

## Supporting Information

### Concise syntheses of (-)-habiterpenol and (+)-2,3-*epi*-habiterpenol via redox radical cyclization of alkenylsilane

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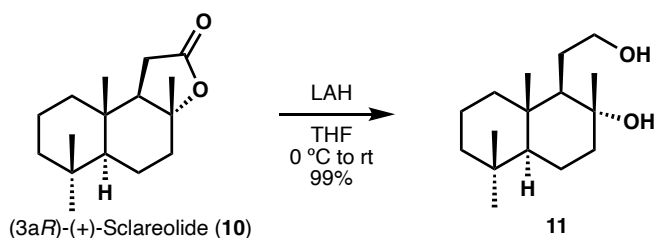
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## 1. Experimental procedure and characterization data

### General

All reactions were performed in flame-dried glassware under nitrogen by using standard techniques for handling air-sensitive materials. Commercial reagents were used without further purification, unless otherwise noted. Organic solvents were distilled and dried over 3 or 4 Å molecular sieves (MS). Cold baths were prepared under the following conditions: 0 °C, wet ice/water; -78 °C, dry ice/acetone. Purification by flash column chromatography was performed over silica gel 60N (spherical, neutral, particle size of 40–50 µm). TLC was performed on 0.25 mm Merck silica gel 60 F254 plates, and the effluents were visualized by UV ( $\lambda = 254$  nm) and by using phosphomolybdic acid and *p*-anisaldehyde TLC stains. Yields corresponded to chromatographically and spectroscopically pure compounds, unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded by using an internal deuterium lock on 400-MR, VNMRs-400, and UNITY-400 spectrometers. All NMR signals were reported in ppm relative to the internal reference standard provided by chloroform (i.e.,  $\delta = 7.26$  or  $77.0$  ppm for  $^1\text{H}$  and  $^{13}\text{C}$  spectra, respectively). Multiplicity data were presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, and dt = doublet of triplets. Coupling constants ( $J$ ) were reported in hertz. IR spectra were recorded on a Horiba FT-710 spectrophotometer and an FT/IR460-plus IR spectrometer. Absorption data were expressed in wavenumbers ( $\text{cm}^{-1}$ ). High-resolution mass spectra were recorded on JEOL JMS 700 MStation, JEOL JMS-AX505HA, and JEOL JMS-T100LP systems equipped with FAB, EI, and ESI high-resolution mass spectrometers.

(1*R*,2*R*,4*aS*,8*aS*)-1-(2-Hydroxyethyl)-2,5,5,8*a*-tetramethyldecahydronaphthalen-2-ol (**11**) <sup>S1)</sup>



A solution of **10** (4.00 g, 16.0 mmol) in THF (40.0 mL) was treated with LAH (909 mg, 24.0 mmol) at 0 °C. After stirring for 15 min at room temperature, the reaction mixture was quenched with EtOAc and 2 M HCl *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 100:1) to afford **11** (4.03 g, 99%) as a white solid.

**Rf**: 0.62 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 20 : 1, phosphomolybdic acid)

[ $\alpha$ ]<sub>D</sub><sup>25</sup> -18.03 (*c* 1.0, CHCl<sub>3</sub>).

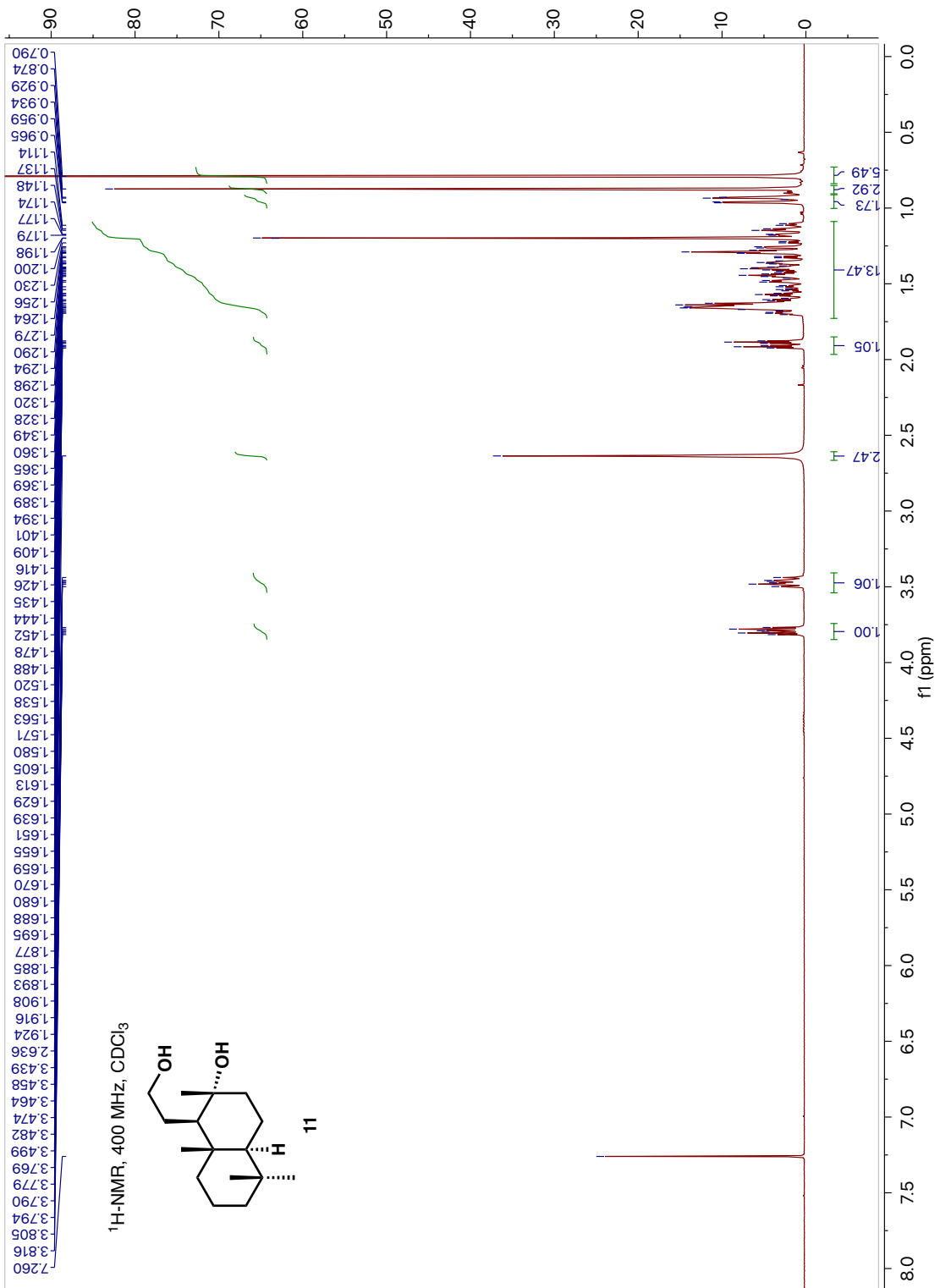
**IR (KBr thin film)** 3396, 2965, 2840, 1388, 1216, 1052 cm<sup>-1</sup>.

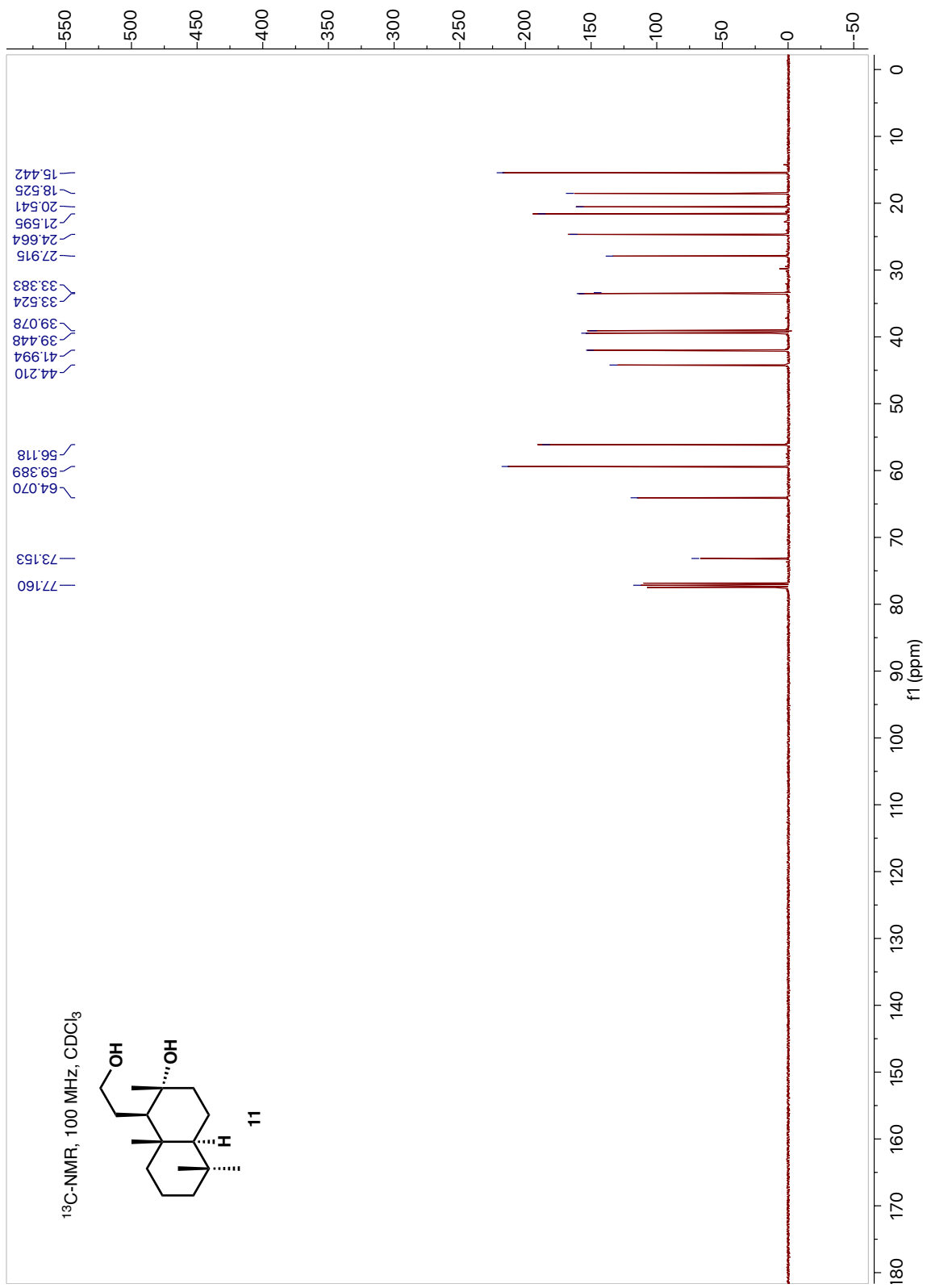
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  3.82–3.77 (m, 1H), 3.50–3.44 (m, 1H), 2.64 (brs, 2H), 1.90 (dt, 1H, *J* = 12.4, 3.2 Hz), 1.70–0.89 (m, 13H), 1.20 (s, 3H), 0.87 (s, 3H), 0.79 (s, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  73.2, 64.2, 59.3, 56.2, 44.4, 42.0, 39.5, 39.1, 33.5, 33.4, 28.0, 24.8, 21.6, 20.6, 18.5, 15.5.

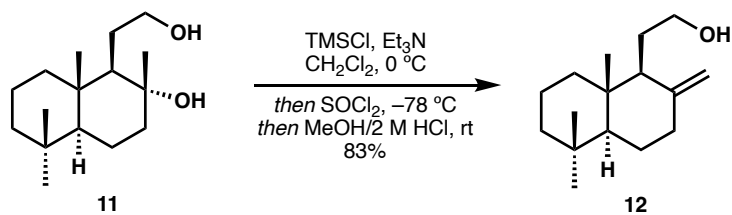
**HRMS (EI)** [*M*]<sup>+</sup> calcd for C<sub>16</sub>H<sub>30</sub>O<sub>2</sub> 254.2246, found 254.2248.

The data for **11** were identical to those reported in the literature <sup>S1)</sup>.





2-((1*S*,4*aS*,8*aS*)-5,5,8*a*-Trimethyl-2-methylenedecahydronaphthalen-1-yl)ethan-1-ol (**12**)<sup>S2</sup>



A solution of a mixture of **11** (254 mg, 1.00 mmol), Et<sub>3</sub>N (2.23 mL, 16.0 mmol) and TMSCl (450  $\mu$ L, 3.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) was stirred for 0.5 h at 0 °C. After cooled to -78 °C, SOCl<sub>2</sub> (218  $\mu$ L, 3.00 mmol) was added, and the mixture was further stirred for 0.5 h at -78 °C. After completing the dehydration reaction checked by TLC, MeOH (1.0 mL) and 2 M HCl aq. (8.0 mL) were added at -78 °C. The mixture was further stirred for 0.5 h after warmed to room temperature. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 30:1) to afford **12** (197 g, 83%) as a white solid.

**Rf**: 0.40 (Hexanes/EtOAc = 2 : 1, anisaldehyde)

$[\alpha]_D^{28}$  +24.79 (*c* 1.0, CHCl<sub>3</sub>).

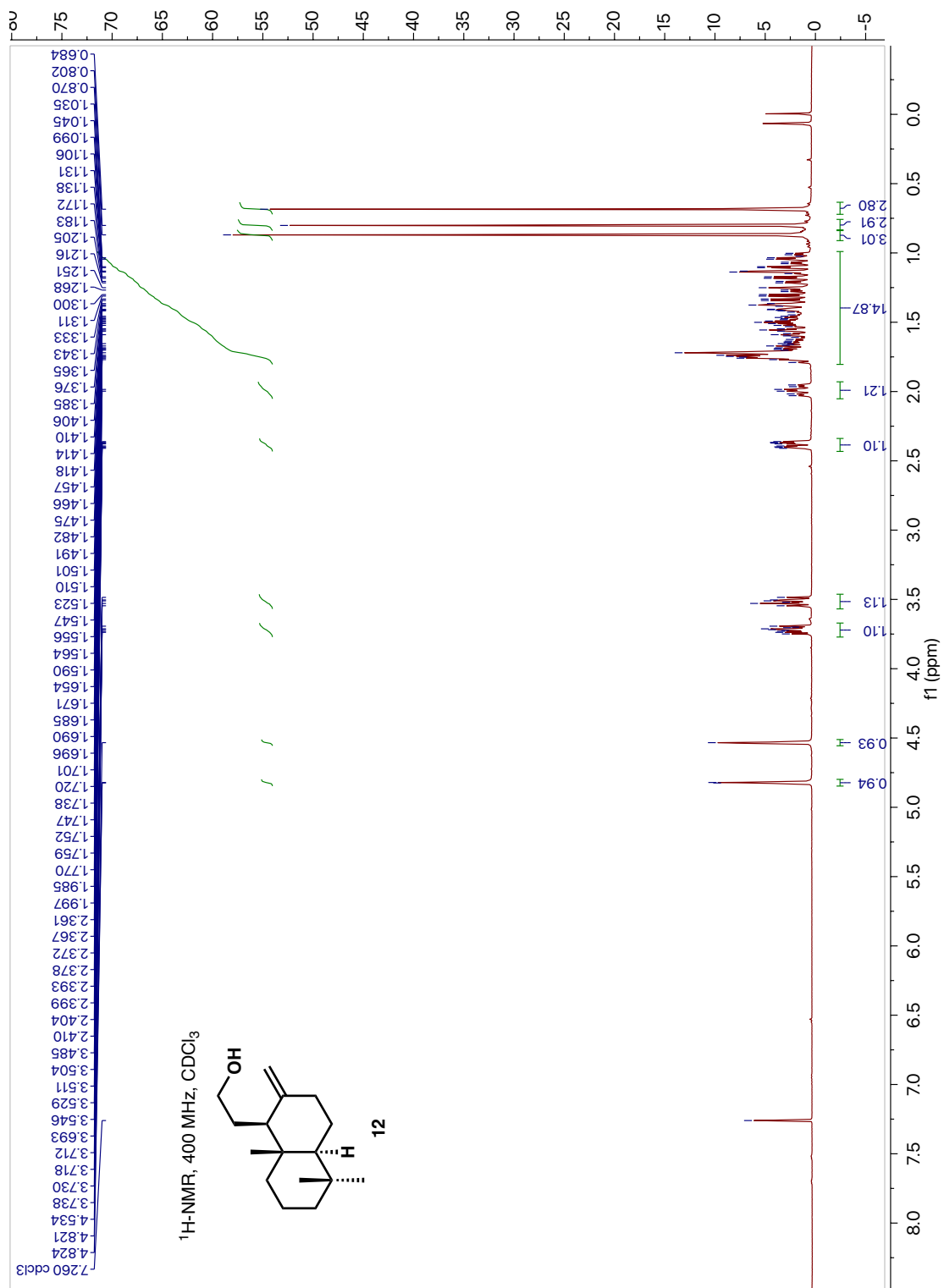
**IR (KBr thin film)** 3383, 2938, 2844, 1441, 1386, 1047 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  4.82 (s, 1H), 4.53 (m, 1H), 3.75–3.69 (m, 1H), 3.55–3.49 (m, 1H), 2.39 (ddd, 1H, *J* = 12.8, 4.0, 2.4 Hz), 1.99 (dt, 1H, *J* = 12.8, 4.8, Hz), 1.79–1.00 (m, 12H), 0.87 (s, 3H), 0.80 (s, 3H), 0.68 (s, 3H).

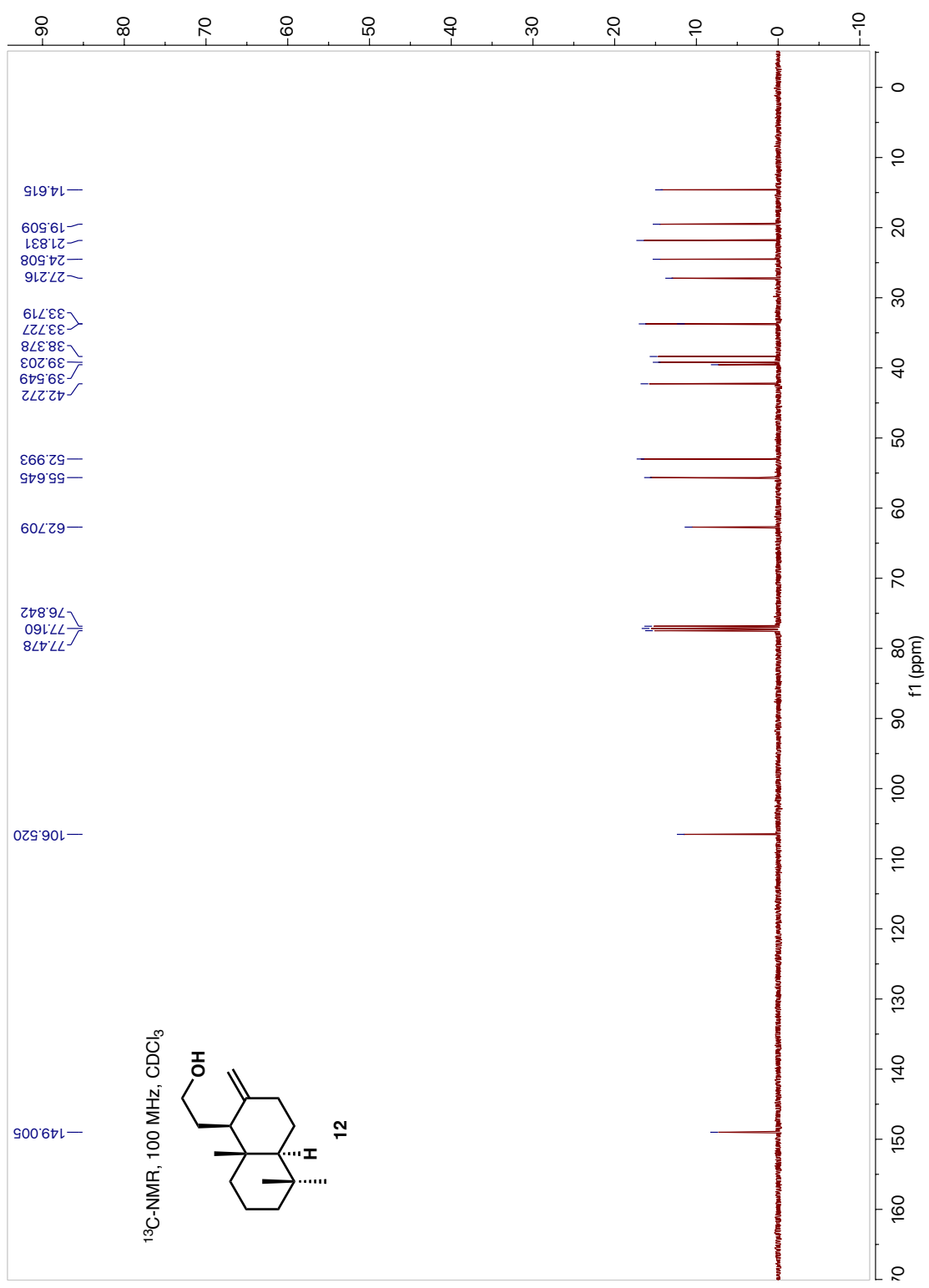
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  149.0, 106.5, 62.7, 55.7, 53.0, 42.3, 39.6, 39.2, 38.4, 33.7, 33.7, 27.2, 24.5, 21.8, 19.5, 14.6.

**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>28</sub>O 236.2140, found 236.2153.

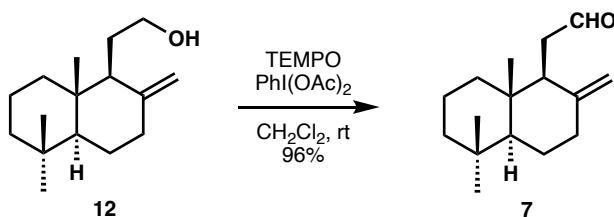
The data for **12** were identical to those reported in the literature<sup>S2</sup>.







2-((1*S*,4*aS*,8*aS*)-5,5,8*a*-Trimethyl-2-methylenedecahydronaphthalen-1-yl)acetaldehyde (**7**)<sup>S3</sup>



A solution of **12** (829 mg, 3.51 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (17.6 mL) was treated with TEMPO (109 mg, 0.701 mmol) and PhI(OAc)<sub>2</sub> (1.36 g, 4.21 mmol) at room temperature. After stirring for 4 h at room temperature, the reaction mixture was quenched with *sat.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 80:1) to afford **7** (4.03 g, 99%) as a colorless liquid.

**Rf:** 0.69 (Hexanes/EtOAc = 4 : 1, anisaldehyde)

$[\alpha]_D^{23}$  -31.10 (*c* 1.0, CHCl<sub>3</sub>).

**IR (KBr thin film)** 2914, 2844, 2716, 1725, 1644, 1459 cm<sup>-1</sup>.

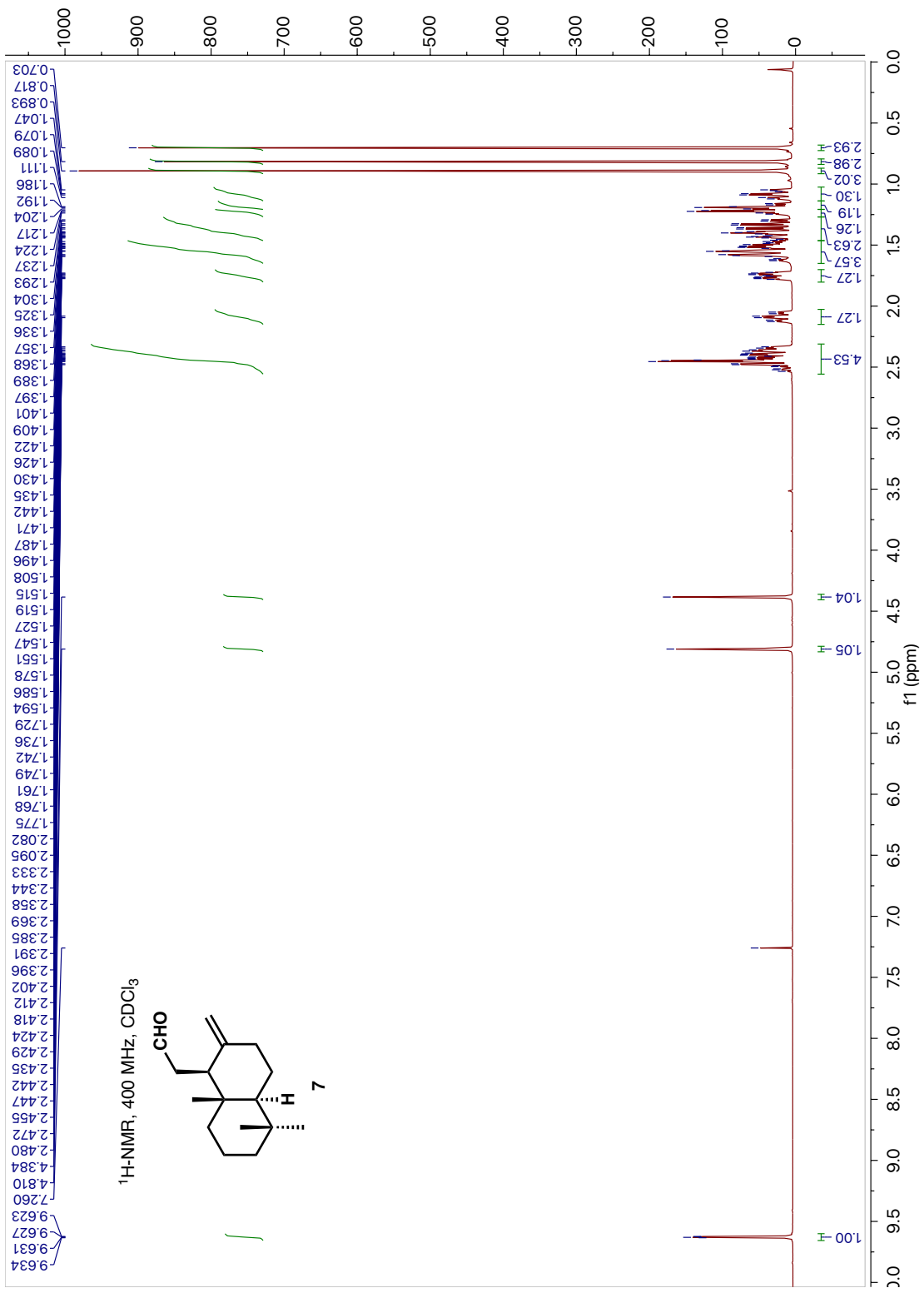
**Rf:** 0.69 (Hexanes/EtOAc = 4 : 1, anisaldehyde)

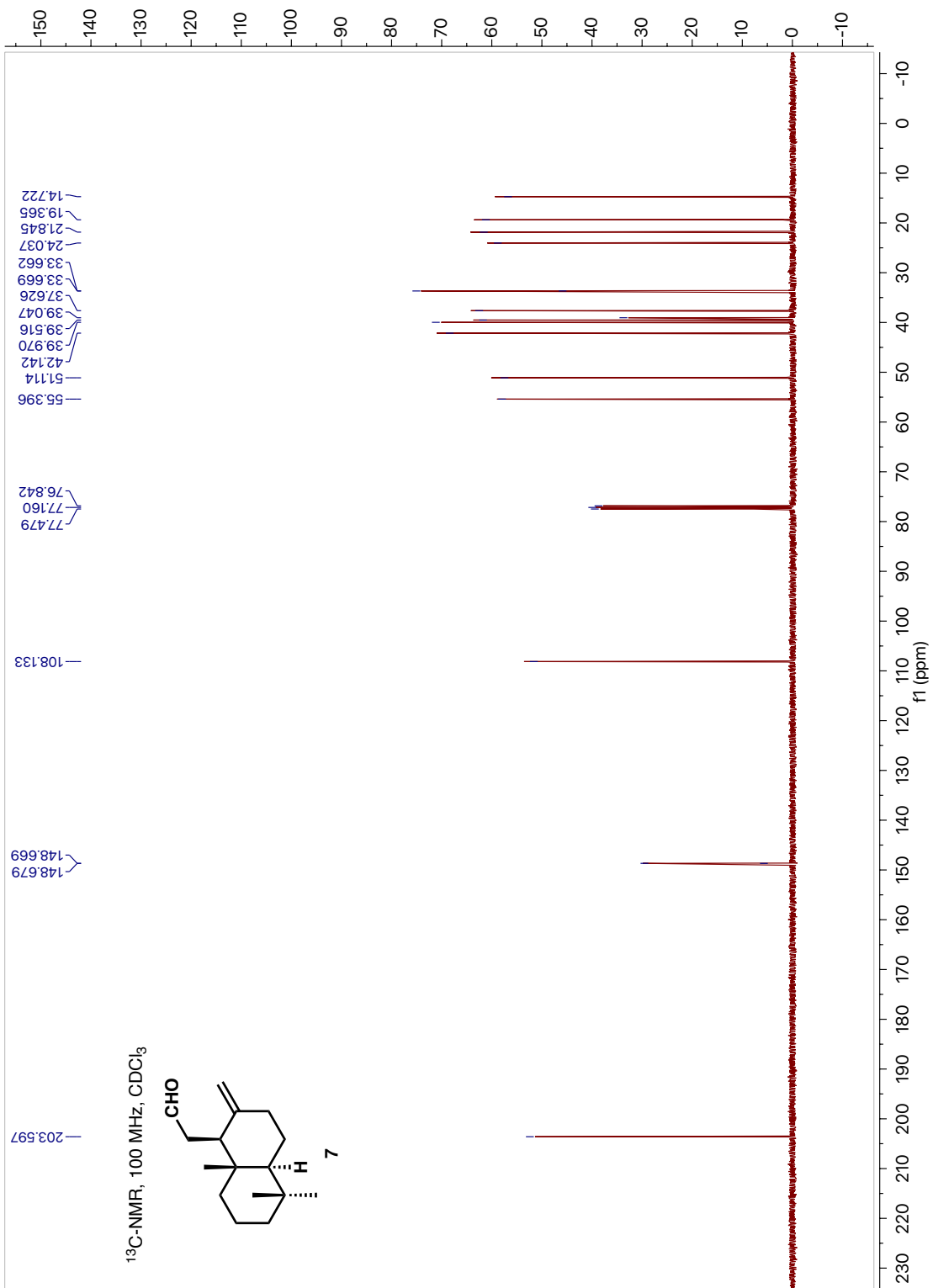
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.63–9.62 (m, 1H), 4.81 (s, 1H), 4.38 (s, 1H), 2.48–2.33 (m, 4H), 2.09 (dt, 1H, *J* = 13.2, 5.2 Hz), 1.79–1.05 (m, 9H), 0.89 (s, 3H), 0.82 (s, 3H), 0.70 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 203.6, 148.7, 108.1, 55.4, 51.1, 42.1, 40.0, 39.5, 39.1, 37.6, 33.7, 33.7, 24.0, 21.9, 19.4, 14.7.

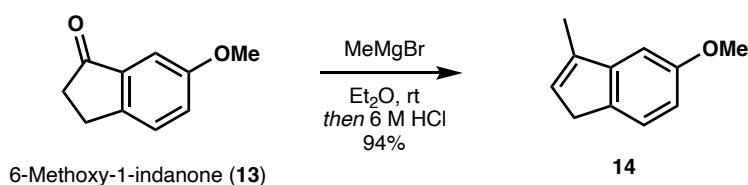
**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>26</sub>O 234.1984, found 234.1985.

The data for **12** were identical to those reported in the literature<sup>S3</sup>.





5-Methoxy-3-methyl-1*H*-indene (**14**)<sup>S4</sup>



Under Ar atmosphere, a solution of **13** (811 mg, 5.00 mmol) in Et<sub>2</sub>O (50.0 mL) was treated with MeMgBr (5.00 mL, 15.0 mmol, 3 M in Et<sub>2</sub>O) at 0 °C. After stirring for 20 min at room temperature, the reaction mixture was quenched with 6 M HCl *aq.* at 0 °C, and the resulting mixture was stirring for 1 h at room temperature. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 100:1) to afford **14** (756 mg, 94%) as a white solid.

