Electronic Supplementary Information

Organocatalytic Deprotonative Functionalization of C(sp^2)–H and C(sp^3)–H Bonds Using *in situ*-Generated Onium Amide Bases

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1. General Comments

All reactions were carried out under an Ar atmosphere unless otherwise noted. Anhydrous solvents were obtained from commercial suppliers and used without further purification. All other chemicals, including P5F (0.3 M in benzene, Aldrich, catalogue #: 87652), were purchased from commercial suppliers and used as received.

Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity. ^{1}H-NMR spectra were recorded on JEOL JNM-AL400 (400 MHz) using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Herts (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, dd = double doublet, m = multiplet, br.s = broad singlet, and br = broad signal. ^{13}C-NMR spectra were recorded on JEOL JNM-AL400 (100 MHz) and chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm). Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and JMS-700/JMS-T 100 GC spectrometer respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

2. Representative Procedure for Deprotonative Functionalization of C(sp^2)–H Bonds

Reaction of Benzothiazole (1a) with Benzophenone (2a) Using P5F and TTMS (3d) (Table 1, Entry 7)

P5F (25 μL, 7.5 μmol, 0.3 M in benzene) was added to a mixture of **1a** (20 mg, 0.15 mmol), **2a** (33 mg, 0.18 mmol), and **3d** (54 mg, 0.23 mmol) in toluene (0.6 mL), and the reaction mixture was stirred at room temperature for 24 h. Saturated aqueous NH_4Cl (5 mL) was added and the whole mixture was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. The solvent was evaporated to give a crude mixture of **4aa** and its trimethylsilylated compound, which was subjected to the desilylation using 2.0 M aqueous NaOH in THF to produce **4aa** (45 mg, 94%).

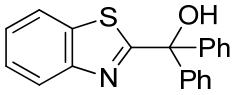
3. Representative Procedure for Deprotonative Functionalization of C(sp^3)–H Bonds

Reaction of ^{t}Butyl Acetate (5a) with Benzophenone (2a) Using TMAF and DMATMS (3c) (Scheme 6)

5a (23 mg, 0.2 mmol) and **3c** (47 mg, 0.4 mmol) were added to a mixture of **2a** (44 mg, 0.24 mmol) and TMAF (1.0 mg, 0.01 mmol) in DMF (0.8 mL), and the reaction mixture was stirred at room temperature for 24 h. Saturated aqueous NH_4Cl (5 mL) was added and the whole mixture was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$, and then the solvent was evaporated. The yield of **6aa** was determined by ^{1}H-NMR spectra using 1,1,2-trichloroethane as an internal standard. Analytically pure **6aa** was obtained by preparative TLC.

4. Characterization Data

(2-Benzothiazolyl)diphenylmethanol (4aa)[1]



Colorless needles [recrystallized from $CHCl_3$, mp 151–153 °C (lit.[1] mp 149.5–150 ºC)].

IR (neat): 3330, 3056, 3027, 2960, 2928, 2364, 2199, 1977, 1588, 1490, 1446, 1435, 1261, 1136, 1041, 887, 751, 728, 696 cm^{-1}.

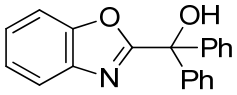
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.37 (s, 1H), 7.33–7.39 (m, 7H), 7.46–7.49 (m 5H), 7.83 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 81.08, 121.60, 123.38, 125.22, 126.15, 127.61, 128.13, 128.19, 135.99, 144.82, 152.81, 177.77.

LRMS (EI) *m/z*: 317 (M^+).

HRMS: Calcd. for $C_{20}H_{15}ONS$: 317.0874, found: 317.0867.

(2-Benzoxazolyl)diphenylmethanol (4ba)[2]



Colorless prisms [recrystallized from $CHCl_3$, mp 164–165 °C (lit.[2] mp 157 ºC)].

IR (neat): 1555, 1491, 1448, 1362, 1240, 1169, 1145, 1093, 1058, 1032, 904, 879, 794, 761, 750, 727 cm^{-1}.

