Supporting Information for

Direct Mannich Reaction of Glycinate Schiff bases with *N*-(8-Quinolyl)sulfonyl Imines: a Catalytic Asymmetric Approach to *anti*-α,β-Diamino Esters

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1. Experimental Section

General methods

All the reactions were carried out in anhydrous solvents and under inert atmosphere. Melting points were taken in open-end capillary tubes. NMR spectra were recorded at 300 MHz (^{1}H), 75 MHz (^{13}C), at room temperature in $CDCl_3$ [calibrated at 7.26 ppm (^{1}H) and 77.0 ppm (^{13}C)] unless indicated. Mass spectra (MS) were determined at an ionizing voltage of 70 eV. HPLC experiments were conducted using Daicel Chiralpak IA column. Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). Methyl (*E*)-*N*-benzylideneglycinate and methyl (*E*)-2-(benzylideneamino)propanoate were prepared according literature procedures.[1]

General procedure for the synthesis of *N*-(8-quinolyl)sulfonyl imines

A mixture of the corresponding aldehyde (5.5 mmol), 8-quinolylsulfonamide[2] (1.0 g, 5 mmol), molecular sieves 4 Å (previously activated) (1.0 g/mmol) and *Amberlist 15* (50 mg) in toluene (5 mL) was heated at 110 ºC in a sealed tube overnight. The mixture was allowed to reach room temperature before it was filtered through Celite and washed with AcOEt (3 times). The solvent was removed under reduced pressure and the crude product was triturated with *n*-hexane/Et_2O at 0 ºC to afford the corresponding pure aryl or heteroaryl *N*-(8-quinolyl)sulfonyl imine.

(*E*)-*N*-Benzylidene-*N*-[(8-quinolyl)sulfonyl]imine (3h): Yield: 83%. Mp = 113-114 ºC. ^{1}H NMR (300 MHz): δ 9.59 (s, 1H), 8.92 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.73 (dd, *J* = 1.3, 7.4 Hz, 1H), 8.21 (dd, *J* = 1.7, 8.3 Hz, 1H), 8.11 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.98 (dd, *J* = 1.5, 7.0 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.60 (tt, *J* = 1.2, 7.4 Hz, 1H), 7.51-7.42 (m, 3H). ^{13}C NMR (75 MHz): δ 175.4, 151.4, 143.5, 136.6, 134.9, 134.8, 134.1, 132.7, 132.6, 131.4, 129.1, 128.8, 125.6, 122.1.

(*E*)-*N*-(4-Methoxybenzylidene)-*N*-[(8-quinolyl)sulfonyl]imine (7h): Yield: 67%. Mp = 171-172 ºC. ^{1}H NMR (300 MHz): δ 9.49 (s, 1H), 8.92 (dd, *J* = 1.8, 4.2 Hz, 1H), 8.72 (dd, *J* = 1.4, 7.5 Hz, 1H), 8.20 (dd, *J* = 1.8, 8.4 Hz, 1H), 8.08 (dd, *J* = 1.4, 8.3 Hz, 1H), 7.95 (dd, *J* = 1.8, 8.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 4.3, 8.4 Hz, 1H), 6.98-6.94 (m, 2H), 3.87 (s, 3H).

(*E*)-*N*-(4-Chlorobenzylidene)-*N*-[(8-quinolyl)sulfonyl]imine (8h): Yield: 91%. Mp = 159-160 ºC. ^{1}H NMR (300 MHz): δ 9.56 (s, 1H), 8.91 (dd, *J* = 1.8, 4.2 Hz, 1H), 8.74

1. a) Cabrera, S.; Gómez Arrayás, R.; Carretero, J. C. *J. Am. Chem. Soc*. **2005**, *127*, 16394; b) Llamas, T.; Gómez Arrayás, R.; Carretero, J. C. *Org. Lett.* **2006**, *8*, 1795.
2. Chivers, G. E.; Cremlyn, R. J.; Guy, R.; Honeyman, R.; Reynolds, P. *Aust. J. Chem.* **1975**, *28*, 413.

(dd, *J* = 1.5, 7.4 Hz, 1H), 8.23 (dd, *J* = 1.8, 8.3 Hz, 1H), 8.13 (dd, *J* = 1.4, 8.3 Hz, 1H), 7.93 (dt, *J* = 1.8, 8.4 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.49-7.43 (m, 3H).

(*E*)-*N*-(2-Methylbenzylidene)-*N*-[(8-quinolyl)sulfonyl]imine (9h): Yield: 78%. Mp = 150-151 ºC. ^{1}H NMR (300 MHz): δ 9.93 (s, 1H), 8.94 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.74 (dd, *J* = 1.4, 7.4 Hz, 1H), 8.21 (dd, *J* = 1.7, 8.3 Hz, 1H), 8.11 (dd, *J* = 1.3, 8.1 Hz, 1H), 8.02 (dd, *J* = 1.1, 7.8 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.49-7.42 (m, 2H), 7.30-7.21 (m, 2H), 2.74 (s, 3H).

(*E*)-*N*-(2-Naphthylmethylene)-*N*-[(8-quinolyl)sulfonyl]imine (10h): Yield: 89%. ^{1}H NMR (300 MHz): δ 9.73 (s, 1H), 8.92 (dd, *J* = 1.5, 4.2 Hz, 1H), 8.76 (dd, *J* = 1.1, 7.4 Hz, 1H), 8.47 (s, 1H), 8.19 (dd, *J* = 1.6, 8.4 Hz, 1H), 8.11 (dd, *J* = 1.3, 8.2 Hz, 1H), 8.06-7.95 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.67-7.56 (m, 2H), 7.42 (dd, *J* = 4.2, 8.3 Hz, 1H).

(*E*)-*N*-[(Furan-2-yl)methylene]-*N*-[(8-quinolyl)sulfonyl]imine (11h): Yield: 75%. Mp = 188-189 ºC. ^{1}H NMR (300 MHz): δ 9.37 (s, 1H), 8.93 (dd, *J* = 1.8, 4.2 Hz, 1H), 8.72 (dd, *J* = 1.5, 7.4 Hz, 1H), 8.21 (dd, *J* = 1.8, 8.3 Hz, 1H), 8.09 (dd, *J* = 1.4, 8.2 Hz, 1H), 7.74-6.67 (m, 2H), 7.45 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.41 (d, *J* = 3.8 Hz, 1H), 6.65 (dd, *J* = 1.7, 3.6 Hz, 1H).

(*E*)-*N*-[(Pyridin-3-yl)methylene]-*N*-[(8-quinolyl)sulfonyl]imine (12h): Yield: 60%. ^{1}H NMR (300 MHz): δ 9.66 (s, 1H), 9.14 (d, *J* = 1.6 Hz, 1H), 8.92 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.81 (dd, *J* = 1.6, 4.8 Hz, 1H), 8.75 (dd, *J* = 1.5, 7.4 Hz, 1H), 8.30 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.23 (dd, *J* = 1.8, 8.3 Hz, 1H), 8.14 (dd, *J* = 1.4, 8.2 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 4.2, 8.3 Hz, 1H), 7.42 (dd, *J* = 4.7, 7.9 Hz, 1H).

(*E*)-*N*-(Phenylethene)-*N*-[(8-quinolyl)sulfonyl]imine (13h): Yield: 83%. Mp = 165-166 ºC. ^{1}H RMN (300 MHz): δ 9.31 (d, *J* = 9.6 Hz, 1H), 8.99 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.71 (dd, *J* = 1.4, 7.4 Hz, 1H), 8.23 (dd, *J* = 1.8, 8.3 Hz, 1H), 8.11 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.70 (dd, *J* = 7.4, 15.7 Hz, 1H), 7.63-7.55 (m, 3H), 7.50-7.42 (m, 4H), 7.02 (dd, *J* = 9.6, 15.7 Hz, 1H).

(*E*)-*N*-[(8-Quinolyl)sulfonyl]-*N*-((thiophen-2-yl)methylene)imine (14h): Yield: 72%. Mp = 152-153 ºC. ^{1}H RMN (300 MHz): δ 9.68 (s, 1H), 8.93 (dd, *J* = 1.5, 4.2 Hz, 1H), 8.71 (d, *J* = 7.4 Hz, 1H), 8.21 (dd, *J* = 1.7, 8.3 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 3.7 Hz, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.22 (t, *J* = 4.1 Hz, 1H).

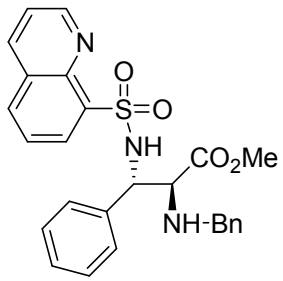
General procedure for the asymmetric Mannich reaction

To a solution of Fesulphos ligand (*R*)-**1**[3] (2.8 mg, 0.082 mmol, 5 mol%,) and $Cu(CH_3CN)_4PF_6$ (3.4 mg, 0.075 mmol, 5 mol%) in THF (0.5 mL), at the optimal temperature (−40 ºC or −78 ºC, as indicated in Table 3), were successively added a solution of the glycinate imine (0.15 mmol) in THF (1.0 mL), Et_3N (3 μL, 0.16 mmol, 10 mol%) and a solution of the corresponding *N*-sulfonyl imine (0.165 mmol, 1.1 equiv) in THF (1.0 mL). Upon consumption of the starting material (TLC monitoring), the reaction mixture was cooled to 0 ºC before it was treated with EtOH (2 mL) and $NaBH_4$ (5.7 mg, 0.15 mmol). The mixture was allowed to reach room temperature and it was stirred at room temperature for 30 min before it was quenched with saturated aq NH_4Cl (2 mL) and extracted with AcOEt (3 x 30 mL). The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was analyzed by ^1H NMR to determine the diastereomeric ratio, and then purified by flash chromatography (the eluent is indicated in each case).

Products **6** and **16**-**22**, obtained from *N*-glycine methyl ester **2a**, were isolated as inseparable mixtures of *anti*+*syn* diastereomers, which were analyzed by chiral HPLC to determine enantioselectivity, as well as diastereoselectivity. In contrast, products **23**-**26** derived from the α-substituted imino ester **2b** could be efficiently separated by chromatography and the pure *anti*-diastereomer was subjected to chiral HPLC analysis for enantiopurity determination.

The racemic mixtures of products **6** and **16**-**26** were prepared under identical conditions at room temperature, but using (±)-Binap (5 mol%) instead of Fesulphos.[4]

(2*S*,3*S*)-Methyl 2-(benzylamino)-3-phenyl-3-[(8-quinolyl)sulfonylamino]propanoate (*anti*-6). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-benzylidene-*N*-[(8-quinolyl)sulfonyl]imine (**3h**) (48.8 mg, 0.165 mmol) in THF at –40 ºC for 3 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**6** as a white solid with 96% ee; yield: 53.1 mg (74%, *anti*/*syn* = 99:1); mp = 102-104 ºC (decomp.).



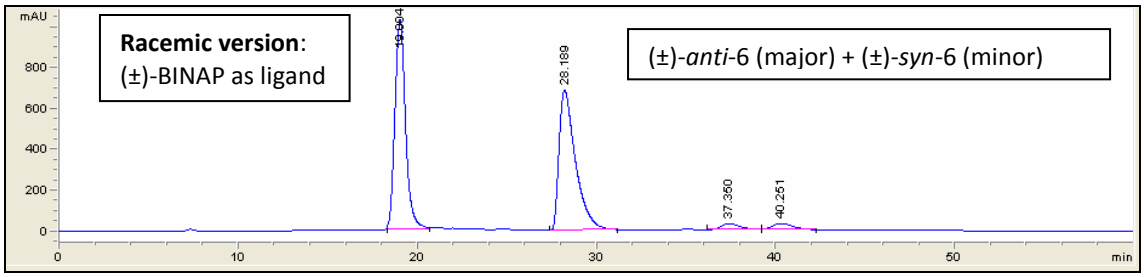
A similar result (77% yield, *anti*/*syn* = 98:2, 96% ee) was obtained when the reaction was performed at 2.0 mmol scale (355 mg of imine **3h**) in the presence of 3 mol% of (*R*)-**1**/$Cu(CH_3CN)_4PF_6$. A single recrystallization from CH_2Cl_2-hexane of the resulting

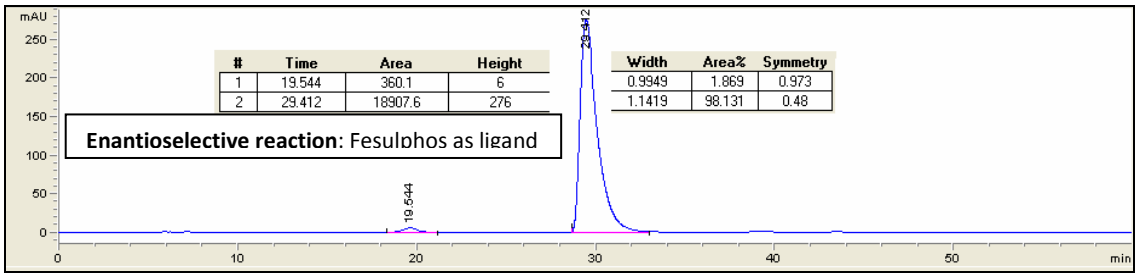
3. a) Priego, J.; García Mancheño, O.; Cabrera, S.; Gómez Arrayás, R.; Llamas, T.; Carretero, J. C.; *Chem. Commun.* **2002**, 2512-2513; b) García Mancheño, O.; Priego, J.; Cabrera, S.; Gómez Arrayás, R.; Llamas, T.; Carretero, J. C. *J. Org. Chem.* **2003**, *68* , 3679.
4. (±)-Binap typically provides lower chemical yields and poorer *anti*-diastereoselectivities than Fesulphos.

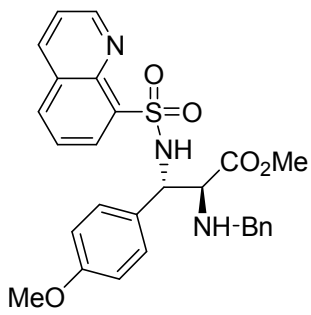
98:2 mixture of *anti*/*syn*-**6** (66% recrystallization yield) provided diastereomerically pure crystalline *anti*–**6** (>99% ee), suitable for X-ray diffraction analysis.

^{1}H NMR (300 MHz): δ 9.02 (dd, *J* = 1.5, 4.2 Hz, 1H), 8.14 (dd, *J* = 1.5, 8.3 Hz, 1H), 8.09 (dd, *J* = 1.1, 7.2 Hz, 1H), 7.84 (dd, *J* = 1.1, 8.3 Hz, 1H), 7.51-7.38 (m, 3H), 7.37-7.26 (m, 5H), 6.88.6.82 (m, 1H), 6.72 (d, *J* = 4.2 Hz, 4H), 4.98 (dd, *J* = 5.1, 9.6 Hz, 1H), 3.72 (d, *J* = 12.5 Hz, 1H), 3.59 (d, *J* = 5.3 Hz, 1H), 3.58 (s, 3H), 3.44 (d, *J* = 12.3 Hz, 1H), 1.79 (bs, 1H). ^{13}C NMR (75 MHz): δ 171.9, 151.0, 150.9, 143.2, 139.3, 137.3, 136.6, 135.8, 132.6, 130.0, 128.3, 128.0, 127.8, 127.6, 127.4, 127.1, 126.8, 125.3, 121.9, 65.1, 59.3, 52.8, 51.8. MS-FAB$^+$ *m/z* 476.0 (M^++H, 100), 297.0 (54), 91 (57). HRMS-FAB$^+$ Calcd. For $C_{26}H_{25}N_3O_4S$: 475.1566. Found: 475.1562. Anal. Calcd. for $C_{26}H_{25}N_3O_4S$: C, 65.67; H, 5.30; N, 8.84; S, 6.74. Found: C, 65.37; H, 5.31; N, 8.45; S, 6.58.

ee = 96%; $[\alpha]_D^{20}$ = –25 (*c* = 0.8, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 254 nm), t_R (*anti*): 19.5 min for (2*R*,3*R*)-isomer and 29.4 min for (2*S*,3*S*)-isomer. t_R (*syn*): 39.1 min and 43.4 min.



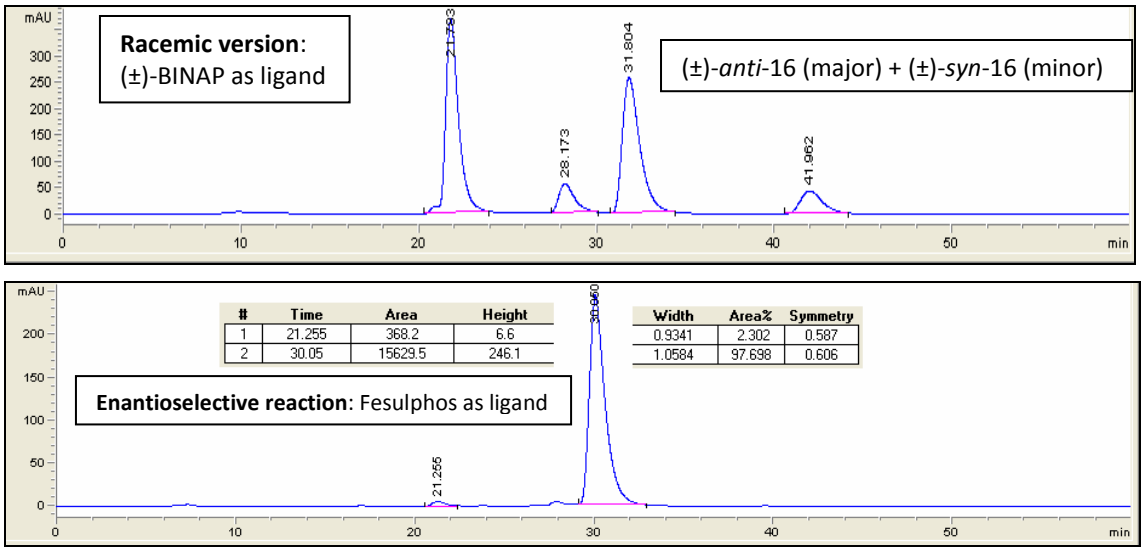


(2*S*,3S)-Methyl 2-(benzylamino)-3-(4-methoxyphenyl)-3-[(8-quinolyl)sulfonylamino]-propanoate (*anti*-16). 

Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-(4-methoxybenzylidene)-*N*-[(8-quinolyl)sulfonyl]imine (**7h**) (53.9 mg, 0.165 mmol) in THF at –78 ºC for 3 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**16** as a white solid; yield: 54.6 mg (72%, *anti*/*syn* = 98:2); mp = 60-61ºC. ^{1}H NMR (300 MHz): δ 9.01 (dd, *J* = 1.7, 4.3 Hz, 1H), 8.14 (dd, *J* = 1.7, 8.3 Hz, 1H), 8.08 (dd, *J* = 1.3, 7.3 Hz, 1H), 7.85 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.47 (dd, *J* = 4.3, 8.3 Hz, 1H) 7.43-7.35 (m, 2H), 7.34-

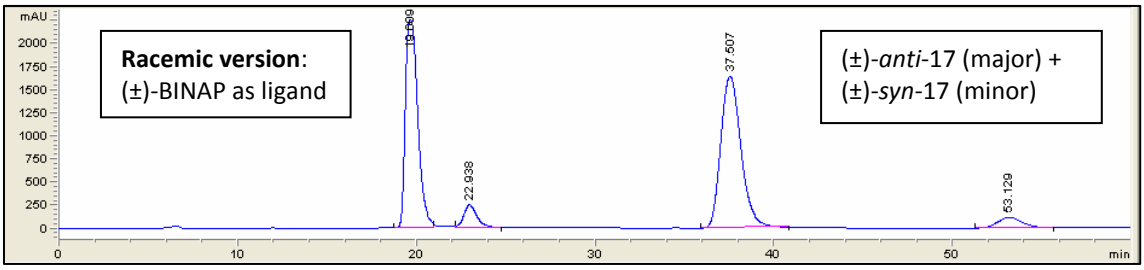
7.25 (m, 5H), 6.63 (d, J = 8.7 Hz, 2H), 6.22 (d, J = 8.7 Hz, 2H), 4.92 (dd, J = 4.9, 9.6 Hz, 1H), 3.73 (d, J = 12.8 Hz, 1H), 3.58 (s, 4H), 3.57 (s, 3H), 3.45 (d, J = 12.8 Hz, 1H), 1.79 (bs, 1H). ^{13}C NMR (75 MHz): δ 172.1, 158.7, 150.9, 139.4, 136.0, 132.5, 130.1, 128.3, 128.1, 128.0, 127.2, 125.4, 121.9, 112.8, 65.2, 58.8, 55.0, 52.9, 51.9. MS-FAB$^+$ *m/z* 506.0 (M^++H, 100), 327.1 (81), 91 (53). HRMS-FAB$^+$ Calcd. For $C_{27}H_{27}N_3O_5S$: 505.1671. Found: 505.1673.

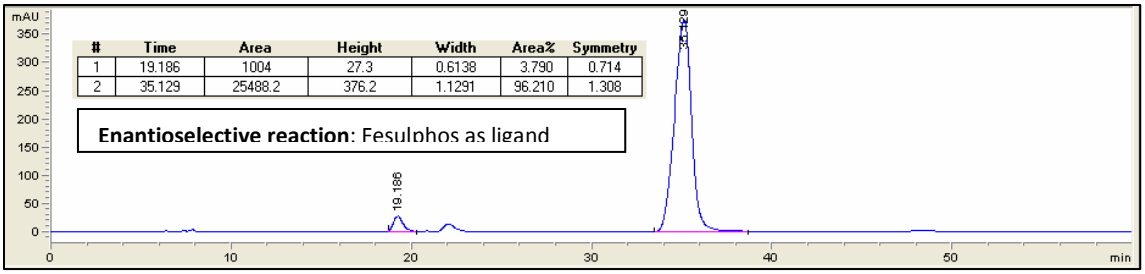
ee = 95%; $[\alpha]_D^{20}$ = –25 (c = 3.0, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 254 nm), t_R (*anti*): 21.2 min for (2*R*,3*R*)-isomer and 30.0 min for (2*S*,3*S*)-isomer. t_R (*syn*): 27.6 min and 41.9 min.



(2*S*,3*S*) Methyl 2-(benzylamino)-3-(4-chlorophenyl)-3-[(8-quinolyl)-sulfonylamino]-propanoate (*anti*-17). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-(4-chlorobenzylidene)-*N*-[(8-quinolyl)sulfonyl]imine (**8h**) (57.4 mg, 0.165 mmol) in THF at –78 ºC for 1 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**17** as a white solid; yield: 72.8 mg (92%, *anti*/*syn* = 98:2); mp = 79-80ºC. ^{1}H NMR (300 MHz): δ 9.00 (dd, J = 1.7, 4.2 Hz, 1H), 8.17 (dd, J = 1.7, 8.3 Hz, 1H), 8.09 (dd, J = 1.4, 7.4 Hz, 1H), 7.90 (dd, J = 1.3, 8.2 Hz, 1H), 7.50 (dd, J = 4.3, 8.3 Hz, 1H), 7.45-7.27 (m, 7H), 6.66 (s, 4H), 4.93 (dd, J = 5.0, 9.8 Hz, 1H), 3.74 (d, J = 12.7 Hz, 1H), 3.60 (d, J = 5.1 Hz, 1H), 3.58 (s, 3H), 3.47 (d, J = 12.7 Hz, 1H), 1.78 (bs, 1H).^{13}C NMR (75 MHz): δ 171.9, 151.0, 143.1, 139.2, 137.3, 136.7, 134.6, 133.5, 132.7, 130.2, 128.5, 128.4, 128.3, 128.1, 127.5, 127.3, 125.4, 122.1, 64.9, 58.7, 53.0, 52.0. MS-FAB$^+$ *m/z* 510.0 (M^++H, 100), 331.0 (53), 91 (94), 57 (48). HRMS-FAB$^+$ Calcd. For $C_{26}H_{24}ClN_3O_4S$: 509.1176. Found: 509.1171.

ee = 93%; $[\alpha]_D^{20}$ = –22 (*c* = 1.4, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 254 nm), t_R (*anti*): 19.2 min for (2*R*,3*R*)-isomer and 35.1 min for (2*S*,3*S*)-isomer. t_R (*syn*): 22.0 min and 53.1 min.





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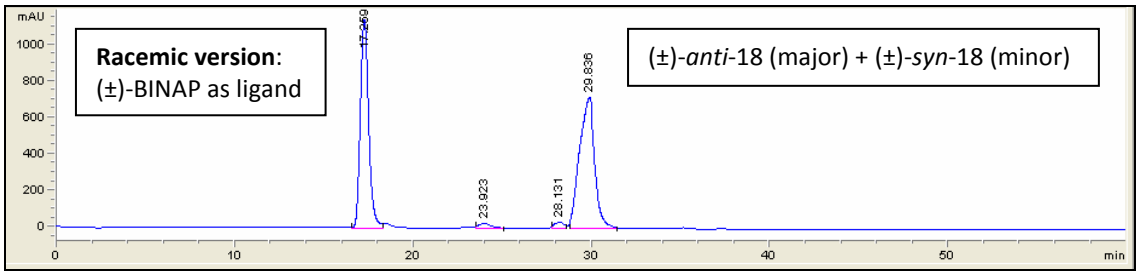
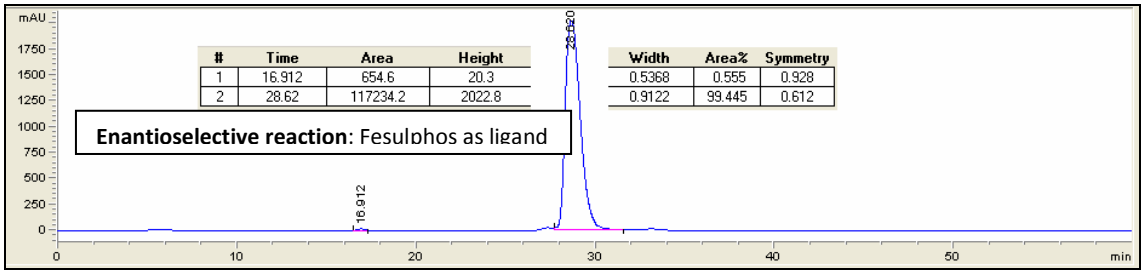
(2*S*,3*S*) Methyl 2-(benzylamino)-3-[(8-quinolyl)sulfonylamino]-3-(*o*-tolyl)propanoate (*anti*-18). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-(*o*-methylbenzylidene)-*N*-[(8-quinolyl)sulfonyl] imine (**9h**) (51.3 mg, 0.165 mmol) in THF at –40 ºC for 1.5 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**18** as a white solid; yield: 58.9 mg (80%, *anti*/*syn* = 98:2); mp = 57-59ºC. ^{1}H NMR (300 MHz): δ 9.00 (dd, *J* = 1.7, 4.3 Hz, 1H), 8.08 (dd, *J* = 1.7, 8.4 Hz, 1H), 8.04 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.76 (dd, *J* = 1.2, 8.3 Hz, 1H), 7.44 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.36-7.21 (m, 7H), 6.70-6.53 (m, 3H), 6.18 (t, *J* = 7.5 Hz, 1H), 5.22 (dd, *J* = 5.6, 9.8 Hz, 1H), 3.73 (d, *J* = 12.9 Hz, 1H), 3.62 (d, *J* = 5.6 Hz, 1H), 3.57 (d, *J* = 12.9 Hz, 1H), 3.55 (s, 3H), 2.14 (s, 3H), 1.98 (bs, 1H). ^{13}C NMR (75 MHz): δ 172.5, 150.8, 143.1, 139.2, 137.2, 136.5, 135.2, 134.4, 132.6, 129.8, 129.6, 128.4, 128.3, 128.1, 127.1, 126.0, 125.2, 124.6, 121.9, 64.6, 54.4, 52.6, 51.8, 19.0. MS-FAB$^+$ *m/z* 490.2 (M^++H, 100), 311.1 (58), 91 (40). HRMS-FAB$^+$ Calcd. For $C_{27}H_{27}N_3O_4S$: 489.1722. Found: 489.1720.

ee = 99%; $[\alpha]_D^{20}$ = –66 (*c* = 3.7, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 25/75, flow rate 0.7 mL/min (λ = 210 nm), t_R (*anti*): 16.9 min for (2*R*,3*R*)-isomer and 28.6 min for (2*S*,3*S*)-isomer. t_R (*syn*): 23.1 min and 27.4 min.





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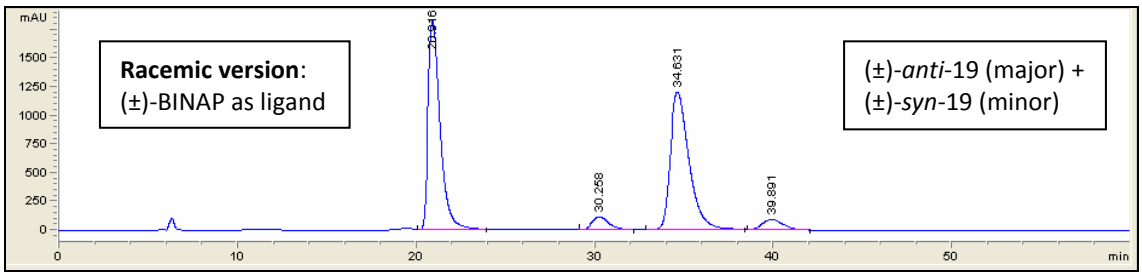
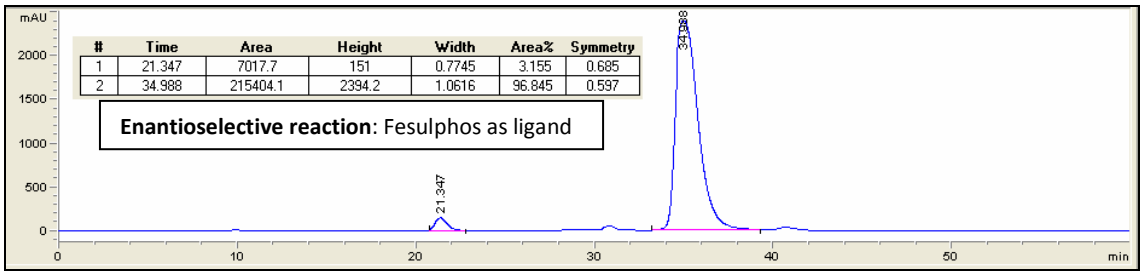
Width	Area%	Symmetry
0.5368	0.555	0.928
0.9122	99.445	0.612

(2*S*,3*S*) Methyl 2-(benzylamino)-3-(naphthalen-2-yl)-3-[(8-quinolyl)sulfonylamino]-propanoate (*anti*-19). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-(2-naphthylmethylene)-*N*-[(8-quinolyl)sulfonyl] imine (**10h**) (57.1 mg, 0.165 mmol) in THF at −78 ºC for 2 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**19** as a white solid; yield: 59.1 mg (75%, *anti*/*syn* = 97:3); mp = 99-100ºC. ^{1}H NMR (300 MHz): δ 9.03 (dd, *J* = 1.7, 4.3 Hz, 1H), 8.04-7.97 (m, 2H), 7.62-7.41 (m, 5H), 7.37-7.22 (m, 7H), 7.20-7.12 (m, 3H), 6.83 (dd, *J* = 1.7, 8.5 Hz, 1H), 5.13 (dd, *J* = 5.3, 9.8 Hz, 1H), 3.78 (d, *J* = 12.9 Hz, 1H), 3.72 (d, *J* = 5.2 Hz, 1H), 3.59 (s, 3H), 3.54 (d, *J* = 12.9 Hz, 1H), 1.91 (bs, 1H). ^{13}C NMR (75 MHz): δ 172.1, 150.9, 143.1, 139.3, 137.2, 136.5, 133.4, 132.5, 132.4, 132.2, 130.0, 128.4, 128.3, 128.1, 127.6, 127.2, 127.1, 127.0, 126.5, 125.9, 125.7, 125.1, 124.6, 121.9, 65.1, 59.6, 52.9, 51.9. MS-FAB^{+} *m/z* 526.0 (M^{+}+H, 100), 347.0 (66), 91 (49). HRMS-FAB^{+} Calcd. For $C_{30}H_{27}N_3O_4S$: 525.1722. Found: 525.1723.

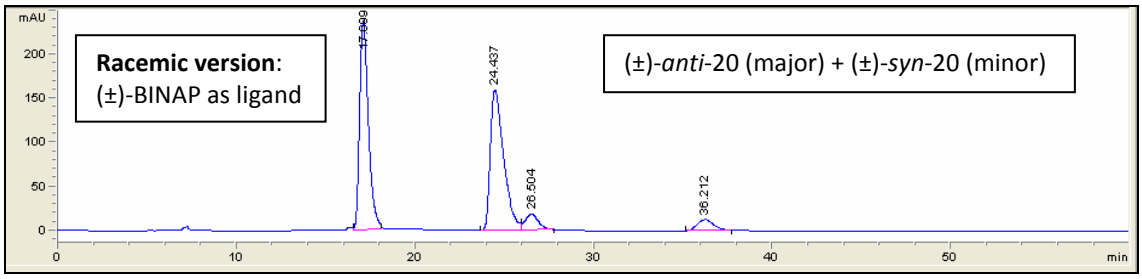
ee = 94%; $[\alpha]_D^{20}$ = −39 (*c* = 2.3, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 210 nm), t_R (*anti*): 21.4 min for (2*R*,3*R*)-isomer and 35.0 min for (2*S*,3*S*)-isomer. t_R (*syn*): 30.8 min and 40.6 min.

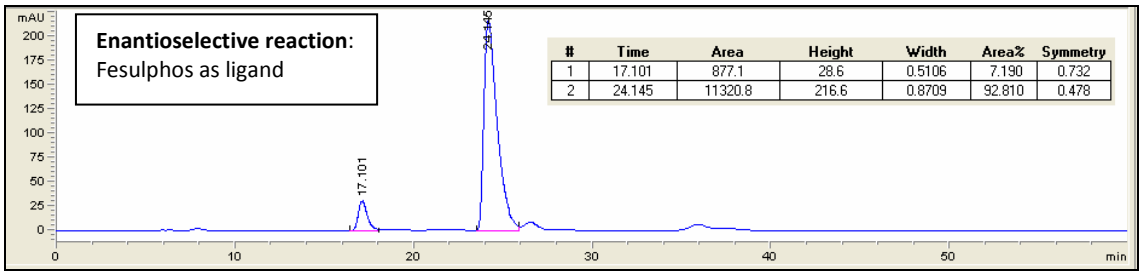




(2*S*,3*S*) Methyl 2-(benzylamino)-3-(furan-2-yl)-3-[(8-quinolyl)sulfonylamino]-propanoate (*anti*-20). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-[(furan-2-yl)methylene]-*N*-[(8-quinolyl)sulfonyl]imine (**11h**) (47.2 mg, 0.165 mmol) in THF at –78 ºC for 1h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**20** as a colourless amorphous solid; yield: 51.4 mg (71%, *anti*/*syn* = 95:5). ^{1}H NMR (300 MHz): δ 8.96 (dd, *J* = 1.7, 4.3 Hz, 1H), 8.19-8.14 (m, 2H), 7.90 (dd, *J* = 1.3, 8.3 Hz, 1H), 7.62 (d, *J* = 9.9 Hz, 1H), 7.51-7.44 (m, 2H), 7.37-7.26 (m, 5H), 6.43 (d, *J* = 1.7 Hz, 1H), 5.76 (d, *J* = 3.2 Hz, 1H), 5.70 (dd, *J* = 1.8, 3.2 Hz, 1H), 5.03 (dd, *J* = 5.1, 9.9 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.67 (d, *J* = 5.1 Hz, 1H), 3.61 (s, 3H), 3.48 (d, *J* = 12.8 Hz, 1H).^{13}C NMR (75 MHz): δ 171.8, 150.9, 149.5, 143.1, 141.7, 139.4, 136.9, 136.4, 132.6, 130.0, 128.4, 128.3, 128.1, 127.1, 125.3, 121.9, 109.3, 108.9, 63.9, 53.0, 52.5, 52.0. MS-FAB^{+} *m/z* 466.0 (M^{+}+H, 100), 287.0 (56), 91 (77), 55 (46). HRMS-FAB^{+} Calcd. For $C_{24}H_{23}N_3O_5S$: 465.1358. Found: 465.1360.

