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Supporting Information

Pseudopeptide Foldamers Designed for PhotoinducedIntramolecular Electron Transfer

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Synthetic details

2-(6-dodecyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f]isoindol-2(1H,3H,5H)-yl)acetic acid 4. For the preparation and characterization see ref. 1.

Methyl 2-(6-dodecyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f]isoindol-2(1H,3H,5H)-yl)acetate 6. $SOCl_2$ (500 μL, 6.85 mmol) was slowly added to a solution of **4** (50 mg, 0.11 mmol) in CH_3OH (5 mL). The mixture was stirred 24 h at room temperature, then it was concentrated in vacuo. The crude was purified by column chromatography (*c*-Hex/ethyl acetate 9:1 → 85:15 → 80:20) and the product **4** was obtained in 45% yield (0.05 mmol, 23 mg). M.p. 139-141°C; IR (CH_2Cl_2, 3 mM): ν 2928, 2855, 1775, 1755, 1729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 3H, *J* = 6.5 Hz, CH_3), 1.21-1.26 (m, 12H, 6 x CH_2), 1.29-1.34 (m, 4H, 2 x CH_2), 1.57 (s, 2H, CH_2), 1.65-1.70 (m, 2H, CH_2-CH_2N), 3.70 (t, 2H, *J* = 7.5 Hz, NCH_2), 3.80 (s, 3H, OCH_3), 4.50 (s, 2H, CH_2 Gly), 8.30 (s, 2H, 2 x Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 26.8, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 38.8, 39.1, 52.9, 118.5, 137.0, 137.5, 165.3, 166.1, 167.1. Anal. Calcd. for $C_{25}H_{32}N_2O_6$: C, 65.77; H, 7.07; N, 6.14. Found: C, 65.79; H, 7.09; N, 6.11.

5-(Heptyloxy)naphthalen-1-ol 7 and 1,5-bis(heptyloxy)naphthalene 5. Potassium carbonate (1.5 g, 11 mmol), potassium iodide (0.83 g, 5 mmol) and *n*-heptyl bromide (786 μL, 5 mmol) were added to a stirred solution of 1,5-dihydroxynaphthalene (0.80 g, 5 mmol) in acetone (18 mL) at room temperature. The suspension was stirred at reflux for 10 h, then cooled to room temperature. The solid was filtered off, the solvent was concentrated under reduced pressure and replaced with ethyl acetate (30 mL). The homogenous mixture was washed with 1 N aqueous HCl (6 mL), water (6 mL), brine (6 mL), dried over sodium sulfate and concentrated *in vacuo*. The crude was purified by flash chromatography (*c*-Hex/ethyl acetate 6:1). The product **7** was obtained in 37% yield (1.85 mmol, 0.48 g) and the by-product **5** was obtained in 30% yield (1.5 mmol, 0.53 g).

7: M.p.: 83-85°C (dec.); IR (CH_2Cl_2, 3 mM): ν 3580, 2994, 2957, 2932, 2872, 2859, 1598, 1517, 1464, 1415, 1386, 1354 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J* = 6.3 Hz, CH_3), 1.27-133 (m, 4H, 2 CH_2), 1.38 (t, 2H, *J* = 7.0 Hz), 1.49-1.58 (m, 4H, 2 CH_2), 1.85-1.93 (m, 2H, OCH_2CH_2), 4.10 (t, 2H, *J* = 6.3 Hz, OCH_2), 5.16 (bs, 1H, OH), 6.81 (t, 2H, *J* = 7.0 Hz, Ar), 7.27 (t, 1H, *J* = 8.0 Hz, Ar), 7.34 (t, 1H, *J* = 8.0 Hz, Ar), 7.68 (d, 1H, *J* = 8.5 Hz, Ar), 7.85 (d, 1H, *J* = 8.5 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 26.2, 29.1, 29.3, 31.8, 68.2, 105.2, 109.4, 113.3, 114.9, 125.0, 125.3, 127.1, 151.1, 154.8. Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; N, 12.39. Found: C, 79.04; H, 8.61; N, 12.36.

5: for the characterization see ref. 2.

(*S*)-5-(heptyloxy)naphthalen-1-yl 2-((tert-butoxycarbonyl)amino)propanoate 8. Into a solution of Boc-L-Ala-OH (0.33 g, 1.73 mmol) in CH_2Cl_2 (15 mL) were added consecutively *N*,*N*-dicyclohexylcarbodiimide (0.36 g, 1.73 mmol), **7** (0.41 g, 1.57 mmol) and 4-(dimethylamino)pyridine (18 mg, 0.15 mmol). The reaction was stirred at room temperature for 24 h. The final suspension was filtered and the solution was concentrated *in vacuo*. The crude was purified by column chromatography (*c*-Hex/ethyl acetate 95:5), and the product was obtained in 55% yield (0.95 mmol, 0.41 g). M.p. 76-77°C (dec.); $[\alpha]_D^{20}$ -33,4 (c 0.12, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3439, 1763, 1714, 1600, 1581 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 3H, *J* = 6.9 Hz, CH_3), 1.30-1.35 (m, 4H, 2 x CH_2), 1.35-1.43 (m, 2H, CH_2), 1.47 (s, 9H, *t*-Boc), 1.50-1.55 (m, 4H, 2 x CH_2), 1.65 (d, 3H, *J* = 7.3 Hz, CH_3-Ala), 1.85-2.00 (m, 2H, CH_2-CH_2O), 4.10 (t, 2H, *J* = 6.3 Hz, OCH_2), 4.65-4.75 (m, 1H, CH-Ala), 5.10-5.15 (m, 1H, NH), 6.80 (d, 1H, *J* = 7.0 Hz, Ar), 7.25 (d, 1H, *J* = 6.2 Hz, Ar), 7.35-7.45 (m, 3H, 3 x Ar), 8.20 (d, 1H, *J* = 8.6 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 18.7, 22.6, 26.2, 28.3, 29.1, 29.2, 31.8, 49.6, 68.3, 80.1, 105.2, 112.9, 118.4, 120.6, 124.4, 126.8, 127.1, 127.7, 146.1, 155.0, 155.2, 172.2. Anal. Calcd. for $C_{25}H_{35}NO_5$: C, 69.90; H, 8.21; N, 3.26. Found: C, 69.87; H, 8.22; N, 3.25.

Boc-L-Ala-D-Oxd-L-Ala-5-(heptyloxy)naphthalen-1-yl ester 9a. Compound **8** (67.4 mg, 0.157 mmol) was dissolved in dry CH_2Cl_2 (1.5 mL) and then TFA (217 µL, 2.82 mmol) was added. The reaction mixture was stirred in a nitrogen atmosphere for 4 h at room temperature. The corresponding ammonium trifluoroacetate salt was obtained pure after solvent removal *in vacuo*.

A solution of Boc-L-Ala-D-Oxd-OH (48 mg, 0.157 mmol) and HATU (65.5 mg, 0.157 mmol) in dry CH_3CN was stirred in a nitrogen atmosphere for 10 min at room temperature, then a solution of the ammonium trifluoroacetate salt and DIEA (82.0 µL, 0.47 mmol) in dry CH_3CN was then added dropwise. The solution was stirred for 1 h in a nitrogen atmosphere, and then CH_3CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL) and 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried over sodium sulfate and concentrated *in vacuo*. The product was obtained pure after silica gel chromatography (6:4 *c*-Hex/ethyl acetate → 1:1 *c*-Hex/ethyl acetate as eluent) in 75% yield (0.118 mmol, 74.1 mg). M.p. 133-138°C; $[\alpha]_D^{20}$ 14.7 (c 0.18, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3444, 3369, 1789, 1722, 1698, 1602, 1509 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 3H, *J* = 6.4 Hz, CH_3), 1.31-1.35 (m, 4H, 2 x CH_2), 1.42 (s, 12H, t-Bu + CH_3-Ala), 1.56 (d, 5H, *J* = 6.2 Hz, CH_2 + CH_3-Oxd) 1.60-1.63

(m, 2H, CH_2), 1.79 (d, 3H, *J* = 7.3 Hz, CH_3-Ala), 1.92 (q, 2H, *J* = 7.4 Hz, C*H*$_2$-CH_2O), 4.15 (t, 2H, *J* = 6.2 Hz, OCH_2), 4.53 (d, 1H, *J* = 5.2 Hz, CHN-Oxd), 4.79 (q, 1H, *J* = 6.1 Hz, CHO-Oxd), 4.89 (q, 1H, *J* = 7.0 Hz, CH-Ala), 5.09-5.12 (m, 1H, NH), 5.20 (q, 1H, *J* = 6.7 CHα-Ala), 6.83 (d, 1H, *J* = 7.3 Hz, Ar), 7.24 (d, 1H, *J* = 7.6 Hz, Ar), 7.35-7.50 (m, 4H, 3 x Ar + NH), 8.19 (d, 1H, *J* = 8.5 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.6, 17.0, 21.0, 22.6, 26.2, 28.3, 29.1, 29.2, 31.8, 31.9, 49.0, 49.4, 62.9, 68.3, 75.3, 80.5, 105.2, 112.9, 118.3, 120.6, 124.3, 126.8, 127.1, 127.7, 146.1, 151.8, 154.9, 167.6, 170.9, 174.3. Anal. Calcd. for $C_{33}H_{45}N_3O_9$: C, 63.17; H, 7.23; N, 6.69. Found: C, 63.21; H, 7.27; N, 6.70.

Dyad 1. Compound **9a** (74.1 mg, 0.118 mmol) was dissolved in dry CH_2Cl_2 (1.2 mL), then TFA (164 µL, 2.12 mmol) was added. The reaction mixture was stirred under nitrogen atmosphere for 4 h at room temperature. The corresponding ammonium trifluoroacetate salt was obtained pure after solvent removal *in vacuo*. A solution of **6** (52.2 mg, 0.118 mmol) and HBTU (49 mg, 0.130 mmol) in dry DMF (1 mL) was stirred under nitrogen atmosphere for 10 min at room temperature, then a solution of the ammonium trifluoroacetate salt and DIEA (64.3 µL, 0.369 mmol) in dry DMF (1 mL) was added. The mixture was stirred for 2 h under nitrogen atmosphere, then CH_3CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL), 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried over sodium sulfate and concentrated in vacuo. The product was obtained pure after silica gel chromatography (6:4 Hex/ethyl acetate → 1:1 Hex/ethyl acetate as eluent) in 50% (0.059 mmol, 56.1 mg) yield. M.p. 178-183°C; $[\alpha]_D^{20}$ 10.9 (c 0.29, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3427, 3342, 1788, 1773, 1727, 1684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83-0.91 (m, 6H, 2 x CH_3), 1.23 (bs, 18H, 9 x CH_2), 1.29-1.35 (m, 8H, 4 x CH_2), 1.50 (d, 3H, *J* = 6.7 Hz, CH_3-Ala), 1.53 (d, 3H, *J* = 6.9 Hz, CH_3-Ala), 1.61 (d, 3H, *J* = 6.2 Hz, CH_3-Oxd), 1.62-1.65 (m, 2H, C*H*$_2$-CH_2N), 1.88-1.96 (m, 2H, C*H*$_2$-CH_2O), 3.63 (t, 2H, *J* = 7.4 Hz, NCH_2), 4.06-4.16 (m, 3H, OCH_2 + C*H*H-Gly), 4.50 (d, 1H, *J* = 3.5 Hz, CHN-Oxd), 4.51 (d, 1H, *J* = 26.6 Hz, CH*H*-Gly), 4.78 (t, 1H, *J* = 6.5 Hz, CHO-Oxd), 4.85 (t, 1H, *J* = 6.9 Hz, CHα-Ala), 5.08 (t, 1H, *J* = 6.3 Hz, CHα-Ala), 6.70 (d, 1H, *J* = 7.5 Hz, Ar), 6.85 (d, 1H, *J* = 5.6 Hz, NH), 7.00 (d, 1H, *J* = 7.5, Ar), 7.10 (d, 1H, *J* = 8.2 Hz, Ar), 7.20-7.25 (m, 2H, 2 x Ar), 7.45 (d, 1H, *J* = 7.5 Hz, NH), 7.80 (s, 2H, 2 x Ar) 8.00 (d, 1H, *J* = 8.4 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 15.8, 16.9, 20.6, 22.6, 22.7, 26.2, 26.9, 28.4, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7, 31.8, 31.9, 38.6, 40.6, 48.4, 50.1, 63.7, 68.2, 75.5, 105.0, 112.5, 118.3, 118.5, 120.2, 124.3, 126.6, 126.9, 127.2, 136.3, 136.6, 145.9, 152.4, 154.8, 165.6, 165.7, 166.4, 166.9, 170.4, 172.8. Anal. Calcd. for $C_{52}H_{65}N_5O_{12}$: C, 65.60; H, 6.88; N, 7.36. Found: C, 65.63; H, 6.90; N, 7.33.

Boc-(-L-Ala-D-Oxd-)$_2$-L-Ala-5-(heptyloxy)naphthalen-1-yl ester 9b. Compound **8** (35.6 mg, 0.08 mmol) was dissolved in dry CH_2Cl_2 (0.1M, 0.8 mL) and then TFA (143 µL, 1.44 mmol) was added. The reaction mixture was stirred under nitrogen atmosphere for 4 h at room temperature. The corresponding ammonium trifluoroacetate salt was obtained pure after solvent removal *in vacuo*.
A solution of Boc-(-L-Ala-D-Oxd-)$_2$-OH (48.3 mg, 0.08 mmol) and HATU (33.5 mg, 0.088 mmol) in dry CH_3CN was stirred under nitrogen atmosphere for 10 min at room temperature, then a solution of the ammonium trifluoroacetate salt and DIEA (41.8 µL, 0.24 mmol) in dry CH_3CN was added dropwise. The solution was stirred for 1 h under nitrogen atmosphere, then CH_3CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL), 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried over sodium sulfate and concentrated in vacuo. The product was obtained pure after silica gel chromatography (6:4 *c*-Hex/ethyl acetate → 1:1 *c*-Hex/ethyl acetate as eluent) in 58% (0.046 mmol, 38.3 mg) yield. M.p. 98-101°C; $[\alpha]_D^{20}$ 19.3 (c 0.23, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3441, 3360, 1790, 1721, 1696, 1600, 1533, 1509 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*= 6.5 Hz, CH_3), 1.23 (bs, 4H, 2 x CH_2), 1.29-1.32 (m, 4H, 2 x CH_2), 1.35-1.44 (m, 15H, *t*-Boc + CH_3-Ala + CH_3-Oxd), 1.48-1.55 (m, 6H, CH_3-Ala, CH_3-Oxd), 1.70 (d, 3H, *J* = 8.3 Hz, CH_3-Ala), 1.89 (q, 2H, *J* = 6.8 Hz, C*H*$_2$-CH_2O), 4.10 (t, 2H, *J* = 6.3, OCH_2), 4.42 (d, 1H, *J* = 4.7, CHN-Oxd), 4.50 (d, 1H, *J* = 5.0 Hz, CHN-Oxd), 4.62-4.67 (m, 1H, CHO-Oxd), 4.78 (q, 1H, *J* = 5.9 Hz, CHO-Oxd), 4.87 (q, 1H, *J* = 6.8 Hz, CHα-Ala), 5.10 (bs, 1H, NH), 5.21 (d, 1H, *J* = 6.8 Hz, CHα-Ala), 5.27-5.34 (m, 1H, CHα-Ala), 6.80 (d, 1H, *J* = 7.7 Hz, Ar), 7.21-7.23 (d, 1H, *J* = 7.6 Hz Ar), 7.35-7.43 (m, 4H, 3 x Ar + NH), 7.57 (d, 1H, *J* = 5.9 Hz, NH), 8.16 (d, 1H, *J* = 8.3 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 15.5, 16.8, 21.0, 21.1, 22.6, 26.2, 28.2, 29.1, 29.2, 29.6, 29.7, 31.8, 48.9, 49.2, 62.4, 62.6, 68.3, 74.8, 75.3, 80.7, 105.2, 112.8, 118.4, 120.6, 124.4, 126.9, 127.0, 127.7, 146.1, 151.6, 151.7, 154.9, 167.7, 168.2, 171.0, 174.8. Anal. Calcd. for $C_{41}H_{55}N_5O_{13}$: C, 59.62; H, 6.71; N, 8.48. Found: C, 59.58; H, 6.73; N, 8.50.

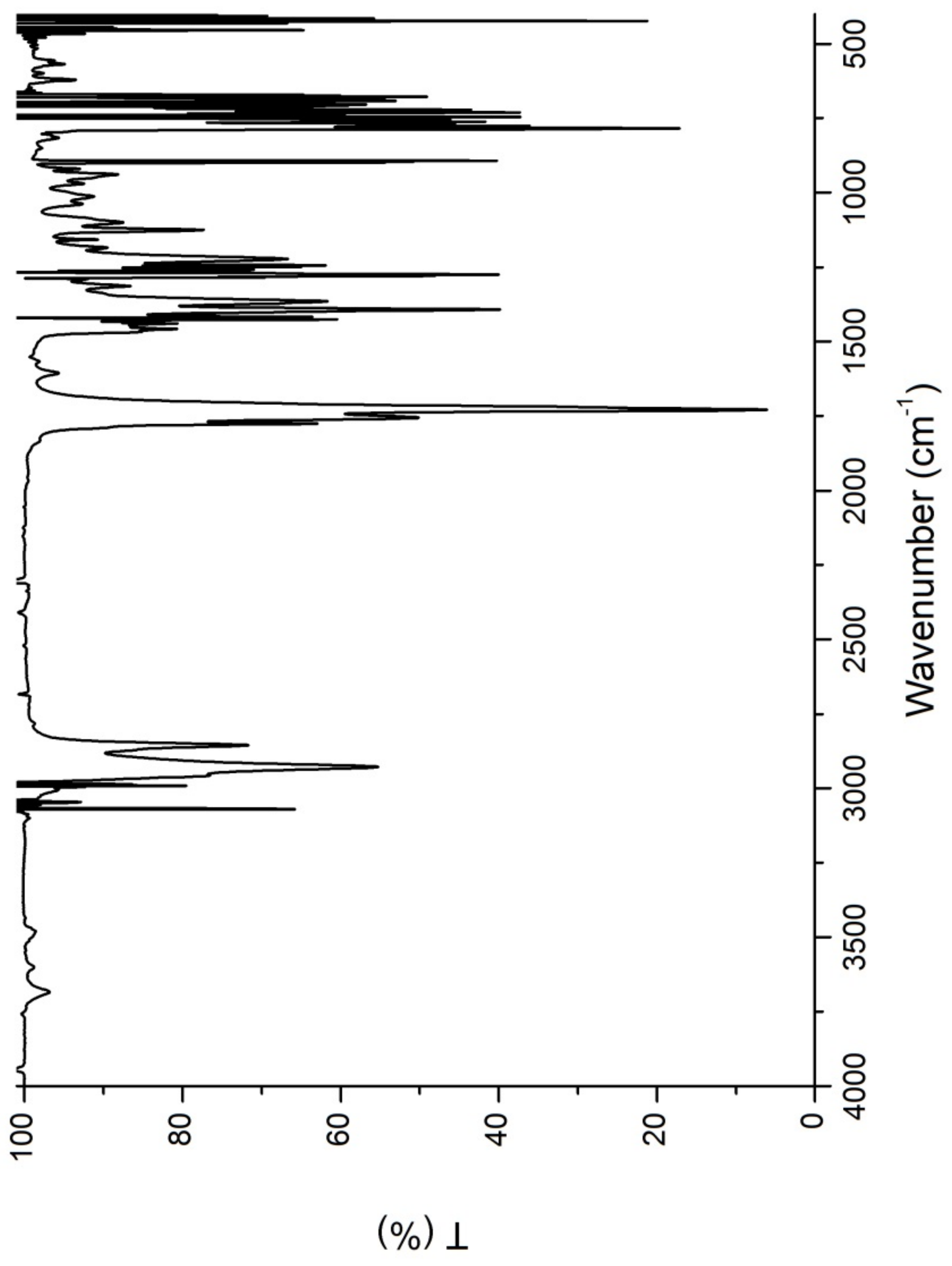
Dyad 2. Compound **9b** (38.0 mg, 0.046 mmol) was dissolved in dry CH_2Cl_2 (0.1M, 460 µL), and then TFA (63.9 µL, 0.829 mmol) was added. The reaction mixture was stirred in a nitrogen atmosphere for 4 h at room temperature. The corresponding ammonium trifluoracetate salt was obtained pure after solvent removal *in vacuo*. A solution of **6** (20.3 mg, 0.046 mmol) and HBTU (19.2 mg, 0.050 mmol) in dry DMF (1 mL) was stirred in a nitrogen atmosphere for 10 min at room temperature. A solution of the corresponding ammonium trifluoracetate salt and DIEA (24.0 µL, 0.138 mmol) in dry DMF (1 mL) was then added dropwise. The solution was stirred for 2 h in a nitrogen atmosphere, and then CH_3CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL), 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried over sodium sulfate and concentrated in vacuo. The product was obtained pure after silica gel chromatography (1:1 Hex/ethyl acetate → 2:8 Hex/ethyl acetate as eluent) in 45% (0.021 mmol, 23.8 mg) yield. M.p. 182-187°C; $[\alpha]_D^{20}$ 9.4 (c 0.34, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3424, 3412, 3359, 3350, 3336, 1789, 1775, 1728, 1719, 1683 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.83-0.90 (m, 6H, CH_3), 1.14 (m, 2H, CH_2), 1.23 (bs, 12H, 6 x CH_2), 1.27-1.34 (m, 9H, 3 x CH_2 + CH_3-Ala), 1.35-1.39 (m, 3H, CH_3-Oxd), 1.40-1.45 (m, 6H, CH_3-Ala + CH_3-Oxd), 1.52 (m, 6H, 3 x CH_2), 1.65 (m, 3H, CH_3-Ala), 1.86-1.92 (m, 4H, C*H*$_2$-CH_2O + C*H*$_2$-CH_2N), 3.66-3.72 (m, 2H, NCH_2), 4.07-4.11 (m, 2H, OCH_2), 4.30-4.50 (m, 4H, 2 CHN-Oxd + CH_2-Gly), 4.62-4.68 (m, 1H, CHO-Oxd), 4.70-4.76 (m, 1H, CHO Oxd), 4.80-4.86 (m, 1H, CHα-Ala), 5.11-5.17 (m, 1H, CHα-Ala), 5.35-5.41 (m, 1H, CHα-Ala), 6.76-6.81 (m, 2H, Ar + NH), 7.17 (d, 1H, *J* = 7.3 Hz, Ar), 7.18-7.22 (m, 2H, Ar), 7.32-7.42 (m, 3H, Ar + 2 x NH), 8.12 (d, 1H, *J* = 7.8 Hz, Ar), 8.18 (s, 2H, 2 x Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 15.5, 16.9, 20.8, 22.6, 26.2, 26.9, 28.4, 29.1, 29.2, 29.3, 29.6, 31.6, 31.8, 31.9, 38.7, 40.5, 48.9, 49.1, 62.8, 68.3, 75.0, 75.4, 105.2, 112.7, 118.8, 118.3, 120.3, 124.3, 126.8, 126.9, 127.3, 127.5, 136.5, 136.9, 145.9, 151.7, 154.8, 165.3, 165.7, 166.0, 166.3, 167.6, 168.1, 171.1, 173.2. Anal. Calcd. for $C_{60}H_{75}N_7O_{16}$: C, 62.65; H, 6.57; N, 8.52. Found: C, 62.62; H, 6.63; N, 8.56.

