Supporting Information for

A New Entry to Enantiopure Polysubstituted Cyclopropanes: Stereoselective Denitrogenation of Sulfinylpyrazolines under $Yb(OTf)_3$ Catalysis

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General Methods. All moisture sensitive reactions were performed in flame–dried glasswares equipped with rubber septa under positive pressure of argon. THF and diethyl ether were distilled from sodium-benzophenone under argon and CH_2Cl_2 over P_2O_5. Lewis acids are commercially available and were used without further purification. $ZnBr_2$ was flame-dried in the reaction flask prior to use. Flash chromatography was carried out with silica gel Merck 60 (230-400 mesh ASTM). NMR spectra were determined in $CDCl_3$ solutions at 300 and 75 MHz for ^1H and ^{13}C NMR, respectively; *J* values are given in hertz. Melting points were measured using a Gallenkamp apparatus in open capillary tubes and are uncorrected. The optical rotations were measured at room temperature (20-23 ºC) using a Perkin-Elmer 241 MC polarimeter (concentration in g/100 mL).

Extrusion reactions.

A) To a solution of pyrazolines **3-7** (0.5 mmol) in THF (5 mL) under argon, was added a solution of $Eu(fod)_3$ (0.5 mmol) in THF (5 mL). The mixture was stirred at the temperature indicated in table 1 or scheme 2. When the reaction was completed (time indicated in table 1 or scheme 2), the reaction was quenched with aqueous potassium sodium tartrate and extracted with AcOEt (3 x 8 mL). The organic extracts were washed with brine (7 mL) and dried (Na_2SO_4). The solvent was removed under vacuum.

B) To a solution of pyrazolines **3-7** (0.5 mmol) in THF (5 mL) under argon, was added a solution of $Yb(OTf)_3$ (0.25 mmol) in THF (5 mL). The mixture was stirred at the temperature indicated in table 1 or scheme 2. When the reaction was completed (time indicated in table 1 or scheme 2), the reaction was quenched with aqueous potassium sodium tartrate and extracted with AcOEt (3 x 8 mL). The organic extracts were washed with brine (7 mL) and dried (Na_2SO_4). The solvent was removed under vacuum.

(1*R*,5*S*,S_S)-1-[(4-Methylphenyl)sulfinyl]-3-oxabicyclo[3.1.0]hexan-2-one (8A). Prepared from **3A**. It was purified by dissolving the crude reaction in AcOEt and further precipitation with hexane. mp: 102-104 ºC (white solid, 97% yield). $[\alpha]_D$ +58 (*c* 0.5, $CHCl_3$). IR (film) 1784. ^1H NMR δ 7.55 and

7.31 (AA'BB' system, 4H), 4.15 (d, 1H, *J* = 9.6 Hz), 4.02 (dd, 1H, *J* = 9.6 and 4.7 Hz), 2.65-2.60 (m, 1H), 2.40 (s, 3H), 2.04 (dd, 1H, *J* = 8.5 and 5.3 Hz), 1.39 (t, 1H, *J* = 5.3 Hz). ^{13}C NMR δ 170.7, 142.6, 138.8, 130.1, 124.2, 68.3, 47.3, 21.4, 21.0, 17.3. Anal. Calcd. for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12; S, 13.57. Found: C, 61.03; H, 5.35; S, 13.77.

(1*S*,5*R*,S$_S$)-1-[(4-Methylphenyl)sulfinyl]-3-oxabicyclo[3.1.0] hexan-2-one (8B). Prepared from **3B**. It was purified by dissolving the crude reaction in AcOEt and further precipitation with Et_2O:hexane. mp: 96-98 ºC (white solid, 91% yield). $[\alpha]_D$ +162 (*c* 0.5, $CHCl_3$). IR (film) 1789. ^{1}H NMR δ 7.69 and 7.42 (AA'BB' system, 4H), 4.46 (dd, 1H, *J* = 9.6 and 4.8 Hz), 4.22 (d, 1H, *J* = 9.6 Hz), 2.84 (m, 1H), 2.41 (s, 3H), 1.80 (dd, 1H, *J* = 8.5 and 5.2 Hz), 1.14 (t, 1H, *J* = 5.2 Hz). ^{13}C NMR δ 170.9, 142.4, 138.3, 129.8, 124.7, 68.2, 45.8, 25.5, 21.5, 13.8. Anal. Calcd. for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12; S, 13.57. Found: C, 61.12; H, 5.29; S, 13.68.

(1*R*,5*S*,6*R*,S$_S$)-6-Methyl-1-[(4-methylphenyl)sulfinyl]3-oxabicyclo [3.1.0]hexan-2-one (9A). Prepared from **4A**. The residue was crystallized from AcOEt-hexane. mp: 101-102 ºC (white solid, 87% yield). $[\alpha]_D$ +62 (*c* 0.5, $CHCl_3$). IR (film) 1754. ^{1}H NMR δ 7.62 and 7.27 (AA'BB' system, 4H), 4.13 (m, 2H), 2.78 (m, 1H), 2.43 (s, 3H), 1.72 (qd, 1H, *J* = 7.0 and 5.2 Hz), 1.51 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR δ 169.9, 142.4, 138.5, 129.7, 125.2, 67.8, 50.3, 28.1, 27.7, 21.4, 11.7. Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64; S, 12.81. Found: C, 62.07; H, 5.58; S, 12.75.

