Supporting Information

1,6-Conjugate addition initiated formal [4+2] annulation of *p*-quinone methides with sulfonyl allenols: a unique access to spiro[5.5]undeca-1,4-dien-3-one scaffolds

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1. General information

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining 2,4 DNP and charring on a hot gun. Solvents were removed in vacuo and heated with a water bath at 40 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet. ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system.

Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AV 400/500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet) etc. High-resolution mass spectrometry (HRMS) was performed on a TOF/Q-TOF mass spectrometer.

1.1 Preparation of *p*-quinone methides and sulfonyl allenols:

All solvents and inorganic reagents were obtained from commercial sources and used without purification unless otherwise noted. The *p*-quinone methides and sulfonyl allenols derivatives were prepared following the literature procedures.[1-5]

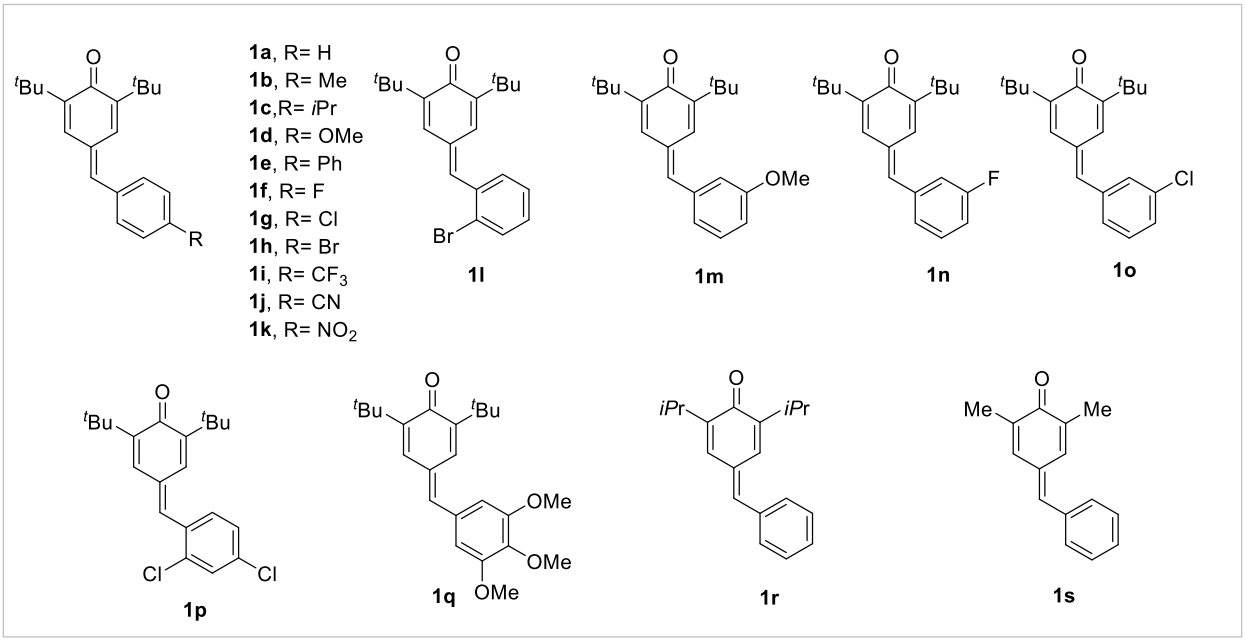


Fig. 1 Substituted *p*-quinone methides

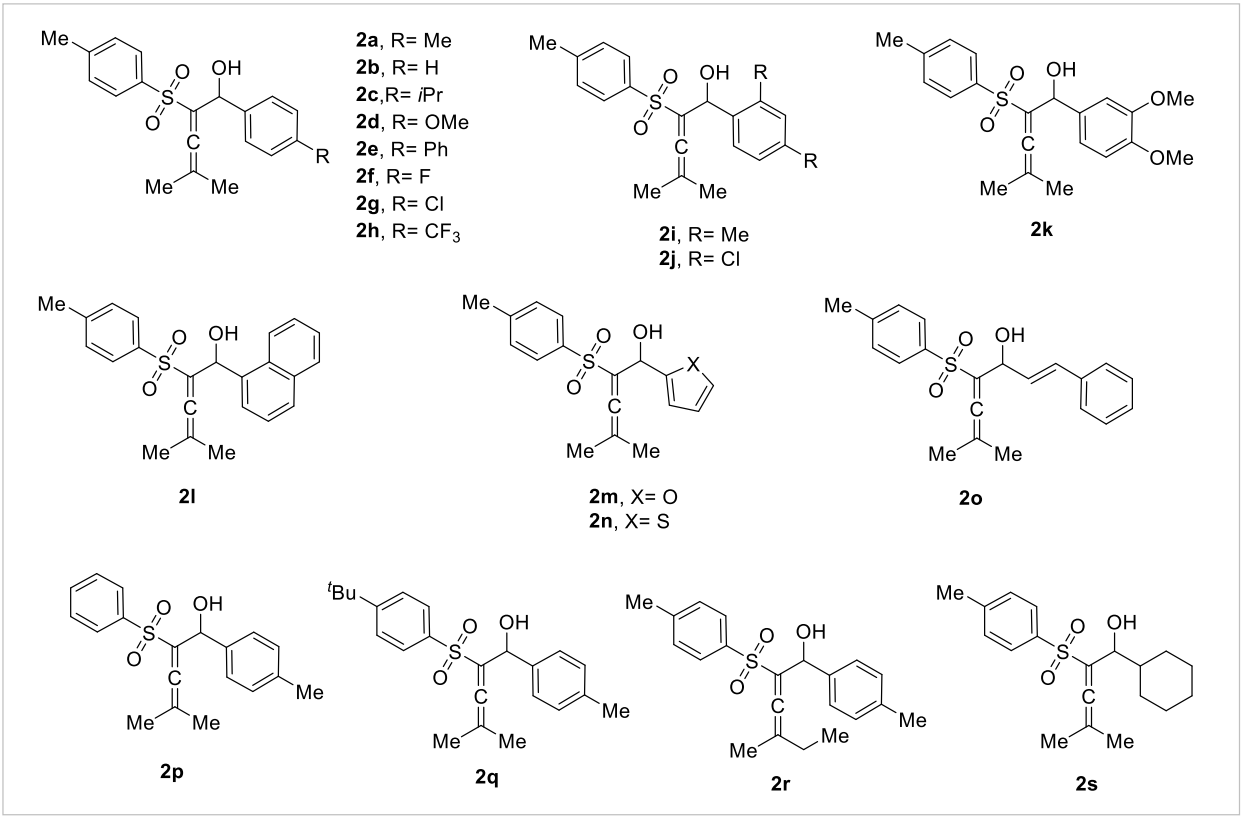
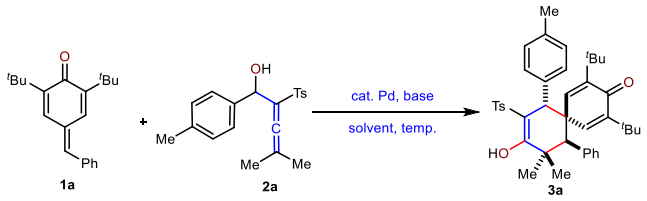


Fig.2 Substituted sulfonyl allenols

1.2 Optimization studies

Table S1. Optimization of Reaction Conditions[a]



Entry	Catalyst	Base	Solvents	Temp	Yield[b] (%)
1	$Pd(PPh_3)_4$	K_2CO_3	DMF	rt	10
2	$Pd(PPh_3)_4$	K_2CO_3	DMF	rt	22[c]
3	$Pd(PPh_3)_4$	K_2CO_3	DMF	55 °C	60
4	$Pd(PPh_3)_4$	Na_2CO_3	DMF	55 °C	NR
5	$Pd(PPh_3)_4$	K_3PO_4	DMF	55 °C	18
6	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	55 °C	28
7	$Pd(PPh_3)_4$	K_2CO_3	THF	55 °C	10
8	$Pd(PPh_3)_4$	K_2CO_3	DMSO	55 °C	NR
9	$Pd(PPh_3)_4$	K_2CO_3	ACN	55 °C	NR
10	$Pd(PPh_3)_2Cl_2$	K_2CO_3	DMF	55 °C	NR
11	$Pd_2(dba)_3$	K_2CO_3	DMF	55 °C	NR
12	$Pd(OAc)_2$	K_2CO_3	DMF	55 °C	NR
13	$Pd(OAc)_2$	K_2CO_3	DMF	55 °C	NR[d]
14	$Pd(PPh_3)_4$	K_2CO_3	DMF	70 °C	46
15	**$Pd(PPh_3)_4$**	**K_2CO_3**	**DMF**	**55 °C**	**82[e]**
16	$Pd(PPh_3)_4$	K_2CO_3	DMF	55 °C	83[f]
17	--	K_2CO_3	DMF	55 °C	NR

[a]All reactions were performed using with 0.33 mmol **1a**, 0.51 mmol **2**, 0.51 mmol base, 5 mol % $Pd(PPh_3)_4$, dry DMF (2.0 mL), 12 h; [b]Isolated yields; [c]3.0 equiv. of K_2CO_3 was employed; [d]20 mol % PPh_3 ligand was employed; [e]10 mol % $Pd(PPh_3)_4$ catalyst was employed; [f]15 mol% $Pd(PPh_3)_4$ catalyst was employed.

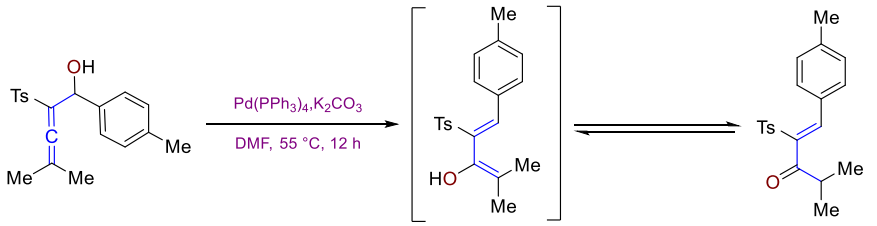
2 General procedure:

2.1 General procedure for preparation spiro[5.5]undeca-1,4-dien-3-one from *p*-QMs (3):

1 **2** **3**

To a 5 mL screw-cap vial containing a stir bar were added *p*-QMs **1** (0.33 mmol, 1.0 equiv), substituted-1-(*p*-tolyl)-2-tosylpenta-2,3-dien-1-ol **2** (0.51 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to afford a crude mixture which was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the corresponding substituted spiro[5.5]undeca-1,4-dien-3-one **3**.

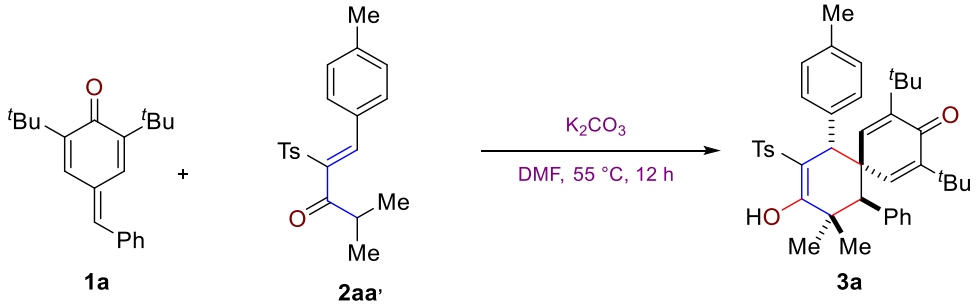
2.2 Procedure for the preparation of intermediate 2aa':



To a 5 mL screw-cap vial containing a stir bar were added 4-methyl-1-(*p*-tolyl)-2-tosylpenta-2,3-dien-1-ol **2a** (0.29 mmol, 1 equiv), $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to afford a crude mixture which was purified by column

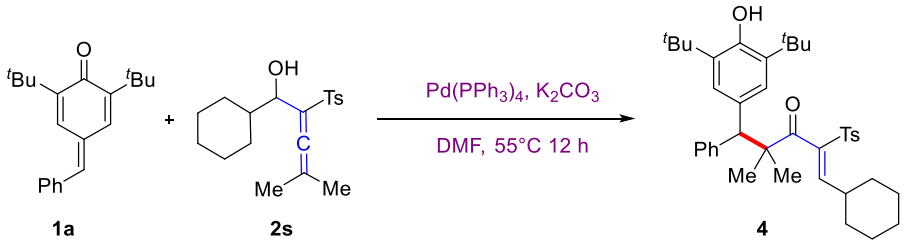
chromatography (silica gel, petroleum ether/EtOAc) to afford the corresponding intermediate **2aa'**as 57 % yield.

2.3 Control Experiment:



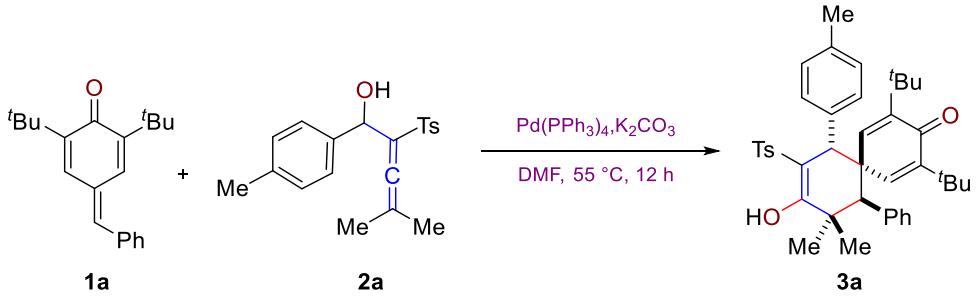
To a seal tube containing a stir bar were added *p*-QM **1a** (33 mmol, 1.0 equiv), 4-methyl-1-(*p*-tolyl)-2-tosylpent-1-en-3-one **2aa'** (0.51 mmol, 1.5 equiv), K_2CO_3 (3.0 equiv,) and dry DMF (3 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and work up with cold H_2O (3 X 10 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one **3a** in 79 %

2.4 Procedure for the preparation 1-Cyclohexyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-2-tosylpent-1-en-3-one (4):



To a 5 mL screw-cap vial containing a stir bar were added *p*-QM **1a** (0.33 mmol, 1.0 equiv), 1-Cyclohexyl-4-methyl-2-tosylpenta-2,3-dien-1-ol **2s** (0.51 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (3.0 equiv) and dry DMF (2 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and the organic layer was washed with ice cold water (3 X 10 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding **4** as 76 % yield.

2.5 Procedure for preparation 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3a):

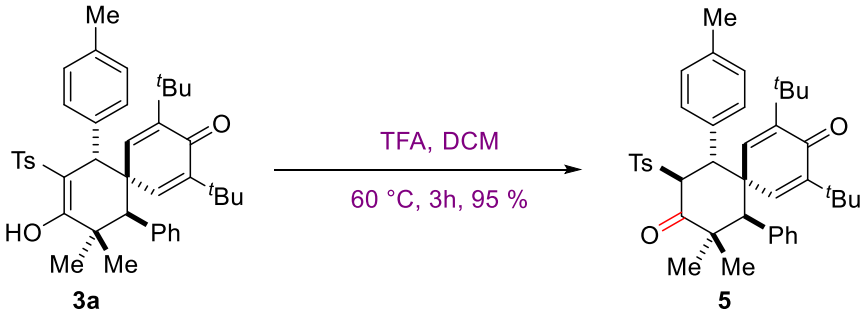


1a **2a** **3a**

To a seal tube containing a stir bar were added *p*-QM **1a** (3.3 mmol, 1.0 equiv), 4-methyl-1-(p-tolyl)-2-tosylpenta-2,3-dien-1-ol **2a** (5.1 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (3.0 equiv,) and dry DMF (30 mL). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 55 °C for 12 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with EtOAc and work up with cold H_2O (3 X 25 mL). After completion of the work up, EtOAc was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate / petroleum ether to afford corresponding 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one **3a** in 79 % yield.

2.6 Procedure for product transformations.

2.6.1 Procedure for the Synthesis of 5:

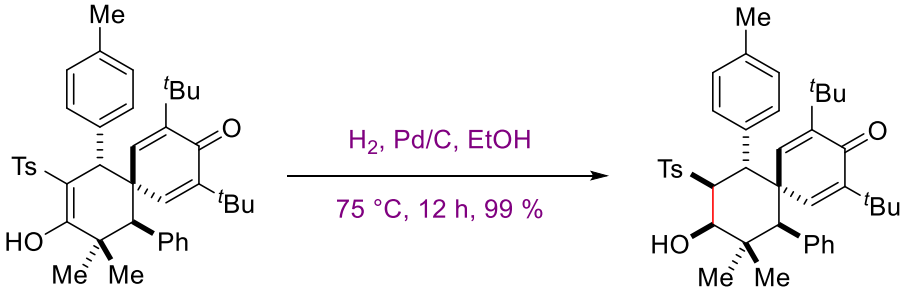


3a **5**

To a 5 mL screw-cap vial containing a stir bar were added 2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one **3a** (0.33 mmol, 1 equiv.), DCM (2.0 mL) and trifluoroacetic acid (0.5 ml). The reaction vial was fitted with a cap, evacuated, and filled with nitrogen and heated at 60 °C for 3 h. The reaction mixture was allowed to warm to ambient temperature. The reaction mixture was diluted with DCM and work up with ice cold H_2O (3 X 10 mL). After completion of the work up, DCM was evaporated on rotary evaporator and purified by flash silica gel column using a gradient of ethyl acetate /

petroleum ether to afford corresponding 2,4-di-tert-butyl-8,8-dimethyl-7-phenyl-11-(*p*-tolyl)-10-tosylspiro[5.5]undeca-1,4-diene-3,9-dione **5** in 95% yield.

2.6.2 Procedure for Synthesis of 6:



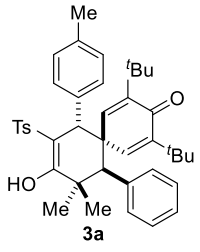
3a **6**

To the solution of **3a** (0.15 mmol, 1 equiv.) in EtOH (5 mL) was added palladium on carbon (10 mg, 10 wt %) in hydrogenation reactor and the reaction mixture was stirred under hydrogen (300 psi) with 75 °C for 12 h. After the completion of the reaction (indicated by TLC), the catalyst was filtered over a plug of Celite bed (EtOAc eluent) and the solvent was evaporated under reduced pressure to afford the corresponding product 2,4-di-tert-butyl-9-hydroxy-8,8-dimethyl-7-phenyl-11-(*p*-tolyl)-10-tosylspiro[5.5]undeca-1,4-dien-3-one **6** in 99% yield.

3. Characterization data:

All reactions were performed on 100 mg scale of *p*-Quinone Methides.

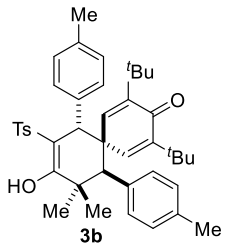
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3a):



3a

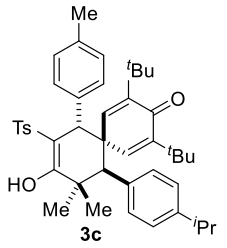
White Solid, 178 mg, 82 % yield; mp = 180-182 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (500 MHz, $CDCl_3$) δ** = 11.25 (s, 1 H), 7.64 - 7.58 (d, *J* = 8.0 Hz, 2 H), 7.25 - 7.20 (d, *J* = 8.0 Hz, 2 H), 7.14 - 7.02 (m, 5 H), 6.98 (s, 1 H), 6.95 (s, 1 H), 6.91 (d, *J* = 2.7 Hz, 1 H), 6.76 (d, *J* = 7.6 Hz, 2 H), 5.25 (d, *J* = 2.7 Hz, 1 H), 3.40 (s, 1 H), 3.23 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 9 H), 0.66 (s, 9 H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** =185.7, 169.5, 147.6, 145.6, 145.4, 144.5, 141.4, 137.4, 137.0, 136.9, 135.7, 131.9, 131.5, 129.9, 128.7, 128.6, 128.5, 128.4, 127.6, 127.4, 127.1, 127.0, 105.1, 53.5, 50.6, 44.5, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.7, 21.5, 21.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{49}O_4S$ 637.3346, found 637.3344.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7,11-di-*p*-tolyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3b):



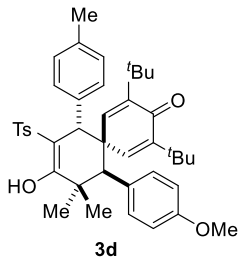
Yellow Solid, 156 mg, 74 % yield; mp = 206-207 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.24 (s, 1 H), 7.64 - 7.58 (d, *J* = 8.4 Hz, 2 H), 7.25 - 7.20 (d, *J* = 7.6 Hz, 2 H), 7.14 - 7.01 (d, 3 H), 6.87 (d, *J* = 3.1 Hz, 2 H), 6.84 - 6.72 (m, 3 H), 6.62 (s, 1 H), 5.25 (d, *J* = 3.1 Hz, 1 H), 3.38 (s, 1 H), 3.17 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 2.18 (s, 3 H), 1.40 (s, 3 H), 1.27 (s, 3 H), 1.12 (s, 9 H), 0.66 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 169.6, 147.5, 145.8, 145.2, 144.5, 141.5, 137.4, 137.0, 136.8, 135.8, 133.7, 131.8, 131.5, 129.9, 128.7, 128.6, 128.3, 128.0, 127.74, 127.70, 127.3, 105.1, 53.1, 50.5, 44.5, 40.5, 34.9, 34.4, 29.0, 28.6, 28.3, 22.7, 21.5, 21.1, 20.8; **HRMS (ESI-TOF)** m/z: $[M+H]^+$calcd for $C_{42}H_{51}O_4S$ 651.3503, found 651.3502.

2,4-Di-*tert*-butyl-9-hydroxy-11-(4-*iso*propylphenyl)-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3c):



White Solid, 146 mg, 73 % yield; mp = 193-194 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.24 (s, 1 H), 7.66 - 7.56 (m, *J* = 8.2 Hz, 2 H), 7.25 - 7.19 (m, *J* = 7.8 Hz, 2 H), 7.15 - 7.09 (m, 1 H), 7.09 - 7.00 (m, 2 H), 6.94 - 6.87 (m, 1 H), 6.87 (d, *J* = 2.7 Hz, 1 H), 6.83 (br. s., 2 H), 6.76 (d, *J* = 7.3 Hz, 1 H), 6.63 (d, *J* = 6.4 Hz, 1 H), 5.23 (d, *J* = 3.2 Hz, 1 H), 3.38 (s, 1 H), 3.18 (s, 1 H), 2.73 (spt, *J* = 6.9 Hz, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.28 (s, 3 H), 1.12 (s, 9 H), 1.09 (d, *J* = 6.9 Hz, 6 H), 0.64 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 169.7, 147.8, 147.5, 145.7, 145.2, 144.5, 141.5, 137.4, 136.9, 135.8, 134.0, 131.9, 131.5, 129.9, 128.7, 128.6, 128.5 128.4, 127.4, 125.4, 125.1, 105.0, 53.2, 50.4, 44.5, 40.5, 34.9, 34.3, 33.6, 29.0, 28.6, 28.3, 23.9, 22.7, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{44}H_{55}O_4S$ 679.3816, found 679.3820.

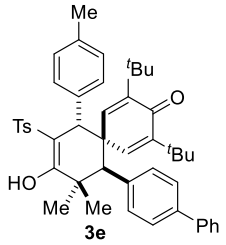
2,4-Di-tert-butyl-9-hydroxy-11-(4-methoxyphenyl)-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3d):



White Solid, 147 mg, 72 % yield; mp = 164-165 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.24 (s, 1 H), 7.63 - 7.58 (m, 2 H), 7.25 - 7.20 (m, *J* = 8.2 Hz, 2 H), 7.13 - 7.02 (m, 3 H), 6.87 (d, *J* = 3.2 Hz, 1 H), 6.84 (br. s., 1 H), 6.76 (d, *J* = 7.3 Hz, 1 H),

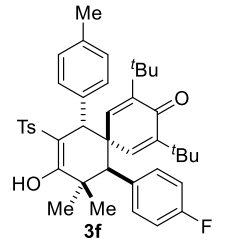
6.71 - 6.63 (m, 1 H), 6.63 - 6.57 (m, 1 H), 6.57 - 6.48 (m, 1 H), 5.26 (d, *J* = 2.7 Hz, 1 H), 3.67 (s, 3 H), 3.38 (s, 1 H), 3.17 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.25 (s, 3 H), 1.12 (s, 9 H), 0.69 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 169.6, 158.7, 147.6, 145.9, 145.3, 144.5, 141.5, 137.4, 137.0, 135.8, 133.0, 131.5, 129.9, 129.4, 129.3, 129.0, 128.7, 128.6, 128.4, 127.4, 125.3, 105.1, 55.2, 52.6, 50.6, 44.6, 40.6, 35.0, 34.4, 29.0, 28.7, 28.3, 22.6, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{51}O_5S$ 667.3452, found 667.3445.

11-([1,1'-biphenyl]-4-yl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3e):



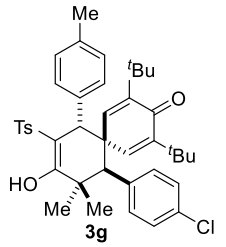
White Solid, 128 mg, 67 % yield; mp = 160-162 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.46 - 7.41 (m, 2 H), 7.40 - 7.35 (m, 2 H), 7.33 - 7.27 (m, 2 H), 7.26 - 7.20 (m, 3 H), 7.16 - 7.12 (m, 1 H), 7.11 - 7.05 (m, 2 H), 7.01 (d, *J* = 7.3 Hz, 1 H), 6.91 (d, *J* = 3.2 Hz, 1 H), 6.86 - 6.74 (m, 2 H), 5.29 (d, *J* = 2.7 Hz, 1 H), 3.42 (s, 1 H), 3.27 (s, 1 H), 2.41 (s, 3 H), 2.35 (s, 3 H), 1.46 (s, 3 H), 1.33 (s, 3 H), 1.15 (s, 10 H), 0.66 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.7, 169.4, 147.7, 145.5, 145.4, 144.5, 141.4, 140.6, 140.2, 137.3, 137.0, 136.0, 135.7, 132.4, 131.5, 129.9, 128.8, 128.8, 128.7, 128.4, 127.4, 127.2, 126.9, 126.2, 125.8, 105.1, 53.3, 50.5, 44.5, 40.5, 35.0, 34.4, 29.0, 28.6, 28.38 22.7, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{47}H_{53}O_4S$ 713.3659, found 713.3657.

2,4-Di-tert-butyl-11-(4-fluorophenyl)-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3f):



White solid, 163 mg, 78 % yield; mp = 186-188 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1 H), 7.64 - 7.55 (d, *J* = 8.4 Hz, 2 H), 7.25 - 7.18 (d, *J* = 8.4 Hz, 2 H), 7.11 - 7.02 (m, 3 H), 6.91 (s, 1 H), 6.88 (d, *J* = 3.1 Hz, 1 H), 6.73 (s, 2 H), 6.77 (s, 2 H), 5.24 (d, *J* = 3.1 Hz, 1 H), 3.39 (s, 1 H), 3.22 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.69 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.2, 163.2, 160.8, 147.9, 145.5, 144.6, 141.1, 137.2, 135.6, 133.3, 132.7, 131.5, 129.9, 128.7, 128.3, 127.4, 114.2, 105.2, 52.7, 50.6, 44.4, 40.4, 35.0, 34.4, 29.0, 28.7, 28.3, 22.5, 21.5, 21.1; **^{19}F NMR (376 MHz, CDCl$_3$) δ** = -115.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{48}O_4FS$ 655.3252, found 655.3251.

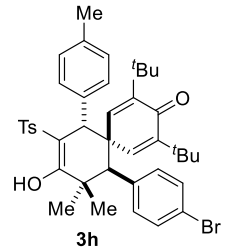
2,4-Di-tert-butyl-11-(4-chlorophenyl)-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3g):



3g

White solid, 161 mg, 79 % yield; mp = 226-227 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1 H), 7.63 - 7.56 (m, *J* = 8.3 Hz, 2 H), 7.24 - 7.19 (m, *J* = 8.1 Hz, 2 H), 7.11 - 7.03 (m, 4 H), 7.03 - 6.95 (m, 1 H), 6.95 - 6.84 (m, 2 H), 6.76 (d, *J* = 7.3 Hz, 1 H), 6.73 - 6.61 (m, 1 H), 5.23 (d, *J* = 3.2 Hz, 1 H), 3.40 (s, 1 H), 3.20 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.70 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.0, 147.9, 145.7, 145.2, 144.6, 141.0, 137.3, 137.1, 135.5, 135.5, 133.2, 131.5, 129.9, 129.6, 128.7, 128.7, 128.3, 127.6, 127.4,127.3, 127.2, 105.2, 52.9, 50.5, 44.4, 40.4, 35.0, 34.5, 29.0, 28.6, 28.3, 22.6, 21.5, 21.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{48}O_4ClS$ 671.2956, found 671.2946.

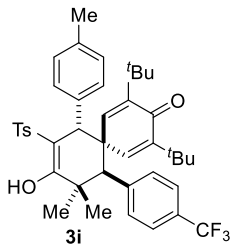
11-(4-bromophenyl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3h):



3h

Yellow Solid, 159 mg, 83 % yield; mp = 228-230 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1 H), 7.60 (d, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 3 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 7.10 - 7.02 (m, 3 H), 6.86 (d, *J* = 3.1 Hz, 1 H), 6.83 (d, J = 7.6 Hz, 1 H), 6.76 (d, *J* = 7.6 Hz, 1 H), 6.68 - 6.57 (d, 1 H), 5.23 (d, *J* = 3.1 Hz, 1 H), 3.40 (s, 1 H), 3.18 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.39 (s, 3 H), 1.24 (s, 3 H), 1.12 (s, 9 H), 0.70 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.0, 148.0, 145.7, 145.2, 144.6, 141.0, 137.2, 137.1, 136.0, 135.5, 133.5, 131.5, 130.7, 130.6, 130.2, 129.9, 128.8, 128.7, 128.2, 127.4, 121.3, 105.2, 53.0, 50.5, 44.3, 40.3, 35.0, 34.5, 29.0, 28.6, 28.3, 22.5, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{41}H_{47}O_4{}^{81}BrNaS$ 739.2250, found 739.2253.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosyl-11-(4-(trifluoromethyl) phenyl)spiro[5.5]undeca-1,4,8-trien-3-one (3i):

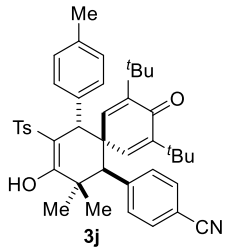


3i

White solid, 145 mg, 83 % yield; mp = 215-216 °C; R_f = 0.8 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.60 (d, *J* = 8.3 Hz, 2 H), 7.41 - 7.32 (m, 1 H), 7.25 (br. s., 1 H), 7.23 (s, 2 H), 7.14 - 7.01 (m, 4 H), 6.95 - 6.84 (m, 2 H), 6.76 (d, *J* = 8.1 Hz, 1 H), 5.22 (d, *J* = 2.9 Hz, 1 H), 3.43 (s, 1 H), 3.30 (s, 1 H), 2.40 (s, 3 H), 2.35 (s,

3 H), 1.41 (s, 3 H), 1.27 (s, 3 H), 1.14 (s, 9 H), 0.64 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.4, 168.8, 148.1, 146.5, 146.0, 144.8, 144.6, 141.2, 140.9, 137.2, 135.4, 132.1, 132.0, 131.5, 131.5, 129.9, 129.8, 129.4, 128.8, 128.8, 128.7, 128.3, 127.4, 105.3, 53.5, 50.5, 44.3, 40.4, 35.1, 34.4, 29.0, 28.6, 28.3 22.6, 21.5, 21.1; **^{19}F NMR (376 MHz, CDCl$_3$) δ** = -62.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{48}O_4F_3S$ 705.3220, found 705.3210.

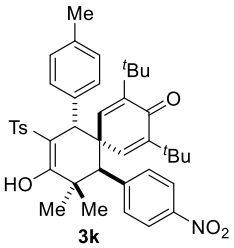
4-(8,10-Di-tert-butyl-3-hydroxy-2,2-dimethyl-9-oxo-5-(*p*-tolyl)-4-tosylspiro[5.5]undeca-3,7, 10-trien-1-yl)benzonitrile (3j):



3j

White solid, 169 mg, 82 % yield; mp = 219-220 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.68 - 7.53 (d, *J* = 7.9 Hz, 2 H), 7.40 - 7.31 (d, 2 H), 7.25 - 7.15 (d, *J* = 7.9 Hz, 2 H), 7.06 (m, 4 H), 6.89 (d, *J* = 2.4 Hz, 2 H), 6.76 (d, *J* = 7.3 Hz, 1 H), 5.20 (d, *J* = 2.4 Hz, 1 H), 3.43 (s, 1 H), 3.29 (s, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H), 1.40 (s, 3 H), 1.24 (s, 3 H), 1.13 (s, 9 H), 0.67 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.2, 168.5, 148.3, 146.3, 144.7, 144.5, 142.7, 140.7, 137.3, 137.2, 135.2, 132.5, 131.5,130.7, 130.6, 129.9, 129.2, 128.8, 128.7, 128.2, 127.4, 118.3, 111.2, 105.4, 53.7, 50.6, 44.2, 40.4, 35.1, 34.5, 29.0, 28.6, 28.3, 22.6, 21.5, 21.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{48}O_4NS$ 662.3299, found 662.3295.

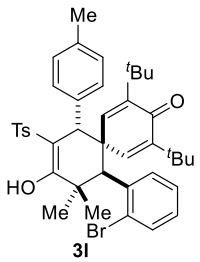
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-(4-nitrophenyl)-7-(*p*-tolyl)-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3k):



3k

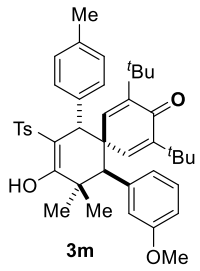
White solid, 138 mg, 69 % yield; mp = 206-207 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.28 (s, 1 H), 7.97 (d, *J* = 7.3 Hz, 1 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.62 - 7.57 (m, *J* = 8.2 Hz, 2 H), 7.24 - 7.20 (m, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 7.09 - 7.04 (m, 3 H), 6.97 (d, *J* = 7.8 Hz, 1 H), 6.91 (d, *J* = 2.7 Hz, 1 H), 6.76 (d, *J* = 7.8 Hz, 1 H), 5.22 (d, *J* = 3.2 Hz, 1 H), 3.44 (s, 1 H), 3.37 (s, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H), 1.41 (s, 3 H), 1.25 (s, 3 H), 1.14 (s, 9 H), 0.65 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ =** 185.2, 168.4, 148.5, 147.0, 146.3, 144.9, 144.7, 144.4, 140.6, 137.4, 137.1, 135.1, 132.7, 131.5, 129.9, 129.1, 128.9, 128.8, 128.2, 127.4, 122.8, 122.1, 105.4, 53.4, 50.6, 44.2, 40.3, 35.1, 34.5, 29.0, 28.6, 28.4, 22.6, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{48}O_6NS$ 682.3197, found 682.3187.

11-(2-bromophenyl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3l):



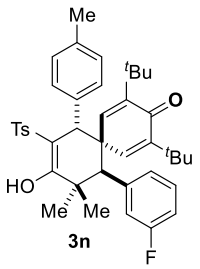
White solid, 107 mg, 56 % yield; mp = 188-189 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.26 (s, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.46 - 7.38 (m, 1 H), 7.24 - 7.14 (m, 3 H), 7.08 - 6.99 (m, 3 H), 6.98 - 6.90 (m, 2 H), 6.86 (d, *J* = 3.1 Hz, 1 H), 6.75 (d, *J* = 7.3 Hz, 1 H), 5.37 (d, *J* = 3.1 Hz, 1 H), 4.24 (s, 1 H), 3.44 (s, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 1.42 (s, 3 H), 1.35 (s, 3 H), 1.13 (s, 9 H), 0.65 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.0, 148.1, 146.0, 144.5, 144.3, 140.8, 137.5, 137.0, 136.2, 135.4, 132.9, 131.4, 130.8, 129.8, 128.8, 128.7, 128.5, 127.5, 127.4, 125.8, 105.4, 50.4, 49.4, 45.8, 41.5, 35.0, 34.4, 29.1, 28.7, 28.0 23.3, 22.6, 21.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{41}H_{47}O_4{}^{81}BrNaS$ 739.2250, found 739.2248.

2,4-Di-tert-butyl-9-hydroxy-11-(3-methoxyphenyl)-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3m):



White solid, 131 mg, 64 % yield; dr = 54:46 mp = 116-117 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1.90 H), 7.59 (d, *J* = 7.6 Hz, 3.87 H), 7.21 (d, *J* = 7.6 Hz, 3.96 H), 7.05 (t, *J* = 7.8 Hz, 5.97 H), 7.01 - 6.92 (m, 2.44 H), 6.90 (d, *J* = 9.0 Hz, 1.55 H), 6.76 (d, *J* = 6.8 Hz, 1.87 H), 6.70 - 6.61 (m, 1.94 H), 6.52 (d, *J* = 7.6 Hz, 0.85 H), 6.48 (s, 1 H), 6.35 (d, *J* = 7.6 Hz, 1 H), 6.31 (s, 0.78 H), 5.27 (d, *J* = 2.9 Hz, 1.91H), 3.68 (s, 2.72 H), 3.56 (s, 3 H), 3.40 (s, 1.92 H), 3.26 (s, 1 H), 3.15 (s, 0.84 H), 2.39 (s, 5.79 H), 2.34 (s, 5.90 H), 1.42 (s, 5.81 H), 1.28 (br. s., 6.24 H), 1.13 (s, 17.53 H), 0.69 (s, 17.45 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 185.7, 169.6, 169.4, 158.9, 158.7, 147.6, 147.5, 145.6, 145.4, 145.3, 144.5, 141.9, 141.3, 138.4, 137.3, 137.0, 135.5, 131.4, 129.8, 129.7, 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.3, 124.4, 121.2, 119.0, 114.5, 113.1, 110.7, 105.1, 55.4, 55.2, 53.6, 53.0, 50.9, 50.6, 44.4, 41.7, 40.5, 34.9, 34.4, 29.1, 29.0, 28.6, 28.3, 22.7, 22.4, 21.6, 21.5, 21.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{51}O_5S$ 667.3452, found 667.3444.

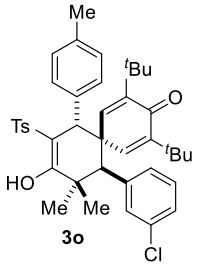
2,4-Di-tert-butyl-11-(3-fluorophenyl)-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3n):



White solid, 141 mg, 67 % yield; dr = 58:42; mp = 223-224 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.26 (s, 1.76

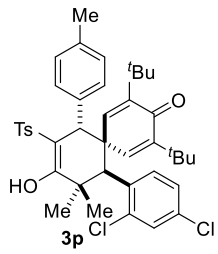
H), 7.60 (d, *J* = 7.6 Hz, 3.59 H), 7.22 (d, *J* = 7.6 Hz, 3.58 H), 7.13 - 7.01- 6.97 (m, 7.30 H), 6.87 (m, 1.89 H), 6.85 - 6.81 (m, 1.55 H), 6.81 - 6.73 (m, 2.49 H), 6.68 (d, *J* = 10.5 Hz, 1.34 H), 6.61 - 6.53 (m, 1 H), 6.53 - 6.41 (m, 0.70 H), 5.25 (br. s., 1.79 H), 3.39 (br. s., 1.77 H), 3.25 (s, 1 H), 3.18 (s, 0.73 H), 2.40 (s, 5.42 H), 2.34 (s, 5.38 H), 1.42 (s, 5.43 H), 1.27 (s, 5.50 H), 1.13 (s, 16.18 H), 0.69 (s, 16.14 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.1, 145.8, 145.7, 145.1, 144.6, 144.6, 140.8, 139.5, 139.4, 137.3, 137.2, 135.5, 135.4, 131.5, 131.5, 131.5, 129.9, 128.8, 128.7, 128.2, 127.4, 105.2, 50.6, 44.4, 40.4, 35.0, 34.4, 29.0, 28.7, 28.4, 22.7, 21.5, 21.1; **^{19}F NMR (376 MHz, CDCl$_3$) δ** = -113.6, -114.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{48}O_4FS$ 655.3252, found 655.3249.

2,4-Di-tert-butyl-11-(3-chlorophenyl)-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3o):



White solid, 161 mg, 79 % yield; dr = 57:43; mp = 190-191 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.26 (s, 1.70 H), 7.60 (m, 3.51 H), 7.23 (m, *J* = 7.3 Hz, 3.55 H), 7.14 - 7.01 (m, 7.83 H), 7.01 - 6.91 (m, 2.20 H), 6.87 (m, 2.70 H), 6.76 (d, *J* = 6.9 Hz, 2.48 H), 6.65 (d, *J* = 7.3 Hz, 1 H), 5.25 (br. s., 0.73 H), 5.21 (br. s., 1 H), 3.41 (s, 0.75 H), 3.39 (s, 1 H), 3.21 (s, 1 H), 3.16 (s, 0.76 H), 2.40 (s, 5.18 H), 2.34 (s, 5.19 H), 1.42 (s, 5.40 H), 1.26 (s, 5.54 H), 1.19 - 1.09 (m, 15.78 H), 0.69 (s, 15.71 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.0, 148.2, 147.9, 145.8, 145.1, 145.0, 144.6, 141.0, 140.8, 139.0, 137.2, 135.5, 135.4, 133.5, 133.3, 131.5, 129.9, 128.7, 128.7, 128.6, 128.2, 127.4, 127.2, 126.7, 105.1, 53.4, 53.0, 50.5, 44.3, 40.3, 35.0, 34.4, 29.0, 28.7, 28.4, 22.6, 22.4, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{41}H_{47}O_4ClNaS$ 693.2776, found 693.2780.

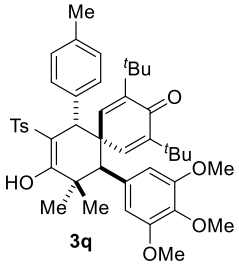
2,4-Di-tert-butyl-11-(2,4-dichlorophenyl)-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3p):



White solid, 121 mg, 62 % yield; mp = 115-117 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.26 (s, 1 H), 7.61 - 7.55 (m, *J* = 8.3 Hz, 2 H), 7.25 (d, *J* = 2.2 Hz, 1 H), 7.22 - 7.17 (m, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 6.8 Hz, 1 H), 7.04 (d, *J* = 8.1 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 1 H), 6.90 (dd, *J* = 2.2, 8.8 Hz, 1 H), 6.84 (d, *J* = 2.9 Hz, 1 H), 6.75 (d, *J* = 7.1 Hz, 1 H), 5.29 (d, *J* = 2.9 Hz, 1 H), 4.22 (s, 1 H), 3.45 (s, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 1.38 (s, 3 H), 1.32 (s, 3 H), 1.13 (s, 9 H), 0.68 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.3,

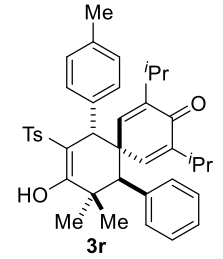
168.7, 148.3, 146.4, 144.5, 143.8, 140.6, 137.4, 137.2, 136.4, 135.2, 133.6, 133.3, 131.4, 131.2, 129.8, 129.0, 128.8, 128.6, 128.4, 127.3, 125.5, 105.4, 50.3, 46.0, 45.4, 41.2, 35.0, 34.4, 34.1, 29.1, 28.6, 28.1 23.1, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{41}H_{46}O_4Cl_2NaS$ 727.2386, found 727.2385.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(*p*-tolyl)-8-tosyl-11-(3,4,5-trimethoxyphenyl) spiro[5.5]undeca-1,4,8-trien-3-one(3q):



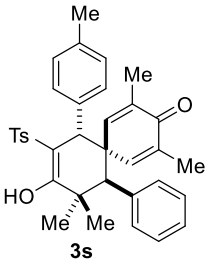
White solid, 107 mg, 57 % yield; mp = 192-194 °C; R_f = 0.3 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.59 - 7.53 (m, *J* = 8.2 Hz, 2 H), 7.20 - 7.16 (m, *J* = 8.2 Hz, 2 H), 7.07 - 7.01 (m, 3 H), 7.00 (d, *J* = 3.2 Hz, 1 H), 6.76 (d, *J* = 8.2 Hz, 1 H), 6.14 (d, *J* = 1.8 Hz, 1 H), 5.94 (d, *J* = 1.8 Hz, 1 H), 5.32 (d, *J* = 2.7 Hz, 1 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.55 (s, 3 H), 3.42 (s, 1 H), 3.17 (s, 1 H), 2.38 (s, 3 H), 2.34 (s, 3 H), 1.43 (s, 3 H), 1.27 (s, 3 H), 1.12 (s, 9 H), 0.74 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 186.0, 169.6, 152.5, 152.0, 147.6, 145.7, 145.5, 144.5, 142.5, 137.8, 137.3, 137.0, 135.4, 132.7, 131.5, 129.8, 128.7, 128.6, 128.5, 127.4, 110.0, 106.5, 105.3, 60.8, 56.6, 56.5, 53.4, 51.3, 44.5, 40.7, 35.0, 34.5, 29.3, 28.7, 28.4, 22.3, 21.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{44}H_{55}O_7S$ 727.3663, found 727.3657.

9-Hydroxy-2,4-diisopropyl-10,10-dimethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3r):



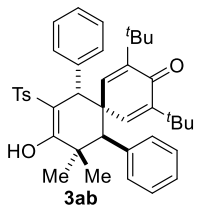
White solid, 153 mg, 67 % yield; mp = 166-168 °C; R_f = 0.4 (Pet. ether/Ethyl acetate- 95:05); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.28 (s, 1 H), 7.60 - 7.55 (m, *J* = 8.2 Hz, 2 H), 7.21 - 7.16 (m, *J* = 8.2 Hz, 2 H), 7.12 - 6.99 (m, 5 H), 6.99 - 6.86 (m, 3 H), 6.75 (d, *J* = 7.3 Hz, 2 H), 5.28 (d, *J* = 2.3 Hz, 1 H), 3.43 (s, 1 H), 3.28 (s, 1 H), 3.01 (spt, *J* = 6.8 Hz, 1 H), 2.63 (spt, *J* = 6.8 Hz, 1 H), 2.39 (s, 3 H), 2.34 (s, 3 H), 1.40 (s, 3 H), 1.27 (s, 3 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 0.85 (d, *J* = 6.9 Hz, 3 H), 0.63 (d, *J* = 6.9 Hz, 3 H), 0.09 (d, *J* = 6.9 Hz, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 184.5, 169.5, 145.8, 145.7, 144.5, 144.0, 141.9, 137.3, 137.0, 136.8, 135.5, 131.9, 131.6, 129.8, 128.6, 128.4, 127.6, 127.4, 127.2, 105.1, 53.3, 50.4, 44.6, 40.6, 28.1, 26.6, 25.4, 22.6, 21.6, 21.5, 21.5, 21.3, 21.0, 20.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{39}H_{45}O_4S$ 609.3033, found 609.3024.

9-Hydroxy-2,4,10,10-tetramethyl-11-phenyl-7-(*p*-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3s):



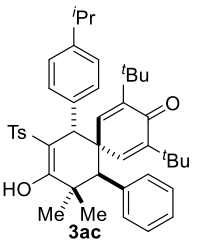
White solid, 162 mg, 62 % yield; mp = 164-166 °C; R_f = 0.3 (Pet. ether/Ethyl acetate- 95:05); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.21 (s, 1 H), 7.76 (dd, *J* = 1.4, 8.2 Hz, 1 H), 7.54 - 7.50 (m, 3 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 7.13 - 7.05 (m, 2 H), 7.05 - 6.98 (m, 4 H), 6.93 (m, 1 H), 6.76 (m, 1 H), 5.43 (dd, *J* = 1.4, 3.2 Hz, 1 H), 3.45 (s, 1 H), 3.23 (s, 1 H), 2.40 (s, 3 H), 2.32 (s, 3 H), 2.29 (s, 3 H), 1.81 (s, 3 H), 1.40 (s, 3 H), 1.20 (s, 3 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 186.5, 169.3, 156.5, 149.5, 146.1, 144.4, 138.4, 137.2, 137.0, 136.7, 136.1, 135.3, 134.4, 131.7, 131.5, 129.7, 129.5, 128.7, 128.1, 127.5, 127.2, 122.8, 105.2, 52.9, 51.0, 45.5, 40.6, 28.0, 22.7, 21.5, 21.0, 16.7, 15.9, 15.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{35}H_{37}O_4S$ 553.2412, found 553.2412.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7,11-diphenyl-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ab) :



White solid, 160 mg, 76 % yield; mp = 217-218 °C; R_f = 0.8 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.65 - 7.57 (m, 2 H), 7.29 - 7.20 (m, 6 H), 7.12 - 7.04 (m, 2 H), 7.02 - 6.92 (m, 2 H), 6.91 (d, *J* = 3.2 Hz, 1 H), 6.90 - 6.86 (m, 1 H), 6.77 - 6.68 (m, 1 H), 5.19 (d, *J* = 3.2 Hz, 1 H), 3.44 (s, 1 H), 3.22 (s, 1 H), 2.39 (s, 3 H), 1.42 (s, 3 H), 1.29 (s, 3 H), 1.14 (s, 9 H), 0.64 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.7, 169.6, 147.6, 145.4, 144.6, 141.3, 138.8, 137.2, 136.7, 131.9, 131.7, 129.9, 128.5, 128.4, 128.0, 127.8, 127.6, 127.4, 127.2, 127.0, 104.9, 53.5, 50.9, 44.4, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.7, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{40}H_{47}O_4S$ 623.3190, found 623.3186.

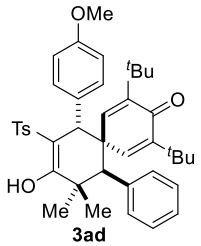
2,4-Di-tert-butyl-9-hydroxy-7-(4-isopropylphenyl)-10,10-dimethyl-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3ac):



White solid, 159 mg, 71 % yield; mp = 207-209 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.24 (s, 1 H), 7.58 - 7.53 (m, 2 H), 7.19 - 7.14 (m, 2 H), 7.13 - 7.07 (m, 2 H), 7.05 (s, 3 H), 6.98 (d, *J* = 3.2 Hz, 3 H), 6.78 (d, *J* = 8.1 Hz, 2 H), 5.19 (d, *J* = 2.9 Hz, 1 H), 3.49 (s, 1 H), 3.23 (s, 1 H), 2.87 (spt, *J* = 6.9 Hz, 1 H), 2.37 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.25 (d, *J* = 2.7 Hz, 3 H), 1.23 (d, *J* = 2.4 Hz, 3 H), 1.18 (s, 9 H), 0.64 (s, 9

H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 185.7, 169.4, 147.9, 147.6, 145.6, 145.3, 144.2, 141.5, 137.6, 136.9, 135.9, 131.9, 131.6, 129.7, 128.6, 128.1, 127.3, 127.1, 127.0, 125.9, 125.8, 105.2, 53.5, 50.6, 44.5, 40.5, 35.0, 34.3, 33.6, , 29.1, 28.5, 28.3, 24.1, 23.8, 22.8, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{43}H_{53}O_4S$ 665.3659, found 665.3660.

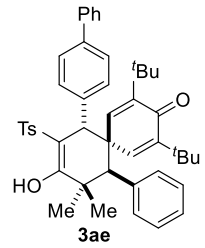
2,4-Di-tert-butyl-9-hydroxy-7-(4-methoxyphenyl)-10,10-dimethyl-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3ad):



3ad

White solid, 164 mg, 74 % yield; mp = 170-172 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 11.24 (s, 1 H), 7.66 - 7.57 (d, *J* = 8.4 Hz, 2 H), 7.26 - 7.19 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 7.11 - 7.04 (m, 2 H), 7.01 - 6.88 (m, 3 H), 6.83 - 6.71 (m, 4 H), 5.26 (d, *J* = 3.1 Hz, 1 H), 3.81 (s, 3 H), 3.40 (s, 1 H), 3.20 (s, 1 H), 2.40 (s, 3 H), 1.40 (s, 3 H), 1.28 (s, 3 H), 1.13 (s, 9 H), 0.66 (s, 9 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 185.7, 169.4, 158.8, 147.6, 145.6, 145.4, 144.5, 141.4, 137.4, 136.8, 132.5, 131.9, 130.7, 129.9, 129.5, 128.5, 127.6, 127.3, 127.1, 127.0, 113.5, 113.0, 105.2, 55.2, 53.5, 50.2, 44.6, 40.5, 35.0, 34.3, 29.0, 28.6, 28.3, 22.6, 21.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{41}H_{48}O_5NaS$ 675.3115, found 675.3109.

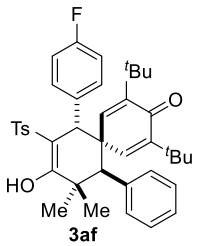
7-([1,1'-biphenyl]-4-yl)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3ae):



3ae

White solid, 168 mg, 71 % yield; mp = 227-228 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 11.30 (s, 1 H), 7.64 - 7.58 (m, 4 H), 7.50 - 7.45 (m, 4 H), 7.40 - 7.35 (m, 1 H), 7.26 (m, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.13 - 7.05 (m, 2 H), 7.04 - 6.91 (m, 4 H), 6.77 (s, 1 H), 5.29 (d, *J* = 2.7 Hz, 1 H), 3.53 (s, 1 H), 3.26 (s, 1 H), 2.34 (s, 3 H), 1.45 (s, 3 H), 1.31 (s, 3 H), 1.17 (s, 9 H), 0.67 (s, 9 H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** = 185.7, 169.7, 147.7, 145.6, 145.3, 144.6, 141.3, 140.4, 140.1, 137.8, 137.4, 136.7, 132.1, 131.9, 130.3, 129.9, 129.0, 128.9, 128.8, 128.5, 127.7, 127.4, 127.2, 127.0, 126.6, 126.4, 105.0, 53.7, 50.7, 44.5, 40.6, 35.0, 34.4, 29.1, 28.6, 28.3, 22.7, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{46}H_{51}O_4S$ 699.3503, found 699.3502.

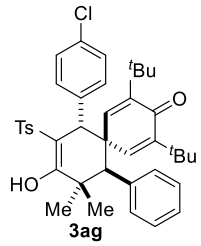
2,4-Di-tert-butyl-7-(4-fluorophenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3af):



3af

White solid, 176 mg, 81 % yield; mp = 209-211 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.27 (s, 1 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.24 (dd, *J* = 0.7, 8.6 Hz, 2 H), 7.19 (br. s., 1 H), 7.13 - 7.06 (m, 2 H), 7.04 - 6.91 (m, 4 H), 6.90 (d, *J* = 3.2 Hz, 1 H), 6.89 - 6.81 (m, 1 H), 6.73 (m, 1 H), 5.19 (d, *J* = 3.2 Hz, 1 H), 3.43 (s, 1 H), 3.15 (s, 1 H), 2.41 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.14 (s, 9 H), 0.65 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.6, 169.8, 163.2, 160.8, 147.8, 145.8, 144.8, 141.1, 137.2, 136.6, 134.7, 133.1, 133.0, 131.9, 130.0, 128.4, 127.7, 127.3, 127.0, 114.9, 114.7, 105.0, 53.6, 50.3, 44.4, 44.3, 40.5, 35.0, 34.4, 29.0, 28.6, 28.4, 22.7, 21.5; **^{19}F NMR (376 MHz, CDCl$_3$) δ** = -114.9; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{40}H_{45}O_4FNaS$ 663.2915, found 663.2899.

2,4-Di-tert-butyl-7-(4-chlorophenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3ag):

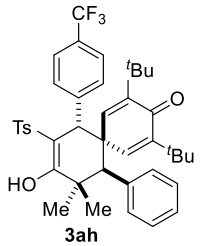


3ag

White solid, 176 mg, 79 % yield; mp = 201-202 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.28 (s, 1 H), 7.62 - 7.55 (m, 2 H), 7.23 (dd, *J* = 5.3, 7.6 Hz, 4 H), 7.17 - 7.05 (m, 3 H), 6.99 (m, 1 H), 6.94 (m, 1 H), 6.91 (d, *J* = 2.7 Hz, 1 H), 6.83 (d, *J* = 7.3 Hz, 1 H), 6.78 - 6.67 (m, 1 H), 5.19 (d, *J* = 2.7 Hz, 1 H), 3.42 (s, 1 H), 3.12 (s, 1 H), 2.42 (s, 3 H), 1.40 (s, 3 H), 1.28 (s, 3 H), 1.14 (s, 9 H), 0.66 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 169.9, 147.9, 145.9, 144.9, 144.8, 141.0, 137.5, 137.1, 136.5, 133.3, 132.8, 131.9, 130.0, 129.8, 128.4, 128.2, 127.9, 127.7, 127.3, 127.1, 104.8, 53.7, 50.4, 44.3, 40.6, 35.0, 34.4, 29.0, 28.6, 28.4, 22.7, 21.5; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{40}H_{45}O_4ClNaS$ 679.2619, found 679.2613.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosyl-7-(4 (trifluoromethyl)phenyl) spiro[5.5]undeca-1,4,8-trien-3-one (3ah):

White solid, 190 mg, 81 % yield; mp = 258-260 °C; R_f = 0.8 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.32 (s, 1 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 6.8 Hz, 2 H),

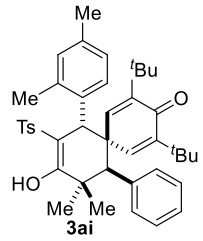


3ah

7.31 - 7.23 (m, 1 H), 7.21 - 7.16 (m, 2 H), 7.11 (d, *J* = 6.6 Hz, 2 H), 7.06 - 6.90 (m, 4 H), 6.81 - 6.66 (m, 1 H), 5.12 (d, *J* = 3.2 Hz, 1 H), 3.57 (s, 1 H), 3.12 (s, 1 H), 2.38 (s, 3 H), 1.42 (s, 3 H), 1.31 (s, 3 H), 1.18 (s, 9 H), 0.64 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.5, 170.2, 148.0, 146.2, 144.9, 144.3, 143.1, 140.8, 137.1, 136.3, 132.1, 129.9, 129.4, 128.8, 128.4,

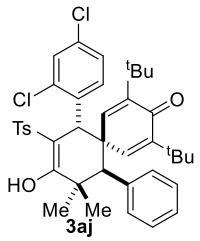
127.8, 127.4, 127.3, 127.1, 125.3, 124.9, 124.5, 122.6, 104.6, 53.8, 50.8, 44.2, 40.7, 35.1, 34.4, 29.1, 28.6, 28.4, 22.8, 21.4; **^{19}F NMR (376 MHz, $CDCl_3$) δ** = -62.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{46}O_4F_3S$ 691.3063, found 691.3058.

