Catalytic Alkylation Reactions of Weakly Acidic Carbonyl and Related Compounds Using Alkenes as Electrophiles

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Supporting Information

General:

Melting points were measured with Büchi Melting Point D-545. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA400, JEOL JNM-ECA500 and JNM-ECX600 spectrometers in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (δ= 0) for ^{1}H NMR, and $CDCl_3$ served as internal standard (δ= 77.0) for ^{13}C NMR. IR spectra were measured using JASCO FT/IR-4200 spectrometer. Preparative thin-layer chromatography (pTLC) was carried out using Wakogel B-5F. Potassium bis(trimethylsilyl)amide (KHMDS) was purchased as a solid from Aldrich Co., Ltd. 18-Crown-6 ether was purchased from Tokyo Chemical Industry Co., Ltd. KHMDS and the crown ether were stored in glove box and used without further purification. THF, CPME, TBME, toluene, and ethylbenzene were distilled in the presence of benzophenone and sodium just before use. *N*,*N*-dimethylpropionamide, styrene and stilbene were purchased from Tokyo Chemical Industry Co., Ltd. *N*-methylcaprolactam was purchased from Aldrich Co., Ltd. Other lactams were synthesized from N-free lactams purchased and methyl iodide. Other nucleophiles were synthesized from corresponding acid chlorides and amines or alcohols following typical procedures. Electrophiles except styrene derivatives were synthesized from corresponding chlorides and vinyl Grignard reagents following typical procedures. Styrene derivatives were synthesized from corresponding aldehydes or ketone and methyl triphenylphosphonium bromide. All compounds employed were purified by distillation or recrystallization before conducting the reactions.

General experimental procedure for the reactions (Table 1, entry 9): the procedure is described for the reaction for **3aa** as an example. Under Ar atmosphere, KHMDS (4.0 mg, 0.020 mmol), 18-crown-6 ether (5.8 mg, 0.022 mmol) and triphenylvinylsilane **1a** (114.6 mg, 0.400 mmol) were placed in a well-dried test tube with rubber septum, and CPME (1.0 mL) was added at 25 °C. After 30 min stirring at the same temperature, *N*,*N*-dimethylpropionamide **2a** (48.6 mg, 0.480 mmol) was added, and the whole was stirred for 6 h. After addition of water (1 mL) to stop the reaction, the mixture was extracted by CH_2Cl_2 (30 mL) three times. The organic layers were combined and dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product obtained was purified by pTLC

(silica gel, hexane/ethyl acetate = 1/1) to afford the desired product **3aa** (144.6 mg, 93%).

***N*,*N*,2-trimethyl-4-(triphenylsilyl)butanamide (3aa)**; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53-7.52 (6H, m), 7.38-7.32 (9H, m), 2.91 (3H, s), 2.89 (3H, s), 2.64 (1H, m), 1.91 (1H, m), 1.55 (1H, m), 1.40 (1H, m), 1.31 (1H, m), 1.07 (3H, d, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.95, 135.48, 134.83, 129.27, 127.73, 38.57, 36.91, 35.41, 27.93, 16.82, 10.89; IR (neat, cm^{-1}): 3049, 3017, 2930, 2236, 1962, 1893, 1826, 1641, 1489, 1424, 1333, 1262, 1165, 1109, 1066, 1026, 1001, 910, 734, 705, 669; HRMS (DART) calcd for $C_{25}H_{30}NOSi$ $[M + H]^+$ 388.2097, found 388.2108.

4-(dimethyl(phenyl)silyl)-*N*,*N*,2-trimethylbutanamide (3ba); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-7.47 (2H, m), 7.32-7.31 (3H, m), 2.94 (3H, s), 2.91 (3H, s), 2.59 (1H, m), 1.68 (1H, m), 1.35 (1H, m), 1.05 (3H, d, J = 6.80 Hz), 0.71-0.67 (2H, m), 0.25 (3H, s), 0.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.38, 139.09, 133.44, 128.73, 127.63, 38.50, 37.02, 35.42, 28.09, 16.91, 13.42, −3.20, −3.43; IR (neat, cm^{-1}): 3481, 3048, 2955, 1645, 1492, 1400, 1334, 1253, 1196, 1168, 1116, 1065, 1020, 910, 820, 781, 731, 703; HRMS (DART) calcd for $C_{15}H_{26}NOSi$ $[M + H]^+$ 264.1784, found 264.1763.