(1*S*,5*R*,6*S*,S$_S$)-6-Methyl-1-[(4-methylphenyl)sulfinyl]3-oxabicyclo [3.1.0]hexan-2-one (9B). Prepared from **4B**. The residue was purified by flash chromatography (AcOEt-hexane, 1:2) and crystallized from AcOEt-hexane. mp: 92-94 ºC (white solid, 68% yield). $[\alpha]_D$ +150 (*c* 0.5, $CHCl_3$). IR (film) 1749. ^{1}H NMR δ 7.68 and 7.38 (AA'BB' system, 4H), 4.44 (m, 2H), 2.82 (m, 1H), 2.42 (s, 3H), 1.64 (qd, 1H, *J* = 7.1 and 5.3 Hz), 1.32 (d, 3H, *J* = 7.1 Hz). ^{13}C NMR δ 170.2, 142.6, 138.2, 129.4, 125.4, 67.6, 49.5, 28.6, 26.4, 21.5, 11.3. Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64; S, 12.81. Found: C, 62.41; H, 5.72; S, 13.04.

(1*R*,5*S*,S_S)-5-Methyl-1-[(4-methylphenyl)sulfinyl]-3-oxabicyclo[3.1.0]hexan-2-one (10A). Prepared from **5A**. It was purified by dissolving the crude reaction in AcOEt and further precipitation with hexane. mp: 115-116 ºC (white solid, 98% yield). $[\alpha]_D$ +75 (*c* 0.5, $CHCl_3$). IR (film) 1768. ^{1}H NMR δ 7.60 and 7.32 (AA'BB' system, 4H), 4.02 (AB system, 2H), 2.41 (s, 3H), 1.97 (d, 1H, *J* = 5.1 Hz), 1.49 (s, 3H), 1.43 (d, 1H, *J* = 5.1 Hz). ^{13}C NMR δ 170.9, 141.9, 137.8, 129.8, 124.6, 72.1, 46.7, 34.0, 22.2, 21.4, 13.8. MS (FAB^+) *m/z* 251 (M+1, 100), 237 (27), 113 (32); HRMS calcd for $C_{13}H_{14}O_3S$ [M +1] 251.0664, found 251.0666.

(1*R*,5*S*,6*R*,S_S)-5,6-Dimethyl-1-[(4-methylphenyl)sulfinyl]-3-oxabicyclo[3.1.0]hexan-2-one (12A). Prepared from **6A**. It was purified by flash chromatography (AcOEt-hexane, 1:2). mp: 122-123 ºC (white solid, 94% yield). $[\alpha]_D$ +88 (*c* 0.5, $CHCl_3$). IR (film) 1771. ^{1}H NMR δ 7.68 and 7.32 (AA'BB' system, 4H), 4.80 (s, 2H), 2.40 (s, 3H), 1.87 (q, 1H, *J* = 7.0 Hz), 1.42 (s, 3H), 1.25 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR δ 168.8, 142.3, 136.8, 130.9, 125.3, 73.5, 47.5, 34.8, 22.6, 21.4, 14.0, 12.7. MS (FAB^+) *m/z* 265 (M+1, 100), 251 (21). HRMS calcd for $C_{14}H_{16}O_3S$ [M +1] 265.0820, found 265.0818.

(1*R*,5*S*,6*S*,S_S)-5,6-Dimethyl-1-[(4-methylphenyl)sulfinyl]-3-oxabicyclo[3.1.0]hexan-2-one (13A). Prepared from **7A**. It was purified by flash chromatography (AcOEt-hexane, 1:2). mp: 115-116 ºC (white solid, 93% yield). $[\alpha]_D$ +111 (*c* 0.5, $CHCl_3$). IR (film) 1761. ^{1}H NMR δ 7.68 and 7.32 (AA'BB' system, 4H), 4.80 (s, 2H), 2.39 (s, 3H), 2.18 (q, 1H, *J* = 7.0 Hz), 1.19 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR δ 169.7, 142.2, 136.7, 130.4, 125.3, 72.3, 47.0. 34.4, 22.6, 21.4, 14.0, 12.7. MS (FAB^+) *m/z* 265 (M+1, 100), 251 (42), 237 (7). HRMS calcd for $C_{14}H_{16}O_3S$ [M +1] 265.0820, found 265.0819.

