Supporting Information

AuCl₃-Catalyzed [4+2] Benzannulation: Synthesis of Naphthylketone Derivatives from *o*-Alkynylbenzaldehyde with Alkyne

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Phenyl-(2-propyl-naphthalen-1-yl)-methanone (3a). Pale yellow oil; ¹H-NMR (CDCl₃, 300 MHz) δ 7.89 – 7.80 (m, 4H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.22 (m, 6H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.60 (tq, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ¹³C-NMR (CDCl₃, 75 MHz) δ 200.1, 137.8, 137.0, 135.6, 133.7, 131.6, 130.6, 129.7, 128.9, 128.7, 127.9, 127.4, 126.5, 125.4, 125.1, 35.7, 24.3, 14.0. IR (neat) 2959, 1668, 1595, 1448, 915, 823, 749 cm⁻¹. Ms (EI) *m/z* 274 (M⁺). HRMS Calcd for C₂₀H₁₈O (M⁺) 274.1353, Found 274.1367.

Phenyl-(3-propyl-naphthalen-1-yl)-methanone (4a). Yellow oil; ¹H-NMR (CDCl₃, 300 MHz) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.85 (m, 3H), 7.79 (s, 1H), 7.61 – 7.56 (m, 1H), 7.52 – 7.41 (m, 5H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.73 (tq, *J* = 7.5, 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ¹³C-NMR (CDCl₃, 75 MHz) δ 198.0, 138.6, 138.3, 136.2, 133.9, 133.1, 130.3, 129.7, 129.4, 129.2, 128.3, 127.8, 126.3, 126.3, 125.4, 37.7, 24.2, 13.7. IR (neat) 3057, 2959, 1661, 1597, 1504, 1448, 1248, 1055, 750 cm⁻¹. Ms (EI) *m/z* 274 (M⁺). HRMS Calcd for C₂₀H₁₈O (M⁺) 274.1353, Found 274.1356.

Phenyl-(2-phenyl-naphthalen-1-yl)-methanone (3b). Yellow solid; ¹H-NMR (CDCl₃, 300 MHz) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.54 - 7.32 (m, 5H), 7.22 - 7.12 (m, 5H). ¹³C-NMR (CDCl₃, 75 MHz) δ 199.6, 140.2, 137.9, 137.4, 135.7, 133.2, 132.4, 130.6, 129.5, 129.5, 129.5, 128.3, 128.2, 128.1, 127.6, 127.4, 127.2, 126.3, 125.5. IR (KBr) 3046, 1665, 1659, 1593, 1447, 1285, 1234, 1171, 1020, 914, 831, 770, 719 cm⁻¹. Ms (EI) *m/z* 308 (M⁺). Anal. Calcd for C₂₃H₁₆O: C, 89.6; H, 5.20. Found C, 89.4; H, 5.50. mp 123 °C.

Phenyl-(2-phenyl-naphthalen-1-yl)-methanone (d-3b). Yellow solid; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 8.00 (s, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.54 - 7.31 (m, 5H), 7.24 - 7.12 (m, 5H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 199.7, 140.2, 137.9, 137.4, 135.7, 133.2, 132.4, 130.6, 129.6, 129.5, 129.3, 128.3, 128.2, 128.2, 128.2, 127.4, 127.2, 126.3, 125.5. IR (KBr) 3044, 1661, 1595, 1578, 1448, 1231, 1173, 1022, 920, 895, 772, 716 cm^{-1} . Ms (EI) m/z 305 (M^+). HRMS Calcd for $\text{C}_{23}\text{H}_{15}\text{OD}$ (M^+) 305.1263, Found 305.1284. mp 122 $^{\circ}\text{C}$.

Phenyl-(3-trimethylsilanyl-naphthalen-1-yl)-methanone (4c). White solid; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 8.15 (s, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 7.93 - 7.87 (m, 3H), 7.67 (s, 1H), 7.60 - 7.46 (m, 5H), 0.33 (s, 9H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 198.5, 138.3, 136.9, 136.6, 135.5, 133.2, 133.0, 131.4, 131.0, 130.4, 128.5, 128.4, 127.4, 126.4, 125.5, -1.21. IR (KBr) 3051, 2959, 1827, 1578, 1450, 1369, 1252, 1153, 1020, 943, 872 cm^{-1} . Ms (EI) m/z 304 (M^+). HRMS Calcd for $\text{C}_{20}\text{H}_{20}\text{OSi}$ (M^+) 304.1278, Found 304.1302. mp 88 $^{\circ}\text{C}$.

