Supporting Information

Sequential Pericyclic Reaction of Ene-diallenes: An Efficient Approach to the Steroid Skeleton

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General. Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^{1}H NMR spectra were taken in $CDCl_3$. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group was used as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230-400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4. PhSCl was prepared by literature procedure[1] and stored in the freezer.

General Procedure for the Pericyclic Reaction of 10a-c with PhSCl. To a solution of **10** (0.100 mmol) and Et_3N (0.10 mL, 0.70 mmol) in THF (8.5 mL) was gradually added a solution of PhSCl (86.5 mg, 0.600 mmol) in THF (1.5 mL) at room temperature, and the mixture was stirred for 1 h at that temperature and for 15 h at refluxing temperature. The reaction was quenched with water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt to afford the crude sulfoxide. To a solution of the sulfoxide in CH_2Cl_2 (1.0 mL) was added *m*CPBA (4 eq) at room temperature. After stirring until complete disappearance of sulfoxide monitored by TLC, the reaction was quenched with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, and the mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with CH_2Cl_2 (for **11a**) or hexane–AcOEt (for **11b,c**).

Methyl (4b*R,8a*R**,9*R**)-1,4-bis(benzenesulfonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthrene-9-carboxylate (11a).** Colorless powder; m.p. 212-215 °C ($CHCl_3$–hexane); IR 1732, 1447, 1385, 1308 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.95 (1H, d, J = 8.5 Hz), 7.86-7.79 (4H, m), 7.69-7.47 (7H, m), 3.72 (3H, s), 3.68-3.40 (2H, m), 2.89 (1H, dd, J = 17.8, 12.0 Hz), 2.54 (1H, dd, J = 12.3, 0.7 Hz), 2.28 (1H, ddd, J = 11.2, 11.2, 3.6 Hz), 1.83-1.58 (3H, m), 1.43-1.09 (5H, m); ^{13}C NMR (67.8 MHz) δ 174.6, 145.4, 144.5, 142.6, 141.6, 139.5, 137.9, 133.9, 133.7, 129.3, 129.3, 128.2, 127.7, 126.3, 51.7, 45.11, 45.05, 43.9, 39.2, 31.9, 30.8, 27.1, 26.2; MS *m/z* 524 (M$^+$, 9.6). Anal. Calcd for $C_{28}H_{28}O_6S_2$: C, 64.10; H, 5.38. Found: C, 63.79; H, 5.42.

Methyl (2*E*,7*E*)-8-[3,6-bis(benzenesulfonyl)-2-methylphenyl]-2,7-octadienoate (15a). Colorless needles: m.p. 119-120 °C (CH_2Cl_2–hexane); IR 1718, 1657, 1447, 1383, 1315 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.31 (2H, s), 7.87-7.83 (2H, m), 7.74-7.70 (2H, m), 7.69-7.44 (6H, m), 6.92 (1H, td, J = 15.8, 6.9 Hz), 6,26 (1H, d, J = 16.5 Hz) 5.81 (1H, td, J = 15.8, 1.7 Hz), 5.13 (1H, td, *J* = 16.5, 6.6 Hz), 3.74 (3H, s), 2.33 (3H, s), 2.24-2.15 (2H, m), 2.08-2.00 (2H, m), 1.52-1.41 (2H, m); ^{13}C NMR (67.8 MHz) δ 166.9, 148.5, 144.3, 143.9, 141.0, 140.7, 140.0, 139.0, 138.5, 133.6, 133.4, 129.3, 128.8, 128.3, 127.9, 127.8, 126.6, 123.7, 121.4, 51.4, 32.4, 31.5, 26.6, 17.5. Anal. Calcd for $C_{28}H_{28}O_6S_2$: C, 64.10; H, 5.38. Found: C, 63.82; H, 5.39.

(4b*R,8a*S**)-1,4-Bis(benzenesulfonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (11b).** Colorless powder: m.p. 186-188 °C ($CHCl_3$–hexane); IR 1448, 1385, 1308 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.94-7.82 (5H, m), 7.66-7.35 (7H, m), 3.33-3.26 (1H, m), 3.21-3.15 (1H, m), 2.73-2.62 (1H, m), 2.55-2.50 (1H, m), 1.85-1.54 (4H, m), 1.39-1.05 (6H, m); ^{13}C NMR (67.8 MHz) δ 145.9, 145.6, 142.5, 141.9, 140.6, 140.0, 133.6, 133.5, 129.3, 129.2, 128.8, 128.0, 127.7, 126.0, 45.4, 42.9, 38.9, 34.0, 29.2, 27.8, 27.4, 26.6; MS *m/z* 466 (M$^+$, 41.3). Anal. Calcd for $C_{26}H_{26}O_4S_2$: C, 66.92; H, 5.62. Found: C, 66.78; H, 5.72.

