A Novel *cis*-β-Iron(III) SALPN Catalyst For Hydrogen Atom Transfer Reductions and Olefin Cross Couplings

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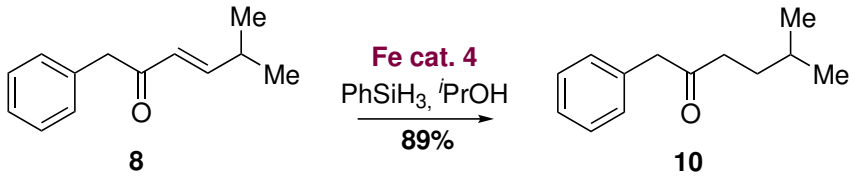
1 Experimental Section

General Procedures

^{1}H-NMR spectra (500MHz and 600MHz) and proton-decoupled ^{13}C-NMR spectra (126MHz and 151 MHz) were recorded on Varian 500 and Bruker 600 spectrometers. HRMS were obtained on an Orbi-TRAP Infusion instrument. Anhydrous MeOH was distilled from magnesium methoxide. $CDCl_3$ was filtered through basic alumina immediately prior to use. All other reagents were used as received. Column chromatography was conducted on SiliCycle SiliaFlash 60Å. Thin layer chromatography was conducted on Merck Kieselgel 60 F_{254} pre-coated plates and visualised under 20% v/v phosphomolybdic acid in EtOH solution. Lactone **18**[1] (81% *ee*) was donated by Circa Group. Stereoselectivity of inseparable mixtures of diastereoisomers were determined by ^{1}H-NMR spectroscopy. In most cases minor diastereoisomers were not detected.

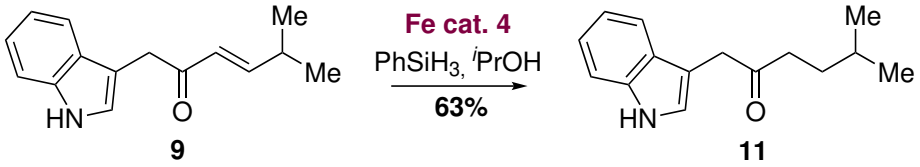
Experimental Procedures and Characterisation

Ketone 10



Prepared according to the general procedure using enone **8**[2] (104.0 mg, 0.552 mmol) with stirring for 3 hours. Column chromatography (2.5% EtOAc/hexane) afforded the ketone **10** (94.0 mg, 0.494 mmol, 89%) as a clear colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 2H), 7.28 - 7.25 (m, 1H), 7.22 - 7.21 (m, 2H), 3.69 (s, 2H), 2.45 (t, J = 7.5 Hz, 2H), 1.54 - 1.43 (m, 3H), 0.85 (d, J = 6.4 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 208.8, 134.5, 129.5, 128.8, 127.0, 50.2, 40.1, 32.6, 27.7, 22.4. HRMS (ESI) Calc. for $C_{13}H_{19}O$ $[M+H]^+$ 191.1430; found 191.1431. All data were in agreement with the literature.[3]

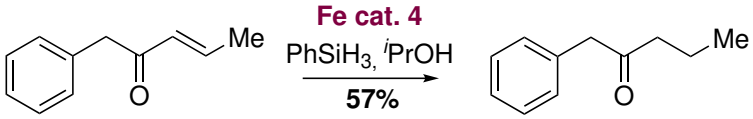
Ketone 11



Prepared according to the general procedure using enone **9**[2] (64.5 mg, 0.284 mmol) and Fe cat. **4** (7.4 mg, 0.0142 mmol), in EtOH (3 mL). After stirring for 1.5 hours, further Fe cat. **4** (7.4 mg, 0.0142 mmol) was added, and the mixture was stirred for 1 hour. 2x Column chromatography (15% EtOAc/hexane then 10% to 15% EtOAc/hexane) afforded ketone **11** (40.9 mg, 0.0.178 mmol, 63%)

as a yellow crystalline solid. M.P 46.3°C - 48.8°C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.56 (J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.1 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 3.83 (s, 2H), 2.51 (t, J = 7.4 Hz, 2H), 1.51 - 1.46 (m, 3H), 0.85 (d, J = 6.3 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 209.9, 136.3, 127.5, 123.3, 122.3, 119.8, 118.8, 111.4, 108.9, 40.0, 39.7, 32.9, 27.8, 22.4. HRMS (ESI) Calc. for $C_{15}H_{20}NO$ $[M+H]^+$ 230.1539; found 230.1538.

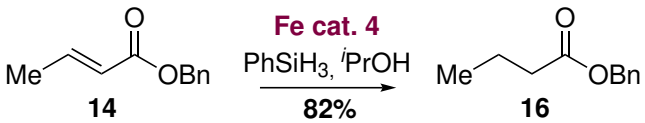
Ketone 13



12 **13**

Prepared according to the general procedure using enone **12**[2] (59.4 mg, 0.371 mmol), with stirring for 2 hours. Column chromatography (1% to 2.5% to 5% EtOAc/hexane) afforded the ketone **13** (34.0 mg, 0.210 mmol, 57%) as a clear colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 2H), 7.28 - 7.25 (m, 1H), 7.22 - 7.20 (m, 2H), 3.68 (s, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.58 (sextet, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 208.6, 134.5, 129.5, 128.8, 127.1, 50.3, 44.0, 17.3, 13.8. All data were in agreement with the literature.[4]

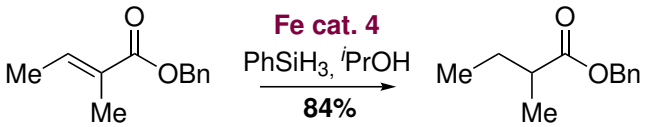
Ester 16



14 **16**

Prepared according to the general procedure using enone **14** (101.7 mg, 0.577 mmol), and Fe cat. **4** (90.6 mg, 0.173 mmol) with stirring for 72 hours. Column chromatography (2.5% Et_2O/hexane, reaction mixture dry loaded onto celite) afforded benzyl butanoate **16** (84.8 mg, 0.476 mmol, 82%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.38 - 7.32 (m, 5H), 5.14 (s, 2H), 2.36 (t, J = 7.4 Hz, 2H), 1.71 (sextet, J = 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 173.5, 136.3, 128.6, 128.2, 66.1, 36.3, 18.5, 13.7 All data were in agreement with the literature.[5]

Ester 17

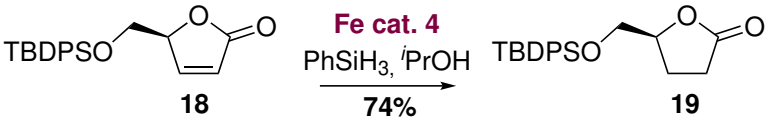


15 **17**

Prepared according to the general procedure using ester **15** (178.5 mg, 0.938 mmol), with stirring for 1.5 hours. Column chromatography (2.5% EtOAc/hexane) afforded ester **17** (143.0 mg, 0.744 mmol,

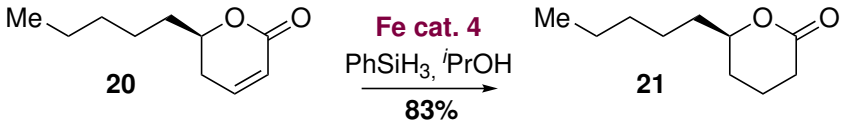
79%) as a clear colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.33 (m, 5H), 5.14 (s, 2H), 2.45 (sextet, J = 6.9 Hz, 1H), 1.78 - 1.69 (m, 1H), 1.56 - 1.49 (m, 1H), 1.19 (d, J = 7.0 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H). All data were in agreement with the literature.[6]

Lactone 19



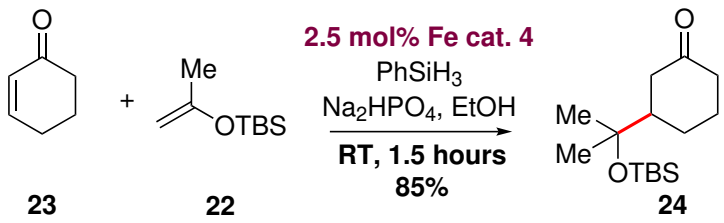
Prepared according to the general procedure using lactone **18**[1] (118.4 mg, 0.336 mmol) with stirring overnight. Column chromatography (20% EtOAc/hexane) afforded lactone **19** (88.4 mg, 0.249 mmol, 74%) as a white crystalline solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.67 (m, 4H), 7.45 - 7.39 (m, 6H), 4.61 (ddt, J = 8.1, 5.1, 3.2 Hz, 1H), 3.89 (dd, J = 11.4, 3.3 Hz, 1H), 3.70 (dd, J = 11.4, 3.3 Hz, 1H), 2.69 (ddd, J = 17.6, 10.3, 7.2 Hz, 1H), 2.52 (ddd, J = 17.5, 10.4, 6.8 Hz, 1H), 2.33 - 2.19 (m, 2H), 1.07 (s, 9H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 177.6, 135.7, 135.6, 133.0, 132.6, 130.0, 127.9, 80.1, 65.5, 28.7, 26.8, 23.7, 19.3. All data were in agreement with the literature.[7]

Lactone 21



Prepared according to the general procedure using lactone **20** (172.1 mg, 1.02 mmol) with stirring for 5 hours. Column chromatography (20% EtOAc/hexane) afforded lactone **21** (145.2 mg, 0.853 mmol, 83%) as a clear colourless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.26 (dddd, J = 10.7, 7.6, 4.9, 2.9 Hz, 1H), 2.60 - 2.54 (m, 1H), 2.46 - 2.39 (m, 1H), 1.93 - 1.79 (m, 3H), 1.69 (dddd, J = 13.4, 10.4, 7.4, 4.7 Hz, 1H), 1.58 - 1.46 (m, 3H), 1.39 - 1.25 (m, 5H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 172.1, 80.7, 35.9, 31.7, 29.6, 27.9, 24.7, 22.6, 18.6, 14.1. All data were in agreement with the literature.[8]

Ketone 24



Method 1: 2.5 mol% Fe cat. **4**.

Prepared according to the general procedure using cyclohexenone **23** (74 μL, 73 mg, 0.764 mmol), silyl enol ether **22**[9] (401 mg, 2.33 mmol), Na_2HPO_4 (110 mg, 0.776 mmol) and Fe cat. **4** (10.15 mg 0.0194 mmol) with stirring for 1.5 hours. Column chromatography (2.5% EtOAc/hexane) afforded ketone **24** (176.6 mg, 0.653 mmol, 85%) as a clear colourless oil.

Method 2: 1 mol% Fe cat. **4**.

Prepared according to the general procedure using cyclohexenone **23** (74 μL, 73 mg, 0.764 mmol), silyl enol ether **22**[9] (401 mg, 2.33 mmol), Na_2HPO_4 (110 mg, 0.776 mmol) and Fe cat. **4** (4.06 mg, 0.00776 mmol) with stirring for 1.5 hours. Column chromatography (2.5% EtOAc/hexane) afforded ketone **24** (160 mg, 0.591 mmol, 77%) as a clear colourless oil.

Method 3: 5 mol% Fe cat. **4**, without Na_2HPO_4 additive.

Prepared according to the general procedure using cyclohexenone **23** (10 μL, 9.9 mg, 0.103 mmol), silyl enol ether **22**[9] (56.5 mg, 0.328 mmol) and Fe cat. **4** (2.5 mg, 0.00478 mmol) with stirring for 1 hour 20 minutes. Column chromatography (5% EtOAc/hexane) afforded ketone **24** (17.4 mg, 0.0643 mmol, 62%) as a clear colourless oil.

Method 4: 2.5 mol% Fe cat. **4**, Ph(^{i}PrO)SiH_2.

Prepared according to the general procedure using cyclohexenone **23** (114.8 μL, 114 mg, 1.195 mmol), enol ether **22**[9] (616.8 mg, 3.585 mmol), Na_2HPO_4 (169.6 mg, 1.195 mmol), Ph(^{i}PrO)SiH_2 (429 μL, 2.39 mmol) and Fe cat. **4** (15.64 mg, 0.0298 mmol) with stirring for 1.5 hours afforded ketone **24** (229 mg, 0.847 mmol, 71%) as a clear colourless oil.

Method 5: 5 mol% Fe(acac)$_3$ (**1**), 60°C.

Prepared according to the general procedure using cyclohexenone **23** (46.3 μL, 46 mg, 0.480 mmol), silyl enol ether **22**,[9] (248 mg, 1.44 mmol), Na_2HPO_4 (67.8 mg, 0.479 mmol) and Fe(acac)$_3$ (**1**) (8.46 mg, 0.02395 mmol) with stirring for 3 hours at 60°C. Column chromatography (2.5% EtOAc/hexane) afforded ketone **24** (47.3 mg, 0.175 mmol, 36%) as a colourless oil.

Method 6: 10 mol% Fe(acac)$_3$ (**1**), Ph(^{i}PrO)SiH_2, 60°C.

Prepared according to the general procedure using cyclohexenone **23** (46.3 μL, 46 mg, 0.48 mmol), silyl enol ether **22**[9] (246.8 mg, 1.43 mmol), Na_2HPO_4 (82.3 mg, 0.0.48 mmol), Ph(^{i}PrO)SiH_2 (171.7 μL, 158.9 mg, 0.926 mmol) and Fe(acac)$_3$ (**1**) (16.9 mg, 0.048 mmol) with heating to 60°C and stirring for 3 hours. Column chromatography (2.5% EtOAc/hexane) afforded ketone **24** (51.3 mg, 0.189 mmol, 40%) as a clear colorless oil.

Method 7: 5 mol% Fe(dibm)$_3$ (**2**), Ph(^{i}PrO)SiH_2, 60°C.

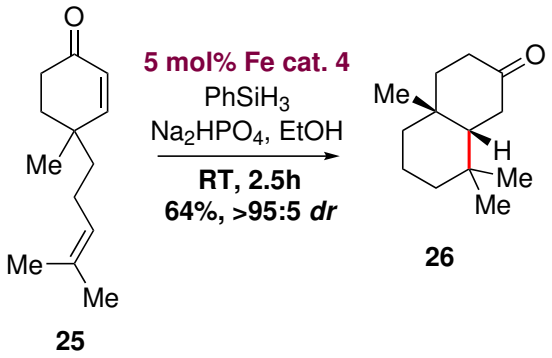
Prepared according to the general procedure using cyclohexenone **23** (88.6 μL, 88.0 mg, 0.92 mmol), silyl enol ether **22**[9] (472.7 mg, 2.75 mmol), Na_2HPO_4 (130.0 mg, 0.916 mmol), Ph(^{i}PrO)SiH_2 (328.9 μL, 304.6 mg, 1.83 mmol) and Fe(dibm)$_3$ (**2**) (23.8 mg, 0.05 mmol), with heating at 60°C and stirring 1.5 hours. Column chromatography (2.5% EtOAc/hexane) afforded ketone **24** (145.9 mg, 0.539 mmol, 59%) as a clear colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.48 (ddt, J = 14.0, 4.0, 2.1 Hz, 1H), 2.36 - 2.33 (m, 1H), 2.25 - 2.19

(m, 2H), 2.09 (ddq, J = 13.1, 6.4, 3.2 Hz, 1H), 1.99 - 1.96 (m, 1H), 1.67 - 1.62 (m, 1H), 1.60 - 1.52 (m, 2H), 1.45 (qd, J = 12.4, 3.5 Hz, 1H), 1.23 (s, 3H), 1.19 (s, 3H), 0.87 (s, 8H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 213.2, 74.6, 50.9, 43.3, 41.4, 28.06, 27.95, 26.0, 25.8, 25.3, 18.4, -2.0. HRMS (ESI) Calc. for $C_{15}H_{31}O_2Si$ $[M+H]^+$ 271.2088; found 271.2088. All data were in agreement with the literature.[10]

Figure 1: TLC (10% EtOAc/hexane) of reaction between cyclohexenone **23** and silyl enol ether **22**, t = 1.5 hours.

Ketone 26



Method 1: 5 mol% Fe cat. **4**.

Prepared according to the general procedure using alkene enone **25**[11] (86.8 mg, 0.451 mmol), with stirring for two hours and 30 minutes. Column chromatography (2.5 % EtOAc/hexane) afforded *cis*-decalin **26** (56.0 mg, 0.288 mmol, 64%) >95:5 *dr* as an oil which solidified to a waxy solid. Slow evaporation from hexane afforded diffraction quality crystals.

Method 2: 10 mol% Fe cat. **4**.

Prepared according to the general procedure using alkene enone **25**[11] (113.3 mg, 0.589 mmol) and Na_2HPO_4 (83.6 mg, 0.589 mmol), with stirring for two hours and 30 minutes. Column chromatography (2.5 % EtOAc/hexane) afforded *cis*-decalin **26** (82.6, 0.425 mmol, 72%) >95:5 *dr*.

Method 3: 5 mol% Fe cat. **4**, Ph(^{i}PrO)SiH_2.

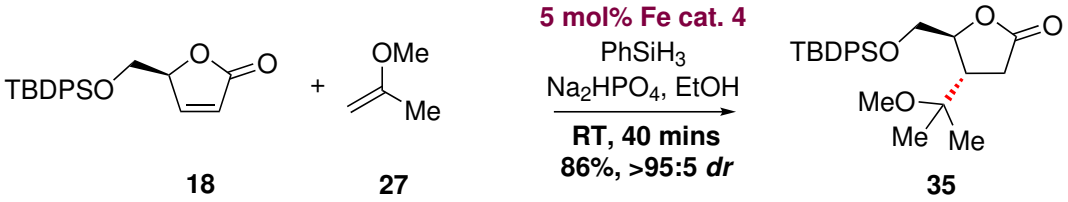
Prepared according to the general procedure using alkene enone **25**[11] (84.29 mg, 0.438 mmol), Na_2HPO_4 (62.06 mg, 0.438 mmol), Ph(^{i}PrO)SiH_2 (157.5 μL, 145.8 mg, 0.876 mmol) and Fe cat. **4** (11.46 mg, 0.0219 mmol) with stirring for 1 hour. Column chromatography (2.5% EtOAc/hexane) afforded *cis*-decalin **26** (43.5 mg, 0.224 mmol, 51%).

Method 4: 5 mol% Fe(dibm)$_3$ (**2**) at 60°C.

Prepared according to the general procedure using alkene enone **25**[11] (56.4 mg, 0.293 mmol), Na_2HPO_4 (41.6 mg, 0.293 mmol) and Fe(dibm)$_3$ (**2**) (7.6 mg, 0.0147 mmol), with stirring for overnight at 60°C. Column chromatography (2.5% EtOAc/hexane) afforded *cis*-decalin **26** (24 mg, 0.124 mmol, 42%, containing ~15% unreacted **25**) as a yellow oil.

M.P 67.7°C - 70.8°C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.51 - 2.42 (m, 3H), 2.33 - 2.22 (m, 2H), 1.56 - 1.48 (m, 3H), 1.41 - 1.28 (m, 4H), 1.17 (s, 3H), 0.90 (s, 3H), 0.80 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 213.2, 52.0, 42.2, 40.6, 39.2, 37.4, 34.7, 33.08, 33.07, 33.03, 30.3, 23.2, 18.4. HRMS (ESI) Calc. for $C_{13}H_{23}O$ $[M+H]^+$ 195.1743; found 195.1739. All data were in agreement with the literature.[10]

Lactone 35



18 **27** **35**

*The following procedure is general for gram scale coupling of **18** and **27***

Method 1: 5 mol% Fe cat. **4**, gram scale.

To a solution of lactone **18**[1] (1.19 g, 3.38 mmol) and 2 methoxypropene **27** (6.5 mL, 4.9 g, 67.5 mmol) in EtOH (17 mL) was added Na_2HPO_4 (480 mg, 3.38 mmol), Fe cat. **4** (88.3 mg, 0.169 mmol) and $PhSiH_3$ (834 μL, 731 mg, 0.877 mmol). The mixture was stirred for 45 minutes at RT, then concentrated *in vacuo* and purified by column chromatography (15% EtOAc/hexane), affording lactone **35** (1.219 g, 2.86 mmol, 85%) >95:5 *dr* as a colourless solid.

Method 2: 5 mol%, Fe cat. **4**, 0.2 mmol scale.

Prepared according to the general procedure using lactone **18**[1] (68.8 mg, 0.195 mmol) and 2-methoxypropene **27** (374 μL, 281 mg, 3.90 mmol) with stirring for 40 minutes. Column chromatography (20% EtOAc/hexane) afforded lactone **35** (71.6 mg, 0.168 mmol, 86%) >95:5 *dr* as a colourless solid.

Method 3: 5 mol% Fe cat. **4**, Ph(^{i}PrO)SiH_2.

Prepared according to the general procedure using lactone **18**[1] (99.62 mg, 0.2826 mmol) and 2-methoxypropene **27** (541 μL, 407.5 mg, 5.652 mmol), Na_2HPO_4 (40 mg, 0.2826 mmol), Ph(^{i}PrO)SiH_2 (101 μL, 94 mg, 0.565 mmol) and Fe cat. **4** (7.397 mg, 0.0141 mmol) with stirring for 40 minutes. Column chromatography (15% EtOAc/hexane) afforded lactone **35** (95.27 mg, 0.224 mmol, 79%) as a colorless solid.

Method 4: 5 mol%, Fe(dibm)$_3$ (**2**), RT.

Prepared according to the general procedure using lactone **18**[1] (114.8 mg, 0.326 mmol), 2-methoxypropene **27** (624 μL, 469 mg, 6.51 mmol), Na_2HPO_4 (46.2 mg, 0.326 mmol) and Fe(dibm)$_3$ (**2**) (8.49 mg, 0.0163 mmol) with stirring for 1 hour. Column chromatography (15% EtOAc/hexane) afforded lactone **35** (67.8 mg, 0.159 mmol, 49%) >95:5 *dr* as a colourless solid.

Method 5: 5 mol%, Fe(dibm)$_3$ (**2**), Ph(^{i}PrO)SiH_2, 60°C.

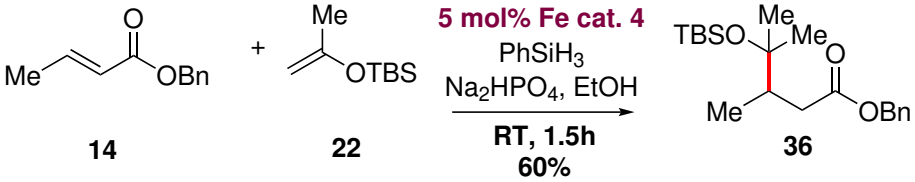
To a solution of lactone **18**[1] (204.0 mg, 0.579 mmol) and 2 methoxypropene **27** (1.6 mL, 1.3 g, 17.4 mmol) in EtOH (3 mL) was added Na_2HPO_4, Fe(dibm)$_3$ (**2**) (15.1 mg, 0.0289 mmol) and $PhSiH_3$ (143 μL, 125 mg, 1.16 mmol). The mixture was stirred for 45 minutes at 60°C in a pressure tube, concentrated *in vacuo* and purified by column chromatography (15% EtOAc/hexane), affording lactone **35** (189.3 mg, 0.444 mmol, 77%) >95:5 *dr* as a colourless solid.

Method 6: 6 mol%, Fe(dibm)$_3$ (**2**), Ph(^{i}PrO)SiH_2, 60°C.

Prepared according to the general procedure using lactone **18**[1] (120 mg, 0.34 mmol), 2-methoxypropene **27** (651.2 μL, 490.4 mg, 0.68 mmol), Na_2HPO_4 (40 mg, 0.28 mmol), Ph(^{i}PrO)SiH_2, (122 μL, 112.9 mg, 0.68 mmol) and Fe(dibm)$_3$ (**2**) (8.86 mg, 0.02 mmol), with heating at 60°C and stiring for 40 mins. Column chromatography (15% EtOAc/hexane) affording lactone **35** (102.5 mg, 0.24 mmol, 71%) as a colorless solid.

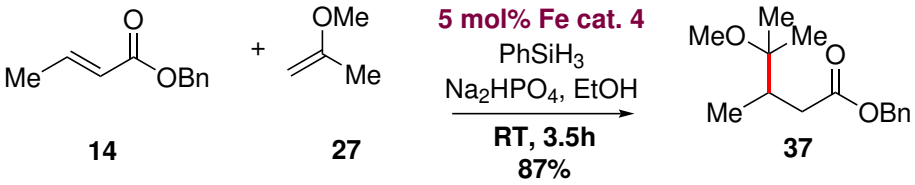
Recrystallisation from MeOH afforded diffraction quality crystals of the racemate. M.P. 102.0°C - 103.0°C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67 (ddt, J = 6.6, 2.7, 1.4 Hz, 4H), 7.46 - 7.39 (m, 7H), 4.56 (q, J = 3.1 Hz, 1H), 3.94 (dd, J = 11.4, 2.9 Hz, 1H), 3.64 (dd, J = 11.4, 2.9 Hz, 1H), 3.14 (s, 3H), 2.72 (dd, J = 18.0, 10.3 Hz, 1H), 2.56 (dt, J = 10.3, 3.7 Hz, 1H), 2.47 (dd, J = 18.0, 4.1 Hz, 1H), 1.10 (s, 3H), 1.09 (s, 3H), 1.07 (s, 9H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.3, 135.8, 135.7, 133.2, 132.7, 130.0, 128.0, 81.3, 75.1, 66.1, 49.3, 45.6, 31.1, 26.9, 22.0, 21.3, 19.3 HRMS (ESI) Calc. for $C_{25}H_{35}O_4Si$ $[M+H]^+$ 427.2299; found 427.2301. $[\alpha]_D^{19.9}$ 13.3 (c 1.51, CH_2Cl_2).

Ester 36



Prepared according to the general procedure using benzyl crotonate **14** (113.3 mg, 0.643 mmol), silyl enol ether **22**[9] (332.3 mg, 1.93 mmol) and Na_2HPO_4 (91 mg, 0.643 mmol), with stirring for 90 minutes. Column chromatography (0.5% EtOAc/hexane) afforded ester **36** (135 mg, 0.385 mmol 60%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.37 - 7.31 (m, 5H), 5.14 (s, 2H), 2.77 (dd, J = 14.6, 2.5 Hz, 1H), 2.08 (dd, J = 14.6, 10.5 Hz, 1H), 2.05 - 1.99 (m, 1H), 1.22 (s, 3H), 1.15 (s, 3H), 0.93 (d, J = 6.4 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 174.1, 136.4, 128.6, 128.26, 128.22, 75.3, 66.2, 42.3, 37.2, 28.4, 26.4, 26.0, 18.3, 15.4, -1.95, -1.98. HRMS (ESI) Calc. for $C_{20}H_{35}O_3Si$ $[M+H]^+$ 351.2350; found 351.2347.

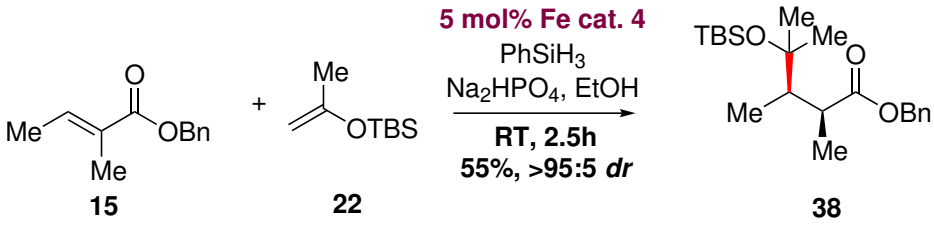
Ester 37



Prepared according to the general procedure using benzyl crotonate **14** (117.0 mg, 0.664 mmol) and 2-methoxypropene **27** (1.3 mL, 959 mg, 13.3 mmol) with stirring for 3.5 hours. Column chromatography (2.5% to 5% EtOAc/hexane) afforded ester **37** (144.9 mg, 0.579 mmol, 87%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.36 - 7.29 (m, 5H), 5.12 (s, 2H), 3.16 (s, 3H), 2.66 (dd, J = 15.1, 3.7 Hz, 1H), 2.27 (dqd, J = 10.3, 6.8, 3.5 Hz, 1H), 2.06 (dd, J = 15.1, 10.1 Hz, 1H), 1.13 (s, 3H), 1.05 (s, 3H), 0.92 (d, J = 6.9 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 176.1, 136.4, 128.5, 128.3,

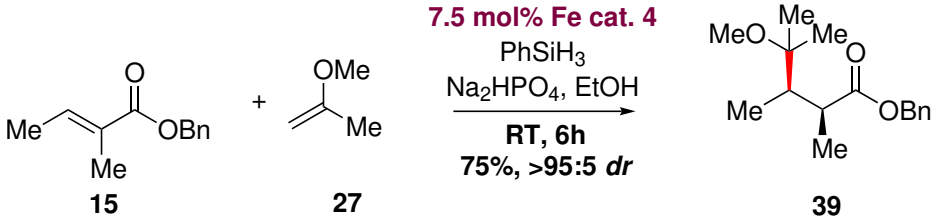
128.1, 77.3, 65.9, 48.8, 45.8, 39.7, 23.6, 21.8, 17.8, 11.4. HRMS (ESI) Calc. for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1642; found 251.1635.

Ester 38



Prepared according to the general procedure using benzyl tiglate **15** (66.7 mg, 0.351 mmol) and silyl enol ether **22**[9] (367.4 mg, 2.13 mmol), with stirring for 2.5 hours. Column chromatography (2% Et_2O/pentane) afforded ester **38** (70.3 mg, 0.193 mmol, 55%) >95:5 *dr* as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.37 - 7.30 (m, 5H), 5.11 and 5.07 (AB_q, J_{AB} = 12.4 Hz, 2H), 2.97 (qd, J = 7.2, 3.1 Hz, 1H), 1.63 (qd, J = 7.3, 3.1 Hz, 1H), 1.22 (d, J = 7.2 Hz, 3H), 1.18 (s, 3H), 1.17 (s, 3H), 0.99 (d, J = 7.3 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 176.3, 136.4, 128.6, 128.4, 128.2, 76.6, 65.9, 50.3, 39.5, 28.8, 26.6, 26.0, 18.6, 18.3, 11.6, -1.8. HRMS (ESI) Calc. for $C_{21}H_{37}O_3Si$ $[M+H]^+$ 365.2507; found 365.2504.

Ester 39



Method 1: 7.5 mol% Fe cat. **4**.

Conducted according to the general procedure using benzyl tiglate **15** (127.0 mg, 0.668 mmol) and 2-methoxypropene **27** (1.3 mL, 966 mg, 13.4 mmol) with stirring for 4 hours, followed by the addition of further 2-methoxypropene **27** (650 μL, 483 mg, 6.7 mmol), Fe cat. **4** (8.8 mg, 0.0168 mmol), and $PhSiH_3$ (82 μL, 72 mg, 0.67 mmol) and the mixture was stirred for a further 2 hours. Column chromatography (2.5% to 5% EtOAc/hexane) afforded ester **39** (132.8 mg, 0.502 mmol, 75%) >95:5 *dr* as a clear colourless oil.

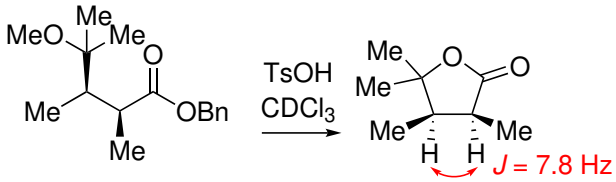
Method 2: 7.5 mol% $Fe(dibm)_3$ (**2**), 60°C.

Conducted according to the general procedure using benzyl tiglate **15** (139.5 mg, 0.733 mmol), 2-methoxypropene **27** (1.4 mL, 1.1 g, 14.7 mmol) Na_2HPO_4 (104 mg, 0.733 mmol), $Fe(dibm)_3$ (**2**) (19.1 mg, 0.0367 mmol) and $PhSiH_3$ (172 μL, 151 mg, 1.39 mmol) with stirring for 1 hour at 60°C in a sealed tube, followed by the addition of further 2-methoxypropene **27** (1.4 mL, 1.1 g, 14.7 mmol), (**2**) (9.6 mg, 0.0184 mmol), and $PhSiH_3$ (86 μL, 75 mg, 0.693 mmol) and the mixture was stirred for

a further 3.5 hours. Column chromatography (2.5% to 5% EtOAc/hexane) afforded ester **39** (121.2 mg, 0.458 mmol, 63%) 4:1 *dr* as a clear colourless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.38 - 7.29 (m, 5H), 5.11 and 5.06 (AB_q, J_{AB} = 12.4 Hz, 2H), 3.13 (s, 3H), 2.84 (qd, J = 7.1, 4.1 Hz, 1H), 1.81 (qd, J = 7.2, 4.1 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H), 1.13 (s, 3H), 1.11 (s, 3H), 1.00 (d, J = 7.2 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 176.1, 136.4, 128.5, 128.3, 128.1, 77.3, 65.9, 48.8, 45.8, 39.7, 23.6, 21.8, 17.8, 11.4. HRMS (ESI) Calc. for $C_{16}H_{25}O_3$ $[M+H]^+$ 265.1798; found 265.1794.

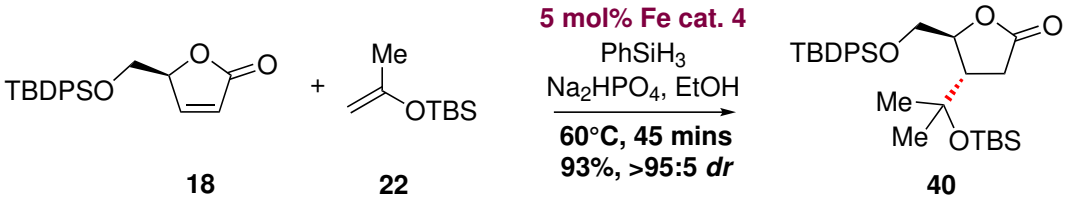
Lactone 54



39 **54**

To a solution of ester **39** (42.6 mg, 0.161 mmol) in $CDCl_3$ (2 mL) was added TsOH (9.2 mg, 0.0484 mmol) and the solution was heated at reflux for 1.5 hours. The organic phase was washed with $NaHCO_3$ and dried over Na_2SO_4 then transfered to an NMR tube for analysis. (Lactone **54** was volatile). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.95 (quintet, J = 7.8 Hz, 1H), 2.31 (quintet, J = 7.7 Hz, 1H), 1.41 (s, 3H), 1.34 (s, 3H), 1.18 (d, J = 7.5 Hz, 3H), 0.94 (d, J = 7.3 Hz, 3H), 0.94 (d, J = 7.3 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 179.2, 85.1, 42.2, 39.1, 27.8, 24.0, 11.1, 11.0. HRMS (ESI) Calc. for $C_8H_{15}O_2$ $[M+H]^+$ 143.1067; found 143.1068. Analysis of the ^3J coupling (J = 7.8 Hz), suggests a *cis* configuration of the methyl groups.[12]

Lactone 40



18 **22** **40**

Method 1: 5 mol% Fe cat. **4**, 60°C:

Conducted according to the general procedure on lactone **18**[1] (204.9 mg, 0.581 mmol), with silyl enol ether **22**[9] (300.8 mg, 1.75 mmol) and Fe cat. **4** (15.2 mg, 0.0291 mmol) with stirring for 45 minutes at 60°C. Column chromatography (5% to 10% EtOAc/hexane) afforded lactone **40** (284.0 mg, 0.539 mmol, 93%) >95:5 *dr* as a clear colourless oil.