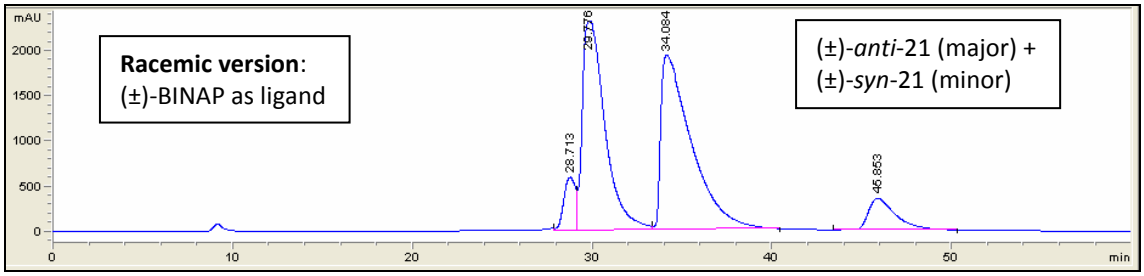
ee = 85%; $[\alpha]_D^{20}$ = –13 (*c* = 2.5, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 210 nm), t_R (*anti*): 17.1 min for (2*R*,3*R*)-isomer and 24.1 min for (2*S*,3*S*)-isomer. t_R (*syn*): 26.2 min and 35.9 min.

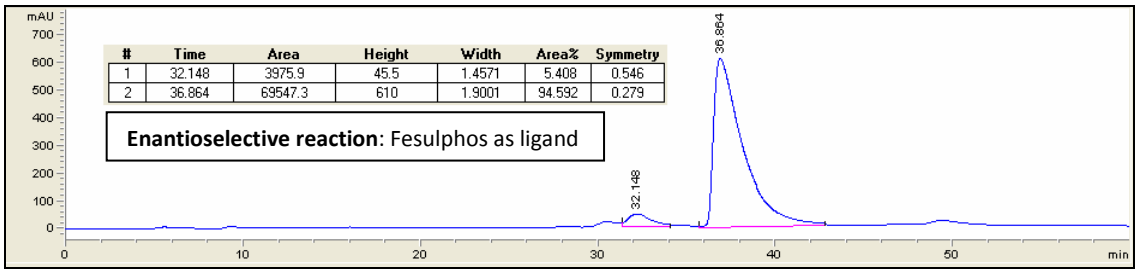




(2*S*,3*S*) Methyl 2-(benzylamino)-3-(pyridin-3-yl)-3-[(8-quinolyl)-sulfonylamino]-propanoate (*anti*-21). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-((pyridin-3-yl)methylene)-*N*-[(8-quinolyl)sulfonyl]imine (**12h**) (49.0 mg, 0.165 mmol) in THF at –78 ºC for 1.5h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**21** as a white solid; yield: 51.5 mg (72%, *anti*/*syn* = 98:2); mp = 63-65 ºC. ^{1}H NMR (300 MHz): δ 9.02 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.20-8.11 (m, 3H), 8.04 (d, *J* = 1.8 Hz, 1H), 7.89 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.53-7.44 (m, 3H), 7.36-7.25 (m, 5H), 7.11 (dt, *J* = 1.9, 7.9 Hz, 1H), 6.64 (dd, *J* = 4.7, 7.9 Hz, 1H), 5.02 (dd, *J* = 4.9, 9.6 Hz, 1H), 3.76 (d, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 4.9 Hz, 1H), 3.61 (s, 3H), 3.51 (d, *J* = 12.8 Hz, 1H), 1.82 (bs, 1H).^{13}C NMR (75 MHz): δ 171.7, 151.1, 149.0, 148.5, 143.0, 139.0, 137.1, 136.8, 134.3, 133.0, 131.8, 130.1, 128.5, 128.4, 128.1, 127.3, 125.5, 122.2, 64.8, 57.2, 53.1, 52.2. MS-FAB$^+$ *m/z* 477.2 (M^++H, 100), 298.1 (24), 91 (42), 71 (28). HRMS-FAB$^+$ Calcd. For $C_{25}H_{24}N_4O_4S$: 476.1518. Found: 476.1522.

ee = 90%; $[\alpha]_D^{20}$ = –17 (*c* = 2.6, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 30/70, flow rate 0.7 mL/min (λ = 210 nm), t_R (*anti*): 32.1 min for (2*R*,3*R*)-enantiomer and 36.9 min for (2*S*,3*S*)-enantiomer. t_R (*syn*): 30.5 min and 49.4 min.

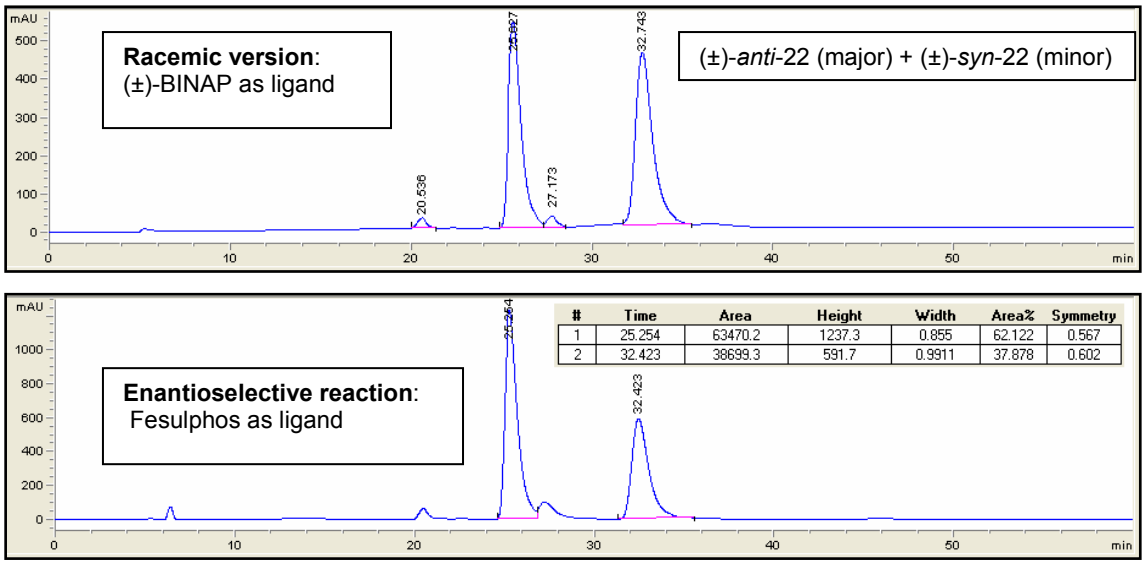




(2*S*,3*S*) methyl 2-(benzylamino)-5-phenyl-3-[(8-quinolyl)-sulfonylamino]pent-4-enoate (*anti*-22). Following the general procedure, the reaction of methyl (*E*)-*N*-benzylideneglycinate (**2a**) (26.6 mg, 0.15 mmol) with (*E*)-*N*-(phenylallylidene)-*N*-[(8-quinolyl)sulfonyl]imine (**13h**) (53.2 mg, 0.165 mmol) in THF at –78 ºC for 3 h afforded, after chromatography (*n*-hexane-EtOAc 3:1), *anti*-**22** as a colourless oil; yield: 48.1 mg (64%, *anti/syn* = 85:15). ^{1}H

NMR (300 MHz): δ 9.01 (dd, *J* = 1.7, 4.2 Hz, 1H), 8.31 (dd, *J* = 1.4, 7.3 Hz, 1H), 8.13 (dd, *J* = 1.8, 8.3 Hz, 1H), 7.79 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.48 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.43-7.39 (m, 1H), 7.38-7.27 (m, 6H), 7.13-7.05 (m, 3H), 6.73 (d, *J* = 4.4 Hz, 1H), 6.62 (dd, *J* = 1.1, 7.6, 2H), 6.20 (d, *J* = 15.6, 1H), 5.24 (dd, *J* = 5.1, 9.6 Hz, 1H), 4.61-4.52 (m, 1H), 3.78 (d, *J* = 12.7 Hz, 1H), 3.66 (s, 3H), 3.48 (d, *J* = 12.7 Hz, 1H), 1.83 (bs, 1H). ^{13}C NMR (75 MHz): δ 172.2, 151.0, 143.2, 138.4, 138.0, 136.7, 135.4, 133.8, 132.6, 130.3, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 127.2, 126.2, 126.1, 125.5, 122.6, 122.0, 64.6, 58.3, 53.0, 52.0. MS-FAB$^+$ *m/z* 502.2 (M^++H, 100), 323.1 (54), 294.1 (35), 91.1 (96). HRMS-FAB$^+$ Calcd. For $C_{28}H_{27}N_3O_4S$: 501.1722. Found: 501.1722.

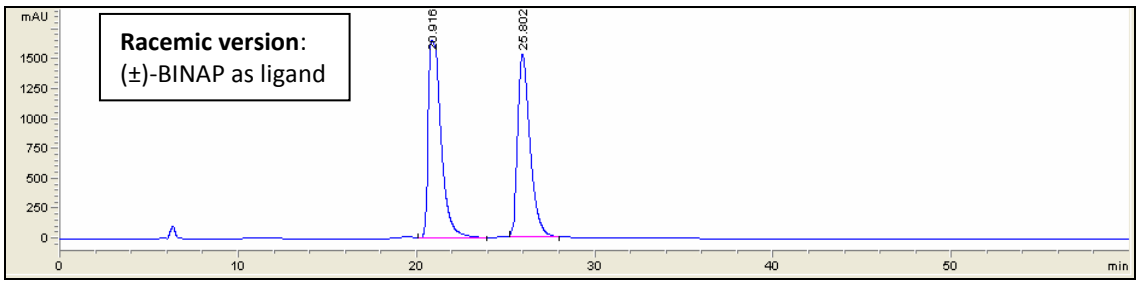
ee = 25%; $[\alpha]_D^{20}$ = + 3.5 (*c* = 3.1, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ = 210 nm), t_R (*anti*): 25.2 min for (2*R*,3*R*)-isomer and 32.4 min for (2*S*,3*S*)-isomer. t_R (*syn*): 20.5 min and 27.1 min.

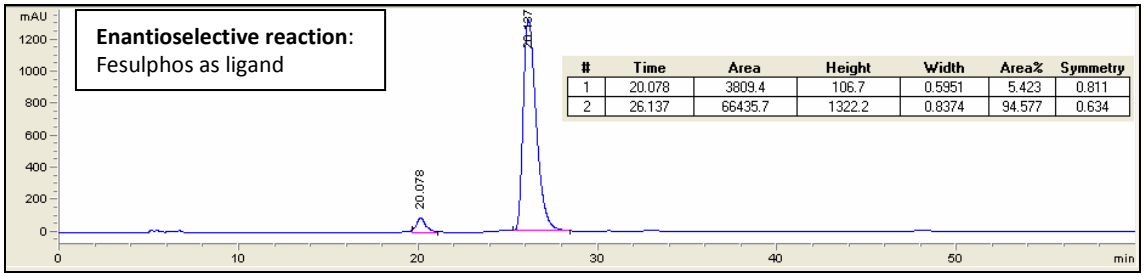


(2*S*,3*S*) Methyl 2-(benzylamino)-2-methyl-3-phenyl-3-[(8-quinolyl)-sulfonylamino]-propanoate (*anti*-23). Following the general procedure, the reaction of methyl (*E*)- 2-(benzylideneamino)propanoate (**2b**) (28.7 mg, 0.15 mmol) with (*E*)-*N*-benzylidene-*N*-[(8-quinolyl)sulfonyl] imine (**3h**) (48.8 mg, 0.165 mmol) in THF at –40 ºC for 3 h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**23** as a colourless amorphous solid; yield: 40.3 mg (55%). ^{1}H NMR (300 MHz): δ 9.08 (dd, *J* = 1.6, 4.2 Hz, 1H), 8.12 (dd, *J* = 1.6, 8.3 Hz, 1H), 7.97 (dd, *J* = 1.3, 7.2 Hz, 1H), 7.77 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.51 (dd, *J* = 4.3, 8.2 Hz, 1H), 7.42-7.26 (m, 7H), 6.79-6.72 (m, 1H), 6.62-6.54 (m, 4H), 4.77 (d, *J* = 10.3 Hz, 1H), 3.77 (d, *J* = 12.0 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 3.56 (s, 3H), 2.22 (bs, 1H), 1.50 (s, 3H). ^{13}C NMR (75 MHz): δ 174.5, 150.8, 143.3, 140.4, 137.6, 136.6,

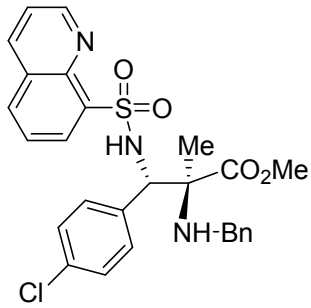
135.7, 132.4, 129.8, 128.4, 128.2, 127.5, 127.2, 127.0, 125.3, 121.9, 65.8, 65.1, 51.9, 48.0, 20.1.

ee = 89%; $[\alpha]_D^{20}$ = –36 (*c* = 1.3, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 20.1 min for (2*R*,3*R*)-enantiomer and 26.1 min for (2*S*,3*S*)-enantiomer.

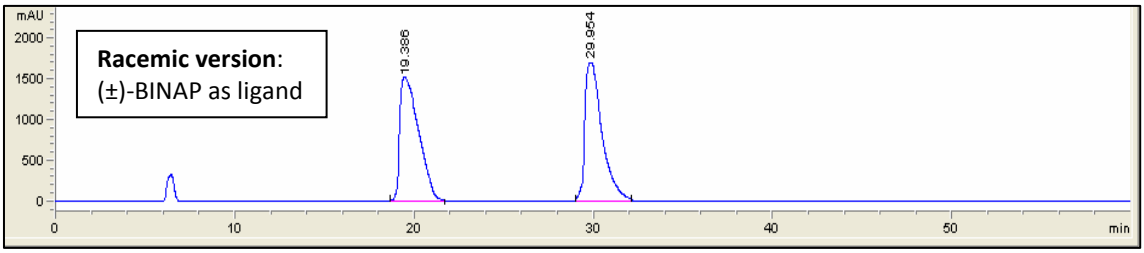


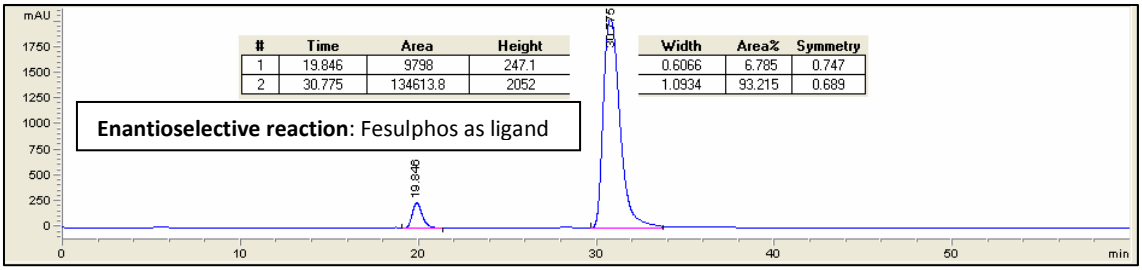


(2*S*,3*S*) Methyl 2-(benzylamino)-3-(4-chlorophenyl)-2-methyl-3-[(8-quinolyl)-sulfonylamino]propanoate (*anti*-24). Following the general procedure, the reaction of methyl (*E*)-2-(benzylideneamino)-propanoate (**2b**) (28.7 mg, 0.15 mmol) with (*E*)-*N*-(4-chlorobenzylidene)-*N*-[(8-quinolyl)sulfonyl] imine (**8h**) (57.4 mg, 0.165 mmol) in THF at –78 ºC for 2h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**24** as a white solid; yield: 52.7 mg (65%); mp = 64-65 ºC. ^{1}H NMR (300 MHz): δ 9.04 (dd, *J* = 1.7, 4.3 Hz, 1H), 8.16 (dd, *J* = 1.7, 8.3 Hz, 1H), 7.99 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.84 (dd, *J* = 1.2, 8.3 Hz, 1H), 7.52 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.39-7.28 (m, 7H), 6.56-6.49 (m, 4H), 4.74 (d, *J* = 10.2 Hz, 1H), 3.76 (d, *J* = 11.8 Hz, 1H), 3.62 (d, *J* = 11.8 Hz, 1H), 3.56 (s, 3H), 2.15 (bs, 1H), 1.48 (s, 3H). ^{13}C NMR (75 MHz): δ 174.4, 150.9, 143.2, 140.1, 137.4, 136.7, 134.6, 133.4, 132.5, 129.9, 128.6, 128.5, 128.4, 128.1, 127.3, 127.1, 125.3, 122.0, 65.6, 64.4, 52.0, 48.1, 20.1. MS-FAB$^+$ *m/z* 524.1 (M^++H, 100), 331.0 (43), 192.1 (88), 91 (98), 57 (53). HRMS-FAB$^+$ Calcd. For $C_{27}H_{26}ClN_3O_4S$: 523.1300. Found: 523.1320.



ee = 87%; $[\alpha]_D^{20}$ = –33 (*c* = 2.9, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 19.8 min for (2*R*,3*R*)-enantiomer and 30.8 min for (2*S*,3*S*)-enantiomer.





