Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

for

Electrophilic iodine(I) compounds induced semipinacol rearrangement via C–X bond cleavage

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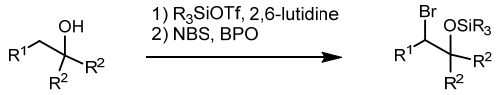
CONTENTS

1. General information

All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise noted. Solvents and materials were obtained from commercial suppliers and used without further purification. Column chromatography was performed on Cica silica gel 60 (230−400 mesh) or Fuji Silysia silica gel (NH, 100−200 mesh), gel permeation chromatography was performed with LC-9201 and flash column chromatography was performed on Cica silica gel 60 (spherical/40−100 μm). Reactions and chromatography fractions were analyzed employing pre-coated silica gel plate (Merck Silica Gel 60 F_{254}). All melting points were measured on BÜCHI M-565 melting point apparatus and are uncorrected. IR spectra were measured on JASCO FT/IR-4100. Unless otherwise noted, NMR spectra were obtained in $CDCl_3$. ^1H NMR (500 MHz) spectra were recorded with JEOL ECP-500 spectrometers and chemical shifts are reported in δ (ppm) relative to TMS (in $CDCl_3$) as internal standard. Unless otherwise noted, ^{13}C NMR (126 MHz) spectra were also recorded using JEOL ECP-500 spectrometers and referenced to the residual $CHCl_3$ signals. ^1H NMR multiplicities are reported as follows: br = broad; m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet; sep = septet. Low-resolution mass spectra were recorded on a JMS-HX/HX 110A or MS700 mass spectrometer. High-resolution mass spectra were obtained on a JMS-HX/MS700 (FAB) or a Shimazu LCMS-IT-TOF fitted with an ESI. Optical rotations were recorded on a JASCO P-2200 polarimater with a path length of 1 cm; concentrations are quoted in grams per 100 mL. $[\alpha]_D$ values are measured in 10^{-1} deg cm^2g^{-1}. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) analyses. Unless otherwise noted, all materials and solvent were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used without purification. All non-commercially available substrates were prepared according to the literature procedure as indicated below.

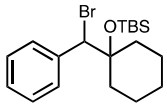
2. Preparation of substrates

General procedure for the preparation of benzyl bromide 1.



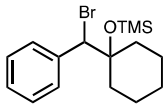
To a solution of tertiary alcohol (2.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) under argon atmosphere was added 2,6-lutidine (4.0 mmol, 2.0 equiv) and TBSOTf or TMSOTf (2.4 mmol, 1.2 equiv) at 0 °C. The resulting mixture was stirred at room temperature until consumption of the starting material, as monitored by TLC (hexane/EtOAc = 9:1). The reaction was quenched with H_2O, and the product was extracted with $CHCl_3$ three

times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was filtered through a plug of silica gel with hexane to yield the corresponding silyl ether. To the solution of the obtained silyl ether (0.5 mmol, 1.0 equiv) in CCl_4 (10 mL) under argon atmosphere was added *N*-bromosuccinimide (0.55 mmol, 1.1 equiv) and benzoyl peroxide (0.05 mmol, 0.1 equiv). The resulting mixture was stirred under reflux until consumption of the starting material, as monitored by TLC (hexane). The reaction was quenched with aqueous $Na_2S_2O_3$ solution, and the product was extracted with $CHCl_3$ three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane) to yield the corresponding benzyl bromide **1**.



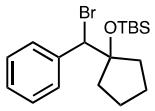
[1-(α-Bromobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1a)

Colorless solid (75%, 2 steps); Mp: 38–42 °C; IR (ATR): 2930, 2857, 1453, 1254, 1106, 1001, 890, 836, 774, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.55–7.53 (m, 2H), 7.30–7.25 (m, 3H), 5.25 (s, 1H), 2.28–2.15 (m, 1H), 1.76–1.68 (m, 1H), 1.60–1.16 (m, 8H), 0.98 (s, 9H), 0.24 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 129.7, 128.1, 127.9, 77.3, 62.1, 38.6, 35.7, 26.2, 25.5, 23.4, 23.3, 18.8, –1.57, –1.65; LRMS (FAB): *m/z* (relative intensity) 327 ($[M–tBu]^+$, 5), 325 ($[M–tBu]^+$, 5), 303 ($[M–Br]^+$, 15), 73 (100); HRMS (FAB): calcd for $C_{15}H_{22}{}^{81}BrOSi$ ($[M–tBu]^+$): 327.0603; found 327.0608



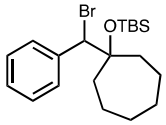
[1-(α-Bromobenzyl)cyclohexyl]oxytrimethylsilane (1b)

Colorless solid (62%, 2 steps); Mp: 56–59 °C; IR (ATR): 2935, 2858, 1494, 1352, 1249, 1164, 1114, 1076, 1030, 1003, 894, 835, 752, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.52–7.45 (m, 2H), 7.31–7.23 (m, 3H), 5.12 (s, 1H), 2.02–1.90 (m, 1H), 1.74–1.60 (m, 2H), 1.59–1.30 (m, 7H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 129.7, 128.1, 127.9, 77.7, 63.7, 38.2, 36.0, 25.6, 23.0, 2.9; LRMS (FAB): *m/z* (relative intensity) 261 ($[M–Br]^+$, 45), 73 (100); HRMS (FAB): calcd for $C_{16}H_{25}OSi$ ($[M–Br]^+$): 261.1675; found 261.1664



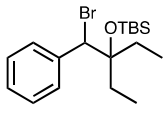
[1-(α-Bromobenzyl)cyclopentyl]oxy(*tert*-butyl)dimethylsilane (1e)

Yellow oil (71%, 2 steps); IR (ATR): 2954, 2856, 1471, 1253, 1089, 1005, 925, 834, 805, 771, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.52–7.50 (m, 2H), 7.30–7.23 (m, 3H), 4.90 (s, 1H), 2.15–2.08 (m, 1H), 1.87–1.68 (m, 4H), 1.67–1.52 (m, 3H), 0.90 (s, 9H), 0.16 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 129.6, 128.1, 128.0, 87.5, 64.3, 39.7, 38.4, 26.1, 24.3, 24.0, 18.7, 2.27, 2.34; LRMS (FAB): *m/z* (relative intensity) 289 ($[M–Br]^+$, 40), 73 (100); HRMS (FAB): calcd for $C_{18}H_{29}OSi$ ($[M–Br]^+$): 289.1988; found 289.1982



[1-(α-Bromobenzyl)cycloheptyl]oxy(*tert*-butyl)dimethylsilane (1f)

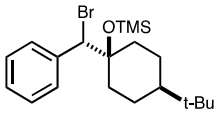
Colorless oil (17%, 2 steps, not optimized); IR (ATR): 2926, 2855, 1461, 1360, 1253, 1219, 1090, 1002, 949, 872, 833, 804, 772, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.57–7.50 (m, 2H), 7.30–7.23 (m, 3H), 5.00 (s, 1H), 2.23 (dd, *J* = 14.5, 8.1 Hz, 1H), 1.89–1.82 (m, 1H), 1.67–1.20 (m, 10H), 0.95 (s, 9H), 0.26 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 129.8, 128.1, 127.9, 81.6, 65.4, 41.5, 39.5, 30.0, 29.8, 26.3, 23.3, 23.1, 18.9, –1.45, –1.53; LRMS (FAB): *m/z* (relative intensity) 317 ($[M–Br]^+$, 25), 73 (100); HRMS (FAB): calcd for $C_{20}H_{33}OSi$ ($[M–Br]^+$): 317.2301; found 317.2299



[3-(α-Bromobenzyl)pentyl]oxy(*tert*-butyl)dimethylsilane (1g)

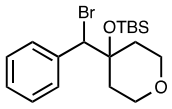
Colorless oil (54%, 2 steps); IR (ATR): 2967, 2929, 2855, 1472, 1255, 1131, 1071, 887, 836, 806, 746, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.55–7.50 (m, 2H), 7.30–7.24 (m, 3H), 4.94 (s, 1H), 2.04 (dt, *J* = 14.0, 7.2 Hz, 1H), 1.83 (dt, *J* = 14.0, 7.1 Hz, 1H), 1.45–1.41 (m, 2H), 0.97 (s, 9H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.81 (t,

J = 7.5 Hz, 3H), 0.26 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 130.1, 128.1, 127.8, 81.1, 62.7, 31.5, 29.4, 26.5, 19.1, 9.4, 8.7, –1.0, –1.1; LRMS (FAB): *m/z* (relative intensity) 291 ($[M–Br]^+$, 22), 73 (100); HRMS (FAB): calcd for $C_{18}H_{31}OSi$ ($[M–Br]^+$): 291.2144; found 291.2145



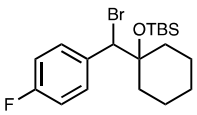
[1-(α-Bromobenzyl)-4-*tert*-butylcyclohexyl]oxytrimethylsilane (1h)

Colorless solid (57%, 2 steps); Mp: 72–75 °C; IR (ATR): 2951, 2870, 1450, 1369, 1248, 1139, 1058, 892, 836, 772, 699, 672 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): δ = 7.43–7.36 (m, 2H), 7.30–7.21 (m, 3H), 4.86 (s, 1H), 2.04–1.98 (m, 1H), 1.78–1.71 (m, 1H), 1.58–1.48 (m, 2H), 1.40–1.33 (m, 5H), 0.83 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 129.7, 128.1, 128.0, 78.0, 68.1, 47.6, 36.8, 35.0, 32.4, 27.7, 23.0, 22.6, 3.0; LRMS (FAB): *m/z* (relative intensity) 317 ($[M–Br]^+$, 12), 73 (100); HRMS (FAB): calcd for $C_{20}H_{33}OSi$ ($[M–Br]^+$): 317.2295; found 317.2304



[1-(α-Bromobenzyl)-4-oxocyclohexyl]oxy(*tert*-butyl)dimethyl silane (1i)

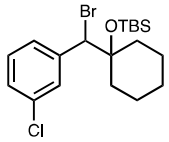
Yellowish solid (30%, 2 steps); Mp: 50–54 °C; IR (ATR): 2957, 2927, 2857, 1251, 1225, 1158, 1095, 1018, 1005, 938, 893, 836, 805, 776, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): δ = 7.46–7.42 (m, 2H), 7.32–7.25 (m, 3H), 5.22 (s, 1H), 3.84 (ddd, *J* = 11.6, 7.2, 4.0 Hz, 1H), 3.77 (ddd, *J* = 11.4, 7.1, 4.0 Hz, 1H), 3.65–3.57 (m, 2H), 1.98–1.94 (m, 1H), 1.85 (ddd, *J* = 12.9, 8.1, 4.2 Hz, 1H), 1.75–1.63 (m, 2H), 0.99 (s, 9H), 0.31 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 129.7, 128.5, 128.2, 75.2, 64.7, 64.5, 63.2, 38.0, 35.4, 26.3, 18.9, –1.5, –1.6; LRMS (FAB): *m/z* (relative intensity) 305 ($[M–Br]^+$, 9), 73 (100); HRMS (FAB): calcd for $C_{18}H_{29}O_2Si$ ($[M–Br]^+$): 305.1931; found 305.1942



[1-(α-Bromo-4-fluorobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1j)

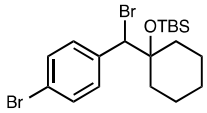
Colorless needle (62%, 2 steps); Mp: 56–59 °C; IR (ATR): 2927, 2855, 1605, 1509, 1457, 1359, 1254, 1230,

1160, 1102, 1000, 892, 836, 801, 773, 738, 688, 648, 620 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.54–7.52 (m, 2H), 6.98–6.95 (m, 2H), 5.26 (s, 1H), 2.31–2.20 (m, 1H), 1.73 (dt, *J* = 9.2, 4.5 Hz, 1H), 1.63–1.38 (m, 6H), 1.34–1.18 (m, 2H), 0.97 (s, 9H), 0.24 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, *J* = 247.1 Hz), 135.7 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 8.1 Hz), 114.8 (d, *J* = 21.5 Hz), 77.3, 60.7, 38.7, 36.0, 26.2, 25.5, 23.4 (2C), 18.8, –1.6, –1.7; LRMS (FAB): *m/z* (relative intensity) 345 ($[M–tBu]^+$, 13), 343 ($[M–tBu]^+$, 12), 73 (100) ; HRMS (FAB): calcd for $C_{15}H_{21}{}^{79}BrFOSi$ ($[M–tBu]^+$): 343.0524; found 343.0525



[1-(α-Bromo-3-chlorobenzyl)cycloheptyl]oxy(*tert*-butyl)dimethylsilane (1k)

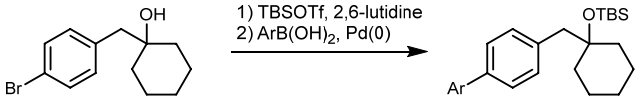
Colorless solid (71%, 2 steps); Mp: 59–63 °C; IR (ATR): 2929, 2857, 1472, 1255, 1219, 1164, 1102, 1000, 878, 836, 773, 726, 706, 681 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.67 (s, 1H), 7.37–7.30 (m, 2H), 7.25–7.16 (m, 3H), 5.21 (s, 1H), 2.34–2.25 (m, 1H), 1.76–1.15 (m, 9H), 0.99 (s, 9H), 0.23 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 133.9, 130.1, 129.0, 128.3, 127.4, 60.0, 38.7, 36.0, 26.2, 25.5, 23.5, 23.4, 18.8, –1.6, –1.7 (One peak of quaternary carbon is missing due to overlapping); LRMS (FAB): *m/z* (relative intensity) 337 ($[M–Br]^+$, 8), 73 (100); HRMS (FAB): calcd for $C_{19}H_{30}ClOSi$ ($[M–Br]^+$): 337.1754; found 337.1756



[1-(α-Bromo-4-bromobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1l)

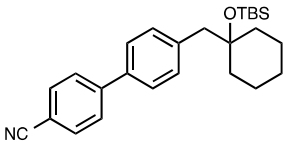
Colorless solid (75%); Mp: 91–94 °C; IR (ATR): 2940, 2851, 1485, 1254, 1219, 1163, 1105, 1071, 999, 892, 830, 775, 730, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.46–7.38 (m, 4H), 5.21 (s, 1H), 2.27–2.23 (m, 1H), 1.75–1.71 (m, 1H), 1.63–1.37 (m, 6H), 1.33–1.17 (m, 2H), 0.97 (s, 9H), 0.23 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 131.3, 131.1, 122.1, 77.3, 60.4, 38.6, 36.0, 26.2, 25.5, 23.4, 18.8, –1.58, –1.63; LRMS (FAB) : *m/z* (relative intensity) 383 ($[M–Br]^+$, 8), 381 ($[M–Br]^+$, 8), 73 (100); HRMS (FAB): calcd for $C_{19}H_{30}{}^{79}BrOSi$ ($[M–Br]^+$): 381.1249; found 381.1252

1l and **1m** were synthesized by silylation, Suzuki–Miyaura coupling followed by radical bromination.



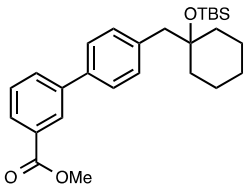
S-1l, S-1m

1-[(4-Bromobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (**S-1l**) was synthesized by silylation of 1-[(4-bromophenyl)methyl]cyclohexanol[2] in the same procedure as described above. To the solution of the resulting silyl ether (0.3 mmol) in DME/H_2O (4:1, 1.0 mL) under argon atmosphere was added sodium carbonate (0.75 mmol, 2.5 equiv), boronic acid (0.36 mmol, 1.2 eqiv), and $Pd(PPh_3)_4$ (0.015 mmol, 5 mol %) at room temperature. The resulting mixture was stirred at 80 °C until consumption of the starting material, as monitored by TLC (hexane). The reaction was quenched with H_2O, and the product was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc) to yield the corresponding biaryl (**S-1l** and **S-1m**).



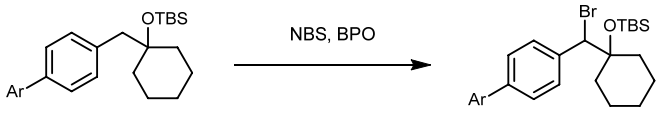
[1-[4-(4-Cyanophenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (S-1m)

Yellow solid (68%, 2 steps); Mp: 85–87 °C; IR (ATR): 2928, 2855, 2227, 1725, 1607, 1494, 1470, 1255, 1147, 1063, 1006, 835, 772, 683 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.72–7.67 (m, 4H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.9 (s, 2H), 1.72–1.65 (m, 2H), 1.55–1.34 (m, 7H), 1.28–1.22 (m, 1H), 0.89 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.7, 139.5, 136.8, 132.7, 131.6, 127.6, 126.5, 119.2, 110.6, 76.1, 47.9, 37.5, 26.2, 25.6, 22.9, 18.6, 1.51; HRMS (ESI): calcd. for $C_{26}H_{35}NaNOSi$ ($[M+Na]^+$): 428.2380, Found: 428.2387



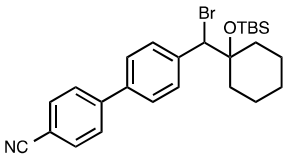
[1-[4-(3-Methoxycarbonylphenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (S-1n)

Yellow oil (42%, 2 steps); IR (ATR): 2928, 2855, 1725, 1471, 1442, 1307, 1244, 1216, 1146, 1111, 1083, 1059, 1007, 833, 811, 756, 683 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 8.28–8.26 (m, 1H), 7.99 (dt, *J* = 7.76, 1.37 Hz, 1H), 7.79 (ddd, *J* = 7.7, 1.9, 1.1 Hz, 1H), 7.54–7.47 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.94 (s, 3H), 2.86 (s, 2H), 1.72–1.65 (m, 2H), 1.55–1.35 (m, 7H), 1.25–1.18 (m, 1H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 141.4, 138.4, 137.8, 131.5, 131.4, 130.7, 128.9, 128.2, 128.2, 126.5, 76.1, 52.3, 37.4, 26.2, 25.6, 22.8, 18.6, 1.5; LRMS (FAB): *m/z* (relative intensity) 381 ($[M–tBu]^+$, 4), 73 (100), HRMS (FAB): calcd for $C_{23}H_{29}O_3Si$ ($[M–tBu]^+$): 381.1891; found 381.1890



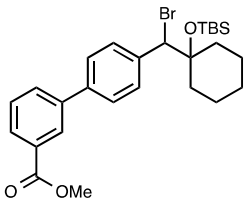
S-1l, S-1m **1l, 1m**

To the solution of **S-1m** (0.12 mmol, 1.0 equiv) in CCl_4 (5 mL) under argon atmosphere was added *N*-bromosuccinimide (0.13 mmol, 1.1 equiv) and benzoyl peroxide (0.01 mmol, 0.1 equiv). The resulting mixture was stirred under reflux until consumption of the starting material, as monitored by TLC (hexane). The reaction was quenched with aqueous $Na_2S_2O_3$ solution, and the product was extracted with $CHCl_3$ three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc) to yield the corresponding benzyl bromide **1m**.



