

# Organocatalytic Enantioselective Friedel-Crafts Alkylation of the Sterically Encumbered $\alpha$ -Alkyl Enal: One-pot Biomimetic Total Synthesis of Yuehchukene.

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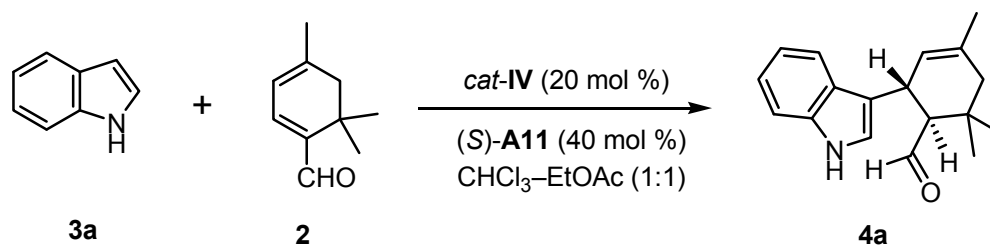
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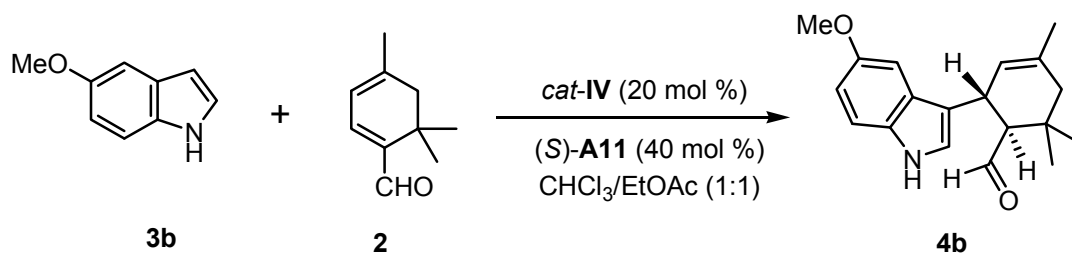
**General Procedure.** All solvents were reagent grade. L-proline (99+%) was purchased from Bachem. Other chemicals were purchased from Aldrich or Acros Chemical Co. Reactions were normally carried out under argon atmosphere in glassware. Silica gel 60 (Merck Geduran Si 60, particle size 0.063 – 0.200 nm) was employed for flash chromatography. Melting points are uncorrected. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub> unless otherwise noted at 400 MHz (Bruker DPX-400) or 500 MHz (Varian-Unity INOVA-500). <sup>13</sup>C NMR spectra were obtained at 100 MHz or 125 MHz. *E.e.* values were measured by HITACHI L-2130 HPLC with HITACHI Diode Array detector L-2455 on a chiral column (chiralpak IC, 0.46 cm ID x 25 cm, particle size 5  $\mu$ ; or chiralpak IA 0.46 cm ID x 25 cm, particle size 5  $\mu$ ) by elution with IPA-hexane. The flow rate of the indicated elution solvent is maintained at 1.0 mL/min, and the retention time of a compound is recorded accordingly. Focused microwave irradiation was carried out at atmospheric pressure with a CEM Discover microwave reactor (5 mL reactors). The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected. The optical rotation values were recorded with a Jasco-P-2000 digital polarimeter.

## Preparation of 4a

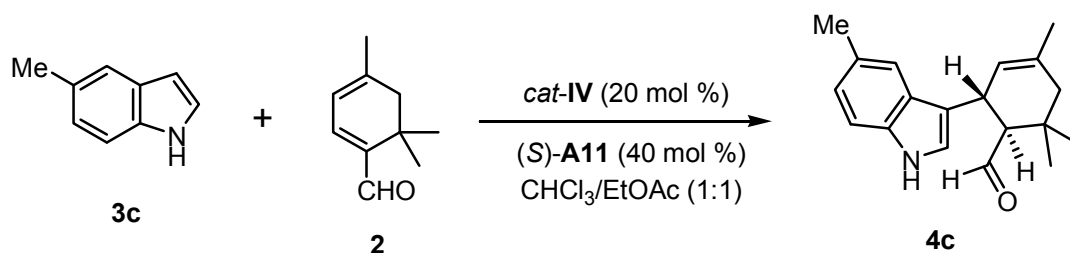


To a solution of aldehyde **2** (102 mg, 0.68 mmol, 2 equiv), catalyst-**IV** (22.1 mg, 0.068 mmol, 0.2 equiv) and additive-(*S*)-**A11** (47.3 mg, 0.14 mmol, 0.4 equiv) in  $\text{CHCl}_3$ -EtOAc (1:1, 1 mL) was added indole **3a** (40 mg, 0.34 mmol, 1 equiv) at  $\sim 25^\circ\text{C}$ . The resulting solution was stirred at ambient temperature for 15 days. To the reaction mixture was added  $\text{Et}_3\text{N}$  (34 mg, 0.34 mmol, 1 equiv) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give the residue. The crude product was purified by flash column chromatography with 8 % EtOAc-hexane ( $R_f = 0.54$  for *trans*-**4a** after developing three times in 15 % EtOAc-hexane and  $R_f = 0.51$  for *cis*-**4a** after developing three times in 15 % EtOAc-hexane) to afford product **4a** as mixture of diastereomers (23 mg, 25 % yield) as a yellow oil. Further purification of **4a** provided the pure *trans*-**4a** for spectra analysis. Selected spectroscopic data for *trans*-**4a**:  $[\alpha]_{\text{D}}^{26} -95.5$  ( $c$  1,  $\text{CHCl}_3$ ) for 88% *ee* of *trans*-**4a**; IR (neat): 3417, 2963, 2825, 1712, 1457, 1260, 1096, 1011, 803, 742  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.70 (d,  $J = 4.5$  Hz, 1 H), 7.96 (bs, 1 H), 7.58 (d,  $J = 8.0$  Hz, 1 H), 7.31 (d,  $J = 8.0$  Hz, 1 H), 7.18 – 7.14 (m, 1 H), 7.09 – 7.05 (m, 1 H), 6.93 (d,  $J = 2.5$  Hz, 1 H), 5.50 (s, 1 H), 4.08 – 4.05 (m, 1 H), 2.63 (dd,  $J = 11.0, 4.0$  Hz, 1 H), 2.18 (d,  $J = 17.0$  Hz, 1 H), 1.71 (s, 3 H), 1.69 (d,  $J = 17$  Hz, 1 H), 1.12 (s, 3 H), 1.11 (s, 3 H),  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5 (CH), 136.7 (C), 131.7 (C), 126.4 (C), 123.0 (CH), 122.0 (CH), 121.9 (CH), 119.4 (CH), 119.2 (CH), 117.5 (C), 111.3 (CH), 60.8 (CH), 46.5 ( $\text{CH}_2$ ), 33.8 (C), 32.2 (CH), 29.3 ( $\text{CH}_3$ ), 23.4 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ); MS ( $m/z$ , relative intensity): 268 ( $\text{M}^+ + 1$ , 20) 267 ( $\text{M}^+$ , 100), 238 (80), 222 (39), 182 (76), 168 (77), 130 (26), 117 (44), exact mass calculated for  $\text{C}_{18}\text{H}_{21}\text{NO}$  ( $\text{M}^+$ ): 267.1623; found : 267.1624.

