Supporting Information

Lanthanum Aryloxide/Pybox-Catalyzed Direct Asymmetric Mannich-Type Reactions Using a Trichloromethyl Ketone as a Propionate Equivalent Donor

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Experimental Section

General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on JEOL JNM-LA500 and JNM-ECX500 spectrometers, operating at 500 MHz for ^1H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in CDCl_3 , C_6D_6 and acetone- d_6 were reported in the scale relative to CHCl_3 and $\text{C}_6\text{D}_5\text{H}$ (7.26 and 7.16 ppm for ^1H NMR) and CDCl_3 , C_6D_6 and acetone- d_6 (77.0, 128.06 and 29.84 ppm for ^{13}C NMR) as an internal reference, respectively. ESI mass spectra (for LRMS) were measured on a Waters ZQ4000 spectrometer. FAB mass spectra (for HRMS) were measured on a JEOL JMS-700 spectrometer. The enantiomeric excess (ee) was determined by HPLC analysis (JASCO HPLC systems; pump: PU-2080; detector: UV-2075, measured at 254 nm; column: DAICEL CHIRALPAK OD-H). Column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM). Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dichloromethane and toluene were dried over activated MS $4\text{\AA}$ before use. Reactions were carried out using flame-dried glasswares in dry solvents under an argon atmosphere, unless otherwise stated.

Preparation of Non-Isomerizable N-Heteroarenesulfonyl Imines:

N-(2-Pyridinesulfonyl) imine **2a** and *N*-(2-thiophenesulfonyl) imines **2b-2e** and **2g** were prepared according to the literature method (González, A. S.; Gómez Arrayás, R.; Carretero, J. C. *Org. Lett.* **2006**, 8, 2977) with slight modification (Procedure A). *N*-(2-Thiophenesulfonyl) imines **2f** and **2h** were prepared based on the literature method (Esquivias, J.; Gómez Arrayás, R.; Carretero, J. C. *J. Am. Chem. Soc.* **2007**, 129, 1480 and references therein, Procedure B). Spectral data of the imines were identical with the reported values.

General Procedure for Preparation of Non-Isomerizable *N*-(2-Thiophenesulfonyl)

Imines (Procedure A): To a round-bottomed flask was placed MS 4Å (Fluka, powder, 1600 mg, 400 mg/mmol) and the flask was flame-dried under reduced pressure (around 1.0 kPa). After cooling to room temperature, argon gas was refilled and Amberlyst® 15 (20 mg, 5 mg/mmol), 2-thiophenesulfonamide (653 mg, 4.0 mmol), toluene (dried over activated MS 4Å, 13.4 mL) and benzaldehyde (0.49 mL, 4.8 mmol, 1.2 equiv) were sequentially added. To the flask was attached a reflux condenser and the mixture was refluxed under argon atmosphere for 11 h at 120 °C (bath temp.). The resulting hot brown suspension was immediately diluted with CH₂Cl₂ and filtered through a pad of Celite. The pad was washed with CH₂Cl₂ and the filtrate was evaporated to give crude imine, which was recrystallized from a minimum amount of AcOEt and hexane twice to afford pure imine **2b** as a pale brown and a yellow solid (660 + 206 mg, 86% combined yield).

General Procedure for Preparation of Non-Isomerizable *N*-(2-Thiophenesulfonyl)

Imines (Procedure B): To a round-bottomed flask was sequentially added 2-thiophenesulfonamide (164 mg, 1.0 mmol), CH₂Cl₂ (3.0 mL) and (*E*)-cinnamaldehyde (0.126 mL, 1.0 mmol, 1.0 equiv), and the mixture was cooled to 0 °C. To the mixture was added Et₃N (0.279 mL, 2.0 mmol, 2.0 equiv) and then TiCl₄ (0.11 mL, 1.0 mmol, 1.0 equiv) dropwise and the resulting mixture was stirred for 1 h at 0 °C. The mixture was filtered through a pad of Celite and the filtrate was evaporated to give yellow-orange sticky oil, which was purified by flash silica gel column chromatography (hexane/AcOEt = 3/1) and

recrystallization (hexane/AcOEt = 2/1) to afford pure imine **2h** (207.8 mg, 75% yield). Following the same procedure, imine **2f** derived from furfural was obtained in 73% yield.

Preparation of Aliphatic *N*-(2-Thiophenesulfonyl) Imines: Aliphatic *N*-(2-thiophenesulfonyl) imines **2i**, **2j** and **2k** were prepared according to the literature method (González, A. S.; Gómez Arrayás, R.; Carretero, J. C. *Org. Lett.* **2006**, 8, 2977) with slight modification. α -Amidosulfones were prepared and purified by recrystallization according to the literature (Ooi, T.; Uematsu, Y.; Maruoka, K. *J. Am. Chem. Soc.* **2006**, 128, 2548). The α -amidosulfones were treated with Na₂CO₃/H₂O (1/1) mixture at 0 °C for 1 h as described below to give aliphatic imines, which were used for the Mannich-type reactions without further purification.

General Procedure for Preparation of Aliphatic *N*-(2-Thiophenesulfonyl) Imines: To a mixture of α -amidosulfone (0.20 mmol) in CH₂Cl₂ (0.57 mL) at 0 °C was added freshly prepared sat. aq. Na₂CO₃/H₂O = 1/1 (v/v) mixture (2.9 mL, 14 mL/mmol). The two-phase mixture was vigorously stirred for 1 h at 0 °C and diluted with H₂O and CH₂Cl₂. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was used for the Mannich-type reaction without further purification.

Preparation of Trichloromethyl Ketones: Trichloromethyl ketones **1a–1c** were prepared according to literature ((a) Corey, E. J.; Link, J. O.; Shao, Y. *Tetrahedron Lett.* **1992**, 33,

3435. (b) Morimoto, H.; Wiedemann, S. H.; Yamaguchi, A.; Harada, S.; Chen, Z.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3146 and references therein).

Preparation Method of a La(OAr)₃ Solution (Ar = *p*-MeO-C₆H₄-): To a round-bottomed flask was added *p*-methoxyphenol (37.2 mg, 0.30 mmol, 3.0 equiv) and the flask was cooled to 0 °C. A solution of La(O-*i*-Pr)₃ (0.50 mL, 0.20 M in THF, 0.10 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 30 min to afford a pale yellow solution (0.20 M for La(OAr)₃), which was immediately used without further manipulation.