Boc-(-L-Ala-D-Oxd-)$_3$-L-Ala-5-(heptyloxy)naphthalen-1-yl ester 9c. Compound **8** (71.4 mg, 0.166 mmol) was dissolved in dry CH_2Cl_2 (1.6 mL), then TFA (231 μL, 2.99 mmol) was added. The mixture was stirred under nitrogen atmosphere for 4 h at room temperature. The corresponding ammonium trifluoroacetate salt was obtained pure after solvent removal *in vacuo*. A solution of Boc-(-L-Ala-D-Oxd-)$_3$-OH (118.2 mg, 0.166 mmol) and HATU (33.5 mg, 0.088 mmol) in dry CH_3CN was stirred under nitrogen atmosphere for 10 min at room temperature, then a solution of the ammonium trifluoroacetate salt and DIEA (86.7 μL, 0.498 mmol) in dry CH_3CN was added dropwise. The mixture was stirred for 1 h in a nitrogen atmosphere, then CH_3CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL), 5% (w/v) aqueous $NaHCO_3$ (1 × 30 mL), dried over sodium sulfate and concentrated *in vacuo*. The product was obtained pure after silica gel chromatography (6:4 *c*-Hex/ethyl acetate → 1:1 *c*-Hex/ethyl acetate as eluent) in 40% (0.066 mmol, 68.0 mg) yield. M.p. 140-144°C; $[\alpha]_D^{20}$ -5.3 (c 0.3, CH_2Cl_2); IR (CH_2Cl_2, 3 mM): ν 3402, 3351, 1790, 1694, 1600, 1535, 1509 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 3H, *J* = 6.9 Hz, CH_3), 1.24-1.27 (m, 2H, CH_2), 1.30-1.35 (m, 4H, 2 x CH_2), 1.36-1.57 (24H, *t*-Bu, CH_3-Oxd, 4 x CH_3-Ala), 1.71-1.75

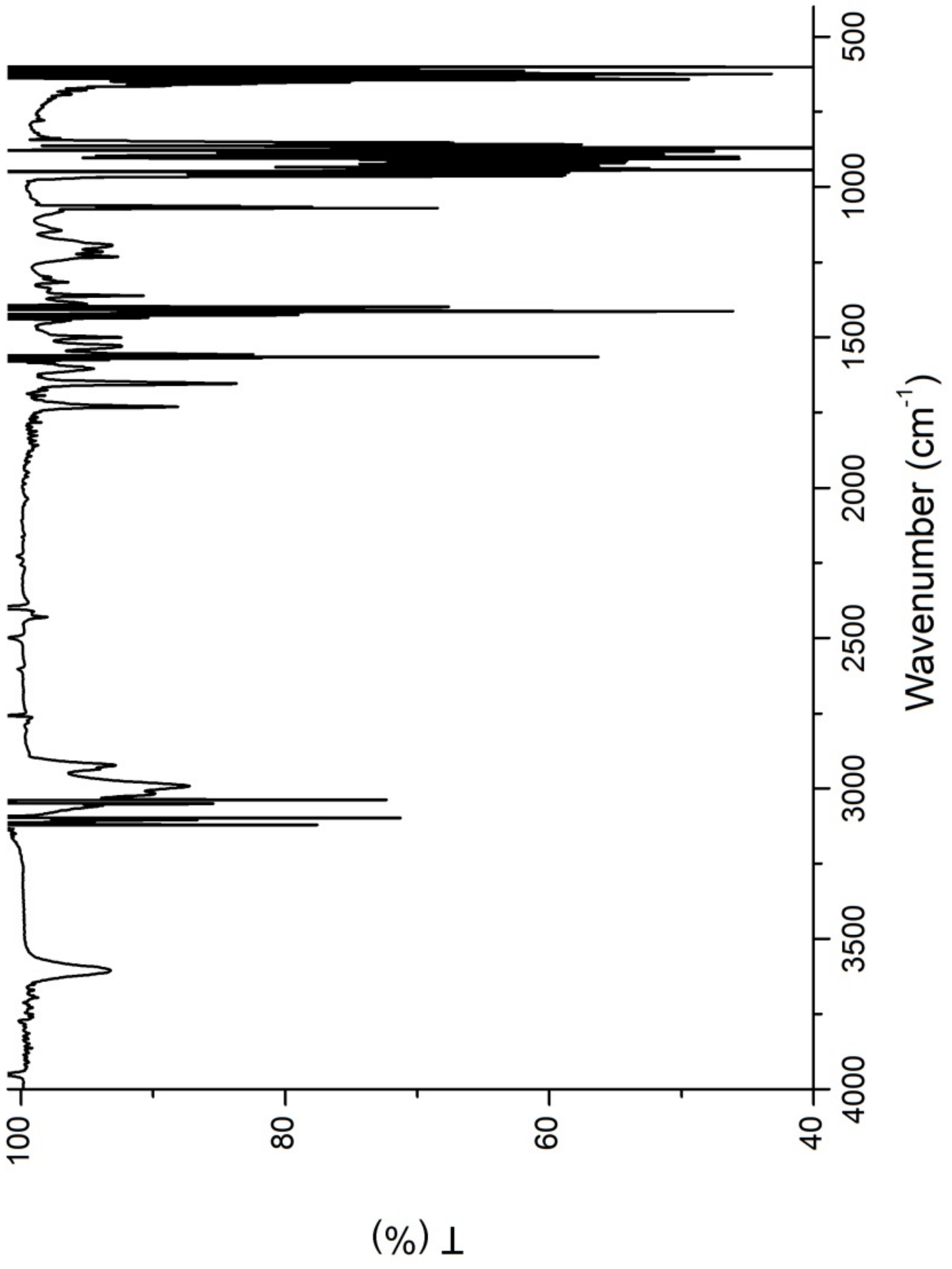
(m, 3H, CH$_3$-Oxd), 1.77-1.82 (m, 5H, CH$_2$ + CH$_3$-Oxd), 1.87-1.95 (m, 2H, C*H*$_2$-CH$_2$O), 4.11 (t, 2H, *J* = 6.4 Hz, OCH$_2$), 4.38-4.40 (m, 1H, CHN-Oxd), 4.42-4.45 (m, 1H, CHN-Oxd), 4.50-4.54 (m, 1H, CHO-Oxd), 4.60-4.64 (m, 1H, CHO-Oxd), 4.65-4.70 (m, 1H, NH), 4.73-4.78 (m, 1H, CHα-Ala), 4.92 (q, 1H, *J*=6.7, CHα-Ala), 5.17-5.24 (m, 2H, CHα-Ala), 5.32-5.40 (m, 2H, CHα-Ala), 6.80-6.84 (m, 1H, Ar), 7.21-7.23 (m, 1H, Ar), 7.37-7.44 (m, 3H, Ar), 7.50-7.54 (m, 2H, 2 x NH), 7.59-7.62 (m, 1H, NH), 8.19 (d, 1H, *J* = 8.2 Hz, Ar); ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.0, 15.8, 16.9, 17.1, 20.5, 20.7, 22.6, 26.2, 28.2, 29.1, 29.2, 29.6, 31.8, 38.6, 48.9, 49.0, 49.3, 62.4, 62.6, 68.3, 74.9, 75.4, 80.5, 105.1, 112.5, 112.7, 118.4, 120.7, 124.2, 127.0, 127.6, 146.0, 151.7, 151.8, 154.9, 167.8, 168.1, 171.4, 171.5, 173.0, 174.2. Anal. Calcd. for $C_{49}H_{65}N_7O_{17}$: C, 57.47; H, 6.40; N, 9.57. Found: C, 57.50; H, 6.43; N, 9.61.

Dyad 3. Compound **9c** (68.9 mg, 0.067 mmol) was dissolved in dry CH$_2$Cl$_2$ (0.5 mL), then TFA (93.0 µL, 1.2 mmol) was added. The reaction mixture was stirred under nitrogen atmosphere for 4 h at room temperature. The corresponding trifluoracetate salt was obtained pure after solvent removal *in vacuo*. A solution of **6** (29.6 mg, 0.067 mmol) and HBTU (28.1 mg, 0.0.074 mmol) in dry DMF (1 mL) was stirred under nitrogen atmosphere for 10 min at room temperature. A solution of the corresponding trifluoracetate salt and DIEA (64.3 µL, 0.20 mmol) in dry DMF (1 mL) was then added dropwise. The mixture was stirred for 2 h in a nitrogen atmosphere, then CH$_3$CN was removed under reduced pressure and replaced with ethyl acetate (30 mL). The mixture was washed with brine (1 × 30 mL), 1 N aqueous HCl (1 × 30 mL), and 5% (w/v) aqueous NaHCO$_3$ (1 × 30 mL), dried over sodium sulfate and concentrated in vacuo. The product was obtained pure after silica gel chromatography (1:1 Hex/ethyl acetate → 2:8 Hex/ethyl acetate as eluent) in 40% (0.027 mmol, 36.1 mg) yield. M.p. 90-98°C; $[\alpha]_D^{20}$ = -7.4 (c 0.4, CH$_2$Cl$_2$); IR (CH$_2$Cl$_2$, 3 mM): v 3418, 3412, 3366, 3353, 3344, 1787, 1774, 1727, 1687, 1683 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.85-0.90 (m, 6H, 2 x CH$_3$), 1.21-1.26 (m, 16H, 8 x CH$_2$), 1.28-1.33 (m, 11H, CH$_3$-Ala + 4 x CH$_2$), 1.35-1.45 (m, 8H, 2 x CH$_3$-Oxd + CH$_2$), 1.49-1.54 (m, 9H, 3 x CH$_3$-Ala), 1.65-1.72 (m, 3H, CH$_3$-Oxd), 1.87-1.94 (m, 4H, C*H*$_2$-CH$_2$O + C*H*$_2$-CH$_2$N), 3.67-3.75 (m, 3H, 3 x CHN-Oxd), 3.98-4.05 (m, 2H, CH$_2$-Gly), 4.07-4.13 (m, 4H, OCH$_2$ + NCH$_2$), 4.34-4.52 (m, 4H, 2 x CH-Ala + 2 x CHO-Oxd), 4.55-4.65 (m, 1H, CHα-Ala), 4.67-4.74 (m, 2H, CHα-Ala + CH Oxd), 4.87-4.95 (m, 1H, NH), 6.79 (d, 1H, *J* = 7.0 Hz, Ar), 7.18-7.24 (m, 3H, Ar + 2 x NH), 7.32-7.41 (m, 4H, 3 x Ar + NH), 8.17 (d, 1H, *CH* = 8.7 Hz, Ar), 8.22 (s, 2H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.0, 17.6, 21.0, 22.6, 22.7, 26.2, 26.8, 28.4, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 30.9, 31.8, 31.9, 38.8, 40.7, 48.5, 48.8, 52.2, 61.9, 62.8, 68.3, 68.7, 75.4, 105.2, 112.6, 118.3, 118.4, 120.7, 124.3, 127.0, 127.5, 129.5, 136.9, 137.0, 137.3, 137.4, 145.9, 155.0, 159.3, 165.5, 165.6, 165.7, 166.0, 166.1, 166.2, 169.6, 171.3. Anal. Calcd. for $C_{68}H_{85}N_9O_{20}$: C, 60.57; H, 6.35; N, 9.35. Found: C, 60.60; H, 6.32; N, 9.37.