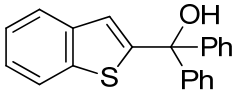
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.26 (s, 1H), 7.32–7.38 (m, 8H), 7.43–7.46 (m, 4H), 7.50–7.53 (m, 1H), 7.74–7.70 (m, 1H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm): 78.59, 111.00, 120.35, 124.63, 125.28, 127.38, 128.20 (2C), 140.12, 142.98, 151.38, 168.54.

LRMS (EI) *m/z*: 301 (M^+).

HRMS: Calcd. for $C_{20}H_{15}NO_2$: 301.1103, found: 301.1117.

(2-Benzothienyl)diphenylmethanol (4ca)[3]



Colorless prisms [recrystallized from acetone/hexane, mp 79–80 °C (lit.[3] mp 70–72 ºC)].

IR (neat): 3453, 3056, 1490, 1457, 1446, 1436, 1329, 1304, 1250, 1156, 1032, 1000, 761, 746 cm^{-1}.

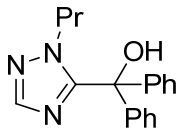
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.03 (s, 1H), 6.93 (s, 1H), 7.30–7.37 (m, 8H), 7.40–7.44 (m, 4H), 7.65 (dd, J = 7.3, 2.0 Hz, 1H), 7.78 (dd, J = 7.3, 2.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 77.89, 122.27, 123.58, 123.73, 124.26, 124.36, 127.33, 127.80, 128.06, 139.22, 140.14, 145.82, 152.63.

LRMS (EI) *m/z*: 316 (M^+).

HRMS: Calcd. for $C_{21}H_{16}OS$: 316.0922, found: 316.0902.

[3-(1-Propyl-1*H*-1,2,4-triazolyl)]diphenylmethanol (4da)



Colorless plates (recrystallized from hexane/EtOAc, mp 144–146 °C).

IR (neat): 3200, 2963, 1491, 1398, 1279, 770, 745, 703 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6) δ (ppm): 0.69 (t, J = 7.6 Hz, 3H), 2.10 (sext, J =7.6 Hz, 2H), 4.06 (t, J = 7.6 Hz. 2H), 5.90 (s, 1H), 7.28–7.36 (m, 10H), 7.71 (s, 1H).

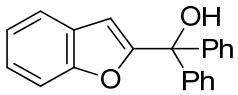
$^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ (ppm): 11.25, 23.34, 52.23, 78.72, 128.11, 128.25, 128.54, 145.80, 149.62, 158.91.

LRMS (EI) *m/z*: 293 (M^+).

HRMS: Calcd. for $C_{18}H_{19}N_3O$: 293.1528, found: 293.1513.

Anal. Calcd. for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.32. Found: C, 73.54; H, 6.60; N, 14.29.

(2-Benzofuryl)diphenylmethanol (4ea)[4]



Colorless prisms [recrystallized from $CHCl_3$, mp 137–138 °C (lit.[4] mp 135 ºC)].

IR (neat): 3542, 1492, 1452, 1343, 1257, 1167, 1135, 1032, 1019, 1001, 967, 903, 875, 751, 745 cm^{-1}.

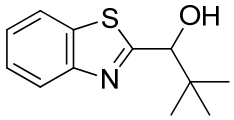
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.22 (s, 1H), 6.31 (s, 1H), 7.21–7.25 (m, 1H), 7.28–7.30 (m, 1H), 7.32–7.40 (m, 10H), 7.45 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm): 80.67, 106.54, 107.79, 116.66, 122.96, 124.47, 127.32, 127.89, 128.10 (2C), 143.98, 157.22, 161.48.

LRMS (EI) *m/z*: 300 (M^+).

HRMS: Calcd. for $C_{21}H_{16}O_2$: 300.1150, found: 300.1175.

1-(2-Benzothiazolyl)-2,2-dimethylpropan-1-ol (4ab)[1]



Colorless needles [recrystallized from MeOH, mp 98–100 °C (lit.[1] mp 110–111 ºC)].

IR (neat): 3420, 2962, 2929, 2867, 1510, 1437, 1367, 1314, 1237, 1187, 1017, 901, 758, 732 cm^{-1}.

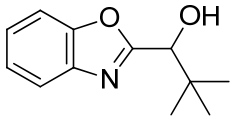
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.08 (s, 9H), 3.07 (d, J = 5.4 Hz, 1H), 4.76 (d, J = 5.4 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.83, 35.98, 79.91, 121.50, 122.83, 124.95, 125.90, 134.78, 152.19, 174.05.

