# Supplementary Material (ESI) for Chemical Communications


**Supporting Information**

# The Antituberculosis, Antitumor, Multibranched Dodecafuranoarabinan of *Mycobacterium* Species has been Assembled from a Single n-Pentenylfuranoside Source

Jun Lu and Bert Fraser-Reid*,

*Natural Products and Glycotechnology Research Institute, Inc.*
*4118 Swarthmore Road*
*Durham, NC 27707 USA*
dglucose@aol.com

**3,5-Di-*O*-chloroacetyl-β-D-arabinofuranose 1,2-(Pent-4-enyl orthobenzoate) (4d)**

To a solution of **4b**[1] (645 mg, 2.08 mmol), Py. (1mL) and DMAP (50 mg) in $CH_2Cl_2$ (10 mL) at –10 °C was added $(ClAc)_2O$ (1.07 g, 6.24 mmol). The mixture was stirred for 30 min at –10 °C. Water (2 mL) was added to quench the reaction. The aqueous phase was extracted with $CH_2Cl_2$ (2x10 mL). The organic phase was dried ($Na_2SO_4$) and was evaporated. The residue was purified by column chromatography (Hexane: EtOAc: $Et_3N$, 4:1:0.1) to give compound **4d** (706 mg, 73%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.52 (m, 2H), 7.27 – 7.31 (m, 3H), 6.12 (d, J=6.0 Hz, 1H), 5.58 – 5.71 (m, 1H), 5.11 – 5.12 (d, J = 0.6 Hz, 1H), 4.90 – 4.92 (m, 1H), 4.86 (s, 1H), 4.83 (m, 1H), 4.24 (t, J=7.2, 7.2 Hz, 1H), 4.00 (s, 1H), 3.96 (d, J=6.9 Hz, 1H), 3.89 (d, J=1.8 Hz, 1H), 3.20 (m, 2H), 1.97 (m, 1H), 3.89 (d, J=1.8 Hz, 1H), 3.20 (m, 2H), 1.97 (m, 1H), 1.52 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.7, 166.2, 137.8, 135.5, 129.7, 128.4, 128.6, 126.1, 123.1, 115.0, 106.3, 84.3, 83.4, 78.7, 64.5, 32.2, 40.7, 40.6, 30.3, 28.7. MS (MALDI) for $C_{21}H_{24}Cl_2O_8$ Calcd. 474.0, Found 473.0 ($M\text{-}H^+$).

**Pent-4-enyl 5-*O*-(2-*O*-benzoyl-3,5-di-*O*-chloroacetyl-α-D-arabinofuranosyl)-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (6a).**

# Supplementary Material (ESI) for Chemical Communications


To a solution of acceptor **5**[1] (200 mg, 0.48 mmol), NIS (311 mg, 1.45 mmol) and Yb $(OTf)_3$ (90 mg, 0.14 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C was added donor **4d** (460 mg, 0.97 mmol in $CH_2Cl_2$ (10 mL)) dropwise until the acceptor was consumed. Aqueous $Na_2S_2O_3$ (10%, 5 mL) was added to quench the reaction. The aqueous phase was extracted with $CH_2Cl_2$ (2x10 mL). The organic phase was dried ($Na_2SO_4$) and was evaporated. The residue was purified through column chromatography to give compound **6a** (265 mg, 69%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.96 – 8.06 (m, 4H), 7.22 – 7.60 (m, 11H), 5.80 (m, 1H), 5.39 (s, 1H), 5.29 (d, J=8.1 Hz, 2H), 5.17 (s, 1H), 4.85 – 5.06 (m, 4H), 4.66 (d, J=12.6 Hz, 1H), 4.50 (dd, J=3.6, 11.7 Hz, 1H), 4.31 (m, 2H), 3.86 – 4.13 (m, 6H), 3.60 – 3.78 (m, 3H), 3.48 (m, 1H), 2.15 (m, 2H), 1.74 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.9, 166.5, 165.4, 165.0, 138.1, 137.8, 133.8, 133.9, 129.7, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 114.9, 106.1, 105.6, 82.6, 81.9, 81.6, 81.2, 80.6, 78.7, 71.9, 67.00, 66.1, 64.4, 40.7, 40.4, 30.4, 28.8. MS (MALDI) for $C_{40}H_{42}Cl_2O_{13}$ Calcd. 800.2, Found 824.0 ($M+Na^+$)

**Pent-4-enyl 5-*O*-(2-*O*-benzoyl-α-D-arabinofuranosyl)-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (6b).**

The solution of compound **6a** (85 mg, 0.10 mmol) and thiourea (35 mg, 0.46 mmol) in THF (1 mL) and EtOH (1 mL) was refluxed for 5h until **6a** was consumed. The solvent was evaporated. The residue was purified by column chromatography (Hexane: EtOAc 1:1) to give compound **6b** (39 mg, 61%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.94 – 8.02 (m, 4H), 7.21 – 7.57 (m, 11H), 5.79 (m, 1H), 5.37 (s, 1H), 5.29 (s, 1H), 5.14 (s, 1H), 5.05 (s, 1H), 4.96 (m, 1H), 4.80 (d, J=12.0 Hz, 1H), 4.60 (d, J=12.0 Hz, 1H), 4.33 (m, 3H), 4.00 – 4.14 (m, 3H), 3.69 – 3.93 (m, 5H), 3.49 (m, 1H), 2.14 (m, 2H), 1.73 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.6, 165.5, 138.2, 137.6, 137.2, 133.7, 133.5, 129.8, 128.5, 128.4, 128.0, 127.9, 120.6, 114.9, 106.2, 105.3, 86.1, 84.3, 83.4, 82.1, 81.5, 76.5, 72.4, 67.1, 66.2, 61.9, 30.4, 28.8. MS (MALDI) for $C_{36}H_{40}O_{11}$ Calcd. 648.2, Found 672.2 ($M+Na^+$)

