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ELECTRONIC SUPPLEMENTARY INFORMATION

Cagelike Manganesesilsesquioxanes. Features of Synthesis, Unique Structure and Catalytic Activity in Oxidative Amidation

Grigorii S. Astakhov,[‡] Victor N. Khrustalev,[‡,//] Marina S. Dronova,[†] Evgenii I. Gutsul,[†] Alexander A. Korlyukov,[†,ɣ] Dmitri Gelman,[Δ] Yan V. Zubavichus,[§] Daniil Novichkov,[¥] Alexander L. Trigub,[$] Elena S. Shubina,[†] Alexey N. Bilyachenko*[,†‡]*

[†]A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street, 28, 119991 Moscow, Russia

[‡]Peoples' Friendship University of Russia, Miklukho-Maklay Street, 6, 117198 Moscow, Russia

[//]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow 119991, Russia

[ɣ]Pirogov Russian National Research Medical University, Ostrovitianov Str., 1, Moscow 117997, Russia

[Δ]Institute of Chemistry, Edmond J. Safra Campus, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

[§]Boreskov Institute of Catalysis SB RAS, prosp. Akad. Lavrentieva, 5, Novosibirsk 630090, Russia

[¥]Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1, Bld. 3, Moscow 119991, Russian Federation

[$]National Research Center "Kurchatov Institute", Akademika Kurchatova pl., 1, 123182 Moscow, Russia

General information

Commercially available compounds were purchased from Aldrich Chemical Co., Fluka, abcr Chemie Rus LLC, Alfa Aesar, Merck and used without further purification. All reactions, that

required heating, were proceeded in a silicon oil bath. Elemental analyses were carried out with a XRF spectrometer VRA-30 (Laboratory of Microanalysis at the INEOS RAS). IR spectra were recorded on FT-IR Shimadzu IR Prestige21 spectrometers in KBr pellets. UV-Vis spectra (10 mm optical path length) were recorded on a Cary 50 spectrophotometer. NMR measurements were performed at the INEOS RAS (Laboratory for Nuclear Magnetic Resonance) and at the Shared research and educational center of the Peoples' Friendship University of Russia (SREC PFUR, RUDN University). ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer and Bruker Avance 300 (75 MHz). Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 7.26 ppm, DMSO-D_6 at 2.50 ppm). Data are reported as br = broad, s = singlet, d = doublet, t = triplet, q = quadruplet, td = triplet of doublets, qt = quintuplet, sept = septuplet, ddd = doublet of doublets of doublets, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on Bruker Avance III HD 100 MHz spectrometer, on Bruker Avance 400 (100 MHz). Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 77.16 ppm, DMSO-D_6 at 39.52 ppm). For column chromatography were used commercially available silica gel 60 from Merck© (0.062-0.200 mm). TLC plates were purchased from Merck© (silica gel 60, F_{254}). TLC analysis were visualized by UV light and/or stained by slightly acidic aqueous solution of $KMnO_4$.

Mn K – edge XANES data were acquired on a laboratory spectrometer of the Department of Radiochemistry, Moscow State University (Moscow, Russia). Spectrometer was based on the design of Rowland circle 0.5 m. was equipped with an X-ray tube with a silver anode with a power of 1.5 kW, silicon drift detector (SDD; Amptek Inc.). and crystal-monochromator.
To monochromatize and focus the beam, Si (440) SBCA was used to scan the energy range 6520 – 6720 eV, with a step size of 1 eV and constant count time of 5s / point in the XANES region. The beam size was chosen to be 5 mm×5 mm. The data were collected in the transmission mode with sample (I) and without the sample (I0), as well as background measurements using the same scan parameters. Data integration time was 4h per spectrum.

Synthesis of **1:** 1000 mg (5.04 mmol) of $PhSi(OMe)_3$ and 242 mg (6.05 mmol) of NaOH were heated under reflux in 50 ml of mixture ethanol/methanol (1:1 v:v) for 2 h. Then 211 mg (1.68 mmol) of $MnCl_2$ was added and resulted brown-colored mixture was stirred without heating 24 h and was filtered from precipitate. Crystallization of the solution gave in ~1 week a brown crystalline material; several single crystals were used for X-ray diffraction analysis. Analysis of vacuum dried complex $[(Ph_6Si_6O_{12})_2Mn^{II}_2Mn^{III}_2Na_6O_2(EtOH)_9(MeOH)_{0.5}(H_2O)_{1.5}] \cdot 2EtOH$ **1** – calculated for $(Ph_6Si_6O_{12})_2Mn_4Na_6O_2$: Si, 16.55; Mn, 10.79; Na, 6.78. Found: Si, 16.40; Mn, 10.66; Na, 6.69. Yield: 0.79 g (73 %).

Synthesis of **2:** 1000 mg (5.04 mmol) of $PhSi(OMe)_3$ and 218 mg (5.46 mmol) of NaOH were heated under reflux in 50 ml of mixture ethanol/methanol (1:1 v:v) for 2 h. Then 317 mg (2.52 mmol) of $MnCl_2$ and 20 mL of 1,4-dioxane were added to the corresponding solution. The resulted brown-colored mixture was stirred without heating 24 h and was filtered from precipitate. Crystallization of the solution gave in ~1 week a brown crystalline material; several

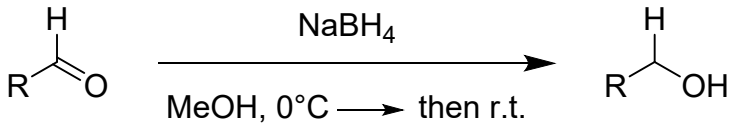
single crystals were used for X-ray diffraction analysis. Analysis of vacuum dried complex $[(Ph_6Si_6O_{12})_2Mn^{II}_6Cl(C_4H_8O_2)_3(H_2O)_3][Na(C_4H_8O_2)_{0.875}(H_2O)_{5.125}] \bullet 0.75C_4H_8O_2$ **2** – calculated for $NaCl(Ph_6Si_6O_{12})_2Mn_6$: Si, 16.57; Mn, 16.20; Na, 1.13. Found: Si, 16.49; Mn, 16.12; Na, 1.07. Yield: 0.73 g (60 %).

Synthesis of **3:** 1000 mg (5.04 mmol) of $PhSi(OMe)_3$ and 235 mg (5.88 mmol) of NaOH were heated under reflux in 50 ml of ethanol for 2 h. Then 211 mg (1.68 mmol) of $MnCl_2$ in 20 mL of DMF were added to the corresponding solution. The resulted brown-colored mixture was stirred without heating 24 h and mixed with 76 mg (0.42 mmol) of 1,10-phenanthroline. Mixture was stirred for 3 h, filtered from precipitate and mixed with 15 mL of pyridine. Crystallization of the solution gave in ~5 days a brown crystalline material; several single crystals were used for X-ray diffraction analysis. Analysis of vacuum dried complex $[(Ph_6Si_6O_{12})_2Mn^{II}Mn^{III}_3Na_2Cl(Phen)(Py)_2(DMF)_{2.5}] \bullet 1¼DMF$ **3** – calculated for $(phen)(Ph_6Si_6O_{12})_2ClMn_5Na_2$: Si, 15.84; Mn, 10.33, N, 1.32; Na, 2.16. Found: Si, 15.79; Mn, 10.26, N, 1.25; Na, 2.09. Yield: 0.73 g (60 %).

Synthesis of **4:** 1000 mg (5.04 mmol) of $PhSi(OMe)_3$ and 202 mg (5.04 mmol) of NaOH were heated under reflux in 50 ml of ethanol for 2 h. Then 317 mg (2.52 mmol) of $MnCl_2$ in 20 mL of DMF were added to the corresponding solution. The resulted brown-colored mixture was stirred without heating 24 h and mixed with 182 mg (1.01 mmol) of 1,10-phenanthroline. Mixture was stirred for 3 h and filtered from precipitate. Crystallization of the solution gave in ~1 week a brown crystalline material; several single crystals were used for X-ray diffraction analysis. Analysis of vacuum dried complex $[(Ph_5Si_5O_{10})_2Mn^{II}_3Mn^{III}_2Cl(OH)(Phen)_2(DMF)_2] \bullet 2⅓EtOH$ **4** – calculated for $(phen)_2[(Ph_5Si_5O_{10})_5]_2Cl(OH)Mn_5$: Si, 13.64; Mn, 13.34; N, 2.72. Found: Si, 13.60; Mn, 13.28; N, 2.63. Yield: 0.53 g (48 %).

Synthesis of **5:** 1000 mg (5.04 mmol) of $PhSi(OMe)_3$ and 202 mg (5.04 mmol) of NaOH were heated under reflux in 50 ml of ethanol for 2 h. Then 317 mg (2.52 mmol) of $MnCl_2$ in 20 mL of DMF were added to the corresponding solution. The resulted brown-colored mixture was stirred without heating 24 h and mixed with 454 mg (2.52 mmol) of 1,10-phenanthroline Mixture was stirred for 3 h and filtered from precipitate. Crystallization of the solution gave in ~5 days a brown crystalline material; several single crystals were used for X-ray diffraction analysis. Analysis of vacuum dried complex $[(Ph_4Si_4O_8)_2Mn^{II}_2Mn^{III}_2(OH)_2(Phen)_4] \bullet 4½DMF$ **5** – calculated for $(phen)_4[(PhSiO_2)_4]_2(OH)_2Mn_4$ Si, 10.84; Mn, 10.61; N, 5.41. Found: Si, 10.76; Mn, 10.53; N, 5.34. Yield: 0.52 g (39 %).

General procedure for the synthesis of alcohols by the reduction of aldehydes:



R=Aryl, alkenyl

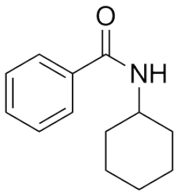
Synthesis of **(4-nitrophenyl)methanol**, (**4-methylphenyl)methanol** and **(E)-3-phenylprop-2-en-1-ol.** To a solution of the corresponding aldehyde (1.0 equiv.) in methanol (0.4 M) was added sodium borohydride (2.5 equiv.) at 0°C. The mixture was stirred at r.t. until complete by TLC analysis. The mixture was concentrated under reduced pressure before being diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and further under vacuum to afford the product without further purification[s1,s2] [**(4-nitrophenyl)methanol**, yield 85%; (**4-methylphenyl)methanol**, yield 90%; **(E)-3-phenylprop-2-en-1-ol**, yield 82%).

Procedure A for the synthesis of amides from alcohols: In a sealed vial (10 mL) were added amine hydrochloride (0.5 mmol), $CaCO_3$ (≥99%, 50.0 mg, 0.5 mmol), manganese catalyst **1** (13 mg), dried MeCN (1 mL), alcohol (1.0 mmol), and TBHP (5.0-6.0 M in decane, 225 μL, 1.25 mmol) respectively. The sealed vial with reaction mixture was purged by argon and was stirred at 80°C for 2h. Thereafter a new portion of TBHP (5.0-6.0 M in decane, 225 μL, 1.25 mmol) was added to the reaction mixture, purged by argon and the reaction was carried out for 22h at 80°C. Afterwards all volatiles was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (gradients of cyclohexane/AcOEt) to afford the corresponding amides.

Procedure B for the synthesis of amides from aldehydes: In a sealed vial (10 mL) were added amine hydrochloride (1.1 mmol), $CaCO_3$ (≥99%, 120.0 mg, 1.2 mmol), manganese catalyst **1** (13 mg), dried MeCN (0.2 mL), aromatic aldehyde (1.0 mmol), and TBHP (5.0-6.0 M in decane, 220 μL, 1.2 mmol) respectively. The sealed vial with reaction mixture was purged by argon and was stirred at 45°C for 8h. Afterwards all volatiles was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (gradients of cyclohexane/AcOEt) to afford the corresponding amides.

NMR data of synthesized amides

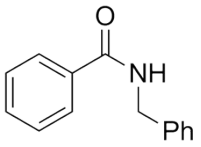
***N*-cyclohexylbenzamide (8)**



Following the procedure **A**, the main product was obtained as colorless solid (85 mg, 84% yield; eluent: EtOAc/hexane = 1:5); Following the procedure **B**, the main product was obtained as

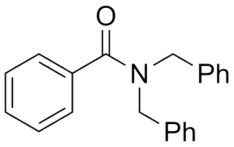
colorless solid (128 mg, 63%); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 7.4 Hz, 2H, *o*-H-Ar), 7.50-7.47 (m, 1H, *p*-H-Ar). 7.44-7.40 (t, *J* = 7.2 Hz, 2H, *m*-H-Ar), 5.97 (br, 1H, -CO-N*H*-), 4.03-3.93 (m, 1H, -CO-NH-C*H*(R'R'')), 2.05-2.02 (m, 2H, aliph.), 1.78-1.73 (m, 2H, aliph.), 1.67-1.63 (m, 1H, aliph.), 1.45-1.38 (m, 2H, aliph.), 1.25-1.19 (m, 3H, aliph.) **(Fig. S1)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 135.2, 131.3, 128.6, 126.9, 48.8, 33.3, 25.7, 25.0 **(Fig. S2)**.

***N*-benzylbenzamide (9)**



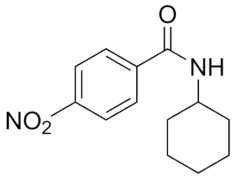
Following the procedure **A**, the main product was obtained as colorless solid (73 mg, 69% yield; eluent: EtOAc/hexane = 1:2); Following the procedure **B**, the main product was obtained as colorless solid (137 mg, 65%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.79 (d, *J* = 7.4 Hz, 2H, *o*-H-Ar), 7.53-7.31 (m, 8H, H-Ar), 6.39 (br, 1H, -CO-N*H*-), 4.67 (d, *J* = 5.1 Hz, 2H, -CH_2-C_6H_5) **(Fig. S3)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.6, 138.3, 134.4, 131.6, 128.8, 128.6, 127.9, 127.6, 127.1, 44.2 **(Fig. S4)**.

***N*,*N*-dibenzylbenzamide (10)**



Following the procedure **A**, the main product was obtained as colorless solid (116 mg, 77% yield; eluent: EtOAc/hexane = 1:4); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.50 (s, 2H, *o*-H-Ar), 7.39-7.31 (m, 11H, H-Ar), 7.15 (s, 2H, H-Ar), 4.71 (s, 2H, -CH_2-C_6H_5), 4.41 (s, 2H, -CH_2-C_6H_5) **(Fig. S5)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 172.4, 136.2, 129.8, 129.0, 128.8, 128.6, 128.5, 127.8, 127.6, 127.1, 126.8, 51.6, 47.0 **(Fig. S6)**.

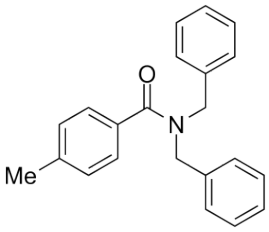
***N*-cyclohexyl-4-nitrobenzamide (11)**



Following the procedure **A**, the main product was obtained as slightly yellowish solid (114 mg, 92% yield; eluent: EtOAc/hexane = 1:5); **^{1}H NMR (400 MHz, DMSO-d_6)**: δ 8.29 (d, *J* = 8.6 Hz, 2H, *o*-H-Ar), 8.07 (d, *J* = 9.0 Hz, 2H, *m*-H-Ar), 3.80-3.73 (m, 1H, -CO-N*H*-), 1.84-1.80 (m, 2H,

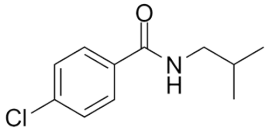
aliph.), 1.75-1.71 (m, 2H, aliph.), 1.63-1.62 (m, 1H, aliph.), 1.33-1.27 (m, 3H, aliph.), 1.16-1.11 (m, 1H, aliph.) **(Fig. S7)**; **^{13}C NMR (100 MHz, DMSO-*d*$_6$)**: *δ* 163.8, 148.9, 140.6, 128.9, 123.4, 48.8, 32.3, 25.3, 24.9 **(Fig. S8)**.

***N*,*N*-dibenzyl-4-methylbenzamide (12)**



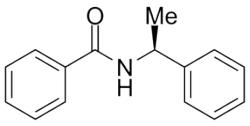
Following the procedure **A**, the main product was obtained as colorless solid (123 mg, 78% yield; eluent: EtOAc/hexane = 1:4); **^{1}H NMR (400 MHz, CDCl$_3$)**: *δ* 7.42-7.28 (m, 10H, H-Ar), 7.19-7.17 (m, 4H, H-Ar), 4.69 (s, 2H, -C*H*$_2$-C$_6$H$_5$), 4.42 (s, 2H, -C*H*$_2$-C$_6$H$_5$), 2.35 (s, 3H, CH$_3$) **(Fig. S9)**; **^{13}C NMR (100 MHz, CDCl$_3$)**: *δ* 172.5, 139.9, 137.1, 136.6, 133.2, 129.7, 129.2, 128.8, 128.6, 128.5, 127.6, 127.0, 126.9, 126.8, 51.6, 46.9, 21.4 **(Fig. S10)**.

4-chloro-*N*-(2-methylpropyl)benzamide (13)



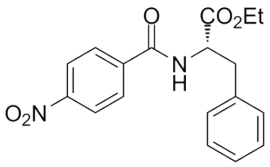
Following the procedure **A**, the main product was obtained as colorless solid (94 mg, 89% yield; eluent: EtOAc/hexane = 1:2); **^{1}H NMR (400 MHz, CDCl$_3$)**: *δ* 7.70 (d, *J* = 8.3 Hz, 2H, *o*-H-Ar), 7.39 (d, *J* = 8.3 Hz, 2H, *m*-H-Ar), 6.20 (br, 1H, -CO-N*H*-), 3.28 (t, *J* = 6.0 Hz, 2H, -C*H*$_2$-CH(CH$_3$)$_2$), 1.94-1.84 (m, 1H, -CH$_2$-C*H*(CH$_3$)$_2$), 0.97 (d, *J* = 7.0 Hz, 6H, -CH$_2$-CH(C*H*$_3$)$_2$) **(Fig. S11)**; **^{13}C NMR (100 MHz, CDCl$_3$)**: *δ* 166.8, 137.6, 133.3, 128.9, 128.4, 47.6, 28.7, 20.3 **(Fig. S12)**.

(-)-*N*-[(1*S*)-1-phenylethyl]benzamide (14)



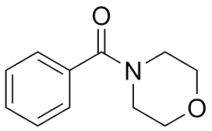
Following the procedure **A**, the main product was obtained as colorless solid (83 mg, 75% yield; eluent: EtOAc/hexane = 1:4); **^{1}H NMR (400 MHz, CDCl$_3$)**: *δ* 7.77 (d, *J* = 8.3 Hz, 2H, *o*-H-Ar), 7.51-7.47 (m, 1H, H-Ar), 7.44-7.34 (m, 6H, H-Ar), 7.29 (d, *J* = 7.0 Hz, 1H, H-Ar), 6.36 (d, *J* = 4.7 Hz, 1H, -CO-N*H*-), 5.34 (p, *J* = 7.0 Hz, 1H, -NH-C*H*(Ph)-CH$_3$), 1.61 (d, *J* = 7.0 Hz, 3H, CH$_3$) **(Fig. S13)**; **^{13}C NMR (100 MHz, CDCl$_3$)**: *δ* 166.7, 143.6, 131.5, 128.8, 128.6, 127.5, 127.1, 126.3, 49.3, 21.8 **(Fig. S14)**.