LRMS (EI) *m/z*: 221 (M^+).

HRMS: Calcd. for $C_{12}H_{15}NOS$: 221.0874, found: 221.0876.

1-(2-Benzoxazolyl)-2,2-dimethylpropan-1-ol (4bb)



Colorless plates (recrystallized from MeOH, mp 100–102 °C).

IR (neat): 3323, 2972, 1567, 1456, 1243, 1083, 901, 836, 750, 706 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.07 (s, 9H), 2.80 (d, J = 7.3 Hz, 1H), 4.60 (d, J = 7.3 Hz, 1H), 7.34–7.37 (m, 2H), 7.53–7.55 (m, 1H), 7.72–7.74 (m, 1H).

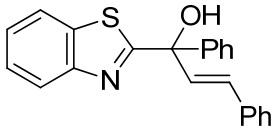
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.63, 36.25, 76.19, 110.73, 119.95, 124.45, 125.02, 140.25, 150.63, 167.03.

LRMS (EI) *m/z*: 205 (M^+).

HRMS: Calcd. for $C_{12}H_{15}NO_2$: 205.1103, found: 205.1095.

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.94; H, 7.35; N, 6.67.

(*E*)-1-(2-Benzothiazolyl)-1,3-diphenyl-2-propen-1-ol (4ac)[1]



Colorless needles [recrystallized from MeOH, mp 172.5–173.5 °C (lit.[1] mp 169.5–170 ºC)].

IR (neat): 3303, 1316, 1099, 1073, 994, 907, 811, 773, 754, 727, 705 cm^{-1}.

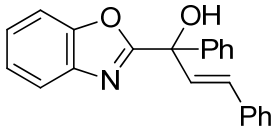
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.06 (s, 1H), 6.85 (d, J = 15.9 Hz, 1H), 7.01 (d, J = 15.9 Hz, 1H), 7.24–7.47 (m, 10H), 7.61 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 79.09, 121.70, 123.26, 125.16, 126.12, 126.58, 126.91, 128.05, 128.28, 128.54, 128.57, 130.62, 132.43, 135.61, 136.10, 143.67, 152.84, 176.98.

LRMS (EI) *m/z*: 343 (M^+).

HRMS: Calcd. for $C_{22}H_{17}NOS$: 343.1031, found: 343.1041.

(*E*)-1-(2-Benzoxazolyl)-1,3-diphenyl-2-propen-1-ol (4bc)



Colorless plates (recrystallized from MeOH, mp 120–121 °C).

IR (neat): 3213, 1564, 1455, 1241, 1128, 1016, 983, 773, 740, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.91 (s, 1H), 6.91 (d, J = 16.1 Hz, 1H), 6.96 (d, J = 16.1 Hz, 1H), 7.24–7.41 (m, 8H), 7.46 (d, J = 7.3 Hz, 2H), 7.52–7.54 (m, 1H), 7.58 (d, J = 16.1 Hz, 2H), 7.75–7.77 (m, 1H).

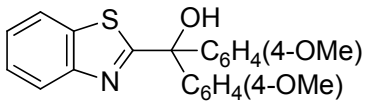
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 76.23, 110.98, 120.31, 124.67, 125.32, 126.28, 126.92, 128.10, 128.36, 128.57, 128.59, 130.12, 130.86, 136.05, 140.22, 142.00, 151.33, 167.97.

LRMS (EI) *m/z*: 327 (M^+).

HRMS: Calcd. for $C_{22}H_{17}NO_2$: 327.1259, found: 327.1250.

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.76; H, 5.30; N, 4.12.

(2-Benzothiazolyl)-bis(4-methoxyphenyl)methanol (4ad)



Colorless plates (recrystallized from hexane, mp 135–137 °C).

IR (neat): 3288, 1605, 1508, 1251, 1165, 1023, 829, 820, 765, 733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.80 (s, 6H), 4.18 (s, 1H), 6.84–6.88 (m, 4H), 7.35–7.39 (m, 5H), 7.47 (t, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H).