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Width	Area%	Symmetry
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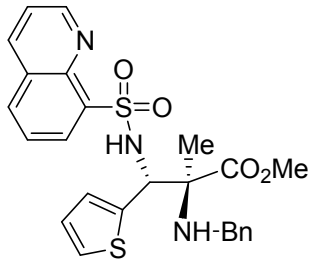
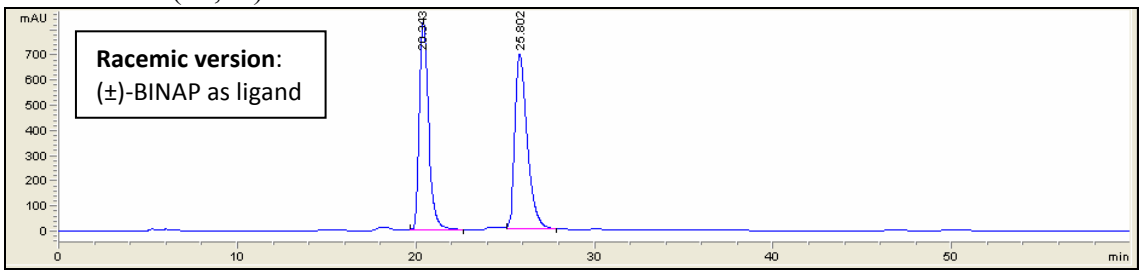
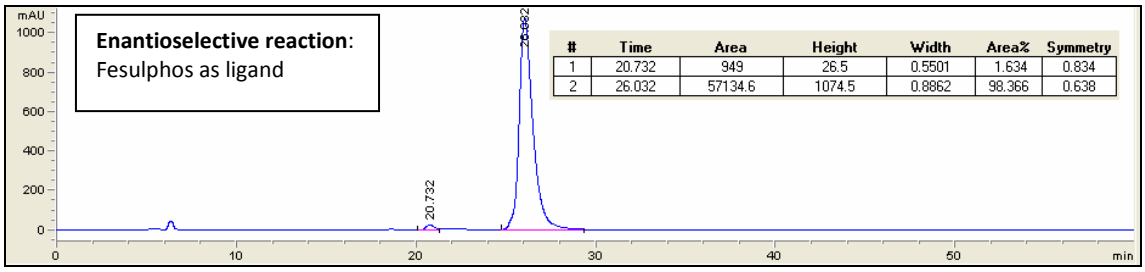
1.0934	93.215	0.689



(2*S*,3*S*) Methyl 2-(benzylamino)-2-methyl-3-[(8-quinolyl)-sulfonylamino]-3-(thiophen-2-yl)propanoate (*anti*-25). Following the general procedure, the reaction of methyl (*E*)- 2-(benzylideneamino)propanoate (**2b**) (28.7 mg, 0.15 mmol) with (*E*)-*N*-[(8-quinolyl)sulfonyl]-*N*-((thiophen-2-yl)methylene) imine (**14h**) (52.8 mg, 0.165 mmol) in THF at −78 ºC for 2h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**25** as a sticky solid; yield: 40.1 mg (52%). ^{1}H NMR (300 MHz): δ 8.99 (dd, *J* = 1.6, 4.2 Hz, 1H), 8.13 (dd, *J* = 1.6, 8.3 Hz, 1H), 8.07 (dd, *J* = 1.2, 7.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.43-7.28 (m, 7H), 6.57 (t, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 2H), 5.08 (d, *J* = 10.3 Hz, 1H), 3.84 (d, *J* = 12.1 Hz, 1H), 3.76 (d, *J* = 12.1 Hz, 1H), 3.60 (s, 3H), 2.37 (bs, 1H), 1.55 (s, 3H). ^{13}C NMR (75 MHz): δ 174.4, 150.8, 143.2, 140.3, 138.0, 137.3, 136.5, 132.5, 129.7, 128.4, 128.0, 127.0, 126.4, 125.3, 125.2, 124.7, 121.9, 65.6, 60.9, 52.0, 48.0, 19.9. MS-FAB^{+} *m/z* 496.1 (M^{+}+H, 61), 303.0 (38), 192.1 (42), 91 (47), 55 (38). HRMS-FAB^{+} Calcd. For $C_{25}H_{25}N_3O_4S_2$: 495.1286. Found: 495.1279. Anal. Calcd. for $C_{25}H_{25}N_3O_4S_2$: C, 60.58; H, 5.08; N, 8.48; S, 12.94. Found: C, 59.36; H, 5.06; N, 8.04; S, 12.70.

ee = 96%; $[\alpha]_D^{20}$ = –30 (*c* = 2.7, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 20.7 min for (2*R*,3*R*)-enantiomer and 26.0 min for (2*S*,3*S*)-enantiomer.





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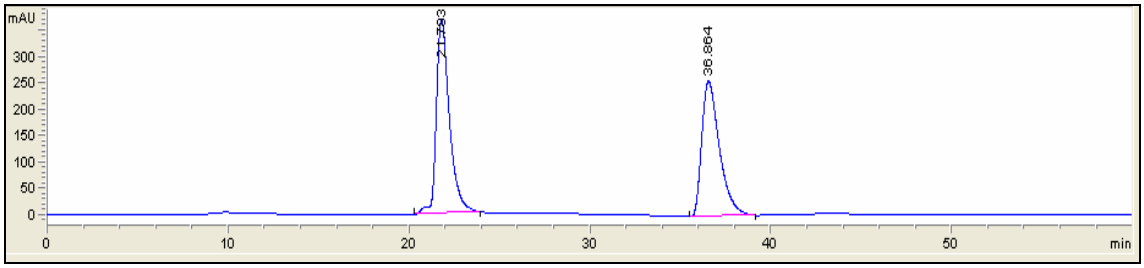
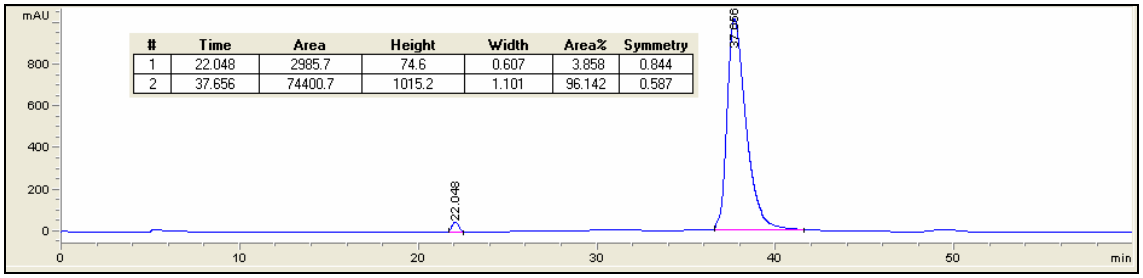
(2*S*,3*S*) Methyl 2-(benzylamino)-3-(2-bromophenyl)-2-methyl-3-[(8-quinolyl)-sulfonylamino]-propanoate (*anti*-26). Following the general procedure the reaction of methyl (*E*)- 2-(benzylideneamino)propanoate (**2b**) (28.7 mg, 0.15 mmol) with (*E*)-*N*-(2-bromobenzylidene)-*N*-[(8-quinolyl)sulfonyl] imine (**15h**) (48.8 mg, 0.165 mmol) in THF at –40 ºC for 3h afforded, after chromatography (*n*-hexane-EtOAc 2:1), *anti*-**26** as a white solid; yield: 52.0 mg (61%). Mp = 64-65 ºC. ^{1}H NMR (300 MHz): δ 9.01 (dd, *J* = 1.8, 4.3 Hz, 1H), 8.20 (dd, *J* = 1.4, 7.2 Hz, 1H), 8.04 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.74 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.44 (dd, *J* = 4.3, 8.3 Hz, 1H), 7.39-7.30 (m, 6H), 7.18 (d, *J* = 10.5 Hz, 1H), 7.03 (dd, *J* = 1.2, 8.0 Hz, 1H), 6.58 (t, *J* = 7.6 Hz, 2H), 6.20 (t, *J* = 7.5 Hz, 1H), 5.39 (d, *J* = 10.6 Hz, 1H), 3.82 (d, *J* = 12.1 Hz, 1H), 3.68 (s, 3H), 3.55 (d, *J* = 12.1 Hz, 1H), 2.50 (bs, 1H), 1.47 (s, 3H). ^{13}C NMR (75 MHz): δ 174.4, 150.8, 140.1, 136.6, 135.5, 133.1, 132.8, 132.3, 130.7, 128.6, 128.4, 128.3, 127.0, 125.8, 125.7, 125.4, 121.9, 65.7, 61.7, 52.2, 47.9, 19.2.

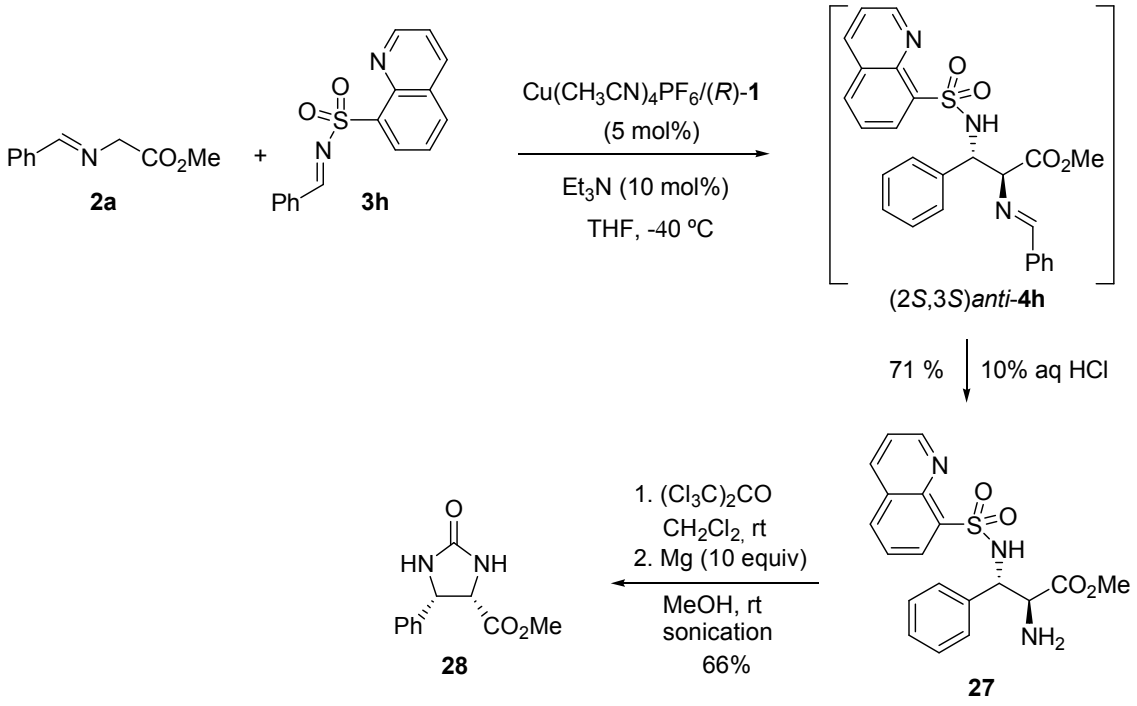
ee = 92%; $[\alpha]_D^{20}$ = – 75 (*c* = 2.7, CH_2Cl_2). HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ = 210 nm), t_R (major): 22.0 min for (2*R*,3*R*)-isomer and 37.7 min for (2*S*,3*S*)-isomer.





#	Time	Area	Height	Width	Area%	Symmetry
1	22.048	2985.7	74.6	0.607	3.858	0.844
2	37.656	74400.7	1015.2	1.101	96.142	0.587

Chemical correlation to thiourea 28



(4*S*,5*S*)-4-(Methoxycarbonyl)-5-phenyl-2-imidazolidinone (28).[5] To a solution of Fesulphos ligand (*R*)-**1** (5 mol%, 12.9 mg) and $Cu(CH_3CN)_4PF_6$ (5 mol%, 10.4 mg) in THF (1.5 mL), at – 40 ºC, were successively added a solution of (*E*)-*N*-benzylideneglycinate (**2a**) (100 mg, 0.56 mmol) in THF (1 mL), Et_3N (10 mol%, 9 μL) and **3h** (182.3 mg, 0.62 mmol). Upon consumption of the starting material (TLC monitoring), the solution was washed with 10% aq HCl (3 mL), and the aqueous phase was carefully basified with 10% aq NaOH to reach pH = 11 before it was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated to afford the aminoester **27** as a white solid (154.4 mg, 71%).

To a solution of **27** (100 mg, 0.26 mmol) in CH_2Cl_2 (3 mL), was added a solution of triphosgene (77 mg, 0.26 mmol) at 0 ºC. The mixture was allowed to reach room temperature and it was stirred at room temperature for 2 h. The solvent was evaporated, the residue was dissolved in MeOH (1 mL) and it was added drop-wise to a suspension of Mg turnings (63.2 mg, 2.6 mmol) in MeOH (5 mL). The reaction mixture was immersed into an ultrasound bath for 2 h, and then quenched with saturated $NaHCO_3$. The mixture was treated with CH_2Cl_2 (3 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure, to give the crude product, which was recrystallized from AcOEt to afford **28** as white solid; yield:

37.8 mg, (66% overall over two steps). Mp = 204-206 ºC (with decomposition). ^{1}H NMR (CD_3OD, 300 MHz): δ 7.36-7.29 (m, 5H), 5.21 (d, J = 9.7 Hz, 1H), 4.65 (d, J = 9.7 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (CD_3OD, 75 MHz): δ 171.9, 166.1, 138.9, 129.6, 129.4, 128.4, 61.7, 60.1, 52.1. $[\alpha]_D^{25}$ = +69 (c = 0.72, MeOH). (lit.[5] $[\alpha]_D^{20}$ = +123.2 (c = 1, MeOH).

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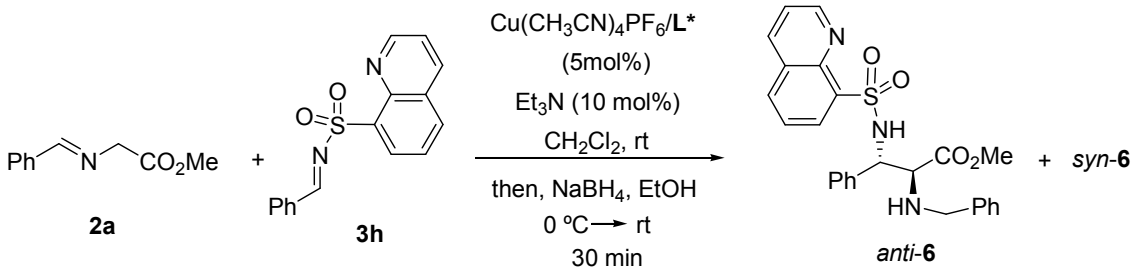
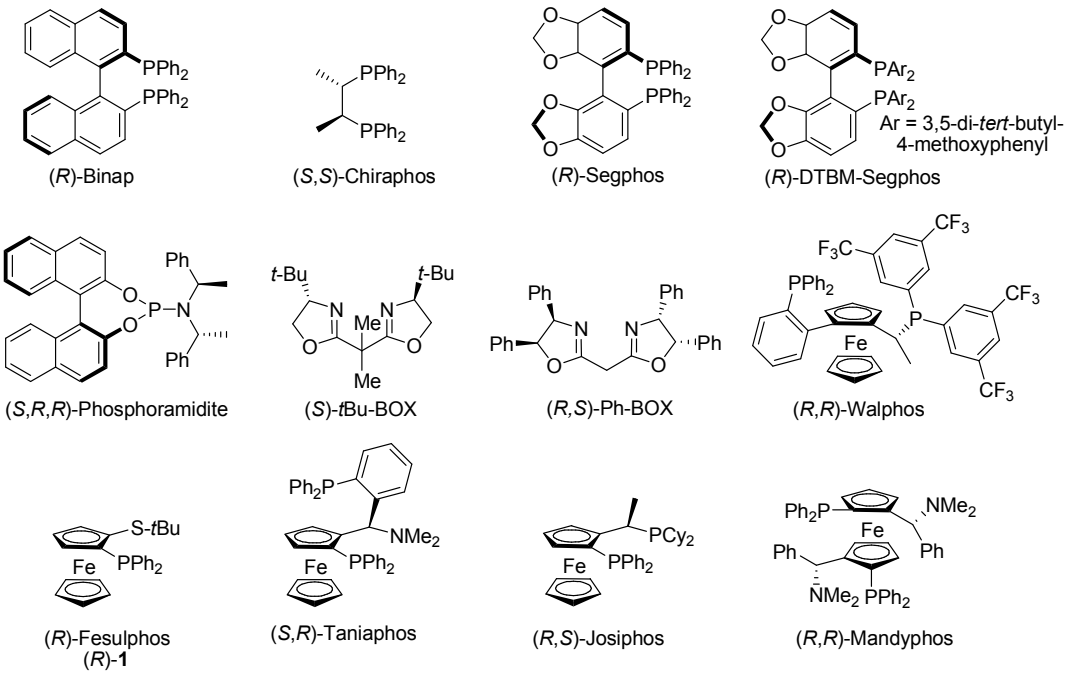
2. Chiral ligand screening



L*	t (h)[a]	conv(%)[a]	*anti/syn*[b]	yield (%)	*ee* (%)
(*R*)-BINAP	2	100	92:8	81	60
(*S*,*S*)-Chiraphos	12	40	73:27	-	–15
Segphos	12	85	84:16	69	–10
DTBM Segphos	24	10	70:30	-	-
(*S*,*R*,*R*)-Fosf. Feringa	2	100	90:10	77	53
(*S*)-*t*Bu-BOX	24	25	75:25	-	-
(*R*, *S*)-Ph-BOX	12	100	60:40	-	0
(*R*,*R*)-Walphos	2	100	52:48	73	–20
(*R*)-Fesulphos	**2**	**100**	**92:8**	**79**	**91**
(*S*,*R*)-Taniaphos	2	100	90:10	77	10
(*R*,*S*)-Josiphos	5	90	83:17	71	57
(*R*,*R*)-Mandyphos	2	100	90:10	70	81

[a] For the direct Manich reaction step. [b] Determined by NMR from the crude reaction mixture.



3. Determination of *syn*/*anti*-diastereoselectivity and absolute configuration: X-ray data of *anti*-6

The determination of the relative and absolute configuration of the Mannich adducts has been established by X-ray diffraction analysis of (–)-*anti*-**6** (recrystallyzed sample of >99% ee), as well as by chemical correlation between (–)-*anti*-**6** and the cyclic known urea (+)-**28**. The *anti*-configuration of the rest of Mannich products (compounds **16**-**26**) has been assigned by chemical analogy with that of *anti*-**6**. In agreement with this assignment, all *anti*-Mannich adducts show rather homogeneous NMR signal patterns and HPLC behaviour. The *anti*/*syn*-configuration of *o*-nosyl-protected adducts **4g** was determined by comparison of their characteristic ^{1}H signal patterns with those of compounds **6** and **16**-**26**.

