Supporting Information

An Unusual Cyclopropanation of 9-Bromocamphor Derivatives: A Novel Formal C(1)–C(7) Bond Cleavage of Camphor

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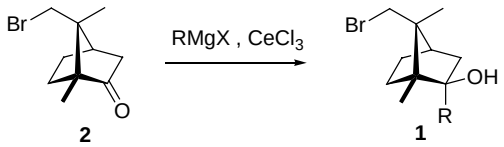
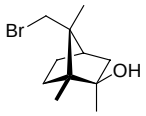
Experimental

General

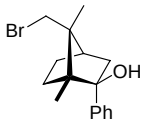
For product purification by flash column chromatography, silica gel (200~300 mesh) and petroleum ether (bp. 60~90 °C) are used unless otherwise noted. All solvents were purified and dried by standard techniques, and distilled prior to use. All organic extracts were dried over anhydrous sodium sulfate, unless otherwise noted. IR spectra were recorded on a *Nicolet* NEXU 670 FT spectrometer as liquid film. ^{1}H and ^{13}C NMR spectra were taken on a *Varian* Mercury-300, *Bruker* AM-200 or AM-400 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. EI-MS was obtained on HP-5988A GC/MS instrument. HRMS were determined on a *Bruker Daltonics* APEXII 47e FT-ICR spectrometer. Melting points were measured on a *Kofler* hot stage and are uncorrected. Optical rotations were recorded on a Perkin Elmer 341 polarimeter. All moisture-sensitive reactions were performed in flame-dried glassware under stream of nitrogen. Other commercially available reagents and solvents were used as received without further purification unless indicated otherwise.



Typical Procedure for the preparation of 9-bromocamphor derivative 1.[1] – $CeCl_3 \cdot 7H_2O$ (5.58 g, 15.0 mmol) was grounded to fine powders in a mortar and transferred into a 250-mL two-necked flask. The flask was immersed in an oil bath and heated gradually to 140–150 °C under reduced pressure (at 0.2 mmHg) for 5 h. While the flask was still hot, a stream of argon gas was passed through the flask was then cooled in an ice bath. The resulting anhydrous $CeCl_3$ (fine powder) was treated with THF (60 mL) and stirred vigorously for 3 h at room temperature under argon. The flask was immersed in an ice bath, to which a freshly prepared Grignard reagent (1.0 M, 15 mL) in THF was added dropwise. After stirring for 1.5 h at 0 °C, the slurry mixture was treated with a THF (10 mL) solution of 9-bromocamphor **2** (2.31 g, 10.0 mmol) and the stirring was continued for 1–2 h. The reaction was then quenched with 10% aqueous acetic acid carefully, extracted with ether, combined organic extracts were washed with brine, aqueous saturated $NaHCO_3$ solution, brine, and dried. The solvent was removed in vacuum and the residue was purified by chromatography on silica gel to afford the *endo*-addition product **1**.



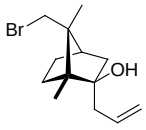
1a, white solids, mp. 79–81 °C; $[\alpha]_D^{21}$ +4 (*c* 1.6, $CHCl_3$); IR (film) ν_{max} 3464, 3410, 2963, 1453, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.26 (s, 3 H), 1.31 (s, 3 H), 1.11–2.09 (m, 8 H), 3.22 (d, *J* = 9.9 Hz, 1 H), 3.65 (d, *J* = 9.9 Hz, 1 H) ppm; ^{13}C NMR /DEPT (100 MHz, $CDCl_3$) δ 10.4 (q), 17.4 (q), 26.2 (t), 26.8 (q), 31.1 (t), 42.7 (t), 44.0 (d), 46.5 (t), 53.5 (s), 53.6 (s), 80.7 (s) ppm; LRMS (EI) *m/z* 231 ($[M–Me]^+$, 0.2%), 186 (3), 108 (77), 95 (37), 93 (32), 67 (24), 43 (100).



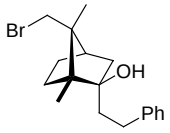
1b, white solids, mp. 116–117 °C; $[\alpha]_D^{21}$ –52 (*c* 2.0, $CHCl_3$); IR (film) ν_{max} 3542, 3514, 2949, 1456, 1059, 761, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 3 H), 1.49 (s, 3 H), 1.00–2.42 (m, 8 H), 3.23 (d, *J* = 10 Hz, 1 H), 3.68 (d, *J* = 10 Hz, 1 H), 7.28–7.55 (m, 5 H) ppm; ^{13}C NMR/DEPT

[1] Cf.: (a) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392. (b) Dimitrov, V.; Bratovanov, S.; Simova, S.; Kostova, K. *Tetrahedron Lett.* **1994**, *35*, 6713.

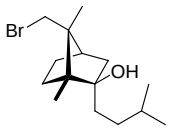
(100 MHz, $CDCl_3$) δ 10.3 (q), 17.5 (q), 25.9 (t), 31.1 (t), 42.8 (t), 44.2 (d), 44.6 (t), 54.6 (s), 54.9 (s), 84.6 (s), 126.8 (d), 126.8 (d), 127.2 (d), 127.8 (d), 127.8 (d), 145.3 (s) ppm; LRMS (EI) *m/z* 229 ($[M–Br]^+$, 5%), 211 (7), 120 (20), 108 (44), 105 (100), 77 (36).



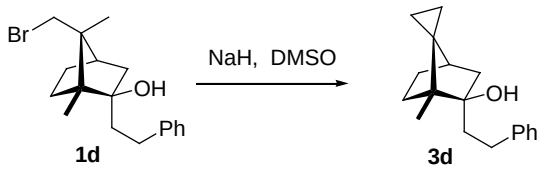
1c, colorless oil, $[\alpha]_D^{21}$ +34 (*c* 1.2, $CHCl_3$); IR (film) ν_{max} 3483, 2958 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.31 (s, 3 H), 1.05–2.09 (m, 8 H), 2.30 (d, *J* = 7.4 Hz, 2 H), 3.20 (d, *J* = 10 Hz, 1 H), 3.65 (d, *J* = 10 Hz, 1 H), 5.12–5.22 (m, 2 H), 5.80–5.97 (m, 1 H) ppm; LRMS (EI) *m/z* 272 (M^+, 0.4%), 231 (6), 109 (50), 69 (74), 41 (100).



1d, white solids, mp. 89–91 °C; $[\alpha]_D^{21}$ –11.3 (*c* 4.8, $CHCl_3$); IR (film) ν_{max} 3369, 2946 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (s, 3 H), 1.33 (s, 3 H), 0.98–2.10 (m, 10 H), 2.65–2.82 (m, 2 H), 3.20 (d, *J* = 10 Hz, 1 H), 3.65 (d, *J* = 10 Hz, 1 H), 7.28–7.33 (m, 5 H) ppm; LRMS (EI) *m/z* 318 ($[M–H_2O]^+$, 0.1%), 186 (8), 108 (90), 91 (100), 79 (16).



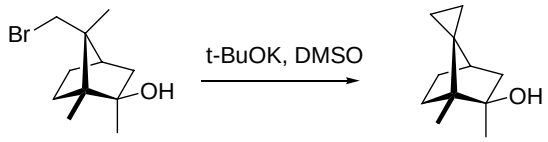
1e, colorless oil, $[\alpha]_D^{21}$ +31 (*c* 1.4, $CHCl_3$); IR (film) ν_{max} 3499, 2956, 2873, 1460, 641 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88–0.92 (12 H, 4 Me), 1.00–2.10 (m, 13 H), 3.23 (d, *J* = 10 Hz, 1 H), 3.70 (d, *J* = 10 Hz, 1 H) ppm; LRMS (EI) *m/z* 302 (M^+, 0.2%), 231 (4), 186 (8), 166 (8), 108 (100), 93 (32).



1d **3d**

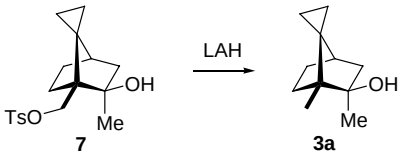
Representative procedure (A) for the spiral-cyclopropanation of 1 with sodium hydride. – A mixture of NaH (dispersion in 60% oil, 320 mg, 8.0 mmol) in DMSO (5 mL) was stirred at 70 °C for 0.5 h under Ar atmosphere, to which a solution of **1d** (1.35 g, 4.0 mmol) in DMSO (6 mL) was added dropwise at the same temperature. The resulting reaction mixture was stirred at 70

°C for 1.5 h. After cooling to rt., 15 mL of water was added and the resulting mixture was extracted thoroughly with ether. The combined organic phases were washed with water, brine, dried, filtered, and concentrated in vacuum. The residue was purified by chromatography on silica gel to afford 0.936 g (90%) of **3d** as a colorless oil. $[\alpha]_D^{28}$ +10 (*c* 1.4, $CHCl_3$); IR (film) ν_{max} 3483, 3063, 3026, 2949, 1454, 1004, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.26 (t, J = 7.2 Hz, 2 H), 0.60 (t, J = 7.2 Hz, 2 H), 0.69 (s, 3 H), 1.18–1.93 (m, 10 H), 2.70 (ddd, J_1 = 4.3 Hz, J_2 = 12.6 Hz, J_3 = 13.2 Hz, 1 H), 2.93 (ddd, J_1 = 5.1 Hz, J_2 = 12.6 Hz, J_3 = 13.2 Hz, 1 H), 7.18–7.32 (m, 5H) ppm; ^{13}C NMR/DEPT (100 MHz, $CDCl_3$) δ 0.96 (t), 4.25 (t), 10.2 (q), 28.5 (t), 30.8 (t), 31.1 (t), 36.2 (s), 38.0 (t), 42.2 (d), 47.4 (t), 49.1 (s), 81.7 (s), 125.6 (d), 128.3 (d), 128.3 (d), 128.4 (d), 128.4 (d), 143.4 (s) ppm; LRMS (EI) *m/z* 256 (M^+, 1%), 241 (2), 151 (10), 133 (24), 108 (100), 91 (76); HRMS (ESI) *m/z* $[M–H_2O+H]^+$ found 239.1796, calcd 239.1794 for $C_{18}H_{23}$.

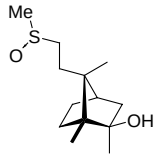


1a **3a**

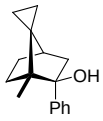
Representative procedure (B) for the spiral-cyclopropanation of 1 with potassium *tert*-butoxide. – A flask was charged with *t*-BuOK (448 mg, 4.0 mmol) under Ar, to which was added dropwise a solution of **1a** (494 mg, 2.0 mmol) in DMSO (6 mL) with stirring at 30 °C. The resulting mixture was continued to stir at 40 °C for 6 h and monitored by TLC. After cooling to rt, 10 mL of water was added and the resulting mixture was extracted thoroughly with ether. The combined organic phases were washed with water, brine, dried, filtered, and the solvent removed in vacuum. The residue was purified by chromatography on silica gel to afford 280 mg (85%) of **3a** and **3a'** (ca. 5%) as white solids. **3a**, mp. 80–82 °C; $[\alpha]_D^{28}$ +17.8 (*c* 4.4, $CHCl_3$); IR (film) ν_{max} 3408, 3066, 2949, 2868, 1099, 1064 cm^{-1}; ^{1}HNMR (200 MHz, $CDCl_3$) δ 0.27 (t, J = 6.8 Hz, 2 H), 0.55 (t, J = 6.8 Hz, 2 H), 0.66 (s, 3 H), 1.22 (s, 3 H), 0.88–1.81 (m, 8 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 1.04 (t), 4.05 (t), 9.52 (q), 22.1 (q), 28.3 (t), 31.7 (t), 35.8 (s), 42.4 (d), 48.5 (s), 49.3 (t), 79.9 (s) ppm; HRMS (SMS) *m/z* $[M–H_2O+H]^+$ found 149.1325, calcd 149.1325 for $C_{11}H_{17}$.



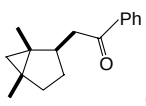
Alternative preparation of 3a by LAH reductive deoxygenation of tosylate 7. – To a stirred solution of tosylate **7**[2] (mixture of isomers at C(2), 140 mg, 0.42 mmol) in anhydrous ether (10 mL) was added $LiAlH_4$ (100 mg, 2.6 mmol) in one portion. The reaction mixture was brought to reflux for 2 h, cooled to room temperature, and quenched with dilute aqueous NaOH. The mixture was extracted with ether, dried over anhydrous sodium sulfate, filtered, and concentrated. Chromatography on silica gel of the crude residue provided 30 mg (42%) of **3a** (spectroscopically identical with the above obtained **3a**) along with 15 mg (22%) of its C(2) isomer.