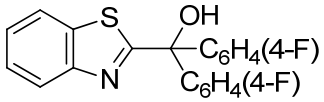
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 55.26, 80.51, 113.43, 121.57, 123.34, 125.11, 126.07, 128.92, 135.96, 137.24, 152.94, 159.29, 178.57.

LRMS (EI) *m/z*: 377 (M^+).

HRMS: Calcd. for $C_{22}H_{19}NO_3S$: 377.1086, found: 377.1040.

Anal. Calcd. for $C_{22}H_{19}NO_3S$: C, 70.00; H, 5.07; N, 3.71. Found: C, 69.93; H, 5.15; N, 3.67.

(2-Benzothiazolyl)-bis(4-fluorophenyl)methanol (4ae)



Colorless plates (recrystallized from MeOH/ hexane, mp 99–102 °C).

IR (neat): 3372, 1600, 1504, 1225, 1158, 1014, 835, 794, 758, 729 cm^{-1}.

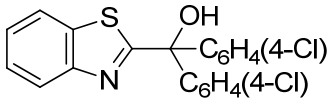
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.35 (s, 1H), 7.01–7.06 (m, 4H), 7.39–7.45 (m, 5H), 7.50 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 80.33, 115.23 (d, J = 18 Hz), 121.77, 123.52, 125.56, 126.46, 129.56 (d, J = 7.2 Hz), 135.93, 140.64, 152.89, 162.6 (J = 205 Hz), 177.40.

LRMS (EI) *m/z*: 353 (M^+).

HRMS: Calcd. for $C_{20}H_{13}F_2NOS$: 353.0686, found: 353.0684.

(2-Benzothiazolyl)-bis(4-chlorophenyl)methanol (4af)



Colorless prisms (recrystallized from hexane, mp 113–115 °C).

IR (neat): 3303, 1488, 1398, 1172, 1092, 1043, 1014, 903, 814, 759, 732 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.47 (s, 1H), 7.30–7.34 (m, 4H), 7.37–7.42 (m, 5H), 7.51 (t, J = 7.9 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H).

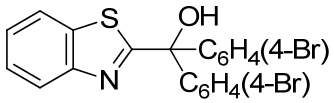
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 80.23, 121.67, 123.43, 125.53, 126.41, 128.45, 128.97, 134.38, 135.76, 142.94, 152.73, 176.68.

LRMS (EI) *m/z*: 385 (M^+).

HRMS: Calcd. for $C_{20}H_{13}{}^{35}Cl_2NOS$: 385.0095, found: 385.0076.

Anal. Calcd. for $C_{20}H_{13}{}^{35}Cl_2NOS$: C, 62.18; H, 3.39; N, 3.63. Found: C, 62.22; H, 3.48; N, 3.64.

(2-Benzothiazolyl)-bis(4-bromophenyl)methanol (4ag)



Colorless needles (recrystallized from hexane, mp 130–133 °C).

IR (neat): 3324, 1483, 1396, 1169, 1073, 1041, 1009, 902, 811, 759, 733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.45 (s, 1H), 7.30–7.34 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.45–7.52 (m, 5H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H).

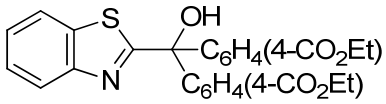
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 80.46, 121.79, 122.78, 123.56, 125.66, 126.53, 129.38, 131.55, 135.92, 143.49, 152.80, 176.44.

LRMS (EI) *m/z*: 472 (M^+).

HRMS: Calcd. for $C_{20}H_{13}{}^{79}Br_2NOS$: 472.9085, found: 472.9074.

Anal. Calcd. for $C_{20}H_{13}{}^{79}Br_2NOS$: C, 50.55; H, 2.76; N, 2.95. Found: C, 50.63; H, 2.84; N, 2.87.

(2-Benzothiazolyl)-bis(4-ethoxycarbonylphenyl)methanol (4ah)



IR (neat): 3392, 2980, 1714, 1696, 1607, 1270, 1103, 1019, 758, 709 cm^{-1}.

