One-pot Solvent-Free Reductive Amination of Aldehydes with a Solidified Amine

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Table of Contents

1. Experimental details ---------------------------------------------------------------S3
2. General procedure for the preparation of secondary amine using catalytic hydrogenation
   between solidified amine 2 and aldehydes 3 ----------------------------------------S4
3. General procedure for the preparation of secondary amine using stoichiometric reduction
   between solidified amine 2 and aldehydes 3 ----------------------------------------S4
4. Crystal growth of (S,E)-N,N-dimethyl-4-(((1-phenylethyl)-imino)methyl)aniline 4a ------S4
5. X-ray crystallography data for 4a -----------------------------------------------------S5
6. Table S1. Structural data for single crystal data of 4a -----------------------------S6
7. Table S2. Selected bond distances and bond angles(Å, °) of 4a ------------------------S7
8. Table S3. Check CIF for 4a -------------------------------------------------------------S8
9. Crystal image of 4a ---------------------------------------------------------------------S11
10. Analytical data of amines obtained from reductive amination between 2 and 3---------S12
11. Characterization of 2 ---------------------------------------------------------------S18
12. NMR data for 4a -----------------------------------------------------------------------S22
13. NMR data for 5a–5r ---------------------------------------------------------------------S24
14. References -----------------------------------------------------------------------------S60
Experimental Details

Materials. (S)-(−)-phenylethylamine was purchased from Lancaster, benzaldehyde was purchased from Hanawa, Platinum(IV) oxide hydrate (80–81% Pt) and Platinum 10% on activated carbon were purchased from Strem chemicals Inc., p-anisaldehyde, 3-methoxybenzaldehyde, 2-furaldehyde, 3-furaldehyde, 1-naphthaldehyde, 2-methoxy-1-naphthaldehyde, 4-tert-butylbenzaldehyde, 4-(diphenylamino)benzaldehyde, N-Methyl-2-pyrolecarboxaldehyde, 1-methylindole-3-carbaldehyde, 3-thiophenecarboxaldehyde, sodium borohydride, isobutyraldehyde, platinum on activated charcoal (Pt 5 wt%), trimethylacetaldehyde, cyclohexanecarboxaldehyde, cyclopentanecarboxaldehyde were purchased from Sigma-Aldrich, 3,4-dimethoxybenzaldehyde, 4-(dimethylamino)benzaldehyde were purchased from Acros, 3-fluorobenzaldehyde, 3-chlorobenzaldehyde, thiophene-2-carbaldehyde were purchased from TCI. All of the reagents were used without any further purification. Chiral amine carbamate salt 2 was prepared by previously reported method.81

Instrumentation

All reactions were carried out in oven-dried glasswares with magnetic stirring. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, or by immersion in solutions of ninhydrin followed by heating on a hot plate for about 10 s. Purification of reaction products was carried out by flash chromatography using Kieselgel 60 Art 9385 (230-400 mesh). Powder X-ray diffraction (XRD) data were collected using a Rigaku DMAX 2500 diffractometer (Cu Ka) operating at 40 kV and 150 mA. A Nicolet 205 instrument was used to measure infrared spectra. Melting point was measured with a SMP10-BIBBY. Thermogravimetric analysis (TGA) was performed with a TA Instrument TGA 2050 where temperature was increased by 10 °C/min. GC/MS data were recorded on an Agilent 5973N and elemental analyses were obtained using a Carlo Erba EA1180 at the Organic Chemistry Research Center in Sogang University. 1H NMR and 13C NMR spectra in solution were recorded on a Varian 400-MHz Gemini operating at 400 MHz for 1H and 100 MHz for 13C, and a Varian UNITY INOVA 500 at 500 MHz for 1H and 125 MHz for 13C, respectively. Chemical shifts are reported relative to TMS (δ = 0.0) for 1H NMR and chloroform (δ = 77.16) for 13C NMR. Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet). Coupling constants are given in Hz. Ambiguous assignments were resolved
on the basis of standard one dimensional proton decoupling experiments. Optical rotations were obtained using a Rudolph Autopol III digital polarimeter and optical rotation data were reported as follows: \([\alpha]^{24}_D\) (concentration \(c = g/100 \text{ mL, solvent})\).

**General procedure for the preparation of secondary amine using catalytic hydrogenation between solidified amine 2 and aldehydes 3**

4-(dimethylamino)-benzaldehyde 3a (149.2 mg, 1.00 mmol) was placed in a vial, the solidified amine 2 (143.2 mg, 0.500 mmol) was added and the vial warmed to 60 °C for 1 hour, then allowed to cool to room temperature. To the vial was added PtO\(_2\) (4.3 mg), Pt/C (35.1 mg), or Pd/C (18.6 mg) and the hydrogenation proceeded at room temperature under 1 atm of H\(_2\) for 17h. The crude product was purified by silica gel flash column chromatography (30% EA / 70% Hexane).

**General procedure for the preparation of secondary amine using stoichiometric reduction between solidified amine 2 and aldehydes 3**

4-(Dimethylamino)benzaldehyde 3a (149 mg, 1.00 mmol) was placed in a vial, the solidified amine 2 (143 mg, 0.50 mmol) was added, and the mixture was warmed to 60 °C for 1 hour, then allowed to cool to room temperature. To the mixture was added methanol (0.7 mL) and sodium borohydride (42 mg, 1.10 mmol) under air at room temperature. After 0.5h, the reaction mixture was diluted with ethyl acetate and treated with water. The organic layer was extracted from the aqueous layer using Pasteur pipette. The solvent of organic layer was removed in vacuo. The crude product was purified by silica gel flash column chromatography (30% EA / 70% Hexane).