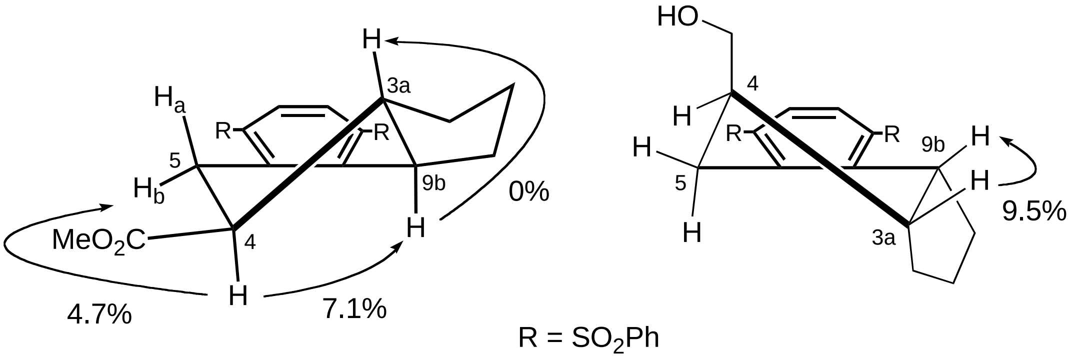
(6*E*)-7-[2,5-Bis(benzenesulfonyl)-6-methylphenyl]-1,2-epoxy-6-heptene (15b). Colorless oil: IR 1448, 1315 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.30 (2H, s), 7.88-7.84 (2H, m), 7.76-7.72 (2H, m), 7.66-7.45 (6H, m), 6.27 (1H, d, *J* = 16.5 Hz), 5.16 (1H, td, *J* = 16.5, 6.6 Hz), 2.90-2.86 (1H, m), 2.75 (1H, dd, *J* = 4.9, 3.9 Hz), 2.45 (1H, dd, *J* = 4.9, 2.6 Hz), 2.33 (3H, s), 2.10-2.04 (2H, m), 1.59-1.41 (4H, m); ^{13}C NMR (67.8 MHz) δ 144.4, 143.9, 141.1, 140.8, 140.1, 139.3, 138.6, 133.6, 133.3, 129.3, 128.8, 128.0, 127.9, 127.8, 126.6, 123.5, 51.9, 46.9, 32.8, 32.0, 24.8, 17.5; FAB MS *m/z* 483 (M$^+$+1, 13.7). FABHRMS calcd for $C_{26}H_{27}O_5S_2$ 483.1299, found 483.1306.

Reaction of 10c. According to the general procedure, reaction of **10c** was performed. The crude oxidation product was passed through a short pad of silica gel with hexane–AcOEt (1:1) to afford a mixture of *trans*-**11c**, *cis*-**11c**, and **15c**. The product ratio was determined by HPLC analysis: KANTO CHEMICAL Mightysil Si 60 250–4.6 (5 μm), hexane:AcOEt =2:1, 1.0 mL/min, t_R = 9.6 min (*trans*-**11c**), t_R = 10.7 min (*cis*-**11c**), t_R = 11.5 min (**15c**). Chromatography of the mixture with $CHCl_3$–hexane–*i*-Pr_2O (30:1:1) afforded pure *trans*-**11c** and a mixture of *cis*-**11c** and **15c**. A mixture of *cis*-**11c** and **15c** was treated with DIBAL-H in THF at –78 °C for 1 h to give the crude alcohols. Chromatography of the crude alcohols with CH_2Cl_2–Et_2O (10:1) afforded *cis*-**11c'** and **15c'**. The stereochemistries of *trans*-**11c** and *cis*-**11c'** were verified by diagnostic ^{1}H NOE correlation shown in Figure 1.

Methyl (3a*R,4*R**,9b*R**)-6,9-bis(benzenesulfonyl)-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene-4-carboxylate (*trans*-11c).** Colorless powder: m.p. 196-198 °C ($CHCl_3$–hexane); IR 1732, 1447, 1445, 1383, 1308 cm^{-1}; ^{1}H NMR (270 MHz, [D6]acetone) δ 8.23 (1H, d, *J* = 8.6 Hz), 8.02-7.72 (11H, m), 3.80 (3H, s), 3.53 (1H, dd, *J* = 18.2, 5.6 Hz, C5-Hb), 3.38 (1H, dd, *J* = 18.2, 11.2 Hz, C5-Ha), 3.24-3.13 (1H, m, C9b-H), 3.07-2.96 (1H, m), 2.69 (1H, ddd, *J* = 11.2, 11.2, 5.6 Hz, C4-H), 1.90-1.25 (6H, m); ^{13}C NMR (67.8 MHz, [D6]acetone) δ 174.9, 146.3, 144.2, 143.5, 142.2, 139.4, 134.8, 134.7, 130.4, 129.0, 128.9, 128.5, 128.0, 51.9, 47.7, 47.4, 43.4, 33.1, 32.4, 27.8, 22.4; MS *m/z* 510 (M^+, 3.1). Anal. Calcd for $C_{27}H_{26}O_6S_2$: C, 63.51; H, 5.13. Found: C, 63.29; H, 5.02.

(3a*R,4*S**,9b*S**)-6,9-Bis(benzenesulfonyl)-4-hydroxymethyl-2,3,3a,4,5,9b-hexahydro-1*H*-benz[*e*]indene (*cis*-11c').** Colorless solid: m.p. 149-151 °C ($CHCl_3$–hexane); IR 3537, 1448, 1398, 1308, 1223 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 8.04 (1H, d, *J* = 8.5Hz), 7.95 (1H, d, *J* = 8.5 Hz), 7.70-7.62 (4H, m), 6.92-6.80 (6H, m), 3.83 (1H, dd, *J* = 19.5, 8.8 Hz, C9b-H), 3.72 (1H, dd, *J* = 15.9, 2.7 Hz, C5-H), 2.86-2.85 (1H, m, C*H*HOH), 2.58-2.53 (1H, m, CH*H*OH), 2.25 (1H, dd, *J* = 15.9, 4.2 Hz, C5-H), 2.08 (1H, brs, OH), 1.95-1.90 (1H, m), 1.68-1.58 (2H, m), 1.44-1.39 (1H, m, C3a-H), 1.26-1.22 (1H, m), 1.20-1.11 (1H, m), 1.04-0.97 (1H, m), 0.71-0.62 (1H, m); ^{13}C NMR (125 MHz) δ 144.8, 144.3, 143.4, 140.9, 140.0, 138.4, 133.9, 133.7, 129.5, 129.3, 127.9, 127.5, 127.3, 126.1, 64.0, 42.2, 39.6, 36.7, 35.2, 34.2, 25.5, 24.9.