(S_S)-4-Ethyl-3-[(4-methylphenyl)sulfinyl]furan-2(5*H*)-one (11). Prepared from **4A**, **4B**, **5A**, or **5B**. The residue was crystallized from AcOEt-hexane. mp: 110-111 ºC (orange solid, 96% yield from **5A**). $[\alpha]_D$ +110 (*c* 0.5, $CHCl_3$). IR (film) 1748. ^{1}H NMR δ 7.70 and 7.35 (AA'BB' system, 4H), 4.76 (AB system, 2H, *J* = 12.9 Hz), 3.00 (m, 2H), 2.40 (s, 3H), 1.22 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR δ 172.9, 168.3, 142.2, 139.1, 130.1, 129.4, 124.7, 71.6, 21.4, 19.9, 12.6. Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64; S, 12.81. Found: C, 61.92; H, 5.78; S, 12.70.

Desulfinylation Reaction. General Procedure. To a solution of the corresponding sulfinyl cyclopropane **8-13** in THF (2 mL/0.2 mmol) was added a suspension of activated Raney nickel in THF. The reaction was stirred at 0 ºC for 30-45 min. The reaction mixture was filtered through a celite pad and the filtrate was concentrated under reduced pressure.

(1*S*,5*R*)-3-Oxabicyclo[3.1.0]hexan-2-one [(-)-15].[1] Prepared by desulfinylation of **8A**. It was purified by flash chromatography (AcOEt-hexane, 1:5). Yellow oil (58% yield). $[\alpha]_D$ -69 (*c* 1, $CHCl_3$). [Lit.[1] $[\alpha]_D$ –68 (*c* 2.50, $CHCl_3$]. ^{1}H NMR δ 4.39 (dd, 1H, *J* = 9.1 and 4.8 Hz), 4.22 (d, 1H, *J* = 9.1 Hz), 2.24 (m, 1H), 2.10 (m, 1H), 1.31 (ddd, 1H, *J* = 9.0, 7.5 and 4.9 Hz), 0.90 (dt, 1H, *J* = 4.6 and 3.4 Hz).

(1*R*,5*S*)-3-Oxabicyclo[3.1.0]hexan-2-one [(+)-15].[1] Prepared by desulfinylation of **8B**. It was purified by flash chromatography (AcOEt-hexane, 1:5). Yellow oil (61% Yield). $[\alpha]_D$ +67 (*c* 1, $CHCl_3$). [Lit.[1] $[\alpha]_D$ +67.8 (*c* 1.20, $CHCl_3$].

(1*S*,5*R*,6*R*)-6-Methyl-3-oxabicyclo[3.1.0]hexan-2-one [(-)-16].[2] Prepared by desulfinylation of **9A**. It was purified by flash chromatography (AcOEt-hexane, 1:6). Yellow oil (62% yield). $[\alpha]_D$ -77 (*c* 1, $CHCl_3$). [Lit.[2] $[\alpha]_D$ –68.5 (*c* 1, CH_2Cl_2 (64% *ee*)]. ^{1}H NMR δ 4.32 (m, 2H), 2.02 (m, 1H), 1.82 (m, 1H), 1.27 (m, 1H), 1.18 (d, 3H, *J* = 4.9 Hz).

(1*R*,5*S*,6*S*)-6-Methyl-3-oxabicyclo[3.1.0]hexan-2-one [(+)-16]. Prepared by desulfinylation of **9B**. It was purified by flash chromatography (AcOEt-hexane, 1:6). Yellow oil (61% yield). $[\alpha]_D$ +76 (*c* 1, $CHCl_3$).

(1*S*,5*R*)-5-Methyl-3-oxabicyclo[3.1.0]hexan-2-one [(-)-17].[3] Prepared by desulfinylation of **10A**. It was purified by flash chromatography (AcOEt-hexane, 1:4). White solid (61% yield). $[\alpha]_D$ -54 (*c* 1, EtOH). [Lit.[3] $[\alpha]_D$ –53 (*c* 1.0, EtOH]. ^{1}H NMR δ 4.23 and 4.53(AB system, 2H, *J* = 9.1 Hz), 1.87 (dd, 1H, *J* = 9.0 and 3.2 Hz), 1.41 (s, 3H), 1.21 (dd, 1H, *J* = 9.0 and 4.6 Hz), 1.05 (dd, 1H, *J* = 4.6 and 3.2 Hz).