(*S*)-ethyl-*N*-(4-nitrobenzoyl)-phenylalaniate (15)



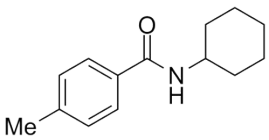
Following the procedure **A**, the main product was obtained as slightly yellowish solid (99 mg, 58% yield; eluent: EtOAc/hexane = 1:7); **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 8.28 (d, *J* = 8.7 Hz, 2H, *o*-H-Ar), 7.87 (d, *J* = 8.7 Hz, 2H, *m*-H-Ar), 7.33-7.28 (m, 3H, H-Ar), 7.14-7.11 (m, 2H, H-Ar), 6.65 (d, *J* = 6.9 Hz 1H, -CO-N*H*-), 5.05 (td, *J* = 7.4, 5.5 Hz, 1H, -NH-C*H*(CO_2Et)-Bn), 4.25 (q, *J* = 7.3 Hz, 2H, -CO_2C*H*$_2$$CH_3$), 3.29 (ddd, *J* = 19.6, 13.7, 5.9 Hz, 2H, -C*H*$_2$-C_6H_5), 1.30 (t, *J* = 7.3 Hz, 3H, -CO_2CH_2C*H*$_3$) **(Fig. S15)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 171.5, 165.0, 149.8, 139.5, 135.7, 129.4, 128.7, 128.3, 127.4, 123.9, 62.0, 53.9, 37.8, 14.2 **(Fig. S16)**.

Morpholin-4-yl(phenyl)methanone (16)



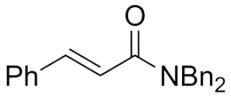
Following the procedure **A**, the main product was obtained as colorless solid (60 mg, 63% yield; eluent: EtOAc/hexane = 1:2); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 7.43-7.39 (m, 5H, H-Ar), 3.76 (br, 4H, aliph.), 3.64 (br, 2H, aliph.), 3.45 (br, 2H, aliph.) **(Fig. S17)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 170.4, 135.3, 129.9, 128.6, 127.1, 66.9, 48.3, 42.5 **(Fig. S18)**.

***N*-cyclohexyl-4-methylbenzamide (17)**



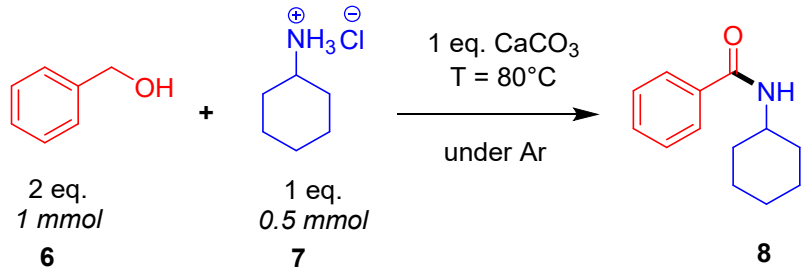
Following the procedure **A**, the main product was obtained as colorless solid (68 mg, 63% yield; eluent: EtOAc/hexane = 1:5); Following the procedure **B**, the main product was obtained as colorless solid (112 mg, 52%); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (d, *J* = 7.6 Hz, 2H, *o*-H-Ar), 7.22 (d, *J* = 7.6 Hz, 2H, *m*-H-Ar), 5.95 (br, 1H, -CO-N*H*-), 4.01-3.94 (m, 1H, -CO-NH-C*H*(R'R'')), 2.93 (s, 3H, CH_3), 2.04-2.01 (m, 2H, aliph.), 1.76-1.73 (m, 2H, aliph.), 1.66-1.63 (m, 1H, aliph.), 1.47-1.38 (m, 2H, aliph.), 1.26-1.18 (m, 3H, aliph.) **(Fig. S19)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 141.7, 132.2, 129.2, 127.0, 48.7, 33.3, 25.7, 25.0, 21.5 **(Fig. S20)**.

(2*E*)-*N*,*N*-dibenzyl-3-phenylprop-2-enamide (18)



Following the procedure A, the main product was obtained as colorless solid (50 mg, 31% yield; eluent: EtOAc/hexane = 1:5); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.86 (d, *J* = 15.3 Hz, 1H, 3-H), 7.47-7.46 (m, 2H, H-Ar), 7.40 – 7.29 (m, 11H, H-Ar), 7.23 (d, *J* = 7.3 Hz, 2H, H-Ar), 6.91 (d, *J* = 15.3 Hz, 1H, 2-H), 4.72 (s, 2H, -C$\underline{H_2}$-C_6H_5), 4.61 (s, 2H, -C$\underline{H_2}$-C_6H_5). **(Fig. S21)**; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.3, 143.9, 137.4, 136.8, 135.3, 129.8, 129.1, 128.9, 128.7, 128.5, 128.0, 127.8, 127.5, 126.7, 117.31, 50.1, 48.9 **(Fig.S22).**

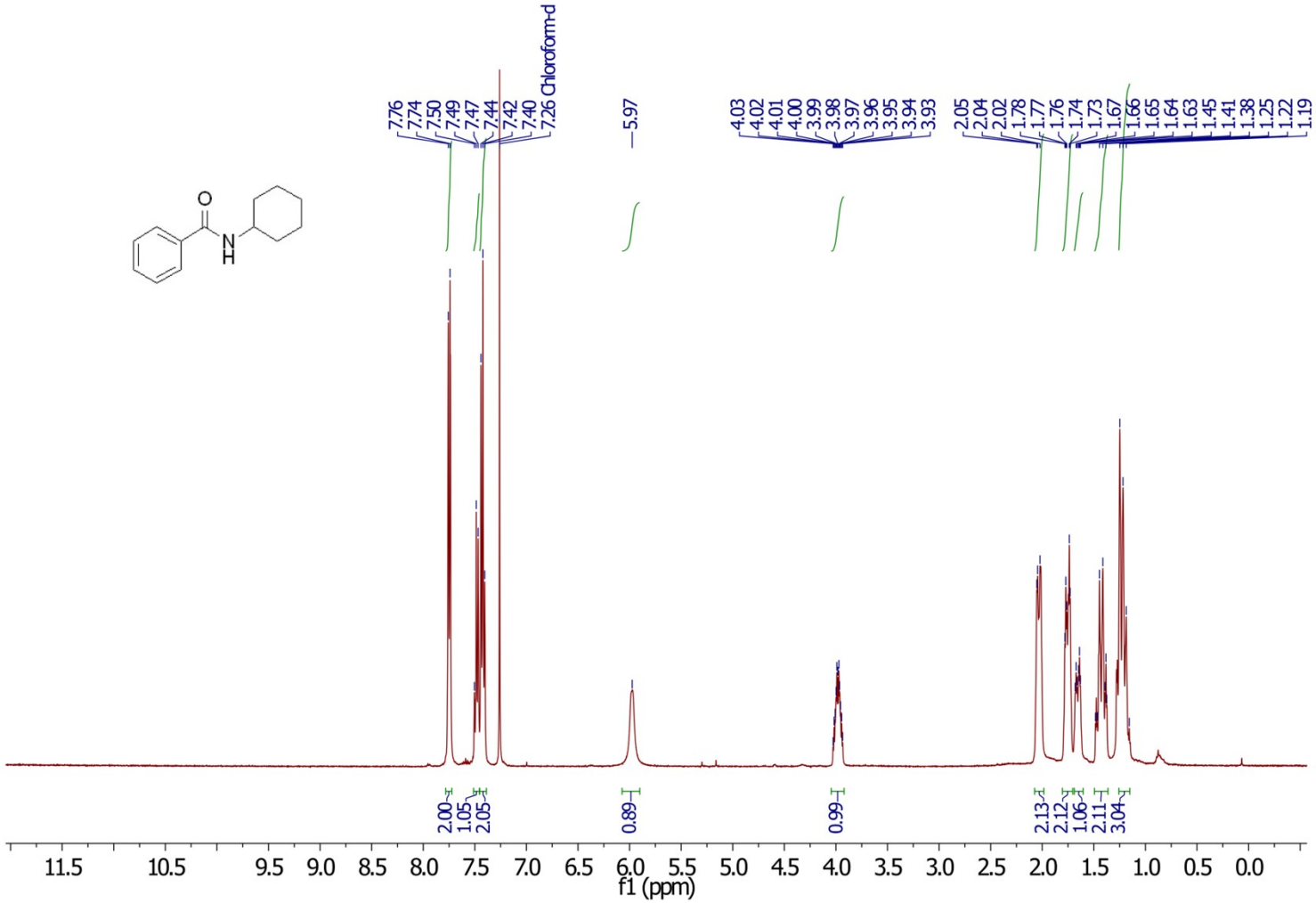
Table S1. Variation of reaction conditions for amidation of benzylic alcohol (7)



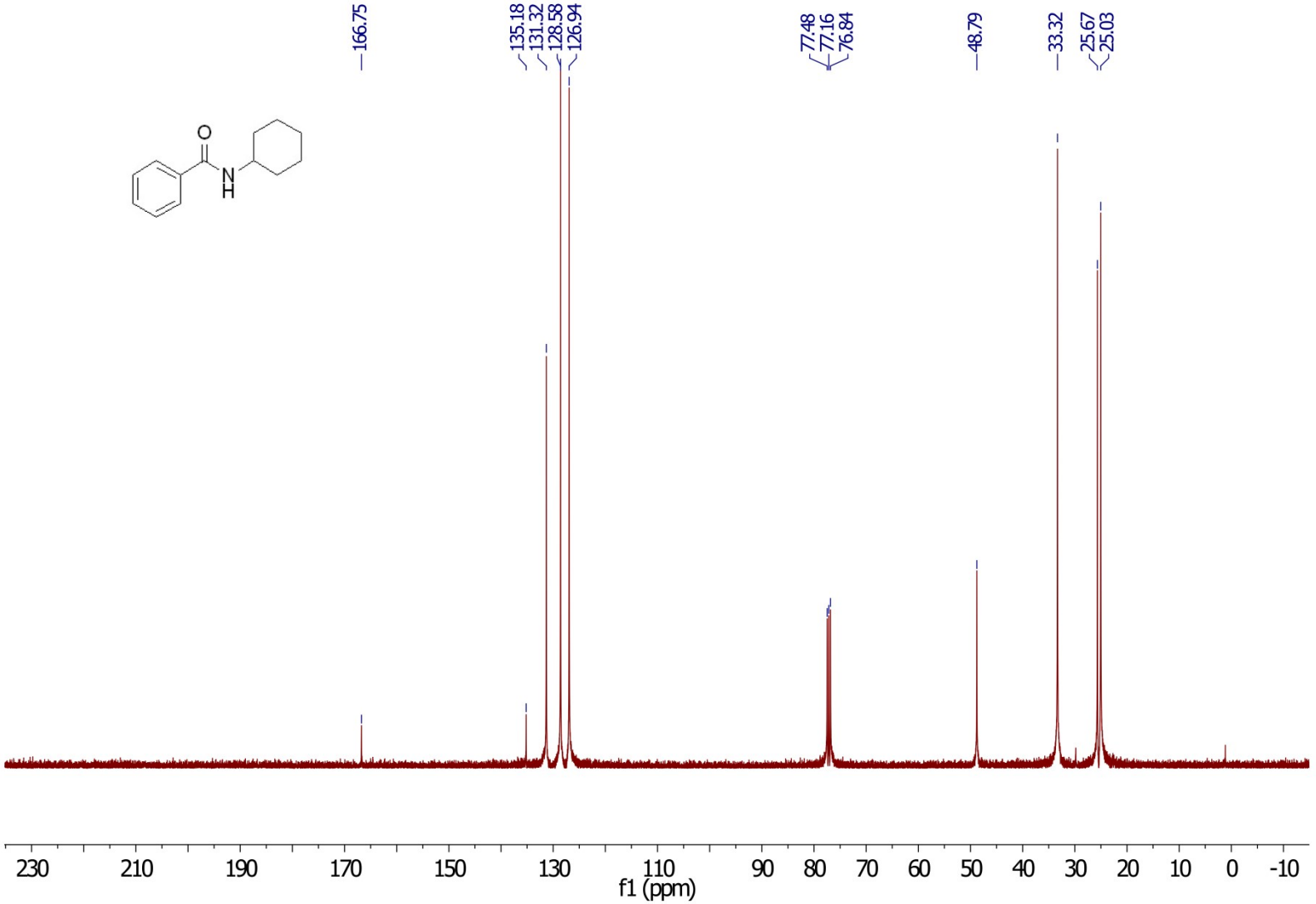
Entry	Catalyst loading (mol% of Mn)	t, hours	Oxidant	Solvent, 1 mL	8, isolated yield, %
1.	-	24	TBHP (5.5M in decane), 5 eq.	MeCN	11
2.	**2** (5)	4	TBHP (70% in water), 5 eq.	MeCN	25
3.	**2** (1)	24	TBHP (5.5M in decane), 5 eq.	MeCN	56
4.	**1** (5)	24	MCPBA, 4 eq.	MeCN, 1.5 mL	26
5.	**1** (2.5)	24	TBHP (5.5M in decane), 5 eq.	MeCN	59
6.	$Mn(OAc)_2$*$4H_2O$ (5)	24	TBHP (5.5M in decane), 5 eq.	MeCN	38
7.	$MnCl_{2\ anhydrous}$ (5)	24	TBHP (5.5M in decane), 5 eq.	MeCN	43
8.	MOF-Manganese (II) Terephtalate (5; 7.5% wt)	24	TBHP (5.5M in decane), 5 eq.	MeCN	49
9.	$Mn(acac)_2$ (5) 1,10-Phenanthroline (6 mol %)	24	TBHP (5.5M in decane), 5 eq.	MeCN	56
10.	$Mn(acac)_2$ (5)	24	TBHP (5.5M in decane), 5 eq.	MeCN	42
11.	$Mn(acac)_2$ (15)	24	TBHP (5.5M in decane), 5 eq.	MeCN	53
12.	$Mn(acac)_2$ (15) 1,10-Phenanthroline (18 mol %)	24	TBHP (5.5M in decane), 5 eq.	MeCN	42

