Enantioselective Conjugate Silyl Additions to Cyclic and Acyclic Unsaturated Carbonyls Catalyzed by Cu Complexes of Chiral *N*-Heterocyclic Carbenes

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SUPPORTING INFORMATION, PART I

List of Contents

General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, bs = broad singlet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility at Boston College. Enantiomer ratios were determined by HPLC analysis (Chiral Technologies Chiralpak AD-H, 4.6 x 250 mm, Chiral Technologies Chiralcel OD, 4.6 x 250 mm, Chiral Technologies Chiralcel AS, 4.6 x 250 mm, and Chiral Technologies Chiralcel OB-H, 4.6 x 250 mm) in comparison with authentic racemic materials. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard dry box or vacuum-line techniques. Tetrahydrofuran (THF) was purified by distillation from sodium benzophenone ketyl immediately prior to use. All work-up and purification procedures were carried out in air. All solvents were purchased from Doe and Ingalls. (Dimethylphenylsilyl)boronic acid pinacol ester [$PhMe_2Si(Bpin)$] was purchased from Aldrich and distilled prior to use. All substrates were purchased from Aldrich and distilled prior to use. 2-Cyclooctenone and dienones (**17** and **18**) were prepared based on a previously reported procedure.[1] Sodium *t*-butoxide and copper(I) chloride were purchased from Strem and used as received.

NOTE: It is imperative that dry and pure reagents, Cu salt and imidazolinium salt are utilized in order to achieve optimal efficiency and enantioselectivity.

■ **Representative Procedure for NHC–Cu-Catalyzed Enantioselective Conjugate Silyl Additions:** Preparation of the desired NHC–CuO*t*-Bu: In an oven-dried vial (6 x 1 cm) equipped with a stir bar, imidazolinium tetrafluoroborate salt **12** (22 mg, 0.036 mmol), NaO*t*-Bu (6.9 mg, 0.072 mmol), and CuCl (3.3 mg, 0.033 mmol) were placed and 5.0 mL of THF was added. After the solution was allowed to stir for two hours at 22 °C under a dry N_2 atmosphere, it was filtered through a short plug of flame-dried Celite.

An appropriate portion of the solution of NHC–CuO*t*-Bu (0.0033 mmol in 0.50 mL THF) was placed in a separate oven-dried vial (6 x 1 cm), and the resulting solution was charged with $PhMe_2Si(Bpin)$ [96 mg (0.36 mmol) in 0.50 mL THF]. The vessel was then removed from the glovebox, placed in a fume hood and cooled to –78 °C. 2-Cyclohexenone (32 mg, 0.33 mmol)

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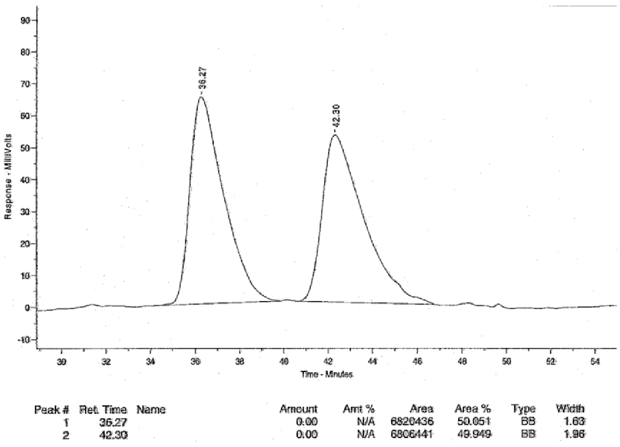
[1] (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011–1013. (b) Hayashi, T.; Yamamoto, S.; Tokunaga, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4224–4227. (c) Henon, H.; Mauduit, M.; Alexakis, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9122–9124.

was added and the mixture was allowed to stir for one hour at –78 °C, after which the reaction was quenched by the addition of H_2O (3 mL) and the mixture was allowed to warm to 22 °C and stir for an additional 15 minutes. The layers were separated, and the aqueous layer was washed with Et_2O (10 mL x 3). The combined organic layers were dried over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the resulting light yellow oil was purified by silica gel chromatography (hexanes/Et_2O:5/1) to afford 71 mg (0.31 mmol, 92% yield) of (*S*)-3-(dimethyl(phenyl)silyl)-cyclohexanone **6**, as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.45 (2H, m), 7.41-7.34 (3H, m), 2.40-2.21 (3H, m), 2.21-2.06 (2H, m), 1.85-1.78 (1H, m), 1.77-1.64 (1H, m), 1.42 (1H, ddd, *J* = 25.6, 12.8, 3.6 Hz), 1.33-1.25 (1H, m), 0.31 (3H, s), 0.31(3H, s). Optical rotation:[2] $[\alpha]_D^{20}$ –75.6 (*c* 1.00, $CHCl_3$) for a sample with 97.4:2.6 er. The spectroscopic data match those reported previously.[3] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97.4:2.6 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.7/0.3 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



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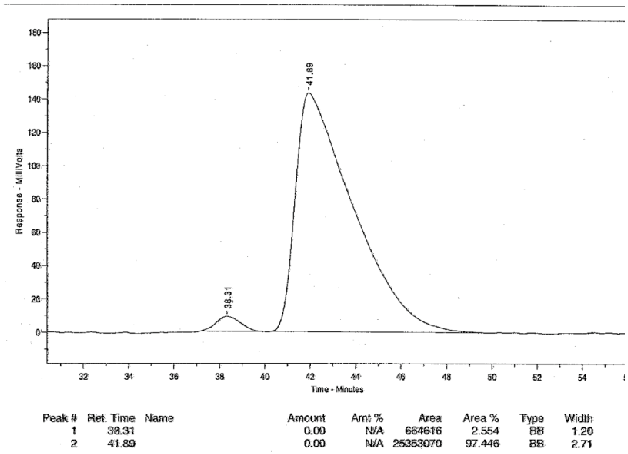

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1	38.31		0.00	N/A	664616	2.554	BB	1.20
2	41.89		0.00	N/A	25353070	97.446	BB	2.71

Retention time	Area	Area %	Retention time	Area	Area %
36.27	6820436	50.051	38.31	664616	2.554
42.30	6806440	49.949	41.89	25353070	97.446

(*S*)-3-(Dimethyl(phenyl)silyl)cyclopentanone (Table 2, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (2H, m), 7.40-7.33 (3H, m), 2.29-2.17 (2H, m), 2.14-2.04 (2H, m), 1.92-1.84 (1H, m), 1.73-1.61 (1H, m), 1.58-1.48 (1H, m), 0.31 (6H, s). Optical rotation:[2] $[\alpha]_D^{20}$ –42.9 (*c* 2.06, $CHCl_3$) for a sample with 90:10 er. The spectroscopic data match those reported previously.[3] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (90:10 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

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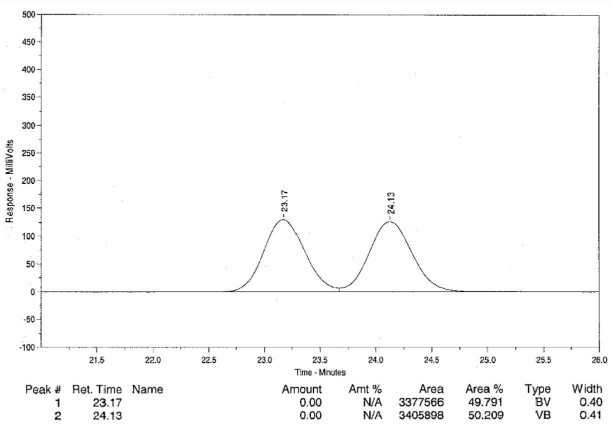
(2) Walter, C.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5675–5677.

(3) Ito, H.; Ishizuka, T.; Tateiwa, J.-i.; Sonoda, M.; Hosomi, A. *J. Am. Chem. Soc.* **1998**, *120*, 11196–11197.



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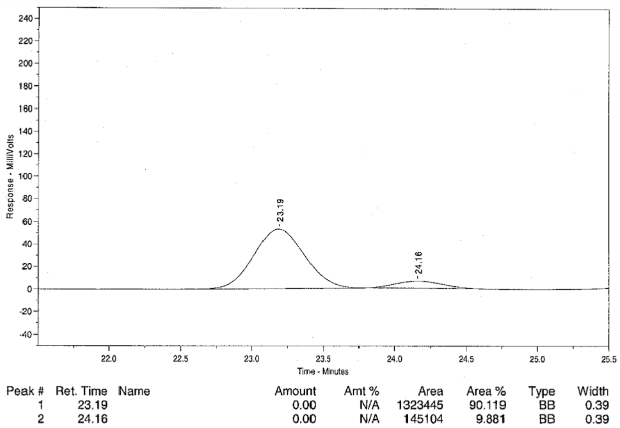
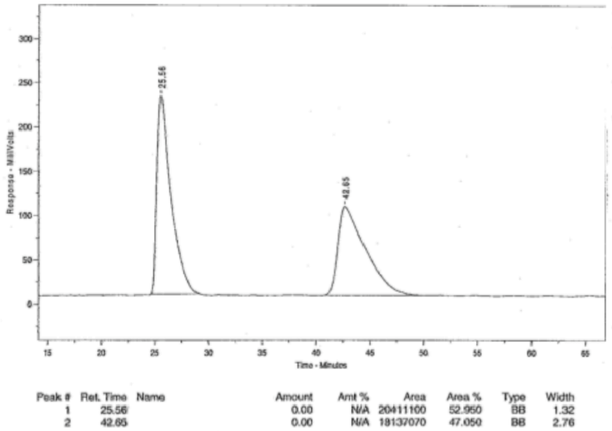


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	23.19		0.00	N/A	1323445	90.119	BB	0.39
2	24.16		0.00	N/A	145104	9.881	BB	0.39

Retention time	Area	Area %	Retention time	Area	Area %
23.17	3377566	49.791	23.19	1323445	90.119
24.13	3405898	50.209	24.16	145104	9.881

(*S*)-3-(Dimethyl(phenyl)silyl)cycloheptanone (Table 2, entry 3). IR (neat): 2921 (m), 2849 (w), 1696 (s), 1443 (m), 1248 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49-7.46 (2H, m), 7.38-7.32 (3H, m), 2.59-2.26 (4H, m), 2.08-1.85 (3H, m), 1.54-1.42 (1H, m), 1.33-1.03 (3H, m), 0.29 (3H, s), 0.28 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 216.0, 137.7, 134.6, 129.9, 128.5, 45.2, 44.1, 32.5, 31.8, 25.0, 24.0, –4.3, –4.5; HRMS (ES$^+$) Calcd for $C_{15}H_{22}SiONa$ [M+Na]: 269.1338, Found: 269.1329. Optical rotation:[2] $[\alpha]_D^{20}$ –75.0 (*c* 1.00, CHCl$_3$) for a sample with 97:3 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.7/0.3 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
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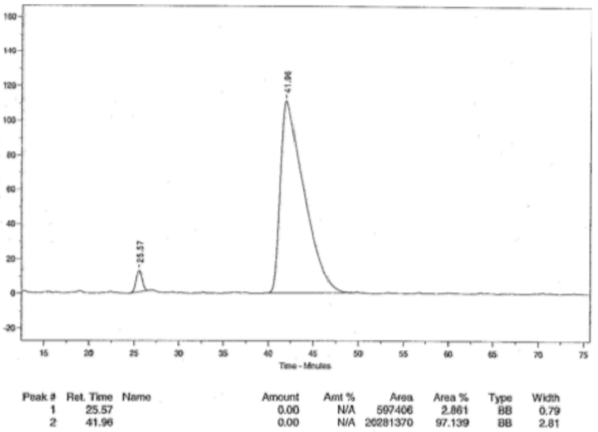

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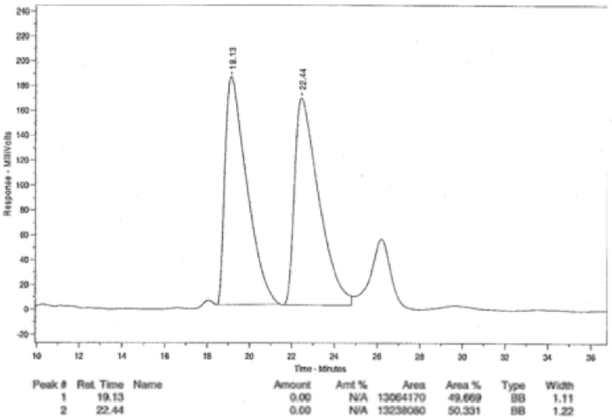
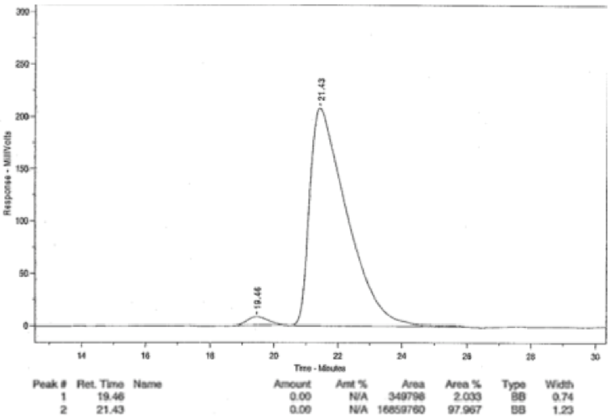
1	25.57		0.00	N/A	597406	2.861	BB	0.79
2	41.96		0.00	N/A	20281370	97.139	BB	2.81

Retention time	Area	Area %	Retention time	Area	Area %
25.56	20411100	52.950	25.57	597406	2.861
42.65	18137070	47.050	41.96	20281370	97.139

3-(Dimethyl(phenyl)silyl)cyclooctanone (Table 2, entry 4). IR (neat): 2927 (m), 2857 (w), 1697 (s), 1408 (m), 1248 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52-7.48 (2H, m), 7.40-7.33 (3H, m), 2.57-2.50 (1H, m), 2.34-2.18 (3H, m), 1.88-1.76 (2H, m), 1.70-1.53 (3H, m), 1,48-1.19 (4H, m), 0.31 (3H, s), 0.31 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 219.6, 137.5, 134.1, 129.4, 128.1, 43.2, 41.7, 28.3, 27.1, 26.5, 26.2, 24.1, –4.6, –4.8; HRMS (ES$^+$) Calcd for $C_{16}H_{24}SiONa$

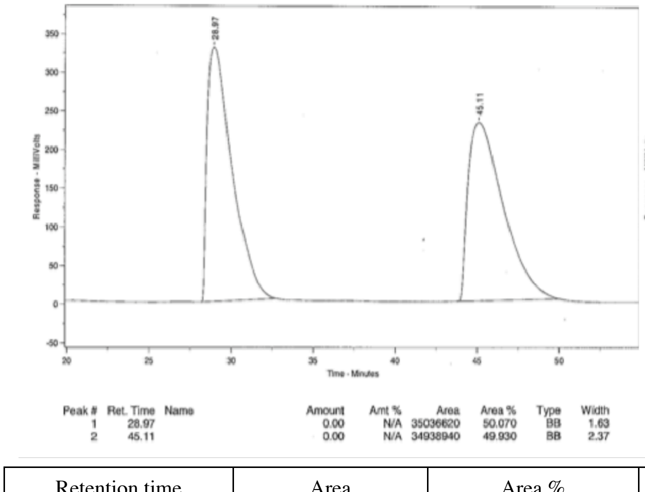
[M+Na]: 283.1494, Found: 283.1495. Optical rotation: $[\alpha]_D^{20}$ +25.4 (*c* 1.45, $CHCl_3$) for a sample with 98:2 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.7/0.3 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

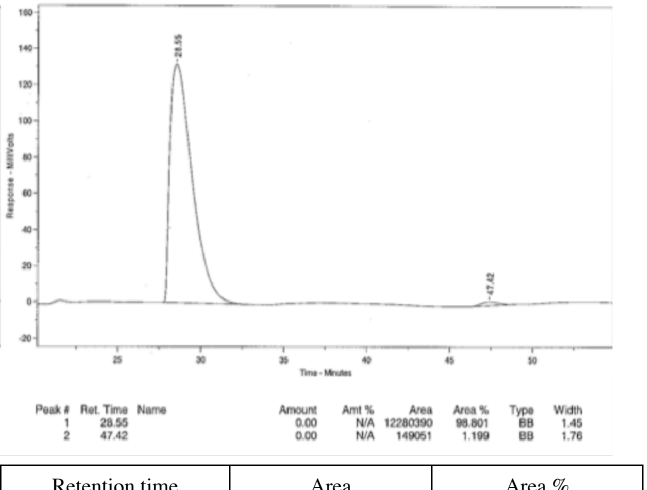




Retention time	Area	Area %	Retention time	Area	Area %
19.13	13064170	49.669	19.46	349798	2.033
22.44	13238080	50.331	21.43	16859760	97.967

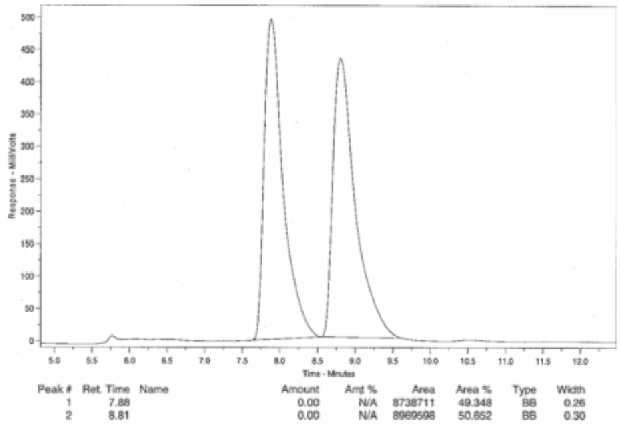
(*R*)-4-(Dimethyl(phenyl)silyl)-3,3-dimethylcyclopentanone (Table 2, entry 5). IR (neat): 2954 (m), 1738 (s), 1427 (m), 1402 (m), 1250 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (2H, m), 7.38-7.33 (3H, m), 2.38-2.23 (2H, m), 2.63 (2H, dd, *J* = 29.6, 17.6 Hz), 1.51 (1H, dd, *J* = 12.8, 9.2 Hz), 1.10 (3H, s), 1.00 (3H, s), 0.42 (3H, s), 0.38 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.6, 139.1, 134.4, 129.8, 128.6, 57.3, 40.7, 40.6, 36.8, 30.8, 26.3, –1.6, –2.2; HRMS (ES$^+$) Calcd for $C_{15}H_{22}SiONa$ [M+Na]: 269.1338, Found: 269.1335. Optical rotation: $[\alpha]_D^{20}$ –118.6 (*c* 1.05, $CHCl_3$) for a sample with 99:1 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown below; chiracel OD column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).





Retention time	Area	Area %	Retention time	Area	Area %
28.97	35036620	50.070	28.55	12280390	98.801
45.11	34938940	49.930	47.42	149051	1.199

(*R*)-3-(Dimethyl(phenyl)silyl)-4,4-dimethylcyclohexanone (Table 2, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.46 (2H, m), 7.36-7.33 (3H, m), 2.45-2.19 (4H, m), 1.73-1.61 (2H, m), 1.37 (1H, dd, *J* = 14.0, 3.6 Hz), 1.10 (3H, s), 0.98 (3H, s), 0.39 (3H, s), 0.36 (3H, s). Optical rotation: $[\alpha]_D^{20}$ –71.7 (*c* 1.30, $CHCl_3$) for a sample with 99:1 er. The spectroscopic data match those reported previously.[4] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (99:1 er shown below; chiracel OD column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



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Peak #  Ret. Time  Name     Amount  Amt %     Area   Area %  Type  Width
   1       7.88              0.00    N/A   8738711   49.348   BB    0.26
   2       8.81              0.00    N/A   8969598   50.652   BB    0.30
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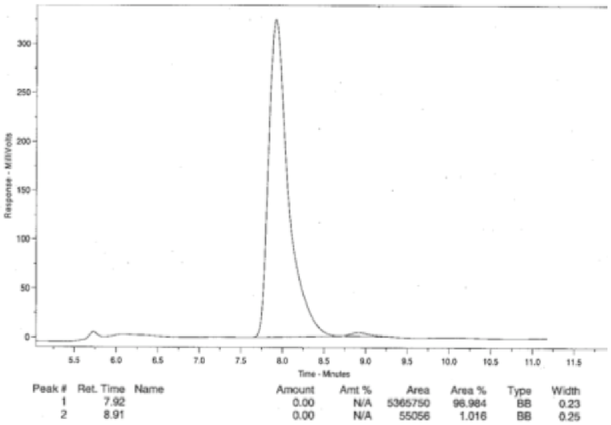

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Peak #  Ret. Time  Name     Amount  Amt %     Area   Area %  Type  Width
   1       7.92              0.00    N/A   5365750   98.984   BB    0.23
   2       8.91              0.00    N/A     55056    1.016   BB    0.25
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Retention time	Area	Area %	Retention time	Area	Area %
7.88	8738711	49.348	7.92	5365750	98.984
8.81	8969598	50.652	8.91	55056	1.016

(*S*)-7-(Dimethyl(phenyl)silyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (Table 2, entry 7). IR (neat): 2951 (m), 1672 (s), 1598 (m), 1427 (m), 1250 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (1H, dd, *J* = 6.0, 1.2 Hz), 7.53-7.50 (2H, m), 7.45 (1H, td, *J* = 6.0, 1.2 Hz), 7.43-7.32 (4H, m), 7.18 (1H, d, *J* = 6.0 Hz), 2.97-2.91 (1H, m), 2.89-2.73 (2H, m), 2.54 (1H, dd, *J* = 13.6, 10.4 Hz), 1.90-1.78 (2H, m), 1.30-1.23 (1H, m), 0.35 (3H, s), 0.34 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 140.9, 138.7, 137.1, 134.2, 132.6, 129.7, 129.5, 128.9, 128.1, 127.0, 41.9, 33.3, 27.1, 18.9, –4.7, –4.8; HRMS (ES$^+$) Calcd for $C_{19}H_{26}SiNO$ [M+NH$_4$]: 312.1784, Found: 312.1770. Optical rotation: $[\alpha]_D^{20}$ +2.80 (*c* 1.00, $CHCl_3$) for a sample with 96.5:3.5 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (96.5:3.5 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.9 mL/min, 220 nm).

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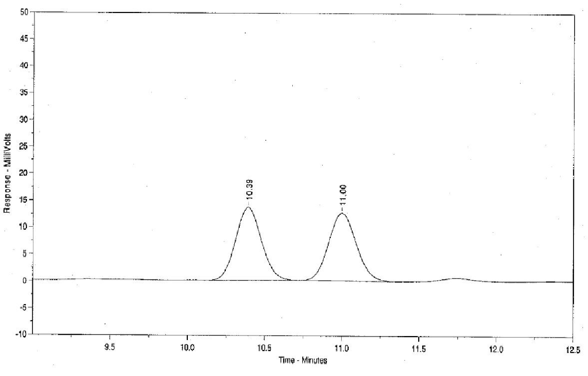
(4) Auer, G.; Weiner, B.; Oestreich, M. *Synthesis* **2006**, 2113–2116.



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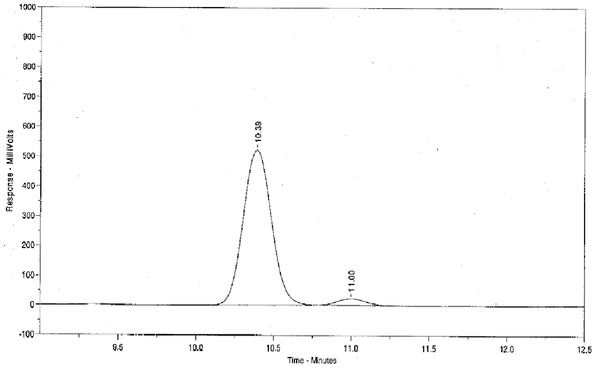
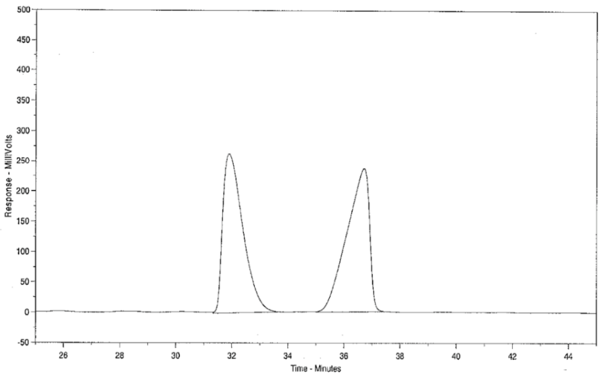


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	10.39		0.00	N/A	6586232	96.420	BB	0.20
2	11.00		0.00	N/A	244545	3.580	BB	0.19

Retention time	Area	Area %	Retention time	Area	Area %
10.39	158719	50.098	10.39	6586232	96.420
11.00	158096	49.902	11.00	244545	3.580

(*S*)-4-(Dimethyl(phenyl)silyl)tetrahydro-2*H*-pyran-2-one (Table 2, entry 8). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49-7.46 (2H, m), 7.43-7.35 (3H, m), 4.34 (1H, dt, *J* = 10.8, 4.8 Hz), 4.25 (1H, ddd, *J* = 10.8, 10.0, 4.0 Hz), 2.57 (1H, ddd, *J* = 17.2, 6.0, 1.6 Hz), 2.28 (1H, dd, *J* = 17.6, 13.2 Hz), 1.88-1.81 (1H, m), 1.70-1.60 (1H, m), 1.44-1.36 (1H, m), 0.34 (6H, s). Optical rotation: $[\alpha]_D^{20}$ –29.6 (*c* 1.50, CHCl$_3$) for a sample with 92:8 er. The spectroscopic data match those reported previously.[5] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (92:8 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.9 mL/min, 220 nm).



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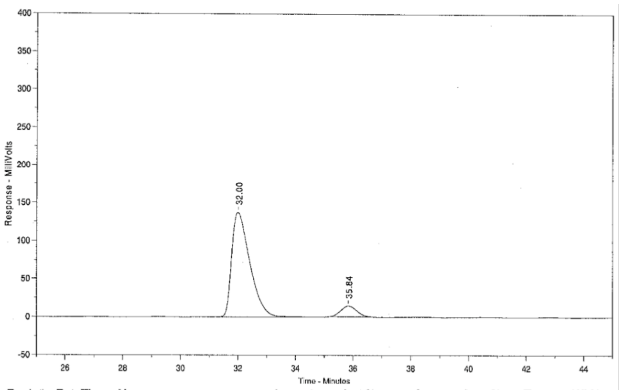

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1	32.00		0.00	N/A	6052143	91.779	BB	0.67
2	35.84		0.00	N/A	542116	8.221	BB	0.60

Retention time	Area	Area %	Retention time	Area	Area %
31.90	13093070	49.829	32.00	6052143	91.779
36.71	13182690	50.171	35.84	542116	8.221

(*S*)-4-(Dimethyl(phenyl)silyl)pentan-2-one (Table 3, entry 1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52-7.47 (2H, m), 7.39-7.33 (3H, m), 2.42 (1H, dd, *J* = 16.4, 3.6 Hz), 2.18 (1H, dd, *J* = 16.0, 10.8 Hz), 2.07 (3H, s), 1.54-1.45 (1H, m), 0.93 (3H, d, *J* = 7.2 Hz), 0.29 (3H, s), 0.28 (3H, s). Optical rotation: $[\alpha]_D^{20}$ +26.2 (*c* 0.55, CHCl$_3$) for a sample with 97:3 er. The spectroscopic data

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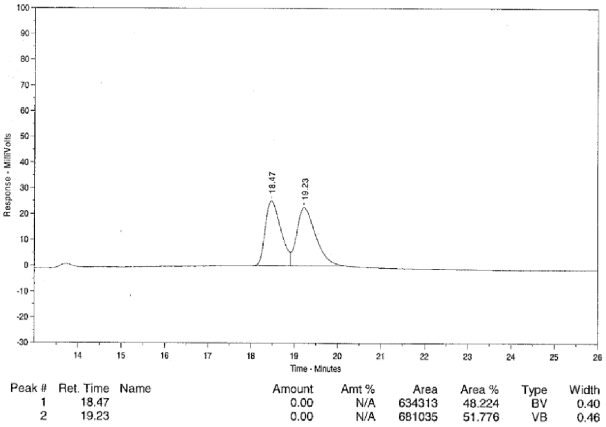
(5) Crump, R. A. N. C.; Fleming, I.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 701–706.

match those reported previously and the absolute configuration was assigned by comparison with reported data.[6] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99.8/0.2 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



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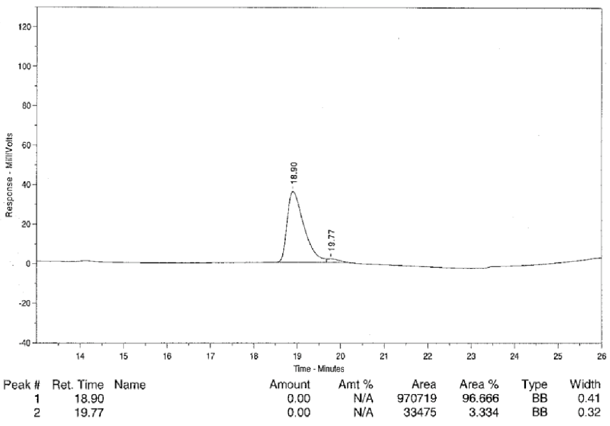
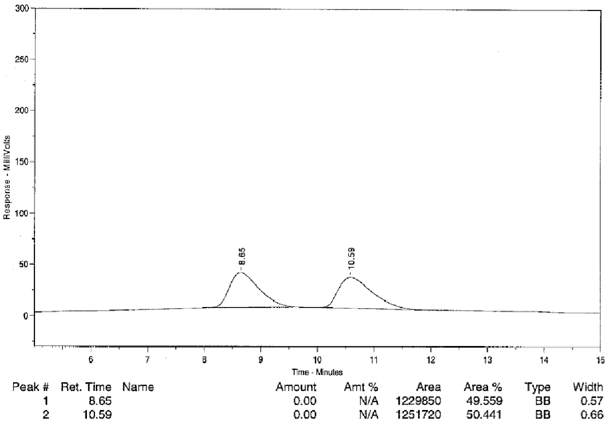
  1      18.47                0.00     N/A    634313   48.224    BV    0.40
  2      19.23                0.00     N/A    681035   51.776    VB    0.46
```



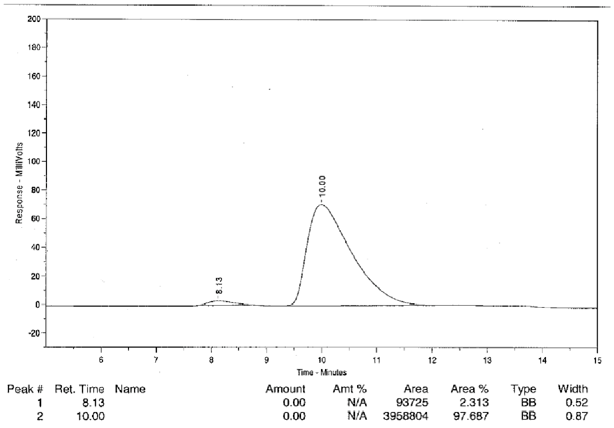
```
Peak #  Ret. Time  Name      Amount   Amt %   Area     Area %   Type  Width
  1      18.90                0.00     N/A    970719   96.666    BB    0.41
  2      19.77                0.00     N/A    33475     3.334    BB    0.32
```

Retention time	Area	Area %	Retention time	Area	Area %
18.47	634313	48.224	18.90	970719	96.666
19.23	681035	51.776	19.77	33475	3.334

(*S*)-4-(Dimethyl(phenyl)silyl)nonan-2-one (Table 3, entry 2). IR (neat): 2955 (m), 2925 (m), 1716 (s), 1427 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51-7.48 (2H, m), 7.36-7.31 (3H, m), 2.41 (1H, dd, J = 17.2, 5.2 Hz), 2.31 (1H, dd, J = 17.2, 8.0 Hz), 2.03 (3H, s), 1.54-1.38 (2H, m), 1.30-1.10 (7H, m), 0.85-0.82 (3H, m), 0.28 (3H, s), 0.27 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 209.2, 138.2, 133.9, 128.9, 127.7, 44.5, 32.0, 30.5, 29.8, 28.8, 22.5, 20.3, 14.0, –3.9, –4.4; HRMS (ESI$^+$) Calcd for $C_{17}H_{28}SiO$ [M+]: 276.1909, Found: 276.1923. Optical rotation: $[\alpha]_D^{20}$ +36.0 (*c* 1.97, CHCl$_3$) for a sample with 98:2 er. The absolute configuration was assigned by analogy to entry 1 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



```
Peak #  Ret. Time  Name      Amount   Amt %   Area      Area %   Type  Width
  1      8.65                 0.00     N/A    1229850   49.559    BB    0.57
  2      10.59                0.00     N/A    1251720   50.441    BB    0.66
```



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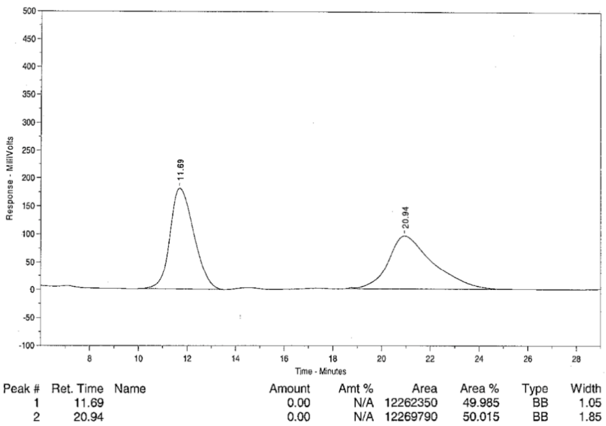
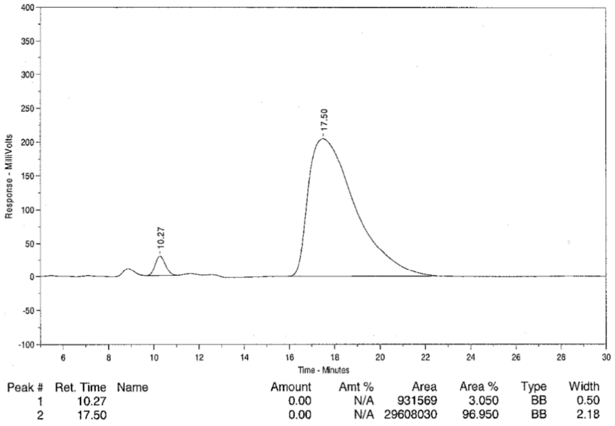
Peak #  Ret. Time  Name      Amount   Amt %   Area      Area %   Type  Width
  1      8.13                 0.00     N/A    93725      2.313    BB    0.52
  2      10.00                0.00     N/A    3958804   97.687    BB    0.87
```

Retention time	Area	Area %	Retention time	Area	Area %
8.65	1229850	49.559	8.13	93725	2.313
10.59	1251720	50.441	10.00	3958804	97.687

(*R*)-4-(Dimethyl(phenyl)silyl)-5-methylhexan-2-one (Table 3, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (2H, m), 7.36-7.32 (3H, m), 2.45 (1H, dd, *J* = 17.6, 7.2 Hz), 2.36 (1H, dd, *J* = 17.6, 5.2 Hz), 2.00 (3H, s), 1.93-1.82 (1H, m), 1.63-1.57 (1H, m), 0.88 (3H, d, *J* = 6.8 Hz), 0.82 (3H, d, *J* = 7.2 Hz), 0.33 (3H, s), 0.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 139.6, 134.6, 129.5, 128.4, 42.0, 30.4, 29.5, 28.2, 23.6, 21.9, –1.6, –2.4. Optical rotation: $[\alpha]_D^{20}$ +18.6 (*c* 2.45, $CHCl_3$) for a sample with 97:3 er. The spectroscopic data match those reported previously[6] and the absolute configuration was assigned by analogy to entry 1 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



```
Peak #  Ret. Time  Name        Amount   Amt %      Area   Area %   Type   Width
  1      11.69                  0.00     N/A   12262350   49.985    BB     1.05
  2      20.94                  0.00     N/A   12269790   50.015    BB     1.85
```



```
Peak #  Ret. Time  Name        Amount   Amt %      Area   Area %   Type   Width
  1      10.27                  0.00     N/A     931569    3.050    BB     0.50
  2      17.50                  0.00     N/A   29608030   96.950    BB     2.18
```

Retention time	Area	Area %	Retention time	Area	Area %
11.69	12262350	49.985	10.27	931569	3.050
20.94	12269790	50.015	17.50	29608030	96.950

(*R*)-4-(Dimethyl(phenyl)silyl)-4-phenylbutan-2-one (Table 3, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (5H, m), 7.19-7.15 (2H, m), 7.09-7.04 (1H, m), 6.93-6.91 (2H, m), 2.93-2.83 (2H, m), 2.62 (1H, dd, *J* = 22.8, 11.2 Hz), 1.92 (3H, s), 0.23 (3H, s), 0.20 (3H, s). Optical rotation: $[\alpha]_D^{20}$ +11.7 (*c* 1.00, $CHCl_3$) for a sample with 98.5:1.5 er. The spectroscopic data match those reported previously and the absolute configuration was assigned by comparison with reported data.[7] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (98.5:1.5 er shown below; chiracel OD column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

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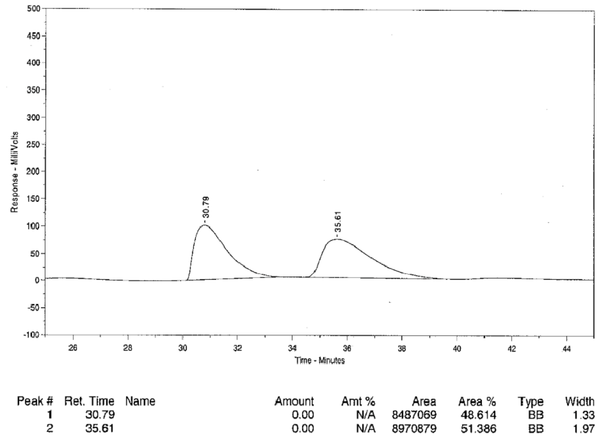
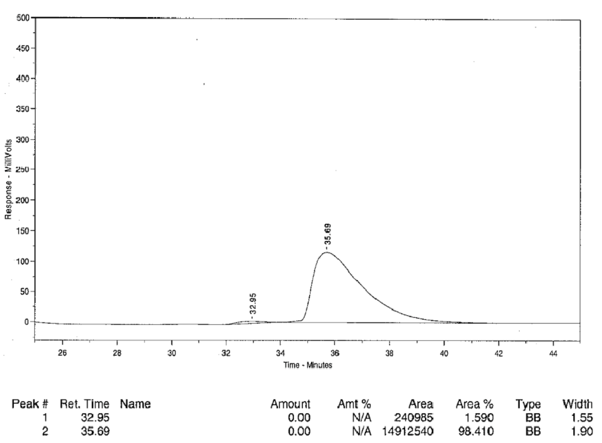
(6) Barbero, A.; Blakemore, D. C.; Fleming, I.; Wesley, R. N. *J. Chem. Soc. Perkin Trans. 1* **1997**, 1329–1352.

(7) Kacprzynski, M. A.; Kazane, S. A.; May, T. L.; Hoveyda, A. H. *Org. Lett.* **2007**, *9*, 3187–3190.



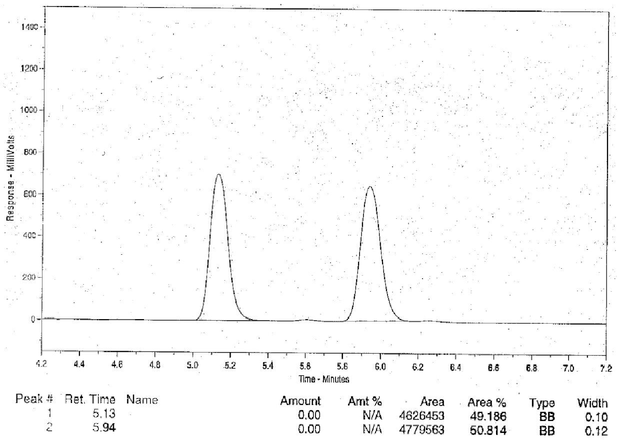
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	30.79		0.00	N/A	8487069	48.614	BB	1.33
2	35.61		0.00	N/A	8970879	51.386	BB	1.97



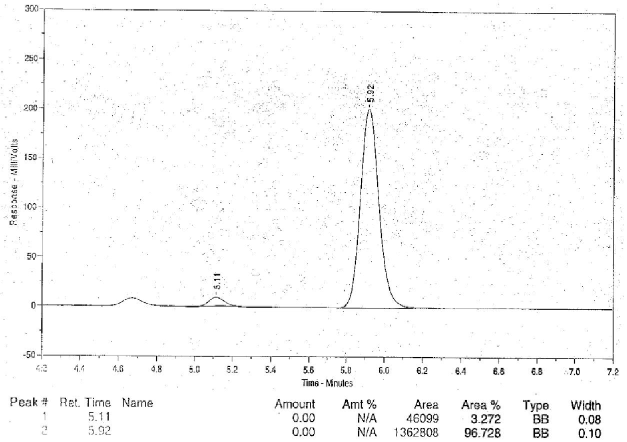
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	32.95		0.00	N/A	240985	1.590	BB	1.55
2	35.69		0.00	N/A	14912540	98.410	BB	1.90

Retention time	Area	Area %	Retention time	Area	Area %
30.79	8487069	48.614	32.95	240985	1.590
35.61	8970879	51.386	35.69	14912540	98.410

(*R*)-4-(Dimethyl(phenyl)silyl)-4-(4-methoxyphenyl)butan-2-one (Table 3, entry 5). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40-7.30 (5H, m), 6.84 (2H, d, *J* = 8.4 Hz), 6.73 (2H, d, *J* = 8.4 Hz), 3.74 (3H, s), 2.87-2.77 (2H, m), 2.59 (1H, dd, *J* = 26.4, 13.2 Hz), 1.92 (3H, s), 0.22 (3H, s), 0.19 (3H, s). Optical rotation: $[\alpha]_D^{20}$ –1.84 (*c* 1.30, CHCl$_3$) for a sample with 97:3 er. The spectroscopic data match those reported previously[6] and the absolute configuration was assigned by analogy to entry 4 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97:3 er shown below; chiracel AD-H column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 0.9 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	5.13		0.00	N/A	4626453	49.186	BB	0.10
2	5.94		0.00	N/A	4779563	50.814	BB	0.12