3a', yield 5%, white solids (mixture of isomers, ca. 1:1), mp. 155–157 °C, IR (film) ν_{max} 3385, 2957, 2874, 1453, 1105, 1026 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (s, 3 H), 1.17 (s, 3 H), 1.27 (s, 3 H), 1.10–2.08 (m, 8 H), 2.58 (s, 3 H), 2.56–2.80 (m, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 10.0 (q), 10.0 (q), 17.4 (q), 17.6 (q), 25.9 (t), 26.1 (t), 26.3 (t), 26.5 (t), 27.1 (q), 27.1 (q), 30.9 (t), 30.9 (t), 38.2 (q), 38.4 (q), 42.3 (d), 42.4 (d), 46.7 (t), 46.7 (t), 50.7 (t), 51.3 (t), 51.4 (s), 51.4 (s), 53.0 (s), 53.0 (s), 79.3 (s), 79.3 (s) ppm; HRMS (ESI) *m/z* $[M+H]^+$ found 245.1565, calcd 245.1470 for $C_{13}H_{25}O_2S$.



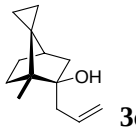
3b, colorless oil, $[\alpha]_D^{21}$ –27 (*c* 2.6, $CHCl_3$); IR (film) ν_{max} 3452, 3060, 2958, 1450, 1060, 759, 703 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.33 (t, *J* = 7.4 Hz, 2 H), 0.62 (s, 3 H), 0.72 (t, *J* = 7.4 Hz, 2 H), 1.17–2.46 (m, 8 H), 7.28–7.51 (m, 5 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 1.68 (t), 4.52 (t), 9.48 (q), 28.2 (t), 31.2 (t), 37.5 (s), 42.6 (d), 48.2 (t), 50.5 (s), 83.8 (s), 126.0 (d), 126.8 (d), 126.8 (d), 127.4 (d), 127.4 (d), 142.5 (s) ppm; LRMS (EI) *m/z* 228 (M^+, 0.7%), 213 (4), 210 (18), 108 (97), 105 (60), 93 (100), 79 (86), 51 (26).



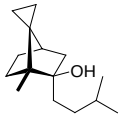
3b', colorless oil, $[\alpha]_D^{21}$ +50 (*c* 1.7, $CHCl_3$); IR (film) ν_{max} 2953, 2864, 1684, 1596, 1449,

[2] Prepared from 10-hydroxy-7-spiral-cyclopropylcamphor by methylation with MeLi and tosylation (TsCl, Pyr.) in moderate yield, cf.: Föhlisch, B.; Bakr, D. A.; Fischer, P. *J. Org. Chem.* **2002**, *67*, 3682.

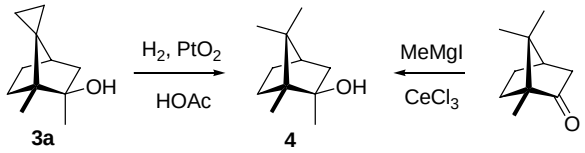
1274, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ –0.08 (d, *J* = 4.2 Hz, 1 H), 0.57 (d, *J* = 4.5 Hz, 1 H), 1.09 (s, 3 H), 1.16 (s, 3 H), 1.18–1.33 (m, 2 H), 1.64–1.69 (m, 2 H), 2.60–2.68 (m, 2 H), 3.13–3.22 (m, 1 H), 7.42–7.96 (m, 5 H) ppm; ^{13}C NMR/DEPT (75 MHz, $CDCl_3$) δ 15.7 (q), 18.1 (q), 20.9 (t), 25.7 (t), 27.5 (s), 29.5 (s), 32.6 (t), 40.8 (d), 41.2 (t), 128.0 (d), 128.0 (d), 128.5 (d), 128.5 (d), 132.7 (d), 137.3 (s), 200.6 (s) ppm; LRMS (EI) *m/z* 228 (M^+, 0.5%), 121 (3), 108 (100), 105 (64), 93 (60), 77 (40); HRMS (ESI) *m/z* $[M+H]^+$ found 229.1588, calcd 229.1587 for $C_{16}H_{21}O$.



3c, colorless oil, $[\alpha]_D^{28}$ +24 (*c* 1.0, $CHCl_3$); IR (film) ν_{max} 3481, 3069, 2950, 2872, 1639, 1456, 1065, 988, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.22 (t, *J* = 7.0 Hz, 2 H), 0.56 (t, *J* = 7.0 Hz, 2 H), 0.67 (s, 3 H), 1.17–1.77 (m, 8 H), 2.29 (t, *J* = 6.0 Hz, 2 H), 5.08–5.16 (m, 2 H), 5.93–6.02 (m, 1 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 1.02 (t), 4.30 (t), 10.3 (q), 28.3 (t), 31.3 (t), 36.2 (s), 40.8 (t), 42.2 (d), 47.2 (t), 48.9 (s), 80.9 (s), 117.2 (t), 135.2 (d) ppm; LRMS (EI) *m/z* 192 (M^+, 0.1%), 177 (1), 151 (29), 109 (69), 108 (88), 93 (100), 77 (44).

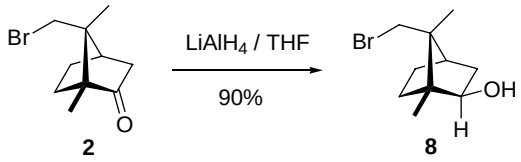


3e, colorless oil, $[\alpha]_D^{28}$ +16 (*c* 1.2, $CHCl_3$); IR (film) ν_{max} 3484, 3065, 2953, 1464 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.22 (t, *J* = 7.1 Hz, 2 H), 0.56 (t, *J* = 7.1 Hz, 2 H), 0.66 (s, 3 H), 0.90 (d, *J* = 6.2 Hz, 6 H), 1.16–1.68 (m, 13 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 0.86 (t), 4.20 (t), 10.2 (q), 22.6 (q), 22.7 (q), 28.5 (t), 28.7 (d), 31.1 (t), 33.1 (t), 33.3 (t), 36.1 (s), 42.1 (d), 47.3 (t), 48.9 (s), 81.8 (s) ppm; LRMS (EI) *m/z* 222 (M^+, 0.1%), 207 (1), 133 (12), 108 (100), 93 (90), 79 (84); HRMS (ESI) *m/z* $[M–H_2O+H]^+$ found 205.1956, calcd 205.1951 for $C_{15}H_{25}$.



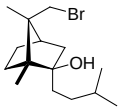
Hydrogenolysis of spiral-cyclopropyl camphor 3a. – A solution of spiral-cyclopropyl camphor derivative **3a** (56 mg, 0.34 mmol) in glacial acetic acid (2 mL) was charged with platinum oxide (6 mg) and stirred under hydrogen atmosphere (balloon pressure) for 2 h. The mixture was diluted with *sat.* $NaHCO_3$ and extracted with ether, washed with *sat.* $NaHCO_3$, brine, dried, filtered, and concentrated in vacuum. The residue was purified by chromatography to afford **4** (44 mg, yield

80%) as white solids, which is identical spectroscopically with the organocerium methylation adduct of D-camphor as shown above. Mp. 86–88 °C; $[\alpha]_D^{21}$ –5 (*c* 2.2, $CHCl_3$);[3] IR (film) ν_{max} 3469, 2947, 1452, 1371, 1094 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 1.10 (s, 3 H), 1.24 (s, 3 H) ppm; LRMS (EI) *m/z* 168 (M^+, 3%), 150 (4), 108 (25), 95 (100), 43 (41).

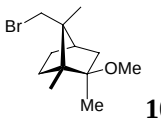


2 **8**

Preparation of *exo*-9-Bromobornan-2-ol (8). − To a suspension of lithium aluminum hydride (120 mg, 3.2 mmol) in 4 mL of THF was added dropwise a solution of 1.0 g (4.3 mmol) of 9-bromocamphor (**2**) in 4 mL of THF at –78 °C. The mixture was stirred at same temperature for an additional hour. The reaction was quenched with 1.5 mL of aqueous NaOH (2.0 M). The crude product was diluted with ether, filtered, dried, and concentrated. The resulting solid residue was recrystallized from hexane to give 900 mg (yield 90%) of *exo*-9-bromobornan-2-ol (**8**). Mp. 105–107 °C [lit. 105–107°C][4]; $[\alpha]_D^{21}$ –3 (*c* 0.04, $CHCl_3$); IR (film) ν_{max} 3389, 2954, 2883, 1454, 1241, 1068, 1001, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 3 H), 1.22 (s, 3 H), 1.04–1.85 (m, 7 H), 2.08 (s, 1 H), 3.19 (d, *J* = 9.9 Hz, 1 H), 3.52 (d, *J* = 9.9 Hz, 1 H), 3.71 (s, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.7, 16.2, 26.4, 33.6, 39.4, 42.4, 43.4, 50.3, 51.2, 81.0 ppm; LRMS (EI) *m/z* 232 (M^+, 0.1%), 173 (5), 153 (47), 135 (37), 107 (42), 95 (100), 79 (31), 69 (63).



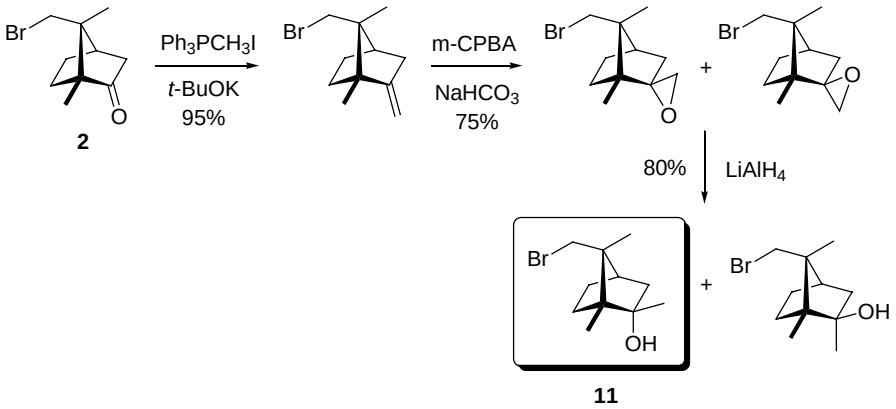
9, colorless oil; IR (film) ν_{max} 3448, 2952, 2869, 1463, 1015 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.79–0.91 (m, 12 H, 4 Me), 1.01–2.05 (m, 13 H), 3.41 (d, *J* = 7.8 Hz, 1 H), 3.65 (d, *J* = 7.8 Hz, 1 H) ppm.



10, colorless oil; IR (film) ν_{max} 2964, 2867, 1453, 1122, 1065 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.89 (s, 3 H), 1.15 (s, 3 H), 1.21 (s, 3 H), 3.12 (s, 3 H), 0.94–2.11 (m, 7H), 3.22 (d, *J* = 10 Hz,

[3] Cf.: (a) *Dictionary of Natural Products;* Buckingham, J. Eds.; Chapman & Hall, 1994; Vol. 4, p. 3890. (b) Toivonen, H. *Tetrahedron Lett.* **1968**, *26*, 3041.
[4] Cf.: Vaillancourt, V.; Agharahimi, M. R.; Sundram, U. N.; Richou, O.; Faulkner, D. J.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 378.

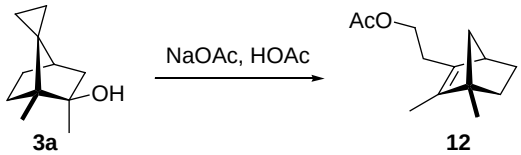
1 H), 3.71 (d, J = 10 Hz, 1 H); LRMS (EI) *m/z* 260 (M^+, 0.1%), 186 (8), 149 (12), 121 (16), 109 (76), 95 (39), 79 (22), 43 (94), 41 (100).



Preparation of compound 11. – (a) methylenation[5] **of 2. –** To a stirred suspension of *t*-BuOK (784 mg, 7.0 mmol) in anhydrous benzene (15 mL) under Ar was added methyltriphenylphosphorium iodide powder (2.82 g, 7 mmol) and the yellowish mixture was heated to reflux for 1 h followed by evaporation of the solvent under a stream of Ar at ca. 90–100 °C, until a slurry remained. To which was then added dropwise a mixture of 9-bromocamphor (1.15 g, 5.0 mmol) and benzene (2 mL) at the same temperature under Ar. After stirring for 10 minutes, the reaction mixture was cooled to room temperature and was diluted with water (15 mL), extracted with ether. The combined organic phases were washed with water, brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford 1.08 g (95%) of the olefin as a colorless oil. IR (film) ν_{max} 2957, 2877, 1658, 1445, 1379, 1245, 879, 631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 6 H, 2 Me), 1.26–2.39 (m, 7H), 3.22 (d, J = 9.9 Hz, 1 H), 3.62 (d, J = 9.9 Hz, 1 H), 4.67 (d, J = 14 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 16.2, 27.2, 34.7, 36.0, 41.0, 42.8, 51.9, 52.6, 101.7, 158.7 ppm; EIMS m/z 228 (M^+, 1%), 149 (94), 121 (16), 107 (97), 93 (100), 79 (47), 41 (53). **(b) Preparation of epoxide intermediates.** To a solution of the above olefin (230 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) was added *m*-CPBA (350 mg, 1.4 mmol, 70%) and $NaHCO_3$ (840 mg, 10.0 mmol) with stirring at 0 °C. The resulting mixture was stirred for 1 h then quenched with aqueous Na_2SO_3, extracted with CH_2Cl_2 and the organic phases were washed with sat. $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by chromatography on silica gel to afford 180 mg (75%) of the

[5] Cf.: Fitjer, L.; Quabeck, U. *Synth. Commun.* **1985**, *15*, 855.