Preparation Method of a LiOAr Solution (Ar = *p*-MeO-C₆H₄-): To a round-bottomed flask was added *p*-methoxyphenol (186.2 mg, 1.5 mmol) and THF (14.1 mL) and the flask was cooled to 0 °C. A solution of *n*-BuLi (Aldrich, 0.94 mL, 1.6 M in hexanes, 1.5 mmol, 1.0 equiv) was added dropwise and the resulting mixture was stirred at room temperature for 1 h to afford a colorless solution (0.10 M for LiOAr). The solution was kept to be active for several months when stored at room temperature under argon atmosphere in dark.

General Procedure for Mannich-type Reaction of *N*-(2-Thiophenesulfonyl) Imine (Table 2, entry 1): MS 3Å (40 mg, 200 mg/mmol) was placed on a test tube and was well dried under reduced pressure (around 1.0 kPa) using a heat gun. After cooling to room temperature, argon gas was re-filled and (*S,S*)-*i*-Pr-pybox (6.0 mg, 0.020 mmol, 10 mol %) and a solution of La(OAr)₃ (0.10 mL, 0.20 M in THF, 0.020 mmol, 10 mol %) were charged. The resulting orange suspension was stirred at 40 °C for 30 min and a solution of LiOAr (0.10 mL, 0.10 M in THF, 0.010 mmol, 5 mol %) was added. After stirring for additional 30 min at 40 °C, the solvent was removed under reduced pressure. After drying for 30 min under reduced pressure, THF (0.10 mL) was charged. The mixture was cooled to -40 °C and trichloromethyl ketone **1** (54 µL, 0.40 mmol, 2.0 equiv) was added. After 5 min, imine **2b** (50.3 mg, 0.20 mmol) was added as a solid and wall of the test tube was washed with toluene (0.10 mL). The resulting yellow to orange suspension was stirred for 9 h at

–40 °C and quenched with saturated aqueous NH_4Cl , extracted with AcOEt, washed with brine and dried over Na_2SO_4 . After evaporation of the solvent, the crude mixture was purified by flash silica gel column chromatography (hexane/ Et_2O = 6/1 to 1/1) to give the Mannich adduct **3b** (82.4 mg, 96% yield).

For reactions with 5 and 2.5 mol % of catalyst loading (Table 2, entry 13–15), 0.40 and 0.80 mmol of imine **2b** and **2g** were used, respectively.

(+)-N-[(1S,2S)-4,4,4-Trichloro-2-methyl-3-oxo-1-phenylbutan-1-yl]-2-thiophenesulfonamide (3b): a colorless solid; IR (KBr) ν 3365,

3111, 1739, 1456, 1405, 1334, 1155, 1090, 1055, 1021 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.30 (d, J = 6.7 Hz, 3 H), 3.22 (dq, J = 6.7, 9.2 Hz, 1 H), 4.81, (dd, J = 9.2, 9.2 Hz, 1 H), 4.89 (d, J = 9.2 Hz, 1 H), 6.10

(dd, J = 3.7, 5.0 Hz, 1 H), 6.44 (dd, J = 1.6, 5.0 Hz, 1 H), 6.64–6.72 (m, 2 H), 6.76–6.85 (m, 3 H), 7.08 (dd, J = 1.6, 3.7 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 17.9, 46.8, 61.1, 96.4, 127.0, 127.4, 128.1, 128.5, 131.7, 132.7, 138.6, 142.0, 190.9; LRMS (ESI): m/z 448, 450, 452 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{15}\text{H}_{14}^{35}\text{Cl}_2^{37}\text{ClCsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 559.8505, found: 559.8508; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 6.7 min (minor) and 11.2 min (major); $[\alpha]_D^{26}$ = +36.6 (c = 1.0, CHCl_3 , data for 95% ee sample).

(+)-N-[(1S,2S)-4,4,4-Trichloro-1-(4-chlorophenyl)-2-methyl-3-oxobutan-1-yl]-2-thiophenesulfonamide (3c): a colorless solid; IR

(KBr) ν 3279, 1744, 1496, 1437, 1406, 1345, 1229, 1163, 1094, 1058, 1026 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.26 (d, J = 7.0 Hz, 3 H), 3.16, (qd, J = 7.0, 9.0 Hz, 1 H), 4.72 (dd, J = 9.0, 9.5 Hz, 1

H), 5.03 (d, J = 9.5 Hz, 1 H), 6.11 (dd, J = 3.8, 5.0 Hz, 1 H), 6.44 (dd, J = 1.5, 5.0 Hz, 1 H), 6.49 (d, J = 8.5 Hz, 2 H), 6.78 (d, J = 8.5 Hz, 2 H), 7.06 (dd, J = 1.5, 3.8 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 17.7, 46.3, 60.3, 96.2, 127.0, 128.6, 128.9, 131.9, 132.8, 134.1, 137.1, 141.8, 190.7; LRMS (ESI): m/z 482, 484, 486 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{15}\text{H}_{13}^{35}\text{Cl}_2^{37}\text{Cl}_2\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 595.8086, found: 595.8084; HPLC

(chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 9.3 min (minor) and 16.8 min (major); $[\alpha]_D^{26}$ = +19.7 (c = 1.1, CHCl_3).

(+)-*N*-[(1*S*,2*S*)-4,4,4-Trichloro-2-methyl-1-(4-methylphenyl)-3-oxobutan-1-yl]-2-thiophenesulfonamide (3d):

a colorless solid; IR (KBr) ν 3378, 2926, 1744, 1437, 1406, 1345, 1164, 1058, 1025 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.36 (d, J = 6.8 Hz, 3 H), 1.92 (s, 3 H), 3.31 (qd, J = 6.8, 9.2 Hz, 1 H), 4.84 (dd, J = 9.2, 9.2 Hz, 1 H), 5.16 (d, J = 9.2 Hz, 1 H), 6.14 (dd, J = 3.7, 4.9 Hz, 1 H), 6.47 (dd, J = 1.2, 4.9 Hz, 1 H), 6.65 (d, J = 8.3 Hz, 2 H), 6.68 (d, J = 8.3 Hz, 2 H), 7.15 (dd, J = 1.2, 3.7 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 17.9, 20.9, 46.8, 60.9, 96.5, 126.9, 127.4, 129.1, 131.5, 132.6, 135.8, 137.7, 142.2, 191.0; LRMS (ESI): m/z 462, 464, 466 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{15}\text{H}_{14}^{35}\text{Cl}_2^{37}\text{ClCsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 573.8662, found: 573.8669; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 8.4 min (minor) and 14.9 min (major); $[\alpha]_D^{26}$ = +26.3 (c = 1.0, CHCl_3).