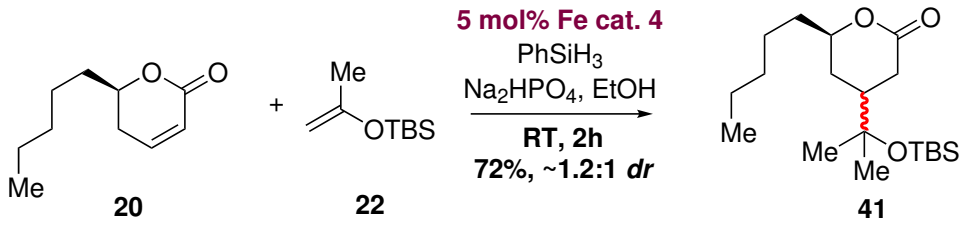
Method 2: 5 mol% $Fe(dibm)_3$ (**2**), 60°C:

Conducted according to the general procedure on lactone **18**[1] (104.8 mg, 0.297 mmol), with silyl enol ether **22**[9] (153.6 mg, 0.892 mmol), Na_2HPO_4 (42.2 mg, 0.297 mmol) and $Fe(dibm)_3$ (**2**) (7.7 mg,

0.01485 mmol) with stirring 1 hour and 30 minutes at 60°C. Column chromatography (5% to 10% EtOAc/hexane) afforded lactone **40** (136.1 mg, 0.258 mmol, 87%) >95:5 *dr* as a clear colourless oil.

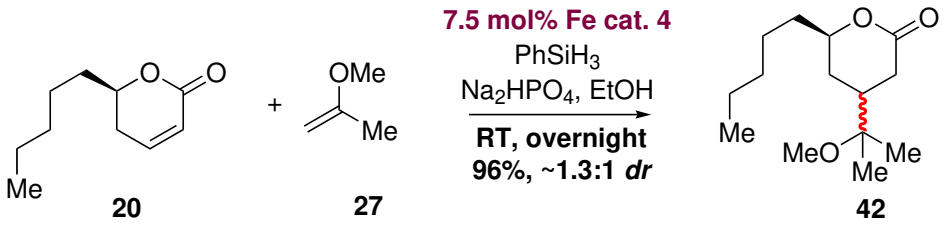
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 6.7 Hz, 4H), 7.46 - 7.39 (m, 7H), 4.58 (q, J = 3.0 Hz, 1H), 3.96 (dd, J = 11.4, 2.7 Hz, 1H), 3.63 (dd, J = 11.4, 2.8 Hz, 1H), 2.69 (dd, J = 18.1, 10.4 Hz, 1H), 2.50 (dd, J = 18.1, 4.5 Hz, 1H), 2.40 (dt, J = 10.3, 4.1 Hz, 1H), 1.18 (s, 3H), 1.14 (s, 3H), 1.06 (s, 9H), 0.82 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.3, 135.8, 135.7, 133.2, 132.7, 130.0, 128.0, 81.7, 73.9, 66.1, 48.0, 31.3, 27.8, 27.4, 27.0, 25.8, 19.4, 18.2, -2.03, -2.06. HRMS (ESI) Calc. for $C_{30}H_{47}O_4Si_2$ $[M+H]^+$ 527.3007; found 527.3011. $[\alpha]_D^{20.1}$ 8.61 (c 1.75, CH_2Cl_2).

Lactone 41



Prepared according to the general procedure using massoia lactone **20** (143.4 mg, 0.852 mmol) and silyl enol ether **22**[9] (592.0 mg, 3.44 mmol) with stirring for 2 hours. Column chromatography (5% to 10% to 20% EtOAc/hexane) afforded lactone **41** (210.2 mg, 0.614 mmol, 72%) as a clear colourless oil and a 1.2:1 mixture of stereoisomers. Further elution afforded reduced lactone **21**[8] (38.3 mg, 0.225 mmol, 26%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.25 - 4.21 (m, 1H), 4.18 (dtd, J = 10.3, 6.8, 3.2 Hz, 1H), 2.60 - 2.56 (m, 1H), 2.52 - 2.45 (m, 2H), 2.40 (dt, J = 17.5, 8.6 Hz, 1H), 1.92 - 1.83 (m, 4H), 1.74 - 1.44 (m, 7H), 1.38 - 1.25 (m, 11H), 1.22 (s, 2H), 1.19 (s, 2H), 1.19 (s, 3H), 1.18 (s, 3H), 0.87 (app. td, = 7.0, 1.4 Hz, 5H), 0.84 (s, 7H), 0.83 (s, 8H), 0.09 (s, 4H), 0.07 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 174.5, 172.6, 80.1, 78.0, 74.7, 74.0, 43.6, 40.9, 36.2, 35.2, 31.71, 31.66, 31.4, 30.9, 30.1, 29.4, 28.1, 27.8, 27.44, 27.34, 25.95, 25.91, 25.0, 24.6, 22.60, 22.58, 18.3, 14.05, 14.02, -2.04, -2.05, -2.07. HRMS (ESI) Calc. for $C_{19}H_{39}O_3Si$ $[M+H]^+$ 343.2663; found 343.2669.

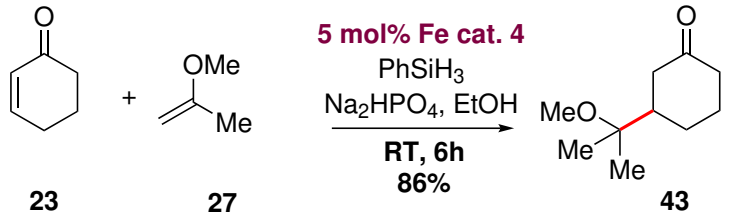
Lactone 42



Prepared according to the general procedure using massoia lactone **20** (121.7 mg, 0.723 mmol), 2-methoxypropene **27** (3.6 mL, 2.7 g, 37.6 mmol) and Fe cat. **4** (28.4 mg, 0.0543 mmol) with stirring overnight. Column chromatography (20% EtOAc/hexane) afforded lactone **42** (167.6 mg, 0.692 mmol, 96%) as a colourless oil and 1.3:1 mixture of stereoisomers. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.25 (ddtd, J = 8.6, 8.4, 4.4, 4.1 Hz, 1H), 4.20 (dddd, J = 11.8, 7.2, 4.8, 2.5 Hz, 1H), 3.17 (s, 2H),

3.17 (s, 3H), 2.57 (ddd, J = 17.7, 6.9, 1.5 Hz, 1H), 2.49 - 2.36 (m, 3H), 2.09 - 2.02 (m, 2H), 1.94 - 1.87 (m, 2H), 1.71 - 1.47 (m, 8H), 1.41 -1.23 (m, 11H), 1.14 (s, 2H), 1.12 (s, 2H), 1.11 (s, 3H), 1.10 (s, 3H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 174.2, 172.4, 80.2, 78.1, 75.7, 75.3, 49.25, 49.14, 40.8, 38.5, 36.1, 35.2, 31.69, 31.66, 31.3, 30.8, 30.0, 29.1, 25.0, 24.6, 22.6, 22.07, 21.96, 21.58, 21.48, 14.0. HRMS (ESI) Calc. for $C_{14}H_{27}O_3$ $[M+H]^+$ 243.1955; found 243.1958.

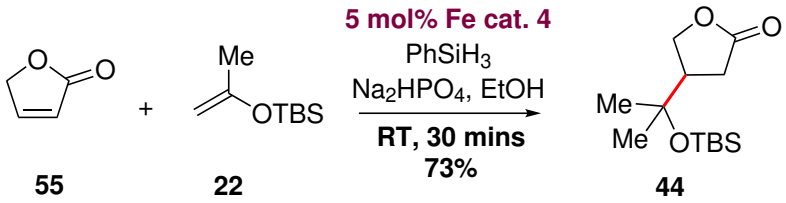
Ketone 43



23 **27** **43**

Prepared according to the general procedure using cyclohexenone **23** (100 μL, 99.3 mg, 1.03 mmol) and 2-methoxypropene **27** (2.9 mL, 2.23 g, 31.0 mmol) with stirring for 6 hours. Column chromatography (15% Et_2O/pentane) afforded ketone **43** (151.3 mg, 0.889 mmol, 86%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.09 (s, 3H), 2.35 (ddt, J = 13.9, 4.0, 2.0 Hz, 1H), 2.28 (ddq, J = 14.3, 4.1, 2.1 Hz, 1H), 2.20 – 2.14 (m, 1H), 2.09 (td, J = 13.5, 0.8 Hz, 1H), 2.03 (ddq, J = 13.2, 6.5, 3.2 Hz, 1H), 1.86 (dtq, J = 11.3, 3.5, 1.8 Hz, 1H), 1.79 (ddt, J = 12.9, 11.9, 3.6 Hz, 1H), 1.51 (qdd, J = 13.2, 4.4, 3.7 Hz, 1H), 1.36 (tdd, J = 12.9, 11.9, 3.6 Hz, 1H), 1.07 (s, 3H), 1.05 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 212.2, 75.7, 48.9, 47.2, 43.1, 41.3, 25.8, 25.4, 22.16, 22.15. HRMS (ESI) Calc. for $C_{10}H_{19}O_2$ $[M+H]^+$ 171.1380; found 171.1380.

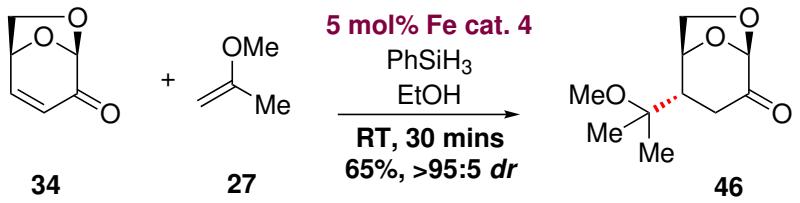
Lactone 44



55 **22** **44**

Prepared according to the general procedure using lactone **33** (19.98 mg, 0.238 mmol) and silyl enol ether **22**[9] (123.1 mg, 0.714 mmol), with stirring for half an hour. Column chromatography (15% EtOAc/hexane) afforded lactone **44** (45.1 mg, 0.175 mmol, 73%) as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.32 (t, J = 8.4 Hz, 1H), 4.25 (t, J = 8.4 Hz, 1H), 2.60 - 2.49 (m, 2H), 2.43 (dd, J = 16.4, 8.3 Hz, 1H), 1.22 (s, 3H), 1.20 (s, 3H), 0.85 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.5, 72.5, 69.4, 47.6, 29.7, 28.6, 28.0, 25.9, 18.3, -2.09, -2.12. HRMS (ESI) Calc. for $C_{13}H_{27}O_3Si$ $[M+H]^+$ 259.1724; found 259.1723.

Ketone 46



Method 1: 5 mol% Fe cat. **4**.

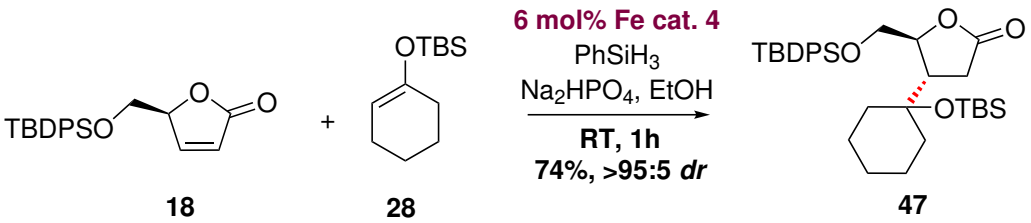
Conducted according to the general procedure, without Na_2HPO_4, using levoglucoscenone (**34**) (227.1 mg, 1.80 mmol), 2-methoxypropene **27** (5.2 mL, 3.9 g, 54.0 mmol) and Fe cat. **4** (47.1 mg, 0.0900 mmol) with stirring for 30 minutes. Column chromatography (30% EtOAc/hexane) afforded ketone **46** (236.1 mg, 1.18 mmol, 65%) >95:5 *dr* as a clear colourless oil.

Method 2: 5 mol% $Fe(dibm)_3$ (**2**), 60°C.

Conducted according to the general procedure, without Na_2HPO_4, using levoglucoscenone (**34**) (68.2 mg, 0.541 mmol), 2-methoxypropene **27** (1.6 mL, 1.20 g, 16.23 mmol) and $Fe(dibm)_3$ (**2**) (14.1 mg, 0.0271 mmol) with heating for 40 minutes at 60°C in a sealed tube. Column chromatography (30% EtOAc/hexane) afforded afforded ketone **46** (65.6 mg, 0.328 mmol, 61%) >95:5 *dr* as a clear colourless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 5.04 (s, 1H), 4.90 (dd, J = 5.2, 0.7 Hz, 1H), 3.92 (dd, J = 7.3, 5.3 Hz, 1H), 3.87 (dd, J = 7.3, 0.9 Hz, 1H), 3.18 (s, 3H), 2.57 (dd, J = 17.4, 9.1 Hz, 1H), 2.38 (dddd, J = 17.4, 3.0, 1.4, 0.8 Hz, 1H), 2.07 (dd, J = 9.1, 3.0 Hz, 1H), 1.21 (s, 3H), 1.15 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 201.4, 100.8, 76.6, 73.2, 69.6, 49.1, 48.5, 32.8, 22.6, 21.4. HRMS (ESI) Calc. for $C_{10}H_{17}O_4$ $[M+H]^+$ 201.1121; found 201.1121. $[\alpha]_D^{20.4}$ -137.7 (c 2.210, CH_2Cl_2).

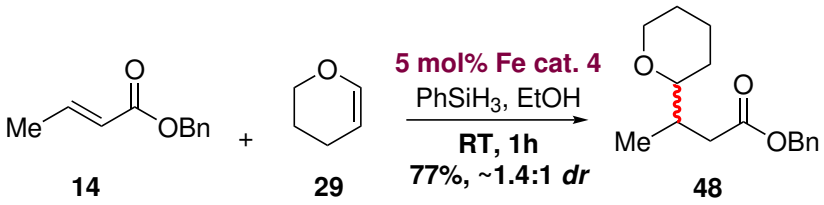
Lactone 47



Prepared according to the general procedure using lactone **18**[1] (66.6 mg, 0.189 mmol), silyl enol ether **28**[10] (127.4 mg, 0.600 mmol) and Fe cat. **4** (6.25 mg, 0.0119 mmol) with stirring for 1 hour. Column chromatography (5% EtOAc/hexane) afforded lactone **47** (79.6 mg 0.140 mmol, 74%) >95:5 *dr* as a clear colourless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.68 - 7.66 (m, 4H), 7.45 - 7.42 (m, 2H), 7.41 - 7.38 (m, 4H), 4.56 (dt, J = 4.7, 2.4 Hz, 1H), 3.99 (dd, J = 11.5, 2.3 Hz, 1H), 3.58 (dd, J = 11.5, 2.9 Hz, 1H), 2.96 (ddd, J = 9.5, 6.6, 4.6 Hz, 1H), 2.66 - 2.62 (m, 1H), 2.60 (dd, J = 15.6, 7.3 Hz, 1H), 1.67 (dt, J = 11.6, 3.6 Hz, 2H), 1.55 - 1.42 (m, 5H), 1.30 - 1.12 (m, 3H), 1.08 (s, 9H), 0.85 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.2, 135.82, 135.69, 133.2, 132.7,

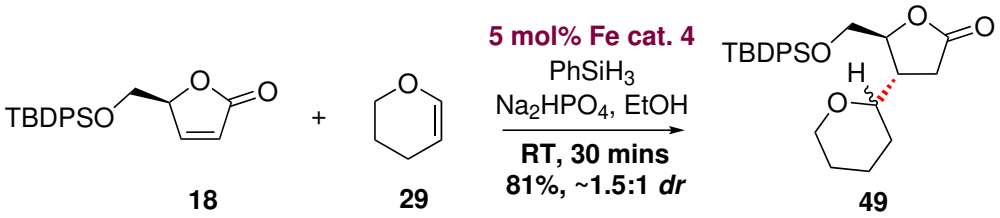
130.0, 128.0, 81.3, 75.8, 65.8, 37.7, 36.2, 30.5, 27.0, 25.9, 25.6, 23.3, 23.1, 19.4, 18.4, -1.7. HRMS (ESI) Calc. for $C_{33}H_{51}O_4Si_2$ $[M+H]^+$ 567.3320; found 567.3324. $[\alpha]_D^{21.9}$ 11.2 (*c* 1.56, CH_2Cl_2).

Ester 48



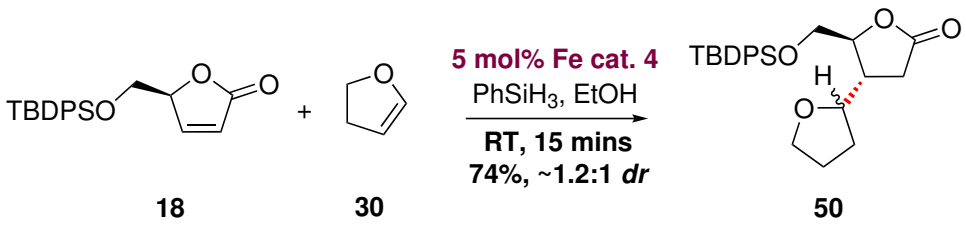
Prepared according to the general procedure, without Na_2HPO_4 using benzyl crotonate **14** (117.6 mg, 0.667 mmol) and dihydropyran **29** (1.8 mL, 1.68 g, 20 mmol), with stirring for 1 hour. Column chromatography (2.5% to 5% EtOAc/hexane) afforded the ester **48** (135.6 mg, 0.517 mmol, 77%) as a clear colourless oil and a 1.4:1 mixture of stereoisomers. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.36 - 7.29 (m, 9H), 5.15 - 5.09 (m, 4H), 3.96 - 3.91 (m, 2H), 3.35 (tdd, J = 11.6, 9.4, 2.3 Hz, 2H), 3.16 (ddd, J = 11.1, 4.3, 1.8 Hz, 1H), 3.00 (ddd, J = 11.0, 7.2, 2.0 Hz, 1H), 2.65 (dd, J = 15.2, 5.0 Hz, 1H), 2.57 - 2.55 (m, 1H), 2.20 (ddd, J = 22.8, 15.2, 7.6 Hz, 2H), 2.13 - 2.04 (m, 2H), 1.84 - 1.82 (m, 2H), 1.65 - 1.63 (m, 1H), 1.57 - 1.40 (m, 7H), 1.35 - 1.28 (m, 1H), 1.26 - 1.20 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.8 Hz, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 173.36, 173.22, 136.40, 136.31, 128.56, 128.53, 128.23, 128.22, 128.16, 128.11, 81.4, 80.6, 68.79, 68.68, 66.06, 65.99, 38.14, 38.01, 35.9, 35.3, 28.9, 28.1, 26.30, 26.21, 23.76, 23.64, 16.2, 15.1 HRMS (ESI) Calc. for $C_{16}H_{23}O_3$ $[M+H]^+$ 263.1642; found 263.1644.

Lactone 49



Prepared according to the general procedure, using lactone **18**[1] (102.2 mg, 0.290 mmol), dihydropyran **29** (794 μL, 732 mg, 8.70 mmol) and Na_2HPO_4 (41 mg, 0.290 mmol), with stirring for half an hour. Column chromatography (10% EtOAc/hexane) afforded lactone **49** (103 mg, 0.235 mmol, 81%) as a colourless oil and a 1.5:1 mixture of stereoisomers. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.69 - 7.66 (m, 7H), 7.45 - 7.38 (m, 11H), 4.60 (q, J = 3.5 Hz, 1H), 4.46 (dt, J = 4.8, 3.3 Hz, 1H), 3.98 - 3.87 (m, 4H), 3.70 (ddd, J = 11.2, 7.4, 3.5 Hz, 2H), 3.37 (tdd, J = 11.1, 7.4, 3.4 Hz, 2H), 3.25 - 3.19 (m, 2H), 2.77 (dd, J = 17.8, 10.0 Hz, 1H), 2.64 (d, J = 8.0 Hz, 1H), 2.55 - 2.49 (m, 2H), 2.34 (dd, J = 17.8, 5.4 Hz, 1H), 1.87 - 1.84 (m, 2H), 1.57 - 1.44 (m, 7H), 1.27 - 1.17 (m, 2H), 1.07 (s, 6H), 1.06 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.0, 176.81, 135.76, 135.75, 135.68, 135.65, 133.2, 133.1, 132.8, 132.7, 130.0, 129.9, 127.92, 127.87, 82.4, 81.8, 79.1, 77.2, 68.67, 68.65, 65.9, 65.1, 41.9, 41.5, 32.1, 30.2, 29.48, 29.36, 26.9, 25.94, 25.92, 23.4, 23.3, 19.3. HRMS (ESI) Calc. for $C_{26}H_{35}O_4Si$ $[M+H]^+$ 439.2299; found 439.2300.

Lactone 50



Method 1: 5 mol% Fe cat. **4**.

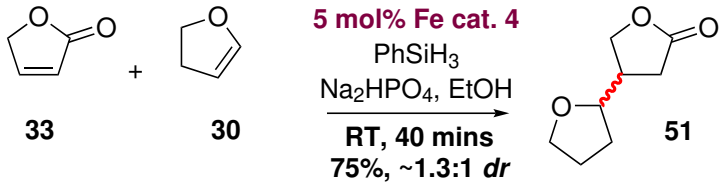
Prepared according to the general procedure, without Na_2HPO_4 using lactone **18**[1] (53.8 mg, 0.153 mmol) and dihydrofuran **30** (117 μL, 107 mg, 1.53 mmol) with stirring for 15 minutes. Column chromatography (15% EtOAc/hexane) afforded lactone **50** (48.1 mg, 0.113 mmol, 74%) as a clear colourless oil and a 1.2:1 mixture of stereoisomers.

Method 2: 5 mol% $Fe(dibm)_3$ (**2**), 60°C.

Prepared according to the general procedure using lactone **18**[1] (102.3 mg, 0.290 mmol), dihydrofuran **30** (219 μL, 203 mg, 2.90 mmol), Na_2HPO_4 (41.2 mg, 0.290 mmol) and $Fe(dibm)_3$ (**2**) (7.56 mg, 0.0145 mmol) with stirring at 60°C for 40 minutes. Column chromatography (15% EtOAc/hexane) afforded lactone **50** (72.8 mg, 0.171 mmol, 59%) as a clear colourless oil and a 1.2:1 mixture of stereoisomers.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67 - 7.65 (m, 8H), 7.44 - 7.39 (m, 12H), 4.55 (q, J = 3.3 Hz, 1H), 4.40 (q, J = 3.4 Hz, 1H), 3.97 (dd, J = 11.4, 2.6 Hz, 1H), 3.91 (dd, J = 11.5, 3.2 Hz, 1H), 3.86 (q, J = 7.5 Hz, 1H), 3.81 (dtd, J = 11.1, 7.4, 3.7 Hz, 3H), 3.76 - 3.68 (m, 4H), 2.82 - 2.67 (m, 3H), 2.61 – 2.57 (m, 1H), 2.51 (dd, J = 16.1, 3.7 Hz, 1H), 2.27 (dd, J = 17.8, 5.1 Hz, 1H), 2.00 (dt, J = 12.6, 6.4 Hz, 1H), 1.96 - 1.88 (m, 5H), 1.49 - 1.41 (m, 2H), 1.06 (s, 8H), 1.06 (s, 8H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 176.8, 176.6, 135.8, 135.70, 135.69, 133.2, 133.1, 132.8, 132.7, 130.1, 130.00, 129.98, 127.98, 127.94, 83.1, 82.2, 80.7, 79.3, 68.5, 68.2, 65.6, 65.1, 41.2, 40.9, 32.3, 31.0, 29.8, 29.2, 26.9, 26.0, 25.7, 19.3. HRMS (ESI) Calc. for $C_{25}H_{33}O_4Si$ $[M+H]^+$ 425.2143; found 425.2143.

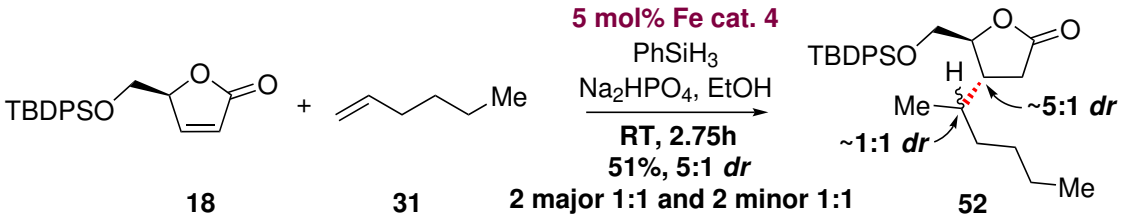
Lactone 51



Prepared according to the general procedure using butenolide **33** (100.4 mg, 1.20 mmol), dihydrofuran **30** (905 μL, 841 mg, 12.0 mmol) and Na_2HPO_4 (170 mg, 1.20 mmol) with stirring for 40 minutes. Column chromatography (30% to 50% EtOAc/hexane) afforded lactone **51** (140.5 mg, 0.900 mmol, 75%) as a clear colourless oil and a 1.3:1 mixture of stereoisomers. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.37 (dd, J = 9.2, 7.5 Hz, 1H), 4.32 (dd, J = 9.1, 8.0 Hz, 1H), 4.20 (dd, J = 9.3, 6.4 Hz, 1H), 4.07 (dd, J = 9.2, 6.5 Hz, 1H), 3.84 - 3.80 (m, 2H), 3.79 - 3.74 (m, 2H), 3.71 (dt, J = 14.6, 7.1 Hz, 2H), 2.66 (dq, J = 14.8, 7.4 Hz, 1H), 2.62 - 2.58 (m, 1H), 2.52 (dt, J = 17.5, 8.8 Hz, 2H), 2.46 - 2.42 (m,

1H), 2.25 (dd, J = 17.3, 7.3 Hz, 1H), 2.02 - 1.94 (m, 2H), 1.90 - 1.85 (m, 4H), 1.47 - 1.41 (m, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.0, 176.7, 80.0, 79.1, 70.8, 70.2, 68.34, 68.25, 40.3, 39.8, 31.3, 30.5, 29.9, 29.4, 25.8, 25.7. HRMS (ESI) Calc. for $C_8H_{13}O_3$ $[M+H]^+$ 157.0859; found 157.0859.

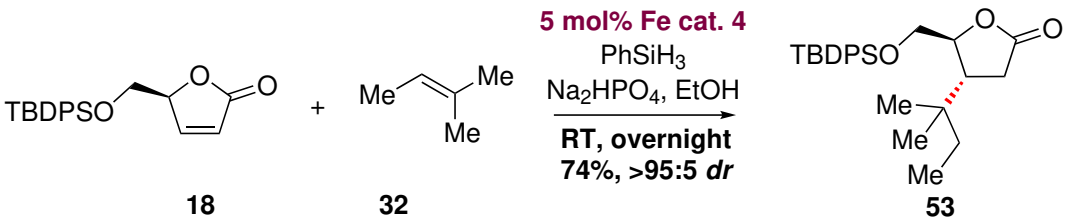
Lactone 52



18 **31** **52**

Prepared according to the general procedure using lactone **18**[1] (112.2 mg, 0.318 mmol) and 1-hexene **31** (398 μL, 267 mg, 3.18 mmol), with stirring for 2 hours and 45 minutes. Column chromatography (5% EtOAc/hexane) afforded lactone **52** (70.7 mg, 0.161 mmol, 51%) as a clear colourless oil, and a mixture of 4 stereoisomers, (~5:1 *dr* 2 major 1:1 and 2 minor 1:1). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67 - 7.66 (m, 7H), 7.45 - 7.39 (m, 12H), 4.34 (q, J = 3.5 Hz, 1H), 4.31 (q, J = 3.8 Hz, 1H), 3.89 (ddd, J = 11.3, 6.6, 3.2 Hz, 1H), 3.66 (ddd, J = 21.3, 11.4, 3.3 Hz, 1H), 2.77 (dd, J = 18.0, 10.0 Hz, 1H), 2.66 (dd, J = 17.9, 9.9 Hz, 1H), 2.46 (ddq, J = 24.4, 9.8, 4.9 Hz, 1H), 2.30 (ddd, J = 18.2, 13.4, 5.0 Hz, 2H), 1.56 - 1.50 (m, 1H), 1.33 - 1.17 (m, 11H), 1.07 (s, 15H), 0.91 - 0.85 (m, 10H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.4, 177.3, 135.8, 135.7, 133.1, 132.8, 132.7, 130.0, 128.0, 83.7, 82.7, 65.9, 65.5, 41.1, 40.9, 36.3, 35.5, 34.1, 33.4, 33.1, 31.3, 29.5, 29.4, 26.9, 23.0, 22.9, 19.3, 16.2, 15.5, 14.17, 14.16. HRMS (ESI) Calc. for $C_{27}H_{39}O_3Si$ $[M+H]^+$ 439.2663; found 439.2663.

Lactone 53



18 **32** **53**

Method 1: 5 mol% Fe cat. **4**.

Prepared according to the general procedure on lactone **18**[1] (105.3 mg, 0.299 mmol) and 2-methyl-2-butene **32** (948 μL, 629 mg, 8.97 mmol), with stirring overnight. Column chromatography, (5% EtOAc/hexane) afforded lactone **53** (94.5 mg, 0.223 mmol, 74%) >95:5 *dr* as a clear colourless oil.

Method 2: 5 mol% Fe(dibm)$_3$ (**2**), 60°C.

Prepared according to the general procedure on lactone **18**[1] (246.0 mg, 0.698 mmol) and 2-methyl-2-butene **32** (2.2 mL, 1.5 g, 20.9 mmol), Na_2HPO_4 (99 mg, 0.698 mmol) and Fe(dibm)$_3$ (**2**) (18.2 mg, 0.0349 mmol) with stirring overnight at 60°C in a sealed tube. Column chromatography, (5% EtOAc/hexane) afforded lactone **53** (178.7 mg, 0.420 mmol, 60%) >95:5 *dr* as a clear colourless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.67 - 7.66 (m, 4H), 7.45 - 7.39 (m, 7H), 4.43 (q, J = 2.8 Hz, 1H), 3.90 (dd, J = 11.3, 3.0 Hz, 1H), 3.59 (dd, J = 11.3, 3.1 Hz, 1H), 2.71 - 2.66 (m, 1H), 2.39 - 2.33 (m, 2H), 1.21 (qd, J = 7.5, 2.5 Hz, 2H), 1.07 (s, 9H), 0.82 - 0.79 (m, 9H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 177.6, 135.83, 135.72, 133.1, 132.7, 130.1, 128.0, 81.4, 66.4, 44.5, 34.9, 32.1, 30.8, 27.0, 23.16, 23.01, 19.4, 8.2. HRMS (ESI) Calc. for $C_{26}H_{37}O_3Si$ $[M+H]^+$ 425.2507; found 425.2506. $[\alpha]_D^{20.9}$ 10.1 (c 0.689, CH_2Cl_2).

Crystallographic Information

Intensity data for the solvated polymorph of Fe cat. **4** was collected on a Rigaku XtalLAB Synergy at 100.0(2) K. Data for the non-solvated polymorph of Fe cat. **4** was collected on the MX2 beamline[13] at the Australian Synchrotron at 100.0(2) K. The temperature was maintained using an Oxford Cryostream cooling device. The structures were solved by direct methods and difference Fourier synthesis.[14] Thermal ellipsoid plots were integrated within the WINGX[15] suite of programs or Olex2.[16]

Solvated Polymorph of 4 CCDC: 2204667

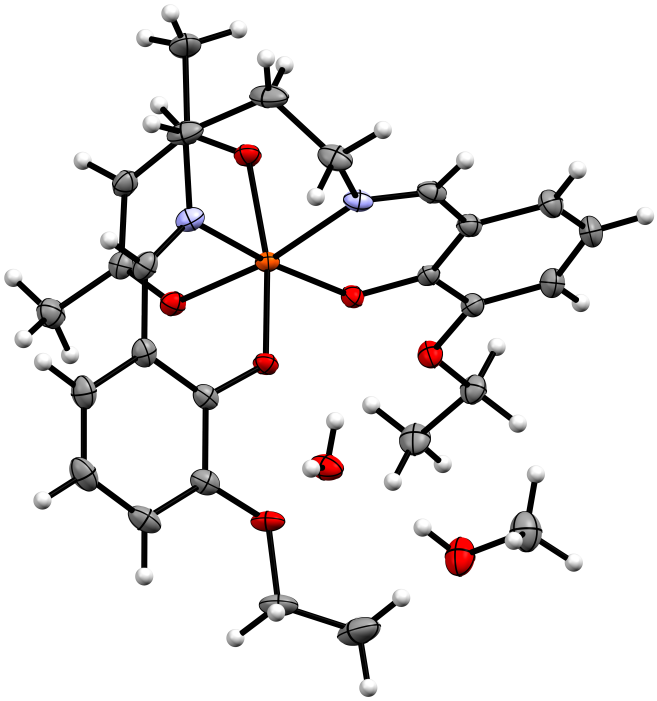


Figure 2: ORTEP representation of single crystal X-ray structure of Fe cat. **4**, as a mixed water and methanol solvate, ellipsoids at 50% probability. Selected bond lengths (Å): [Fe-N1 2.150(1), Fe-N2 2.148(1), Fe-O2 1.935(1), Fe-O3 1.940(1), Fe-O5 2.025(1), Fe-O6 2.008(1)].

