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A novel and simple procedure for the enantiospecific synthesis of bridgehead norbornane thioethers and thiocyanates

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Abstract—An easy three-step route for the enantiospecific synthesis of novel 1-norbornyl thioethers and thiocyanates from readily available natural fenchone and camphor is described. The key step of the synthetic route is the nucleophilic substitution over the sulfenyl sulfur atom of the intermediate thiotriflates by the corresponding *C*-nucleophiles.

1. Introduction

There is a great deal of current interest in the use of chiral sulfides in asymmetric synthesis.[1,2] This interest is mainly focused on sulfur ylide-mediated catalytic enantioselective aziridination of imines,[1,3] cyclopropanation of olefins[1,3b] and epoxidation of aldehydes and ketones.[1,4] These methodologies involve ylide generation either by deprotonation of the corresponding chiral sulfonium salt (from alkylation of the starting sulfide),[5] or by coupling of the latter with a carbene or carbenoid generated from a diazomethane derivative.[6] Since the pioneering work of Furukawa et al.[7] on the catalytic asymmetric epoxidation of aldehydes, using 10-camphoryl sulfides as ligands, a huge number of chiral sulfides have been synthesised and tested as chiral auxiliaries or catalysts for the above mentioned reactions.[1–7] Among these, camphor-based sulfides[8] (e.g. camphoroxathianes, mainly developed by Aggarwal et al.)[9] are the most extensively used and have played an important role in this field. Camphor-derived ketosulfides are also key intermediates in syntheses of other interesting C10–S(II)- and C10–S(IV)-substituted camphor derivatives.[10] In addition, homochiral camphor-based acetylene thioethers have recently found interesting applications in both intra- and intermolecular Pauson–Khand reactions.[11] On the other hand, thiocyanates are very important synthetic intermediates for the preparation of a wide variety of organosulfur compounds.[12] As a result of these applications, the development of new chiral camphor– or norbornane–S(II) derivatives is of particular interest and, in order to rapidly screen a series of these compounds for their use in asymmetric synthesis, the development of a method allowing rapid synthetic entry to these compounds is desirable.

Over the last decade, we have been interested in the chemistry of homochiral bridgehead norbornane derivatives, which have been widely used by us as starting materials for the preparation of chiral ligands,[13] virostatics,[14] homochiral cyclopentane derivatives[15] and other interesting camphor- or fenchone-based intermediates.[16] In continuation of our studies in this field, we wish to report herein an easy and convenient procedure for the enantiospecific synthesis of optically active bridgehead norbornane thioethers and thiocyanates, which find interesting applications as chiral controllers in asymmetric synthesis.

2. Results and discussion

Previously, we have shown[17] that the reaction of optically active thiocamphor and thiofenchone **2** with tri-

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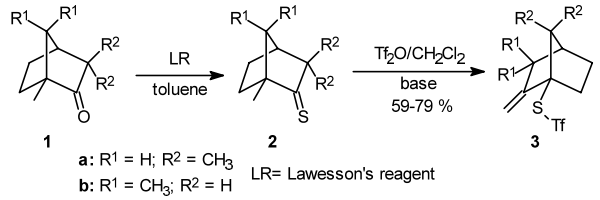
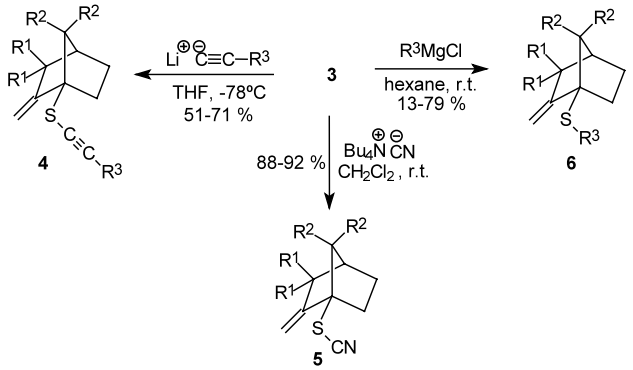
fluoromethanesulfonic anhydride constitutes the key step for the introduction of a sulfur atom at the bridgehead position of the norbornane framework, leading to the corresponding 2-methylene-1-norbornyl thiotriflates **3** (Scheme 1) which, like other thiosulfonates, are good sulfenylating reagents. Thus, the solvolysis of these homochiral bridgehead thiotriflates in EtOH and Et_2NH takes place smoothly, by nucleophilic attack at the sulfenyl sulfur atom, giving the corresponding sulfenates and sulfenamides, which can be oxidised easily to their sulfonic derivatives.[18]

Taking advantage of the powerful sulfenylating character of thiotriflates **3**, favoured by the strong nucleofugicity of the triflinate group, we have now assayed their reactivity with various *C*-nucleophiles, including metal acetylides, cyanide ion, organolithium and organomagnesium reagents (Scheme 2). The results are summarised in Table 1.



