Supporting Information

Ni-Catalyzed α-Arylation of Esters and Amides with Phenol Derivatives

Eva Koch,[a] Ryosuke Takise,[b] Armido Studer,[a] Junichiro Yamaguchi,[b,*]
and Kenichiro Itami[b,c,*]

[a] *Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Corrensstraße 40, 48149 Münster, Germany.* [b] *Institute of Transformative Bio-Molecules (WPI-ITbM) and Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan.* [c] *JST, ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Chikusa, Nagoya 464-8602, Japan*

E-mail: junichiro@chem.nagoya-u.ac.jp, itami@chem.nagoya-u.ac.jp

Table of Contents

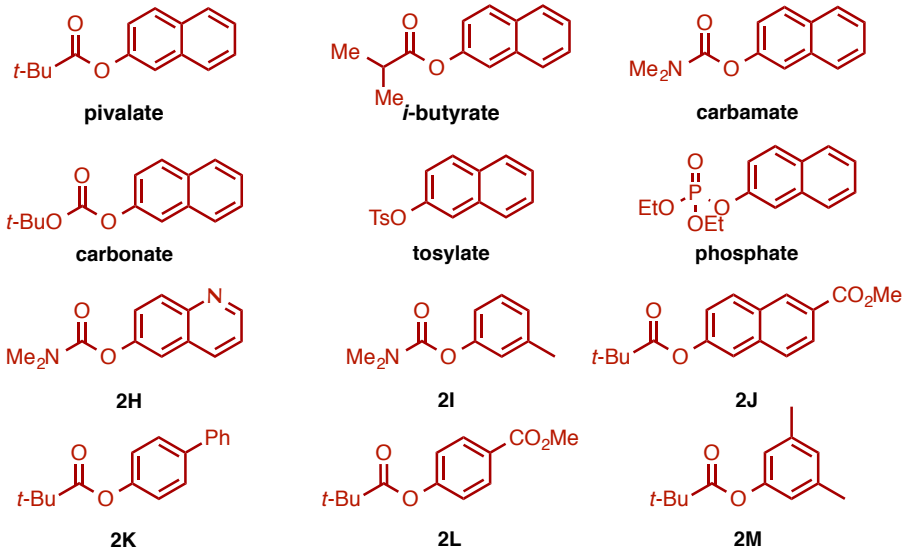
1. General

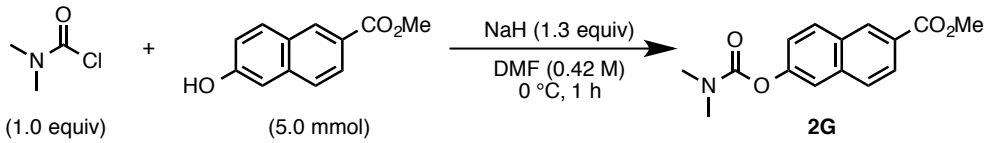
Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. $Ni(cod)_2$ was obtained from KANTO Chemical and K_3PO_4 was obtained from Wako Chemicals. 1,2-Bis(dicyclohexylphosphino)ethane was obtained from Sigma-Aldrich. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in dried glassware using standard vacuum-line techniques. All α-arylation reactions were performed in 20-mL glass vessel tubes equipped with J. Young® O-ring tap and heated in an oil bath (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). The high- resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer and a JEOL JNM-ECA-400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

2. Synthesis of Phenol Derivatives as Arylating Agents

Note: **pivalate**[1], ***i*-butyrate**[2], **carbamate**[3], **carbonate**[4], **tosylate**[5], **phosphate**[6], **2H**[7], **2I**[8], **2J**[1], **2K**[9], **2L**[10], **2M**[11] were synthesized according to procedures reported in the literature.





Methyl 6-((dimethylcarbamoyl)oxy)-2-naphthoate (2G)

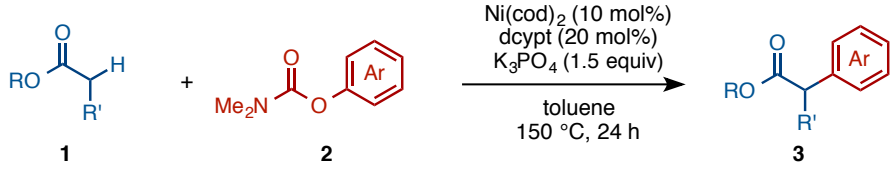
Methyl 6-hydroxy-2-naphthoate (1.01 g, 5.00 mmol, 1.0 equiv) was dissolved in DMF (0.42 M) in a round bottom flask. Sodium hydride (60% oil dispersion, 1.3 equiv) was added at 0 °C in small portions and stirred for 30 min. Dimethylcarbamic chloride (1.0 equiv) was slowly added and the reaction mixture was stirred at room temperature for 30 min. The reaction was slowly quenched by addition of ice and the mixture was extracted with ethyl acetate, washed with 2M NaOH and brine. The crude product was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude mixture

[1] K. W. Quasdorf, X. Tian and N. K. Garg, *J. Am. Chem. Soc.,* 2008, **130**, 14422.
[2] A. K. Chakraborti and Shivani, *J. Org. Chem*., 2008, **71**, 5785.
[3] B.-J. Li, L. Xu, Z.-H. Wu, B.-T. Guan, C.-L. Sun, B.-Q. Wang and Z.-J. Shi, *J. Am. Chem. Soc.,* 2009, **131**, 14656.
[4] K. W. Quasdorf, M. Riener, K.V. Petrova and N. K. Garg, *J. Am. Chem. Soc.,* 2009, **131**, 17748.
[5] T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.,* 2008, **130**, 13848.
[6] A. Guzmán and E. Diaz, *Synth. Commun*., 1997, **27**, 3035.
[7] D. Silvaa, F. Norbertoa, S. Santosa and J. Iley, *J. Phys. Org. Chem*., 2011, **24**, 1081.
[8] N. Schröder, J. Wencel-Delord and F. Glorius, *J. Am. Chem. Soc.,* 2012, **134**, 8298.
[9] R. Takise, K. Muto, J. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed*., 2014, **53**, 6791.
[10] S. T. A. Shah, K. M. Khan, H. Hussain, M. U. Anwar, M. Feckera and W. Voelter, *Tetrahedron*, 2005, **61**, 6652.
[11] A. Hatano, K. Tanaka, M. Shiroc and M. Shionoya, *Tetrahedron*, 2002, **58**, 2965.

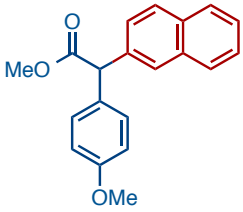
was purified by column chromatography (*n*-hexane/ethyl acetate = 3:1) to provide **2G** as a white crystal (1.18 g, 4.35 mmol, 87%).

R_f = 0.43 (*n*-hexane/ethyl acetate = 2/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.05 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.97 (s, 3H), 3.15 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 154.8, 151.2, 136.3, 131.0, 130.8, 130.3, 127.9, 127.1, 125.9, 122.7, 118.5, 52.4, 36.9, 36.7. HRMS (ESI): calculated for $C_{15}H_{16}NO_4$ $[M+H]^+$ = 274.1074, found: 274.1063.

3. Ni-Catalyzed α-Arylation of Esters with Phenol Derivatives



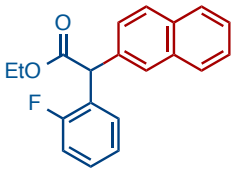
General Procedure for the reaction of Esters and Phenol Derivatives: A 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar and K_3PO_4 (95.5 mg, 0.45 mmol, 1.5 equiv) was dried with a heat-gun under reduced pressure and filled with argon after cooling to room temperature. After adding esters **1** (0.60 mmol, 2.0 equiv) and phenol derivatives **2** (0.30 mmol, 1.0 equiv) to the mixture, the vessel was introduced inside an argon-atmosphere glovebox. In the glovebox, $Ni(cod)_2$ (8.3 mg, 0.03 mmol, 10 mol%), 3,4-bis(dicyclohexylphosphino)thiophene (dcypt: 28.6 mg, 0.06 mmol, 20 mol%), and toluene (1.2 mL) were added to the vessel, which was sealed with O-ring tap and then taken out of the glovebox. The vessel was heated at 150 °C for 24 h in an oil bath with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short pad of silica gel with EtOAc. The filtrate was concentrated and the residue was subjected to preparative thin-layer chromatography to afford α-arylated carbonyl compounds **3** as coupling product.



Methyl 2-(4-methoxyphenyl)-2-(naphthalen-2-yl)acetate (3B)[12]: Purification by PTLC (toluene) provided **3B** as a white solid (42.9 mg, 141 μmol, 47%).

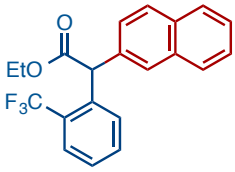
[12] W. A. Moradi and S. L. Buchwald, *J. Am. Chem. Soc*., 2001, **123**, 7996.

R_f = 0.74 (*n*-hexane/ethyl acetate = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.77 (m, 3H), 7.74 (s, 1H), 7.49–7.43 (m, 2H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.4, 159.0, 136.5, 133.5, 132.6, 130.8, 129.9, 128.5, 128.1, 127.7, 127.2, 126.8, 126.3, 126.1, 114.2, 56.4, 55.4, 52.5. HRMS (ESI): calculated for $C_{20}H_{18}NaO_3$ $[M+Na]^+$ = 329.1148, found: 329.1140.



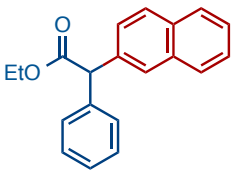
Ethyl 2-(2-fluorophenyl)-2-(naphthalen-2-yl)acetate (3D): Purification by PTLC (toluene) provided **3D** as a white solid (72.0 mg, 234 µmol, 78%).

R_f = 0.86 (*n*-hexane/ethyl acetate = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84–7.79 (m, 3H), 7.78 (s, 1H) 7.49–7.42 (m, 3H), 7.28–7.21 (m, 2H), 7.09–7.02 (m, 2H), 5.44 (s, 1H), 4.29–4.19 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.0, 160.6 (d, J_{CF} = 247.5 Hz), 134.8, 133.5, 132.8, 130.2 (d, J_{CF} = 4.5 Hz), 129.2 (d, J_{CF} = 7.5 Hz), 128.6, 128.1, 127.8, 127.7, 126.9, 126.38, 126.38 (d, J_{CF} = 15.0 Hz), 126.3, 124.3 (d, J_{CF} = 4.5 Hz), 115.5 (d, J_{CF} = 22.5 Hz), 61.6, 50.2, 14.3. HRMS (ESI): calculated for $C_{20}H_{17}FNaO_2$ $[M+Na]^+$ = 331.1105, found: 331.1099.



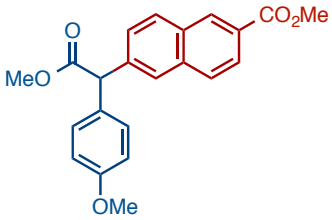
Ethyl 2-(naphthalen-2-yl)-2-(2-(trifluoromethyl)phenyl)acetate (3E): Purification by PTLC (toluene) provided **3E** as a white solid (64.6 mg, 180 µmol, 60%).

R_f = 0.83 (*n*-hexane/ethyl acetate = 3:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83–7.76 (m, 4H), 7.65 (s, 1H), 7.57–7.51 (m, 2H), 7.50–7.45 (m, 2H), 7.45–7.39 (m, 2H), 5.22 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.0, 139.8, 135.5, 133.5, 132.8, 132.3 (q, J_{CF} = 1.5 Hz), 131.0 (q, J_{CF} = 33.0 Hz), 129.2, 128.8, 128.1, 127.8, 127.4, 126.54, 126.53, 126.4, 125.6 (q, J_{CF} = 4.5 Hz), 124.4 (q, J_{CF} = 4.5 Hz), 124.2 (q, J_{CF} = 273.0 Hz), 61.7, 57.1, 14.2. HRMS (ESI): calculated for $C_{21}H_{17}F_3NaO_2$ $[M+Na]^+$ = 381.1073, found: 381.1065.



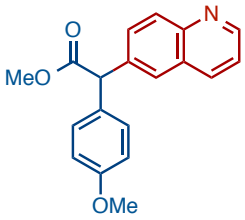
Ethyl 2-(naphthalen-2-yl)-2-phenylacetate (3F)[12]: Purification by PTLC (toluene) provided **3F** as a white solid (47.5 mg, 165 µmol, 55%).

R_f = 0.89 (*n*-hexane/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.75 (m, 4H), 7.48–7.39 (m, 3H), 7.38–7.28 (m, 4H), 7.28–7.23 (m, 1H), 5.18 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 138.8, 136.3, 133.4, 132.6, 128.8, 128.7, 128.4, 128.1, 127.7, 127.40, 127.35, 126.9, 126.3, 126.1, 61.4, 57.3, 14.3. HRMS (ESI): calculated for $C_{20}H_{18}NaO_2$ $[M+Na]^+$ = 313.1199, found: 313.1193.



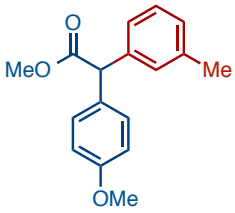
Methyl 6-(2-methoxy-1-(4-methoxyphenyl)-2-oxoethyl)-2-naphthoate (3G): Purification by PTLC (*n*-hexane/ethyl acetate = 3:1) provided **3G** as slightly reddish oil (68.8 mg, 189 µmol, 63%).

R_f = 0.30 (*n*-hexane/ethyl acetate = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.04 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.48 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.16 (s, 1H), 3.97 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.0, 167.3, 159.1, 139.2, 135.6, 131.7, 130.8, 130.3, 129.9, 129.8, 128.3, 127.7, 127.6, 127.0, 125.7, 114.3, 56.4, 55.4, 52.6, 52.4. HRMS (ESI): calculated for $C_{22}H_{20}NaO_5$ $[M+Na]^+$ = 387.1203, found: 387.1196.



Methyl 2-(4-methoxyphenyl)-2-(quinolin-6-yl)acetate (3H): Purification by PTLC (ethyl acetate) provided **3H** as a white-reddish solid (36.0 mg, 117 µmol, 39%).

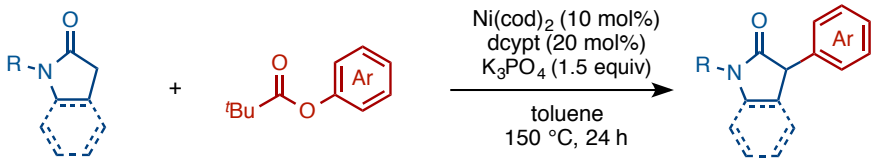
R_f = 0.35 (*n*-hexane/ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.37 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.30–7.24 (m, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 5.17 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 159.0, 150.4, 147.5, 137.3, 136.0, 130.4, 130.2, 129.73, 129.70, 128.1, 126.8, 121.3, 114.1, 56.0, 55.2, 52.4. HRMS (ESI): calculated for $C_{19}H_{18}NO_3$ $[M+H]^+$ = 308.1281, found: 308.1277.



Methyl 2-(4-methoxyphenyl)-2-(m-tolyl)acetate (3I): Purification by PTLC (toluene) provided **3I** as colorless oil (22.0 mg, 66.0 μmol, 27%).

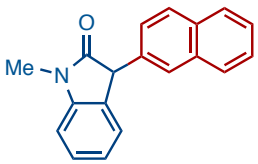
R_f = 0.61 (*n*-hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.18 (m, 3H), 7.12–7.04 (m, 3H), 6.85 (d, *J* = 9.2 Hz, 2H), 4.94 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 158.8, 138.9, 138.4, 130.9, 129.8, 129.2, 128.6, 128.1, 125.5, 114.0, 56.2, 55.3, 52.4, 21.6. HRMS (ESI): calculated for $C_{17}H_{19}O_3$ $[M+H]^+$ = 271.1329, found: 271.1318.

4. Ni-Catalyzed α-Arylation of Amides with Phenol Derivatives



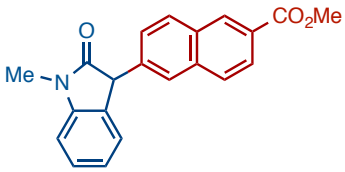
1 **2** **3**

General Procedure for Amides and Phenol Derivatives: A 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar and K_3PO_4 (95.5 mg, 0.45 mmol, 1.5 equiv) was dried with a heat-gun under reduced pressure and filled with argon after cooling to room temperature. After adding amides **1** (0.45 mmol, 1.5 equiv) and phenol derivatives **2** (0.30 mmol, 1.0 equiv) to the mixture, the vessel was introduced inside an argon-atmosphere glovebox. In the glovebox, $Ni(cod)_2$ (8.3 mg, 0.03 mmol, 10 mol%), 3,4-bis(dicyclohexylphosphino)thiophene (dcypt: 28.6 mg, 0.06 mmol, 20 mol%), and toluene (1.2 mL) were added to the vessel, which was sealed with O-ring tap and then taken out of the glovebox. The vessel was heated at 150 °C for 24 h in an oil bath while stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short pad of silica gel with EtOAc. The filtrate was concentrated and the residue was subjected to preparative thin-layer chromatography to afford α-arylated carbonyl compounds **3** as a coupling product.



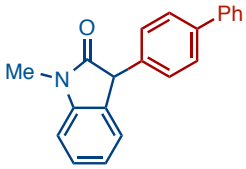
1-Methyl-3-(naphthalen-2-yl)indolin-2-one (3C)[13]: Purification by PTLC (*n*-hexane/ethyl acetate = 2:1) provided **3C** as a white-reddish solid (55.9 mg, 204 µmol, 68%).

R_f = 0.46 (*n*-hexane/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.74 (m, 3H), 7.70 (s, 1H), 7.47–7.40 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.77 (s, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 144.5, 134.0, 133.5, 132.8, 128.9, 128.7, 128.5, 127.8, 127.6, 127.5, 126.2, 126.1, 125.9, 125.1, 122.8, 108.2, 52.2, 26.5. HRMS (ESI): calculated for $C_{19}H_{15}NNaO$ $[M+Na]^+$ = 296.1046, found: 296.1040.