2,4-Di-tert-butyl-7-(2,4-dimethylphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3ai):



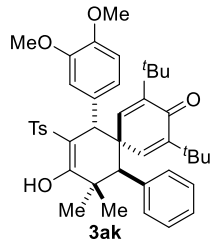
White solid, 183 mg, 83 % yield; mp = 215-217 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz**, **$CDCl_3$) δ** = 11.17 (s, 1 H), 7.59 - 7.51 (d, *J* = 8.4 Hz, 2 H), 7.22 - 7.17 (d, *J* = 7.6 Hz, 2 H), 7.08 (d, *J* = 3.8 Hz, 2 H), 7.03 - 6.96 (m, 2 H), 6.96 - 6.91 (m, 1 H), 6.91 - 6.85 (m, 3 H), 6.79 - 6.70 (m, 1 H), 5.28 (d, *J* = 2.3 Hz, 1 H), 3.82 (s, 1 H), 3.40 (s, 1 H), 2.40 (s, 3 H), 2.29 (s, 3 H), 2.05 (s, 3 H), 1.40 (s, 3 H), 1.30 (s, 3 H), 1.16 (s, 9 H), 0.57 (s, 9 H); **^{13}C NMR (100 MHz**, **$CDCl_3$) δ** = 185.4, 169.2, 147.4, 145.9, 144.4, 144.2, 141.3, 137.7, 136.7, 136.5, 134.1, 132.1, 131.5, 129.7, 128.7, 128.5, 127.7, 127.1, 127.0, 126.5, 105.8, 53.3, 44.5, 44.2, 40.3, 35.0, 34.1, 29.1, 28.3, 28.1, 22.8, 21.5, 20.9, 20.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{51}O_4S$ 651.3503, found 651.3497.

2,4-Di-tert-butyl-7-(2,4-dimethylphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3aj):



White solid, 183 mg, 78 % yield; mp = 239-241 °C; R_f = 0.8 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz**, **$CDCl_3$) δ** = 11.30 (s, 1 H), 7.75 - 7.69 (m, 2 H), 7.38 (d, *J* = 1.8 Hz, 1 H), 7.34 - 7.27 (m, 4 H), 7.15 - 7.08 (m, 2 H), 7.03 - 6.95 (m, 1 H), 6.91 (d, *J* = 8.2 Hz, 1 H), 6.76 (br. s., 1 H), 6.70 (d, *J* = 3.2 Hz, 1 H), 5.18 (d, *J* = 3.2 Hz, 1 H), 4.05 (s, 1 H), 3.19 (s, 1 H), 2.43 (s, 3 H), 1.41 (s, 3 H), 1.29 (s, 3 H), 1.08 (s, 9 H), 0.61 (s, 9 H); **^{13}C NMR (100 MHz**, **$CDCl_3$) δ** = 185.1, 170.1, 148.0, 146.6, 145.1, 142.4, 139.7, 136.6, 136.2, 136.0, 135.6, 133.8, 132.0, 131.1, 130.1, 129.6, 128.4, 127.8, 127.6, 127.4, 127.1, 127.0, 104.5, 53.7, 44.6, 44.0, 40.4, 34.9, 34.2, 28.9, 28.4, 28.2, 22.7, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{40}H_{45}O_4Cl_2S$ 691.2410, found 691.2402.

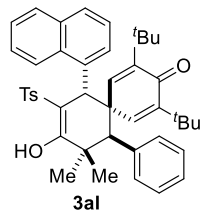
2,4-Di-tert-butyl-7-(3,4-dimethoxyphenyl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosyl spiro[5.5]undeca-1,4,8-trien-3-one (3ak):



3ak

White solid, 153 mg, 66 % yield; dr = 57:43; mp = 199-201 °C; R_f = 0.4 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.24 (s, 0.72 H), 11.20 (s, 1 H), 7.59 (d, *J* = 7.8 Hz, 2 H), 7.54 (d, *J* = 7.8 Hz, 1.46 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 7.8 Hz, 1.60 H), 7.14 - 7.05 (m, 3.53 H), 7.03 - 6.89 (m, 5.32 H), 6.75 (d, *J* = 8.2 Hz, 1.70 H), 6.72 (s, 2.81 H), 6.59 (s, 0.75 H), 6.48 (d, *J* = 7.3 Hz, 0.75 H), 6.35 (s, 1 H), 5.31 (d, *J* = 2.7 Hz, 1 H), 5.24 (d, *J* = 2.7 Hz, 0.70 H), 3.89 (s, 5.37 H), 3.82 (d, *J* = 4.6 Hz, 5.38 H), 3.53 (s, 0.75 H), 3.38 (s, 1 H), 3.27 (s, 1.76 H), 2.39 (s, 5.31 H), 1.40 (s, 5.37 H), 1.29 (d, *J* = 4.6 Hz, 5.73 H), 1.18 (d, *J* = 7.3 Hz, 16 H), 0.65 (s, 16 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 185.7, 169.4, 148.3, 148.2, 148.1, 147.7, 145.5, 145.4, 144.4, 141.6, 141.3, 137.6, 136.8, 136.7, 131.9, 131.1, 129.8, 129.7, 128.5, 127.7, 127.3, 127.2, 127.0, 123.9, 121.2, 114.0, 111.7, 110.5, 110.2, 105.7, 105.5, 55.7, 55.7, 55.6, 53.8, 53.7, 50.5, 44.7, 40.5, 40.5, 35.0, 34.3, 29.1, 28.7, 28.7, 28.3, 22.7, 22.6, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{51}O_6S$ 683.3401, found 683.3408.

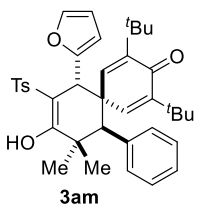
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-7-(naphthalen-1-yl)-11-phenyl-8-tosylspiro [5.5]undeca-1,4,8-trien-3-one (3al):



3al

White solid, 155 mg, 68 % yield; mp = 258-260 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.32 (s, 1 H), 7.84 - 7.80 (m, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.52 - 7.36 (m, 7 H), 7.05 (dd, *J* = 2.3, 5.5 Hz, 4 H), 7.03 - 6.91 (m, 3 H), 6.67 (d, *J* = 7.3 Hz, 1 H), 4.85 (d, *J* = 3.2 Hz, 1 H), 4.47 (s, 1 H), 3.42 (s, 1 H), 2.32 (s, 3 H), 1.47 (s, 3 H), 1.35 (s, 3 H), 1.24 (s, 9 H), 0.19 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.4, 169.6, 148.0, 145.1, 145.0, 144.5, 141.1, 136.7, 136.6, 134.8, 133.7, 132.1, 131.9, 129.6, 128.8, 128.4, 128.1, 127.6, 127.53, 127.5, 127.1, 127.0, 126.3, 125.6, 124.6, 123.9, 105.4, 53.6, 44.8, 43.6, 40.5, 35.1, 33.8, 29.2, 28.1, 27.6, 22.9, 21.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{44}H_{49}O_4S$ 673.3346, found 673.3328.

2,4-Di-tert-butyl-7-(furan-2-yl)-9-hydroxy-10,10-dimethyl-11-phenyl-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3am):

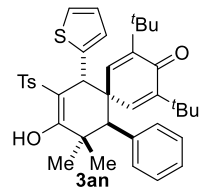


3am

White solid, 162 mg, 78 % yield; mp = 183-184 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.15 (s, 1 H), 7.70 - 7.66 (m, 2 H), 7.29 (dd, *J* = 1.0, 1.7 Hz, 2 H), 7.27 (d, *J* = 0.7 Hz, 1 H), 7.12 (s, 2

H), 7.00 (s, 1 H), 6.93 (s, 1 H), 6.84 (s, 1 H), 6.79 (d, *J* = 3.2 Hz, 1 H), 6.32 - 6.28 (m, 1 H), 6.09 (dd, *J* = 0.6, 2.6 Hz, 1 H), 5.37 (d, *J* = 3.2 Hz, 1 H), 3.49 (s, 1 H), 3.39 (s, 1 H), 2.41 (s, 3 H), 1.37 (s, 3 H), 1.25 (s, 3 H), 1.11 (s, 9 H), 0.70 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.6, 169.9, 152.8, 148.4, 146.2, 144.6, 144.4, 141.8, 139.7, 137.3, 136.9, 130.0, 127.2, 110.7, 109.9, 103.6, 54.9, 44.8, 44.2, 40.5, 35.0, 34.2, 29.0, 28.6, 28.4, 22.5, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{38}H_{45}O_5S$ 613.2982, found 613.2976.

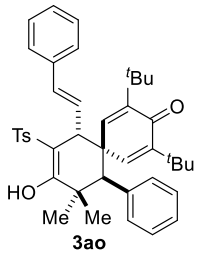
2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-(thiophen-2-yl)-8-tosylspiro[5.5] undeca-1,4,8-trien-3-one (3an):



3an

White solid, 134 mg, 63 % yield; mp = 213-215 °C; R_f = 0.8 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.17 (s, 1 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.20 (dd, *J* = 0.9, 5.0 Hz, 1 H), 7.12 (d, 2 H), 7.01 (m, 1 H), 6.96 (m, 1 H), 6.91 (dd, *J* = 3.7, 5.0 Hz, 1 H), 6.87 (d, *J* = 3.2 Hz, 1 H), 6.84 (m, 1 H), 6.73 (d, *J* = 3.2 Hz, 1 H), 5.51 (d, *J* = 3.2 Hz, 1 H), 3.70 (s, 1 H), 3.52 (s, 1 H), 2.41 (s, 3 H), 1.41 (s, 3 H), 1.27 (s, 3 H), 1.13 (s, 9 H), 0.69 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.6, 169.5, 148.2, 145.9, 145.0, 144.6, 143.6, 140.4, 137.4, 136.8, 131.9, 129.9, 128.4, 127.8, 127.7, 127.2, 127.1, 126.7, 125.3, 106.6, 54.1, 46.0, 44.5, 40.5, 35.0, 34.4, 29.0, 28.6, 28.3, 22.7, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{38}H_{45}O_4S_2$ 629.2754, found 629.2749.

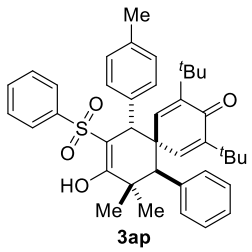
(*E*)-2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-7-styryl-8-tosylspiro[5.5]undeca -1,4,8-trien-3-one (3ao):



3ao

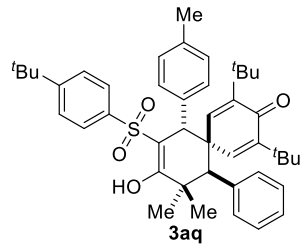
White solid, 146 mg, 66 % yield; mp = 247-249 °C; R_f = 0.6 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (500 MHz, CDCl$_3$) δ** = 11.21 (s, 1 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 7.2 Hz, 2 H), 7.30 - 7.21 (m, 5 H), 7.15 (m, 2 H), 7.03 (m, 1 H), 6.94 (m, 2 H), 6.90 (d, *J* = 3.1 Hz, 1 H), 6.32 (d, *J* = 15.6 Hz, 1 H), 6.09 - 5.98 (m, 2 H), 3.26 (s, 1 H), 3.03 (d, *J* = 7.6 Hz, 1 H), 2.30 (s, 3 H), 1.36 (s, 3 H), 1.25 (s, 3 H), 1.16 (s, 9 H), 0.79 (s, 9 H); **^{13}C NMR (125 MHz, CDCl$_3$) δ** = 185.6, 169.5, 148.0, 146.4, 144.8, 140.8, 137.7, 137.0, 136.4, 135.0, 131.9, 131.4, 130.1, 129.1, 128.6, 128.5, 128.3, 127.8, 127.5, 127.3, 127.1, 126.4, 104.9, 55.2, 47.9, 45.1, 40.7, 35.0, 34.5, 29.0, 28.9, 28.7, 22.6, 21.4; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{42}H_{48}O_4SNa$ 671.3448, found 671.3448.

2,4-Di-tert-butyl-9-hydroxy-10,10-dimethyl-11-phenyl-8-(phenylsulfonyl)-7-(p-tolyl)spiro [5.5]undeca-1,4,8-trien-3-one (3ap):



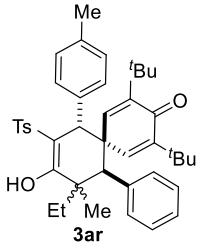
White solid, 150 mg, 71 % yield; mp = 192-194 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1 H), 7.75 - 7.68 (m, 2 H), 7.58 - 7.51 (m, 1 H), 7.45 - 7.38 (m, 2 H), 7.14 - 6.98 (m, 6 H), 6.96 (d, *J* = 3.2 Hz, 2 H), 6.82 - 6.68 (m, 2 H), 5.25 (d, *J* = 3.2 Hz, 1 H), 3.47 (s, 1 H), 3.23 (s, 1 H), 2.32 (s, 3 H), 1.41 (s, 3 H), 1.30 (s, 3 H), 1.15 (s, 9 H), 0.66 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.7, 170.1, 147.7, 145.5, 145.4, 141.4, 140.5, 137.0, 136.8, 135.5, 133.3, 131.6, 129.2, 128.6, 128.5, 128.3, 127.3, 127.2, 105.0, 53.5, 50.6, 44.5, 40.6, 35.0, 34.4, 29.2, 28.6, 28.3, 22.7, 21.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{40}H_{46}O_4SNa$ 645.3439, found 645.3439.

2,4-Di-tert-butyl-8-((4-(tert-butyl)phenyl)sulfonyl)-9-hydroxy-10,10-dimethyl-11-phenyl-7-(p-tolyl)spiro[5.5]undeca-1,4,8-trien-3-one (3aq):



White solid, 180 mg, 78 % yield; mp = 192-194 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.25 (s, 1 H), 7.64 - 7.60 (m, 2 H), 7.43 - 7.38 (m, 2 H), 7.12 - 7.06 (m, 2 H), 7.06 - 7.00 (m, 3 H), 7.00 - 6.92 (m, 3 H), 6.79 (d, *J* = 7.3 Hz, 1 H), 6.74 (s, 1 H), 5.25 (d, *J* = 3.2 Hz, 1 H), 3.51 (s, 1 H), 3.22 (s, 1 H), 2.31 (s, 3 H), 1.41 (s, 3 H), 1.32 (s, 9 H), 1.29 (s, 3 H), 1.15 (s, 9 H), 0.65 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.7, 169.7, 157.3, 147.5, 145.6, 145.5, 145.5, 141.6, 137.5, 136.9, 136.8, 135.7, 132.0, 131.9, 131.6, 128.6, 128.5, 128.3, 127.6, 127.2, 127.1, 126.2, 105.2, 53.5, 50.6, 44.5, 40.5, 35.2, 35.1, 34.4, 31.0, 29.3, 28.6, 28.3, 22.7, 21.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{44}H_{54}O_4SNa$ 701.8619, found 701.8619.

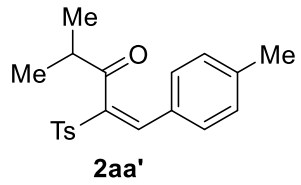
2,4-Di-tert-butyl-10-ethyl-9-hydroxy-10-methyl-11-phenyl-7-(p-tolyl)-8-tosylspiro[5.5]undeca-1,4,8-trien-3-one (3ar):



White solid, 152 mg, 69 % yield; dr = 67:34; mp = 185-186 °C; R_f = 0.7 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 11.34 (s, 0.97 H), 11.28 (s, 0.51 H), 7.64 - 7.56 (m, 3.13 H), 7.26 - 7.20 (m, 3.36 H), 7.18 - 7.13 (m, 0.92 H), 7.09 - 7.05 (m, 3 H), 7.04 - 7.02 (m, 3.38 H), 7.00 - 6.94 (m, 1.64 H), 6.94 - 6.86 (m, 2.98 H), 6.76 (d, *J* = 6.1 Hz, 2.25 H), 5.25 (d, *J*

= 2.9 Hz, 1 H), 5.20 (d, *J* = 2.9 Hz, 0.51 H), 3.45 (s, 1 H), 3.38 (s, 1 H), 3.37 (s, 0.50 H), 3.24 (s, 0.51 H), 2.41 (s, 4.76 H), 2.36 - 2.31 (m, 4.71 H), 2.07 - 1.97 (m, 0.53 H), 1.93 - 1.83 (m, 1 H), 1.64 (qd, *J* = 7.4, 14.6 Hz, 0.68 H), 1.45 (s, 1.62 H), 1.39 - 1.34 (m, 1.17 H), 1.32 (s, 3.30 H), 1.25 - 1.19 (m, 3.30 H), 1.14 (s, 9.40 H), 1.12 (s, 4.72 H), 0.77 (t, *J* = 7.5 Hz, 1.93 H), 0.66 (s, 4.80 H), 0.63 (s, 9.50 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.8, 170.4, 169.0, 147.0, 146.8, 146.1, 146.0, 145.3, 145.0, 144.5, 144.5, 142.3, 142.0, 137.7, 137.6, 137.3, 137.1, 137.0, 136.9, 136.0, 135.8, 129.9, 129.8, 128.5, 127.7, 127.3, 127.2, 127.1, 106.8, 105.4, 76.7, 54.3, 51.1, 50.2, 48.9, 44.5, 44.2, 44.2, 42.9, 35.0, 34.9, 34.4, 34.3, 32.7, 29.0, 29.0, 28.6, 28.6, 27.8, 24.5, 23.2, 21.5, 21.5, 21.1, 21.0, 10.8, 10.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{42}H_{51}O_4S$ 651.3499, found 651.3499.

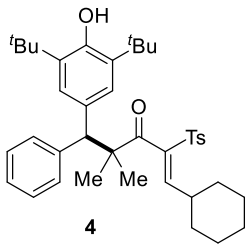
4-Methyl-1-(*p*-tolyl)-2-tosylpent-1-en-3-one (2aa'):



2aa'

Brown liquid, 57 mg, 57 % yield; R_f = 0.3 (Pet. ether/Ethyl acetate-80:20); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.97 (s, 1 H), 7.79 (d, *J* = 8.7 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.18 (s, 4 H), 2.69 (spt, *J* = 6.9 Hz, 1 H), 2.43 (s, 3 H), 2.37 (s, 3 H), 1.06 (d, *J* = 6.9 Hz, 6 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 206.0, 144.5, 141.9, 141.8, 141.0, 137.5, 129.8, 129.7, 129.5, 129.2, 128.5, 41.7, 21.6, 21.4, 18.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{20}H_{23}O_3S$ 343.1362, found 343.1359.

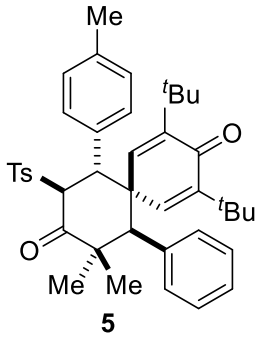
1-Cyclohexyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-2-tosylpent-1-en-3-one (4):



4

Brown liquid, 0.162 mg, 76 % yield; R_f = 0.6 (Pet. ether/Ethyl acetate-80:20); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.53 (d, *J* = 8.2 Hz, 2 H), 7.41 (d, *J* = 7.8 Hz, 2 H), 7.27 (s, 1 H), 7.25 - 7.18 (m, 5 H), 7.17 - 7.11 (m, 1 H), 6.58 (d, *J* = 10.1 Hz, 1 H), 5.04 (s, 1 H), 4.55 (s, 1 H), 2.41 (s, 3 H), 1.52 (s, 3 H), 1.45 (d, *J* = 12.4 Hz, 3 H), 1.39 (s, 18 H), 1.25 (s, 3 H), 1.19 (d, *J* = 8.7 Hz, 1 H), 1.16 - 0.99 (m, 2 H), 0.97 - 0.70 (m, 5 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 207.6, 152.4, 149.4, 144.3, 142.5, 140.5, 136.8, 135.1, 131.8, 130.7, 129.6, 128.3, 128.1, 127.0, 126.4, 57.4, 53.8, 37.2, 34.3, 31.0, 30.9, 30.4, 26.4, 25.2, 23.9, 23.7, 21.7; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{40}H_{52}O_4NaS$ 651.3479, found 651.3474.

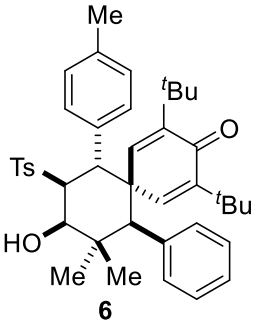
2,4-Di-tert-butyl-8,8-dimethyl-7-phenyl-11-(*p*-tolyl)-10-tosylspiro[5.5]undeca-1,4-diene-3,9-dione (5):



5

White solid, 71 mg, 71 % yield; mp = 107-109 °C; R_f = 0.5 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.59 (d, *J* = 8.2 Hz, 2 H), 7.29 - 7.24 (m, 1 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 7.19 - 7.14 (m, 2 H), 7.03 (t, *J* = 7.3 Hz, 1 H), 6.90 (d, *J* = 7.8 Hz, 1 H), 6.85 - 6.78 (m, *J* = 7.8 Hz, 2 H), 6.71 - 6.63 (m, *J* = 8.2 Hz, 2 H), 6.55 (d, *J* = 3.2 Hz, 1 H), 6.12 (s, 1 H), 4.62 (d, *J* = 9.2 Hz, 1 H), 4.24 (d, *J* = 8.7 Hz, 1 H), 3.84 (s, 1 H), 2.38 (s, 3 H), 2.18 (s, 3 H), 1.48 (s, 3 H), 1.17 (s, 9 H), 1.17 (s, 3 H), 0.67 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 206.7, 185.1, 149.8, 147.3, 145.3, 144.8, 137.3, 137.0, 136.6, 134.6, 134.6, 131.3, 129.7, 129.6, 128.8, 128.5, 128.4, 128.1, 127.9, 127.8, 127.4, 127.3, 76.5, 60.3, 52.8, 48.3, 47.9, 35.4, 34.1, 28.8, 28.5, 28.4, 24.6, 21.6, 20.9; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{49}O_4S$ 637.3346, found 637.3345.

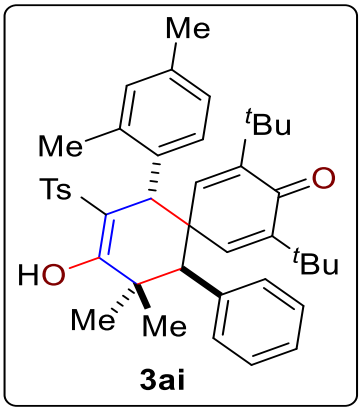
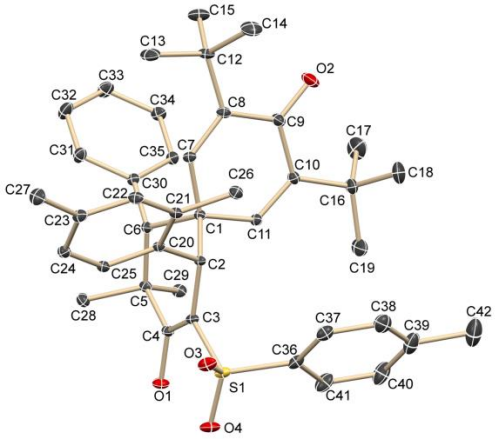
2,4-Di-tert-butyl-9-hydroxy-8,8-dimethyl-7-phenyl-11-(p-tolyl)-10-tosylspiro[5.5]undeca-1,4-dien-3-one (6):



6

White solid, 99 mg, 99 % yield; mp = 173-175 °C; R_f = 0.3 (Pet. ether/Ethyl acetate- 90:10); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.17 - 7.06 (m, 5 H), 7.00 (d, *J* = 9.2 Hz, 5 H), 6.76- 6.69 (d, *J* = 7.3 Hz, 2 H), 6.36 - 6.20 (m, 3 H), 5.30 (s, 1 H), 4.73 - 4.60 (d, 1 H), 4.28 (d, *J* = 12.2 Hz, 1 H), 3.87 (d, *J* = 12.2 Hz, 1 H), 3.50 (s, 1 H), 3.30 (d, *J* = 4.3 Hz, 1 H), 2.38 (s, 3 H), 2.13 (s, 3 H), 1.44 (s, 3 H), 1.12 (s, 9 H), 0.92 (s, 3 H), 0.70 (s, 9 H); **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 185.0, 148.4, 146.9, 146.7, 143.6, 138.1, 137.6, 137.4, 136.5, 132.6, 131.6, 131.4, 129.0, 128.8, 128.5, 127.9, 127.6, 127.1, 126.8, 126.6, 126.2, 74.6, 65.6, 55.5, 53.4, 50.7, 47.8, 40.1, 35.2, 34.0, 28.6, 28.5, 23.5, 21.5, 20.9; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ calcd for $C_{41}H_{51}O_4S$ 639.3506, found 639.3506.

4. X-ray crystallography:

Sr. No	Compound Structure	ORTEP Diagram
1	 CCDC No - **1950350**	

An X-ray intensity data measurement of compound **3ai** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out at 100(2) K temperature with Mo micro-focus sealed tube diffraction source (MoK_α= 0.71073 Å). The X-ray generator was operated at 50 kV and 1.4. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[6] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016).[6] Using APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[7] structure solution program, using direct methods. The model was refined with version of ShelXL-2013 (Sheldrick, 2015)[8] using Least Squares minimisation. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. An *ORTEP* III[9] view of compounds was drawn with 30% probability displacement ellipsoids and H atoms are omitted for clarity.

Crystal data of **3ai:** $C_{42}H_{50}O_4S$, M = 650.88, colorless block, 0.48 x 0. 23 x 0.14 mm^3, monoclinic, space group $P2_1/c$, a = 17.0878(7) Å, b = 10.7963(4) Å, c = 21.0437(9) Å, β = 109.074(2)°, V = 3669.1(3) $Å^3$, Z = 4, T = 100(2) K, $2\theta_{max}$= 61.052°, D_{calc} (g cm^{-3}) = 1.178, $F(000)$ = 1400, μ (mm^{-1}) = 0.128, 130989 reflections collected, 11176 unique reflections (R_{int} = 0.0458, R_{sig} = 0.0219), 9223 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.941, T_{max} = 0.982, 436 refined parameters, Good of Fit = S = 1.069, $R1$ = 0.0391, $wR2$ = 0.0968 (all data R = 0.0530, $wR2$ = 0.1089), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.392, $\Delta\rho_{min}$= -0.386 (e $Å^{-3}$), **CCDC No. 1950350** .

5. References:

1. (a) W. Chu, L. Zhang, X. Bao, X. Zhao,C. Zeng, J. Du, G. Zhang, F. Wang, X. Ma and C. A. Fan, *Angew. Chem., Int. Ed.* 2013, **52**, 9229. (b) S. R.Shirsath, G. H. Shinde, A. C. Shaikh and Muthukrishnan, M. *J. Org. Chem*. 2018, **83**, 12305-12314.

2. R. R. Tata, C. S. Hampton, E. F. Altenhofer, M. Topinka, W. Ying, X. Gao and M. Harmata, *Chem. Eur. J*. 2014, **20**, 13547-13550.

3. R.R. Tata and M. Harmata, *J. Org. Chem***.** 2015, **80**, 6839-6845.

4. C. S. Hampton and M. Harmata *Org. Lett*. 2014, **16**, 1256–1259.

5. R. R. Tata and M. Harmata, *Org. Lett.* 2016**, 18**, 5684-5687.

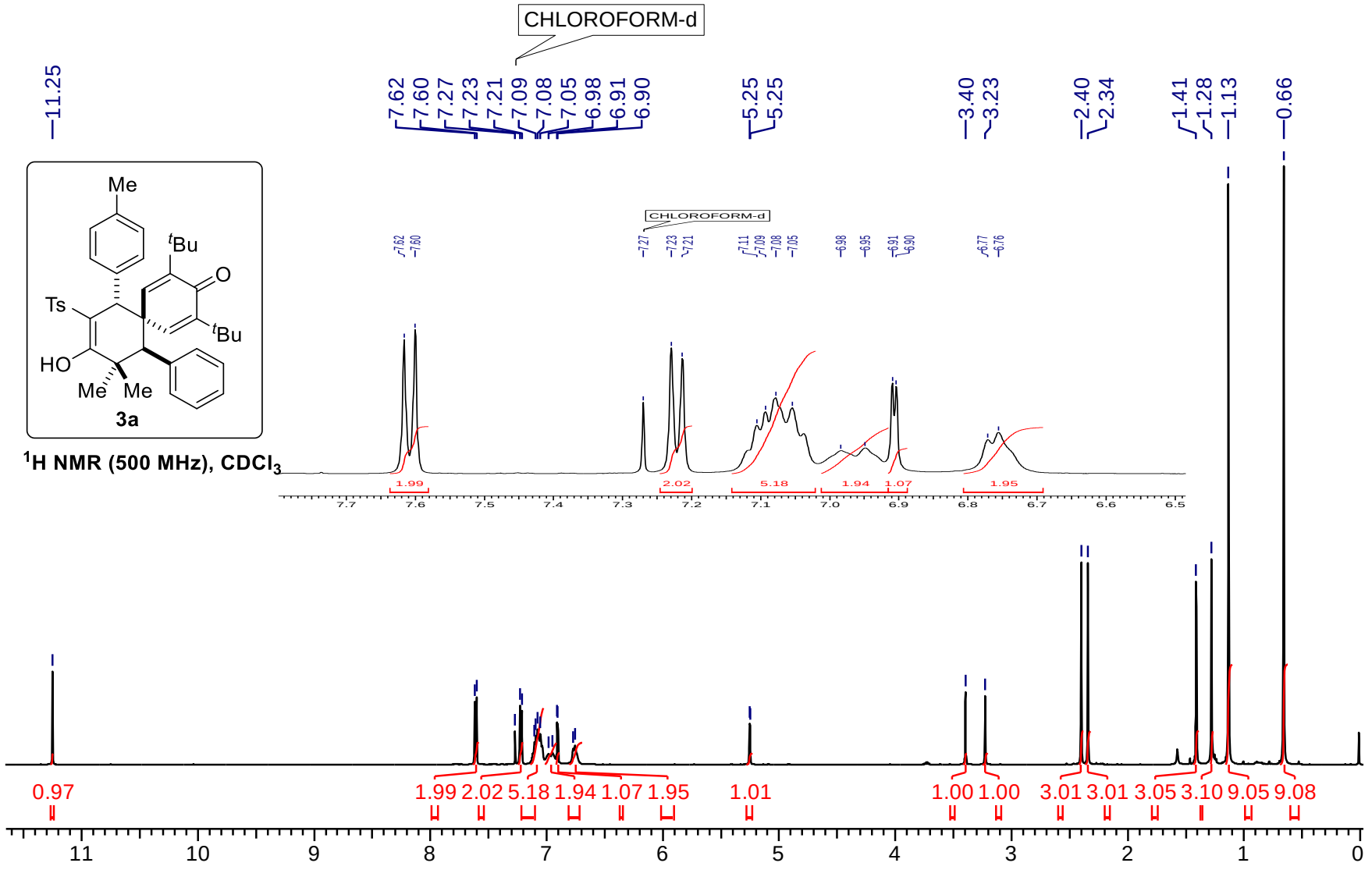
6. Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

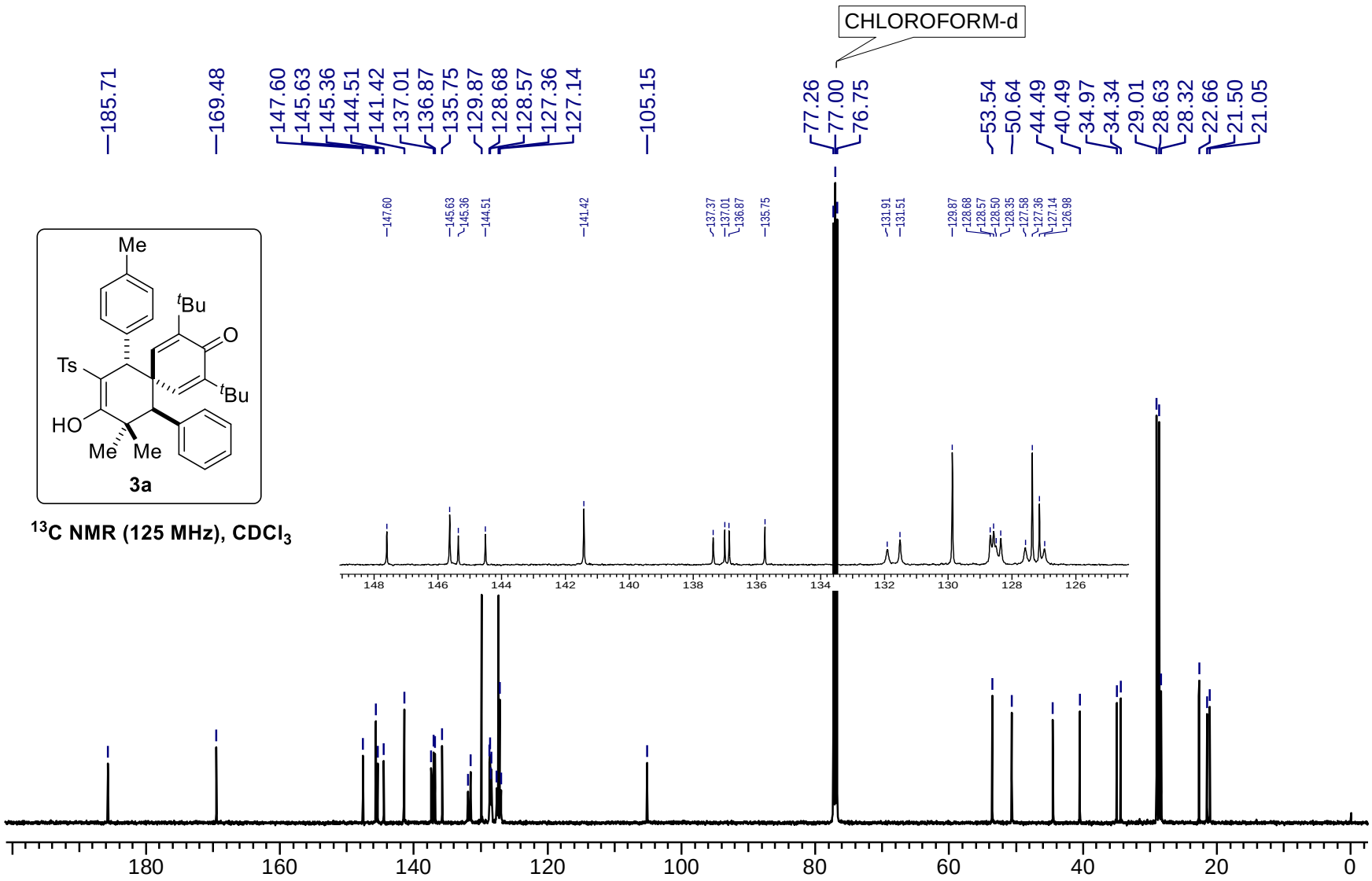
7. G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

8. G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3–8.

9. L. J. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849–854.

6. Spectral Data

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129.87
128.68
128.57
127.36
127.14
105.15
77.26
77.00
76.75
53.54
50.64
44.49
40.49
34.97
34.34
29.01
28.63
28.32
22.66
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O
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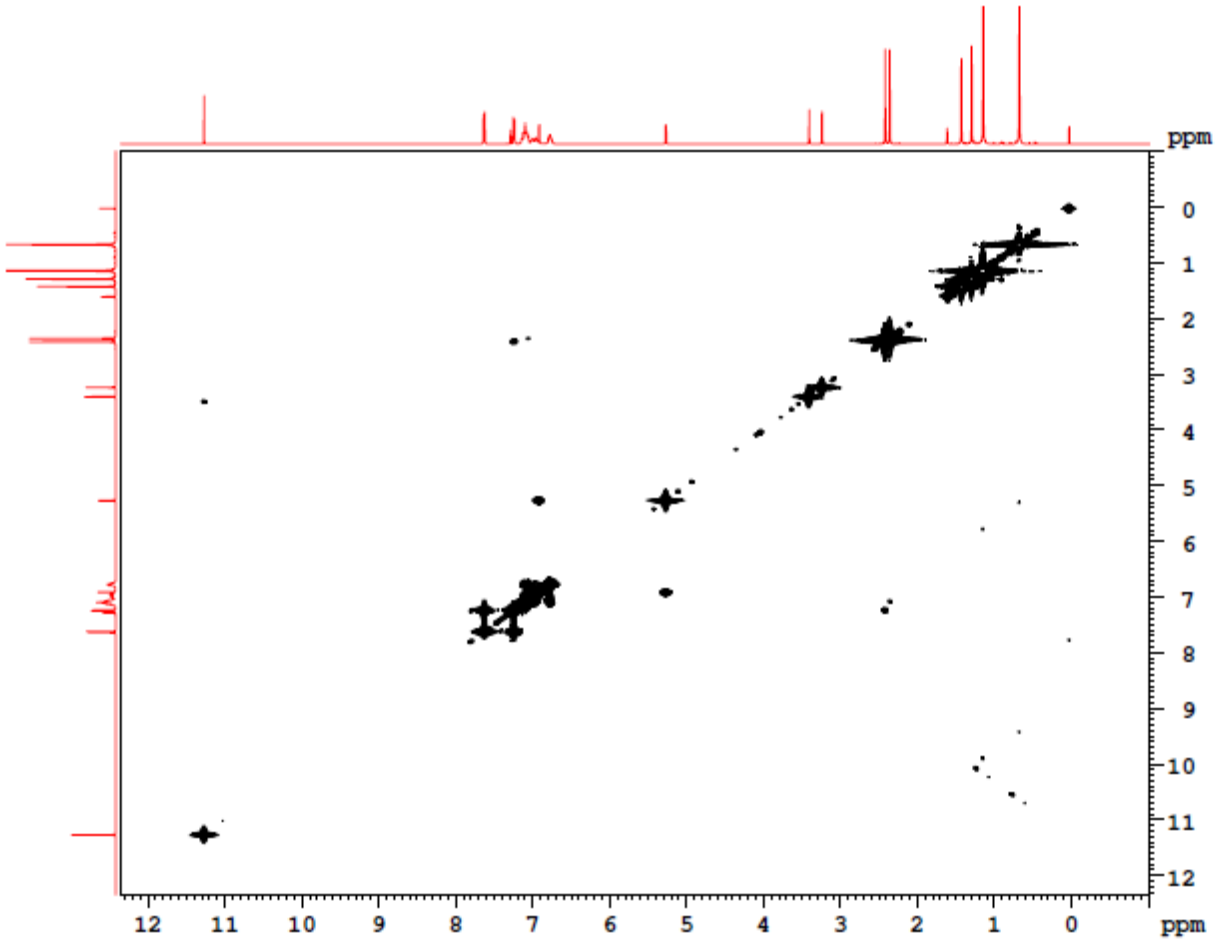
tBu
HO
Me
Me
3a
13C NMR (125 MHz), CDCl3

COSY: 3a



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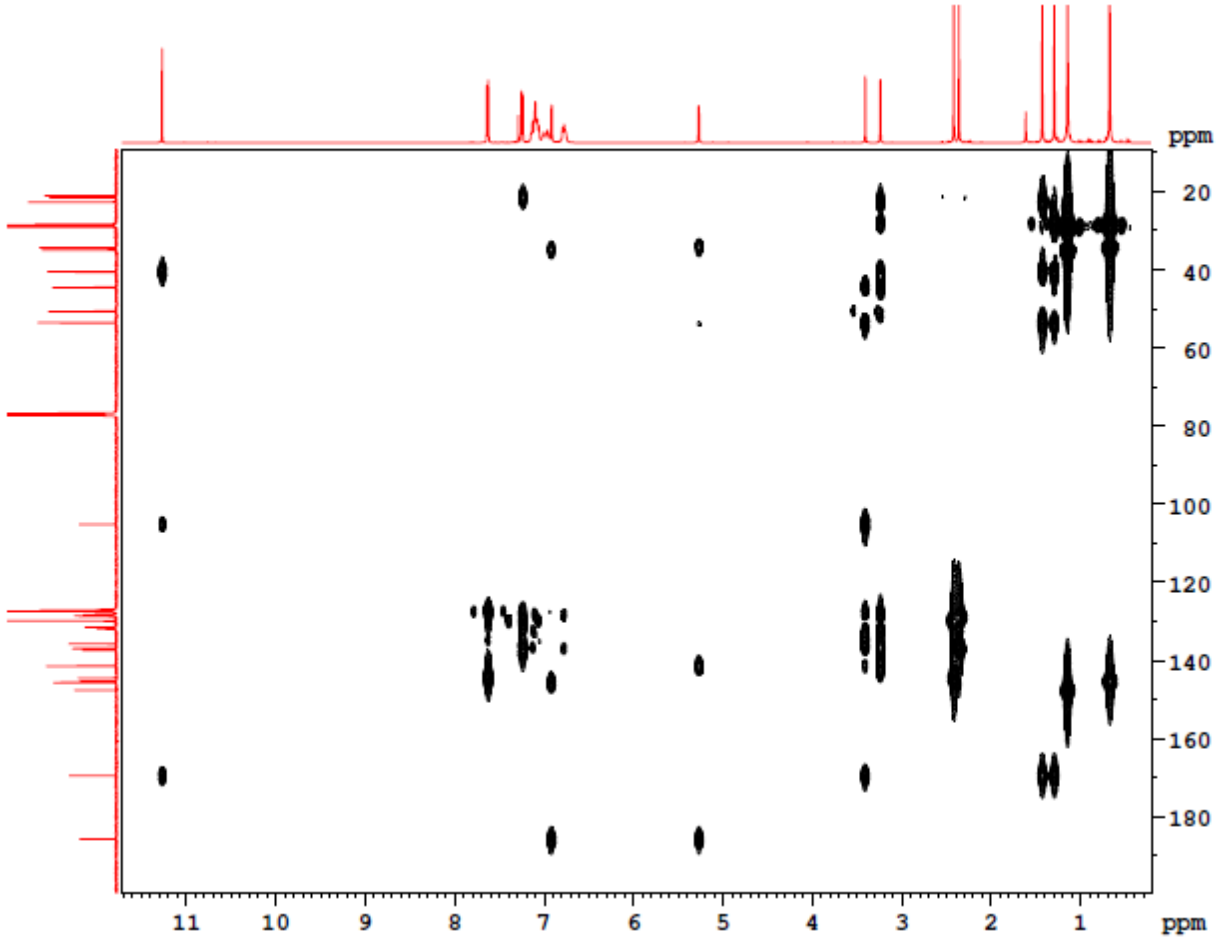

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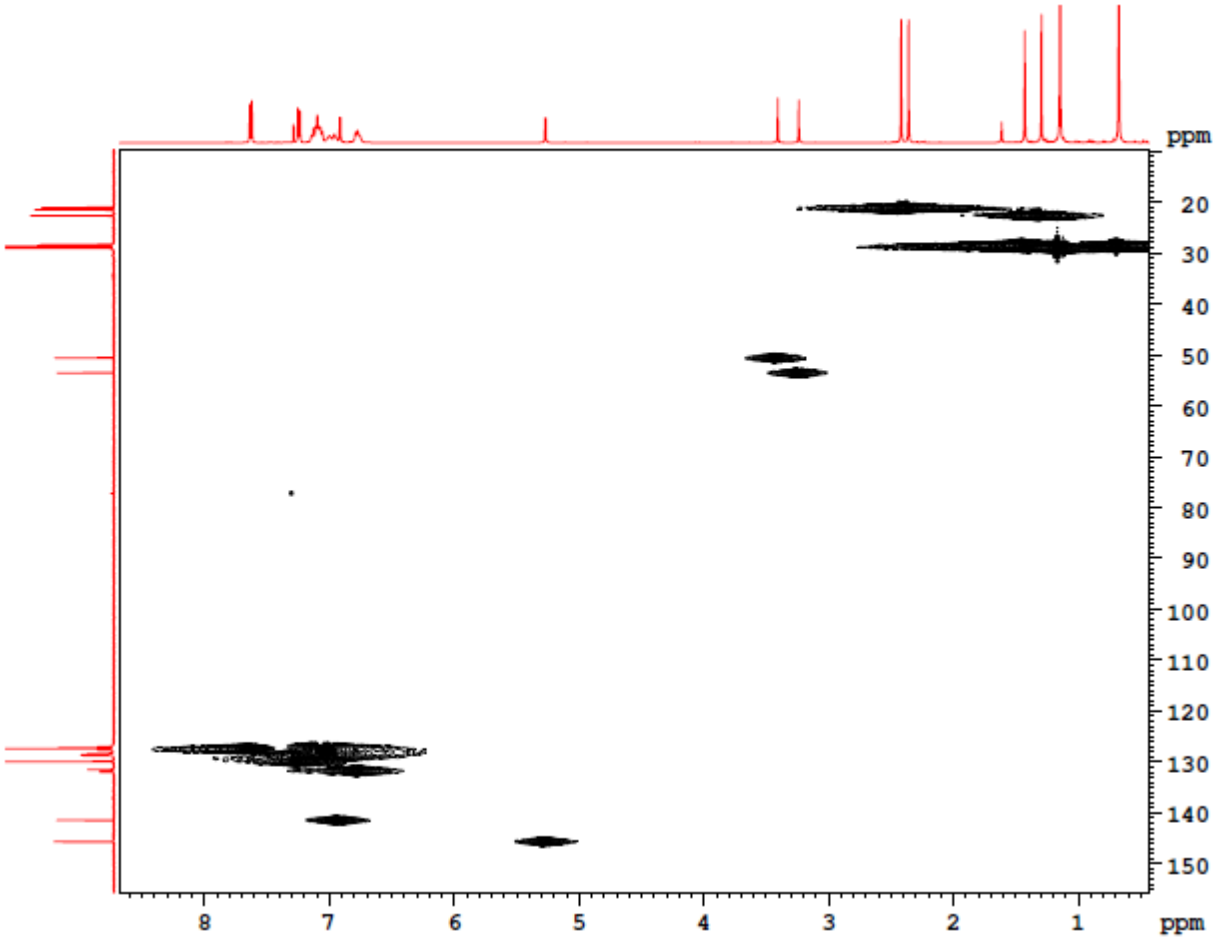