## Preparation of 4b

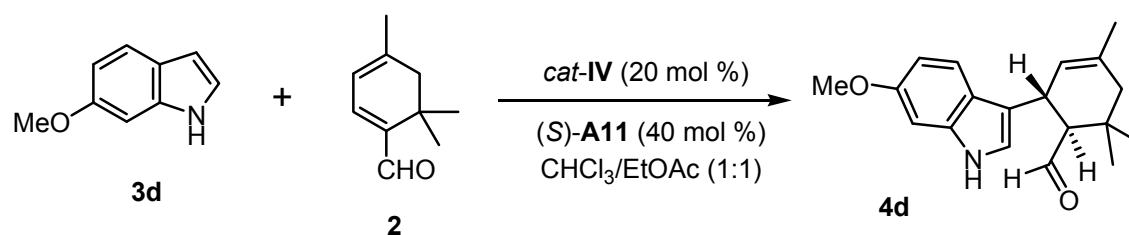


To a solution of aldehyde **2** (81.6 mg, 0.54 mmol, 2 equiv), catalyst-**IV** (17.7 mg, 0.05 mmol, 0.2 equiv) and additive-(*S*)-**A11** (37.8 mg, 0.11 mmol, 0.4 equiv) in  $\text{CHCl}_3$ -EtOAc (1:1, 0.77 mL) was added indole **3b** (40 mg, 0.27 mmol, 1 equiv) at  $\sim 25^\circ\text{C}$ . The resulting solution was stirred at ambient temperature for 15 days. To the reaction mixture was added  $\text{Et}_3\text{N}$  (27 mg, 0.27 mmol, 1 equiv) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give the residue. The crude product was purified by flash column chromatography with 10 % EtOAc-hexane ( $R_f = 0.49$  for *trans*-**4b** after developing three times in 15 % EtOAc-hexane and  $R_f = 0.46$  for *cis*-**4b** after developing three times in 15 % EtOAc-hexane) to afford product **4b** as mixture of diastereomers (24 mg, 30 % yield) as yellow oil; Selected spectroscopic data for *trans*-**4b**:  $[\alpha]_D^{26} -59.2$  ( $c$  1,  $\text{CHCl}_3$ ) for 58% *ee* of *trans*-**4b**; IR (neat): 3414, 2964, 2828, 1716, 1486, 1457, 1439, 1260, 1217, 1027, 800,  $756\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.70 (d,  $J = 4.5$  Hz, 1 H), 7.84 (bs, 1 H), 7.21 (d,  $J = 8.5$  Hz, 1 H), 7.03 (d,  $J = 2.0$  Hz, 1 H), 6.91 (d,  $J = 2.5$  Hz, 1 H), 6.82 (dd,  $J = 8.5, 2.5$  Hz, 1 H), 5.49 (s, 1 H), 4.04 – 4.00 (m, 1 H), 3.83 (s, 3 H), 2.60 (dd,  $J = 11, 4$  Hz, 1 H), 2.16 (d,  $J = 17$  Hz, 1 H), 1.78 – 1.68 (m, 1 H), 1.71 (s, 3 H), 1.11 (s, 3 H), 1.10 (s, 3 H),  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5 (CH), 153.6 (C), 131.82 (C), 131.76 (C), 126.8 (C), 122.9 (CH), 122.7 (CH), 117.2 (C), 111.9 (CH), 111.8 (CH), 101.6 (CH), 60.6 (CH), 55.9 (CH<sub>3</sub>), 46.5 (CH<sub>2</sub>), 33.8 (C), 32.1 (CH), 29.3 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>); MS ( $m/z$ , relative intensity): 298 ( $\text{M}^+ + 1$ , 21), 297 ( $\text{M}^+$ , 100), 268 (76), 252 (26), 212 (74), 198 (52), 147 (40), 101 (39), exact mass calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}_2$  ( $\text{M}^+$ ): 297.1729; found : 297.1728.

Preparation of **4c**

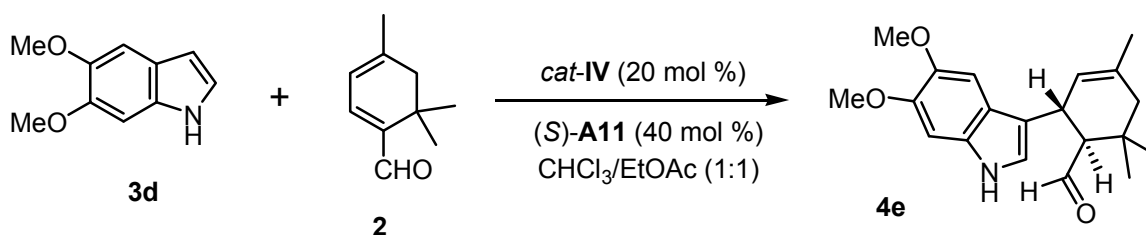
To a solution of aldehyde **2** (91.5 mg, 0.61 mmol, 2 equiv), catalyst-**IV** (19.8 mg, 0.06 mmol, 0.2 equiv) and additive-(*S*)-**A11** (42.4 mg, 0.12 mmol, 0.4 equiv) in  $\text{CHCl}_3$ -EtOAc (1:1, 0.87 mL) was added indole **3c** (40 mg, 0.30 mmol, 1 equiv) at  $\sim 25^\circ\text{C}$ . The resulting solution was stirred at ambient temperature for 15 days. To the reaction mixture was added  $\text{Et}_3\text{N}$  (31 mg, 0.305 mmol, 1 equiv) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give the residue. The crude product was purified by flash column chromatography with 8 % EtOAc-hexane ( $R_f = 0.35$  for *trans*-**4c** after developing two times in 15 % EtOAc-hexane and  $R_f = 0.32$  for *cis*-**4c** after developing two times in 15 % EtOAc-hexane) to afford product **4c** as mixture of diastereomers (23 mg, 27 % yield) as yellow oil; Selected spectroscopic data for *trans*-**4c**:  $[\alpha]_{\text{D}}^{26} -72.1$  ( $c$  0.8,  $\text{CHCl}_3$ ) for 72% *ee* of *trans*-**4c**; IR (neat): 3375, 3012, 2963, 2825, 1719, 1543, 1484, 1466, 1369, 1317, 1205, 1157, 1021, 990, 858, 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.68 (d,  $J = 4.5$  Hz, 1 H), 7.84 (bs, 1 H), 7.34 (s, 1 H), 7.20 (d,  $J = 8.0$  Hz, 1 H), 6.98 (dd,  $J = 8.5, 1.5$  Hz, 1 H), 6.89 (d,  $J = 2.5$  Hz, 1 H), 5.49 (s, 1 H), 4.06 – 4.02 (m, 1 H), 2.60 (dd,  $J = 11.0, 4.0$  Hz, 1 H), 2.43 (s, 3 H) 2.17 – 2.14 (m, 1 H), 1.78 – 1.67 (m, 1 H), 1.70 (s, 3 H), 1.11 (s, 6 H),  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.6 (CH), 135.0 (C), 131.6 (C), 128.4 (C), 126.6 (C), 123.7 (CH), 123.0 (CH), 122.0 (CH), 118.9 (CH), 117.0 (C), 110.9 (CH), 60.6 (CH), 46.5 ( $\text{CH}_2$ ), 33.8 (C), 32.1 (CH), 29.3 ( $\text{CH}_3$ ), 23.4 ( $\text{CH}_3$ ), 21.62 ( $\text{CH}_3$ ), 21.57 ( $\text{CH}_3$ ); MS ( $m/z$ , relative intensity): 282 ( $\text{M}^+ + 1$ , 22), 281 ( $\text{M}^+$ , 100), 252 (92), 236 (33), 196 (75), 182 (58), 131 (35), 59 (55), exact mass calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}$  ( $\text{M}^+$ ): 281.1780; found : 281.1782.