Methyl 6-(1-methyl-2-oxoindolin-3-yl)-2-naphthoate (3J): Purification by PTLC (*n*-hexane/ethyl acetate = 2:1) provided **3J** as a white-reddish solid (62.4 mg, 189 µmol, 63%).

R_f = 0.63 (*n*-hexane/ethyl acetate = 1:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.04 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.74 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.08 (td, *J* = 7.2, 1.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.78 (s, 1H), 3.96 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.6, 167.2, 144.6, 136.8, 135.7, 131.9, 130.9, 130.2, 128.8, 128.5, 128.2, 127.6, 127.5, 127.1, 125.7, 125.2, 123.0, 108.5, 52.3, 26.6. There is one overlapping carbon signal as 1 peak is missing even with prolonged scans. HRMS (ESI): calculated for $C_{21}H_{18}NO_3$ $[M+H]^+$ = 332.1281, found: 332.1272.

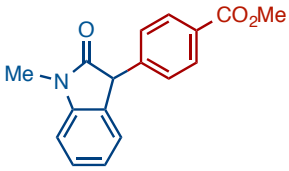


3-([1,1'-Biphenyl]-4-yl)-1-methylindolin-2-one (3K)[14]: Purification by PTLC (*n*-hexane/ethyl acetate = 2:1) provided **3K** as a white-reddish solid (52.7 mg, 177 µmol, 59%).

R_f = 0.71 (*n*-hexane/ethyl acetate = 1:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57–7.53 (m, 4H), 7.41 (t, *J* = 8.4 Hz, 2H), 7.36–7.31 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.65 (s, 1H), 3.26 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 176.1, 144.6, 140.9, 140.7, 135.7, 128.92, 128.86, 128.8, 128.6, 127.8, 127.4, 127.2, 125.2, 122.9, 108.3, 51.8, 26.6. HRMS (ESI): calculated for $C_{21}H_{18}NO$ $[M+H]^+$ = 300.1383, found: 300.1375.

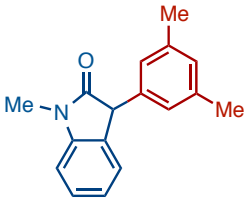
---

[13] B. M. Trost and Y. Zhang, *J. Am. Chem. Soc*., 2007, **129**, 14548.
[14] B. M. Trost and M. U. Frederiksen, *Angew. Chem., Int. Ed*., 2005, **44,** 308.



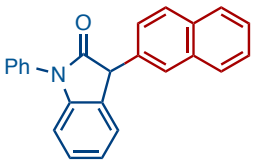
Methyl 4-(1-methyl-2-oxoindolin-3-yl)benzoate (3L): Purification by PTLC (*n*-hexane/ethyl acetate = 1:2) provided **3L** as a white solid (53.3 mg, 189 µmol, 63%).

R_f = 0.75 (*n*-hexane/ethyl acetate = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 3.90 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 166.9, 144.5, 141.8, 130.2, 129.5, 128.8, 128.6, 128.1, 125.1, 123.0, 108.5, 52.2, 52.0, 26.6. HRMS (ESI): calculated for $C_{17}H_{15}NNaO_3$ $[M+Na]^+$ = 304.0944, found: 304.0936.



3-(3,5-Dimethylphenyl)-1-methylindolin-2-one (3M): Purification by PTLC (*n*-hexane/ethyl acetate = 4:1) provided **3M** as a brown solid (25.6 mg, 102 µmol, 34%).

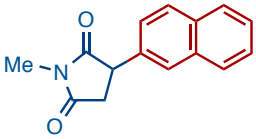
R_f = 0.45 (*n*-hexane/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92–6.87 (m, 2H), 6.78 (s, 2H), 4.52 (s, 1H), 3.26 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 144.4, 138.4, 136.4, 129.3, 129.2, 128.2, 126.2, 125.0, 122.7, 108.0, 52.1, 26.4, 21.3. HRMS (ESI): calculated for $C_{17}H_{17}NNaO$ $[M+Na]^+$ =274.1202, found: 274.1196.



3-(Naphthalen-2-yl)-1-phenylindolin-2-one (3N): Purification by PTLC (*n*-hexane/ethyl acetate = 2:1) provided **3N** as a brown solid (55.3 mg, 165 µmol, 55%).

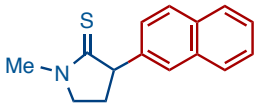
R_f = 0.69 (*n*-hexane/ethyl acetate = 2:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85–7.80 (m, 3H), 7.79 (s, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.49–7.46 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.26–7.24 (m, 1H), 7.11 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 144.4, 134.5, 134.1, 133.5, 132.8, 129.6,

128.8, 128.7, 128.4, 128.1, 127.8, 127.7, 127.6, 126.6, 126.2, 126.1, 126.0, 125.5, 123.2, 109.6, 52.4. HRMS (ESI): calculated for $C_{24}H_{17}NNaO$ $[M+Na]^+$ = 358.1202, found: 358.1194.



1-Methyl-3-(naphthalen-2-yl)pyrrolidine-2,5-dione (3O): Purification by PTLC (*n*-hexane/ethyl acetate = 2:1) provided **3O** as white crystals (18.9 mg, 78.0 µmol, 26%).

R_f = 0.32 (*n*-hexane/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.78 (m, 3H), 7.70 (s, 1H), 7.53–7.46 (m, 2H), 7.29 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.20 (dd, *J* = 9.6, 4.8 Hz, 1H), 3.28 (dd, *J* = 18.8, 9.6 Hz, 1H), 3.11 (s, 3H), 2.93 (dd, *J* = 18.8, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 176.4, 134.4, 133.5, 132.9, 129.4, 127.9, 127.8, 126.8, 126.7, 126.5, 124.9, 46.2, 37.3, 25.4. HRMS (ESI): calculated for $C_{15}H_{14}NO_2$ $[M+H]^+$ = 240.1019, found: 240.1012.

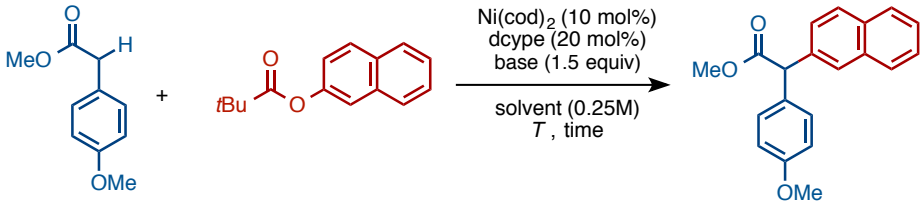


1-Methyl-3-(naphthalen-2-yl)pyrrolidine-2-thione (3P): Naphthalen-2-yl dimethylcarbamate was employed as a phenol derivative and dcype was employed as a ligand in this reaction. Purification by PTLC (ethyl acetate) provided **3P** as white crystals (40.3 mg, 168 µmol, 56%).

R_f = 0.49 (*n*-hexane/ethyl acetate = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.75 (m, 3H), 7.69 (s, 1H), 7.47–7.41 (m, 2H), 7.30 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.29 (t, *J* = 8.4 Hz, 1H), 3.94–3.85 (m, 1H), 3.84–3.75 (m, 1H), 3.39 (s, 3H), 2.69–2.58 (m, 1H), 2.30–2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 138.9, 133.4, 132.6, 128.6, 127.8, 127.6, 127.1, 126.1, 125.9, 125.8, 60.4, 55.5, 36.0, 29.6. HRMS (ESI): calculated for $C_{15}H_{16}NS$ $[M+H]^+$ = 242.0998, found: 242.0987.

5. Screening of Reaction Parameters

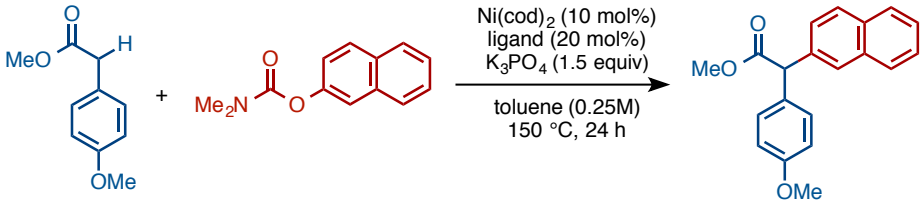
Table S1



1B (1.5 equiv) **2: pivalate** (0.30 mmol) **3B**

entry	base	solvent	T (°C)	time (h)	NMR yield (%)
1	Li_3PO_4	toluene	150	24	0
2	KO^tBu	toluene	150	24	0
3	Na_2CO_3	toluene	150	24	0
4	Cs_2CO_3	toluene	150	24	9
5	**K_3PO_4**	**toluene**	150	24	9
6	K_3PO_4	1,4-dioxane	140	24	1
7	K_3PO_4	m-xylene	140	24	2
8	K_3PO_4	DMF	140	24	0
9	K_3PO_4	CH_2Cl_2	140	24	0
10	K_3PO_4	THF	120	24	3
11	K_3PO_4	Et_2O	120	24	4

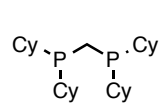
Table S2

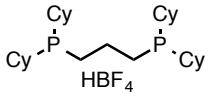


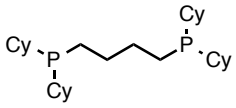
1B (0.30 mmol) **2: carbamate** (1.1 equiv) **3B**

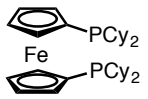
entry	ligand	NMR yield (%)
1[a]	dcypt	63
2	dcypm	0
3[a]	dcype	36
4	dcypp·HBF_4	0
5	dcypb	0
6	dcypf	0
7[b]	PCy_3	0
8	dppe	0
9[b]	IPr·HCl	0
10	BINAP	9
11	CyJohnPhos	0
12	L1	0

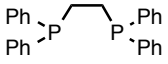
[a] **1** (0.60 mmol), **2** (0.30 mmol). [b] ligand (40 mol%).

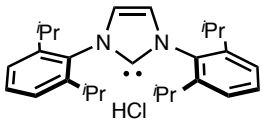

dcypm

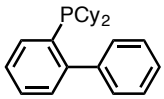

dcypp·HBF$_4$


dcypb


dcypf


dppe


IPr·HCl


CyJohnPhos

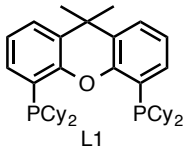
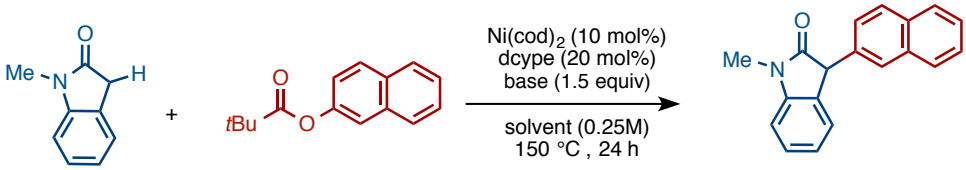

L1

Table S3



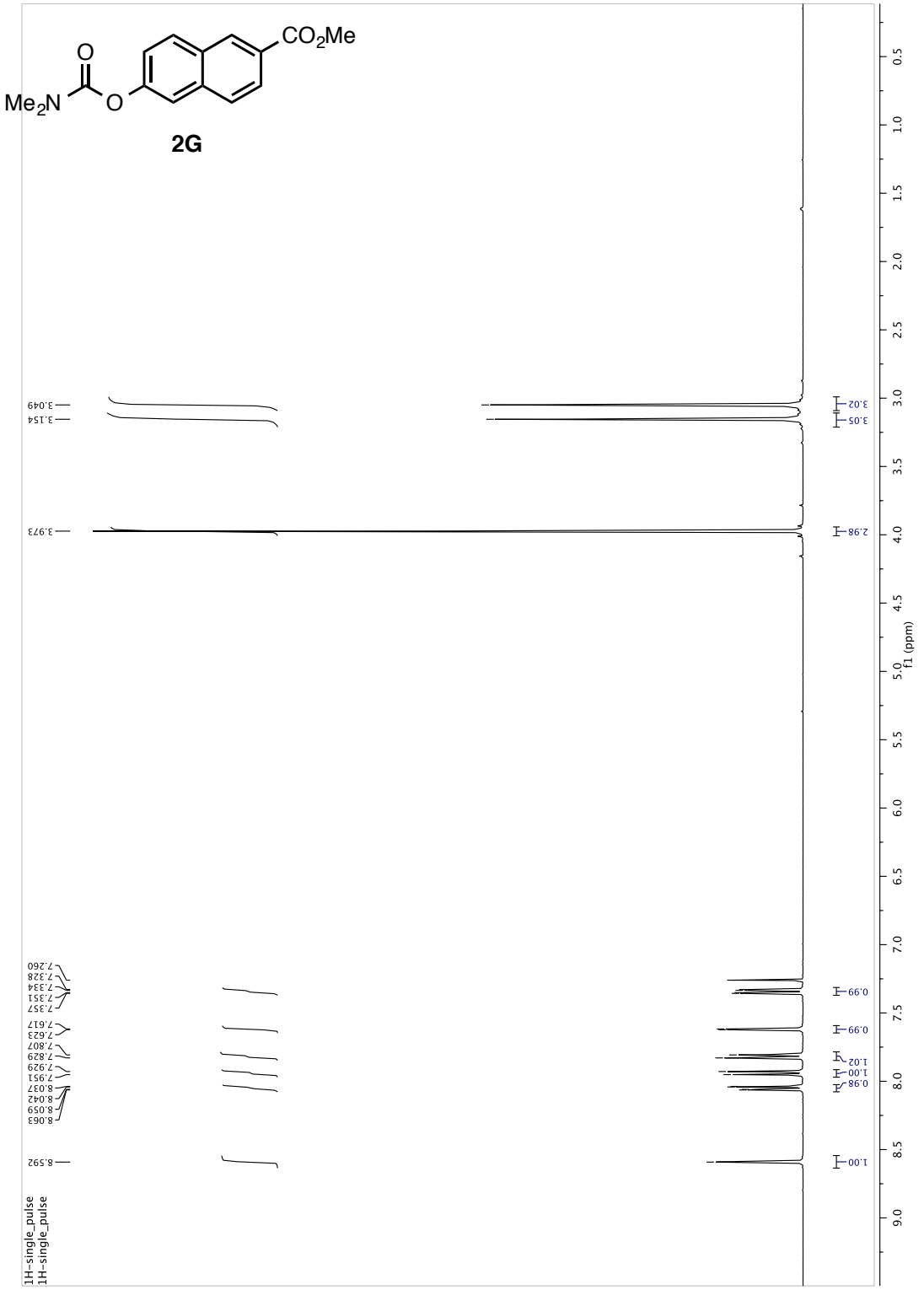
1C (1.5 equiv) **2: pivalate** (0.30 mmol) **3C**

entry	base	solvent	NMR yield (%)
1	KO^{t}Bu	toluene	13
2	K_2CO_3	toluene	65
3	Cs_2CO_3	toluene	54
4	CsOPiv	toluene	0
5	K_3PO_4	toluene	76
6	K_3PO_4	toluene	76[a,b]
7	K_3PO_4	1,4-dioxane	35
8	K_3PO_4	DMF	0
9	K_3PO_4	THF	9

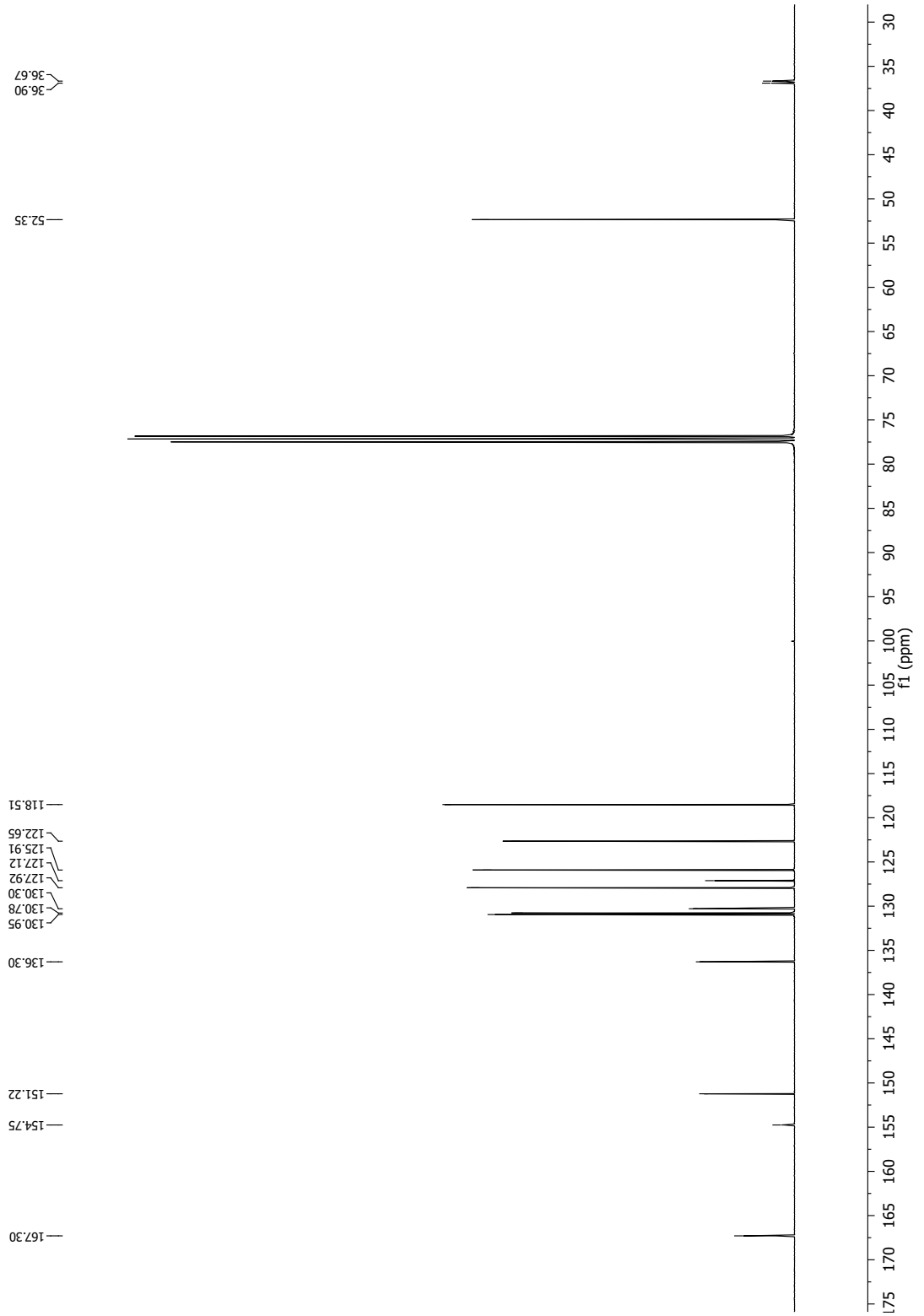
[a]Ni(cod)$_2$ (5 mol%), dcypt (5 mol%). [b]isolated yield