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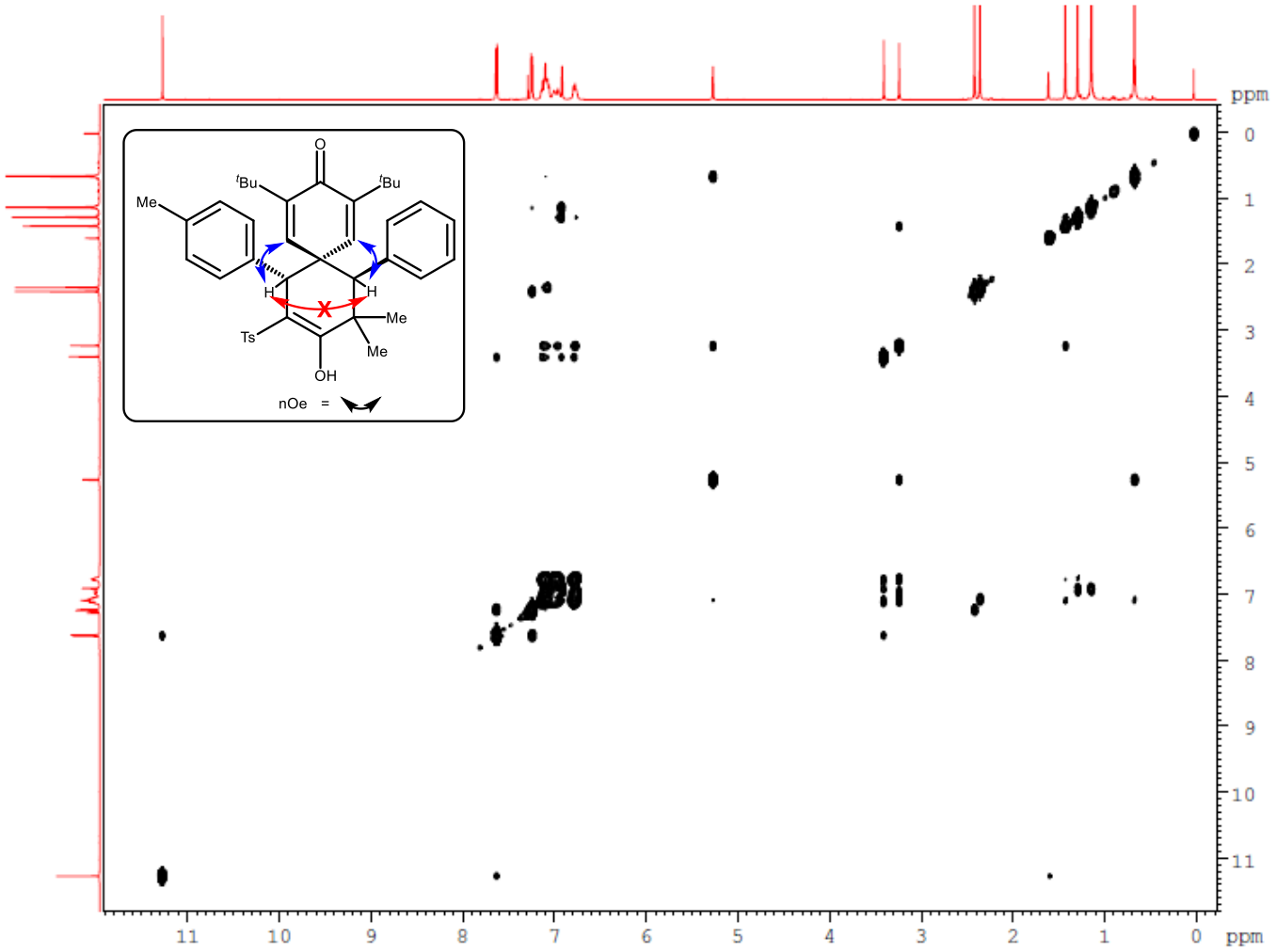
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Me
H
H
Ts
Me
Me
OH
nOe =
ppm
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1
2
3
4
5
6
7
8
9
10
11
11
10
9
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7
6
5
4
3
2
1
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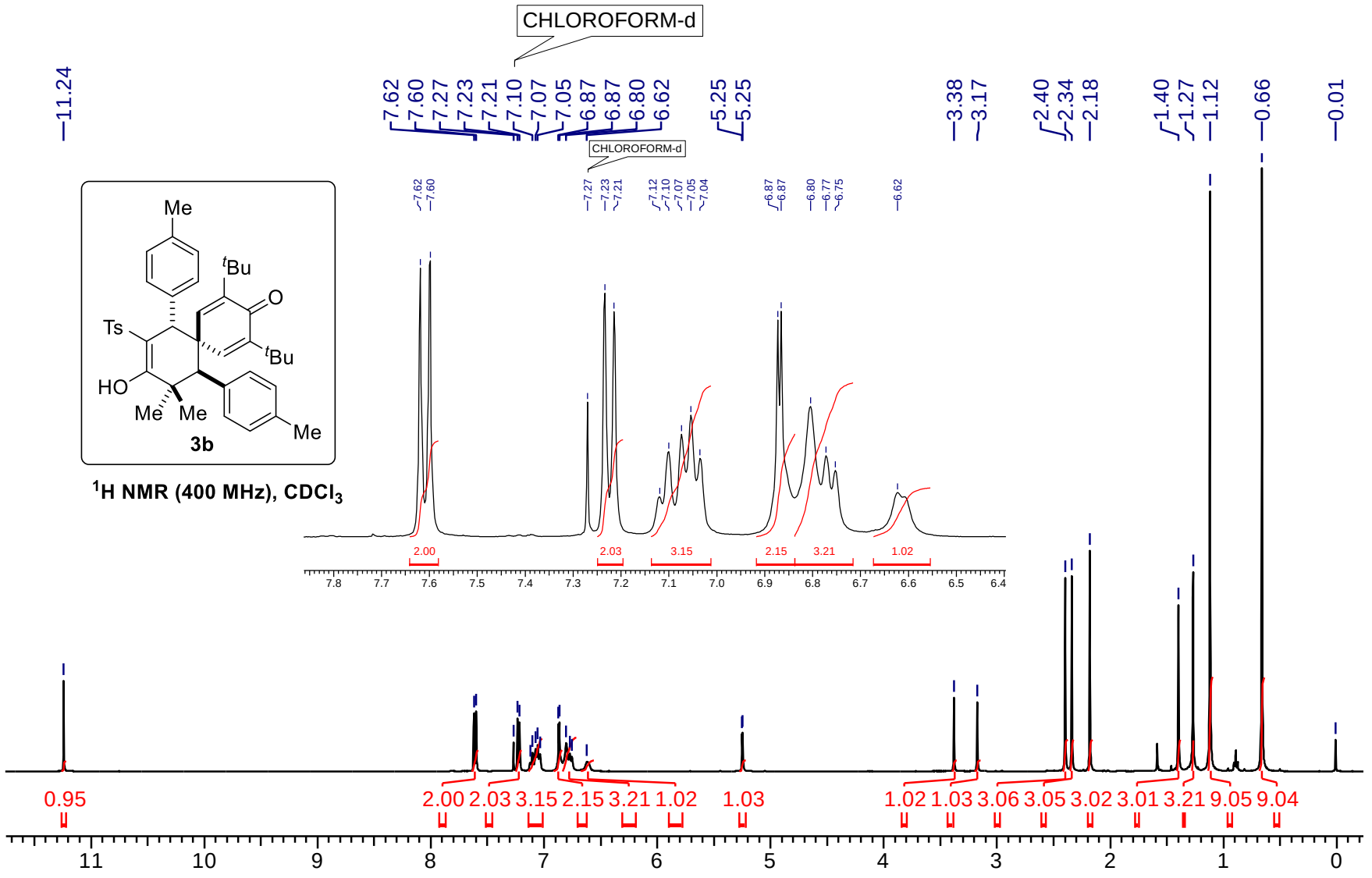
ppm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7.27
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7.21
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6.80
6.62
5.25
5.25
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3.17
2.40
2.34
2.18
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1.27
1.12
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O
Ts
tBu
HO
Me
Me
Me
3b
1H NMR (400 MHz), CDCl3
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2.03
3.15
2.15
3.21
1.02
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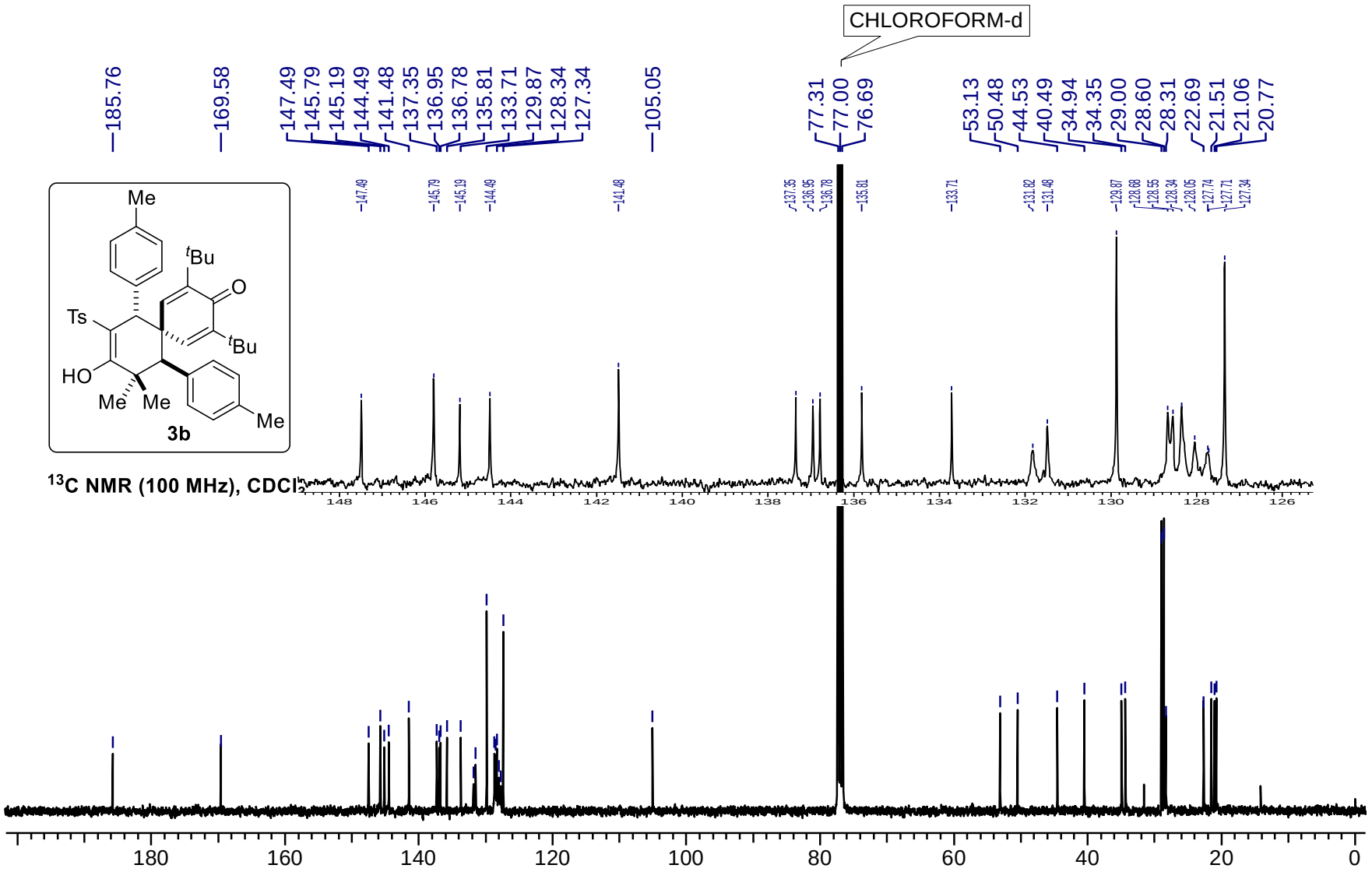
1.03
1.02 1.03 3.06 3.05 3.02 3.01 3.21 9.05 9.04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129.87
128.34
127.34
105.05
77.31
77.00
76.69
53.13
50.48
44.53
40.49
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34.35
29.00
28.60
28.31
22.69
21.51
21.06
20.77
Me
tBu
O
Ts
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Me
Me
Me
3b
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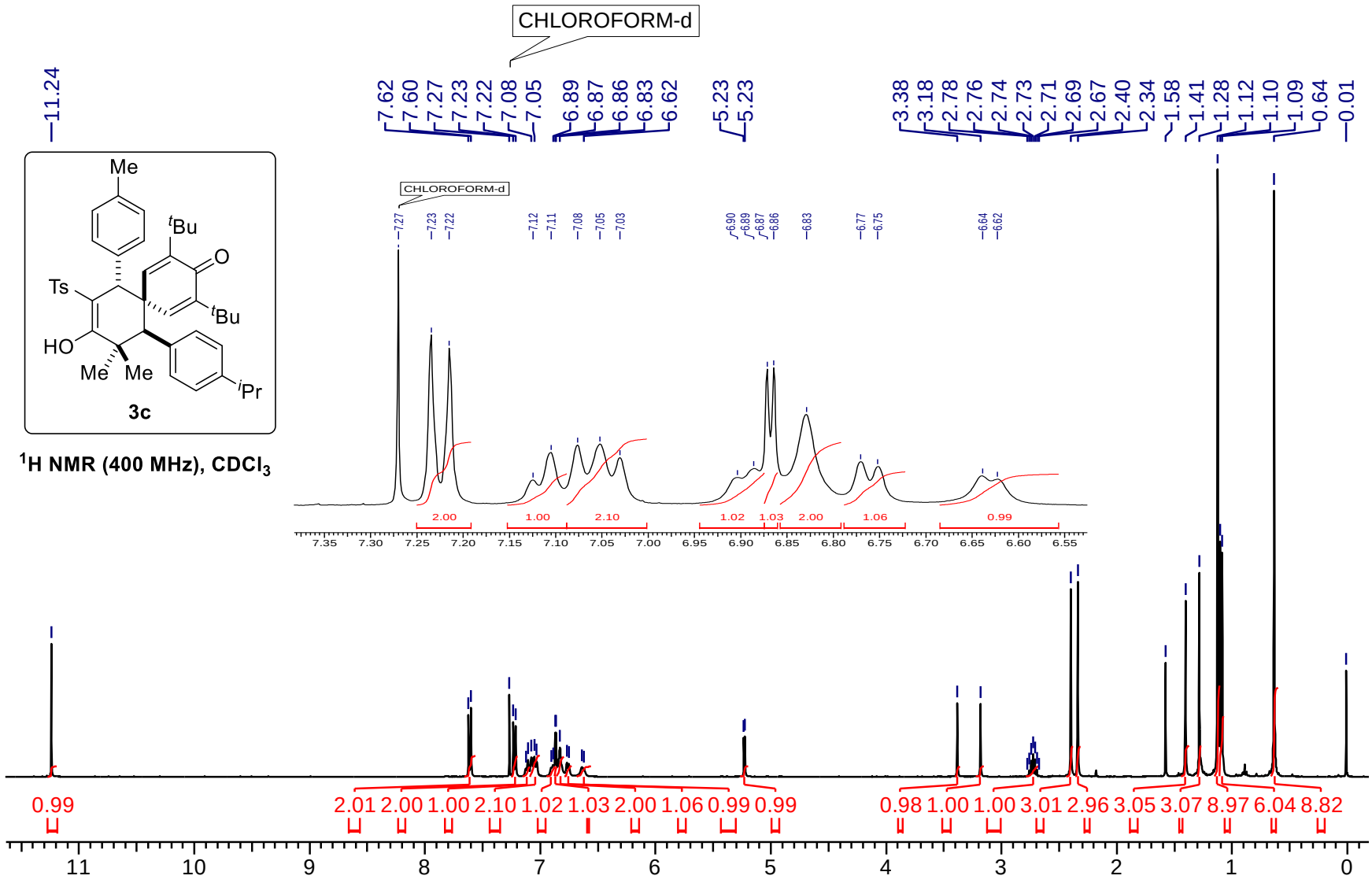
140
120
100
80
60
40
20
0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3.38 3.18 2.78 2.76 2.74 2.73 2.71 2.69 2.67 2.40 2.34 1.58 1.41 1.28 1.12 1.10 1.09 0.64 0.01
Me
tBu
O
Ts
tBu
HO
Me Me
iPr
3c
1H NMR (400 MHz), CDCl3
0.99
2.01 2.00 1.00 2.10 1.02 1.03 2.00 1.06 0.99 0.99
0.98 1.00 1.00 3.01 2.96 3.05 3.07 8.97 6.04 8.82
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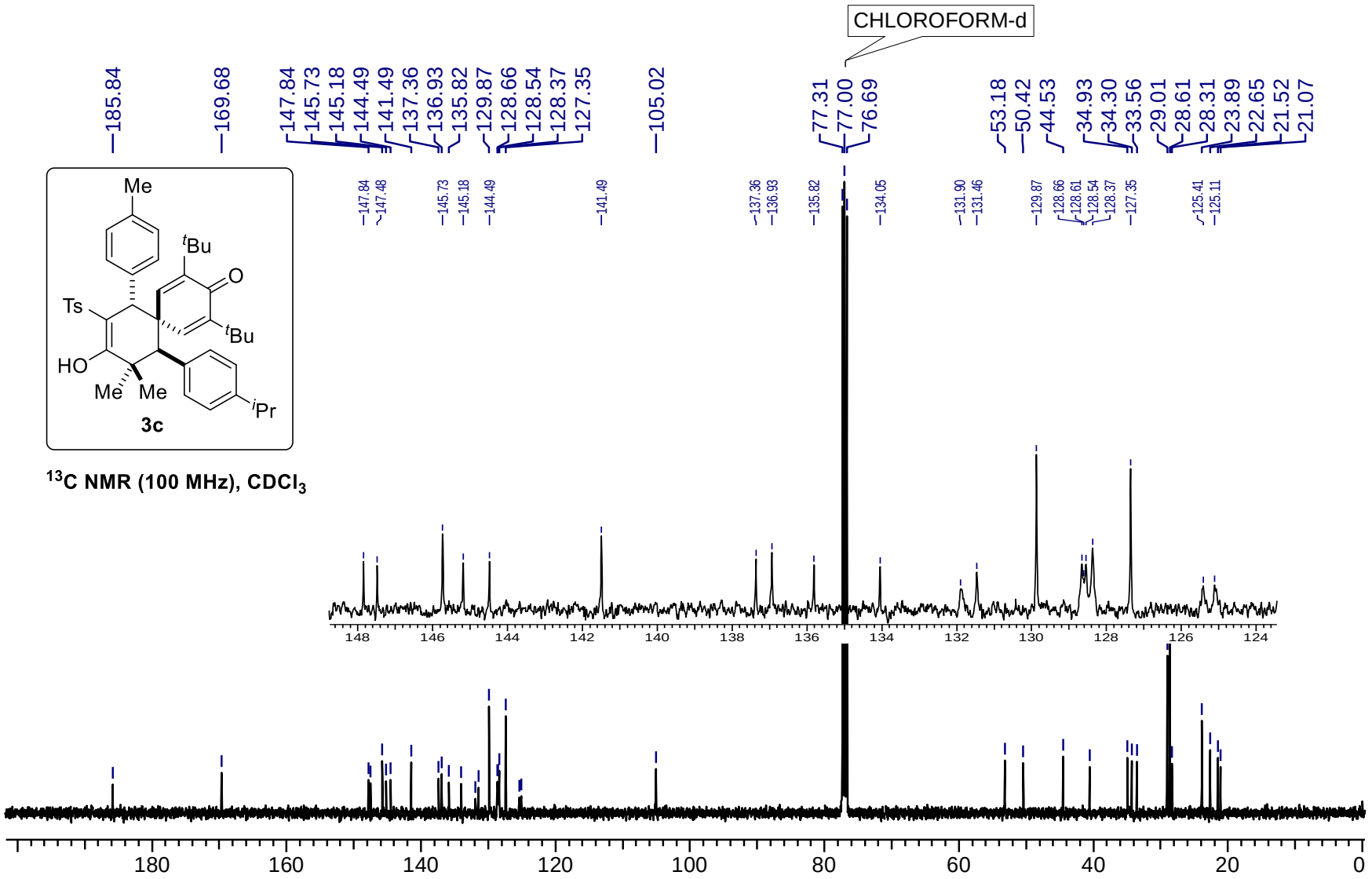
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136.93
135.82
129.87
128.66
128.54
128.37
127.35
105.02
77.31
77.00
76.69
53.18
50.42
44.53
34.93
34.30
33.56
29.01
28.61
28.31
23.89
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Me
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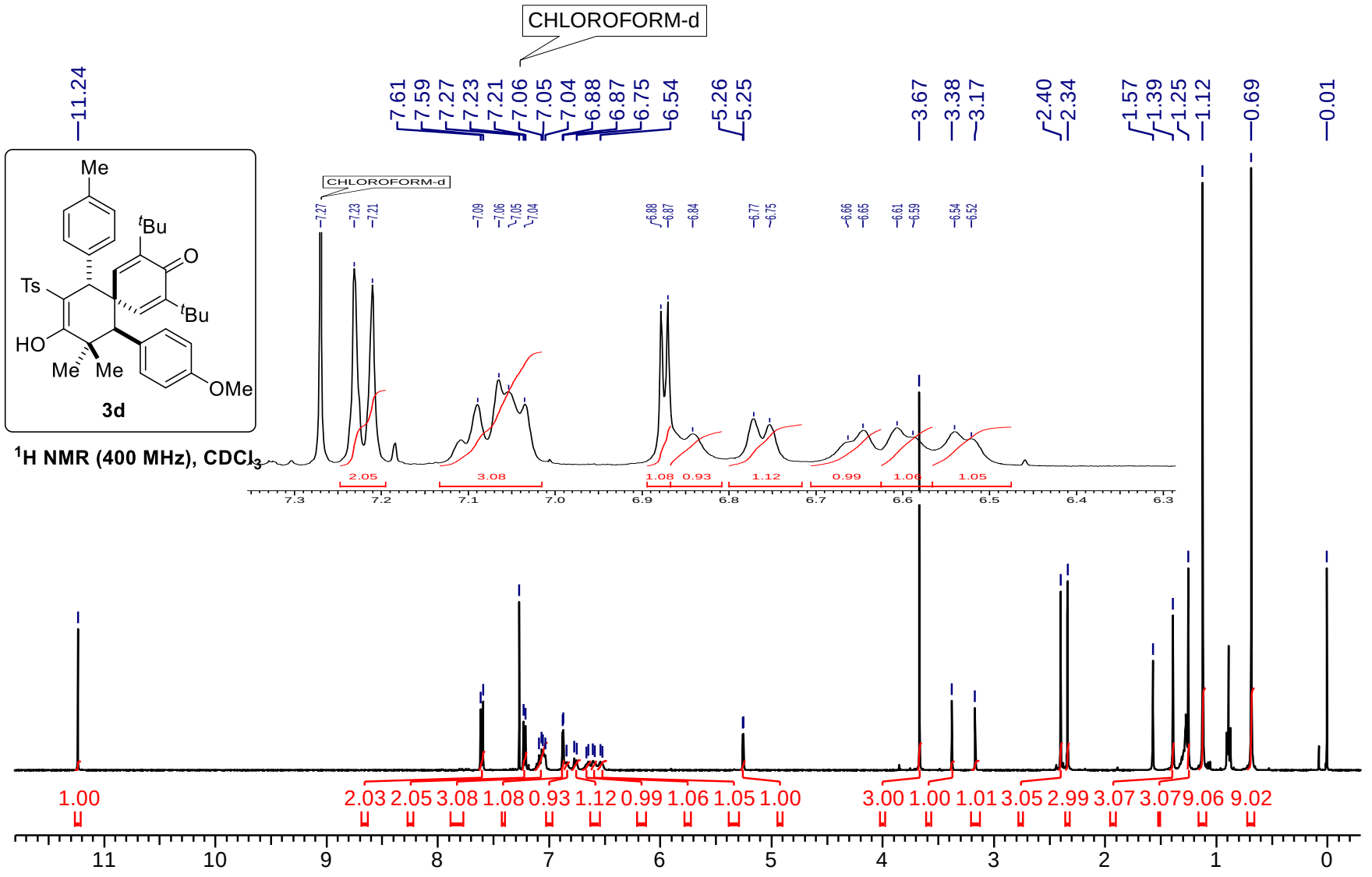
3c
13C NMR (100 MHz), CDCl3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7.59
7.27
7.23
7.21
7.06
7.05
7.04
6.88
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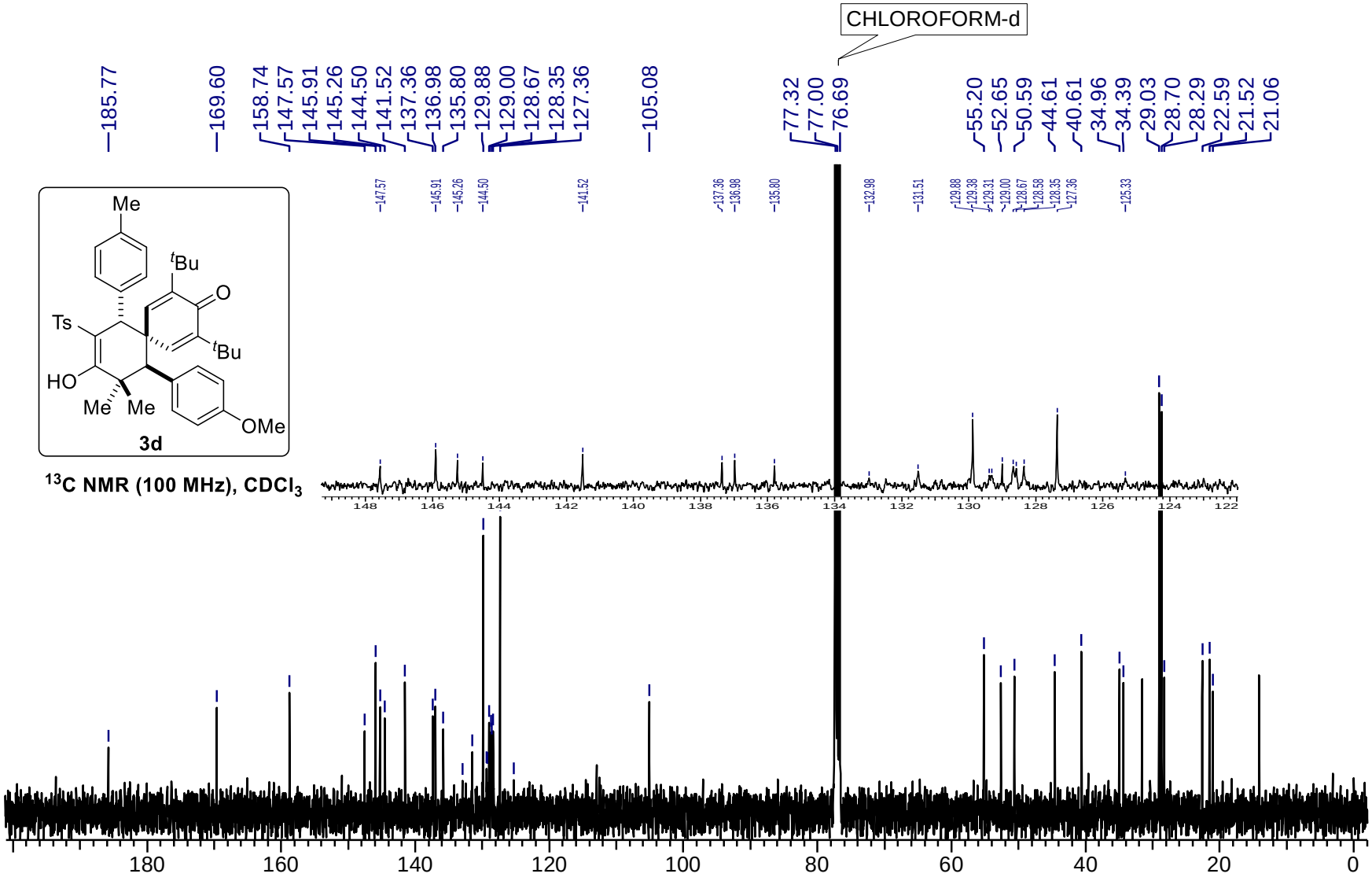
6.75
6.54
5.26
5.25
3.67
3.38
3.17
2.40
2.34
1.57
1.39
1.25
1.12
0.69
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
OMe
3d
1H NMR (400 MHz), CDCl3
1.00
2.03 2.05 3.08 1.08 0.93 1.12 0.99 1.06 1.05 1.00
3.00 1.00 1.01 3.05 2.99 3.07 3.07 9.06 9.02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128.67
128.35
127.36
105.08
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77.00
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55.20
52.65
50.59
44.61
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34.96
34.39
29.03
28.70
28.29
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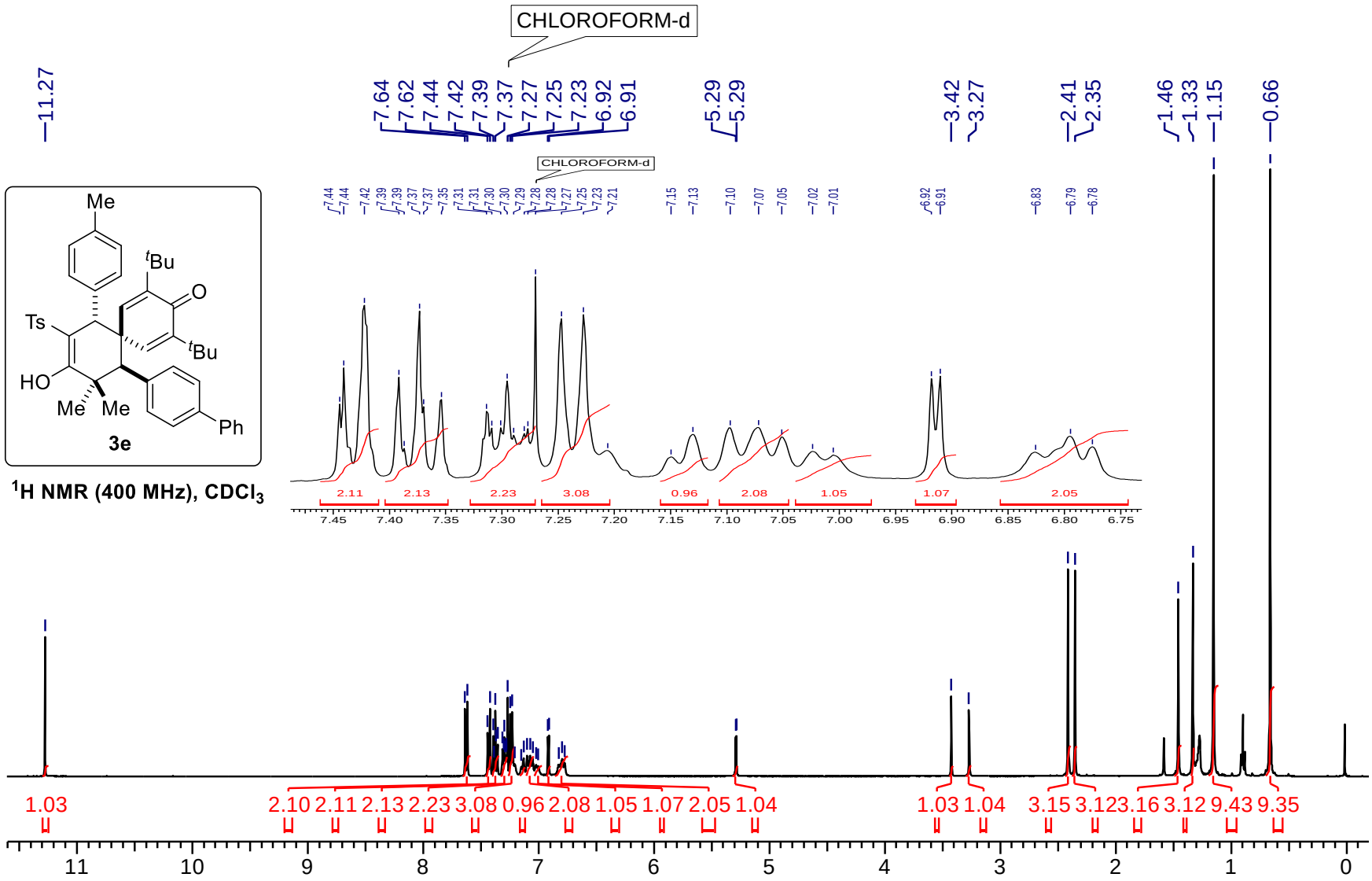
Me
OMe
3d
13C NMR (100 MHz), CDCl3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7.27
7.25
7.23
6.92
6.91
5.29
5.29
3.42
3.27
2.41
2.35
1.46
1.33
1.15
0.66
Me
tBu
O
Ts
tBu
HO
Me
Me
Ph
3e
1H NMR (400 MHz), CDCl3
2.11
2.13
2.23
3.08
0.96
2.08
1.05
1.07
2.05
1.03
2.10 2.11 2.13 2.23 3.08 0.96 2.08 1.05 1.07 2.05 1.04
1.03 1.04
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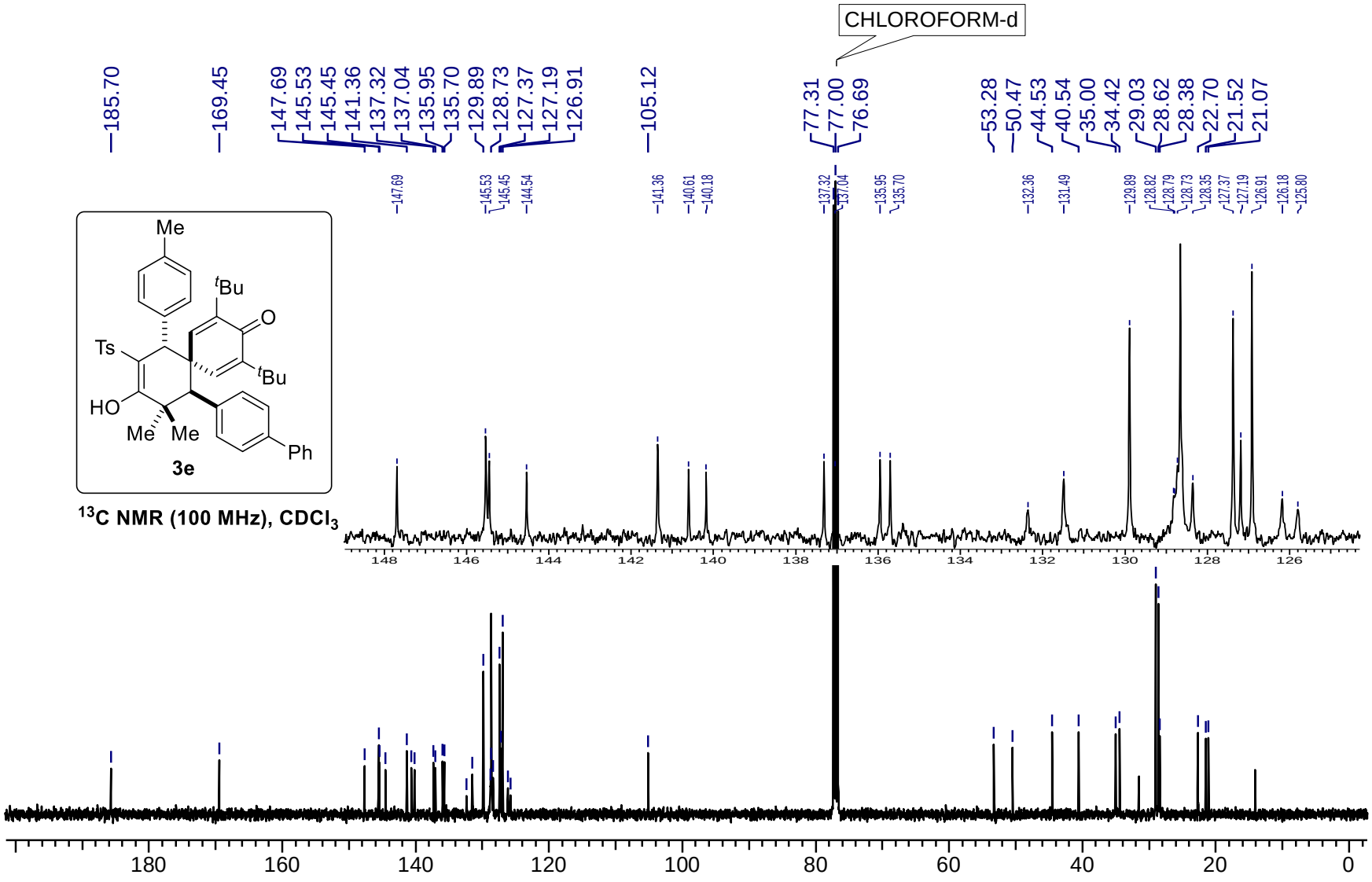
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Ts
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Me
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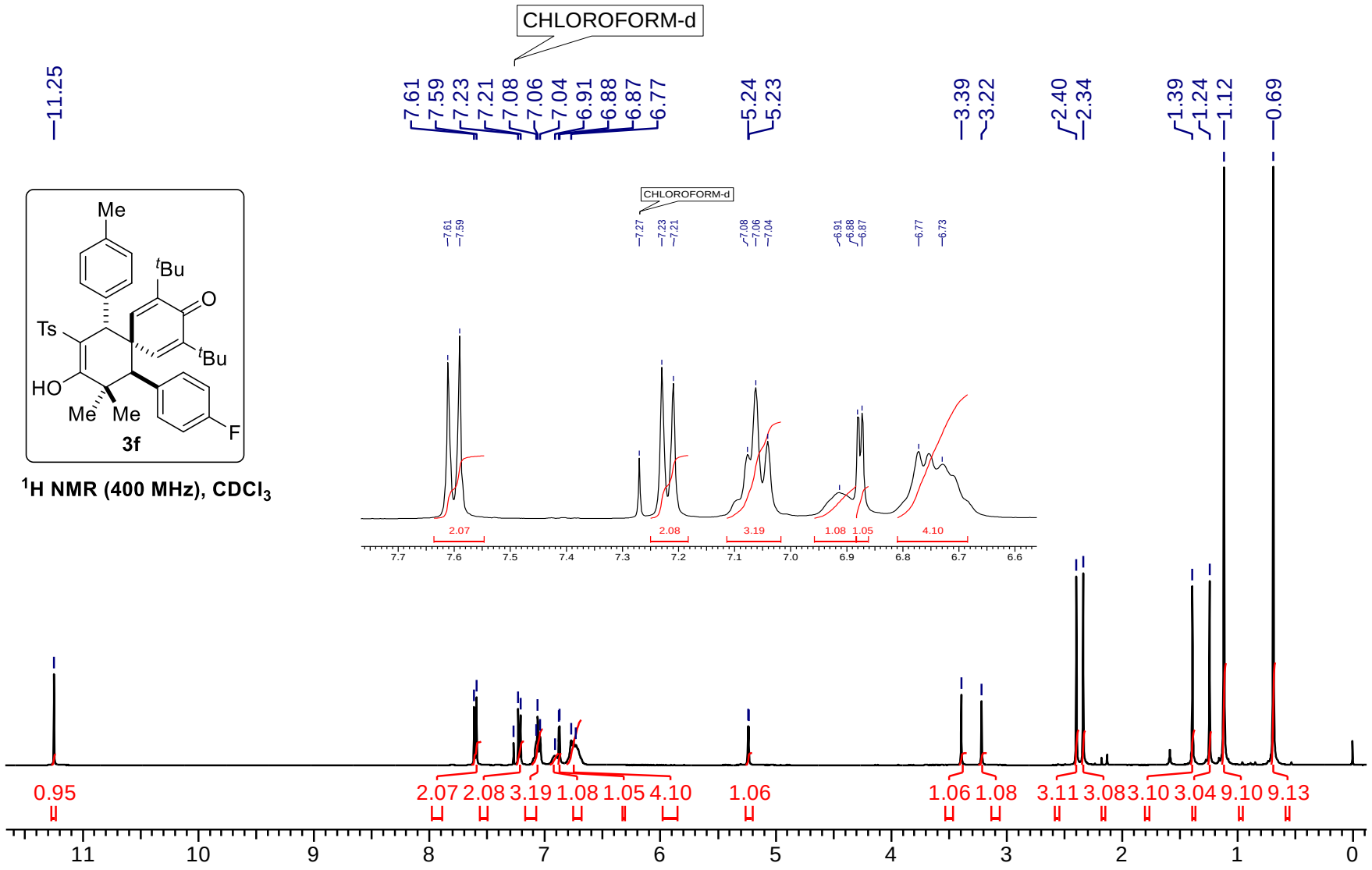
Ph
3e
13C NMR (100 MHz), CDCl3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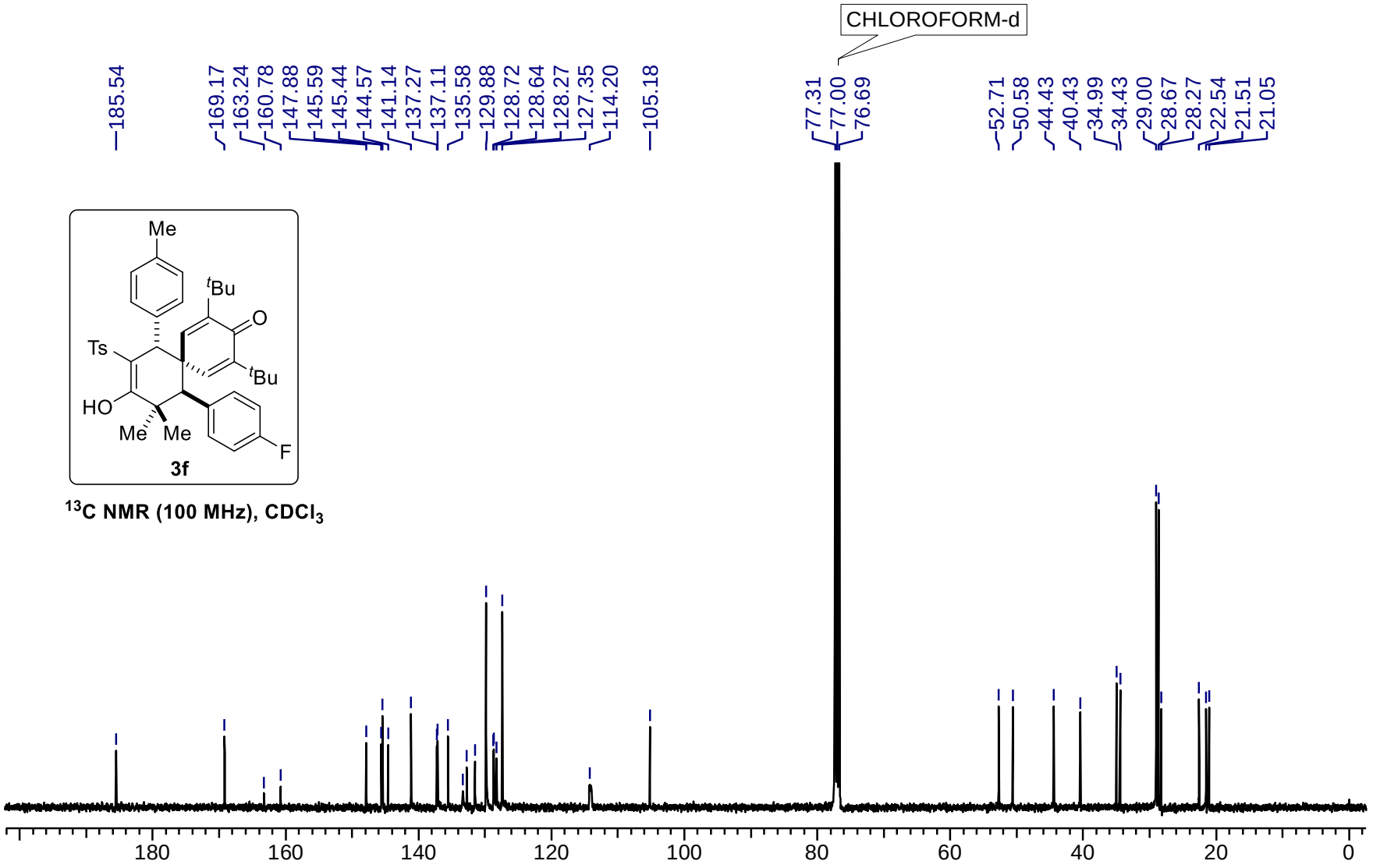
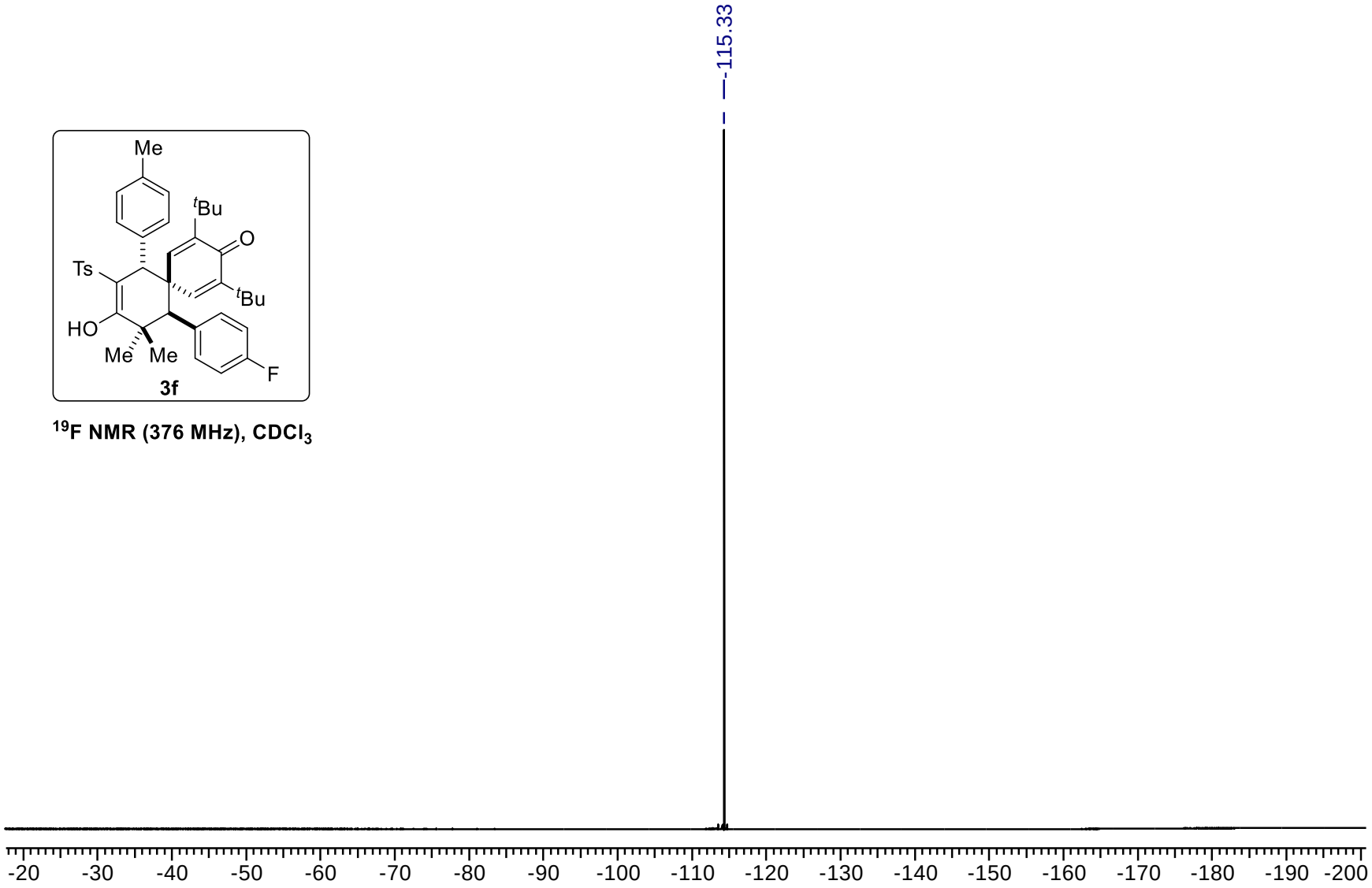
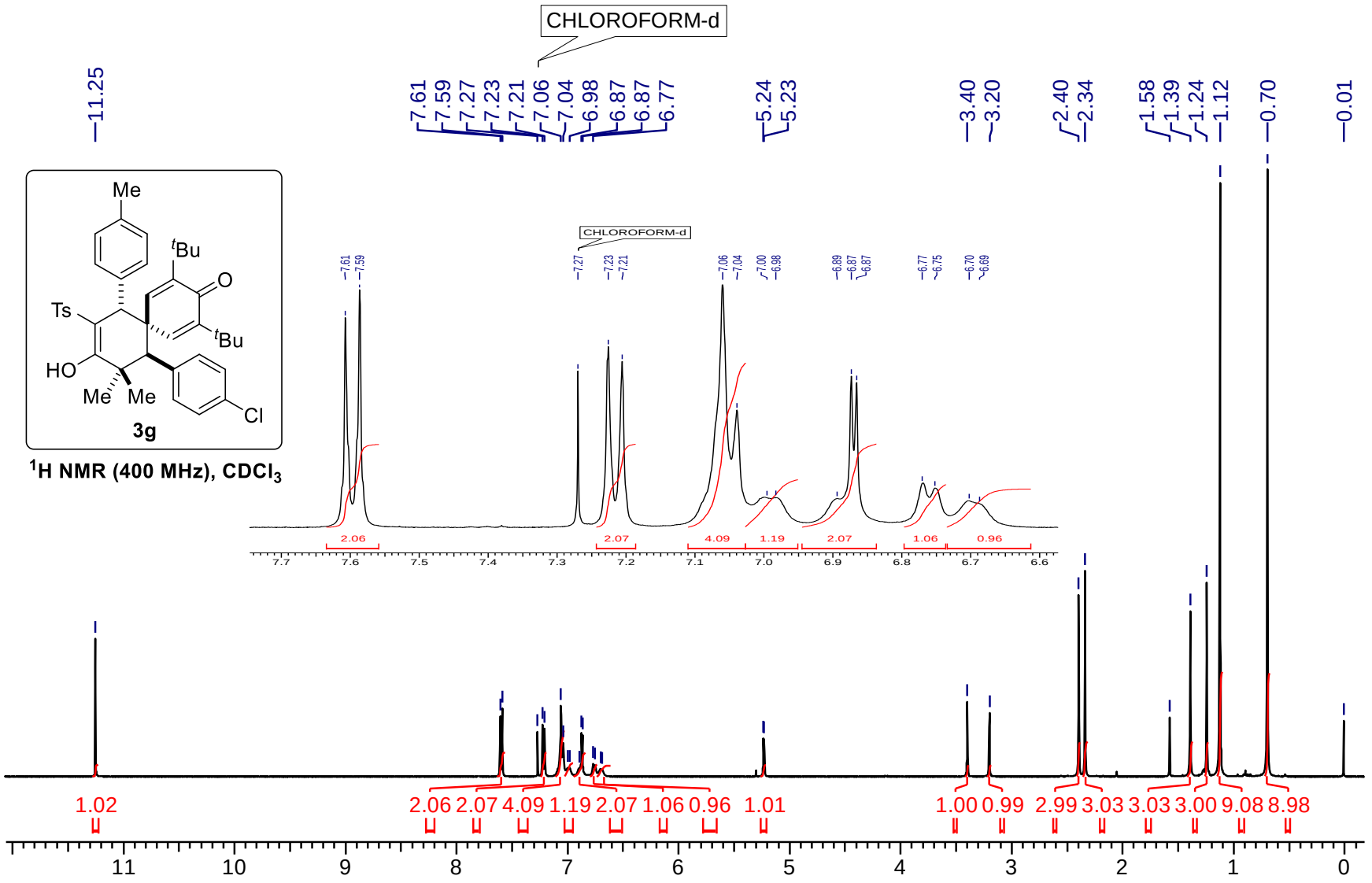
6.87
6.77
5.24
5.23
3.39
3.22
2.40
2.34
1.39
1.24
1.12
0.69
Me
tBu
O
Ts
tBu
HO
Me
Me
F
3f
1H NMR (400 MHz), CDCl3
2.07
2.08
3.19
1.08
1.05
4.10
0.95
1.06
1.06
1.08
3.11
3.08
3.10
3.04
9.10
9.13



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

^{19}F NMR (376 MHz), $CDCl_3$

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7.61
7.59
7.27
7.23
7.21
7.06
7.04
6.98
6.87
6.87
6.77
5.24
5.23
3.40
3.20
2.40
2.34
1.58
1.39
1.24
1.12
0.70
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
Cl
3g
1H NMR (400 MHz), CDCl3
1.02
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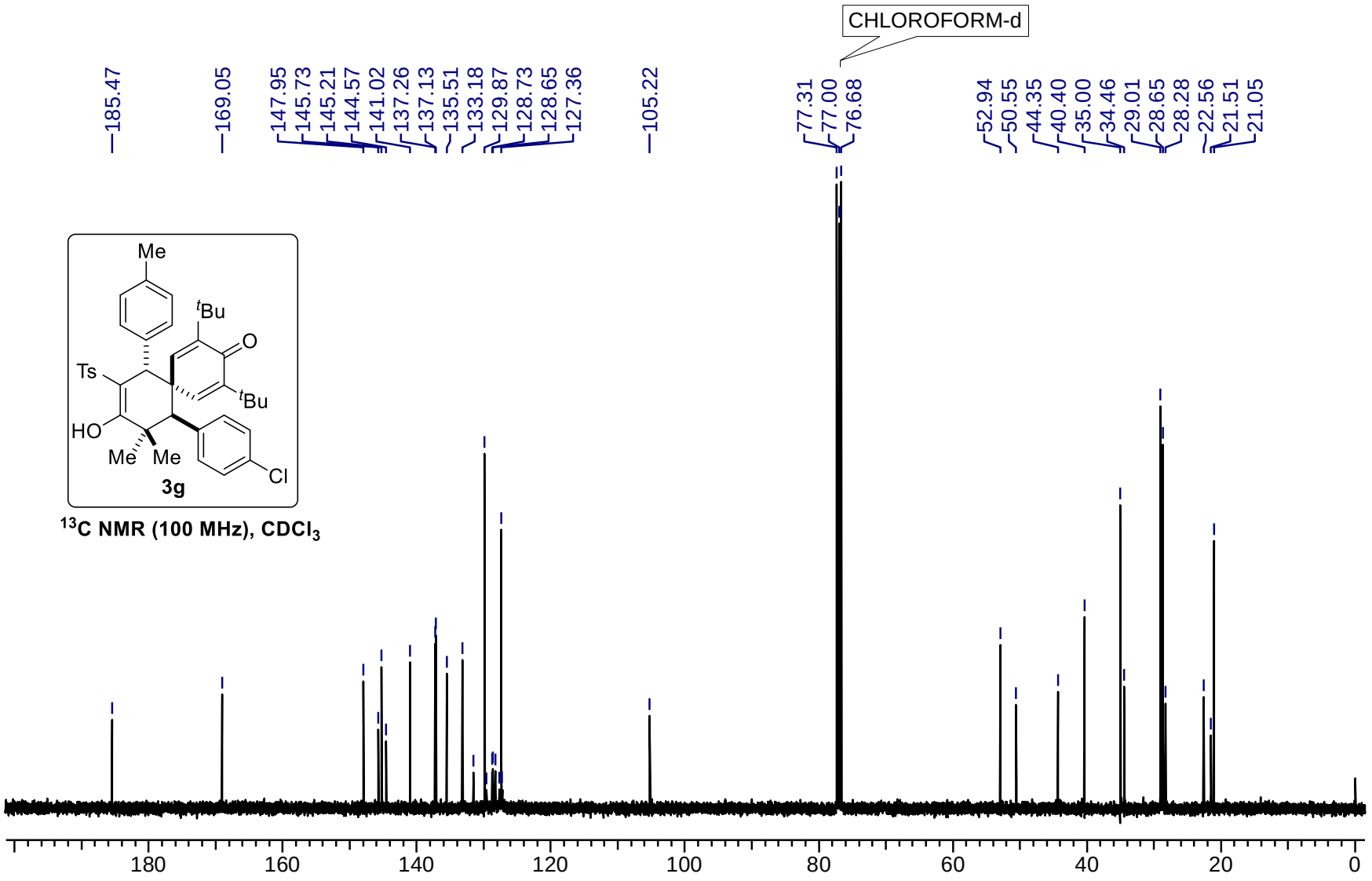
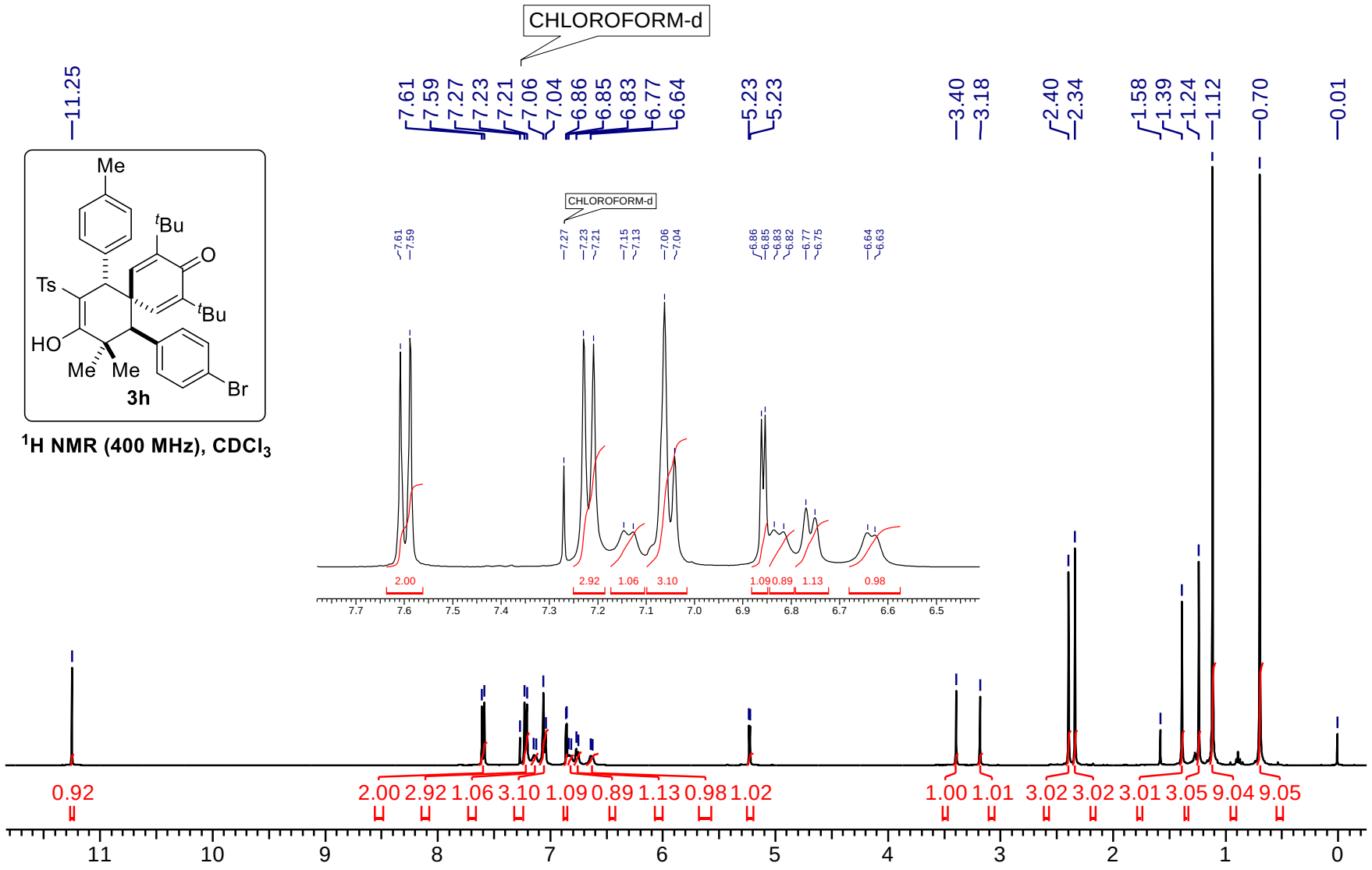
1.00 0.99 2.99 3.03 3.03 3.00 9.08 8.98



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


CHLOROFORM-d
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7.61
7.59
7.27
7.23
7.21
7.06
7.04
6.86
6.85
6.83
6.77
6.64
5.23
5.23
3.40
3.18
2.40
2.34
1.58
1.39
1.24
1.12
0.70
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
Br
3h
1H NMR (400 MHz), CDCl3
0.92
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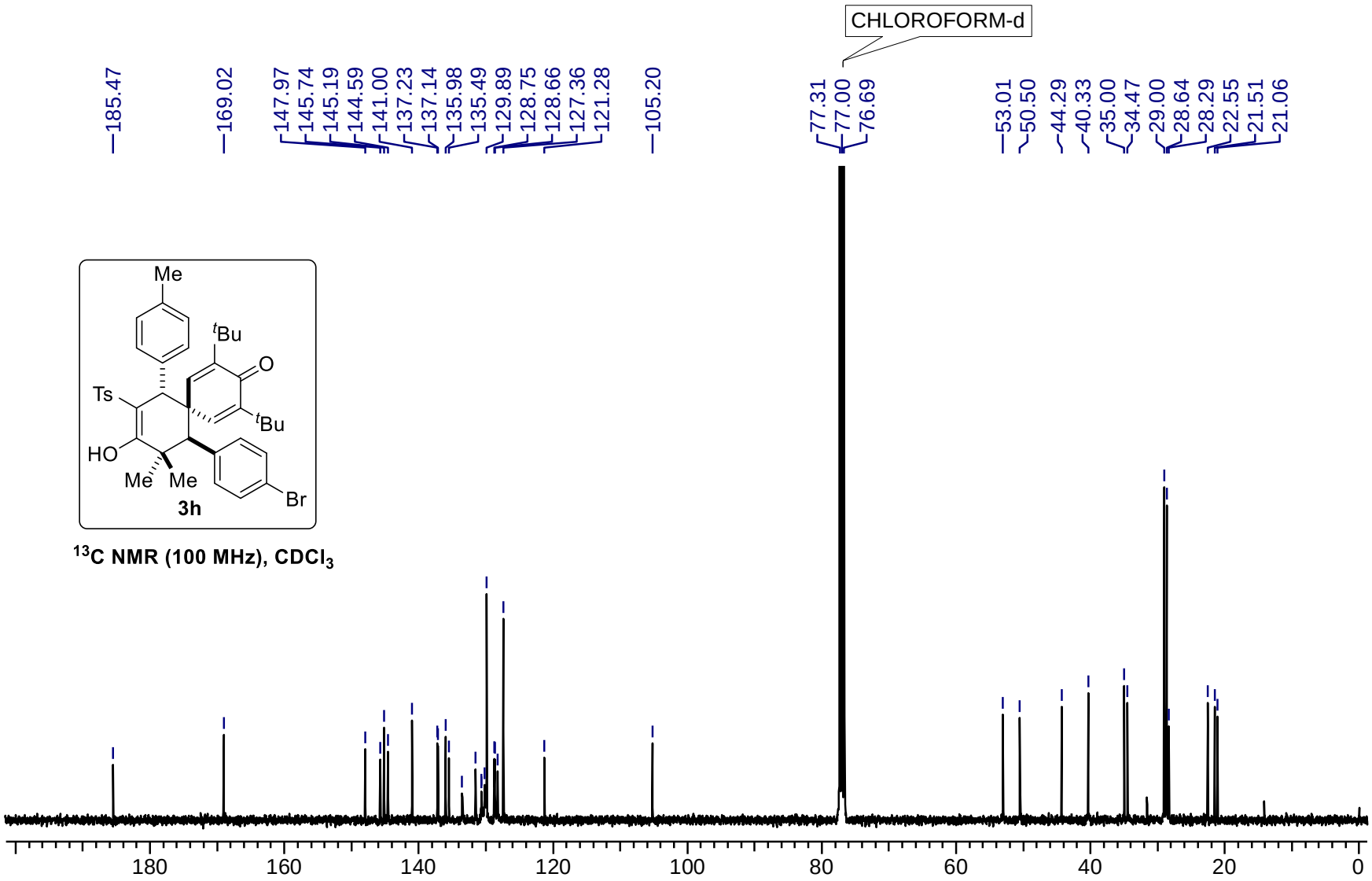
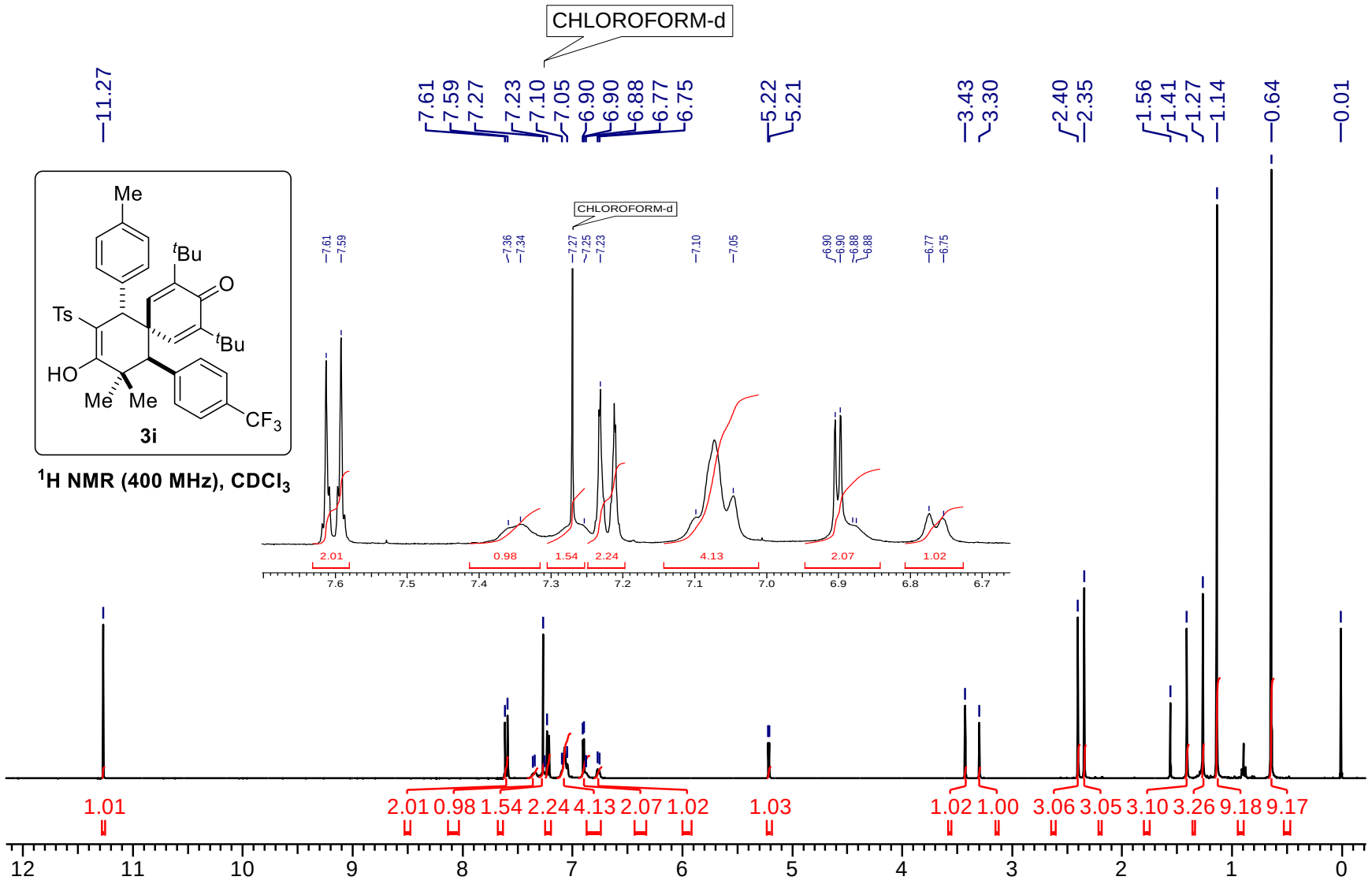
1.00 1.01 3.02 3.02 3.01 3.05 9.04 9.05