## Preparation of 4d

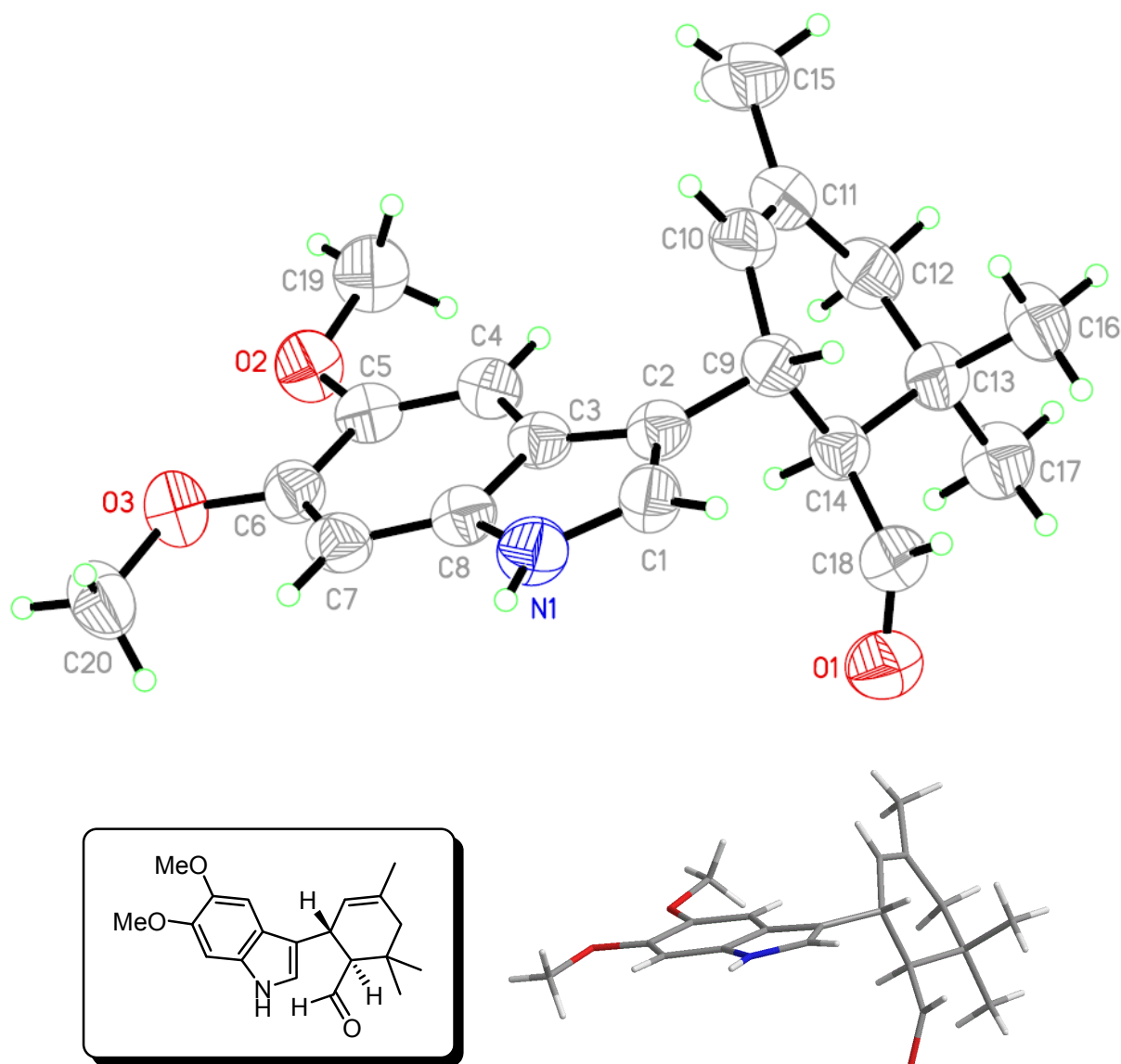


To a solution of aldehyde **2** (81.6 mg, 0.54 mmol, 2 equiv), catalyst-**IV** (17.7 mg, 0.05 mmol, 0.2 equiv) and additive-(*S*)-**A11** (37.8 mg, 0.11 mmol, 0.4 equiv) in  $\text{CHCl}_3$ -EtOAc (1:1, 0.77 mL) was added indole **3d** (40 mg, 0.27 mmol, 1 equiv) at  $\sim 25^\circ\text{C}$ . The resulting solution was stirred at ambient temperature for 15 days. To the reaction mixture was added  $\text{Et}_3\text{N}$  (27 mg, 0.27 mmol, 1 equiv) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give the residue. The crude product was purified by flash column chromatography with 10 % EtOAc-hexane ( $R_f = 0.47$  for *trans*-**4d** after developing two times in 15 % EtOAc-hexane and  $R_f = 0.44$  for *cis*-**4d** after developing two times in 15 % EtOAc-hexane) to afford product **4d** as mixture of diastereomers (19 mg, 23 % yield) as yellow oil; Selected spectroscopic data for *trans*-**4d**:  $[\alpha]_D^{26} -83.3$  ( $c$  1,  $\text{CHCl}_3$ ) for 78% *ee* of *trans*-**4d**; IR (neat): 3369, 3015, 2963, 2825, 1718, 1484, 1466, 1317, 1205, 1156, 1021, 857, 752, 666  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.69 (d,  $J = 4.0$  Hz, 1 H), 7.80 (bs, 1 H), 7.43 (d,  $J = 9.0$  Hz, 1 H), 6.81 (dd,  $J = 6.5, 2.0$  Hz, 2 H), 6.74 (dd,  $J = 8.5, 2.0$  Hz, 1 H), 5.48 (s, 1 H), 4.02 – 3.99 (m, 1 H), 3.81 (s, 3 H), 2.58 (dd,  $J = 11.0, 4.0$  Hz, 1 H), 2.17 – 2.14 (m, 1 H), 1.77 – 1.66 (m, 1 H), 1.70 (s, 3 H), 1.10 (s, 3 H), 1.09 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5 (CH), 156.5 (C), 137.4 (C), 131.7 (C), 123.0 (CH), 120.7 (C), 120.5 (CH), 120.0 (CH), 117.5 (C), 109.3 (CH), 94.8 (CH), 60.7 (CH), 55.7 ( $\text{CH}_3$ ), 46.5 ( $\text{CH}_2$ ), 33.8 (C), 32.3 (CH), 29.3 ( $\text{CH}_3$ ), 23.5 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), MS ( $m/z$ , relative intensity): 298 ( $\text{M}^+ + 1$ , 21), 297 ( $\text{M}^+$ , 100), 268 (100), 212 (61), 198 (39), 147 (38), 59 (44), exact mass calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}_2$  ( $\text{M}^+$ ): 297.1729; found : 297.1731.