X-Ray data of *anti*-6

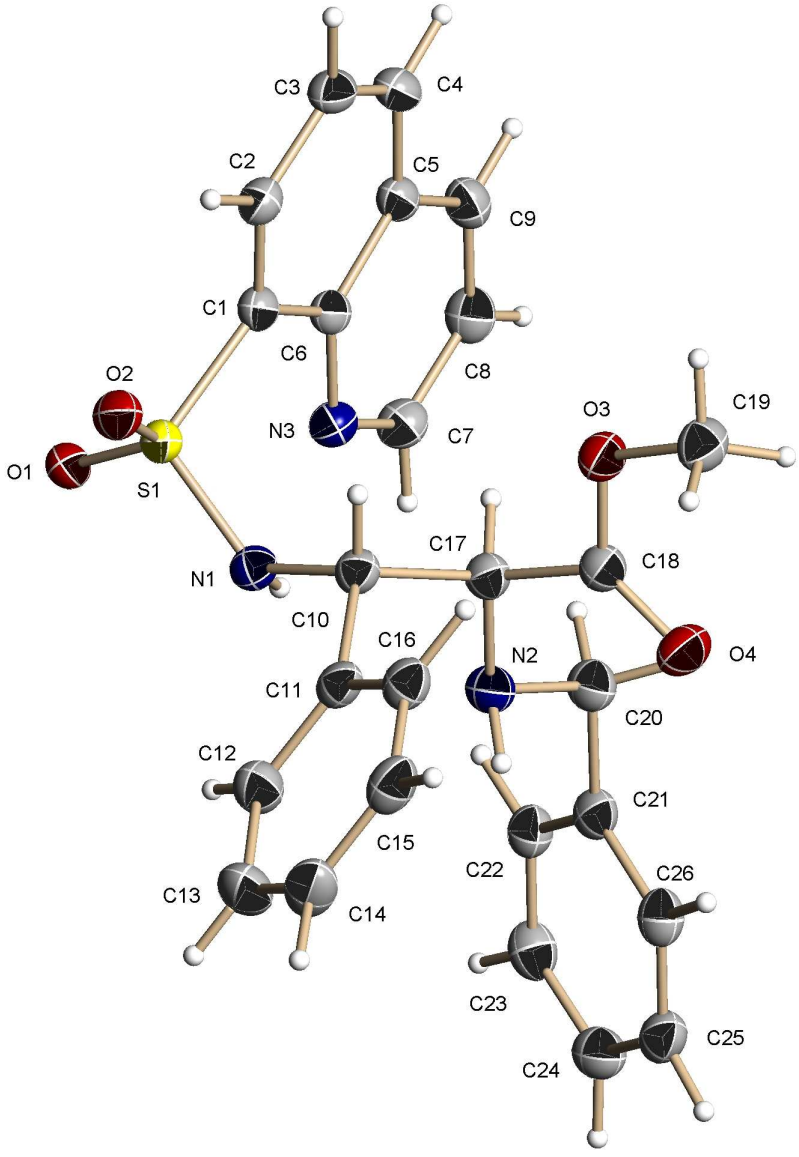


Table 1. Crystal data and structure refinement for *anti*-**6**.

Empirical formula	C26 H25 N3 O4 S	
Formula weight	475.55	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.58980(10) Å	α = 90°.
	b = 13.8415(3) Å	β = 90°.
	c = 17.3475(3) Å	γ = 90°.
Volume	2302.66(7) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	1.574 mm^{-1}	
F(000)	1000	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	4.09 to 72.05°.	
Index ranges	-11<=h<=11, -16<=k<=17, -19<=l<=21	
Reflections collected	18910	
Independent reflections	4330 [R(int) = 0.0326]	
Completeness to theta = 72.05°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4330 / 0 / 407	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0764	
R indices (all data)	R1 = 0.0309, wR2 = 0.0854	
Absolute structure parameter	-0.003(14)	
Largest diff. peak and hole	0.293 and -0.204 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *anti*-**6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

S(1)	8797(1)	9840(1)	1134(1)	23(1)
C(1)	8818(2)	10937(1)	1663(1)	23(1)
C(2)	8439(2)	11772(1)	1292(1)	26(1)
C(3)	8493(2)	12666(1)	1682(1)	29(1)
C(4)	8957(2)	12711(1)	2426(1)	29(1)
C(5)	9341(2)	11860(1)	2824(1)	25(1)
C(6)	9237(2)	10948(1)	2450(1)	22(1)
C(7)	9884(2)	10139(2)	3546(1)	29(1)
C(8)	10053(2)	11009(1)	3966(1)	31(1)
C(9)	9781(2)	11865(1)	3603(1)	29(1)
C(10)	6308(2)	9303(1)	1659(1)	24(1)
C(11)	5425(2)	8514(1)	1280(1)	26(1)
C(12)	5964(2)	7614(1)	1104(1)	33(1)
C(13)	5117(3)	6914(2)	761(1)	42(1)
C(14)	3745(3)	7116(2)	582(1)	40(1)
C(15)	3201(2)	8019(2)	756(1)	34(1)
C(16)	4030(2)	8715(1)	1102(1)	29(1)
C(17)	5978(2)	9437(1)	2528(1)	25(1)
C(18)	4469(2)	9756(1)	2654(1)	26(1)
C(19)	2788(2)	10932(2)	2367(1)	33(1)
C(20)	6440(2)	8693(1)	3780(1)	30(1)
C(21)	6658(2)	7719(1)	4155(1)	27(1)
C(22)	7986(2)	7401(2)	4345(1)	28(1)
C(23)	8176(2)	6497(2)	4679(1)	32(1)
C(24)	7042(2)	5904(2)	4818(1)	33(1)
C(25)	5701(2)	6212(2)	4614(1)	31(1)
C(26)	5525(2)	7117(2)	4289(1)	30(1)
N(1)	7801(2)	9083(1)	1591(1)	25(1)
N(2)	6342(2)	8563(1)	2939(1)	28(1)
N(3)	9506(2)	10094(1)	2815(1)	26(1)
O(1)	10173(1)	9437(1)	1141(1)	27(1)
O(2)	8143(1)	10047(1)	412(1)	30(1)
O(3)	4219(1)	10608(1)	2321(1)	30(1)
O(4)	3619(2)	9305(1)	3015(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for *anti*-**6**.

S(1)-O(2)	1.4299(14)
S(1)-O(1)	1.4325(14)
S(1)-N(1)	1.6247(16)
S(1)-C(1)	1.7746(17)
C(1)-C(2)	1.372(3)
C(1)-C(6)	1.422(2)
C(2)-C(3)	1.411(3)
C(2)-H(2)	0.97(2)
C(3)-C(4)	1.367(3)
C(3)-H(3)	0.98(3)
C(4)-C(5)	1.414(3)
C(4)-H(4)	0.94(3)
C(5)-C(9)	1.416(3)
C(5)-C(6)	1.423(2)
C(6)-N(3)	1.366(2)
C(7)-N(3)	1.321(2)
C(7)-C(8)	1.417(3)
C(7)-H(7)	0.93(2)
C(8)-C(9)	1.367(3)
C(8)-H(8)	0.95(3)
C(9)-H(9)	0.96(2)
C(10)-N(1)	1.469(2)
C(10)-C(11)	1.530(2)
C(10)-C(17)	1.550(2)
C(10)-H(10)	0.95(2)
C(11)-C(12)	1.383(3)
C(11)-C(16)	1.400(3)
C(12)-C(13)	1.398(3)
C(12)-H(12)	0.92(2)
C(13)-C(14)	1.381(4)
C(13)-H(13)	0.89(3)
C(14)-C(15)	1.387(3)
C(14)-H(14)	0.97(3)
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.93(3)
C(16)-H(16)	1.00(3)

C(17)-N(2)	1.448(2)
C(17)-C(18)	1.529(3)
C(17)-H(17)	0.98(2)
C(18)-O(4)	1.202(2)
C(18)-O(3)	1.336(2)
C(19)-O(3)	1.445(2)
C(19)-H(19A)	0.90(3)
C(19)-H(19B)	0.97(3)
C(19)-H(19C)	0.95(3)
C(20)-N(2)	1.472(2)
C(20)-C(21)	1.512(3)
C(20)-H(20A)	1.00(3)
C(20)-H(20B)	0.98(3)
C(21)-C(22)	1.387(3)
C(21)-C(26)	1.390(3)
C(22)-C(23)	1.391(3)
C(22)-H(22)	1.02(2)
C(23)-C(24)	1.384(3)
C(23)-H(23)	1.00(3)
C(24)-C(25)	1.400(3)
C(24)-H(24)	0.98(3)
C(25)-C(26)	1.385(3)
C(25)-H(25)	0.96(2)
C(26)-H(26)	1.00(3)
N(1)-H(1)	0.84(3)
N(2)-H(2A)	0.95(3)
O(2)-S(1)-O(1)	119.33(8)
O(2)-S(1)-N(1)	107.38(8)
O(1)-S(1)-N(1)	106.59(8)
O(2)-S(1)-C(1)	106.68(8)
O(1)-S(1)-C(1)	108.58(8)
N(1)-S(1)-C(1)	107.81(8)
C(2)-C(1)-C(6)	121.05(16)
C(2)-C(1)-S(1)	118.35(13)
C(6)-C(1)-S(1)	120.60(13)
C(1)-C(2)-C(3)	120.27(16)
C(1)-C(2)-H(2)	120.3(13)
C(3)-C(2)-H(2)	119.4(13)

C(4)-C(3)-C(2)	120.27(16)
C(4)-C(3)-H(3)	121.7(15)
C(2)-C(3)-H(3)	118.0(15)
C(3)-C(4)-C(5)	120.57(16)
C(3)-C(4)-H(4)	121.0(15)
C(5)-C(4)-H(4)	118.4(15)
C(4)-C(5)-C(9)	122.67(16)
C(4)-C(5)-C(6)	119.81(16)
C(9)-C(5)-C(6)	117.47(16)
N(3)-C(6)-C(1)	119.26(15)
N(3)-C(6)-C(5)	122.86(15)
C(1)-C(6)-C(5)	117.88(15)
N(3)-C(7)-C(8)	124.39(18)
N(3)-C(7)-H(7)	116.0(14)
C(8)-C(7)-H(7)	119.5(14)
C(9)-C(8)-C(7)	118.63(17)
C(9)-C(8)-H(8)	117.4(14)
C(7)-C(8)-H(8)	123.9(14)
C(8)-C(9)-C(5)	119.43(17)
C(8)-C(9)-H(9)	119.9(15)
C(5)-C(9)-H(9)	120.6(15)
N(1)-C(10)-C(11)	110.94(15)
N(1)-C(10)-C(17)	107.58(14)
C(11)-C(10)-C(17)	112.97(14)
N(1)-C(10)-H(10)	110.7(13)
C(11)-C(10)-H(10)	107.6(12)
C(17)-C(10)-H(10)	107.0(12)
C(12)-C(11)-C(16)	119.14(18)
C(12)-C(11)-C(10)	122.06(18)
C(16)-C(11)-C(10)	118.79(17)
C(11)-C(12)-C(13)	120.1(2)
C(11)-C(12)-H(12)	121.0(15)
C(13)-C(12)-H(12)	118.9(15)
C(14)-C(13)-C(12)	120.5(2)
C(14)-C(13)-H(13)	120.1(18)
C(12)-C(13)-H(13)	119.3(18)
C(13)-C(14)-C(15)	119.5(2)
C(13)-C(14)-H(14)	118.2(16)

C(15)-C(14)-H(14)	122.3(16)
C(16)-C(15)-C(14)	120.3(2)
C(16)-C(15)-H(15)	117.8(16)
C(14)-C(15)-H(15)	121.7(16)
C(15)-C(16)-C(11)	120.34(19)
C(15)-C(16)-H(16)	120.7(15)
C(11)-C(16)-H(16)	119.0(15)
N(2)-C(17)-C(18)	113.50(15)
N(2)-C(17)-C(10)	109.28(14)
C(18)-C(17)-C(10)	111.55(15)
N(2)-C(17)-H(17)	109.3(13)
C(18)-C(17)-H(17)	106.5(13)
C(10)-C(17)-H(17)	106.4(13)
O(4)-C(18)-O(3)	124.23(17)
O(4)-C(18)-C(17)	124.50(17)
O(3)-C(18)-C(17)	111.27(15)
O(3)-C(19)-H(19A)	110.2(17)
O(3)-C(19)-H(19B)	109.0(14)
H(19A)-C(19)-H(19B)	113(2)
O(3)-C(19)-H(19C)	106.6(17)
H(19A)-C(19)-H(19C)	110(2)
H(19B)-C(19)-H(19C)	108(2)
N(2)-C(20)-C(21)	109.05(15)
N(2)-C(20)-H(20A)	110.2(16)
C(21)-C(20)-H(20A)	112.8(15)
N(2)-C(20)-H(20B)	113.4(14)
C(21)-C(20)-H(20B)	111.2(13)
H(20A)-C(20)-H(20B)	100(2)
C(22)-C(21)-C(26)	119.19(17)
C(22)-C(21)-C(20)	120.84(18)
C(26)-C(21)-C(20)	119.93(18)
C(21)-C(22)-C(23)	120.37(19)
C(21)-C(22)-H(22)	118.4(12)
C(23)-C(22)-H(22)	121.2(12)
C(24)-C(23)-C(22)	120.18(19)
C(24)-C(23)-H(23)	120.7(14)
C(22)-C(23)-H(23)	118.9(14)
C(23)-C(24)-C(25)	119.85(18)

C(23)-C(24)-H(24)	120.1(17)
C(25)-C(24)-H(24)	120.0(17)
C(26)-C(25)-C(24)	119.37(19)
C(26)-C(25)-H(25)	122.6(13)
C(24)-C(25)-H(25)	118.0(13)
C(25)-C(26)-C(21)	121.03(19)
C(25)-C(26)-H(26)	121.4(14)
C(21)-C(26)-H(26)	117.6(14)
C(10)-N(1)-S(1)	118.64(13)
C(10)-N(1)-H(1)	112.7(18)
S(1)-N(1)-H(1)	109.9(18)
C(17)-N(2)-C(20)	113.69(15)
C(17)-N(2)-H(2A)	108.3(16)
C(20)-N(2)-H(2A)	110.1(16)
C(7)-N(3)-C(6)	117.18(16)
C(18)-O(3)-C(19)	114.86(15)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for *anti*-**6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	25(1)	22(1)	21(1)	-1(1)	2(1)	-1(1)
C(1)	22(1)	23(1)	25(1)	-1(1)	4(1)	0(1)
C(2)	25(1)	28(1)	24(1)	3(1)	3(1)	-1(1)
C(3)	29(1)	23(1)	33(1)	5(1)	4(1)	2(1)
C(4)	31(1)	21(1)	35(1)	-3(1)	5(1)	0(1)
C(5)	22(1)	24(1)	29(1)	-2(1)	3(1)	-1(1)
C(6)	19(1)	22(1)	26(1)	0(1)	2(1)	1(1)
C(7)	29(1)	30(1)	27(1)	4(1)	-2(1)	0(1)
C(8)	30(1)	37(1)	25(1)	-2(1)	-2(1)	0(1)
C(9)	26(1)	30(1)	30(1)	-7(1)	2(1)	-1(1)
C(10)	26(1)	25(1)	22(1)	1(1)	1(1)	-1(1)
C(11)	30(1)	29(1)	20(1)	0(1)	2(1)	-6(1)
C(12)	30(1)	33(1)	36(1)	-4(1)	3(1)	-2(1)
C(13)	47(1)	33(1)	48(1)	-15(1)	9(1)	-8(1)
C(14)	41(1)	44(1)	35(1)	-14(1)	7(1)	-17(1)
C(15)	29(1)	45(1)	29(1)	-1(1)	2(1)	-10(1)

C(16)	31(1)	34(1)	23(1)	0(1)	1(1)	-3(1)
C(17)	27(1)	26(1)	22(1)	-1(1)	1(1)	-1(1)
C(18)	26(1)	27(1)	24(1)	-2(1)	0(1)	-2(1)
C(19)	26(1)	35(1)	38(1)	6(1)	4(1)	4(1)
C(20)	37(1)	31(1)	23(1)	0(1)	1(1)	0(1)
C(21)	31(1)	30(1)	19(1)	-3(1)	1(1)	-2(1)
C(22)	27(1)	33(1)	24(1)	-2(1)	2(1)	-1(1)
C(23)	32(1)	38(1)	26(1)	-2(1)	-2(1)	6(1)
C(24)	42(1)	31(1)	26(1)	-1(1)	-1(1)	0(1)
C(25)	35(1)	34(1)	25(1)	-2(1)	4(1)	-5(1)
C(26)	28(1)	39(1)	24(1)	-3(1)	0(1)	1(1)
N(1)	26(1)	24(1)	23(1)	2(1)	-1(1)	-1(1)
N(2)	35(1)	26(1)	22(1)	0(1)	-1(1)	-1(1)
N(3)	26(1)	26(1)	26(1)	2(1)	-1(1)	-1(1)
O(1)	26(1)	24(1)	31(1)	-2(1)	4(1)	1(1)
O(2)	37(1)	30(1)	23(1)	-1(1)	2(1)	-4(1)
O(3)	27(1)	29(1)	33(1)	5(1)	4(1)	2(1)
O(4)	31(1)	34(1)	41(1)	6(1)	6(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for *anti*-**6**.

	x	y	z	U(eq)
H(1)	8170(30)	8934(18)	2016(16)	36(6)
H(2)	8160(20)	11755(15)	756(13)	22(5)
H(2A)	5670(30)	8082(19)	2821(15)	42(7)
H(3)	8200(30)	13245(19)	1402(15)	41(7)
H(4)	9050(30)	13308(19)	2682(14)	37(6)
H(7)	10010(20)	9548(16)	3794(13)	25(5)
H(8)	10290(30)	11034(16)	4494(15)	31(6)
H(9)	9900(30)	12462(17)	3875(15)	35(6)
H(10)	6090(20)	9894(15)	1412(12)	23(5)
H(12)	6880(30)	7466(16)	1208(14)	28(5)
H(13)	5470(30)	6330(20)	657(15)	41(7)
H(14)	3190(30)	6613(19)	343(15)	42(7)
H(15)	2300(30)	8196(18)	608(14)	36(6)

H(16)	3640(30)	9365(19)	1232(15)	39(6)
H(17)	6570(20)	9967(17)	2707(13)	29(5)
H(19A)	2240(30)	10546(19)	2083(16)	39(7)
H(19B)	2510(20)	10957(16)	2901(15)	28(5)
H(19C)	2770(30)	11570(20)	2166(16)	47(7)
H(20A)	7190(30)	9163(18)	3906(16)	40(6)
H(20B)	5640(30)	9028(17)	4002(14)	32(6)
H(22)	8810(20)	7846(15)	4234(12)	25(5)
H(23)	9150(30)	6259(17)	4768(14)	36(6)
H(24)	7180(30)	5260(20)	5031(16)	47(7)
H(25)	4940(20)	5769(16)	4688(12)	25(5)
H(26)	4580(30)	7360(17)	4139(13)	32(6)

Table 6. Torsion angles [°] for *anti*-**6**.