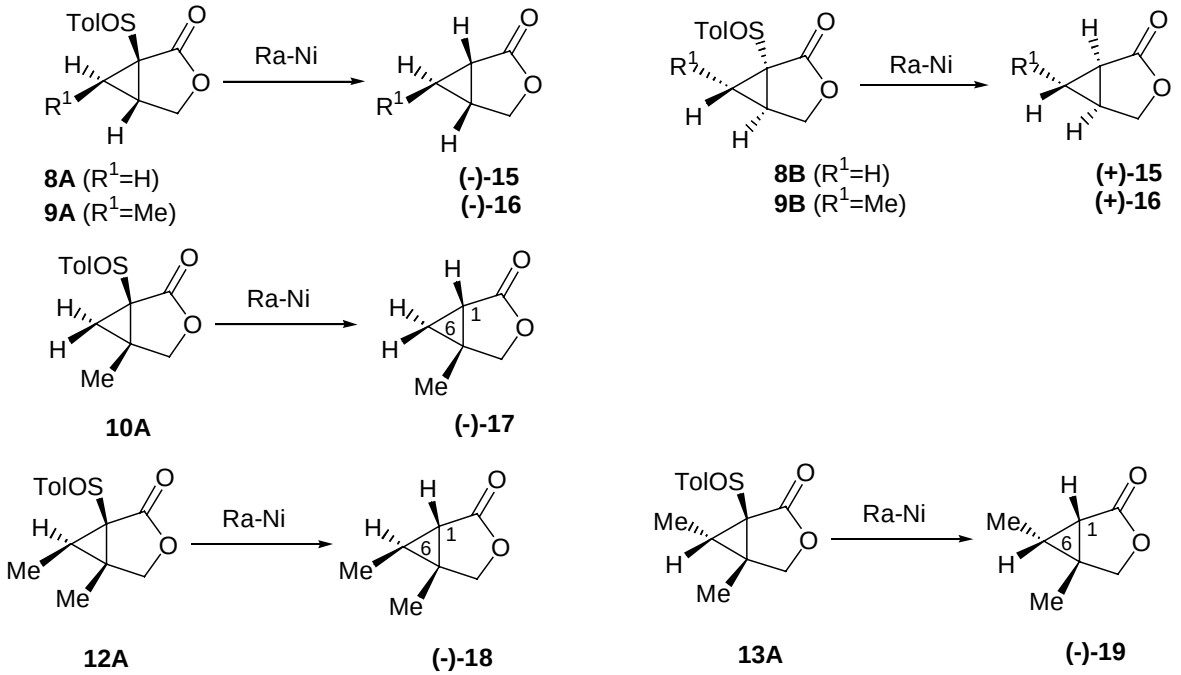
(1*S*,5*R*,6*S*)-5,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one [(-)-18]. Prepared by desulfinylation of **12A**. It was purified by flash chromatography (AcOEt-hexane, 1:6). Colourless oil (55% yield). $[\alpha]_D$

-64 (*c* 1, $CHCl_3$). IR (film) 1762.^{1}H NMR δ 4.79 and 4.69 (AB system, 2H, *J* = 9.1 Hz), 1.78 (d, 1H, *J* = 3.6 Hz), 1.39 (s, 3H), 1.09 (d, 3H, *J* = 7.0 Hz), 0.99 (dq, 1H, *J* = 7.0 and 3.4 Hz). ^{13}C NMR δ 169.9, 73.9, 26.7, 24.9, 21.3, 16.8, 13.8. Calcd. for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.66; H, 8.03.

(1*S*,5*R*,6*R*)-5,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one [(-)-19]. Prepared by desulfinylation of **13A**. It was purified by flash chromatography (AcOEt-hexane, 1:7). Yellow oil (58% yield). $[\alpha]_D$ -86 (*c* 1, $CHCl_3$). IR (film) 1773.^{1}H NMR δ 4.60 and 4.53 (AB system, 2H, *J* = 9.1 Hz), 2.06 (d, 1H, *J* = 8.9 Hz), 1.39 (s, 3H), 1.24-1.12 (m, 1H), 1.18 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR δ 174.7, 74.2, 27.6, 25.2, 21.4, 15.0, 13.1. Calcd. for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.72; H, 8.15.

Configurational assignment:

The absolute configuration of compounds **8A, 9A, 10A** and **8B, 9B** have been assigned by chemical correlation. The reactions of **8A, 8B, 9A,** and **10A** with Ra-Ni afforded compounds (-)-**15**,[1] **(+)-15**[1], **(-)-16**[2] and **(-)-17,**[3] whose spectroscopical data and optical rotations are in coincident with those previously reported in the literature. Desulfinylation of **9B** yielded **(+)-16**, with identical spectroscopics parameters but the opposite optical rotation that (-)-**16**.[2] The relative configuration of **12A** was established from its Ra-Ni desulfynilated derivative **(-)-18**. Compound **(-)-18** exhibits a $J_{1,6}$ 3.6 Hz, indicative of a *trans* arrangement between the involved protons, which allowed us to conclude that the relative stereochemistry of the sulfinyl group at **12A** and the methyl group at C-6 is *cis*. Desulfinylation of **13A** yielded **(-)-19**, that has a value $J_{1,6}$ 8.9 Hz evidences the *cis* arrangement of the protons H_1 and H_6 . This means that the relative configuration of the SOTol and the Me group at C-6 in **13A** implies in a *trans*-arrangement. The absolute configuration of **12A** and **13A** was assigned taking from the stereochemical course of nitrogen extrusion.