NMR Spectra

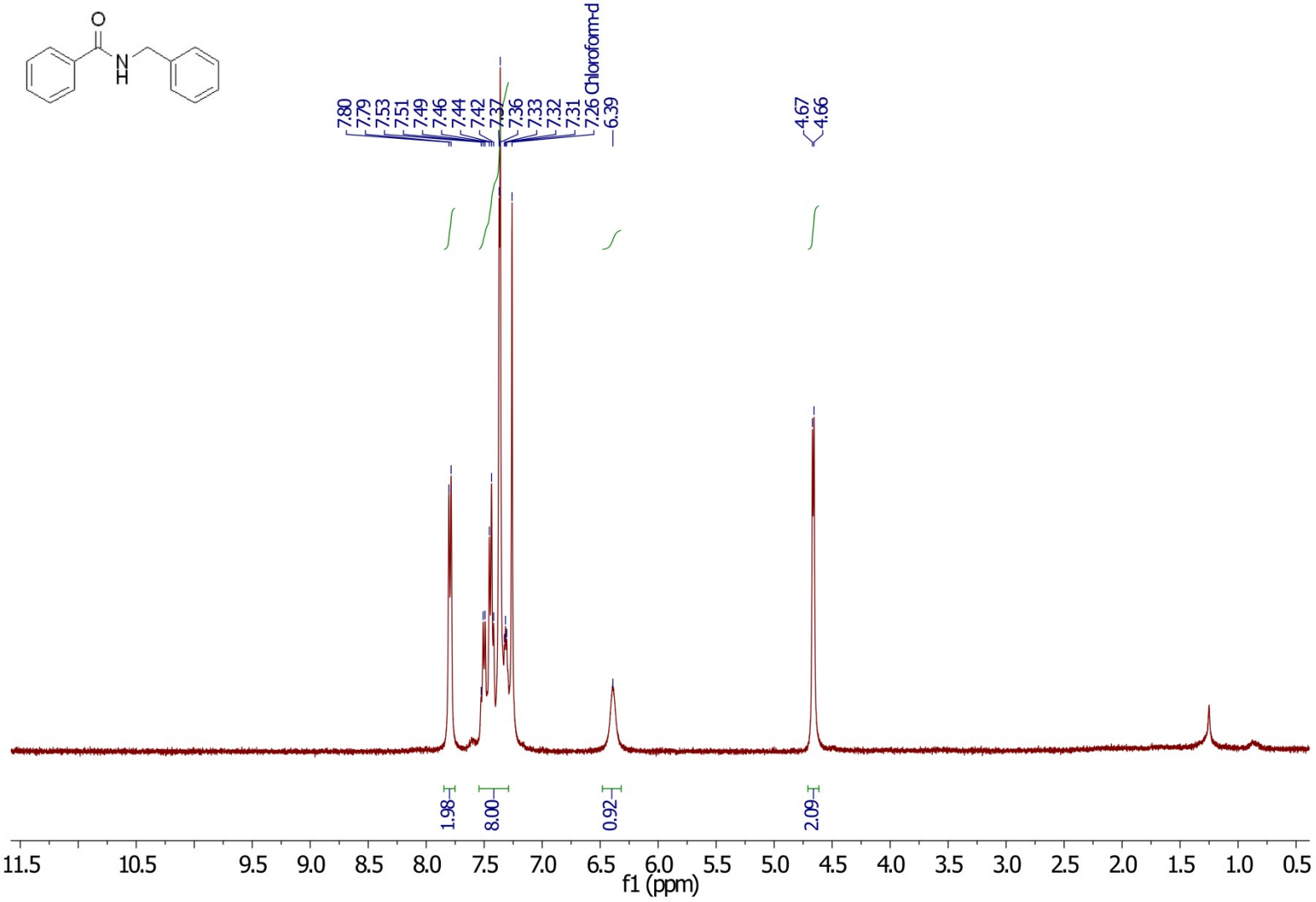
^{1}H of **8 (Fig. S1)**



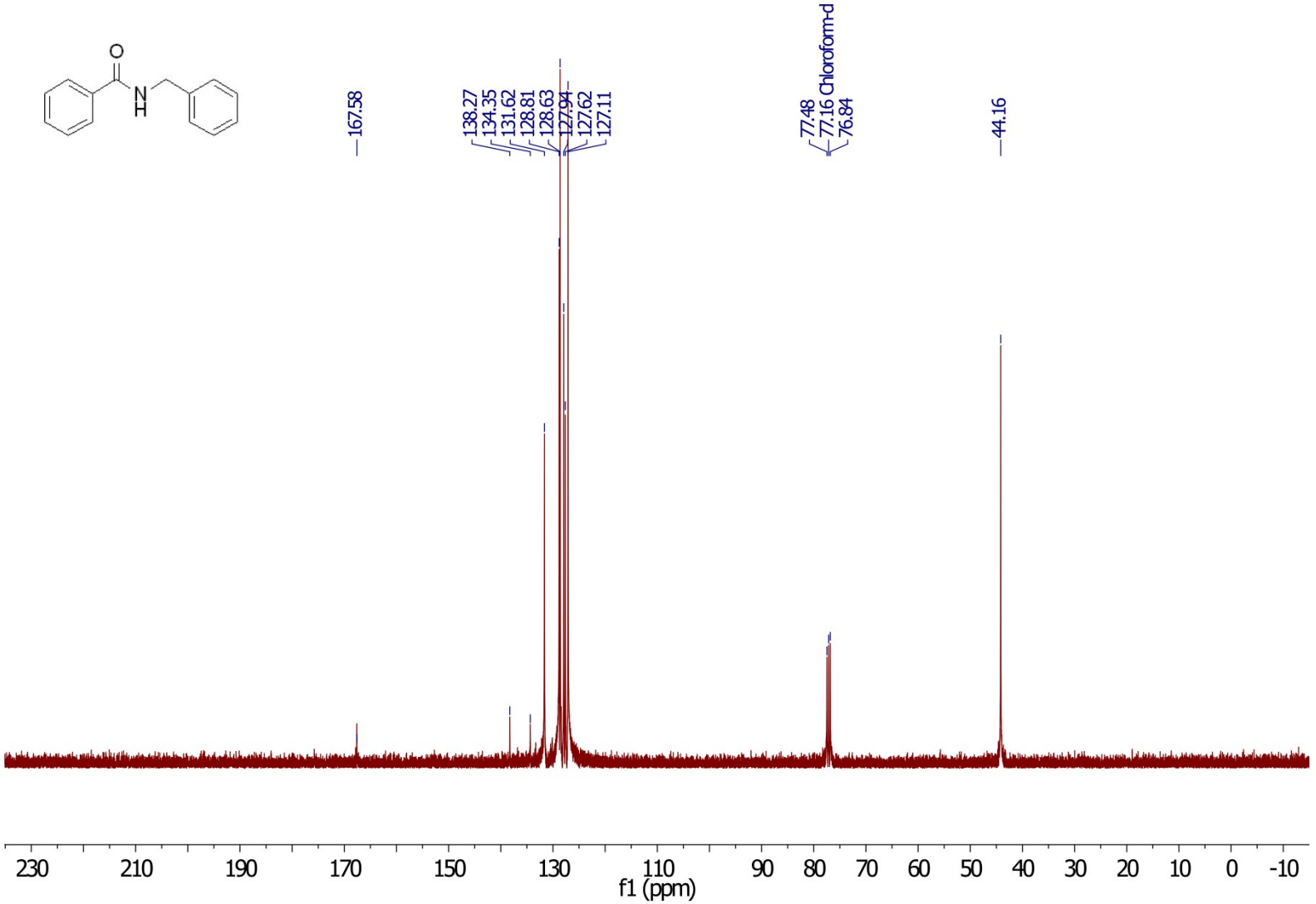
^{13}C of **8 (Fig. S2)**



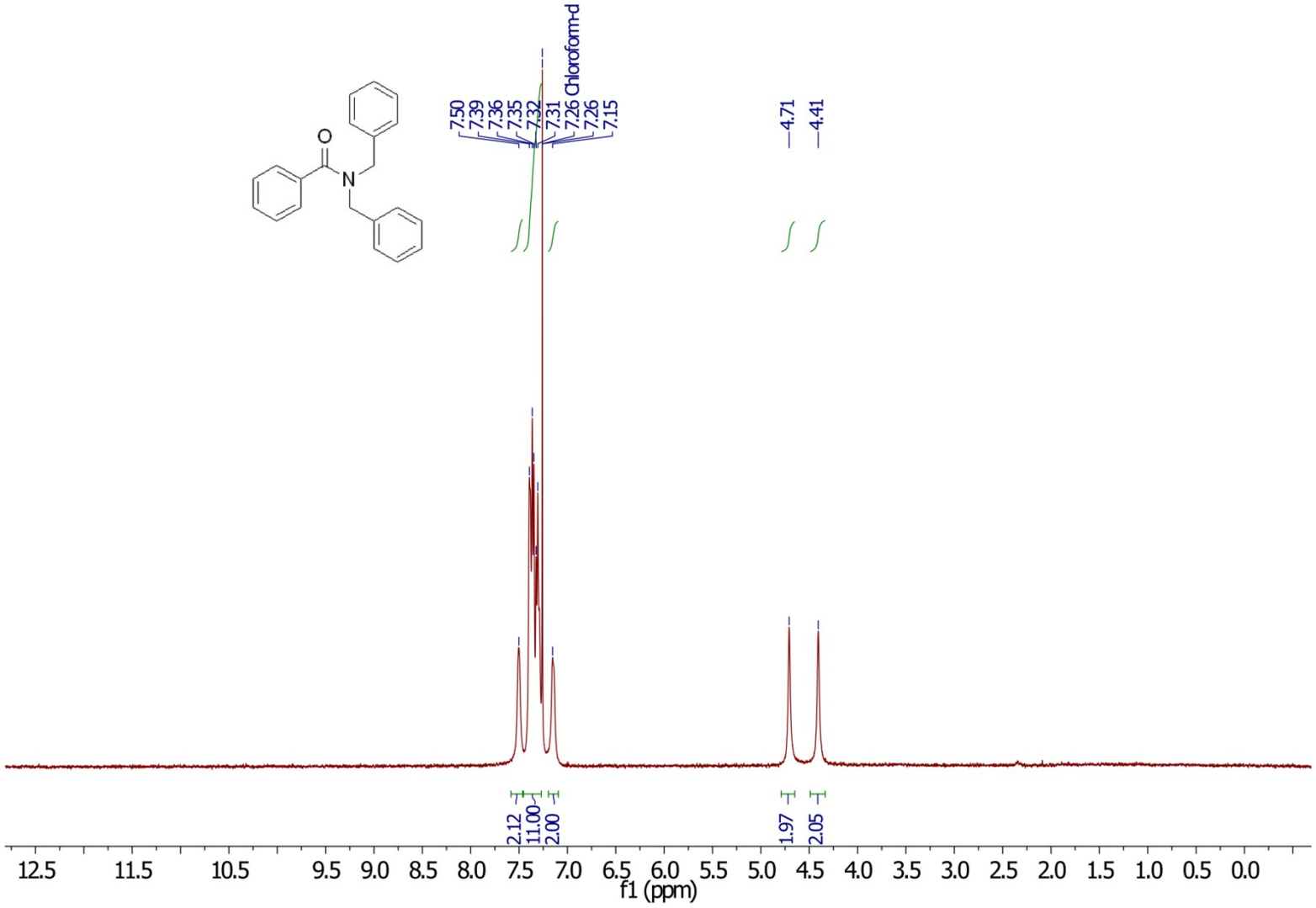
^{1}H of **9 (Fig. S3)**


O
N
H
7.80
7.79
7.53
7.51
7.49
7.46
7.44
7.42
7.37
7.36
7.33
7.32
7.31
7.26 Chloroform-d
6.39
4.67
4.66
1.98
8.00
0.92
2.09
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