(+)-*N*-[(1*S*,2*S*)-4,4,4-Trichloro-1-(4-methoxyphenyl)-2-methyl-3-oxobutan-1-yl]-2-thiophenesulfonamide (3e):

a colorless solid; IR (KBr) ν 3271, 2933, 1752, 1612, 1517, 1442, 1403, 1377, 1328, 1275, 1254, 1164, 1128, 1111, 1093, 1071, 1027 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.32 (d, J = 6.7 Hz, 3 H), 3.12–3.22 (m, 1 H), 3.15 (s, 3 H), 4.60 (d, J = 9.2 Hz, 1 H), 4.78 (dd, J = 9.2, 9.2 Hz, 1 H), 6.13 (dd, J = 4.0, 5.2 Hz, 1 H), 6.43 (d, J = 8.6 Hz, 2 H), 6.45 (dd, J = 1.6, 5.2 Hz, 1 H), 6.57 (d, J = 8.6 Hz, 2 H), 7.10 (dd, J = 1.6, 4.0 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 18.2, 47.0, 54.7, 60.8, 96.6, 113.9, 127.0, 128.7, 130.6, 131.7, 132.7, 142.1, 159.7, 191.1; LRMS (ESI): m/z 478, 480, 482 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{16}\text{H}_{16}^{35}\text{Cl}_2^{37}\text{ClCsNO}_4\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 589.8611, found: 589.8615; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min;

detection: at 254 nm): t_R = 11.9 min (minor) and 21.0 min (major) ; $[\alpha]_D^{22}$ = +29.8 (c = 1.1, CHCl_3).

(+)-*N*-[(1*S*,2*S*)-4,4,4-Trichloro-1-(2-furyl)-2-methyl-3-oxobutan-1-yl]-2-thiophenesulfonamide (3f): a colorless solid; IR (KBr) ν 3332,

1749, 1445, 1403, 1335, 1230, 1155, 1056, 1023 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.30 (d, J = 6.9 Hz, 3 H), 3.27 (qd, J = 6.9, 10.3 Hz, 1 H), 4.51 (d, J = 10.3 Hz, 1 H), 4.81 (dd, J = 10.3, 10.3 Hz, 1 H), 5.49 (brd, J = 3.1 Hz, 1 H), 5.57 (dd, J = 1.7, 3.1 Hz, 1 H), 6.16 (dd, J = 3.5, 4.9 Hz, 1 H), 6.48 (dd, J = 1.2, 4.9 Hz, 1 H), 6.56 (brd, J = 1.7 Hz, 1 H), 7.05 (dd, J = 1.2, 3.5 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 18.2, 45.3, 55.0, 96.9, 108.7, 110.6, 127.0, 131.6, 132.4, 141.8, 142.0, 149.9, 190.8; LRMS (ESI): m/z 438, 440, 442 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{13}\text{H}_{12}^{35}\text{Cl}_2^{37}\text{ClCsNO}_4\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 549.8298, found: 549.8291; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 8.8 min (minor) and 14.1 min (major); $[\alpha]_D^{26}$ = +20.6 (c = 1.2, CHCl_3).

(+)-*N*-[(1*S*,2*S*)-4,4,4-Trichloro-2-methyl-3-oxo-1-(2-thienyl)butan-1-yl]-2-thiophenesulfonamide (3g): a colorless wax; IR (KBr) ν 3347,

1743, 1449, 1402, 1335, 1228, 1154, 1093, 1069, 1050, 1019 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.23 (d, J = 6.7 Hz, 3 H), 3.20 (qd, J = 6.7, 9.5 Hz, 1 H), 4.44 (d, J = 9.5 Hz, 1 H), 5.13 (dd, J = 9.5, 9.5 Hz, 1 H), 6.17 (dd, J = 3.7, 5.0 Hz, 1 H), 6.32 (dd, J = 3.2, 4.9 Hz, 1 H), 6.37 (brd, J = 3.2 Hz, 1 H), 6.48–6.54 (m, 2 H), 7.12 (dd, J = 1.5, 5.0 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 18.1, 47.8, 56.8, 96.4, 125.1, 126.6, 126.7, 127.1, 131.8, 132.7, 142.0, 142.2, 190.9; LRMS (ESI): m/z 454, 456, 458 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{13}\text{H}_{12}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_3^+$ [$\text{M}+\text{Cs}^+$]: 563.8099, found: 563.8101; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 9.5 min (minor) and 17.1 min (major); $[\alpha]_D^{22}$ = +43.8 (c = 1.2, CHCl_3).

(+)-*N*-[(3*R*,4*S*)-6,6,6-Trichloro-4-methyl-5-oxo-1-phenylhex-1-en

-3-yl]-2-thiophenesulfonamide (3h): a colorless solid; IR (KBr) ν

3326, 1738, 1430, 1404, 1341, 1286, 1224, 1158, 1089, 1058, 1017 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 1.25 (d, J = 6.7 Hz, 3 H), 3.11

(qd, J = 6.7, 8.6 Hz, 1 H), 3.97 (d, J = 8.6 Hz, 1 H), 4.22 (ddd, J =

8.6, 8.6, 8.6 Hz, 1 H), 5.44 (dd, J = 8.6, 15.6 Hz, 1 H), 5.92 (d, J = 15.6 Hz, 1 H), 6.19 (dd, J = 3.7, 4.9 Hz, 1 H), 6.46 (dd, J = 1.3, 4.9 Hz, 1 H), 6.89–6.96 (m, 2 H), 6.97–7.08 (m, 3

H), 7.26 (brd, J = 3.7 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 18.0, 45.9, 59.9, 96.7, 125.1,

126.8, 127.1, 128.3, 128.8, 131.7, 132.8, 133.5, 136.2, 142.5, 191.1; LRMS (ESI): m/z 474,

476, 478 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{17}\text{H}_{16}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]:

583.8691, found: 583.8691; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent:

hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 10.7 min

(minor) and 15.4 min (major); $[\alpha]_D^{27}$ = +8.2 (c = 0.99, CHCl_3).