[1-[α-Bromo-4-(4-cyanophenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1m)

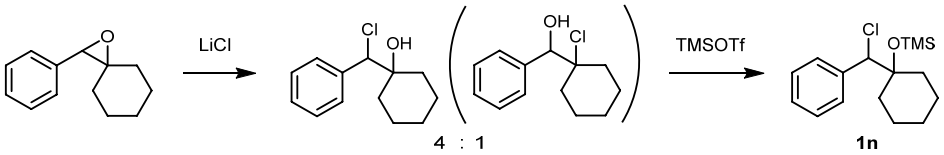
Colorless oil (68%); IR (ATR): 2929, 2856, 2227, 1606, 1494, 1470, 1349, 1254, 1164, 1101, 1001, 893, 826, 772, 751, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.73–7.66 (m, 6H), 7.52 (d, *J* = 8.5 Hz, 2H), 5.31 (s, 1H), 2.31–2.28 (m, 1H), 1.77–1.73 (m, 1H), 1.65–1.23 (m, 8H), 0.93 (s, 9H), 0.26 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 140.9, 138.8, 132.7, 130.4, 127.7, 126.8, 119.0, 111.1, 77.3, 61.0, 38.7, 36.1, 26.2, 25.5, 23.5, 18.8, –1.5, –1.6; LRMS (FAB): *m/z* (relative intensity) 404 ($[M–Br]^+$, 5), 73 (100); HRMS (FAB): calcd for $C_{26}H_{34}NOSi$ ($[M–Br]^+$): 404.2410; found 404.2407



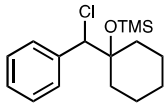
[1-[α-Bromo-4-(3-methoxycarbonylphenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1l)

Colorless oil (90%); IR (ATR): 2929, 2856, 1725, 1442, 1308, 1244, 1165, 1110, 1001, 893, 836, 761, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 8.29–8.26(m, 1H), 8.02–8.00 (m, 1H), 7.81–7.76 (m, 1H), 7.67–7.63 (m, 2H), 7.57–7.48 (m, 3H), 5.32 (s, 1H), 3.94 (s, 3H), 2,32–2.23 (m, 1H), 1.77–1.72 (m, 1H), 1.68–1.20 (m, 8H), 1.00 (s, 9H), 0.26 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 141.0, 139.8, 139.4, 131.5, 130.8, 130.2, 129.0, 128.5, 128.3, 126.7, 77.3, 61.5, 52.3, 38.6, 36.1, 26.2, 25.5, 23.5, 23.4, 18.9, –1.5, –1.6; LRMS (FAB): *m/z* (relative intensity) 437 ([M–Br]$^+$, 8), 73 (100); HRMS (FAB): calcd for $C_{27}H_{37}O_3Si$ ([M–Br]$^+$): 437.2512; found 437.2516

Substrate bearing benzyl chloride **1d** was prepared from 2-phenyl-1-oxaspiro[2.5]octane.



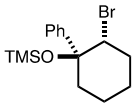
To the solution of 2-phenyl-1-oxaspiro[2.5]octane (1.5 mmol) in MeCN/DMF (4:1, 15 mL) was added LiCl (7.5 mmol, 5 equiv) and Amberlyst 15R (520 mg). The resulting heterogeneous mixture was stirred at room temperature until consumption of the starting material, as monitored by TLC (hexane). The reaction mixture was filtrated and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc) to yield the regioisomeric mixture of chlorohydrin (desired : undesired = 4:1). To the solution of this inseparable mixture (0.7 mmol in total) in CH_2Cl_2 (7 mL) under argon atmosphere was added 2,6-lutidine (1.4 mmol, 2.0 equiv) and TMSOTf (0.85 mmol, 1.2 equiv) at 0 °C. The resulting mixture was stirred at room temperature until consumption of the starting material, as monitored by TLC (hexane/EtOAc 9:1). The reaction was quenched with H_2O, and the product was extracted with $CHCl_3$ three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was filtered through silica gel with hexane to yield the regioisomeric mixture of the silyl ether. These regioisomers were separated by gel permeation chromatography (GPC) to afford **1d** as colorless oil.



[1-(α-Chlorobenzyl)cyclohexyl]oxytrimethylsilane (1d)

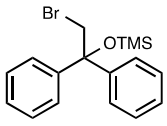
Colorless oil (39%, 2 steps); IR (ATR): 2936, 2858, 1452, 1249, 1166, 1149, 1117, 1076, 1030, 104, 897, 835, 740, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.51–7.40 (m, 2H), 7.39–7.27 (m, 3H), 4.96 (s, 1H), 1.89–1.33 (m, 10H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 129.4, 1281, 127.8, 78.0, 70.1, 36.7, 35.4, 25.6, 22.7, 22.7, 2.8; LRMS (FAB): *m/z* (relative intensity) 261 ($[M–Cl]^+$, 18), 73 (100); HRMS (FAB): calcd for $C_{16}H_{25}OSi$ ($[M–Cl]^+$): 261.1675; found 261.1678

1o and **1p** were synthesized by the silylation of the corresponding bromohydrin[1]. The procedure for the silylation is same as described above.



(2-Bromo-1-phenylcyclohexyl)oxytrimethylsilane (1o)

Colorless oil (59%); IR (ATR): 2938, 2359, 1447, 1250, 1155, 1087, 1067, 1023, 1005, 930, 906, 868, 837, 752, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.41–7.25 (m, 5H), 4.52–4.47 (m, 1H), 2.60–2.45 (m, 2H), 2.00–1.92 (m, 2H), 1.84–1.67 (m, 3H), 1.59–1.52 (m, 1H), –0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 128.0, 127.7, 126.1, 76.7, 61.5, 30.6, 29.4, 21.2, 19.9, 1.9; LRMS (FAB): *m/z* (relative intensity) 247 ($[M–Br]^+$, 20), 73 (100) ; HRMS (FAB): calcd for $C_{15}H_{23}OSi$ ($[M–Br]^+$): 247.1518; found 247.1523

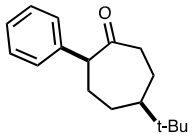


(2-Bromo-1,1-diphenylethyl)oxytrimethylsilane (1p)

Colorless oil (92%); IR (ATR): 3059, 2956, 1492, 1447, 1250, 1185, 1150, 1120, 1073, 1017, 921, 837, 753, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.41–7.24 (m, 10H), 4.17 (1, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 128.0, 127.5, 127.2, 79.8, 43.2, 1.94; LRMS (FAB): *m/z* (relative intensity) 269 ($[M–Br]^+$, 13), 73 (100) ; HRMS (FAB): calcd for $C_{17}H_{21}OSi$ ($[M–Br]^+$): 269.1362; found 269.1366

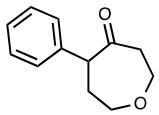
3. General procedure for iodine(I)-mediated semipinacol rearrangement.

To a homogeneous solution of benzyl bromide **1** (0.05 mmol, 1.0 equiv) in nitromethane (1.0 mL) under argon atmosphere was added *N*-iodosuccinimide (0.055 mmol, 1.1 equiv) in the dark. The resulting mixture was stirred under exclusion of light at room temperature until consumption of the starting material, as monitored by TLC (hexane/EtOAc). The reaction was quenched with saturated aqueous $Na_2S_2O_3$ solution, and the product was extracted with $CHCl_3$ five times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/EtOAc) to yield the corresponding ketone **2**. The compound characterization data for **2a**,[3] **2e**,[4] **2f**,[3] **2g**,[5] **2l**[6] were all identical to the literature data.



***cis*-5-*tert*-Butyl-2-phenylcycloheptan-1-one (2h)**

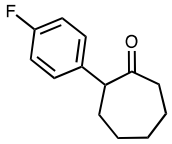
Colorless solid; Mp: 37–40 °C; IR (ATR): 2949, 2859, 1702, 1450, 1366, 1219, 954, 904, 768, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.35–7.29 (m, 2H), 7.26–7.18 (m, 3H), 3.80 (dd, *J* = 6.1, 6.1 Hz, 1H), 2.72–2.67 (m, 1H), 2.62–2.55 (m, 1H), 2.30–2.23 (m, 1H), 2.14–2.07 (m, 1H), 1.99–1.89 (m, 2H), 1.47–1.32 (m, 3H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.3, 140.3, 128.5, 128.3, 126.8, 57.4, 49.4, 41.9, 33.7, 30.2, 27.6, 26.7, 25.1; HRMS (ESI): calcd. for $C_{17}H_{25}O$ ($[M+H]^+$): 245.1900, Found: 245.1904.



5-Oxo-2-phenylcycloheptan-1-one (2i)

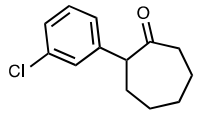
Colorless solid; Mp: 33–35 °C; IR (ATR): 2944, 2855, 1708, 1495, 1450, 1261, 1221, 1150, 1032, 772, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.35–7.32 (m, 2H), 7.28–7.24 (m, 1H), 7.20–7.18 (m, 1H), 4.21 (ddd, *J* = 12.8, 4.4, 3.1 Hz, 1H), 4.10 (ddd, *J* = 12.9, 4.5, 4.5, 1H), 3.92 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.76 (ddd, *J* = 13.0, 10.4, 2.6 Hz, 1H), 3.66 (ddd, *J* = 12.7, 10.6, 2.0 Hz, 1H), 3.00 (ddd, *J* = 15.3, 10.7, 4.5 Hz, 1H), 2.66 (ddd, *J* = 15.5, 4.5, 2.8 Hz, 1H), 2.30 (dddd, *J* = 14.9, 11.6, 10.6, 3.2 Hz, 1H), 2.09–2.04 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 210.1, 139.5, 128.7, 128.2, 127.3, 71.9, 66.6, 57.7, 46.3, 33.9; HRMS (ESI): calcd. for $C_{12}H_{15}O_2$ ($[M+H]^+$): 191.1067, Found: 191.1064.



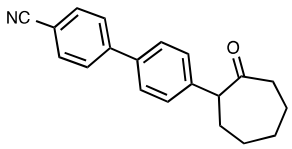
2-(4-Fluorophenyl)cycloheptan-1-one (2j)

Yellow oil; IR (ATR): 2966, 2932, 2879, 1703, 1602, 1509, 1455, 1224, 1160, 1130, 936, 835 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.21–7.13 (m, 2H), 7.03–6.96 (m, 2H), 3.71 (dd, *J* = 11.4, 3.9 Hz, 1H), 2.68–2.59 (m, 1H), 2.57–2.49 (m, 1H), 2.14–1.86 (m, 5H), 1.71–1.60 (m, 1H), 1.52–1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 161.9 (d, *J* = 244.9 Hz), 136.2 (d, *J* = 3.6 Hz), 129.5 (d, *J* = 7.5 Hz), 115.4 (d, *J* =21.5 Hz), 57.8, 42.9, 32.4, 29.9, 28.8, 25.1; HRMS (ESI): calcd. for $C_{13}H_{15}FNaO$ ($[M+Na]^+$): 229.0999, Found: 229.0981.



2-(3-Chlorophenyl)cycloheptan-1-one (2k)

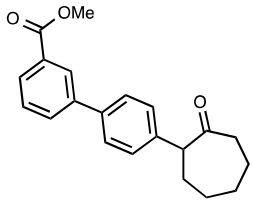
Colorless oil; IR (ATR): 2930, 2856, 1703, 1596, 1572, 1478, 1455, 1430, 1160, 1129, 1082, 937, 871, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.30–7.19 (m, 3H), 7.10–7.07 (m, 1H), 3.70 (dd, *J* = 11.4, 3.9 Hz, 1H), 2.68–2.62 (m, 1H), 2.57–2.53 (m, 1H), 2.13–1.88 (m, 5H), 1.69–1.60 (m, 1H), 1.51–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8, 142.5, 134.3, 129.8, 128.2, 127.1, 126.3, 58.3, 43.0, 32.1, 29.9, 29.0, 25.1; HRMS (ESI): calcd. for $C_{13}H_{16}ClO$ ($[M+H]^+$): 223.0884, Found: 223.0874.



2-[4-(4-Cyanophenyl)phenyl]cycloheptan-1-one (2m)

Colorless solid; Mp: 125–128 °C; IR (ATR): 2923, 2853, 2225, 1701, 1607, 1493, 1452, 1353, 1129, 1006, 931, 900, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.33(d, *J* = 8.1 Hz, 2H), 3.80 (dd, *J* = 11.3, 3.8 Hz, 1H), 2.74–2.66 (m, 1H), 2.60–2.56 (m,

1H), 2.18–1.95 (m, 5H), 1.73–1.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.2, 145.4, 141.3, 137.8, 132.7, 128.8, 127.7, 127.4, 119.1, 110.9, 58.4, 43.1, 32.2, 29.9, 28.9, 25.1; HRMS (ESI): calcd. for $C_{20}H_{20}NO$ ($[M+H]^+$): 290.1539, Found: 290.1532.

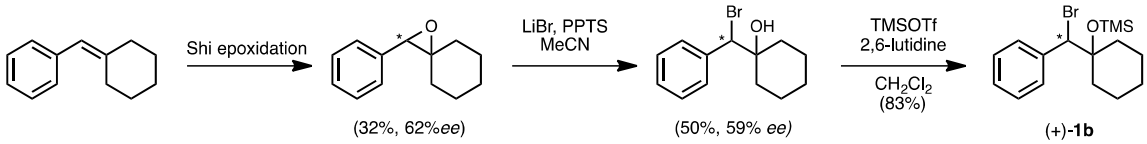


2-[4-(3-Methoxycarbonylphenyl)phenyl]cycloheptan-1-one (2n)

Yellow oil; IR (ATR): 2927, 2855, 1723, 1442, 1308, 1246, 1111, 841, 741, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): δ = 8.25 (s, 1H), 8.02–7.99 (m, 1H), 7.78–7.75 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.49 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.78 (dd, *J* = 11.3, 4.0 Hz, 1H), 2.73–2.67 (m, 1H), 2.60–2.54 (m, 1H), 2.20–2.14 (m, 1H), 2.14–1.96 (m, 4H), 1.73–1.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 167.2, 141.2, 140.1, 138.8, 131.5, 130.8, 128.9, 128.5, 128.4, 128.3, 127.4, 58.5, 52.3, 43.0, 32.2, 30.0, 28.8, 25.3; HRMS (ESI): calcd. for $C_{21}H_{23}O_3$ ($[M+H]^+$): 323.1642, Found: 323.1641.

4. Preparation of the chiral substrate 1b

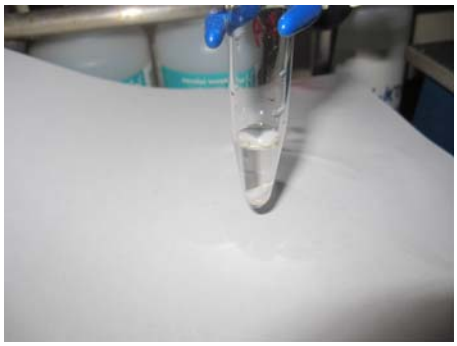
As indicated below, (+)-**1b** was synthesized via Shi epoxidation.[7]



To the chiral 2-phenyl-1-oxaspiro[2.5]octane (0.32 mmol) in MeCN (3.0 mL) was added PPTS (0.64 mmol, 2.0 eqiv) and LiBr (1.6 mmol, 5.0 equiv) at room temperature, and the resulting mixture was stirred at room temperature for three days. After quenched with H_2O, the reaction mixture was extracted with EtOAc three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc/hexane) to yield the chiral bromohydrin as colorless oil, whose enantiomeric excess was determined by chiral HPLC analysis. Then, silylation afford chiral (+)-**1b**, and its spectrum was identical with the racemic **1b**. The optical rotation was $[\alpha]^{24}_D$ (*c* 0.47, $CHCl_3$) +40.3 (for 59% ee)

5. The appearance of reaction mixture with substrate 1b

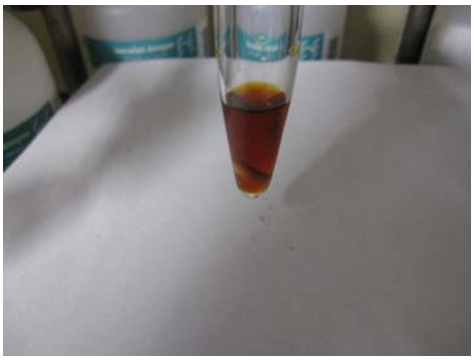
30 sec



5 min

10 min

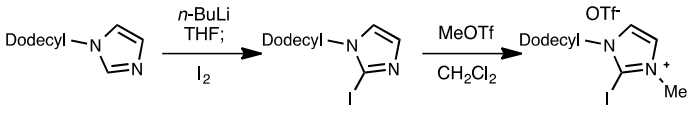
15 min (All SM was consumed)



The transition of their appearances also supports the idea that iodine bromide was generated during the reaction *in situ*.

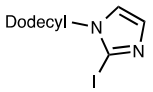
6. Preparation of iodoimidazolium salt

Iodoimidazolium triflate **4** was synthesized from 1-dodecylimidazole[8].



To the solution of 1-dodecylimidazole (18.0 mmol) in THF (50 mL) was added *n*-BuLi solution in hexane (21.6 mmol, 1.2 equiv) dropwise over 10 min at –78 °C. The resulting solution was stirred at –78 °C for 2

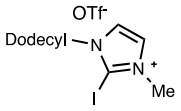
hours, and then iodone (1.0 equiv) at –78 °C. The solution was allowed to warm up to room temperature, and kept stirred overnight. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ solution, and the product was extracted with $CHCl_3$ three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was filtered through silica gel with hexane to yield the corresponding 1-dodecyl-2-iodoimidazole as yellow oil (65%).



1-Dodecyl-2-iodoimidazole

Yellow oil; IR (ATR): 2922, 2852, 1735, 1507, 1461, 1425, 1375, 1336, 1267, 1127, 1095, 908, 770, 732, 658 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.06 (s, 1H), 7.01 (s, 1H), 3.86 (t, *J* = 7.3 Hz, 2H), 1.77–1.68 (m, 2H), 1.31–1.20 (m, 18H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 122.9, 90.1, 49.6, 32.0, 30.7, 29.7, 29.6, 29.5, 29.4, 29.1, 26.5, 22.7, 14.2 (one carbon peak is missing due to overlapping); HRMS (ESI): calcd. for $C_{15}H_{28}IN_2$ ($[M+H]^+$): 363.1292, Found: 363.1286.

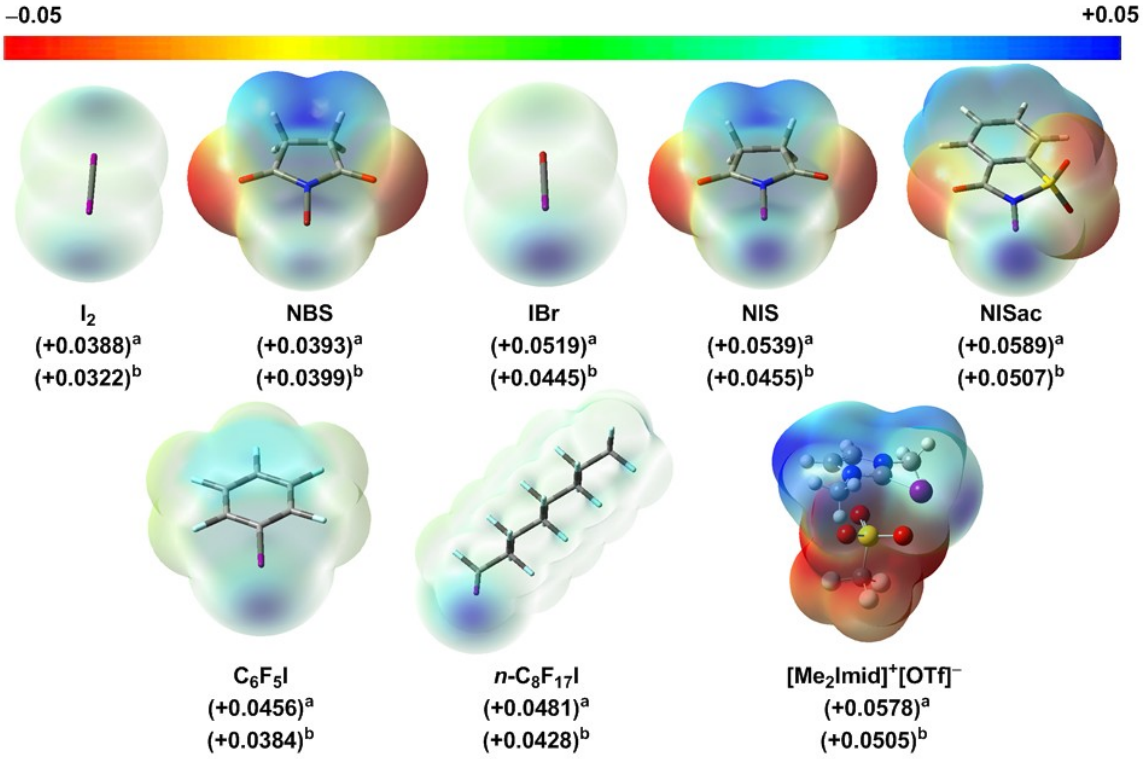
To the solution of iodoimidazole (0.72 mmol) in CH_2Cl_2 (7 mL) under argon atmosphere was added methyl triflate (1.5 mmol, 2.0 equiv) at room temperature. The resulting mixture was stirred at room temperature until consumption of the starting material, as monitored by TLC (hexane/EtOAc 9:1). The solvent was evaporated *in vacuo*, and then the residue was washed with Et_2O and hexane to afforded iodoimidazolium triflate **4** as colorless solid (59%).