Scheme 1.



Scheme 2.

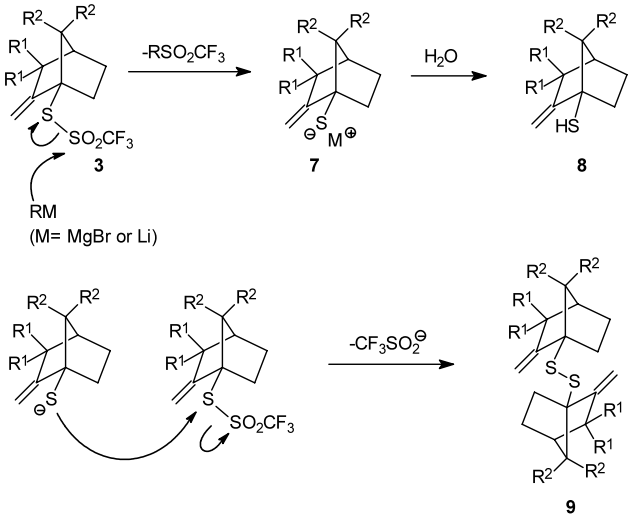
Table 1.

Entry	Product	R^1	R^2	R^3	Yield (%)[a]
1	**4a**	H	Me	CO_2Et	71
2	**4b**	Me	H	CO_2Et	51
3	**5a**	H	Me		88
4	**5b**	Me	H		92
5	**6a**	H	Me	Me	72
6	**6b**	H	Me	Et	79
7	**6c**	H	Me	*i*-Pr	76
8	**6d**	H	Me	Bu	71
9	**6e**	H	Me	*t*-Bu	13
10	**6f**	H	Me	Ph	45
11	**6g**	Me	H	Et	79
12	**6h**	Me	H	*i*-Pr	70

[a] The yields are given in isolated product.

The reaction of **3** with alkylmagnesium chlorides, lithium acetylides and tetrabutylammonium cyanide takes place under very mild conditions, by nucleophilic attack mainly at the more electrophilic sulfenyl sulfur atom,[19] leading to the corresponding sulfide (or thiocyanate) in moderate to good yields. Thus, the treatment of **3** with the in situ-generated acetylide[20] afforded the acetylene thioethers **4**. Thiocyanates **5** were obtained in good yield by treatment of **3** with tetrabutylammonium cyanide in dry dichloromethane. Finally, the reaction of **3** with the corresponding organomagnesium reagent leads to a series of bridgehead norbornane thioethers **6**, with different degrees of steric hindrance around the sulfur atom, in moderate to good yields.

It is noteworthy that the use of alkylmagnesium chlorides leads to the highest yields in the corresponding sulfide. The reaction of **3** with the more reactive analoguous organometallic reagents, such as alkyllithiums or alkylmagnesium bromides, under the same conditions, is much less selective, leading to complex reaction mixtures and lower yield of sulfide. As revealed by GC/MS monitorisation of the process, a competitive nucleophilic attack over the sulfonyl sulfur atom take place in these cases leading to both thiol **8**[17] and disulfide **9** in variable proportions, depending on the nature of the organometallic reagent (Scheme 3), together with the sulfide **6** formed by nucleophilic attack over the sulfenyl sulfur atom.



Scheme 3.

The formation of disulfide **9** can be explained by competitive nucleophilic attack of the thiolate anion **7** at the sulfenyl sulfur of thiotriflate **3**. A similar mechanism has been proposed by Langlois et al.[21] for the formation of disulfides in the reaction of thiols with trifluoromethanesulfonic anhydride in the presence of a base. Low selectivity was also observed in the reaction of **3** with the bulky *tert*-butylmagnesium chloride, probably due to the high steric hindrance for the nucleophilic attack over the sulfenyl sulfur atom directly

attached to the bridgehead position. As a result, only a 13% yield of **6e** was obtained, disulfide **9** being the main product.