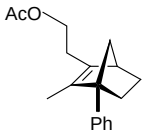
epoxides as a colorless oil (mixture of diastereomers as shown). IR (film) ν_{max} 2959, 2880, 1450, 1380, 1248, 1037, 799, 626 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.65 (s, 6 H, 2Me), 1.14 (s, 3H), 1.18 (s, 3 H), 1.30–2.23 (m, 14 H), 2.61 (d, *J* = 4.2 Hz, 1 H), 2.66 (d, *J* = 4.5 Hz, 2 H), 2.87 (d, *J* = 4.5 Hz, 1 H), 3.22 (d, *J* = 9.9 Hz, 2 H), 3.54 (d, *J* = 10.2 Hz, 1 H), 3.61 (d, *J* = 10.5 Hz, 1 H) ppm; ^{13}C NMR (75MHz, $CDCl_3$) δ 8.85, 10.5, 16.0, 16.1, 26.6, 26.9, 30.2, 32.2, 35.6, 36.9, 40.6, 40.9, 42.7, 42.9, 46.7, 48.3, 48.7, 52.3, 52.4, 54.0, 68.5, 68.5 ppm; LRMS (EI) *m/z* 244 (M^+, 0.1%), 165 (90), 135 (20), 121 (17), 107 (69), 93 (85), 91 (60), 79 (52). **(c) Preparation of 11.** To a suspension of lithium aluminum hydride (30 mg, 0.8 mmol) in THF (1 mL) was added a solution of the above epoxides (100 mg, 0.41 mmol) in THF (1 mL). After the reaction mixture was stirred for 10 minutes under refluxing and cooled to ambient temperature, saturated aqueous sodium sulfate was added. The crude product was filtered through a short pad of Celite with diethyl ether, the filtrate was concentrated, and then purified by chromatography on silica gel to give 50 mg (50%) of the *endo*- hydroxyl product **11** along with 30 mg (30%) of **1a**. **11**, white solids, mp. 96–98 °C; $[\alpha]_D^{21}$ –17.2 (*c* 4.7 $CHCl_3$); IR (film) ν_{max} 3403, 2953, 1450, 1115, 1071, 731, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0 .84 (s, 3 H), 1.13 (s, 3 H), 1.33 (s, 3 H), 1.12–1.76 (m, 5 H), 1.99–2.02 (m, 2 H), 2.23–2.35 (m, 1 H), 3.20 (d, *J* = 10.2 Hz, 1 H), 3.73 (d, *J* = 10 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6, 17.5, 26.4, 29.1, 29.3, 43.0, 43.6, 45.8, 53.6, 54.0, 79.5 ppm; LRMS (EI) *m/z* 231 ($[M–Me]^+$, 0.4%), 186 (6), 108 (95), 95 (39), 43 (100).



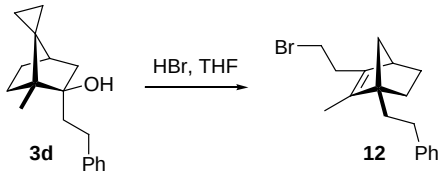
3a **12**

Preparation of acetate 12a (X = OAc, R = Me). – To a solution of spiral-cyclopropyl camphor derivative **3a** (50 mg, 0.3 mmol) in glacial acetic acid (1 mL) was added sodium acetate (246 mg, 3.0 mmol), and the mixture was heated to reflux with stirring for 2 h. After cooling to rt., the reaction mixture was neutralized with powdered $NaHCO_3$, diluted with ether, washed with sat. aqueous $NaHCO_3$, water, and brine respectively, dried over $MgSO_4$, filtered and concentrated in vacuum. The residue was purified by chromatography on silica gel to afford the norborenyl acetate **12a** as a colorless oil. $[\alpha]_D^{21}$ –18 (*c* 1.4, $CHCl_3$); IR (film) ν_{max} 2952, 1743, 1243, 1039 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.00–2.42 (m, 8 H), 1.22 (s, 3 H), 1.53 (s, 3 H), 2.03 (s, 3 H), 2.62 (brs, 1 H), 4.08 (t, *J* = 7.4 Hz, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 8.87 (q), 17.6 (q), 20.9 (q), 26.9 (t), 28.9 (t), 32.6 (t), 44.9

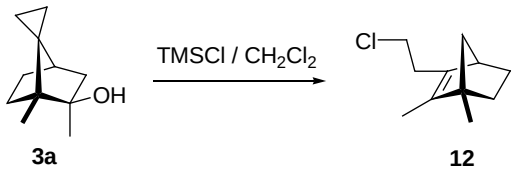
(d), 51.6 (s), 53.3 (t), 63.3 (t), 136.0 (s), 140.3 (s), 171.0 (s) ppm; LRMS (EI) *m/z* 208 (M^+, 0.3%), 148 (20), 120 (100), 105 (70), 91 (30); HRMS (ESI) *m/z* $[M+H]^+$ found 209.1537, calcd 209.1536 for $C_{13}H_{21}O_2$.



12b (X = OAc, R = Ph), colorless oil; IR (film) ν_{max} 2956, 1741, 1239, 1231, 1034, 760, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.29 (s, 3 H), 2.05 (s, 3 H), 1.22–1.95 (m, 6 H), 2.40 (m, 2 H), 2.81 (s, 1 H), 4.15 (t, *J* = 7.2 Hz, 2 H), 7.22–7.38 (m, 5 H) ppm; LRMS (EI) *m/z* 270 (M^+, 1%), 242 (12), 210 (24), 182 (100), 167 (86), 43 (80).

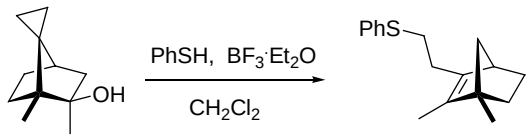


Preparation of bromide 12d (X = Br, R = phenethyl). – To a stirred solution of spiral-cyclopropyl camphor derivative **3d** (380 mg, 1.48 mmol) in 4 mL of THF was added dropwise 5 mL of HBr (40% aqueous) at 0 °C and the resulting mixture was stirred for 10 min, then quenched and neutralized with sat. aqueous $NaHCO_3$. The aqueous phase was separated and extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford 400 mg (85%) of the norborenyl bromide **12d** as a colorless oil. $[\alpha]_D^{21}$ –21 (*c* 1.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 0.95–1.28 (m, 4 H), 1.61 (s, 3 H), 1.72–2.03 (m, 4 H), 2.56–2.74 (m, 5 H), 3.42 (t, *J* = 7.8 Hz, 2 H), 7.18–7.33 (m, 5 H) ppm; LRMS (EI) *m/z* 318 (M^+, 1%), 290 (13), 239 (10), 199 (100), 119 (23), 91 (77), 77 (15).



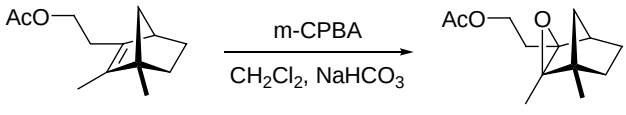
Preparation of chloride 12a' (X = Cl, R = Me). – To a solution of spiral-cyclopropyl camphor derivative **3a** (20 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was added freshly distilled TMSCl (0.2 mL) at –15 °C with stirring and the reaction mixture was stirred for 30 minutes, then quenched with sat. aqueous $NaHCO_3$. The mixture was extracted with ether, washed with sat. aqueous $NaHCO_3$, brine,

dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by chromatography on silica gel to afford 13 mg (60%) of the chloride **12a'** as a colorless oil. $[\alpha]_D^{18}$ –23 (*c* 0.6, $CHCl_3$); IR (film) ν_{max} 2952, 2863, 1655, 1447, 660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.91–1.81 (m, 6 H), 1.23 (s, 3 H), 1.55 (s, 3 H), 2.36–2.60 (m, 3 H), 3.55 (t, *J* = 7.6 Hz, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 9.01 (q), 17.5 (q), 29.1 (t), 31.2 (t), 32.6 (t), 43.5 (t), 44.6 (d), 51.8 (s), 53.3 (t), 136.5 (s), 141.0 (s) ppm; LRMS (EI) *m/z* 184 (M^+, 5%), 156 (32), 107 (100), 91 (30).



3a **12**

Preparation of sulfide 12a'' (X = SPh, R = Me). – To the mixture of spiral-cyclopropyl camphor derivative **3a** (20 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was added thiophenol (50 μL, 0.48 mmol) at –78 °C, the mixture was treated with a catalytic amount of BF_3 etherate (ca. 10μl) at the same temperature and was stirred for 30 min and monitored by TLC. After the starting material was consumed completely, the reaction mixture was treated with an aqueous $CuSO_4$ to remove the excess thiophenol and extracted with CH_2Cl_2. The organic extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was removed in vacuum and the residue was purified by chromatography on silica gel (petroleum ether) to give 19 mg (60%) of the sulfide **12a''** as a colorless oil. $[\alpha]_D^{18}$ –32 (*c* 0.7, $CHCl_3$); IR (film) ν_{max} 2950, 1581, 1478, 1440, 738, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.03–1.56 (m, 4 H), 1.22 (s, 3 H), 1.49 (s, 3 H), 1.75 –2.40 (m, 4 H), 2.63 (s, 1 H), 2.98 (t, *J* = 8.0 Hz, 2 H), 7.19–7.52 (m, 5 H) ppm; HRMS (ESI) *m/z* $[M+H]^+$ found 259.1516, calcd 259.1515 for $C_{17}H_{23}S$.

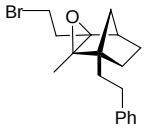


12a **13a**

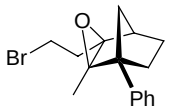
Preparation of norborenyl epoxide 13. – To a solution of the acetate **12a** (86 mg, 0.41 mmol) in CH_2Cl_2 (1.5 mL) was added *m*-CPBA (153 mg, 0.62 mmol, 70%) and $NaHCO_3$ (420 mg, 5 mmol) with stirring at 0 °C. The mixture was stirred for 1 h and quenched with an aqueous Na_2SO_3, extracted with CH_2Cl_2 and the organic phases were washed with sat. aqueous $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by chromatography to afford 77 mg

(85%) of the exo-epoxide **13a** as a colorless oil. **13a** (X = OAc, R = Me), $[\alpha]_D^{21}$ +33 (*c* 1.0, $CHCl_3$); IR (film) ν_{max} 2955, 1742, 1242, 1042 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.62 (d, *J* = 9.2 Hz, 1 H), 1.14 (s, 3 H), 1.19 (s, 3 H), 1.22–1.68 (m, 6 H), 2.07 (s, 3 H), 2.02–2.35 (m, 2 H), 4.28 (t, *J* = 7.0 Hz, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 8.33 (q), 15.3 (q), 21.0 (q), 25.3 (t), 26.0 (t), 31.7 (t), 35.6 (t), 39.7 (d), 46.4 (s), 61.9 (t), 63.7 (s), 64.6 (s), 170.9 (s) ppm; LRMS (EI) *m/z* 224 (M^+, 0.04%), 164 (10), 109 (40), 43 (100); HRMS (ESI) *m/z* $[M+Na]^+$ found 247.1309, calcd 247.1305 for $C_{13}H_{20}O_3Na$.

13a' (X = Br, R = Me), colorless oil, $[\alpha]_D^{20}$ +27 (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 0.62 (d, *J* = 9.4 Hz, 1 H), 1.12 (s, 3 H), 1.18 (s, 3 H), 1.21–1.34 (m, 4 H), 1.58–1.95 (m, 2 H), 2.32–2.48 (m, 2 H), 3.51 (t, *J* = 9.0 Hz, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 8.41 (q), 15.3 (q), 26.0 (t), 28.8 (t), 30.2 (t), 31.6 (t), 35.5 (t), 39.1 (d), 46.4 (s), 64.1 (s), 65.8 (s) ppm; LRMS (EI) *m/z* 244 (M^+, 0.4%), 215 (13), 137 (27), 109 (100), 91 (14), 79 (19).