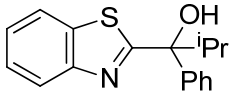
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.38 (t, *J* = 7.2 Hz, 6H), 4.37 (q, *J* = 7.2 Hz, 4H), 4.53 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.49–7.55 (m, 5H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.01–8.05 (m, 5H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 14.38, 61.18, 80.82, 121.79, 123.58, 125.68, 126.53, 127.61, 129.65, 130.52, 135.91, 148.96, 152.80, 166.22, 176.18.

LRMS (EI) *m/z*: 461 (M^+).

HRMS: Calcd. for $C_{26}H_{23}NO_5S$: 461.1297, found: 461.1285.

1-(2-Benzothiazolyl)-2-methyl-1-phenylpropan-1-ol (4ai)



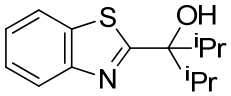
^1H NMR (400 MHz, acetone-d_6) δ (ppm): 0.80 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 3.09 (sept, *J* = 6.9 Hz, 1H), 5.30 (s, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 7.28–7.34 (m, 3H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.93 (t, *J* = 8.3 Hz, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ (ppm): 16.79, 17.40, 38.99, 82.61, 122.59, 123.57, 125.52, 126.57, 127.76, 128.71, 136.07, 145.13, 154.68, 181.10.

LRMS (EI) *m/z*: 283 (M^+).

HRMS: Calcd. for $C_{17}H_{17}NOS$: 283.1031, found: 283.1012.

1-(2-Benzothiazolyl)-2-methyl-1-isopropylpropan-1-ol (4aj)



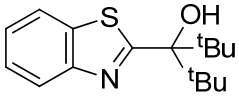
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.95 (dd, J = 6.8, 5.2 Hz, 12H), 2.36 (sept, J = 6.8 Hz, 2H), 3.43 (br.s, 1H), 7.37 (t, J = 8.1 Hz, 1H), 7.47 (t, J = 8.1 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 16.55, 17.13, 35.24, 82.69, 121.48, 122.82, 124.69, 125.76, 135.27, 152.15, 176.47.

LRMS (EI) *m/z*: 249 (M^+).

HRMS: Calcd. for $C_{14}H_{19}NOS$: 249.1187, found: 249.1172.

1-(2-Benzothiazolyl)-1-*tert*-butyl-2,2-dimethylpropan-1-ol (4ak)



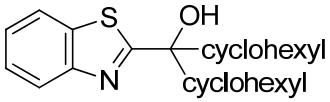
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.20 (br, 18H), 5.46 (br, 1H), 7.32 (br, 1H), 7.42 (br, 1H), 7.86 (d, J = 5.0 Hz, 1H), 7.99 (d, J = 5.0 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 28.90, 42.15, 85.26, 121.13, 123.06, 124.27, 125.24, 134.75, 153.88, 179.81.

LRMS (EI) *m/z*: 220 (M^+–57).

HRMS: Calcd. for $C_{12}H_{14}NOS$: 220.0874, found: 220.0787.

1-(2-Benzothiazolyl)-1,1-dicyclohexylmethanol (4al)



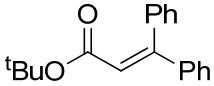
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.86–0.92 (m, 2H), 1.01–1.12 (m, 2H), 1.22–1.48 (m, 10H), 1.53–1.77 (m, 4H), 1.91–2.04 (m, 4H), 3.43 (brs, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/TMS) δ (ppm): 26.38, 26.48, 26.53, 26.56, 26.92, 44.85, 82.38, 121.47, 122.81, 124.63, 125.73, 135.22, 152.20, 177.39.

LRMS (EI) *m/z*: 329 (M^+).

HRMS: Calcd. for $C_{20}H_{27}NOS$: 329.1813, found: 329.1796.

^{t}Butyl 3,3-Diphenylpropenoate (6aa)[5]



IR (neat): 2977, 1718, 1692, 1446, 1366, 1292, 1258, 1140, 990, 767 cm^{-1}.

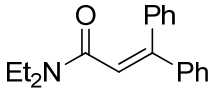
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.27 (s, 9H), 6.27 (s, 1H), 7.18–7.37 (m, 10H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 27.71, 80.19, 119.85, 127.77, 127.80, 128.12, 128.22, 128.98, 129.17, 139.38, 140.91, 154.21, 165.67.

LRMS (EI) *m/z*: 280 (M^+).