3. Conclusion

In summary, we have developed an easy and short enantiospecific route to novel bridgehead norbornane thioethers and thiocyanates. The procedure takes place in only three steps starting from natural camphor and fenchone. All these compounds offer interesting applications as chirality transfer agents in asymmetric synthesis. Acetylene thioethers **4** can be used, for example, as chiral auxiliaries in stereoselective [2+2] and [4+2] cycloadditions. Sulfides **6** and its derivatives, find applications in catalytic enantioselective epoxidation or aziridination reactions. Thiocyanates **5** can be used as masked thiols, when required, and starting substrates for the access to other interesting chiral ligands bearing a sulfur-containing heterocyclic ring attached to the bridgehead position of the norbornane skeleton.[12] The presence of the methylene group at C-2 in all these compounds, in conjunction with all of the possible different degrees of oxidation of the sulfur atom, opens a way to other interesting homochiral norbornane derivatives. Further work in this field is currently in progress.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker-AC 200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) with TMS as internal standard; J values are given in hertz. IR spectra were recorded on a Shimadzu FTIR spectrometer. Reaction solvents were distilled from an appropriate drying agent before use. Mass spectra were recorded on a GC–MS Shimadzu QP5000 (60 eV) mass spectrometer. For gas chromatography, a Shimadzu 17 AAF chromatograph equipped with a capillary SGL-1 column was used. High-resolution electron-impact mass spectra (HREIMS) were measured on a VG Auto Spec instrument. Molecular rotation data were recorded on a Perkin–Elmer 241 polarimeter, concentrations are given as g/100 mL of solvent.

4.2. Typical procedure for the synthesis of acetylene thioethers, 4

A stirred solution of $(Me_3Si)_2NLi$ (2.0 mmol) in THF (2.0 mL) cooled at −78°C under an argon atmosphere, was treated with ethyl propiolate (2.0 mmol). After stirring for 15 min, the reaction mixture was diluted with THF (8 mL) and a solution of thiotriflate **3** (1.8 mmol) in THF (5 mL) was added dropwise. The mixture was stirred at −78°C for 24 h (the reaction progress was monitored by GC). After completion of the reaction, CH_2Cl_2 (15 mL) was added. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude oil was purified by column chromatography (silica gel/diethyl ether) to yield pure **4**.

4.2.1. Ethyl 3-{[(1*S*)-7,7-dimethyl-2-methylenebicyclo-[2.2.1]hept-1-yl]sulfanyl}-2-propynoate, 4a. Yield 71%. $[\alpha]_D^{20}$ −31.4 (*c* 2.39, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.11 (m, 1H), 4.89 (m, 1H), 4.19 (q, $J=7.1$ Hz, 2H), 2.51 (dm, $J=16.1$ Hz, 1H), 2.36–2.20 (m, 1H), 2.10–1.79 (m, 3H), 1.71 (ddd, $J=12.1$, 9.3, 4.1 Hz, 1H), 1.45–1.27 (m, 1H), 1.28 (t, $J=7.1$ Hz, 3H), 1.08 (s, 3H), 0.97 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.0, 152.0, 106.0, 87.5, 83.2, 65.9, 61.5, 50.8, 43.6, 36.6, 34.5, 27.9, 19.7, 19.4, 14.1 ppm. FTIR (CCl_4): ν 3078, 2147, 1705, 1236, 1036 cm^{-1}. MS m/z 264 (M^+, 2), 249 (1), 235 (8), 220 (7), 209 (7), 192 (21), 177 (13), 163 (7), 149 (32), 135 (23), 105 (14), 91 (54), 77 (38), 69 (26), 53 (19), 41 (100). HREIMS calcd for $C_{15}H_{20}O_2S$ (M^+): 264.11840. Found: 264.11835.

4.2.2. Ethyl 3-{[(1*R*)-3,3-dimethyl-2-methylenebicyclo-[2.2.1]hept-1-yl]sulfanyl}-2-propynoate, 4b. Yield 51%. $[\alpha]_D^{20}$ −74.2 (*c* 1.46, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.97 (s, 1H), 4.79 (s, 1H), 4.21 (q, $J=7.1$ Hz, 2H), 2.10–1.48 (m, 7H), 1.29 (t, $J=7.1$ Hz, 3H), 1.12 (s, 3H), 1.08 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 161.8, 153.0, 101.9, 88.3, 82.6, 61.7, 61.6, 45.9, 44.1, 43.5, 34.6, 29.3, 25.9, 25.6, 14.1 ppm. FTIR (film): ν 3072, 2149, 1705, 1236 cm^{-1}. MS m/z 264 (M^+, 1) 220 (18), 192 (31), 177 (37), 163 (15), 149 (81), 135 (17), 115 (16), 105 (23), 91 (73), 77 (56), 69 (30), 53 (32), 41 (100). HREIMS calcd for $C_{15}H_{20}O_2S$ (M^+): 264.11840. Found: 264.11758.