4-Benzoyl-naphthalene-2-carboxylic acid ethyl ester (4d). White crystal; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 8.74 (s, 1H), 8.14 (s, 1H), 8.14 - 8.01 (m, 2H), 7.85 (d, $J = 7.1$ Hz, 2H), 7.63 - 7.57 (m, 3H), 7.46 (dd, $J = 7.9, 7.5$ Hz, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 197.3, 166.0, 137.8, 136.9, 133.6, 133.6, 133.0, 132.9, 130.4, 129.9, 129.9, 129.5, 128.6, 127.2, 126.5, 125.7, 61.4, 14.4. IR (KBr) 3057, 2986, 1728, 1655, 1620, 1597, 1506, 1448, 1383, 1298, 1202, 1024, 770, 704 cm^{-1} . Ms (EI) m/z 304 (M^+). HRMS Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3$ (M^+) 304.1095, Found 304.1091. mp 82 $^{\circ}\text{C}$.

1-(4-benzoyl-naphthalen-2-yl)-ethanone (4e). White solid; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 8.58 (s, 1H), 8.11 - 8.02 (m, 3H), 7.84 (bd, $J = 7.6$ Hz, 2H), 7.63 - 7.58 (m, 3H), 7.45 (bdd, $J = 7.9, 7.6$ Hz, 2H), 2.71 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 197.3, 137.7, 137.1, 133.6, 133.0, 133.0, 133.0, 132.7, 130.4, 130.0, 129.7, 128.7, 128.6, 127.4, 125.8, 125.2, 26.6. IR (KBr) 3017, 2941, 1682, 1665, 1593, 1448, 1350, 1313, 1240, 1192, 1022, 920 cm^{-1} . Ms (EI) m/z 274 (M^+). HRMS Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_2$ (M^+) 274.0990, Found 274.0998. mp 123 $^{\circ}\text{C}$.

(2,3-Dipropyl-naphthalen-1-yl)-phenyl-methanone (3f=4f). Pale yellow solid; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.81 - 7.71 (m, 4H), 7.53 (dd, $J = 7.5, 7.3$ Hz, 1H), 7.40 - 7.33 (m, 4H),

7.24 (dd, $J = 7.9, 6.4$ Hz, 1H), 2.77 (t, $J = 6.2$ Hz, 2H), 2.66 (br, 1H), 2.41 (br, 1H), 1.76 (sextet, $J = 7.5$ Hz, 2H), 1.56 (br, 1H), 1.42 (br, 1H), 1.05 (t, $J = 7.3, 7.5$ Hz, 3H), 0.86 (t, $J = 7.3, 7.5$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 200.6, 139.1, 137.9, 136.4, 136.3, 133.6, 131.9, 129.7, 127.3, 128.7, 128.4, 127.4, 125.7, 125.4, 124.8, 34.6, 33.0, 24.6, 24.3, 14.6, 14.3. IR (KBr) 3046, 2957, 2926, 1665, 1593, 1450, 1332, 1267, 1234, 1011, 910 cm^{-1} . Ms (EI) m/z 316 (M^+). HRMS Calcd for $\text{C}_{23}\text{H}_{24}\text{O}$ (M^+) 316.1821, Found 316.1827. mp 87 $^{\circ}\text{C}$.

Phenyl-(2-phenyl-3-trimethylsilanyl-naphthaen-1-yl)-methanone (3g). Yellow solid; ^1H -NMR (CDCl_3 , 300 MHz) δ 8.26 (s, 1H), 8.00 (d, $J = 8.3$ Hz, 1H), 7.64 - 7.54 (m, 5H), 7.51 - 7.44 (m, 2H), 7.32 (m, 6H). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 200.0, 142.0, 140.1, 138.4, 137.8, 136.5, 136.5, 133.0, 131.5, 130.4, 129.4, 128.3, 128.2, 128.1, 127.6, 127.3, 127.3, 126.2, 125.2, 0.5. IR (KBr) 3048, 2966, 1665, 1597, 1491, 1448, 1234, 1211, 1173, 949, 853, 793 cm^{-1} . Ms (EI) m/z 380 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{OSi}$: C, 82.11; H, 6.32. Found C, 81.87; H, 6.45. mp 129 $^{\circ}\text{C}$.

(3-Methyl-2-phenyl-naphthalen-1-yl)-phenyl-methanone (3h). White solid; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.87(d, $J = 5.2$ Hz, 1H), 7.85 (s, 1H), 7.59 (dd, $J = 8.9, 8.1$ Hz, 3H), 7.51 - 7.35 (m, 4H), 7.26 - 7.15 (m, 6H), 2.29 (s, 3H). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 199.5, 138.3, 138.3, 138.0, 137.0, 134.1, 133.0, 132.7, 129.4, 129.4, 129.1, 129.1, 128.1, 127.7, 127.4, 127.1, 126.3, 126.2, 125.3, 21.0. IR (KBr) 3046, 1666, 1595, 1578, 1445, 1292, 1231, 1024, 885, 822 cm^{-1} . Ms (EI) m/z 322 (M^+). HRMS Calcd for $\text{C}_{24}\text{H}_{18}\text{O}$ (M^+) 322.1353, Found 322.1357. mp 157 $^{\circ}\text{C}$.