1-Dodecyl-2-iodo-3-methyliodoimidazolium triflate (4)

Colorless solid; Mp: 89–92 °C; IR (ATR): 2918, 2853, 1546, 1501, 1471, 1444, 1257, 1220, 1159, 1033, 779, 686, 674 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): δ = 7.82 (s, 1H), 7.67 (s, 1H), 4.17 (t, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 1.90–1.75 (m, 2H), 1.34–1.21 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.3, 125.6, 120.6 (q, *J* = 320.3 Hz), 97.2, 53.2, 40.0, 32.0, 29.9, 29.7, 29.6, 29.4, 29.4, 29.1, 26.3, 22.8, 14.2; HRMS (ESI): calcd. for $C_{16}H_{30}IN_2$ ($[M–OTf^-]^+$): 377.1448, Found: 377.1441.

7. Maximum values of electrostatic potential energy



[a] MP2/6-31+G(d,p)-LANL2DZdp level [b] MP2/6-311+G(d,p) level

The electrostatic potential energy surface was calculated using the Gaussian 09[9] suite of programs. The molecular geometry was optimized at 1) the MP2/6-31+G (d,p) level of theory[10,11] for all atoms except bromine and iodine, for which the double-ζ LANL2DZ basis set and effective core potential were used,[12–14] or 2) MP2/6-311+G (d,p) level of theory, where extrabasis was set for bromine and iodine atoms.[15] The maximum values of electrostatic potential energy surface (Isovalue: MO = 0.02, density = 0.0004) were indicated above. Blue colors represent positive potential (the darker the color the more positive), green, yellow, and red represent an increasing negative potential (in that order). Here σ-holes on iodine atoms in the listed molecules can be seen.

8. Calculated energetic properties of XB-donors and Cartesian coordinates of calculated structures

Table S1. Calculated energetic properties of XB-donors optimized with MP2/6-31+G(d,p)-LANL2DZdp

XB-donor	Energy (Hartrees)	LUMO Energy (Hartrees)	HOMO Energy (Hartrees)
I_2	–22.54810012	–0.03025	–0.36287
NBS	–372.12868251	0.04363	–0.40166
C_6F_5I	–737.25675902	0.03656	–0.36726
n-$C_8F_{17}I$	–2008.68242112	0.02716	–0.40988
IBr	–2581.28281663	–0.02283	–0.38130
NIS	–370.33104682	0.02673	–0.37573
$[Me_2Imid]^+[OTf]^-$	–1274.78793727	0.03192	–0.35801
NISac	–956.92158627	0.01622	–0.37688

Table S2. Calculated energetic properties of XB-donors optimized with MP2/6-311+G(d,p)

XB-donor	Energy (Hartrees)	LUMO Energy (Hartrees)	HOMO Energy (Hartrees)
I_2	–13834.15714418	0.06888	–0.01592
NBS	–2931.82942975	0.05397	–0.40466
C_6F_5I	–7643.41597608	0.03820	–0.36577
n-$C_8F_{17}I$	–8915.56047554	0.02879	–0.41219
IBr	–9489.71939993	–0.00963	–0.37953
NIS	–7276.26980044	0.03037	–0.37505
$[Me_2Imid]^+[OTf]^-$	–8180.99118170	0.03084	–0.35713
NISac	–7862.94280262	0.02191	–0.37656

Cartesian coordinates for all the calculated structures (optimized with MP2/6-31+G(d,p)-LANL2DZdp)

I_2

0 1

I	0.00000000	0.00000000	1.35027600
I	0.00000000	0.00000000	–1.35027600

NBS

0 1

C	2.37102100	0.76654900	0.00037300
C	2.37102100	–0.76654900	0.00037300
H	2.84852900	1.19772000	–0.87918300
H	2.84818200	1.19771300	0.88012400
H	2.84852900	–1.19772000	–0.87918300
H	2.84818200	–1.19771300	0.88012400
C	0.91112200	–1.18757900	0.00008500
C	0.91112200	1.18757900	0.00008500
N	0.15706000	0.00000000	0.00019900
O	0.45131200	2.31553800	–0.00007900
O	0.45131200	–2.31553800	–0.00007900
Br	–1.68855900	0.00000000	–0.00021500

C_6F_5I

0 1

C	0.22130300	0.00001900	–0.00074700
C	–0.50015100	–1.19657000	0.00030100
C	–0.50018000	1.19659200	0.00031100
C	–1.89356400	–1.20598700	–0.00051400
C	–1.89361000	1.20597300	–0.00051900
C	–2.59153300	–0.00001600	0.00038500
F	0.13792200	–2.38393000	0.00014500
F	–2.56777400	–2.36997200	–0.00007000
F	–3.93541000	–0.00004600	0.00026000
F	–2.56781100	2.36996300	–0.00008100
F	0.13786700	2.38396500	0.00015400
I	2.30383500	0.00000200	0.00002000

***n*-$C_8F_{17}I$**

0 1

C	–0.46973000	5.68353300	0.00000000
C	0.41028900	4.40613900	0.00000000
C	–0.37474000	3.06611600	0.00000000
C	0.51801300	1.78991800	0.00000000
C	–0.27614200	0.44827000	0.00000000
C	0.61801700	–0.82896500	0.00000000
C	–0.17195500	–2.17075700	0.00000000
C	0.70986500	–3.44814800	0.00000000
I	–0.50043700	–5.23029200	0.00000000
F	1.50521400	–3.44263600	1.09843700
F	1.50521400	–3.44263600	–1.09843700
F	–0.95722400	–2.20681300	1.10858800
F	–0.95722400	–2.20681300	–1.10858800
F	1.40428700	–0.79934500	1.10782200
F	1.40428700	–0.79934500	–1.10782200
F	–1.06240300	0.41989600	1.10776200
F	–1.06240300	0.41989600	–1.10776200
F	1.30371100	1.82512700	1.10789800
F	1.30371100	1.82512700	–1.10789800
F	–1.16263200	3.04656800	–1.10786700
F	–1.16263200	3.04656800	1.10786700
F	1.19415100	4.46594700	–1.10787800
F	1.19415100	4.46594700	1.10787800
F	–1.24648500	5.73378100	–1.09446200
F	0.34737000	6.75148700	0.00000000
F	–1.24648500	5.73378100	1.09446200

IBr

0 1

I	0.00000000	0.00000000	0.99419600
Br	0.00000000	0.00000000	–1.50549700

NIS

0 1

C	–0.00048100	2.76903900	0.76584000
C	–0.00048100	2.76903900	–0.76584000
H	–0.88002200	3.24498300	1.19887400
H	0.87892900	3.24524200	1.19886000
H	–0.88002200	3.24498300	–1.19887400
H	0.87892900	3.24524200	–1.19886000
C	–0.00025600	1.30676000	–1.18231800
C	–0.00025600	1.30676000	1.18231800
N	0.00004000	0.54578300	0.00000000
I	0.00028000	–1.49781100	0.00000000
O	–0.00025600	0.85459200	2.31470200
O	–0.00025600	0.85459200	–2.31470200

$[Me_2Imid]^+[OTf]^-$

0 1

C	0.62611800	2.58297000	–0.78020000
H	0.14061800	3.23372000	–1.48448600
C	0.83990300	2.71669000	0.56765500
H	0.57962900	3.51021000	1.24511800
N	1.42870100	1.55606300	1.00517700
N	1.07849800	1.33805100	–1.14090600
C	1.55203000	0.70813800	–0.04141700
I	2.34689800	–1.17735900	0.01757600

C	0.95107000	0.74519600	–2.47604600
H	0.36820200	–0.16885100	–2.38303100
H	1.94118600	0.55715600	–2.88530000
H	0.41153900	1.45811300	–3.09083600
H	0.74312200	0.55271300	2.68406600
C	1.58392800	1.18801400	2.41198700
H	1.57469700	2.10438600	2.99457400
H	2.53151800	0.67560000	2.55190100
S	–1.70498800	0.09867100	–0.15583100
O	–1.18917300	0.51652200	1.17649100
O	–1.98176300	1.21356600	–1.09460100
C	–3.37564800	–0.59442500	0.22664100
F	–4.16697000	0.34476700	0.78810000
F	–3.27993500	–1.63015700	1.08827600
F	–3.98180400	–1.03723200	–0.89475000
O	–0.97315300	–1.04714700	–0.75770100

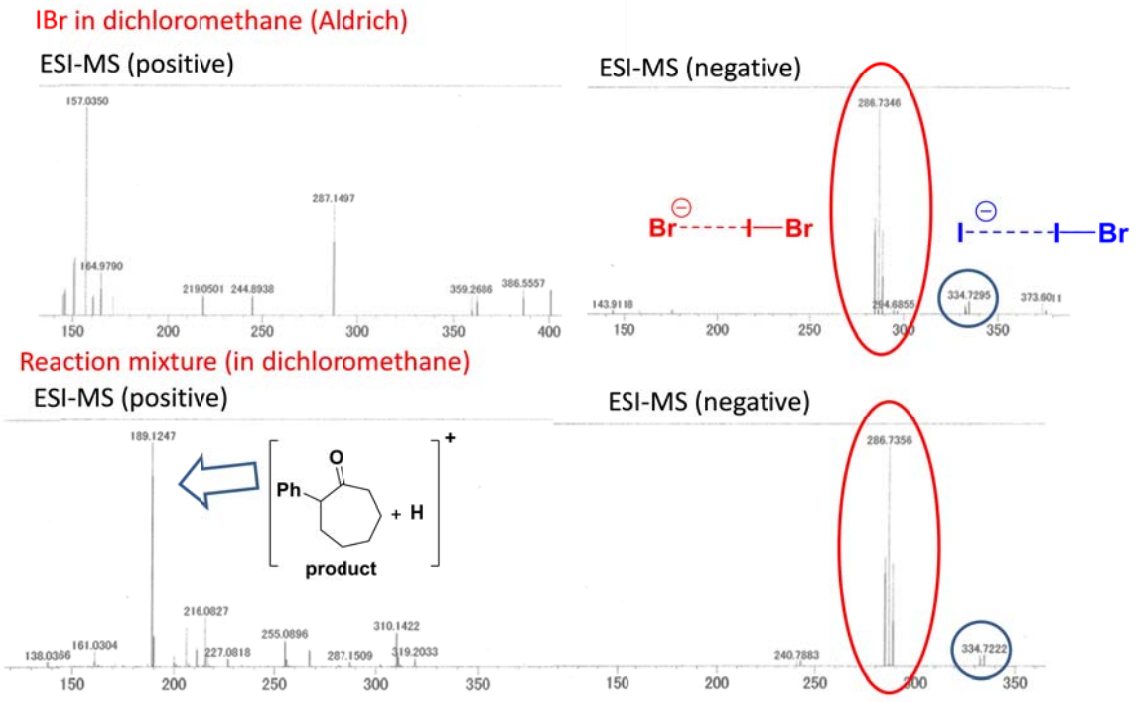
NISac

0 1

C	0.32334500	1.30311700	–0.05417300
I	–2.49026800	0.21909100	0.00336700
O	0.08105200	–1.86701300	1.34281600
O	–0.10490100	2.44729100	0.02795900
C	1.94250100	–0.49515700	–0.00568400
C	1.75186000	0.88608500	–0.02059100
C	2.85085100	1.74441700	–0.00854900
H	2.69860300	2.81631000	–0.02091800
C	4.12934900	1.17820700	0.01497000
H	4.99952700	1.82234700	0.02470300
C	4.30444400	–0.21479700	0.02189700

H	5.30503900	–0.62823500	0.03615300
C	3.20429500	–1.08027500	0.00790400
H	3.32980300	–2.15562800	0.01179100
S	0.38941600	–1.34887400	0.00890300
O	0.22249600	–2.19247700	–1.17250200
N	–0.45835600	0.15476300	–0.24192400

9. Detection of MS signal of IBr



10. References

1) L. Li, P. Cai, Q. Guo, S. Xue, *Org. Lett.*, **2008**, *73*, 3516.

2) T. Kuribayashi, H. Kubota, T. Fukuda, R. Takano, T. Tsuji, K. Sasaki and N. Tanaka, *PCT Int. Appl.*

WO2009131129 A1, 2009

3) V. L. Rendina, H. Z. Kaplan, J. S. Kingsbury, *Synthesis*, **2012**, *44*, 686.

4) D. Leung and E. V. Anslyn, *Org. Lett.*, **2011**, *13*, 2298.

5) T. Miyoshi, T. Miyakawa, M. Ueda and O. Miyata, *Angew. Chem. Int. Ed.*, **2010**, *50*, 928.

6) F. D. King and S. Caddick, *Org. Biomol. Chem.*, **2012**, *10*, 3244.

7) Z-X. Wang, Y. Tu, M. Frohn, J-R. Zhang and Y. Shi, *J. Am. Chem. Soc.*, **1997**, *119*, 11224.

8) M. Lee, Z. Niu, D. V. Schoonover, C. Slebodnick and H. W. Gibson, *Tetrahedron*, **2010**, *66*, 7077.

9) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.

10) (a) C. Møller and M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618. (b) M. Head-Gordon, J. A. Pople and M. J. Frisch, *Chem. Phys. Lett.* **1988**, *153*, 503.

11) W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

12) J. P. Hay and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.

13) C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert and L. S. Sunderlin, *J. Phys. Chem. A* **2001**, *105*, 8111.

14) https://bse.pnl.gov/bse/portal. K. L. Schuchardt, B. T. Didier, T. Eisethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045.

15) https://bse.pnl.gov/bse/portal. M.N. Glukhovstev, A. pross, M.P. McGrath, L. Radom, *J. Chem. Phys.* **1995**, *103*, 1878.

11. Copies of ^{1}H and ^{13}C NMR charts

[1-(α-Bromobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1a)

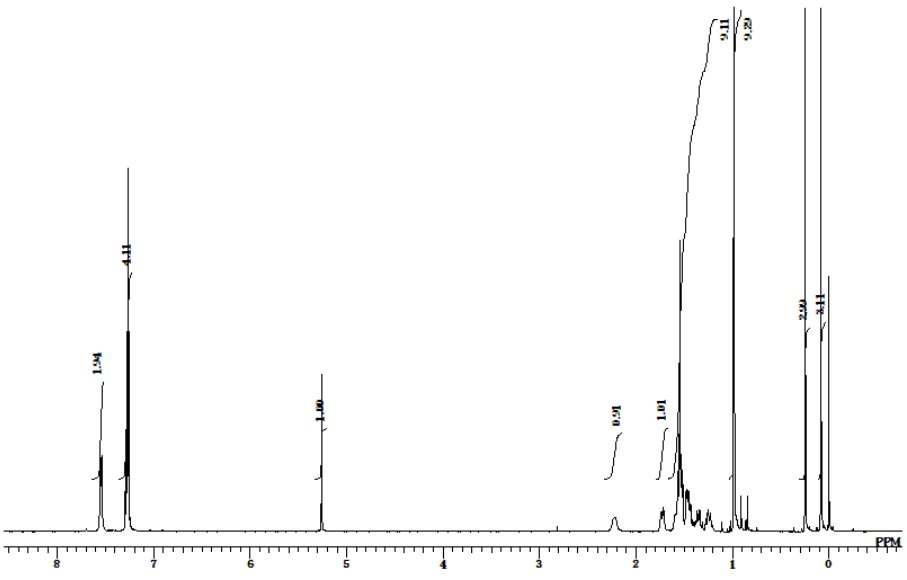


Figure S1. ^{1}H NMR of **1a**

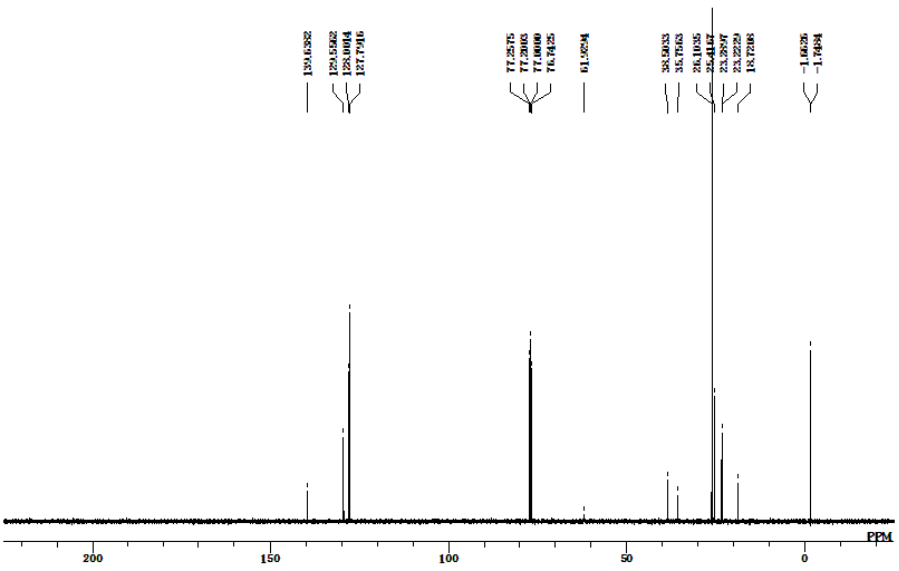
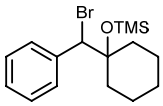


Figure S2. ^{13}C NMR of **1a**



[1-(α-Bromobenzyl)cyclohexyl]oxytrimethylsilane (1b)

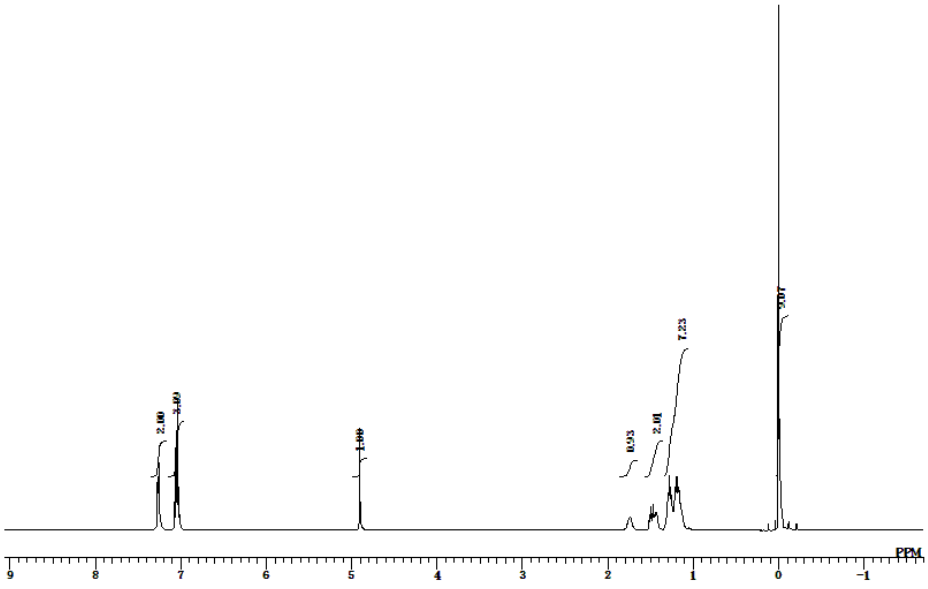


Figure S3. ^{1}H NMR of **1b**

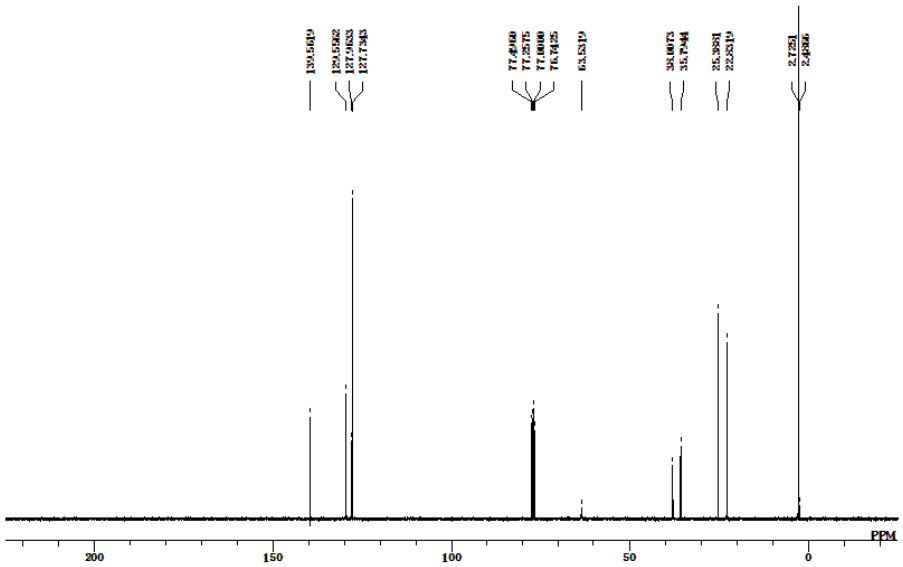
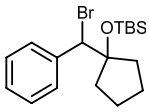