13d (X = Br, R = phenethyl), colorless oil, $[\alpha]_D^{21}$ +36 (*c* 1.9, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.62 (d, *J* = 9.0 Hz, 1 H), 1.25 (s, 3 H), 1.27–1.96 (m, 8 H), 2.38– 2.48 (m, 2 H), 2.67 (t, *J* = 10 Hz, 2 H), 3.50–3.57 (m, 2 H), 7.15–7.31 (m, 5 H) ppm; ^{13}C NMR/DEPT (75 MHz, $CDCl_3$) δ 8.79 (q), 25.7 (t), 28.8 (t), 30.1 (t), 30.1 (t), 32.1 (t), 32.1 (t), 32.8 (t), 39.0 (d), 50.5 (s), 63.6 (s), 65.0 (s), 125.7 (d), 128.1 (d), 128.1 (d), 128.3 (d), 128.3 (d), 142.8 (s) ppm; LRMS (EI) *m/z* 334 (M^+, 0.3%), 215 (7), 135 (19), 118 (55), 107 (93), 91 (100), 77 (20), 43 (61); HRMS (ESI) *m/z* $[M+H]^+$ found 352.1274, calcd 352.1271 for $C_{18}H_{24}OBr$.



13b (X = Br, R = Ph), crystalline solids, mp. 56–57 °C (*n*-Hexane), $[\alpha]_D^{25}$ +65 (*c* 1.1, $CHCl_3$); IR (film)ν_{max} 2958, 1601, 1445, 759, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (d, *J* = 10 Hz, 1 H), 1.02 (s, 3 H), 1.50–1.98 (m, 6 H), 2.44–2.54 (m, 1 H), 2.62 (brs, 1 H), 3.54–3.60 (m, 2 H), 7.24–7.34 (m, 5 H) ppm; ^{13}C NMR/DEPT (75 MHz, $CDCl_3$) δ 9.3 (q), 25.8 (t), 28.0 (t), 28.7 (t), 30.2 (t), 36.1 (t), 39.4 (d), 54.5 (s), 65.2 (s), 65.4 (s), 126.5 (d), 127.2 (d), 127.2 (d), 128.2 (d), 128.2 (d), 141.0 (s) ppm; HRMS (ESI) *m/z* $[M+H]^+$ found 307.0691, calcd 307.0692 for $C_{16}H_{20}OBr$.

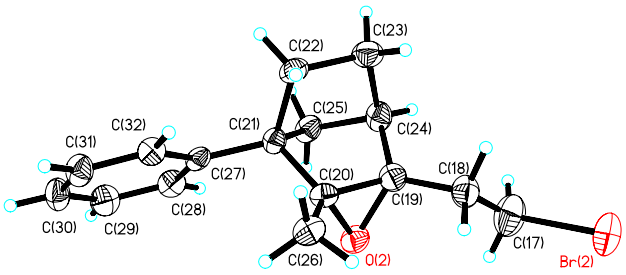
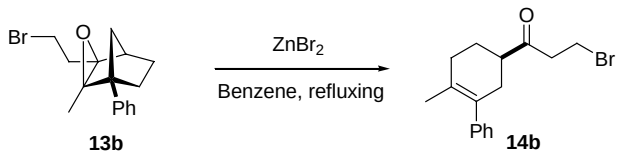


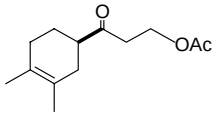
Table 1. Crystal data and structure refinement for epoxide **13b** (X = Br, R = Ph).

Empirical formula	$C_{16}H_{19}BrO$	
Formula weight	307.22	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.9507(8) Å	α= 90°.
	b = 25.614(2) Å	β= 90°.
	c = 30.160(3) Å	γ = 90°.
Volume	6914.4(11) $Å^3$	
Z	20	
Density (calculated)	1.476 Mg/m^3	
Absorption coefficient	2.959 mm^{-1}	
F(000)	3160	
Crystal size	0.10 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.35 to 27.88°.	
Index ranges	-11<=h<=11, -33<=k<=29, -37<=l<=39	
Reflections collected	45643	
Independent reflections	16373 [R(int) = 0.0643]	
Completeness to theta = 27.88°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16373 / 0 / 816	
Goodness-of-fit on F^2	0.908	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0541	
R indices (all data)	R1 = 0.1065, wR2 = 0.0628	
Absolute structure parameter	-0.018(5)	
Largest diff. peak and hole	0.730 and -0.607 $e.Å^{-3}$	

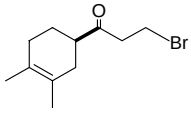


13b **14b**

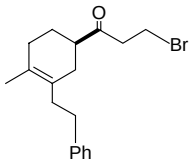
Meinwald rearrangement of 13 to 14. – To a solution of the epoxide **13** (35 mg, 0.11 mmol) in benzene (3 mL) was added anhydrous zinc bromide (117 mg, 0.52 mmol), and the mixture was stirred at 70 °C for about 10 min. After cooling to room temperature, the reaction mixture was diluted with ether, washed with water, brine, and dried over $MgSO_4$. The solvent was removed in vacuum and the residue was purified by chromatography on silica gel to give 27 mg (80%) of ketone **14b** (X = Br, R = Ph) as a colorless oil, $[\alpha]_D^{25}$ + 48 (*c* 1.6, $CHCl_3$); IR (film) ν_{max} 2914, 1711 (vs), 1440, 1073, 762, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3 H), 1.65–2.50 (m, 6 H), 2.69–2.79 (m, 1 H), 3.04–3.14 (m, 2 H), 3.58 (t, *J* = 6.9 Hz, 2 H), 7.13–7.35 (m, 5 H) ppm; ^{13}C NMR/DEPT (75 MHz, $CDCl_3$) δ 20.3 (q), 24.6 (t), 25.5 (t), 30.9 (t), 33.0 (t), 43.3 (t), 47.6 (d), 126.3 (d), 128.1 (d), 128.1 (d), 128.4 (d), 128.4 (d), 128.9 (s), 130.4 (s), 143.2 (s), 209.9 (s) ppm; HRMS (ESI) *m/z* $[M+Na]^+$ found 329.0514, calcd 329.0511 for $C_{16}H_{19}OBrNa$.



14a (X = OAc, R = Me), colorless oil, $[\alpha]_D^{18}$ + 95 (*c* 1.0, $CHCl_3$); IR (film) ν_{max} 2915, 1741, 1711, 1368, 1239 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.92–2.14 (m, 6 H), 1.62 (s, 6 H, 2 Me), 2.03 (s, 3 H), 2.52–2.83 (m, 3 H), 4.33 (t, *J* = 7.0 Hz, 2 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 18.8 (q), 19.0 (q), 20.9 (q), 25.0 (t), 31.1 (t), 32.8 (t), 39.2 (t), 47.8 (d), 59.5 (t), 123.8 (s), 125.4 (s), 171.0 (s), 210.5 (s) ppm; HRMS (ESI) *m/z* $[M+Na]^+$ found 247.1308, calcd 247.1305 for $C_{13}H_{20}O_3Na$.

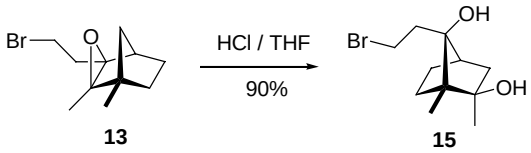


14a' (X = Br, R = Me), colorless oil, $[\alpha]_D^{18}$ + 73 (*c* 1.2, $CHCl_3$); IR (film) ν_{max} 2917, 1711, 1444, 1381, 911 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.62 (s, 6 H, 2 Me), 1.89–2.23 (m, 5 H), 2.51–2.56 (m, 1 H), 3.06 (t, *J* = 6.8 Hz, 2 H), 3.57 (t, *J* = 6.9 Hz, 2 H) ppm; HRMS (ESI) *m/z* $[M+H]^+$ found 245.0537, calcd 245.0536 for $C_{11}H_{18}OBr$.



14d (X = Br, R = phenethyl), colorless oil, $[\alpha]_D^{21}$ + 55 (*c* 1.8, $CHCl_3$); IR (film) ν_{max}

2921, 2856, 1710, 1452, 1075, 909, 733, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.49–2.32 (m, 8 H), 2.50–2.71 (m, 3 H), 3.00–3.14 (m, 2 H), 3.57 (t, *J* = 6.7 Hz, 2 H), 7.16–7.30 (m, 5 H) ppm; ^{13}C NMR/DEPT (75 MHz, $CDCl_3$) δ 18.5 (q), 24.9 (t), 25.6 (t), 31.0 (t), 31.2 (t), 34.5 (t), 35.5 (t), 43.3 (t), 47.7 (d), 125.8 (d), 126.7 (s), 127.4 (s), 128.2 (d), 128.2 (d), 128.4 (d), 128.4 (d), 142.2 (s), 210.4 (s) ppm; LRMS (EI) *m/z* 334 (M^+, 3%), 199 (12), 165 (9), 137 (31), 107 (100), 91 (96), 77 (21), 65 (26); HRMS (ESI) *m/z* $[M+H]^+$ found 352.1273, calcd 352.1271 for $C_{18}H_{24}OBr$.



13 **15**

Preparation of bicyclic diol 15 from epoxide 13. – A solution of the epoxide **13** (24 mg, 0.1 mmol) in 0.5 mL of THF was treated dropwise with 0.5 mL of 20% HCl at room temperature. The reaction mixture was stirred for 25 minutes and quenched with powdered $NaHCO_3$, and extracted with EtOAc (15 mL). Combined extracts were washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by chromatography on silica gel to afford 23 mg (90%) of diol **15** as crystalline solids, mp. 135–136°C (ethyl acetate); $[\alpha]_D^{20}$ + 33 (*c* 1.0, $CHCl_3$); IR (film) ν_{max} 3356, 3194, 2962, 1448 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (s, 3 H), 1.28 (s, 3 H), 0.85–1.60 (m, 6 H), 2.07–2.16 (m, 3 H), 2.61 (s, 1 H), 3.46–3.71 (m, 2 H), 3.97 (s, 1 H) ppm; ^{13}C NMR/DEPT (50 MHz, $CDCl_3$) δ 9.53 (q), 24.1 (q), 25.2 (t), 29.2 (t), 29.3 (t), 35.8 (t), 42.3 (d), 46.7 (t), 51.3 (s), 80.5 (s), 88.5 (s) ppm; LRMS (EI) *m/z* 244 ($[M-H_2O]^+$, 4%), 186 (15), 137 (24), 109 (100), 93 (21), 43 (36).

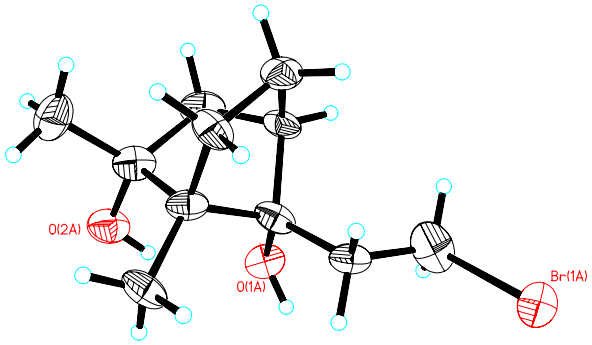
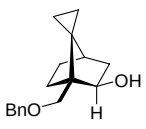


Table 2. Crystal data and structure refinement for diol **15**.

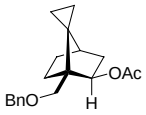
Empirical formula	$C_{11}H_{19}BrO_2$	
Formula weight	263.17	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.2349(15) Å	α= 90°.
	b = 7.3055(15) Å	β= 90°.
	c = 44.210(9) Å	γ = 90°.
Volume	2336.7(8) $Å^3$	
Z	8	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	3.493 mm^{-1}	
F(000)	1088	
Crystal size	0.20 x 0.18 x 0.10 mm^3	
Theta range for data collection	0.92 to 27.89°.	
Index ranges	-9<=h<=9, -9<=k<=6, -58<=l<=58	
Reflections collected	15105	
Independent reflections	5525 [R(int) = 0.0799]	
Completeness to theta = 27.89°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7214 and 0.5417	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5525 / 0 / 261	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1417	
R indices (all data)	R1 = 0.0921, wR2 = 0.1490	
Absolute structure parameter	0.061(17)	
Largest diff. peak and hole	0.551 and -0.684 $e.Å^{-3}$	



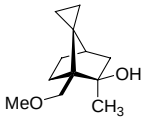
16, colorless oil.[6] IR (film) ν_{max} 3449, 2950, 2866, 1451, 1364, 1074, 1006, 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22–0.83 (m, 4H), 1.14–1.89 (m, 7H), 2.91 (d, *J* = 3.6 Hz, 1H, OH),

[6] Prepared from 10-hydroxy-7-spiral-cyclopropylcamphor by benzylation and carbonyl reduction, cf.: Föhlisch, B.; Bakr, D. A.; Fischer, P. *J. Org. Chem.* **2002**, *67*, 3682.