4.3. Typical procedure for synthesis of thiocyanates, 5

To a stirred solution of thiotriflate **3** (3.0 mmol) in dry CH_2Cl_2 (25 mL), 3.3 mmol of tetrabutylammonium cyanide were added. The reaction mixture was stirred for 20 min at room temperature. After that, the reaction was quenched with water and extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude oil was purified by column chromatography (silica gel/hexane) to yield pure **5**.

4.3.1. (1*S*)-7,7-Dimethyl-2-methylenebicyclo[2.2.1]hept-1-yl thiocyanate, 5a. Yield 88%. $[\alpha]_D^{20}$ −43.3 (*c* 1.59, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.16 (t, $J=2.2$ Hz, 1H), 4.96 (t, $J=2.1$ Hz, 1H), 2.54 (dm, $J=16.0$ Hz, 1H), 2.31–1.89 (m, 4H), 1.87–1.72 (m, 1H), 1.47–1.32 (m, 1H), 1.12 (s, 3H), 0.96 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 151.0, 111.1, 106.5, 66.3, 50.9, 43.3, 36.5, 35.3, 27.9, 19.6, 19.2 ppm. FTIR (CCl_4): ν 3100, 2154, 1659, 1450 cm^{-1}. MS m/z 193 (M^+, 7), 178 (10), 164 (7), 150 (30), 137 (19), 124 (25), 119 (13), 105 (19), 91 (57), 79 (25), 77 (31), 69 (28), 65 (19), 41 (100). HREIMS calcd for $C_{11}H_{15}NS$ (M^+): 193.09252. Found: 193.09254.

4.3.2. (1*R*)-3,3-Dimethyl-2-methylenebicyclo[2.2.1]hept-1-yl thiocyanate, 5b. Yield 92%. $[\alpha]_D^{20}$ −45.6 (*c* 2.04, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.01 (bs, 1H), 4.85 (bs, 1H), 2.12 (dm, $J=10.0$ Hz, 1H), 2.07–1.54 (m, 6H), 1.13 (s, 3H), 1.10 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 161.0, 111.3, 102.5, 61.4, 45.9, 44.8, 43.4, 35.1, 29.4, 25.9, 25.6 ppm. FTIR (CCl_4): *v* 3080, 2160, 1660, 1460 cm^{-1}. MS *m*/*z* 193 (M^+, 9), 178 (6), 164 (6), 150 (42), 124 (28), 119 (16), 105 (15), 91 (80), 79 (24), 77 (28), 69 (44), 65 (25), 41 (100). HREIMS calcd for $C_{11}H_{15}NS$ (M^+): 193.09252. Found: 193.09256.

4.4. Typical procedure for the synthesis of thioethers, 6

To a stirred solution, cooled at 0°C, of thiotriflate **3** (2.0 mmol) in hexane (10 mL), a solution of the corresponding alkylmagnesium chloride (10.0 mmol) in THF was added dropwise. The mixture was stirred at room temperature until disappearance of starting thiotriflate (the reaction was monitored by CG). After that, the reaction was quenched with 10% aqueous hydrochloric acid and extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the crude oil was purified by column chromatography (silica gel/hexane) to yield pure **6**.

4.4.1. (1*S*)-7,7-Dimethyl-2-methylene-1-(methylsulfanyl)-bicyclo[2.2.1]heptane, 6a. Yield 72%. $[\alpha]_D^{20}$ −32.1 (*c* 5.58, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.13 (m, 1H), 4.85 (m, 1H), 2.45 (dm, $J=16.1$ Hz, 1H), 2.09 (s, 3H), 2.11–2.01 (m, 1H), 2.00–1.73 (m, 3H), 1.60–1.43 (m, 1H), 1.39–1.20 (m, 1H) 1.03 (s, 3H), 0.89 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 153.9, 104.9, 62.2, 50.4, 44.3, 36.8, 34.7, 28.0, 20.8, 19.7, 12.2 ppm. FTIR (CCl_4): *v* 3078, 1657, 1472, 1448, 1385, 1367, 1298 cm^{-1}. MS *m*/*z* 182 (M^+, 35), 167 (41), 140 (33), 127 (54), 119 (30), 105 (40), 91 (91), 69 (38), 41 (100). HREIMS calcd for $C_{11}H_{18}S$ (M^+): 182.11292. Found: 182.11267.