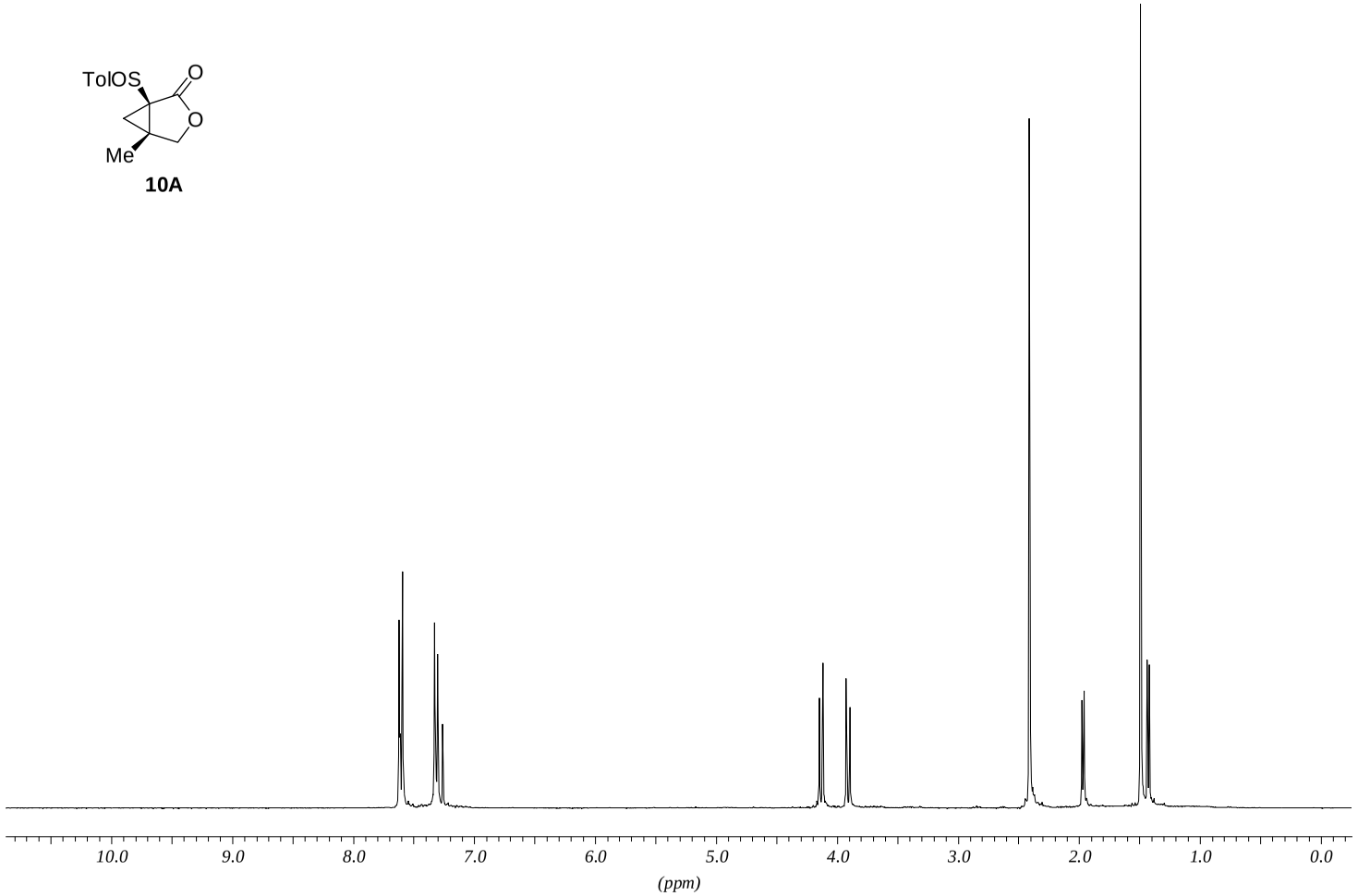


References

[1] a) Hasegawa, D.; Uchiro, H.; Kobayashi, S. *Tetrahedron Lett.* **2002**, *43*, 7185. b) Jakovac I. J.; Goodbrand, H. B.; Lok, K. P.; Jones, J. *J. Am. Chem. Soc.* **1982**,*104*, 4659.

[2]Collado, I.; Pedregal, C.; Mazon, A.; Espinosa, J. F.; Blanco-Urgoiti, J.; Schoepp, D. D.; Wright, R. A.; Jonson, B. G.; Kingston, A. E. *J. Med. Chem.* **2002**, *45*, 3619.