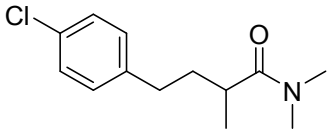
4-(diphenylphosphaneyl)-*N*,*N*,2-trimethylbutanamide (3ca); yellowish oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.44-7.38 (4H, m), 7.34-7.30 (6H, m), 2.95 (3H, s), 2.92 (3H, s), 2.83 (1H, m), 2.09 (1H, m), 1.98 (1H, m), 1.90 (1H, m), 1.50 (1H, m), 1.09 (3H, d, J = 6.80 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 175.67, 138.60 (d, $J_{P\text{-}C}$ = 11.9 Hz), 138.35 (d, $J_{P\text{-}C}$ = 11.9 Hz), 132.70, 132.55, 128.47 (d, $J_{P\text{-}C}$ = 2.38 Hz), 128.36 (d, $J_{P\text{-}C}$ = 2.39 Hz), 128.30 (d, $J_{P\text{-}C}$ = 2.38 Hz), 37.03, 36.36 (d, $J_{P\text{-}C}$ = 13.1 Hz), 35.54, 29.97 (d, $J_{P\text{-}C}$ = 16.7 Hz), 25.56 (d, $J_{P\text{-}C}$ = 11.9 Hz), 17.16; ^{31}P NMR (243 MHz, $CDCl_3$) δ: −15.7; IR (neat, cm^{-1}): 2903, 2336, 1893, 1635, 1488, 1435, 1403, 1175, 1122, 743, 697, 467, 402; HRMS (DART) calcd for $C_{19}H_{25}NOP$ $[M + H]^+$ 314.16738, found 314.16589.

***N*,*N*,2-trimethyl-4-(phenylthio)butanamide (3da)**; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31 (2H, d, J = 6.87 Hz), 7.29-2.25 (2H, m), 7.15 (1H, t, J = 7.56 Hz), 3.01-2.95 (5H, m), 2.92 (3H, s), 2.87 (1H, m), 2.10 (1H, m), 1.66 (1H, m), 1.10 (3H, d, J = 6.87 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.39, 136.27, 128.73, 128.61, 125.61, 36.95, 35.47, 33.89, 32.86, 31.11, 17.17; IR (neat, cm^{-1}): 3054, 2932, 2236, 1639, 1583, 1480, 1443, 1401, 1342, 1265, 1138, 1104, 916, 736, 695; HRMS (DART) calcd for $C_{13}H_{20}NOS$ $[M + H]^+$ 238.1266, found 238.1252.

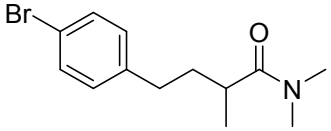
***N*,*N*,2-trimethyl-4-phenylbutanamide (3ea)**; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.26 (2H, t, J = 7.56 Hz), 7.18-7.15 (3H, m), 2.95 (3H, s), 2.89 (3H, s), 2.69-2.61 (2H, m), 2.57 (1H, m), 2.05 (1H, m), 1.67 (1H, m), 1.12 (3H, d, J = 6.87 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.12, 141.80, 128.28, 128.18, 125.67, 36.90, 35.48, 35.36, 34.44, 33.36, 17.29; IR (neat, cm^{-1}): 3481, 3026, 2932, 2234, 1643, 1495, 1457, 1400, 1335, 1260, 1143, 1108, 1053, 921, 732, 702; HRMS (DART) calcd for

$C_{13}H_{20}NO$ $[M + H]^+$ 206.1545, found 206.1568.