Crystal data for: $C_{27}H_{37}N_2O_8Fe$ (M = 573.43 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 11.2988(4) Å, b = 29.2753(7) Å, c = 8.8713(3) Å, β = 108.177(4)°, V = 2787.98(16) Å^3, Z = 4, T = 100.0(2) K, μ(Mo Kα) = 0.592 mm^{-1}, $Dcalc$ = 1.366 g/cm^3, 43657 reflections measured (4.706°$\leq 2\Theta \leq$ 67.338°), 9552 unique (R_{int} = 0.0544, R_{sigma} = 0.0515) which were used in all calculations. The final R_1 was 0.0399 (I $> 2\sigma$(I)) and wR_2 was 0.0950 (all data).

Non-Solvated Polymorph of 4 CCDC: 2204669

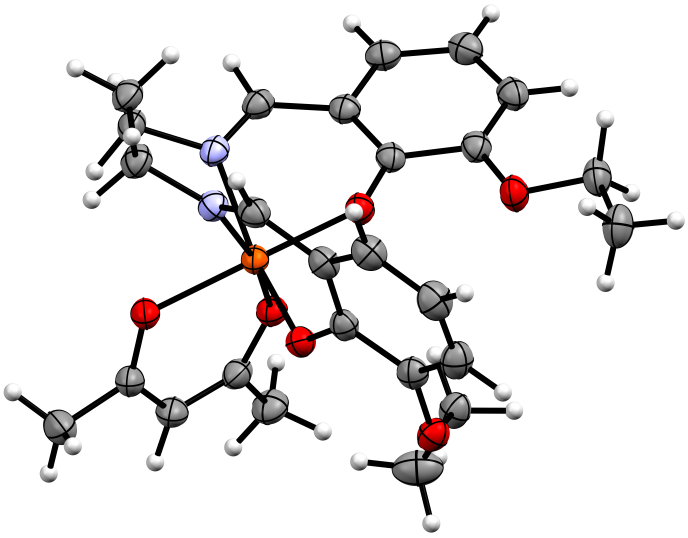


Figure 3: ORTEP representation of single crystal X-ray structure of Fe cat. **4**, as a non solvated polymorph, ellipsoids at 50% probability. Selected bond lengths (Å): [Fe-N1 2.120(2), Fe-N2 2.143(2), Fe-O2 1.942(2), Fe-O3 1.925(1), Fe-O5 2.035(1), Fe-O6 2.036(2)].

Crystal data for: $C_{26}H_{31}FeN_2O_6$ (M = 523.38 g/mol): monoclinic, space group C2/c (no. 15), a = 33.115(7) Å, b = 8.0690(16) Å, c = 23.502(5) Å, β = 128.93(3)°, V = 4885(2)Å^3, Z = 8, T = 100.0(2) K, μ(Synchrotron) = 0.662 mm^{-1}, $Dcalc$ = 1.423 g/cm^3, 43326 reflections measured (3.162°≤ 2Θ ≤ 64.474°), 7263 unique (R_{int} = 0.0821, R_{sigma} = 0.0622) which were used in all calculations. The final R_1 was 0.0466 (I > 2σ(I)) and wR_2 was 0.1313 (all data).

Lactone 35 CCDC: 2224866

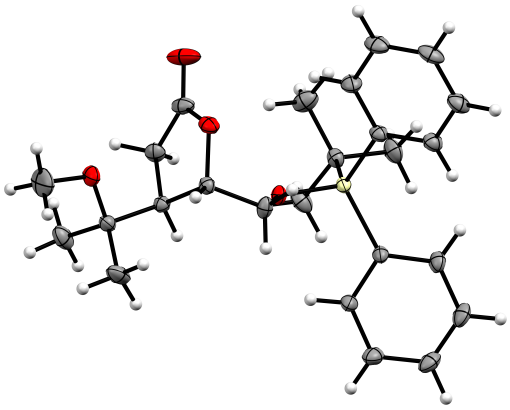


Figure 4: ORTEP representation of single crystal X-ray structure of lactone **35** ellipsoids at 50% probability.

Crystal Data for $C_{25}H_{34}O_4Si$ (M = 426.61 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.35425(16) Å, b = 11.58392(18) Å, c = 21.9396(3) Å, β = 93.5438(15)°, V = 2372.80(7) Å^3, Z =

4, T = 100.00(10) K, μ(Mo Kα) = 0.126 mm^{-1}, *Dcalc* = 1.194 g/cm^3, 278224 reflections measured (4.362°≤ 2Θ ≤ 102.83°), 26138 unique (R_{int} = 0.0902, R_{sigma} = 0.0502) which were used in all calculations. The final R_1 was 0.0555 (I > 2σ(I)) and wR_2 was 0.1572 (all data).

Decalin 26 CCDC: 2205204

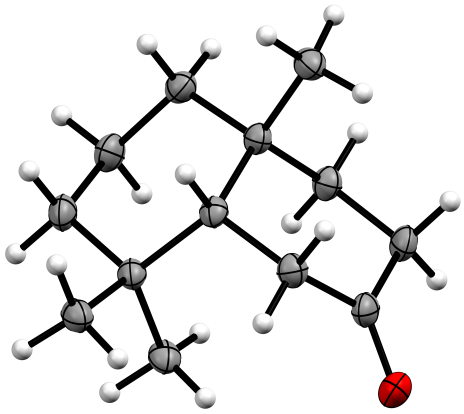


Figure 5: ORTEP representation of single crystal X-ray structure of decalin **26** ellipsoids at 50% probability.

Crystal data for: $C_{13}H_{22}O$ (M = 194.30 g/mol): monoclinic, space group P2$_1$ (no. 4), a = 7.31970(10) Å, b = 7.14910(10) Å, c = 10.9080(2) Å, β = 96.041(2)°, V= 567.638(15) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 0.524 mm^{-1}, *Dcalc* = 1.137 g/cm^3, 11992 reflections measured (8.15°≤ 2Θ ≤ 159.764°), 2370 unique (R_{int} = 0.0546, R_{sigma} = 0.0356) which were used in all calculations. The final R_1 was 0.0355 (I > 2σ(I)) and wR_2 was 0.0951 (all data).

Cost benefit analysis

Table 1: Cost of materials for the synthesis of $Fe(dibm)_3$ **2** and Fe cat. **4**. All prices in USD.

Compound	**Supplier**	**Cost USD/g**
$Fe(dibm)_3$ **2**	Strem	\$87.9
$Fe(acac)_3$ **1**	AKSci	\$ 0.14
$FeCl_3{\cdot}6H_2O$	Sigma	\$ 0.13
Ligand (dibm)	Sigma	\$ 8.52
Aldehyde **5**	Sigma	\$ 0.72
1,3-diaminopropane	Alfa Aeser	\$ 0.098

While $Fe(dibm)_3$ **2** is a highly effective catalyst in the C–C bond forming reaction, it is costly. The Fe complex **4** is an active catalyst at low loadings (<5 mol%). Both catalysts have similar molecular masses, (Fe cat. **4** = 523.4 g/mol, $Fe(dibm)_3$ **2** = 521.5 g/mol) which make the comparison simple.

$Fe(dibm)_3$ **2** is commercially available, however, at the cheapest cost of \$87.9/g it is essentially prohibitively expensive. On the other hand, calculating the cost to synthesise complex **2**, on the scale and yield reported by Baran, a price of \$11.2/g is obtained. Conducting the same analysis for Fe cat. **4** on the scale and yield described in this report, a price of \$0.77/g is obtained. Thus, per gram and given near identical molar masses, per mol, Fe cat. **4** is 14-fold cheaper than $Fe(dibm)_3$ **2**.

Table 1 lists the prices of the key reagents for the production of $Fe(dibm)_3$ **2** and Fe cat. **4**. Solvents and other reagents which all research laboratories would have on hand are not included.

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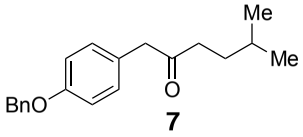
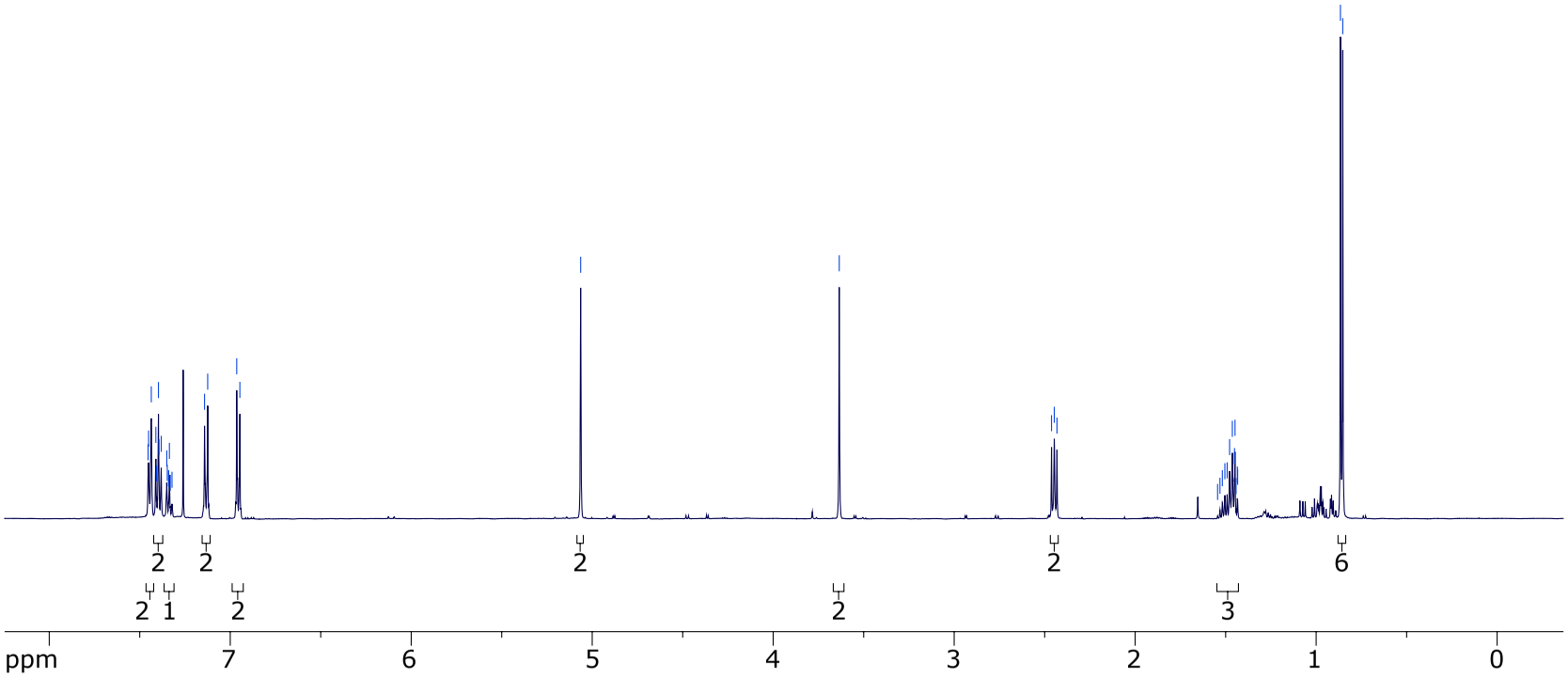
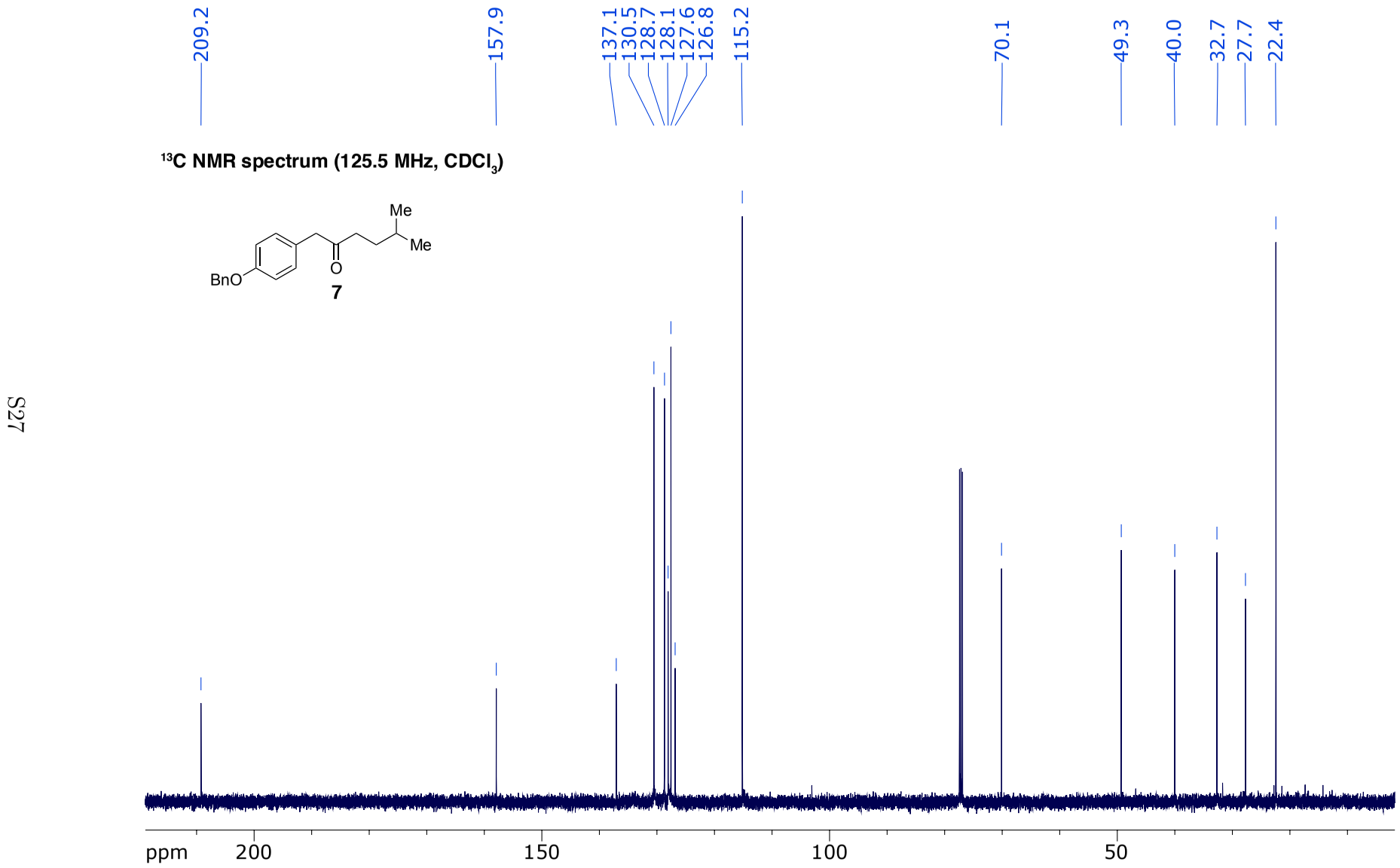
[16] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

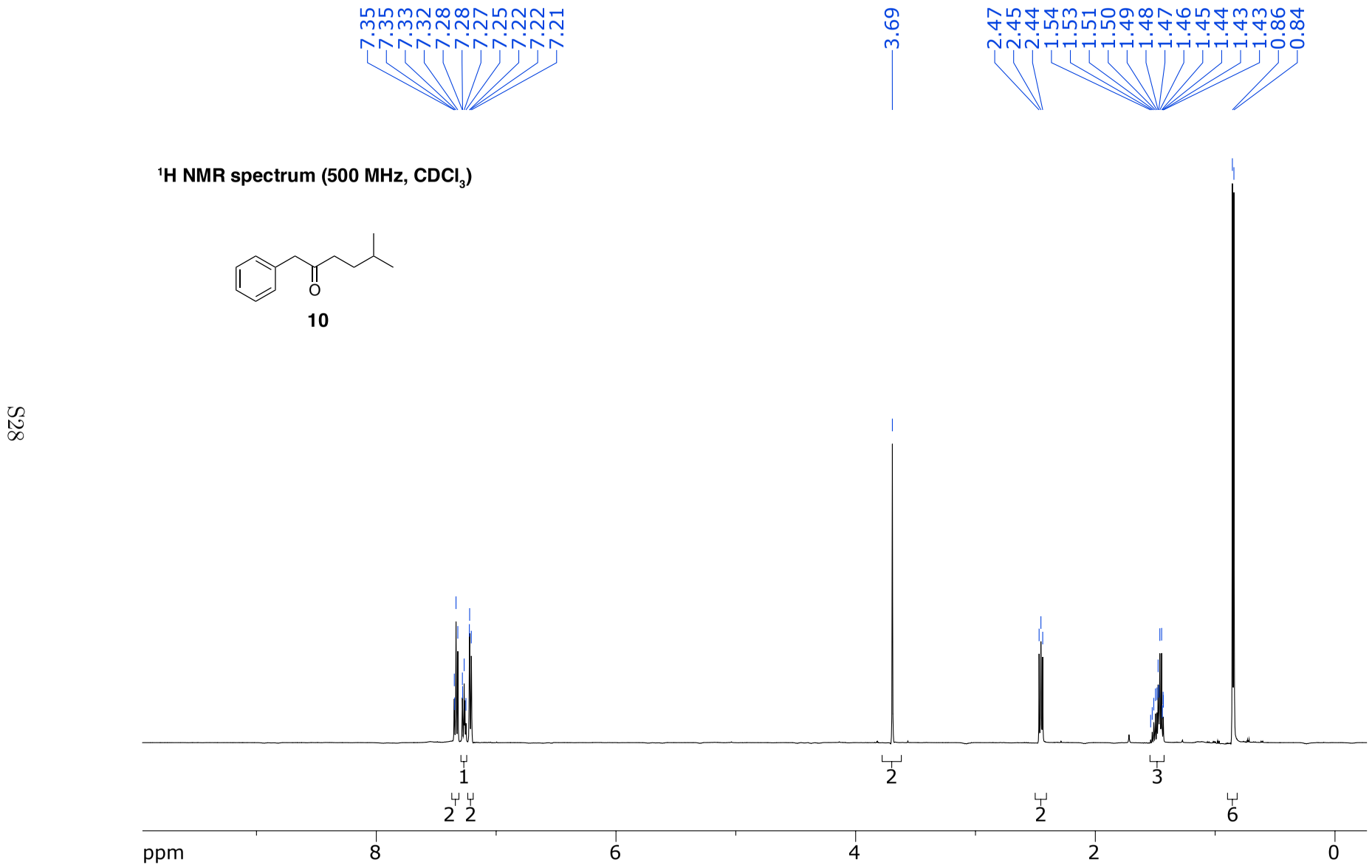


7





^{13}C NMR spectrum (125.5 MHz, $CDCl_3$)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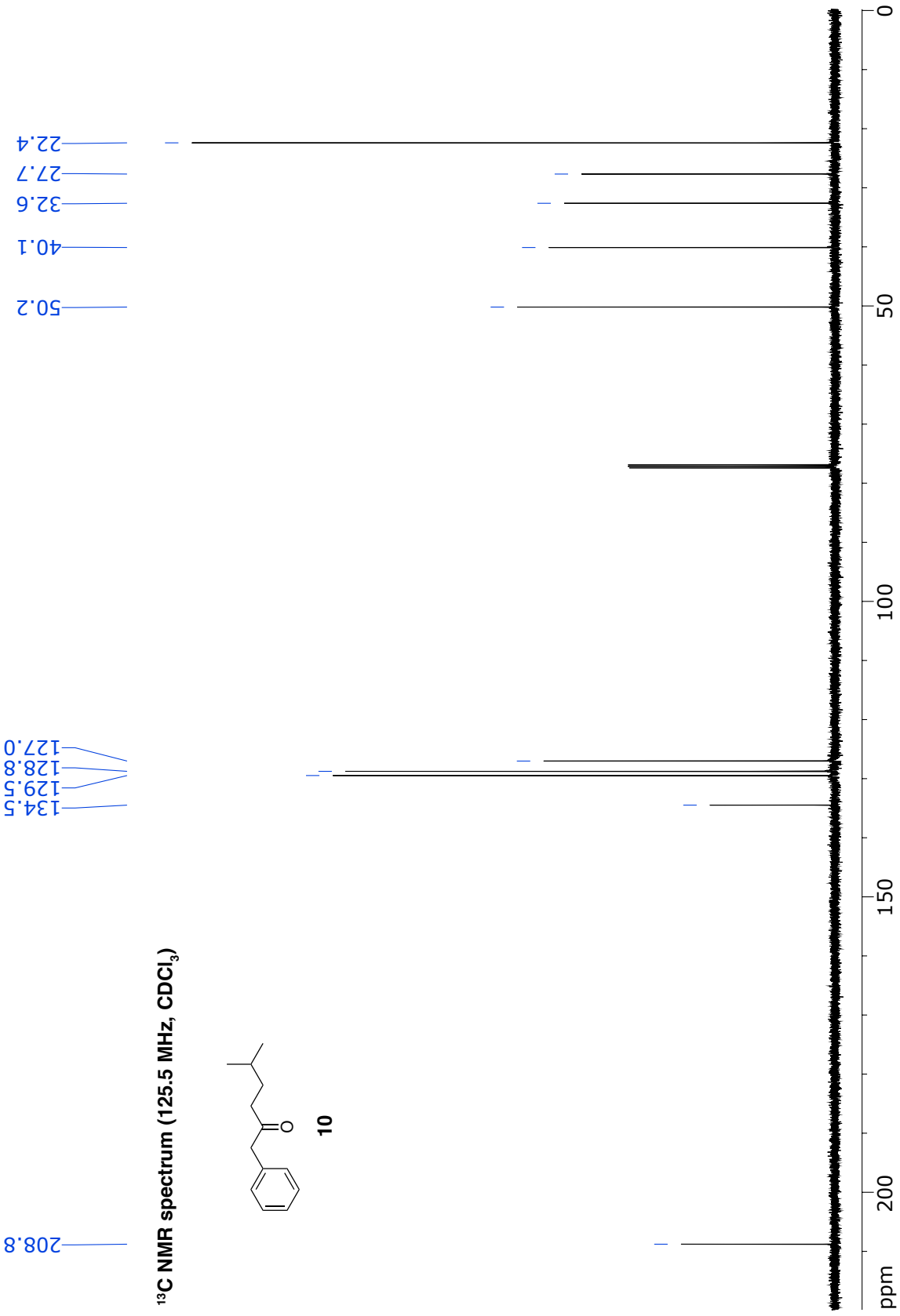
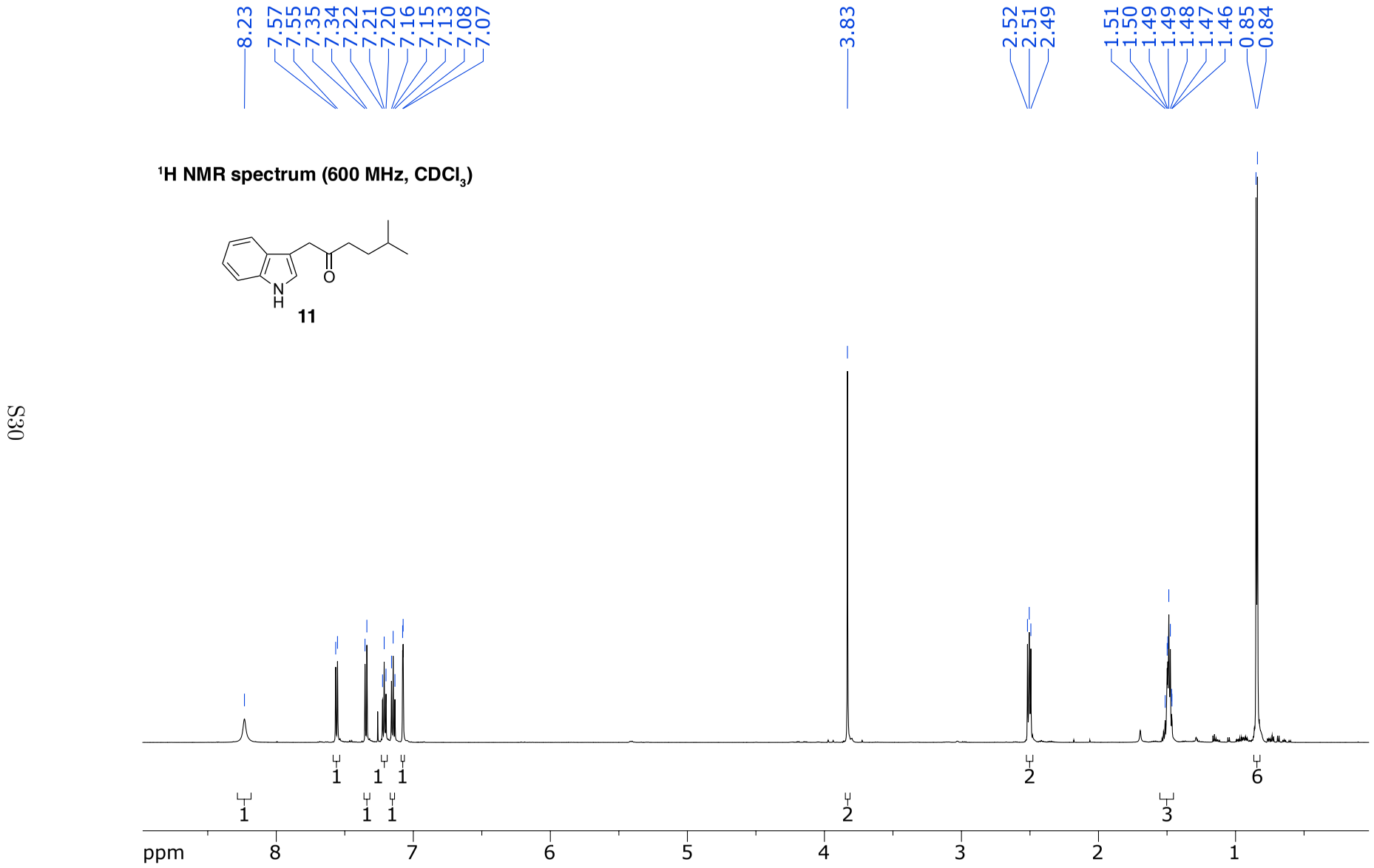
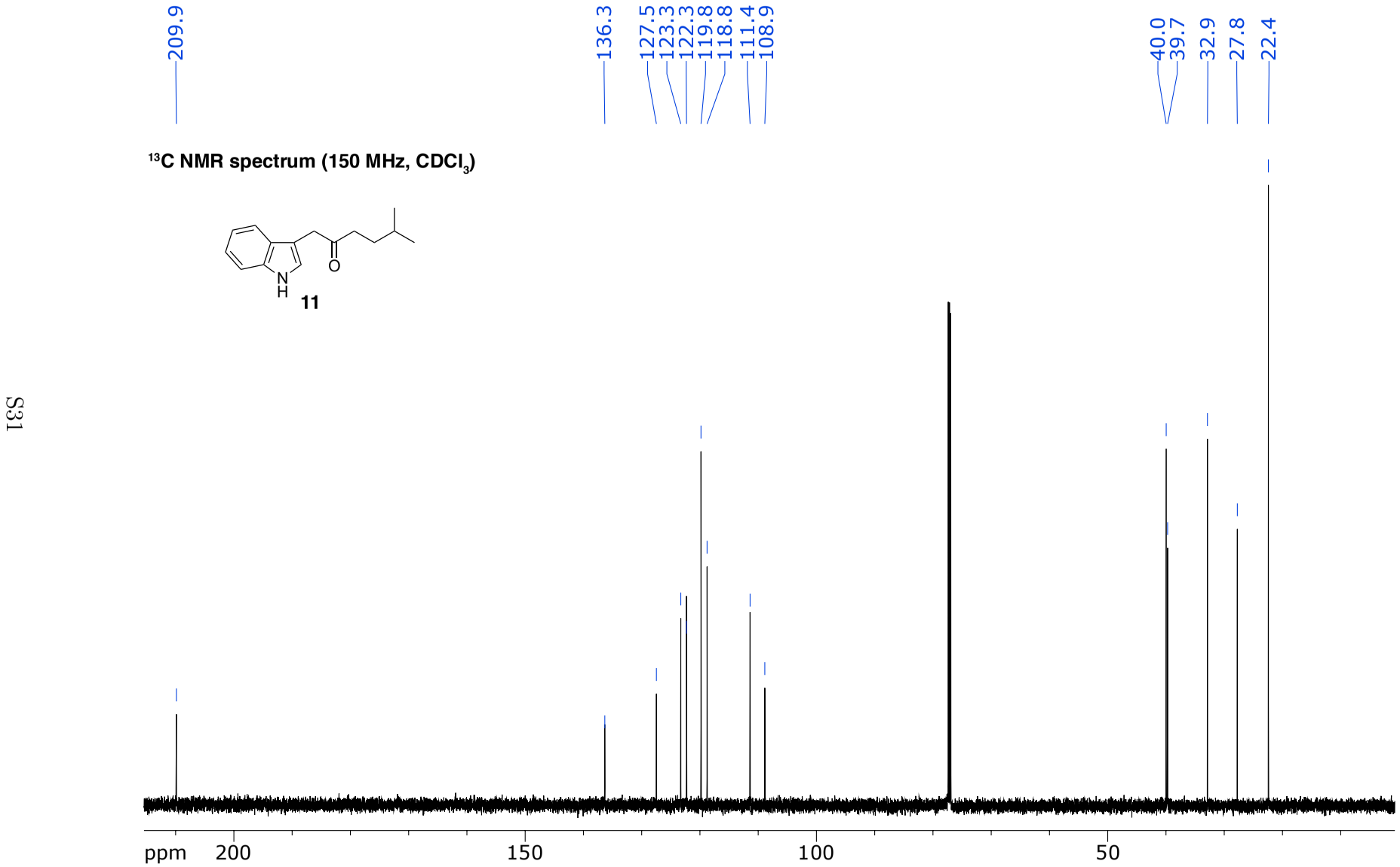
7.35
7.33
7.32
7.28
7.28
7.27
7.25
7.22
7.22
7.21
3.69
2.47
2.45
2.44
1.54
1.53
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.44
1.43
1.43
0.86
0.84
¹H NMR spectrum (500 MHz, CDCl3)
O
10
1
2
3
2 2
2
6
ppm
8
6
4
2
0

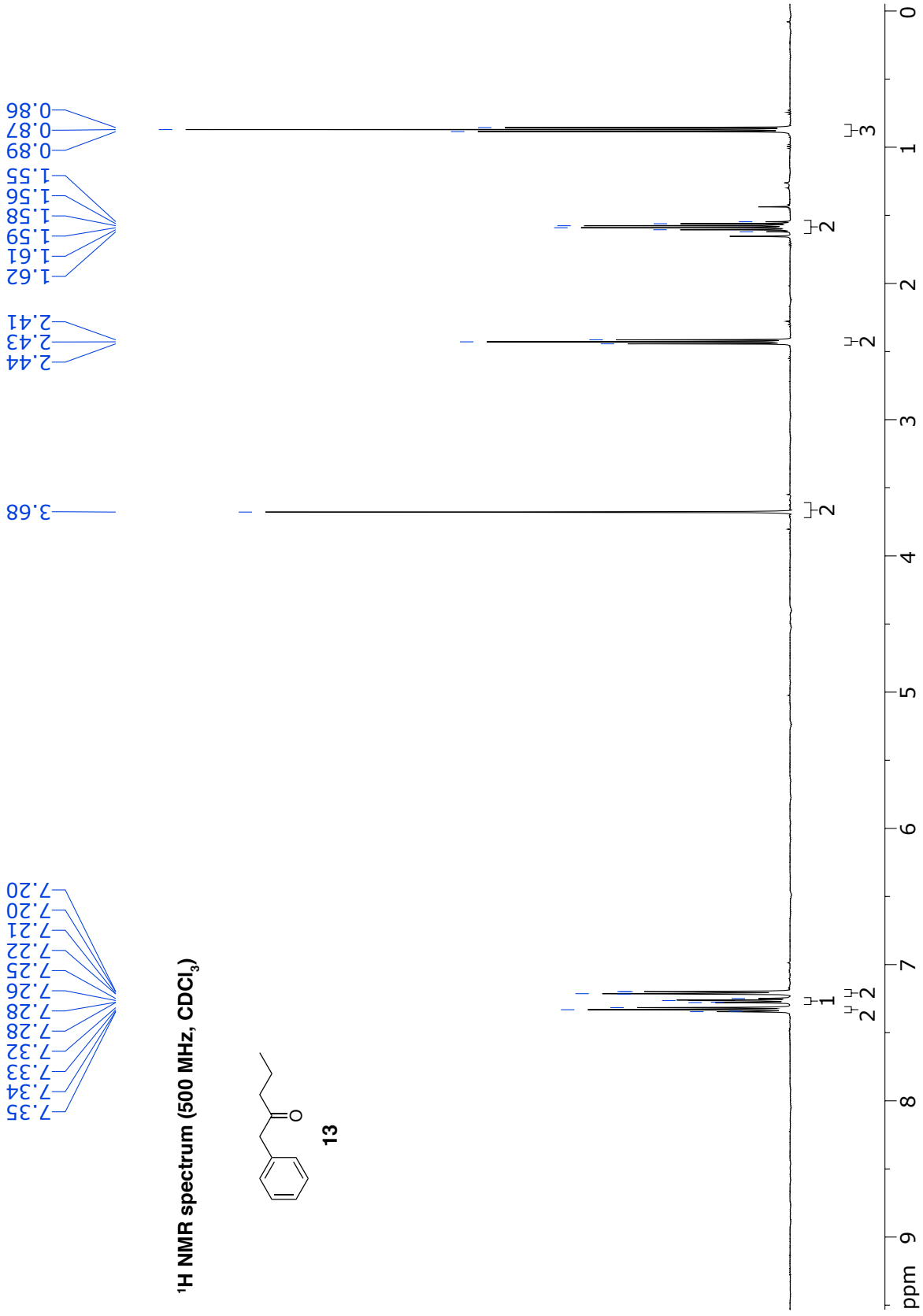

^{13}C NMR spectrum (125.5 MHz, $CDCl_3$)
10
208.8
134.5
129.5
128.8
127.0
50.2
40.1
32.6
27.7
22.4
ppm
0
50
100
150
200