(+)-*N*-[(1*R*,2*S*)-4,4,4-Trichloro-1-cyclohexyl-2-methyl-3-oxobutan-

1-yl]-2-thiophenesulfonamide (3i): a colorless solid; IR (KBr) ν

3355, 2932, 2849, 1741, 1450, 1405, 1335, 1229, 1152, 1118, 1094, 1065, 1034 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 0.45–0.59 (m, 1 H),

0.76–0.95 (m, 4 H), 1.05 (d, J = 7.0 Hz, 3 H), 1.03–1.15 (m, 1 H),

1.23–1.55 (m, 5 H), 3.17 (qd, J = 7.0, 7.0 Hz, 1 H), 3.87 (ddd, J = 3.7, 7.0, 9.8 Hz, 1 H),

4.04 (d, J = 9.8 Hz, 1 H), 6.33 (dd, J = 3.8, 5.1 Hz, 1 H), 6.63 (dd, J = 1.2, 5.1 Hz, 1 H),

7.36 (dd, J = 1.2, 3.8 Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 16.9, 26.1, 26.2, 26.4, 27.5,

31.2, 41.3, 41.9, 61.8, 96.9, 127.2, 131.2, 132.4, 143.8, 192.0; LRMS (ESI): m/z 454, 456,

458 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{15}\text{H}_{20}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 563.9004,

found: 563.9012; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent:

hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.6 min

(minor) and 10.1 min (major); $[\alpha]_D^{24}$ = +46.5 (c = 1.0, CHCl_3).

(+)-*N*-[(3*S*,4*R*)-1,1,1-Trichloro-3,6-dimethyl-2-oxoheptan-4-yl]-2-thiophenesulfonamid

e (3j): a colorless solid; IR (KBr) ν 3266, 2959, 1755, 1465, 1441, 1402, 1342, 1160, 1141,

1091, 1030, 1014 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 0.63 (d, $J = 6.4$ Hz, 3 H), 0.69 (d, $J = 6.4$ Hz, 3 H), 1.04 (d, $J = 7.0$ Hz, 3 H), 1.06–1.25 (m, 3 H), 3.32 (dd, $J = 7.0, 7.0$ Hz, 1 H), 3.70–3.81 (m, 1 H), 4.18 (d, $J = 8.6$ Hz, 1 H), 6.34 (dd, $J = 3.7, 5.0$ Hz, 1 H), 6.63 (dd, $J = 1.4, 5.0$ Hz, 1 H), 7.37 (dd, $J = 1.4, 3.7$ Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 16.8, 21.5, 23.2, 24.5, 43.0, 44.0, 55.7, 96.8, 127.1, 131.4, 132.2, 143.3, 191.6; LRMS (ESI): m/z 428, 430, 432 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{13}\text{H}_{18}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 537.8848, found: 537.8856; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R = 7.6$ min (minor) and 9.8 min (major); $[\alpha]_D^{26} = +43.3$ ($c = 1.1$, CHCl_3).

(+)-N-[(3S,4R)-6,6,6-Trichloro-2,4-dimethyl-5-oxohexan-3-yl]-2-thiophenesulfonamide (3k): a colorless solid; IR (KBr) ν 3357, 3116, 2974, 2931, 2876, 1739, 1451, 1406, 1374, 1344, 1327, 1231, 1152, 1131, 1095, 1067, 1031 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 0.45 (d, $J = 6.7$ Hz, 3 H), 0.60 (d, $J = 6.7$ Hz, 3 H), 1.11 (d, $J = 6.9$ Hz, 3 H), 1.44 (dq, $J = 3.7, 6.7, 6.7$ Hz, 1 H), 3.13 (qd, $J = 6.9, 8.4$ Hz, 1 H), 3.88 (ddd, $J = 3.7, 8.4, 9.9$ Hz, 1 H), 4.33 (d, $J = 9.9$ Hz, 1 H), 6.34 (dd, $J = 3.7, 4.9$ Hz, 1 H), 6.64 (dd, $J = 1.2, 4.9$ Hz, 1 H), 7.37 (dd, $J = 1.2, 3.7$ Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 16.6, 17.4, 20.7, 31.1, 42.6, 62.3, 96.9, 127.1, 131.2, 132.3, 143.9, 192.1; LRMS (ESI): m/z 414, 416, 418 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calculated for $\text{C}_{12}\text{H}_{16}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 523.8691, found: 523.8694; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R = 8.1$ min (minor) and 11.8 min (major); $[\alpha]_D^{26} = +24.2$ ($c = 1.5$, CHCl_3).

(+)-N-[(1S,2S)-4,4,4-Trichloro-2-ethyl-3-oxo-1-phenylbutan-1-yl]-2-thiophenesulfonamide (3l): a colorless solid; IR (KBr) ν 3362, 1737, 1458, 1403, 1332, 1154, 1062, 1048, 1019 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 0.81 (dd, $J = 7.6, 7.6$ Hz, 3 H), 1.54–1.68 (m, 1 H),

1.72–1.84 (m, 1 H), 3.32 (ddd, $J = 3.7, 7.4, 7.8$ Hz, 1 H), 4.87 (d, $J = 8.6$ Hz, 1 H), 4.99 (dd, $J = 7.8, 8.6$ Hz, 1 H), 6.11 (dd, $J = 4.0, 5.1$ Hz, 1 H), 6.46 (dd, $J = 1.4, 5.1$ Hz, 1 H), 6.71–6.79 (m, 2 H), 6.80–6.87 (m, 3 H), 7.09 (dd, $J = 1.4, 4.0$ Hz, 1 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 10.4, 22.7, 52.3, 59.1, 96.6, 127.1, 127.4, 127.9, 128.5, 131.7, 132.7,

138.7, 141.8, 189.4; LRMS (ESI): m/z 462, 464, 466 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calculated for $\text{C}_{16}\text{H}_{16}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ $[\text{M}+\text{Cs}^+]$: 571.8691, found: 571.8699; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R = 8.7$ min (minor) and 14.6 min (major); $[\alpha]_D^{26} = +5.5$ ($c = 1.0$, CHCl_3).