**Crystal growth of \((S,E)-N,N\text{-Dimethyl-4-((1-phenylethyl-imino)methyl)aniline 4a}\)**

For the growth of 4a crystals, methylene chloride was added to the solid powder (252 mg) until the powder was completely dissolved at ambient temperature (1 mL total), followed by addition of hexane (1 mL) without mixing in a 5 mL vial. The resulting solution was carefully stored in the refrigerator for one day. Yellow crystals grew from the solution, which were separated by filtering and washing with pentane (3 × 3 mL).
X-ray crystallography. A single crystal of (S,E)-N,N-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline 4a was selected by a nylon loop (Hampton Research Co.) placed on a handmade cooper plate, which was placed inside a liquid N\(_2\) Dewar vessel at approximately -40 °C and was mounted on a goniometer head in a N\(_2\) cryostream. Data collections were carried out in a Bruker SMART AXS diffractometer equipped with a monochromator with a Mo K\(\alpha\) (\(\lambda = 0.71073\) Å) incident beam. The charge-coupled device (CCD) data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V 6.12\(^{52}\) Hydrogen atoms were located in the calculated positions. The crystal data for (S,E)-N,N-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline 4a: \(\text{C}_{17}\text{H}_{20}\text{N}_2\), Monoclinic, \(P2(1)\), \(Z = 2\), \(a = 8.5299(3)\), \(b = 6.0689(2)\), \(c = 13.7293(5)\) Å, \(\beta = 91.554(2)\) °, \(V = 710.46(4)\) Å\(^3\), \(\mu = 0.070\) mm\(^{-1}\), \(\rho\text{calcd} = 1.180\) g/cm\(^3\), \(R_1 = 0.0353\), and \(wR_2 = 0.0930\) for 3410 unique reflections and 175 variables. The crystallographic data for (S,E)-N,N-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline 4a are listed in Table S1, while Table S2 lists the selected bond distances and angles. CCDC-953131 for (S,E)-N,N-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline 4a contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
<table>
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<tr>
<th>Table S1. Structural data for (S,E)-N,N-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline 4a</th>
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<td>Final $R$ indices [$I &gt; 2\sigma(I)$]</td>
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<td>$R$ indices (all data)</td>
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<td>Largest difference peak and hole (e/Å³)</td>
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**Table S2.** Selected bond distances and bond angles (Å, °) $(S,E)$-$N,N$-dimethyl-4-((1-phenylethyl)imino)methyl)aniline 4a

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<td>N2-C17</td>
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<td>C16-N2-C17</td>
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<td>C17-N2-C13</td>
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<td>C13-N2-C16</td>
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Table S3. checkCIF/PLATON report

Structure factors have been supplied for datablock(s) chem260

No syntax errors found. CIF dictionary Interpreting this report

**Datablock: chem260**

Bond precision: C-C = 0.0018 Å Wavelength=0.71073

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Correction method= MULTI-SCAN

Data completeness= 1.77/0.97 Theta(max)= 28.290

R(reflections)= 0.0353( 2859) \( wR2 \text{(reflections)} = 0.1008( 3410) \)

S = 0.641 Npar= 175

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

**Alert level B**

PLAT035_ALERT_1_B No _chemical_absolute_configuration info given .
Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as multi-scan.

GOODF01_ALERT_2_C The least squares goodness of fit parameter lies outside the range 0.80 <> 2.00.

Goodness of fit given = 0.641

STRVA01_ALERT_4_C Flack parameter is too small.

From the CIF: _refine_ls_abs_structure_Flack -4.000
From the CIF: _refine_ls_abs_structure_Flack_su 2.000

PLAT033_ALERT_4_C Flack x Parameter Value Deviates from Zero. -4.000

Alert level G

REFT03_ALERT_4_G ALERT: MoKa measured Friedel data cannot be used to determine absolute structure in a light-atom study EXCEPT under VERY special conditions.

   It is preferred that Friedel data is merged in such cases. From the CIF: _diffrn_reflns_theta_max 28.29
   From the CIF: _reflns_number_total 3410
   Count of symmetry unique reflns 1922
   Completeness (_total/calc) 177.42% TEST3: Check
   Friedels for noncentro structure Estimate of Friedel pairs measured 1488
   Fraction of Friedel pairs measured 0.774
   Are heavy atom types Z>Si present no

PLAT05_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?

PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High. 2.000

PLAT791_ALERT_4_G Note: The Model has Chirality at C7 (Verify) S

PLAT916_ALERT_2_G Hooft y and Flack x Parameter values differ by. 4.30

0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special details" fields of the CIF. Check CIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation); however, if you intend to submit to Acta Crystallographica Section C or E, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the Notes for Authors of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/04/2012; check.def file version of 14/04/2012
Analytical data of amines obtained from reductive amination between 2 and 3

(S)-1-Phenylethaniminium (S)-(1-phenylethyl)carbamate (2): white solid; mp N/A (totally sublimed at ~100 °C); 1H NMR (400 MHz, CDCl3) δ 7.13-7.31 (m, 9H), 6.44 (s, br, 2H), 4.36-4.41 (m, 1H), 3.93-3.94 (d, 1H, J = 6.4 Hz) 1.31-1.33 (d, 3H, J = 6.4 Hz), 1.15-1.17 (d, 3H, J = 6.4 Hz); 13C NMR (100 MHz, CDCl3) δ 162.2, 146.2, 143.8, 128.5, 128.2, 127.3, 126.3, 126.0, 125.8, 50.74, 50.52, 23.44; vmax (powder)/cm⁻¹ = 1621 (w) and 1554 (m) for ν(C=O); Anal. Calcd for C17H22N2O2: C, 71.30; H, 7.74; N, 9.78. found: C, 71.23; H, 7.65; N, 9.89