3.43 (q, *J* = 9.6 Hz, 2H), 3.96–3.99 (m, 1H), 4.46 (q, *J* = 12 Hz, 2H), 7.26–7.37 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.90, 5.16, 27.9, 30.0, 32.9, 41.4, 43.1, 48.9, 70.2, 73.5, 77.4, 127.4, 127.4, 127.6, 128.4, 128.4, 138.0 ppm; LRMS (EI) *m/z* 258 (M^+, 0.1%), 167 (2), 150 (26), 106 (32), 91 (100), 79 (23); HRMS (ESI) *m/z* $[2M+H]^+$ found 517.3316; calcd 517.3312 for $C_{34}H_{45}O_4$.



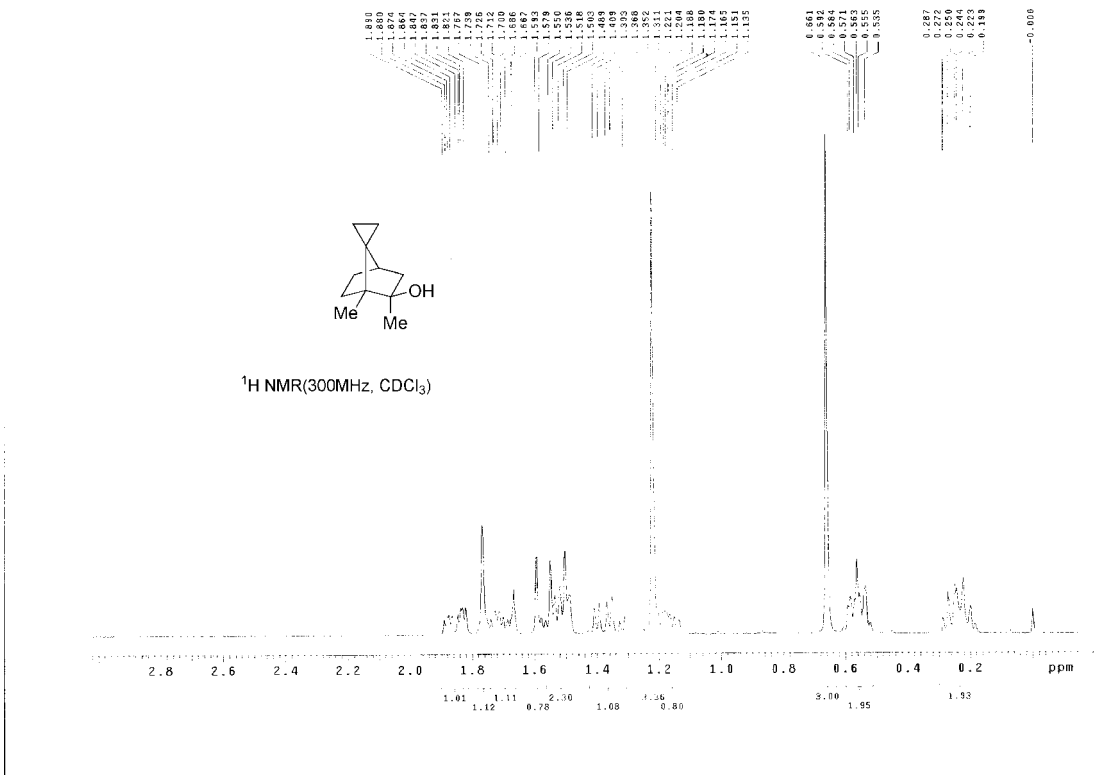
17, colorless oil. IR (film) ν_{max} 2952, 2867, 1734, 1367, 1246, 1099, 1053, 1018, 740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27–0.61 (m, 4H), 1.25–2.02 (m, 7H), 1.91 (s, 3H), 3.12 (d, *J* = 9.0 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 4.41 (q, *J* = 12 Hz, 2H), 4.86–4.90 (m, 1H), 7.26–7.33 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.29, 4.58, 21.2, 27.7, 29.5, 33.5, 39.7, 43.1, 48.5, 68.2, 73.3, 78.3, 127.3, 127.3, 127.3, 128.2, 128.2, 138.7, 170.7 ppm; LRMS (EI) *m/z* 300 (M^+, 0.1%), 209 (2), 134 (30), 106 (19), 91(100), 79 (12); HRMS (SMS) *m/z* $[M+H]^+$ found 301.1792; calcd 301.1798 for $C_{19}H_{25}O_3$.



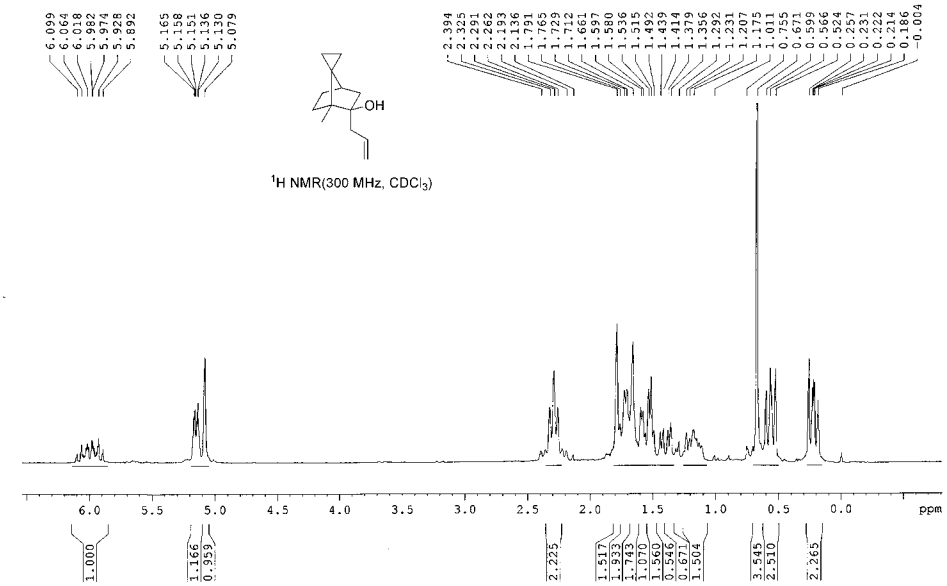
18, colorless oil.[7] IR (film)ν_{max} 3496, 2934, 2870, 1187, 1103 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24–0.92 (m, 4H), 1.14–1.96 (m, 8H), 1.34 (s, 3H), 3.26 (s, 3H), 3.32–3.41 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.7, 6.4, 24.3, 27.9, 28.3, 35.5, 43.3, 49.2, 51.4, 59.4, 72.3, 80.3 ppm; LRMS (EI) *m/z* 164 ($[M–32]^+$, 4%), 149 (14), 121 (26), 106 (100), 91 (62).

19, colorless oil (mixture of inseparable isomers, *ca* 1:1), prepared from methyl ether **18** by acidolysis with catalytic amount of *p*-TsOH in refluxing benzene in 80% yield. IR (film) ν_{max} 2953, 2869, 1716, 1669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20–0.69 (m, 8H), 1.17 (s, 3H), 1.23 (s, 3H), 1.25–2.13 (m, 16H), 9.47 (d, *J* = 6.6 Hz, 1H), 9.62 (d, *J* = 5.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.0, 6.8, 11.5, 13.4, 18.3, 20.4, 27.6, 28.4, 28.6, 28.9, 30.5, 37.7, 43.4, 45.8, 46.8, 47.3, 49.3, 51.3, 62.3, 63.8, 203.7, 206.9 ppm; LRMS (EI) *m/z* 164 (M^+, 7%), 135 (31), 107 (43), 91 (100), 79 (91).

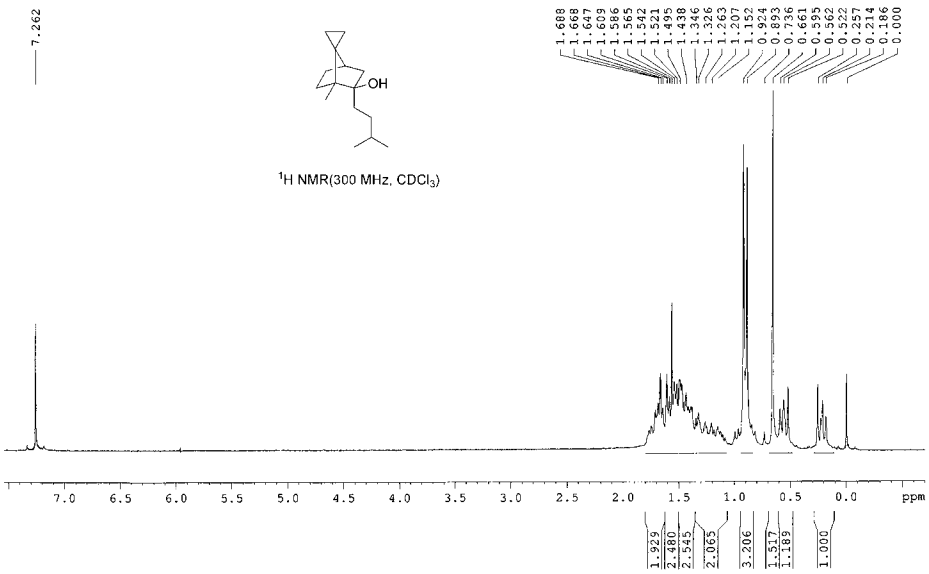
[7] Prepared from 10-hydroxy-7-spiral-cyclopropylcamphor by O-methylation and C(2) carbonyl methylation, cf.: Föhlisch, B.; Bakr, D. A.; Fischer, P. *J. Org. Chem.* **2002**, *67*, 3682.



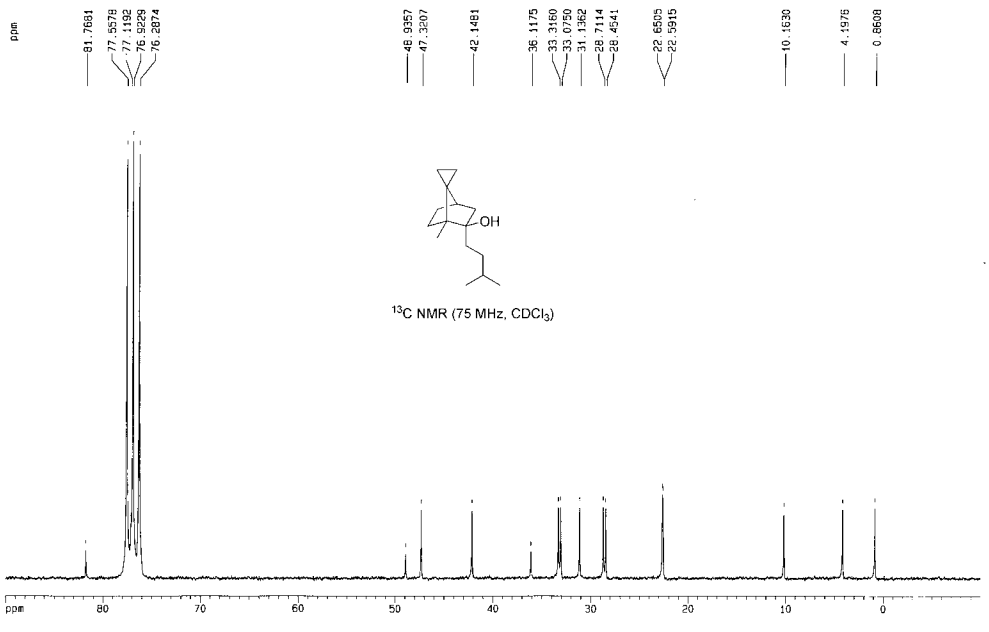
^{1}H NMR(300MHz, $CDCl_3$)



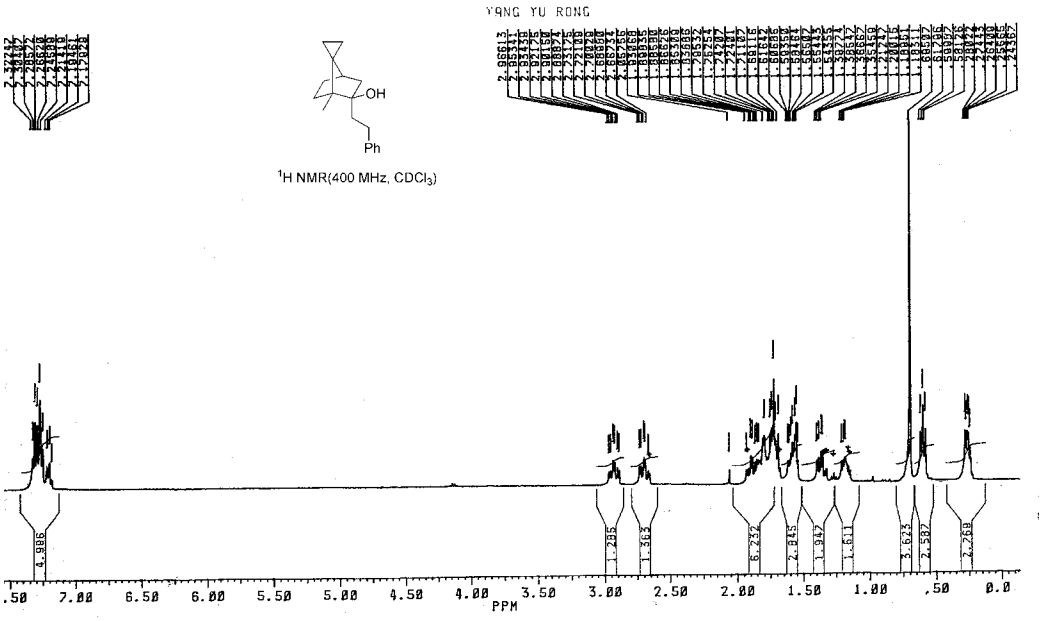
^{1}H NMR(300 MHz, $CDCl_3$)