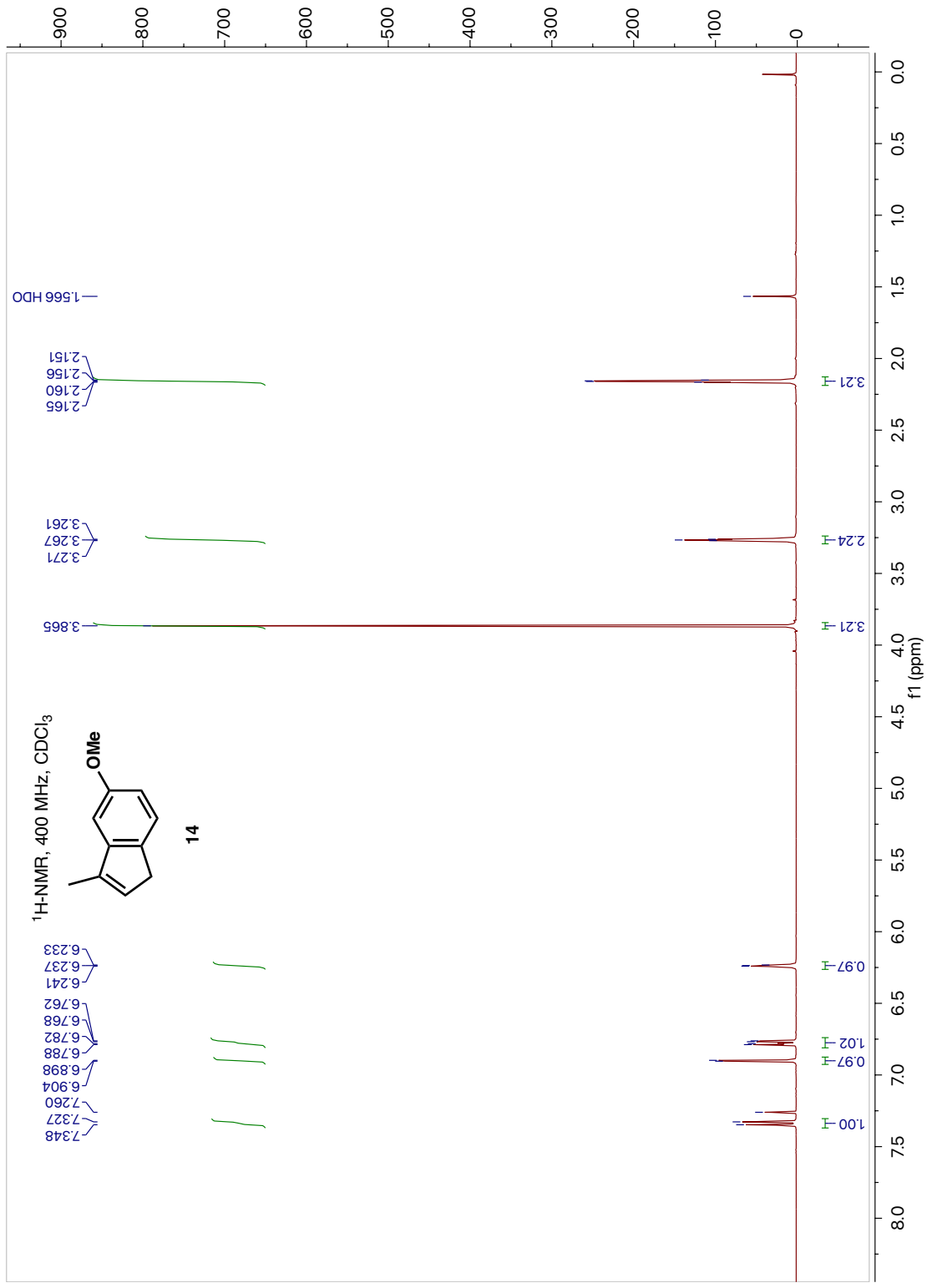
**Rf**: 0.73 (Hexanes/EtOAc = 4 : 1, anisaldehyde)

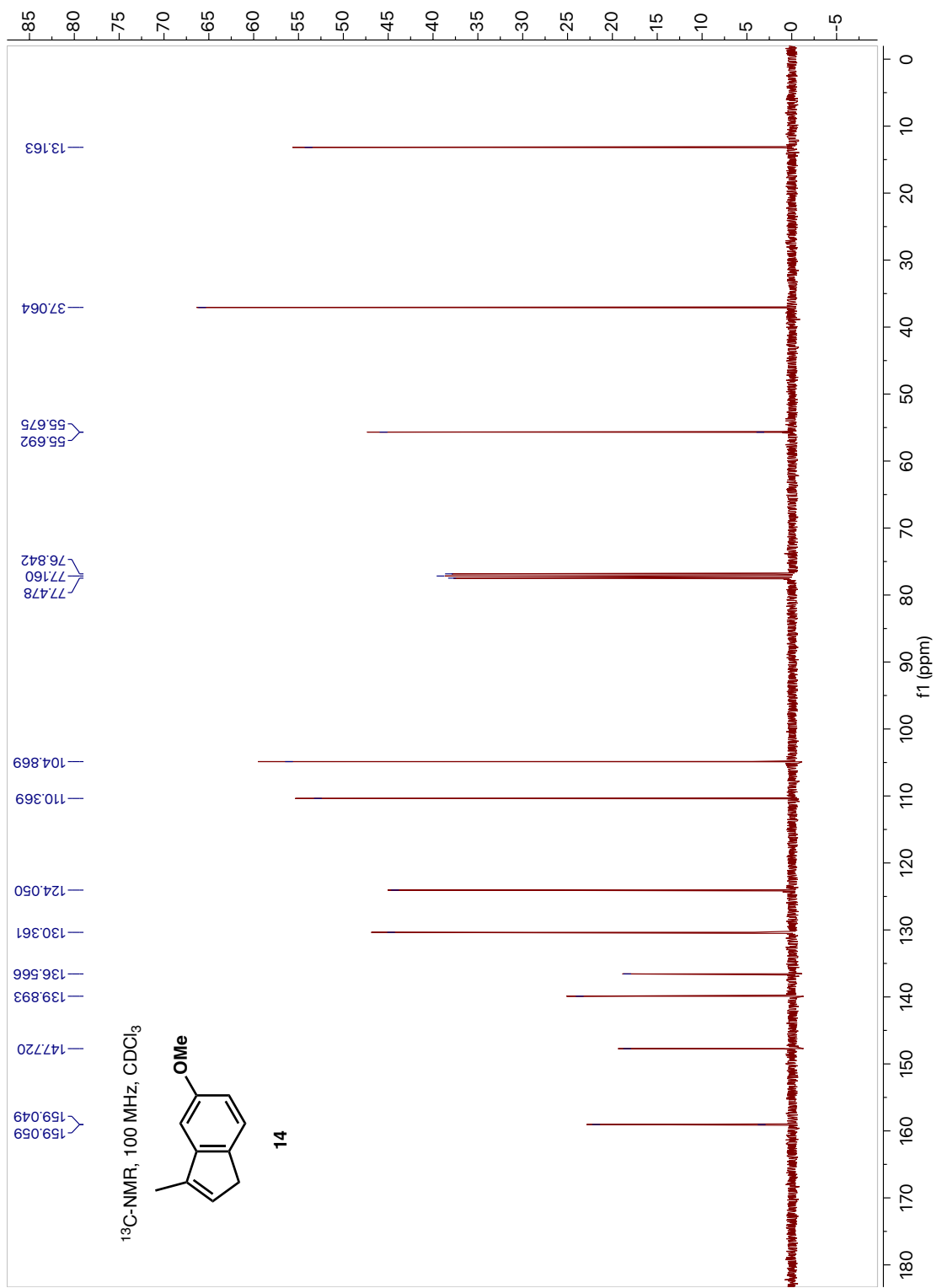
**IR (KBr thin film)** 3066, 2997, 2938, 2832, 1608, 1578, 1473, 1258, 1220 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.34 (d, 1H, *J* = 8.4 Hz), 6.90 (d, 1H, *J* = 2.4 Hz), 6.78 (dd, 1H, *J* = 8.4, 2.4 Hz), 6.24 (d, 1H, *J* = 2.4 Hz), 3.87 (s, 3H), 3.27 (t, 2H, *J* = 2.4 Hz), 2.17–2.15 (m, 3H).

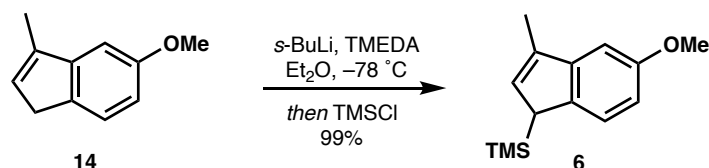
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 159.1, 147.7, 139.9, 136.6, 130.4, 124.1, 110.4, 104.9, 55.7, 37.1, 13.2.

**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>11</sub>H<sub>12</sub>O 160.0888, found 160.0867.





(5-Methoxy-3-methyl-1*H*-inden-1-yl)trimethylsilane (**6**)



Under Ar atmosphere, a solution of **14** (1.28 g, 7.89 mmol) in Et<sub>2</sub>O (40.0 mL) was treated with TMEDA (3.53 mL, 27.3 mmol) and *s*-BuLi (24.9 mL, 23.7 mmol, 0.95 M in cyclohexane, *n*-hexane) at -78 °C. After stirring for 2 h at -78 °C, TMSCl (7.01 mL, 55.2 mmol) was added to the solution. After stirring for 1 h at -78 °C, the reaction mixture was quenched with H<sub>2</sub>O. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 300:1) to afford **6** (1.82 g, 99%) as a yellow solid.

**Rf**: 0.74 (Hexanes/EtOAc = 4 : 1, anisaldehyde)

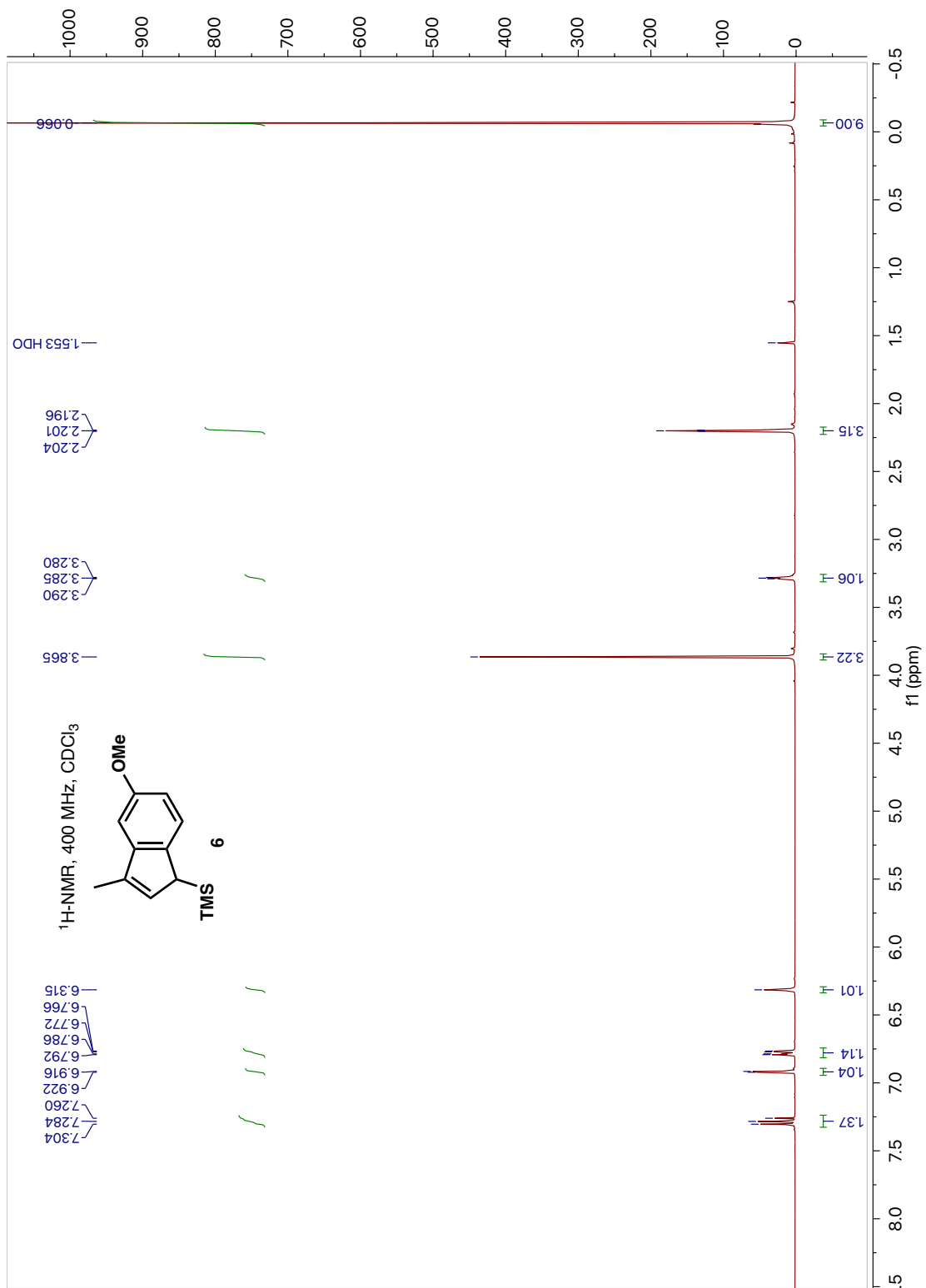
**IR (KBr thin film)** 2955, 2830, 1610, 1469, 1247, 1213 cm<sup>-1</sup>.

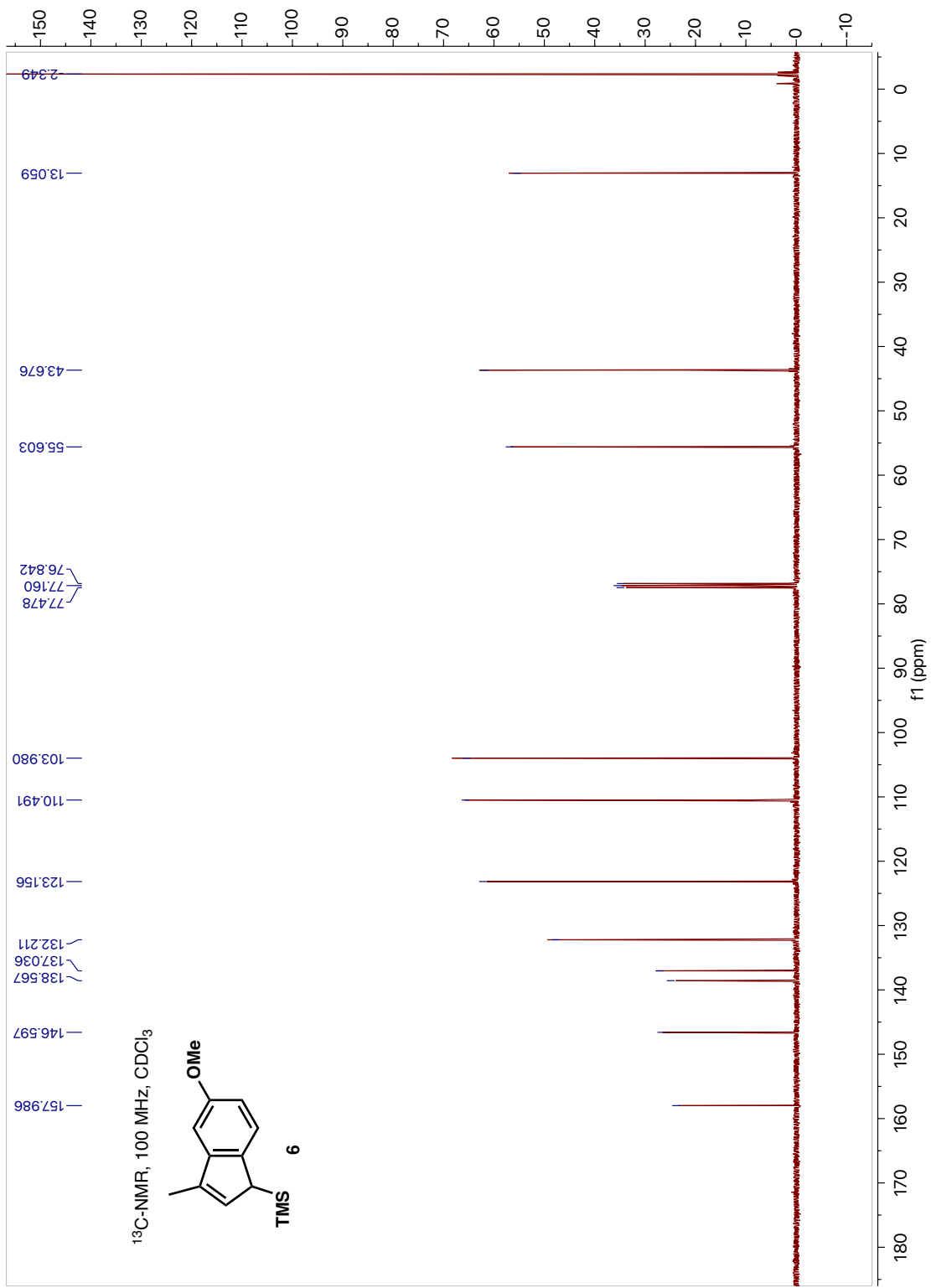
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.30 (d, 1H, *J* = 8.0 Hz), 6.92 (d, 1H, *J* = 2.4 Hz), 6.78 (dd, 1H, *J* = 8.0, 2.4 Hz), 6.32 (s, 1H), 3.87 (s, 3H), 3.29–3.26 (m, 1H), 2.20–2.19 (m, 3H), -0.07 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 158.0, 146.6, 138.6, 137.0, 132.2, 123.2, 110.5, 104.0, 55.6, 43.7, 13.1, -2.48.

**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>20</sub>OSi 232.1283, found 232.1272.

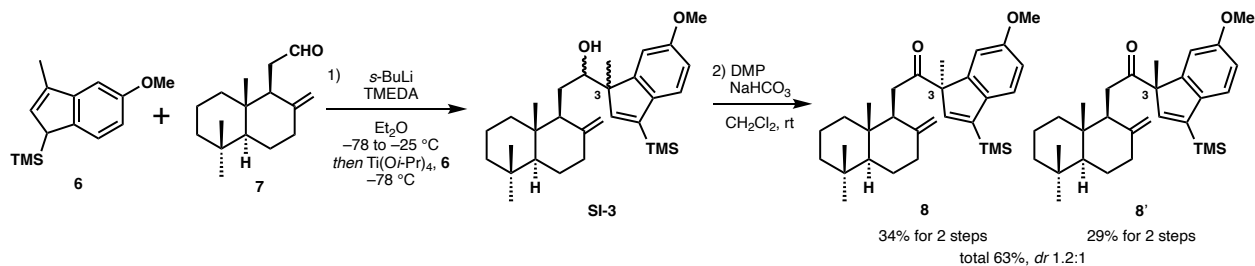






1-((*R*)-6-Methoxy-1-methyl-3-(trimethylsilyl)-1*H*-inden-1-yl)-2-((1*S*,4*aS*,8*aS*)-5,5,8*a*-trimethyl-2-methylenedecahydronaphthalen-1-yl)ethan-1-one (**8**)

1-((*S*)-6-Methoxy-1-methyl-3-(trimethylsilyl)-1*H*-inden-1-yl)-2-((1*S*,4*aS*,8*aS*)-5,5,8*a*-trimethyl-2-methylenedecahydronaphthalen-1-yl)ethan-1-one (**8'**)



Under Ar atmosphere, a solution of **6** (789 mg, 3.39 mmol) in Et<sub>2</sub>O (25.2 mL) was treated with TMEDA (1.52 mL, 4.50 mmol) and *s*-BuLi (8.36 mL, 10.2 mmol, 1.22 M in cyclohexane, *n*-hexane) at -78 °C. After stirring for 2 h at -78 °C, a solution of Ti(O*i*-Pr)<sub>4</sub> (6.02 mL, 20.3 mmol) and **9** (2.38 g, 10.2 mmol) in Et<sub>2</sub>O (8.5 mL) was added, and the resulting mixture was stirred for 2 h at -78 °C. The reaction mixture was quenched with MeOH and 2 M HCl *aq.* After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by flash silica gel column chromatography (Hexanes/EtOAc = 40:1) to afford a crude **SI-3**.

A solution of the crude **SI-3** in CH<sub>2</sub>Cl<sub>2</sub> (23.1 mL) was treated with DMP (1.96 g, 4.62 mmol) and NaHCO<sub>3</sub> (358 mg, 4.62 mmol) at room temperature. After stirring for 0.5 h at room temperature, the reaction mixture was quenched with *sat.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.* and *sat.* NaHCO<sub>3</sub> *aq.*. After extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 80:1) to afford a mixture of **8** and **8'** (987 mg, *dr* = 1.2:1, 63% for 2 steps) as a colorless oil.

A sole compound of **8** and **8'** derived by the purification of a part of the mixture of **8** and **8'** by PTLC (3 times).

### Data for **8**

**Rf**: 0.57 (Hexanes/EtOAc = 5 : 1, anisaldehyde)

$[\alpha]_D^{25}$  -162.61 (*c* 1.0, CHCl<sub>3</sub>).

**IR (KBr thin film)** 2930, 2869, 2843, 1710, 1643, 1473, 1286, 1249, 1213  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.36 (d, 1H,  $J = 8.4$  Hz), 6.88 (dd, 1H,  $J = 8.4, 2.4$  Hz), 6.83 (d, 1H,  $J = 2.4$  Hz), 6.38 (s, 1H), 4.65 (s, 1H), 4.25 (s, 1H), 3.81 (s, 3H), 2.30–1.92 (m, 5H), 1.68–0.78 (m, 9H), 1.43 (s, 3H), 0.83 (s, 3H), 0.72 (s, 3H), 0.40 (s, 3H), 0.31 (s, 9H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  208.8, 158.6, 150.8, 149.7, 148.1, 146.2, 141.0, 123.2, 113.2, 109.2, 106.0, 68.7, 55.8, 55.2, 50.6, 42.1, 38.9, 38.8, 37.8, 33.6, 33.6, 33.5, 24.2, 21.8, 19.3, 18.7, 14.5, -1.2.

**HRMS (EI)**  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{44}\text{O}_2\text{Si}$  464.3111, found 464.3118.

### Data for 8'

**Rf:** 0.57 (Hexanes/EtOAc = 5 : 1, anisaldehyde)

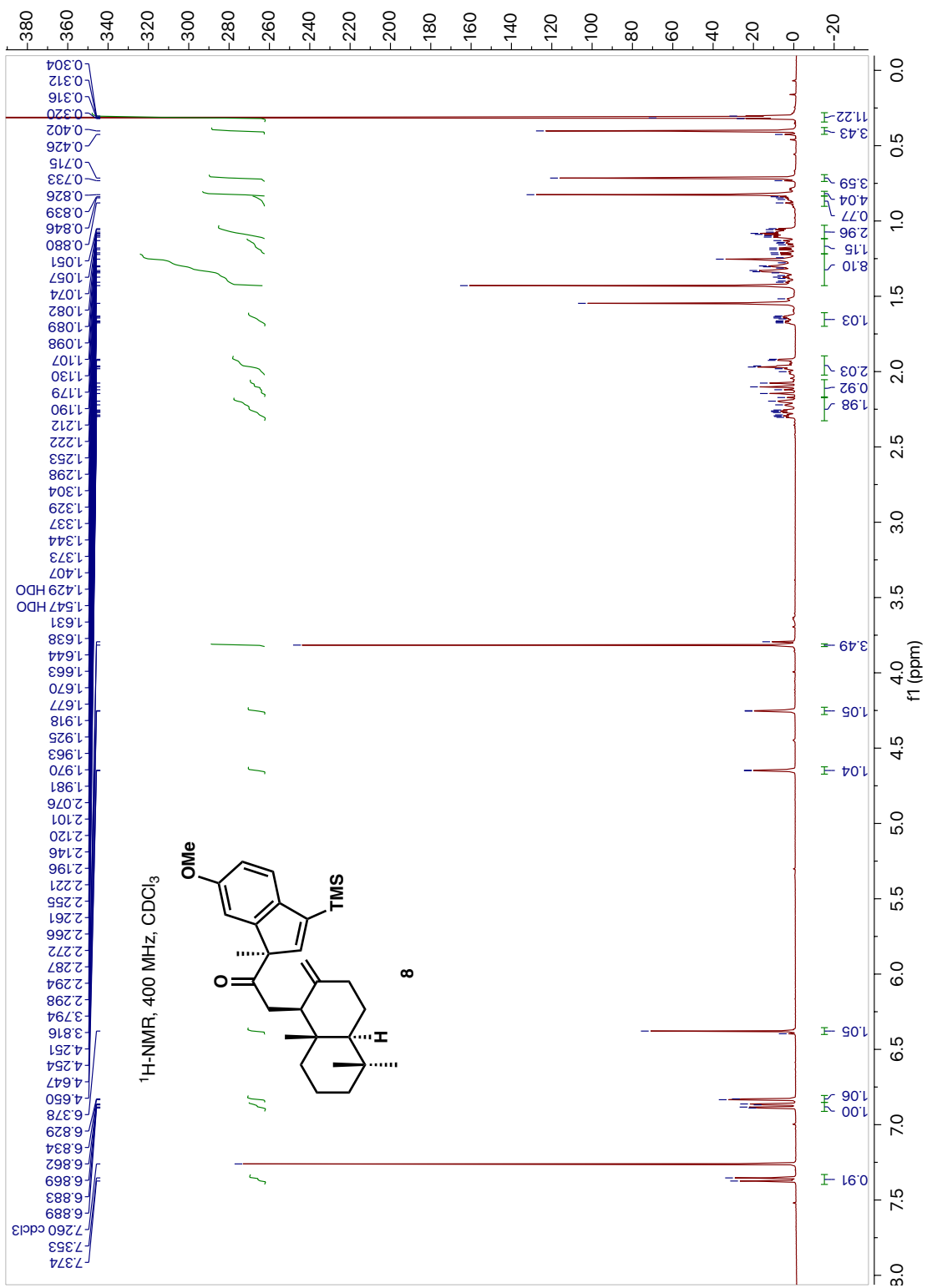
$[\alpha]_{\text{D}}^{25} +157.57$  ( $c$  1.0,  $\text{CHCl}_3$ ).

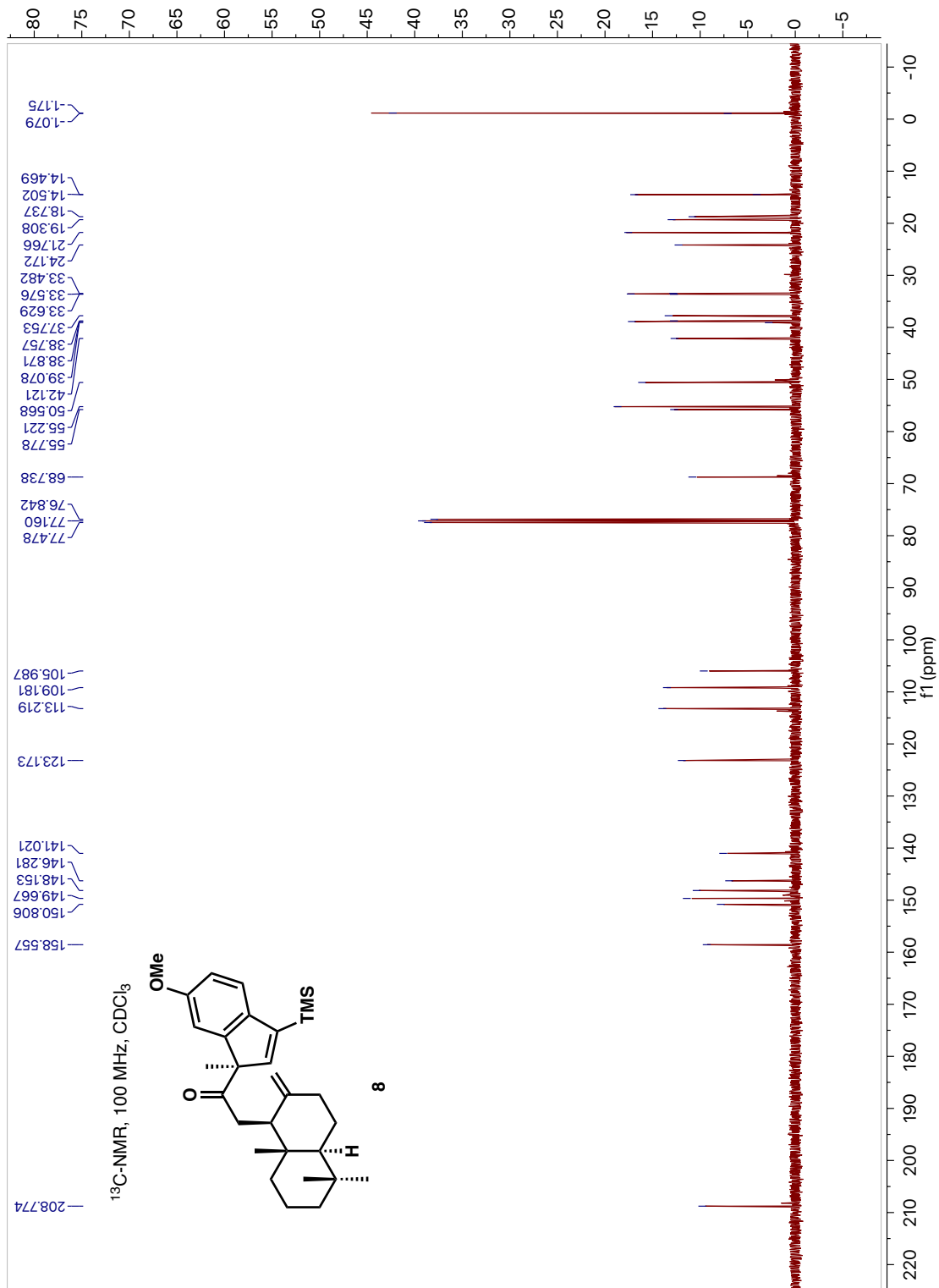
**IR (KBr thin film)** 2952, 2870, 2844, 1710, 1644, 1473, 1285, 1249, 1214  $\text{cm}^{-1}$ .

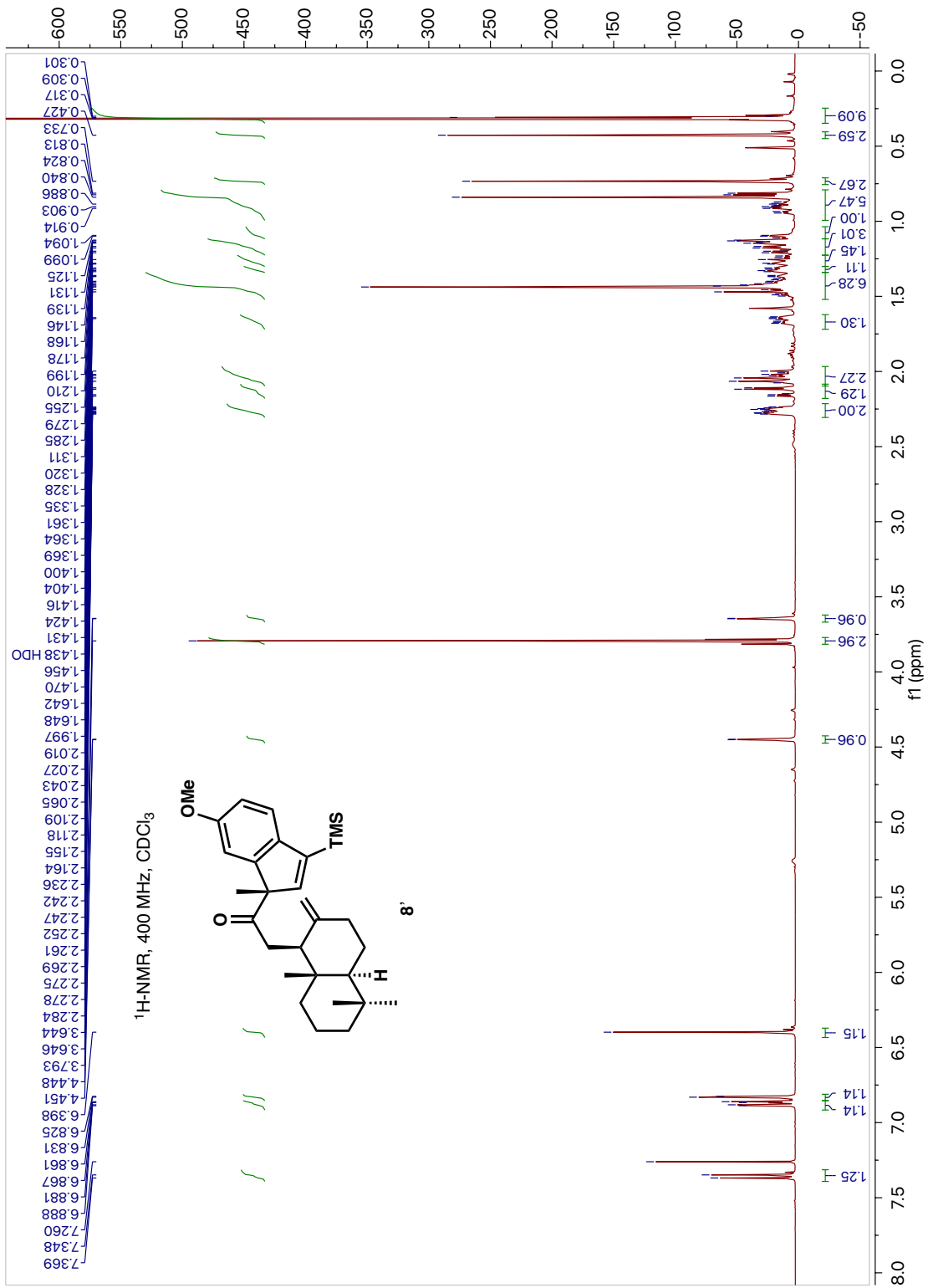
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.36 (d, 1H,  $J = 8.0$  Hz), 6.87 (dd, 1H,  $J = 8.0, 2.4$  Hz), 6.83 (d, 1H,  $J = 2.4$  Hz), 6.40 (s, 1H), 4.45 (s, 1H), 3.79 (s, 3H), 3.65 (s, 1H), 2.28–1.97 (m, 5H), 1.68–0.81 (m, 9H), 1.44 (s, 3H), 0.84 (s, 3H), 0.73 (s, 3H), 0.43 (s, 3H), 0.32 (s, 9H).