Analytical data of amines obtained from the reductive amination reactions between 2 and aldehydes 3

(S,E)-N,N-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline (4a): pale yellow crystal; mp 87.7 °C; [α]24D +184 (c 1.00, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 8.24 (s, 1H), 7.64-7.66 (d, 2H, J = 8.5 Hz), 7.41-7.43 (d, 2H, J = 8 Hz), 7.30-7.33 (t, 2H, J = 7.5 Hz), 7.20-7.23 (m, 1H), 6.68-6.70 (d, 2H, J = 8.5 Hz), 4.46-4.49 (q, 1H, J = 6.5 Hz) 3.00 (s, 6H), 1.62 (br, s, 1H) 1.57-1.58 (d, 3H, J = 6.5 Hz); 13C NMR (125 MHz, CDCl3) δ 159.6, 152.3, 146.0, 129.8, 128.5, 126.9, 125.0, 111.8, 69.6, 40.4, 25.0; Anal. Calcd for C17H20N2: C, 80.91; H, 7.99; N, 11.10. found: C, 80.76; H, 7.86; N, 11.33; MS (EI+) m/z = 252, 237, 221, 210, 193, 175, 165, 147, 134, 122, 105, 91, 77; GC-MS retention time Rt = 12.72 min.

(S)-N,N-Dimethyl-4-((1-phenylethlamino)methyl)aniline (5a): colorless oil; [α]24D +17.7 (c 0.015, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.23-7.37 (m, 5H), 7.14-7.16 (d, 2H, J = 8.4 Hz), 6.70-6.72 (d, 2H, J = 8.8 Hz), 3.78-3.83 (q, 1H, J = 6.4 Hz), 3.55-3.58 (d, 1H, J = 12.8 Hz), 3.48-3.51 (d, 1H, J = 12.8 Hz), 2.93 (s, 6H), 1.34-1.36 (d, 3H, J = 6.4 Hz); 13C NMR (100 MHz, CDCl3) δ 149.9, 145.8, 129.2, 128.7, 128.5, 127.0, 126.9, 112.8, 57.3, 51.1, 40.9, 24.6; Anal. Calcd. for C17H22N2: C, 80.27; H, 8.72; N, 11.01. found: C, 80.31; H, 8.62; N, 10.86; MS (EI+) m/z = 254, 149, 134, 118, 105, 91, 77; GC-MS retention time Rt = 12.20 min.

(S)-N-(3-Fluorobenzyl)-1-phenylethamine (5b): colorless oil; [α]24D -26.9 (c 0.0067, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.19-7.33 (m, 6H), 6.87-7.02 (m, 3H), 3.74-3.79 (q, 1H, J = 6.4 Hz), 3.60-3.64 (d, 1H, J = 14.0 Hz), 3.54-3.57 (d, 1H, J = 14.0 Hz), 1.34-1.35 (d, 3H, J = 6.4 Hz); 13C NMR (100 MHz, CDCl3) δ 163.0 (d, JCF = 254, 149, 134, 118, 105, 91, 77; GC-MS retention time Rt = 12.20 min.
244.1 Hz), 145.4, 143.5 (d, $^3J_{C-F} = 6.7$ Hz), 129.9 (d, $^3J_{C-F} = 7.4$ Hz), 128.6, 127.1, 126.7, 123.7, 129.8 (d, $^2J_{C-F} = 20.9$ Hz), 113.7 (d, $^2J_{C-F} = 20.9$ Hz); Anal. Calcd for C\textsubscript{13}H\textsubscript{16}FN: C, 78.57; H, 7.03; N, 6.11. found: C, 78.56; H, 6.98; N, 5.98. MS (EI\textsuperscript{+}) m/z = 229, 214, 152, 124, 109, 91, 77; GC-MS retention time Rt = 9.83 min.

(S)-N-(3-Chlorobenzyl)-1-phenylethanamine (5c): colorless oil; $[\alpha]_{D}^{24}$ -37.7 (c 0.0060, CH\textsubscript{2}Cl\textsubscript{2}); $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.13-7.34 (m, 9H), 3.75-3.80 (q, 1H, $J = 6.4$ Hz), 3.59-3.63 (d, 1H, $J = 13.2$ Hz), 3.53-3.57 (d, 1H, $J = 13.2$ Hz), 1.35-1.37 (d, 3H, $J = 6.4$ Hz); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 145.4, 142.9, 134.3, 129.7, 128.6, 128.3, 127.2, 127.1, 126.7, 126.3, 57.7, 51.2, 24.6; Anal. Calcd for C\textsubscript{15}H\textsubscript{16}ClN: C, 73.31; H, 6.56; N, 5.70. found: C, 73.28; H, 6.61; N, 5.64. MS (EI\textsuperscript{+}) m/z = 245, 230, 168, 125, 105, 89, 77; GC-MS retention time Rt = 10.94 min.

(S)-1-Phenyl-N-(thiophen-3-ylmethyl)ethanamine (5d): colorless oil; $[\alpha]_{D}^{24}$ -28.6 (c 0.010, CH\textsubscript{2}Cl\textsubscript{2}); $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.28-7.36 (m, 4H), 7.18-7.26 (m, 2H), 7.03 (s, 1H), 6.97-6.98 (d, 1H, $J = 4.4$ Hz), 3.75-3.80 (q, 1H, $J = 6.4$ Hz), 3.61 (s, 2H), 1.33-1.35 (d, 3H, $J = 6.4$ Hz); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 145.5, 141.7, 128.5, 127.7, 127.1, 126.7, 125.7, 121.4, 57.5, 46.7, 24.6; Anal. Calcd for C\textsubscript{13}H\textsubscript{15}NS: C, 71.84; H, 6.96; N, 6.44; S, 14.75. found: C, 71.80; H, 6.95; N, 6.44; S, 14.80. MS(EI\textsuperscript{+}) m/z = 216, 202, 140, 120, 112, 105, 97, 91, 85, 77; GC-MS retention time Rt = 10.58 min.

(S)-N-Benzyl-1-phenylethanamine (5e): colorless oil; $[\alpha]_{D}^{24}$ -38.3 (c 0.0073, CH\textsubscript{2}Cl\textsubscript{2}); $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.20-7.33 (m, 10H), 3.76-3.81 (q, 1H, $J = 6.8$ Hz), 3.62-3.65 (d, 1H, $J = 12.8$ Hz), 3.55-3.58 (d, 1H, $J = 12.8$ Hz), 1.33-1.35 (d, 3H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 145.7, 140.8, 128.6, 128.5, 127.1, 126.9, 126.8; Anal. Calcd for C\textsubscript{15}H\textsubscript{17}N: C, 85.26; H, 8.11; N, 6.63. found: C, 85.20; H, 8.10; N, 6.58. MS (EI\textsuperscript{+}) m/z = 196, 105, 91, 77, 65; GC-MS retention time Rt = 9.86 min.

(S)-N-(4-Methoxybenzyl)-1-phenylethanamine (5f): colorless oil; $[\alpha]_{D}^{24}$ -16.4 (c 0.0073, CH\textsubscript{2}Cl\textsubscript{2}); $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.32-7.33 (d, 5H, $J = 4.8$ Hz), 7.22-7.25 (q, 1H, $J = 4$ Hz), 6.27 (s, 1H), 6.07-6.08 (d, 1H, $J = 2.4$ Hz), 3.74-3.79 (q, 1H, $J = 6.4$ Hz), 3.63-3.66 (d, 1H, $J = 14.4$ Hz), 3.54-3.57 (d, 1H, $J = 14.4$ Hz), 1.33-1.35 (d, 3H, $J = 6.4$ Hz); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 154.1, 145.1, 141.81, 128.6, 127.1, 126.8, 110.1, 106.9, 57.1, 44.1, S13
24.4; Anal. Calcd for C_{16}H_{19}NO: C, 79.63; H, 7.94; N, 5.80. found: C, 79.65; H, 7.96; N, 5.95. MS (EI+) m/z = 241, 226, 136, 121, 105, 91, 77, 65; GC-MS retention time Rt = 11.30 min.

(S)-N-(3-Methoxybenzyl)-1-phenylethanamine (5g):^56 colorless oil; [α]^24_D -3.2 (c 0.0090, CH₂Cl₂); ^1H NMR (400 MHz, CDCl₃) δ 7.18-7.33 (m, 6H), 6.75-6.85 (m, 3H), 3.76-3.81 (q, 1H, J = 6.4 Hz), 3.76 (s, 3H), 3.61-3.64 (d, 1H, J = 13.2 Hz), 3.53-3.57 (d, 1H, J = 13.2 Hz), 3.34-3.36 (d, 1H, J = 6.4 Hz); ^13C NMR (100 MHz, CDCl₃) δ 159.8, 145.5, 142.3, 129.4, 128.5, 127.0, 126.8, 120.5, 113.7, 112.3, 57.5, 55.2, 51.6, 24.5; Anal. Calcd for C_{16}H_{19}NO: C, 79.63; H, 7.94; N, 5.80. found: C, 79.74; H, 7.90; N, 5.75. MS (EI+) m/z = 240, 226, 164, 136, 121, 113, 105, 91, 77, 65; GC-MS retention time Rt = 11.19 min.

(S)-N-(Naphthalen-1-ylmethyl)-1-phenylethanamine (5h):^57 colorless oil; [α]^24_D +13.9 (c 0.0067, CH₂Cl₂); ^1H NMR (400 MHz, CDCl₃) δ 7.98-7.99 (d, 1H, J = 7.2 Hz), 7.82-7.84 (d, 1H, J = 7.6 Hz), 7.73-7.75 (d, 1H, J = 7.6 Hz), 7.34-7.50 (m, 8H), 7.28-7.30 (m, 1H), 4.07-4.10 (d, 1H, J = 13.2 Hz), 3.99-4.03 (d, 1H, J = 13.2 Hz), 3.89-3.94 (q, 1H, J = 6.4 Hz), 1.38-1.40 (d, 3H, J = 6.4 Hz); ^13C NMR (100 MHz, CDCl₃) δ 145.7, 136.3, 133.9, 131.9, 128.7, 128.6, 127.7, 127.1, 126.9, 126.2, 126.0, 125.6, 125.5, 123.9, 58.4, 49.6, 24.6; Anal. Calcd for C_{19}H_{19}N: C, 87.31; H, 7.33; N, 5.36. found: C, 87.34; H, 7.33; N, 5.27. MS (EI+) m/z = 261, 246, 156, 141, 115, 105, 91, 77; GC-MS retention time Rt = 12.65 min.

(S)-N-((2-Methoxynaphthalen-1-yl)methyl)-1-phenylethanamine (5i): yellow oil; [α]^24_D +10.6 (c 0.011, CH₂Cl₂); ^1H NMR (400 MHz, CDCl₃) δ 7.74-7.80 (m, 3H), 7.21-7.45 (m, 4H), 4.08-4.11 (d, 1H, J = 12.0 Hz), 4.03-4.00 (d, 1H, J = 12.0 Hz), 3.86-3.98 (m, 4H), 1.36-1.37 (d, 3H, J = 6.4 Hz); ^13C NMR (100 MHz, CDCl₃) δ 155.1, 146.0, 133.3, 129.2, 129.0, 128.5, 128.4, 127.0, 126.6, 123.3, 123.2, 121.4, 113.1, 58.4, 56.4, 41.6, 24.8; Anal. Calcd for C_{20}H_{21}NO: C, 82.44; H, 7.26; N, 4.81; O, 5.49. found: C, 82.37; H, 7.14; N, 4.95. MS (EI+) m/z = 291, 276, 260, 186, 171, 156, 141, 128, 115, 105, 91, 77; GC-MS retention time Rt = 13.36 min.

(S)-N-(4-tert-Butylbenzyl)-1-phenylethanamine (5j): colorless oil; [α]^24_D +4.6 (c 0.0056, CH₂Cl₂); ^1H NMR (400 MHz, CDCl₃) δ 7.20-7.35 (m, 9H), 3.79-3.84 (q, 1H, J = 6.4 Hz), 3.60-3.63 (d, 1H, J = 13.2 Hz), 1.35-1.36 (d, 3H,
J = 6.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.8, 125.8, 127.7, 128.5, 127.9, 127.0, 126.8, 125.4, 57.7, 51.4, 34.5, 31.5, 24.7; Anal. Calcd for C$_{19}$H$_{25}$N: C, 85.34; H, 9.42; N, 5.24. found: C, 85.27; H, 9.52; N, 5.12. MS (EI$^+$) m/z = 265, 252, 162, 147, 132, 117, 105, 91, 77, 65; GC-MS retention time Rt = 11.59 min.

(S)-N-((1-Methyl-1H-pyrrol-2-yl)methyl)-1-phenylethanamine (5k): colorless oil; $[\alpha]_{D}^{24}$ -14.1 ($c$ 0.0064, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22-7.38 (m, 5H) 6.54 (s, 1H), 5.97-6.02 (m, 2H), 3.78-2.82 (q, 1H, $J$ = 6.4 Hz), 3.54-3.58 (d, 1H, $J$ = 13.2 Hz), 3.55 (s, 3H), 3.49-3.52 (d, 1H, $J$ = 13.2 Hz), 1.33-1.35 (d, 3H, $J$ = 6.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.7, 131.4, 128.5, 127.0, 126.7, 122.2, 107.6, 106.5, 58.0, 43.5, 33.7, 24.5; Anal. Calcd for C$_{14}$H$_{18}$N$_2$: C, 78.46; H, 8.47; N, 13.07. found: C, 78.41; H, 8.34; N, 13.07. MS (EI$^+$) m/z = 214, 132, 120, 105, 94, 77; GC-MS retention time Rt = 10.00 min.

(S)-N-((1-Methyl-1H-indol-3-yl)methyl)-1-phenylethanamine (5l): yellow oil; $[\alpha]_{D}^{24}$ +3.6 ($c$ 0.0047, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54-7.56 (d, 1H, $J$ = 8.0 Hz), 7.06-7.39 (m, 8H), 6.89 (s, 1H), 3.84-3.89 (q, 1H, $J$ = 6.4 Hz), 3.80-3.83 (d, 1H, $J$ = 13.2 Hz), 3.74-3.78 (d, 1H, $J$ = 13.2 Hz), 1.34-1.36 (d, 3H, $J$ = 6.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.8, 137.1, 128.5, 127.5, 127.2, 126.9, 126.8, 121.7, 119.1, 119.0, 113.7, 109.3, 57.8, 42.6, 32.6, 24.6; Anal. Calcd for C$_{18}$H$_{20}$N$_2$: C, 81.78; H, 7.63; N, 10.60. found: C, 81.78; H, 7.53; N, 10.50. MS (EI$^+$) m/z = 264, 159, 144, 132, 115, 106, 91, 77; GC-MS retention time Rt = 12.91 min.

(S)-N-(Furan-2-ylmethyl)-1-phenylethanamine (5m):$^{88}$ colorless oil; $[\alpha]_{D}^{24}$ -68.7 ($c$ 0.013, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.38 (m, 5H), 7.21-7.25 (dd, 1H, $J$ = 4.0, 8.0 Hz), 6.26-6.27 (d, 1H, $J$ = 4.0 Hz), 6.07-6.08 (d, 1H, $J$ = 4.0 Hz), 3.74-3.79 (q, 1H, $J$ = 6.4 Hz), 3.63-3.66 (d, 1H, $J$ = 14.4 Hz), 3.54-3.57 (d, 1H, $J$ = 14.4 Hz), 1.33-1.35 (d, 3H, $J$ = 6.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.1, 145.1, 141.8, 128.5, 127.2, 126.9, 126.8, 121.7, 119.1, 119.0, 113.7, 109.3, 57.8, 42.6, 32.6, 44.05, 24.4; Anal. Calcd for C$_{13}$H$_{15}$NO: C, 77.58; H, 7.51; N, 6.96. found: C, 77.56; H, 7.37; N, 6.98. MS (EI$^+$) m/z = 201, 196, 186, 105, 96, 91, 81, 76, 53; GC-MS retention time Rt = 11.31 min.