### Preparation of 4e



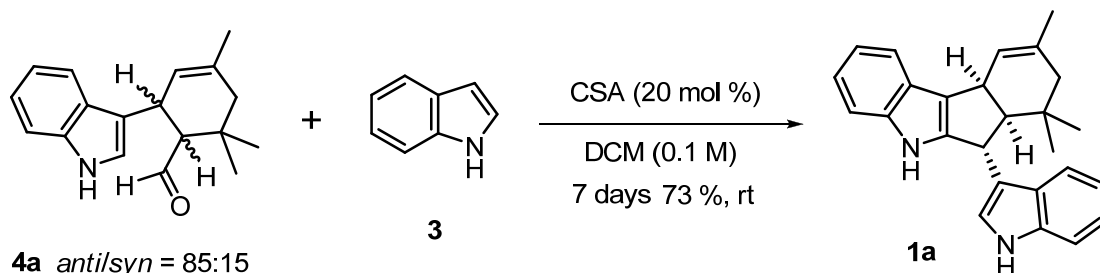
To a solution of aldehyde **2** (68 mg, 0.45 mmol, 2 equiv), catalyst-**IV** (14.3 mg, 0.04 mmol, 0.2 equiv) and additive-(*S*)-**A11** (30.6 mg, 0.09 mmol, 0.4 equiv) in  $\text{CHCl}_3$ -EtOAc (1:1, 0.60 mL) was added indole **3e** (40 mg, 0.23 mmol, 1 equiv) at  $\sim 25^\circ\text{C}$ . The resulting solution was stirred at ambient temperature for 15 days. To the reaction mixture was added  $\text{Et}_3\text{N}$  (23 mg, 0.23 mmol, 1 equiv) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give the residue. The crude product was purified by flash column chromatography with 15 % EtOAc-hexane ( $R_f = 0.30$  for *trans*-**4e** after developing two times in 30 % EtOAc-hexane and  $R_f = 0.27$  for *cis*-**4e** after developing two times in 30 % EtOAc-hexane) to afford product **4e** as mixture of diastereomers (18 mg, 24 % yield) as yellow oil. For purified *trans*-**4e**, darkkhaki solid, m.p. decomposed at  $185^\circ\text{C}$ . Selected spectroscopic data for *trans*-**4e**:  $[\alpha]_{\text{D}}^{26} -78.2$  ( $c$  1.2,  $\text{CHCl}_3$ ) for 79% *ee* of *trans*-**4e**; IR (neat): 3372, 2960, 1718, 1484, 1466, 1317, 1205, 1157, 1022, 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.70 (d,  $J = 4$  Hz, 1 H), 7.80 (bs, 1 H), 7.01 (s, 1 H), 6.82 (s, 1 H), 6.79 (d,  $J = 2.5$  Hz, 1 H), 5.50 (s, 1 H), 4.02 – 3.99 (m, 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 2.56 (dd,  $J = 11.0, 4.5$  Hz, 1 H), 2.15 – 2.02 (m, 1 H), 1.79 – 1.70 (m, 1 H), 1.71 (s, 3 H), 1.11 (s, 3 H), 1.10 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5 (CH), 147.2 (C), 144.6 (C), 131.7 (C), 130.9 (C), 123.0 (CH), 120.2 (CH), 119.1 (C), 117.4 (C), 101.2 (CH), 94.7 (CH), 60.8 (CH), 56.4 ( $\text{CH}_3$ ), 56.2 ( $\text{CH}_3$ ), 46.5 ( $\text{CH}_2$ ), 33.8 (C), 32.1 (CH), 29.3 ( $\text{CH}_3$ ), 23.4 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ); MS ( $m/z$ , relative intensity): 328 ( $\text{M}^+ + 1$ , 22), 327 ( $\text{M}^+$ , 100), 298 (99), 284 (19), 282 (16), 242 (41), 228 (28), 177 (36), 71 (32), exact mass calculated for  $\text{C}_{20}\text{H}_{25}\text{NO}_3$  ( $\text{M}^+$ ): 327.1834; found : 327.1834.



**Figure S1.** ORTEP and Stereo plots for X-ray crystal structures of (-)-*trans*-4e.

CCDC-1011541 contains the supplementary crystallographic data for (-)-*trans*-4e. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Preparation of **1a**



To a solution of aldehyde **4a** (15 mg, 0.06 mmol) and indole **3a** (7.9 mg, 0.07 mmol, 1.2 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.1M, 0.56 mL) was added (*S*)-CSA (2.6 mg, 0.01 mmol, 0.2 equiv) at room temperature. The resulting solution was stirred at ambient temperature for 7 days until the completion of reaction, as monitored by TLC. To the reaction mixture was added Et<sub>3</sub>N (6 mg, 0.06 mmol) and the corresponding reaction mixture was stirred for 30 min. The reaction solution was concentrated in *vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 8 % EtOAc-hexane (*R<sub>f</sub>* = 0.40 for **1a** after developing three times in 15 % EtOAc-hexane) to afford product **1** (15 mg, 73 % yield) as amorphous white powder; m.p. 125-127 °C (decomp.) Lit. 128 °C;<sup>1</sup> 127;<sup>2</sup> Selected spectroscopic data for **1a**:<sup>3</sup> IR (neat): 3410, 2963, 2906, 1454, 1415, 1260, 1114, 1008, 865, 797, 701cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.00 (bs, 1 H), 7.55 (d, *J* = 7.5 Hz, 1 H), 7.48 (bs, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.18 (dd, *J* = 7.5, 7.5 Hz, 1 H), 7.15 – 6.99 (m, 5 H), 5.68 (s, 1 H), 4.56 (d, *J* = 8.5 Hz, 1 H), 4.0 (d, *J* = 6.0 Hz, 1 H), 3.15 (dd, *J* = 8.5, 7.0 Hz, 1 H), 2.25 (d, *J* = 17.0 Hz, 1 H), 1.64 (s, 3 H), 1.61 (d, *J* = 17.0 Hz, 1 H), 1.07 (s, 3 H), 0.85 (s, 3 H), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 145.1 (C), 140.2 (C), 136.5 (C), 130.2 (C), 126.8 (C), 124.2 (C), 122.9 (CH), 122.3 (CH), 122.0 (CH), 120.52 (CH), 120.48 (CH), 119.50 (CH), 119.48 (CH), 119.4 (C), 118.4 (C), 118.2 (CH), 111.7 (CH), 111.2 (CH), 60.7 (CH), 41.0 (CH<sub>2</sub>), 38.3 (CH), 37.6 (CH), 33.5 (C), 29.1 (CH<sub>3</sub>), 28.9 (CH<sub>3</sub>), 24.1 (CH<sub>3</sub>); MS (*m/z*, relative intensity): 366 (M<sup>+</sup>, 17), 351 (8), 284 (12), 267 (82), 245 (25), 238 (58), 222 (35), 182 (91), 168 (94), 117 (62), 97 (47), 85 (82), 71 (100), 57 (100); exact mass calculated for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub> (M<sup>+</sup>): 366.2096; found : 366.2093.