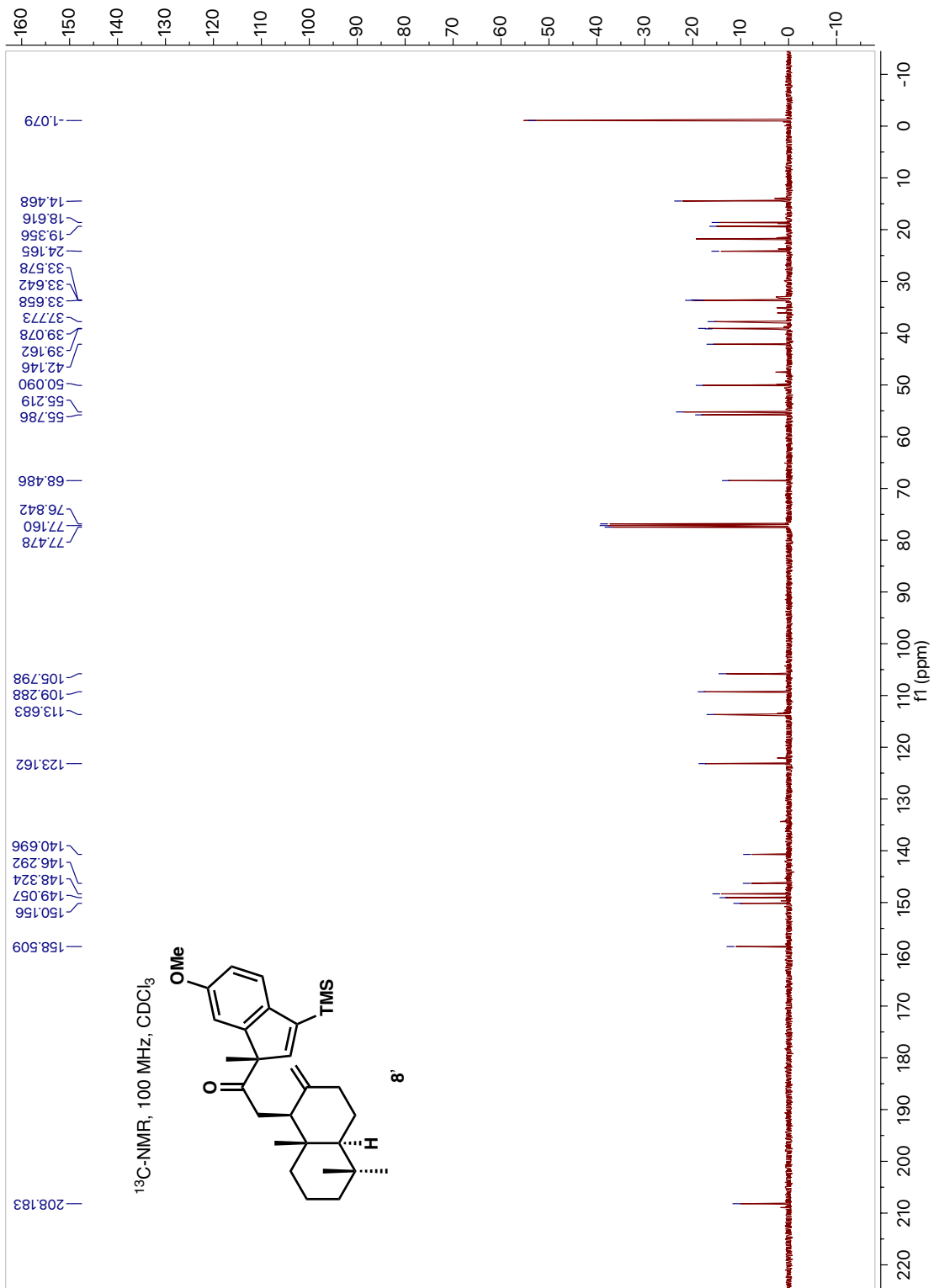
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  208.1, 158.5, 150.2, 149.6, 148.3, 146.3, 140.7, 123.2, 113.7, 109.3, 105.8, 68.5, 55.8, 55.2, 50.1, 42.1, 39.2, 39.1, 37.8, 33.7, 33.6, 33.6, 24.2, 21.8, 19.4, 18.6, 14.5, -1.1.

**HRMS (EI)**  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{44}\text{O}_2\text{Si}$  464.3111, found 464.3116.

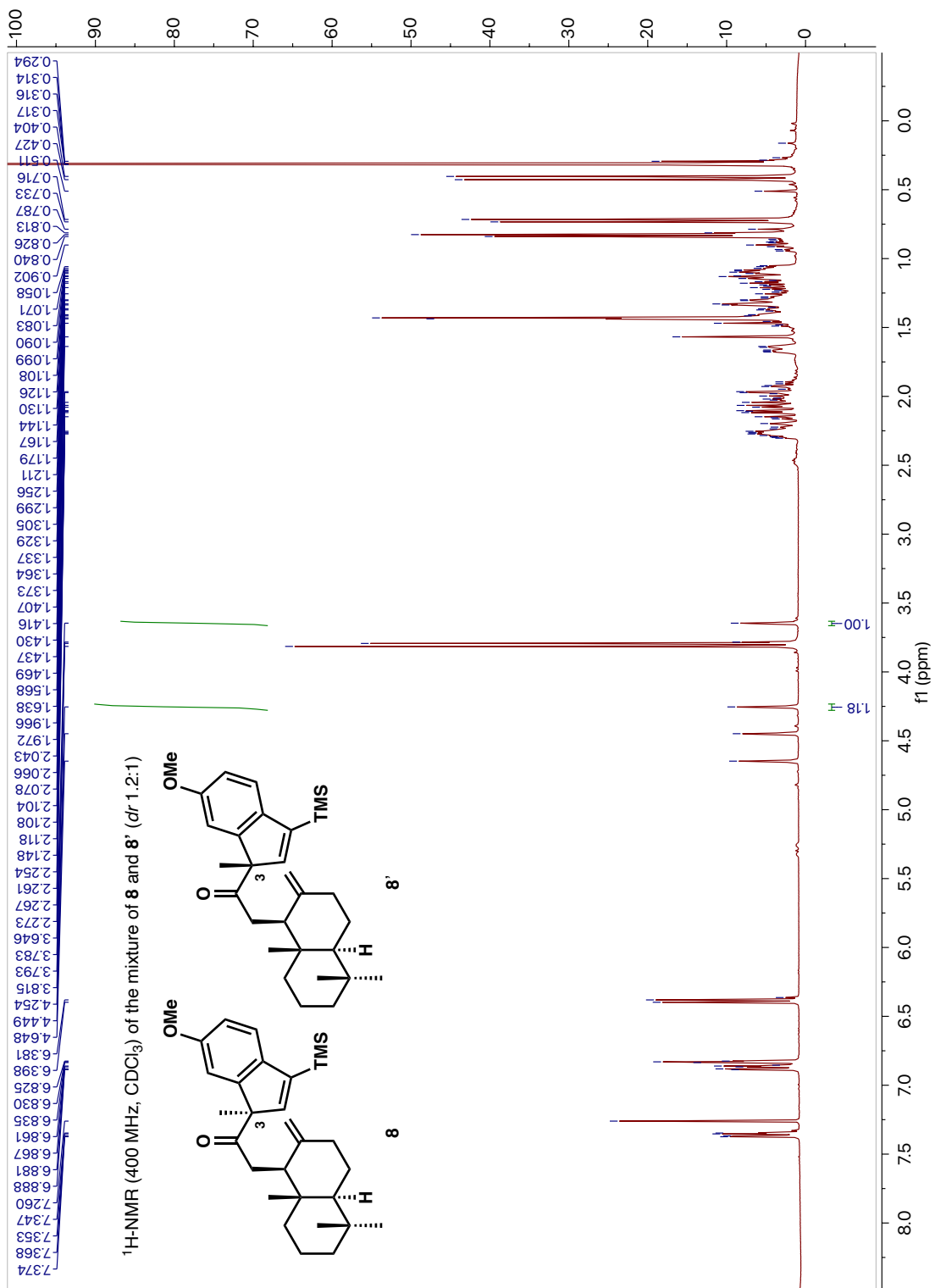




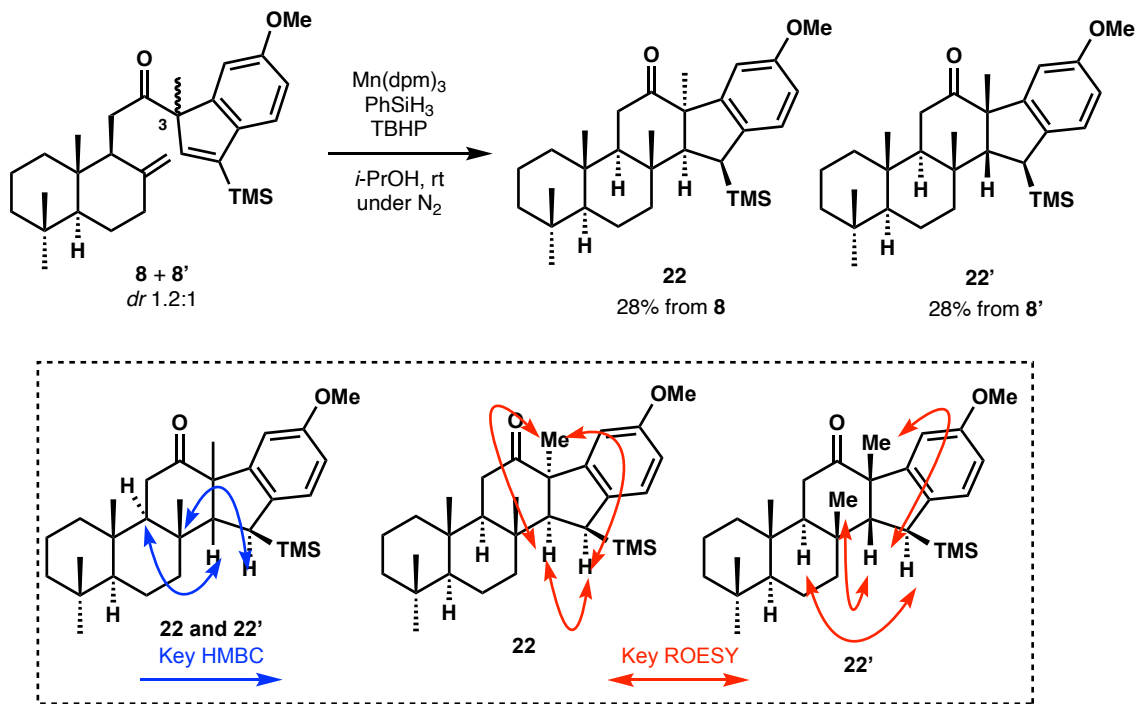








(2a*S*,6a*S*,6b*R*,8a*R*,13*S*,13a*S*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-13-(trimethylsilyl)-1,2,2a,3,4,5,6,6a,6b,7,8a,13,13a,13b-tetradecahydro-8*H*-indeno[2,1-*a*]phenanthren-8-one (**22**)  
 (2a*S*,6a*S*,6b*R*,8a*S*,13*S*,13a*R*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-13-(trimethylsilyl)-1,2,2a,3,4,5,6,6a,6b,7,8a,13,13a,13b-tetradecahydro-8*H*-indeno[2,1-*a*]phenanthren-8-one (**22'**)



A solution of a mixture of **8** and **8'** (20.0 mg, 0.0431 mmol, *dr* 1.2 : 1 (**8**: 10.9 mg (0.0235 mmol), **8'**: 9.1 mg (0.0196 mmol))) in *i*-PrOH (0.4 mL) was treated with Mn(dpm)<sub>3</sub> (8.6 mg, 0.0137 mmol), PhSiH<sub>3</sub> (15.9 μL, 0.129 mmol) and TBHP (11.7 μL, 0.0645 mmol, 5.5 M in decane) at room temperature. After stirring for 18 h at room temperature, the reaction mixture was concentrated *in vacuo*. The residue was purified by PTLC (Hexanes/EtOAc = 5:1) to afford **22** (3.1 mg, 28% from **8**) and **22'** (2.6 mg, 28% from **8'**) as colorless liquids.

#### Data for **22**

**Rf**: 0.43 (Hexanes/EtOAc = 5 : 1, phosphomolybdic acid)

$[\alpha]_D^{25}$  +22.08 (*c* 0.5, CHCl<sub>3</sub>).

**IR (KBr thin film)** 2957, 2932, 1693, 1479, 1279, 1252 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.08 (dd, 1H, *J* = 8.8, 1.6 Hz), 6.67–6.64 (m, 2H), 3.74 (s, 3H),

2.73 (dd, 1H,  $J = 5.6, 1.2$  Hz), 2.42 (dd, 1H,  $J = 17.2, 3.2$  Hz), 2.30–2.22 (m, 1H), 2.29 (d, 1H,  $J = 5.6$  Hz), 2.11–2.06 (m, 1H), 1.64–0.81 (m, 11H), 1.38 (s, 3H, CH<sub>3</sub>), 0.88 (s, 3H, CH<sub>3</sub>), 0.79 (s, 3H, CH<sub>3</sub>), 0.73 (s, 3H), 0.37 (s, 3H), 0.34 (s, 9H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  214.1, 158.3, 149.3, 137.1, 123.8, 112.5, 108.0, 70.8, 59.7, 56.3, 55.5, 54.2, 44.0, 41.9, 39.8, 38.9, 37.8, 36.2, 35.7, 33.5, 33.4, 23.9, 21.7, 18.6, 18.4, 16.5, 15.5, -7.92.

HRMS (EI) [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>46</sub>O<sub>2</sub>Si 466.3267, found 466.3257.

#### Data for 22'

Rf: 0.43 (Hexanes/EtOAc = 5 : 1, phosphomolybdic acid)

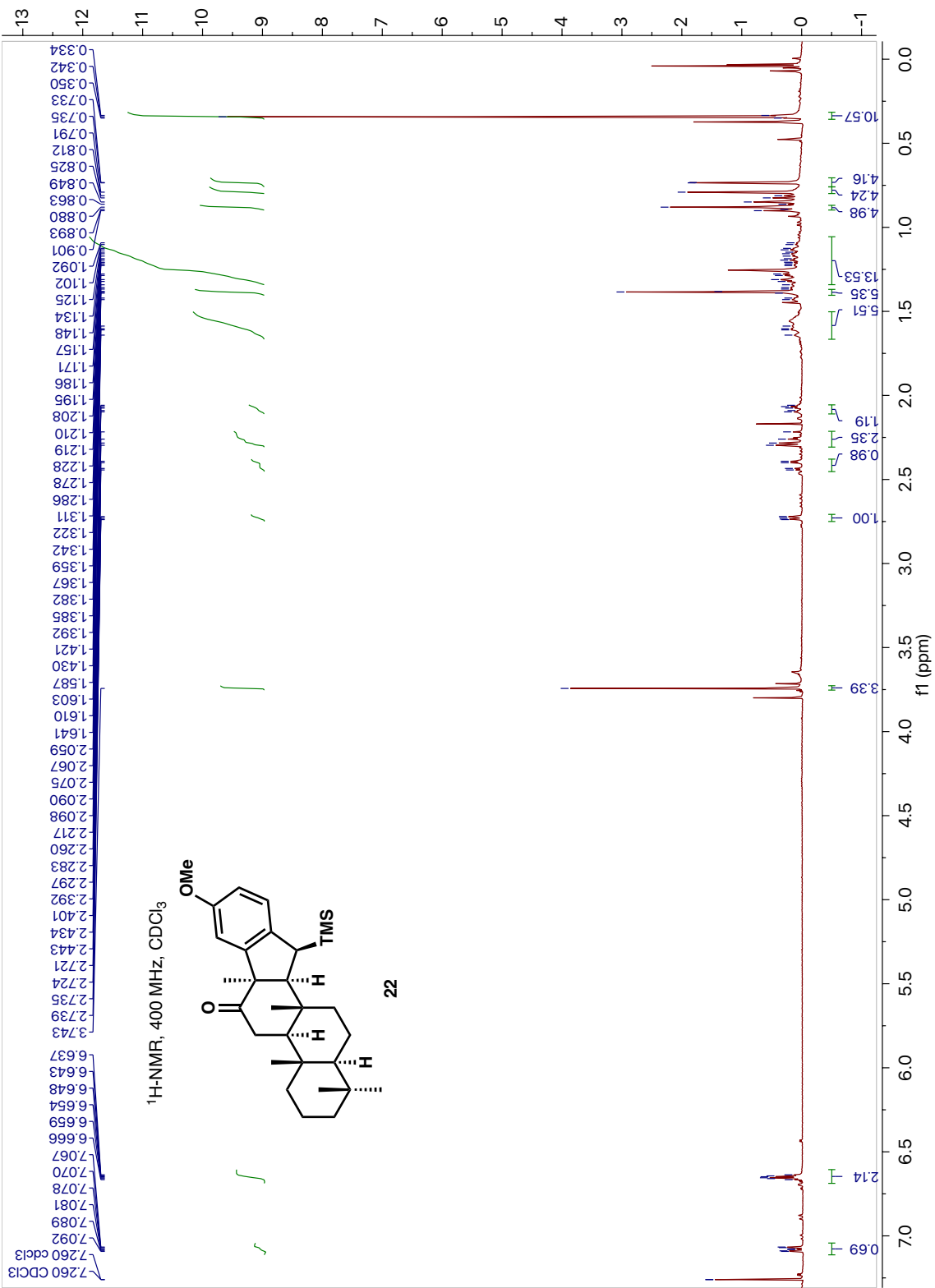
$[\alpha]_D^{24}$  -53.25 ( $c$  0.5, CHCl<sub>3</sub>).

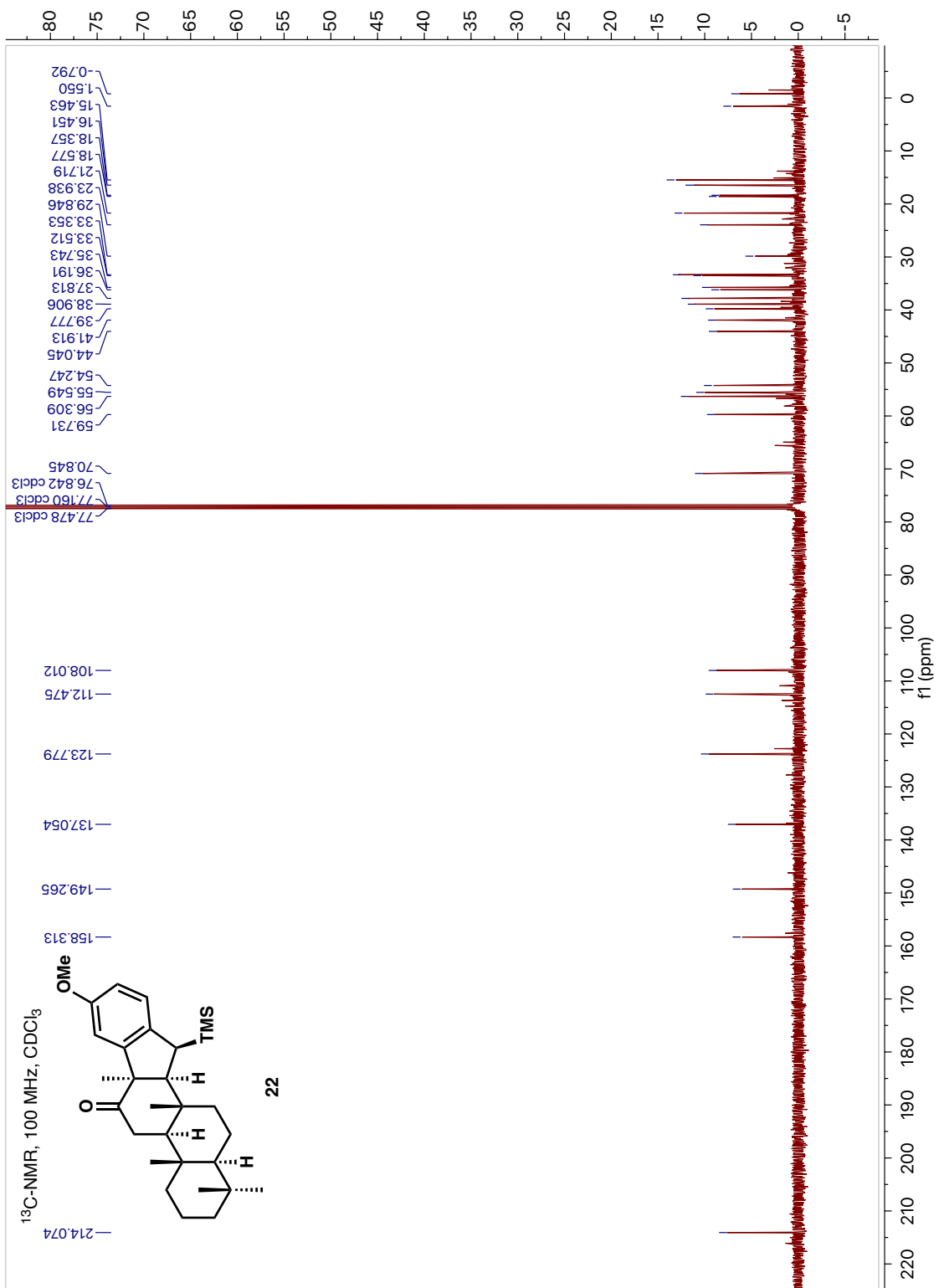
IR (KBr thin film) 2951, 2928, 1695, 1492, 1466, 1273, 1248 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.01 (d, 1H,  $J = 8.8$  Hz), 6.71 (dd, 1H,  $J = 8.8, 2.4$  Hz), 6.43 (d, 1H,  $J = 2.4$  Hz), 3.74 (s, 3H), 2.77 (d, 1H,  $J = 4.4$  Hz), 2.07 (d, 1H,  $J = 4.4$  Hz), 2.09–1.96 (m, 2H), 1.68 (t, 1H,  $J = 9.6$  Hz), 1.58–0.59 (m, 11H), 1.44 (s, 3H), 0.93 (s, 3H), 0.90 (s, 3H), 0.84 (s, 3H), 0.81 (s, 3H), 0.03 (s, 9H).

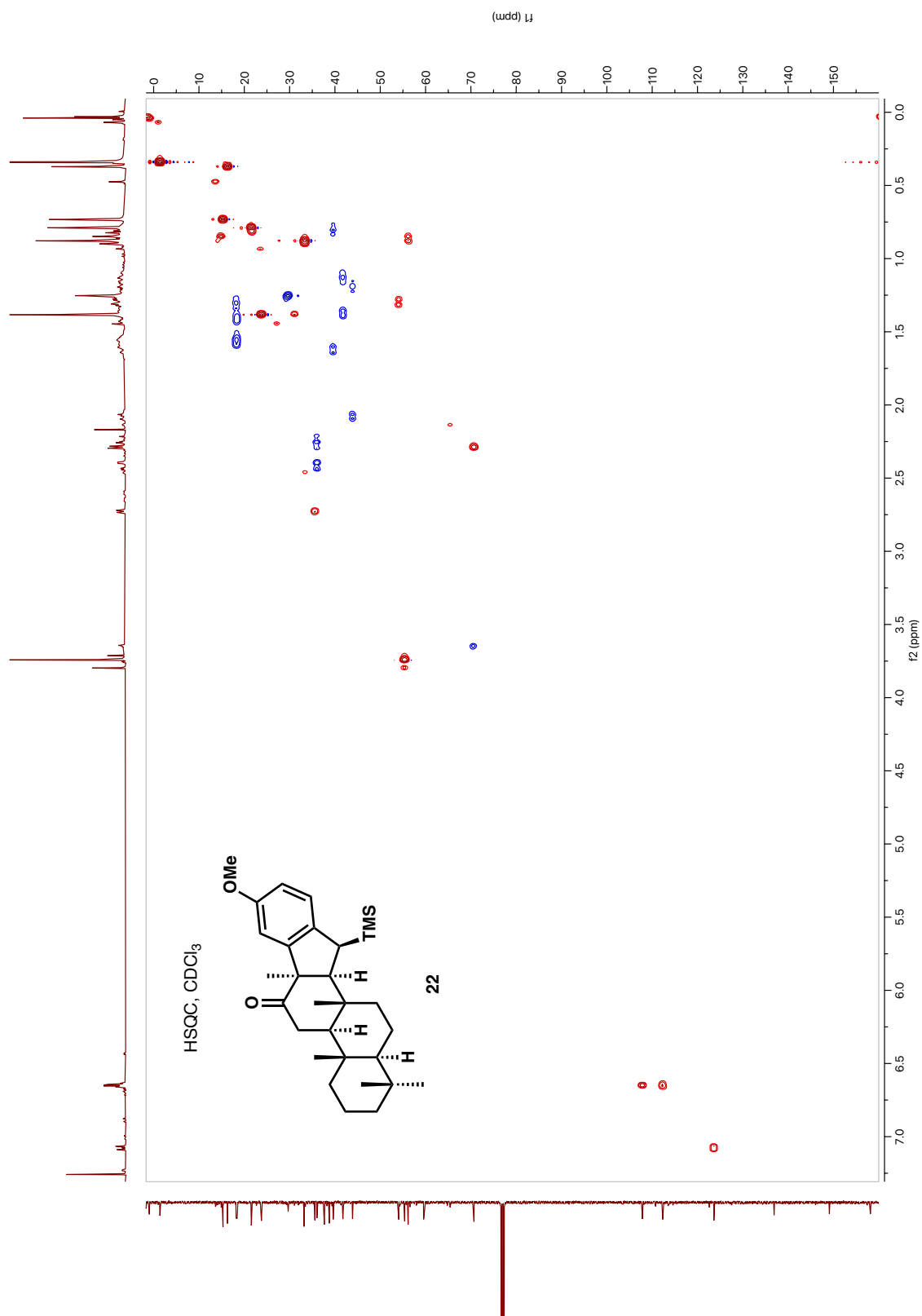
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  215.4, 158.3, 145.6, 139.0, 124.0, 114.7, 108.3, 64.9, 60.5, 55.9, 55.5, 47.4, 41.9, 39.6, 38.9, 38.6, 37.6, 36.3, 35.4, 33.5, 33.2, 27.3, 23.7, 21.9, 18.5, 18.3, 15.0, -1.51.

HRMS (EI) [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>46</sub>O<sub>2</sub>Si 466.3267, found 466.3263.