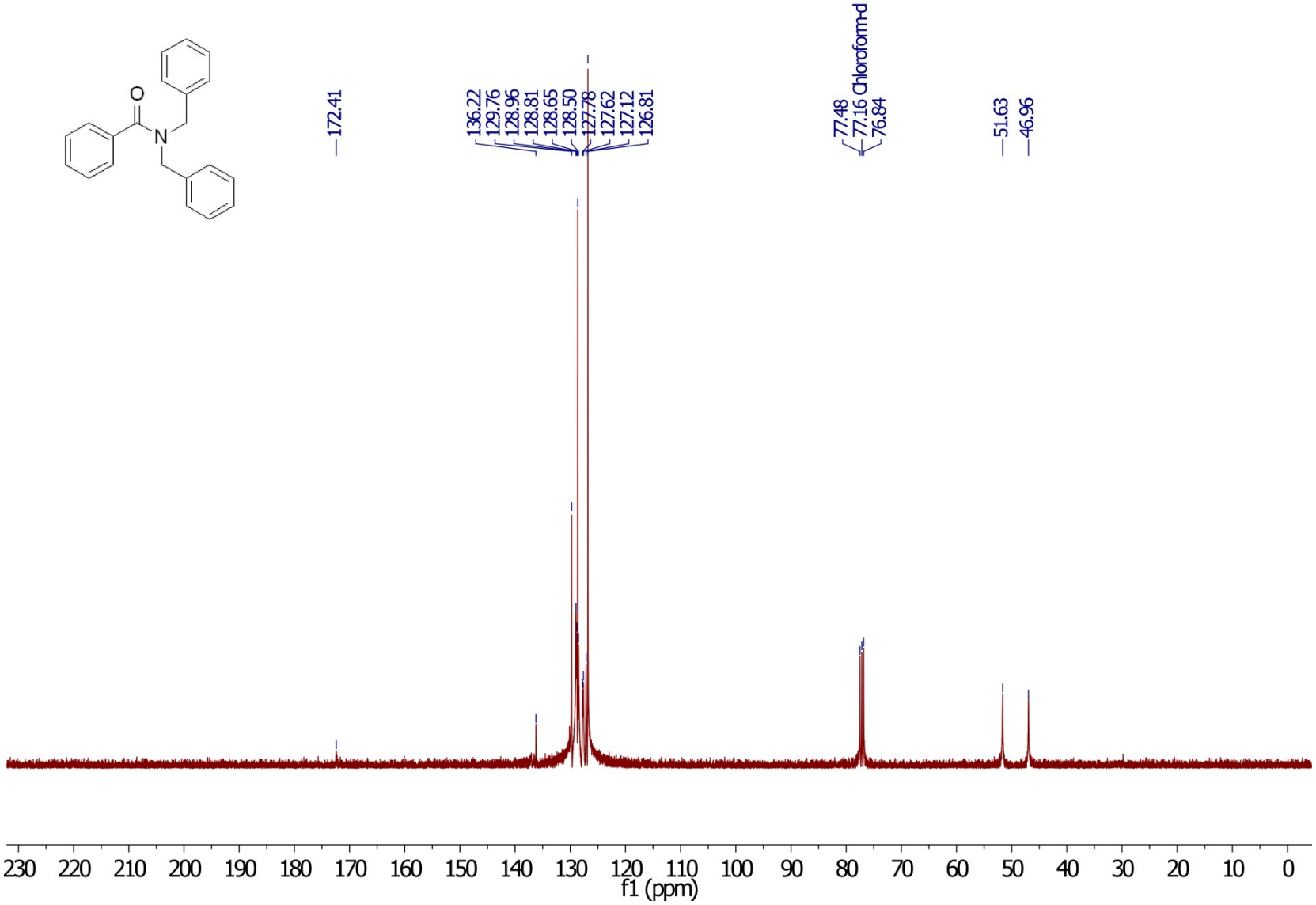
^{13}C of **9 (Fig. S4)**



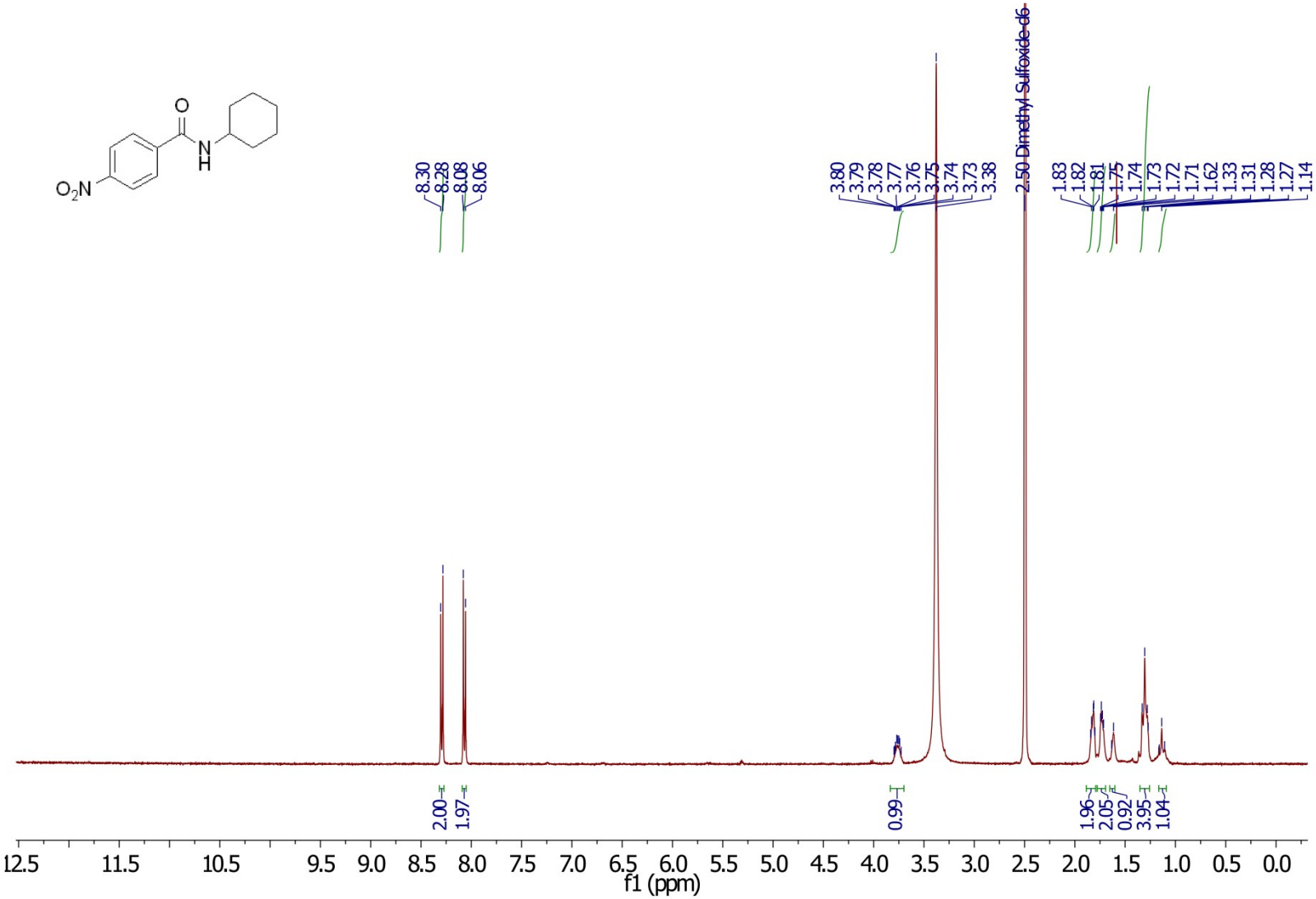
^{1}H of **10 (Fig. S5)**



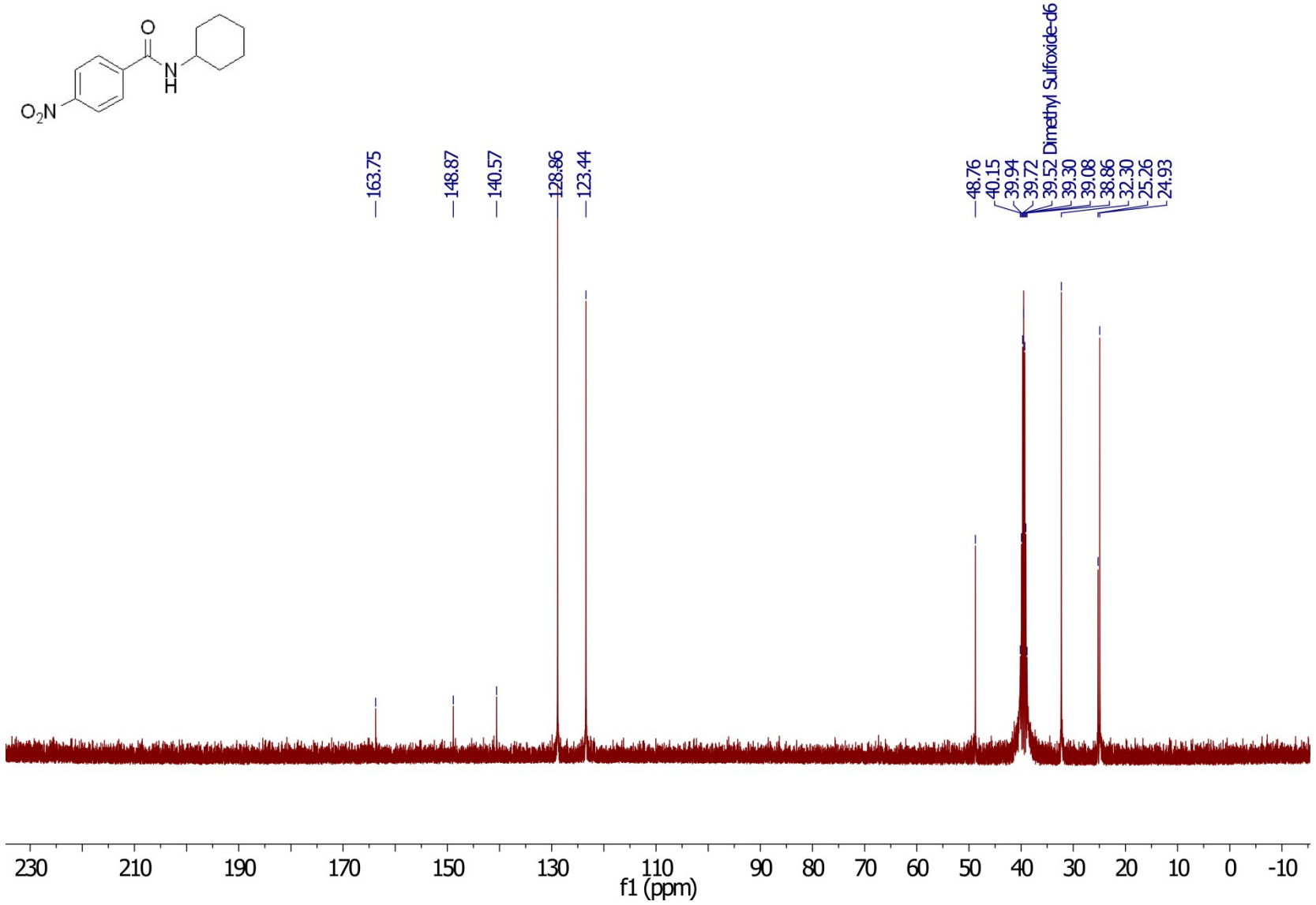
^{13}C of **10 (Fig. S6)**



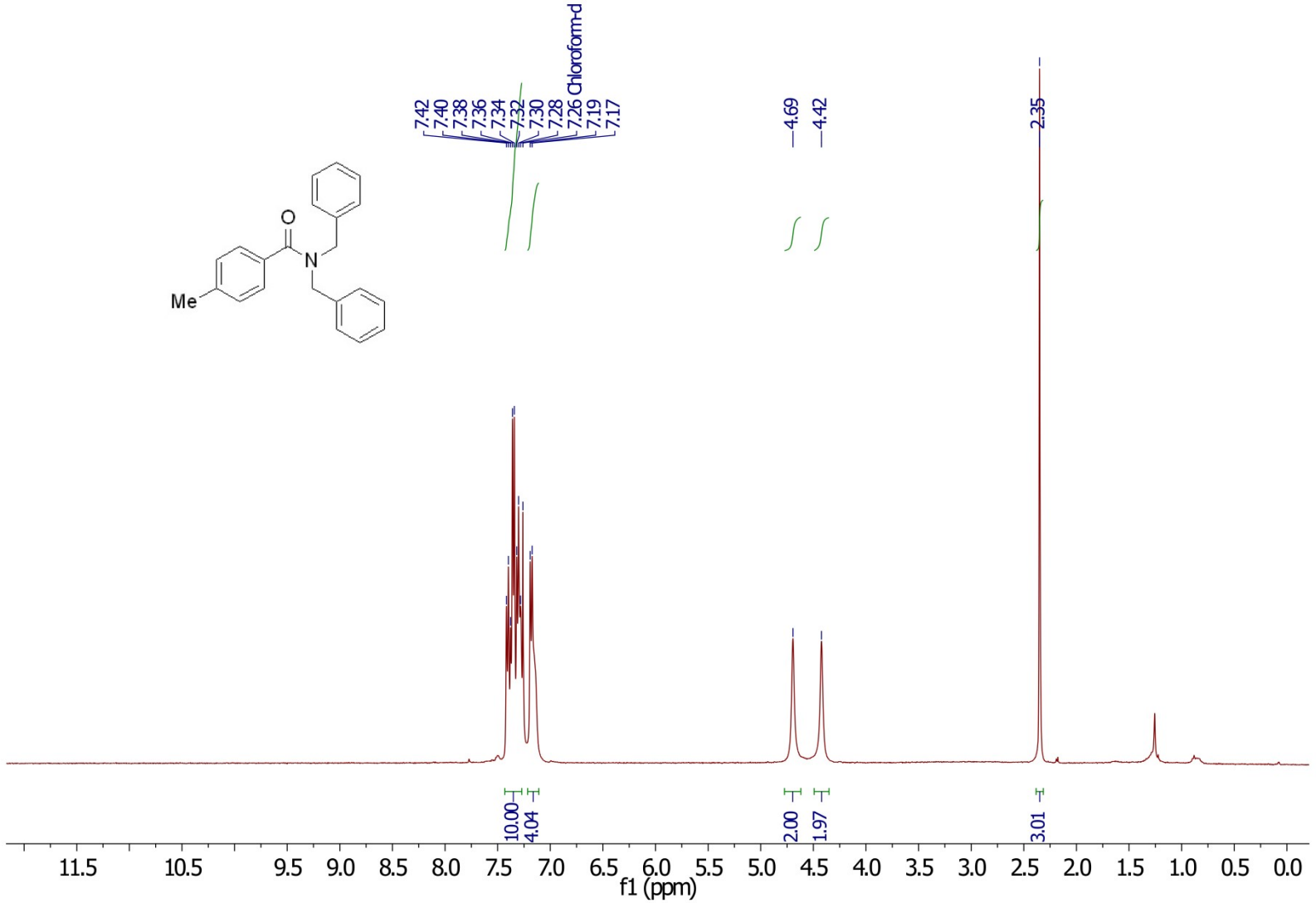
^{1}H of **11 (Fig. S7)**



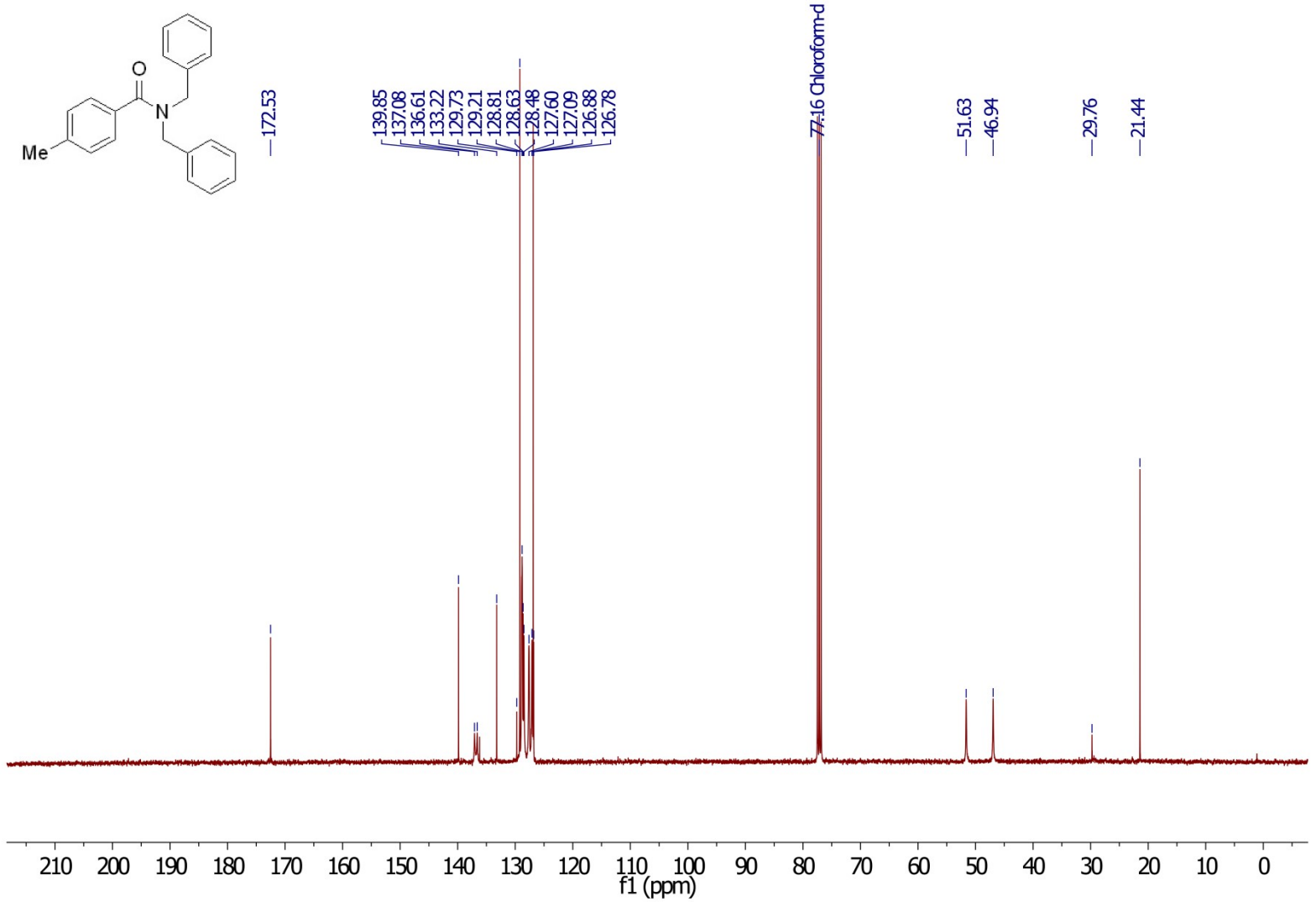
^{13}C of **11 (Fig. S8)**



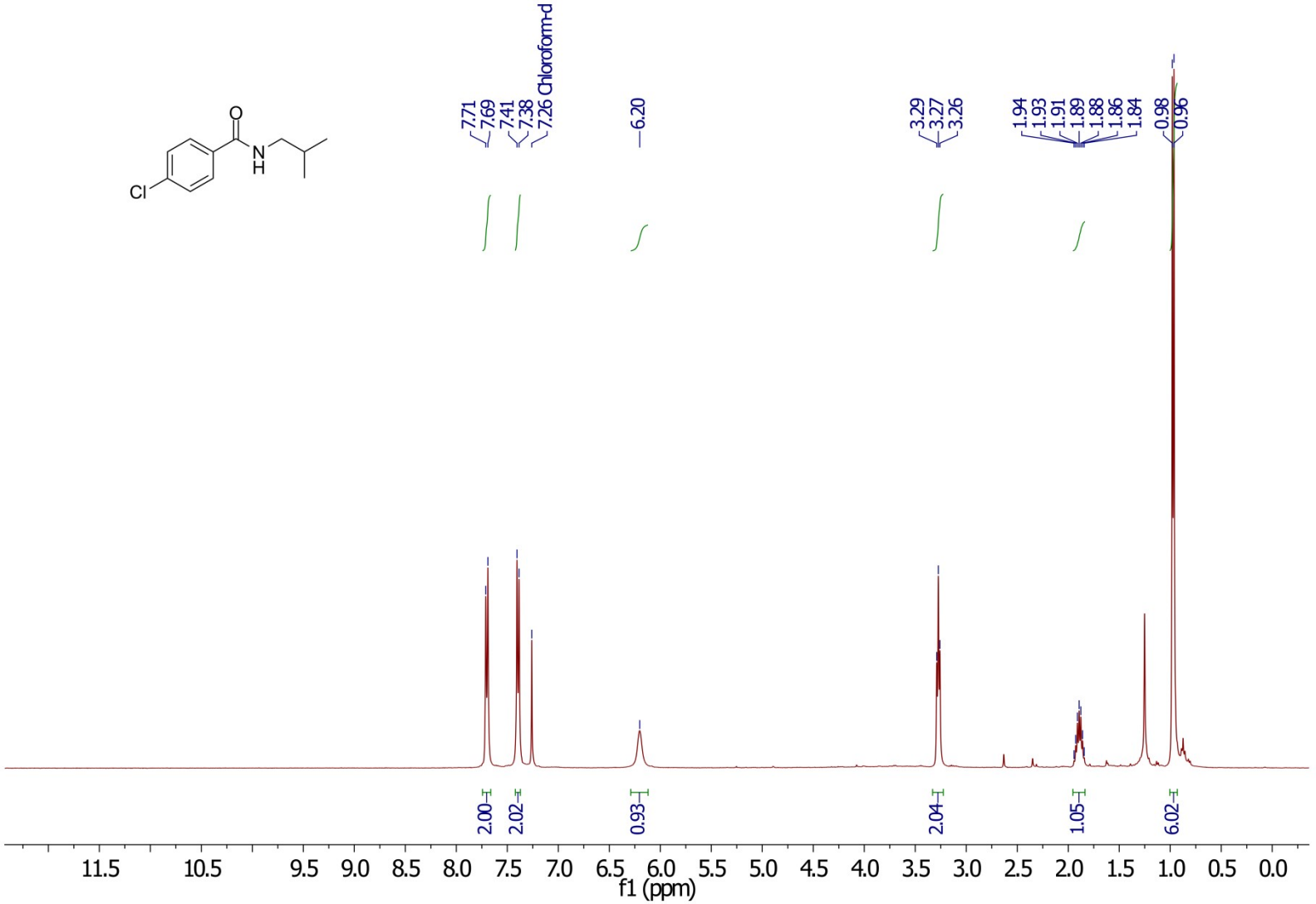
^{1}H of **12 (Fig. S9)**



