Supporting Information

Asymmetric Pauson-Khand Reactions using Camphor-derived Chelating Thiols as Chiral Controllers.

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Experimental Section.

Pauson-Khand reactions of 7b with Norbornadiene. Procedure B using as reagents: **7b** (0.12 g, 0.33 mmol), $Co_2(CO)_8$ (0.12 mg, 0.35 mmol), NMO (0.24 g, 2.06 mmol) and norbornadiene (0.35 mL, 3.3 mmol) was followed. The reaction was performed at 0°C during 48 h, affording 49 mg (31% yield, two steps) of **11b** (25:75 diastereomeric ratio as determined by ^{13}C NMR).

Procedure C using as reagents: **7b** (0.22 g, 0.6 mmol), $Co_2(CO)_8$ (0.22 g, 0.65 mmol), and norbornadiene (0.64 g, 6.3 mmol) was followed. The reaction was performed at 0°C during 40 h, after addition of the olefin at –15°C, affording 168 mg (56% yield, two steps) of **11b** (98:2 diastereomeric ratio as determined by ^{13}C NMR).

Procedure D using as reagents: **10b** (0.2 g, 0.33 mmol), norbornadiene (0.33 g, 3.3 mmol), and hexane (6 mL) was followed. The reaction was performed at 0°C during 48 h, after addition of the