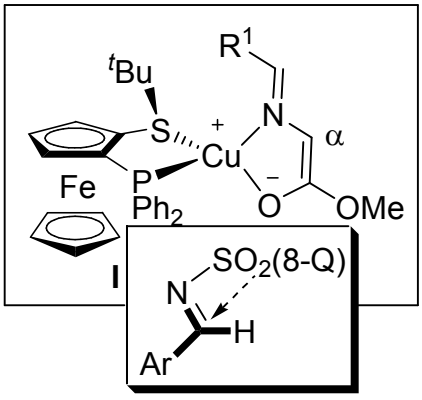
O(2)-S(1)-C(1)-C(2)	-9.17(17)
O(1)-S(1)-C(1)-C(2)	120.65(15)
N(1)-S(1)-C(1)-C(2)	-124.24(15)
O(2)-S(1)-C(1)-C(6)	171.69(14)
O(1)-S(1)-C(1)-C(6)	-58.50(16)
N(1)-S(1)-C(1)-C(6)	56.61(16)
C(6)-C(1)-C(2)-C(3)	1.6(3)
S(1)-C(1)-C(2)-C(3)	-177.52(14)
C(1)-C(2)-C(3)-C(4)	1.7(3)
C(2)-C(3)-C(4)-C(5)	-2.3(3)
C(3)-C(4)-C(5)-C(9)	-177.73(18)
C(3)-C(4)-C(5)-C(6)	-0.3(3)
C(2)-C(1)-C(6)-N(3)	175.17(17)
S(1)-C(1)-C(6)-N(3)	-5.7(2)
C(2)-C(1)-C(6)-C(5)	-4.2(3)
S(1)-C(1)-C(6)-C(5)	174.94(13)
C(4)-C(5)-C(6)-N(3)	-175.80(17)
C(9)-C(5)-C(6)-N(3)	1.7(3)
C(4)-C(5)-C(6)-C(1)	3.5(2)
C(9)-C(5)-C(6)-C(1)	-178.95(16)
N(3)-C(7)-C(8)-C(9)	1.5(3)
C(7)-C(8)-C(9)-C(5)	0.0(3)
C(4)-C(5)-C(9)-C(8)	175.92(18)

C(6)-C(5)-C(9)-C(8)	-1.5(3)
N(1)-C(10)-C(11)-C(12)	16.6(2)
C(17)-C(10)-C(11)-C(12)	-104.3(2)
N(1)-C(10)-C(11)-C(16)	-162.89(15)
C(17)-C(10)-C(11)-C(16)	76.2(2)
C(16)-C(11)-C(12)-C(13)	-0.8(3)
C(10)-C(11)-C(12)-C(13)	179.67(18)
C(11)-C(12)-C(13)-C(14)	1.2(3)
C(12)-C(13)-C(14)-C(15)	-1.0(3)
C(13)-C(14)-C(15)-C(16)	0.4(3)
C(14)-C(15)-C(16)-C(11)	0.0(3)
C(12)-C(11)-C(16)-C(15)	0.2(3)
C(10)-C(11)-C(16)-C(15)	179.75(17)
N(1)-C(10)-C(17)-N(2)	-58.66(18)
C(11)-C(10)-C(17)-N(2)	64.1(2)
N(1)-C(10)-C(17)-C(18)	175.02(14)
C(11)-C(10)-C(17)-C(18)	-62.20(19)
N(2)-C(17)-C(18)-O(4)	-4.8(2)
C(10)-C(17)-C(18)-O(4)	119.2(2)
N(2)-C(17)-C(18)-O(3)	174.41(14)
C(10)-C(17)-C(18)-O(3)	-61.62(19)
N(2)-C(20)-C(21)-C(22)	96.2(2)
N(2)-C(20)-C(21)-C(26)	-81.5(2)
C(26)-C(21)-C(22)-C(23)	-1.2(3)
C(20)-C(21)-C(22)-C(23)	-178.92(17)
C(21)-C(22)-C(23)-C(24)	0.5(3)
C(22)-C(23)-C(24)-C(25)	0.7(3)
C(23)-C(24)-C(25)-C(26)	-1.2(3)
C(24)-C(25)-C(26)-C(21)	0.6(3)
C(22)-C(21)-C(26)-C(25)	0.6(3)
C(20)-C(21)-C(26)-C(25)	178.38(16)
C(11)-C(10)-N(1)-S(1)	119.57(14)
C(17)-C(10)-N(1)-S(1)	-116.40(14)
O(2)-S(1)-N(1)-C(10)	-49.71(15)
O(1)-S(1)-N(1)-C(10)	-178.67(12)
C(1)-S(1)-N(1)-C(10)	64.90(15)
C(18)-C(17)-N(2)-C(20)	-70.7(2)
C(10)-C(17)-N(2)-C(20)	164.11(16)

C(21)-C(20)-N(2)-C(17)	173.50(16)
C(8)-C(7)-N(3)-C(6)	-1.4(3)
C(1)-C(6)-N(3)-C(7)	-179.62(16)
C(5)-C(6)-N(3)-C(7)	-0.3(2)
O(4)-C(18)-O(3)-C(19)	-4.9(3)
C(17)-C(18)-O(3)-C(19)	175.87(15)

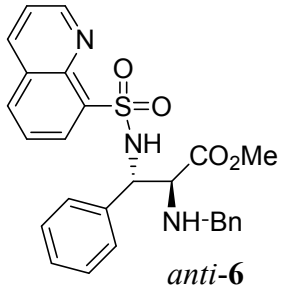
4. Tentative stereochemical model

As a tentative model, the high enantioselectivity observed in this Fesulphos/Cu^{I}-catalyzed Mannich reaction could be rationalized assuming the participation as nucleophile of the Fesulphos-copper-enolate complex intermediate **I** shown in the Figure below. According to our previous computational studies[6] the tetracoordinated complex **I**, showing a highly distorted tetrahedral structure around the copper atom, was found to be the most stable geometry in the coordination of the metal atom with the P,S-ligand Fesulphos and the azomethine species. In this complex the high steric congestion imposed by the *tert*-butyl group linked to the sulfur atom in close proximity to the copper center hinders the approach of the N-(8-quinolyl)sulfonyl imine from the *Si* C-α enolate face of the azomethine. Thus, the approach of **I** from the more accessible *Re* C–α enolate face to the *Re* face of the *N*-sulfonyl imine accounts for the high stereoselectivity attained in the formation of the α,β-diamino esters with (2*S*,3*S*) configuration. The *Re*-face approach of the imine would minimize the steric repulsion between the *N*-sulfonyl substitutent of the imine and the diphenylphosphino fragment of the chiral ligand. We have not yet a conclusive explanation for the role of the 8-quinolyl unit in providing high *anti*-diastereoselectivity. Further mechanistic studies in this direction are underway in our laboratory.

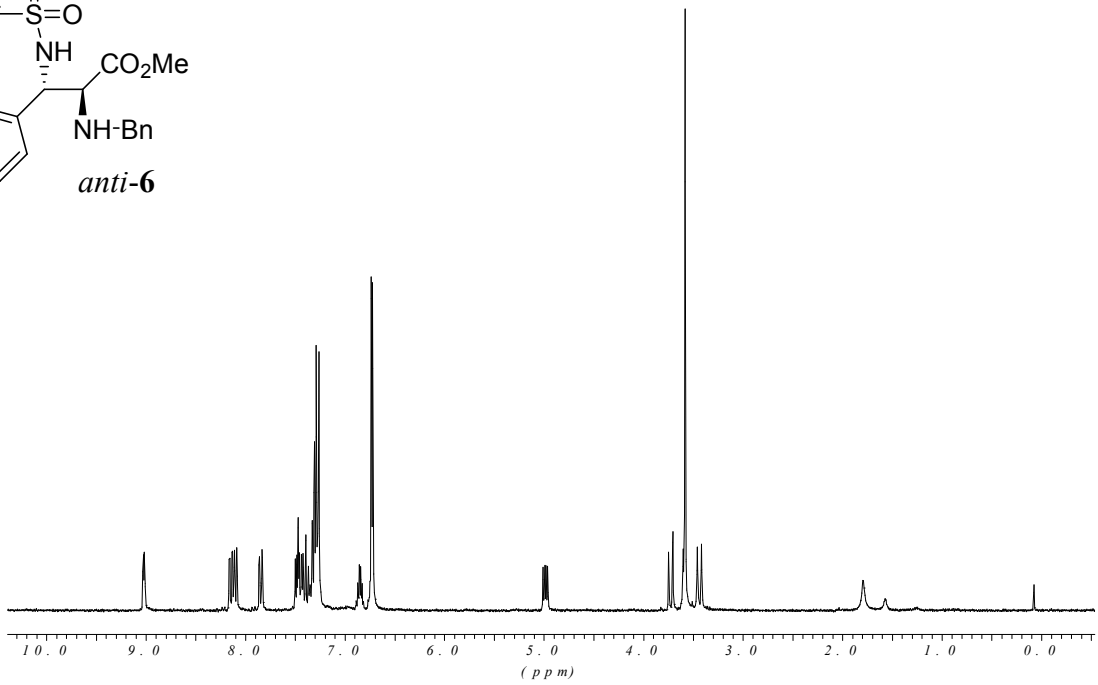


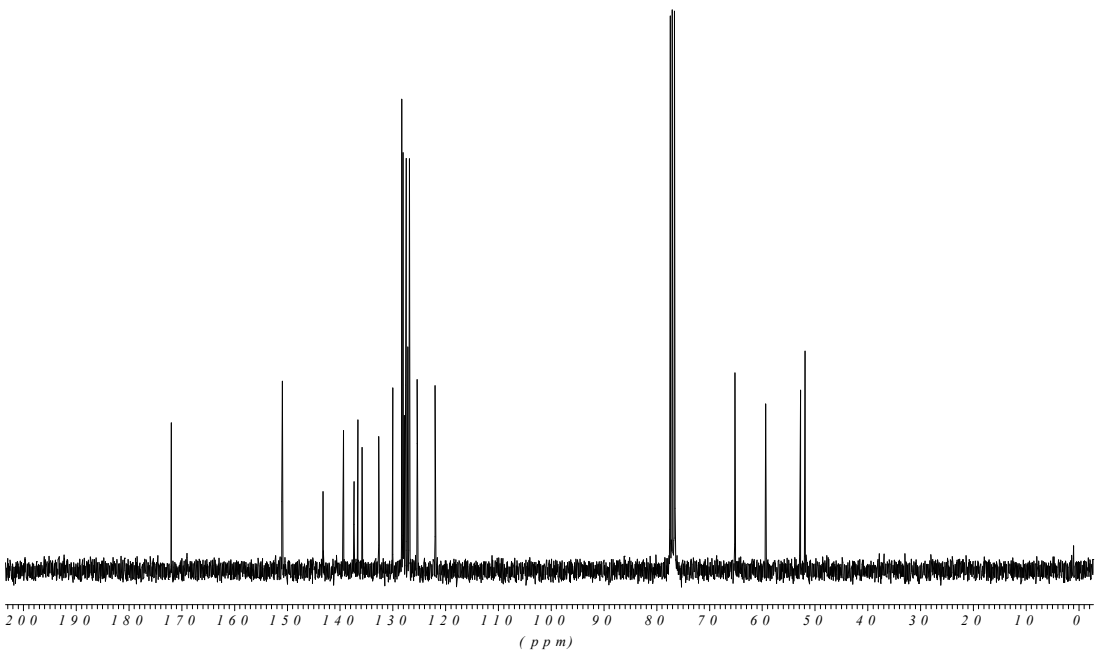
6. Cabrera, S.; Gómez Arrayás, R.; Martín-Matute, B.; Cossío, F.; Carretero, J. C. *Tetrahedron* **2007**, *63*, 6587.

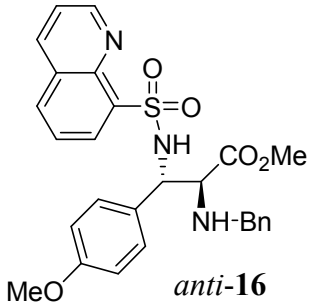
5. NMR Spectra



anti-**6**



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O
S=O
NH
CO2Me
NH-Bn
MeO

anti-**16**

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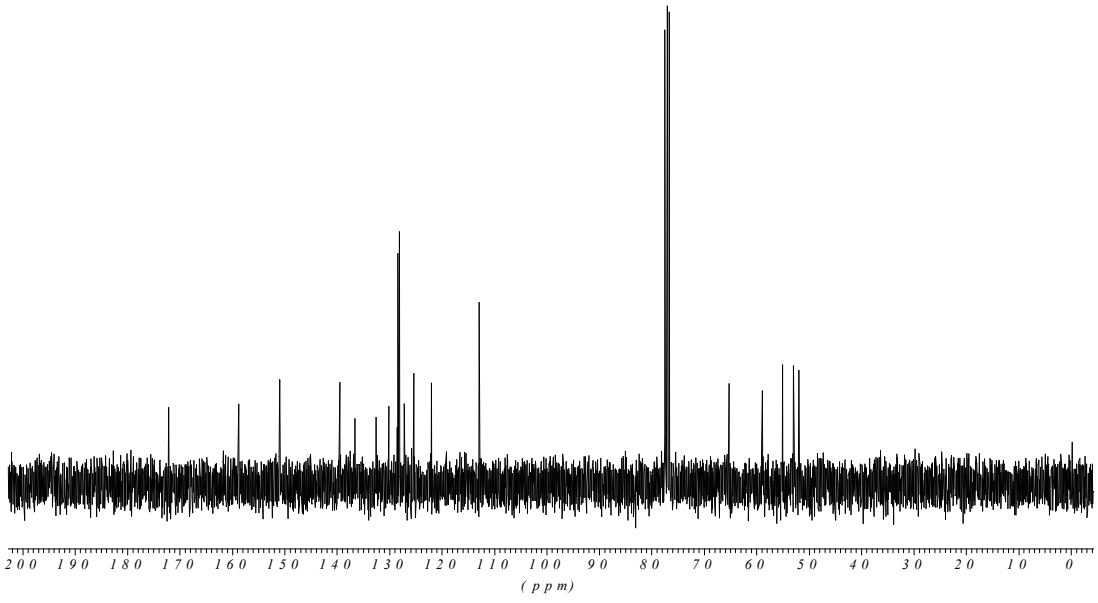
(ppm)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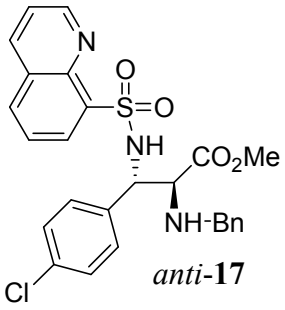
40
30
20
10
0
(ppm)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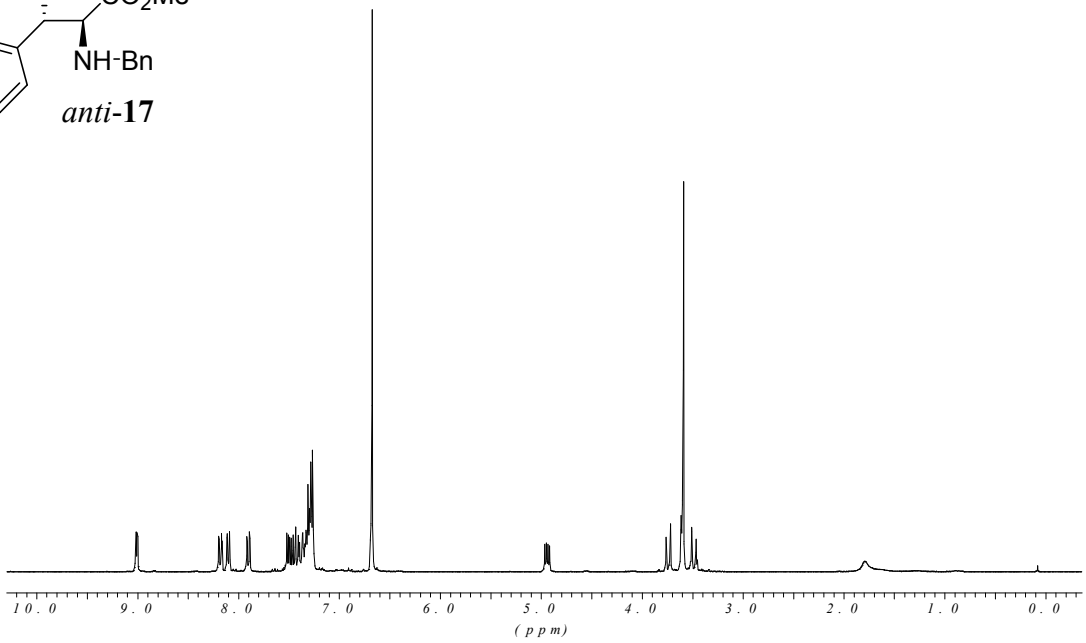
NH
CO2Me
NH-Bn
Cl