(2*E*,6*E*)-7-[3,6-Bis(benzenesulfonyl)-2-methylphenyl]-2,6-heptadien-1-ol (15c'). Colorless oil: IR 3443, 1447, 1383, 1352, 1310, 1219 cm^{-1}; ^1H NMR (500 MHz) δ 8.35-8.27 (2H, m), 7.87-7.85 (2H, m), 7.75-7.74 (2H, m), 7.63-7.29 (6H, m), 6.27 (1H, d, *J* = 16.4 Hz), 5.67-5.61 (2H, m), 5.17-5.13 (1H, m), 4.10-4.07 (2H, m), 2.33 (3H, s), 2.14 2.11 (4H, m); ^{13}C NMR (125 MHz) δ 144.4, 143.9, 141.1, 140.7, 139.1, 138.7, 133.7, 133.4, 131.4, 130.0, 129.3, 128.8, 128.03, 127.95, 127.91, 127.8, 126.6, 123.6, 63.5, 32.6, 30.8, 17.6; FABMS *m/z* 505 (M^++Na, 43.6); FABHRMS calcd for $C_{26}H_{26}O_5S_2Na$ 505.1119, found 505.1123.



trans-**11c** *cis*-**11c'**

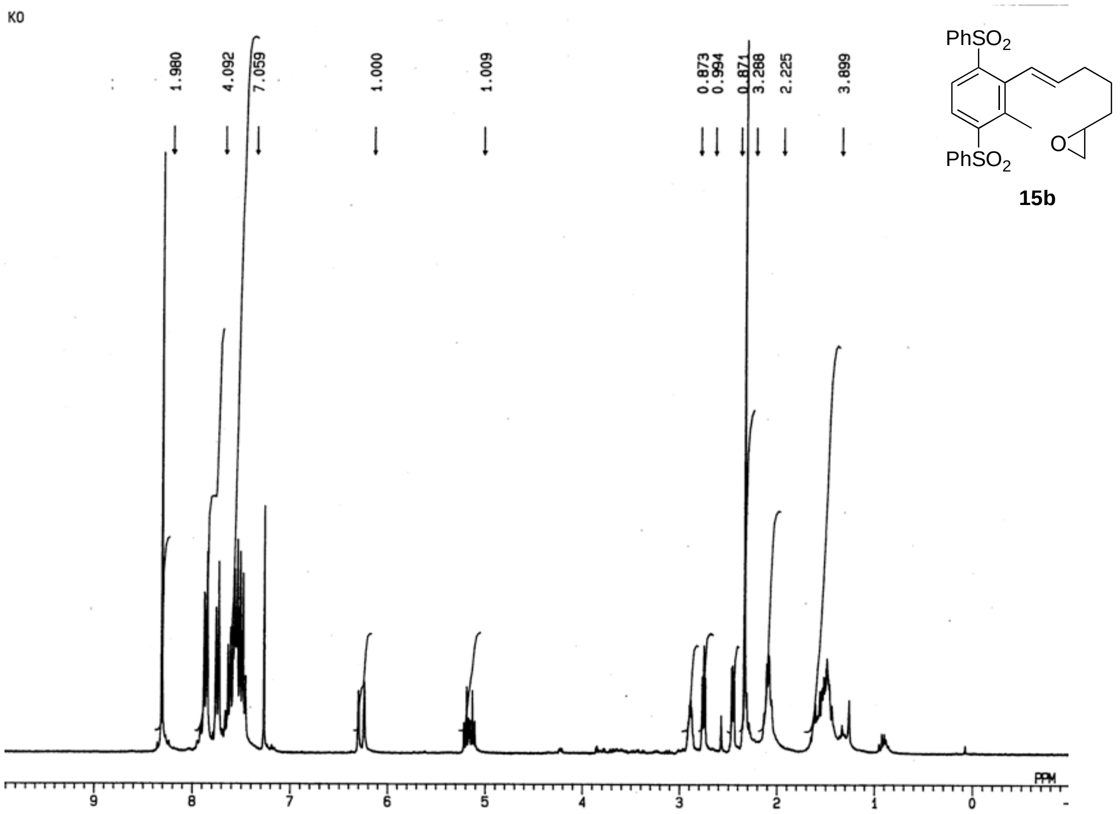
Figure 1. NOE data for *trans*-**11c** and *cis*-**11c'**

***dl*-Estra-1,3,5(10)-trien-17-one (23).** To a solution of **22** (23.2 mg, 8.10 x 10^{-2} mmol) and Et_3N (0.08 mL, 0.6 mmol) in THF (7.0 mL) was gradually added a solution of PhSCl (70.0 mg, 0.486 mmol) in THF (1.1 mL) at room temperature. After the mixture was stirred at that temperature for 0.5 h, the reaction mixture was refluxed for 17 h. The reaction was quenched with water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (1:2) to afford the crude sulfoxide. To a solution of the crude sulfoxide (26.0 mg) in THF (1.0 mL) was added Raney-Ni (W-2, excess) at room temperature. After being stirred at reflux temperature for 1 d, the mixture was filtered and concentrated to dryness. Chromatography of the residue with hexane-AcOEt (9:1) afforded **23** (6.6 mg, 32%) as a colorless solid: IR 2961, 2928, 2855, 1746 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.32-7.29 (1H, m), 7.24-7.08 (3H, m), 2.95-2.90 (2H, m), 2.51 (1H, dd, *J* = 18.4, 8.0 Hz), 2.45-2.28 (2H, m), 2.22-1.94 (4H, m), 1.68-1.30 (6H, m), 0.91 (3H, s).

