Studies Directed Toward The Synthesis of Terreulactone A: Rapid Synthesis of the A,B,C Rings

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General Considerations: All air/moisture sensitive experiments were conducted under a slight static pressure of dry Ar unless indicated otherwise. Anhydrous CH₂Cl₂, THF were obtained using Solv-Tek, Inc. solvent purification system. All other solvents were of anhydrous quality purchased from Aldrich Chemicals Co. All chemicals were purchased from Aldrich Chemical Co. and used as received. Commercial grade solvents were used for routine purposes without further purification. (*i*-Pr)₂NH was distilled from CaH₂ under a N₂ atmosphere prior to use. All NMR spectra were recorded on a Bruker model AMX-400 (¹H: 400 MHz, ¹³C: 100 MHz) NMR spectrometer. Chemical shifts are reported in parts per million (ppm) from the residual solvent signal of CDCl₃. The following abbreviations were used in reporting spectra: s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet. Column chromatography was performed with Merck silica gel 60 (40-63 mesh).

5-(methoxymethoxy)-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (14)

To a solution of 4.0 g (22.4 mmol) Wieland-Miescher ketone in EtOH (32 mL) cooled at 0 °C was added a solution of NaBH₄ (233 mg, 6.16 mmol) in EtOH (48 mL) over 1 hour. After addition was completed, stirring was continued for another 90 min, and the reaction was then quenched with AcOH (2.4 mL, 40 mmol). The reaction mixture was concentrated, diluted with water (50 mL), and extracted with EtOAc (3x50 mL). The combined organic phases were washed with saturated NaHCO₃, water and brine, and dried over Na₂SO₄. After removal of solvent, the crude product was dried on high-vac overnight. The residue was then dissolved in CH₂Cl₂ (200 mL), and DIPEA (35 mL, 200 mmol) and MOMCl (8.4 mL, 110 mmol) were added. After stirring at room temperature for 16 hours, the reaction was quenched with 100 mL of water and 100 mL of saturated NH₄Cl. The aqueous phase was further extracted with CH₂Cl₂ (2x100 mL). The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by silica gel flash chromatography (1:3 – 1:2 EtOAc/Hexanes). 3.541 g product was obtained as a pale yellow oil (78%, two steps). ¹HNMR (400 MHz, CDCl₃) δ 5.70 (d, *J*=1.6 Hz, 1H), 4.68 (d, *J*=6.9 Hz, 1H), 4.54 (d, *J*=6.9 Hz, 1H), 3.32 (s, 1H), 3.22 (dd, *J*=4.3, 11.7 Hz, 1H), 2.42-2.27 (m, 3H), 2.16-2.11 (m, 2H), 1.92 (m, 1H), 1.80 (m, 2H), 1.60 (m, 1H), 1.32 (m, 1H), 1.16 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 199.3, 168.1, 125.2, 95.6, 83.6, 55.6, 41.2, 34.3, 33.6, 32.0, 27.1, 22.9, 16.1. ESI-MS *m/z* 246.8 [(M+Na)⁺; calcd for C₁₃H₂₀O₃Na: 247.1]. HRMS *m/z* 225.1491 [(M+H)⁺; calcd for C₁₃H₂₁O₃: 225.1491].

5-(methoxymethoxy)-1,1,4a-trimethyl-3,4,4a,5,6,7-hexahydronaphthalen-2(1H)-one (15)

