

SUPPORTING INFORMATION

Asymmetric Rh(II)-Catalyzed Cyclopropanation of Alkenes with Diaceptor Diazo Compounds: the *p*-Methoxyphenyl Ketone as a General Stereoselectivity Controlling Group

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General: Unless specified, all non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.¹ All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, Et₂O, CH₂Cl₂, benzene, DMF, CH₃CN, toluene, hexane, methanol) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et₃N, ClCH₂CH₂Cl, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F254). Visualization of the developed chromatogram was performed by UV absorbance or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.² Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm⁻¹). Nuclear magnetic resonance spectra (¹H, ¹³C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a Bruker AV 300, AMX 300, AV 400, AMX 400, or DMX 700 spectrometer. Chemical shifts for ¹H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for ¹³C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.16 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments. Optical rotations were determined with a Perkin-Elmer 341 polarimeter at 589 or 546 nm. Data are reported as follows: $[\alpha]_{\lambda}^{\text{temp}}$, concentration (c in g/100 mL), and solvent. High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l'Université de Montréal. Analytical SFC were performed at Laboratoire d'Analyse et de Séparation Chirale par SFC de l'Université de Montréal and Data are reported as follows: column type, eluent, flow rate, temperature, backpressure, wavelength and retention times (tr).

Reagents : All alkenes used in the cyclopropanation reactions were commercially available from Aldrich, except 4-Nitrostyrene which was prepared according to a standard Wittig methylenation procedure.³ TfN₃ is usually stored at -20°C as a 0.5 - 1M solution in hexane, prepared according to a literature procedure.⁴ The benzoic acids, CDI, MeNO₂, NaH, DIPEA, BzCl, Boc₂O, *p*-Methoxybenzoylacetonitrile, NaBH₄, LiAlH₄, Ni(ClO₄)₂•6H₂O, DIBAL, K₂CO₃, *n*-BuLi, CuCN, benzaldehyde, Sn(OTf)₂, Rh₂(OAc)₄, In powder were purchased from Aldrich, Alfa Aesar, Strem Chemicals or Pressure Chemicals and used without further purification. *m*-CPBA 77% was purchased from Aldrich and was recrystallized in 5% Et₂O/Hexane prior to use. Rh₂(S-TCPTTL)₄ was prepared according to a literature procedure.⁵ 2-chloro-1,3-dimethylimidazolium chloride is commercially available from Aldrich but can be readily prepared by treatment of 1,3-dimethyl-2-imidazolidinone with oxalyl chloride.⁶ 4'-methoxy-2-phenylacetophenone is commercially available from Aldrich but can be prepared by a standard Friedel-Crafts acylation procedure from anisole and phenylacetyl chloride.⁷ Indoline was purchased from Aldrich and purified by SiO₂ column chromatography prior to use.

Safety/Storage: Diazo compounds **1a-1i** were found to be stable for several months when stored neat at -20°C. Diazo compound **1j** readily decomposes within 2 weeks at -20°C, and thus it should be used immediately after its preparation. These compounds should be handled with great care due to their potential explosivity when exposed to heat or shocks. We have not thoroughly studied their behavior in this regard, but it should be noted that diazo **1f** was found to be explosive under shocks in our laboratories.

¹ D. F. Shriver, M. A. Drezdson, *The Manipulation of Air-Sensitive Compounds*; 2nd ed.; Wiley: New York, 1986.

² W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

³ Choi, H.-S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 901.

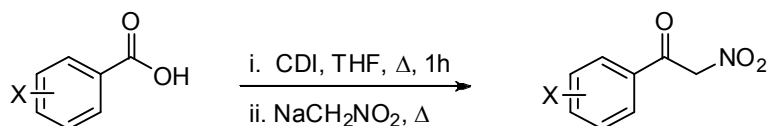
⁴ Charette, A. B.; Wurz, R. P.; Ollevier, T. *J. Org. Chem.* **2000**, *65*, 9252.

⁵ Tsutsui, H.; Yamaguchi, Y.; Kitagaki, S.; Nakamura, S.; Anada, M.; Hashimoto, S., *Tetrahedron: Asymmetry* **2003**, *14*, 817.

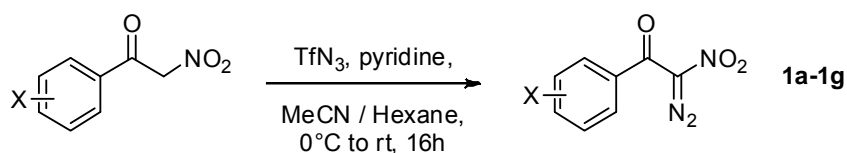
⁶ Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem. Eur. J.* **2005**, *11*, 1833.

⁷ Lubczyk, V.; Bachmann, H.; Gust, R. *J. Med. Chem.* **2002**, *45*, 5358.

Experimental Procedures and Characterization Data

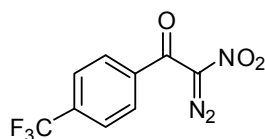
General procedure for the synthesis of α -nitro-diazoacetophenones (**1a-1g**)^{4,8}

A flame-dried, round-bottomed 250 mL flask equipped with a football-shaped magnetic stirring bar and a reflux condenser was charged with the benzoic acid (32.9 mmols, 1 equiv) and CDI (*N,N'*-carbonyldiimidazole; 6.39g, 39.4 mmols, 1.2 equiv). Dry THF was added (100 mL) and the resulting colourless solution was refluxed for 1 hour under Argon (solution A). During that time, NaH (60% in mineral oil) was added (1.6g, 39.4 mmols, 1.2 equiv) to a flame-dried 500 mL flask equipped with a football-shaped magnetic stirring bar, the flask was flushed with Argon and dry THF was added (60 mL) affording a milky heterogenous solution, to which CH₃NO₂ (50 mL, 931 mmols, 28.3 equiv) was slowly added at room temperature (CAUTION: exothermic H₂ formation). The resulting solution was stirred for a further 30 minutes at room temperature (solution B). Solution A was cooled to room temperature, and transferred to the flask containing solution B via cannula. The resulting light-brown heterogenous solution was refluxed overnight with vigorous stirring (16 hours), affording a light-yellow heterogenous solution, which was cooled to room temperature. Approximately 2/3 of the solvent was removed under vacuo, the resulting mixture was filtered on Büchner funnel, and the filter cake was rinsed thoroughly with cold THF. Once relatively dry, this filter cake was transferred into a 2L flask, along with 400 mL EtOAc and 600 mL H₂O. Vigorous stirring was maintained until complete dissolution, and the aqueous layer was acidified to pH 1 by dropwise addition of 12M HCl. The phases were separated, and the aqueous layer was extracted with 2 x 150mL EtOAc. The combined organic layers were washed with brine, dried on MgSO₄ and concentrated under vacuo to afford the pure α -nitroketone, which was used in the next step without further purification.

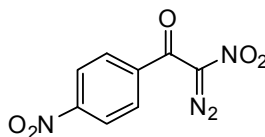


A 0.5M Tf-N₃ solution in hexanes was prepared according to a literature procedure.⁴ A flame-dried, round-bottomed 500 mL flask equipped with a football-shaped magnetic stirring bar was charged with the α -nitroketone (30.7 mmols, 1 equiv), dry MeCN (160 mL) was added followed by a 0.5M solution of Tf-N₃ in hexanes (92 mL, 46.1 mmols, 1.5 equiv). The flask was capped with a rubber septum and purged under Argon for 15 minutes before being cooled to 0°C using an ice/water bath. Freshly distilled pyridine (5 mL, 61.5 mmols, 2 equiv) was added dropwise over a period of 10 minutes at 0°C (maintaining vigorous stirring), and the resulting biphasic yellow solution was stirred and allowed to slowly warm to room temperature overnight (16 hours). The resulting biphasic orange solution was evaporated to dryness without heating and the brown oily residue obtained was rapidly purified by silica-gel chromatography using CHCl₃ as eluent, affording the pure α -nitro-diazoacetophenone **1a-1g**, which was stored in the freezer at -20°C (N.B. In order to minimize product decomposition, do not leave the crude α -nitro-diazoacetophenone neat for more than 15 minutes). ¹⁹F NMR analysis was performed to ensure the absence of TfN₃ and/or TfNH₂ in the final product.

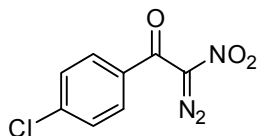
⁸ Baker, D. C.; Putt, S. R. *Synthesis* **1978**, 478.



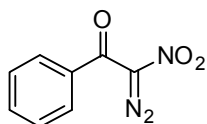
2-diazo-2-nitro-1-[4-(trifluoromethyl)phenyl]ethanone (1a): Yellow solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 58% isolated yield. mp 98-99°C (decomposition). $R_f = 0.46$ (100% CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.77 (s, br, 4H, ArH). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 179.9, 138.2, 134.8 (q, $J = 32.7$ Hz), 129.0 (2C), 125.6 (2C, q, $J = 3.6$ Hz), 123.5 (q, $J = 271.3$ Hz), 111.9 (br, C=N₂). $^{19}\text{F NMR}$ (CDCl_3 , 282 MHz): δ -64.7. IR (neat) 2158, 1629, 1533, 1304, 1171, 1122, 845.



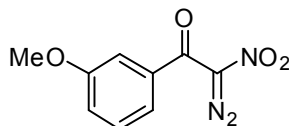
2-diazo-2-nitro-1-(4-nitrophenyl)ethanone (1b): Yellow solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 21% isolated yield. mp 77-78°C (decomposition). $R_f = 0.32$ (100% CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.35 (d, $J = 8.8$ Hz, 2H, ArH), 7.81 (d, $J = 8.8$ Hz, 2H, ArH). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 179.1, 149.8, 139.9, 129.1 (2C), 123.2 (2C), 112.4 (br, C=N₂). IR (neat) 2156, 1633, 1602, 1500, 1287, 1164, 934, 851.



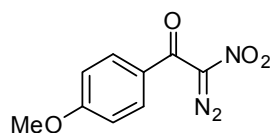
1-(4-chlorophenyl)-2-diazo-2-nitroethanone (1c): Yellow solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 66% isolated yield. mp 95-96°C (decomposition). $R_f = 0.45$ (100% CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.62 (d, $J = 9.2$ Hz, 2H, ArH), 7.49 (d, $J = 9.2$ Hz, 2H, ArH). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 179.5, 140.3, 133.4, 130.2 (2C), 129.0 (2C), 111.6 (br, C=N₂). IR (neat) 2161, 1630, 1588, 1528, 1486, 1290, 1158, 835.



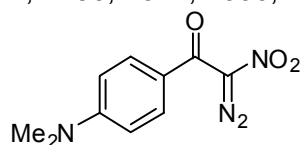
2-diazo-2-nitro-1-phenylethanone (1d): Yellow solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 77% isolated yield. mp 79-82°C (decomposition). $R_f = 0.41$ (100% CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.64 (m, 3H, ArH), 7.50 (m, 2H, ArH). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 180.4, 135.1, 133.8, 128.7 (2C), 128.6 (2C), 111.1 (br, C=N₂). IR (neat) 2133, 1670, 1629, 1596, 1522, 1447, 1294, 1233, 1161, 940, 921, 812, 776, 733, 692, 665.



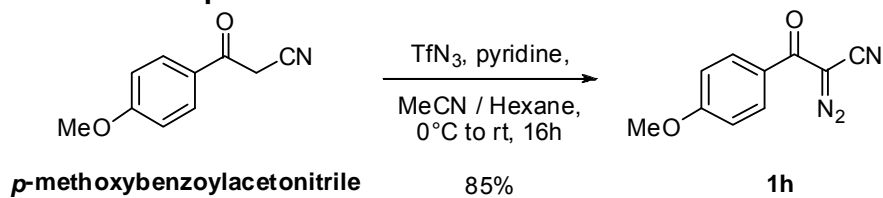
2-diazo-1-[3-(methoxy)phenyl]-2-nitroethanone (1e): Yellow oil. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 75% isolated yield. $R_f = 0.42$ (100% CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.37 (t, $J = 8.0$ Hz, 1H, ArH), 7.21 (d, $J = 8.0$ Hz, 1H, ArH), 7.17-7.12 (m, 2H, ArH), 3.82 (s, 3H, ArOCH₃). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 180.0, 159.8, 136.4, 129.8, 120.9, 120.1, 113.3, 110.8 (br, C=N₂), 55.7. IR (neat) 2941, 2838, 2154, 2128, 1669, 1639, 1597, 1581, 1509, 1290, 1246, 1156, 1038, 735.



2-diazo-1-[4-(methoxy)phenyl]-2-nitroethanone (1f): Yellow solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 80% isolated yield. mp 75-76°C (decomposition). R_f = 0.28 (100% CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 7.70 (d, J = 9.2 Hz, 2H, ArH), 6.98 (d, J = 9.2 Hz, 2H, ArH), 3.91 (s, 3H, ArOCH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 178.5, 164.3, 131.5 (2C), 127.4, 113.9 (2C), 110.7 (br, C=N₂), 55.7. IR (neat) 2977, 2344, 2156, 1624, 1606, 1530, 1503, 1287, 1259, 1165, 1022, 831.

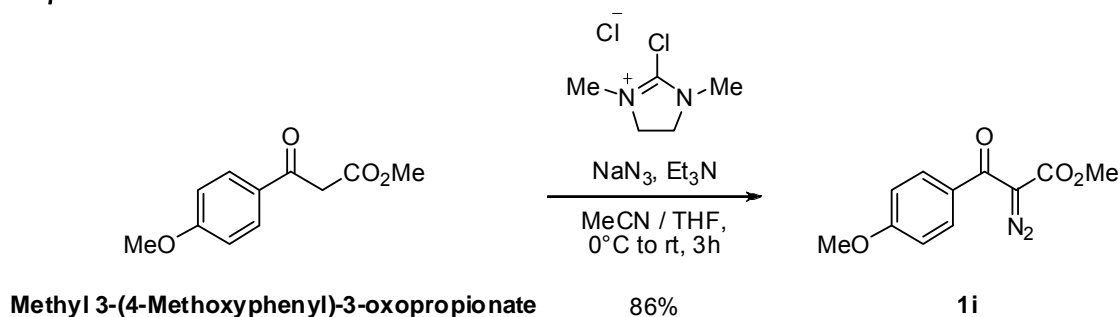


2-diazo-1-[4-(dimethylamino)phenyl]-2-nitroethanone (1g): Red solid. The general procedure for the synthesis of α -nitro-diazoacetophenones was followed. 29% isolated yield. mp 75-76°C (decomposition). R_f = 0.24 (100% CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 7.65 (d, J = 9.2 Hz, 2H, ArH), 6.67 (d, J = 9.2 Hz, 2H, ArH), 3.11 (s, 6H, N(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz): δ 176.7, 154.2, 131.8 (2C), 121.5, 110.5 (2C), 109.3 (br, C=N₂), 40.1 (2C). IR (neat) 2903, 2826, 2155, 2132, 1640, 1586, 1493, 1372, 1286, 1192, 1064, 822, 747.

Synthesis of α -cyano-diazoacetophenone **1h⁹**

2-diazo-3-[4-(methoxy)phenyl]-3-oxopropanenitrile (1h): Yellow solid. A 0.5M Tf-N₃ solution in hexanes was prepared according to a literature procedure.⁴ A flame-dried, round-bottomed 250 mL flask equipped with a football-shaped magnetic stirring bar was charged with *p*-methoxybenzoylacetonitrile (1.80 g, 10.3 mmol, 1.0 equiv), dry MeCN (60 mL) was added and the resulting solution was cooled to 0°C using an ice/water bath. A 0.5M solution of Tf-N₃ in hexanes (30.8 mL, 15.4 mmol, 1.5 equiv) was added, the flask was capped with a rubber septum and flushed with argon for 15 minutes. Freshly distilled pyridine (1.70 mL, 20.5 mmol, 2.0 equiv) was added dropwise over a period of 5 minutes at 0°C (maintaining vigorous stirring), and the resulting biphasic yellow solution was stirred and allowed to slowly warm to room temperature overnight (16 hours). The resulting biphasic brown solution was evaporated to dryness without heating and the brown oily residue obtained was rapidly purified by silica-gel chromatography using 80% CHCl₃ in hexane as eluent, affording the pure α -cyano-diazoacetophenone **1h** (1.76 g, 85%) as a yellow solid, which was stored in the freezer at -20°C (N.B. In order to minimize product decomposition, do not leave the crude α -cyano-diazoacetophenone neat for more than 15 minutes). ¹⁹F NMR analysis was performed to ensure the absence of TfN₃ and/or TfNH₂ in the final product. mp 62°C. R_f = 0.38 (80% CHCl₃/hexane) ¹H NMR (CDCl₃, 400 MHz): δ 7.93 (d, *J* = 12.0 Hz, 2H, ArH), 6.98 (d, *J* = 12.0 Hz, 2H, ArH), 3.89 (s, 3H, ArOCH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 181.2, 164.2, 130.6 (2C), 127.4, 114.2 (2C), 109.8, 58.5, 55.7. IR (neat) 2920, 2221, 2136, 1638, 1602, 1512, 1265, 1252, 1174, 740.

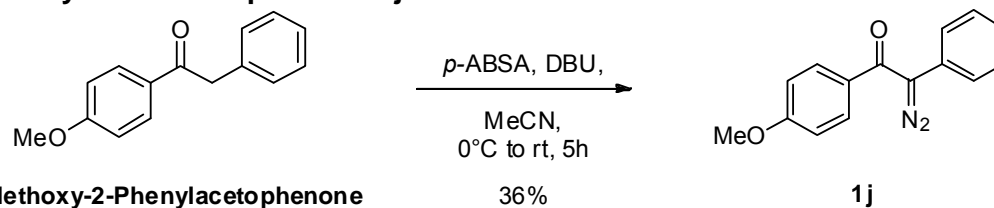
⁹ Wurz, R. P.; Lin, W.; Charette, A. B. *Tetrahedron Lett.* **2003**, *44*, 8845.

Synthesis of β -keto-diazoester **1i**¹⁰

methyl 2-diazo-3-[4-(methoxy)phenyl]-3-oxopropanoate (1i): Yellow oil. (Methyl 3-(4-Methoxyphenyl)-3-oxopropionate was prepared according to a literature procedure).¹¹ A flame-dried, round-bottomed 250 mL flask equipped with a football-shaped magnetic stirring bar was charged with 2-chloro-1,3-dimethylimidazolium chloride (2.92 g, 17.3 mmol, 1.2 equiv), dry MeCN (40 mL) was added and the resulting solution was cooled to 0°C using an ice/water bath, before NaN₃ (1.12 g, 17.3 mmol, 1.2 equiv) was added in one portion. The resulting mixture was stirred at 0°C for 30 minutes (solution A). A separate round-bottomed 200 mL equipped with a football-shaped magnetic stirring bar was charged with methyl 3-(4-methoxyphenyl)-3-oxopropionate (3.00 g, 14.4 mmol, 1.0 equiv), THF (60 mL) and freshly distilled Et₃N (4.1 mL, 28.9 mmol, 2 equiv) (solution B). Solution B was transferred to the flask containing solution A via cannula affording a greenish heterogenous mixture, which was stirred at 0°C until completion of the reaction (follow by TLC, ca. 2 hours). The reaction was quenched by slow addition of H₂O (70 mL) at 0°C and was left to stir 5-10 minutes at this temperature. The mixture was extracted with 3 x 120 mL CH₂Cl₂, the combined organic layers were washed with 1 x 100 mL H₂O, 1 x 100 mL brine, dried on Na₂SO₄, and concentrated under vacuo to afford the crude diazo **1i** as a greenish oil. Purification on silica-gel chromatography using 25% EtOAc in hexane afforded the pure β -keto-diazoester **1i** as a yellow oil (2.91 g, 86%), which was stored in the freezer at -20°C. *R*_f = 0.39 (25% EtOAc/hexane) ¹H NMR (CDCl₃, 400 MHz): δ 7.68 (d, *J* = 6.8 Hz, 2H, ArH), 6.93 (d, *J* = 6.8 Hz, 2H, ArH), 3.87 (s, 3H, ArOCH₃), 3.82 (s, 3H, CO₂CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 185.2, 163.3, 161.9, 131.1 (2C), 129.4, 113.3 (2C), 75.5 (br, C=N₂), 55.5, 52.4. IR (neat) 2131, 1724, 1601, 1306, 1257, 1175, 1121, 532.

¹⁰ Modified from: Kitamura, M.; Tashiro, N.; Okauchi, T. *Synlett* **2009**, 2843.

¹¹ Mordant, C.; Caño de Andrade, C.; Touati, R.; Ratovelomanana-Vidal, V.; Ben Hassine, B.; Genêt, J.-P. *Synthesis* **2003**, 2405.

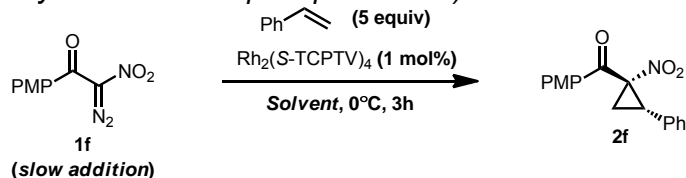
Synthesis of α -phenyl-diazoacetophenone **1j¹²**

2-diazo-1-[4-(methoxy)phenyl]-2-phenylethanone (1j): Yellow solid. A flame-dried, round-bottomed 50 mL flask equipped with a football-shaped magnetic stirring bar was charged with 4'-methoxy-2-phenylacetophenone (500 mg, 2.21 mmol, 1.0 equiv), dry MeCN (22 mL) was added and the resulting solution was cooled to 0°C using an ice/water bath. *p*-ABSA (637 mg, 2.65 mmol, 1.2 equiv) was added in one portion and the mixture was stirred until dissolution. DBU (0.400 mL, 2.67 mmol, 1.21 equiv) was added dropwise over 30 minutes, the mixture was stirred at 0°C for 2 hours before being allowed to warm to room temperature and stirred for 2 more hours. The resulting solution was poured into a mixture of Et₂O (100 mL) and aq. sat. NaHCO₃ (100 mL), stirred for 10 minutes, the organic layer was separated and the aqueous layer was extracted twice with Et₂O. The combined organic layers were dried (MgSO₄) and concentrated under reduced pressure. The resulting dark red residue was rapidly purified on silica gel using 9% EtOAc in Hexane as eluent, and the orange solid obtained was triturated in Hexane (10 mL) for 16 hours, to afford the pure α -phenyl-diazoacetophenone **1j** (202 mg, 36%) as a yellow solid. mp 84-85°C (decomposition). *R*_f = 0.22 (20% Et₂O in hexane) ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (d, *J* = 8.6 Hz, 2H, ArH), 7.47-7.36 (m, 4H, ArH), 7.26 (t, *J* = 7.1 Hz, 1H, ArH), 6.90 (d, *J* = 8.6 Hz, 2H, ArH), 3.85 (s, 3H, ArOCH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 187.4, 162.5, 130.5, 130.2 (2C), 129.1 (2C), 127.0, 126.7, 126.3 (2C), 113.8 (2C), 72.5, 55.5. IR (neat) 2081, 1627, 1593, 1495, 1443, 1328, 1234, 1170, 1020, 836, 757, 691.

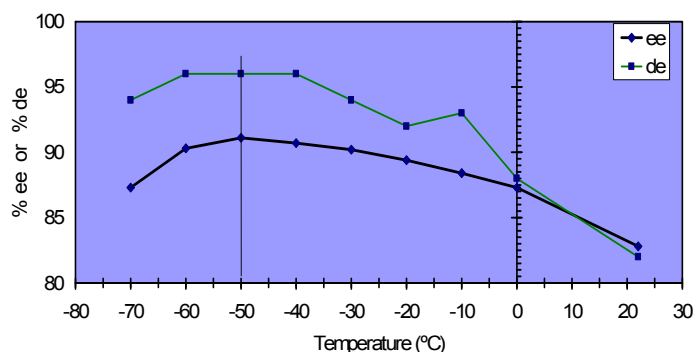
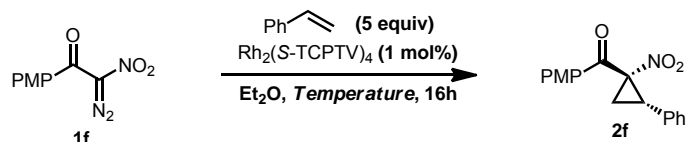
¹² Denton, J. R.; Davies, H. M. L. *Org. Lett.* **2009**, *11*, 787.

Enantioselective Rh(II)-Catalyzed Cyclopropanations**General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation using 1a-1g**

Solvent / Temperature Optimization for the enantioselective cyclopropanation with diazo 1f: (catalyst optimization is already disclosed in a prior publication)¹³



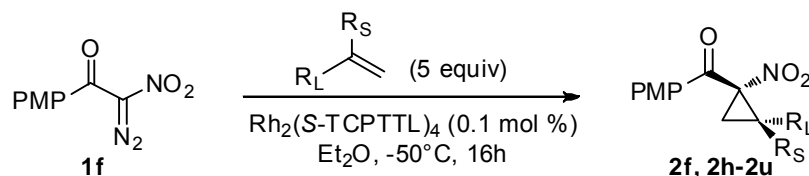
Entry	Solvent	Yield (%) ¹	dr (cis : trans) ²	ee (% , cis) ³
1	CH ₂ Cl ₂	72	91 : 9	71
2	EtOAc	67	92 : 8	78
3	Pentane / EtOAc	64	93 : 7	82
4	Benzene / EtOAc	61	81 : 19	20
5	Toluene	66	86 : 14	65
6	PhCl	25	82 : 18	40
7	PhOMe	9	88 : 12	42
8	THF	0	-	-
9	Et ₂ O	37	93 : 7	87
10	Et ₂ O / EtOAc	64	93 : 7	86
11	DME	27	97 : 3	86
12	Dioxane / EtOAc	64	95 : 5	82
13	<i>t</i> -BuOMe	57	94 : 6	86
14	MeNO ₂	61	88 : 12	68
15	MeNO ₂ / Et ₂ O	65	92 : 8	82
16 ⁴	Et ₂ O	64	93 : 7	87
17 ⁵	Et ₂ O	68	94 : 6	87

¹ Isolated Yield² dr was determined by ¹H NMR analysis of the crude mixture³ ee was determined by SFC on chiral stationary phase (Chiralcel OJ) after flash chrom.⁴ the diazo was added via syringe within 5 minutes and the reaction was run for 16 hours⁵ the diazo was added in the solid state in one portion and the reaction was run for 16 hours¹³ Lindsay, V. N. G.; Lin, W.; Charette, A. B. *J. Am. Chem. Soc.* **2009**, *131*, 16383.

General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation using α -nitrodiazoacetphenones 1a-1g (Table 2 and 5)

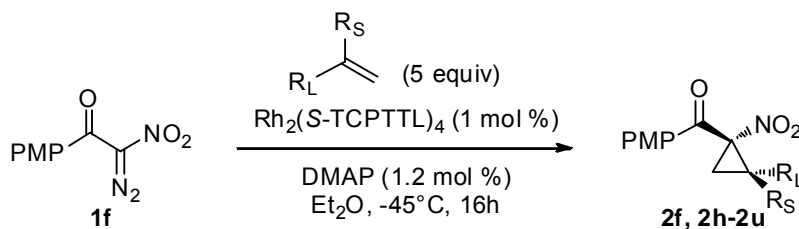
(the racemic products were synthesized according to a literature procedure)¹⁴

(the results in table 2 were obtained using the same procedure, but with 1 mol% of Rh₂(S-TCPTTL)₄ instead of 0.1 mol%)

Table 5, method A (no additive):

A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with 1 mL of a 0.20 mM stock-solution of catalyst Rh₂(S-TCPTTL)₄ in dry Et₂O (0.00020 mmol, 0.001 equiv), followed by 2 mL of dry Et₂O and the alkene (1 mmol, 5 equiv) at room temperature (20-23°C). The resulting green homogenous solution was cooled to -50°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before diazo **1f** (44.2 mg, 0.20 mmol, 1 equiv) was added in the solid state under air, the flask was capped back with the rubber septum and the resulting heterogenous yellow solution was stirred for a further 16 hours at -50°C, keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting milky heterogenous solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH₂Cl₂, and evaporated to dryness. (The d.r. was determined at this point using ¹H NMR). The resulting residue was purified by silica-gel chromatography using CH₂Cl₂/hexanes as eluent (various ratios from 50% CH₂Cl₂/hexanes to 80% CH₂Cl₂/hexanes, depending on the nature of the alkene) to afford the pure cyclopropane product (**2f, 2h-2u**) as a mixture of diastereomers, which was submitted to SFC analysis using a chiral stationary phase for ee determination. The pure *cis*-cyclopropane product could usually be obtained by simple trituration in hexanes, with virtually no loss of yield with respect to the initial *cis/trans* ratio. On a larger scale according to table 8 (14 mmol), the residue obtained after silica-gel chromatography could be recrystallized using 30% CHCl₃/hexane as solvent to obtain the product as a single stereoisomer (>99:1 dr, >99% ee) with various yields of recrystallization (always higher than 90%).

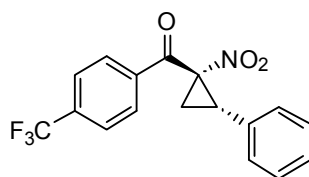
¹⁴ Charette, A. B.; Wurz, R. P.; Ollevier, T. *Helv. Chim. Acta* **2002**, *85*, 4468.

Table 5, method B (with 1.2 mol% DMAP added):

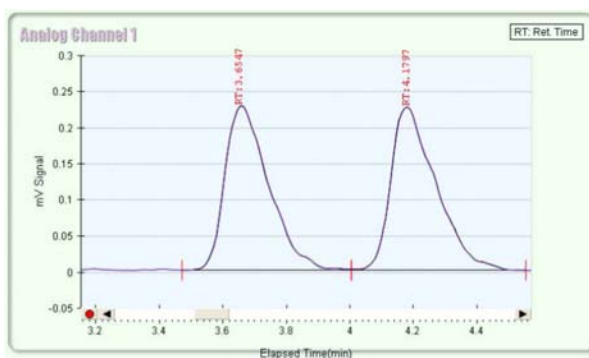
A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with $\text{Rh}_2(\text{S-TCPTTL})_4$ (3.9 mg, 0.0020 mmol, 0.01 equiv) followed by 3 mL of dry Et_2O . A 24 mM solution of DMAP in dry Et_2O (100 μL , 0.0024 mmol, 0.012 equiv) was added, the green homogenous solution rapidly became pink, the alkene (115 μL , 1.00 mmol, 5.00 equiv) was added at room temperature (20-23°C), and the resulting solution was cooled to -45°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before diazo **1f** (44.2 mg, 0.200 mmol, 1.00 equiv) was added in the solid state under air, the flask was capped back with the rubber septum and the resulting heterogenous solution was stirred for a further 16 hours at -50°C , keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting milky yellow heterogenous solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH_2Cl_2 , and evaporated to dryness. (The dr was determined at this point using ^1H NMR). Purification on silica gel chromatography using CH_2Cl_2 /hexanes as eluent (various ratios from 50% CH_2Cl_2 /hexanes to 80% CH_2Cl_2 /hexanes, depending on the nature of the alkene) to afford the pure cyclopropane product (**2f**, **2h-2u**) as a mixture of diastereomers, which was submitted to SFC analysis using a chiral stationary phase for ee determination. The pure *cis*-cyclopropane product could usually be obtained by simple trituration in hexanes, with virtually no loss of yield with respect to the initial *cis/trans* ratio. On a larger scale, the residue obtained after silica-gel chromatography could be recrystallized using 30% CHCl_3 /hexane as solvent to obtain the product as a single stereoisomer (single diastereomer, >99%ee) with various yields of recrystallization.

Absolute Configuration

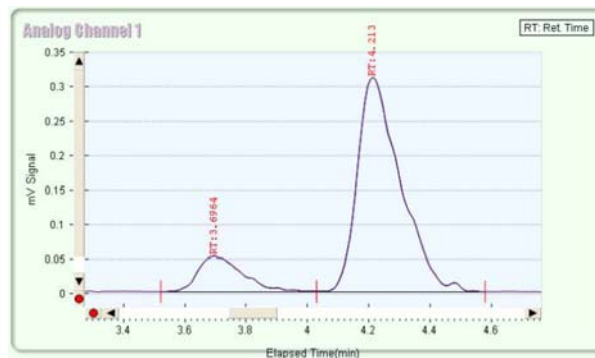
The absolute configuration of α -nitro acetophenones **2a-2u** was assigned by X-Ray (compound **2f**, see page S77) and confirmed by comparison of the sign of optical rotation of the *N*-Boc amino acid **9** with a literature value (See page S65).



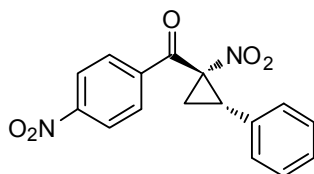
[(1S,2S)-1-nitro-2-phenylcyclopropyl][4-(trifluoromethyl)phenyl]methanone (2a): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1a** was used as substrate). 80% isolated yield, 70:30 (2.3:1) d.r., 71% ee. mp 111-113°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 280 nm, t_r (minor) 3.7 min, t_r (major) 4.2 min. $R_f = 0.55$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -143.5$ (c 0.78, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.98 (d, $J = 8.4$ Hz, 2H, ArH), 7.77 (d, $J = 8.4$ Hz, 2H, ArH), 7.41-7.28 (m, 5H, ArH), 3.91 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.07 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.05 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 188.4, 138.1, 135.3 (q, $J = 32.8$ Hz), 131.1, 129.0 (2C), 128.8 (3C), 128.4 (2C), 126.2 (q, $J = 3.8$ Hz), 125.3, 121.7, 77.3, 33.1, 22.1. ^{19}F NMR (CDCl_3 , 282 MHz): δ -64.7. IR (neat) 3030, 1700 (C=O), 1542, 1528 (NO_2), 1324 (NO_2), 1169, 1124, 1114, 1064, 985, 696. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$: 336.0842, found 336.0841.



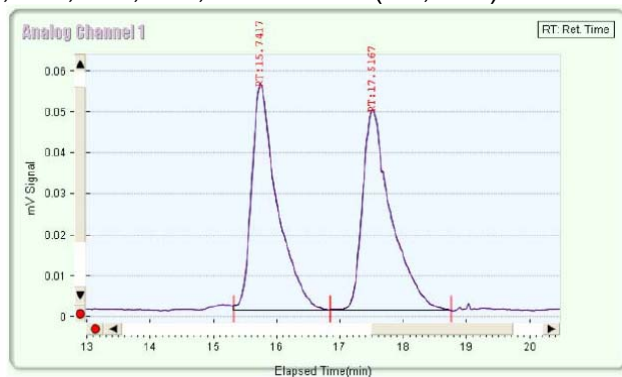
Peak Name	Area %	Area	Retention Time
Peak1	49.4369	2.1462	3.6547 min
Peak3	50.5631	2.1951	4.1797 min



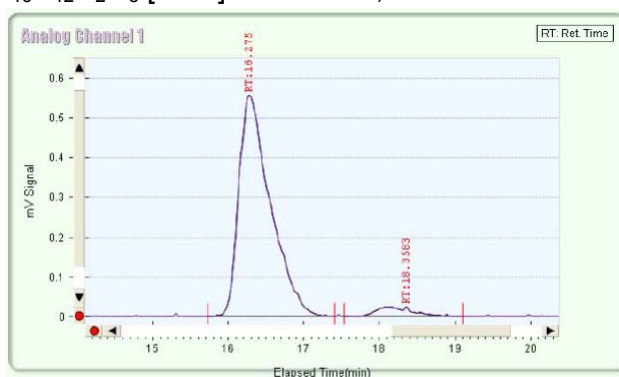
Peak Name	Area %	Area	Retention Time
Peak1	14.5458	0.5086	3.6964 min
Peak3	85.4542	2.9878	4.213 min



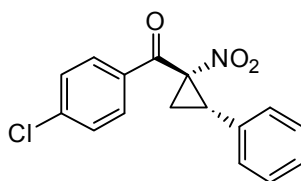
(4-nitrophenyl)[(1S,2S)-1-nitro-2-phenylcyclopropyl]methanone (2b): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1b** was used as substrate). 76% isolated yield, 92:8 (12:1) d.r., 91% ee. mp 148-150°C (decomposition). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (major) 16.3 min, t_r (minor) 18.4 min. R_f = 0.24 (50:50 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -189.4 (c 0.95, CHCl_3 , 12:1 mixture of diastereomers). ^1H NMR (CDCl_3 , 400 MHz): δ 8.35 (d, J = 8.8 Hz, 2H, ArH), 8.02 (d, J = 8.8 Hz, 2H, ArH), 7.41-7.29 (m, 5H, ArH), 3.93 (t, J = 9.6 Hz, 1H, CH cyclopropane), 3.10 (dd, J = 6.4, 9.6 Hz, 1H, CH_2 cyclopropane), 2.07 (dd, J = 6.4, 9.6 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 188.2, 150.7, 140.1, 130.8, 129.0 (7C), 124.4 (2C), 77.3, 33.6, 22.5. IR (neat) 1700 (C=O), 1604, 1530 (NO_2), 1349 (NO_2), 1284, 988, 861, 754, 691. HRMS (ES, Pos) Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 313.0819, found 313.0825.



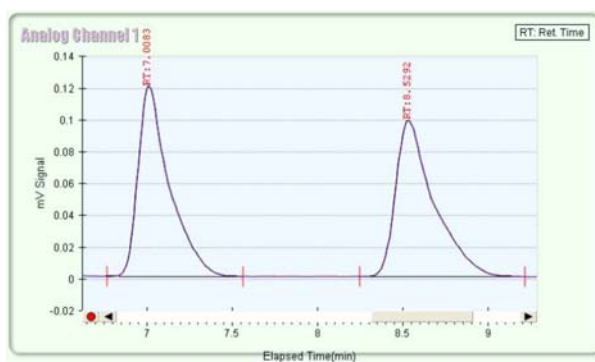
Peak Name	Area %	Area	Retention Time
	50.0933	1.54	15.7417 min
	49.9067	1.5343	17.5167 min



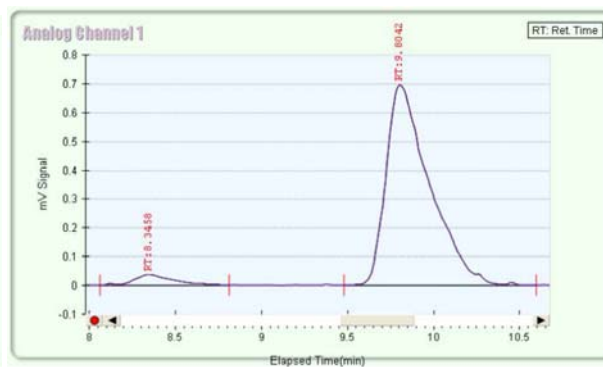
Peak Name	Area %	Area	Retention Time
	95.5633	15.9343	16.275 min
	4.4367	0.7398	18.3583 min



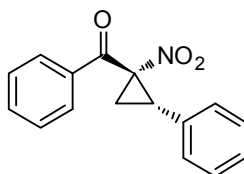
(4-chlorophenyl)[(1S,2S)-1-nitro-2-phenylcyclopropyl]methanone (2c): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1c** was used as substrate). 82% isolated yield, 96:4 (24:1) d.r., 92% ee. mp 105-106°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 8.3 min, t_r (major) 9.8 min. $R_f = 0.51$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -209.0$ (c 0.34, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.83 (d, $J = 8.8$ Hz, 2H, ArH), 7.48 (d, $J = 8.8$ Hz, 2H, ArH), 7.39-7.29 (m, 5H, ArH), 3.86 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.03 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.99 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 187.7, 140.7, 133.4, 131.3, 129.6 (2C), 129.5 (2C), 129.0 (2C), 128.8 (2C), 128.7, 76.9, 32.7, 21.6. IR (neat) 3091, 3065, 3026, 1697 (C=O), 1542, 1528 (NO_2), 1357 (NO_2), 1286, 1085, 983, 829, 695. HRMS (ES, Pos) Calcd for $\text{C}_{16}\text{H}_{12}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 302.0579, found 302.0581.



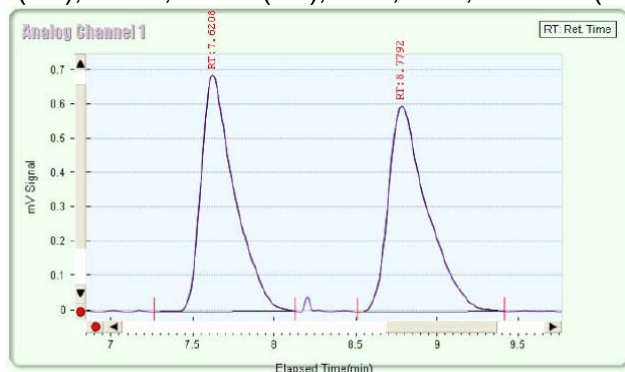
Peak Name	Area %	Area	Retention Time
	50.0146	1.5101	7.0083 min
	49.9854	1.5092	8.5292 min



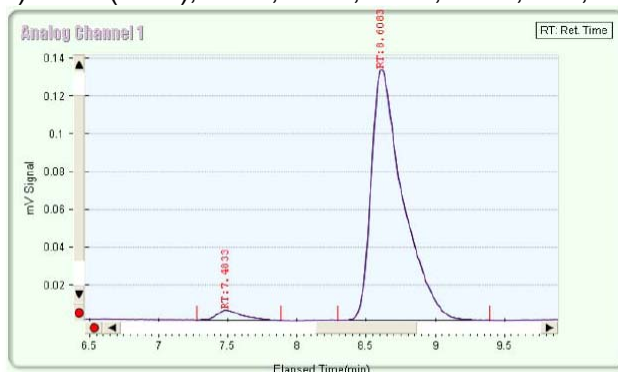
Peak Name	Area %	Area	Retention Time
	4.152	0.524	8.3458 min
	95.848	12.097	9.8042 min



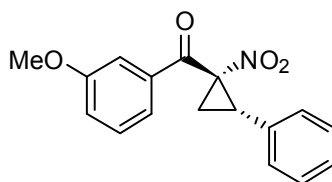
[(1S,2S)-1-nitro-2-phenylcyclopropyl](phenyl)methanone (2d): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1d** was used as substrate). 80% isolated yield, 96:4 (24:1) d.r., 94% ee. mp 141-142°C (decomposition). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm. t_r (minor) 7.4 min, t_r (major) 8.6 min. R_f = 0.52 (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -217.3 (c 0.30, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, J = 7.2 Hz, 2H, ArH), 7.62 (t, J = 7.6 Hz, 1H, ArH), 7.50 (t, J = 7.6 Hz, 2H, ArH), 7.34 (m, 5H, ArH), 3.88 (t, J = 9.6 Hz, 1H, CH cyclopropane), 3.04 (dd, J = 6.8, 9.6 Hz, 1H, CH_2 cyclopropane), 1.99 (dd, J = 6.8, 9.6 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 188.8, 135.0, 134.1, 131.5, 129.2 (2C), 129.1 (2C), 128.8 (2C), 128.6, 128.2 (2C), 77.0, 32.4, 21.5. IR (neat) 1683 (C=O), 1528, 1448, 1351, 1286, 795, 686.



Peak Name	Area %	Area	Retention Time
	49.8425	9.7225	7.6208 min
	50.1575	9.7839	8.7792 min



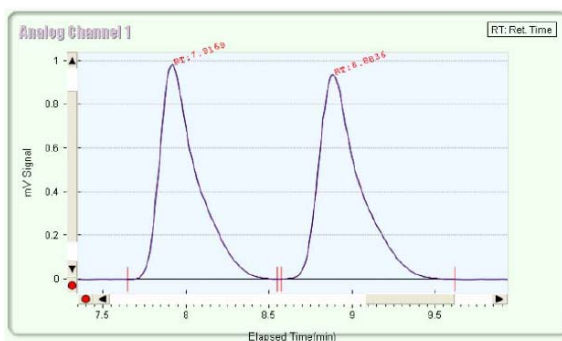
Peak Name	Area %	Area	Retention Time
	2.9683	0.064	7.4833 min
	97.0317	2.093	8.6083 min



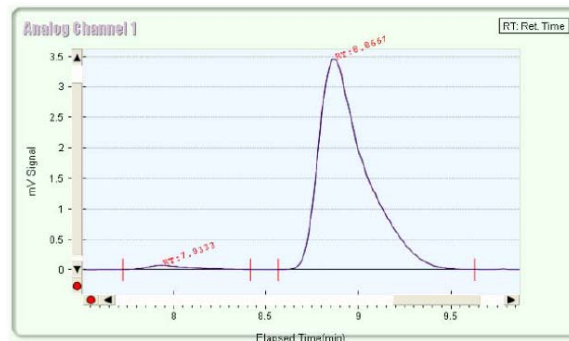
[3-(methoxy)phenyl][(1S,2S)-1-nitro-2-phenylcyclopropyl]methanone (2e): white crystalline solid.

The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1e** was used as substrate).

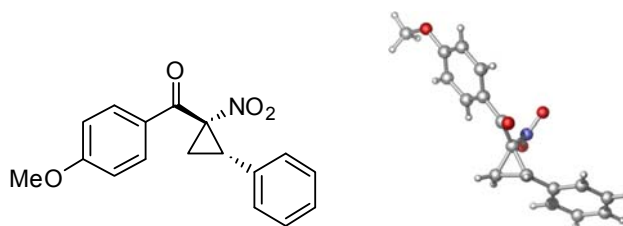
72% isolated yield, 98:2 (49:1) d.r., 96% ee. mp 94-95°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 7.9 min, t_r (major) 8.9 min. R_f = 0.51 (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -281.1 (c 0.63, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.49-7.29 (m, 8H, ArH), 7.18-7.12 (m, 1H, ArH), 3.87 (s, 3H, ArOCH_3), 3.86 (t, J = 9.6 Hz, 1H, CH cyclopropane), 3.03 (dd, J = 6.8, 9.6 Hz, 1H, CH_2 cyclopropane), 1.99 (dd, J = 6.8, 9.6 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.7, 160.2, 136.3, 131.5, 130.1, 129.0 (2C), 128.7 (2C), 128.6, 120.6, 120.5, 112.7, 77.1, 55.6, 32.4, 21.5. IR (neat) 2939, 1687 (C=O), 1598, 1582, 1534 (NO_2), 1452, 1430, 1352 (NO_2), 1290, 1254, 1158. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 298.1074, found 298.1070.



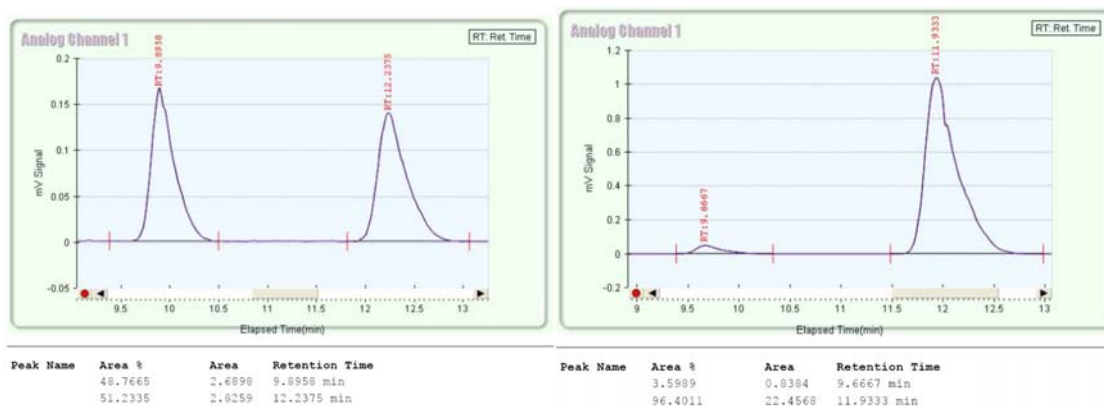
Peak Name	Area %	Area	Retention Time
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Peak2	50.8908	15.758	8.8836 min



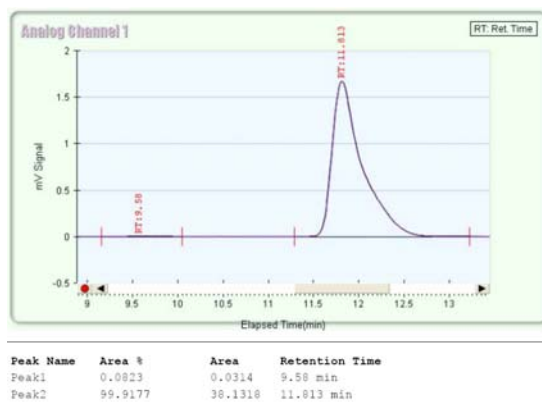
Peak Name	Area %	Area	Retention Time
Peak1	1.8074	1.1018	7.9333 min
Peak2	98.1926	59.8573	8.8667 min

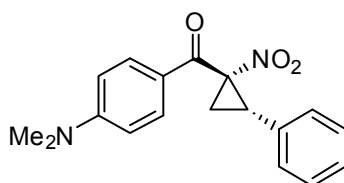


[4-(methoxyphenyl)[(1S,2S)-1-nitro-2-phenylcyclopropyl]methanone (2f): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). **80% isolated yield, 98:2 (49:1) d.r., 93% ee** (method **A**), **78% isolated yield, 97:3 d.r., 95% ee** (method **B**). On a larger scale according to table **8** (14 mmol), the residue obtained after silica-gel chromatography could be recrystallized using 30% CHCl₃/hexane as solvent to obtain the product as a single stereoisomer (>99:1 dr, >99% ee) in 72% overall yield from **1f**. mp 134-135°C. Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, *t*_r (minor) 9.7 min, *t*_r (major) 11.9 min. *R*_f = 0.30 (60:40 CH₂Cl₂:Hexane). [α]_D²⁰ = -203.7 (*c* 1.03, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 7.90 (d, *J* = 8.8 Hz, 2H, ArH), 7.41-7.27 (m, 5H, ArH), 6.97 (d, *J* = 8.8 Hz, 2H, ArH), 3.88 (s, 3H, ArOCH₃), 3.83 (t, *J* = 9.6 Hz, 1H, CH cyclopropane), 3.01 (dd, *J* = 6.8, 9.6 Hz, 1H, CH₂ cyclopropane), 1.94 (dd, *J* = 6.8, 9.6 Hz, 1H, CH₂ cyclopropane). ¹³C NMR (CDCl₃, 75 MHz): δ 186.7, 164.4, 131.8, 130.8 (2C), 129.0 (2C), 128.7 (2C), 128.5, 127.6, 114.5 (2C), 77.4, 55.7, 32.1, 21.0. IR (neat) 3089, 2940, 2844, 1675 (C=O), 1601, 1532 (NO₂), 1350 (NO₂), 1292, 1265, 1018, 982. HRMS (ES, Pos) Calcd for C₁₇H₁₅NO₄ [M+H]⁺: 298.1074, found 298.1068.

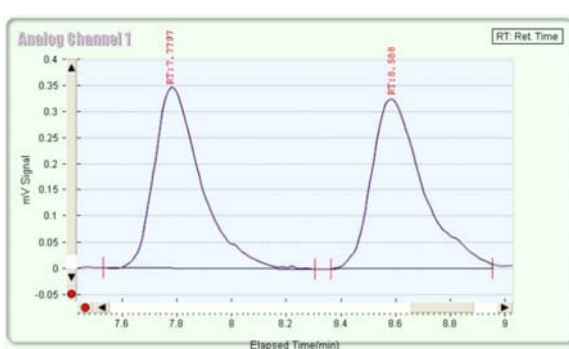


After recrystallization:

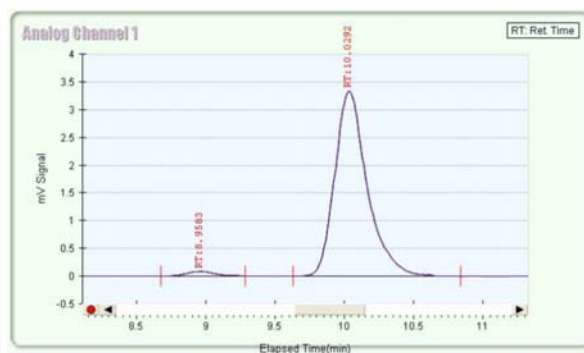




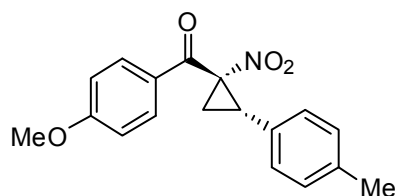
[4-(dimethylamino)phenyl][(1S,2S)-1-nitro-2-phenylcyclopropyl]methanone (2g): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1g** was used as substrate). **38% isolated yield, 98.8:1.2 (83:1) d.r., 96% ee.** mp 211-212°C (decomposition). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 15% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 9.0 min, t_r (major) 10.0 min. $R_f = 0.18$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -183.6$ (c 0.43, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.84 (d, $J = 8.8$ Hz, 2H, ArH), 7.40-7.26 (m, 5H, ArH), 6.66 (d, $J = 8.8$ Hz, 2H, ArH), 3.78 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.08 (s, 6H, ArN(CH₃)₂), 2.97 (dd, $J = 6.4, 9.6$ Hz, 1H, CH₂ cyclopropane), 1.88 (dd, $J = 6.4, 9.6$ Hz, 1H, CH₂ cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 185.4, 154.1, 132.2, 131.0 (2C), 129.1 (2C), 128.6 (2C), 128.3, 121.9, 111.1 (2C), 76.7, 40.1 (2C), 31.8, 20.1. IR (neat) 3018, 2917, 1660 (C=O), 1605, 1524 (NO₂), 1376, 1349 (NO₂), 1165, 821. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 311.1390, found 311.1395.



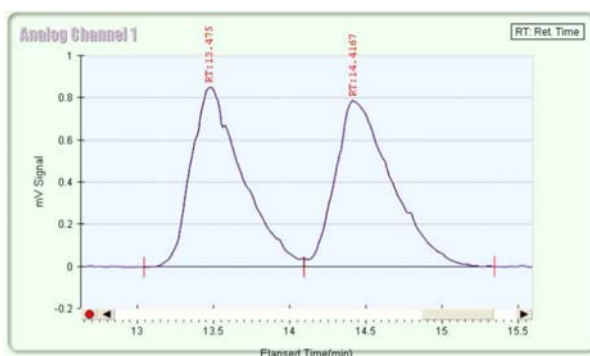
Peak Name	Area %	Area	Retention Time
Peak1	49.1804	4.0523	7.7797 min
Peak2	50.8196	4.1874	8.588 min



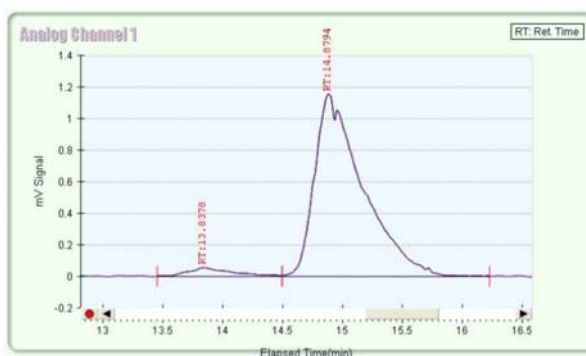
Peak Name	Area %	Area	Retention Time
Peak1	2.0762	1.1389	8.9583 min
Peak2	97.9238	53.7153	10.0292 min



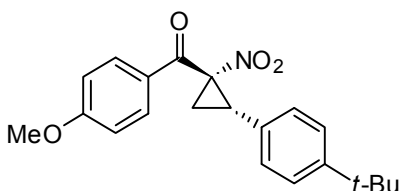
[4-(methoxy)phenyl][(1S,2S)-2-(4-methylphenyl)-1-nitrocyclopropyl]methanone (2h): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). 75% isolated yield, 97:3 d.r., 92% ee (method **A**), 83% isolated yield, 97:3 d.r., 94% ee (method **B**). mp 139-140°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 5% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 13.8 min, t_r (major) 14.9 min. $R_f = 0.32$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -212.1$ (c 1.00, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.89 (d, $J = 8.8$ Hz, 2H, ArH), 7.22 (d, $J = 7.6$ Hz, 2H, ArH), 7.14 (d, $J = 7.6$ Hz, 2H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.80 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 2.98 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.30 (s, 3H, ArCH_3), 1.92 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.9, 164.3, 138.3, 130.7 (2C), 129.4 (2C), 128.9 (2C), 128.6, 127.6, 114.4 (2C), 76.8, 55.7, 32.0, 21.3, 21.1. IR (neat) 3087, 3014, 1668 (C=O), 1596, 1571, 1527 (NO_2), 1346 (NO_2), 1297, 1265, 1160, 1026. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 312.1230, found 312.1237.



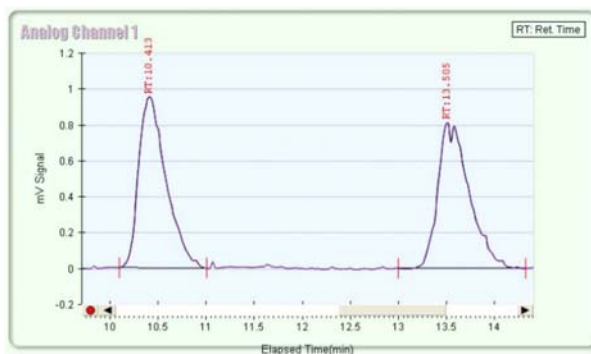
Peak Name	Area %	Area	Retention Time
Peak1	49.4155	19.7257	13.475 min
Peak3	50.5845	20.1923	14.4167 min



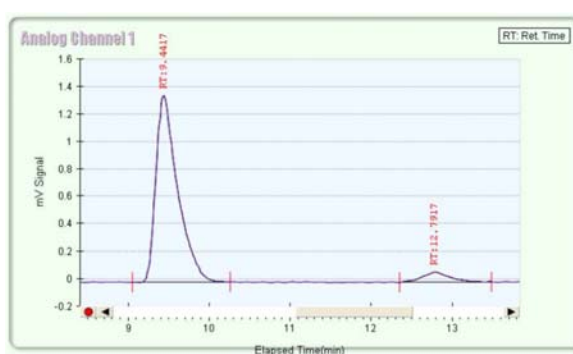
Peak Name	Area %	Area	Retention Time
Peak1	4.0095	1.3406	13.8378 min
Peak3	95.9905	32.0954	14.8794 min



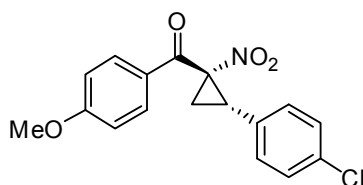
{{(1S,2S)-2-[4-(1,1-dimethylethyl)phenyl]-1-nitrocyclopropyl}[4-(methoxy)phenyl]methanone (2i): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). 65% isolated yield, 94:6 d.r., 87% ee (method **A**), 71% isolated yield, 90:10 d.r., 89% ee (method **B**). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 5% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 9.4 min, t_r (minor) 12.8 min. $R_f = 0.38$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -194.4$ (c 0.22, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.92 (d, $J = 8.8$ Hz, 2H, ArH), 7.37 (d, $J = 8.0$ Hz, 2H, ArH), 7.27 (d, $J = 8.0$ Hz, 2H, ArH), 6.99 (d, $J = 8.8$ Hz, 2H, ArH), 3.90 (s, 3H, ArOCH_3), 3.80 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.00 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.94 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.32 (s, 9H, $\text{ArC}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.9, 164.4, 151.5, 130.8 (2C), 128.7 (2C), 128.6, 127.7, 125.7 (2C), 114.5 (2C), 76.8, 55.7, 34.7, 32.0, 31.4 (3C), 21.1. IR (neat) 2972, 1678 (C=O), 1600, 1535 (NO_2), 1511, 1349 (NO_2), 1291, 1261, 1165, 1018. HRMS (ES, Pos) Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 354.1700, found 354.1697.



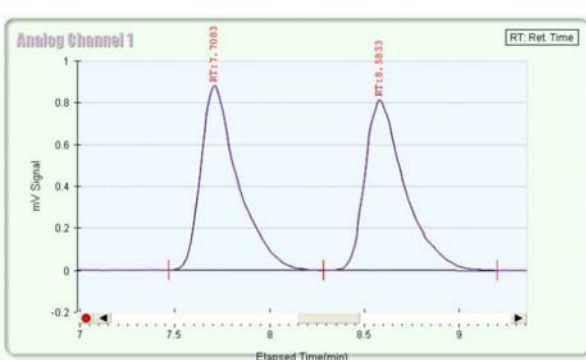
Peak Name	Area %	Area	Retention Time
Peak1	50.6069	18.6797	10.413 min
Peak2	49.3931	18.2316	13.505 min



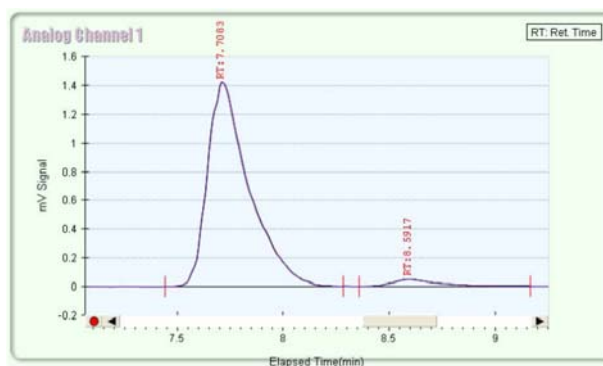
Peak Name	Area %	Area	Retention Time
Peak1	93.6251	25.1563	9.4417 min
Peak2	6.3749	1.7129	12.7917 min



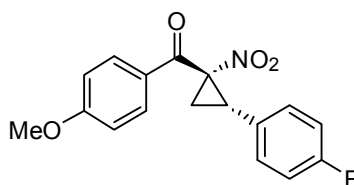
[(1S,2S)-2-(4-chlorophenyl)-1-nitrocyclopropyl][4-(methoxy)phenyl]methanone (2j): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (1f was used as substrate). 91% isolated yield, 98:2 d.r., 93% ee (method A), 80% isolated yield, 97:3 d.r., 94% ee (method B). mp 150-151°C (decomposition). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 10% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 7.7 min, t_r (minor) 8.6 min. $R_f = 0.35$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -200.0$ (c 0.93, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.88 (d, $J = 8.8$ Hz, 2H, ArH), 7.31 (d, $J = 8.4$ Hz, 2H, ArH), 7.26 (d, $J = 8.4$ Hz, 2H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.77 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 2.96 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.95 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.4, 164.5, 134.6, 130.8 (2C), 130.4 (2C), 130.3, 129.0 (2C), 127.4, 114.5 (2C), 76.7, 55.7, 31.3, 21.0. IR (neat) 3100, 3020, 2976, 1670 (C=O), 1595, 1528 (NO_2), 1349 (NO_2), 1268, 1161, 1023, 1015. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_4$ $[\text{M}+\text{H}]^+$: 332.0684, found 332.0690.



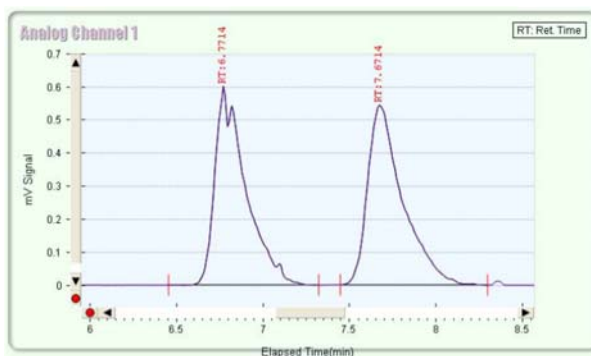
Peak Name	Area %	Area	Retention Time
Peak3	50.1385	11.868	7.7083 min
Peak5	49.8615	11.8024	8.5833 min



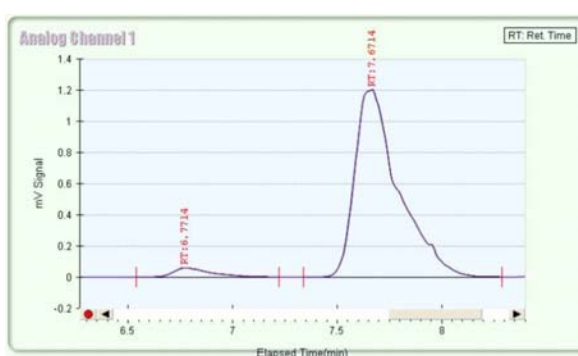
Peak Name	Area %	Area	Retention Time
Peak1	96.4747	19.2077	7.7083 min
Peak2	3.5253	0.7019	8.5917 min



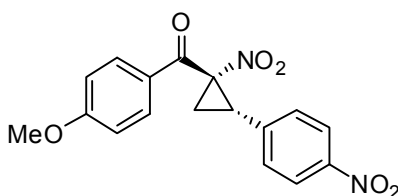
[(1S,2S)-2-(4-fluorophenyl)-1-nitrocyclopropyl][4-(methoxy)phenyl]methanone (2k): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (1f was used as substrate). 88% isolated yield, 98:2 d.r., 92% ee (method A), 85% isolated yield, 96:4 d.r., 95% ee (method B). mp 152-153°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 280 nm, t_r (minor) 6.8 min, t_r (major) 7.7 min. $R_f = 0.32$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -193.4$ (c 0.92, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.89 (d, $J = 8.8$ Hz, 2H, ArH), 7.31 (d, $J = 8.8$ Hz, 2H, ArH), 7.04 (d, $J = 8.8$ Hz, 2H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.78 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 2.96 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.94 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.5, 164.5, 161.2, 130.8, 130.8 (2C), 130.7, 127.6 (d, $J = 3.2$ Hz), 127.5, 115.9, 115.6, 114.5 (2C), 76.7, 55.7, 31.3, 21.2. ^{19}F NMR (CDCl_3 , 282 MHz): δ -114.7. IR (neat) 3103, 3022, 2843, 1670 (C=O), 1597, 1528 (NO_2), 1512, 1346 (NO_2), 1269, 1161, 1025. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{14}\text{FNO}_4$ $[\text{M}+\text{H}]^+$: 316.0980, found 316.0974.



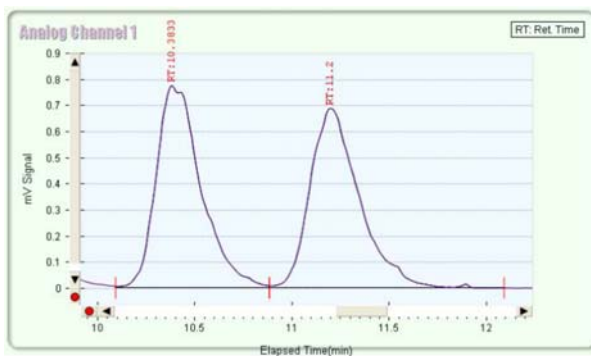
Peak Name	Area %	Area	Retention Time
Peak1	49.2627	7.3304	6.7714 min
Peak2	50.7173	7.5438	7.6714 min



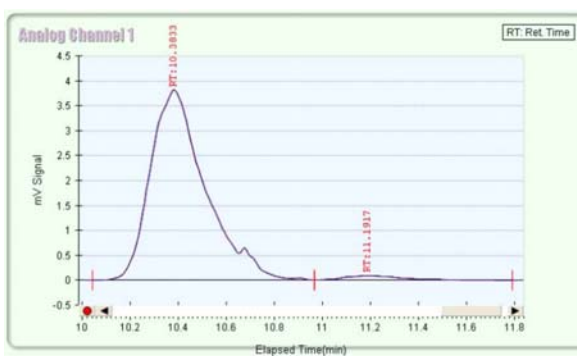
Peak Name	Area %	Area	Retention Time
Peak1	3.9404	0.7127	6.7714 min
Peak2	96.0596	17.3733	7.6714 min



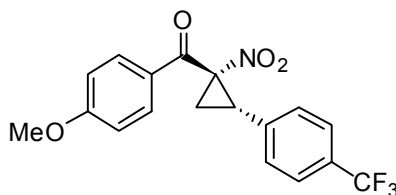
[4-(methoxy)phenyl][(1*S*,2*S*)-1-nitro-2-(4-nitrophenyl)cyclopropyl]methanone (2i): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (1f was used as substrate). 74% isolated yield, 99:1 d.r., 95% ee (method A), 87% isolated yield, 99:1 d.r., 97% ee (method B). mp 171-172°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 10% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 280 nm, t_r (major) 10.4 min, t_r (minor) 11.2 min. $R_f = 0.14$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -187.3$ (c 1.02, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.21 (d, $J = 8.8$ Hz, 2H, ArH), 7.89 (d, $J = 8.8$ Hz, 2H, ArH), 7.51 (d, $J = 8.8$ Hz, 2H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.85 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.05 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.04 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 185.7, 164.7, 148.0, 139.2, 130.9 (2C), 130.1 (2C), 127.0, 123.9 (2C), 114.6 (2C), 76.6, 55.7, 30.9, 20.9. IR (neat) 3094, 2977, 2844, 1666 (C=O), 1597, 1511 (NO_2), 1345 (NO_2), 1265, 1160, 1019, 846. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$: 343.0925, found 343.0921.



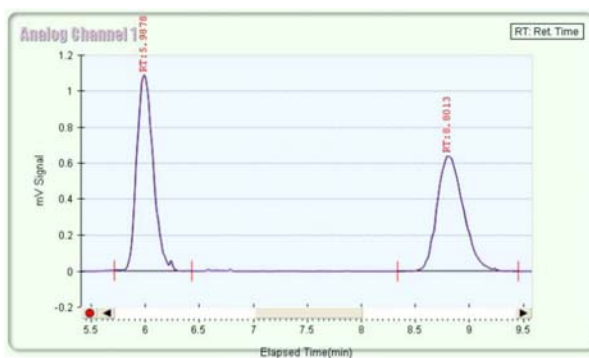
Peak Name	Area %	Area	Retention Time
Peak4	50.5752	12.3391	10.3833 min
Peak5	49.4248	12.0584	11.2 min



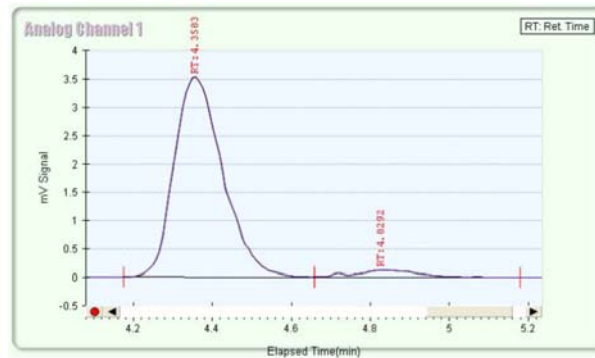
Peak Name	Area %	Area	Retention Time
Peak1	97.5982	60.332	10.3833 min
Peak3	2.4018	1.4847	11.1917 min



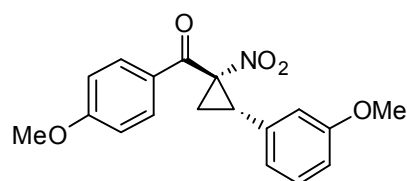
[4-(methoxy)phenyl]cyclopropanecarboxamide derivative (2m): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). 75% isolated yield, 98:2 d.r., 91% ee (method A), 75% isolated yield, 96:4 d.r., 95% ee (method B). mp 104-105°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 5% *i*-PrOH, 3 mL/min, 40°C, 180 bar, 280 nm, t_r (major) 6.0 min, t_r (minor) 8.8 min. $R_f = 0.37$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -185.8$ (c 0.48, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 8.8$ Hz, 2H, ArH), 7.60 (d, $J = 8.0$ Hz, 2H, ArH), 7.45 (d, $J = 8.0$ Hz, 2H, ArH), 6.98 (d, $J = 8.8$ Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.83 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.03 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.99 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.1, 164.6, 135.9, 130.9, 130.9 (2C), 130.5, 129.5 (2C), 127.2, 125.7 (q, 3.7 Hz), 122.2, 114.6 (2C), 76.6, 55.8, 31.2, 20.9. ^{19}F NMR (CDCl_3 , 282 MHz): δ -64.1. IR (neat) 3027, 2976, 2941, 1668 (C=O), 1598, 1531 (NO_2), 1322 (NO_2), 1264, 1163, 1110, 1068, 1016, 840. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_4$ $[\text{M}+\text{H}]^+$: 366.0948, found 366.0960.



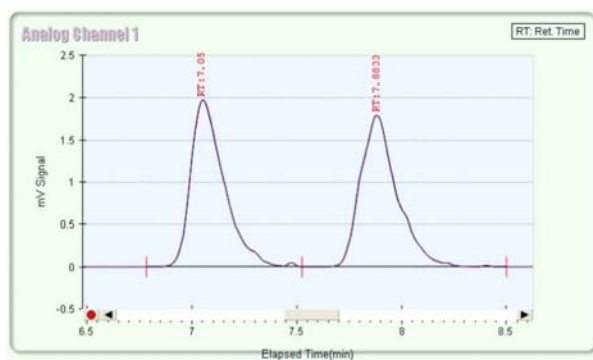
Peak Name	Area %	Area	Retention Time
Peak1	51.5271	11.4098	5.9878 min
Peak2	48.4729	10.7335	8.8013 min



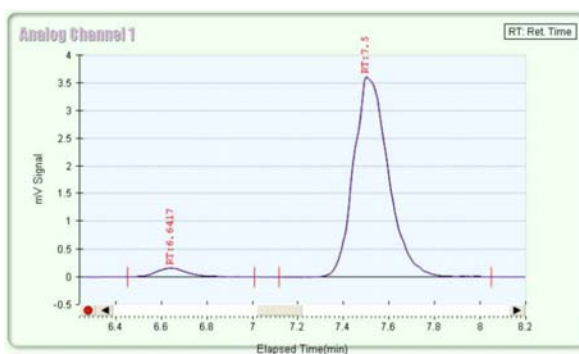
Peak Name	Area %	Area	Retention Time
Peak1	95.6696	29.6225	4.3583 min
Peak3	4.3304	1.3408	4.8292 min



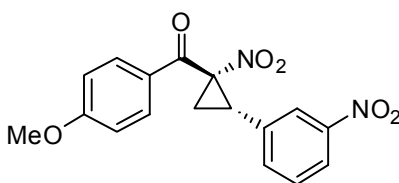
[4-(methoxy)phenyl]((1S,2S)-2-[3-(methoxy)phenyl]-1-nitrocyclopropyl)methanone (2n): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (1f was used as substrate and 1 mol% of $Rh_2(S\text{-TCPTTL})_4$ was used). 85% isolated yield, 97:3 d.r., 92% ee (method A), 61% isolated yield, 94:6 d.r., 94% ee (method B). Diastereomeric ratio was determined by 1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 10% *i*-PrOH, 3 mL/min, 30°C, 150 bar, 280 nm, t_r (minor) 6.6 min, t_r (major) 7.5 min. $R_f = 0.18$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -193.7$ (c 0.98, $CHCl_3$). 1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, $J = 8.8$ Hz, 2H, ArH), 7.29-7.22 (m, 1H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 6.92-6.90 (m, 1H, ArH), 6.88-6.82 (m, 2H, ArH), 3.88 (s, 3H, $ArOCH_3$), 3.80 (s, 3H, $ArOCH_3$), 3.80 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 2.98 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.92 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.7, 164.4, 159.8, 133.3, 130.8, 129.7, 127.6, 121.3, 114.7, 114.5, 114.2, 76.8, 55.7, 55.4, 32.1, 21.2. IR (neat) 3014, 2934, 1678 (C=O), 1590, 1531 (NO_2), 1316 (NO_2), 1253, 1163, 1031, 838. HRMS (ES, Pos) Calcd for $C_{18}H_{17}NO_5$ $[M+H]^+$: 328.1180, found 328.1171.



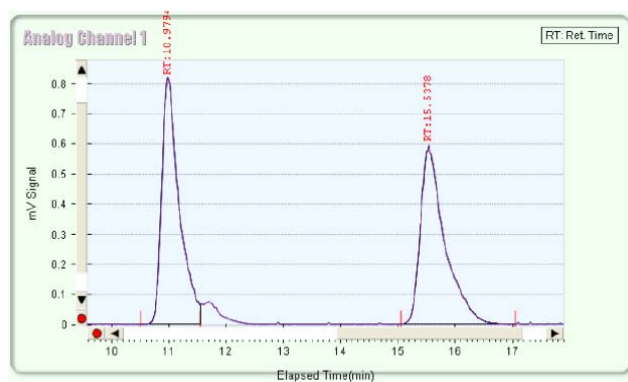
Peak Name	Area %	Area	Retention Time
Peak1	50.0689	21.6389	7.05 min
Peak5	49.9311	21.5793	7.8033 min



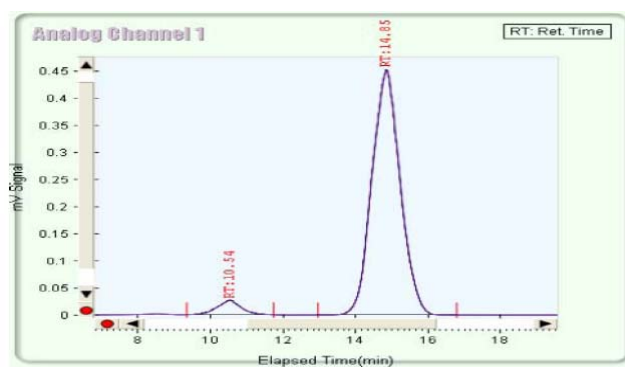
Peak Name	Area %	Area	Retention Time
Peak1	3.7918	1.4929	6.6417 min
Peak2	96.2082	37.8767	7.5 min



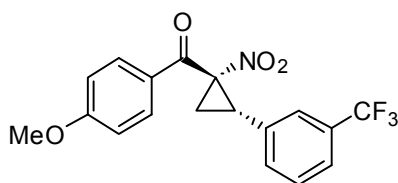
[4-(methoxy)phenyl][(1S,2S)-1-nitro-2-(3-nitrophenyl)cyclopropyl]methanone (2o): white solid. *The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (1f was used as substrate and 1 mol% of $Rh_2(S-TCPTTL)_4$ was used). 54% isolated yield, 95:5 d.r., 91% ee (method A). mp 129-130°C. Diastereomeric ratio was determined by 1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 180 bar, 280 nm, t_r (minor) 10.5 min, t_r (major) 14.8 min. R_f = 0.22 (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -227.0 (c 1.01, $CHCl_3$). 1H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, 1H, ArH), 8.18 (d, J = 8.2 Hz, 1H, ArH), 7.89 (d, J = 8.8 Hz, 2H, ArH), 7.67 (d, J = 7.6 Hz, 1H, ArH), 7.53 (t, J = 8.0 Hz, ArH), 6.98 (d, J = 8.8 Hz, 2H, ArH), 3.88 (s, 3H, $ArOCH_3$), 3.85 (t, J = 9.4 Hz, 1H, CH cyclopropane), 3.07 (dd, J = 7.2, 8.9 Hz, 1H, CH_2 cyclopropane), 2.04 ((dd, J = 7.2, 8.9 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.7, 164.6, 148.4, 135.2, 134.1, 130.9 (2C), 129.8, 127.0, 124.1, 123.6, 114.6 (2C), 76.4, 55.7, 30.8, 20.8. IR (neat) 2937, 2255, 1673, 1599, 1528, 1348, 1261, 1167, 909, 732. HRMS (ES, Pos) Calcd for $C_{17}H_{14}N_2O_6$ $[M+H]^+$: 343.0925, found 343.0921.*



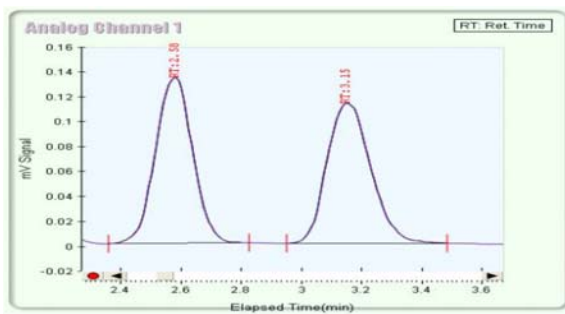
Peak Name	Area %	Area	Retention Time
Peak1	49.9843	17.2189	10.9784 min
Peak2	50.0157	17.2298	15.5378 min



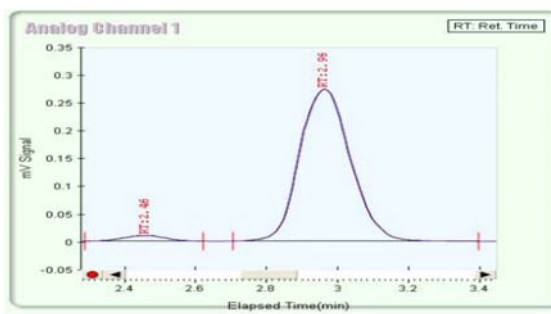
Peak Name	Peak Number	Area %	Area	Retention Time
	1	4.6924	1.2015	10.54 min
	2	95.3076	24.403	14.85 min



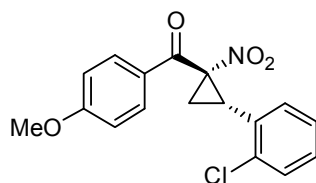
[4-(methoxy)phenyl]((1S,2S)-1-nitro-2-[3-(trifluoromethyl)phenyl]cyclopropyl)methanone (2p): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). 68% isolated yield, 96:4 d.r., 94% ee (method **A**), 60% isolated yield, 95:5 d.r., 96% ee (method **B**). mp 117-118°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel AS-H 25 cm, 5% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 2.5 min, t_r (major) 3.0 min. $R_f = 0.38$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -189.1$ (c 0.47, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 9.2$ Hz, 2H, ArH), 7.63-7.55 (m, 2H, ArH), 7.55-7.43 (m, 2H, ArH), 6.98 (d, $J = 9.2$ Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.83 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.03 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.99 (dd, $J = 6.8, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.1, 164.6, 132.9, 132.4, 131.4, 131.0, 130.9 (2C), 129.3, 127.3, 126.1, 125.4, 114.6 (2C), 76.5, 55.8, 31.3, 20.8. ^{19}F NMR (CDCl_3 , 282 MHz): δ -64.1. IR (neat) 3020, 2943, 2847, 1672 (C=O), 1600, 1542 (NO_2), 1328 (NO_2), 1263, 1161, 1125, 1113, 1019, 843. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_4$ $[\text{M}+\text{H}]^+$: 366.0948, found 366.0955.



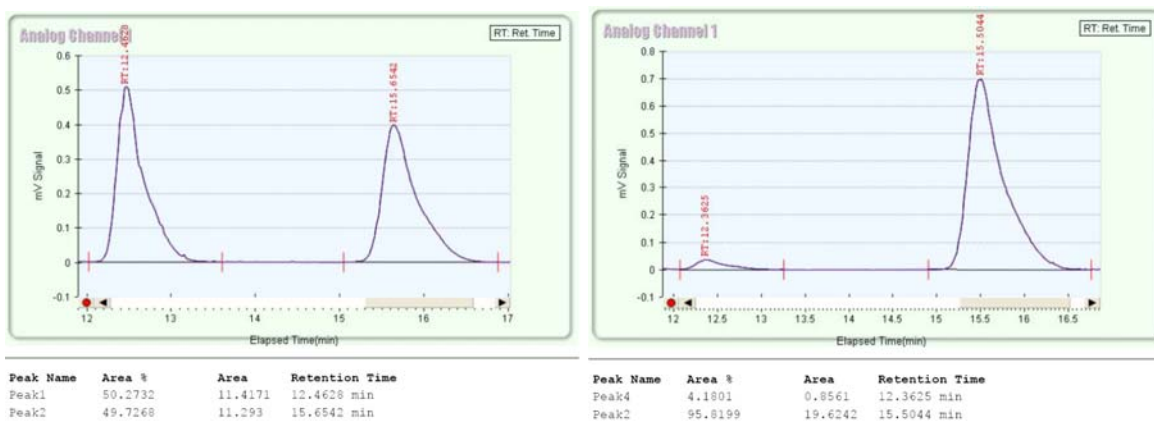
Peak Name	Peak Number	Area %	Area	Retention Time
	1	50.1021	1.1204	2.58 min
	2	49.8979	1.1158	3.15 min

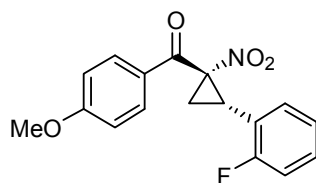


Peak Name	Peak Number	Area %	Area	Retention Time
	1	2.935	0.081	2.46 min
	2	97.065	2.6804	2.96 min

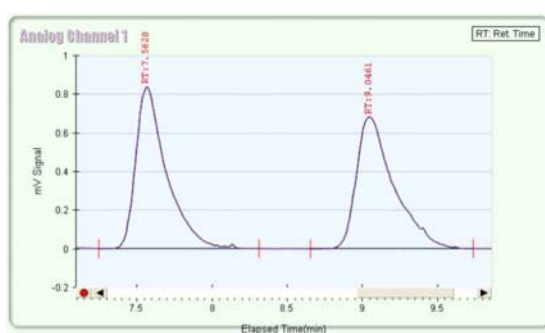


[(1S,2S)-2-(2-chlorophenyl)-1-nitrocyclopropyl][4-(methoxy)phenyl]methanone (2q): white solid. A slightly modified procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed, where the reaction was run at -40°C in method **A** (**1f** was used as substrate). 68% isolated yield, 96:4 d.r., 92% ee (method A), 53% isolated yield, 96:4 d.r., 94% ee (method B). mp $121\text{--}122^\circ\text{C}$. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C , 150 bar, 280 nm, t_r (minor) 12.4 min, t_r (major) 15.5 min. $R_f = 0.32$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -161.0$ (c 0.26, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.89 (d, $J = 8.8$ Hz, 2H, ArH), 7.42–7.36 (m, 1H, ArH), 7.35–7.24 (m, 3H, ArH), 6.97 (d, $J = 8.8$ Hz, 2H, ArH), 3.97 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.88 (s, 3H, ArOCH_3), 3.04 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.99 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.3, 164.4, 136.3, 130.7 (2C), 130.3, 130.1, 129.9, 129.9, 127.6, 126.8, 114.4, 75.8, 55.7, 31.0, 21.3. IR (neat) 3091, 2938, 2846, 1673 (C=O), 1598, 1530 (NO_2), 1345 (NO_2), 1307, 1264, 1159, 1022, 851. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_4$ $[\text{M}+\text{H}]^+$: 332.0684, found 332.0683.

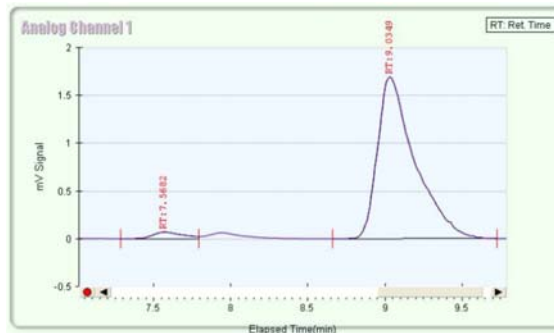




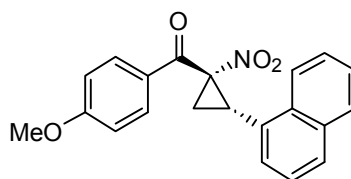
[(1S,2S)-2-(2-fluorophenyl)-1-nitrocyclopropyl][4-(methoxy)phenyl]methanone (2r): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate). 54% isolated yield, 97:3 d.r., 93% ee (method **A**), 36% isolated yield, 98:2 d.r., 94% ee (method **B**). mp 124-125°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 7.6 min, t_r (major) 9.0 min. $R_f = 0.31$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -197.3$ (c 0.67, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 9.2$ Hz, 2H, ArH), 7.36-7.24 (m, 2H, ArH), 7.17-7.12 (m, 1H, ArH), 7.11-7.05 (m, 1H, ArH), 6.97 (d, $J = 9.2$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.81 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.00 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.01 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.4, 164.4, 162.4 (d, $J = 248$ Hz), 130.8 (2C), 130.3 (d, $J = 12.1$ Hz), 130.3, 127.5, 124.2 (d, $J = 3.7$ Hz), 119.4 (d, $J = 14.3$ Hz), 115.8 (d, $J = 21.1$ Hz), 114.4 (2C), 75.7, 55.7, 26.9 (d, $J = 3.5$ Hz), 20.9. ^{19}F NMR (CDCl_3 , 282 MHz): δ -116.7. IR (neat) 3092, 1673 (C=O), 1598, 1529 (NO_2), 1350 (NO_2), 1269, 1163, 1020, 846. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{14}\text{FNO}_4$ $[\text{M}+\text{H}]^+$: 316.0980, found 316.0967.



