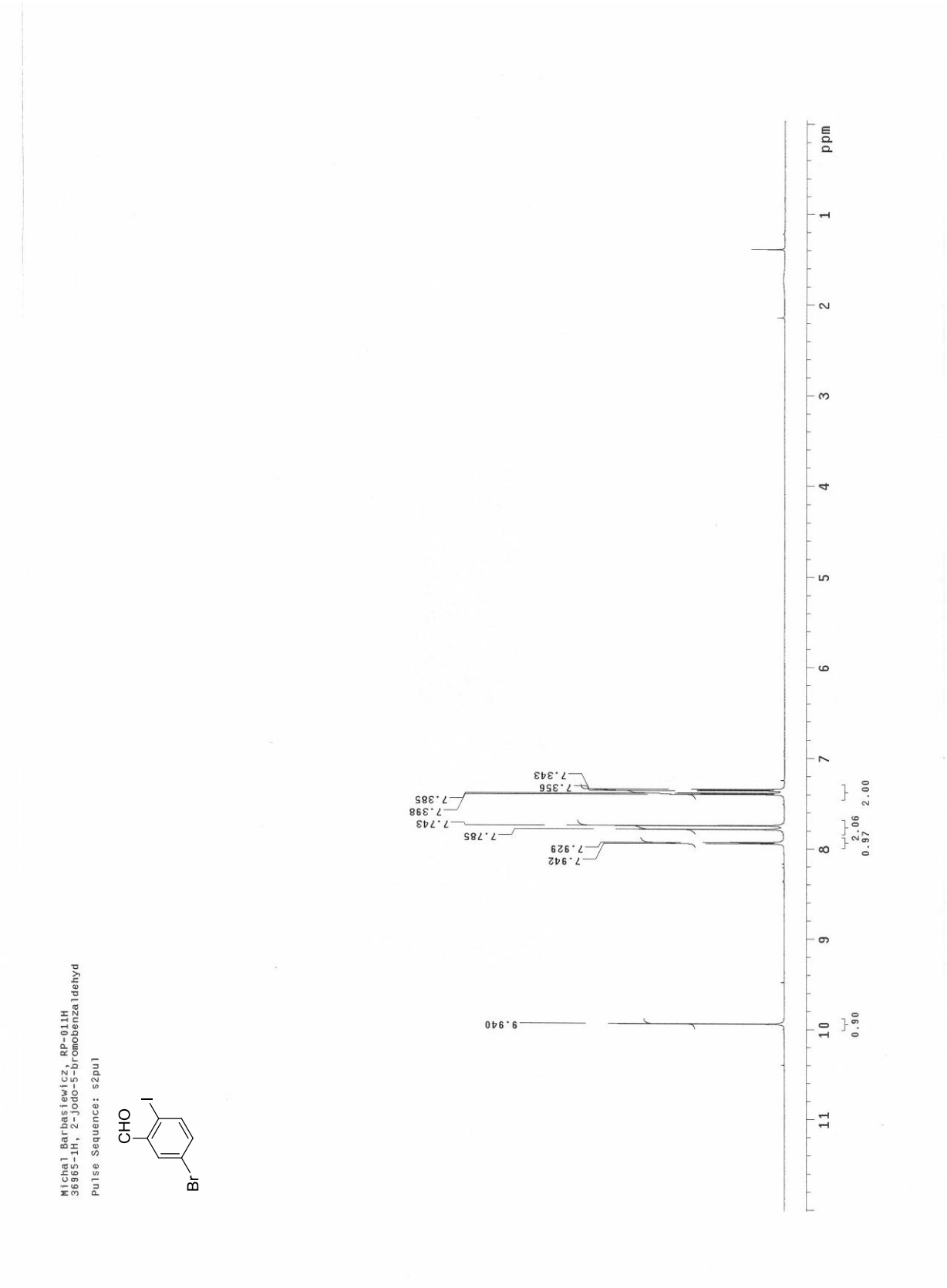
Reproduction of ^{1}H NMR spectrum of compound **9**.



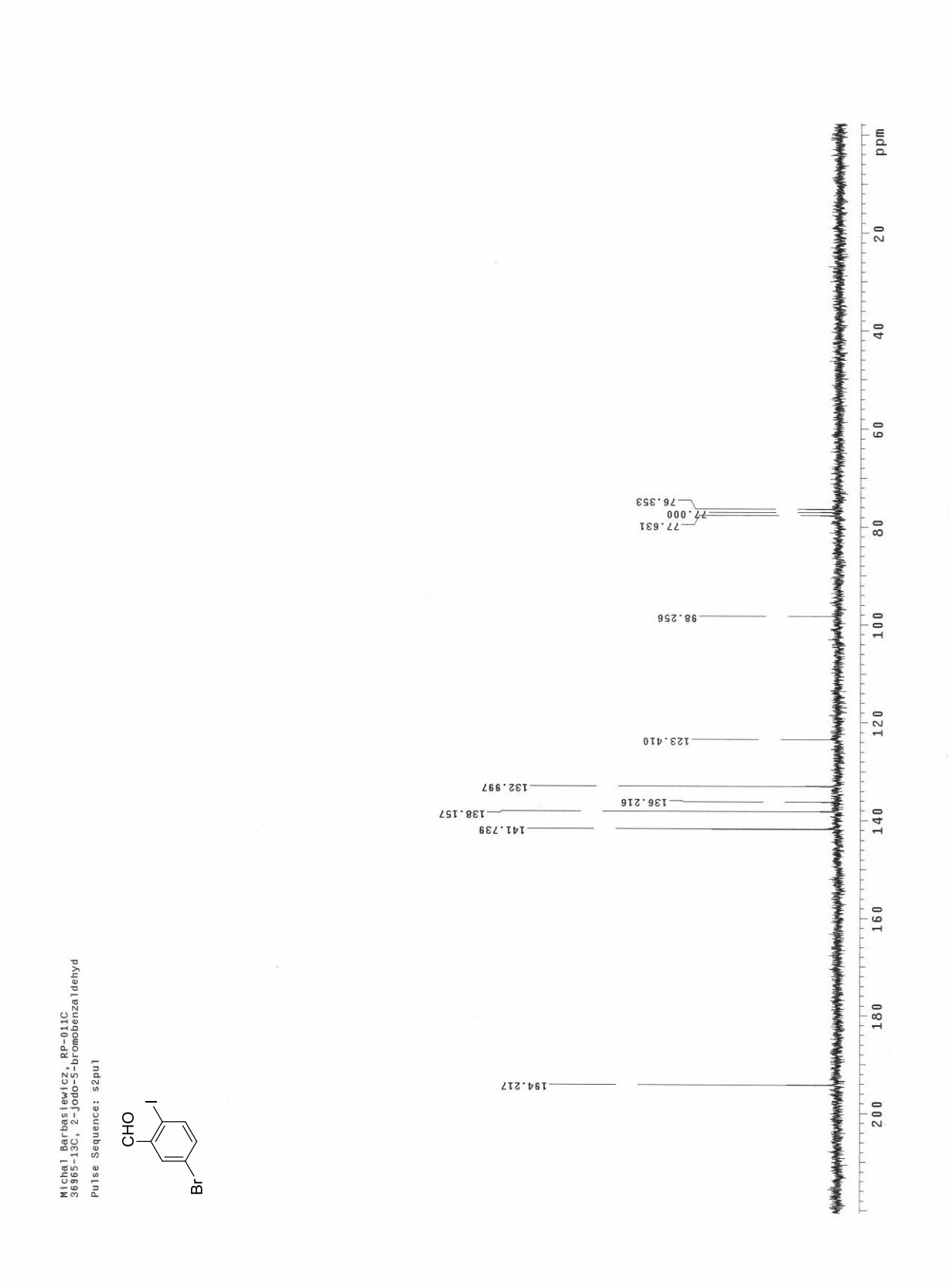
Reproduction of ^{13}C NMR spectrum of compound **9**.