To a solution of compound **14** (3.54 g, 15.8 mmol) in 70 mL of *t*BuOH was added 1.0 M *t*BuOK in *t*BuOH (95 mL, 95 mmol) under Ar atmosphere. After the reaction mixture was stirred at r.t. for 10 min, it was cooled to 10 °C and 13 mL of CH₃I (209 mmol) was added slowly. The cool bath was then removed and stirring continued for another 20 min. The reaction mixture was concentrated, diluted with water (40 mL), and extracted with EtOAc (3x50 mL). The combined organics were washed with brine (30 mL), dried over Na₂SO₄, and concentrated. Purification by flash chromatography (1:4-1:3 EtOAc/Hexanes) furnished 3.05 g product as a pale yellow oil (77%). ¹HNMR (400 MHz, CDCl₃) δ 5.45 (t, *J*=3.5 Hz, 1H), 4.71 (d, *J*=6.9 Hz, 1H), 4.56 (d, *J*=6.9 Hz, 1H), 3.35 (dd, *J*=3.7, 12.2 Hz, 1H), 3.33 (s, 3H), 4.46 (dd, *J*=5.2, 9.5 Hz, 2H), 2.10 (m, 3H), 1.82 (m, 1H), 1.75 (m, 1H), 1.65 (m, 1H), 1.18 (s, 3H), 1.16 (s, 3H), 0.92 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 215.7, 148.0, 119.9, 95.5, 81.7, 55.5, 48.6, 38.8, 33.6, 31.1, 29.1, 27.2, 24.5, 22.9, 18.5. ESI-MS *m/z* 275.1 [(M+Na)⁺; calcd for C₁₅H₂₄O₃Na: 275.2]. HRMS *m/z* 253.1800 [(M+H)⁺; calcd for C₁₅H₂₅O₃: 253.1804].

3-hydroxy-5-(methoxymethoxy)-1,1,4a-trimethyl-4a,5,6,7-tetrahydronaphthalen-2(1H)-one (3)

Compound **15** (3.05 g, 12.1 mmol) was dissolved in 80 mL of anhydrous THF and cooled to -78 °C. Then KHMDS (26.5 mL, 0.5 M in PhMe, 13.3 mmol) was added. After 30 min, a solution of Davis Oxaziridine (3.48 g 13.3 mmol) in 40 mL of anhydrous THF was added. The reaction mixture was stirred at -78 °C for 1 hr before it was quenched by 100 mL of water. After warmed to r.t., the reaction was extracted with EtOAc (3x50 mL). The

combined organics were washed with brine (30 mL), dried over Na₂SO₄, and concentrated to dryness. After drying on high-vac overnight, the residue was dissolved in 120 mL of CH₂Cl₂ and treated with DMP (5.0 g, 11.8 mmol) at r.t. for 1.5 hr. The reaction was then added to 80 mL of 1:1 saturated Na₂S₂O₃ and water and stirred for 2 hr. The reaction mixture was extracted with EtOAc (3x100 mL). The combined organics were washed with 2N NaOH (2x100 mL) and brine (100 mL), dried over Na₂SO₄, and concentrated to dryness. Purification by flash chromatography (1:3 EtOAc/Hexanes) furnished 1.97 g product (62%) as a light yellow oil. ¹HNMR (400 MHz, CDCl₃) δ 6.27 (s, 1H), 5.92 (s, 1H), 5.54 (t, *J*=3.6 Hz, 1H), 4.76 (d, *J*=6.8 Hz, 1H), 4.65 (d, *J*=6.8 Hz, 1H), 3.41 (s, 1H), 3.41 (dd, *J*=4.2, 8.0 Hz, 1H), 2.20 (m, 2H), 1.95 (m, 1H), 1.80 (m, 1H), 1.39 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 199.0, 143.0, 142.6, 121.9, 121.6, 96.2, 80.4, 55.7, 47.0, 40.0, 31.7, 24.1, 23.5, 23.0, 22.2. ESI-MS *m/z* 288.9 [(M+Na)⁺; calcd for C₁₅H₂₂O₄Na: 289.1]. HRMS *m/z* 267.1604 [(M+H)⁺; calcd for C₁₅H₂₃O₄: 267.1596].

methoxy 2-methoxy-4-(methoxymethoxy)-1,1,3a-trimethyl-3-(phenylthio)-2,3,3a,4,5,6-hexahydro-1*H*-indene-2-carboxylate (16)

Compound **3** (530 mg 2.0 mmol) was dissolved in 20 mL of anhydrous THF, to which was added 1.0 M *t*BuOK in THF (5.0 mL, 5.0 mmol) at 0 °C and the reaction mixture was stirred for 15 min. A solution of PhSO₂SPh (751 mg, 3.0 mmol) in 10 mL of dry THF was added and the cold bath was removed after completing addition. The reaction mixture was stirred at r.t. for 5 h before it was quenched with 30 mL of Saturated NH₄Cl, extracted with EtOAc (3x30 mL), and dried over Na₂SO₄. After removal of volatiles, the residue was dried on high-vac overnight. This crude product and KOH (4.5 g, 80 mmol) were suspended in 40 mL of freshly degassed water and heated at 110 °C for 3 hr under Ar atmosphere. After cooling to 0 °C, 4.8 mL (80 mmol) of AcOH was added to the reaction mixture, followed by extraction with EtOAc (3x40 mL). The combined organics