olefin at –15°C, affording 100 mg (64% yield) of **11b** (95:5 diastereomeric ratio as determined by ^{13}C NMR).

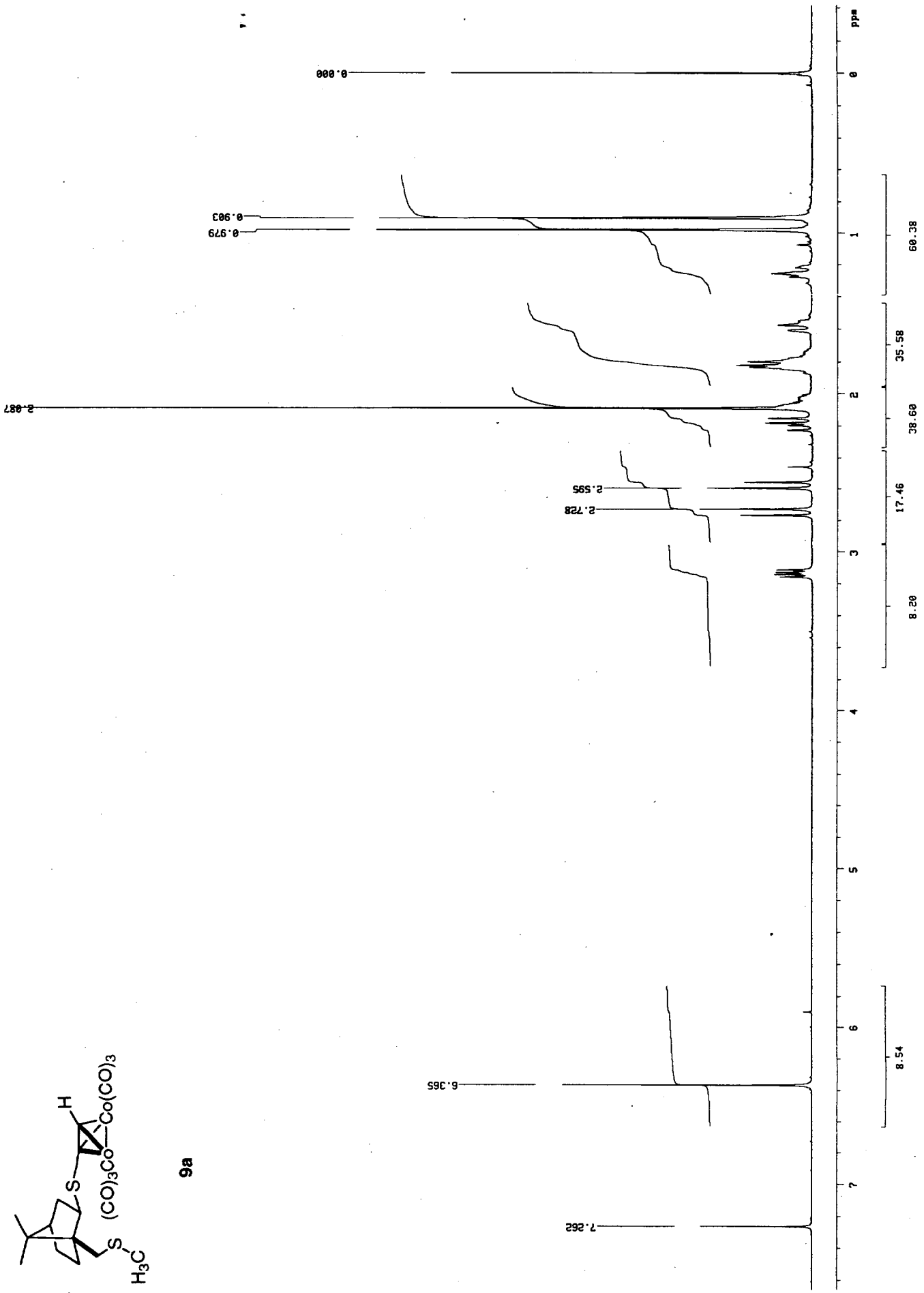
(1*R*,2*R*,6*S*,7*S*)-4-[(1*S*,2*R*,4*R*)-7,7-dimethyl-1-(2,4,6-trimethylbenzylsulfanyl) methylbicyclo[2.2.1]hept-2-ylsulfanyl]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (11b). $[\alpha]_D$ = +16.9 (*c* 1.0, $CDCl_3$). IR (film) ν_{max} = 2954, 1704, 1563, 1457 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 7.05 (d, 1H), 6.78 (broad s, 2H), 6.30-6.15 (m, 2H), 3.8, 3.74 (AB, J= 11Hz, 2H), 3.38-3.25 (dd, 1H), 2.95, 2.85 (AB, J= 12Hz, 2H), 2.95-0.95 (complex signal, 13H), 2.33 (s, 6H), 2.21 (s, 3H), 1.05 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.0 (C), 152.6 (CH), 146.5 (2C), 138.2 (CH), 137.0 (CH), 136.8 (C), 136.3 (C), 131.3 (C), 128.8 (2CH), 53.5 (C), 52.5 (CH), 50.5 (CH), 48.7 (C), 48.5 (CH), 46.4 (CH), 43.8 (CH), 43.5 (CH), 41.5 (CH_2), 41.0 (CH_2), 35.3 (CH_2), 34.1 (CH_2), 33.1 (CH_2), 27.3 (CH_2), 20.9 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 19.6 ($2CH_3$). HRMS Calcd for $C_{30}H_{38}OS_2$: 478.2364, found 478.2381.