**Pent-4-enyl 5-*O*-{2-*O*-benzoyl-3,5-di-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (7a).**

Acceptor **6b** (47 mg, 0.072 mmol) was coupled with **4d** (180 mg, 0.36 mmol) to give compound **7a** (71 mg, 67%), according to the procedure as described for compound **6a**.

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.89 – 8.03 (m, 8H), 7.13 – 7.54 (m, 37H), 5.78 (m, 1H), 5.11 – 5.52 (m, 8H), 4.97 (m, 2H), 4.19 – 4.79 (m, 16H), 3.42 – 4.04 (m, 12H), 2.13 (m, 2H), 1.71 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.4, 165.2, 165.1, 138.2, 137.9, 137.8, 137.8, 137.7, 133.3, 129.8, 129.7, 129.4, 129.00, 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 125.3, 114.8, 106.2, 106.0, 105.4, 83.5, 83.3, 83.2, 82.7, 82.6, 82.4, 82.2,

81.8, 81.7, 81.5, 80.0, 73.4, 73.3, 72.6, 72.2, 71.9, 69.3, 69.1, 66.9, 65.8, 65.3, 30.4, 28.8, 21.6. MS (MALDI) $C_{88}H_{88}O_{21}$, Calcd. 1480.5, Found 1503.4 ($M+Na^+$)

**5-*O*-{2-*O*-Benzoyl-3,5-di-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranose (7b).**

To a solution of compound **7a** (70 mg, 0.047 mmol) in $CH_3CN$ (5 mL) and water (0.5 mL) was added NIS (30 mg, 0.14 mmol). The mixture was stirred at r.t. for 1h. Aqueous $Na_2S_2O_3$ solution (10%, 5 mL) was added to quench the reaction. The aqueous phase was extracted with $CH_2Cl_2$ (2x20 mL). The organic phase was dried ($Na_2SO_4$) and was evaporated. The residue was purified by column chromatography to give compound **7b** (50 mg, 74%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.89 – 8.01 (m, 8H), 7.15 – 7.53 (m, 37H), 5.08 – 5.50 (m, 8H), 4.16 – 4.77 (m, 14H), 3.49 – 4.03 (m, 10H), 3.14 – 3.29 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.4, 165.3, 165.2, 138.1, 138.0, 138.0, 137.9, 137.8, 137.7, 133.4, 133.3, 129.9, 129.8, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.6, 127.6, 106.3, 106.2, 105.6, 105.4, 83.6, 83.4, 82.8, 82.7, 82.5, 81.9, 81.8, 81.1, 80.2, 80.0, 73.5, 72.8, 72.7, 72.6, 72.3, 72.0, 70.6, 69.4, 69.2, 67.3, 66.9, 66.2, 65.5. MS (MALDI) for $C_{83}H_{80}O_{21}$, Calcd. 1412.5, Found 1436.8 ($M+Na^+$).

**5-*O*-{2-*O*-Benzoyl-3,5-di-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl}-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl Trichloroacetamide (7c).**

To a solution of compound **7b** (150 mg, 0.11 mmol) and $Cl_3CCN$ (100 mg, 0.53 mmol) in $CH_2Cl_2$ (5 mL) at 0 °C was added DBU (2 drops). The solution was stirred at 0 °C for 1h. Aqueous $NH_4Cl$ solution (3 mL) was added. The aqueous phase was extracted with $CH_2Cl_2$ (2x10 mL). The organic phase was dried ($Na_2SO_4$) and was evaporated. The residue was purified by column chromatography (Hexane: EtOAc: $Et_3N$ 3:1:0.1) to give compound **7c** (117 mg, 70%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.91 – 8.05 (m, 8H), 7.15 – 7.57 (m, 37H), 6.45 (s, 1H), 5.69 (d, J=1.2 Hz, 1H), 5.29 – 5.53 (m, 6H), 5.11 (d, J=6.4 Hz, 1H), 4.25 – 4.86 (m, 15H), 3.92 – 4.02 (m, 4H), 3.78 (m, 2H), 3.47 – 3.60 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 165.3, 165.2, 161.0, 138.1, 138.0, 137.9, 133.6, 133.4, 133.3, 130.00, 129.9, 128.00, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 106.3, 106.1, 105.4, 103.9, 84.6, 83.5, 83.4, 82.9, 82.8, 82.7, 82.6, 82.5, 82.0, 81.9, 81.8, 80.9, 79.9, 73.5, 73.4, 72.6, 72.5, 72.2, 71.9, 69.3, 69.1, 65.6, 65.3.