were dried over Na₂SO₄, concentrated to dryness, and dried on high-vac overnight. The crude product was then dissolved in 20 mL of dry DMF and treated with NaH (720 mg, 30 mmol) and 1.6 mL (25.7 mmol) of MeI. The reaction mixture was stirred at r.t. for 4 hr, before it was quenched with 30 mL of brine. Crude product was extracted with EtOAc (3x30 mL), dried over Na₂SO₄, and concentrated to dryness. Purification by flash chromatography (1:4 EtOAc/Hexanes) furnished 375 mg compound **16** as a pale yellow solid (45%, three steps). ¹HNMR (400 MHz, CDCl₃) δ 7.56 (d, *J*=7.5 Hz, 2H), 7.22 (t, *J*=7.5 Hz, 2H), 7.10 (t, *J*=7.3 Hz, 1H), 5.31 (dd, *J*=3.1 Hz, 4.5 Hz, 1H), 4.09 (s, 1H), 3.82 (d, *J*=1.2 Hz, 2H), 3.71 (s, 3H), 3.04 (s, 3H), 3.18 (dd, *J*=5.3, 11.4 Hz, 1H), 3.11 (s, 3H), 2.18 (m, 1H), 2.08 (m, 1H), 1.89 (m, 1H), 1.73 (m, 1H), 1.38 (s, 3H), 1.19 (s, 3H), 0.94 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 171.5, 152.6, 138.5, 129.3, 128.7, 125.8, 117.8, 96.9, 93.8, 85.9, 62.7, 57.8, 54.7, 51.6, 48.9, 47.9, 30.1, 24.8, 24.0, 23.4, 17.1. ESI-MS *m/z* 443.2 [(M+Na)⁺; calcd for C₂₃H₃₂O₅SNa: 443.2]. HRMS *m/z* 421.2033 [(M+H)⁺; calcd for C₂₃H₃₃O₅S: 421.2049].

2-methoxy-4-(methoxymethoxy)-1,1,3a-trimethyl-3-(phenylthio)-2,3,3a,4,5,6-hexahydro-1*H*-indene-2-carboxylic acid (4**)**

To a solution of compound **16** (335 mg 0.80 mmol) in 10 mL of anhydrous THF were added water (29 μL, 1.6 mmol) and 1.0 M *t*BuOK in THF (6.4 mL, 6.4 mmol). After the reaction mixture was stirred at r.t. for 6 hr, it was quenched with AcOH (1.2 mL, 20 mmol), diluted with brine (40 mL), and extracted with Et₂O (3x40 mL). The combined organics were dried over Na₂SO₄ and concentrated to dryness. Purification by flash chromatography (1:3-1:1 EtOAc/Hexanes) furnished 300 mg compound **4** as a white solid (93%). ¹HNMR (400 MHz, CDCl₃) δ 7.54 (d, *J*=7.5 Hz, 2H), 7.23 (t, *J*=6.9 Hz, 2H), 7.11 (t, *J*=7.3 Hz, 1H), 5.35 (dd, *J*=3.1, 4.5 Hz, 1H), 4.08 (s, 1H), 3.83 (s, 2H), 3.65 (s, 3H), 3.18 (dd, *J*=5.3, 11.4 Hz, 1H), 3.13 (s, 3H), 2.22 (m, 1H), 2.11 (m, 1H), 1.92 (m, 1H), 1.75 (m, 1H), 1.40 (s, 3H), 1.23 (s, 3H), 1.05 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 175.9, 152.3, 138.3, 129.5, 128.7, 126.0, 118.1, 96.8, 93.6, 85.9, 62.4, 57.9, 55.0, 48.9,

48.0, 30.2, 24.8, 24.0, 23.5, 17.0. ESI-MS m/z 429.2 $[(M+Na)^+]$; calcd for $C_{22}H_{30}O_5SNa$: 429.2]. HRMS m/z 407.1900 $[(M+H)^+]$; calcd for $C_{22}H_{31}O_5S$: 407.1892].