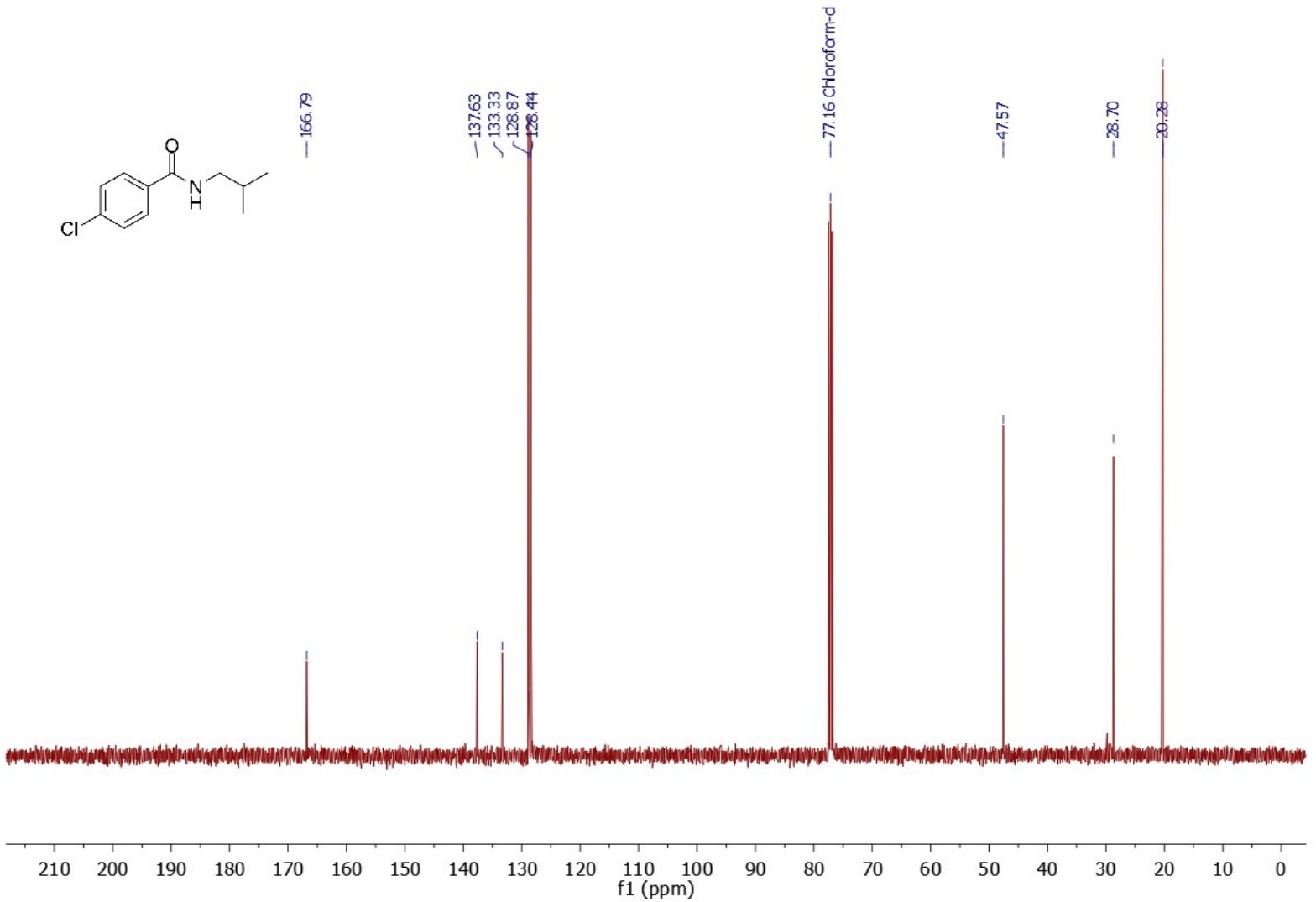
^{13}C of **12 (Fig. S10)**



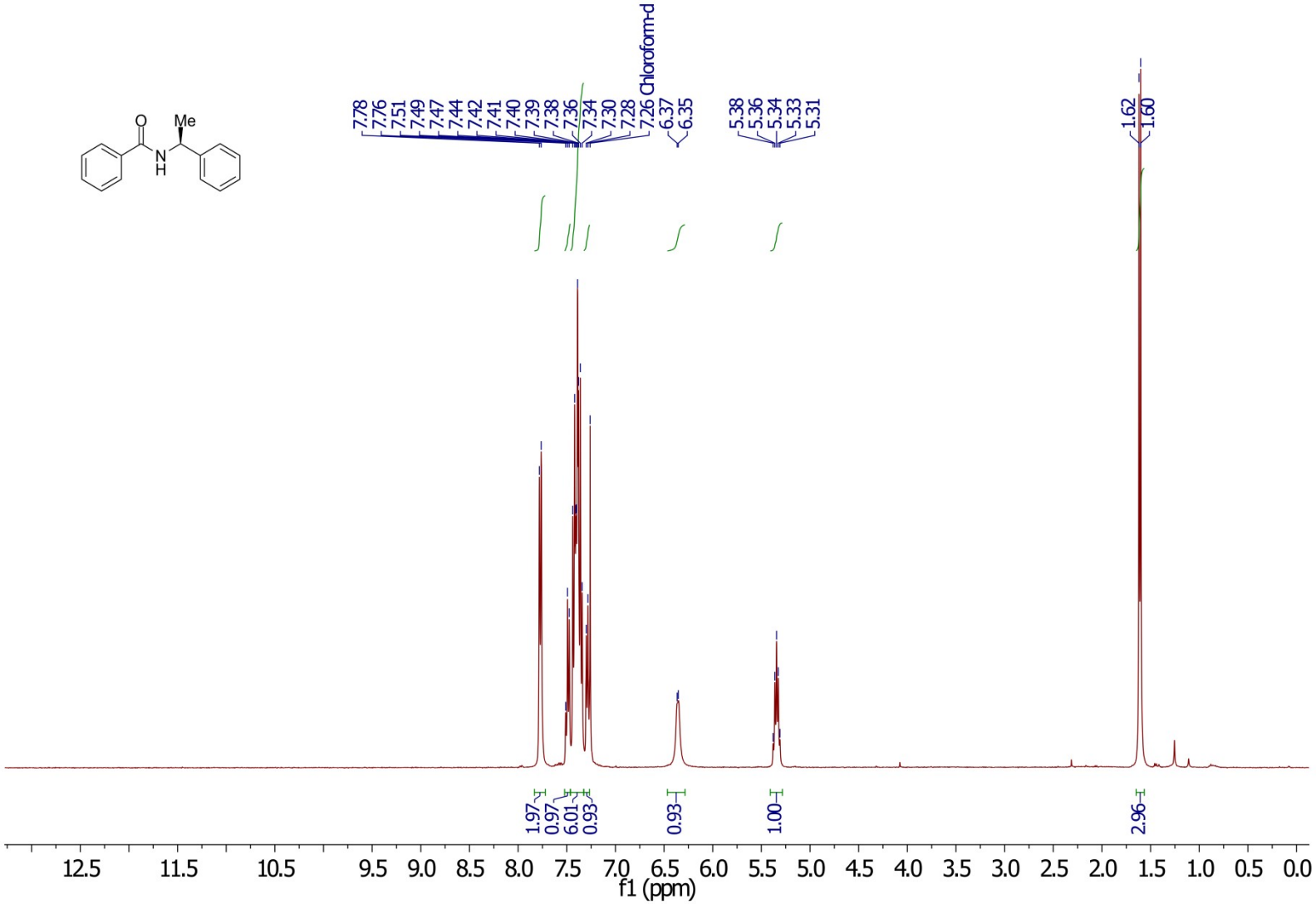
^{1}H of **13 (Fig. S11)**



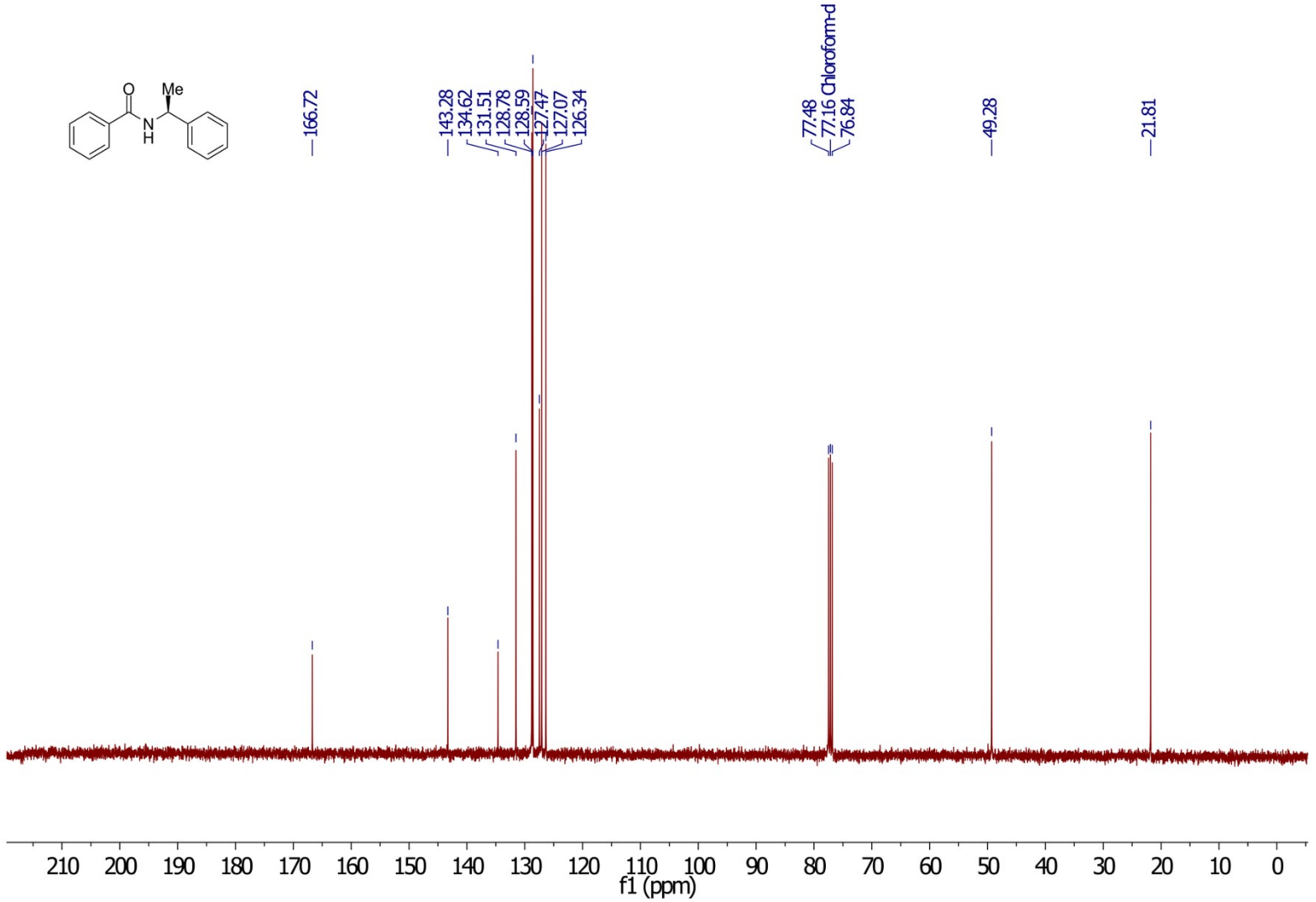
^{13}C of **13 (Fig. S12)**



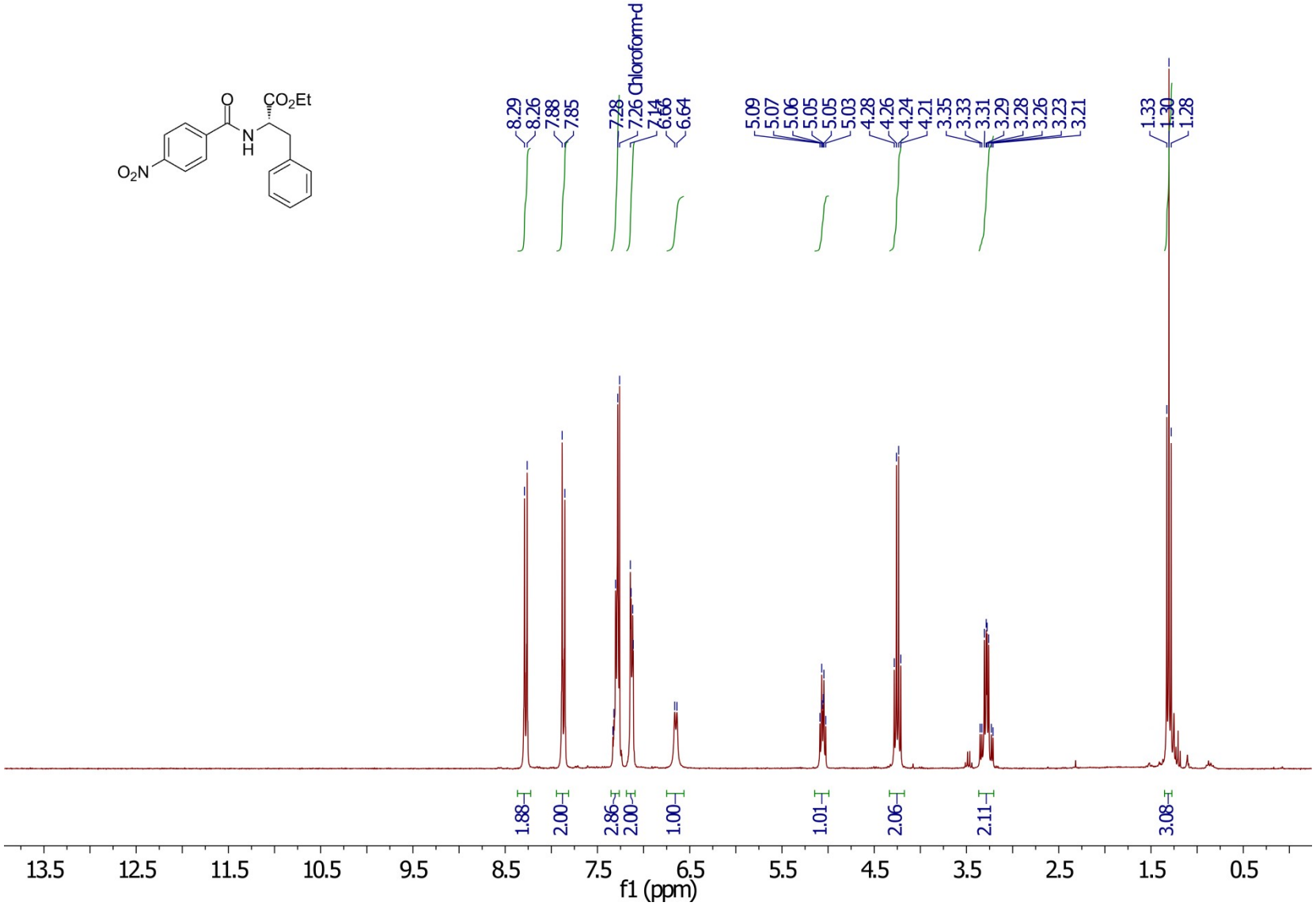
^{1}H of **14 (Fig. S13)**



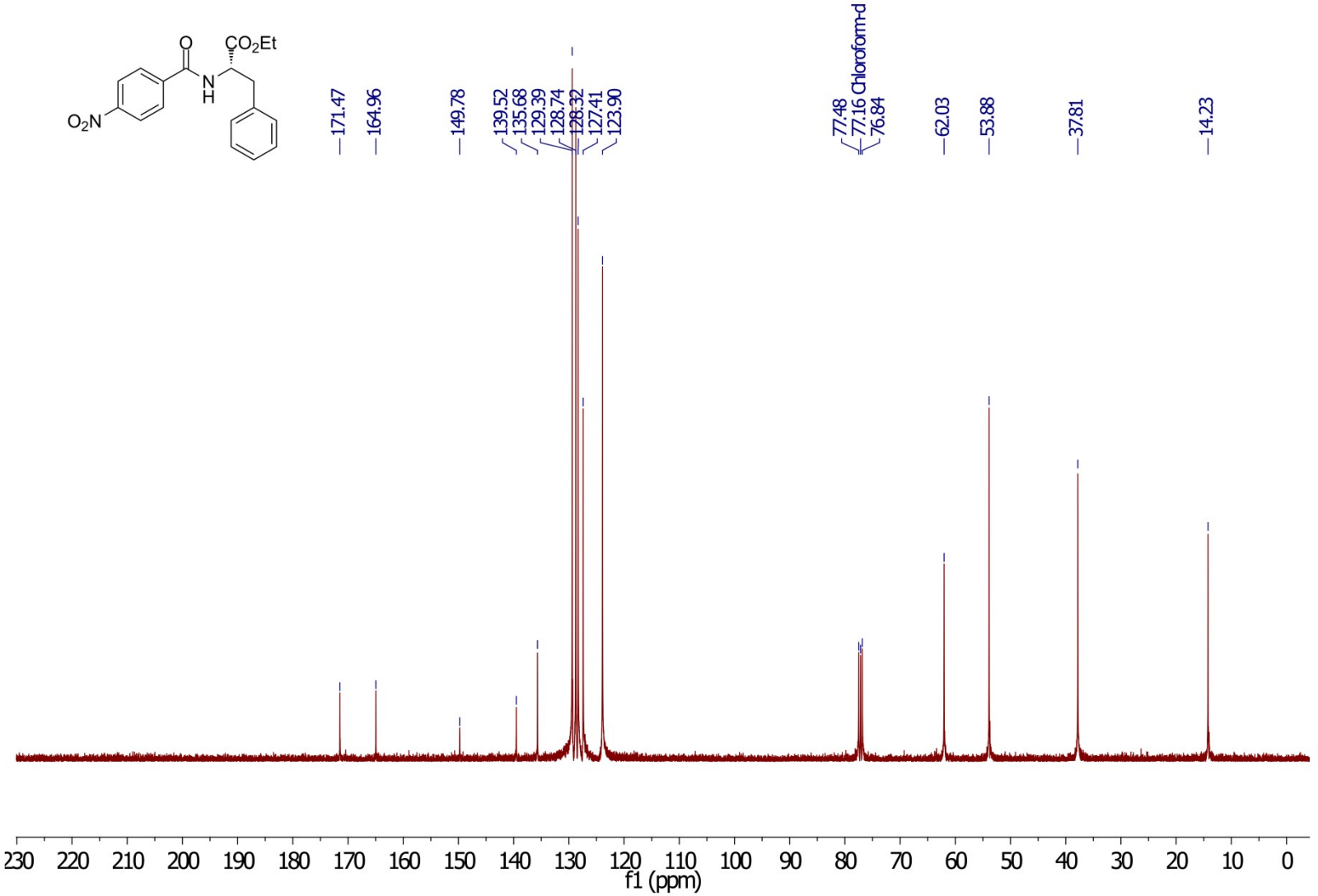
^{13}C of **14 (Fig. S14)**



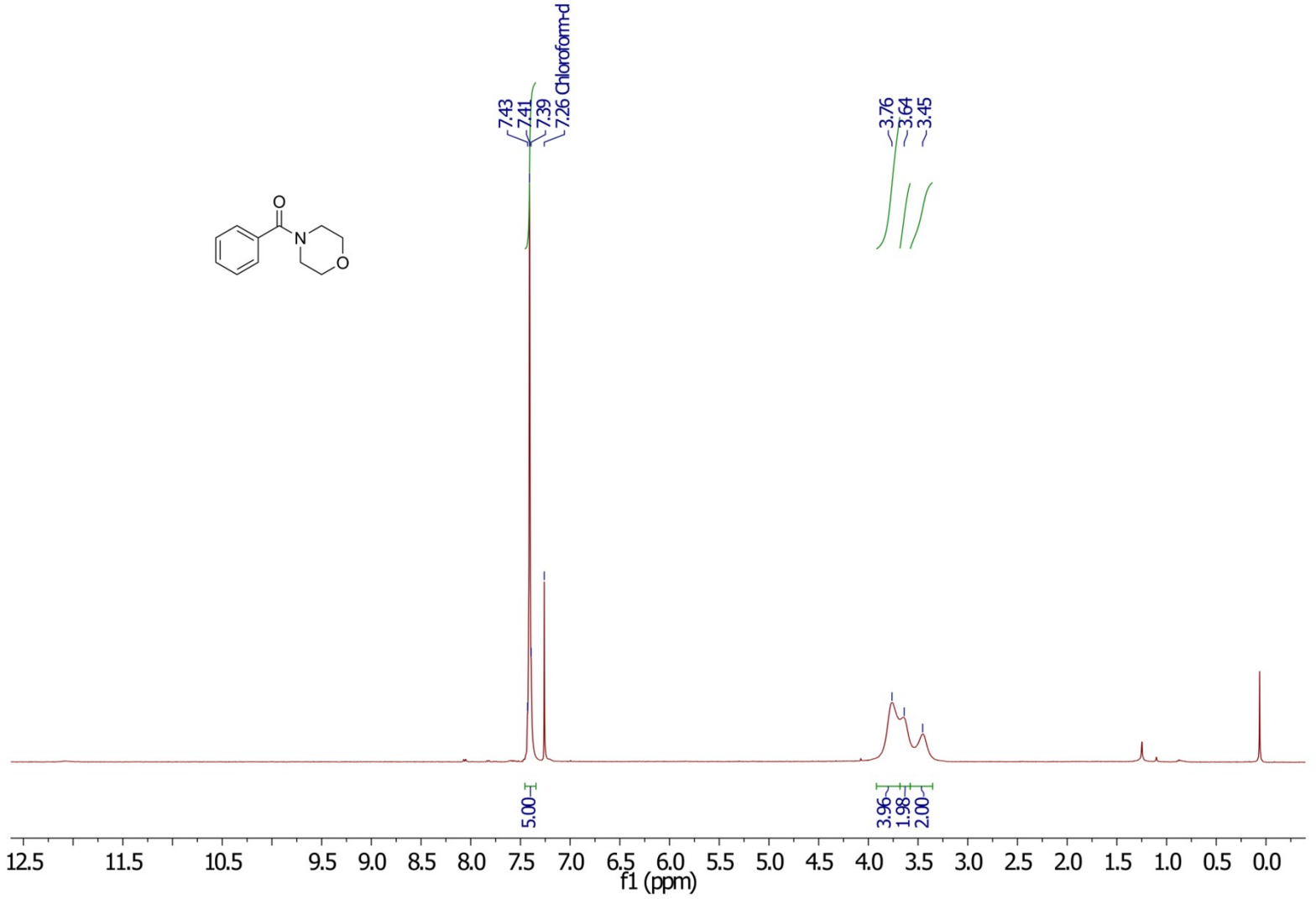