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


CHLOROFORM-d
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7.27
7.23
7.10
7.05
6.90
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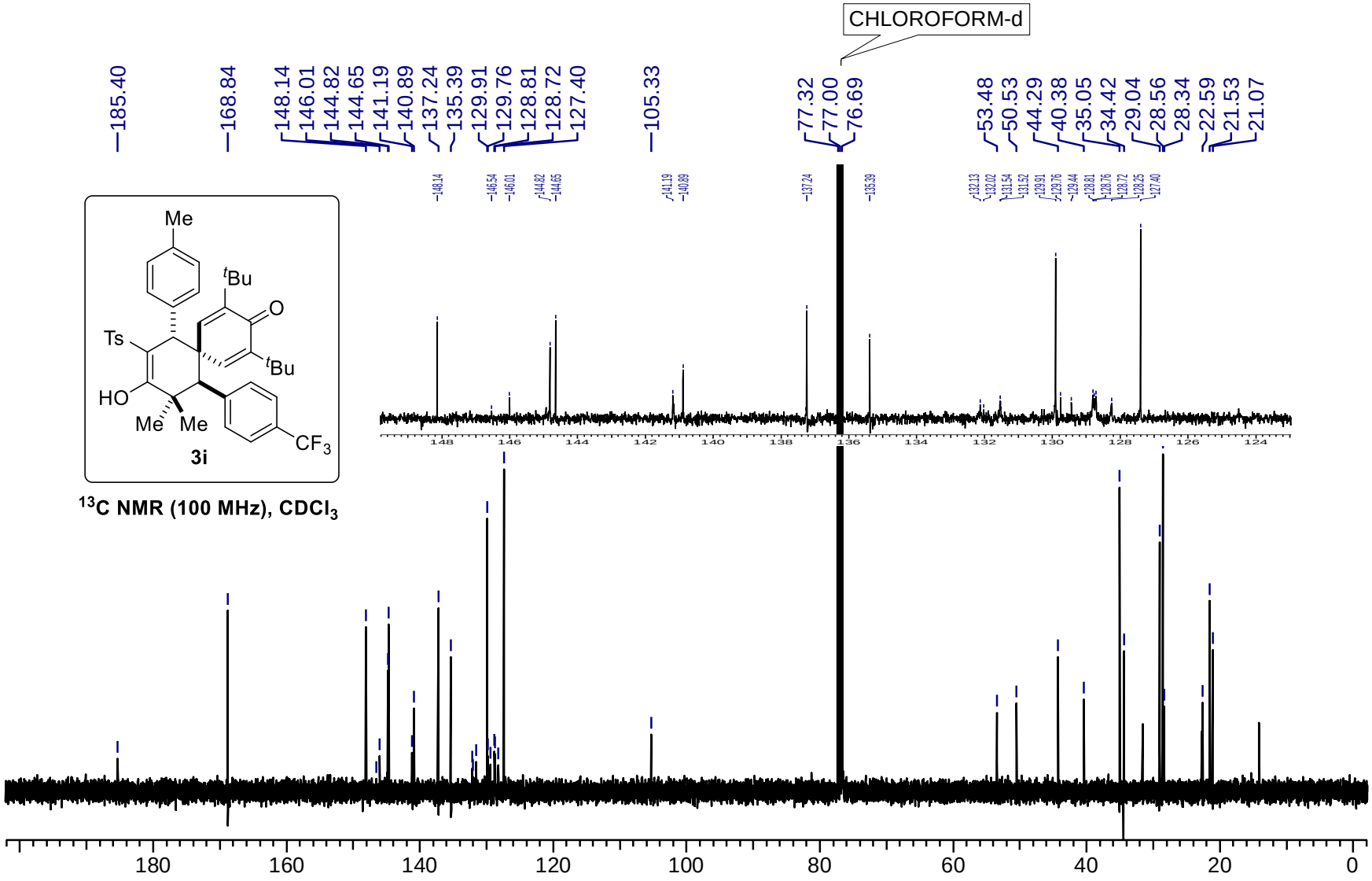
6.88
6.77
6.75
5.22
5.21
3.43
3.30
2.40
2.35
1.56
1.41
1.27
1.14
0.64
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
CF3
3i
1H NMR (400 MHz), CDCl3
2.01
0.98
1.54
2.24
4.13
2.07
1.02
1.01
2.01 0.98 1.54 2.24 4.13 2.07 1.02
1.03
1.02 1.00
3.06 3.05 3.10 3.26 9.18 9.17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144.82
144.65
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137.24
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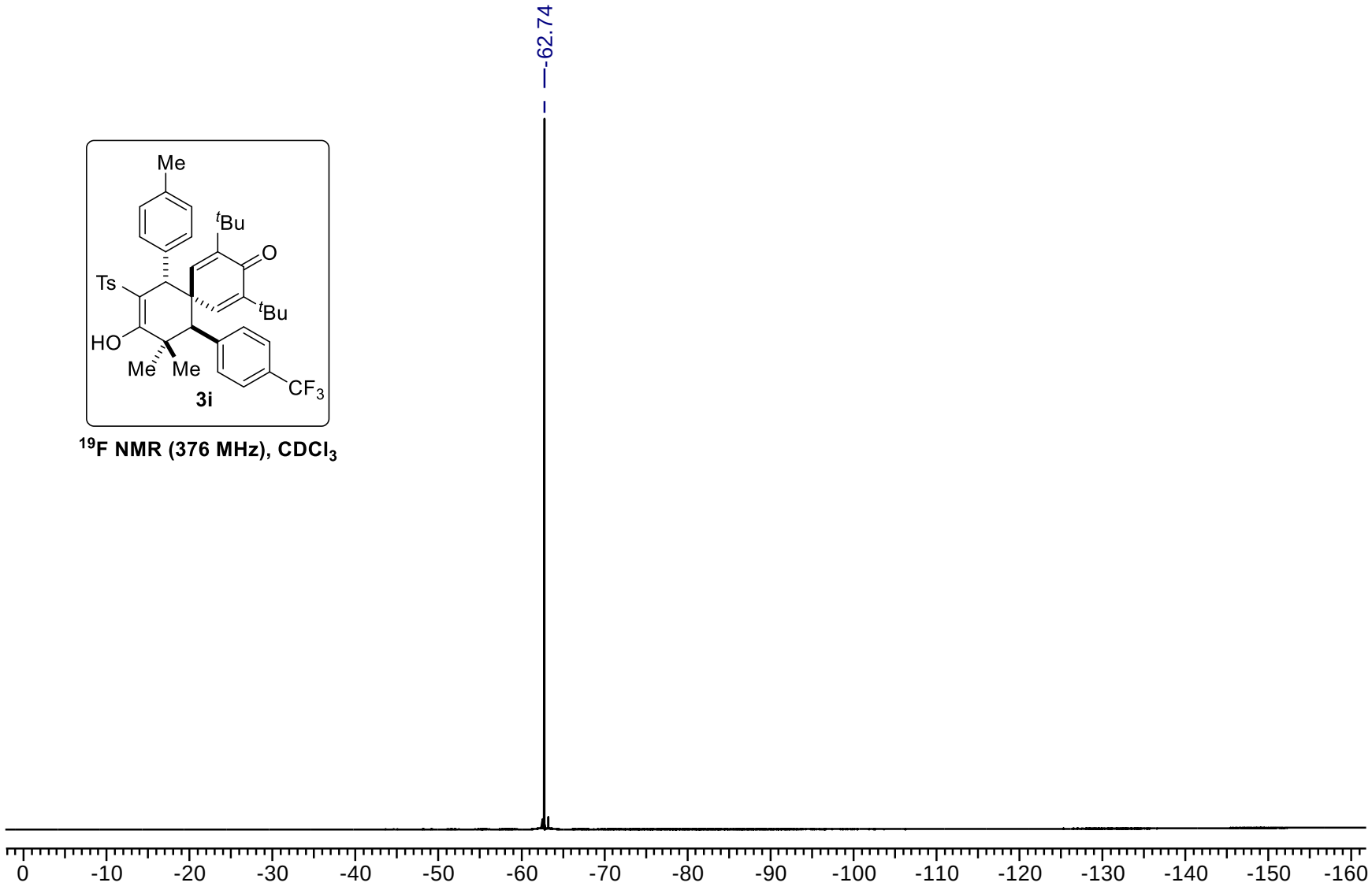
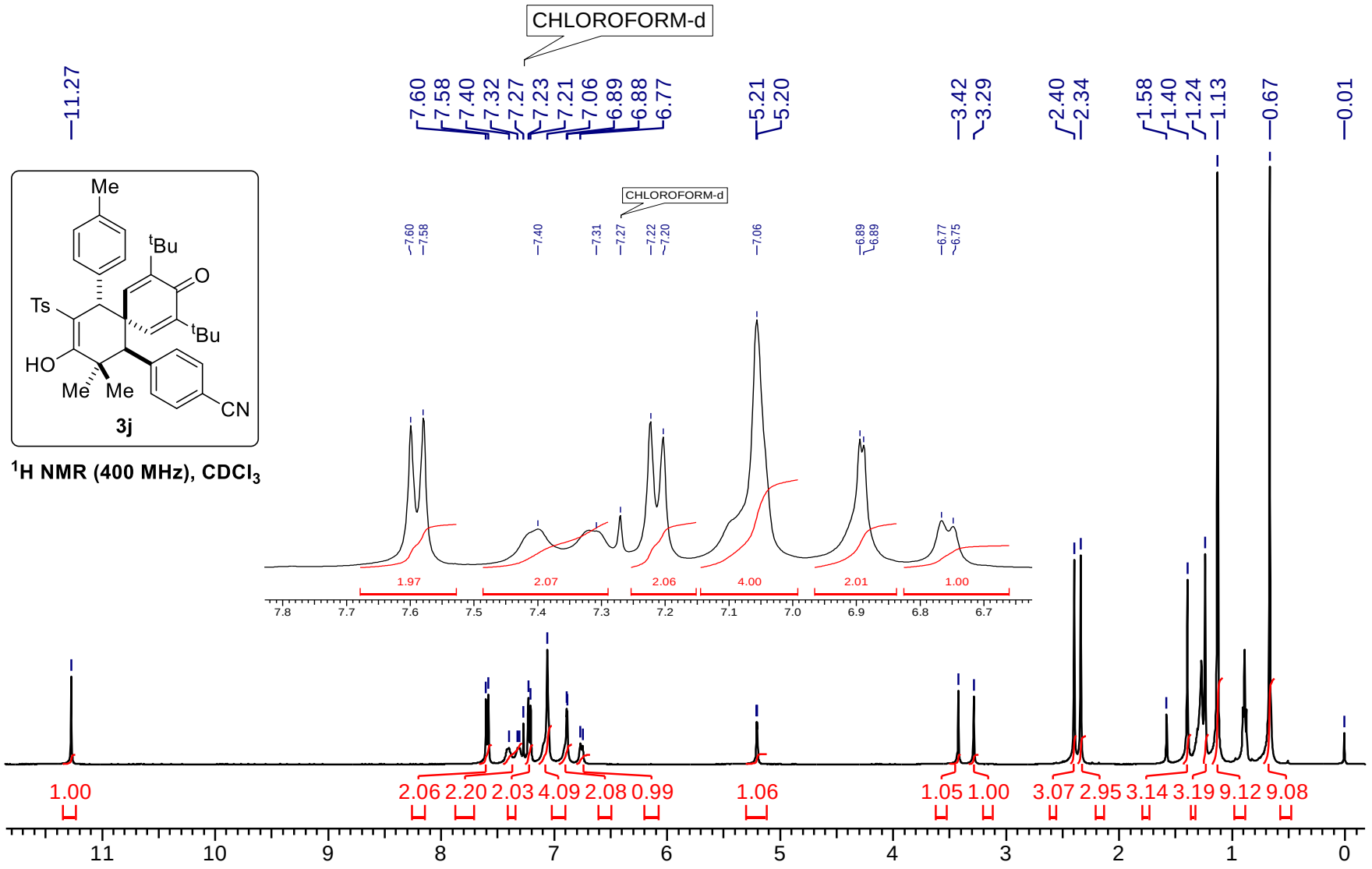
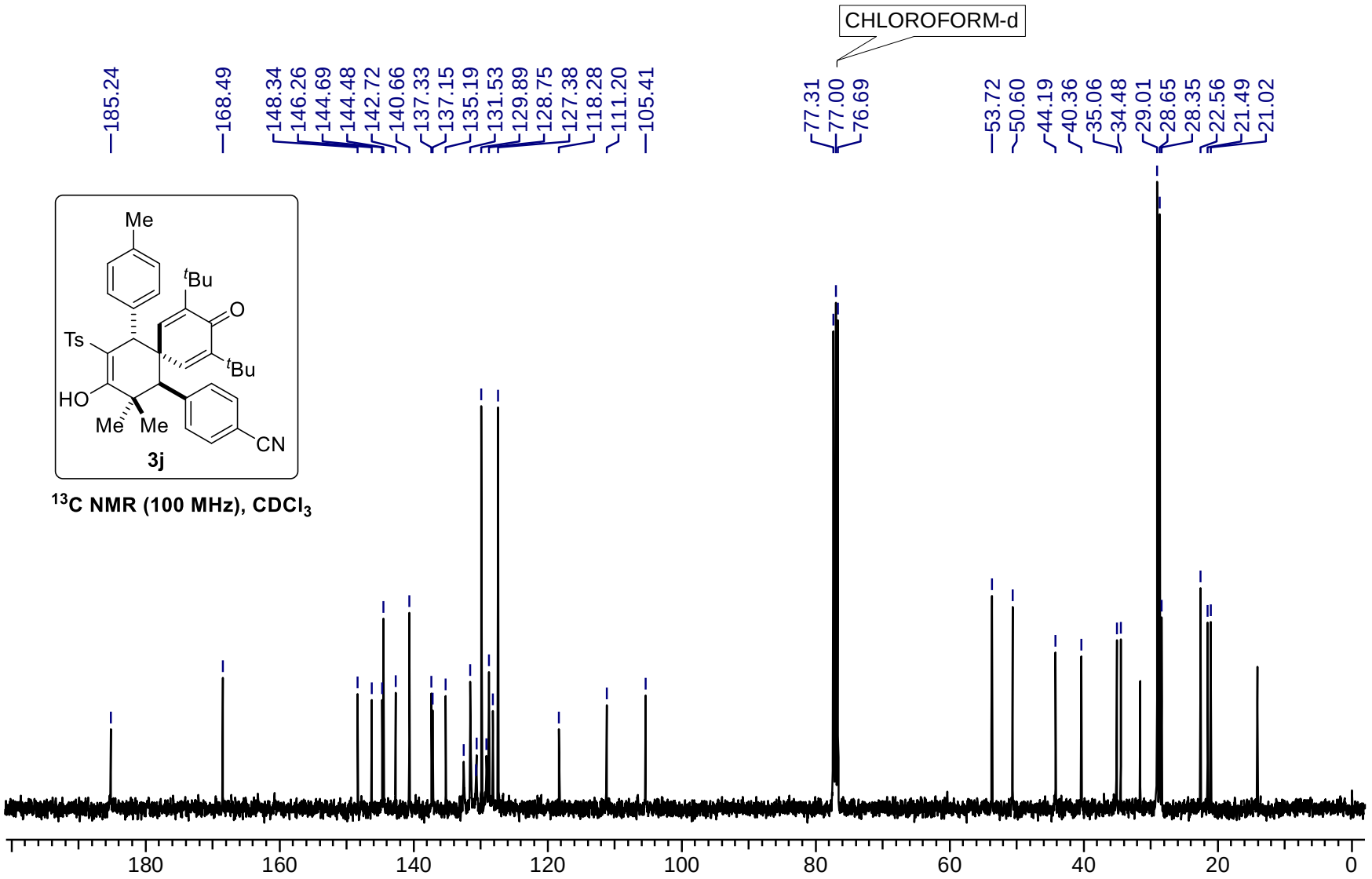
129.76
128.81
128.72
127.40
105.33
77.32
77.00
76.69
53.48
50.53
44.29
40.38
35.05
34.42
29.04
28.56
28.34
22.59
21.53
21.07
Me
tBu
O
Ts
tBu
HO
Me
Me
CF3
3i
13C NMR (100 MHz), CDCl3

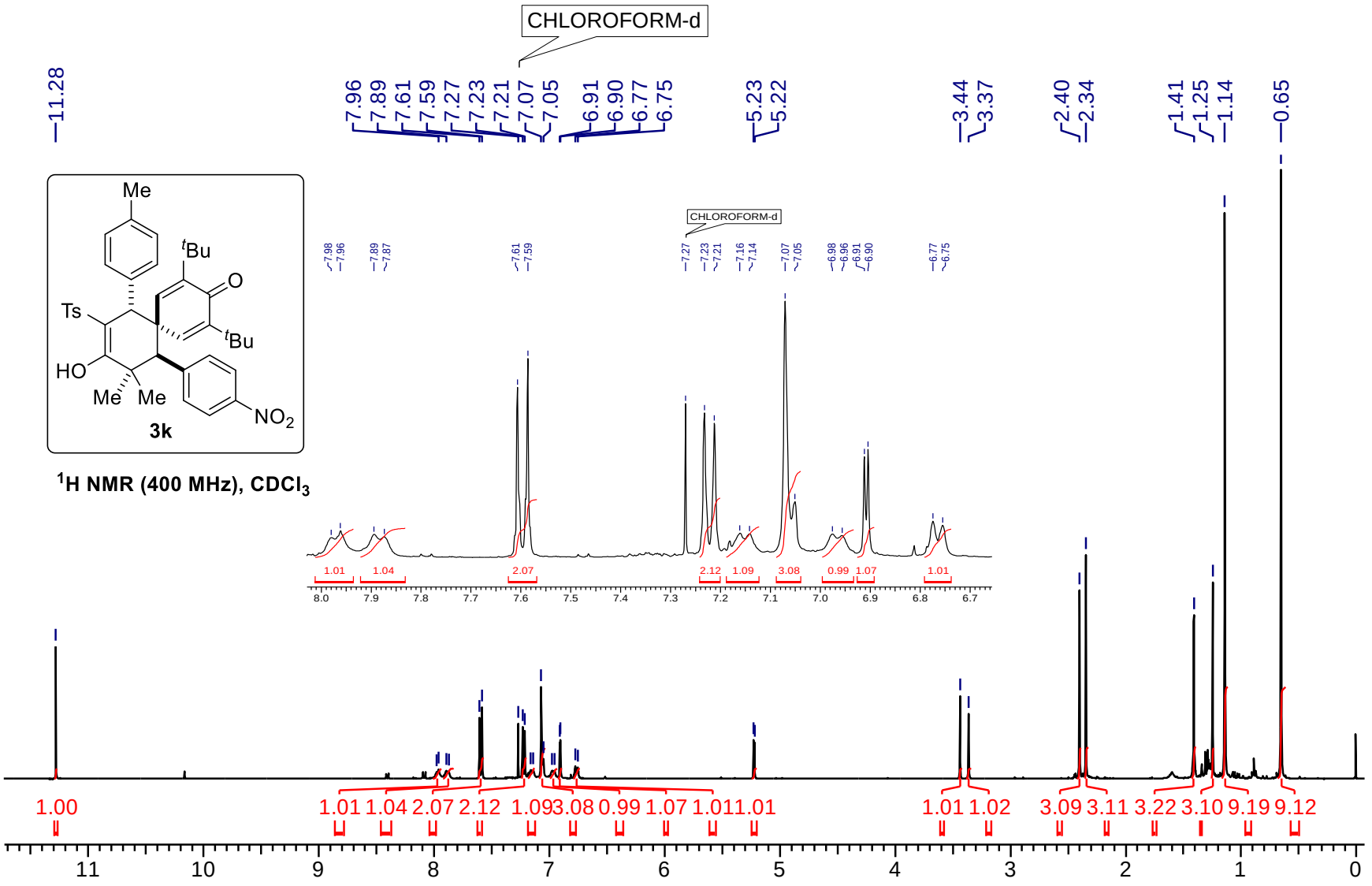
^{19}F NMR (376 MHz), $CDCl_3$

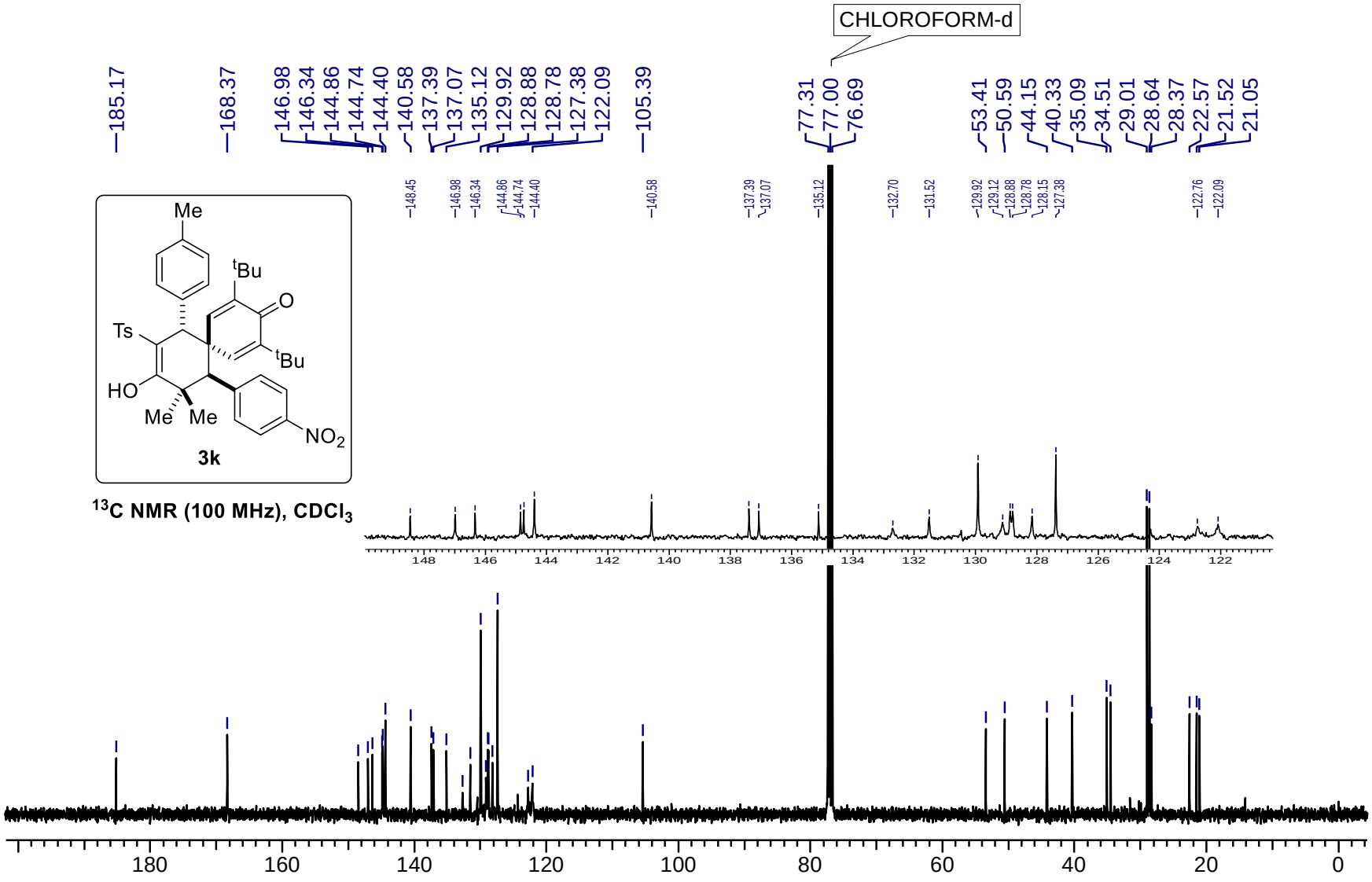



CHLOROFORM-d
11.27
7.60
7.58
7.40
7.32
7.27
7.23
7.21
7.06
6.89
6.88
6.77
5.21
5.20
3.42
3.29
2.40
2.34
1.58
1.40
1.24
1.13
0.67
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
CN
3j
1H NMR (400 MHz), CDCl3
1.97
2.07
2.06
4.00
2.01
1.00
1.00
2.06 2.20 2.03 4.09 2.08 0.99
1.06
1.05 1.00
3.07 2.95 3.14 3.19 9.12 9.08



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


CHLOROFORM-d
11.28
7.96
7.89
7.61
7.59
7.27
7.23
7.21
7.07
7.05
6.91
6.90
6.77
6.75
5.23
5.22
3.44
3.37
2.40
2.34
1.41
1.25
1.14
0.65
Me
tBu
O
Ts
tBu
HO
Me
Me
NO2
3k
1H NMR (400 MHz), CDCl3
1.00
1.01 1.04 2.07 2.12 1.09 3.08 0.99 1.07 1.01 1.01
1.01 1.02
3.09 3.11 3.22 3.10 9.19 9.12


CHLOROFORM-d
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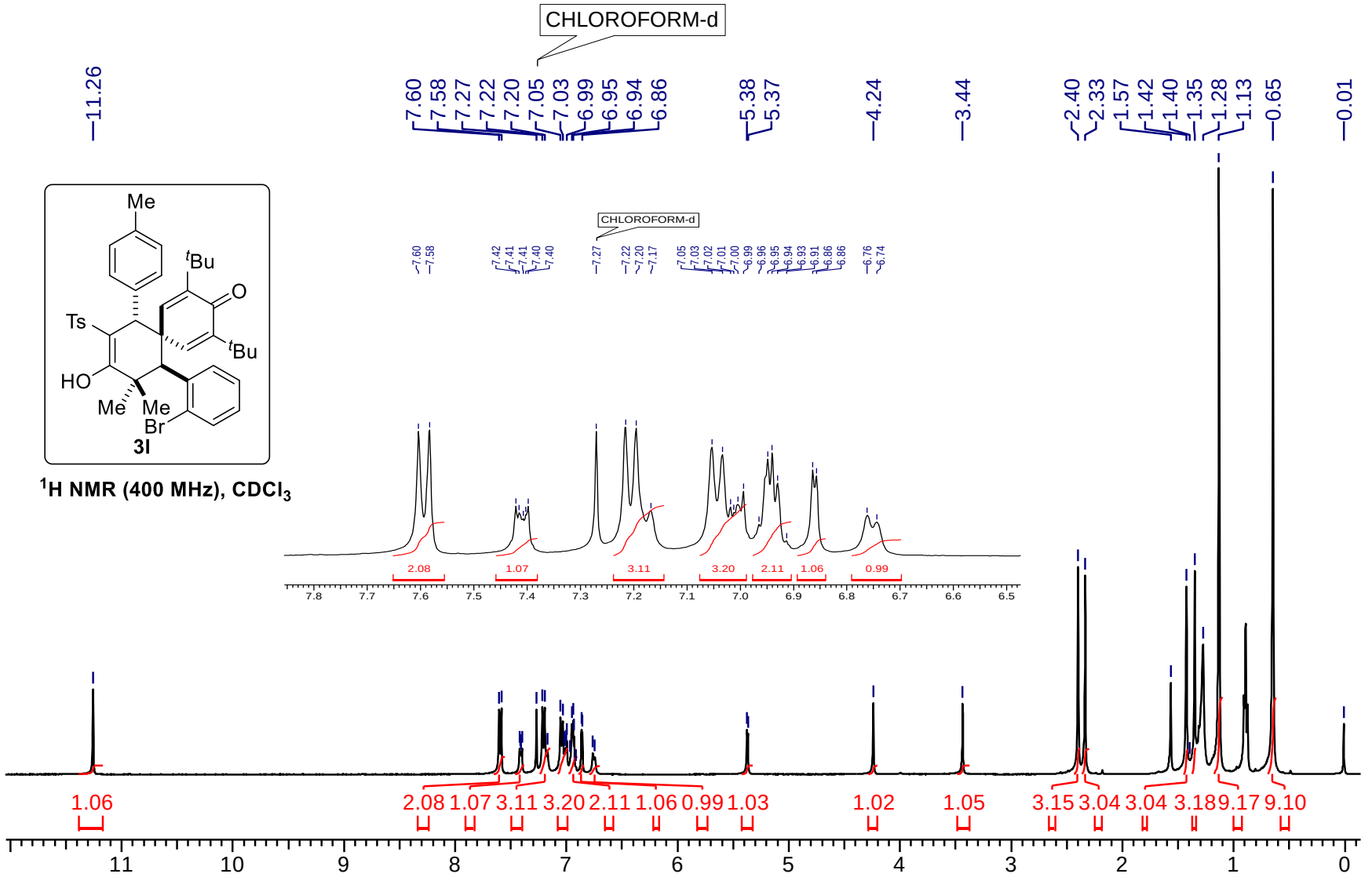
168.37
146.98
146.34
144.86
144.74
144.40
140.58
137.39
137.07
135.12
129.92
128.88
128.78
127.38
122.09
105.39
77.31
77.00
76.69
53.41
50.59
44.15
40.33
35.09
34.51
29.01
28.64
28.37
22.57
21.52
21.05
Me
tBu
O
Ts
tBu
HO
Me
Me
NO2
3k
13C NMR (100 MHz), CDCl3


CHLOROFORM-d
11.26
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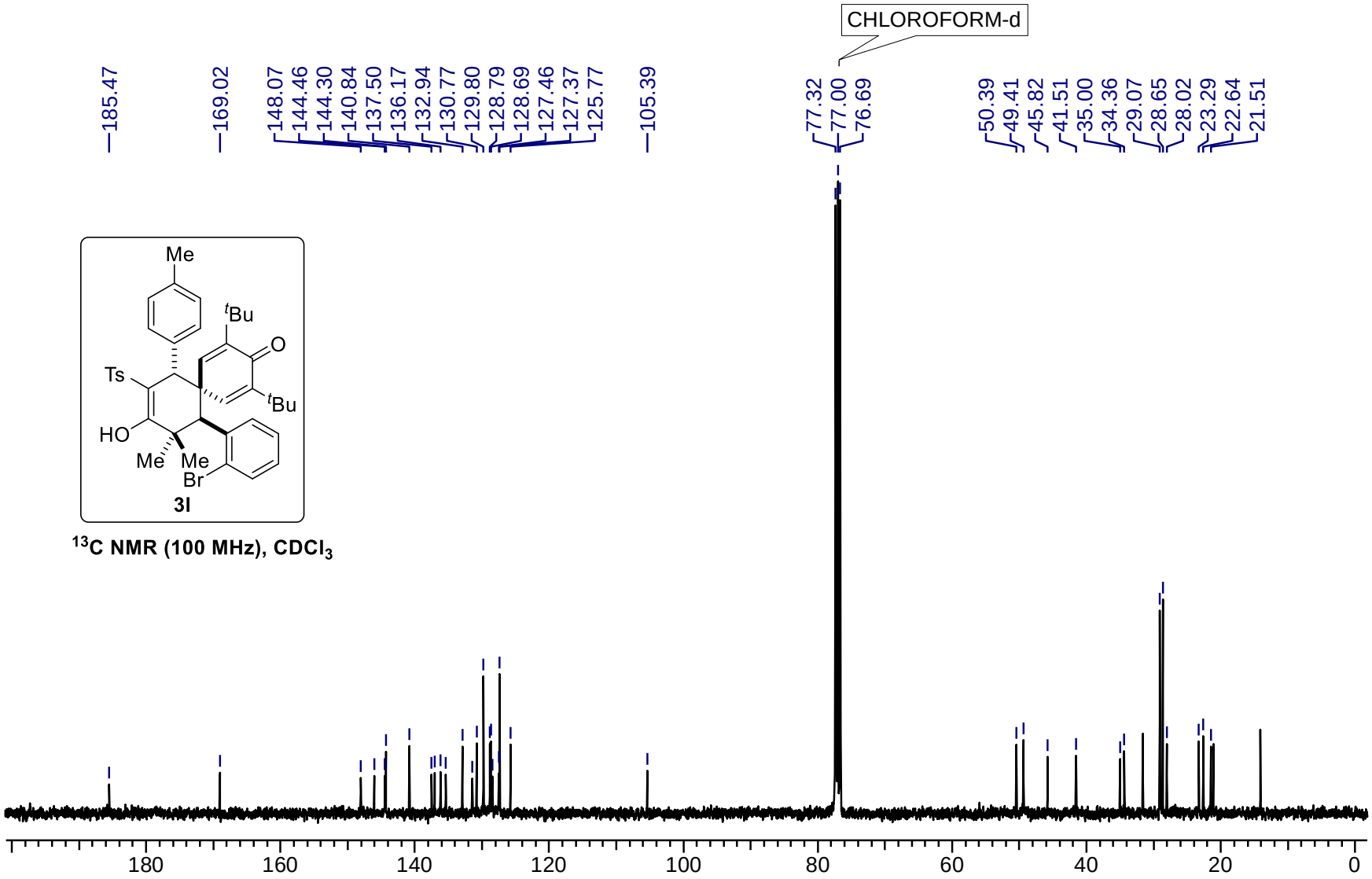
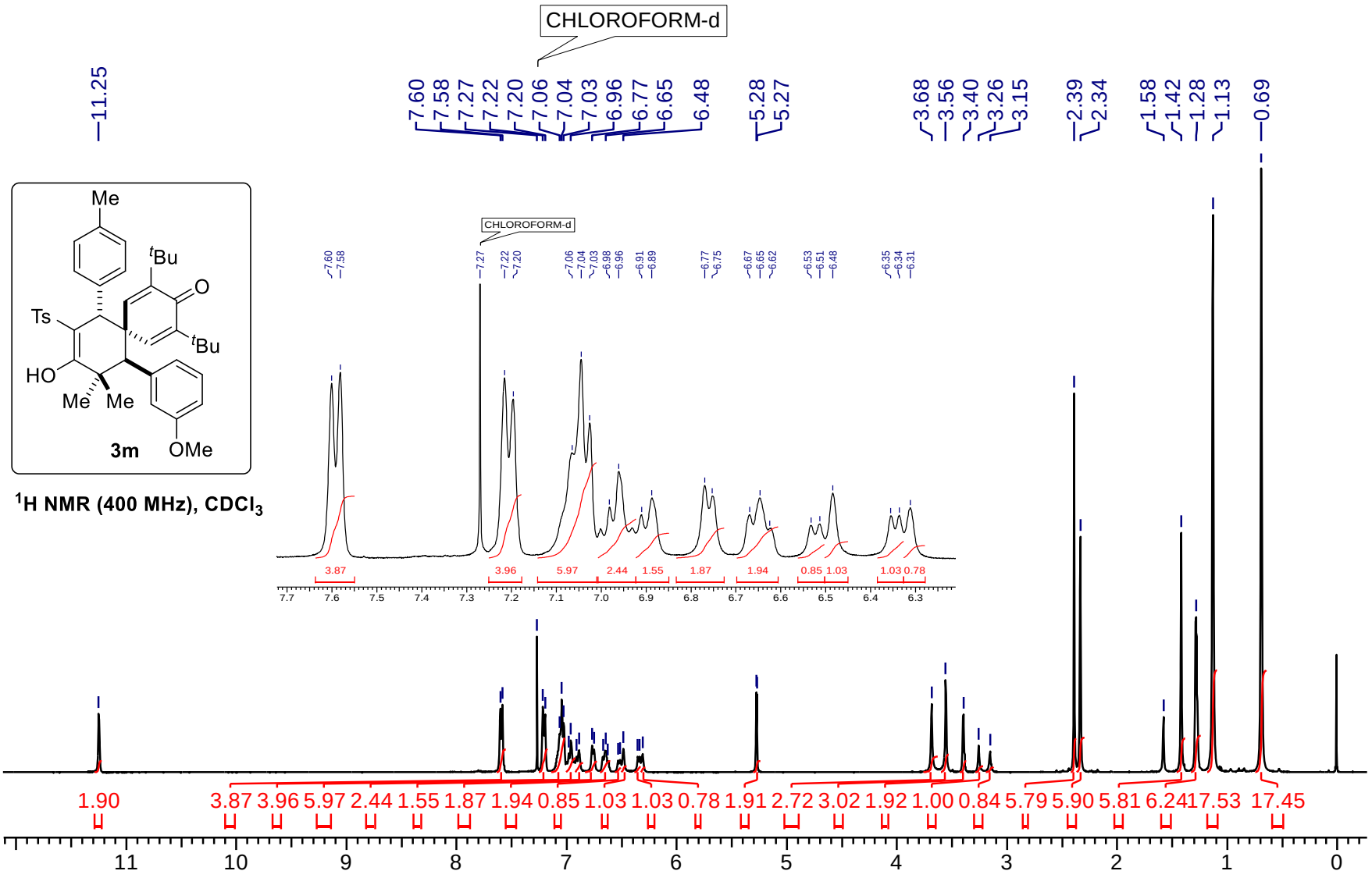
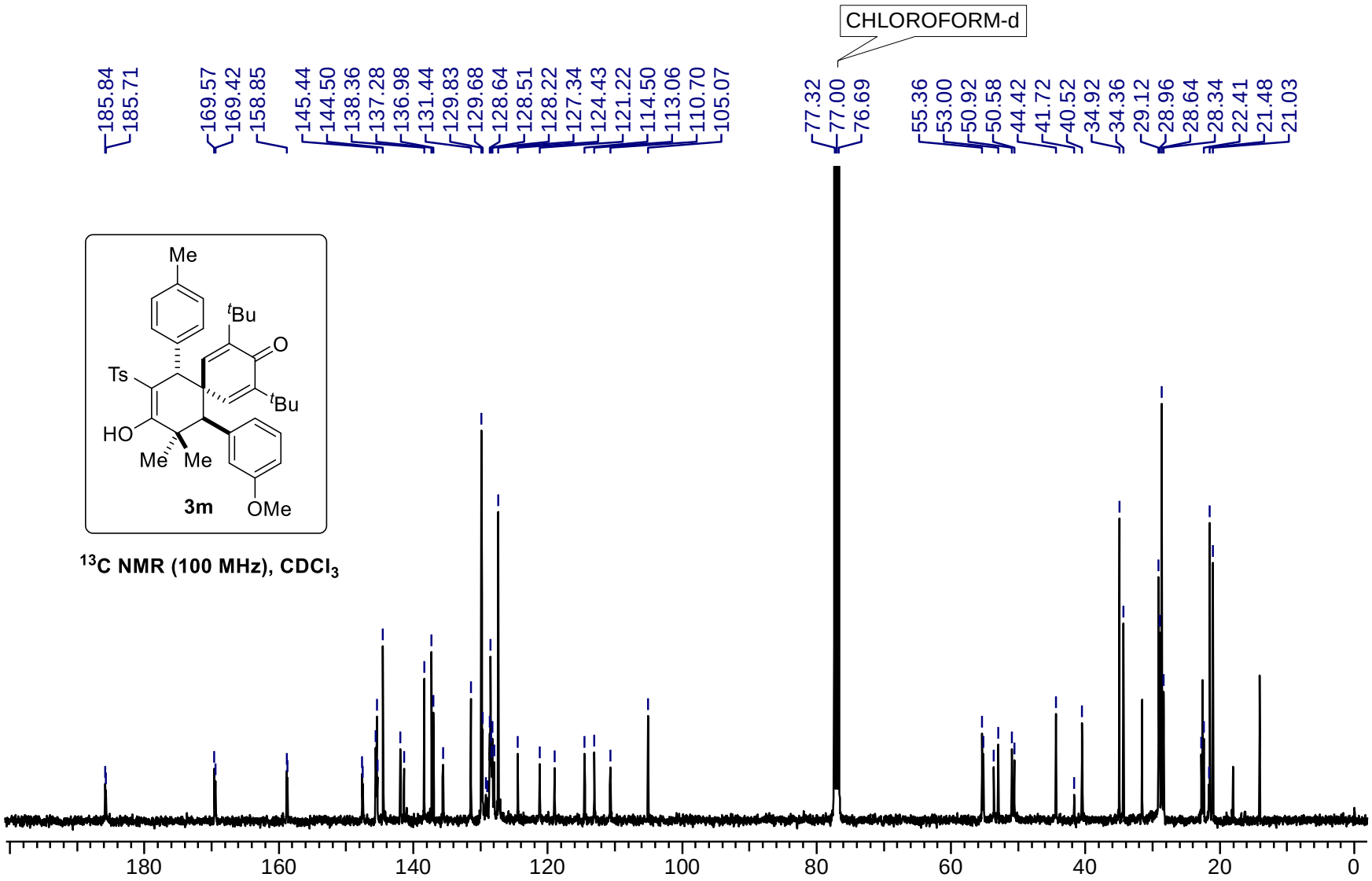
7.58
7.27
7.22
7.20
7.05
7.03
6.99
6.95
6.94
6.86
5.38
5.37
4.24
3.44
2.40
2.33
1.57
1.42
1.40
1.35
1.28
1.13
0.65
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
Br
3l
1H NMR (400 MHz), CDCl3
2.08
1.07
3.11
3.20
2.11
1.06
0.99
1.06
2.08
1.07
3.11
3.20
2.11
1.06
0.99
1.03
1.02
1.05
3.15
3.04
3.04
3.18
9.17
9.10

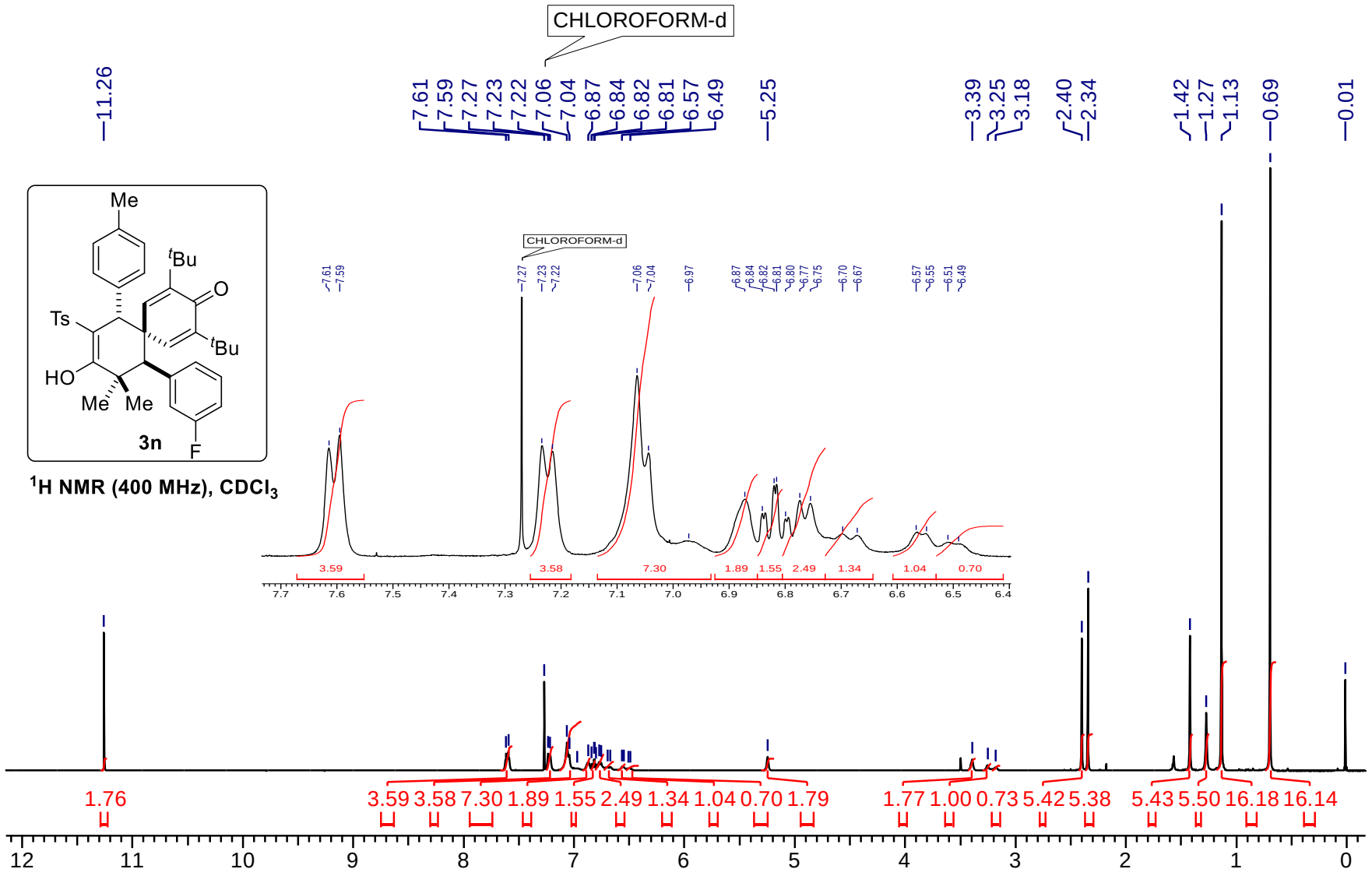


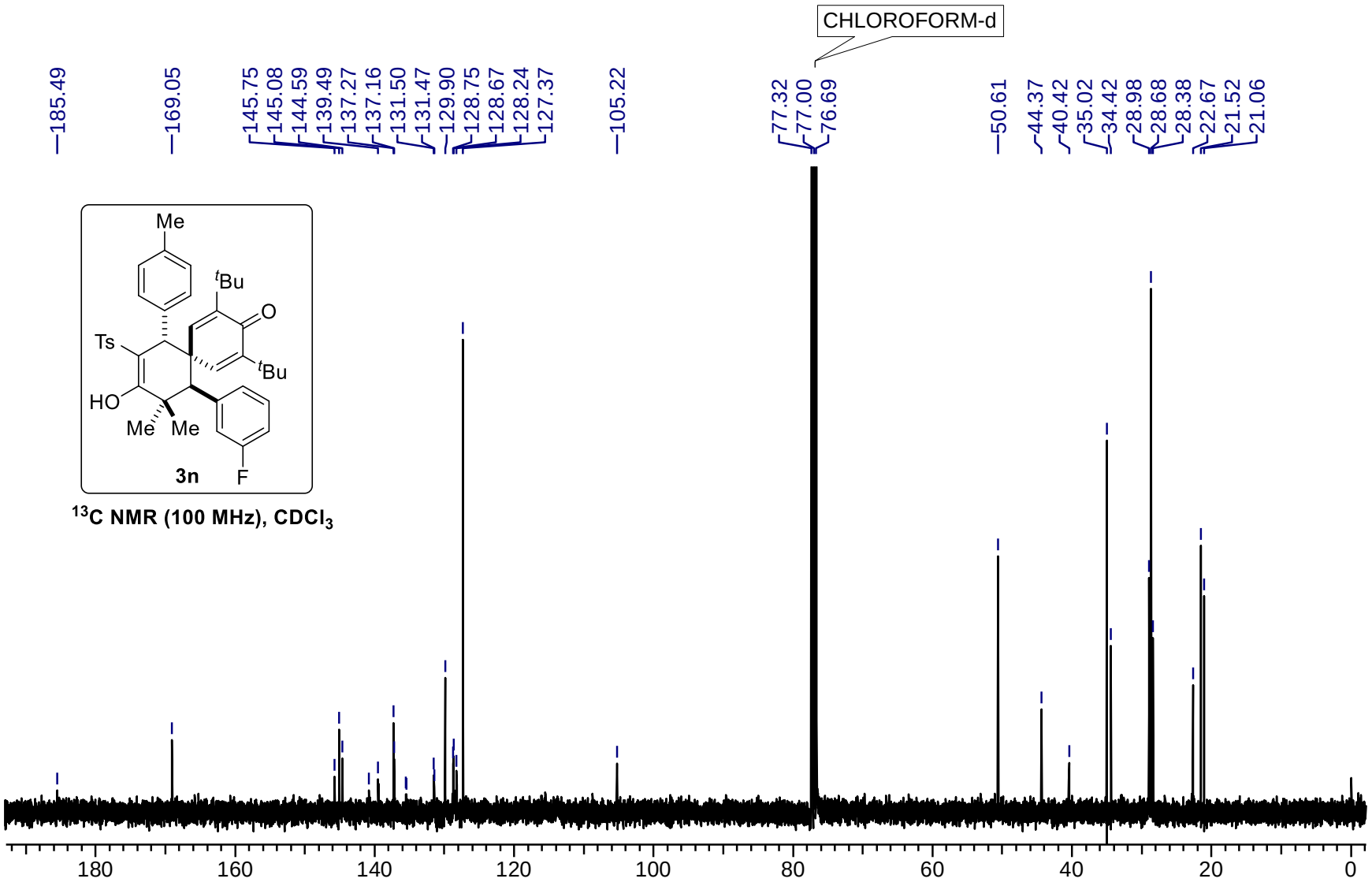
^{13}C NMR (100 MHz), $CDCl_3$


CHLOROFORM-d
11.25
7.60
7.58
7.27
7.22
7.20
7.06
7.04
7.03
6.96
6.77
6.65
6.48
5.28
5.27
3.68
3.56
3.40
3.26
3.15
2.39
2.34
1.58
1.42
1.28
1.13
0.69
Me
tBu
O
Ts
tBu
HO
Me
Me
3m
OMe
1H NMR (400 MHz), CDCl3
3.87
3.96
5.97
2.44
1.55
1.87
1.94
0.85
1.03
1.03
0.78
1.91
2.72
3.02
1.92
1.00
0.84
5.79
5.90
5.81
6.24
17.53
17.45



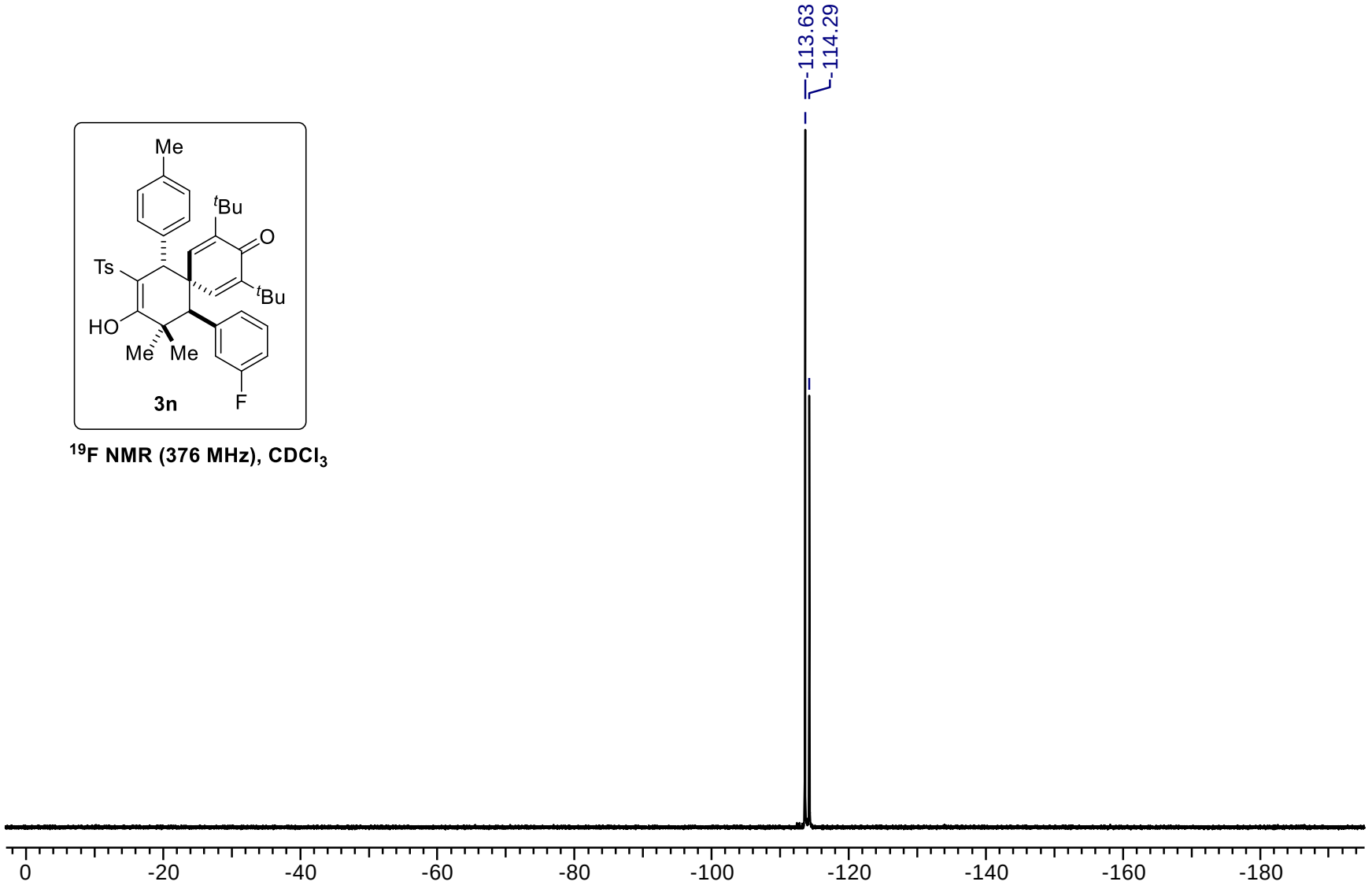
^{13}C NMR (100 MHz), $CDCl_3$

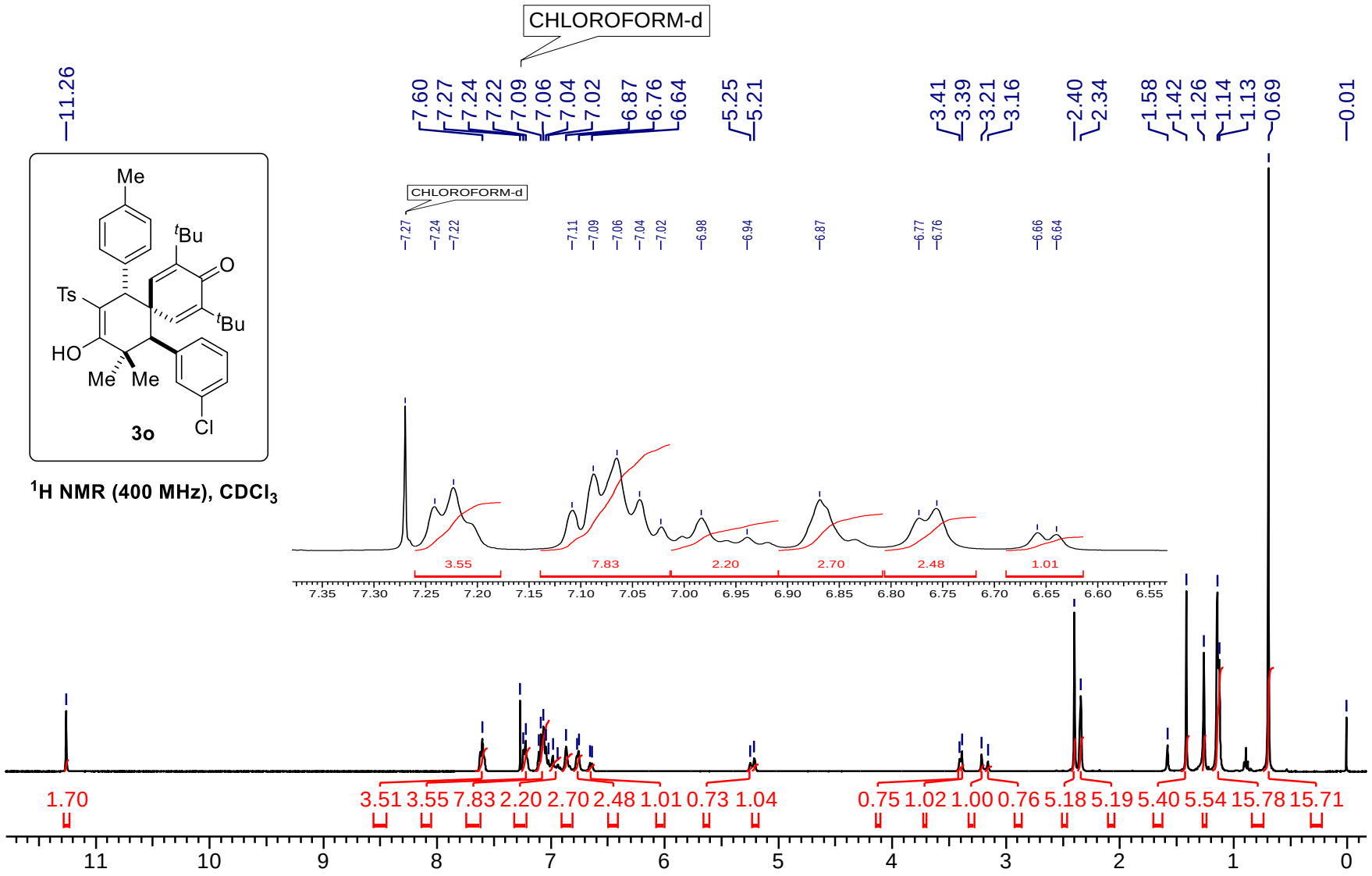

CHLOROFORM-d
11.26
7.61
7.59
7.27
7.23
7.22
7.06
7.04
6.87
6.84
6.82
6.81
6.57
6.49
5.25
3.39
3.25
3.18
2.40
2.34
1.42
1.27
1.13
0.69
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
3n
F
1H NMR (400 MHz), CDCl3
3.59
3.58
7.30
1.89
1.55
2.49
1.34
1.04
0.70
1.76
3.59 3.58 7.30 1.89 1.55 2.49 1.34 1.04 0.70 1.79
1.77 1.00 0.73 5.42 5.38
5.43 5.50 16.18 16.14