[3] Fox, M. E.; Li, C.; Marino Jr, J. P. ; Overman, L. E. *J. Am. Chem. Soc*. **1999**, *121*, 5467.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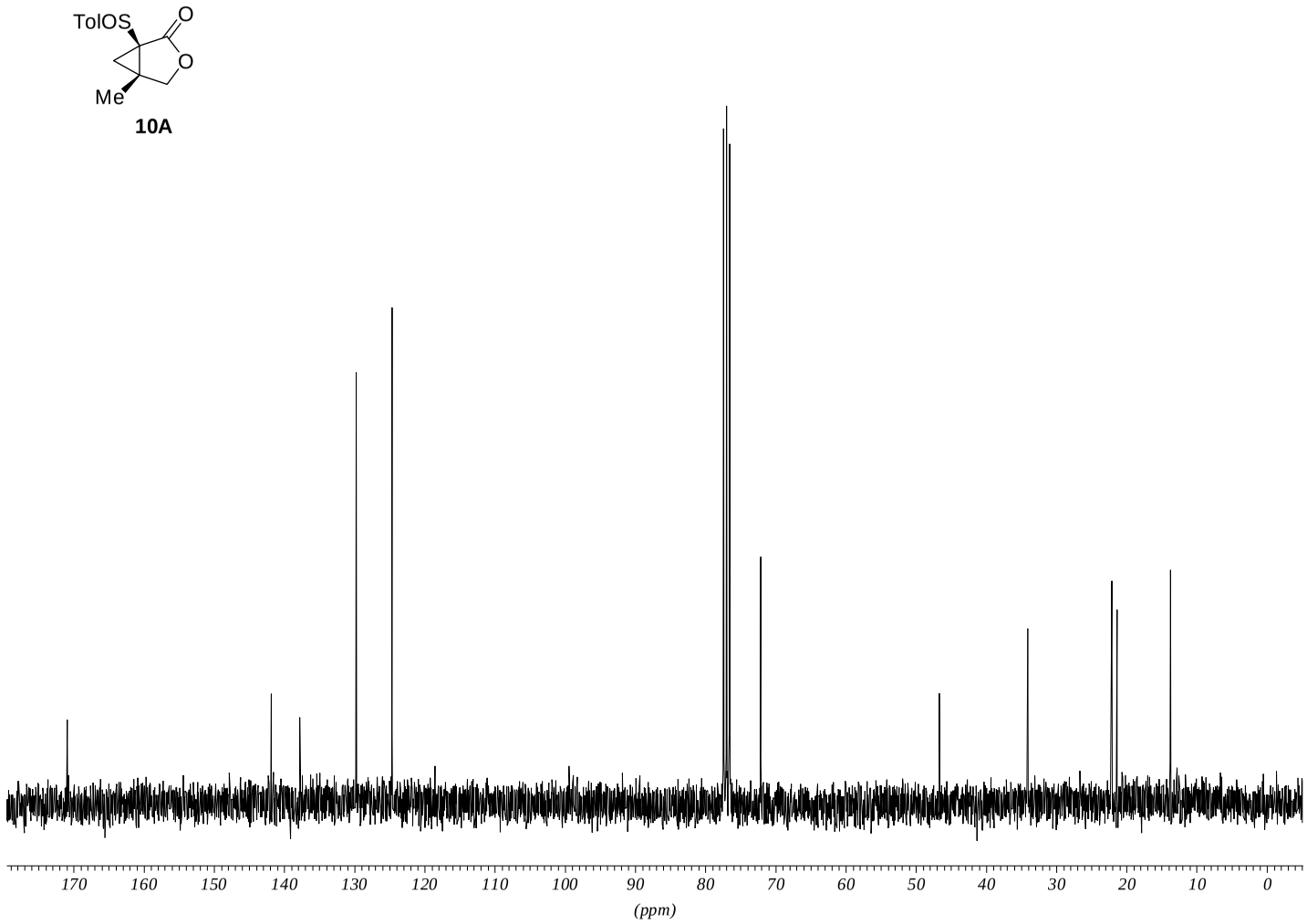