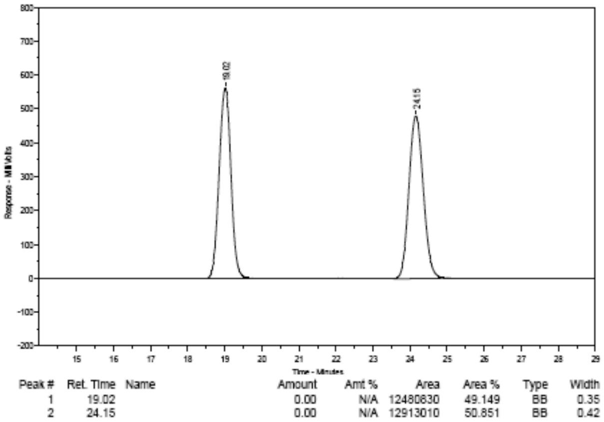


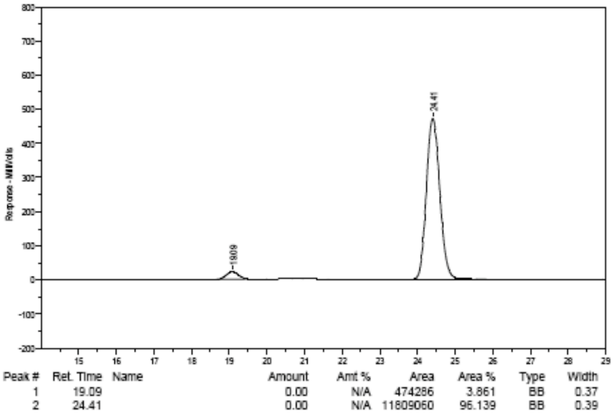
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	5.11		0.00	N/A	46099	3.272	BB	0.08
2	5.92		0.00	N/A	1362808	96.728	BB	0.10

Retention time	Area	Area %	Retention time	Area	Area %
5.13	4626453	49.186	5.11	46099	3.272
5.94	4779563	50.814	5.92	1362808	96.728

(*R*)-4-(Dimethyl(phenyl)silyl)-4-(4-(trifluoromethyl)phenyl)butan-2-one (Table 3, entry 6). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46-7.36 (7H, m), 7.03 (2H, d, *J* = 8.0 Hz), 3.02-2.91 (2H, m), 2.71 (1H, d, *J* = 16.0 Hz), 1.98 (3H, s), 0.26 (3H, s), 0.25 (3H, s); optical rotation: $[\alpha]_D^{20}$ +6.66 (*c* 2.45, CHCl$_3$) for a sample with 96:4 er. The spectroscopic data match those reported previously[6] and the absolute configuration was assigned by analogy to entry 4 in Table 3.

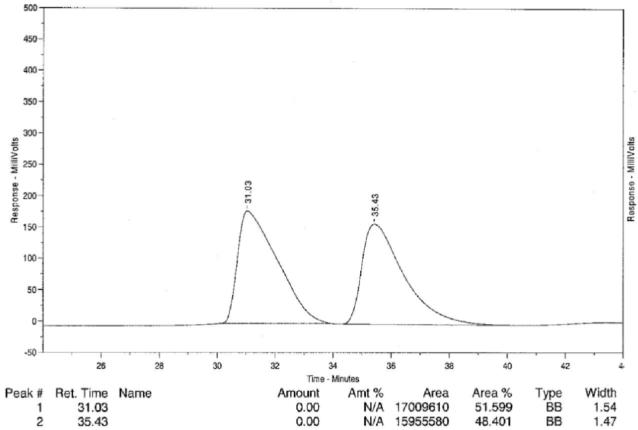
Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99/1 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).

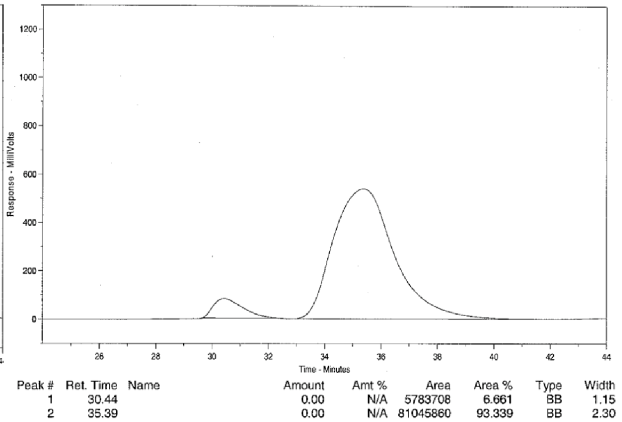




Retention time	Area	Area %	Retention time	Area	Area %
19.02	12480830	49.149	19.09	474286	3.861
24.15	12913010	50.851	24.41	11809060	96.139

(*R*)-4-(Dimethyl(phenyl)silyl)-4-*o*-tolylbutan-2-one (Table 3, entry 7). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40-7.32 (5H, m), 7.10-7.07 (2H, m), 7.02-6.98 (1H, m), 6.88-6.86 (1H, m), 3.16 (1H, dd, *J* = 11.2, 4.0 Hz), 2.96 (1H, dd, *J* = 16.8, 10.8 Hz), 2.68 (1H, dd, *J* = 16.8, 4.0 Hz), 2.24 (3H, s), 1.93 (3H, s), 0.30 (3H, s), 0.21 (3H, s). Optical rotation: $[\alpha]_D^{20}$ +11.3 (*c* 1.08, CHCl$_3$) for a sample with 93.5:6.5 er. The spectroscopic data match those reported previously[8] and the absolute configuration was assigned by analogy to entry 4 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (93.5:6.5 shown below; chiracel OD column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).





Retention time	Area	Area %	Retention time	Area	Area %
31.03	17009610	51.599	30.44	5783708	6.661
35.43	15955580	48.401	35.39	81045860	93.339

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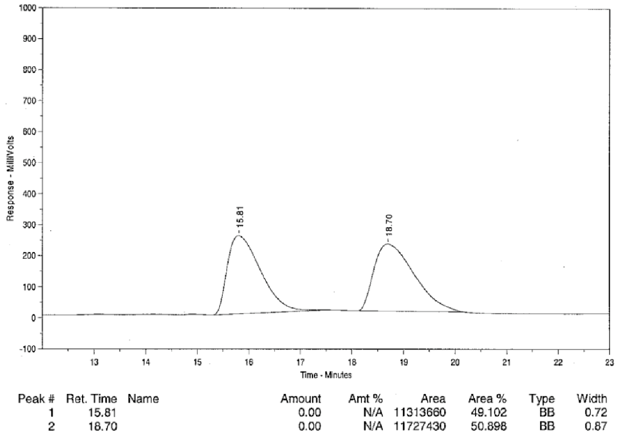
(8) Shintani, R.; Okamoto, K.; Hayashi, T. *Org. Lett.* **2005**, *7*, 4757–4759.

(*S*)-3-(Dimethyl(phenyl)silyl)-1-phenylbutan-1-one (13). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.84-7.81 (2H, m), 7.55-7.49 (3H, m), 7.42-7.35 (5H, m), 3.00 (1H, dd, *J* = 16.0, 3.2 Hz), 2.66 (1H, dd, *J* = 16.0, 11.2 Hz), 1.66-1.57 (1H, m), 0.98 (3H, d, *J* = 7.2 Hz), 0.34 (3H, s), 0.33 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 200.5, 137.6, 137.1, 134.0, 132.7, 129.1, 128.5, 128.1, 127.8, 40.7, 15.9, 14.6, –4.7, –5.4. Optical rotation: $[\alpha]_D^{20}$ +12.4 (*c* 1.10, CHCl$_3$) for a sample with 95.5:4.5 er. The spectroscopic data match those reported previously[9] and the absolute configuration was assigned by comparison with reported data.[10] Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (95.5:4.5 er shown below; chiracel OD column (25 cm x 0.46 cm), 99.9/0.1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



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Peak #  Ret. Time  Name          Amount   Amt %      Area   Area %   Type   Width
   1      15.81                    0.00     N/A  11313660   49.102    BB     0.72
   2      18.70                    0.00     N/A  11727430   50.898    BB     0.87
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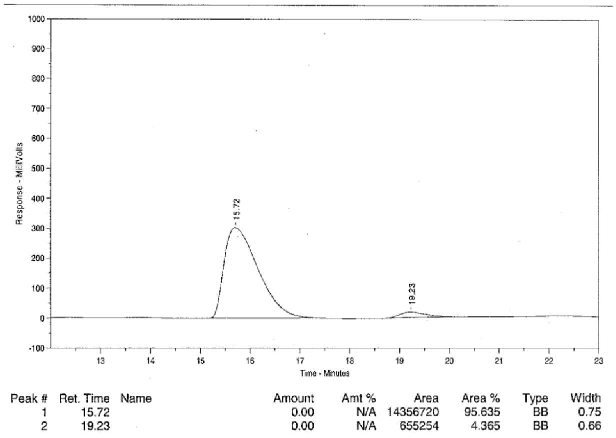

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Peak #  Ret. Time  Name          Amount   Amt %      Area   Area %   Type   Width
   1      15.72                    0.00     N/A  14356720   95.635    BB     0.75
   2      19.23                    0.00     N/A    655254    4.365    BB     0.66
```

Retention time	Area	Area %	Retention time	Area	Area %
15.81	11313660	49.102	15.72	14356720	95.635
18.70	11727430	50.898	19.23	655254	4.365

(*R*)-3-(Dimethyl(phenyl)silyl)-3-phenylpropanenitrile (14). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43-7.33 (5H, m), 7.27-7.23 (2H, m), 7.19-7.14 (1H, m), 6.96-6.93 (2H, m), 2.65-2.56 (3H, m), 0.27 (6H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.3, 135.8, 134.7, 130.5, 129.2, 128.7, 128.1, 126.6, 120.3, 33.7, 19.5, –3.4, –4.9. Optical rotation: $[\alpha]_D^{20}$ –13.4 (*c* 1.16, CHCl$_3$) for a sample with 90:10 er. The spectroscopic data match those reported previously[5] and the absolute configuration was assigned by analogy to entry 1 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (90:10 er shown below; chiracel AS column (25 cm x 0.46 cm), 99.7/0.3 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

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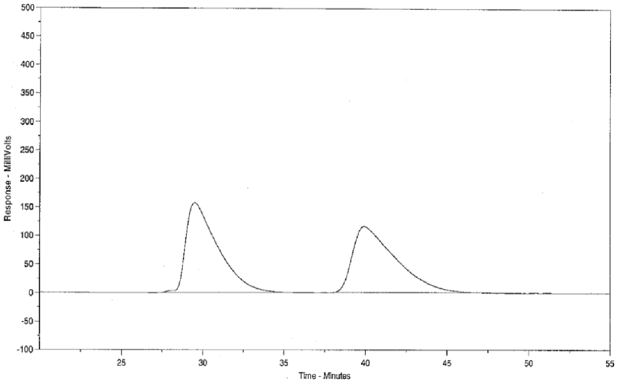
(9) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc., Perkin Trans. 1,* **1995**, 317–337.

(10) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579–5581.



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Peak #  Ret. Time  Name      Amount   Amt %   Area      Area %   Type  Width
  1       29.50               0.00     N/A    21358850  50.210    BB    2.06
  2       39.93               0.00     N/A    21180000  49.790    BB    2.80
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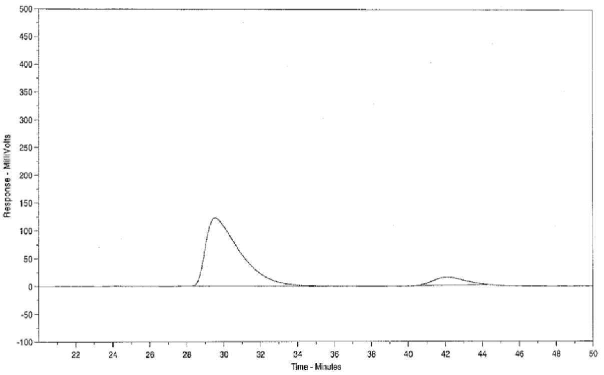

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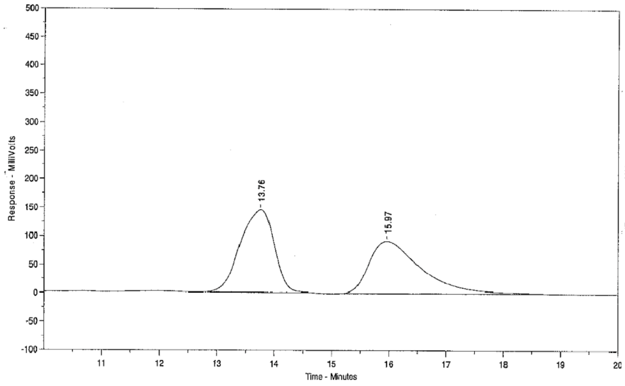
Peak #  Ret. Time  Name      Amount   Amt %   Area      Area %   Type  Width
  1       29.55               0.00     N/A    15804460  90.214    BB    1.94
  2       42.10               0.00     N/A    1714489    9.786    BB    1.99
```