(–)-N-[(1S,2S)-4,4,4-Trichloro-1-(4-chlorophenyl)-2-ethyl-3-oxobutan-1-yl]-2-thiophenesulfonamide (3m): a colorless solid; IR (KBr) ν 3354, 3272, 1748, 1493, 1459, 1443, 1404, 1347, 1162,

1092, 1056, 1025 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 0.82 (dd, $J = 7.3, 7.3$ Hz, 3 H), 1.57 (dq, $J = 3.8, 7.3, 14.7$ Hz, 1 H), 1.78 (dq, $J = 7.3, 7.3, 14.7$ Hz, 1 H), 3.23 (ddd, $J = 3.8, 7.3, 8.1$ Hz, 1 H), 4.88 (dd, $J = 8.1, 8.9$ Hz, 1 H), 4.91 (d, $J = 8.9$ Hz, 1 H), 6.11 (dd, $J = 3.8, 4.9$ Hz, 1 H), 6.45 (dd, $J = 1.4, 4.9$ Hz, 1 H), 6.51 (d, $J = 8.4$ Hz, 2 H), 6.81 (d, $J = 8.4$ Hz, 2 H), 7.05 (dd, $J = 1.4, 3.8$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 10.9, 21.8, 51.6, 58.5, 95.8, 127.4, 128.3, 128.6, 132.5, 132.9, 133.9, 136.7, 140.0, 189.6; LRMS (ESI): m/z 498, 496, 500, 502 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calculated for $\text{C}_{16}\text{H}_{15}^{35}\text{Cl}_2^{37}\text{Cl}_2\text{CsNO}_3\text{S}_2^+$ $[\text{M}+\text{Cs}^+]$: 609.8243, found: 609.8244; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R = 7.8$ min (minor) and 12.4 min (major); $[\alpha]_D^{26} = -8.4$ ($c = 1.2$, CHCl_3).

(–)-N-[(1S,2S)-2-Benzyl-4,4,4-trichloro-3-oxo-1-phenylbutan-1-yl]-2-thiophenesulfonamide: a colorless solid; IR (KBr) ν 3349, 1737, 1456, 1440, 1405, 1329, 1150, 1064, 1019 cm^{-1} ; ^1H NMR (C_6D_6 , 500 MHz) δ 2.78–2.85 (m, 2 H), 3.73 (ddd, $J = 5.5, 5.7, 8.0$ Hz, 1 H), 5.08

(d, $J = 7.5$ Hz, 1 H), 5.13 (dd, $J = 5.7, 7.5$ Hz, 1 H), 6.17 (dd, $J = 3.7, 5.2$ Hz, 1 H), 6.50 (dd, $J = 1.6, 5.2$ Hz, 1 H), 6.86–6.90 (m, 2 H), 6.90–6.97 (m, 6 H), 6.98–7.03 (m, 2 H), 7.16–7.20 (m, 1 H); ^{13}C NMR (acetone- d_6 , 125 MHz) δ 36.2, 55.1, 61.0, 96.8, 127.7, 128.0, 128.7, 129.2, 129.2, 130.4, 132.8, 132.8, 138.4, 139.2, 143.2, 189.5; LRMS (ESI): m/z 524, 526, 528 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calculated for $\text{C}_{21}\text{H}_{18}^{35}\text{Cl}_2^{37}\text{ClCsNO}_3\text{S}_2^+$ $[\text{M}+\text{Cs}^+]$: 635.8815, found: 635.8813; HPLC (chiral column: DAICEL CHIRALPAK OD-H; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): $t_R = 7.2$ min (minor) and 18.4 min (major); $[\alpha]_D^{26} = -13.4$ ($c = 1.0$, CHCl_3).

Determination of relative and absolute configuration of Mannich adducts: Relative and absolute configuration of Mannich adduct **3b** was determined after conversion to known β -amino acid methyl ester **A** as shown in Scheme below. The chemical shifts of ^1H NMR spectrum were matched with the reported values of *syn*-product. Chiral HPLC analysis of **3b** under the reported conditions showed the absolute stereochemistry was (2*S*,3*S*) [Lit. Seerden, J.-P. G.; Kuypers, M. M. M.; Scheeren, H. W. et al. *Tetrahedron: Asymmetry* **1995**, 6, 1441]. Relative and absolute configuration of the Mannich adduct **3j** was determined after conversion to Boc-protected β -amino acid methyl ester **C** as shown in Scheme below. The chemical shifts of ^1H and ^{13}C NMR spectra were matched with reported values of *syn*-product [Lit. Seebach, D.; Abele, S.; Gademann, K.; Guichard, G.; Hintermann, T.; Jaun, B.; Matthews, J. L.; Schreiber, J. V. *Helv. Chim. Acta* **1998**, 81, 932]. The absolute configuration was determined to be (2*S*,3*R*) based on the comparison of reported and observed optical rotation values. Relative and absolute configurations of other Mannich adducts were tentatively assigned by analogy.

Transformation of the Mannich adduct

To ester **4**. (–)-Methyl (2*S*,3*S*)-2-methyl-3-phenyl-3-[(2-thiophenesulfonyl)amino]propionate (**4**):

To a solution of Mannich adduct **3b** (85.4 mg, 0.20 mmol) in MeOH (1 mL) at 0 °C was added NaOMe (4.0 mL, 0.1 M in MeOH, 0.40 mmol, 2.0 equiv) and the mixture was stirred for 20 min at 0 °C.

The reaction mixture was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified by flash silica gel column chromatography to afford **4** as a colorless solid (68.0 mg, quantitative yield). IR (KBr) ν 3259, 2979, 1719, 1329, 1161 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.17 (d, $J = 7.3$ Hz, 3 H), 2.91 (dq, $J = 7.0, 6.7$ Hz, 1 H), 3.53 (s, 3 H), 4.62 (dd, $J = 8.9, 6.7$ Hz, 1 H), 5.71 (d, $J = 8.9$ Hz, 1 H), 6.85 (dd, $J = 4.9, 3.1$ Hz, 1 H), 7.02–7.04 (m, 2 H), 7.16–7.18 (m, 3 H), 7.31 (d, $J = 3.1$ Hz, 1 H), 7.40 (d, $J = 4.9$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.5, 45.8, 51.9, 60.1, 126.9, 127.0, 127.8, 128.3, 131.7, 132.3, 137.7, 141.4, 173.7; LRMS (ESI): m/z 362 [$\text{M}+\text{Na}^+$]; HRMS (FAB): calculated for $\text{C}_{15}\text{H}_{17}\text{CsNO}_4\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 471.9653, found: 471.9652; $[\alpha]_D^{24} = -18.0$ ($c = 1.08$, CHCl_3).