1-(2-Phenyl-naphthalen-1-yl)-heptan-1-one (3i). Pale yellow oil; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.93 - 7.80 (m, 3H), 7.53 - 7.41 (m, 8H), 2.27 (t, $J = 7.3$ Hz, 2H), 1.45 (dd, $J = 7.3, 7.1$ Hz, 2H), 1.18 - 1.04 (m, 6H), 0.80 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 209.9, 140.3, 138.4, 135.9, 132.5, 132.5, 129.4, 129.2, 128.6, 128.2, 127.8, 127.4, 127.3, 126.2, 124.8, 45.1, 31.3, 28.5, 23.5, 22.3, 13.9. IR (neat) 3032, 1695, 1593, 1447, 1423, 1350, 1161, 1094, 1076, 1030, 866 cm^{-1} . Ms (EI) m/z 316 (M^+). HRMS Calcd for $\text{C}_{23}\text{H}_{24}\text{O}$ (M^+) 316.1821, Found 316.1827.

(6,7-Dimethoxy-2-phenyl-naphthalen-1-yl)-phenyl-methanone (3j). White crystal; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.88 (d, $J = 8.3$ Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.46 - 7.33 (m, 4H), 7.28 - 7.15 (m, 6H), 7.07 (s, 1H), 4.05 (s, 3H), 3.84 (s, 3H). ^{13}C -NMR (CDCl_3 , 75 MHz) δ 200.2,

150.3, 149.6, 140.5, 140.5, 138.1, 136.2, 134.1, 133.0, 129.4, 128.5, 128.1, 128.0, 127.9, 127.1, 126.3, 125.8, 106.4, 104.0, 55.8, 55.8. IR (KBr) 3022, 2937, 2251, 1666, 1580, 1416, 1261, 1215, 1097, 914 cm^{-1} . Ms (EI) m/z 368 (M^+). HRMS Calcd for $\text{C}_{23}\text{H}_{15}\text{OD}$ (M^+) 368.1411, Found 368.1434. mp 48 $^{\circ}\text{C}$.

(2,4-Diphenyl-naphthalen-1-yl)-phenyl-methanone (11a). Yellow solid; ^1H -NMR (CDCl_3 , 300 MHz) δ 7.99 (dd, $J = 3.0, 6.0$ Hz, 1H), 7.77 (dd, $J = 3.0, 6.0$ Hz, 1H), 7.68 (d, $J = 7.0$ Hz, 2H), 7.60 - 7.56 (m, 2H), 7.54 (s, 1H), 7.49 (d, $J = 3.0$ Hz, 2H), 7.45 (dd, $J = 3.0, 7.0$ Hz, 2H), 7.42 - 7.35 (m, 3H), 7.28 - 7.14 (m, 6H). ^{13}C -NMR (CDCl_3 , 270 MHz) δ 199.5, 141.7, 140.0, 140.0, 138.0, 136.8, 135.1, 133.1, 131.1, 130.7, 130.0, 129.6, 129.4, 128.5, 128.5, 128.3, 128.2, 128.1, 127.6, 127.4, 126.9, 126.3, 125.8. IR (KBr) 3058, 1661, 1492, 1448, 1257, 1229, 781, 761, 717 cm^{-1} . Ms (EI) m/z 384 (M^+). HRMS Calcd for $\text{C}_{29}\text{H}_{20}\text{O}$ (M^+) 384.1514, Found 384.1499. mp 141.0 $^{\circ}\text{C}$.

(4-Methyl-2-phenyl-naphthalen-1-yl)-phenyl-methanone (11b). Yellow solid; ^1H -NMR (CDCl_3 , 500 MHz) δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.62 (dd, $J = 1.5, 7.5$ Hz, 2H), 7.56 (ddd, $J = 1.5, 7.0, 8.0$ Hz, 1H), 7.46 (ddd, $J = 1.5, 7.0, 8.0$ Hz, 1H), 7.43 (s, 1H), 7.38 (dddd, $J = 0.5, 2.0, 6.5, 7.5$ Hz, 1H), 7.34 (dd, $J = 1.5, 6.0$ Hz, 2H), 7.22 (dd, $J = 7.5, 7.5$ Hz, 2H), 7.21 (dd, $J = 6.0, 6.0$ Hz, 2H), 7.16 (ddt, $J = 1.5, 6.0, 6.0$ Hz, 1H), 2.81 (s, 3H). ^{13}C -NMR (CDCl_3 , 500 MHz) δ 199.9, 140.4, 138.2, 137.1, 136.1, 134.1, 133.1, 131.6, 130.8, 129.6, 129.4, 128.3, 128.2, 128.1, 127.3, 126.8, 126.2, 126.1, 124.3, 19.7. IR (KBr) 3061, 2920, 1659, 1450, 1243, 1226, 893, 750 cm^{-1} . Ms (EI) m/z 322 (M^+). HRMS calcd for $\text{C}_{24}\text{H}_{18}\text{O}$ (M^+) 322.1358, found 322.1363. Anal Calcd for $\text{C}_{24}\text{H}_{18}\text{O}$: C, 89.41; H, 5.63; Found: C, 89.14; H, 5.46. mp. 159.0 $^{\circ}\text{C}$.