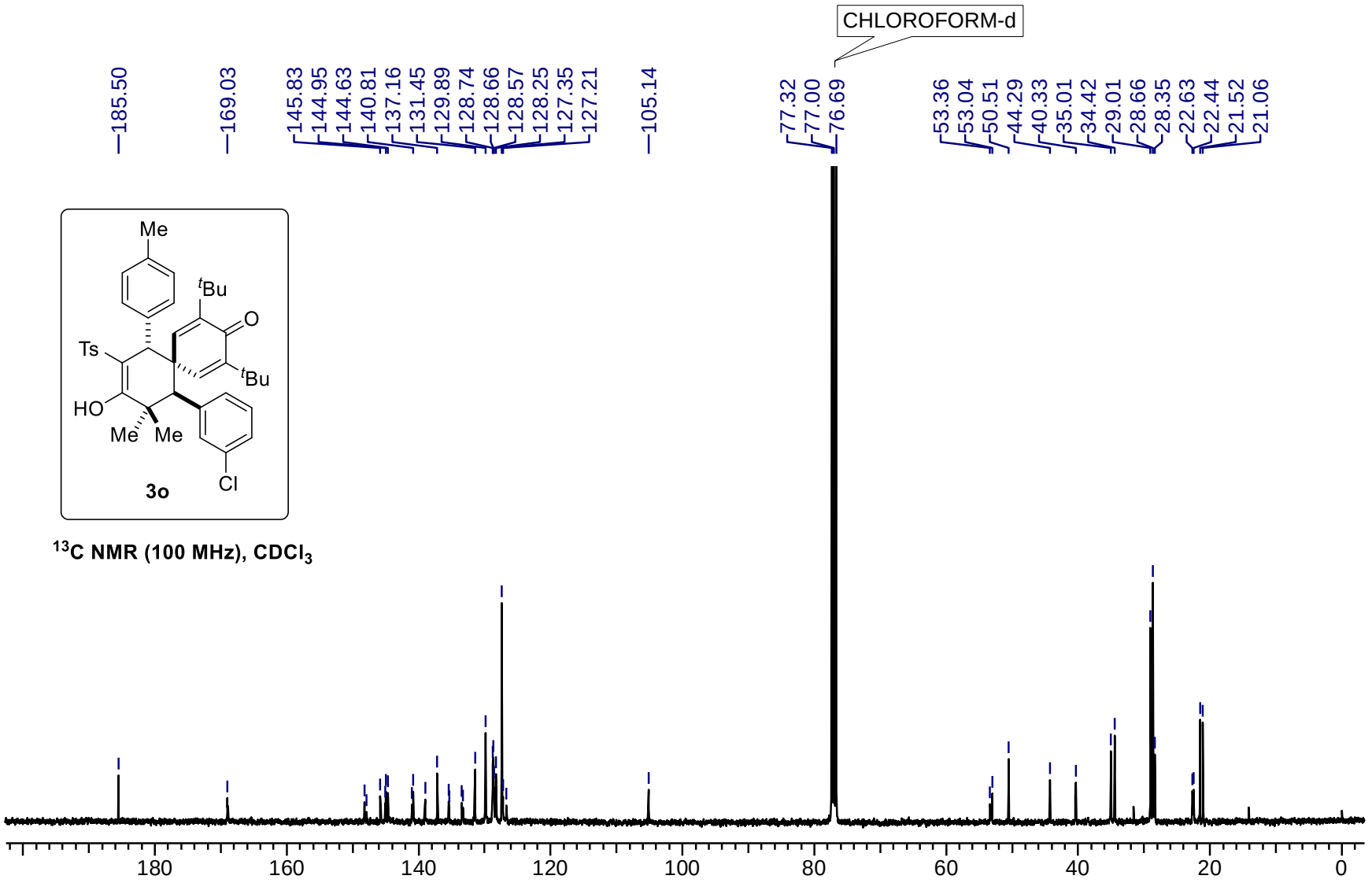


^{13}C NMR (100 MHz), $CDCl_3$

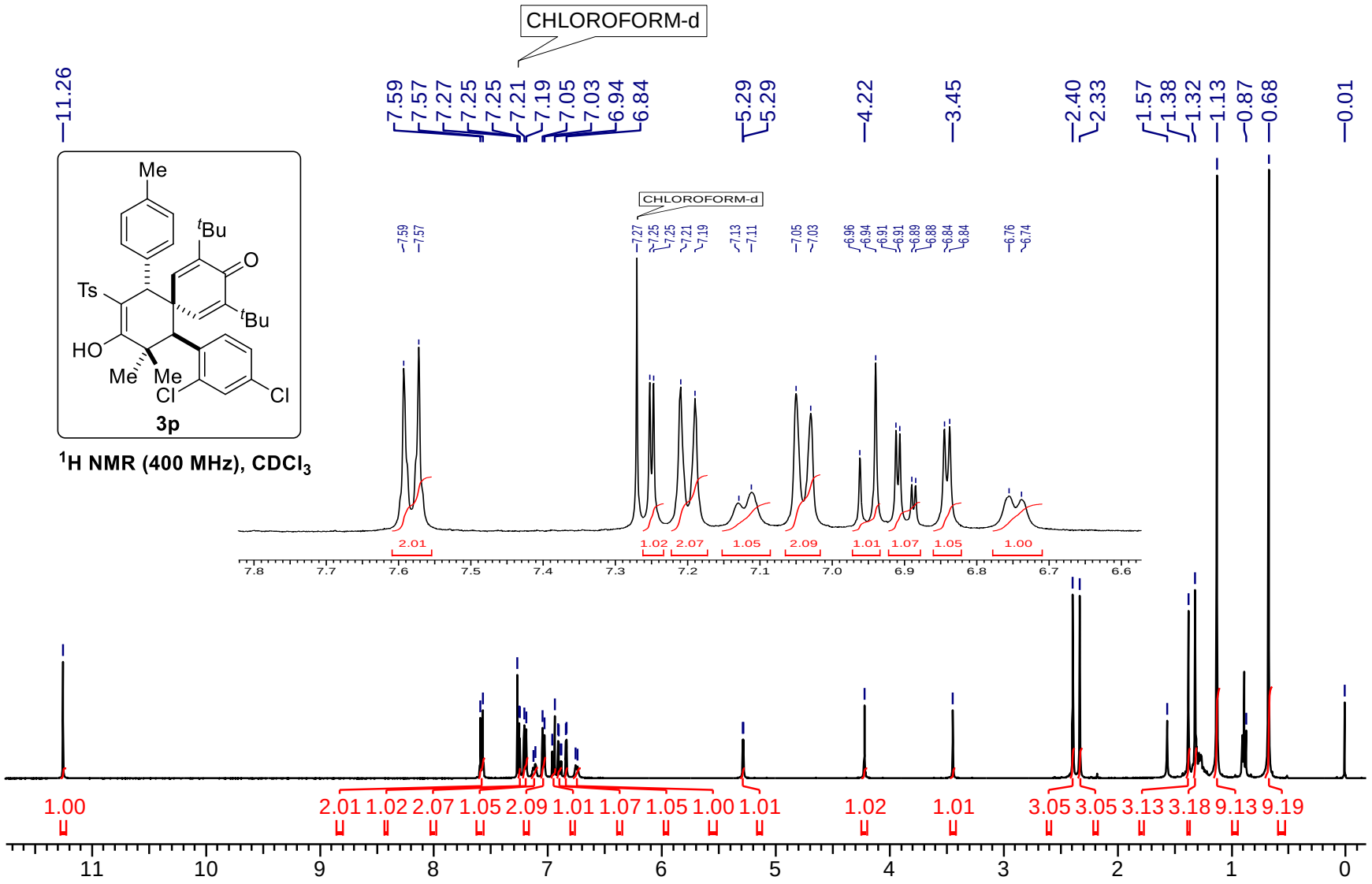
^{19}F NMR (376 MHz), $CDCl_3$

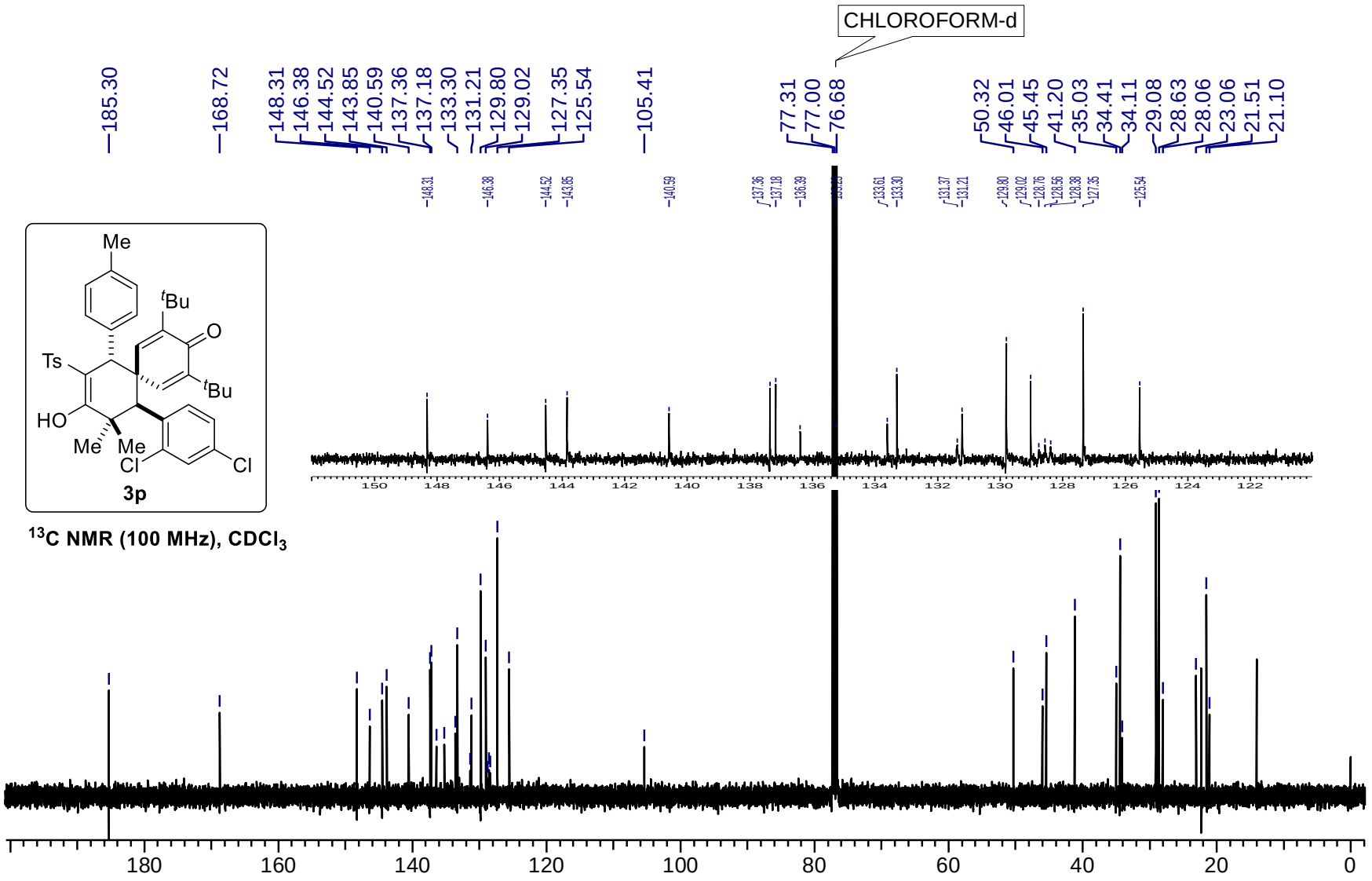



CHLOROFORM-d
11.26
7.60
7.27
7.24
7.22
7.09
7.06
7.04
7.02
6.87
6.76
6.64
5.25
5.21
3.41
3.39
3.21
3.16
2.40
2.34
1.58
1.42
1.26
1.14
1.13
0.69
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
Cl
3o
1H NMR (400 MHz), CDCl3
3.55
7.83
2.20
2.70
2.48
1.01
1.70
3.51 3.55 7.83 2.20 2.70 2.48 1.01 0.73 1.04
0.75 1.02 1.00 0.76 5.18 5.19 5.40 5.54 15.78 15.71



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


CHLOROFORM-d
11.26
7.59
7.57
7.27
7.25
7.25
7.21
7.19
7.05
7.03
6.94
6.84
5.29
5.29
4.22
3.45
2.40
2.33
1.57
1.38
1.32
1.13
0.87
0.68
0.01
Me
tBu
O
Ts
tBu
HO
Me
Me
Cl
Cl
3p
1H NMR (400 MHz), CDCl3
1.00
2.01 1.02 2.07 1.05 2.09 1.01 1.07 1.05 1.00 1.01
1.02
1.01
3.05 3.05 3.13 3.18 9.13 9.19


CHLOROFORM-d
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148.31
146.38
144.52
143.85
140.59
137.36
137.18
133.30
131.21
129.80
129.02
127.35
125.54
105.41
77.31
77.00
76.68
50.32
46.01
45.45
41.20
35.03
34.41
34.11
29.08
28.63
28.06
23.06
21.51
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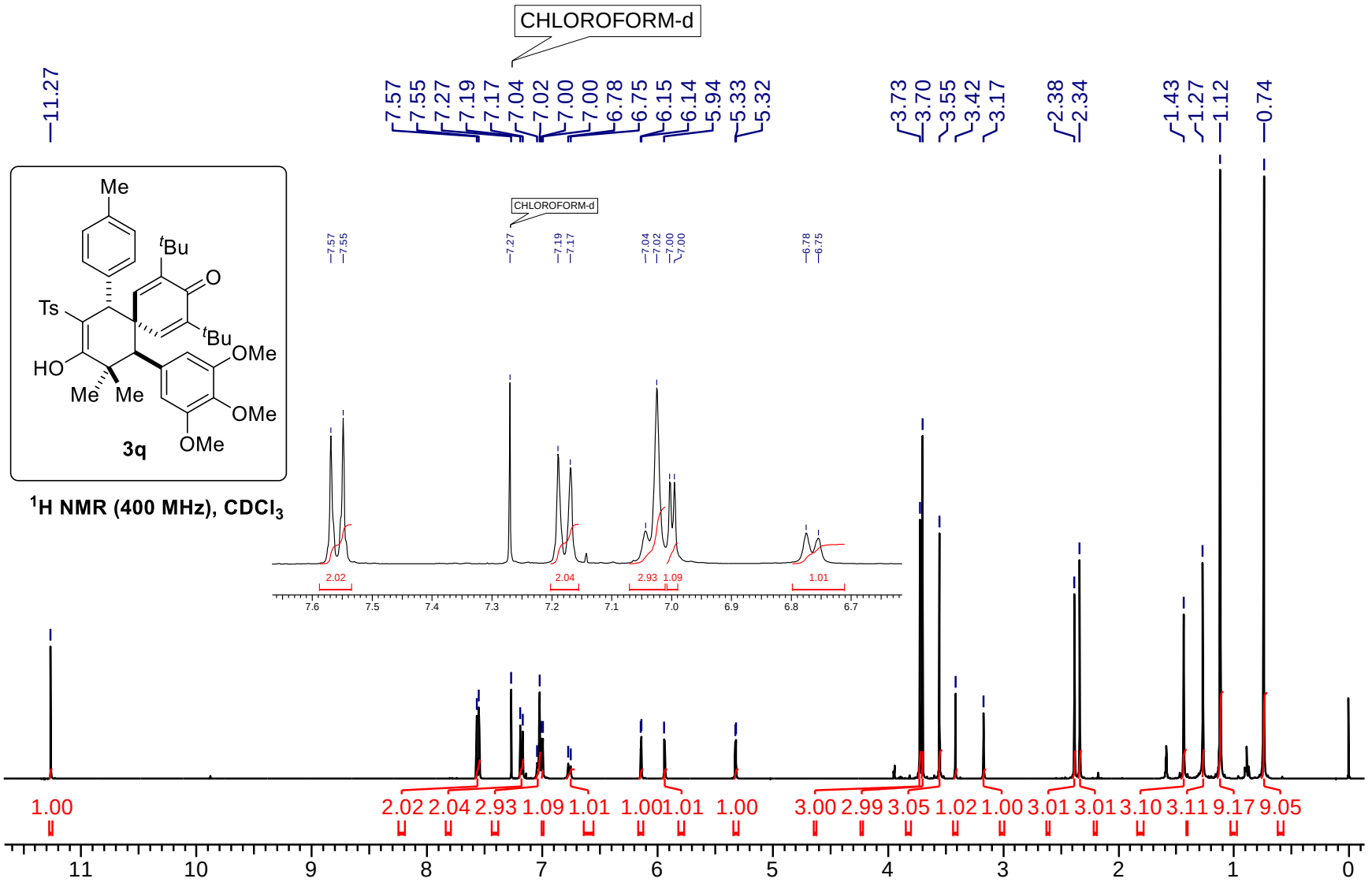
Me
tBu
O
Ts
tBu
HO
Me
Me
Cl
Cl
3p
13C NMR (100 MHz), CDCl3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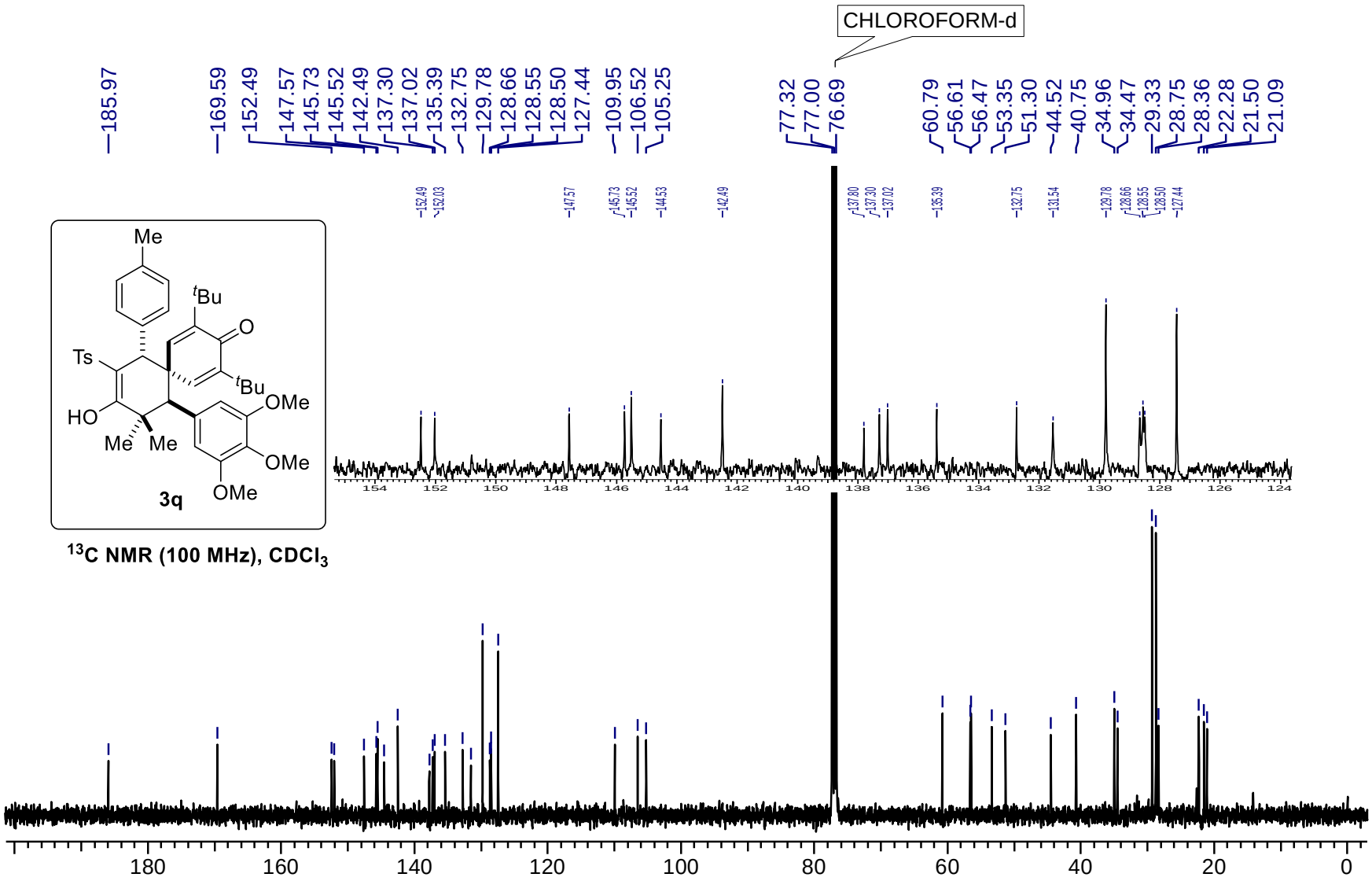
7.55
7.27
7.19
7.17
7.04
7.02
7.00
7.00
6.78
6.75
6.15
6.14
5.94
5.33
5.32
3.73
3.70
3.55
3.42
3.17
2.38
2.34
1.43
1.27
1.12
0.74
Me
tBu
O
Ts
tBu
OMe
HO
Me
Me
OMe
OMe
3q
1H NMR (400 MHz), CDCl3
1.00
2.02 2.04 2.93 1.09 1.01 1.00 1.01 1.00
3.00 2.99 3.05 1.02 1.00 3.01 3.01 3.10 3.11 9.17 9.05


CHLOROFORM-d
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147.57
145.73
145.52
142.49
137.30
137.02
135.39
132.75
129.78
128.66
128.55
128.50
127.44
109.95
106.52
105.25
77.32
77.00
76.69
60.79
56.61
56.47
53.35
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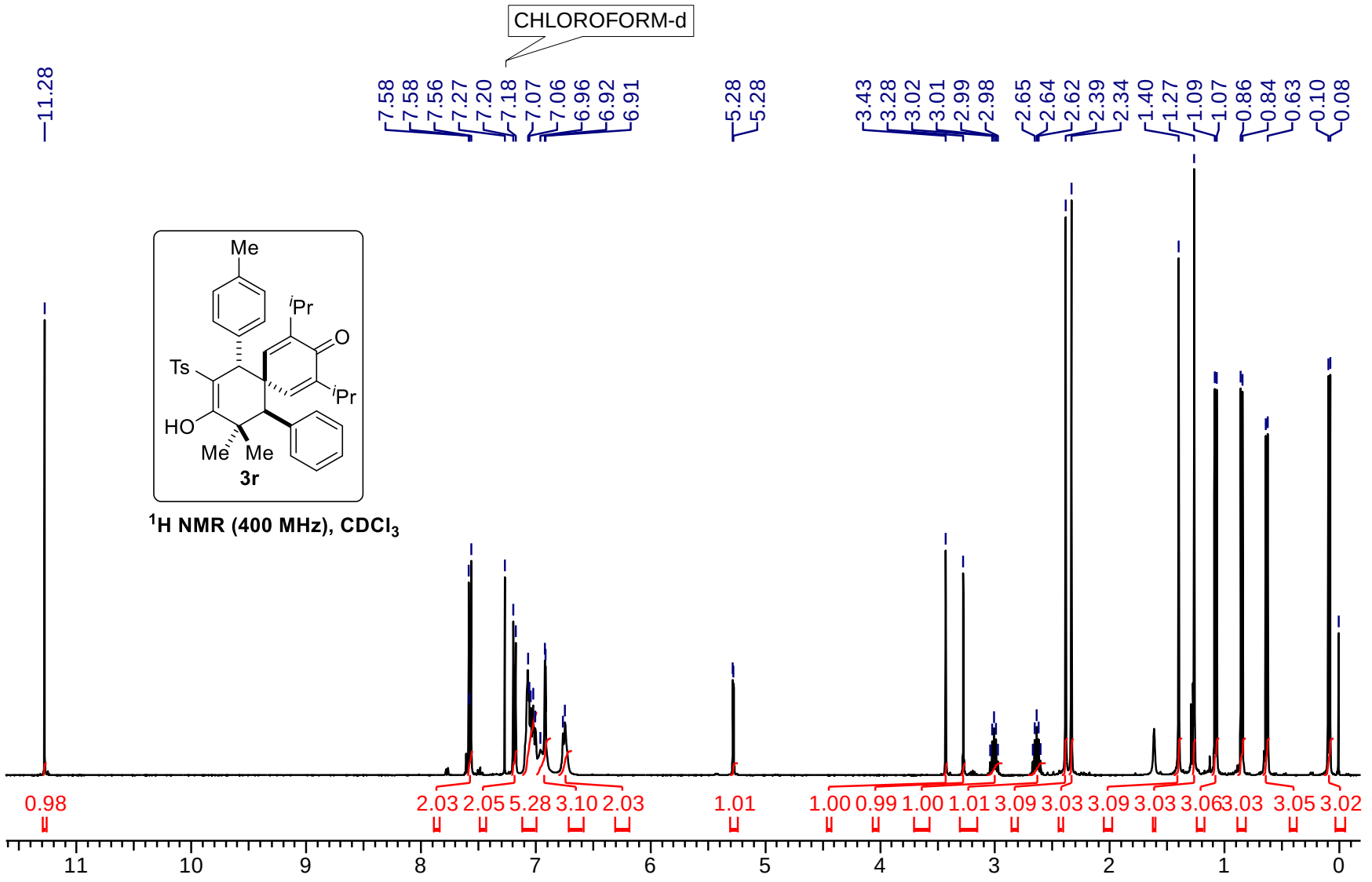
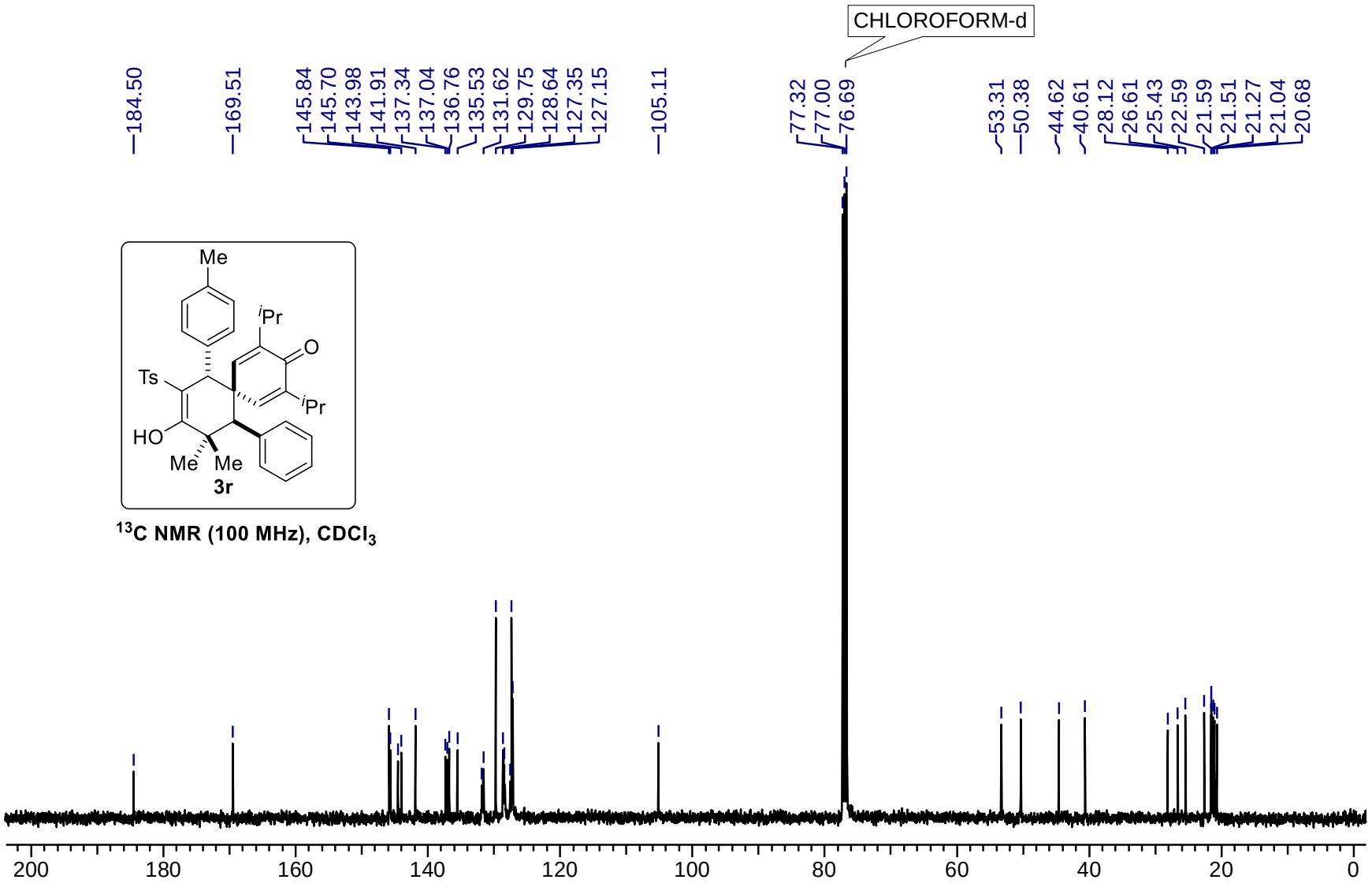
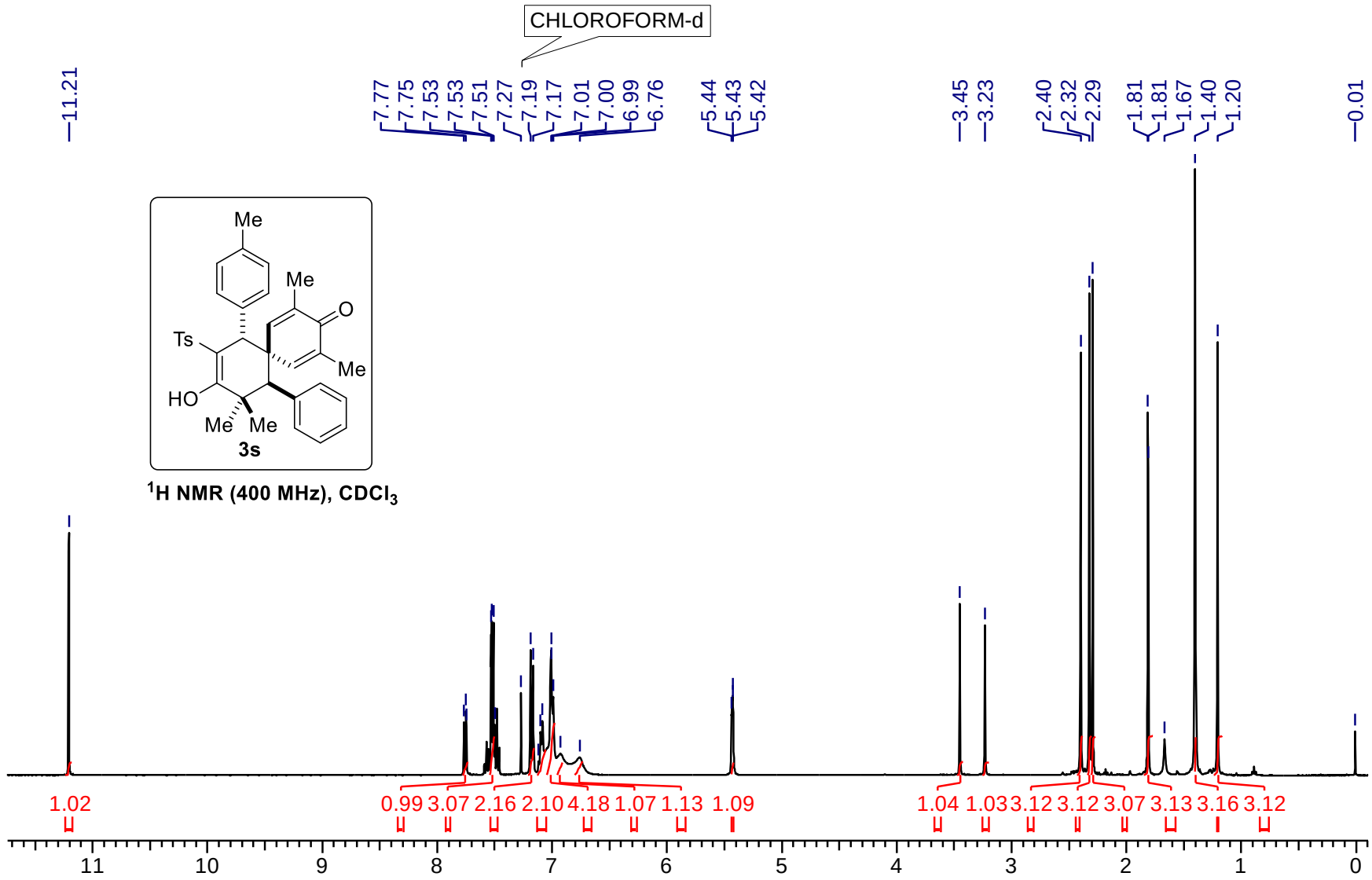
34.96
34.47
29.33
28.75
28.36
22.28
21.50
21.09
Me
tBu
O
Ts
tBu
OMe
HO
Me
Me
OMe
OMe
3q
13C NMR (100 MHz), CDCl3

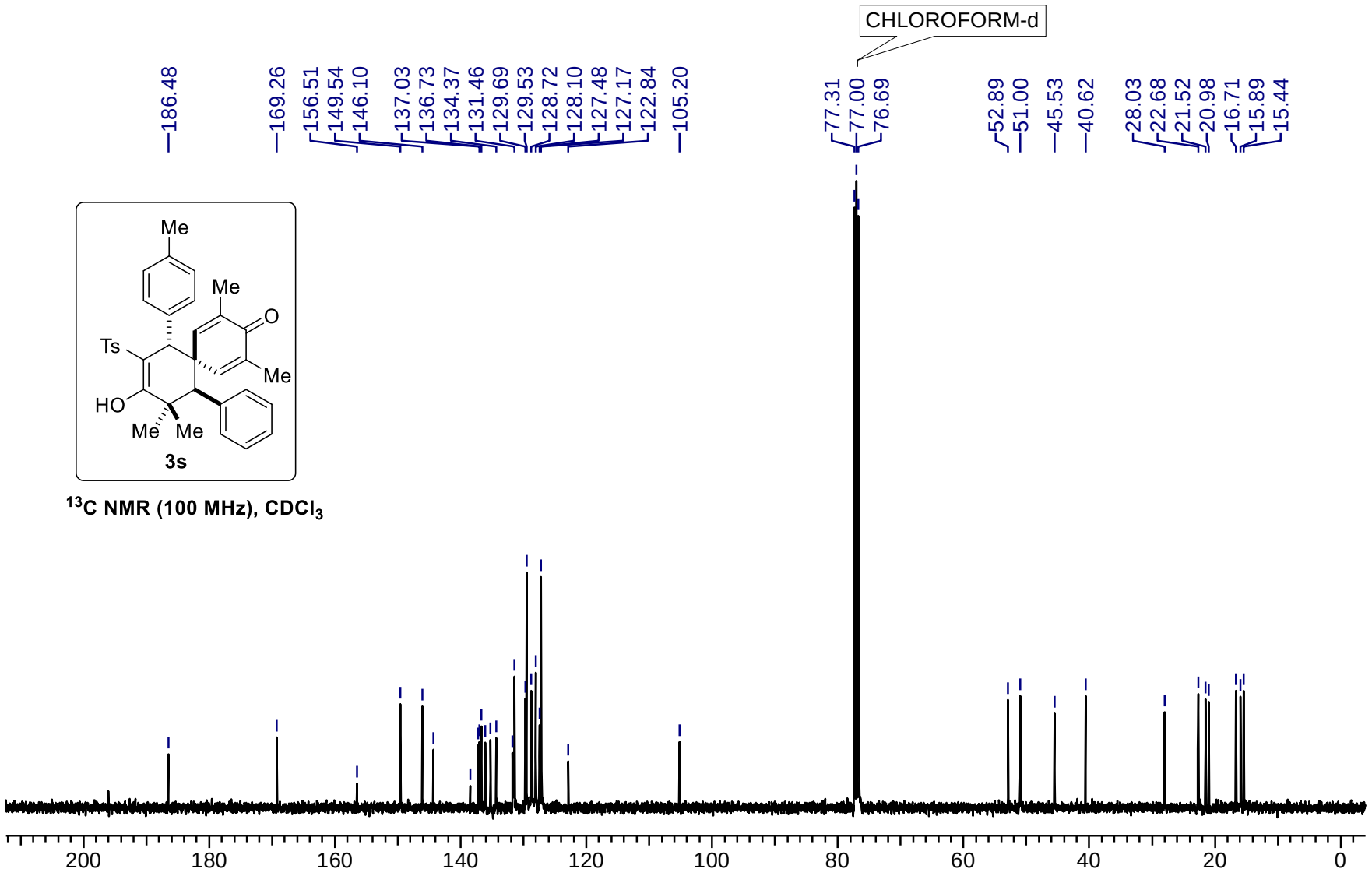

CHLOROFORM-d
11.28
7.58 7.58 7.56 7.27 7.20 7.18 7.07 7.06 6.96 6.92 6.91
5.28 5.28
3.43 3.28 3.02 3.01 2.99 2.98
2.65 2.64 2.62 2.39 2.34
1.40 1.27 1.09 1.07
0.86 0.84 0.63
0.10 0.08
Me
iPr
O
Ts
iPr
HO
Me Me
3r
1H NMR (400 MHz), CDCl3
0.98 2.03 2.05 5.28 3.10 2.03 1.01 1.00 0.99 1.00 1.01 3.09 3.03 3.09 3.03 3.06 3.03 3.05 3.02
11 10 9 8 7 6 5 4 3 2 1 0



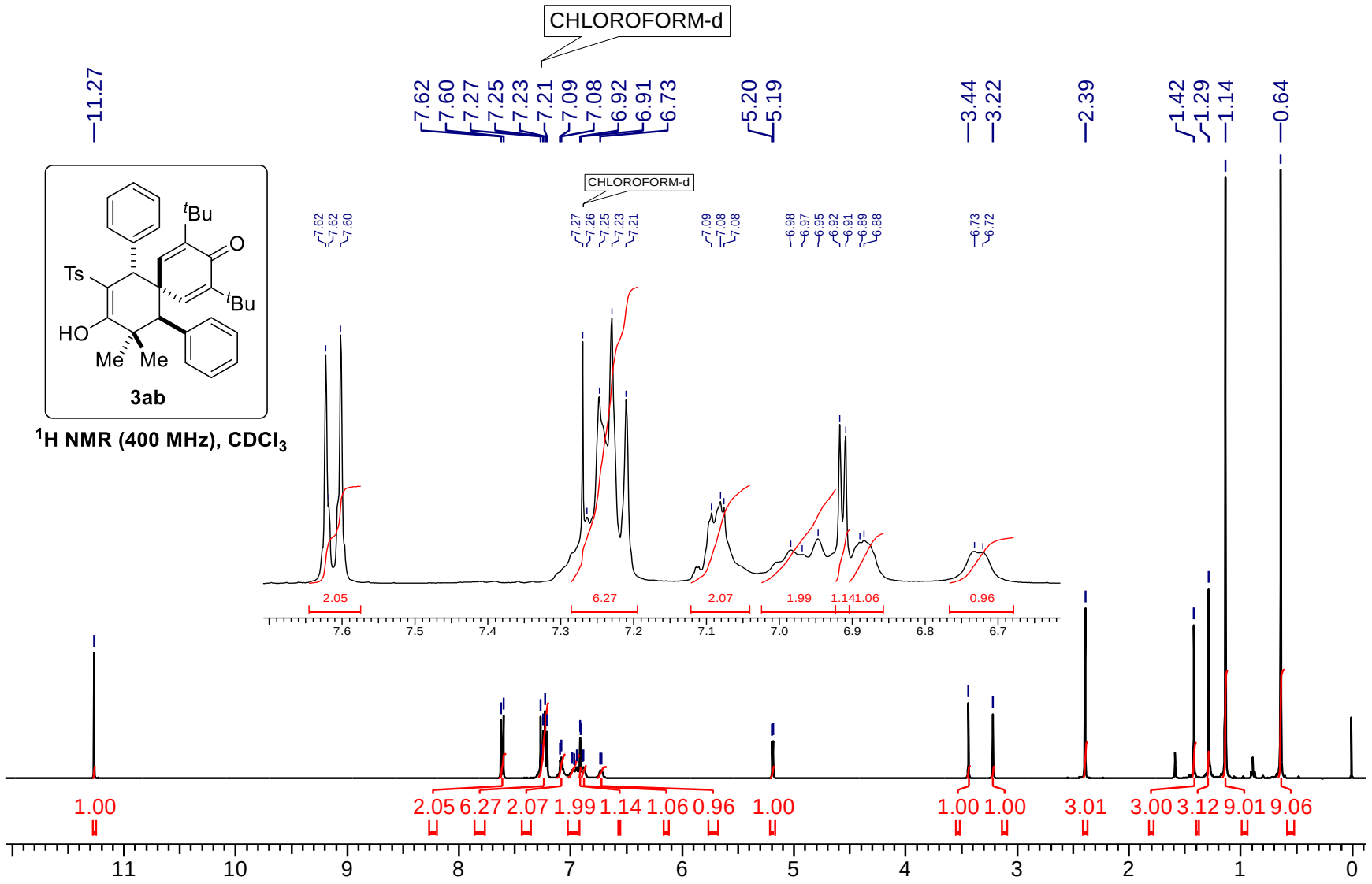
^{13}C NMR (100 MHz), $CDCl_3$

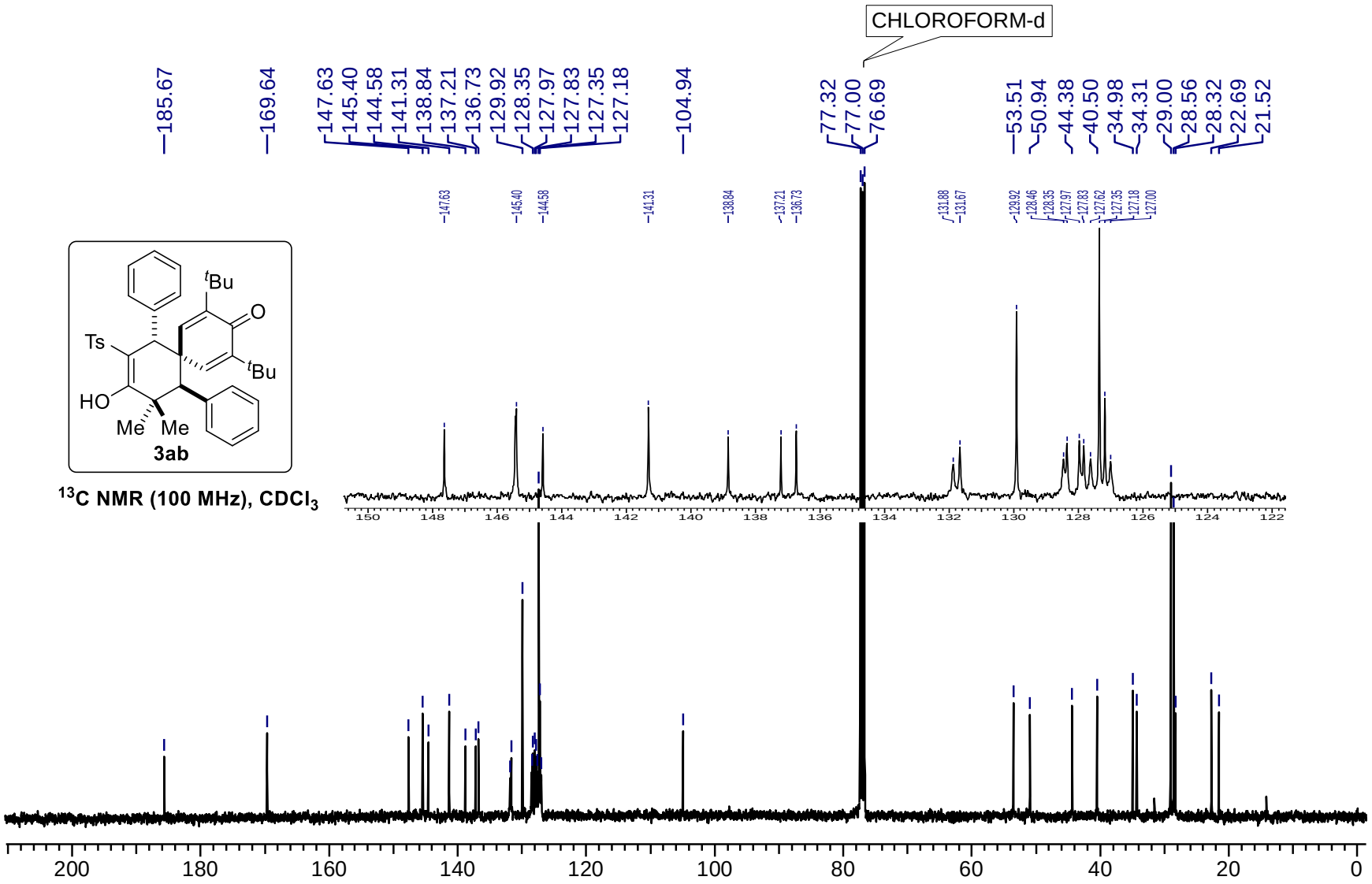


^{1}H NMR (400 MHz), $CDCl_3$



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


CHLOROFORM-d
11.27
7.62
7.60
7.27
7.25
7.23
7.21
7.09
7.08
6.92
6.91
6.73
5.20
5.19
3.44
3.22
2.39
1.42
1.29
1.14
0.64
tBu
O
Ts
tBu
HO
Me
Me
3ab
1H NMR (400 MHz), CDCl3
2.05
6.27
2.07
1.99
1.14
1.06
0.96
1.00
2.05 6.27 2.07 1.99 1.14 1.06 0.96
1.00
1.00 1.00
3.01
3.00 3.12 9.01 9.06


CHLOROFORM-d
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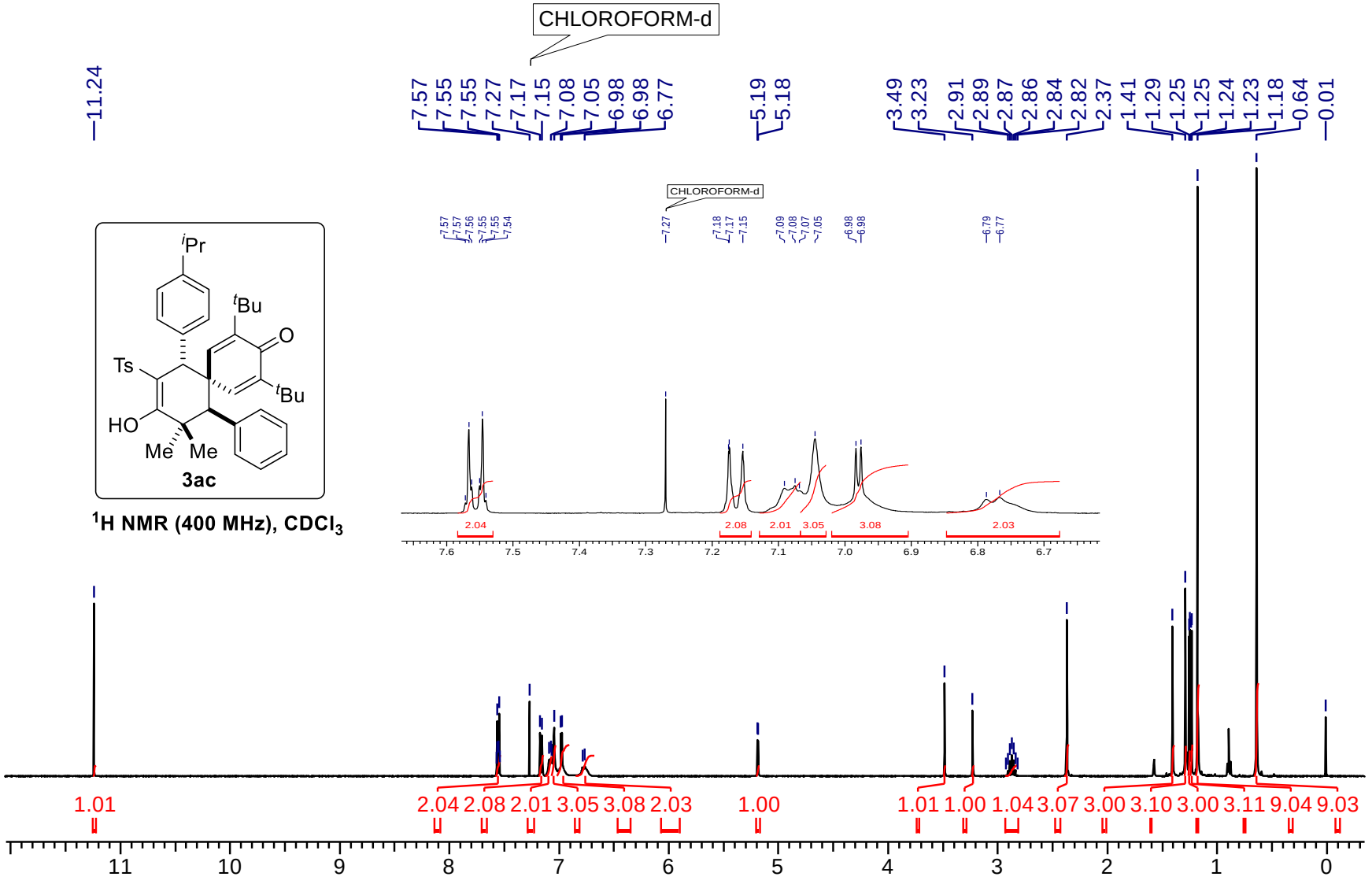
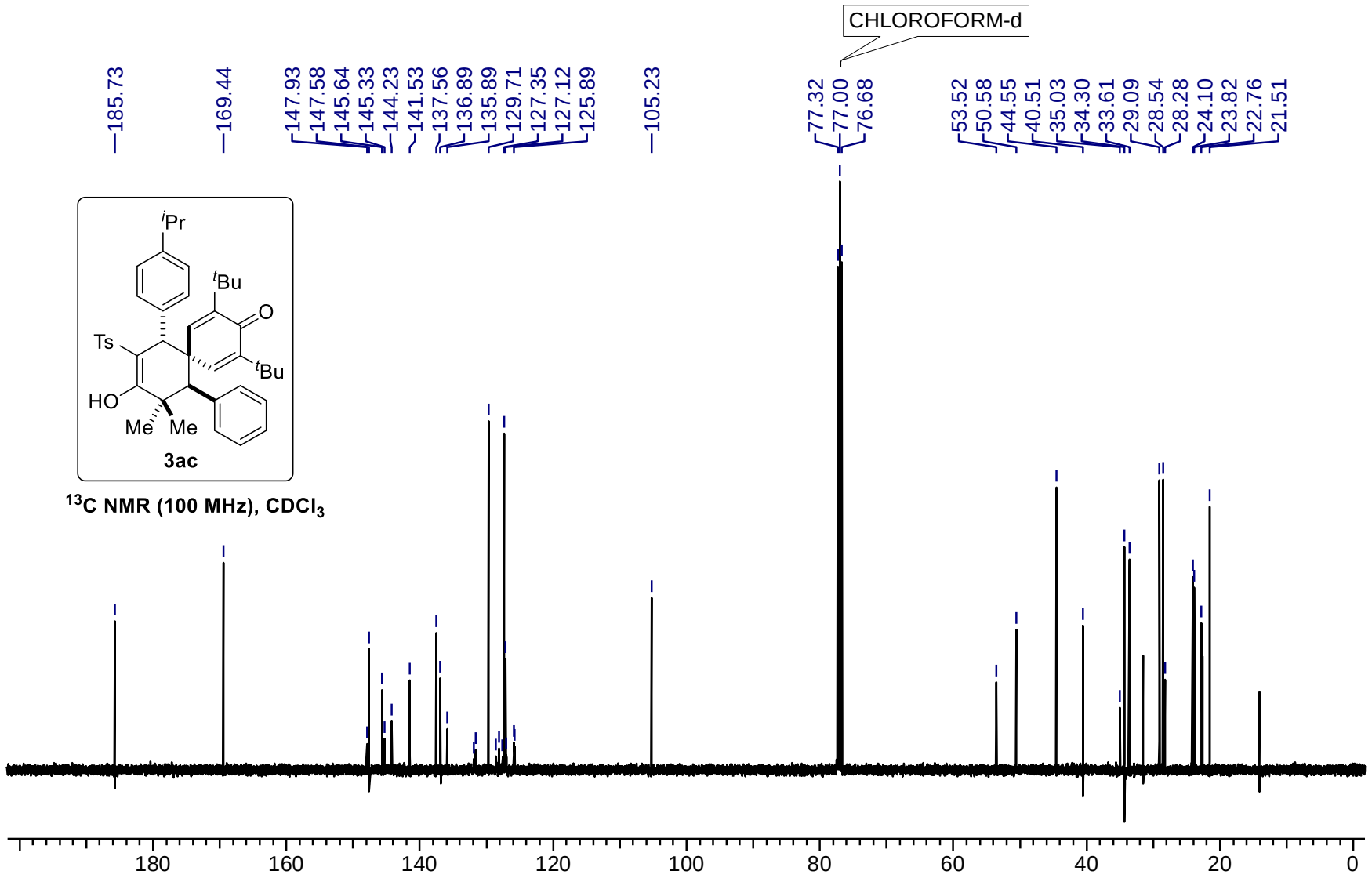
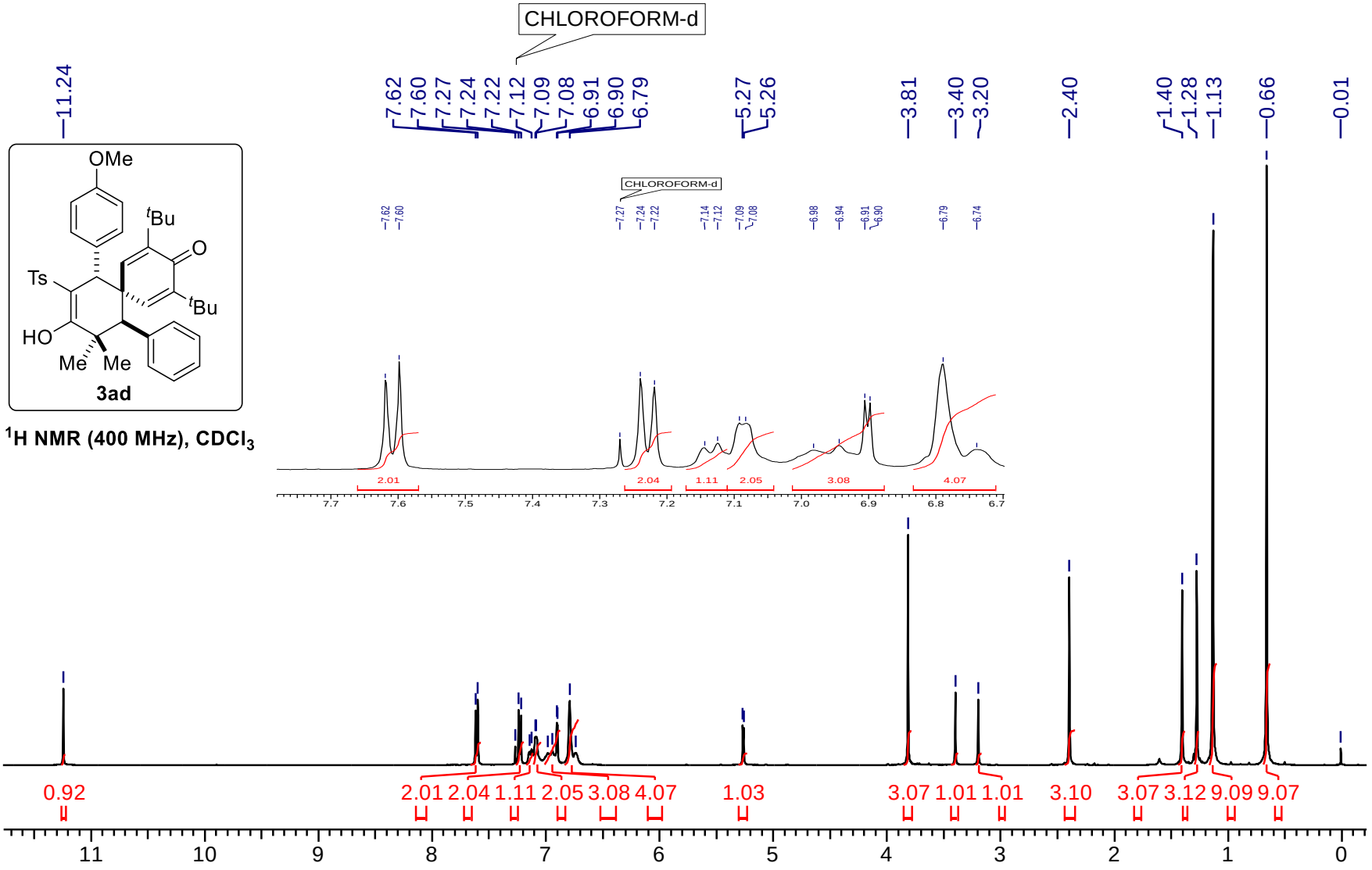
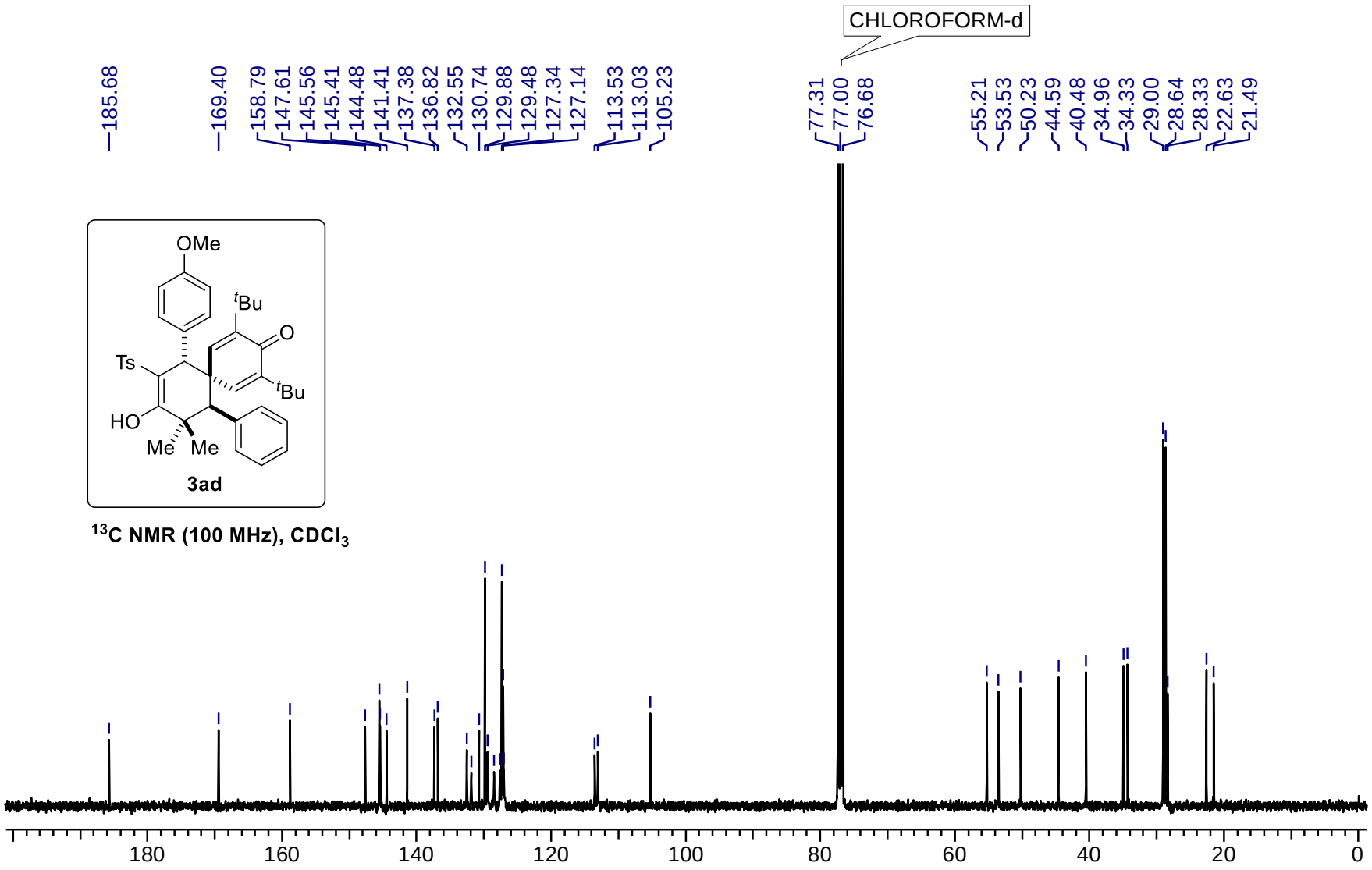
145.40
144.58
141.31
138.84
137.21
136.73
129.92
128.35
127.97
127.83
127.35
127.18
104.94
77.32
77.00
76.69
53.51
50.94
44.38
40.50
34.98
34.31
29.00
28.56
28.32
22.69
21.52
tBu
O
Ts
tBu
HO
Me
Me
3ab
13C NMR (100 MHz), CDCl3