To Boc-protected ester 5. (–)-Methyl

(2*S*,3*S*)-3-[(*tert*-butoxycarbonyl)amino]-2-methyl-3-phenylpropionate (5): To a test tube was added ester **4** (33.9 mg, 0.10 mmol), Boc₂O

(2.0 mL, 0.15 M in MeCN, 0.30 mmol, 3.0 equiv) under argon, and

then DMAP (12.2 mg, 0.10 mmol, 1.0 equiv) was added in one portion. The mixture was stirred at room temperature for 2 h. After removal of the solvent under vacuum, the residue was purified by flash silica gel column chromatography to afford *N*-Boc-protected compound as a colorless oil (42.9 mg, 98% yield), which was transferred into another well dried test tube with 2 mL anhydrous MeOH. Mg (0) (48.6 mg, 212–600 μm, 2.0 mmol, 20 equiv) was added in 2 portions and the mixture was stirred under argon at room temperature for 4 h. Then the reaction was quenched with saturated aq. NH₄Cl and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by flash silica gel column chromatography to afford **5** as a colorless solid (27.4 mg, 95% yield). IR (KBr) ν 3384, 2977, 1734, 1685, 1524, 1264, 1174 cm^{–1}; ¹H NMR (CDCl₃, 500 MHz) δ 1.14 (d, *J* = 7.0 Hz, 3 H), 1.42 (brs, 9 H), 2.92 (brs, 1 H), 3.59 (s, 3 H), 5.00 (brs, 1 H), 5.34 (brs, 1 H), 7.22–7.33 (m, 5 H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.0, 28.3, 45.3, 51.7, 56.4, 79.6, 126.7, 127.5, 128.4, 140.0, 155.1, 174.2; LRMS (ESI): *m/z* 316 [M+Na]⁺; HRMS (FAB): calculated for C₁₆H₂₃N₂O₄⁺ [M+Cs⁺]: 426.0682; found: 426.0681; [α]_D²⁵ = –18.4 (*c* = 1.10, CHCl₃).

To dithiane 6. (+)-*N*-[(2*S*, 3*S*)-4,4-bis(ethylthio)-2-methyl-3-oxo-1-phenylbutan-1-yl]-2-thio

phenesulfonamide (6): To a solution of Mannich adduct **3b** (17.1 mg, 0.040 mmol) in THF (0.40 mL) at 0 °C was added a suspension

of LiSEt/EtSH in THF (0.20 mL, prepared from EtSH (0.15 mL, 97% assay, 1.96 mmol) and *n*-BuLi (1.0 mL, 1.6 M in hexane, 1.6 mmol) in THF (1 mL) at 0 °C). The mixture was stirred at 0 °C for 30 min, quenched with saturated aq. NH₄Cl and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by

flash silica gel column chromatography to afford **6** as a colorless solid (13.9 mg, 79% yield). IR (KBr) ν 3330, 2966, 2926, 1697, 1332, 1155, 1025 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.94 (dd, $J = 7.5, 7.5$ Hz, 3 H), 1.17 (dd, $J = 7.5, 7.5$ Hz, 3 H), 1.31 (d, $J = 7.0$ Hz, 3 H), 1.72-1.79 (m, 1 H), 2.23-2.30 (m, 1 H), 2.30-2.37 (m, 1 H), 2.42-2.49 (m, 1 H), 3.38-3.44 (m, 1 H), 4.13 (s, 1 H), 4.54 (dd, $J = 8.2, 7.7$ Hz, 1 H), 5.18 (d, $J = 7.7$ Hz, 1 H), 6.87 (dd, $J = 5.1, 3.9$ Hz, 1 H), 7.05-7.07 (m, 2 H), 7.16-7.17 (m, 3 H), 7.34 (dd, $J = 3.9, 1.4$ Hz, 1 H), 7.41 (dd, $J = 5.1, 1.4$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.7, 14.0, 15.3, 23.3, 24.2, 48.8, 57.9, 60.5, 127.0, 127.2, 127.8, 128.4, 131.9, 132.6, 138.6, 140.9, 201.8; LRMS (ESI): m/z 466 [$\text{M}+\text{Na}^+$]; HRMS (FAB): calculated for $\text{C}_{19}\text{H}_{25}\text{CsNO}_3\text{S}_4^+$ [$\text{M}+\text{Cs}^+$]: 575.9772, found: 575.9776; $[\alpha]_{\text{D}}^{25} = +19.2$ ($c = 1.00$, CHCl_3).

To *syn*-trichloromethyl carbinol **7**.

(+)-*N*-[(1*S*,2*S*,3*R*)-4,4,4-Trichloro-3-hydroxy-2-methyl-1-phenylbutan-1-yl]-2-thiophenesulfonamide (7): A 20 mL round-bottomed

flask was charged with Mannich adduct **3b** (29.9 mg, 0.070 mmol) and CH_2Cl_2 (3.5 mL) under argon. The solution was cooled to -78°C

and DIBAL-H (0.28 mL, 1.0 M in toluene, 0.28 mmol, 4.0 equiv) was slowly added dropwise by syringe with stirring. The reaction mixture was stirred for 5 h at -78°C and for 2.5 h at -40°C , and then quenched with saturated aq. Rochelle's salt (3 mL) at -40°C with rapid stirring. The product was extracted with ethyl acetate, and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified by flash silica gel column chromatography to afford **7** as a colorless foam (30.6 mg, quantitative yield). IR (neat) ν 3484, 3282, 2926, 1325, 1157, 1020 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.04 (d, $J = 7.0$ Hz, 3 H), 2.64-2.70 (m, 1 H), 2.98 (d, $J = 5.5$ Hz, 1 H), 3.95 (dd, $J = 5.5, 1.6$ Hz, 1 H), 4.63 (dd, $J = 7.9, 5.7$ Hz, 1 H), 5.30 (d, $J = 7.9$ Hz, 1 H), 6.90 (dd, $J = 5.1, 3.9$ Hz, 1 H), 7.09-7.11 (m, 2 H), 7.19-7.23 (m, 3 H), 7.39 (dd, $J = 3.9, 1.6$ Hz, 1 H), 7.45 (dd, $J = 5.1, 1.6$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 8.1, 40.9, 63.0, 82.8, 103.6, 126.4, 127.2, 127.6, 128.4, 132.0, 132.6, 138.4, 140.9; LRMS (ESI): m/z 450 [$\text{M}+\text{Na}^+$]; HRMS (FAB): calculated for $\text{C}_{15}\text{H}_{16}^{35}\text{Cl}_3\text{CsNO}_3\text{S}_2^+$ [$\text{M}+\text{Cs}^+$]: 559.8691, found: 559.8698; $[\alpha]_{\text{D}}^{23} = +4.4$ ($c = 1.09$, CHCl_3).