Figure S4. ^{13}C NMR of **1b**



[1-(α-Bromobenzyl)cyclopentyl]oxy(*tert*-butyl)dimethylsilane (1e)

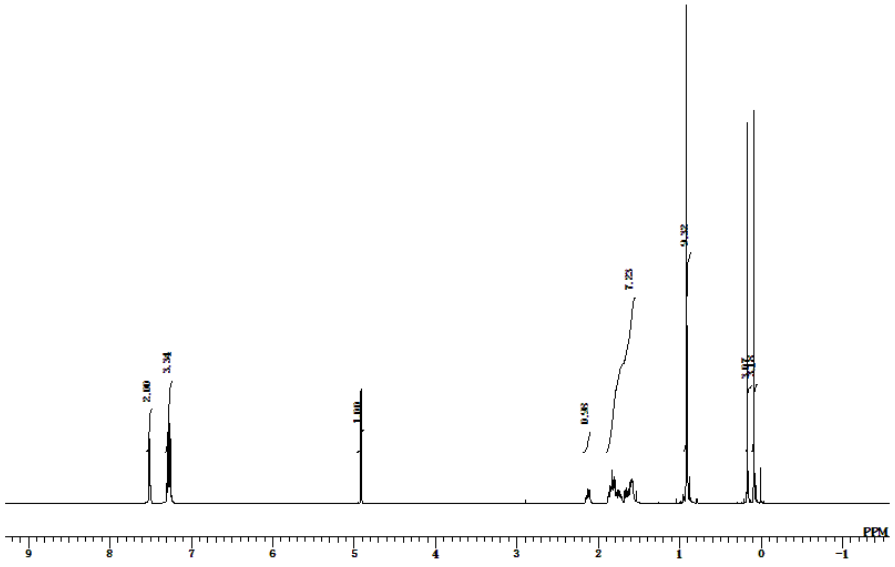


Figure S5. ^{1}H NMR of **1e**

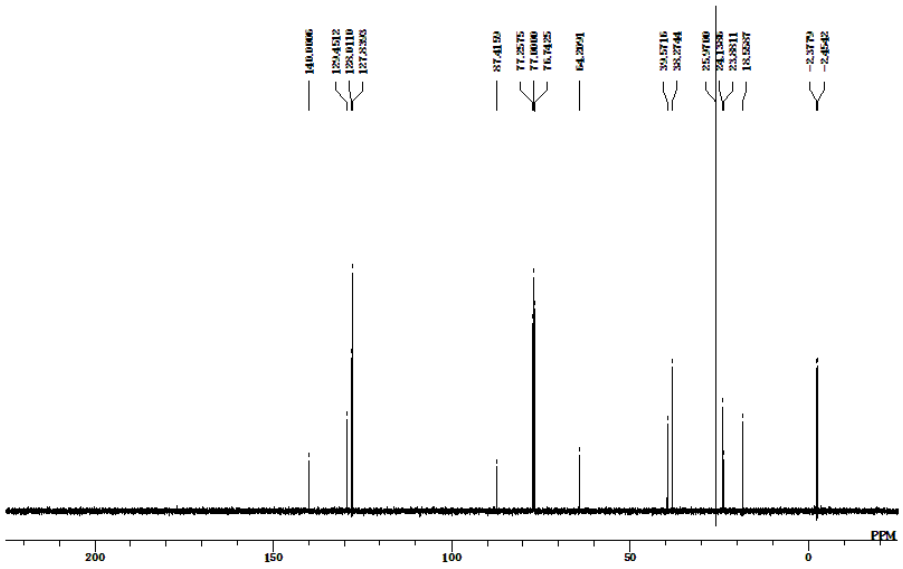
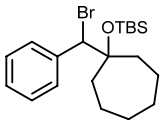


Figure S6. ^{13}C NMR of **1e**



[1-(α-Bromobenzyl)cycloheptyl]oxy(*tert*-butyl)dimethylsilane (1f)

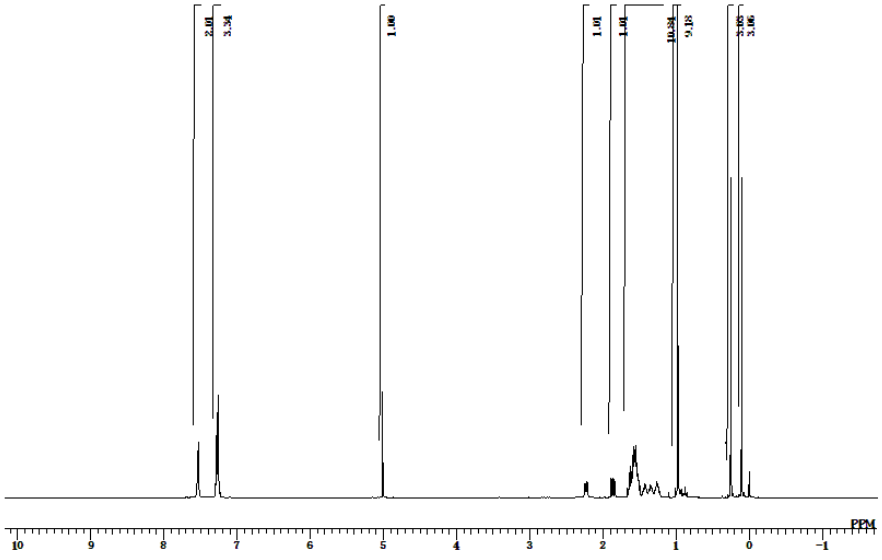


Figure S7. ^{1}H NMR of **1f**

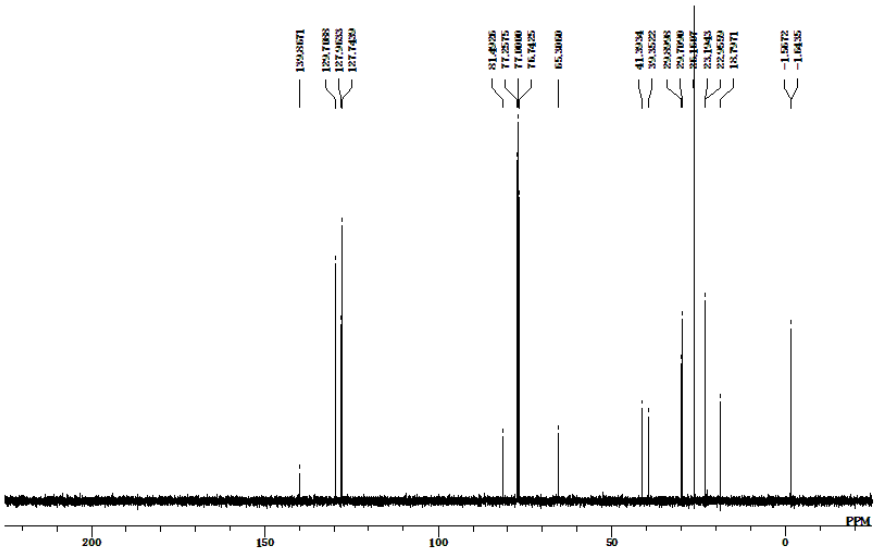
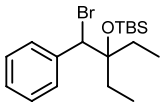


Figure S8. ^{13}C NMR of **1f**



[3-(α-Bromobenzyl)pentyl]oxy(*tert*-butyl)dimethylsilane (1g)

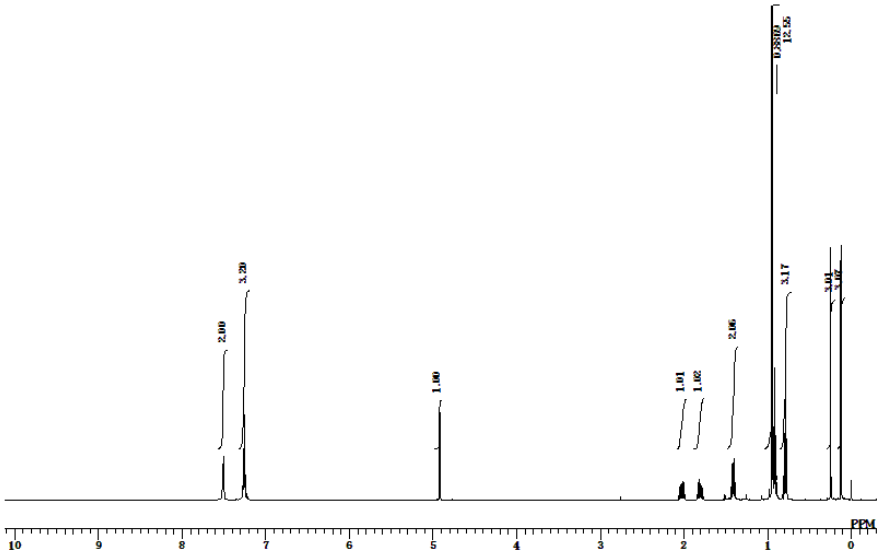


Figure S9. ^{1}H NMR of **1g**

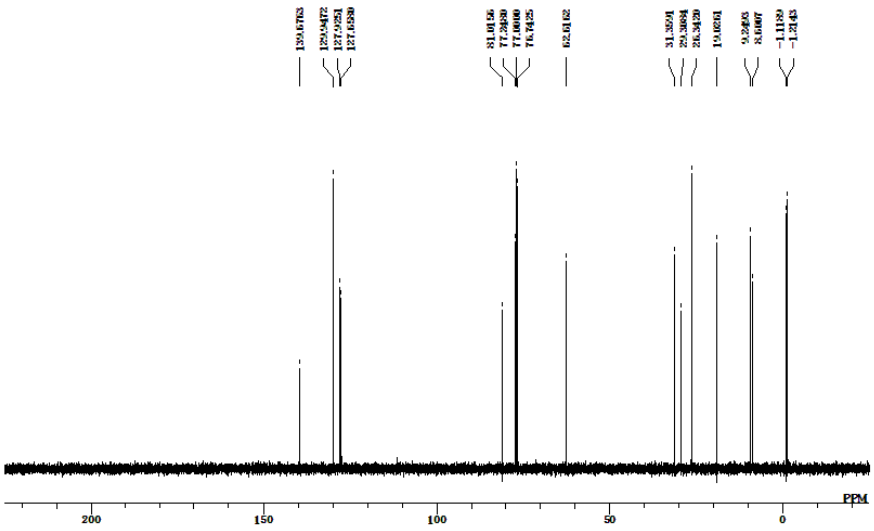
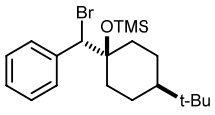


Figure S10. ^{13}C NMR of **1g**



[1-(α-Bromobenzyl)-4-*tert*-butylcyclohexyl]oxytrimethylsilane (1h)

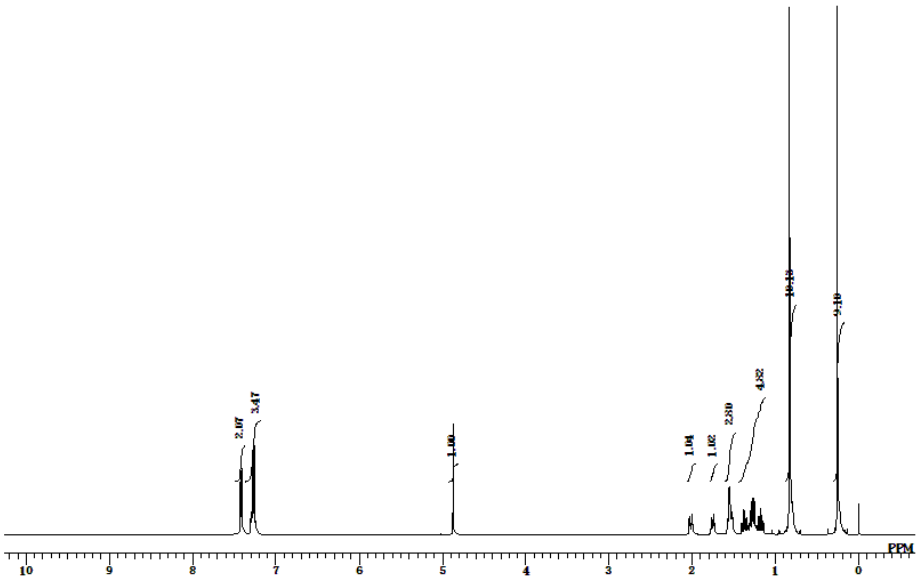


Figure S11. ^{1}H NMR of **1h**

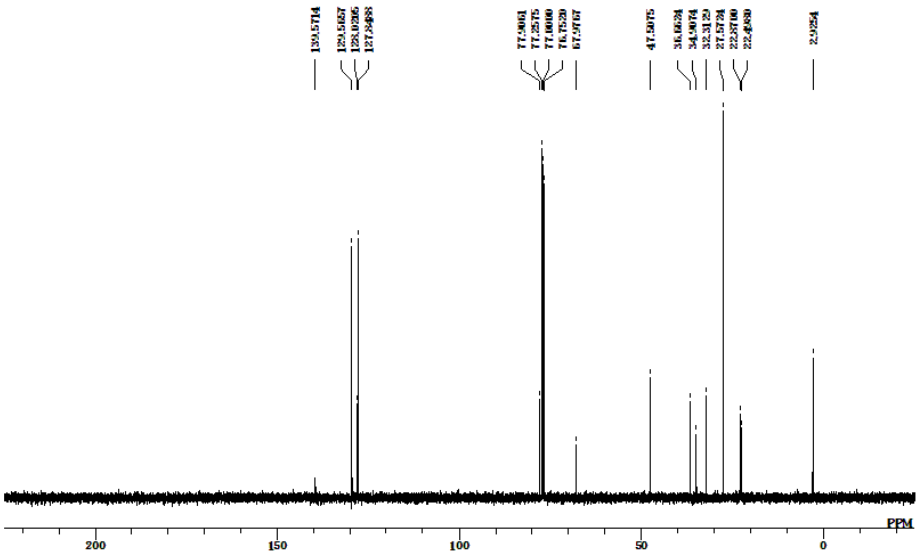
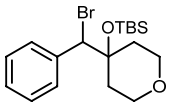


Figure S12. ^{13}C NMR of **1h**



[1-(α-Bromobenzyl)-4-oxocyclohexyl]oxy(*tert*-butyl)dimethyl silane (1i)

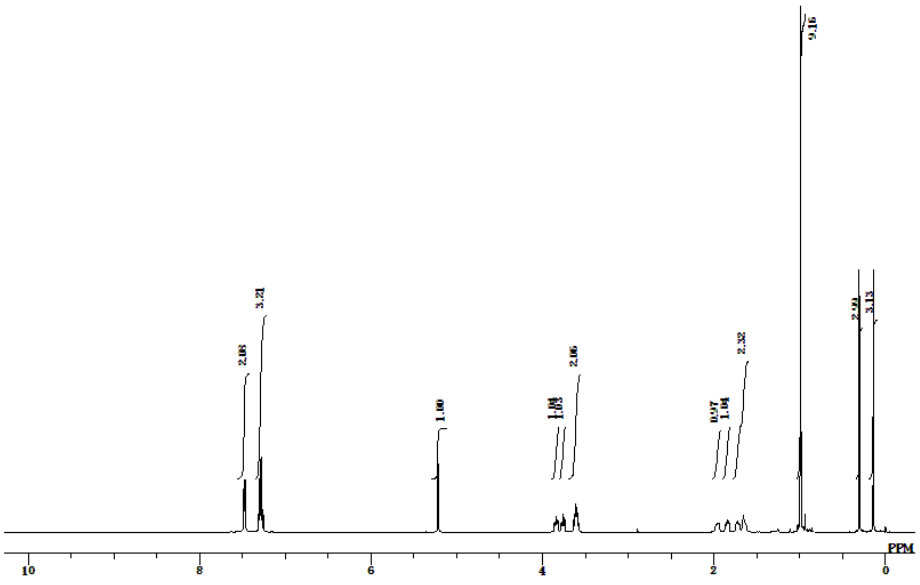


Figure S13. ^{1}H NMR of **1i**

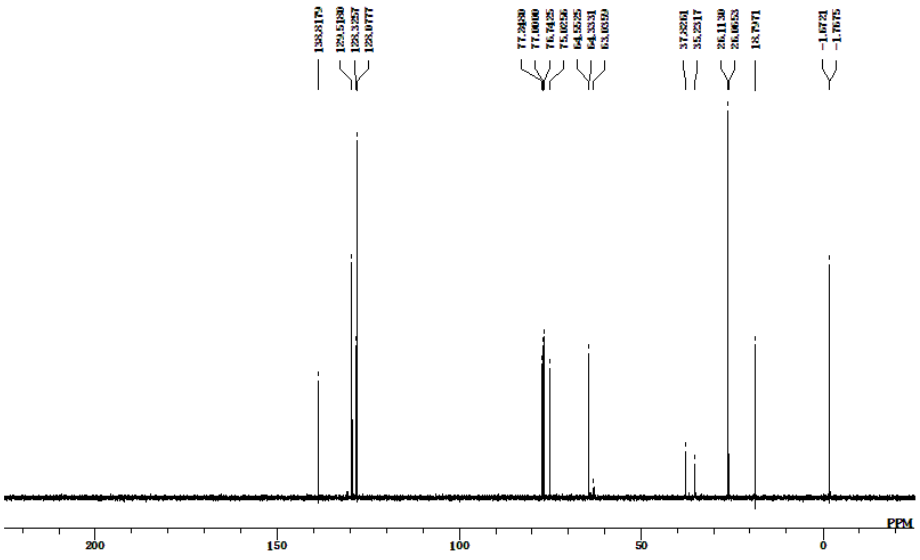
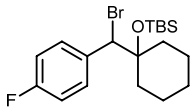


Figure S14. ^{13}C NMR of **1i**



[1-(α-Bromo-4-fluorobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1j)