Retention time	Area	Area %	Retention time	Area	Area %
29.50	21358850	50.210	29.55	15804460	90.214
39.93	21180000	49.790	42.10	1714489	9.786

(*S*)-Methyl 3-(dimethyl(phenyl)silyl)butanoate (15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (2H, m), 7.39-7.33 (3H, m), 3.62 (3H, s), 2.39 (1H, dd, *J* = 15.2, 4.0 Hz), 2.07 (1H, dd, *J* = 15.2, 11.2 Hz), 1.49-1.40 (1H, m), 0.98 (3H, d, *J* = 7.2 Hz), 0.29 (6H, s). Optical rotation: $[\alpha]_D^{20}$ +2.50 (*c* 1.75, $CHCl_3$) for a sample with 96.5:3.5 er. The spectroscopic data match those reported previously[11] and the absolute configuration was assigned by analogy to entry 1 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (96.5:3.5 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99.8/0.2 hexanes/*i*-PrOH, 0.51 mL/min, 220 nm).



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Peak #  Ret. Time  Name      Amount   Amt %   Area     Area %   Type  Width
  1       13.76               0.00     N/A    5976265  50.685    BB    0.67
  2       15.97               0.00     N/A    5814820  49.315    BB    0.94
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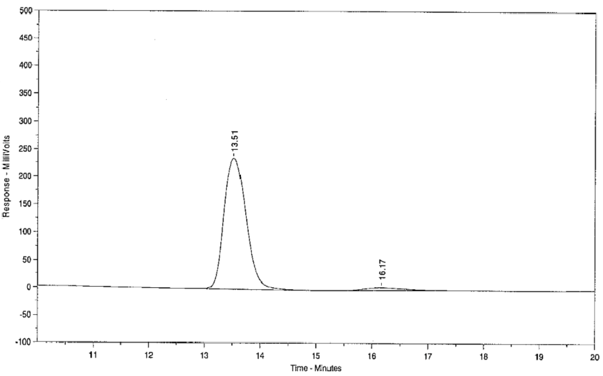

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Peak #  Ret. Time  Name      Amount   Amt %   Area     Area %   Type  Width
  1       13.51               0.00     N/A    6549847  96.495    BB    0.44
  2       16.17               0.00     N/A    237946    3.505    BB    0.85
```

Retention time	Area	Area %	Retention time	Area	Area %
13.76	5976265	50.685	13.51	6549847	96.495
15.97	5814820	49.315	16.17	237946	3.505

(*R*)-Methyl 3-(dimethyl(phenyl)silyl)-3-phenylpropanoate (16). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.32 (5H, m), 7.22-7.19 (2H, m), 7.12-7.08 (1H, m), 6.97-6.95 (2H, m), 3.47 (3H, s), 2.86 (1H, dd, *J* = 11.2, 4.8 Hz), 2.77 (1H, dd, *J* = 15.6, 11.2 Hz), 2.66 (1H, dd, *J* = 15.6, 11.2 Hz), 0.98 (3H, d, *J* = 7.2 Hz), 0.26 (3H, s), 0.23 (3H, s). Optical rotation: $[\alpha]_D^{20}$ +4.98 (*c* 2.30, $CHCl_3$)

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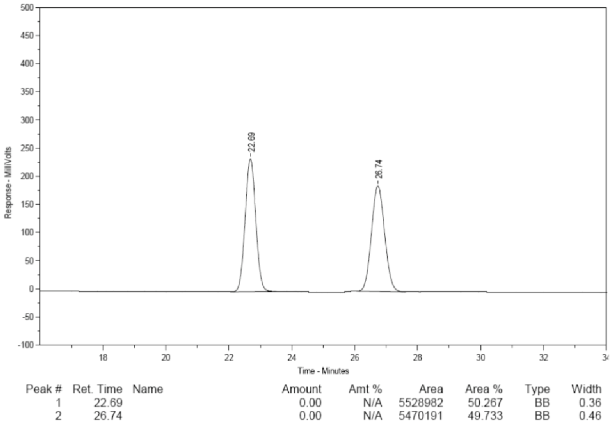
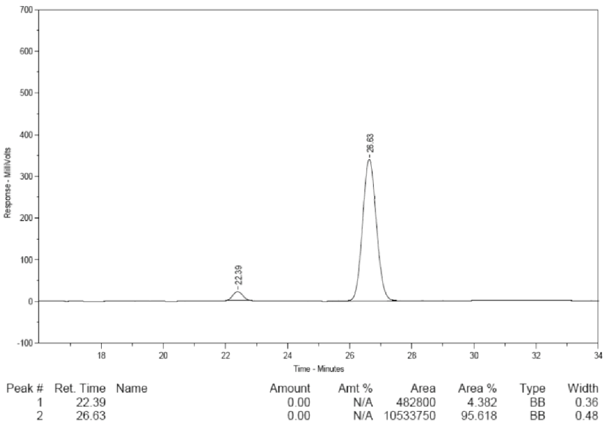
[11] Lipshutz, B. H.; Tanaka, N.; Taft, B. R.; Lee, C-T. *Org. Lett.* **2006**, *8*, 1963–1966.

for a sample with 95.5:4.5 er. The spectroscopic data match those reported previously[12] and the absolute configuration was assigned by analogy to the product entry 4 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (95.5:4.5 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99.2/0.8 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).





Retention time	Area	Area %	Retention time	Area	Area %
22.69	5528982	50.267	22.39	482800	4.382
26.74	5470191	49.733	26.63	10533750	95.618

■ Chiral NHC–Cu-Catalyzed Enantioselective 1,6-Conjugate Silyl Additions

(*R*,*Z*)-3-(2-(Dimethyl(phenyl)silyl)-2-phenylethylidene)cyclohexanone (20). IR (neat): 3023 (m), 2956 (m), 1714 (s), 1248 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (5H, m), 7.18 (2H, t, *J* = 8.0 Hz), 7.07 (1H, t, *J* = 7.4 Hz), 6.97-6.93 (2H, m), 5.67 (1H, d, *J* = 11.6 Hz), 3.25 (1H, d, *J* = 11.6 Hz), 2.94 (1H, d, *J* = 16.4 Hz), 2.69 (1H, dd, *J* = 16.4, 1.6 Hz), 2.38-2.26 (4H, m), 1.80-1.65 (2H, m), 0.22 (3H, s), 0.19 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 142.4, 137.3, 134.9, 132.2, 129.9, 128.9, 128.2, 127.9, 125.4, 124.7, 46.0, 42.0, 38.0, 35.8, 25.6, –3.7, –4.5; HRMS (ES$^+$) Calcd for $C_{22}H_{26}SiONa$ [M+Na]: 357.1651, Found: 357.1645. Optical rotation: $[\alpha]_D^{20}$ –5.90 (*c* 1.81, $CHCl_3$) for a sample with 98:2 er. The absolute configuration was assigned by analogy to entry 4 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).

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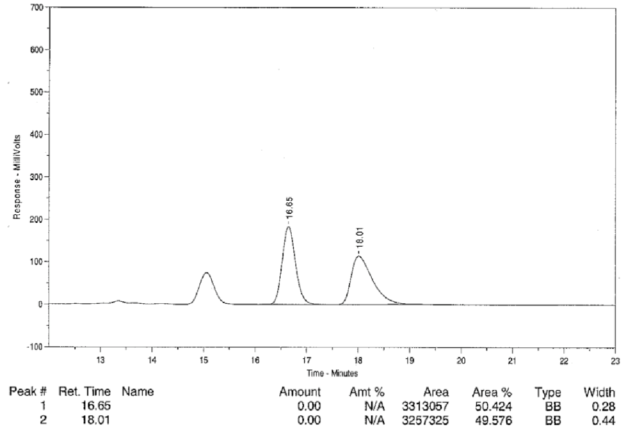
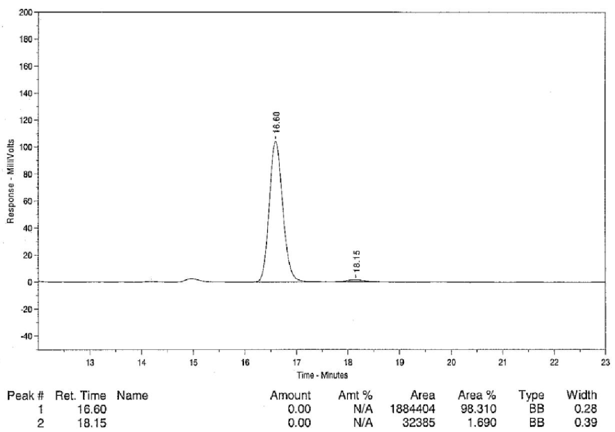
[12] Dambacher, J.; Bergdahl, M. *J. Org. Chem.* **2005**, *70*, 580–589.



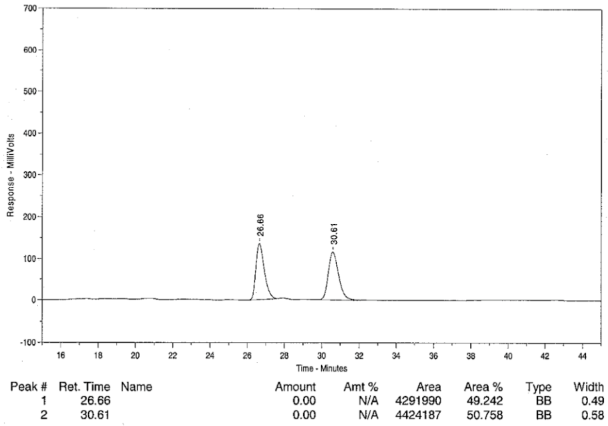
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	16.65		0.00	N/A	3313057	50.424	BB	0.28
2	18.01		0.00	N/A	3257325	49.576	BB	0.44



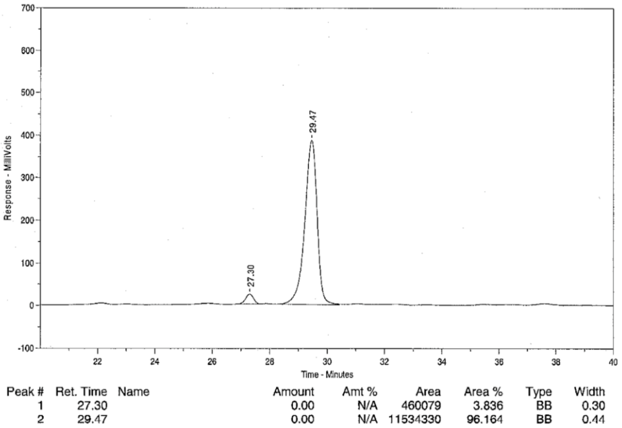
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	16.60		0.00	N/A	1884404	98.310	BB	0.28
2	18.15		0.00	N/A	32385	1.690	BB	0.39

Retention time	Area	Area %	Retention time	Area	Area %
16.65	3313057	50.424	16.60	1884404	98.310
18.01	3257325	49.576	18.15	32385	1.690

(*R*,*E*)-3-(2-(Dimethyl(phenyl)silyl)-2-phenylethylidene)-4,4-dimethylcyclohexanone (21). IR (neat): 2959 (m), 1686 (s), 1253 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37-7.27 (5H, m), 7.19 (2H, t, *J* = 7.6 Hz), 7.08 (1H, t, *J* = 7.4 Hz), 6.95 (2H, d, *J* = 7.2 Hz), 5.69 (1H, d, *J* = 11.6 Hz), 3.16 (1H, d, *J* = 11.6 Hz), 3.04 (1H, d, *J* = 17.2 Hz), 2.73 (1H, dd, *J* = 17.2, 1.6 Hz), 2.33-2.27 (2H, m), 1.59 (2H, t, *J* = 6.8 Hz) 1.18 (3H, s), 1.15 (3H, s), 0.22 (3H, s), 0.19 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 210.5, 142.6, 138.0, 137.3, 134.9, 129.9, 128.9, 128.2, 127.9, 125.4, 122.7, 43.0, 38.2, 38.0, 38.0, 36.7, 28.5, 28.3, –3.7, –4.5; HRMS (ES$^+$) Calcd for $C_{24}H_{30}SiONa$ [M+Na]: 385.1964, Found: 385.1955. Optical rotation: $[\alpha]_D^{20}$ +16.0 (*c* 1.30, CHCl$_3$) for a sample with 96:4 er. The absolute configuration was assigned by analogy to entry 4 in Table 3. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 99.3/0.7 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).



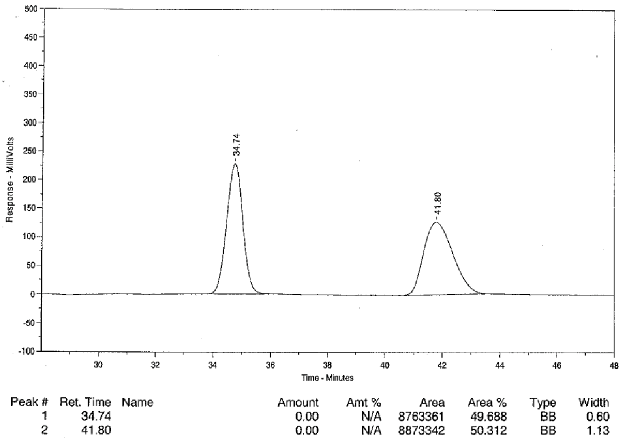
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	26.66		0.00	N/A	4291990	49.242	BB	0.49
2	30.61		0.00	N/A	4424187	50.758	BB	0.58



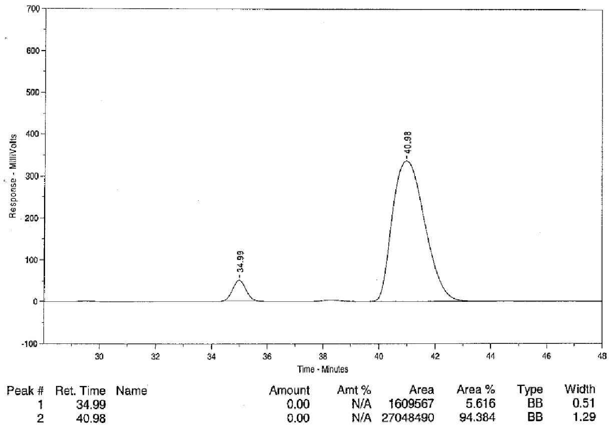
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	27.30		0.00	N/A	460079	3.836	BB	0.30
2	29.47		0.00	N/A	11534330	96.164	BB	0.44

Retention time	Area	Area %	Retention time	Area	Area %
26.66	4291990	49.242	27.30	460079	3.836
30.61	4424187	50.758	29.47	11534330	96.164

(*R*,*E*)-3-(Dimethyl(phenyl)silyloxy)-3-styrylcyclohexanone (22). IR (neat): 2955 (m), 1716 (s), 1427 (m), 1251 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52-7.50 (2H, m), 7.37-7.21 (6H, m), 7.18-7.16 (2H, m), 6.37 (1H, d, *J* = 16.4 Hz), 6.11 (1H, d, *J* = 16.4 Hz), 2.65 (1H, d, *J* = 14 Hz), 2.61 (1H, d, *J* = 14 Hz), 2.91-2.33 (1H, m), 2.90-2.21 (1H, m), 2.11-2.00 (2H, m), 1.91-1.74 (2H, m), 0.35 (3H, s), 0.33 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 210.2, 140.2, 136.8, 135.0, 134.1, 130.0, 129.9, 129.3, 128.6, 128.5, 127.2, 78.9, 54.1, 41.4, 38.1, 21.4, 1.6, 1.5; HRMS (ESI$^+$) Calcd for $C_{22}H_{27}SiO_2$ [M+H]: 351.1780, Found: 351.1769. Optical rotation: $[\alpha]_D^{20}$ +10.4 (*c* 0.90, CHCl$_3$) for a sample with 94.5:5.5 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (94.5:5.5 er shownbelow; chiralpak AD-H column (25 cm x 0.46 cm), 99.3/0.7 hexanes/*i*-PrOH, 0.3 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	34.74		0.00	N/A	8763361	49.688	BB	0.60
2	41.80		0.00	N/A	8873342	50.312	BB	1.13



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	34.99		0.00	N/A	1609567	5.616	BB	0.51
2	40.98		0.00	N/A	27048490	94.384	BB	1.29

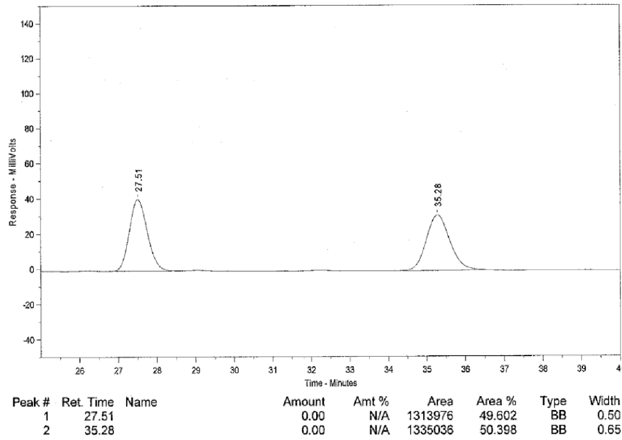
Retention time	Area	Area %	Retention time	Area	Area %
34.74	8763361	49.688	34.99	1609567	5.616
41.80	8873342	50.312	40.98	27048490	94.384

(2*S*,3*S*)-3-(Dimethyl(phenyl)silyl)-2-(hydroxy(phenyl)methyl)cyclopentanone (23). IR (neat): 3434 (w), 2955 (w), 2893 (w), 1724 (s), 1250 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45-7.42 (2H, m), 7.40-7.32 (3H, m), 7.29-7.19 (3H, m), 7.06-7.03 (2H, m), 4.83 (1H, d, *J* = 4.4 Hz), 3.86 (1H, bs), 2.53 (1H, dd, *J* = 9.6, 4.4 Hz), 2.15-2.06 (1H, m), 1.95-1.86 (2H, m), 1.66-1.57 (1H, m), 1.50-1.37 (1H, m), 0.22 (3H, s), 0.20 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 225.2, 142.3, 137.6, 134.5, 130.1, 129.0, 128.7, 128.3, 127.3, 75.8, 56.2, 40.9, 24.4, 23.9, –4.0, –4.2; HRMS (ESI$^+$) Calcd for $C_{20}H_{25}SiO_2$ [M+H]: 325.1624, Found: 325.1635. Optical rotation: $[\alpha]_D^{20}$ –15.1 (*c* 1.40, CHCl$_3$) for a sample with 6:1 dr.