Pauson-Khand Adduct of 7b with Norbornene. Procedure B using as reagents **7b** (0.16 g, 0.45 mmol), $Co_2(CO)_8$ (0.16 g, 0.47 mmol), NMO (0.32 g, 2.8 mmol) and norbornene (0.42 g, 4.5 mmol) was followed. The reaction was performed at 0°C during 6 h, affording 55 mg (26% yield, two steps) of **12b** (39:61 diastereomeric ratio as determined by ^{13}C NMR).

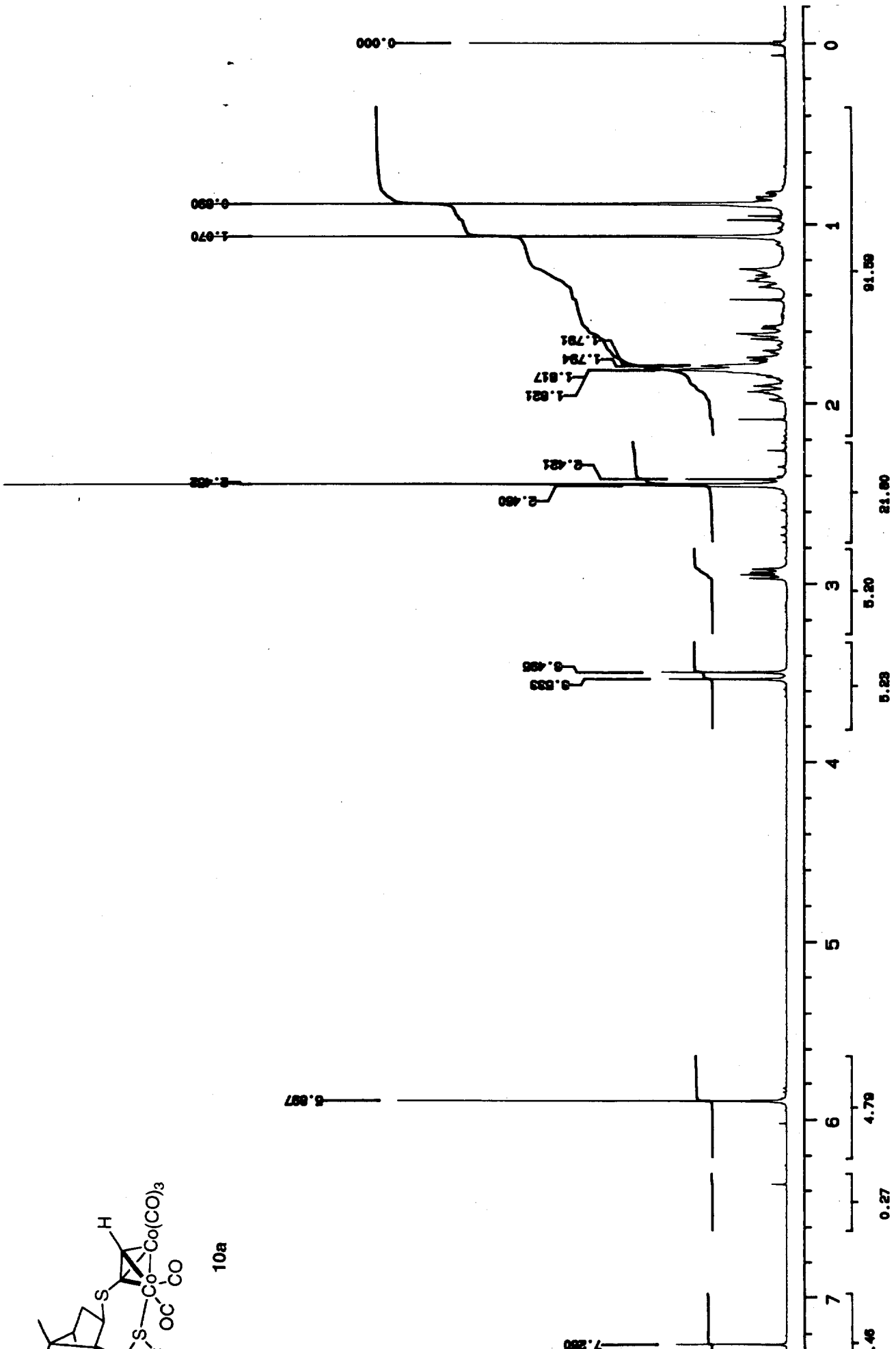
Procedure C using as reagents **7b** (0.15 g, 0.42 mmol), $Co_2(CO)_8$ (0.15 g, 0.43 mmol), and norbornene (0.39 g, 4.2 mmol) was followed. The reaction was performed at 0°C during 4 days affording 100 mg (50% yield, two steps) of **12b** (96:4 diastereomeric ratio as determined by ^{13}C NMR).