Preparation of 26. To a solution of **24** (37.2 mg, 0.200 mmol) in THF (3.0 mL) were successively added dimethyl fumarate (60.0 mg, 0.420 mmol), Et_3N (0.20 mL, 1.4 mmol), and a solution of PhSCl (175 mg, 1.20 mmol) in THF (0.5 mL) at –78 °C. After being stirred for 1.5 h, the reaction mixture was allowed to warm to room temperature. After 2.5 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with CH_2Cl_2–Et_2O (10:1) to afford the crude sulfoxide (92.6 mg). To a solution of 67.9 mg of the crude sulfoxide in CH_2Cl_2 (1.2 mL) was added *m*CPBA (82.8 mg, 0.480 mmol) at 0 °C, and the reaction mixture was allowed to warm to room temperature. After 25 h, the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (2:1) gave **26** (68.5 mg, 84%) as a pale yellow solid: IR 1732, 1325, 1148 cm^{-1}; ^{1}H NMR (270 MHz) δ 9.07-8.90 (2H, m), 7.95-7.82 (4H, m), 7.66-7.42 (8H, m), 3.85-3.73 (4H, m), 3.65 (6H, s), 3.24-3.07 (2H, m); ^{13}C NMR (67.8 MHz) δ 173.8, 143.2, 140.8, 138.5, 133.3, 129.8, 129.3, 127.6, 126.1, 125.4, 52.4, 40.1, 28.2; MS *m/z* 578 (M^+, 3.9). HRMS calcd for $C_{30}H_{26}O_8S_2$ 578.1069, found 578.1064.