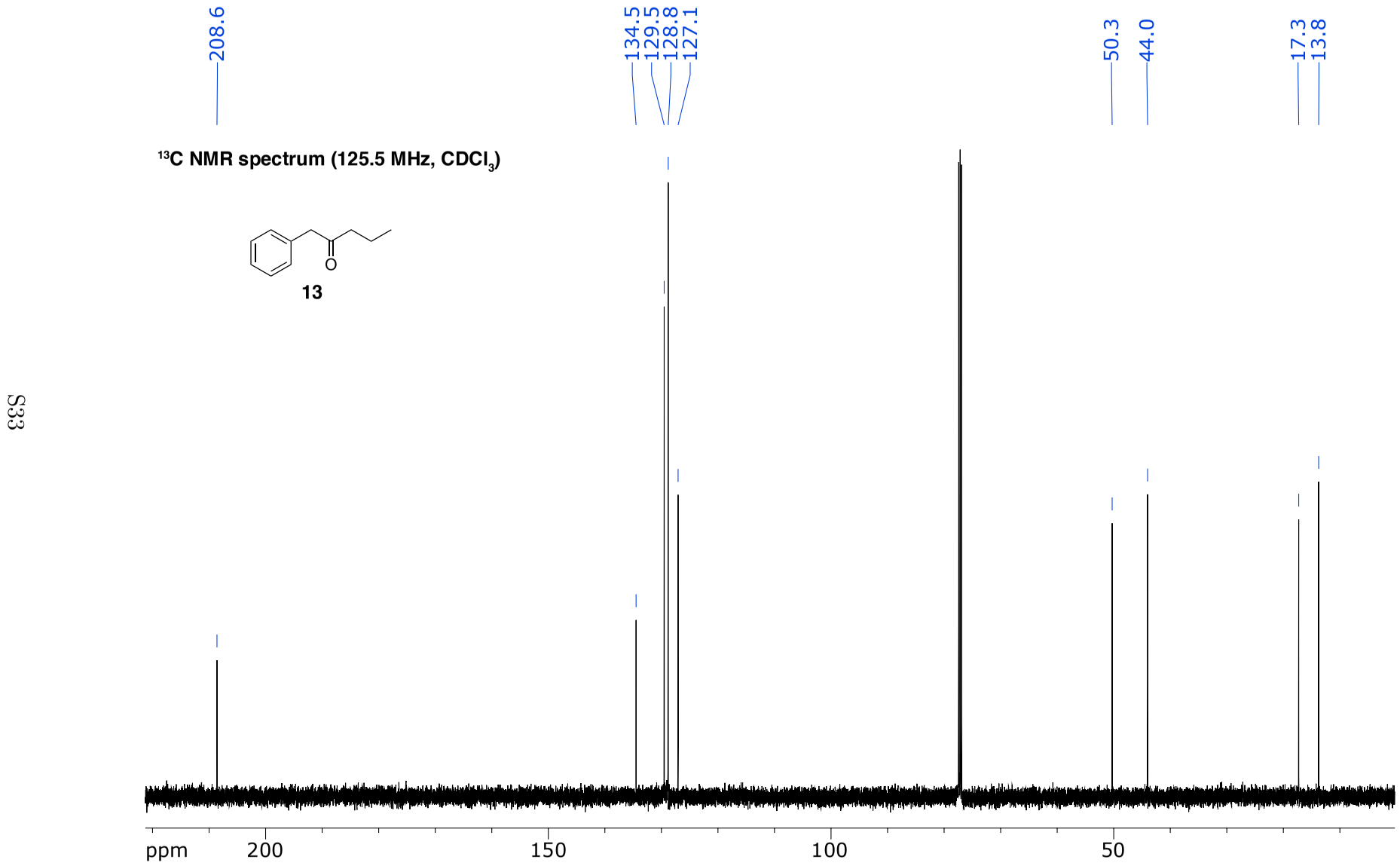

8.23
7.57
7.55
7.35
7.34
7.22
7.21
7.20
7.16
7.15
7.13
7.08
7.07
3.83
2.52
2.51
2.49
1.51
1.50
1.49
1.49
1.48
1.47
1.46
0.85
0.84
¹H NMR spectrum (600 MHz, CDCl3)
N
H
O
11
1
1
1
1
1
1
2
2
6
3
ppm
8
7
6
5
4
3
2
1

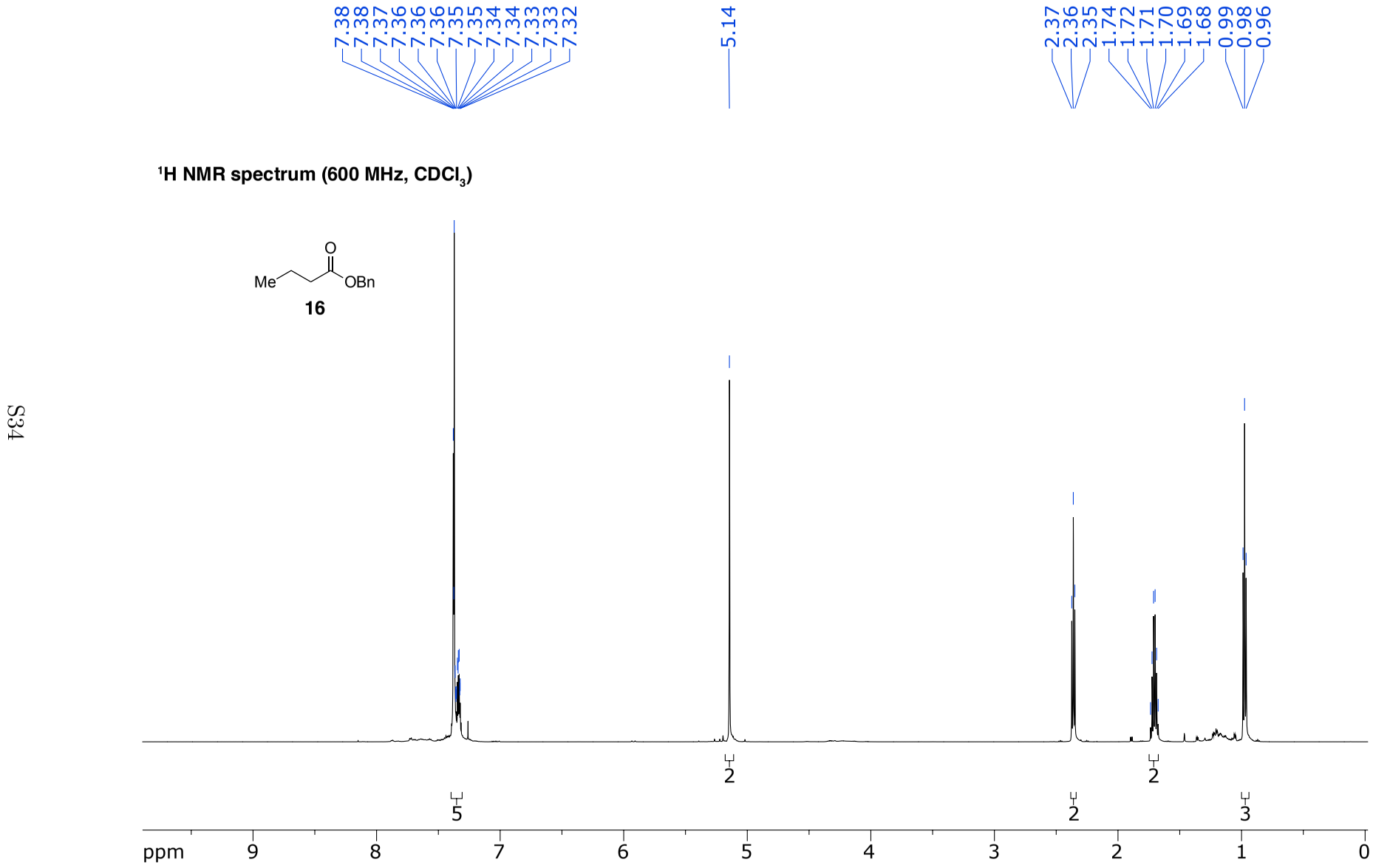


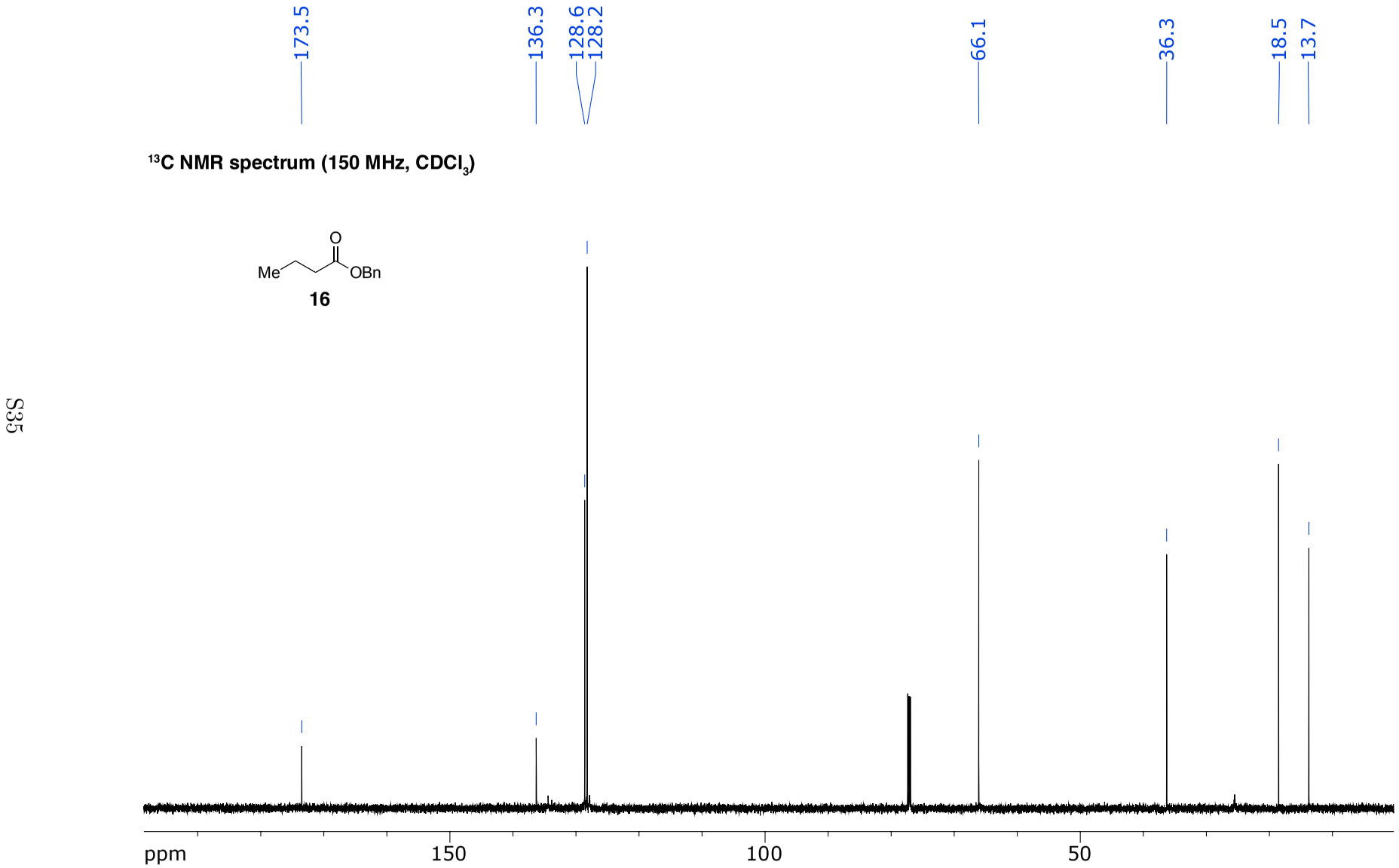
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

11

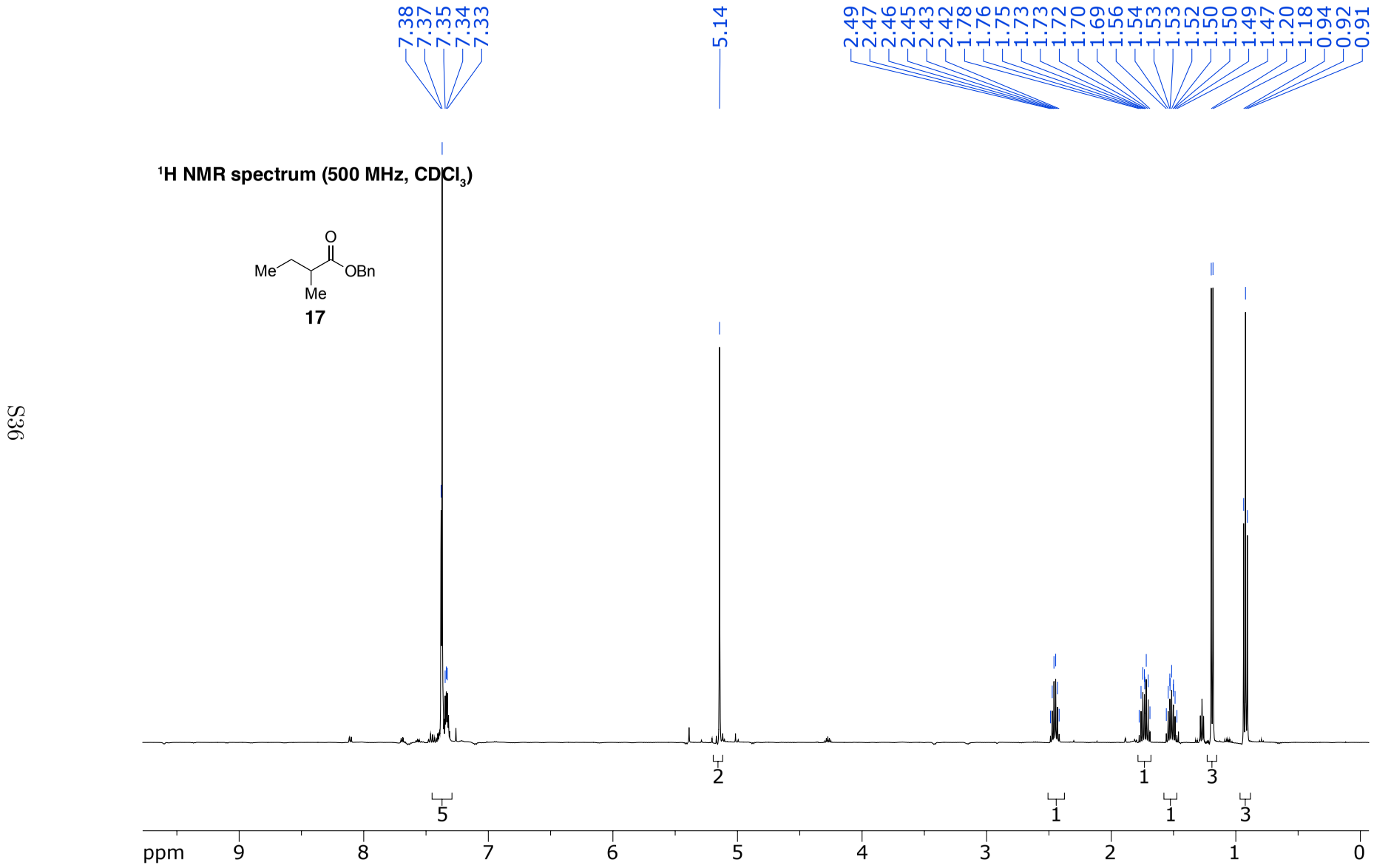

0.86
0.87
0.89
1.55
1.56
1.58
1.59
1.61
1.62
2.41
2.43
2.44
3.68
7.20
7.20
7.21
7.22
7.25
7.26
7.28
7.28
7.32
7.33
7.34
7.35
ppm
0
1
2
3
4
5
6
7
8
9
2
2
1
2
2
3
13
O
1H NMR spectrum (500 MHz, CDCl3)

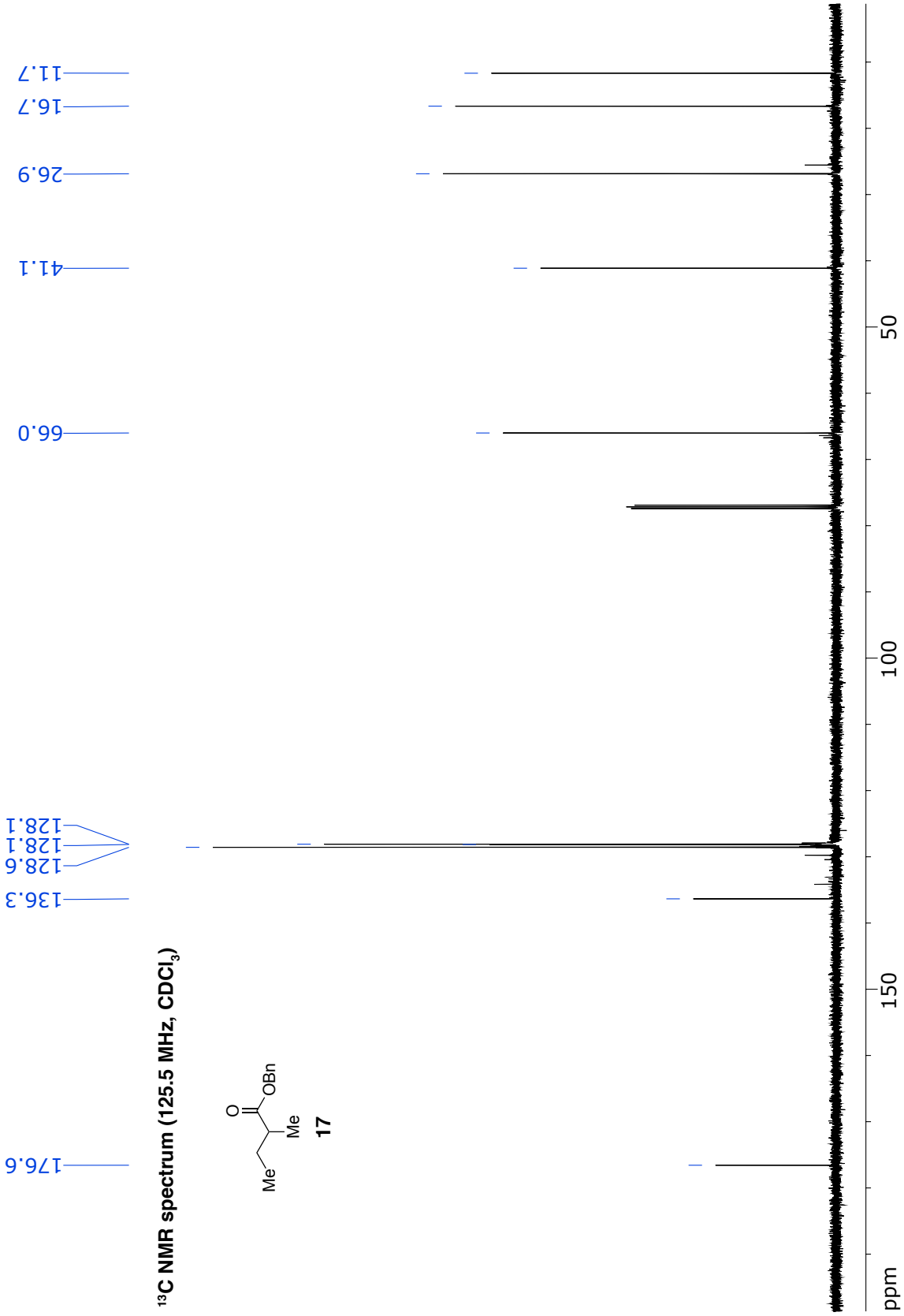

208.6
134.5
129.5
128.8
127.1
50.3
44.0
17.3
13.8
13C NMR spectrum (125.5 MHz, CDCl3)
O
13
ppm
200
150
100
50

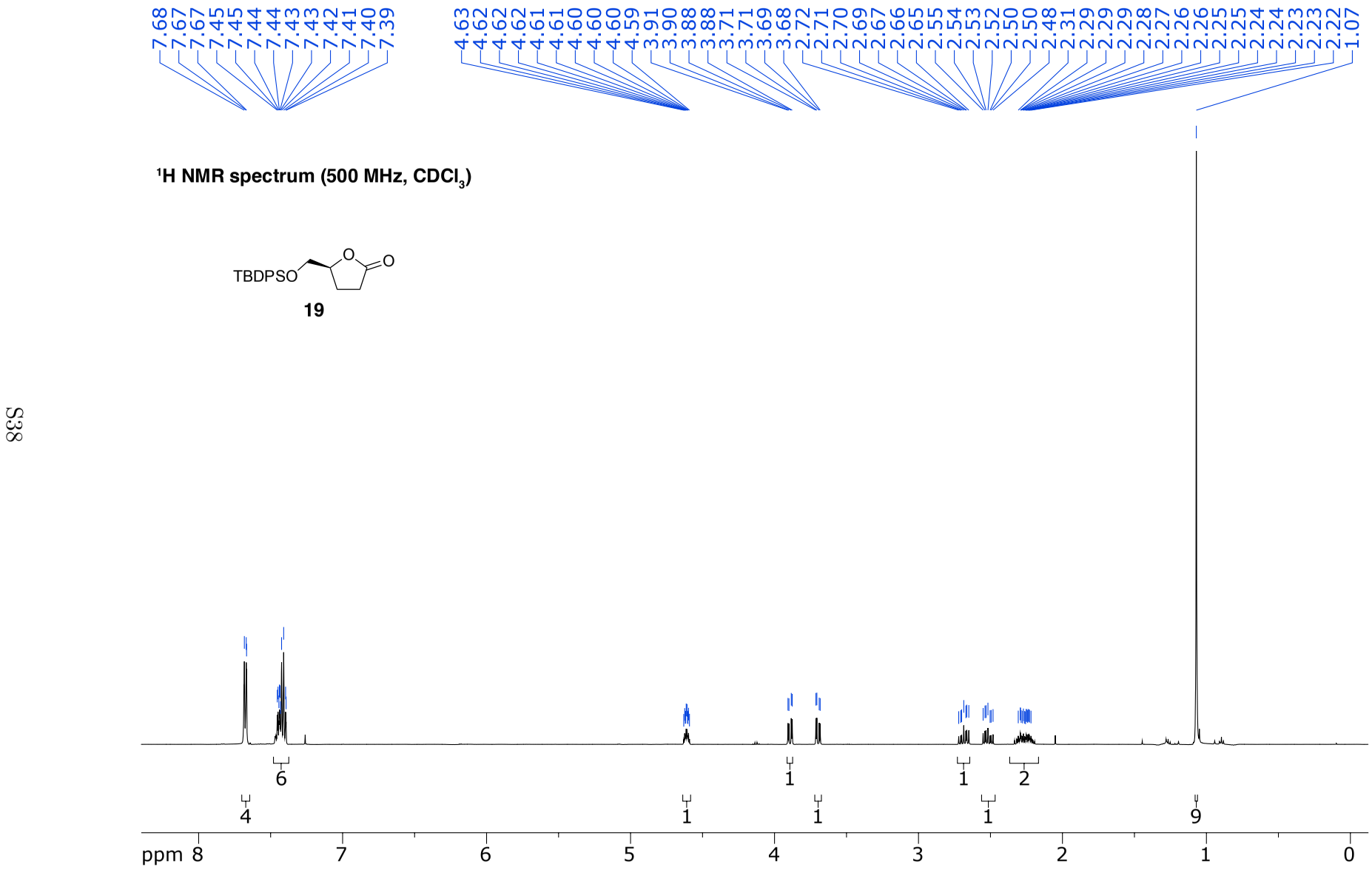

7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
5.14
2.37
2.36
2.35
1.74
1.72
1.71
1.70
1.69
1.68
0.99
0.98
0.96
¹H NMR spectrum (600 MHz, CDCl3)
O
Me
OBn
16
2
2
5
2
3
ppm
9
8
7
6
5
4
3
2
1
0

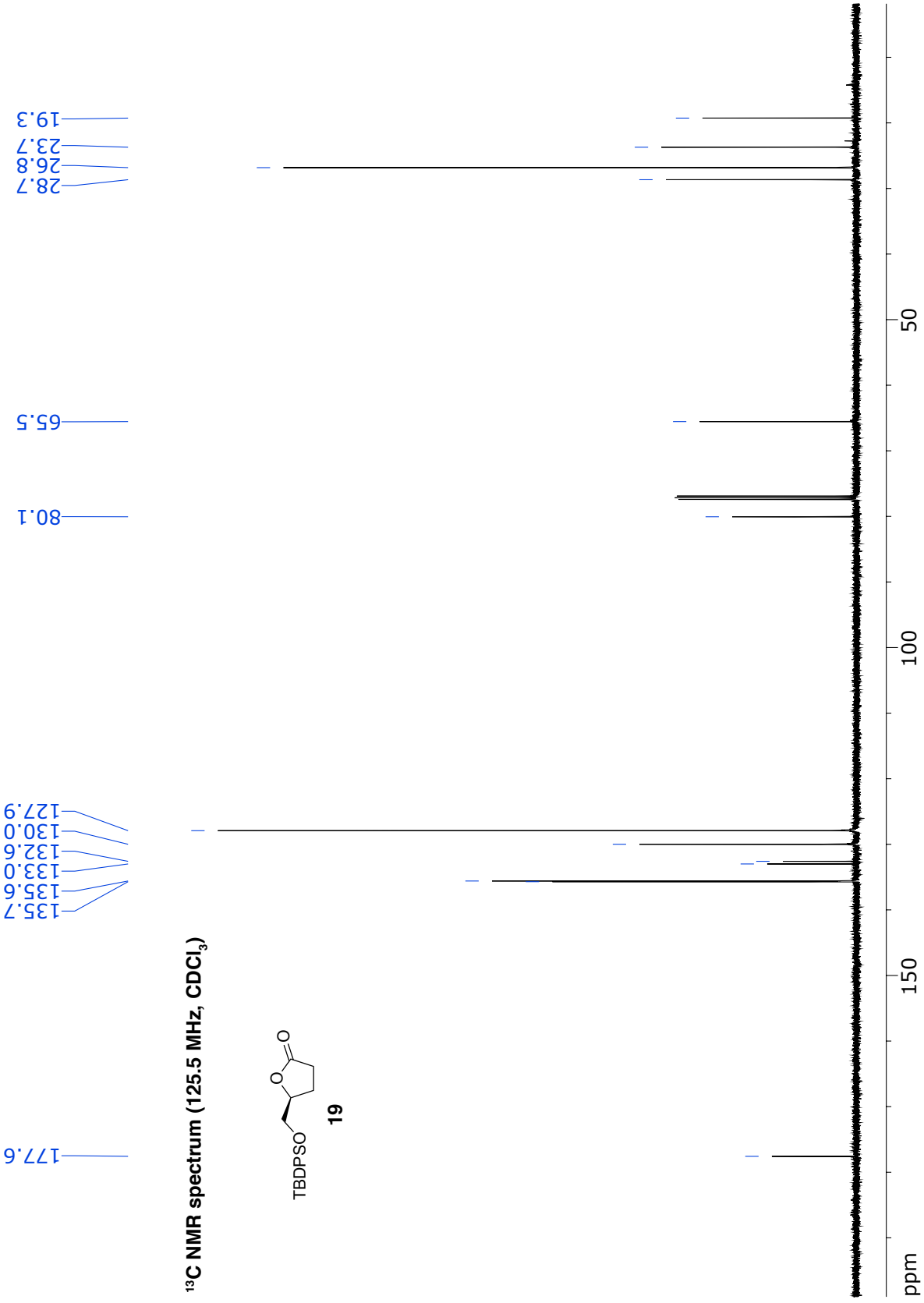


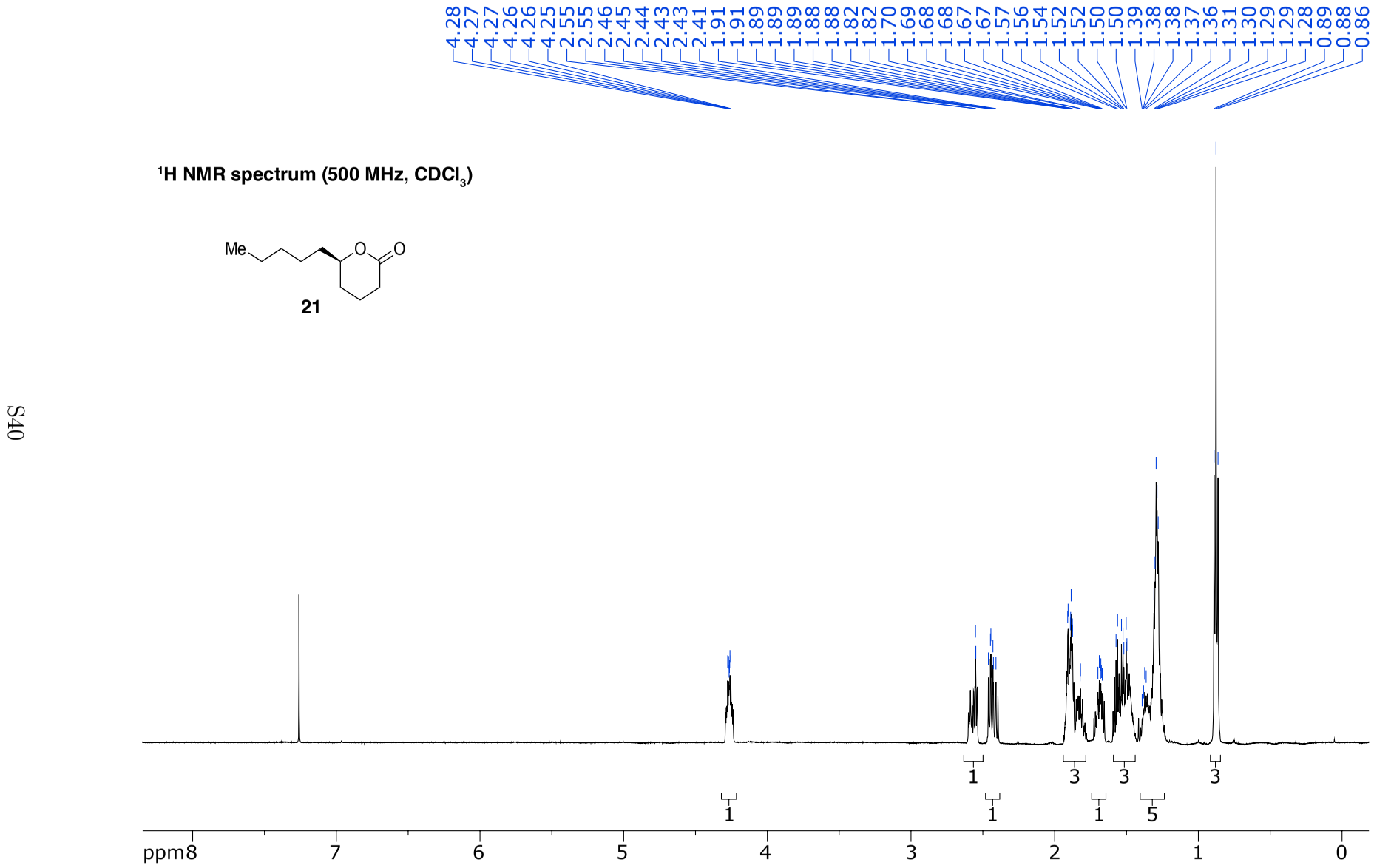
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

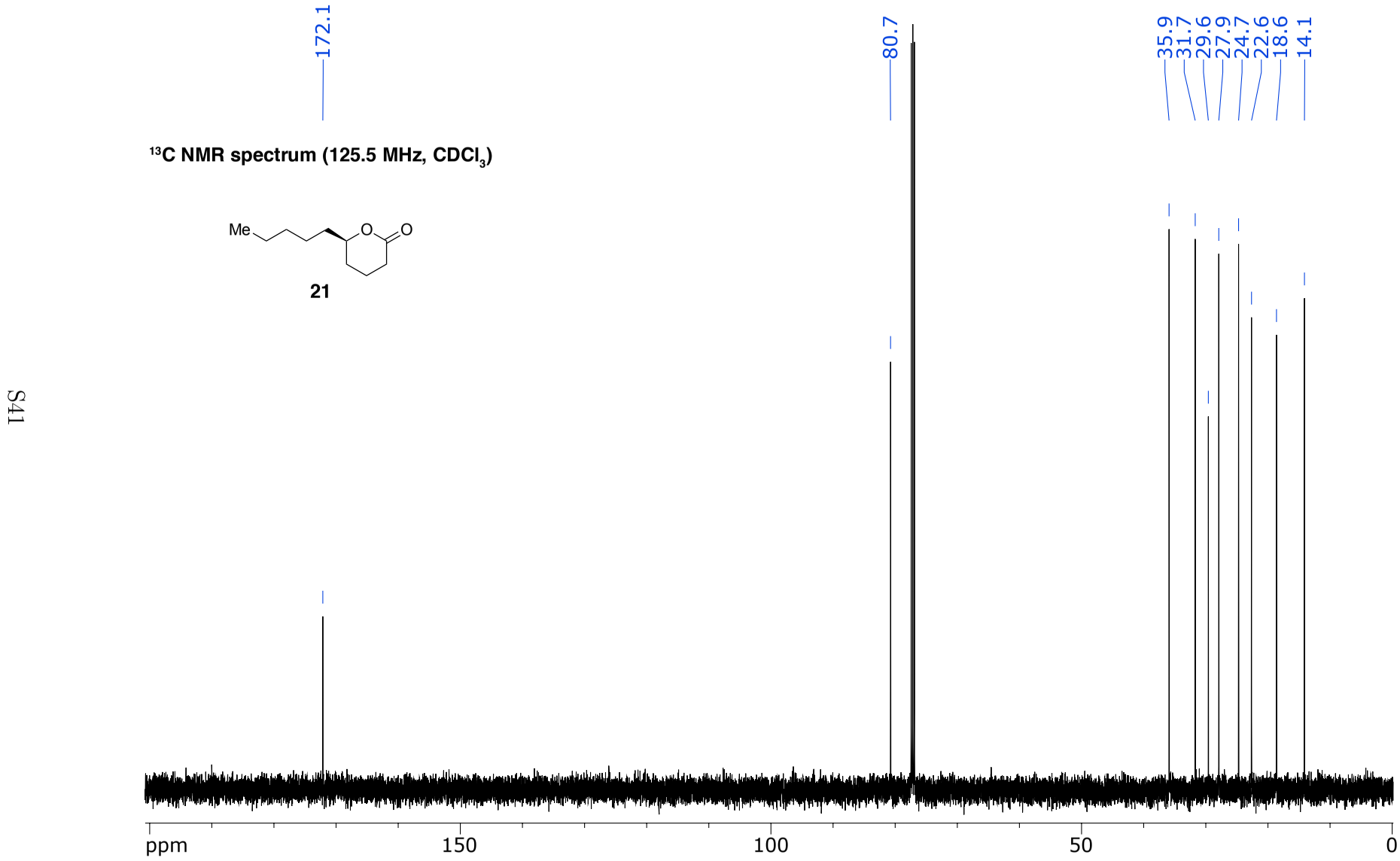

7.38
7.37
7.35
7.34
7.33
5.14
2.49
2.47
2.46
2.45
2.43
2.42
1.78
1.76
1.75
1.73
1.73
1.72
1.70
1.69
1.56
1.54
1.53
1.53
1.52
1.50
1.50
1.49
1.47
1.20
1.18
0.94
0.92
0.91
¹H NMR spectrum (500 MHz, CDCl3)
O
Me
OBn
Me
17
2
1
3
5
1
1
3
ppm
9
8
7
6
5
4
3
2
1
0