To *anti*-trichloromethyl carbinol **8**.

(-)-*N*-[(1*S*,2*S*,3*S*)-4,4,4-Trichloro-3-hydroxy-2-methyl-1-phenylbutan-1-yl]-2-thiophenesulfonamide (**8**):

A 20 mL round-bottomed flask was charged with Mannich adduct **3b** (29.9 mg, 0.070 mmol), Ph₃P=O (79.5 mg, 98% assay, 0.28 mmol, 4.0 equiv) and THF (3.5 mL) under argon. The solution was cooled to -78 °C and DIBAL-H (0.14 mL, 1.0 M in toluene, 0.14 mmol, 2.0 equiv) was slowly added dropwise by syringe with stirring. The reaction mixture was stirred for 1 h at -78 °C and 1 h at -40 °C, and then quenched with saturated aq. Rochelle's salt (3 mL) at -40 °C with rapid stirring. The product was extracted with ethyl acetate, and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by flash silica gel column chromatography to afford **8** as a colorless foam (29.7 mg, 99% yield). IR (neat) ν 3481, 3290, 1323, 1159, 1019 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.09 (d, *J* = 7.3 Hz, 3 H), 2.32-2.39 (m, 1 H), 3.55 (d, *J* = 4.9 Hz, 1 H), 4.07 (dd, *J* = 7.2, 4.9 Hz, 1 H), 5.19 (dd, *J* = 9.1, 2.2 Hz, 1 H), 5.62 (d, *J* = 9.1 Hz, 1 H), 6.86 (dd, *J* = 5.1, 4.0 Hz, 1 H), 7.08 -7.13 (m, 2 H), 7.17-7.24 (m, 3 H), 7.37 (brd, *J* = 4.0 Hz, 1 H), 7.42 (brd, *J* = 5.1 Hz, 1 H); ¹³C NMR (CDCl₃, 125 MHz) δ 12.5, 43.7, 58.9, 83.4, 103.1, 126.5, 127.1, 127.3, 128.3, 132.0, 132.5, 138.3, 140.8; LRMS (ESI): *m/z* 450 [M+Na⁺]; HRMS (FAB): calculated for C₁₅H₁₆³⁵Cl₂³⁷ClSNO₃S₂⁺ [M+Cs⁺]: 561.8662, found: 561.8655; [α]_D²⁵ = -9.6 (*c* = 1.19, CHCl₃).

Determination of relative configuration of trichloromethyl carbinols: Relative configurations of trichloromethyl carbinols **7** and **8** were determined by NOE experiment after conversion to cyclic carbamates **D** and **E**. These experimental results were summarized in Scheme shown below.

To cyclic carbamate **D and **E**:** To a stirred solution of **7** (or **8**) (8.6 mg, 0.020 mmol) in CH_2Cl_2 (0.40 mL) at -78°C was added pyridine (32 μL , 0.40 mmol, 20 equiv) and triphosgene (14.4 mg, 0.050 mmol, 2.5 equiv). The mixture was stirred and gradually warmed to room temperature within 3 h. The reaction was quenched with 1 M aq. HCl, extracted with ethyl acetate. The organic layer was washed with saturated aq. NaHCO_3 and brine, and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was purified by flash silica gel column chromatography to afford cyclic carbamate **D** (or **E**).

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POINT 131072
FREQ 31133.25 Hz
SCANS 212
ACQTM 1.0525 sec
PD 2.0000 sec
PWI 3.57 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.42 Hz
RGAIN 66

DFILE C:\My Documents\PGousei\morimoto070419de1ta8070419fury\rac
COMMIT single_pulse
DATIM 19-04-2007 21:13:19
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 kHz
OBFIN 9.64 Hz
POINT 13107
FREQU 7429.31 Hz
SCANS 12
ACQTM 1.7642 sec
PD 5.0000 sec
PM1 6.20 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.12 Hz
RGAIN 56

DFILE
COMMIT
DATIM
OBNUC
EXMOD
OBERQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PM1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\PGousei\morimoto\070418fury\rac
single pulse decoupled gated NOE
19-04-2007 01:53:43
13C
single pulse dec
124.51 MHz
3.45 KHz
6.00 Hz
104856
31249.52 Hz
1995
0.8889 sec
2.0000 sec
3.57 usec
1H
20.7 c
C6D6
128.06 ppm
0.12 Hz
60

C:\Documents and Settings\NMRmanager\

DFILE COMNT DATIM OBNUC EXMOD OBFRQ OBSET OBFIN POINT FREQU SCANS ACQTM PD PW1 IIRNUC CTEMP SLVNT EXREF BB RGAIN

TH Line 8 21:42:57 2007

1H non

you

500.00 MHz

160.00 KHZ

2160.0 Hz

32768

10000.0 Hz

9
771 0.00001

3.277 sec

3.723 sec

5.7 ns

1H 3.7 us

24.8 c

C6D6
Z4.0 C

7.16 ppm

1.16 ppm
1.20 Hz

1.20 Hz
22

DFILE
CONNT
DATIM
OBNUC
EXMOD
OBERQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWI
TRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\Gousei\morimoto070419del\ta8\070308thierac
single pulse decoupled gated NOE
09-03-2007 00:21:50
13C
single pulse dec
124.51 MHz
3.45 kHz
6.00 Hz
104856
31249.52 Hz
212
0.8389 sec
2.0000 sec
3.57 usec
1H
20.2 c
C6D6
128.06 ppm
0.42 Hz
60

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Sat Mar 10 00:24:02 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 8
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 24.8 c
SLVNT C6D6
EXREF 7.16 ppm
BF 1.20 Hz
RGAIN 23

DFILE C:\My Documents\PGousei\morimoto070419del\ta8\070310thiecin
COMMT single pulse decoupled gated NOE
DATIM 10-03-2007 23:43:35
OBNUC 13C
EXMOD single pulse dec
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 104856
FREQU 31249.52 Hz
SCANS 433
ACQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.22 Hz
RGAIN 60

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Documents and Settings\NMRmanager\
1H Line
Tue Mar 13 17:12:13 2007
1H
non
500.00 MHz
160.00 KHz
2160.0 Hz
32768
10000.0 Hz
8
3.277 sec
3.723 sec
5.7 us
1H
24.8 C
C6D6
7.16 ppm
1.20 Hz
22

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Tue Mar 13 18:39:13 2007
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 92
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 25.7 c
SLVNT C6D6
EXREF 128.06 ppm
BF 1.20 Hz
RGAIN 26