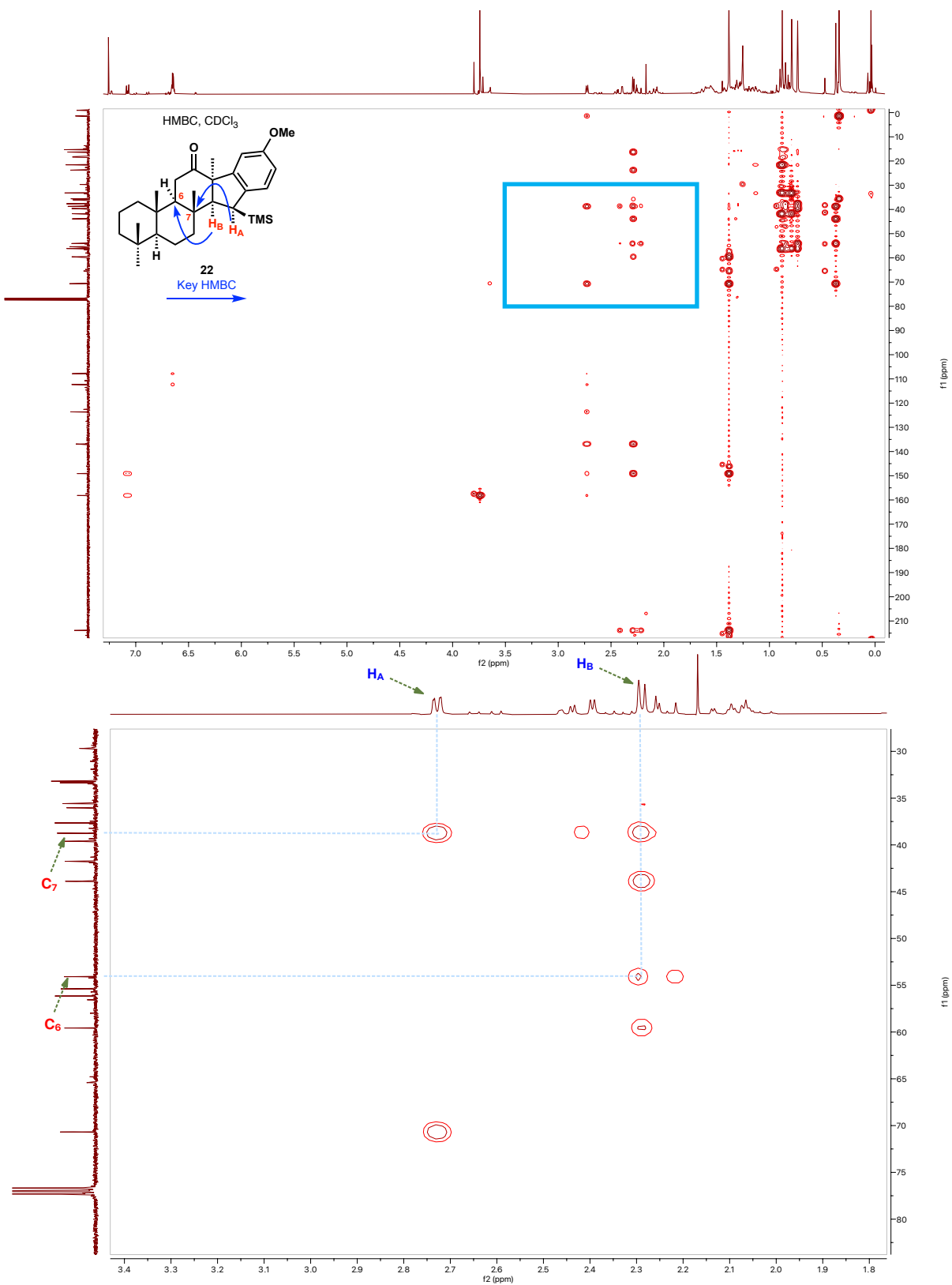




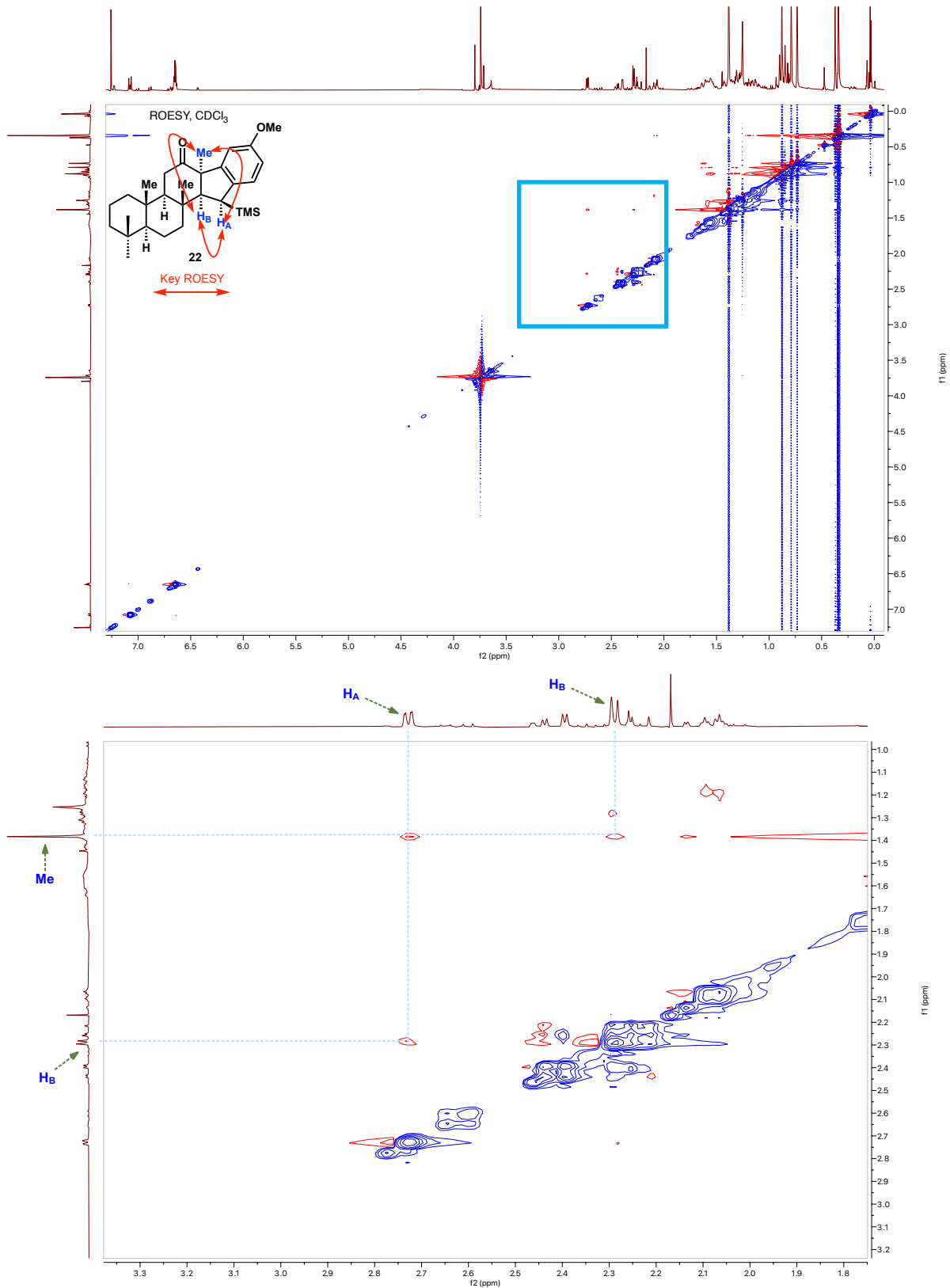
# HSQC spectra of 22



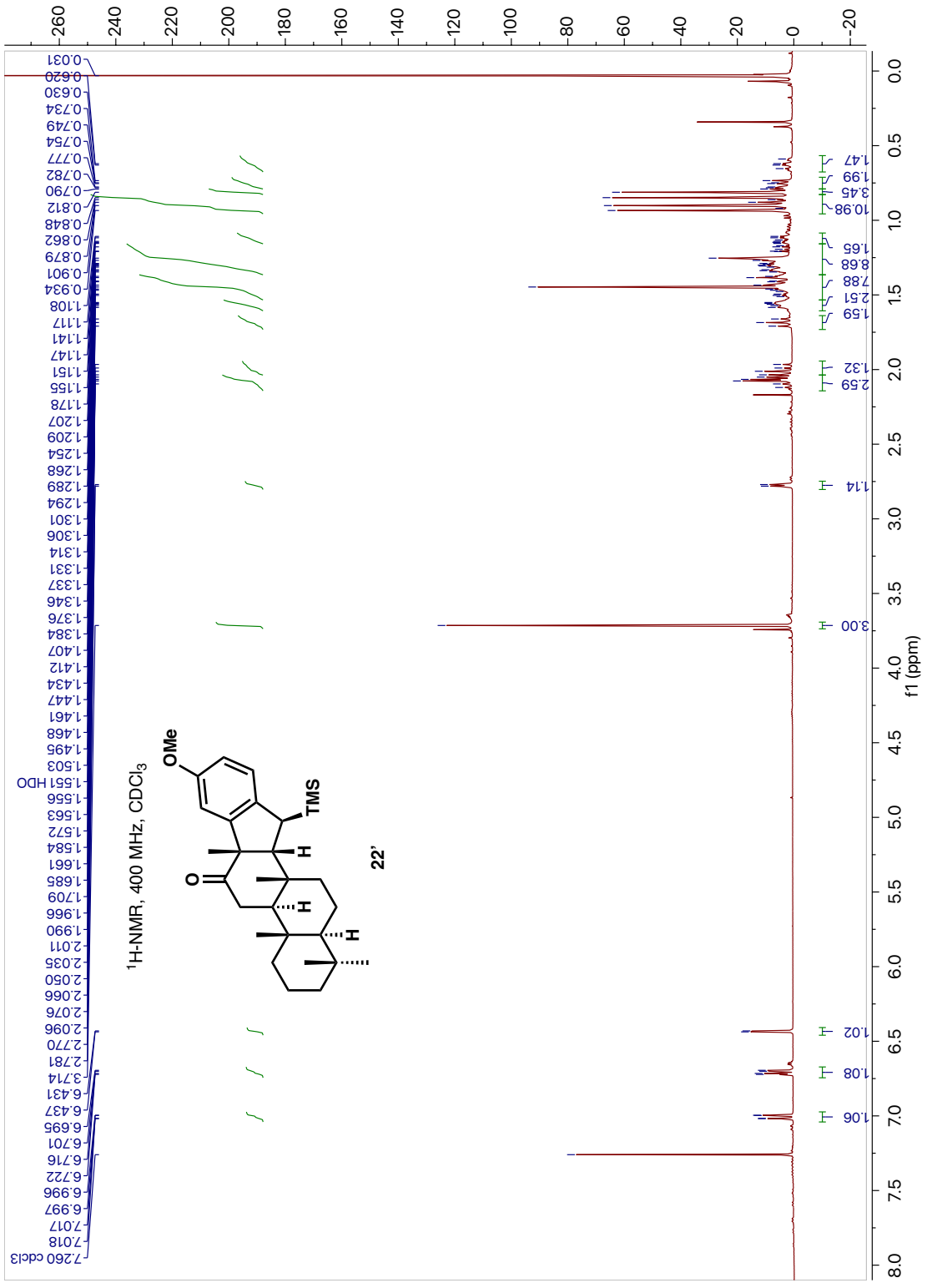
# HMBC spectra of 22

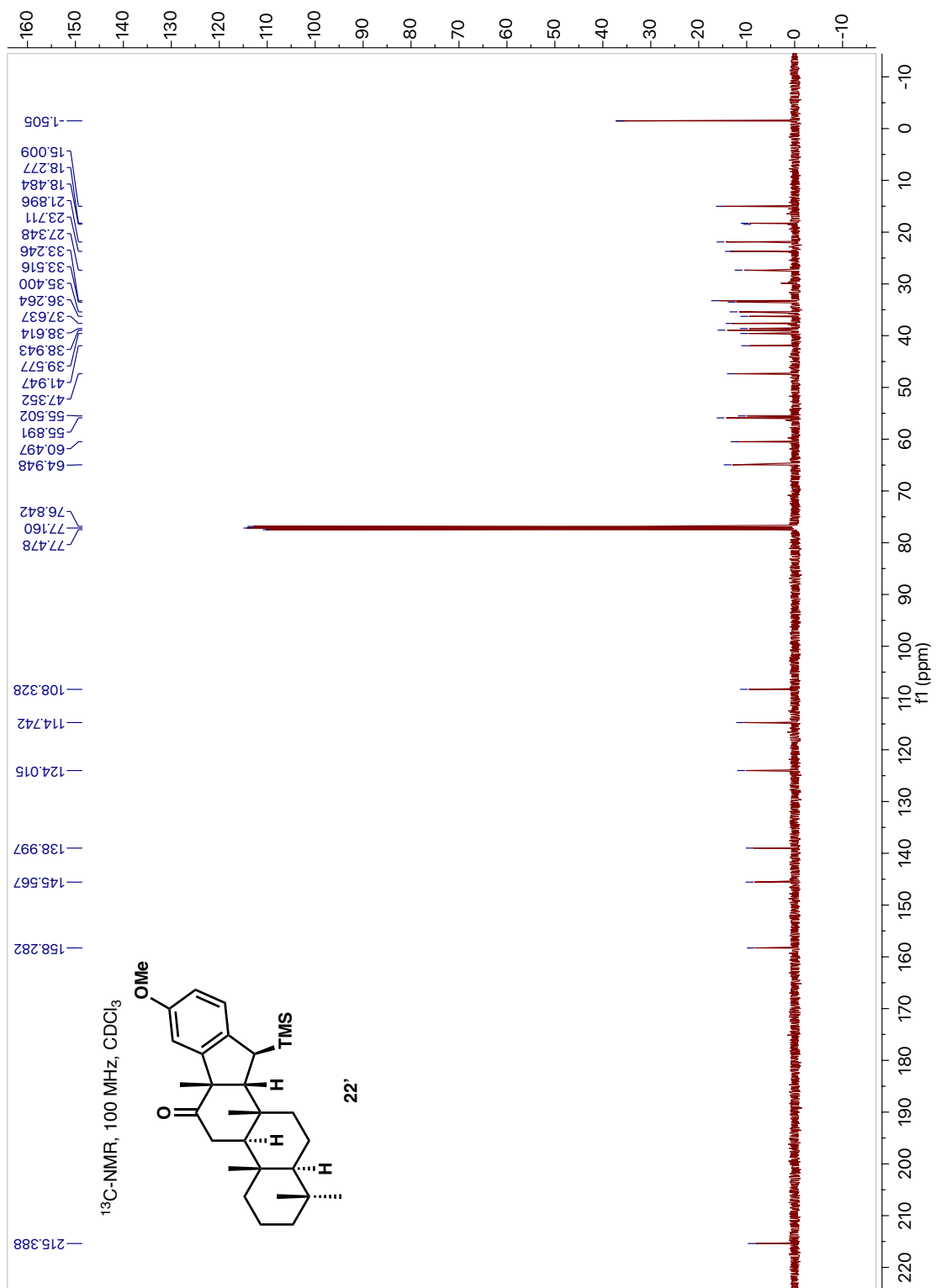


# ROESY spectra of 22

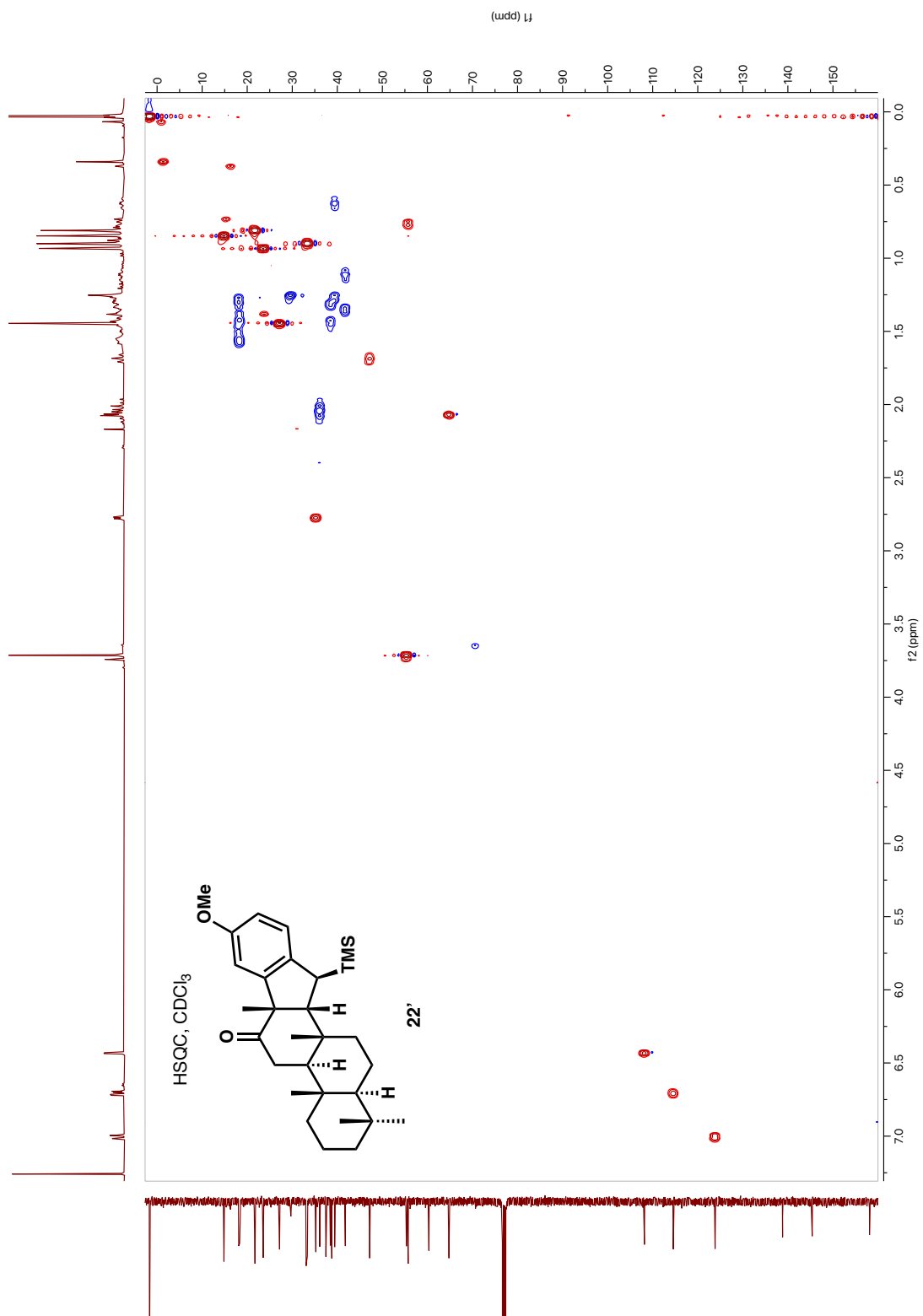




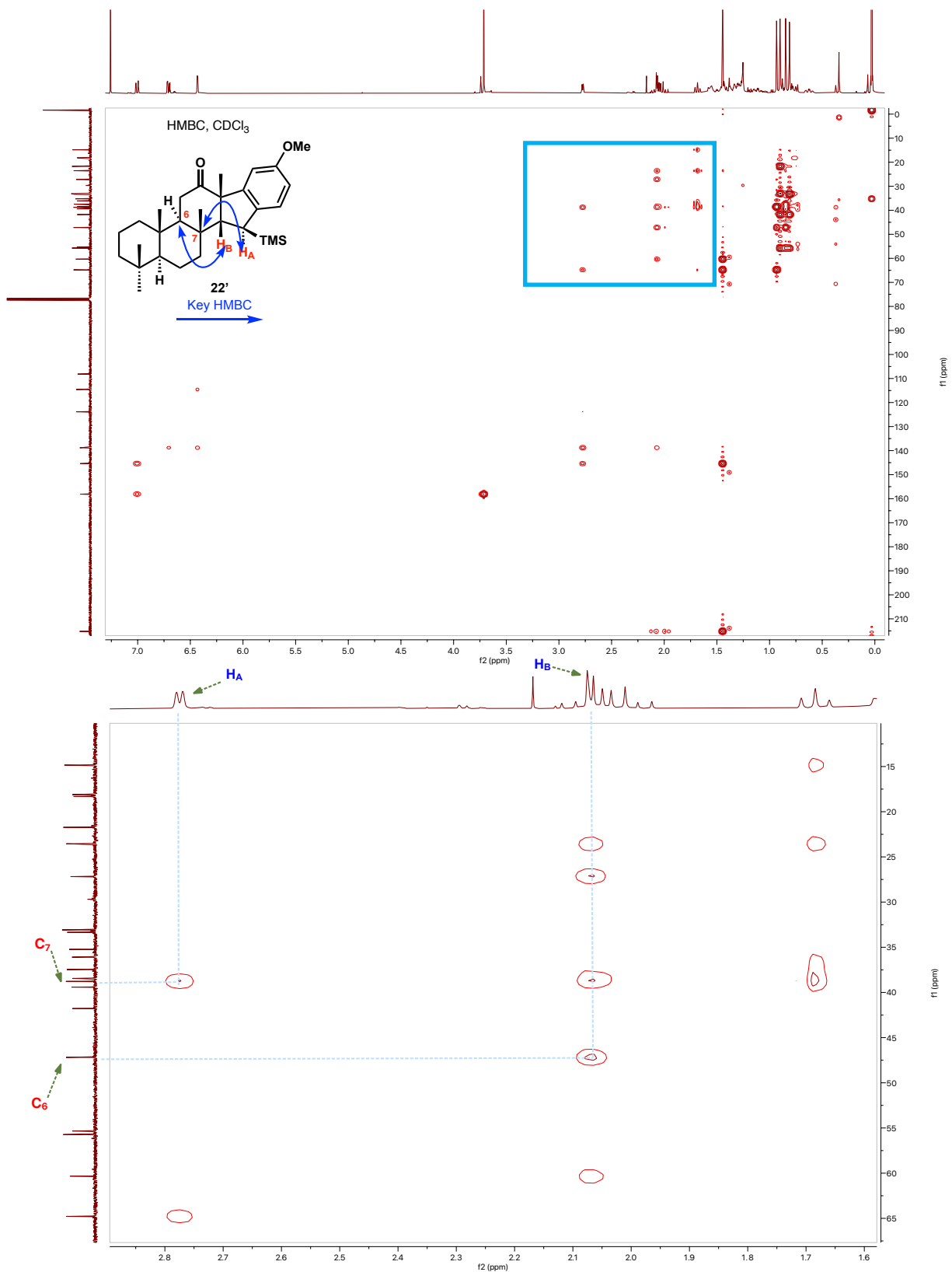




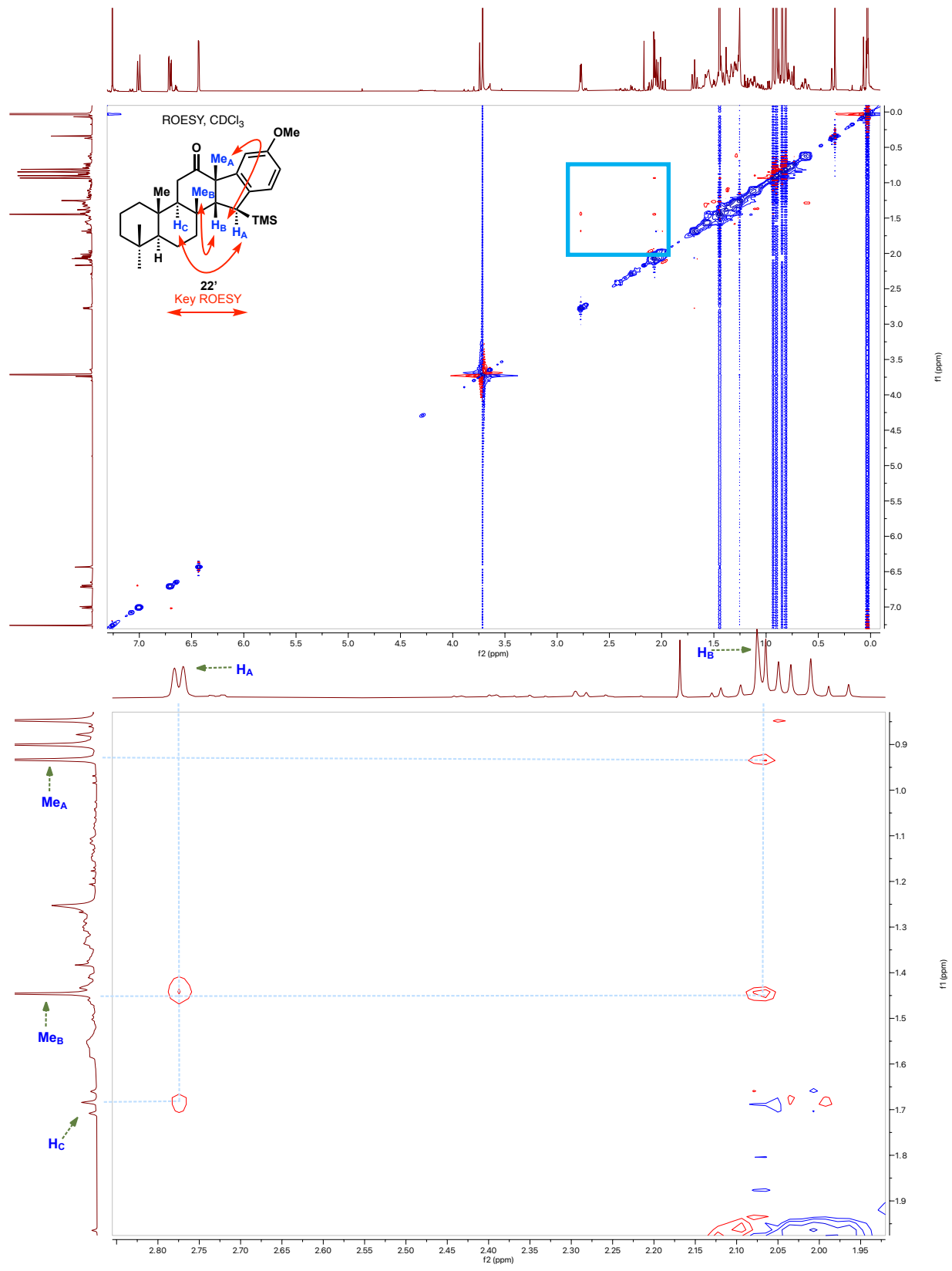
# HSQC spectra of 22'



# HMBC spectra of 22



# ROESY spectra of 22'

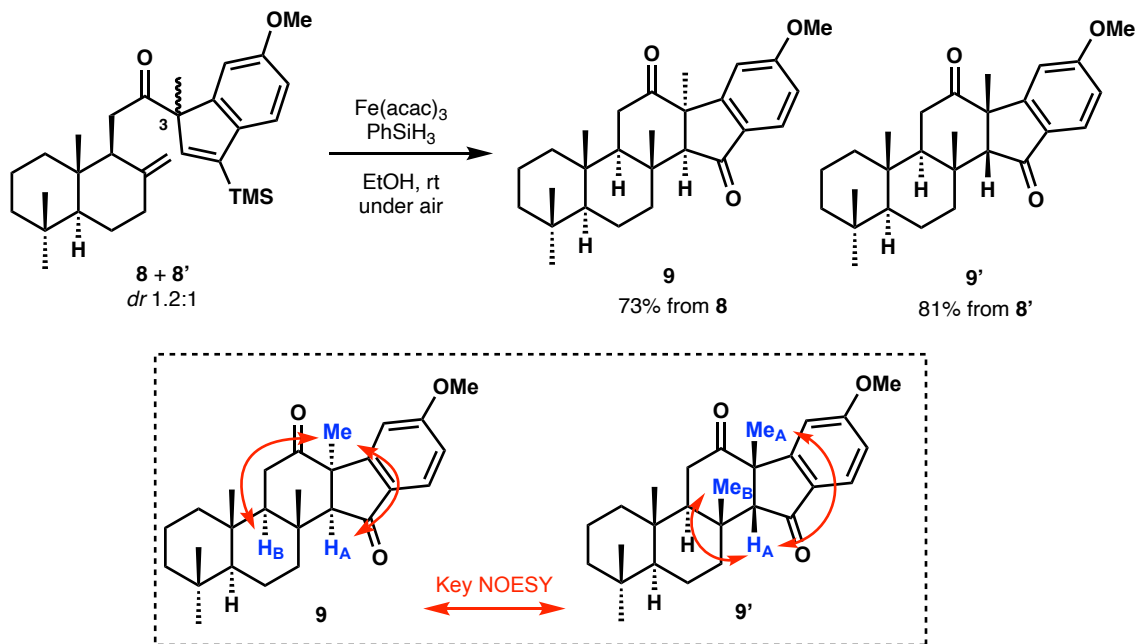


(2a*S*,6a*S*,6b*R*,8a*R*,13a*S*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-

1,2a,3,4,5,6,6a,6b,7,8a,13a,13b-dodecahydro-8*H*-indeno[2,1-*a*]phenanthrene-8,13(2*H*)-dione (**9**)

(2a*S*,6a*S*,6b*R*,8a*S*,13a*R*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-

1,2a,3,4,5,6,6a,6b,7,8a,13a,13b-dodecahydro-8*H*-indeno[2,1-*a*]phenanthrene-8,13(2*H*)-dione (**9'**)



Under air atmosphere, a solution of a mixture of **8** and **8'** (183 mg, 0.394 mmol, *dr* 1.2 : 1 (**8**: 99.8 mg (0.215 mmol), **8'**: 83.2 mg (0.179 mmol))) in EtOH (3.9 mL) was treated with Fe(acac)<sub>3</sub> (69.6 mg, 0.197 mmol) and PhSiH<sub>3</sub> (145  $\mu$ L, 1.18 mmol) at room temperature. After stirring for 18 h at room temperature, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 40:1) to afford **9** (63.8 mg, 73% from **8**) as a pale yellow solid and **9'** (59.0 mg, 81% from **8'**) as a colorless liquid.

#### Data for **9**

**Rf**: 0.26 (Hexanes/EtOAc = 5: 1, KMnO<sub>4</sub>)

$[\alpha]_D^{26}$  -17.79 (*c* 1.0, CHCl<sub>3</sub>).

**IR (KBr thin film)** 2962, 2870, 1696, 1638, 1459, 1298, 1237 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.66 (d, 1H, *J* = 8.8 Hz), 7.36 (d, 1H, *J* = 2.4 Hz), 6.92 (dd, 1H, *J* = 8.8, 2.4 Hz), 3.92 (s, 3H), 2.67 (dd, 1H, *J* = 19.2, 7.6 Hz), 2.60–2.55 (m, 1H), 2.42 (s, 1H), 2.34

(dd, 1H,  $J = 19.2, 12.0$  Hz), 1.84 (dd, 1H,  $J = 12.0, 7.6$  Hz), 1.67–0.86 (m, 10H), 1.53 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.83 (s, 3H), 0.56 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.3, 203.6, 165.4, 159.2, 129.6, 124.8, 116.6, 110.5, 71.1, 56.5, 55.9, 54.0, 52.7, 41.9, 41.8, 39.9, 39.5, 38.0, 35.5, 33.5, 33.2, 31.0, 21.8, 18.5, 18.4, 15.9, 15.2.

HRMS (EI)  $[M]^+$  calcd for  $\text{C}_{27}\text{H}_{36}\text{O}_3$  408.2664, found 408.2665.

### Data for 9'

Rf: 0.32 (Hexanes/EtOAc = 5: 1,  $\text{KMnO}_4$ )

$[\alpha]_D^{26} -89.94$  ( $c$  1.0,  $\text{CHCl}_3$ ).

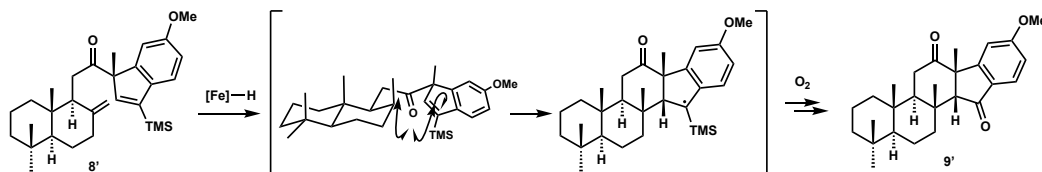
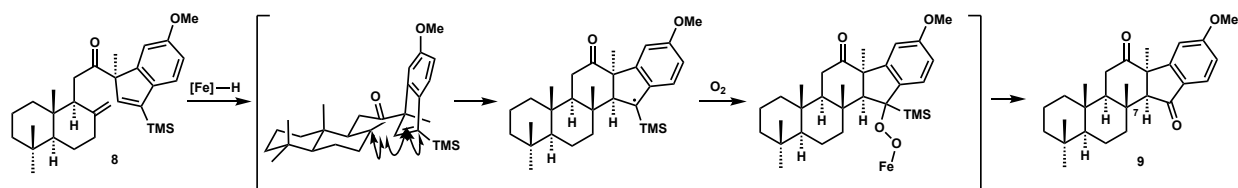
IR (KBr thin film) 2966, 2871, 1696, 1638, 1600, 1489, 1460, 1270  $\text{cm}^{-1}$ .

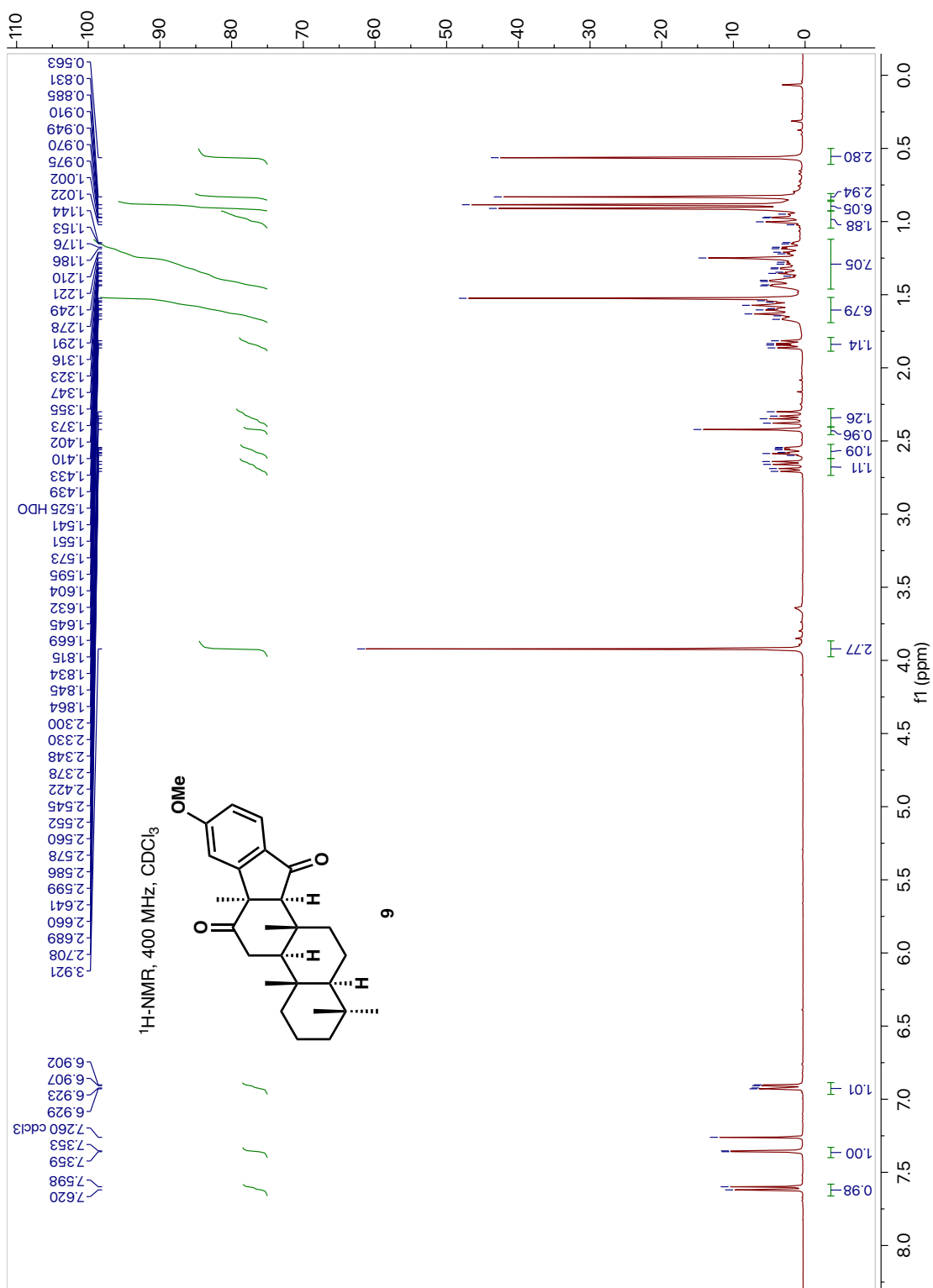
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d, 1H,  $J = 8.0$  Hz), 6.94 (dd, 1H,  $J = 8.0, 2.4$  Hz), 6.75 (d, 1H,  $J = 2.4$  Hz), 3.85 (s, 3H), 2.87–2.80 (m, 1H), 2.25 (dd, 1H,  $J = 18.8, 9.6$  Hz), 2.24 (s, 1H), 2.09 (dd, 1H,  $J = 18.8, 9.6$  Hz), 1.66–0.54 (m, 11H), 1.55 (s, 3H), 1.02 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H), 0.79 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.7, 204.6, 166.1, 158.3, 130.8, 125.8, 117.5, 107.3, 69.7, 56.0, 55.6, 55.4, 50.3, 41.8, 40.9, 39.1, 36.2, 38.1, 35.0, 33.3, 33.2, 26.5, 23.9, 21.8, 18.2, 18.1, 15.1.