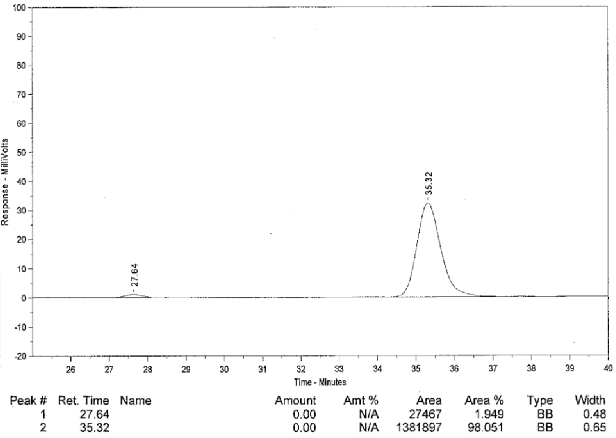
(2*S*,3*S*)-3-(Dimethyl(phenyl)silyl)-2-(hydroxy(phenyl)methyl)cycloheptanone (24). Upon standing, the product undergoes retro-aldol reaction, as evidenced by HRMS and ^{1}H NMR to afford (*S*)-3-(dimethyl(phenyl)silyl)cycloheptanone (entry 3 in Table 2) in 95.5:4.5 er. HRMS of **24** (ESI$^+$) Calcd for $C_{22}H_{32}NSiO_2$ [M+NH$_4$]: 370.2202, Found: 370.2204. The diastereomeric ratio (3:1 dr) was obtained through analysis of ^{1}H NMR spectra of the unpurified mixtures.

■ **Preparation of (1*R*,4*R*)-4-(dimethyl(phenyl)silyl)-3,3-dimethyl-1-phenylcyclopentanol (26):** An oven-dried vial (6 x 1 cm) under a dry N$_2$ atmosphere equipped with a stir bar was charged with **25** (Table 2, entry 1, 99:1 er) (0.12 mmol, 30 mg) and Et$_2$O (2 mL) was added and the solution was allowed to cool to –78 °C. A solution of PhLi (78 μL, 0.13 mmol) in *n*-Bu_2O (1.71 M) was added at –78 °C. After 6 h at -50 °C, the reaction was quenched by the addition of 1M HCl solution (0.5 mL) and H_2O (2 mL) and the mixture was allowed to warm to 22 °C. Layers were separated, and the aqueous layer was washed with Et_2O (5 mL x 2). The combined organic layers were dried over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the resulting light yellow oil was purified by silica gel chromatography (hexanes/Et_2O:3/1) to afford 31 mg (0.097 mmol, 85% yield) of **26** as a colorless oil (>25:1 dr). IR (neat): 3387 (w), 2953 (s), 2687 (m), 1250 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (2H, m), 7.44-7.41 (2H, m), 7.35-7.28 (5H, m), 7.21-7.18 (1H, m), 2.42 (1H, dd, *J* = 13.8, 8.6 Hz), 2.29 (1H, dd, *J* = 13.6, 13.6 Hz), 2.08 (1H, d, *J* = 13.6 Hz), 1.87 (1H, d, *J* = 14.0 Hz), 1.71 (1H, s), 1.42-1.37 (1H, m), 1.23 (3H, s), 0.97 (3H, s), 0.39 (3H, s), 0.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 140.1, 134.5, 129.5, 128.9, 128.4, 127.2, 125.1, 83.7, 62.8, 47.7, 44.3, 41.4, 31.6, 27.4, –1.7, –1.9; HRMS (ES^+) Calcd for $C_{21}H_{28}SiONa$ [M+Na]: 347.1807, Found: 347.1811. Optical rotation: $[\alpha]_D^{20}$ –21.0 (*c* 1.01, $CHCl_3$).

(1*R*,3*R*)-4,4-Dimethyl-1-phenylcyclopentane-1,3-diol (27). IR (neat): 3356 (m), 2957 (s), 2926 (s), 2869 (m), 1448 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (2H, m), 7.38-7.34 (2H, m), 7.31-7.26 (1H, m), 4.13 (1H, dd, *J* = 8.0, 6.0 Hz), 2.77 (1H, dd, *J* = 14.0, 6.0 Hz), 2.22 (1H, dd, *J* = 14.0, 6.0 Hz), 2.08 (2H, s), 1.16 (3H, s), 0.96 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 129.3, 128.4, 126.8, 92.6, 80.3, 50.5, 42.6, 42.0, 28.6, 23.6; Optical rotation: $[\alpha]_D^{20}$ –7.04 (*c* 0.800, $CHCl_3$) for a sample with 98:2 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (98:2 er shown below; chiralpak AD-H column (25 cm x 0.46 cm), 90/10 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



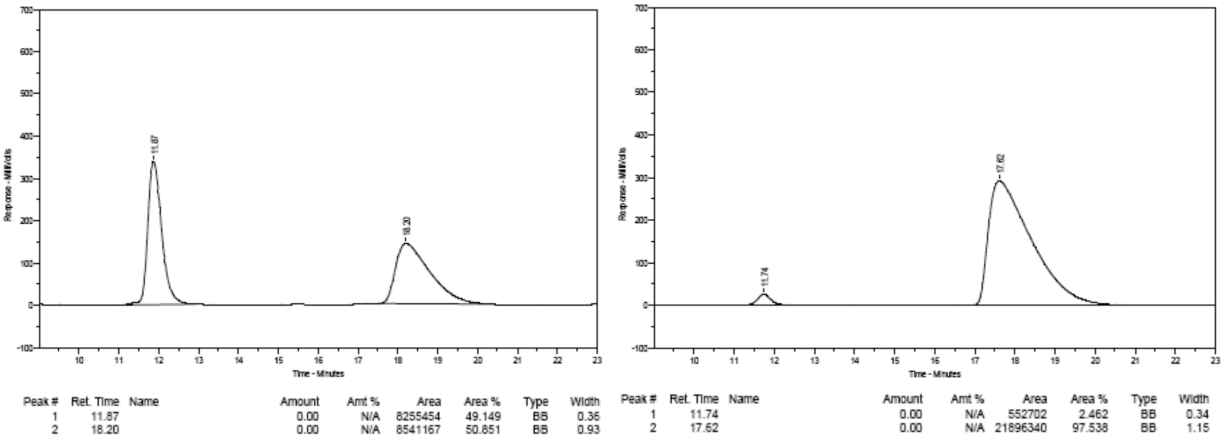
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	27.51		0.00	N/A	1313976	49.602	BB	0.50
2	35.28		0.00	N/A	1335036	50.398	BB	0.65



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	27.64		0.00	N/A	27467	1.949	BB	0.48
2	35.32		0.00	N/A	1381897	98.051	BB	0.65

Retention time	Area	Area %	Retention time	Area	Area %
27.51	1313976	49.602	27.64	27467	1.949
35.28	1335036	50.398	35.32	1381897	98.051

Methyl 2-((1*S*,2*S*)-2-(dimethyl(phenyl)silyl)-6-oxocyclohexyl)acetate (28)[13]**.** IR (neat): 2951 (w), 2858 (w), 1735 (s), 1708 (s), 1428 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (2H, m), 7.40-7.33 (3H, m), 3.58 (3H, s), 2.78 (1H, dddd, *J* = 18.8, 9.6, 3.6, 0.8 Hz), 2.46-2.32 (3H, m), 2.72-2.13 (2H, m), 1.87-1.82 (1H, m), 1.82-1.56 (2H, m), 1.35 (1H, td, *J* = 12.8, 3.6 Hz), 0.38 (3H, s), 0.33 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.9, 173.5, 138.5, 134.3, 130.0, 128.7, 52.2, 48.9, 42.5, 34.6, 32.7, 30.8, 28.2, –2.2, –3.3; HRMS (ES^+) Calcd for $C_{17}H_{25}SiO_3$ [M+H]: 305.1573, Found: 305.1580. Optical rotation: $[\alpha]_D^{20}$ –79.4 (*c* 2.33, $CHCl_3$) for a sample with 97.5:2.5 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (97.5:2.5 er shown below; chiracel AS column (25 cm x 0.46 cm), 90/10 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	11.87		0.00	N/A	8255454	49.149	BB	0.36
2	18.20		0.00	N/A	8541167	50.851	BB	0.93

Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	11.74		0.00	N/A	552702	2.462	BB	0.34
2	17.62		0.00	N/A	21896340	97.538	BB	1.15

Retention time	Area	Area %	Retention time	Area	Area %
11.87	8255454	49.149	11.74	552702	2.462
18.20	8541167	50.851	17.62	21896340	97.538

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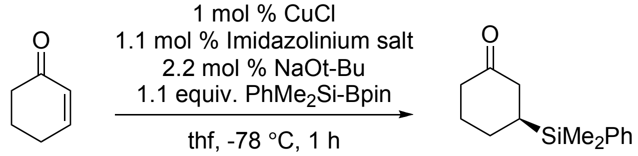
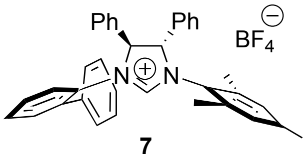
(13) For total synthesis of (+)-erysotramidine, see: (a) Tietze, L. F.; Tolle, N.; Kratzert, D.; Stalke, D. *Org. Lett.* **2009**, *11*, 5230–5233. (b) Blake, A. J.; Gill, C.; Greenhalgh, D. A.; Simpkins, N. S.; Zhang, F. *Synthesis* **2005**, *19*, 3287–3292.

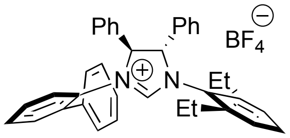
■ Screening of ligands.





7

>98% conv
94.5:5.5 er



8

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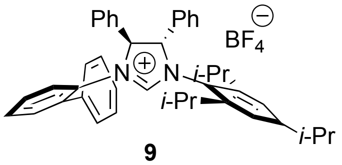
91.5:8.5 er



9

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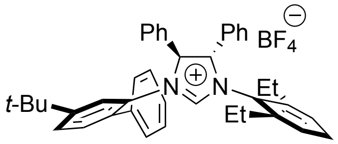
87:13 er



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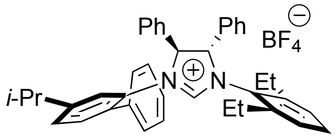
91:9 er



11

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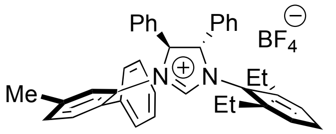
93:7 er



12

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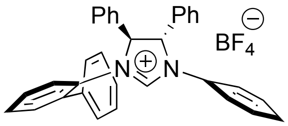
97.5:2.5



Ligand 1

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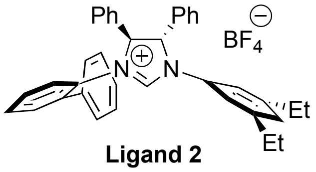
90.5:9.5 er



Ligand 2

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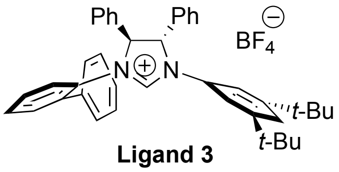
87.5:12.5 er



Ligand 3

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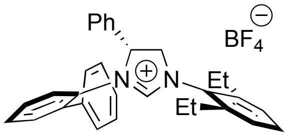
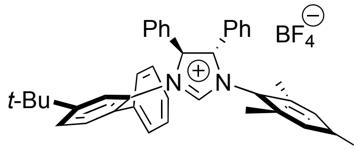
96:4 er



Ligand 4

>98% conv
82:18 er



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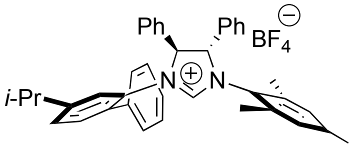
87.5:12.5 er



Ligand 6

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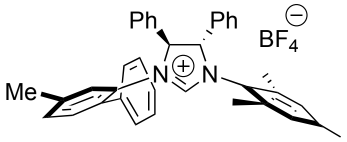
87:13 er



Ligand 7

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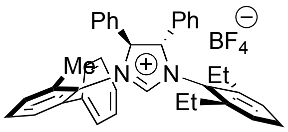
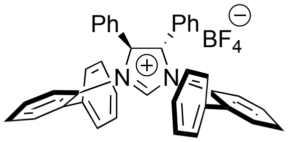
91:9 er



Ligand 8

>98% conv
78.5:21.5 er



Ligand 9

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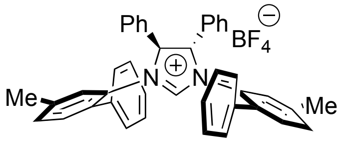
92.5:7.5 er



Ligand 10

>98% conv
97.5:2.5 er