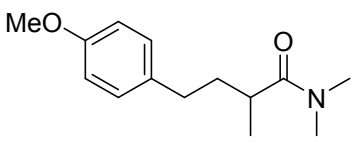
4-(4-chlorophenyl)-*N*,*N*,2-trimethylbutanamide (3fa); yellowish oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.15 (2H, d, *J* = 8.47 Hz), 7.01 (2H, d, *J* = 8.51 Hz), 2.87 (3H, s), 2.85 (3H, s), 2.61-2.41 (3H, m), 1.96 (1H, m), 1.56 (1H, m), 1.04 (3H, d, *J* = 6.78 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 175.94, 140.39, 131.41, 129.56, 128.32, 37.00, 35.56, 35.55, 35.32, 34.60, 32.84, 17.45; IR (neat, cm^{-1}): 3541, 2928, 2336, 1896, 1643, 1491, 1403, 1143, 1094, 1014, 814, 477; HRMS (DART) calcd for $C_{13}H_{189}ClNO$ $[M + H]^+$ 240.11552, found 240.11474.



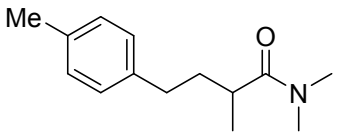
4-(4-bromophenyl)-*N*,*N*,2-trimethylbutanamide (3ga); colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38 (2H, d, *J* = 7.94 Hz), 7.04 (2H, d, *J* = 7.94 Hz), 2.95-2.94 (6H, m), 2.67-2.48 (3H, m), 2.04 (1H, m), 1.64 (1H, m), 1.12 (3H, d, *J* = 6.24 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.89, 140.89, 131.25, 130.10, 119.42, 37.00, 35.55, 35.25, 34.58, 32.90, 17.46; IR (neat, cm^{-1}): 3048, 2934, 2237, 1638, 1488, 1402, 1335, 1265, 1144, 1107, 1073, 1011, 912, 809, 735; HRMS (DART) calcd for $C_{13}H_{19}BrNO$ $[M + H]^+$ 284.0650, found 284.0635.



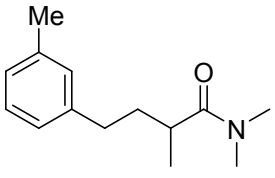
4-(4-methoxyphenyl)-*N*,*N*,2-trimethylbutanamide (3ha); colorless oil; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.08 (2H, d, *J* = 8.94 Hz), 6.82 (2H, d, *J* = 8.94 Hz), 3.78 (3H, s), 2.96 (3H, s), 2.92 (3H, s), 2.66 (1H, m), 2.60-2.49 (2H, m), 2.03 (1H, m), 1.64 (1H, m), 1.12 (3H, d, *J* = 6.87 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.29, 157.72, 134.00, 129.28, 113.70, 55.22, 37.05, 35.71, 35.60, 34.50, 32.54, 17.38; IR (neat, cm^{-1}): 3475, 2934, 2235, 1641, 1511, 1461, 1401, 1333, 1298, 1247, 1178, 1143, 1108, 1037, 920, 826, 734; HRMS (DART) calcd for $C_{14}H_{22}NO_2$ $[M + H]^+$ 236.1651, found 236.1662.



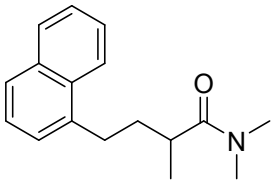
***N*,*N*,2-trimethyl-4-(*p*-tolyl)butanamide (3ia)**; colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.09-7.04 (4H, m), 2.94 (3H, s), 2.91 (3H, s), 2.68-2.49 (3H, m), 2.30 (3H, s), 2.04 (1H, m), 1.65 (1H, m), 1.11 (3H, d, *J* = 6.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.16, 138.70, 135.06, 128.86, 128.16, 36.92, 35.51, 35.48, 34.44, 32.91, 20.85, 17.29; IR (neat, cm^{-1}): 3546, 2929, 2213, 1899, 1644, 1511, 1458, 1399, 1333, 1260, 1142, 1107, 1054, 901, 810, 747; HRMS (DART) calcd for $C_{14}H_{22}NO$ $[M + H]^+$ 220.1701, found 220.1727.