# Supplementary Material (ESI) for Chemical Communications


**Methyl 5-*O*-(2-*O*-benzoyl-3-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (10).**

a ) with NIS

To a solution of donor (0.1 mmol), acceptor (0.1 mmol) and NIS (0.1 mmol) in $CH_2Cl_2$ (2 mL) at 0 °C was added TESOTf (0.05 mmol). The solution was stirred at 0 °C for 30 min. Aqueous $Na_2S_2O_3$ solution (10%, 2 mL) was added to quench the reaction. The aqueous phase was extracted with $CH_2Cl_2$ (2x 10 mL). The organic phase was dried ($Na_2SO_4$) and was evaporated. The residue was purified by column chromatography to give compound 10 (20-30%).

b) without NIS

The same reaction was carried out as in part (a) except that NIS was omitted. Compound **10** was obtained (30%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.89-7.92 (m, 2H), 7.14-7.59 (m, 33H), 5.47 (d, J=0.9 Hz, 1H), 5.27 (s, 1H), 4.93 (d, J= 11.1 Hz, 1H), 4.50-4.82 (m, 9H), 3.93-4.22 (m, 4H), 3.52-3.76 (m, 6H), 3.15 (s, 3H), 0.95 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 265.3, 139.0, 138.6, 138.4, 137.8, 135.6, 133.4, 129.9, 129.8, 129.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 106.6, 98.3, 84.4, 83.5, 82.3, 81.8, 80.2, 77.8, 75.8, 75.2, 73.6, 72.4, 70.1, 65.7, 63.4, 55.3, 27.0, 19.6. MS (MALDI) $C_{64}H_{72}O_{11}Si$ Calcd. 1044.4, Found 1067.8 ($M+Na^+$).

**Methyl 5-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (12).**

Compound **12** was prepared (40%) by the same method as described for compound 10 without addition of NIS.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.96-8.05 (m, 6H), 7.16-7.59 (m, 24H), 5.60 (d, J=0.8 Hz, 1H), 5.52 (d, J= 4.8 Hz, 1H), 5.41 (s, 1H), 4.97 (d, J= 11.2 Hz, 1H), 4.46 (m, 9H), 4.09 (dd, J= 3.6, 11.2 Hz, 1H), 3.99 (t, J= 9.2, 9.2 Hz, 1H), 3.79 (m, 2H), 3.67 (m, 1H), 3.57 (dd, J= 3.6, 9.6 Hz, 1H), 3.33 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.6, 165.4, 165.3, 138.3, 138.2, 133.6, 133.1, 130.0, 129.8, 128.6, 128.5, 128.4, 128.3, 128.2, 129.0, 128.0, 127.8, 127.6, 127.5, 106.3, 98.2, 82.1, 81.9, 78.0, 75.8, 75.2, 73.6, 70.1, 66.2, 64.0, 55.4. MS (MALDI) $C_{54}H_{52}O_{13}$, Calcd. 908.3, Found 933.2 ($M+Na^+$).

**2-(*N*-Benzyloxycarbonyl)aminoethyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (14).**

Acceptor **13**[2] (175 mg, 0.9 mmol) was coupled with donor **4c** (1.17 g, 1.8 mmol) to give silylated compound (560 mg, 82%), according to the procedure as described for **6a**. The

silylated compound was desilylated by TBAF (1.8 mL, 1.8 mmol) in THF with HOAc (108 mg, 1.8 mmol) to give compound **14** (104 mg, 74%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J=7.5 Hz, 2H), 7.16 – 7.54 (m, 13H), 5.56 (m, 1H), 5.32 (d, J=1.8 Hz, 1H), 5.05 (d, J=12.9 Hz, 1H) 4.19 (m, 1H), 4.04 (m, 1H), 3.77 (m, 2H), 3.50 – 3.64 (m, 2H), 3.37 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.4, 156.3, 137.2, 136.5, 133.3, 129.6, 129.2, 128.5, 128.4, 128.0, 127.8, 127.7, 106.0, 83.4, 82.6, 82.2, 72.4, 66.7, 66.4, 62.0, 40.8. MS (MALDI) $C_{29}H_{31}NO_8$ Calcd. 521.2, Found 545.0 ($M+Na^+$).

**2-(*N*-Benzyloxycarbonyl)aminoethyl 5-*O*-{(2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-(1→5)-2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranoside (15).**

Acceptor **14** (284 mg, 0.54 mmol) was coupled with donor **4c** (1.0 g, 1.63 mmol) to give disaccharide (438 mg, 74%), which was desilylated to give compound **15** (280 mg, 85%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 - 8.03 (m, 4H), 7.18 – 7.57 (m, 21H), 5.52 (t, J=5.2 Hz, 1H), 5.38 (s, 1H), 5.36 (d, J=1.6 Hz, 1H), 5.24 (s, 1H), 5.14 (s, 1H), 5.08 (s, 1H), 4.75 (d, J=11.6 Hz, 1H), 4.63 (t, J=12.4, 12.4 Hz, 2H), 4.49 (d, J-11.6 Hz, 1H), 4.34 (m, 1H), 4.18 (d, J=4.8 Hz, 1H), 4.09 (m, 1H), 3.99 (d, J=5.6 Hz, 1H), 3.88 (dd, J=4.4, 11.2 Hz, 1H), 3.71 – 3.84 (m, 3H), 3.55 – 3.59 (m, 2H), 3.41 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.4, 156.6, 137.6, 133.69, 129.9, 129.8, 129.4, 129.3, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 106.3, 106.1, 83.5, 83.00, 82.9, 82.2, 81.9, 81.8, 72.5, 72.3, 66.7, 66.6, 65.8, 61.9, 40.9. MS (MALDI) $C_{48}H_{49}NO_{13}$ Calcd. 847.3, Found 871.3 ($M+Na^+$).