Compound 17

Compound **4** (110 mg, 0.27 mmol) and NBS (52 mg, 0.29 mmol) were cooled to 0 °C, then 8.0 mL of anhydrous THF was added. The reaction was stirred at 0 °C for 30 min and then concentrated and purified by flash chromatography (1:9-1:3 EtOAc/Hexanes). 120 mg was obtained as a white solid (91%). 1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, $J=1.6, 8.3$ Hz, 2H), 7.13 (m, 3H), 4.16 (d, $J=6.8$ Hz, 1H), 4.09 (d, $J=4.7$ Hz, 1H), 3.97 (d, $J=6.8$ Hz, 1H), 3.64 (s, 3H), 3.49 (s, 1H), 3.48 (dd, $J=5.6, 10.5$ Hz, 1H), 3.00 (s, 3H), 2.47 (m, 1H), 1.87 (m, 2H), 1.76 (s, 3H), 1.13 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 136.5, 132.5, 129.0, 127.5, 96.5, 94.2, 87.4, 81.9, 61.9, 55.3, 54.5, 54.4, 52.1, 40.3, 30.7, 25.0, 20.1, 18.5, 18.0. ESI-MS m/z 507.1 $[(M+Na)^+]$; calcd for $C_{22}H_{29}BrO_5SNa$: 507.1]. HRMS m/z 485.1003 $[(M+H)^+]$; calcd for $C_{22}H_{30}BrO_5S$: 485.0997].

Compound 18

Compound (503 mg 1.04 mmol) **17** and AIBN (40 mg, 0.24 mmol) were mixed with Bu_3SnH (10 mL, 37.2 mmol) and the reaction was heated at 80 °C for 5 min. The reaction mixture was partitioned between CH_3CN (40 mL) and Hexanes (40 mL). The

CH₃CN phase was further washed with Hexanes (3x20 mL) to remove residual tin. Purification by flash chromatography (1:4-1:3 EtOAc/Hexanes) furnished 282 mg compound **18** as a white solid (67%). ¹HNMR (400 MHz, CDCl₃) δ 7.55 (d, *J*=7.5 Hz, 2H), 7.23 (m, 3H), 4.28 (d, *J*=6.7 Hz, 1H), 4.09 (d, *J*=6.7 Hz, 1H), 3.87 (s, 3H), 3.59 (s, 1H), 3.57 (dd, *J*=4.7, 9.5 Hz, 1H), 3.10 (s, 3H), 1.92 (m, 1H), 1.79 (m, 1H), 1.66 (m, 2H), 1.57 (m, 1H), 1.49 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 174.9, 136.5, 132.7, 128.9, 127.5, 96.3, 88.8, 82.2, 60.7, 55.2, 54.4, 53.8, 51.7, 27.8, 20.5, 19.6, 18.4, 16.1. ESI-MS *m/z* 429.2 [(M+Na)⁺; calcd for C₂₂H₃₀O₅SNa: 429.2]. HRMS *m/z* 407.1895 [(M+H)⁺; calcd for C₂₂H₃₁O₅S: 407.1892].

Compound 19

Compound **18** (38 mg, 0.09 mmol) was dissolved in 1.2 mL of THF and treated with 0.4 mL of concentrated HCl. The reaction was stirred at r.t. for 50 min before it was diluted with water (8 mL) and extracted with Et₂O (3x8 mL). The combined organics were washed with saturated NaHCO₃ and brine, 8 mL each. Purification by flash chromatography (1:2 EtOAc/Hexanes) furnished 27 mg product as a white solid (84%). ¹HNMR (400 MHz, CDCl₃) δ 7.60 (d, *J*=7.2 Hz, 2H), 7.29 (t, *J*=7.0 Hz, 2H), 7.23 (t, *J*=4.8 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, *J*=4.8, 10.7 Hz, 1H), 3.71 (s, 1H), 1.82 (m, 1H), 1.70 (m, 4H), 1.49 (m, 1H), 1.42 (s, 3H), 1.03 (s, 3H), 0.87 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 174.7, 136.4, 132.2, 129.4, 127.7, 96.6, 88.9, 74.8, 60.6, 54.5, 53.9, 52.1, 29.5, 20.4, 19.6, 19.2, 18.4, 14.9. ESI-MS *m/z* 385.2 [(M+Na)⁺; calcd for C₂₀H₂₆O₄SNa: 385.2]. HRMS *m/z* 363.1635 [(M+H)⁺; calcd for C₂₀H₂₇O₄S: 363.1630].