6. NMR Spectra

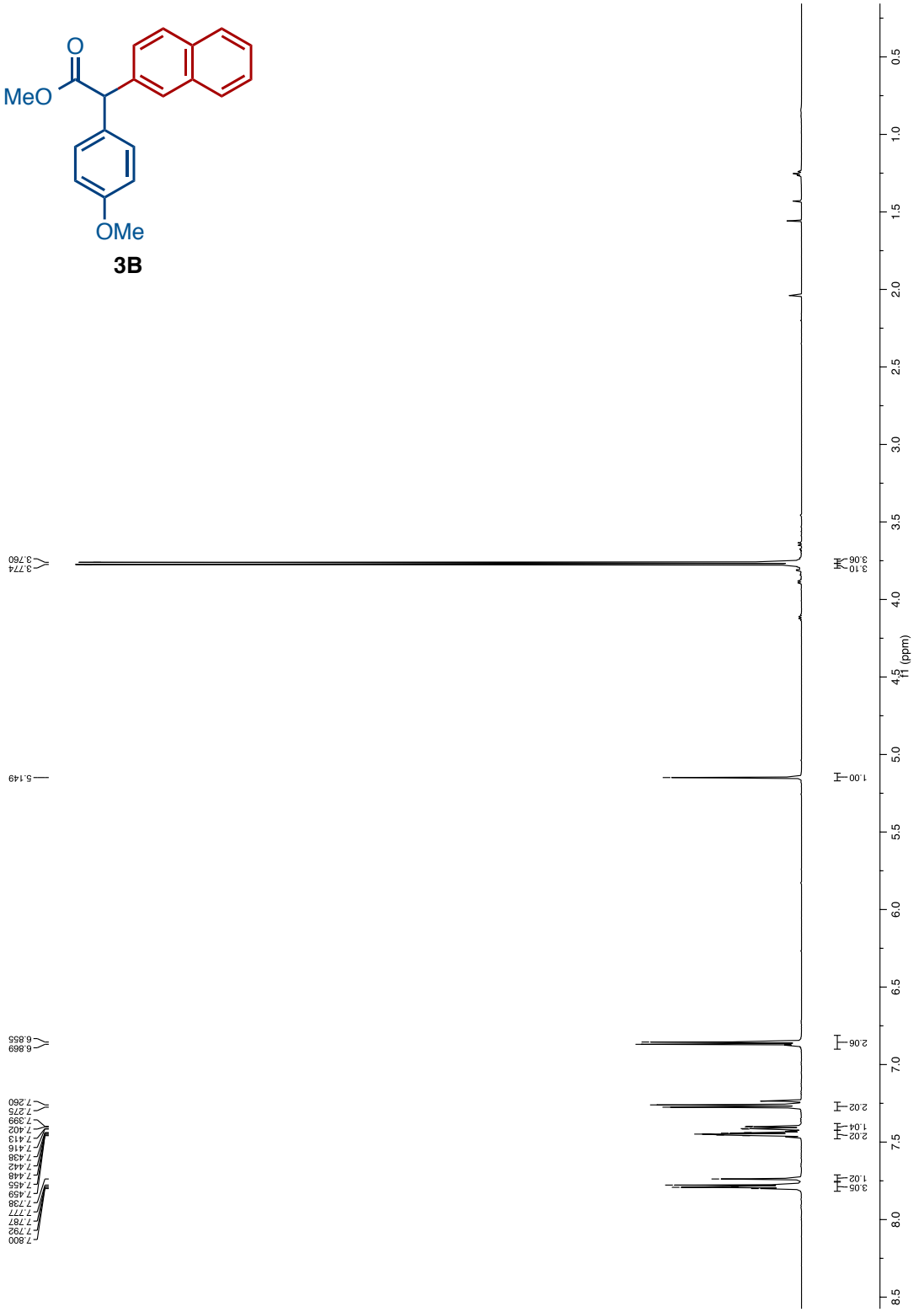
^{1}H NMR (400 MHz, $CDCl_3$) of 2G:



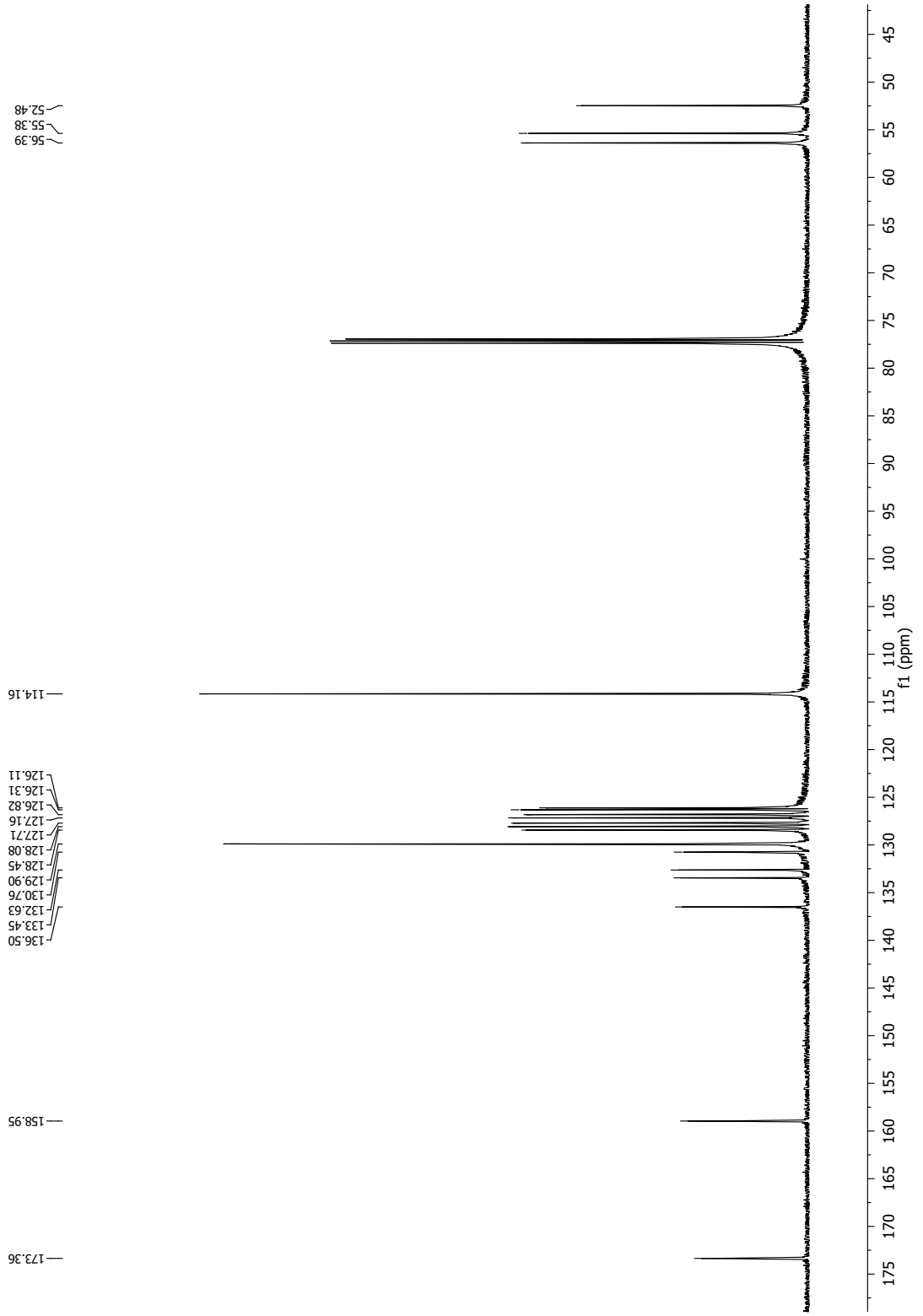
^{13}C NMR (100 MHz, $CDCl_3$) of 2G:



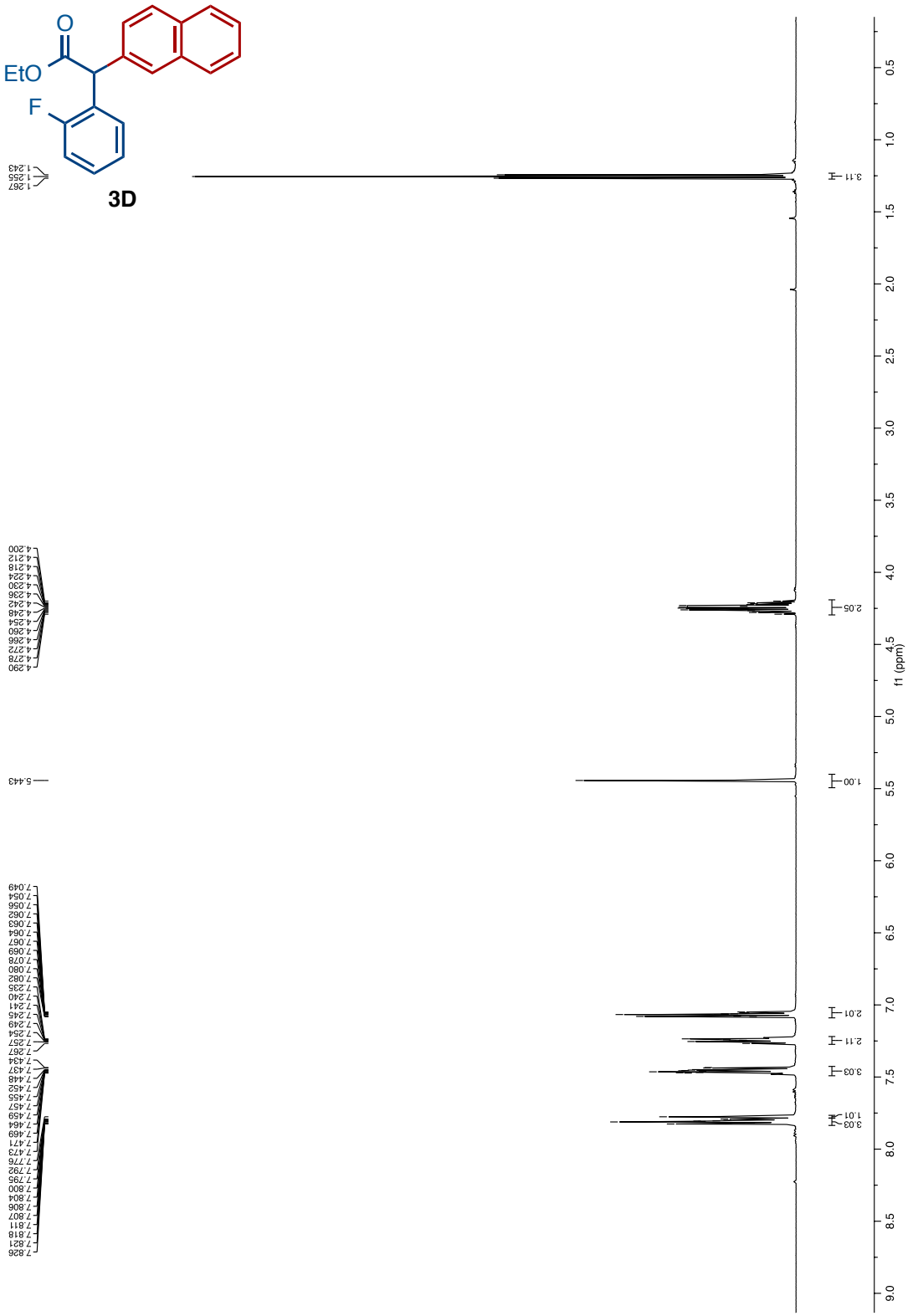
^{1}H NMR (600 MHz, $CDCl_3$) of 3B:



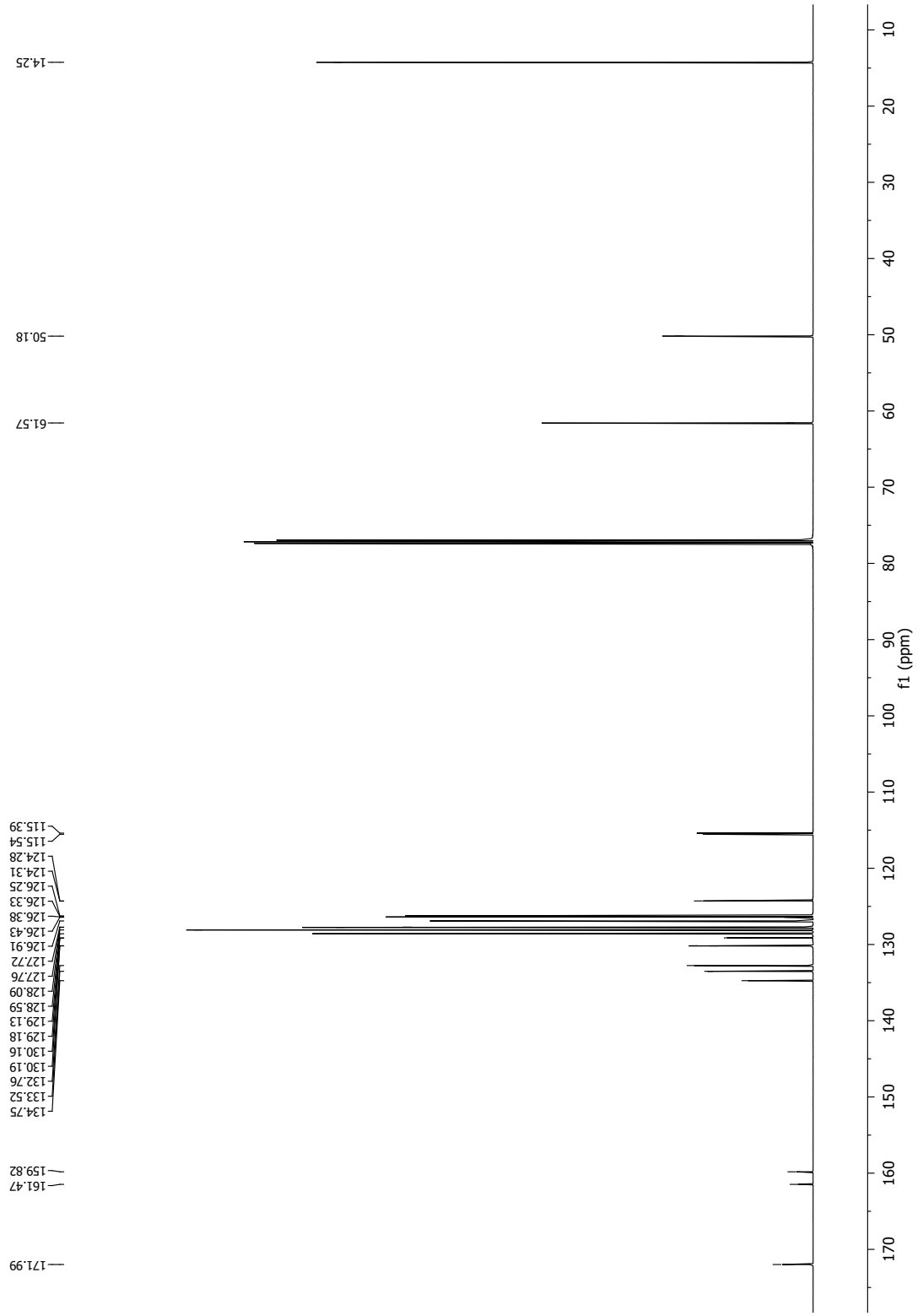
^{13}C NMR (150 MHz, $CDCl_3$) of 3B:



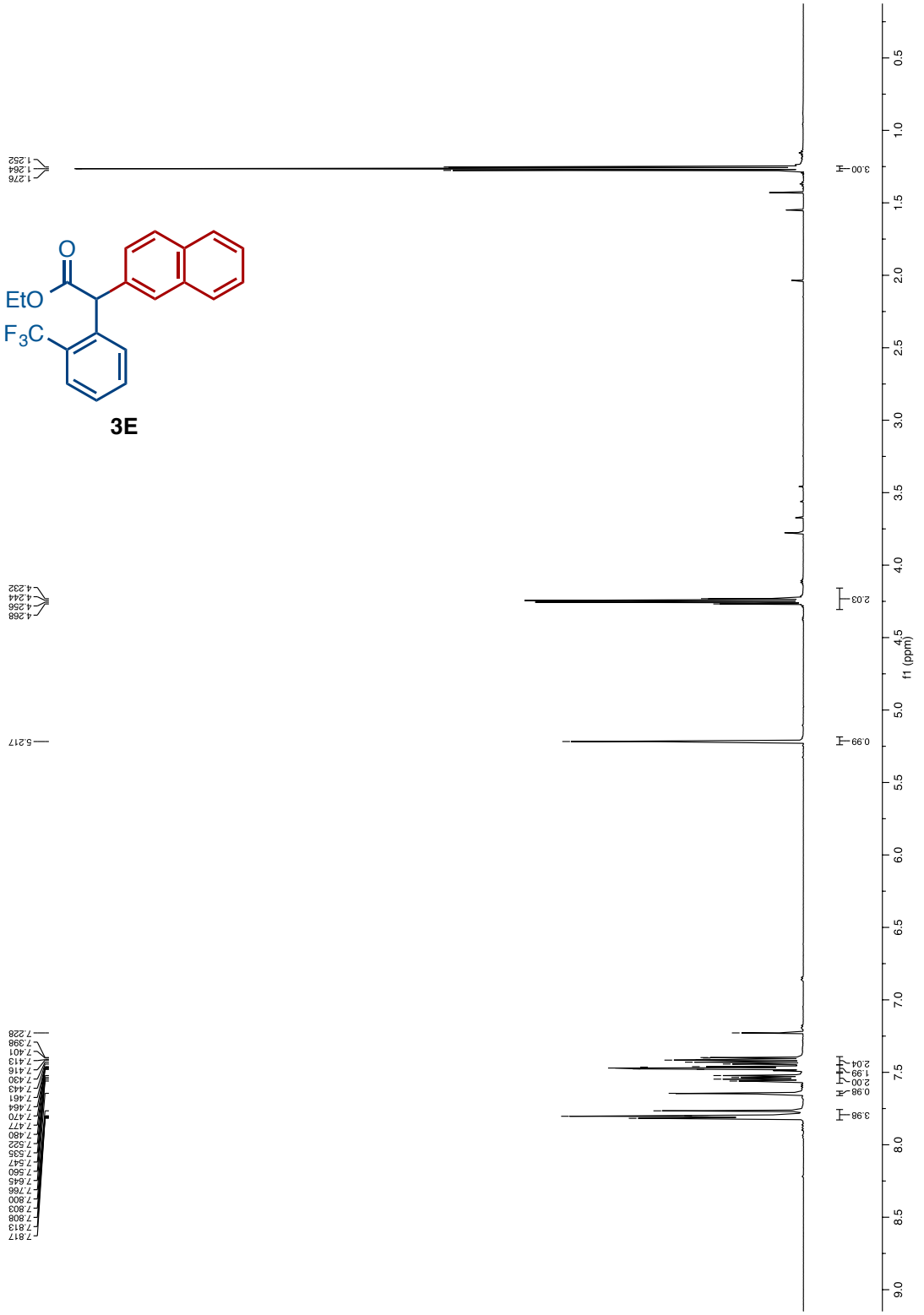
^{1}H NMR (600 MHz, $CDCl_3$) of 3D:



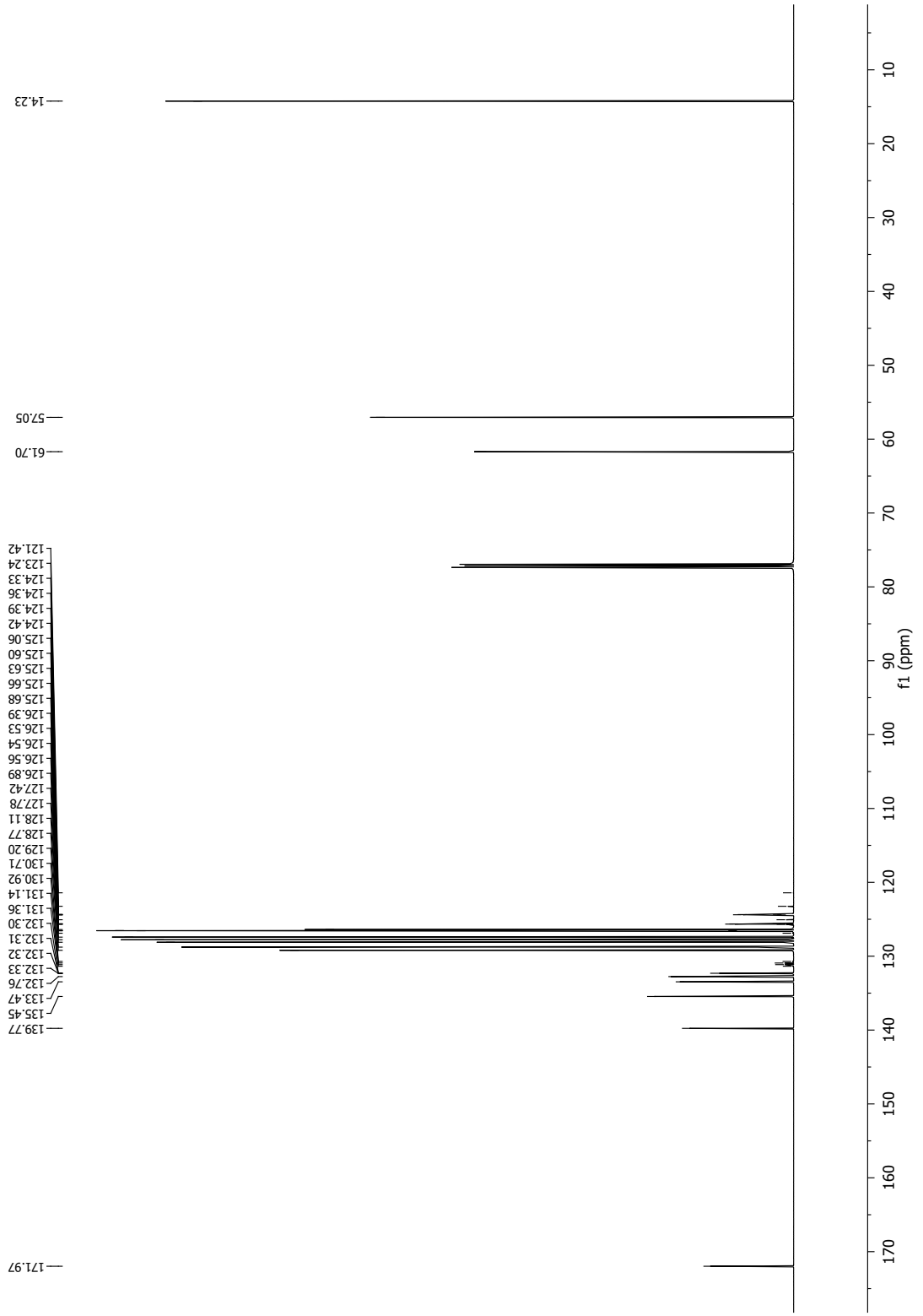
^{13}C NMR (150 MHz, $CDCl_3$) of 3D:



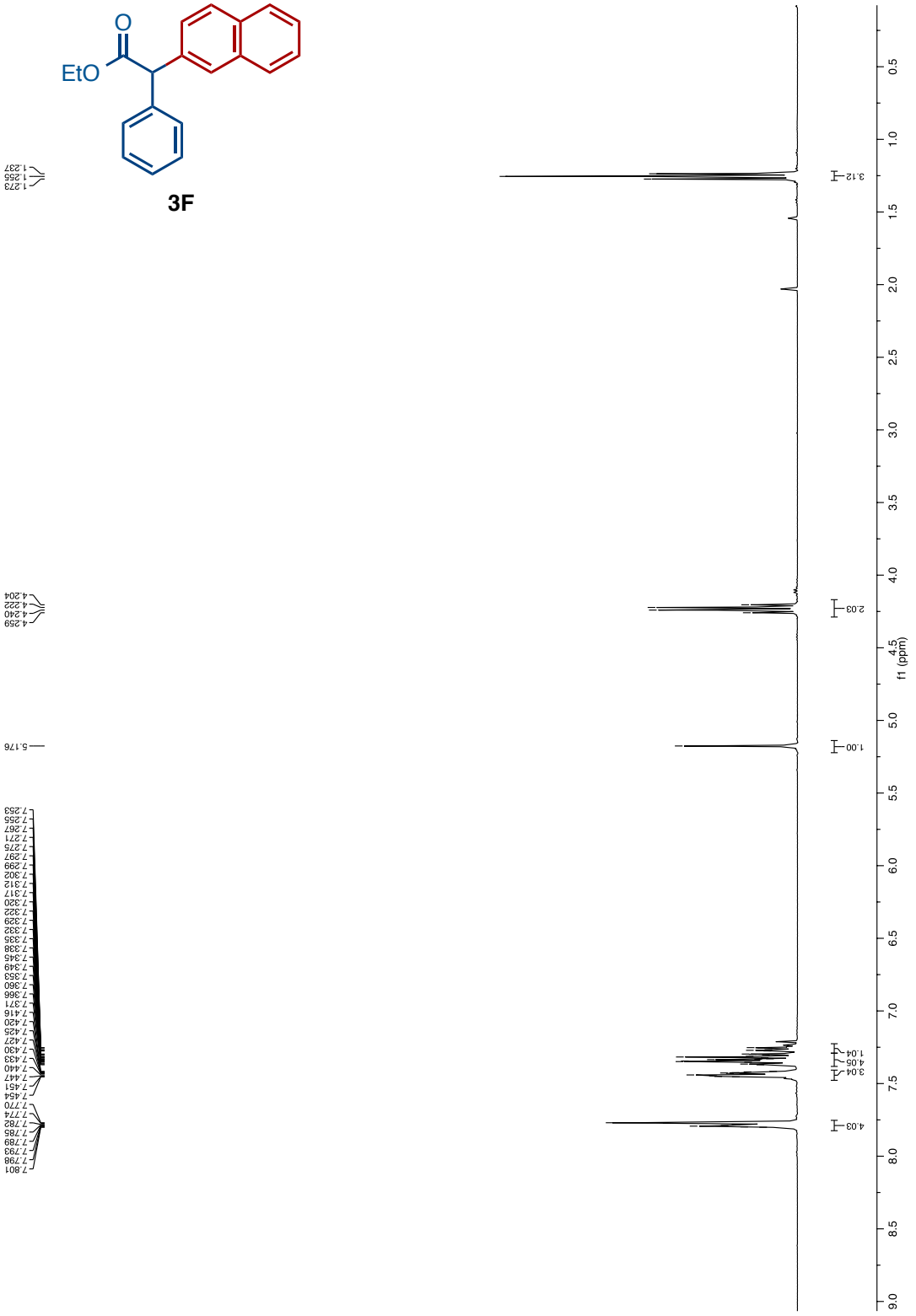
^{1}H NMR (600 MHz, $CDCl_3$) of 3E:



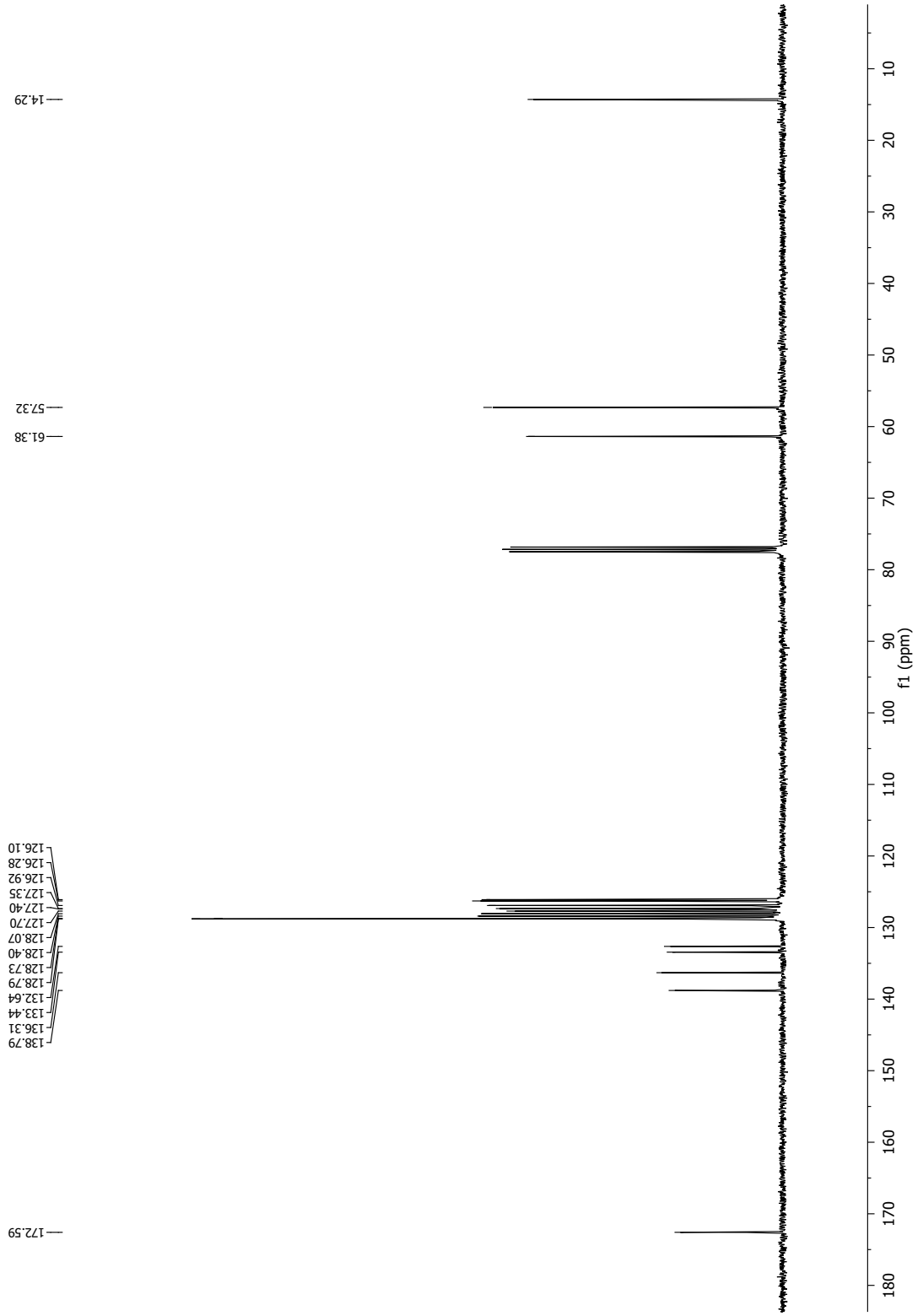
^{13}C NMR (150 MHz, $CDCl_3$) of 3E:



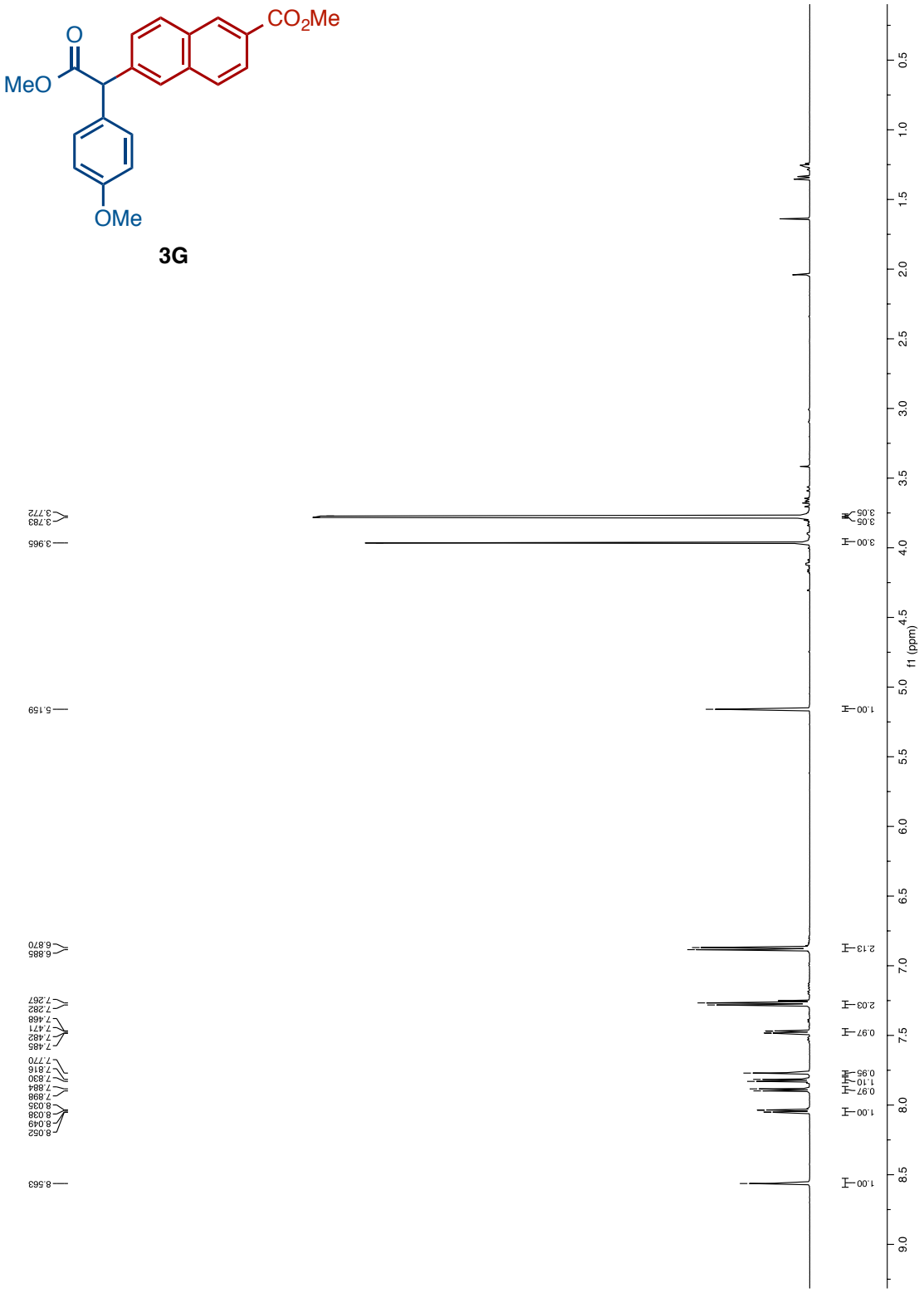
^{1}H NMR (400 MHz, $CDCl_3$) of 3F:



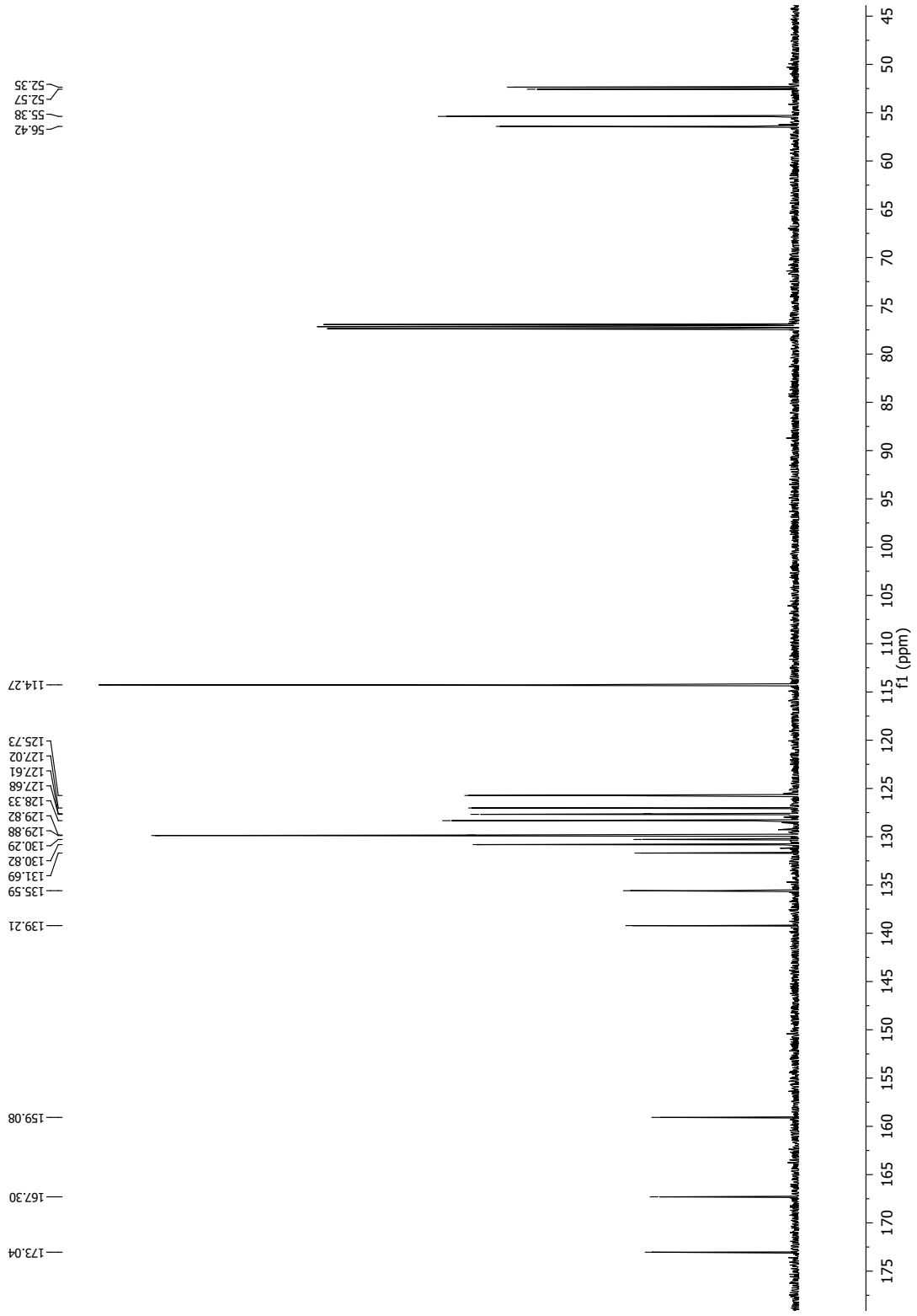
^{13}C NMR (100 MHz, $CDCl_3$) of 3F:



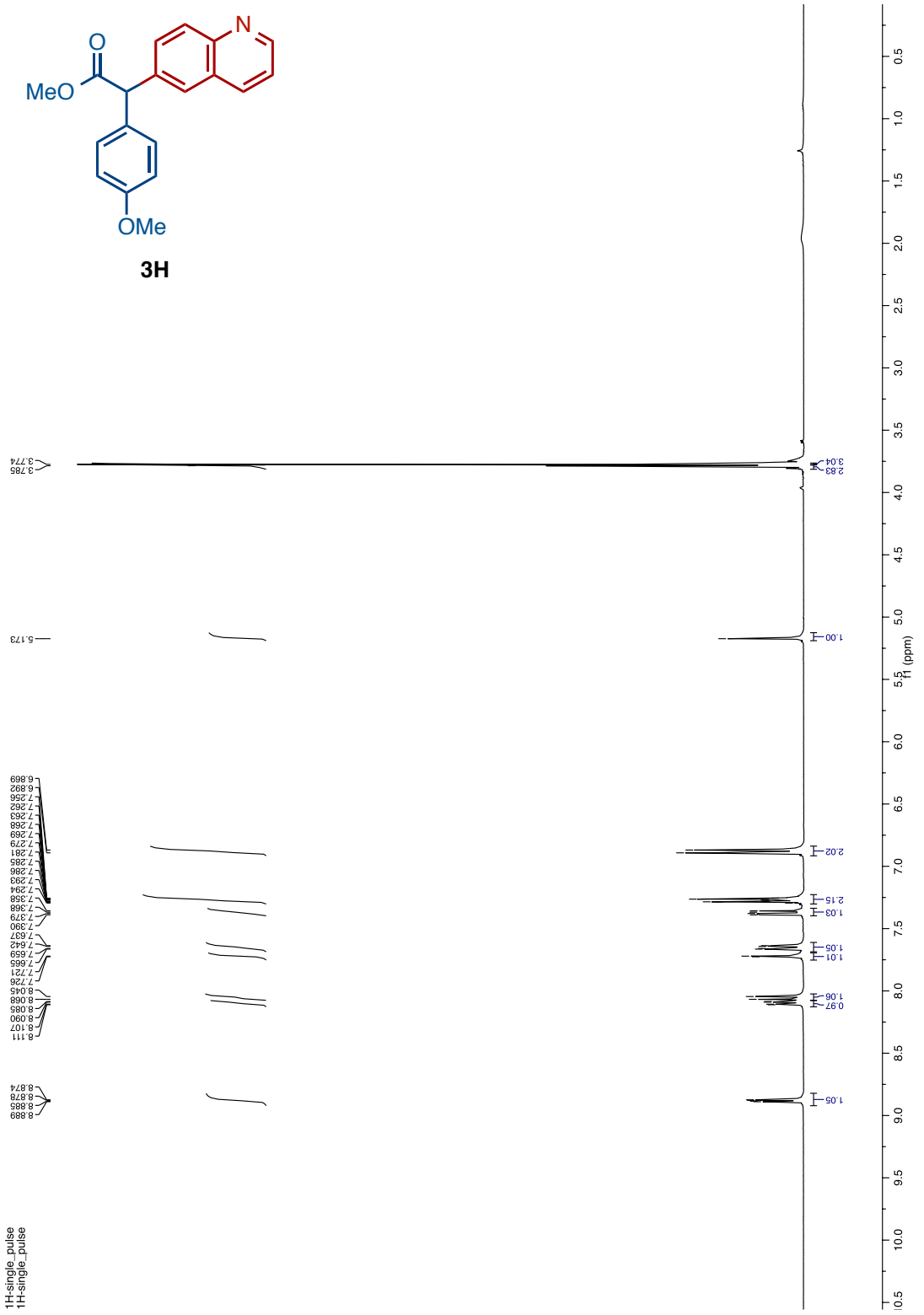
^{1}H NMR (600 MHz, $CDCl_3$) of 3G:



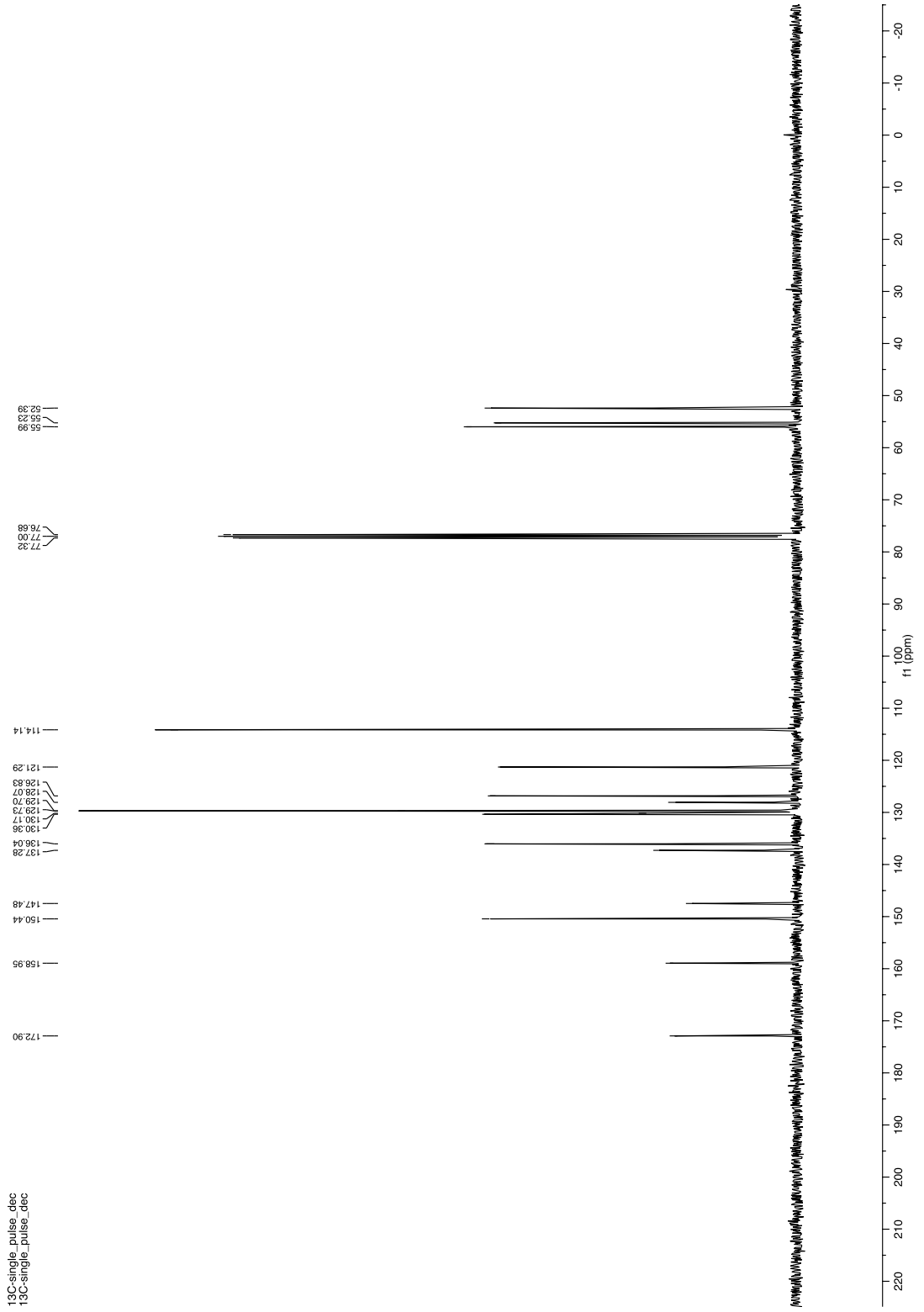
^{13}C NMR (150 MHz, $CDCl_3$) of 3G:



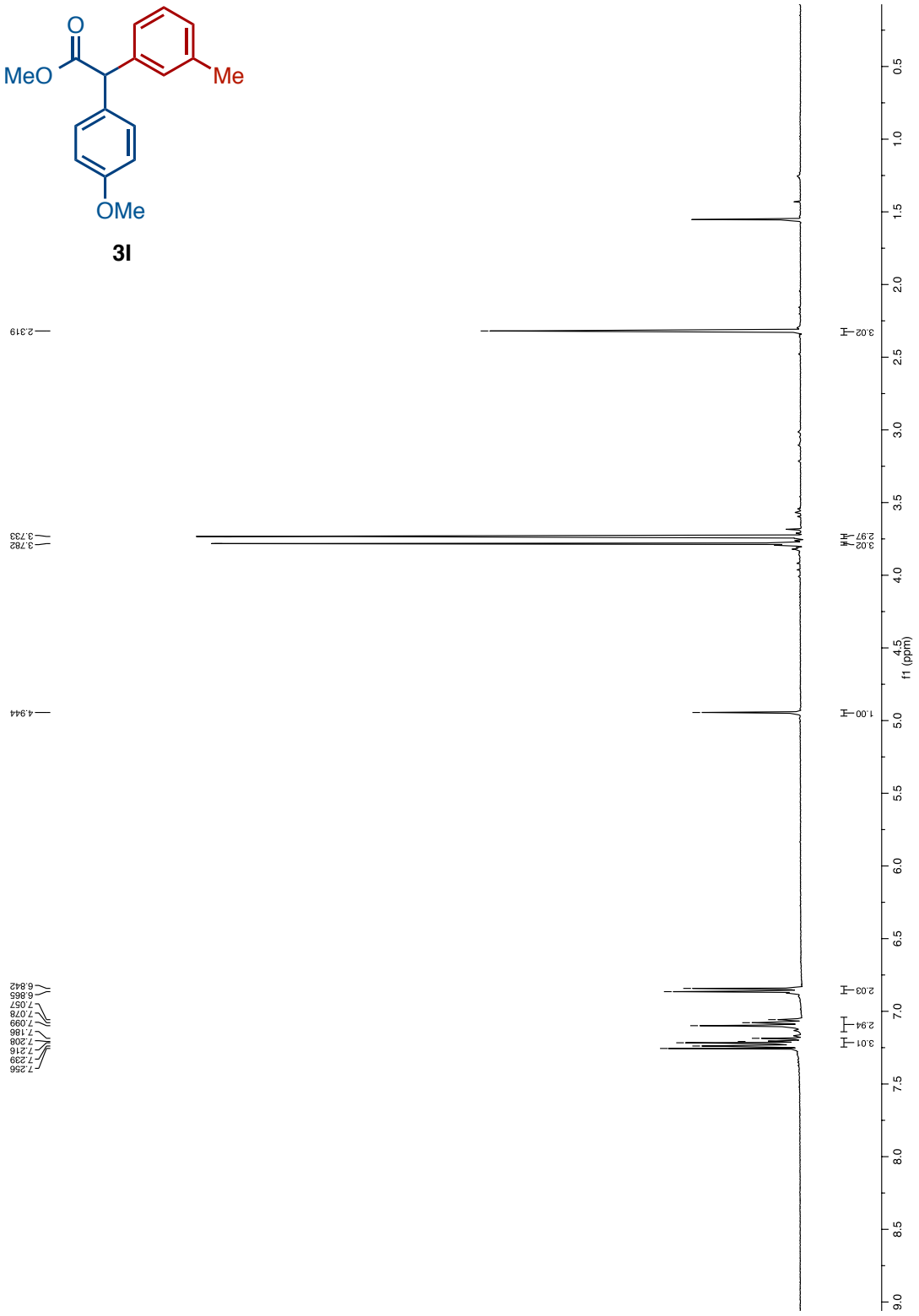
^{1}H NMR (400 MHz, $CDCl_3$) of 3H:



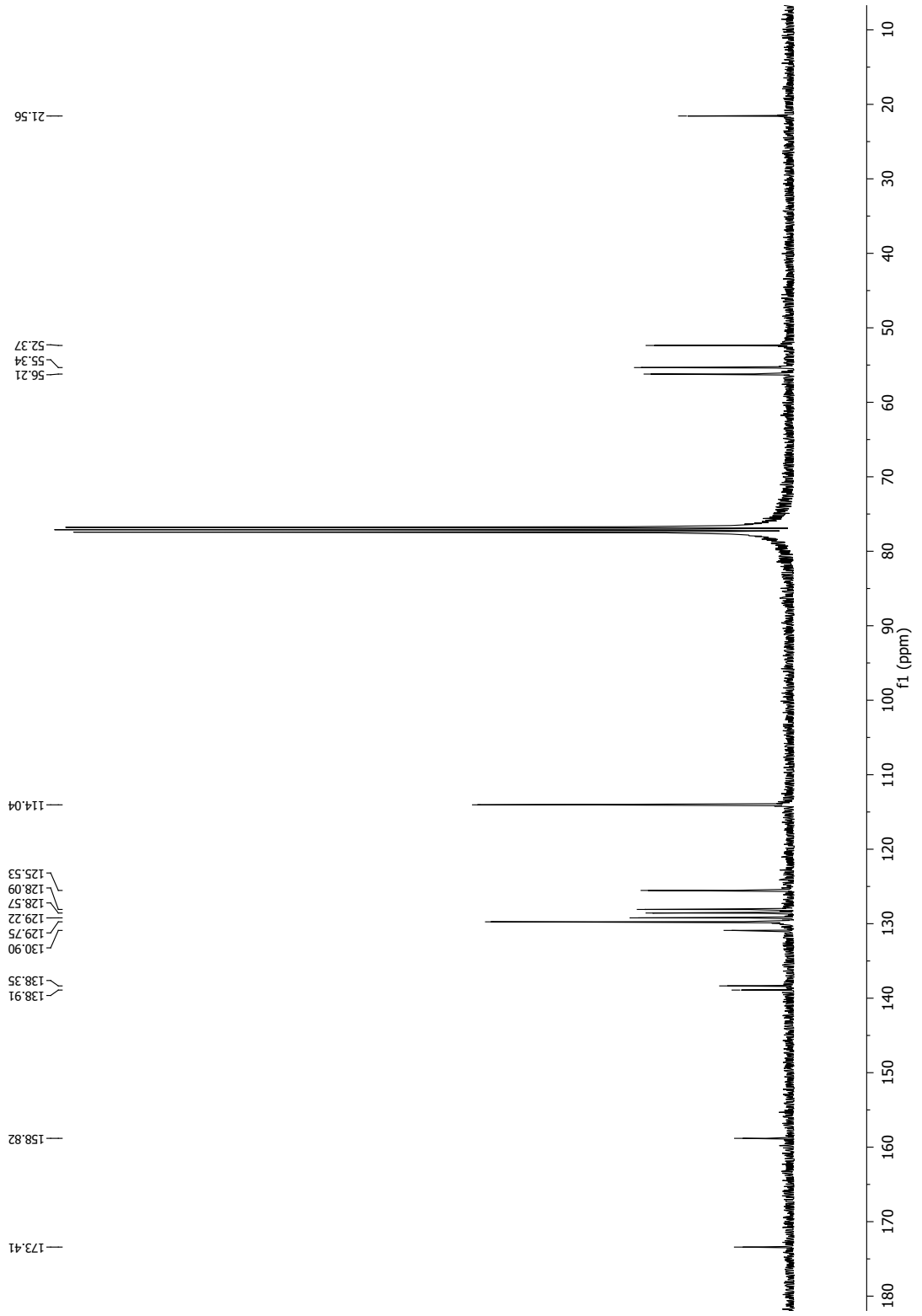
^{13}C NMR (100 MHz, $CDCl_3$) of 3H:



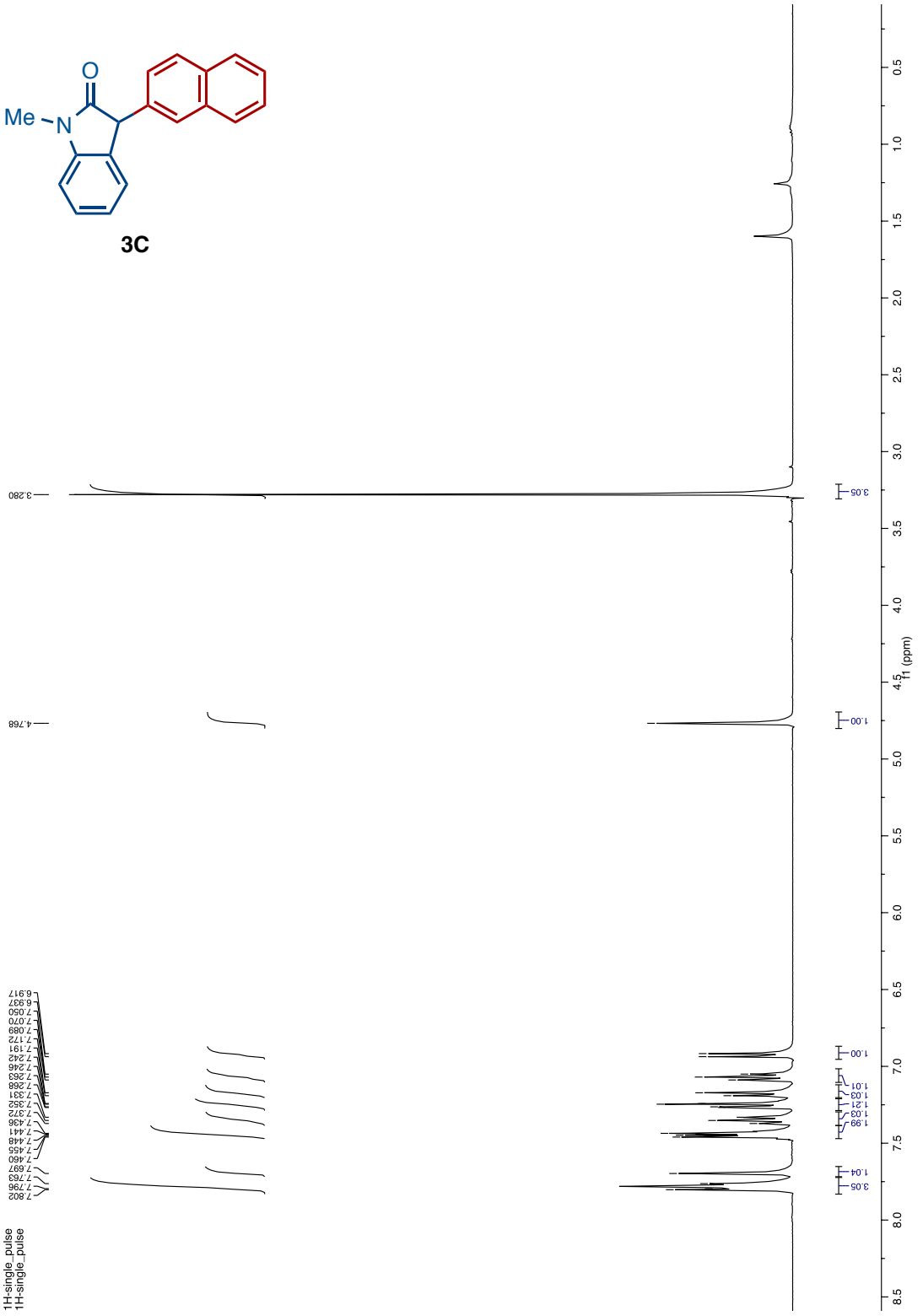
^{1}H NMR (400 MHz, $CDCl_3$) of 3I:



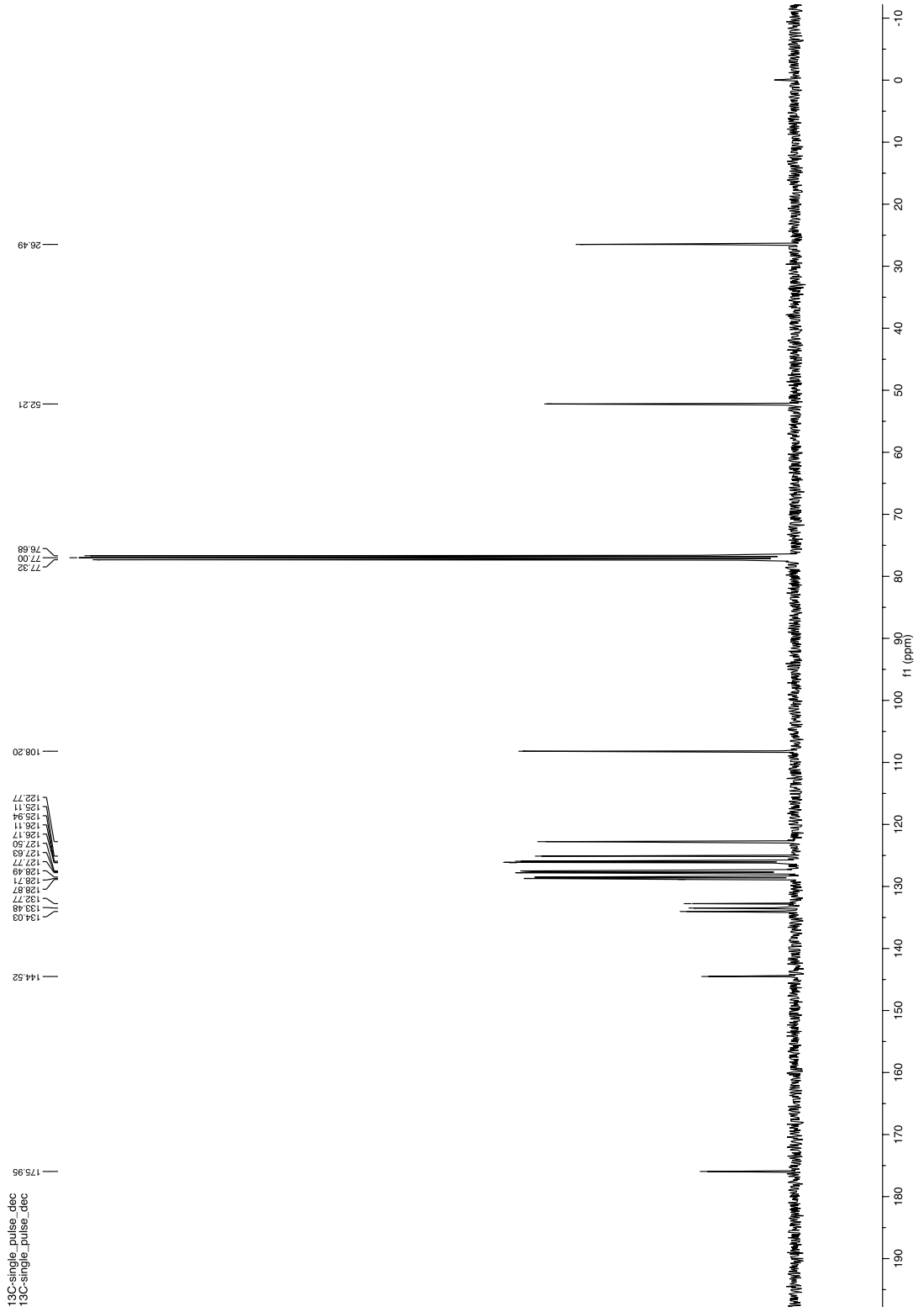
^{13}C NMR (100 MHz, $CDCl_3$) of 3I:



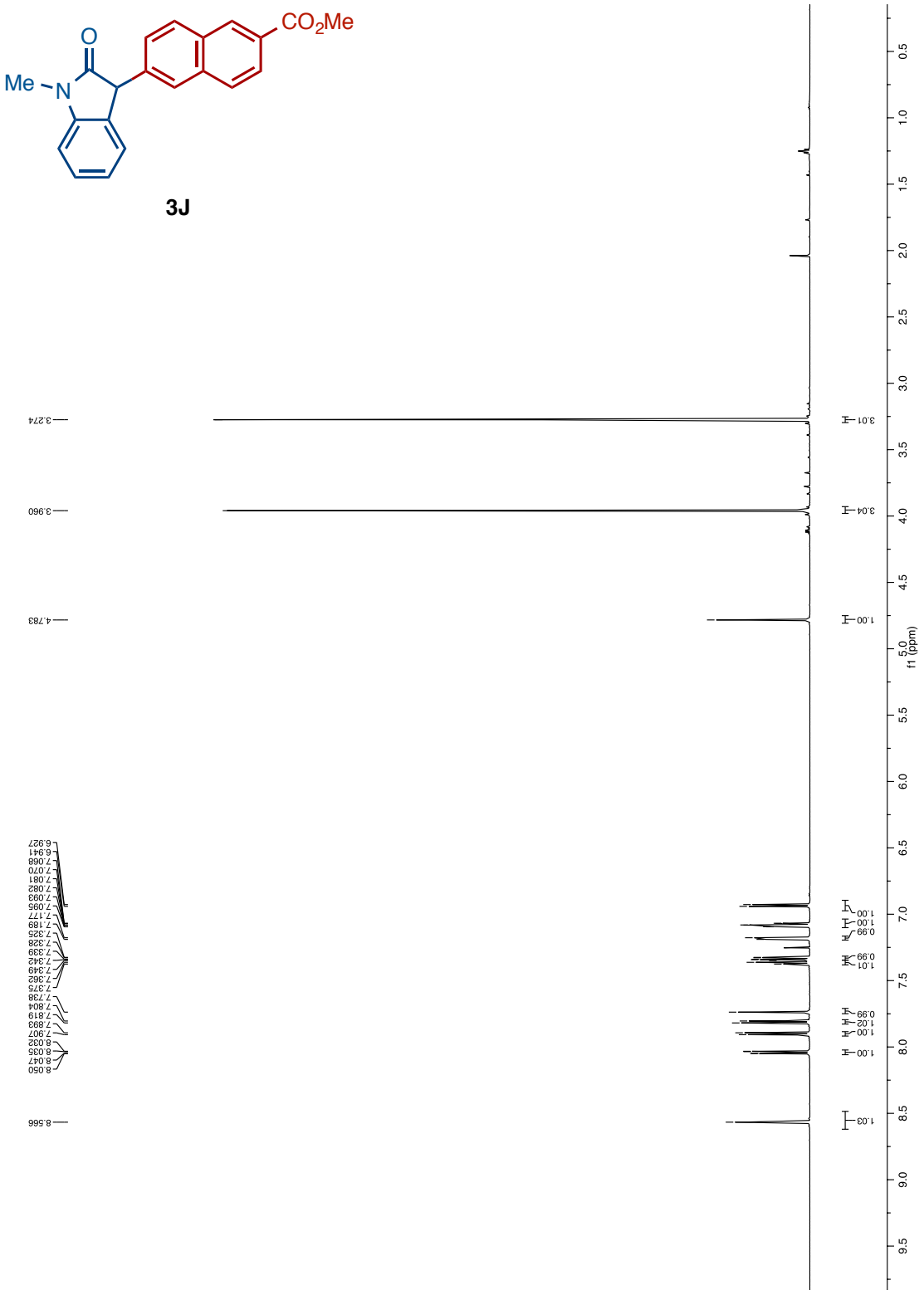
^{1}H NMR (400 MHz, $CDCl_3$) of 3C:



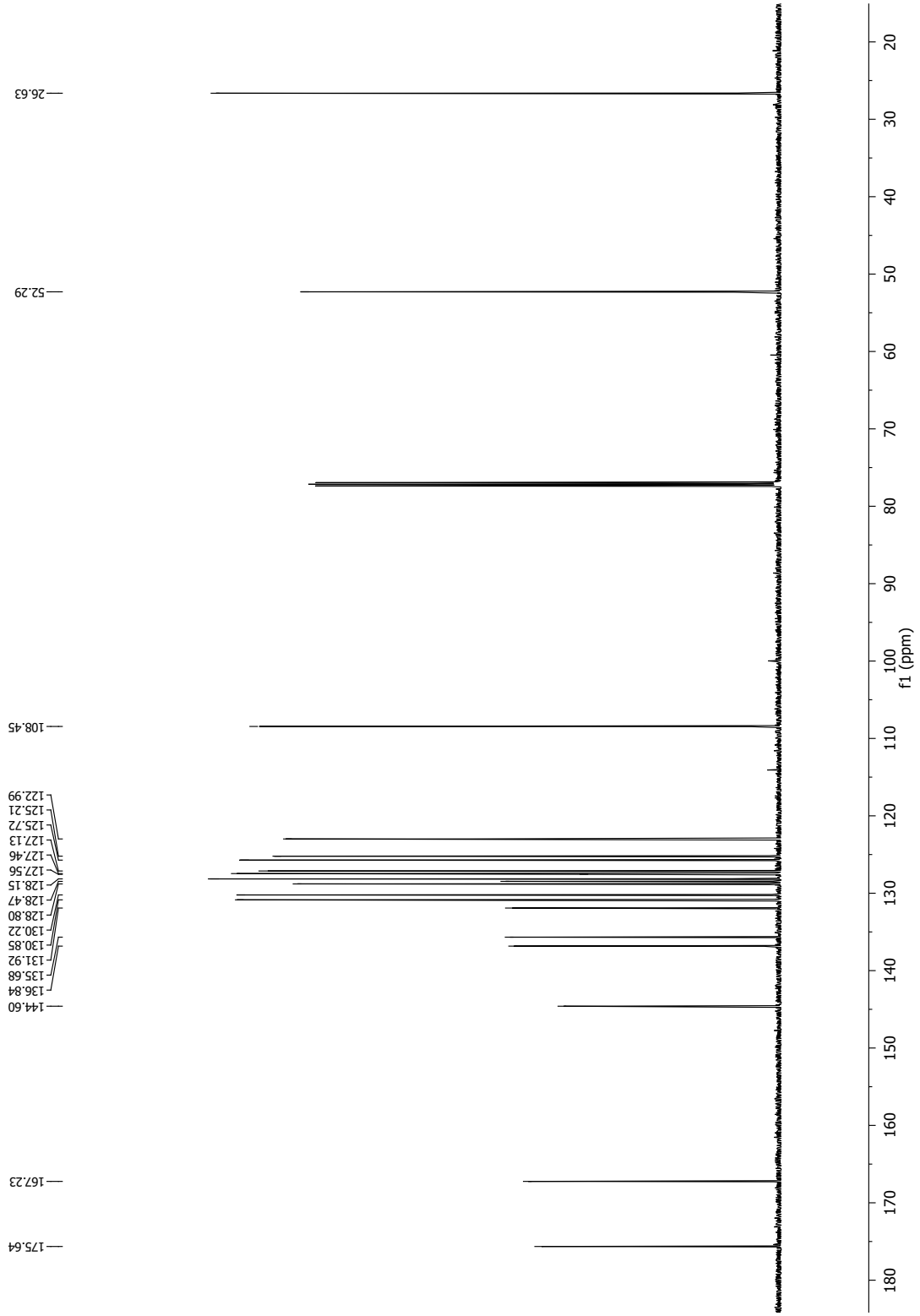
^{13}C NMR (100 MHz, $CDCl_3$) of 3C:



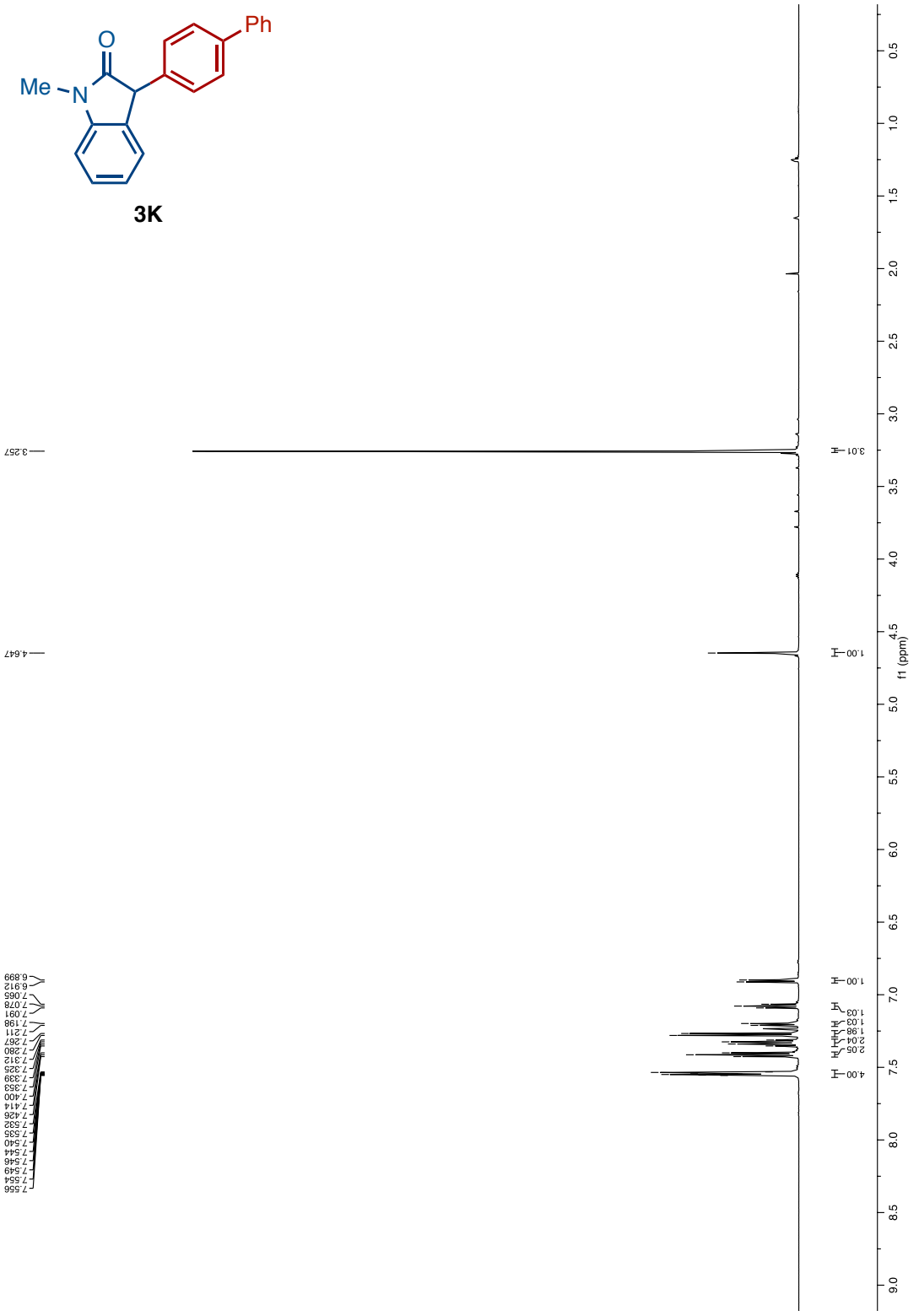
^{1}H NMR (600 MHz, $CDCl_3$) of 3J:



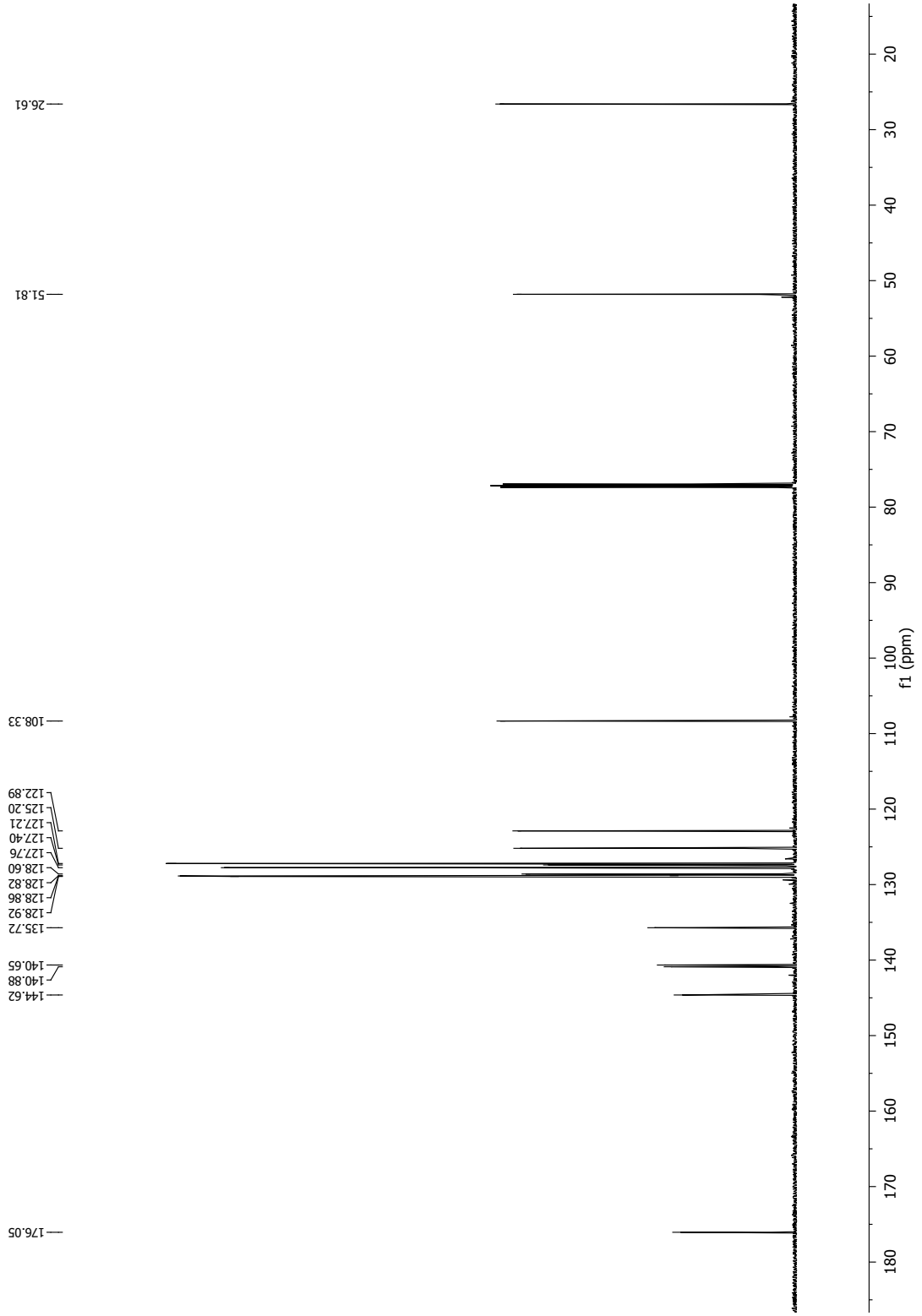
^{13}C NMR (150 MHz, $CDCl_3$) of 3J:



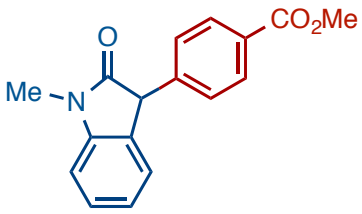
^{1}H NMR (600 MHz, $CDCl_3$) of 3K:



^{13}C NMR (150 MHz, $CDCl_3$) of 3K:

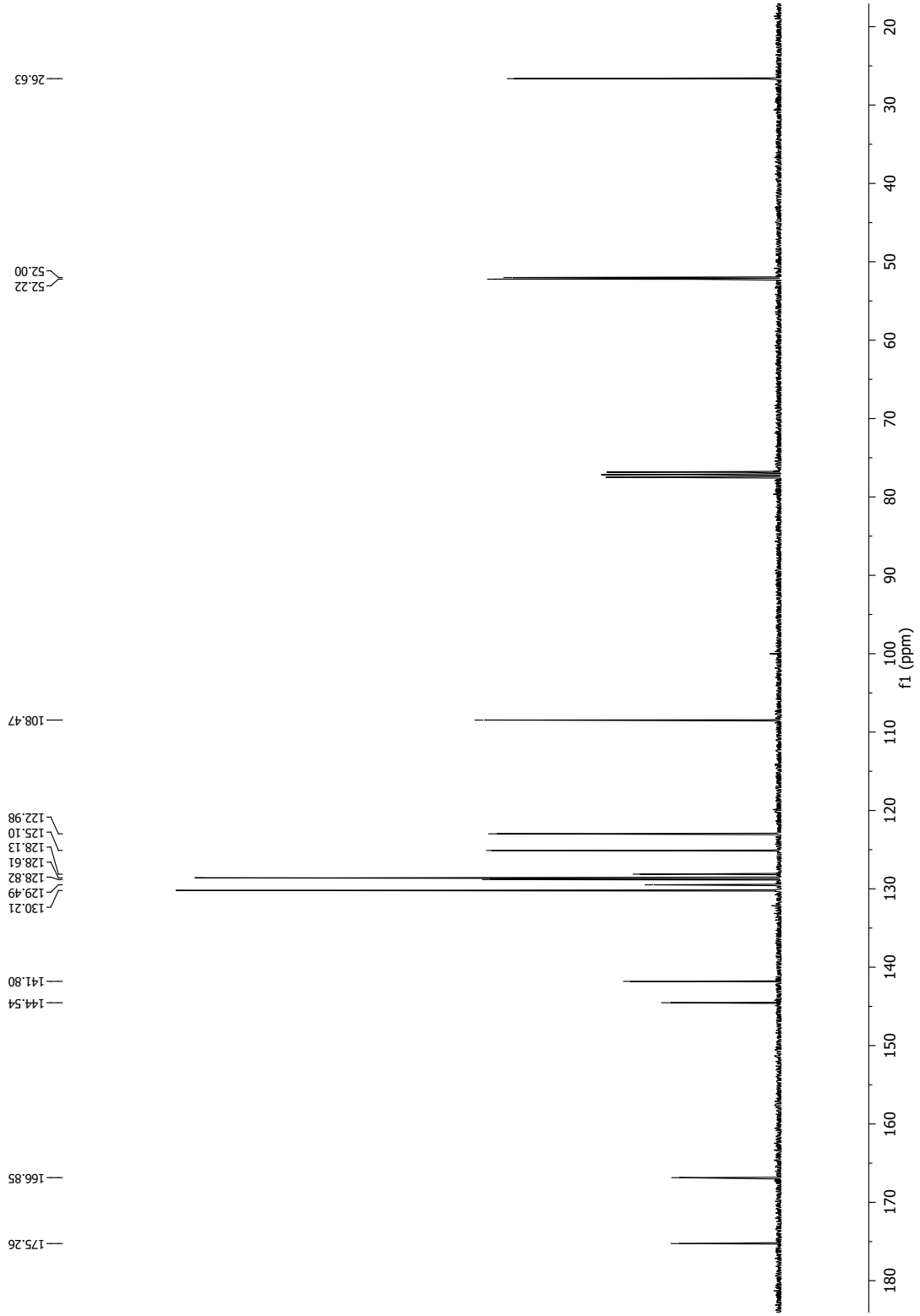


^{1}H NMR (400 MHz, $CDCl_3$) of 3L:

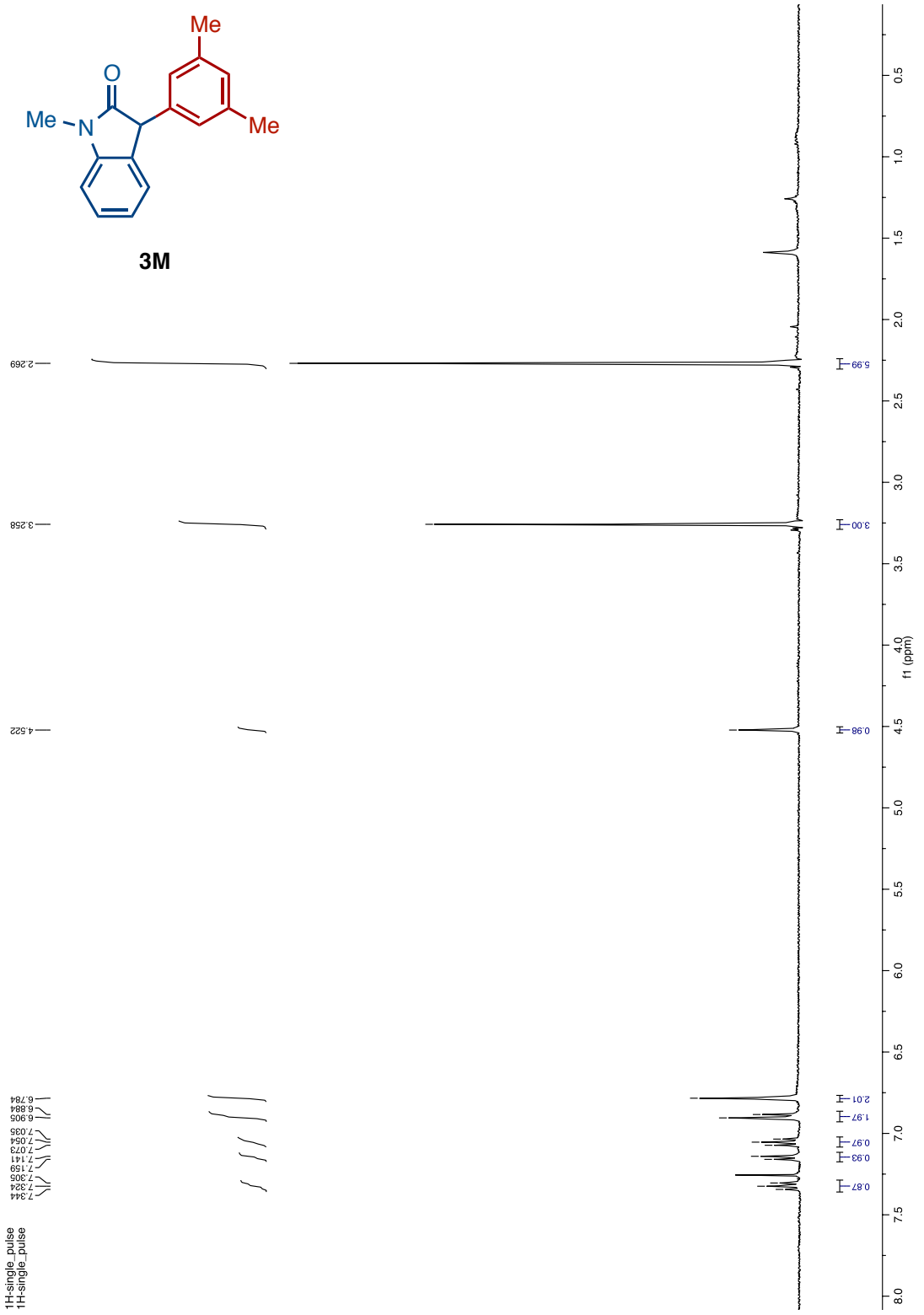


3L

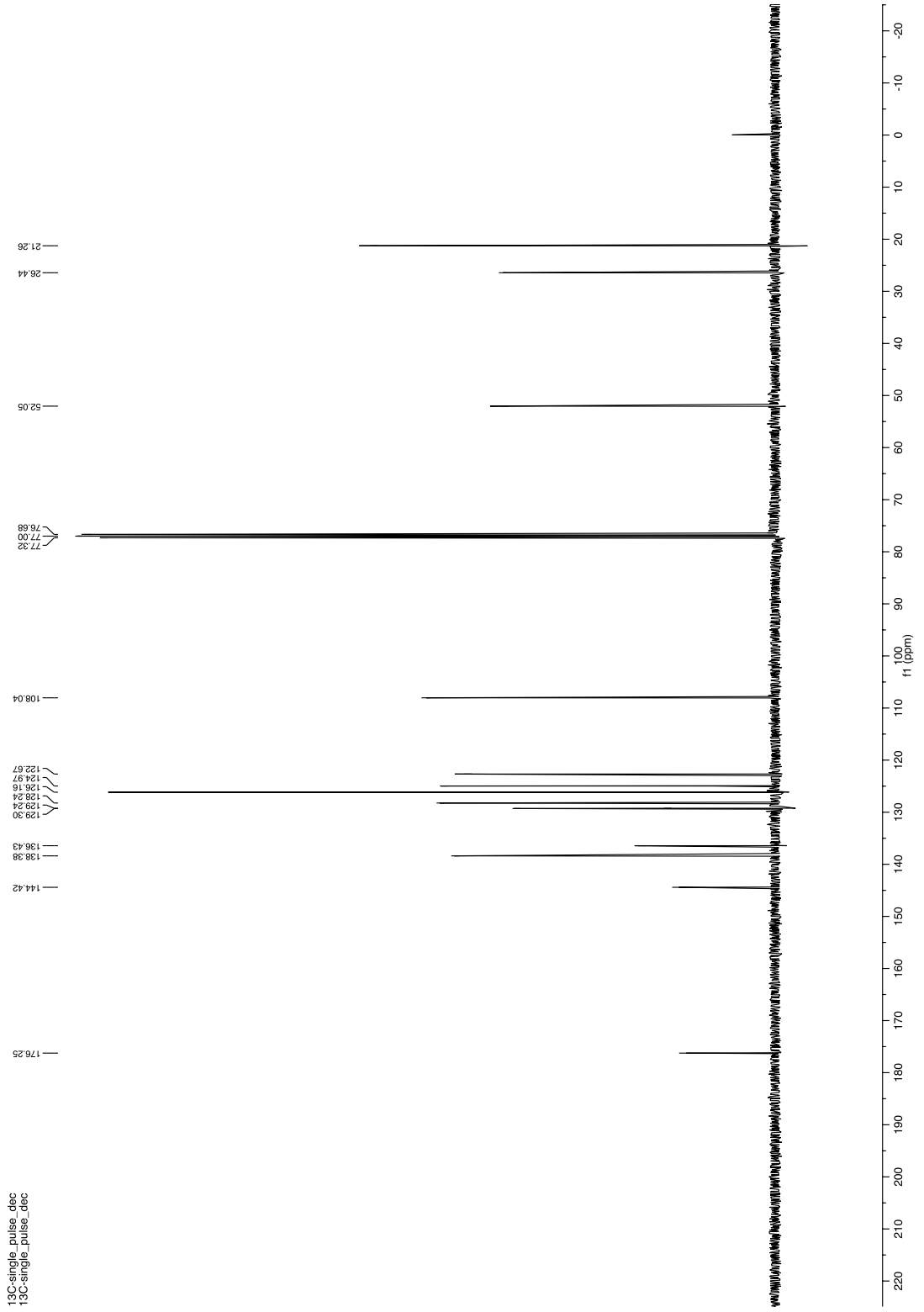
^{13}C NMR (100 MHz, $CDCl_3$) of 3L:



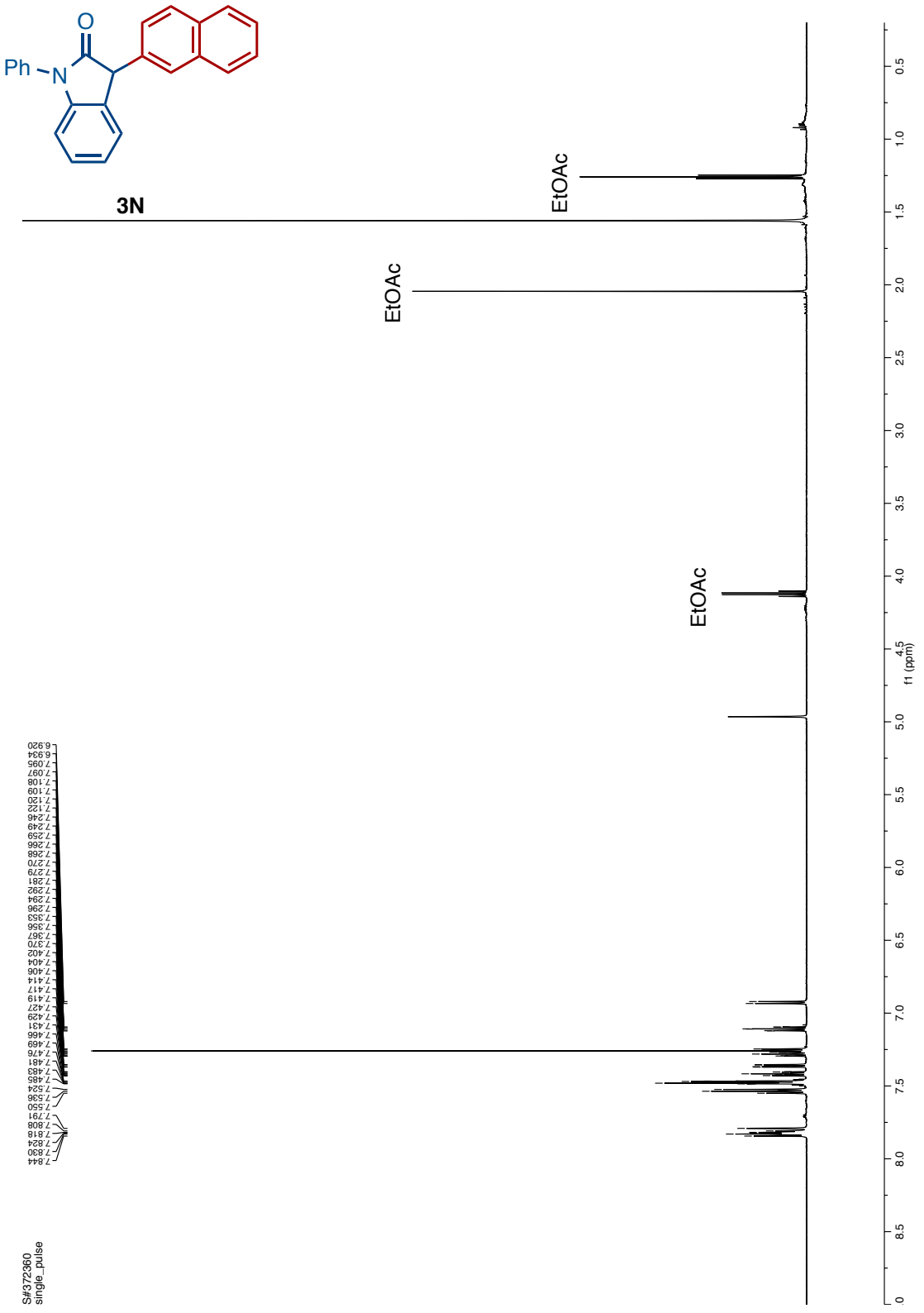
^{1}H NMR (400 MHz, $CDCl_3$) of 3M:



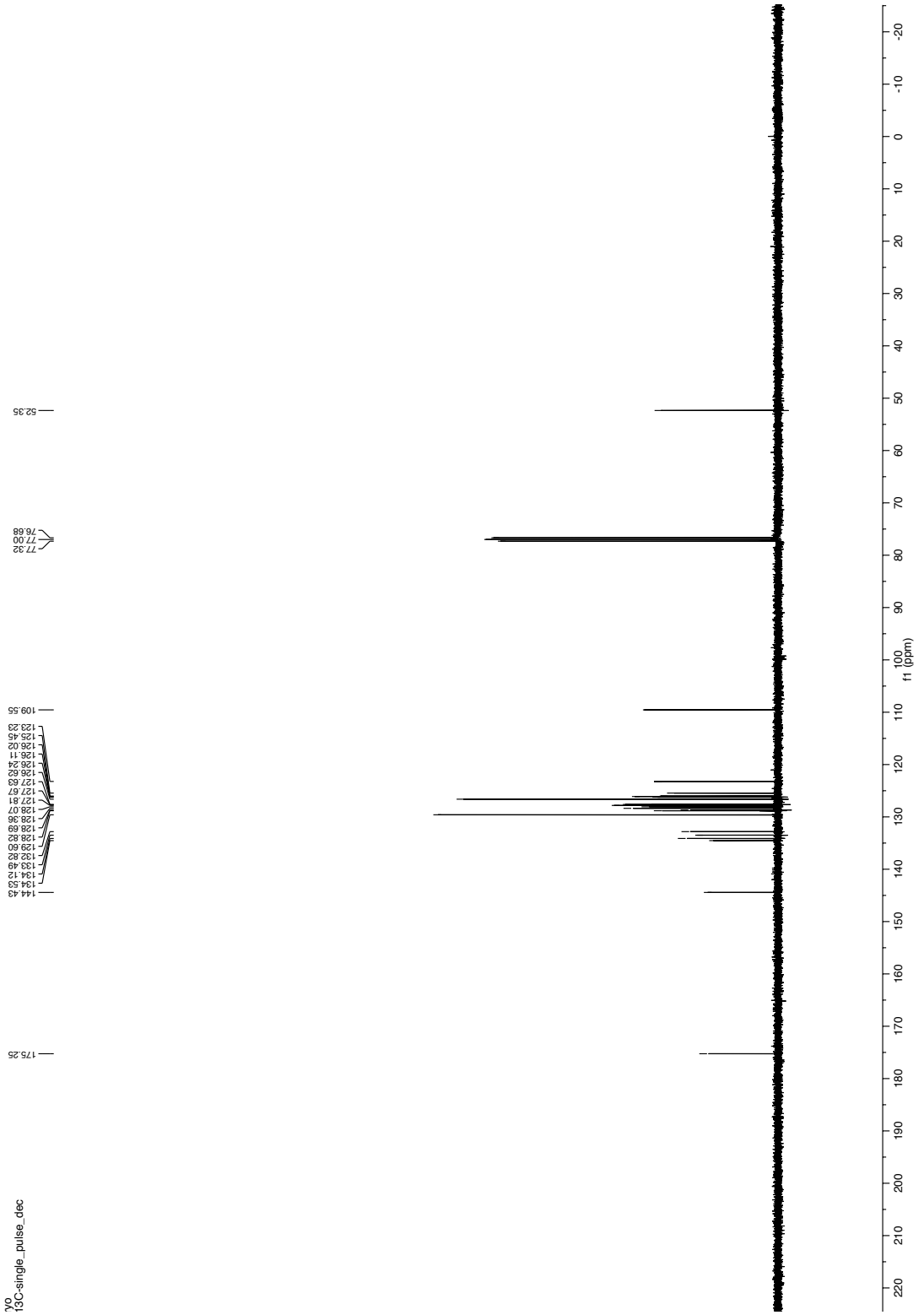
^{13}C NMR (100 MHz, $CDCl_3$) of 3M:



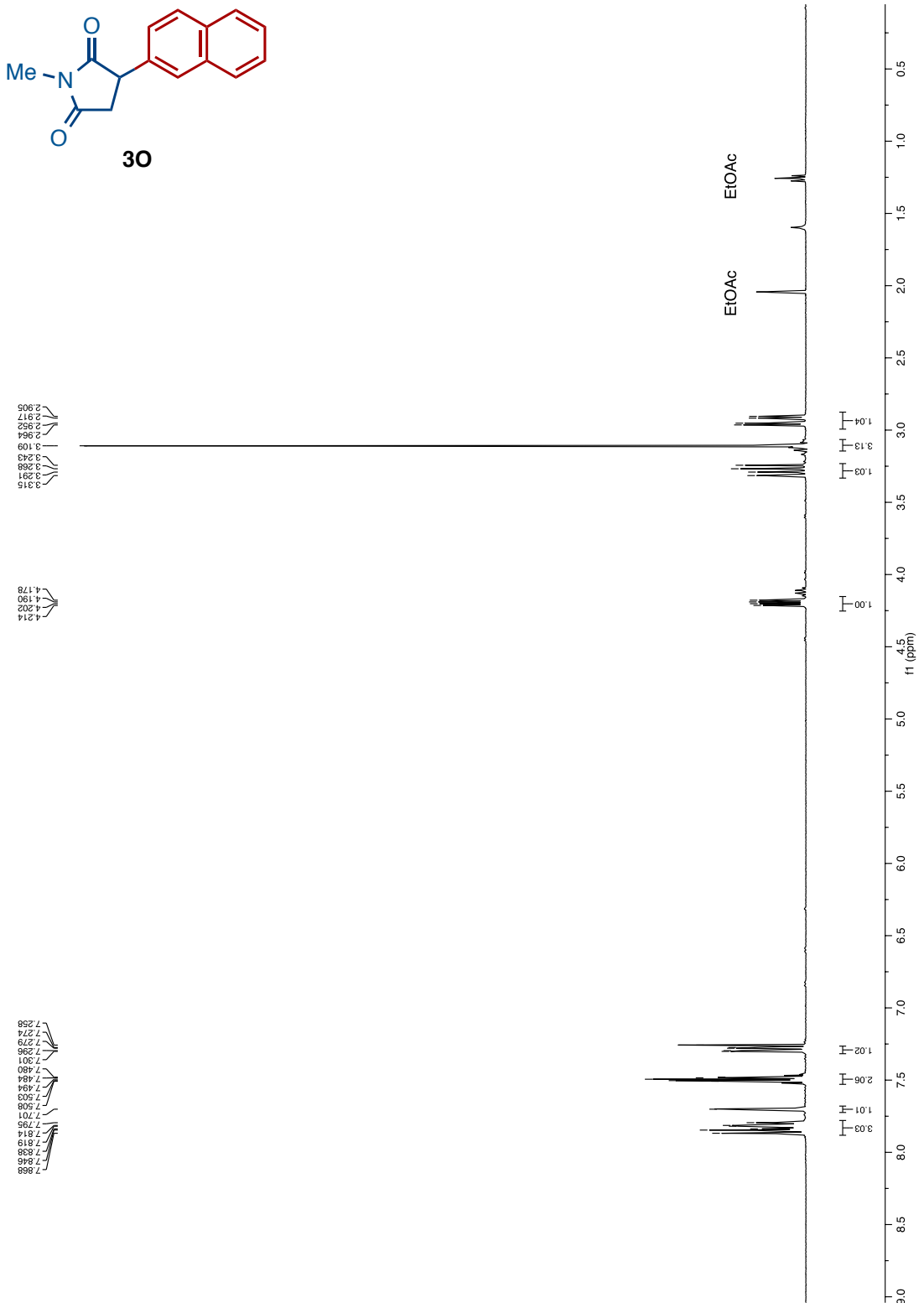
^{1}H NMR (600 MHz, $CDCl_3$) of 3N:



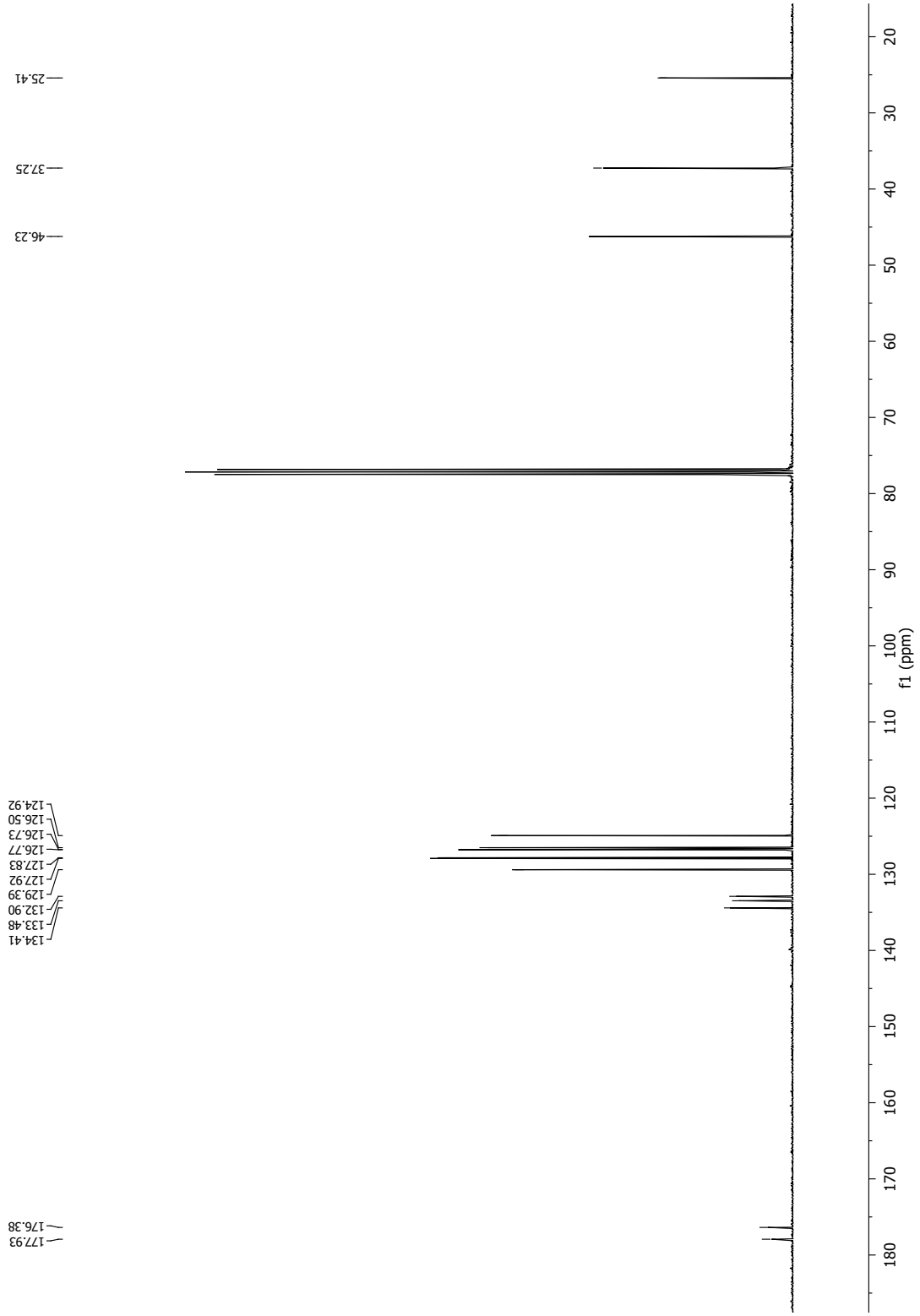
^{13}C NMR (100 MHz, $CDCl_3$) of 3N:



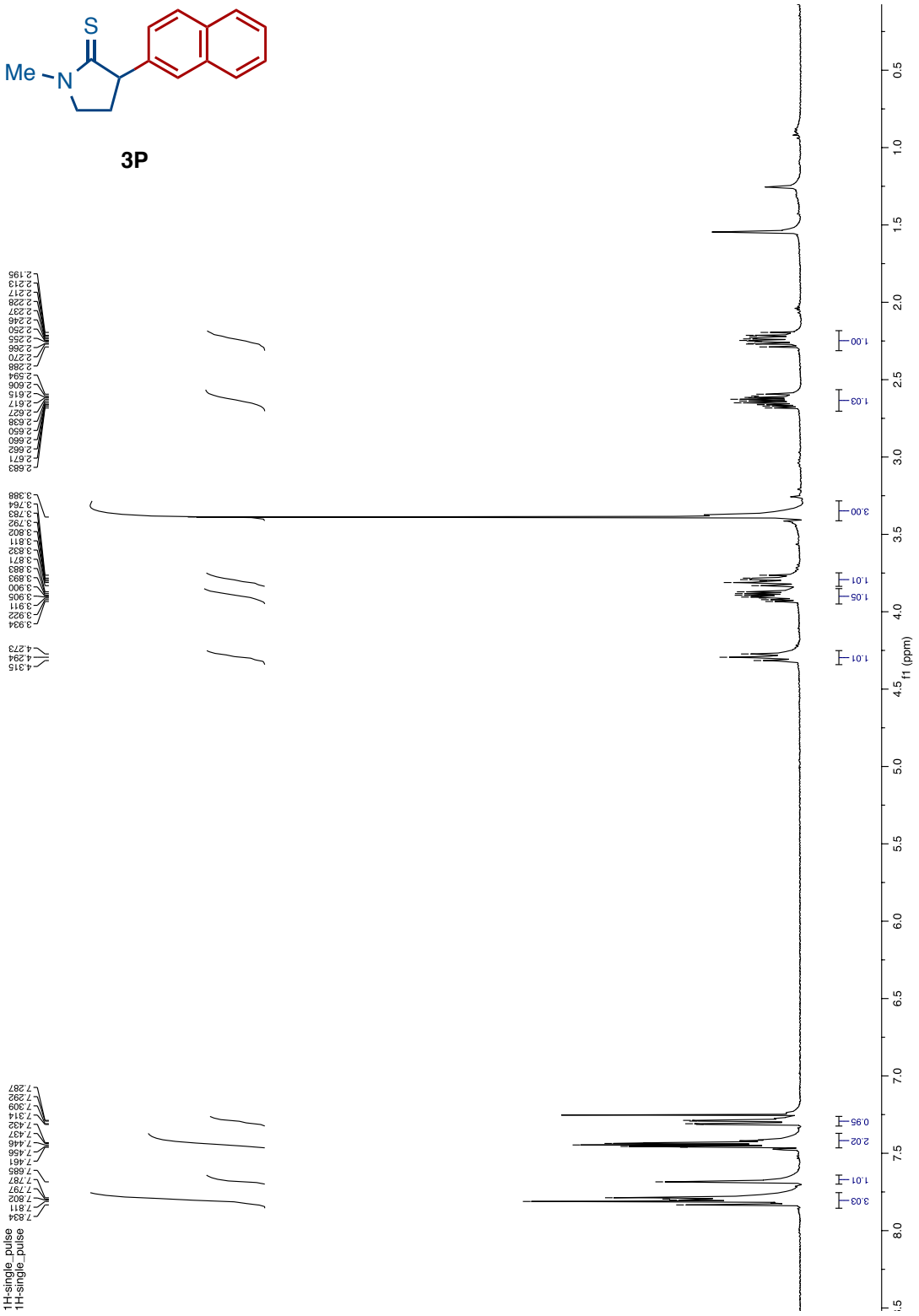
^{1}H NMR (400 MHz, $CDCl_3$) of 3O:



^{13}C NMR (100 MHz, $CDCl_3$) of 3O:



^{1}H NMR (400 MHz, $CDCl_3$) of 3P:



^{13}C NMR (100 MHz, $CDCl_3$) of 3P: