# Supporting Information

## Palladium-Catalyzed Asymmetric Benzylic Substitution of Secondary Benzyl Carbonates with Nitrogen and Oxygen Nucleophiles

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### Instrumentation and Chemicals

$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra were recorded at 400 MHz, 100 MHz, and 376 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by APCI using TOF. GC analysis was carried out using a silicon OV-17 column (2.6 mm i.d. x 1.5 m) or a CBP-1 capillary column (0.5 mm i.d. x 25 m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (Wakosil C-200) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-6AD (pump, SHIMADZU, 3.5 mL/min $CHCl_3$) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line GPC H-2001 (20 x 500 mm, particle size: 15 μm) and H-2002 columns (20 x 500 mm, particle size: 15 μm) (preparative columns, Shodex, $CHCl_3$ eluent) or by LC-20AR (pump, SHIMADZU, 7.5 mL/min EtOAc) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line YMC-GPC T2000 (20 x 600 mm, particle size: 10 μm) (preparative columns, YMC, EtOAc eluent). Unless otherwise noted, materials obtained from commercial suppliers were used as received. MeCN was dried on a Glass Contour Solvent dispensing system (Nikko Hansen & Co., Ltd.) prior to use. DMSO was freshly distilled from $CaH_2$. (*R*)- and (*S*)-BINAP were purchased from Aldrich. [$CpPd(\eta^3\text{–}C_3H_5)$] was prepared according to the literature.[1] Starting carbonates **1**, including (*S*)-**1a**, were synthesized from the corresponding carbinols.[2] All reactions were carried out under nitrogen atmosphere unless otherwise noted.

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1 Tatsuno, Y.; Yoshida, T.; Otsuka, S.; Al-Salem, N.; Shaw, B. L. *Inorg. Synth.* **1990**, *28*, 342.

2 (a) Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A. *J. Org. Chem.* **2008**, *73*, 2879. (b) Tabuchi, S.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2014**, *79*, 5401. (c) Tabuchi, S.; Hirano, K.; Miura, M. *Chem.–Eur. J.* **2015**, *21*, 16823.

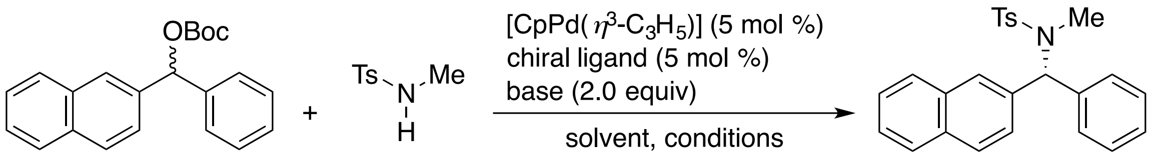
**Experimental Procedures**

Synthesis of (*R*)-**3aa** (0.25 mmol scale; Table 1, entry 1): In a glovebox filled with nitrogen (*R*)-BINAP (7.8 mg, 0.0125 mmol), $K_2CO_3$ (69.1 mg, 0.5 mmol), and CpPd($\eta^3$-$C_3H_5$) (2.7 mg, 0.0125 mmol) were placed in a 20 mL two neck flask. The flask was sealed with a septum and taken out of the glovebox. MeCN (2.0 mL) was added, and the suspension was stirred for 10 min. A solution of *tert*-butyl (2-naphthyl (phenyl) methyl) carbonate (**1a**; 83.6 mg, 0.25 mmol) and *N*-methyl-*N*-tosylamide (**2a**; 55.6 mg, 0.30 mmol) in MeCN (1.0 mL) was then added to the flask, and the suspension was stirred for 6 h at 60 °C. The resulting mixture was quenched with water and then extracted three times with ethyl acetate. The combined organic layer was dried over sodium sulfate. Concentration in vacuo and subsequent purification by column chromatography on silica gel with hexane/ethyl acetate (1/10 to 1/5 v/v) as an eluent gave (*R*)-*N*,4-dimethyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide [(*R*)-**3aa**; 79.3 mg, 0.20 mmol, 92:8 er] in 80% yield: enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic sample (Chiralcel OD-H column, 95/5 hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 24.7 min, minor isomer: $t_R$ = 29.2 min).

Synthesis of (*R*)-**3ia** (1.0 mmol scale; Scheme 3): In a glovebox filled with nitrogen (*R*)-BINAP (31.1 mg, 0.05 mmol), $K_2CO_3$ (276.4 mg, 2.0 mmol), *tert*-butyl (phenanthren-9-yl (phenyl) methyl) carbonate (384.5 mg, 1.0 mmol), and CpPd($\eta^3$-$C_3H_5$) (10.6 mg, 0.05 mmol) were placed in a 50 mL two neck flask. The flask was sealed with a septum and taken out of the glovebox. MeCN (10 mL) was added, and the suspension was stirred for 10 min. A solution of *N*-methyl-*N*-tosylamide (**2a**; 22.3 mg, 1.20 mmol) in MeCN (2.0 mL) was then added to the flask, and the suspension was stirred for 6 h at 60 °C. The resulting mixture was quenched with water and then extracted three times with ethyl acetate. The combined organic layer was dried over sodium sulfate. Concentration in vacuo and subsequent purification by column chromatography on silica gel with hexane/ethyl acetate (1/5 v/v) as an eluent gave (*R*)-*N*,4-dimethyl-*N*-(phenanthren-9-yl(phenyl)methyl)benzenesulfonamide [(*R*)-**3ia**; 421.7 mg, 0.92 mmol, 98:2 er] in 92% yield: enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic sample (Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 27.5 min, minor isomer: $t_R$ = 30.6 min).

**Detailed Optimization Studies**

***Table S1. Optimization Studies***[a]

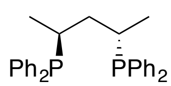



**1a** **2a** (1.2 equiv) **3aa**

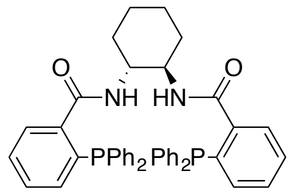
| entry | chiral ligand | base | solvent | conditions | yield (%),[b] er[c] |
|---|---|---|---|---|---|
| 1 | (*S*,*S*)-BDPP | none | MeCN | 80 °C, 3 h | 46, 66:34 |
| 2 | (*R*,*R*)-DPPBA | none | MeCN | 80 °C, 3 h | 0, n.d. |
| 3 | ***(R)-BINAP*** | ***none*** | ***MeCN*** | ***80 °C, 3 h*** | ***77, 86:14*** |
| 4 | (*R*)-Xyl-BINAP | none | MeCN | 80 °C, 3 h | 74, 74:26 |
| 5 | (*R*)-DTBM-BINAP | none | MeCN | 80 °C, 3 h | 60, 72:28 |
| 6 | ***(R)-$H_8$-BINAP*** | ***none*** | ***MeCN*** | ***80 °C, 3 h*** | ***70, 87:13*** |
| 7 | (*R*)-SEGPHOS | none | MeCN | 80 °C, 3 h | trace, n.d. |
| 8 | (*R*)-DM-SEGPHOS | none | MeCN | 80 °C, 3 h | trace, n.d. |
| 9 | (*R*)-DTBM-SEGPHOS | none | MeCN | 80 °C, 3 h | 48, 84:16 |
| 10 | (*R*)-MeO-BIPHEP | none | MeCN | 80 °C, 3 h | 61, 79:21 |
| 11 | (*R*)-DTBM-MeO-BIPHEP | none | MeCN | 80 °C, 3 h | 68, 56:44 |
| 12 | (*R*)-BINAP | none | MeCN | 60 °C, 6 h | 45, 94:6 |
| 13 | (*R*)-BINAP | $Na_2CO_3$ | MeCN | 60 °C, 6 h | 59, 91:9 |
| ***14*** | ***(R)-BINAP*** | ***$K_2CO_3$*** | ***MeCN*** | ***60 °C, 6 h*** | ***79, 92:8*** |
| 15 | (*R*)-BINAP | $Cs_2CO_3$ | MeCN | 60 °C, 6 h | 65, 90:10 |
| 16 | (*R*)-BINAP | NaOAc | MeCN | 60 °C, 6 h | 50, 90:10 |
| 17 | (*R*)-BINAP | KOAc | MeCN | 60 °C, 6 h | 34, 92:8 |
| 18 | (*R*)-BINAP | $Et_3N$ | MeCN | 60 °C, 6 h | 39, 93:7 |
| 19 | (*R*)-BINAP | *i*-$Pr_2NEt$ | MeCN | 60 °C, 6 h | 5 (NMR), n.d. |
| 20 | (*R*)-BINAP | $K_2CO_3$ | DMSO | 60 °C, 6 h | 34, 83:17 |
| 21 | (*R*)-BINAP | none | DMSO | 80 °C, 3 h | 37, 87:13 |
| 22 | (*R*)-$H_8$-BINAP | $K_2CO_3$ | MeCN | 60 °C, 6 h | 17, 93:7 |
| 23 | (*R*)-BINAP | $K_2CO_3$ | MeCN | 50 °C, 24 h | 52, 80:20 |

[a] Reaction conditions: [CpPd($\eta^3$-$C_3H_5$)] (0.013 mmol), ligand (0.013 mmol), base (0.50 mmol), **1a** (0.25 mmol), **2a** (0.30 mmol), MeCN (3.0 mL), $N_2$. [b] Isolated yields are shown. [c] The enantiomeric ratios (er) are determined by HPLC analysis on a chiral stationary phase. n.d. = not

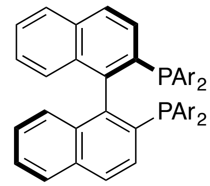
determined.



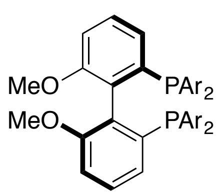
(*S,S*)-BDPP



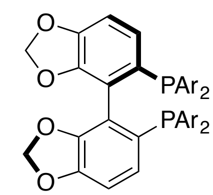
(*R,R*)-DPPBA



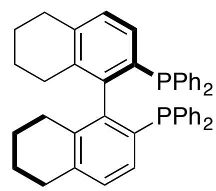
Ar = Ph: (*R*)-BINAP
Ar = 3,5-$Me_2C_6H_3$: (*R*)-Xyl-BINAP
Ar = 3,5-(*t*-Bu)$_2$-4-$MeOC_6H_2$: (*R*)-DTBM-BINAP



Ar = Ph: (*R*)-MeO-BIPHEP
Ar = 3,5-(*t*-Bu)$_2$-4-$MeOC_6H_2$: (*R*)-DTBM-MeO-BIPHEP



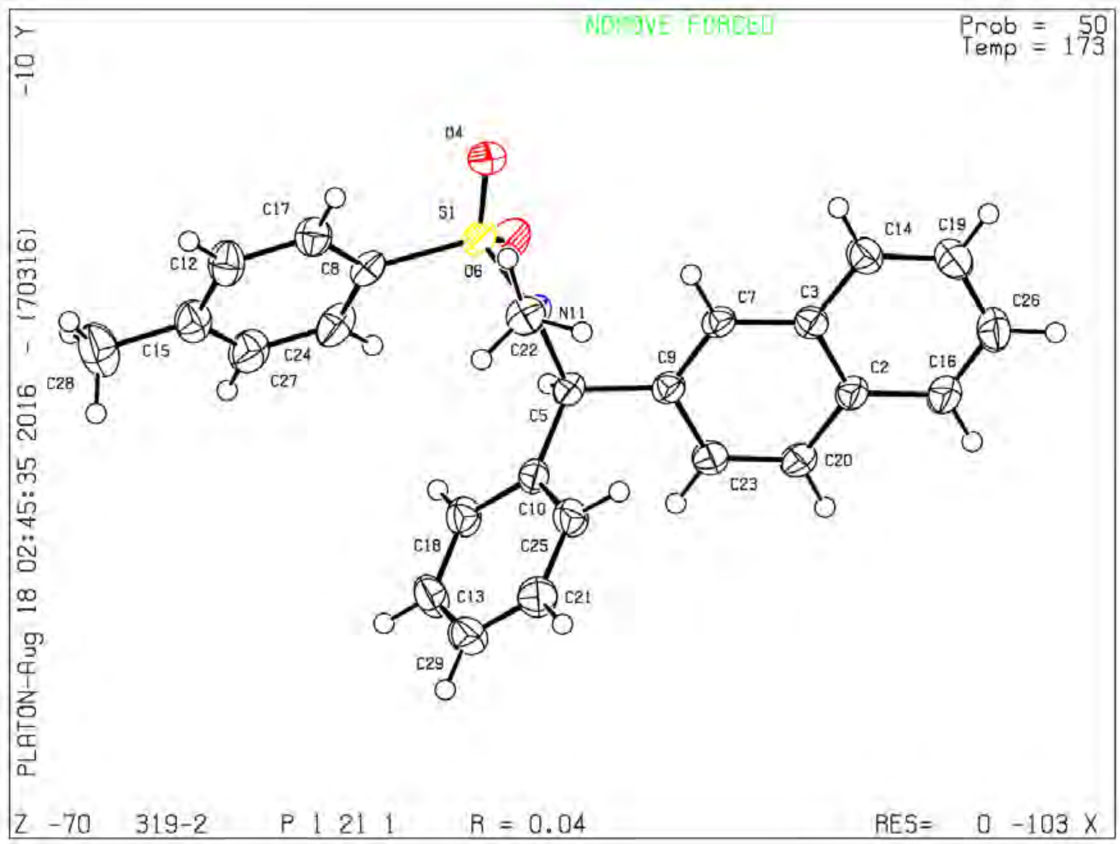
Ar = Ph: (*R*)-SEGPHOS
Ar = 3,5-$Me_2C_6H_3$: (*R*)-DM-SEGPHOS
Ar = 3,5-(*t*-Bu)$_2$-4-$MeOC_6H_2$: (*R*)-DTBM-SEGPHOS

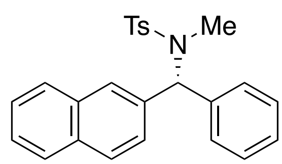


(*R*)-$H_8$-BINAP

## X-Ray Analysis

The X-ray quality crystals of (*R*)-**3aa** were grown from heptane/ethyl acetate.




(*R*)-**3aa**, 92:8 er

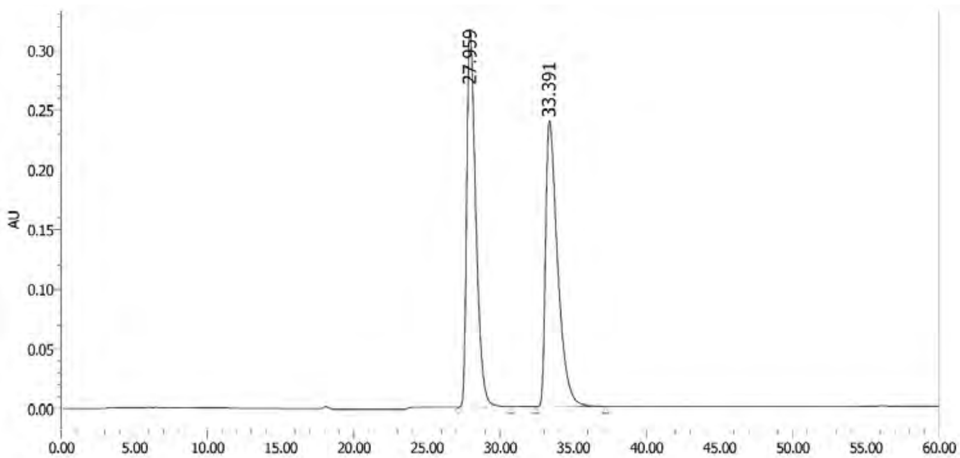
$[\alpha]_D^{20}$ –7.76 (*c* 0.50, $CHCl_3$)

**Figure S1.** ORTEP Drawing (CCDC 1536820) and Specific Rotation of (*R*)-**3aa**

**Chiral HPLC Charts of Enantioenriched Products**

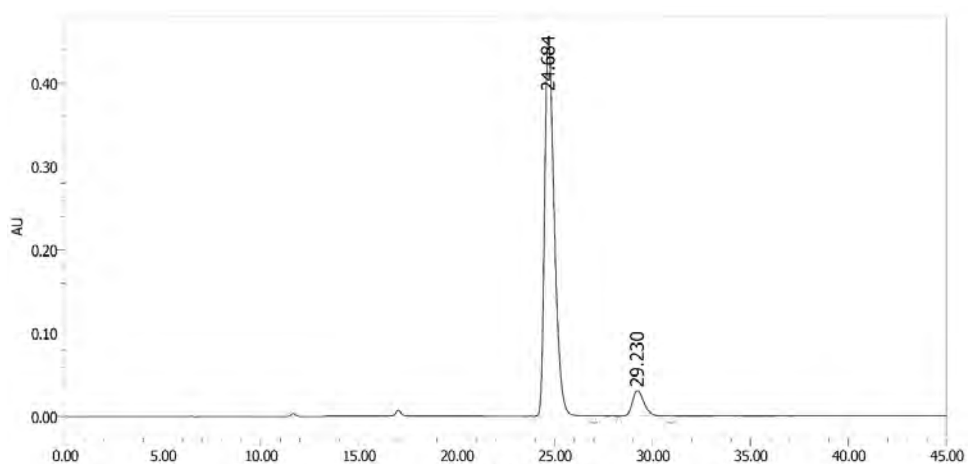
**3aa**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 95/5 *n*-hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 24.7 min, minor isomer: $t_R$ = 29.2 min, UV detection at 250 nm, 30 $^{o}$C).

*rac*-**3aa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 27.959 | 13714526 | 50.12 |
| 2 | 33.391 | 13648943 | 49.88 |

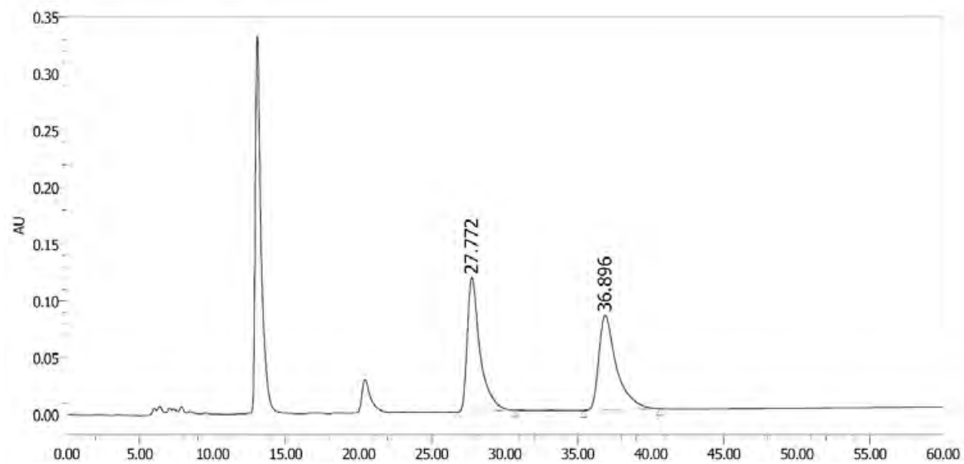
(*R*)-**3aa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 24.684 | 15551430 | 92.41 |
| 2 | 29.230 | 1276979 | 7.59 |

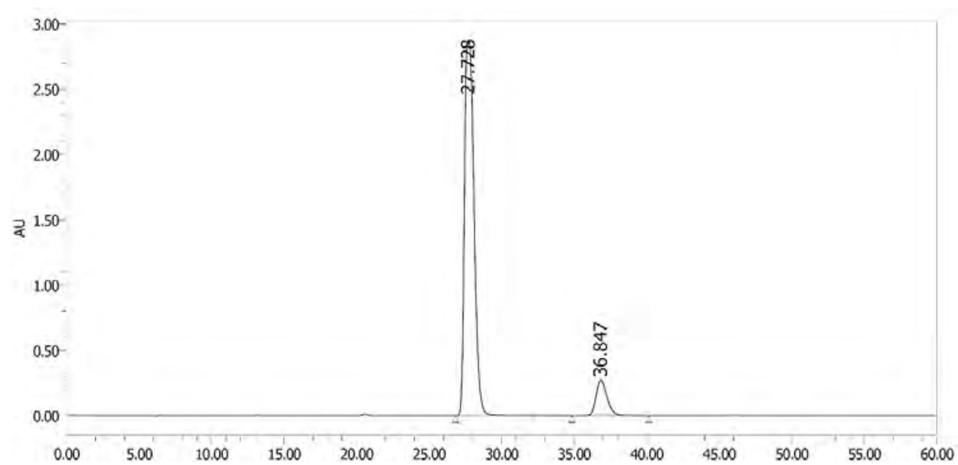
**3ab**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 95/5 *n*-hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 27.7 min, minor isomer: $t_R$ = 36.8 min, UV detection at 220 nm, 30 $^oC$).

*rac*-**3ab**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 27.772 | 7134284 | 50.45 |
| 2 | 36.896 | 7006028 | 49.55 |

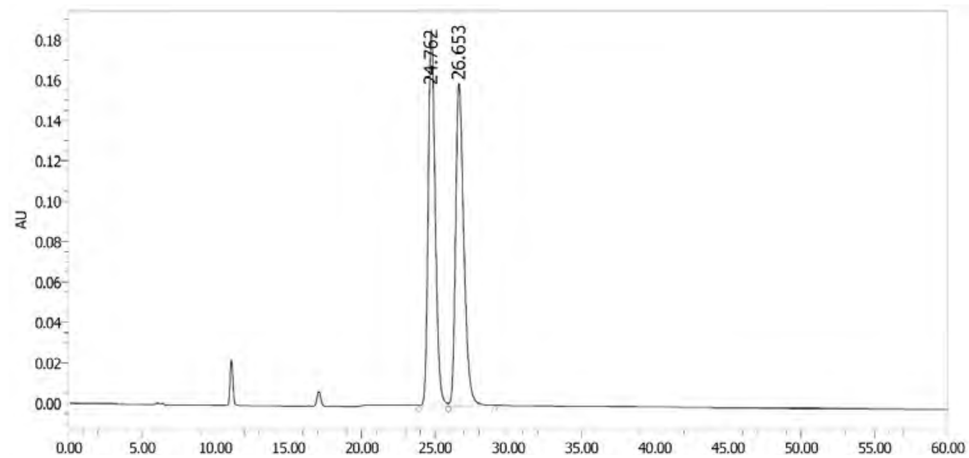
(*R*)-**3ab**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 27.728 | 131073094 | 90.08 |
| 2 | 36.847 | 14439758 | 9.92 |

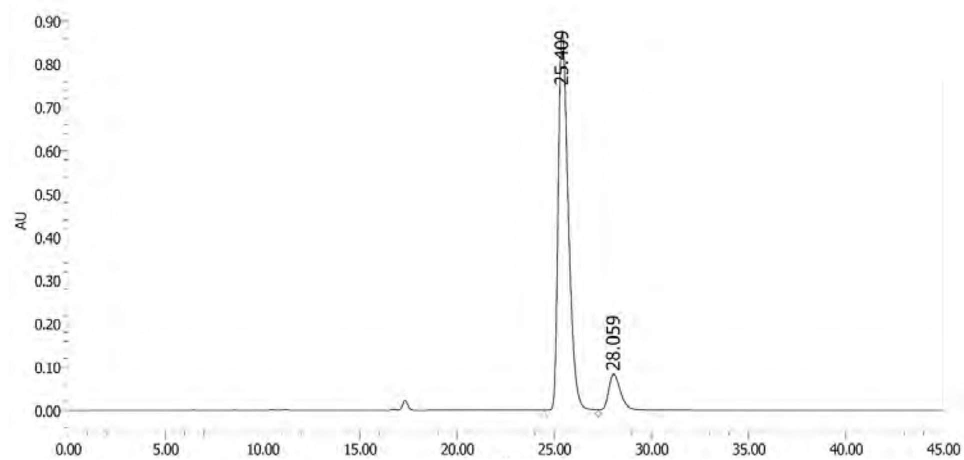
**3ac**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 95/5 *n*-hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 25.4 min, minor isomer: $t_R$ = 28.1 min, UV detection at 250 nm, 30 $^o$C).

*rac*-**3ac**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 24.762 | 6201397 | 49.99 |
| 2 | 26.653 | 6204092 | 50.01 |

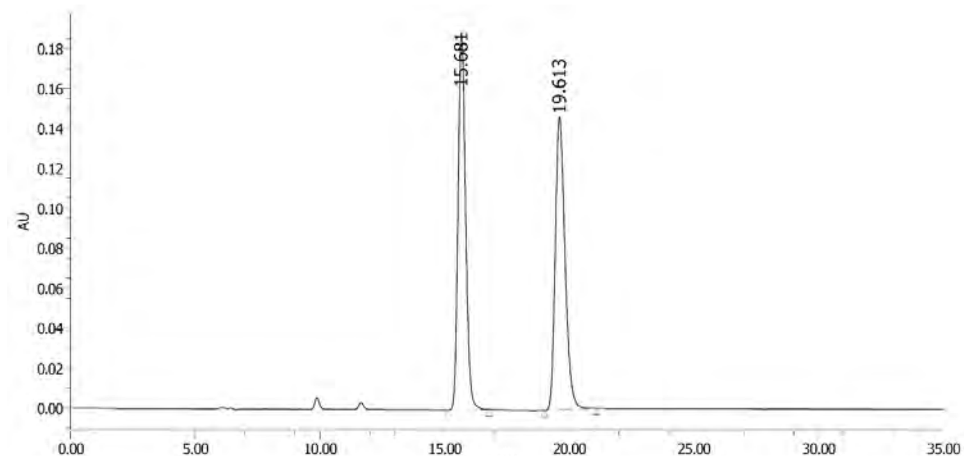
(*R*)-**3ac**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 25.409 | 31479911 | 89.89 |
| 2 | 28.059 | 3539344 | 10.11 |

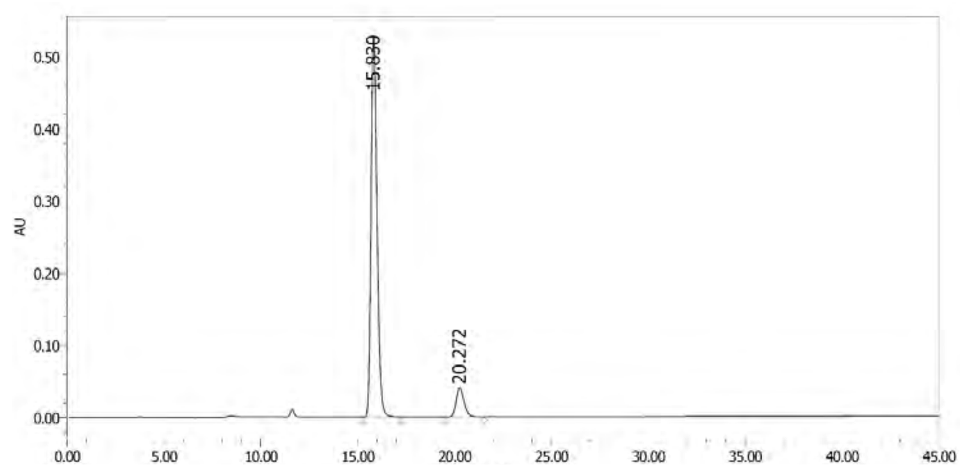
**3ad**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 95/5 *n*-hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 15.8 min, minor isomer: $t_R$ = 20.3 min, UV detection at 250 nm, 30 °C).

*rac*-**3ad**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 15.681 | 3952396 | 49.92 |
| 2 | 19.613 | 3965518 | 50.08 |

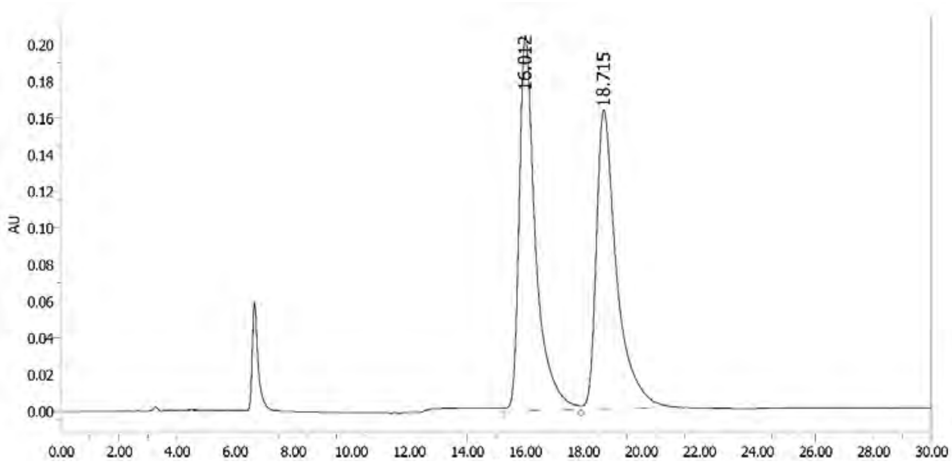
(*R*)-**3ad**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 15.83 | 11383054 | 90.82 |
| 2 | 20.272 | 1150531 | 9.18 |

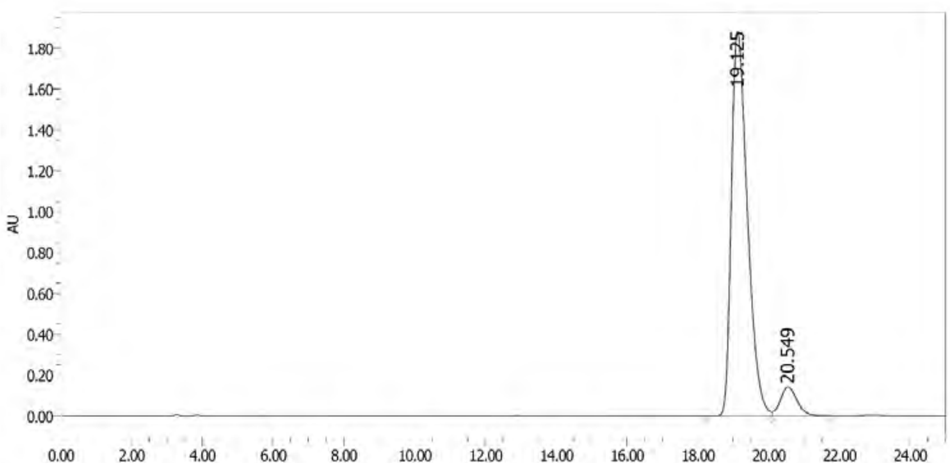
**3ae:** The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 97/3 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 19.1 min, minor isomer: $t_R$ = 20.5 min, UV detection at 210 nm, 30 $^oC$).

*rac*-**3ae**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 16.012 | 8074177 | 50.34 |
| 2 | 18.715 | 7966127 | 49.66 |

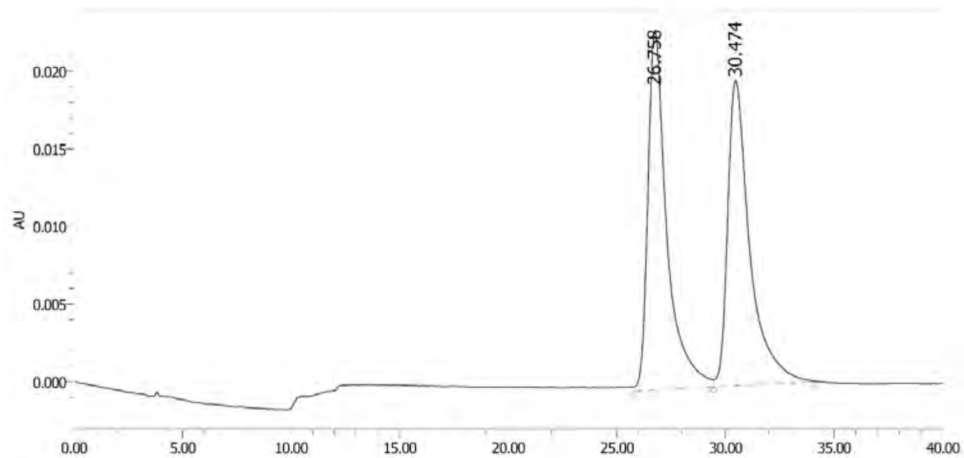
(*R*)-**3ae**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 19.125 | 59148445 | 92.78 |
| 2 | 20.549 | 4600649 | 7.22 |

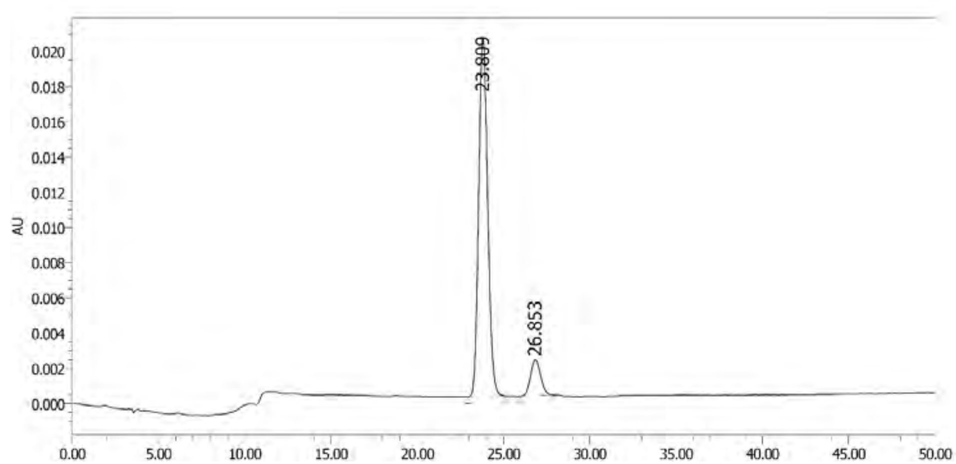
**3af**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 97/3 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 23.8 min, minor isomer: $t_R$ = 26.9 min, UV detection at 270 nm, 30 °C).

*rac*-**3af**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 26.758 | 1413775 | 50.36 |
| 2 | 30.474 | 1393542 | 49.64 |

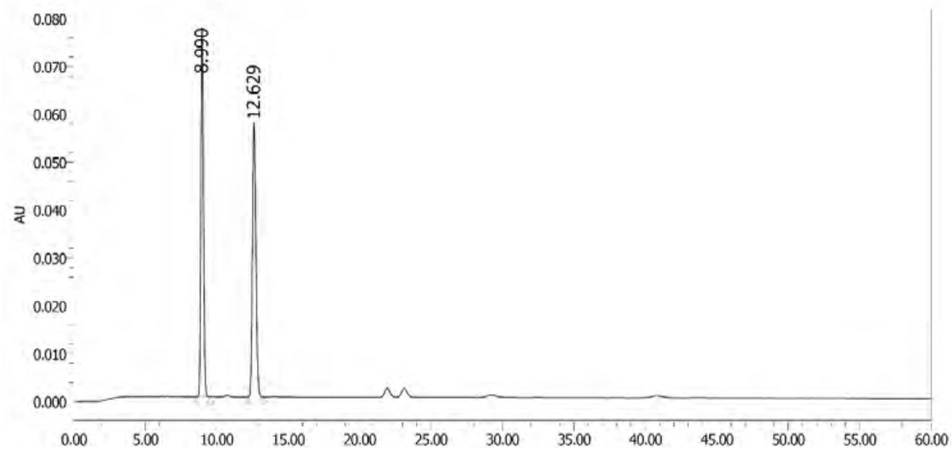
(*R*)-**3af**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 23.809 | 741307 | 89.96 |
| 2 | 26.853 | 82759 | 10.01 |

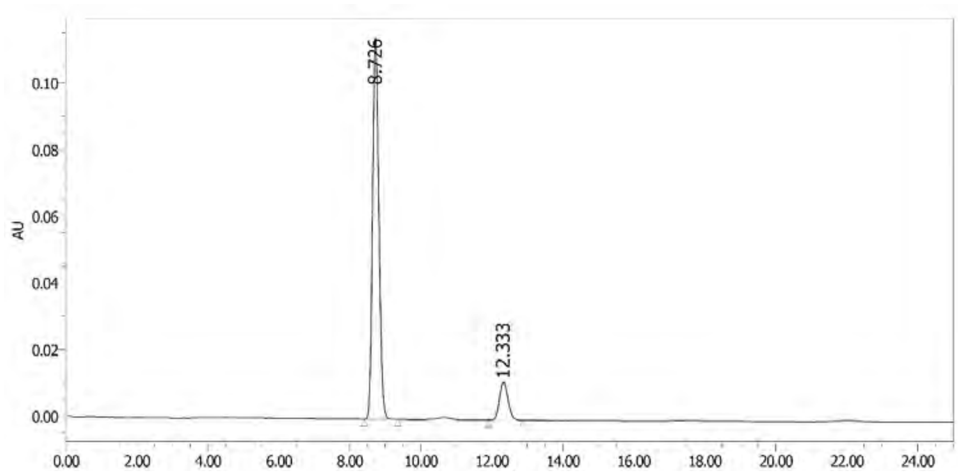
The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 8.7 min, minor isomer: $t_R$ = 12.3 min, UV detection at 260 nm, 30 $^oC$).

*rac*-**3ag**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 8.990 | 962890 | 49.84 |
| 2 | 12.629 | 968909 | 50.16 |

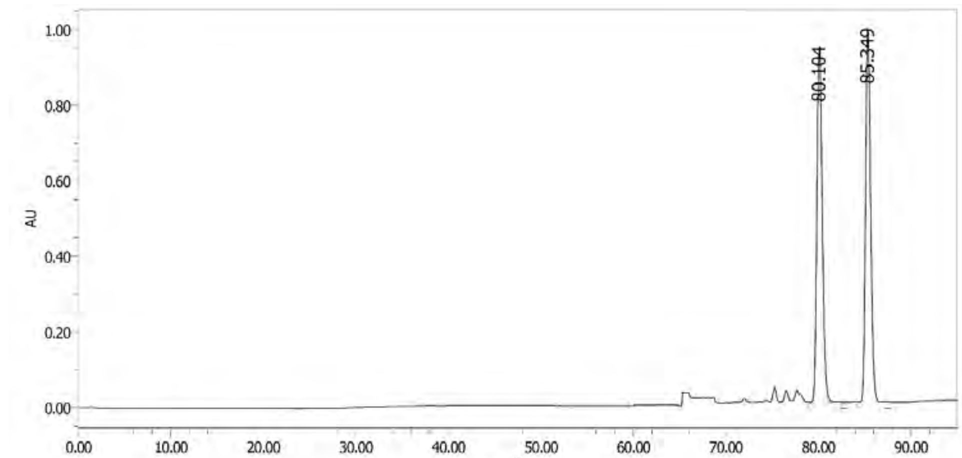
(*R*)-**3ag**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 8.726 | 1415635 | 88.17 |
| 2 | 12.333 | 190016 | 11.83 |

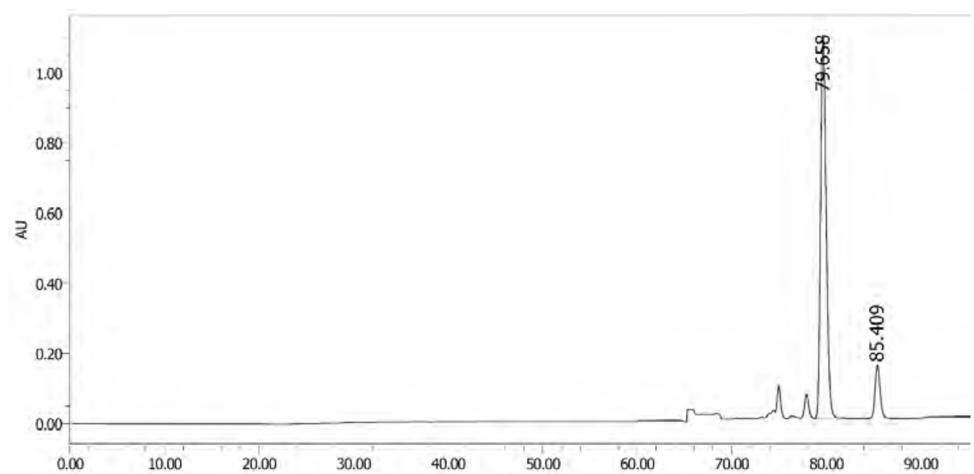
**3ba**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 99.5/0.5 *n*-hexane/2-propanol, 2.5 mL/min (60 min) then 90/10 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 79.7 min, minor isomer: $t_R$ = 85.4 min, UV detection at 228 nm, 30 $^{o}$C).

*rac*-**3ba**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 80.104 | 38236813 | 50.46 |
| 2 | 85.439 | 37543409 | 49.54 |

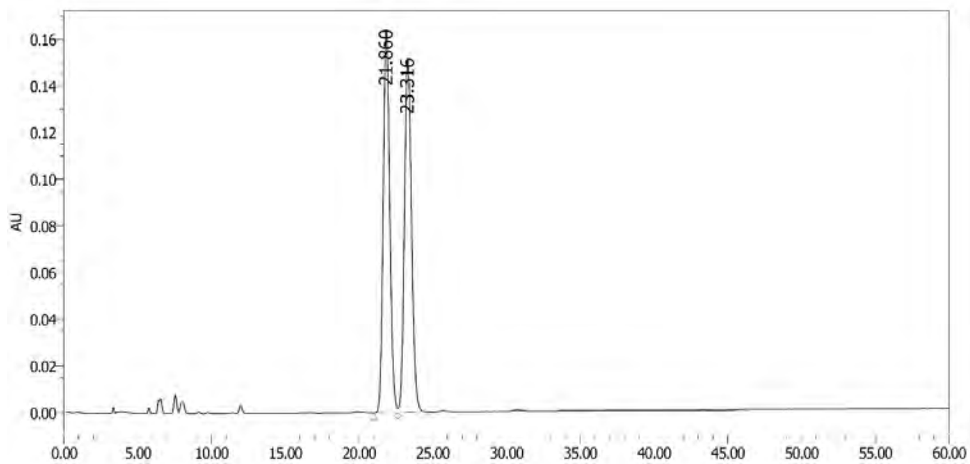
(*R*)-**3ba**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 79.658 | 45175852 | 89.07 |
| 2 | 85.409 | 5543172 | 10.93 |

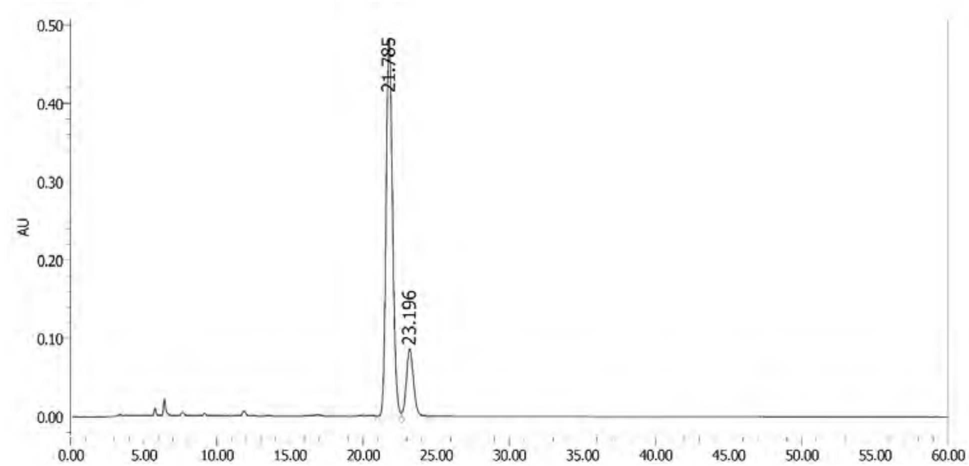
**3ca:** The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 21.8 min, minor isomer: $t_R$ = 23.2 min, UV detection at 220 nm, 30 $^{o}$C).

*rac*-**3ca**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 21.860 | 5048538 | 49.93 |
| 2 | 23.316 | 5063031 | 50.07 |

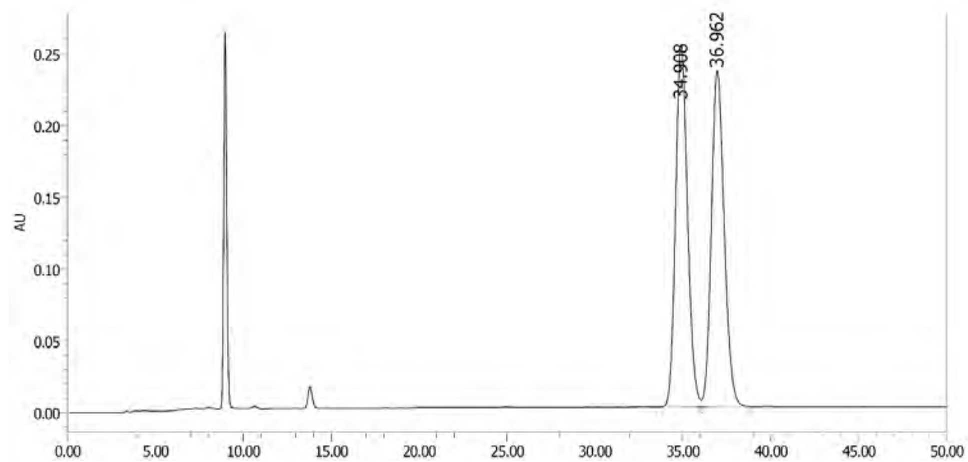
(*R*)-**3ca**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 21.785 | 1413377 | 83.90 |
| 2 | 23.196 | 2841805 | 16.10 |

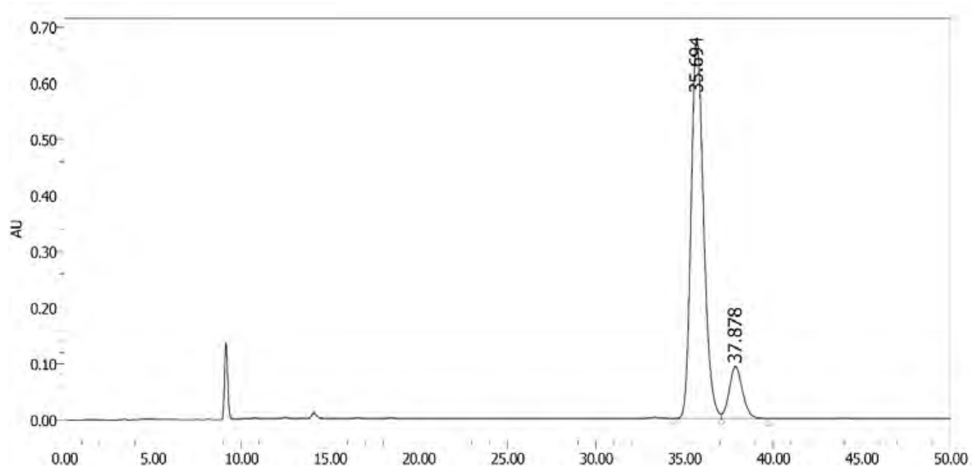
**3da:** The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 35.7 min, minor isomer: $t_R$ = 37.9 min, UV detection at 230 nm, 30 °C).

*rac*-**3da**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 34.908 | 11936773 | 50.12 |
| 2 | 36.962 | 11877382 | 49.88 |

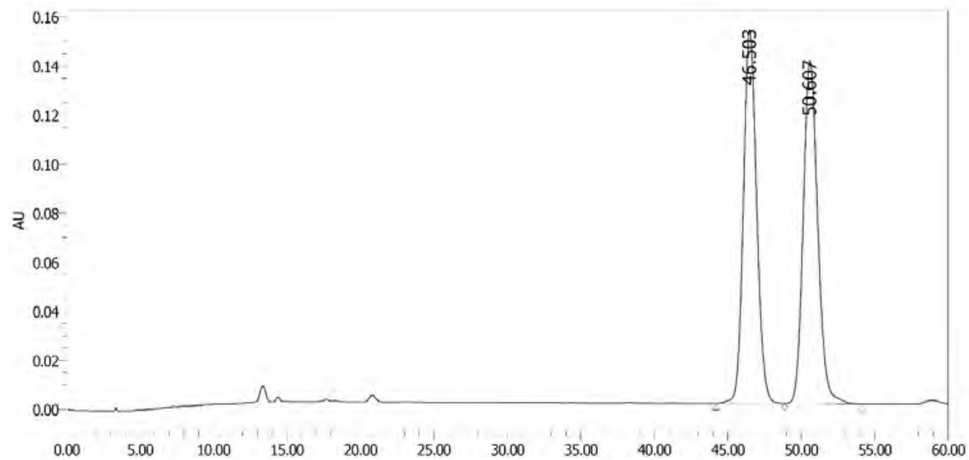
(*R*)-**3da**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 35.694 | 33184230 | 87.32 |
| 2 | 37.878 | 4820616 | 12.68 |

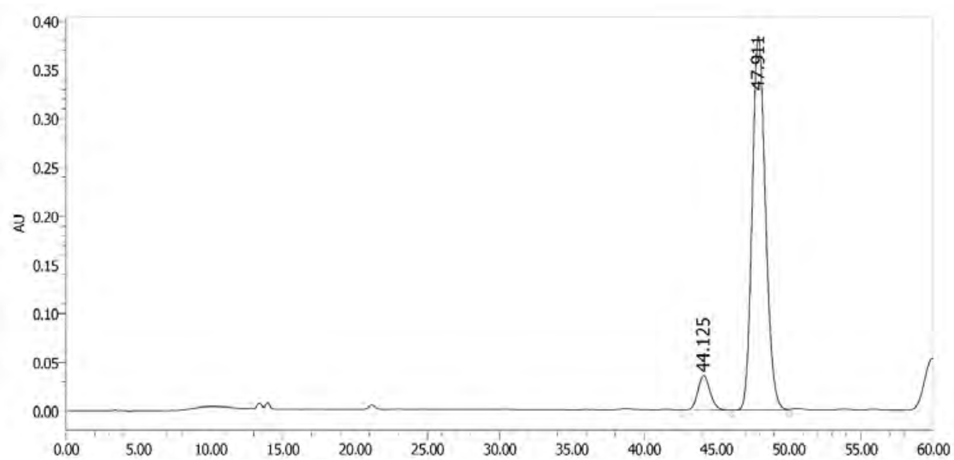
**3ea**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 97/3 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 47.9 min, minor isomer: $t_R$ = 44.1 min, UV detection at 228.0 nm, 30 $^{o}$C).

*rac*-**3ea**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 46.503 | 9507136 | 49.70 |
| 2 | 50.607 | 9620157 | 50.30 |

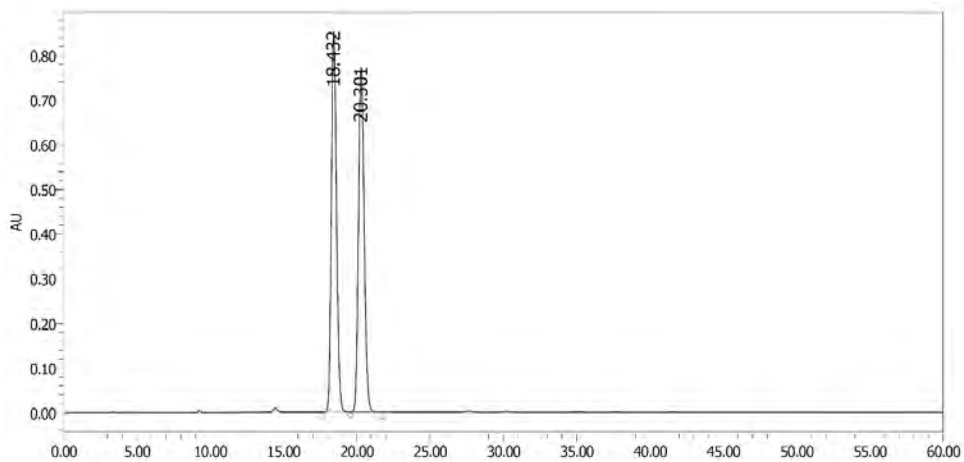
(*S*)-**3ea**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 44.125 | 2072711 | 7.77 |
| 2 | 47.911 | 24604949 | 92.23 |

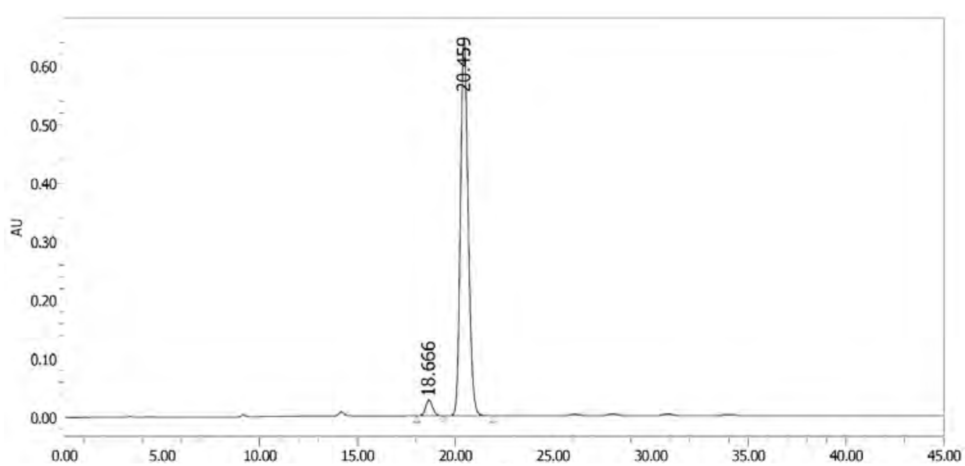
**3fa**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 97/3 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 20.5 min, minor isomer: $t_R$ = 18.7 min, UV detection at 220 nm, 30 $^{o}$C).

*rac*-**3fa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 18.432 | 20786624 | 49.98 |
| 2 | 20.301 | 20802471 | 50.02 |

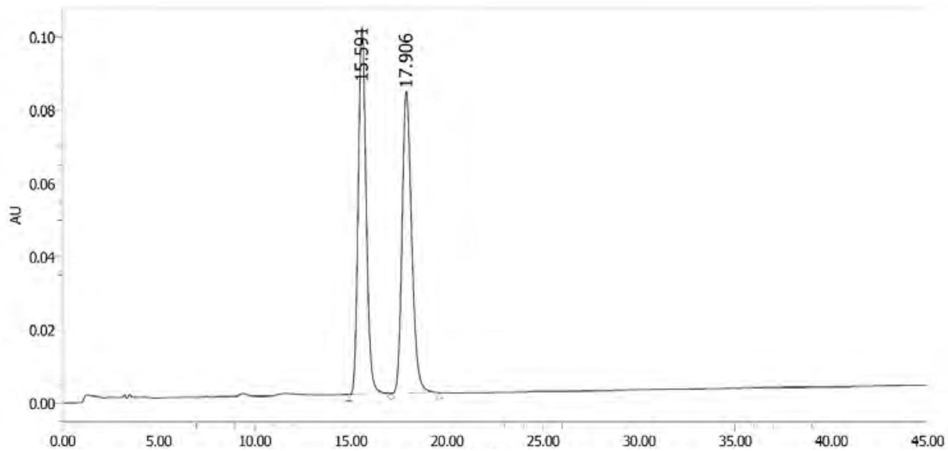
(*S*)-**3fa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 18.666 | 661390 | 3.57 |
| 2 | 20.459 | 17880571 | 96.43 |

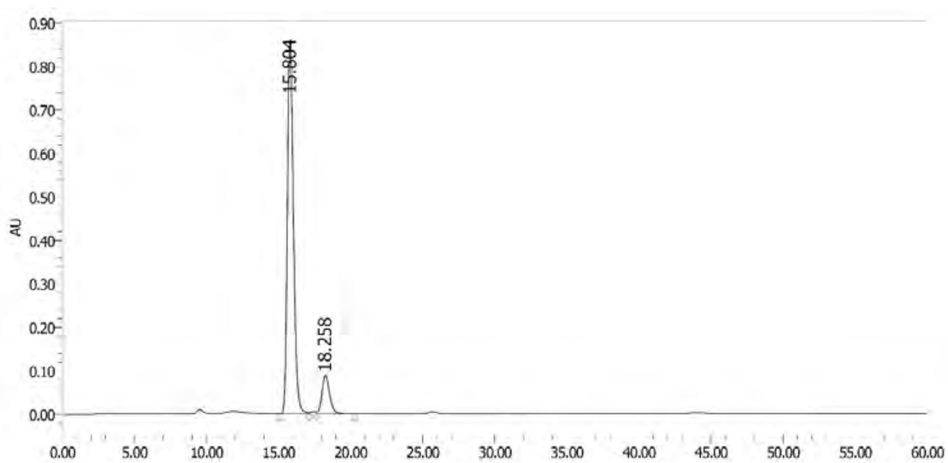
**3ga**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 15.8 min, minor isomer: $t_R$ = 18.3 min, UV detection at 235 nm, 30 $^{o}$C).

*rac*-**3ga**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 15.591 | 2874515 | 50.12 |
| 2 | 17.906 | 2860975 | 49.88 |

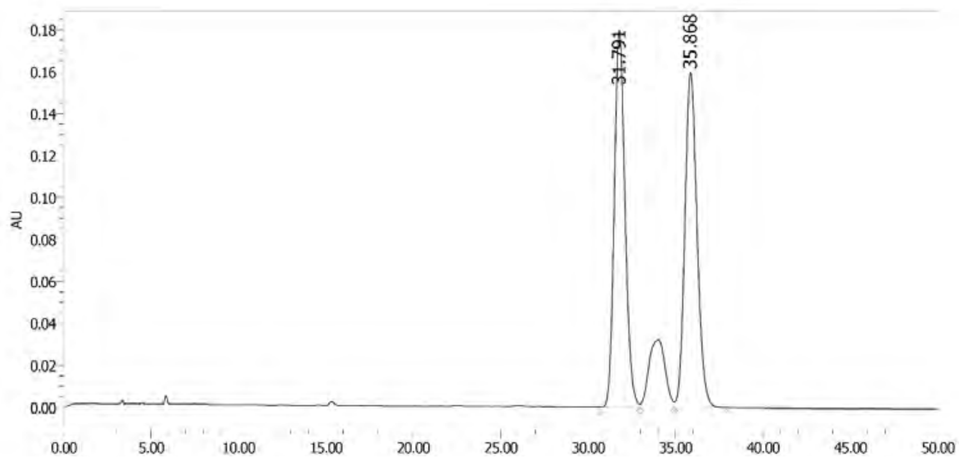
(*R*)-**3ga**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 15.804 | 25047196 | 88.53 |
| 2 | 18.258 | 3245014 | 11.47 |

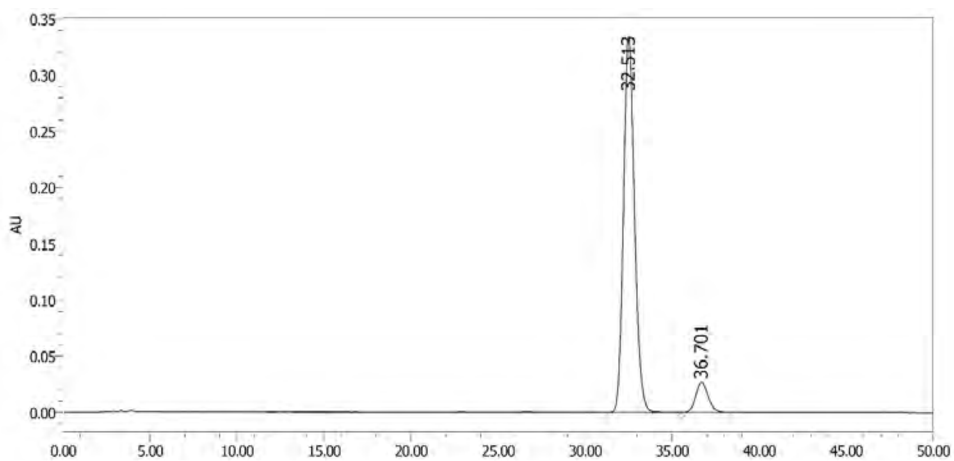
**3ge**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 32.5 min, minor isomer: $t_R$ = 36.7 min, UV detection at 235 nm, 30 $^oC$).

*rac*-**3ge**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 31.791 | 7688374 | 49.95 |
| 2 | 35.868 | 7703532 | 50.05 |

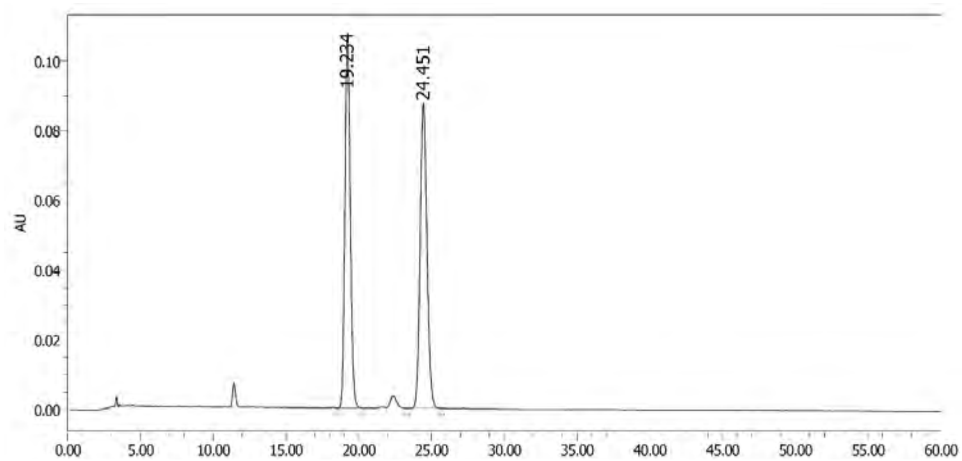
(*R*)-**3ge**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 32.513 | 14703625 | 91.76 |
| 2 | 36.701 | 1320552 | 8.24 |

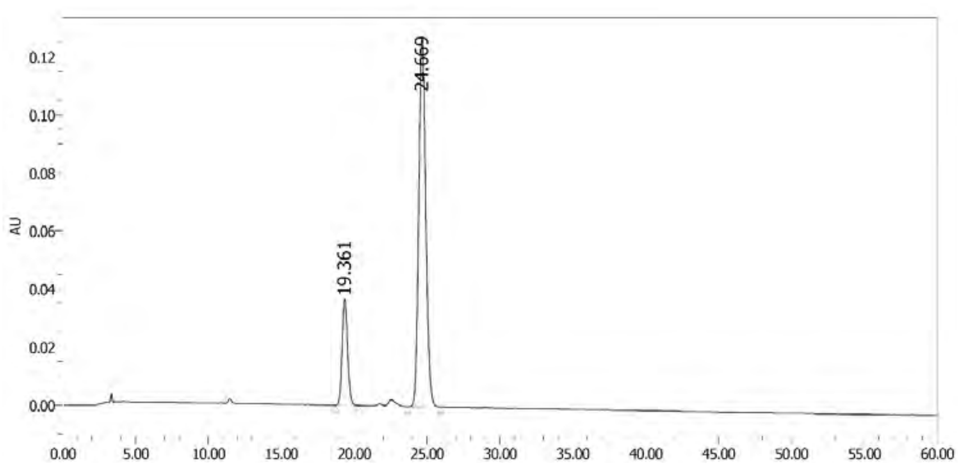
**3ha**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 24.7 min, minor isomer: $t_R$ = 19.4 min, UV detection at 220 nm, 30 °C).

*rac*-**3ha**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 19.234 | 2749972 | 48.93 |
| 2 | 24.451 | 2870476 | 51.07 |

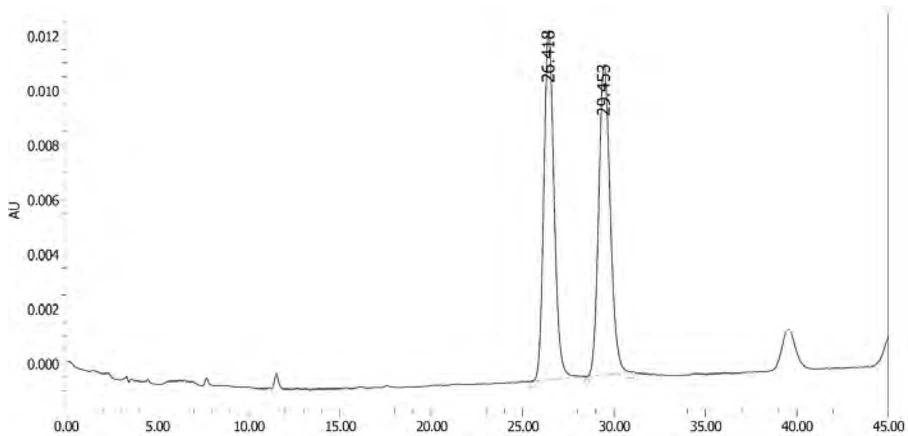
(*R*)-**3ha**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 19.361 | 950478 | 18.27 |
| 2 | 24.669 | 4251350 | 81.73 |

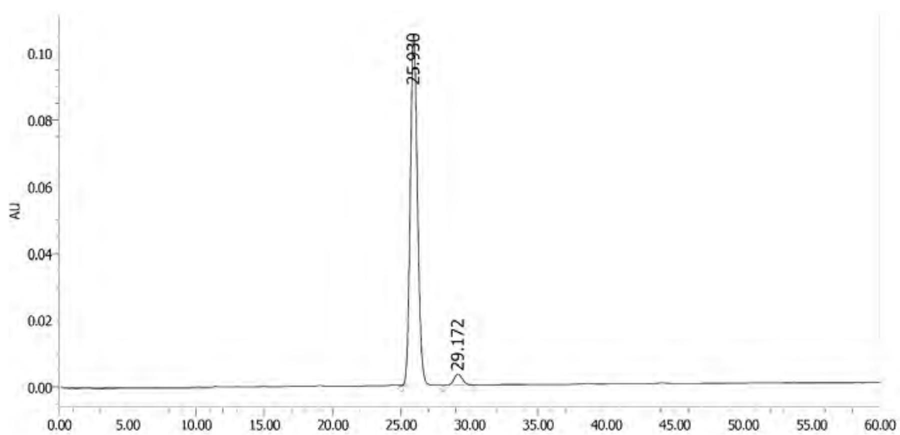
**3ia**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 25.9 1min, minor isomer: $t_R$ = 29.2 min, UV detection at 260 nm, 30 $^o$C).

*rac*-**3ia**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 26.418 | 498744 | 50.08 |
| 2 | 29.453 | 497155 | 49.92 |

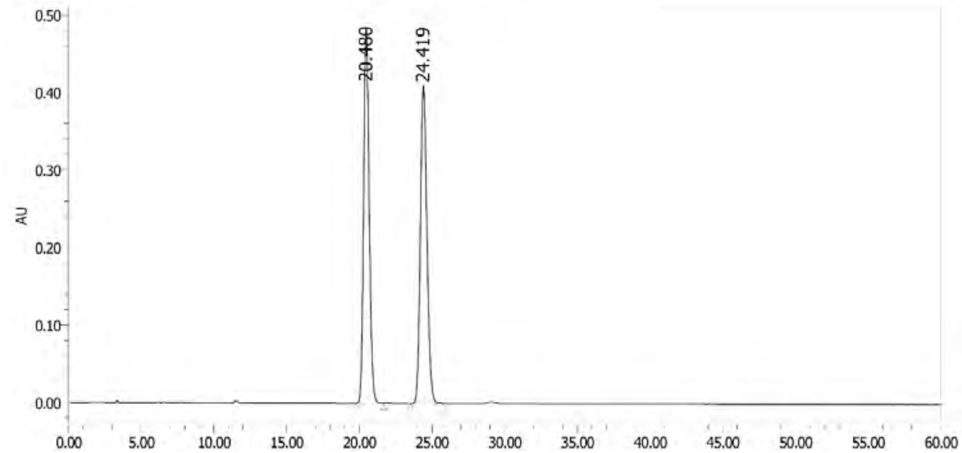
(*R*)-**3ia**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 25.930 | 3859402 | 96.46 |
| 2 | 29.172 | 141765 | 3.54 |

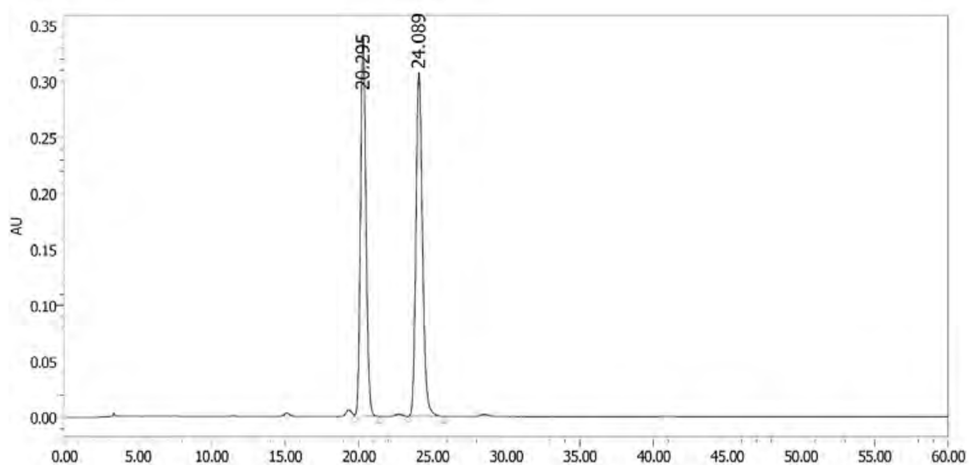
**3ja:** The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 24.0 min, minor isomer: $t_R$ = 20.3 min, UV detection at 220 nm, 30 $^oC$).

*rac*-**3ja**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 20.480 | 12869111 | 49.97 |
| 2 | 24.419 | 12885805 | 50.03 |

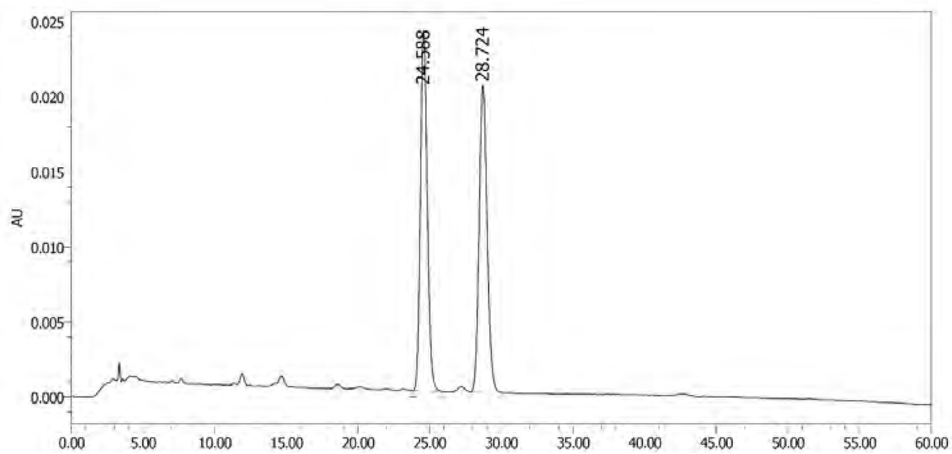
(*R*)-**3ja**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 20.295 | 8760786 | 47.91 |
| 2 | 24.049 | 9526935 | 52.09 |

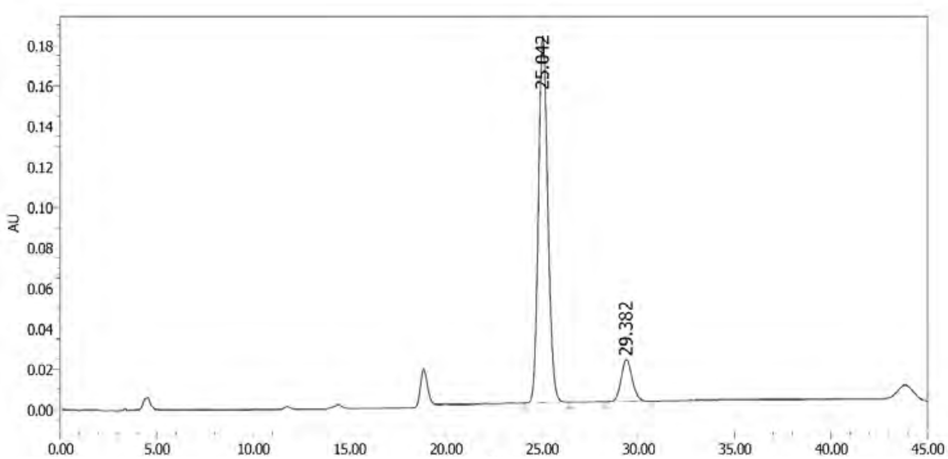
**3ka**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 25.0 min, minor isomer: $t_R$ = 29.4 min, UV detection at 230 nm, 30 $^{o}$C).

*rac*-**3ka**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 24.588 | 795838 | 50.09 |
| 2 | 28.724 | 792830 | 49.91 |

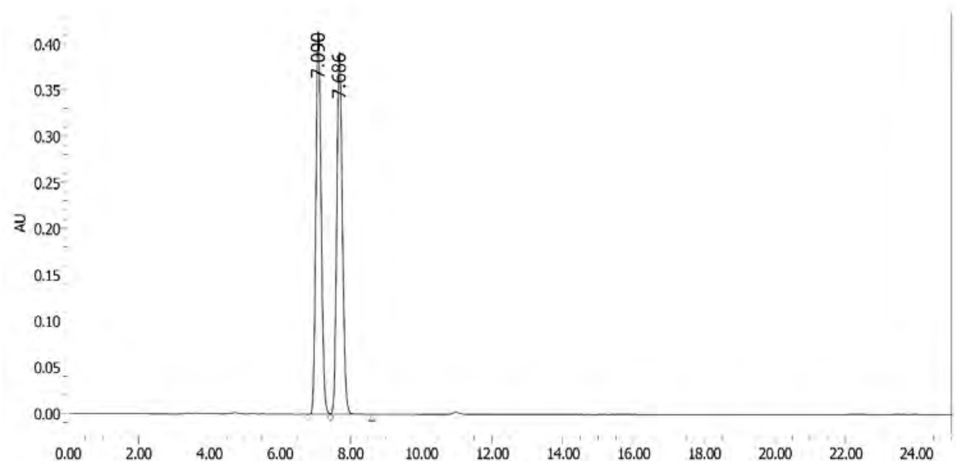
(*R*)-**3ka**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 25.042 | 6146877 | 88.27 |
| 2 | 29.382 | 817012 | 11.73 |

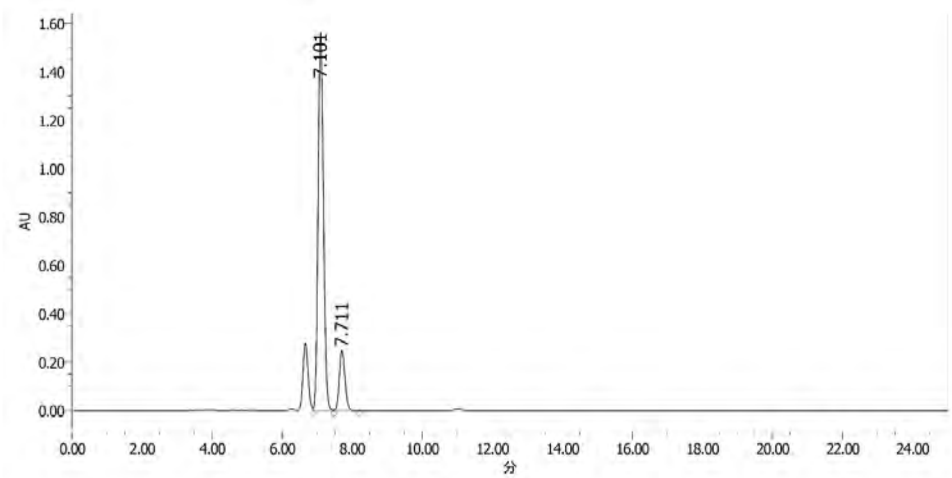
**6aa**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 7.1 min, minor isomer: $t_R$ = 7.7 min, UV detection at 235 nm, 30 $^{o}$C).

*rac*-**6aa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 7.090 | 4313053 | 49.87 |
| 2 | 7.686 | 4335335 | 50.13 |

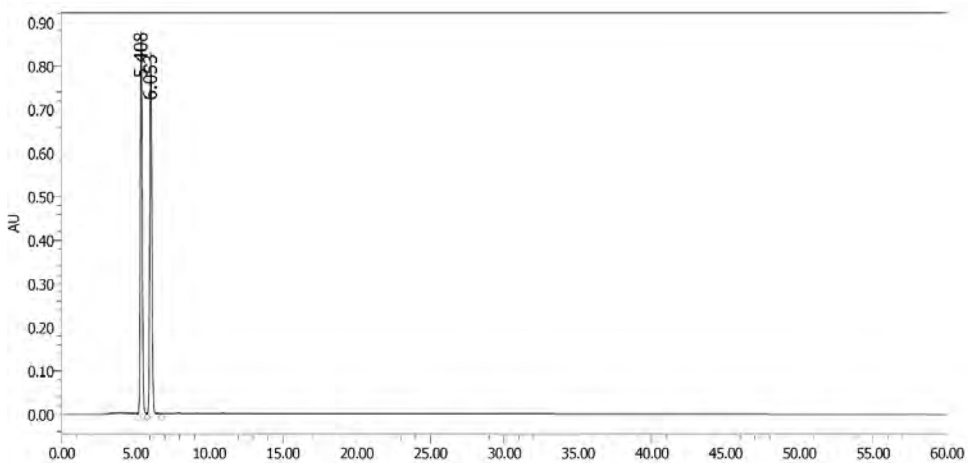
(*R*)-**6aa**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 7.101 | 16618327 | 85.69 |
| 2 | 7.711 | 2774602 | 14.31 |

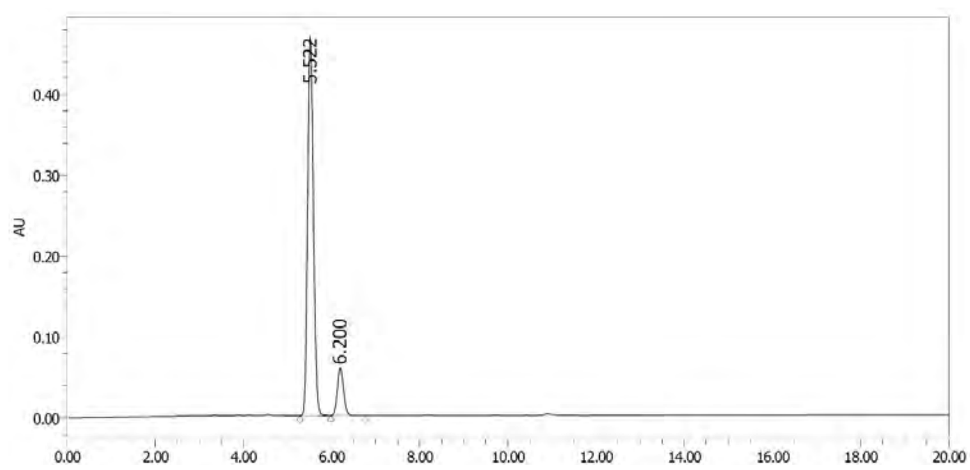
**6ab**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.00 mL/min, major isomer: $t_R$ = 5.5 min, minor isomer: $t_R$ = 6.2 min, UV detection at 235 nm, 30 $^oC$).

*rac*-**6ab**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 5.408 | 8021082 | 49.82 |
| 2 | 6.053 | 8079204 | 50.18 |

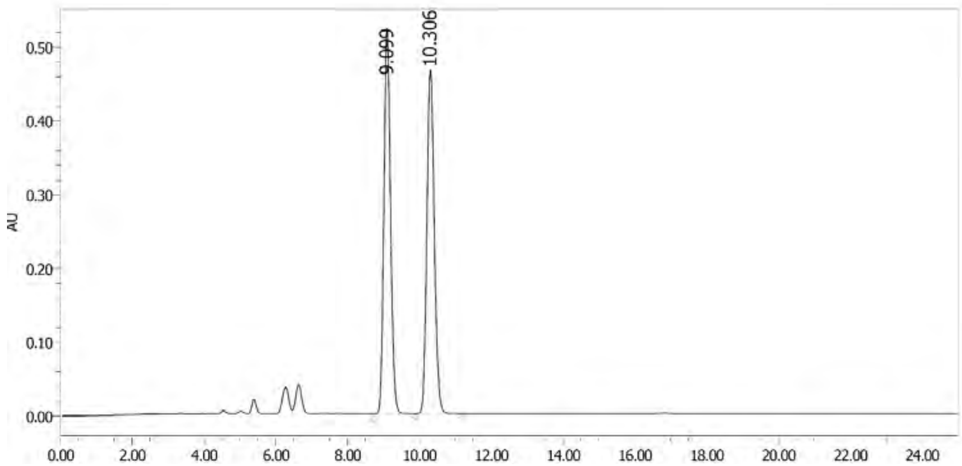
(*R*)- **6ab**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 5.522 | 4280493 | 87.99 |
| 2 | 6.200 | 584371 | 12.01 |

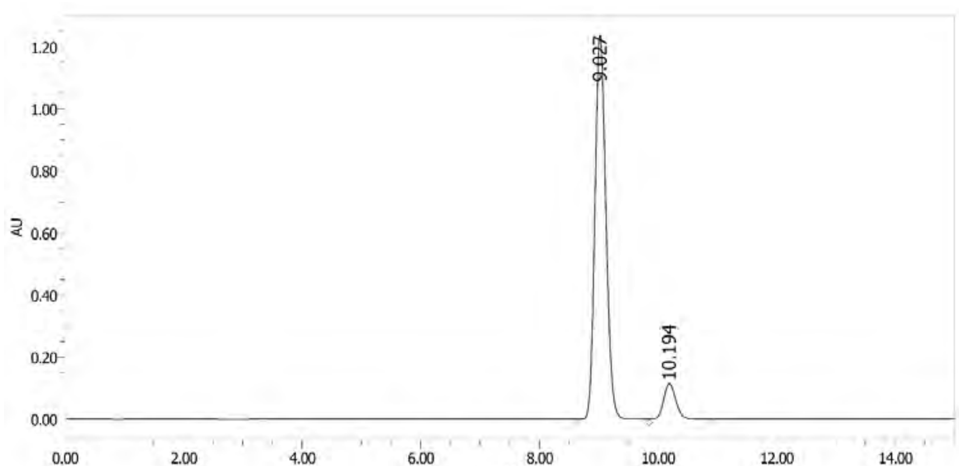
**6ac**: The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALPAK AD-H column, 95/5 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 9.0 min, minor isomer: $t_R$ = 10.2 min, UV detection at 235 nm, 30 $^{o}$C).

*rac*-**6ac**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 9.099 | 6702995 | 49.98 |
| 2 | 10.306 | 6708116 | 50.02 |

(*R*)-**6ac**




| Peak # | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 9.027 | 15840927 | 90.72 |
| 2 | 10.194 | 1619726 | 9.28 |

**Characterization Data for Products**

$^{1}H$, $^{13}C\{^{1}H\}$, and $^{19}F$ NMR spectra for all compounds are attached in the last part.

***N*,4-Dimethyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide (3aa)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 79.3 mg (79%, 92:8 er); white solid; mp 109-110 °C; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.74 (s, 3H), 6.61 (s, 1H), 7.10-7.16 (m, 2H), 7.16-7.22 (m, 3H), 7.27-7.31 (m, 3H), 7.43 (s, 1H), 7.45-7.50 (m, 2H), 7.61-7.67 (m, 3H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.78-7.83 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 21.49, 31.36, 64.36, 126.24, 126.27, 126.60, 127.29, 127.57, 127.71, 127.84, 128.03, 128.04, 128.44, 128.89, 129.48, 132.70, 133.06, 135.82, 136.99, 138.39, 143.16; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{25}H_{22}NO_2S$: 400.1355, found: 400.1366. Chiralcel OD-H column, 95/5 hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 24.7 min, minor isomer: $t_R$ = 29.2 min.

**4-Methoxy-*N*-methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide (3ab)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 49.1 mg (47%, 90:10 er); white solid; mp 102-104 °C; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H), 3.81 (s, 3H), 6.61 (s, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 7.11-7.19 (m, 2H), 7.20 (dd, *J* = 8.6, 1.8 Hz,1H), 7.26-7.34 (m, 3H), 7.41-7.52 (m, 3H), 7.63-7.70 (m, 3H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.78-7.84 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 31.34, 55.57, 64.34, 113.97(two peaks overlapped), 126.24, 126.60, 127.56, 127.70, 127.84, 128.02, 128.04, 128.44, 128.88, 129.35, 131.65, 132.69, 133.06, 135.87, 138.41, 162.67; HRMS (APCI) *m/z* $(M-H)^+$ for $C_{25}H_{22}NO_3S$: 416.1315, found: 416.1319. Chiralcel OD-H column, 95/5 hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 27.7 min, minor isomer: $t_R$ = 36.8 min.

**4-Chloro-*N*-methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide (3ac)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 59.1 mg (56%, 90:10 er); oil; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 6.61 (s, 1H), 7.09-7.17 (m, 2H), 7.21 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.28-7.26 (m, 5H), 7.43 (s, 1H), 7.45-7.52 (m, 2H), 7.61-7.70 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.79-7.85 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 27.90, 64.60, 126.44, 127.59, 127.82, 127.91, 128.00, 128.25, 128.56, 128.65, 128.80, 129.05, 129.08, 129.23, 132.72, 133.00, 135.45, 137.96, 138.29, 138.84; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{24}H_{19}ClNO_2S$: 420.0820, found: 420.0819. Chiralcel OD-H column, 95/5 hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 25.4 min, minor isomer: $t_R$ = 28.1 min.

***N*,2,4,6-Tetramethyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzenesulfonamide (3ad)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/80 v/v) as an eluent; 76.2 mg (71%, 91:9 er); white solid; mp 73−75 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.54 (s, 6H), 2.74 (s, 3H), 6.49 (s, 1H), 6.92 (s, 2H), 7.15-7.22 (m, 2H), 7.26-7.34 (m, 4H), 7.43-7.51 (m, 3H), 7.66-7.73 (m, 1H), 7.77 (d, $J$ = 8.6 Hz, 1H), 7.79-7.85 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 27.93, 31.34, 55.58, 64.32, 113.82, 113.96, 126.25, 126.60, 127.55, 127.70, 127.83, 128.02, 128.05, 128.44, 128.88, 129.35, 129.98, 131.61, 132.68, 135.85, 138.40, 162.66; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{27}H_{26}NO_2S$: 428.1679, found: 428.1679. Chiralcel OD-H column, 95/5 hexane/2-propanol, 0.50 mL/min, major isomer: $t_R$ = 15.8 min, minor isomer: $t_R$ = 20.3 min.

***N*-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)thiophene-2-sulfonamide (3ae)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 78.0 mg (79%, 93:7 er); oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3H), 6.62 (s, 1H), 7.00 (dd, $J$ = 3.8, 5.0 Hz, 1H), 7.11-7.17 (m, 2H), 7.20 (dd, $J$ = 8.6 Hz, 1.8 Hz, 1H), 7.28-7.34 (m, 3H), 7.43-7.53 (m, 5H), 7.67-7.73 (m, 1H), 7.75 (d, $J$ = 8.7 Hz, 1H), 7.79-7.85 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.54, 64.80, 126.33, 126.35, 126.44, 127.16, 127.58, 127.80, 127.86, 128.08, 128.13, 128.49, 128.82, 131.43, 131.91, 132.75, 133.07, 135.56, 138.06, 140.59; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{22}H_{18}NO_2S_2$: 392.0773, found: 392.0767. Chiralcel OD-H column, 97/3 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 19.1 min, minor isomer: $t_R$ = 20.5 min.

***N*-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)methanesulfonamide (3af)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 41.6 mg (51%, 90:10 er); brown solid; mp 116-118 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 3H), 2.83 (s, 3H), 6.57 (s, 1H), 7.31-7.45 (m, 6H), 7.48-7.55 (m, 2H), 7.71 (s, 1H), 7.78-7.84 (m, 1H), 7.84-7.90 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 30.92, 38.29, 64.53, 126.42, 126.48 (two peaks overlapped), 127.65, 127.89, 128.08 (two peaks overlapped), 128.45, 128.74, 128.87, 132.86, 133.15, 135.45, 137.85; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{19}H_{18}NO_2S$: 324.1053, found: 324.1060. Chiralcel OD-H column, 97/3 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 23.8 min, minor isomer: $t_R$ = 26.9 min.

**4-(Naphthalen-2-yl(phenyl)methyl)morpholine (3ag)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/20 to 1/10 v/v) as an eluent; 44.7 mg (59%, 88:12 er); white solid; mp

126-128 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.44 (d, $J$ = 4.6 Hz, 4H), 3.73 (t, $J$ = 4.6 Hz, 4H), 4.37 (s, 1H), 7.17 (tt, $J$ = 7.3, 1.3 Hz, 1H), 7.26-7.30 (m, 2H), 7.42 (dtd, $J$ = 14.6, 6.9, 1.4 Hz, 2H), 7.46-7.53 (m, 2H), 7.60 (dd, $J$ = 8.6, 1.6 Hz, 1H), 7.71-7.82 (m, 3H), 7.84 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 52.78, 67.23, 76.83, 125.70, 125.81, 126.02, 126.67, 127.11, 127.59, 127.78, 128.01, 128.37, 128.58, 132.75, 133.47, 139.91, 142.18; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{21}H_{20}NO$: 302.1539, found: 302.1540. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 8.7 min, minor isomer: $t_R$ = 12.3 min.

***N*-((4-Methoxyphenyl)(naphthalen-2-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (3ba)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 86.3 mg (80%, 89:11 er); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.73 (s, 3H), 3.80 (s, 3H), 6.56 (s, 1H), 6.80 (d, $J$ = 8.8 Hz, 2H), 7.02 (d, $J$ = 8.4 Hz, 2H), 7.15-7.22 (m, 3H), 7.40-7.52 (m, 3H), 7.59-7.68 (m, 3H), 7.73 (d, $J$ = 8.6 Hz, 1H), 7.76-7.84 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.47, 31.22, 55.30, 63.86, 113.74, 126.17, 126.18, 126.46, 127.27, 127.46, 127.54, 127.98, 128.02, 129.45, 130.26, 130.34, 132.65, 133.06, 136.16, 137.05, 143.08, 159.09; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{26}H_{24}NO_3S$: 430.1477, found: 430.1477. Chiralpak AD-H column, 99.5/0.5 hexane/2-propanol, 2.5 mL/min (60 min) then 90/10 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 79.7 min, minor isomer: $t_R$ = 85.4 min.

***N*,4-Dimethyl-*N*-(naphthalen-2-yl(4-trifluoromethyl)phenyl)methyl)benzenesulfonamide (3ca)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 63.4 mg (54%, 84:16 er); white solid; mp 100-102 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.74 (s, 3H), 6.64 (s, 1H), 7.12 (dd, $J$ = 8.7, 1.9 Hz, 1H), 7.21 (d, $J$ = 8.0 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.35 (s, 1H), 7.44-7.52 (m, 2H), 7.56 (d, $J$ = 8.2 Hz, 2H), 7.61-7.66 (m, 3H), 7.75 (d, $J$ = 8.6 Hz, 1H), 7.79-7.84 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.49, 31.43, 64.00, 123.87 (q, $J$ = 271 Hz), 125.42 (q, $J$ = 3.4 Hz), 126.44, 126.8, 126.58, 127.23, 127.61, 128.00, 128.24, 128.36, 128.91, 129.59, 129.92 (q, $J$ = 31.8 Hz), 132.79, 132.98, 134.75, 136.70, 142.70, 143.49; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.51; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{26}H_{21}F_3NO_2S$: 468.1240, found: 468.1238. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 21.8 min, minor isomer: $t_R$ = 23.2 min.

***N*-((4-Chlorophenyl)(naphthalen-2-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (3da)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 67.4 mg (63%, 87:13 er); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.72 (s, 3H), 6.57 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.14 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.24-7.29 (m, 2H), 7.38 (s, 1H), 7.43-7.52 (m, 2H), 7.61-7.67 (m, 3H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.78-7.84 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.52, 31.30, 63.74, 126.39, 126.40, 126.44, 127.25, 127.58, 127.92, 128.00, 128.22, 128.63, 129.57, 130.12, 132.73, 132.99, 133.62, 135.18, 136.80, 137.03, 143.38; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{25}H_{21}ClNO_2S$: 434.0976, found: 434.0975. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 35.7 min, minor isomer: $t_R$ = 37.9 min, UV detection at 230 nm, 30 °C).

***N*-((3-Methoxyphenyl)(naphthalen-2-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (3ea)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 89.7 mg (83%, 92:8 er); white solid; mp 98-100 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.75 (s, 3H), 3.69 (s, 3H), 6.57 (s, 1H), 6.63 (s, 1H), 6.69 (dt, *J* = 7.6, 0.8 Hz, 1H), 6.82 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.15-7.24 (m, 4H), 7.42-7.51 (m, 3H), 7.62-7.67 (m, 3H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.78-7.82 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.49, 31.46, 55.17, 64.30, 113.20, 114.45, 121.27, 126.22, 126.26, 126.60, 127.28, 127.56, 127.80, 128.03, 128.05, 129.41, 129.49, 132.70, 133.04, 135.72, 136.95, 140.01, 143.17, 159.66; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{26}H_{24}NO_3S$: 430.1477, found: 430.1470. Chiralpak AD-H column, 97/3 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 47.9 min, minor isomer: $t_R$ = 44.1 min.

***N*,4-Dimethyl-*N*-(naphthalen-2-yl(*o*-tolyl)methyl)benzenesulfonamide (3fa)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 74.1 mg (71%, 96:4 er); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.36 (s, 3H), 2.72 (s, 3H), 6.73 (s, 1H), 6. 95 (d, *J* = 7.6 Hz, 1H), 7.04-7.18 (m, 4H), 7.16 (s, 1H), 7.18-7.22 (m, 2H), 7.38-7.48 (m, 2H), 7.50 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.55 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 7.3, 1.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 19.78, 21.47, 32.30, 62.01, 125.89, 126.20, 126.22, 126.61, 127.33, 127.43, 127.57, 127.76, 127.95, 128.26, 128.46, 129.34, 130.93, 132.64, 133.03, 136.07, 136.76, 136.98, 137.32, 143.06; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{26}H_{24}NO_2S$: 414.1528, found: 414.1521. Chiralpak AD-H column, 97/3 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 20.5 min, minor isomer: $t_R$ = 18.7 min.

***N*-((6-Methoxynaphthalen-2-yl)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3ga)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 68.2 mg (63%, 89:11 er); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.72 (s, 3H), 3.90 (s, 3H), 6.58 (s, 1H), 7.06-7.20 (m, 7H), 7.25-7.30 (m, 3H), 7.33 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.50, 31.30, 55.36, 64.29, 105.55, 119.02, 126.88, 127.21, 127.29, 127.62, 127.76, 128.40, 128.47, 128.79, 129.46, 129.50, 133.42, 133.88, 137.03, 138.55, 143.10, 157.99; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{26}H_{24}NO_3S$: 430.1471, found: 430.1475. Chiralcel OD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 15.8 min, minor isomer: $t_R$ = 18.3 min.

***N*-((6-Methoxynaphthalen-2-yl)(phenyl)methyl)-*N*-methylthiophene-2-sulfonamide (3ge)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 67.5 mg (62%, 92:8 er); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 3H), 3.91 (s, 3H), 6.58 (s, 1H), 6.99 (dd, *J* = 3.8, 5.0 Hz, 1H), 7.07-7.19 (m, 5H), 7.26-7.32 (m, 3H), 7.40 (s, 1H), 7.44-7.50 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.47, 55.35, 64.75, 105.58, 119.10, 126.94, 127.05, 127.12, 127.58, 127.74, 128.44, 128.50, 128.72, 129.54, 131.35, 131.85, 133.15, 133.95, 138.24, 140.68, 158.07; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{23}H_{20}NO_3S_2$: 422.0879, found: 422.0872. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 32.5 min, minor isomer: $t_R$ = 36.7 min.

***N*,4-Dimethyl-*N*-(naphthalen-1-yl(phenyl)methyl)benzenesulfonamide (3ha)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 62.6 mg (62%, 82:18 er); white solid; mp 142-144 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.69 (s, 3H), 6.96 (d, *J* = 6.8 Hz, 2H), 7.10-7.25 (m, 7H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.39-7.50 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.51, 32.30, 61.70, 124.07, 124.92, 125.85, 126.58, 126.85, 127.07, 127.35, 127.54, 128.49, 128.73, 129.34, 129.71, 131.34, 133.88, 134.73, 136.82, 139.20, 143.02; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{25}H_{22}NO_2S$: 400.1366, found: 400.1369. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 24.7 min, minor isomer: $t_R$ = 19.4 min

***N*,4-Dimethyl-*N*-(phenanthren-9-yl(phenyl)methyl)benzenesulfonamide (3ia)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 v/v) as an eluent; 113.1 mg (>99%, 96:4

er); white solid; mp 98-100 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.76 (s, 3H), 6.99-7.06 (m, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.15 (s, 1H), 7.17-7.27 (m, 3H), 7.31 (s, 1H), 7.48-7.67 (m, 7H), 8.00 (d, $J$ = 8.3 Hz, 1H), 8.65 (d, $J$ = 8.2 Hz, 1H), 8.71 (d, $J$ = 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.46, 32.38, 62.18, 122.44, 123.11, 125.00, 126.56, 126.67, 126.97, 127.06, 127.32, 127.73. 127.93, 128.61, 128.90, 129.00, 129.37, 130.15, 130.34, 130.79, 130.96, 132.83, 136.83, 138.85, 143.08; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{29}H_{24}NO_2S$: 450.1522, found: 450.1523 Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 25.9 min, minor isomer: $t_R$ = 29.2 min.

***N*,4-Dimethyl-*N*-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide (3ja)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 40.0 mg (47%, 52:48 er); white solid; mp 121-123 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, $J$ = 7.0 Hz, 3H), 2.44 (s, 3H), 2.58 (s, 3H), 5.43 (q, $J$ = 7.0 Hz, 1H), 7.32 (d, $J$ = 8.0 Hz, 2H), 7.43-7.51 (m, 3H), 7.64 (s, 1H), 7.72-7.84 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) 15.04, 21.57, 38.46, 54.90, 125.54, 126.08, 126.15, 126.20, 127.17, 127.58, 127.99, 128.24, 129.77, 132.74, 133.01, 137.23, 137.41, 143.21; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{20}H_{20}NO_2S$: 338.1209, found: 338.1207. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 24.0 min, minor isomer: $t_R$ = 20.3 min.

***N*-(Benzo[*b*]thiophen-2-yl(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (3ka)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 v/v) as an eluent followed by GPC with ethyl acetate; 34.9 mg (34%, 88:12 er); white solid; mp 143-145 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.79 (s, 3H), 6.71 (s, 1H), 6.94 (s, 1H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.27-7.35 (m, 7H), 7.60-7.67 (m, 3H), 7.71-7.75 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.50, 31.04, 61.04, 122.19, 123.56, 124.39, 124.52, 124.65, 127.39, 128.26, 128.51, 128.58, 129.43, 136.30, 137.48, 139.13, 140.00, 143.06, 143.33; HRMS (APCI) *m/z* $(M\text{-}H)^+$ Calcd for $C_{23}H_{20}NO_2S_2$: 406.0930, found: 406.0928. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 25.0 min, minor isomer: $t_R$ = 29.4 min.

***N*-(2-Benzylbenzo[*b*]thiophen-3-yl)-*N*,4-dimethylbenzenesulfonamide (3ka')** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 v/v) as an eluent followed by GPC with ethyl acetate; 21.7 mg (21%); oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.22 (s, 3H), 4.18 (d, $J$ = 16 Hz, 1H), 4.31 (d, $J$ = 16 Hz, 1H), 6.80 (d, $J$ = 8.0 Hz, 1H), 7.60 (ddd, $J$ = 8.1, 7.2, 1.0 Hz, 1H), 7.20

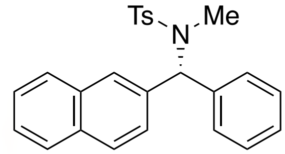
(ddd, $J$ = 8.1, 7.2, 1.0 Hz, 1H), 7.22-7.36 (m, 7H), 7.66 (t, $J$ = 8.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.59, 34.19, 37.72, 121.26, 122.74, 124.01, 124.14, 126.79, 127.66, 128.60, 128.97, 129.27, 129.71, 135.62, 136.72, 136.75, 139.11, 143.70, 145.49; HRMS (APCI) *m/z* $(M+H)^+$ Calcd for $C_{23}H_{22}NO_2S_2$: 408.1086, found: 408.1087.

**2-(Phenoxy(phenyl)methyl)naphthalene (6aa)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/10 to 1/5 v/v) as an eluent; 64.1 mg (83%, 86:14 er); white solid; mp 92-94 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 6.89 (tt, $J$ = 7.3, 1.0 Hz, 1H), 6.95-7.03 (m, 2H), 7.16-7.27 (m, 3H), 7.27-7.36 (m, 2H), 7.38-7.49 (m, 4H), 7.52 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.73-7.83 (m, 3H), 7.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 81.96, 116.27, 121.15, 124.93, 125.80, 126.17, 126.30, 127.13, 127.78, 127.89, 128.18, 128.63, 128.70, 129.48, 133.02, 133.31, 138.77, 141.24, 158.23; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{23}H_{17}O$: 309.1274, found: 309.1274. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 7.1 min, minor isomer: $t_R$ = 7.7 min.

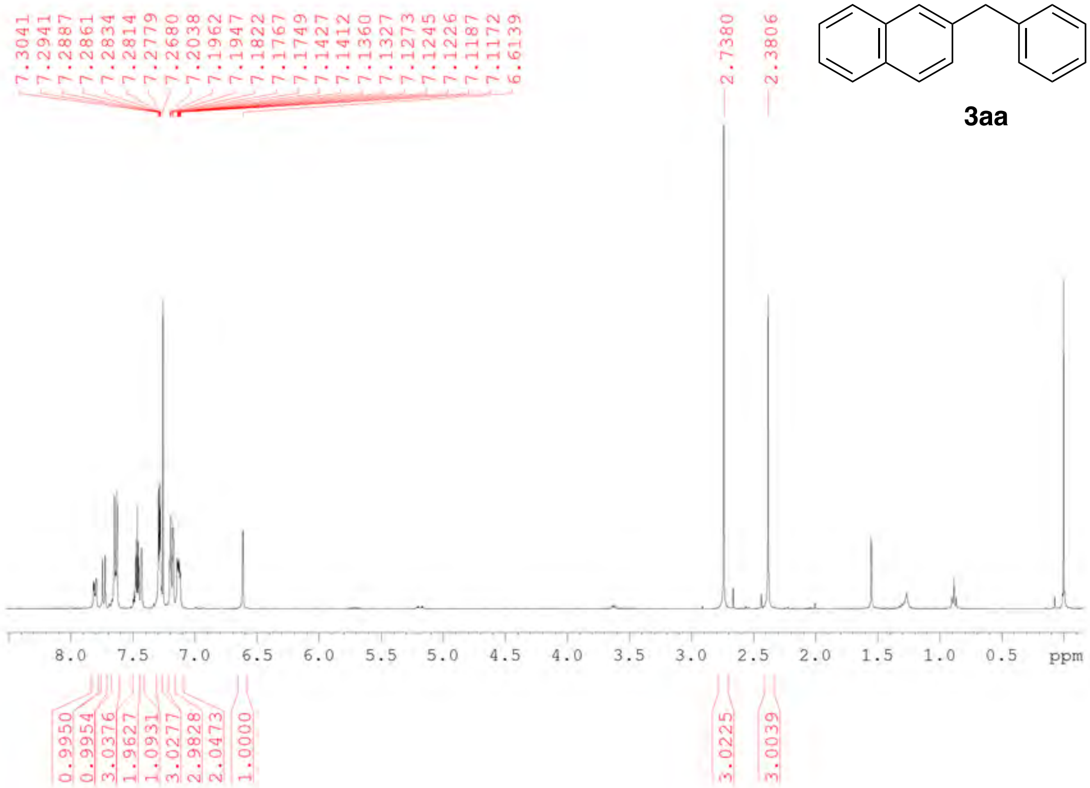
**2-((4-(*tert*-Butyl)phenoxy)(phenyl)methyl)naphthalene (6ab)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/150 v/v) as an eluent followed by GPC with chloroform; 67.8 mg (74%, 88:12 er); white solid; mp 110-112 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 6.33 (s, 1H), 6.90-6.96 (m, 2H), 7.19-7.29 (m, 3H), 7.30-7.37 (m, 2H), 7.40-7.48 (m, 4H), 7.52 (dd, $J$ = 8.6, 1.6 Hz, 1H), 7.76-7.84 (m, 3H), 7.87 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.54, 34.11, 81.97, 115.54, 124.99, 125.78, 126.10, 126.25 (two peaks overlapped), 127.14, 127.75, 127.81, 128.17, 128.57, 128.65, 132.98, 133.30, 138.95, 141.42, 143.67, 156.05; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{27}H_{25}O$: 365.1900, found: 365.1899. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 5.5 min, minor isomer: $t_R$ = 6.2 min.

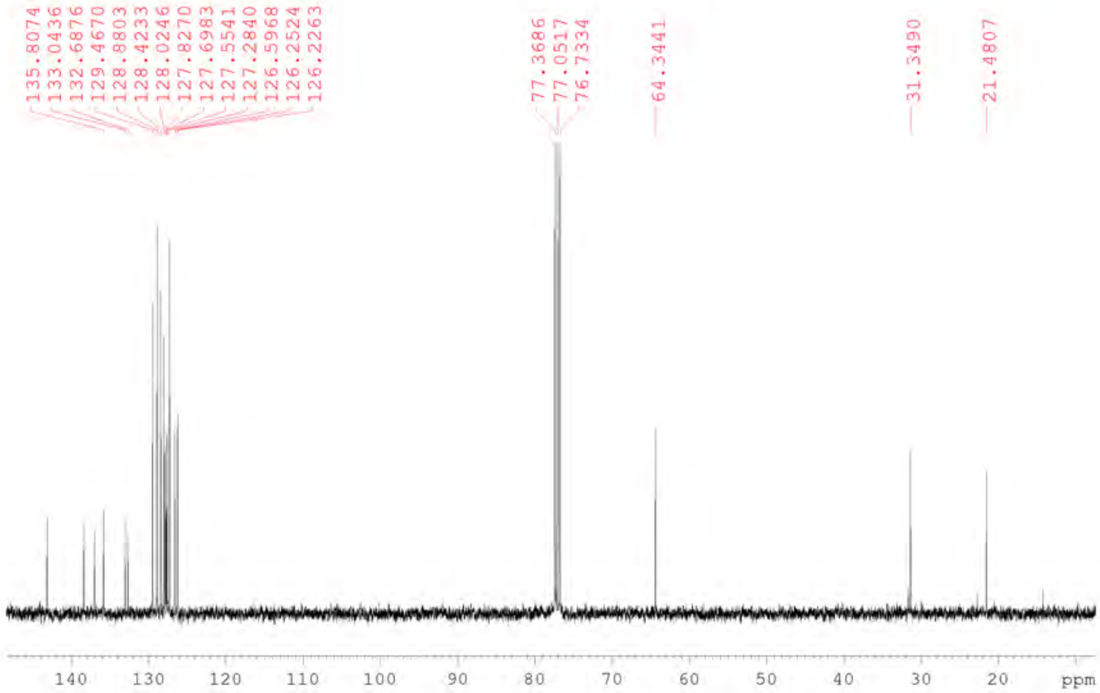
**2-(Naphthalen-2-yl(phenyl)methoxy)naphthalene (6ac)** Purified by column chromatography on silica gel with ethyl acetate/hexane (1/150 v/v) as an eluent followed by GPC with chloroform; 74.8 mg (83%, 91:9 er); white solid; mp 129−130 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 1H), 7.18 (d, $J$ = 2.4 Hz, 1H), 7.25-7.34 (m, 3H), 7.34-7.38 (m, 3H), 7.42-7.50 (m, 2H), 7.49-7.52 (m, 2H), 7.55-7.61 (m, 2H), 7.70-7.77 (m, 2H), 7.78-7.87 (m, 3H), 7.94 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) 81.35, 109.55, 119.47, 123.78, 124.83, 125.74, 126.13, 126.25 (two peaks overlapped), 126.89, 127.09, 127.57, 127.72, 127.90, 128.13, 128.61, 128.69, 129.07, 129.43, 132.98, 133.27, 134.34, 138.54, 141.05, 155.96; HRMS (APCI) *m/z* $(M-H)^+$ Calcd for $C_{27}H_{19}O$: 359.1430, found: 359.1429. Chiralpak AD-H column, 95/5 hexane/2-propanol, 1.0 mL/min, major isomer: $t_R$ = 9.0 min, minor isomer: $t_R$ = 10.2 min.

[$^1$H and $^{13}$C NMR Spectra of **3aa**]

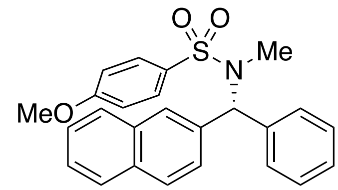



**3aa**

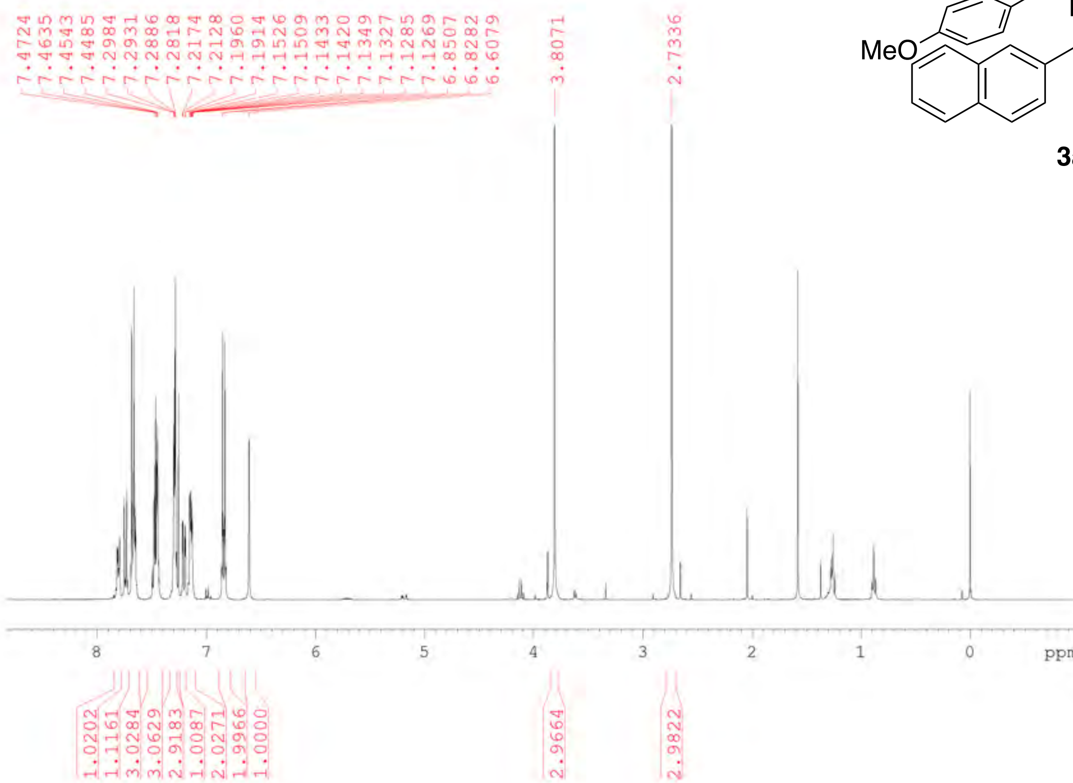


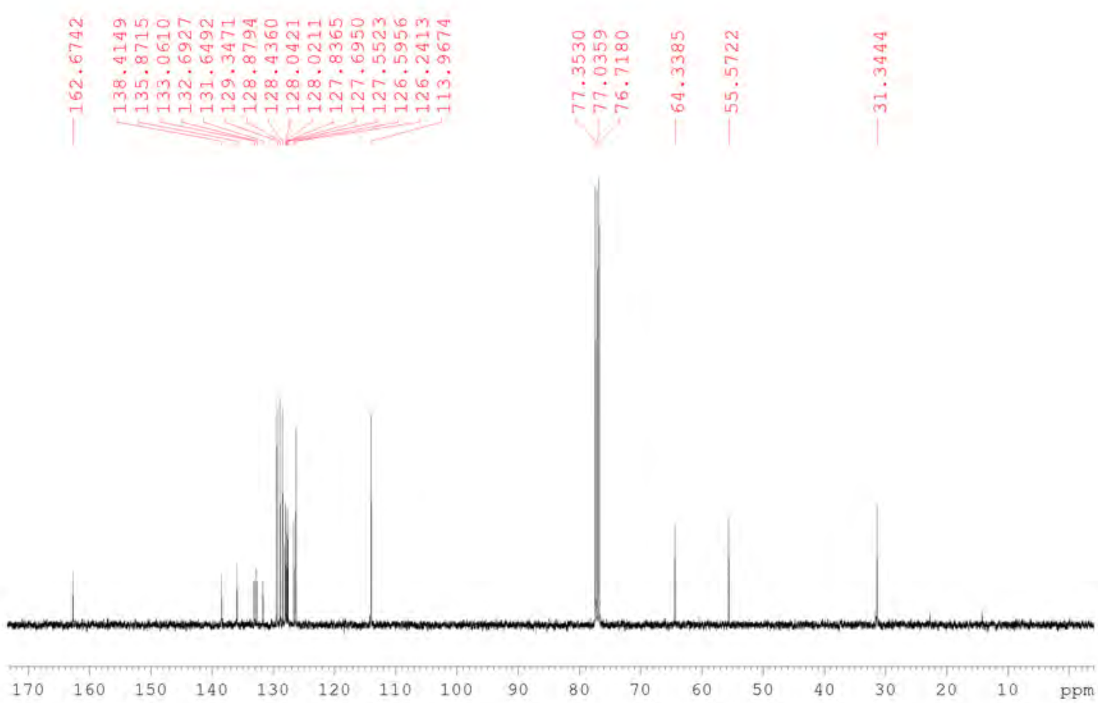



[$^{1}$H and $^{13}$C NMR Spectra of **3ab**]

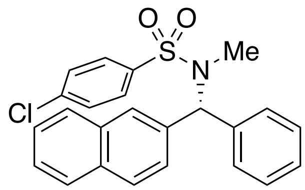


**3ab**

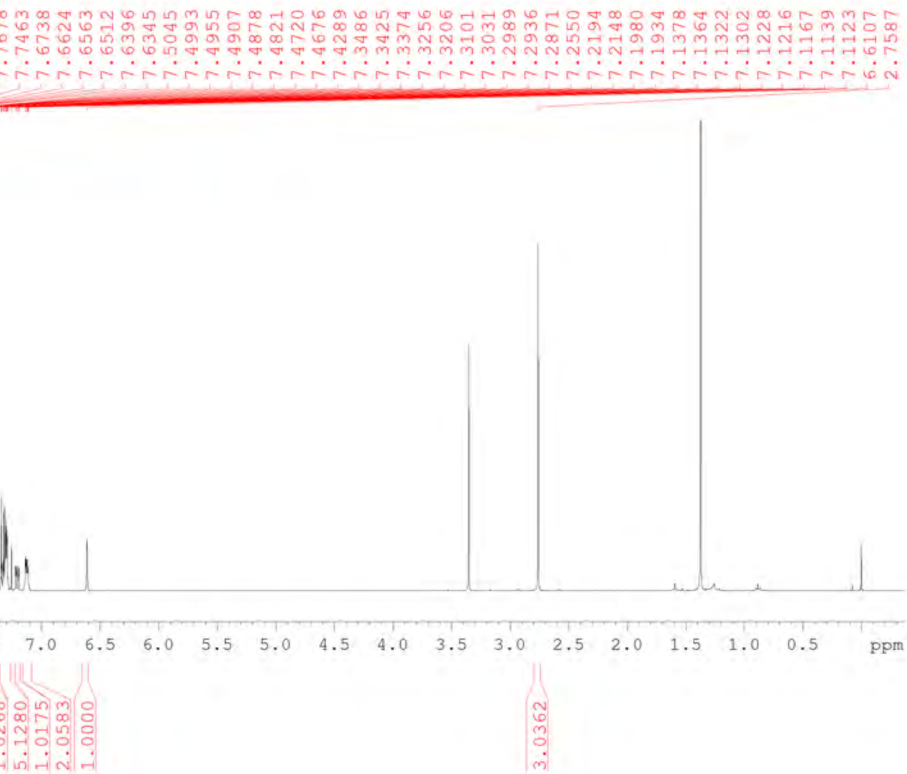


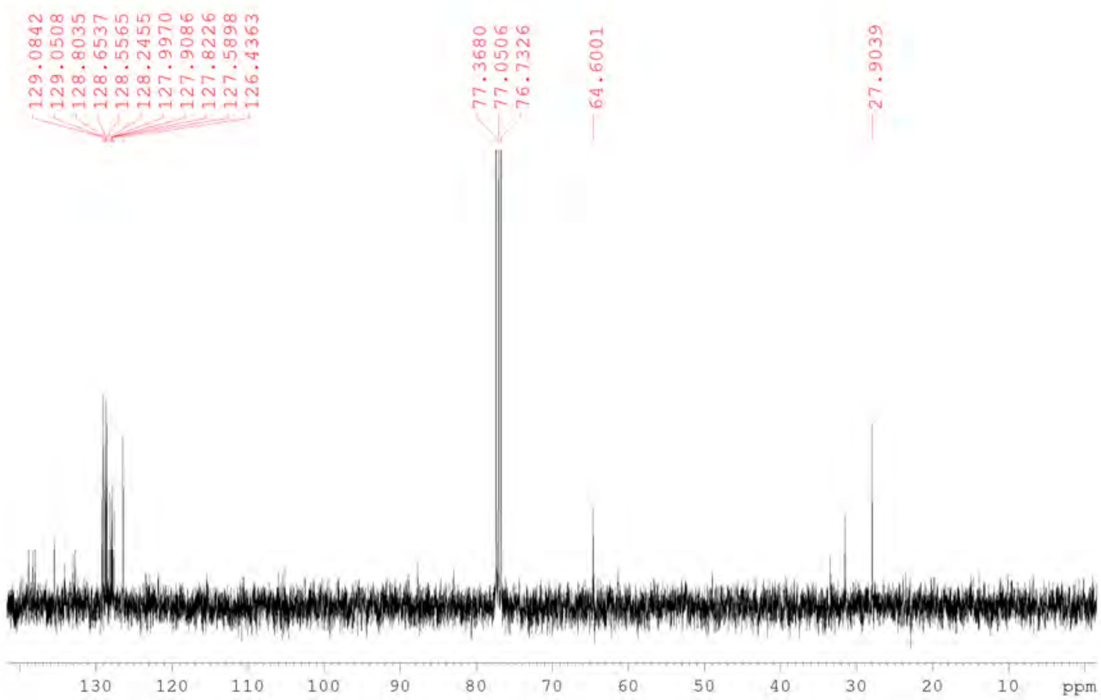


[$^{1}H$ and $^{13}C$ NMR Spectra of **3ac**]

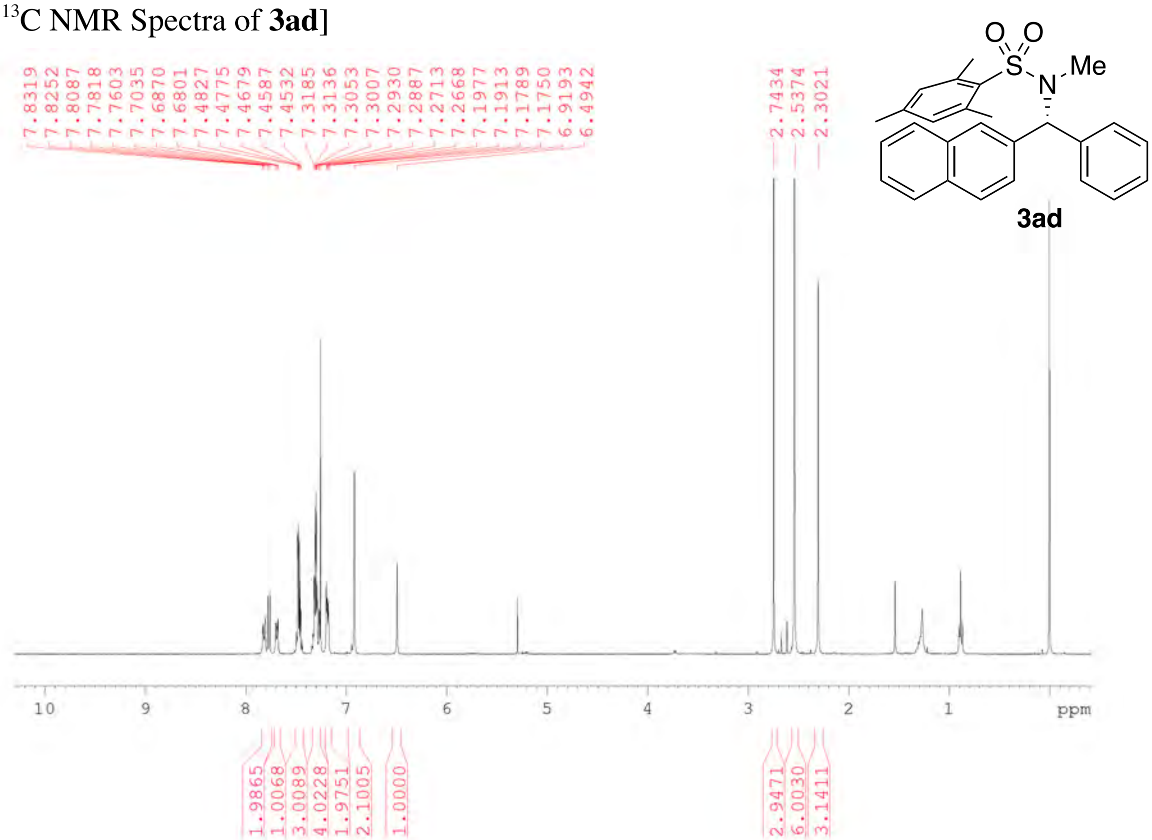



**3ac**

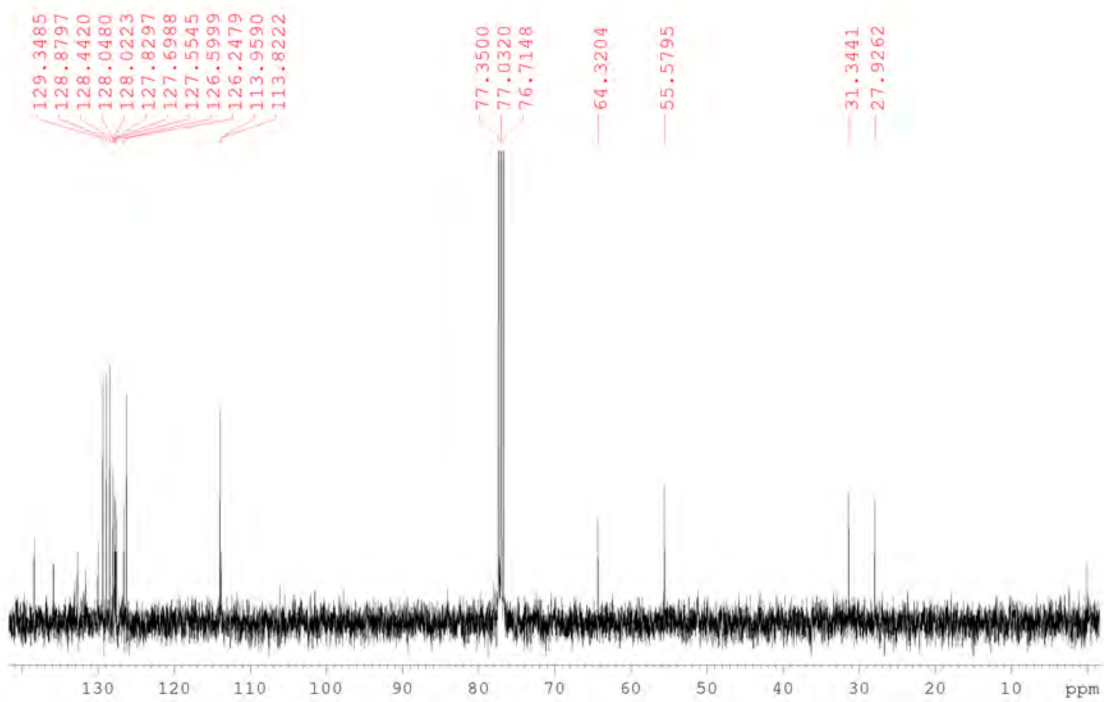


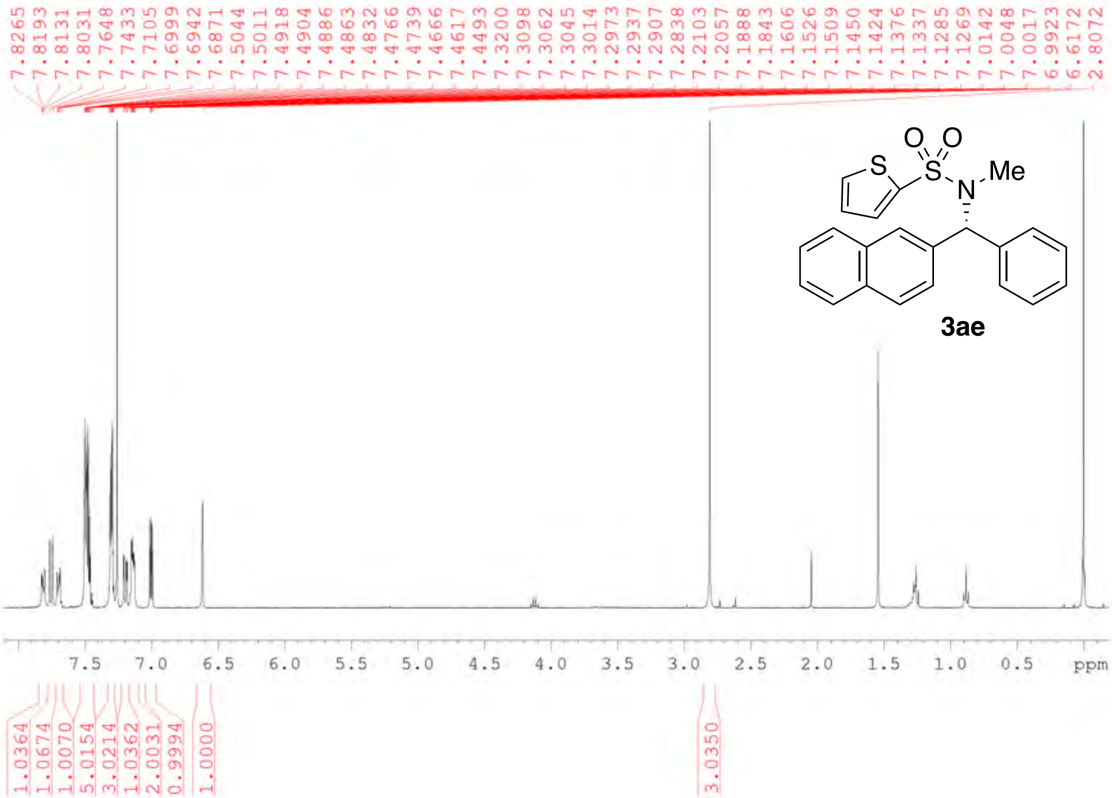
[$^1$H and $^{13}$C NMR Spectra of **3ad**]

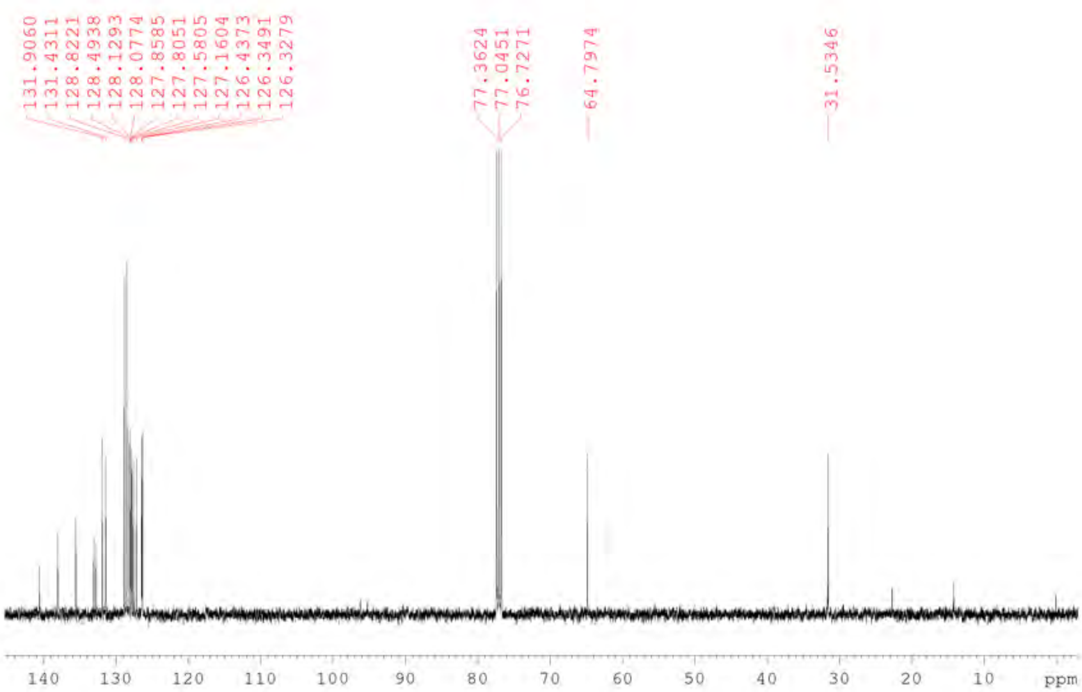



**3ad**

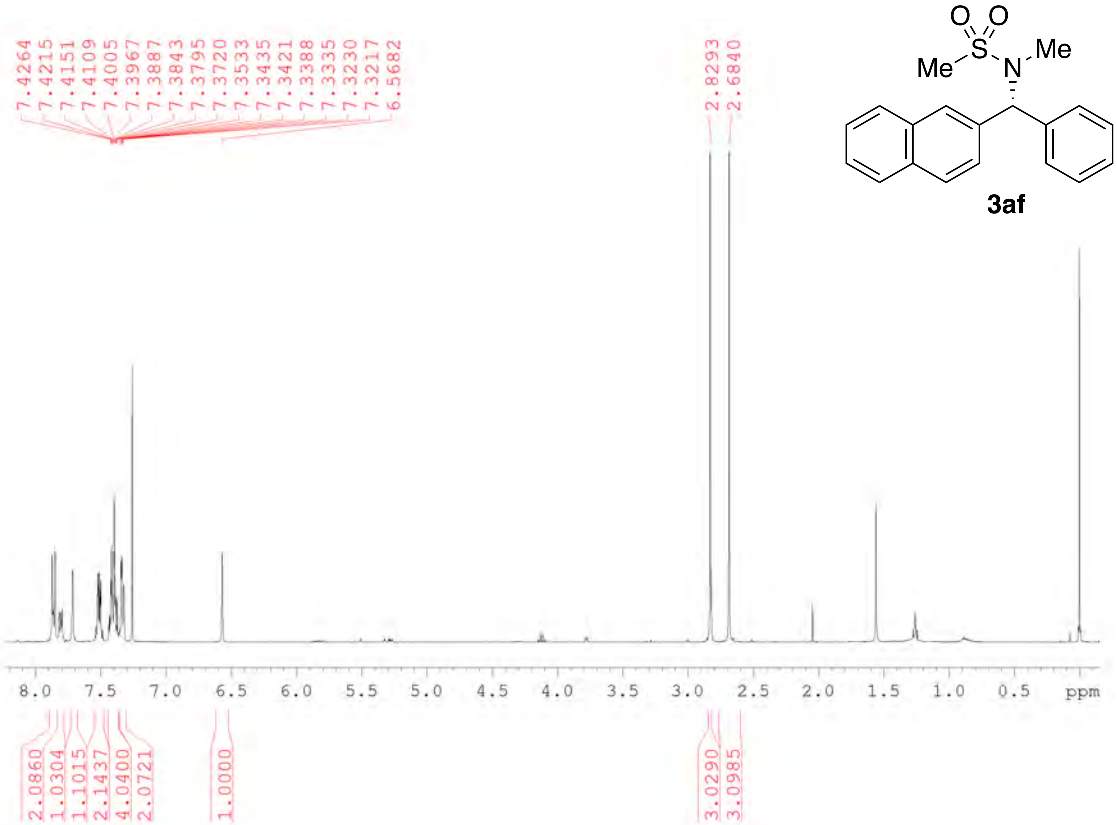


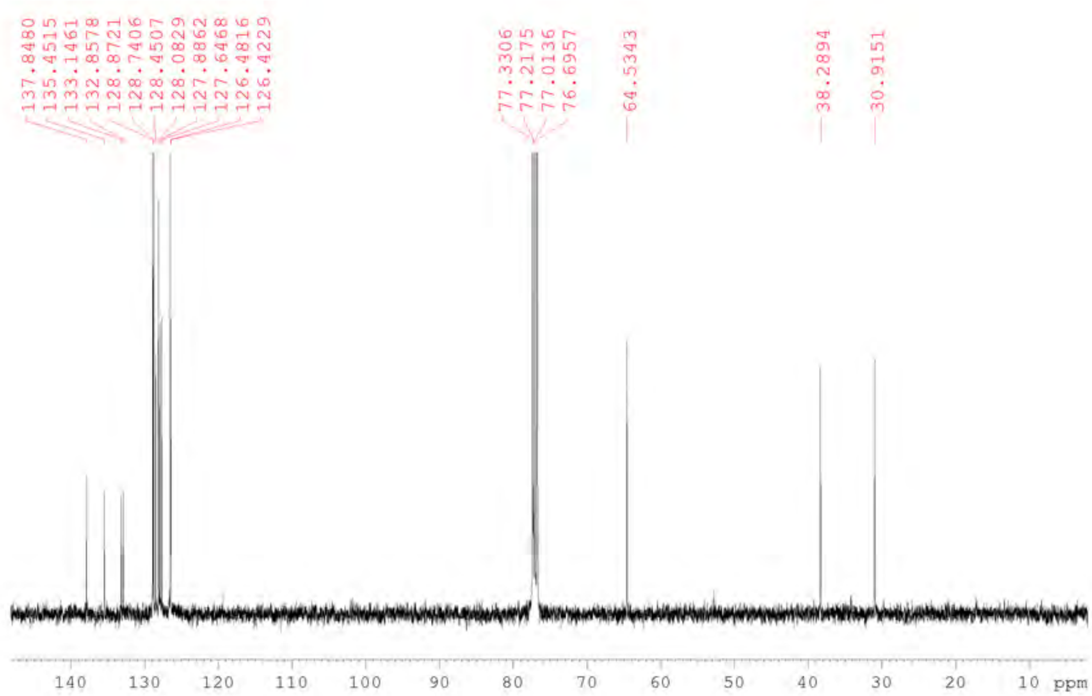
[$^{1}$H and $^{13}$C NMR Spectra of **3ae**]



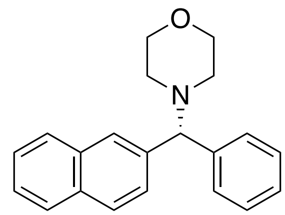



[$^{1}$H and $^{13}$C NMR Spectra of **3af**]

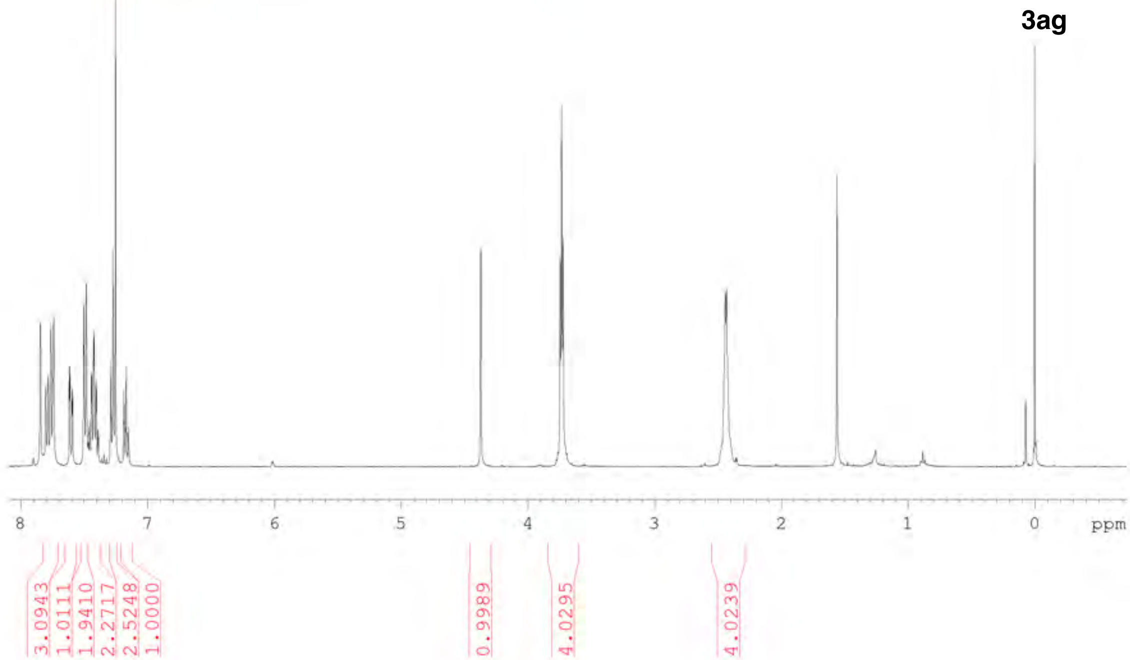


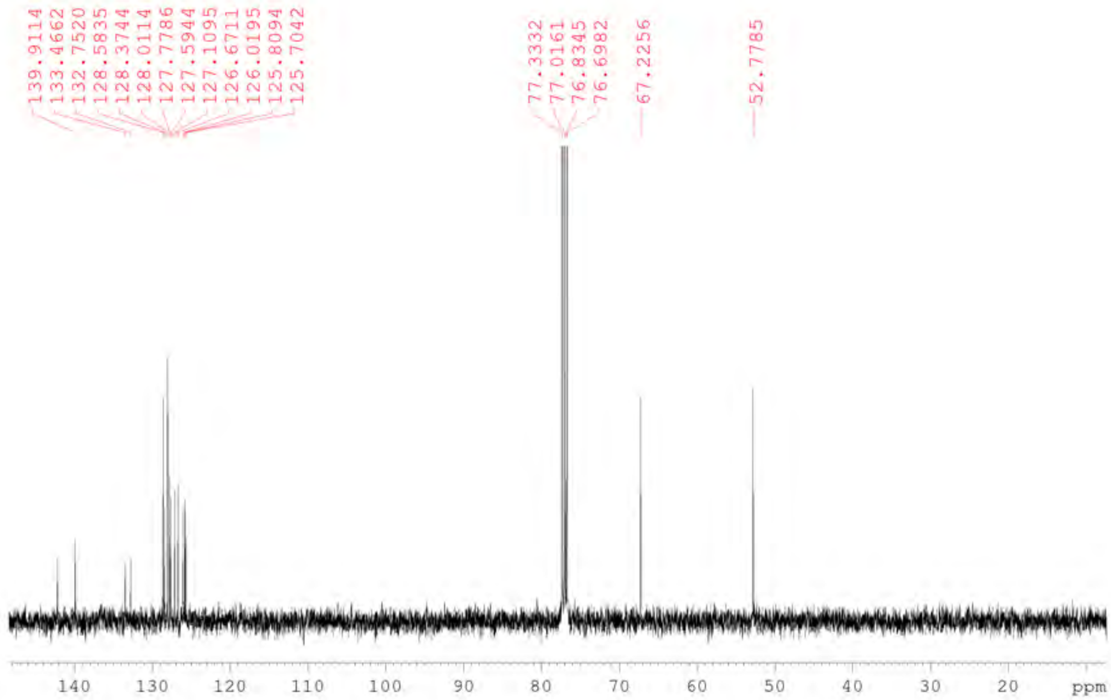



[[1]H and [13]C NMR Spectra of **3ag**]

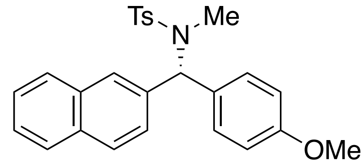



**3ag**

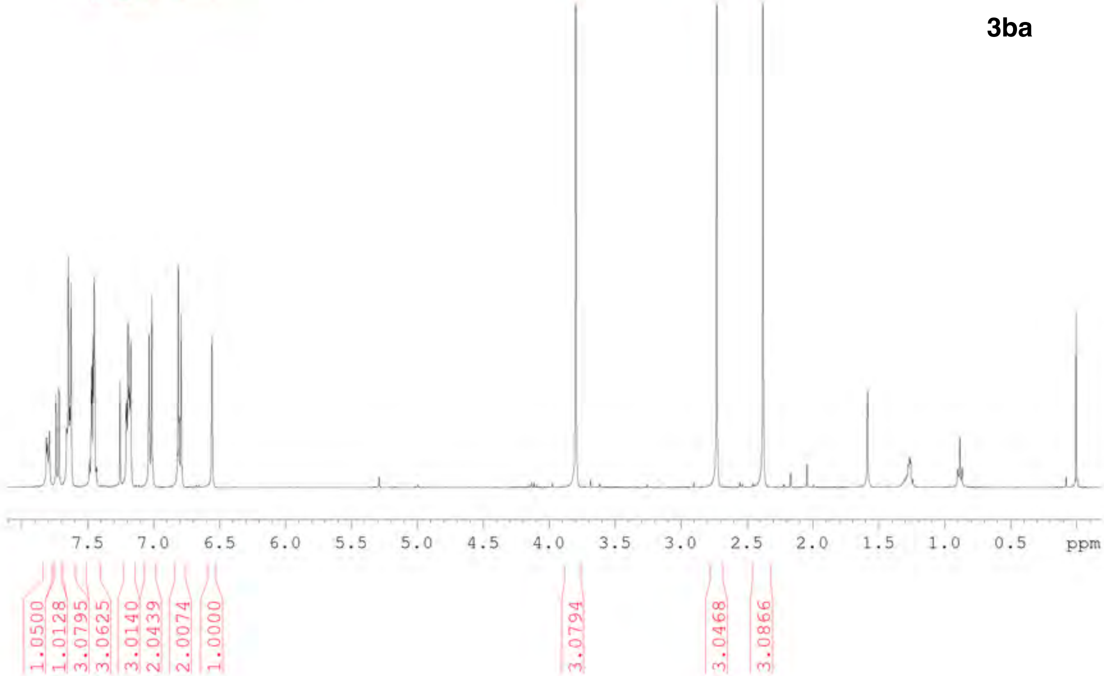


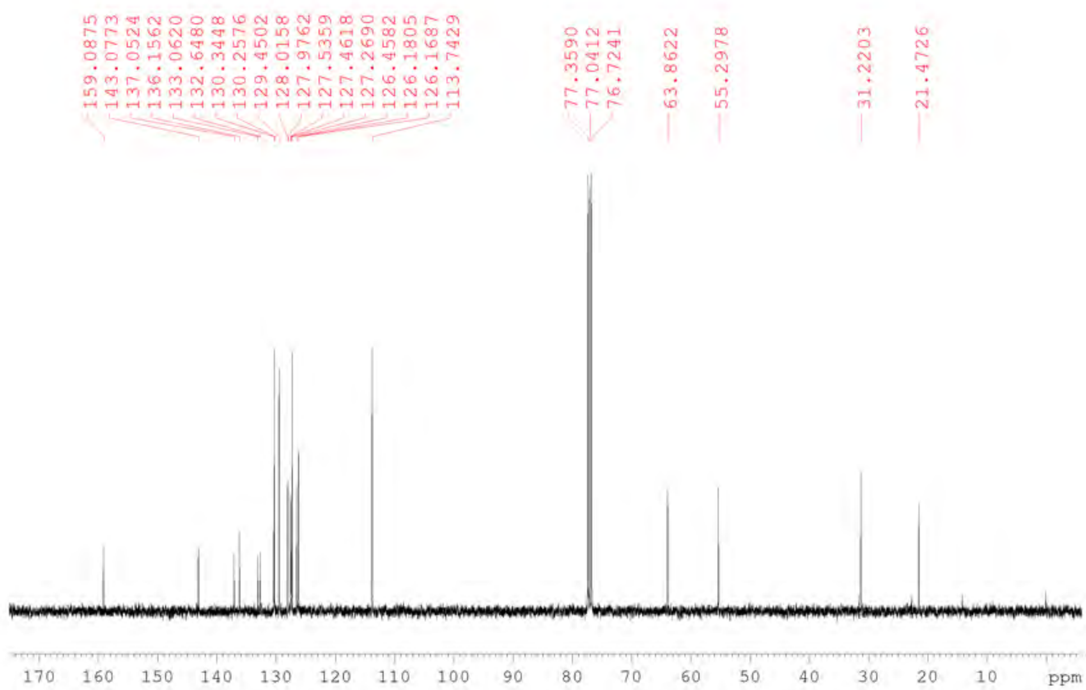



[[1]H and [13]C NMR Spectra of **3ba**]

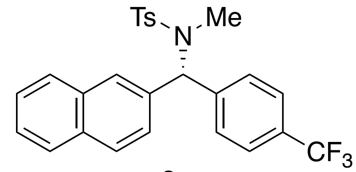



**3ba**

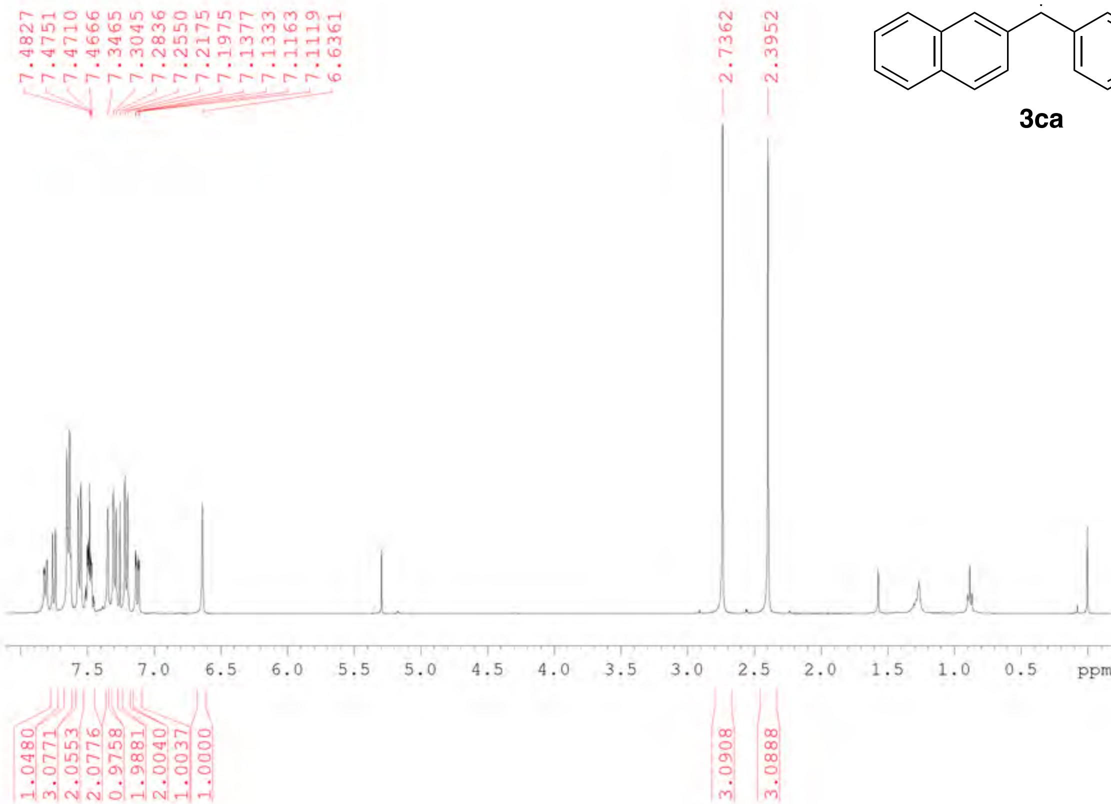


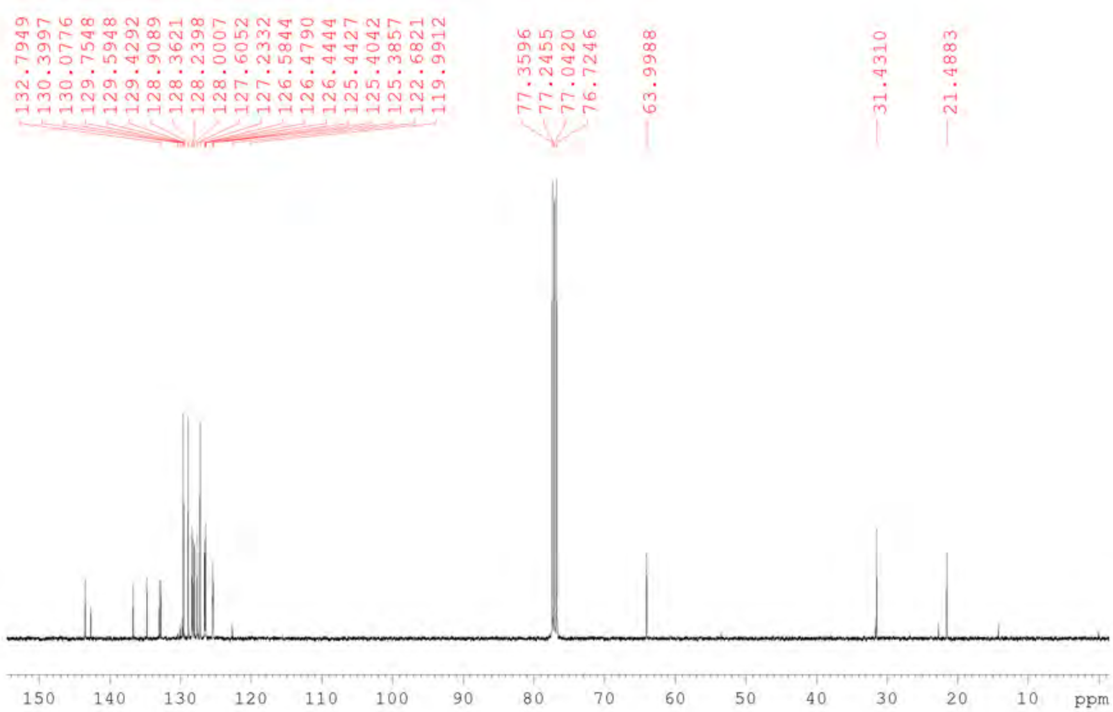



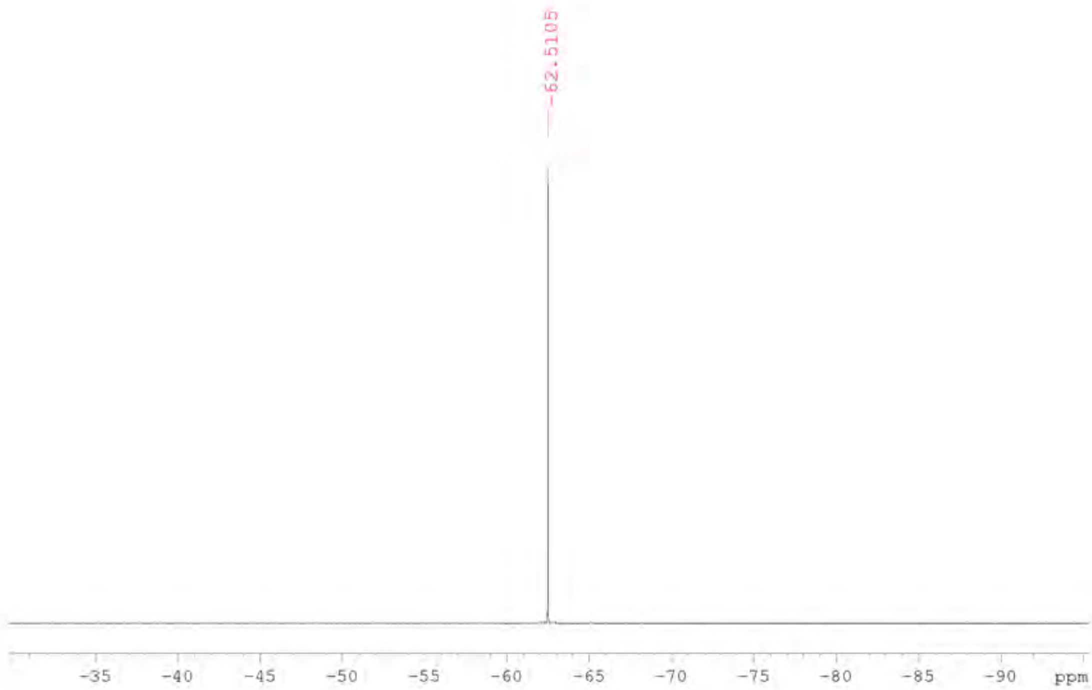
[$^{1}H$, $^{13}C$, and $^{19}F$ NMR Spectra of **3ca**]



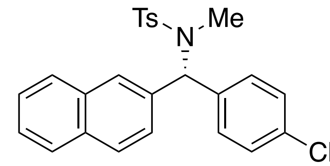

**3ca**



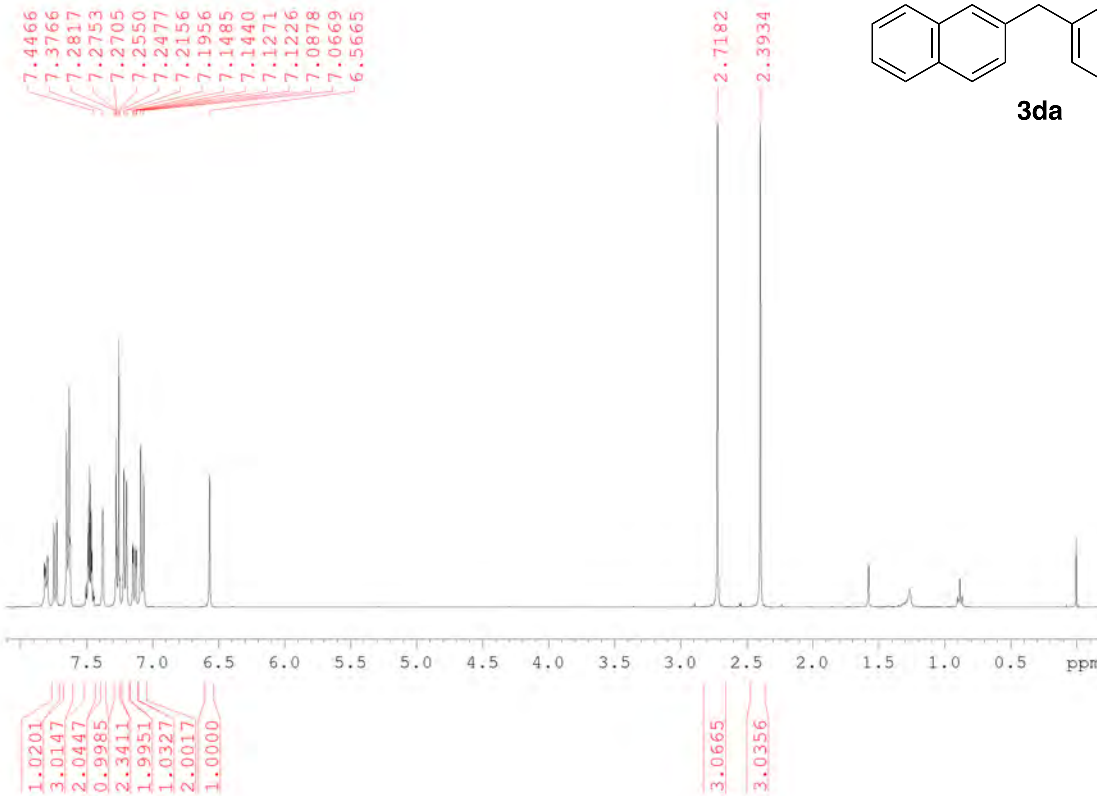



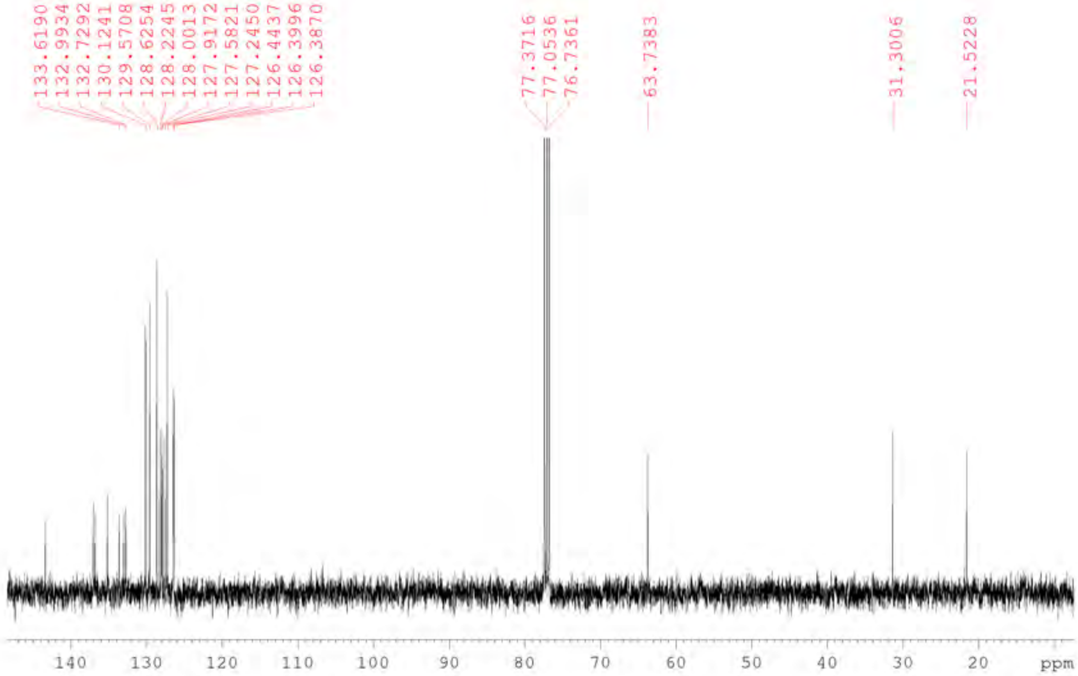

-62.5105
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm

[$^{1}$H and $^{13}$C NMR Spectra of **3da**]

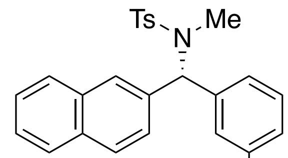



**3da**

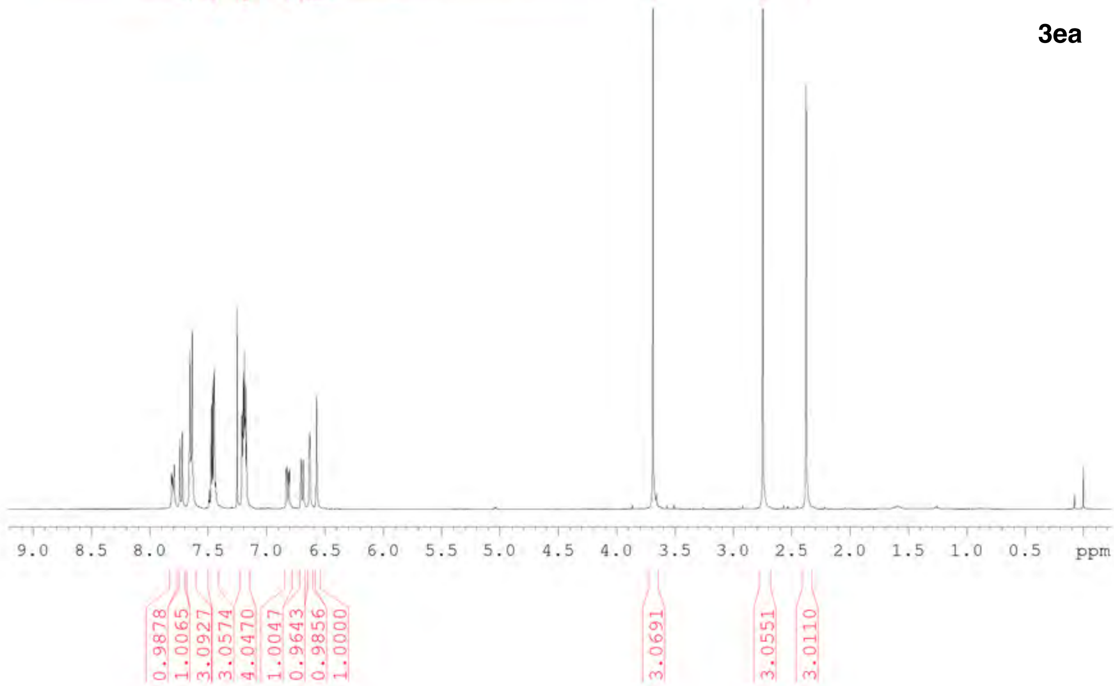


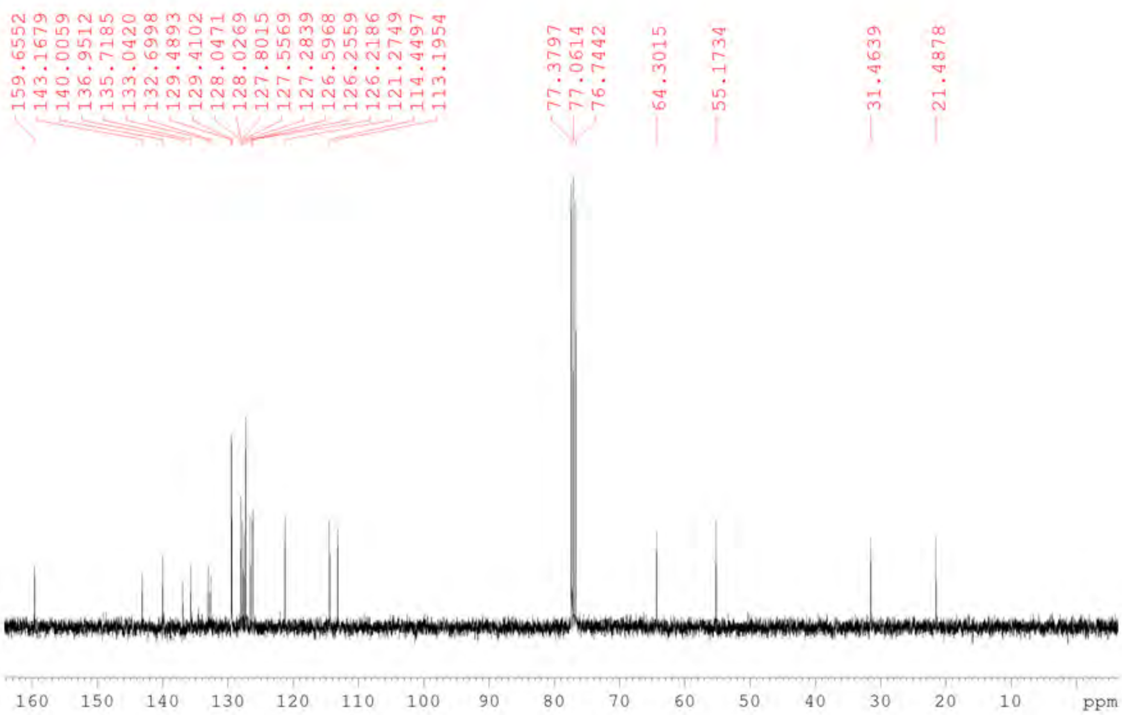



[$^1$H and $^{13}$C NMR Spectra of **3ea**]

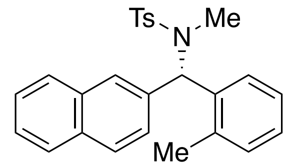



**3ea**

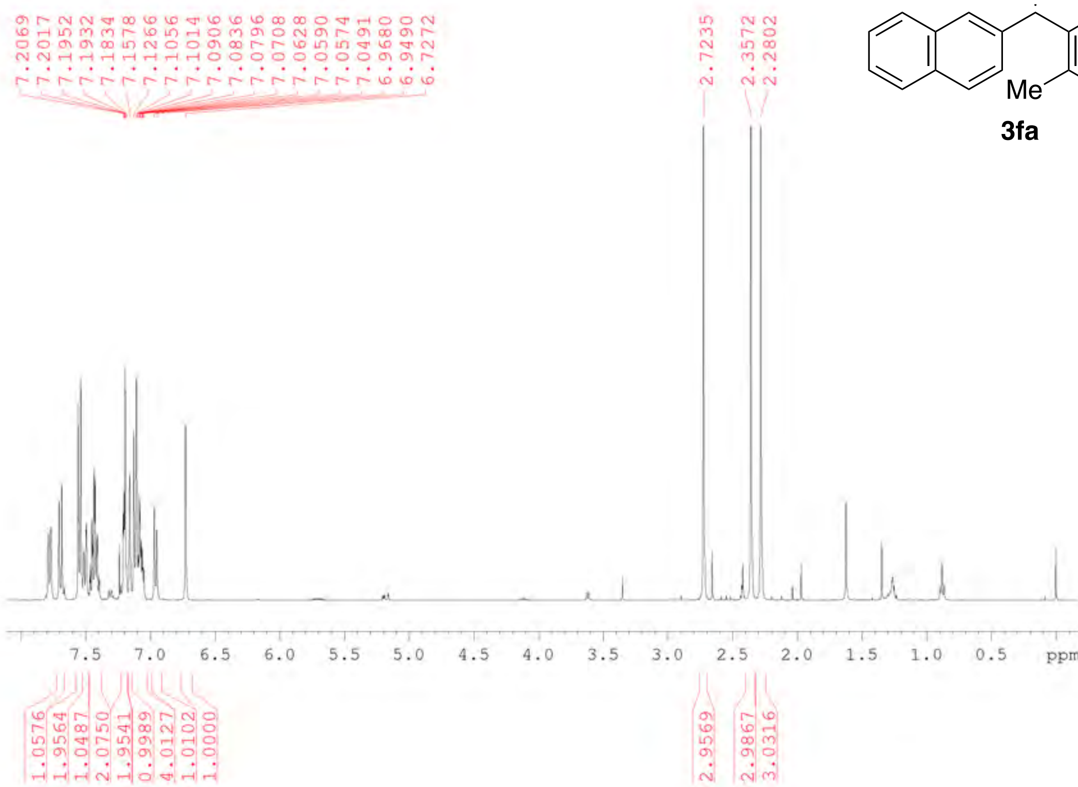


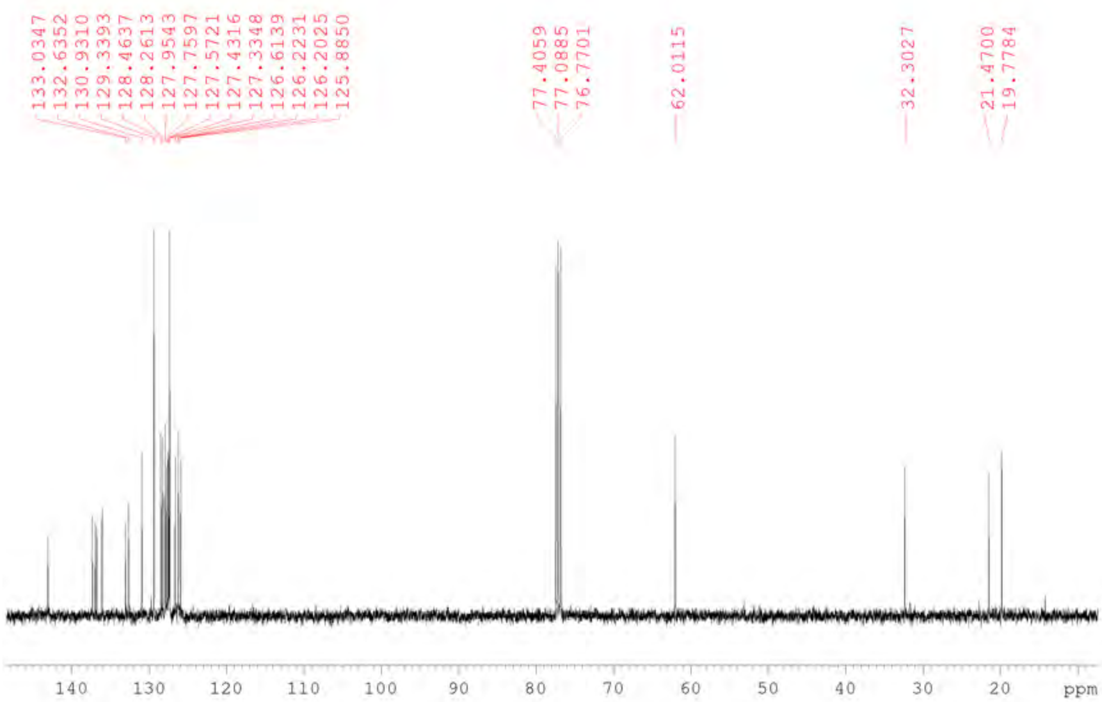



[$^{1}$H and $^{13}$C NMR Spectra of **3fa**]

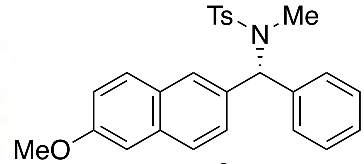


**3fa**

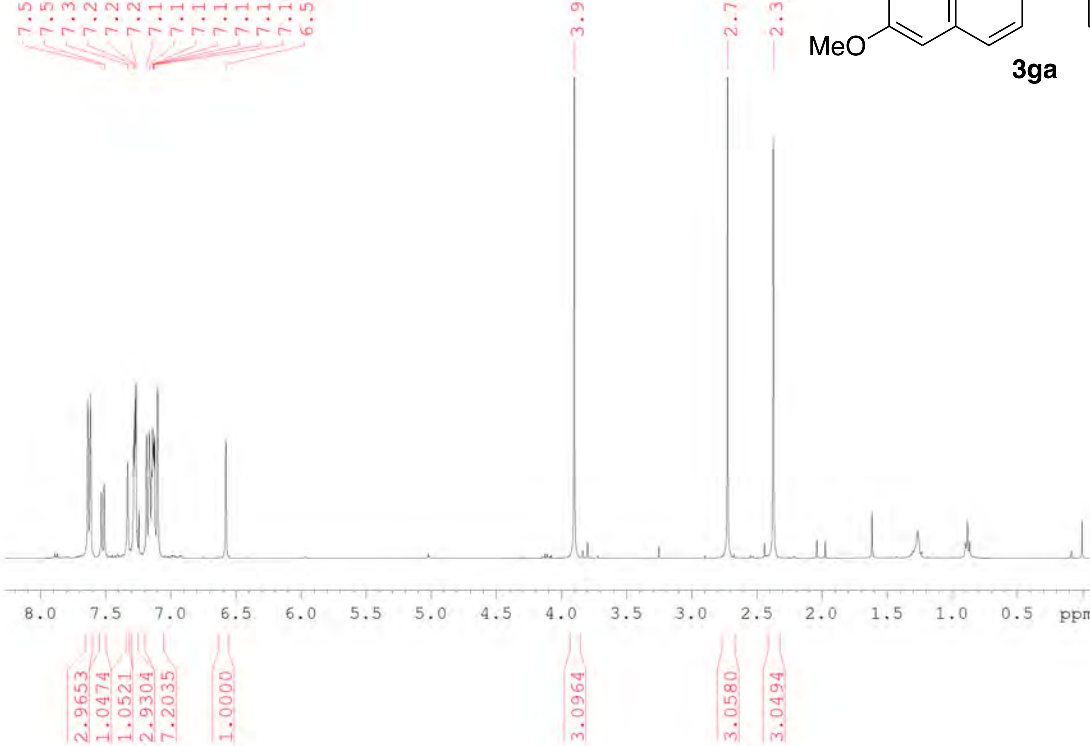


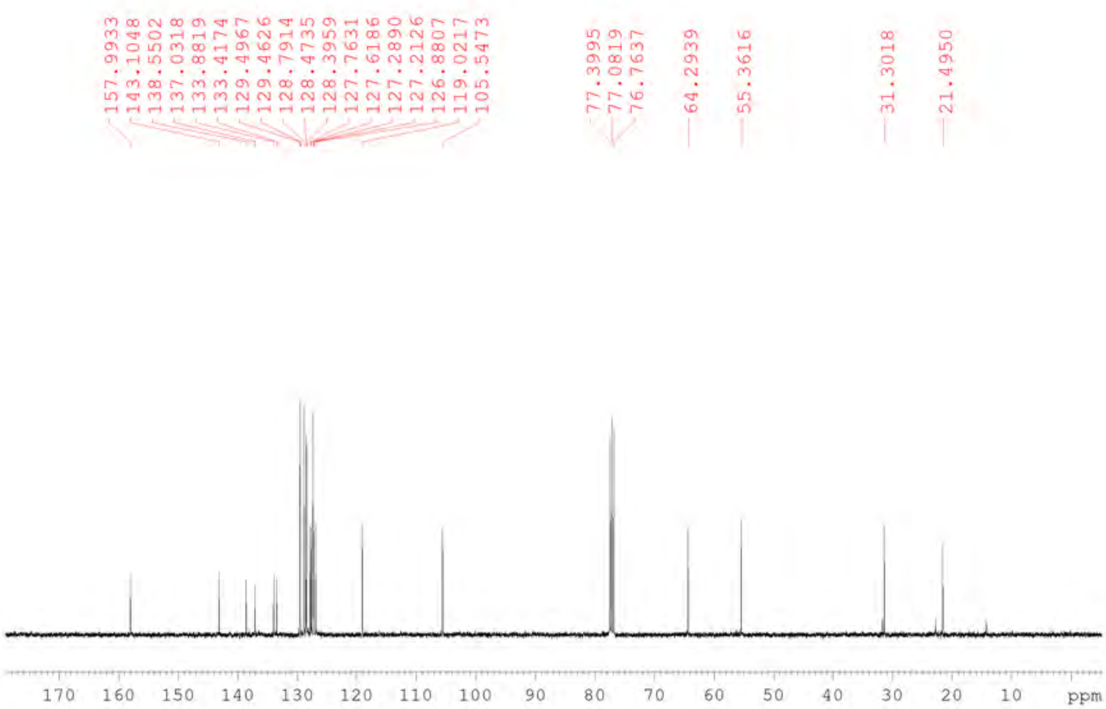


[$^1$H and $^{13}$C NMR Spectra of **3ga**]

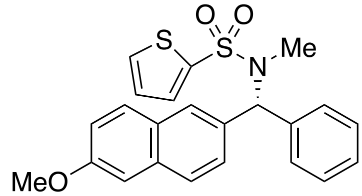



**3ga**

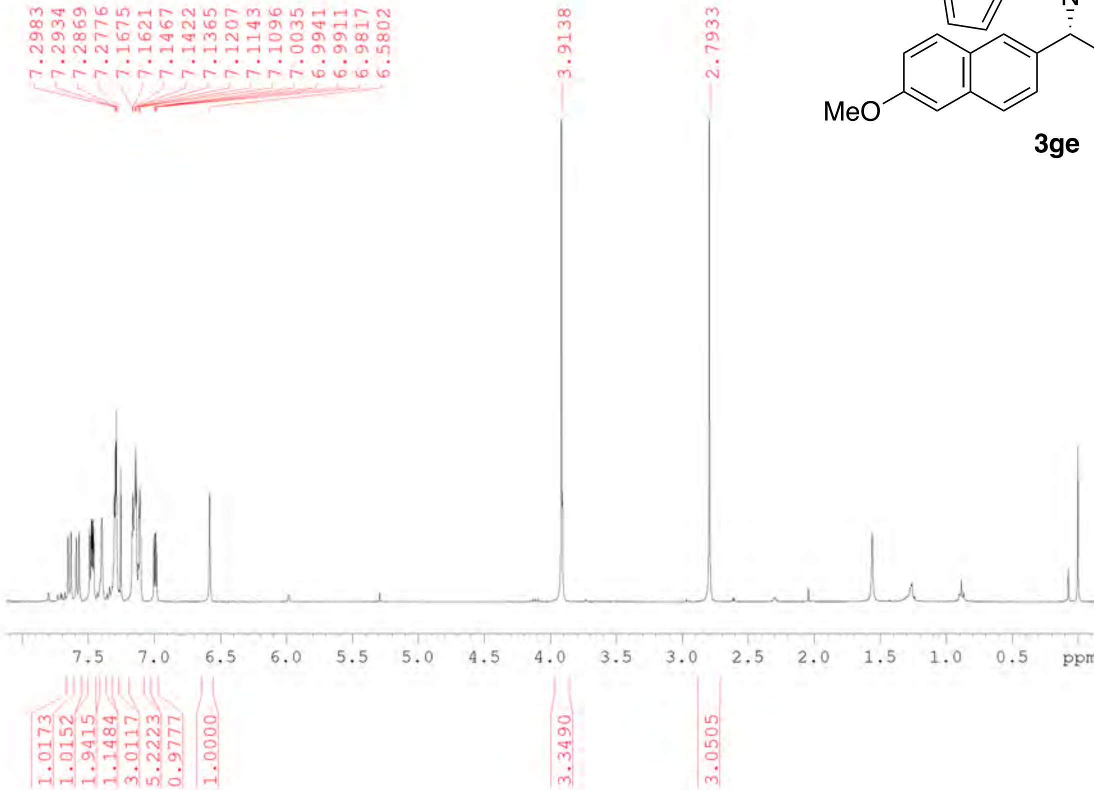


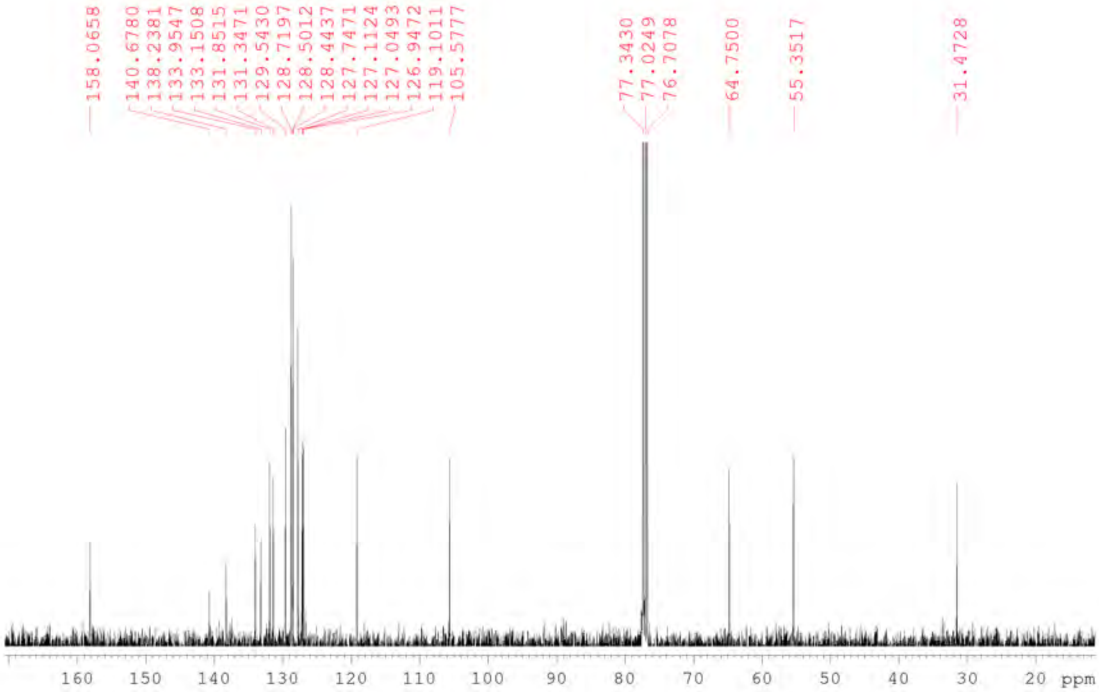



[[1]H and [13]C NMR Spectra of **3ge**]

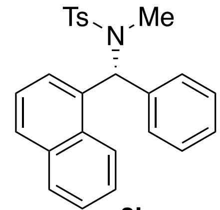


**3ge**

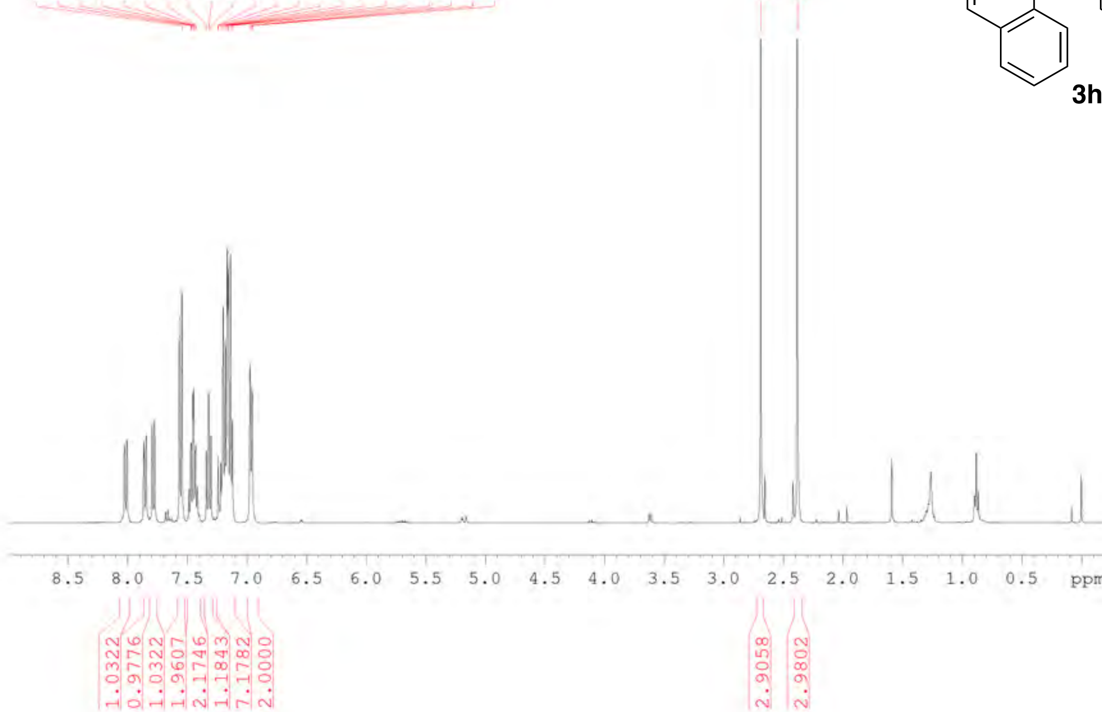


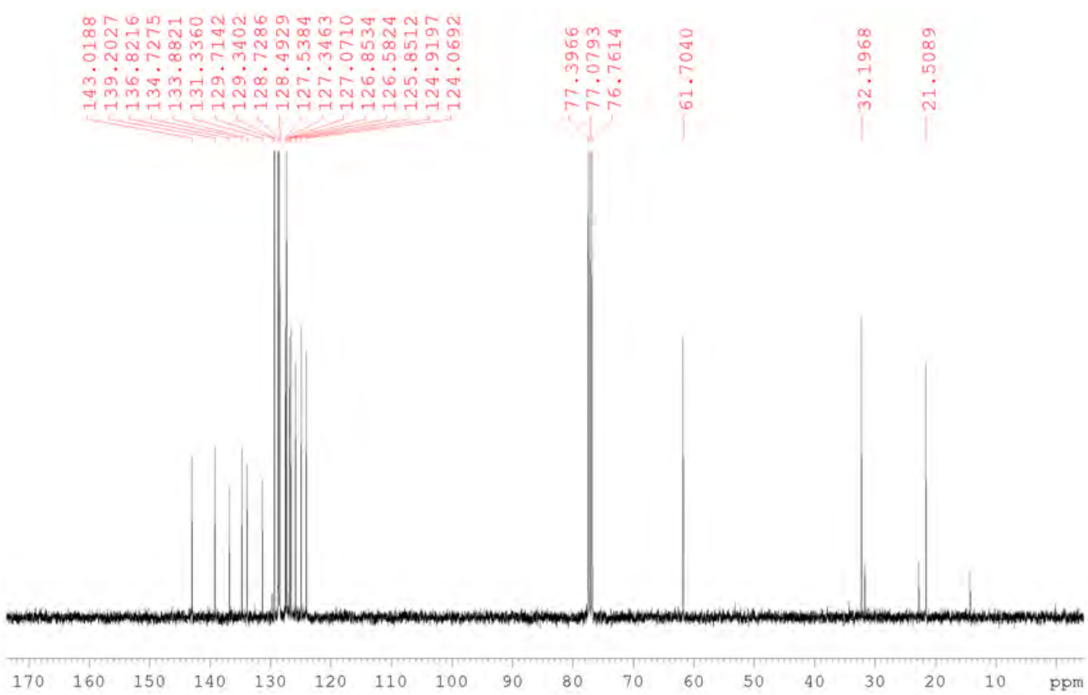


[$^{1}$H and $^{13}$C NMR Spectra of **3ha**]

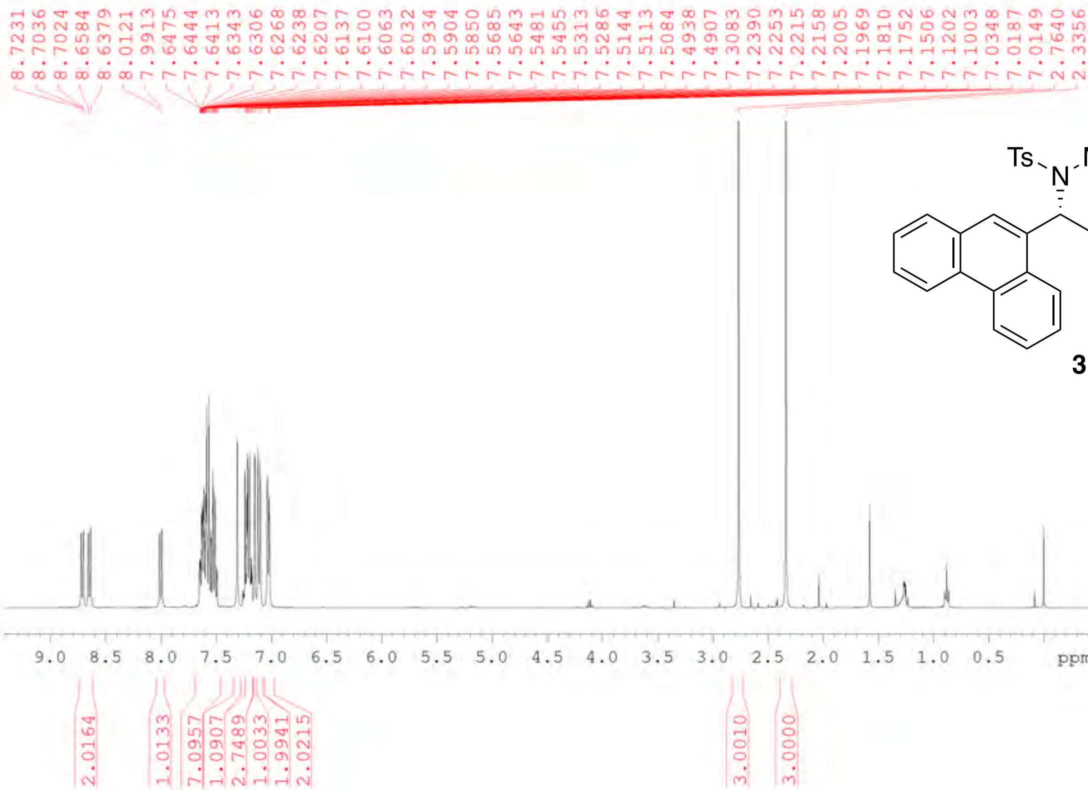


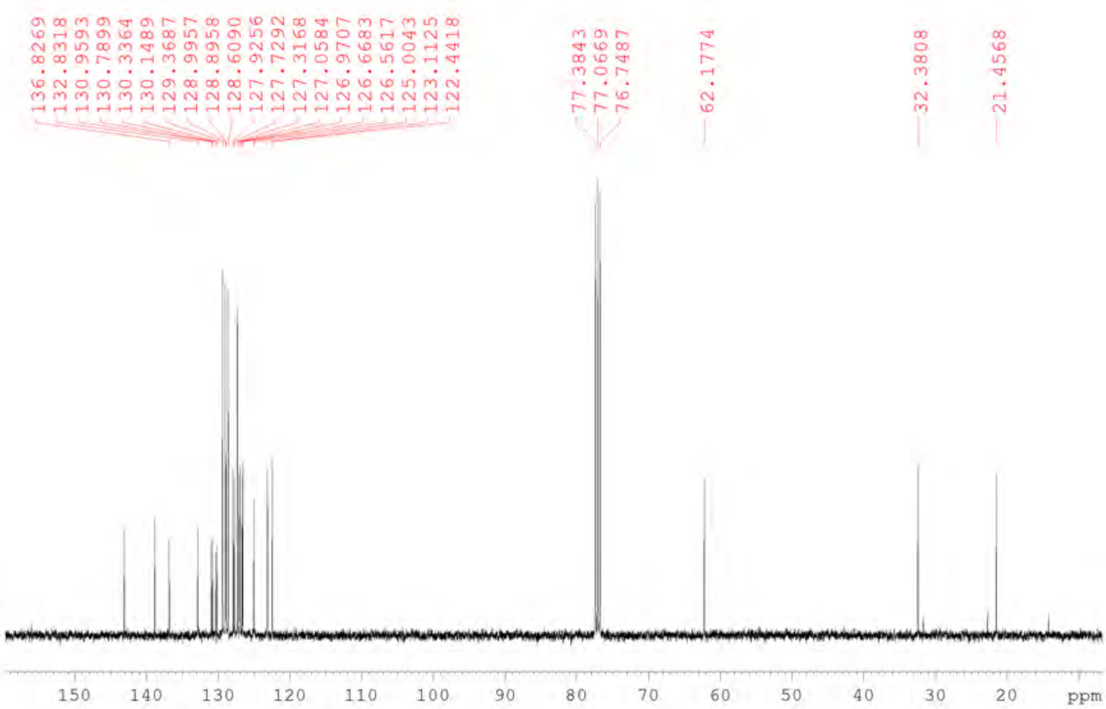

**3ha**



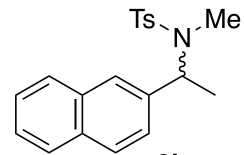



[$^{1}$H and $^{13}$C NMR Spectra of **3ia**]

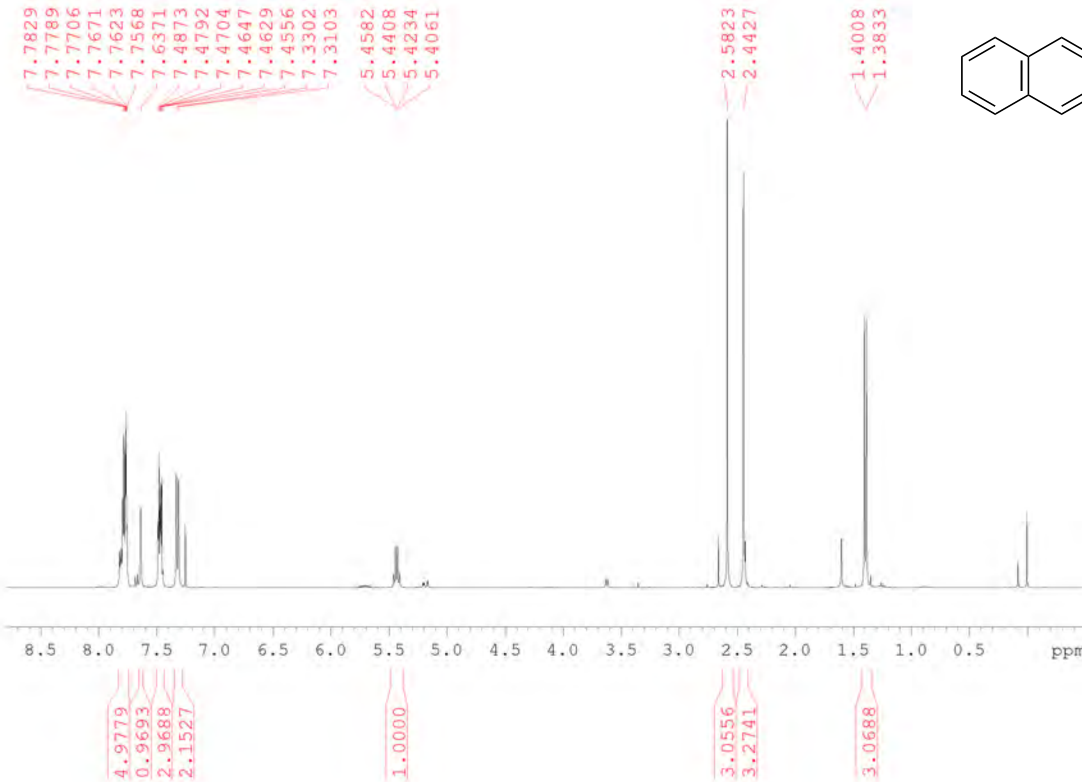


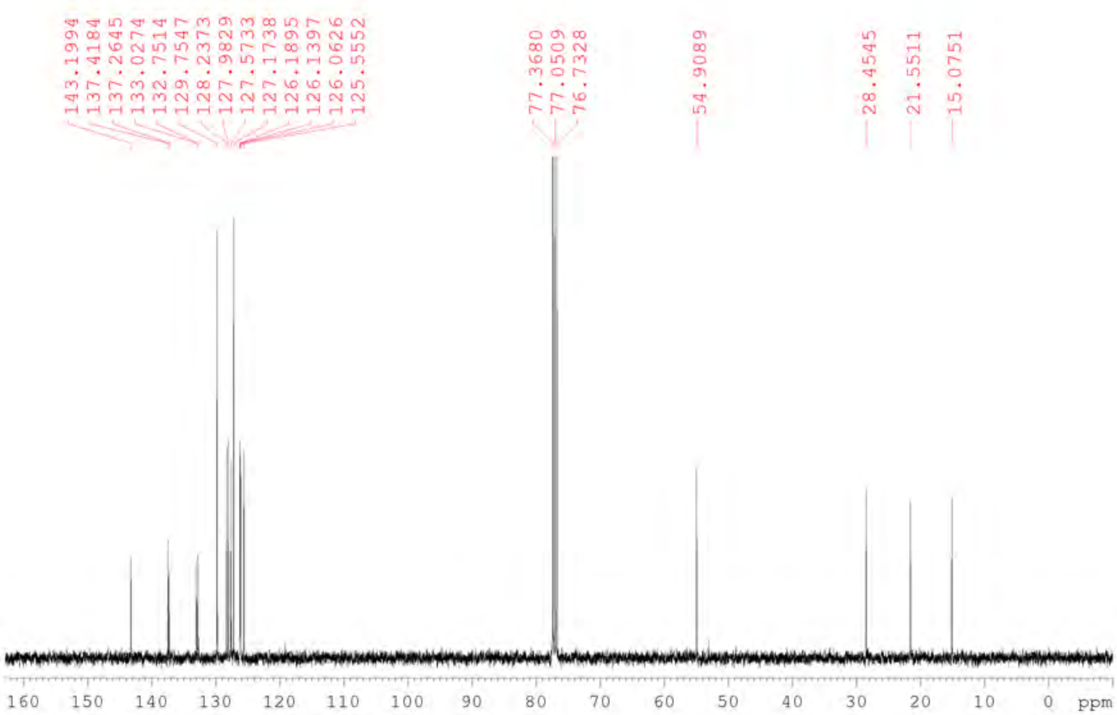



[$^1$H and $^{13}$C NMR Spectra of **3ja**]

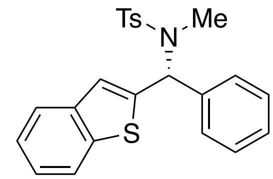



**3ja**

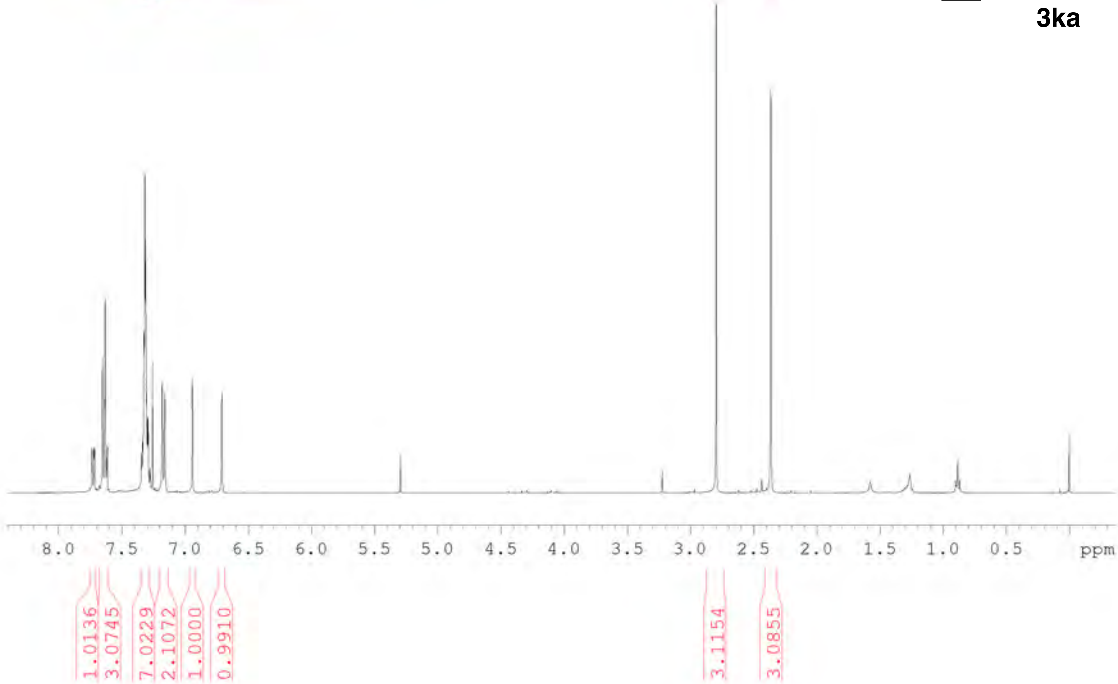


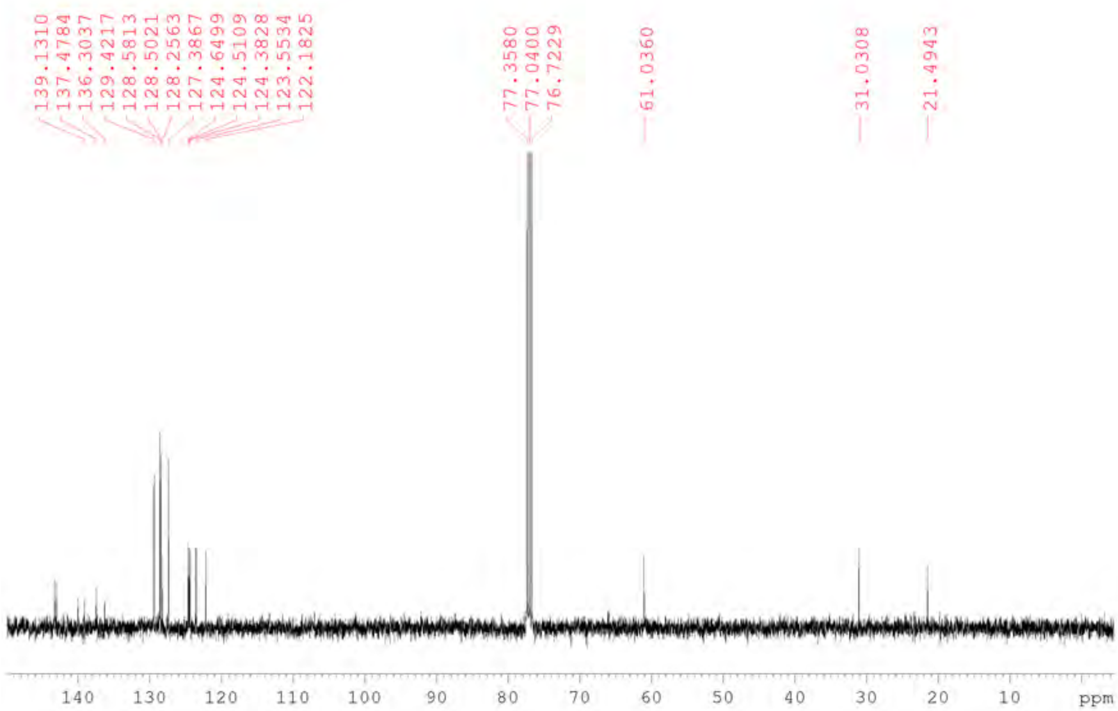



[$^1$H and $^{13}$C NMR Spectra of **3ka**]

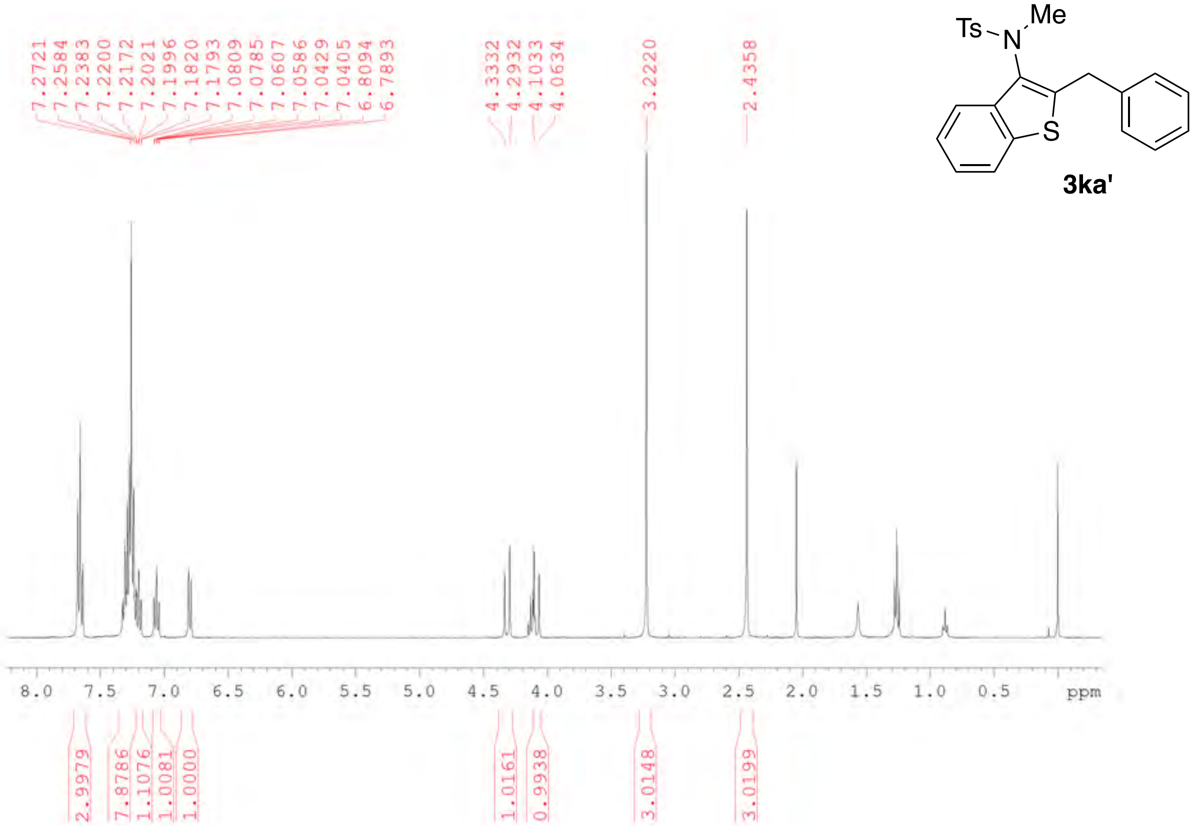


**3ka**

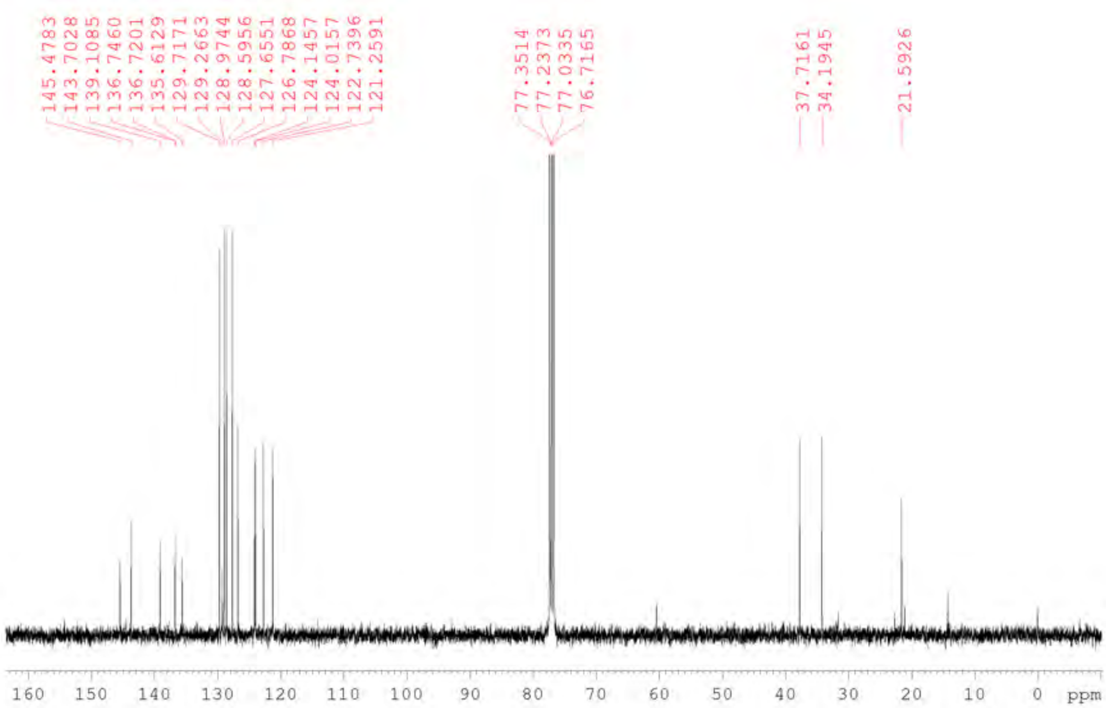


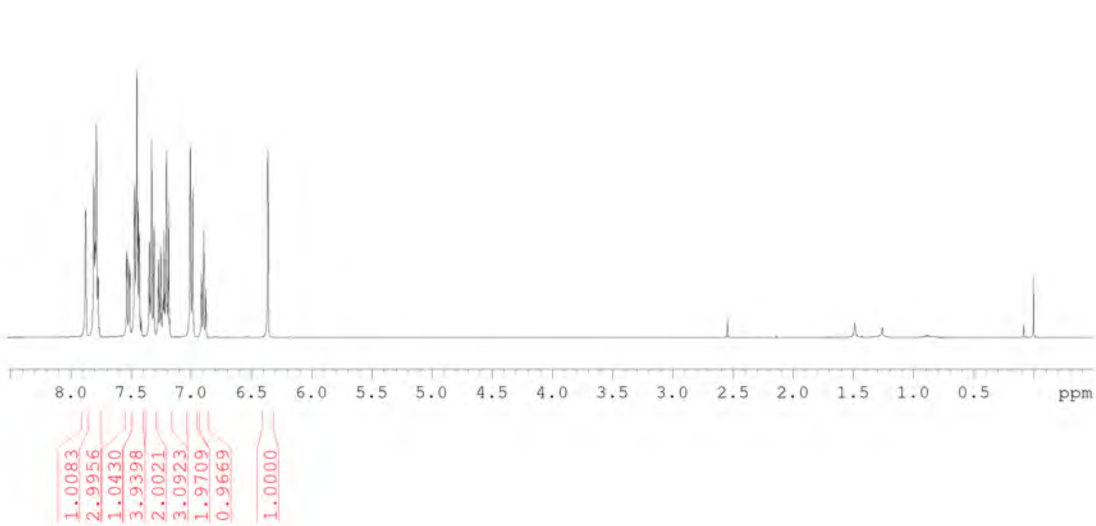
[[1]H and [13]C NMR Spectra of **3ka'**]

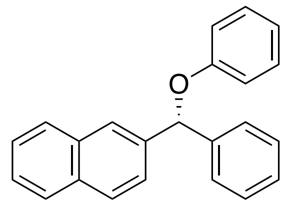


**3ka'**

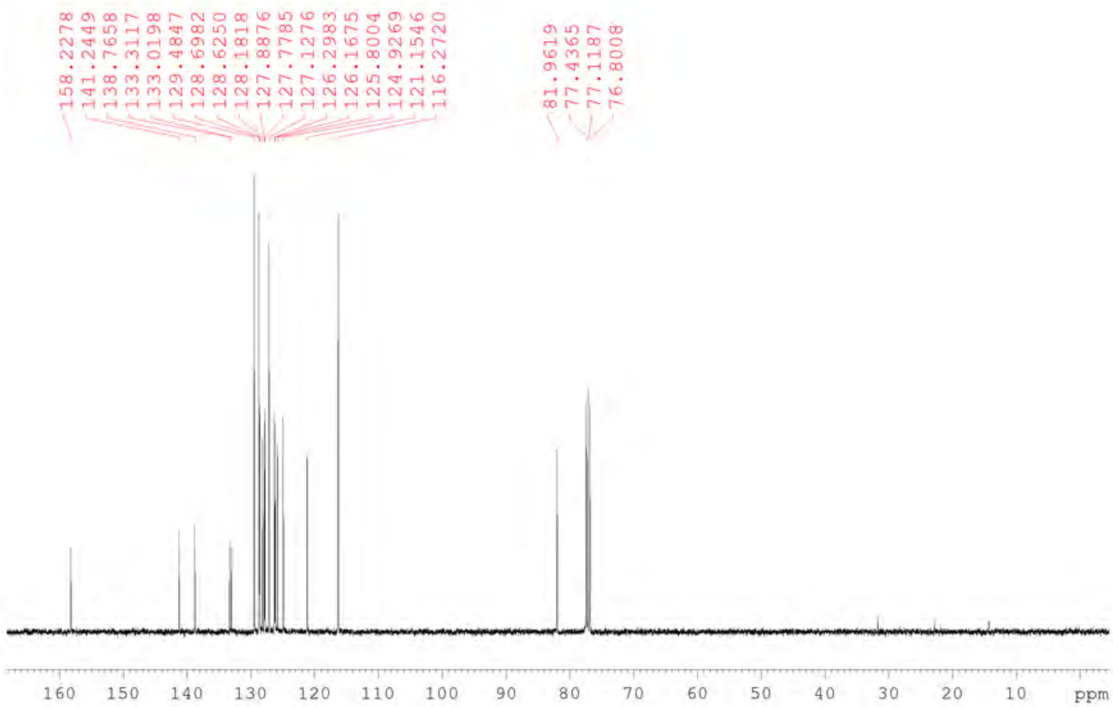


[$^{1}$H and $^{13}$C NMR Spectra of **6aa**]

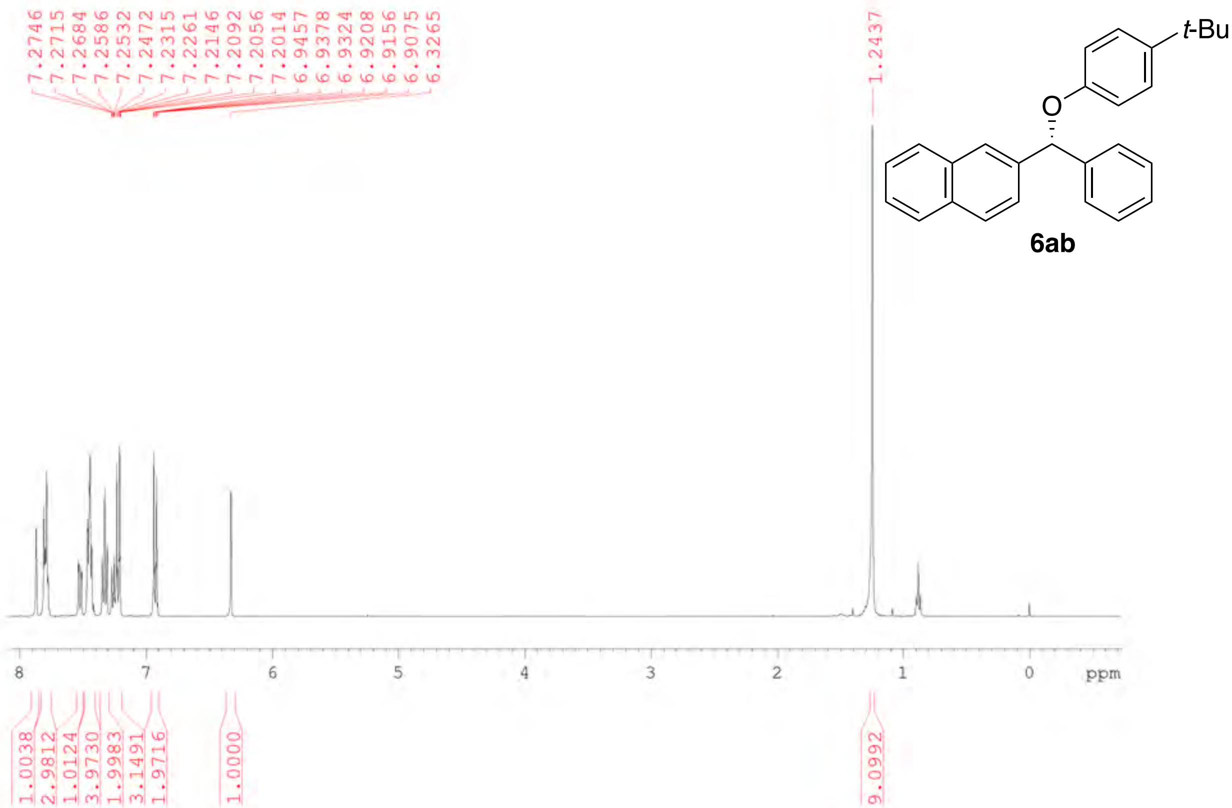


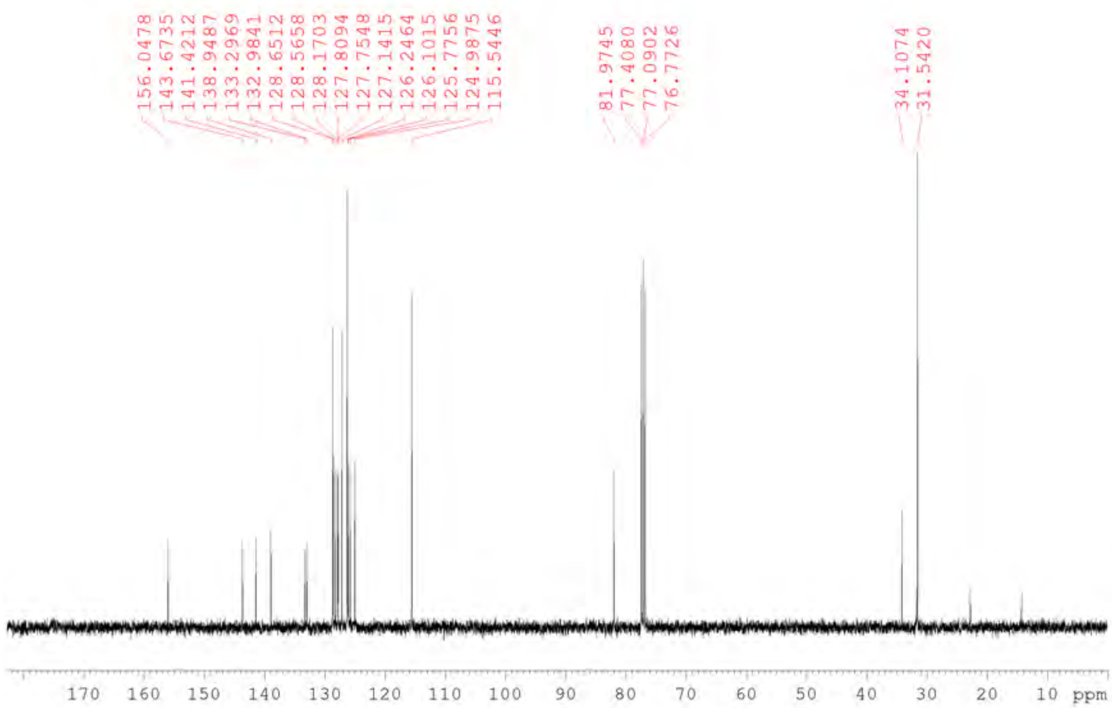




**6aa**



[$^{1}$H and $^{13}$C NMR Spectra of **6ab**]



[$^1$H, $^{13}$C, and $^{19}$F NMR Spectra of **6ac**]