**2-(*N*-Benzyloxycarbonyl)aminoethyl 5-*O*-{(2-*O*-benzoyl-3-*O*-benzyl-a-D-arabinofuranosyl)-(1→5)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-a-D-arabinofuranosyl)-(1→5)}-2-*O*-benzoyl-3-*O*-benzyl-a-D-arabinofuranoside (16).**

Acceptor **15** (280 mg, 0.33 mmol) was coupled with donor **4c** (430 mg, 0.66 mmol) to give trisaccharide (400 mg, 86%). The trisaccharide was desilylated to give compound **16** (278 mg, 85%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.95 – 8.01 (m, 6H), 7.18 – 7.52 (m, 29H), 5.07 – 5.52 (m, 9H), 4.30 – 4.76 (m, 7H), 4.02 – 4.23 (m, 5H), 3.67 – 3.96 (m, 7H), 3.41 – 3.56 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.2, 165.1, 156.4, 137.7, 137.5, 136.6, 133.4, 133.3, 129.8, 129.7, 129.6, 129.4, 129.3, 129.2, 128.5, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 106.2, 106.1, 106.0, 83.5, 83.2, 82.9, 82.9, 82.20, 82.1, 81.8, 72.5, 72.2, 72.2, 66.7, 66.6, 65.8, 65.7, 61.9, 60.5, 40.9. MS (MALDI) $C_{67}H_{67}NO_{18}$ Calcd. 1173.4, Found 1197.3 ($M+Na^+$).

**2-(*N*-Benzyloxycarbonyl)aminoethyl 5-*O*-{(2-*O*-benzoyl-α-D-arabinofuranosyl)-(1→5)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-α-D-arabinofuranosyl)-(1→5)-*O*-(2-**

**_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranosyl)}-2-_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranoside (17).**

Acceptor **16** (260 mg, 0.22 mmol) was coupled with donor **4d** (210 mg, 0.44 mmol) to give tetrasaccharide (288 mg, 83%). The chloroacetate groups were removed according to the procedure as described for **6b** to give compound **17** (184 mg, 71%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.94 – 8.00 (m, 8H), 7.16 – 7.56 (m, 32H), 4.95 – 5.44 (m, 11H), 4.29 – 4.75 (m, 7H), 4.05 – 4.24 (m, 5H), 3.54 – 3.96 (m, 10H), 3.41 (m, 3H), 3.10 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.6, 165.6, 165.3, 165.2, 137.8, 137.6, 137.5, 133.76, 133.6, 133.5, 133.4, 129.9, 129.8, 129.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 106.3, 106.2, 106.1, 105.3, 86.2, 84.2, 83.4, 83.1, 83.0, 82.3, 82.0, 81.9, 81.7, 76.5, 72.6, 72.3, 72.1, 66.7, 66.0, 65.8, 62.0, 41.0. MS (MALDI) C79H79NO23 Calcd. 1409.5, Found 1432.4 ($M+Na^+$).

**2-(_N_-Benzyloxycarbonyl)aminoethyl 5-_O_-[{2-_O_-benzoyl-3,5-di-_O_-(-5-_O_-{2-_O_-benzoyl-3,5-di-_O_-(2-_O_-benzoyl-3,5-di-_O_-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl}-2-_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranosyl-(1→5)-_O_-(2-_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranosyl)-(1→5)-_O_-(2-_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranosyl)}-2-_O_-benzoyl-3-_O_-benzyl-α-D-arabinofuranoside (18a).**

To a solution of Acceptor **17** (40 mg, 0.028 mmol) and donor **7c** (112 mg, 0.07 mmol) in $Et_2O$ (2 mL) at r.t. was added TBDMSOTf (3 μL). The mixture was stirred at r.t. for 20 min. Triethylamine (0.1 mL) was added to quench the reaction. The solvent was evaporated. The residue was purified by column chromatography (Hexane EtOAc 1:1) to give an un-separated mixture of compound **18a** and **19a** (89 mg, 75%).

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.99 (m, 24H), 7.03 – 7.51 (m, 106H), 5.06 – 5.45 (m, 26H), 4.05 – 4.72 (m, 43H), 3.40 – 3.94 (m, 36H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.6, 165.8, 165.6, 165.5, 165.5, 165.4, 165.4, 165.3,165.3,165.2,165.1,165.1, 156.6, 138.2,138.1, 138.1, 137.9, 137.8, 137.7, 137.7, 136.9, 133.6, 133.5, 133.4,133.3, 130.0, 129.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, , 106.4, 106.3, 106.2, 106.1, 105.6, 105.5, 105.4, 105.3, 86.0, 83.7, 83.4, 83.3, 83.1, 82.9, 82.8, 82.6, 82.5, 82.3, 82.1, 82.0, 81.9, 80.1, 73.6, 72.8, 72.7, 72.5, 72.3, 72.2, 72.1, 72.0, 71.9, 69.5, 69.3, 66.9, 66.8, 66.2, 65.9, 65.4, 41.2; MS (MALDI) $C_{245}H_{235}NO_{63}$ Calcd. 4198.5, Found 4225.7 ($M+Na^+$).