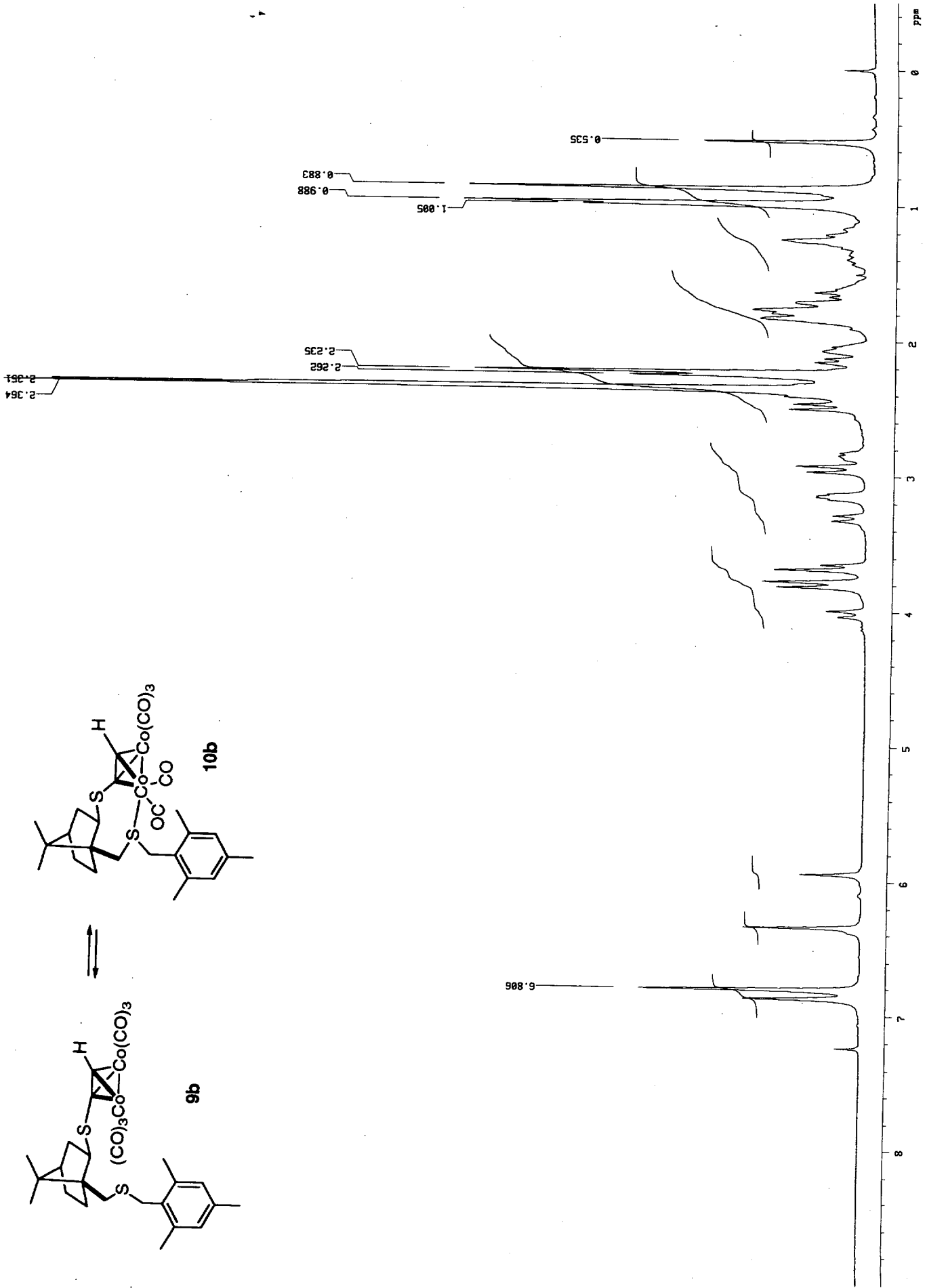
Procedure D using as reagents **7b** (0.127 g, 0.28 mmol), norbornene (0.2 g, 2.12 mmol) and hexane (4 mL) was followed. The reaction was performed, after addition of the olefin at –15°C, at 0°C during 48 h affording 30 mg (30% yield) of **12b** (89:11 diastereomeric ratio as determined by ^{13}C NMR).