^{1}H of **15 (Fig. S15)**



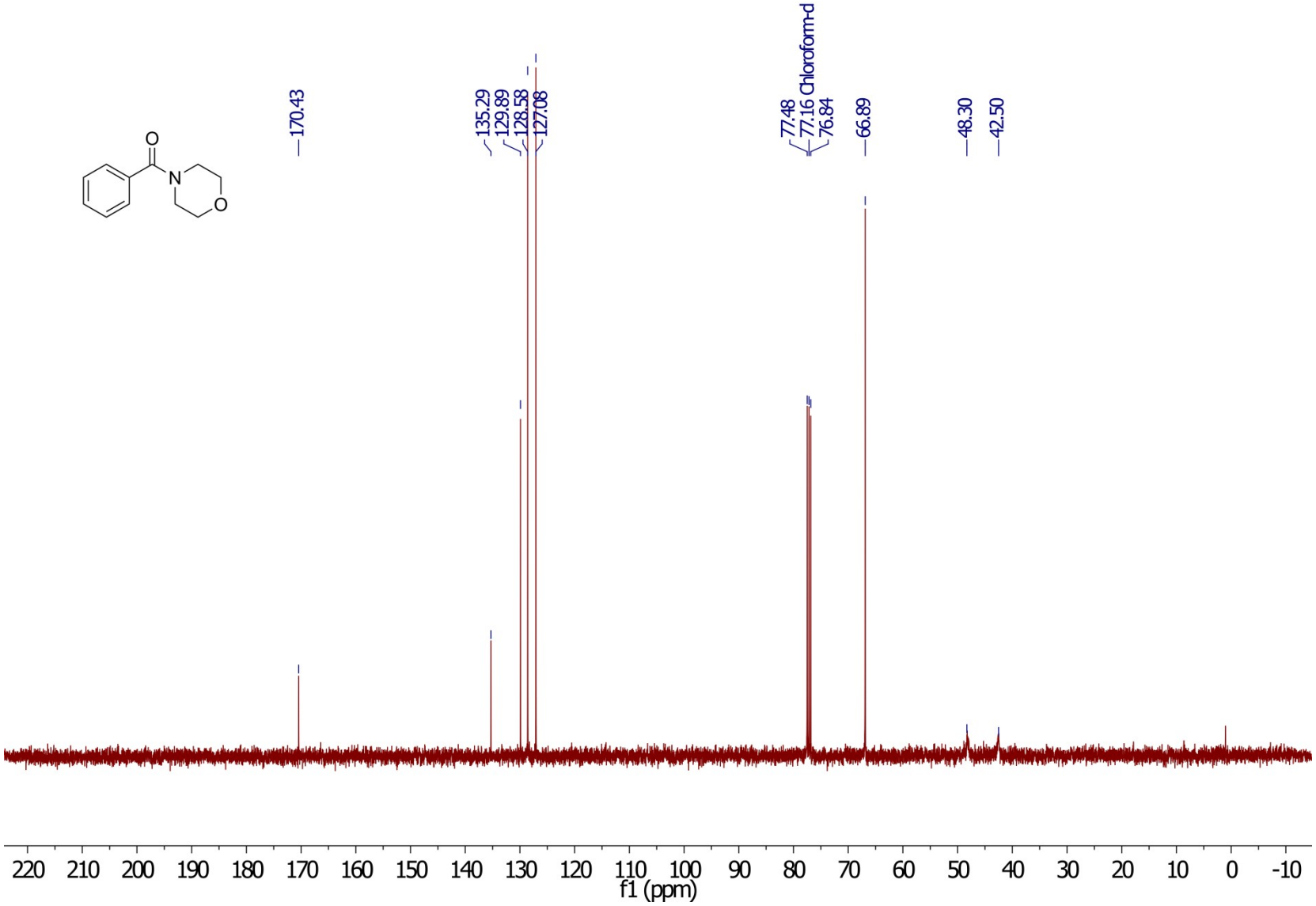
^{13}C of **15 (Fig. S16)**



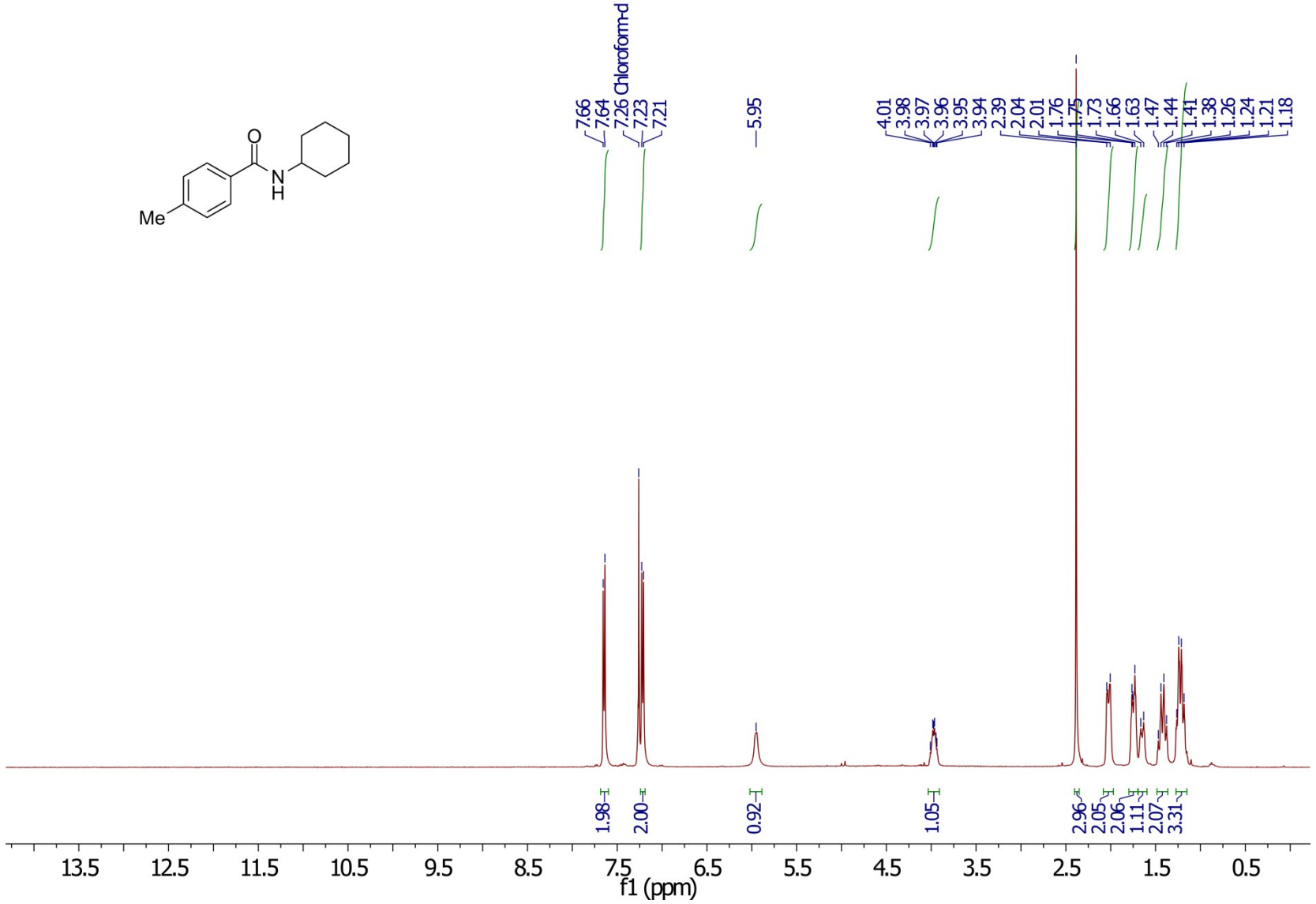
^{1}H of **16 (Fig. S17)**



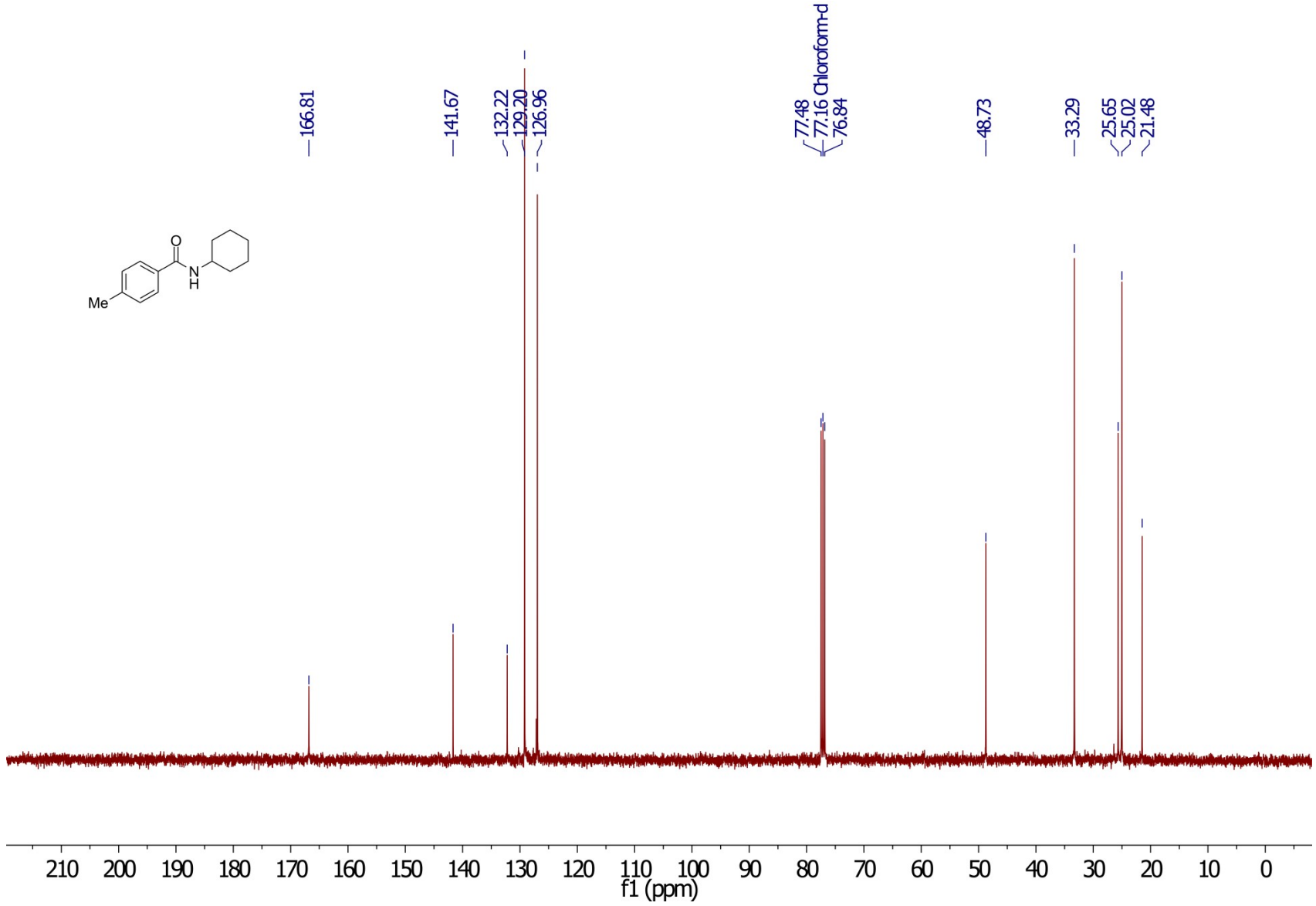
^{13}C of **16 (Fig. S18)**



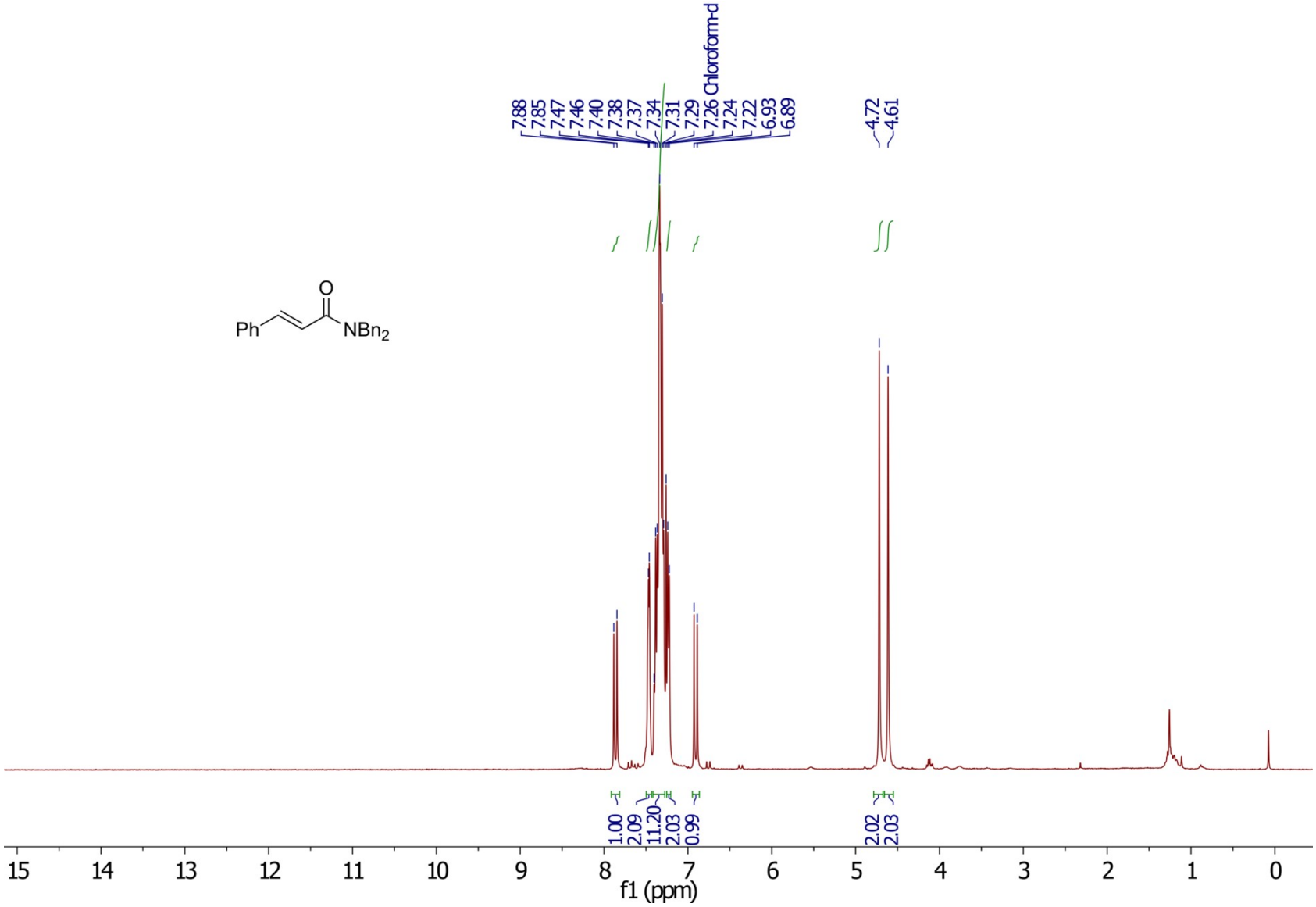
^{1}H of **17 (Fig. S19)**



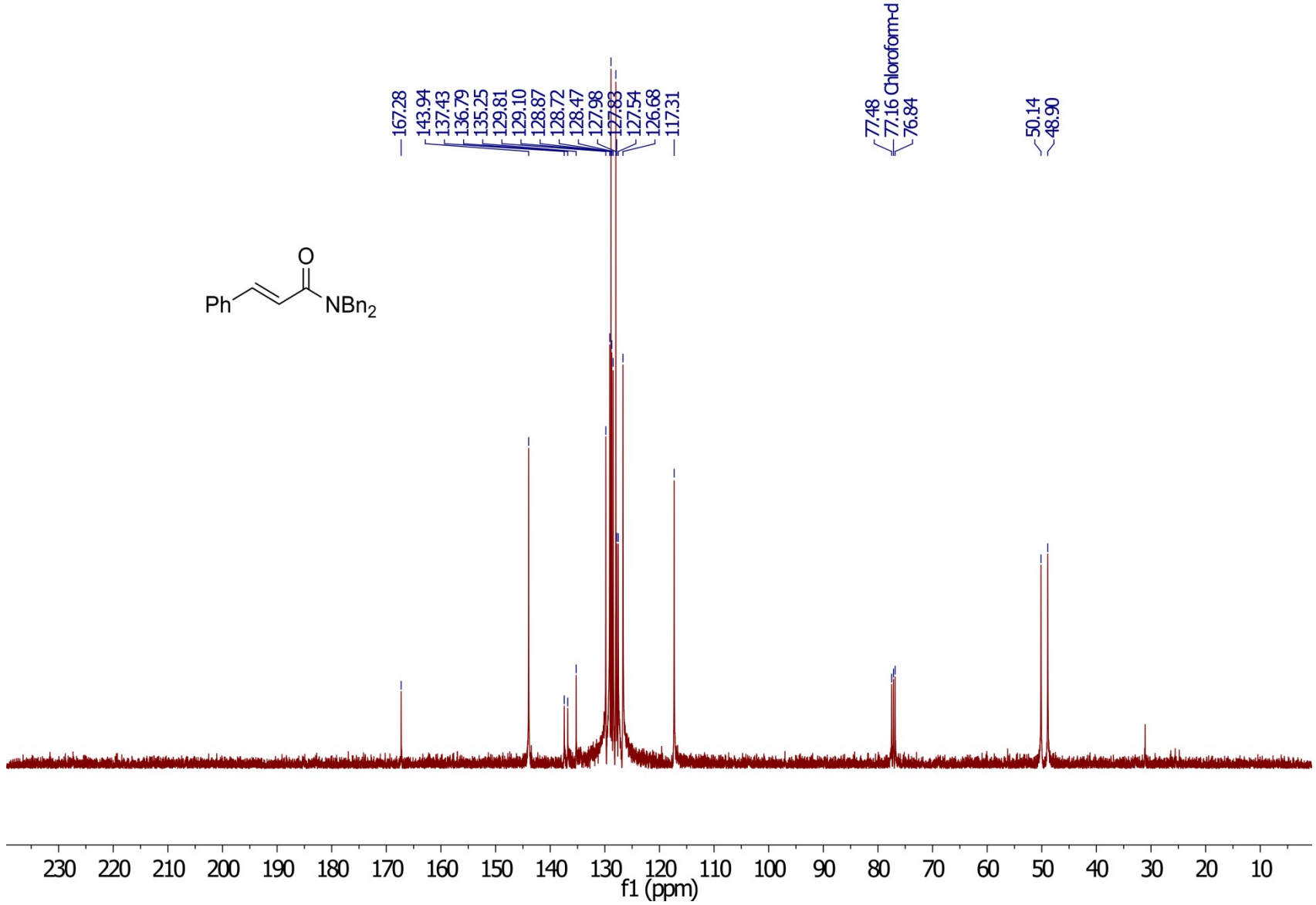
^{13}C of **17 (Fig. S20)**



^{1}H of **18 (Fig. S21)**