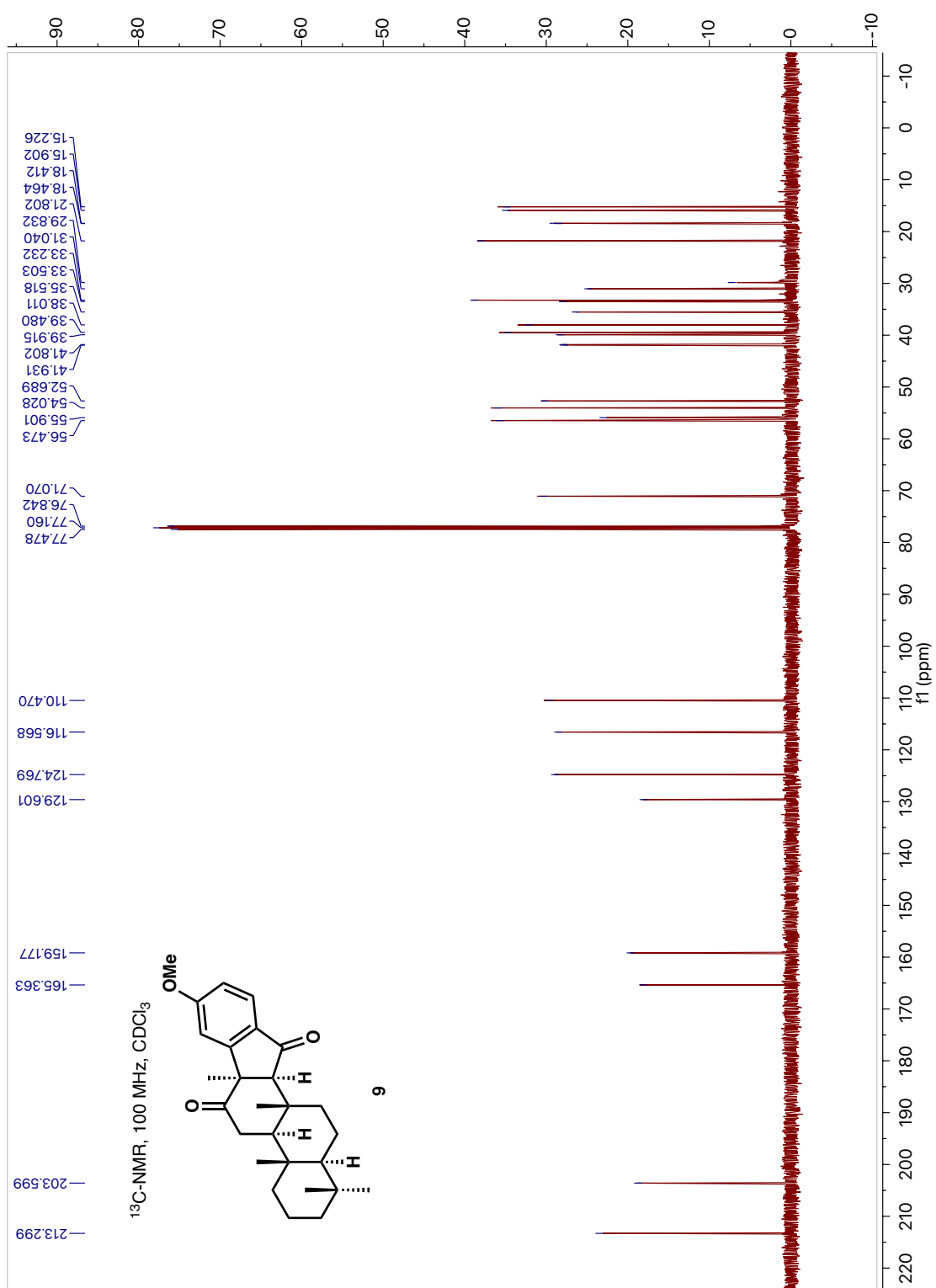
HRMS (EI)  $[M]^+$  calcd for  $\text{C}_{27}\text{H}_{36}\text{O}_3$  408.2665, found 408.2667.

Plausible mechanism of the MHAT-initiated redox cyclization of 8 and 8'.

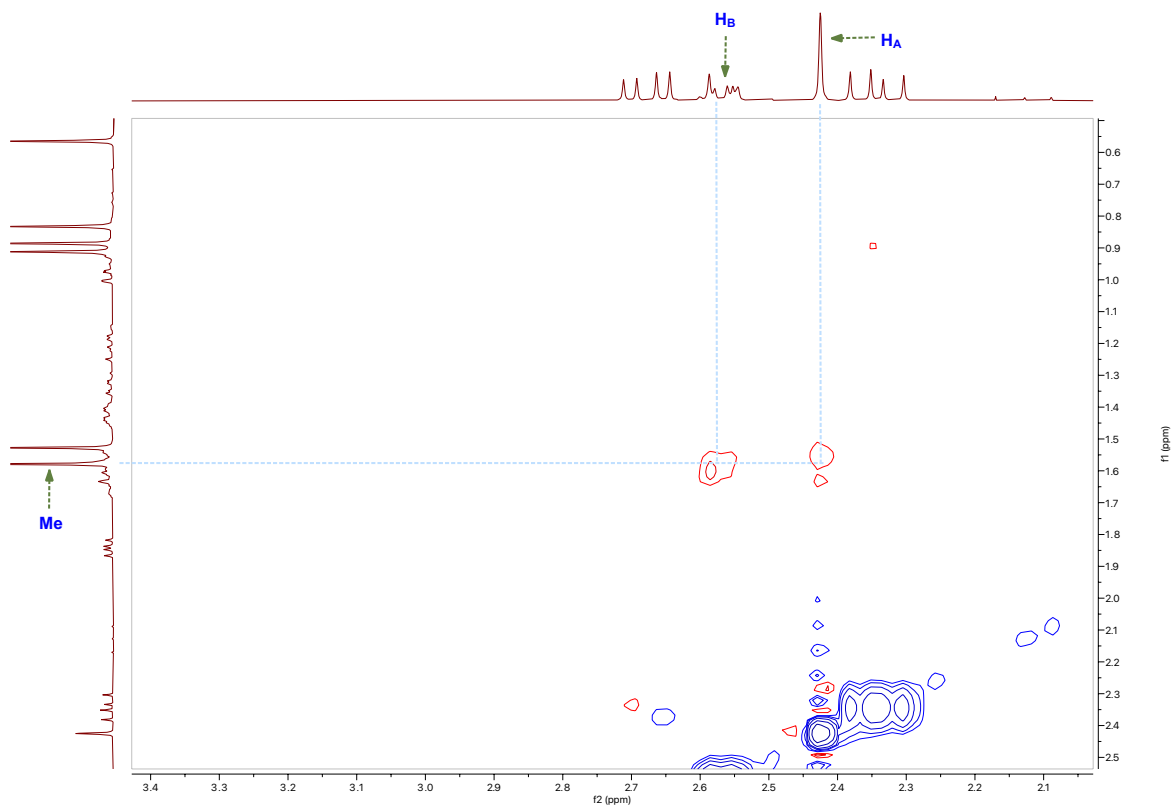
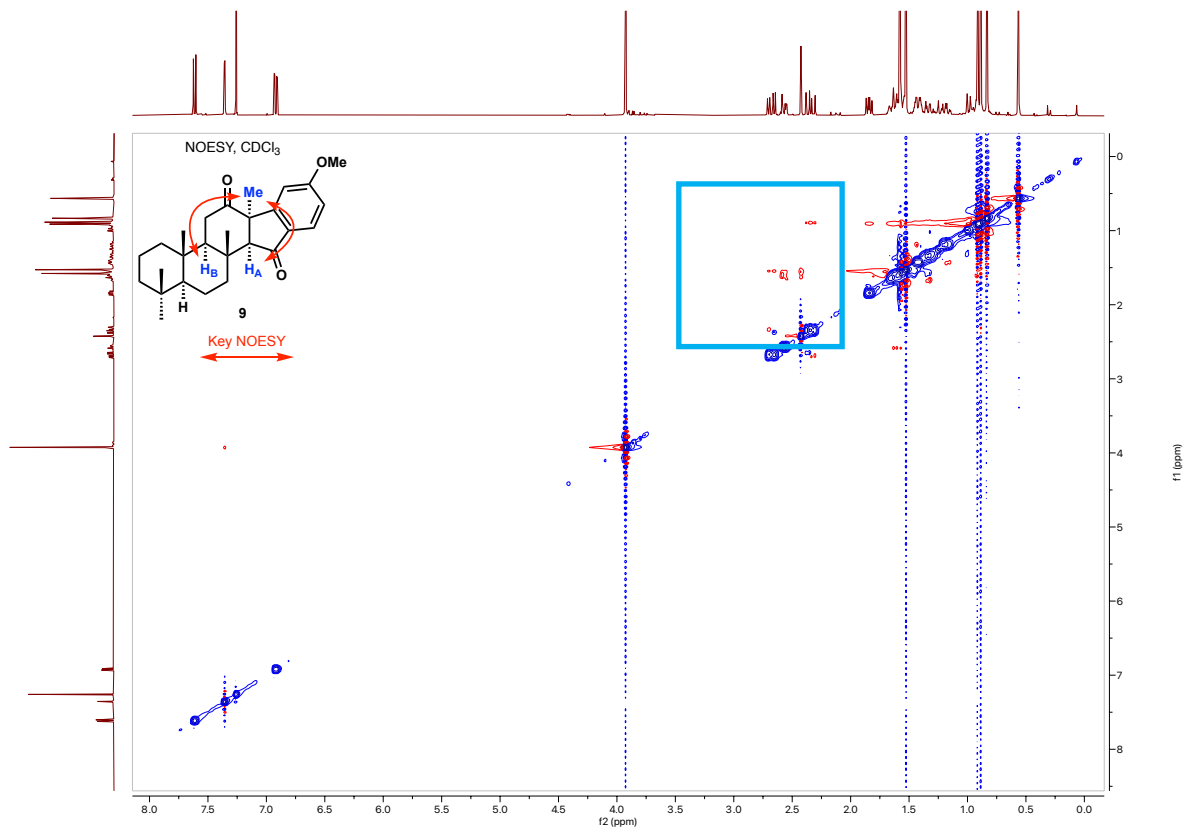


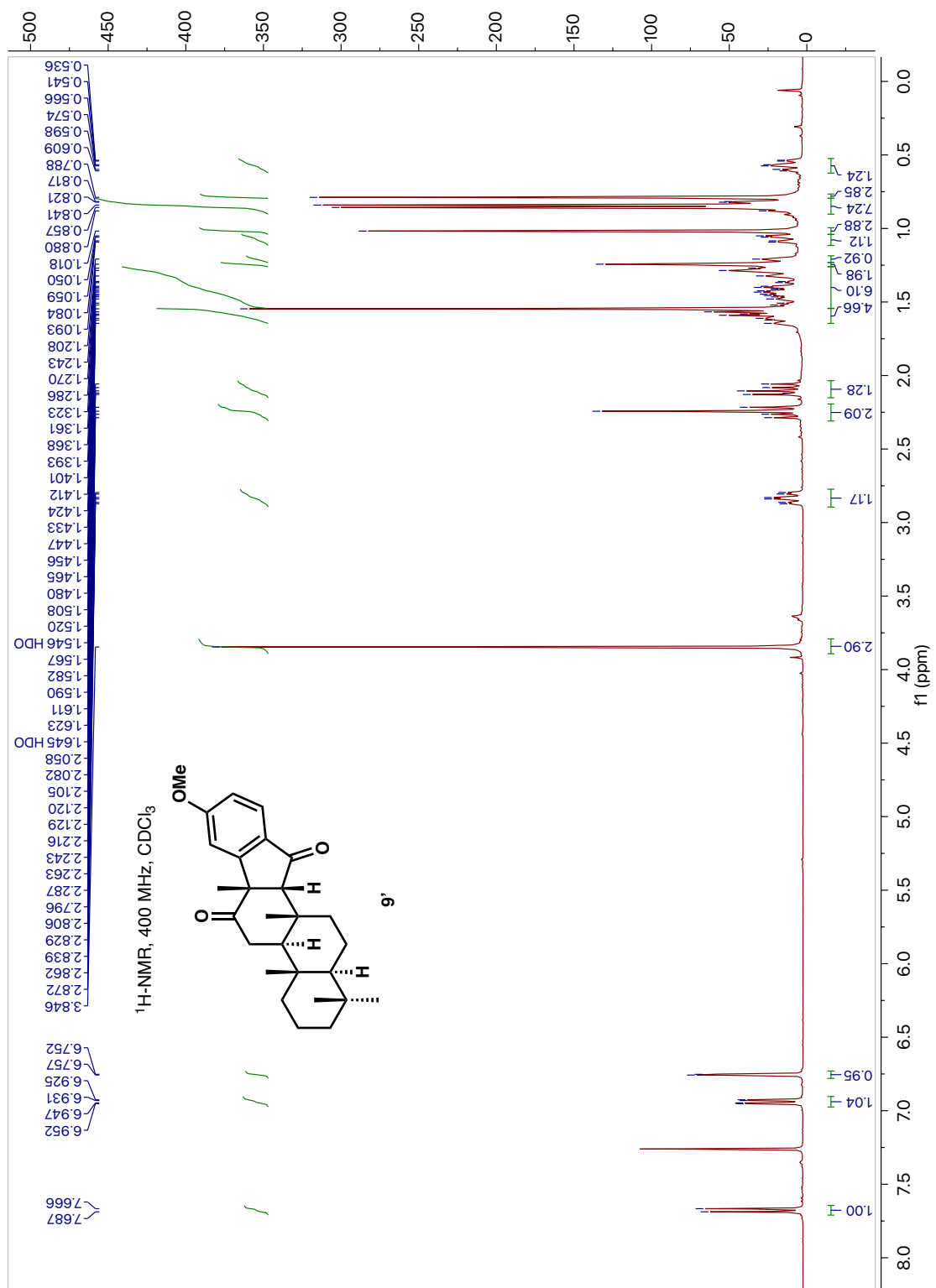


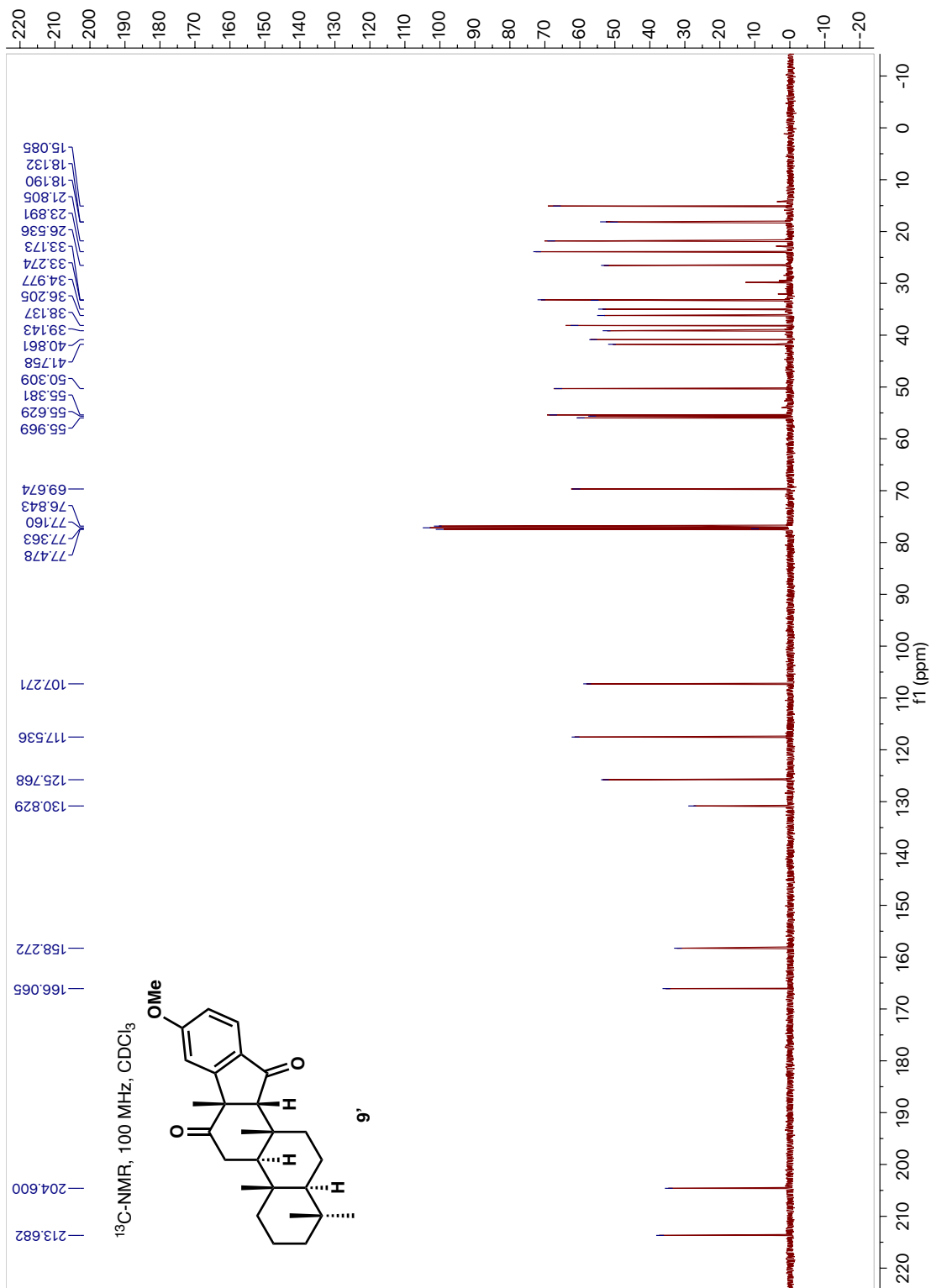




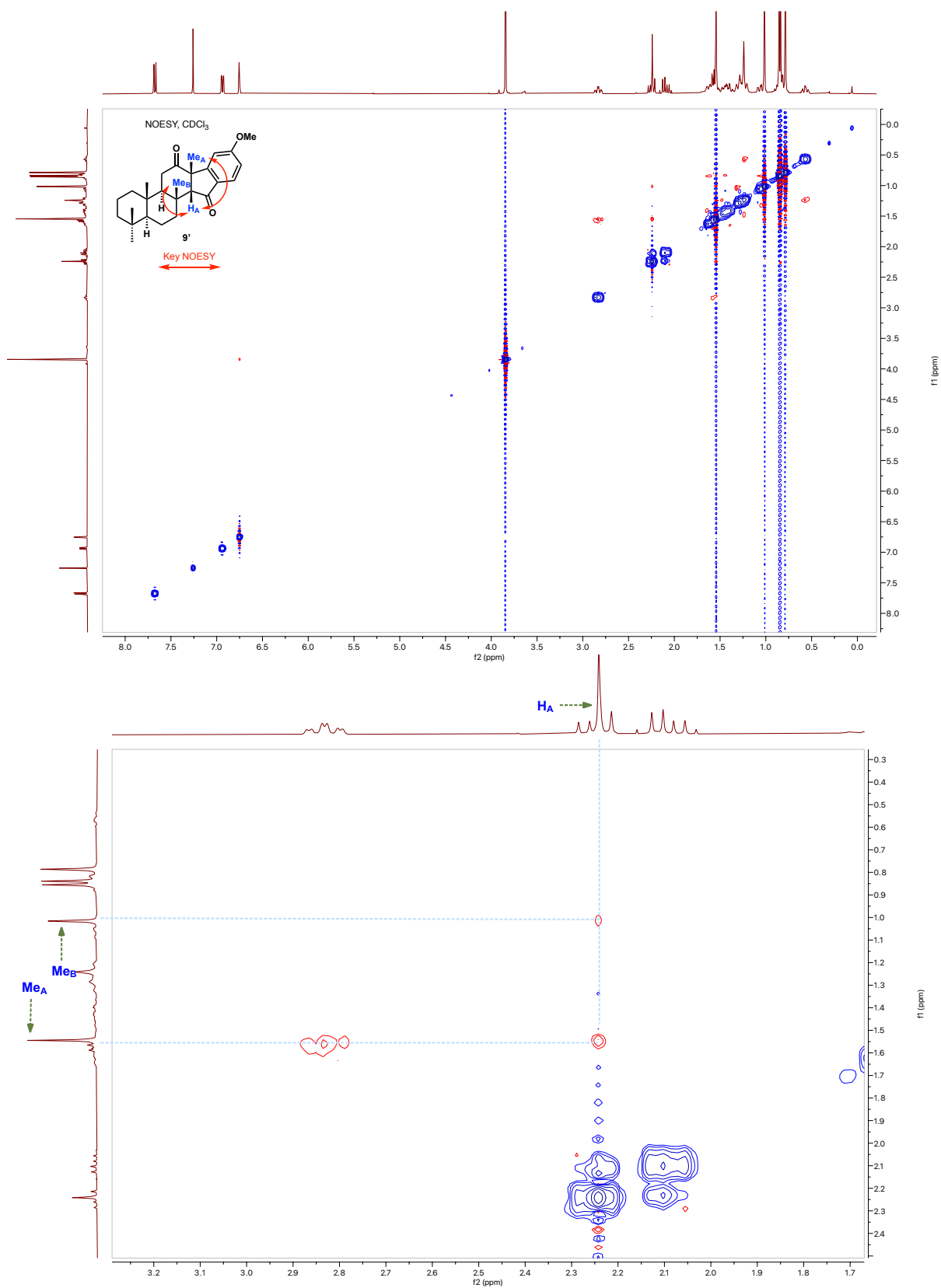
# NOESY spectra of 9



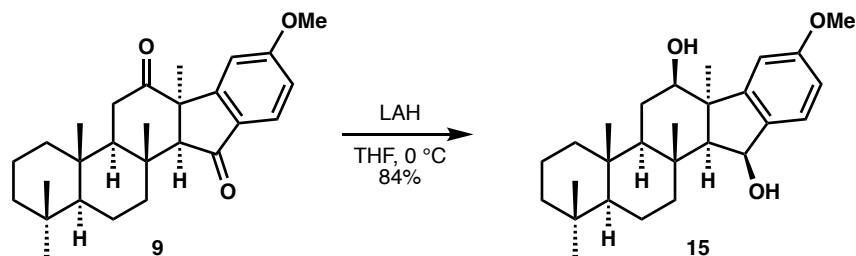




# NOESY spectra of 9'



(2a*S*,6a*S*,6b*R*,8*R*,8a*R*,13*S*,13a*S*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-2,2a,3,4,5,6,6a,6b,7,8,8a,13,13a,13b-tetradecahydro-1*H*-indeno[2,1-*a*]phenanthrene-8,13-diol  
**(15)**



A solution of **9** (63.8 mg, 0.156 mmol) in THF (3.1 mL) was treated with LAH (17.8 mg, 0.468 mmol) at 0 °C. After stirring for 10 min at room temperature, the reaction mixture was quenched with EtOAc and 2 M HCl *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 150:1) to afford **15** (53.8 mg, 84%) as a white solid.

**Rf:** 0.50 (Hexanes/EtOAc = 1 : 1, anisaldehyde)

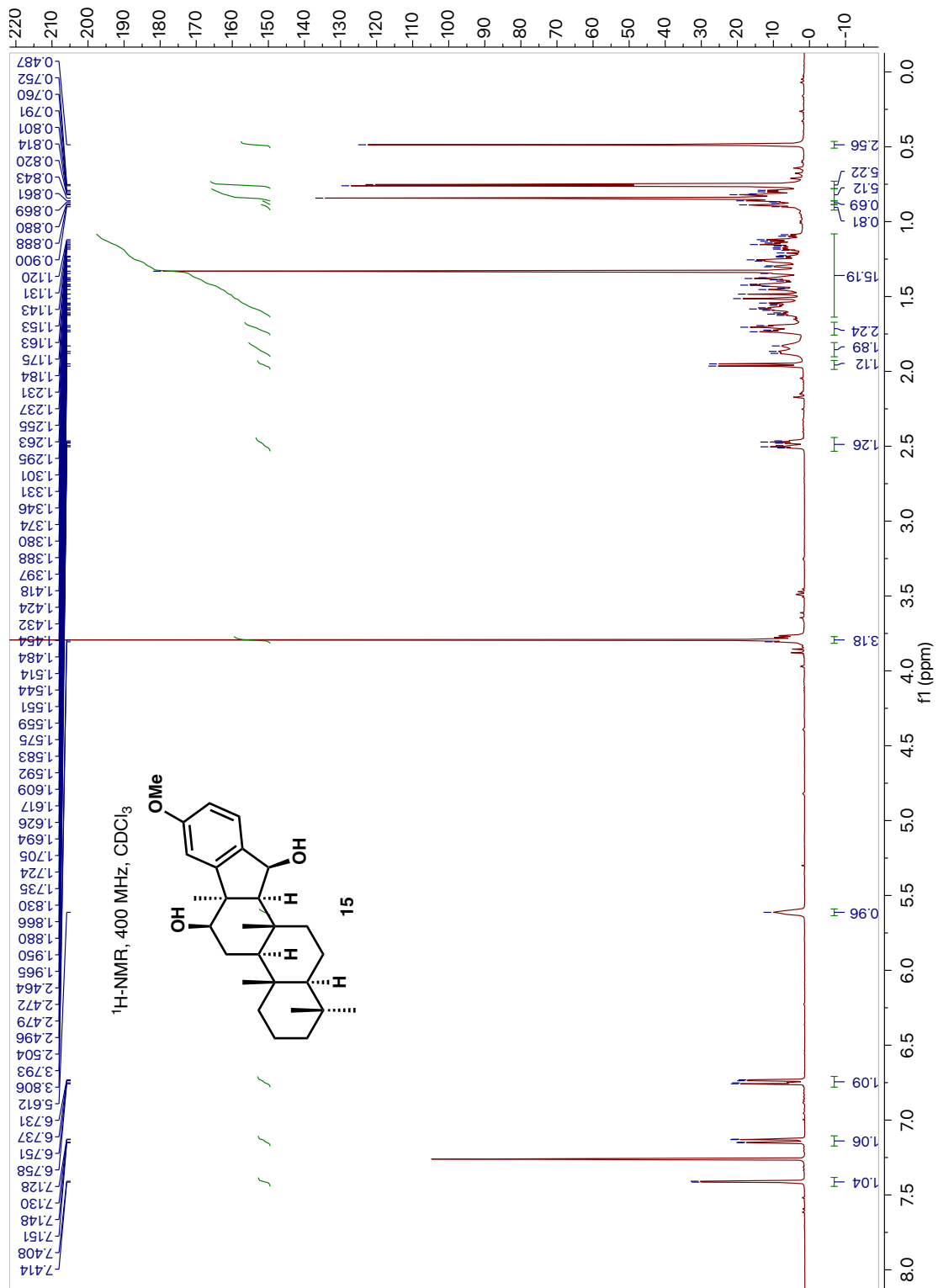
$[\alpha]_{\text{D}}^{25}$  +17.40 (*c* 1.0, CHCl<sub>3</sub>).

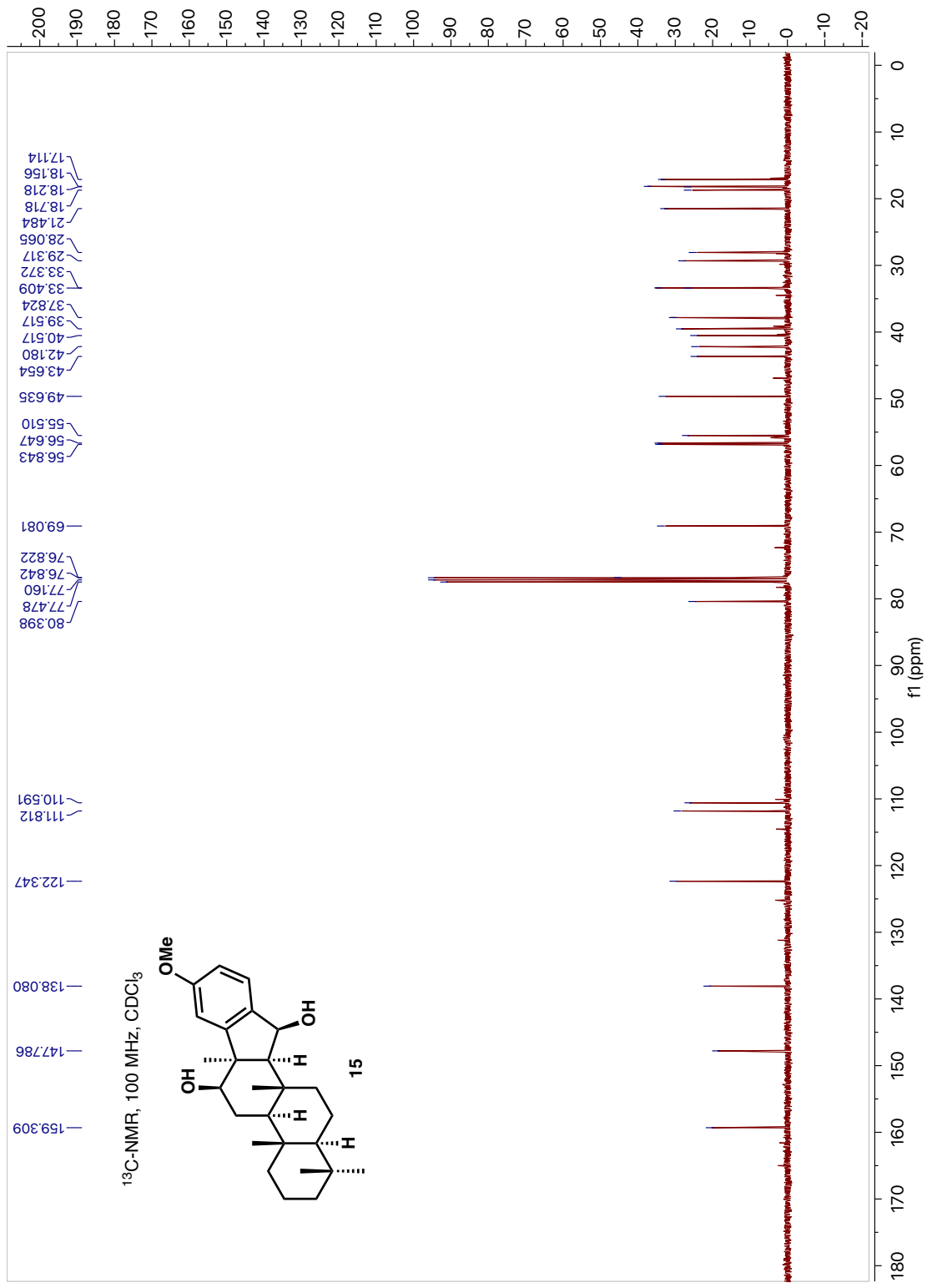
**IR (KBr thin film)** 3423, 2954, 2919, 1543, 1459, 1070 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.41 (d, 1H, *J* = 2.4 Hz), 7.14 (d, 1H, *J* = 8.0 Hz), 6.74 (dd, 1H, *J* = 8.0, 2.4 Hz), 5.61 (s, 1H), 3.81–3.76 (m, 1H), 3.79 (s, 3H), 2.49 (dt, 1H, *J* = 12.8, 3.2 Hz), 2.49 (d, 1H, *J* = 6.0 Hz), 1.73–0.79 (m, 13H), 1.33 (s, 3H), 0.84 (s, 3H), 0.76 (s, 3H), 0.75 (s, 3H), 0.49 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 159.3, 147.8, 138.1, 122.3, 111.8, 110.6, 80.4, 76.82, 69.1, 56.8, 56.6, 55.5, 49.6, 43.7, 42.2, 40.5, 39.5, 37.8, 33.4, 33.3, 29.3, 28.1, 21.5, 18.7, 18.2, 18.2, 17.1.