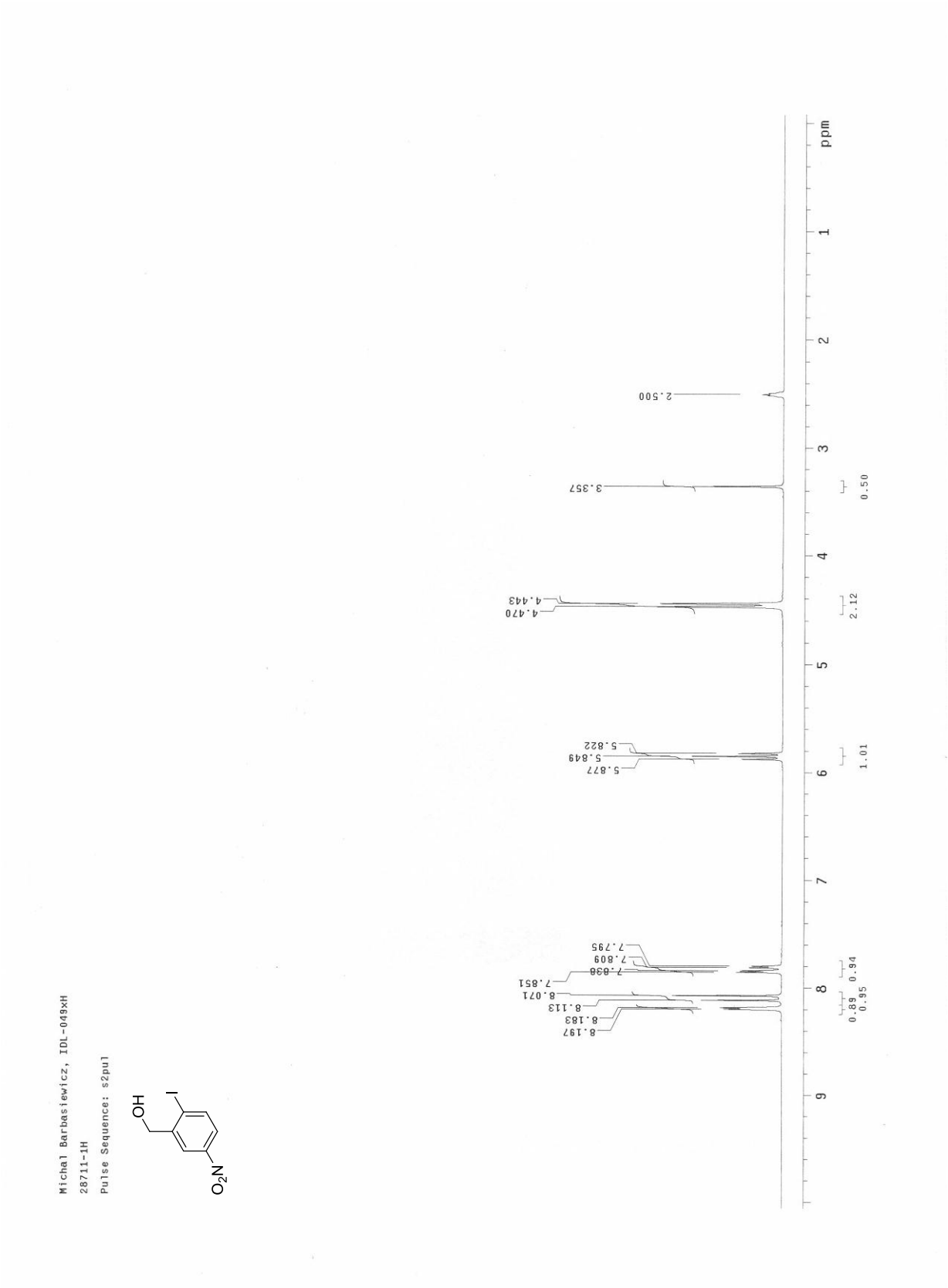
Reproduction of ^{1}H NMR spectrum of compound **10**.