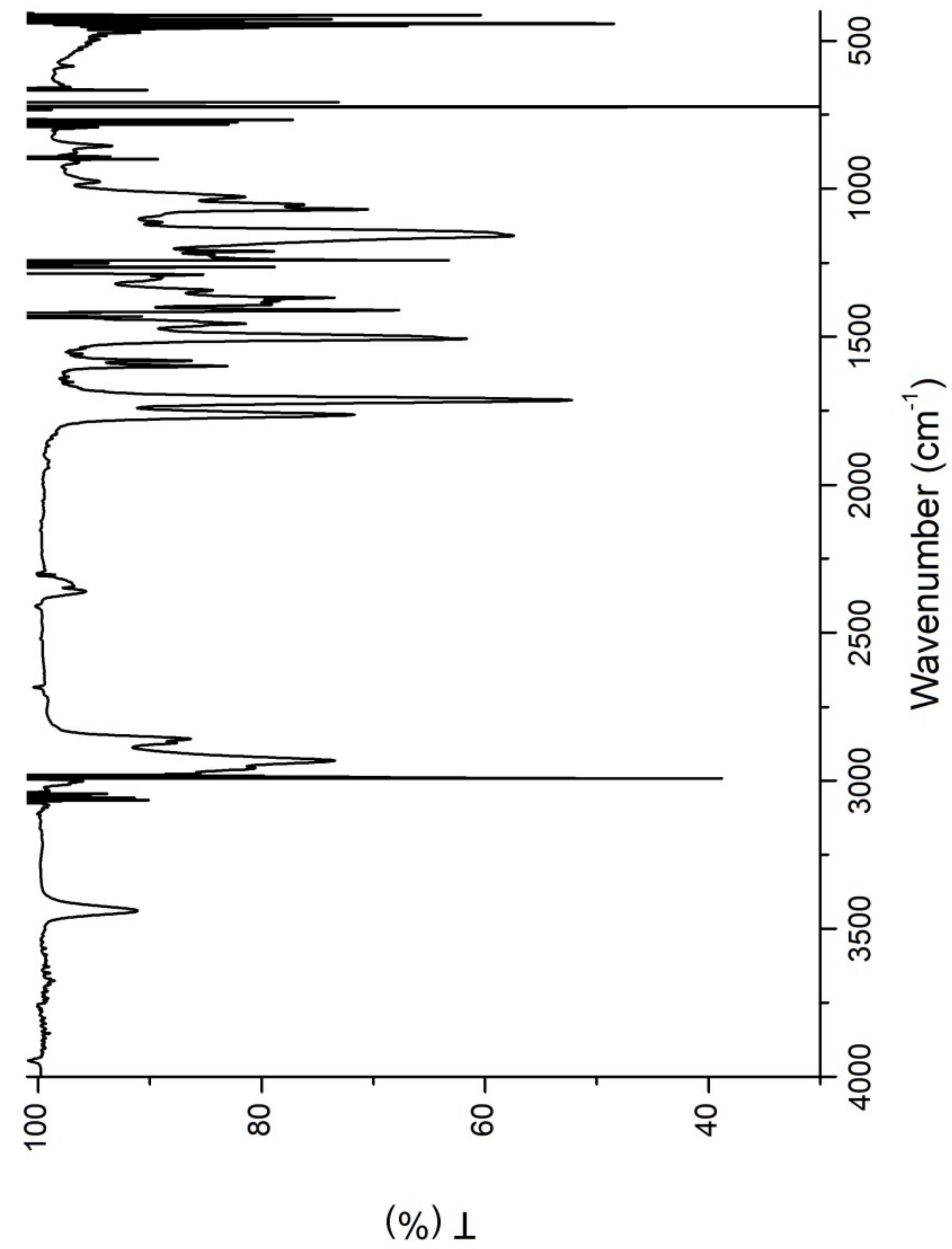
IR spectrum of **4**



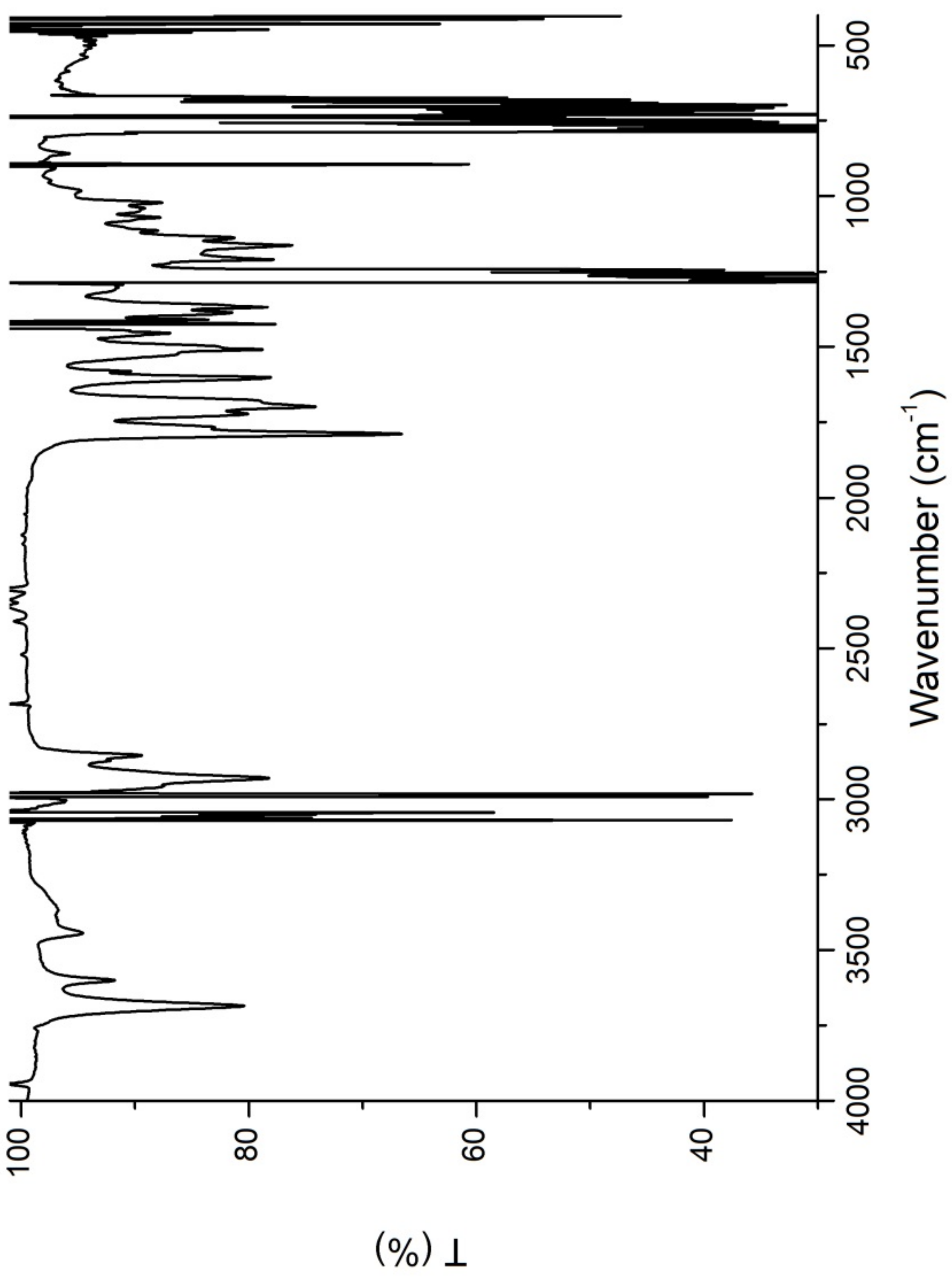
IR spectrum of **7**



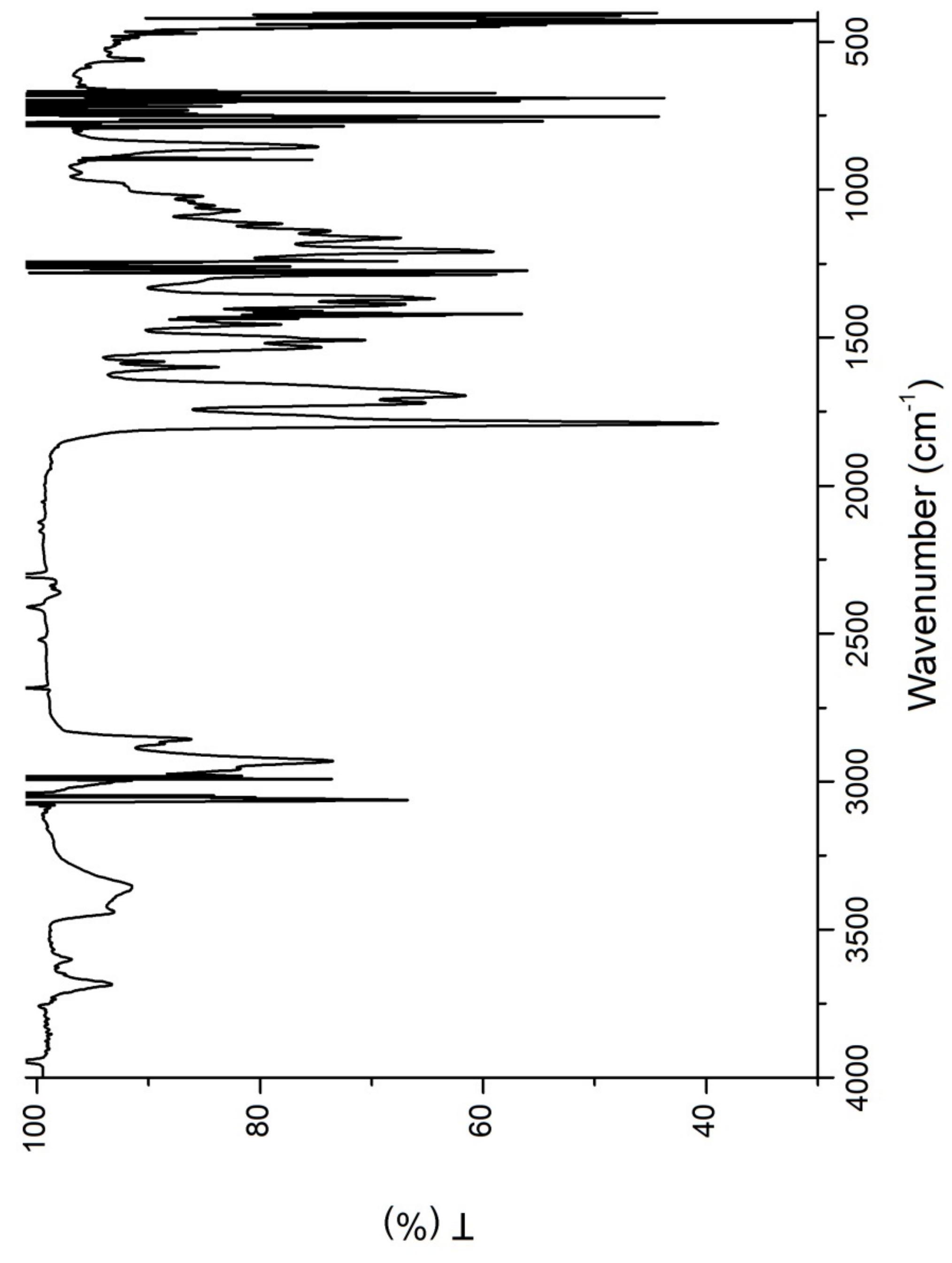
IR spectrum of **8**



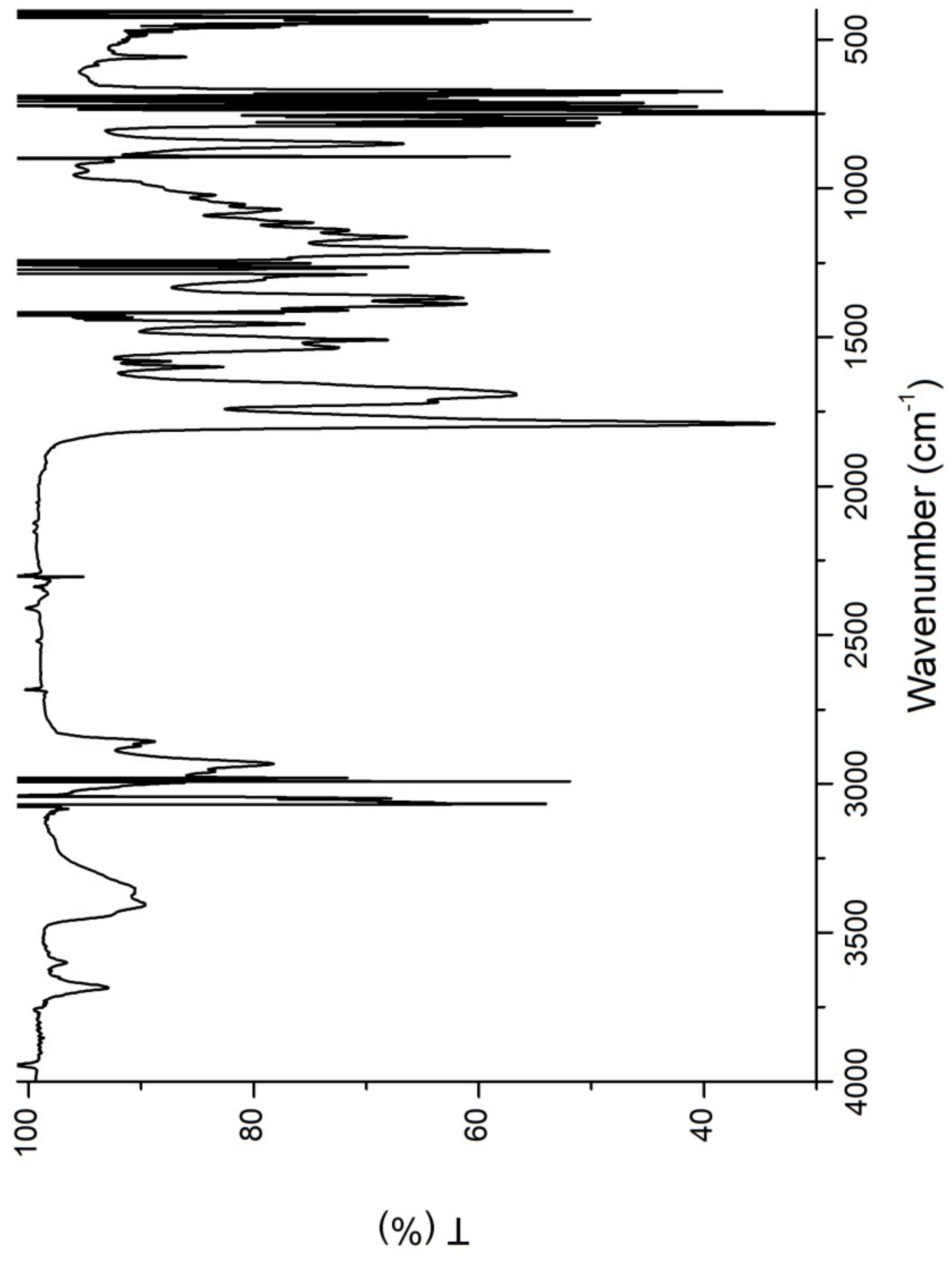
IR spectrum of **9a**



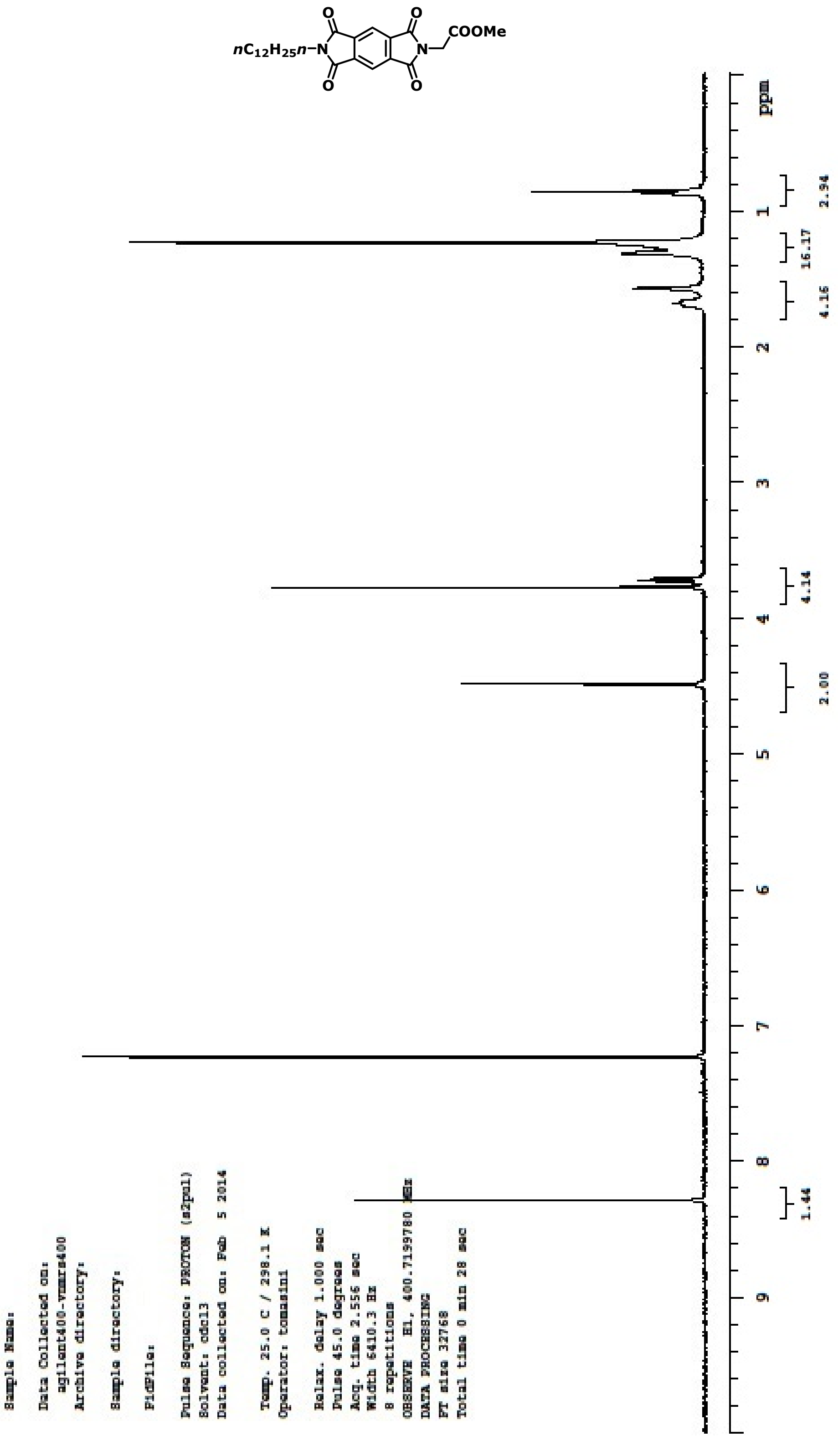
IR spectrum of **9b**

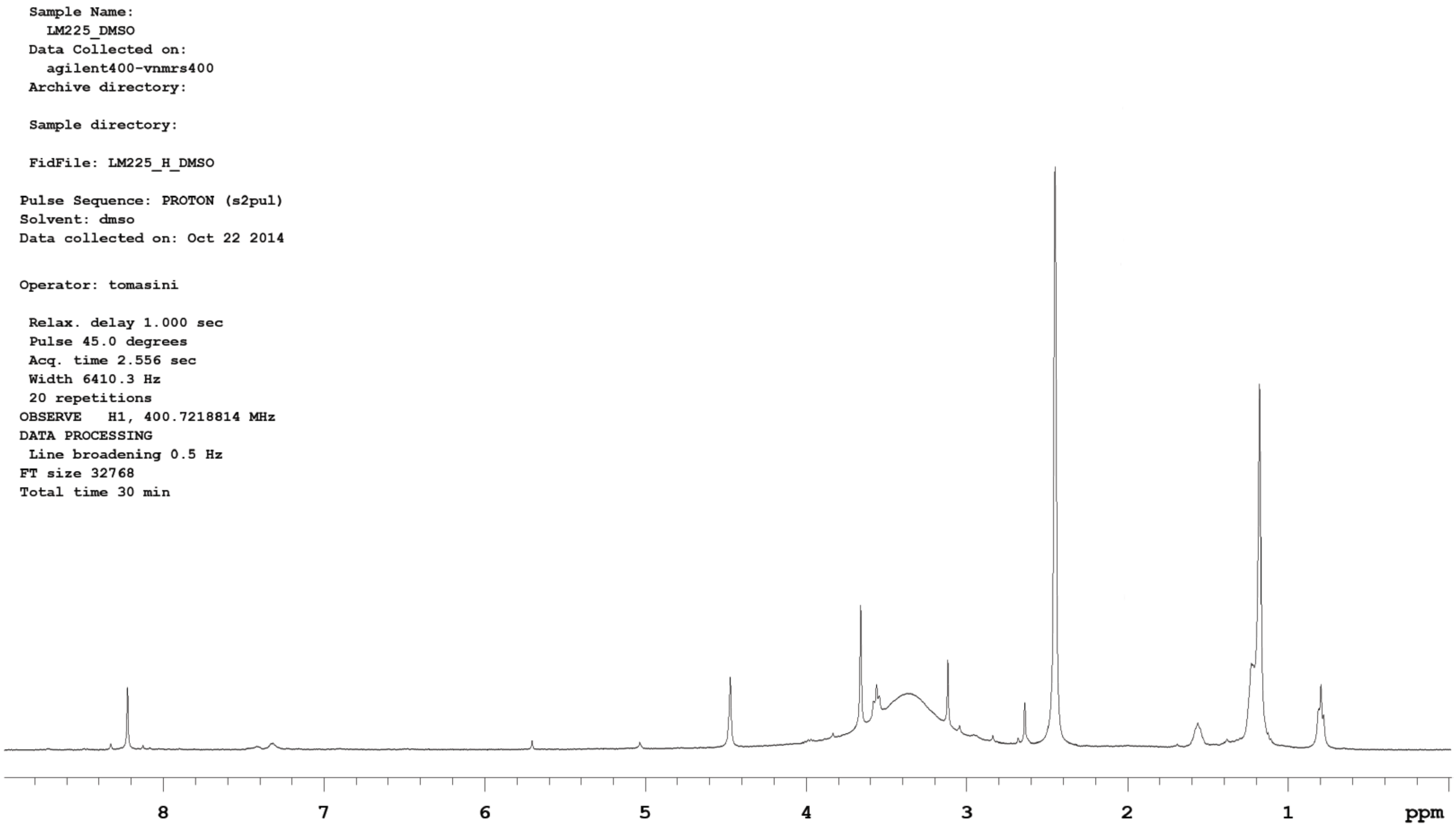


IR spectrum of **9c**



^{1}H NMR spectra of **4**





```
 Sample Name:
   LM225_DMSO
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

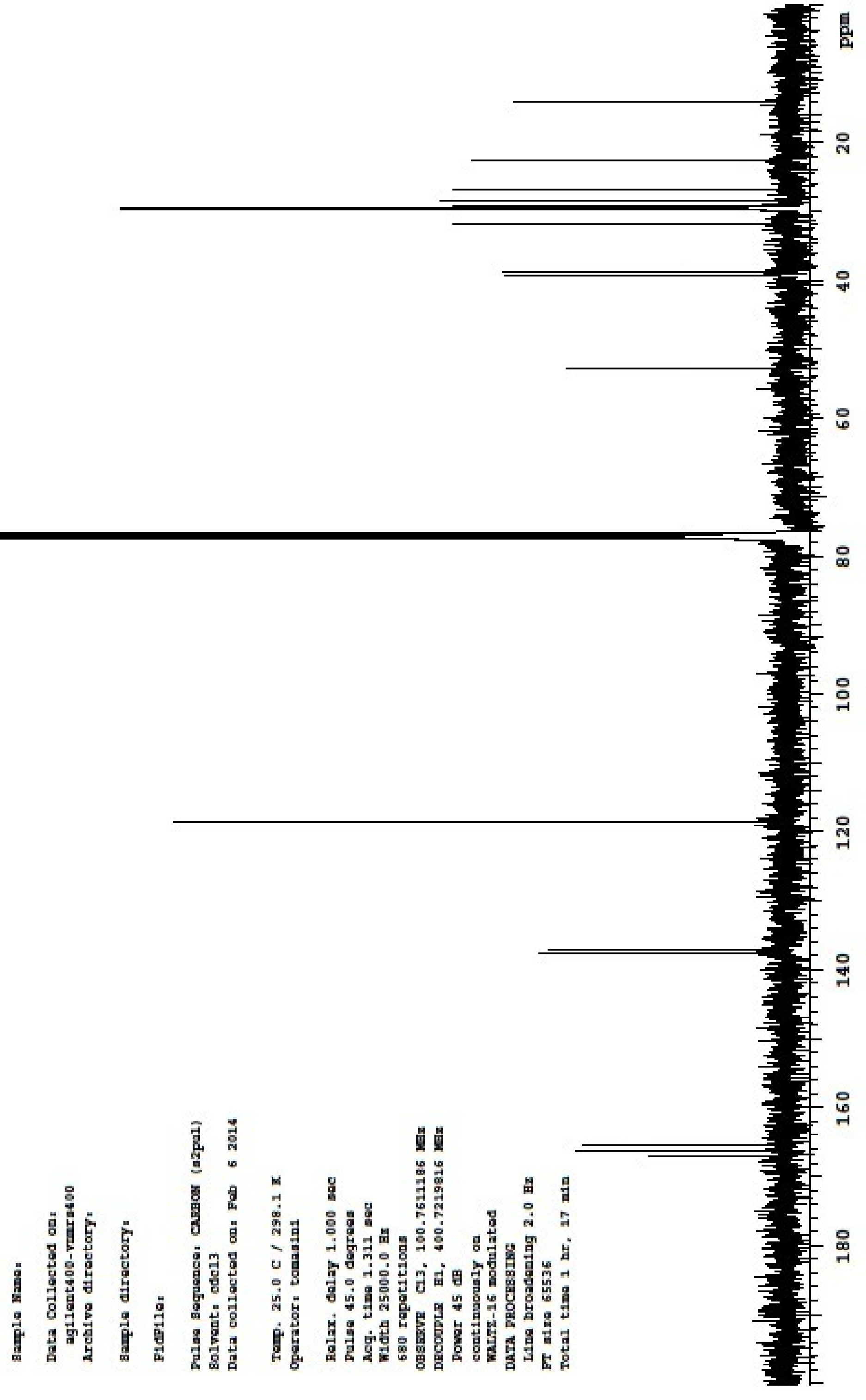
 FidFile: LM225_H_DMSO

Pulse Sequence: PROTON (s2pul)
Solvent: dmso
Data collected on: Oct 22 2014

Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 20 repetitions
OBSERVE   H1, 400.7218814 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 30 min
```

^{13}C NMR spectrum of **4**



Sample Name:

Data Collected on:
agilent400-vnmrs400
Archive directory:

Sample directory:

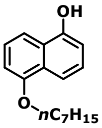
FidFile:

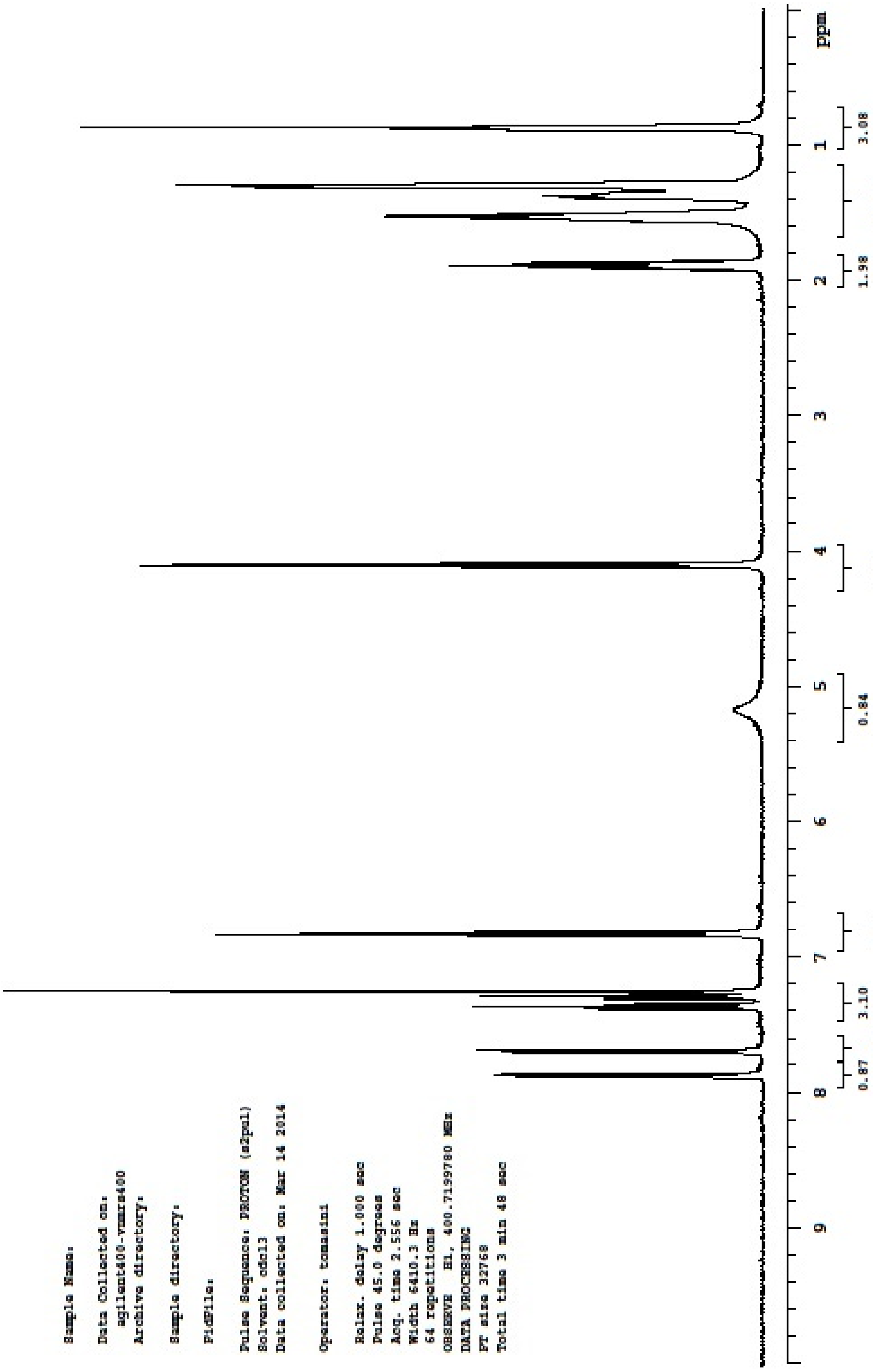
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 6 2014

Temp. 25.0 C / 298.1 K
Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
680 repetitions
OBSERVE C13, 100.7611186 MHz
DECOUPLE H1, 400.7219816 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 17 min

^{1}H NMR spectrum of **7**





```
Sample Name:

Data Collected on:
   agilent400-vnmrs400
Archive directory:

Sample directory:

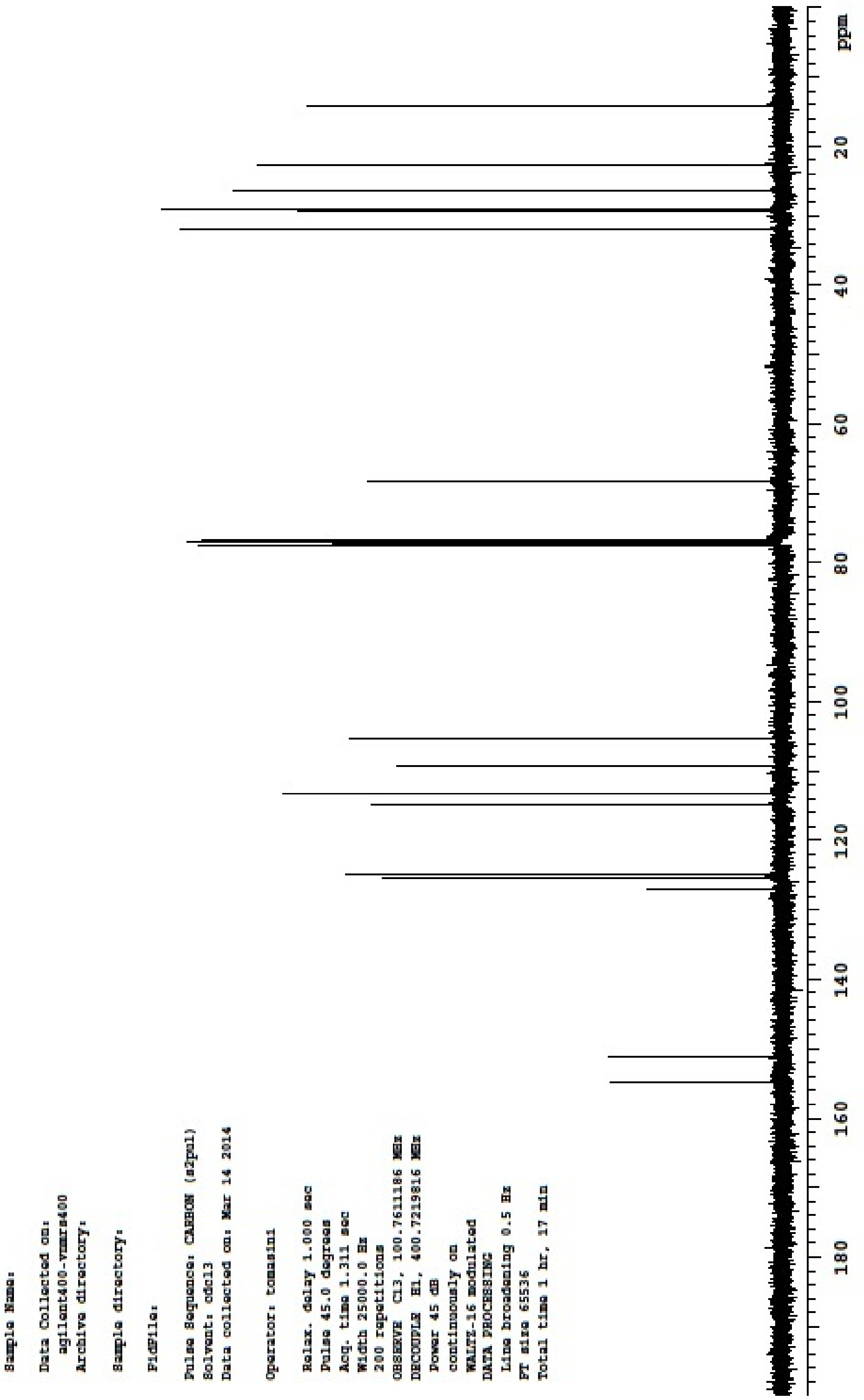
FidFile:

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 14 2014

Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
64 repetitions
OBSERVE  H1, 400.7199780 MHz
DATA PROCESSING
FT size 32768
Total time 3 min 48 sec
```

^{13}C NMR spectrum of **7**



```
 Sample Name:

 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

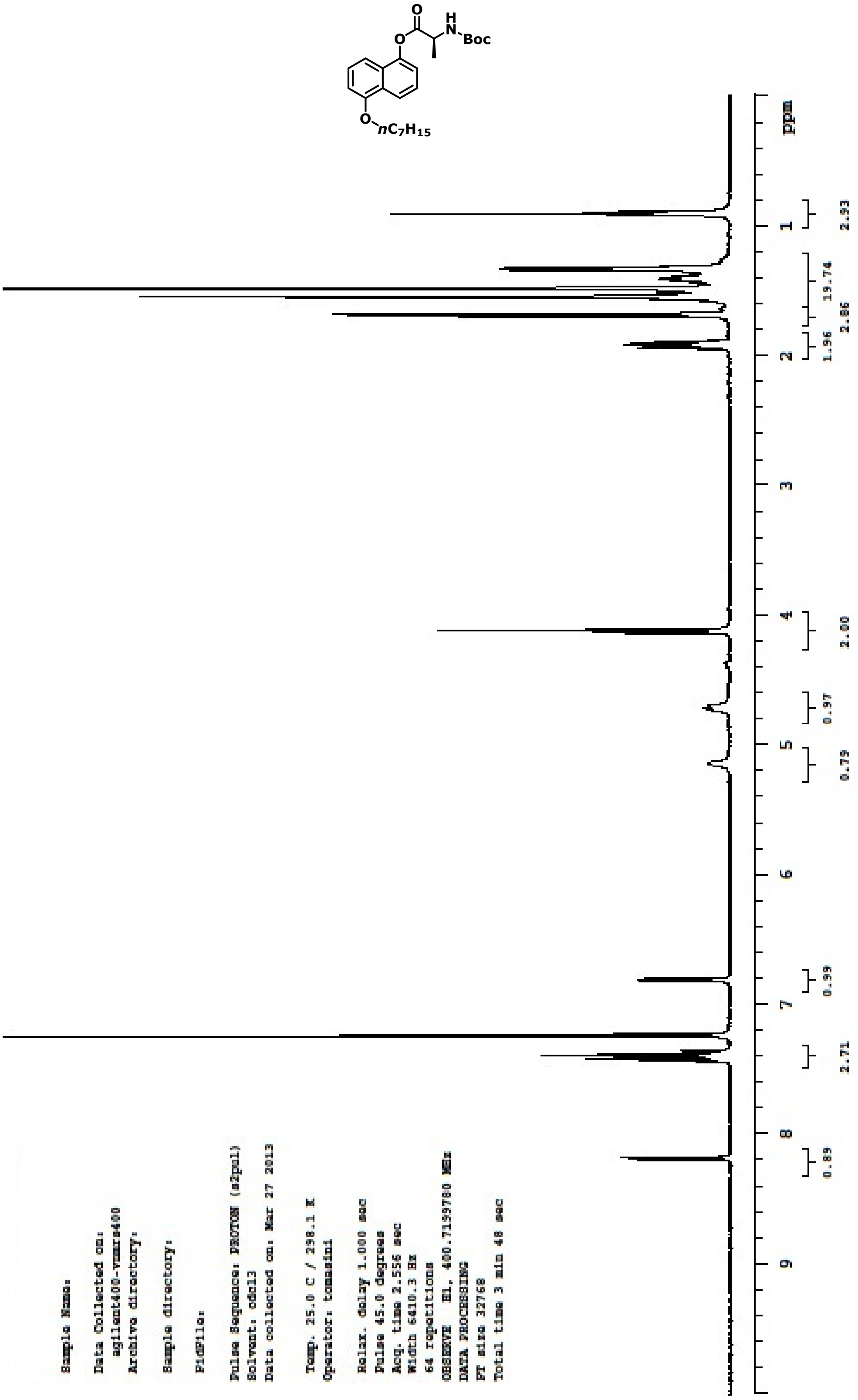
 Sample directory:

 FidFile:

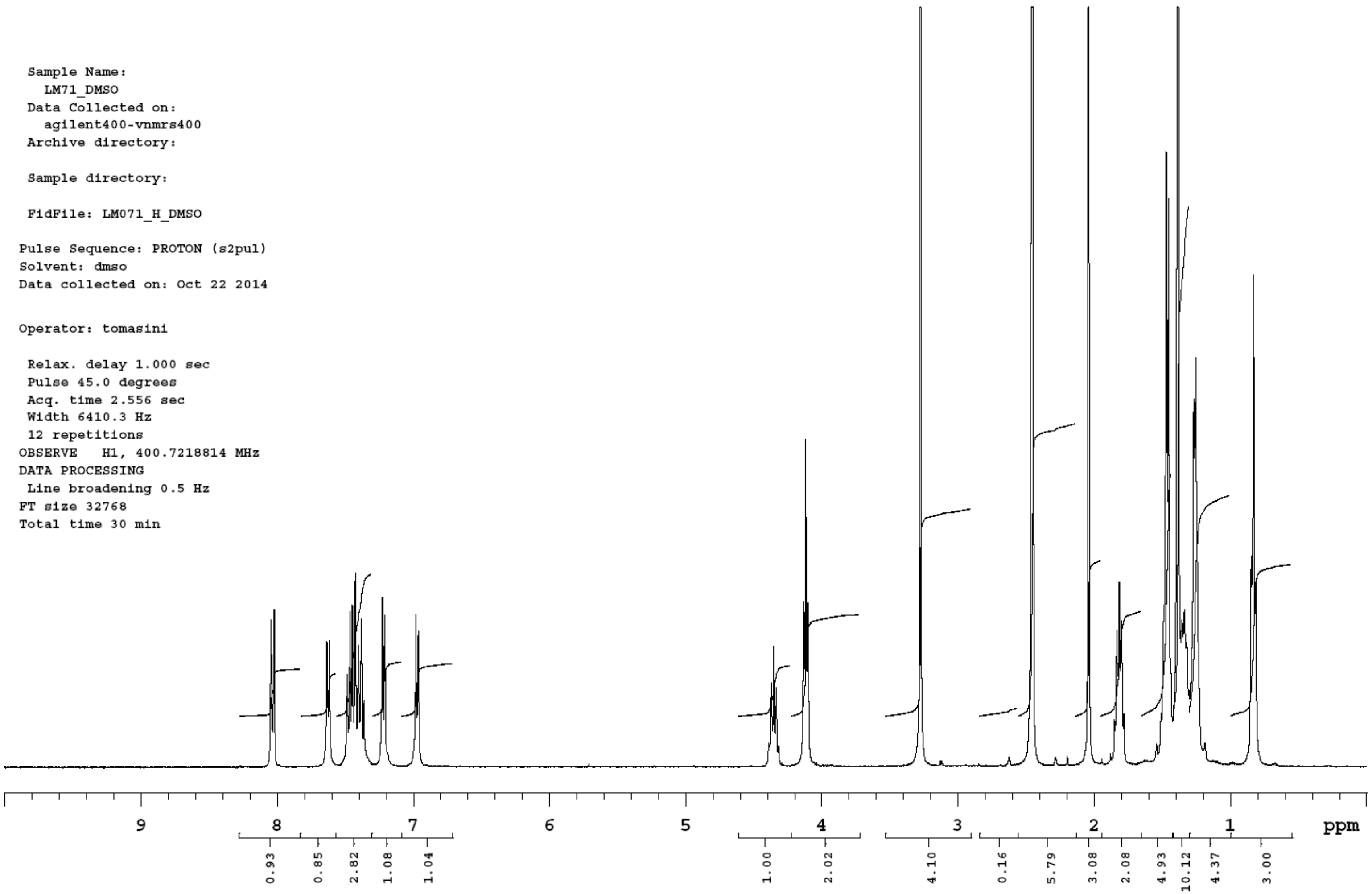
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 14 2014

Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 200 repetitions
OBSERVE  C13, 100.7611186 MHz
DECOUPLE  H1, 400.7219816 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 17 min
```



^{1}H NMR spectra of **8**



```
 Sample Name:
   LM71_DMSO
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

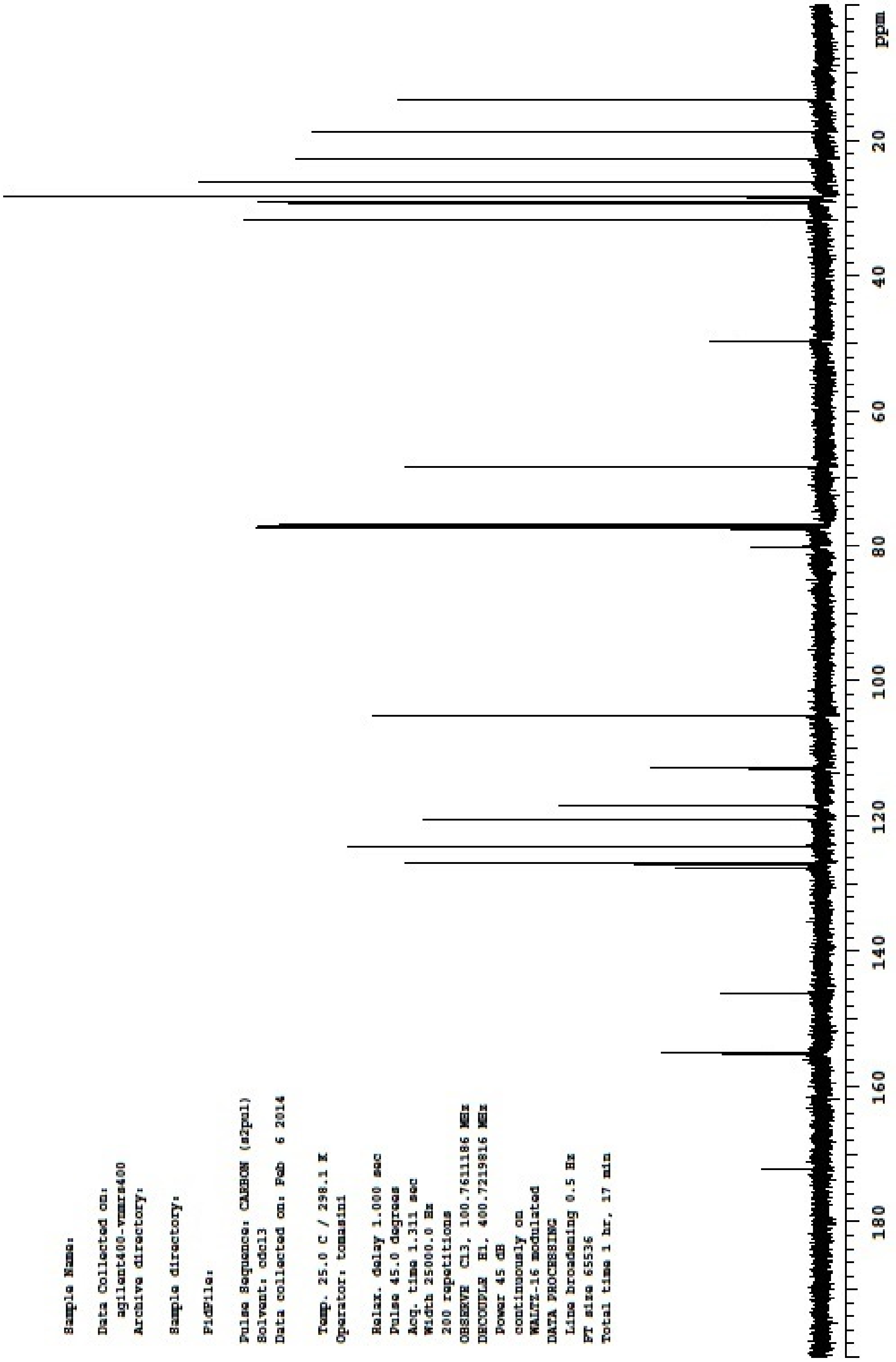
 FidFile: LM071_H_DMSO

Pulse Sequence: PROTON (s2pul)
Solvent: dmso
Data collected on: Oct 22 2014

Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 12 repetitions
OBSERVE   H1, 400.7218814 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 30 min
```

^{13}C NMR spectrum of **8**



```
Sample Name:

Data Collected on:
  agilent400-vnmrs400
Archive directory:

Sample directory:

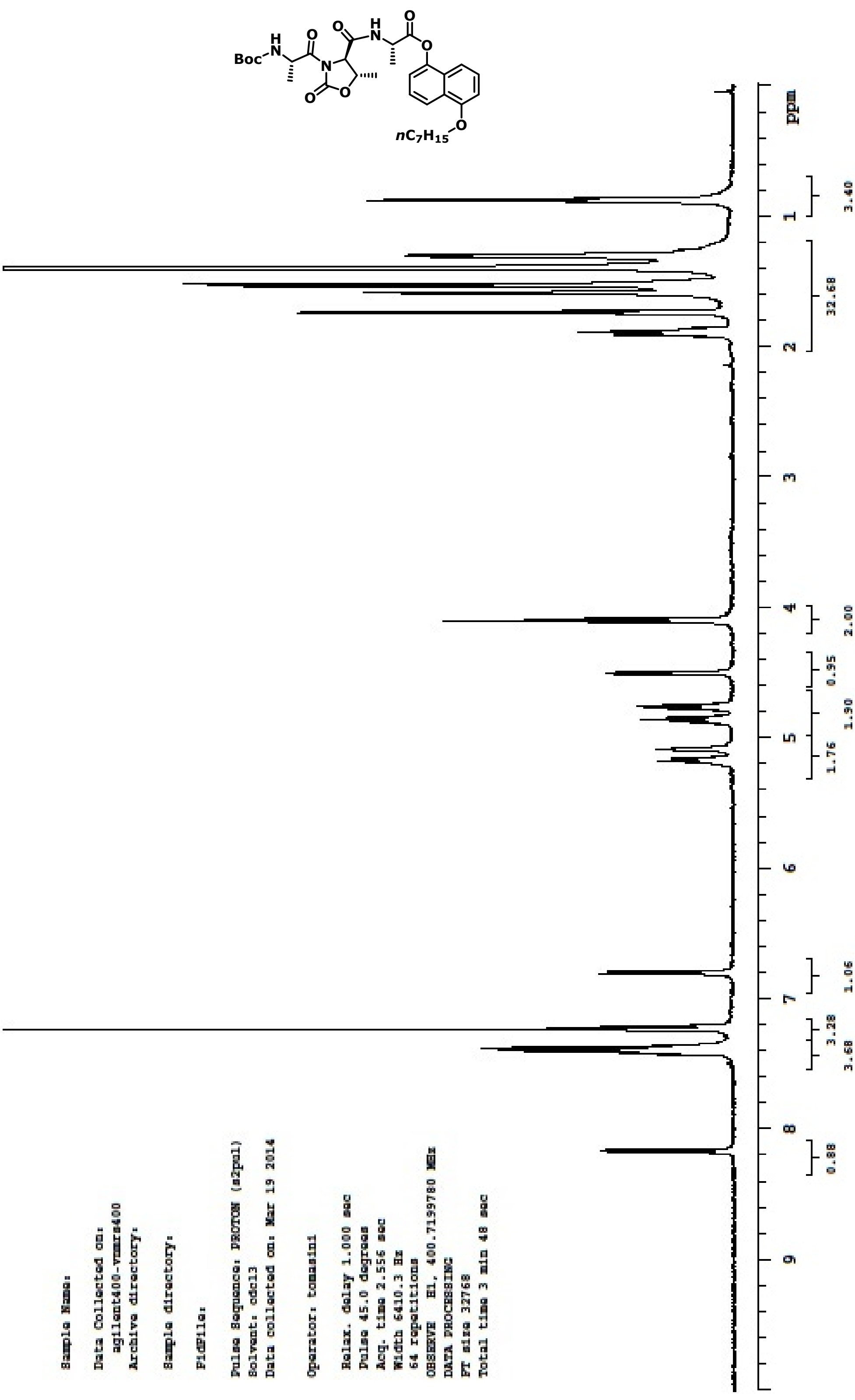
FidFile:

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb  6 2014

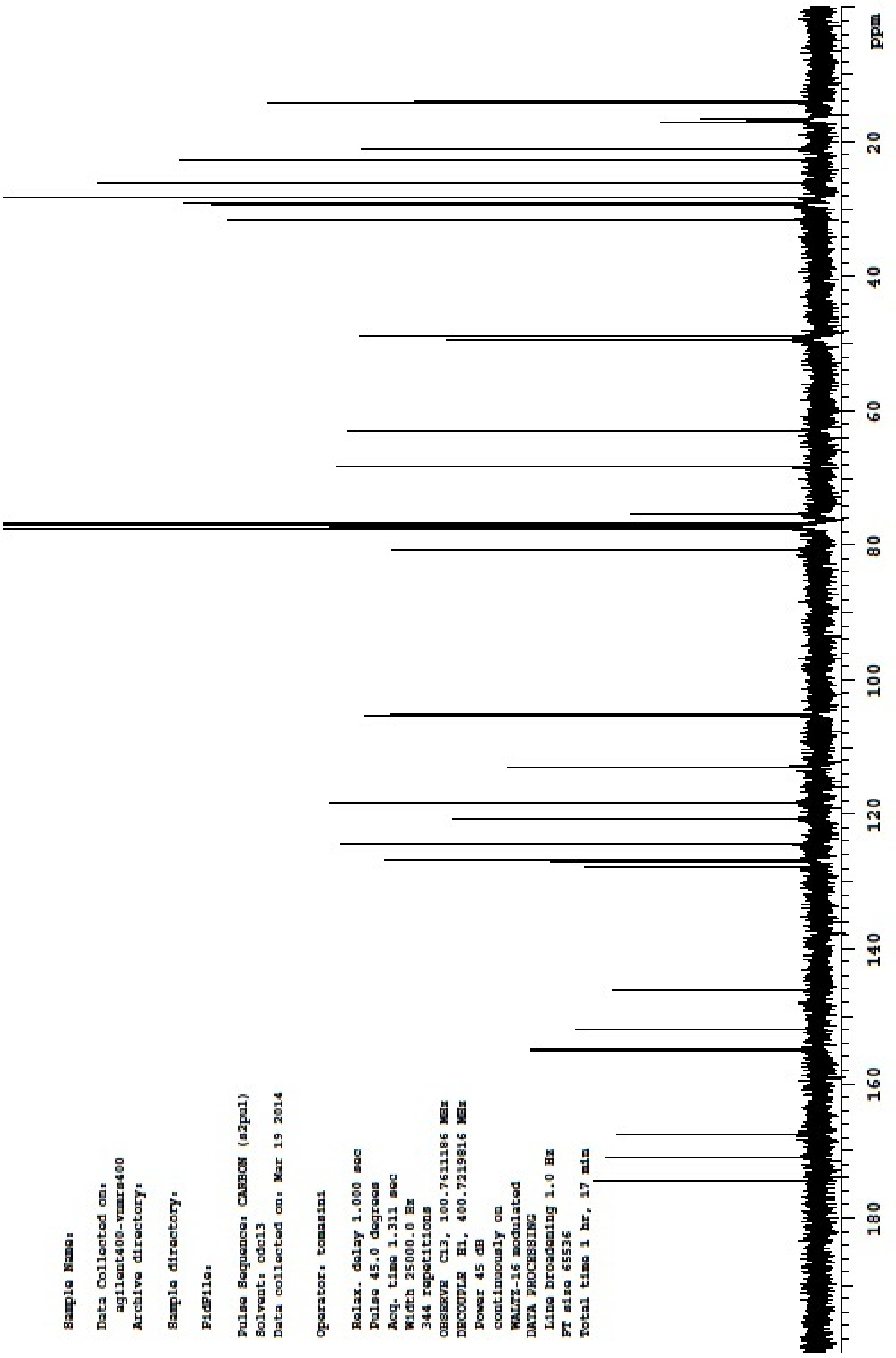
Temp. 25.0 C / 298.1 K
Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
200 repetitions
OBSERVE  C13, 100.7611186 MHz
DECOUPLE  H1, 400.7219816 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 17 min
```

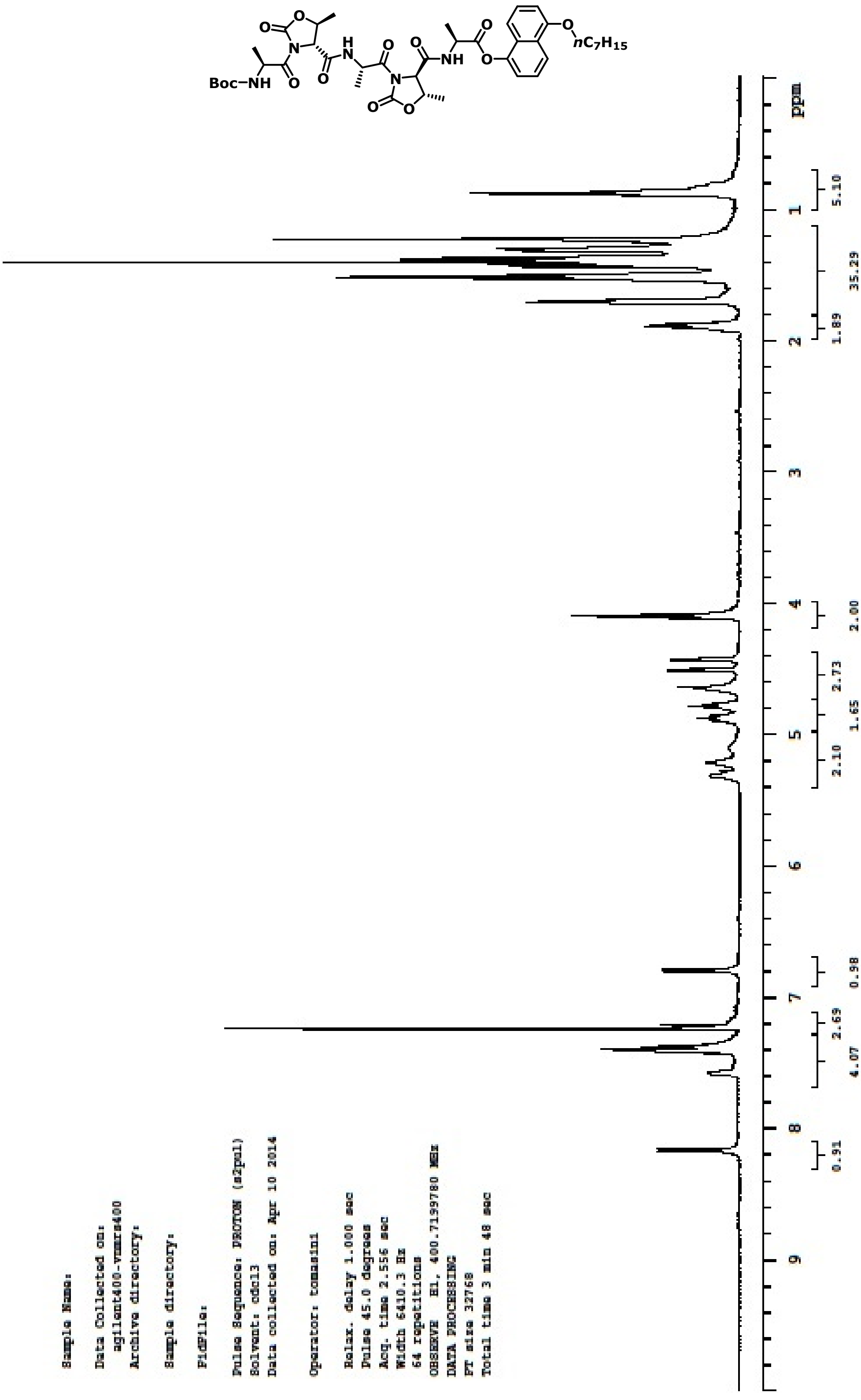
^{1}H NMR spectrum of **9a**



^{13}C NMR spectrum of**9a**



^{1}H NMR spectrum of **9b**



Sample Name:

Data Collected on:
agilent400-vnmrs400
Archive directory:

Sample directory:

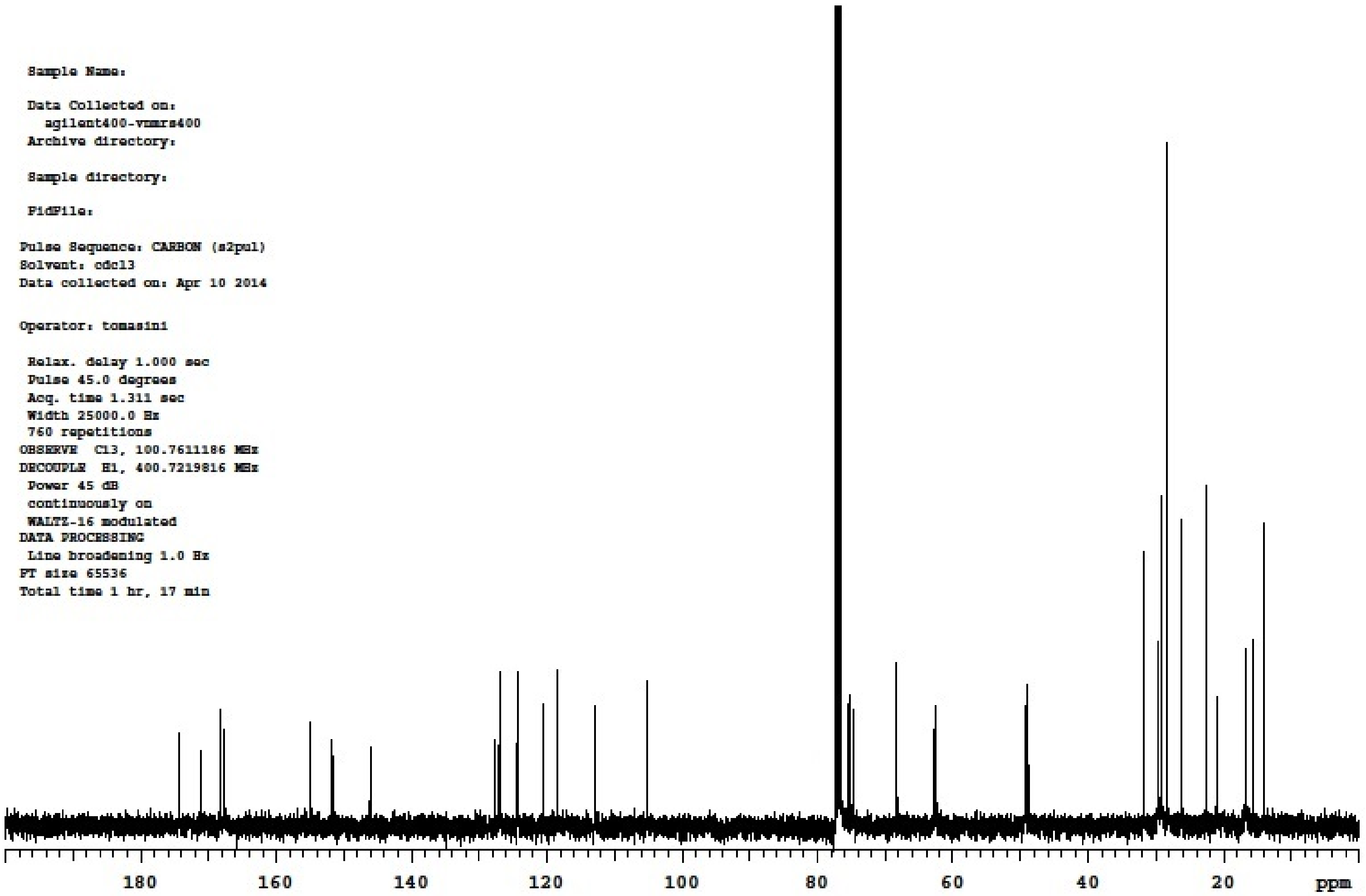
FidFile:

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 10 2014

Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
64 repetitions
OBSERVE H1, 400.7199780 MHz
DATA PROCESSING
FT size 32768
Total time 3 min 48 sec

^{13}C NMR spectrum of **9b**



```
 Sample Name:

 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

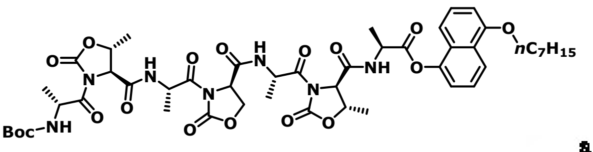
 FidFile:

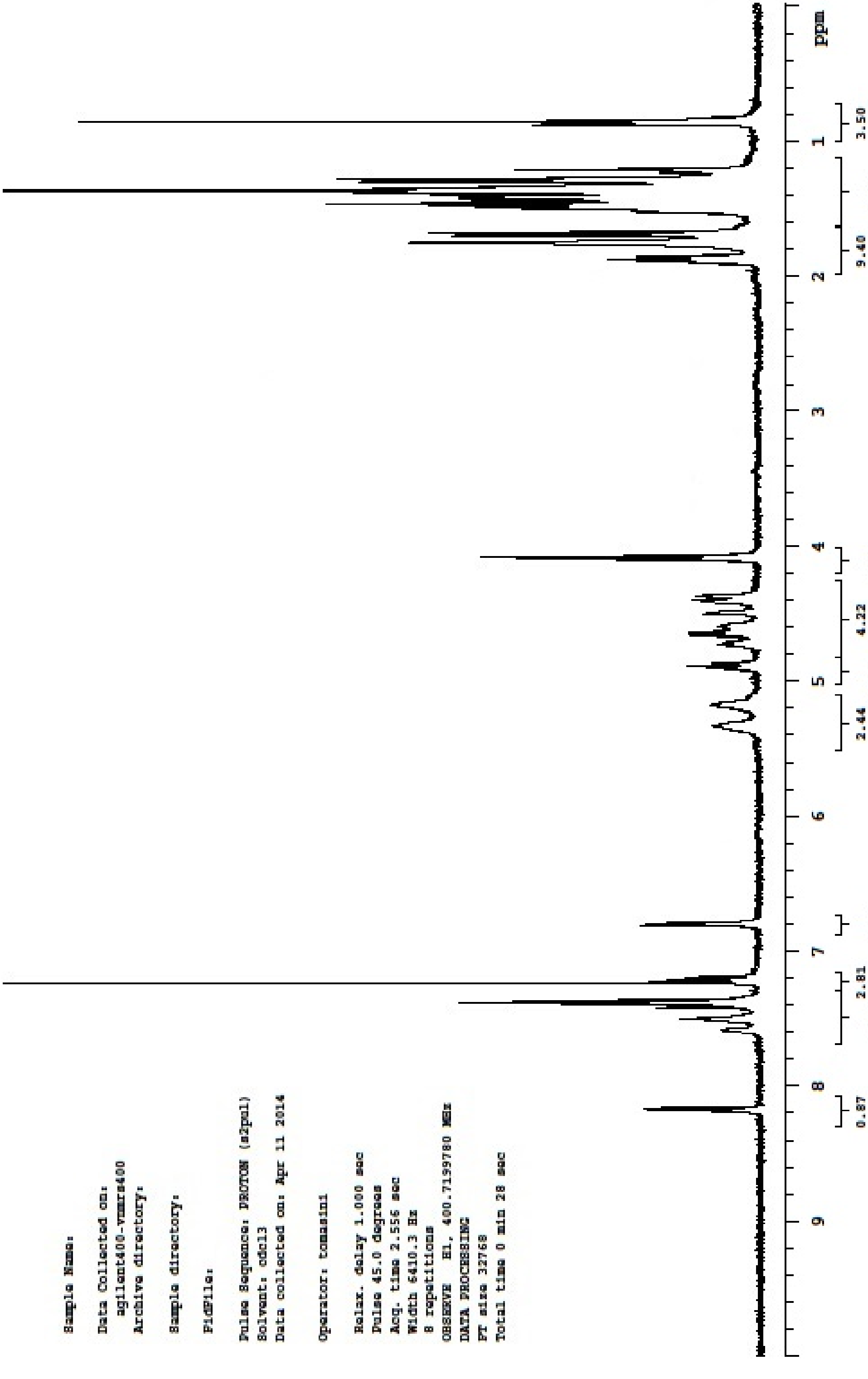
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 10 2014

Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 760 repetitions
OBSERVE  C13, 100.7611186 MHz
DECOUPLE  H1, 400.7219816 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 17 min
```

^{1}H NMR spectrum of **9c**

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Sample Name:

Data Collected on:
   agilent400-vnmrs400
Archive directory:

Sample directory:

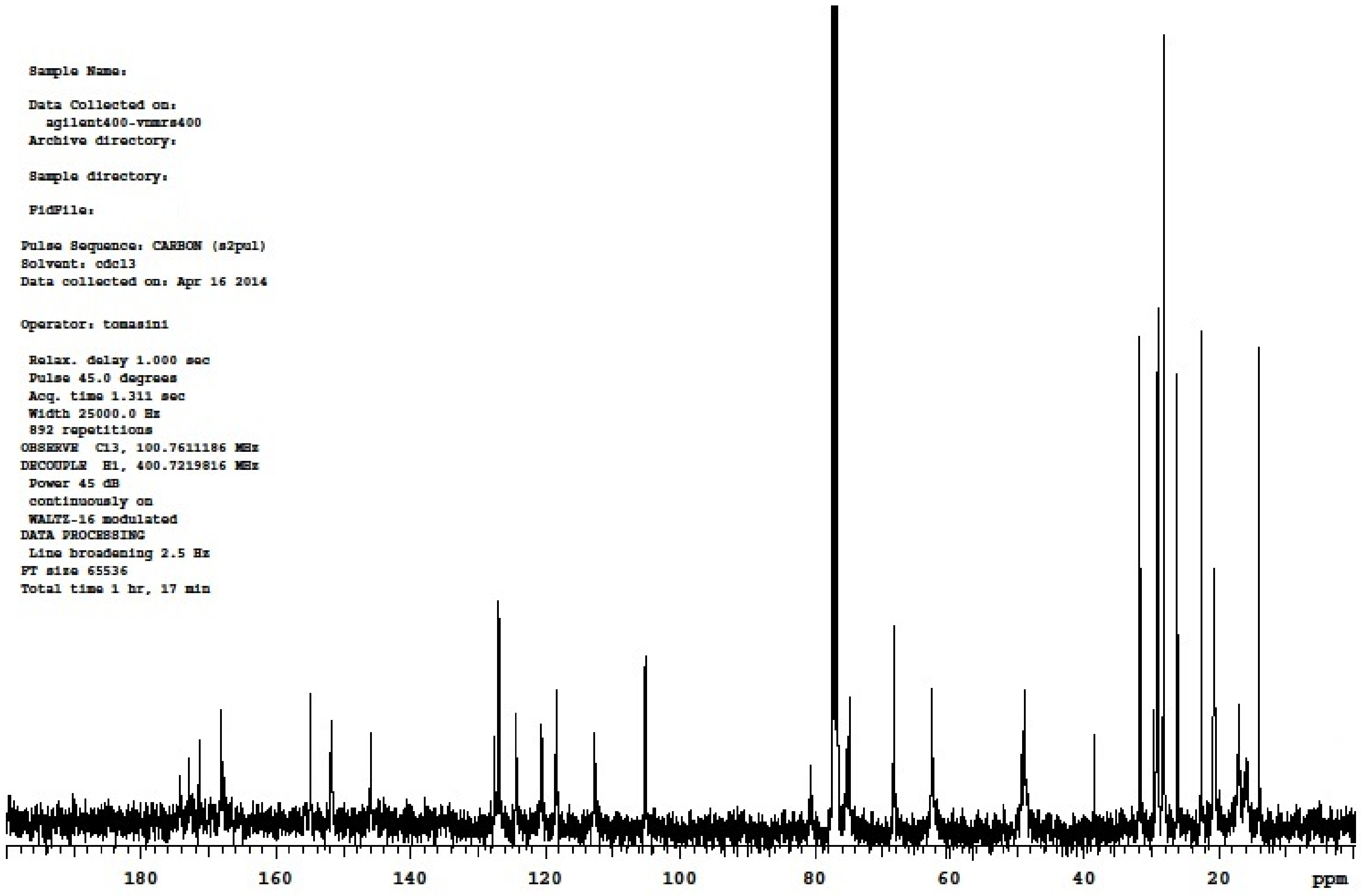
FidFile:

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 11 2014

Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE  H1, 400.7199780 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
```

^{13}C NMR spectrum of **9c**



Sample Name:

Data Collected on:
agilent400-vnmrs400
Archive directory:

Sample directory:

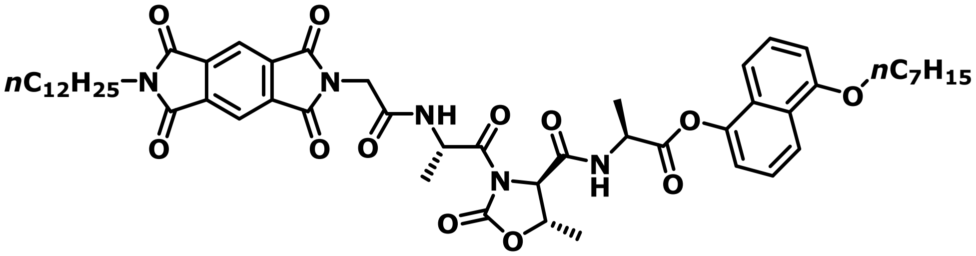
FidFile:

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 16 2014

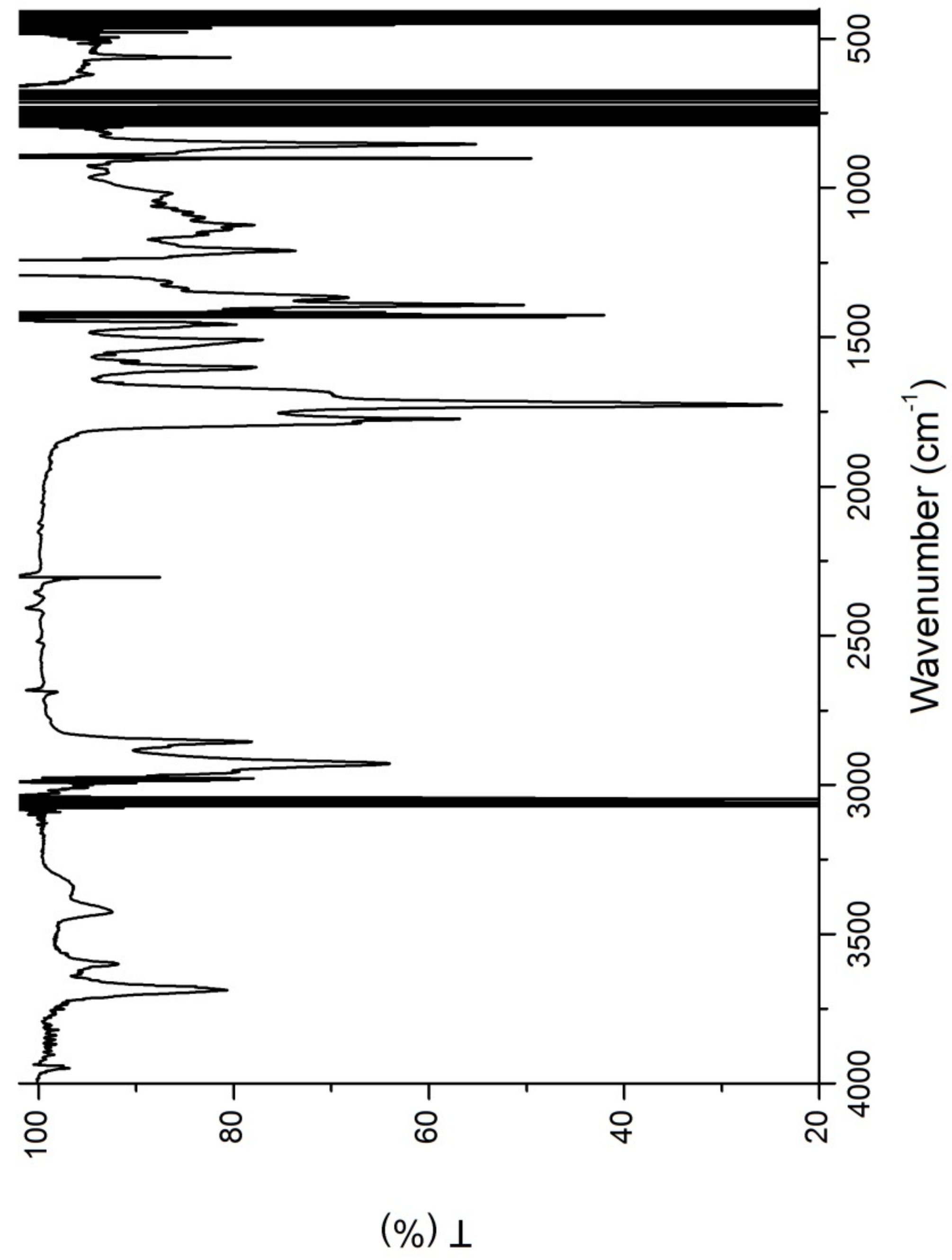
Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
892 repetitions
OBSERVE C13, 100.7611186 MHz
DECOUPLE H1, 400.7219816 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.5 Hz
FT size 65536
Total time 1 hr, 17 min

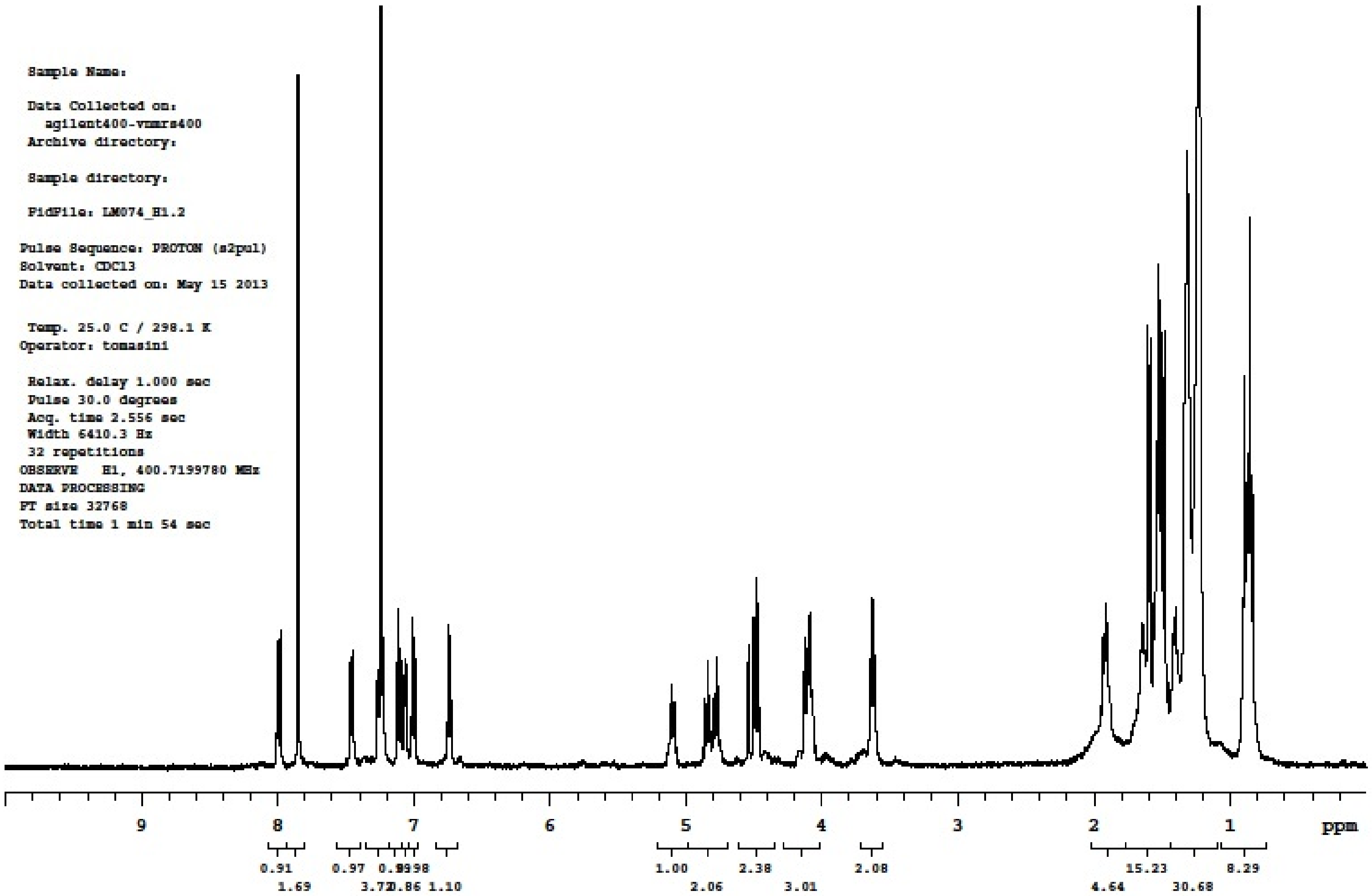
Dyad **1**



IR spectrum of dyad **1**



^{1}H NMR spectra of dyad **1**



```
 Sample Name:

 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

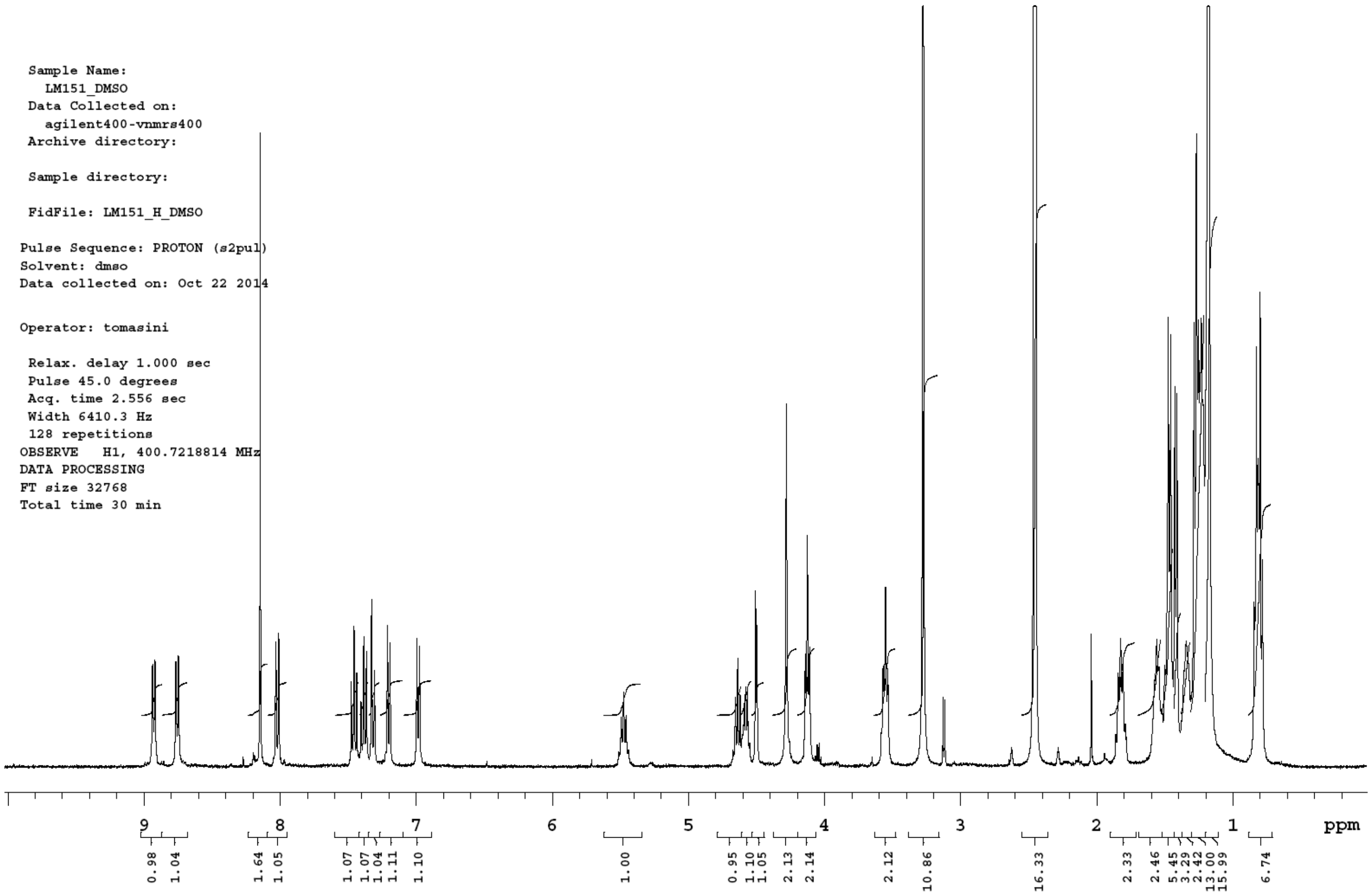
 Sample directory:

 FidFile: LM074_H1.2

Pulse Sequence: PROTON (s2pul)
Solvent: CDCl3
Data collected on: May 15 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 32 repetitions
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 54 sec
```



```
 Sample Name:
   LM151_DMSO
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