CHLOROFORM-d
11.24
7.57 7.55 7.55 7.27 7.17 7.15 7.08 7.05 6.98 6.98 6.77
5.19 5.18
3.49 3.23 2.91 2.89 2.87 2.86 2.84 2.82 2.37
1.41 1.29 1.25 1.25 1.24 1.23 1.18 0.64 0.01
iPr
tBu
O
Ts
tBu
HO
Me Me
3ac
1H NMR (400 MHz), CDCl3
2.04 2.08 2.01 3.05 3.08 2.03
1.01 2.04 2.08 2.01 3.05 3.08 2.03 1.00 1.01 1.00 1.04 3.07 3.00 3.10 3.00 3.11 9.04 9.03

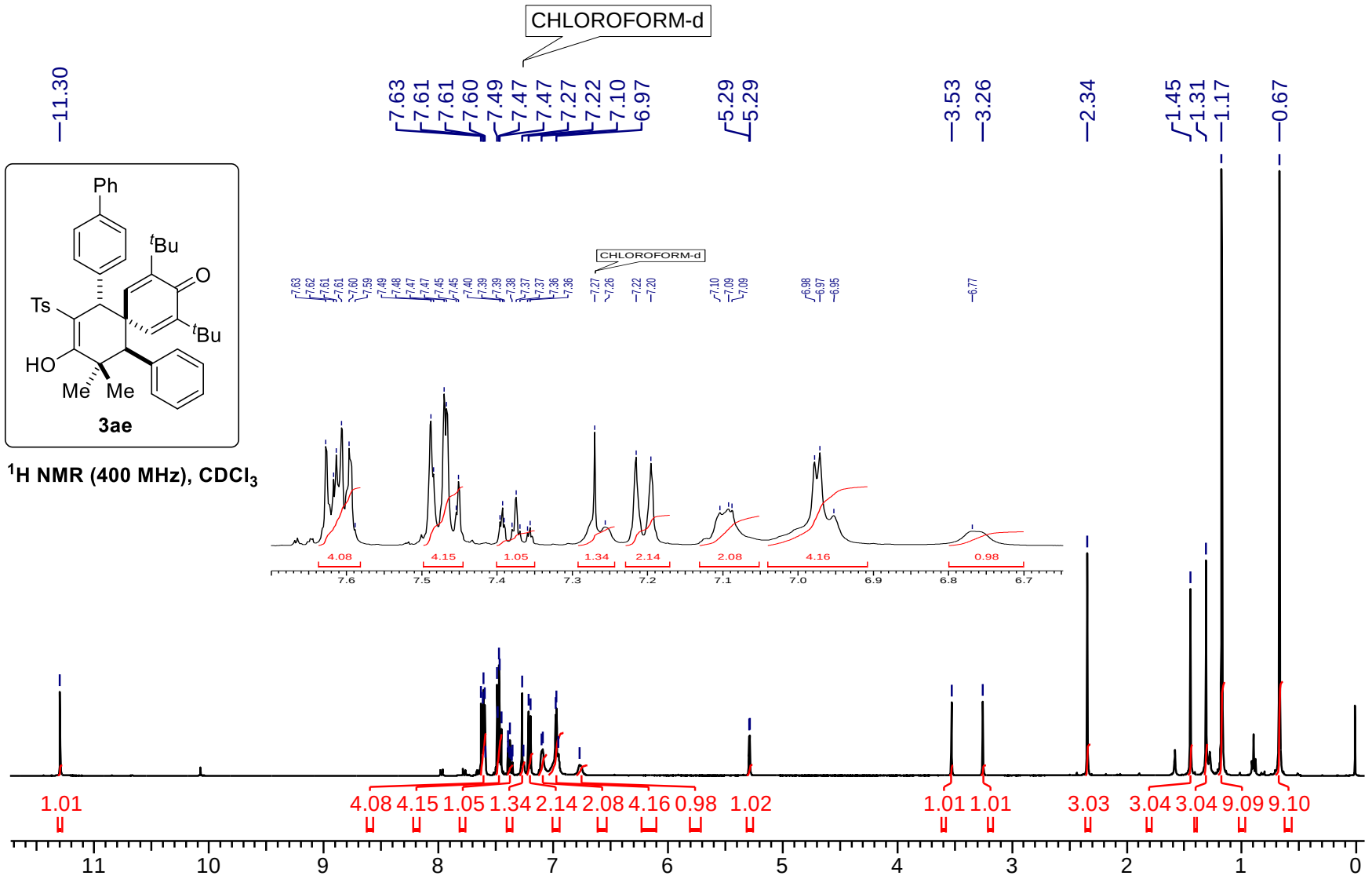


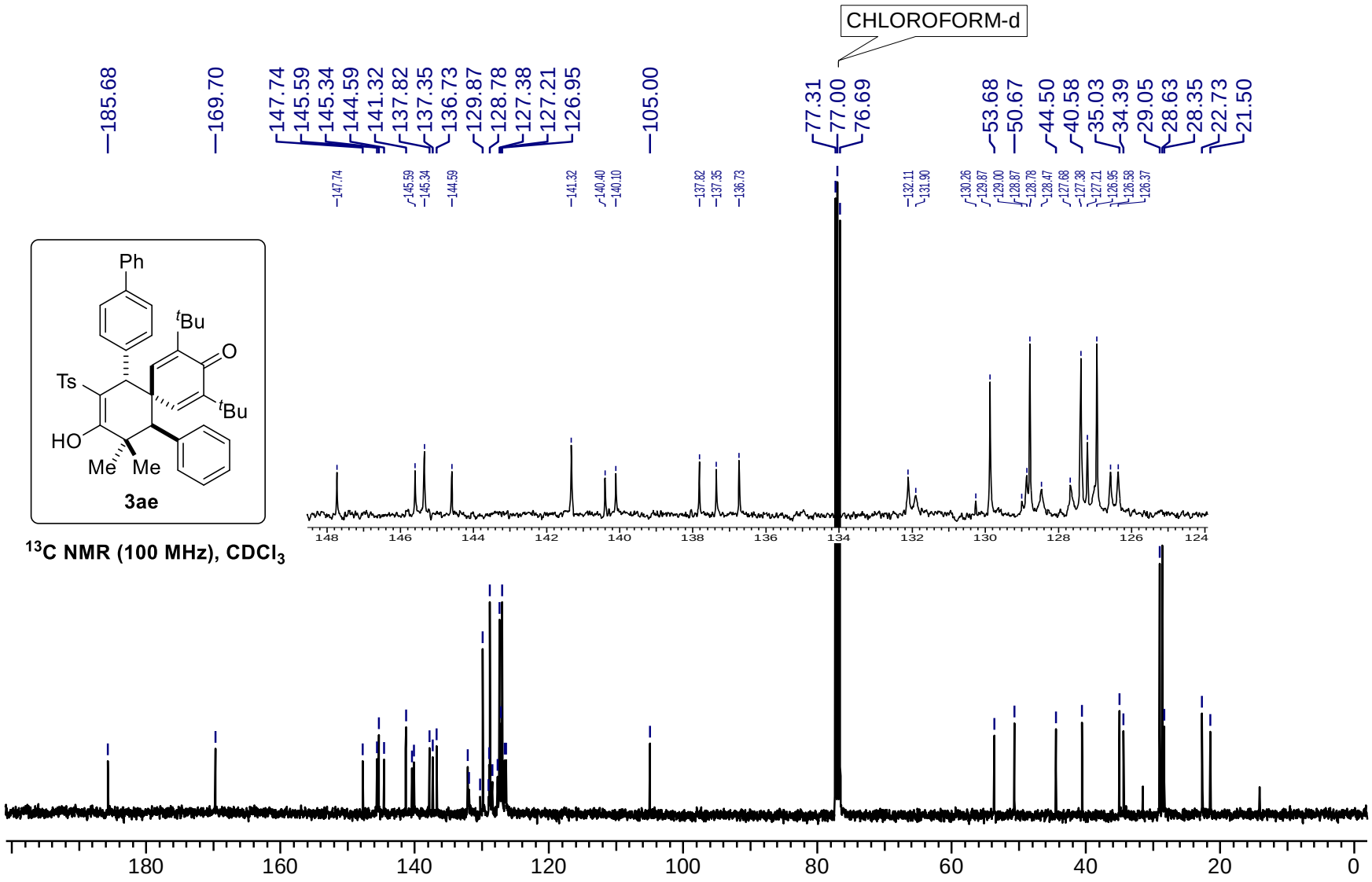
^{13}C NMR (100 MHz), $CDCl_3$

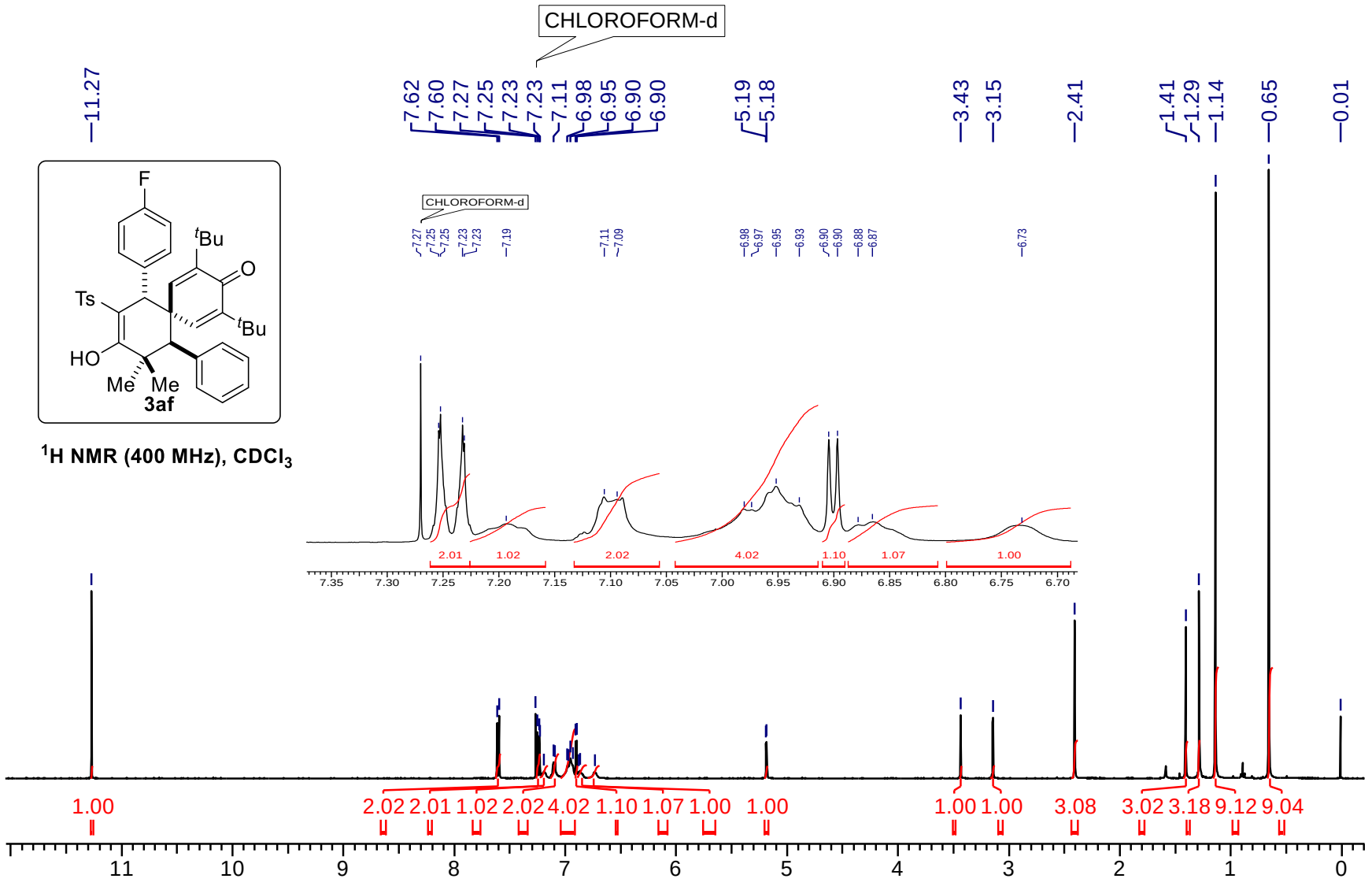

CHLOROFORM-d
11.24
7.62
7.60
7.27
7.24
7.22
7.12
7.09
7.08
6.91
6.90
6.79
5.27
5.26
3.81
3.40
3.20
2.40
1.40
1.28
1.13
0.66
0.01
OMe
tBu
O
Ts
tBu
HO
Me
Me
3ad
1H NMR (400 MHz), CDCl3
2.01
2.04
1.11
2.05
3.08
4.07
0.92
2.01 2.04 1.11 2.05 3.08 4.07
1.03
3.07 1.01 1.01
3.10
3.07 3.12 9.09 9.07

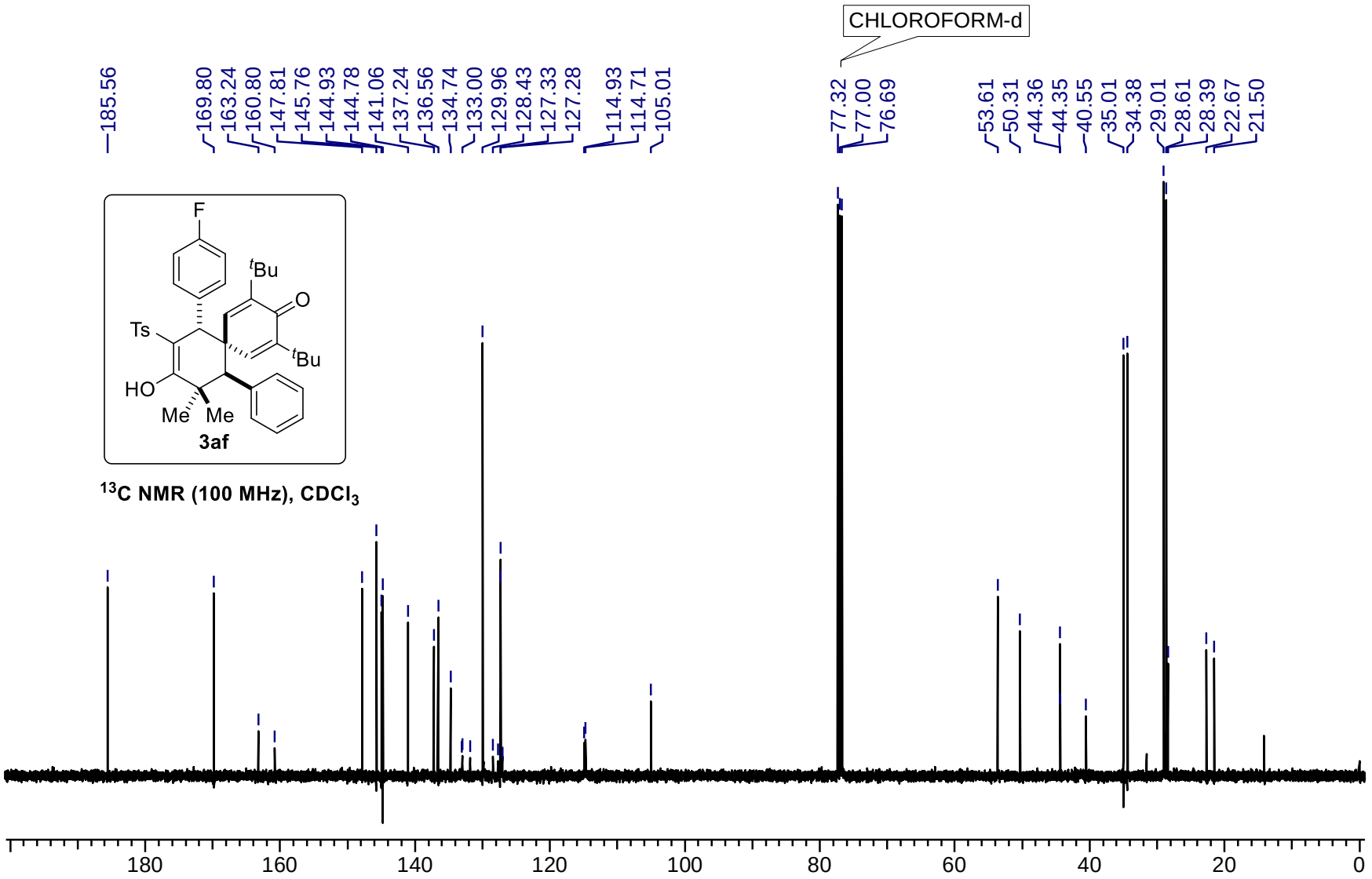


^{13}C NMR (100 MHz), $CDCl_3$


CHLOROFORM-d
11.30
7.63
7.61
7.61
7.60
7.49
7.47
7.47
7.27
7.22
7.10
6.97
5.29
5.29
3.53
3.26
2.34
1.45
1.31
1.17
0.67
Ph
tBu
O
Ts
tBu
HO
Me
Me
3ae
1H NMR (400 MHz), CDCl3
4.08
4.15
1.05
1.34
2.14
2.08
4.16
0.98
1.01
4.08
4.15
1.05
1.34
2.14
2.08
4.16
0.98
1.02
1.01
1.01
3.03
3.04
3.04
9.09
9.10

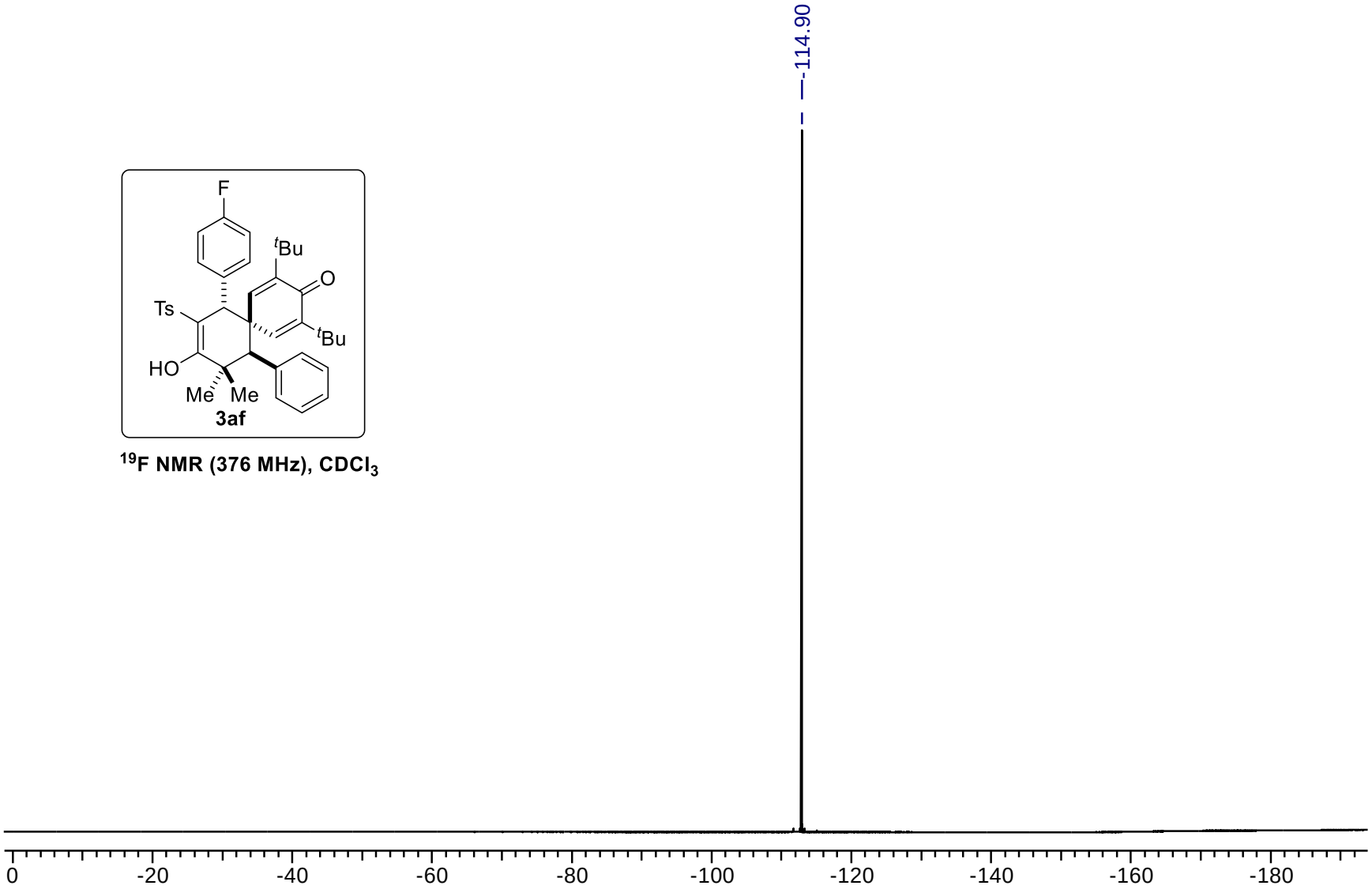

CHLOROFORM-d
185.68
169.70
147.74
145.59
145.34
144.59
141.32
137.82
137.35
136.73
129.87
128.78
127.38
127.21
126.95
105.00
77.31
77.00
76.69
53.68
50.67
44.50
40.58
35.03
34.39
29.05
28.63
28.35
22.73
21.50
Ph
tBu
O
Ts
tBu
HO
Me
Me
3ae
13C NMR (100 MHz), CDCl3

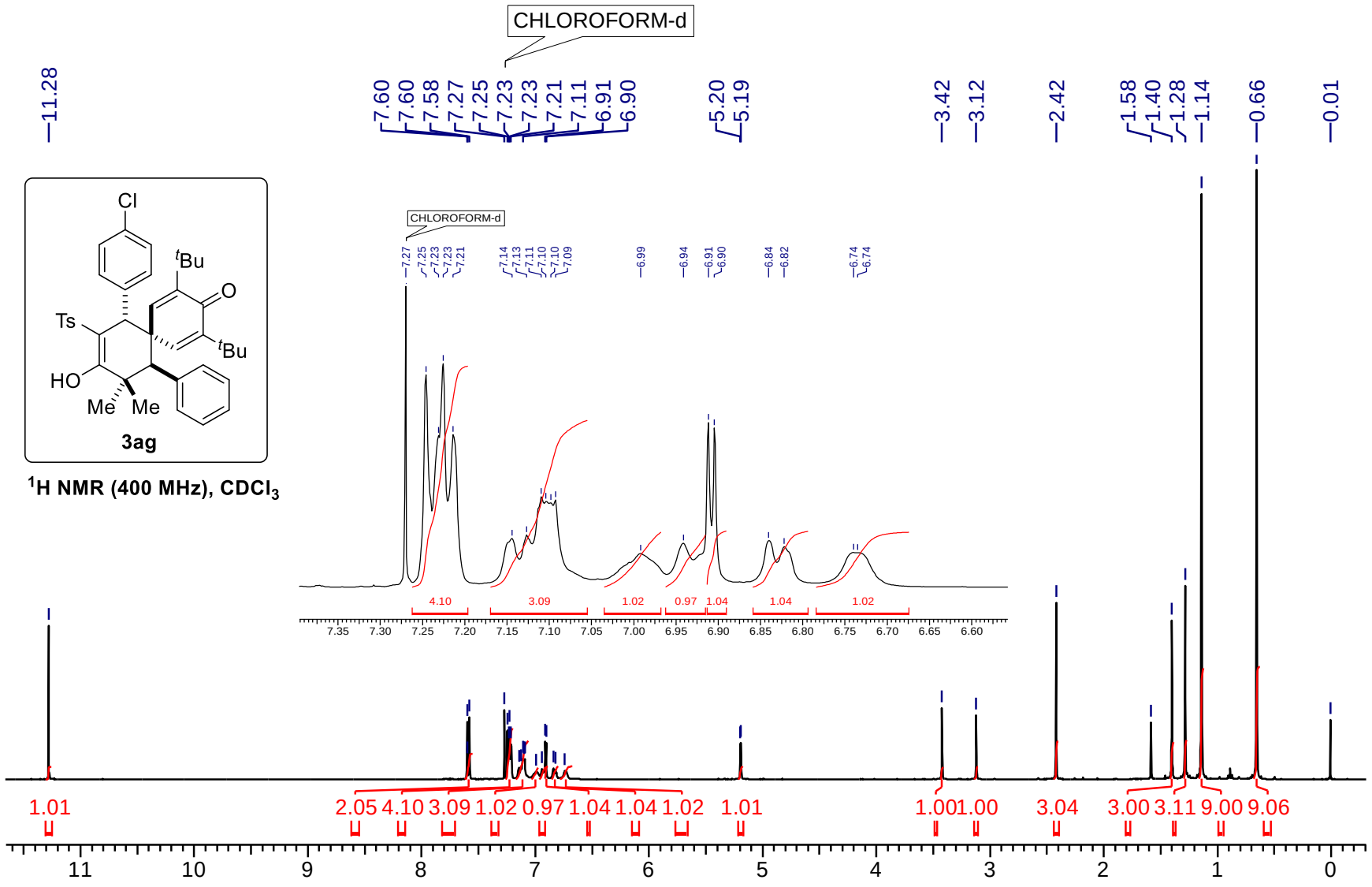

CHLOROFORM-d
11.27
7.62
7.60
7.27
7.25
7.23
7.23
7.11
6.98
6.95
6.90
6.90
5.19
5.18
3.43
3.15
2.41
1.41
1.29
1.14
0.65
0.01
F
tBu
O
Ts
tBu
HO
Me
Me
3af
1H NMR (400 MHz), CDCl3
2.01
1.02
2.02
4.02
1.10
1.07
1.00
1.00
2.02 2.01 1.02 2.02 4.02 1.10 1.07 1.00
1.00
1.00 1.00
3.08
3.02 3.18 9.12 9.04

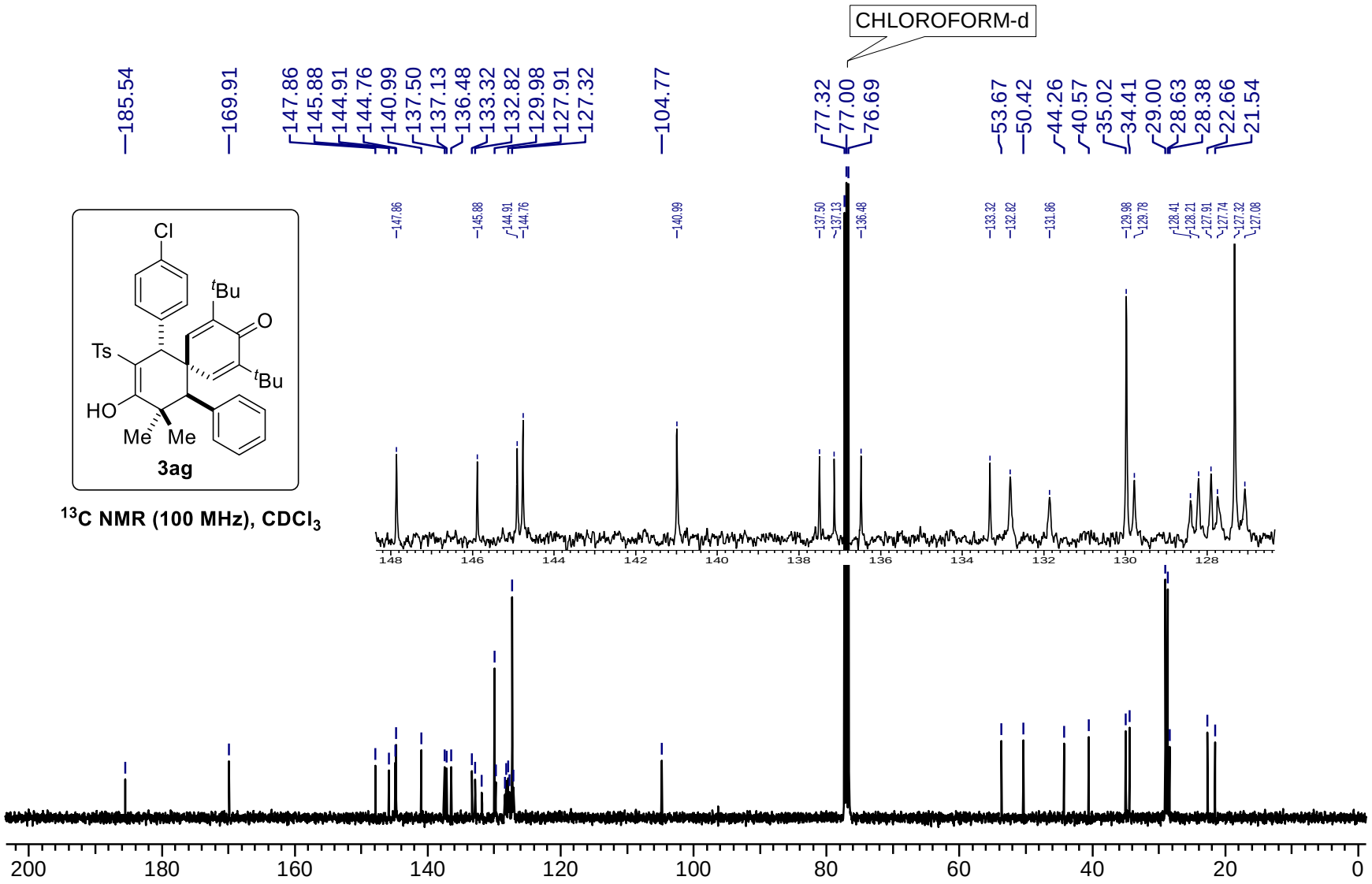

CHLOROFORM-d
185.56
169.80
163.24
160.80
147.81
145.76
144.93
144.78
141.06
137.24
136.56
134.74
133.00
129.96
128.43
127.33
127.28
114.93
114.71
105.01
77.32
77.00
76.69
53.61
50.31
44.36
44.35
40.55
35.01
34.38
29.01
28.61
28.39
22.67
21.50
F
tBu
O
Ts
tBu
HO
Me
Me
3af
13C NMR (100 MHz), CDCl3
180
160
140
120
100
80
60
40
20
0

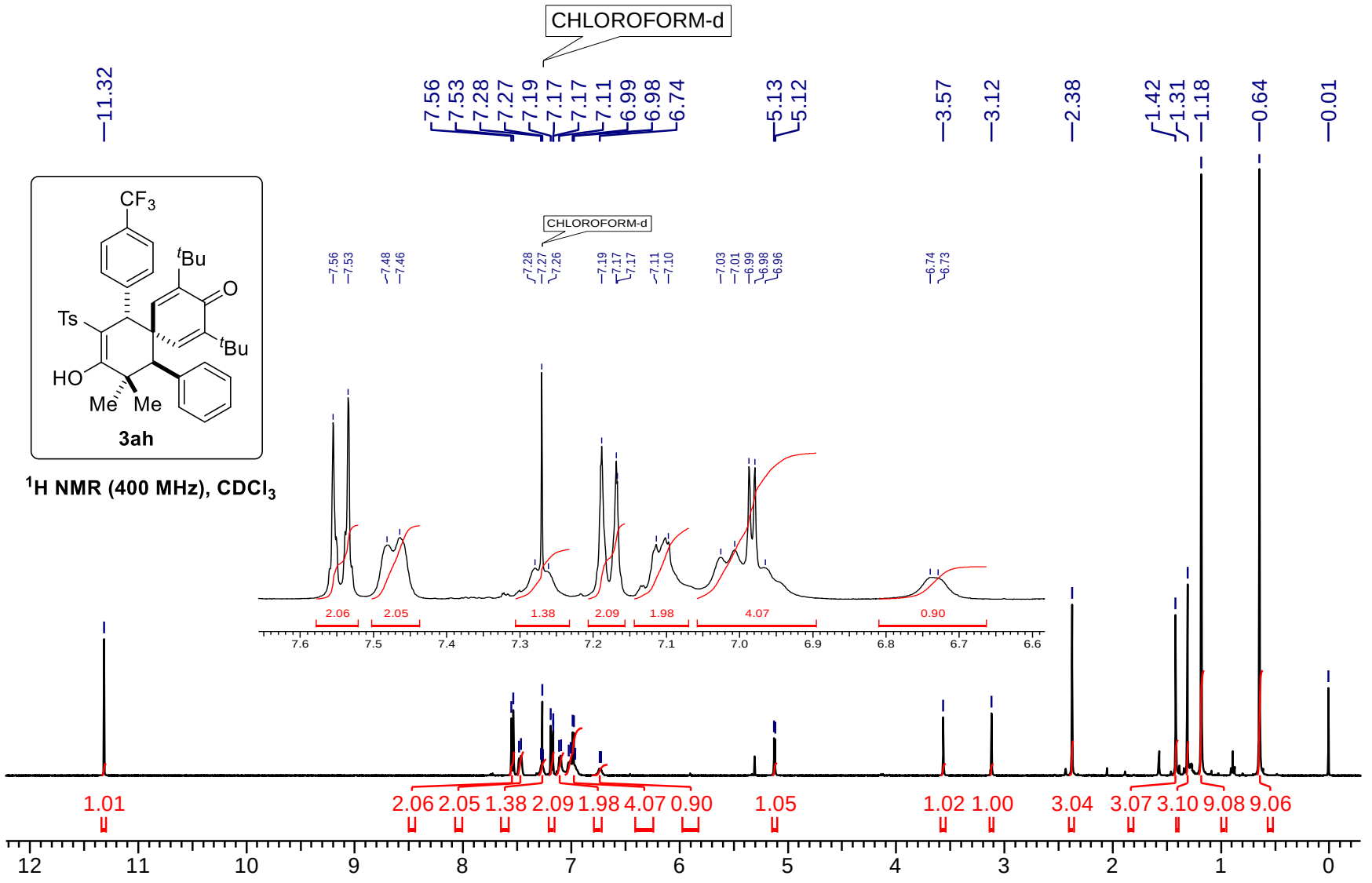
3af

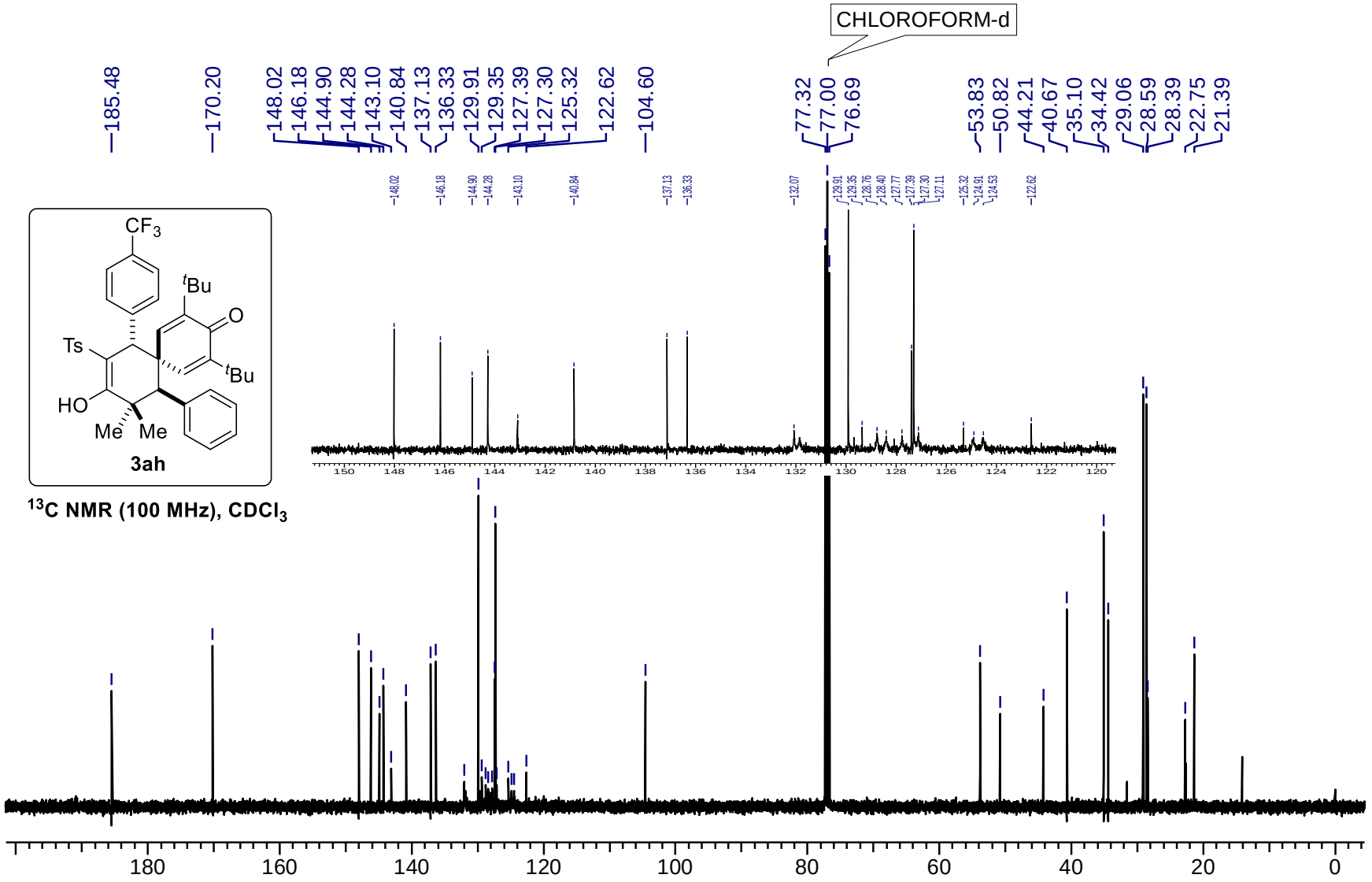
^{19}F NMR (376 MHz), $CDCl_3$

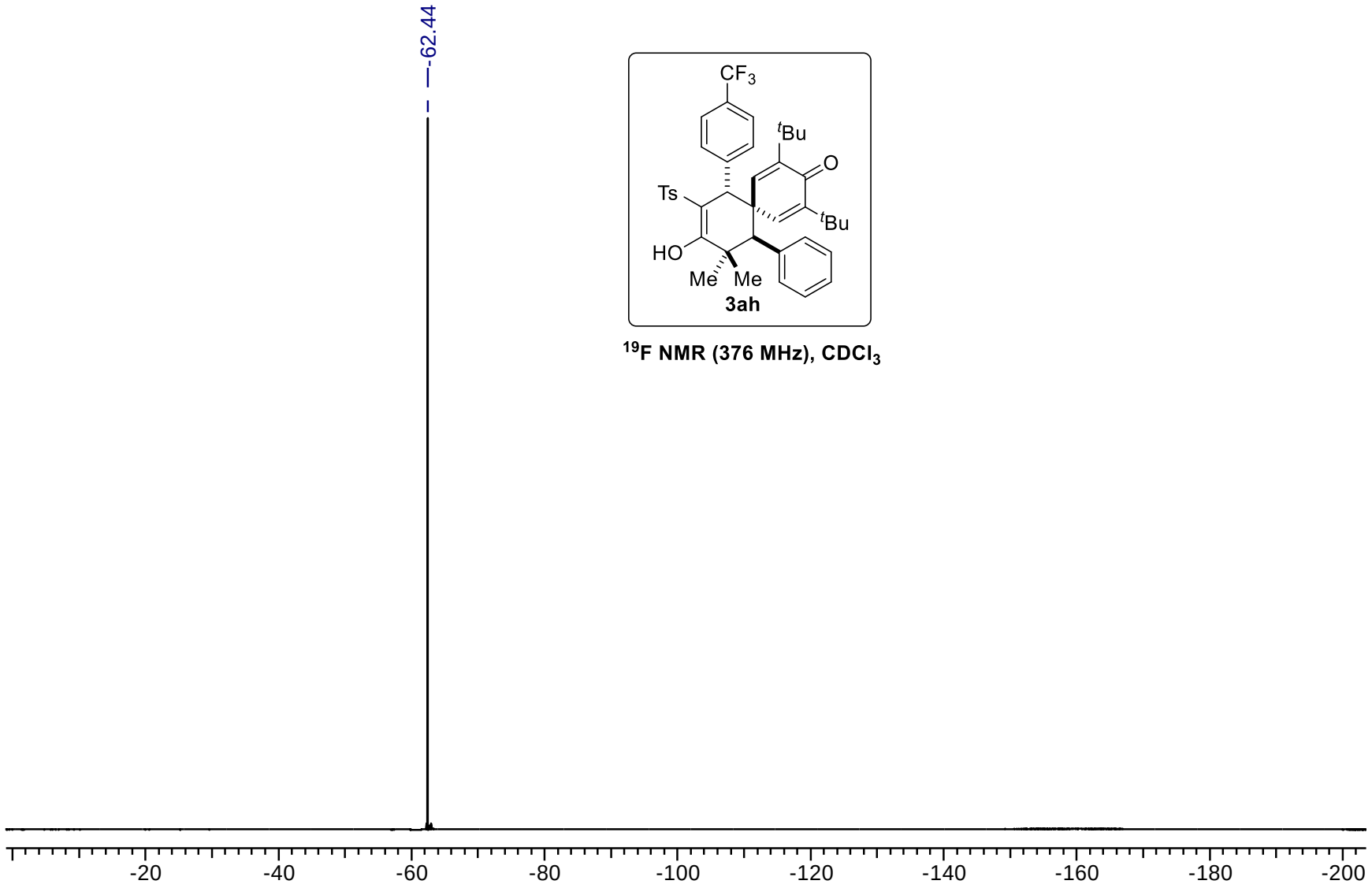



CHLOROFORM-d
11.28
7.60
7.60
7.58
7.27
7.25
7.23
7.23
7.21
7.11
6.91
6.90
5.20
5.19
3.42
3.12
2.42
1.58
1.40
1.28
1.14
0.66
0.01
Cl
tBu
O
Ts
tBu
HO
Me
Me
3ag
1H NMR (400 MHz), CDCl3
4.10
3.09
1.02
0.97
1.04
1.04
1.02
1.01
2.05
4.10
3.09
1.02
0.97
1.04
1.04
1.02
1.01
1.00
1.00
3.04
3.00
3.11
9.00
9.06

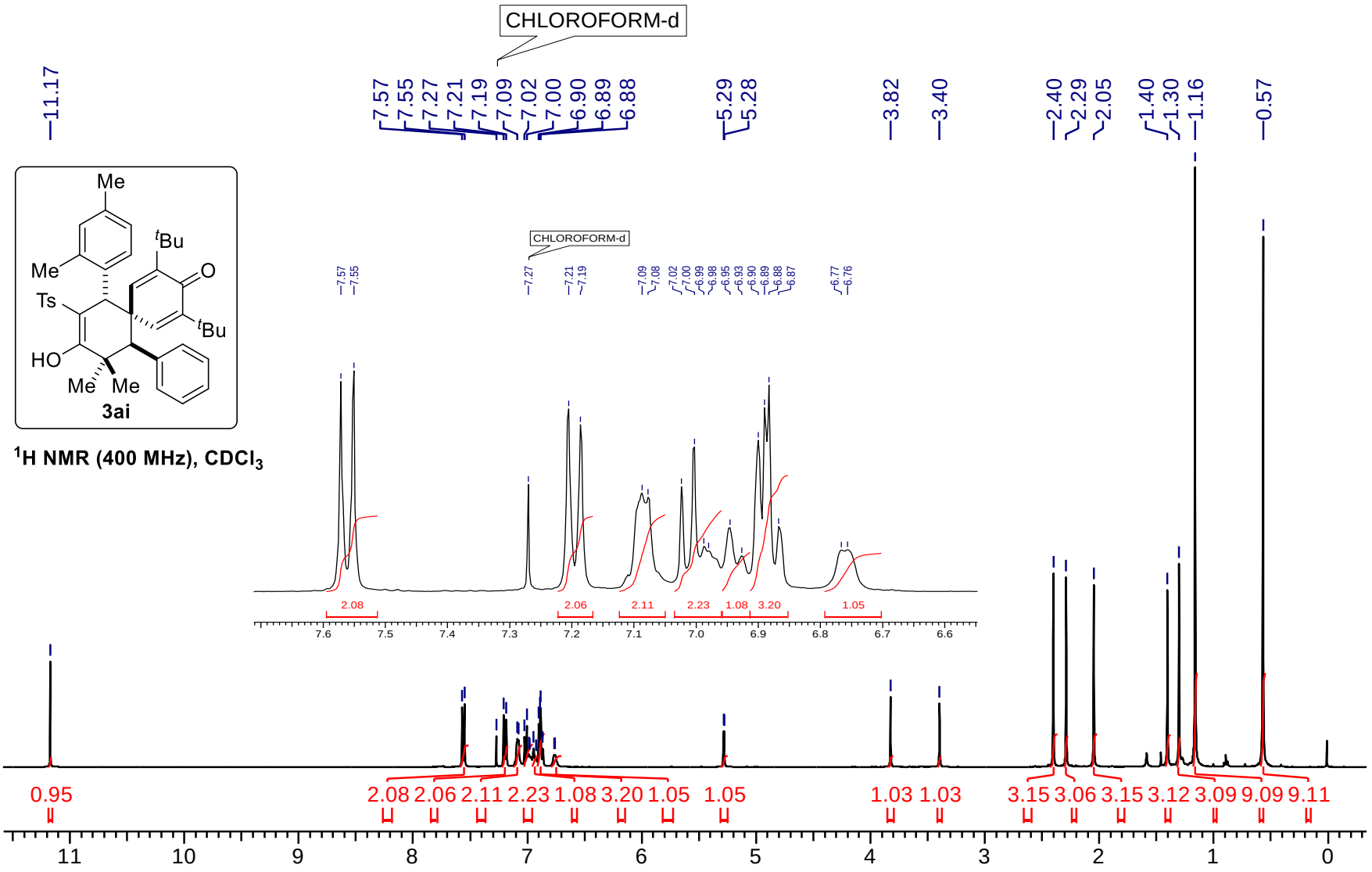

CHLOROFORM-d
185.54
169.91
147.86
145.88
144.91
144.76
140.99
137.50
137.13
136.48
133.32
132.82
129.98
127.91
127.32
104.77
77.32
77.00
76.69
53.67
50.42
44.26
40.57
35.02
34.41
29.00
28.63
28.38
22.66
21.54
Cl
tBu
O
Ts
tBu
HO
Me
Me
3ag
13C NMR (100 MHz), CDCl3

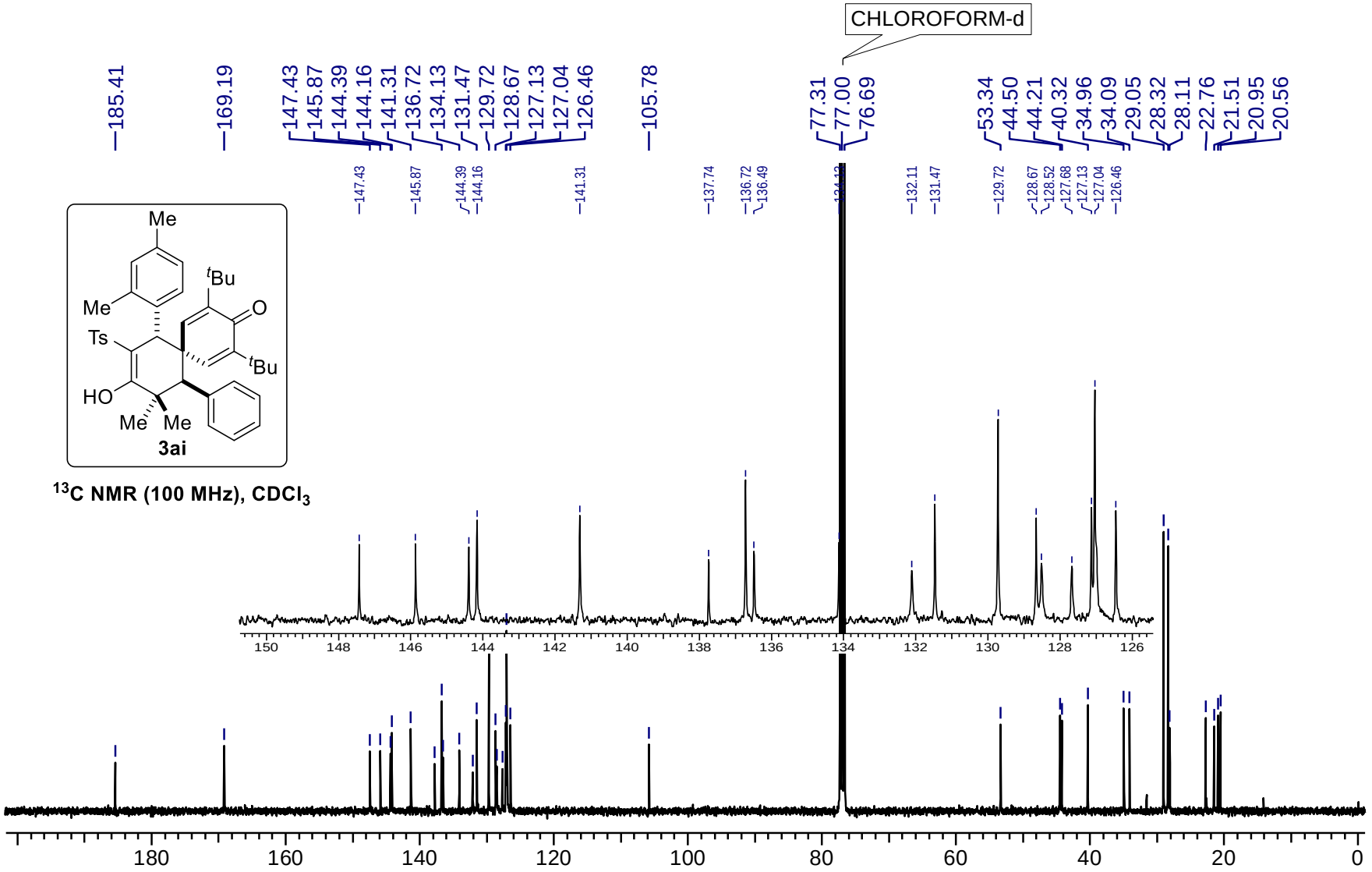

CHLOROFORM-d
11.32
7.56
7.53
7.28
7.27
7.19
7.17
7.17
7.11
6.99
6.98
6.74
5.13
5.12
3.57
3.12
2.38
1.42
1.31
1.18
0.64
0.01
CF3
tBu
O
Ts
tBu
HO
Me
Me
3ah
1H NMR (400 MHz), CDCl3
2.06
2.05
1.38
2.09
1.98
4.07
0.90
1.01
2.06 2.05 1.38 2.09 1.98 4.07 0.90
1.05
1.02 1.00
3.04
3.07 3.10 9.08 9.06