anti-**17**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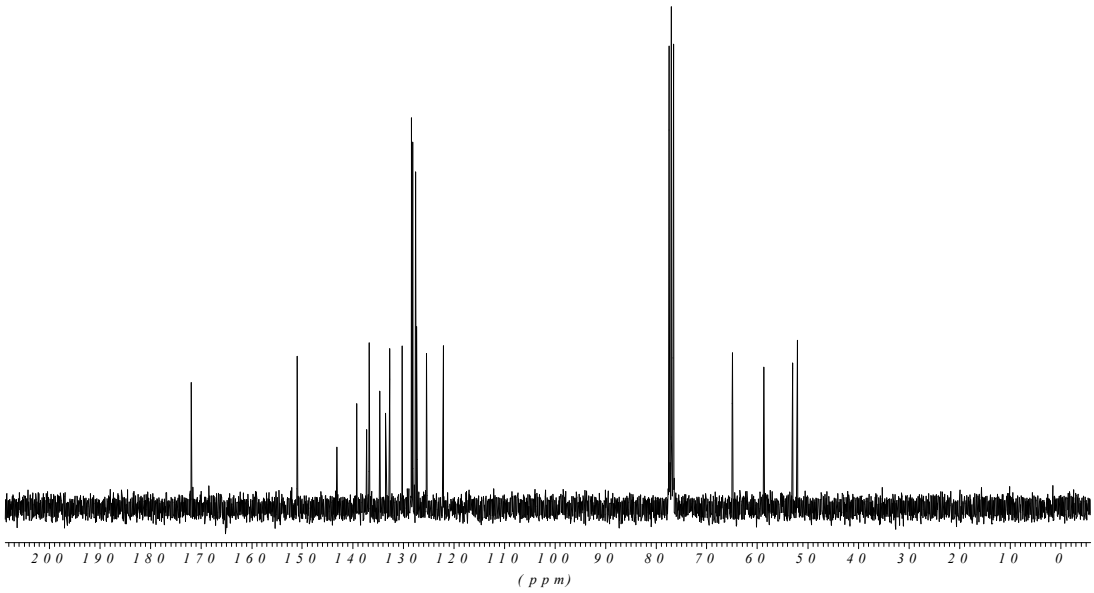
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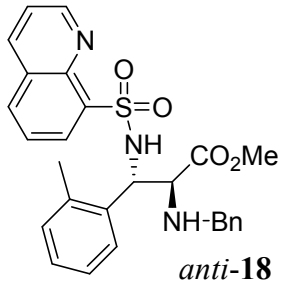
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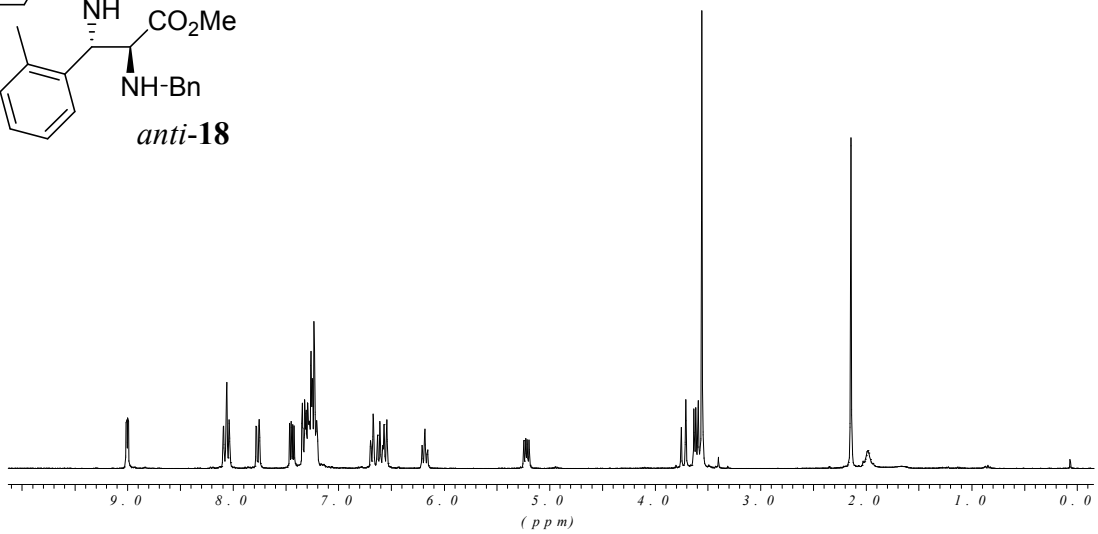
S=O
NH
CO2Me
NH-Bn

anti-**18**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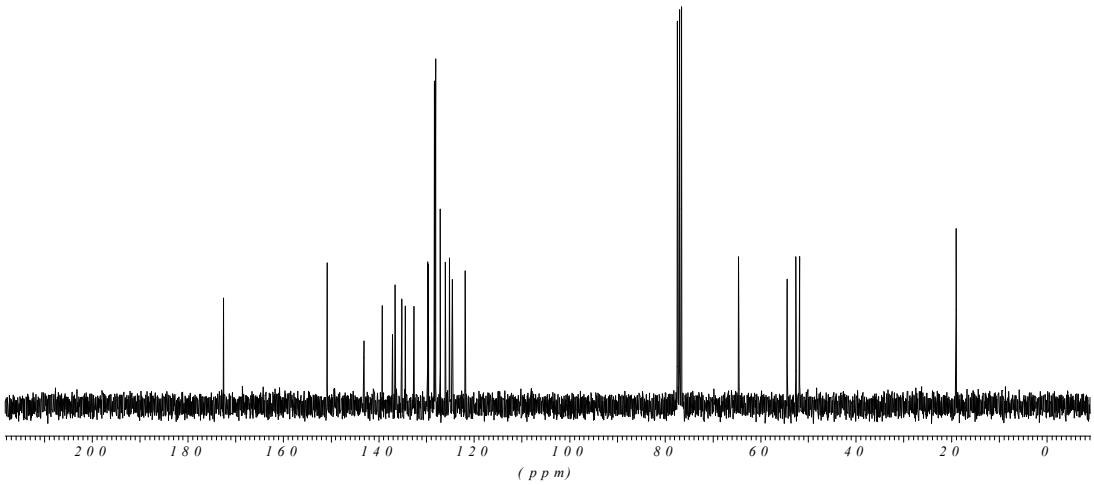
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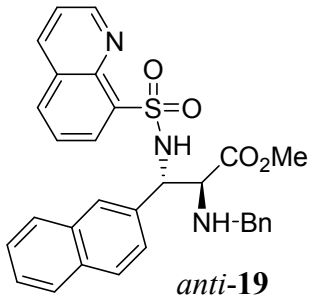
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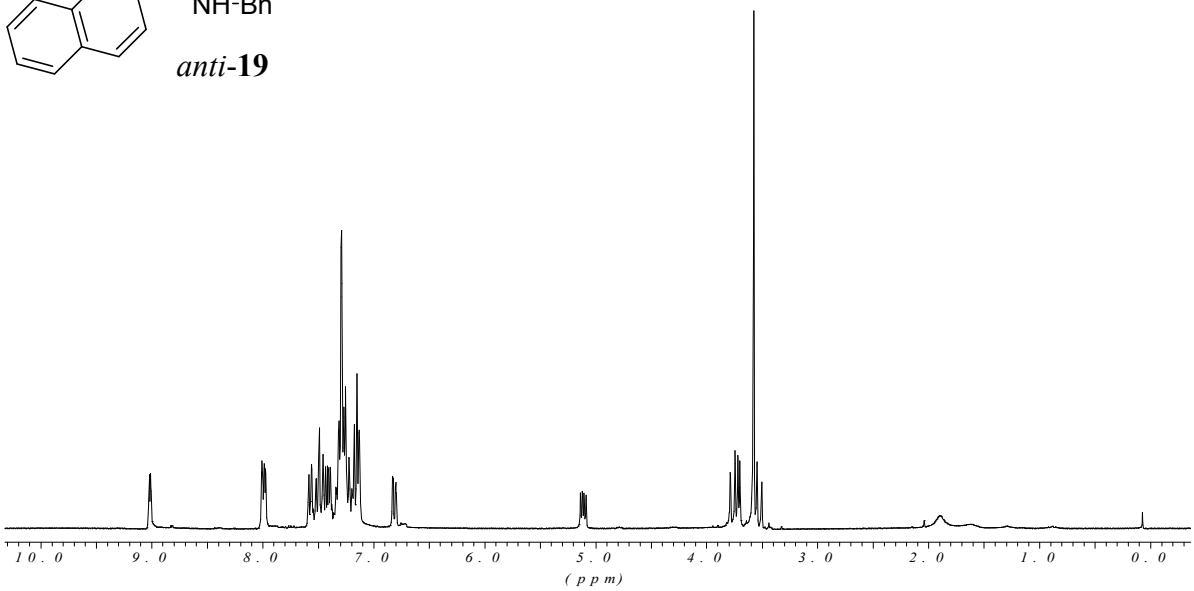
O
S=O
NH
CO2Me
NH-Bn

anti-**19**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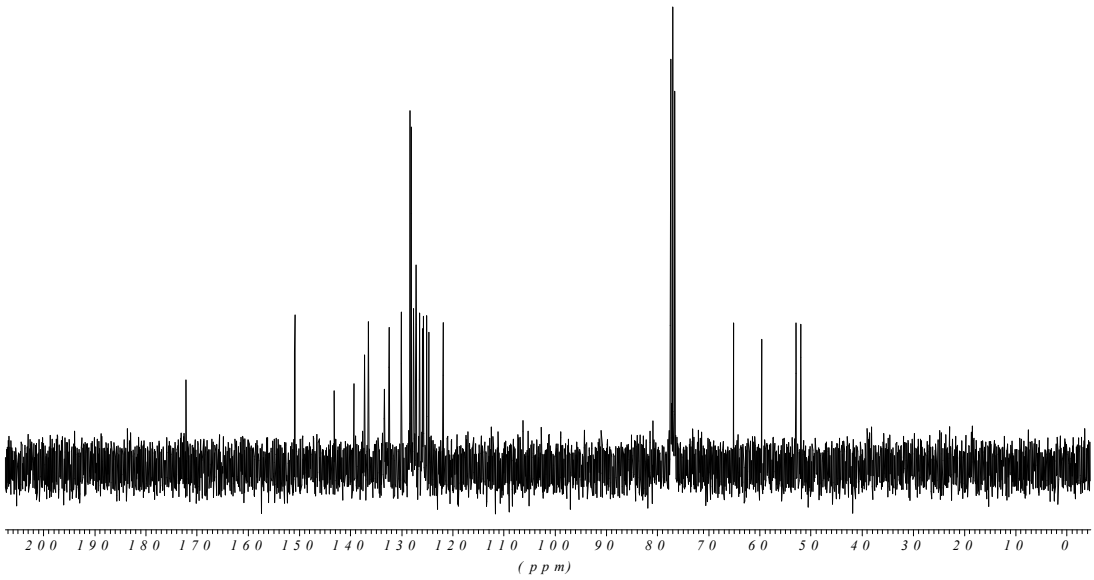
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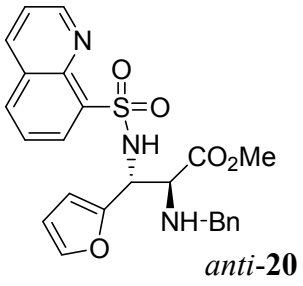
(ppm)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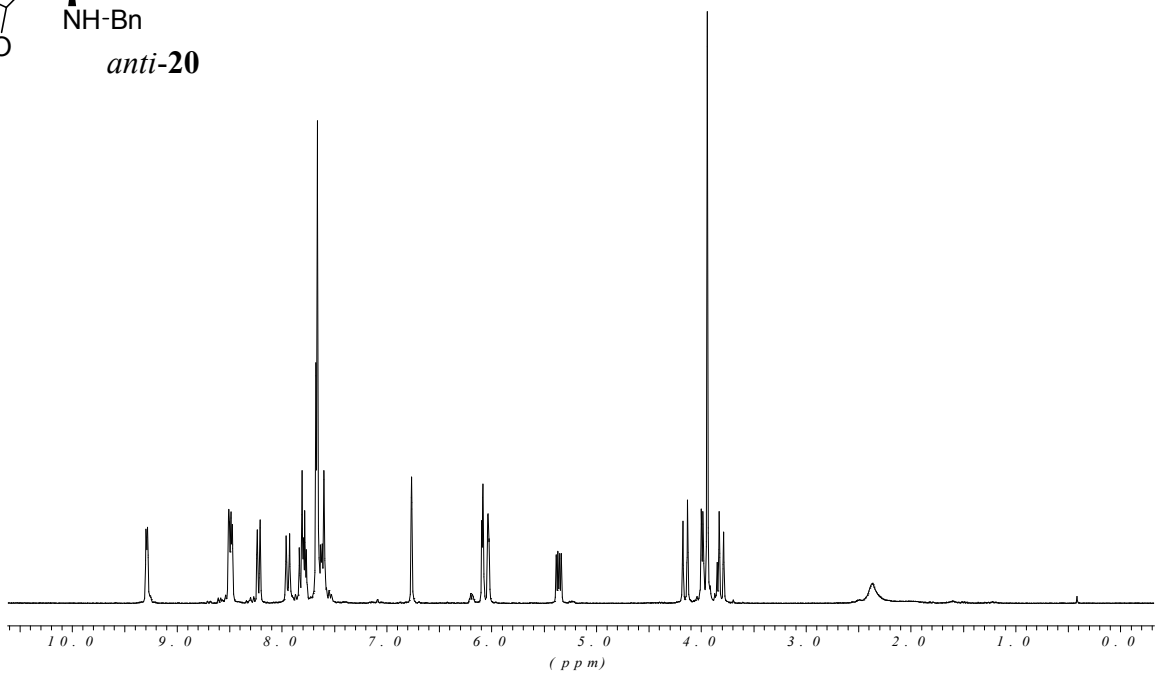
S=O
NH
CO2Me
NH-Bn
O

anti-**20**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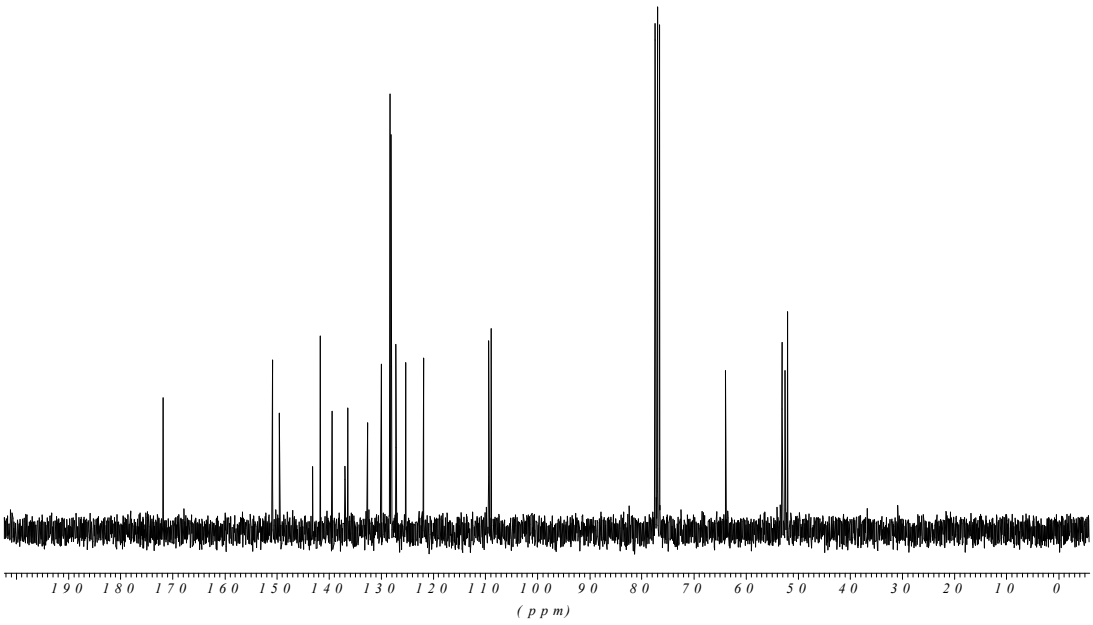
(ppm)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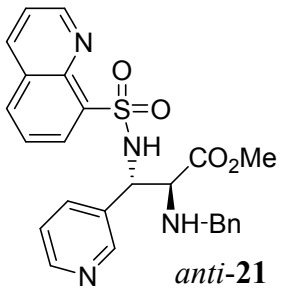
(ppm)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NH
CO2Me
NH-Bn
N