***N*,*N*,2-trimethyl-4-(*m*-tolyl)butanamide (3ja)**; colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.08 (1H, t, *J* = 7.94 Hz), 6.92-6.87 (3H, m), 2.88 (3H, s), 2.84 (3H, s), 2.58 (1H, m), 2.54-2.42 (2H, m), 2.24 (3H, s), 1.97 (1H, m), 1.58 (1H, m), 1.04 (3H, d, *J* = 6.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.15, 141.80, 137.72, 129.15, 128.10, 126.42, 125.32, 36.92, 35.50, 34.51, 33.34, 21.28, 17.37; IR (neat, cm^{-1}): 3482, 3018, 2929, 2867, 2235, 1644, 1490, 1459, 1400, 1334, 1260, 1142, 1107, 1055, 923, 783, 733, 700; HRMS (DART) calcd for $C_{14}H_{22}NO$ $[M + H]^+$ 220.1701, found 220.1686.

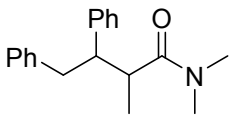


***N*,*N*,2-trimethyl-4-(*o*-tolyl)butanamide (3ka)**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.13-7.06 (4H, m), 2.95 (6H, s), 2.71 (1H, m), 2.64-2.52 (2H, m), 2.30 (3H, s), 2.00 (1H, m), 1.61 (1H, m), 1.14 (3H, d, *J* = 6.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.02, 140.01, 135.81, 130.06, 128.74, 125.83, 125.72, 36.93, 35.51, 34.92, 34.13, 30.86, 19.09, 17.41; IR (neat, cm^{-1}): 3546, 3016, 2933, 2871, 1643, 1492, 1461, 1400, 1333, 1260, 1147, 1108, 1056, 942, 743; HRMS (DART) calcd for $C_{14}H_{22}NO$ $[M + H]^+$ 220.1701, found 220.1701.



***N*,*N*,2-trimethyl-4-(naphthalen-1-yl)butanamide (3la)**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (1H, d, *J* = 7.94 Hz), 7.84 (1H, d, *J* = 7.94 Hz), 7.70 (1H, d, *J* = 8.50 Hz), 7.53-7.45 (2H, m), 7.39-7.36 (1H, m), 7.28 (1H, d, *J* = 6.80 Hz), 3.15-3.10 (1H, m), 3.03-2.98 (4H, m), 2.87 (3H, s), 2.71 (1H, m), 2.24 (1H, m), 1.78 (1H, m), 1.14 (3H, d, *J* = 6.80 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 176.08, 138.22, 133.85, 131.86, 128.64, 126.61, 125.98, 125.76, 125.43, 125.40, 123.95, 36.96, 35.63, 35.07, 34.92, 30.73, 17.60; IR (neat, cm^{-1}): 3478, 3046, 2931, 2872, 2235, 1936, 1640, 1504, 1462, 1398, 1334, 1261, 1142, 1107, 1018, 971, 918, 862, 783, 733; HRMS (DART) calcd for $C_{17}H_{22}NO$ $[M + H]^+$ 256.1701, found 256.1727.

***N*,*N*,2-trimethyl-3,4-diphenylbutanamide (3ma)**; major diastereomer: colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.19 (2H, t, *J* = 7.37 Hz), 7.13 (1H, t, *J* = 7.09 Hz), 7.09-7.01 (5H, m), 6.89 (2H, d, *J* = 6.80 Hz), 3.23 (1H, m), 3.09 (3H, s), 3.06-2.99 (5H, m), 2.69 (1H, dd, *J* = 12.75, 11.05 Hz), 0.88 (3H, d, *J* = 6.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.89, 141.93, 139.98, 129.09, 128.58, 128.03, 127.66, 126.20, 125.50, 51.50, 41.07, 40.77, 37.34, 35.75, 16.47; IR (KBr disc, cm^{-1}): 3449, 3249, 3079, 3025, 2966, 2932, 2343, 2258, 1953, 1876, 1811, 1754, 1628, 1492, 1449, 1414, 1328, 1256, 1142, 1112, 1069, 1006, 953, 909, 810, 757, 700, 631; HRMS (DART) calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1836; m.p. 96-99 °C; minor diastereomer: colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.14 (2H, t, *J* = 7.37 Hz), 7.11-7.02 (6H, m), 6.94 (2H, d, *J* = 6.80 Hz), 3.29-3.20 (2H, m), 3.10 (1H, m), 2.80 (1H, m), 2.75 (3H, s), 2.68 (3H, s), 1.34 (3H ,d, *J* = 6.24 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.47, 142.70, 140.12, 129.05, 128.18, 127.84, 127.82, 126.14, 125.55, 50.42, 41.53, 37.94, 37.16, 35.37, 15.84; IR (KBr disc, cm^{-1}): 3682, 3655, 3433, 3261, 3082, 3060, 3028, 2949, 2923, 2368, 2340, 1941, 1893, 1634, 1493, 1451, 1418, 1396, 1328, 1258, 1148, 1111, 1074, 1048, 765, 739, 701, 611; HRMS (DART) calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1890; m.p. 81-83 °C.