Structure Determinations of Compound **18b** and **19b**:

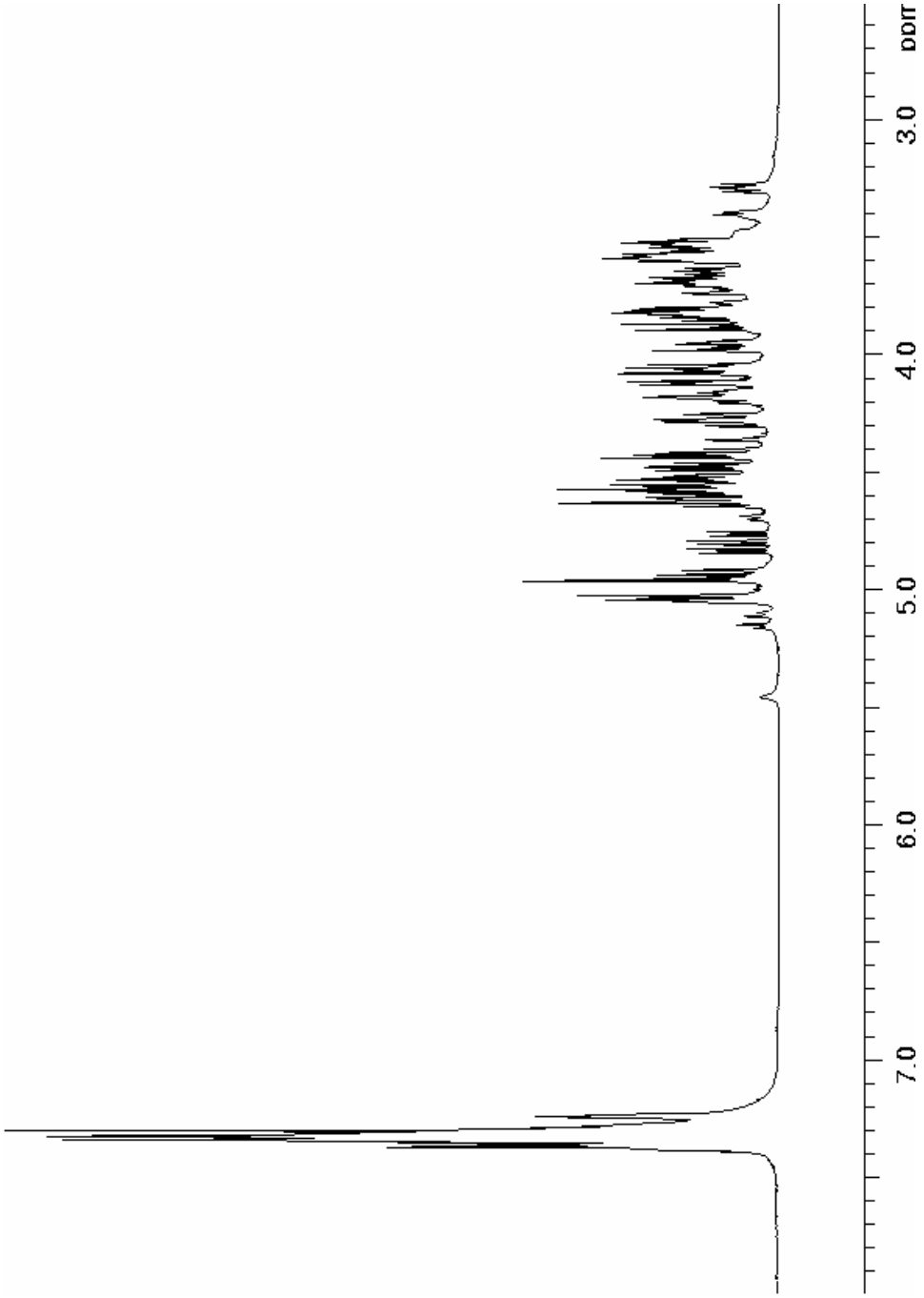
The mixture of compound **18a** and **19a** was subjected to debenzoylation to give compound **18b** and **19b** which were separated by preparative TLC. The structures of **18b** and **19b** were confirmed by MS and COSY(see the attached spectra).