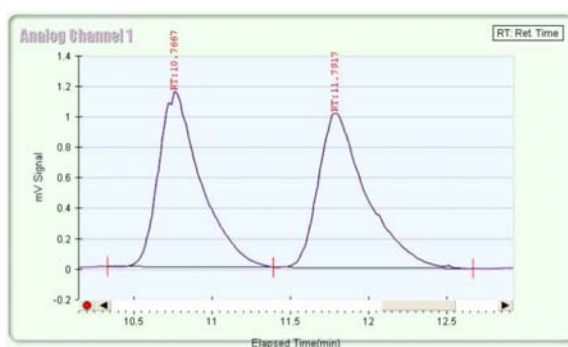
Peak Name	Area %	Area	Retention Time
Peak1	50.155	11.7521	7.5628 min
Peak2	49.845	11.6795	9.0461 min



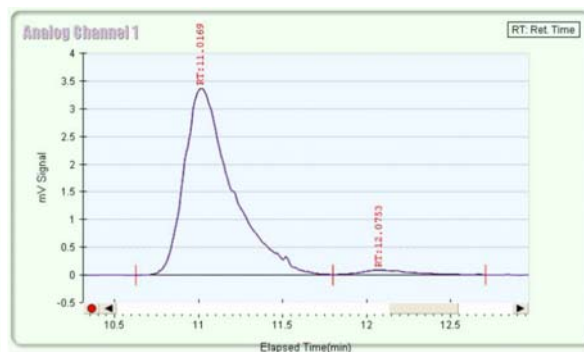
Peak Name	Area %	Area	Retention Time
Peak1	3.3098	0.9671	7.5682 min
Peak2	96.6902	28.2521	9.0349 min



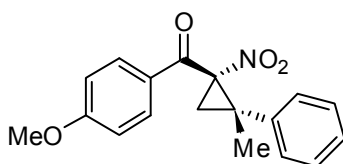
[4-(methoxy)phenyl][(1S,2S)-2-naphthalen-1-yl-1-nitrocyclopropyl]methanone (2s): white solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate and 1 mol% of $Rh_2(S\text{-TCPTTL})_4$ was used). 81% isolated yield, 98:2 d.r., 95% ee (method **A**), 78% isolated yield, 96:4 d.r., 94% ee (method **B**). mp 138-139°C (decomposition). Diastereomeric ratio was determined by 1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 15% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 11.0 min, t_r (minor) 12.1 min. $R_f = 0.35$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = +3.4$ (c 0.93, $CHCl_3$). 1H NMR ($CDCl_3$, 400 MHz): δ 8.39 (d, $J = 8.4$ Hz, 1H, ArH), 7.99 (d, $J = 8.8$ Hz, 2H, ArH), 7.88-7.81 (m, 2H, ArH), 7.62-7.55 (m, 1H, ArH), 7.54-7.45 (m, 3H, ArH), 6.99 (d, $J = 8.8$ Hz, 2H, ArH), 4.27 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 3.87 (s, 3H, $ArOCH_3$), 3.24 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.07 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.7, 164.6, 133.6, 132.8, 131.0 (2C), 129.3, 128.6, 128.1, 127.4, 127.2, 127.0, 126.4, 125.1, 124.1, 114.5 (2C), 75.9, 55.7, 30.6, 20.8. IR (neat) 3049, 2841, 1672 (C=O), 1596, 1531 (NO_2), 1510, 1343 (NO_2), 1261, 1162, 1021, 778. HRMS (ES, Pos) Calcd for $C_{21}H_{17}NO_4$ $[M+H]^+$: 348.1230, found 348.1235.



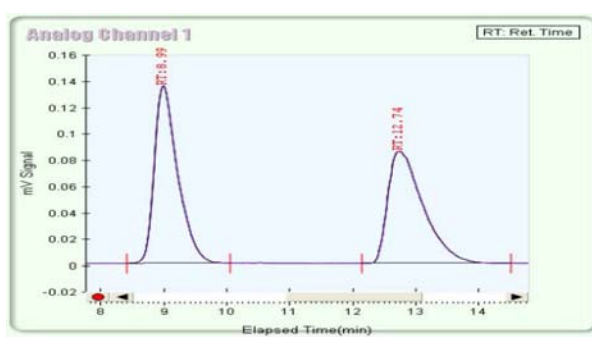
Peak Name	Area %	Area	Retention Time
Peak1	50.0005	21.3946	10.7667 min
Peak3	49.9995	21.3942	11.7917 min



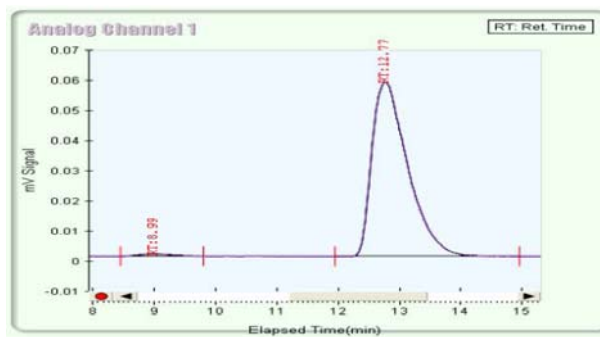
Peak Name	Area %	Area	Retention Time
Peak1	97.3742	66.5122	11.0169 min
Peak3	2.6258	1.7936	12.0753 min



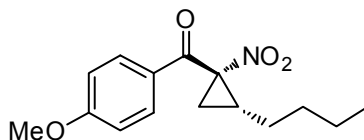
[(1S,2S)-2-methyl-1-nitro-2-phenylcyclopropyl][4-(methoxy)phenyl]methanone (2t): white crystalline solid. A slightly modified procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed, where the compound was purified by recrystallization in CH_2Cl_2 /hexane due to its instability on silica gel (1f was used as substrate). 88% isolated yield, 99:1 d.r., 98% ee (method A). mp 117-118°C (decomposition). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OD-H 25 cm, 4% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 280 nm, t_r (minor) 9.0 min, t_r (major) 12.8 min. $R_f = 0.27$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -232.0$ (c 1.08, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.05 (d, $J = 8.8$ Hz, 2H, ArH), 7.46-7.36 (m, 4H, ArH), 7.35-7.28 (m, 1H, ArH), 7.01 (d, $J = 8.8$ Hz, 2H, ArH), 3.91 (s, 3H, ArOCH_3), 2.92 (d, $J = 6.4$ Hz, 1H, CH_2 cyclopropane), 1.98 (d, $J = 6.4$ Hz, 1H, CH_2 cyclopropane), 1.52 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 185.6, 164.5, 138.6, 131.8 (2C), 128.9 (2C), 128.5, 128.1, 128.0 (2C), 114.3 (2C), 76.4, 55.7, 40.7, 26.8, 25.8. IR (neat) 3011, 2985, 2843, 1677 (C=O), 1602, 1532 (NO_2), 1338 (NO_2), 1265, 1162, 1019, 843. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 312.1230, found 312.1228.



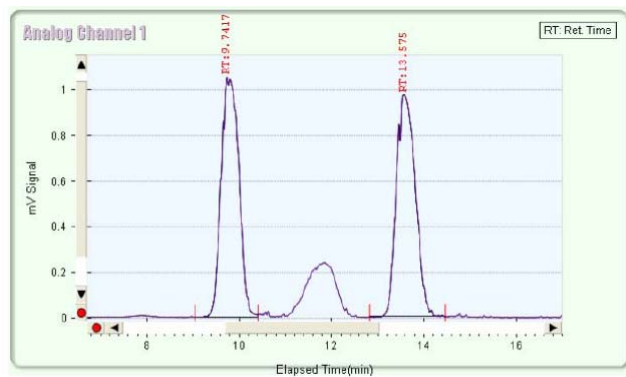
Peak Name	Peak Number	Area %	Area	Retention Time
	1	51.2373	3.4709	8.99 min
	2	48.7627	3.3032	12.74 min



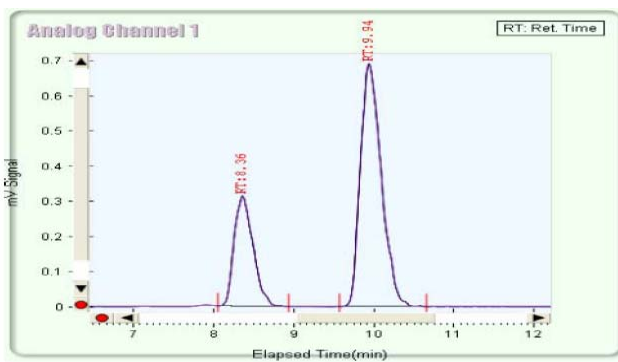
Peak Name	Peak Number	Area %	Area	Retention Time
	1	1.0043	0.0238	8.99 min
	2	98.9957	2.3444	12.77 min



[(1S,2R)-2-butyl-1-nitrocyclopropyl][4-(methoxy)phenyl]methanone (2u): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -nitro-diazoacetophenones described in the experimental section was followed (**1f** was used as substrate and 1 mol% of $Rh_2(S\text{-TCPTTL})_4$ was used). 5% isolated yield, 54:46 d.r. (cis major), 42% ee (for cis) (method **A**). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 3% *i*-PrOH, 3 mL/min, 40°C, 180 bar, 280 nm, t_r (minor) 8.4 min, t_r (major) 9.9 min. R_f = 0.44 (30:70 Et₂O:Hexane). $[\alpha]_D^{20}$ = -38.2 (c 0.72, CHCl₃). ^1H NMR (CDCl₃, 400 MHz): δ 7.85 (d, J = 8.9 Hz, 2H, ArH), 6.95 (d, J = 8.9 Hz, 2H, ArH), 3.88 (s, 3H, ArOCH₃), 2.51-2.40 (m, 1H, CH cyclopropane) 2.26 (dd, J = 6.0, 9.0 Hz, 1H, CH₂ cyclopropane), 1.64-1.30 (m, 7H, AlkH), 0.91 (t, J = 7.2 Hz, 3H, AlkCH₃). ^{13}C NMR (CDCl₃, 75 MHz): δ 187.5, 164.2, 130.6 (2C), 127.8, 114.4 (2C), 75.5, 55.7, 30.6, 28.2, 26.4, 23.4, 22.4, 14.0. IR (neat) 2918, 2849, 1680 (C=O), 1601, 1534 (NO₂), 1352 (NO₂), 1263, 1167, 910, 734. HRMS (ES, Pos) Calcd for C₁₅H₁₉NO₄ [M+H]⁺: 278.1387, found 278.1390.

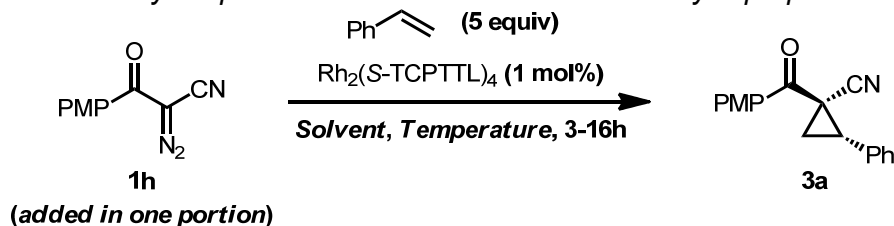


Peak Name	Area %	Area	Retention Time
Peak1	50.1629	27.9109	9.7417 min
Peak2	49.8371	27.7297	13.575 min



Peak Name	Peak Number	Area %	Area	Retention Time
	1	28.9981	5.078	8.36 min
	2	71.0019	12.4336	9.94 min

General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation with 1h
Solvent / Temperature / Catalyst Optimization for the enantioselective cyclopropanation with diazo 1h:

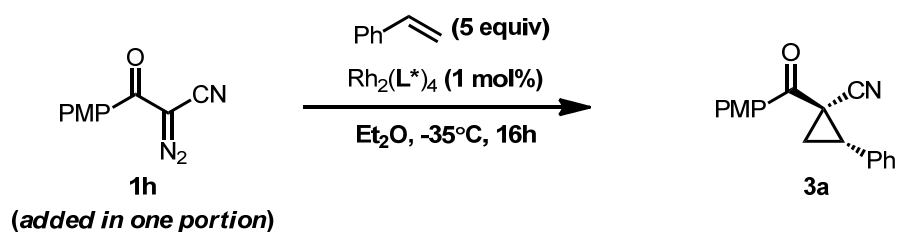


Entry	Solvent	Temperature	Yield (%) ¹	dr (<i>trans</i> : <i>cis</i>) ²	ee (%, <i>trans</i>) ³
1	CH ₂ Cl ₂	0°C	89	89 : 11	60
2	EtOAc	0°C	94	91 : 9	75
3	Toluene	0°C	48	87 : 13	57
4	DME	0°C	94	91 : 9	67
5	<i>t</i> -BuOMe	0°C	72	93 : 7	80
6	Et ₂ O	0°C	88	92 : 8	76
7	<i>t</i> -BuOMe	-15°C	79	93 : 7	82
8	Et ₂ O	-15°C	93	93 : 7	79
9	<i>t</i> -BuOMe	-35°C	78	94 : 6	83
10	Et ₂ O	-35°C	98	95 : 5	84

¹ Isolated Yield

² dr was determined by ¹H NMR analysis of the crude mixture

³ ee was determined by SFC on chiral stationary phase after flash chrom.

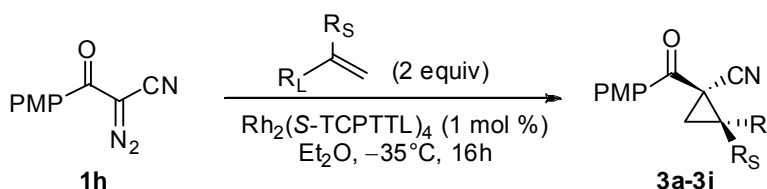


Entry	L*	Yield (%) ¹	dr (<i>trans</i> : <i>cis</i>) ²	ee (%, <i>trans</i>) ³
1	S-TCPTTL	98	95 : 5	84
2	S-TBPTV	97	91 : 9	57
3	S-PTTL	49	61 : 39	3
4	S-NTTL	53	62 : 38	46

¹ Isolated Yield

² dr was determined by ¹H NMR analysis of the crude mixture

³ ee was determined by SFC on chiral stationary phase after flash chrom.



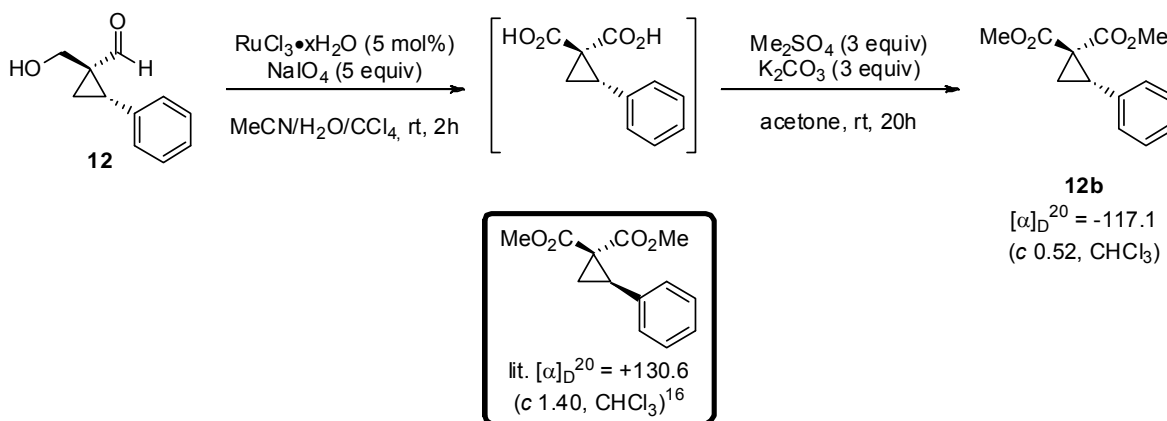
General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation using α -cyanodiazoacetophenone **1h** (Table 6)

(the racemic products were synthesized according to a literature procedure)¹⁵

A flame-dried, round-bottomed 10 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with catalyst $\text{Rh}_2(\text{S-TCPTTL})_4$ (5.8 mg, 0.0030 mmol, 0.01 equiv), followed by 4.5 mL of dry Et_2O and the alkene (0.6 mmol, 2 equiv) at room temperature (20–23°C). The resulting green homogenous solution was cooled to -35°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before diazo **1h** (60.4 mg, 0.30 mmol, 1 equiv) was added in the solid state under air, the flask was capped back with the rubber septum and the resulting heterogenous green solution was stirred for a further 16 hours at -35°C , keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH_2Cl_2 , and evaporated to dryness. (The d.r. was determined at this point using ^1H NMR). The resulting residue was purified by silica-gel chromatography using CH_2Cl_2 /hexanes as eluent (various ratios from 50% CH_2Cl_2 /hexanes to 80% CH_2Cl_2 /hexanes, depending on the nature of the alkene) to afford the pure cyclopropane product (**3a-3i**) as a mixture of diastereomers, which was submitted to SFC analysis using a chiral stationary phase for ee determination. On a larger scale according to table **8** (10 mmol), the residue obtained after the first silica-gel chromatography (mixture of diastereomers) could be repurified on silica-gel chromatography to obtain a diastereopure product using 27% Et_2O in hexane as eluent (for **3a**). Subsequent recrystallizations in either 30% CHCl_3 in hexane or 100% Et_2O permitted isolation of **3a** in >99:1 dr, 98% ee in 66% overall yield from **1h**.

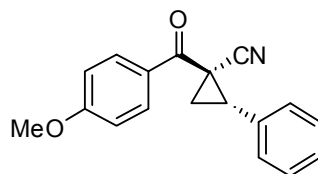
Absolute Configuration

The absolute configuration of α -cyano acetophenones **3a-3i** was assigned by X-Ray (compound **3b**, see page S78) and confirmed by comparison of the sign of optical rotation of the *gem*-diester obtained by oxidation and methylation of β -hydroxyaldehyde **12** with a literature value¹⁶ (See page S69 for the synthesis of **12** and page S70 for experimental procedures of derivatization to *gem*-diester **12b**):

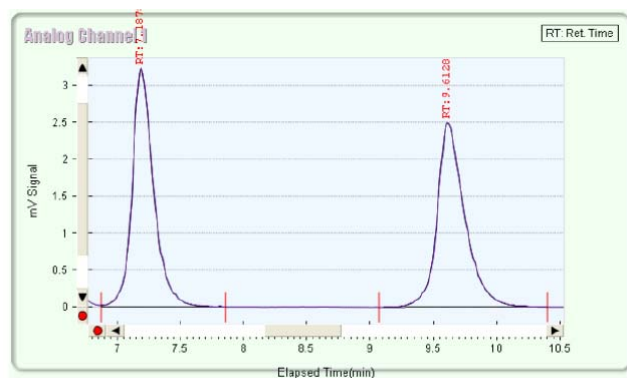


¹⁵ Wurz, R. P.; Charette, A. B. *Org. Lett.* **2005**, *7*, 2313.

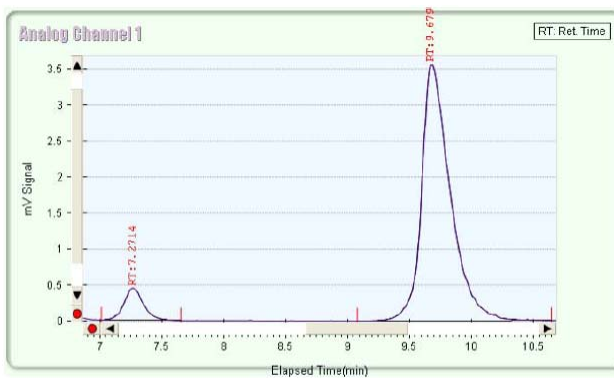
¹⁶ Perreault, C.; Goudreau, S. R.; Zimmer, L. E.; Charette, A. B. *Org. Lett.* **2008**, *10*, 689.



(1R,2S)-1-[(4-(methoxy)phenyl)carbonyl]-2-phenylcyclopropanecarbonitrile (3a): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 92% isolated yield, 95:5 d.r., 84% ee. On a larger scale according to table **8** (10 mmol), the residue obtained after the first silica-gel chromatography (mixture of diastereomers) could be repurified to obtain a diastereopure product on silica-gel chromatography using 27% Et₂O in hexane as eluent. Subsequent recrystallizations in either 30% CHCl₃/hexane or 100% Et₂O permitted isolation of **3a** in >99:1 dr, 98% ee in 66% overall yield from **1h**. mp 106-108°C. Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, *t_r* (minor) 7.3 min, *t_r* (major) 9.7 min. R_f = 0.25 (70:30 CH₂Cl₂:Hexane). [α]_D²⁰ = -190.4 (c 1.08, CHCl₃, 98% ee). ¹H NMR (CDCl₃, 400 MHz): δ 8.02 (d, *J* = 8.8 Hz, 2H, ArH), 7.50-7.30 (m, 5H, ArH), 6.98 (d, *J* = 8.8 Hz, 2H, ArH), 3.89 (s, 3H, ArOCH₃), 3.11 (t, *J* = 8.6 Hz, 1H, CH cyclopropane), 2.53 (dd, *J* = 5.3, 9.0 Hz, 1H, CH₂ cyclopropane), 2.18 (dd, *J* = 5.3, 8.2 Hz, 1H, CH₂ cyclopropane). ¹³C NMR (CDCl₃, 75 MHz): δ 189.5, 164.2, 133.5, 131.5 (2C), 129.0 (2C), 128.7, 128.3 (2C), 128.2, 119.1, 114.1 (2C), 55.7, 37.1, 28.3, 21.9. IR (neat) 2935, 2841, 2237 (C≡N), 1672 (C=O), 1600, 1257, 1168, 1029, 699. HRMS (ES, Pos) Calcd for C₁₈H₁₅NO₂ [M+H]⁺: 278.1176, found 278.1175.

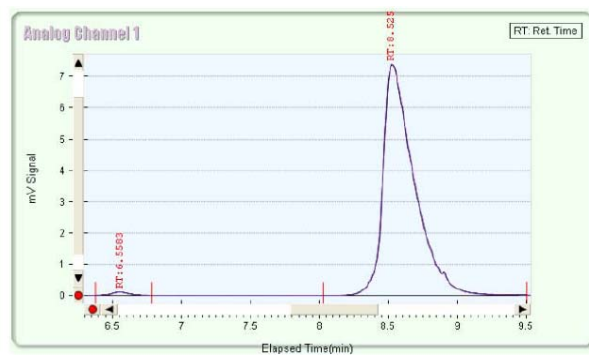


Peak Name	Area %	Area	Retention Time
Peak4	50.4188	38.4135	7.1878 min
Peak6	49.5812	37.7753	9.6128 min

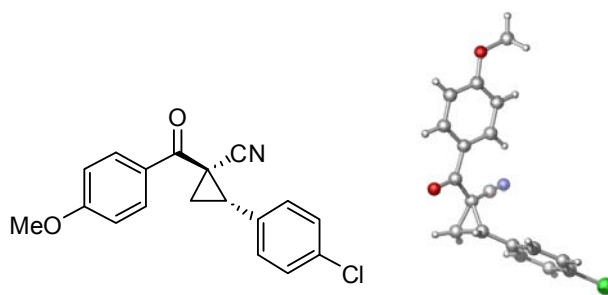


Peak Name	Area %	Area	Retention Time
Peak3	7.766	4.8222	7.2714 min
Peak2	92.234	57.2718	9.6797 min

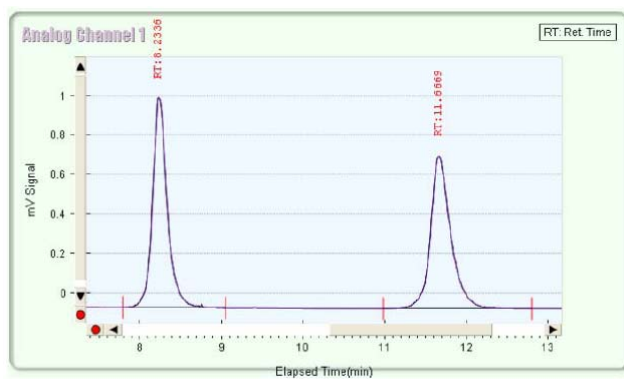
After recrystallization:



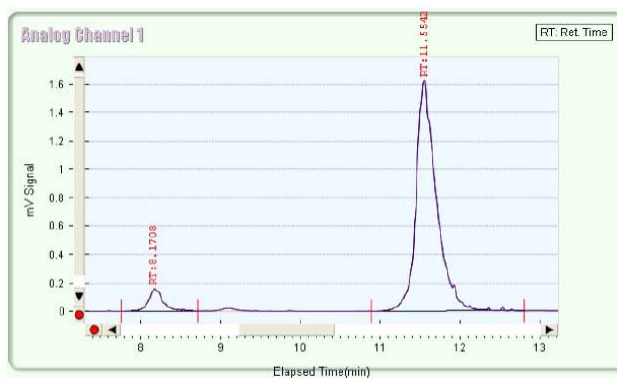
Peak Name	Area %	Area	Retention Time
Peak3	0.7799	0.9053	6.5583 min
Peak2	99.2201	115.1644	8.525 min



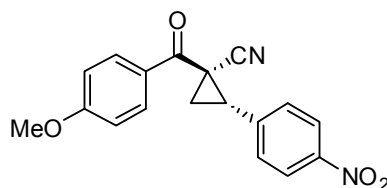
(1*R*,2*S*)-2-(4-chlorophenyl)-1-[[4-(methoxy)phenyl]carbonyl]cyclopropanecarbonitrile (3b): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 94% isolated yield, 97:3 d.r., 88% ee. mp 78-79°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 8.2 min, t_r (major) 11.6 min. R_f = 0.28 (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -180.5 (c 0.98, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.01 (d, J = 8.8 Hz, 2H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.28 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 8.8 Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.09 (t, J = 8.6 Hz, 1H, CH cyclopropane), 2.50 (dd, J = 5.4, 9.0 Hz, 1H, CH_2 cyclopropane), 2.13 (dd, J = 5.4, 8.1 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 189.1, 164.3, 134.6, 132.1, 131.5 (2C), 129.7 (2C), 129.2 (2C), 128.1, 118.9, 114.1 (2C), 55.7, 36.0, 28.1, 22.1. IR (neat) 2935, 2841, 2237 ($\text{C}\equiv\text{N}$), 1670 ($\text{C}=\text{O}$), 1600, 1257, 1167, 1014, 833, 737. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{14}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 312.0786, found 312.0781.



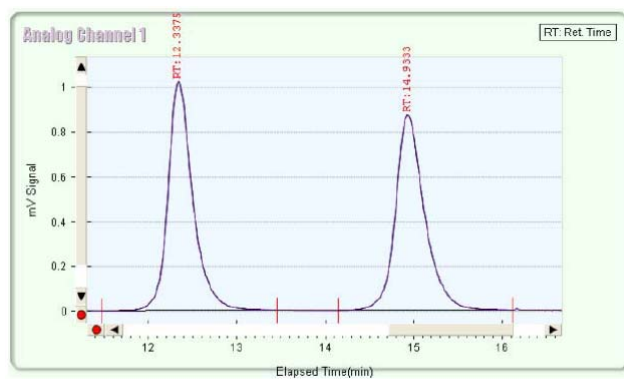
Peak Name	Area %	Area	Retention Time
Peak3	50.1425	13.331	8.2336 min
Peak4	49.8575	13.2553	11.6669 min



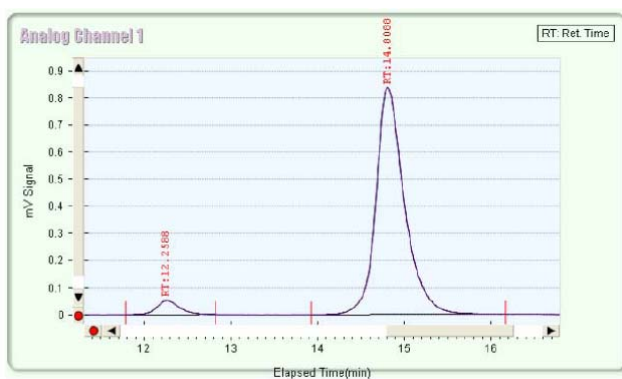
Peak Name	Area %	Area	Retention Time
Peak2	6.234	1.9002	8.1708 min
Peak3	93.766	28.5813	11.5542 min



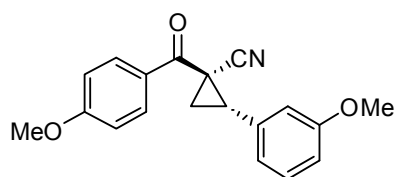
(1R,2S)-1-[(4-methoxyphenyl)carbonyl]-2-(4-nitrophenyl)cyclopropanecarbonitrile (3c): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 90% isolated yield, 99:1 d.r., 91% ee. mp 140-141°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 12.3 min, t_r (major) 14.8 min. $R_f = 0.13$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -174.1$ (c 1.03, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 8.31 (d, $J = 8.7$ Hz, 2H, ArH), 8.03 (d, $J = 8.9$ Hz, 2H, ArH), 7.53 (d, $J = 8.7$ Hz, 2H, ArH), 6.99 (d, $J = 8.9$ Hz, 2H, ArH), 3.90 (s, 3H, ArOCH_3), 3.26 (t, $J = 8.6$ Hz, 1H, CH cyclopropane), 2.53 (dd, $J = 5.5, 9.0$ Hz, 1H, CH_2 cyclopropane), 2.24 (dd, $J = 5.5, 8.1$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 188.4, 164.5, 148.0, 141.0, 131.6 (2C), 129.3 (2C), 127.8, 124.2 (2C), 118.5, 114.2 (2C), 55.8, 35.0, 28.2, 22.7. IR (neat) 2934, 2840, 2237 ($\text{C}\equiv\text{N}$), 1664 ($\text{C}=\text{O}$), 1593, 1513 (NO_2), 1346 (NO_2), 1318, 1258, 1163, 1016, 856, 735. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 323.1026, found 323.1023.



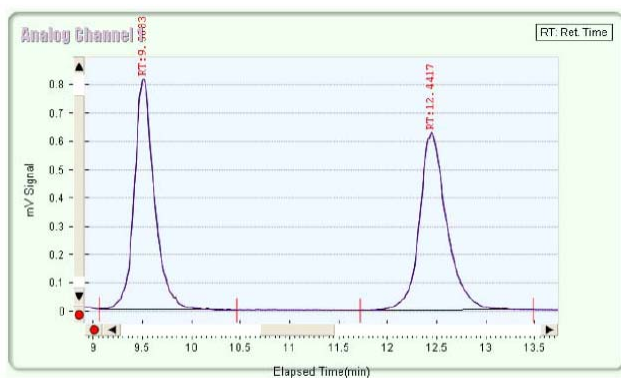
Peak Name	Area %	Area	Retention Time
Peak1	49.114	19.8924	12.3375 min
Peak2	50.886	20.6101	14.9333 min



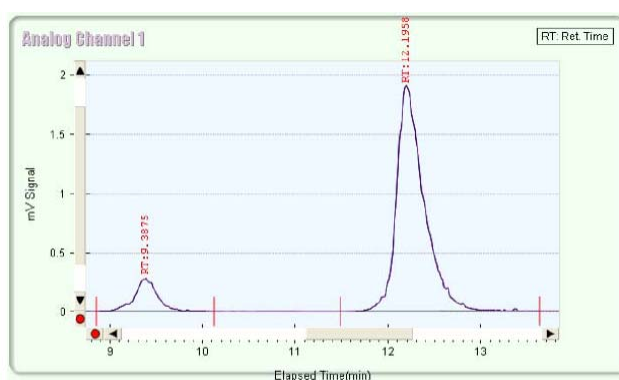
Peak Name	Area %	Area	Retention Time
Peak3	4.6542	0.9301	12.2588 min
Peak2	95.3458	19.0536	14.8088 min



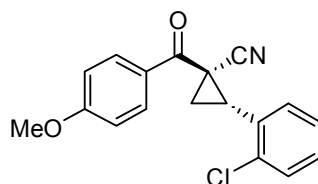
(1*R*,2*S*)-2-[3-(methoxy)phenyl]-1-[4-(methoxy)phenyl]carbonylcyclopropanecarbonitrile (3d): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 92% isolated yield, 95:5 d.r., 79% ee. mp 114-115°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 9.4 min, t_r (major) 12.2 min. $R_f = 0.16$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -137.1$ (c 0.98, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.03 (d, $J = 8.9$ Hz, 2H, ArH), 7.36 (t, $J = 7.9$ Hz, 1H, ArH), 7.04-6.84 (m, 5H, ArH), 3.89 (s, 3H, ArOCH_3), 3.85 (s, 3H, ArOCH_3), 3.07 (t, $J = 8.6$ Hz, 1H, CH cyclopropane), 2.51 (dd, $J = 5.3, 9.0$ Hz, 1H, CH_2 cyclopropane), 2.16 (dd, $J = 5.3, 8.2$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 189.4, 164.2, 160.0, 135.0, 131.5 (2C), 130.0, 128.2, 120.5, 119.0, 114.2, 114.0 (2C), 114.0, 55.7, 55.4, 37.0, 28.2, 21.8. IR (neat) 2938, 2839, 2236 ($\text{C}\equiv\text{N}$), 1670 ($\text{C}=\text{O}$), 1599, 1457, 1255, 1169, 1015, 738, 702. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 308.1281, found 308.1281.



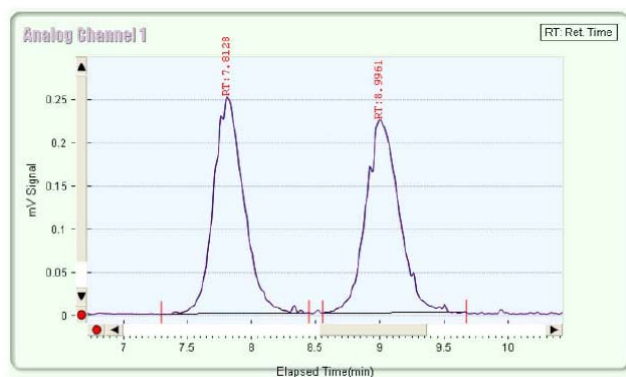
Peak Name	Area %	Area	Retention Time
Peak1	49.0205	11.5724	9.5083 min
Peak2	50.9795	12.0349	12.4417 min



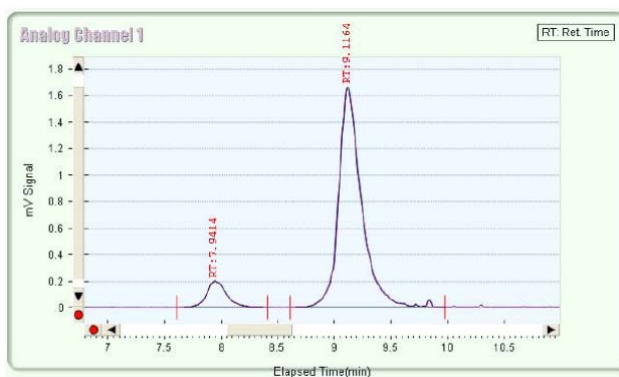
Peak Name	Area %	Area	Retention Time
Peak1	10.7267	4.7144	9.3875 min
Peak2	89.2733	39.2354	12.1958 min



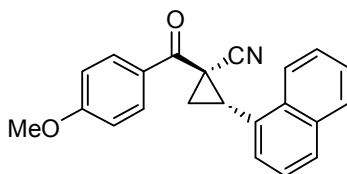
(1*R*,2*R*)-2-(2-chlorophenyl)-1-[(4-(methoxy)phenyl]cyclopropanecarbonitrile (3e): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. **88% isolated yield, 98:2 d.r., 81% ee.** mp 123-124°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 7.9 min, t_r (major) 9.1 min. R_f = 0.27 (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = +38.8 (*c* 1.00, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.14 (d, J = 8.9 Hz, 2H, ArH), 7.55-7.47 (m, 1H, ArH), 7.39-7.24 (m, 3H, ArH), 6.99 (d, J = 8.9 Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.36 (t, J = 8.6 Hz, 1H, CH cyclopropane), 2.56 (dd, J = 5.0, 8.8 Hz, 1H, CH_2 cyclopropane), 2.22 (dd, J = 5.0, 8.4 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 189.8, 164.1, 136.5, 132.1, 131.6 (2C), 130.0, 129.9, 129.0, 128.5, 127.3, 119.1, 113.9 (2C), 55.7, 36.2, 27.1, 23.1. IR (neat) 2937, 2840, 2237 (C \equiv N), 1667 (C=O), 1600, 1511, 1257, 1168, 1014, 738. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{14}\text{ClNO}_2$ [$\text{M}+\text{H}$] $^+$: 312.0786, found 312.0784.



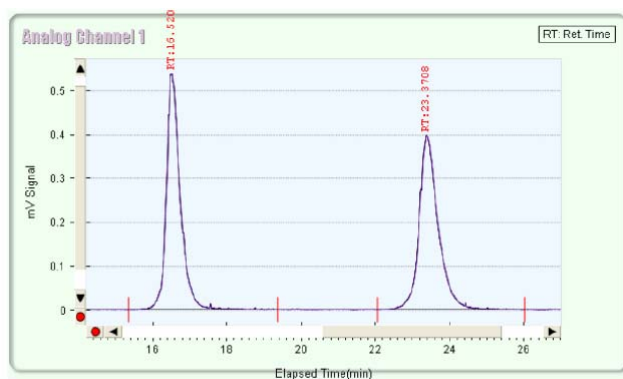
Peak Name	Area %	Area	Retention Time
Peak1	50.4721	4.0636	7.8128 min
Peak2	49.5279	3.9876	8.9961 min



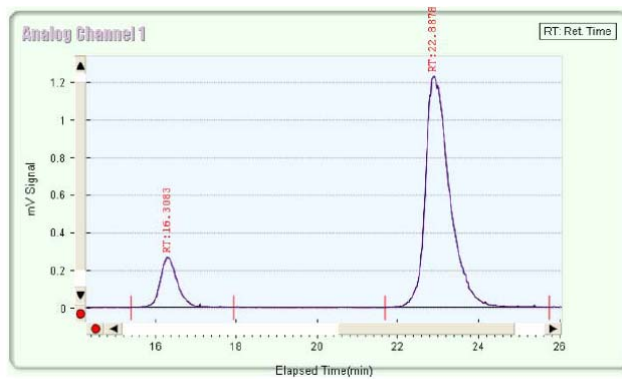
Peak Name	Area %	Area	Retention Time
Peak1	9.4952	2.4411	7.9414 min
Peak2	90.5048	23.2679	9.1164 min



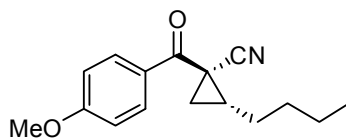
(1R,2S)-1-[[4-(methoxy)phenyl]carbonyl]-2-naphthalen-1-ylcyclopropanecarbonitrile (3f): white foam. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 99% isolated yield, 96:4 d.r., 73% ee. mp <50°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 16.3 min, t_r (major) 22.9 min. R_f = 0.28 (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = +136.6 (c 0.58, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.15 (d, J = 9.0 Hz, 2H, ArH), 8.08-8.01 (m, 1H, ArH), 7.99-7.87 (m, 2H, ArH), 7.61-7.42 (m, 4H, ArH), 6.98 (d, J = 9.0 Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.76 (t, J = 8.6 Hz, 1H, CH cyclopropane), 2.58 (dd, J = 4.9, 8.8 Hz, 1H, CH_2 cyclopropane), 2.44 (dd, J = 4.9, 8.3 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 190.0, 164.3, 133.9, 132.9, 131.7 (2C), 130.1, 129.6, 129.2, 128.4, 127.0, 126.4, 125.6, 125.4, 123.1, 119.2, 114.0 (2C), 55.7, 34.7, 27.7, 23.1. IR (neat) 3053, 2935, 2840, 2236 (C \equiv N), 1667 (C=O), 1599, 1510, 1257, 1171, 1027, 989, 778, 737. HRMS (ES, Pos) Calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 328.1332, found 328.1332.



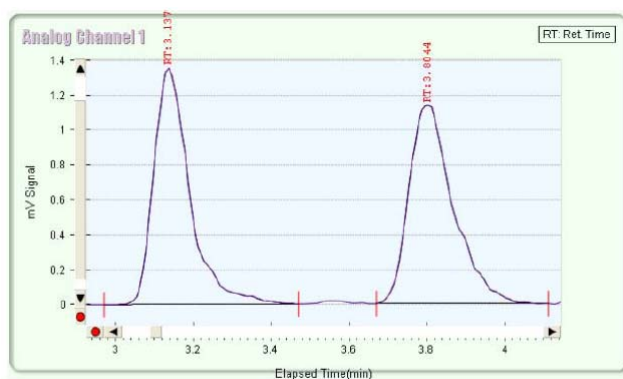
Peak Name	Area %	Area	Retention Time
Peak1	49.5667	13.9146	16.5208 min
Peak2	50.4333	14.1579	23.3708 min



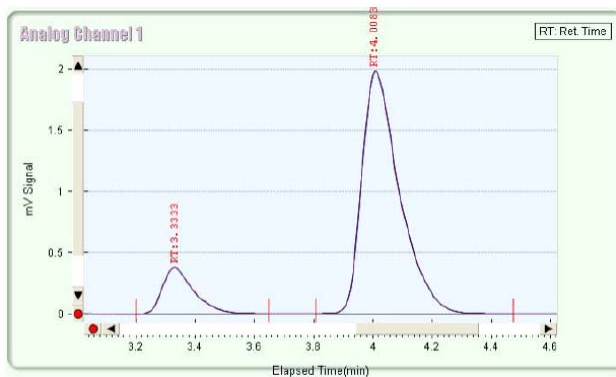
Peak Name	Area %	Area	Retention Time
Peak1	13.2853	7.9159	16.3083 min
Peak2	86.7147	51.6679	22.8878 min



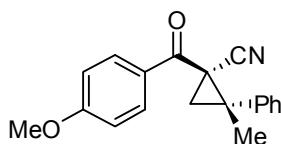
(1R,2R)-2-butyl-1-([4-(methoxy)phenyl]carbonyl)cyclopropanecarbonitrile (3g): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. 75% isolated yield, 81:19 d.r., 73% ee. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OB-H 25 cm, 1% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 210 nm, t_r (minor) 3.3 min, t_r (major) 4.0 min. $R_f = 0.37$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = +0.5$ (c 1.28, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.05 (d, $J = 9.0$ Hz, 2H, ArH), 6.99 (d, $J = 9.0$ Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 2.17-2.08 (m, 1H, CH cyclopropane), 1.99-1.87 (m, 1H, CH_2 cyclopropane), 1.87-1.35 (m, 7H, AlkH), 0.96 (t, $J = 7.2$ Hz, 3H, AlkCH_3). ^{13}C NMR (CDCl_3 , 75 MHz): δ 190.7, 164.0, 131.3 (2C), 128.7, 120.3, 113.9 (2C), 55.7, 33.3, 30.8, 30.4, 25.8, 24.4, 22.4, 14.1. IR (neat) 2957, 2928, 2856, 2235 ($\text{C}\equiv\text{N}$), 1741, 1670 ($\text{C}=\text{O}$), 1601, 1258, 1170, 1028, 991, 846, 755. HRMS (ES, Pos) Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 258.1489, found 258.1478.



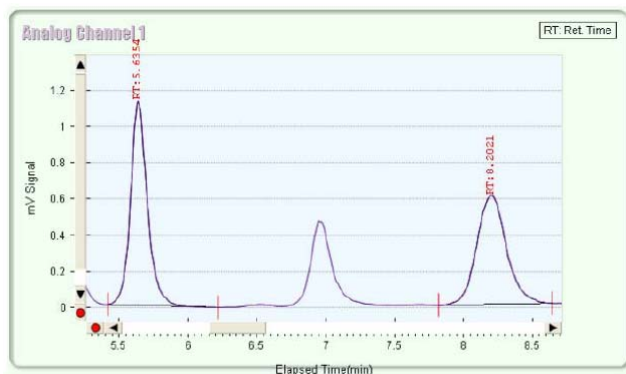
Peak Name	Area %	Area	Retention Time
Peak1	49.3212	8.574	3.1378 min
Peak2	50.6788	8.81	3.8044 min



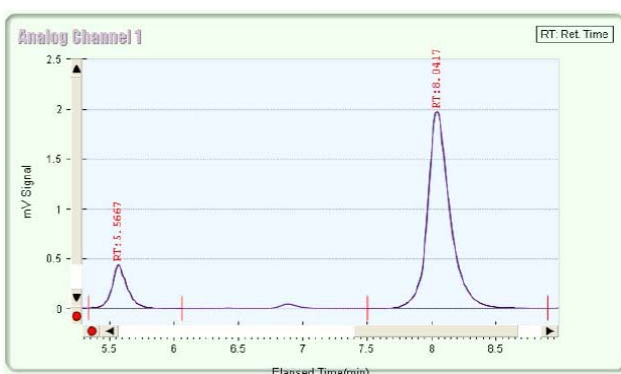
Peak Name	Area %	Area	Retention Time
Peak1	13.6912	2.7402	3.3333 min
Peak2	86.3088	17.2741	4.0083 min



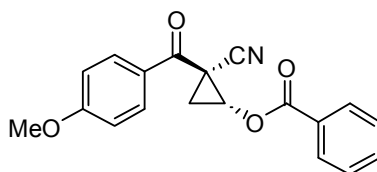
(1R,2S)-2-methyl-1-([4-(methoxy)phenyl]carbonyl)-2-phenylcyclopropanecarbonitrile (3h): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was followed. **97% isolated yield, 84:16 d.r., 75% ee.** Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (minor) 5.6 min, t_r (major) 8.0 min. $R_f = 0.28$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -109.1$ (*c* 0.59, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.11 (d, $J = 9.0$ Hz, 2H, ArH), 7.56-7.34 (m, 5H, ArH), 7.04 (d, $J = 9.0$ Hz, 2H, ArH), 3.91 (s, 3H, ArOCH_3), 2.44 (d, $J = 5.6$, 1H, CH_2 cyclopropane), 2.19 (d, $J = 5.6$ Hz, 1H, CH_2 cyclopropane), 1.43 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz): δ 188.5, 164.4, 139.6, 131.8 (2C), 129.3 (2C), 128.2, 128.5, 127.8 (2C), 119.8, 114.3 (2C), 55.7, 41.1, 31.5, 24.5, 20.4. IR (neat) 3018, 2934, 2230 ($\text{C}\equiv\text{N}$), 1670 ($\text{C}=\text{O}$), 1598, 1256, 1168, 1027, 974, 755. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 292.1332, found 292.1333.



Peak Name	Area %	Area	Retention Time
Peak2	51.6456	9.5614	5.6354 min
Peak3	46.3544	8.9521	8.2021 min

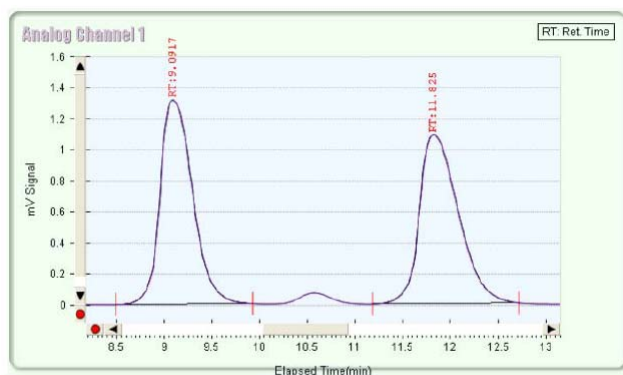


Peak Name	Area %	Area	Retention Time
Peak1	12.6612	3.462	5.5667 min
Peak2	87.3388	23.8814	8.0417 min

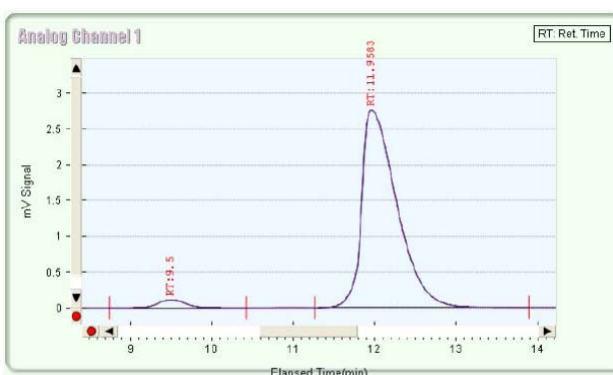


(1R,2S)-2-cyano-2-[[4-(methoxy)phenyl]carbonyl]cyclopropyl benzoate (3i): white crystalline solid.

The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using α -cyano-diazoacetophenone **1h** described in the experimental section was slightly modified, where 10 equiv of alkene (vinyl benzoate) was used. 82% isolated yield, 97:3 d.r., 94% ee. mp 65-66°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 3% *i*-PrOH, 3 mL/min, 25°C, 150 bar, 280 nm, t_r (minor) 9.5 min, t_r (major) 12.0 min. $R_f = 0.21$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -12.5$ (c 1.02, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.19-8.09 (m, 4H, ArH), 7.64 (t, $J = 7.5$ Hz, 1H, ArH), 7.50 (t, $J = 7.9$ Hz, 2H, ArH), 7.01 (d, $J = 9.0$ Hz, 2H, ArH), 4.79 (dd, $J = 5.4, 6.6$ Hz, 1H, CH cyclopropane), 3.89 (s, 3H, ArOCH_3), 2.58 (t, $J = 6.6$ Hz, 1H, CH_2 cyclopropane), 2.14 (dd, $J = 5.5, 6.4$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.1, 166.2, 164.3, 134.2, 131.7 (2C), 130.1 (2C), 128.8 (2C), 128.2, 128.2, 117.6, 114.1 (2C), 60.0, 55.7, 25.5, 22.2. IR (neat) 3061, 2935, 2841, 2239 ($\text{C}\equiv\text{N}$), 1734 ($\text{C}=\text{O}$), 1669 ($\text{C}=\text{O}$), 1600, 1255, 1174, 1021, 848. 712. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 322.1074, found 322.1077.

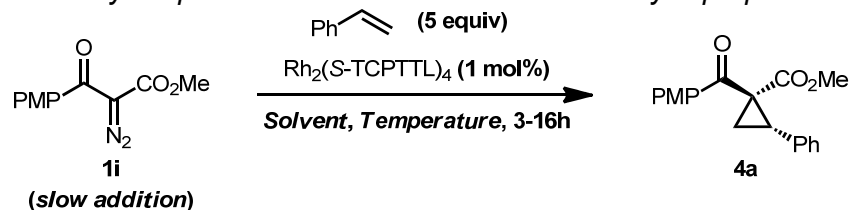


Peak Name	Area %	Area	Retention Time
Peak1	50.2937	30.9996	9.0917 min
Peak3	49.7063	30.6375	11.825 min



Peak Name	Area %	Area	Retention Time
Peak1	3.1228	2.6683	9.5 min
Peak2	96.8772	82.7779	11.9563 min

General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation with 1i
 Solvent / Temperature / Catalyst Optimization for the enantioselective cyclopropanation with diazo 1i:

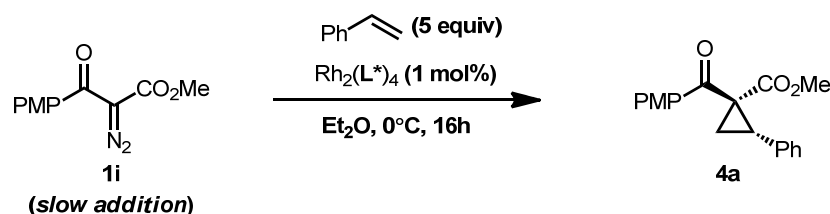


Entry	Solvent	Temperature	Yield (%) ¹	dr (<i>cis</i> : <i>trans</i>) ²	ee (%, <i>cis</i>) ³
1	CH ₂ Cl ₂	0°C	43	98 : 2	73
2	EtOAc	0°C	<5	-	-
3	DCE	0°C	47	98 : 2	69
4	DME	0°C	27	>99 : 1	83
5	<i>t</i> -BuOMe	0°C	<5	-	-
6	<i>i</i> -Pr ₂ O	0°C	9	>90 : 10	79
7	<i>n</i> -Bu ₂ O	0°C	9	>90 : 10	79
8	Et ₂ O / Hex	0°C	57	>99 : 1	81
9	Et ₂ O	0°C	51	>99 : 1	82
10	Et ₂ O	-20°C	57	>99 : 1	87
11	Et ₂ O	-40°C	60	>99 : 1	88
12	Et ₂ O	-60°C	42	>99 : 1	86

¹ Isolated Yield

² dr was determined by ¹H NMR analysis of the crude mixture

³ ee was determined by SFC on chiral stationary phase after flash chrom.

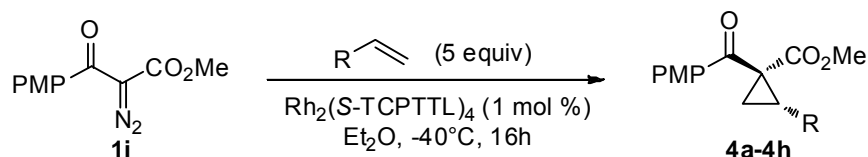


Entry	L*	Yield (%) ¹	dr (<i>cis</i> : <i>trans</i>) ²	ee (%, <i>cis</i>) ³
1	S-TCPTTL	51	>99 : 1	82
2	S-TBPTV	56	>99 : 1	82
3	S-PTTL	23	92 : 8	77
4	S-NTTL	33	87 : 13	11
5	S-1,2-BPTV	23	92 : 8	23
6	S-DOSP	9	>90 : 10	52

¹ Isolated Yield

² dr was determined by ¹H NMR analysis of the crude mixture

³ ee was determined by SFC on chiral stationary phase after flash chrom.



General Procedure for the Rh(II)-Catalyzed Enantioselective Cyclopropanation using β -ketodiazooester **1i**

The racemic products were synthesized as follows:

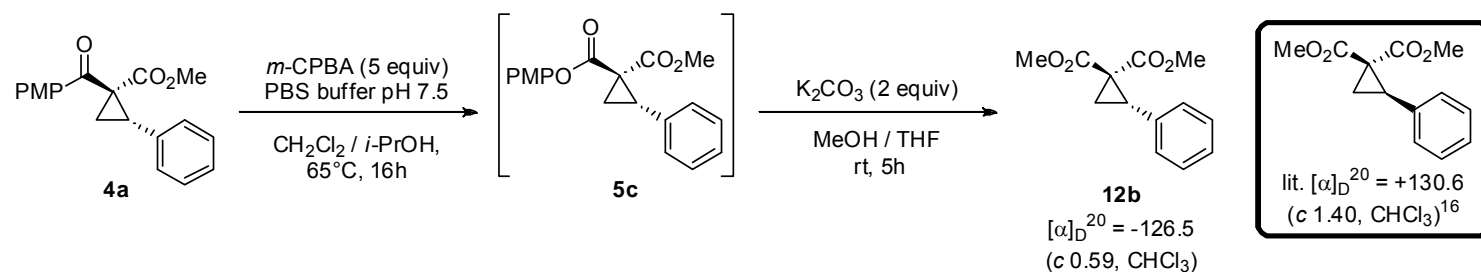
A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with catalyst $\text{Rh}_2(\text{OAc})_4$ (1.9 mg, 0.0043 mmol, 0.01 equiv), 1 mL of dry Et_2O and the alkene (2.13 mmol, 5 equiv) at room temperature (20–23°C). The mixture was cooled to 0–5°C using an ice/water bath, and a solution of diazo **1i** (100 mg, 0.427 mmol, 1.0 equiv) in 0.5 mL of dry Et_2O was added dropwise over a period of 5 minutes, the syringe was rinsed with 0.4 mL of dry Et_2O , and the mixture was left with stirring for 16 hours allowing it to slowly reach room temperature. The resulting solution was evaporated to dryness, and the residue obtained was purified on silica-gel chromatography using 70–85% CH_2Cl_2 in hexane (depending of the alkene) to obtain the pure cyclopropane as a racemic mixture.

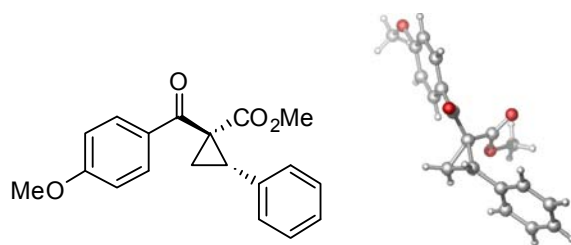
Enantioselective version with $\text{Rh}_2(\text{S-TCPTTL})_4$ as catalyst (Table 7):

A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with catalyst $\text{Rh}_2(\text{S-TCPTTL})_4$ (8.4 mg, 0.0043 mmol, 0.01 equiv), 1 mL of dry Et_2O and the alkene (2.13 mmol, 5 equiv) at room temperature (20–23°C). The mixture was cooled to –40°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before a solution of diazo **1i** (100.0 mg, 0.427 mmol, 1.0 equiv) in 0.5 mL of dry Et_2O was added dropwise over a period of 15 minutes, the syringe was rinsed with 0.4 mL of dry Et_2O , and the mixture was left with stirring for 16 hours at –40°C, keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting milky heterogenous solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH_2Cl_2 , and evaporated to dryness. (The d.r. was determined at this point using ^1H NMR). The resulting solution was evaporated to dryness, and the residue obtained was purified on silica-gel chromatography using 70–85% CH_2Cl_2 in hexane (depending of the alkene) to obtain the pure cyclopropane, which was submitted to SFC analysis using a chiral stationary phase for ee determination. On a larger scale according to table **8** (12 mmol), the residue obtained after silica-gel chromatography could be recrystallized using 20% CH_2Cl_2 in hexane as solvent to obtain the product as a single stereoisomer (>99:1 dr, >99% ee) in 41% isolated yield from **1i** (for **4a**).

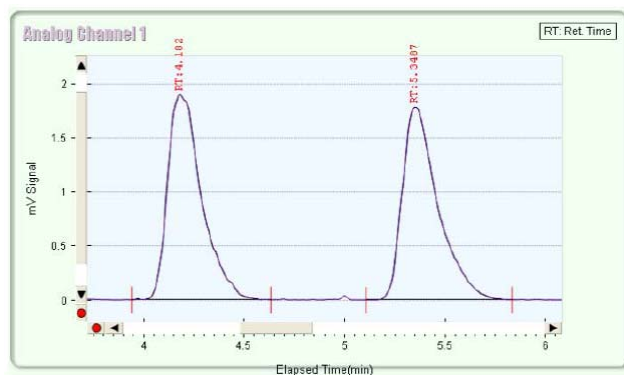
Absolute Configuration

The absolute configuration of β -ketoesters **4a–4h** was assigned by X-Ray (compound **4a**, see page S79) and confirmed by comparison of the sign of optical rotation of the *gem*-diester obtained by Baeyer-Villiger oxidation of **4a** and transesterification with MeOH with a literature value¹⁶ (See page S73 for experimental procedures of derivatization to *gem*-diester **12b**):

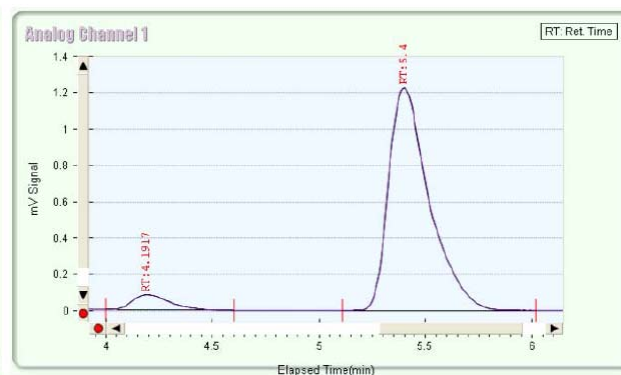




methyl (1S,2S)-1-[(4-(methoxy)phenyl)carbonyl]-2-phenylcyclopropanecarboxylate (4a): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 60% isolated yield, 99:1 d.r., 88% ee. On a larger scale according to table **8** (12 mmol), the residue obtained after silica-gel chromatography could be recrystallized using 20% CH₂Cl₂ in hexane as solvent to obtain the product as a single stereoisomer (>99:1 dr, >99% ee) in 41% isolated yield from **1i**. mp 110°C. Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, *t_r* (minor) 4.2 min, *t_r* (major) 5.4 min. *R_f* = 0.13 (70:30 CH₂Cl₂:Hexane). [α]_D²⁰ = -148.9 (*c* 1.017, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 7.94 (d, *J* = 9.0 Hz, 2H, ArH), 7.36-7.21 (m, 5H, ArH), 6.95 (d, *J* = 9.0 Hz, 2H, ArH), 3.88 (s, 3H, ArOCH₃), 3.52 (t, *J* = 8.5 Hz, 1H, CH cyclopropane), 3.28 (s, 3H, CO₂CH₃), 2.42 (dd, *J* = 4.9, 8.1 Hz, 1H, CH₂ cyclopropane), 1.64 (dd, *J* = 4.9, 9.1 Hz, 1H, CH₂ cyclopropane). ¹³C NMR (CDCl₃, 100 MHz): δ 192.7, 169.3, 163.6, 135.1, 130.8 (2C), 129.7, 129.2 (2C), 128.2 (2C), 127.3, 114.0 (2C), 55.6, 52.4, 42.1, 30.4, 19.6. IR (neat) 3023, 2959, 2839, 1709 (C=O), 1673 (C=O), 1603, 1574, 1438, 1279, 1260, 1172, 1143, 1018, 843, 693. HRMS (ES, Pos) Calcd for C₁₉H₁₈O₄ [M+H]⁺: 311.1278, found 311.1282.

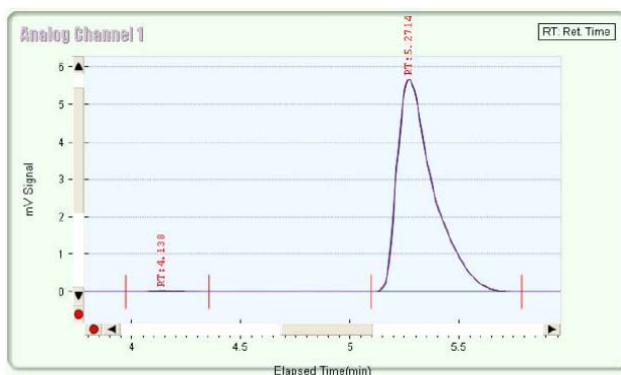


Peak Name	Area %	Area	Retention Time
Peak1	50.4136	22.0588	4.182 min
Peak2	49.5864	21.6969	5.3487 min

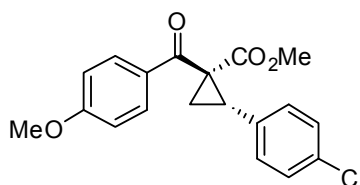


Peak Name	Area %	Area	Retention Time
Peak3	5.7554	0.9868	4.1917 min
Peak2	94.2446	16.1585	5.4 min

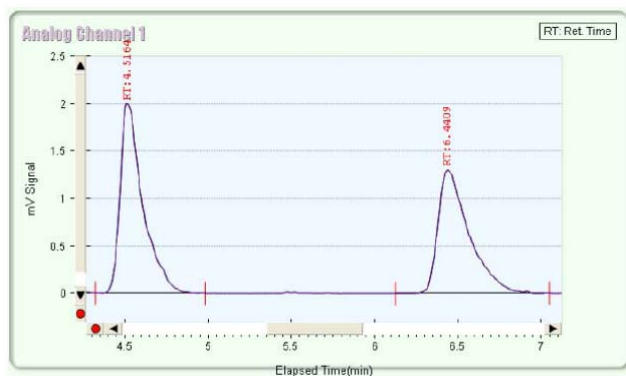
After recrystallization:



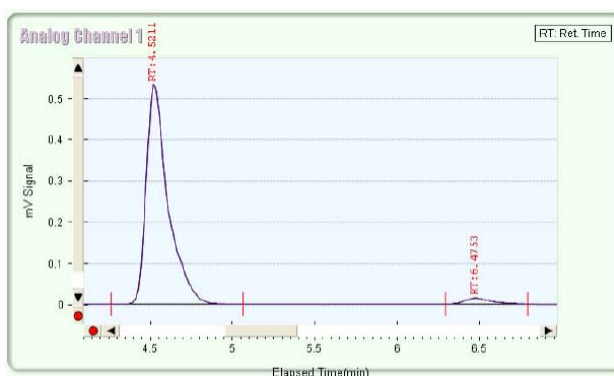
Peak Name	Area %	Area	Retention Time
Peak3	0.3764	0.2455	4.138 min
Peak2	99.6236	64.9935	5.2714 min



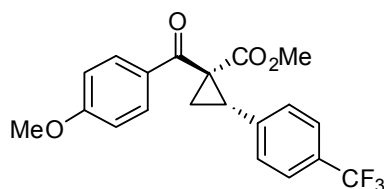
methyl (1S,2S)-2-(4-chlorophenyl)-1-([4-(methoxy)phenyl]carbonyl)cyclopropane-carboxylate (4b): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 31% isolated yield, 99:1 d.r., 94% ee. mp 118°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 4.5 min, t_r (minor) 6.5 min. $R_f = 0.17$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -142.9$ (c 0.55, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.93 (d, $J = 8.8$ Hz, 2H, ArH), 7.28 (m, 4H, ArH), 6.96 (d, $J = 8.8$ Hz, 2H, ArH), 3.90 (s, 3H, ArOCH_3), 3.48 (t, $J = 8.5$ Hz, 1H, CH cyclopropane), 3.33 (s, 3H, CO_2CH_3), 2.39 (dd, $J = 5.0, 8.0$ Hz, 1H, CH_2 cyclopropane), 1.65 (dd, $J = 5.0, 9.0$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.3, 169.1, 163.7, 133.7, 133.2, 130.8 (2C), 130.5 (2C), 129.5, 128.4 (2C), 114.0 (2C), 55.6, 52.5, 42.1, 29.7, 19.6. IR (neat) 2957, 2844, 1710 (C=O), 1672 (C=O), 1604, 1494, 1439, 1282, 1263, 1171, 1145, 1014, 833, 612. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{17}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 345.0888, found 345.0895.



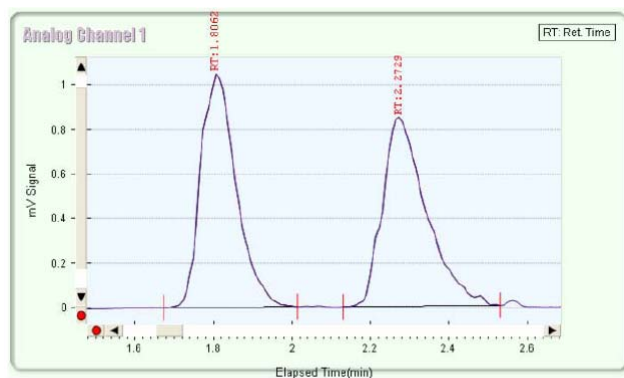
Peak Name	Area %	Area	Retention Time
Peak2	52.8669	18.6604	4.5164 min
Peak3	47.1331	16.6366	6.4409 min



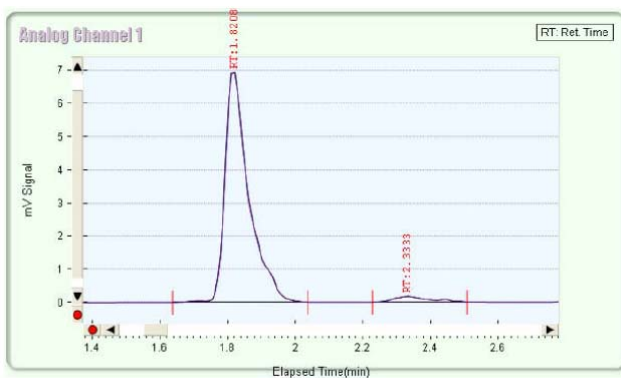
Peak Name	Area %	Area	Retention Time
Peak1	96.8972	4.813	4.5211 min
Peak2	3.1028	0.1541	6.4753 min



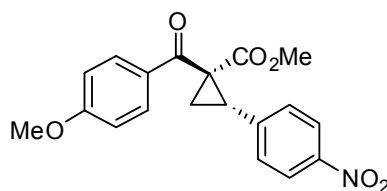
methyl (1S,2S)-1-[(4-(methoxy)phenyl)carbonyl]-2-[4-(trifluoromethyl)phenyl]cyclopropane carboxylate (4c): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 60% isolated yield, 99:1 d.r., 93% ee. mp 100°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 1.8 min, t_r (minor) 2.3 min. $R_f = 0.23$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -99.9$ (*c* 1.01, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 7.94 (d, $J = 8.7$ Hz, 2H, ArH), 7.57 (d, $J = 8.0$ Hz, 2H, ArH), 7.43 (d, $J = 8.0$ Hz, 2H, ArH), 6.96 (d, $J = 8.7$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.54 (t, $J = 8.7$ Hz, 1H, CH cyclopropane), 3.30 (s, 3H, CO_2CH_3), 2.44 (dd, $J = 5.2, 7.8$ Hz, 1H, CH_2 cyclopropane), 1.68 (dd, $J = 5.2, 9.0$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 192.0, 169.0, 163.8, 139.4, 130.9 (2C), 129.5 (2C), 129.3, 129.2, 125.1 (q, $J = 3.6$ Hz, 2C), 124.3 (q, $J = 270.3$ Hz), 114.0 (2C), 55.6, 52.5, 42.3, 29.7, 19.4. ^{19}F NMR (CDCl_3 , 282 MHz): δ -63.9. IR (neat) 2962, 2839, 1726 (C=O), 1671 (C=O), 1655, 1603, 1575, 1323, 1285, 1260, 1173, 1152, 1109, 1069, 1018, 988, 843, 823, 616. HRMS (ES, Pos) Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 379.1152, found 379.1159.



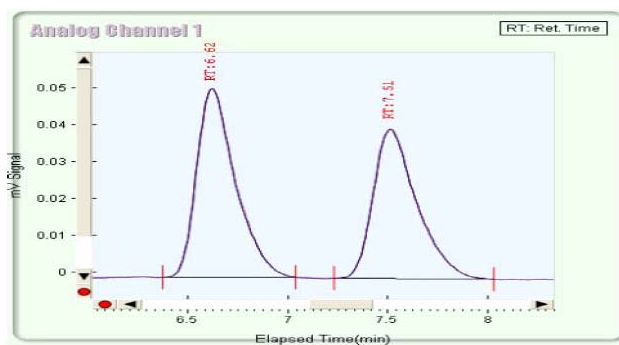
Peak Name	Area %	Area	Retention Time
Peak1	49.8871	6.4302	1.8062 min
Peak2	50.1129	6.4593	2.2729 min



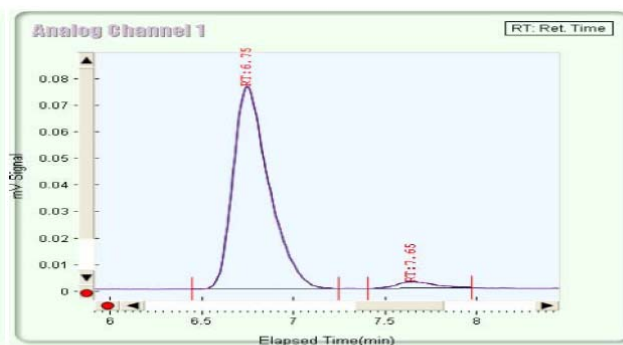
Peak Name	Area %	Area	Retention Time
Peak1	96.5556	33.2462	1.8208 min
Peak2	3.4444	1.186	2.3333 min



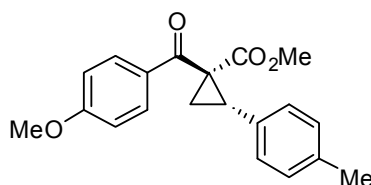
methyl (1S,2S)-1-[[4-(methoxy)phenyl]carbonyl]-2-(4-nitrophenyl)cyclopropanecarboxylate (4d): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 10% isolated yield, 99:1 d.r., 94% ee. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 210 nm, t_r (major) 6.8 min, t_r (minor) 7.7 min. $R_f = 0.14$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -126.3$ (c 0.38, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.18 (d, $J = 8.8$ Hz, 2H, ArH), 7.92 (d, $J = 8.9$ Hz, 2H, ArH), 7.49 (d, $J = 8.5$ Hz, 2H, ArH), 6.96 (d, $J = 8.9$ Hz, 2H, ArH), 3.89 (s, 3H, ArOCH_3), 3.55 (t, $J = 8.5$ Hz, 1H, CH cyclopropane), 3.32 (s, 3H, CO_2CH_3), 2.46 (dd, $J = 5.2, 8.0$ Hz, 1H, CH_2 cyclopropane), 1.73 (dd, $J = 5.2, 9.0$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 191.6, 168.8, 163.9, 147.2, 143.1, 130.9 (2C), 130.1 (2C), 129.1, 123.5 (2C), 114.1 (2C), 55.7, 52.7, 42.6, 29.7, 19.6. IR (neat) 2952, 2843, 1726 (C=O), 1669 (C=O), 1598, 1516, 1344, 1257, 1169, 1145, 1109, 1015, 841, 609. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 356.1129, found 356.1135.



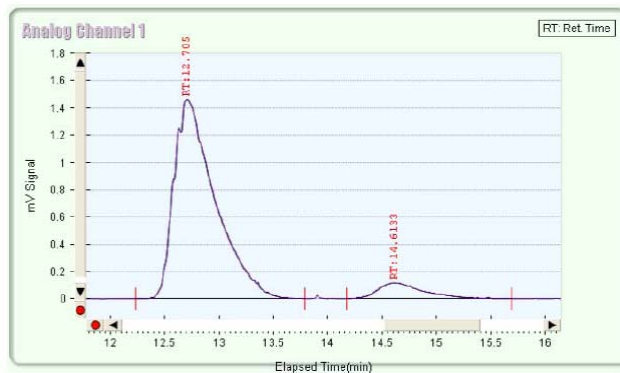
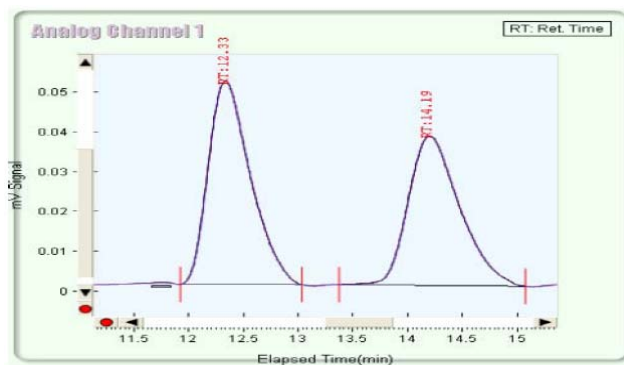
Peak Name	Peak Number	Area %	Area	Retention Time
	1	52.6973	0.6804	6.62 min
	2	47.3027	0.6108	7.51 min



Peak Name	Peak Number	Area %	Area	Retention Time
	1	96.9001	1.0255	6.75 min
	2	3.0999	0.0328	7.65 min

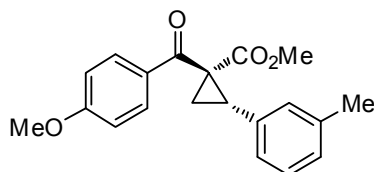


methyl (1S,2S)-1-[4-(methoxy)phenyl]carbonyl-2-(4-methylphenyl)cyclopropane carboxylate (4e): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 70% isolated yield, 99:1 d.r., 84% ee. mp 88°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 1% *i*-PrOH, 3 mL/min, 32°C, 150 bar, 210 nm, t_r (major) 12.7 min, t_r (minor) 14.6 min. $R_f = 0.24$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -144.3$ (c 1.02, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 7.95 (d, $J = 8.9$ Hz, 2H, ArH), 7.22 (d, $J = 8.0$ Hz, 2H, ArH), 7.12 (d, $J = 8.0$ Hz, 2H, ArH), 6.95 (d, $J = 8.9$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.48 (t, $J = 8.6$ Hz, 1H, CH cyclopropane), 3.31 (s, 3H, CO_2CH_3), 2.39 (dd, $J = 4.9, 8.0$ Hz, 1H, CH_2 cyclopropane), 2.33 (s, 3H, Ar- CH_3), 1.64 (dd, $J = 4.9, 9.2$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 192.8, 169.4, 163.5, 136.8, 132.0, 130.8 (2C), 129.8, 129.0 (2C), 128.9 (2C), 113.9 (2C), 55.6, 52.3, 42.0, 30.3, 21.2, 19.7. IR (neat) 2954, 2833, 1732 (C=O), 1666 (C=O), 1602, 1577, 1514, 1423, 1285, 1258, 1172, 1149, 1022, 987, 843, 823, 615. HRMS (ES, Pos) Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$ $[\text{M}+\text{H}]^+$: 325.1434, found 325.1437.

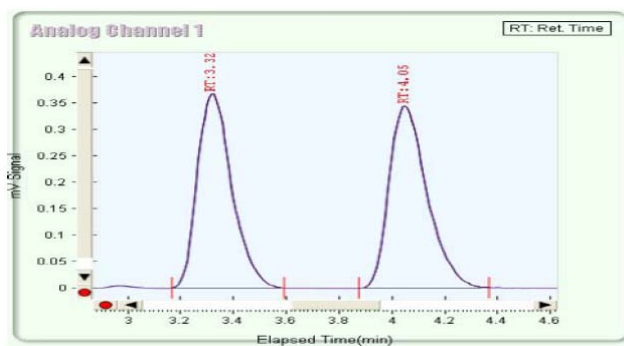


Peak Name	Peak Number	Area %	Area	Retention Time
	1	52.7525	1.3619	12.33 min
	2	47.2475	1.2197	14.19 min

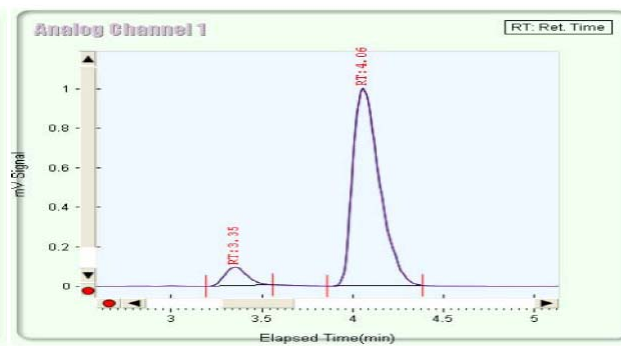
Peak Name	Area %	Area	Retention Time
Peak1	92.0553	38.338	12.705 min
Peak2	7.9447	3.3087	14.6133 min



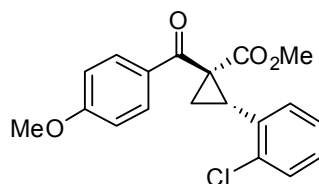
methyl (1S,2S)-1-([4-(methoxy)phenyl]carbonyl)-2-(3-methylphenyl)cyclopropane carboxylate (4f): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 54% isolated yield, 99:1 d.r., 86% ee. mp 70°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 210 nm, t_r (minor) 3.4 min, t_r (major) 4.1 min. $R_f = 0.17$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -142.4$ (c 0.93, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.95 (d, $J = 8.6$ Hz, 2H, ArH), 7.25-7.01 (m, 4H, ArH), 6.95 (d, $J = 8.6$ Hz, 2H, ArH), 3.87 (s, 3H, ArOCH_3), 3.49 (t, $J = 8.4$ Hz, 1H, CH cyclopropane), 3.30 (s, 3H, CO_2CH_3), 2.40 (dd, $J = 4.8, 7.9$ Hz, 1H, CH_2 cyclopropane), 2.34 (s, 3H, Ar- CH_3), 1.63 (dd, $J = 4.8, 9.0$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.7, 169.3, 163.5, 137.7, 135.0, 130.8 (2C), 130.0, 129.7, 128.0, 128.0, 126.0, 113.9 (2C), 55.5, 52.3, 42.0, 30.4, 21.4, 19.6. IR (neat) 2953, 2835, 1731 (C=O), 1668 (C=O), 1600, 1422, 1286, 1259, 1172, 1145, 1024, 987, 839, 700, 615. HRMS (ES, Pos) Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$ $[\text{M}+\text{H}]^+$: 325.1434, found 325.1437.



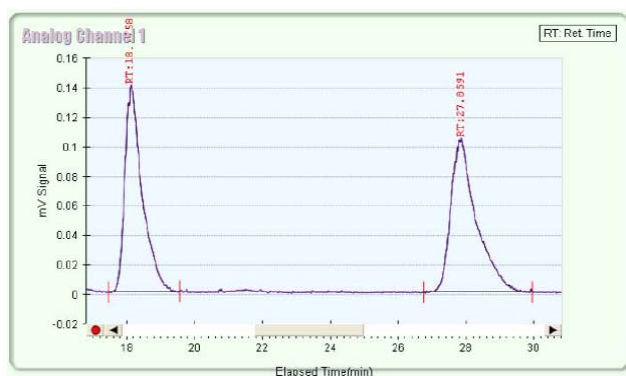
Peak Name	Peak Number	Area %	Area	Retention Time
	1	49.1182	3.2583	3.32 min
	2	50.8818	3.3752	4.05 min



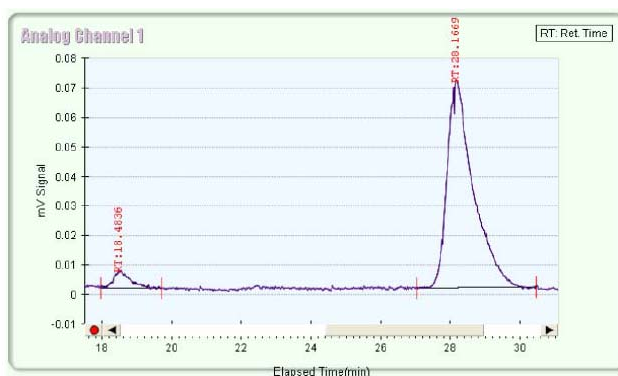
Peak Name	Peak Number	Area %	Area	Retention Time
	1	7.1886	0.7837	3.35 min
	2	92.8114	10.1178	4.06 min



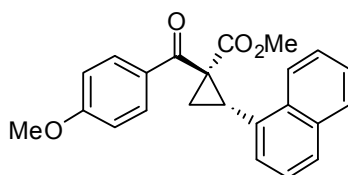
methyl (1S,2R)-2-(2-chlorophenyl)-1-([4-(methoxy)phenyl]carbonyl)cyclopropane carboxylate (4g): colourless oil. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 33% isolated yield, $\geq 97:3$ d.r., 90% ee. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 1% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 18.5 min, t_r (major) 28.2 min. $R_f = 0.37$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -109.6$ (c 3.27, CHCl_3). ^1H NMR (CDCl_3 , 300 MHz): δ 7.93 (d, $J = 8.9$ Hz, 2H, ArH), 7.41-7.33 (m, 1H, ArH), 7.32-7.17 (m, 3H, ArH), 6.95 (d, $J = 8.9$ Hz, 2H, ArH), 3.88 (s, 3H, ArOCH_3), 3.65 (t, $J = 8.6$ Hz, 1H, CH cyclopropane), 3.32 (s, 3H, CO_2CH_3), 2.45 (dd, $J = 4.9, 8.2$ Hz, 1H, CH_2 cyclopropane), 1.68 (dd, $J = 4.9, 8.9$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 75 MHz): δ 192.1, 169.4, 163.6, 136.1, 133.4, 130.8 (2C), 130.4, 129.7, 129.3, 128.7, 126.4, 113.9 (2C), 55.6, 52.4, 41.2, 29.3, 20.0. IR (neat) 2951, 2839, 1727 (C=O), 1666 (C=O), 1601, 1576, 1510, 1316, 1259, 1218, 1172, 1148, 1021, 985, 842, 613. HRMS (ES, Pos) Calcd for $\text{C}_{19}\text{H}_{17}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 345.0888, found 345.0895.



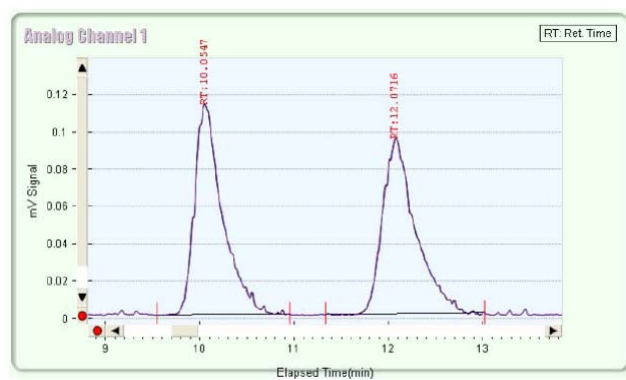
Peak Name	Area %	Area	Retention Time
Peak3	47.7446	4.9353	18.1258 min
Peak4	52.2554	5.4016	27.8591 min



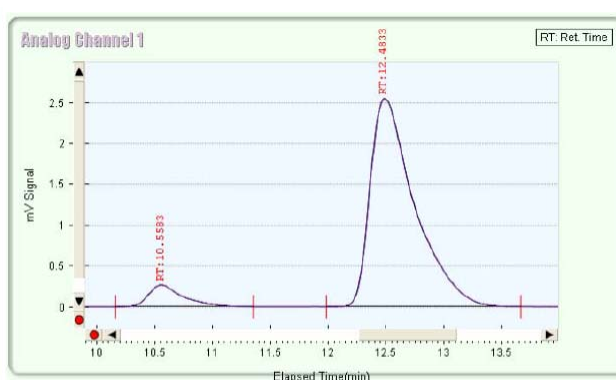
Peak Name	Area %	Area	Retention Time
Peak1	5.1893	0.1997	18.4836 min
Peak2	94.8107	3.6478	28.1669 min



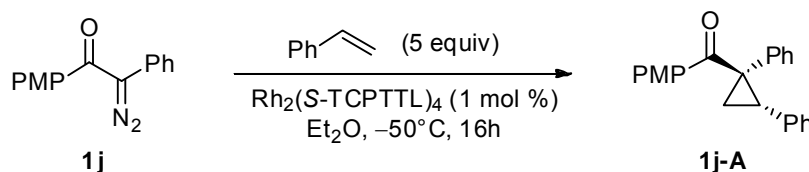
methyl (1S,2S)-1-([4-(methoxy)phenyl]carbonyl)-2-naphthalen-1-ylcyclopropane carboxylate (4h): white crystalline solid. The general procedure for the enantioselective rhodium-catalyzed cyclopropanation of alkenes using β -keto-diazoester **1i** described in the experimental section was followed. 52% isolated yield, 99:1 d.r., 85% ee. mp 115°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 10.6 min, t_r (major) 12.5 min. $R_f = 0.25$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -36.2$ (c 1.02, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 8.46 (d, $J = 8.2$ Hz, 1H, ArH), 8.03 (d, $J = 8.7$ Hz, 2H, ArH), 7.88-7.72 (m, 2H, ArH), 7.61-7.38 (m, 4H, ArH), 6.98 (d, $J = 8.7$ Hz, 2H, ArH), 3.95 (t, $J = 8.6$ Hz, 1H, CH cyclopropane), 3.89 (s, 3H, ArOCH₃), 2.97 (s, 3H, CO₂CH₃), 2.65 (dd, $J = 4.8, 8.0$ Hz, 1H, CH₂ cyclopropane), 1.74 (dd, $J = 4.8, 8.8$ Hz, 1H, CH₂ cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.8, 169.2, 163.8, 133.5, 133.1, 131.6, 131.0 (2C), 129.4, 128.3, 128.1, 126.6, 126.3, 125.9, 125.2, 124.8, 114.1 (2C), 55.6, 52.1, 41.4, 28.5, 19.4. IR (neat) 3007, 2946, 2842, 1729 (C=O), 1667 (C=O), 1602, 1576, 1508, 1434, 1294, 1259, 1172, 1147, 1019, 978, 848, 782, 770, 614. HRMS (ES, Pos) Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4$ $[\text{M}+\text{H}]^+$: 361.1434, found 361.1423.