***N*,*N*,2-trimethyl-4,4-diphenylbutanamide (3na)**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31-7.13 (10H, m), 3.95 (1H, dd, *J* = 9.66, 6.78 Hz), 2.92 (3H, s), 2.60 (3H, s), 2.56-2.44 (2H, m), 2.08 (1H, m), 1.12 (3H, d, *J* = 6.83 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 176.12, 144.76, 144.23, 128.48, 128.31, 128.03, 127.75, 126.26, 126.11, 48.73, 39.98, 36.76, 35.59, 33.38, 17.84; IR (neat, cm^{-1}): 3026, 2931, 1635, 1598, 1494, 1450, 1414, 1397, 1339, 1260, 1147, 1109, 1089, 1053, 1031, 759, 746, 729, 697; HRMS (DART) calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1854.

2-methyl-1-(pyrrolidin-1-yl)-4-(triphenylsilyl)butan-1-one (3ab); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.51 (6H, m), 7.38-7.31 (9H, m), 3.45 (2H, t, J = 6.80 Hz), 3.36-3.25 (2H, m), 2.48 (1H, m), 1.95-1.75 (5H, m), 1.56 (1H, m), 1.44-1.30 (2H, m), 1.09 (3H, d, J = 6.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.58, 135.49, 134.82, 129.24, 127.71, 46.16, 45.48, 40.98, 27.78, 25.96, 24.13, 16.67, 10.92; IR (KBr disc, cm^{-1}): 3753, 3439, 3244, 3130, 3062, 2974, 2926, 2868, 2215, 1961, 1894, 1828, 1775, 1630, 1481, 1431, 1336, 1256, 1227, 1190, 1147, 1110, 1071, 1036, 1002, 955, 882, 704; HRMS (DART) calcd for $C_{27}H_{32}NOSi$ $[M + H]^+$ 414.2253, found 414.2208; m.p. 116-118 °C.

***N*,*N*-diisopropyl-2-methyl-4-(triphenylsilyl)butanamide (3ac)**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.51 (6H, m), 7.40-7.32 (9H, m), 3.92 (1H, br), 3.46 (1H, Br), 2.55 (1H, m), 1.87 (1H, m), 1.53 (1H, m), 1.42-1.30 (8H, m), 1.15 (3H, d, J = 6.24 Hz), 1.09-1.06 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.15, 135.55, 134.94, 129.32, 127.80, 45.51, 28.30, 20.78, 20.70, 17.06, 10.73; IR (neat, cm^{-1}): 3065, 3002, 2967, 2929, 2874, 2237, 1961, 1891, 1824, 1634, 1433, 1371, 1307, 1262, 1212, 1111, 1068, 1039, 1002, 913, 704, 665; HRMS (DART) calcd for $C_{29}H_{38}NOSi$ $[M + H]^+$ 444.2723, found 444.2741.

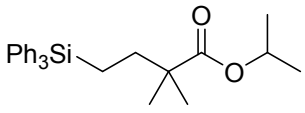
1-methyl-3-(2-(triphenylsilyl)ethyl)pyrrolidin-2-one (3ad); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-7.51 (6H, m), 7.40-7.32 (9H, m), 3.24-3.21 (2H, m), 2.79 (3H, s), 2.46-2.39 (1H, m), 2.15 (1H, m), 2.00 (1H, m), 1.70-1.55 (2H, m), 1.48-1.35 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.15, 135.53, 134.70, 129.34, 127.79, 47.42, 44.12, 29.54, 25.50, 23.96, 10.30; IR (KBr disc, cm^{-1}): 3429, 3128, 3061, 3002, 2973, 2939, 2875, 2342, 2217, 1967, 1893, 1829, 1775, 1688, 1586, 1498, 1429, 1401, 1301, 1260, 1169, 1109, 1026, 1001, 962, 931, 837, 797, 708, 670, 622; HRMS (DART) calcd for $C_{19}H_{22}NOSi$ $[M - Ph]^+$ 308.1471, found 308.1465; m.p. 123-125 °C.