<sup>1</sup> Henry, K. J.; Grieco, P. A. *J. Chem. Soc., Chem. Commun.* **1993**, 510.

<sup>2</sup> (a) Kong, Y.-C.; Cheng, K.-F.; Cambie, R. C.; Waterman, P. G. *J. Chem. Soc., Chem. Commun.*, **1985**, 47-48. (b) Chen, Y.-K.; Chung, H.-F.; Lin, S.-F.; Sheu, J.-H.; Sung, P.-J. *J. Chem. Soc. Perkin Trans. 1*, **1998**, 1959 – 1965

<sup>3</sup> In a separate reaction, starting from 84% *ee* of *trans*-**4a** with (*S*)-**A12** in CH<sub>2</sub>Cl<sub>2</sub> at ~35 °C for 15 days provided 73% yield of **1a** with 21% *ee*. For the yuehchukene (**1a**) obtained (21% *ee*): [α]<sub>D</sub><sup>26</sup> -16.6 (c 1.4, CHCl<sub>3</sub>).



**<sup>1</sup>H NMR Data for Yuehchukene (1a)**

Lit. <sup>1</sup>		Obs. <sup>a</sup>	
	mult, <i>J</i> (Hz)		mult, <i>J</i> (Hz)
8.02	br s, 1H	8.00	br s, 1H
7.56	d (7.8), 1H	7.55	d (7.5), 1H
7.49	br s, 1H	7.47	br s, 1H
7.43	d (8.0), 1H	7.42	d (8.0), 1H
7.37	d (8.3), 1H	7.36	d (8.0), 1H
7.18	t (7.3), 1H	7.18	dd (7.5, 7.5), 1H
6.99-7.20	m, 5H	6.99-7.15	m, 5H
5.68	s, 1H	5.68	s, 1H
4.57	d (7.8), 1H	4.55	d (8.5), 1H
4.0	br s, 1H	4.0	d (6), 1H
3.16	t (8.1), 1H	3.15	dd (8.5, 7), 1H
2.27	d (17), 1H	2.25	d (17), 1H
1.65	s, 3H	1.64	s, 3H
1.60	d (17), 1H	1.61	d (17), 1H
1.08	s, 3H	1.07	s, 3H
0.86	s, 3H	0.85	s, 3H

<sup>a</sup>Spectrum recorded at 500 MHz (Varian Unity INOVA 500) in CDCl<sub>3</sub>

<sup>13</sup>C NMR Data for Yuehchukene (1a)

Lit. <sup>4</sup>	Lit. <sup>5</sup>	Lit. <sup>6</sup>	Lit. <sup>7</sup>	Lit. <sup>8</sup>	Lit. <sup>9</sup>	Obs. <sup>a</sup>	
	$\delta$	$\delta$	$\delta$	$\delta$	$\delta$	$\delta$	Type
145.09	145.0	145.2	145.3	145.2	145.15	145.15	C
140.22	140.1	140.2	140.3	140.2	140.22	140.19	C
136.47	136.4	136.4	136.5	136.5	136.48	136.47	C
130.13	130.1	130.2	130.3	130.2	130.20	130.22	C
126.76	126.7	126.8	126.9	126.8	126.78	126.75	C
124.23	124.1	124.2	124.3	124.2	124.23	124.21	C
122.90	122.9	122.9	123.1	122.3	122.95	122.94	CH
122.16	122.2	122.3	122.5	122.3	122.27	122.29	CH
122.08	121.9	122.0	122.1	122.1	122.06	122.05	CH
120.46	120.5	120.5	120.6	120.6	120.52	120.52	CH
	120.4	120.4	120.5	120.5	120.52	120.48	CH
119.44	119.4	119.5	119.6	119.5	119.50	119.50	CH
				119.5	119.50	119.48	CH
119.24	119.3	119.3	119.4	119.3	119.34	119.36	C
118.50	118.4	118.4	118.5	118.5	118.50	118.46	C
118.19	118.2	118.2	118.4	118.4	118.25	118.25	CH
111.60	111.6	111.7	111.8	111.7	111.68	111.69	CH
111.14	111.2	111.2	111.4	111.2	111.21	111.22	CH
60.80	60.8	60.8	60.9	60.8	60.80	60.74	CH
41.03	41.0	41.0	41.1	41.0	41.02	40.98	CH <sub>2</sub>
	38.3	38.3	38.4	38.3	38.32	38.30	CH
37.54	37.7	37.5	37.7	37.6	37.61	37.61	CH
33.41	33.6	33.5	33.6	33.5	33.50	33.50	C
	29.2	29.1	29.2	29.0	29.09	29.14	CH <sub>3</sub>
28.83	29.0	28.9	29.0	28.9	28.90	28.90	CH <sub>3</sub>
23.91	24.1	24.1	24.2	24.1	24.05	24.07	CH <sub>3</sub>

<sup>a</sup>Spectrum recorded at 125 MHz (Varian Unity INOVA 500) in CDCl<sub>3</sub>

<sup>4</sup> Kong, Y. C. Novel indole derivative, processes for its preparation and its use as fertility control agent Eur. Pat. Appl. EP0130067 A3 1985.

<sup>5</sup> Naka, H.; Akagi, Y.; Yamada, K.; Imahori, T.; Kasahara, T.; Kondo, Y. *Eur. J. Org. Chem.* **2007**, 4635 – 4637.

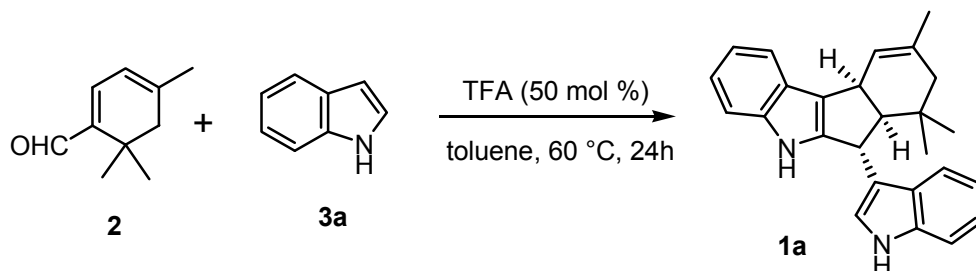
<sup>6</sup> Imaizumi, Katsuaki; Ishikura, Minoru; Katagiri, Nobuya *Heterocycles*, **2000**, *53*, 2201 – 2220.