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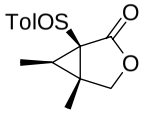
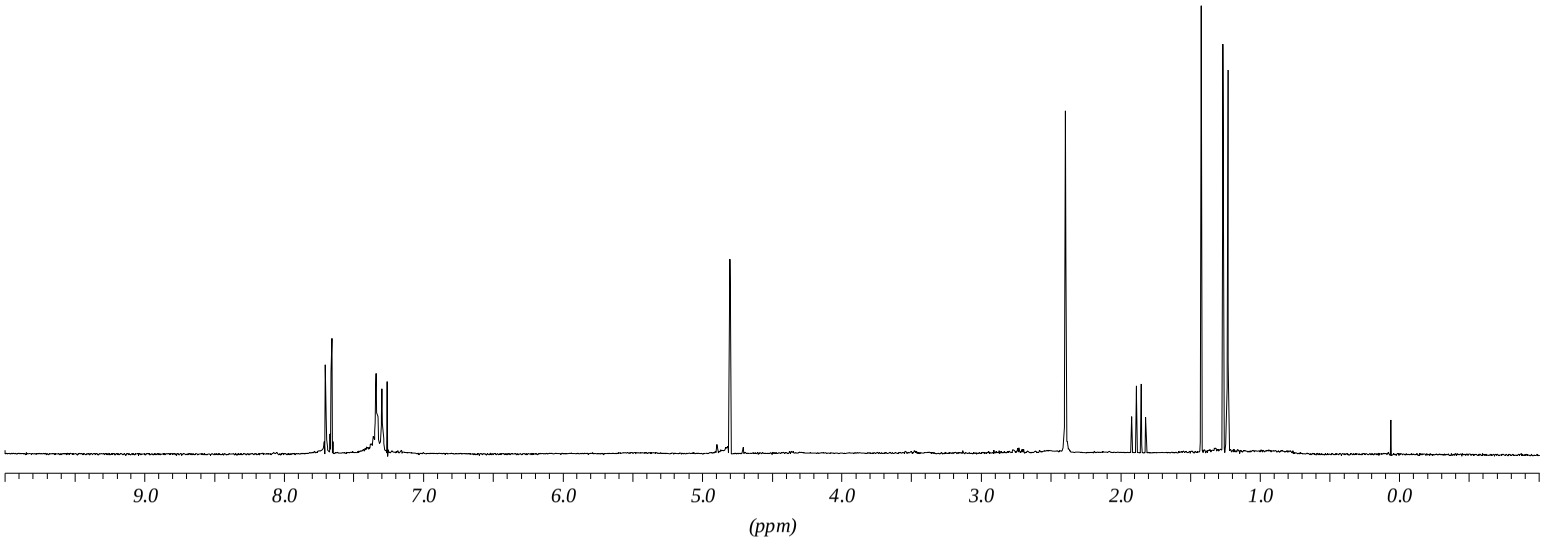
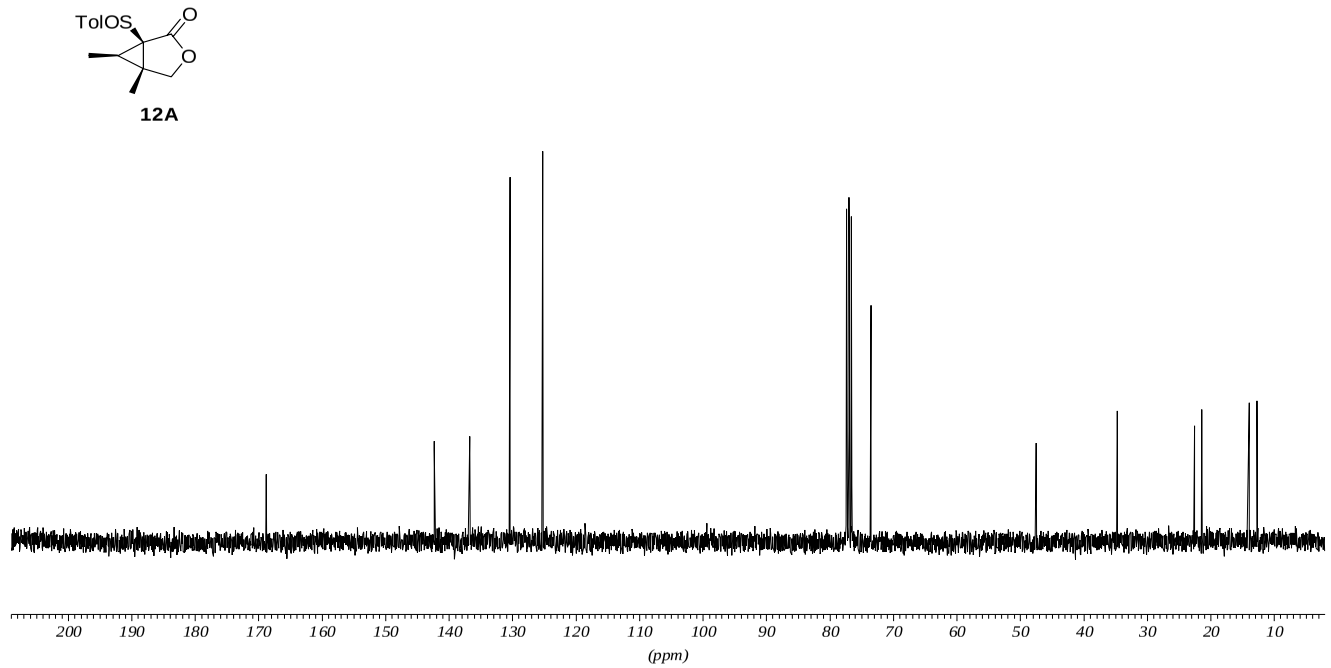