Compound 20

Compound **19** (27 mg, 0.075 mmol) and DMP (40 mg, 0.094 mmol) were suspended in 2.0 mL of CH₂Cl₂ and stirred at r.t. for 1.5 hr. 5.0 mL of 1:1 saturated Na₂S₂O₃ and water were then added into the reaction mixture. After another 2 hr, the reaction was extracted with CH₂Cl₂ (3x5 mL) and dried over Na₂SO₄. Purification by flash chromatography (1:2 EtOAc/Hexanes) furnished desired product as a white solid in quantitative yield (27 mg). ¹HNMR (400 MHz, CDCl₃) δ 7.52 (d, *J*=7.7 Hz, 2H), 7.30 (t, *J*=7.8 Hz, 2H), 7.17 (t, *J*=7.4 Hz, 1H), 4.68 (s, 1H), 3.78 (s, 3H), 2.66 (m, 1H), 2.45 (m, 1H), 2.09 (m, 3H), 1.94 (m, 1H), 1.59 (s, 3H), 1.20 (s, 3H), 1.04 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 207.7, 173.6, 136.6, 129.1, 128.8, 126.4, 95.8, 88.8, 60.7, 54.6, 54.3, 50.7, 35.1, 20.4, 19.8, 18.7, 18.43, 18.38. ESI-MS *m/z* 382.8 [(M+Na)⁺; calcd for C₂₀H₂₄O₄SNa: 383.1]. HRMS *m/z* 383.1282 [(M+Na)⁺; calcd for C₂₀H₂₄O₄SNa: 383.1293].

Compound 21

Compound **20** (9 mg, 0.025 mmol) was dissolved in 1.0 mL of absolute EtOH and anhydrous hydrazine (0.5 mL, 16.0 mmol) and AcOH (0.1 mL, 1.7 mmol) were added. The reaction mixture was heated at 90 °C for 23 hr. The reaction was then concentrated and partitioned between Et₂O (8 mL) and 0.5 N NaOH (4 mL, 2 mmol). The organic phase was dried over Na₂SO₄, concentrated, and dried on high-vac. The residue was then dissolved in 1.0 mL of Et₂O and DBU (0.6 mL, 4.0 mmol). iodine (30 mg, 0.12 mmol) was added into the reaction mixture. After 30 min, the reaction was quenched with saturated NaHCO₃ (2 mL) and extracted with Et₂O (2x5 mL). The organics were dried

over Na₂SO₄ and purified by flash chromatography (1:3 EtOAc/Hexanes). 8 mg product was obtained as a white solid in 68% overall yield. ¹HNMR (400 MHz, CDCl₃) δ 7.62 (d, *J*=7.7 Hz, 2H), 7.30 (t, *J*=7.9 Hz, 2H), 7.20 (t, *J*=5.1 Hz, 1H), 6.07 (t, *J*=3.9 Hz, 1H), 3.95 (s, 1H), 3.73 (s, 3H), 2.38 (m, 1H), 2.25 (m, 1H), 1.98 (m, 2H), 1.55 (s, 3H), 1.27 (s, 3H), 1.11 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 174.6, 135.7, 135.1, 132.6, 129.0, 127.6, 107.2, 94.2, 87.8, 61.3, 55.6, 55.2, 54.8, 26.4, 25.5, 20.6, 19.5, 18.0. ESI-MS *m/z* 493.0 [(M+Na)⁺; calcd for C₂₀H₂₃IO₃SNa: 493.0]. HRMS *m/z* 471.0493 [(M+H)⁺; calcd for C₂₀H₂₄IO₃S: 471.0491].