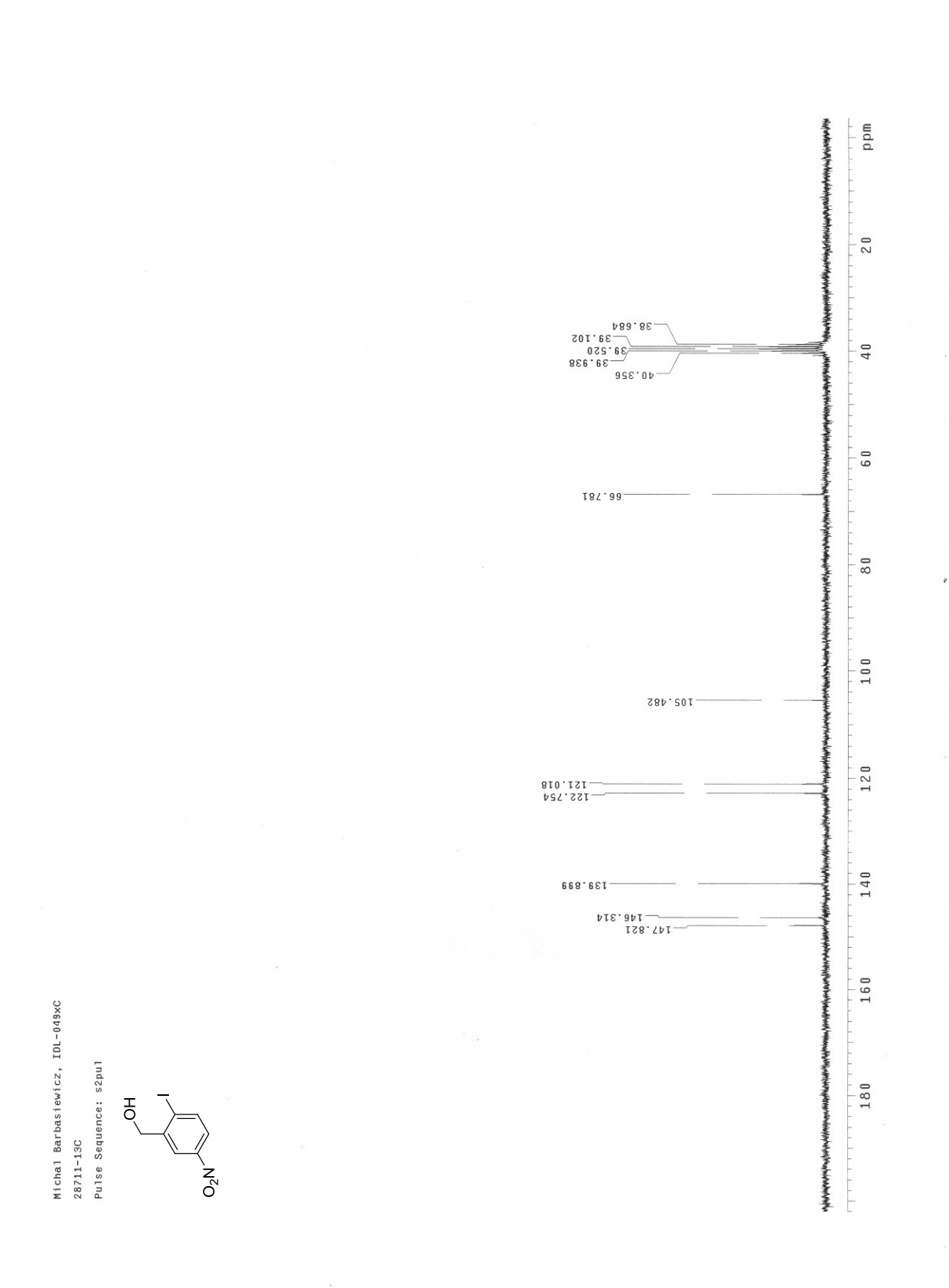
Reproduction of ^{13}C NMR spectrum of compound **10**.



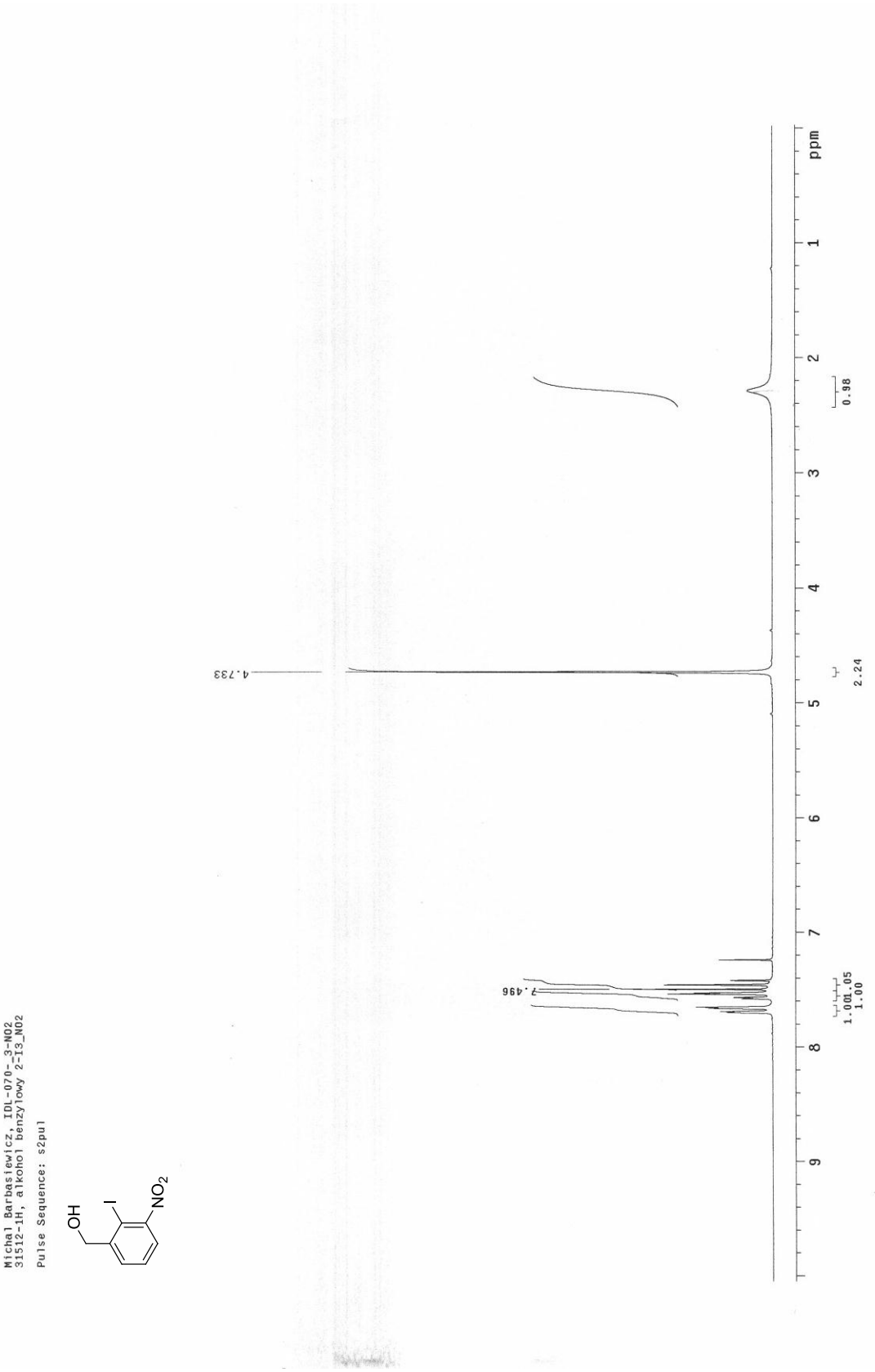
Reproduction of ^{1}H NMR spectrum of compound **11a**.



