Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Phosphazene base-catalyzed condensation of trimethylsilylacetate with carbonyl compounds

K. Kobayashi, M. Ueno, Y. Kondo

General Commments

THF was distilled from sodium benzophenone ketyl. Reagents were purchased from commercial sources and used without further purification.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian Gemini 2000 (300 MHz) or JEOL ECA-400 (400 MHz) using tetramethylsilane as internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constans are expressed in herts (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet, m= mutiplet, brs= broad singlet and dd= double doublet. Mass spectra were recorded on JEOL JMS-DX303 or JEOL JMS-AX500 spectrometer. IR specrtra were measured with SensIR ATR FT-IR.

General Procedure (A)

Under argon atmosphere, a base (0.03 mmol) was added to a mixture of benzophenone (55.2 mg 0.3 mmol), ethyl trimethylsilylacetate (97.1 mg 0.6 mmol) and dry THF (1.0 mL) at -78 ˚C, and the mixture was stirred for 6 - 24 h at -78 ˚C. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography.

General Procedure (B)

Under argon atmosphere, *t*-Bu-P4 base (0.03 ml 1.0 M in hexane, 0.03 mmol) was added to a mixture of electrophile (0.3 mmol), ethyl trimethylsilylacetate (97.1 mg 0.6 mmol) or trimethylsilyl acetonitrile (67.9 mg 0.6 mmol) or *N,N*-diethyl trimethylsilylacetamide (112.4 mg 0.6 mmol) and dry THF (1.0 mL) at -78 ˚C, and the mixture was stirred for 6 h at -78 ˚C. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography.

General Procedure (C)

Under argon atmosphere, *t*-Bu-P4 base (0.03 ml 1.0 M in hexane, 0.03 mmol) was added to a mixture of electrophile (0.3 mmol), ethyl trimethylsilylacetate (97.1 mg 0.6

mmol) or trimethylsilylacetonitrile (67.9 mg 0.6 mmol) and dry THF (0.3 mL) or no solvent at room temperature, and the mixture was stirred for 20 - 48 h at room temperature. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography.

(*E*)-3,3-Diphenylpropanoic acid ethyl ester (2)

Prepared according to the general procedure (A) in the presence of *t*-Bu-P4 base (0.03 mL, 1.0 M in hexane, 0.03 mmol). The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1) to give the title compound as a colorless oil [94% yield (71.2 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.11 (t, J = 7.1 Hz, 3H), 4.05 (q, J = 7.1 Hz, 2H), 6.34 (s, 1H), 7.15-7.25 (m, 2H), 7.27-7.41 (m, 8H)

IR (cm^{-1}): 2979, 1721, 1445, 1368, 1262, 1148, 1027, 769, 694

LRMS (EI) *m/z* 252 (M^+)

HRMS: Calcd. For $C_{17}H_{16}O_2$: 252.1150, Found 252.1132

β-Phenyl-β-trimethylsilyloxybenzenepropanoic acid ethyl ester

Prepared according to the general procedure (A) in the presence of TBAF (0.03 mL, 1.0 M in THF, 0.03 mmol). The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1) to give the title compound as a colorless oil [38% yield (34.0 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): -0.06 (s, 9H), 0.99 (t, J = 7.0 Hz, 3H), 3.34 (s, 2H), 3.89 (q, J = 7.0 Hz, 2H), 7.18-7.35 (m, 10H)

IR (cm^{-1}): 2956, 1733, 1447, 1248, 1146, 1071, 860, 837, 752, 696

LRMS (EI) *m/z* 342 (M^+)

HRMS: Calcd. For $C_{20}H_{26}O_3Si$: 342.1651, Found 342.1640

***N*,*N*-Diethyl-3,3-diphenyl-2-propenamide (4a)**

Under argon atmosphere, *t*-Bu-P4 base (0.03 ml 1.0 M in hexane, 0.03 mmol) was added to a mixture of benzophenone (55.2 mg, 0.3 mmol),

N,N-diethyltrimethylsilylacetamide (112.4 mg 0.6 mmol) and dry THF (1.0 mL) at room temperature and the mixture was stirred for 6 h at room temperature and for 6 h at 50 ˚C. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography (eluting with hexane/ethyl acetate = 7:3) to give the title compound as an orange oil [87% yield (72.9 mg)].

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 0.97 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2Hz, 3H), 3.25 (q, *J* = 7.2Hz, 2H), 3.34 (q, *J* = 7.2 Hz, 2H), 6.37 (s, 1H), 7.24-7.36 (m, 10H)

IR (cm^{-1}): 2973, 1627, 1607, 1443, 1426, 1275, 764, 733, 696

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

HRMS: Calcd. For $C_{19}H_{21}NO$: 279.1623, Found 279.1614

3,3-Diphenyl-2-propenenitrile (4b)

Prepared according to the general procedure (B) using benzophenone (55.2 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as an yellowish oil [78% yield (48.0 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 5.73 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.40-7.47 (m, 6H)

IR (cm^{-1}): 3058, 2211, 1592, 1569, 1445, 1077, 775, 760, 731, 692

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

HRMS: Calcd. For $C_{15}H_{11}N$: 205.0892, Found 205.0829

(*E*)-3-Phenylpropenoic acid ethyl ester (4c)

Prepared according to the general procedure (B) using benzaldehyde (31.8 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as a colorless oil [89% yield (47.0 mg)].

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.34 (t, *J* = 7.1 Hz, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 7.38-7.40 (m, 3H), 7.52-7.55 (m, 2H), 7.69 (d, *J* = 15.9 Hz, 1H)

IR (cm^{-1}): 2981, 1706, 1636, 1308, 1164, 1036, 1027, 978, 766, 710, 683
LRMS (EI) *m/z* 176 (M^+)
HRMS: Calcd. For $C_{11}H_{12}O_2$: 176.0837, Found 176.0833

(*E*)-3-(4-Tolyl)propenoic acid ethyl ester (4d)

Prepared according to the general procedure (B) using *p*-tolaldehyde (37.9 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as a colorless oil [91% yield (50.4 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.34 (t, *J* = 7.1 Hz, 3H), 2.37 (s, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J*= 15.9 Hz, 1H)
IR (cm^{-1}): 2981, 1708, 1636, 1308, 1258, 1204, 1162, 1036, 982, 812
LRMS (EI) *m/z* 190 (M^+)
HRMS: Calcd. For $C_{12}H_{14}O_2$: 190.0994, Found 190.0984

(*E*)-3-(4-Methoxyphenyl)propenoic acid ethyl ester (4e)

Prepared according to the general procedure (B) using 4-methoxybenzaldehyde (40.8 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as a colorless oil [69% yield (41.9 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.32 (t, *J* = 7.1 Hz, 3H), 3.82 (s, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 6.30 (d, *J* = 16.2 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 16.2 Hz, 1H)
IR (cm^{-1}): 2958, 1702, 1634, 1603, 1511, 1248, 1160, 1030, 827
LRMS (EI) *m/z* 206 (M^+)
HRMS: Calcd. For $C_{12}H_{14}O_3$: 206.0943, Found 206.0942

(*E*)-3-(2-Furanyl)propenoic acid ethyl ester(4f)

Prepared according to the general procedure (B) using furfural (29.4 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as an orange oil [85% yield (41.0 mg)].

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.32 (t, *J* = 7.1 Hz, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 6.31 (d, *J* = 15.9 Hz, 1H), 6.46 (dd, *J* = 3.6 Hz, *J* = 2.1 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 7.43 (d, *J* = 15.9 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H)
IR (cm^{-1}): 2981, 1702, 1636, 1302, 1258, 1208, 1158, 1017, 970, 746, 731
LRMS (EI) *m/z* 166 (M^+)
HRMS: Calcd. For $C_{19}H_{10}O_3$: 166.0630, Found 166.0624

3-Phenyl-3-(trimethylsilyloxy)butanoic acid ethyl ester (4g)

Prepared according to the general procedure (B) using acetophenone (36.0 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as a colorless oil [29% yield (24.4 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 0.08 (s, 9H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.82 (s, 3H), 2.70 (d, *J* = 13.6 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 3.94-4.02 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H)
IR (cm^{-1}): 2958, 1733, 1250, 1703, 1009, 837, 754, 698
LRMS (EI) *m/z* 265 (M^+-15)
HRMS: Calcd. For $C_{14}H_{21}O_3Si$: 265.1260, Found 265.1245

3-Phenyl-(2*E/Z*)-butenenitrile (4h)

Under argon atmosphere, *t*-Bu-P4 base (0.03 ml 1.0 M in hexane, 0.03 mmol) was added to a mixture of acetophenone (97.1 mg 0.3 mmol), trimethylsilylacetonitrile (67.9 mg 0.6 mmol) and dry THF (1.0 mL) at -78 ˚C and the mixture was stirred for 4 h at -78 ˚C and for 9 h at 50 ˚C. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography (eluting with hexane/ethyl acetate = 10:1) to give the title compound as an yellow oil [63% yield (27.0 mg)].
400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm):
Z-isomar; 2.48 (d, *J* = 0.8 Hz, 3H), 5.62 (q, *J* = 0.8 Hz, 1H), 7.39-7.45 (m, 3H), 7.49-7.58 (m, 2H)
E-isomar; 2.29 (d, *J* = 1.6 Hz, 3H), 5.40 (q, *J* = 1.6 Hz, 1H), 7.40-7.45 (m, 3H), 7.53-7.58

(m, 2H)
IR (cm^{-1}): 2981, 2215, 1735, 1437, 1243, 1044, 1027, 804, 766, 694
LRMS (EI) *m/z* 143 (M^+)
HRMS: Calcd. For $C_{10}H_9N$: 143.0736, Found 143.0733

(2*E*,4*E*)-3,5-Diphenylpentadienoic acid ethyl ester (4i)

Prepared according to the general procedure (B) using (*E*)-chalcone (65.1 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as an yellow oil [81% yield (67.6 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.34 (t, *J* = 7.1 Hz, 3H), 4.26 (d, *J* = 7.1 Hz, 2H), 5.81 (s, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 7.20-7.55 m, 10H), 8.54 (d, *J* = 16.2 Hz, 1H)
IR (cm^{-1}): 2979, 1702, 1586, 1286, 1154, 1025, 754, 700, 690
LRMS (EI) *m/z* 278 (M^+)
HRMS: Calcd. For $C_{19}H_{18}O_2$: 278.1307, Found 278.1287

3,5-Diphenyl-(2*E/Z*,4*E*)-pentadienenitrile (4j)

Under argon atmosphere, *t*-Bu-P4 base (0.03 ml 1.0 M in hexane, 0.03 mmol) was added to a mixture of (*E*)-chalcone (65.1 mg 0.3 mmol), trimethylsilylacetonitrile (67.9 mg 0.6 mmol) and dry THF (1.0 mL) at -78 ˚C and the mixture was stirred for 4 h at -78 ˚C and for 9 h at 50 ˚C. After the reaction, saturated aq. NH_4Cl and H_2O were added to the mixture. The mixture was extracted with AcOEt (30 mL x 3). The combined organic layers were then washed with saturated aq. NaCl (50 mL). The solution was dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by SiO_2 column chromatography (eluting with hexane/ethyl acetate = 10:1) to give the title compound as a pale yellow oil [80% yield (55.5 mg)].
400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm) :
E-isomar; 5.29 (s, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 7.32-7.39 (m, 5H), 7.42-7.49 (m, 5H), 7.52 (d, *J* = 16.0 Hz, 1H)
Z-isomar; 5.55 (s, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 7.28-7.36 (m, 3H), 7.37-7.43 (m, 4H), 7.46-7.51 (m, 3H)
IR (cm^{-1}): 3058, 2207, 1735, 1617, 1447, 1241, 996, 750, 688
LRMS (EI) *m/z* 231 (M^+)

HRMS: Calcd. For $C_{17}H_{13}N$: 231.1049, Found 231.1044

E-Octenoic acide ethyl ester (4k)

Prepared according to the general procedure (B) using hexenal (30.0 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 10:1) to give the title compound as an coloress oil [35% yield (17.9 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm) : 0.89 (t, *J*= 7.2 Hz, 3H), 1.25-1.65 (m, 6H), 2.19 (qd, *J*= 6.8 Hz, *J*= 1.6 Hz, 2H), 4.18 (q, *J*= 7.2 Hz, 2H), 5.81 (dt, *J*=15.6 Hz, *J*= 1.6 Hz, 1H), 6.96 (dt, *J*= 15.6 Hz, *J*= 6.8 Hz, 1H)

IR (cm^{-1}): 2958, 2931, 1737, 1250, 1096, 1046, 837, 750

LRMS (EI) *m/z* 170 (M^+)

HRMS: Calcd. For $C_{10}H_{18}O_2$: 170.1307, Found 170.1287

(*E*)-β-(*N*-Methylanilino)acrylic acid ethyl ester (6a)

Prepared according to the general procedure (C) using *N*-methylformanilide (40.5 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as an yellow oil [entry 1: 90% yield (55.4 mg), entry 2: 92% (56.6 mg)].

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.28 (t, *J* = 7.2 Hz, 3H), 3.24 (s, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.94 (d, *J* = 13.2 Hz, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.34 (dd, *J* = 6.8 Hz, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 13.2 Hz, 1H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) d (ppm): 14.55, 36.53, 59.28, 90.44, 119.82, 124.12, 129.41, 146.59, 148.41, 169.16

IR (cm^{-1}): 2979, 1737, 1692, 1617, 1258, 1152, 1096, 1044, 756, 694

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

HRMS: Calcd. For $C_{12}H_{15}NO_2$: 205.1103, Found 205.1122

(*E*)- β-(*N*-Methylanilino)acrylonitrile (6b)

Prepared according to the general procedure (C) using *N*-methylformanilide (40.5 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as orange oil [78% yield (37.0 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 3.21 (s, 3H), 4.17 (d, *J* = 13.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 13.6 Hz, 1H)
100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 150.77, 145.96, 129.65, 126.74, 124.89, 121.07, 120.12, 36.34
IR (cm^{-1}): 2198, 1617, 1586, 1493, 1328, 1127, 756, 692
LRMS (EI) *m/z* 158 (M^+)
HRMS: Calcd. For $C_{10}H_{10}N_2$: 158.0845, Found 158.0832

(*E*)-β-(4-Methyl-*N*-methylanilino)acrylic acid ethyl ester (6c)

Prepared according to the general procedure (C) using *N*-methyl-*N*-(4-tolyl)formamide (44.8 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as an yellow oil [74% yield (48.6 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.28 (t, *J* = 7.1 Hz, 3H), 2.32 (s, 3H), 3.22 (s, 3H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.90 (d, *J* = 13.2 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 13.2 Hz, 1H)
100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 14.51, 20.60, 59.15, 89.62, 119.94, 129.62, 129.87, 133.89, 144.22, 148.71, 169.24
IR (cm^{-1}): 1688, 1596, 1513, 1256, 1152, 1121, 796
LRMS (EI) *m/z* 219 (M^+)
HRMS: Calcd. For $C_{13}H_{17}NO_2$ 219.1260 Found 219.1271

(*E*)-β-(4-Methoxy-*N*-methylanilino)acrylic acid ethyl ester (6d)

Prepared according to the general procedure (C) using *N*-(4-methoxyphenyl)-*N*-methylformamide (49.6 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as an yellow oil [47% yield (33.2 mg)].
300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.28 (t, *J* = 7.1 Hz, 3H), 3.21 (s, 3 H), 3.81 (s, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.85 (d, *J* = 13.2 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 2H), 7.01 (d, *J* = 9.1 Hz, 2H), 7.83 (d, *J* = 13.2 Hz, 1H)
IR (cm^{-1}): 1686, 1617, 1600, 1511, 1245, 1154, 1125, 1044, 831, 796
LRMS (EI) *m/z* 235 (M^+)

HRMS: Calcd. For $C_{13}H_{17}NO_3$ 235.1209 Found 235.1190

(*E*)-β-(4-Ethoxycarbonyl-*N*-methylanilino)acrylic acid ethyl ester (6e)

Prepared according to the general procedure (C) using *N*-(4-ethoxycarbonylphenyl)-*N*-methylformamide (62.2 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as pale yellow oil [85% yield (70.7 mg)].

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.30 (t, *J* = 7.1 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 3.28 (s, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 5.09 (d, *J* = 13.2 Hz, 1H), 7.16 (d, *J* = 9.1 Hz, 2H), 8.02 (d, *J* = 13.2 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 2H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 14.32, 14.49, 35.76, 59.58, 60.89, 93.07, 117.91, 125.94, 131.11, 131.42, 146.69, 149.67, 165.94, 168.73

IR (cm^{-1}): 1696, 1588, 1254, 1233, 1158, 1108, 769

LRMS (EI) *m/z* 277 (M^+)

HRMS: Calcd. For $C_{15}H_{19}NO_4$ 277.1315 Found 277.1299

(*E*)-3-(4-Ethoxycarbonyl-*N*-methylanilino)acrylonitrile (6f)

Prepared according to the general procedure (C) using *N*-(4-ethoxycarbonylanilino)-*N*-methylformamide (48.1 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as white crystals [87% yield (44.0 mg)]. mp 82-86 □

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.40 (t, *J* = 7.2 Hz, 3H), 3.25 (s, 3H), 4.33 (d, *J* = 14.0 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 14.0 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 2H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 35.51, 60.92, 61.03, 69.33, 118.17, 120.16, 125.93, 130.93, 148.79, 149.18, 161.65, 165.47

IR (cm^{-1}): 2991, 2204, 1698, 1684, 1596, 1517, 1111, 972, 768, 752, 692

LRMS (EI) *m/z* 230 (M^+)

HRMS: Calcd. For $C_{13}H_{14}N_2O_2$: 230.1055, Found 230.1057

Anal. Calcd. For $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17, Found: C, 66.62; H, 6.13; N, 10.79.

(*E*)-β-(4-Cyano-*N*-methylanilino)acrylic acid ethyl ester (6g)

Prepared according to the general procedure (C) using *N*-(4-cyanophenyl)-*N*-methylformamide(48.1 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as colorless prisms [80% yield (55.3 mg)]. mp 113 □

300 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.30 (t, *J* = 7.1 Hz, 3 H), 3.27 (s, 3H), 4.21 (q, *J* = 9.1 Hz, 2H), 5.15 (d, *J* = 13.5 Hz, 1H), 7.20 (d, *J* = 9.1 Hz, 2H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.98 (d, *J* = 13.5 Hz, 1H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 14.46, 35.54, 59.76, 94.64, 106.21, 118.41, 118.67, 133.62, 145.76, 149.33, 168.37

IR (cm^{-1}): 2217, 1688, 1578, 1567, 1258, 1111, 1040, 823, 800

LRMS (EI*) m/z* 230(M^+)

HRMS: Calcd. For $C_{13}H_{14}N_2O_2$ 230.1056 Found 230.1050

Anal. Calcd. For $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.78; H, 6.13; N, 12.12.

(*E*)-3-(4-Cyano-*N*-methylanilino)acrylonitrile (6h)

Prepared according to the general procedure (C) using *N*-(4-cyanophenyl)-*N*-methylformamide(48.1 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as colorless crystals [80% yield (44.0 mg)]. mp 160 □

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 3.25 (s, 3H), 4.26 (d, *J* = 13.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 13.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 35.27, 70.98, 107.05, 118.28, 118.83, 119.68, 120.93, 133.67, 148.62

IR (cm^{-1}): 3089, 2219, 2204, 1627, 1596, 1511, 1337, 966, 825, 764

LRMS (EI) *m/z* 183 (M^+)

HRMS: Calcd. For $C_{11}H_9N_3$: 183.0796, Found 183.0793

Anal. Calcd. For $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 71.60; H, 5.19; N, 22.48.

(*E*)-β-(*N*-Allylanilino)acrylic acid ethyl ester (6i)

Prepared according to the general procedure (C) using *N*-allyl-*N*-phenyl formamide (48.3 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as pale an yellow oil [83% yield (57.5 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.28 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.25 (br, 2H), 4.94 (d, *J* = 13.6 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.86 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 13.6 Hz, 1H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 14.49, 52.54, 59.28, 91.03, 117.23, 120.04, 124.32, 129.39, 130.97, 145.89, 147.24, 169.20

IR (cm^{-1}): 2979, 1690, 1613, 1580, 1497, 1275, 1142, 1048, 798, 754, 694

LRMS (EI) *m/z* 231 (M^+)

HRMS: Calcd. For $C_{14}H_{17}NO_2$: 231.1260, Found 231.1266

(*E*)-3-(*N*-Allylanilino)acrylonitrile (6j)

Prepared according to the general procedure (C) using *N*-allyl-*N*-phenyl formamide(48.4 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as a pale yellow oil [42% yield (23.2 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 4.17 (d, *J* = 14.0 Hz, 1H), 4.18-4.22 (m, 2H), 5.17-5.25 (m, 1H), 5.25-5.33 (m, 1H), 5.75-5.89 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 14.0 Hz, 1H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 30.89, 67.57, 117.81, 120.56, 121.00, 125.20, 129.67, 130.38, 145.27, 149.76

IR (cm^{-1}): 3083, 2918, 1618, 1588, 1492, 1345, 1214, 953, 756, 694

LRMS (EI) *m/z* 184 (M^+)

HRMS: Calcd. For $C_{12}H_{12}N_2$: 184.1001, Found 184.0999

(*E*)-β-(*N*-benzylanilino)acrylic acid ethyl ester (6k)

Prepared according to the general procedure (C) using *N*-benzyl-*N*-phenyl formamide (63.4 mg 0.3 mmol) and ethyl trimethylsilylacetate. The crude material was purified by

column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as an yellow oil [99% yield (83.5 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 1.25 (t, *J* = 7.6 Hz, 3H), 4.13 (q, *J* = 7.6 Hz, 2H), 4.88 (s, 2H), 4.90 (d, *J* = 13.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz), 7.16 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.30-7.37 (m, 5H), 8.08 (d, *J* = 13.6 Hz, 1H)

IR (cm^{-1}): 2979, 1686, 1615, 1578, 1497, 1138, 1508, 996, 800, 756, 724, 692

LRMS (EI) *m/z* 281 (M^+)

HRMS: Calcd. For $C_{18}H_{19}NO_2$: 281.1417, Found 281.1408

(*E*)-3-(Benzylphenylamino)acrylonitrile (6l)

Prepared according to the general procedure (C) using *N*-benzyl-*N*-phenyl formamide(63.4 mg 0.3 mmol) and trimethylsilylacetonitrile. The crude material was purified by column chromatography on silicagel (eluting with hexane/ethyl acetate = 7:3) to give the title compound as a pale yellow oil [88% yield (71.9 mg)].

400 MHz ^{1}H-NMR($CDCl_3$/TMS) δ (ppm): 4.11 (d, *J* = 13.6 Hz, 1H), 4.82 (s, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.14-7.21 (m, 3H), 7.27-7.38 (m, 5H), 7.51 (d, *J* = 13.6 Hz, 1H)

100 MHz ^{13}C-NMR($CDCl_3$/TMS) δ (ppm): 14.46, 59.24, 91.57, 119.73, 124.19, 126.04, 127.17, 128.62, 129.34, 135.57, 145.83, 147.20, 168.87

IR (cm^{-1}): 3064, 2200, 1617, 1584, 1492, 1343, 1329, 729, 692

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

HRMS: Calcd. For $C_{16}H_{14}N_2$: 234.1158, Found 234.1138