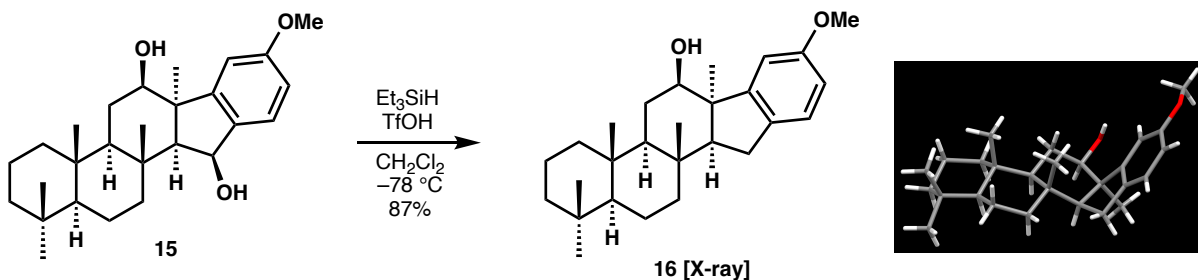
**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>40</sub>O<sub>3</sub> 412.2977, found 412.2984.







(2a*S*,6a*S*,6b*R*,8*R*,8a*R*,13a*S*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-2,2a,3,4,5,6,6a,6b,7,8,8a,13,13a,13b-tetradecahydro-1*H*-indeno[2,1-*a*]phenanthren-8-ol (**16**)



A solution of **15** (10.8 mg, 0.0262 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.1 mL) was treated with Et<sub>3</sub>SiH (20.8 μL, 0.131 mmol) and TfOH (4.6 μL, 0.0524 mmol) at –78 °C. After stirring for 20 min at –78 °C, the reaction mixture was quenched with *sat.* NaHCO<sub>3</sub> *aq.*. After extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by preparative TLC (Hexanes/EtOAc = 2:1) to afford **16** (9.0 mg, 99%) as a white solid.

**Rf**: 0.50 (Hexanes/EtOAc = 2 : 1, anisaldehyde)

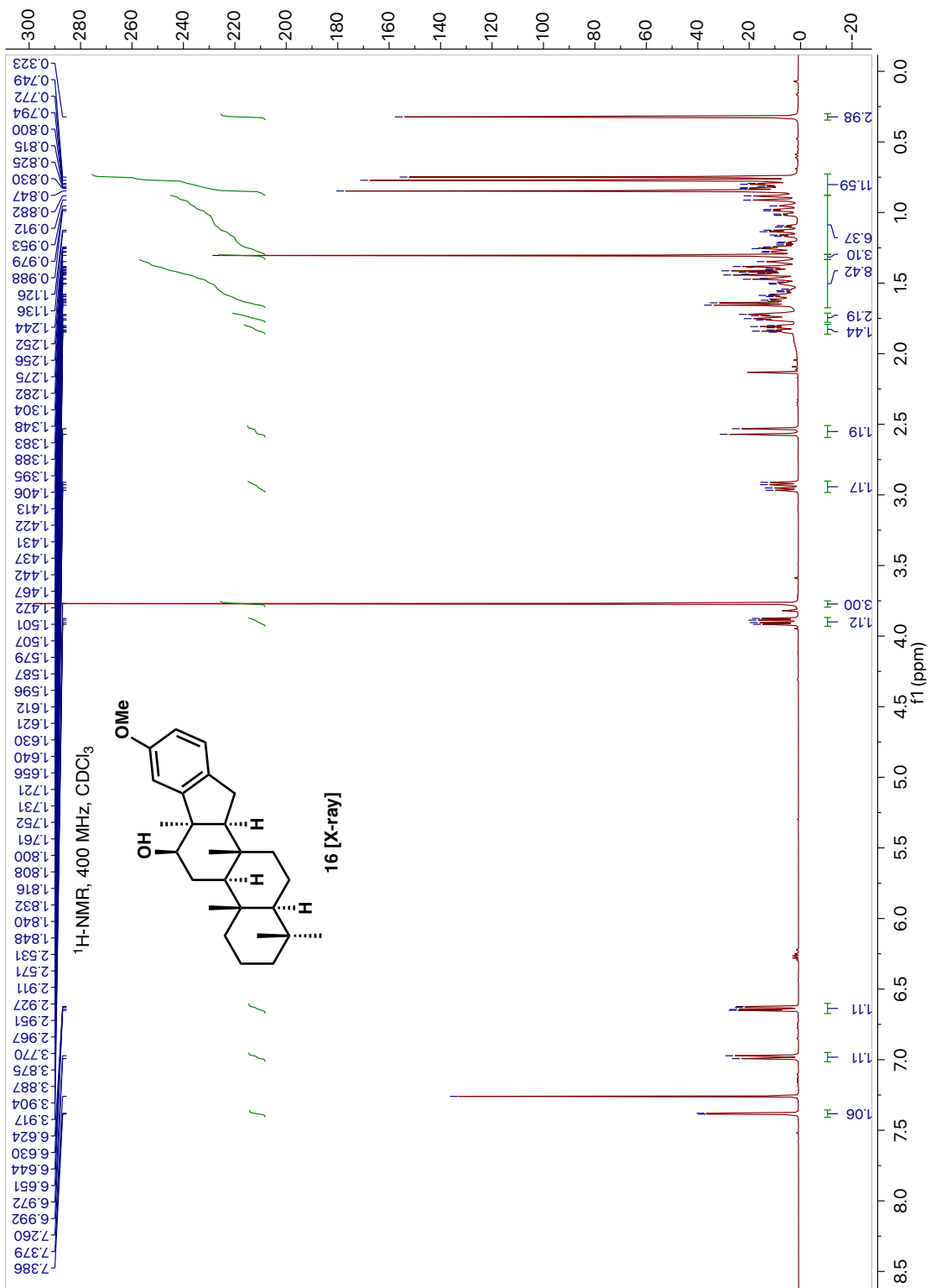
[α]<sub>D</sub><sup>26</sup> –10.35 (*c* 1.0, CHCl<sub>3</sub>).

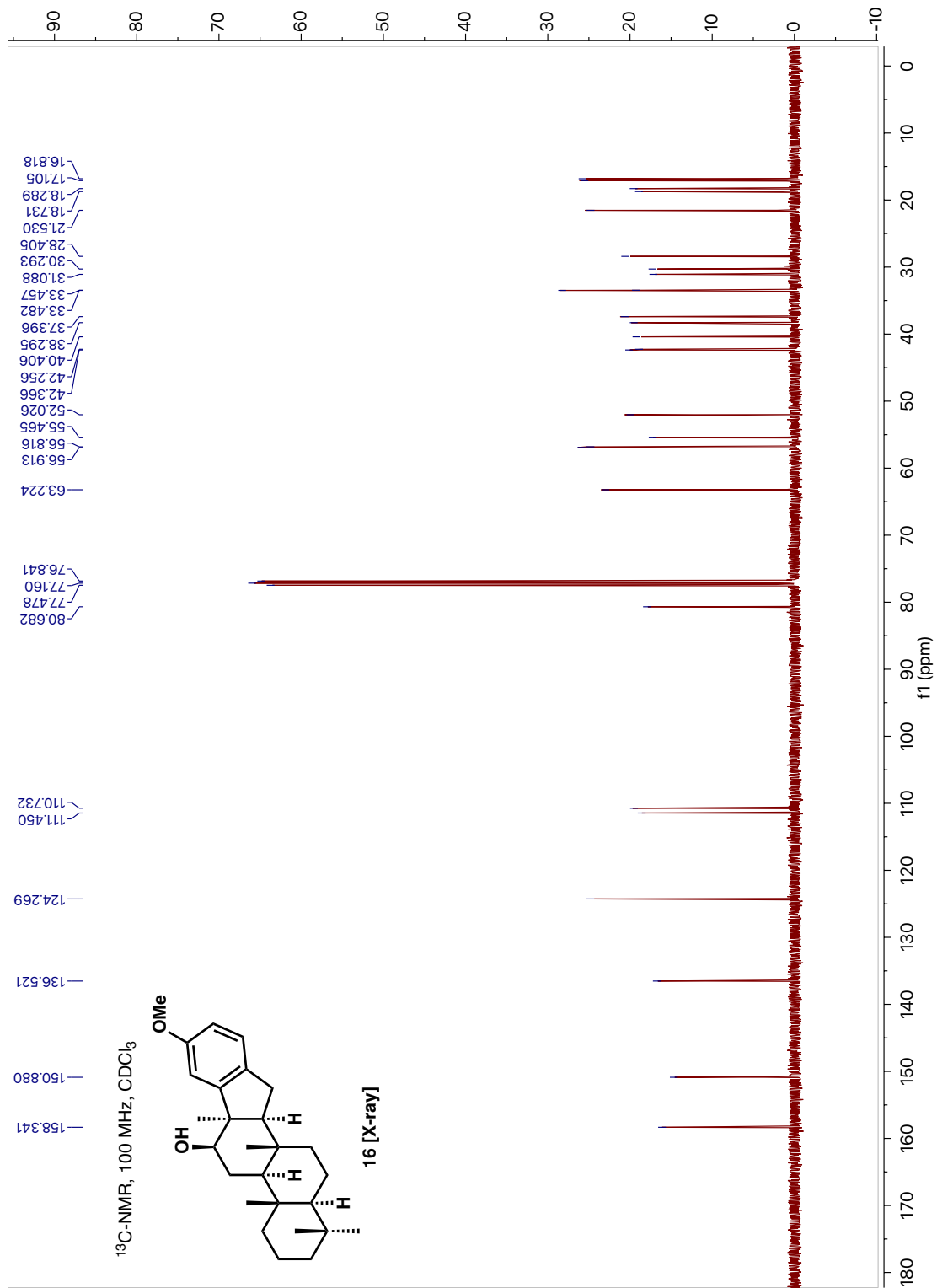
**IR (KBr thin film)** 3430, 2951, 2867, 1481, 1467, 1279, 1220 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.38 (d, 1H, *J* = 2.4 Hz), 6.98 (d, 1H, *J* = 8.0 Hz), 6.64 (dd, 1H, *J* = 8.0, 2.4 Hz), 3.89 (dd, 1H, *J* = 12.0, 4.8 Hz), 3.77 (s, 3H), 2.94 (dd, 1H, *J* = 16.0, 6.8 Hz), 2.55 (d, 1H, *J* = 16.0 Hz), 1.83 (dt, 1H, *J* = 12.8, 3.2 Hz), 1.76–0.80 (m, 13H), 1.65 (d, 1H, *J* = 6.8 Hz), 1.31 (s, 3H), 0.85 (s, 3H), 0.77 (s, 3H), 0.75 (s, 3H), 0.32 (s, 3H).

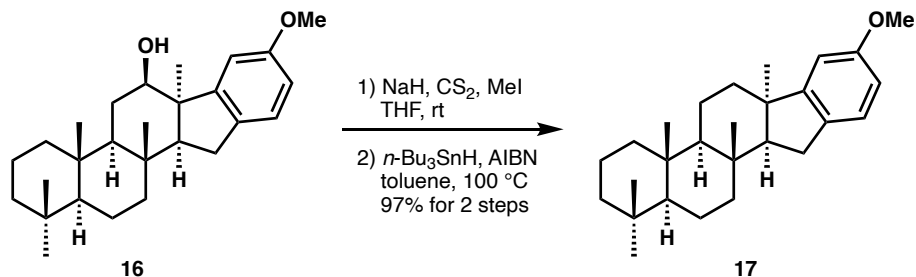
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 158.3, 150.9, 136.5, 124.3, 111.5, 110.7, 80.7, 63.2, 56.9, 56.8, 55.5, 52.0, 42.4, 42.3, 40.4, 38.3, 37.4, 33.5, 33.5, 31.1, 30.3, 28.4, 21.5, 18.7, 18.3, 17.1, 16.8.

**HRMS (EI) [M]<sup>+</sup>** calcd for C<sub>27</sub>H<sub>40</sub>O<sub>2</sub> 396.3028, found 396.3025.





(2a*S*,6a*S*,6b*R*,8*R*,8a*R*,13a*S*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-2,2a,3,4,5,6,6a,6b,7,8,8a,13,13a,13b-tetradecahydro-1*H*-indeno[2,1-*a*]phenanthren-8-ol (**17**)



A solution of **16** (12.2 mg, 0.0308 mmol) in THF (0.6 mL) was treated with NaH (55%, 10.7 mg, 0.246 mmol) at 0 °C. After stirring for 30 min at room temperature, CS<sub>2</sub> (18.6 μL, 0.308 mmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, MeI (23.0 μL, 0.370 mmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, the reaction mixture was quenched with *sat.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by preparative TLC (Hexanes : EtOAc = 5 : 1) to afford crude xanthate.

A solution of the crude xanthate in toluene (0.7 mL) was treated with *n*-Bu<sub>3</sub>SnH (19.3 μL, 0.0719 mmol) and AIBN (1.2 mg, 0.00720 mmol) at room temperature. After stirring for 40 min at 100 °C, the reaction mixture was concentrated *in vacuo*. The residue was purified by preparative TLC (Hexanes : EtOAc = 10 : 1) to afford **17** (11.0 mg, 97% for 2 steps) as a colorless oil.

**Rf**: 0.63 (Hexanes/EtOAc = 8 : 1, phosphomolybdic acid)

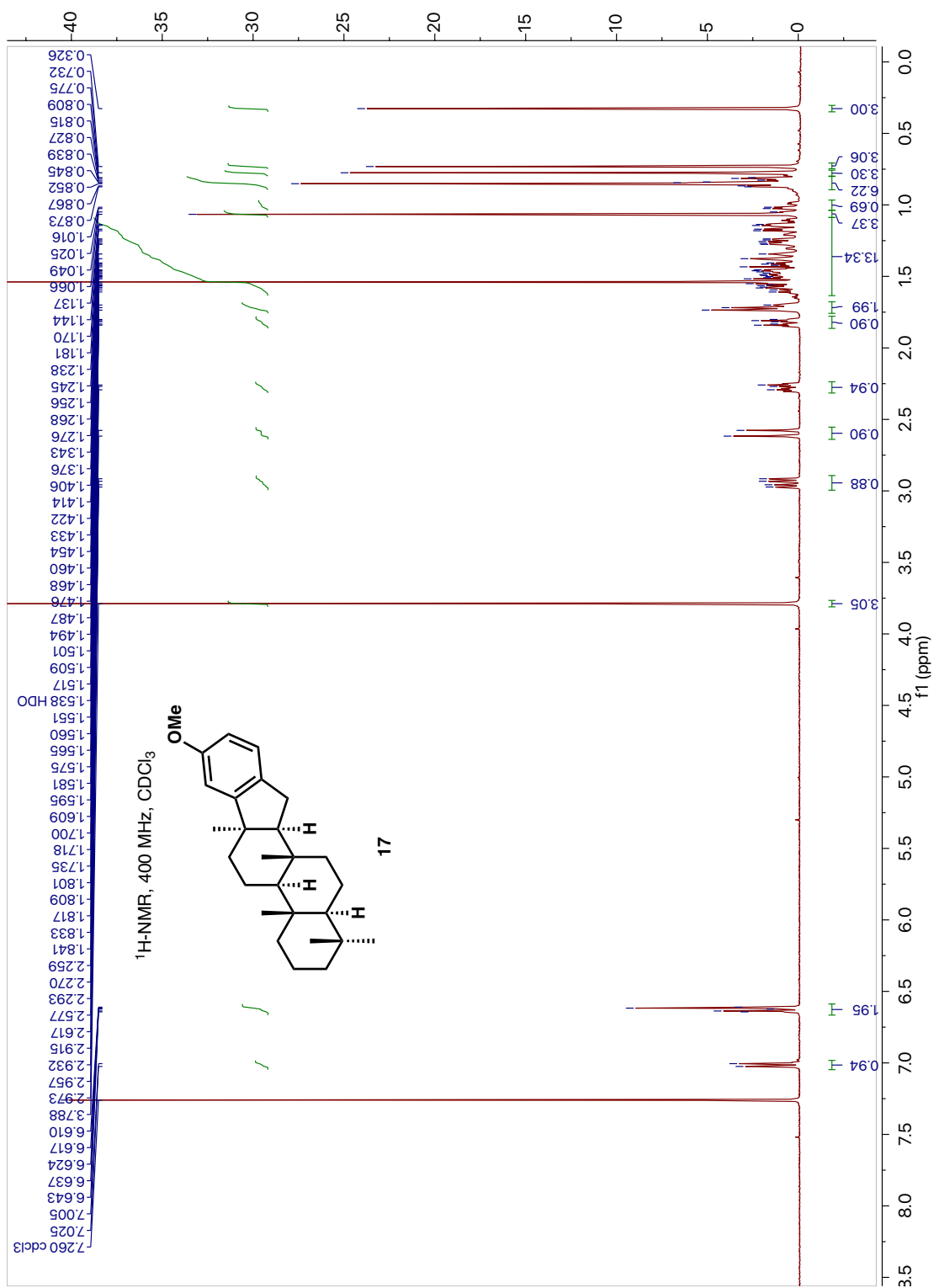
[α]<sub>D</sub><sup>23</sup> −49.53 (*c* 1.0, CHCl<sub>3</sub>).

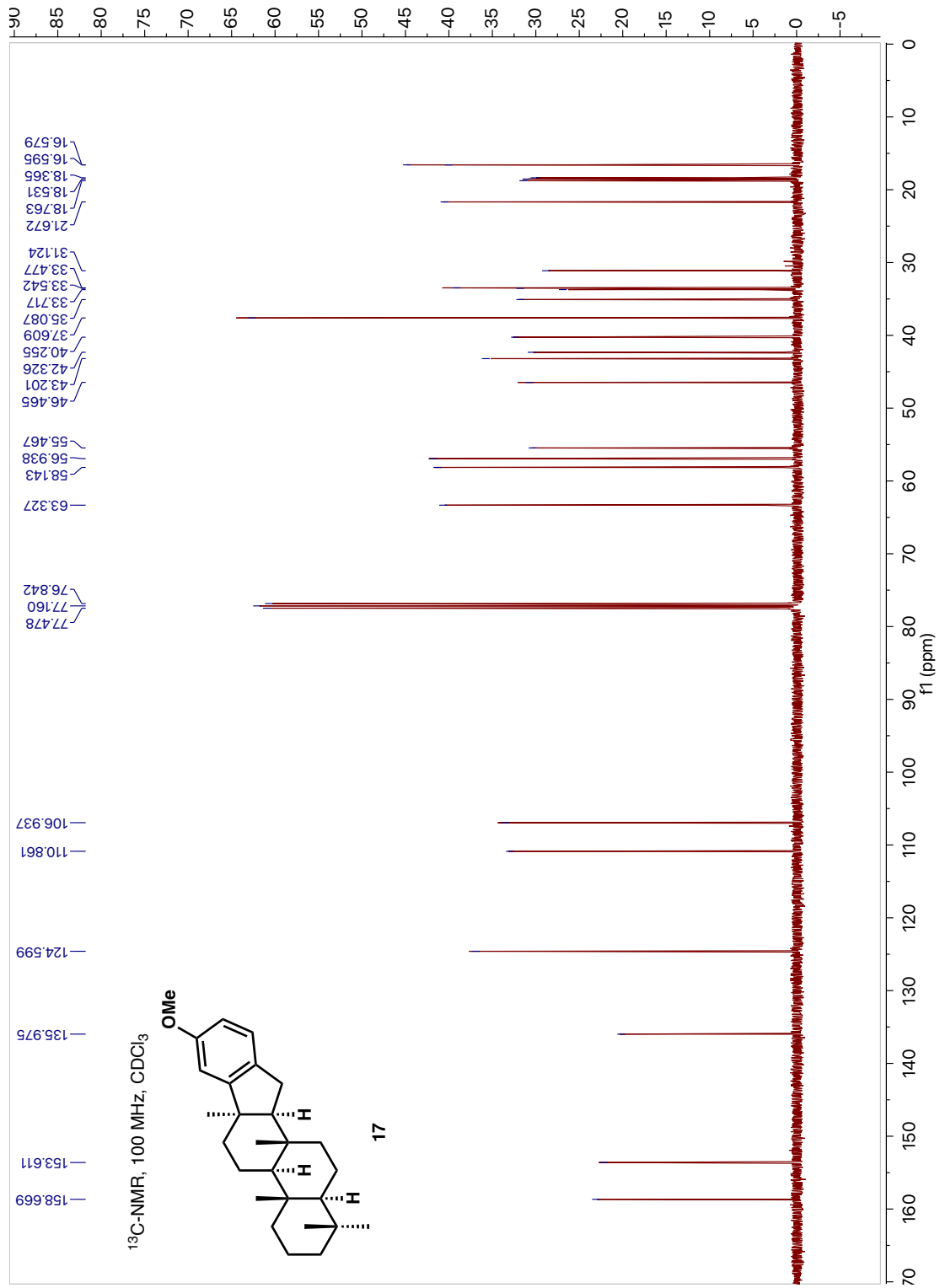
**IR (KBr thin film)** 2948, 2844, 1638, 1482, 1461, 1384, 1333, 1281, 1249 cm<sup>−1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.02 (d, 1H, *J* = 2.4 Hz), 6.65–6.62 (m, 2H), 3.79 (s, 3H), 2.95 (dd, 1H, *J* = 16.0, 7.2 Hz), 2.60 (d, 1H, *J* = 16.0 Hz), 2.31 (dt, 1H, *J* = 13.6, 4.0 Hz), 1.83 (dt, 1H, *J* = 12.4, 3.2 Hz), 1.74–0.82 (m, 14H), 1.73 (d, 1H, *J* = 7.2 Hz), 1.07 (s, 3H), 0.86 (s, 3H), 0.78 (s, 3H), 0.74 (s, 3H), 0.33 (s, 3H).

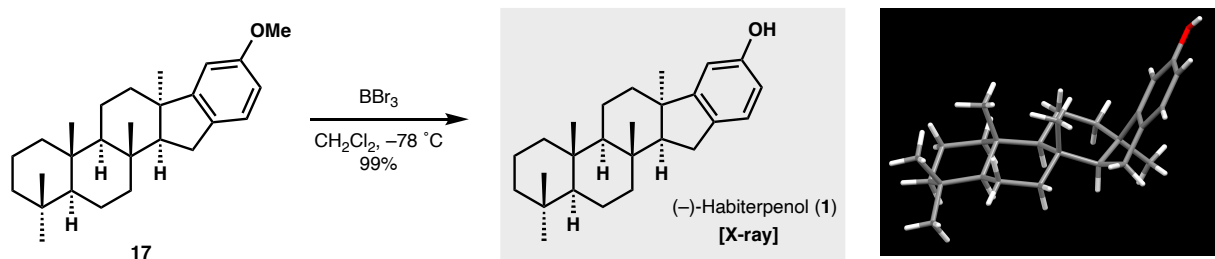
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 158.7, 153.6, 136.0, 124.6, 110.9, 106.9, 63.3, 58.1, 56.9, 55.5, 46.5, 43.2, 42.3, 40.3, 37.6, 37.6, 35.1, 33.7, 33.5, 33.5, 31.1, 21.7, 18.8, 18.5, 18.4, 16.6, 16.6.

**HRMS (EI) [M]<sup>+</sup>** calcd for C<sub>27</sub>H<sub>40</sub>O 380.3079, found 380.3083.





(-)-Habiterpenol (**1**)



A solution of **17** (27.0 mg, 0.0709 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.4 mL) was treated with  $\text{BBr}_3$  (284  $\mu\text{L}$ , 0.284 mmol, 1.0 M in  $\text{CH}_2\text{Cl}_2$ ) at  $-78^\circ\text{C}$ . After stirring for 1 h at room temperature, the reaction mixture was quenched with *sat.*  $\text{NaHCO}_3$  *aq.*. After extraction with  $\text{CH}_2\text{Cl}_2$ , the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 15:1) to afford **1** <sup>SI-5</sup> (25.8 mg, 99%) as a white solid.

**Rf**: 0.30 (Hexanes/EtOAc = 8 : 1, phosphomolybdic acid)

$[\alpha]_{\text{D}}^{27} -53.58$  (*c* 0.1, MeOH).

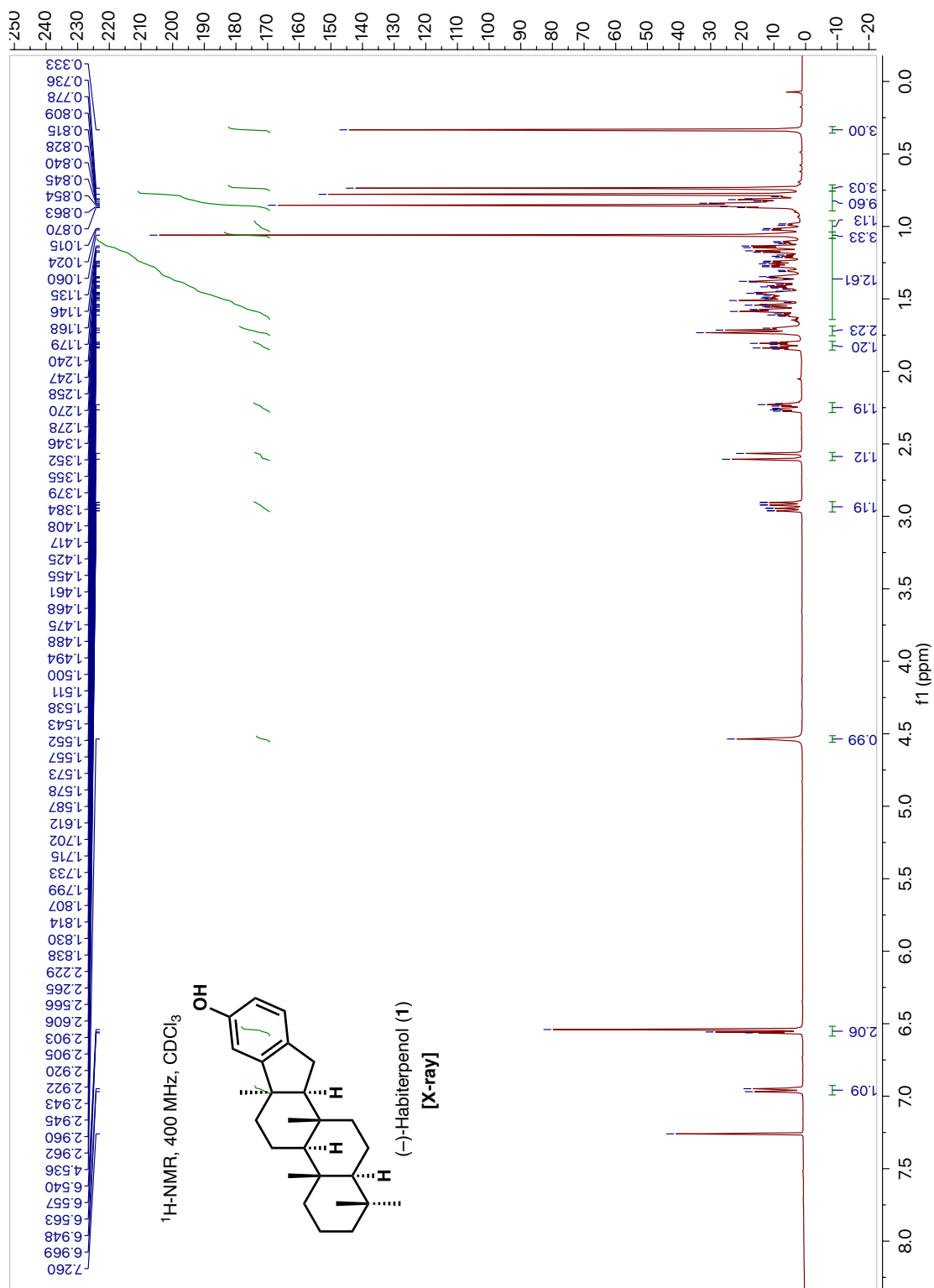
**IR (KBr thin film)** 3434, 2947, 2844, 1719, 1638, 1459, 1384, 1334, 1268, 1183  $\text{cm}^{-1}$ .

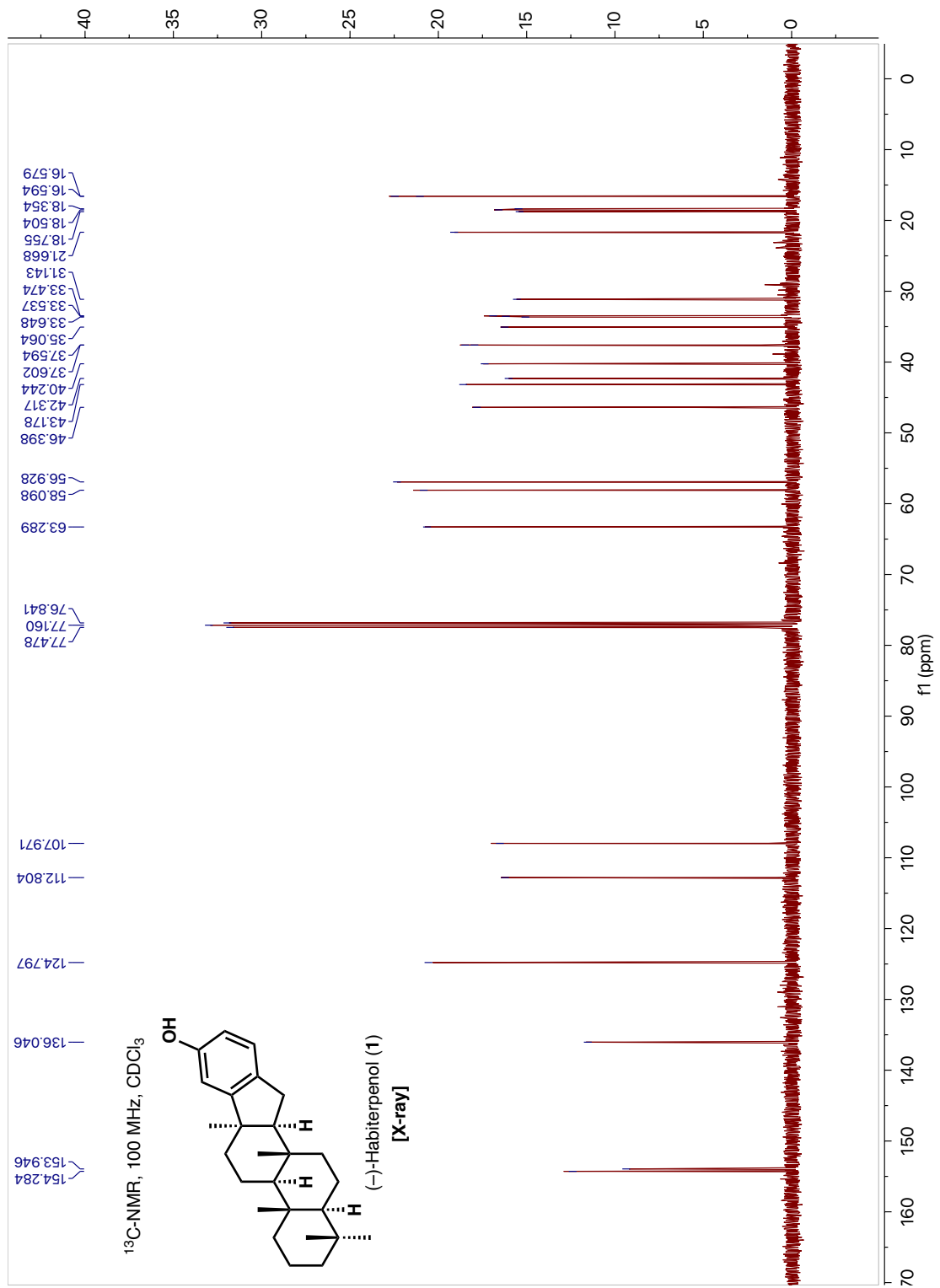
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  6.96 (d, 1H,  $J = 8.4$  Hz), 6.56 (dd, 1H,  $J = 8.4, 2.4$  Hz), 6.54 (s, 1H), 4.64 (brs, 1H), 2.93 (ddd, 1H,  $J = 16.0, 7.2, 0.8$  Hz), 2.59 (d, 1H,  $J = 16.0$  Hz), 2.24 (dt, 1H,  $J = 14.0, 4.0$  Hz), 1.83 (dt, 1H,  $J = 12.8, 3.2$  Hz), 1.73–0.81 (m, 13H), 1.72 (d, 1H,  $J = 7.2$  Hz), 1.06 (s, 3H), 1.02 (dt, 1H,  $J = 12.8, 3.6$  Hz), 0.86 (s, zf3H), 0.78 (s, 3H), 0.74 (s, 3H), 0.34 (s, 3H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  154.3, 153.9, 136.0, 124.8, 112.8, 108.0, 63.3, 58.1, 56.9, 46.4, 43.2, 42.3, 40.2, 37.6, 37.6, 35.0, 33.6, 33.5, 33.5, 31.1, 21.7, 18.8, 18.5, 18.4, 16.6, 16.6.