HRMS: Calcd. for $C_{19}H_{20}O_2$: 280.1463, found: 280.1464.

_N,N_-Diethyl 3,3-Diphenylpropenamide (6ba)[6]



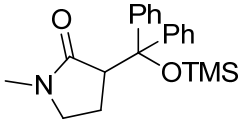
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.97 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 3.26 (q, *J* = 7.2 Hz, 2H), 3.34 (q, *J* = 7.2 Hz, 2H), 6.37 (s, 1H), 7.26–7.35 (m, 10H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 12.26, 13.97, 38.75, 42.36, 121.71, 128.03, 128.08, 128.17, 128.26, 128.31, 129.43, 138.84, 141.30, 146.78, 167.60.

LRMS (EI) *m/z*: 279 (M^+).

HRMS: Calcd. for $C_{19}H_{21}NO$: 279.1623, found: 279.1612.

3-{diphenyl[(trimethylsilyl)oxy]methyl}-1-methyl-2-pyrrolidone (6ca)



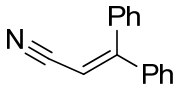
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): –0.15 (s, 9H), 1.98–2.17 (m, 3H), 2.53 (s, 3H), 2.82–2.87 (m, 1H), 3.72–3.75 (m, 1H), 7.24–7.29 (m, 6H), 7.38–7.47 (m, 2H), 7.486–7.491 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 1.55, 21.22, 29.44, 46.71, 49.42, 82.32, 127.04, 127.30, 127.42, 127.97, 129.25, 144.29, 144.31, 172.95.

LRMS (EI) *m/z*: 353 (M^+).

HRMS: Calcd. for $C_{21}H_{27}NO_2Si$: 353.1811, found: 353.1825.

3,3-Diphenylacrylonitrile (6da)[7]



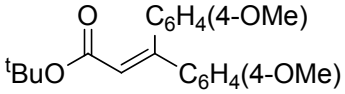
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 5.74 (s, 1H), 7.25–7.46 (m, 10H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 94.82, 117.79, 128.38, 128.47, 128.58, 129.47, 129.94, 130.34, 136.99, 138.85, 163.05.

LRMS (EI) *m/z*: 205 (M^+).

HRMS: Calcd. for $C_{15}H_{11}N$: 205.0892, found: 205.0883.

***tert*-Butyl 3,3-Bis(4-methoxyphenyl)propenoate (6ad)[5]**



IR (neat): 2975, 1711, 1690, 1597, 1507, 1456, 1366, 1288, 1244, 1135, 1032, 830 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.33 (s, 9H), 3.80 (s, 3H), 3.84 (s, 3H), 6.14 (s, 1H), 6.82 (d, 2H, *J* = 9.2 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 7.13 (d, 2H, *J* = 8.8 Hz), 7.21 (d, 2H, *J* = 9.2 Hz).

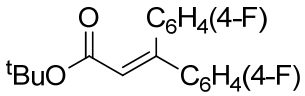
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 27.90, 55.19, 55.26, 79.91, 113.17, 113.57, 117.39, 129.80,

130.81, 131.73, 133.97, 154.23, 159.47, 160.45, 166.04.

LRMS (EI) *m/z*: 340 (M^+).

HRMS: Calcd. for $C_{21}H_{24}O_4$: 340.1675, found: 340.1677.

tert-Butyl 3,3-Bis(4-fluorophenyl)propenoate (6ae)[5]



Colorless scales [recrystallized from hexane/EtOAc, mp 98–100 °C (lit.[5] mp 98–99 ºC)].

IR (neat): 2982, 2360, 1680, 1598, 1505, 1366, 1299, 1219, 1162, 1149, 991, 884, 848, 837 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.31 (s, 9H), 6.23 (s, 1H), 6.98–7.25 (m, 8H).

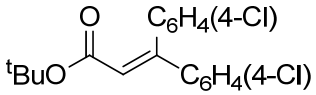
$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm): 27.84, 80.56, 115.01 (d, J = 21.6 Hz), 115.38 (d, J = 21.5 Hz), 119.93, 130.02 (d, J = 8.6 Hz), 131.04 (d, J = 7.2 Hz), 134.99 (d, J = 4.4 Hz), 137.00 (d, J = 2.9 Hz), 152.32, 162.65 (d, J = 246 Hz), 163.39 (d, J = 246 Hz), 165.40.

LRMS (EI) *m/z*: 316 (M^+).

HRMS: Calcd. for $C_{19}H_{18}F_2O_2$: 316.1275, found: 316.1271.

Anal. Calcd. for $C_{19}H_{18}F_2O_2$: C, 72.14; H, 5.74. Found: C, 72.17; H, 5.80.

tert-Butyl 3,3-Bis(4-chlorophenyl)propenoate (6af)[5]



Colorless needles [recrystallized from hexane, mp 122–124 °C (lit.[5] mp 121 ºC)].

IR (neat): 2926, 2358, 1684, 1587, 1490, 1364, 1313, 1300, 1161, 1150, 1093, 1013, 830 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.32 (s, 9H), 6.25 (s, 1H), 7.11–7.19 (m, 4H), 7.29 (d, 2H, J = 8.8 Hz), 7.36 (d, 2H, J = 8.8 Hz).

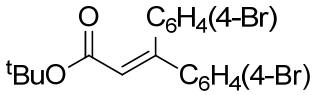
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 27.83, 80.79, 120.54, 128.27, 128.64, 129.40, 130.62, 134.21, 135.43, 137.27, 139.04, 151.97, 165.15.

LRMS (EI) *m/z*: 348 (M^+).

HRMS: Calcd. for $C_{19}H_{18}{}^{35}Cl_2O_2$: 348.0684, found: 348.0684.

Anal. Calcd. for $C_{19}H_{18}Cl_2O_2$: C, 65.34; H, 5.19. Found: C, 65.26; H, 5.20.

tert-Butyl 3,3-Bis(4-bromophenyl)propenoate (6ag)



Colorless needles (recrystallized from hexane/acetone, mp 128–130 °C).

IR (neat): 2359, 1685, 1653, 1490, 1364, 1314, 1302, 1161, 1009, 828 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.32 (s, 9H), 6.26 (s, 1H), 7.05–7.12 (m, 4H), 7.44 (d, 2H, J = 8.8 Hz), 7.51 (d, 2H, J = 8.8 Hz).

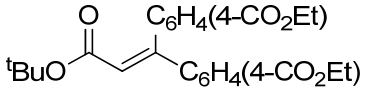
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 27.83, 80.84, 120.55, 122.43, 129.67, 130.92, 131.23, 131.41, 131.63, 131.76, 137.68, 152.06, 165.13.

LRMS (EI) *m/z*: 435 (M^+).

HRMS: Calcd. for $C_{19}H_{18}{}^{79}Br_2O_2$: 435.9674, found: 435.9677.

Anal. Calcd. for $C_{19}H_{18}Br_2O_2$: C, 52.08; H, 4.14. Found: C, 52.06; H, 4.19.

tert-Butyl 3,3-Bis(4-ethoxycarbonylphenyl)propenoate (6ah)



IR (neat): 2979, 1715, 1608, 1457, 1405, 1392, 1367, 1296, 1145, 1100, 1020, 992, 917, 857, 774, 706 cm^{-1}.

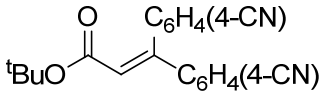
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.30 (s, 9H), 1.39–1.43 (m, 6H), 4.35–4.41 (m, 4H), 6.38 (s, 1H), 7.28–7.31 (m, 4H), 7.98 (d, 2H, J = 8.0 Hz), 8.08 (d, 2H, J = 8.0 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 14.29, 14.34, 27.80, 61.05, 61.14, 81.03, 122.05, 127.96, 129.15, 129.33, 129.62, 130.15, 131.06, 143.52, 144.42, 152.17, 164.94, 166.02, 166.28.

LRMS (EI) *m/z*: 424 (M^+).

HRMS: Calcd. for $C_{25}H_{28}O_6$: 424.1886, found: 424.1885.

tert-Butyl 3,3-Bis(4-cyanophenyl)propenoate (6ai)



Colorless needles (recrystallized from hexane/EtOAc, mp 167–168 °C).

IR (neat): 2922, 2361, 2231, 1694, 1604, 1499, 1458, 1409, 1366, 1300, 1163, 1163, 993, 847, 840 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.32 (s, 9H), 6.41 (s, 1H), 7.30–7.34 (m, 4H), 7.63 (d, 2H, J = 8.4 Hz), 7.71 (d, 2H, J = 8.4 Hz).

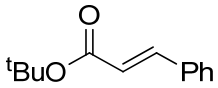
$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm): 27.80, 81.64, 112.35, 113.16, 118.15, 118.42, 123.57, 128.49, 129.88, 132.04, 132.39, 142.97, 143.93, 150.28, 164.19.

LRMS (EI) *m/z*: 330 (M^+).

HRMS: Calcd. for $C_{21}H_{18}N_2O_2$: 330.1368, found: 330.1383.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.26; H, 5.53; N, 8.44.

tert-Butyl (_E_)-Cinnamate (6aj)[8]



Pale yellow oil.

IR (neat): 2978, 1704, 1637, 1328, 1315, 1145, 978, 767 cm^{-1}.

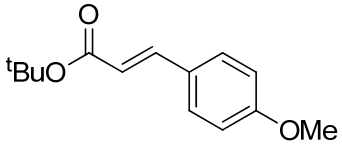
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.54 (s, 9H), 6.36 (d, J = 15.9 Hz, 1H), 7.36–7.37 (m, 3H), 7.49–7.52 (m, 2H), 7.58 (d, J = 15.9 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 28.16, 80.46, 120.14, 127.91, 128.78, 129.91, 134.62, 143.50, 166.29.

LRMS (EI) *m/z*: 204 (M^+).

HRMS: Calcd. for $C_{13}H_{16}O_2$: 204.1150, found: 204.1151.

***tert*-Butyl (*E*)-3-(4-Methoxyphenyl)propenoate (6ak)[8]**



IR (neat): 2977, 1701, 1634, 1604, 1576, 1511, 1458, 1421 cm^{-1}.

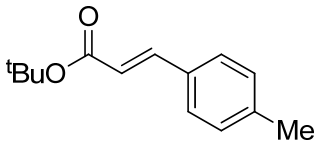
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.53 (s, 9H), 3.82 (s, 3H), 6.24 (d, J = 16.1 Hz, 1H), 6.88 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 16.1 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 28.19, 55.28, 80.17, 114.20, 117.67, 127.35, 129.50, 143.15, 161.08, 166.64.

LRMS (EI) *m/z*: 234 (M^+).

HRMS: Calcd. for $C_{14}H_{18}O_3$: 234.1256, found: 234.1257.

***tert*-Butyl (*E*)-3-(4-Methylphenyl)propenoate (6al)[8]**



Brown oil.

IR (neat): 2977, 1705, 1636, 1609, 1367, 1323, 1282, 1145, 981, 812 cm^{-1}.

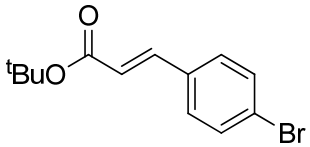
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.53 (s, 9H), 2.36 (s, 3H), 6.32 (d, J = 16.1 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 16.1 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 21.41, 28.19, 80.33, 119.05, 127.91, 129.52, 131.89, 140.27, 143.52, 166.52.

LRMS (EI) *m/z*: 218 (M^+).

HRMS: Calcd. for $C_{14}H_{18}O_2$: 218.1307, found: 218.1302.

***tert*-Butyl (*E*)-3-(4-Bromophenyl)propenoate (6am)[8]**



Colorless plates [recrystallized from acetone/hexane, mp 55–56 °C (lit.[8] mp 64.8–65.9 ºC)].

IR (neat): 2964, 1707, 1634, 1487, 1309, 1259, 1144, 1067, 1011, 994, 814 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.53 (s, 9H), 6.35 (d, J = 16.6 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.49–7.53 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 28.14, 80.68, 120.90, 124.10, 129.29, 132.02, 133.58, 142.10, 165.97.

LRMS (EI) *m/z*: 282 (M^+).

HRMS: Calcd. for $C_{13}H_{15}{}^{79}BrO_2$: 282.0255, found: 282.0229.

5. References

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