3a

d-3b

1H

DFILE : ALPHA
SFILE : DUA0: HANN01948

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COMNT : 1H
EXMOD : SINGL
IRMOD : NON
POINT : 65536
FREQU : 1000.00 Hz
SCANS : 16
DUMMY : 2
ACQTM : 6.5536 sec
PD : 1.4464 sec
RGAIN : 12
PW1 : 5.83 usec

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OBNUC : 1H
OBFRQ : 500.00 MHZ
OBSET : 162410.00 HZ
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IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 160568.87 Hz
IRATN : 140
IRRPW : 50.0 usec
IRBP1 : 25
IRBP2 : 6.
IRANS : 0
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ADBIT : 16
CTEMP : 23.9
CSPED : 11
SLVNT : COCL3
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RESOL :	0.15 Hz
BF :	0.00 Hz
T1 :	0.00 %
T2 :	0.00 %
T3 :	100.00 %
T4 :	100.00 %
REFVL :	0.00 ppm
XE :	4850.77 Hz
XS :	237.88 Hz
operator

19-JUN-2002 13:14:53.78

DFILE : ALPHA
SFIL : QUAO: HANNO1942COMNT : 1H
EXMOD : SINGL
IRMOD : NON
POINT : 65536
FREQ : 10000.00 Hz
SCANS : 32
DUMY : 2
ACQTM : 6.5536 sec
PD : 1.4464 sec
RGAIN : 12
PW1 : 5.83 usecOBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 HzIRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 160568.87 Hz
IRATN : 140
IRRPW : 50.0 usec
IRBP1 : 25
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 23.7 C
CSPED : 13 Hz
SLVNT : CDCL3RESOL : 0.15 Hz
BF : 0.00 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 100.00 %
T4 : 100.00 %
REFVL : 7.26 ppm
XE : 5001.53 Hz
XS : 240.63 Hz
operator

1H

13-MAY-2002 13: 46: 27.30

DFILE : ALPHA
SFIL : DUA0: HANNO1891

COMNT : 1H
EXMOD : SINGL
IRMOD : NON
POINT : 65536
FREQ : 1000.00 Hz
SCANS : 16
DUMMY : 2
ACQTM : 6.5536 sec
PD : 1.4464 sec
RGAIN : 12
PW1 : 5.85 usec

OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz

IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 160568.87 Hz
IRATN : 140
IRPW : 50.0 usec
IRBP1 : 25
IRBP2 : 6
IRNS : 0

ADBIT : 16
CTEMP : 26.6 c
CSPED : 12 Hz
SLVNT : CDCL3

RESOL : 0.15 Hz
BF : 0.00 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 100.00 %
T4 : 100.00 %
REFVL : 7.26 ppm
XE : 5001.53 Hz
XS : 241.09 Hz
operator

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OFFILE : ALPHA
SFILE  : DUA0: HANNO1895

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COMINT : 1H
EXMOD : SINGL
IRMOD : NON
POINT : 65536
FREQU : 10000.00 Hz
SCANS : 16
DUMMY : 2
ACQTM : 6.5536 sec
PD : 1.4464 sec
RGAIN : 12
PW1 : 5.85 usec

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OBNUC : 1H
OBFRQ : 500.00 MHZ
OBSET : 162410.00 HZ
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```
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 160568.87 Hz
IRATN : 140
IRRPW : 50.0 usec
IRBP1 : 25
IRBP2 : 6
IRRNS : 0
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ADBIT : 16
CTEMP : 26.7 c
CSPED : 11 HZ
SLVNT : CDCL3
```

RESOL :	0.15 HZ
BF	0.00 HZ
T1	0.00 %
T2	0.00 %
T3	100.00 %
T4	100.00 %
REFVL :	7.26 ppm
XE	5001.53 HZ
XS	241.09 HZ
operator

11a

The results of NOE experiments.