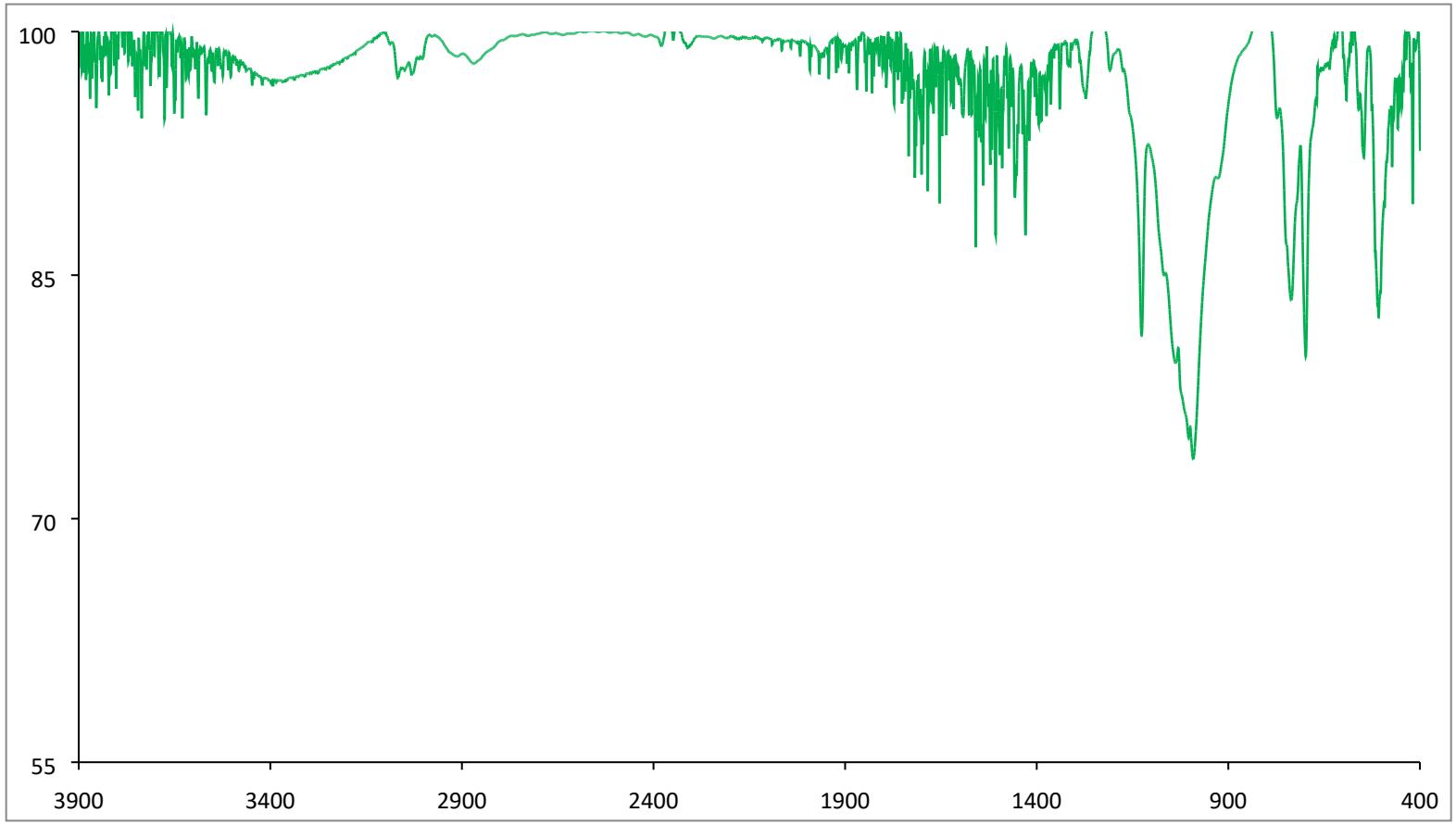


^{13}C of **18 (Fig. S22)**

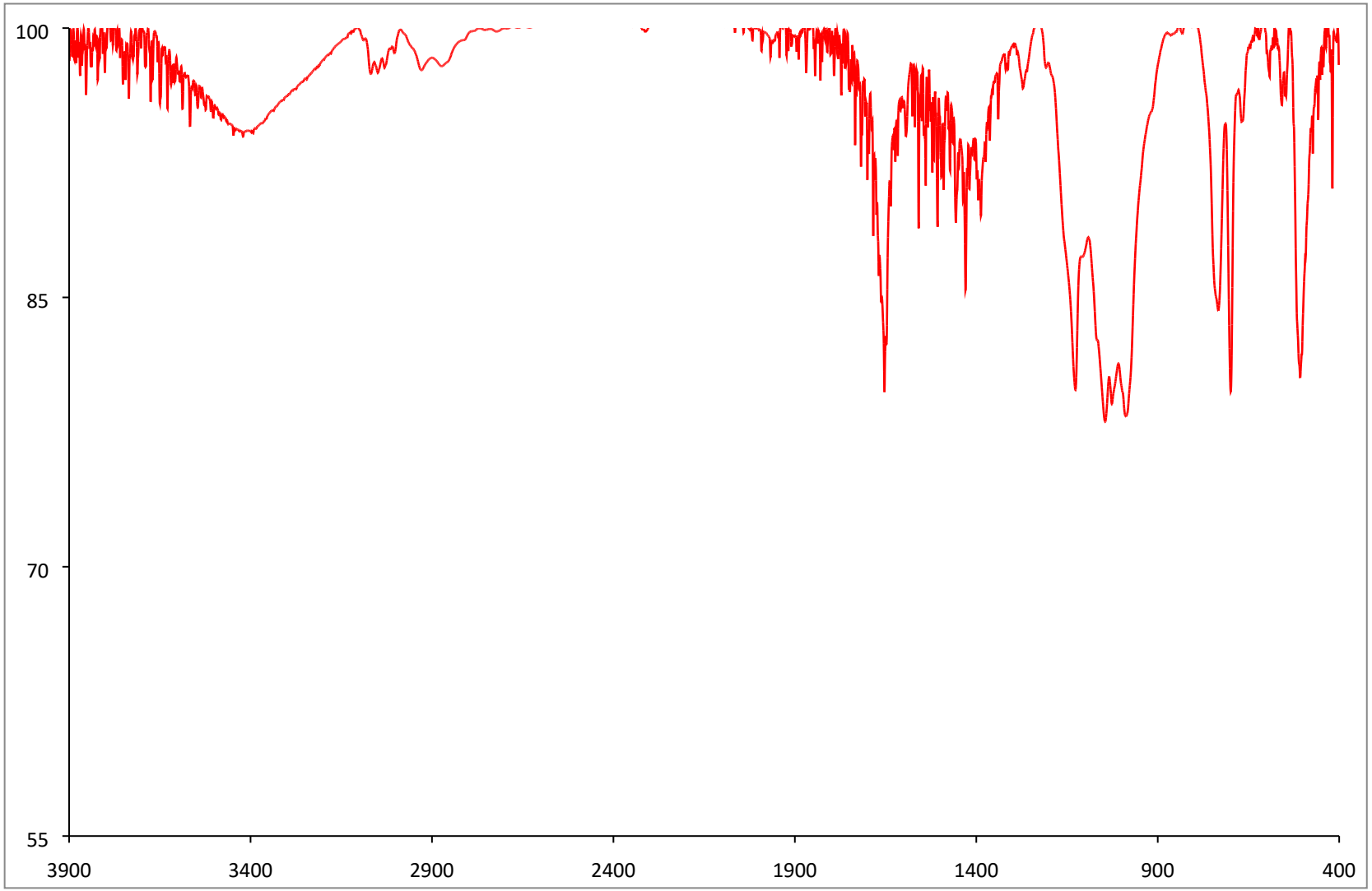


IR-spectra of Mn-silsesquioxanes (pellets in KBr)

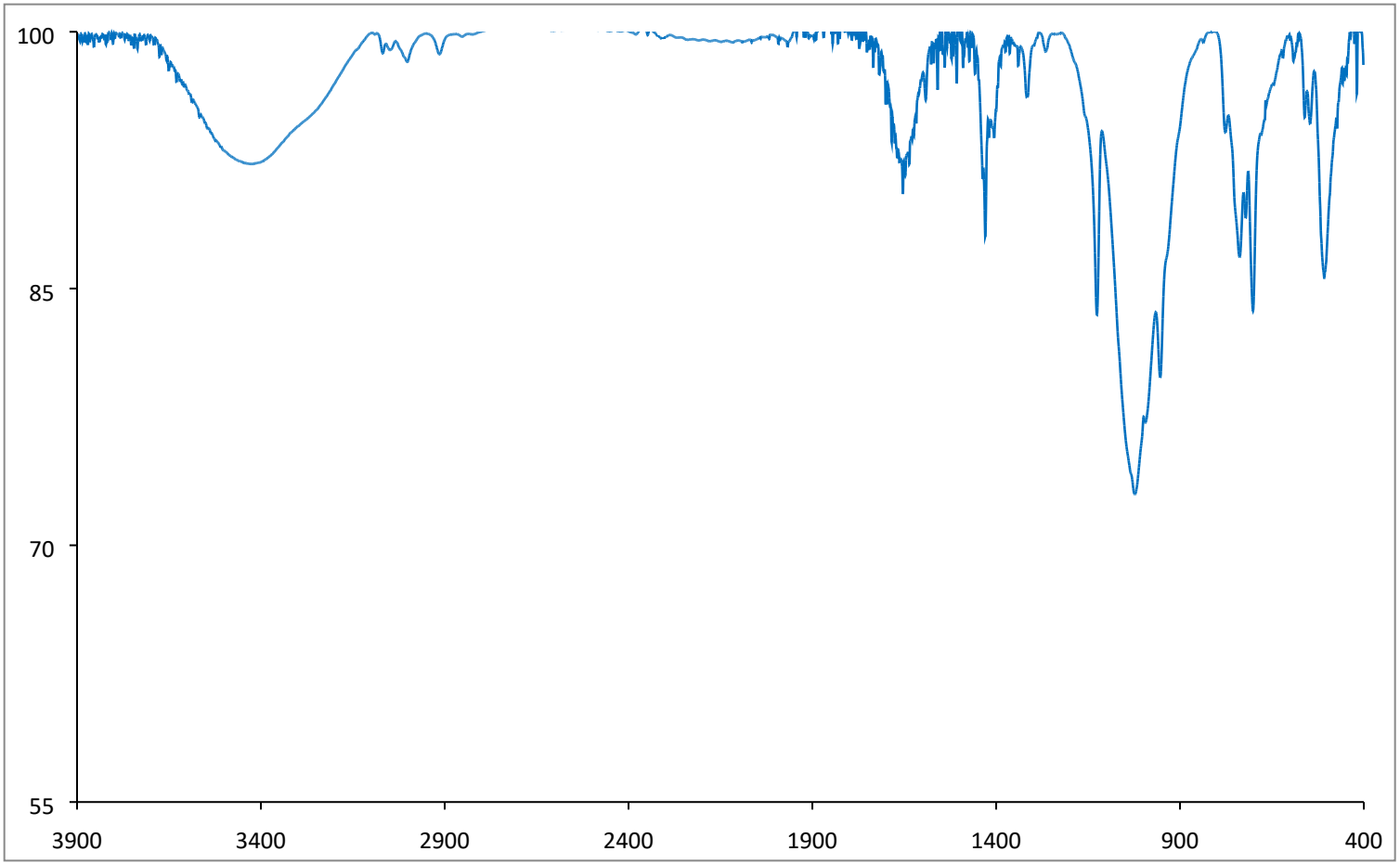
1 (Fig. S23)



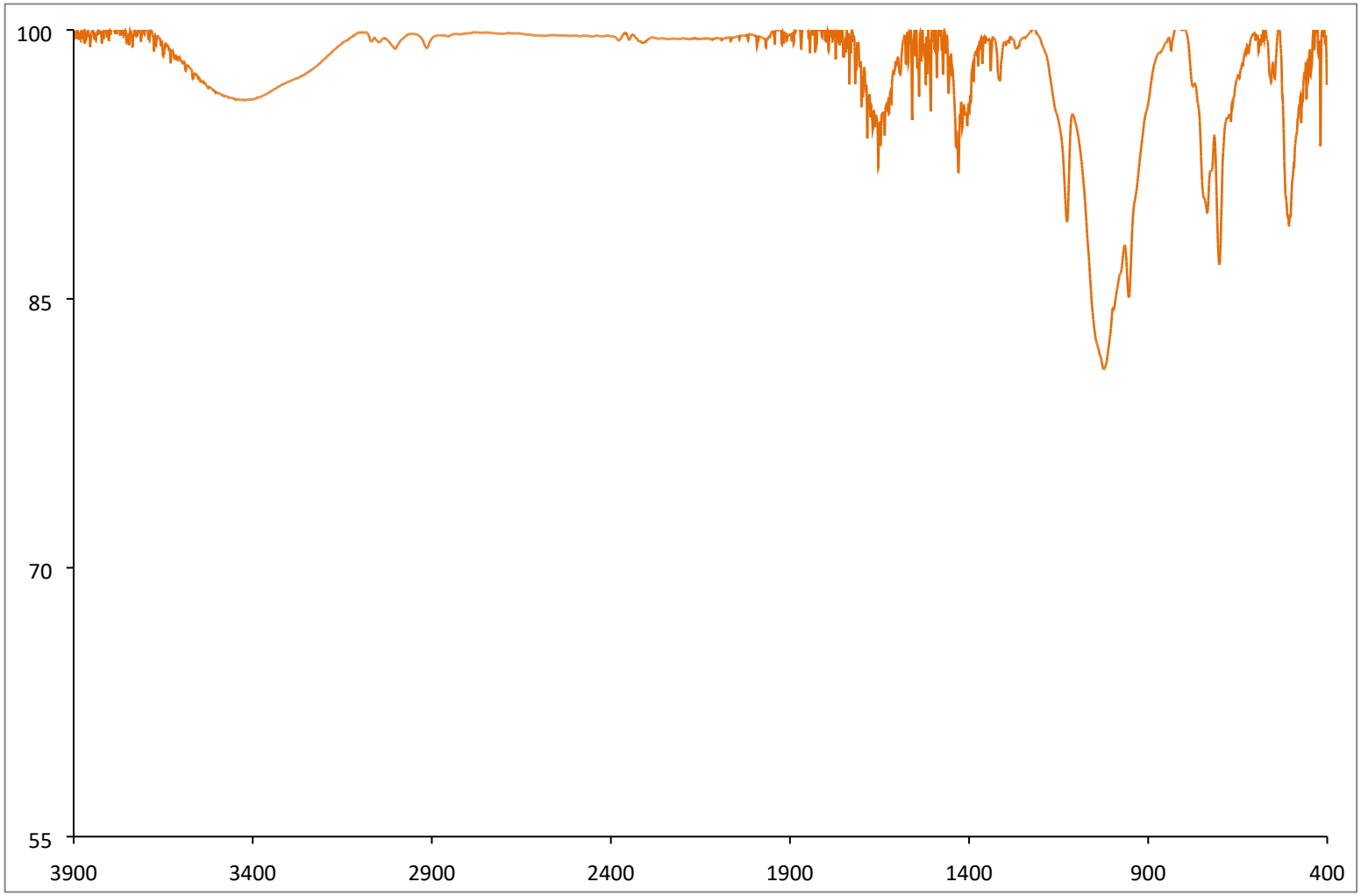
2 (Fig. S24)



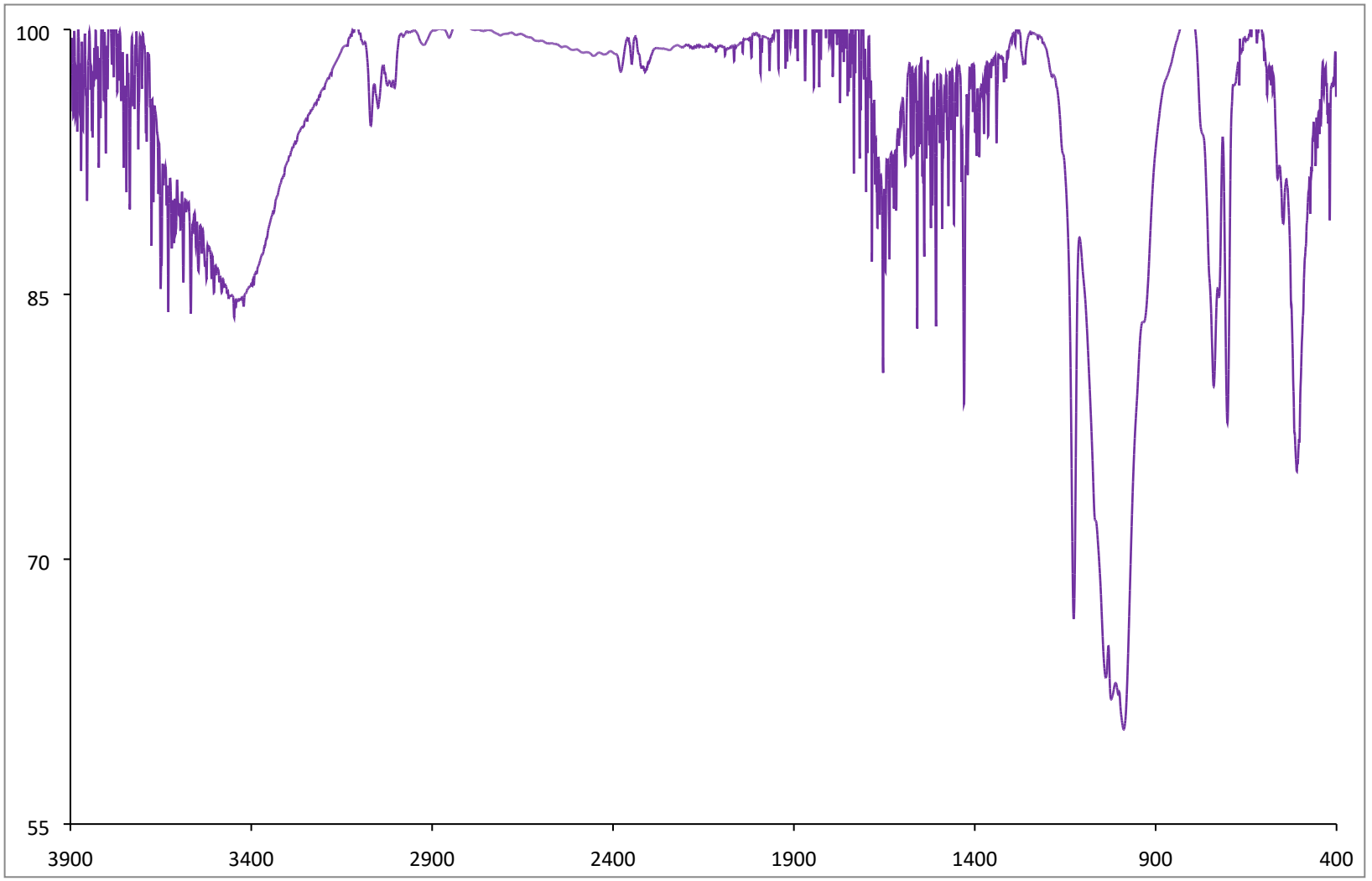
3 (Fig. S25)



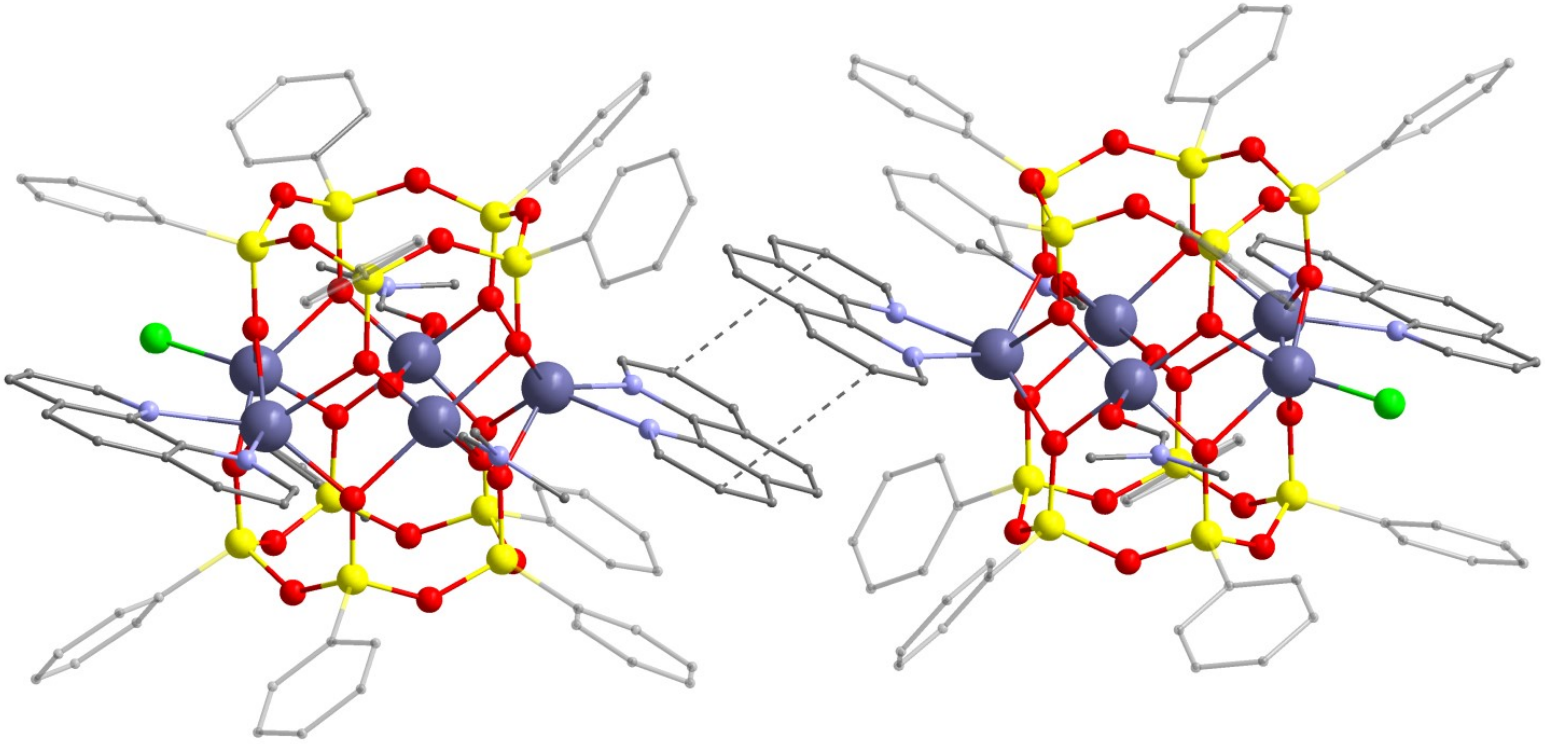
4 (Fig. S26)