Compound 5

To a solution of compound **21** (25 mg, 0.053 mmol) in 1.3 mL of degassed PhMe was added Pd(Ph₃P)₄ (4.5 mg in 0.45 mL of PhMe, 3.9x10⁻³ mmol) at 50 °C. A solution of 20 μL (0.07 mmol) of Bu₃SnH in 0.4 mL of PhMe was added into the reaction mixture over 2 hr via a syringe pump. Heating continued for another 20 min after addition of Bu₃SnH. The reaction mixture was concentrated and purified by flash chromatography (1:2 EtOAc/Hexanes), which furnished 18 mg product as a white solid (91%). ¹HNMR (400 MHz, CDCl₃) δ 9.27 (s, 1H), 7.67 (d, *J*=7.4 Hz, 2H), 7.31 (t, *J*=7.9 Hz, 2H), 7.21 (t, *J*=5.3 Hz, 1H), 6.62 (t, *J*=3.8 Hz, 1H), 4.30 (s, 1H), 3.50 (s, 3H), 2.66 (m, 2H), 2.01 (m, 2H), 1.51 (s, 3H), 1.32 (s, 3H), 1.12 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 192.0, 174.9, 151.3, 148.9, 136.2, 131.4, 128.9, 127.1, 93.3, 88.2, 55.6, 55.0, 52.3, 48.6, 26.0, 23.8, 20.4, 19.1, 18.3. ESI-MS *m/z* 395.1 [(M+Na)⁺; calcd for C₂₁H₂₄O₄SNa: 395.1]. HRMS *m/z* 373.1490 [(M+H)⁺; calcd for C₂₁H₂₅O₄S: 371.1474].

* haibo HU-192H (1 1) CDCl3 25.0C October_27,2004_20:53 AMX 400MHz zg30 1H *

. * haibo HL13C (1 1) CDCl3 25.0C December_07, 2005 21:33 AMX 400MHz zgpg30 13C; 1H O2=5999.783 *.

29.569
29.139
26.776
26.444
25.948
24.645
22.783

49.691
47.483
45.056

85.877
77.722
77.405
77.087
75.184
73.154

116.686

154.484

180.954

ppm

13

* haibo HL-I242C (1 1) CDCl3 25.0C January_08,2005_14:07 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

14

* haibo HL-I250 (1 1) CDCl3 25.0C January_12,2005_13:18 AMX 400MHz zg30 1H *

15

* haibo HL-I250C (1) CDCl3 25.0C January_12, 2005_13:22 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

* haibo Comp-4 (1 1) CDCl3 25.0C September_06,2005_19:15 AMX 400MHz zg30 1H *

. * haibo Comp-4C (1 1) CDCl3 25.0C September_06, 2005_19:18 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

* haibo HL-I284 (1 1) CDCl3 25.0C January_21,2005_14:28 AMX 400MHz zg30 1H *

* haibo HL-I284C (1 1) CDCl3 25.0C January_21, 2005_14:32 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

16

* haibo HL-I291 (1 1) CDCl3 25.0C January_24,2005_10:02 AMX 400MHz zg30 1H *

* haibo HL-T291C (1 1) CDCl3 25.0C January_24,2005_10:05 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

4

* haibo HL-I252 (1 1) CDCl3 25.0C January_12,2005_19:43 AMX 400MHz zg30 1H *

* haibo HL-T252C (1 1) CDCl3 25.0C January_12,2005_19:47 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

* haibo HL-III25a (1 1) CDCl3 25.0C August_17, 2005_22:58 AMX 400MHz zg30 1H *

. * haibo HL-III25Ca (1 1) CDCl3 25.1C August_17, 2005_23:02 AMX 400MHz zgpg30 13C; 1H O2=5999.783 *.

. * haibo HL-III29C (1 1) CDCl3 25.0C August_18_2005_23:28 AMX 400MHz zgpg30 13C; 1H O2=5999.783 *

19

20

* haibo HL-III30C (1 1) CDCl3 25.0C August_19,2005_19:57 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

21

. * haibo HL-III33C (1 1) CDCl3 25.0C August_22,2005_20:10 AMX 400MHz zgpg30 13C; 1H 02=5999.783 *.

21

* haibo HL-III34 (1 1) CDCl3 25.10 August_24, 2005_21:38 AMX 400MHz zg30 1H *

. * haibo HL-III34C (1 1) CDCl3 25.0C August_24_2005_21:40 AMX 400MHz zgpg30 13C; 1H O2=5999.783 *

5