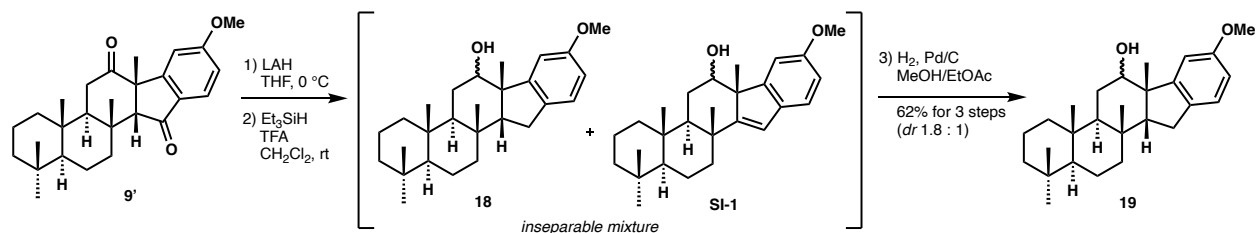
**HRMS (EI)**  $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{38}\text{O}$  366.2923, found 366.2926.







(2*aS*,6*aS*,6*bR*,8*aS*,13*aR*,13*bR*)-10-Methoxy-3,3,6*a*,8*a*,13*b*-pentamethyl-2,2*a*,3,4,5,6,6*a*,6*b*,7,8,8*a*,13,13*a*,13*b*-tetradecahydro-1*H*-indeno[2,1-*a*]phenanthren-8-ol (**19**)



A solution of **9'** (204 mg, 0.500 mmol) in THF (5.0 mL) was treated with LAH (56.9 mg, 1.50 mmol) at 0 °C. After stirring for 15 min at room temperature, the reaction mixture was quenched with EtOAc and 2 M HCl *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by flash silica gel column chromatography (Hexanes/EtOAc = 9:1) to afford crude diol as a diastereo mixture.

A solution of crude diol in THF (5.0 mL) was treated with Et<sub>3</sub>SiH (359 μL, 2.25 mmol) and TFA (172 μL, 2.25 mmol) at 0 °C. After stirring for 50 min at room temperature, the reaction mixture was quenched with *sat.* NaHCO<sub>3</sub> *aq.*. After extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by flash silica gel column chromatography (Hexanes/EtOAc = 40:1) to afford crude **18** and **SI-1** as an inseparable mixture.

Under H<sub>2</sub> atmosphere, a solution of crude **18** and **SI-1** in EtOAc (7.5 mL) and MeOH (7.5 mL) was treated with Pd/C (10% on carbon, 18.6 mg, 10% w/w) at room temperature. After stirring for 5 h at room temperature, the reaction mixture was through a celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/EtOAc = 40:1) to afford **19** (diastereomer A: 42.5 mg, diastereomer B: 76.7 mg, total 62% for 3 steps, *dr* 1.8 : 1) as white solids.

#### Diastereomer A

**Rf**: 0.53 (Hexanes/EtOAc = 2 : 1, anisaldehyde)

$[\alpha]_D^{24} +102.91$  (*c* 0.9, CHCl<sub>3</sub>).

**IR (KBr thin film)** 3467, 2995, 2944, 2864, 1489, 1465, 1386, 1283, 1211 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.13 (d, 1H, *J* = 8.0 Hz), 6.74 (dd, 1H, *J* = 8.0, 2.4 Hz), 6.70 (d,

1H,  $J = 2.4$  Hz), 3.81 (s, 3H), 3.72 (s, 1H), 2.89 (dd, 1H,  $J = 14.4, 11.6$  Hz), 2.68 (dd, 1H,  $J = 14.4, 8.4$  Hz), 1.93 (dd, 1H,  $J = 11.6, 8.4$  Hz), 1.75–0.84 (m, 14H), 1.44 (s, 3H), 1.19 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 149.5, 136.3, 125.3, 112.7, 108.5, 75.7, 62.7, 57.2, 55.6, 50.2, 43.5, 42.3, 40.0, 39.9, 36.8, 36.8, 34.5, 33.6, 33.6, 26.0, 25.5, 24.2, 21.7, 18.7, 18.3, 16.7.

HRMS (EI)  $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{40}\text{O}_2$  396.3028, found 396.3015.

#### Diastereomer B

Rf: 0.47 (Hexanes/EtOAc = 2 : 1, anisaldehyde)

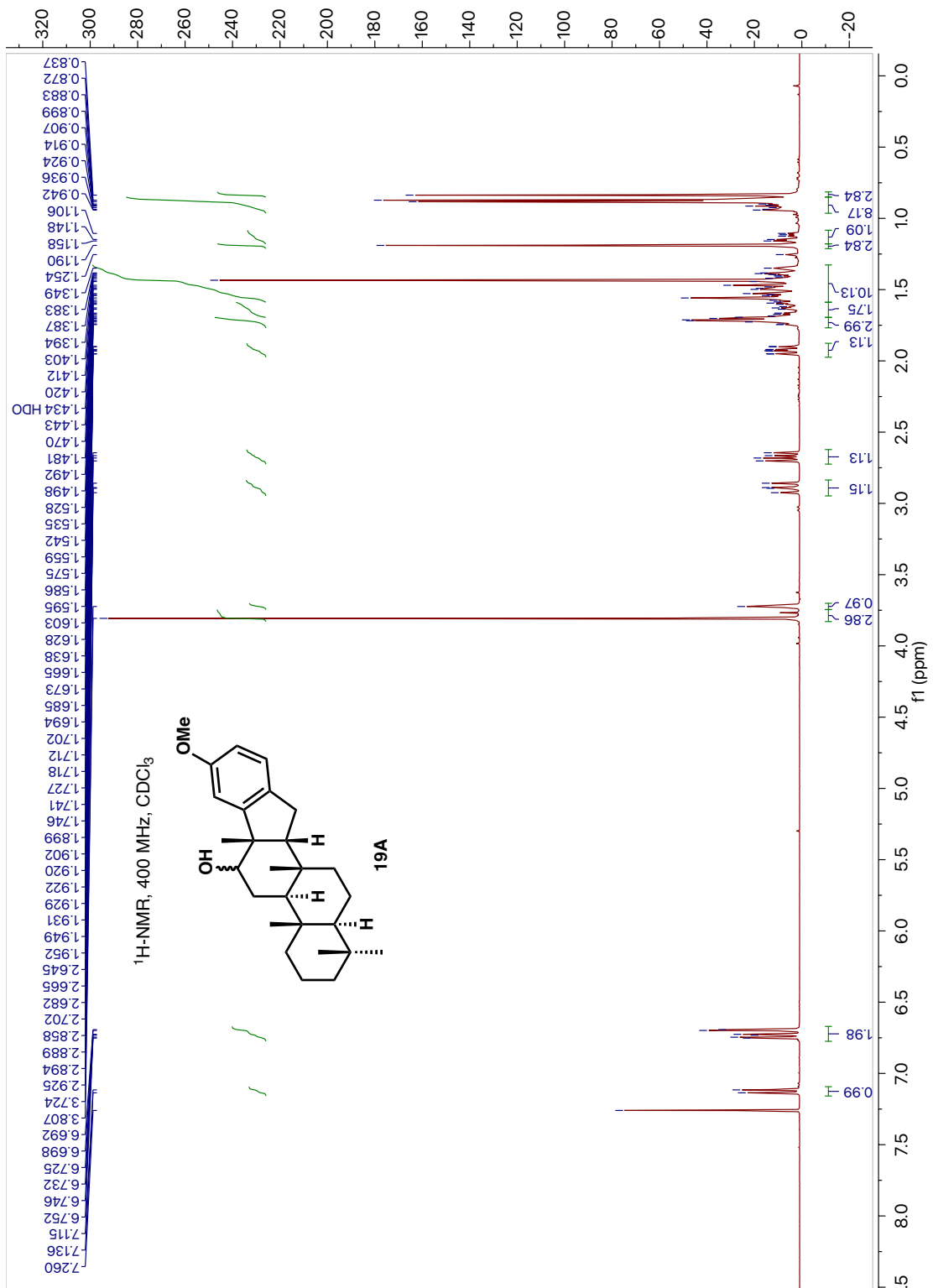
$[\alpha]_{\text{D}}^{24} +51.01$  ( $c$  1.0,  $\text{CHCl}_3$ ).

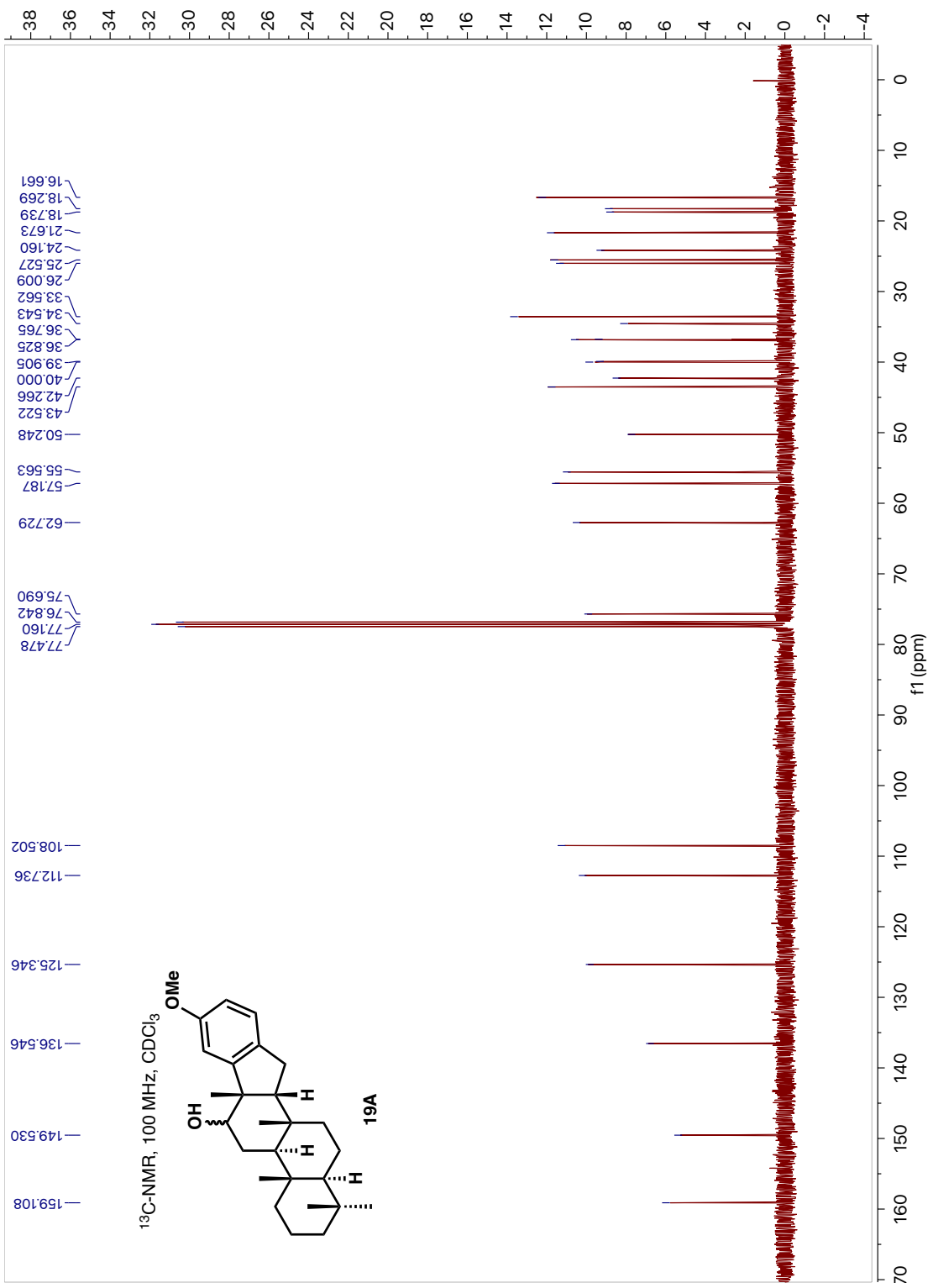
IR (KBr thin film) 3448, 2995, 2943, 2855, 1488, 1467, 1387, 1283, 1209  $\text{cm}^{-1}$ .

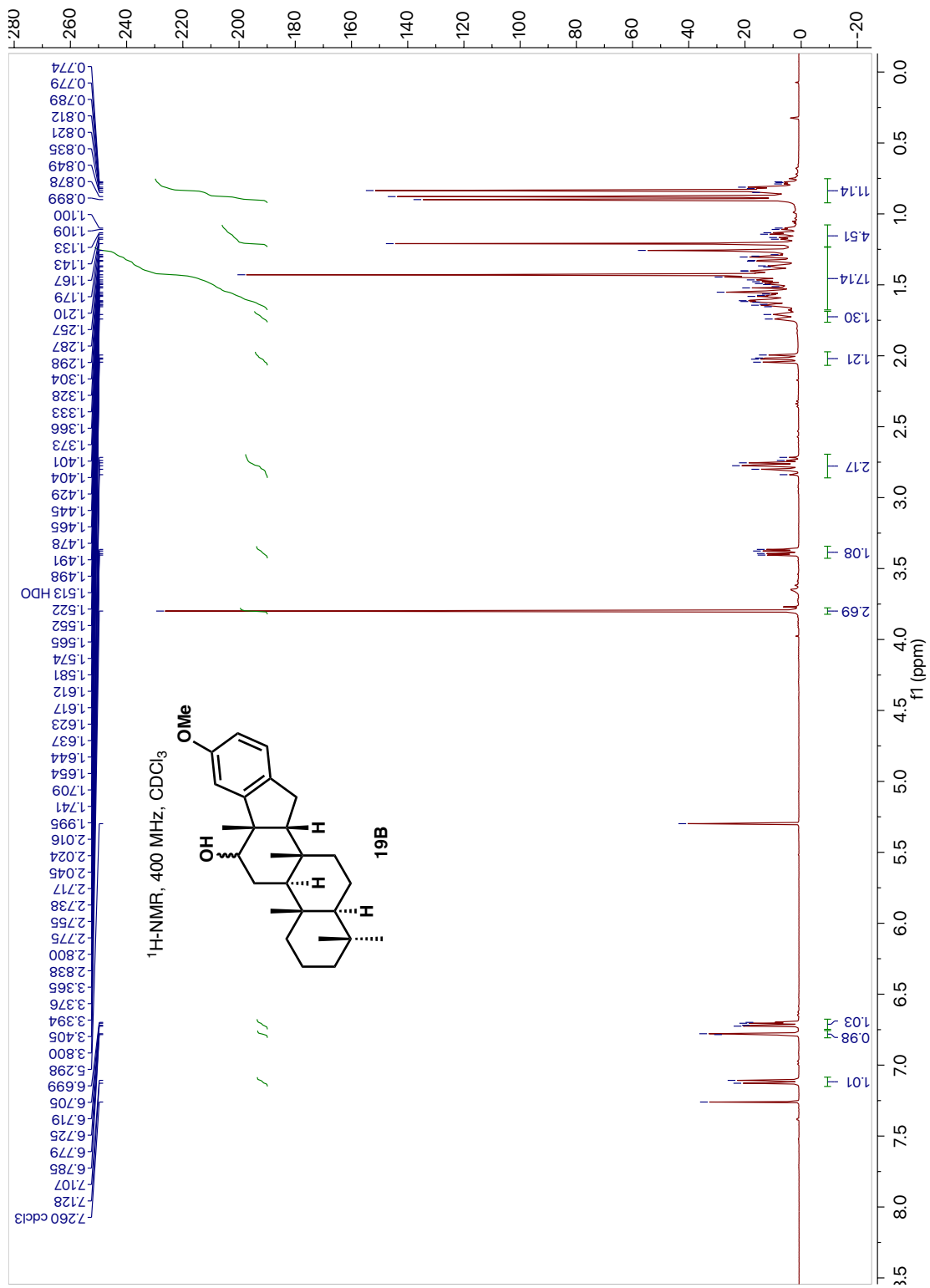
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (d, 1H,  $J = 8.0$  Hz), 6.78 (dd, 1H,  $J = 8.0, 2.4$  Hz), 6.71 (d, 1H,  $J = 2.4$  Hz), 3.80 (s, 3H), 3.39 (dd, 1H,  $J = 11.6, 4.4$  Hz), 2.84–2.72 (m, 2H), 2.02 (dd, 1H,  $J = 12.0, 8.4$  Hz), 1.75–0.84 (m, 14H), 1.43 (s, 3H), 1.21 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

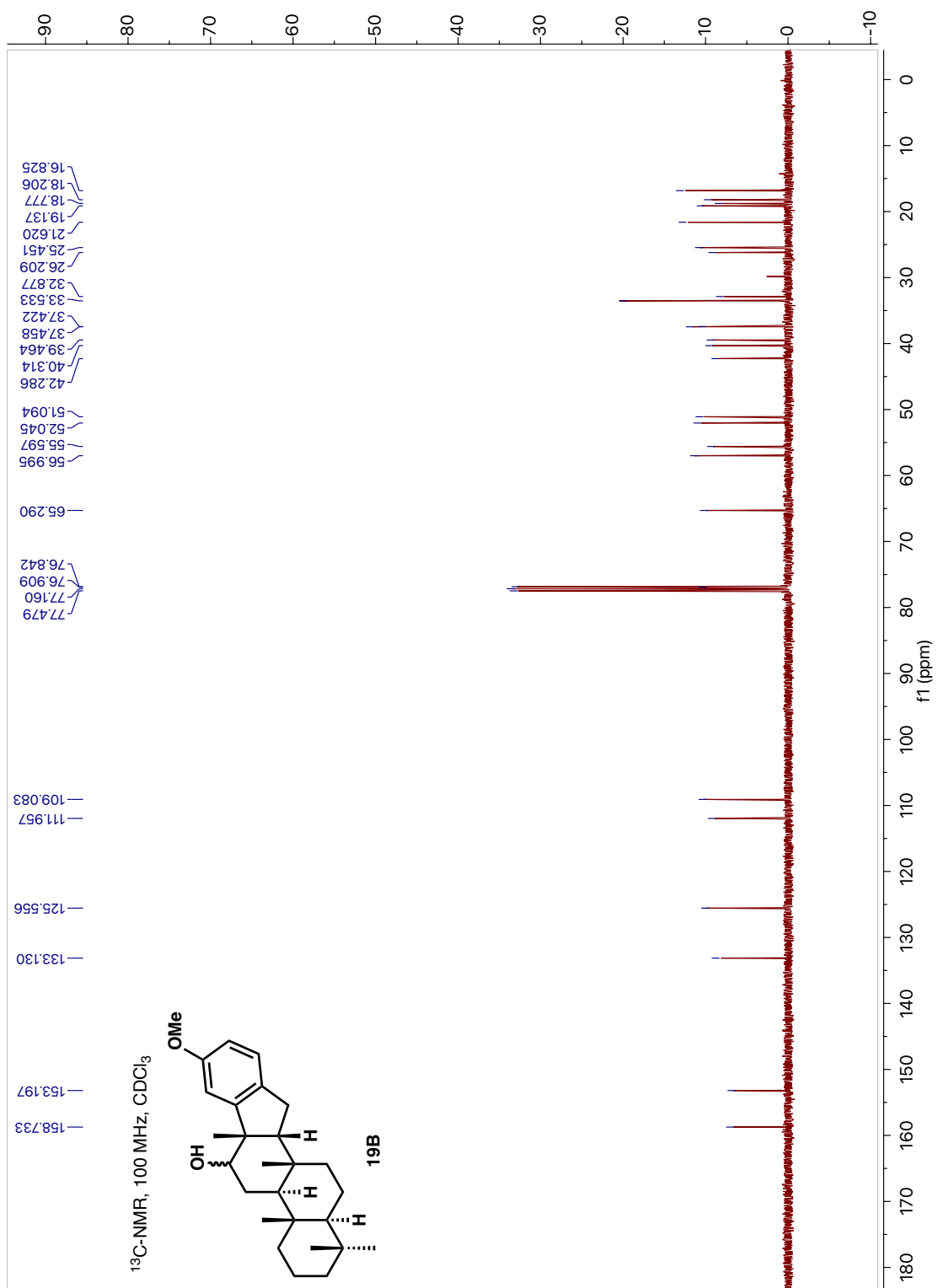
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 153.2, 133.1, 125.6, 112.0, 109.1, 76.9, 65.3, 57.0, 55.6, 52.0, 51.1, 42.3, 40.3, 39.5, 37.5, 37.4, 33.5, 33.5, 32.9, 26.2, 25.5, 21.6, 19.1, 18.8, 18.2, 16.8.

HRMS (EI)  $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{40}\text{O}_2$  396.3028, found 396.3019.



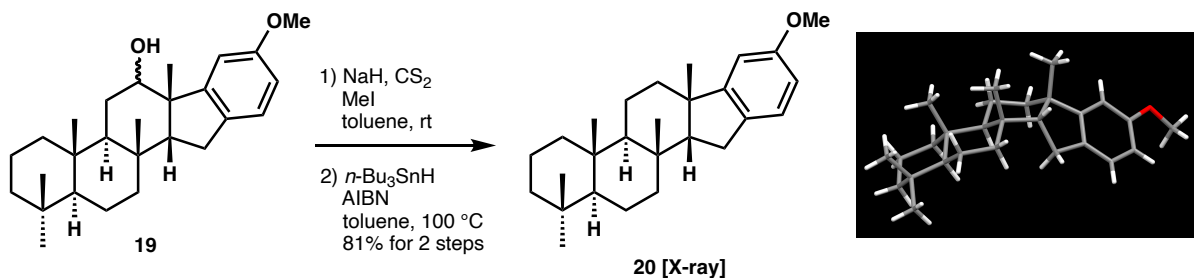








(2a*S*,6a*S*,6b*R*,8a*S*,13a*R*,13b*R*)-10-Methoxy-3,3,6a,8a,13b-pentamethyl-2,2a,3,4,5,6,6a,6b,7,8,8a,13,13a,13b-tetradecahydro-1*H*-indeno[2,1-*a*]phenanthrene (**20**)



A solution of diastereomer A of **19** (42.5 mg, 0.107 mmol) in THF (2.9 mL) was treated with NaH (55%, 37.3 mg, 0.856 mmol) at 0 °C. After stirring for 30 min at room temperature, CS<sub>2</sub> (64.5 μL, 1.07 mmol) was added to the reaction mixture at room temperature. After stirring for 2 h at room temperature, MeI (75.9 μL, 1.22 mmol) was added to the reaction mixture at room temperature. After stirring for 2 h at room temperature, the reaction mixture was quenched with *sat.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by flash silica gel column chromatography (Hexanes : EtOAc = 50 : 1) to afford crude xanthate.

A solution of the crude xanthate in toluene (7.2 mL) was treated with *n*-Bu<sub>3</sub>SnH (144 μL, 0.535 mmol) and AIBN (1.7 mg, 0.0107 mmol) at room temperature. After stirring for 40 min at 100 °C, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes) to afford **20** (27.8 mg) as a white solid.

On the other hand, a solution of diastereomer B of **19** (76.7 mg, 0.193 mmol) in THF (3.9 mL) was treated with NaH (55%, 67.2 mg, 1.54 mmol) at 0 °C. After stirring for 30 min at room temperature, CS<sub>2</sub> (117 μL, 1.93 mmol) was added to the reaction mixture at room temperature. After stirring for 2 h at room temperature, MeI (144 μL, 2.32 mmol) was added to the reaction mixture at room temperature. After stirring for 2 h at room temperature, the reaction mixture was quenched with *sat.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> *aq.*. After extraction with EtOAc, the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was semi-purified by flash silica gel column chromatography (Hexanes : EtOAc = 75 : 1) to afford crude xanthate.

A solution of the crude xanthate in toluene (9.7 mL) was treated with *n*-Bu<sub>3</sub>SnH (259 μL, 0.965 mmol) and AIBN 3.2 mg, 0.0193 mmol) at room temperature. After stirring for 1 h at 100 °C, the

reaction mixture was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes) to afford **20** (64.7 mg) as a white solid.

After combining each compound **20** (92.5 mg, 0.243 mmol) from diastereomers A and B of **19**, the total yield was 81% in 2 steps.

**Rf:** 0.57 (Hexanes/EtOAc = 8 : 1, phosphomolybdic acid)

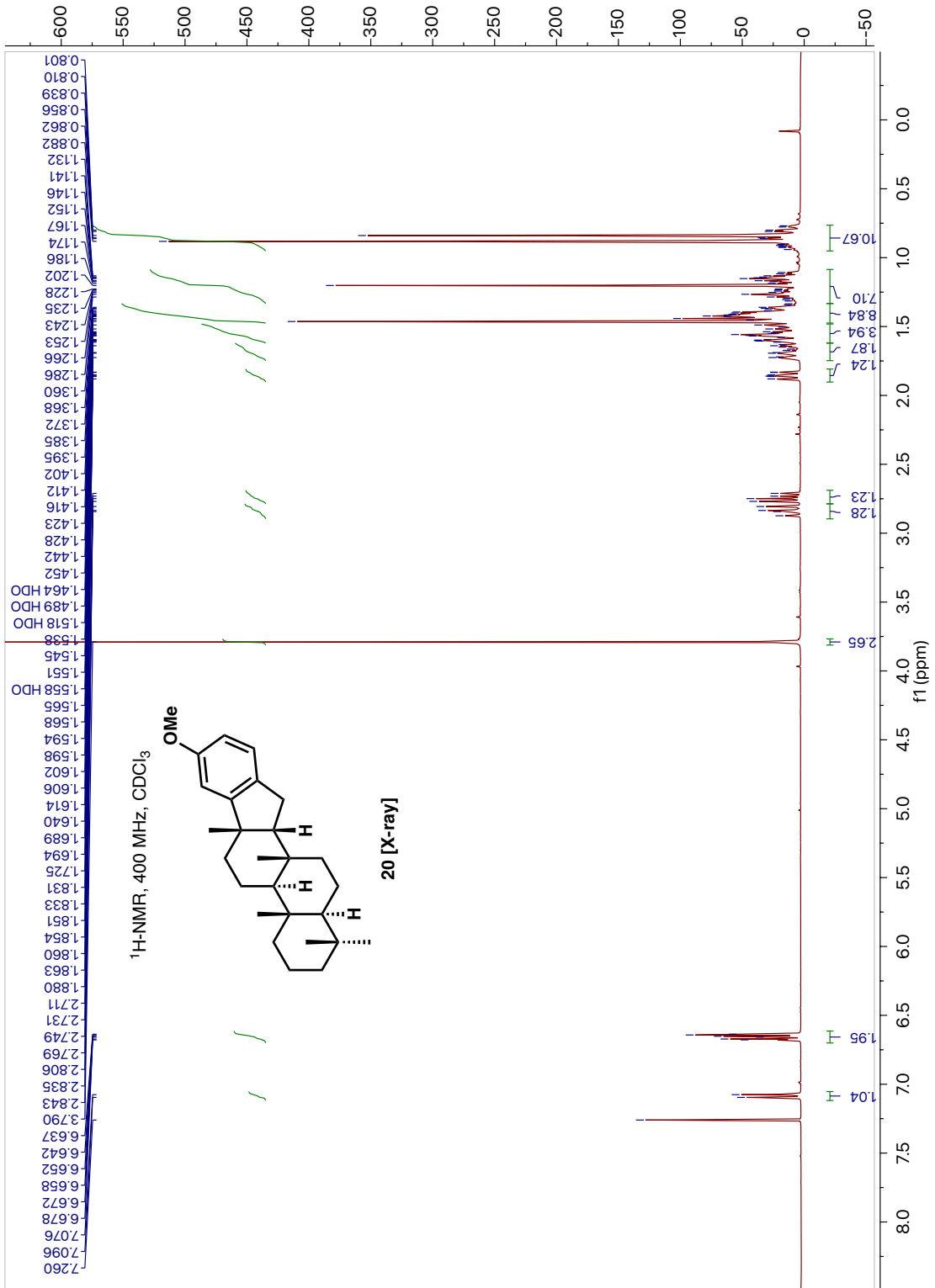
$[\alpha]_D^{25} +61.02$  (*c* 1.0, CHCl<sub>3</sub>).

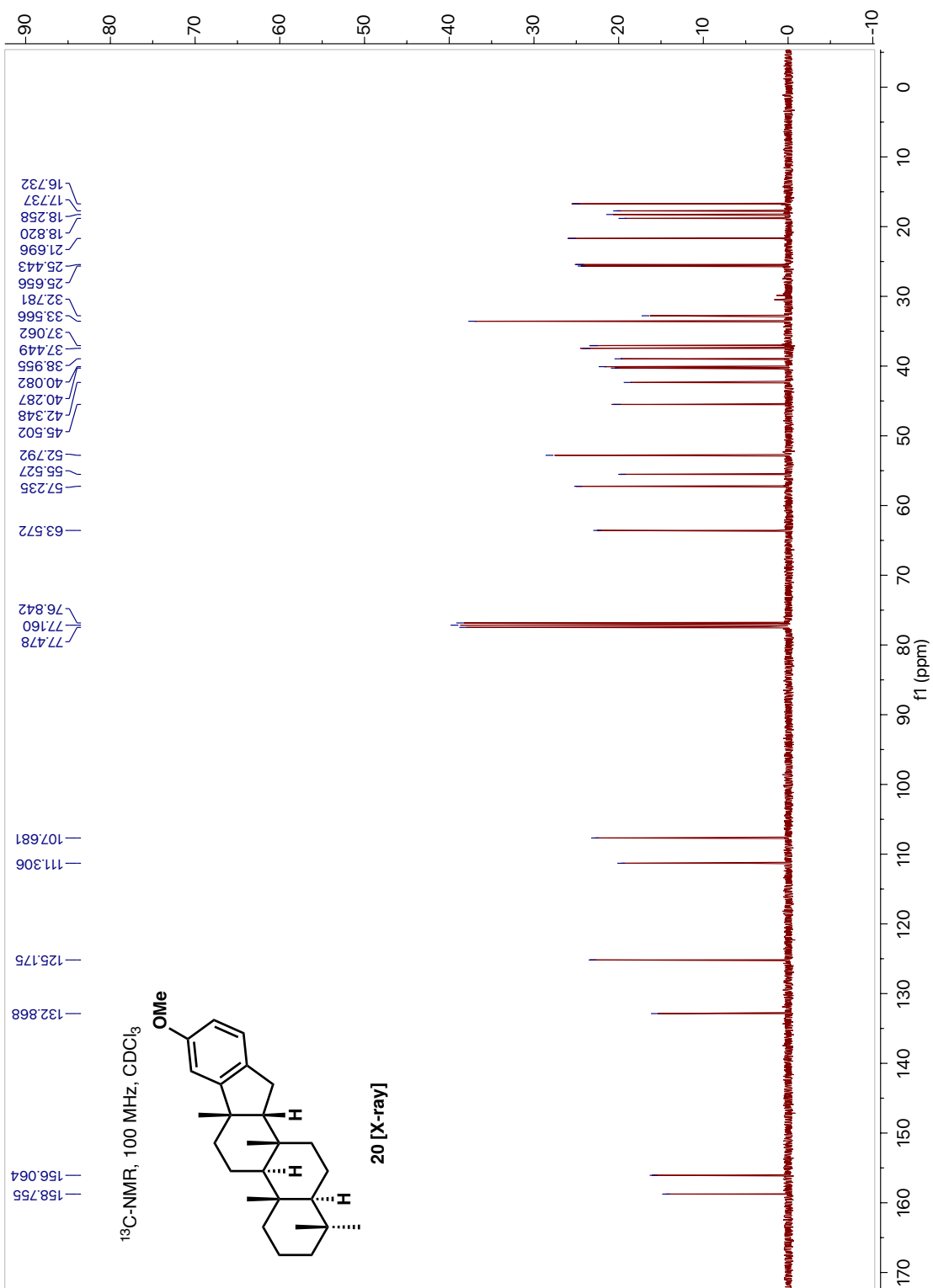
**IR (KBr thin film)** 2995, 2944, 2852, 1493, 1465, 1386, 1283, 1220 cm<sup>-1</sup>.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.09 (d, 1H, *J* = 8.0 Hz), 6.68–6.64 (m, 2H), 3.79 (s, 3H), 2.84 (dd, 1H, *J* = 15.2, 12.0 Hz), 2.74 (dd, 1H, *J* = 15.2, 8.4 Hz), 1.86 (dd, 1H, *J* = 12.0, 8.0 Hz), 1.73–0.77 (m, 16H), 1.47 (s, 3H), 1.20 (s, 3H), 0.88 (s, 6H), 0.84 (s, 3H).