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line 16 23:40:33 2007
DATIM Fri Mar 16 23:40:33 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQ 10000.0 Hz
SCANS 6
ACQTM 3.277 sec
PD 3.723 sec
PW 5.7 us
IRNUC 1H
CTEMP 23.8 c
SIVNT C6D6
EXREF 7.16 ppm
BF 1.20 Hz
RGAIN 19

DFILE
COMMIT
DATIM
OBNUC
EXMOD
OBFREQ
OBFSET
OBFIN
POINT
FREQ
SCANS
AQTM
PD
PWI
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\PPGousei\morimoto070419del\ta8\070316thierBur
single pulse decoupled gated NOE
16-03-2007 23:50:58
13C
single pulse dec
124.51 MHz
3.45 KHz
6.00 Hz
104856
31249.52 Hz
176
0.8389 sec
2.0000 sec
3.57 usec
20.7 c
C6D6
128.06 ppm
0.12 Hz
60

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Wed Jun 20 22:49:14 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 9
ACQTM 3.277 sec
PD 3.723 sec
PWL 5.7 us
IRNUC 1H
CTEMP 26.3 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.12 Hz
RGAIN 20

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Sat Jun 23 19:00:45 2007
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 131072
FREQU 33898.3 Hz
SCANS 90
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 26.9 c
SLVNT C6D6
EXREF 128.06 ppm
BF 0.12 Hz
RGAIN 26

C:\Documents and Settings\NMRmanager\
1H Line Wed Apr 4 10:21:48 2007
1H
EXMOD non
OBFQ 500.00 MHz
OBSE 160.00 KHz
OBFN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 9
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 25.2 C
SLVNT C6D6
EXREF 7.16 ppm
BF 1.20 Hz
RGAIN 22

C:\My Documents\PGousei\morimoto070419delta8¥070404LithiePrTCMKracMP13C.als
single pulse decoupled gated NOE

```

C:\my Documents\wpGousei\mori\moto070419del\ta070404\lithiepr
single_pulse decoupled gated NOE
04-04-2007 14:55:50
13C
single_pulse_dec
124.51 MHz
3.45 KHz
6.00 Hz
104856
31249.52 Hz
327
0.8359 sec
2.0000 sec
3.57 usec
1H
C066
128.06 ppm
0.12 Hz
60
BF
RGAIN

```

1H Line

DFILE C:\Documents and Settings\NMRmanager\
 1H Line 1H Line
 DATIM Sun Jun 17 00:01:04 2007
 OBNUC 1H
 EXMOD non
 OBSFQ 500.00 MHz
 OBSST 160.00 KHz
 OBFIN 2160.0 Hz
 POINT 32768
 FREQU 10000.0 Hz
 SCANS 6
 ACQTM 3.277 sec
 PD 3.723 sec
 PW1 5.7 us
 IRNUC 1H
 CTEMP 25.0 C
 SLVNT C6D6
 EXREF 7.16 ppm
 BF 0.12 Hz
 RGAIN 22

DFILE C:\My Documents\Gousei\morimoto\070419del\ta8\070622pClPrchi
COMMIT single pulse decoupled gated NOE
DATIM 22-06-2007 16:57:10
OBNUC 13C
EXMOD single pulse dec
OBSFQ 124.51 MHz
OBSF 3.45 kHz
OBFIN 6.00 Hz
POINT 104856
FREQU 31249.52 Hz
SCANS 52
AQTM 0.8389 sec
PD 2.0000 sec
PW1 3.57 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

DFILE
COMNT 1H Line
DATIM Thu Apr 26 21:24:12 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREOU 10000.0 Hz
SCANS 16
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 24

DFILE C:\Documents and Settings\NMRmanager\
1H Line
COMNT Wed Feb 28 14:35:17 2007
DATIM 13C
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 70
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Sun Mar 25 17:10:21 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 16
ACQTM 3.277 sec
PD 3.723 sec
PWL 5.7 us
IRNUC 1H
CTEMP 25.2 c
SIVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 21

DFILE C:\Documents and Settings\NMRmanager\

COMNT 1H Line
DATIM Sun Mar 25 18:09:34 2007

OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 1066
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30

S-45

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Thu Mar 1 14:05:54 2007
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 17
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 26

DFILE
COMNT 1H Line
DATIM Thu Mar 1 14:38:53 2007
OBNUC 13C
EXMOD bcm
OBFREQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 343
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 31

DFILE 1H Line
COMET 1H Line
DATIM Thu Mar 1 11:11:09 2007
OBNUC 1H
EXMOD non
OBFRO 500.00 MHz
OBFSE 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 20
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 25.3 c
SIVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 26

DFILE C:\Documents and Settings\NMRmanager\
COMNT 1H Line
DATIM Thu Mar 1 11:50:33 2007
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 202
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 26.6 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30

DFILE C:\Documents and Settings\NMRmanager\
 COMNT 1H Line
 DATIM Sat Mar 10 14:39:19 2007
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.0 Hz
 POINT 32768
 FREQU 10000.0 Hz
 SCANS 16
 ACQTM 3.277 sec
 PD 3.723 sec
 PW1 5.7 us
 IRNUC 1H
 CTEMP 24.5 c
 SILVT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 26

DFILE
COMNT 1H Line
DATIM Sat Mar 10 15:09:24 2007
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 519
ACQTM 0.967 sec
PD 2.033 sec
PW1 6.2 us
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30

C:\Documents and Settings\NMRmanager\

DFILE 1H Line
COMET Wed Apr 4 10:43:06 2007
OBNUC 1H
EXMOD non
OBFREQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 10
ACQTM 3.277 sec
PD 3.723 sec
PW1 5.7 us
IRNUC 1H
CTEMP 25.8 c
SLVNT C6D6
EXREF 7.16 ppm
BF 0.12 Hz
RGAIN 23

DFILE
CONIT
DATIM
OBNUC
EXMOD
OBFREQ
OBFSET
OBFIN
POINT
FREQ
SCANS
ACQTM
PD
PM1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\Gousei\morimoto070419del1ta070404L1thiePh
single pulse decoupled gated NOE
04-04-2007 23:51:01
13C
single pulse dec
124.51 MHz
3.45 KHz
6.00 Hz
104856
31249.52 Hz
433
0.8389 sec
2.0000 sec
3.57 usec
1H
20.6 c
ACETN
29.84 ppm
0.12 Hz
60