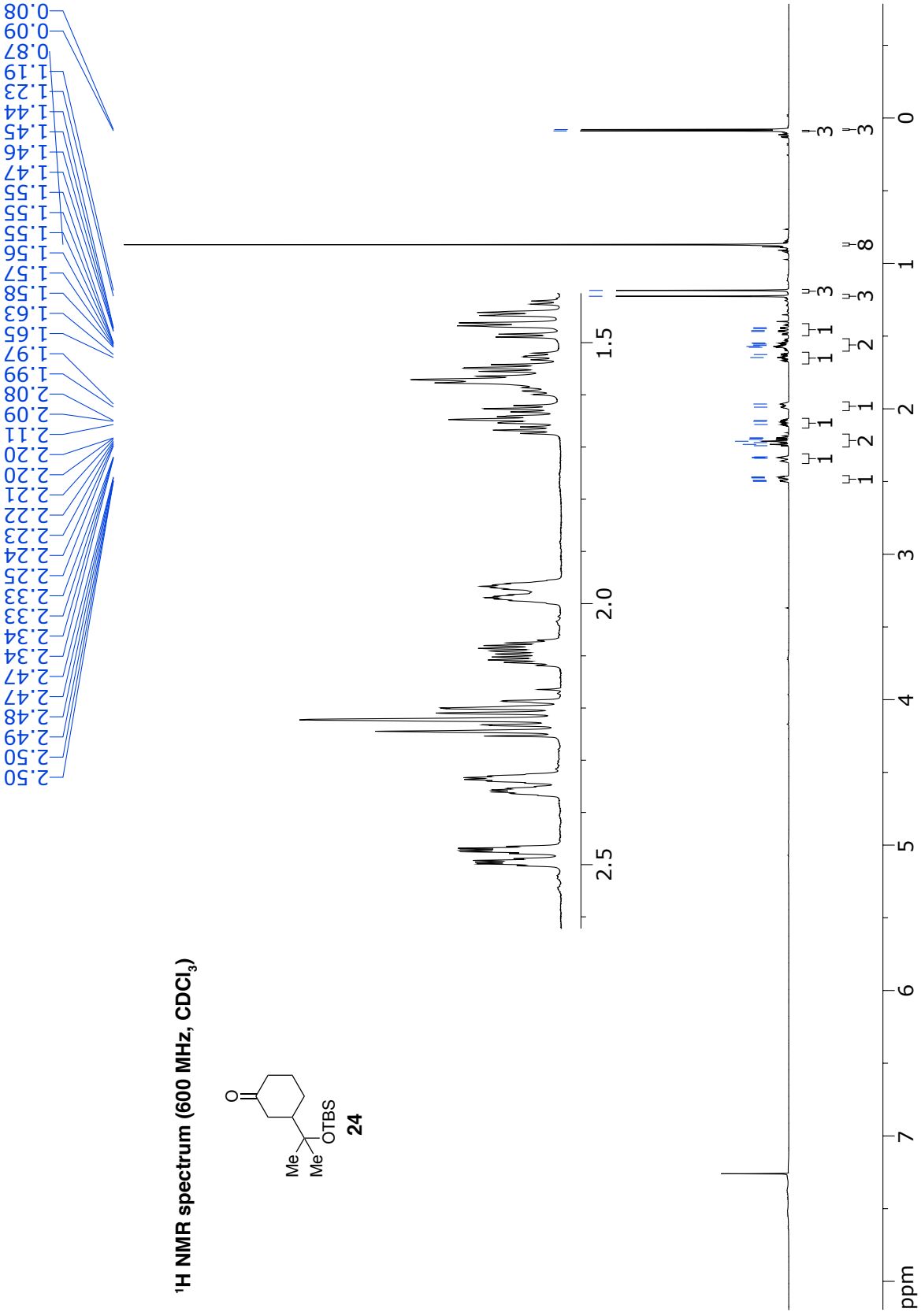

11.7
16.7
26.9
41.1
66.0
128.1
128.1
128.6
136.3
176.6
^{13}C NMR spectrum (125.5 MHz, $CDCl_3$)
O
OBn
Me
Me
17
50
100
150
ppm

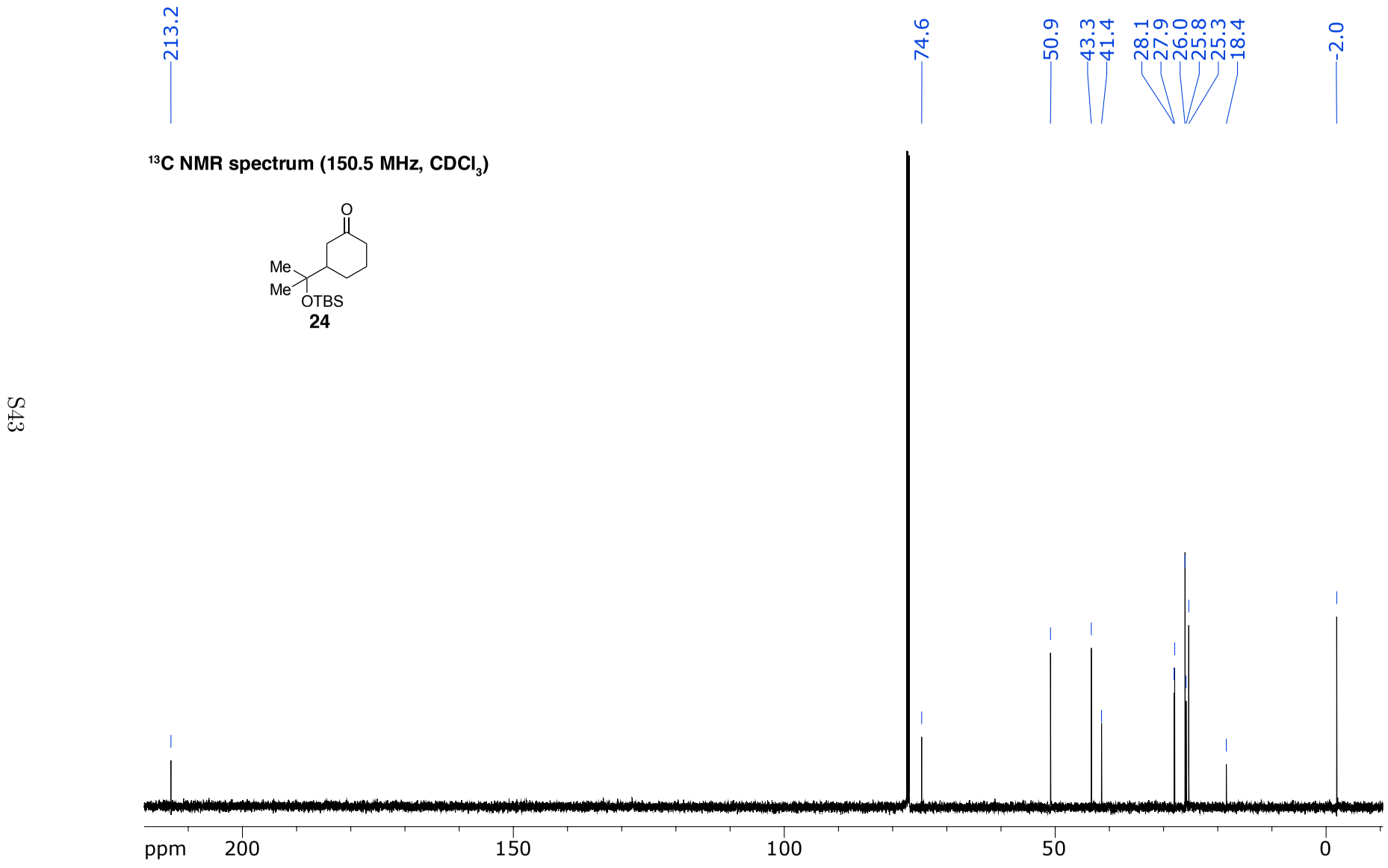

7.68
7.67
7.67
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.39
4.63
4.62
4.62
4.62
4.61
4.61
4.60
4.60
4.60
4.59
3.91
3.90
3.88
3.88
3.71
3.71
3.69
3.68
2.72
2.71
2.70
2.69
2.67
2.66
2.65
2.55
2.54
2.53
2.52
2.50
2.50
2.48
2.31
2.29
2.29
2.29
2.28
2.27
2.26
2.26
2.25
2.24
2.24
2.23
2.23
2.22
1.07
¹H NMR spectrum (500 MHz, CDCl3)
TBDPSO
O
O
19
6
1
1
2
4
1
1
1
9
ppm 8
7
6
5
4
3
2
1
0


^{13}C NMR spectrum (125.5 MHz, $CDCl_3$)
19
TBDPSO
O
O
O
177.6
135.7
135.6
133.0
132.6
130.0
127.9
80.1
65.5
28.7
26.8
23.7
19.3
ppm
150
100
50

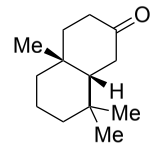

4.28
4.27
4.27
4.26
4.26
4.25
2.55
2.55
2.46
2.45
2.44
2.43
2.43
2.41
1.91
1.91
1.89
1.89
1.89
1.88
1.88
1.82
1.82
1.70
1.69
1.68
1.68
1.67
1.67
1.57
1.56
1.54
1.52
1.52
1.50
1.50
1.39
1.38
1.38
1.37
1.36
1.31
1.30
1.29
1.29
1.28
0.89
0.88
0.86
1H NMR spectrum (500 MHz, CDCl3)
Me
O
O
21
1
1
3
3
3
1
1
1
5
ppm8
7
6
5
4
3
2
1
0


172.1
80.7
35.9
31.7
29.6
27.9
24.7
22.6
18.6
14.1
^{13}C NMR spectrum (125.5 MHz, $CDCl_3$)
Me
O
O
21
ppm
150
100
50
0

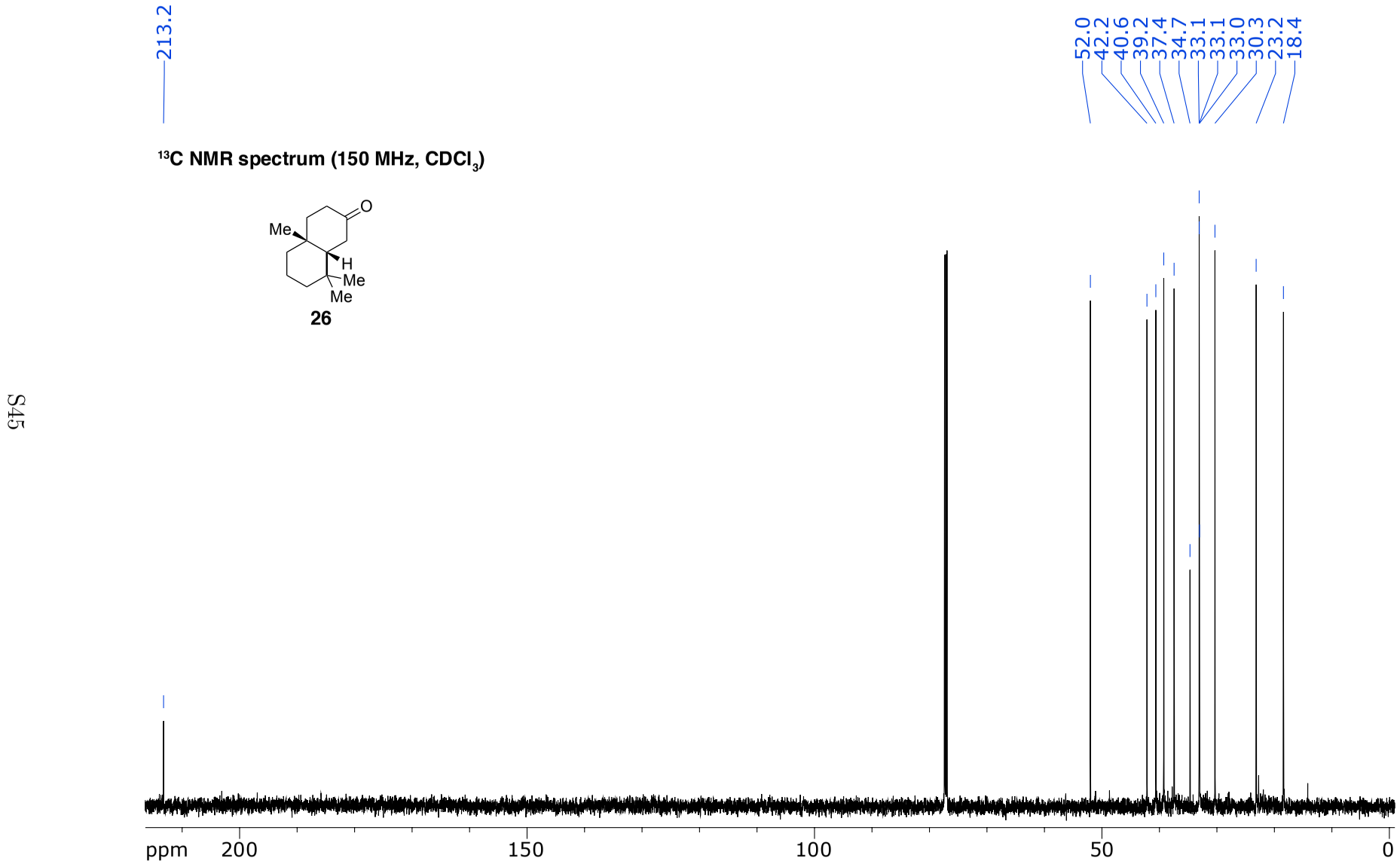

0.08
0.09
0.87
1.19
1.23
1.44
1.45
1.46
1.47
1.55
1.55
1.55
1.56
1.57
1.58
1.63
1.65
1.97
1.99
2.08
2.09
2.11
2.20
2.20
2.21
2.22
2.23
2.24
2.25
2.33
2.33
2.34
2.34
2.47
2.47
2.48
2.49
2.50
2.50
1H NMR spectrum (600 MHz, CDCl3)
O
Me
Me
OTBS
24
ppm


213.2
74.6
50.9
43.3
41.4
28.1
27.9
26.0
25.8
25.3
18.4
-2.0
^{13}C NMR spectrum (150.5 MHz, $CDCl_3$)
O
Me
Me
OTBS
24
ppm
200
150
100
50
0

^{1}H NMR spectrum (600 MHz, $CDCl_3$)

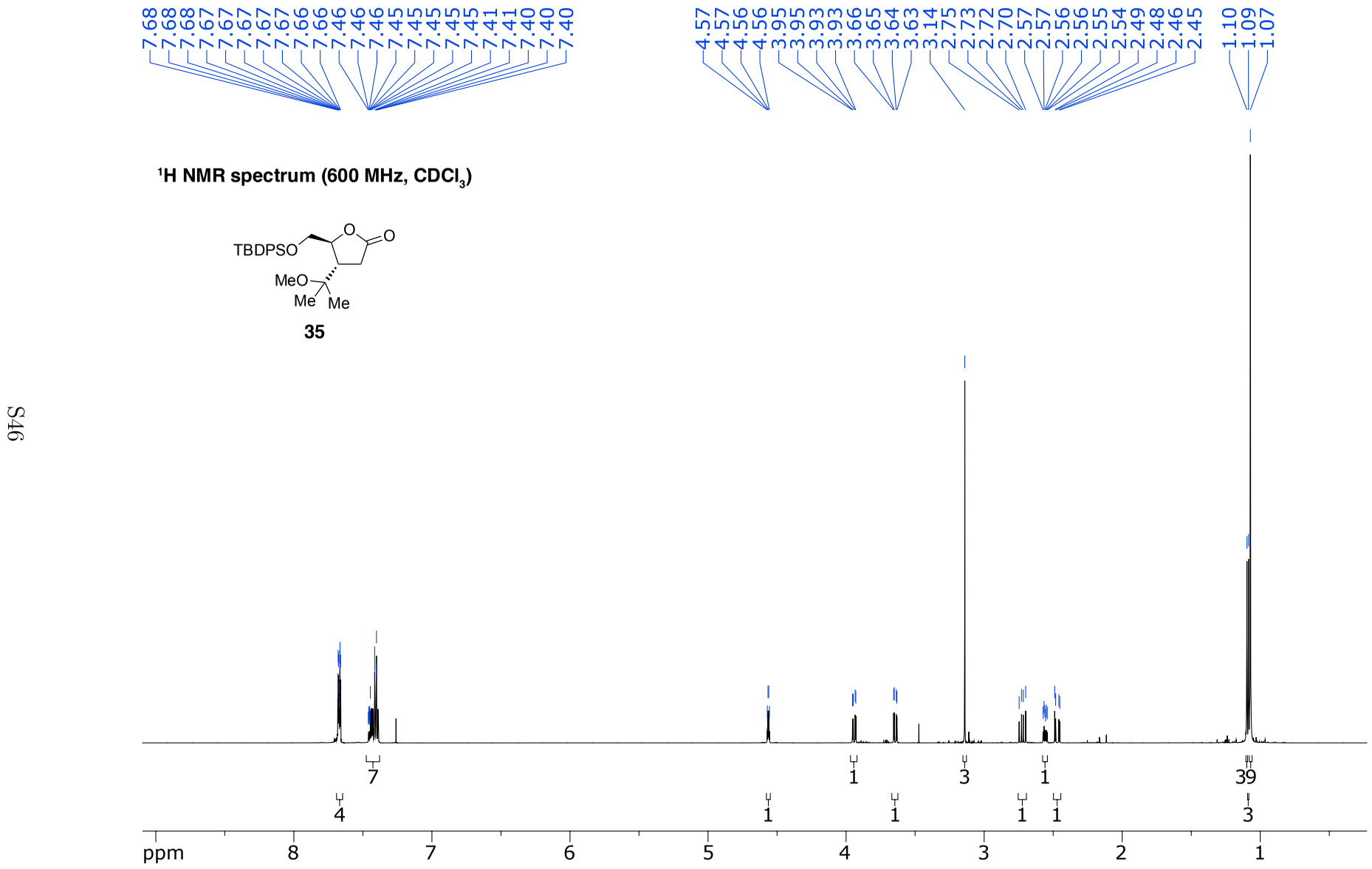


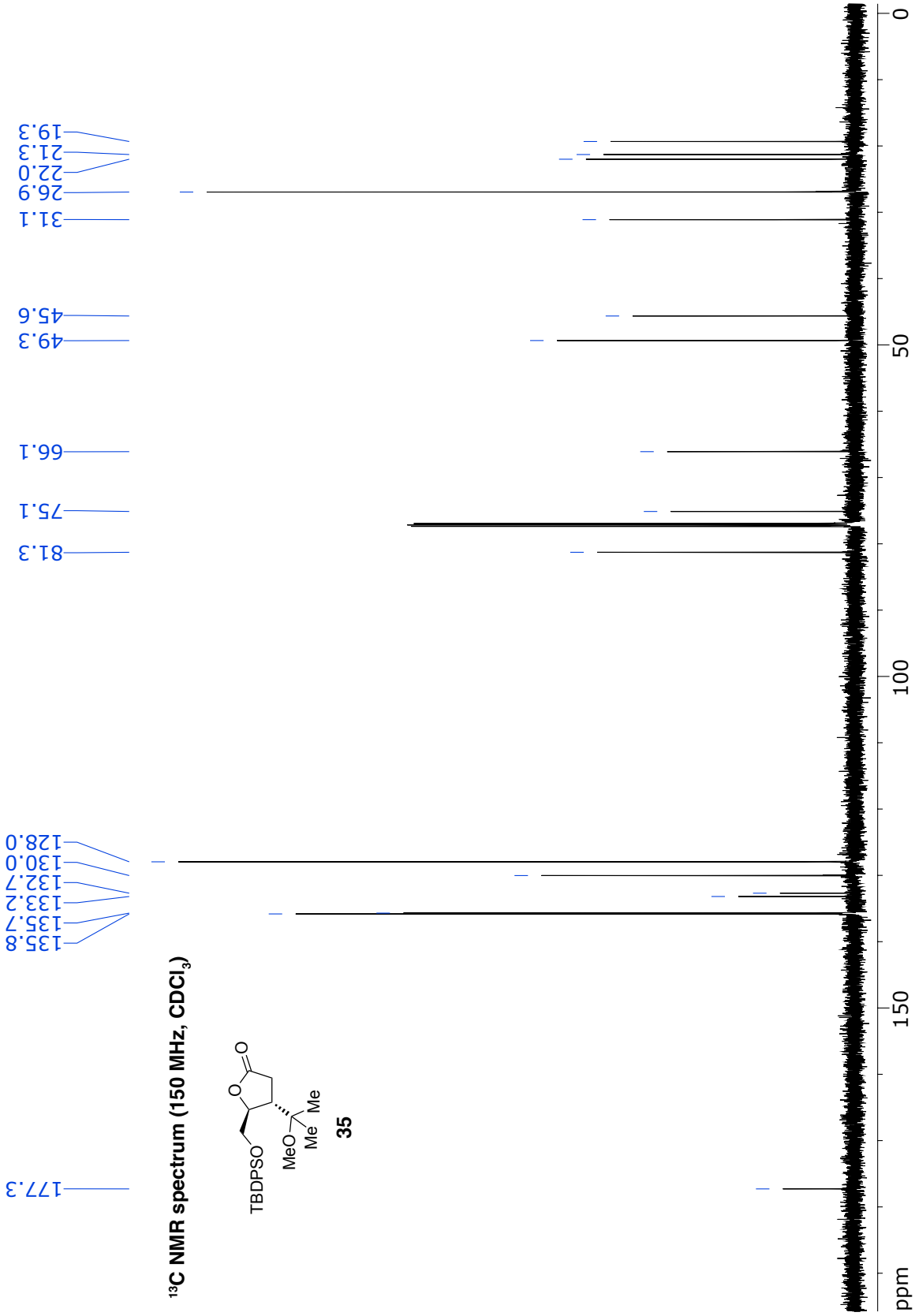
26

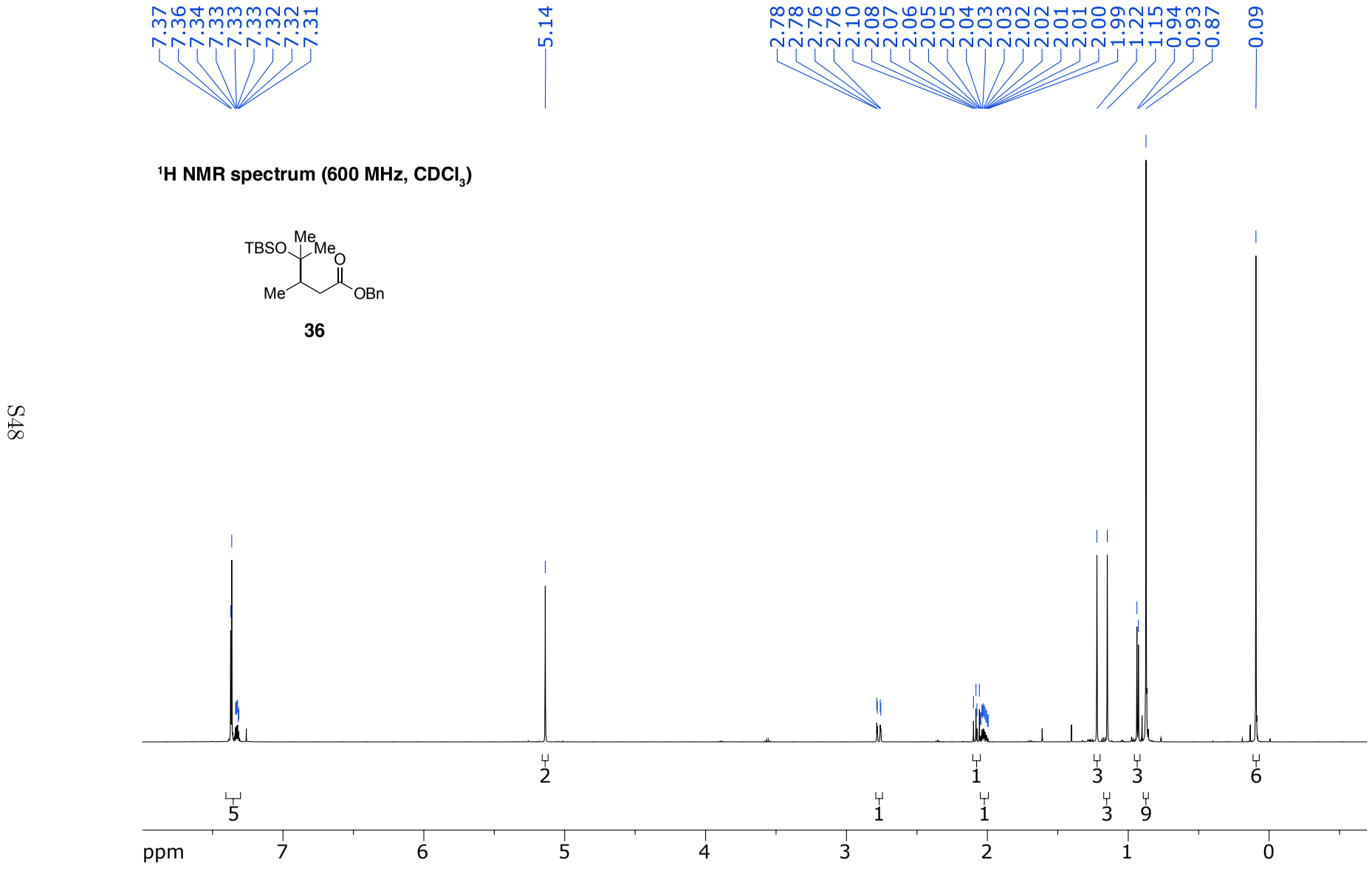


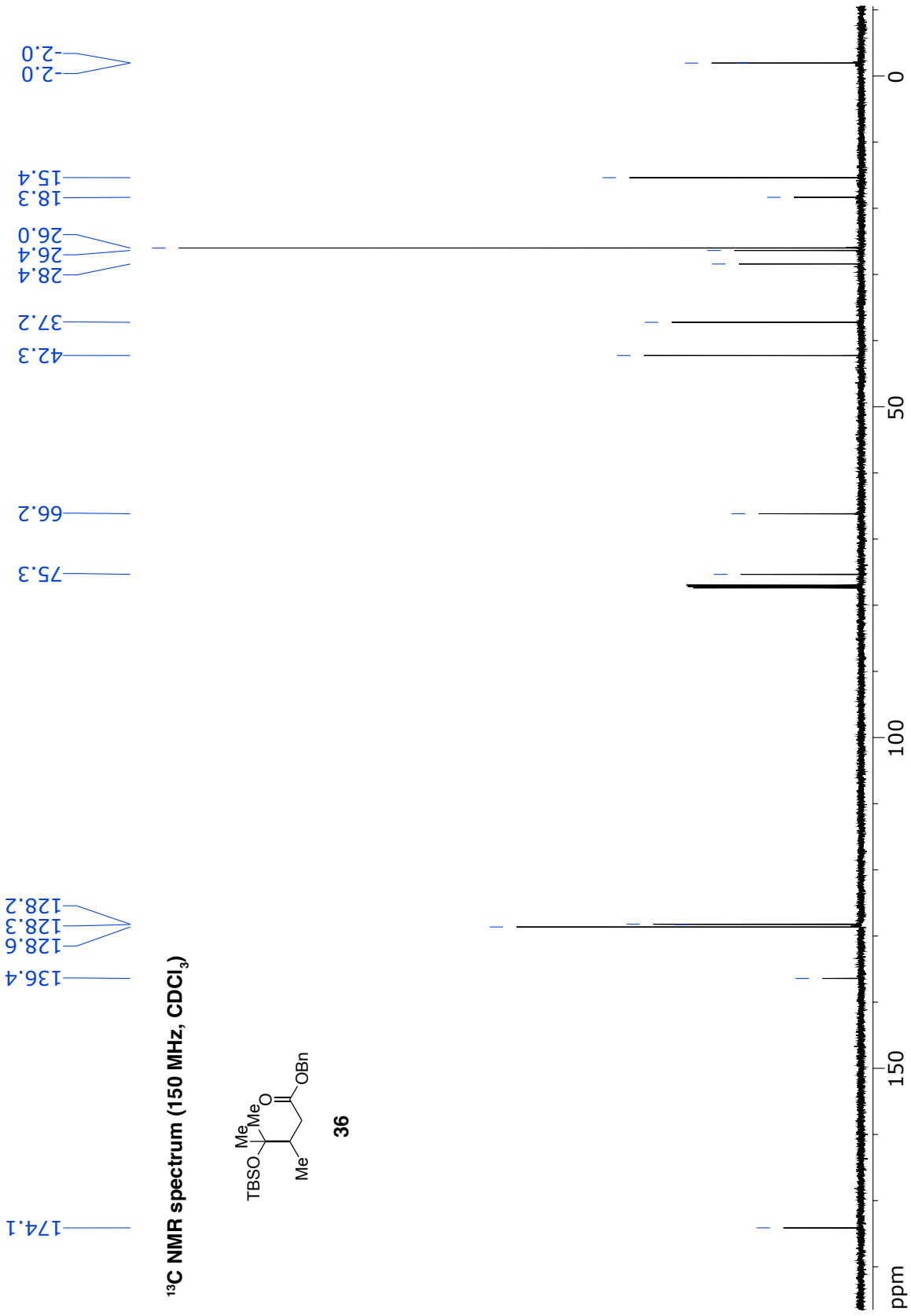
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

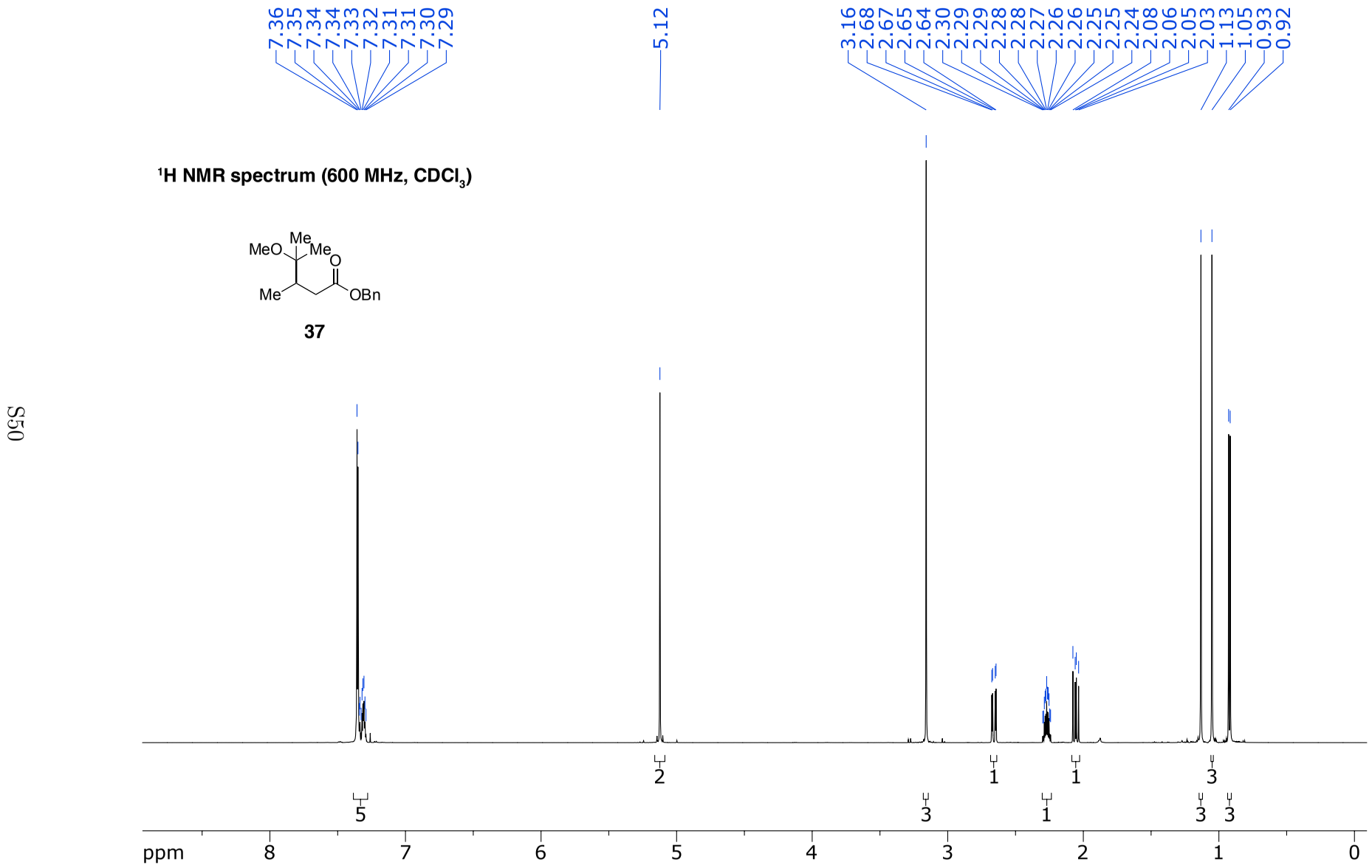
26

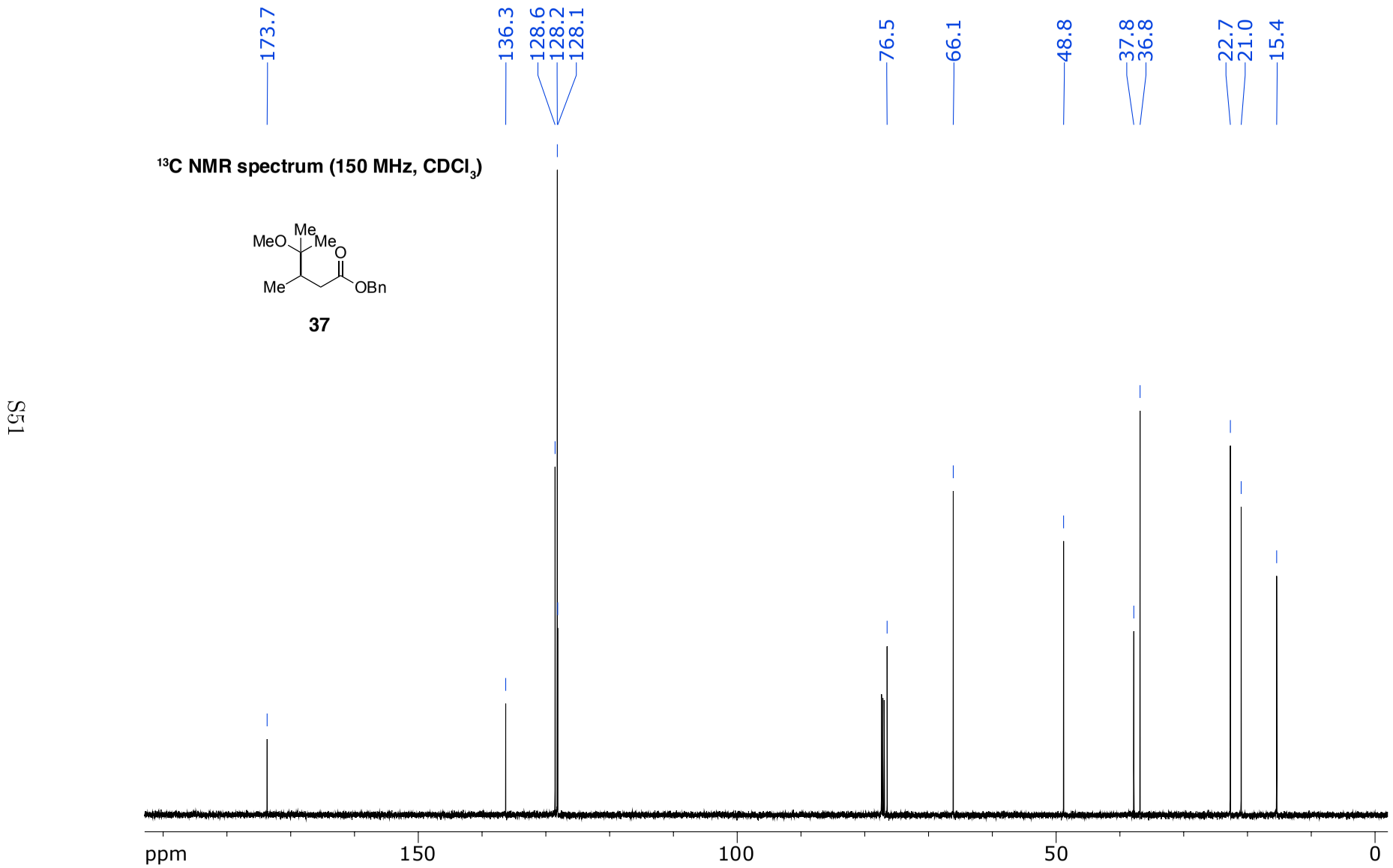

7.68
7.68
7.68
7.67
7.67
7.67
7.67
7.66
7.66
7.46
7.46
7.46
7.45
7.45
7.45
7.45
7.45
7.41
7.41
7.40
7.40
7.40
4.57
4.57
4.56
4.56
3.95
3.95
3.93
3.93
3.66
3.65
3.64
3.63
3.14
2.75
2.73
2.72
2.70
2.57
2.57
2.56
2.56
2.55
2.54
2.49
2.48
2.46
2.45
1.10
1.09
1.07
¹H NMR spectrum (600 MHz, CDCl3)
TBDPSO
O
O
MeO
Me
Me
35
7
1
3
1
39
4
1
1
1
1
3
ppm
8
7
6
5
4
3
2
1