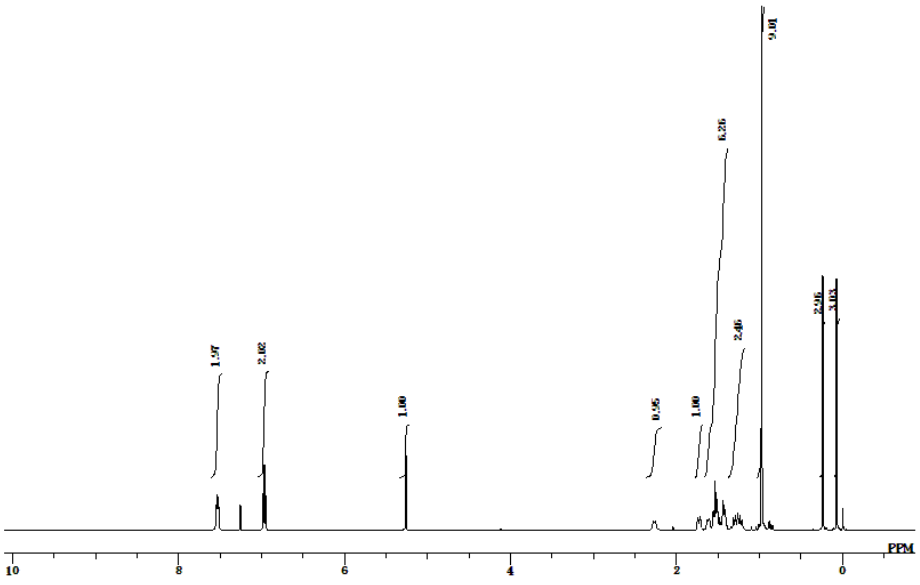


Figure S15. ^{1}H NMR of **1j**

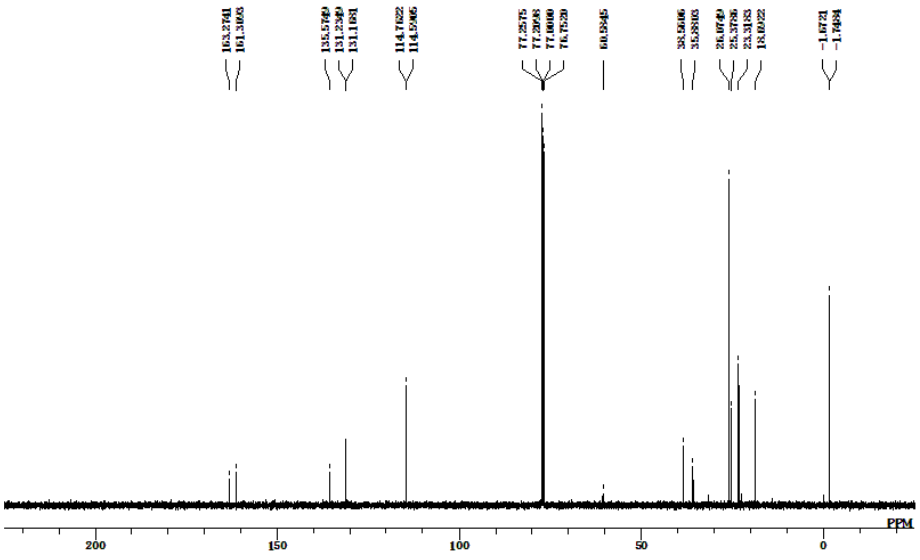
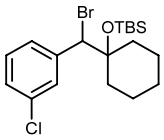


Figure S16. ^{13}C NMR of **1j**



[1-(α-Bromo-3-chlorobenzyl)cycloheptyl]oxy(*tert*-butyl)dimethylsilane (1k)

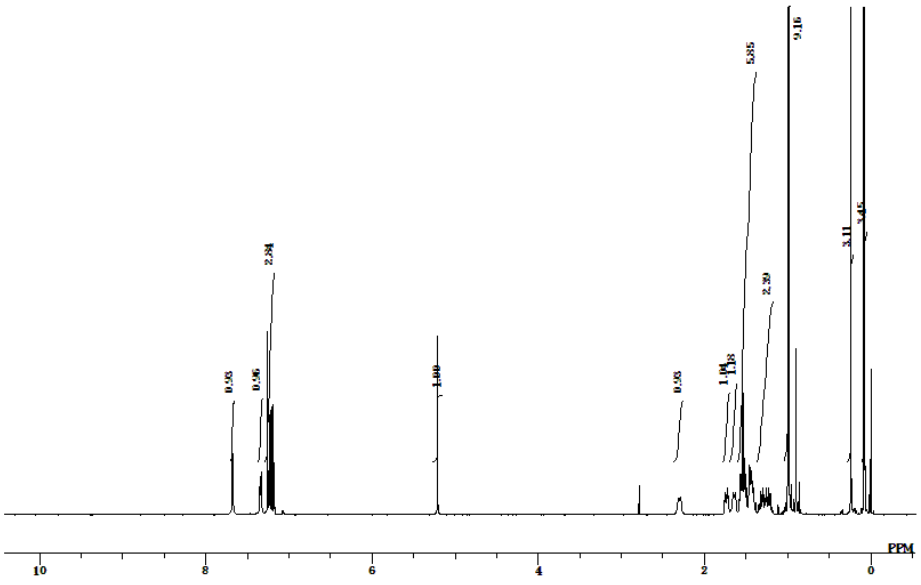


Figure S17. ^{1}H NMR of **1k**

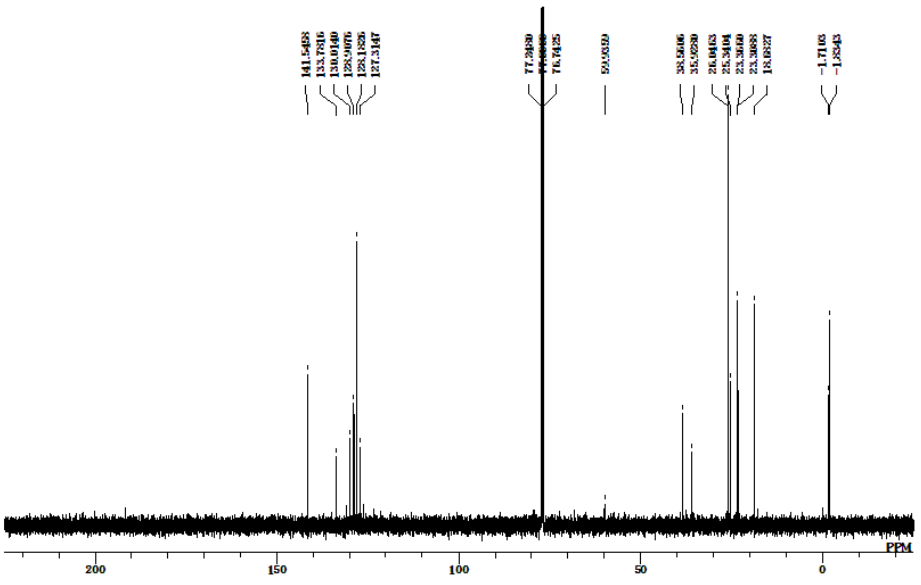
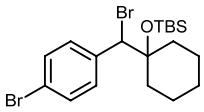


Figure S18. ^{13}C NMR of **1k**



[1-(α-Bromo-4-bromobenzyl)cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1l)

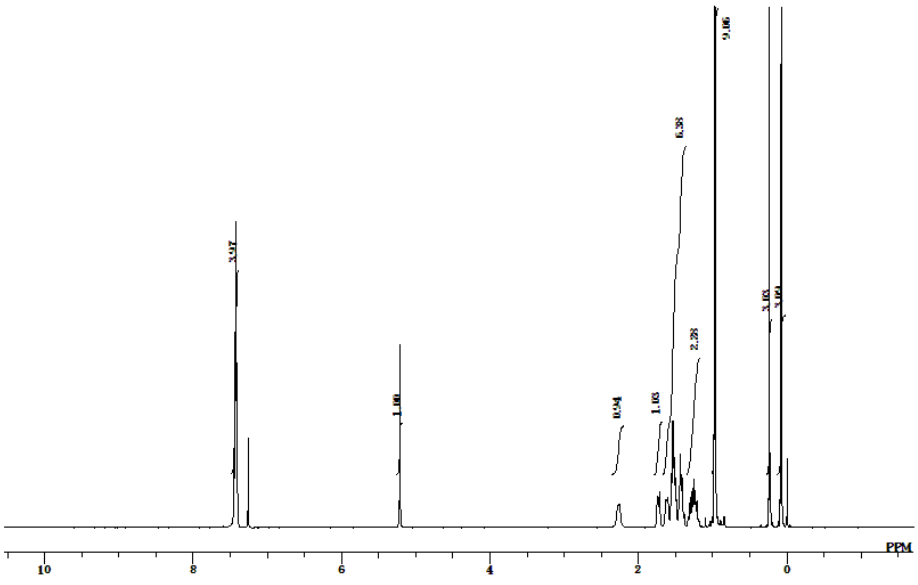


Figure S19. ^{1}H NMR of **1l**

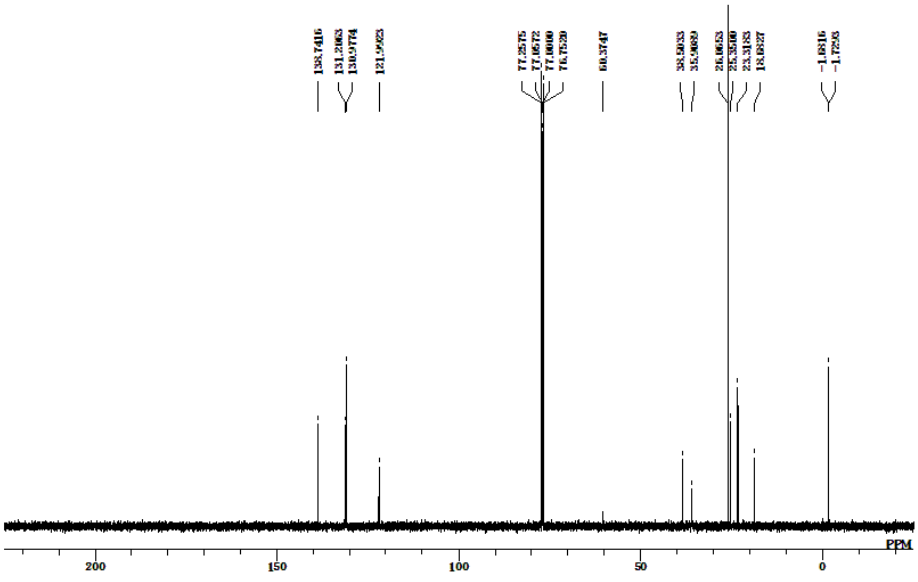
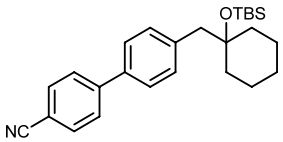


Figure S20. ^{13}C NMR of **1l**



[1-[4-(4-cyanophenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (S-1m)

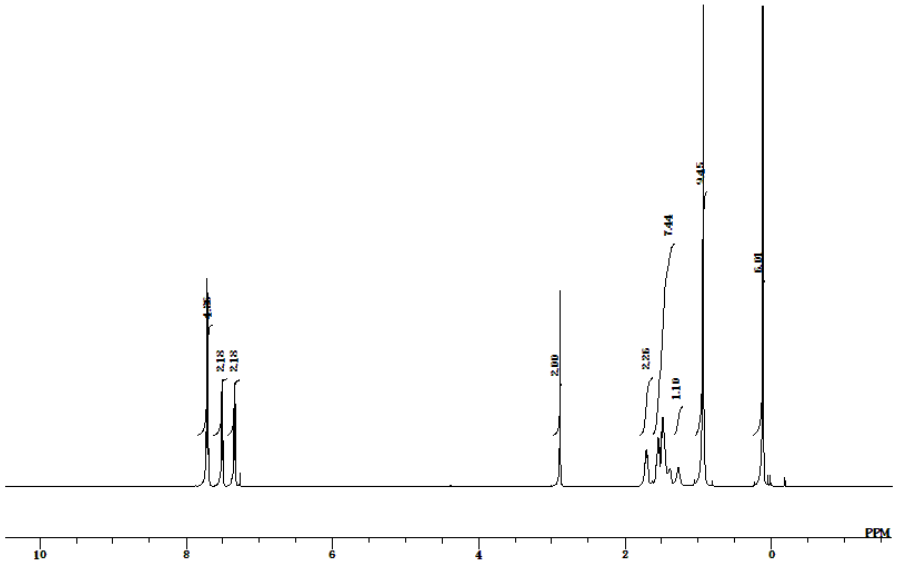


Figure S21. ^{1}H NMR of **S-1m**

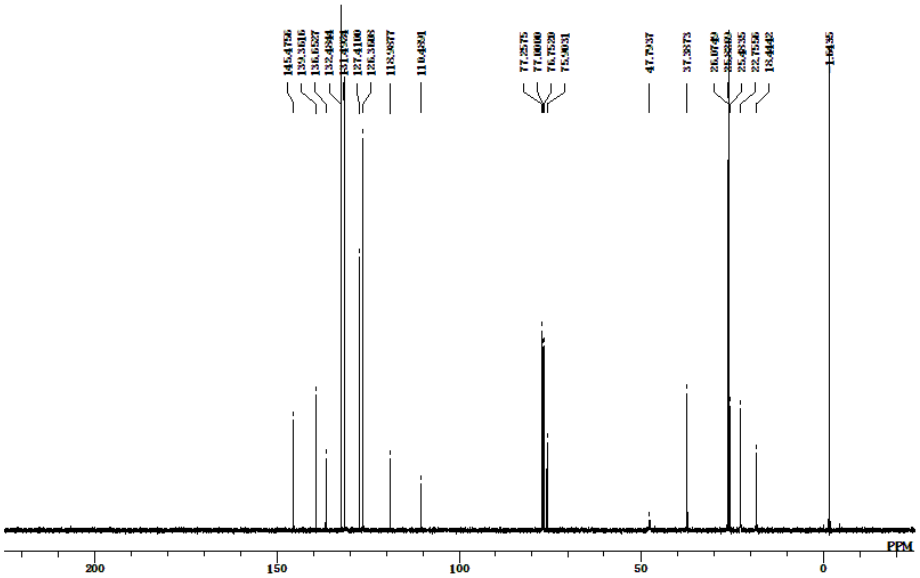
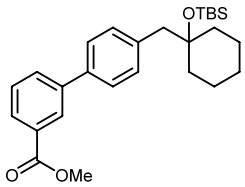


Figure S22. ^{13}C NMR of **S-1m**



[1-[4-(3-methoxycarbonylphenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (S-1n)

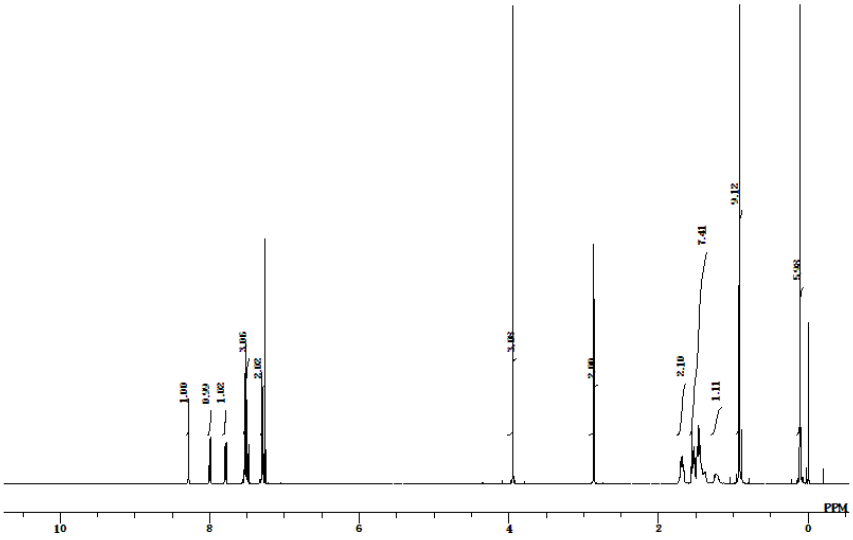


Figure S23. ^{1}H NMR of **S-1n**

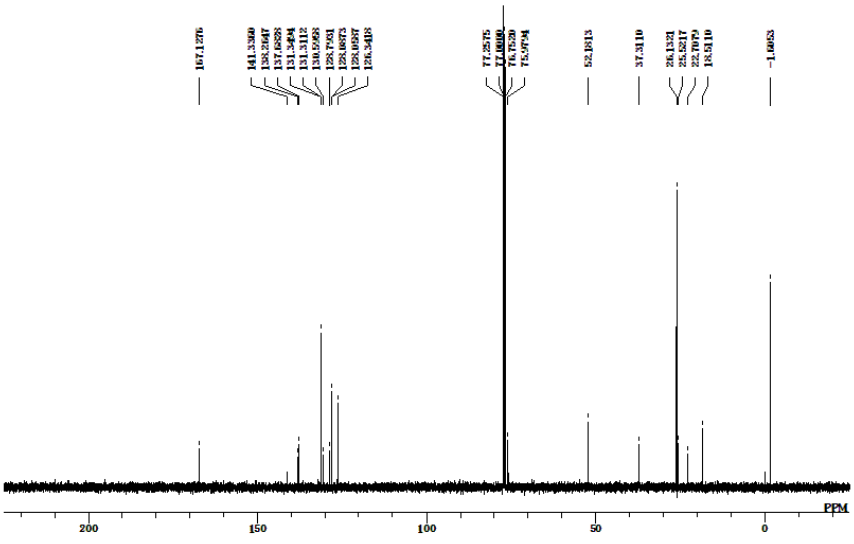
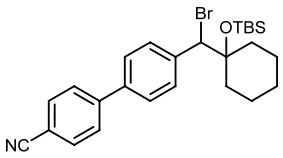


Figure S24. ^{13}C NMR of **S-1n**



[1-[α-Bromo-4-(4-cyanophenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1m)

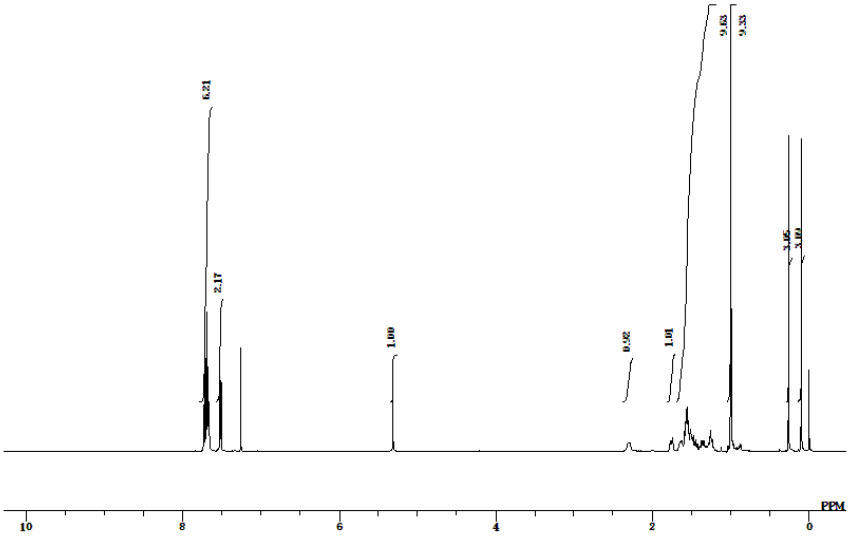


Figure S25. ^{1}H NMR of **1m**

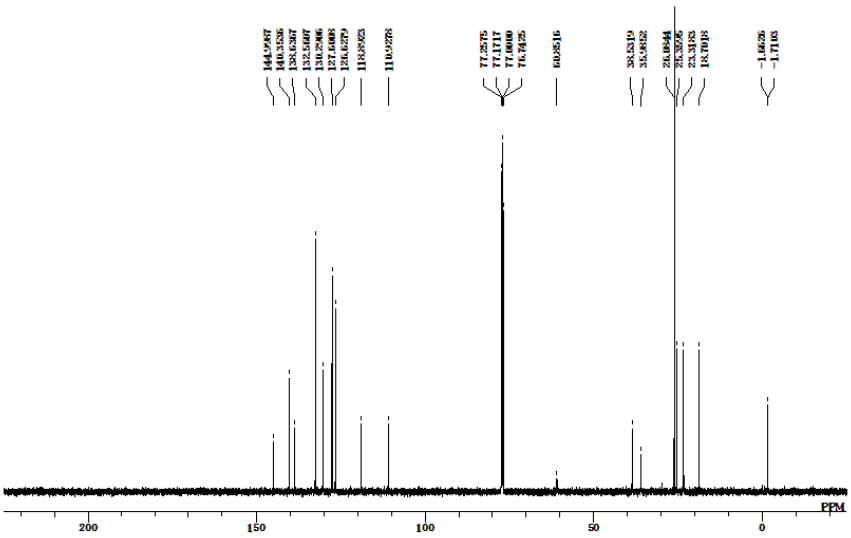
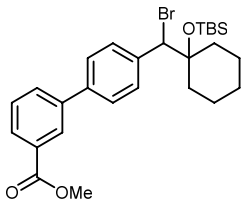