anti-**21**

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1.0
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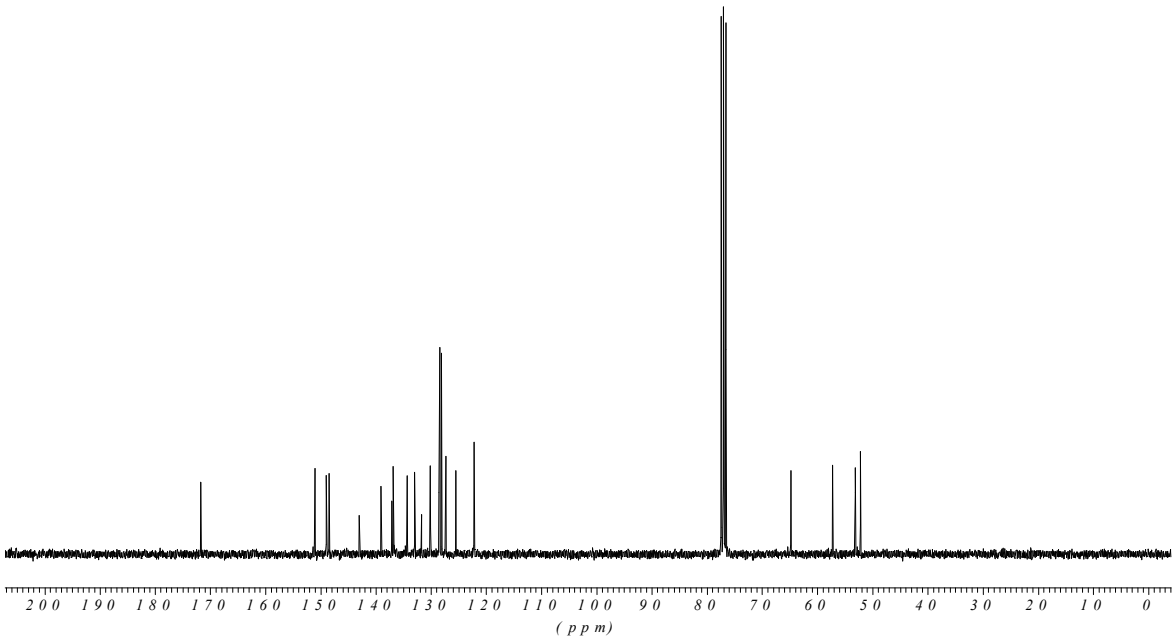
(ppm)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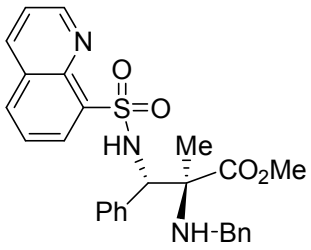
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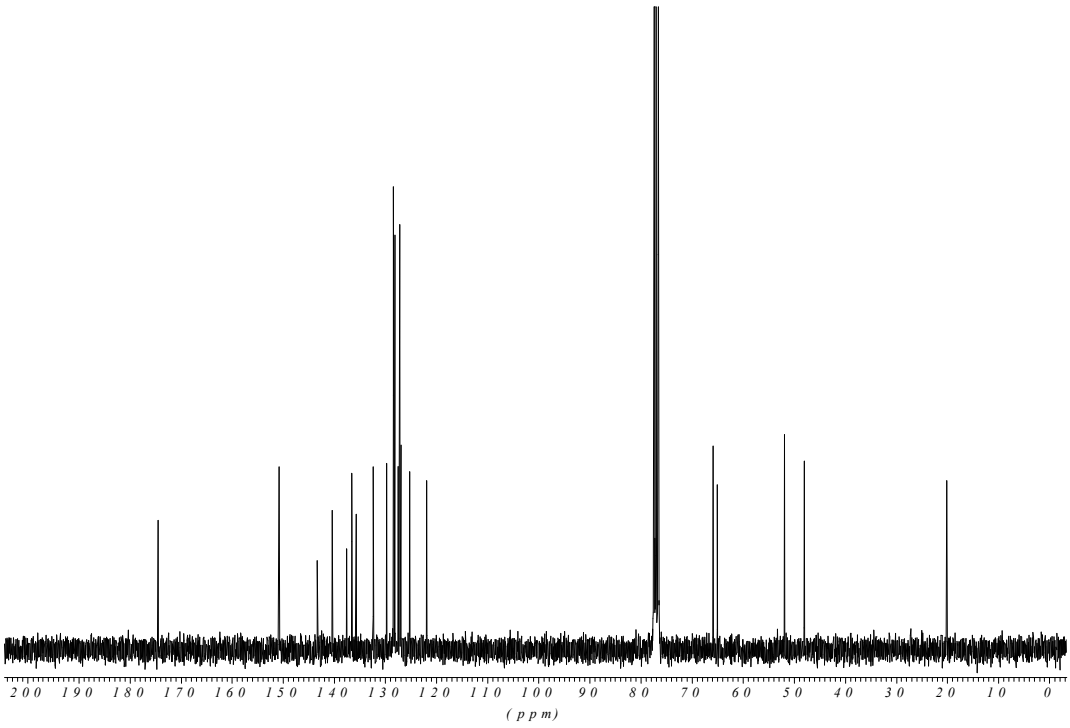
HN
Me
CO2Me
Ph
NH-Bn

anti-**23**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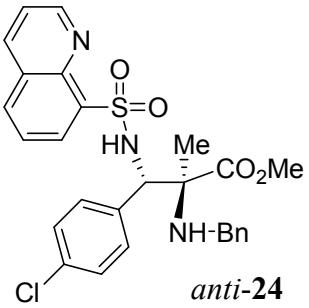
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CO2Me
NH-Bn
Cl

anti-**24**

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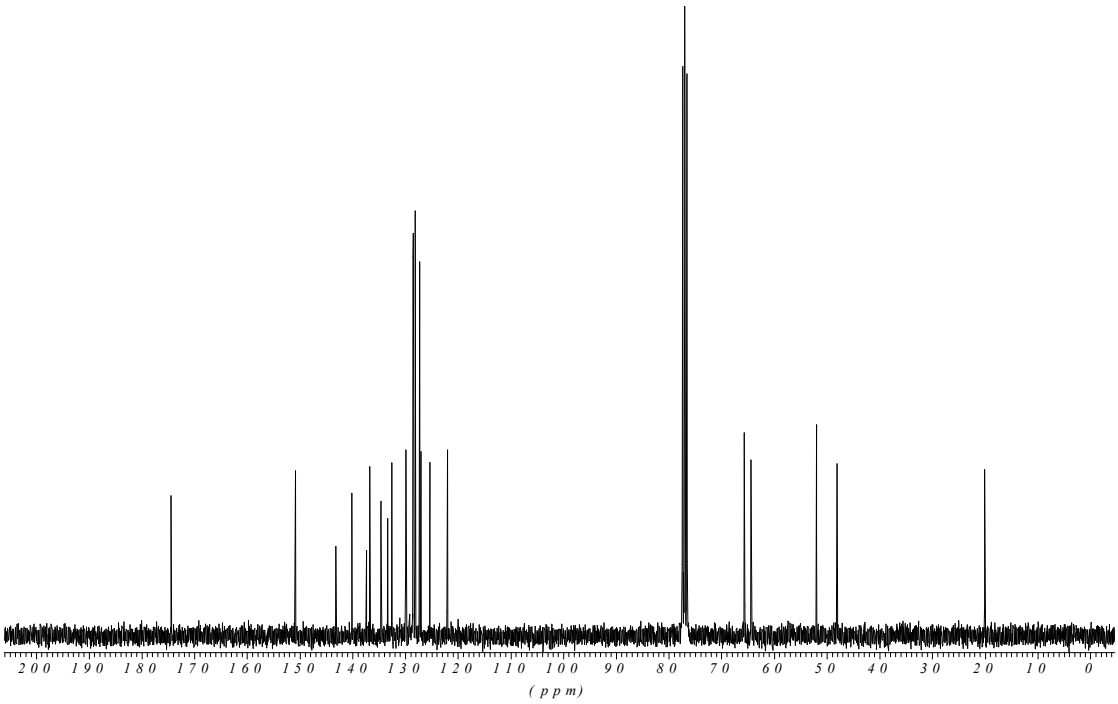
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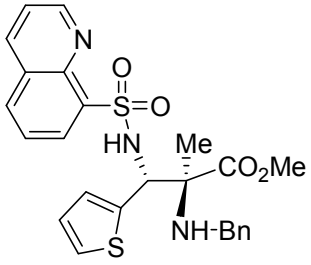
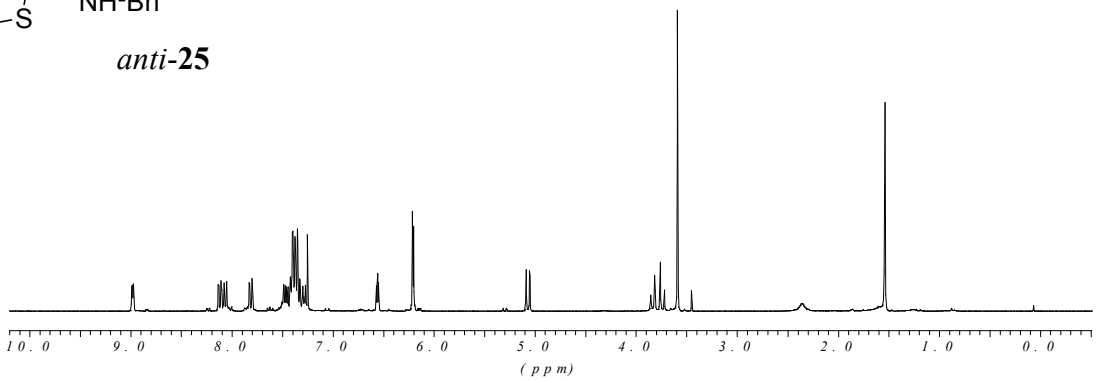
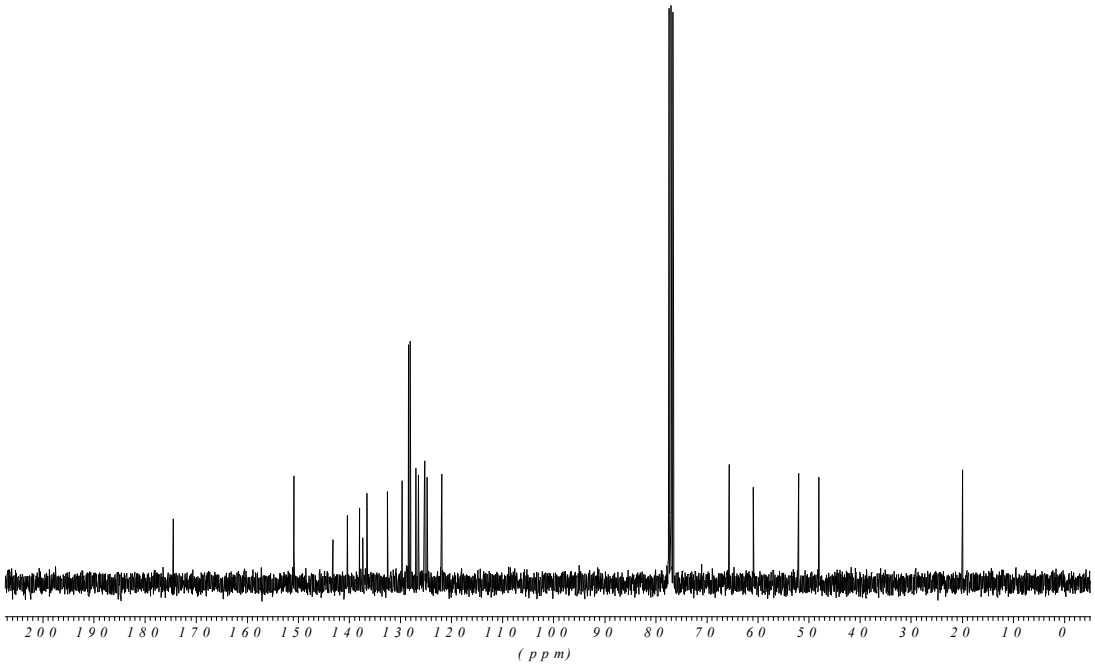
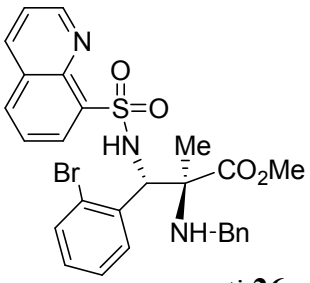
80
70
60
50
40
30
20
10
0
(ppm)


N
O
S=O
HN
Me
CO2Me
NH-Bn
S

anti-**25**

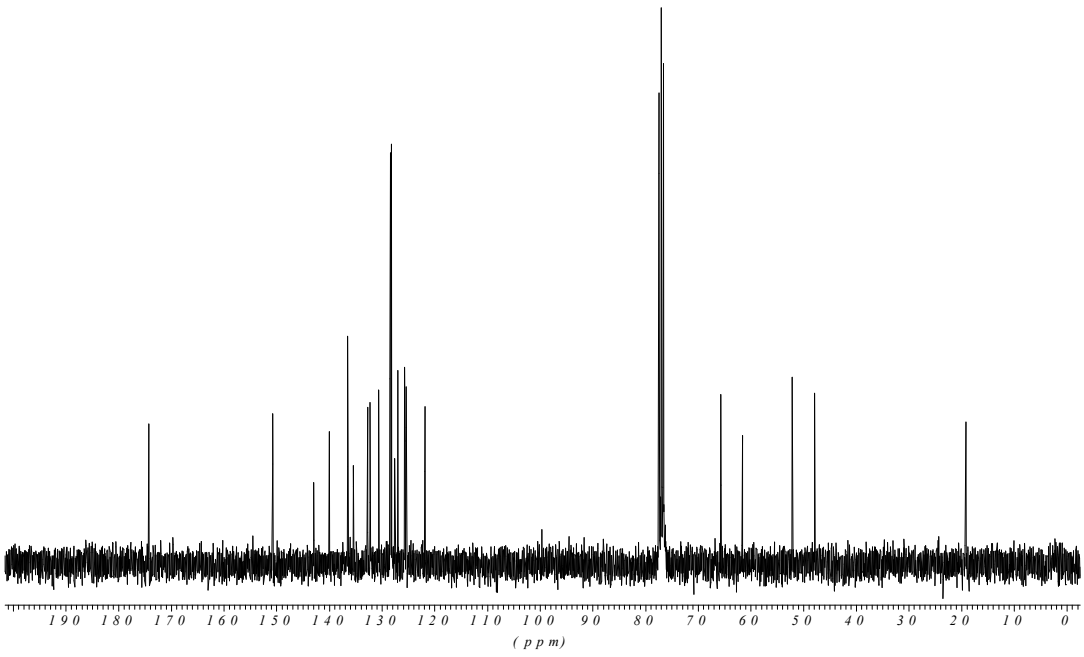

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

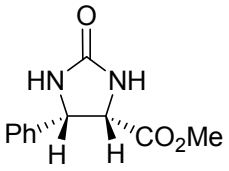

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


N
O
S=O
HN
Me
CO2Me
Br
NH-Bn

anti-**26**

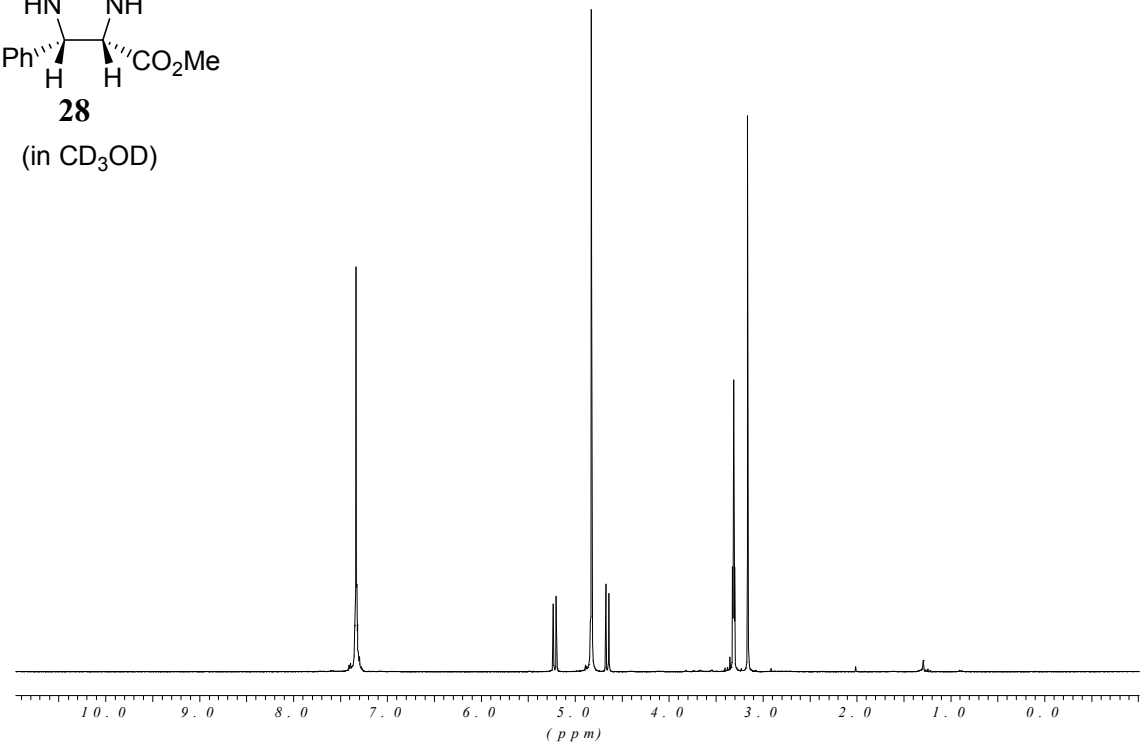
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

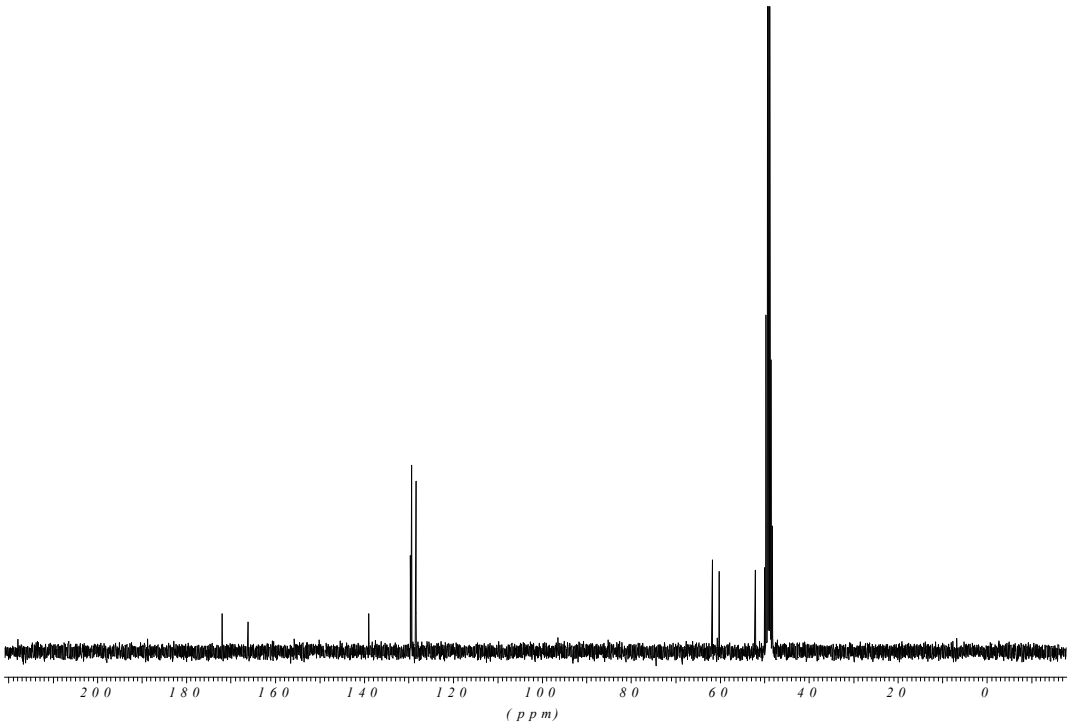

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


O
HN
NH
Ph
H
H
CO2Me

28

(in CD_3OD)


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


200
180
160
140
120
100
80
60
40
20
0
(ppm)