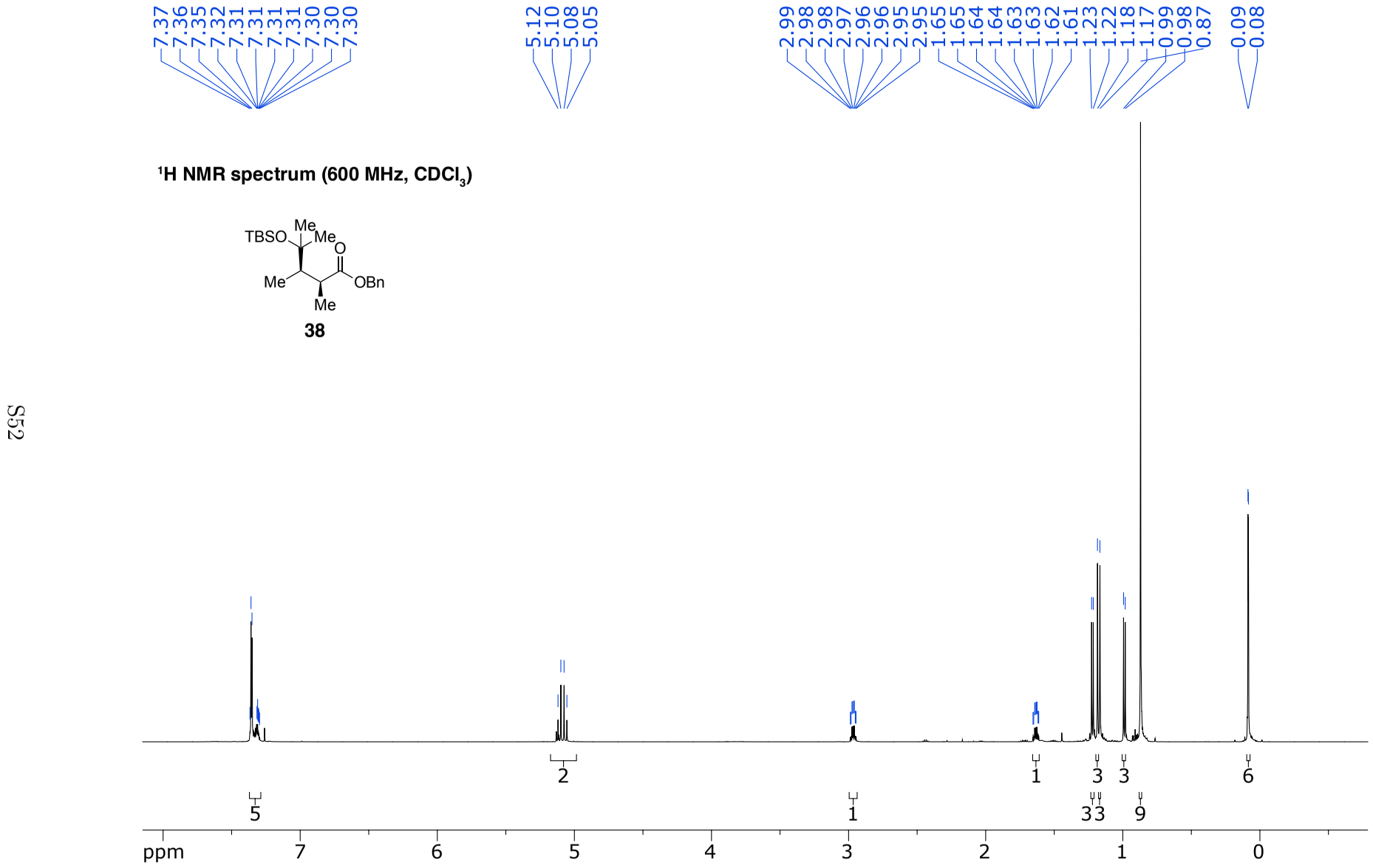

177.3
135.8
135.7
133.2
132.7
130.0
128.0
81.3
75.1
66.1
49.3
45.6
31.1
26.9
22.0
21.3
19.3
0
50
100
150
ppm
13C NMR spectrum (150 MHz, CDCl3)
TBDPSO
MeO
Me
Me
35

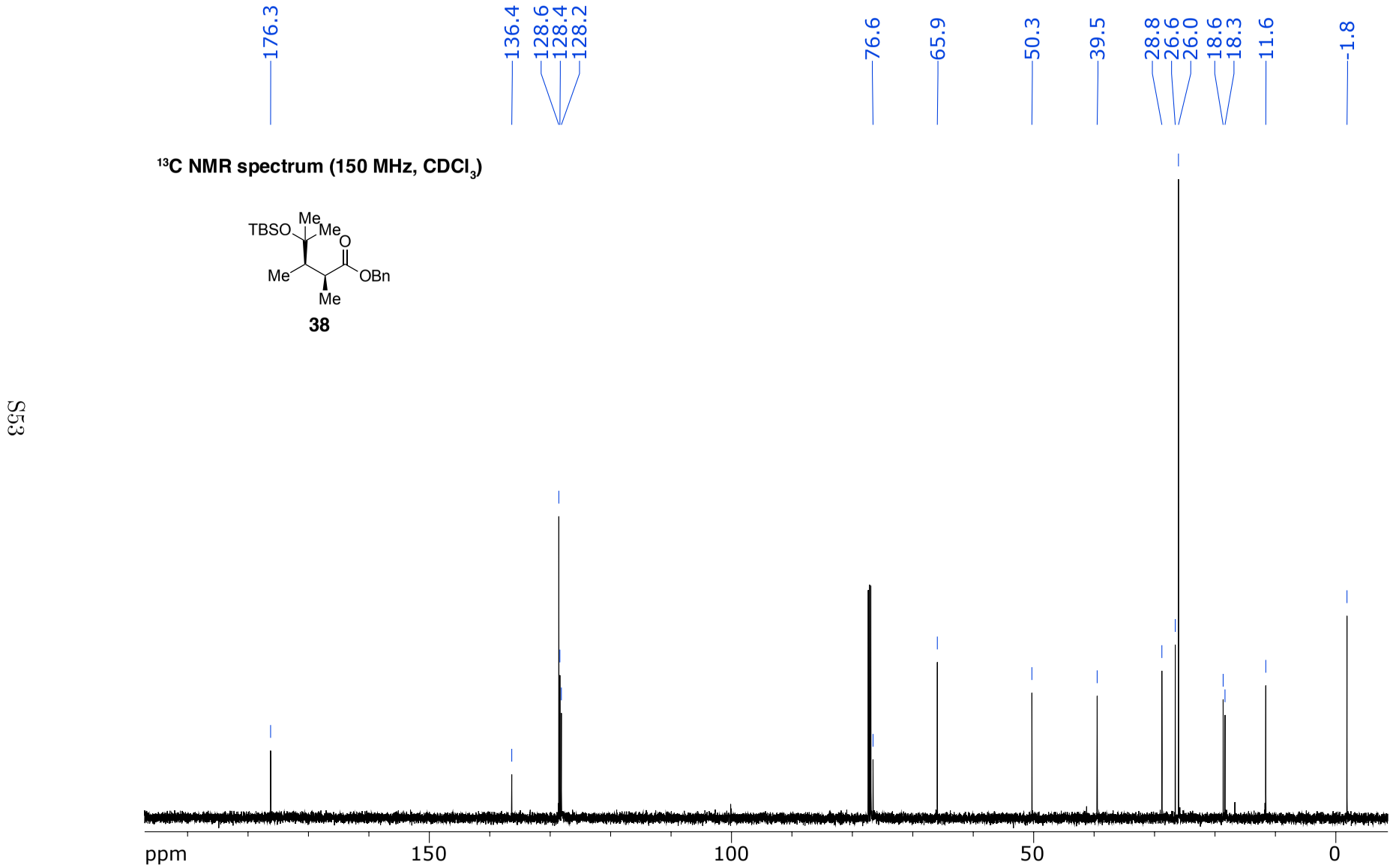

7.37
7.36
7.34
7.33
7.33
7.33
7.32
7.32
7.31
5.14
2.78
2.78
2.76
2.76
2.10
2.08
2.07
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.02
2.01
2.01
2.00
1.99
1.22
1.15
0.94
0.93
0.87
0.09
¹H NMR spectrum (600 MHz, CDCl3)
TBSO
Me
Me
O
Me
OBn
36
2
1
3
3
6
5
1
1
3
9
ppm
7
6
5
4
3
2
1
0


-2.0
-2.0
15.4
18.3
26.0
26.4
28.4
37.2
42.3
66.2
75.3
128.2
128.3
128.6
136.4
174.1
ppm
0
50
100
150
^{13}C NMR spectrum (150 MHz, $CDCl_3$)
TBSO
Me
Me
O
OBn
Me
36


7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
5.12
3.16
2.68
2.67
2.65
2.64
2.30
2.29
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.25
2.24
2.08
2.06
2.05
2.03
1.13
1.05
0.93
0.92
¹H NMR spectrum (600 MHz, CDCl3)
MeO
Me
Me
O
Me
OBn
37
2
1
1
3
5
3
1
3
3
ppm
8
7
6
5
4
3
2
1
0

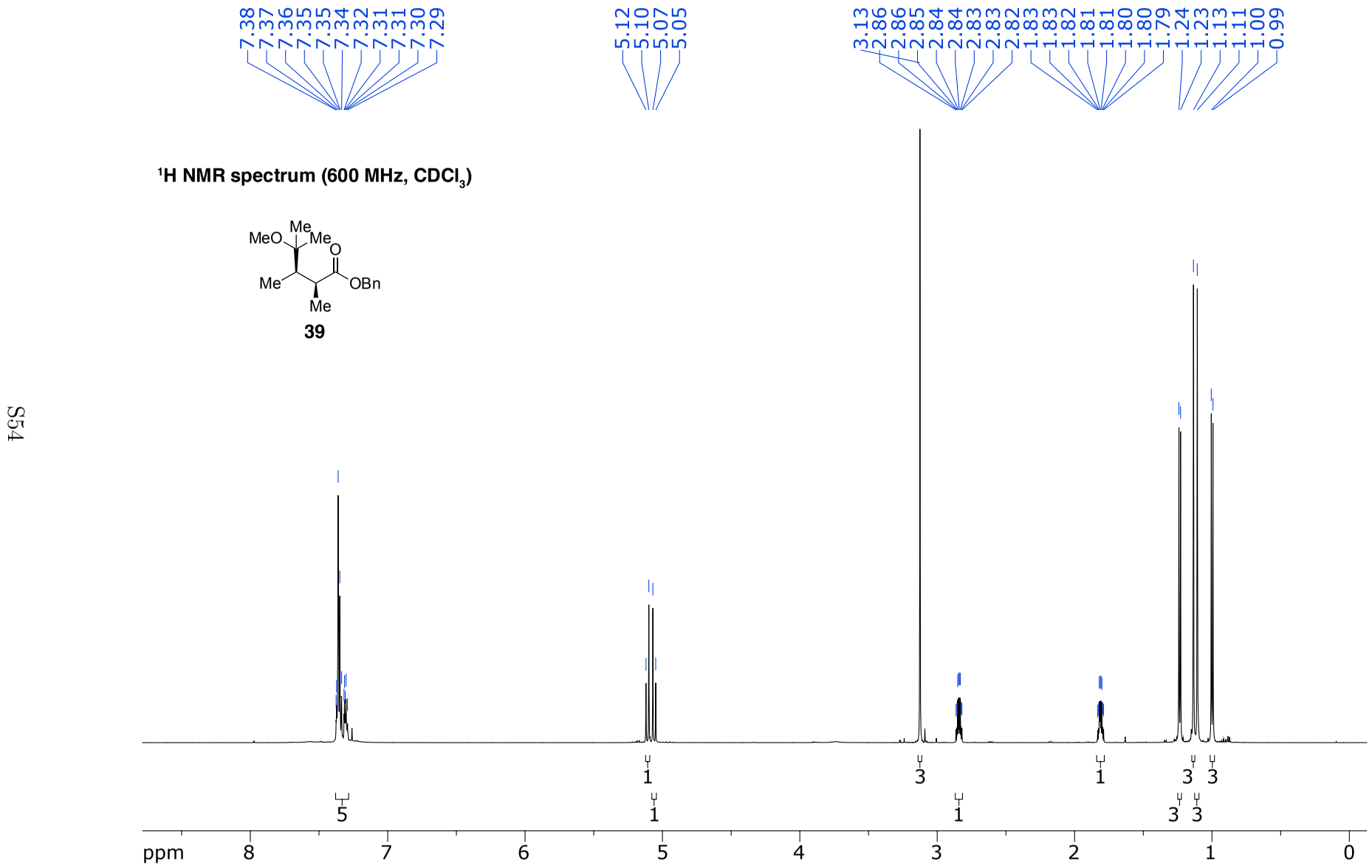

173.7
136.3
128.6
128.2
128.1
76.5
66.1
48.8
37.8
36.8
22.7
21.0
15.4
13C NMR spectrum (150 MHz, CDCl3)
MeO
Me
Me
O
Me
OBn
37
ppm
150
100
50
0

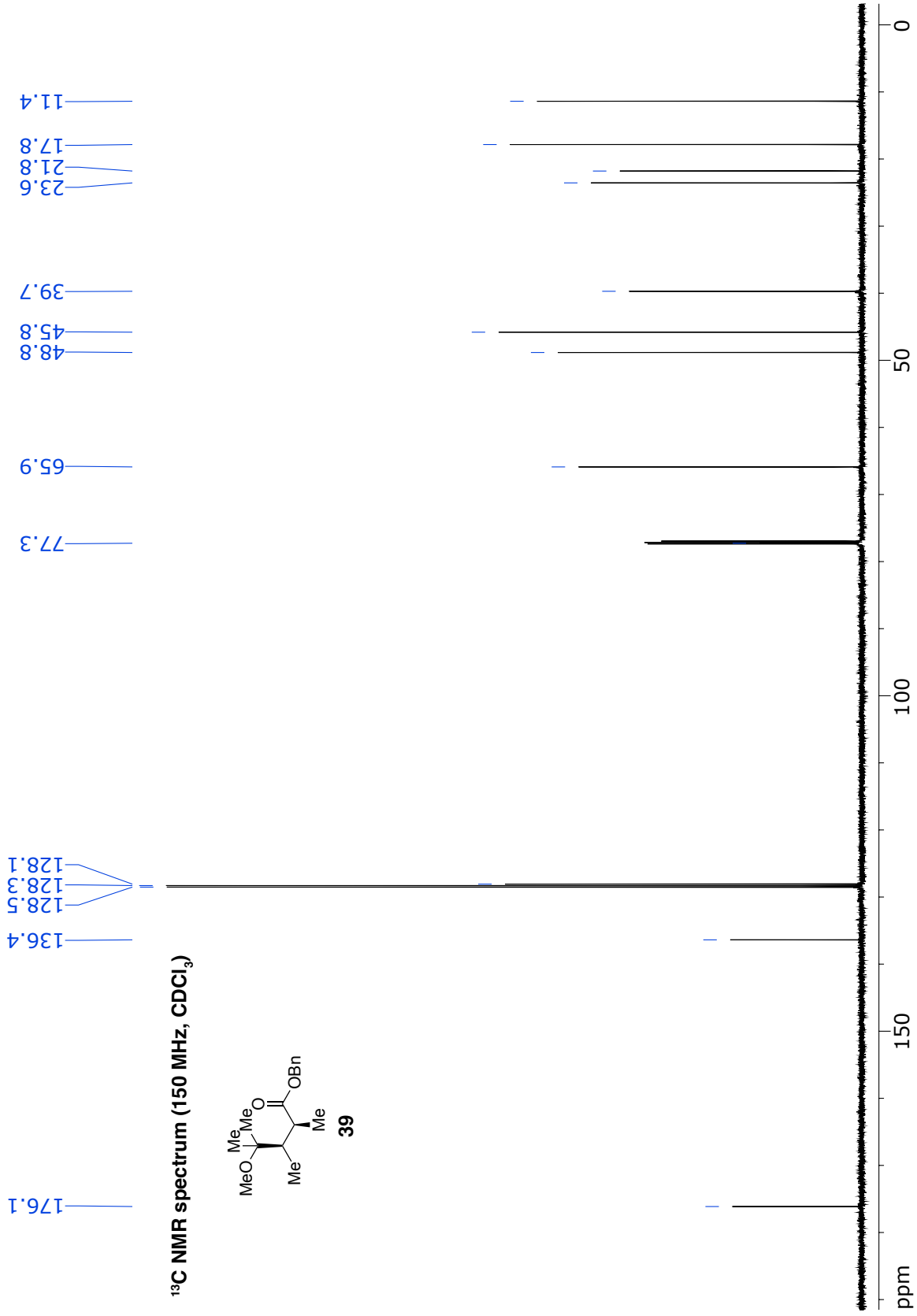

7.37
7.36
7.35
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
5.12
5.10
5.08
5.05
2.99
2.98
2.98
2.97
2.96
2.96
2.95
2.95
1.65
1.65
1.64
1.64
1.63
1.63
1.62
1.61
1.23
1.22
1.18
1.17
0.99
0.98
0.87
0.09
0.08
¹H NMR spectrum (600 MHz, CDCl3)
TBSO
Me
Me
O
Me
OBn
Me
38
2
1
3
3
6
5
1
3
3
9
ppm
7
6
5
4
3
2
1
0

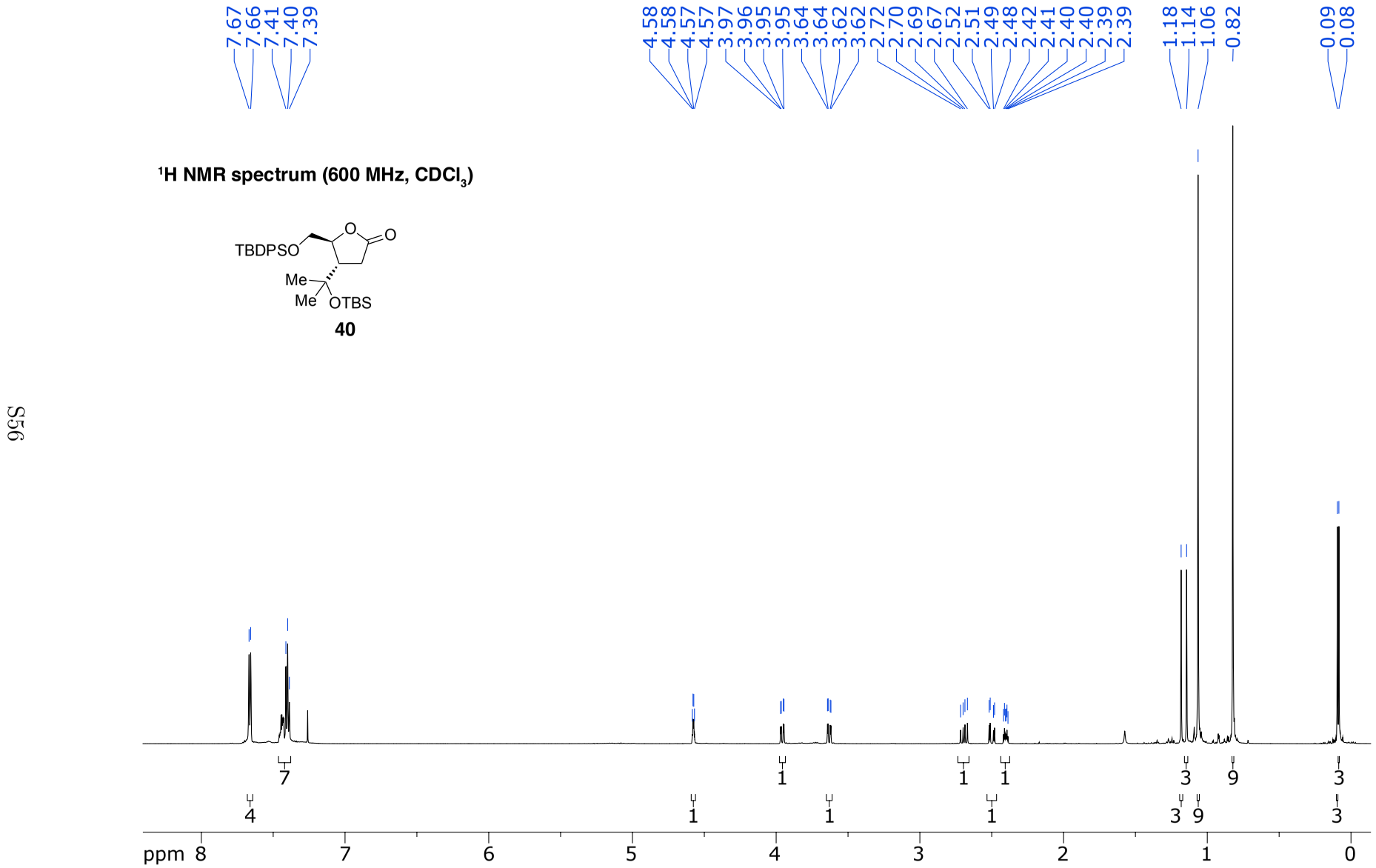


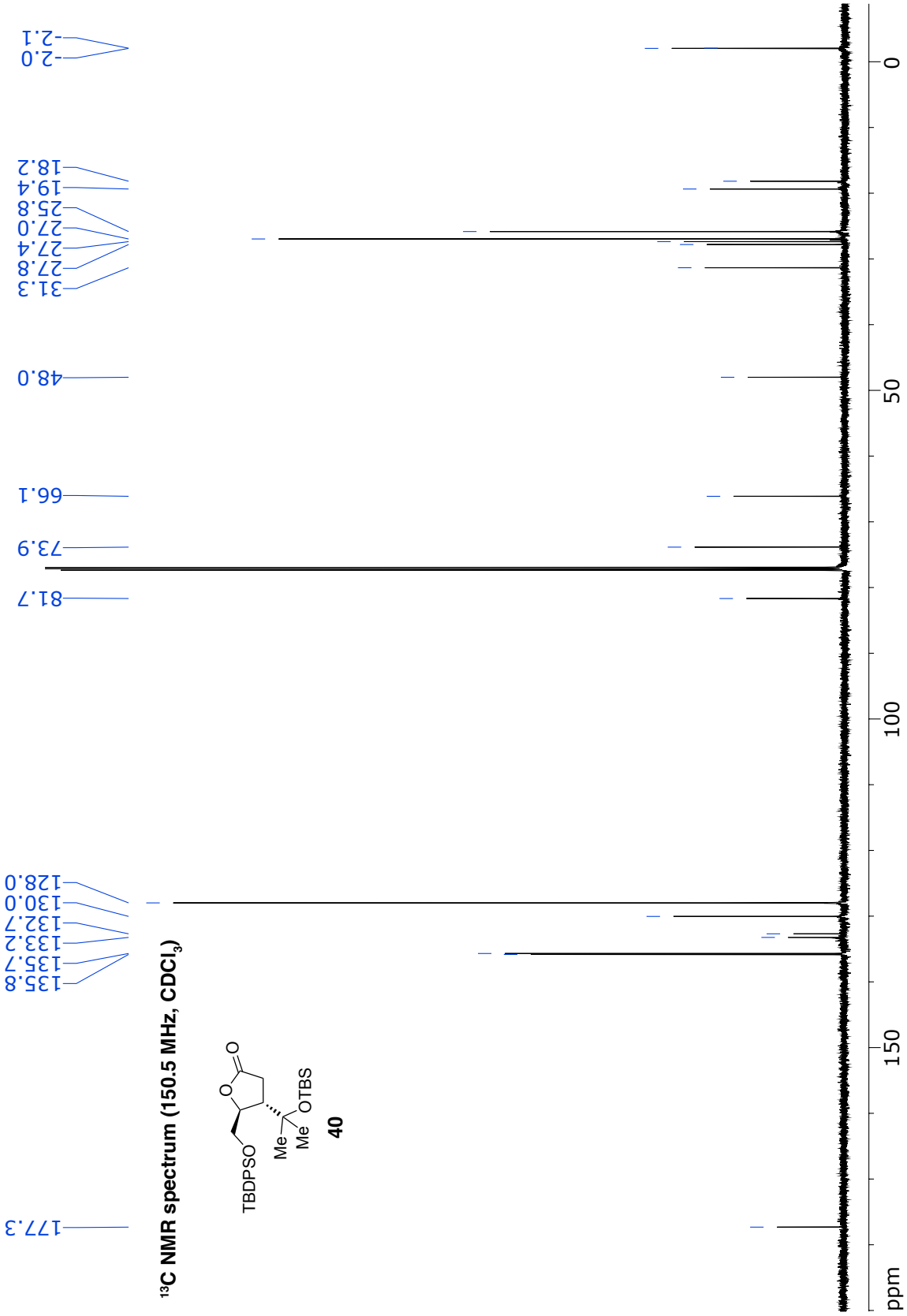
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

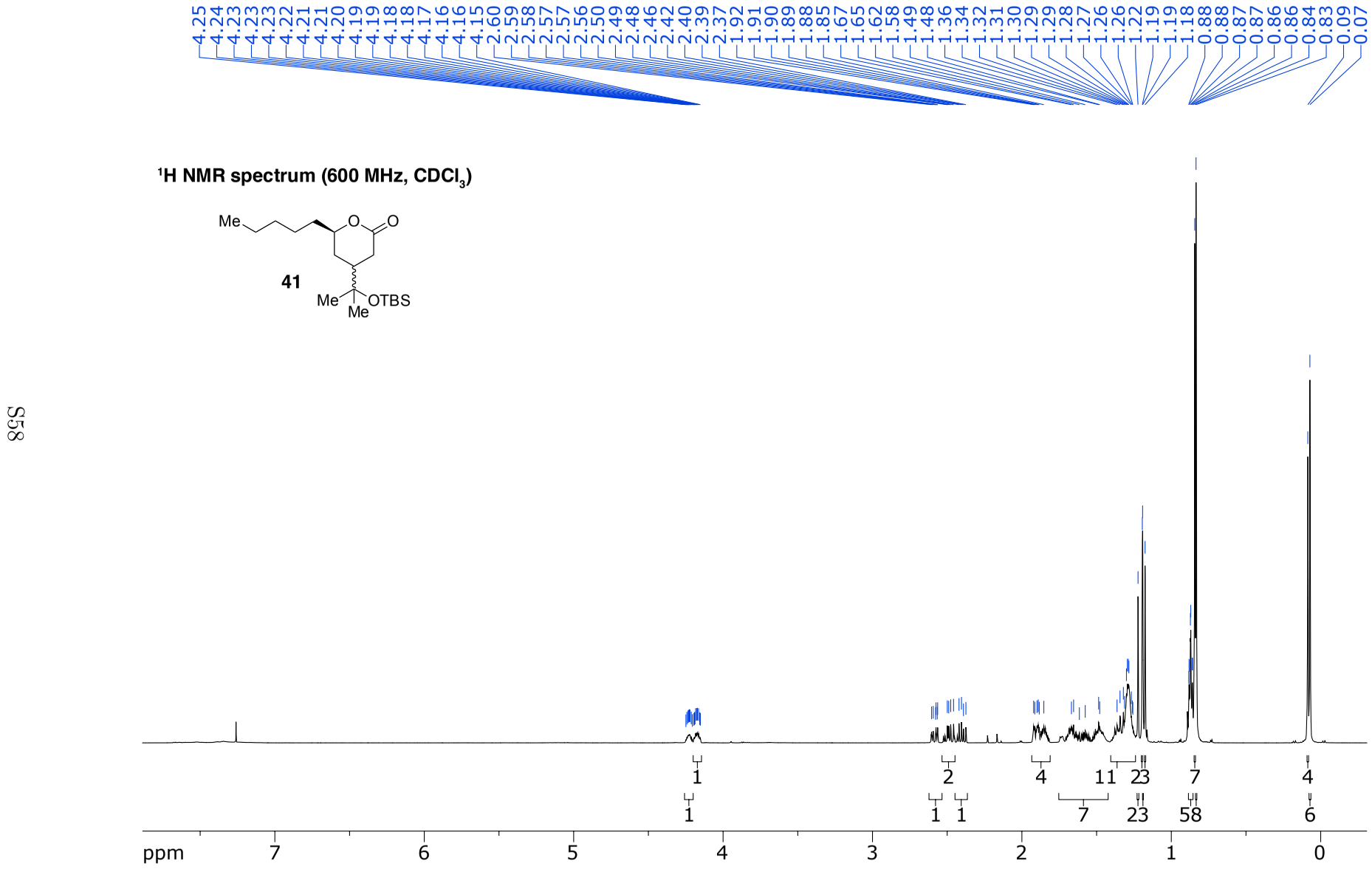
38


7.38
7.37
7.36
7.35
7.35
7.34
7.32
7.31
7.31
7.30
7.29
5.12
5.10
5.07
5.05
3.13
2.86
2.86
2.85
2.84
2.84
2.83
2.83
2.82
1.83
1.82
1.81
1.81
1.80
1.80
1.79
1.24
1.23
1.13
1.11
1.00
0.99
¹H NMR spectrum (600 MHz, CDCl3)
Me
MeO
Me
O
Me
OBn
Me
39
1
3
1
3
3
5
1
1
3
3
ppm
8
7
6
5
4
3
2
1
0

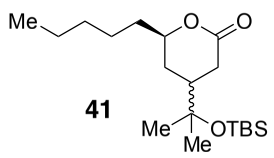

^{13}C NMR spectrum (150 MHz, $CDCl_3$)
176.1
136.4
128.5
128.3
128.1
77.3
65.9
48.8
45.8
39.7
23.6
21.8
17.8
11.4
ppm
0
50
100
150
39
Me
Me
MeO
Me
Me
O
OBn


7.67
7.66
7.41
7.40
7.39
4.58
4.58
4.57
4.57
3.97
3.96
3.95
3.95
3.64
3.64
3.62
3.62
2.72
2.70
2.69
2.67
2.52
2.51
2.49
2.48
2.42
2.41
2.40
2.40
2.39
2.39
1.18
1.14
1.06
0.82
0.09
0.08
¹H NMR spectrum (600 MHz, CDCl3)
TBDPSO
O
O
Me
Me
OTBS
40
7
1
1
1
3
9
3
4
1
1
1
3
9
3
ppm 8
7
6
5
4
3
2
1
0