Figure S26. ^{13}C NMR of **1m**



[1-[α-Bromo-4-(3-methoxycarbonylphenyl)benzyl]cyclohexyl]oxy(*tert*-butyl)dimethylsilane (1n)

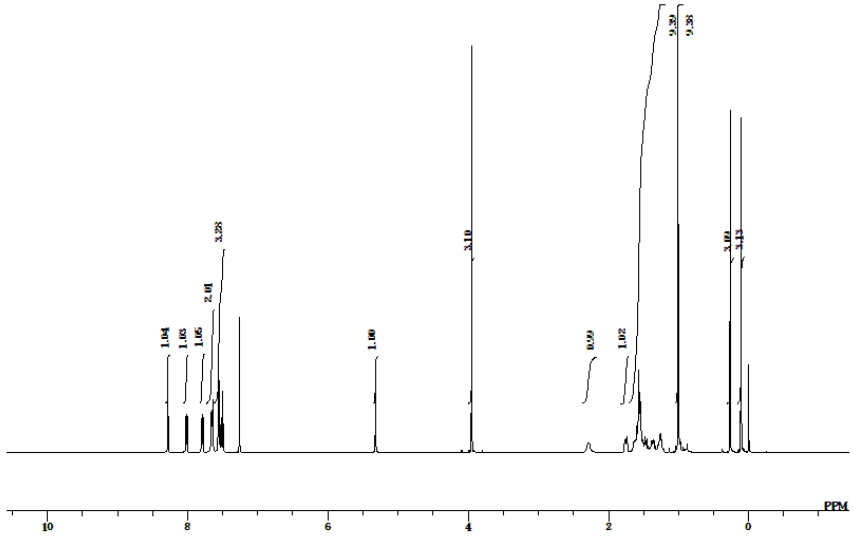


Figure S27. ^{1}H NMR of **1n**

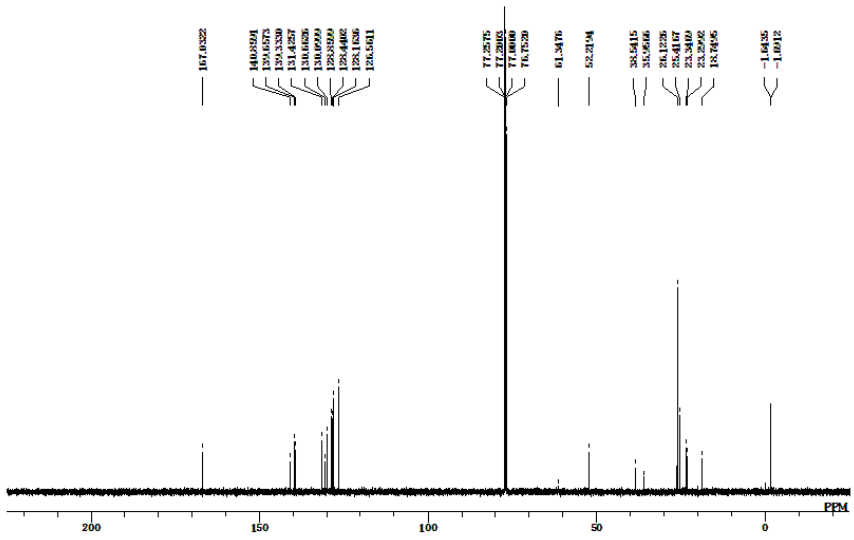
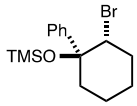


Figure S28. ^{13}C NMR of **1n**



(2-Bromo-1-phenylcyclohexyl)oxytrimethylsilane (1o)

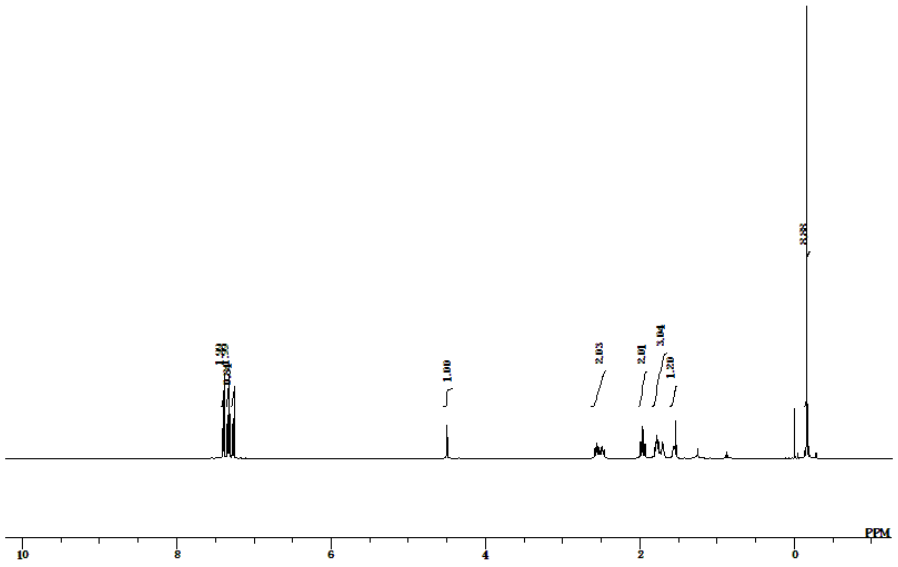


Figure S29. ^{1}H NMR of **1o**

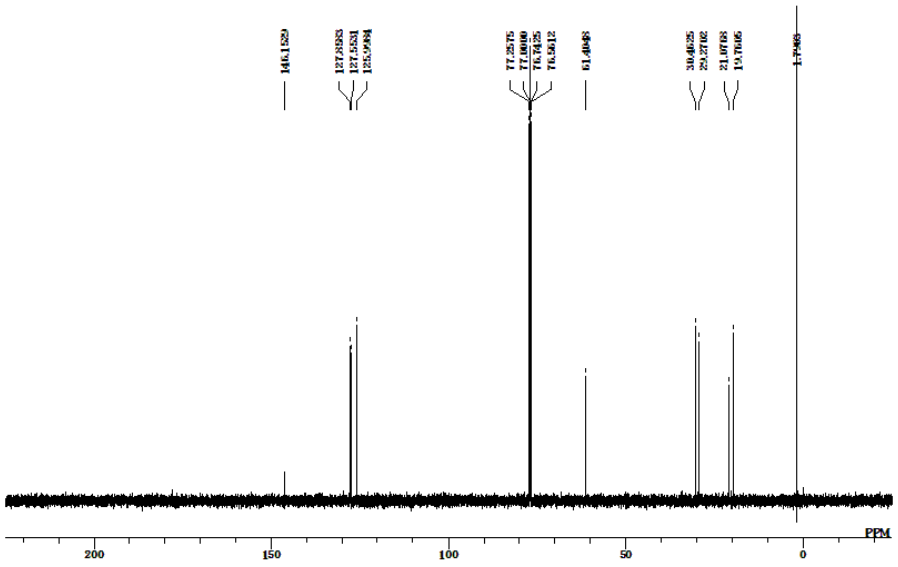
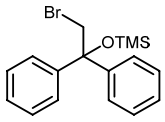


Figure S30. ^{13}C NMR of **1o**



(2-Bromo-1,1-diphenylethyl)oxytrimethylsilane (1p)

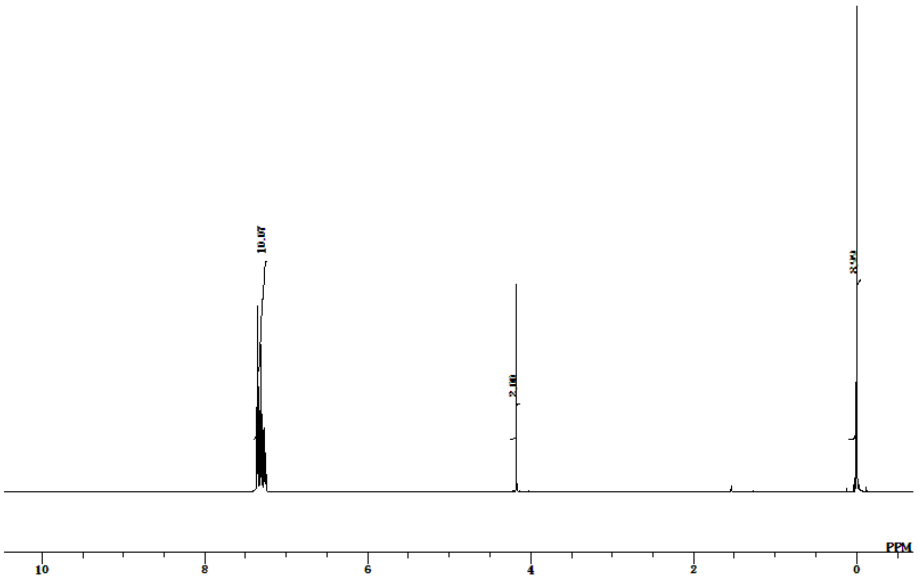


Figure S31. ^{1}H NMR of **1p**

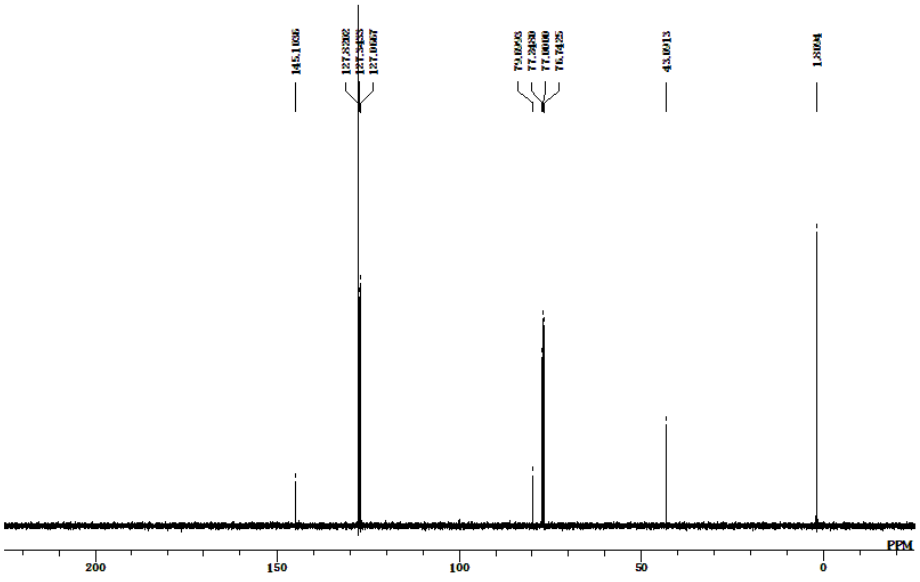
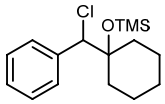


Figure S32. ^{13}C NMR of **1p**



[1-(α-Chlorobenzyl)cyclohexyl]oxytrimethylsilane (1d)

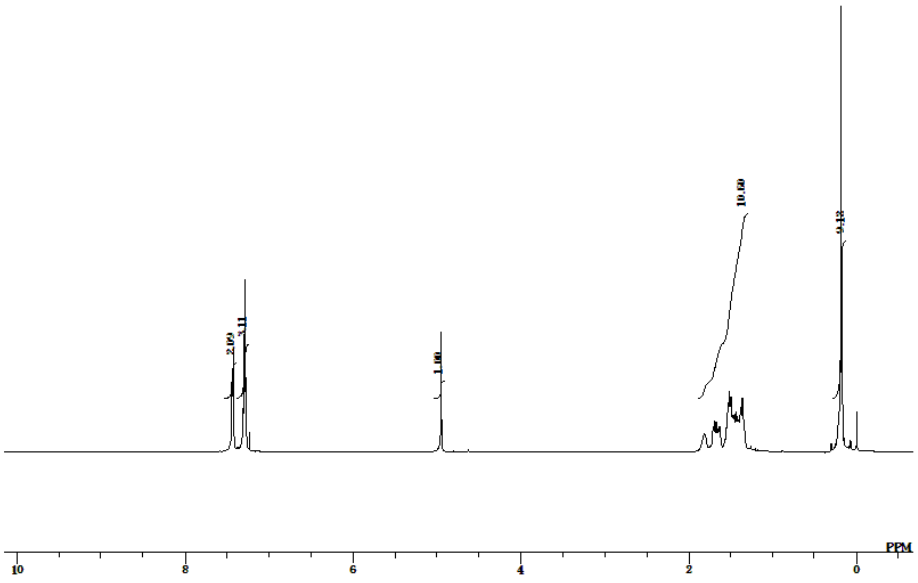


Figure S33. ^{1}H NMR of **1d**

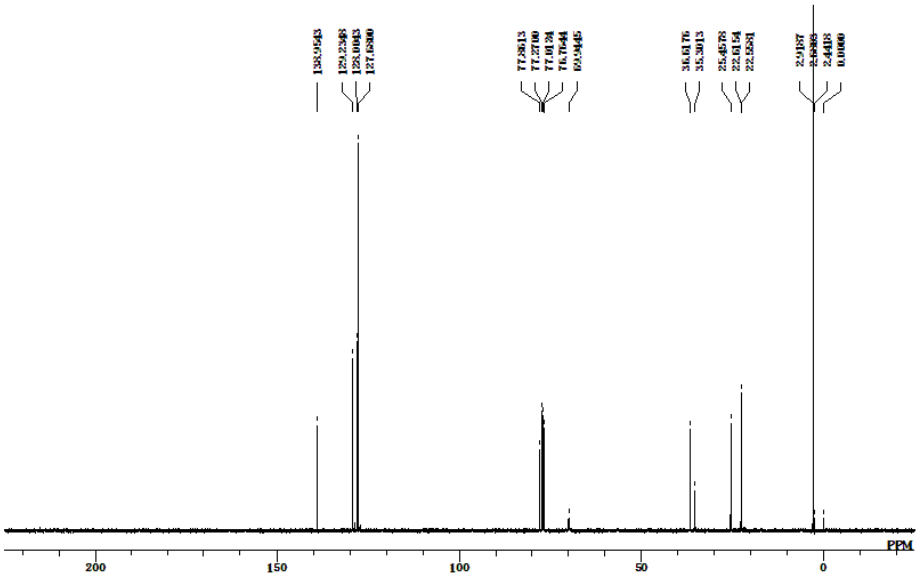
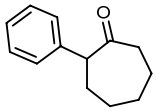


Figure S34. ^{13}C NMR of **1d**



2-phenylcycloheptanone (2a)

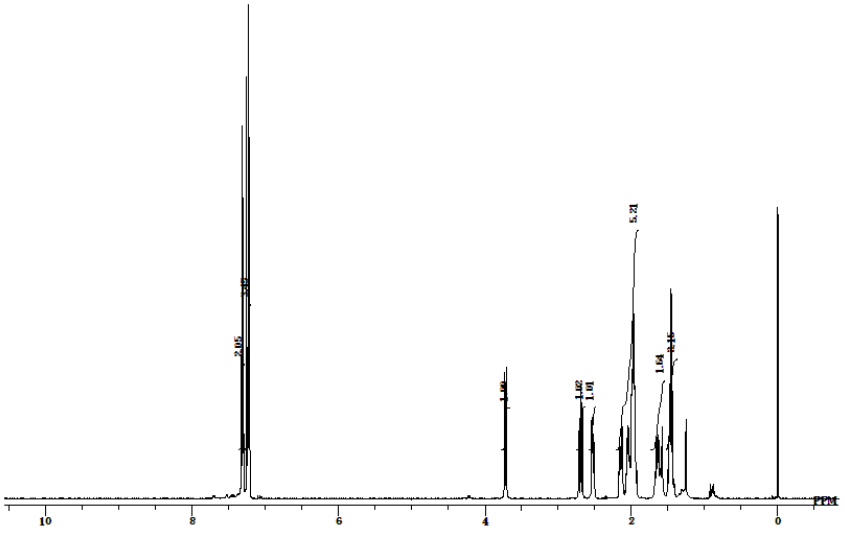
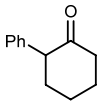


Figure S35. ^{1}H NMR of **2a**



2-phenylcyclohexanone (2e)

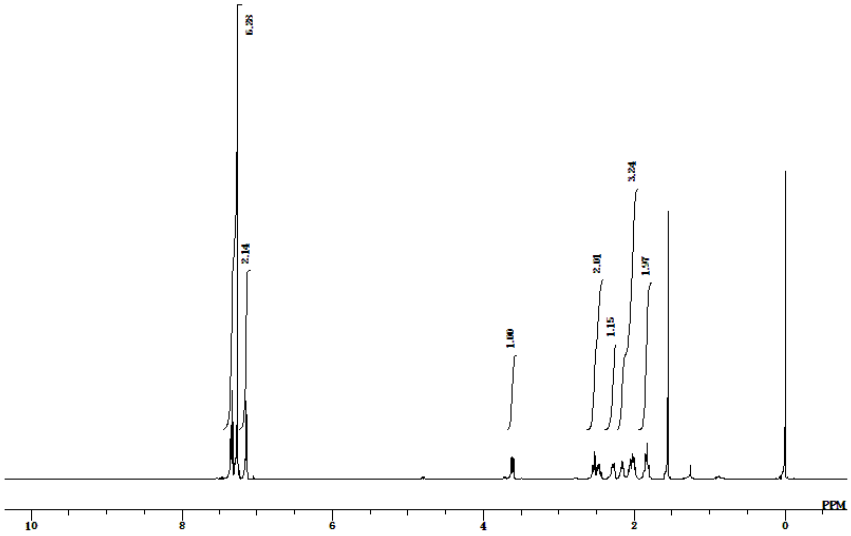
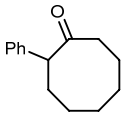


Figure S36. ^{1}H NMR of **2e**



2-phenylcyclooctanone (2f)

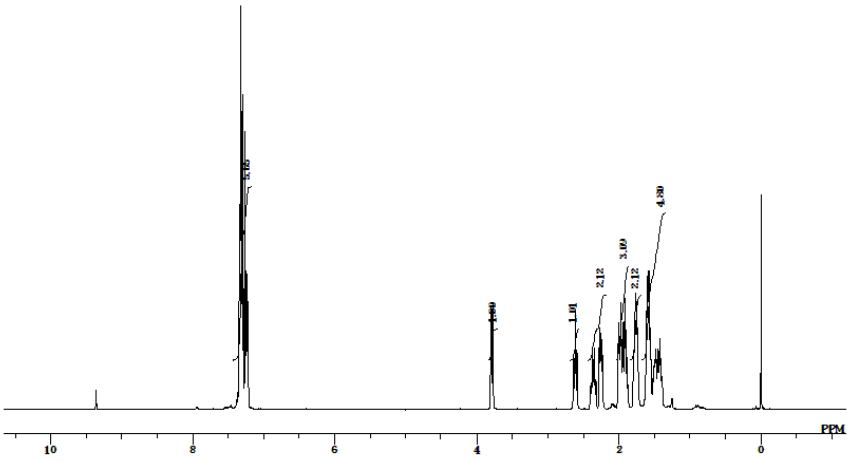
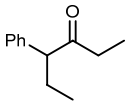


Figure S37. ^{1}H NMR of **2f**



4-phenylhexan-3-one (2g)