1. Lu, J.; Fraser-Reid, B *Org. Lett.*. **2004,** *6,* 3051 – 3054.

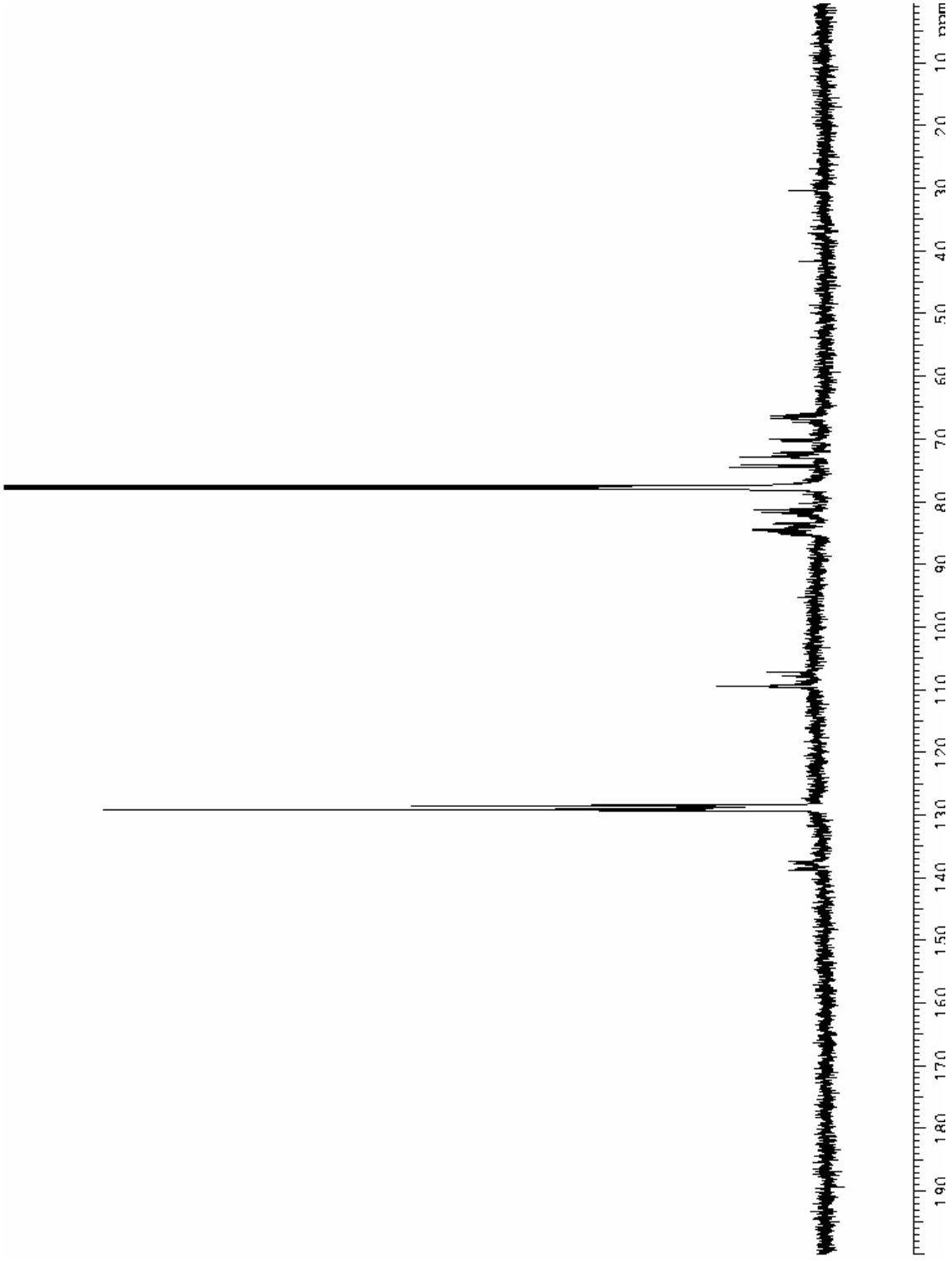
2. Campbell, A. .; Fraser-Reid, B. *Bioorg. Med. Chem.* **1994,** *2,* 1209 – 1219.

# Supplementary Material (ESI) for Chemical Communications


$^{1}H$, $^{13}C$ and COSY Spectra of **18b** and **19b** were recorded on a 800 MHz NMR machine.