Reference

1) A. G. M. Barrett, D. Dhanak, G. G. Graboski, S. J. Taylor, *Org. Syn.* **1990**, *68*, 8–12.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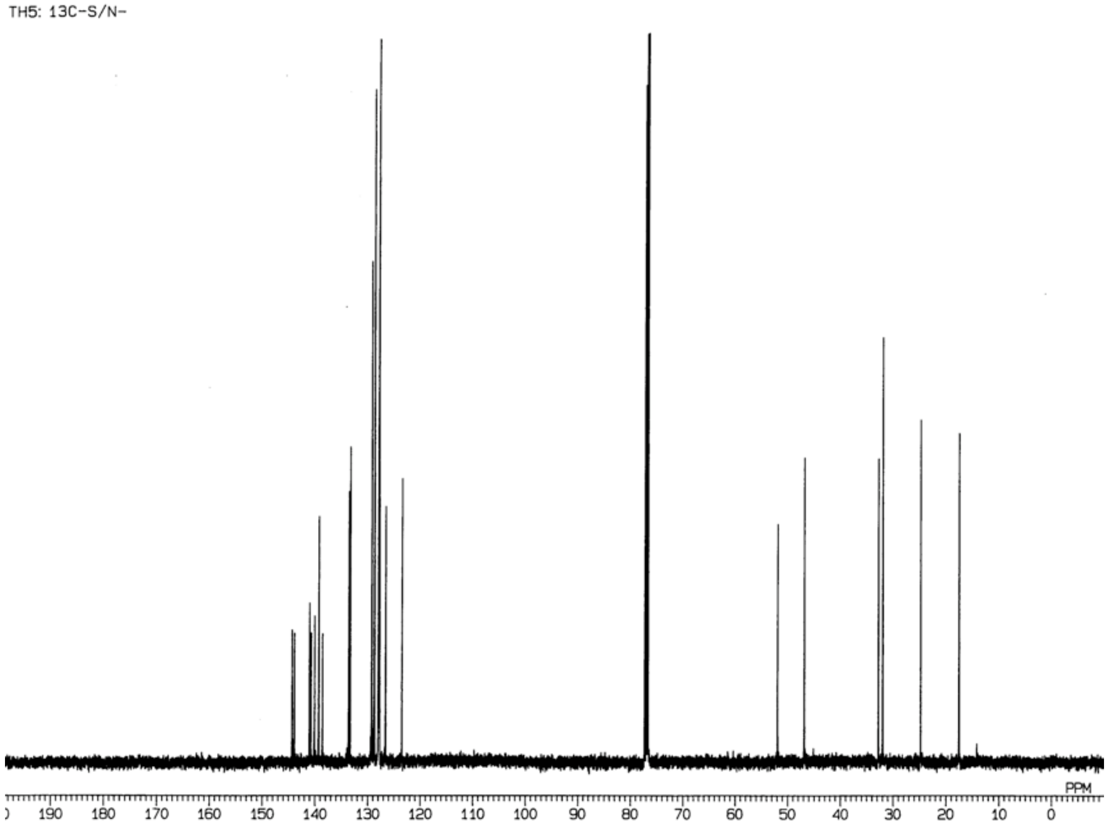
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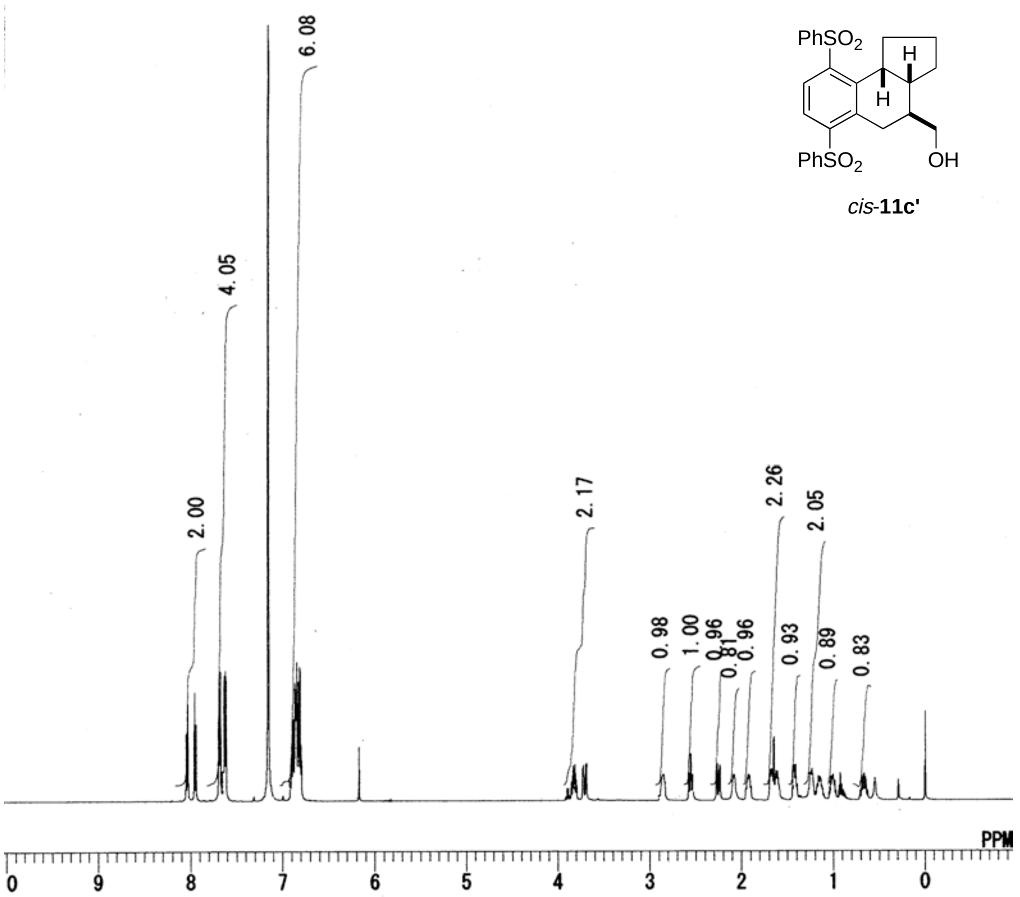
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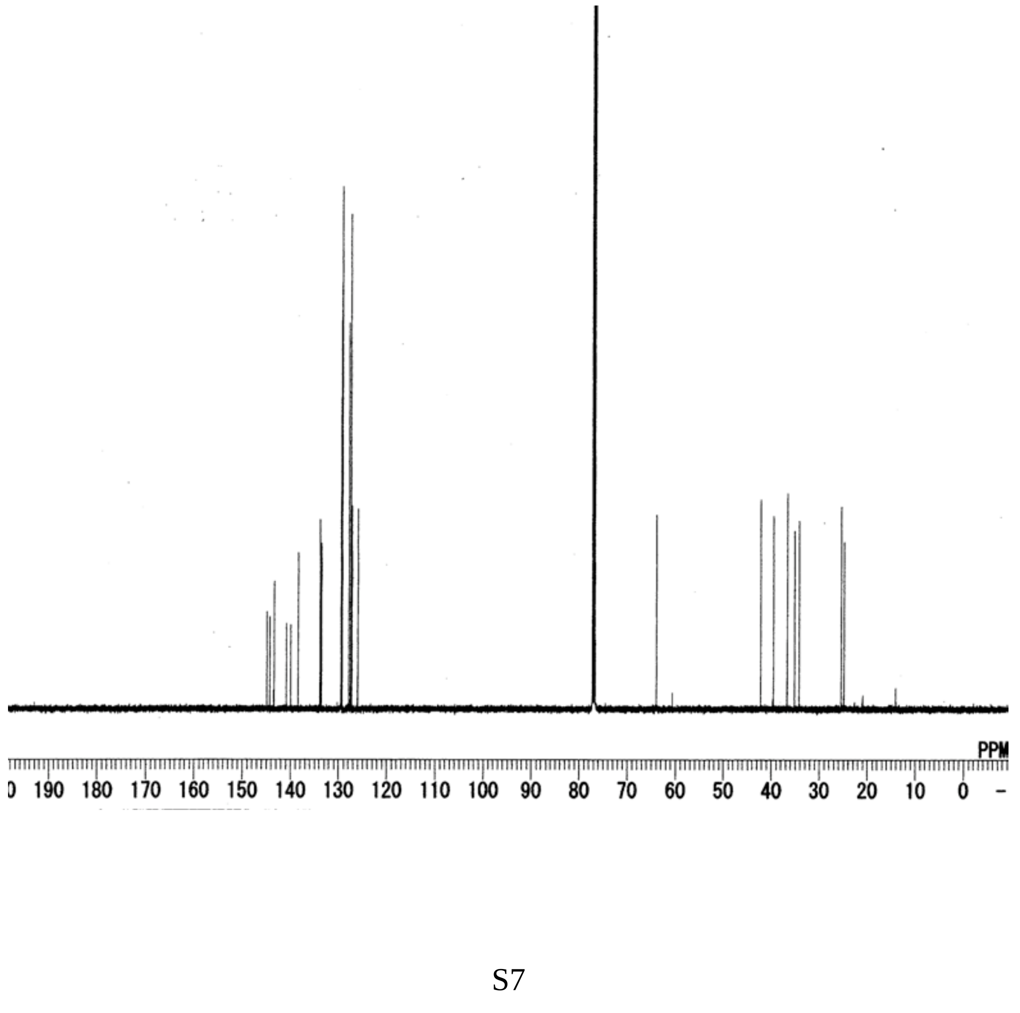
cis-**11c'**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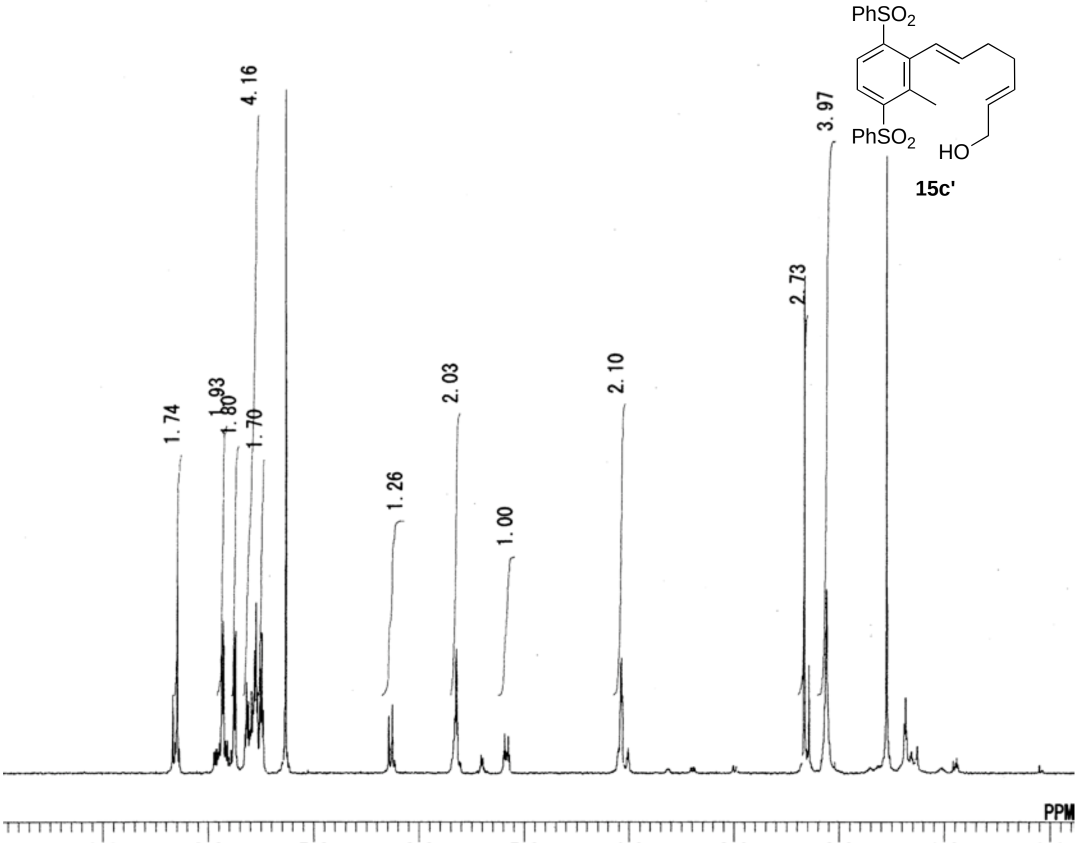