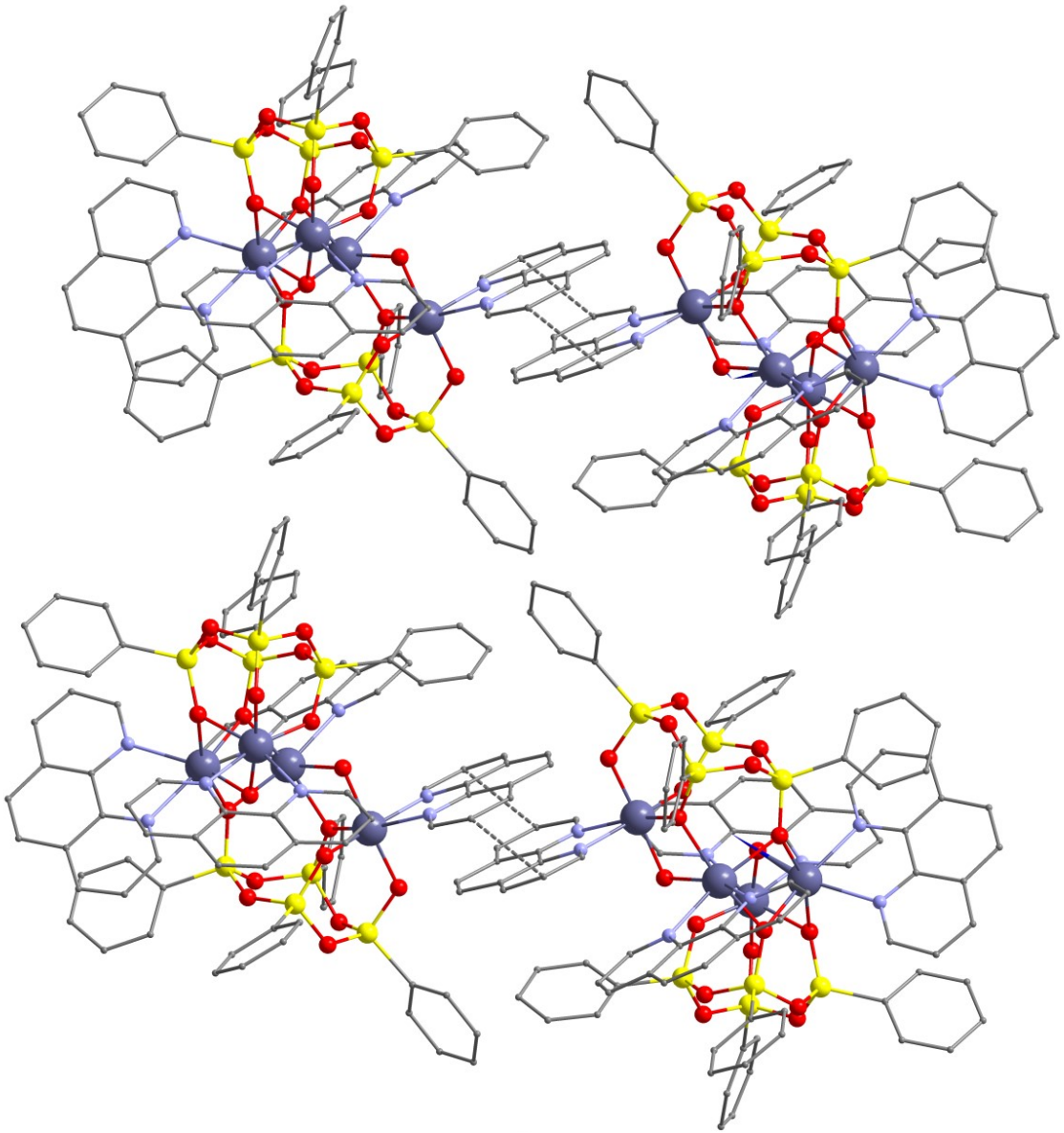
5 (Fig. S27)



π-π stacking interactions of phenanthrolines' ligands in crystal packing of 4 (Figure S28)

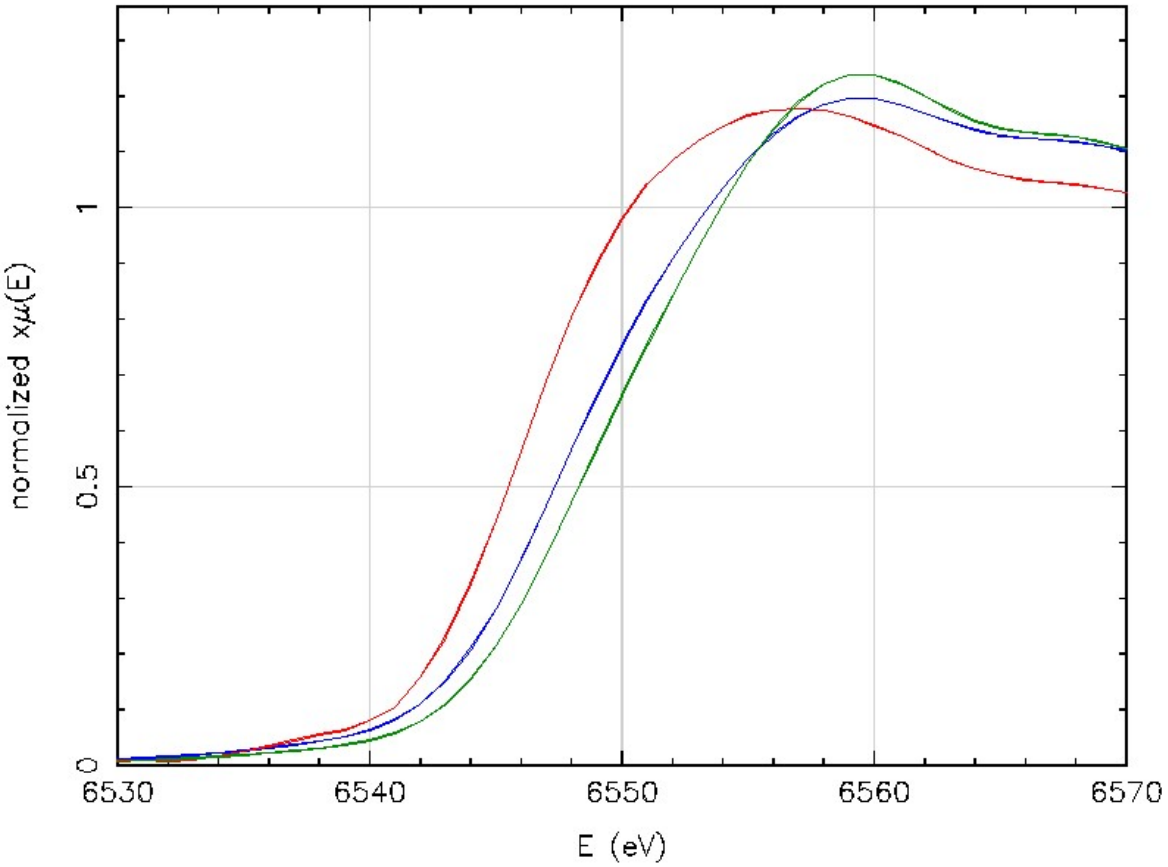


π-π stacking interactions of phenanthrolines' ligands in crystal packing of 5 (Figure S29)

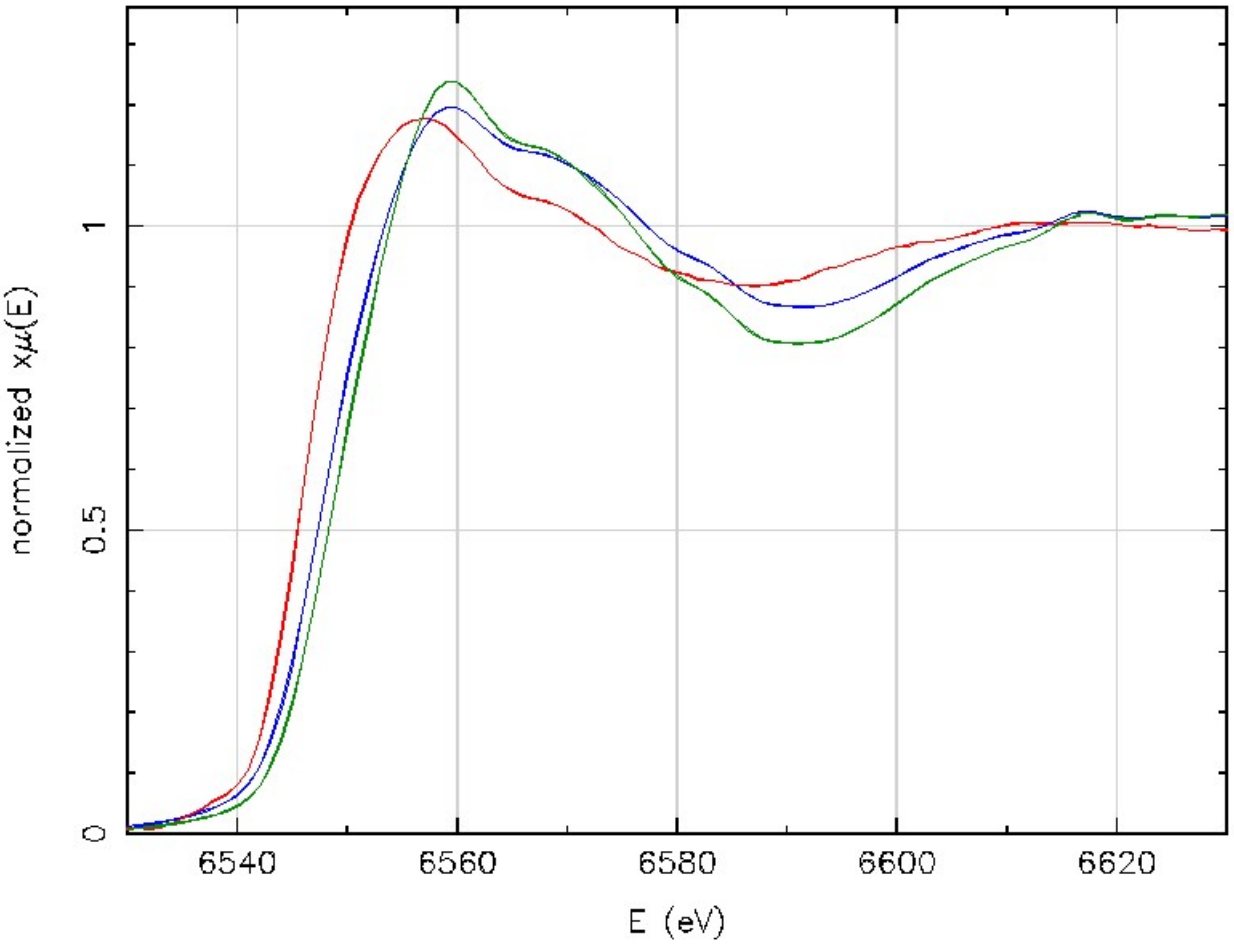


XANES spectra of Mn-silsesquioxanes

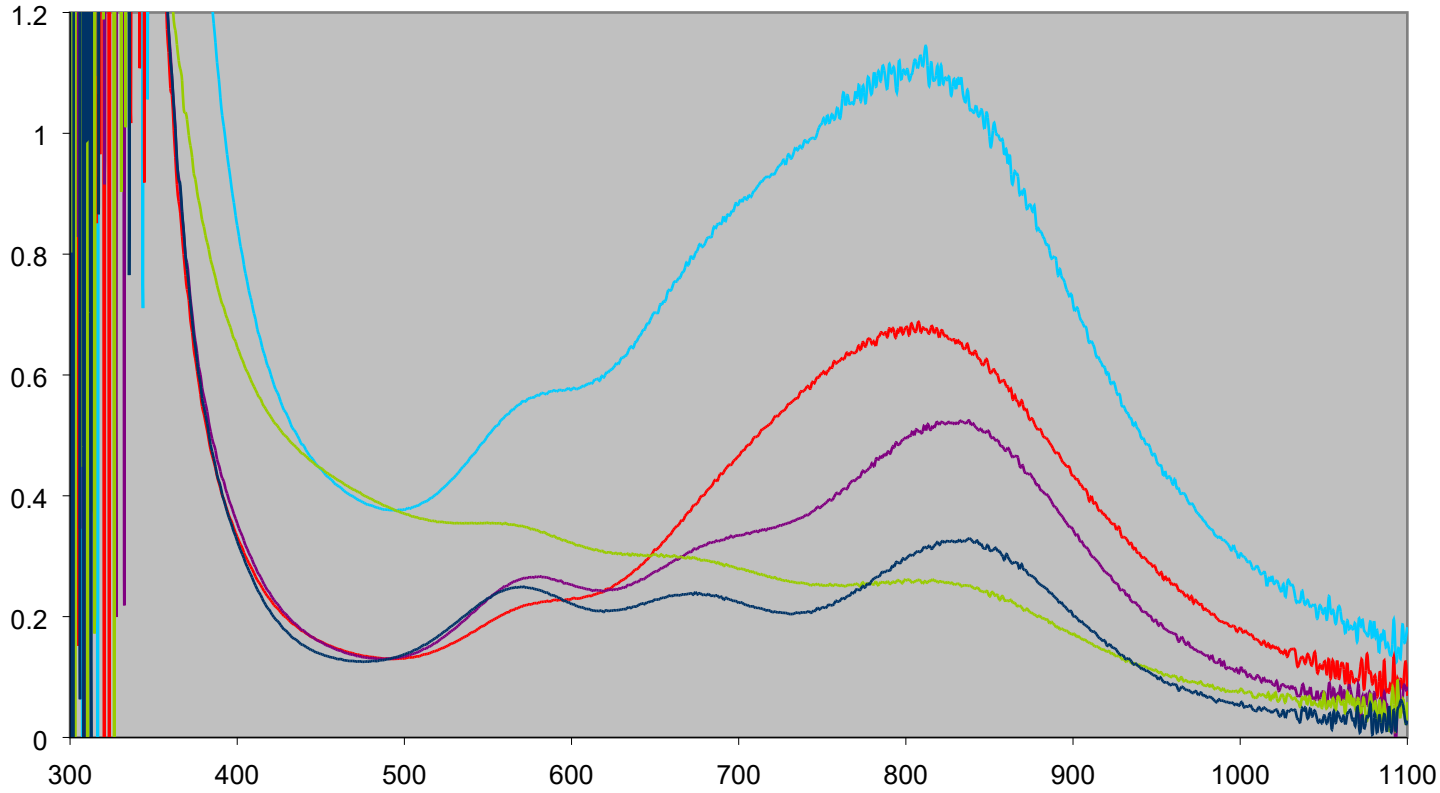
Red curve – 2; blue curve – 3; green curve – 5 (Figure S30).



Red curve – 2; blue curve – 3; green curve – 5 (Figure S31).



UV-vis spectra of 1-5
(Figure S32)



Experimental UV-vis spectra of **1-5** in PhCN. Deep blue: **1**; Blue: **2**; Red: **3**; Purple: **4**; Green: **5**.

X-ray crystal structure determination

X-ray diffraction data for **1**, **2** and **5** were collected on three-circle Bruker APEX-II CCD (for **1** and **2**) and Bruker D8 QUEST PHOTON-III CCD (for **5**) diffractometers (graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program [S3]. The data were indexed and integrated using the SAINT program [S4]. X-ray diffraction data for **3** and **4** were collected at the 'Belok' beamline of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. A total of 720 images were collected with an oscillation range of 1.0° in the *φ* scanning mode using two different orientations for each crystal, and corrected for absorption using the *Scala* program [S5]. The data were indexed, integrated and scaled using the utility *iMOSFLM* in CCP4 program [S6]. For details, see Table S2. The structures were solved by intrinsic phasing modification of direct methods [S7] and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. In the case of **4**, all attempts to model and refine positions of the ethanol solvate molecules were unsuccessful. Therefore, their contribution to the total scattering pattern was removed by use of the utility *SQUEEZE* in PLATON06 [S8]. The hydrogen atoms of the OH-groups and the water molecules were localized in the difference-Fourier maps and included in the refinement within the riding model with fixed isotropic displacement parameters. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite [S9].

Crystallographic data for **1-5** have been deposited with the Cambridge Crystallographic Data Center, CCDC 2168292-2168296. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Table S2. Crystal data and structure refinement for complexes **1-5**.

Identification code	**1 • 2EtOH**	**2 • ¾dioxane**	**3 • 1¼DMF**	**4 • *2⅓EtOH***	**5 • 4½DMF**
Empirical formula	$C_{94.5}H_{131}Mn_4Na_6O_{39}Si_{12}$	$C_{90.5}H_{113.25}ClMn_6NaO_{41.375}Si_{12}$	$C_{105.25}H_{104.25}ClMn_4Na_2N_{7.75}O_{27.75}Si_{12}$	$C_{90}H_{81}ClMn_5N_6O_{23}Si_{10}$	$C_{109.5}H_{105.5}Mn_4N_{12.5}O_{22.5}Si_8$
Formula weight	2585.77	2588.21	2559.98	2205.66	2401.05
Temperature, K	100(2)	296(2)	100(2)	100(2)	100(2)
Crystal size, mm	0.27 × 0.23 × 0.21	0.35 × 0.30 × 0.25	0.15 × 0.10 × 0.01	0.15 × 0.13 × 0.08	0.21 × 0.13 × 0.11
Wavelength, Å	0.71073	1.54178	Synchrotron (λ = 0.96600)	Synchrotron (λ = 0.96600)	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_12_12_1$	*P*bca	$P2_1/n$	*P*-1
a, Å	18.1516(9)	17.1275(8)	19.612(4)	19.940(4)	17.4280(4)
b, Å	17.2212(8)	26.9431(12)	30.698(6)	18.944(4)	18.2428(4)
c, Å	19.6391(10)	32.7551(14)	40.431(8)	32.358(7)	20.8324(5)
α, deg.	90	90	90	90	75.8116(7)
β, deg.	103.8220(10)	90	90	102.70(3)	67.7941(6)
γ, deg.	90	90	90	90	79.8932(7)
V, Å^3	5961.3(5)	15115.4(12)	24342(8)	11924(5)	5919.7(2)
Z	2	4	8	4	2
Density (calc.), mg/m^3	1.441	1.137	1.397	1.229	1.347
μ, mm^{-1}	0.635	5.595	0.841	1.619	0.570
F(000)	2688.0	5333.0	10552.0	4516.0	2484.0
Theta range, deg.	1.751 – 30.964	2.698 – 67.968	1.585 – 31.034	3.251 – 30.409	2.236 – 27.549
Index ranges	-26 ≤ h ≤ 25, -24 ≤ k ≤ 24, -28 ≤ l ≤ 28	-19 ≤ *h* ≤ 20, -31 ≤ *k* ≤ 31, -38 ≤ *l* ≤ 38	-25 ≤ *h* ≤ 24, -39 ≤ *k* ≤ 39, -52 ≤ *l* ≤ 52	-20 ≤ h ≤ 20, -17 ≤ k ≤ 19, -33 ≤ l ≤ 33	-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -27 ≤ l ≤ 27
Reflections collected	79185	185704	222737	61320	73374
Independent	18539 (R_{int} = 0.0570)	26336 (R_{int} = 0.0940)	27772 (R_{int} = 0.0527)	13768 (R_{int} = 0.0924)	27062 (R_{int} = 0.0582)
Reflections observed	12318	18467	22061	8555	17949
Restraints /	127 / 670	589 / 1133	165 / 1125	228 / 1131	132 / 1345
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0666 / 0.1671	0.1469 / 0.2969	0.0927 / 0.2077	0.0932 / 0.1974	0.0880 / 0.2025
R_1 / wR_2 (all data)	0.1111 / 0.2061	0.1723 / 0.3104	0.1104 / 0.2198	0.1404 / 0.2252	0.1296 / 0.2283
Goodness-of-fit on F^2	1.020	1.030	1.027	1.011	1.032
T_{min} / T_{max}	0.798 / 0.846	0.123 / 0.234	0.870 / 0.980	0.780 / 0.870	0.877 / 0.931
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	2.080 / -1.475	1.140 / -1.138	2.30 / -1.41	0.678 / -0.494	2.674 / -1.569

References:

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