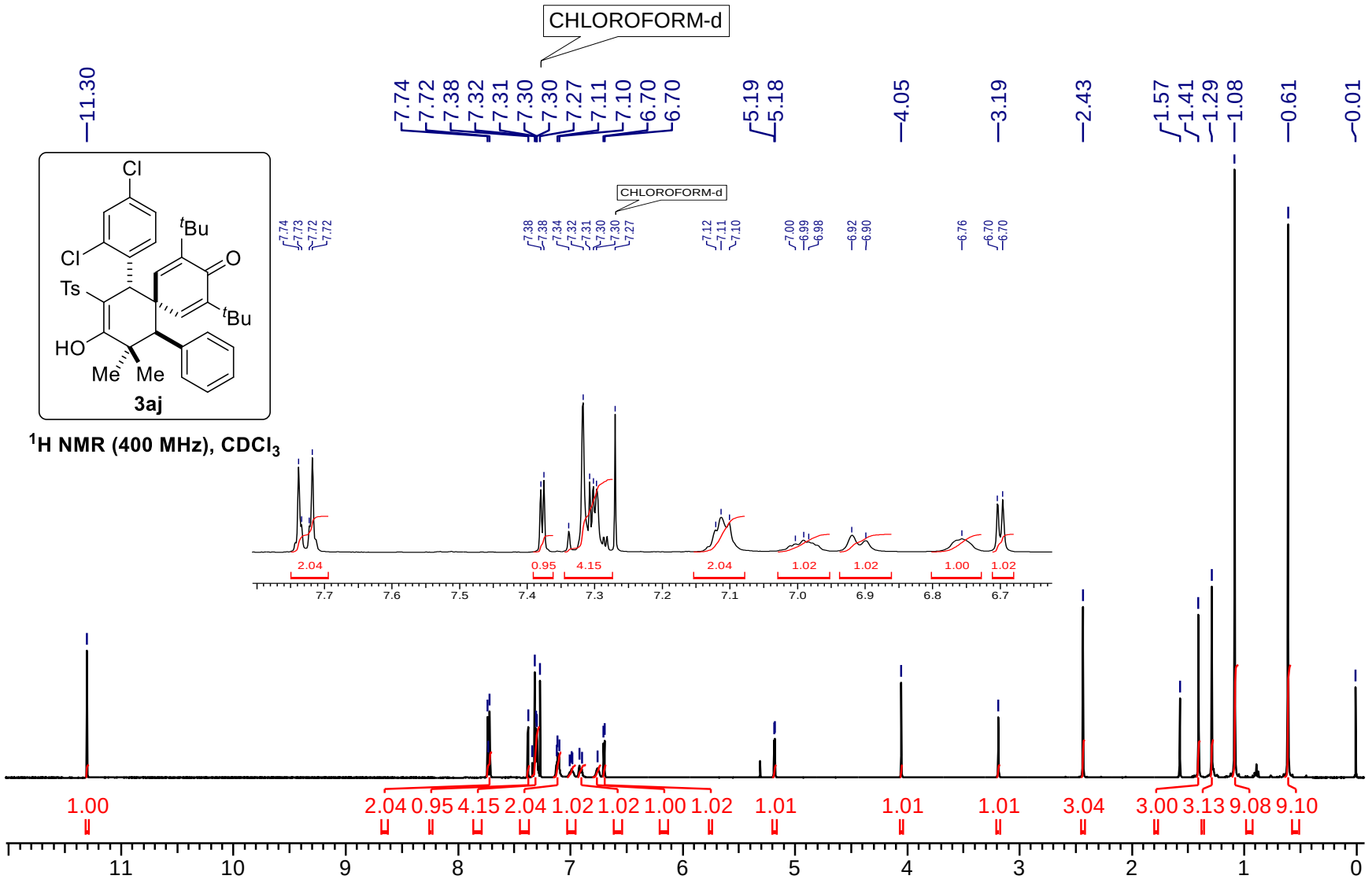

CHLOROFORM-d
185.48
170.20
148.02
146.18
144.90
144.28
143.10
140.84
137.13
136.33
129.91
129.35
127.39
127.30
125.32
122.62
104.60
77.32
77.00
76.69
53.83
50.82
44.21
40.67
35.10
34.42
29.06
28.59
28.39
22.75
21.39
CF3
tBu
O
Ts
tBu
HO
Me
Me
3ah
13C NMR (100 MHz), CDCl3

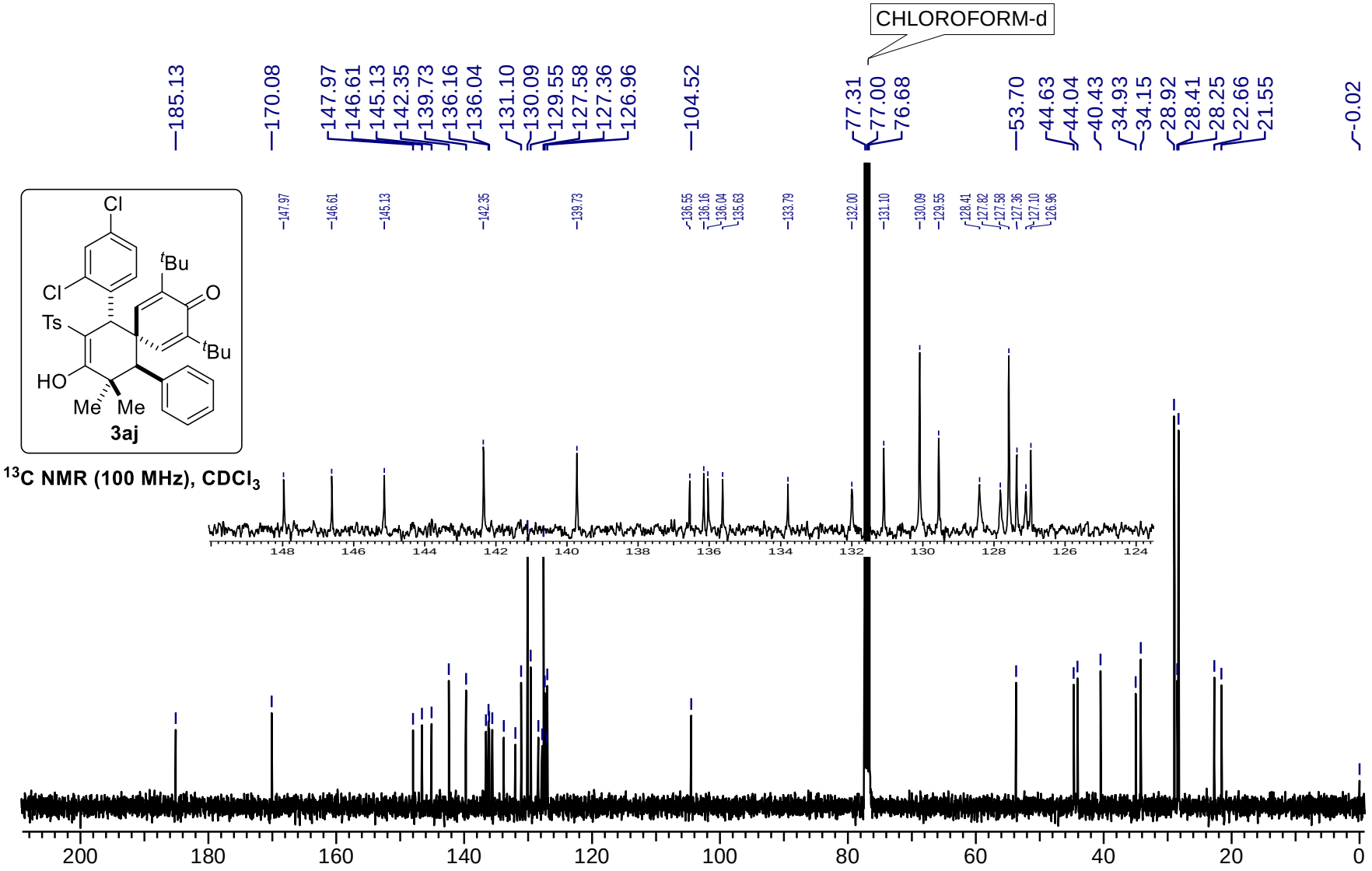


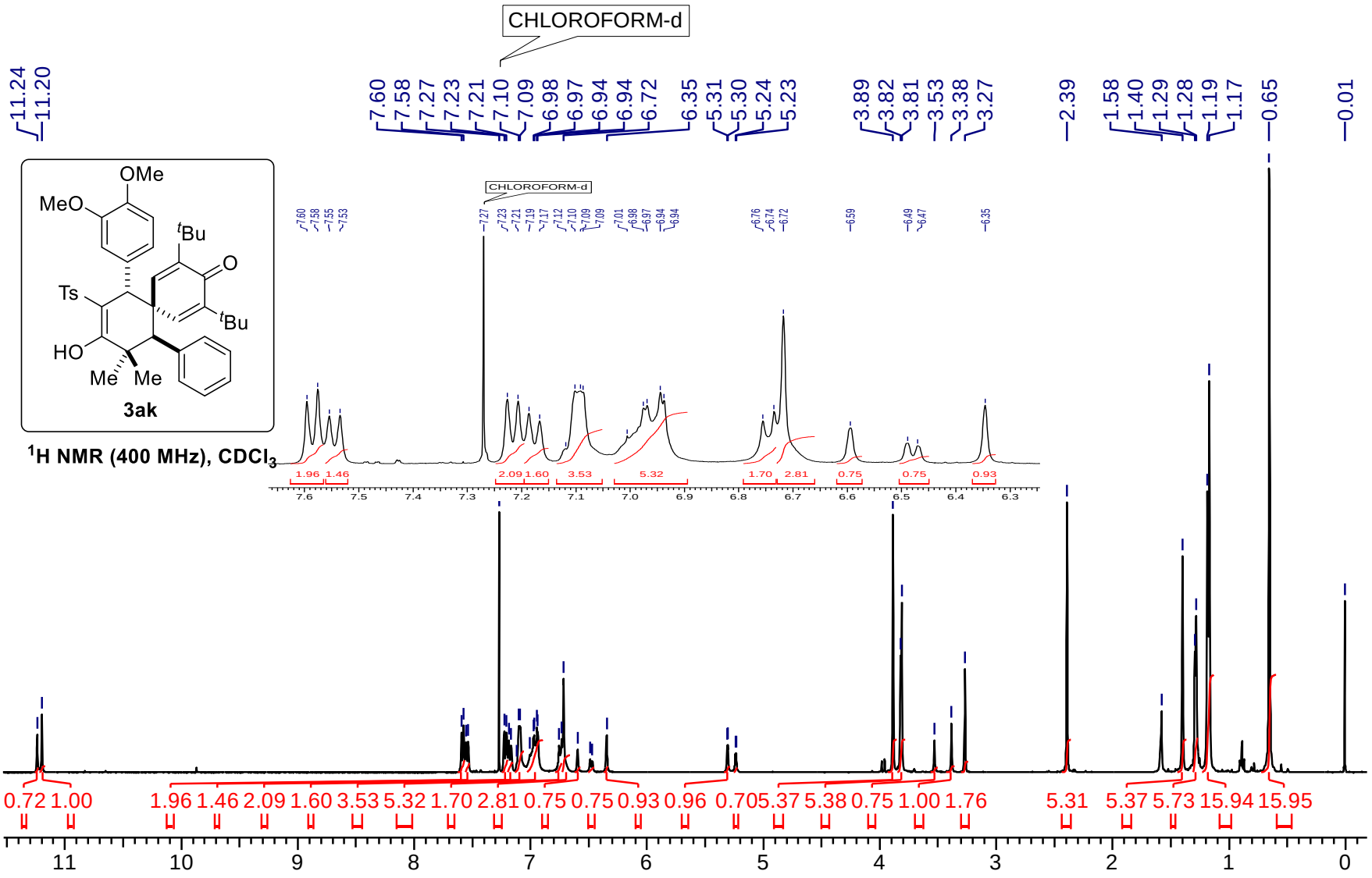
^{19}F NMR (376 MHz), $CDCl_3$

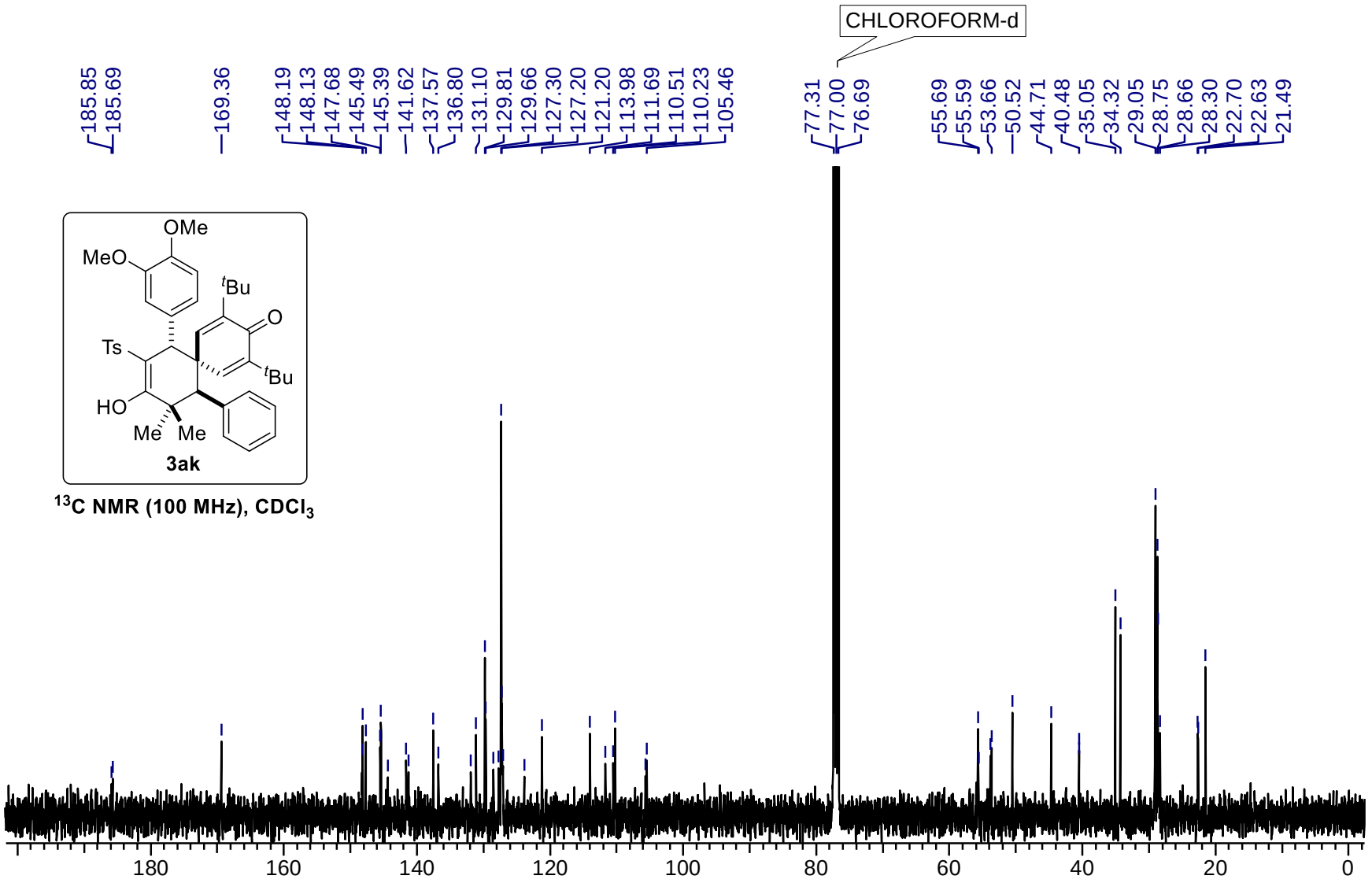

CHLOROFORM-d
11.17
7.57
7.55
7.27
7.21
7.19
7.09
7.02
7.00
6.90
6.89
6.88
5.29
5.28
3.82
3.40
2.40
2.29
2.05
1.40
1.30
1.16
0.57
Me
tBu
Me
O
Ts
tBu
HO
Me
Me
3ai
1H NMR (400 MHz), CDCl3
2.08
2.06
2.11
2.23
1.08
3.20
1.05
0.95
2.08 2.06 2.11 2.23 1.08 3.20 1.05
1.05
1.03 1.03
3.15 3.06 3.15 3.12 3.09 9.09 9.11


CHLOROFORM-d
185.41
169.19
147.43
145.87
144.39
144.16
141.31
136.72
134.13
131.47
129.72
128.67
127.13
127.04
126.46
105.78
77.31
77.00
76.69
53.34
44.50
44.21
40.32
34.96
34.09
29.05
28.32
28.11
22.76
21.51
20.95
20.56
Me
tBu
Me
O
Ts
tBu
HO
Me
Me
3ai
13C NMR (100 MHz), CDCl3

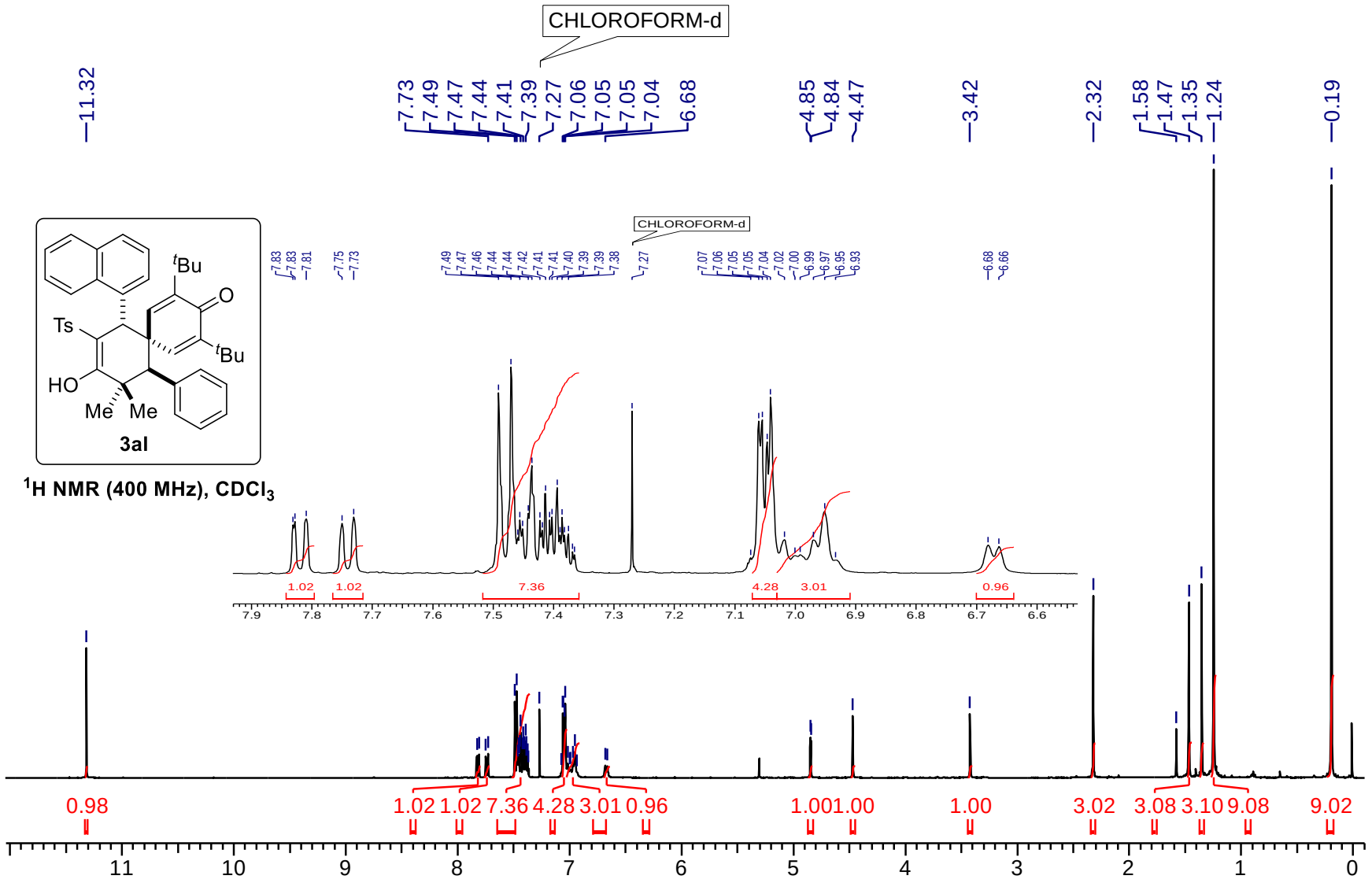

CHLOROFORM-d
11.30
7.74
7.72
7.38
7.32
7.31
7.30
7.30
7.27
7.11
7.10
6.70
6.70
5.19
5.18
4.05
3.19
2.43
1.57
1.41
1.29
1.08
0.61
0.01
Cl
Cl
tBu
O
Ts
tBu
HO
Me
Me
3aj
1H NMR (400 MHz), CDCl3
2.04
0.95
4.15
2.04
1.02
1.02
1.00
1.02
1.00
2.04
0.95
4.15
2.04
1.02
1.02
1.00
1.02
1.01
1.01
1.01
3.04
3.00
3.13
9.08
9.10

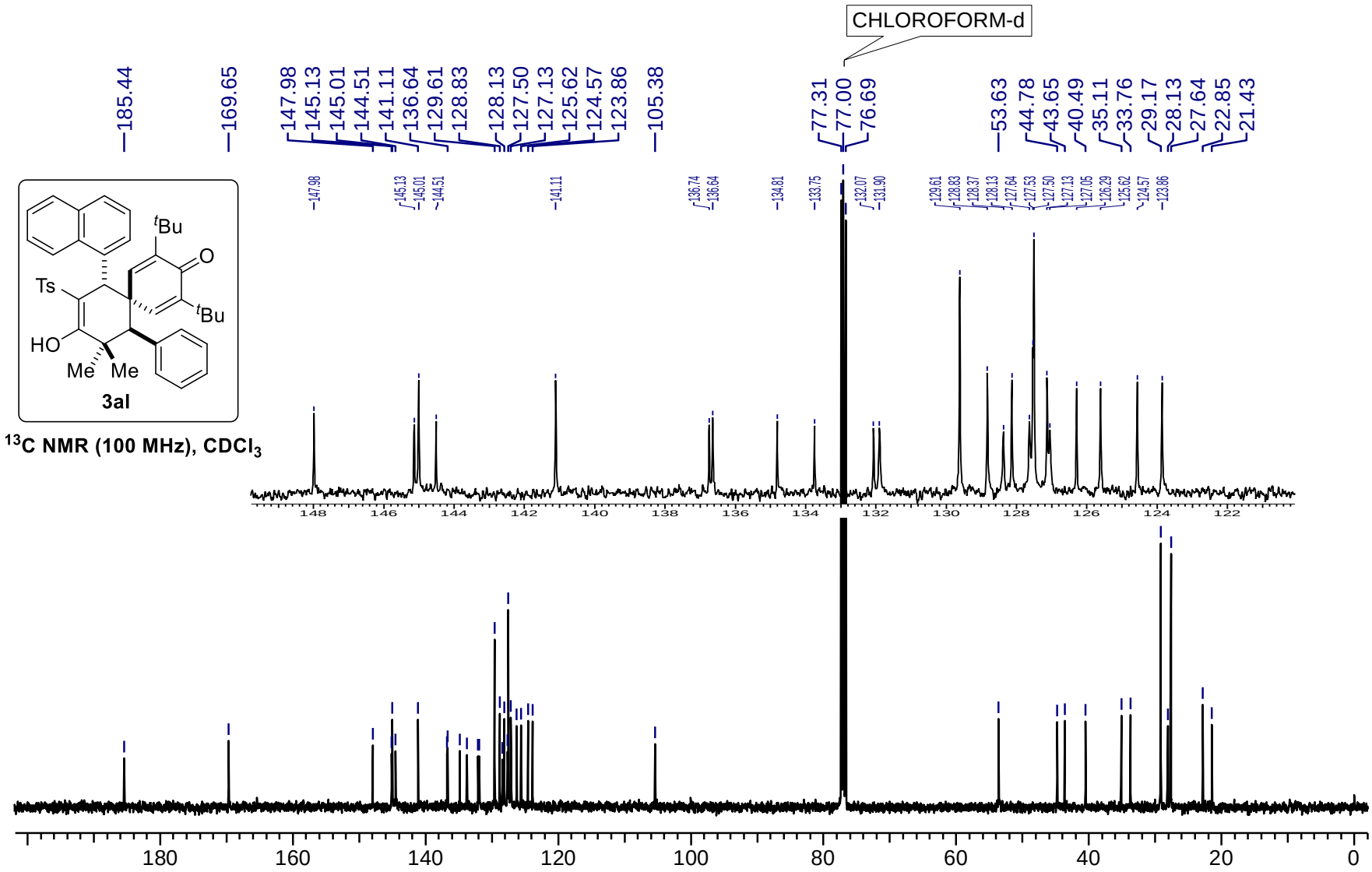

CHLOROFORM-d
185.13
170.08
147.97
146.61
145.13
142.35
139.73
136.16
136.04
131.10
130.09
129.55
127.58
127.36
126.96
104.52
77.31
77.00
76.68
53.70
44.63
44.04
40.43
34.93
34.15
28.92
28.41
28.25
22.66
21.55
-0.02
Cl
Cl
tBu
O
Ts
tBu
HO
Me
Me
3aj
13C NMR (100 MHz), CDCl3

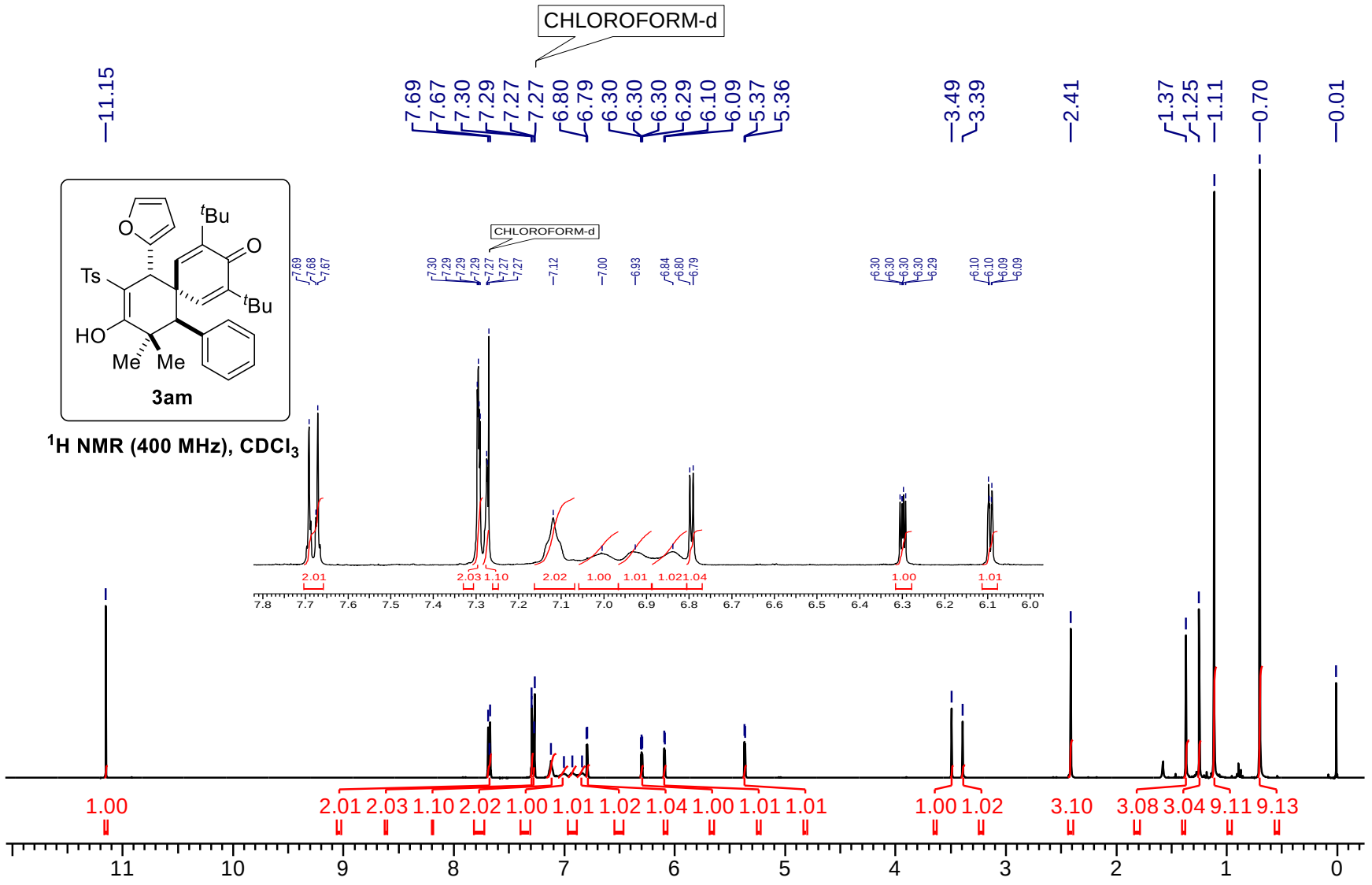

CHLOROFORM-d
11.24
11.20
7.60
7.58
7.27
7.23
7.21
7.10
7.09
6.98
6.97
6.94
6.94
6.72
6.35
5.31
5.30
5.24
5.23
3.89
3.82
3.81
3.53
3.38
3.27
2.39
1.58
1.40
1.29
1.28
1.19
1.17
0.65
0.01
OMe
MeO
tBu
O
Ts
tBu
HO
Me
Me
3ak
1H NMR (400 MHz), CDCl3
0.72 1.00
1.96 1.46 2.09 1.60 3.53 5.32 1.70 2.81 0.75 0.75 0.93 0.96 0.70 5.37 5.38 0.75 1.00 1.76
5.31
5.37 5.73 15.94 15.95
11
10
9
8
7
6
5
4
3
2
1
0

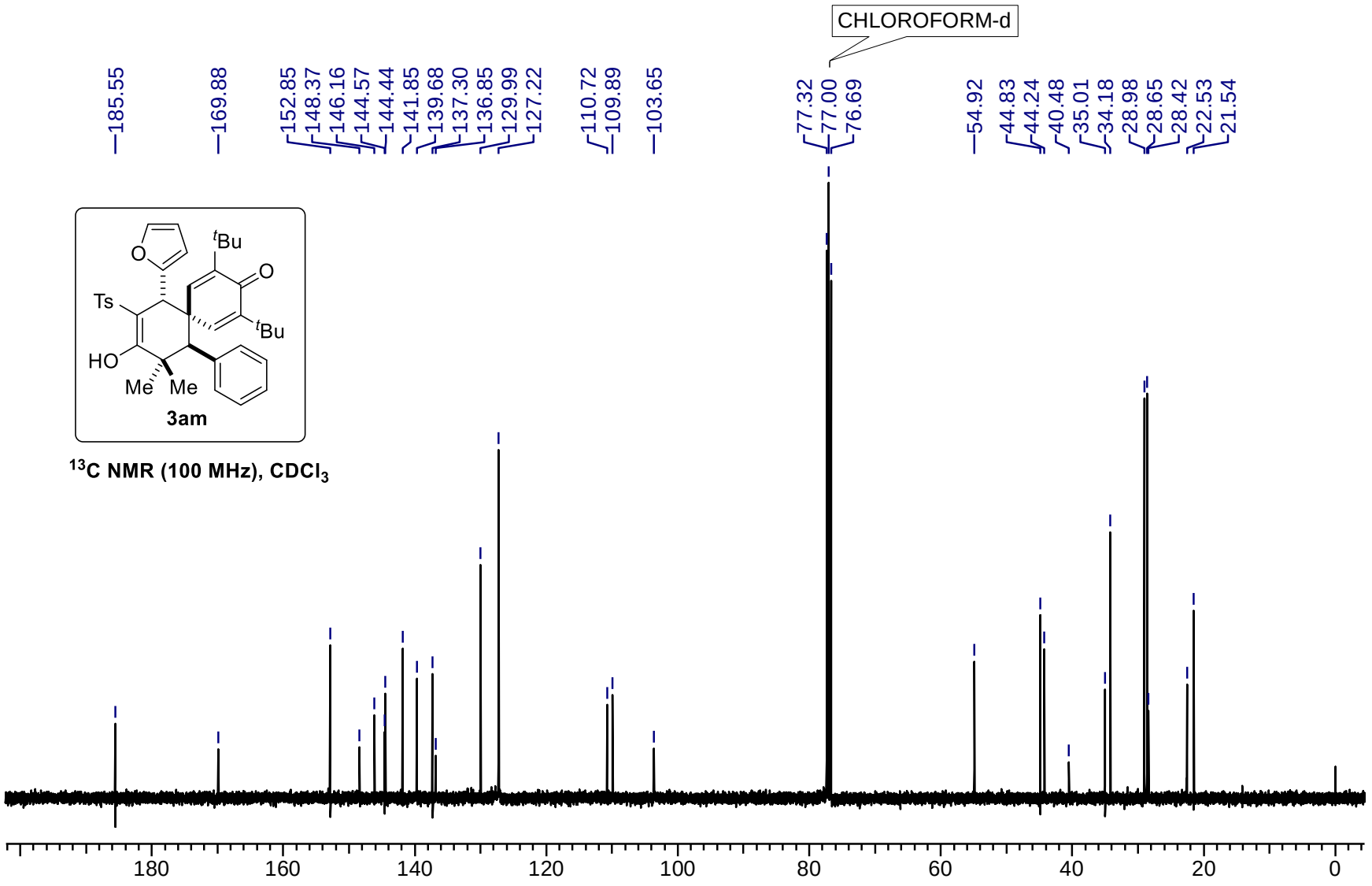


^{13}C NMR (100 MHz), $CDCl_3$

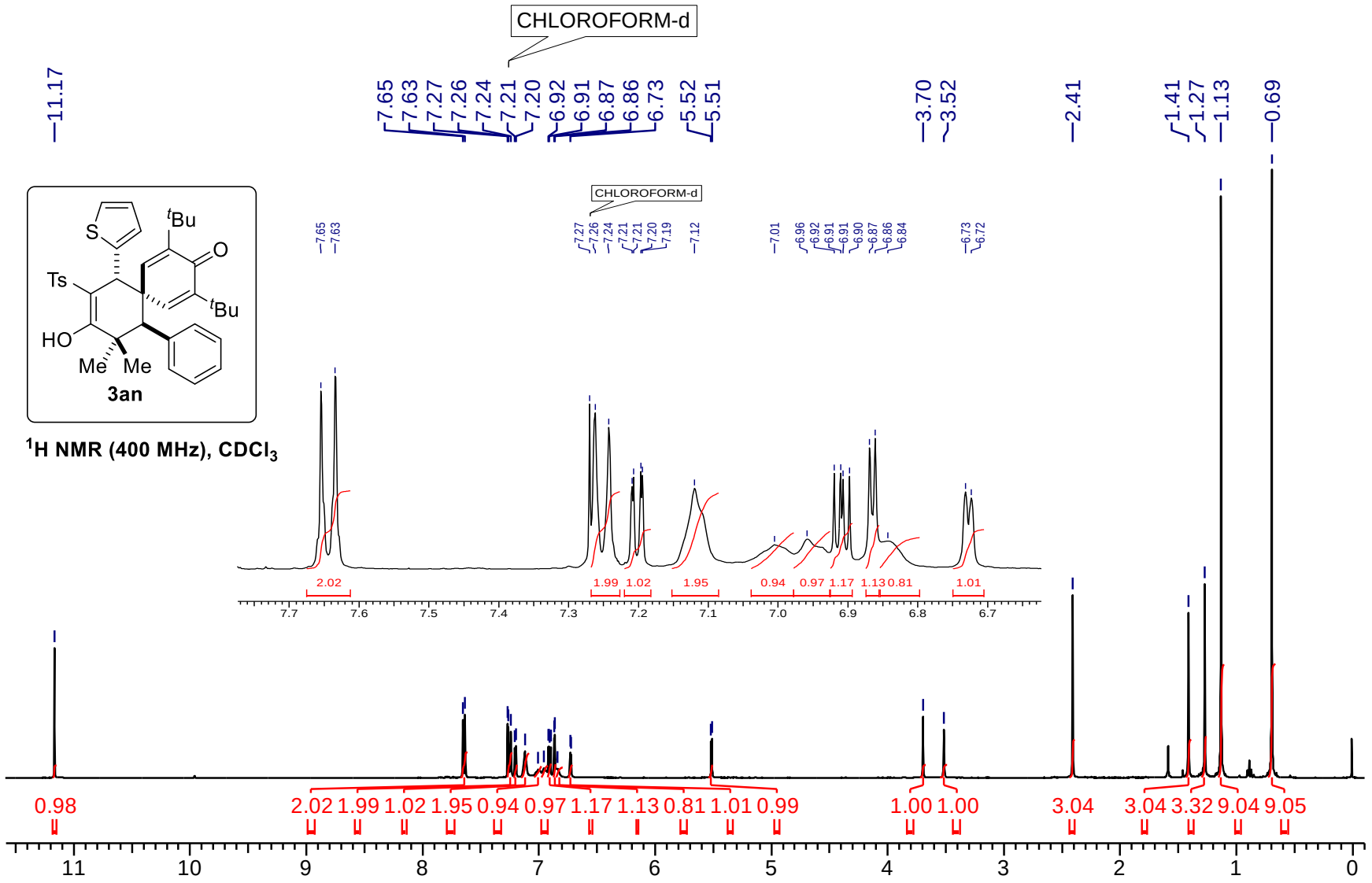

CHLOROFORM-d
11.32
7.73
7.49
7.47
7.44
7.41
7.39
7.27
7.06
7.05
7.05
7.04
6.68
4.85
4.84
4.47
3.42
2.32
1.58
1.47
1.35
1.24
0.19
tBu
O
Ts
tBu
HO
Me
Me
3al
1H NMR (400 MHz), CDCl3
1.02
1.02
7.36
4.28
3.01
0.96
0.98
1.02
1.02
7.36
4.28
3.01
0.96
1.00
1.00
1.00
3.02
3.08
3.10
9.08
9.02

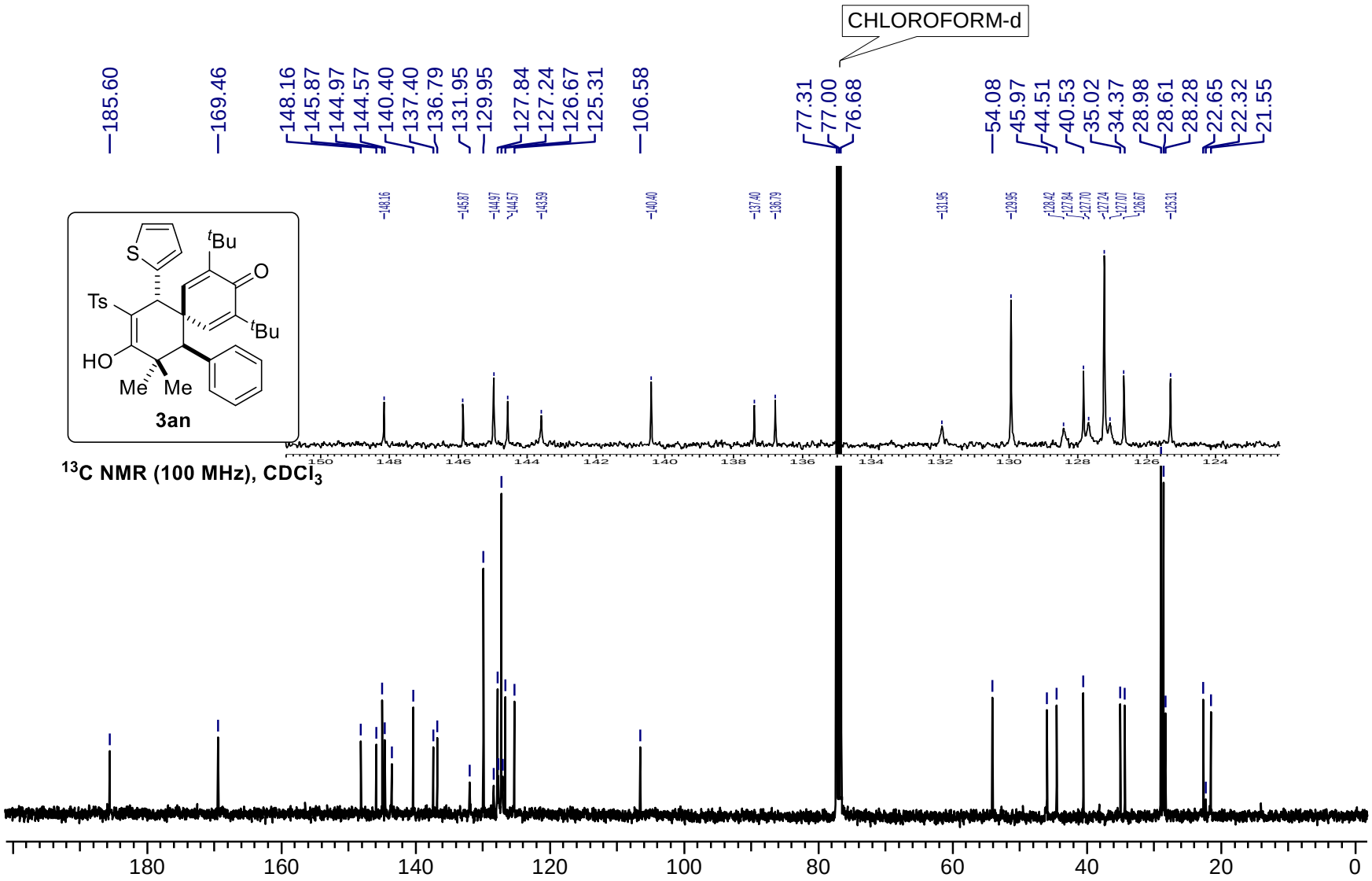

CHLOROFORM-d
185.44
169.65
147.98
145.13
145.01
144.51
141.11
136.64
129.61
128.83
128.13
127.50
127.13
125.62
124.57
123.86
105.38
77.31
77.00
76.69
53.63
44.78
43.65
40.49
35.11
33.76
29.17
28.13
27.64
22.85
21.43
tBu
O
Ts
tBu
HO
Me
Me
3al
13C NMR (100 MHz), CDCl3

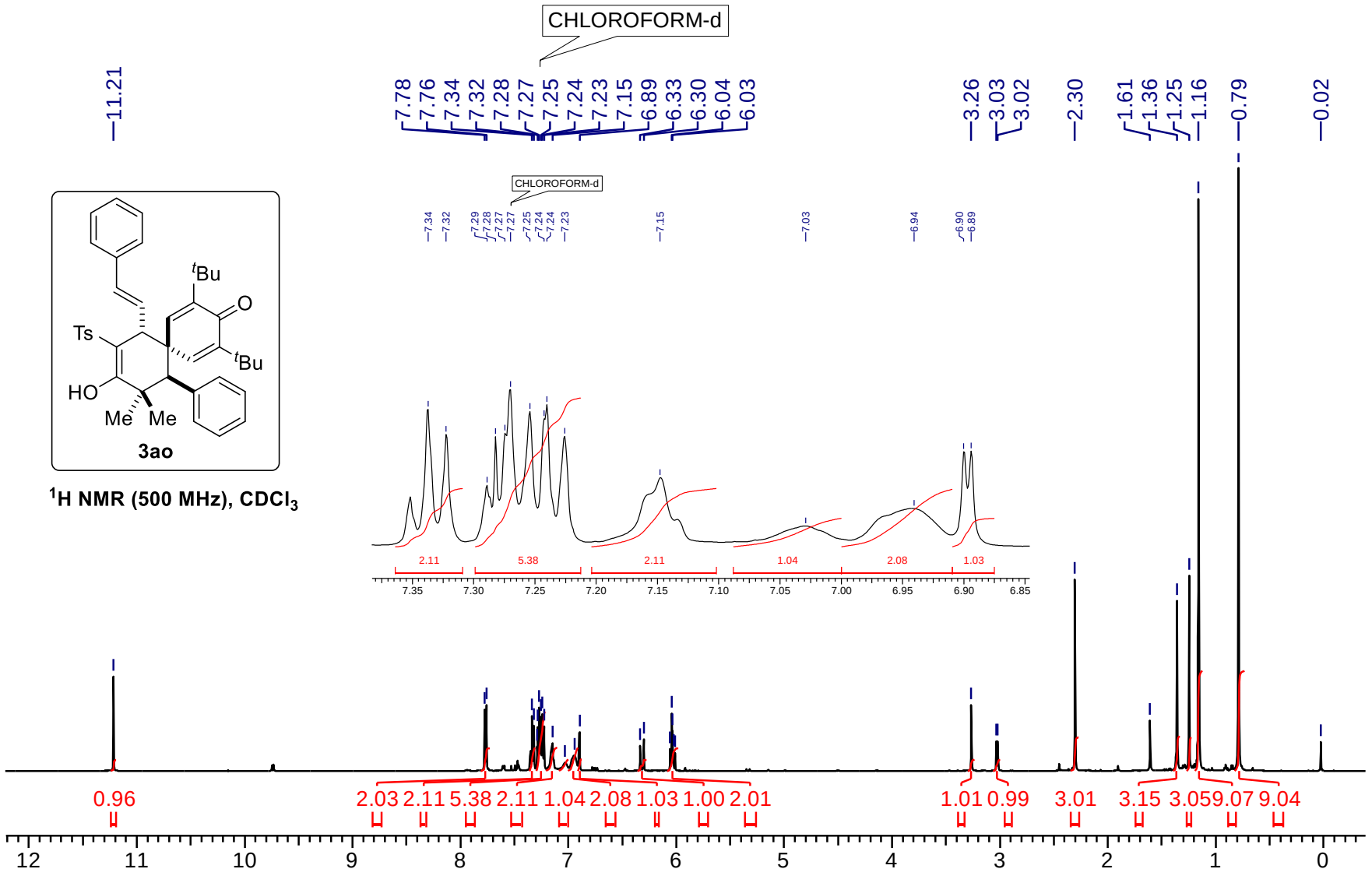

CHLOROFORM-d
11.15
7.69
7.67
7.30
7.29
7.27
7.27
6.80
6.79
6.30
6.30
6.30
6.29
6.10
6.09
5.37
5.36
3.49
3.39
2.41
1.37
1.25
1.11
0.70
0.01
tBu
O
O
Ts
tBu
HO
Me
Me
3am
1H NMR (400 MHz), CDCl3
1.00
2.01 2.03 1.10 2.02 1.00 1.01 1.02 1.04 1.00 1.01 1.01
1.00 1.02
3.10
3.08 3.04 9.11 9.13

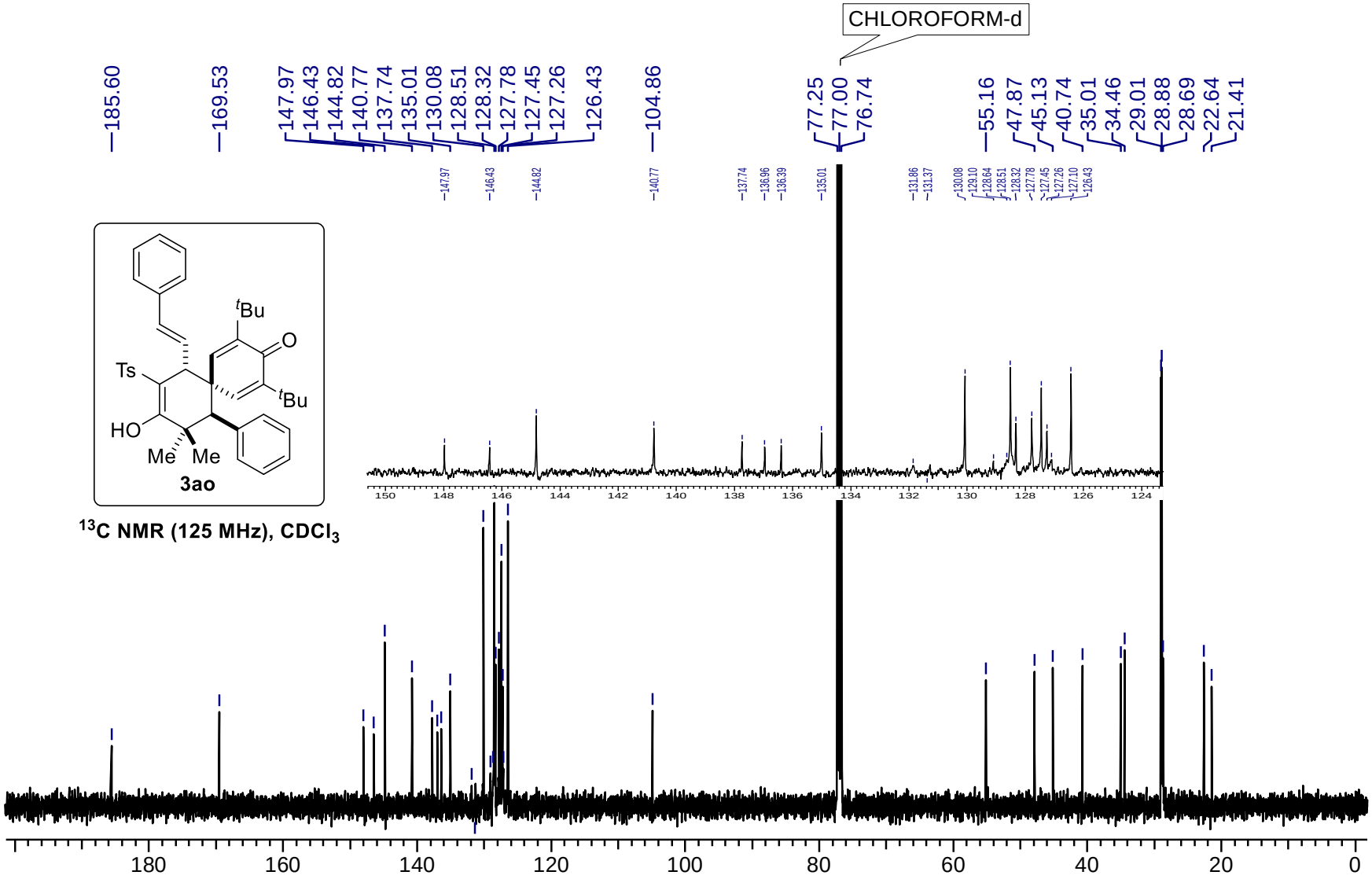


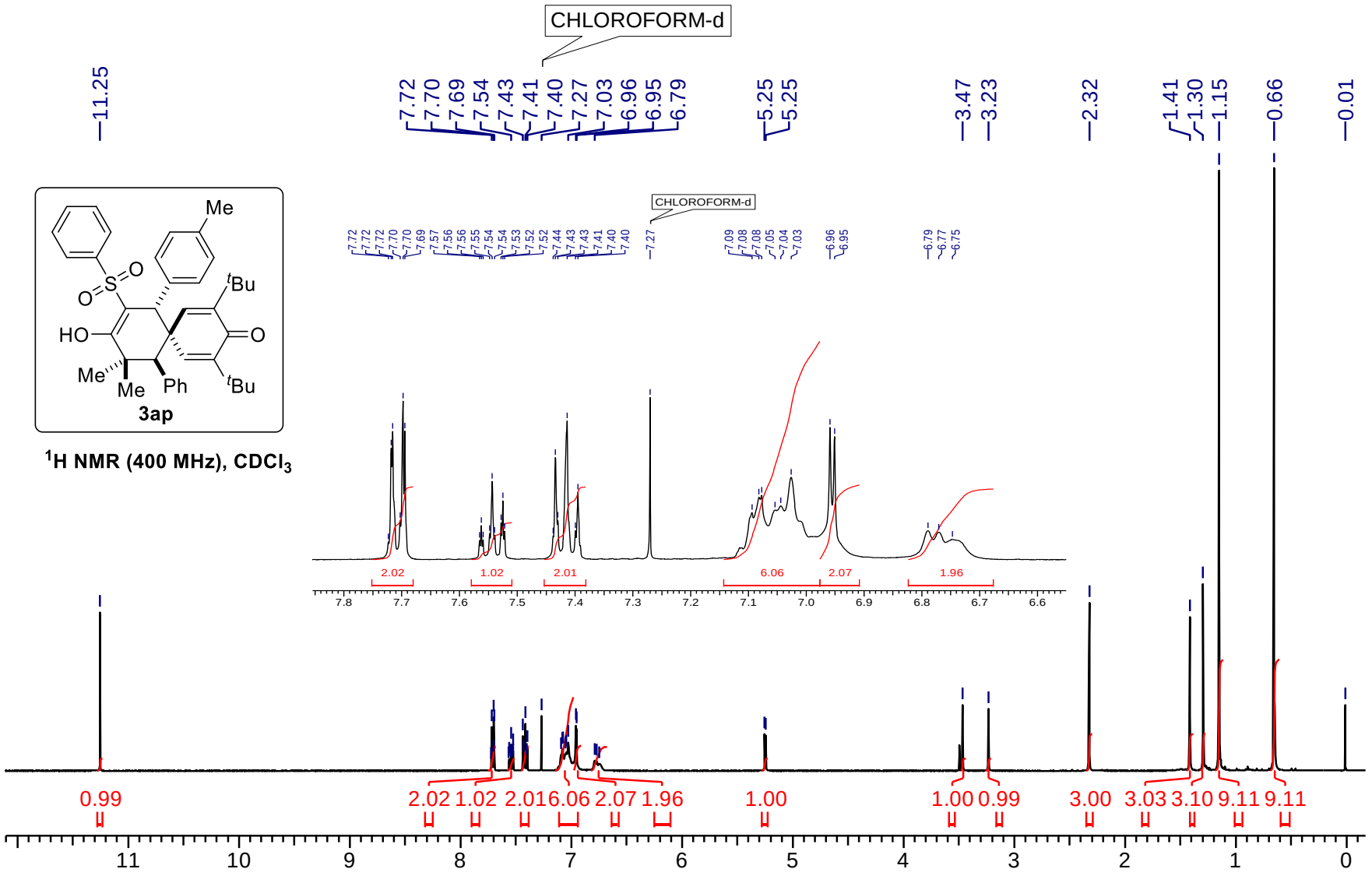
^{13}C NMR (100 MHz), $CDCl_3$

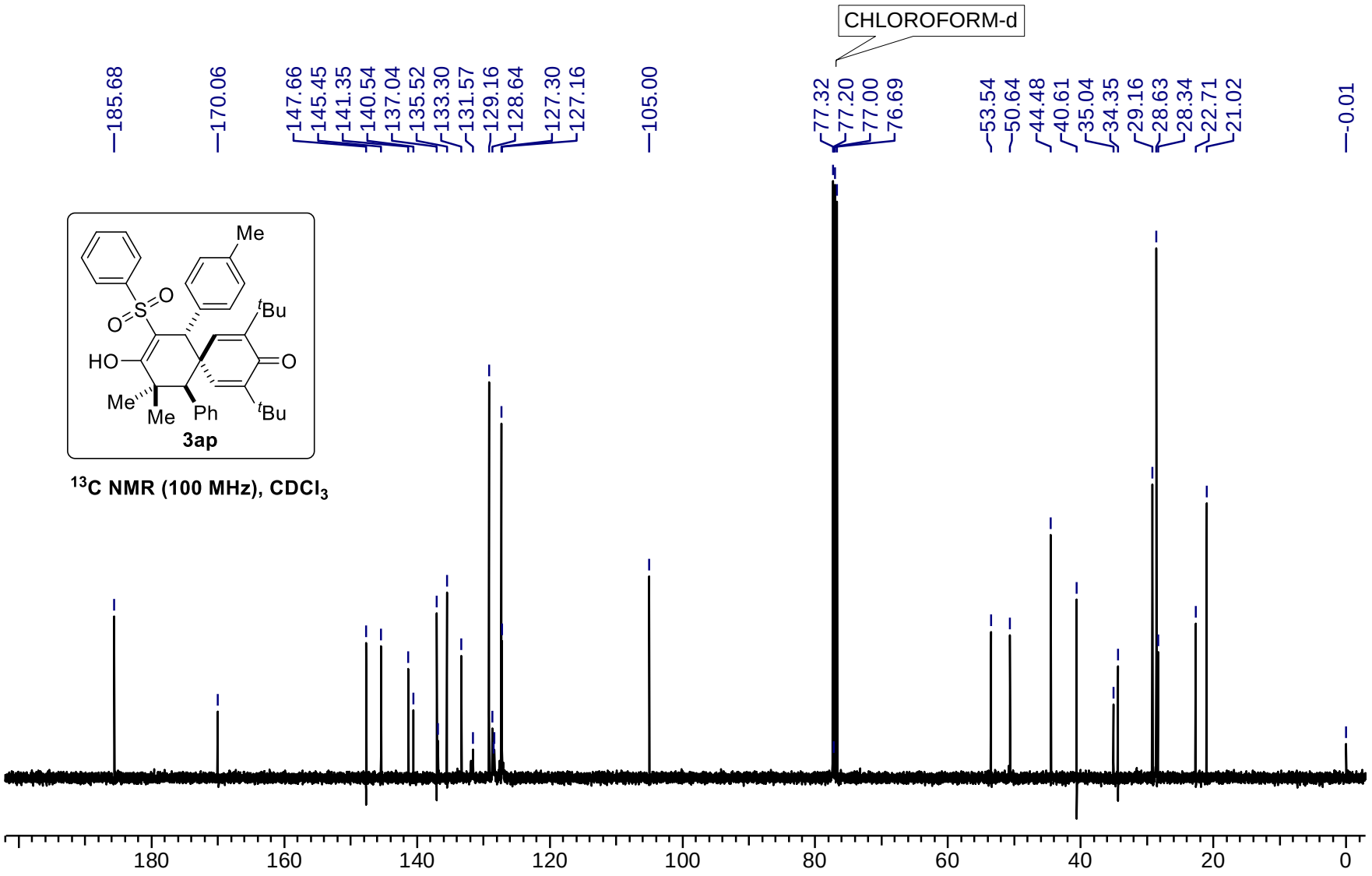

CHLOROFORM-d
11.17
7.65
7.63
7.27
7.26
7.24
7.21
7.20
6.92
6.91
6.87
6.86
6.73
5.52
5.51
3.70
3.52
2.41
1.41
1.27
1.13
0.69
S
tBu
O
Ts
tBu
HO
Me
Me
3an
1H NMR (400 MHz), CDCl3
0.98
2.02 1.99 1.02 1.95 0.94 0.97 1.17 1.13 0.81 1.01 0.99
1.00 1.00
3.04
3.04 3.32 9.04 9.05