(S)-N-(Furan-3-ylmethyl)-1-phenylethanamine (5n): yellow oil; $[\alpha]_{D}^{24}$ -35.5 ($c$ 0.020, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21-7.34 (m, 7H), 6.33 (s, 1H), 3.77-3.82 (q, 1H, $J$ = 6.4 Hz), 3.47 (s, 2H), 1.34-1.35 (d, 3H, $J$ =
6.4 Hz); 13C NMR (100 MHz, CDCl3) δ 145.4, 143.1, 139.8, 128.5, 127.0, 126.7, 124.2, 110.5, 57.5, 42.1, 24.4;
Anal. Calcd for C13H15NO: C, 77.58; H, 7.51; N, 6.96. found: C, 77.42; H, 7.45; N, 6.99. MS (EI+) m/z = 200, 186, 120, 105, 96, 81, 53; GC-MS retention time Rt = 8.70 min.

(S)-2,2-Dimethyl-N-(1-phenylethyl)propan-1-amine (5o): yellow oil; [α]D24 −55.6 (c 1.00, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 7.29-7.33 (m, 4H), 7.20-7.24 (m, 1H), 3.68-3.72 (q, 1H, J = 6.5 Hz), 2.25-2.27 (d, 1H, J = 11 Hz), 2.12-2.14 (d, 1H, J = 11 Hz), 1.32-1.33 (d, 3H, J = 6.5 Hz), 0.88 (s, 9H); 13C NMR (125 MHz, CDCl3) δ 146.7, 128.4, 126.7, 60.2, 59.1, 31.5, 27.9, 25.1; Anal. Calcd for C13H15NO: C, 81.61; H, 11.06; N, 7.32. found: C, 81.63; H, 11.05; N, 7.35. MS (EI+) m/z = 191, 176, 134, 105, 91, 77; GC-MS retention time Rt = 10.11 min.

(S)-2-Methyl-N-(1-phenylethyl)propan-1-amine (5p): yellow oil; [α]D24 −56.2 (c 1.00, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 7.30-7.34 (m, 4H), 7.21-7.25 (m, 1H), 3.71-3.75 (q, 1H, J = 6.5 Hz), 2.32-2.35 (d of d, 1H, J = 11.5, 6 Hz), 2.22-2.25 (d of d, 1H, J = 11.5, 7 Hz), 1.66-1.74 (heptet, 1H, J = 7.0 Hz), 1.34-1.35 (d, 3H, J = 6.5 Hz), 0.87-0.88 (d of d, 6H, J = 6.5, 2.0 Hz); 13C NMR (125 MHz, CDCl3) δ 146.2, 128.5, 126.9, 126.7, 58.5, 56.0, 24.7, 20.9, 20.8; Anal. Calcd for C13H15NO: C, 81.61; H, 10.80; N, 7.90. found: C, 81.24; H, 10.71; N, 7.86. MS (EI+) m/z = 177, 162, 134, 105, 91, 77; GC-MS retention time Rt = 9.91 min.

(S)-N-(Cyclohexylmethyl)-1-phenylethanamine (5q): yellow oil; [α]D24 −30.6 (c 1.00, CH2Cl2); 1H NMR (500 MHz, CDCl3) δ 7.30-7.35 (m, 4H), 7.21-7.24 (m, 1H), 3.70-3.74 (q, 1H, J = 6.5 Hz), 2.33-2.36 (d of d, 1H, J = 11.5, 6 Hz), 2.22-2.25 (d of d, 1H, J = 11.5, 7 Hz), 1.63-1.76 (m, 5H), 1.33-1.34 (d, 3H, J = 6.5 Hz), 1.09-1.30 (m 4H), 0.80-0.91 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 146.3, 128.5, 126.9, 126.7, 58.6, 54.8, 38.3, 31.7, 31.6, 26.8, 26.3, 26.2, 24.7; Anal. Calcd for C13H15NO: C, 82.70; H, 10.41; N, 6.89. found: C, 82.61; H, 10.44; N, 6.91. MS (EI+) m/z = 203, 188, 134, 105, 91, 79, 41; GC-MS retention time Rt = 9.23 min.

(S)-N-(Cyclopentylmethyl)-1-phenylethanamine (5r): yellow oil; [α]D24 −36.0 (c 1.00, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.21-7.35 (m, 5H), 3.72-3.77 (q, 1H, J = 6.8 Hz), 2.43-2.47 (q, 1H, J = 6.8, 11.2 Hz), 2.30-2.34 (q, 1H, J = 7.2, 11.2 Hz), 1.32-1.33 (sept, 1H, J = 7.2 Hz), 1.68-1.78 (m, 2H), 1.47-1.58 (m, 4H), 1.34-1.35 (d, 3H, J
= 6.8 Hz), 1.06-1.12 (m, 2H) ; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.2, 128.5, 126.9, 126.7, 58.7, 53.9, 40.3, 31.0, 25.4, 24.7; Anal. Calcd for C$_{13}$H$_{15}$NO: C, 82.89; H, 10.67; N, 6.44. found: C, 82.76; H, 10.77; N, 6.56. MS (El$^+$) m/z = 217, 202, 134, 105, 91, 79, 55, 41; GC-MS retention time Rt = 9.94 min.
Fig. S1 ¹H NMR Spectrum of 2.
Fig. S2 $^{13}$C NMR Spectrum of 2.
Fig. S3 TGA data of 2: the temperature is increased by 10 °C per minute from 20 to 300 °C.
Fig. S4 (a) X-ray powder diffraction (XRD) pattern and (b) IR spectrum of 2.
Fig. S5 $^1$H NMR Spectrum of 4a.