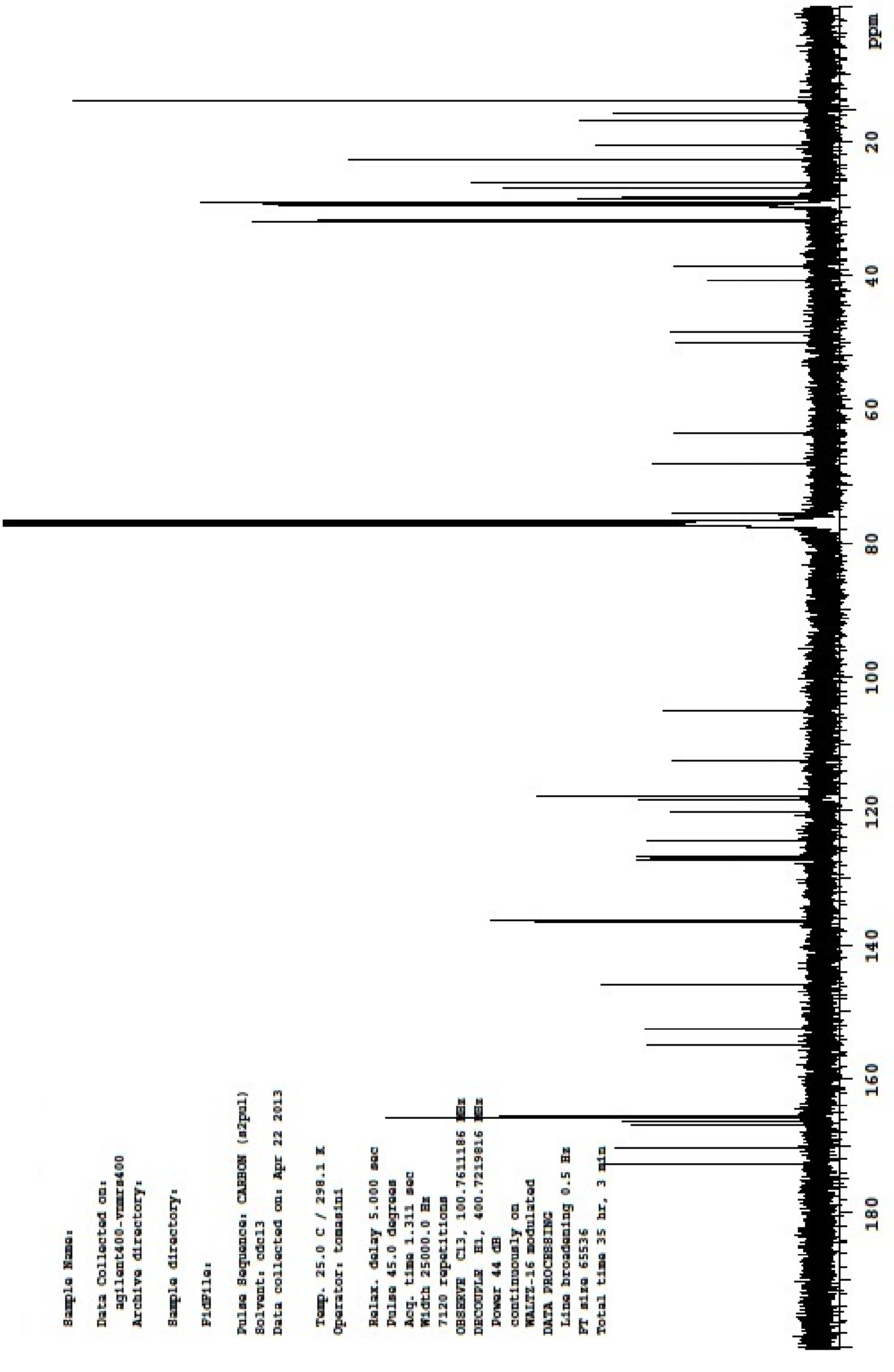
 FidFile: LM151_H_DMSO

Pulse Sequence: PROTON (s2pul)
Solvent: dmso
Data collected on: Oct 22 2014

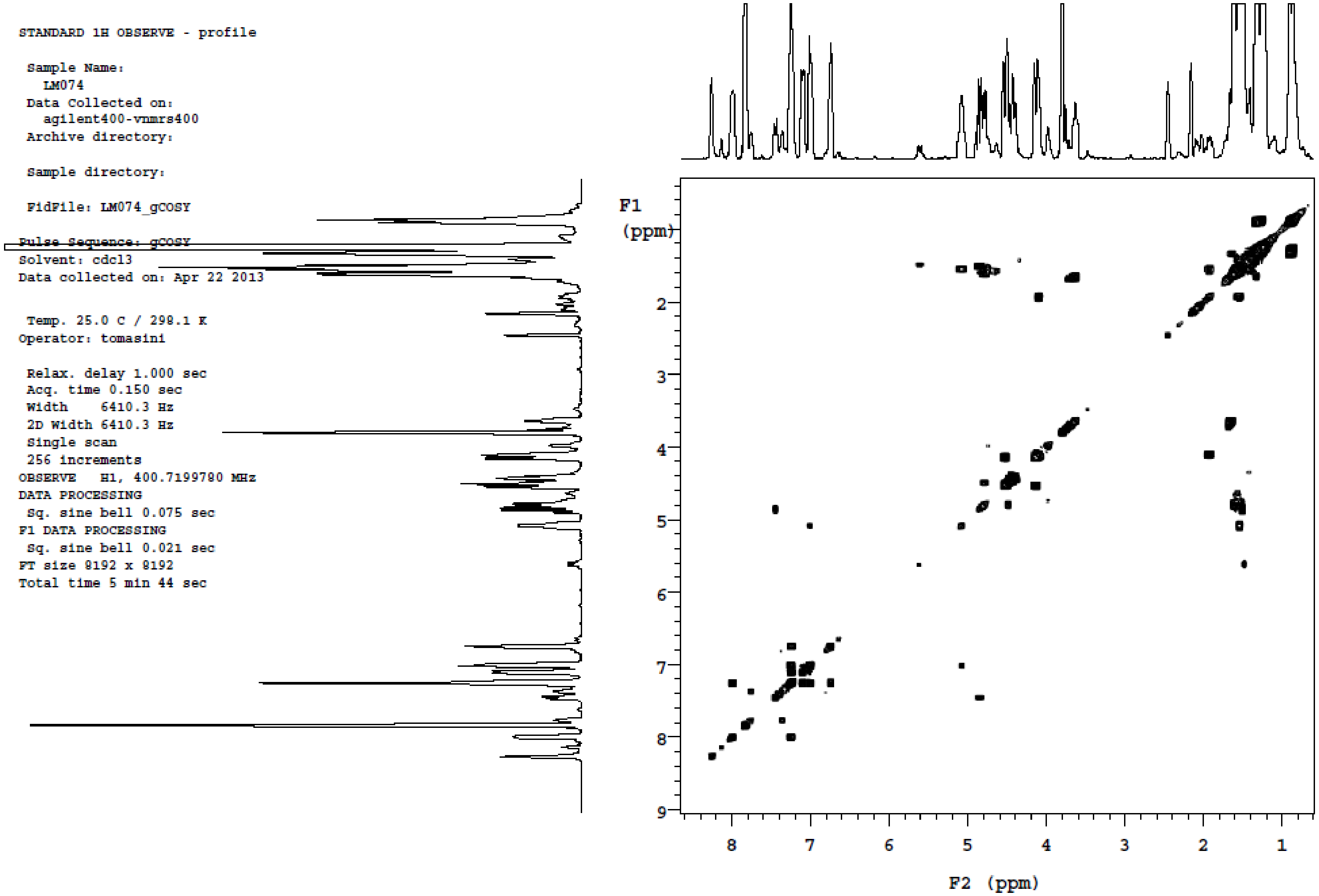
Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 128 repetitions
OBSERVE   H1, 400.7218814 MHz
DATA PROCESSING
FT size 32768
Total time 30 min
```

^{13}C NMR spectrum of dyad **1**



COSY spectrum of dyad **1**



```
STANDARD 1H OBSERVE - profile

 Sample Name:
   LM074
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: LM074_gCOSY

Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Apr 22 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     6410.3 Hz
 2D Width 6410.3 Hz
 Single scan
 256 increments
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Sq. sine bell 0.021 sec
FT size 8192 x 8192
Total time 5 min 44 sec
```

ROESY spectrum of dyad **1**

```
 Sample Name:
   LM074
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

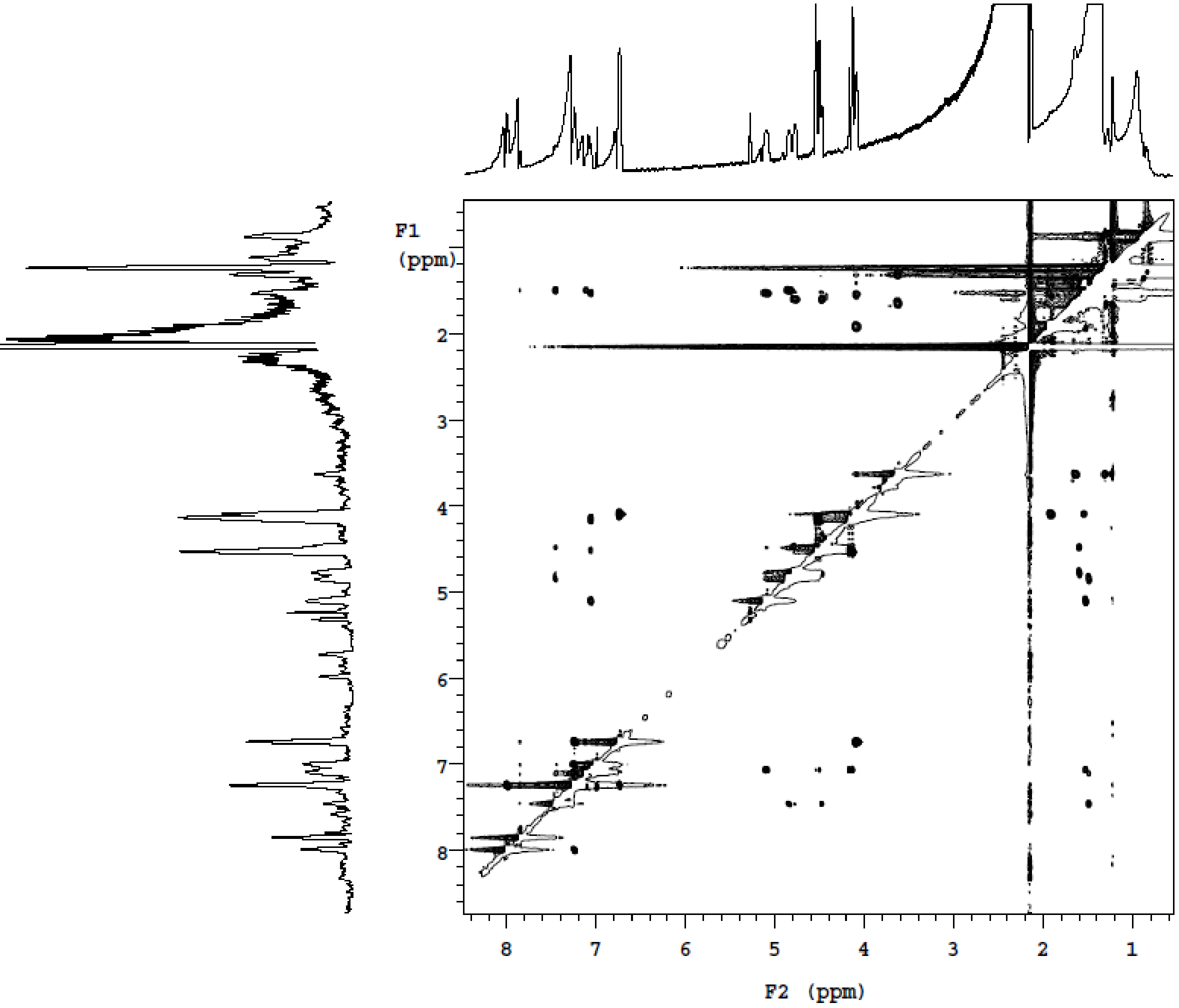
 Sample directory:

 FidFile: LM074_ROESY_400

Pulse Sequence: ROESY
Solvent: CDCl3
Data collected on: May 15 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     6410.3 Hz
 2D Width 6410.3 Hz
 16 repetitions
 2 x 256 increments
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.037 sec
FT size 8192 x 8192
Total time 3 hr, 35 min
```



```
 Sample Name:
   LM074
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

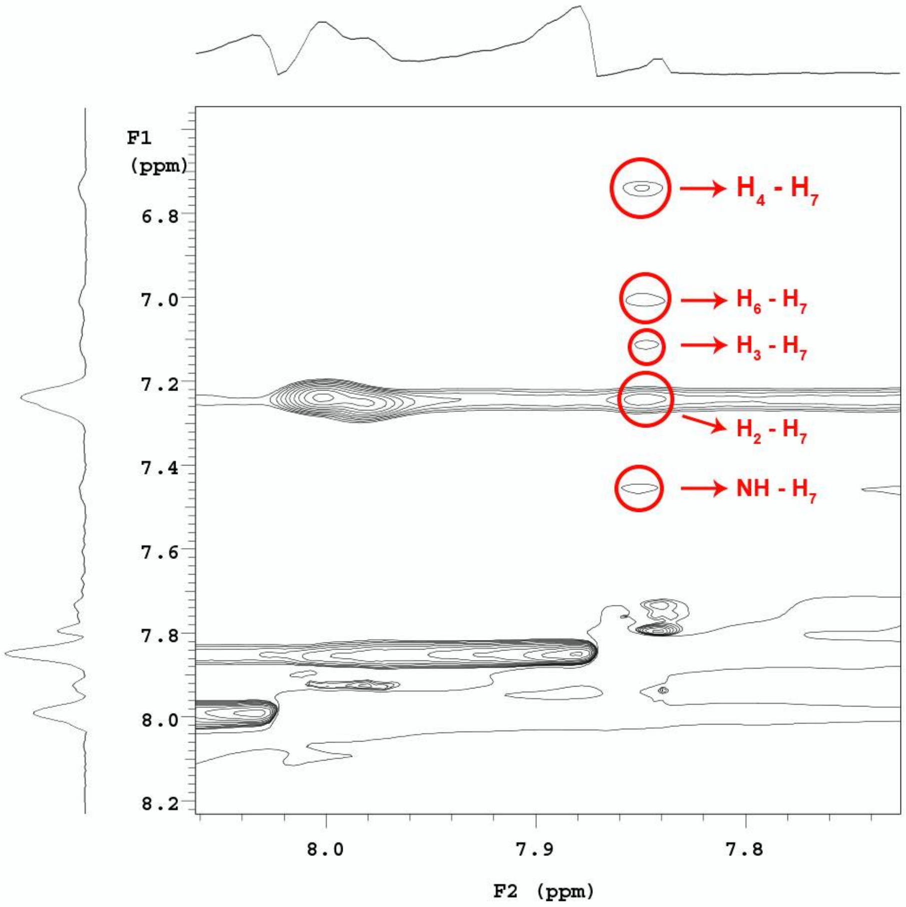
 Sample directory:

 FidFile: LM074_ROESY_400

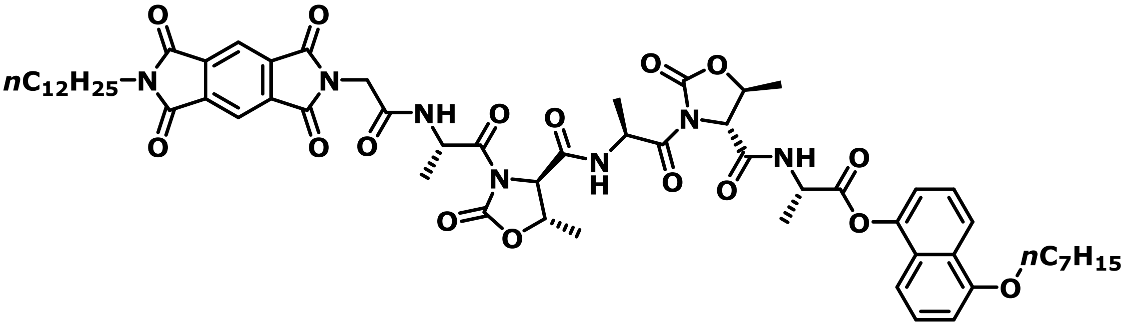
Pulse Sequence: ROESY
Solvent: CDCl3
Data collected on: May 15 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

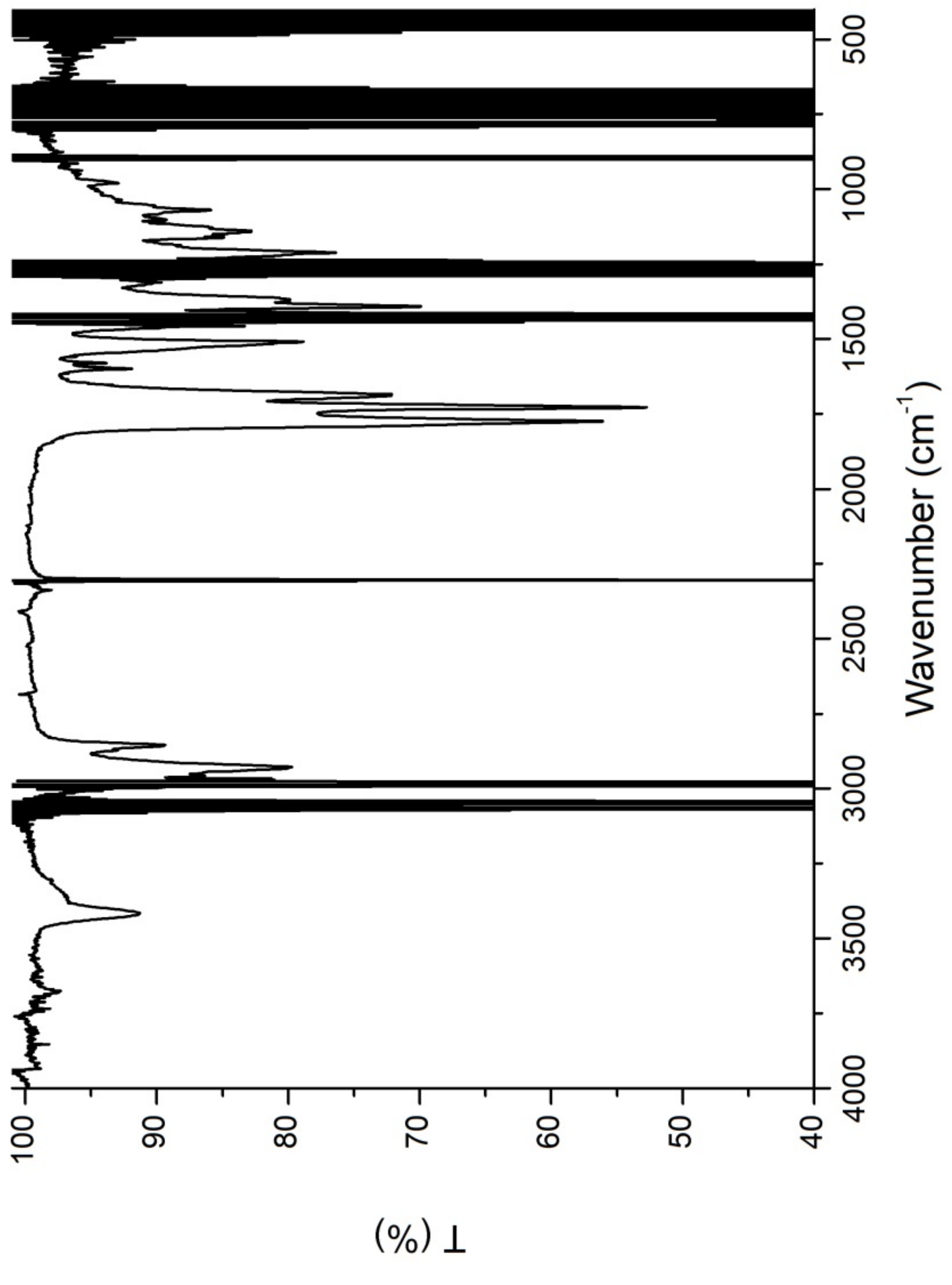
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    6410.3 Hz
 2D Width 6410.3 Hz
 16 repetitions
 2 x 256 increments
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.037 sec
FT size 8192 x 8192
Total time 3 hr, 35 min
```



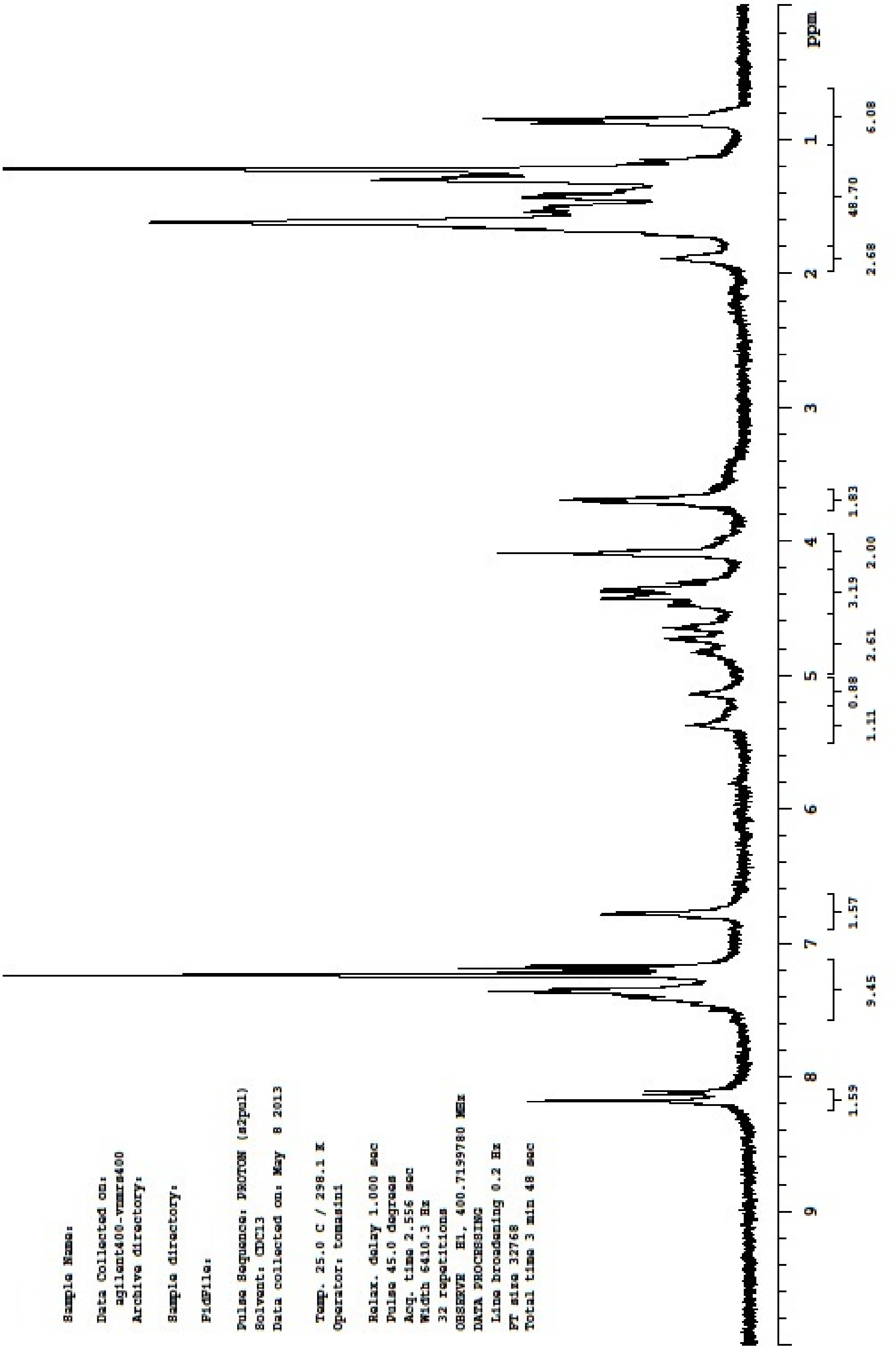
Dyad **2**



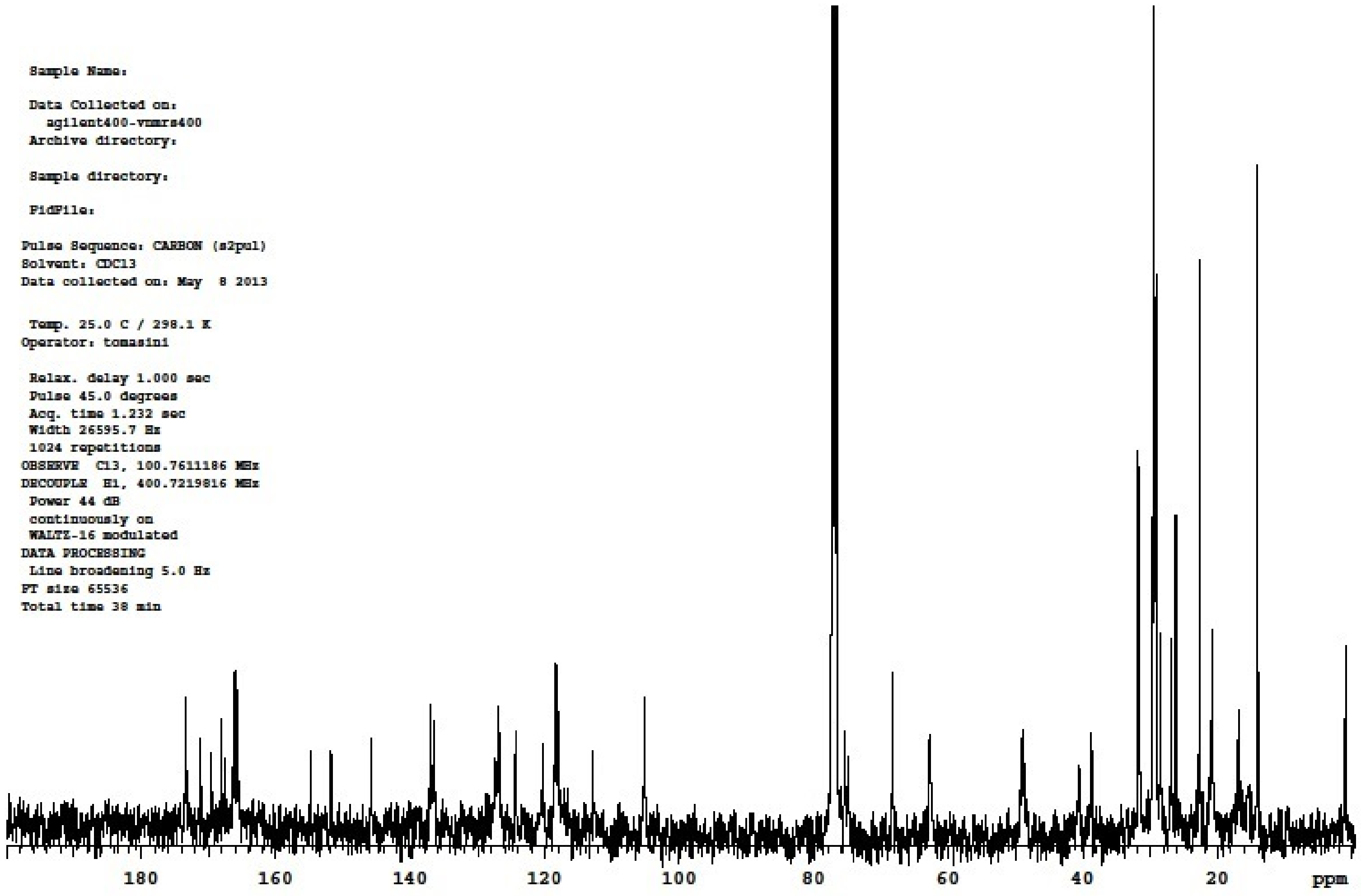
IR spectrum of dyad **2**



^{1}H NMR spectrum of dyad **2**



^{13}C NMR spectrum of dyad **2**