<sup>7</sup> Abe, T.; Komatsu, H.; Ikeda, T.; Hatae, N.; Toyota, E.; Ishikura, M. *Heterocycles*, **2012**, *86*, 505 – 513.

<sup>8</sup> Chen, Y.-K.; Chung, H.-F.; Lin, S.-F.; Sheu, J.-H.; Sung, P.-J. *J. Chem. Soc. Perkin Trans. 1*, **1998**, 1959 – 1965.

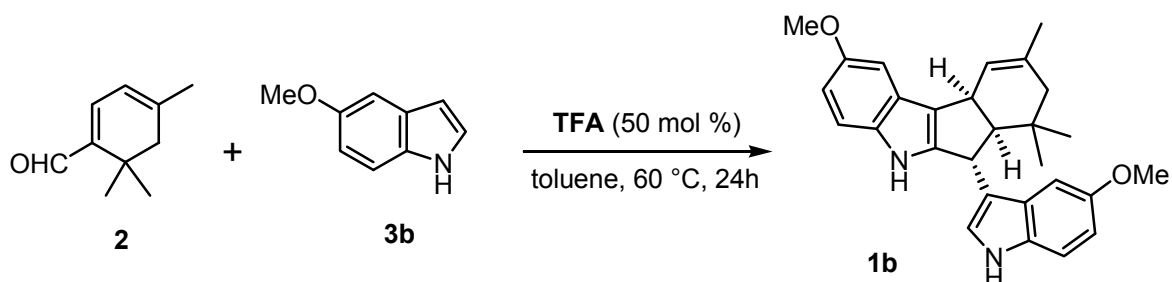
<sup>9</sup> Sheu, J.-H.; Chen, Y.-K.; Hong, Y.-L. *V. J. Org. Chem.* **1993**, *58*, 5784 – 5787.

### One-pot synthesis of (±)-yuehchukene (**1a**) from aldehyde **2** and indole (**3a**)



To a solution of aldehyde **2** (100 mg, 0.67 mmol) and indole **3a** (156 mg, 1.33 mmol, 2 equiv) in toluene (0.2 M, 3.3 mL) was added TFA (38 mg, 0.33 mmol, 0.5 equiv) at room temperature. The resulting solution was heated to 60 °C and stirred at the same temperature for 24 h until the completion of reaction, as monitored by TLC. The solution was cooled to 0 °C, followed by the addition of Et<sub>3</sub>N (67 mg, 0.66 mmol), and the corresponding reaction mixture was stirred for 30 min. The reaction mixture was diluted with EtOAc (50 mL) and washed with H<sub>2</sub>O (10 mL). The organic reaction solution was concentrated in *vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 8 % EtOAc-hexane ( $R_f$  = 0.40 for **1a** after developing three times in 15 % EtOAc-hexane) to afford product **1** (40 mg, 16 % yield) as white solid.

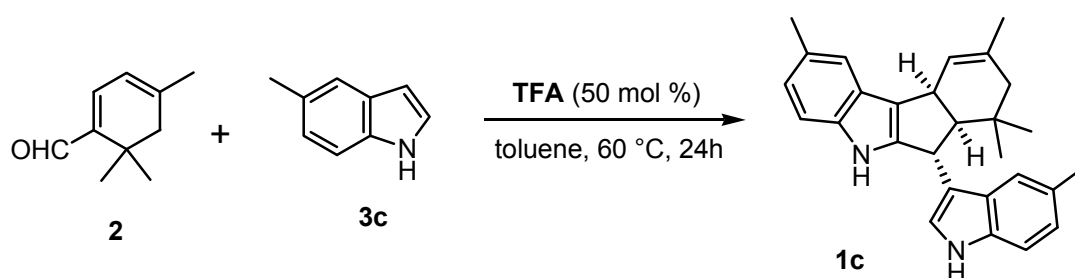
### One-pot synthesis of (±)-**1b** from aldehyde **2** and indole **3b**



To a solution of aldehyde **2** (100 mg, 0.67 mmol) and indole **3b** (196 mg, 1.33 mmol, 2 equiv) in toluene (0.2 M, 3.3 mL) was added TFA (38 mg, 0.33 mmol, 0.5 equiv) at room temperature. The resulting solution was heated to 60 °C and stirred at the same temperature for 24 h until the completion of reaction, as monitored by TLC. The solution was cooled to 0 °C, followed by the addition of Et<sub>3</sub>N (67 mg, 0.66 mmol), and the corresponding reaction mixture was stirred for 30 min. The reaction mixture was diluted with EtOAc (50 mL) and washed with H<sub>2</sub>O (10 mL). The organic solution was concentrated in *vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 10 %

EtOAc-hexane ( $R_f = 0.50$  for **1b** after developing two times in 20 % EtOAc-hexane) to afford product **1b** (30 mg, 13 % yield) as yellow solid. m.p. 160 °C (decomp). Selected spectroscopic data for **1b**: IR (neat): 3403, 2947, 1586, 1484, 1211, 1034, 799, 760 $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.26 (d,  $J = 2.5$  Hz, 1 H), 7.07 (dd,  $J = 9.0, 2.5$  Hz, 1 H), 6.95 – 7.01 (m, 3 H), 6.77 (d,  $J = 9.0$  Hz, 1 H), 6.67 (bs, 1 H), 6.48 (d,  $J = 2.0$  Hz, 2 H), 5.87 (s, 1 H), 4.50 (d,  $J = 8.0$  Hz, 1 H), 4.05 – 4.10 (m, 1 H), 3.59 (s, 3 H), 3.39 (s, 3 H), 3.17 (dd,  $J = 8.0, 8.0$  Hz, 1 H), 2.29 (d,  $J = 17.0$  Hz, 1 H), 1.66 (s, 3 H), 1.59 (d,  $J = 17.0$  Hz, 1 H), 1.15 (s, 3 H), 0.95 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  155.3 (2 C), 146.7 (C), 136.2 (C), 132.2 (C), 130.2 (2 C), 125.5 (C), 124.3 (CH), 123.2 (CH), 120.8 (C), 119.0 (C), 113.3 (CH), 113.0 (CH), 112.6 (CH), 111.0 (CH), 101.6 (CH), 101.4 (CH), 62.2 (CH), 55.8 ( $\text{CH}_3$ ), 55.7 ( $\text{CH}_3$ ), 41.8 ( $\text{CH}_2$ ), 39.1 (CH), 38.2 (CH), 34.0 (C), 29.7 ( $\text{CH}_3$ ), 29.6 ( $\text{CH}_3$ ), 24.5 (CH); MS ( $m/z$ , relative intensity): 427 ( $\text{M}^+ + 1$ , 31), 426 ( $\text{M}^+$ , 100), 411 (43), 359 (56), 264 (35), 185 (45), 160 (38), 57 (54); exact mass calculated for  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_2$  ( $\text{M}^+$ ): 426.2307; found: 426.2310.