4.4.2. (1*S*)-1-(Ethylsulfanyl)-7,7-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6b. Yield 79%. $[\alpha]_D^{20}$ −22.3 (*c* 0.40, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.15 (m, 1H), 4.84 (m, 1H), 2.73–2.53 (m, 2H), 2.49 (dm, $J=16.1$ Hz, 1H), 2.08–1.74 (m, 4H), 1.54 (m, 1H), 1.36–1.24 (m, 1H), 1.24 (t, $J=7.6$ Hz, 3H), 1.03 (s, 3H), 0.88 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.6, 104.9, 63.2, 50.3, 44.1, 36.8, 34.9, 28.1, 22.8, 20.6, 19.7, 15.3 ppm. FTIR (CCl_4): *v* 3078, 1655, 1558, 1448, 1384, 1367 cm^{-1}. MS *m*/*z* 196 (M^+, 41), 167 (47), 153 (42), 141 (57), 133 (18), 134 (18), 125 (27), 119 (49), 105 (35), 119 (49), 111 (31), 105 (35), 91 (98), 77 (47), 69 (54), 41 (100). HREIMS calcd for $C_{12}H_{20}S$ (M^+): 196.12857. Found: 196.12820.

4.4.3. (1*S*)-1-(Isopropylsulfanyl)-7,7-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6c. Yield 76%. $[\alpha]_D^{20}$ −21.4 (*c* 1.99, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.23 (m, 1H), 4.82 (m, 1H), 3.05 (sept., $J=6.8$ Hz, 1H), 2.47 (dm, $J=16.1$ Hz, 1H), 2.18–1.75 (m, 4H), 1.63 (ddd, $J=11.3$, 9.3, 3.5 Hz, 1H), 1.36 (d, $J=6.8$ Hz, 3H), 1.36–1.34 (m, 1H), 1.32 (d, $J=6.8$ Hz, 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 155.6, 105.3, 63.9, 50.1, 43.7, 36.8, 34.2, 33.2, 28.3, 27.1, 25.8, 20.0, 19.5 ppm. FTIR (CCl_4): *v* 3080, 1655, 1450, 1383, 1367 cm^{-1}. MS *m*/*z* 210 (M^+, 28), 167 (52), 153 (21), 133 (18), 125 (47), 111 (29), 91 (53), 77 (31), 69 (32), 43 (47), 41 (100). HREIMS calcd for $C_{13}H_{22}S$ (M^+): 210.14422. Found: 210.14372.

4.4.4. (1*S*)-1-(Butylsulfanyl)-7,7-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6d. Yield 71%. $[\alpha]_D^{20}$ −25.2 (*c* 1.16, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.15 (m, 1H), 4.85 (m, 1H), 2.70–2.40 (m, 3H), 2.07–1.75 (m, 4H), 1.67–1.20 (m, 6H), 1.04 (s, 3H), 0.96 (t, $J=7.3$ Hz, 3H), 0.89 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.5, 104.9, 63.0, 50.3, 44.1, 36.8, 35.0, 32.6, 28.4, 28.1, 22.2, 20.7, 19.7, 13.7 ppm. FTIR (film): *v* 3076, 1657, 1448 cm^{-1}. MS *m*/*z* 224 (M^+, 30), 181 (16), 169 (34), 168 (33), 167 (34), 153 (5), 135 (14), 125 (30), 105 (30), 91 (59), 77 (28), 69 (24), 55 (25), 41 (100). HREIMS calcd for $C_{14}H_{24}S$ (M^+): 224.15987. Found: 224.16005.