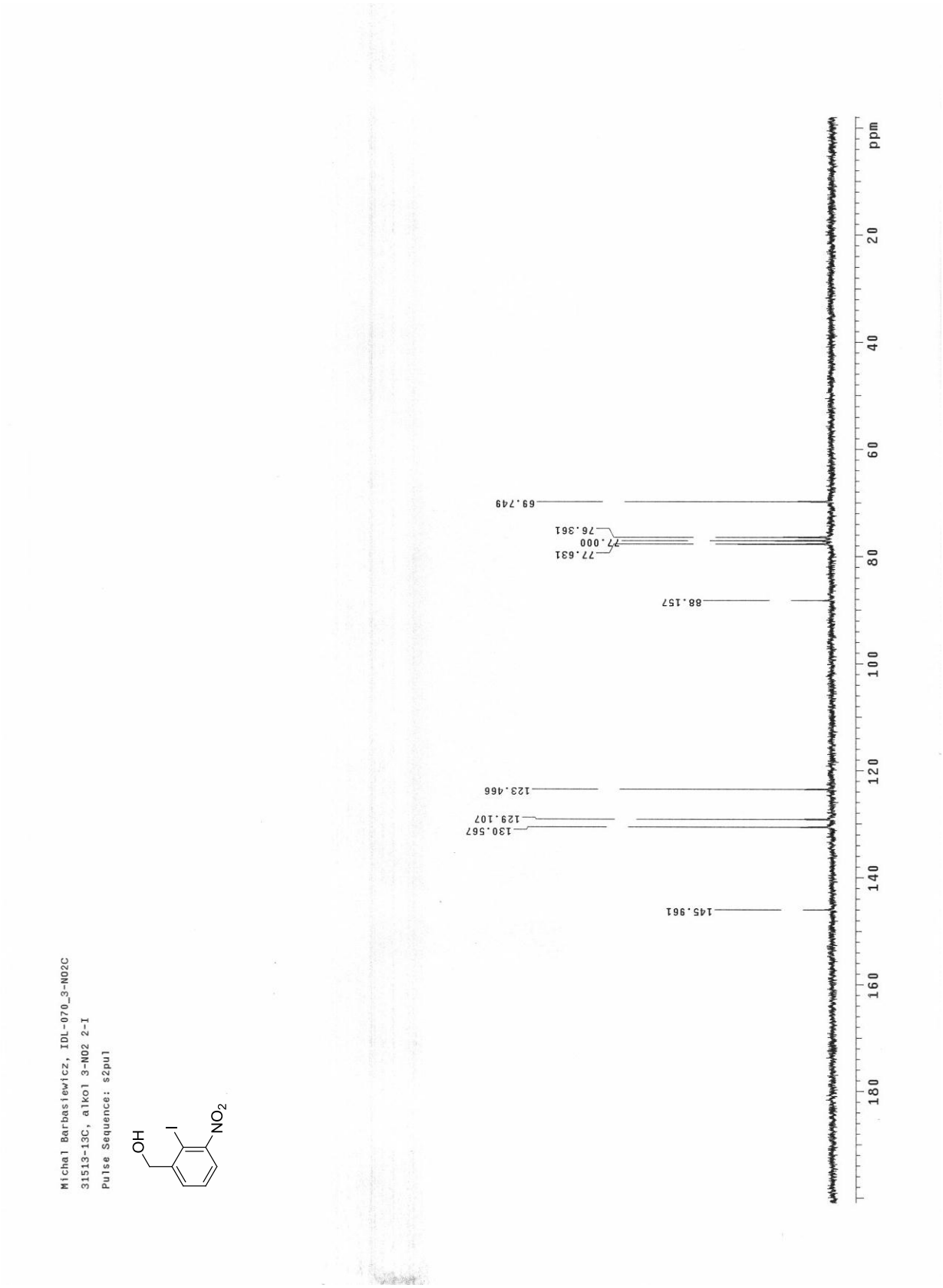
Reproduction of ^{13}C NMR spectrum of compound **11a**.



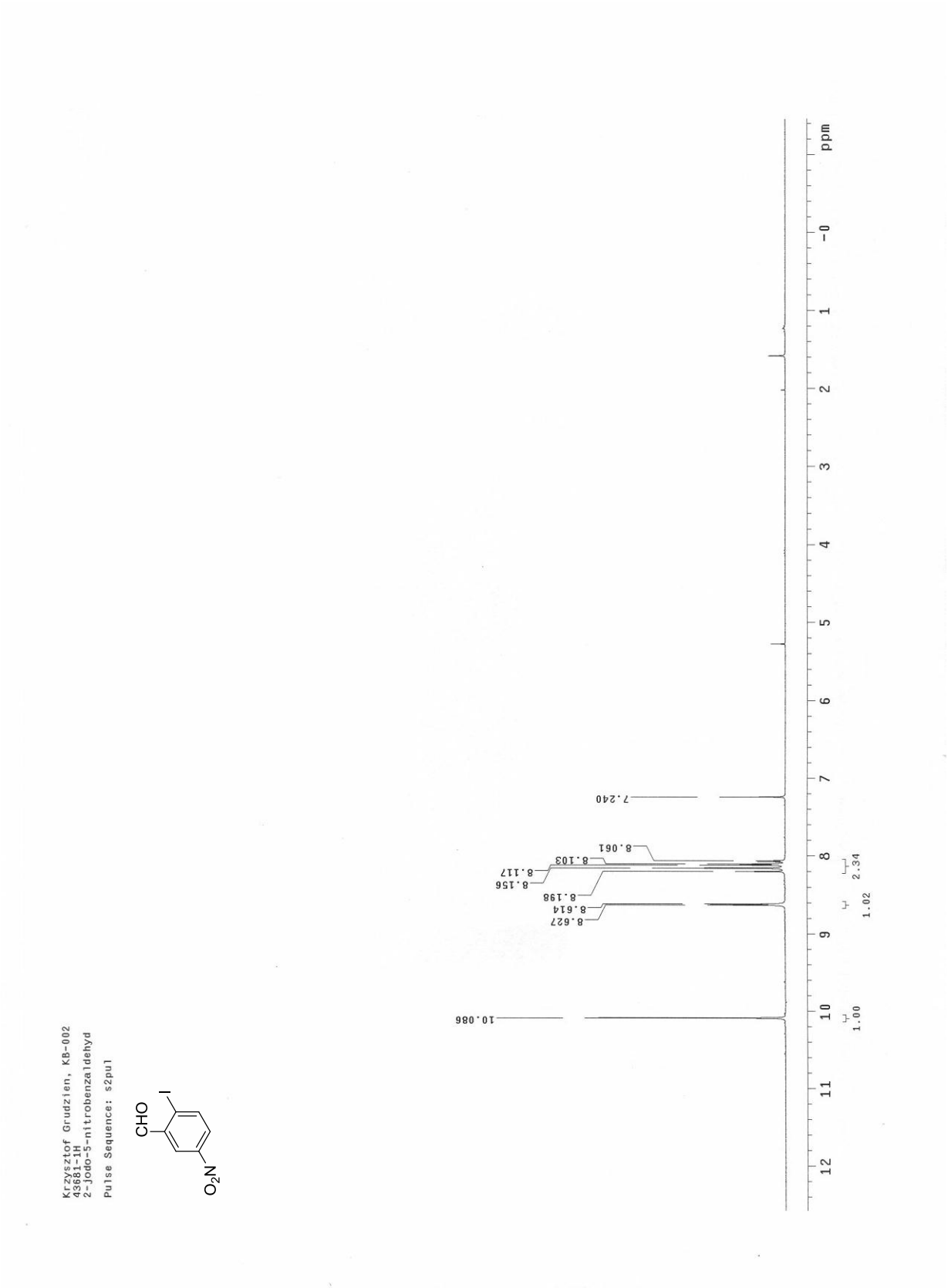
Reproduction of ^{1}H NMR spectrum of compound **11b**.