Peak Name	Area %	Area	Retention Time
Peak1	50.5176	2.3137	10.0547 min
Peak2	49.4824	2.2662	12.0716 min

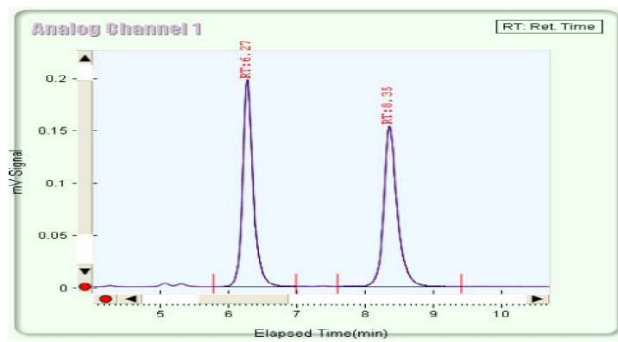


Peak Name	Area %	Area	Retention Time
Peak1	7.4161	5.4255	10.5583 min
Peak2	92.5839	67.7325	12.4833 min

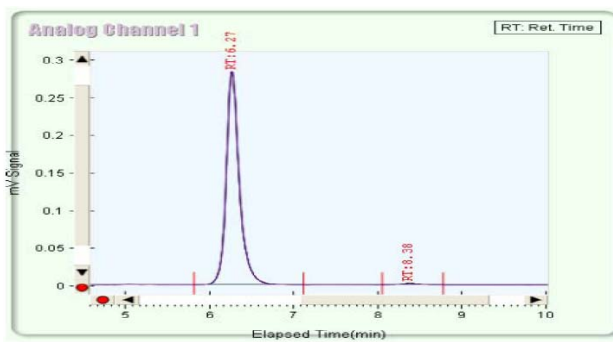


[(1*R*,2*S*)-1,2-diphenylcyclopropyl][4-(methoxy)phenyl]methanone (1j-A): white solid.
 (the racemic product was synthesized according to a literature procedure)¹²

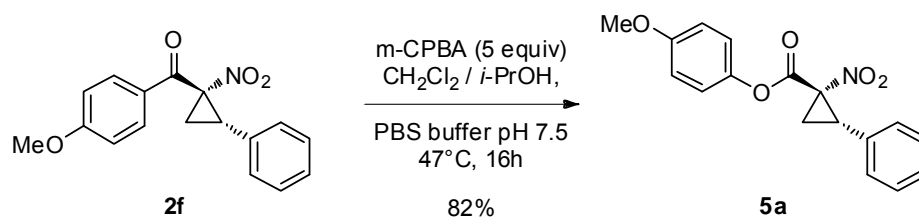
A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with catalyst $\text{Rh}_2(\text{S-TCPTTL})_4$ (3.9 mg, 0.0020 mmol, 0.01 equiv), followed by 3 mL of dry Et_2O and styrene (0.115 mL, 1.0 mmol, 5 equiv) at room temperature (20–23°C). The resulting green homogenous solution was cooled to -50°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before diazo **1j** (50.5 mg, 0.20 mmol, 1 equiv) was added in the solid state under air, the flask was capped back with the rubber septum and the resulting heterogenous green solution was stirred for a further 16 hours at -50°C , keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH_2Cl_2 , and evaporated to dryness. (The dr was determined at this point using ^1H NMR). The resulting residue was purified twice by silica-gel chromatography using 1) 60% CH_2Cl_2 in hexanes, and 2) 20% Et_2O in Hexane, to afford the pure cyclopropane product **1j-A** as a white solid (6 mg, 9%), which was submitted to SFC analysis using a chiral stationary phase for ee determination. mp 118–119°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (>95:5 dr, 98% ee) (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 280 nm, t_r (major) 6.3 min, t_r (minor) 8.4 min. $R_f = 0.28$ (20:80 Et_2O :Hexane). $[\alpha]_D^{20} = -247.4$ (*c* 0.47, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.81 (d, $J = 9.0$ Hz, 2H, ArH), 7.13–6.96 (m, 10H, ArH), 6.77 (d, $J = 9.0$ Hz, 2H, ArH), 3.78 (s, 3H, ArOCH₃), 3.45 (dd, $J = 7.1, 9.1$ Hz, 1H, CH cyclopropane), 2.23 (dd, $J = 5.2, 7.1$ Hz, 1H, CH₂ cyclopropane), 1.89 (dd, $J = 5.2, 9.1$ Hz, 1H, CH₂ cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.9, 162.7, 137.0, 136.5, 132.0 (2C), 130.3 (2C), 129.7, 128.7 (2C), 128.2 (2C), 127.8 (2C), 126.7, 126.1, 113.3 (2C), 55.4, 43.6, 30.5, 19.0. IR (neat) 2931, 1660 (C=O), 1598, 1309, 1252, 1163, 1028, 841, 697. HRMS (ES, Pos) Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$: 329.1536, found 329.1544.



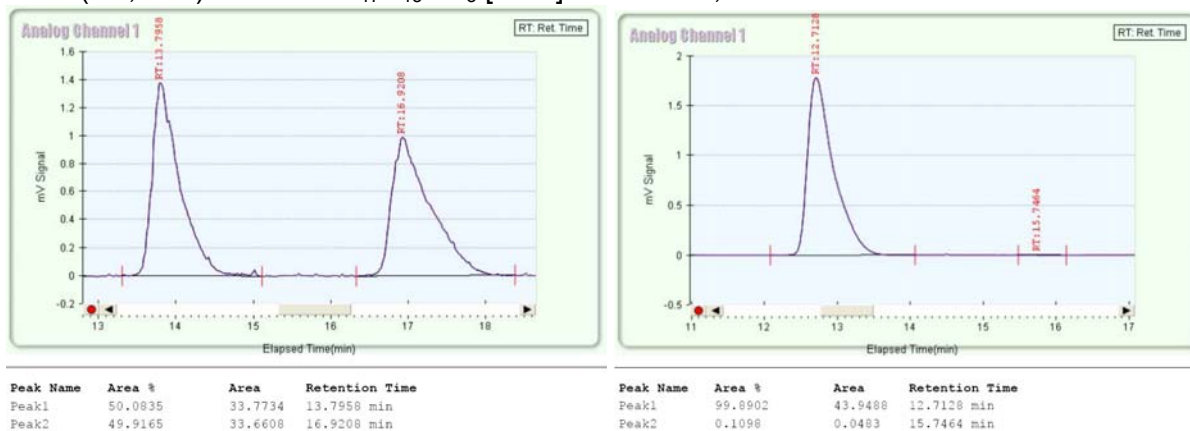
Peak Name	Peak Number	Area %	Area	Retention Time
	1	50.208	2.1218	6.27 min
	2	49.792	2.1042	8.35 min

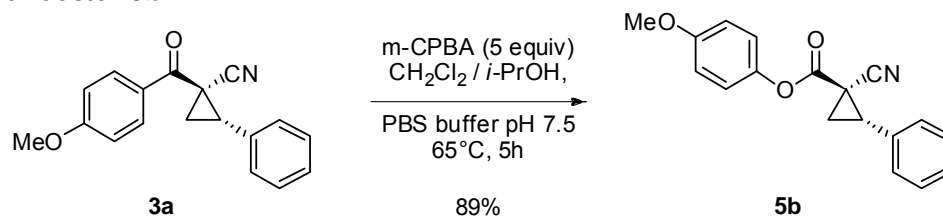


Peak Name	Peak Number	Area %	Area	Retention Time
	1	99.1815	3.0787	6.27 min
	2	0.8185	0.0254	8.38 min

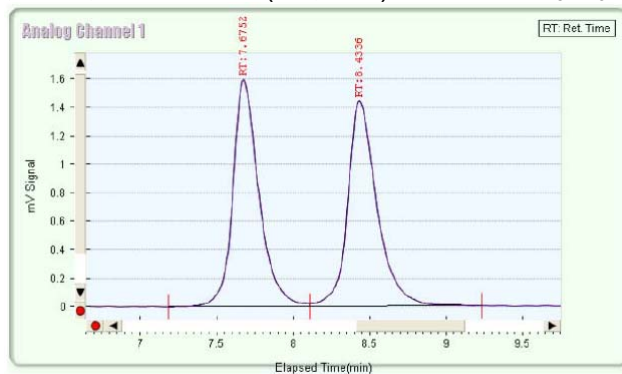
Baeyer-Villiger Oxidations of α -EWG acetophenonesSynthesis of α -nitroester **5a** :

4-(methoxyphenyl) (1S,2S)-1-nitro-2-phenylcyclopropanecarboxylate (5a). In a round-bottomed 100 mL flask equipped with a football-shaped magnetic stirring bar and a reflux condenser, cyclopropane **2f** (single dias., >99%ee, 1.25g, 4.21 mmols) was dissolved in 25 mL CH_2Cl_2 , 25 mL *i*-PrOH and 5.1 mL Phosphate Buffer (PBS) pH 7.5. Recrystallized *m*-CPBA (99% pure, 3.64g, 21.1 mmols, 5 equiv) was added, and the resulting homogeneous colorless solution was heated at 47°C for 16h. The resulting yellow solution was allowed to cool to room temperature and diluted with 300 mL EtOAc. The organic layer was washed successively with 3 x 300 mL 2% $\text{Na}_2\text{SO}_3(\text{aq})$, 3 x 300 mL 1% $\text{NaHCO}_3(\text{aq})$, 1 x 200 mL sat. $\text{NaCl}(\text{aq})$, dried on Na_2SO_4 and concentrated under reduced pressure to afford the crude α -nitro ester **5a** as a yellow solid. SiO_2 column chromatography using 40% to 60% CH_2Cl_2 in hexane (slow elution gradient) afforded the pure α -nitroester **5a** (1.08g, 82%) as a white crystalline solid (>99:1 dr, >99%ee). mp $117\text{-}118^\circ\text{C}$. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 10% *i*-PrOH, 3 mL/min, 40°C , 150 bar, 220 nm, t_r (major) 12.7 min, t_r (minor) 15.7 min. $R_f = 0.23$ (60:40 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -136.0$ (c 1.55, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.26 (m, 5H, ArH), 7.13 (d, $J = 6.8$ Hz, 2H, ArH), 6.94 (d, $J = 6.8$ Hz, 2H, ArH), 3.83 (s, 3H, ArOCH_3), 3.64 (t, $J = 9.6$ Hz, 1H, CH cyclopropane), 2.84 (dd, $J = 7.2, 9.6$ Hz, 1H, CH_2 cyclopropane), 2.20 (dd, $J = 7.2, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 164.5, 158.0, 143.7, 131.2, 128.9, 128.9 (2C), 128.6 (2C), 122.0 (2C), 114.7 (2C), 72.6, 55.7, 34.3, 20.7. IR (neat) 3082, 2937, 2838, 1752 (C=O), 1533 (NO_2), 1505, 1358 (NO_2), 1280, 1250, 1191, 1054, 1031. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 314.1023, found 314.1020.

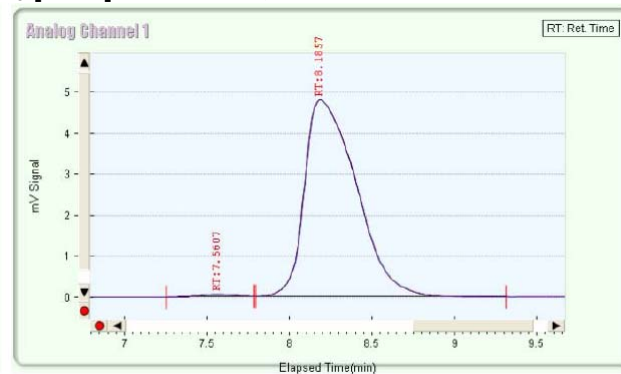


Synthesis of α -cyanoester **5b** :

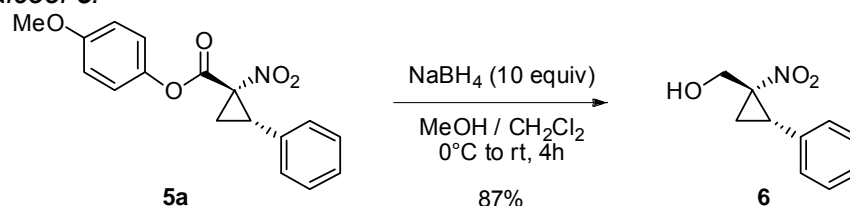
4-(methoxy)phenyl (1*R*,2*S*)-1-cyano-2-phenylcyclopropanecarboxylate (5b). In a round-bottomed 100 mL flask equipped with a football-shaped magnetic stirring bar and a reflux condenser, cyclopropane **3a** (>99:1 dr, 98% ee, 554.6 mg, 2.00 mmol, 1.0 equiv) was dissolved in 12 mL CH_2Cl_2 , 12 mL *i*-PrOH and 2.5 mL Phosphate Buffer (PBS) 1M pH 7.5. Recrystallized *m*-CPBA (99% pure, 1.73 g, 10.0 mmol, 5 equiv) was added, and the resulting homogeneous colorless solution was heated to $65\text{--}70^\circ\text{C}$ (reflux) and stirred at this temperature for 5 hours. The resulting yellow solution was allowed to cool to room temperature, diluted with 250 mL CH_2Cl_2 , and washed successively with 4 x 150 mL 2% aq. Na_2SO_3 , 1 x 200 mL sat. aq. NaHCO_3 , dried on Na_2SO_4 and concentrated under reduced pressure to afford the crude α -cyanoester **5b**. SiO_2 column chromatography using 25% to 30% Et_2O in hexane (slow elution gradient) afforded the pure α -cyanoester **5b** (522.4 mg, 89%) as a white crystalline solid (>99:1 dr, 98% ee). mp $101\text{--}102^\circ\text{C}$. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 7% *i*-PrOH, 3 mL/min, 40°C , 150 bar, 210 nm, t_r (minor) 7.6 min, t_r (major) 8.2 min. $R_f = 0.22$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -234.0$ (c 1.03, CHCl_3 , 98% ee). ^1H NMR (CDCl_3 , 400 MHz): δ 7.47–7.33 (m, 5H, ArH), 7.12 (d, $J = 9.2$ Hz, 2H, ArH), 6.93 (d, $J = 9.2$ Hz, 2H, ArH), 3.82 (s, 3H, ArOCH_3), 3.32 (t, $J = 8.9$ Hz, 1H, CH cyclopropane), 2.31 (dd, $J = 5.4$, 9.3 Hz, 1H, CH_2 cyclopropane), 2.26 (dd, $J = 5.4$, 8.5 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 166.6, 157.8, 144.0, 132.7, 129.0 (2C), 128.9, 128.5 (2C), 122.0 (2C), 116.2, 114.6 (2C), 55.7, 36.4, 23.7, 23.1. IR (neat) 3021, 2838, 2838, 2243 (C \equiv N), 1747 (C=O), 1505, 1294, 1248, 1190, 1143, 1094, 1031, 762. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 294.1125, found 294.1124.



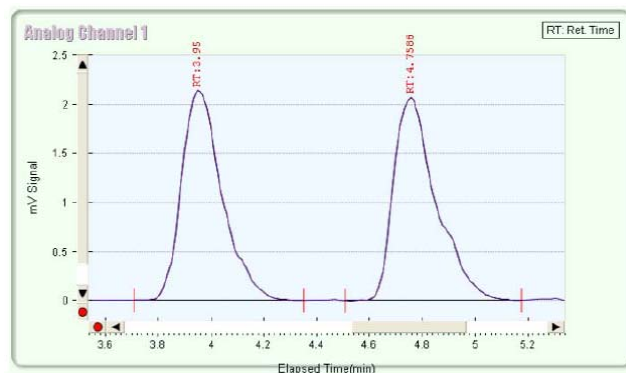
Peak Name	Area %	Area	Retention Time
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Peak3	50.4007	19.0598	8.4336 min



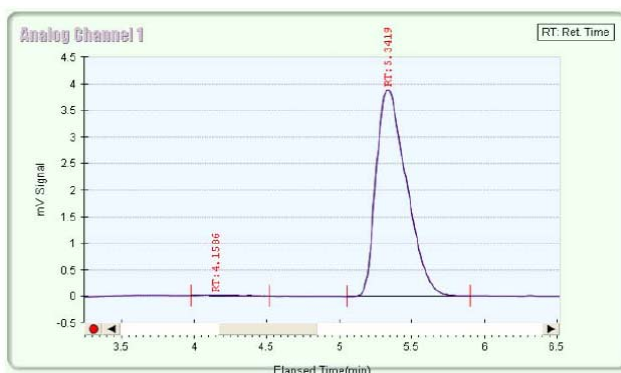
Peak Name	Area %	Area	Retention Time
Peak1	0.8367	0.8778	7.5607 min
Peak2	99.1633	104.0288	8.1857 min

Applications of α -nitro PMP-ester **5a** (Scheme1)Synthesis of β -Nitroalcohol **6**:

[(1S,2S)-1-nitro-2-phenylcyclopropyl]methanol (6). In a round-bottomed 50 mL flask equipped with a football-shaped magnetic stirring bar, cyclopropane **5a** (>99:1 dr., >99% ee, 150 mg, 0.48 mmol, 1 equiv) was dissolved in 2 mL of dry CH_2Cl_2 , 15 mL of dry MeOH was added and the resulting solution was cooled to 0°C using an ice/water bath. Sodium borohydride (NaBH_4 , 181 mg, 4.8 mmol, 10 equiv) was added in one portion, and the reaction was stirred for 4 hours, allowing to slowly warm to room temperature after 2 hours at 0°C . 1 M HCl (20 mL) and EtOAc (10 mL) were added and the mixture was allowed to vigorously stir at room temperature for 10 minutes. The layers were separated, the aqueous layer was extracted with 3 x 25 mL EtOAc, the combined organic layers were dried on Na_2SO_4 and concentrated under vacuum to afford the crude β -nitroalcohol **6**. SiO_2 column chromatography using 40% EtOAc in hexane afforded the pure β -nitroalcohol **6** (81 mg, 87%) as a white crystalline solid (>99:1 dr., >99% ee). mp 60 - 61°C . Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 20% MeOH, 2 mL/min, 40°C , 150 bar, 210 nm, t_r (minor) 4.2 min, t_r (major) 5.3 min. $R_f = 0.33$ (50:50 EtOAc:Hexane). $[\alpha]_D^{20} = -90.3$ (c 0.93, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.46-7.21 (m, 5H, ArH), 4.32 (d, $J = 13.3$ Hz, 1H, CH_2OH), 4.01 (d, $J = 13.3$ Hz, 1H, CH_2OH), 3.06 (s, br, 1H, OH), 2.99 (t, $J = 9.2$ Hz, 1H, CH cyclopropane), 2.63 (dd, $J = 6.9, 8.4$ Hz, 1H, CH_2 cyclopropane), 1.71 (dd, $J = 6.6, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 132.4, 129.1 (2C), 128.5 (2C), 128.1, 72.6, 64.9, 33.3, 18.9. IR (neat) 3263 (O-H), 2953, 2924, 2852, 1530 (NO_2), 1450, 1378 (NO_2), 1348, 1037, 696. HRMS (ES, Pos) Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 194.0812, found 194.0810.

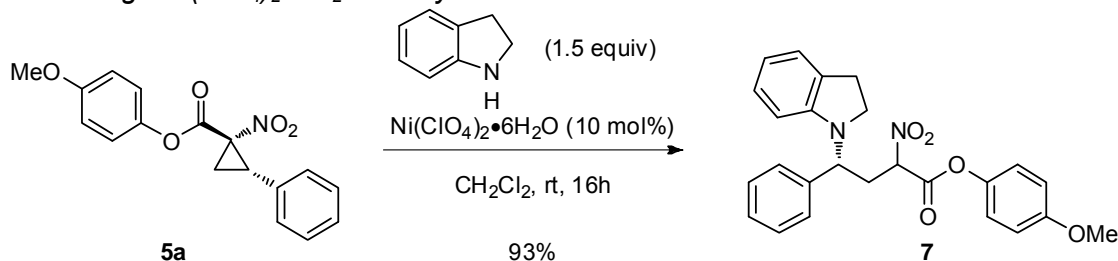


Peak Name	Area %	Area	Retention Time
Peak1	49.5401	22.5065	3.95 min
Peak2	50.4599	22.9243	4.7586 min



Peak Name	Area %	Area	Retention Time
Peak2	0.3401	0.1909	4.1586 min
Peak1	99.6599	55.9314	5.3419 min

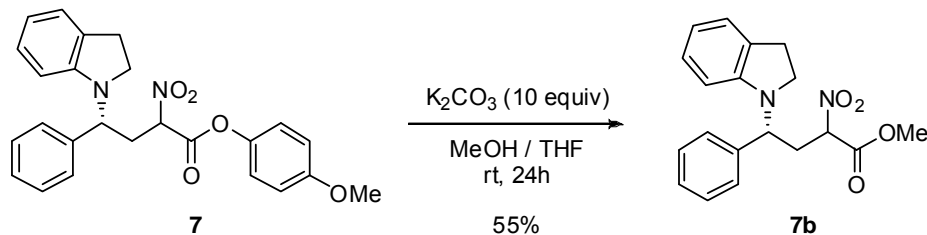
Synthesis of **7** through $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ catalyzed addition of indoline:¹⁷



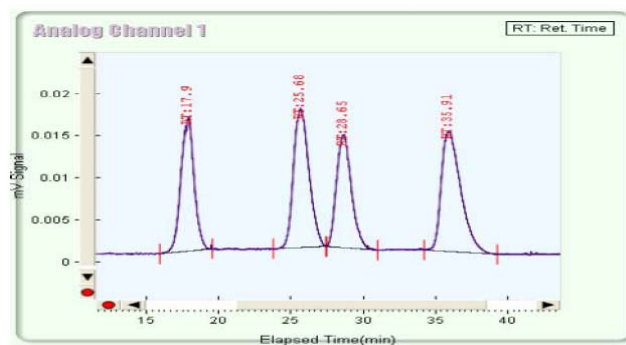
4-(methoxy)phenyl (4R)-4-(2,3-dihydro-1H-indol-1-yl)-2-nitro-4-phenylbutanoate (7). A 2 mL microwave vial equipped with a V-shaped magnetic stirring bar was charged with α -nitroester **5a** (>99:1 dr, >99%ee, 72.1 mg, 0.23 mmol, 1 equiv), a 2.5 M solution of indoline in CH_2Cl_2 was added (138 μL , 0.345 mmol, 1.5 equiv) followed by $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (8.4 mg, 0.023 mmol, 0.10 equiv) in one portion, the vial was sealed and the mixture was stirred vigorously at room temperature for 20 hours. The mixture was evaporated to dryness and the resulting residue was purified by silica-gel chromatography using 20% EtOAc in hexane as eluent, affording the pure γ -amino- α -nitroester **7** (92.7 mg, 93%) as a mixture of diastereomers (epimers at the α position) (yellow solid, 59:41 dr, >99%ee). mp 127-128°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture. $R_f = 0.31$ (20:80 EtOAc:Hexane). $[\alpha]_D^{20} = +89.7$ (c 0.98, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 59:41 inseparable mixture of diastereomers): δ 7.44-7.21 (m, 5H, ArH), 7.19-6.94 (m, 3H, ArH), 6.94-6.81 (m, 3H, ArH), 6.76-6.61 (m, 2H, ArH), 5.63 (t, $J = 6.6$ Hz, 1H *major diastereomer*, α -C-H), 5.49 (t, $J = 6.9$ Hz, 1H *minor diastereomer*, α -C-H), 4.99 (m, 1H, γ -C-H), 3.81 (s, 3H, ArOCH_3), 3.50-3.31 (m, 1H, AlkH), 3.24-2.77 (m, 5H, AlkH). ^{13}C NMR (CDCl_3 , 100 MHz, 59:41 inseparable mixture of diastereomers): *major diastereomer*: δ 163.7, 157.9, 150.8, 143.5, 137.2, 129.9, 128.8 (2C), 128.3, 127.7 (2C), 127.7, 125.0, 121.9 (2C), 118.3, 114.6 (2C), 107.5, 86.2, 55.7, 55.7, 46.4, 32.4, 28.2. *minor diastereomer*: δ 163.5, 158.0, 150.7, 143.5, 137.2, 129.8, 128.9 (2C), 128.3, 127.9 (2C), 127.6, 125.0, 121.9 (2C), 118.2, 114.7 (2C), 107.2, 85.8, 55.8, 55.6, 46.8, 32.2, 28.2. IR (neat) 2849, 1765 (C=O), 1605, 1560, 1504, 1485, 1251, 1189, 1032, 746. HRMS (ES, Pos) Calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 433.1758, found 433.1763. Enantiomeric excess was determined by transesterification of **7** and SFC analysis of the resulting methylic ester (**7b**).

¹⁷ Modified from: Lifchits, O.; Charette, A. B. *Org. Lett.* **2008**, *10*, 2809.

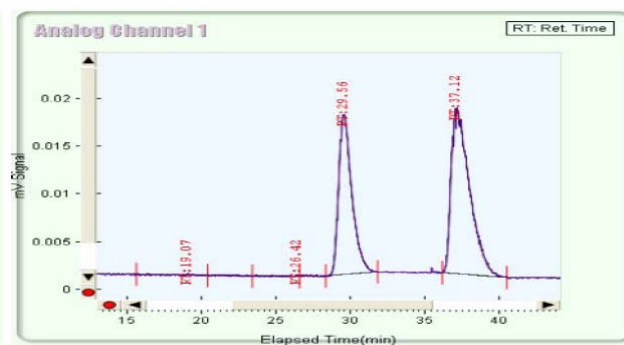
Transesterification of α -Nitroester **7** for ee determination:



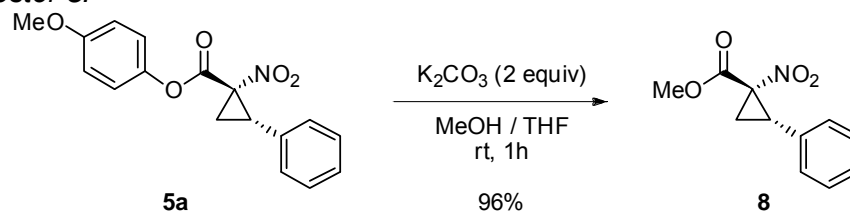
methyl (4R)-4-(2,3-dihydro-1H-indol-1-yl)-2-nitro-4-phenylbutanoate (7b). A 10 mL flame-dried round-bottomed flask equipped with a corn-shaped magnetic stirring bar was charged with finely powdered potassium carbonate (K_2CO_3 , 123 mg, 0.89 mmol, 10 equiv), dry MeOH (2 mL) was added, followed by a solution of γ -amino- α -nitroester **7** (59:41 dr, 38.3 mg, 0.089 mmol, 1 equiv) in dry THF (1 mL) dropwise via syringe, the syringe was rinsed with dry THF (0.5 mL), and the resulting heterogeneous mixture was stirred for 24 hours at room temperature or until full consumption of the starting material (follow by TLC). H_2O (2 mL) and CH_2Cl_2 (5 mL) were added, the layers were separated and the aqueous layer was extracted with 2 x 20 mL CH_2Cl_2 , the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under vacuum to obtain the crude γ -amino- α -nitroester **7b**, which was purified by silica-gel chromatography using 50% CH_2Cl_2 in hexane as eluent, yielding the pure γ -amino- α -nitroester **7b** as a beige solid (16.6 mg, 55%, 72:28 dr, >99% ee for both diastereomers). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC Analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 3% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 220 nm, t_r (minor diastereomer, minor enantiomer) 17.9 min, t_r (major diastereomer, minor enantiomer) 25.7 min, t_r (minor diastereomer, major enantiomer) 29.6 min, t_r (major diastereomer, major enantiomer) 37.1 min. $R_f = 0.76$ (30:70 EtOAc:Hexane). mp 82-83°C. $[\alpha]_D^{20} = +151.0$ (c 1.09, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 72:28 inseparable mixture of diastereomers): δ 7.44-7.22 (m, 5H, ArH), 7.12-7.00 (m, 2H, ArH), 6.66 (t, $J = 7.4$ Hz, 1H, ArH), 6.58 (d, $J = 7.9$ Hz, 1H, ArH), 5.49 (dd, $J = 5.0, 9.0$ Hz, 1H *major diastereomer*, α -C-H), 5.25 (t, $J = 6.9$ Hz, 1H *minor diastereomer*, α -C-H), 4.89 (dd, $J = 6.6, 9.1$ Hz, 1H *minor diastereomer*, γ -C-H), 4.82 (dd, $J = 4.6, 10.9$ Hz, 1H *major diastereomer*, γ -C-H), 3.79 (s, 3H, CO_2CH_3), 3.44-3.33 (m, 1H, AlkH), 3.13-2.77 (m, 5H, AlkH). ^{13}C NMR (CDCl_3 , 75 MHz, 72:28 inseparable mixture of diastereomers): *major diastereomer*: δ 165.5, 150.7, 137.4, 129.7, 128.8 (2C), 128.1, 127.7 (2C), 127.6, 124.9, 118.1, 107.3, 85.7, 55.1, 53.7, 46.3, 32.4, 28.2. *minor diastereomer*: δ 165.1, 150.7, 137.3, 129.8, 128.9 (2C), 128.3, 127.9 (2C), 127.5, 124.9, 118.1, 107.2, 85.8, 55.9, 53.8, 46.8, 31.9, 28.2. All other analysis were consistent with literature values.¹⁷



Peak Name	Peak Number	Area %	Area	Retention Time
	1	22.3408	1.02	17.9 min
	2	27.0172	1.2335	25.68 min
	3	21.2472	0.9701	28.65 min
	4	29.3948	1.3421	35.91 min

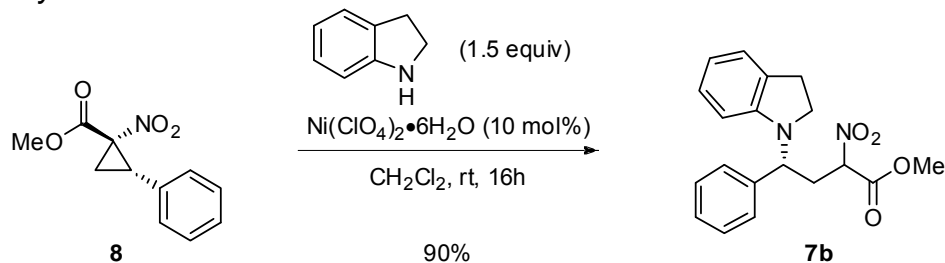


Peak Name	Peak Number	Area %	Area	Retention Time
	1	0.1847	0.0047	19.07 min
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	3	40.8656	1.0345	29.56 min
	4	58.6483	1.4847	37.12 min

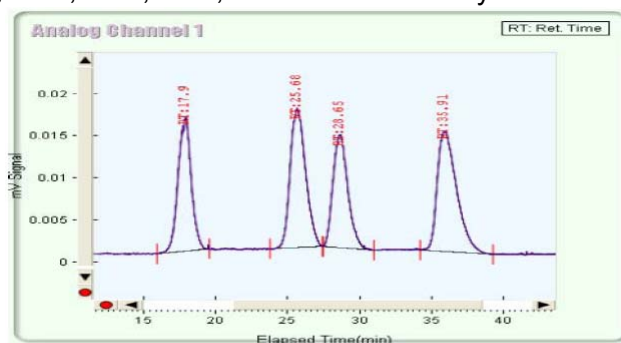
Synthesis of α -Nitroester **8**:

methyl (1S,2S)-1-nitro-2-phenylcyclopropanecarboxylate (8). A 50 mL flame-dried round-bottomed flask equipped with a football-shaped magnetic stirring bar was charged with finely powdered potassium carbonate (K_2CO_3 , 276.4 mg, 2.0 mmol, 2 equiv), dry MeOH (15 mL) was added, followed by a solution of α -nitroester **5a** (>99:1 dr, >99%ee, 313.3 mg, 1.0 mmol, 1 equiv) in dry THF (4 mL) dropwise via syringe, the syringe was rinsed with dry THF (1 mL), and the resulting heterogenous mixture was stirred for 1 hour at room temperature or until full consumption of the starting material (follow by TLC). The mixture was poured into H_2O (100 mL) and CH_2Cl_2 (100 mL), the layers were separated and the aqueous layer was extracted with 2 x 100 mL CH_2Cl_2 , the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under vacuum to obtain the crude α -nitroester **8**, which was purified by silica-gel chromatography using 40% CH_2Cl_2 in hexane as eluent, yielding the pure α -nitroester **8** as a white solid (212.7 mg, 96%, >99:1 dr, >99%ee). mp 55°C. Diastereomeric ratio was determined by 1H NMR analysis of the crude mixture. $R_f = 0.17$ (40:60 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = -71.4$ (c 1.08, $CHCl_3$). 1H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.28 (m, 3H, ArH), 7.28-7.16 (m, 2H, ArH), 3.90 (s, 3H, CO_2CH_3), 3.50 (t, $J = 9.5$ Hz, 1H, CH cyclopropane), 2.70 (dd, $J = 7.0, 9.2$ Hz, 1H, CH_2 cyclopropane), 2.05 (dd, $J = 7.0, 9.9$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.9, 131.4, 128.8 (2C), 128.8, 128.4 (2C), 72.6, 53.9, 33.9, 20.1. IR (neat) 2958, 1743 (C=O), 1544, 1437, 1359, 1295, 1153, 741. HRMS (ES, Pos) Calcd for $C_{11}H_{11}NO_4$ $[M+H]^+$: 222.0761, found 222.0756. Enantiomeric excess was determined by $Ni(ClO_4)_2 \cdot 6H_2O$ catalyzed addition of indoline and SFC analysis of the resulting product (**7b**, see next page).

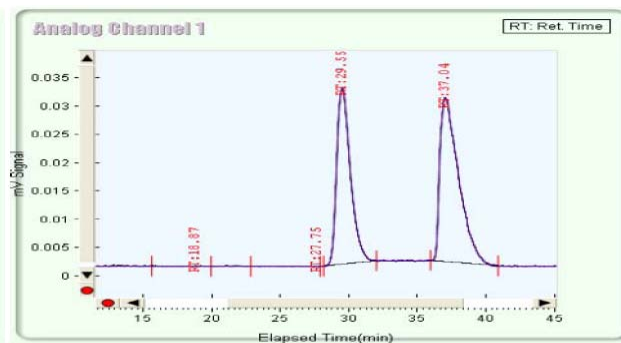
$Ni(ClO_4)_2 \cdot 6H_2O$ catalyzed addition of indoline to **8** for ee determination:¹⁷



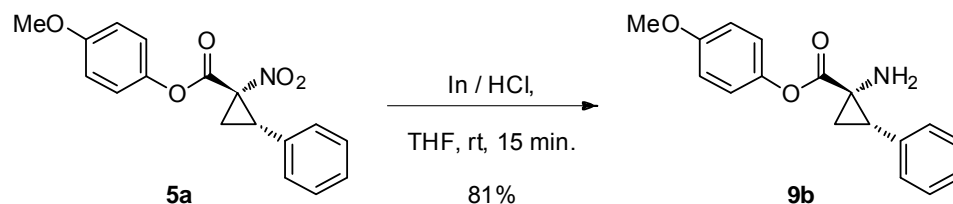
methyl (4R)-4-(2,3-dihydro-1H-indol-1-yl)-2-nitro-4-phenylbutanoate (7b). A 2 mL microwave vial equipped with a V-shaped magnetic stirring bar was charged with α -nitroester **8** (>99:1 dr, 50.9 mg, 0.23 mmol, 1 equiv), a 2.5 M solution of indoline in CH_2Cl_2 was added (138 μL , 0.345 mmol, 1.5 equiv) followed by $\text{Ni(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (8.4 mg, 0.023 mmol, 0.10 equiv) in one portion, the vial was sealed and the mixture was stirred vigorously at room temperature for 20 hours. The mixture was evaporated to dryness and the resulting residue was purified by silica-gel chromatography using 20% EtOAc in hexane as eluent, affording the pure γ -amino- α -nitroester **7b** (70.7 mg, 90%) as a mixture of diastereomers (epimers at the α position) (beige solid, 57:43 dr, >99%ee). mp 82-83°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC Analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 3% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 220 nm, t_r (minor diastereomer, minor enantiomer) 17.9 min, t_r (major diastereomer, minor enantiomer) 25.7 min, t_r (minor diastereomer, major enantiomer) 29.6 min, t_r (major diastereomer, major enantiomer) 37.0 min. $R_f = 0.76$ (30:70 EtOAc:Hexane). $[\alpha]_D^{20} = +151.0$ (c 1.09, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 57:43 inseparable mixture of diastereomers): δ 7.44-7.22 (m, 5H, ArH), 7.12-7.00 (m, 2H, ArH), 6.66 (t, $J = 7.4$ Hz, 1H, ArH), 6.58 (d, $J = 7.9$ Hz, 1H, ArH), 5.49 (dd, $J = 5.0, 9.0$ Hz, 1H *major diastereomer*, α -C-H), 5.25 (t, $J = 6.9$ Hz, 1H *minor diastereomer*, α -C-H), 4.89 (dd, $J = 6.6, 9.1$ Hz, 1H *minor diastereomer*, γ -C-H), 4.82 (dd, $J = 4.6, 10.9$ Hz, 1H *major diastereomer*, γ -C-H), 3.79 (s, 3H, CO_2CH_3), 3.44-3.33 (m, 1H, AlkH), 3.13-2.77 (m, 5H, AlkH). ^{13}C NMR (CDCl_3 , 75 MHz, 57:43 inseparable mixture of diastereomers): *major diastereomer*: δ 165.5, 150.7, 137.4, 129.7, 128.8 (2C), 128.1, 127.7 (2C), 127.6, 124.9, 118.1, 107.3, 85.7, 55.1, 53.7, 46.3, 32.4, 28.2. *minor diastereomer*: δ 165.1, 150.7, 137.3, 129.8, 128.9 (2C), 128.3, 127.9 (2C), 127.5, 124.9, 118.1, 107.2, 85.8, 55.9, 53.8, 46.8, 31.9, 28.2. All other analysis were consistent with literature values.¹⁷



Peak Name	Peak Number	Area %	Area	Retention Time
	1	22.3408	1.02	17.9 min
	2	27.0172	1.2335	25.68 min
	3	21.2472	0.9701	28.65 min
	4	29.3948	1.3421	35.91 min

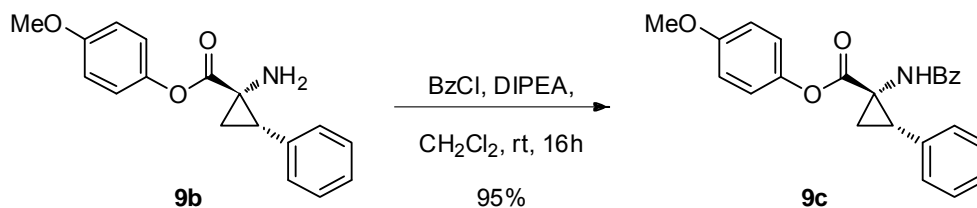


Peak Name	Peak Number	Area %	Area	Retention Time
	1	0.0301	0.0015	18.87 min
	2	0.1062	0.0052	27.75 min
	3	44.0941	2.1774	29.55 min
	4	55.7695	2.7539	37.04 min

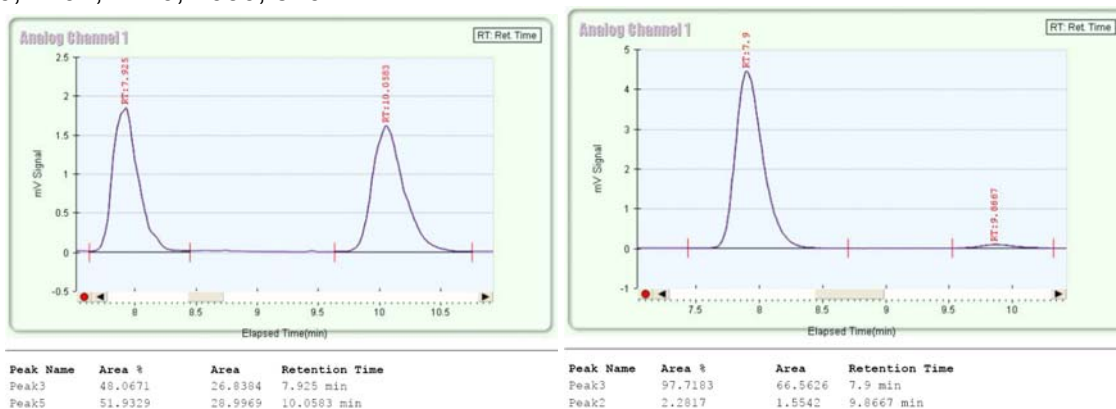
Synthesis of (*S,S*)-Boc- ν^Z Phe **9**:1. Nitro Reduction:¹⁸

4-(methoxy)phenyl (1*S*,2*S*)-1-amino-2-phenylcyclopropanecarboxylate (9b). In a 100 mL round-bottomed flask equipped with a football-shaped magnetic stirring bar, α -nitroester **5a** (>99:1 d.r., >99%ee, 200 mg, 0.638 mmols) was dissolved in 3 mL THF at room temperature, aqueous HCl 2N was added (11.5 mL, 23.0 mmols, 36.0 equiv) followed by In powder (1.466g, 12.8 mmols, 20.0 equiv) in one portion. The gray heterogenous solution rapidly became clear and a metallic precipitate appeared. The resulting solution was stirred at room temperature for 15 minutes before 20 mL EtOAc and 60 mL of sat. $\text{NaHCO}_3(\text{aq})$ was added slowly. The resulting mixture was stirred for 10 more minutes, the phases were separated and the aqueous layer was extracted with 5 x EtOAc. Combined organic layers were dried on Na_2SO_4 , concentrated under vacuum, and the crude α -aminoester **9b** was purified on silica-gel chromatography using 35% EtOAc in hexane as eluent (146.3 mg, 81% yield, colourless oil). $R_f = 0.17$ (35:65 EtOAc:Hexane). $[\alpha]_D^{20} = -108.7$ (c 2.43, CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.42-7.25 (m, 5H, ArH), 7.06 (d, $J = 9.2$ Hz, 2H, ArH), 6.92 (d, $J = 9.2$ Hz, 2H, ArH), 3.82 (s, 3H, ArOCH_3), 3.03 (dd, $J = 8.0, 9.6$ Hz, 1H, CH cyclopropane), 2.04 (dd, $J = 5.2, 8.0$ Hz, 1H, CH_2 cyclopropane), 1.79 (s, br, 2H, NH_2), 1.61 (dd, $J = 5.2, 8.0$ Hz, 1H, CH_2 cyclopropane). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 174.3, 156.9, 143.9, 135.0, 128.9, 127.9, 126.7, 121.8, 114.1, 55.3, 40.8, 33.4, 22.2. IR (neat) 2928, 1736 (C=O), 1605, 1506, 1247, 1194, 1132, 734. HRMS (ES, Pos) Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 284.1281, found 284.1295. Enantiomeric excess was determined by benzoylation procedure and SFC analysis of the resulting compound (**9c**):

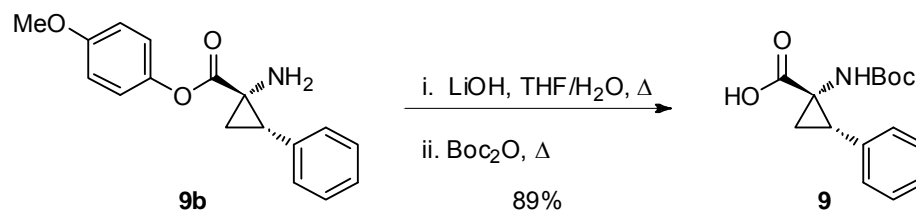
¹⁸ Modified from: He, L.; Srikanth, G. S. C.; Castle, S. L. *J. Org. Chem.* **2005**, *70*, 8140.

Determination of enantiomeric excess of **9b** through *N*-benzylation:

4-(methoxyphenyl) (1S,2S)-2-phenyl-1-[(phenylcarbonyl)amino]cyclopropanecarboxylate (9c). In a 100 mL round-bottomed flask equipped with a football-shaped magnetic stirring bar, α -amino ester **9b** (41.0 mg, 0.145 mmol) was dissolved in 10 mL CH_2Cl_2 at room temperature. DIPEA (32.8 μL , 0.188 mmol, 1.3 equiv) was added, followed by BzCl (20.2 μL , 0.174 mmol, 1.2 equiv). The resulting mixture was stirred overnight (16h) and quenched with 10 mL aqueous sat. NaHCO_3 ; the phases were separated and the aqueous layer was extracted with 2 x CH_2Cl_2 . Combined organic layers were dried on Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by silica-gel chromatography using 1) 80% CH_2Cl_2 in hexane 2) 35% EtOAc in hexane (53.1 mg, 95% yield, >95:5 d.r., 95% ee, white solid). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 15% *i*-PrOH, 3mL/min, 40°C, 150bar, t_r (major) 7.9 min, t_r (minor) 9.9 min. $R_f = 0.21$ (35:65 EtOAc:Hexane). $[\alpha]_D^{20} = -70.0$ (c 0.83, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.58-7.21 (m, 10H, ArH), 7.06 (d, $J = 8.8$ Hz, 2H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, ArH), 6.12 (s, 1H, NH-Bz) 3.80 (s, 3H, ArOCH_3), 3.21 (t, $J = 8.8$ Hz, 1H, CH cyclopropane), 2.49 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane), 1.99 (dd, $J = 6.4, 9.6$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 168.2, 157.2, 144.2, 133.9, 133.8, 131.6, 128.6, 128.5, 128.4, 127.7, 126.8, 122.1, 114.3, 55.4, 38.8, 33.3, 21.7. IR (neat) 3330 (N-H), 1749 (C=O ester), 1642 (C=O amide), 1504, 1485, 1246, 1191, 1140, 1030, 846.

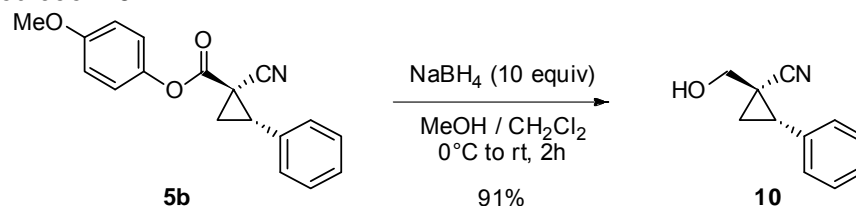


2. Saponification/Boc protection:

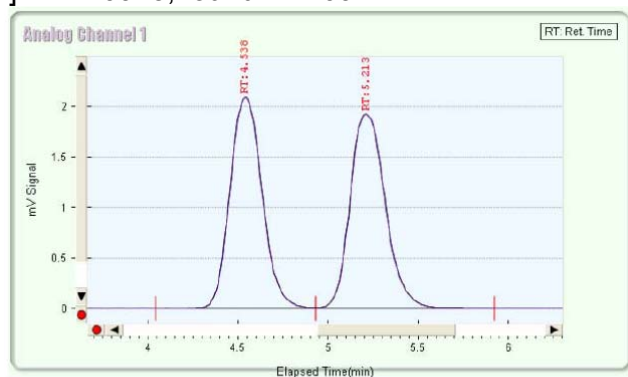


(1S,2S)-1-(((1,1-dimethylethyl)oxy)carbonyl)amino)-2-phenylcyclopropanecarboxylic acid (9).¹⁹ In a 50 mL round-bottomed flask equipped with a football-shaped magnetic stirring bar, the α -aminoester **9b** (114.0 mg, 0.402 mmol, >95:5 dr, 95% ee) was dissolved in a mixture of 10 mL THF and 10 mL H₂O, LiOH (28.9 mg, 1.21 mmol, 3 equiv) was added and the resulting mixture was heated to 40°C for 2 hours or until no starting material was left (follow by TLC). After this time, Boc₂O (263.4 mg, 1.21 mmol, 3 equiv) was added and the reaction was heated to 60°C for 24h. The reaction mixture was allowed to cool to room temperature, 50 mL EtOAc and 50 mL H₂O were added and the pH was adjusted to 8 using aqueous NaOH 1N. The phases were separated and the aqueous layer was extracted with 3 x EtOAc to remove the excess Boc₂O and the phenol byproduct. The aqueous layer was acidified to pH 1 using aqueous HCl 1N, and reextracted with 5 x EtOAc. These last extracts were combined, dried over Na₂SO₄, filtered and concentrated to dryness to afford the pure *N*-Boc-amino acid **9** as a white solid (99.5 mg, 89% yield). mp 177-178°C (lit. 179-181°C)¹⁹. $[\alpha]_{\text{D}}^{20} = -87.4$ (c 0.47, CH₂Cl₂) (lit. $[\alpha]_{\text{D}}^{20} = -106.8$ (c 1.4, CH₂Cl₂)).¹⁹ ¹H NMR (CDCl₃, 400 MHz): δ 7.42-7.25 (m, 3H, ArH), 7.25-7.16 (m, 2H, ArH), 4.65 (s (br), 1H, NHBoc), 3.05 (t, $J = 8$ Hz, 1H, CH cyclopropane), 2.22 (s (br), 1H, CH₂ cyclopropane major rotamer), 2.09 (s (br), 1H, CH₂ cyclopropane minor rotamer), 1.83 (s (br), 1H, CH₂ cyclopropane major rotamer), 1.67 (s (br), 1H, CH₂ cyclopropane minor rotamer), 1.37 (s, 9H, *t*-Bu major rotamer), 1.28 (s, 9H, *t*-Bu minor rotamer). ¹³C NMR (75 MHz, CDCl₃): δ 178.1, 156.2, 134.5, 128.8, 128.3, 127.3, 80.0, 39.4, 33.1, 27.8, 21.4. IR (neat) 3385 (N-H), 2982, 2928, 1689 (C=O), 1504, 1242, 1162, 730, 696. HRMS (ES, Pos) Calcd for C₁₅H₁₉NO₄ [M+Na]⁺: 300.1211, found 300.1206.

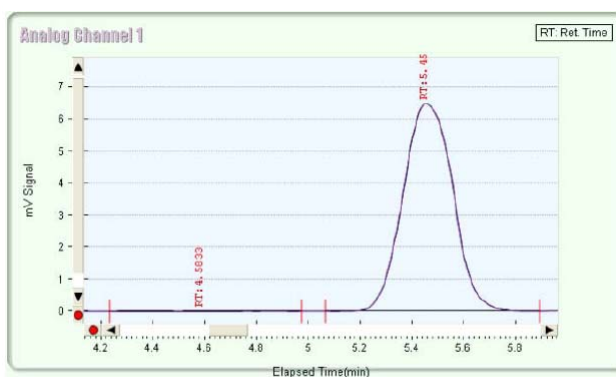
¹⁹ Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

Applications of α -cyano PMP-ester **5b** (Scheme 2)Synthesis of β -Cyanoalcohol **10**:

(1*R*,2*S*)-1-(hydroxymethyl)-2-phenylcyclopropanecarbonitrile (10). In a round-bottomed 50 mL flask equipped with a football-shaped magnetic stirring bar, cyclopropane **5b** (>99:1 dr., 98% ee, 117.3 mg, 0.40 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (2 mL), dry MeOH (13 mL) was added and the resulting solution was cooled to 0°C using an ice/water bath. Sodium borohydride (NaBH_4 , 151 mg, 4.0 mmol, 10 equiv) was added in one portion, and the reaction was stirred for 4 hours, allowing to slowly warm to room temperature after 2 hours at 0°C . 1 M HCl (20 mL) and EtOAc (10 mL) were added and the mixture was allowed to vigorously stir at room temperature for 10 minutes. The layers were separated, the aqueous layer was extracted with 3 x 25 mL EtOAc, the combined organic layers were dried on Na_2SO_4 and concentrated under vacuum to afford the crude β -cyanoalcohol **10**. SiO_2 column chromatography using 40% EtOAc in hexane afforded the pure β -cyanoalcohol **10** (63.4 mg, 91%) as a white solid (>99:1 dr., >99% ee). mp 40 – 41°C . Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 7% MeOH, 3 mL/min, 40°C , 150 bar, 210 nm, t_r (minor) 4.6 min, t_r (major) 5.5 min. $R_f = 0.13$ (25:75 EtOAc:Hexane). $[\alpha]_D^{20} = -51.0$ (c 0.92, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.43–7.21 (m, 5H, ArH), 3.78 (d, $J = 11.7$ Hz, 1H, CH_2OH), 3.64 (d, $J = 11.7$ Hz, 1H, CH_2OH), 3.18 (s, br, 1H, CH_2OH), 2.48 (t, $J = 7.8$ Hz, 1H, CH cyclopropane), 1.72 (t, $J = 6.1$ Hz, 1H, CH_2 cyclopropane), 1.46 (t, $J = 6.9$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 135.2, 128.6 (2C), 128.1 (2C), 127.7, 120.4, 65.6, 28.4, 22.5, 17.1. IR (neat) 3419 (O–H), 3021, 2925, 2237 ($\text{C}\equiv\text{N}$), 1711, 1500, 1456, 1218, 1045, 928, 755, 699. HRMS (ES, Pos) Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$ $[\text{M}+\text{H}]^+$: 174.0913, found 174.0912.

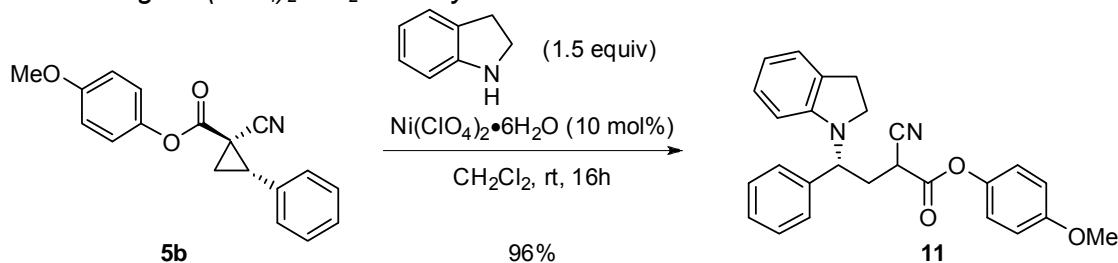


Peak Name	Area %	Area	Retention Time
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Peak3	50.2855	25.8068	5.213 min



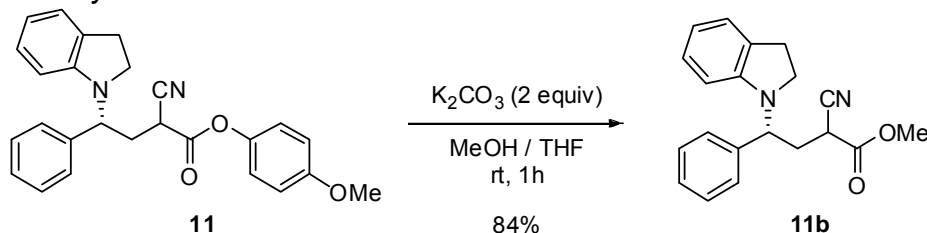
Peak Name	Area %	Area	Retention Time
Peak2	0.043	0.0369	4.5833 min
Peak1	99.957	85.6852	5.45 min

Synthesis of **11** through $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ catalyzed addition of indoline:¹⁷

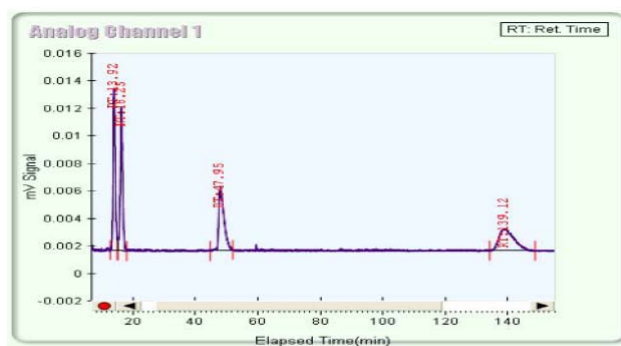


4-(methoxy)phenyl (4R)-2-cyano-4-(2,3-dihydro-1H-indol-1-yl)-4-phenylbutanoate (11). A 2 mL microwave vial equipped with a V-shaped magnetic stirring bar was charged with α -cyanoester **5b** (>99:1 dr, 98%ee, 67.5 mg, 0.23 mmol, 1 equiv), a 2.5 M solution of indoline in CH_2Cl_2 was added (138 μL , 0.345 mmol, 1.5 equiv) followed by $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (8.4 mg, 0.023 mmol, 0.10 equiv) in one portion, the vial was sealed and the mixture was stirred vigorously at room temperature for 20 hours. The mixture was evaporated to dryness and the resulting residue was purified by silica-gel chromatography using 80% CH_2Cl_2 in hexane as eluent, affording the pure γ -amino- α -cyanoester **11** (90.9 mg, 96%) as a mixture of diastereomers (epimers at the α position) (white solid, 54:46 dr, 98%ee). mp 43-44°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture. $R_f = 0.37$ (25:75 EtOAc:Hexane). $[\alpha]_D^{20} = +120.5$ (c 0.84, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.43-7.23 (m, 5H, ArH), 7.17 (q, $J = 8.0$ Hz, 1H, ArH), 7.06 (t, $J = 9.0$ Hz, 1H, ArH), 7.01-6.95 (m, 1H, ArH), 6.95-6.77 (m, 3H, ArH), 6.77-6.66 (m, 2H, ArH), 5.24 (dd, $J = 5.0, 10.7$ Hz, 1H *major diastereomer*, α -C-H), 5.12 (dd, $J = 3.8, 11.7$ Hz, 1H *minor diastereomer*, α -C-H), 4.13 (dd, $J = 5.3, 9.4$ Hz, 1H *minor diastereomer*, γ -C-H), 3.95 (t, $J = 6.0$ Hz, 1H *major diastereomer*, γ -C-H), 3.82 (s, 3H *minor diastereomer*, ArOCH_3), 3.79 (s, 3H *major diastereomer*, ArOCH_3), 3.45-3.36 (m, 1H *minor diastereomer*, Alk-H), 3.32-3.23 (m, 1H *major diastereomer*, Alk-H), 3.11-2.84 (m, 3H, Alk-H), 2.82-2.55 (m, 2H, Alk-H). ^{13}C NMR (CDCl_3 , 100 MHz, mixture of 2 diastereomers): δ 165.4, 164.9, 157.9, 157.7, 150.9, 150.9, 143.7, 143.7, 137.4, 137.3, 130.2, 129.8, 128.8 (2C), 128.8 (2C), 128.3, 128.2, 127.9 (2C), 127.9 (2C), 127.8 (2C), 127.7 (2C), 125.0, 124.9, 121.9 (2C), 121.9 (2C), 118.4, 118.2, 116.5, 116.4, 114.6, 114.4, 108.2, 107.5, 56.6, 56.4, 55.7, 55.7, 46.4, 46.2, 35.6, 35.4, 32.0, 31.2, 28.2, 28.1. IR (neat) 2928, 1760 (C=O), 1605, 1505, 1485, 1250, 1217, 1189, 1032, 752. HRMS (ES, Pos) Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 413.1860, found 413.1863. Enantiomeric excess was determined by transesterification of **11** and SFC analysis of the resulting methylic ester (**11b**).

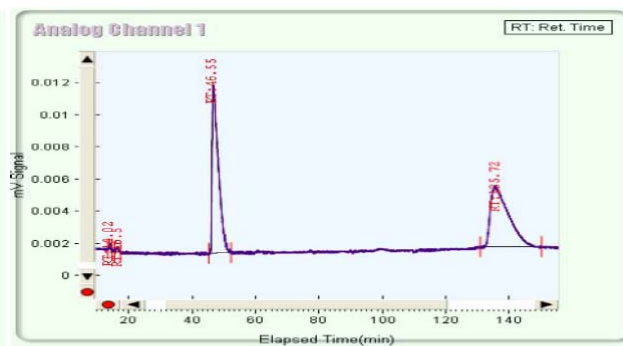
Transesterification of α -cyanoester **11** for ee determination:



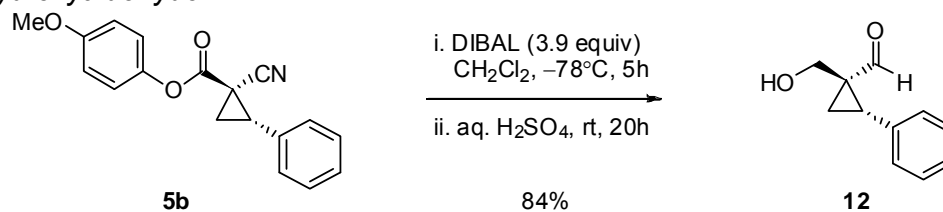
methyl (4R)-2-cyano-4-(2,3-dihydro-1H-indol-1-yl)-4-phenylbutanoate (11b). A 10 mL flame-dried round-bottomed flask equipped with a corn-shaped magnetic stirring bar was charged with finely powdered potassium carbonate (K_2CO_3 , 24.5 mg, 0.177 mmol, 2 equiv), dry MeOH (2 mL) was added, followed by a solution of γ -amino- α -cyanoester **11** (54:46 dr, 36.5 mg, 0.089 mmol, 1 equiv) in dry THF (1 mL) dropwise via syringe, the syringe was rinsed with dry THF (0.5 mL), and the resulting heterogenous mixture was stirred for 1 hour at room temperature or until full consumption of the starting material (follow by TLC). H_2O (2 mL) and CH_2Cl_2 (5 mL) were added, the layers were separated and the aqueous layer was extracted with 2 x 20 mL CH_2Cl_2 , the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under vacuum to obtain the crude γ -amino- α -cyanoester **11b**, which was purified by silica-gel chromatography using 70% CH_2Cl_2 in hexane as eluent, yielding the pure γ -amino- α -cyanoester **11b** as a colourless oil (23.8 mg, 84%, 51:49 dr, >98%ee for both diastereomers). Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC Analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 5% *i*-PrOH, 3 mL/min, 35°C, 150 bar, 280 nm, t_r (minor diastereomer, minor enantiomer) 14.0 min, t_r (major diastereomer, minor enantiomer) 16.5 min, t_r (minor diastereomer, major enantiomer) 46.6 min, t_r (major diastereomer, major enantiomer) 135.7 min. $R_f = 0.24$ (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20} = +170.2$ (c 1.33, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 51:49 inseparable mixture of diastereomers): δ 7.43-7.21 (m, 5H, ArH), 7.19-7.09 (m, 1H, ArH), 7.05 (t, $J = 6.6$ Hz, 1H, ArH), 6.77 (dd, $J = 8.0, 15.3$ Hz, 1H, ArH), 6.68 (t, $J = 7.5$ Hz, 1H, ArH), 5.13-5.01 (m, 1H, AlkH), 3.93 (dd, $J = 4.8, 10.2$ Hz, 1H *major diastereomer*, AlkH), 3.82 (s, 3H *major diastereomer*, CO_2CH_3), 3.70 (t, $J = 6.2$ Hz, 1H *minor diastereomer*, AlkH), 3.68 (s, 3H *minor diastereomer*, CO_2CH_3), 3.44-3.30 (m, 1H, AlkH), 3.13-2.71 (m, 4H, AlkH), 2.68-2.56 (m, 1H *minor diastereomer*, AlkH), 2.56-2.43 (m, 1H *major diastereomer*, AlkH). ^{13}C NMR (CDCl_3 , 100 MHz, mixture of 2 diastereomers): δ 166.9, 166.4, 150.9, 150.7, 137.5, 137.4, 129.8, 129.7, 128.9 (2C), 128.8 (2C), 128.2, 128.1, 127.9 (2C), 127.8 (2C), 127.7, 127.6, 124.9, 124.8, 118.1, 118.0, 116.7, 116.6, 107.7, 107.5, 56.6, 56.1, 53.7, 53.4, 46.7, 46.2, 35.2, 35.0, 32.0, 31.3, 28.2, 28.2. IR (neat) 3028, 2953, 2849, 2251 (C \equiv N), 2150, 1743 (C=O), 1604, 1485, 1460, 1436, 1254, 1180, 909, 733, 700. HRMS (ES, Pos) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 321.1598, found 321.1601.



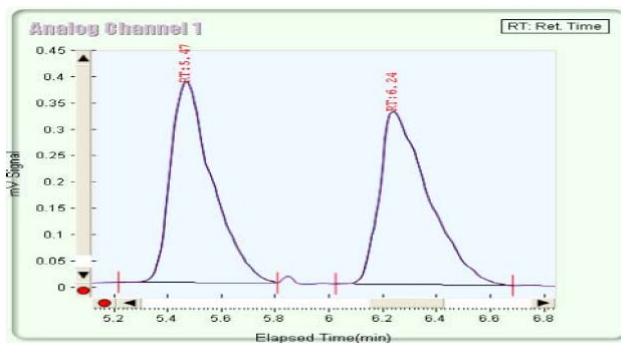
Peak Name	Peak Number	Area %	Area	Retention Time
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	3	24.1551	0.5314	47.95 min
	4	24.2825	0.5342	139.12 min



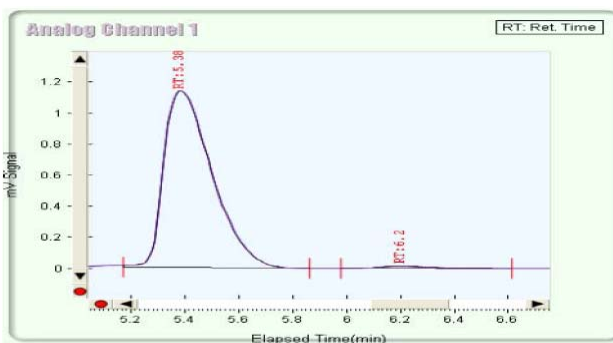
Peak Name	Peak Number	Area %	Area	Retention Time
	1	0.3507	0.0102	14.02 min
	2	0.5364	0.0156	16.5 min
	3	48.3447	1.4096	46.55 min
	4	50.7682	1.4802	135.72 min

Synthesis of β -Hydroxyaldehyde **12**:

(1S,2S)-1-(hydroxymethyl)-2-phenylcyclopropanecarbaldehyde (12). In a flame-dried round-bottomed 20 mL flask equipped with a football-shaped magnetic stirring bar, α -cyanoester **5b** (>99:1 dr, 98% ee, 117.3 mg, 0.40 mmol, 1 equiv) was dissolved in CH₂Cl₂ (6 mL), the colourless solution was cooled to -78°C using an acetone/CO₂ bath, stirred 5 minutes at this temperature before neat DIBAL (280 μ L, 1.56 mmol, 3.9 equiv) was slowly added via syringe over 2 minutes, and the resulting white heterogenous mixture was stirred at -78°C for 5 hours. Aqueous H₂SO₄ 0.5 M (5 mL, 2.5 mmol, 6.3 equiv) was added dropwise at -78°C via syringe, the bath was removed and the resulting mixture was stirred for 20 hours at room temperature. H₂O (15 mL) and CH₂Cl₂ (10 mL) were added, the layers were separated and the aqueous layer was extracted with 3 x 25 mL CH₂Cl₂, the combined organic layers were washed with 1 x 50 mL aq. sat. NaHCO₃, 1 x 50 mL brine, dried over Na₂SO₄ and concentrated under reduced pressure to afford the crude β -hydroxyaldehyde **12**. SiO₂ column chromatography using 40% EtOAc in hexane afforded the pure β -hydroxyaldehyde **12** (59.3 mg, 84%) as a colourless oil (>99:1 dr, 98% ee). Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 20% MeOH, 2 mL/min, 40°C, 150 bar, 210 nm, t_r (major) 5.4 min, t_r (minor) 6.2 min. R_f = 0.13 (25:75 EtOAc:Hexane). [α]_D²⁰ = -176.2 (c 0.81, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 8.60 (s, 1H, CHO), 7.40-7.17 (m, 5H, ArH), 3.89 (d, J = 12.0 Hz, 1H, CH₂OH), 3.77 (d, J = 12.0 Hz, 1H, CH₂OH), 2.87 (t, J = 7.7 Hz, 1H, CH cyclopropane), 2.77 (s, br, 1H, CH₂OH), 2.04 (t, J = 6.0 Hz, 1H, CH₂ cyclopropane), 1.62 (dd, J = 5.8, 8.4 Hz, 1H, CH₂ cyclopropane). ¹³C NMR (CDCl₃, 100 MHz): δ 203.2, 135.3, 129.1 (2C), 128.7 (2C), 127.4, 64.4, 40.4, 31.5, 16.6. IR (neat) 3404 (O-H), 3026, 2924, 1694 (C=O), 1498, 1452, 1387, 1216, 1033, 908, 768, 699. HRMS (ES, Pos) Calcd for C₁₁H₁₂O₂ [M+Na]⁺: 199.0730, found 199.0730.

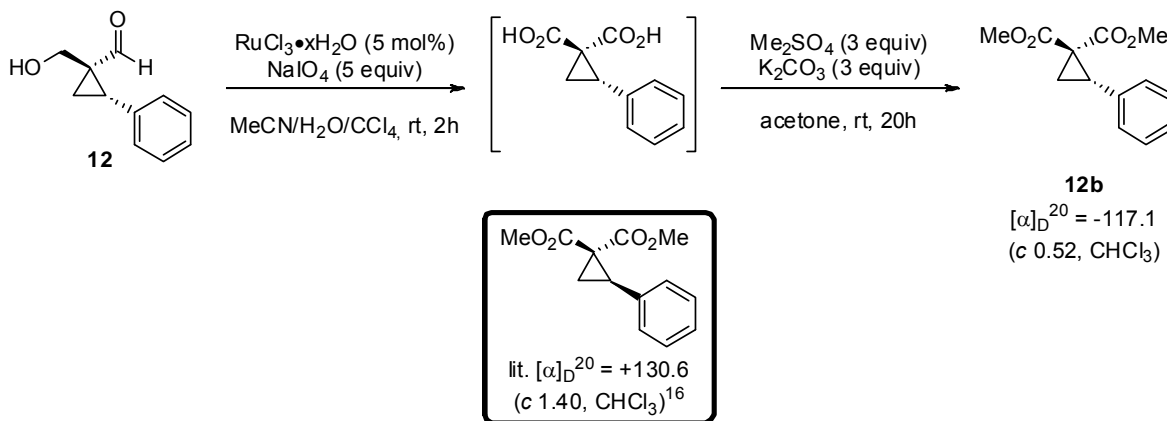


Peak Name	Peak Number	Area %	Area	Retention Time
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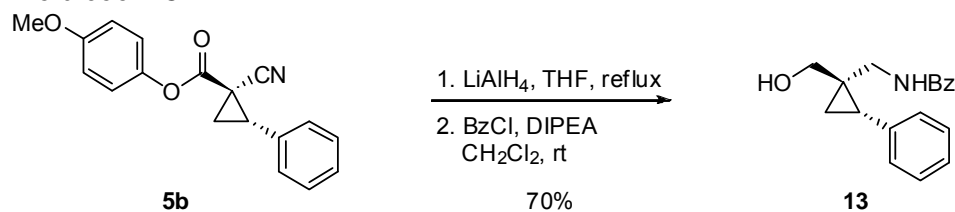


Peak Name	Peak Number	Area %	Area	Retention Time
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	2	1.1663	0.1651	6.2 min

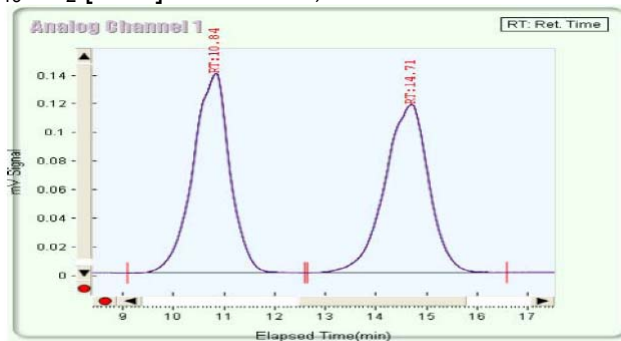
Derivatization of β -Hydroxyaldehyde **12** into *gem*-diester **12b** for absolute configuration determination :



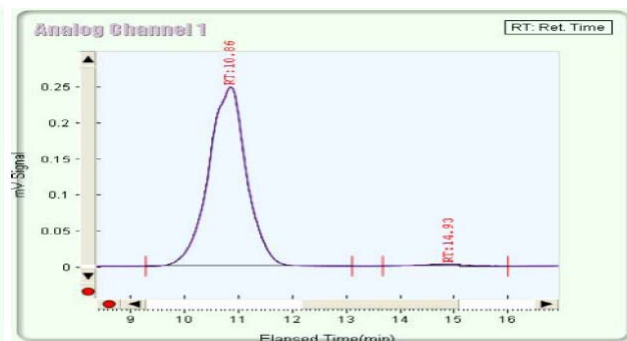
Dimethyl (2S)-2-phenylcyclopropane-1,1-dicarboxylate (12b).¹⁶ In a round-bottomed 10 mL flask equipped with a football-shaped magnetic stirring bar, β -hydroxyaldehyde **12** (>99:1 dr, 98% ee, 43.4 mg, 0.25 mmol, 1 equiv) was dissolved in CCl_4 (0.7 mL), MeCN (0.7 mL), and H_2O (1 mL), the mixture was vigorously stirred at room temperature and NaIO_4 (263.4 mg, 1.23 mmol, 5 equiv) was added in one portion, followed by $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (2.6 mg, 0.012 mmol, 0.05 equiv), and the resulting brown heterogenous mixture was stirred at room temperature for 3 hours. CH_2Cl_2 (5 mL) and H_2O (5 mL) were added, the layers were separated and the aqueous layer was extracted with 3 x 15 mL CH_2Cl_2 , the combined organic layers were dried (Na_2SO_4) and concentrated to afford the crude *gem*-dicarboxylic acid which was used in the next step without further purification. In a round-bottomed 25 mL flask equipped with a football-shaped magnetic stirring bar, the crude *gem*-dicarboxylic acid was dissolved in acetone (4 mL), K_2CO_3 (102.1 mg, 0.74 mmol, 3 equiv) was added, followed by Me_2SO_4 (70 μL , 0.74 mmol, 3 equiv), and the resulting mixture was stirred at room temperature for 20 hours. The mixture was filtered over Celite (rinse thoroughly with Et_2O) and concentrated under vacuum to afford the crude *gem*-diester **12b**, which was purified on silica-gel chromatography using 10% EtOAc in Hexane as eluent, furnishing the pure *gem*-diester **12b** (12.2 mg, 21% over 2 steps) as a colourless oil. $[\alpha]_{\text{D}}^{20} = -117.1$ (c 0.52, CHCl_3) (lit. $[\alpha]_{\text{D}}^{20} = +130.6$ (c 1.40, CHCl_3) for *R* enantiomer).¹⁶ All analysis was consistent with literature values.¹⁶

Synthesis of γ -Amino alcohol **13**.²⁰

***N*-{[(1*R*,2*S*)-1-(hydroxymethyl)-2-phenylcyclopropyl]methyl}benzamide (13)**. A flame-dried 20 mL round-bottomed flask equipped with a football-shaped magnetic stirring bar and a reflux condenser was charged with LiAlH_4 (21.3 mg, 0.56 mmol, 1.4 equiv), dry THF (2 mL) was added and the resulting heterogenous mixture was cooled to 0°C using an ice/water bath. A solution of α -cyanoester **5b** (>99:1 dr, 98% ee, 117.3 mg, 0.40 mmol, 1 equiv) in THF (3 mL) was added dropwise at 0°C via syringe, the syringe was rinsed with dry THF (1 mL), and the reaction was stirred at 0°C for 30 minutes. The ice/water bath was removed and the mixture was heated to reflux for 24 hours. The resulting heterogenous solution was cooled to 0°C, and H_2O (4 mL) was slowly added, leaving the flask open, the solution was allowed to come back to room temperature and stirred for a further 2 hours. The mixture was filtered over celite, rinsing with THF (130 mL), and the filtrate was concentrated under reduced pressure to afford the crude γ -amino alcohol. To a flame-dried 100 mL round-bottomed flask equipped with a football-shaped magnetic stirring bar containing the crude γ -amino alcohol dissolved in dry CH_2Cl_2 (20 mL) was added diisopropylethylamine (DIPEA, 90.6 μL , 0.52 mmol, 1.3 equiv) and benzoyl chloride (BzCl, 55.7 μL , 0.48 mmol, 1.2 equiv), and the resulting colourless solution was stirred at room temperature for 16 hours. Aqueous sat. NaHCO_3 (40 mL) was added, the layers were separated, the aqueous layer was extracted with 2 x 20 mL CH_2Cl_2 , the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to afford the crude *N*-Bz- γ -amino alcohol **13**, which was purified by silica-gel chromatography using 40% EtOAc in hexane as eluent (colourless oil, 79.2 mg, 70% yield over 2 steps. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 34°C, 150 bar, 210 nm, t_r (major) 10.9 min, t_r (minor) 14.9 min. $R_f = 0.23$ (50:50 EtOAc:Hexane). $[\alpha]_D^{20} = -143.0$ (c 0.59, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (d, $J = 7.3$ Hz, 2H, ArH), 7.50 (t, $J = 7.4$ Hz, 1H, ArH), 7.41 (t, $J = 7.7$ Hz, 2H, ArH), 7.38-7.30 (m, 2H, ArH), 7.30-7.21 (m, 3H, ArH), 6.31 (s, br, 1H, NHBz), 4.13 (s, br, 1H, CH_2OH), 3.77-3.62 (m, 2H), 3.39 (d, $J = 12.0$ Hz, 1H), 2.94 (dd, $J = 5.4, 14.6$ Hz, 1H), 2.17 (dd, $J = 6.4, 8.0$ Hz, 1H, CH cyclopropane), 1.18 (t, $J = 5.8$ Hz, 1H, CH_2 cyclopropane), 1.03 (dd, $J = 5.6, 8.5$ Hz, 1H, CH_2 cyclopropane). ^{13}C NMR (CDCl_3 , 100 MHz): δ 168.6, 138.0, 133.8, 131.8, 128.9 (2C), 128.7 (2C), 128.6 (2C), 126.9 (2C), 126.7, 68.1, 41.0, 30.3, 26.2, 14.3. IR (neat) 3337 (O-H), 3061, 2924, 1637, 1536, 1488, 1306, 1028, 700, 586. HRMS (ES, Pos) Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 282.1489, found 282.1484.

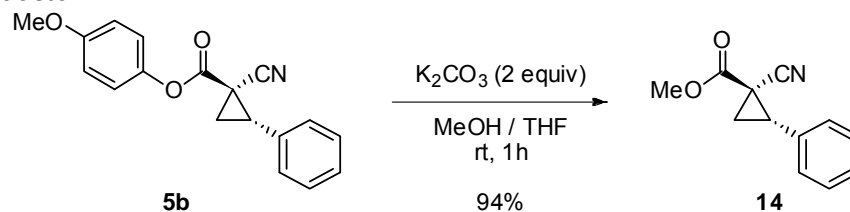


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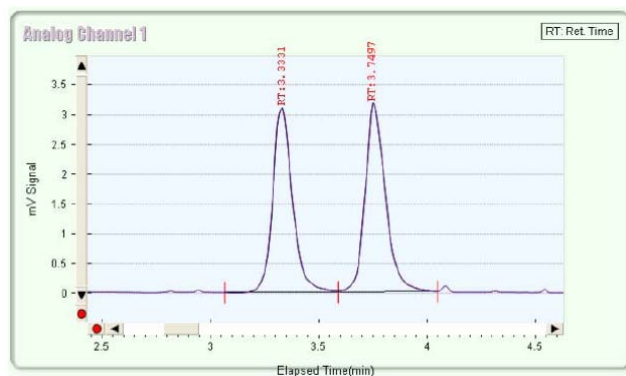


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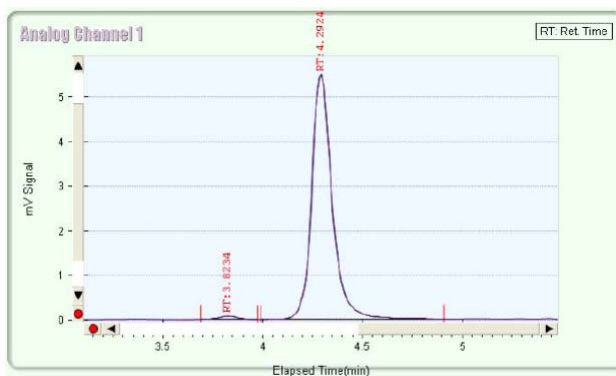
²⁰ Modified from: Archer, E. A.; Krische, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 5074.

Synthesis of α -Cyanoester **14**:

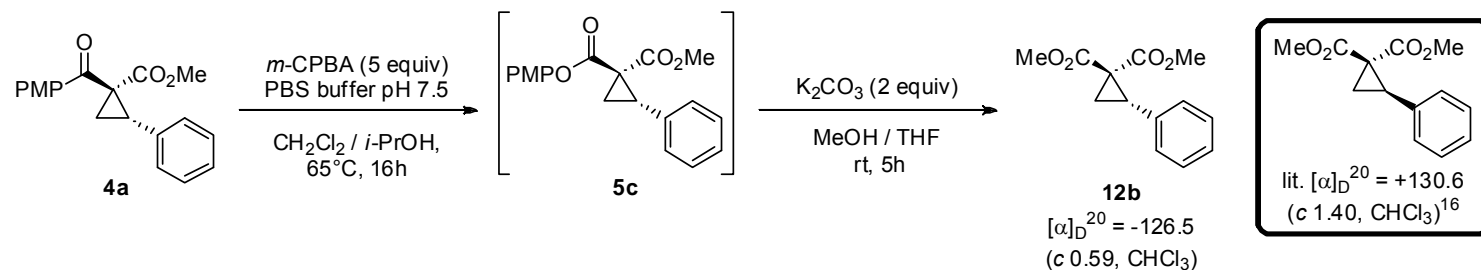
methyl (1*R*,2*S*)-1-cyano-2-phenylcyclopropanecarboxylate (14). A 10 mL flame-dried round-bottomed flask equipped with a football-shaped magnetic stirring bar was charged with finely powdered potassium carbonate (K_2CO_3 , 48.9 mg, 0.354 mmol, 2 equiv), dry MeOH (3 mL) was added, followed by a solution of α -cyanoester **5b** (>99:1 dr, 98%ee, 51.9 mg, 0.177 mmol, 1 equiv) in dry THF (1 mL) dropwise via syringe, the syringe was rinsed with dry THF (0.5 mL), and the resulting heterogenous mixture was stirred for 1 hour at room temperature or until full consumption of the starting material (follow by TLC). The mixture was poured into H_2O (30 mL) and CH_2Cl_2 (30 mL), the layers were separated and the aqueous layer was extracted with 2 x 25 mL CH_2Cl_2 , the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated under vacuum to obtain the crude α -cyanoester **14**, which was purified by silica-gel chromatography using 70% CH_2Cl_2 in hexane as eluent, yielding the pure α -cyanoester **14** as a white solid (33.6 mg, 94%, >99:1 dr, 98%ee). mp 48°C. Diastereomeric ratio was determined by 1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (RR Whelk-O 1, 3% *i*-PrOH, 3 mL/min, 40°C, 150 bar, 210 nm, t_r (minor) 3.8 min, t_r (major) 4.3 min. R_f = 0.28 (70:30 CH_2Cl_2 :Hexane). $[\alpha]_D^{20}$ = -202.7 (*c* 0.98, $CHCl_3$). 1H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.33 (m, 3H, ArH), 7.33-7.24 (m, 2H, ArH), 3.88 (s, 3H, CO_2CH_3), 3.20 (t, J = 8.8 Hz, 1H, CH cyclopropane), 2.19 (dd, J = 5.4, 9.3 Hz, 1H, CH_2 cyclopropane), 2.13 (dd, J = 5.4, 8.4 Hz, 1H, CH_2 cyclopropane). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.0, 132.9, 128.9 (2C), 128.7, 128.4 (2C), 116.4, 53.8, 35.6, 23.0, 22.9. IR (neat) 2956, 2245 (C \equiv N), 1736 (C=O), 1437, 1298, 1267, 1206, 1159, 967, 894, 764, 697. HRMS (ES, Pos) Calcd for $C_{12}H_{11}NO_2$ [M+H] $^+$: 202.0863, found 202.0859.



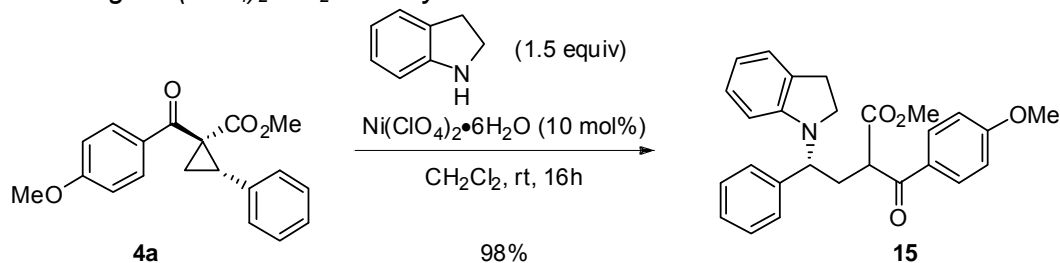
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Peak3	51.0898	20.2676	3.7497 min



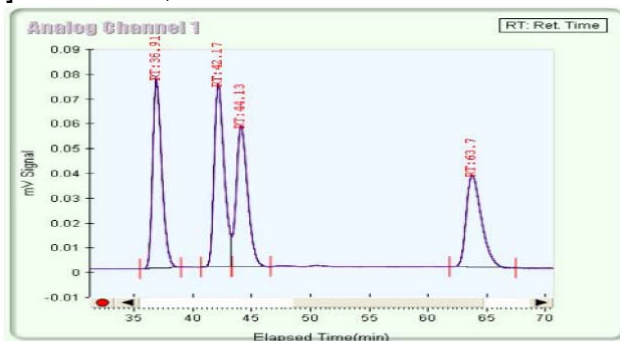
Peak Name	Area %	Area	Retention Time
Peak3	1.0938	0.4417	3.8234 min
Peak2	98.9062	39.9426	4.2924 min

Applications of β -ketoester **4a** (Scheme 3)Derivatization of β -Ketoester **4a** into *gem*-diester **12b** for absolute configuration determination :

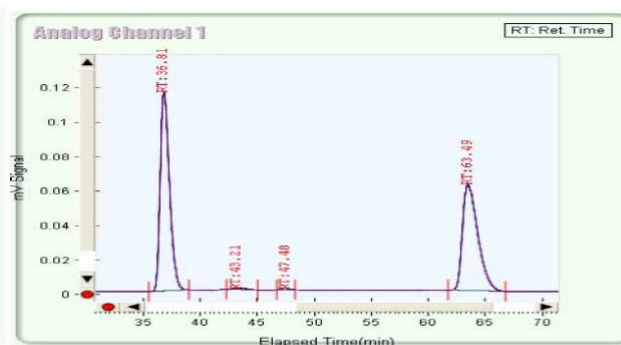
Dimethyl (2S)-2-phenylcyclopropane-1,1-dicarboxylate (12b).¹⁶ In a round-bottomed 50 mL flask equipped with a football-shaped magnetic stirring bar and a reflux condenser, β -ketoester **4a** (>99:1 dr, >99% ee, 270 mg, 0.87 mmol, 1 equiv) was dissolved in CH_2Cl_2 (5.2 mL), *i*-PrOH (5.2 mL) and Phosphate Buffer (PBS) 1M pH 7.5 (1.1 mL). Recrystallized *m*-CPBA (99% pure, 751 mg, 4.35 mmol, 5 equiv) was added, and the resulting homogeneous colorless solution was heated to 65–70°C (reflux) and stirred at this temperature for 16 hours. The resulting yellow solution was allowed to cool to room temperature, diluted with 50 mL CH_2Cl_2 , and washed successively with 4 x 50 mL 2% aq. Na_2SO_3 , 1 x 50 mL sat. aq. NaHCO_3 , dried on Na_2SO_4 and concentrated under reduced pressure to afford the crude diester **5c**, which was submitted to the next step without further purification. Crude diester **5c** was dissolved in THF (5 mL) and MeOH (10 mL), finely powdered K_2CO_3 (241 mg, 1.74 mmol, 2 equiv) was added and the resulting mixture was stirred at room temperature for 5 hours. CH_2Cl_2 (30 mL) and H_2O (30 mL) were added, the layers were separated and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL), the combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under vacuum to afford the crude diester **12b**. SiO_2 column chromatography (70% CH_2Cl_2 in hexane, then 20% Et_2O in hexane) furnished the pure *gem*-diester **12b** (31.4 mg, 15% over 2 steps) as a colourless oil. $[\alpha]_{\text{D}}^{20} = -126.5$ (c 0.59, CHCl_3) (lit. $[\alpha]_{\text{D}}^{20} = +130.6$ (c 1.40, CHCl_3) for *R* enantiomer).¹⁶ All analysis was consistent with literature values.¹⁶

Synthesis of **15** through $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ catalyzed addition of indoline:¹⁷**methyl (4R)-4-(2,3-dihydro-1H-indol-1-yl)-2-([4-(methoxy)phenyl]carbonyl)-4-phenylbutanoate (15).**

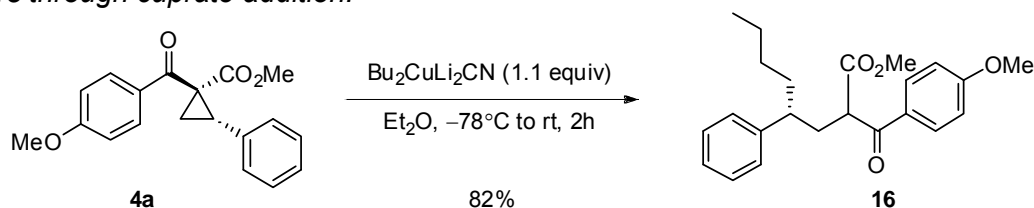
A 2 mL microwave vial equipped with a V-shaped magnetic stirring bar was charged with β -ketoester **4a** (>99:1 dr, >99%ee, 71.4 mg, 0.23 mmol, 1 equiv), a 2.5 M solution of indoline in CH_2Cl_2 was added (138 μL , 0.345 mmol, 1.5 equiv) followed by $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (8.4 mg, 0.023 mmol, 0.10 equiv) in one portion, the vial was sealed and the mixture was stirred vigorously at room temperature for 20 hours. The mixture was evaporated to dryness and the resulting residue was purified by silica-gel chromatography using 2% EtOAc in benzene as eluent, affording the pure γ -amino- β -ketoester **15** (96.5 mg, 98%) as a mixture of diastereomers (epimers at the α position) (yellow solid, 56:44 dr, 99%ee for both diastereomers). mp <50°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 6% *i*-PrOH, 2 mL/min, 40°C, 180 bar, 280 nm, t_r (major diastereomer, major enantiomer) 36.8 min, t_r (major diastereomer, minor enantiomer) 43.2 min, t_r (minor diastereomer, minor enantiomer) 47.5 min, t_r (minor diastereomer, major enantiomer) 63.5 min. $R_f = 0.37$ (2:98 EtOAc:Benzene). $[\alpha]_D^{20} = +88.8$ (c 1.00, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 56:44 inseparable mixture of diastereomers): δ 7.96-7.84 (m, 2H, ArH), 7.39-7.22 (m, 5H, ArH), 7.11-6.80 (m, 4H, ArH), 6.65-6.54 (m, 1H, ArH), 6.65-6.54 (m, 1H *major diastereomer*, ArH), 6.44 (d, $J = 8.0$ Hz, 1H *minor diastereomer*, ArH), 4.87 (dd, $J = 5.2, 10.4$ Hz, 1H *major diastereomer*, α -C-H), 4.74 (dd, $J = 5.7, 10.0$ Hz, 1H *minor diastereomer*, α -C-H), 4.63-4.51 (m, 1H, γ -C-H), 3.88 (s, 3H *minor diastereomer*, ArOCH_3), 3.86 (s, 3H *major diastereomer*, ArOCH_3), 3.70 (s, 3H *major diastereomer*, CO_2CH_3), 3.65 (s, 3H *minor diastereomer*, CO_2CH_3), 3.56-3.45 (m, 1H *minor diastereomer*, AlkH), 3.38-3.28 (m, 1H *major diastereomer*, AlkH), 3.22-3.09 (m, 1H *minor diastereomer*, AlkH), 3.06-2.95 (m, 1H *major diastereomer*, AlkH), 3.03-2.61 (m, 4H, AlkH). ^{13}C NMR (CDCl_3 , 100 MHz, 56:44 inseparable mixture of diastereomers): *major diastereomer*: δ 193.4, 170.7, 163.8, 151.2, 138.8, 131.0 (2C), 129.6, 129.1, 128.5 (2C), 127.9 (2C), 127.6, 127.3, 124.6, 117.2, 113.8 (2C), 107.0, 57.0, 55.6, 52.6, 50.6, 46.5, 31.1, 28.0. *minor diastereomer*: δ 193.6, 170.7, 164.0, 151.1, 139.2, 131.2 (2C), 129.6, 129.2, 128.5 (2C), 127.9 (2C), 127.6, 127.3, 124.5, 117.2, 113.9 (2C), 107.1, 56.8, 55.6, 52.5, 50.8, 46.8, 31.2, 28.1. IR (neat) 3026, 2950, 2841, 1736 (C=O), 1670 (C=O), 1598, 1485, 1459, 1251, 1168, 1024, 839, 742, 699. HRMS (ES, Pos) Calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 430.2013, found 430.2018.