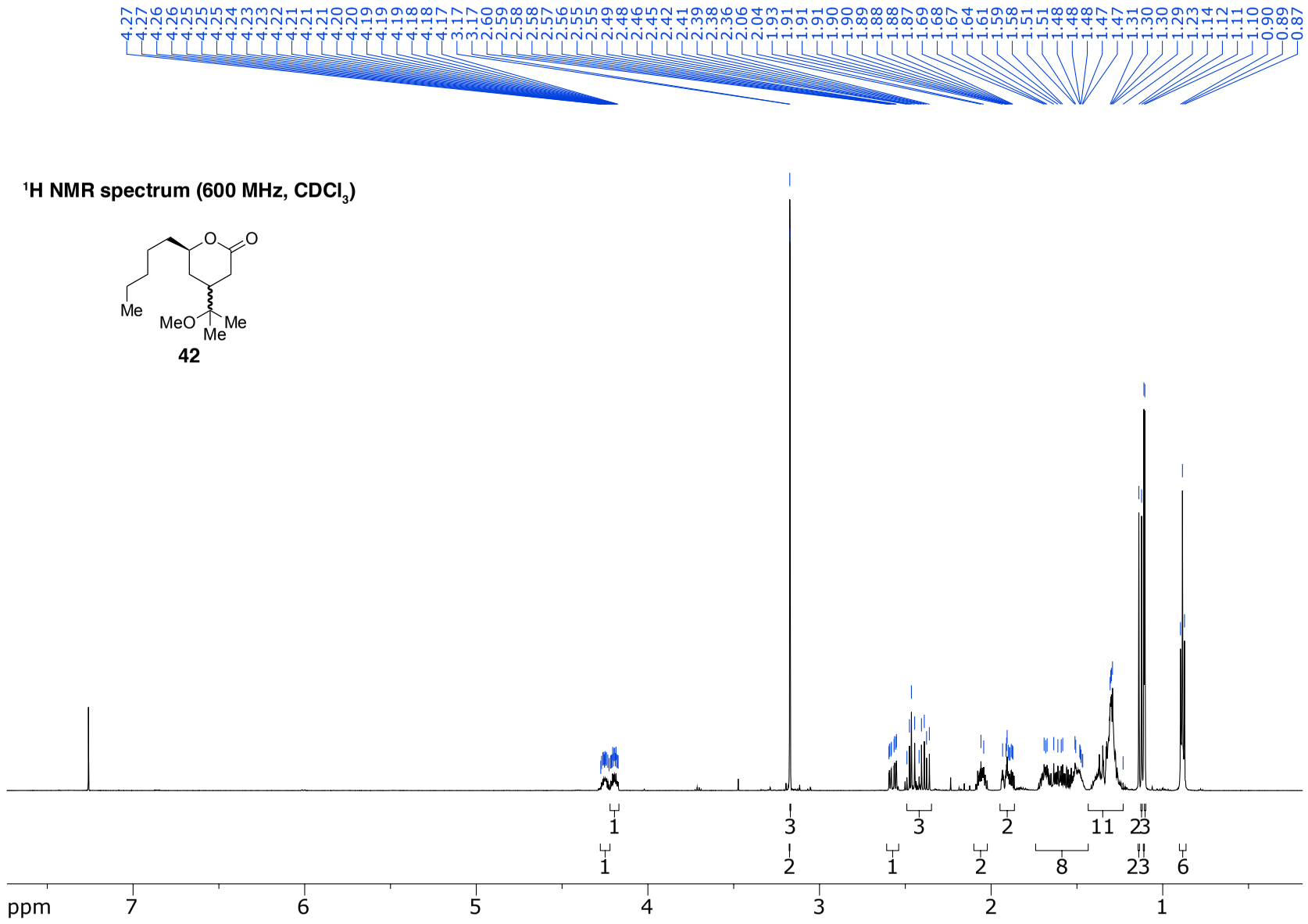

-2.1
-2.0
18.2
19.4
25.8
27.0
27.4
27.8
31.3
48.0
66.1
73.9
81.7
128.0
130.0
132.7
133.2
135.7
135.8
177.3
ppm
0
50
100
150
^{13}C NMR spectrum (150.5 MHz, CDCl$_3$)
TBDPSO
Me
Me
OTBS
40

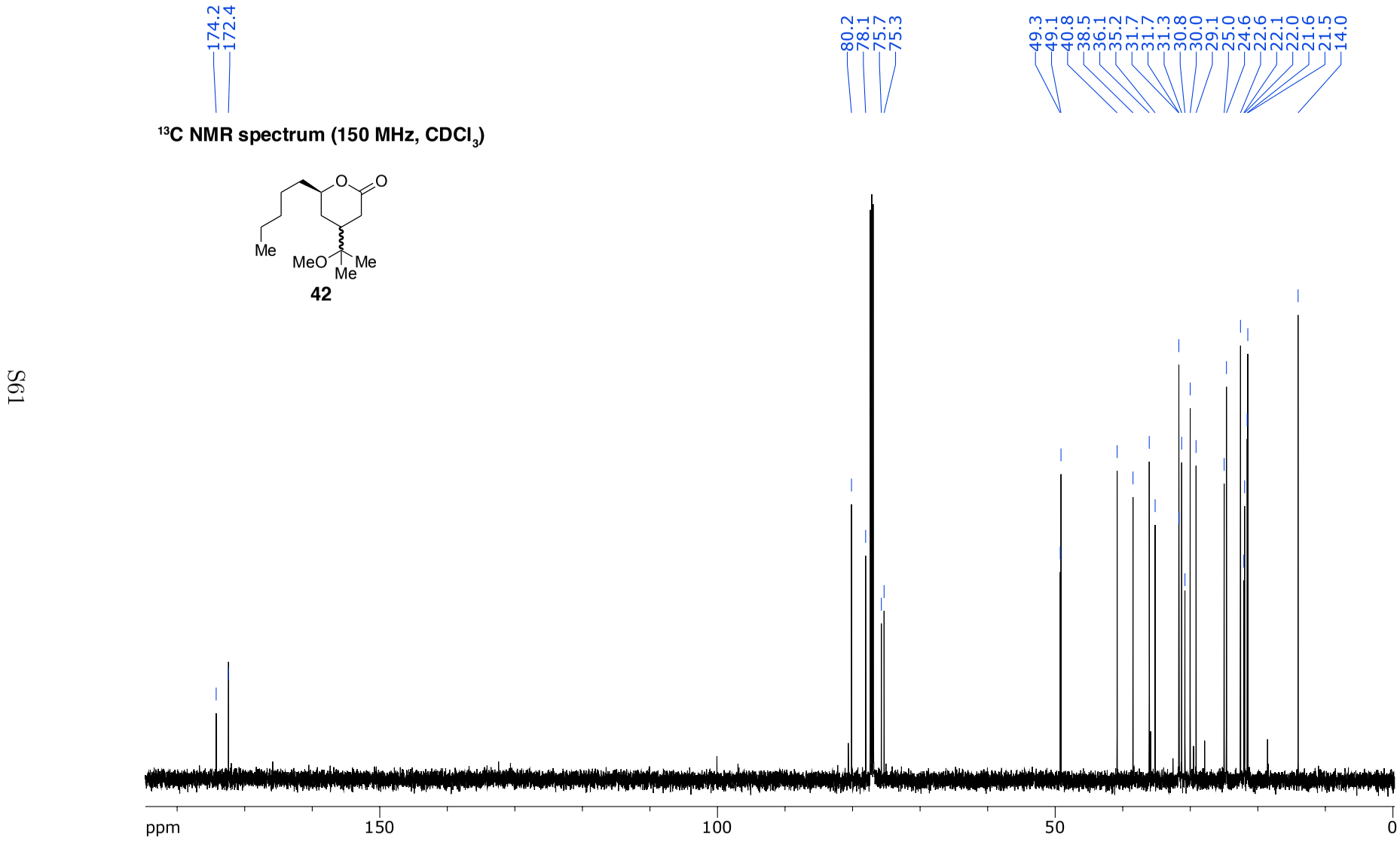

4.25 4.24 4.23 4.23 4.23 4.22 4.21 4.21 4.20 4.19 4.19 4.18 4.18 4.17 4.16 4.16 4.15 2.60 2.59 2.58 2.57 2.57 2.56 2.50 2.49 2.48 2.46 2.42 2.40 2.39 2.37 1.92 1.91 1.90 1.89 1.88 1.85 1.67 1.65 1.62 1.58 1.49 1.48 1.36 1.34 1.32 1.31 1.30 1.29 1.29 1.28 1.27 1.26 1.26 1.22 1.19 1.19 1.18 0.88 0.88 0.87 0.87 0.86 0.86 0.84 0.83 0.09 0.07
¹H NMR spectrum (600 MHz, CDCl3)
Me
O
O
41
Me
OTBS
Me
1
2
4
11
23
7
4
1
1
1
7
23
58
6
ppm
7
6
5
4
3
2
1
0

^{13}C NMR spectrum (150 MHz, $CDCl_3$)

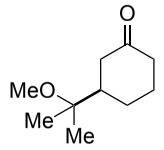


41

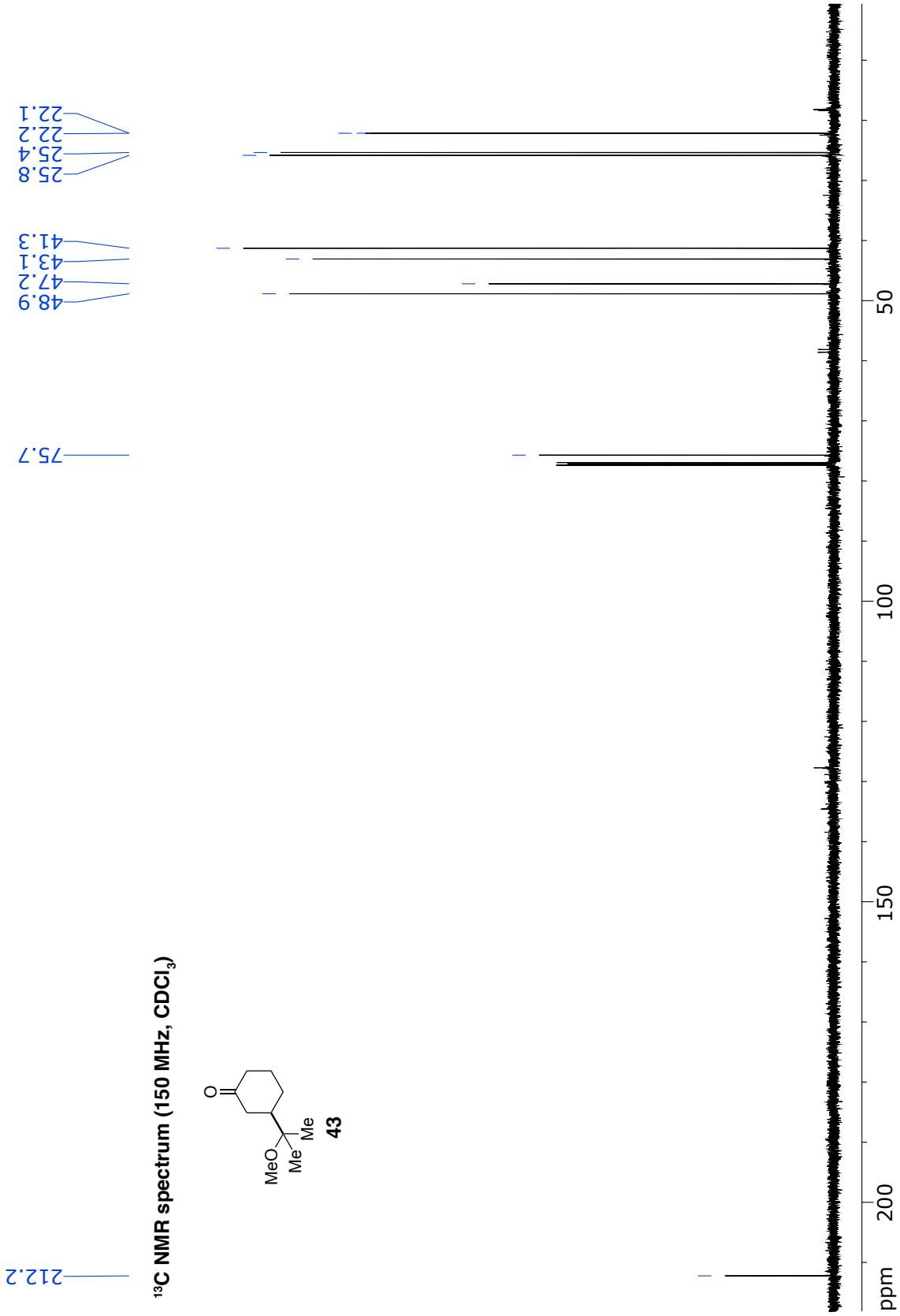

4.27 4.27 4.26 4.26 4.25 4.25 4.24 4.23 4.23 4.22 4.21 4.21 4.21 4.20 4.20 4.19 4.19 4.19 4.18 4.18 4.17 3.17 3.17 2.60 2.59 2.58 2.58 2.57 2.56 2.55 2.55 2.49 2.48 2.46 2.45 2.42 2.41 2.39 2.38 2.36 2.06 2.04 1.93 1.91 1.91 1.91 1.90 1.90 1.89 1.88 1.88 1.87 1.69 1.68 1.67 1.64 1.61 1.59 1.58 1.51 1.51 1.48 1.48 1.48 1.47 1.47 1.31 1.30 1.30 1.29 1.23 1.14 1.12 1.11 1.10 0.90 0.89 0.87
¹H NMR spectrum (600 MHz, CDCl3)
Me
MeO
Me
Me
42
1 3 3 2 11 23
1 2 1 2 8 23 6
ppm 7 6 5 4 3 2 1


174.2
172.4
80.2
78.1
75.7
75.3
49.3
49.1
40.8
38.5
36.1
35.2
31.7
31.7
31.3
30.8
30.0
29.1
25.0
24.6
22.6
22.1
22.0
21.6
21.5
14.0
13C NMR spectrum (150 MHz, CDCl3)
O
O
Me
MeO
Me
Me
42
ppm
150
100
50
0

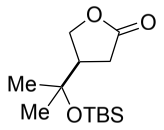
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



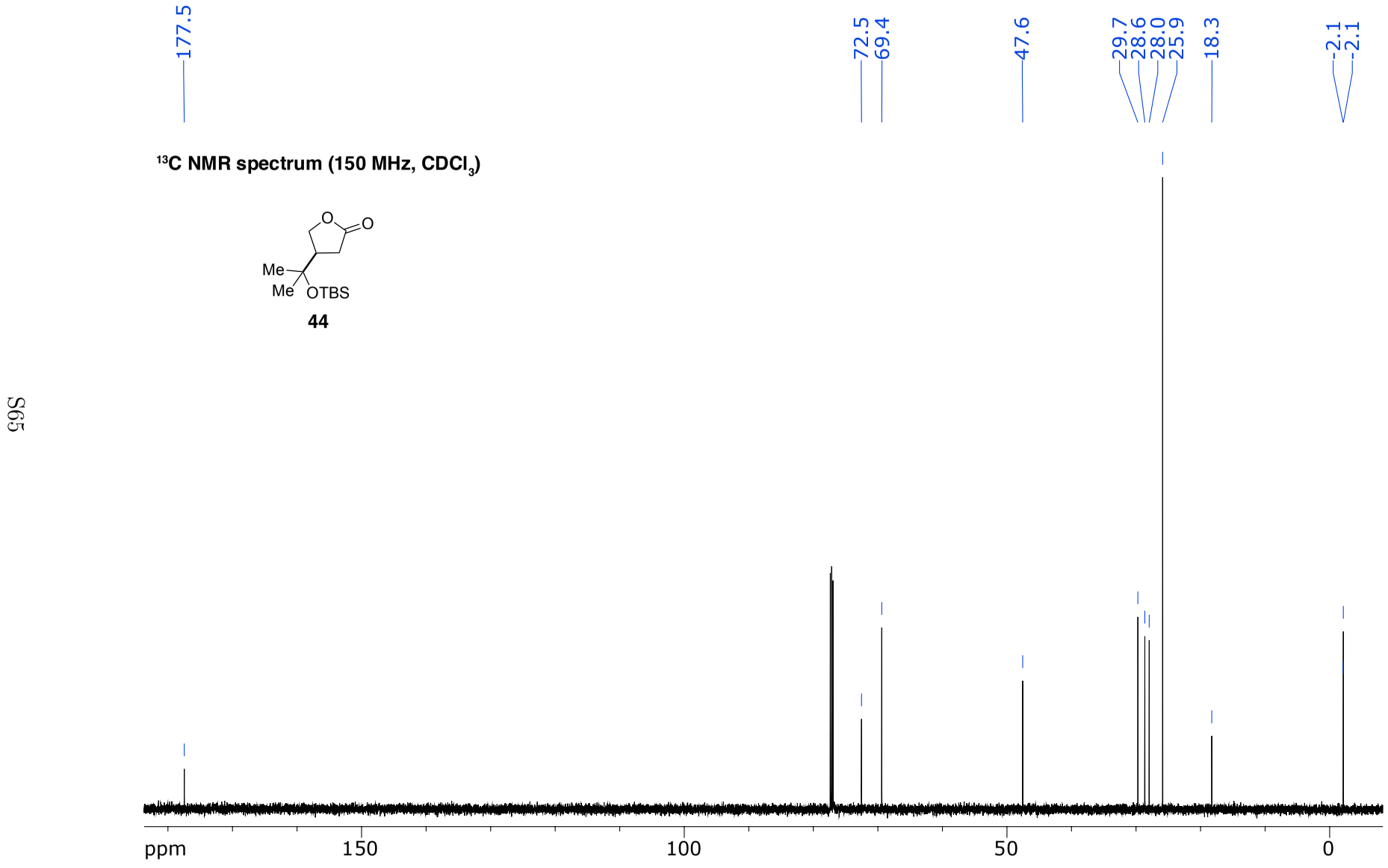
43


212.2
75.7
48.9
47.2
43.1
41.3
25.8
25.4
22.2
22.1
^{13}C NMR spectrum (150 MHz, $CDCl_3$)
O
MeO
Me
Me
Me
43
ppm
200
150
100
50

^{1}H NMR spectrum (600 MHz, $CDCl_3$)



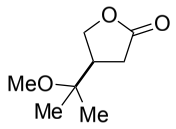
44



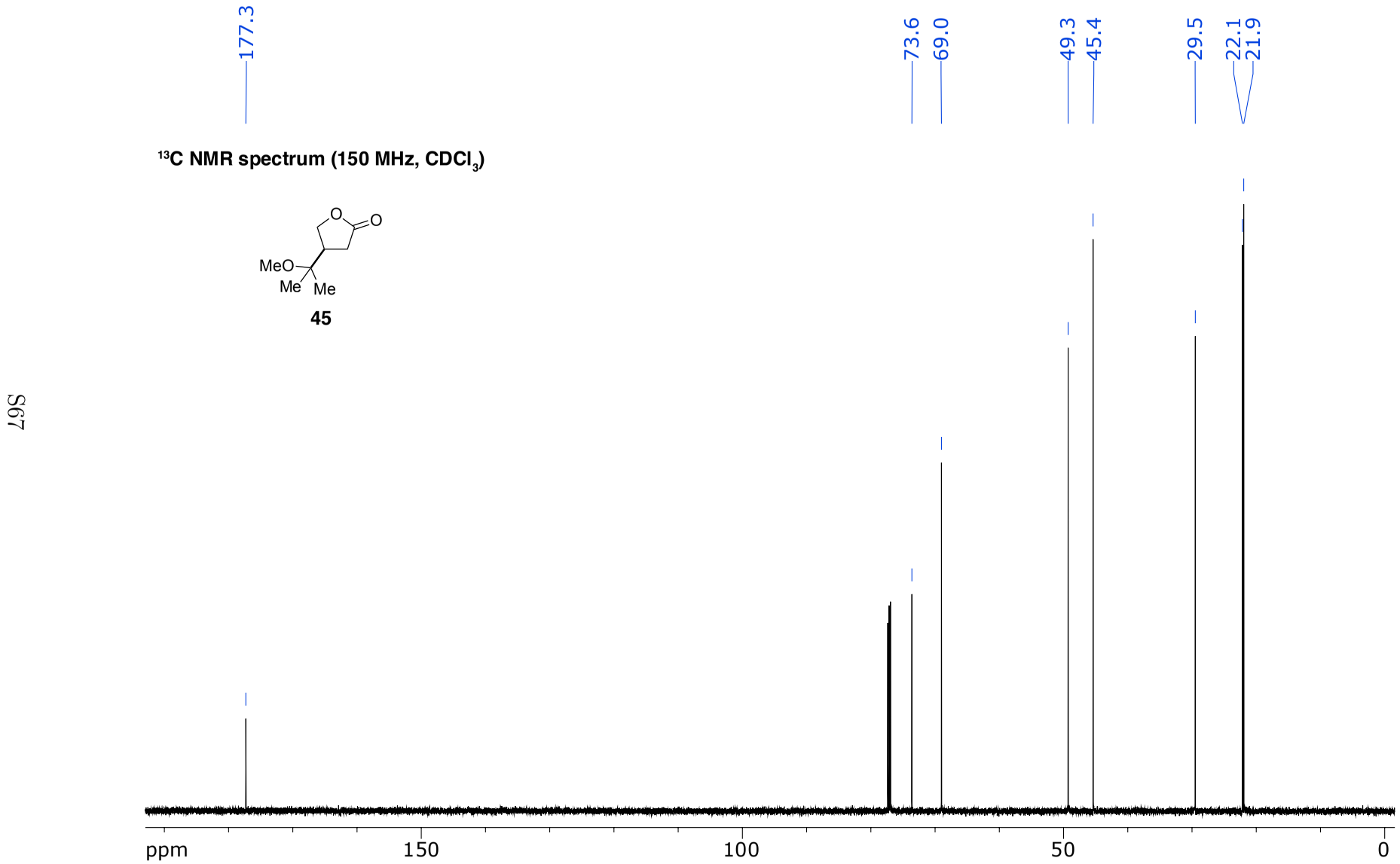
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

44

^{1}H NMR spectrum (600 MHz, $CDCl_3$)



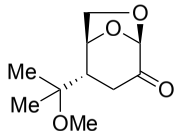
45



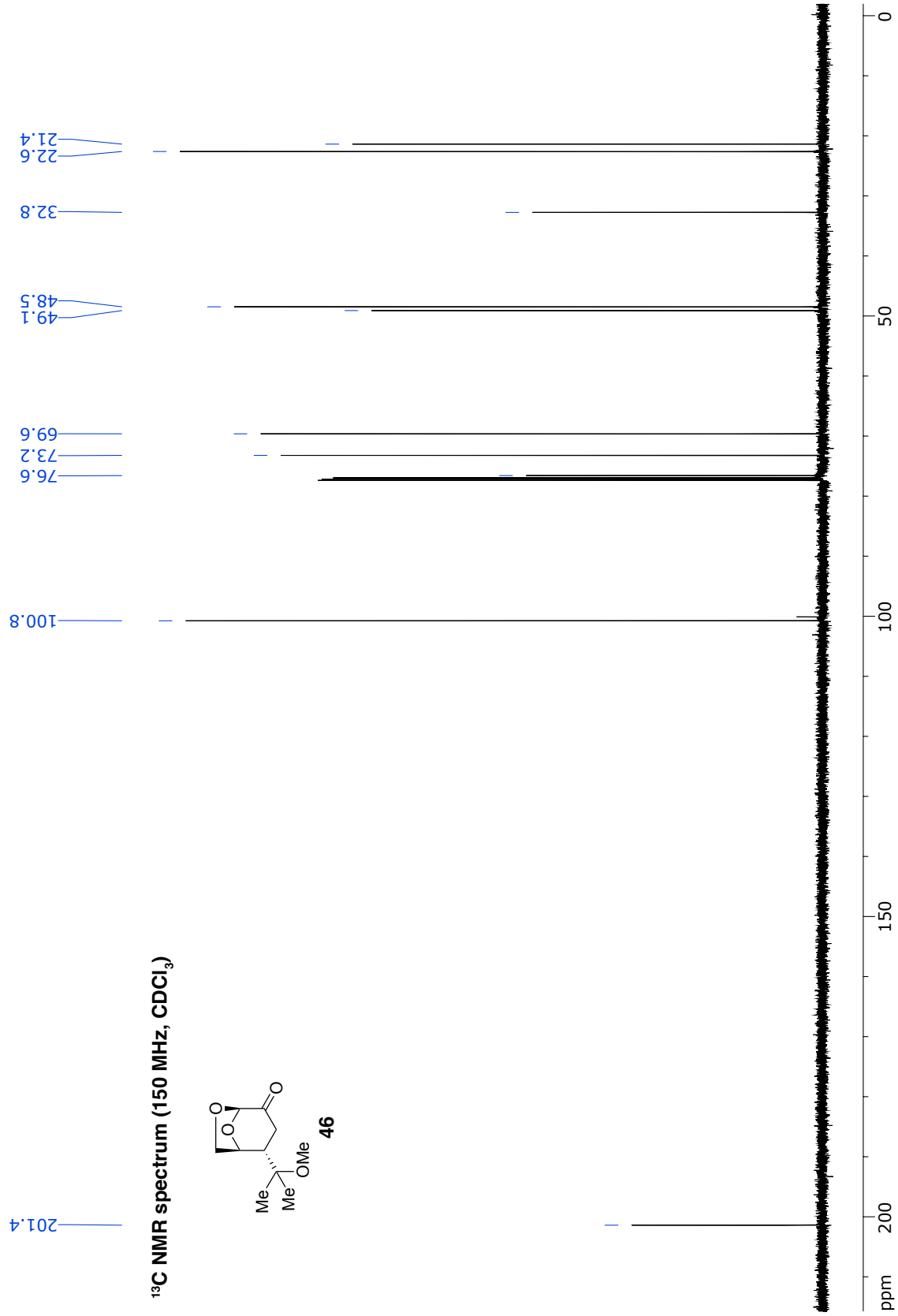
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

45

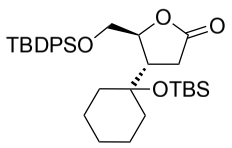
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



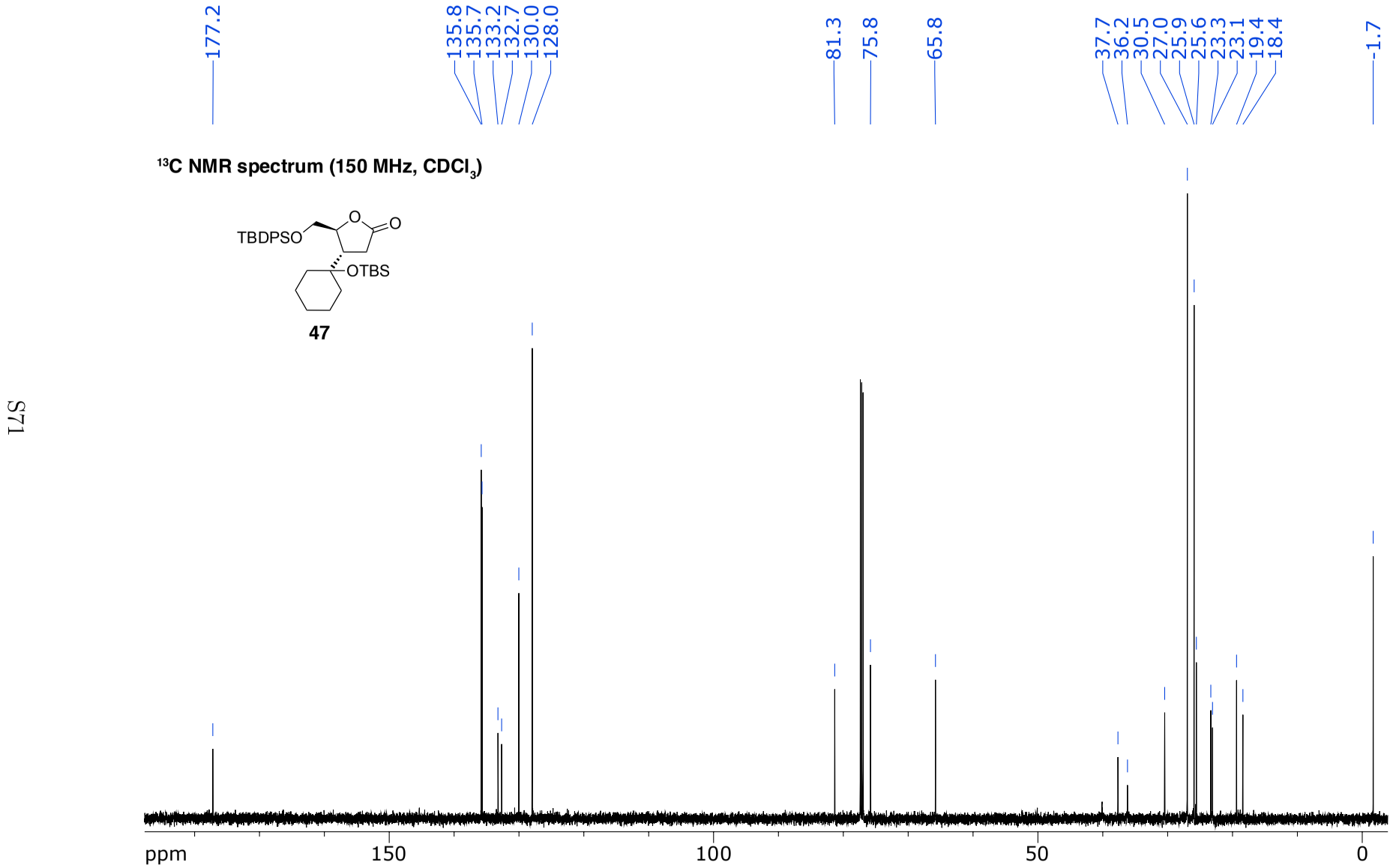
46


^{13}C NMR spectrum (150 MHz, $CDCl_3$)
46
Me
Me
OMe
O
O
O
201.4
100.8
76.6
73.2
69.6
49.1
48.5
32.8
22.6
21.4
ppm
0
50
100
150
200

^{1}H NMR spectrum (600 MHz, $CDCl_3$)

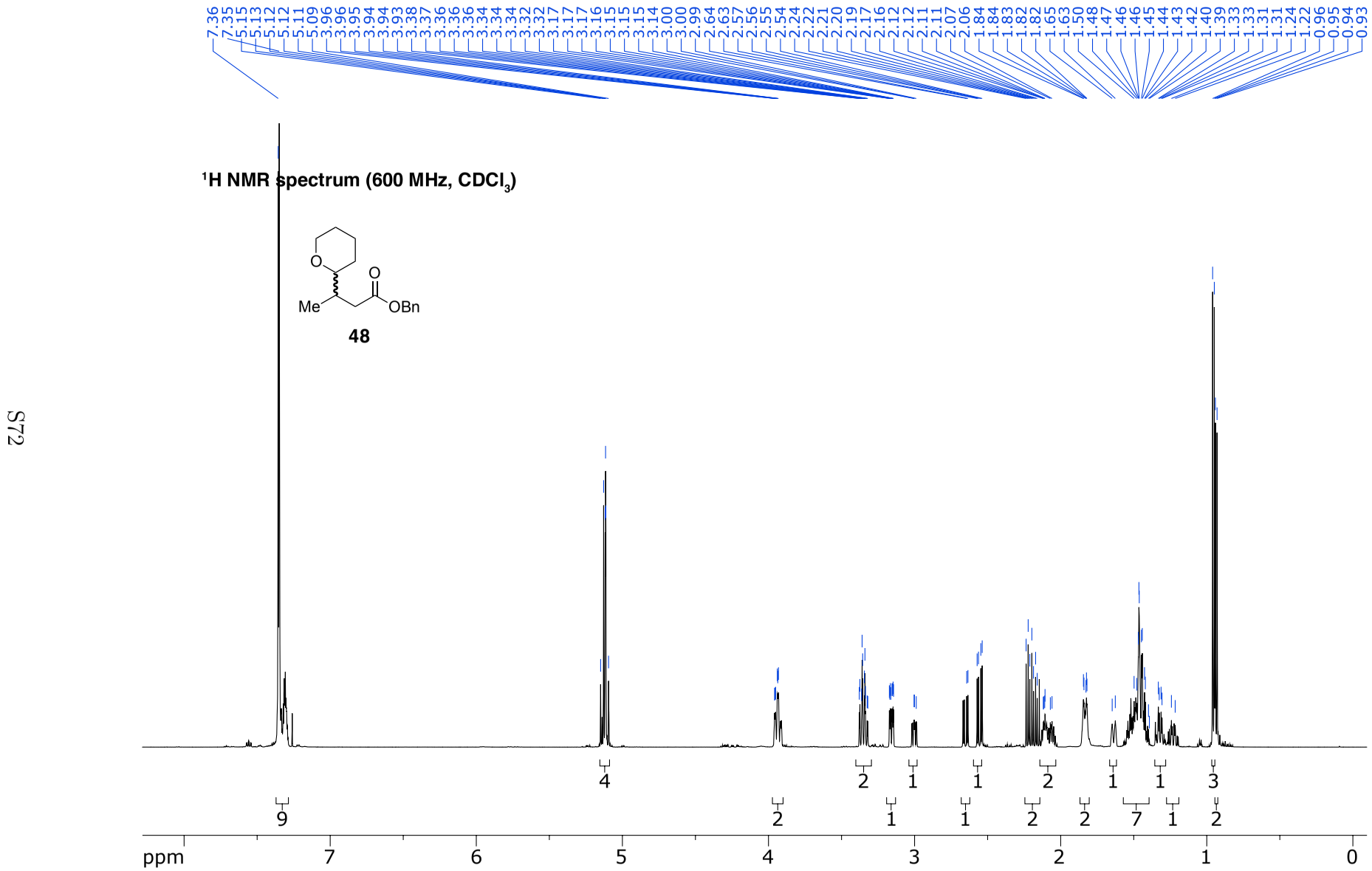


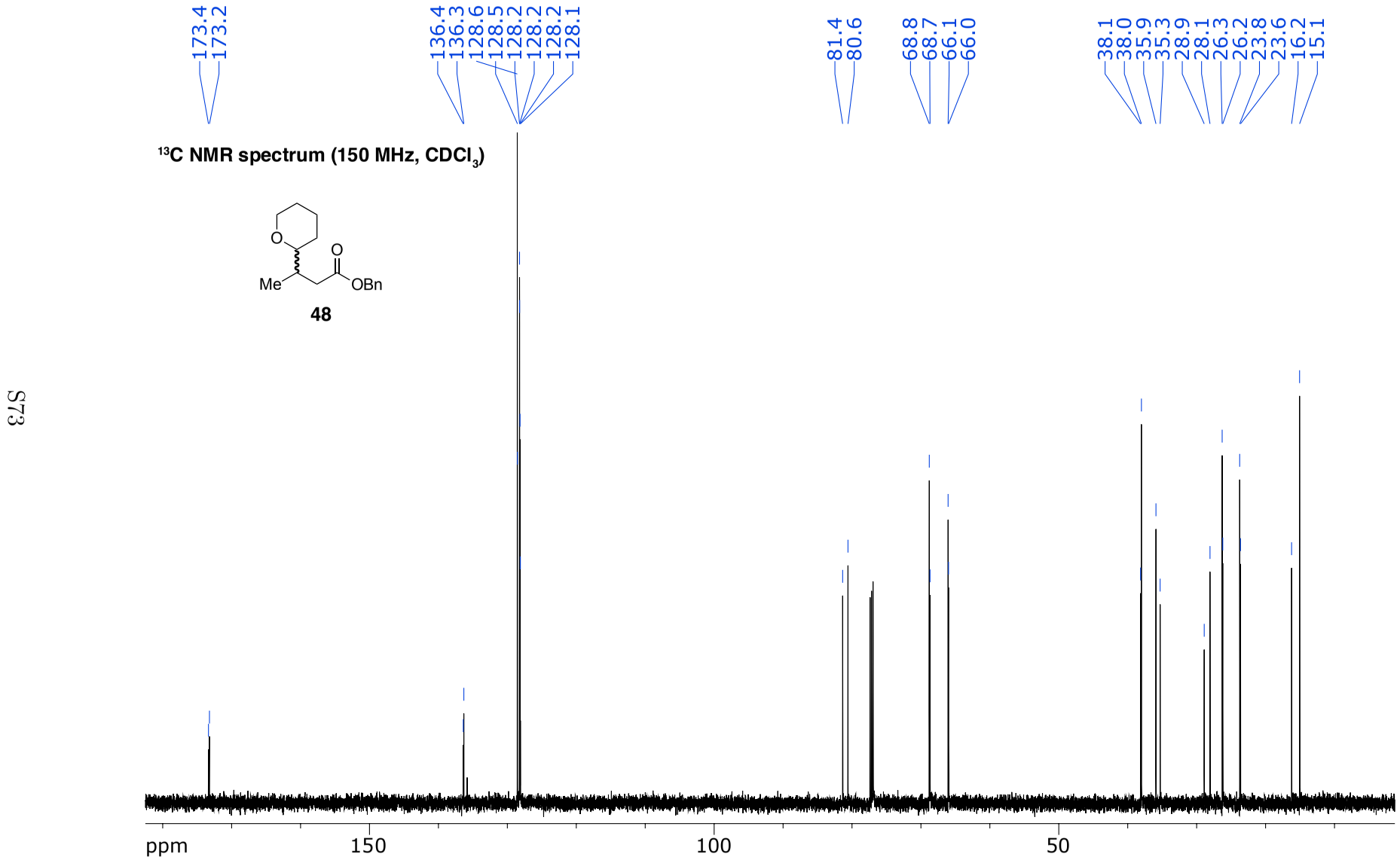
47



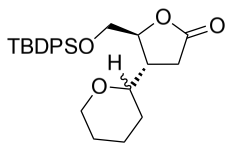
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