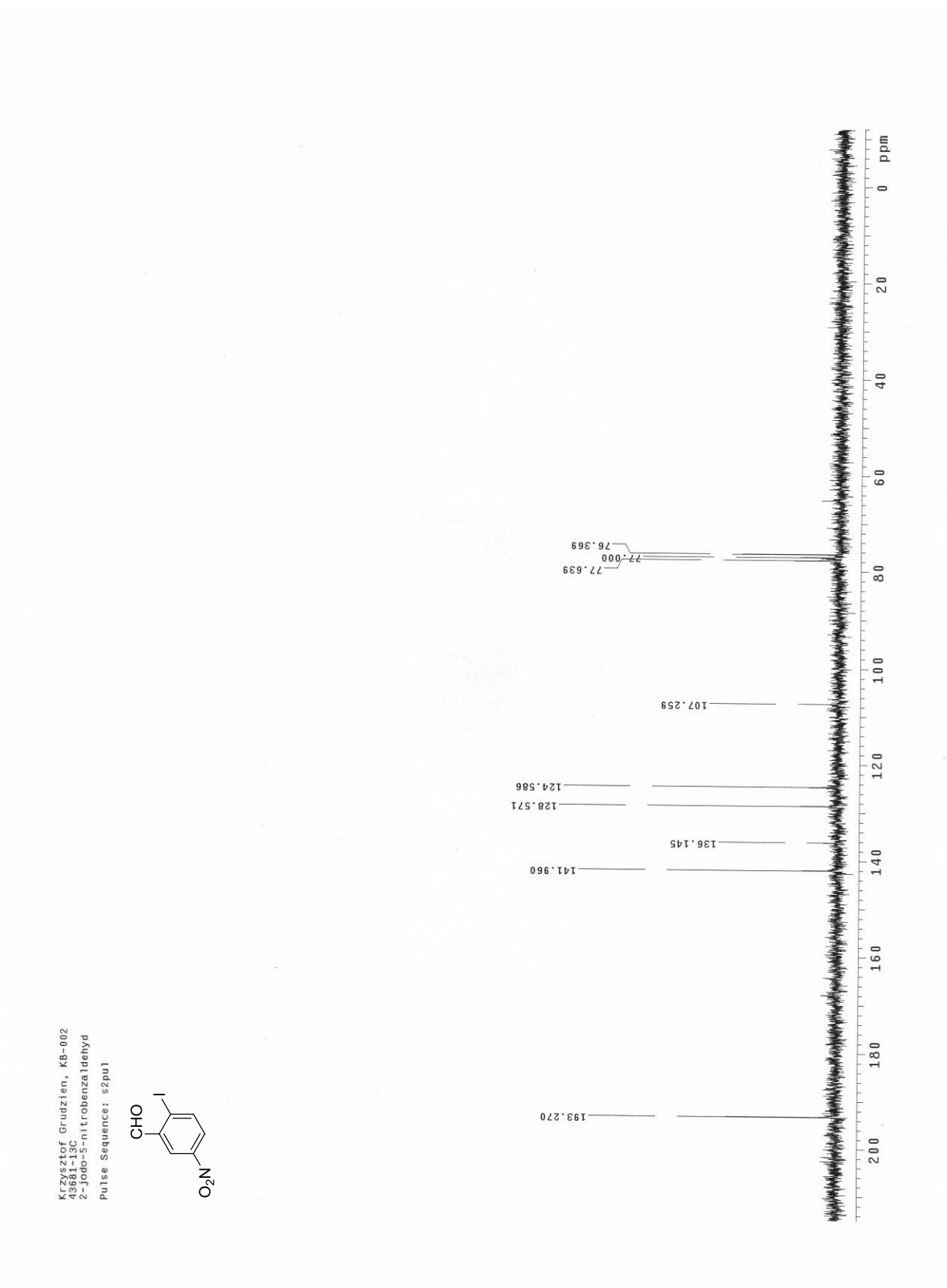
Reproduction of ^{13}C NMR spectrum of compound **11b**.