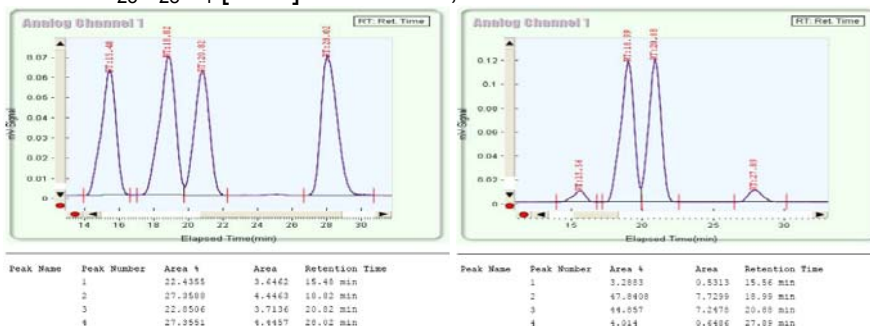
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	3	24.3495	3.8051	44.13 min
	4	21.3728	3.3399	63.7 min



Peak Name	Peak Number	Area %	Area	Retention Time
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	3	0.3367	0.0416	47.48 min
	4	46.4642	5.7435	63.49 min

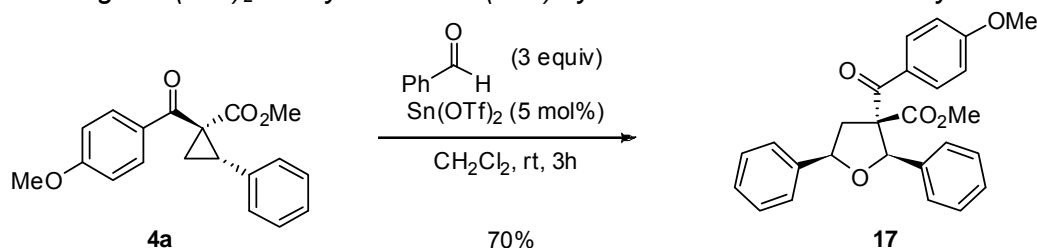
Synthesis of **16** through cuprate addition:²¹

methyl (4R)-2-[[4-(methoxy)phenyl]carbonyl]-4-phenyloctanoate (16). A flame-dried round-bottomed 20 mL flask equipped with a football-shaped magnetic stirring bar was charged with CuCN (19.7 mg, 0.22 mmol, 1.1 equiv), the flask was flushed with argon for 15 minutes, dry Et₂O (4 mL) was added and the resulting heterogenous solution was cooled to -78°C using an acetone/CO₂ bath. *n*-BuLi (2.40 M in hexane, 183 μL, 0.44 mmol, 2.2 equiv) was added dropwise at -78°C, the bath was removed and replaced by a 25°C water bath, and the solution was stirred at this temperature for 20 minutes. The resulting brown homogenous solution was cooled back to -78°C, and a solution of cyclopropane **4a** (>99:1 dr, >99%ee, 62.1 mg, 0.20 mmol, 1.0 equiv) in dry Et₂O (2.5 mL) was added dropwise at -78°C via syringe, the syringe was rinsed with dry Et₂O (0.5 mL), the bath was removed and the resulting solution was allowed to warm to room temperature and to stir at this temperature for 2 more hours. The resulting black mixture was quenched with saturated aq. NH₄Cl (10 mL) dropwise, Et₂O (10 mL) was added and the mixture was stirred at room temperature for 20 minutes. The layers were separated, the aqueous layer was extracted with 3 x 20 mL Et₂O, the combined organic layers were washed with brine (40 mL), dried over MgSO₄ and concentrated under reduced pressure to afford the crude β-ketoester **16**. Purification on silica-gel chromatography using 1) 30% Et₂O in hexane 2) 60% CH₂Cl₂ in hexane afforded the pure β-ketoester **16** as a colourless oil (60.5 mg, 82% yield, 52:48 inseparable mixture of diastereomers, epimers at the α-position, 85% ee for both diastereomers). Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralpak AD-H 25 cm, 2% *i*-PrOH, 3 mL/min, 40°C, 180 bar, 280 nm, *t_r* (minor diastereomer, minor enantiomer) 15.6 min, *t_r* (major diastereomer, major enantiomer) 19.0 min, *t_r* (minor diastereomer, major enantiomer) 20.9 min, *t_r* (major diastereomer, minor enantiomer) 27.9 min. *R_f* = 0.31 (30:70 Et₂O:Hexane). [α]_D²⁰ = -12.9 (c 0.94, CHCl₃). ¹H NMR (CDCl₃, 400 MHz, 52:48 inseparable mixture of diastereomers): δ 7.78 (d, *J* = 8.9 Hz, 2H *minor diastereomer*, ArH), 7.59 (d, *J* = 8.9 Hz, 2H *major diastereomer*, ArH), 7.39-7.31 (m, 1H, ArH), 7.30-7.12 (m, 3H, ArH), 7.00 (d, *J* = 6.8 Hz, 1H, ArH), 6.89 (d, *J* = 8.9 Hz, 2H *minor diastereomer*, ArH), 6.82 (d, *J* = 8.9 Hz, 2H *major diastereomer*, ArH), 4.09 (dd, *J* = 4.4, 10.0 Hz, 1H *minor diastereomer*, α-C-H), 4.02 (dd, *J* = 3.0, 10.7 Hz, 1H *major diastereomer*, α-C-H), 3.87 (s, 3H *minor diastereomer*, ArOCH₃), 3.85 (s, 3H *major diastereomer*, ArOCH₃), 3.72 (s, 3H *major diastereomer*, CO₂CH₃), 3.54 (s, 3H *minor diastereomer*, CO₂CH₃), 2.53 (m, 2H, β-CH₂), 2.16 (m, 1H *minor diastereomer*, γ-C-H), 1.93 (m, 1H *major diastereomer*, γ-C-H), 1.73-1.51 (m, 2H, AlkH), 1.35-0.97 (m, 4H, AlkH), 0.87-0.75 (m, 3H, AlkCH₃). ¹³C NMR (CDCl₃, 100 MHz, 52:48 mixture of 2 diastereomers): δ 194.3, 194.0, 170.8, 170.7, 164.0, 163.9, 144.4, 144.3, 131.2 (2C), 131.1 (2C), 129.8, 128.8 (2C), 128.6 (2C), 128.4, 128.1 (2C), 128.0 (2C), 126.7, 126.5, 113.9 (2C), 113.9 (2C), 55.6, 55.6, 52.5, 52.4, 51.9, 51.0, 44.4, 43.8, 37.2, 36.8, 36.6, 36.0, 29.8, 29.7, 22.8, 22.8, 14.1. IR (neat) 2954, 2927, 2855, 1740 (C=O), 1675 (C=O), 1599, 1511, 1453, 1262, 1170, 1029, 842, 739, 702. HRMS (ES, Pos) Calcd for C₂₃H₂₈O₄ [M+H]⁺: 369.2060, found 369.2062.



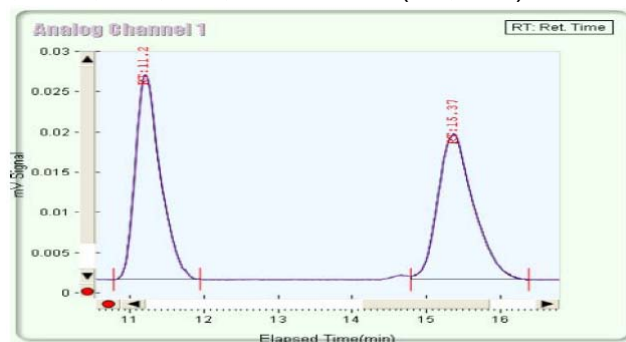
²¹ Modified from: Marcoux, D.; Goudreau, S. R.; Charette, A. B. *J. Org. Chem.* **2009**, *74*, 8939.

Synthesis of **17** through $\text{Sn}(\text{OTf})_2$ -catalyzed formal (3+2) cycloaddition with benzaldehyde.²²

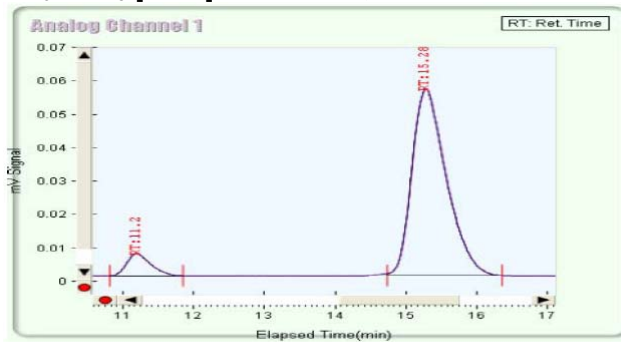


2-(methoxy)-1-[(2*R*,3*R*,5*R*)-3-[[4-(methoxy)phenyl]carbonyl]-2,5-diphenyltetrahydrofuran-3-yl]ethanone (17).

A 2 mL microwave vial equipped with a V-shaped magnetic stirring bar was charged with β -ketoester **4a** (>99:1 dr, >99% ee, 105.5 mg, 0.34 mmol, 1 equiv), CH_2Cl_2 (600 μL) was added, followed by benzaldehyde (104 μL , 1.02 mmol, 3 equiv) and $\text{Sn}(\text{OTf})_2$ (7.1 mg, 0.017 mmol, 0.05 equiv) in one portion, the vial was sealed and the mixture was stirred vigorously at room temperature for 3 hours. The mixture was evaporated to dryness and the resulting residue was purified by silica-gel chromatography using 15% EtOAc in hexane as eluent, affording the pure tetrahydrofuran **17** as a white solid (99.8 mg, 70%, 89:11 dr, 85% ee). mp 40°C. Diastereomeric ratio was determined by ^1H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% *i*-PrOH, 3 mL/min, 33°C, 150 bar, 280 nm, t_r (minor) 11.2 min, t_r (major) 15.3 min. $R_f = 0.21$ (15:85 EtOAc:Hexane). $[\alpha]_D^{20} = +79.1$ (c 1.00, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz, 89:11 inseparable mixture of diastereomers): *major diastereomer*: δ 7.84 (d, $J = 8.9$ Hz, 2H, ArH), 7.69-7.58 (m, 4H, ArH), 7.50-7.22 (m, 6H, ArH), 6.92 (d, $J = 8.9$ Hz, 2H, ArH), 6.19 (s, 1H, α -C-H), 4.97 (dd, $J = 6.8, 9.8$ Hz, 1H, ω -C-H), 3.86 (s, 3H, ArOCH_3), 3.36 (dd, $J = 10.0, 13.2$ Hz, 1H, γ - CH_2), 2.95 (s, 3H, CO_2CH_3), 2.72 (dd, $J = 6.8, 13.2$ Hz, 1H, γ - CH_2). ^{13}C NMR (CDCl_3 , 100 MHz, 89:11 inseparable mixture of diastereomers): *major diastereomer*: δ 193.3, 171.7, 163.6, 140.4, 137.9, 131.2 (2C), 128.6 (2C), 128.2, 128.0, 127.9, 127.9 (2C), 127.3 (2C), 126.8 (2C), 114.0 (2C), 84.1, 80.0, 69.5, 55.6, 52.2, 44.5. IR (neat) 2948, 2839, 1731 (C=O), 1670 (C=O), 1598, 1511, 1454, 1254, 1167, 1019, 842, 748, 697. HRMS (ES, Pos) Calcd for $\text{C}_{26}\text{H}_{24}\text{O}_5$ $[\text{M}+\text{H}]^+$: 417.1697, found 417.1690.

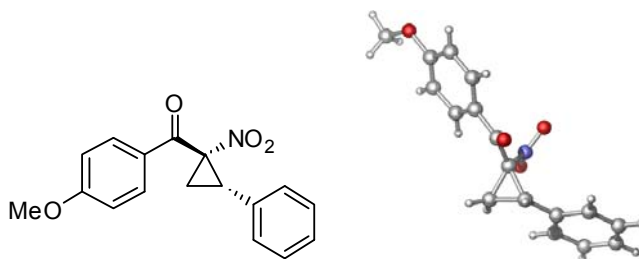


Peak Name	Peak Number	Area %	Area	Retention Time
	1	49.5667	0.5934	11.2 min
	2	50.4333	0.6038	15.37 min



Peak Name	Peak Number	Area %	Area	Retention Time
	1	7.6054	0.1542	11.2 min
	2	92.3946	1.8736	15.28 min

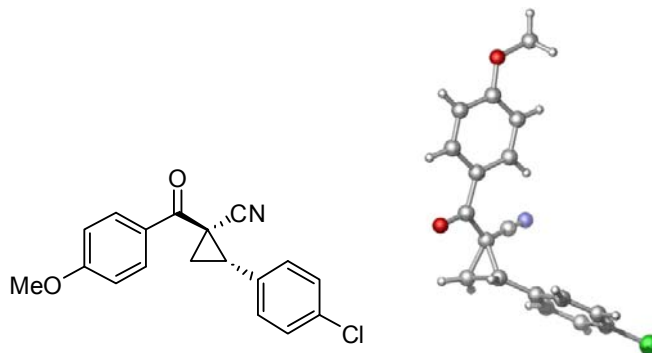
²² Modified from: Pohlhaus, P. D.; Sanders, S. D.; Parsons, A. T.; Li, W.; Johnson, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 8642.

X-Ray Data of compounds 2f, 3b and 4a*X-Ray Data of compound 2f:*

(performed on a Bruker Smart 6000)

Crystal data and structure refinement for C₁₇ H₁₅ N O₄.

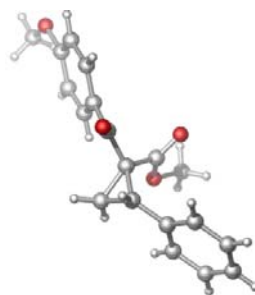
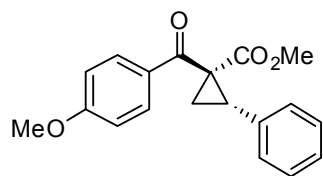
Identification code	cha172
Empirical formula	C ₁₇ H ₁₅ N O ₄
Formula weight	297.30
Temperature	150K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	a = 8.1895(14) Å α = 90° b = 5.7464(9) Å β = 97.801(5)° c = 16.269(3) Å γ = 90°
Volume	758.6(2) Å ³
Z	2
Density (calculated)	1.302 g/cm ³
Absorption coefficient	0.772 mm ⁻¹
F(000)	312
Crystal size	0.16 x 0.06 x 0.05 mm
Theta range for data collection	2.74 to 72.53°
Index ranges	-9 ≤ h ≤ 9, -6 ≤ k ≤ 6, -20 ≤ l ≤ 19
Reflections collected	9944
Independent reflections	1641 [R _{int} = 0.067]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9621 and 0.8086
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1641 / 1 / 201
Goodness-of-fit on F ²	1.140
Final R indices [I > 2σ(I)]	R ₁ = 0.0535, wR ₂ = 0.1166
R indices (all data)	R ₁ = 0.0914, wR ₂ = 0.1303
Absolute structure parameter	0.2(4)
Extinction coefficient	0.021(2)
Largest diff. peak and hole	0.200 and -0.223 e/Å ³

X-Ray Data of compound **3b**:

(performed on a Bruker Smart 6000)

Crystal data and structure refinement for C₁₈ H₁₄ Cl N O₂.

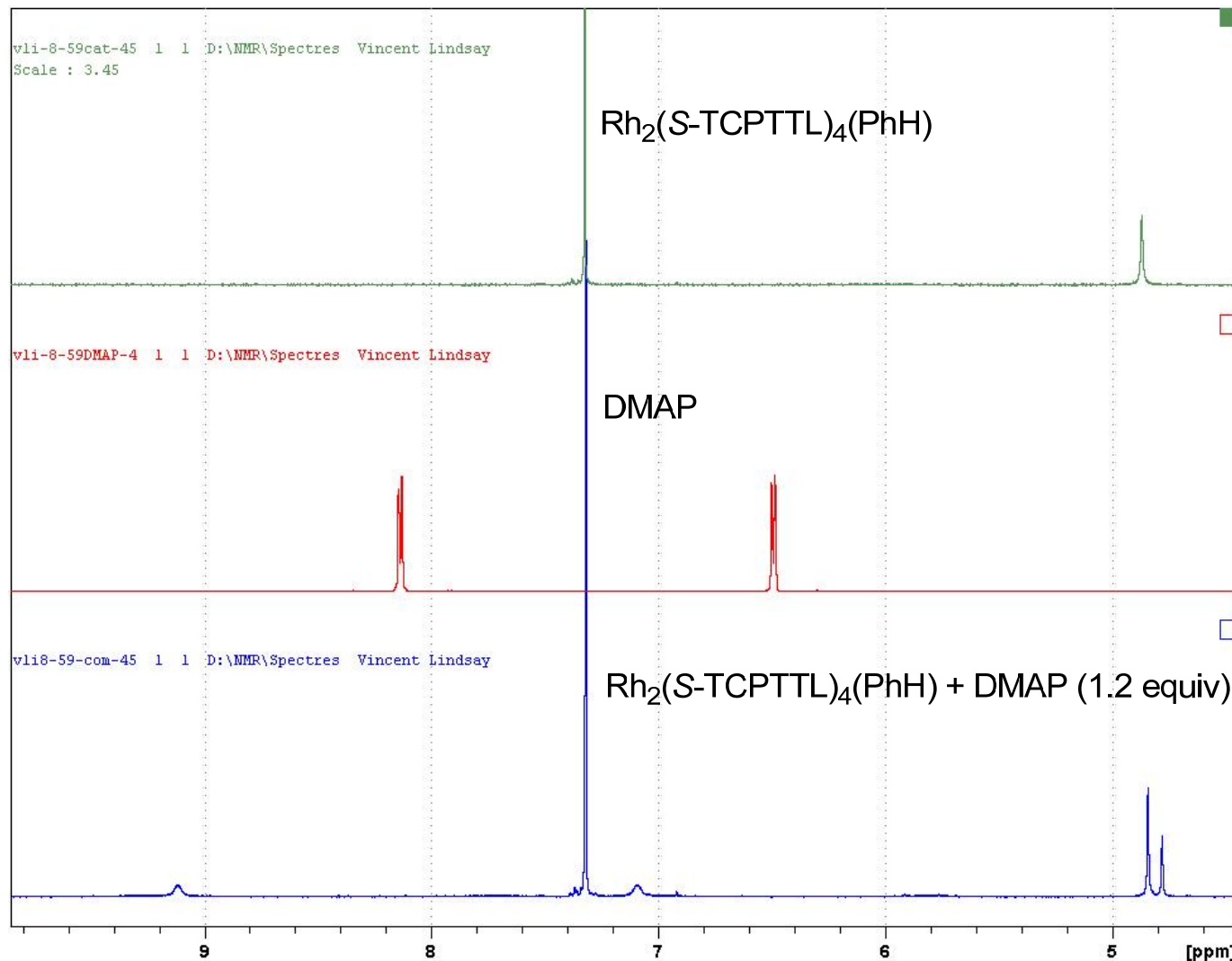
Identification code	cha203
Empirical formula	C ₁₈ H ₁₄ Cl N O ₂
Formula weight	311.75
Temperature	200K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	a = 11.94(4) Å α = 90° b = 5.2913(18) Å β = 94.675(16)° c = 12.294(4) Å γ = 90°
Volume	774.1(4) Å ³
Z	2
Density (calculated)	1.337 g/cm ³
Absorption coefficient	2.234 mm ⁻¹
F(000)	324
Crystal size	0.26 x 0.04 x 0.02 mm
Theta range for data collection	3.61 to 72.63°
Index ranges	-14 ≤ h ≤ 14, -5 ≤ k ≤ 6, -15 ≤ l ≤ 15
Reflections collected	10910
Independent reflections	2472 [R _{int} = 0.035]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9563 and 0.7571
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2472 / 1 / 200
Goodness-of-fit on F ²	1.030
Final R indices [I > 2σ(I)]	R ₁ = 0.0416, wR ₂ = 0.1022
R indices (all data)	R ₁ = 0.0530, wR ₂ = 0.1138
Absolute structure parameter	0.03(2)
Largest diff. peak and hole	0.206 and -0.266 e/Å ³

X-Ray Data of compound 4a:

(performed on a Bruker Smart 6000)

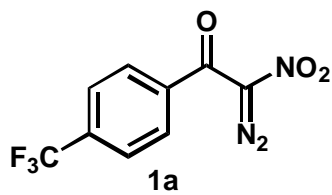
Crystal data and structure refinement for C₁₉ H₁₈ O₄.

Identification code	cha200
Empirical formula	C ₁₉ H ₁₈ O ₄
Formula weight	310.33
Temperature	150K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	a = 7.9911(1) Å α = 90° b = 5.5915(1) Å β = 91.981(1)° c = 17.4447(3) Å γ = 90°
Volume	779.00(2) Å ³
Z	2
Density (calculated)	1.323 g/cm ³
Absorption coefficient	0.754 mm ⁻¹
F(000)	328
Crystal size	0.24 x 0.14 x 0.04 mm
Theta range for data collection	2.53 to 72.73°
Index ranges	-9 ≤ h ≤ 9, -6 ≤ k ≤ 6, -21 ≤ l ≤ 21
Reflections collected	10190
Independent reflections	2839 [R _{int} = 0.031]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9703 and 0.8490
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2839 / 1 / 211
Goodness-of-fit on F ²	1.079
Final R indices [I > 2σ(I)]	R ₁ = 0.0343, wR ₂ = 0.0887
R indices (all data)	R ₁ = 0.0358, wR ₂ = 0.0901
Absolute structure parameter	-0.03(16)
Extinction coefficient	0.036(2)
Largest diff. peak and hole	0.168 and -0.239 e/Å ³

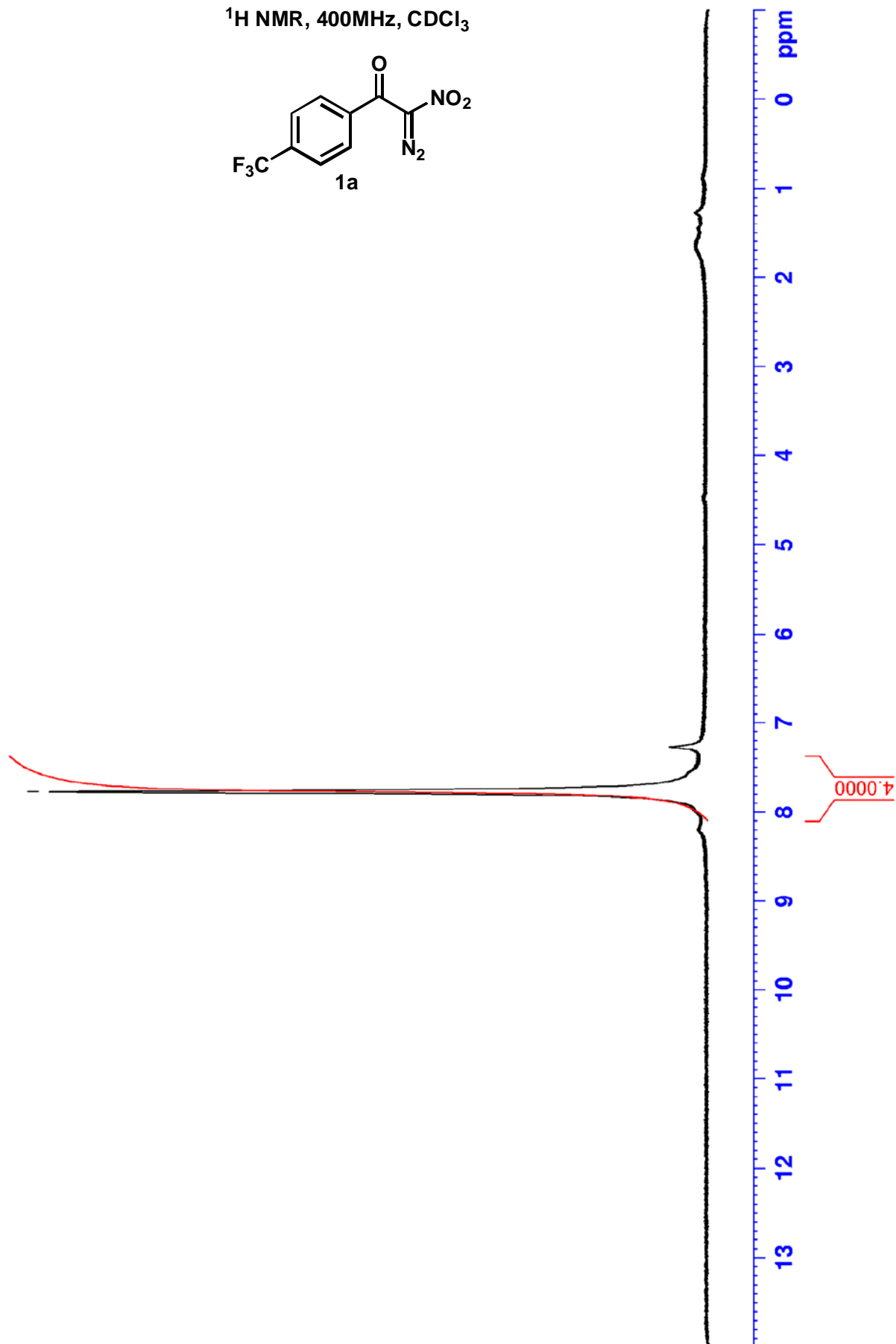
Low Temperature ^1H NMR Experiment with $\text{Rh}_2(\text{S-TCPTTL})_4$ and DMAP ^1H NMR experiments performed at -45°C in $\text{Et}_2\text{O}-d_{10}$ (400 MHz DRX apparatus, aromatic region)Notes:

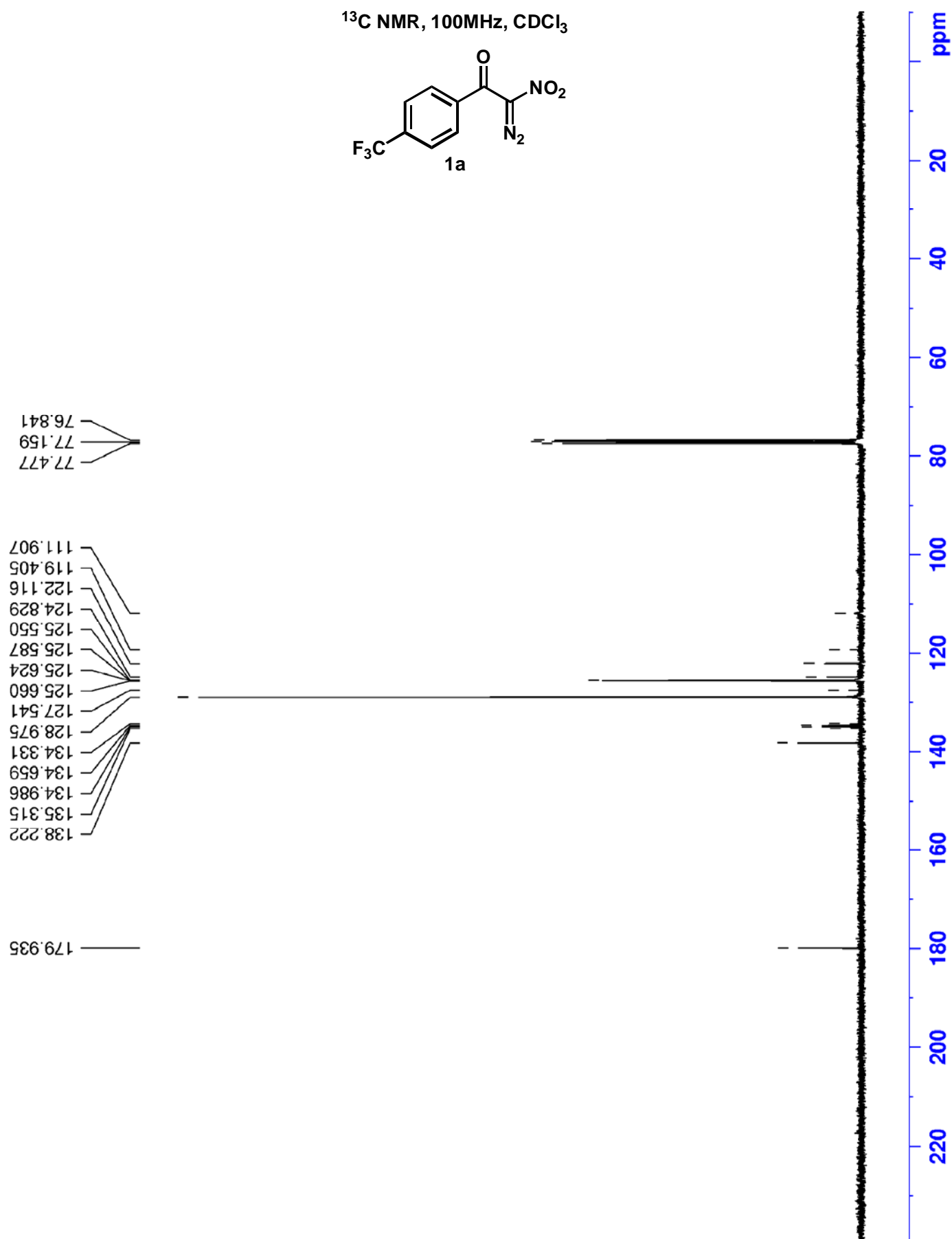
- A clear downfield shift of the aromatic protons of DMAP is observed after addition of 1.2 equiv to a catalyst solution in $\text{Et}_2\text{O}-d_{10}$ at -45°C .
- This result suggests that under the reaction conditions (Conditions B, Et_2O , -45°C), DMAP efficiently competes with Et_2O for catalyst complexation.

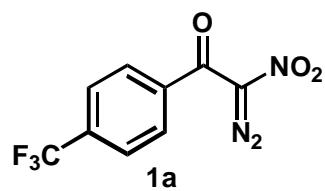
^1H NMR, 400MHz, CDCl_3



7.772





¹⁹F NMR, 282MHz, CDCl₃

-64.656

ppm

-160

-140

-120

-100

-80

-60

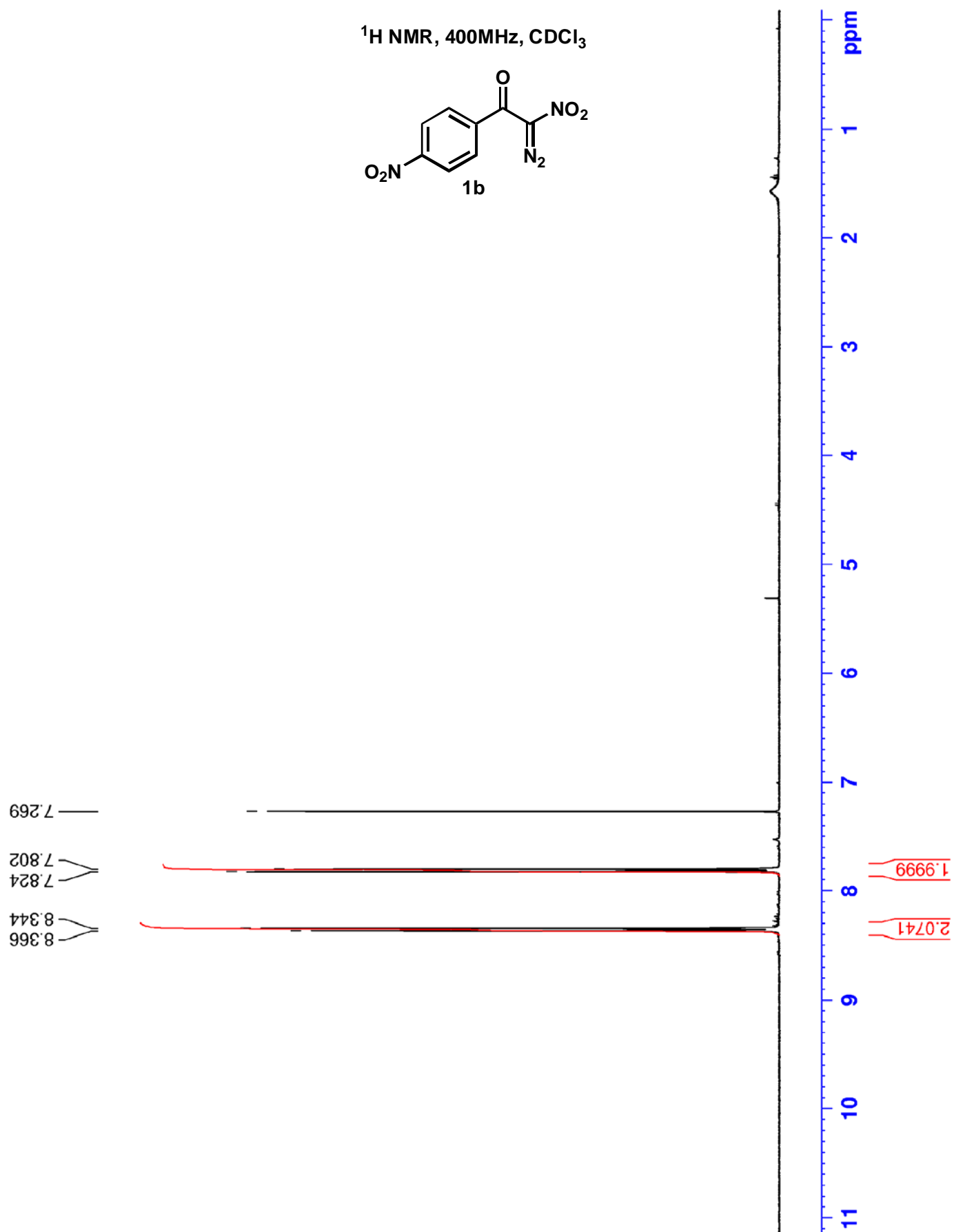
-40

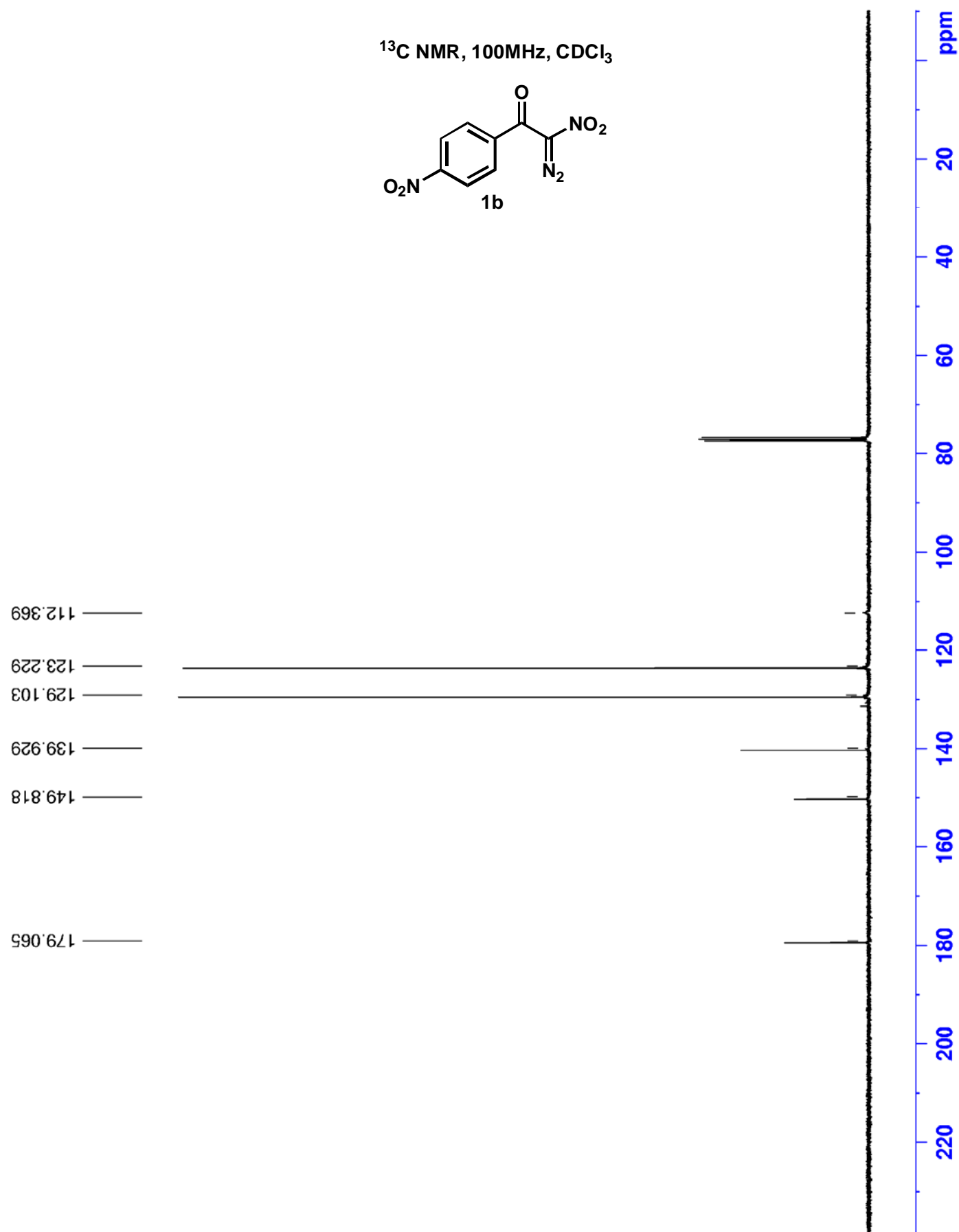
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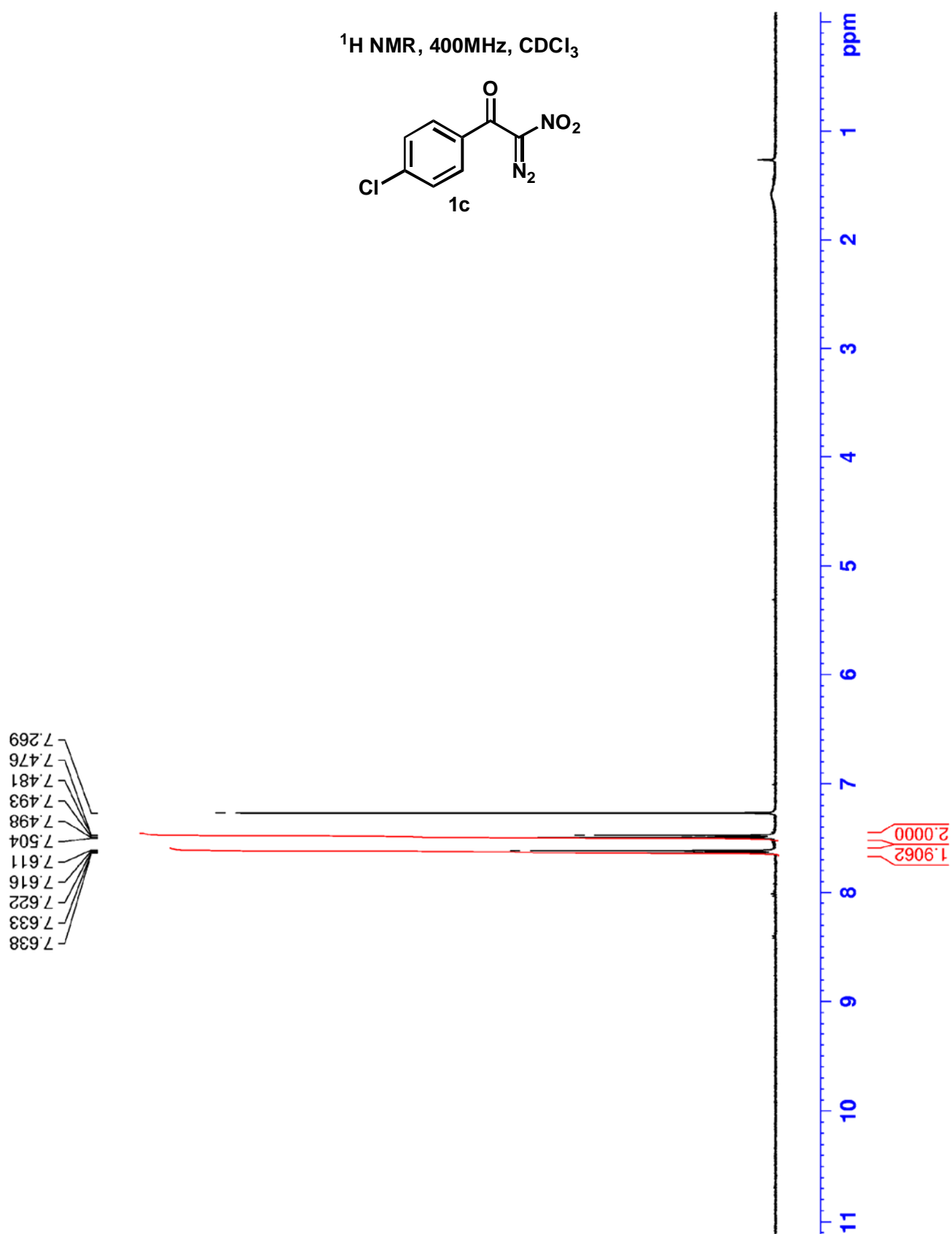
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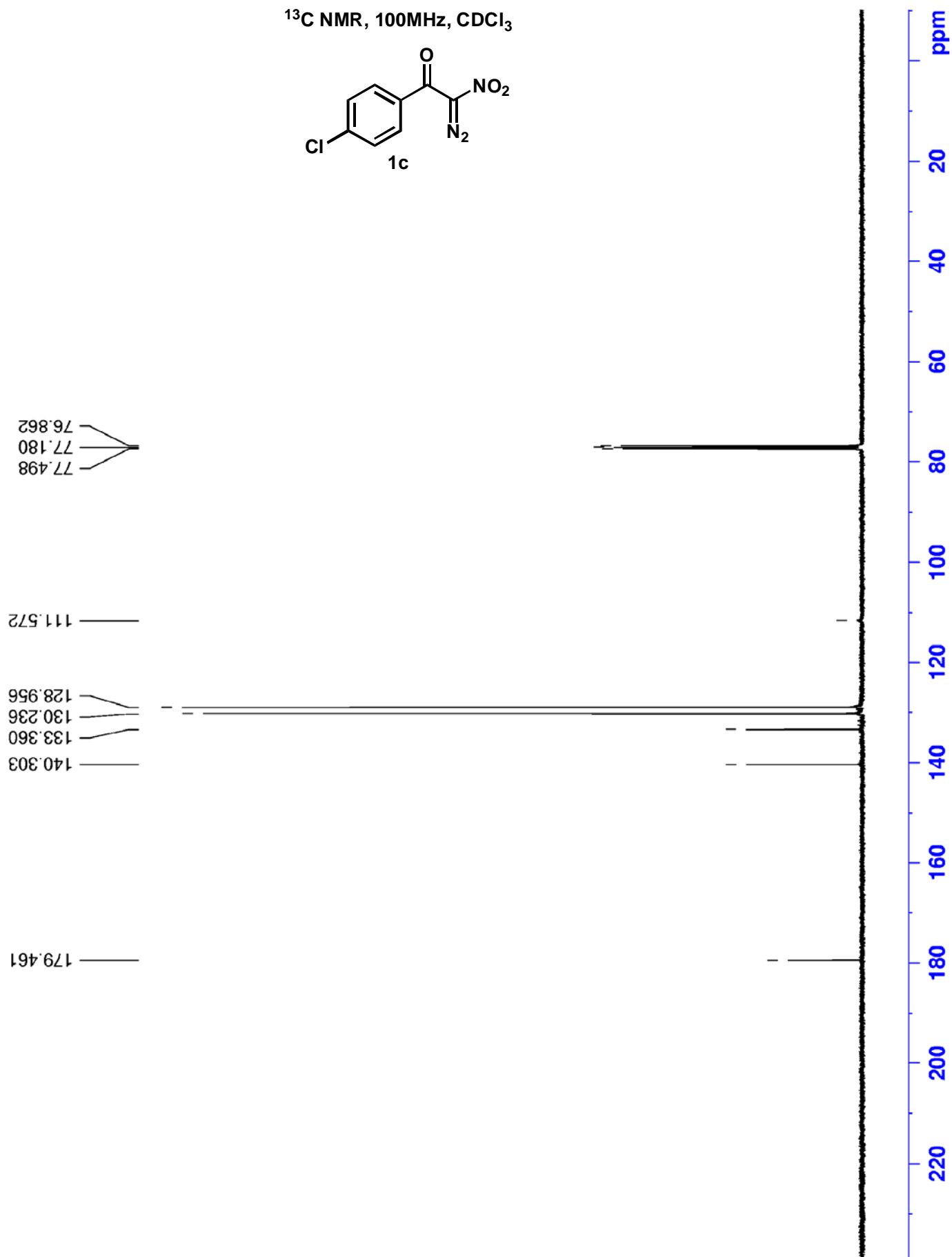
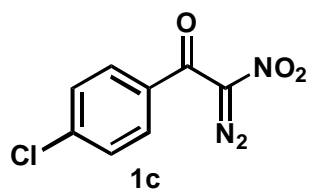
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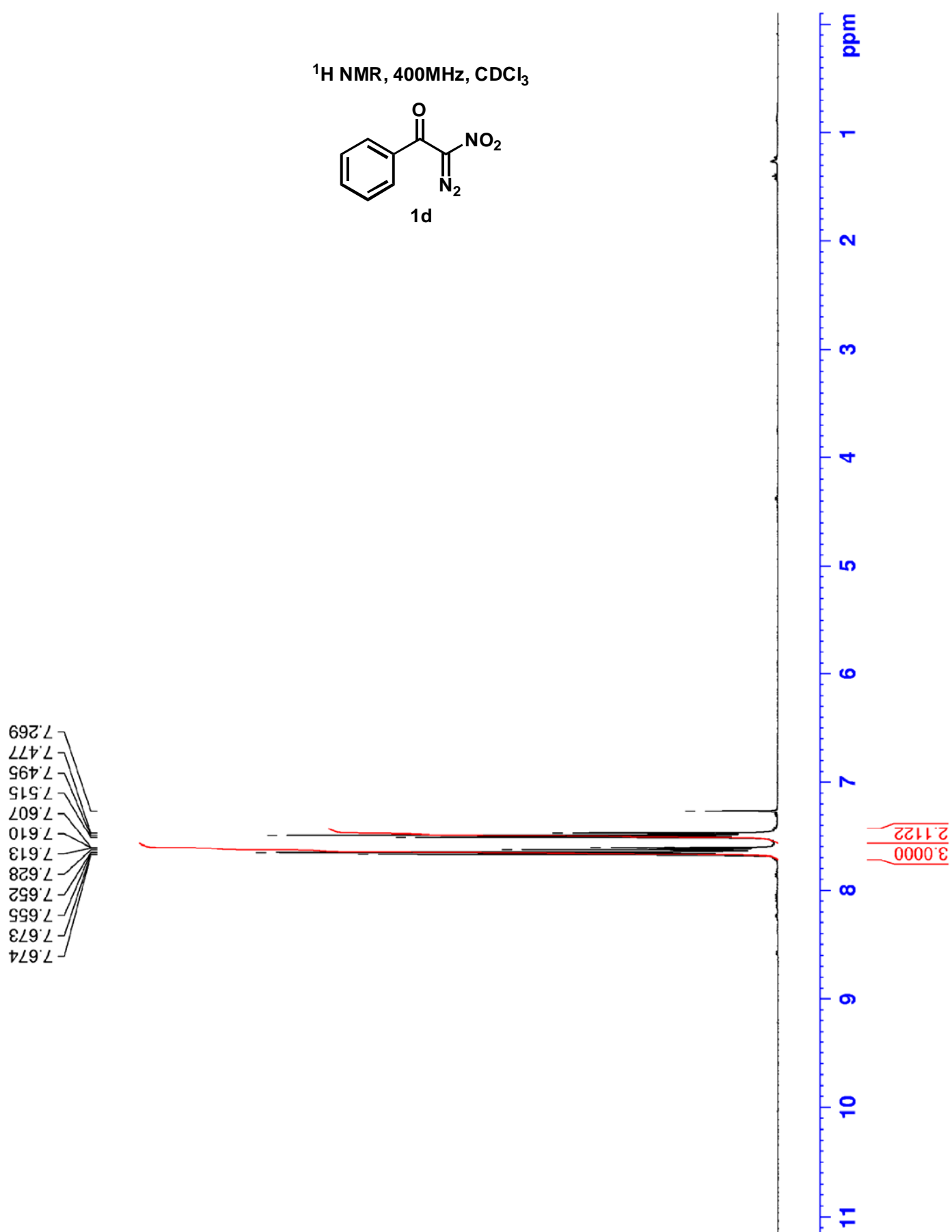
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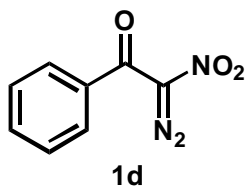






^{13}C NMR, 100MHz, CDCl_3 



^{13}C NMR, 100MHz, CDCl_3 

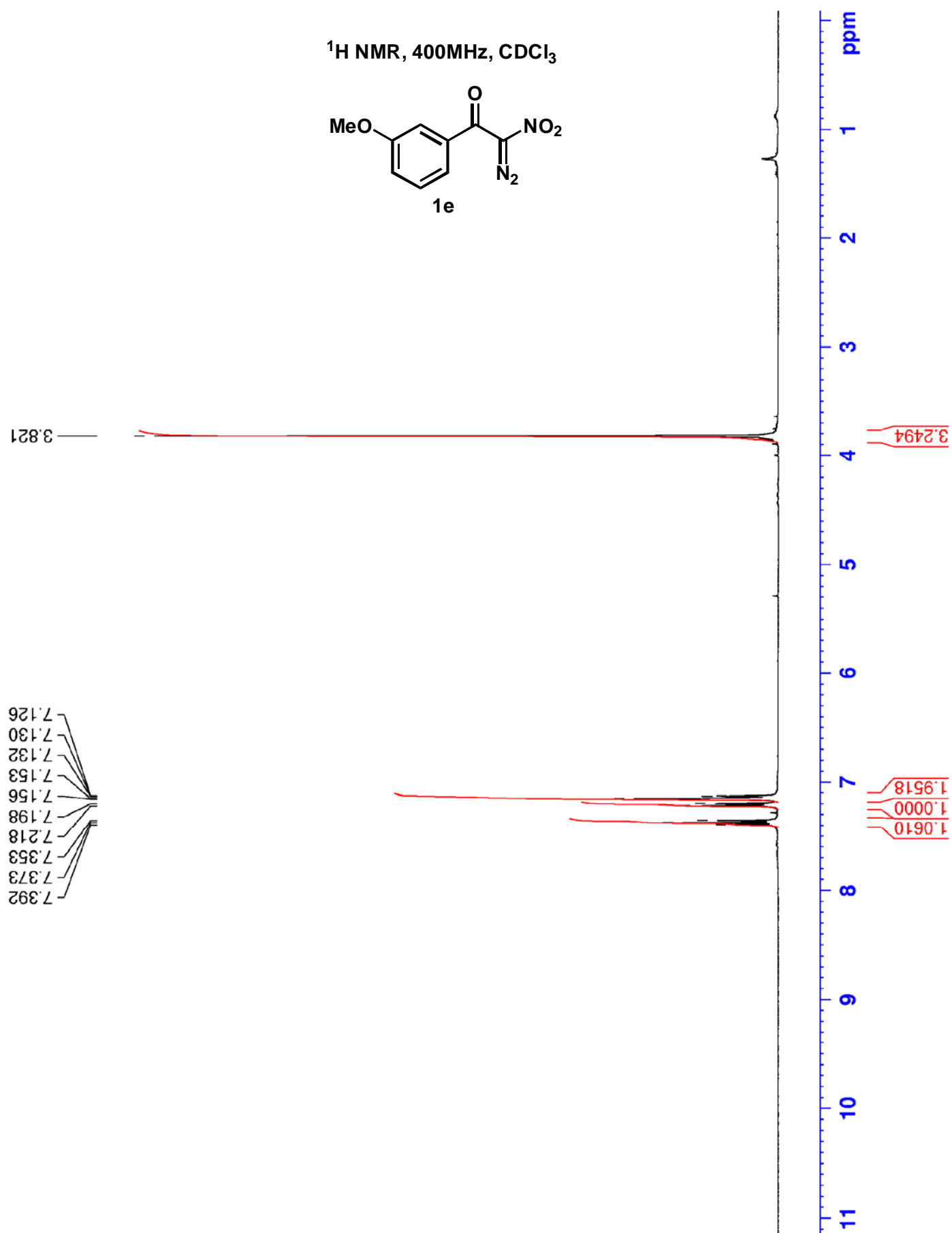
76.841
77.159
77.477

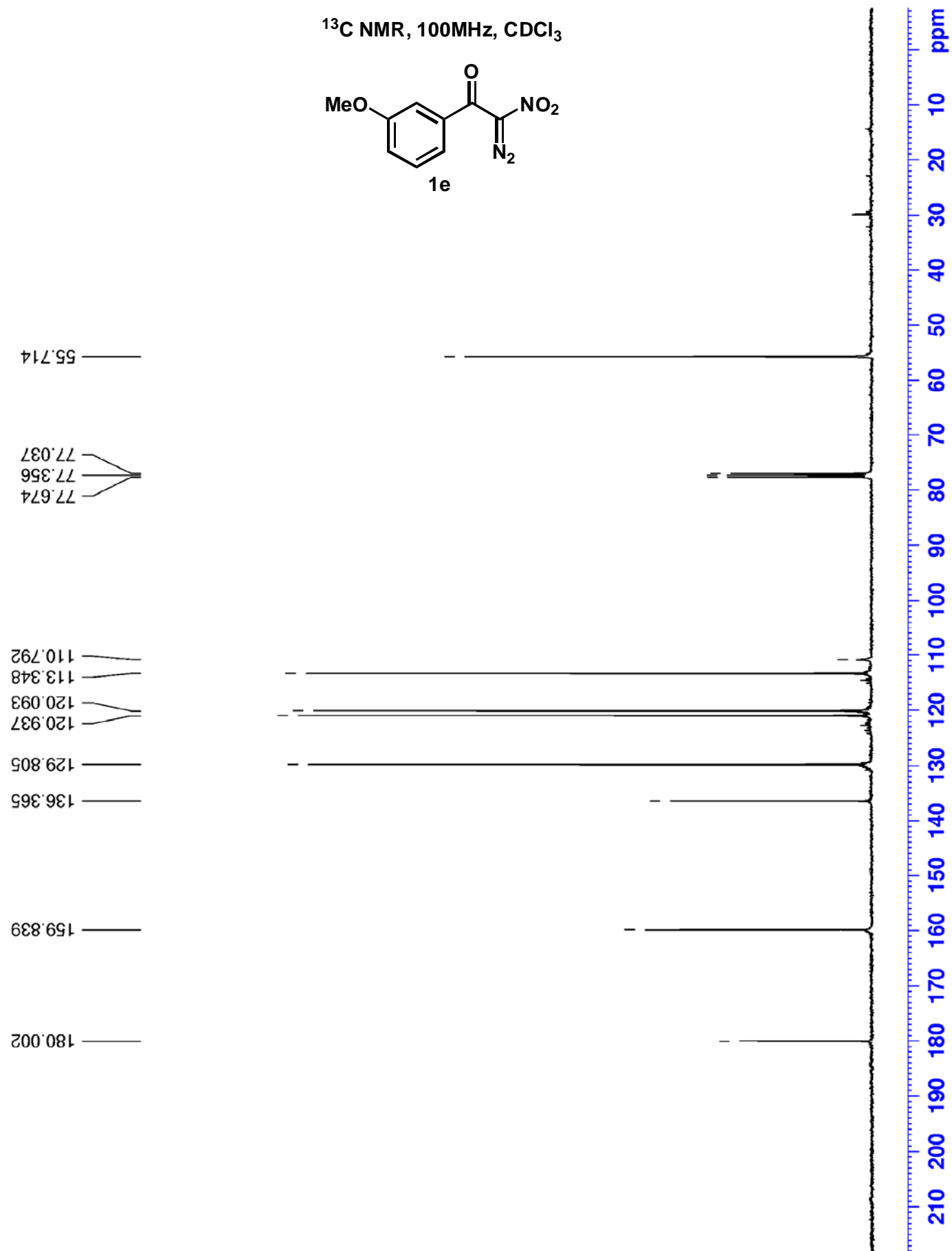
111.140

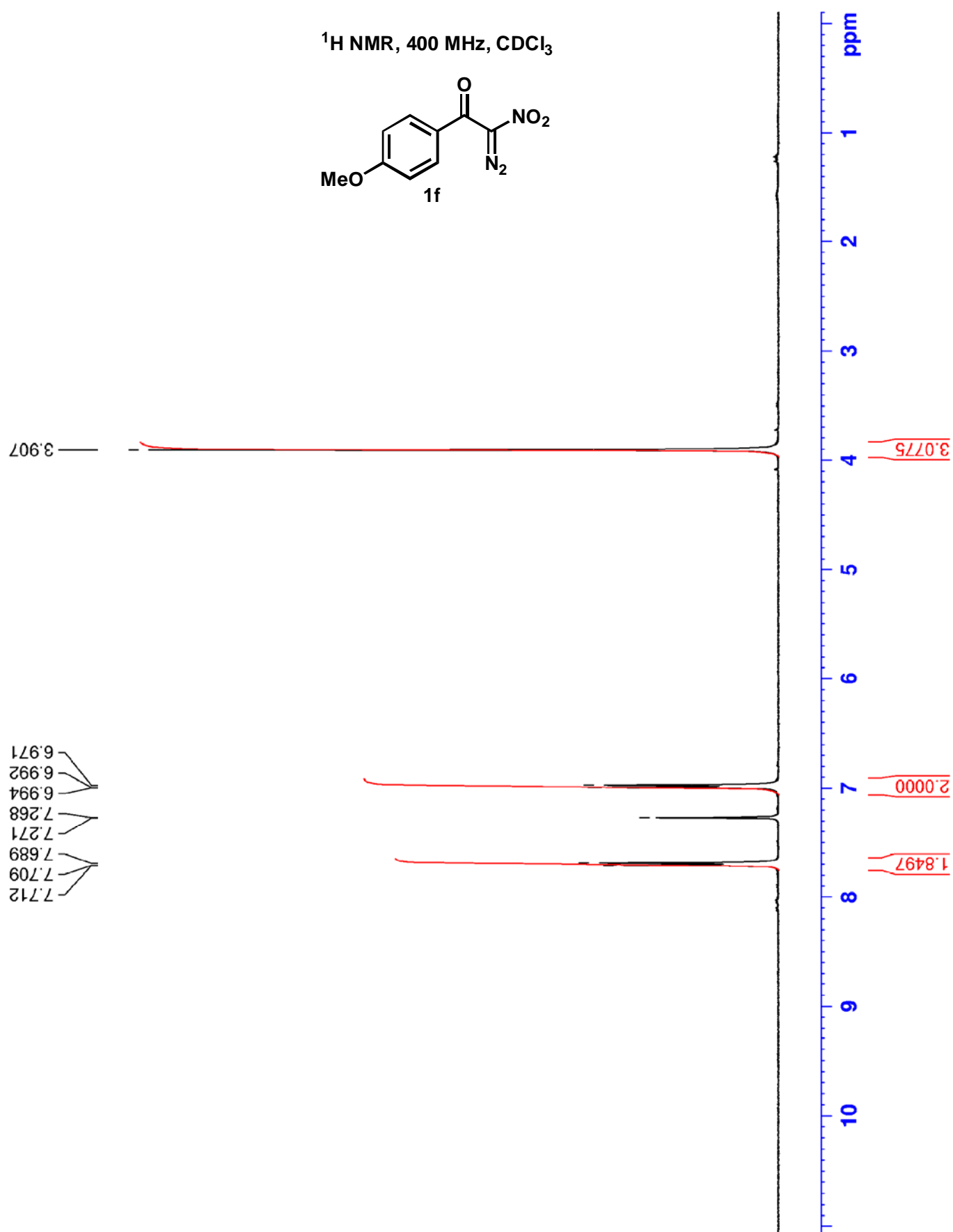
128.619
128.668
133.788
135.101

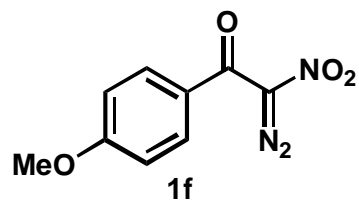
180.368

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm







^{13}C NMR, 100MHz, CDCl_3 

55.695

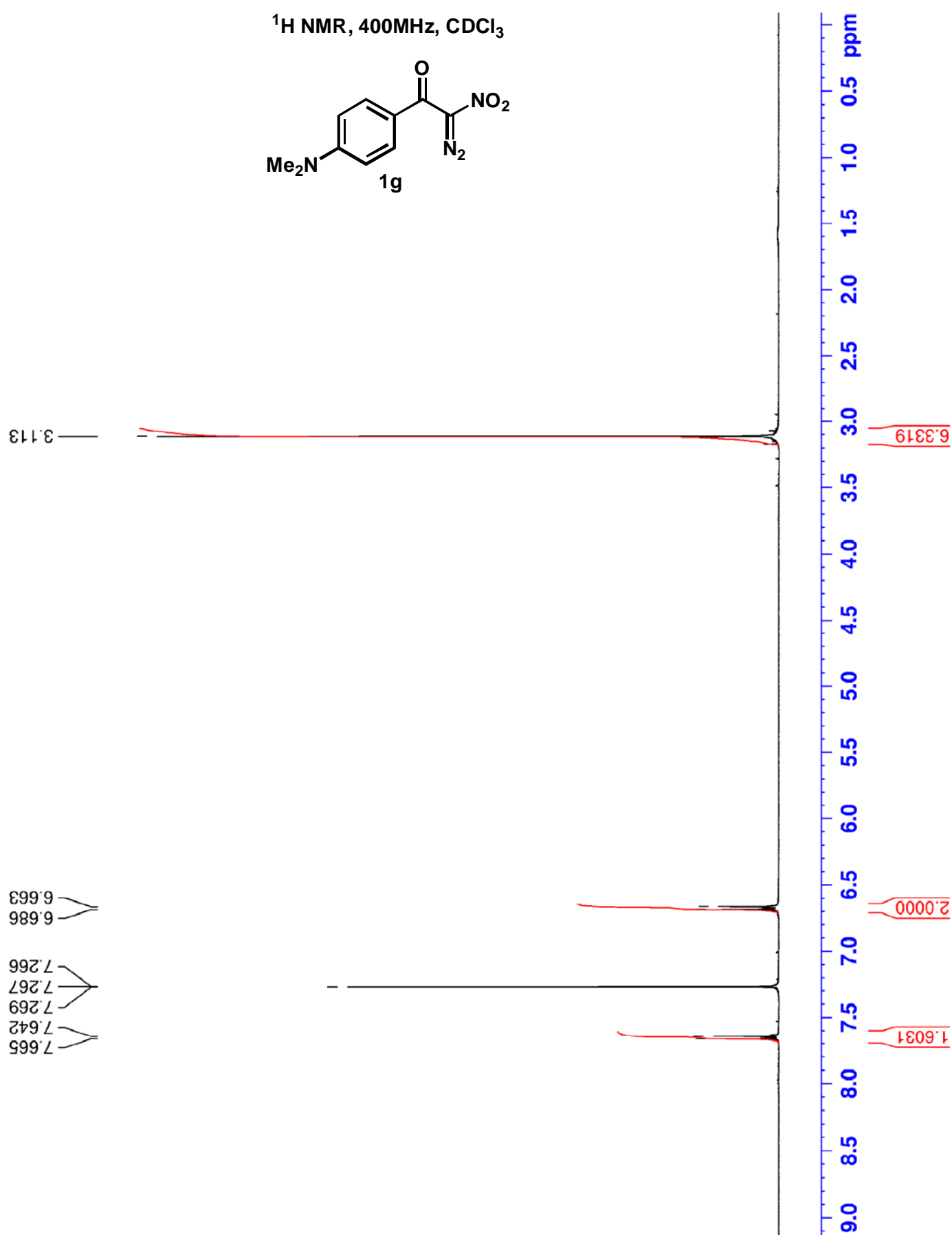
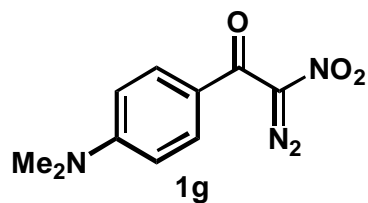
76.839
77.157
77.475110.711
113.926127.366
131.504

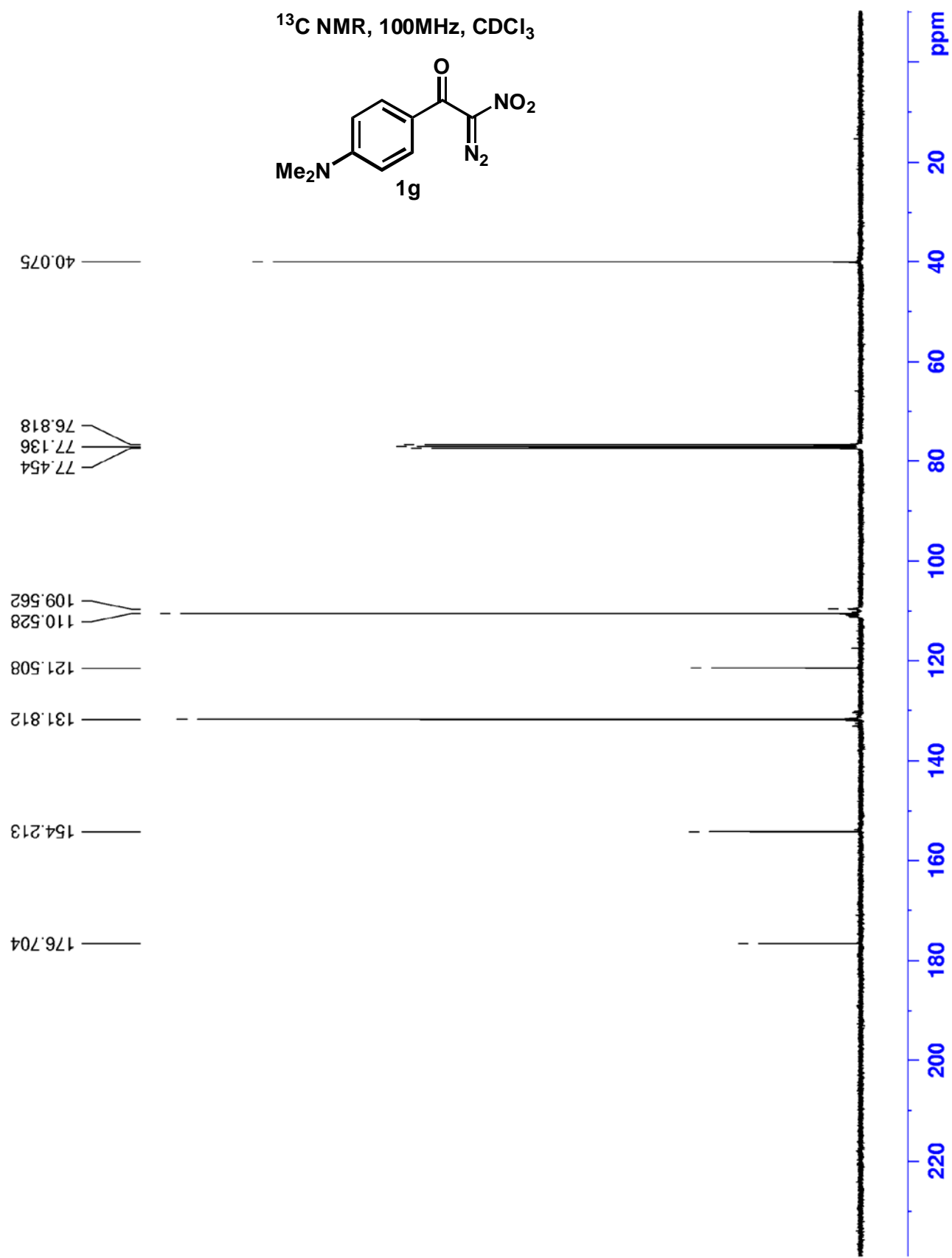
164.334

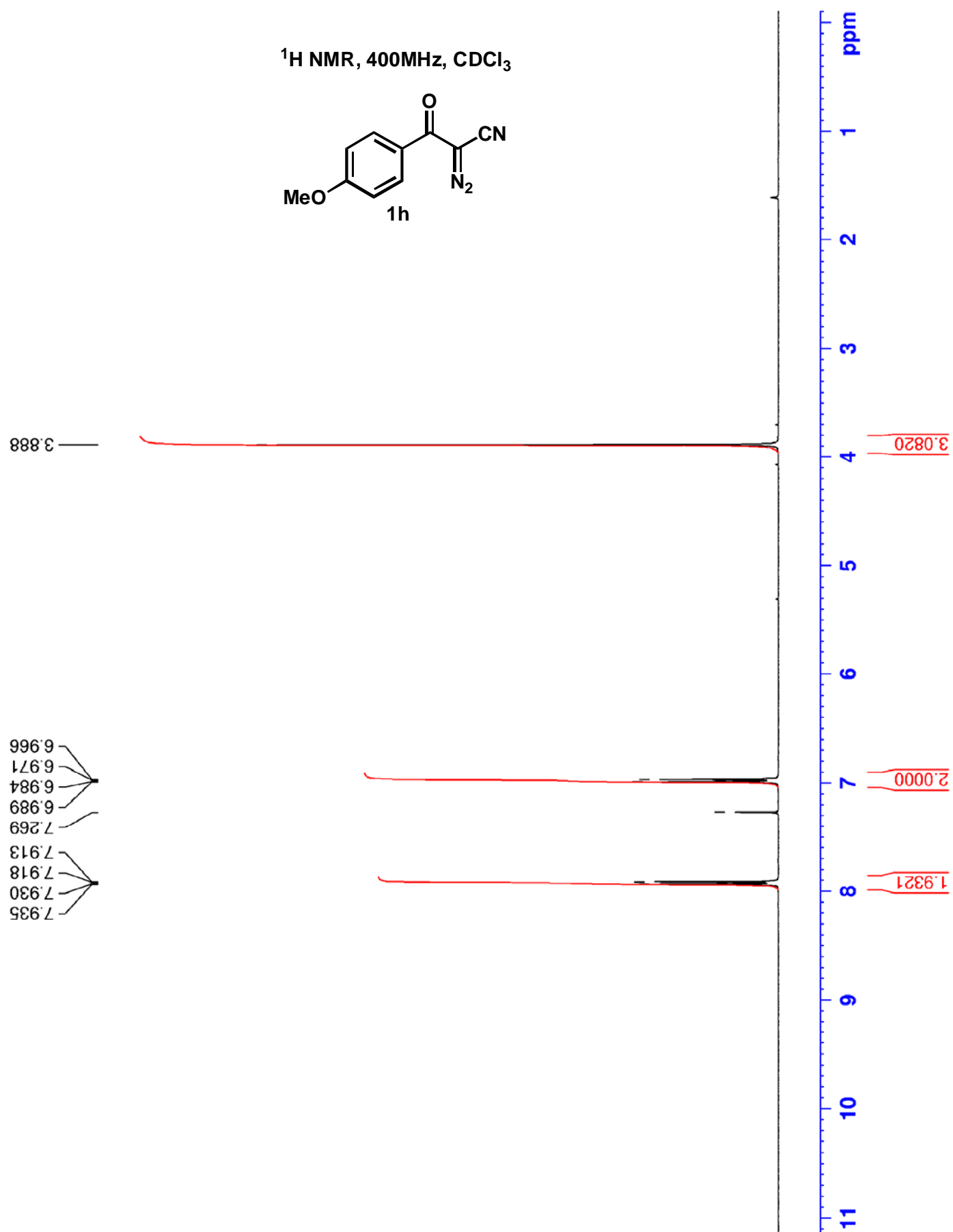
178.543

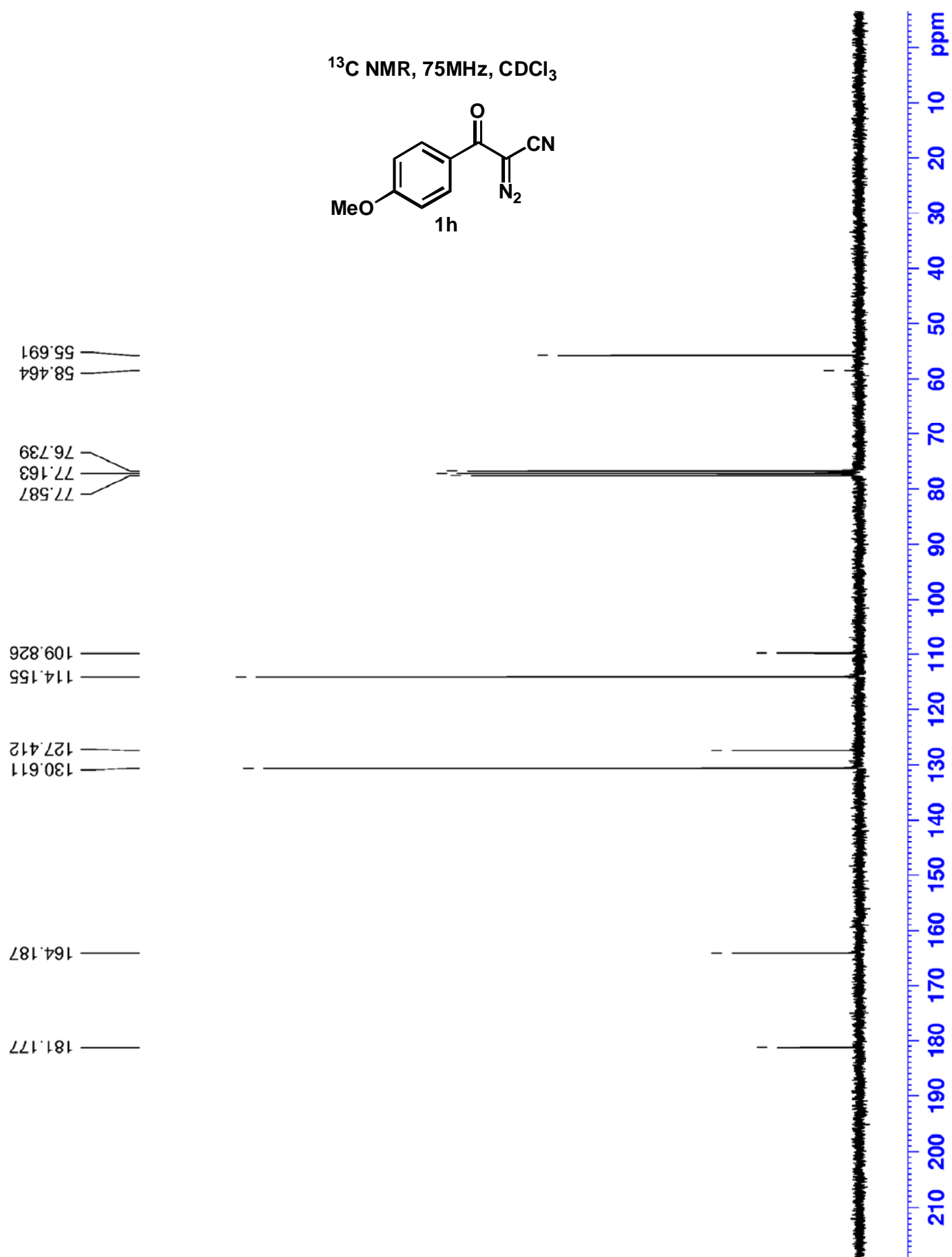
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

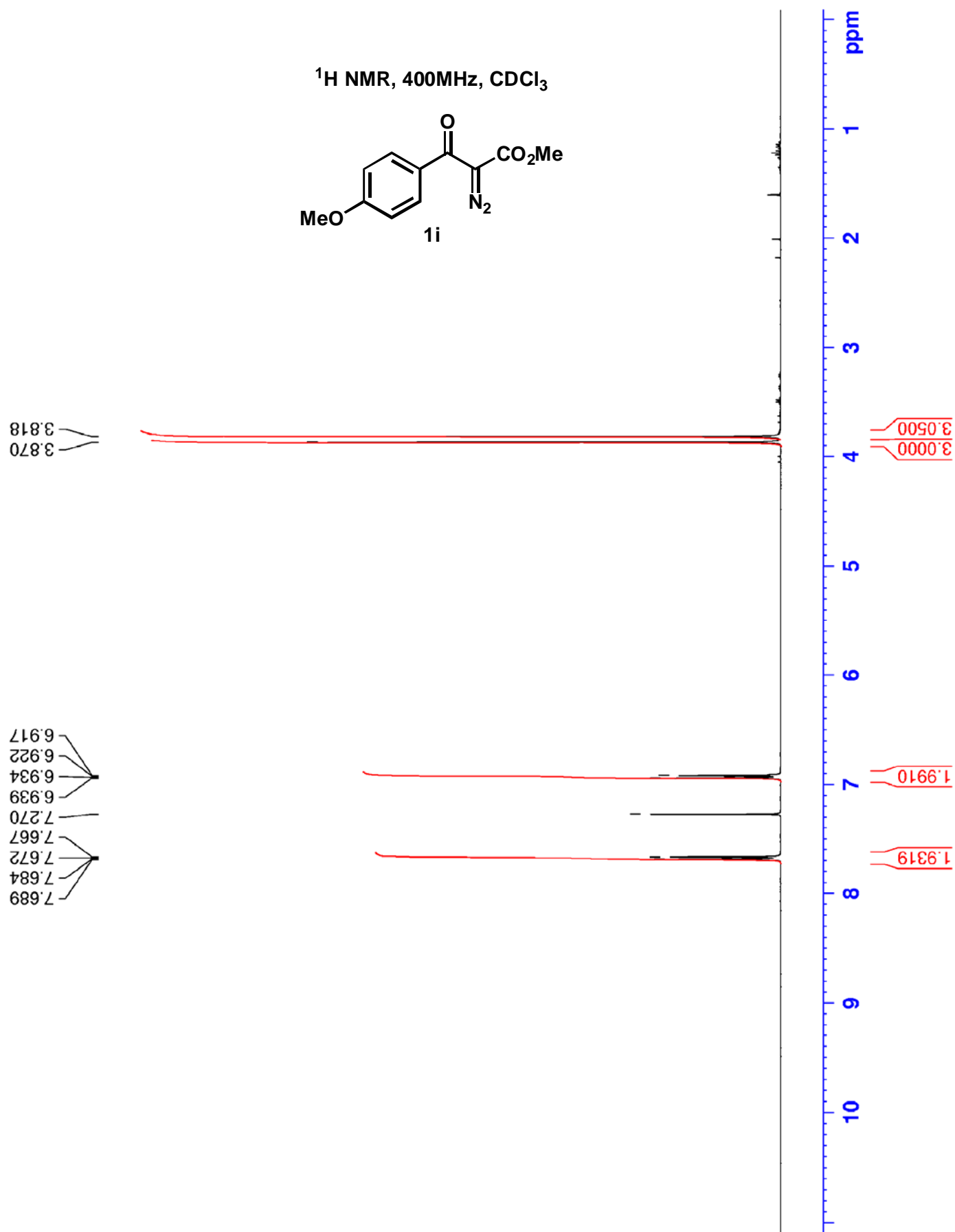
^1H NMR, 400MHz, CDCl_3

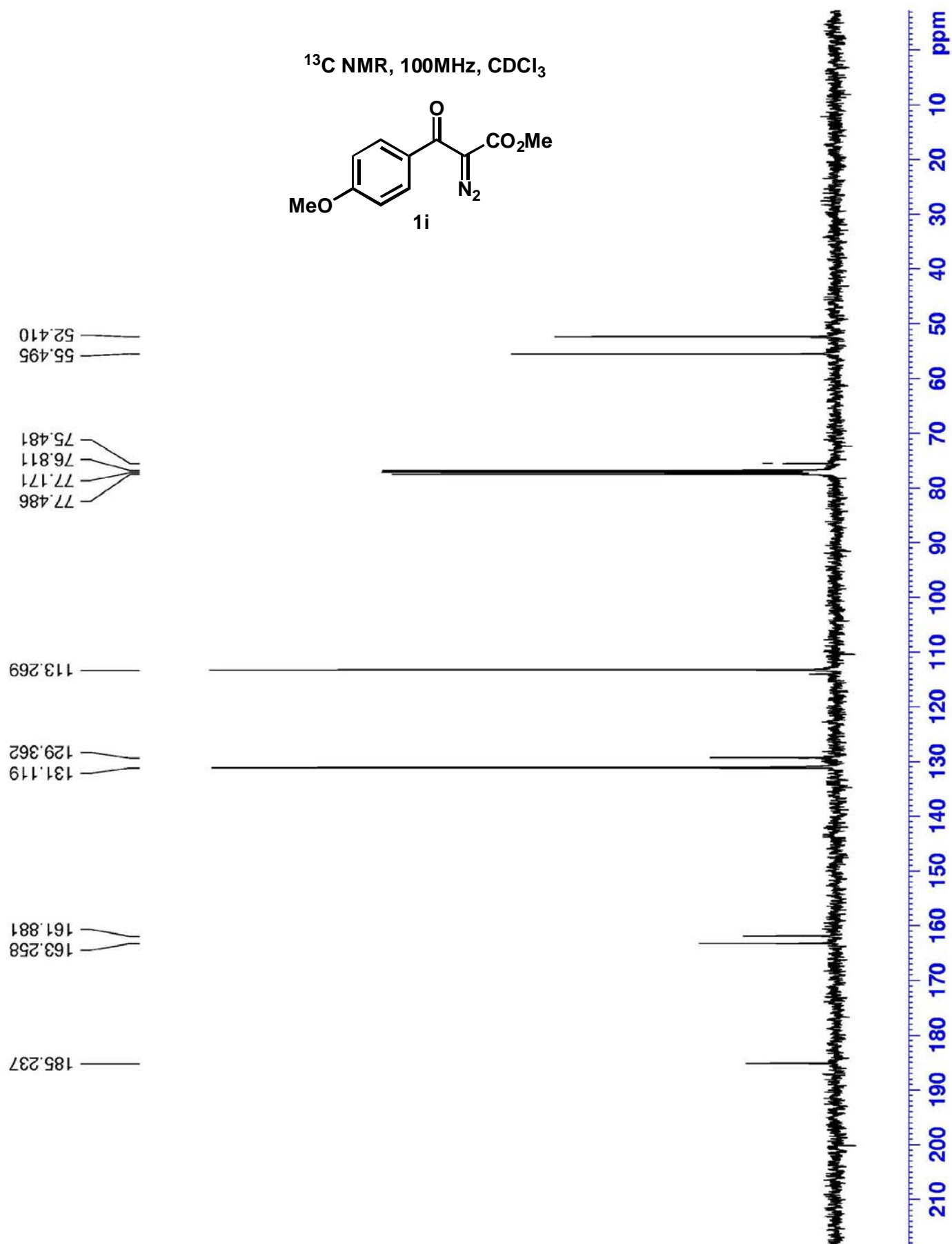


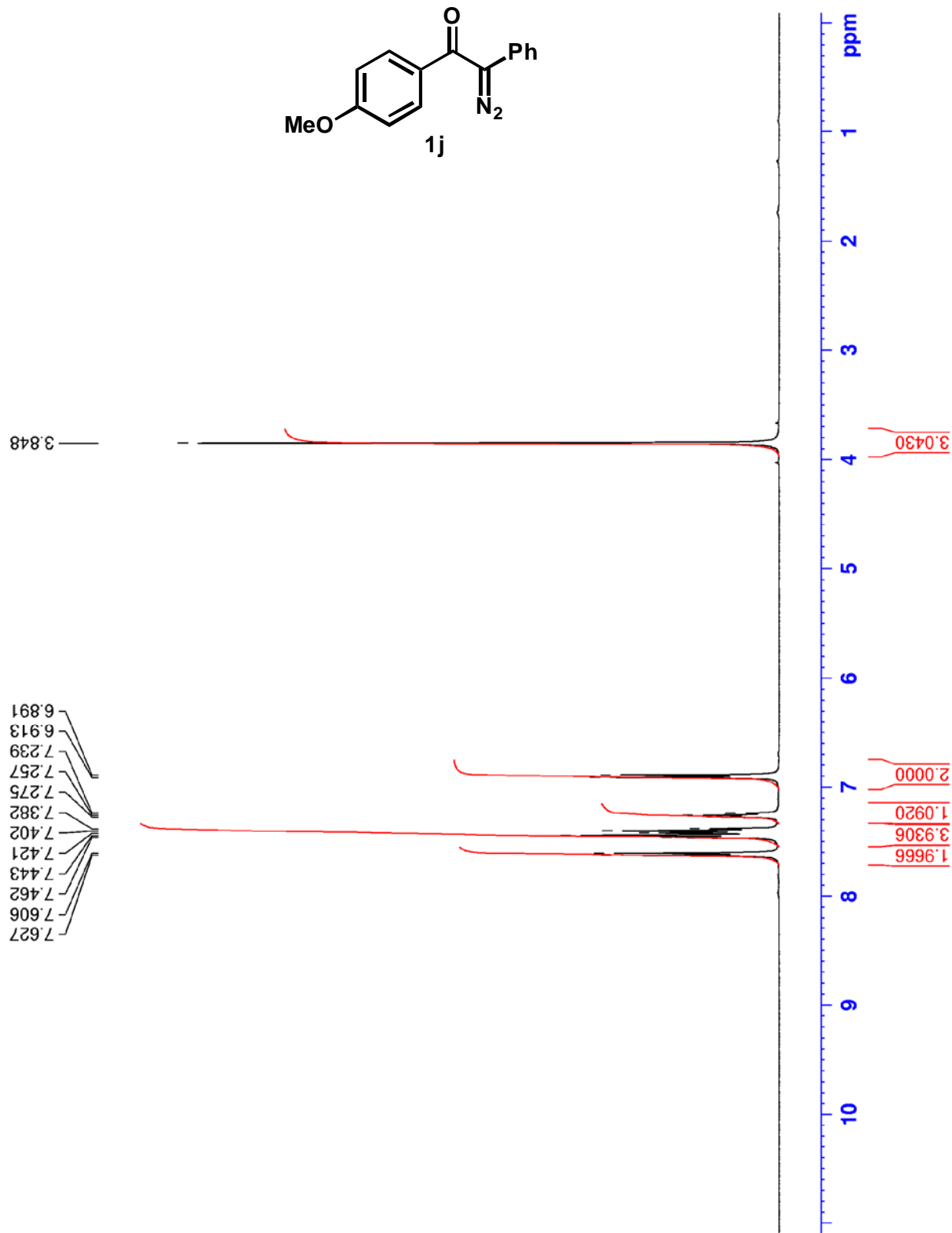
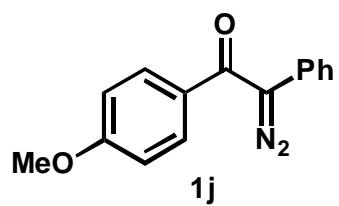