```
 Sample Name:

 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

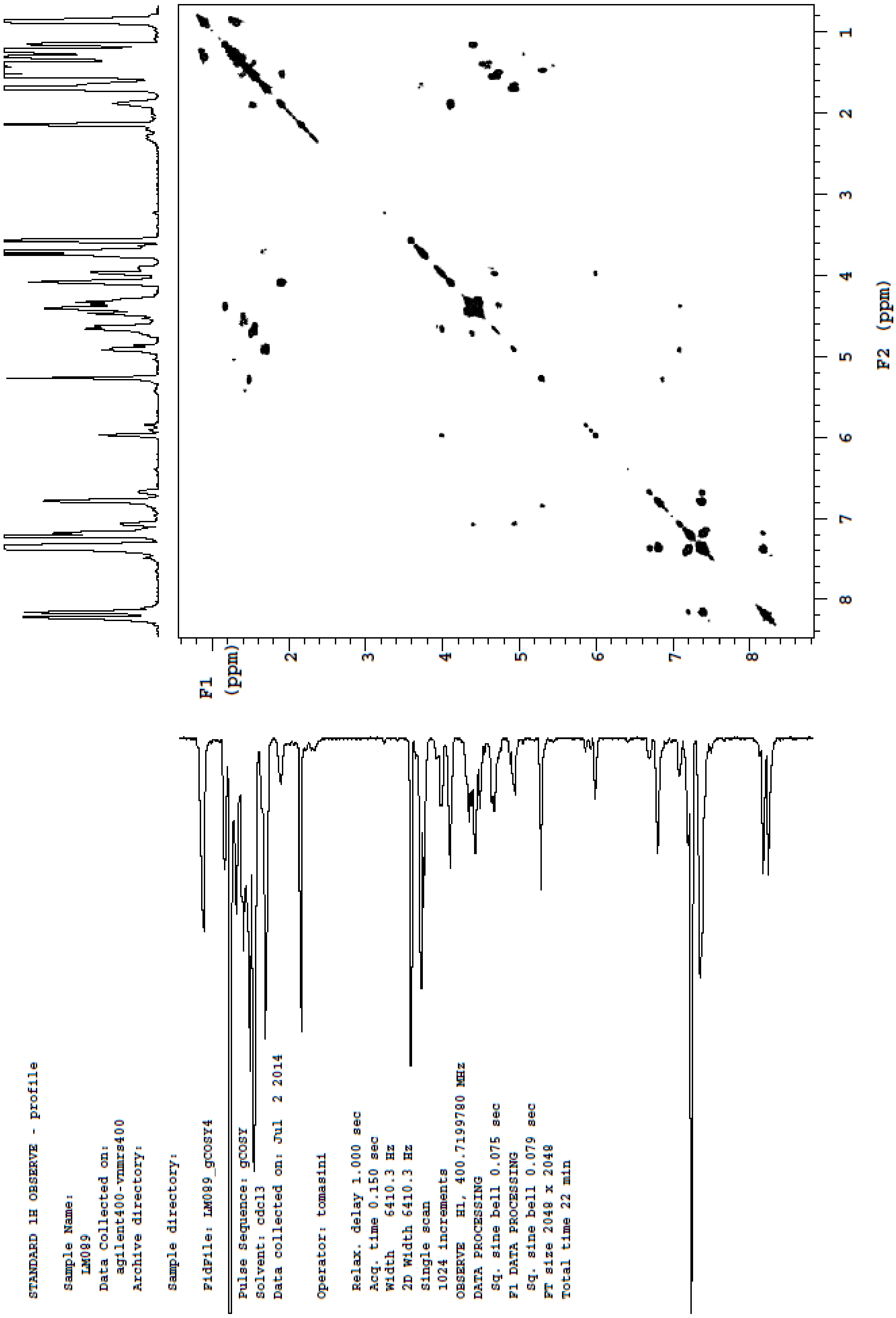
 FidFile:

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: May  8 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.232 sec
 Width 26595.7 Hz
 1024 repetitions
OBSERVE  C13, 100.7611186 MHz
DECOUPLE  H1, 400.7219816 MHz
 Power 44 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 5.0 Hz
FT size 65536
Total time 38 min
```

COSY spectrum of dyad **2**



```
STANDARD 1H OBSERVE - profile

Sample Name:
    LM089
Data Collected on:
    agilent400-vnmrs400
Archive directory:

Sample directory:

FidFile: LM089_gCOSY4

Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul  2 2014

Operator: tomasini

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width    6410.3 Hz
2D Width 6410.3 Hz
Single scan
1024 increments
OBSERVE  H1, 400.7199780 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Sq. sine bell 0.079 sec
FT size 2048 x 2048
Total time 22 min
```

ROESY spectrum of dyad **2**

```
 Sample Name:
   LM089
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

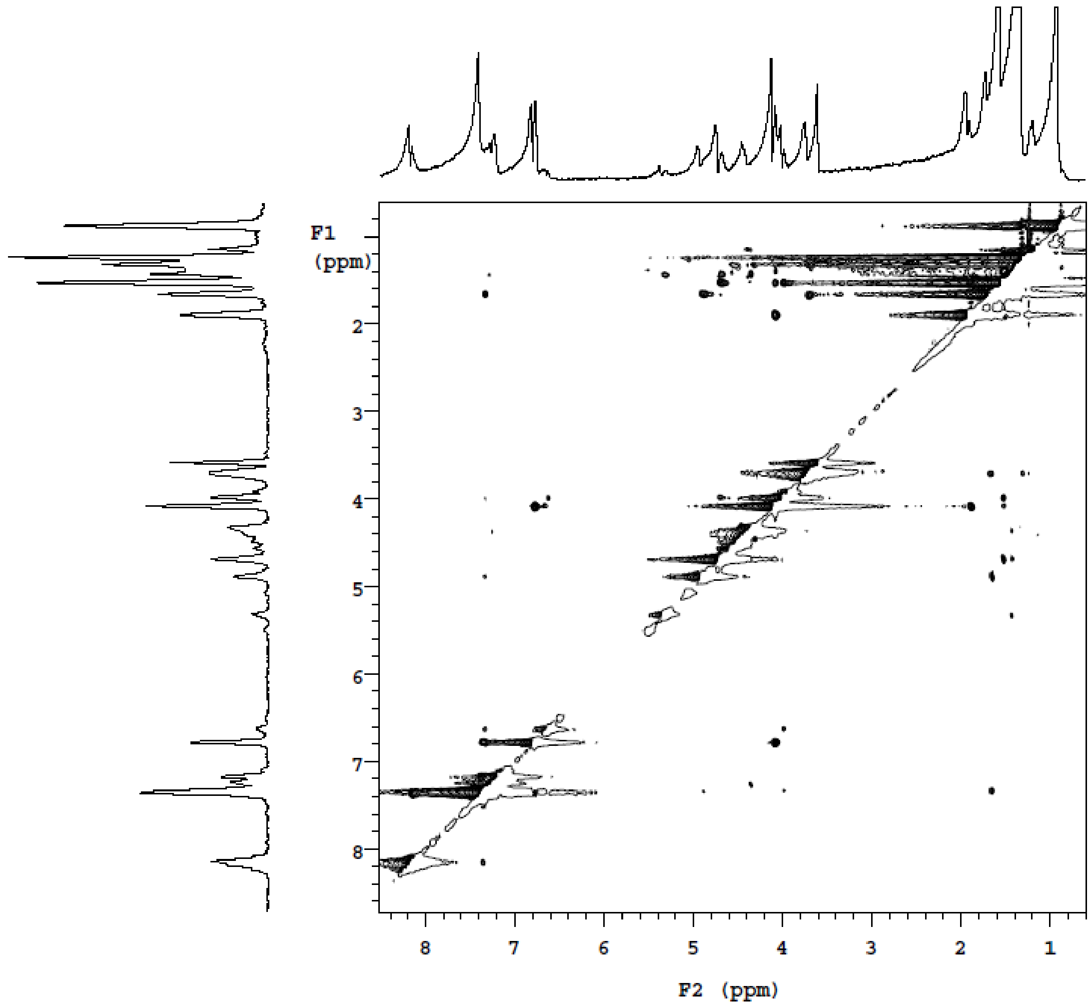
 Sample directory:

 FidFile: LM089_ROESY_400

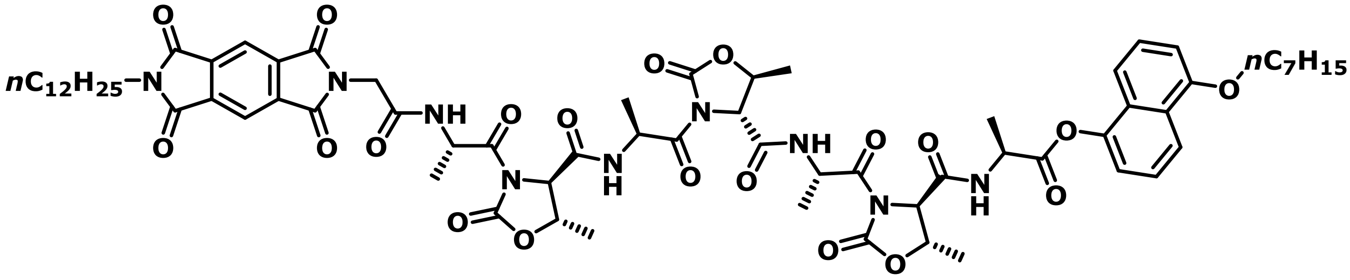
Pulse Sequence: ROESY
Solvent: CDCl3
Data collected on: Oct 28 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

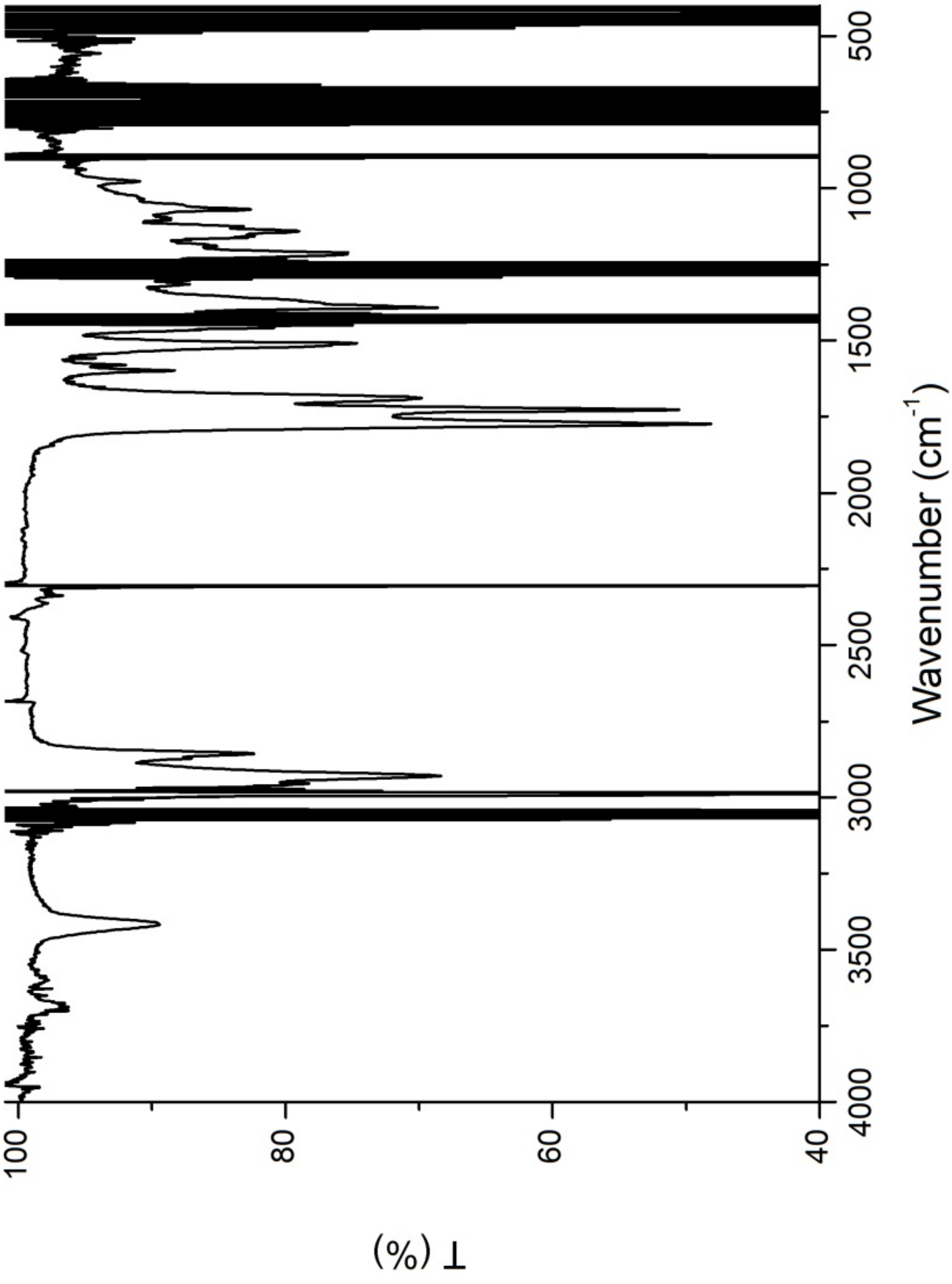
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    6410.3 Hz
 2D Width 6410.3 Hz
 16 repetitions
 2 x 256 increments
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 3 hr, 35 min
```



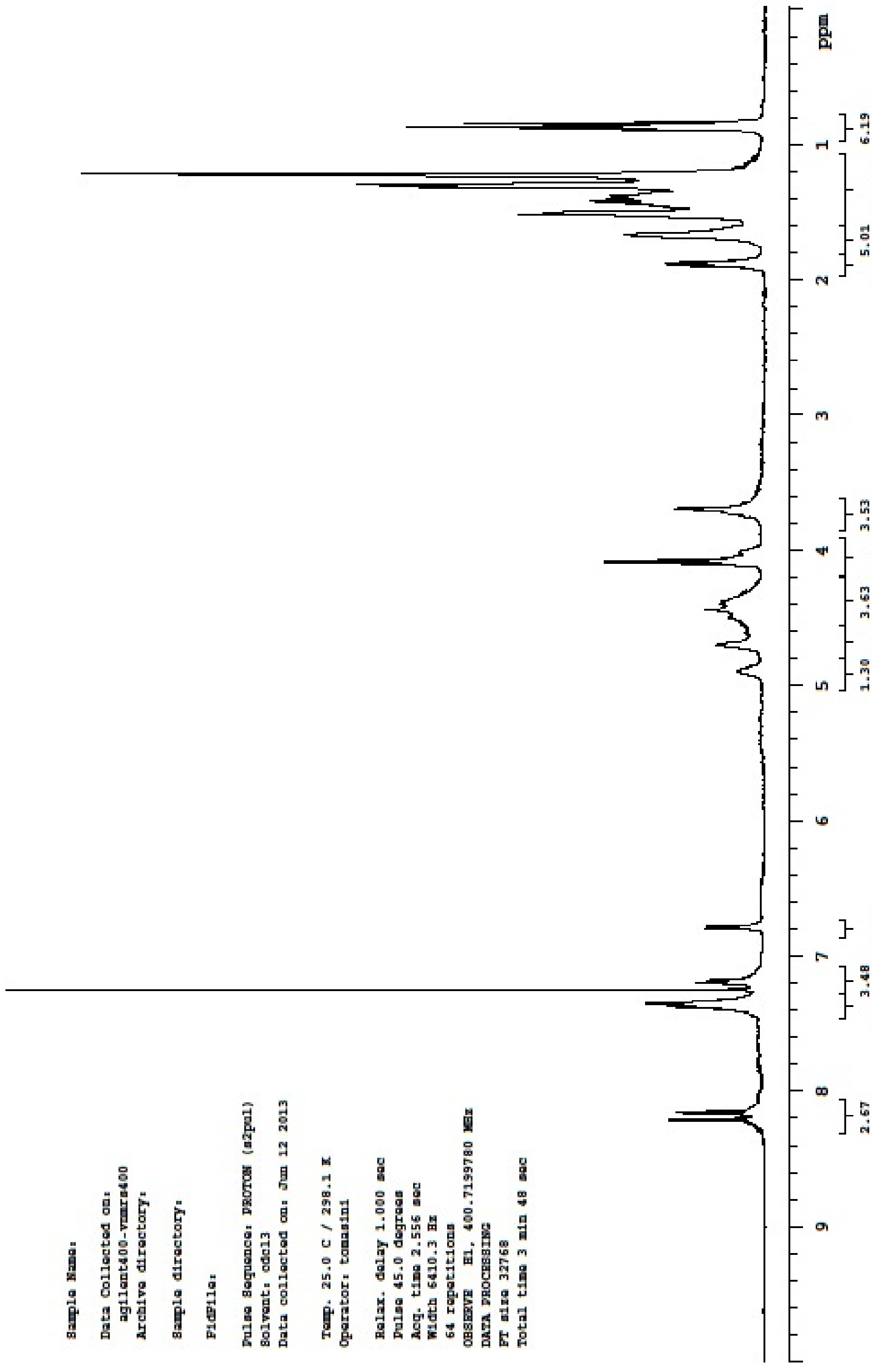
Dyad **3**



IR spectrum of dyad **3**



^1H NMR spectrum of dyad **3**



```
Sample Name:

Data Collected on:
  agilent400-vnmrs400
Archive directory:

Sample directory:

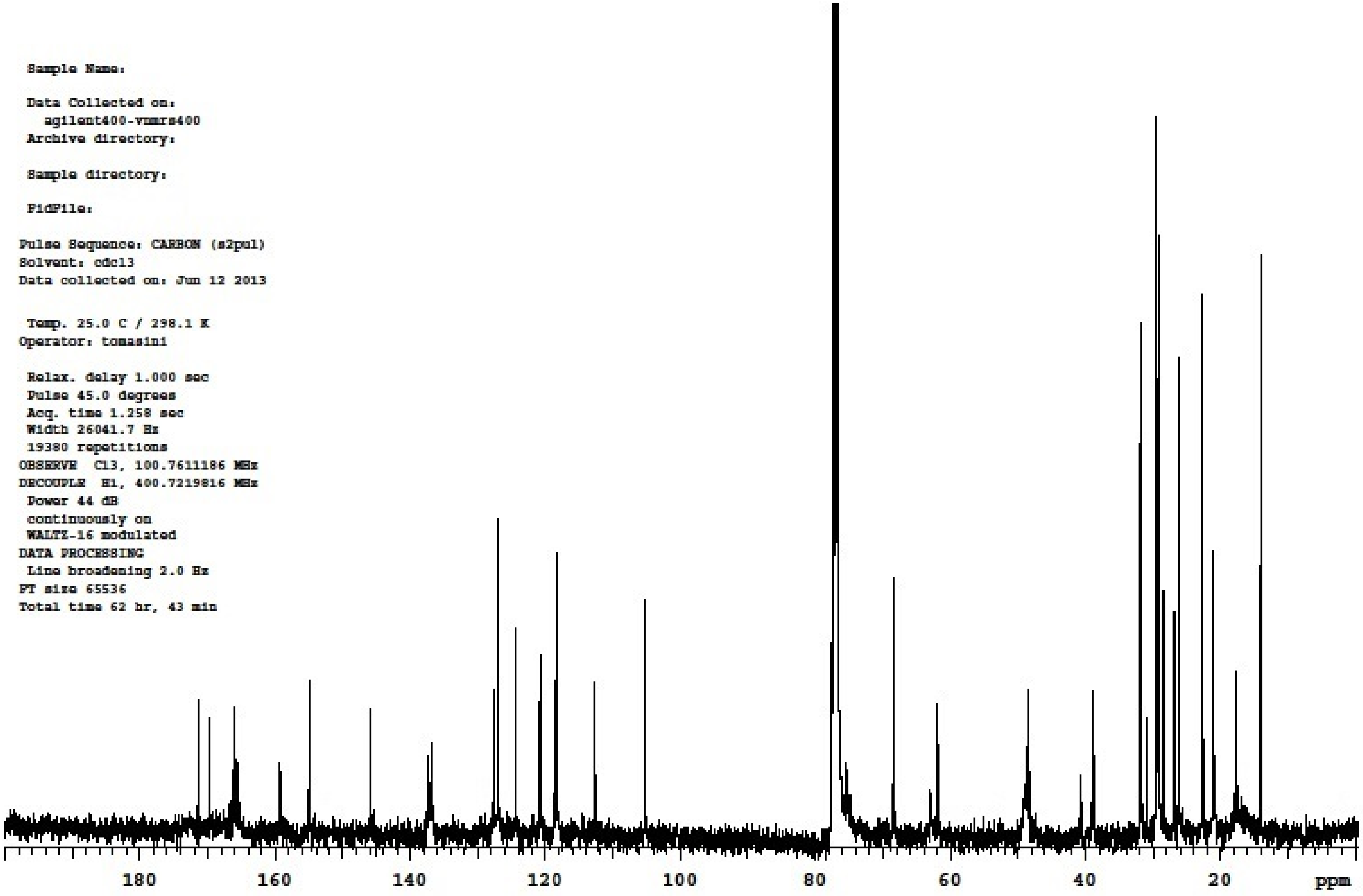
FidFile:

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 12 2013

Temp. 25.0 C / 298.1 K
Operator: tomasini

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
64 repetitions
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
FT size 32768
Total time 3 min 48 sec
```

^{13}C NMR spectrum of dyad **3**



```
 Sample Name:

 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

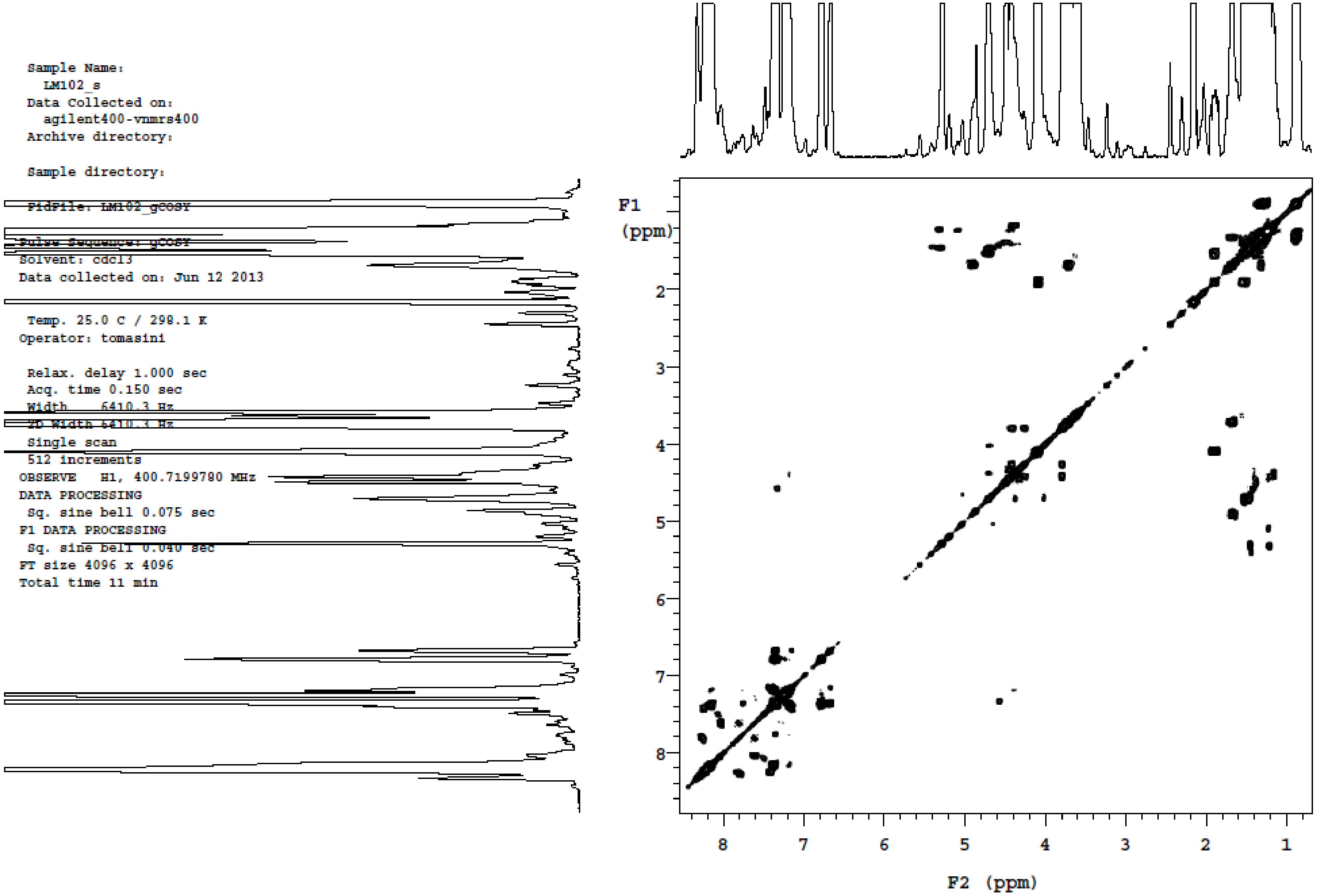
 FidFile:

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 12 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.258 sec
 Width 26041.7 Hz
 19380 repetitions
OBSERVE  C13, 100.7611186 MHz
DECOUPLE  H1, 400.7219816 MHz
 Power 44 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 65536
Total time 62 hr, 43 min
```

COSY spectrum of dyad **3**



```
 Sample Name:
   LM102_s
 Data Collected on:
   agilent400-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: LM102_gCOSY

Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jun 12 2013

 Temp. 25.0 C / 298.1 K
Operator: tomasini

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    6410.3 Hz
 2D Width 6410.3 Hz
 Single scan
 512 increments
OBSERVE   H1, 400.7199780 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Sq. sine bell 0.040 sec
FT size 4096 x 4096
Total time 11 min
```

ROESY spectrum of dyad **3**

Sample Name:
LM102
Data Collected on:
agilent400-vnmrs400
Archive directory:

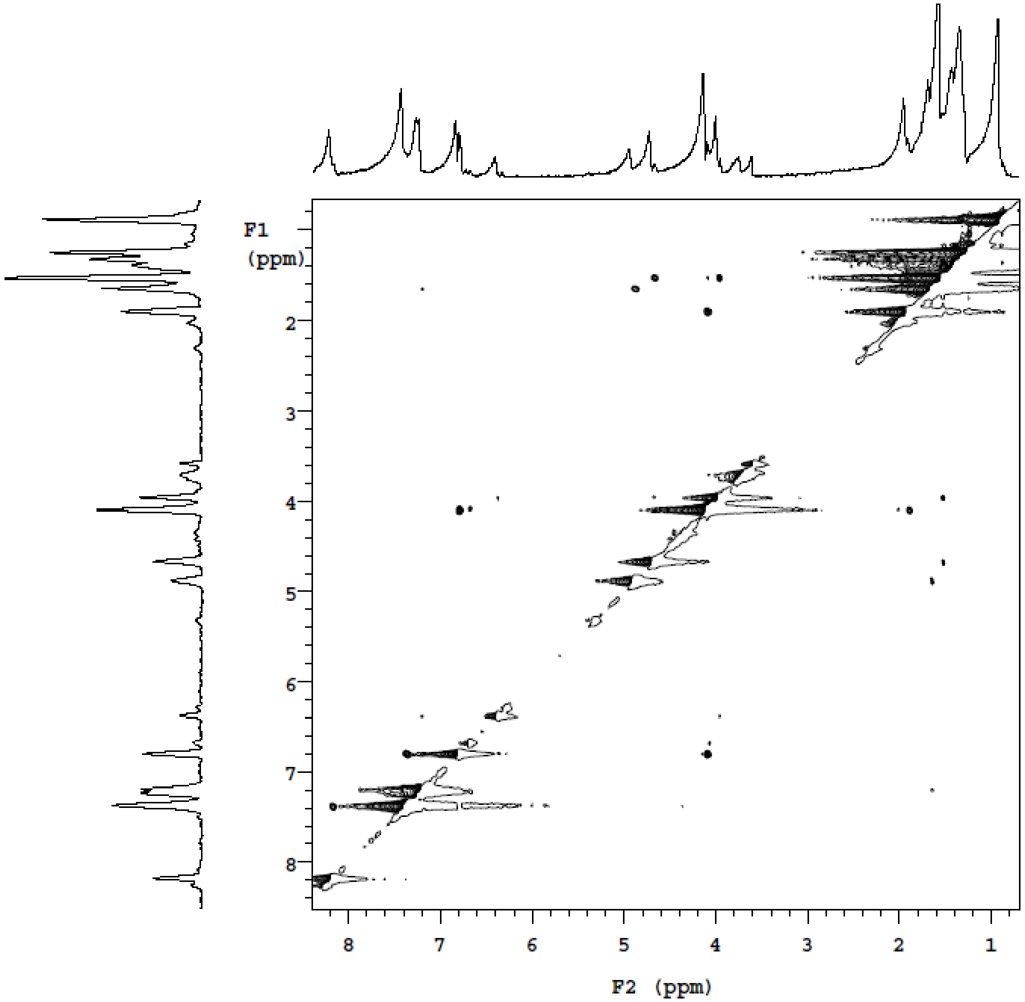
Sample directory:

FidFile: LM102_ROESY_400

Pulse Sequence: ROESY
Solvent: cdcl3
Data collected on: Nov 6 2013

Temp. 25.0 C / 298.1 K
Operator: tomasini

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6410.3 Hz
2D Width 6410.3 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 400.7199780 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 3 hr, 35 min



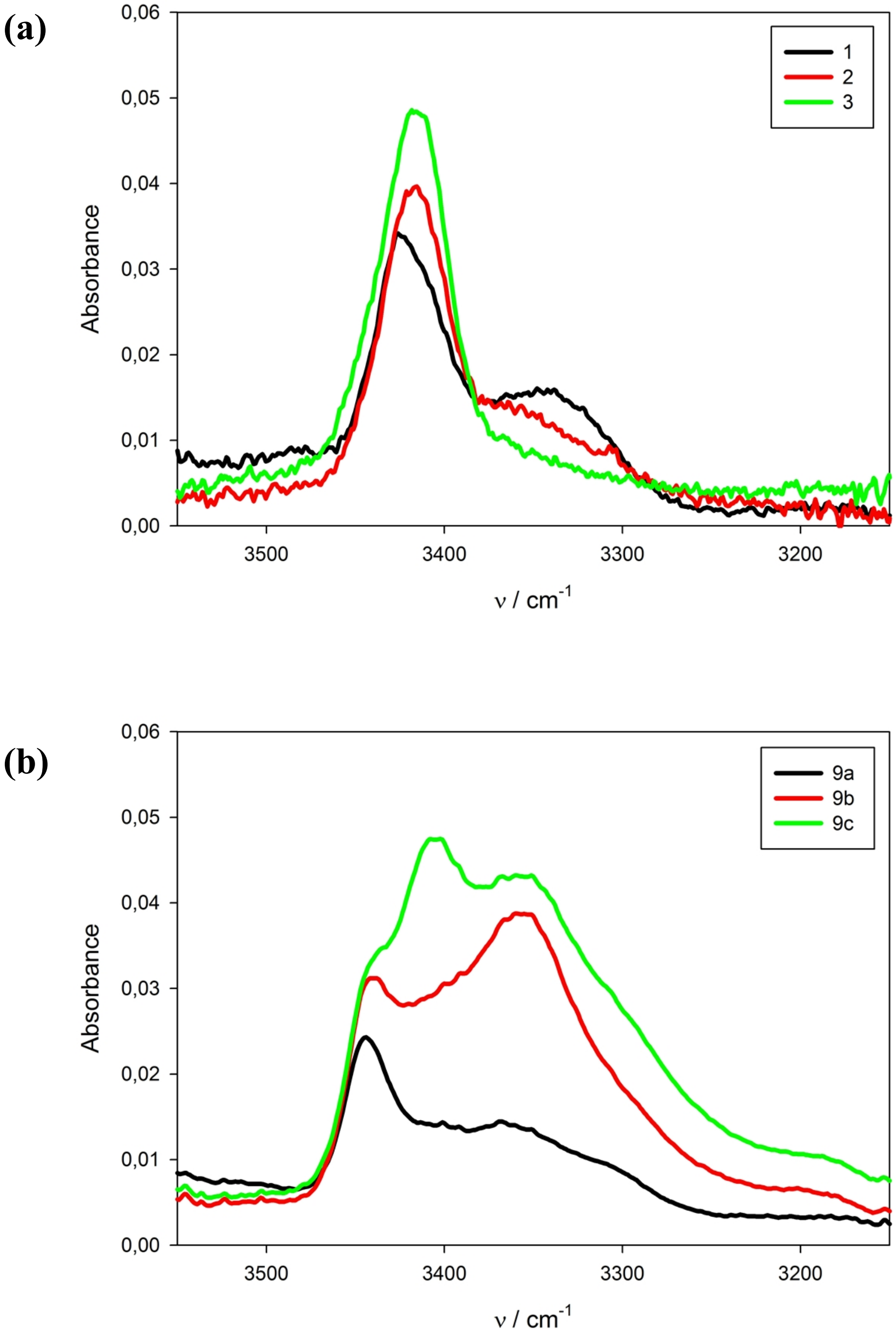


Figure S1. (a) N-H stretching regions of the FT-IR absorption spectra in pure CH_2Cl_2 at room temperature for 3 mM concentration of dyads **1** (black line), **2** (red line) and **3** (green line); (b) N-H stretching regions of the FT-IR absorption spectra in pure CH_2Cl_2 at room temperature for 3 mM concentration of **9a** (black line), **9b** (red line) and **9c** (green line).

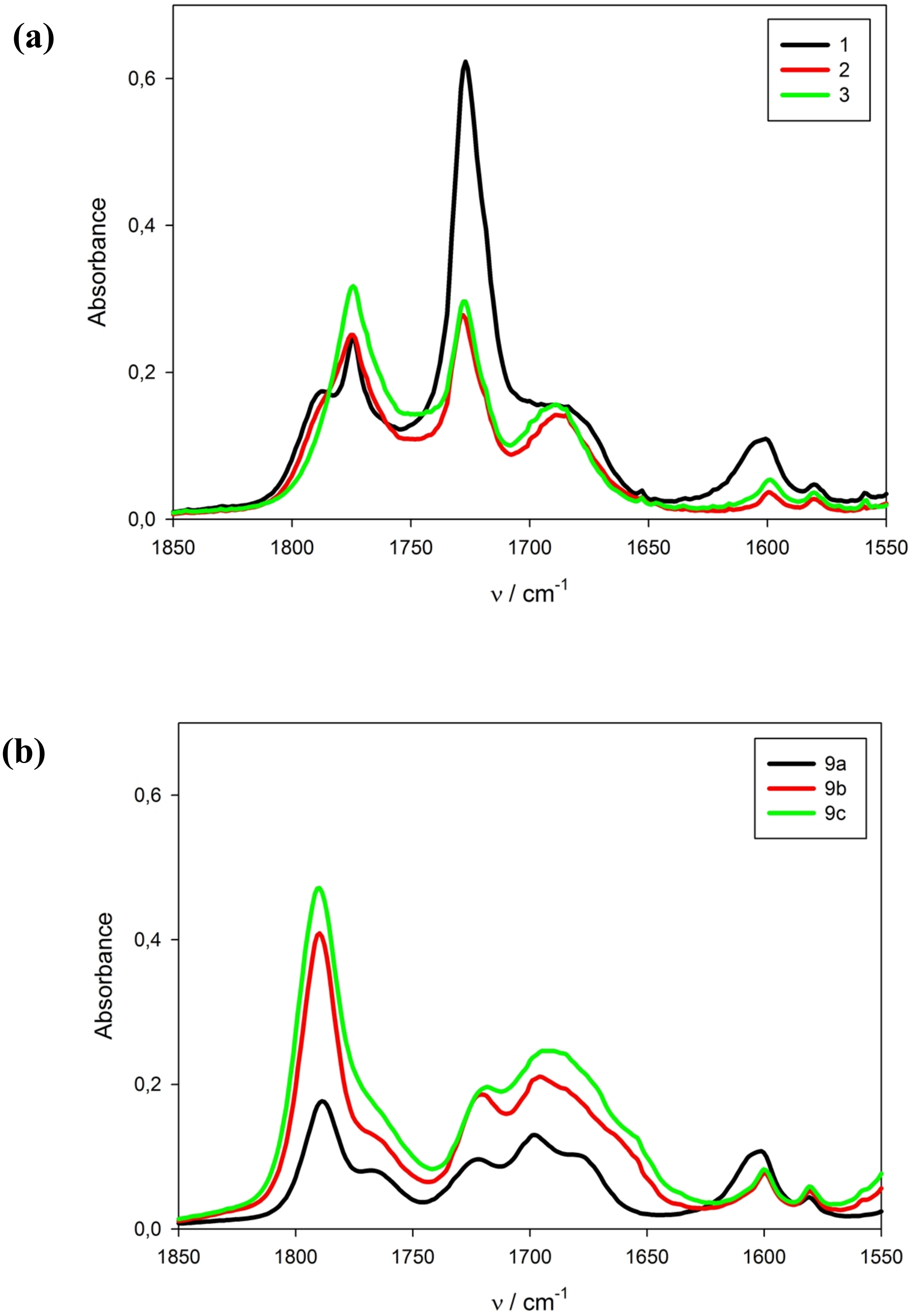


Figure S2. (a) C=O stretching regions of the FT-IR absorption spectra in pure CH_2Cl_2 at room temperature for 3 mM concentration of dyads **1** (black line), **2** (red line) and **3** (green line); (b) C=O stretching regions of the FT-IR absorption spectra in pure CH_2Cl_2 at room temperature for 3 mM concentration of **9a** (black line), **9b** (red line) and **9c** (green line).

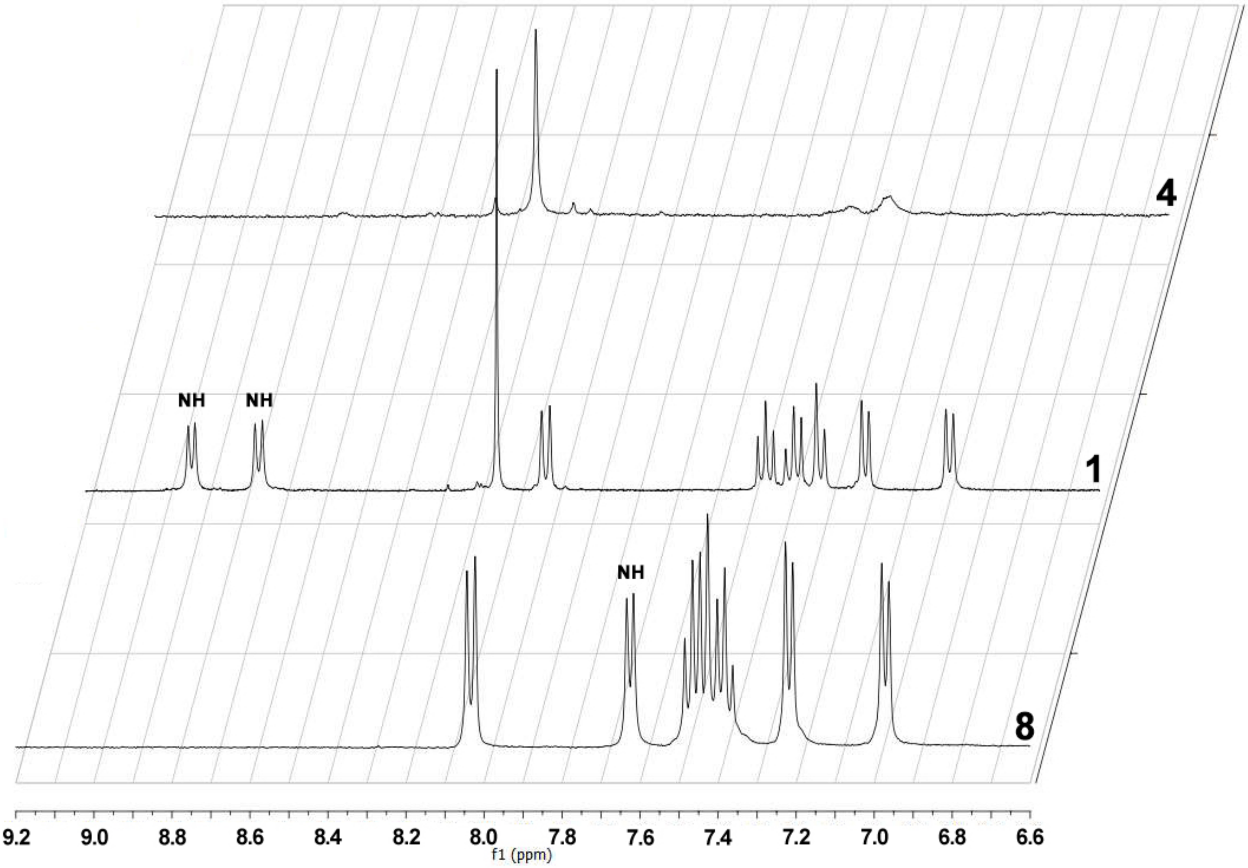


Figure S3. Superimposition of the ^{1}H NMR spectra in DMSO,d_6 of **1**, **4** and **8** in the aromatic region.

Ultrafast Absorption Spectroscopy Apparatus

Ultrafast absorption spectroscopy experiments were carried upon 266 nm excitation out using a pump-probe detection system based on the Spectra-Physics Hurricane Ti:sapphire laser source and the Ultrafast Systems Helios spectrometer. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450-800 nm). Effective time resolution ca. 300 fs, temporal chirp over the white-light 450-750 nm range ca. 200 fs, temporal window of the optical delay stage 0-1000 ps.

Quenching efficiency calculations

To estimate the quenching efficiency of the donor subunits in the dyads we collected the emission spectra of isoabsorbing solutions of the three dyads and model donor compound **5** at the excitation wavelength of 286 nm (A_{286nm} = 0.395). At this wavelength both the donor and the acceptor absorbs light in the dyads, so that we need to correct the emission spectra to take into account the lower amount of light adsorbed by the donor unit in the three dyads compared to the reference compound **5**. The adsorbed fraction of incident light ($1\text{-}10^{-A286nm}$ = 59.7%) is the same for all the compounds, but only 90% of the adsorbed light is directly adsorbed by the donor units in the dyads (53.6%), considering the molar absorption coefficients for the donor model **5** (7400 $M^{-1}cm^{-1}$) and acceptor model **4** (850 $M^{-1}cm^{-1}$) at 286 nm. Taking into account this difference, we corrected the experimental emission intensities, according to the formula:

$$I_{em}^{corr} = I_{em} * \frac{59.7}{53.6}$$

The quenching efficiency (η) of the donor subunit in the dyads was estimated by the ratio of the corrected emission intensity for each dyad and the emission intensity of the model compound **5** (see **Table 2** in the text).

The quenching efficiency was estimated also by comparing excited state lifetimes of the dyads and the donor model compound **5**: $\eta=1-(\tau/\tau^0)$ [3] where τ is the lifetime of the fluorescent excited state of the donor subunit in each dyad and τ^0 is the lifetime of the fluorescent excited state of the model compound **5** (6.3 ns).

The results are the following:

dyad **1**: η = 98%

dyad **2**: η = 95%

dyad **3**: η = 92%.

Same results (within experimental errors) are obtained considering 5.3 ns (the long lifetime of the fitting of the decay curves of the three dyads) as τ^0.

Electrochemical measurements

Table S1. Half-wave potentials ($E_{1/2}$ in V vs. SCE), unless otherwise noted, of acceptor **4** and donor **5** model compounds in CH_2Cl_2 solution at 298K. Working electrode: glassy carbon.

	$E_{1/2}$ V vs. SCE				
4	-1.41	-0.83	+1.64[a]		
5			+1.22[a]	+1.64[a]	+1.97[a]

[a] Anodic peak potential, $E_{p.a.}$ at scan rate v = 0.2 Vs^{-1}.

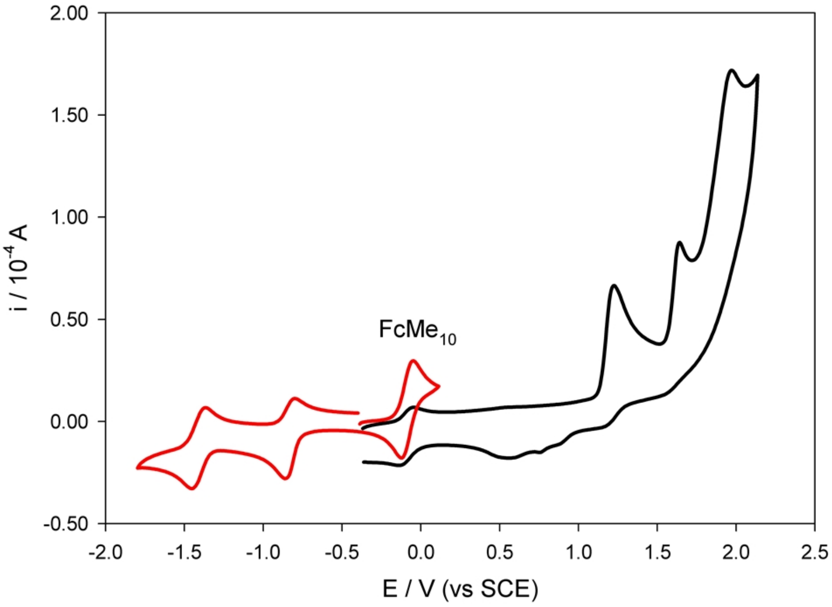


Figure S4. Cyclic voltammograms of a 1.0 mM solution of the acceptor **4** (red line) and donor **5** (black line) model compounds in $CH_2Cl_2/TBAPF_6$. T= 298 K; v=0.2 V/s; working electrode: glassy carbon. Decamethylferrocene ($FcMe_{10}$) has been added as internal standard.

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1. a) G. Luppi, C. Soffrè, C. Tomasini, *Tetrahedron: Asymmetry* **2004**, *15*, 1645-1650; b) C. Tomasini, G. Luppi, M. Monari, *J. Am. Chem. Soc.* **2006**, *128*, 2410-2420; c) G. Angelici, G. Luppi, B. Kaptein, Q. B. Broxterman, H.-J. Hofmann, C. Tomasini, *Eur. J. Org. Chem.* **2007**, 2713-2721; d) G. Longhi, S. Abbate, F. Lebon, N. Castellucci, P. Sabatino, C. Tomasini, *J. Org. Chem.* **2012**, 6033-6042; e) N. Castellucci, G. Falini, L. Milli, M. Monari, S. Abbate, G. Longhi, E. Castiglioni, G. Mazzeo, C. Tomasini, *ChemPlusChem* **2014**, *79*, 114-121.
2. P. M. Alvey, J. J. Reczek, V. Lynch, B. L. Iverson, *J. Org. Chem.* **2010**, *75*, 7682-7690.
3. V. Balzani, P. Ceroni, A. Juris, *Photochemistry and Photophysics: Concepts, Research, Applications*, Wiley-VCH, Weinheim, **2014.**