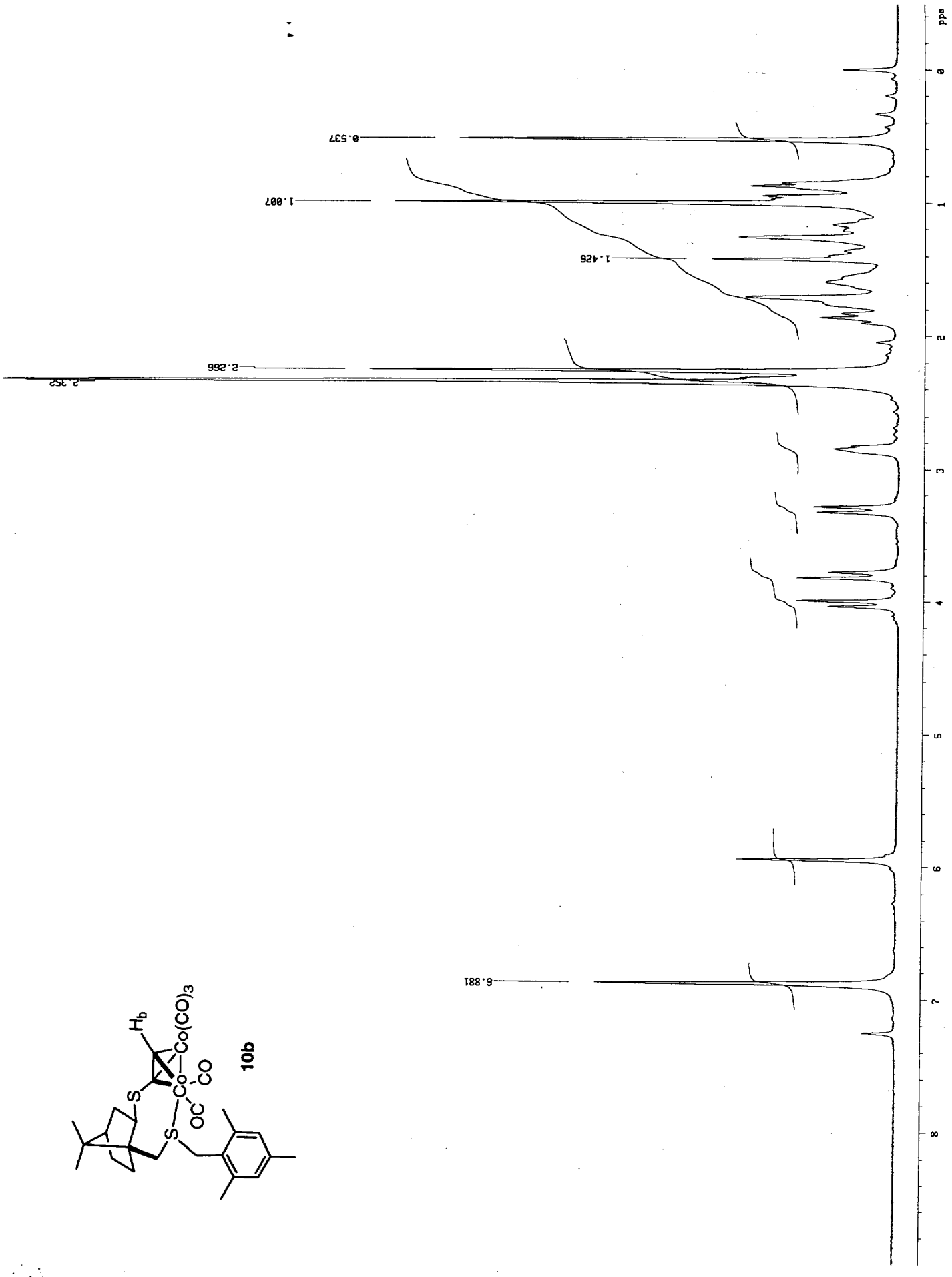
4-[(1*S*,2*R*,4*R*)-7,7-Dimethyl-1-[(2,4,6-trimethylbenzylsulfanyl)methyl]bicyclo [2.2.1]hept-2-ilsulfanyl]tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one (12b). $[\alpha]_D$ = -19.75 (c 1.2, $CHCl_3$). IR (film) ν_{max} = 2956, 1698, 1565, 1457 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 6.96 (d, 1H), 6.79 (broad s, 2H), 3.80, 3.70 (AB, J=11Hz, 2H), 3.35-3.30 (dd, 1H), 2.93, 2.66 (AB, J= 12Hz, 2H), 2.33 (s, 6H), 2.22 (s, 3H), 2.6-0.95 (complex signal 17H), 1.05 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.5 (C), 152.7 (minor), 152.3 (major) (CH), 144.6 (2C), 136.8 (C), 136.3 (C), 131.3 (C), 128.8 (2CH), 53.9 (CH), 53.5 (C), 50.5 (CH major), 50.4 (CH minor), 49.2 (CH), 48.6 (C), 46.4 (CH), 40.9 (CH_2), 39.2 (CH), 38.6 (CH), 35.3 (CH_2), 34.1 (CH_2), 33.0 (CH_2), 31.3 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 27.3 (CH_2), 20.9 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 19.6 ($2CH_3$) ppm. HRMS Calcd for $C_{30}H_{41}OS_2$ (M+1): 481.2599, found 481.2568.



9a







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