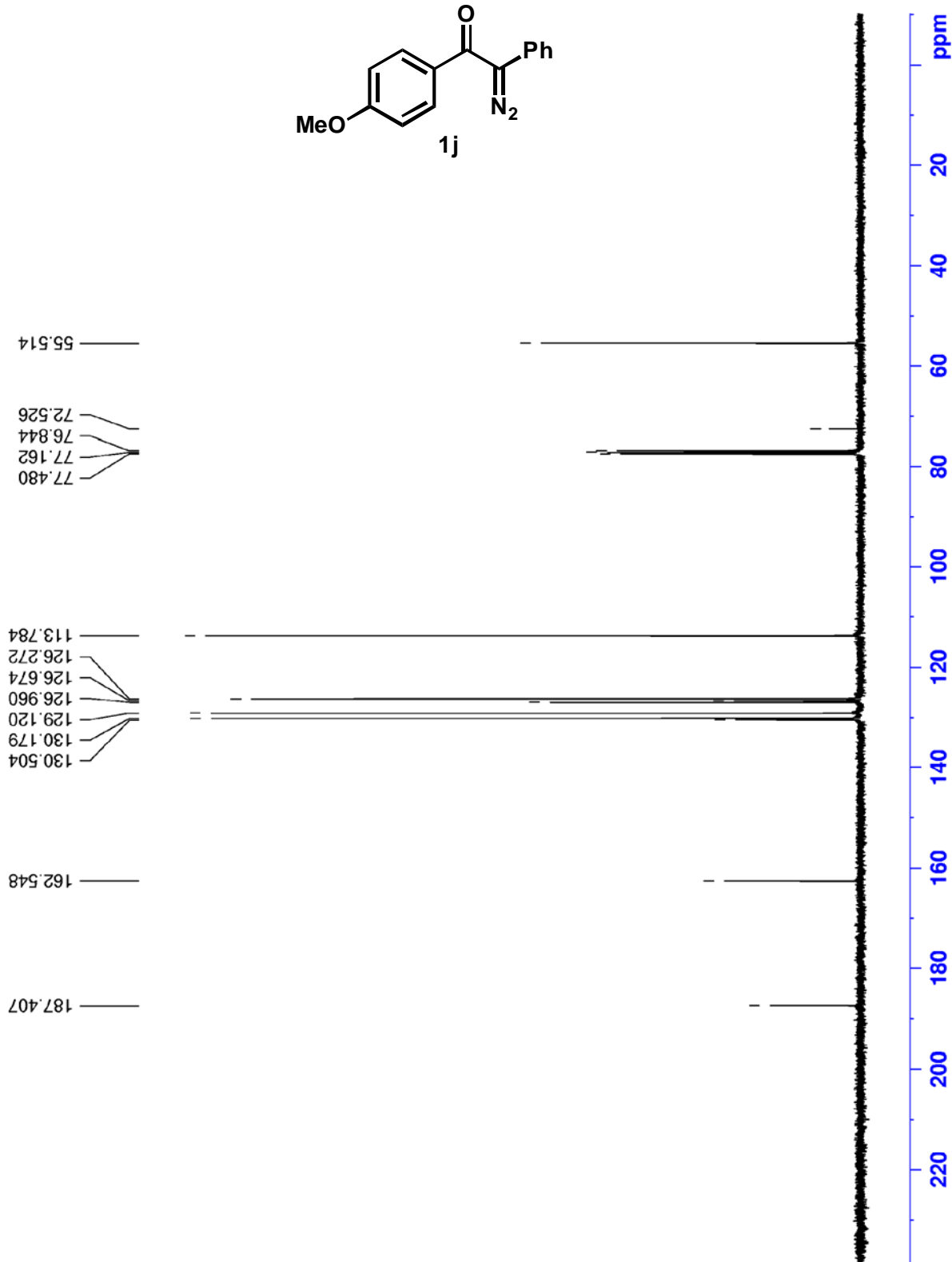
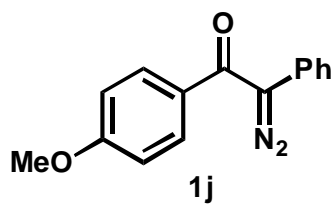


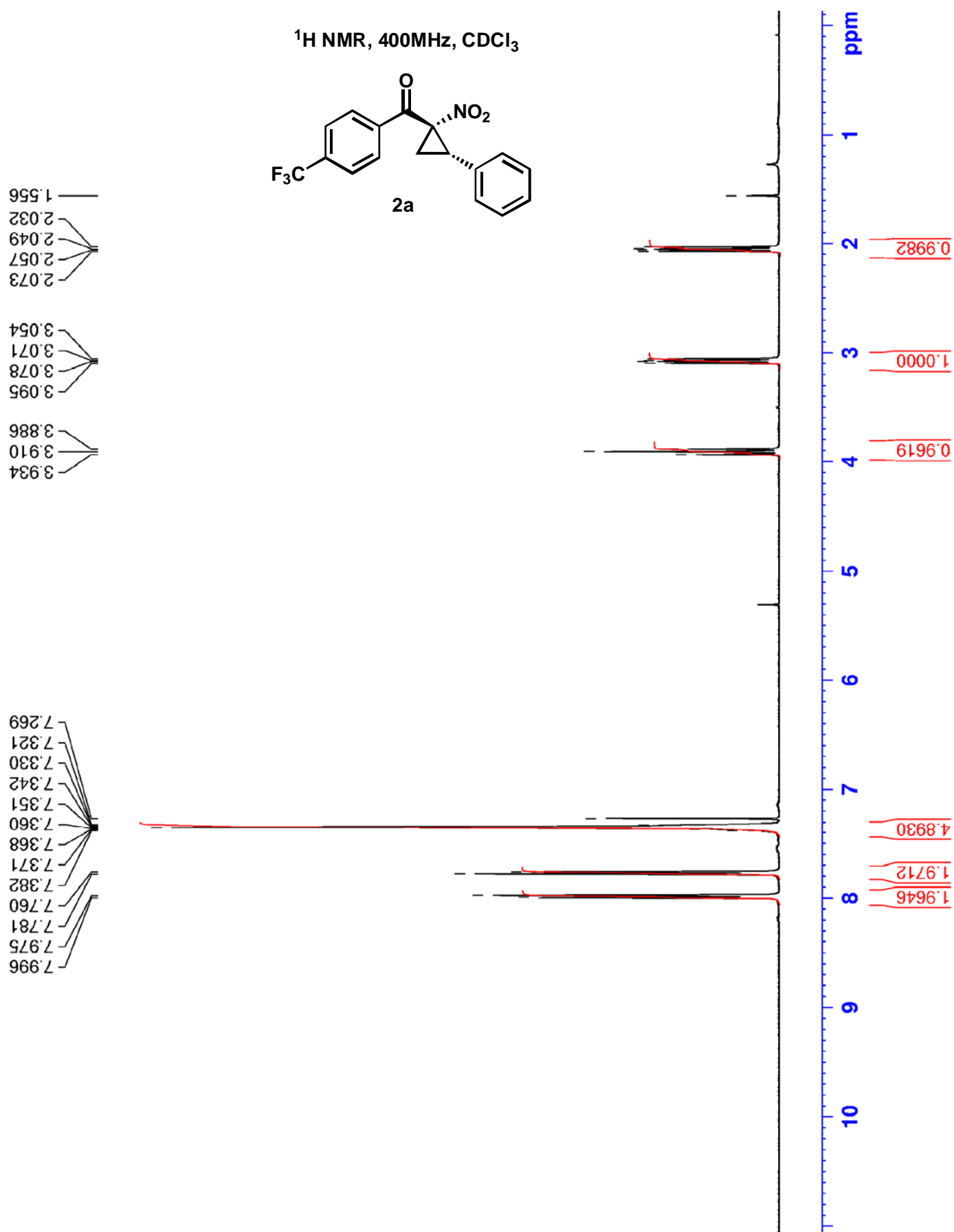


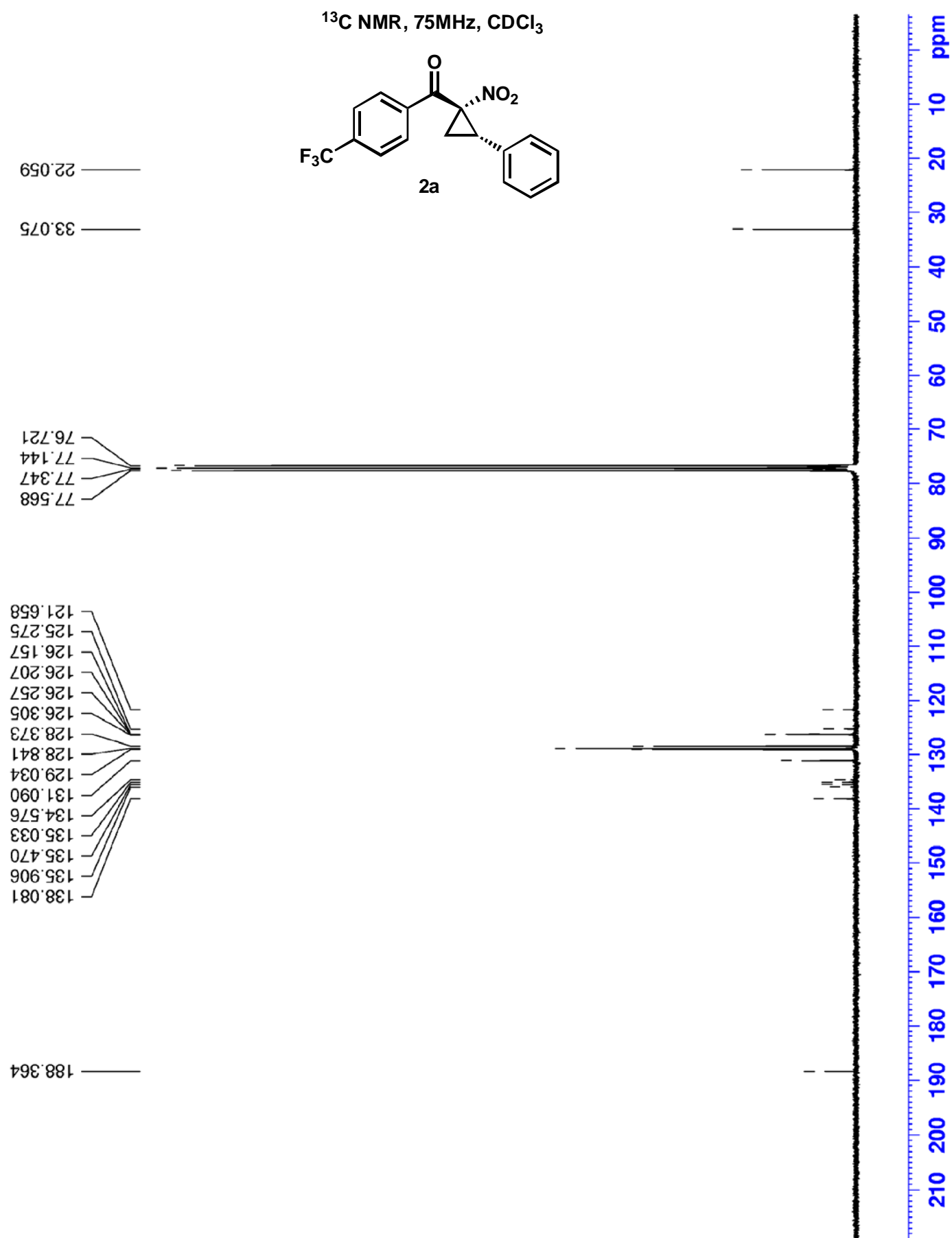




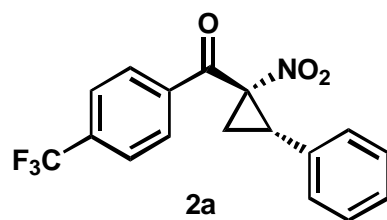
$^1\text{H NMR}$, 400MHz, CDCl_3 

^{13}C NMR, 100MHz, CDCl_3 





^{19}F NMR, 282MHz, CDCl_3



-64.710

ppm

-160

-140

-120

-100

-80

-60

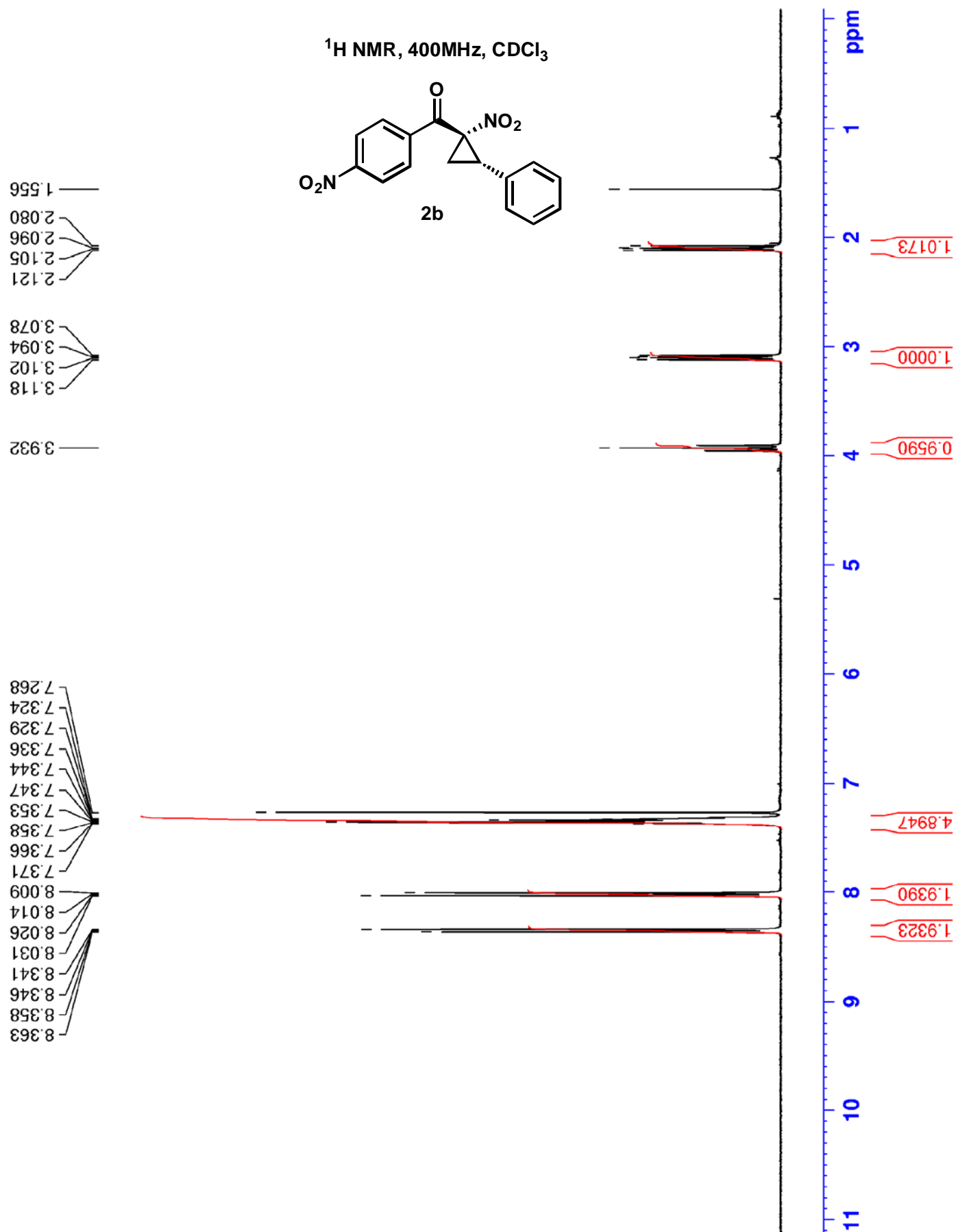
-40

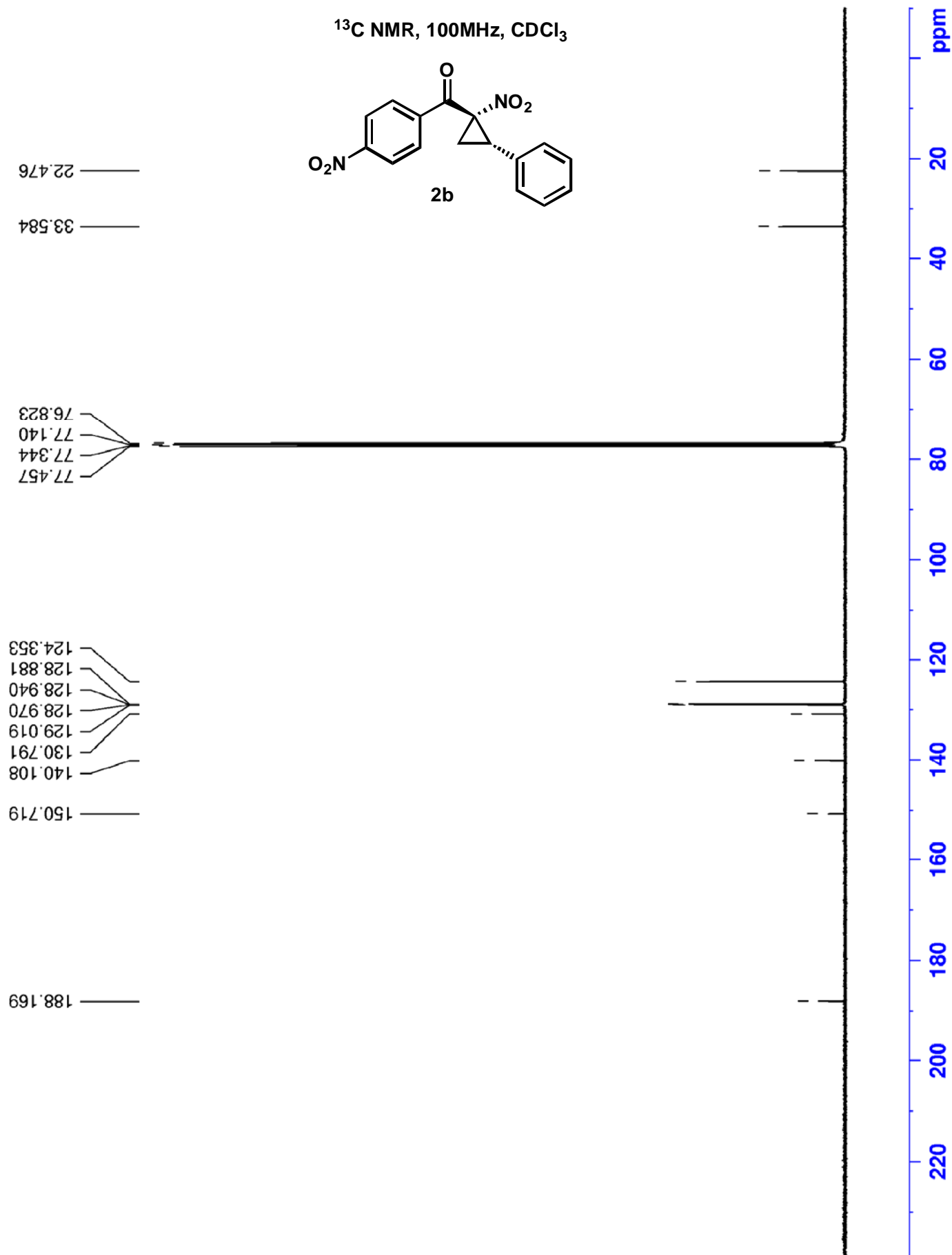
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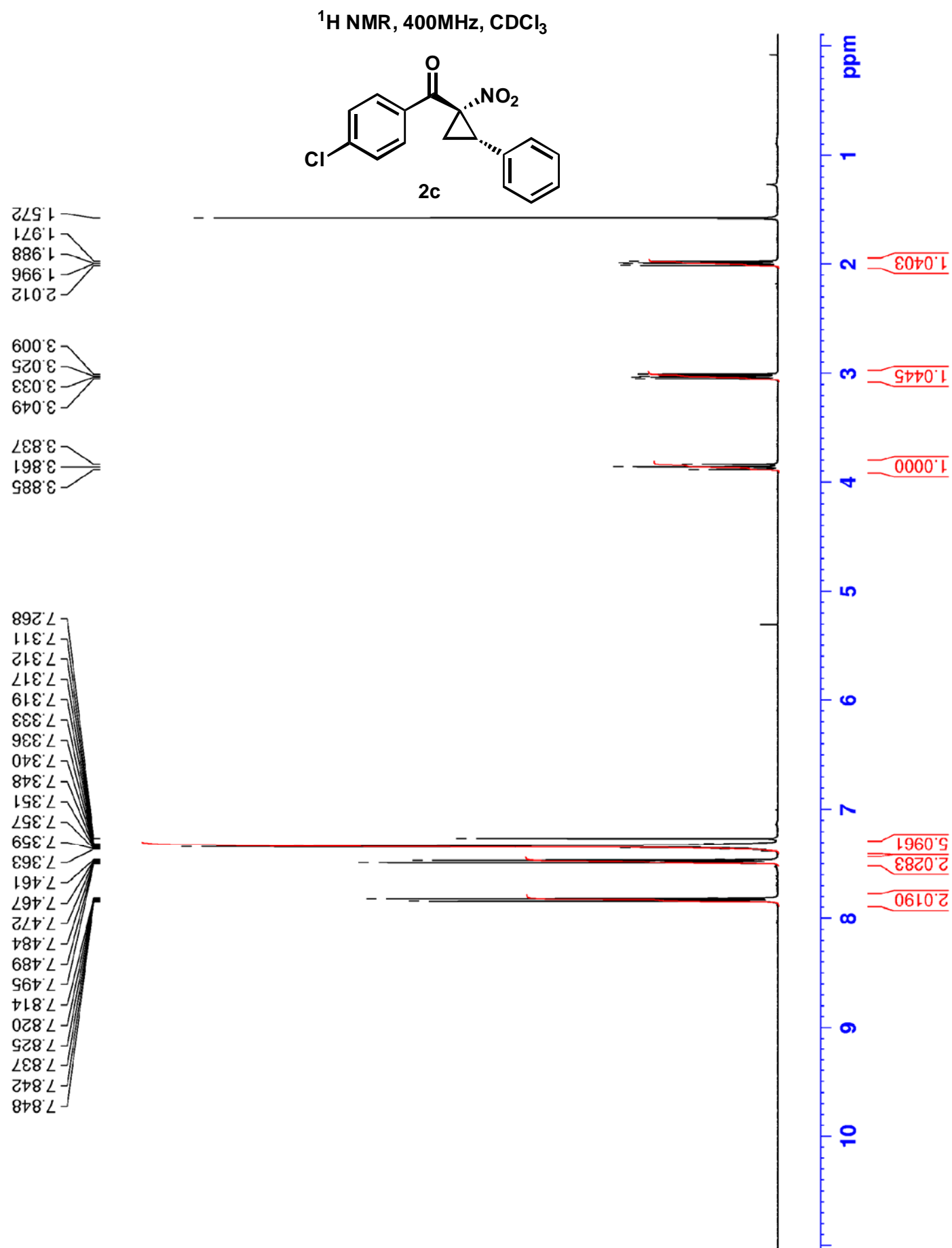
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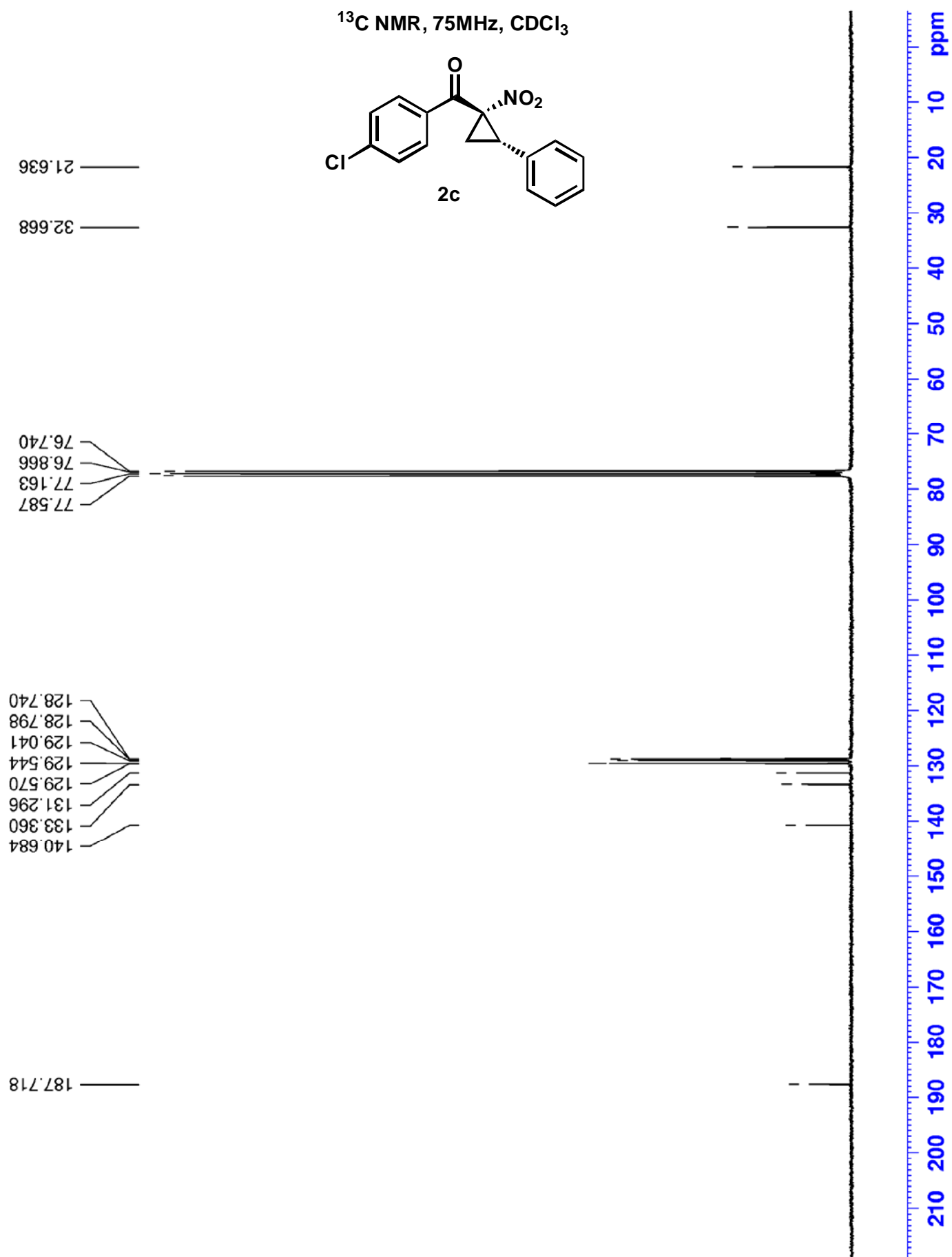
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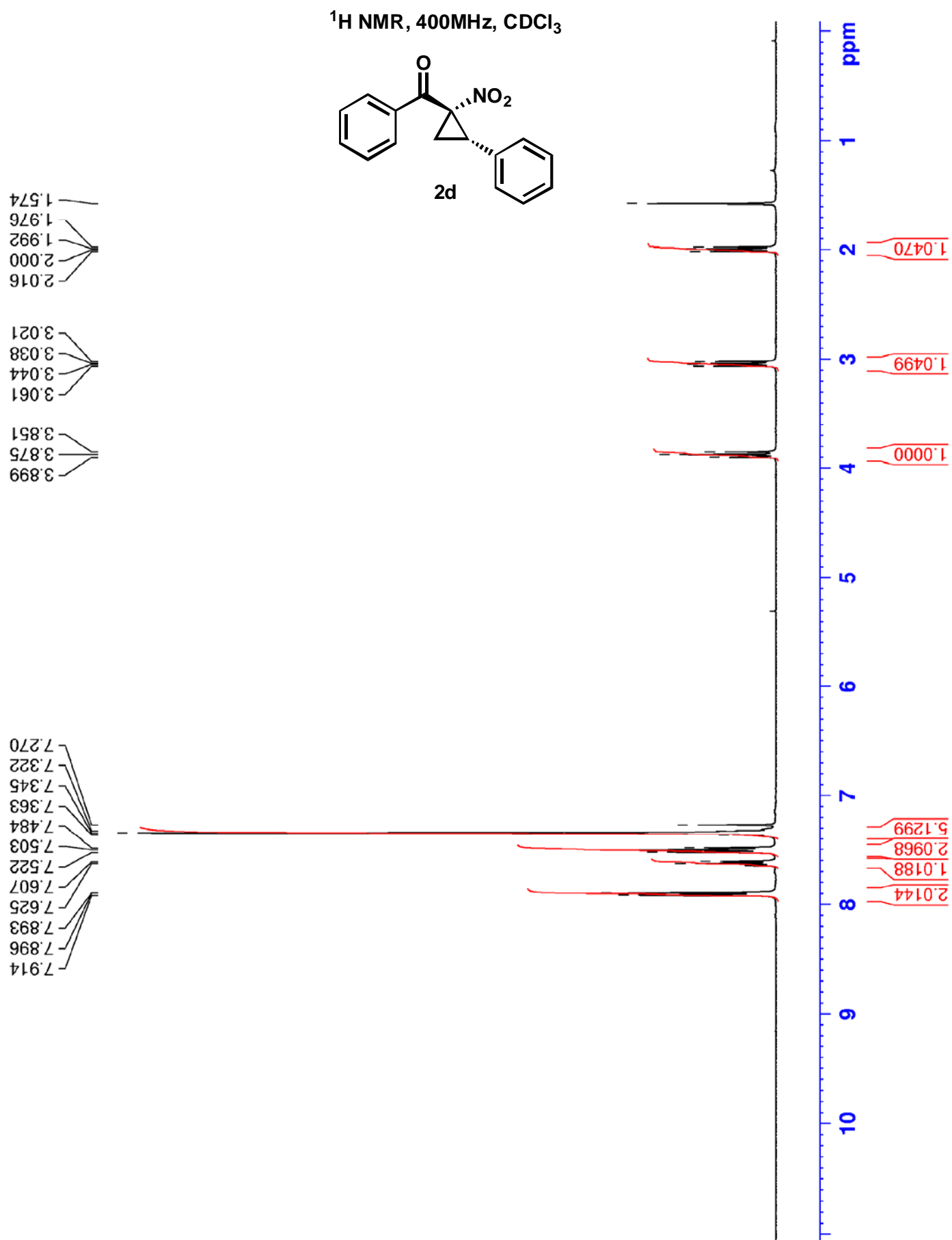
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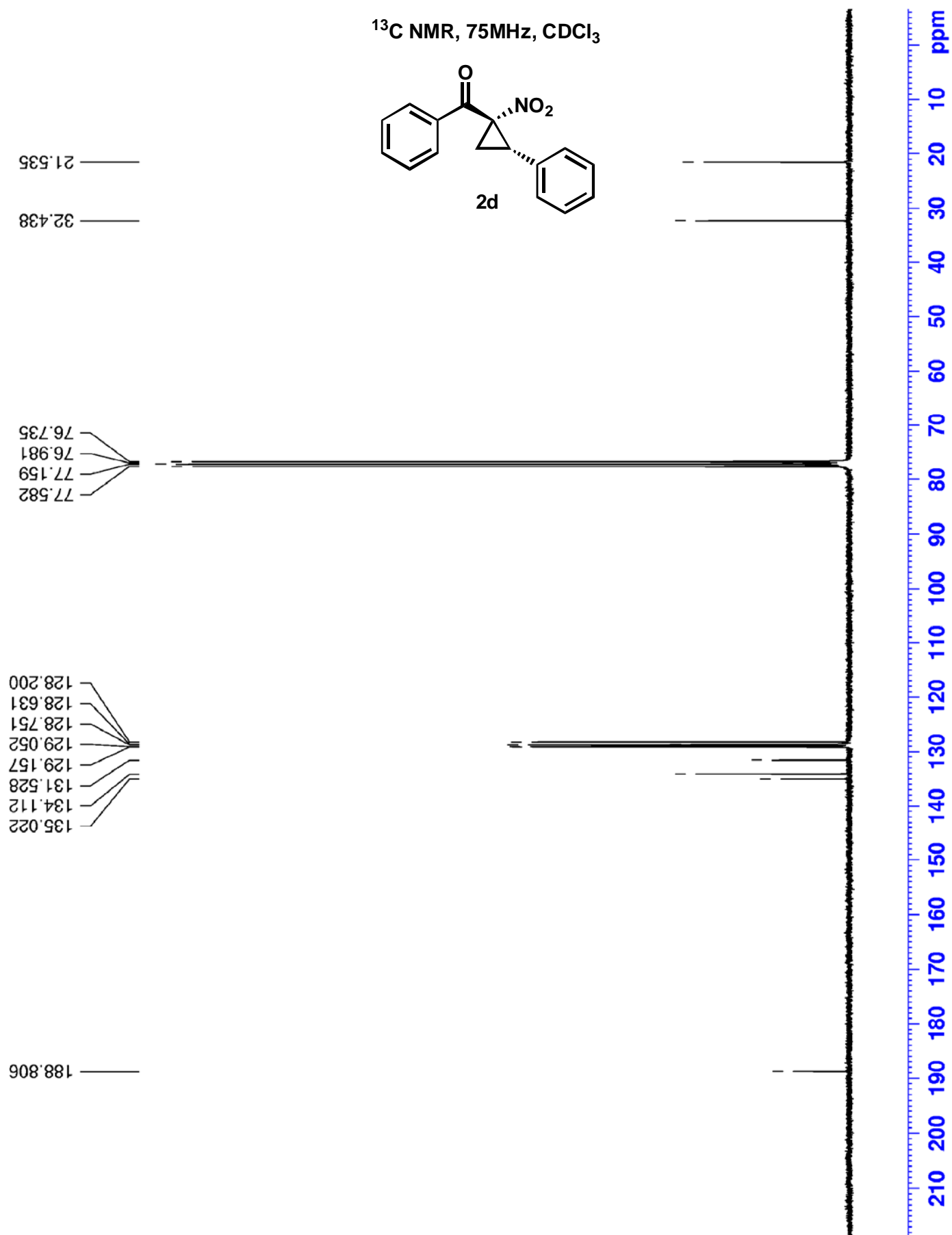