15c'

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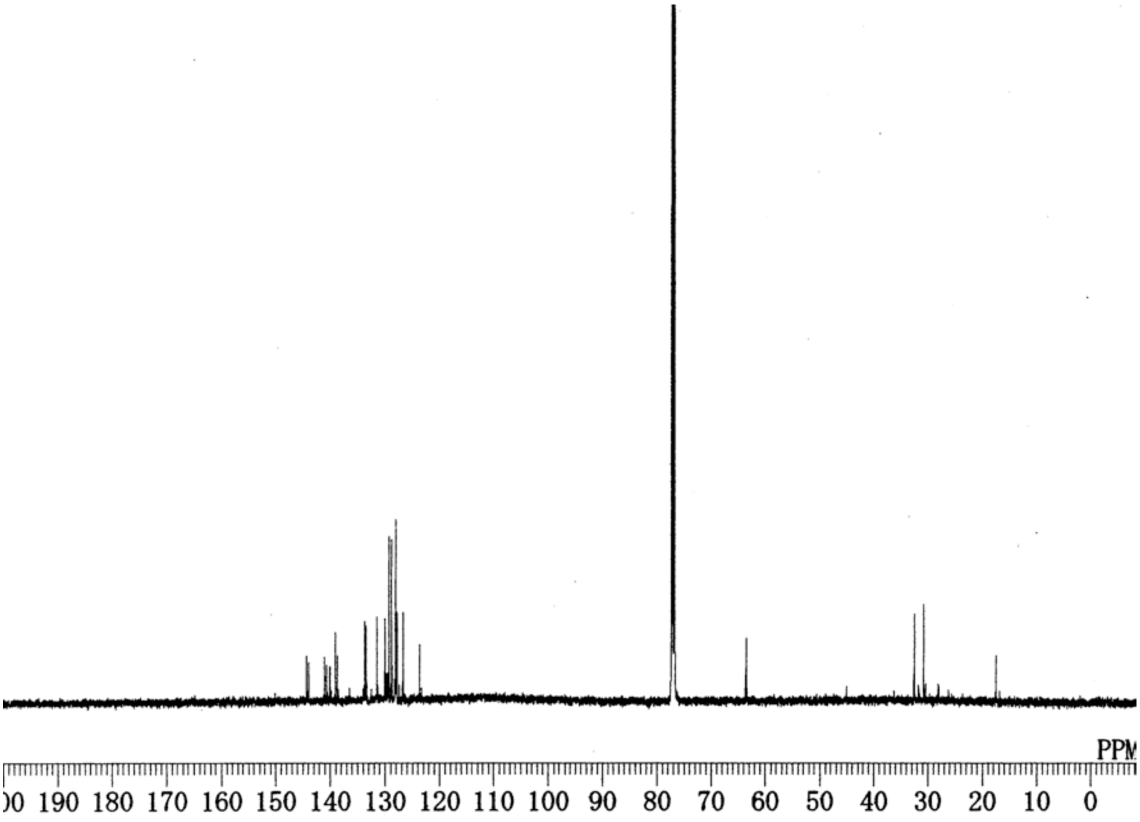