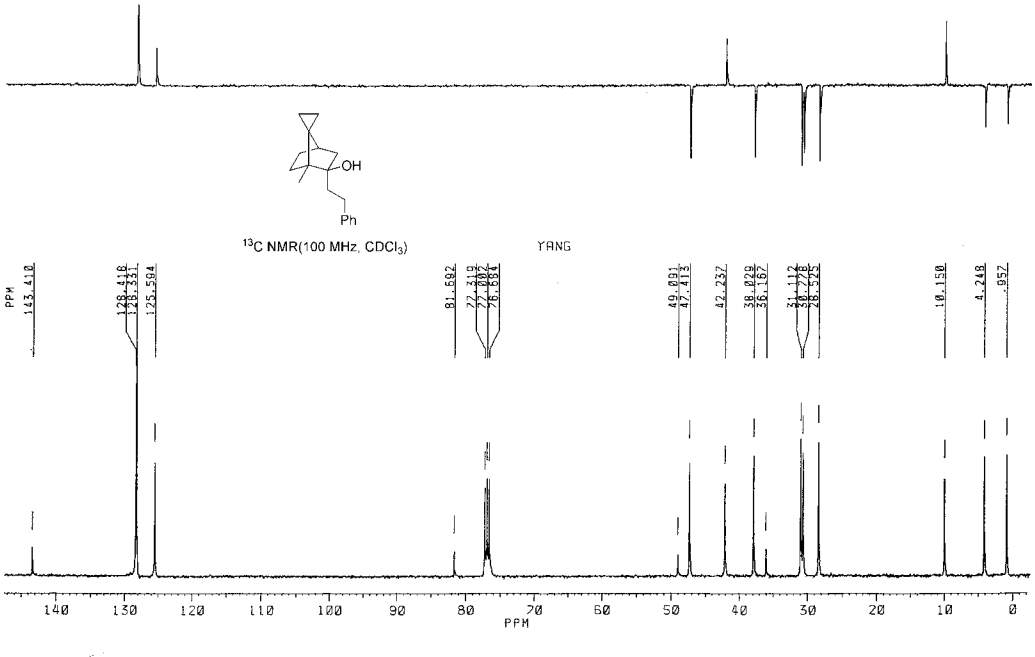


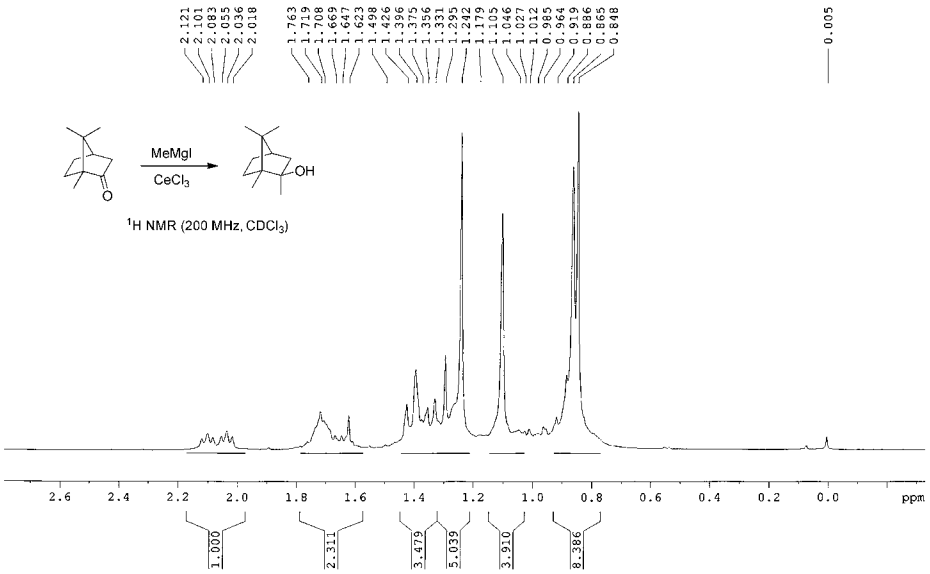
^{1}H NMR(300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)


YANG YU RONG
OH
Ph
^{1}H NMR(400 MHz, CDCl$_3$)
PPM


OH
Ph
^{13}C NMR(100 MHz, CDCl$_3$)
YANG
PPM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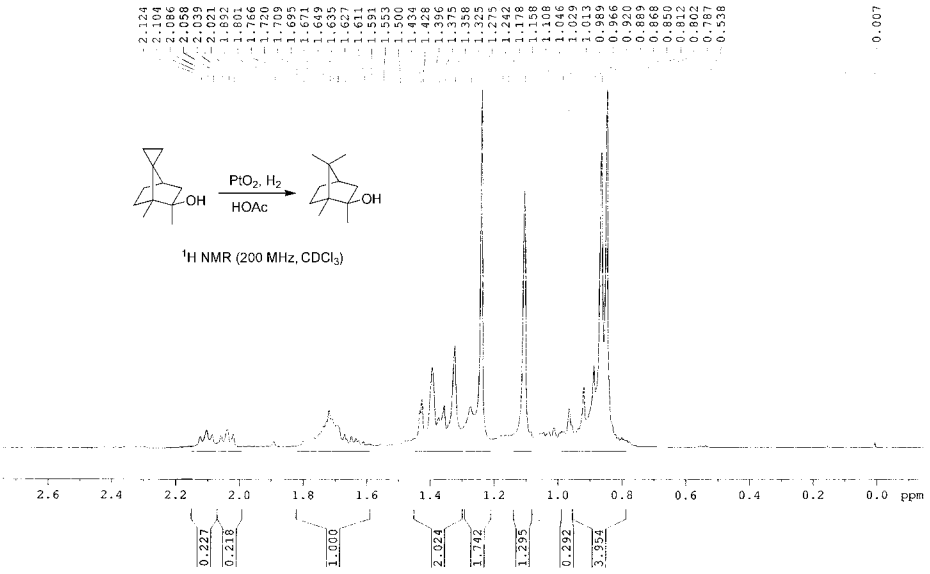
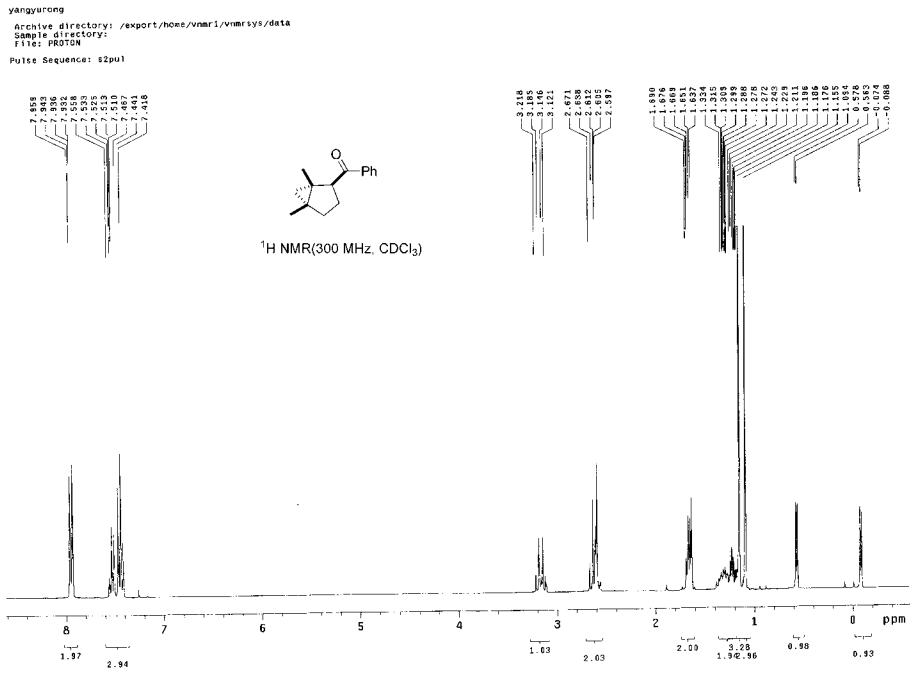
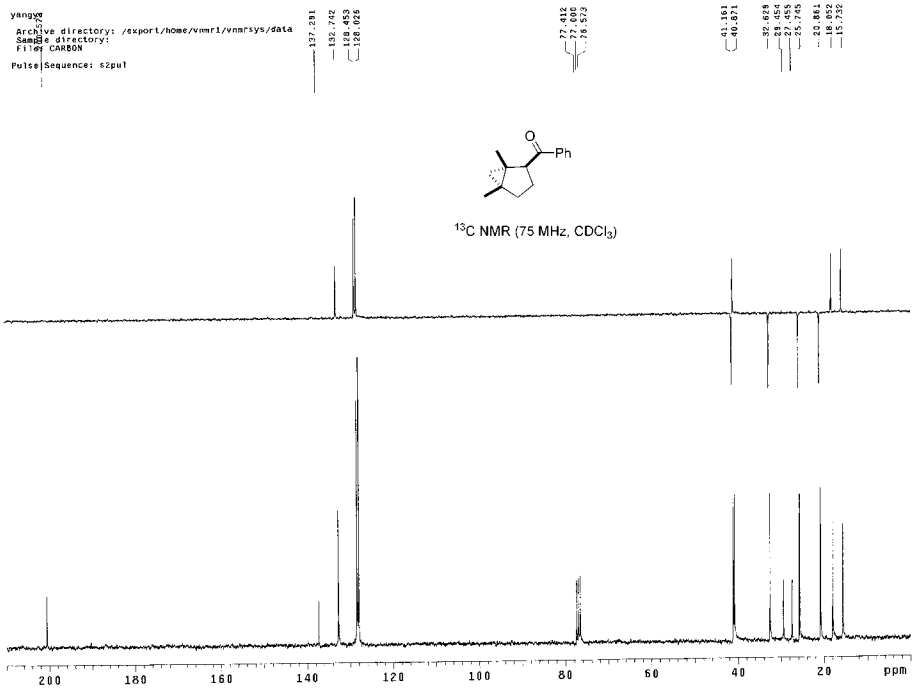
CeCl3
OH
O
1H NMR (200 MHz, CDCl3)
ppm