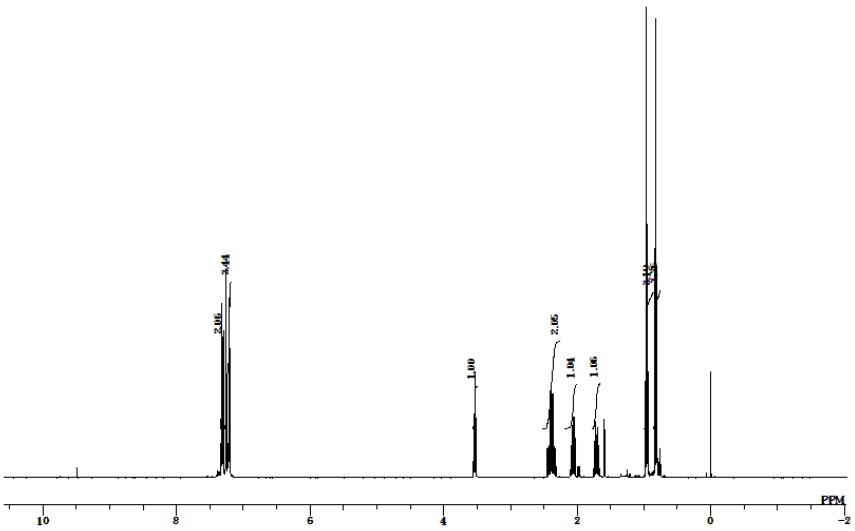
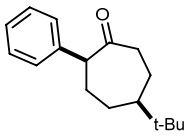


Figure S38. ^{1}H NMR of **2g**



***cis*-5-*tert*-butyl-2-phenylcycloheptan-1-one (2h)**

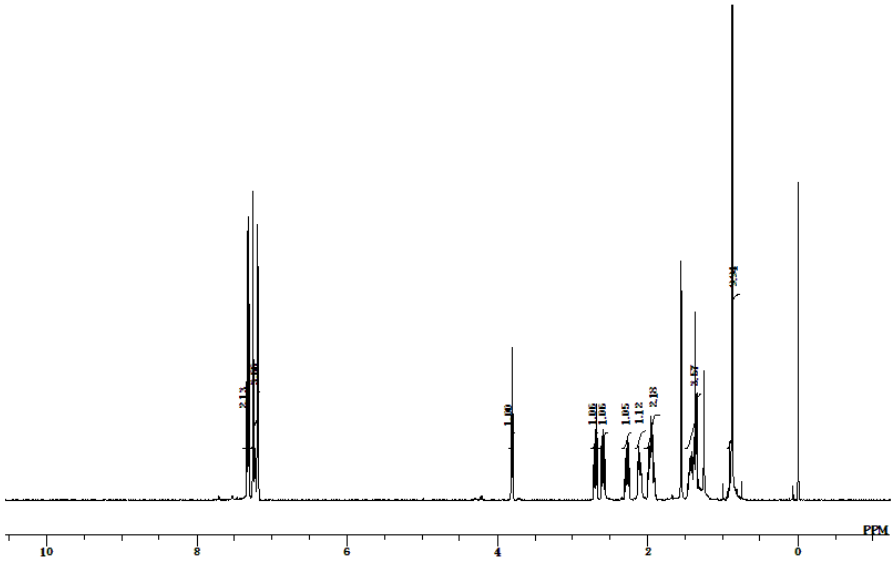


Figure S39. ^{1}H NMR of **2h**

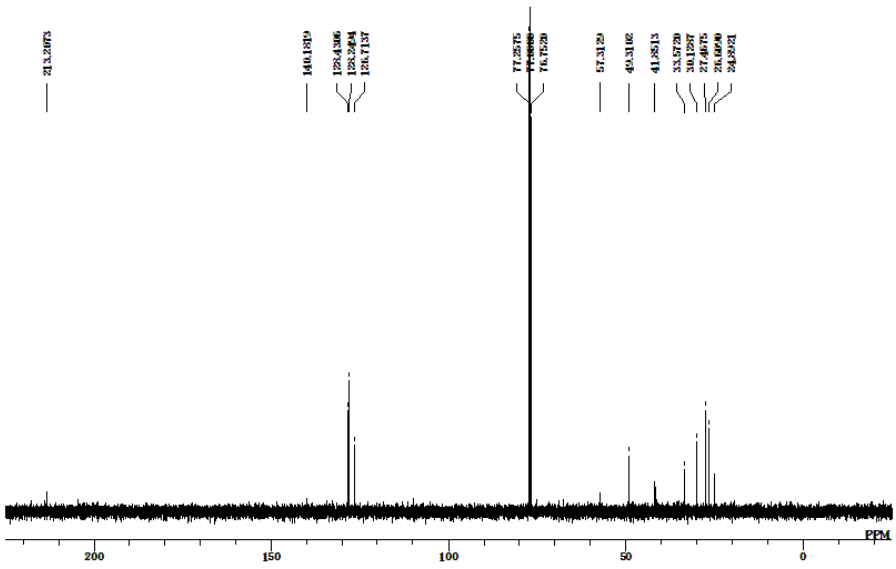
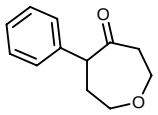


Figure S40. ^{13}C NMR of **2h**



5-oxo-2-phenylcycloheptan-1-one (2i)

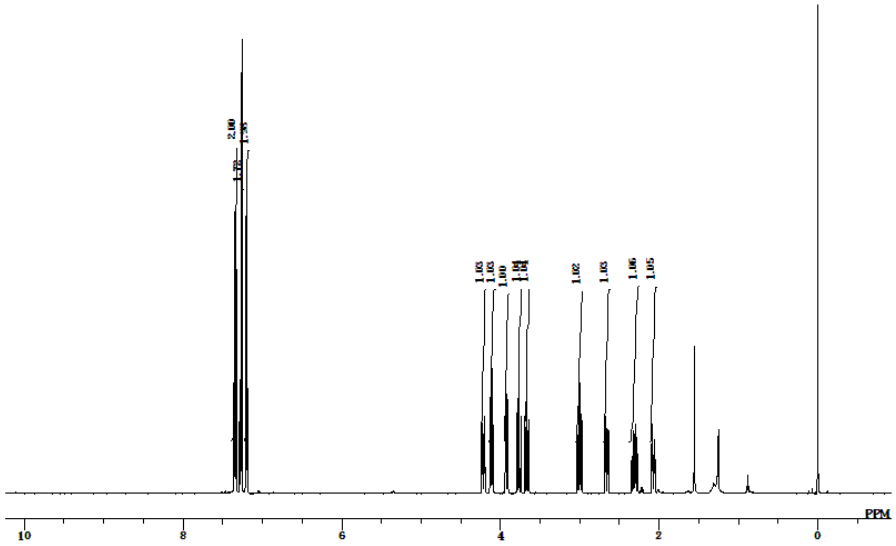


Figure S41. ^{1}H NMR of **2i**

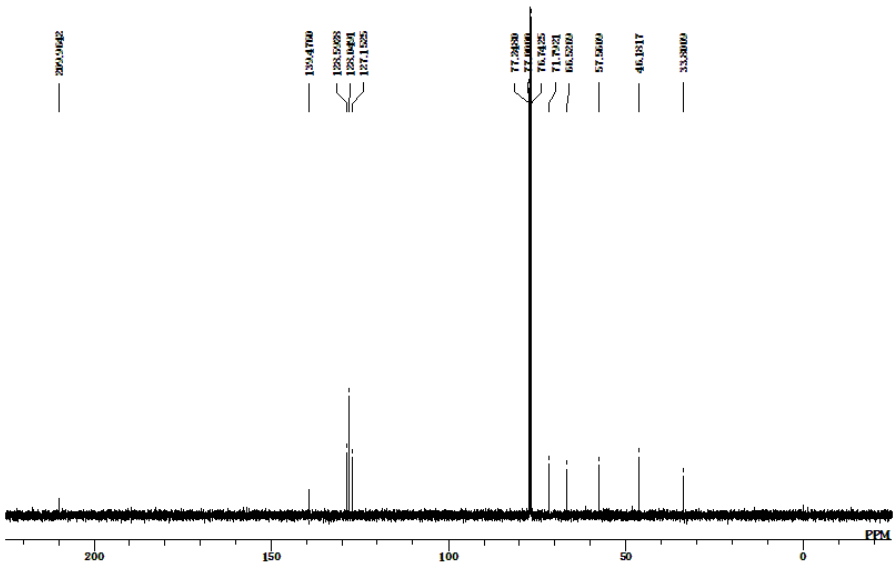
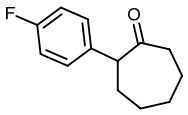


Figure S42. ^{13}C NMR of **2i**



2-(4-fluorophenyl)cycloheptan-1-one (2j)

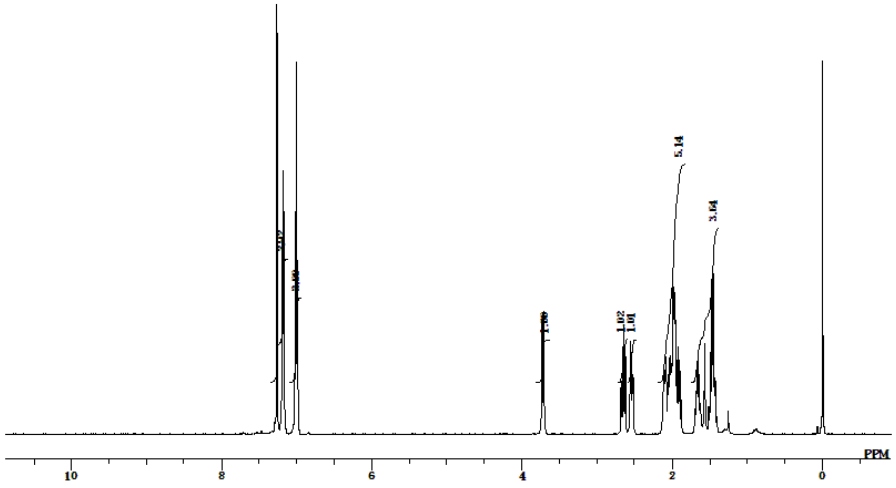


Figure S43. ^{1}H NMR of **2j**

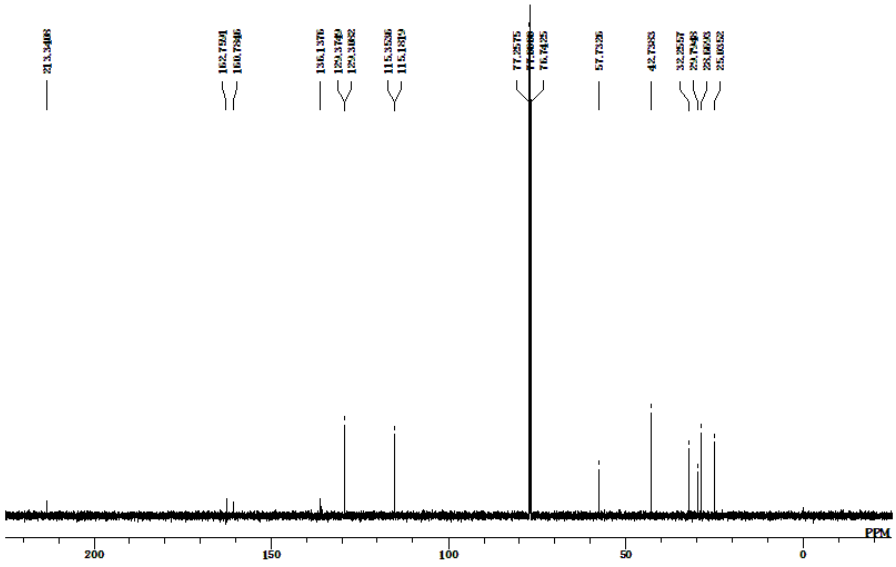


Figure S44. ^{13}C NMR of **2j**

2-(3-chlorophenyl)cycloheptan-1-one (2k)

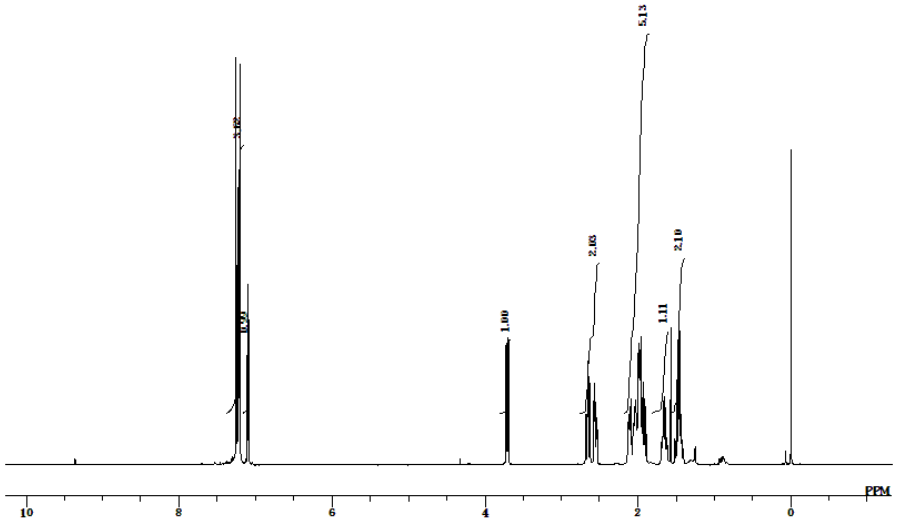


Figure S45. ^{1}H NMR of **2k**

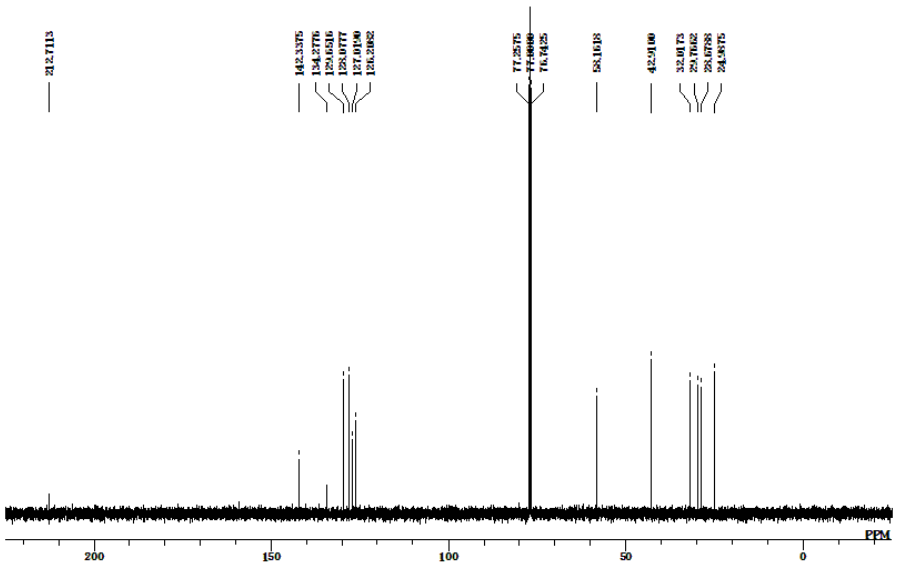
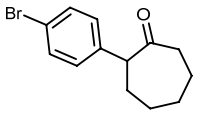


Figure S46. ^{13}C NMR of **2k**



2-(4-bromophenyl)cycloheptan-1-one (2l)

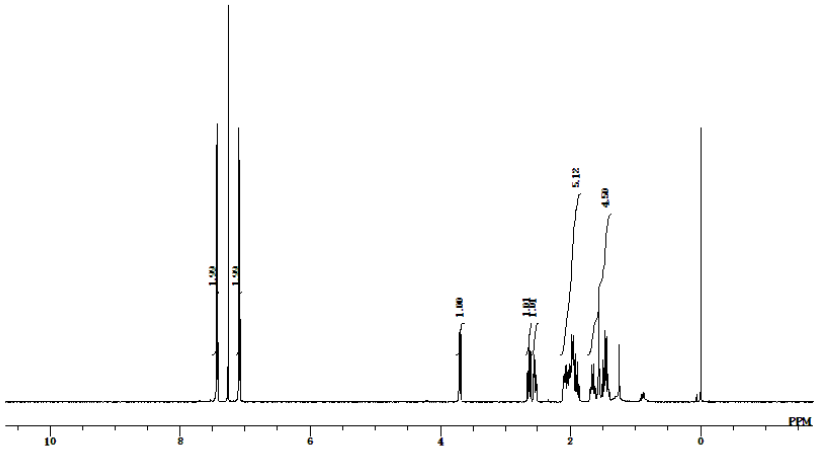
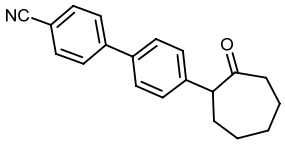


Figure S47. ^{1}H NMR of **2l**



2-[4-(4-cyanophenyl)phenyl]cycloheptan-1-one (2m)

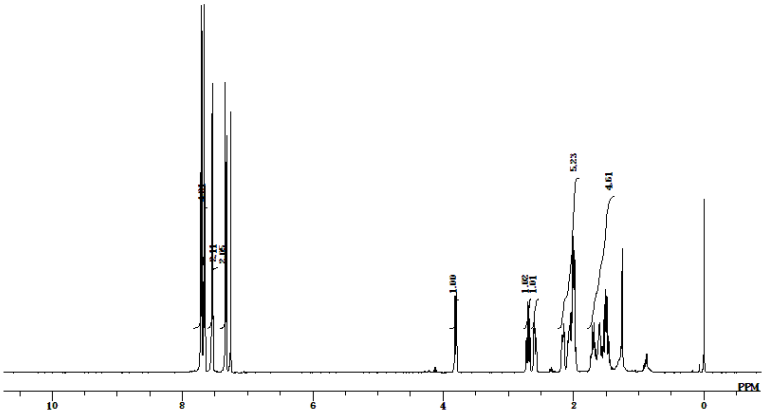


Figure S48. ^{1}H NMR of **2m**

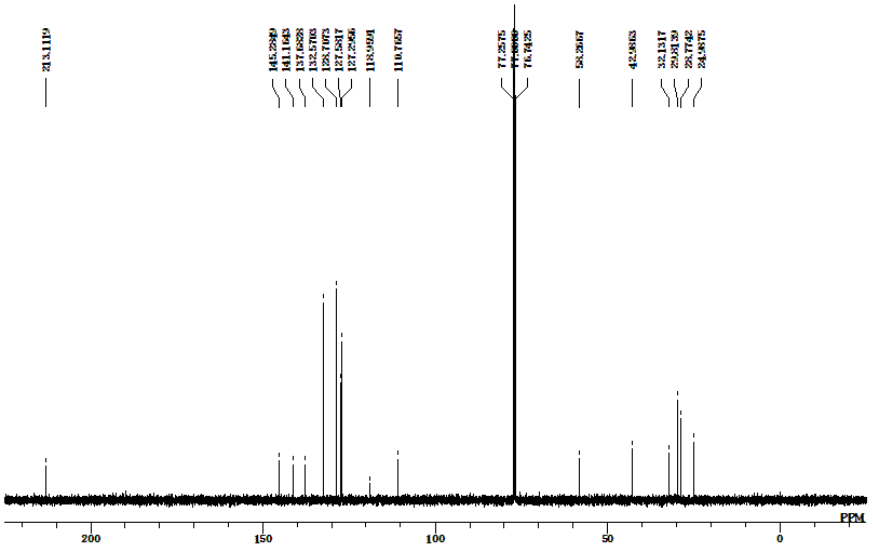
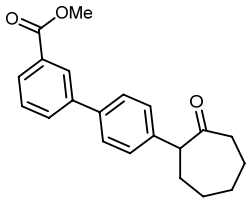


Figure S49. ^{13}C NMR of **2m**



2-[4-(3-methoxycarbonylphenyl)phenyl]cycloheptan-1-one (2n)