Temp. 25.0 °C / 298.1 K
Operator: EWR
INOVA-500 "sokang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 7996.4 Hz
40 repetitions

OBSERVE $^1$H: 498.90 MHz 129 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 8 sec

4a

$^1$H NMR Spectrum:

- Ph
- N

- ppm:
  - 0.95
  - 1.80, 1.90
  - 1.90, 2.02
  - 3.00
  - 5.43
  - 0.97, 2.03
Fig. S6 $^{13}$C NMR Spectrum of 4a.

Operator: LWK
IROYA-500 "sokang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.8 degrees
Acq. time 1.200 sec
Width 30185.5 Hz
5900 repetitions
OBSERVE G13, 125.7011538 MHz
DECOUPLE H1, 49.8074048 MHz
Power 37 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 3 hr, 12 min, 26 sec
Fig. S7 $^1$H NMR Spectrum of 5a.
Fig. S8 $^{13}$C NMR Spectrum of 5a.

Relax. delay 1,000 sec
Pulse 45.0 degrees
Acq. time 1,390 sec
Width 24508.8 Hz
56 repetitions
Observe C13, 100.5127788 MHz
Decouple H1, 399.7344008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
Data processing
Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
Fig. S9 $^1$H NMR Spectrum of 5b.
Fig. S10 $^{13}$C NMR Spectrum of 5b.

Ambient temperature
Operator: LVE
VNMRS-400 "Varian-NMR"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24508.0 Hz
80 repetitions
OBSERVE C13, 100.5127833 MHz
DECOUPLE H1, 398.7344008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 85536
Total time 36 min, 21 sec
Fig. S11 $^1$H NMR Spectrum of 5c.
Fig. S12 $^{13}$C NMR Spectrum of 5c.

Pulse Sequence: s2pu1
Solvent: d6c13
Ambient temperature
Operator: LWK
VNMRS-600 "Varian-NMR"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24508.8 Hz
46 repetitions
OBSERVE C13, 100.5127818 MHz
DECOUPLE H, 398.7344008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
Fig. S13 $^1$H NMR spectra of 5d.
Fig. S14 $^{13}$C NMR Spectrum of 5d.

Solvent: dcd19
Ambient temperature
Operator: LWR
VNMR-400 "Varian-NMR"

Delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24508.8 Hz
72 repetitions

Observe C13, 160.5127900 MHz
DECOUPLE H1, 399.7944000 MHz
Power 37 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
fT size 65536
Total time 38 min, 21 sec
Fig. S15 $^1$H NMR Spectrum of 5e.

Solvent: cdcl$_3$
Operator: LWK
VNNRS-490 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.649 sec
Width 8410.3 Hz
Single scan

OBSERVE : H1, 399.7324555 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total Time 0 min, 8 sec

![NMR Spectrum of 5e](image)
Fig. S16 $^{13}$C NMR Spectrum of 5e.

Solvent: cdCl$_3$
Ambient temperature
Operator: L.W.
VNMR-400 "Varian-NMR"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24508.8 Hz
64 repetitions

OBSERVE C13, 100.5127833 MHz
DECouple H1, 399.7344000 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 30 min, 21 sec
Fig. S17 $^1$H NMR Spectrum of 5f.

Solvent: cdcl3
Ambient temperature
Operator: LWK
VNIIRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 6410.3 Hz
Single scan

OBSERVE H1, 399.7324360 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 9 min, 9 sec

![NMR Spectrum of 5f](image)
Fig. S18 $^{13}$C NMR Spectrum of 5f.
Fig. S19 $^1$H NMR Spectrum of 5g.
Fig. S20 $^{13}$C NMR Spectrum of 5g.

Solvent: cdcl3
Ambient temperature
Operator: LWK
VMNRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 49.0 degrees
Acq. time 1.360 sec
Width 2559.8 Hz
40 repetitions

OBSERVE C13, 100.5127878 MHz
DECOUPLE H1, 399.7944008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 36 min, 21 sec
Fig. S21 $^1$H NMR Spectrum of 5h.

Operator: LWK
File: 1024-column_product
VNMRS-400 "Varian-NMR2"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
28 repetitions
OBSERVE H1, 0.089564689 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min, 31 sec
Fig. S22 $^{13}$C NMR Spectrum of 5h.
Fig. S23 ¹H NMR Spectrum of 5i.

Solvent: cdcl₃
Ambient temperature
Operator: LWK
VNMRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
Single scan
OBSERVE H1, 399.7324185 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 9 sec
Fig. S24 $^{13}$C NMR Spectrum of 5i.

Solvent: ddc13
Ambient temperature
Operator: LWK
VNMRS-400 "Varian-NMR"

Relax. delay 1.600 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24595.8 Hz
80 repetitions
OBSERVE C13, 100.5127988 MHz
DECOUPLE H1, 390.7344008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 65536
Total time 36 min, 21 sec
Fig. S25 $^1$H NMR Spectrum of 5j.
Fig. S26 $^{13}$C NMR Spectrum of 5j.

Solvent: dcd13
Ambient temperature
Operator: LWK
VRMRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.250 sec
Width 24505.8 Hz
64 repetitions
OBSERVE C13, 100.5127855 MHz
DECOUPLE H1, 399.7344808 MHz
Power 37 dB
continuously on
WALTZ-19 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
Fig. S27 $^1$H NMR Spectrum of 5k.