PtO2, H2
HOAc
OH
OH
1H NMR (200 MHz, CDCl3)
ppm


yangyurong
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Ph
^{1}H NMR(300 MHz, $CDCl_3$)
ppm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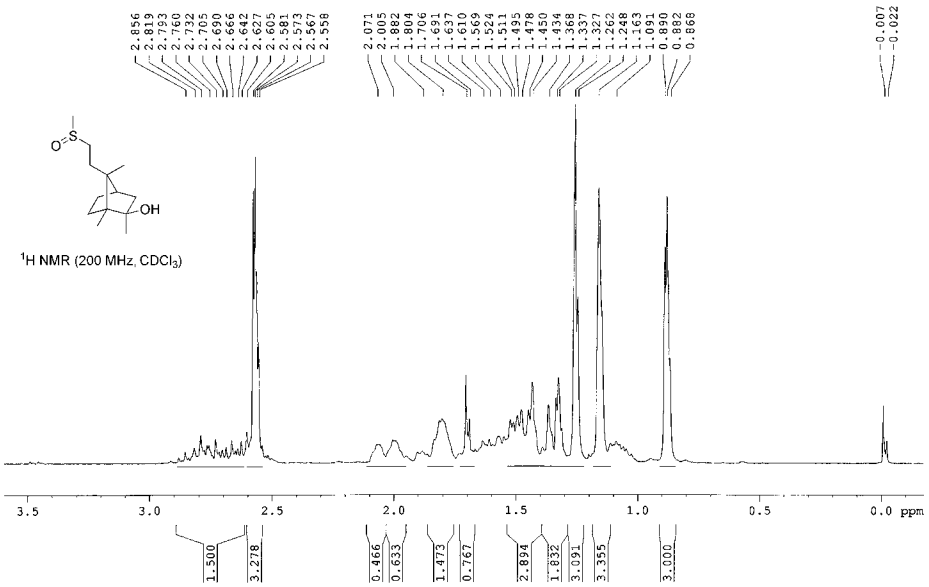
ppm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2.819
2.793
2.760
2.732
2.705
2.690
2.666
2.642
2.627
2.605
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2.573
2.567
2.558
2.071
2.005
1.882
1.804
1.706
1.691
1.637
1.610
1.569
1.524
1.511
1.495
1.478
1.450
1.434
1.368
1.337
1.327
1.262
1.248
1.163
1.091
0.890
0.882
0.868
0.007
-0.022
O=S
OH
^{1}H NMR (200 MHz, CDCl$_3$)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.500
3.278
0.466
0.633
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0.767
2.894
1.832
3.091
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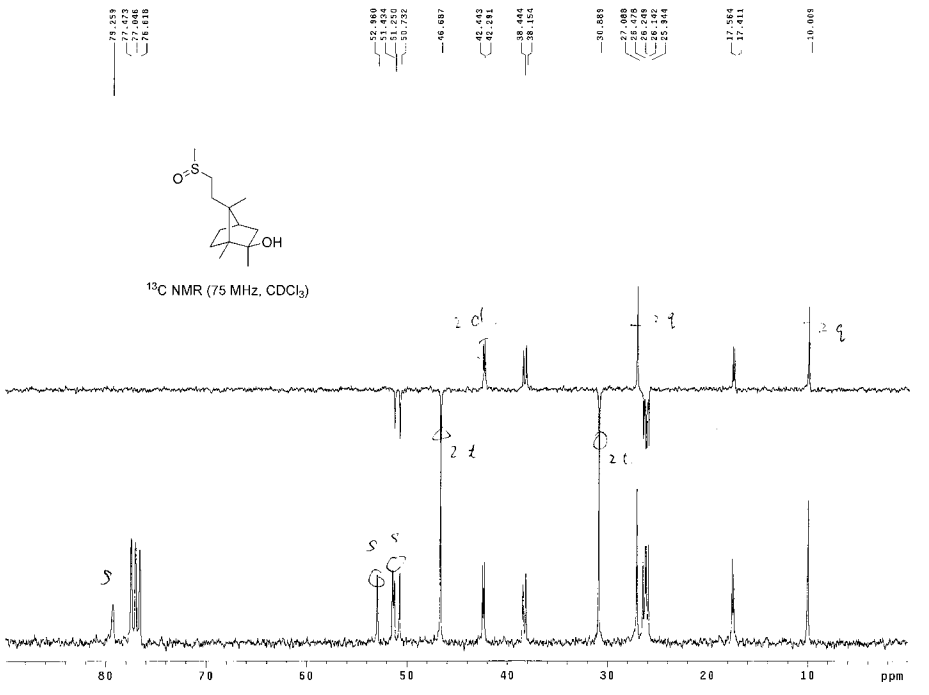
3.000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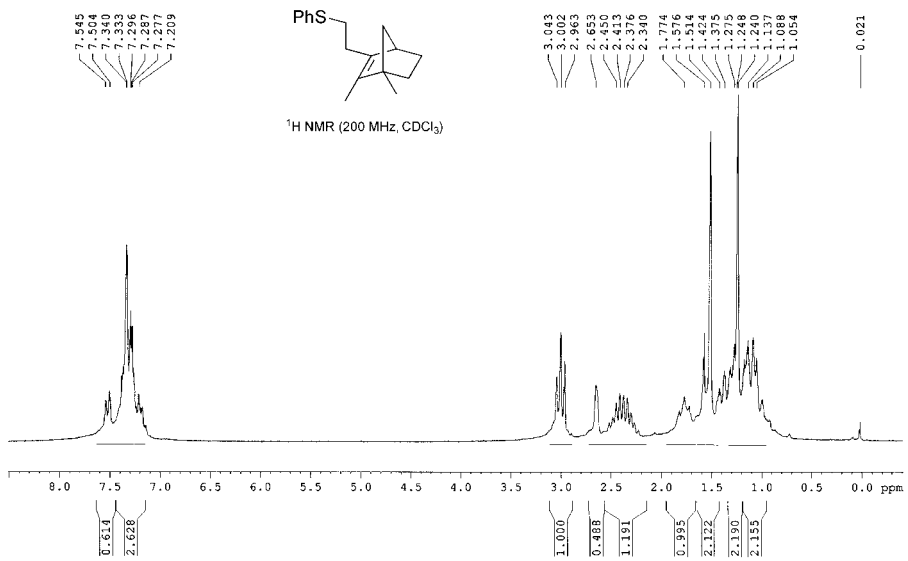
77.473
77.046
76.618
52.960
51.454
51.220
50.732
46.687
42.648
42.291
38.446
38.154
30.889
27.008
26.498
26.248
26.142
25.944
17.564
17.411
10.009
O=S
OH
^{13}C NMR (75 MHz, CDCl$_3$)
2 d
2 t
2 q
2 t
2 t
S
S
S
80
70
60
50
40
30
20
10
ppm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7.340
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7.296
7.287
7.277
7.209
3.043
3.002
2.963
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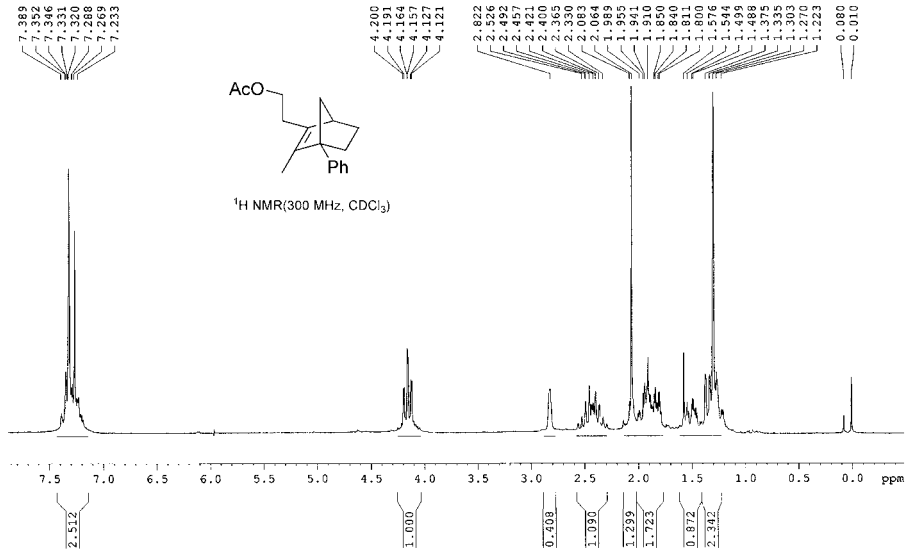
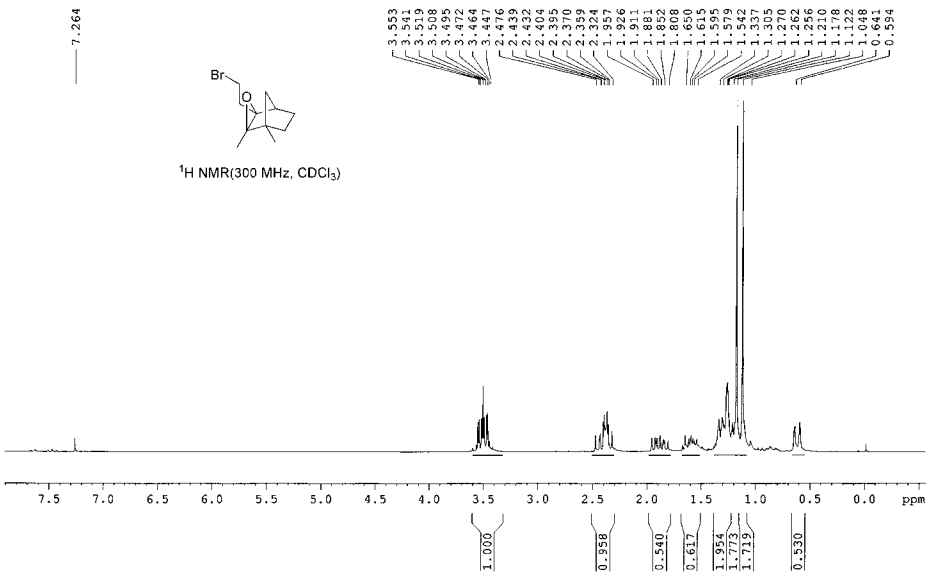
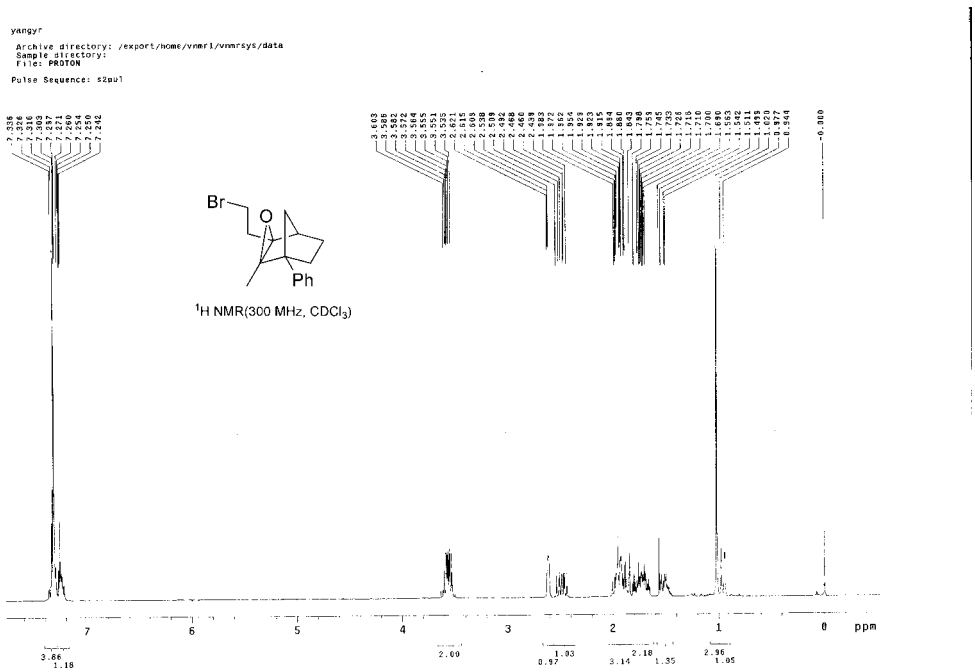
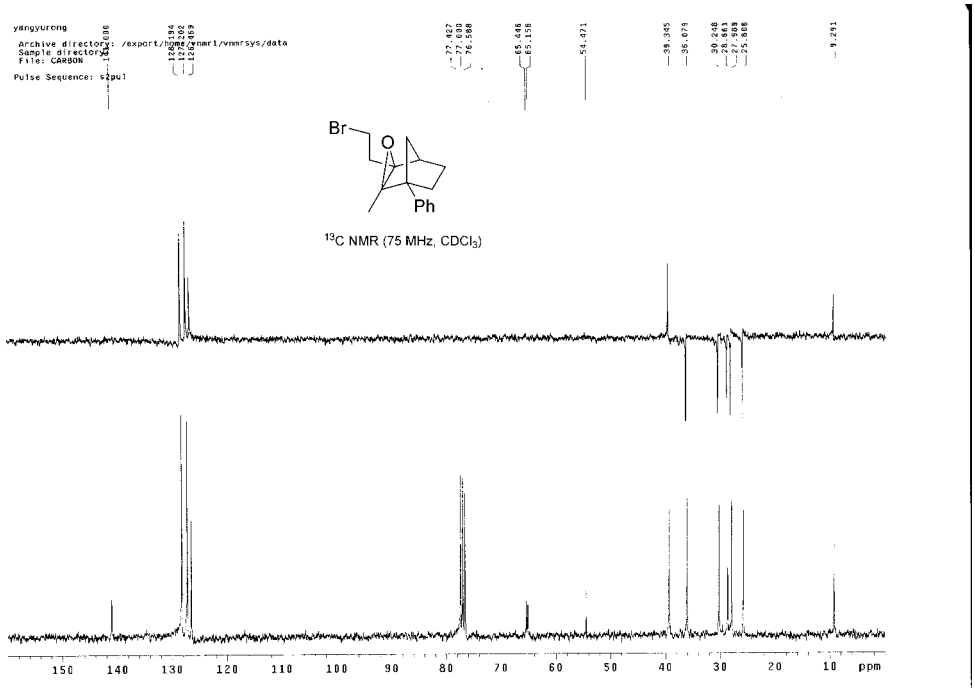
2.450
2.413
2.376
2.340
1.774
1.576
1.514
1.424
1.375
1.275
1.248
1.240
1.137
1.088
1.054
0.021
^{1}H NMR (200 MHz, $CDCl_3$)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.614
2.628
1.000
0.488
1.191
0.995
2.122
2.190
2.155