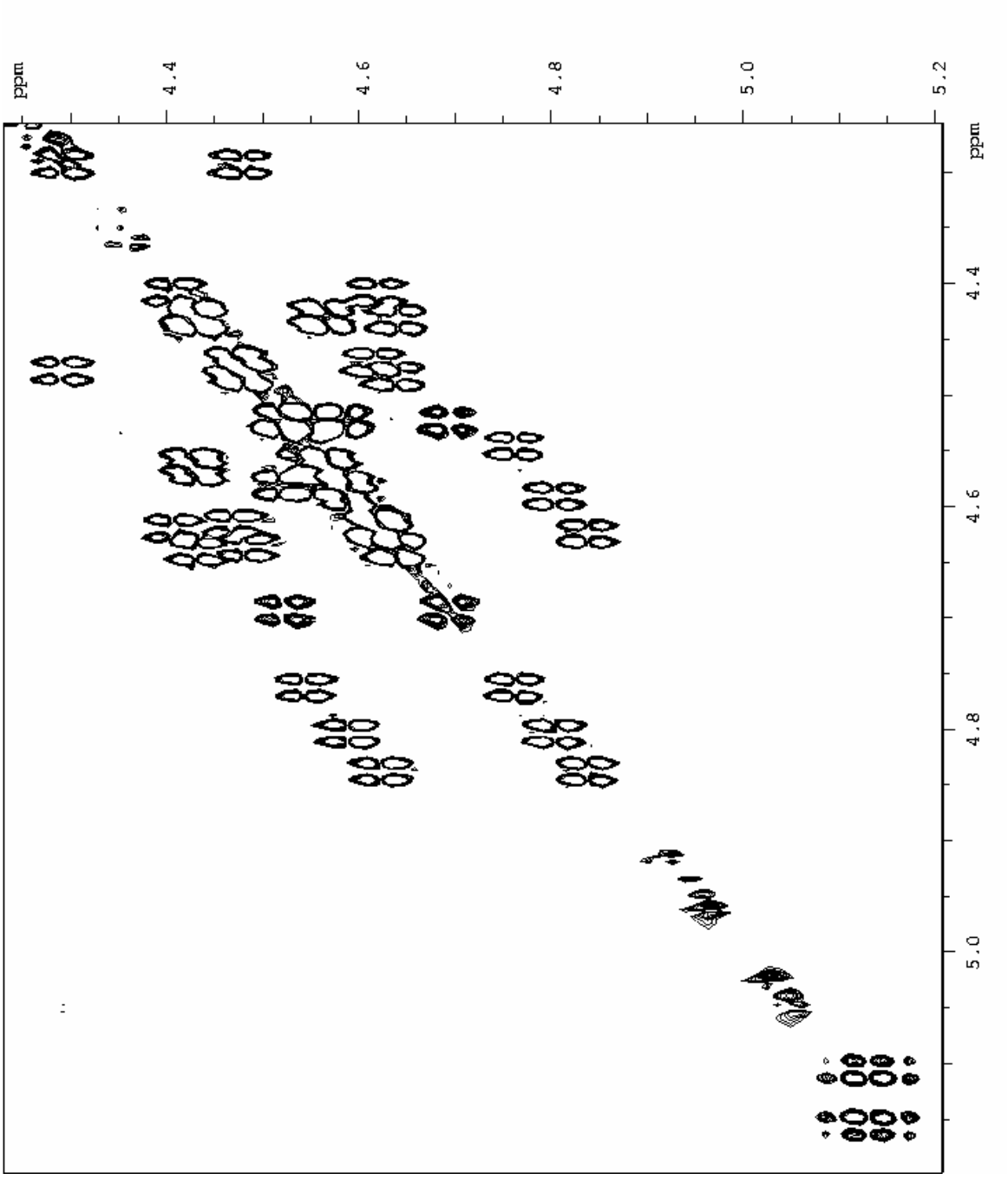



$^{1}$H NMR of **18b**



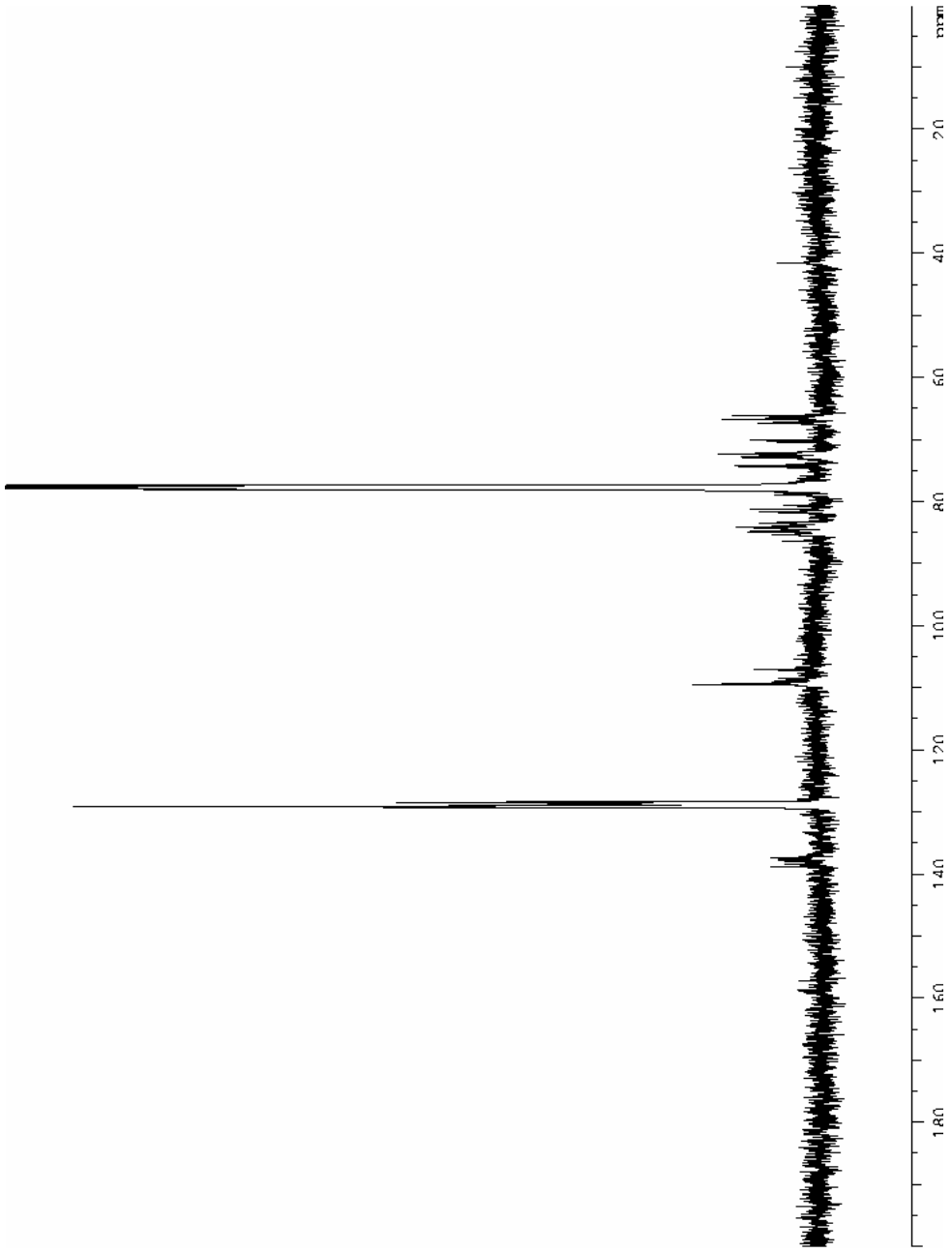

$^{13}$C NMR of **18b**

# Supplementary Material (ESI) for Chemical