### One-pot synthesis of ( $\pm$ )-**1c** from aldehyde **2** and indole **3c**



To a solution of aldehyde **2** (100 mg, 0.67 mmol) and indole **3c** (175 mg, 1.33 mmol, 2 equiv) in toluene (0.2 M, 3.3 mL) was added TFA (38 mg, 0.33 mmol, 0.5 equiv) at room temperature. The resulting solution was heated to 60 °C and stirred at the same temperature for 24 h until the completion of reaction, as monitored by TLC. The solution was cooled to 0 °C, followed by the addition of  $\text{Et}_3\text{N}$  (67 mg, 0.66 mmol), and the corresponding reaction mixture was stirred for 30 min. The reaction mixture was diluted with EtOAc (50 mL) and washed with  $\text{H}_2\text{O}$  (10 mL). The organic solution was concentrated in *vacuo* to give a crude residue. The crude product was purified by flash column chromatography with 8 % EtOAc-hexane ( $R_f = 0.60$  for **1c** after developing two times in 15 % EtOAc-hexane) to afford product **1c** (40 mg, 15 % yield) as yellow oil. Selected spectroscopic data for **1c**: IR (neat): 3404, 2917, 1716, 1620, 1454, 1297, 1096, 798  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.54 (s, 1 H), 7.41 (s, 1 H), 6.98 – 7.16 (m, 3 H), 6.81 (d,  $J = 8.5$  Hz, 1 H), 6.68 (bs, 1 H), 6.51 (bs, 1 H),

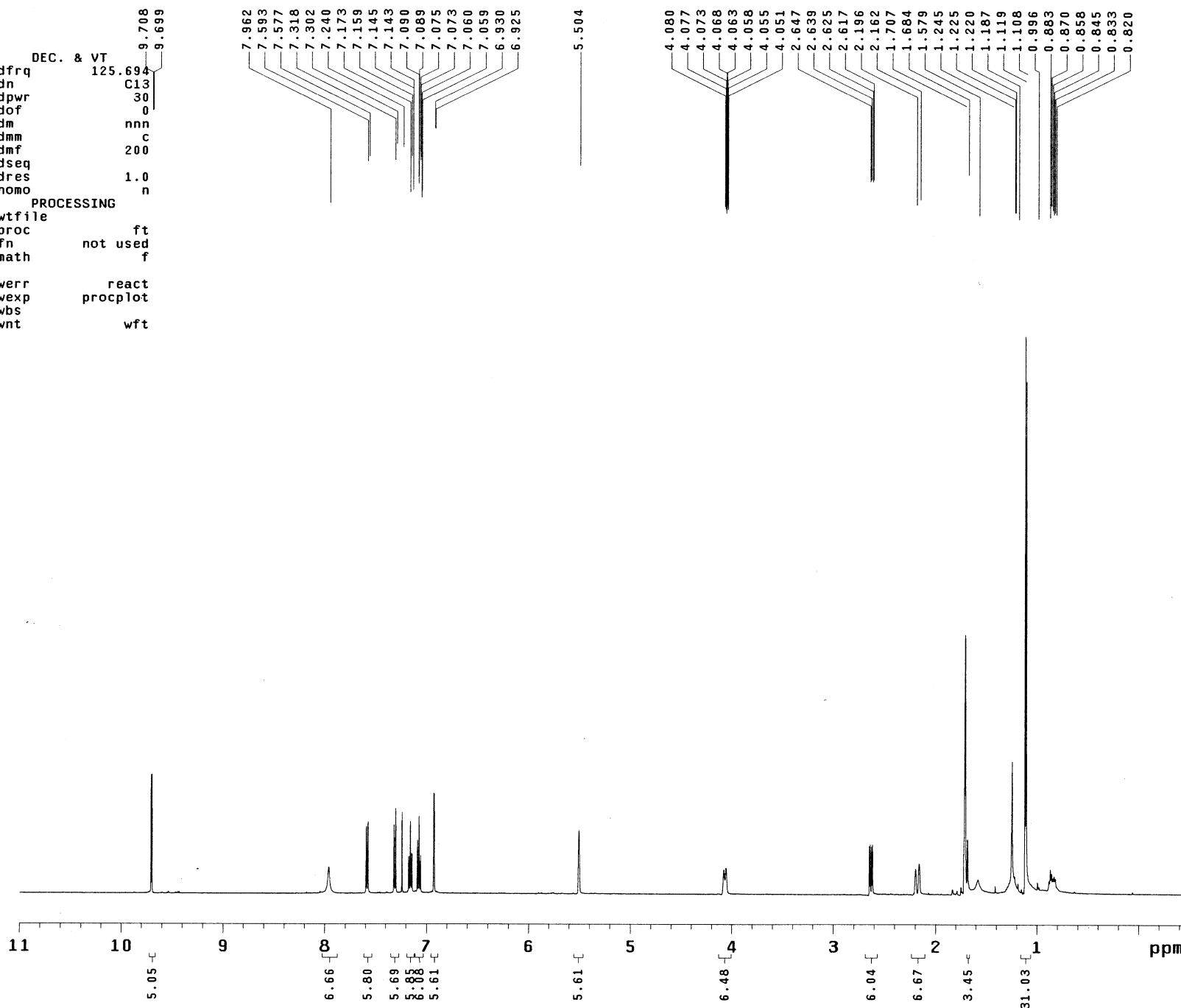
6.45 (d,  $J = 2.5$  Hz, 1 H), 5.88 (s, 1 H), 4.52 (d,  $J = 8.5$  Hz, 1 H), 4.05 – 4.11 (m, 1 H), 3.20 (dd,  $J = 8.0, 8.0$  Hz, 1 H), 2.48 (s, 3 H), 2.31 (s, 3 H), 2.26 – 2.28 (m, 1 H), 1.65 (s, 3 H), 1.56 (d,  $J = 16.5$  Hz, 1 H), 1.14 (s, 3 H), 1.01 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  146.1 (C), 139.6 (C), 135.5 (C), 130.1 (C), 129.2 (C), 128.9 (C), 128.7 (C), 125.6 (C), 124.5 (CH), 124.4 (CH), 122.64 (CH), 122.63 (CH), 120.3 (C), 119.4 (CH), 119.1 (CH), 118.9 (C), 112.1 (CH), 111.6 (CH), 62.3 (CH), 41.8 ( $\text{CH}_2$ ), 39.1 (CH), 38.1 (CH), 34.0 (C), 29.8 ( $\text{CH}_3$ ), 29.5 ( $\text{CH}_3$ ), 24.5 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_3$ ); MS ( $m/z$ , relative intensity): 395 ( $\text{M}^+ + 1$ , 12), 394 ( $\text{M}^+$ , 34), 379 (17), 248 (15), 221 (18), 207 (13), 198 (13), 149 (34), 85 (42), 71 (62), 58 (100); exact mass calculated for  $\text{C}_{28}\text{H}_{30}\text{N}_2$  ( $\text{M}^+$ ): 394.2409; found : 394.2407.