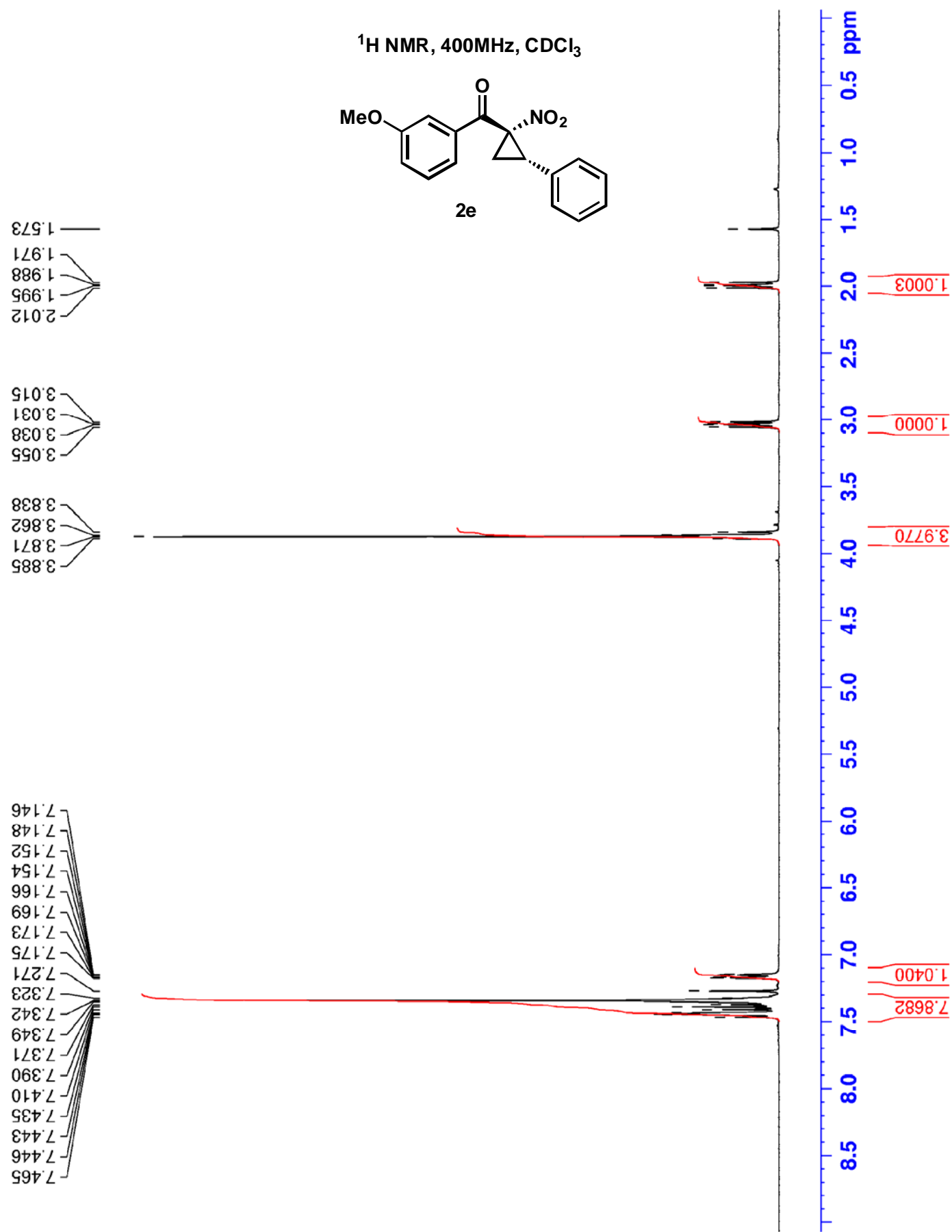


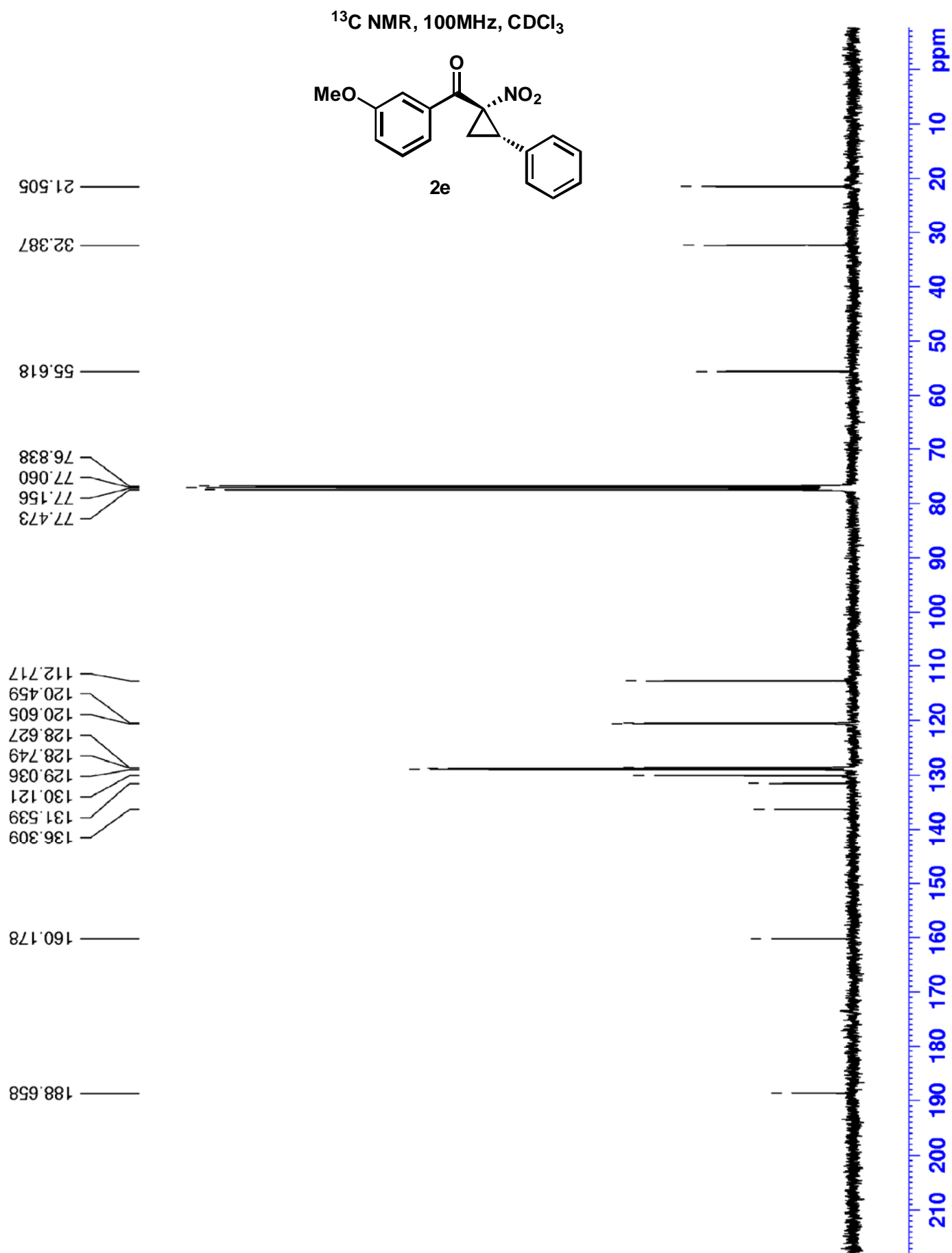


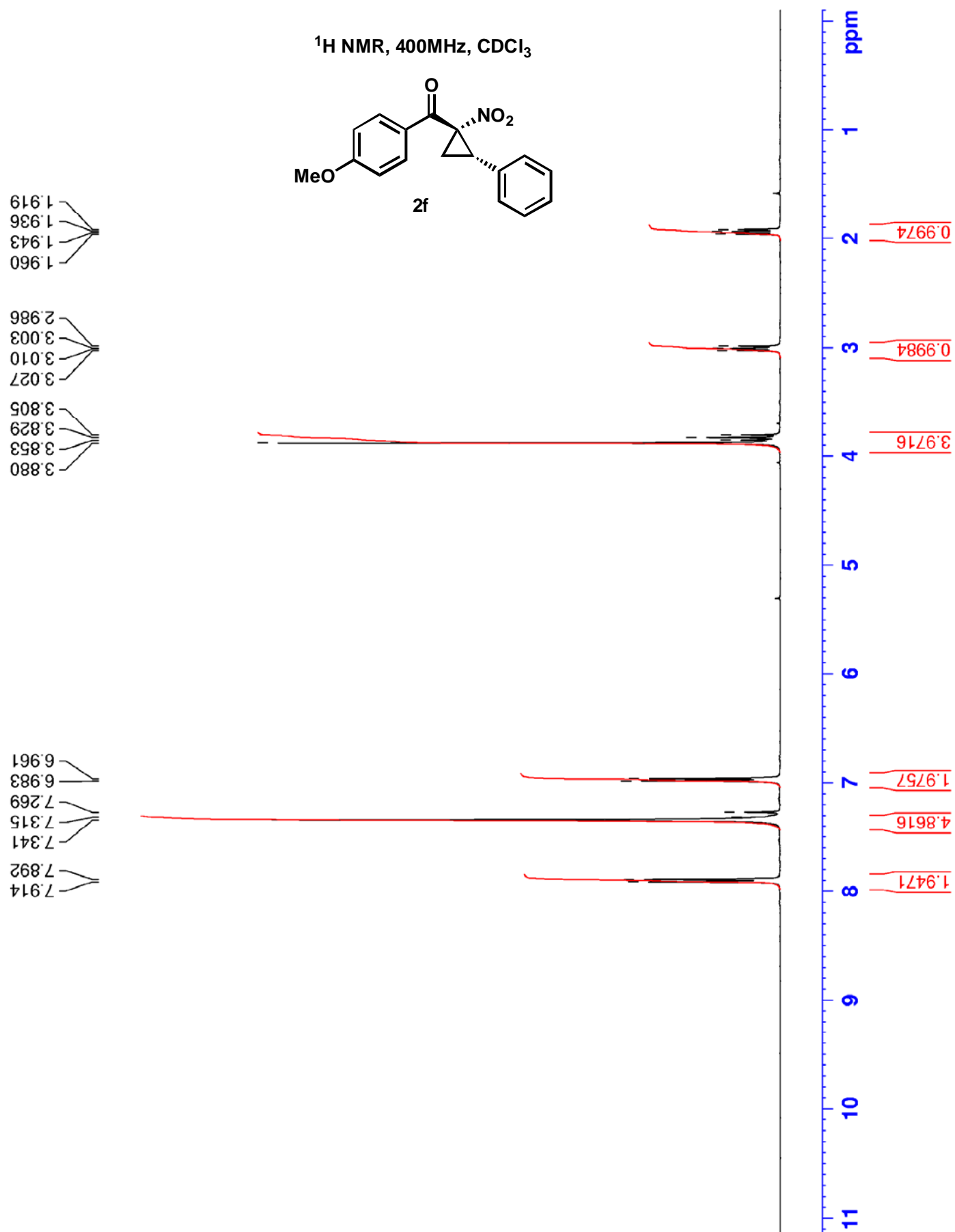


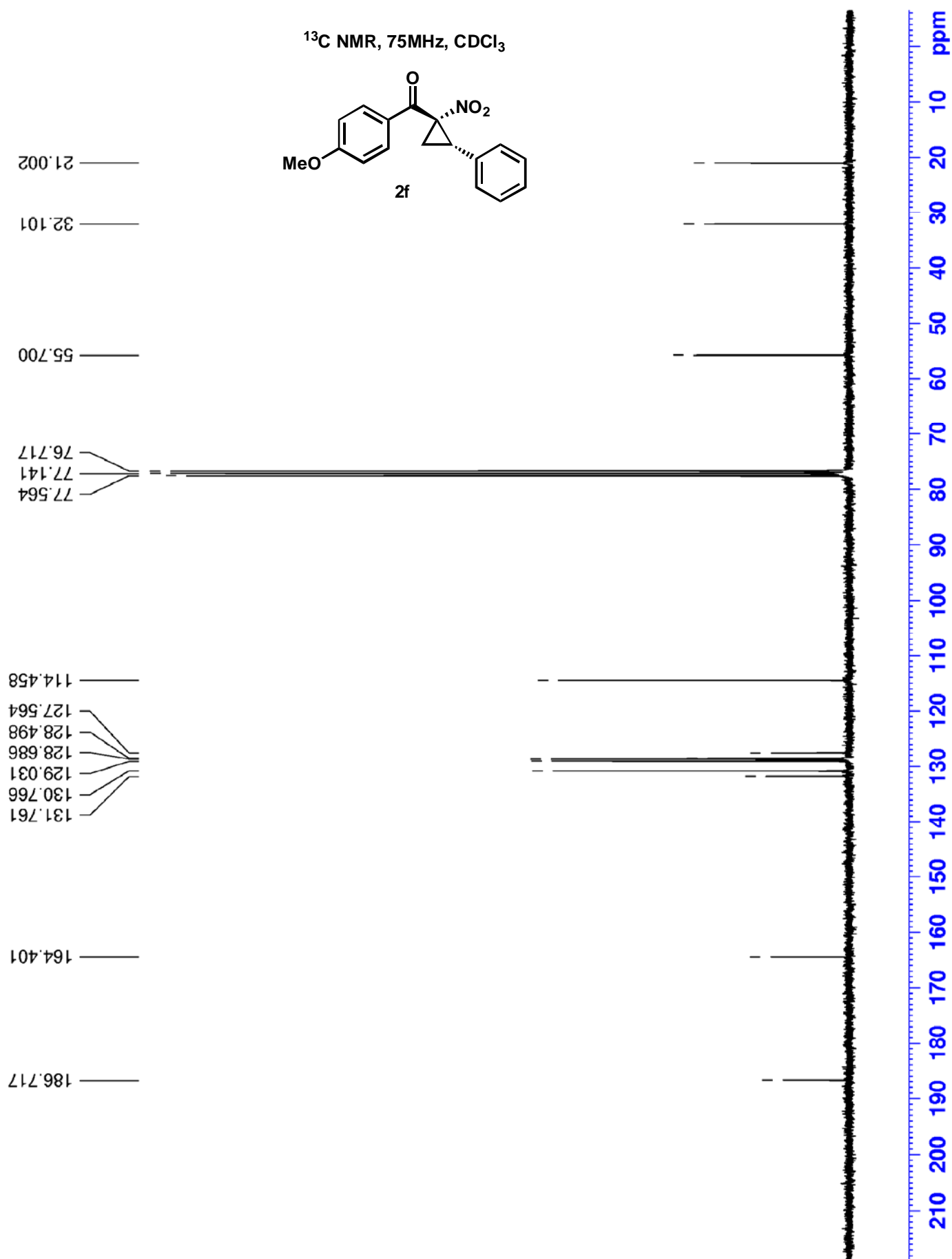




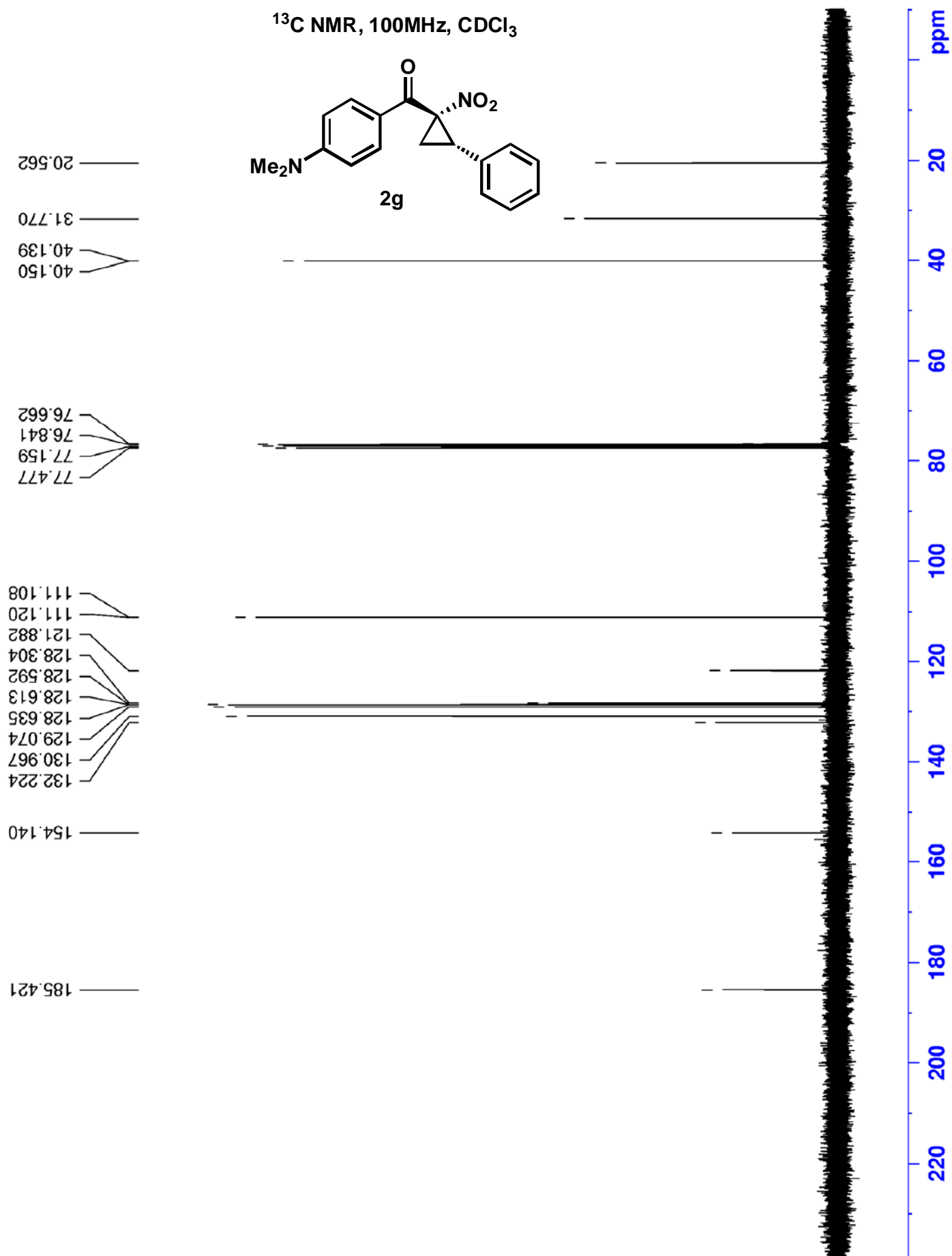


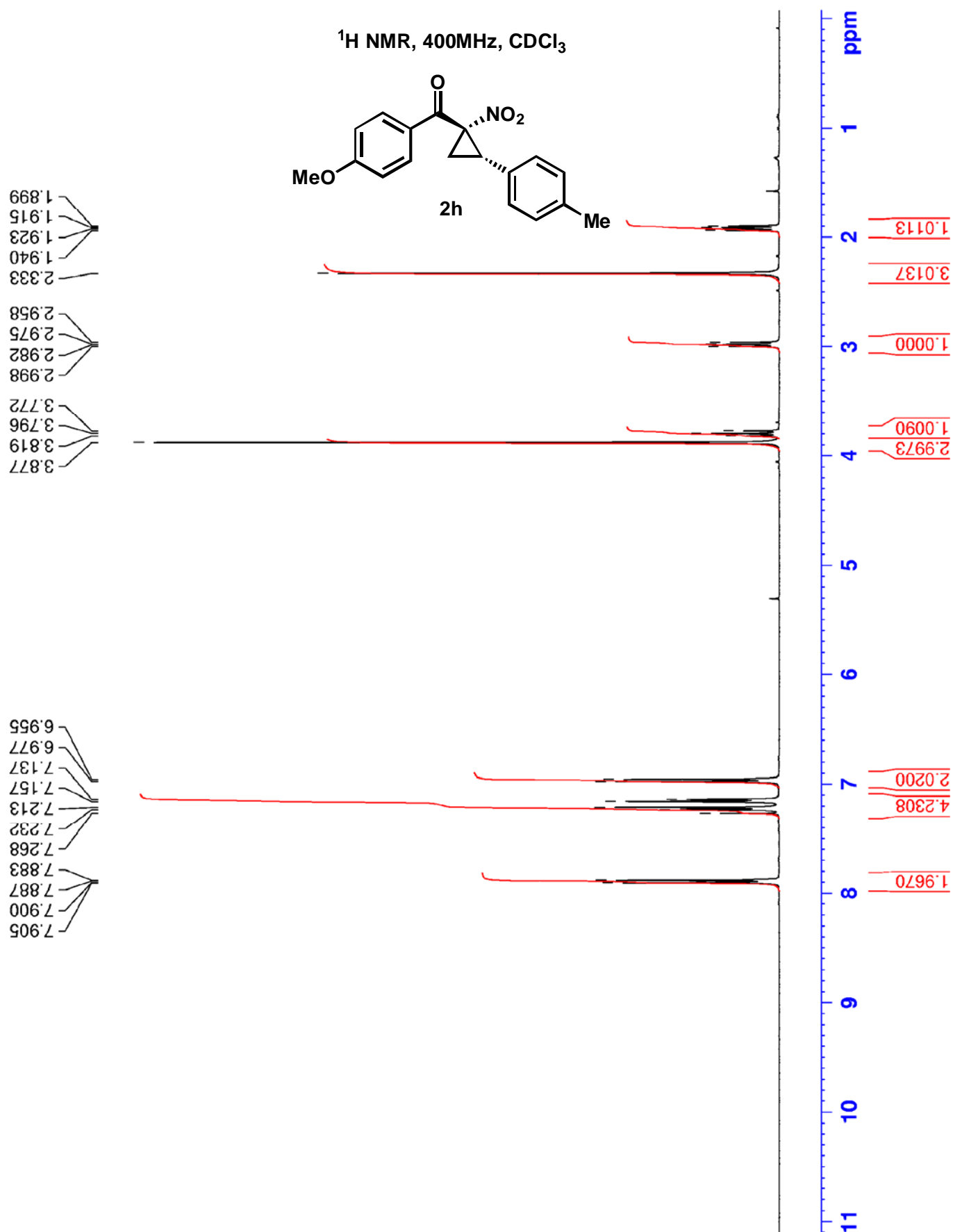


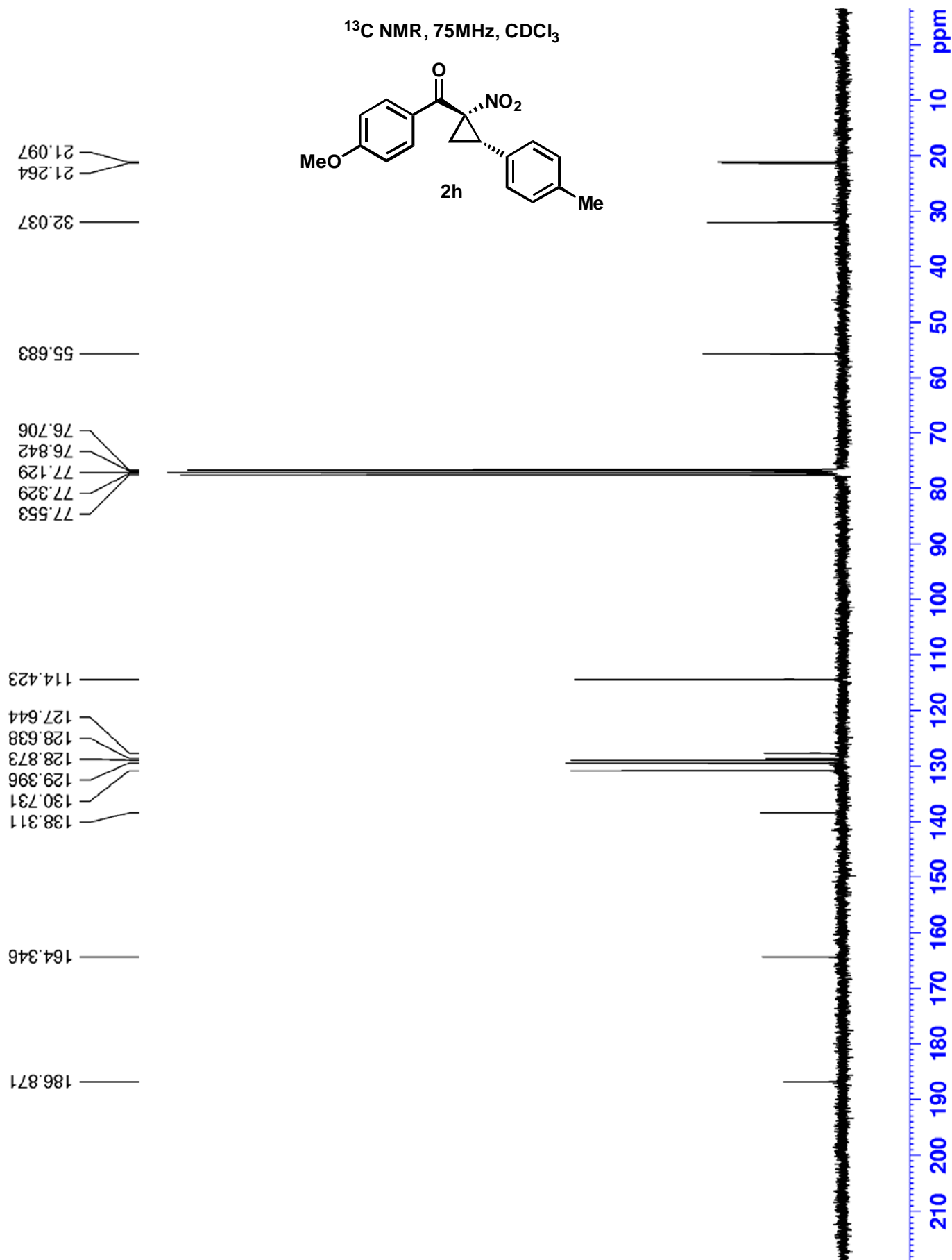


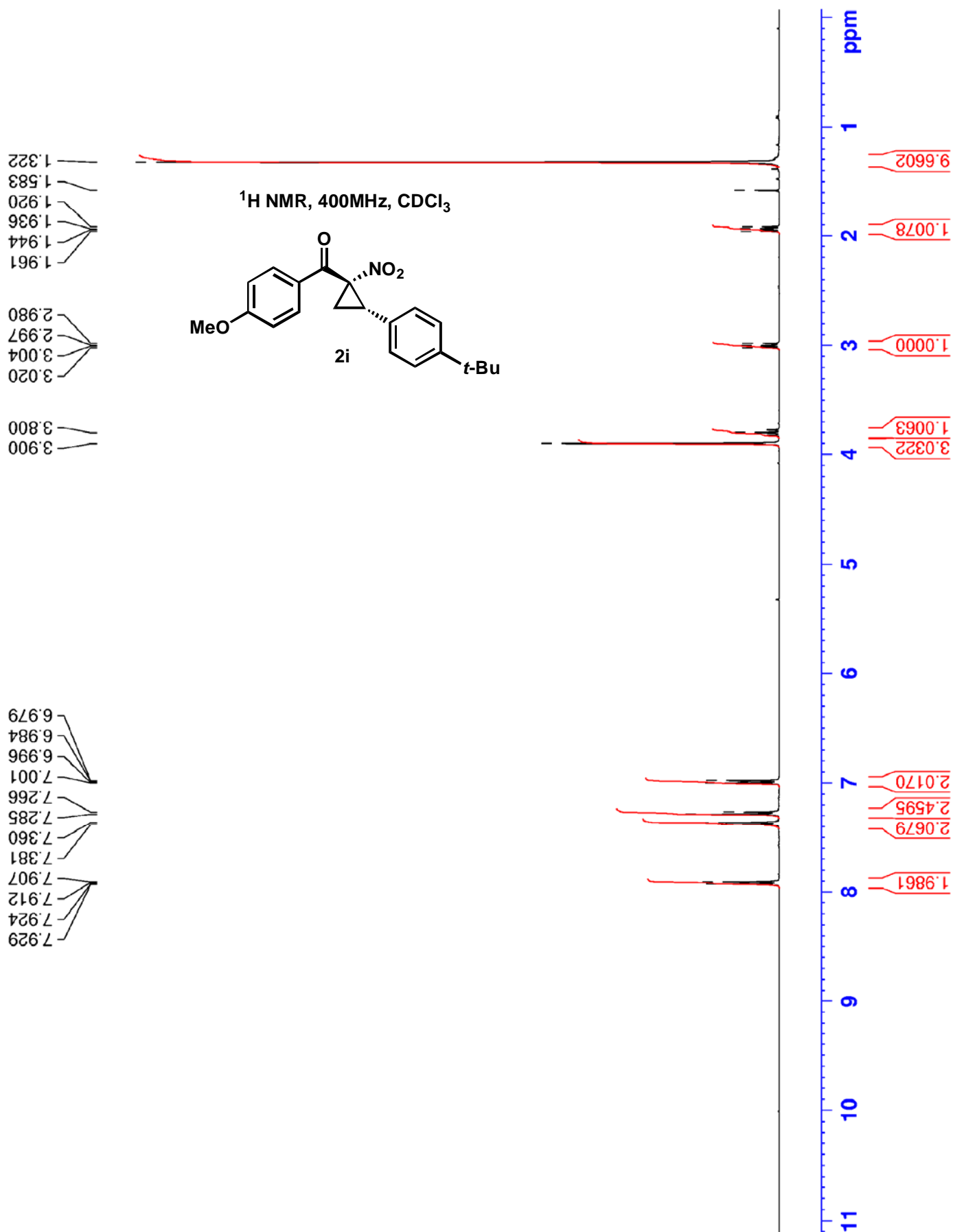


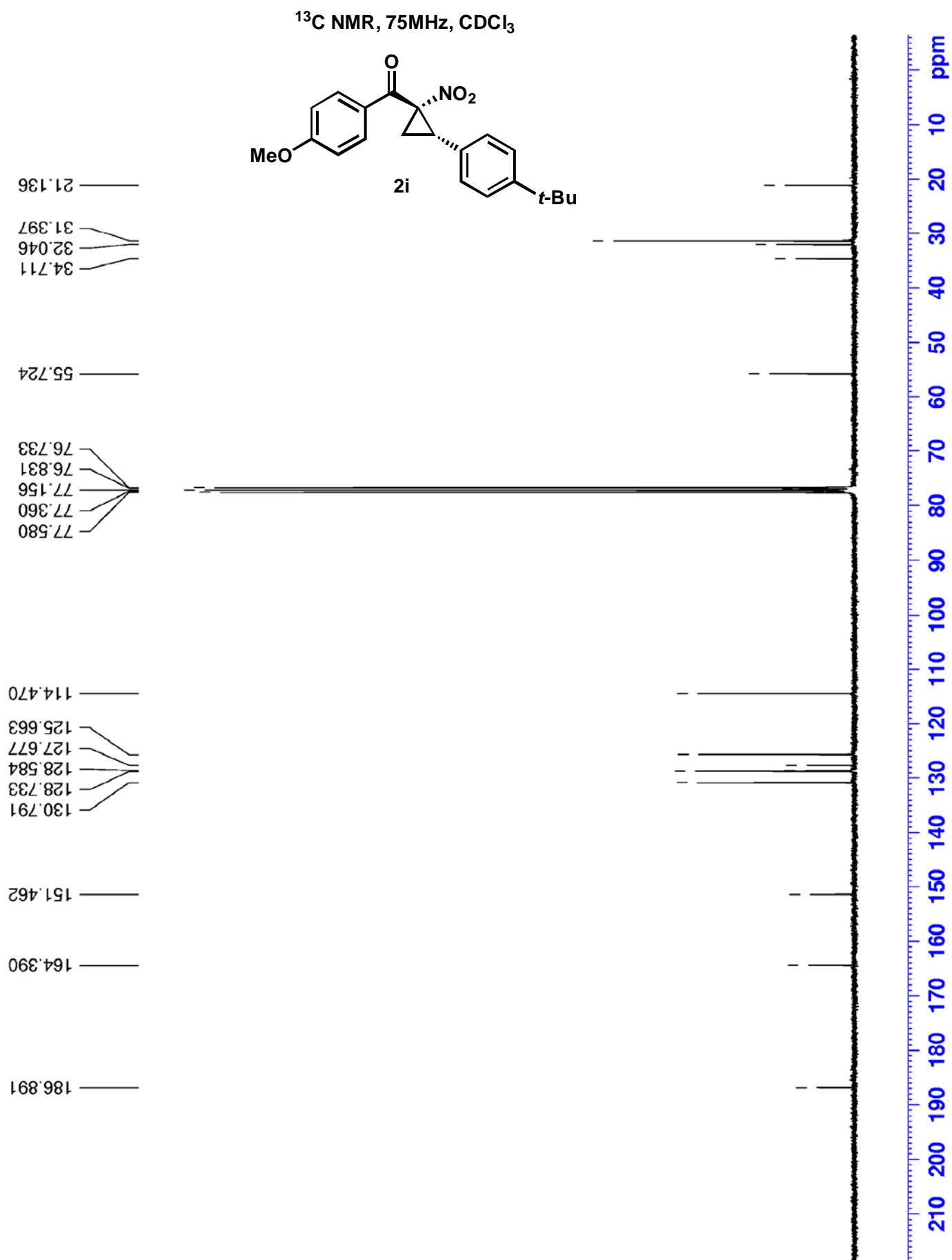


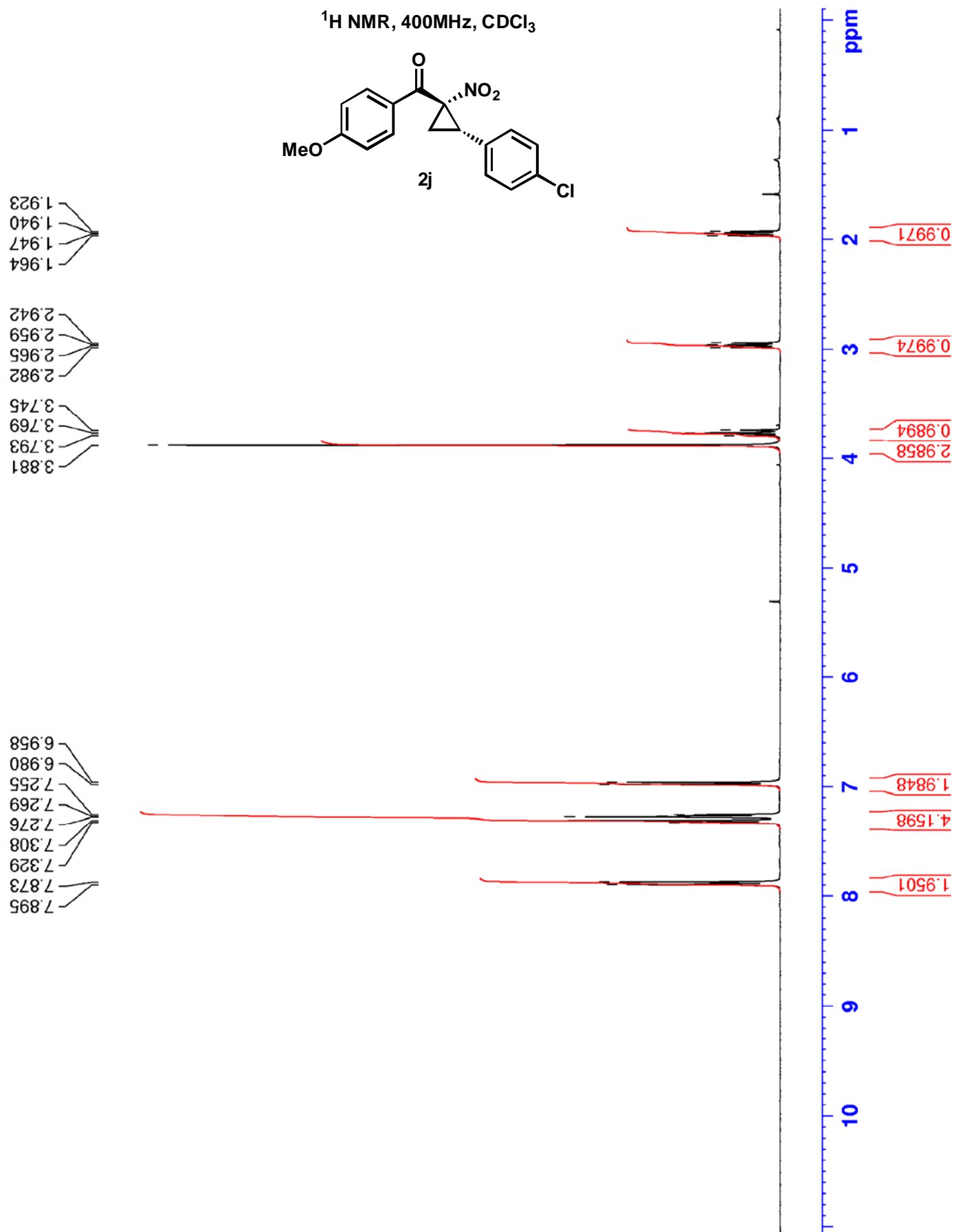


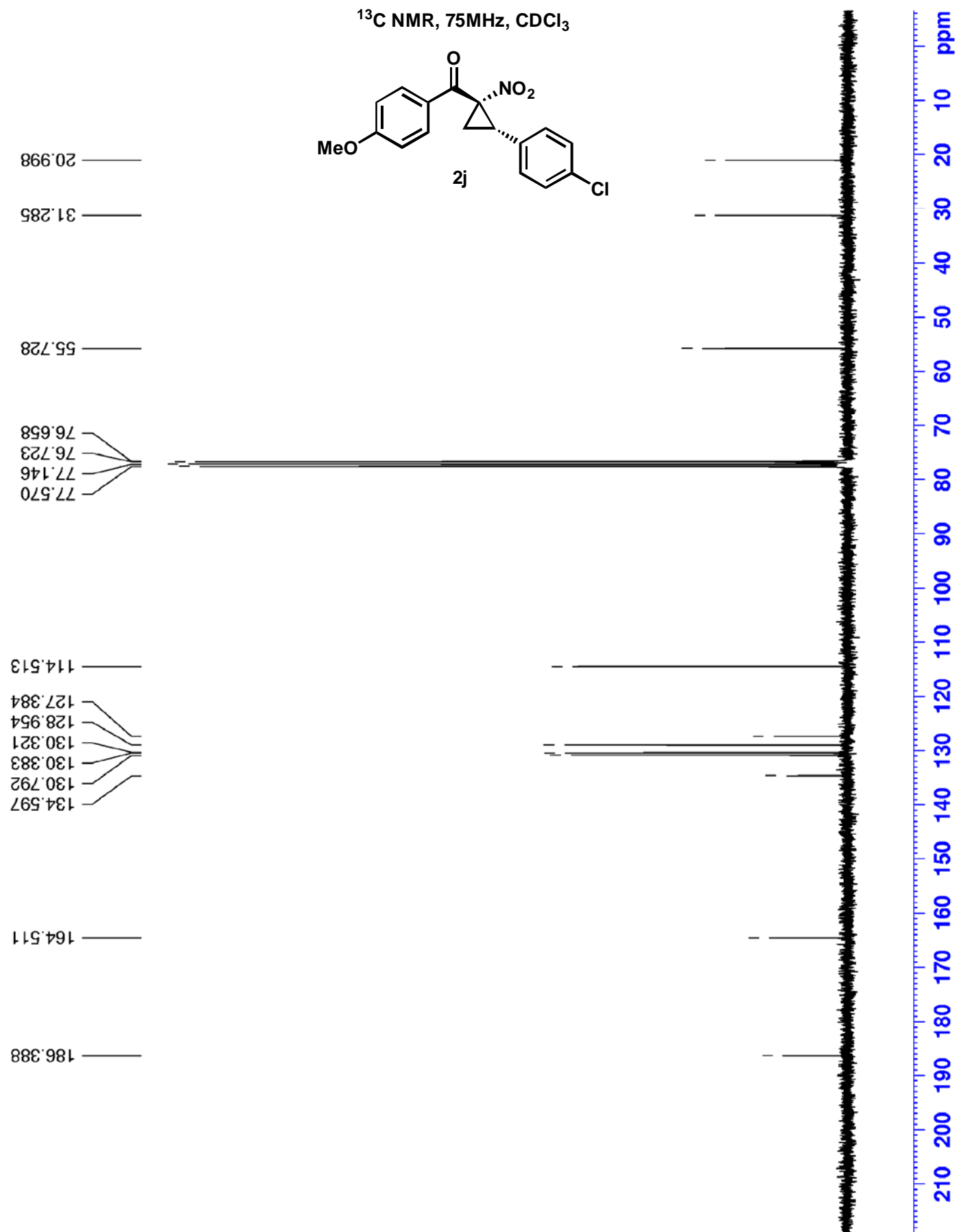


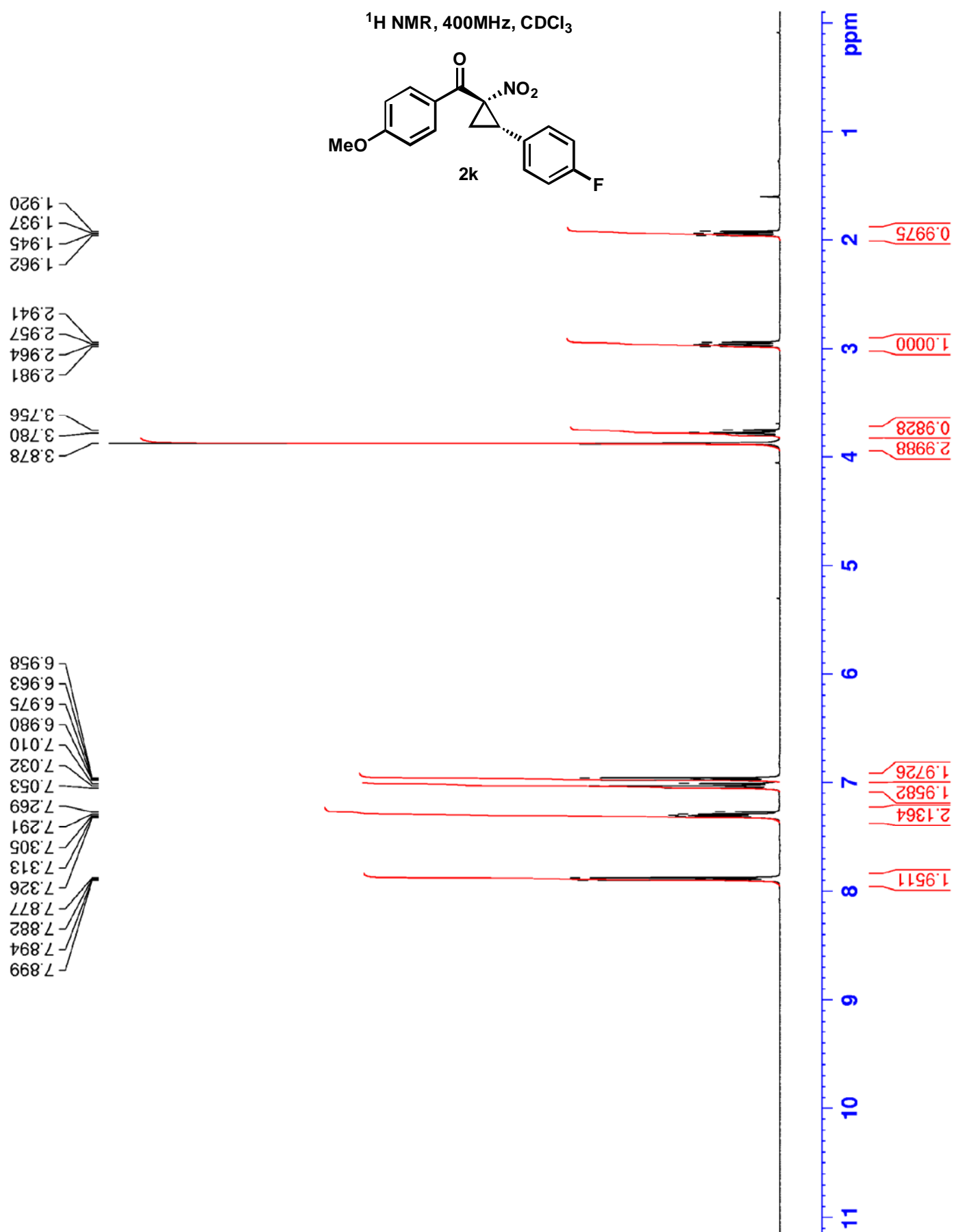


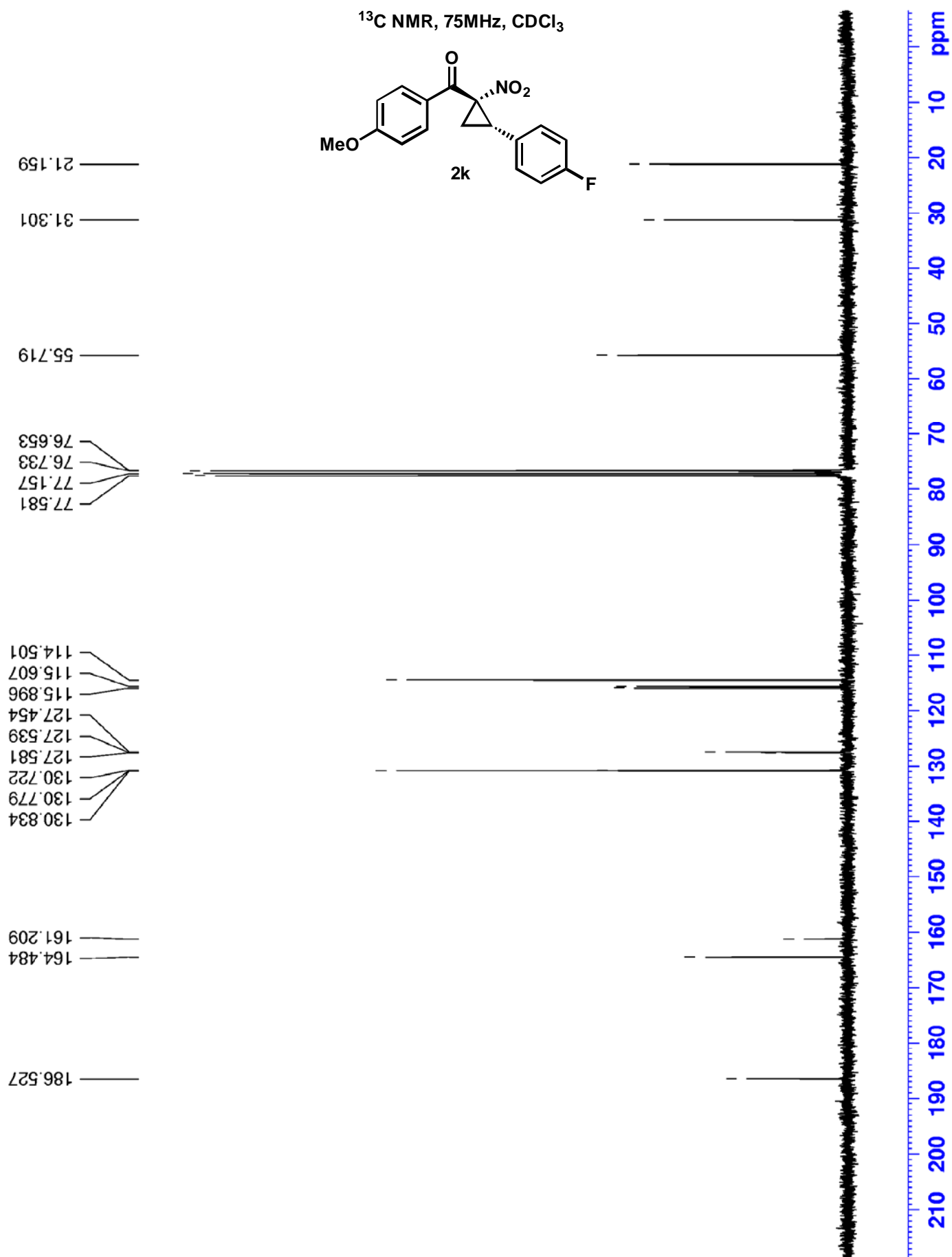


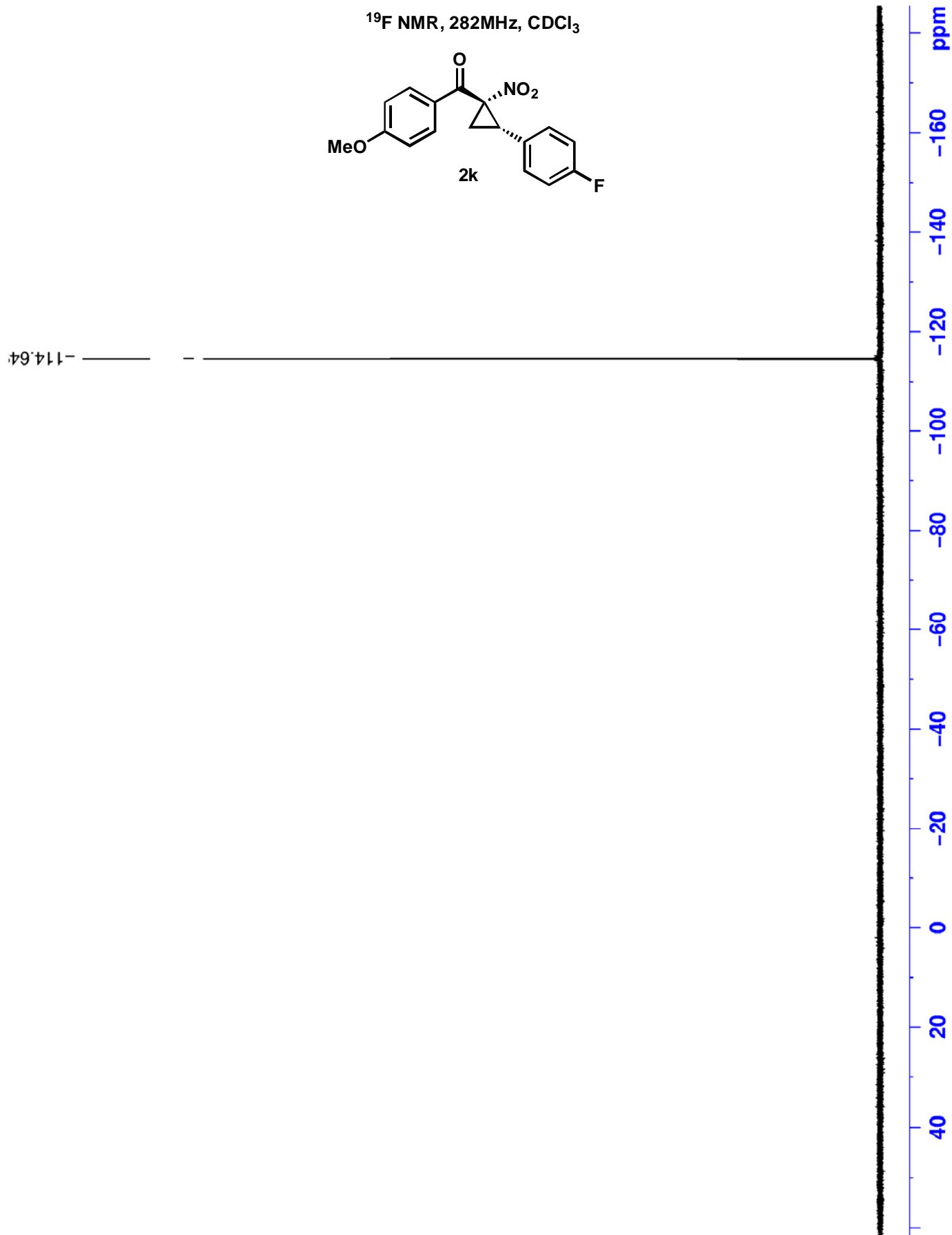


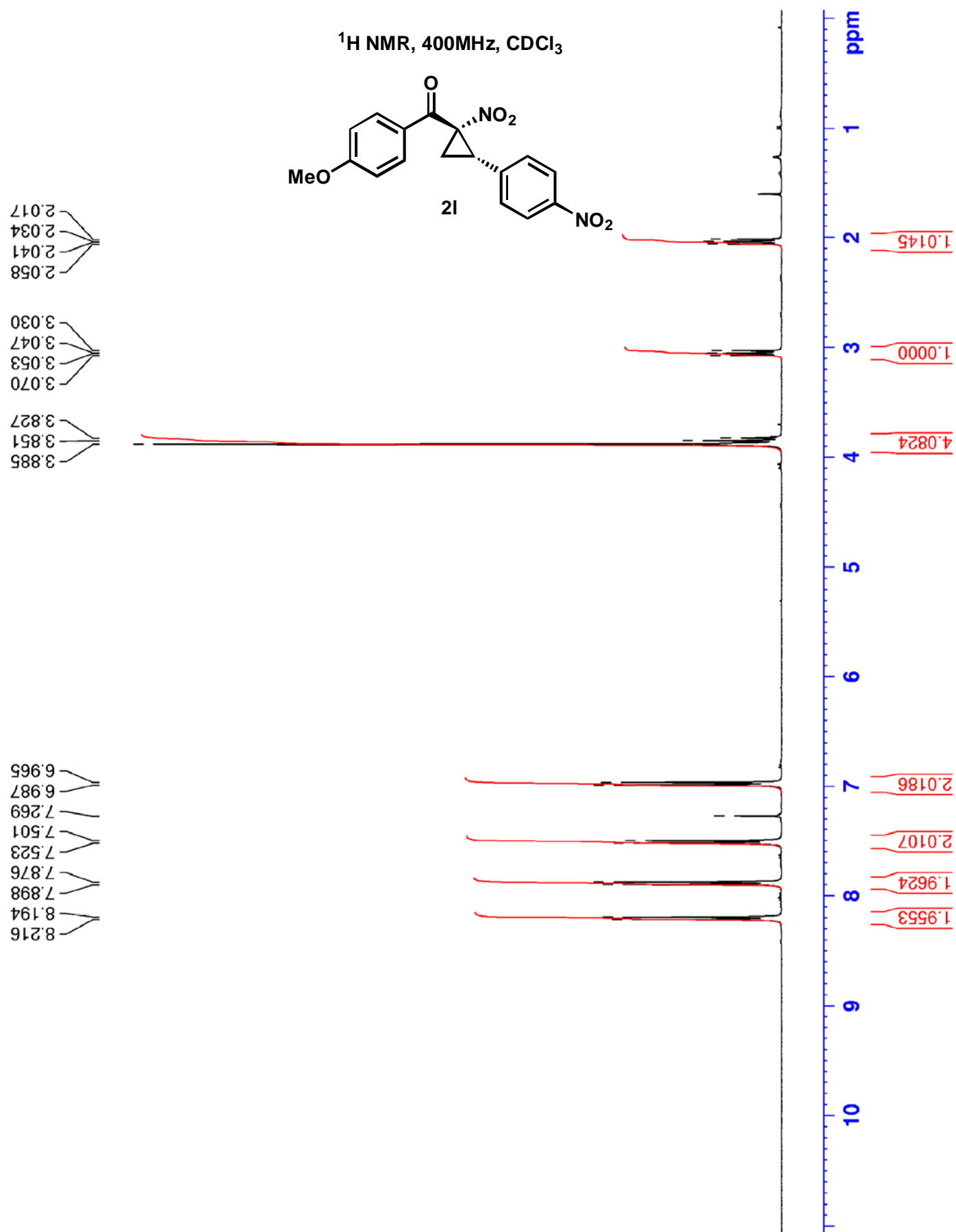


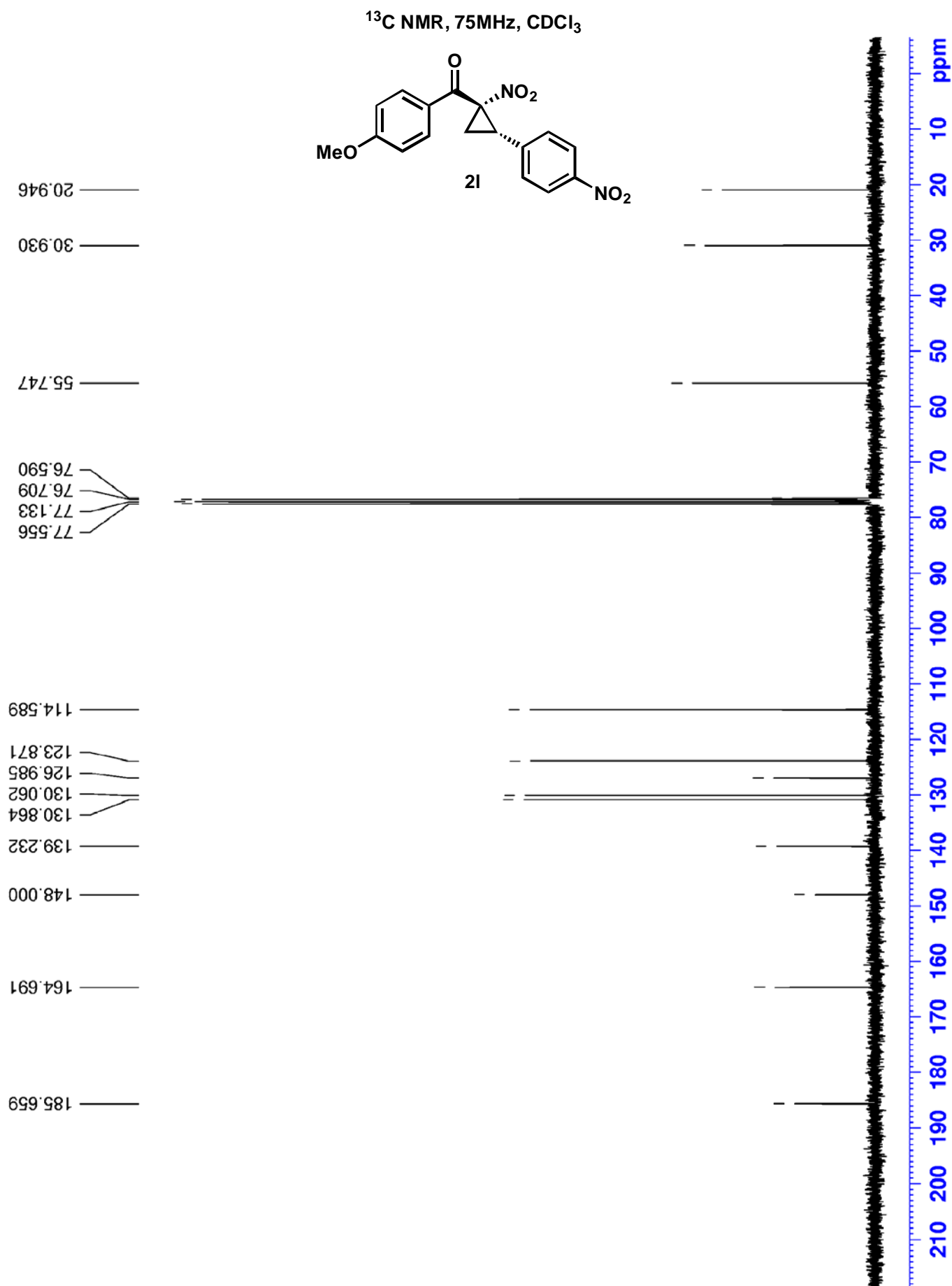


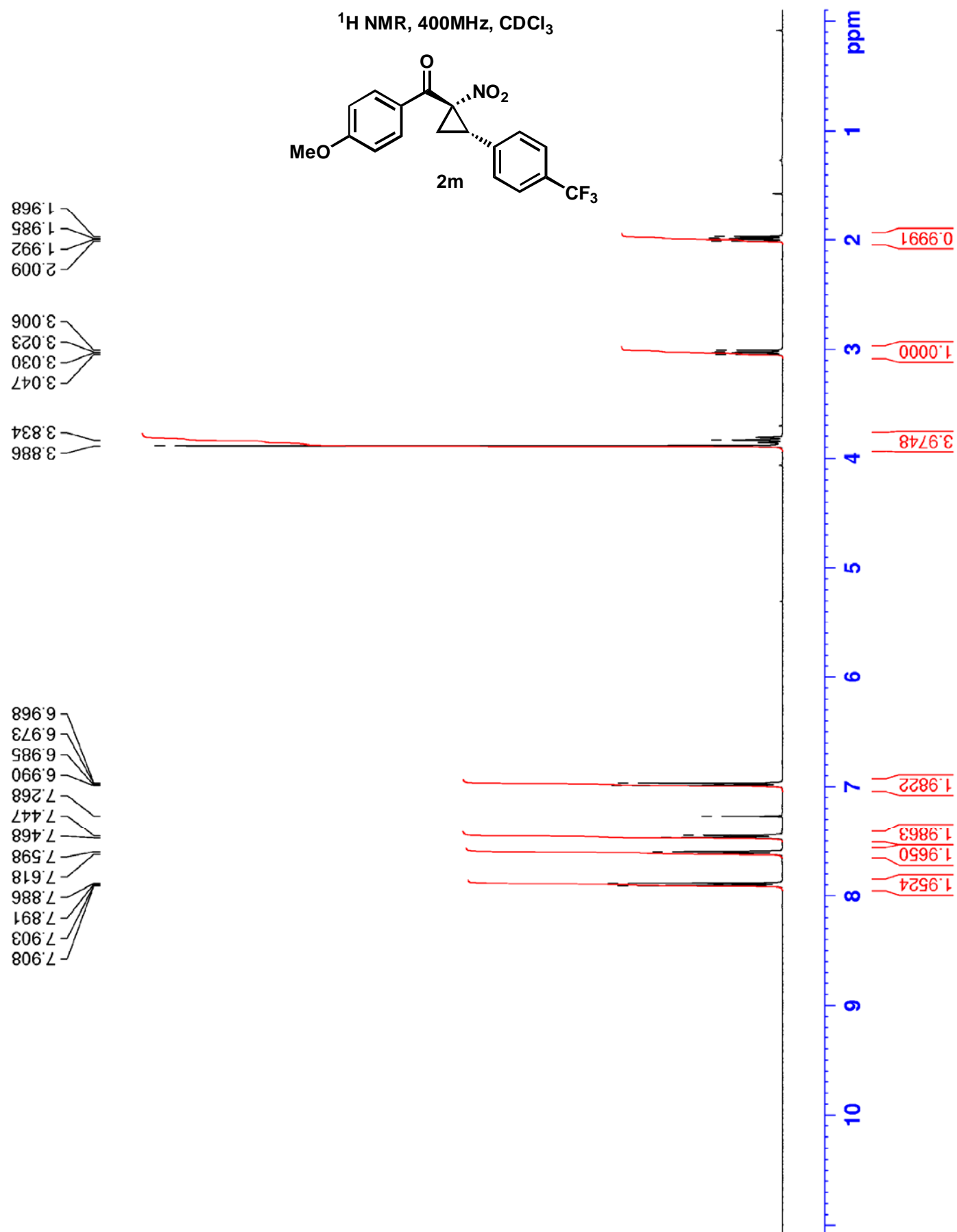


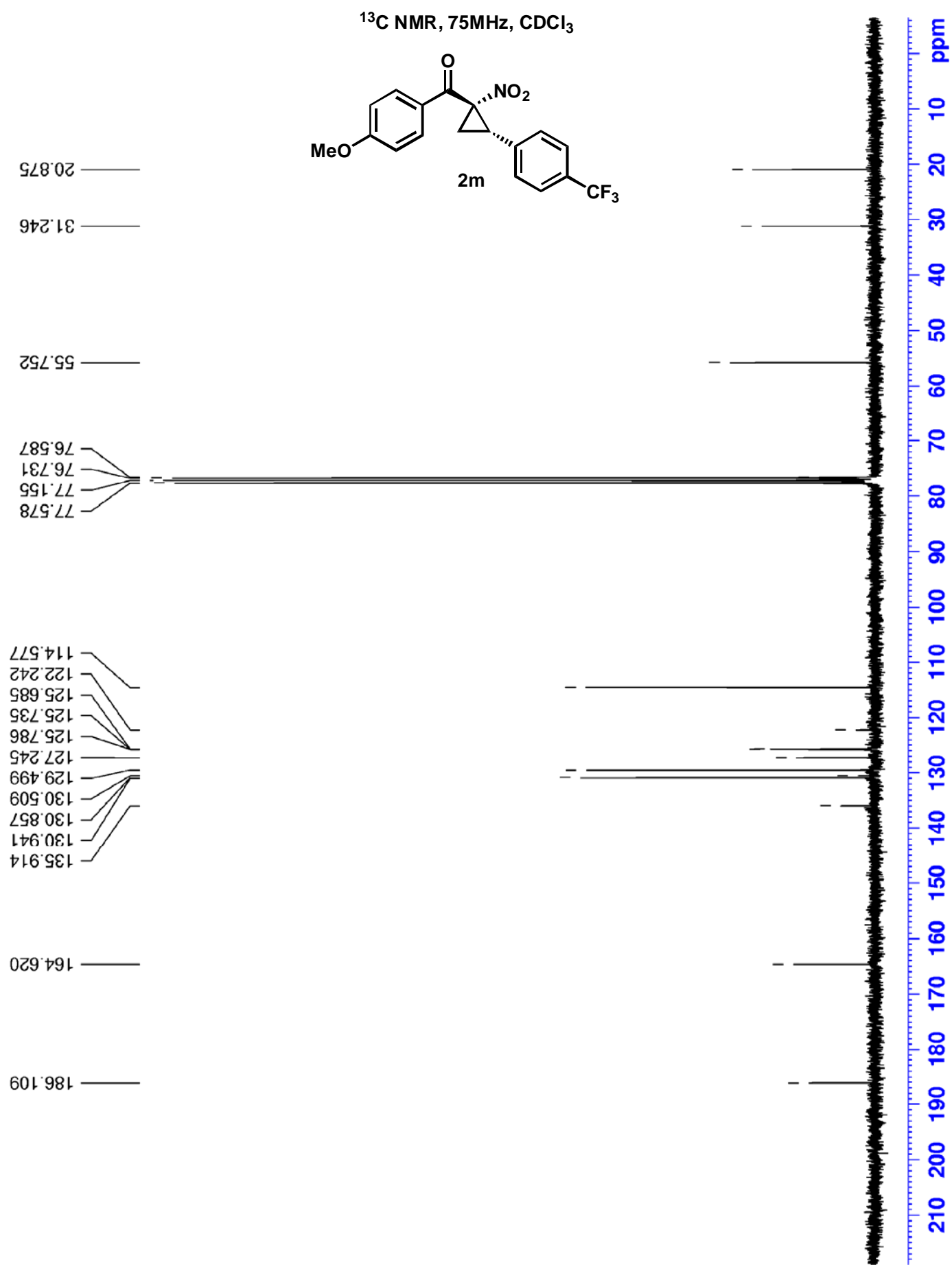


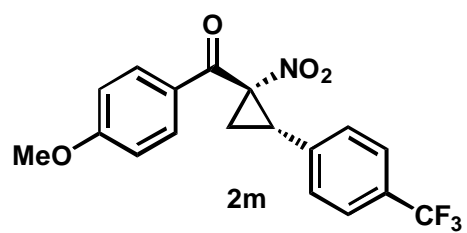










^{19}F NMR, 282MHz, CDCl_3 

-64.119

ppm

-160

-140

-120

-100

-80

-60

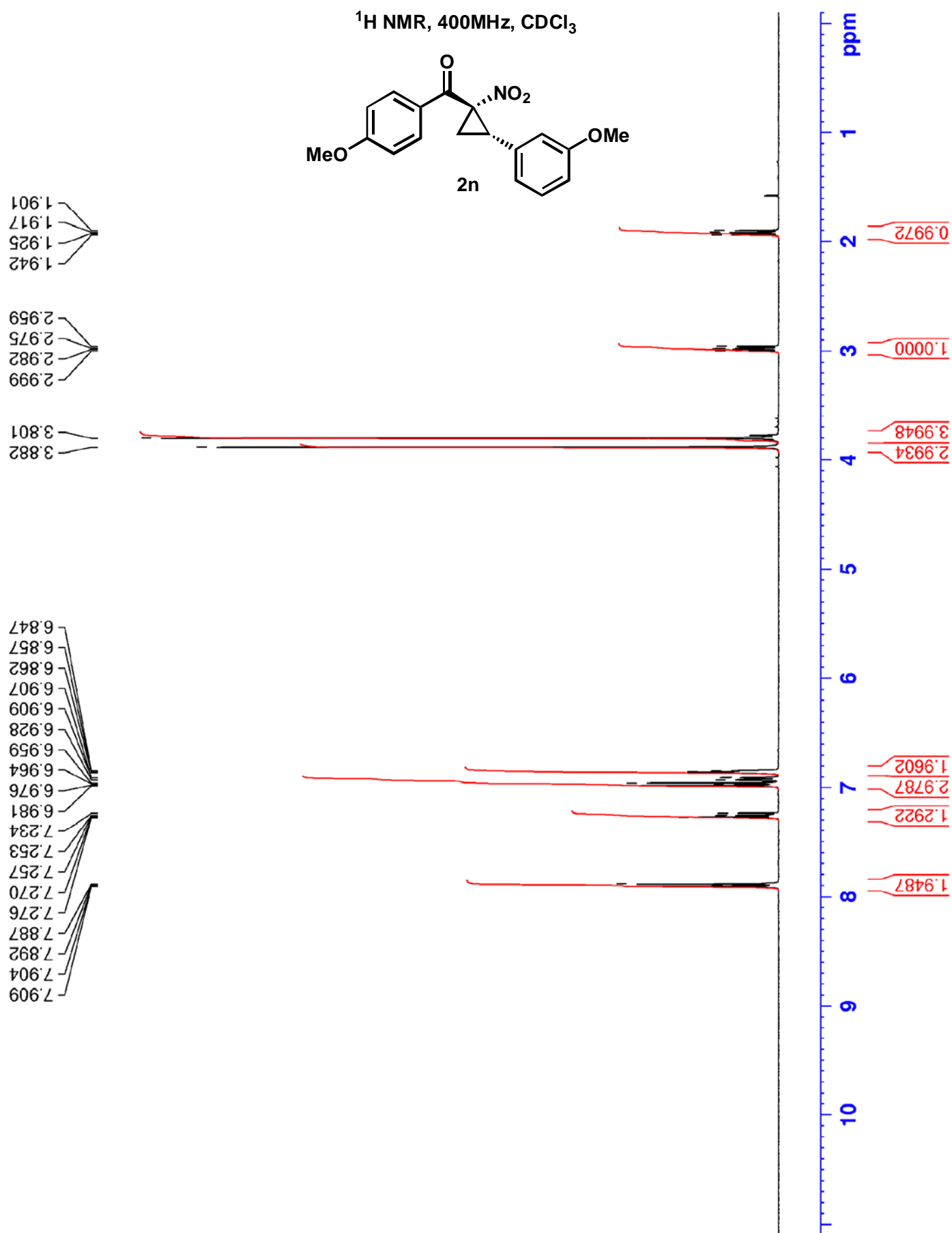
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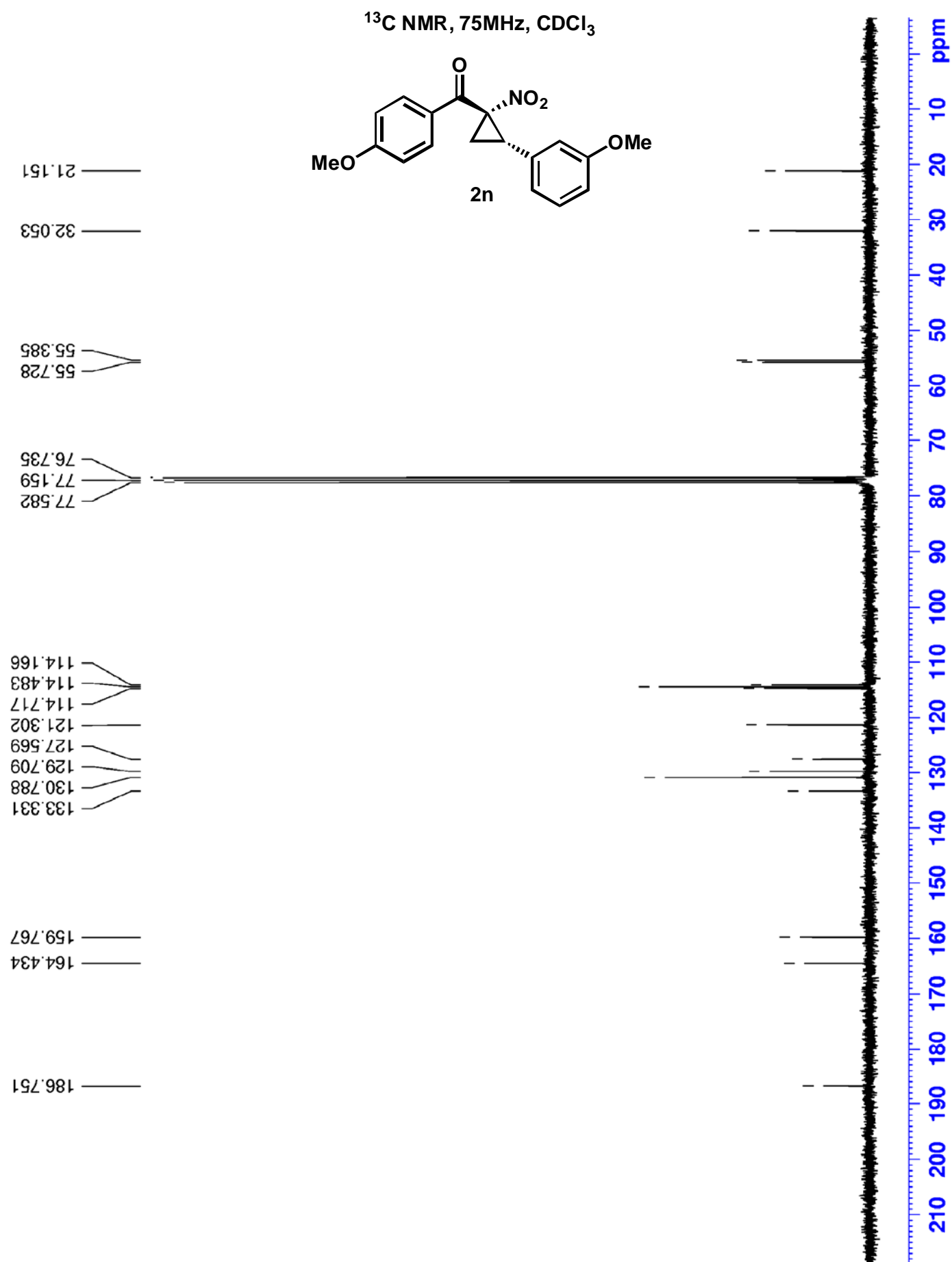
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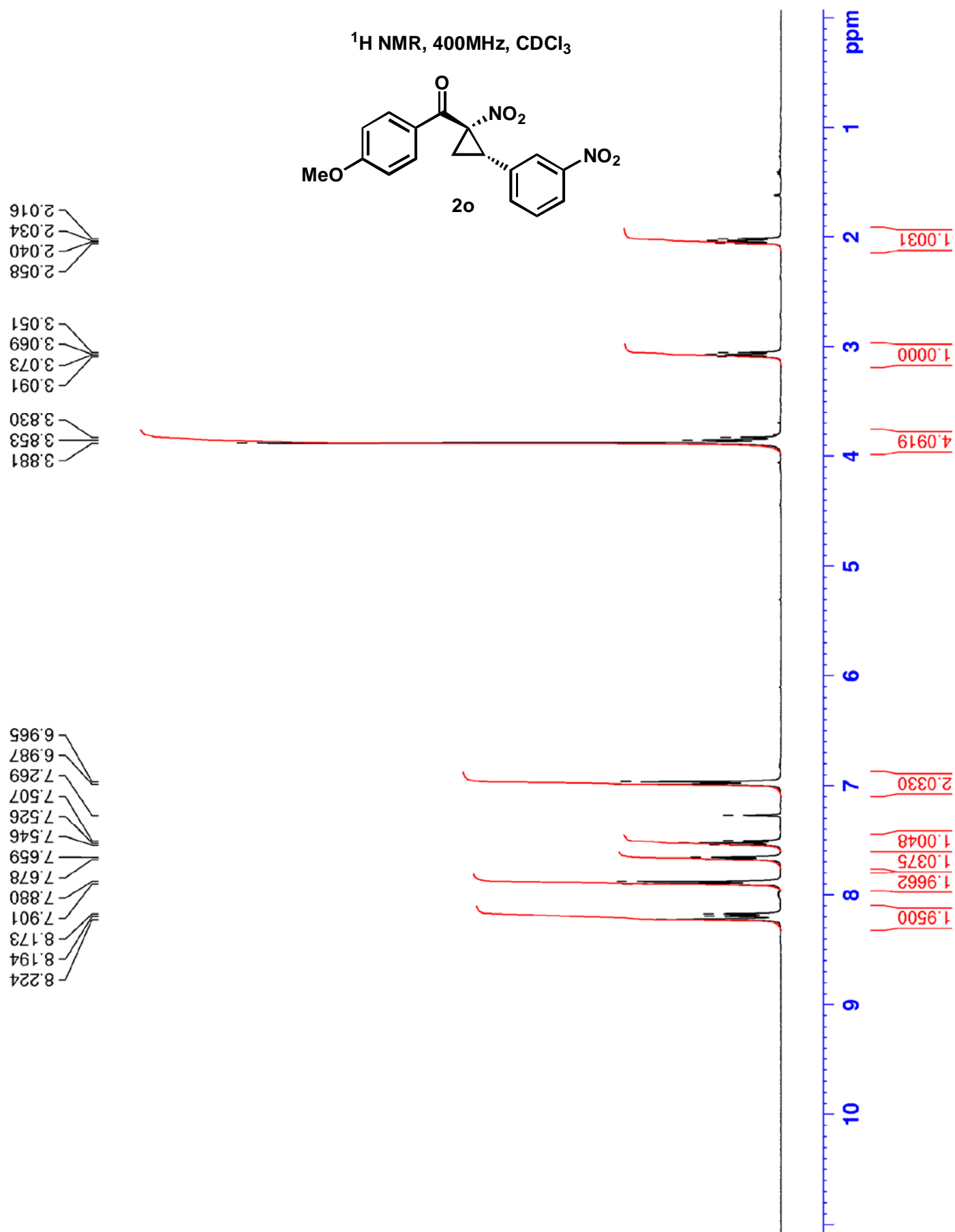
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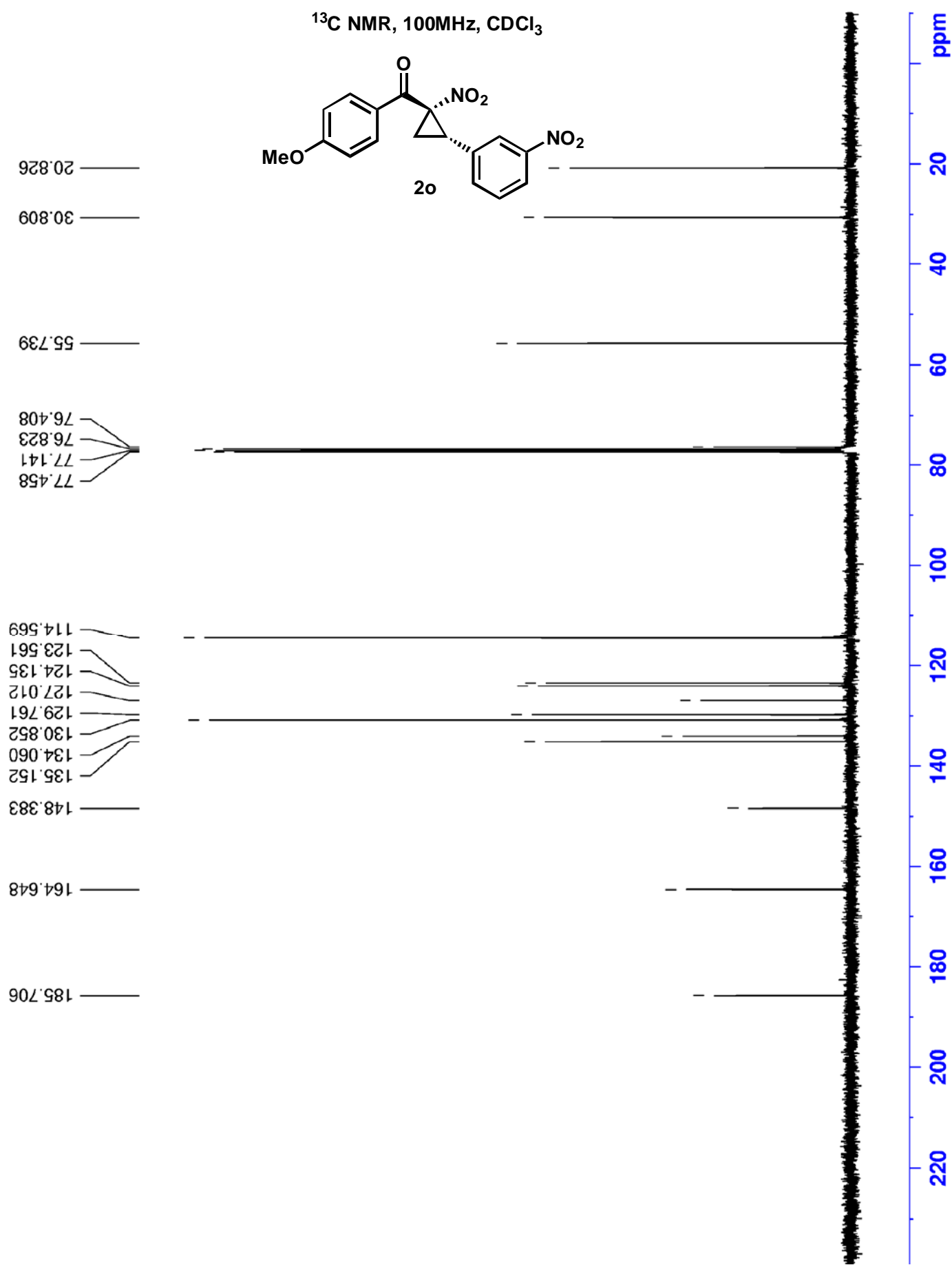
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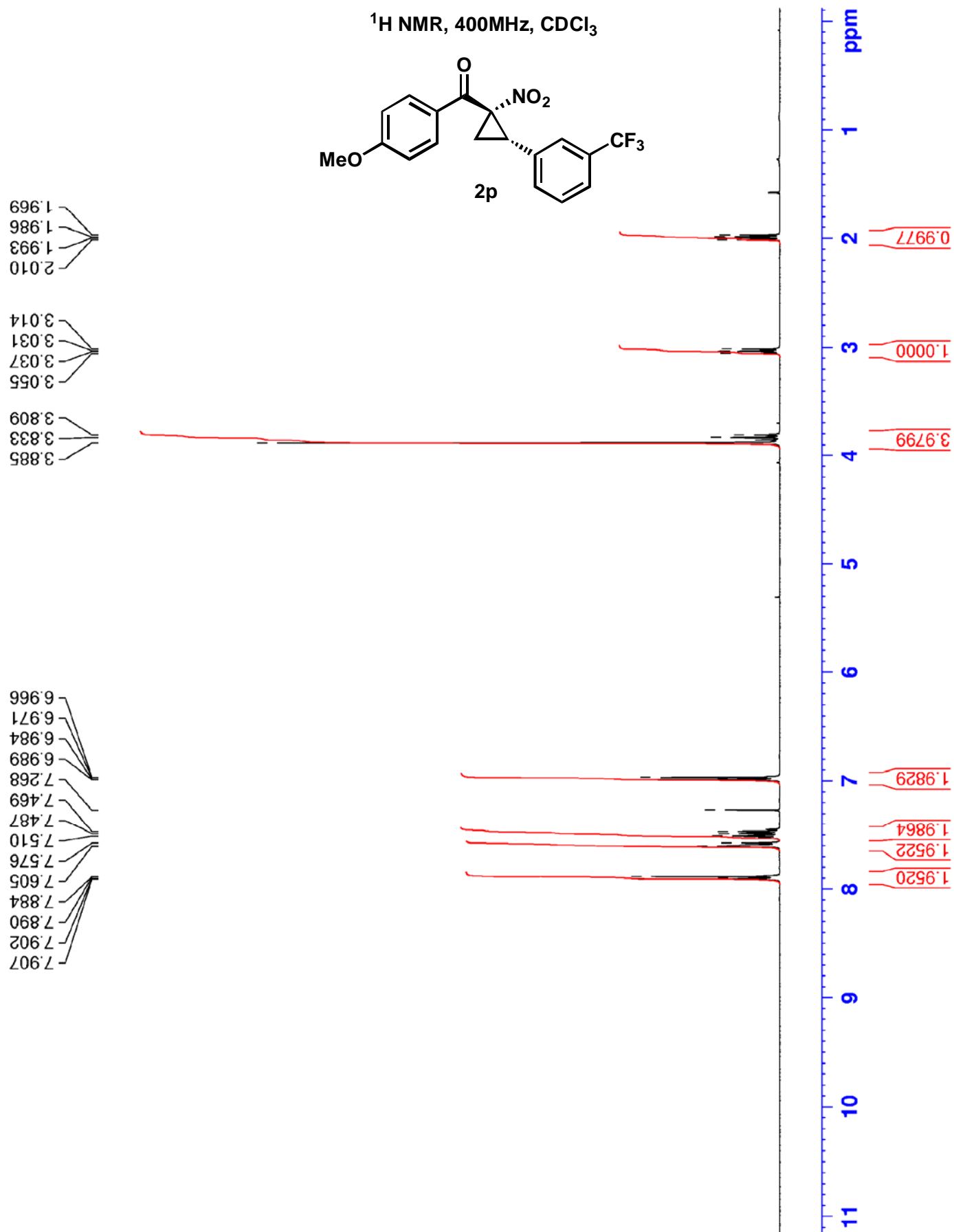
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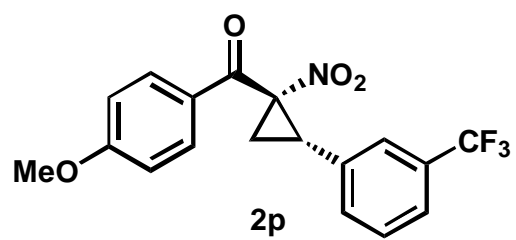






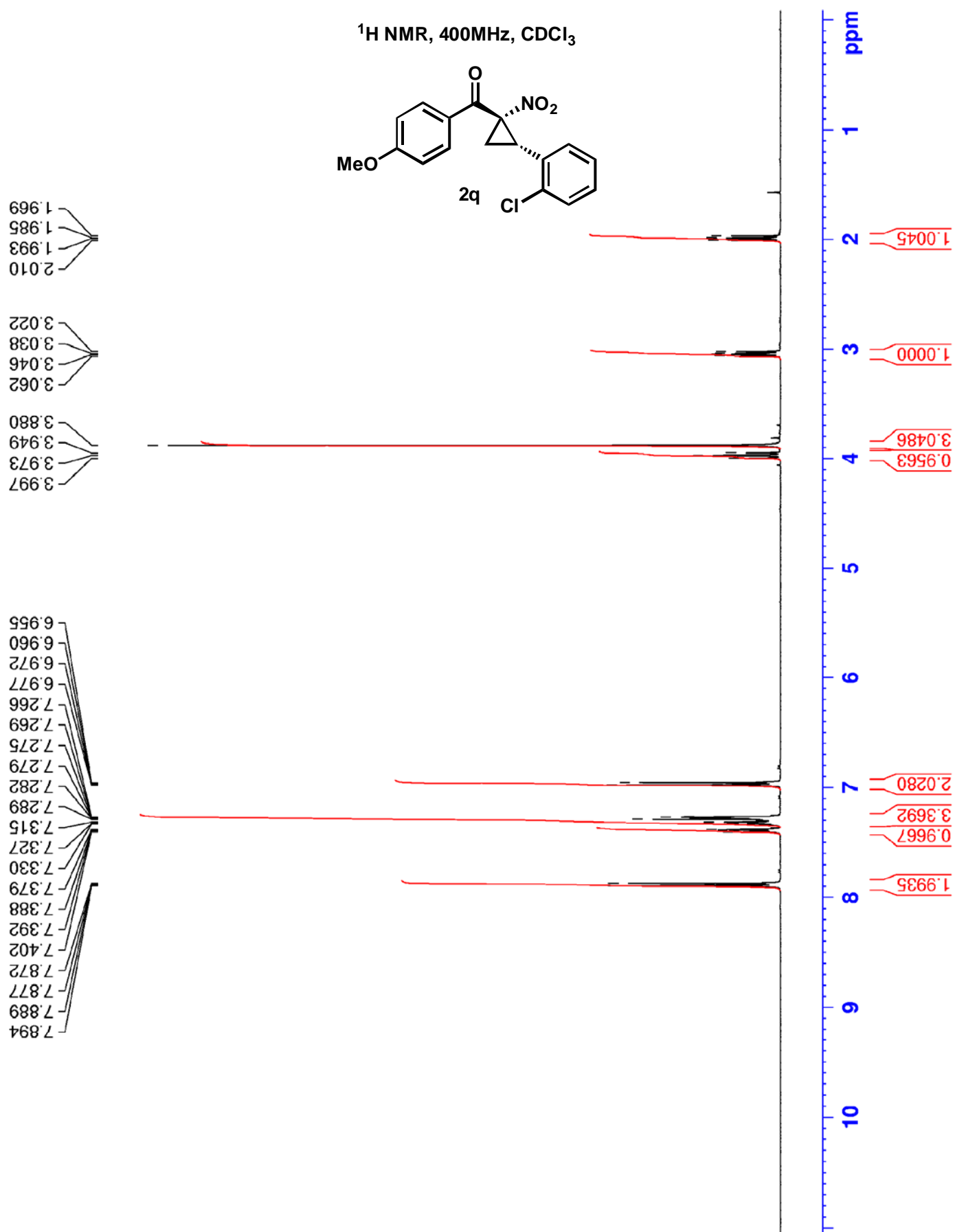


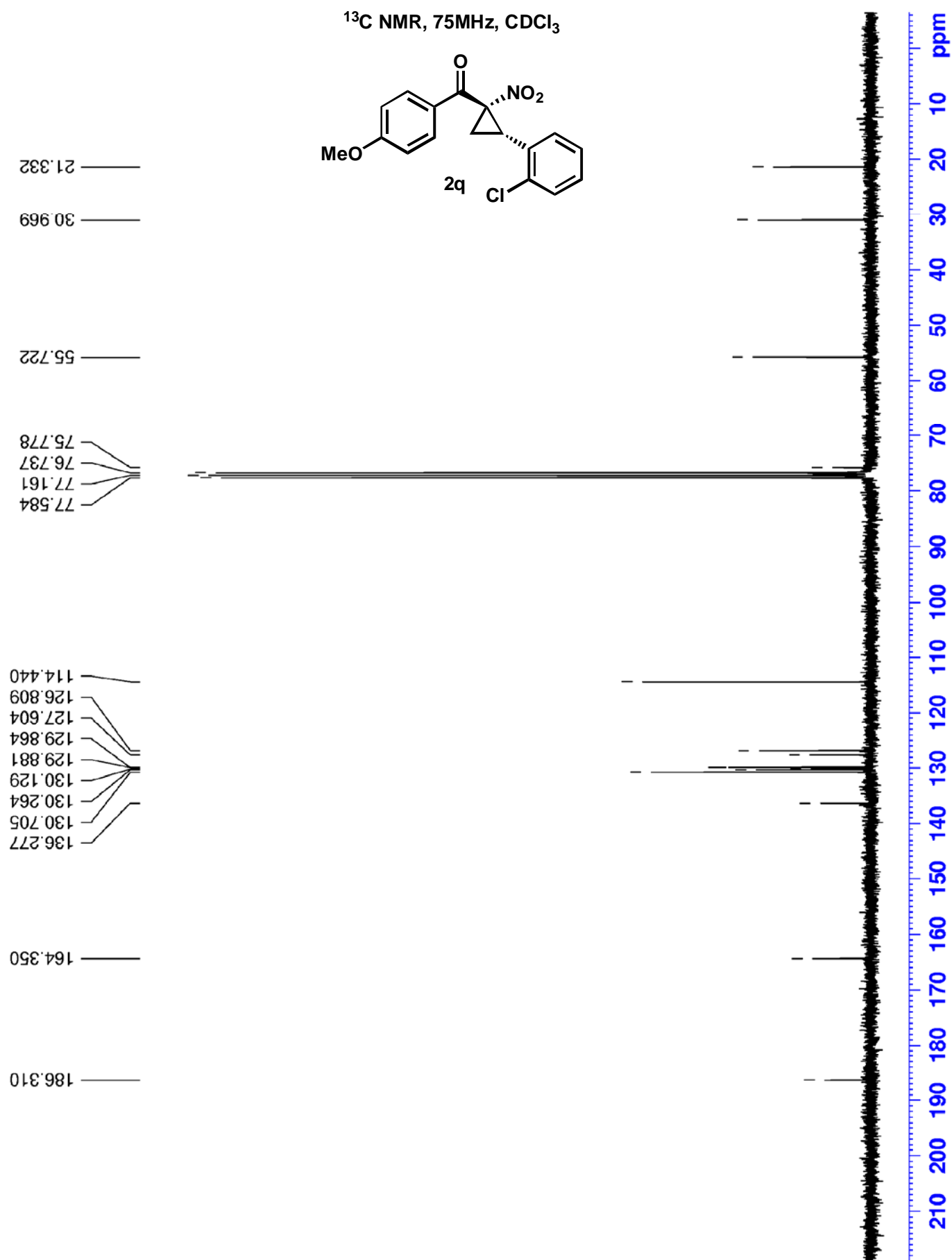
^{19}F NMR, 282MHz, CDCl_3

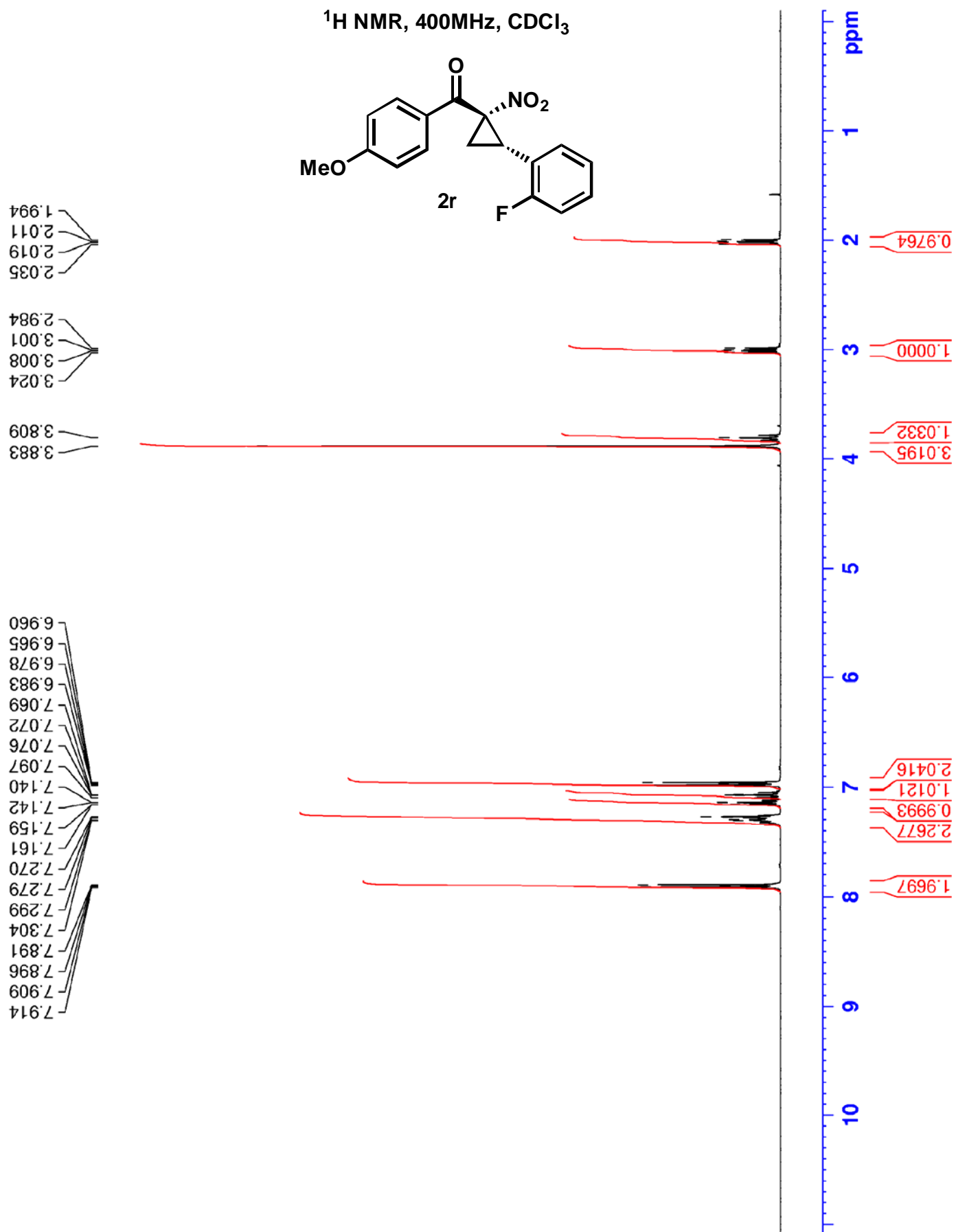


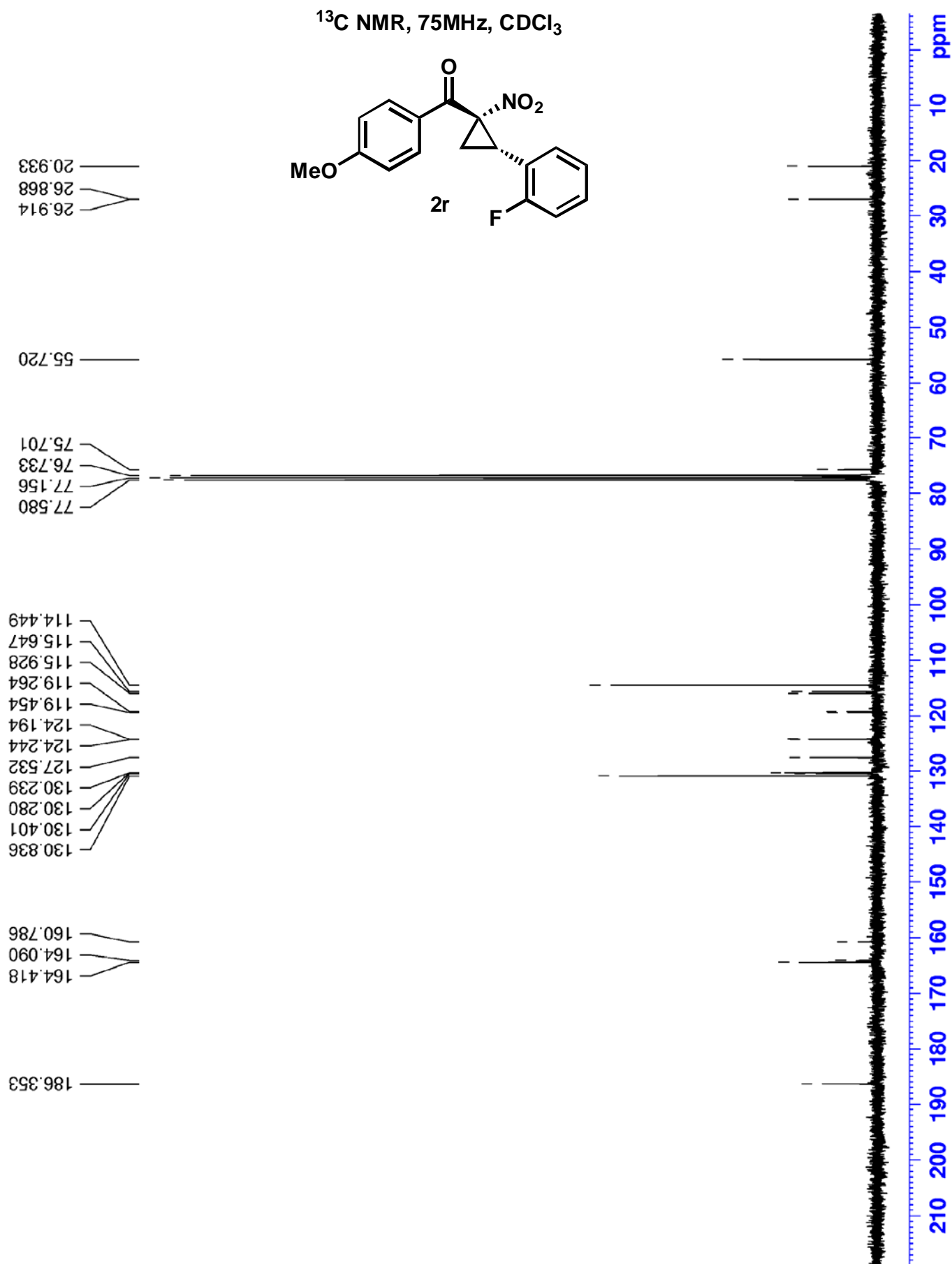
-64.122

ppm
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40

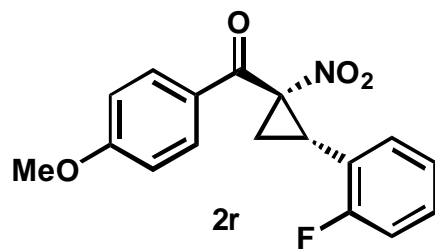








^{19}F NMR, 282MHz, CDCl_3



2r

99.911-

ppm

-160

-140

-120

-100

-80

-60

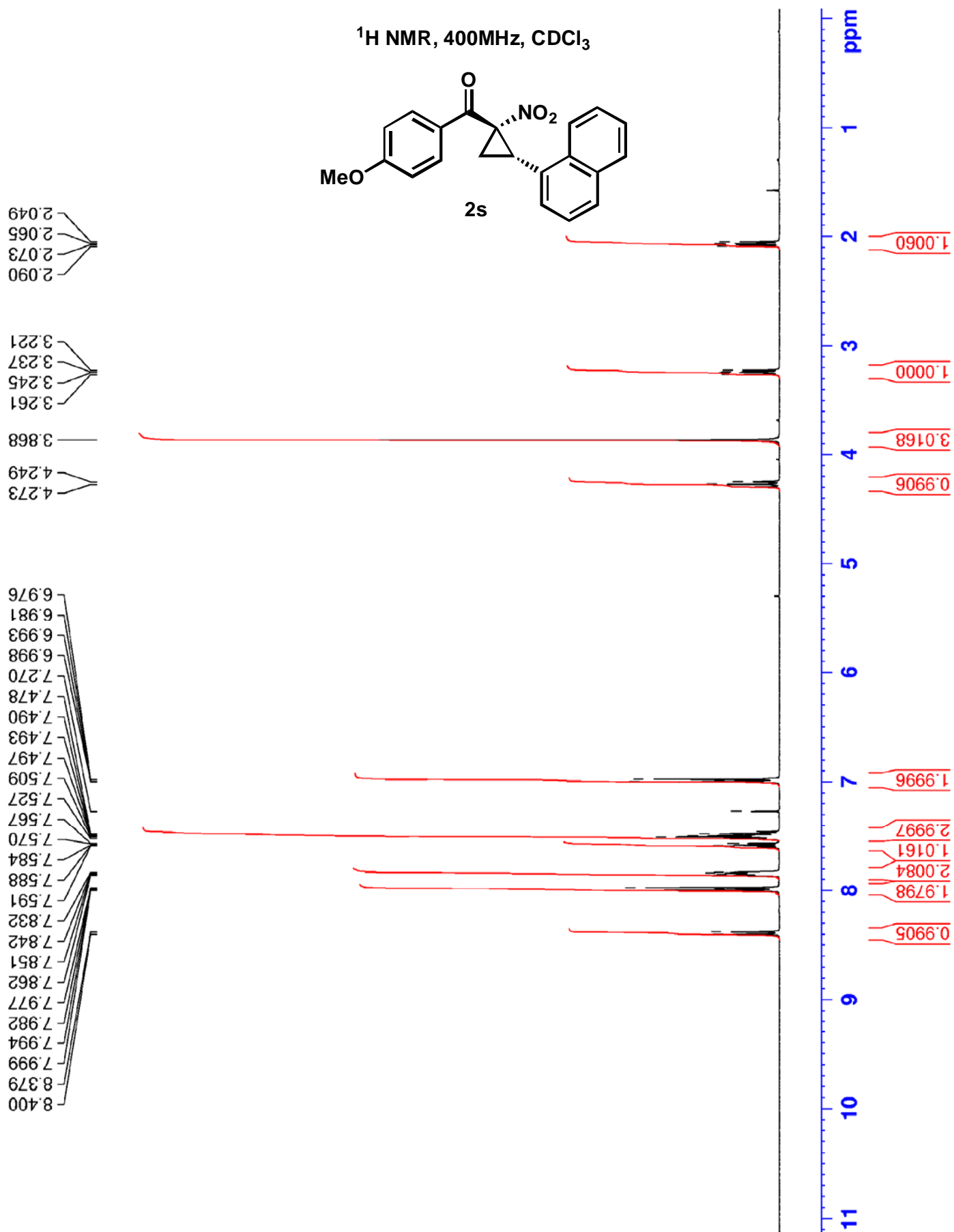
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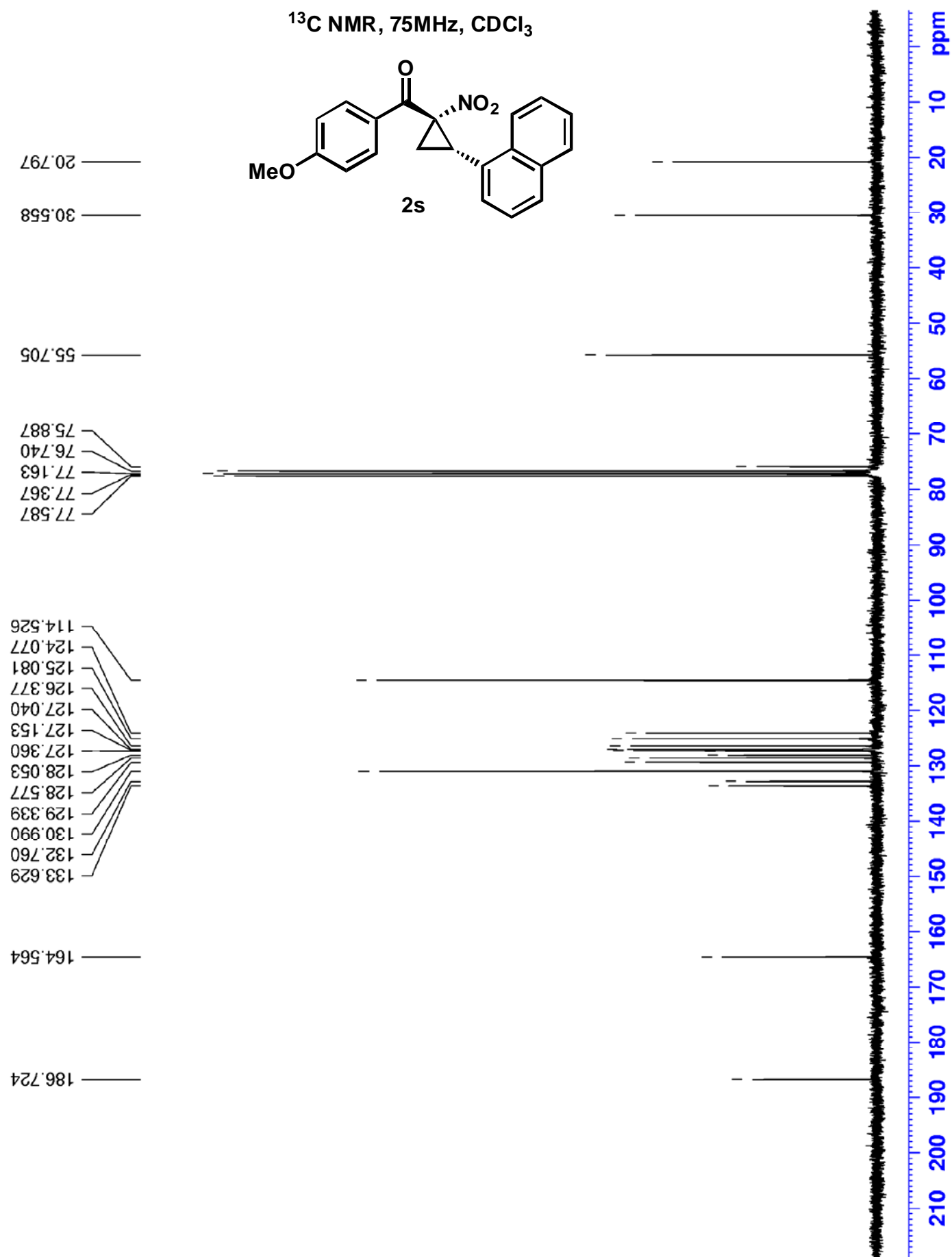
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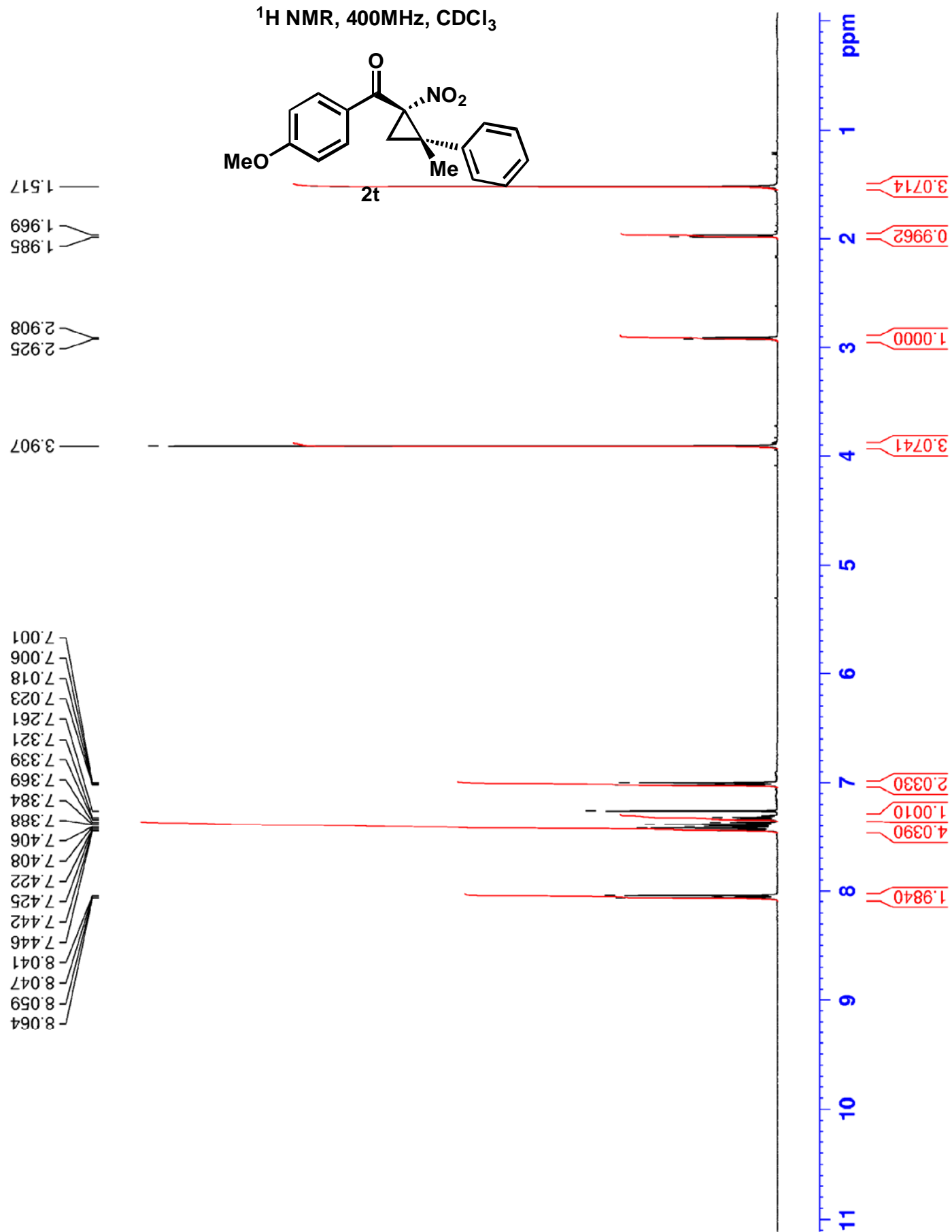
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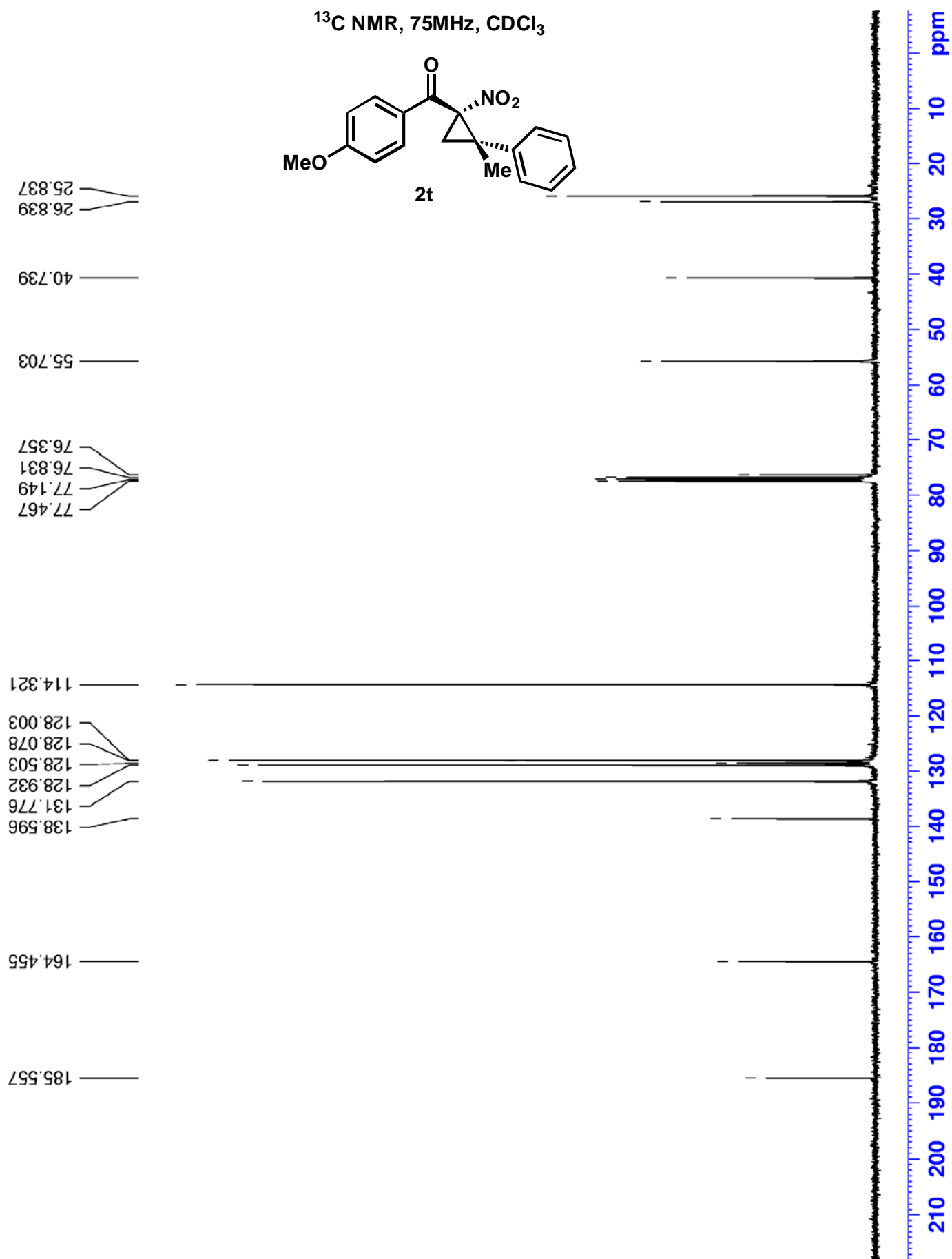
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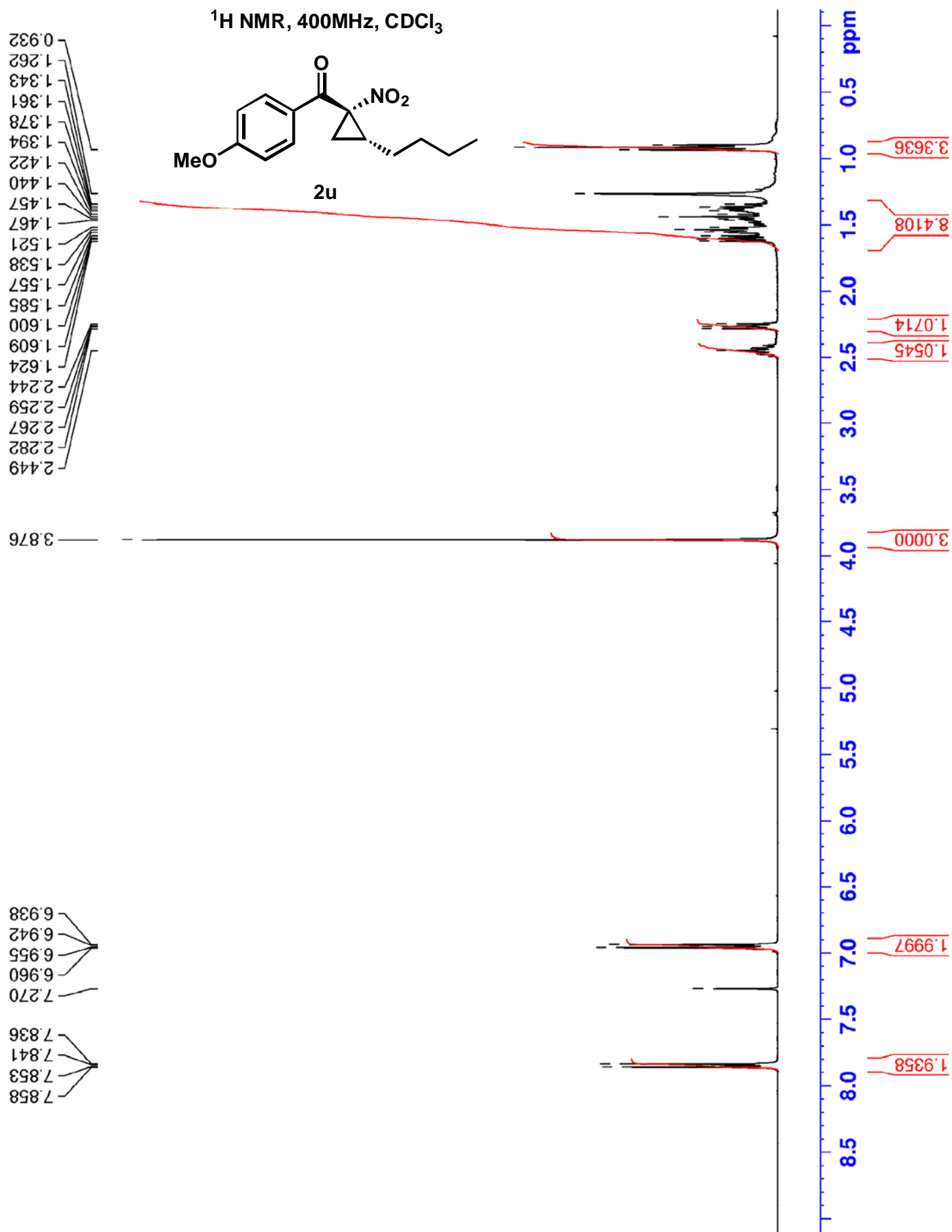
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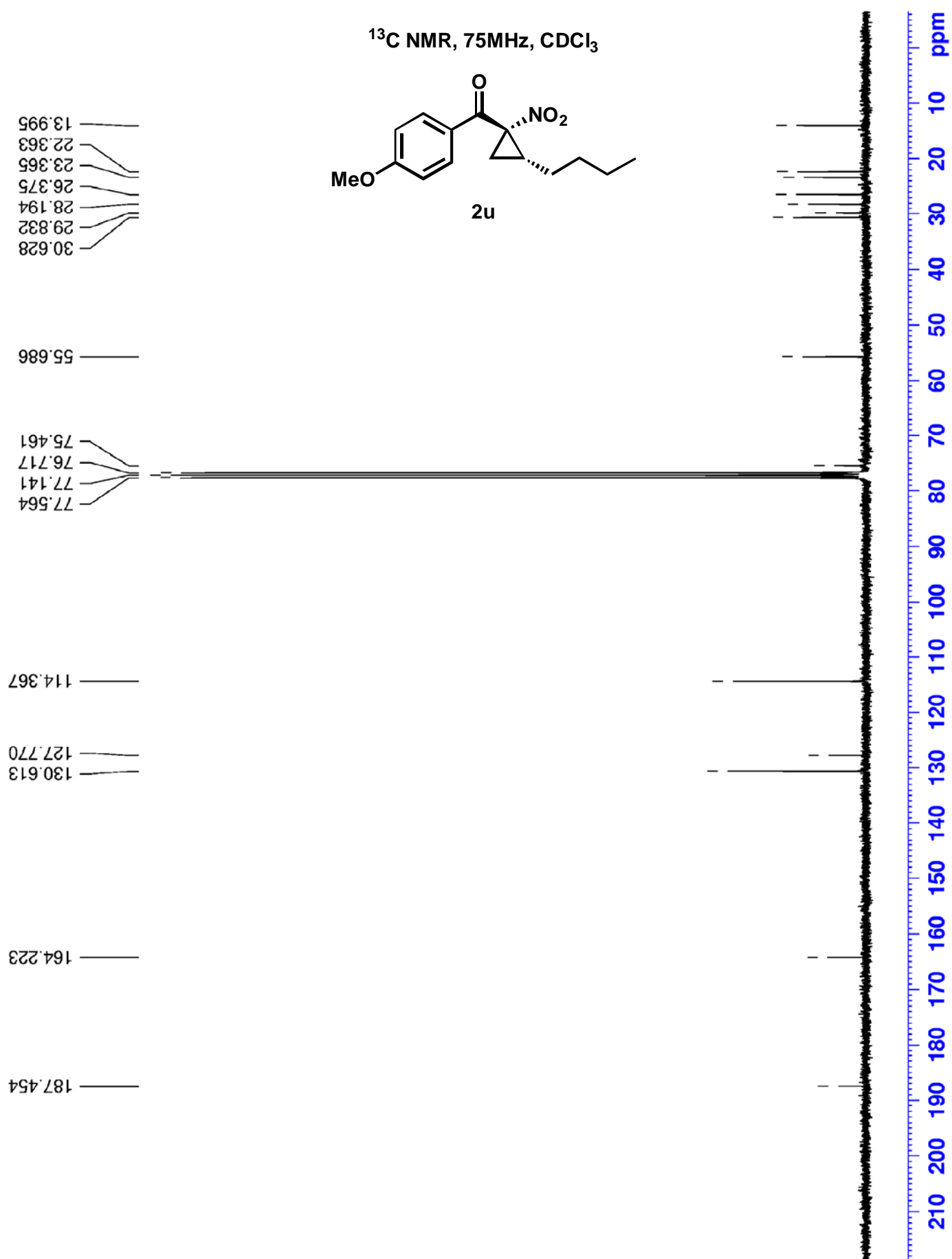