47

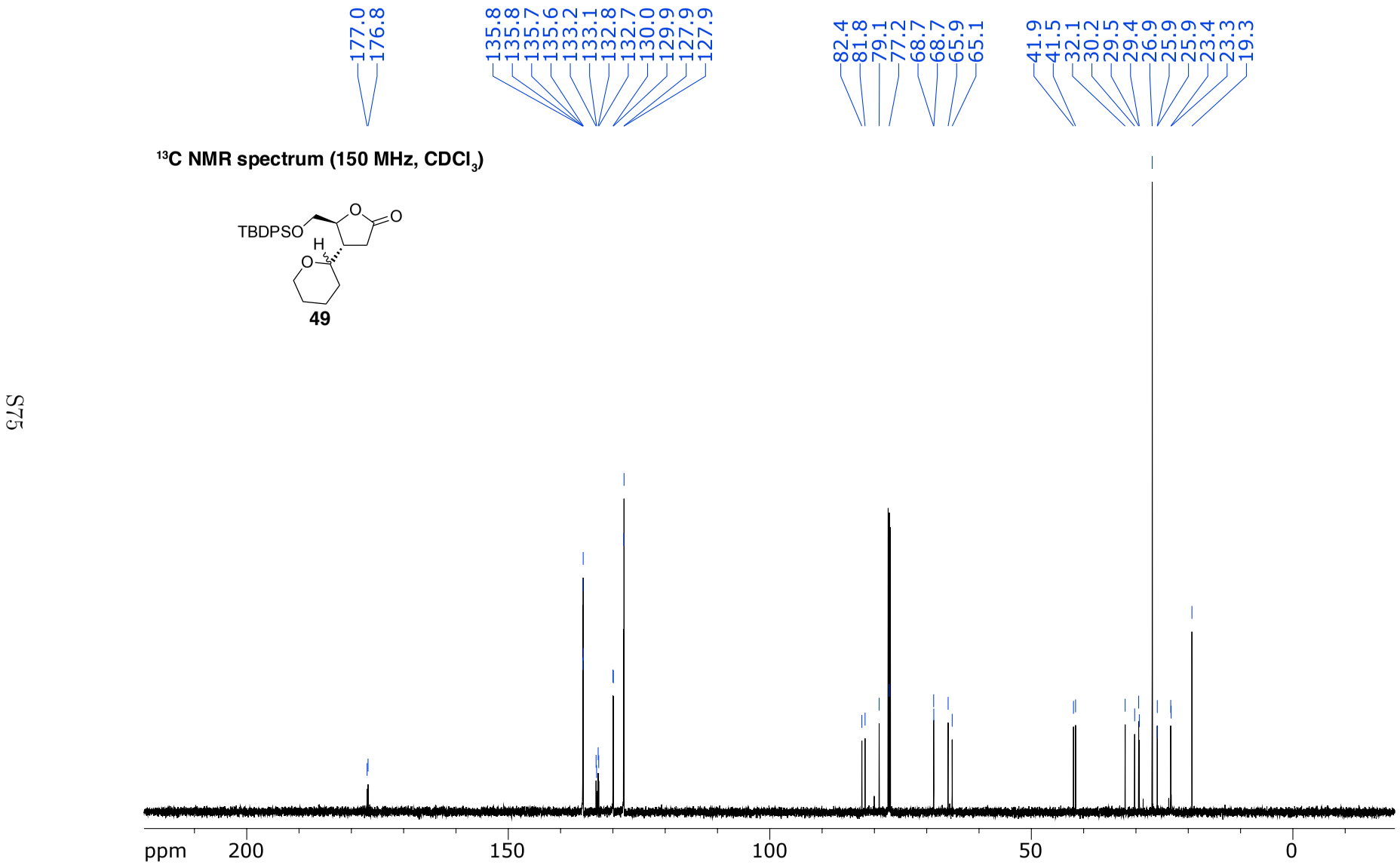

7.36
7.35
5.15
5.13
5.12
5.12
5.11
5.09
3.96
3.96
3.95
3.94
3.94
3.93
3.38
3.37
3.36
3.36
3.36
3.34
3.34
3.34
3.32
3.32
3.17
3.17
3.17
3.16
3.15
3.15
3.15
3.14
3.00
3.00
2.99
2.64
2.63
2.57
2.56
2.55
2.54
2.24
2.22
2.21
2.20
2.19
2.17
2.16
2.12
2.12
2.11
2.11
2.07
2.06
1.84
1.84
1.83
1.82
1.82
1.65
1.63
1.50
1.48
1.47
1.46
1.46
1.45
1.44
1.43
1.42
1.40
1.39
1.33
1.33
1.31
1.31
1.24
1.22
0.96
0.95
0.94
0.93
¹H NMR spectrum (600 MHz, CDCl3)
O
O
Me
OBn
48
4
2
1
1
1
2
1
1
3
9
2
1
1
2
2
7
1
2
ppm
7
6
5
4
3
2
1
0


173.4
173.2
136.4
136.3
128.6
128.5
128.2
128.2
128.2
128.1
81.4
80.6
68.8
68.7
66.1
66.0
38.1
38.0
35.9
35.3
28.9
28.1
26.3
26.2
23.8
23.6
16.2
15.1
13C NMR spectrum (150 MHz, CDCl3)
O
O
Me
OBn
48
ppm
150
100
50

^{1}H NMR spectrum (600 MHz, $CDCl_3$)



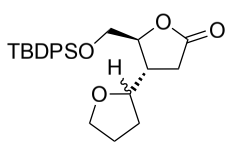
49



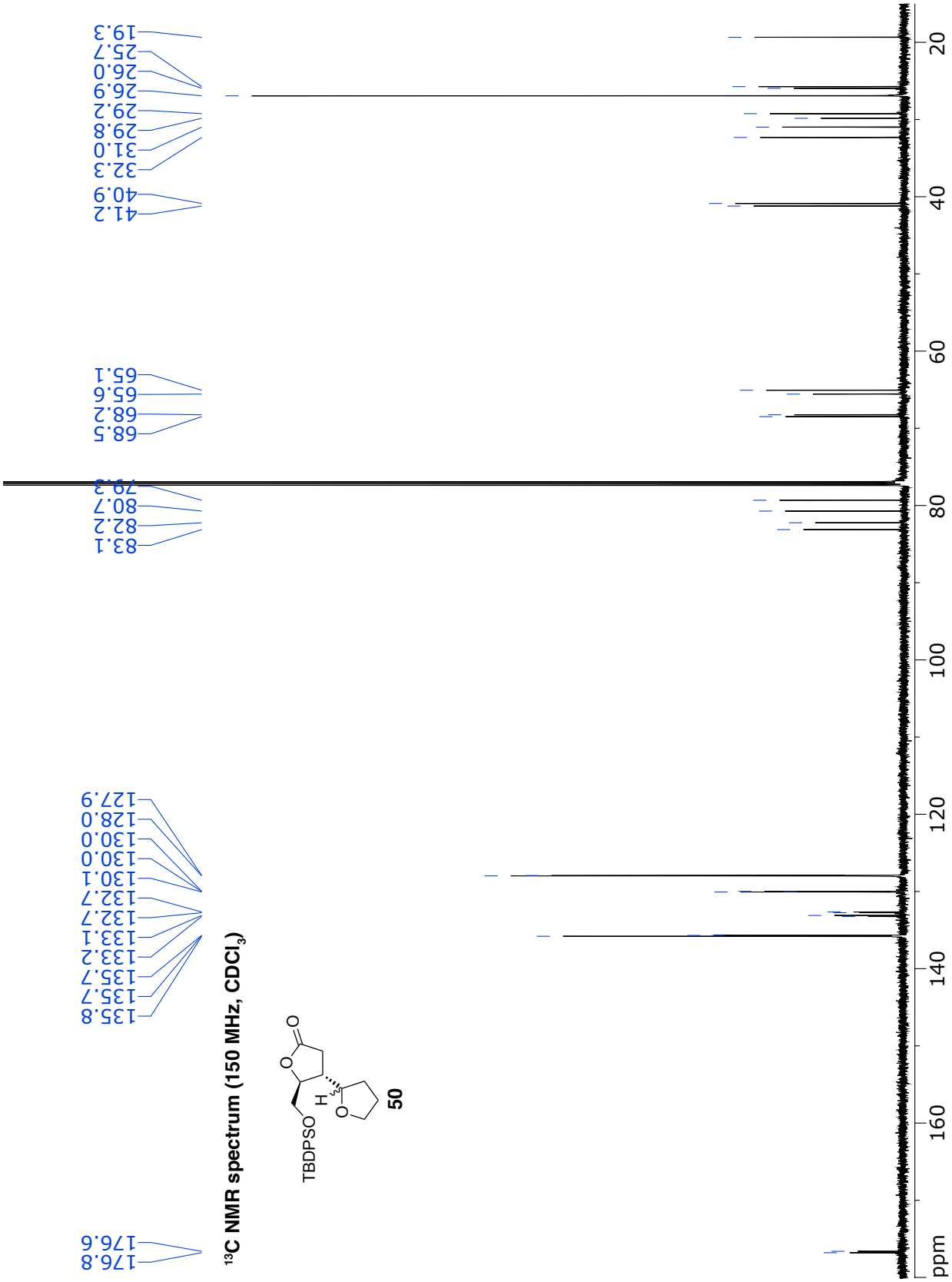
^{13}C NMR spectrum (150 MHz, $CDCl_3$)

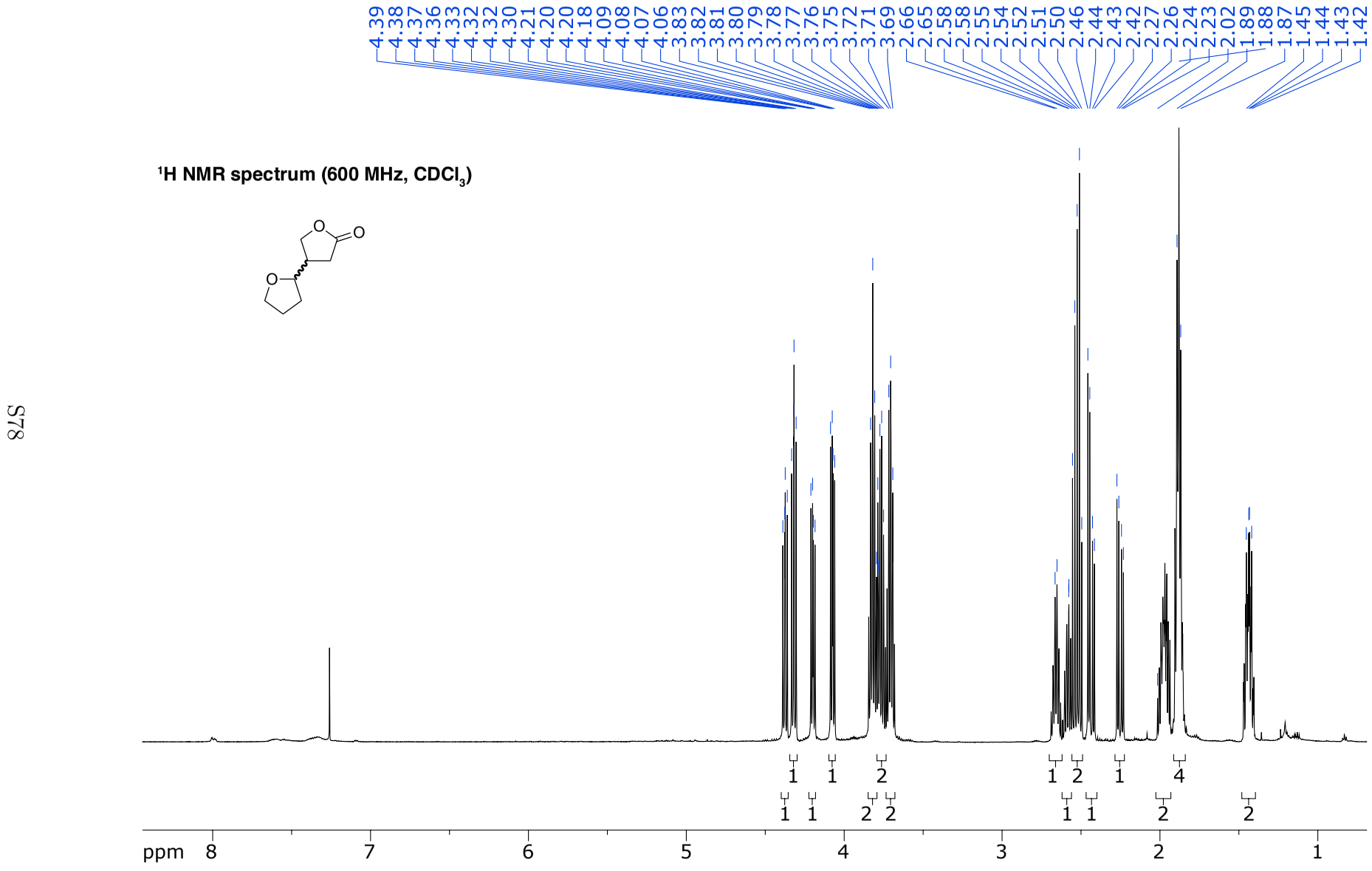
49

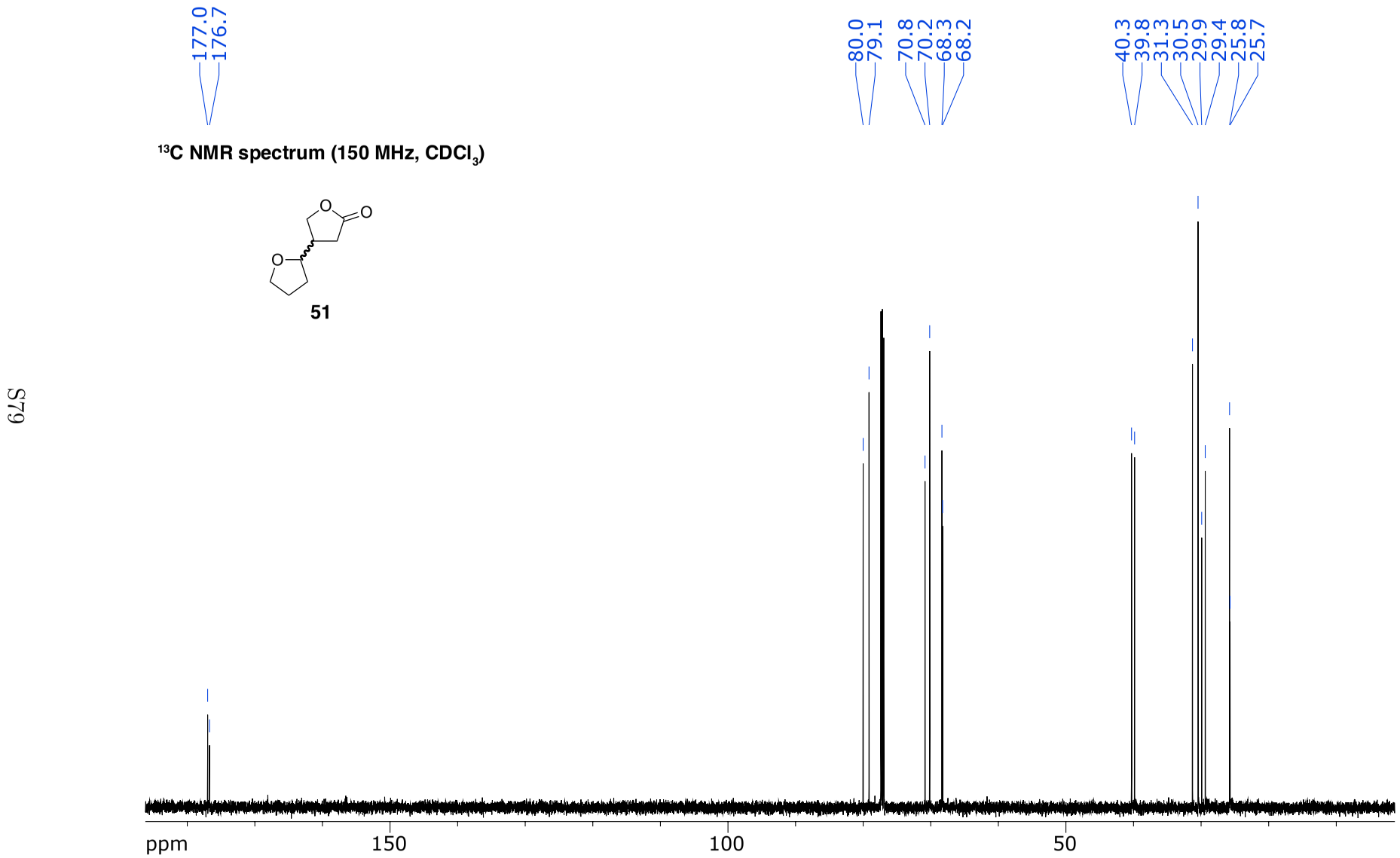
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



50


19.3
25.7
26.0
26.9
29.2
29.8
31.0
32.3
40.9
41.2
65.1
65.6
68.2
68.5
79.3
80.7
82.2
83.1
127.9
128.0
130.0
130.0
130.1
132.7
132.7
133.1
133.2
135.7
135.7
135.8
176.6
176.8
13C NMR spectrum (150 MHz, CDCl3)
TBDPSO
50
ppm
20
40
60
80
100
120
140
160


4.39
4.38
4.37
4.36
4.33
4.32
4.32
4.30
4.21
4.20
4.20
4.18
4.09
4.08
4.07
4.06
3.83
3.82
3.81
3.80
3.79
3.78
3.77
3.76
3.75
3.72
3.71
3.69
2.66
2.65
2.58
2.58
2.55
2.54
2.52
2.51
2.50
2.46
2.44
2.43
2.42
2.27
2.26
2.24
2.23
2.02
1.89
1.88
1.87
1.45
1.44
1.43
1.42
^{1}H NMR spectrum (600 MHz, CDCl$_3$)
O
O
O
1
1
2
1
2
1
4
1
1
2
2
1
1
2
2
ppm
8
7
6
5
4
3
2
1

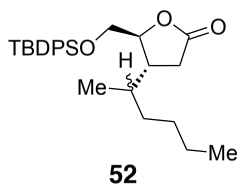


^{13}C NMR spectrum (150 MHz, $CDCl_3$)

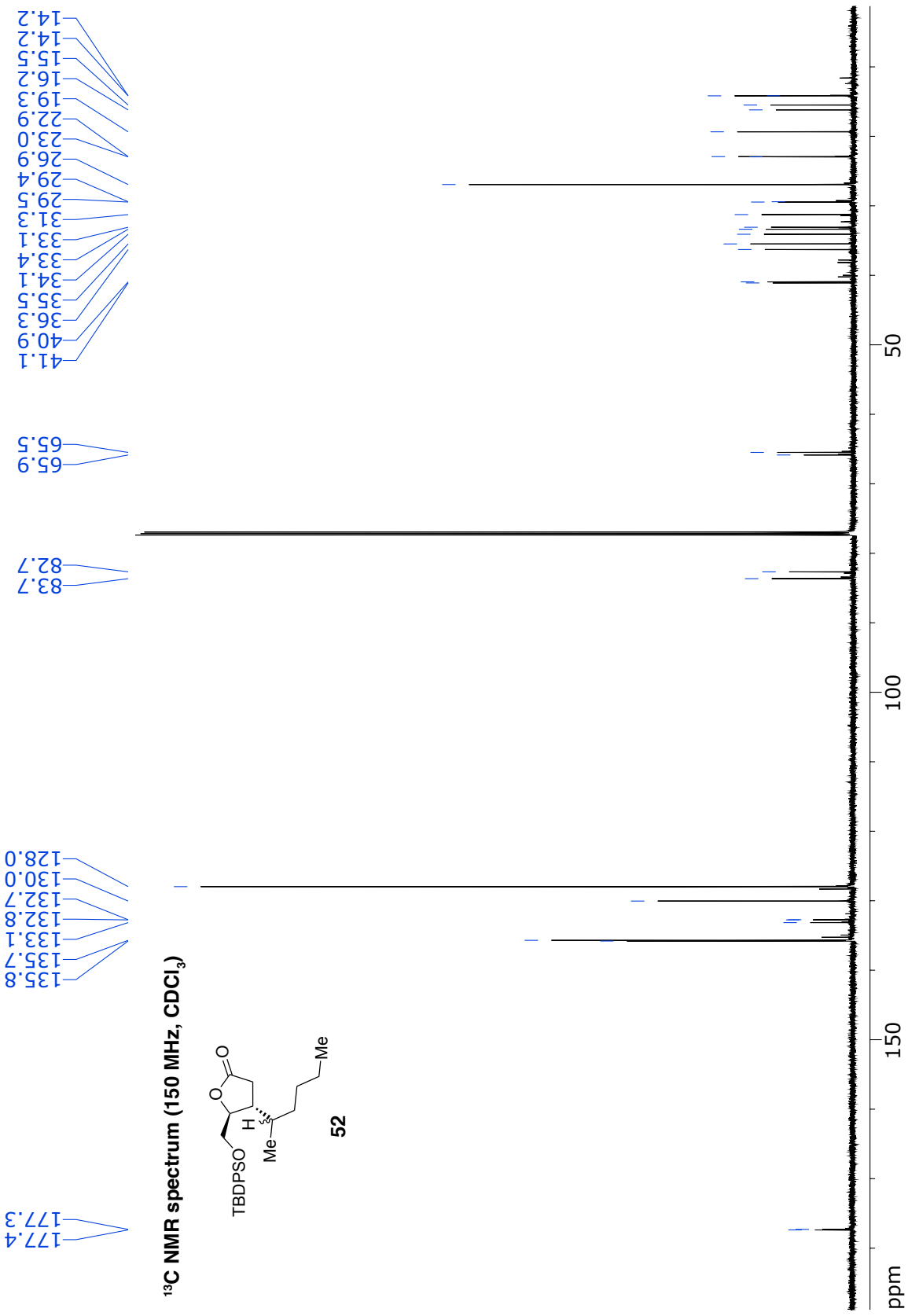
51

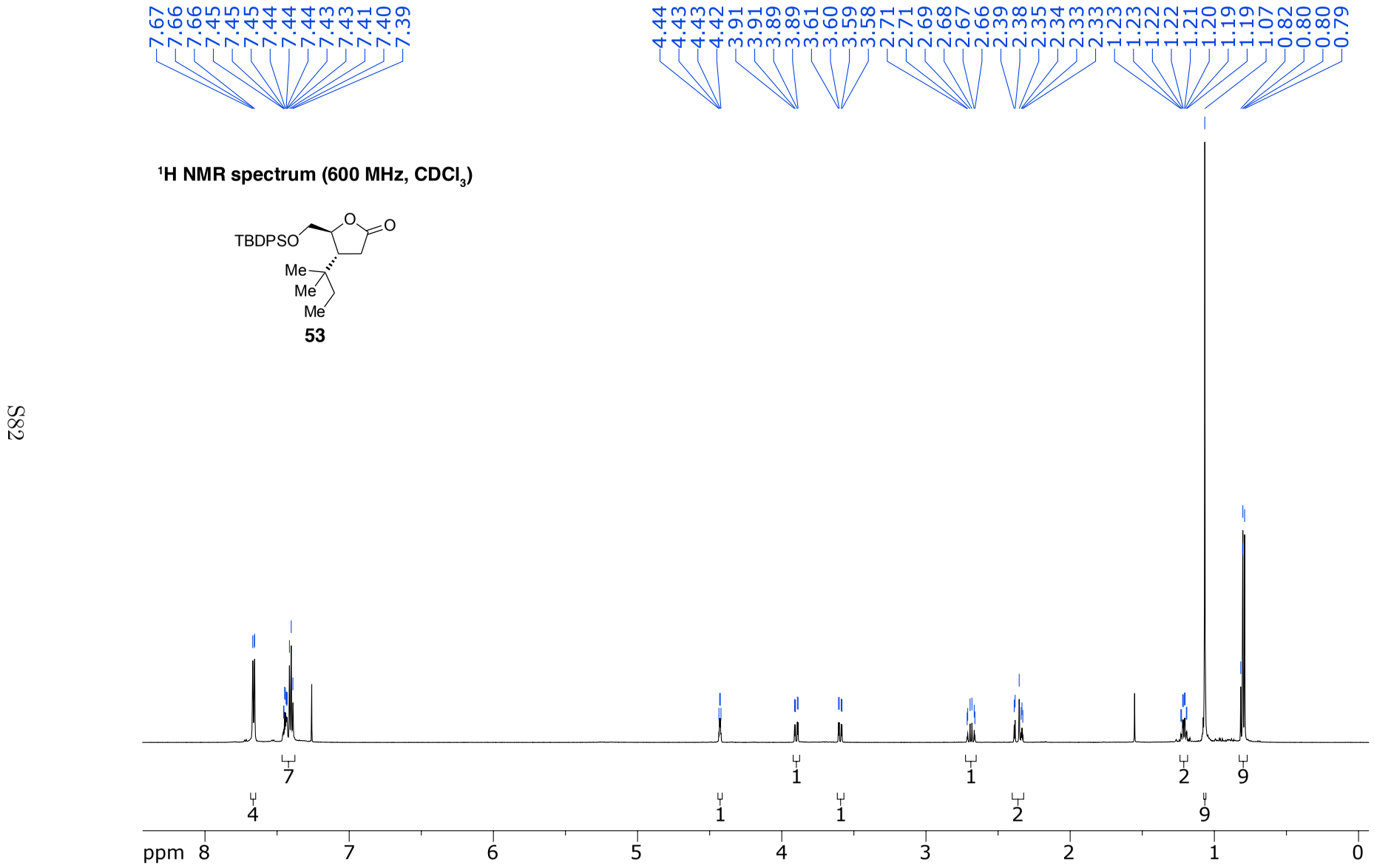
7.67 7.66 7.66 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.40 7.40 7.39 7.39 4.34 4.34 4.32 4.31 3.89 3.89 3.88 3.88 3.87 3.87 3.69 3.68 3.67 3.66 3.65 3.64 2.78 2.77 2.75 2.68 2.66 2.65 2.63 2.49 2.49 2.48 2.33 2.32 2.31 2.30 2.29 2.28 1.31 1.30 1.30 1.29 1.29 1.28 1.27 1.26 1.25 1.24 1.06 1.06 0.91 0.90 0.89 0.87 0.86 0.86 0.85

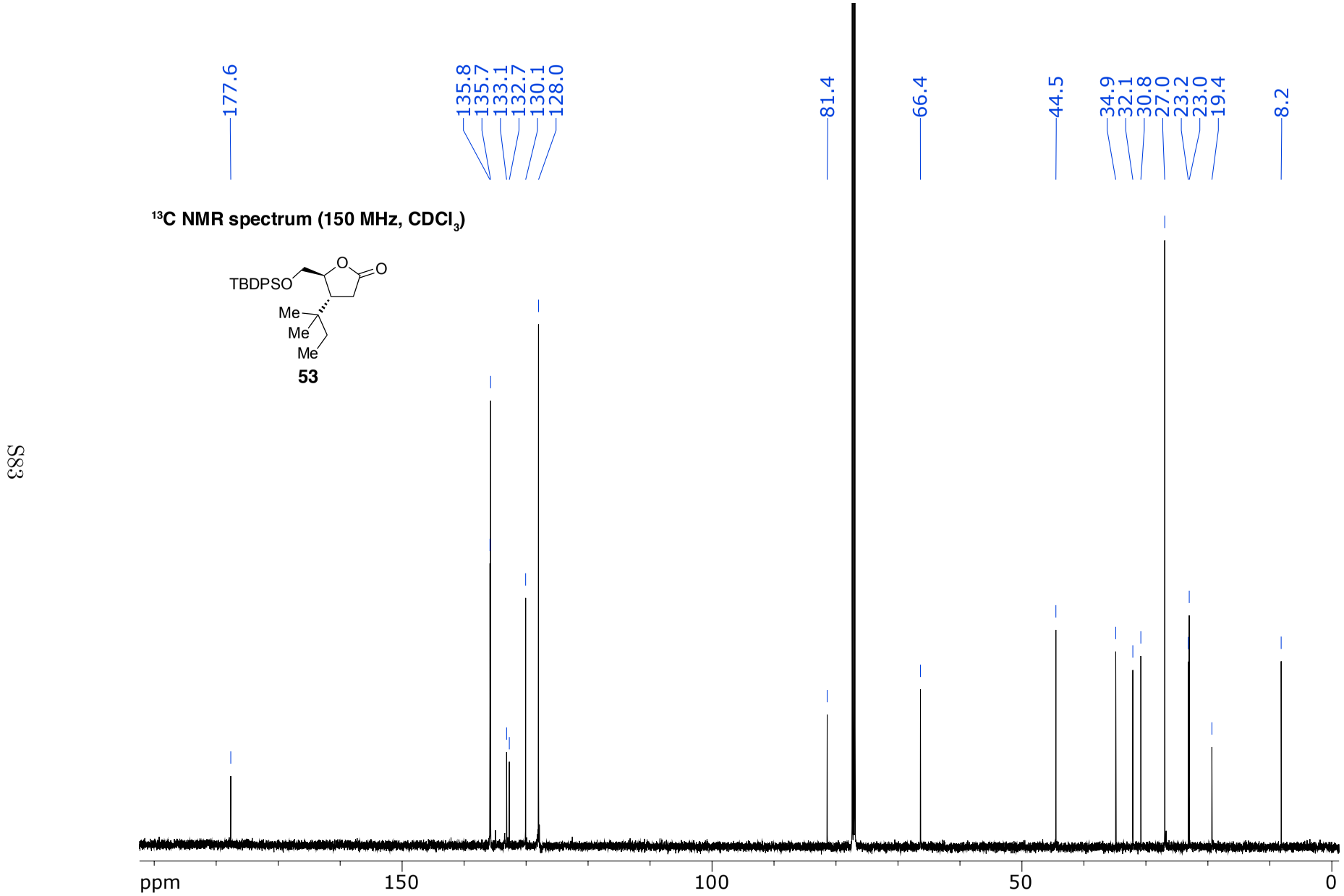
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



52


14.2
14.2
15.5
16.2
19.3
22.9
23.0
26.9
29.4
29.5
31.3
33.1
33.4
34.1
35.5
36.3
40.9
41.1
65.5
65.9
82.7
83.7
128.0
130.0
132.7
132.8
133.1
135.7
135.8
177.3
177.4
^{13}C NMR spectrum (150 MHz, CDCl$_3$)
TBDPSO
H
Me
Me
O
O
52
ppm
50
100
150


7.67
7.66
7.66
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.41
7.40
7.39
4.44
4.43
4.43
4.42
3.91
3.91
3.89
3.89
3.61
3.60
3.59
3.58
2.71
2.71
2.69
2.68
2.67
2.66
2.39
2.38
2.35
2.34
2.33
2.33
1.23
1.23
1.22
1.22
1.21
1.20
1.19
1.19
1.07
0.82
0.80
0.80
0.79
¹H NMR spectrum (600 MHz, CDCl3)
TBDPSO
O
O
Me
Me
Me
53
7
1
1
2
9
4
1
1
2
9
ppm 8
7
6
5
4
3
2
1
0



^{13}C NMR spectrum (150 MHz, $CDCl_3$)

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