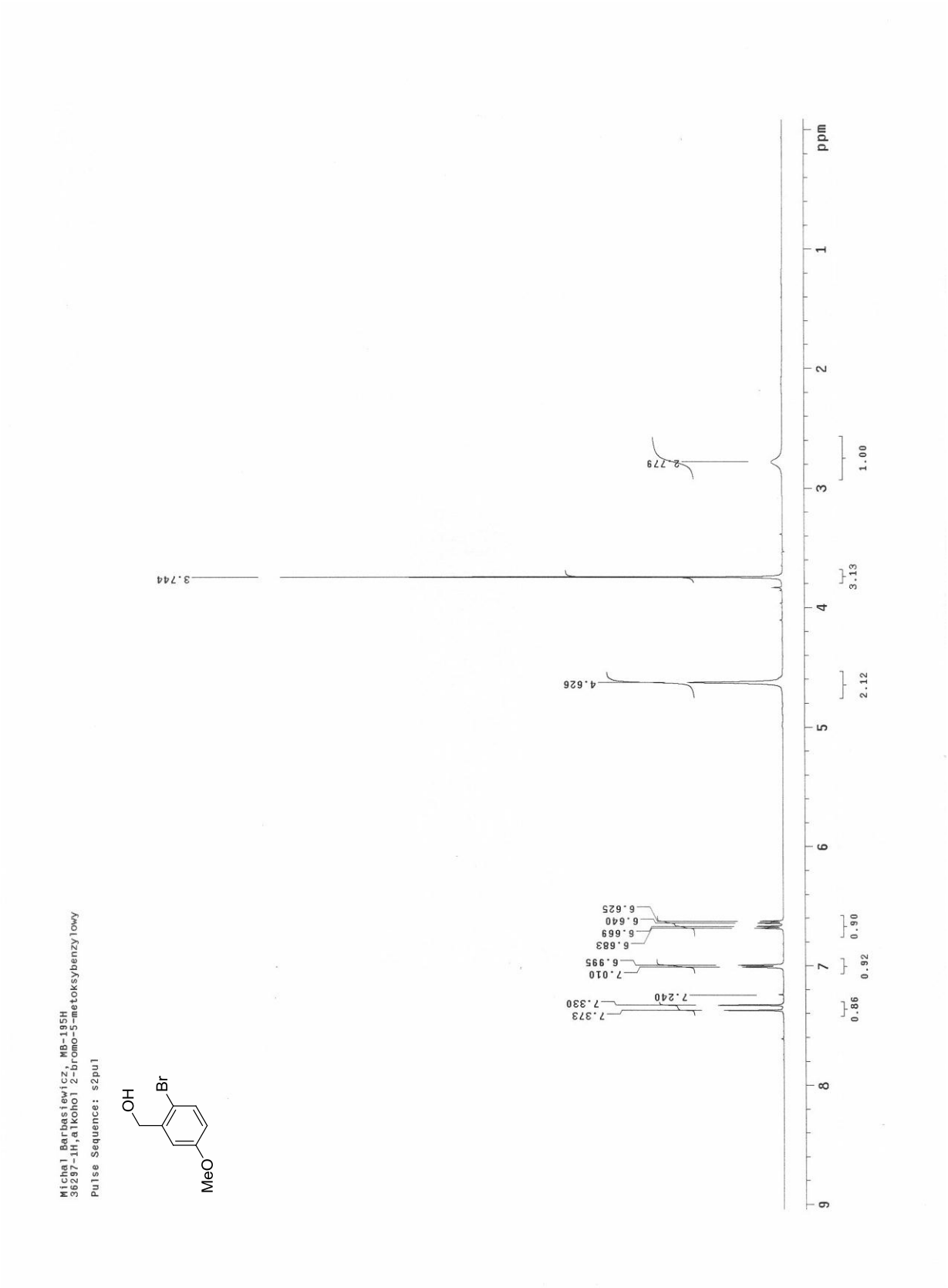
Reproduction of ^{1}H NMR spectrum of compound **12**.



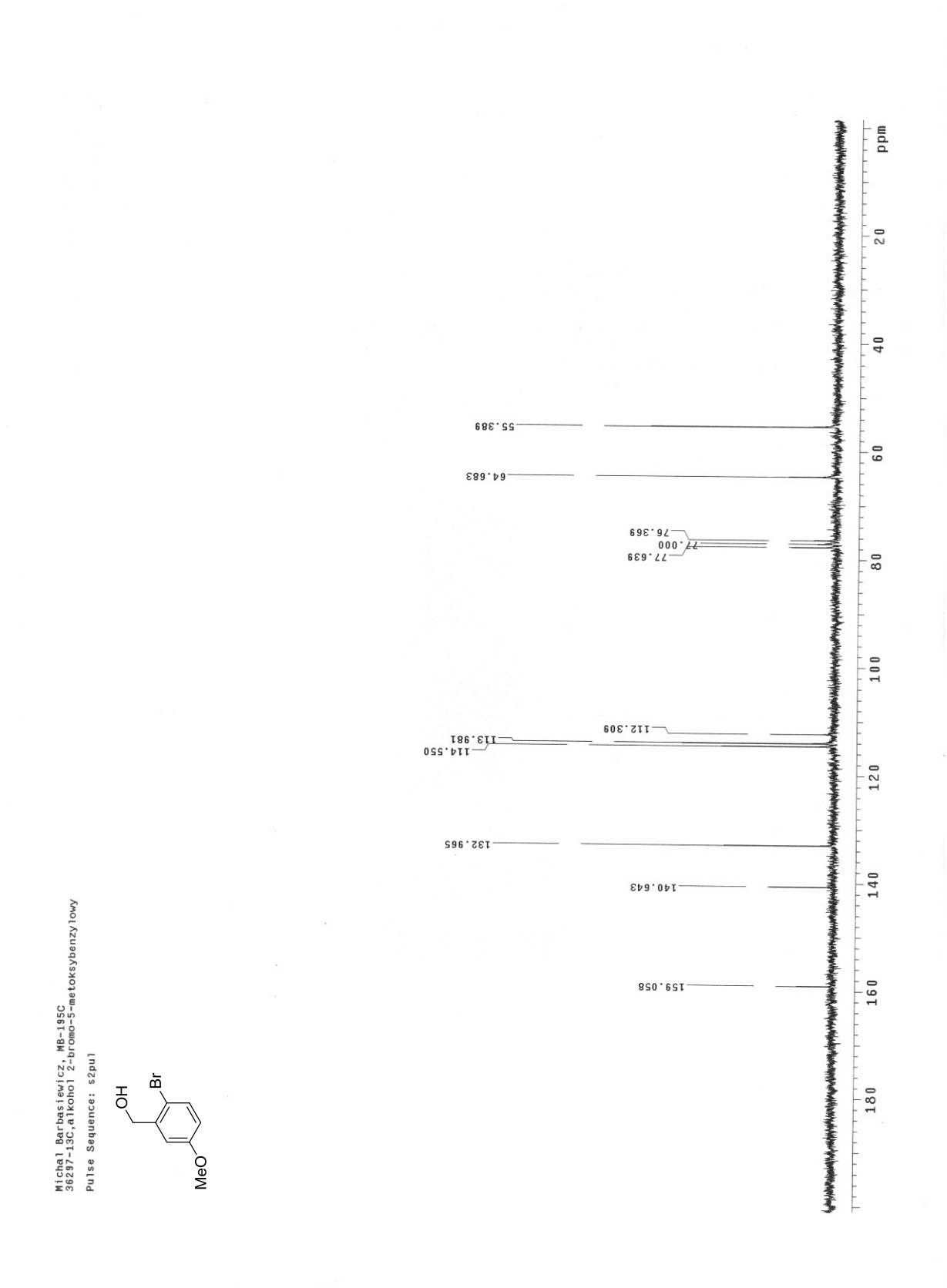
Reproduction of ^{13}C NMR spectrum of compound **12**.