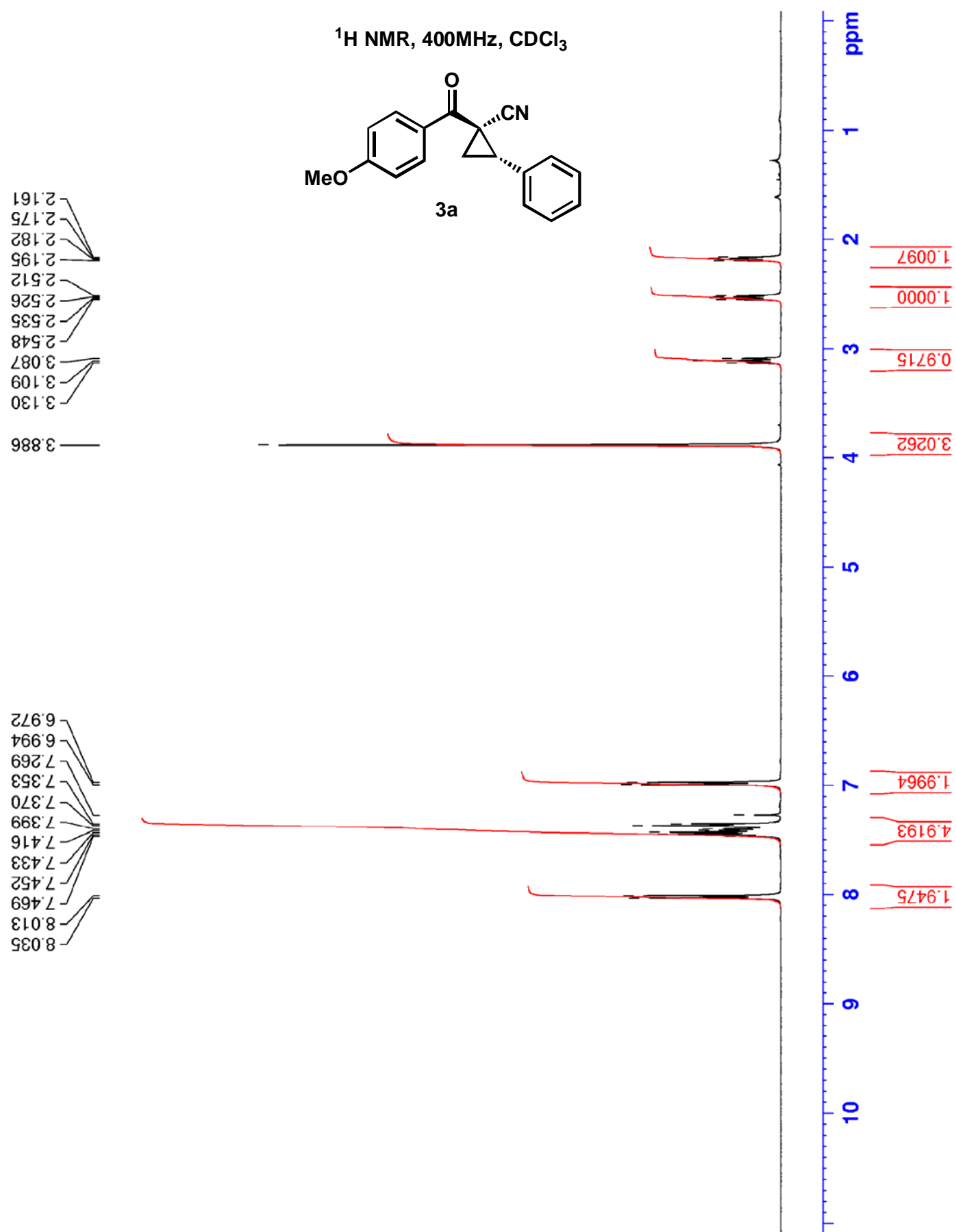


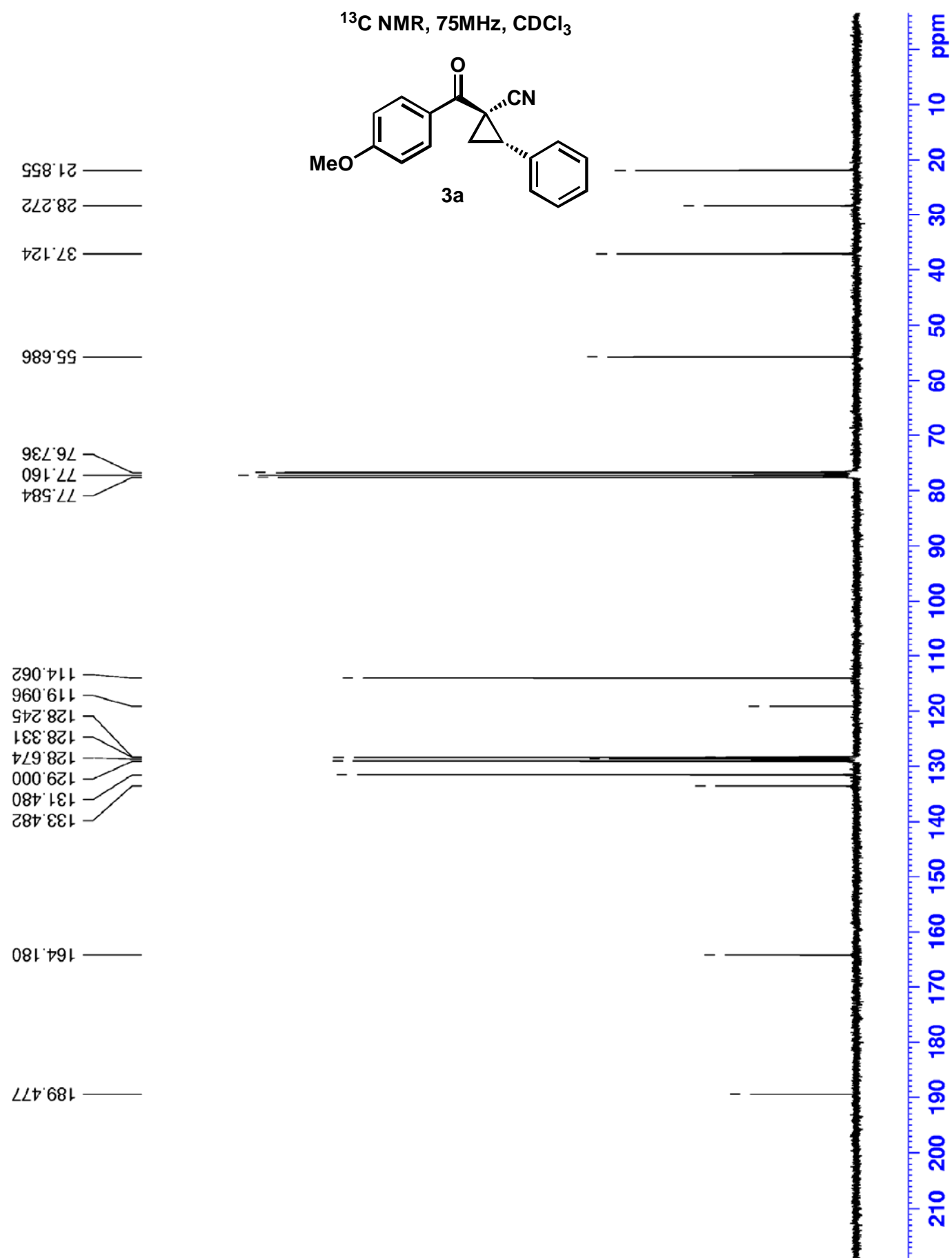
^1H NMR, 400MHz, CDCl_3 

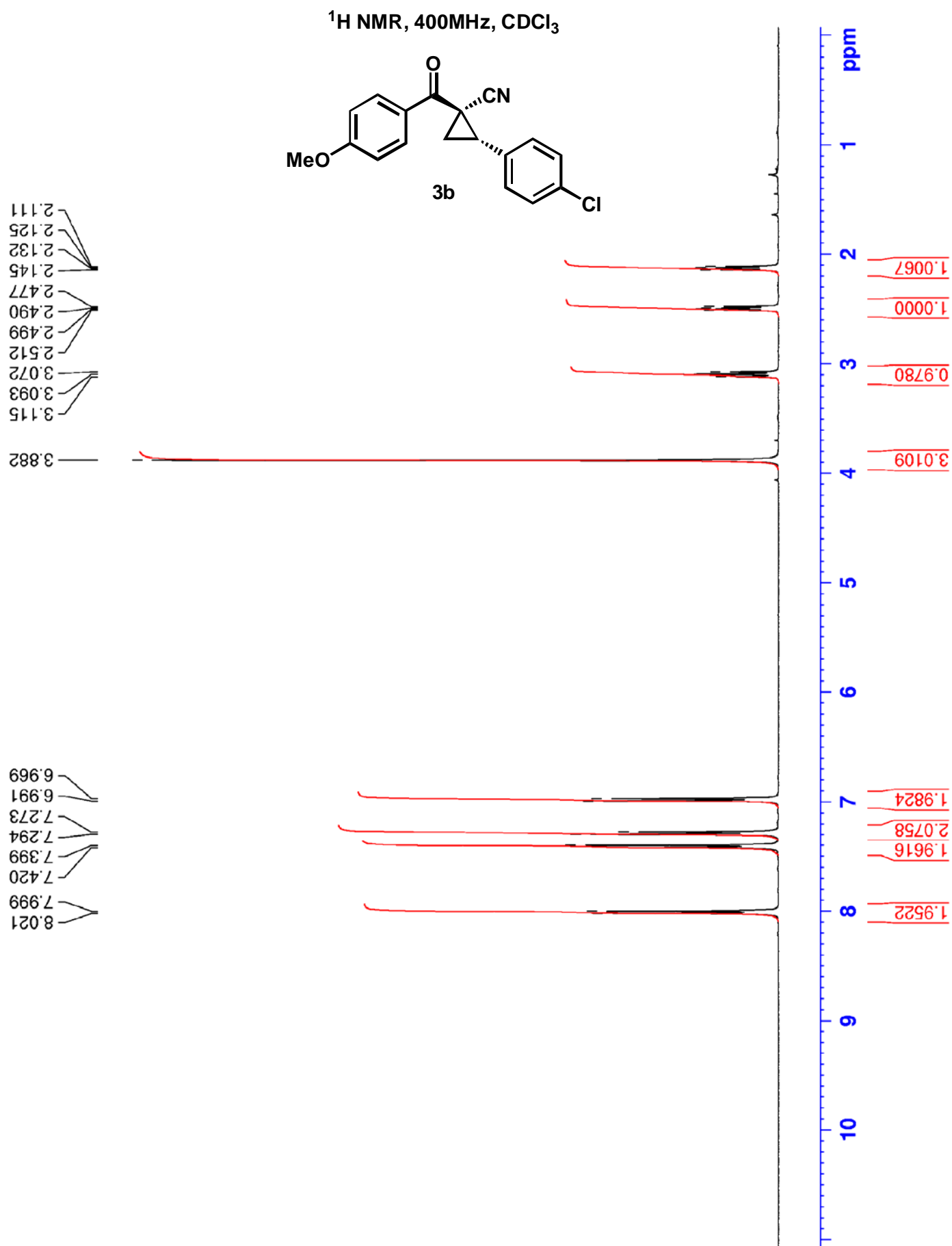


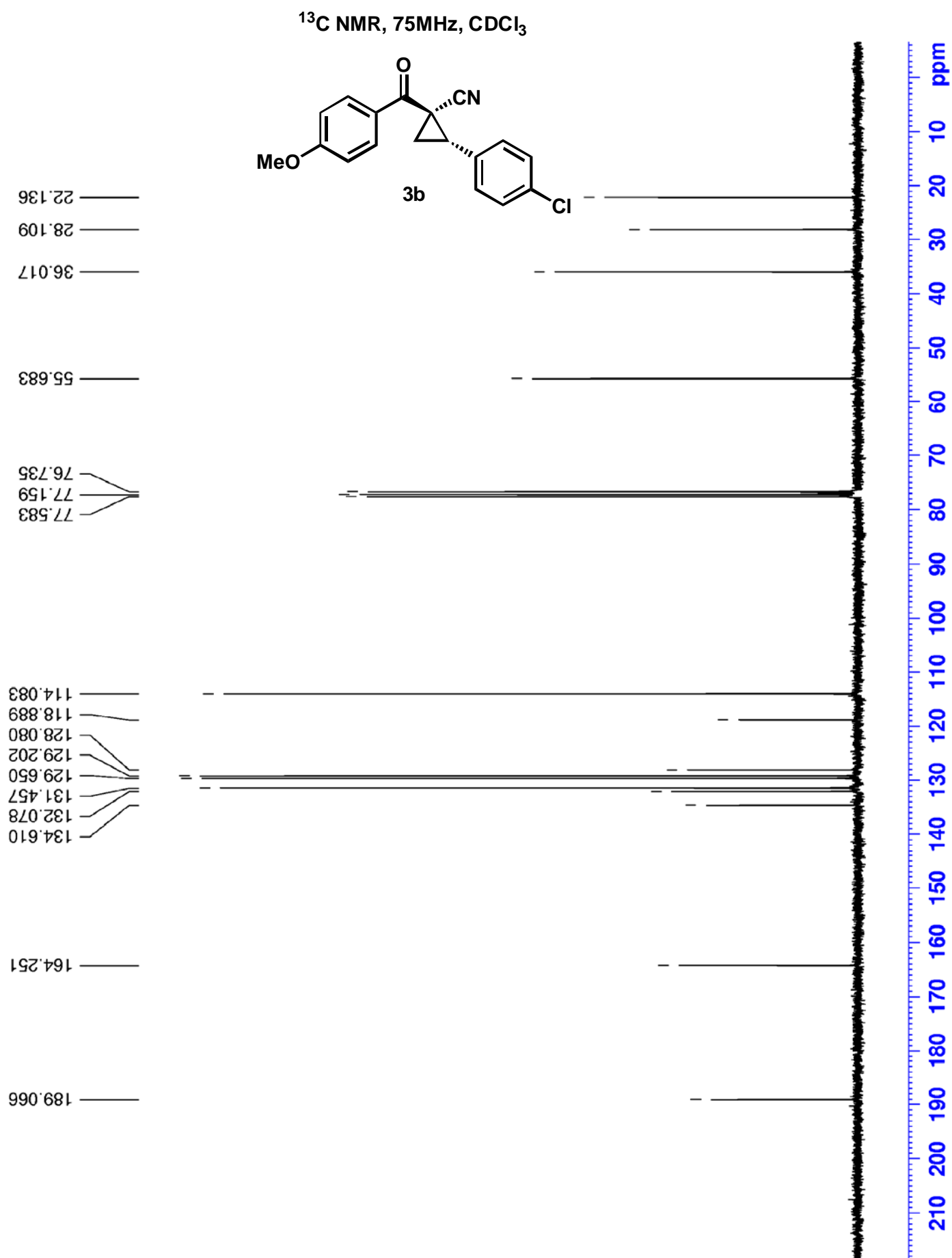


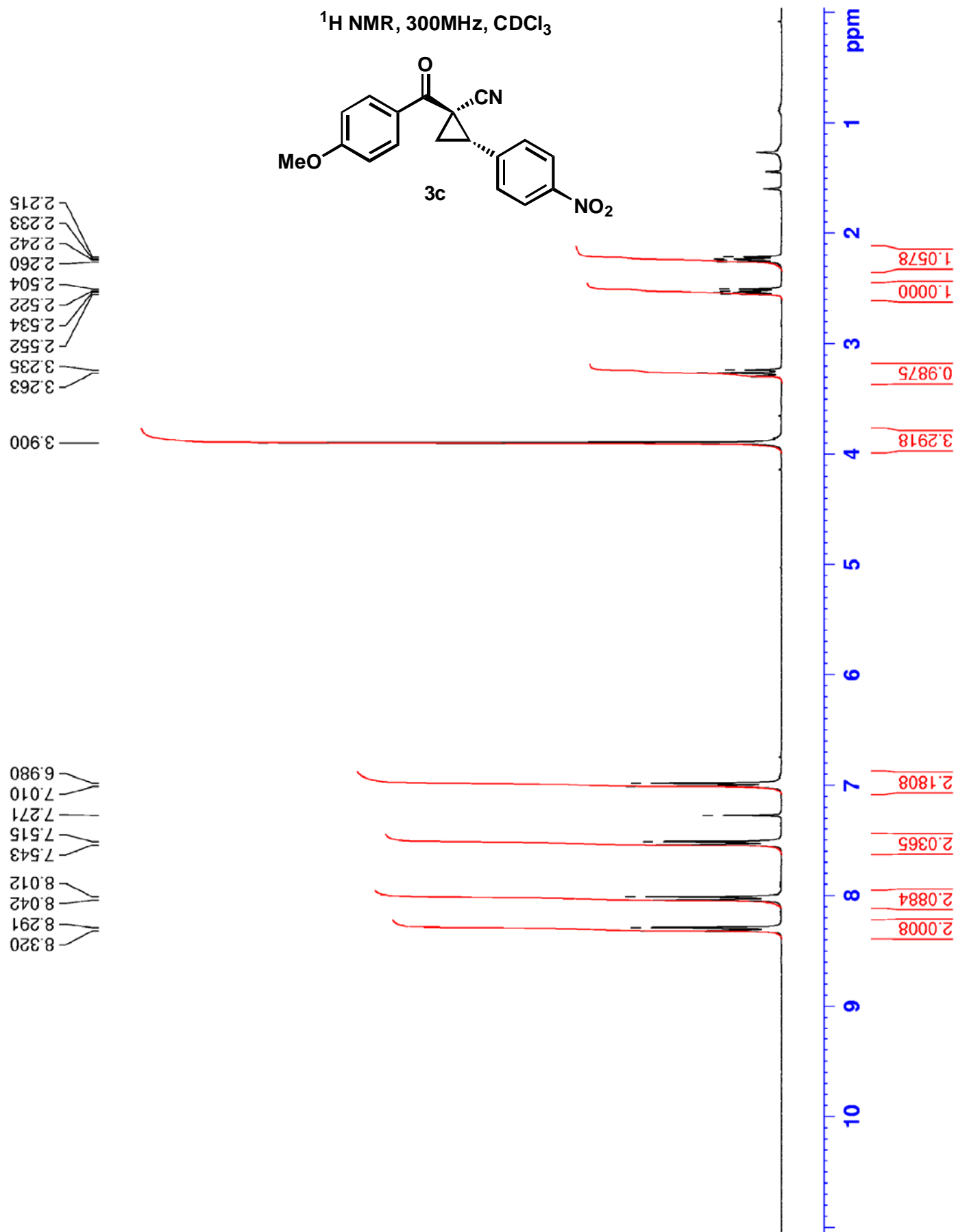


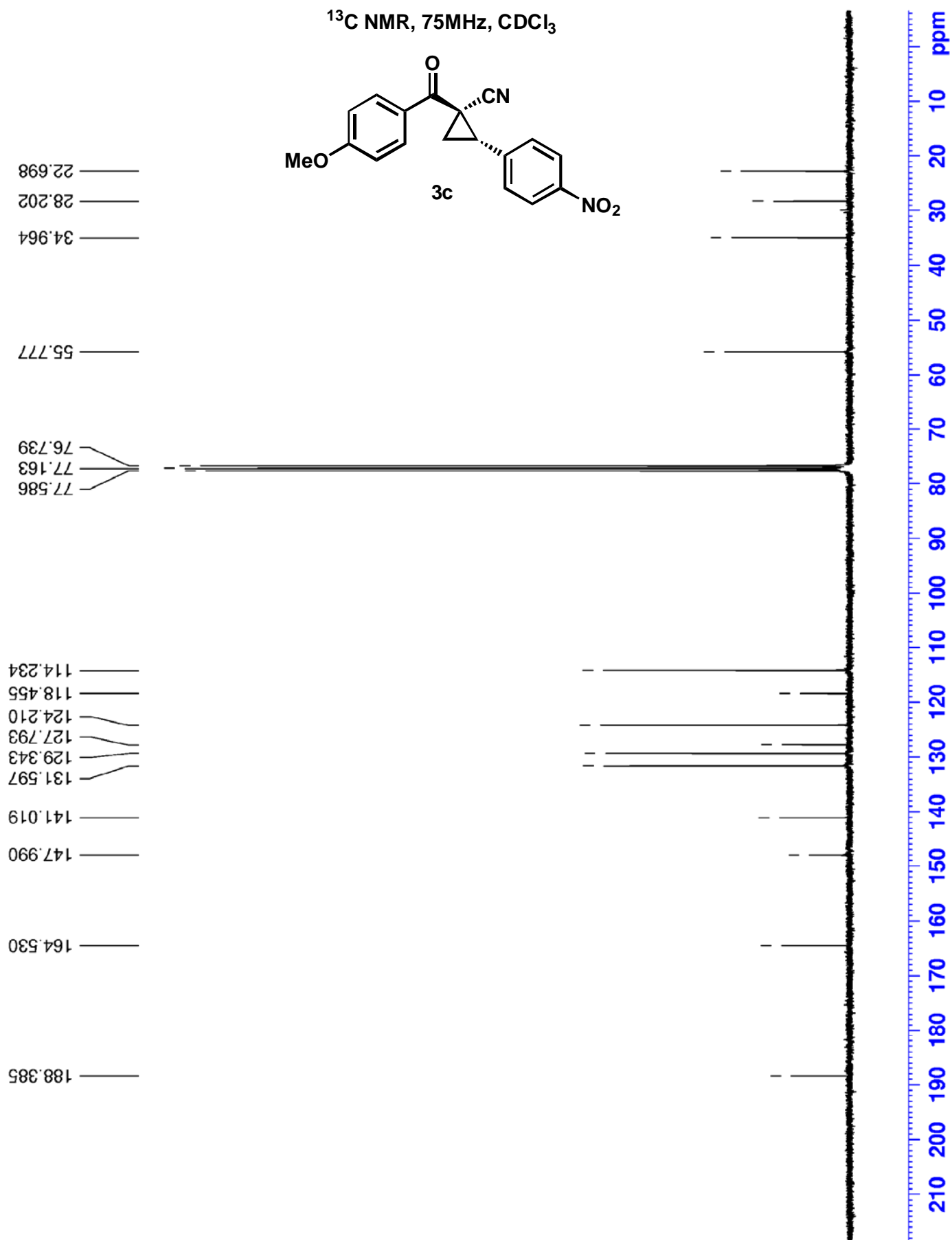


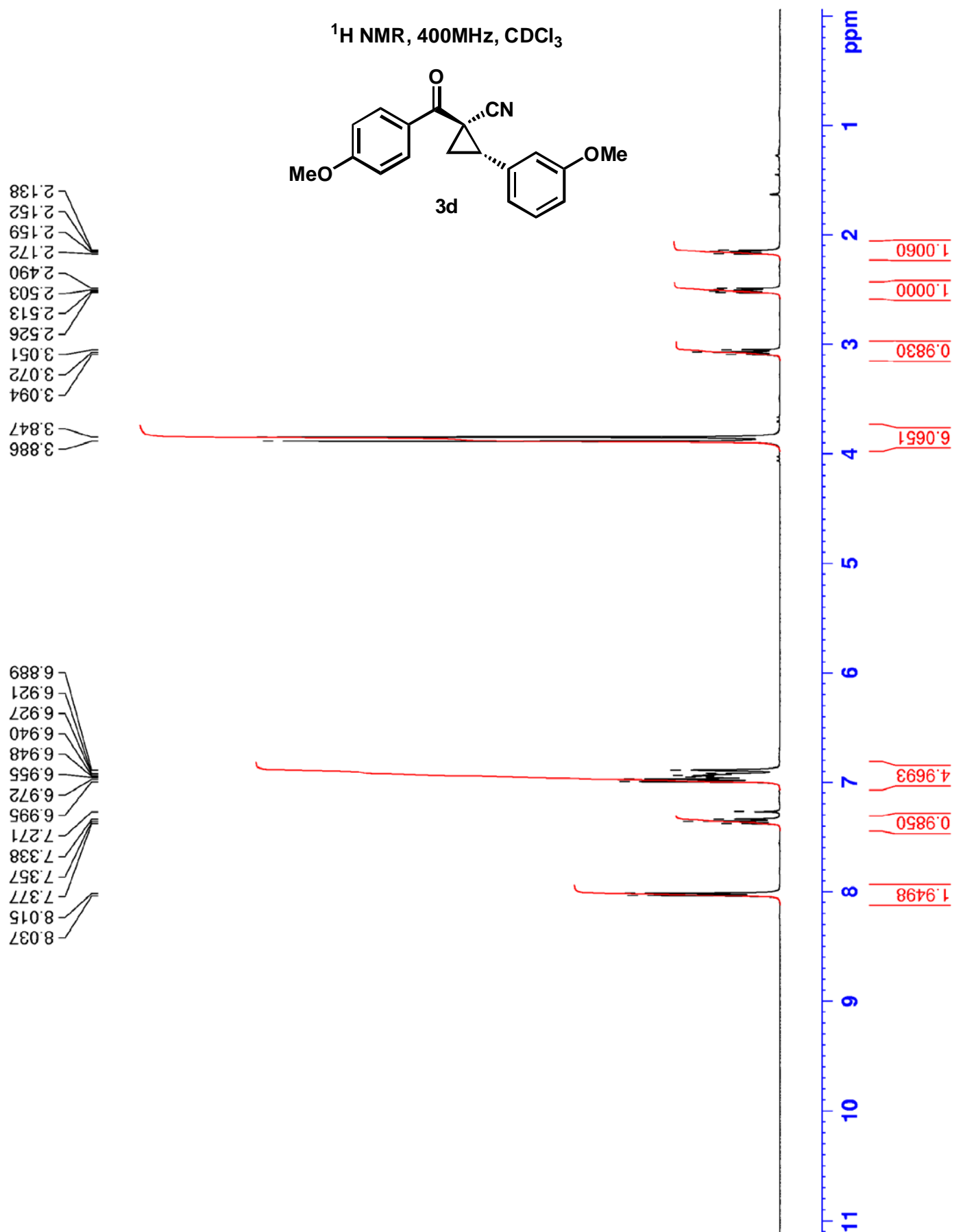


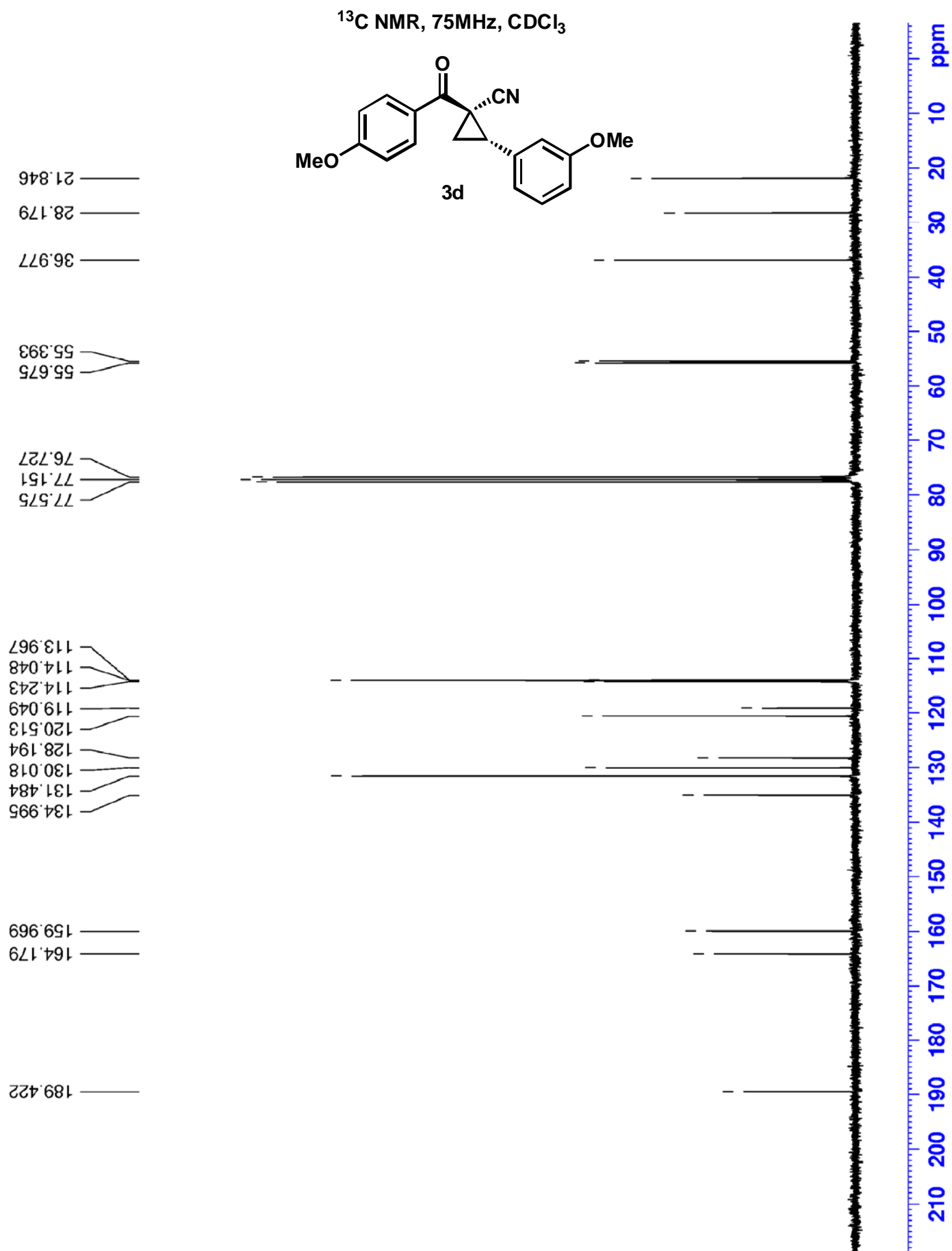


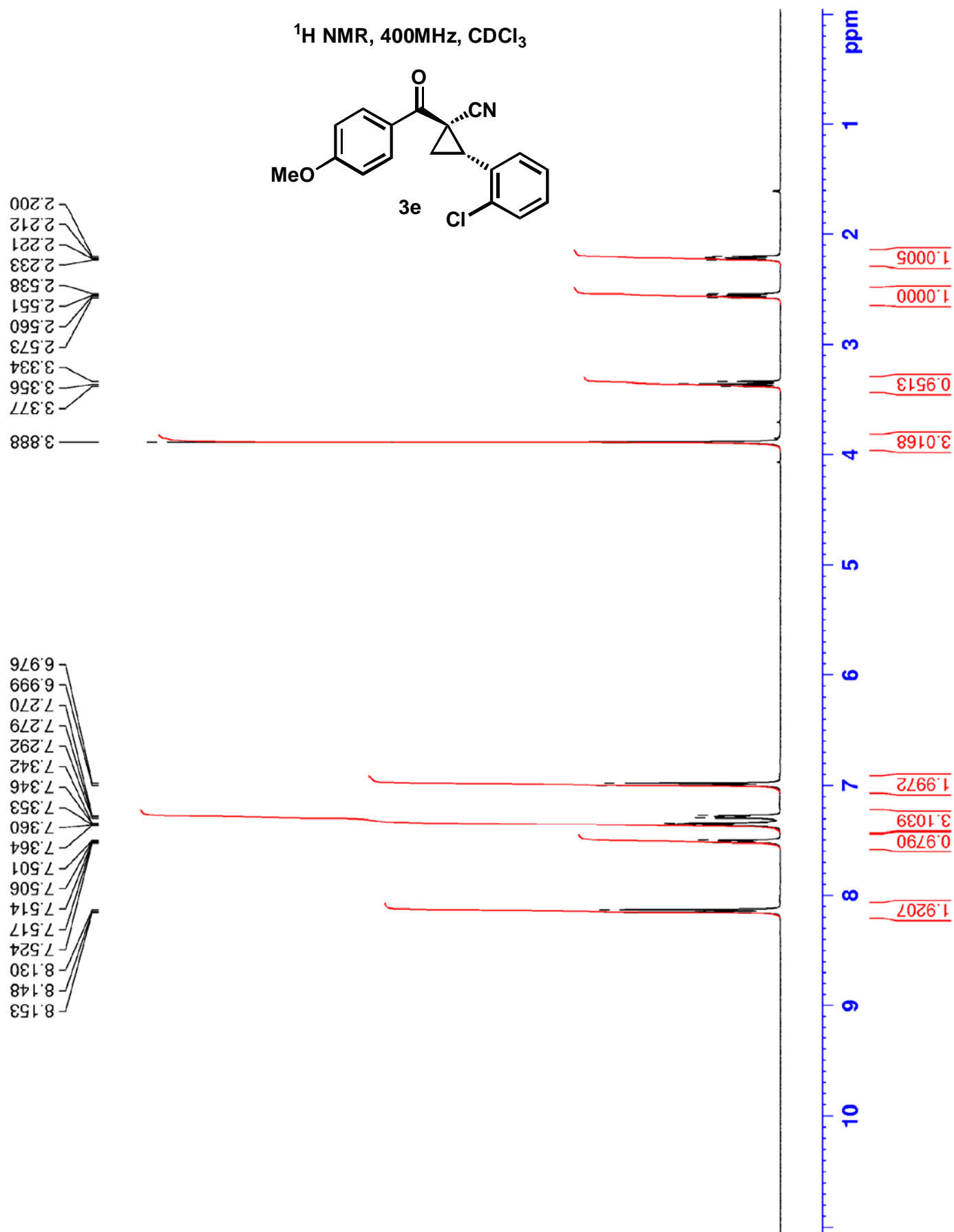


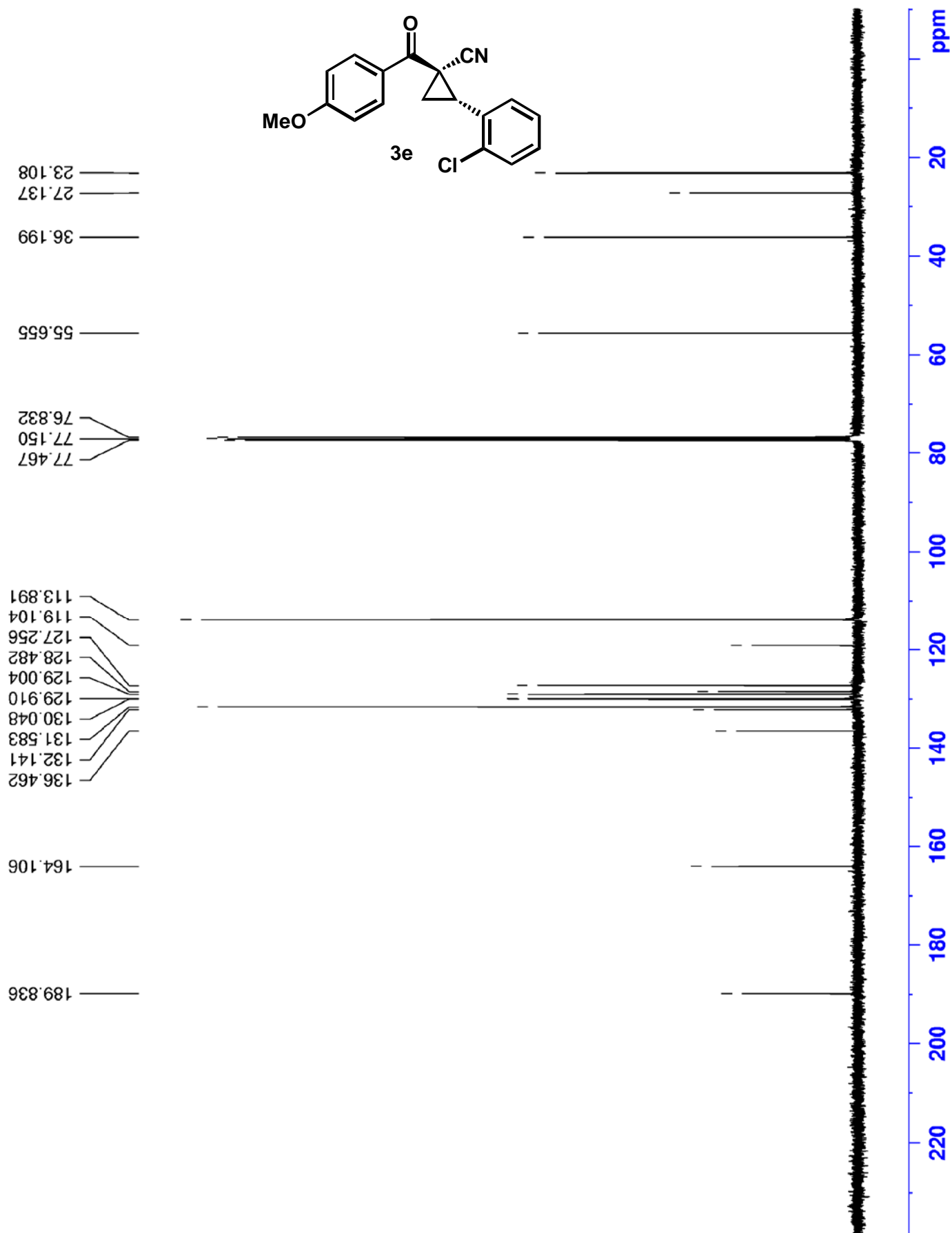


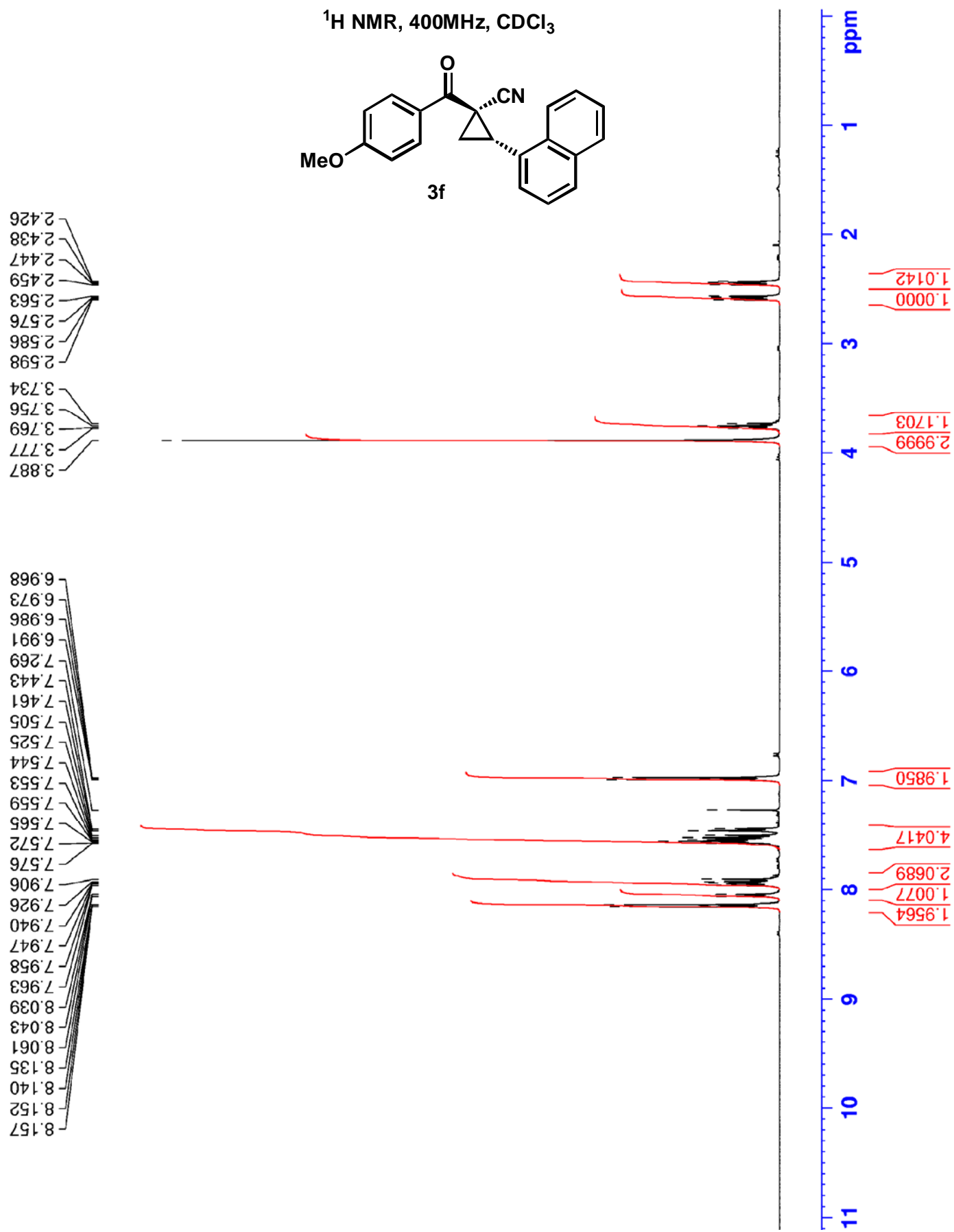


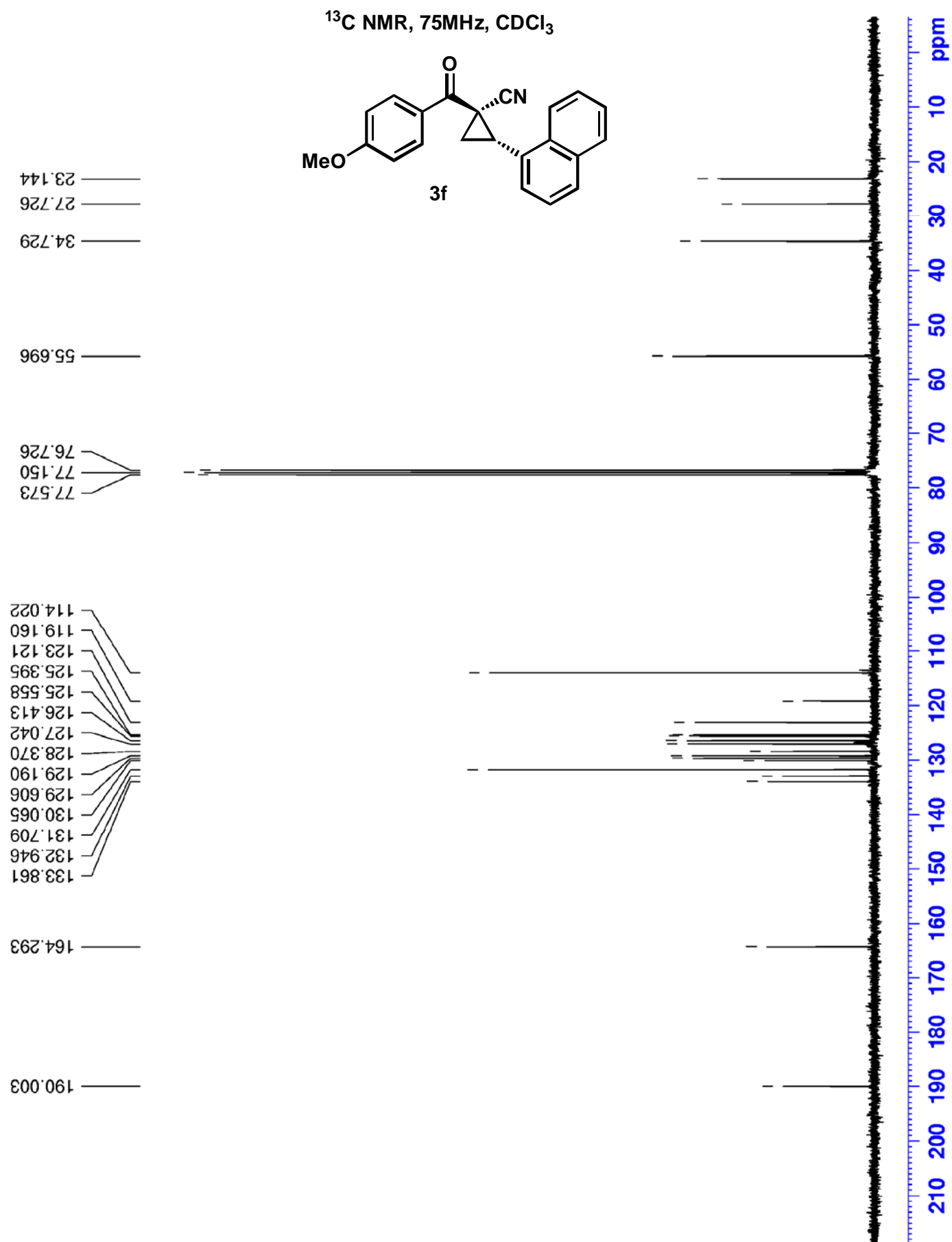


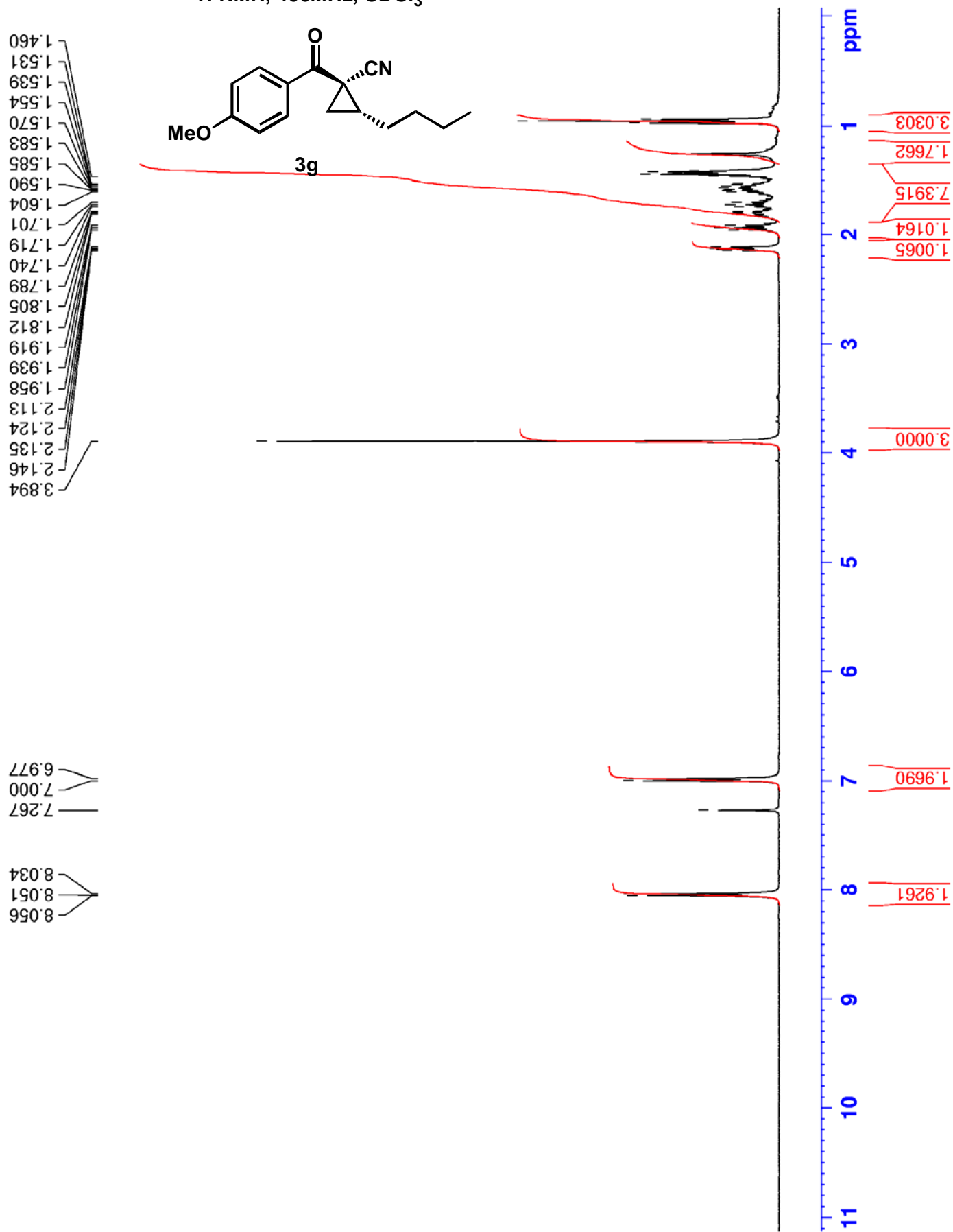


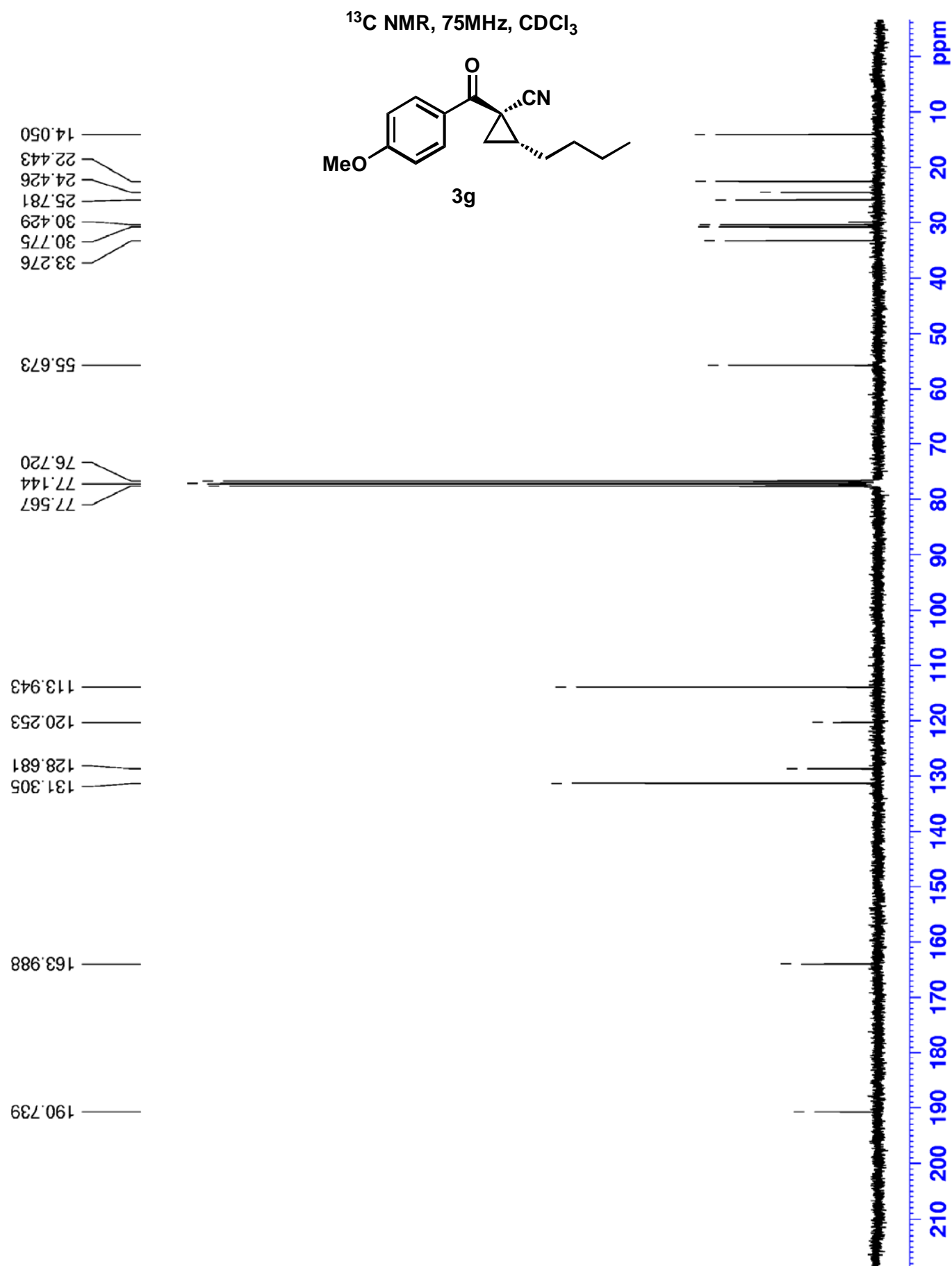


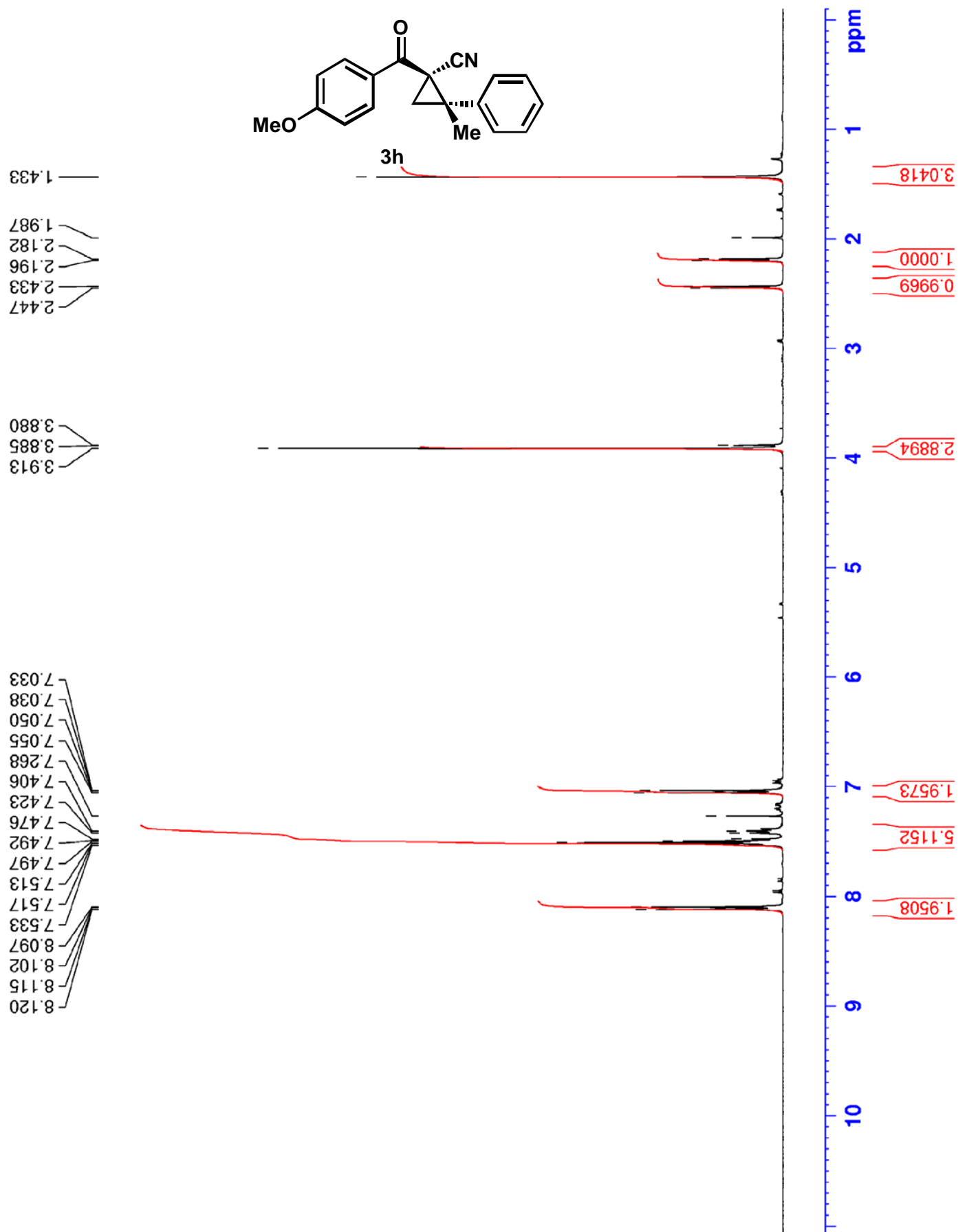
^{13}C NMR, 100MHz, CDCl_3 

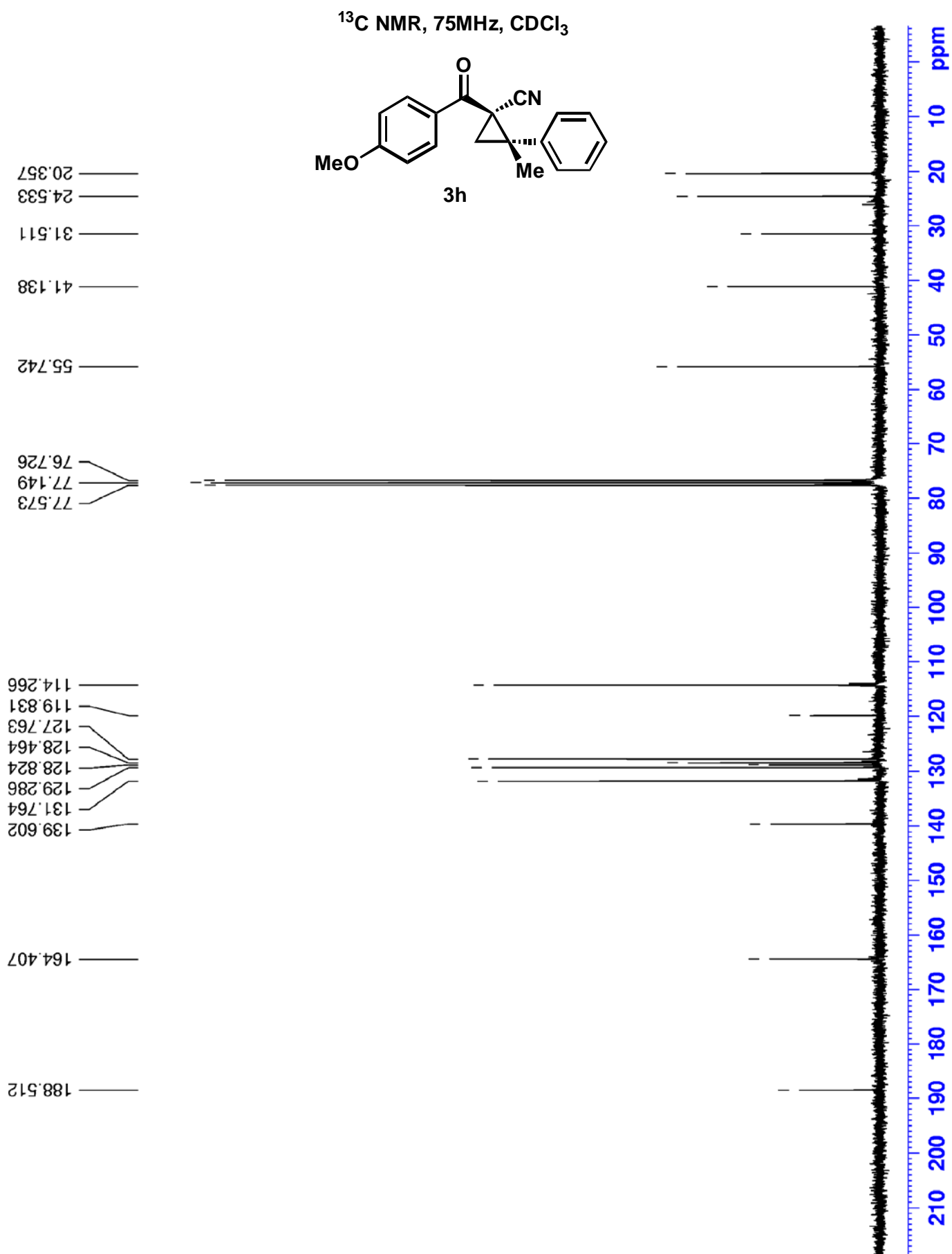


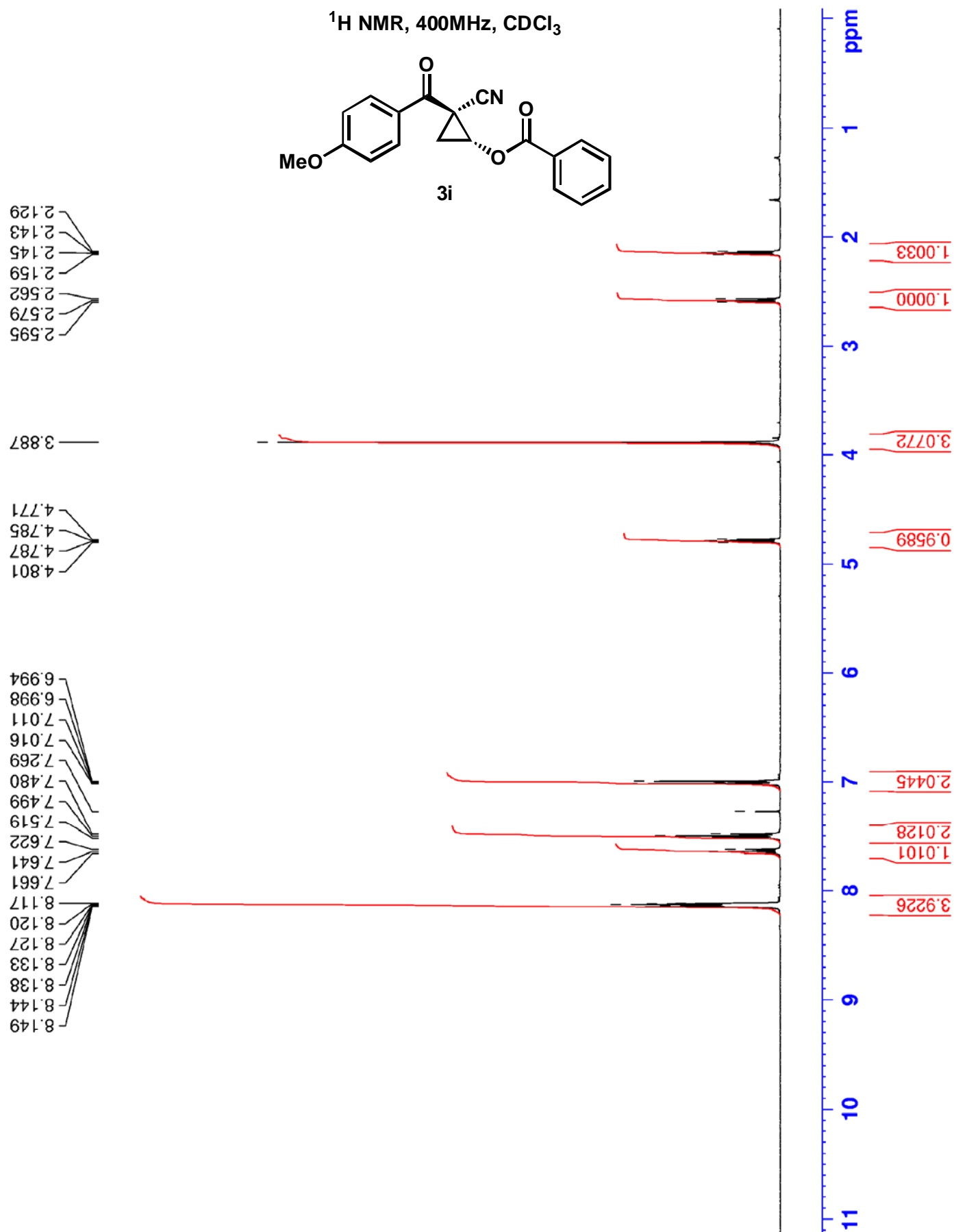


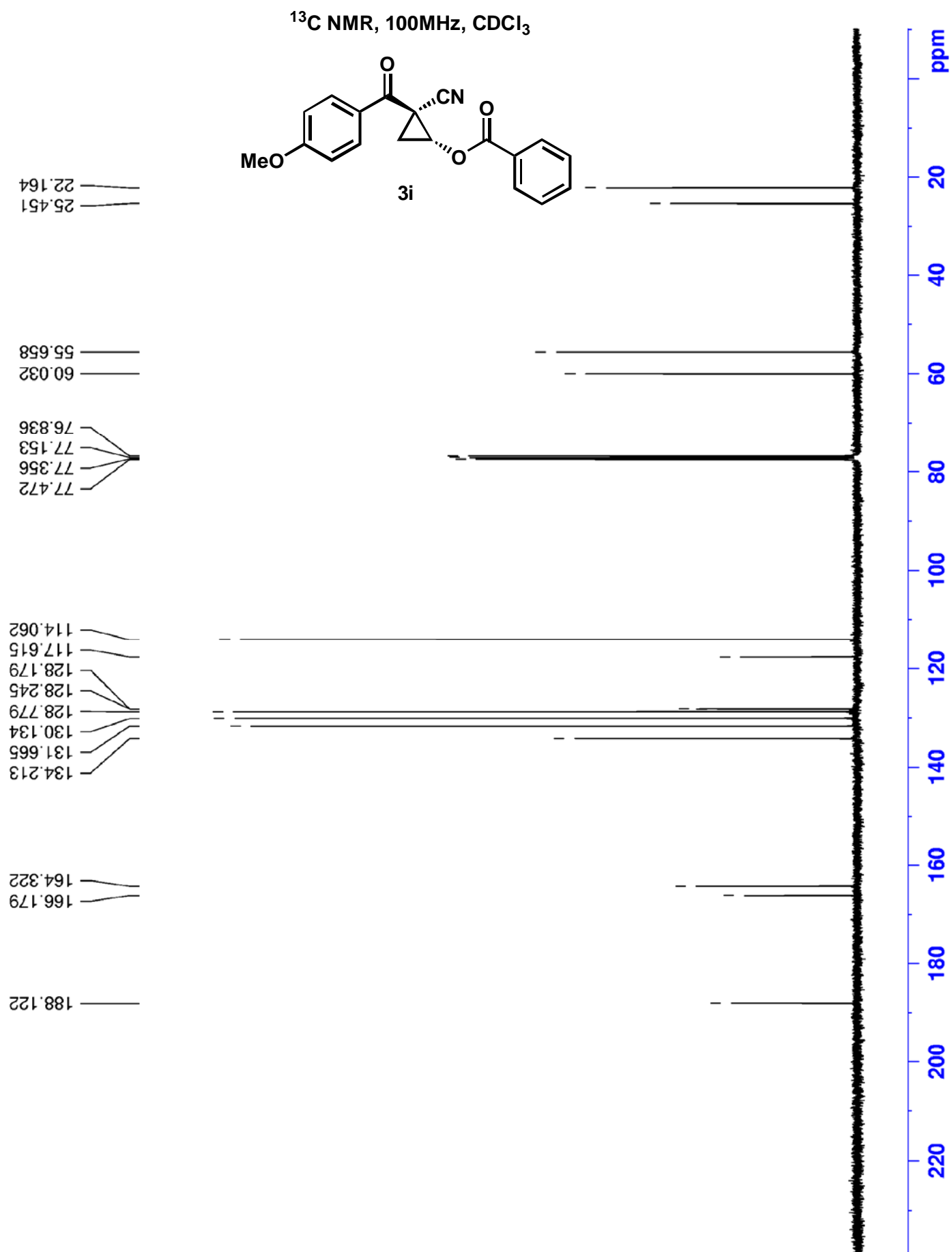
^1H NMR, 400MHz, CDCl_3 

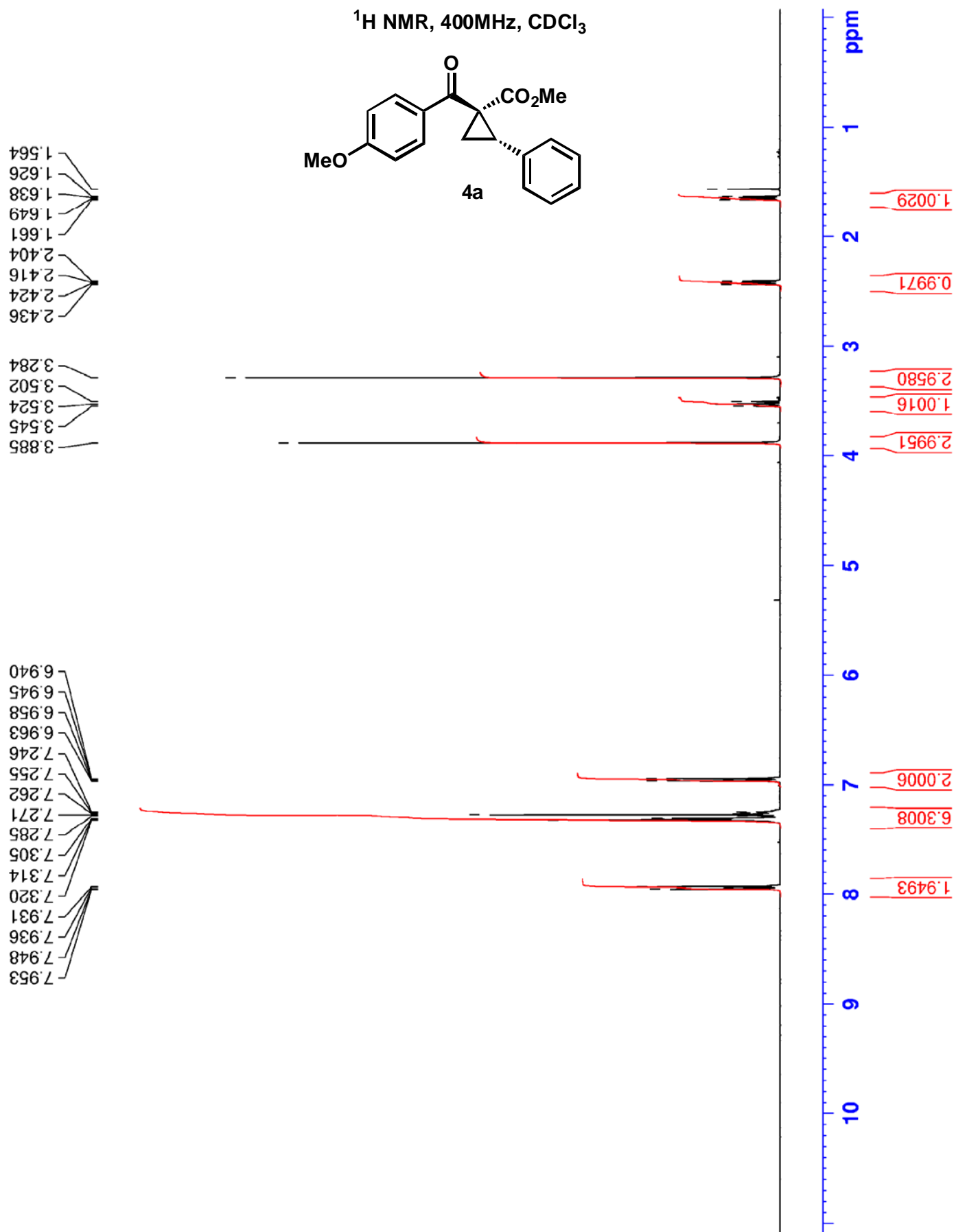


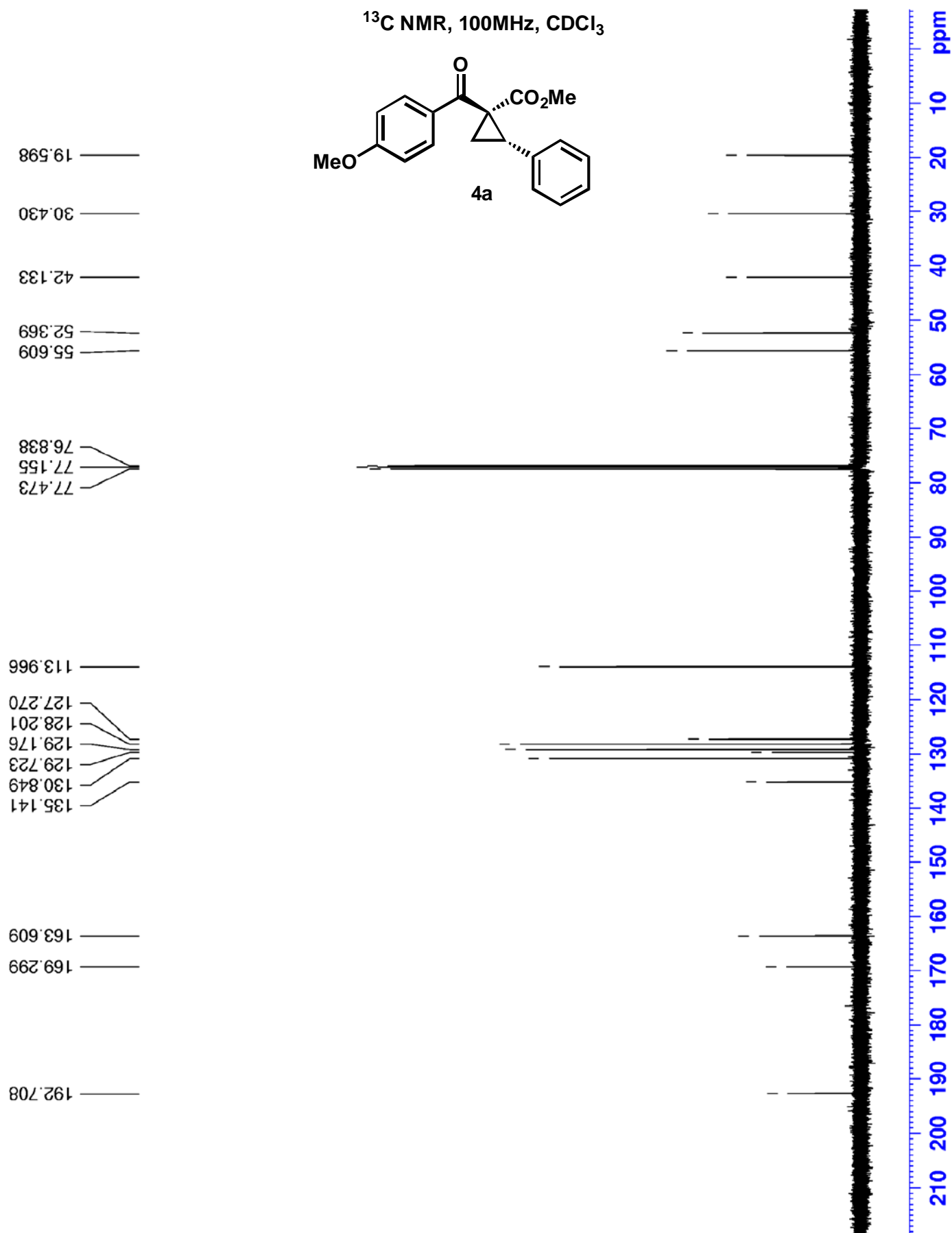
^1H NMR, 400MHz, CDCl_3 

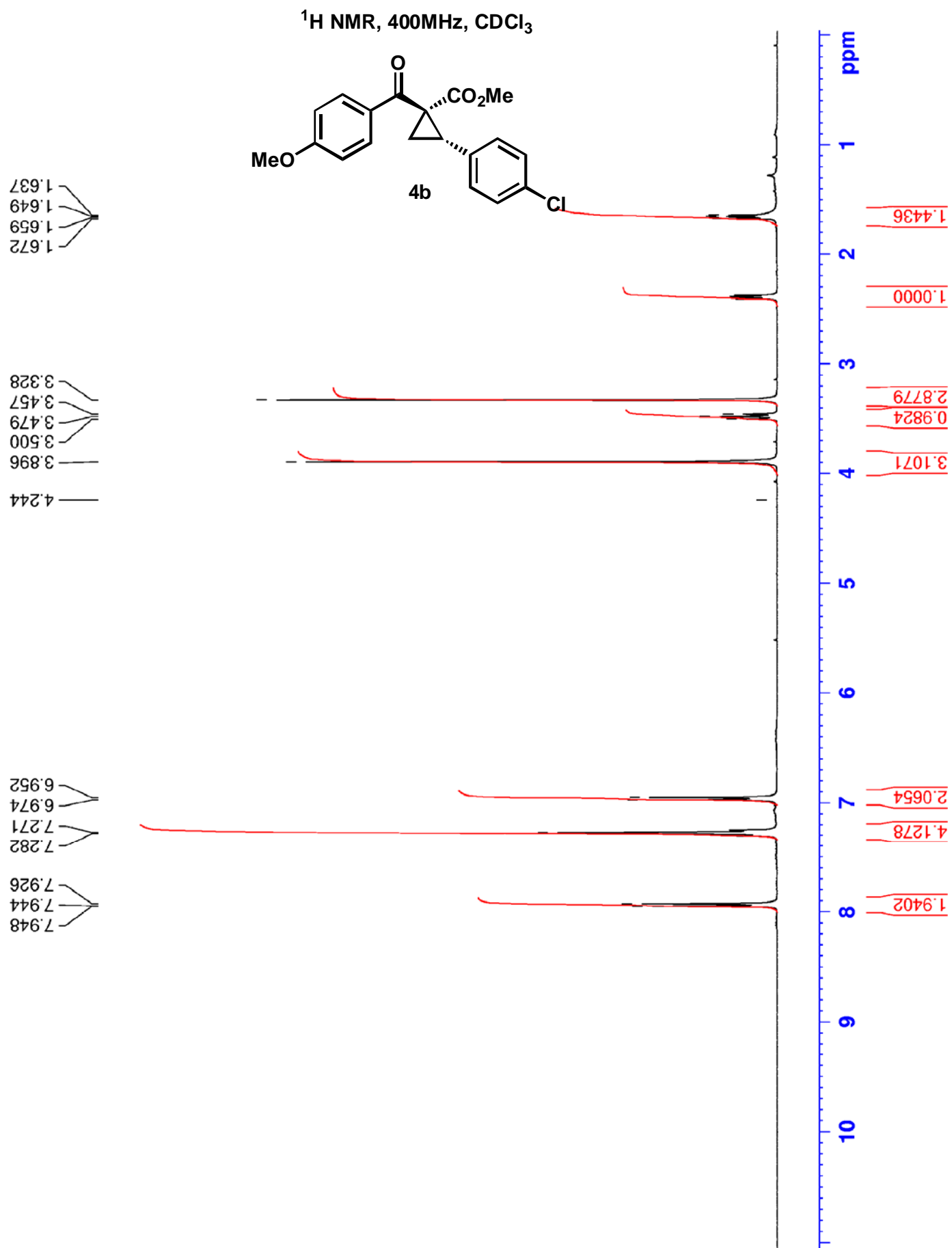


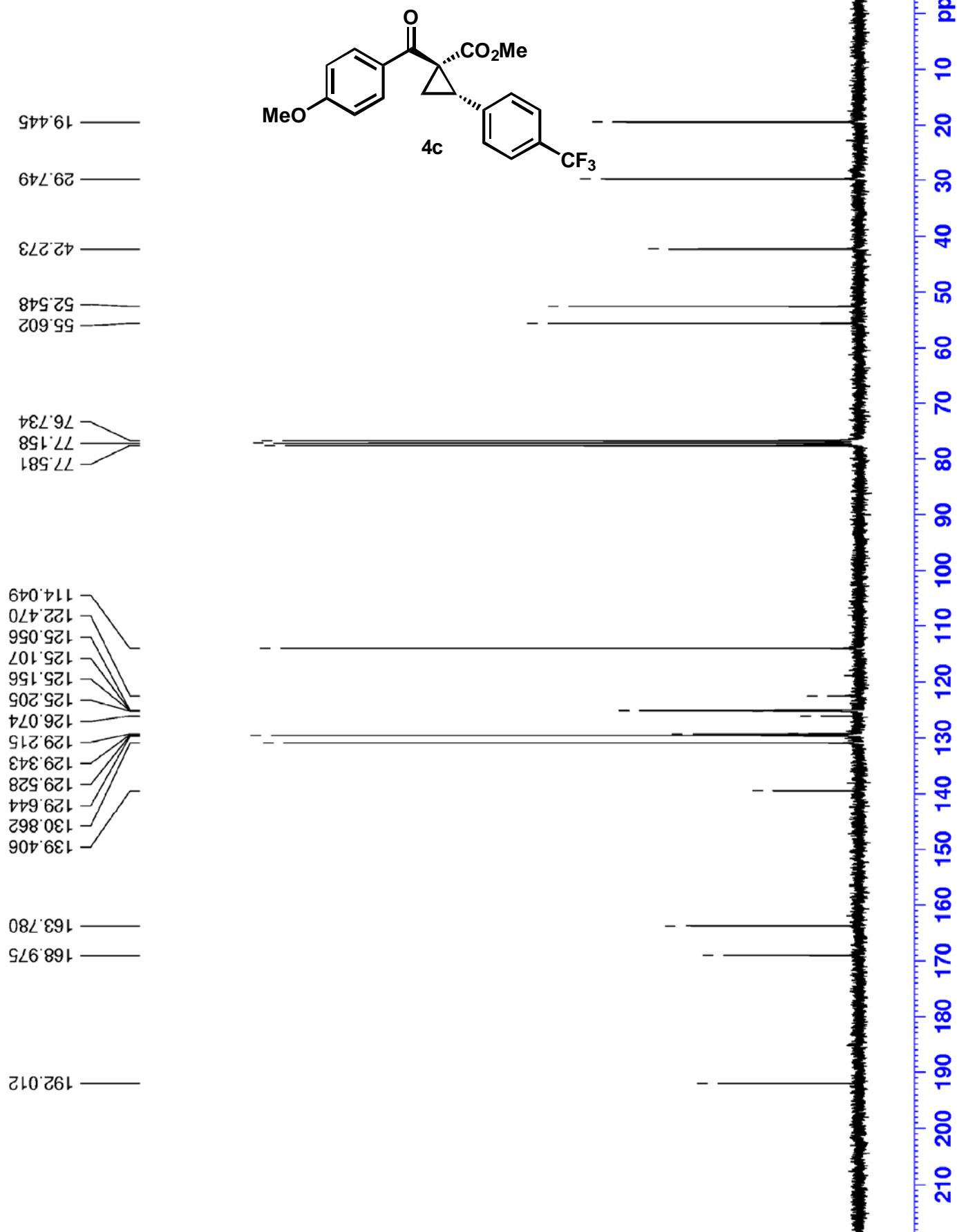


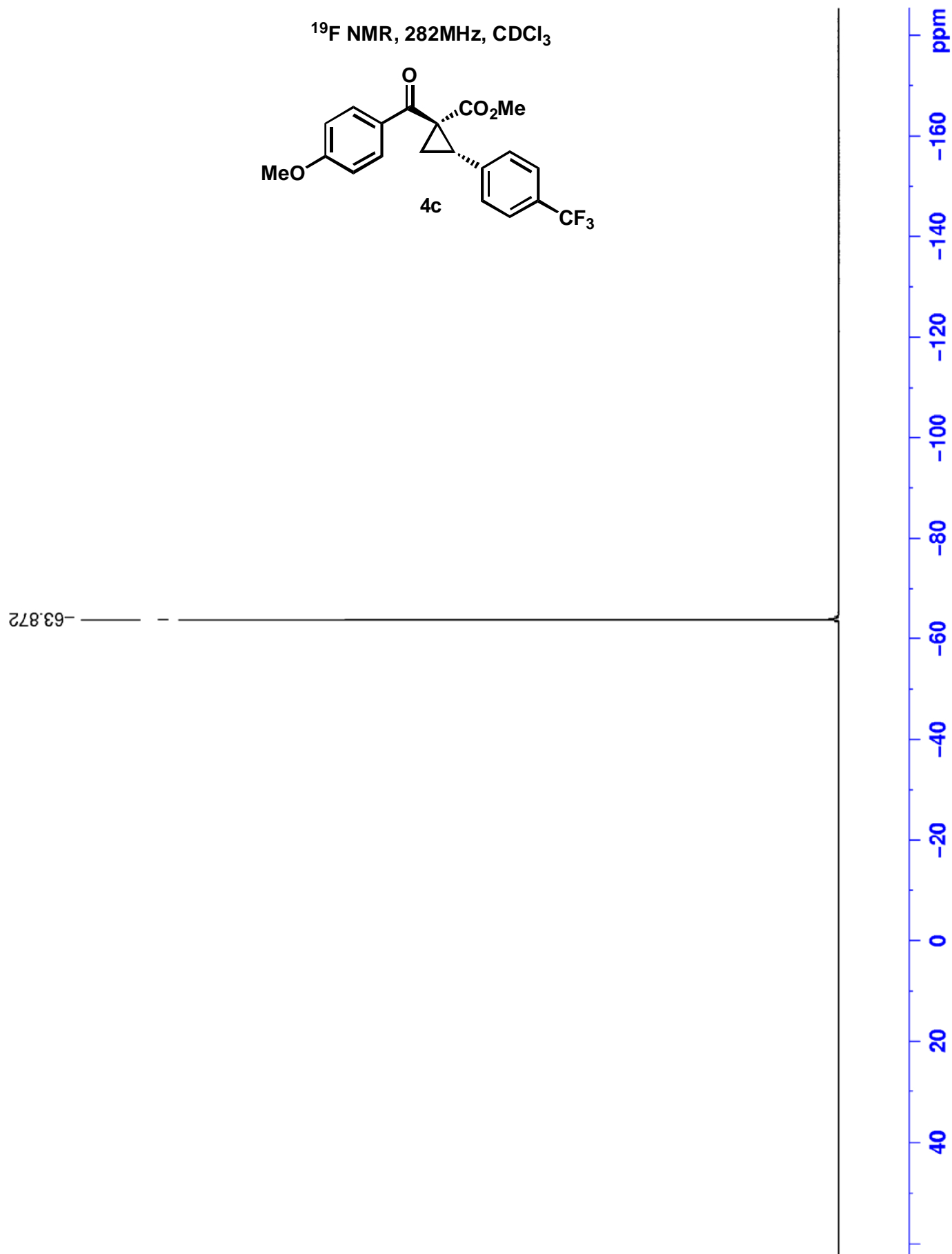


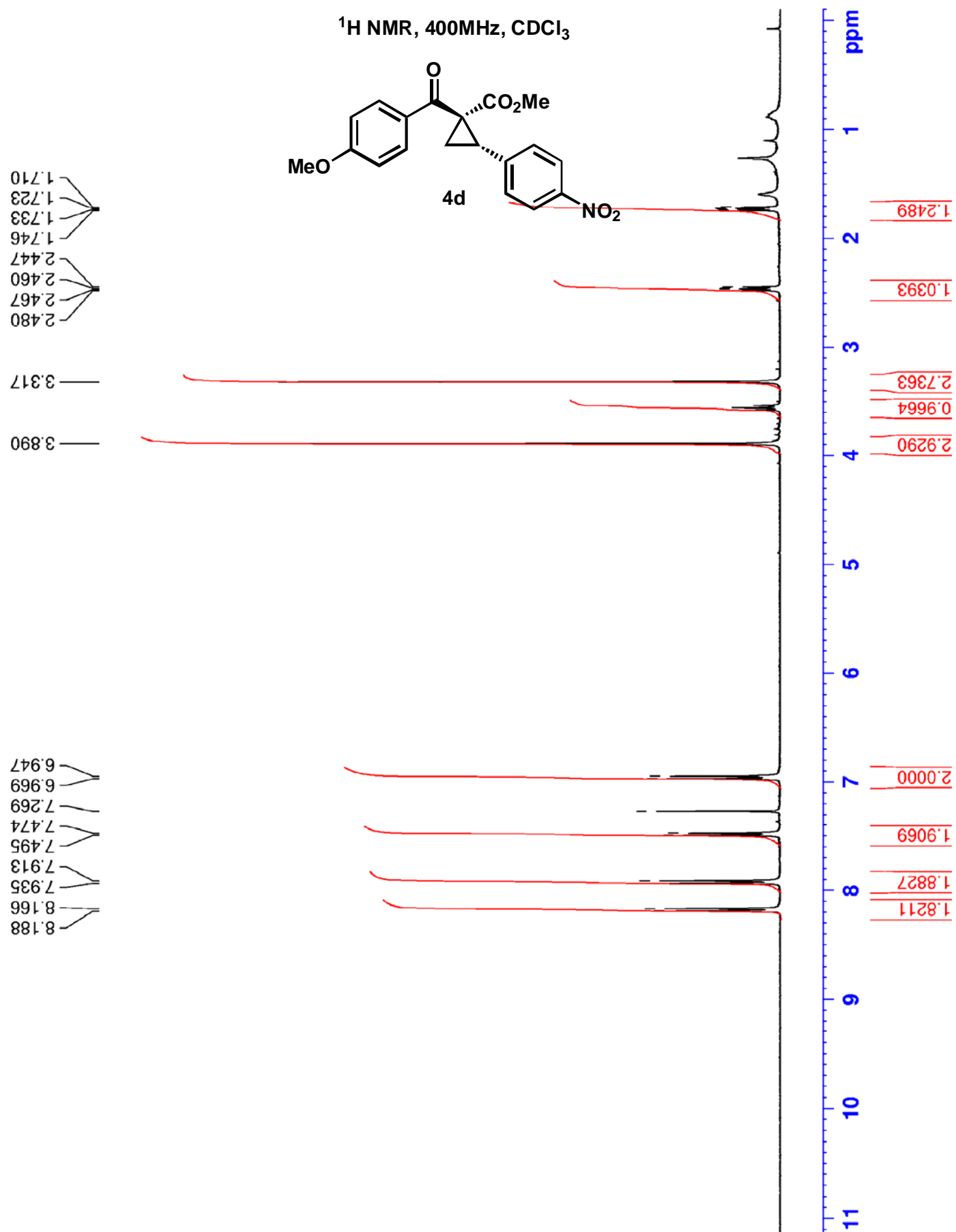


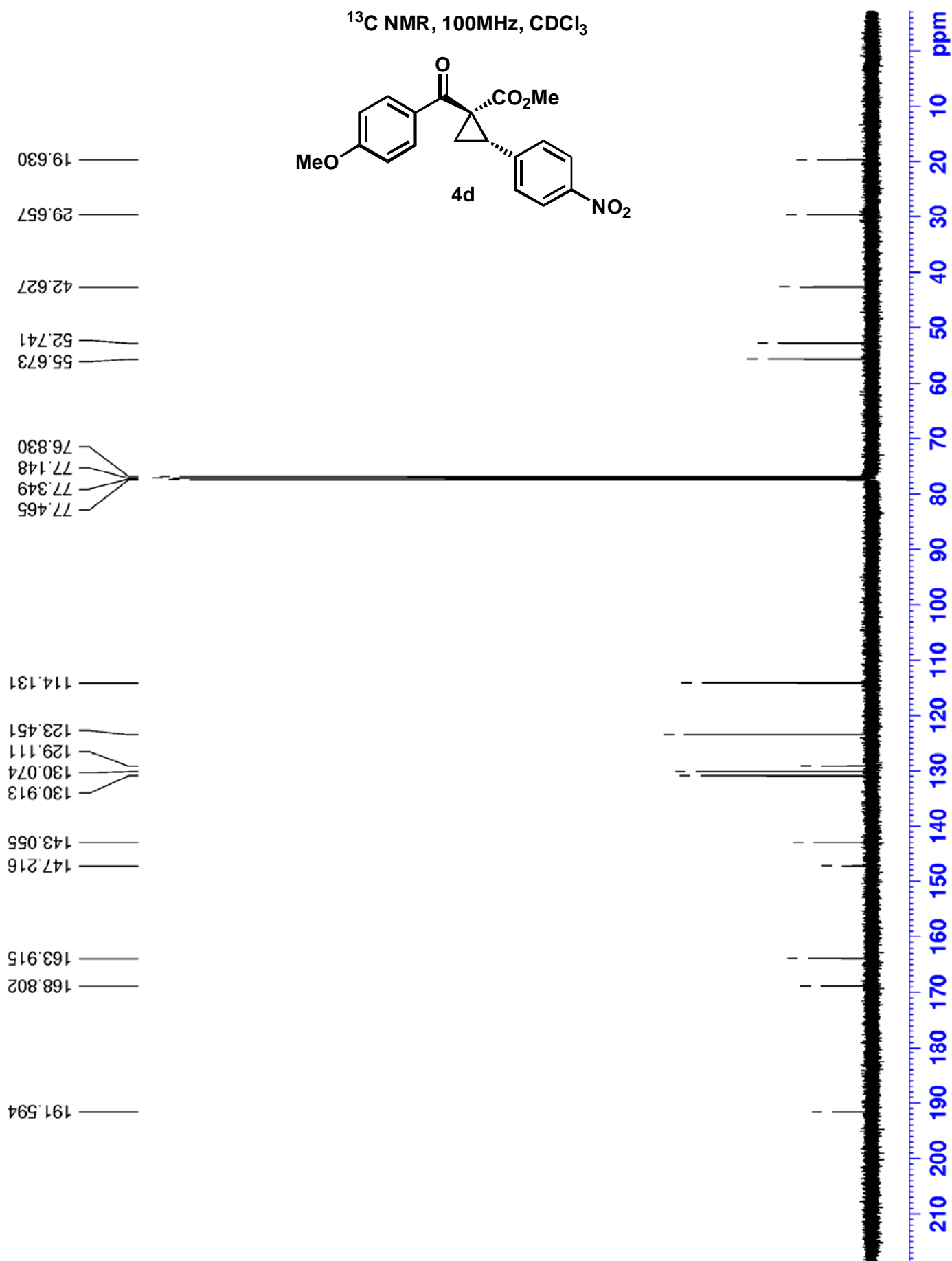


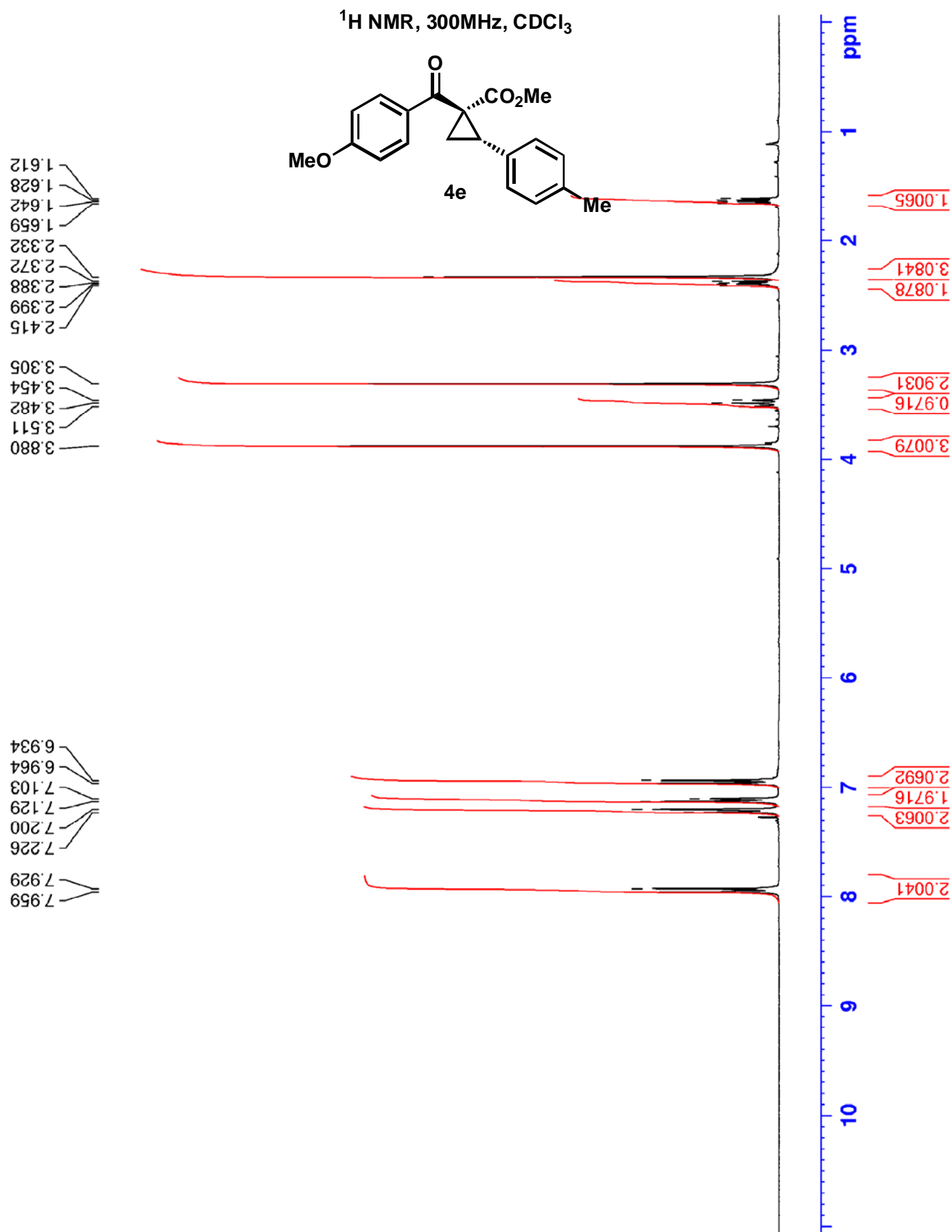