CHLOROFORM-d
185.60
169.46
148.16
145.87
144.97
144.57
140.40
137.40
136.79
131.95
129.95
127.84
127.24
126.67
125.31
106.58
77.31
77.00
76.68
54.08
45.97
44.51
40.53
35.02
34.37
28.98
28.61
28.28
22.65
22.32
21.55
tBu
O
Ts
tBu
HO
Me
Me
3an
13C NMR (100 MHz), CDCl3

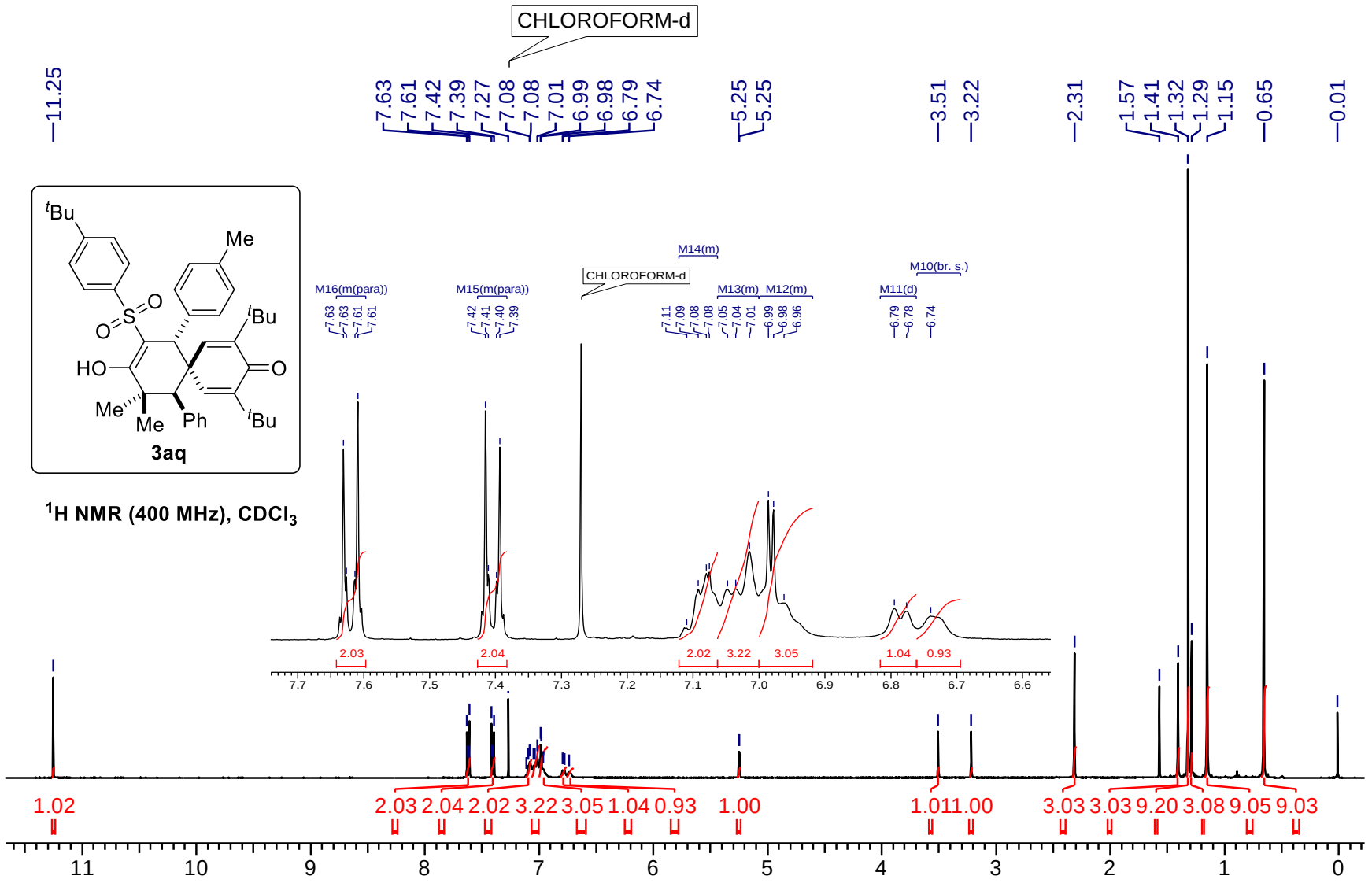

CHLOROFORM-d
11.21
7.78
7.76
7.34
7.32
7.28
7.27
7.25
7.24
7.23
7.15
6.89
6.33
6.30
6.04
6.03
3.26
3.03
3.02
2.30
1.61
1.36
1.25
1.16
0.79
0.02
tBu
O
Ts
tBu
HO
Me
Me
3ao
1H NMR (500 MHz), CDCl3
2.11
5.38
2.11
1.04
2.08
1.03
0.96
2.03 2.11 5.38 2.11 1.04 2.08 1.03 1.00 2.01
1.01 0.99 3.01 3.15 3.05 9.07 9.04

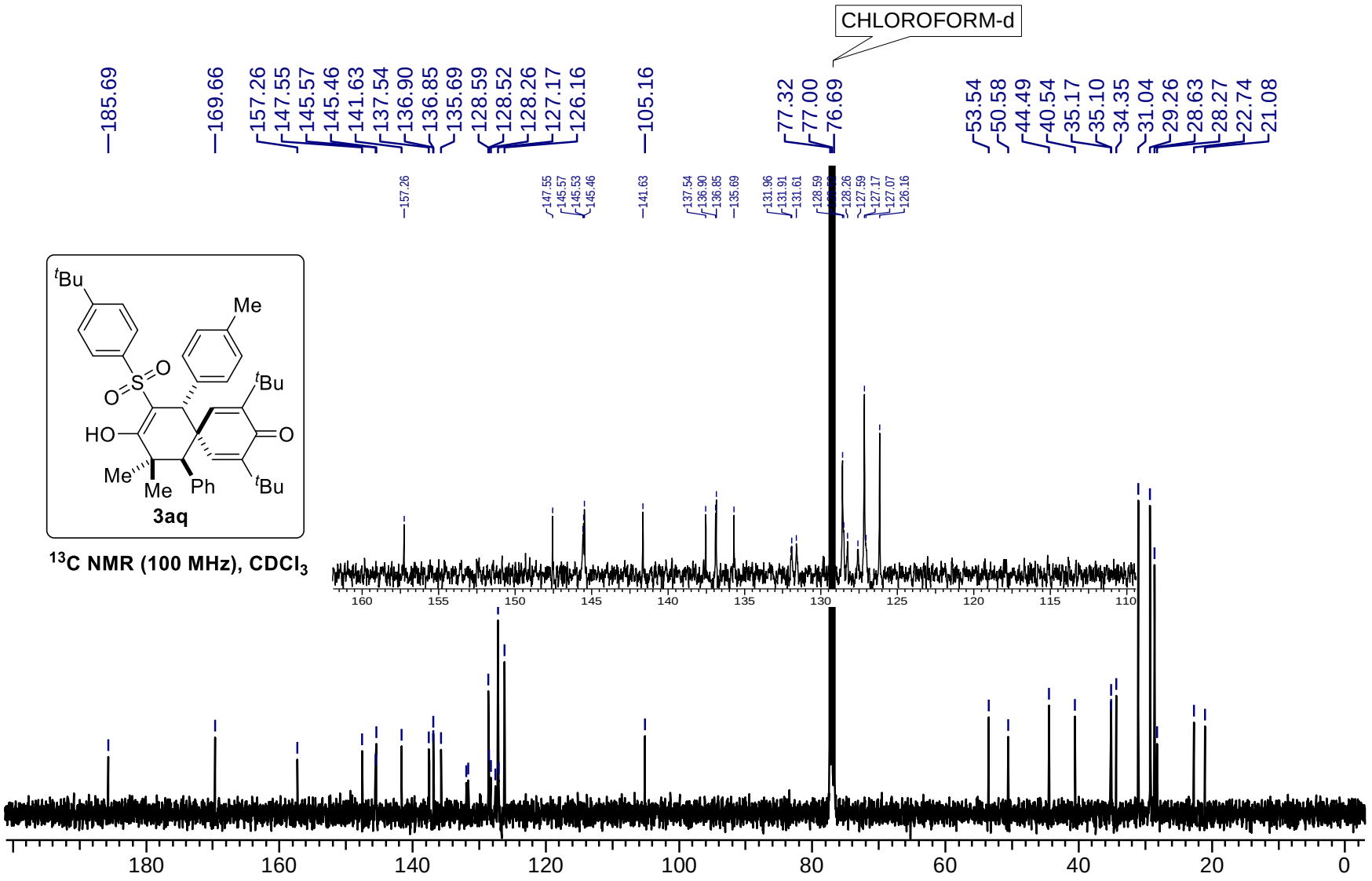

CHLOROFORM-d
185.60
169.53
147.97
146.43
144.82
140.77
137.74
135.01
130.08
128.51
128.32
127.78
127.45
127.26
126.43
104.86
77.25
77.00
76.74
55.16
47.87
45.13
40.74
35.01
34.46
29.01
28.88
28.69
22.64
21.41
Ts
HO
Me
Me
tBu
O
tBu
3ao
13C NMR (125 MHz), CDCl3

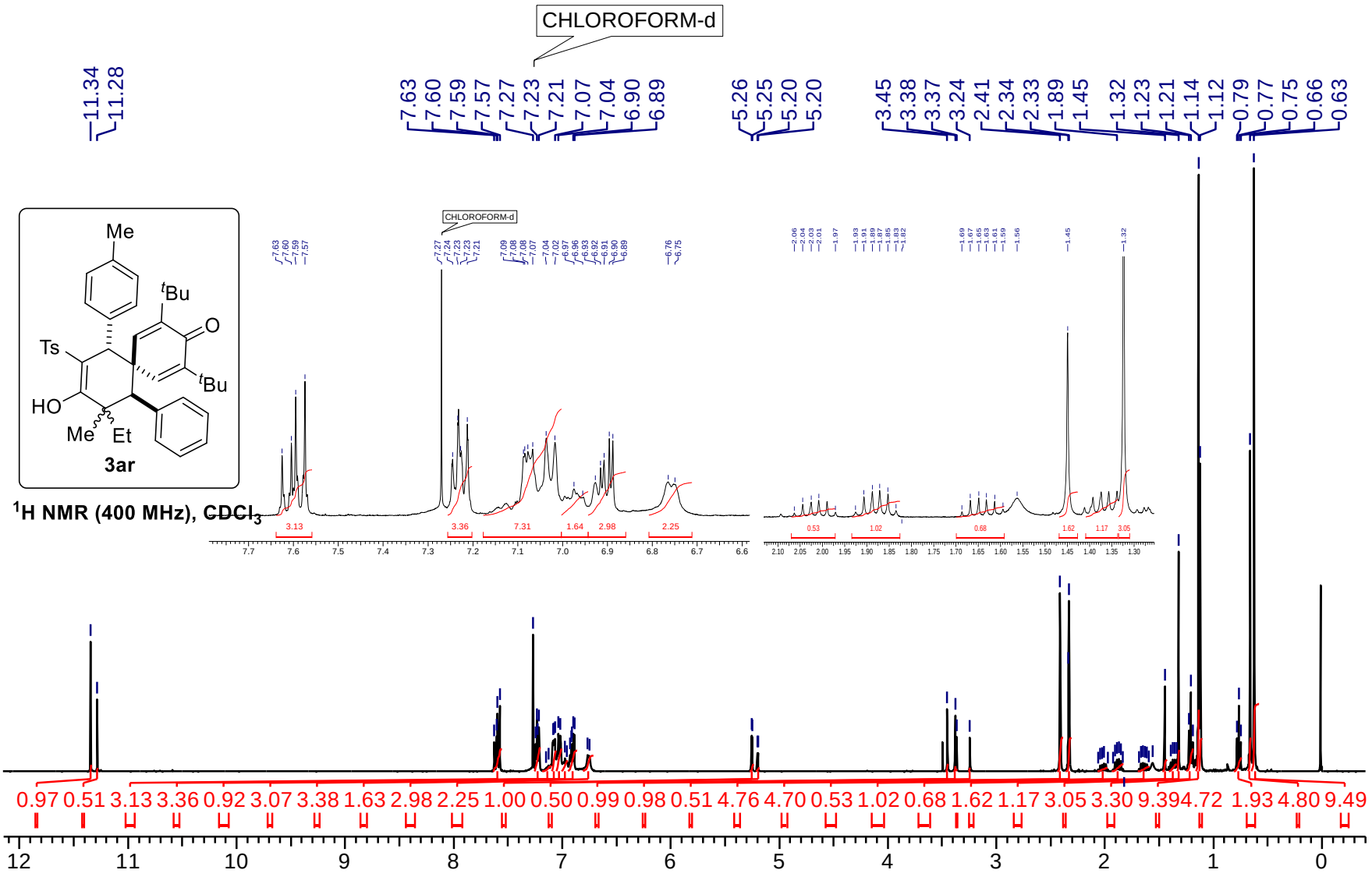

CHLOROFORM-d
11.25
7.72
7.70
7.69
7.54
7.43
7.41
7.40
7.27
7.03
6.96
6.95
6.79
5.25
5.25
3.47
3.23
2.32
1.41
1.30
1.15
0.66
0.01
Me
tBu
O
S
O
HO
O
Me
Me
Ph
tBu
3ap
1H NMR (400 MHz), CDCl3
2.02
1.02
2.01
6.06
2.07
1.96
0.99
2.02 1.02 2.01 6.06 2.07 1.96
1.00
1.00 0.99
3.00
3.03 3.10 9.11 9.11

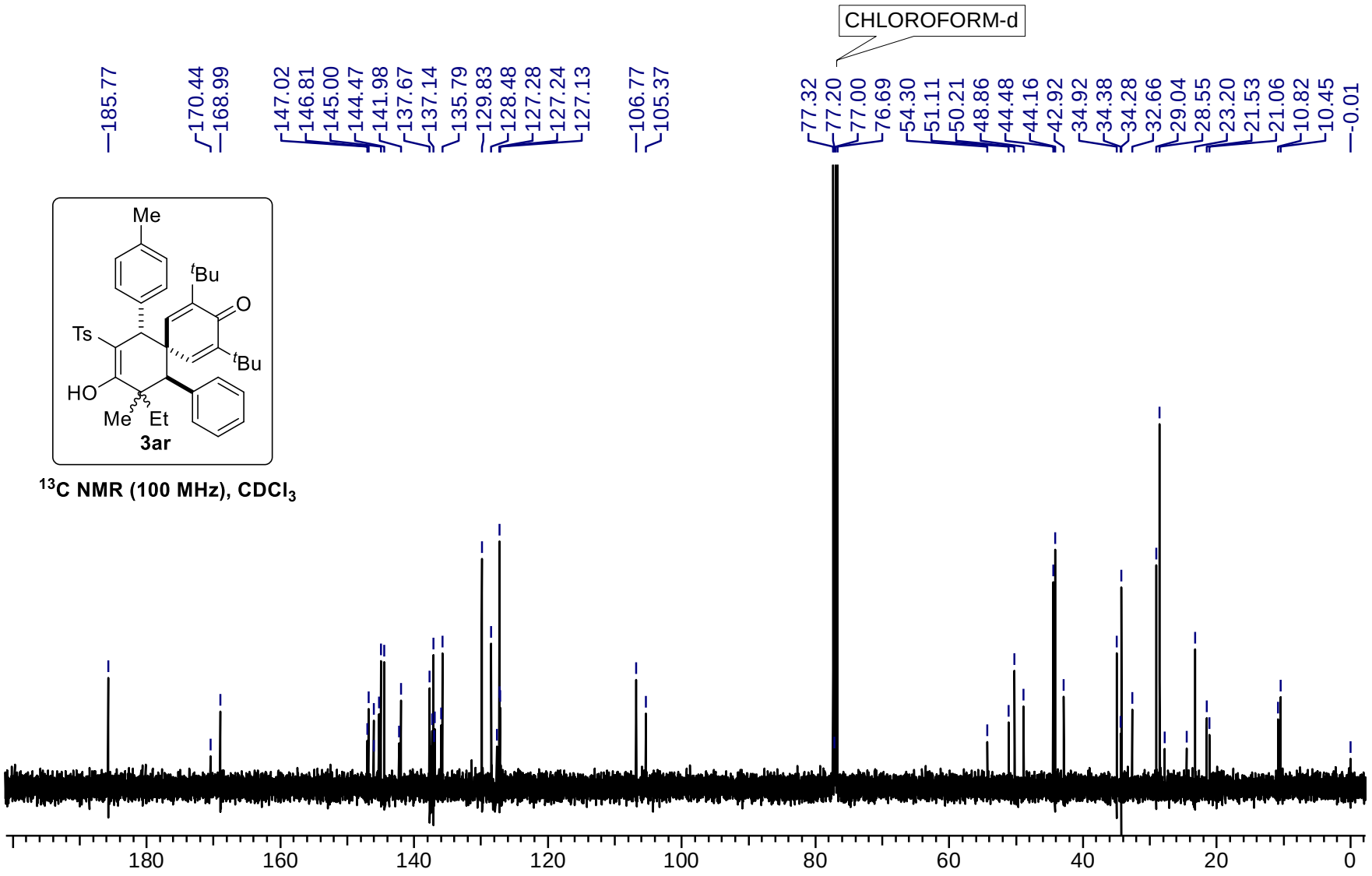


^{13}C NMR (100 MHz), $CDCl_3$

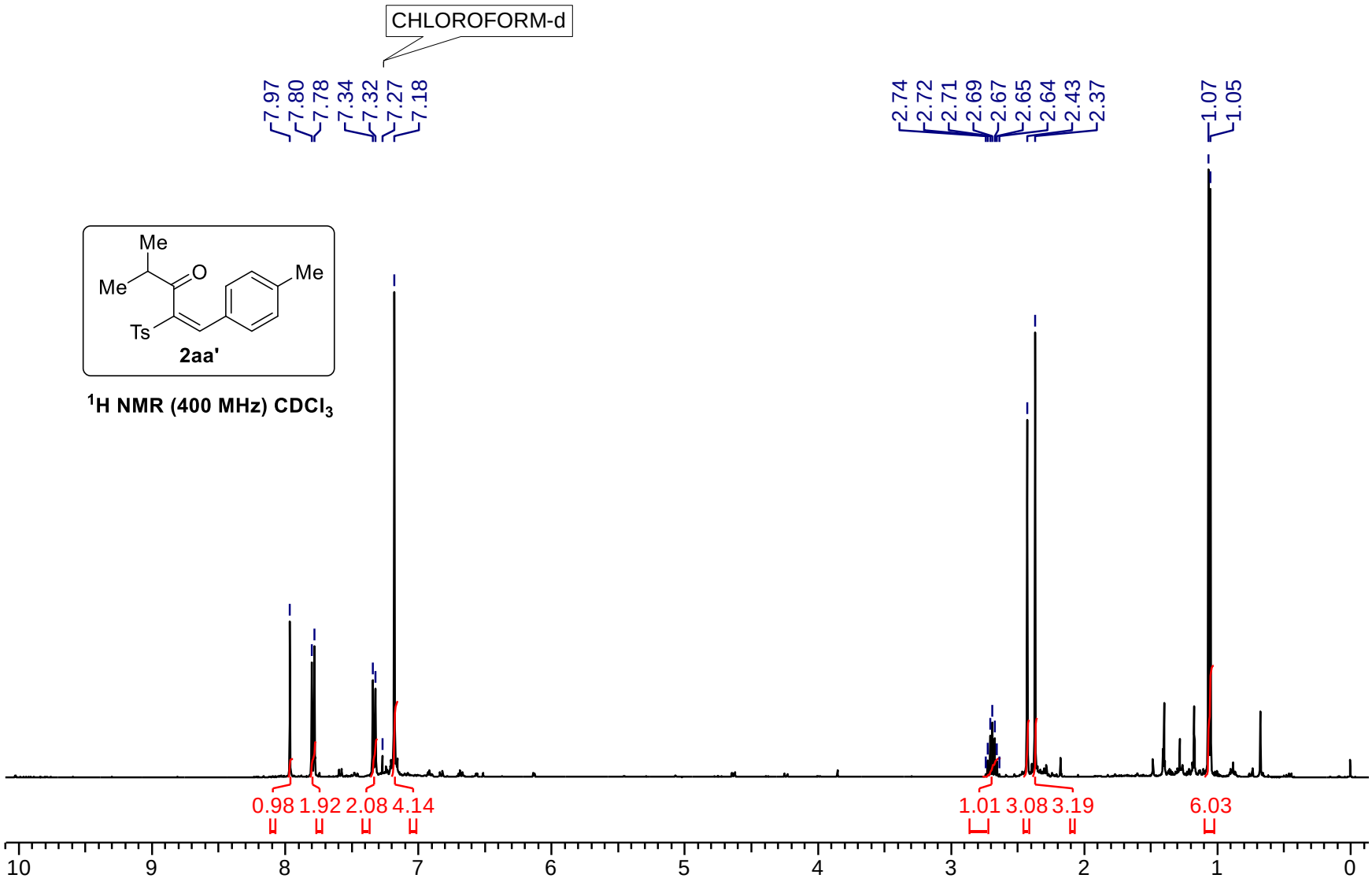

CHLOROFORM-d
11.25
7.63
7.61
7.42
7.39
7.27
7.08
7.08
7.01
6.99
6.98
6.79
6.74
5.25
5.25
3.51
3.22
2.31
1.57
1.41
1.32
1.29
1.15
0.65
0.01
tBu
Me
O
S
O
HO
O
tBu
Me
Me
Ph
tBu
3aq
1H NMR (400 MHz), CDCl3
M16(m(para))
M15(m(para))
CHLOROFORM-d
M14(m)
M13(m)
M12(m)
M11(d)
M10(br. s.)
2.03
2.04
2.02
3.22
3.05
1.04
0.93
1.02
2.03 2.04 2.02 3.22 3.05 1.04 0.93
1.00
1.01 1.00
3.03 3.03 9.20 3.08 9.05 9.03


CHLOROFORM-d
185.69
169.66
157.26
147.55
145.57
145.46
141.63
137.54
136.90
136.85
135.69
128.59
128.52
128.26
127.17
126.16
105.16
77.32
77.00
76.69
53.54
50.58
44.49
40.54
35.17
35.10
34.35
31.04
29.26
28.63
28.27
22.74
21.08
tBu
Me
O
S
O
tBu
HO
O
Me
Me
Ph
tBu
3aq
13C NMR (100 MHz), CDCl3
180
160
140
120
100
80
60
40
20
0

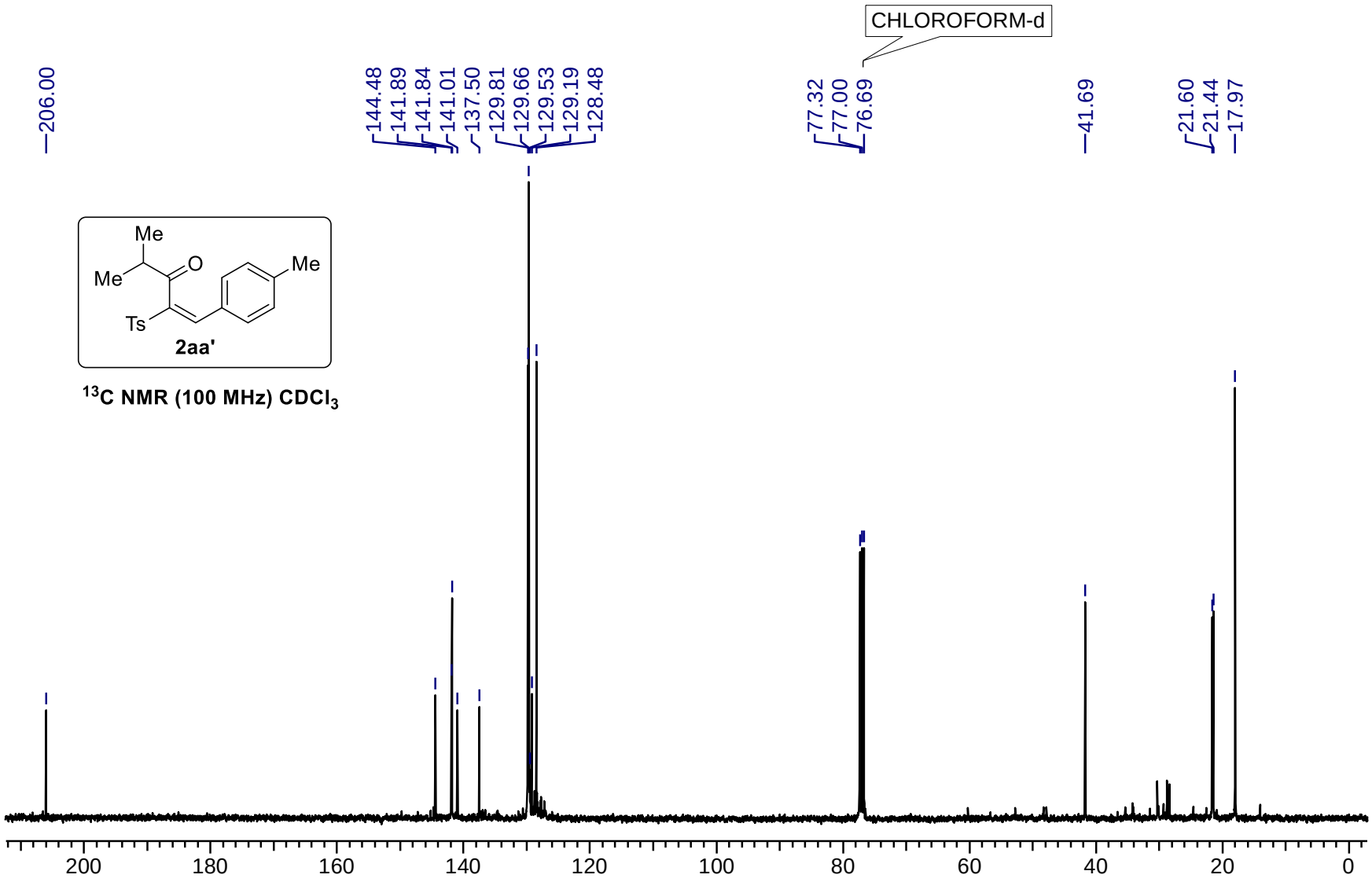

CHLOROFORM-d
11.34
11.28
7.63
7.60
7.59
7.57
7.27
7.23
7.21
7.07
7.04
6.90
6.89
5.26
5.25
5.20
5.20
3.45
3.38
3.37
3.24
2.41
2.34
2.33
1.89
1.45
1.32
1.23
1.21
1.14
1.12
0.79
0.77
0.75
0.66
0.63
Me
tBu
O
Ts
tBu
HO
Me
Et
3ar
1H NMR (400 MHz), CDCl3
0.97 0.51 3.13 3.36 0.92 3.07 3.38 1.63 2.98 2.25 1.00 0.50 0.99 0.98 0.51 4.76 4.70 0.53 1.02 0.68 1.62 1.17 3.05 3.30 9.39 4.72 1.93 4.80 9.49



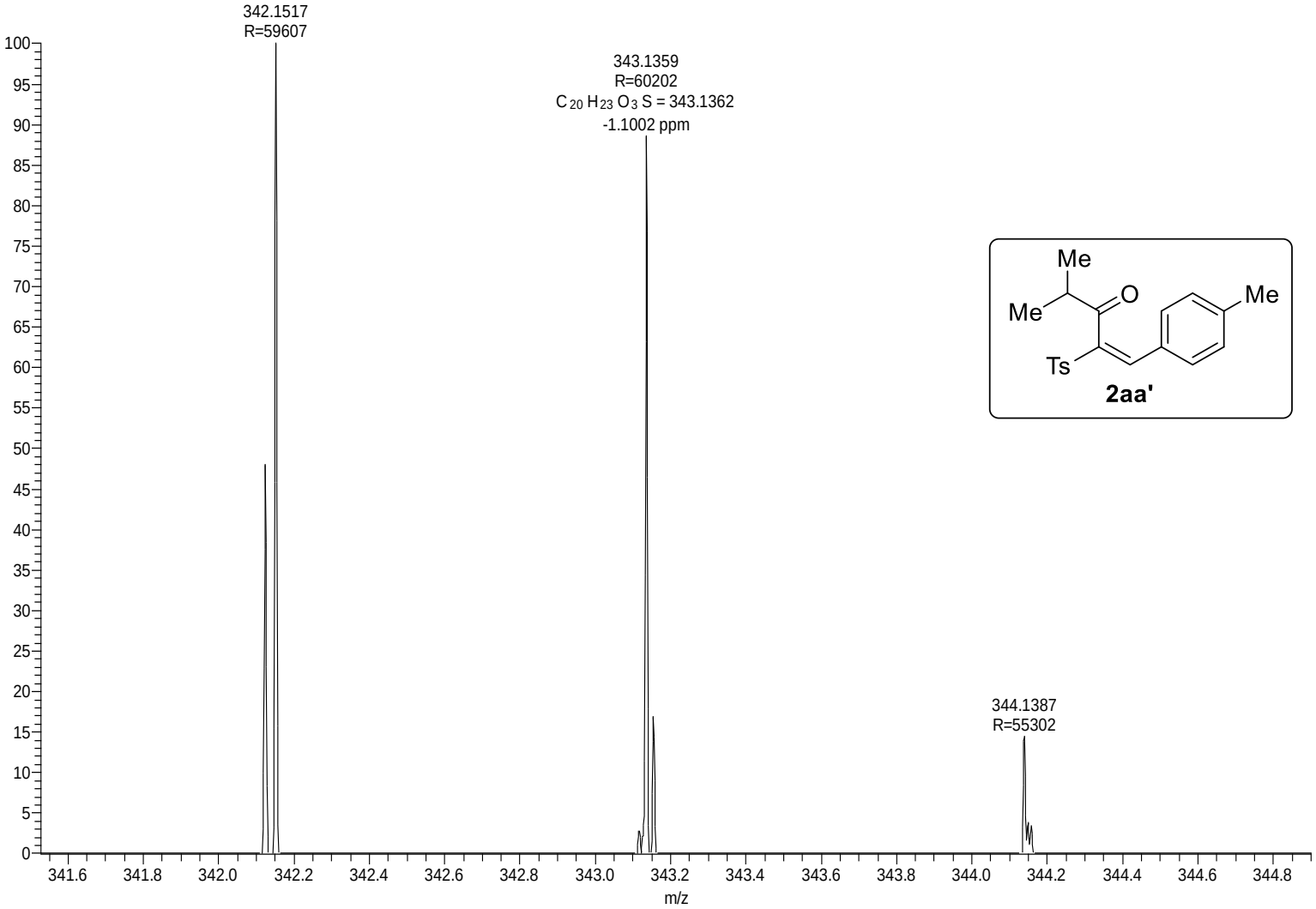
^{13}C NMR (100 MHz), $CDCl_3$

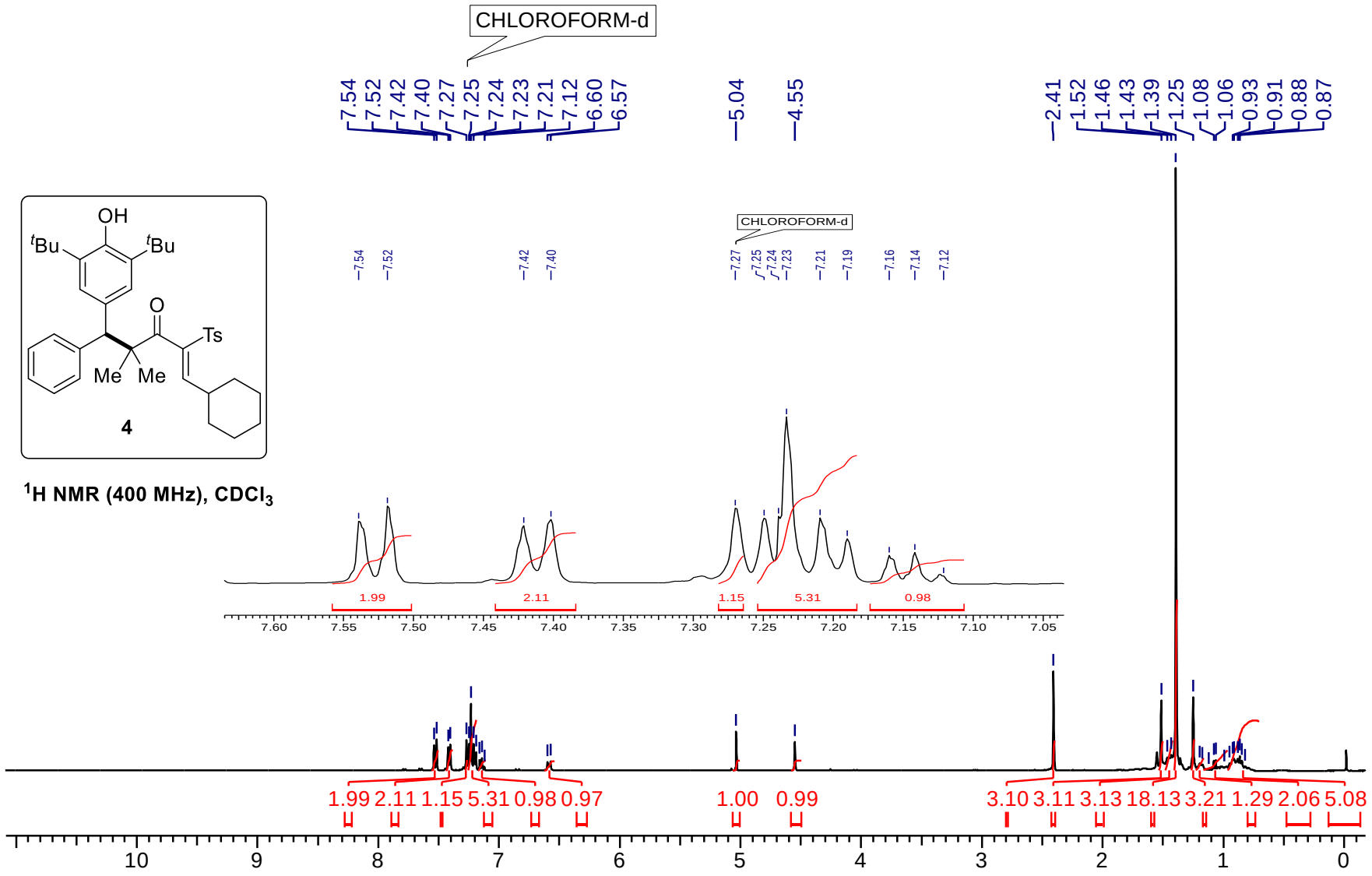


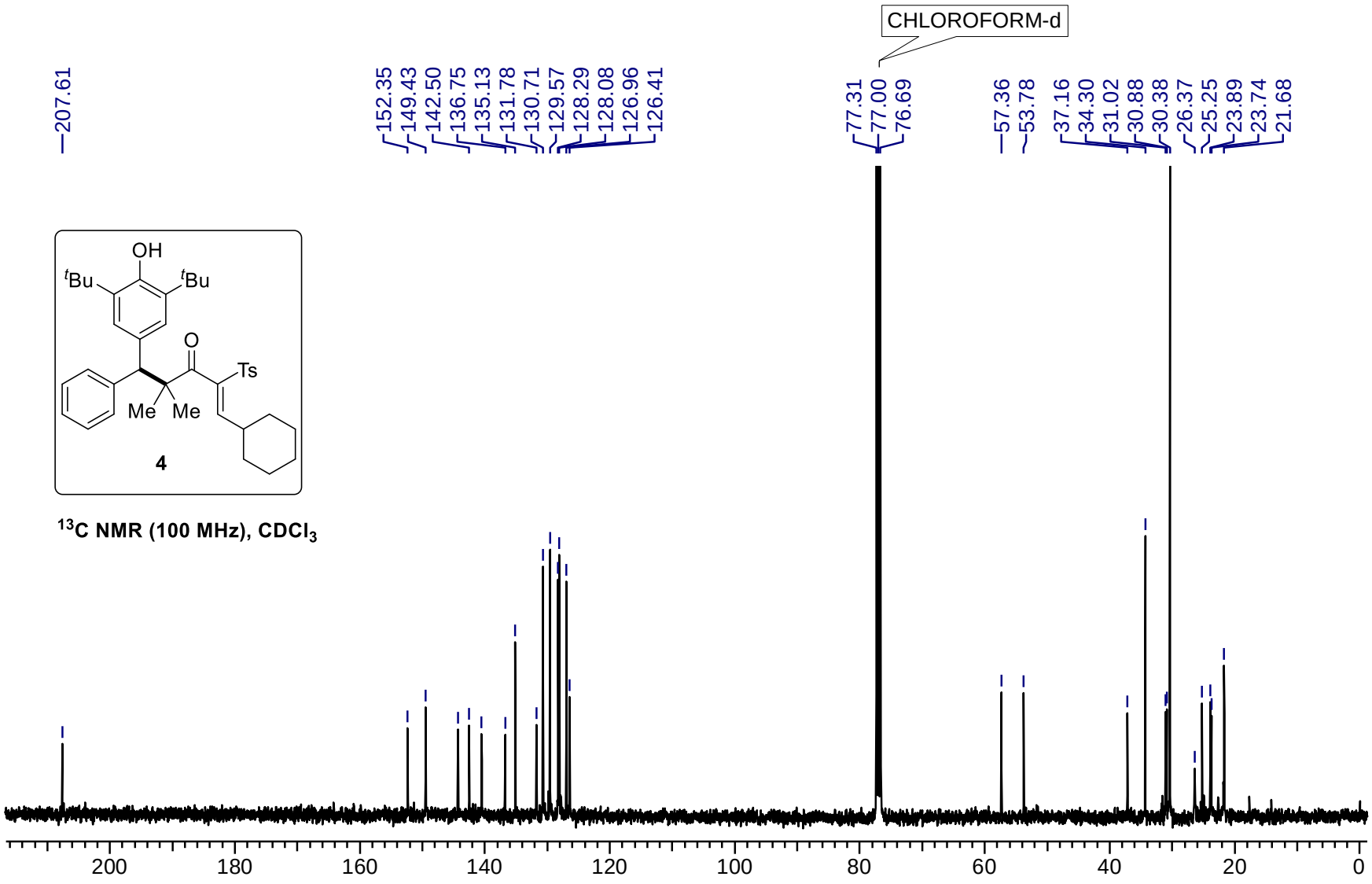
^{1}H NMR (400 MHz) $CDCl_3$

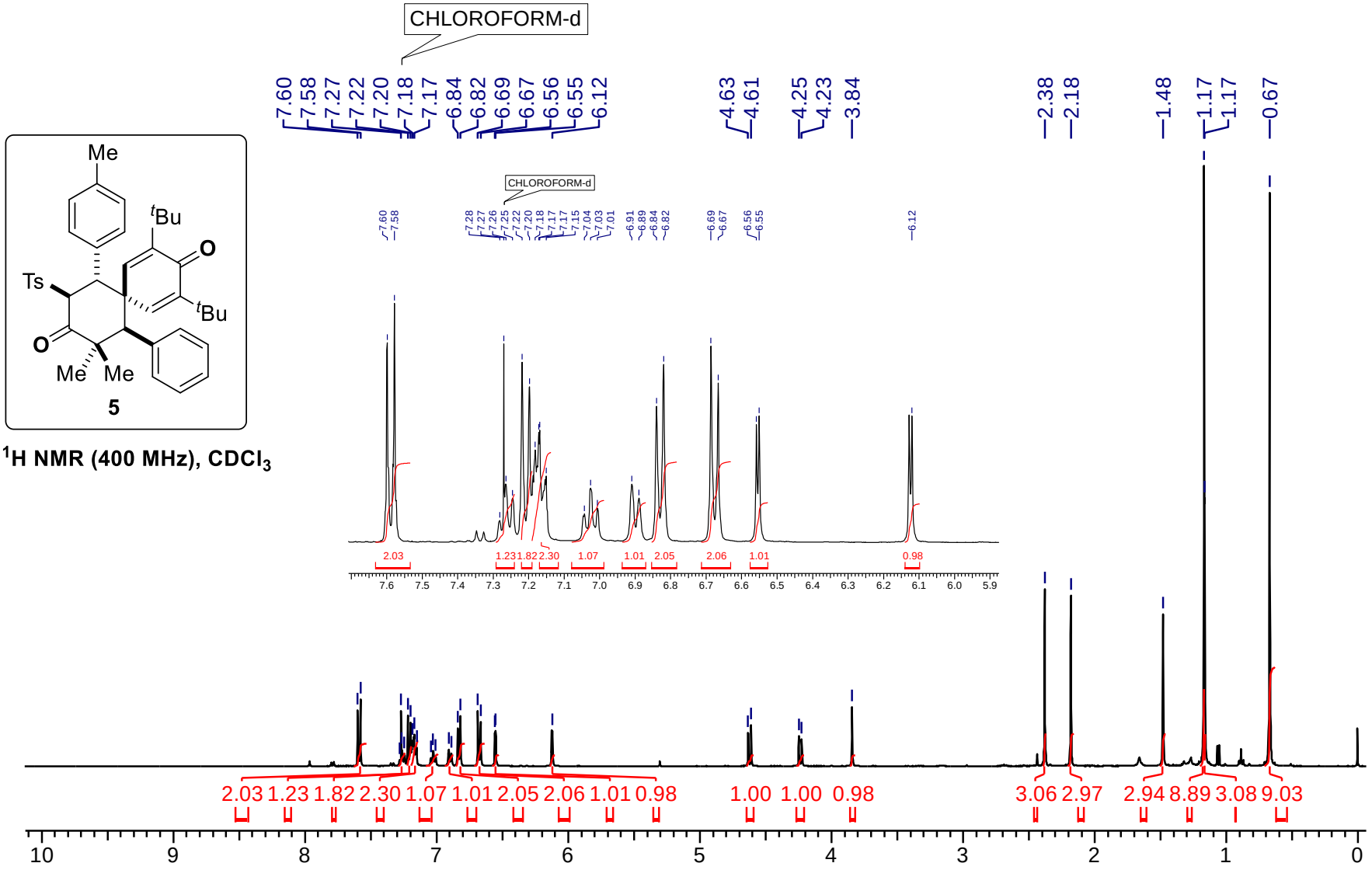

CHLOROFORM-d
206.00
144.48
141.89
141.84
141.01
137.50
129.81
129.66
129.53
129.19
128.48
77.32
77.00
76.69
41.69
21.60
21.44
17.97
Me
Me
O
Me
Ts
2aa'
13C NMR (100 MHz) CDCl3
200
180
160
140
120
100
80
60
40
20
0

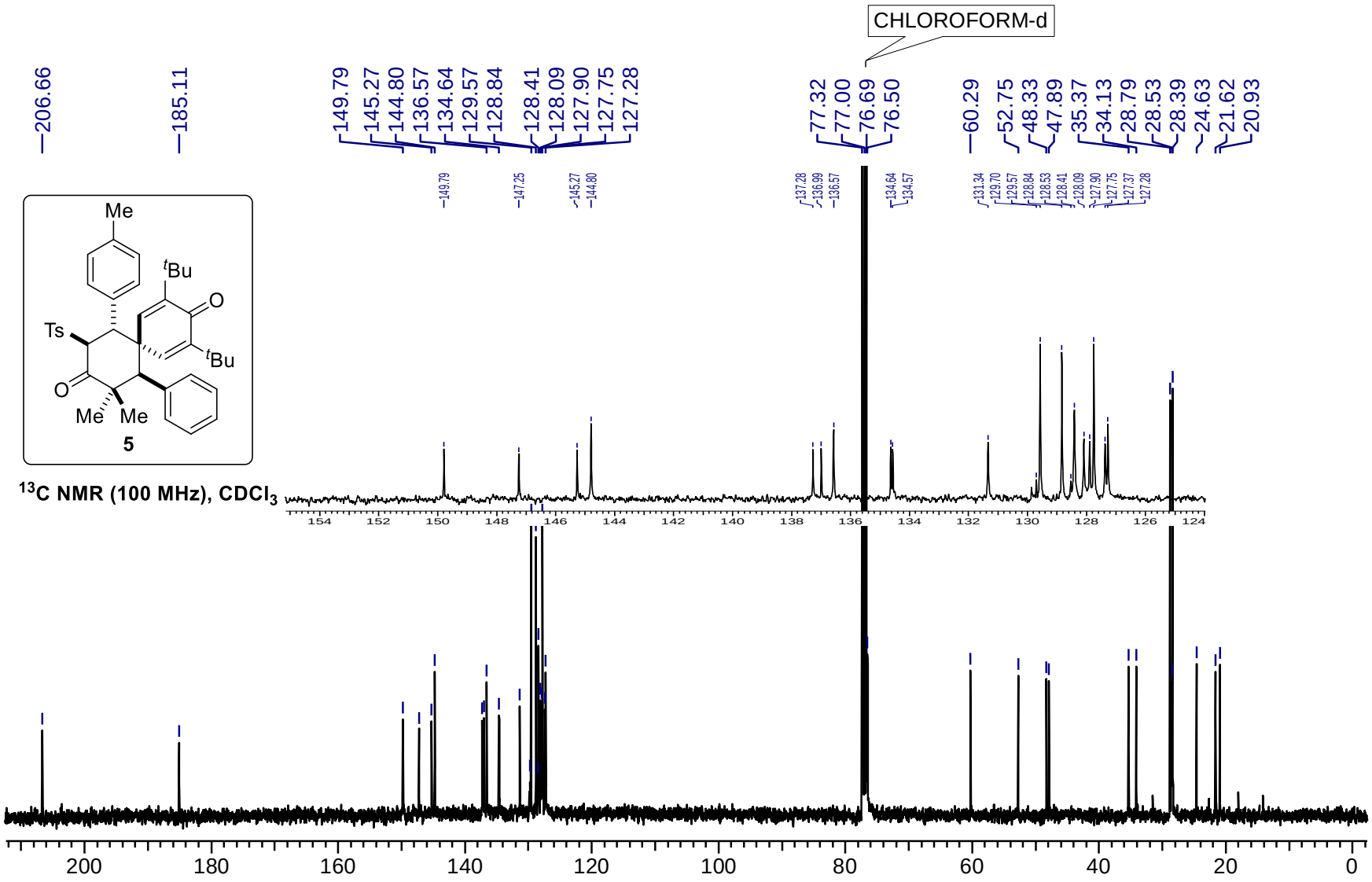
GSG-G-821 #264 RT: 1.17 AV: 1 NL: 2.55E7
T: FTMS + p ESI Full ms [133.4000-2000.0000]

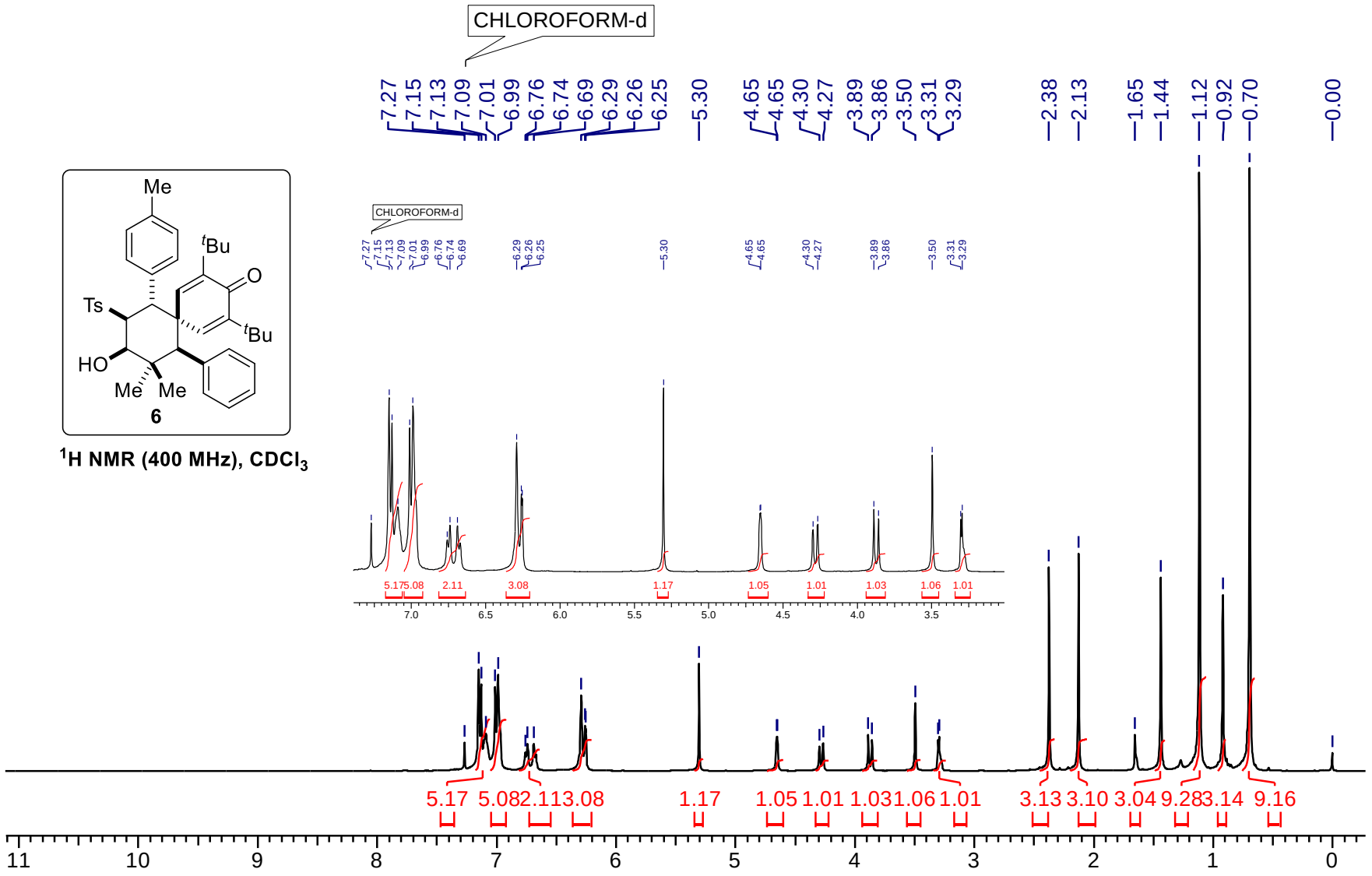


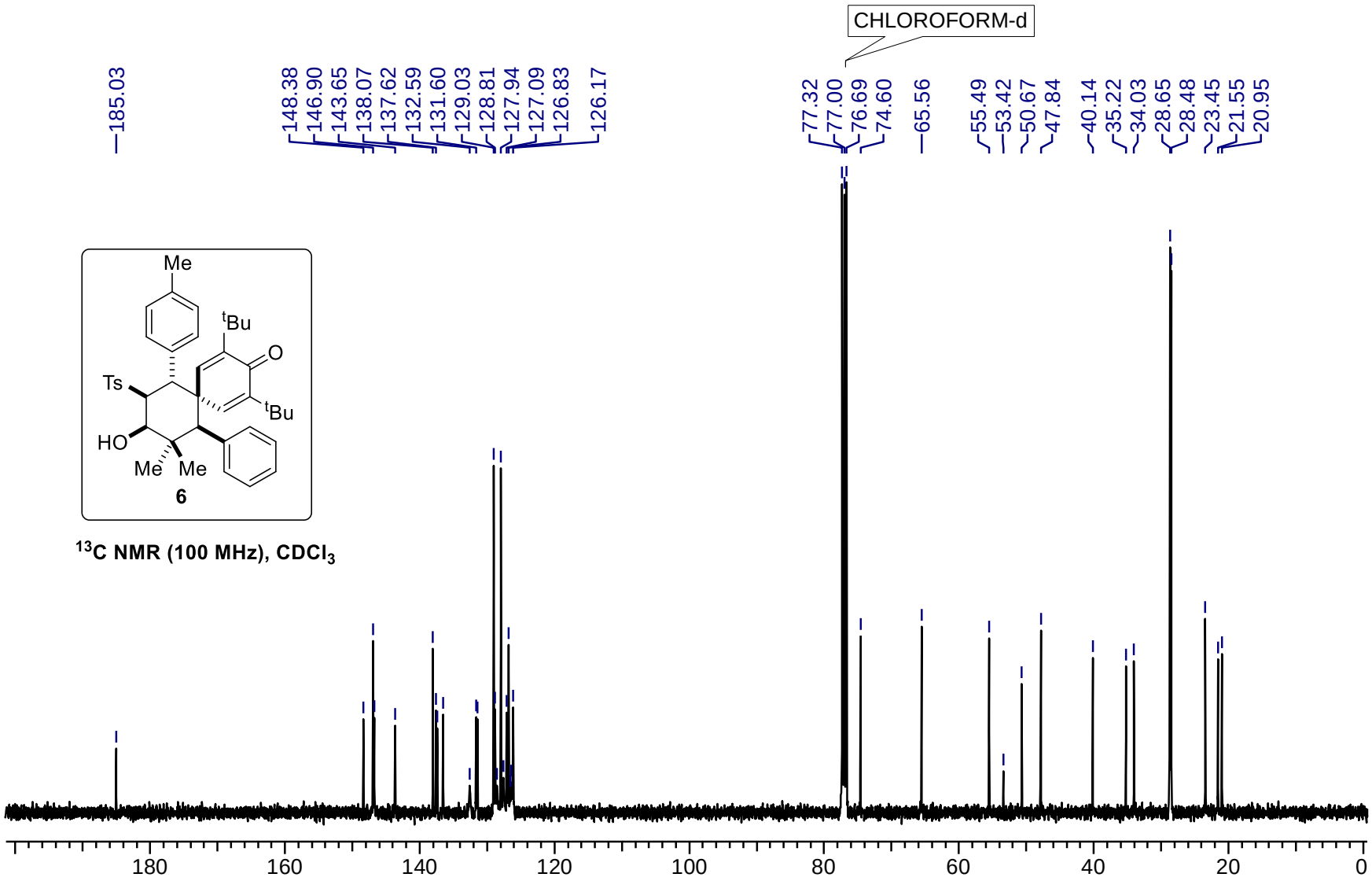

CHLOROFORM-d
7.54 7.52 7.42 7.40 7.27 7.25 7.24 7.23 7.21 7.12 6.60 6.57
5.04
4.55
2.41 1.52 1.46 1.43 1.39 1.25 1.08 1.06 0.93 0.91 0.88 0.87
OH
tBu
tBu
O
Ts
Me Me
4
1H NMR (400 MHz), CDCl3
CHLOROFORM-d
1.99 2.11 1.15 5.31 0.98
1.99 2.11 1.15 5.31 0.98 0.97
1.00 0.99
3.10 3.11 3.13 18.13 3.21 1.29 2.06 5.08


CHLOROFORM-d
207.61
152.35
149.43
142.50
136.75
135.13
131.78
130.71
129.57
128.29
128.08
126.96
126.41
77.31
77.00
76.69
57.36
53.78
37.16
34.30
31.02
30.88
30.38
26.37
25.25
23.89
23.74
21.68
OH
tBu
tBu
O
Ts
Me
Me
4
13C NMR (100 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0


CHLOROFORM-d
7.60 7.58 7.27 7.22 7.20 7.18 7.17 6.84 6.82 6.69 6.67 6.56 6.55 6.12 4.63 4.61 4.25 4.23 3.84 2.38 2.18 1.48 1.17 1.17 0.67
Me
tBu
O
Ts
tBu
O
Me Me
5
1H NMR (400 MHz), CDCl3
2.03 1.23 1.82 2.30 1.07 1.01 2.05 2.06 1.01 0.98 1.00 1.00 0.98 3.06 2.97 2.94 8.89 3.08 9.03
10 9 8 7 6 5 4 3 2 1 0


CHLOROFORM-d
206.66
185.11
149.79
145.27
144.80
136.57
134.64
129.57
128.84
128.41
128.09
127.90
127.75
127.28
77.32
77.00
76.69
76.50
60.29
52.75
48.33
47.89
35.37
34.13
28.79
28.53
28.39
24.63
21.62
20.93
Me
tBu
O
Ts
tBu
O
Me
Me
5
13C NMR (100 MHz), CDCl3


CHLOROFORM-d
7.27 7.15 7.13 7.09 7.01 6.99 6.76 6.74 6.69 6.29 6.26 6.25 5.30 4.65 4.65 4.30 4.27 3.89 3.86 3.50 3.31 3.29 2.38 2.13 1.65 1.44 1.12 0.92 0.70 0.00
Me
tBu
O
Ts
tBu
HO
Me Me
6
1H NMR (400 MHz), CDCl3
5.17 5.08 2.11 3.08 1.17 1.05 1.01 1.03 1.06 1.01
3.13 3.10 3.04 9.28 3.14 9.16
11 10 9 8 7 6 5 4 3 2 1 0



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