Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Low-valent Nb(III)-mediated synthesis of 1,1,2-trisubstituted-1*H*-indenes from aliphatic ketones and aryl-substituted alkynes

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Materials: The reagents and the solvents were dried and purified before use by usual procedures.[1] $NbCl_3$(DME) was prepared according to the published method,[2] or can be purchased from Aldrich.

Analytical Procedures: All manipulations were performed under argon atmosphere in conventional Schlenk-type glasswares on a dual-manifold Schlenk line. NMR spectra were recorded on a Bruker ARX-400 (^{1}H, 400 Hz; ^{13}C, 100 MHz). The mass spectra were measured on a Shimadzu QP-5050A (EI) and a JEOL JMS-700TZ (HRMS, EI). The GC analysis was made on a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-1, 0.25 mm i.d. × 25 m). Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University.

3b: ^{1}H NMR ($CDCl_3$) δ 0.50-0.59 (m, 2H), 0.73 (t, J = 7 Hz, 6H), 0.78-0.83 (m, 2H), 1.60-1.69 (m, 2H), 1.76-1.83 (m, 2H), 1.88 (d, J = 1 Hz, 3H), 6.42 (brs, 1H), 7.10-7.46 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.9 (CH_3), 14.9 ($2CH_3$), 17.0 ($2CH_2$), 40.2 ($2CH_2$), 58.7 (C), 119.9 (CH), 121.7 (CH), 124.0 (CH), 126.5 (CH), 126.9 (CH), 145.3 (C), 150.8 (C), 152.0 (C); MS (relative intensity) *m/z* 115 (26), 126 (13), 128 (46), 129 (52), 130 (12),

141 (29), 142 (14), 143 (100), 144 (12), 171 (11), 172 (12), 185 (40), 214 (M^+, 44); HRMS calc. for $C_{16}H_{22}$: *m/z* 214.1721. Found *m/z* 214.1722.

3c: ^{1}H NMR ($CDCl_3$) δ 0.47-0.54 (m, 2H), 0.70-0.81 (m, 8H), 1.11-1.19 (m, 2H), 1.60-1.70 (m, 2H), 1.78-1.88 (m, 2H), 1.87 (d, *J* = 1 Hz, 3H), 6.44 (d, *J* = 1 Hz, 1H), 7.11-7.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.3 (CH_3), 14.3 (CH_3), 15.0 (CH_3), 17.0 (CH_2), 23.5 (CH_2), 25.8 (CH_2), 37.4 (CH_2), 40.3 (CH_2), 58.5 (C), 119.9 (CH), 121.7 (CH), 124.0 (CH), 126.5 (CH), 127.0 (CH), 145.3 (C), 150.7 (C), 152.0 (C); MS (relative intensity) *m/z* 115 (22), 126 (10), 128 (37), 129 (44), 141 (22), 142 (100), 144 (18), 157 (10), 185 (24), 199 (15), 228 (M^+, 35); HRMS calc. for $C_{17}H_{24}$: *m/z* 228.1878. Found 228.1875. Anal. Calc. For $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.26; H, 10.47.

3d: ^{1}H NMR ($CDCl_3$) δ 0.77 (t, *J* = 7 Hz, 6H), 0.89-0.93 (m, 4H), 1.11-1.19 (m, 4H), 1.61-1.68 (m, 2H), 1.79-1.86 (m, 2H), 1.89 (d, *J* = 1 Hz, 3H), 6.45 (d, *J* = 1 Hz, 1H), 7.09-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 14.3 ($2CH_3$), 23.5 ($2CH_2$), 25.8 ($2CH_2$), 37.6 ($2CH_2$), 58.4 (C), 119.9 (CH), 121.7 (CH), 124.0 (CH), 126.5 (CH), 127.0 (CH), 145.3 (C), 150.7 (C), 151.9 (C); MS (relative intensity) *m/z* 115 (16), 128 (36), 129 (42), 141 (20), 143 (100), 144 (28), 157 (15), 199 (21), 242 (M^+, 25); HRMS calc. for $C_{18}H_{26}$: *m/z* 242.2035. Found *m/z* 242.2035. Anal. Calc. For $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.60; H, 10.36.

3e: ^{1}H NMR ($CDCl_3$) δ 0.35 (t, *J* = 7 Hz, 6H), 1.66-1.73 (m, 2H), 1.84-1.92 (m, 5H), 6.48 (s, 1H), 7.10-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 8.3 ($2CH_3$) 13.1 (CH_3), 30.2 ($2CH_2$), 59.5 (C), 119.9 (CH), 121.7 (CH), 124.0 (CH), 126.5 (CH), 127.6 (CH), 145.8 (C), 149.9 (C), 151.0 (C); MS (relative intensity) *m/z* 115 (52), 128 (26), 129 (33), 141 (53), 142 (87), 143 (29), 157 (100), 158 (13), 171 (20), 186 (M^+, 64); HRMS calc. for $C_{14}H_{18}$: *m/z* 186.1409. Found *m/z* 186.1402.

3f: ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3H), 1.80-1.86 (m, 2H), 2.00 (d, 3H, J = 1 Hz), 2.01-2.19 (m, 2H), 6.48 (d, 1H, J = 1 Hz), 7.04-7.34 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 13.1 (CH_3), 24.4 (CH_3), 30.7 (CH_2), 39.7 (CH_2), 54.3 (C), 120.4 (CH), 121.7 (CH), 124.4 (CH), 126.0 (CH), 126.9 (CH), 128.6 (2CH), 128.7 (3CH), 143.2 (C), 144.3 (C), 151.8 (C), 153.1 (C); HRMS calc. for $C_{19}H_{20}$: *m/z* 248.1565. Found *m/z* 248.1474.

3g: ^{1}H NMR ($CDCl_3$) δ 0.99-1.23 (m, 2H), 1.25 (s, 3H), 1.85-2.03 (m, 2H), 1.94 (d, J = 1 Hz, 3H), 3.28-3.37 (m, 2H), 6.41 (d, J=1 Hz, 1H), 7.13-7.27 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.0 (CH_3), 24.3 (CH_3), 27.6 (CH_2), 34.7 (CH_2), 46.0 (CH_2), 53.8 (C), 120.4 (CH), 121.6 (CH), 124.5 (CH), 126.2 (CH), 127.0 (CH), 144.1 (C), 151.6 (C), 152.9 (C); MS (relative intensity) *m/z* 115 (31), 127 (17), 128 (83), 129 (30), 141 (41), 142 (28), 143 (91), 144 (27), 157 (100), 158 (18), 220 (M^+(^{35}Cl), 35), 222 (M^+(^{37}Cl), 15); HRMS calc. for $C_{14}H_{17}{}^{35}Cl$: *m/z* 220.1019. Found *m/z* 220.1022.

3h: ^{1}H NMR ($CDCl_3$) δ 1.16 (t, J = 7 Hz, 3H), 1.25 (s, 3H), 1.47-1.55 (m, 1H), 1.67-1.73 (m, 1H), 1.91 (s, 3H), 2.00-2.08 (m, 1H), 2.15-2.22 (m, 1H), 3.98 (m, 2H), 6.41 (s, 1H), 7.05-7.45 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.5 (CH_3), 14.1 (CH_3), 23.6 (CH_3), 29.0 (CH_2), 31.6 (CH_2), 53.1 (C), 60.1 (CH_2), 120.0 (CH), 121.4 (CH), 124.1 (CH), 126.1 (CH), 126.7 (CH), 143.7 (C), 150.5 (C), 151.9 (C), 173.8 (C); MS (relative intensity) *m/z* 128 (27), 141 (31), 142 (12), 143 (20), 155 (11), 156 (100), 157 (25), 244 (M^+, 17); HRMS calc. for $C_{16}H_{20}O_2$: *m/z* 244.1463. Found *m/z* 244.1463.

3i: ^{1}H NMR ($CDCl_3$) δ 0.70-0.79 (m, 8H), 0.90-1.00 (m, 2H), 1.28 (t, J = 7 Hz, 3H), 1.59-1.68 (m, 2H), 1.76-1.82 (m, 2H), 2.13 (q, J = 7 Hz, 2H), 6.46 (s, 1H), 7.08-7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.9 (CH_3), 14.8 ($2CH_3$), 17.0 ($2CH_2$), 20.1 (CH_2), 40.6 ($2CH_2$), 58.9 (C), 120.0 (CH), 121.5 (CH), 123.9 (CH), 124.3 (CH), 126.5 (CH), 145.3 (C), 150.9 (C), 158.1 (C); MS (relative intensity) *m/z* 115 (36), 127 (13), 128 (50), 129 (100), 130

(11), 141 (40), 142 (14), 143 (62), 144 (12), 156 (63), 185 (21), 186 (20), 199 (66), 200 (11), 228 (M^+, 56); HRMS calc. for $C_{17}H_{24}$: *m/z* 228.1878. Found *m/z* 228.1882.

3j: ^{1}H NMR ($CDCl_3$) δ 0.51-0.59 (m, 2H), 0.72 (t, J = 6 Hz, 6H), 0.75-0.80 (m, 2H), 1.56-1.63 (m, 2H), 1.73-1.79 (m, 2H), 1.84 (d, J = 1 Hz, 3H), 2.38 (s, 3H), 6.37 (d, J = 1 Hz, 1H), 6.98 (d, J = 7 Hz, 1H), 7.00 (s, 1H), 7.08 (d, J = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.3 (CH_3), 14.9 ($2CH_3$), 17.0 ($2CH_2$), 22.0 (CH_3), 40.3 ($2CH_2$), 58.5 (C), 119.4 (CH), 122.7 (CH), 126.6 (CH), 127.1 (CH), 133.4 (C), 142.7 (C), 150.9 (C), 151.0 (C); MS (relative intensity) 115 (16), 128 (22), 129 (11), 141 (31), 142 (29), 143 (36), 144 (10), 155 (18), 156 (15), 157 (100), 158 (14), 185 (19), 186 (20), 199 (62), 200 (10), 228 (M^+, 58); HRMS calc. for $C_{17}H_{24}$: *m/z* 228.1878. Found *m/z* 228.1871.

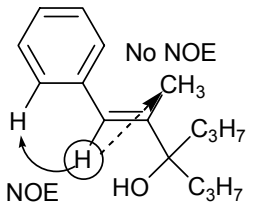
3k: ^{1}H NMR ($CDCl_3$) δ 0.74 (t, J = 7 Hz, 6H), 0.80-0.98 (m, 4H), 1.60-1.70 (m, 2H), 1.80-1.91 (m, 5H), 6.46 (brs, 1H), 7.2-7.7 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 15.0 ($2CH_3$), 17.1 ($2CH_2$), 40.3 ($2CH_2$), 58.9 (C), 120.1 (CH), 120.6 (CH), 125.7 (CH), 127.1 (CH), 127.4 (CH), 127.5 (2CH), 129.1 (2CH), 137.1 (C), 142.5 (C), 144.7 (C), 151.5 (C), 152.8 (C); MS (relative intensity) *m/z* 95 (11), 101 (13), 107 (14), 115 (10), 191 (11), 202 (35), 203 (31), 204 (31), 205 (37), 206 (12), 215 (22), 217 (30), 218 (33), 219 (100), 220 (20), 247 (18), 248 (19), 261 (55), 262 (12), 290 (M^+, 92); HRMS calc. for $C_{22}H_{26}$: *m/z* 290.2034. Found *m/z* 290.2028.

3l: ^{1}H NMR ($CDCl_3$) δ 0.40 (t, J = 7 Hz, 6H), 1.74 (q, J = 7 Hz, 2H), 1.88-1.98 (m, 5H), 6.51 (brs, 1H), 7.2-7.7 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 8.4 ($2CH_3$), 13.3 (CH_3), 30.3 ($2CH_2$), 59.6 (C), 120.0 (CH), 120.6 (CH), 125.8 (CH), 127.0 (CH), 127.3 (CH), 127.4 (2CH), 129.1 (2CH), 137.1 (C), 142.6 (C), 145.2 (C). 150.6 (C), 151.8 (C); MS (relative intensity) *m/z* 95 (14), 101 (16), 108 (19), 202 (26), 203 (23), 204 (10), 205 (10), 215 (16), 217 (24), 218 (64), 219 (22), 233 (100), 234 (20), 247 (31), 262 (M^+, 76); HRMS calc. for

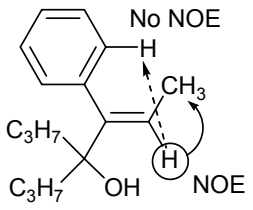
$C_{20}H_{22}$: *m/z* 262.1721. Found *m/z* 262.1711.

3m: ^{1}H NMR ($CDCl_3$) δ 0.45-0.53 (m, 2H), 0.72 (t, *J* = 7 Hz, 6H), 0.75-0.82 (m, 2H), 1.69-1.77 (m, 2H), 1.89-1.97 (m, 2H), 2.00 (d, *J* = 1 Hz, 3H), 7.03 (d, *J* = 1 Hz, 1H), 7.42-7.52 (m, 3H), 7.66 (d, *J* = 8 Hz, 1H), 7.89 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 14.9 ($2CH_3$), 16.9 ($2CH_2$), 39.9 ($2CH_2$), 59.7 (C), 120.7 (CH), 124.1 (CH), 124.2 (CH), 124.4 (CH), 125.0 (CH), 125.6 (CH), 127.5 (C), 128.8 (CH), 133.3 (C), 141.1 (C), 147.8 (C), 152.8 (C); MS (relative intensity) *m/z* 165 (13), 178 (40), 179 (33), 180 (12), 189 (25), 190 (15), 191 (44), 192 (34), 193 (100), 194 (18), 221 (15), 222 (25), 235 (84), 236 (16), 264 (M^+, 65); HRMS calc. for $C_{20}H_{24}$: *m/z* 264.1878. Found *m/z* 264.1888.

4a: ^{1}H NMR ($CDCl_3$) δ 0.93(t, *J* = 7 Hz, 6H), 1.46-1.61(m, 8H), 1.77(s, 3H), 6.63(s, 1H), 7.06(d, *J* = 7 Hz, 2H), 7.20-7.30(m, 3H); ^{13}C NMR ($CDCl_3$) δ 15.0($2CH_3$), 15.1(CH_3), 17.0($2CH_2$), 42.6($2CH_2$), 78.7(C), 124.8(CH), 126.4(CH), 128.4(2CH), 129.5(2CH), 139.0(C), 142.0(C). Stereostructure of **4a** was confirmed by NOESY spectrum. NOE correlation of olefinic proton (6.63 ppm) was observed with *ortho*-phenyl proton (7.06 ppm) and not with methyl proton (1.77 ppm).

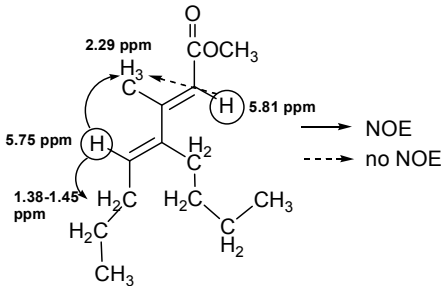


4a': ^{1}H NMR ($CDCl_3$) δ 0.91(t, *J* = 7 Hz, 6H), 1.40(d, *J* = 7 Hz, 3H), 1.42-1.51(m, 8H), 5.82(q, *J* = 7 Hz, 1H), 7.05(d, *J* = 7 Hz, 2H), 7.20-7.37(m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.8($2CH_3$), 15.0(CH_3), 17.2($2CH_2$), 42.1($2CH_2$), 78.1(C), 122.0(CH), 127.0(CH), 128.4(2CH), 129.8(2CH), 139.8(C), 146.3(C). Stereostructure of **4a'** was confirmed by NOESY spectrum. NOE correlation of olefinic proton (5.82 ppm) was observed with methyl proton (1.40 ppm) and not with *ortho*-phenyl proton (7.05 ppm).



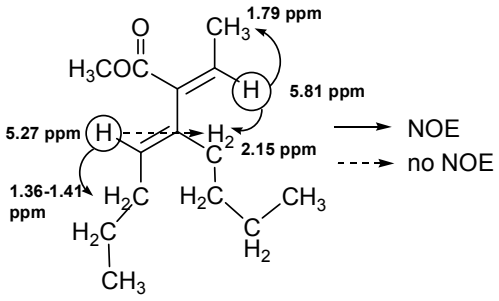
5a: ^{1}H NMR ($CDCl_3$) δ 0.86-0.93(m, 6H), 1.27-1.30(m, 4H), 1.38-1.45(m, 2H), 2.09(q, *J*=7 Hz, 2H), 2.22-2.24(m, 2H), 2.29(s, 3H), 3.69(s, 3H), 5.75(t, *J* = 7 Hz, 1H), 5.81(s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9(CH_3), 14.0(CH_3), 16.2(CH_3), 22.8(CH_2), 22.9(CH_2), 27.6(CH_2), 30.6(CH_2), 31.1(CH_2), 50.8(CH_3), 114.1(CH), 135.6(CH), 144.8(C), 157.4(C), 168.0(C); HRMS calc. for $C_{14}H_{24}O_2$: *m/z* 224.1776. Found: *m/z* 224.1766.

NOESY spectrum supported (*E*), (*E)*-structure of **5a** as shown below.



5a': ^{1}H NMR ($CDCl_3$) δ 0.85-0.92(m, 6H), 1.28-1.35 (m, 4H), 1.36-1.41 (m, 2H), 1.79(d, *J* = 7 Hz, 3H), 2.04(q, *J* = 7 Hz, 2H), 2.15 (t, *J* = 7 Hz, 2H), 3.76(s, 3H), 5.27(t, *J* = 7 Hz, 1H), 5.81(q, *J* = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9(CH_3), 14.0(CH_3), 15.5(CH_3), 22.8(2CH_2), 28.0(CH_2), 30.2(CH_2), 30.8(CH_2), 51.5(CH_3), 127.9(CH), 129.7(CH), 137.4(C), 138.2(C), 169.7(C); HRMS calc. for $C_{14}H_{24}O_2$: *m/z* 224.1776. Found: *m/z* 224.1778.

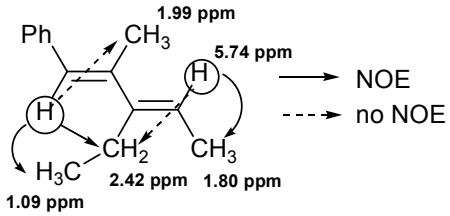
NOESY spectrum supported (*E*), (*E)*-structure of **5a'** as shown below.



5b: ^{1}H NMR ($CDCl_3$) δ 1.09(t, *J*=8 Hz, 3H), 1.80(d, *J* = 7 Hz, 3H), 1.99(d, *J* = 1 Hz, 3H), 2.42(q, *J* = 8 Hz, 2H), 5.74(q, *J* = 7 Hz, 1H), 6.60(s, 1H), 7.20-7.37(m, 5H); ^{13}C NMR

($CDCl_3$) δ 14.0(CH_3), 14.3(CH_2), 16.3(CH_3), 21.1(CH_3), 121.6(CH), 125.3(CH), 126.4(CH), 128.2(2CH), 129.7(2CH), 138.2(C), 139.4(C), 144.8(C); HRMS calc. for $C_{14}H_{18}$: *m/z* 186.1409. Found *m/z* 186.1401.

NOESY spectrum supported (*E*), (*E)*-structure of **5b** as shown below.



References

(1) W. L. F. Armagego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, UK, 1997.

(2) E. J. Roskamp, S. F. Pedersen, *J. Am. Chem. Soc.,* 1987, **109**, 6551.