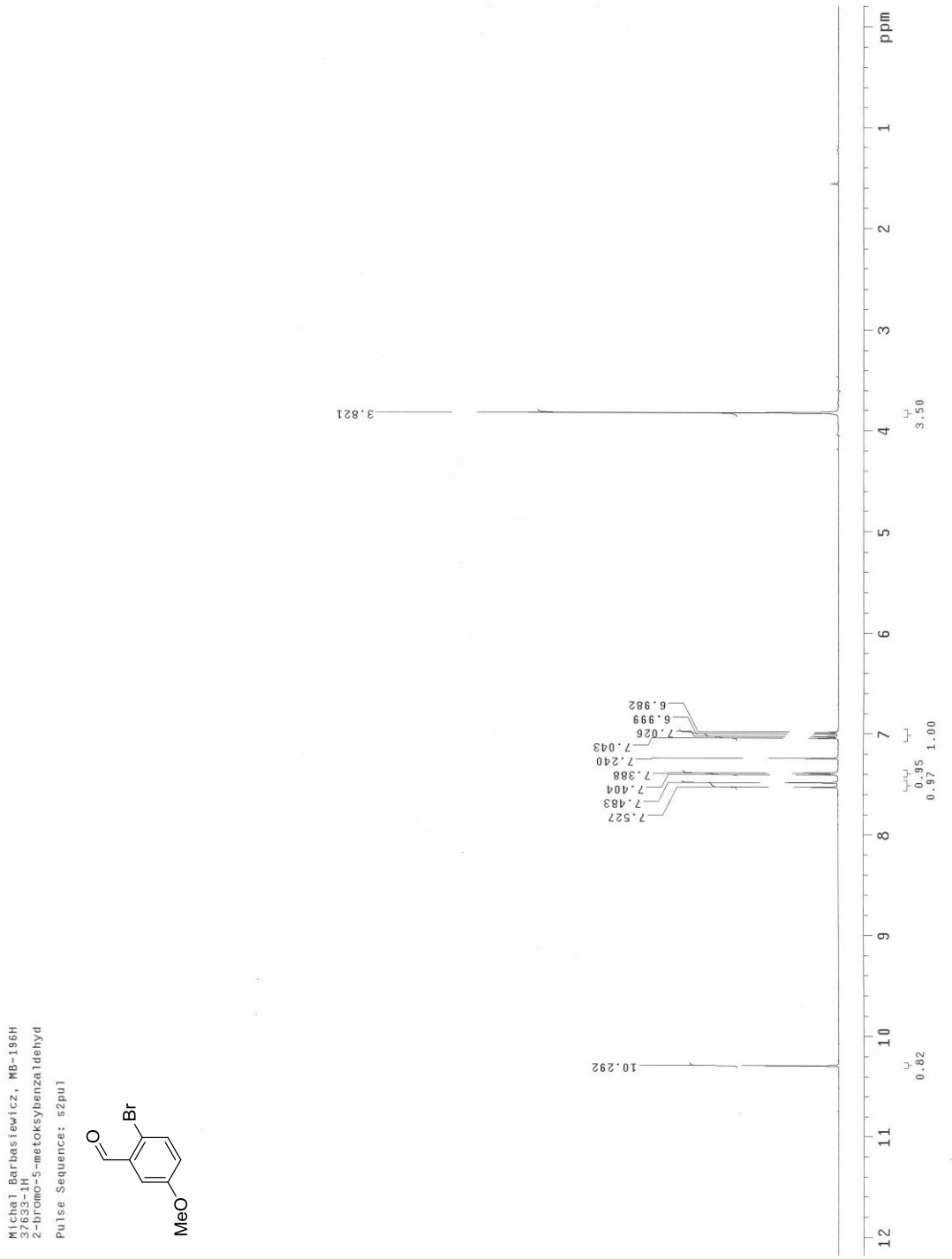
Reproduction of ^{1}H NMR spectrum of compound **13**.