4.4.5. (1*S*)-1-(*tert*-Butylsulfanyl)-7,7-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6e. Yield 13%. $[\alpha]_D^{20}$ +4.8 (*c* 1.43, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.43 (m, 1H), 4.84 (m, 1H), 2.52–2.27 (m, 2H), 2.09–1.70 (m, 4H), 1.39–1.22 (m, 1H), 1.44 (s, 9H), 1.02 (s, 3H), 0.81 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 156.6, 106.6, 65.6, 51.0, 44.8, 42.6, 36.9, 34.2, 32.9, 28.8, 19.8, 19.5 ppm. FTIR (CCl_4): *v* 3082, 1657, 1471, 1458, 1383, 1363, 1159 cm^{-1}. MS *m*/*z* 224 (M^+, 4), 168 (21), 167 (11), 153 (7), 135 (8), 113 (23), 112 (20), 91 (25), 77 (15), 57 (56), 41 (100). HREIMS calcd for $C_{14}H_{24}S$ (M^+): 224.15987. Found: 224.15936.

4.4.6. (1*S*)-7,7-Dimethyl-2-methylene-1-(phenylsulfanyl)-bicyclo[2.2.1]heptane, 6f. Yield 45%. $[\alpha]_D^{20}$ +29.7 (*c* 3.20, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.64–7.54 (m, 2H), 7.27–7.19 (m, 3H), 5.49 (m, 1H), 4.9 (m, 1H), 2.51 (dm, $J=16.1$ Hz, 1H), 2.04 (dt, $J=13.9$; 2.1 Hz, 1H), 1.83–1.77 (m, 3H), 1.58–1.20 (m, 2H), 0.99 (s, 3H), 0.91 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 151.4, 135.8, 133.6, 128.2, 127.5, 106.0, 65.8, 50.4, 43.9, 36.8, 34.8, 28.1, 20.0, 19.5 ppm. FTIR (film): *v* 3084, 1657, 1471, 1458, 1382, 1363 cm^{-1}. MS *m*/*z* 244 (M^+, 25), 189 (20), 167 (25), 134 (4), 124 (11), 119 (11), 105 (11), 91 (6), 77 (38), 65 (32), 41 (100). HREIMS calcd for $C_{16}H_{20}S$ (M^+): 244.12857. Found: 244.12860.

4.4.7. (1*R*)-1-(Ethylsulfanyl)-3,3-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6g. Yield 79%. $[\alpha]_D^{20}$ −54.6 (*c* 0.93, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ 5.02 (s, 1H), 4.73 (s, 1H), 2.50 (q, $J=7.5$ Hz, 2H), 1.97 (dm, $J=9.5$ Hz, 1H), 1.89 (m, 1H), 1.87–1.65 (m, 2H), 1.64–1.50 (m, 1H), 1.49–1.30 (m, 2H), 1.23 (t, $J=7.5$ Hz, 3H), 1.10 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 163.3, 100.8, 59.5, 46.0, 43.6, 42.8, 35.5, 29.3, 26.0, 25.1, 23.5, 14.9 ppm. FTIR (film): *v* 3070, 1655, 1458 cm^{-1}. MS *m*/*z* 196 (M^+, 33), 167 (48), 153 (96), 91 (62), 77 (35), 59 (33), 41 (100). HREIMS calcd for $C_{12}H_{20}S$ (M^+): 196.12857. Found: 196.12850.

4.4.8. (1*R*)-1-(Isopropylsulfanyl)-3,3-dimethyl-2-methylenebicyclo[2.2.1]heptane, 6h. Yield 70%. $[\alpha]_D^{20}$ −87.2 (*c* 2.10, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz): δ

5.06 (s, 1H), 4.71 (s, 1H), 2.86 (sept., $J=6.8$ Hz, 1H), 2.05–1.97 (m, 1H), 1.90 (m, 1H), 1.85–1.69 (m, 2H), 1.65–1.45 (m, 2H), 1.43–1.34 (m, 1H), 1.31 (d, $J=6.8$ Hz, 3H), 1.26 (d, $J=6.8$ Hz, 3H), 1.10 (s, 3H), 1.04 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 164.0, 100.9, 59.9, 46.1, 44.2, 42.8, 36.2, 34.1, 29.4, 26.2, 26.1, 25.1, 24.9 ppm. FTIR (CCl_4): ν 3070, 1653, 1460, 1388, 1363, 1209, 1149 cm^{-1}. MS m/z 210 (M^+, 25), 181 (6), 167 (70), 139 (19), 125 (25), 105 (20), 91 (41), 77 (21), 59 (20), 41 (100). HREIMS calcd for $C_{13}H_{22}S$ (M^+): 210.14422. Found: 210.14357.

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