12A

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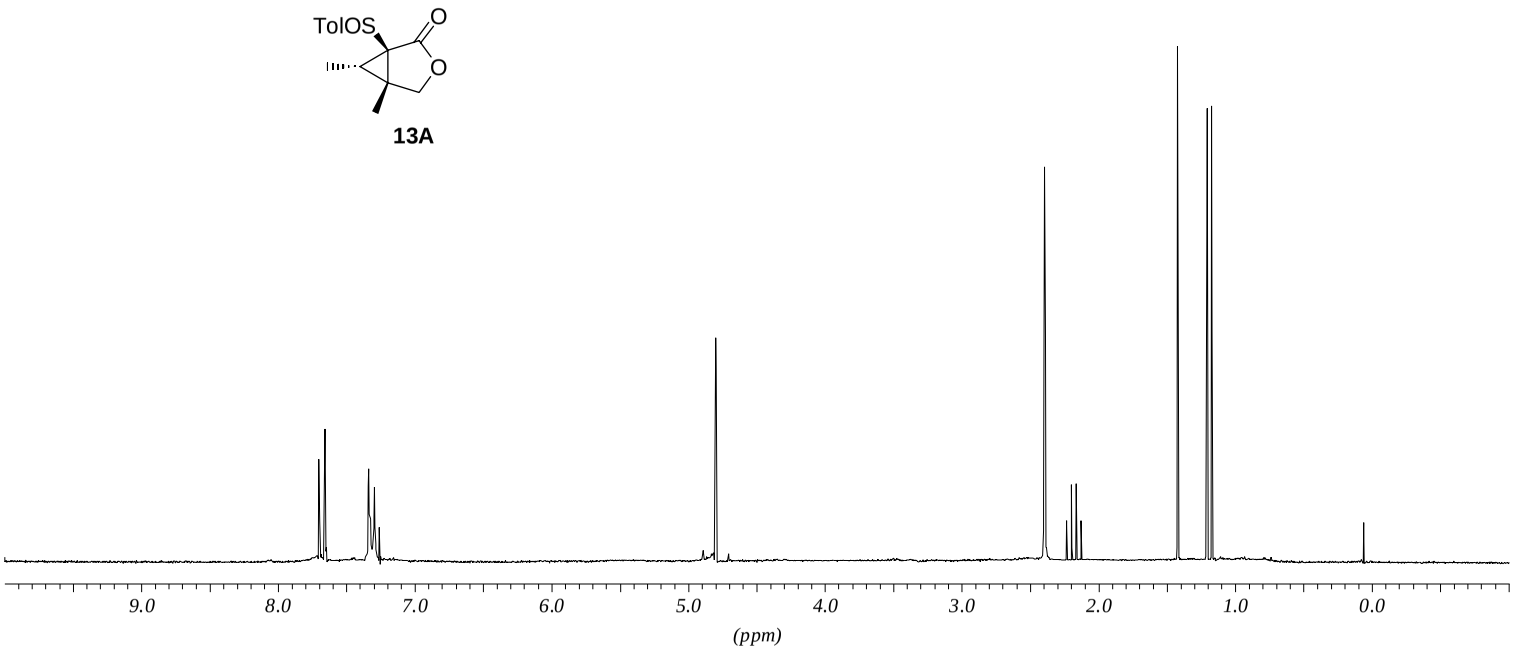
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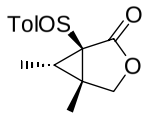
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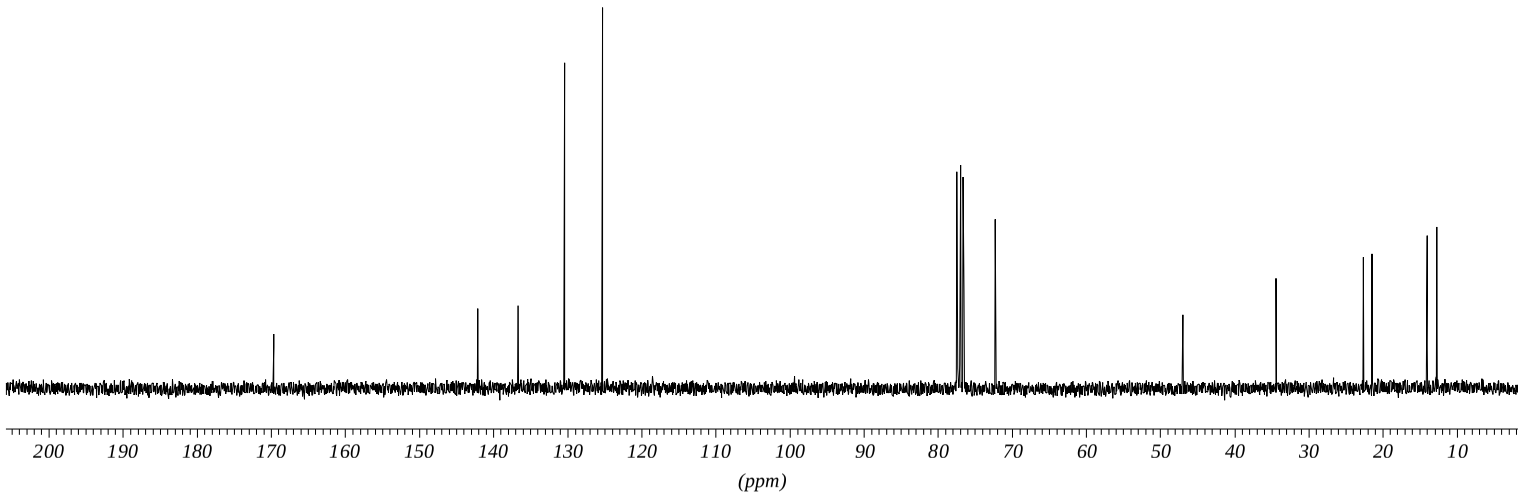
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