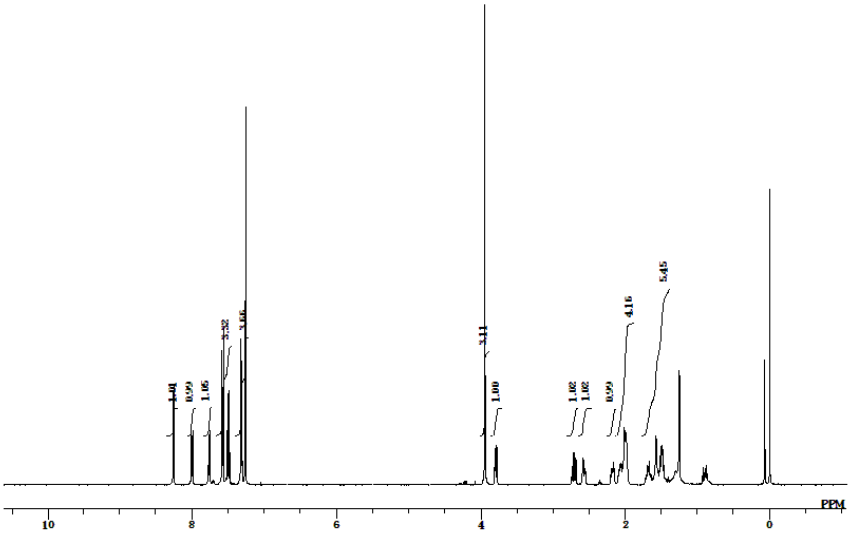


Figure S50. ^{1}H NMR of **2n**

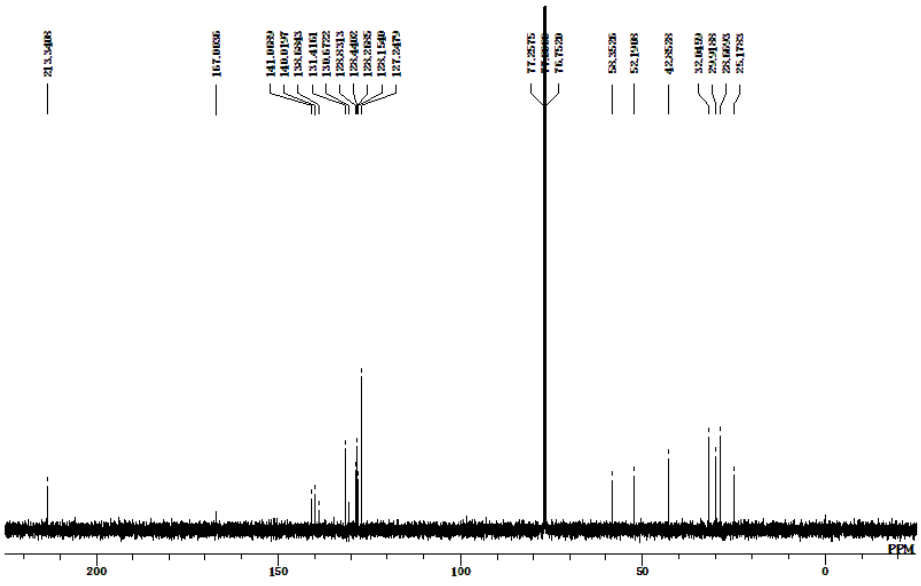
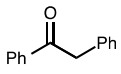


Figure S51. ^{13}C NMR of **2n**



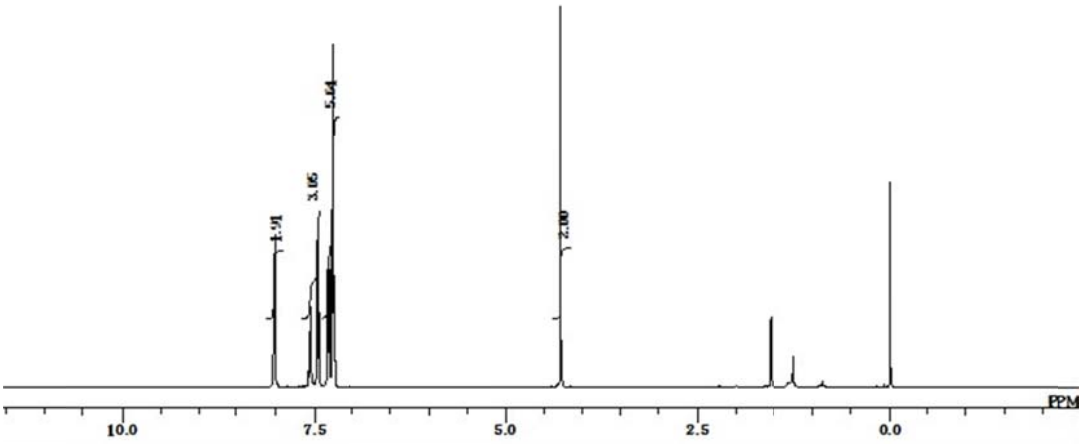
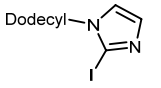


Figure S52. ^{1}H NMR of **2p**



1-Dodecyl-2-iodoimidazole

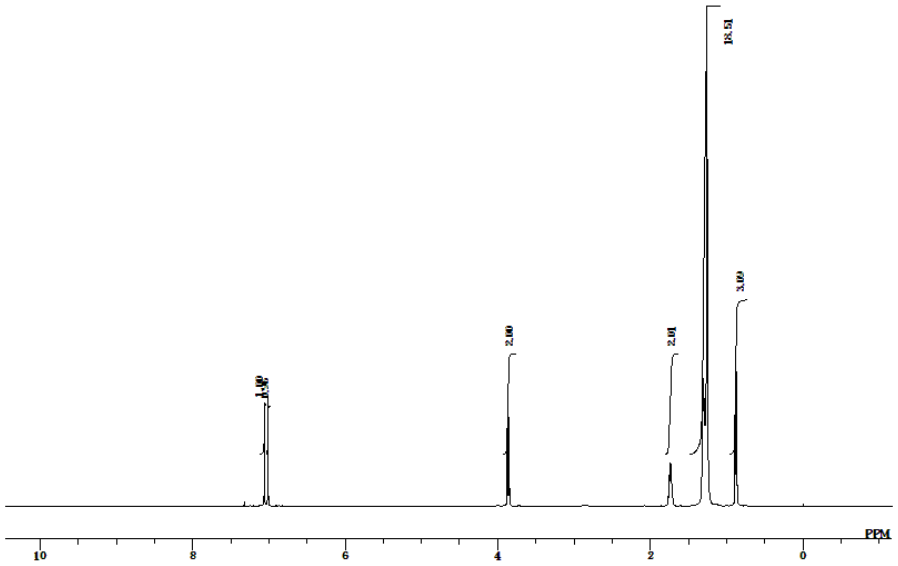


Figure S53. ^{1}H NMR of the titled compound

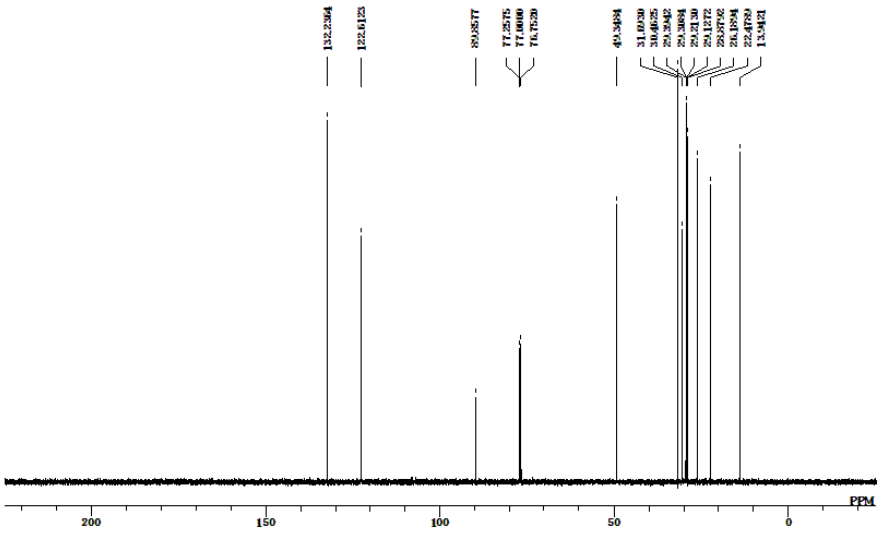
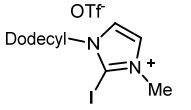


Figure S54. ^{13}C NMR of the titled compound



1-Dodecyl-2-iodo-3-methyliodoimidazolium triflate (4)

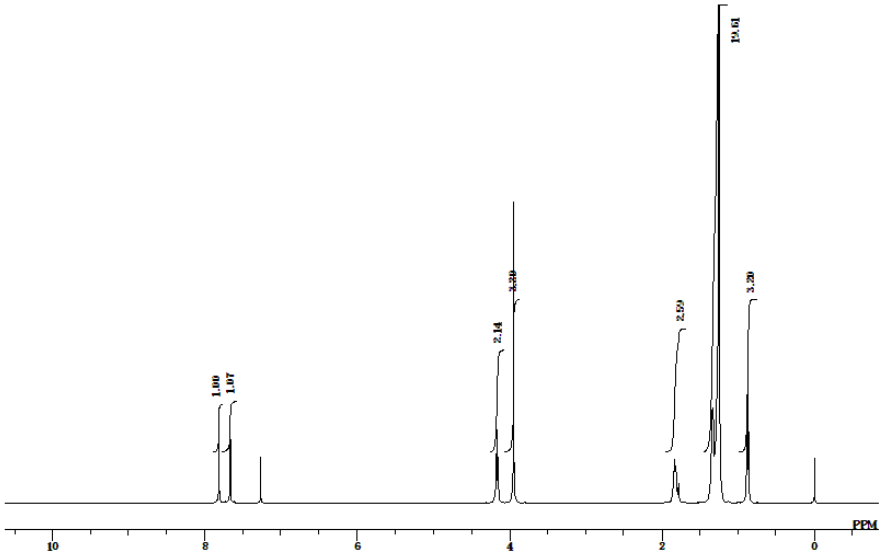


Figure S55. ^{1}H NMR of **4**

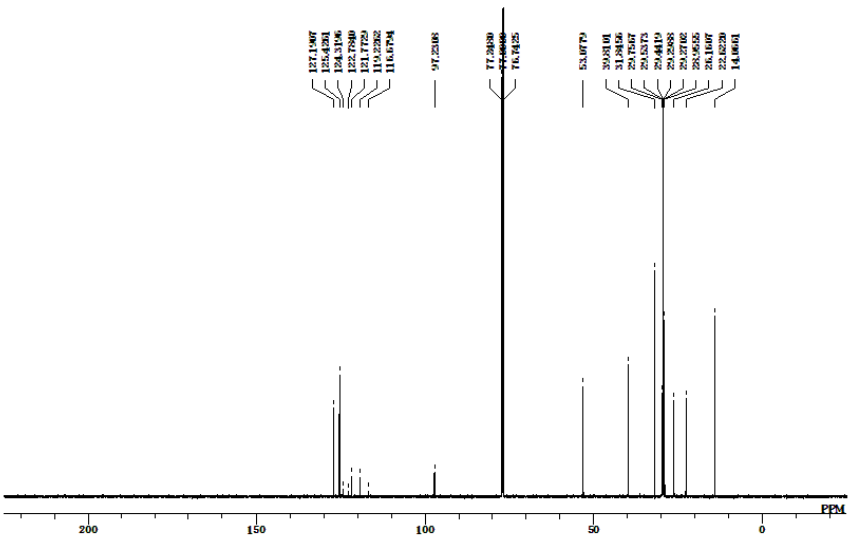
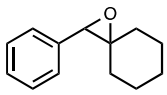


Figure S56. ^{13}C NMR of **4**

12. Copies of HPLC charts



2014/05/30 22:18:35 1 / 1

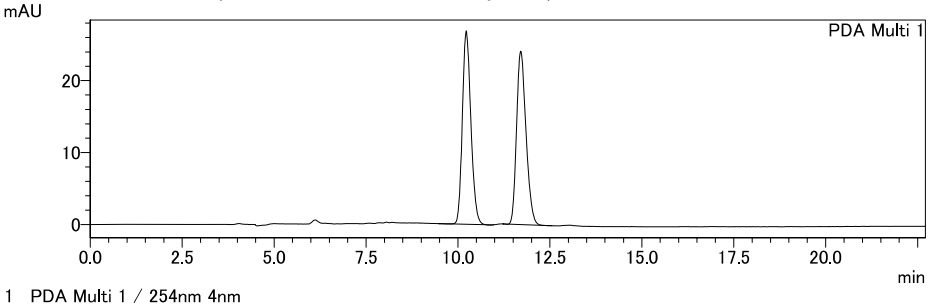
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kobayashi¥epoxide-racem-AD.lcd

sample ID : epoxide-rac
method name : 99-IPA 0.5mL 30min no2.lcm
acquisition date : 2014/03/18 15:28:47
modified date : 2014/03/18 15:51:33

<Chromatogram>

chromatogram
epoxide-rac C:¥data_131217¥Kobayashi¥epoxide-racem-AD.lcd



1 PDA Multi 1 / 254nm 4nm

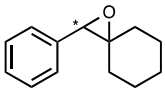
<Peak Report>

peak table C:¥data_131217¥Kobayashi¥epoxide-racem-AD.lcd

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	10.218	433237	50.264
2	11.701	428690	49.736

Figure S57. HPLC chart of (±)-2-phenyl-1-oxaspiro[2.5]octane.



2014/05/30 22:21:11 1 / 1

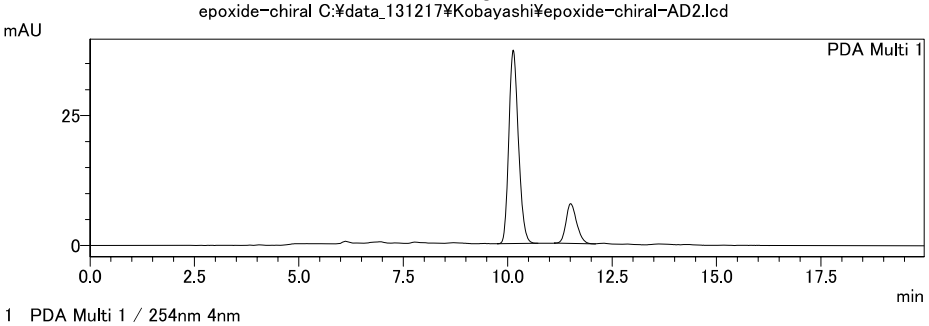
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kobayashi¥epoxide-chiral-AD2.lcd

sample ID : epoxide-chiral
method name : 99-IPA 0.5mL 30min no2.lcm
acquisition date : 2014/03/18 17:13:59
modified date : 2014/03/18 17:33:59

<Chromatogram>

chromatogram
epoxide-chiral C:¥data_131217¥Kobayashi¥epoxide-chiral-AD2.lcd



1 PDA Multi 1 / 254nm 4nm

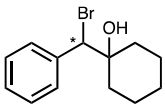
<Peak Report>

peak table C:¥data_131217¥Kobayashi¥epoxide-chiral-AD2.lcd

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	10.126	595869	81.400
2	11.503	136155	18.600

Figure S58. HPLC chart of the chiral 2-phenyl-1-oxaspiro[2.5]octane.



(+)–**1c**

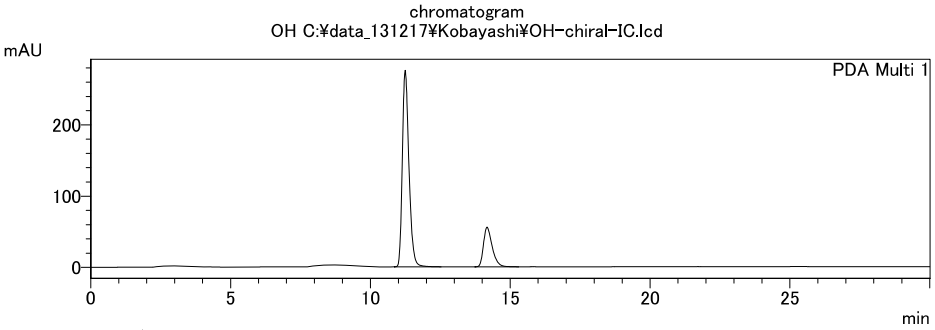
2014/05/30 22:23:39 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kobayashi¥OH-chiral-IC.lcd

sample ID	: OH
method name	: 99-IPA 0.5mL 30min no1.lcm
acquisition date	: 2014/03/24 13:23:58
modified date	: 2014/03/24 13:54:04

<Chromatogram>



1 PDA Multi 1 / 254nm 4nm

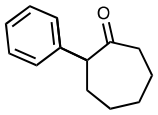
<Peak Report>

peak table C:¥data_131217¥Kobayashi¥OH-chiral-IC.lcd

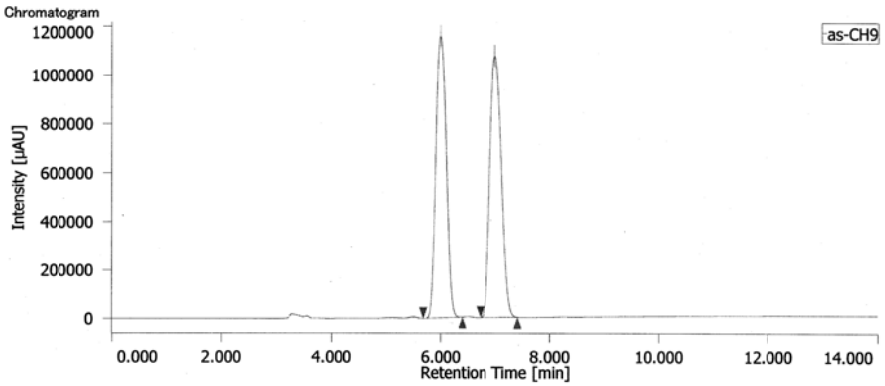
PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	11.238	4464290	79.093
2	14.164	1180078	20.907

Figure S59. HPLC chart of the chiral **1c**.



Analysis Report– Chromatogram



Chromatogram Info

modification time	2013/10/26 14:35:57
commen:	
acquisition date	2013/10/26 14:21:54
injection volume	5.00 [μL]
sample#	1
control method	1.0 mL 2-propanol 5% in hexane 3

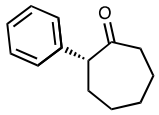
Channel Info

chromatogram name	as-CH9

Peak Info

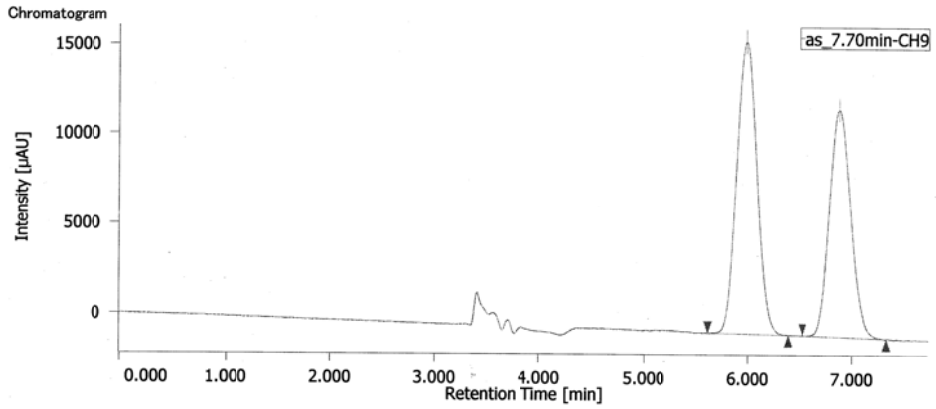
#	CH	tR [min]	Area [μV·sec]	Area (%)
1	9	5.993	15658527	49.440
2	9	7.005	16012982	50.560

Figure S60. HPLC chart of (±)-**2a**.



(11% ee)

Analysis Report– Chromatogram



Chromatogram Info

modification time	2014/07/17 11:38:39
comment	
acquisition date	2014/07/17 11:30:56
injection volume	5.00 [μL]
sample#	1
control method	1.0 mL 2-propanol 5% in hexane 3 2

Channel Info

chromatogram name	as_7.70min-CH9

Peak Info

#	CH	tR [min]	Area [μV·sec]	Area (%)
1	9	5.982	220498	55.521
2	9	6.875	176646	44.479

Figure S61. HPLC chart of the chiral **2a**.