Solvent: d$^2$C$_3$D$_6$
Ambient temperature
Operator: LWR
VARIAN-400 "Varian-NMR"
Relax. delay 1.000 sec
Pulse 45.8 degrees
Acq. time 2.645 sec
Width 6413.3 Hz
Single scan
OBSERVE H1, 398.3924150 MHz
DATA PROCESSING
Recal. enhancement ~0.0 Hz
FT size 65536
Total time 8 min, 9 sec
Fig. S28 $^{13}$C NMR Spectrum of 5k.

Solvent: cdcl3
Ambient temperature
Operator: LWK
NMR3-400 "Varian-NMR"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.360 sec
Width 24509.8 Hz
60 repetitions
Observe CH, 100.5127938 MHz
Decouple H1, 99.70644008 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
Fig. S29 $^1$H NMR Spectrum of 5l.
Fig. S30 $^{13}$C NMR Spectrum of 5I.

Solvent: cdCl$_3$
Ambient temperature
Operator: LKC
VNMRS-400 "Varian-NMR"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24500.6 Hz
40 repetitions
OSERVE C13, 100.5127960 MHz
DECOUPLE H1, 399.7344000 MHz
Power 37 dB
continuously on
VALT2-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 30 min, 21 sec
Fig. S31 $^1$H NMR Spectrum of 5m.

Operator: LWK
File: 1056-column_product
VNMRS-000 "Varian-NMR2"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 6410.3 Hz
24 repetitions
OBSERVE: H1, 399.6646457 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min, 19 sec
Fig. S32 $^{13}$C NMR Spectrum of 5m.

Solvent: dcl3
Ambient temperature
Operator: EW
VNMRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24589.8 Hz

104 repetitions

OBSERVE C13, 100.515083 MHz
DECOUPLE H1, 399.743510 MHz

Power 37 dB
continuously on

WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 85536
Total time 38 min, 21 sec
Fig. S33 1H NMR Spectrum of 5n.

Solvent: dcd19
Ambient temperature
Operator: LWE
VNMR-600 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6018.3 Hz
Single scan

OBSERVE H1, 398.7324192 MHz
DATA PROCESSING
Resol. enhancement 0.0 Hz
FT size 65536
Total time 8 min, 9 sec
Fig. S34 $^{13}$C NMR Spectrum of 5n.

Ambient temperature
Operator: LWK
Varian-NMR

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24599.8 Hz
44 repetitions

OBSERVE C13, 106.5127855 MHz
DECOUPLE H1, 138.734008 MHz
Power 37 dB
Continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 30 min, 21 sec
Fig. S35 $^1$H NMR Spectrum of 5o.

Solvent: cdcl3
Ambient temperature
Operator: LWK
INOVAS-500 "sokang.ac.kr"

Relax. delay 1,000 sec
Pulse 45.0 degrees
Acq. time 2.066 sec
Width 7998.4 Hz
40 repetitions
OBSERVE Hl, 499.9049138 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 8 sec
Fig. S36 $^{13}$C NMR Spectrum of 5o.

Solvent: cdc13
Ambient temperature
Operator: LWK
INOVA-500 "soxang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.360 sec
Width 30165.9 Hz
4744 repetitions
OBSERVE C13, 125.7011712 MHz
DECouple H1, 499.9074948 MHz
Power 37 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 151872
Total time 3 hr, 12 min, 26 sec
Fig. S37 $^1$H NMR Spectrum of 5p.

Operator: LWK
File: 844-proton
VMR2-400 "Varian-NMR2"

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
40 repetitions

OBSERVE H1, 399.6770224 MHz
DATA PROCESSING
Resol. enhancement 0.0 Hz
FT size 65536
Total time 2 min, 8 sec
Fig. S38 $^{13}$C NMR Spectrum of 5p.

Ambient temperature
Operator: LWK
INOVA-500 "sokang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. Time 1.300 sec
Width 30165.9 Hz
5744 repetitions
OBSERVE C13, 125.7011712 MHz
DECOUPLE H1, 498.8674948 MHz
Power 37 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 151872
Total time 5 hr, 7 min, 55 sec
Fig. S39 $^1$H NMR Spectrum of 5q.

Temp. 25.0 C / 298.1 K
Operator: LWK
INOVA-500 "sokang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 7980.4 Hz
40 repetitions

OBSERVE H1, 499.9049128 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 85536
Total time 2 min, 8 sec
Fig. S40 $^{13}$C NMR Spectrum of 5q.

Temp. 25.0°C / 298.1 K  
Operator: LWK  
INOVA-500 "sokang.ac.kr"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 30165.3 Hz  
5000 repetitions  
OBSERVE CI3, 125.7011707 MHz  
DECOUPLE HI, 499.8074048 MHz  
Power 37 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 3 hr, 12 min, 26 sec
Fig. S41 $^1$H NMR Spectrum of 5r.

Temp. 22.0 °C / 295.1 K
Operator: LWE
VNMRS-400 "Varian-NMR"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 6418.3 Hz
20 repetitions
OBSERVE H1, 399.6646449 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min, 7 sec
Fig. S42 $^{13}$C NMR Spectrum of 5r.

Temp. 25.0°C / 298.1 K
Operator: LWK
INOVA-500 "sokang.ac.kr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30185.9 Hz
2628 repetitions
OBSERVE C13, 125.7011707 MHz
DECOUPLE H1, 488.30407408 MHz
Power 37 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 55 min, 28 sec
References