Communications

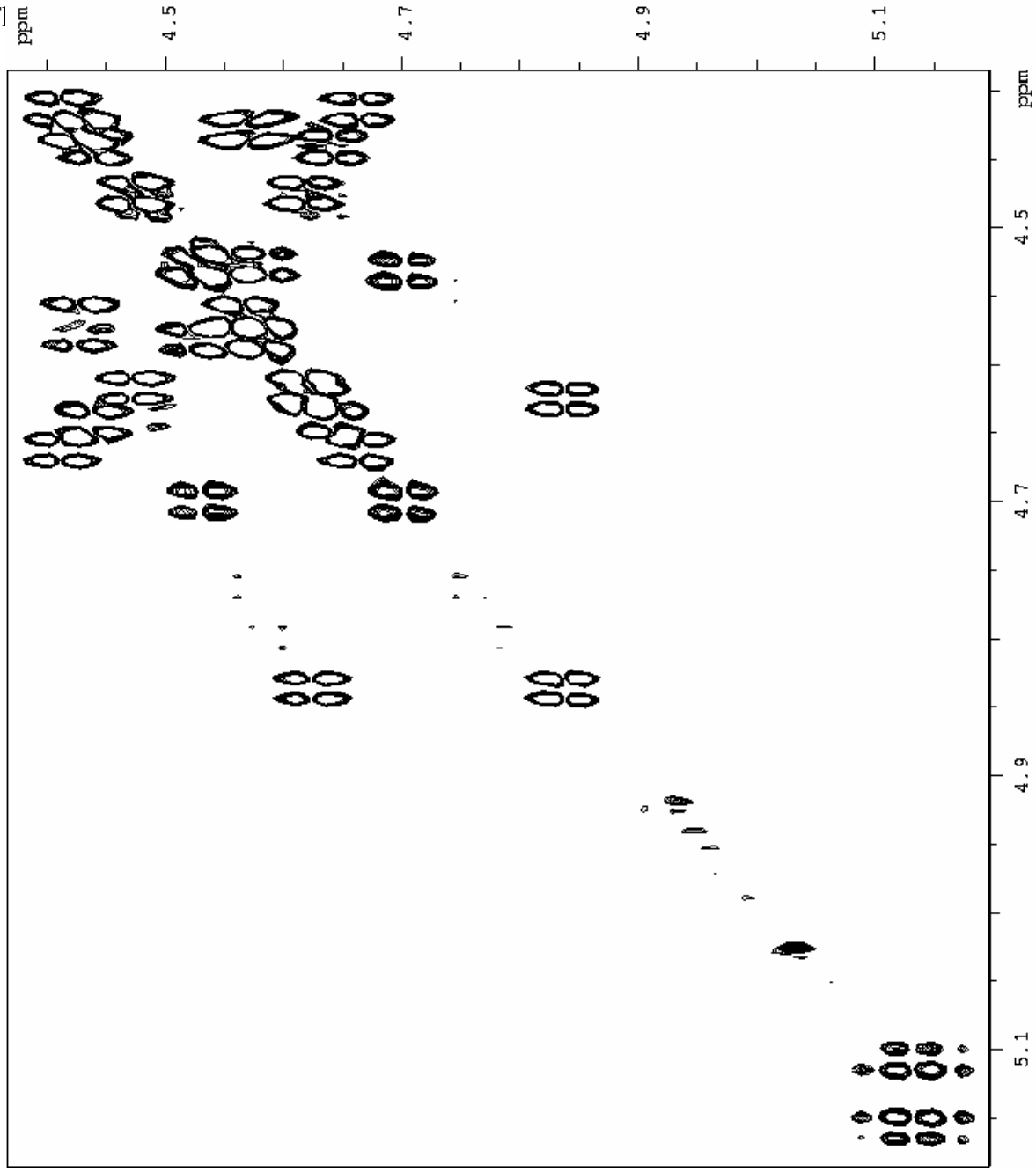

COSY of **18b**

# Supplementary Material (ESI) for Chemical Communications


$^{13}$C NMR of **19b**

# Su
# Th




COSY of **19b**