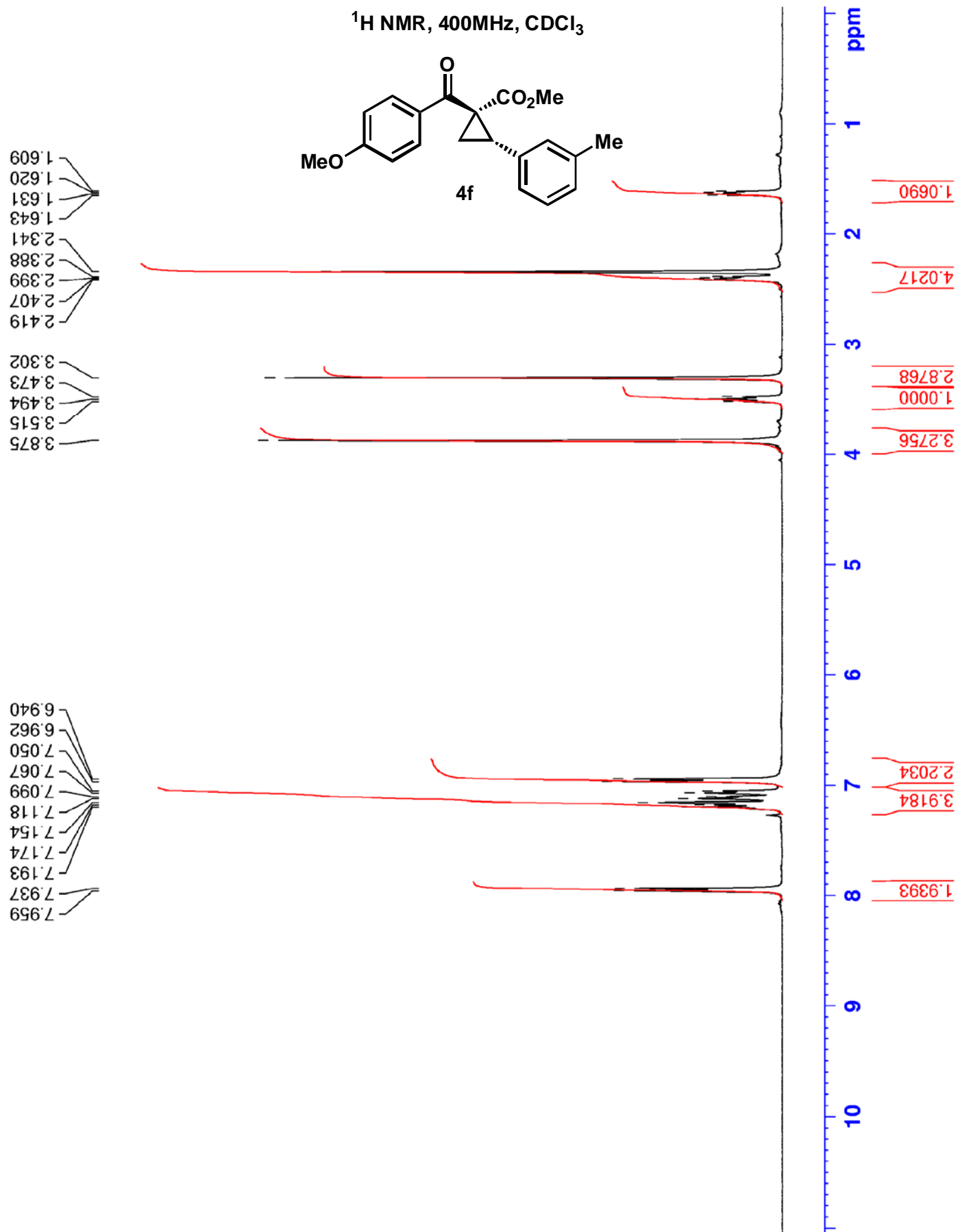
^{13}C NMR, 75MHz, CDCl_3 

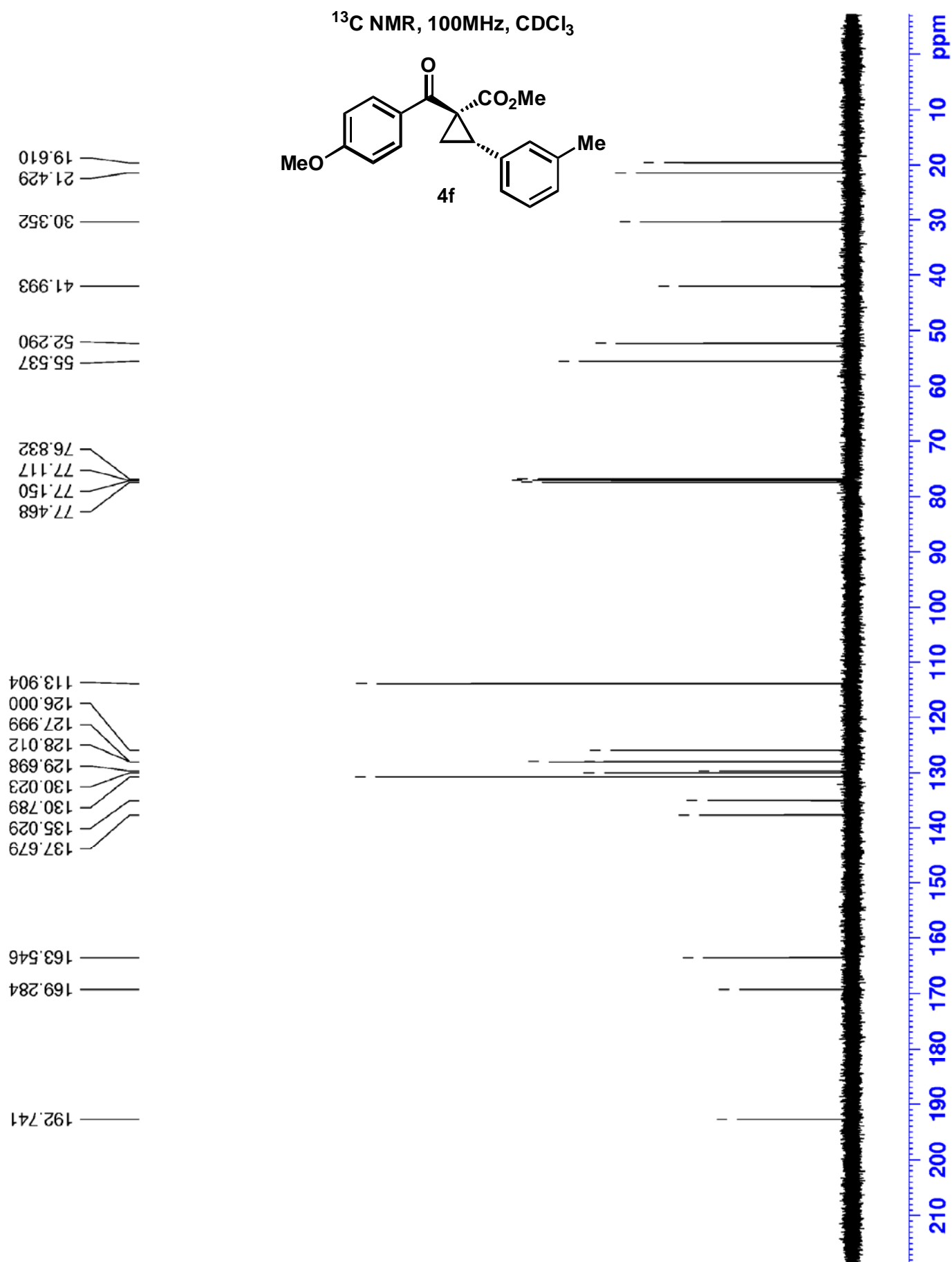


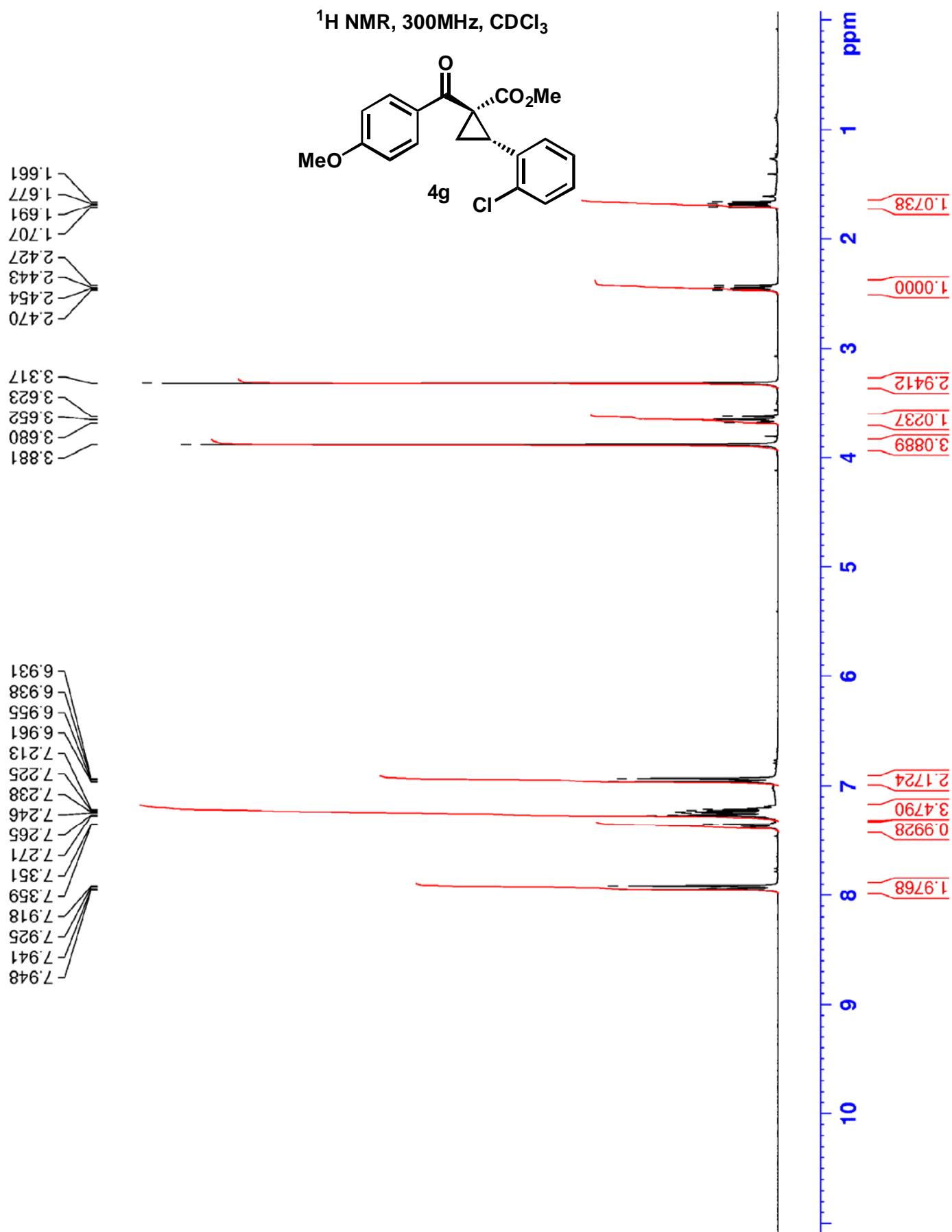


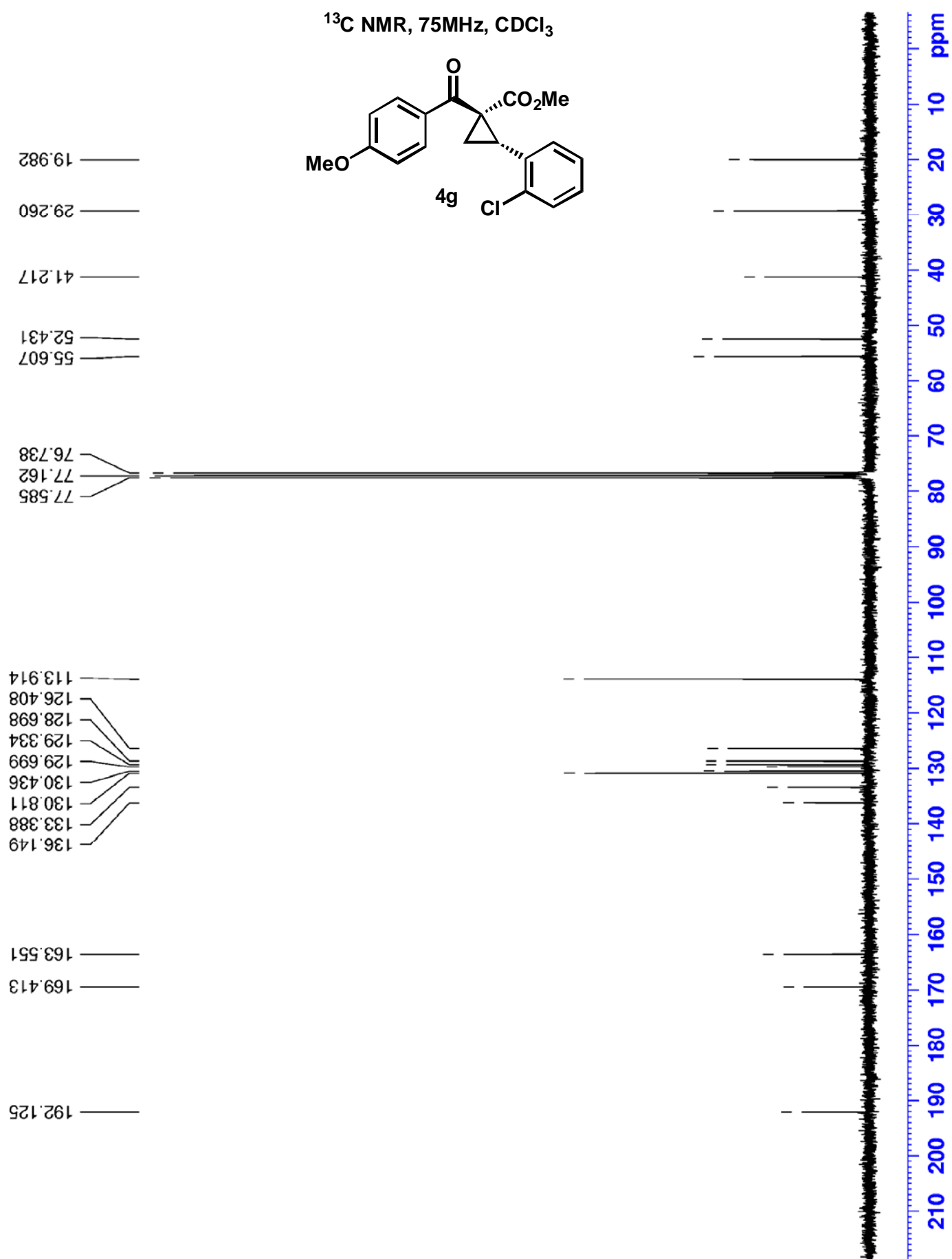


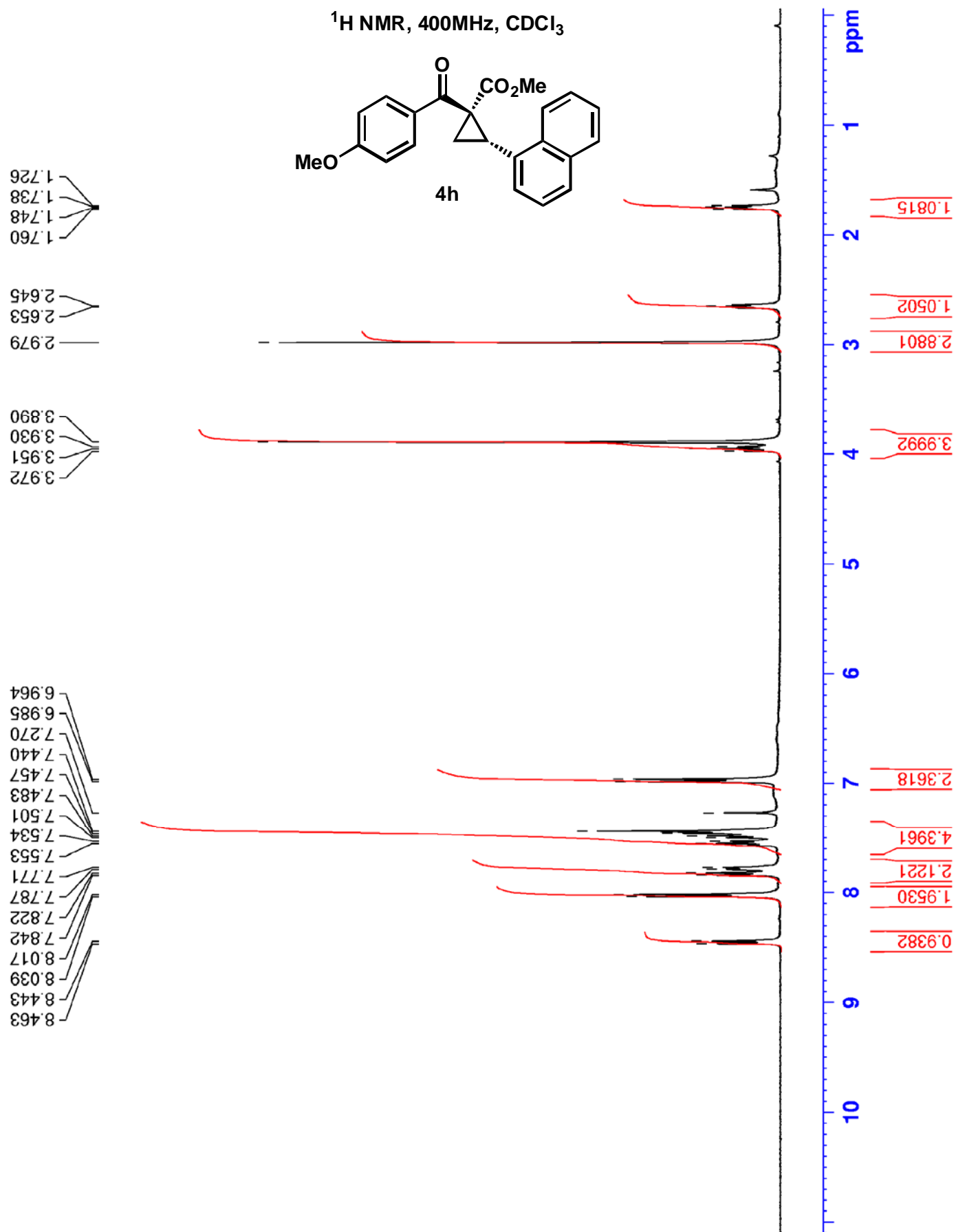


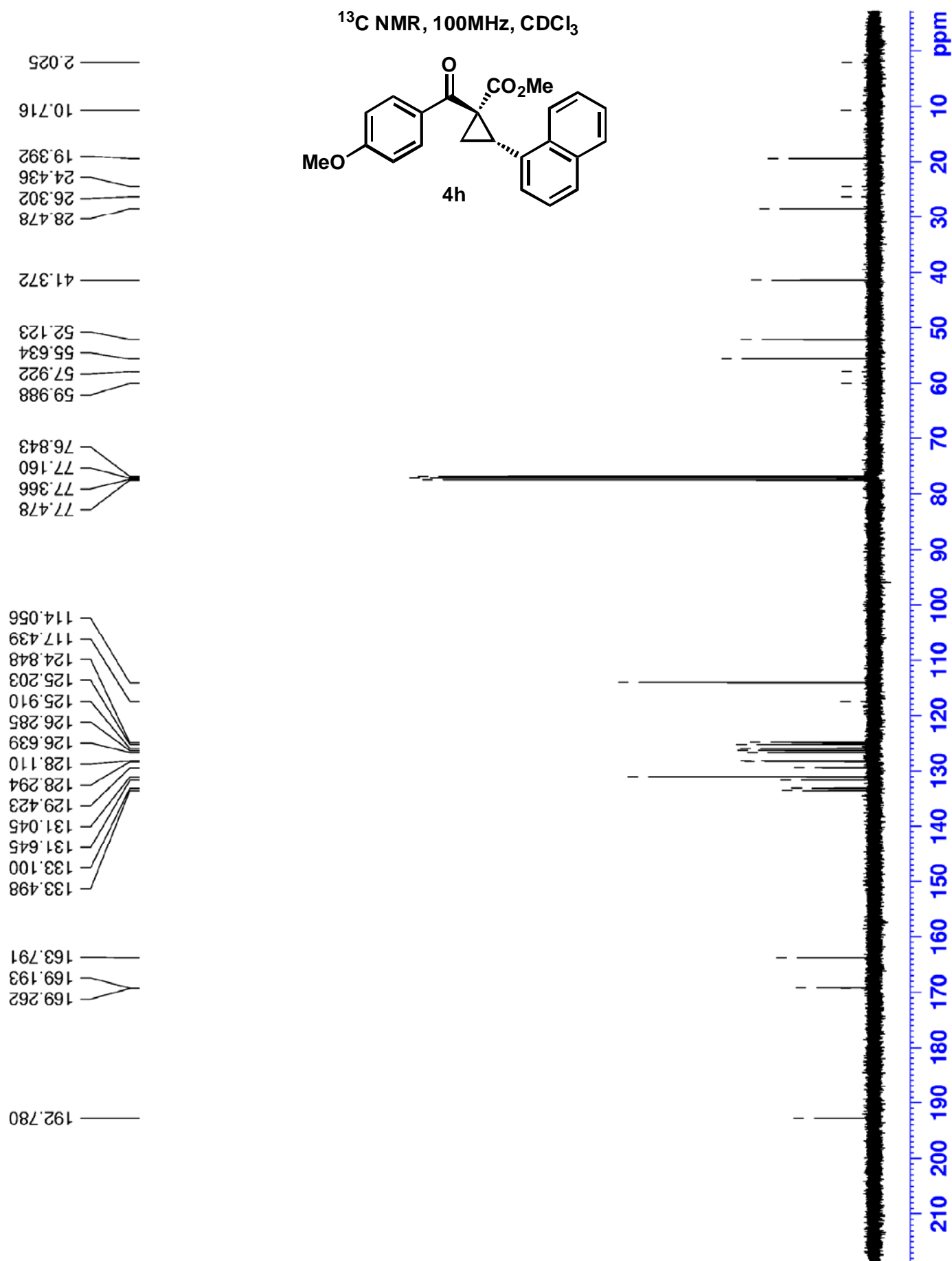


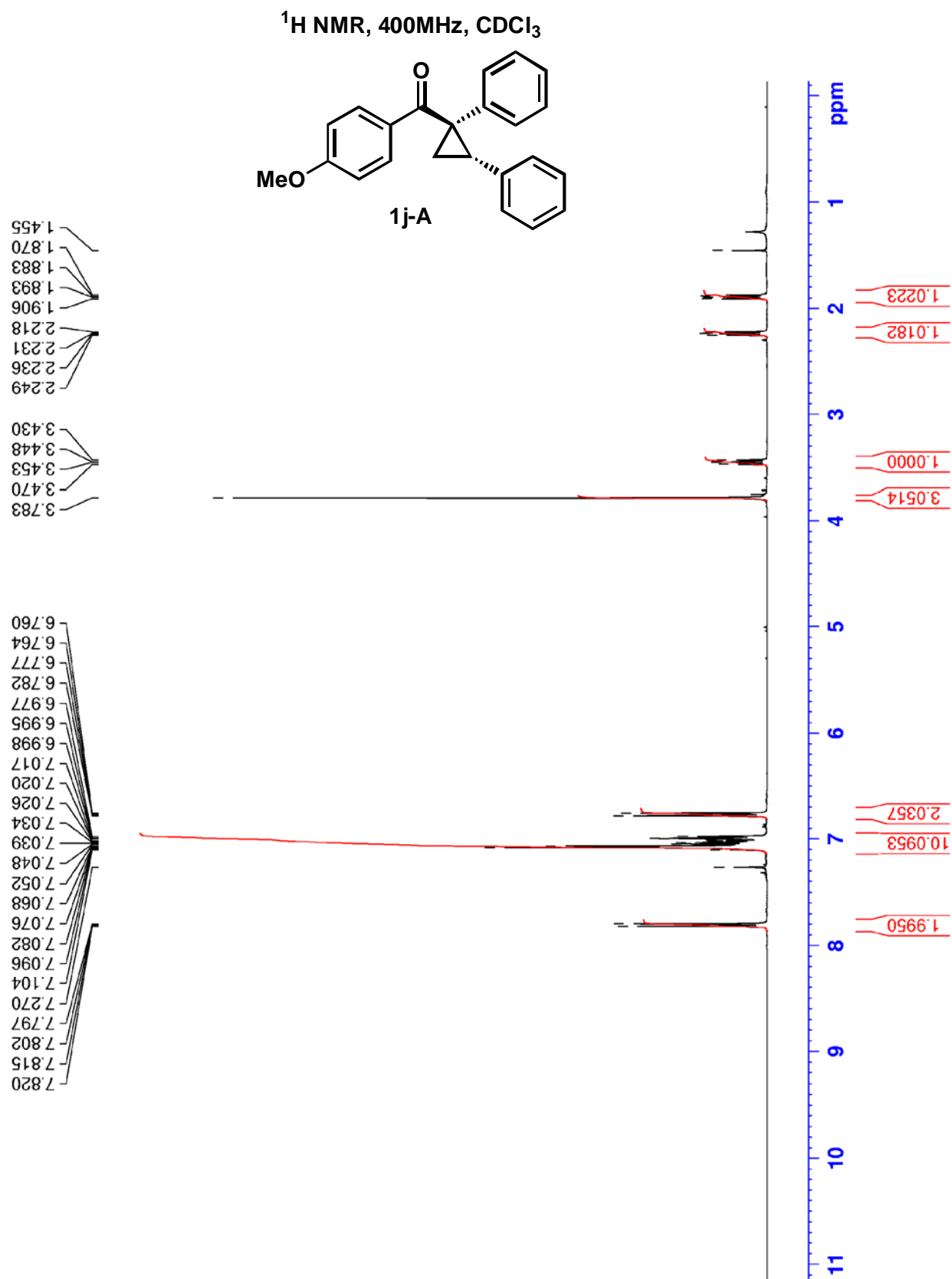


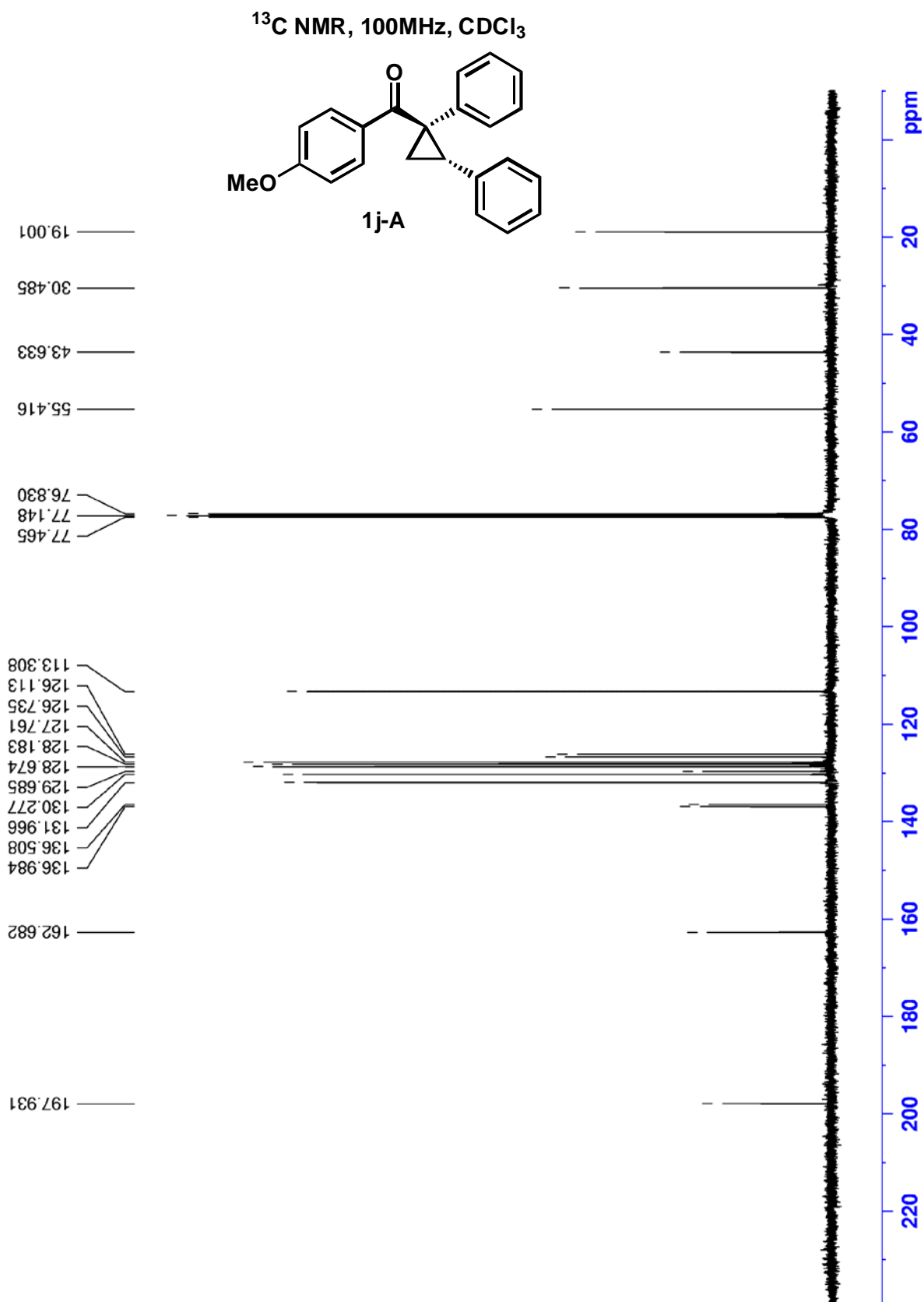


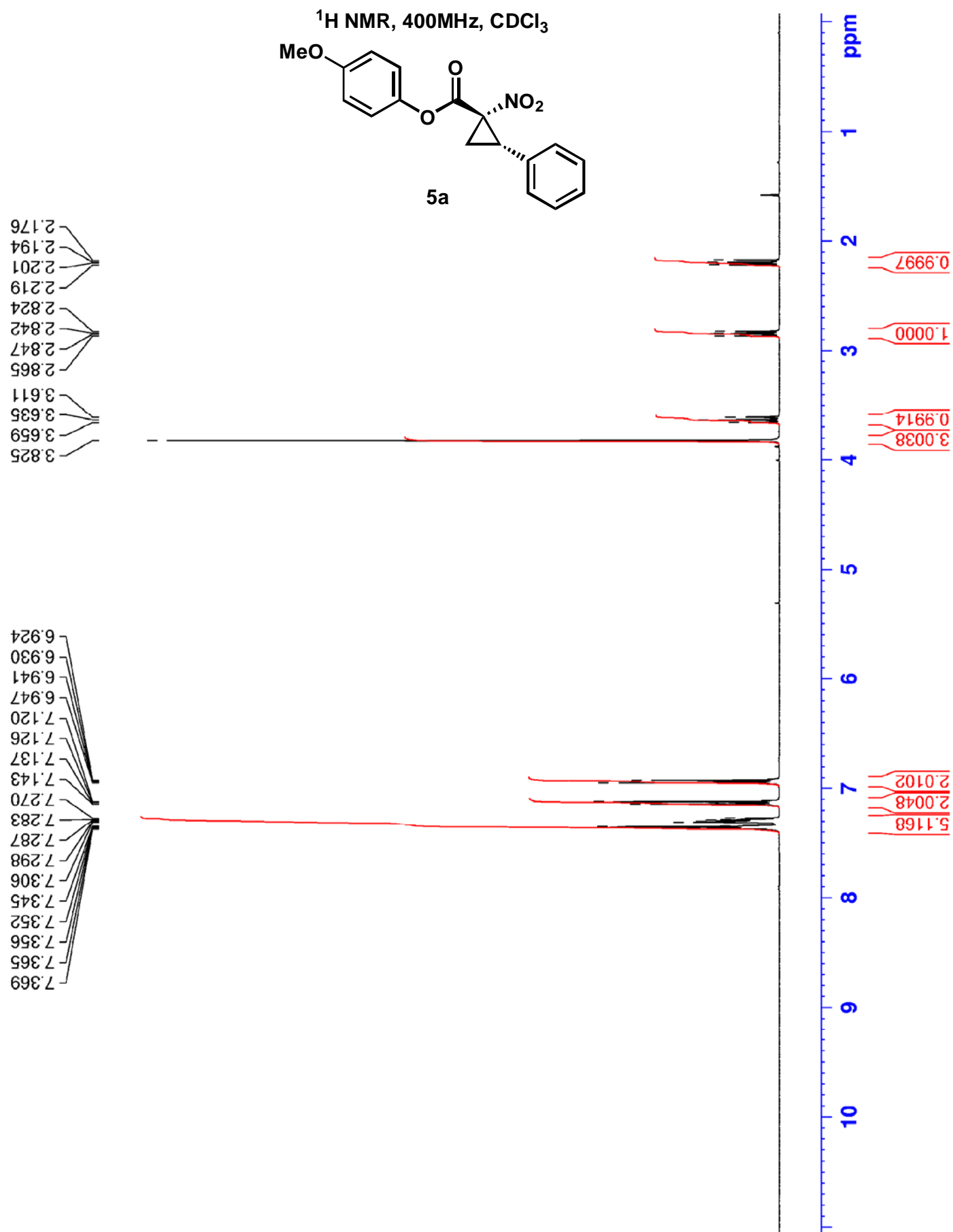


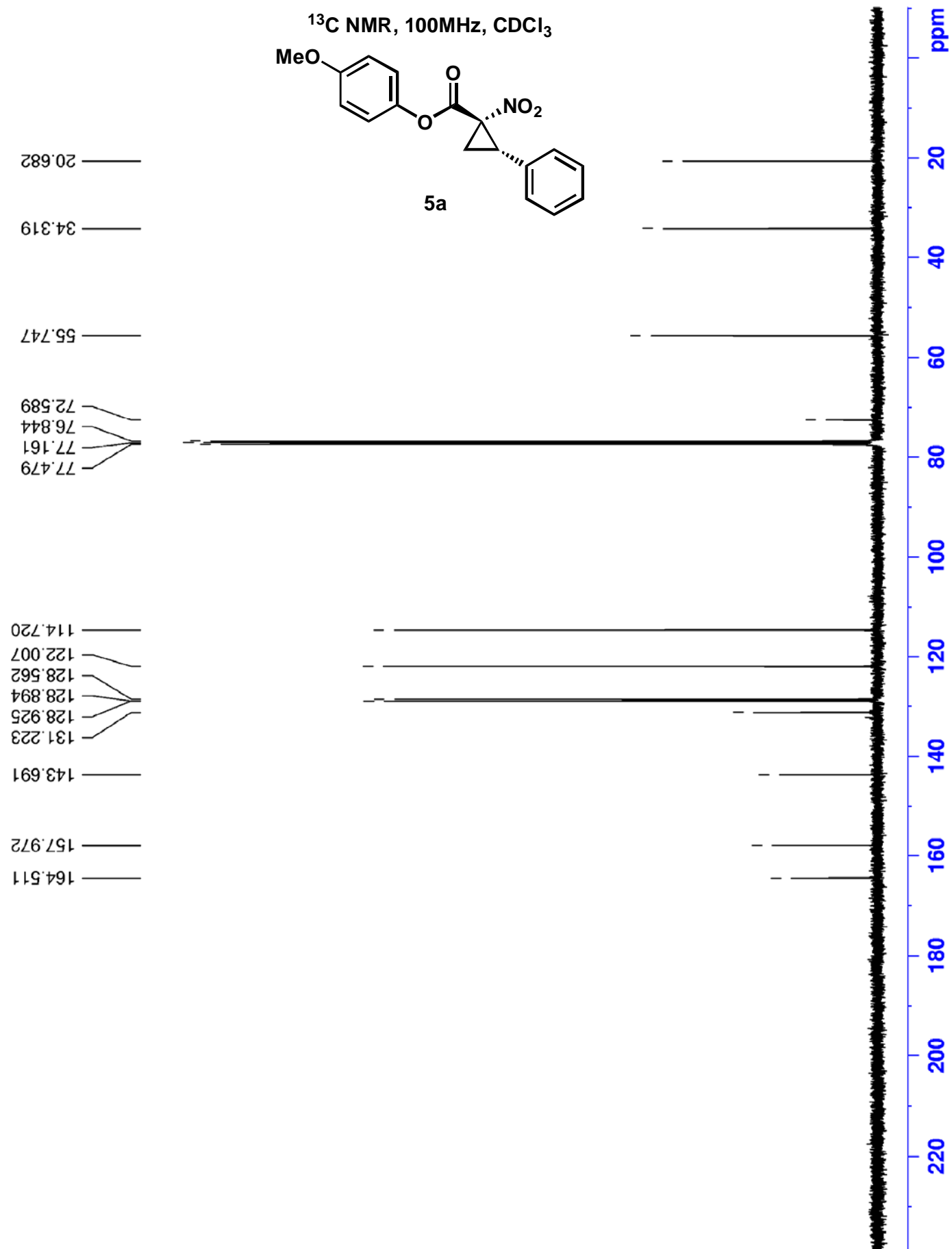


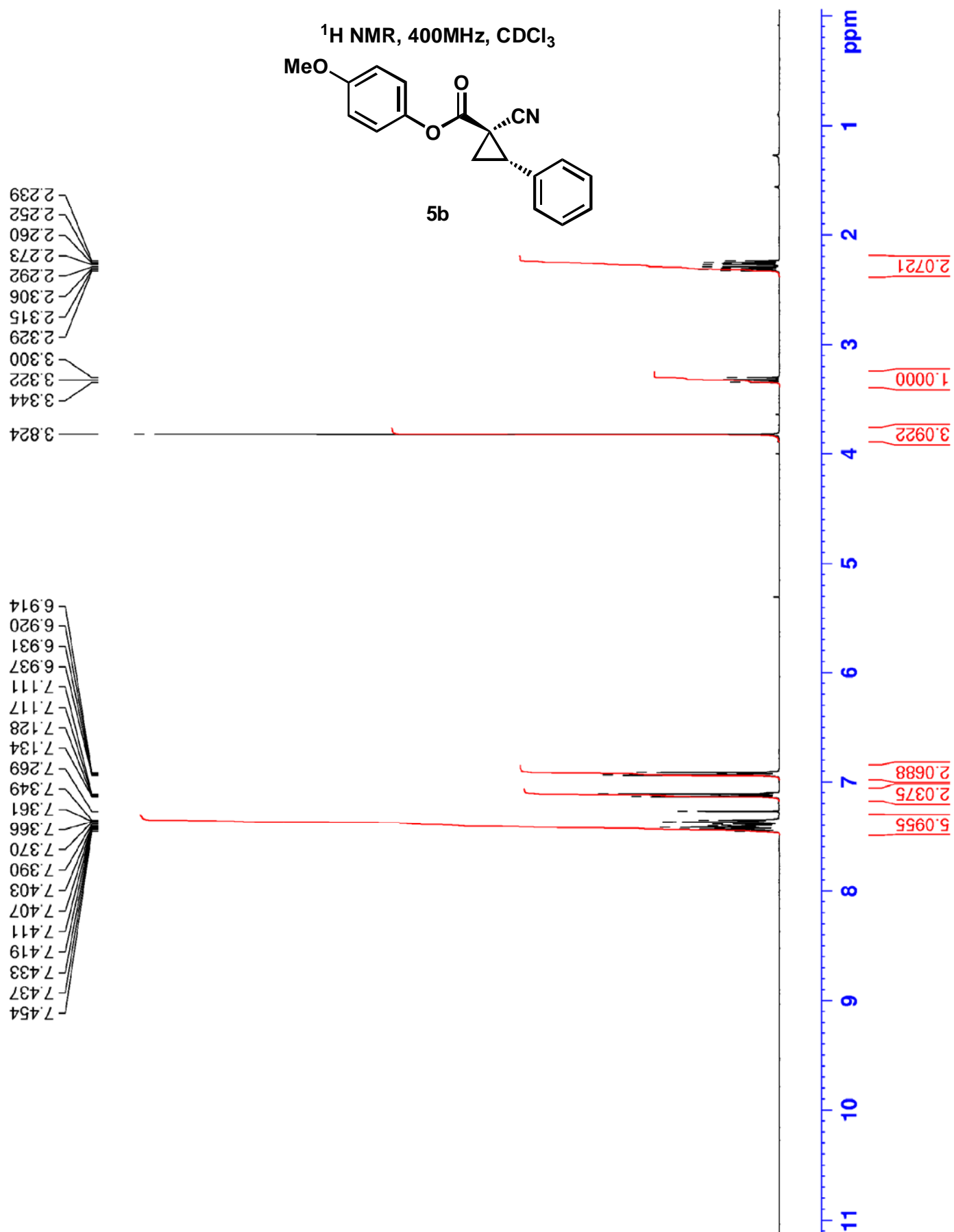


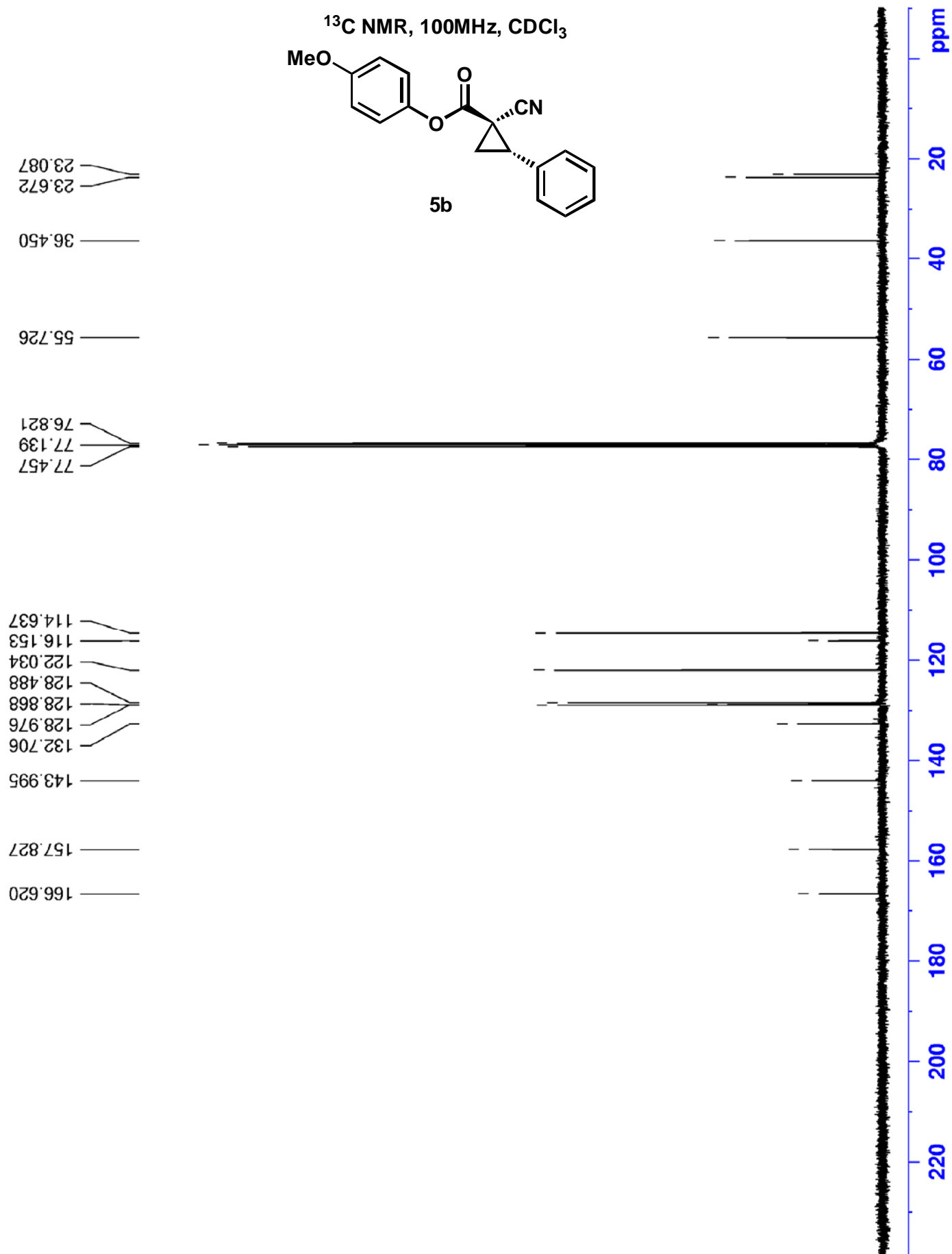


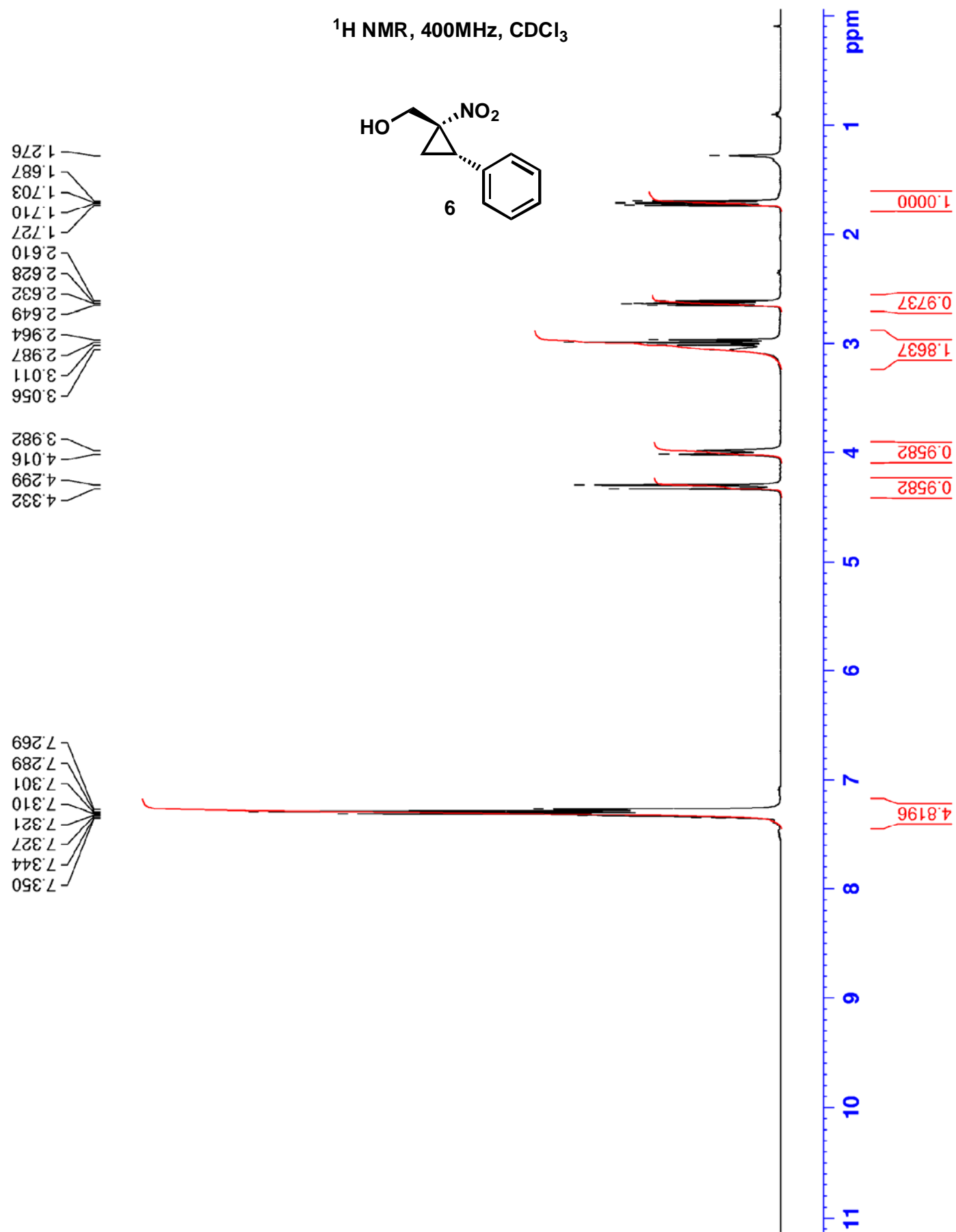


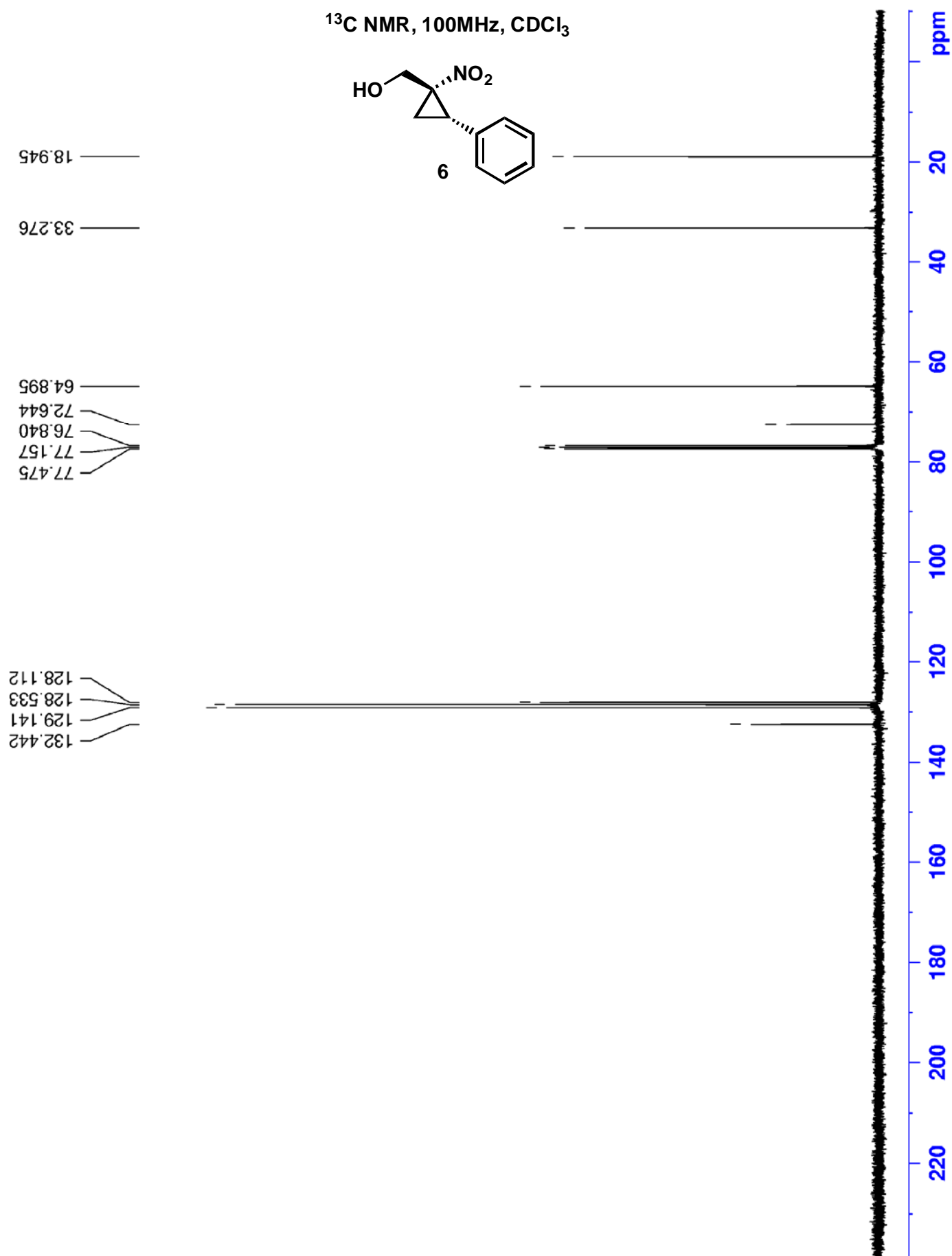


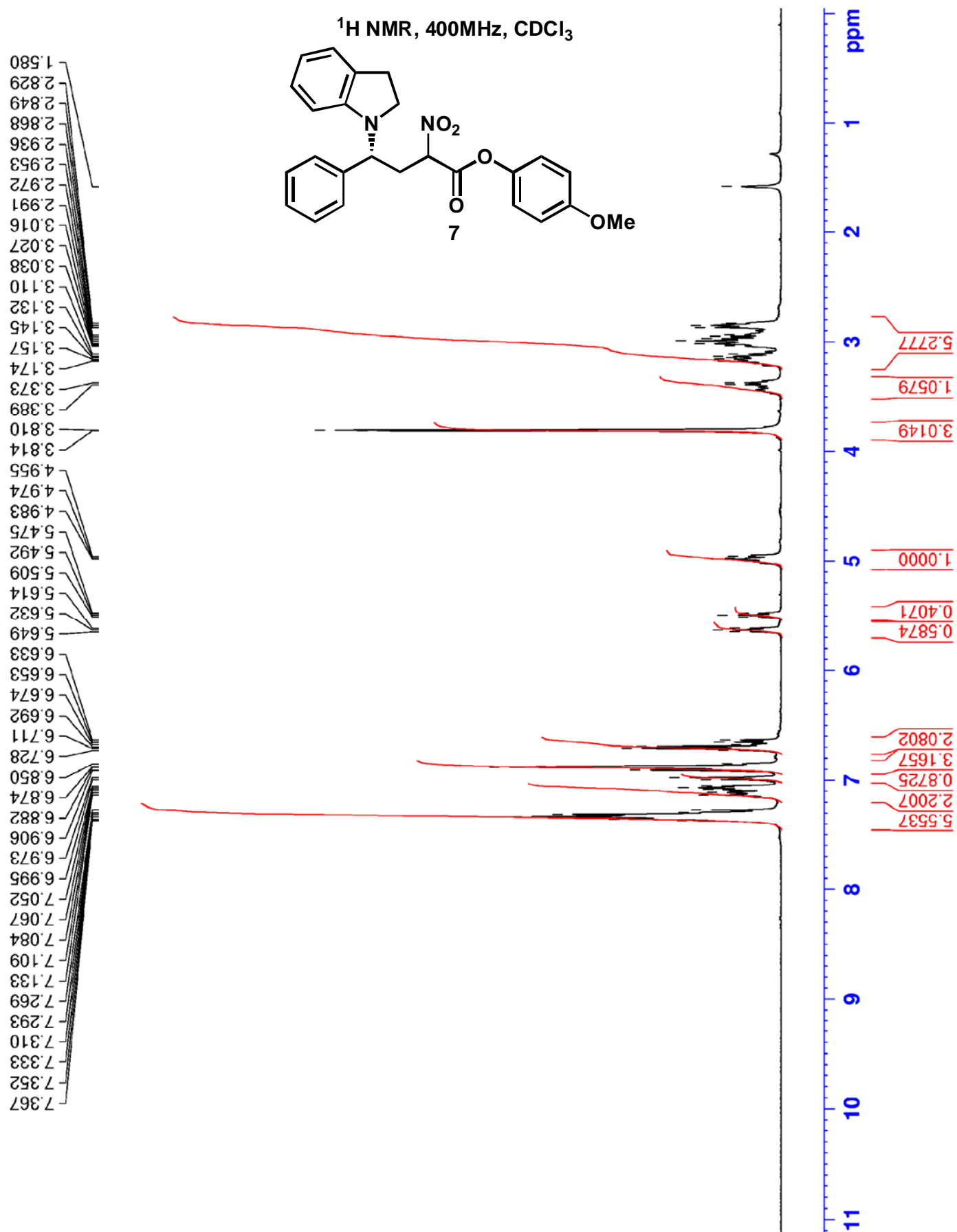


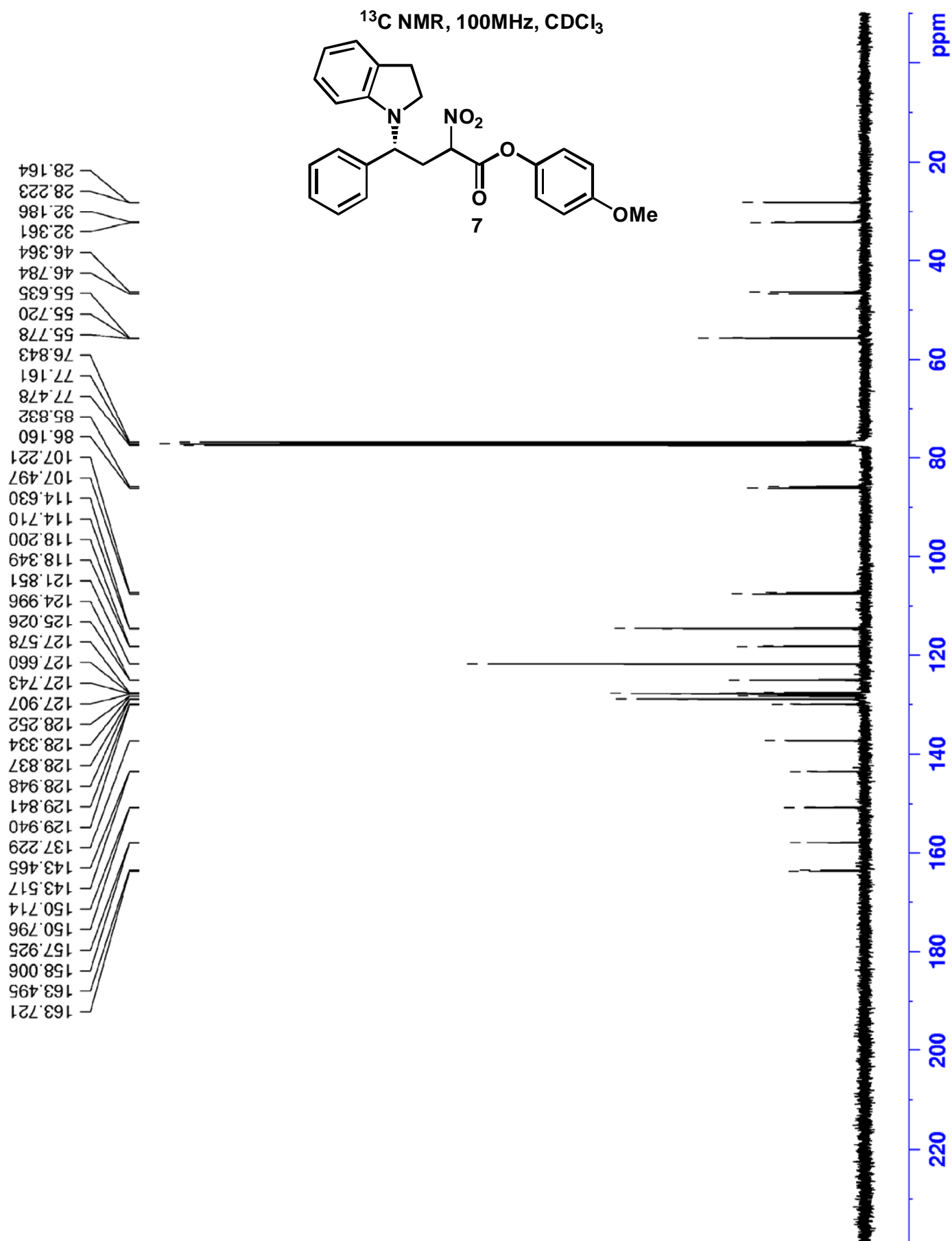


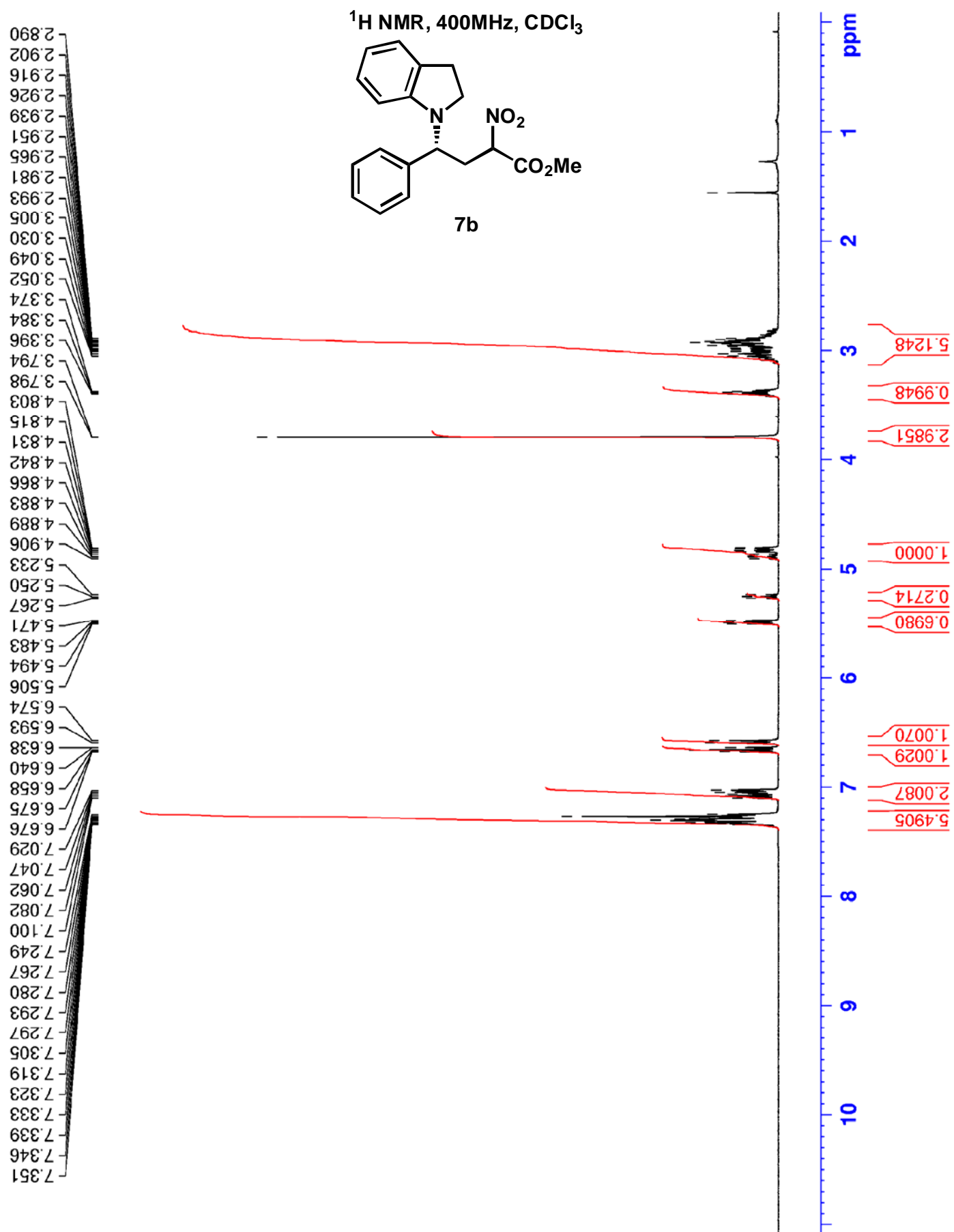


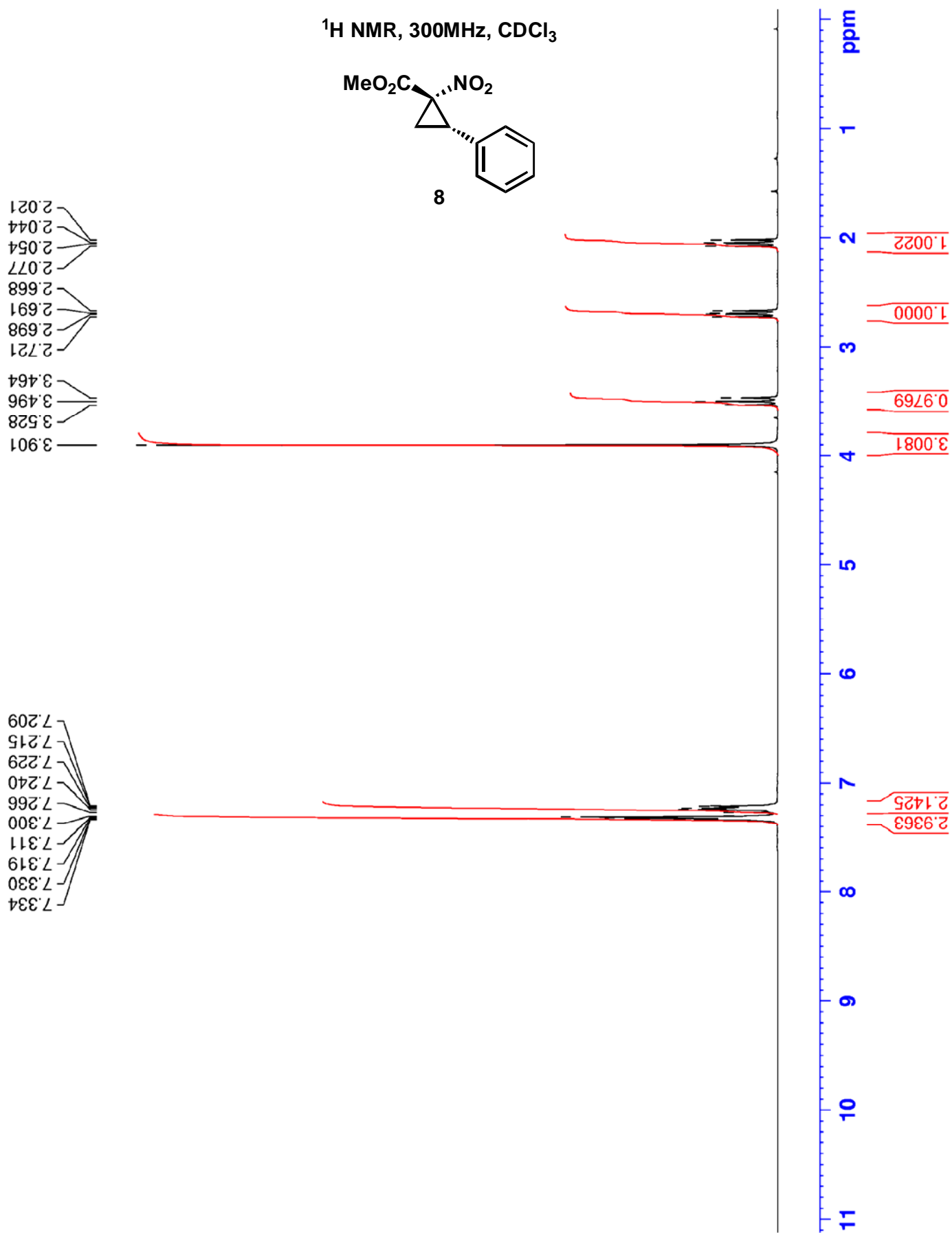


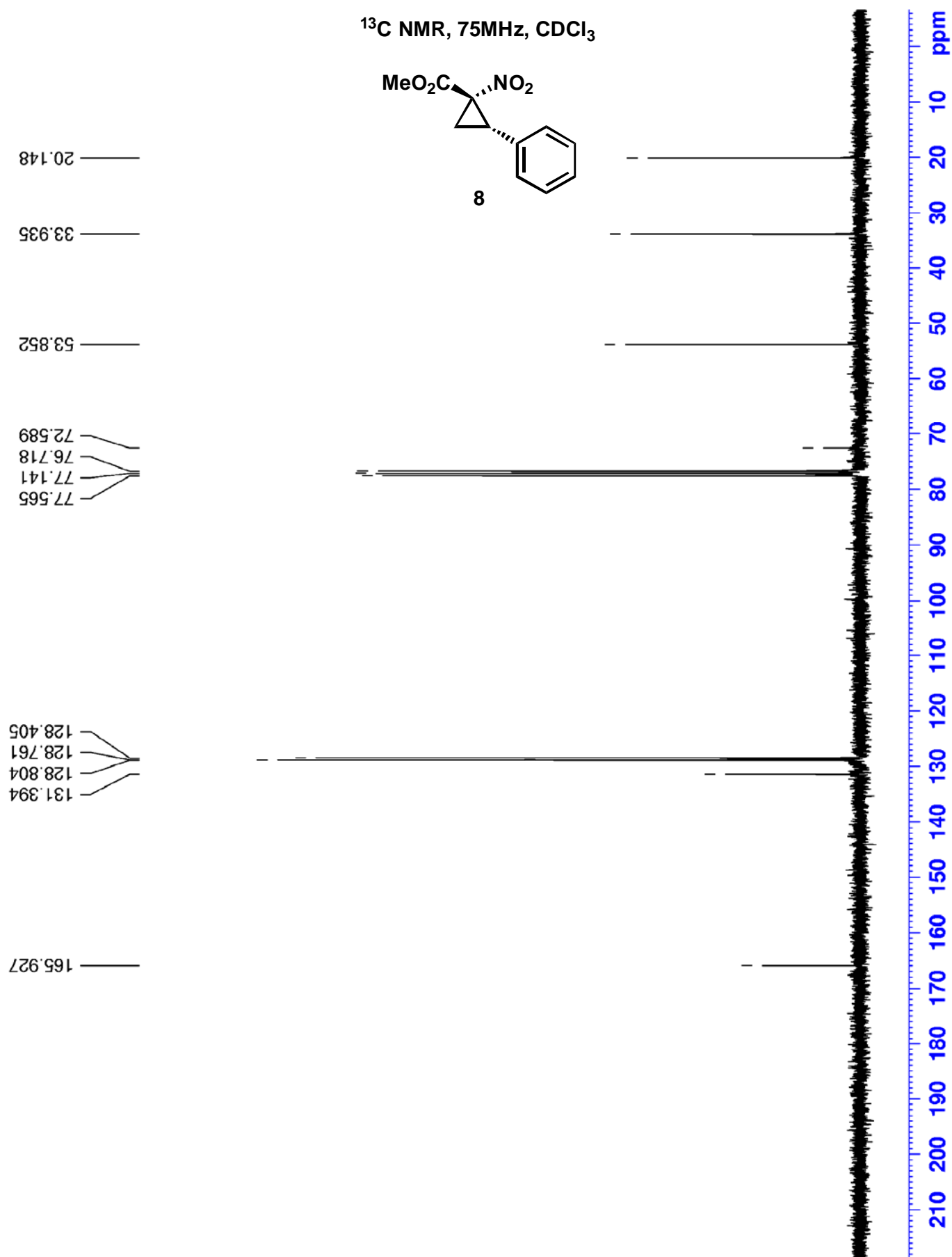


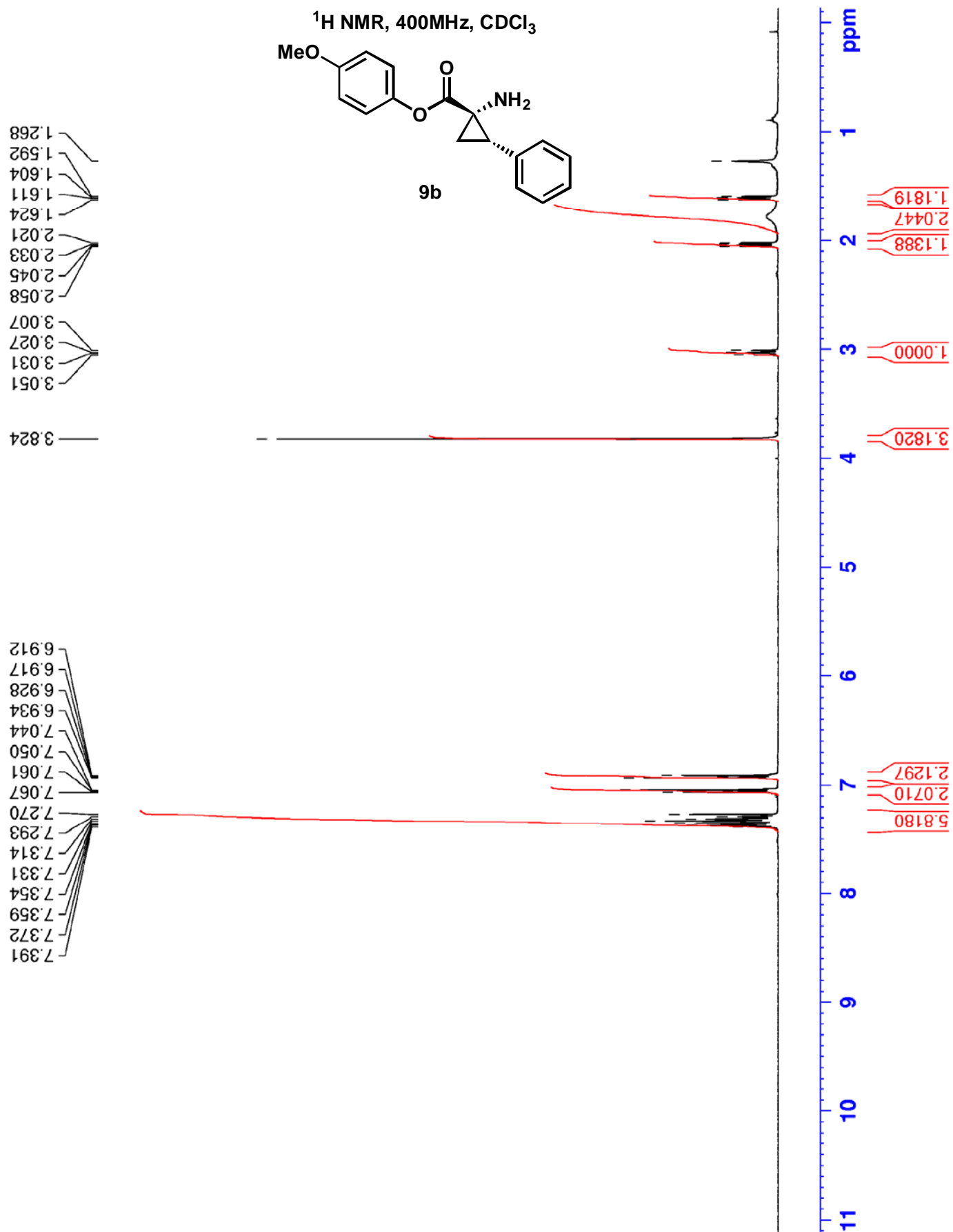


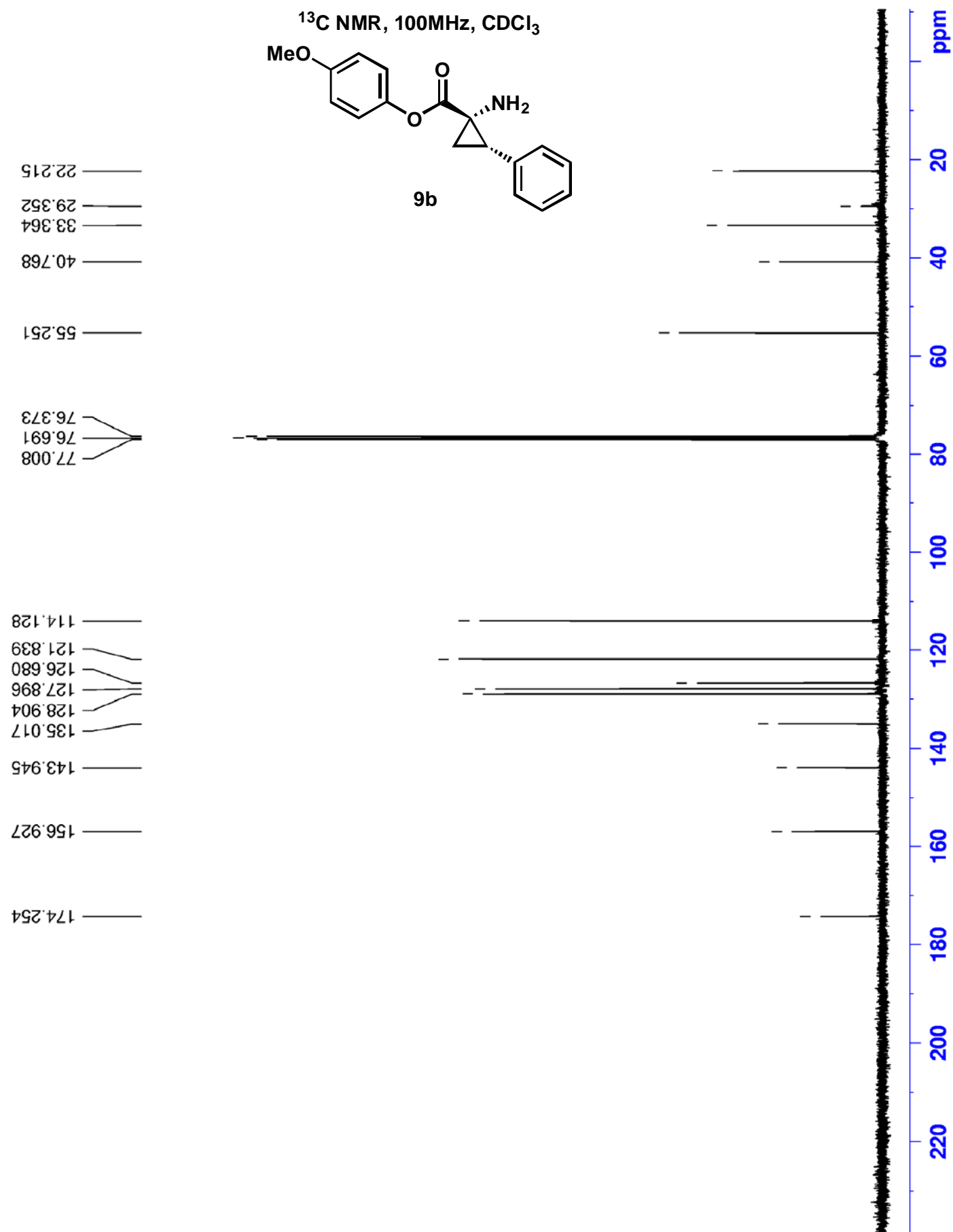


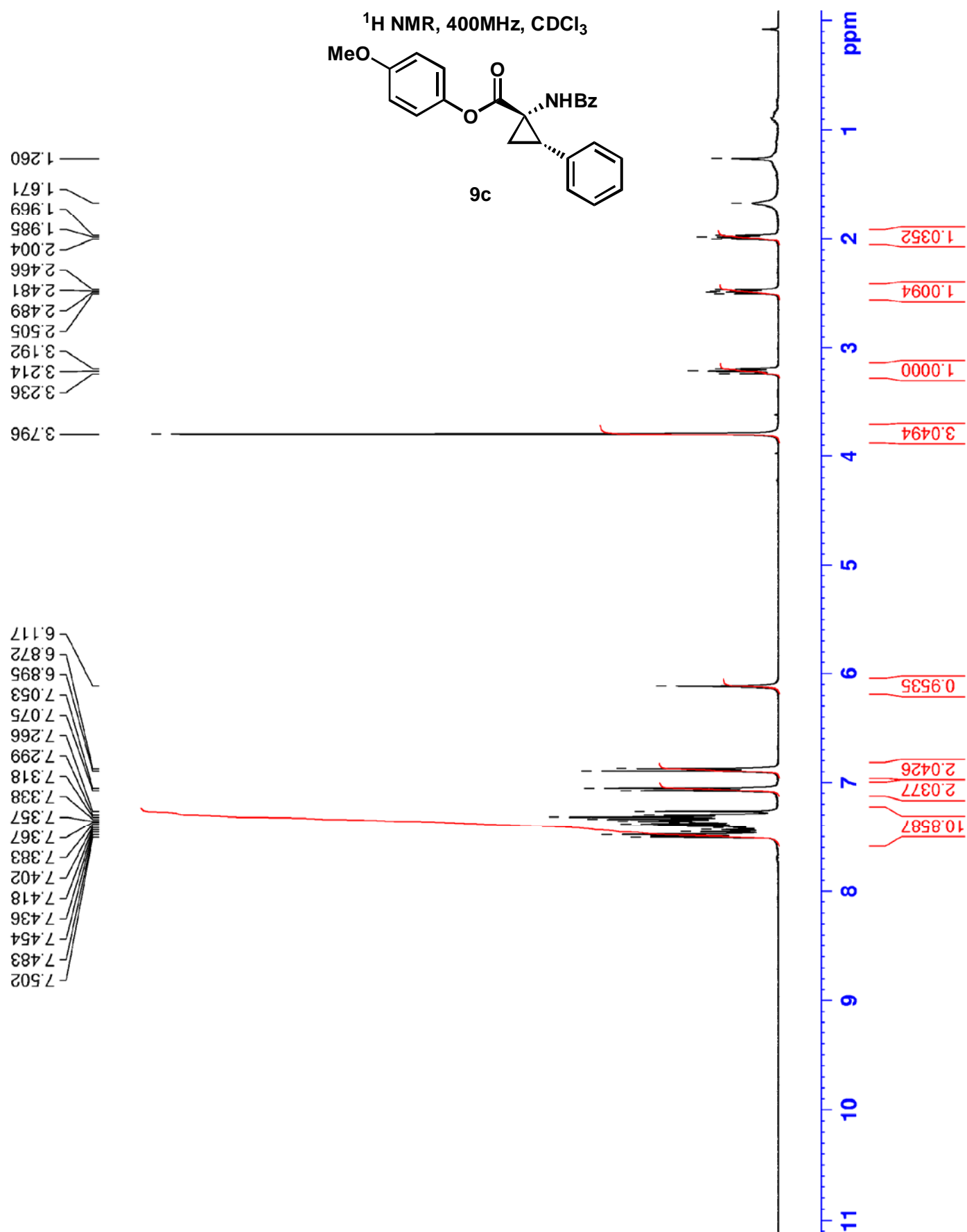


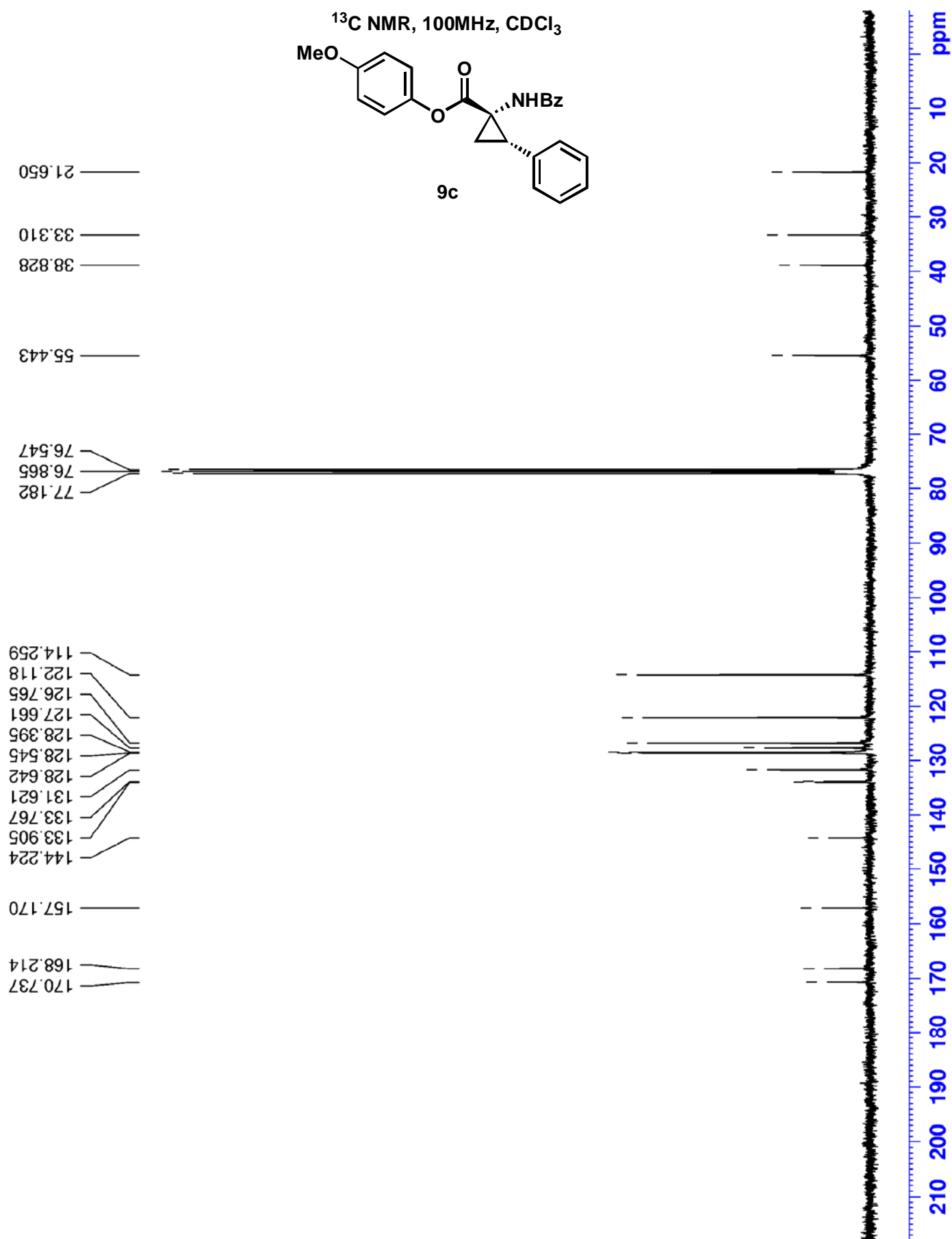


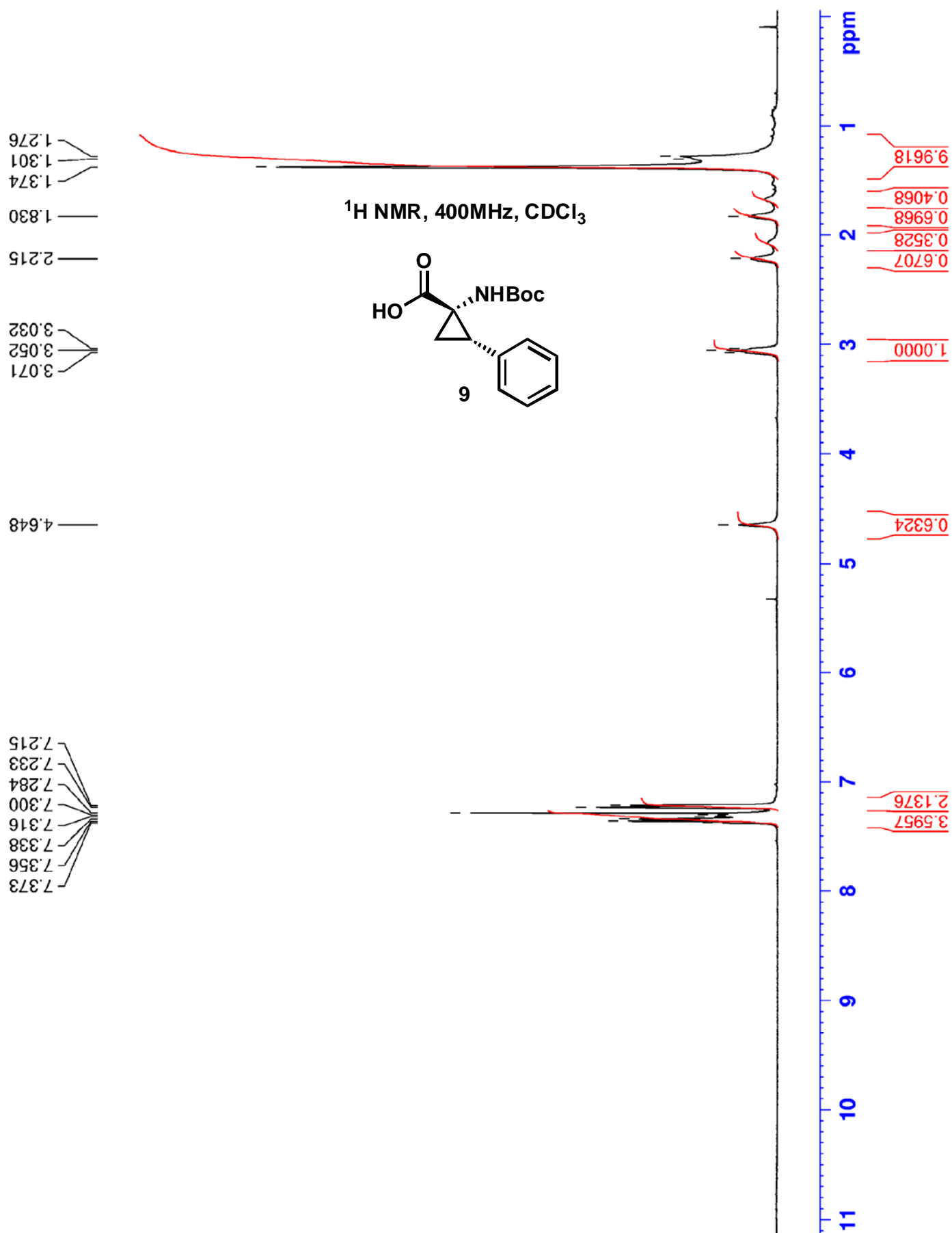


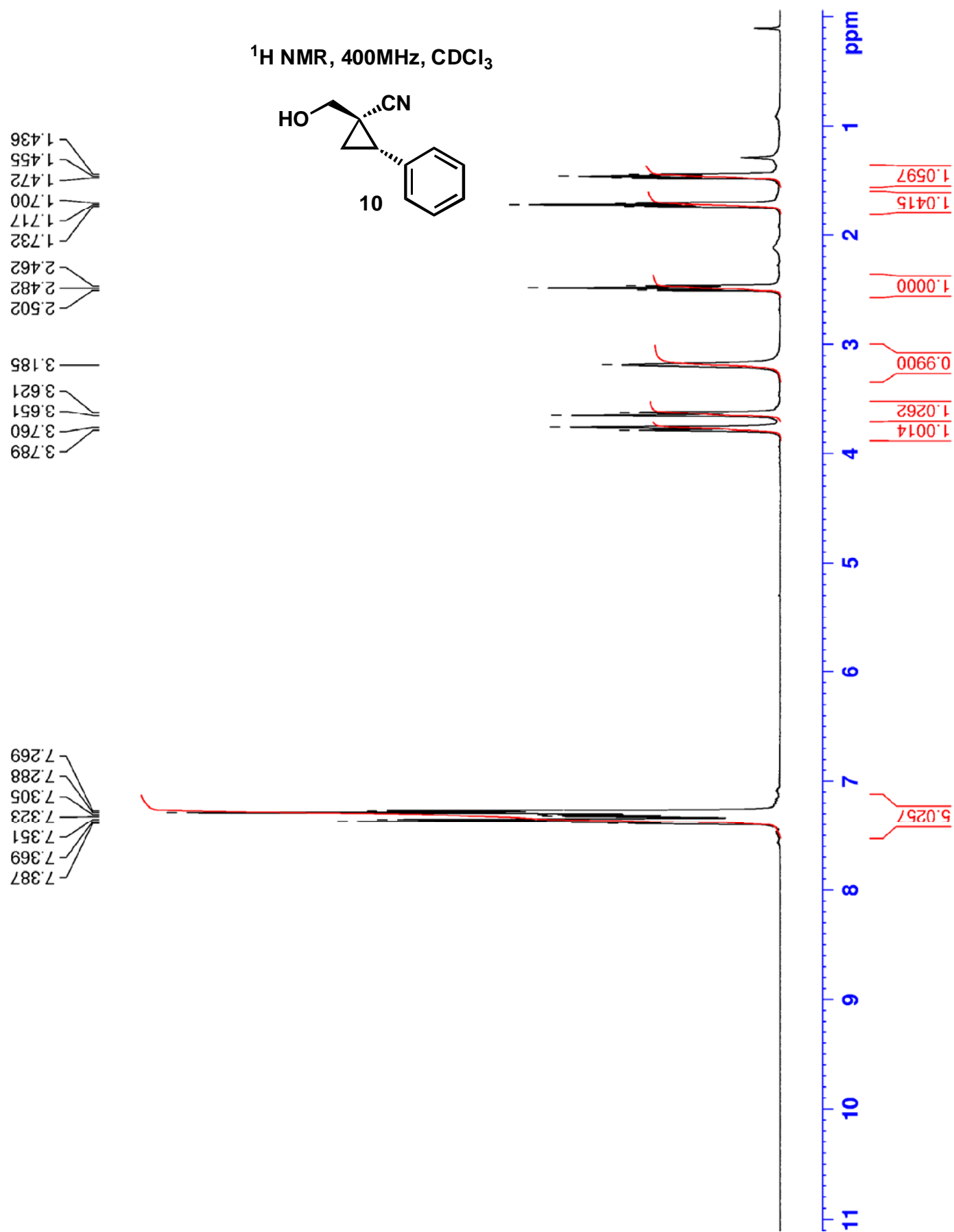


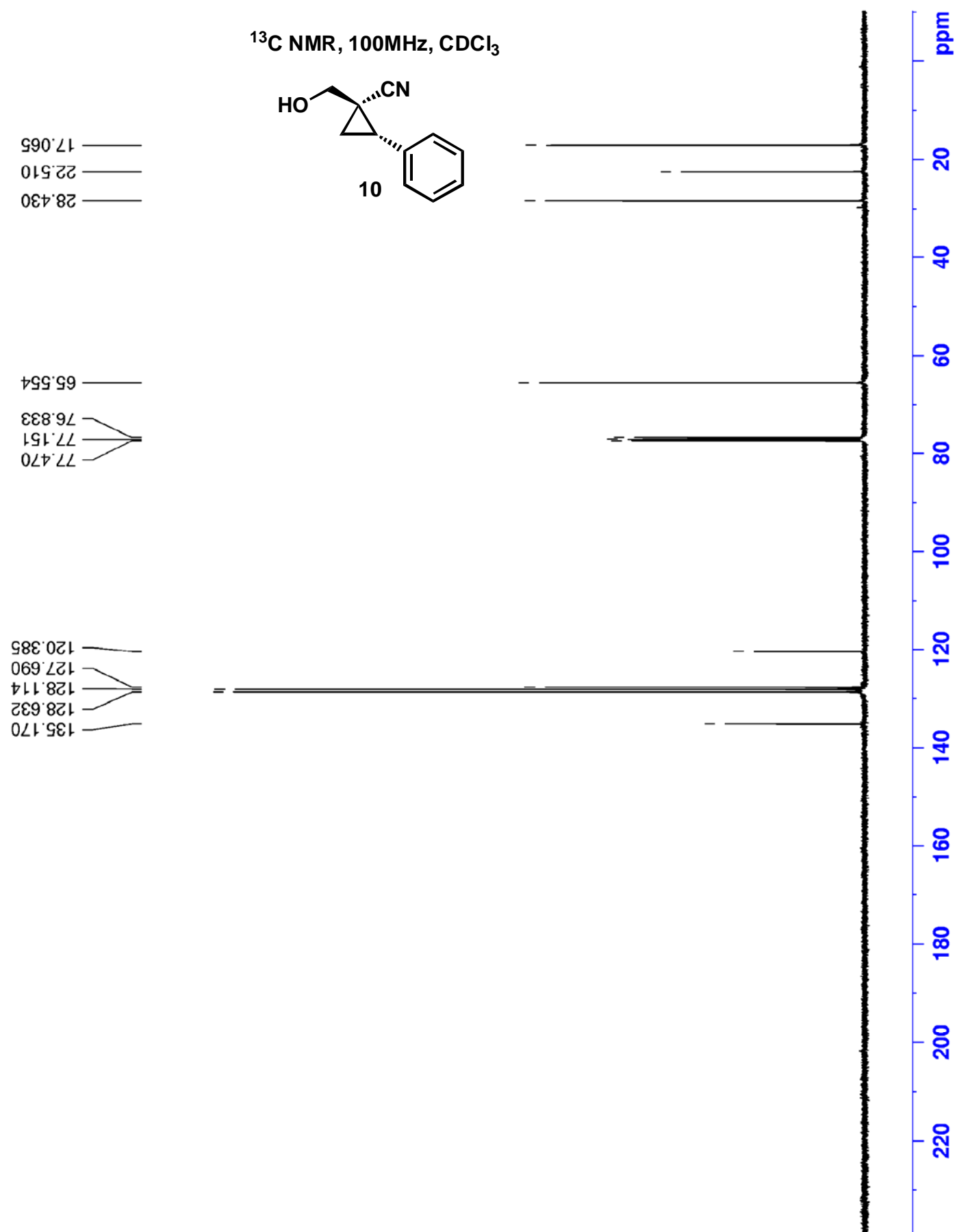




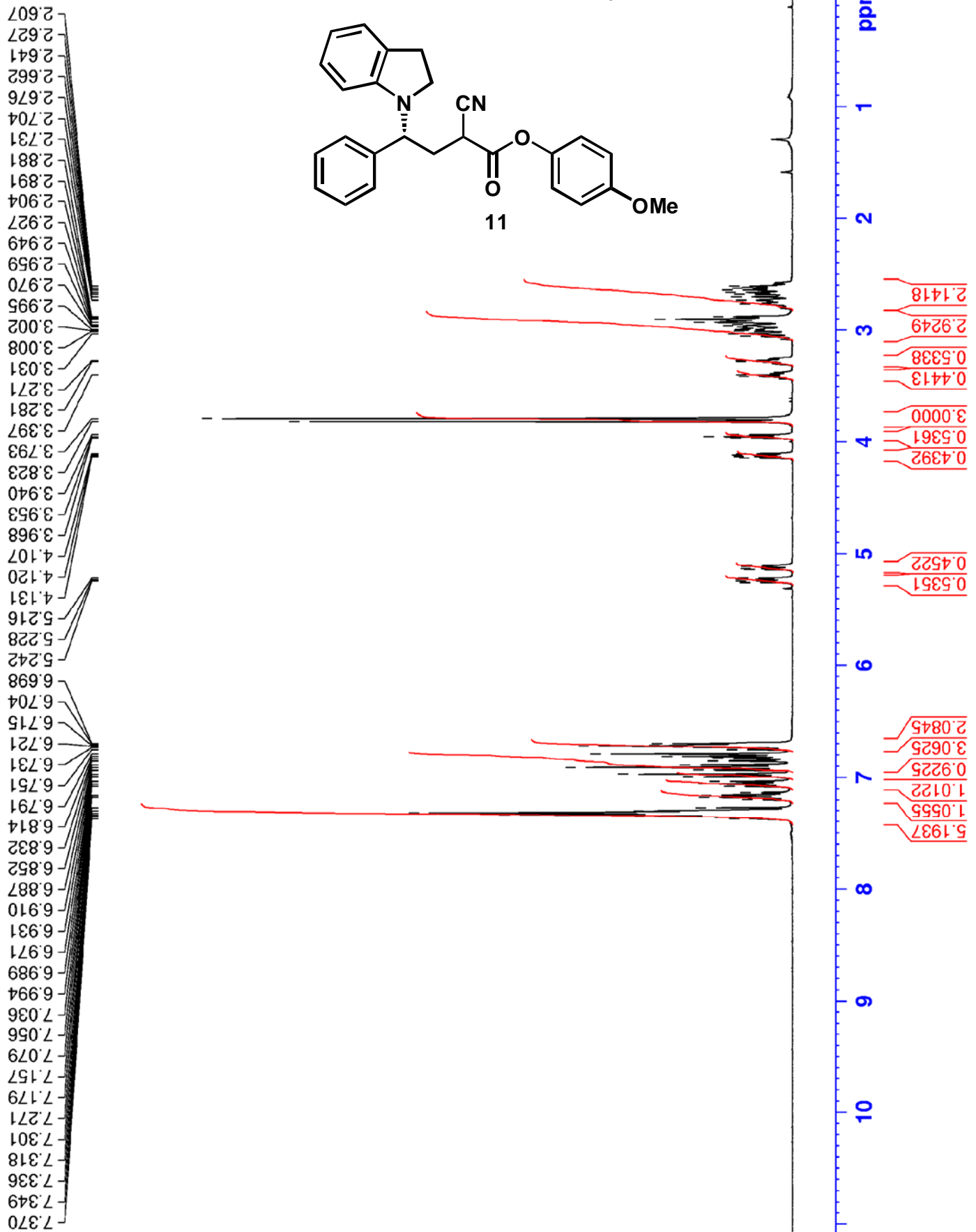








¹H NMR, 400MHz, CDCl₃



^{13}C NMR, 100MHz, CDCl_3 