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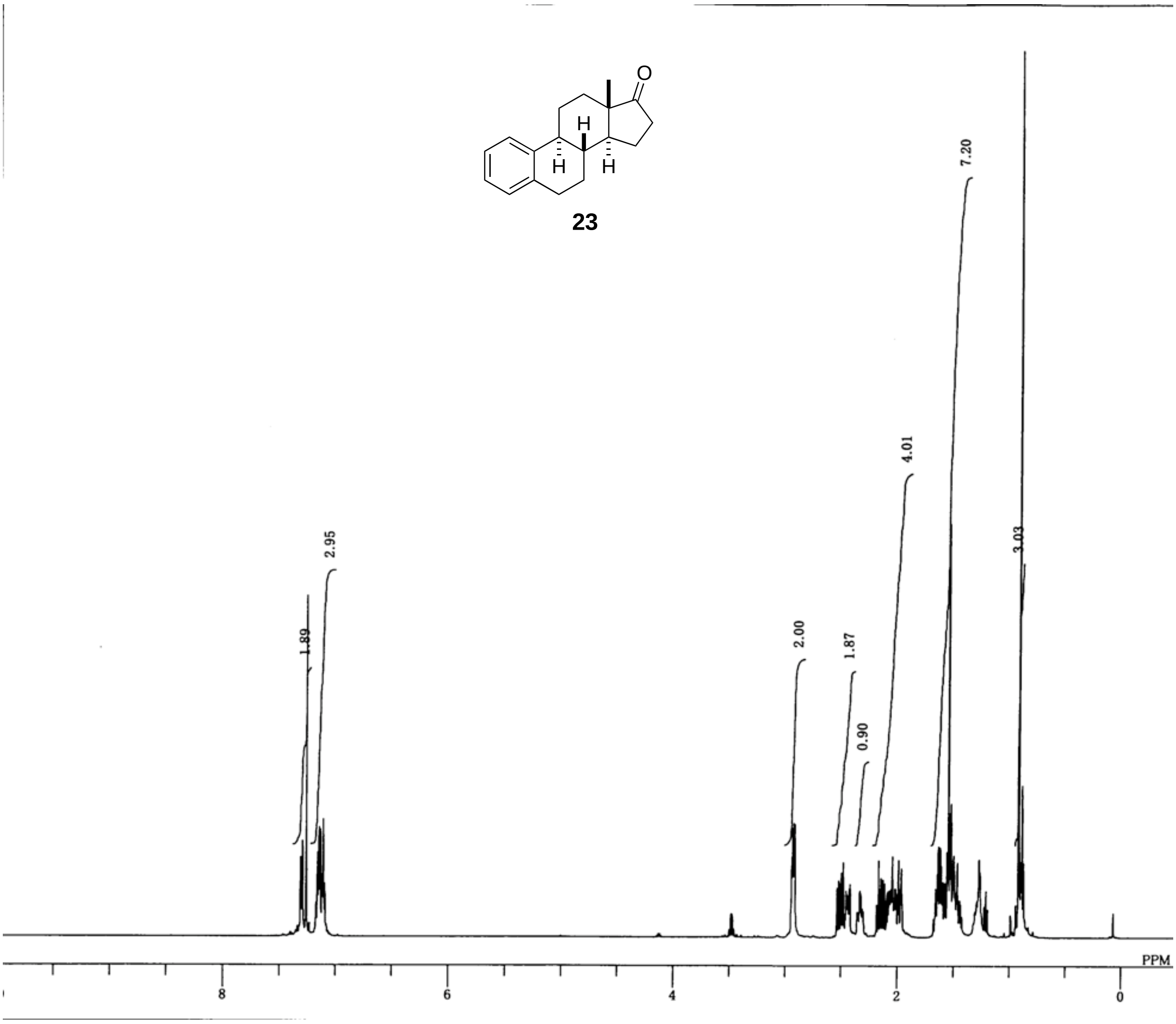