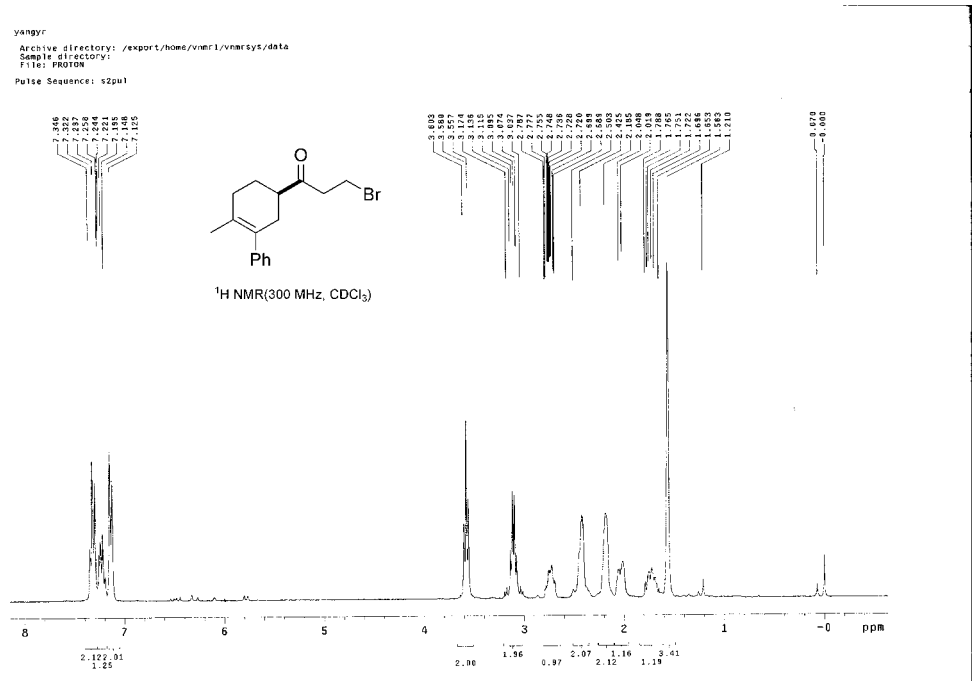

7.389
7.352
7.346
7.331
7.320
7.288
7.269
7.233
4.200
4.191
4.164
4.157
4.127
4.121
2.822
2.526
2.492
2.457
2.421
2.400
2.365
2.330
2.083
2.064
1.989
1.955
1.941
1.910
1.850
1.840
1.811
1.800
1.576
1.544
1.499
1.488
1.375
1.335
1.303
1.270
1.223
0.080
0.010
AcO
Ph
^{1}H NMR(300 MHz, $CDCl_3$)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.512
1.000
0.408
1.090
1.299
1.723
0.872
2.342


Br
O
^{1}H NMR(300 MHz, $CDCl_3$)
7.264
3.553
3.541
3.519
3.508
3.495
3.472
3.464
3.447
2.476
2.439
2.432
2.404
2.395
2.370
2.359
2.324
1.957
1.926
1.911
1.851
1.808
1.650
1.615
1.595
1.579
1.542
1.337
1.305
1.270
1.262
1.256
1.210
1.178
1.122
1.048
0.641
0.594
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000
0.958
0.540
0.617
1.954
1.773
1.719
0.530

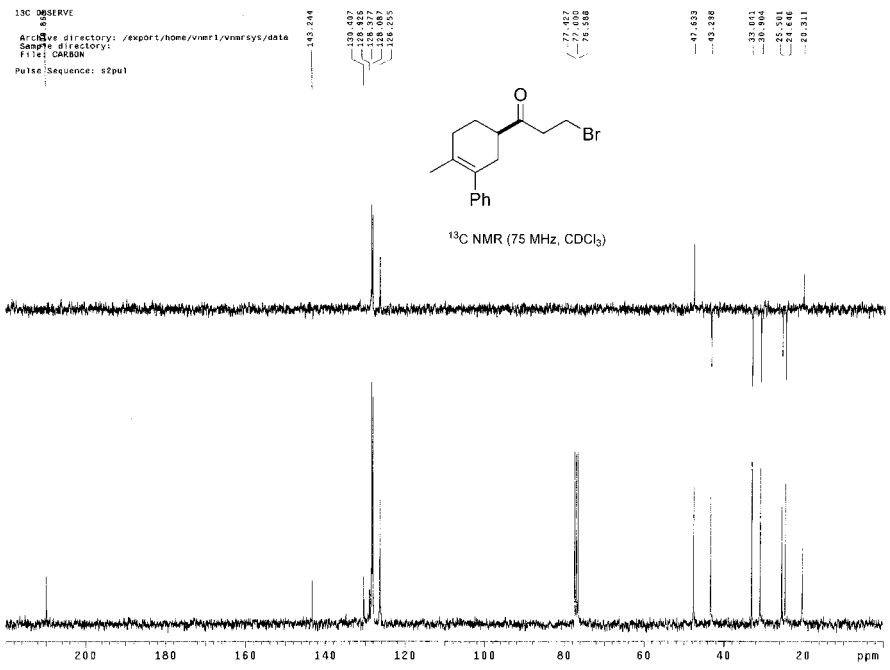

yangyr
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Br
O
Ph
^{1}H NMR(300 MHz, $CDCl_3$)
7 6 5 4 3 2 1 0 ppm
3.66
1.18
2.00
1.03
0.97
2.18
3.14
1.35
2.96
1.05



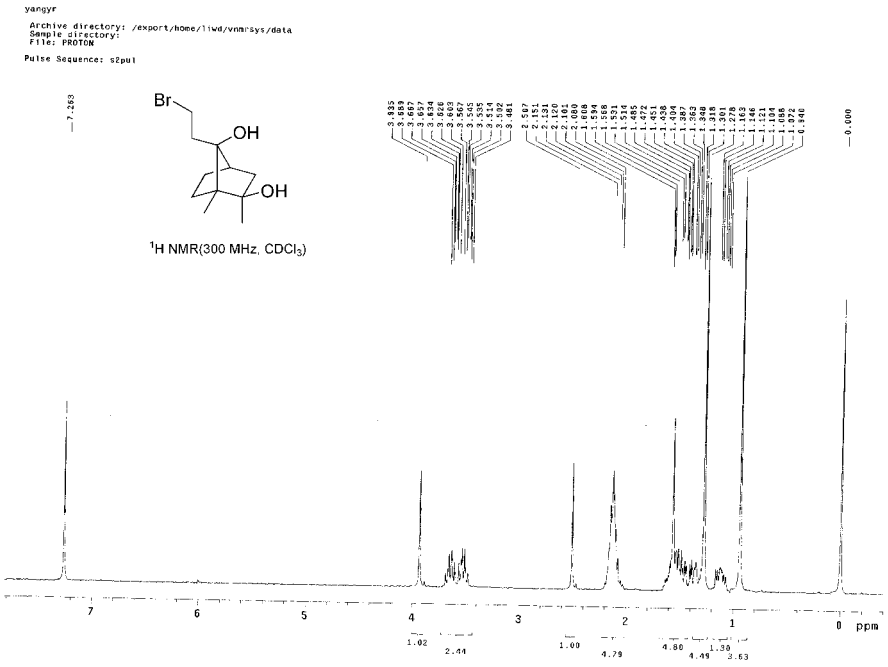
^{13}C NMR (75 MHz, $CDCl_3$)



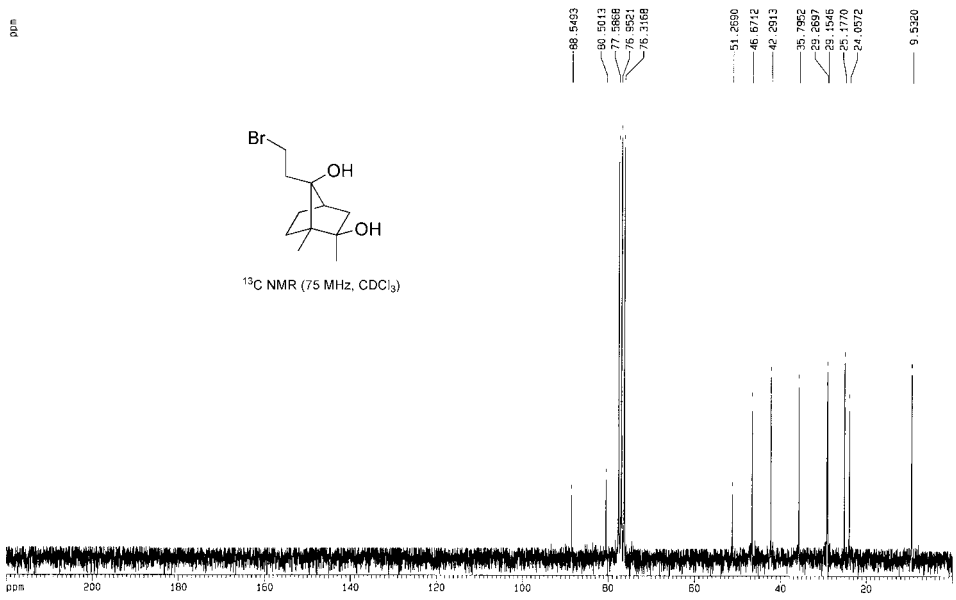
^{1}H NMR(300 MHz, $CDCl_3$)

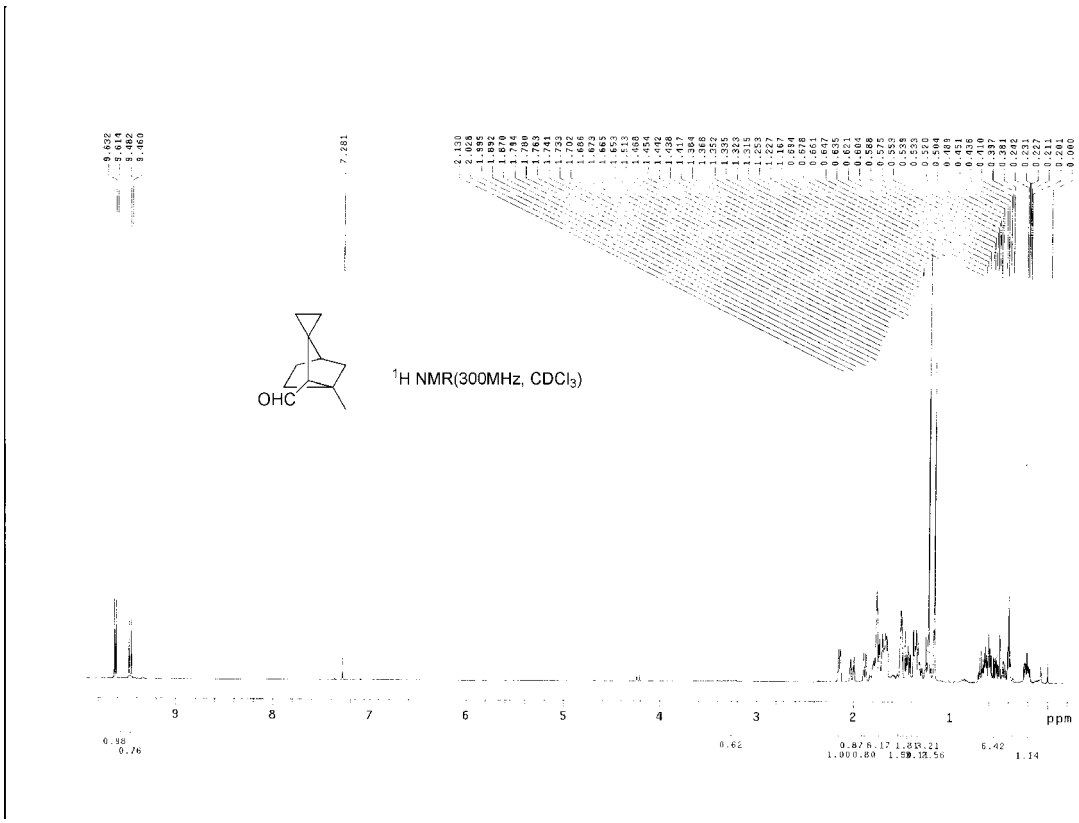


^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR(300 MHz, $CDCl_3$)


Br
OH
OH
^{13}C NMR (75 MHz, CDCl$_3$)
ppm
88.5493
80.5013
77.5868
76.9521
76.3168
51.2690
46.6712
42.2913
35.7952
29.2697
29.1546
25.1770
24.0572
9.5320
200
180
160
140
120
100
80
60
40
20


OHC
^{1}H NMR(300MHz, CDCl$_3$)
9.692
9.614
9.482
9.460
7.281
ppm