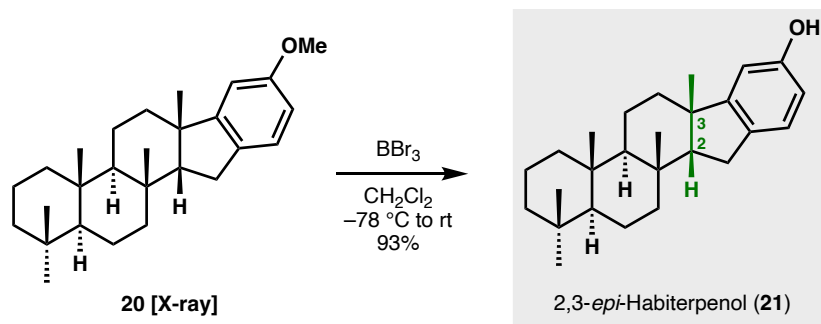
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  158.8, 156.1, 132.9, 125.2, 111.3, 107.7, 63.6, 57.2, 55.5, 52.8, 45.5, 42.3, 40.3, 40.1, 39.0, 37.4, 37.1, 33.6, 33.6, 32.8, 25.7, 25.4, 21.7, 18.8, 18.3, 17.7, 16.7.

**HRMS (EI)** [M]<sup>+</sup> calcd for C<sub>27</sub>H<sub>40</sub>O 380.3079, found 380.3076.





## 2,3-*epi*-(+)-Habiterpenol (**21**)



A solution of **20** (27.8 mg, 0.0730 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) was treated with  $\text{BBr}_3$  (292  $\mu\text{L}$ , 0.292 mmol, 1.0 M in  $\text{CH}_2\text{Cl}_2$ ) at  $-78\text{ }^\circ\text{C}$ . After stirring for 1 h at room temperature, the reaction mixture was quenched with *sat.*  $\text{NaHCO}_3$  *aq.*. After extraction with  $\text{CH}_2\text{Cl}_2$ , the combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (Hexanes/ $\text{EtOAc}$  = 50:1) to afford **21** (25.0 mg, 93%) as a colorless oil.

**Rf:** 0.30 (Hexanes/ $\text{EtOAc}$  = 8 : 1, phosphomolybdic acid)

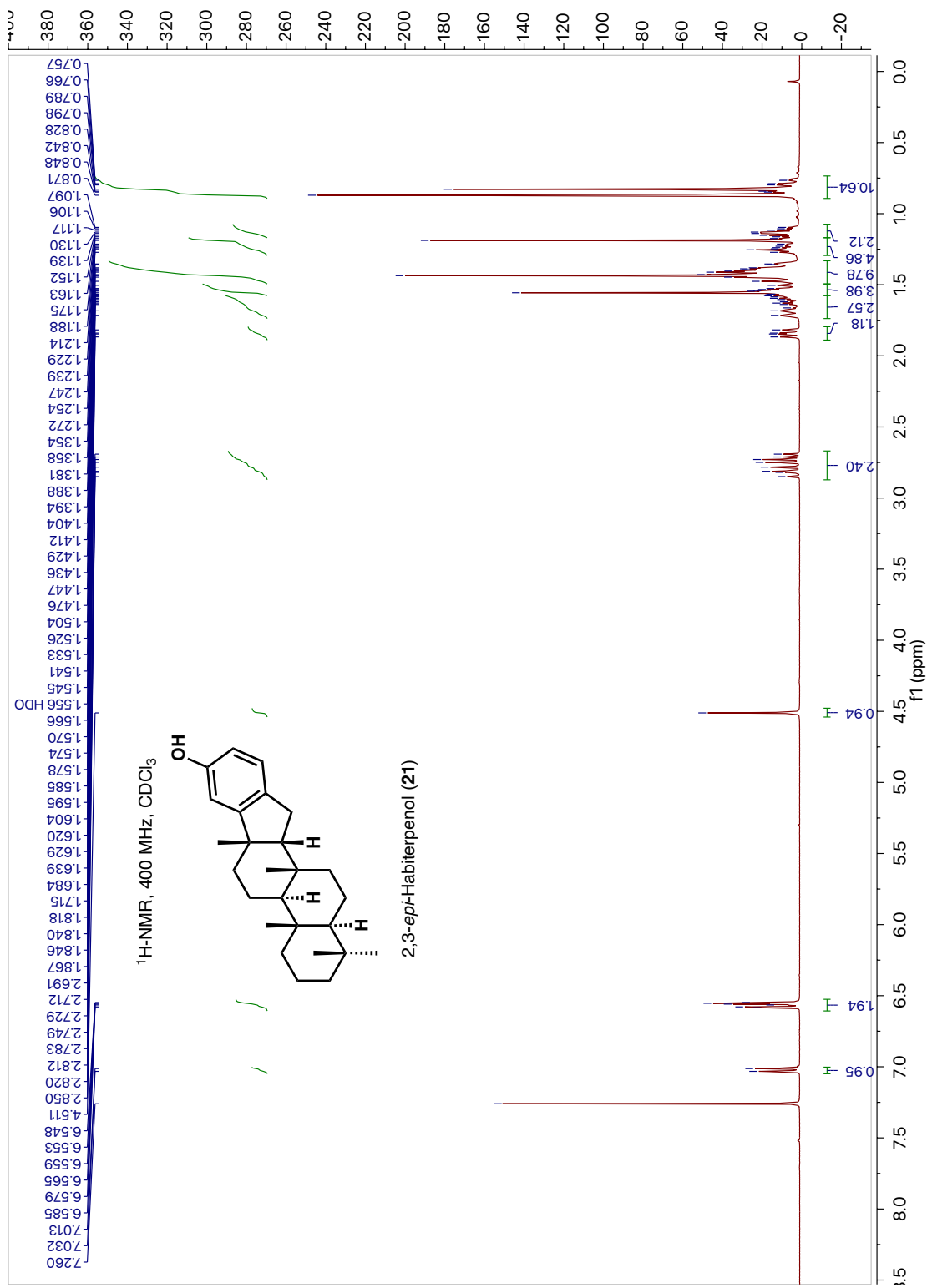
$[\alpha]_{\text{D}}^{27} +57.06$  ( $c$  1.0,  $\text{CHCl}_3$ ).

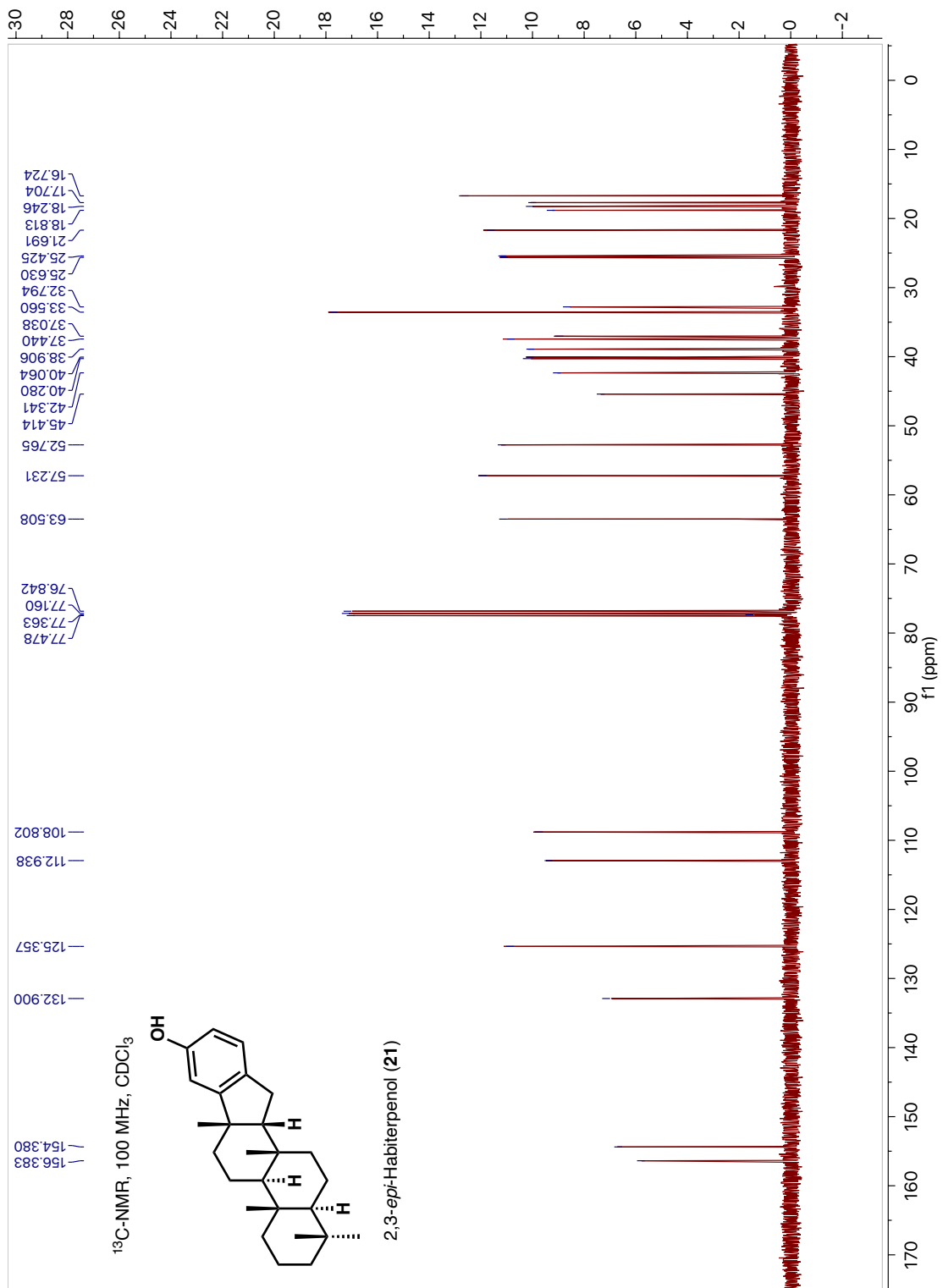
**IR (KBr thin film)** 3447, 2943, 2852, 1466, 1386, 1279  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.03 (d, 1H,  $J$  = 7.6 Hz), 6.59–6.55 (m, 2H), 4.51 (brs, 1H), 2.82 (dd, 1H,  $J$  = 15.2, 12.0 Hz), 2.73 (dd, 1H,  $J$  = 15.2, 8.0 Hz), 1.85 (dd, 1H,  $J$  = 12.0, 8.0 Hz), 1.72–0.77 (m, 16H), 1.44 (s, 3H), 1.20 (s, 3H), 0.88 (s, 6H), 0.84 (s, 3H).

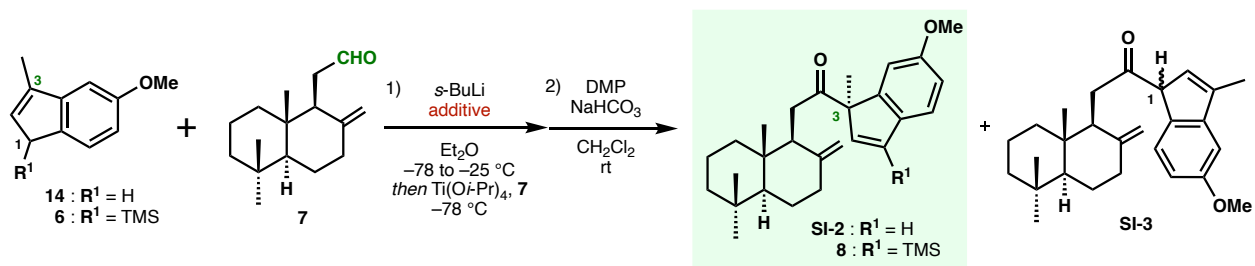
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  156.4, 154.4, 132.9, 125.4, 112.9, 108.8, 63.5, 57.2, 52.8, 45.4, 42.3, 40.3, 40.1, 38.9, 37.4, 37.0, 33.6, 33.6, 32.8, 25.6, 25.4, 21.7, 18.8, 18.2, 17.7, 16.7.

**HRMS (EI)**  $[\text{M}]^+$  calcd for  $\text{C}_{26}\text{H}_{38}\text{O}$  366.2923, found 366.2923.





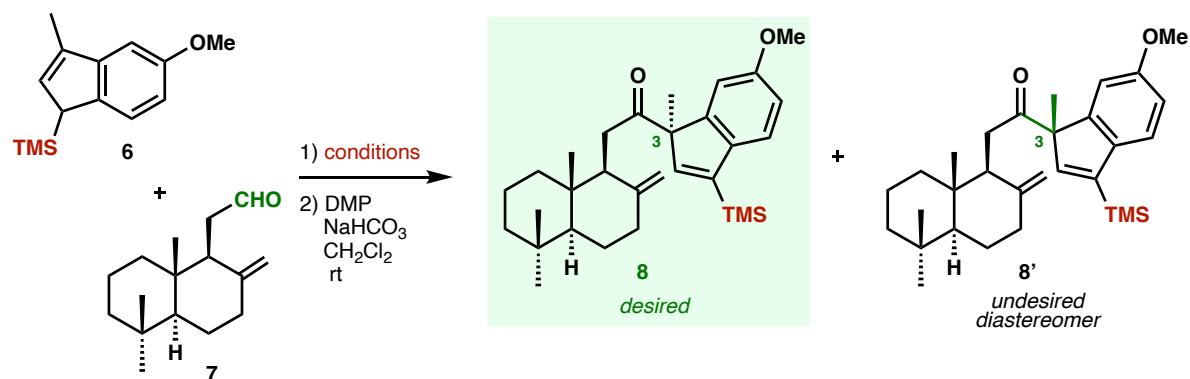
## 2. Examination of the regio- and stereoselective coupling of indenenes 14 or 6 and aldehyde 7.



entry	indene	additive	results (2 steps from 7)
1	14 (R <sup>1</sup> = H)	TMEDA	SI-2: 19% ( <i>dr</i> 1.1:1 at C3), SI-3: 34% ( <i>dr</i> 1:1 at C1)
2	14 (R <sup>1</sup> = H)	(-)-sparteine	SI-2: 42% ( <i>dr</i> 1:3.1 at C3), SI-3: 2% ( <i>dr</i> 1:1 at C1)
3	14 (R <sup>1</sup> = H)	(+)-sparteine	SI-2: 38% ( <i>dr</i> 2.5:1 at C3), SI-3: 10% ( <i>dr</i> 1:1 at C1)
-----			
4	6 (R <sup>1</sup> = TMS)	TMEDA	8: 63% ( <i>dr</i> 1.2:1 at C3)
5	6 (R <sup>1</sup> = TMS)	(-)-sparteine	8: 46% ( <i>dr</i> 1:1.6 at C3)
6	6 (R <sup>1</sup> = TMS)	(+)-sparteine	8: 50% ( <i>dr</i> 1:1 at C3)



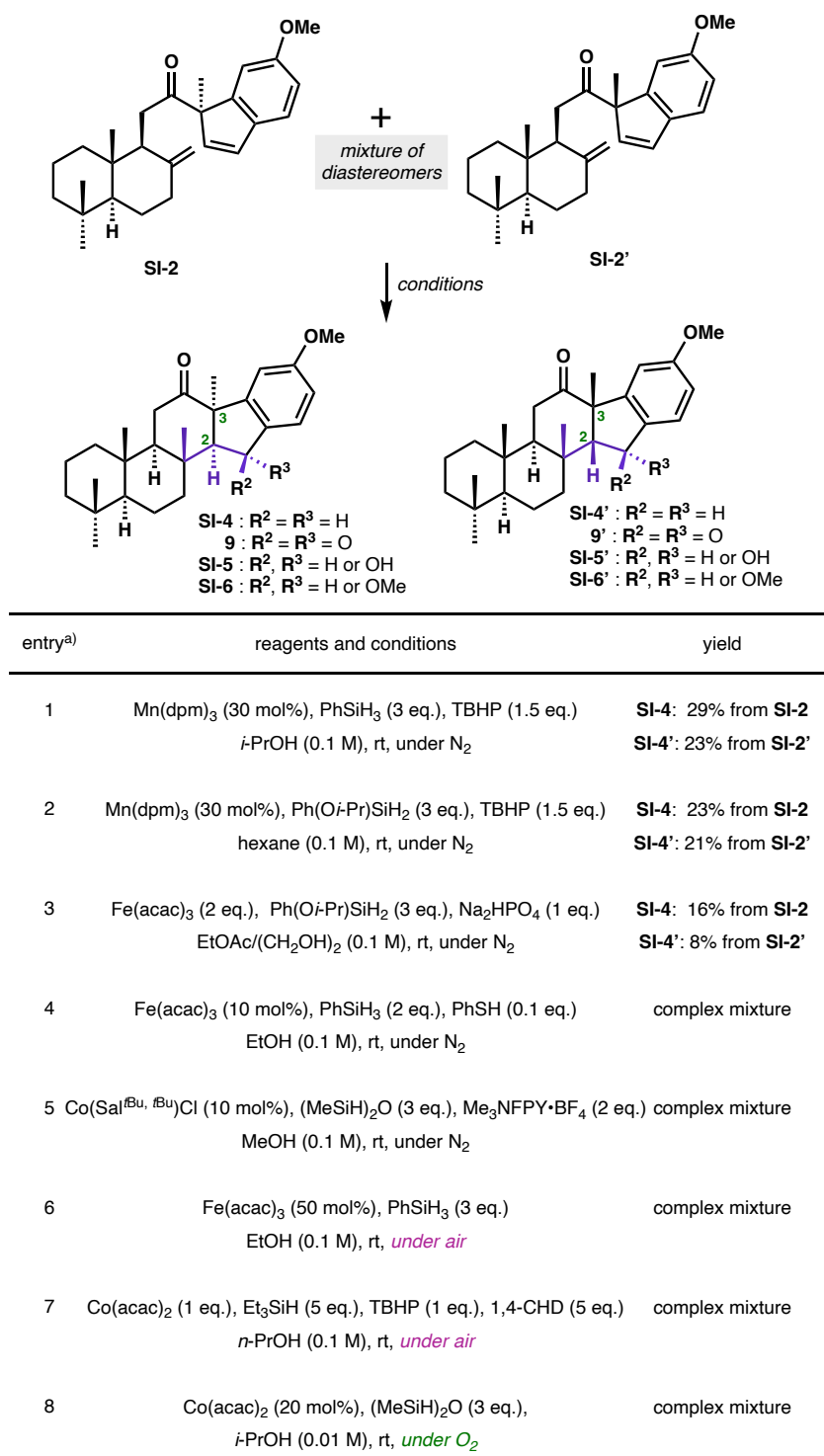
### 3. Trial for the stereoselective coupling of TMS-indene 6 and aldehyde 7.



entry	conditions	yield of <b>8</b> for 2 steps*	yield of <b>8'</b> for 2 steps*
0	<i>s</i> -BuLi, TMEDA, Et <sub>2</sub> O, -78 to 25 °C then Ti(O <i>i</i> -Pr) <sub>4</sub> , <b>7</b> , -78 °C	34%	29%
1	(-)-sparteine, <i>s</i> -BuLi, Et <sub>2</sub> O, -78 to 25 °C then Ti(O <i>i</i> -Pr) <sub>4</sub> , <b>7</b> , -78 °C	18%	28%
2	(+)-sparteine, <i>s</i> -BuLi, Et <sub>2</sub> O, -78 to 25 °C then Ti(O <i>i</i> -Pr) <sub>4</sub> , <b>7</b> , -78 °C	25%	25%
3	<i>s</i> -BuLi, TMEDA, Et <sub>2</sub> O, -78 °C then ( <i>R</i> )-BINOL-Ti, <b>7</b> , -78 °C	15%	13%
4	<i>s</i> -BuLi, TMEDA, Et <sub>2</sub> O, -78 °C then ( <i>S</i> )-BINOL-Ti, <b>7</b> , -78 °C	34%	31%
5	<i>s</i> -BuLi, TMEDA, Et <sub>2</sub> O, -78 °C then ( <i>R,R</i> )-TADDOL-Ti, <b>7</b> , -78 °C	31%	26%

\*Calculated from <sup>1</sup>H-NMR

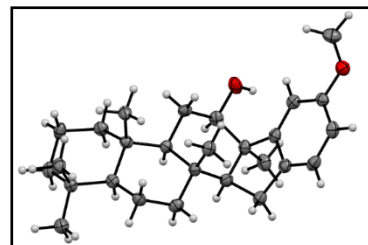
#### 4. Examination of the MHAT-initiated radical cyclization for SI-2 and SI-2'.



a) Ratio of SI-2:SI-2' as a starting material was 2.3:1.

## 5. Data for X-Ray Crystallography

### 5-1. Compound 16



#### Experimental

##### Data Collection

A colorless block crystal of  $C_{27}H_{40}O_2$  having approximate dimensions of 0.300 x 0.300 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID diffractometer using graphite monochromated Cu-K $\alpha$  radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

$$a = 11.4252(2) \text{ \AA}$$

$$b = 14.3062(3) \text{ \AA}$$

$$c = 27.6008(5) \text{ \AA}$$

$$V = 4511.37(14) \text{ \AA}^3$$

For  $Z = 8$  and F.W. = 396.61, the calculated density is 1.168 g/cm<sup>3</sup>. The reflection conditions of:

$$h00: h = 2n$$

$$0k0: k = 2n$$

$$00l: l = 2n$$

uniquely determine the space group to be:

$P2_12_12_1$  (#19)

The data were collected at a temperature of  $-180 \pm 1^\circ\text{C}$  to a maximum  $2\theta$  value of  $136.3^\circ$ . A total of 180 oscillation images were collected. A sweep of data was done using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $5.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $30.0$  [sec./ $^\circ$ ]. A second sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $5.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 90.0^\circ$ . The exposure rate was  $30.0$  [sec./ $^\circ$ ]. Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $5.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 180.0^\circ$ . The exposure rate was  $30.0$  [sec./ $^\circ$ ]. Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $5.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 270.0^\circ$ . The exposure rate was  $30.0$  [sec./ $^\circ$ ]. Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $5.00^\circ$  step, at  $\chi=0.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $30.0$  [sec./ $^\circ$ ]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

## Data Reduction

Of the 53122 reflections were collected, where 8205 were unique ( $R_{\text{int}} = 0.0585$ ); equivalent reflections were merged.

The linear absorption coefficient,  $\mu$ , for Cu-K $\alpha$  radiation is  $5.436 \text{ cm}^{-1}$ . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.789 to 0.947. The data were corrected for Lorentz and polarization effects.

## Structure Solution and Refinement

The structure was solved by direct methods <sup>S6)</sup> and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement <sup>S7)</sup> on  $F^2$  <sup>S7)</sup> was based on 8205 observed reflections and 523 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0554$$

$$wR2 = [ \Sigma ( w (F_o^2 - F_c^2)^2 ) / \Sigma w(F_o^2)^2 ]^{1/2} = 0.1396$$

The goodness of fit <sup>S8)</sup> was 1.02. Unit weights were used. Plots of  $\Sigma w (|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and  $-0.32 \text{ e}^-/\text{\AA}^3$ , respectively. The final Flack parameter <sup>S9)</sup> was 0.07(10), indicating that the present absolute structure is correct. <sup>S10)</sup>

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 <sup>S11)</sup>. Anomalous dispersion effects were included in  $F_{\text{calc}}$  <sup>S12)</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley <sup>S13)</sup>. The values for the mass attenuation coefficients are those of Creagh and Hubbell <sup>S14)</sup>. All calculations were performed using the CrystalStructure <sup>S15)</sup> crystallographic software package except for refinement, which was performed using SHELXL2013 <sup>S16)</sup>.

### **A. Crystal Data**

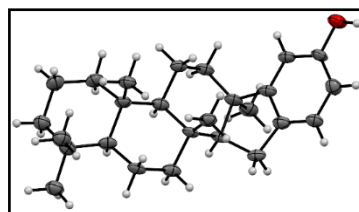
Empirical Formula	C <sub>27</sub> H <sub>40</sub> O <sub>2</sub>
Formula Weight	396.61
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.300 X 0.300 X 0.100 mm
Crystal System	orthorhombic
Lattice Type	Primitive

Lattice Parameters	a = 11.4252(2) Å
	b = 14.3062(3) Å
	c = 27.6008(5) Å
	V = 4511.37(14) Å <sup>3</sup>
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
Z value	8
D <sub>calc</sub>	1.168 g/cm <sup>3</sup>
F <sub>000</sub>	1744.00
m(CuKα)	5.436 cm <sup>-1</sup>

## 5-2. (-)-Habiterpenol (1)

### Experimental

#### Data Collection



A colorless platelet crystal of C<sub>26</sub>H<sub>38</sub>O having approximate dimensions of 0.200 x 0.100 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID diffractometer using graphite monochromated Cu-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a C-centered monoclinic cell with dimensions:

$$a = 49.6825(9) \text{ \AA}$$

$$b = 6.41808(12) \text{ \AA} \quad \beta = 95.324(7)^\circ$$

$$c = 13.2630(2) \text{ \AA}$$

$$V = 4210.86(14) \text{ \AA}^3$$

For Z = 8 and F.W. = 366.59, the calculated density is 1.156 g/cm<sup>3</sup>. Based on the reflection conditions of:

$$\text{hkl: } h+k = 2n$$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2 (#5)

The data were collected at a temperature of  $-180 \pm 1^\circ\text{C}$  to a maximum  $2\theta$  value of  $136.4^\circ$ . A total

of 90 oscillation images were collected. A sweep of data was done using  $\omega$  scans from 80.0 to 260.0° in 10.00° step, at  $\chi=54.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was 30.0 [sec./°]. A second sweep was performed using  $\omega$  scans from 80.0 to 260.0° in 10.00° step, at  $\chi=54.0^\circ$  and  $\phi = 90.0^\circ$ . The exposure rate was 30.0 [sec./°]. Another sweep was performed using  $\omega$  scans from 80.0 to 260.0° in 10.00° step, at  $\chi=54.0^\circ$  and  $\phi = 180.0^\circ$ . The exposure rate was 30.0 [sec./°]. Another sweep was performed using  $\omega$  scans from 80.0 to 260.0° in 10.00° step, at  $\chi=54.0^\circ$  and  $\phi = 270.0^\circ$ . The exposure rate was 30.0 [sec./°]. Another sweep was performed using  $\omega$  scans from 80.0 to 260.0° in 10.00° step, at  $\chi=0.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was 30.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

### Data Reduction

Of the 53122 reflections were collected, where 8205 were unique ( $R_{\text{int}} = 0.0585$ ); equivalent reflections were merged.

The linear absorption coefficient,  $\mu$ , for Cu-K $\alpha$  radiation is 5.436 cm<sup>-1</sup>. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.789 to 0.947. The data were corrected for Lorentz and polarization effects.

### Structure Solution and Refinement

The structure was solved by direct methods <sup>S6)</sup> and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement <sup>S7)</sup> on  $F^2$  <sup>S7)</sup> was based on 7211 observed reflections and 487 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0870$$

$$wR2 = [ \sum ( w (F_o^2 - F_c^2)^2 ) / \sum w(F_o^2)^2 ]^{1/2} = 0.2154$$

The goodness of fit <sup>S8)</sup> was 1.02. Unit weights were used. Plots of  $\sum w (|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.39 and -0.32 e<sup>-</sup>/Å<sup>3</sup>, respectively. The final Flack parameter <sup>S9)</sup> was 0.0(4), indicating that inversion-distinguishing power is too weak. <sup>S10)</sup> It is required to average Friedel pairs and do least-squares structure refinement again.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 <sup>S11)</sup>. Anomalous dispersion effects were included in  $F_{\text{calc}}$  <sup>S12)</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley <sup>S13)</sup>. The values for the mass attenuation coefficients

are those of Creagh and Hubbell <sup>S14</sup>). All calculations were performed using the CrystalStructure <sup>S15</sup>) crystallographic software package except for refinement, which was performed using SHELXL2013 <sup>S16</sup>).

### A. Crystal Data

Empirical Formula	C <sub>26</sub> H <sub>38</sub> O
Formula Weight	366.59
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.200 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 49.6825(9) Å b = 6.41808(12) Å c = 13.2630(2) Å β = 95.324(7) ° V = 4210.86(14) Å <sup>3</sup>
Space Group	C2 (#5)
Z value	8
D <sub>calc</sub>	1.156 g/cm <sup>3</sup>
F <sub>000</sub>	1616.00
m(CuKα)	5.071 cm <sup>-1</sup>

### 5-3. Compound 20

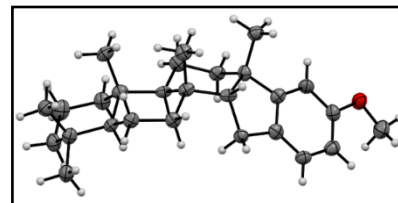
#### Experimental

##### Data Collection

A colorless needle crystal of C<sub>27</sub>H<sub>40</sub>O having approximate dimensions of 0.300 x 0.100 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis RAPID diffractometer using graphite monochromated Cu-Kα radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive



monoclinic cell with dimensions:

$$a = 13.3948(3) \text{ \AA}$$

$$b = 6.52070(14) \text{ \AA} \quad b = 111.239(8)^\circ$$

$$c = 13.5565(3) \text{ \AA}$$

$$V = 1103.65(7) \text{ \AA}^3$$

For  $Z = 2$  and F.W. = 380.61, the calculated density is  $1.145 \text{ g/cm}^3$ . Based on the reflection conditions of:

$$0k0: k = 2n$$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P2_1$  (#4)

The data were collected at a temperature of  $-180 \pm 1^\circ\text{C}$  to a maximum  $2\theta$  value of  $136.4^\circ$ . A total of 45 oscillation images were collected. A sweep of data was done using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $10.0 \text{ [sec./}^\circ]$ . A second sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 90.0^\circ$ . The exposure rate was  $10.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 180.0^\circ$ . The exposure rate was  $10.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=54.0^\circ$  and  $\phi = 270.0^\circ$ . The exposure rate was  $10.0 \text{ [sec./}^\circ]$ . Another sweep was performed using  $\omega$  scans from  $80.0$  to  $260.0^\circ$  in  $20.00^\circ$  step, at  $\chi=0.0^\circ$  and  $\phi = 0.0^\circ$ . The exposure rate was  $10.0 \text{ [sec./}^\circ]$ . The crystal-to-detector distance was  $127.40 \text{ mm}$ . Readout was performed in the  $0.100 \text{ mm}$  pixel mode.

#### Data Reduction

Of the 12436 reflections were collected, where 3832 were unique ( $R_{\text{int}} = 0.0552$ ); equivalent reflections were merged.

The linear absorption coefficient,  $\mu$ , for Cu-K $\alpha$  radiation is  $5.002 \text{ cm}^{-1}$ . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.731 to 0.951. The data were corrected for Lorentz and polarization effects.

#### Structure Solution and Refinement

The structure was solved by direct methods <sup>S6)</sup> and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement <sup>S7)</sup> on  $F$  <sup>S7)</sup> was based on 8205 observed reflections and 523 variable parameters and converged (largest parameter shift was 0.00 times its



esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0707$$

$$wR2 = [ \Sigma ( w (F_o^2 - F_c^2)^2 ) / \Sigma w(F_o^2)^2 ]^{1/2} = 0.1614$$

The goodness of fit <sup>S8)</sup> was 1.05. Unit weights were used. Plots of  $\Sigma w (|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.25 and -0.23  $e^-/\text{\AA}^3$ , respectively. The final Flack parameter <sup>S9)</sup> was 0.5(3), indicating that inversion-distinguishing power is too weak. <sup>S10)</sup> It is required to average Friedel pairs and do least-squares structure refinement again.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 <sup>S11)</sup>. Anomalous dispersion effects were included in  $F_{calc}$  <sup>S12)</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley <sup>S13)</sup>. The values for the mass attenuation coefficients are those of Creagh and Hubbell <sup>S14)</sup>. All calculations were performed using the CrystalStructure <sup>S15)</sup> crystallographic software package except for refinement, which was performed using SHELXL2013 <sup>S16)</sup>.

#### A. Crystal Data

Empirical Formula	C <sub>27</sub> H <sub>40</sub> O
Formula Weight	380.61
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.300 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 13.3948(3) Å b = 6.52070(14) Å c = 13.5565(3) Å β = 111.239(8) ° V = 1103.65(7) Å <sup>3</sup>
Space Group	P2 <sub>1</sub> (#4)
Z value	2
D <sub>calc</sub>	1.145 g/cm <sup>3</sup>
F <sub>000</sub>	420.00
m(CuKα)	5.002 cm <sup>-1</sup>

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$$[S_w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$
  
where:  $N_o$  = number of observations  
 $N_v$  = number of variables
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