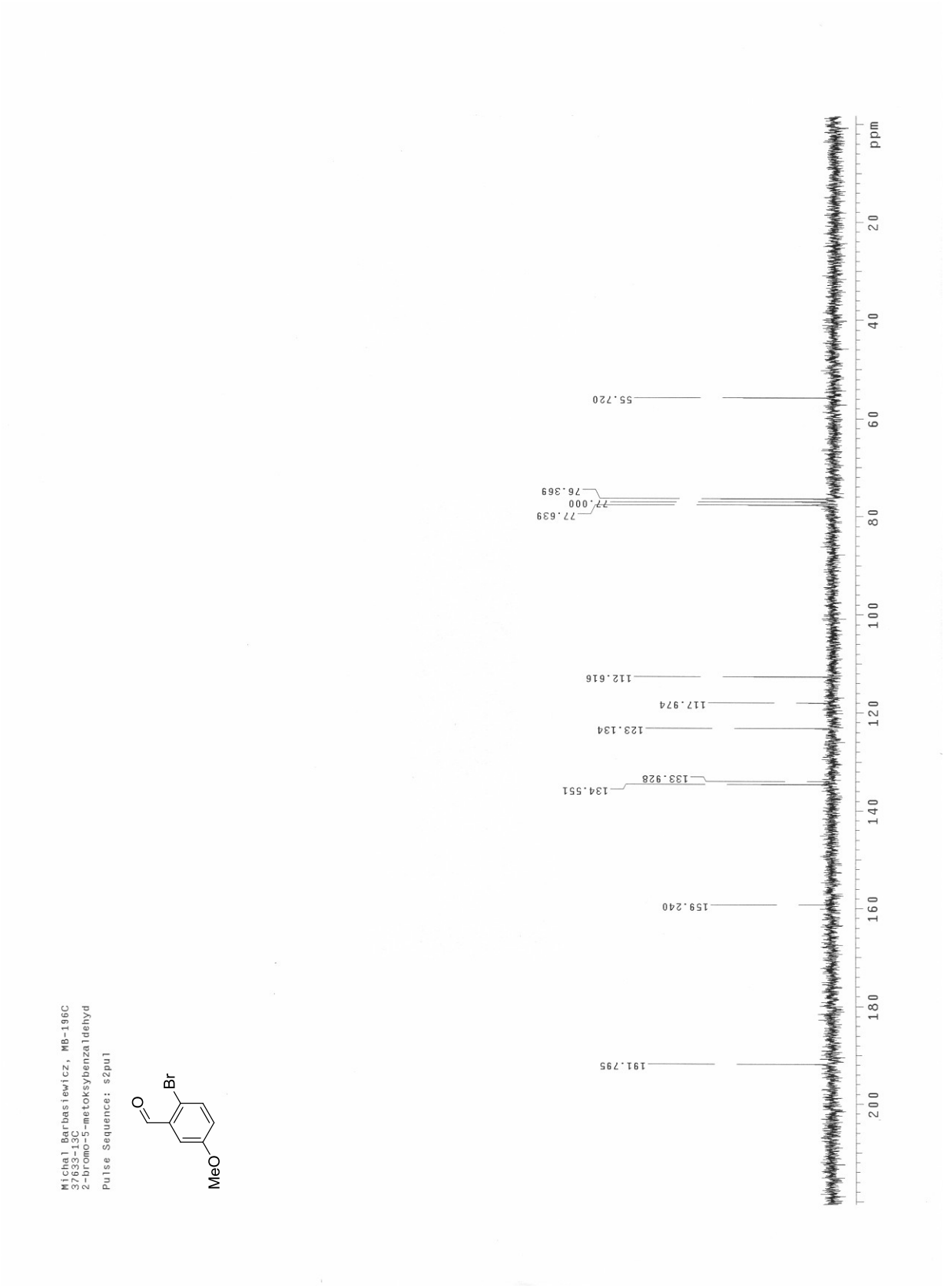
Reproduction of ^{13}C NMR spectrum of compound **13**.



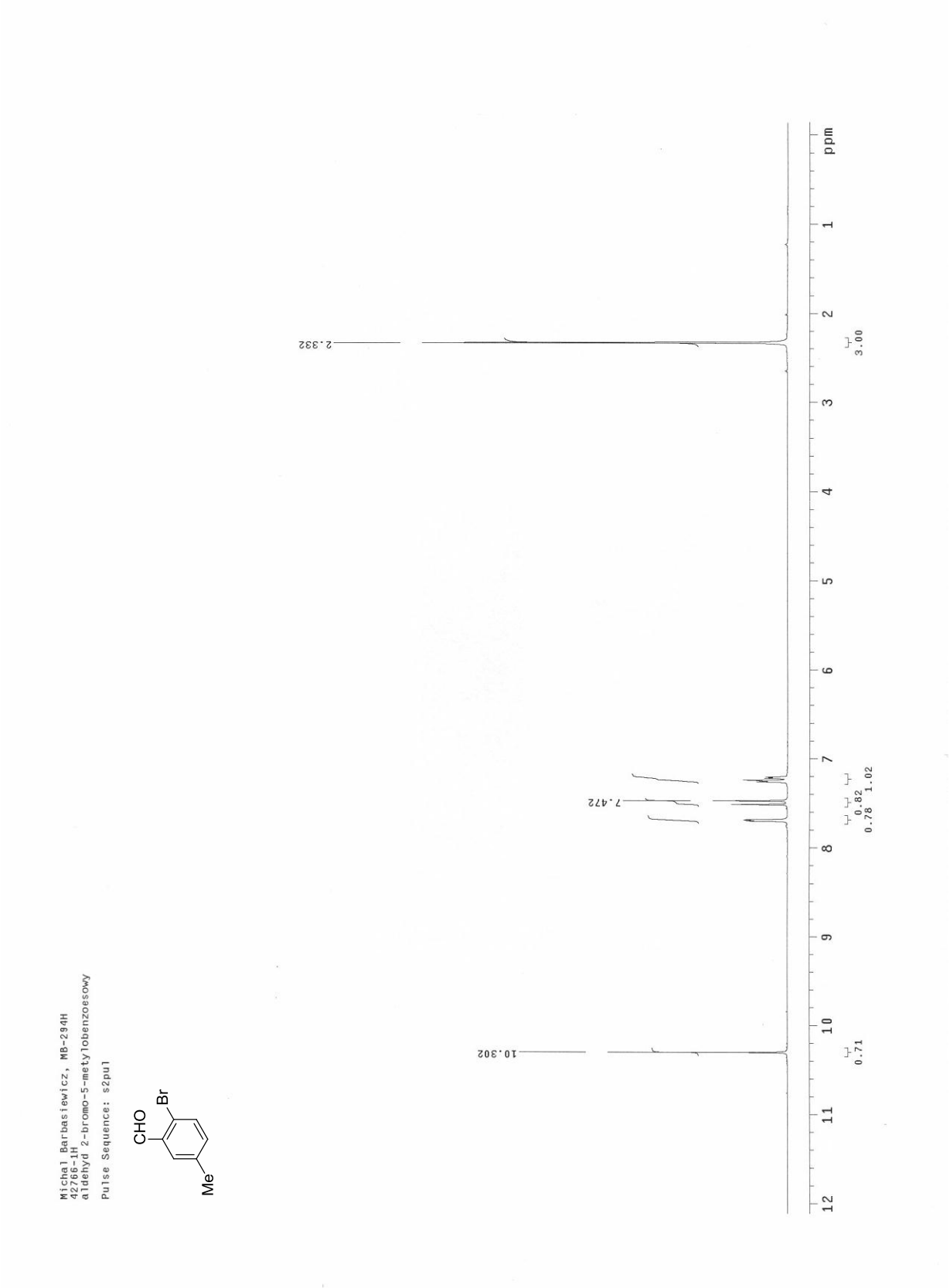
Reproduction of ^{1}H NMR spectrum of compound **14**.



Reproduction of ^{13}C NMR spectrum of compound **14**.



Reproduction of ^{1}H NMR spectrum of compound **15**.



Reproduction of ^{13}C NMR spectrum of compound **15**.