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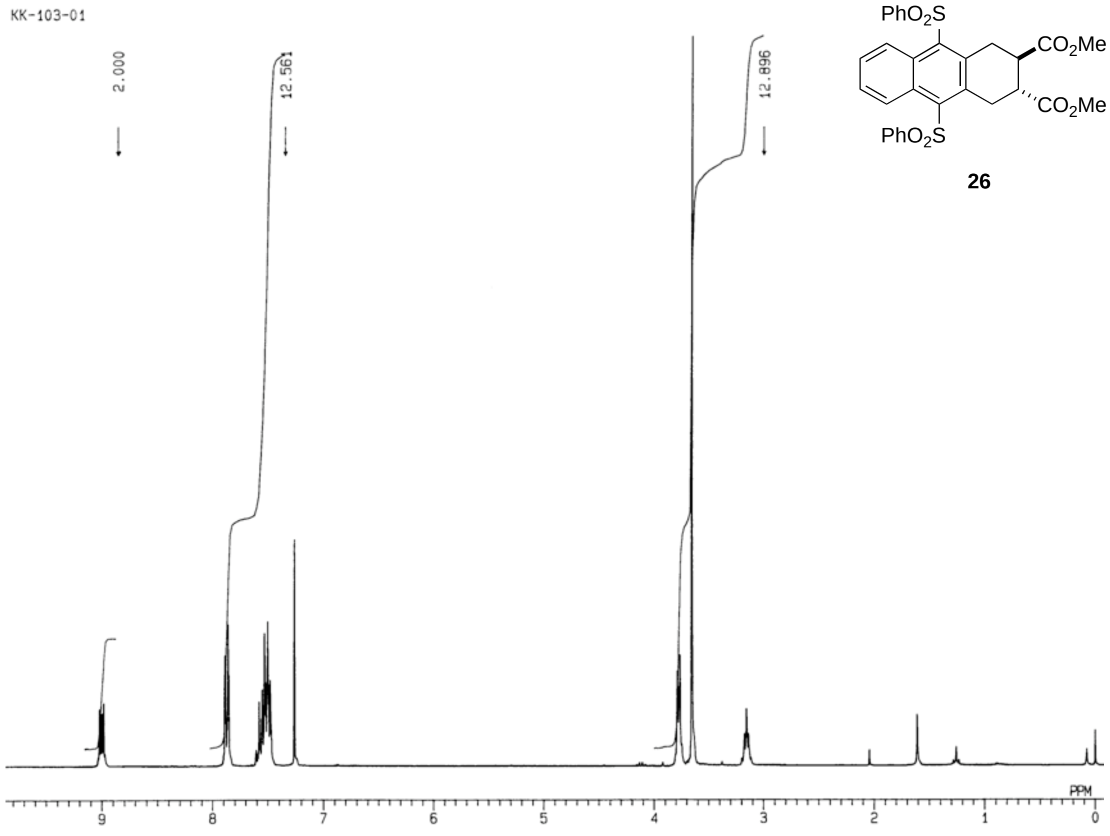
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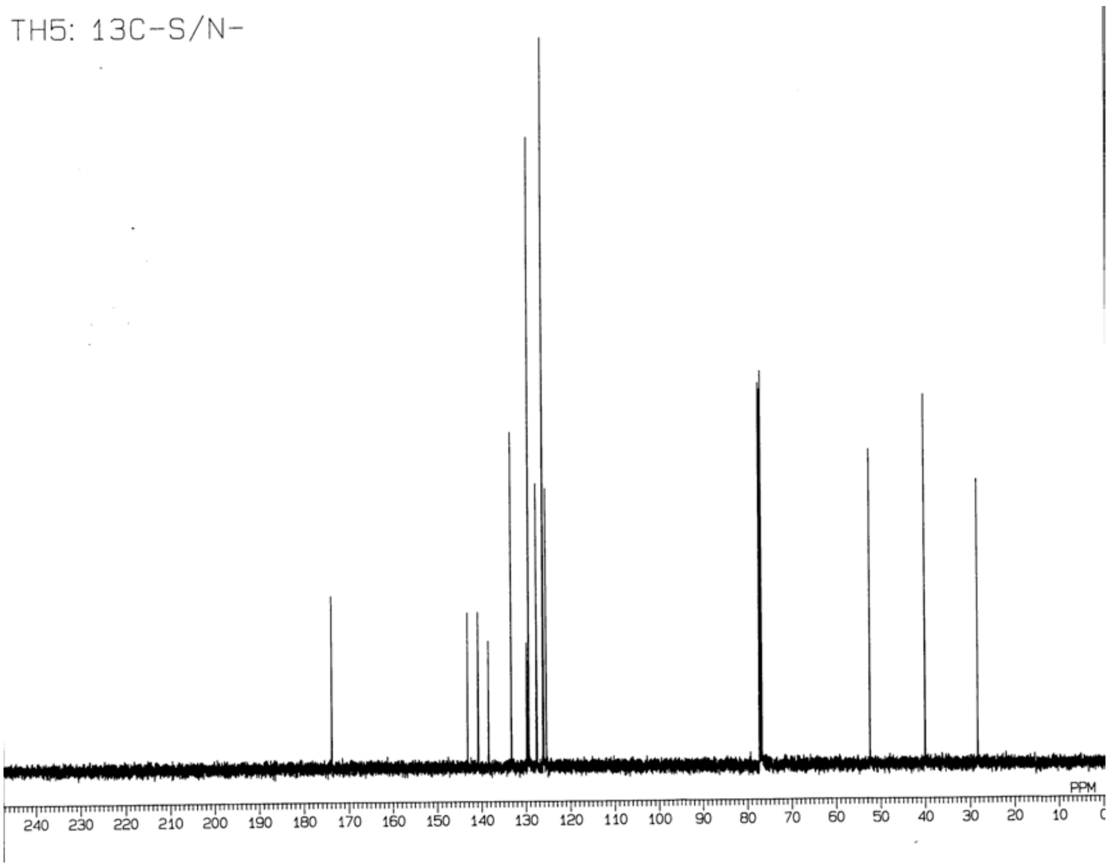
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