1-methyl-3-(2-(triphenylsilyl)ethyl)piperidin-2-one (3ae); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54-7.49 (6H, m), 7.38-7.31 (9H, m), 3.23-3.14 (2H, m), 2.87 (3H, s), 2.30-2.24 (1H, m), 2.15-2.07 (1H, m), 1.93-1.88 (1H, m), 1.81-1.75 (1H, m), 1.72-1.64 (2H, m), 1.60-1.53 (1H, m), 1.48-1.34 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.24, 135.52, 134.87, 129.25, 127.72, 49.88, 43.79, 34.68, 25.99, 25.61, 21.32, 10.38; IR (KBr disc, cm^{-1}): 3753, 3436, 3236, 3063, 3013, 2925, 2865, 2691, 2291, 1964, 1889, 1823, 1775, 1632, 1590, 1494, 1427, 1395, 1354, 1328, 1248, 1215, 1175, 1108, 1058, 1026, 999, 924, 877, 851, 782, 739, 705, 616; HRMS (DART) calcd for $C_{26}H_{30}NOSi$ $[M + H]^+$ 400.2097, found 400.2076; m.p. 113-116 °C.

1-methyl-3-(2-(triphenylsilyl)ethyl)azepan-2-one (3af); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57-7.55 (6H, m), 7.39-7.32 (9H, m), 3.46 (1H, dd, J = 15.3, 11.3 Hz), 3.04 (1H, dd, J = 15.0, 4.25 Hz), 2.96 (3H, s), 2.42 (1H, m), 2.13 (1H, m), 1.83 (1H, m), 1.66 (1H, m), 1.61-1.55 (2H, m), 1.51-1.24 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.75, 135.64, 135.28, 129.23, 127.76, 50.18, 46.72, 35.57, 30.23, 29.07, 27.09, 26.75, 11.65; IR (KBr disc, cm^{-1}): 3754,

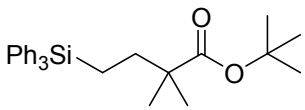
3698, 3628, 3440, 3267, 3129, 3045, 3021, 2923, 2863, 2688, 2613, 2586, 2361, 1971, 1904, 1831, 1776, 1645, 1482, 1428, 1394, 1330, 1262, 1212, 1183, 1159, 1108, 1073, 1026, 993, 950, 905, 851, 816, 716, 671; HRMS (DART) calcd for $C_{27}H_{32}NOSi$ $[M + H]^+$ 414.2253, found 414.2209; m.p. 106-108 °C.

isopropyl 2,2-dimethyl-4-(triphenylsilyl)butanoate (3ag); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55-

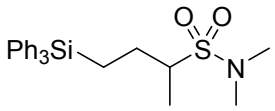


7.53 (6H, m), 7.44-7.36 (9H, m), 5.01 (1H, m), 1.73-1.69 (2H, m), 1.35-1.30 (2H, m), 1.20 (6H, d, J = 6.24 Hz), 1.16 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.20, 135.58, 134.89, 129.40, 127.83, 67.23, 43.54, 34.70, 24.73, 21.75, 8.19; IR (KBr disc, cm^{-1}): 3753, 3417, 3132, 3067, 3048, 3018, 2976, 2917, 2873, 1953, 1885, 1818, 1717, 1586, 1468, 1427, 1380, 1324, 1262, 1176, 1107, 1034, 1001, 925, 897, 833, 805, 738, 704, 674; HRMS (DART) calcd for $C_{21}H_{27}O_2Si$ $[M - Ph]^+$ 339.1780, found 339.1794; m.p. 61-63 °C.

***tert*-butyl 2,2-dimethyl-4-(triphenylsilyl)butanoate (3ah)**; colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-

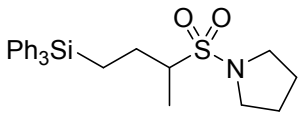


7.51 (6H, m), 7.40-7.33 (9H, m), 1.68-1.64 (2H, m). 1.39 (9H, s), 1.33-1.30 (2H, m), 1.11 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.00, 135.57, 134.92, 129.38, 127.82, 79.56, 44.07, 34.83, 27.97, 24.75, 8.20; IR (KBr disc, cm^{-1}): 3415, 3133, 3050, 2972, 2926, 2872, 1963, 1896, 1829, 1775, 1718, 1591, 1480, 1453, 1426, 1388, 1367, 1330, 1262, 1151, 1108, 1033, 1003, 889, 853, 818, 736, 706, 673; HRMS (DART) calcd for $C_{22}H_{29}O_2Si$ $[M - Ph]^+$ 353.1934, found 353.1948; m.p. 91-95 °C.



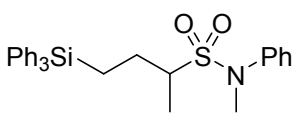
***N*,*N*-dimethyl-4-(triphenylsilyl)butane-2-sulfonamide (3ai)**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-7.51 (6H, m), 7.41-7.33 (9H, m), 3.05-2.98 (1H, m), 2.74 (6H, s), 2.17 (1H, m), 1.70 (1H, m), 1.59 (1H, m), 1.36-1.30 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.45, 134.14, 129.58, 127.93, 59.29, 37.54, 24.97, 13.36, 10.14; IR (neat, cm^{-1}): 3066, 3016, 2939, 2812, 1964, 1895, 1827, 1589, 1482, 1456, 1428, 1379, 1323, 1280, 1190, 1137, 1111, 1064, 966, 893, 860, 772, 707, 658; HRMS (DART) calcd for $C_{24}H_{30}NO_2SSi$ $[M + H]^+$ 424.1767, found 424.1741.

1-((4-(triphenylsilyl)butan-2-yl)sulfonyl)pyrrolidine (3aj); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53-



7.51 (6H, m), 7.41-7.33 (9H, m), 3.25-3.20 (4H, m), 3.03 (1H, m), 2.09 (1H, m), 1.78-1.66 (5H, m), 1.59 (1H, td, J = 13.9, 4.53 Hz), 1.38-1.30 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.45, 134.19, 129.56, 127.91, 59.77, 47.89, 25.77, 24.90, 13.22, 10.18; IR (KBr disc, cm^{-1}): 3440, 3133, 3063, 2979, 2939, 2875, 2276, 1972, 1902, 1833, 1779, 1669, 1587, 1485, 1456, 1425, 1375, 1315, 1254, 1194, 1142, 1113, 1077, 1012, 903, 861, 777, 743, 703; HRMS (DART) calcd for $C_{26}H_{32}NO_2SSi$ $[M + H]^+$ 450.1923, found 450.1898; m.p. 116-118 °C.

***N*-methyl-*N*-phenyl-4-(triphenylsilyl)butane-2-sulfonamide (3ak)**; colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$)



δ: 7.50-7.49 (6H, m), 7.43-7.30 (9H, m), 7.26-7.23 (2H, m), 7.19-7.15 (3H, m), 3.18 (3H, s), 3.04 (1H, m), 2.09 (1H, m), 1.73 (1H, m), 1.55 (1H, m), 1.37 (3H, d, J = 6.80

Hz), 1.21 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.49, 135.46, 134.07, 129.63, 129.14, 127.95, 126.58, 125.80, 59.50, 39.19, 24.85, 13.13, 10.08; IR (KBr disc, cm^{-1}): 3067, 3021, 2983, 2946, 2920, 1968, 1896, 1838, 1778, 1669, 1589, 1488, 1456, 1424, 1383, 1326, 1262, 1188, 1136, 1110, 1069, 1020, 878, 770, 744, 706, 667; HRMS (DART) calcd for $C_{23}H_{26}NO_2SSi$ $[M - Ph]^+$ 408.1454, found 408.1423; m.p. 129-132 °C.