Fig S14. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of compound 4a.

NSD-09-68-F1

exp58 s2pul

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date	Aug 1 2013	dfrq	125.694
solvent	cdcl3	dn	C13
file	/export/home/~	dpwr	30
vnmr1/vnmr	sys/data~	dof	0
/NSD/NSD-09-68/F1/~		dm	nnn
		dmm	c
ACQUISITION		PROCESSING	
sfrq	499.833	dseq	200
tn	H1	dres	1.0
at	3.000	homo	n
np	48000	wtfile	
sw	8000.0	proc	ft
fb	not used	fn	not used
bs	4	math	f
tpwr	61	werr	react
pw	4.8	wexp	procplot
d1	1.000	wbs	
tof	499.7	wnt	wft
nt	4		
ct	4		
alock	y		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	100		
sc	0		
wc	210		
hzmm	27.37		
is	33.57		
rfl	4636.0		
rfp	3618.8		
th	2		
ins	100.000		
nm	cdc ph		



```

NSD-09-68-F1
exp4 s2pu1
SAMPLE
date Aug 1 2013 dfrq DEC. & VT 499.833
solvent cdc13 dn H1
file exp dpwr 44
ACQUISITION dof 0
sfrq 125.697 dm yyy
tn C13 dmm w
at 1.000 dmf 11765
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16 PROCESSING
ss 2 lb 1.00
tpwr 59 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 1024
ct 1024 werr react
alock y wexp procp
gain not used wbs testsn
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1257.0
wp 28906.3
vs 150
sc 0
wc 210
hzmm 137.65
is 500.00
rfl 10980.6
rfp 9677.5
th 9
ins 100.000
nm cdc ph

```

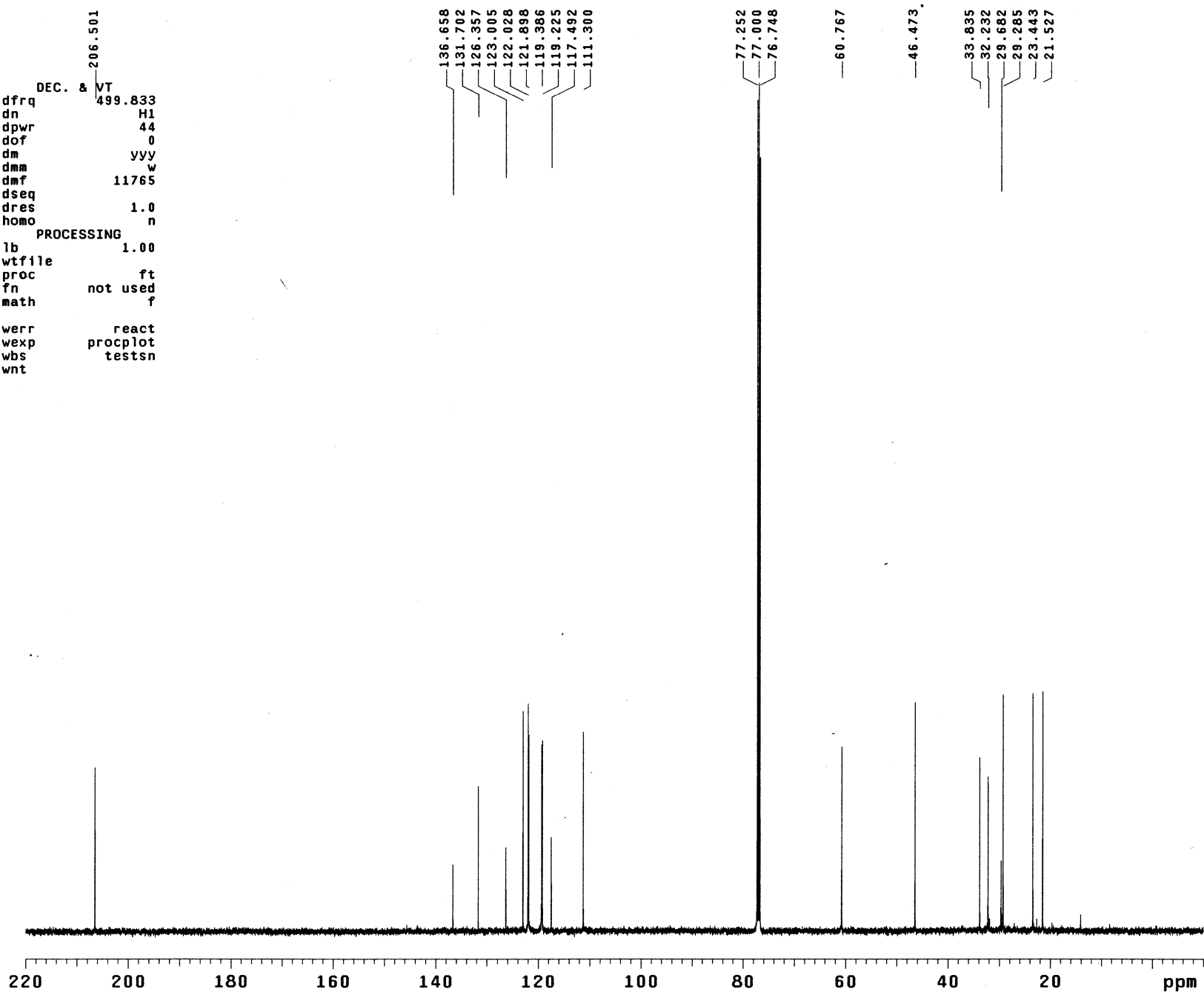
Fig S15.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of compound 4a.

Fig S16. DEPT of compound 4a.

NSD-09-68-F1

exp5 DEPT

date	Aug 1 2013	j1xh	140.0	array	mult
solvent	cdcl3	mult	arrayed	arraydim	3
sample	undefined	SPECIAL			
ACQUISITION		temp	not used	1	mult
sw	31446.5	gain	20	1	0.5
at	1.000	spin	0	2	1
np	62894	PROCESSING		3	1.5
bs	16	lb	1.00		
ss	-4	fn	not used		
d1	1.000	SPECTRUM			
nt	512	wp	27650.1		
ct	512	sp	-1257.0		
TRANSMITTER		rp	-29.8		
tn	C13	lp	125.7		
tof	2512.2	ai	cdc ph		
tpwr	59	REFERENCE			
pw	10.600	rfl	1302.1		
DECOUPLER		rfp	0		
dn	H1	PLOT			
dof	0	wc	210		
dpwr	44	sc	0		
dm	nny	vs	300		
dmm	11765	ccw	131.67		
dmf	59	th	68		
pp1v1	15.300				

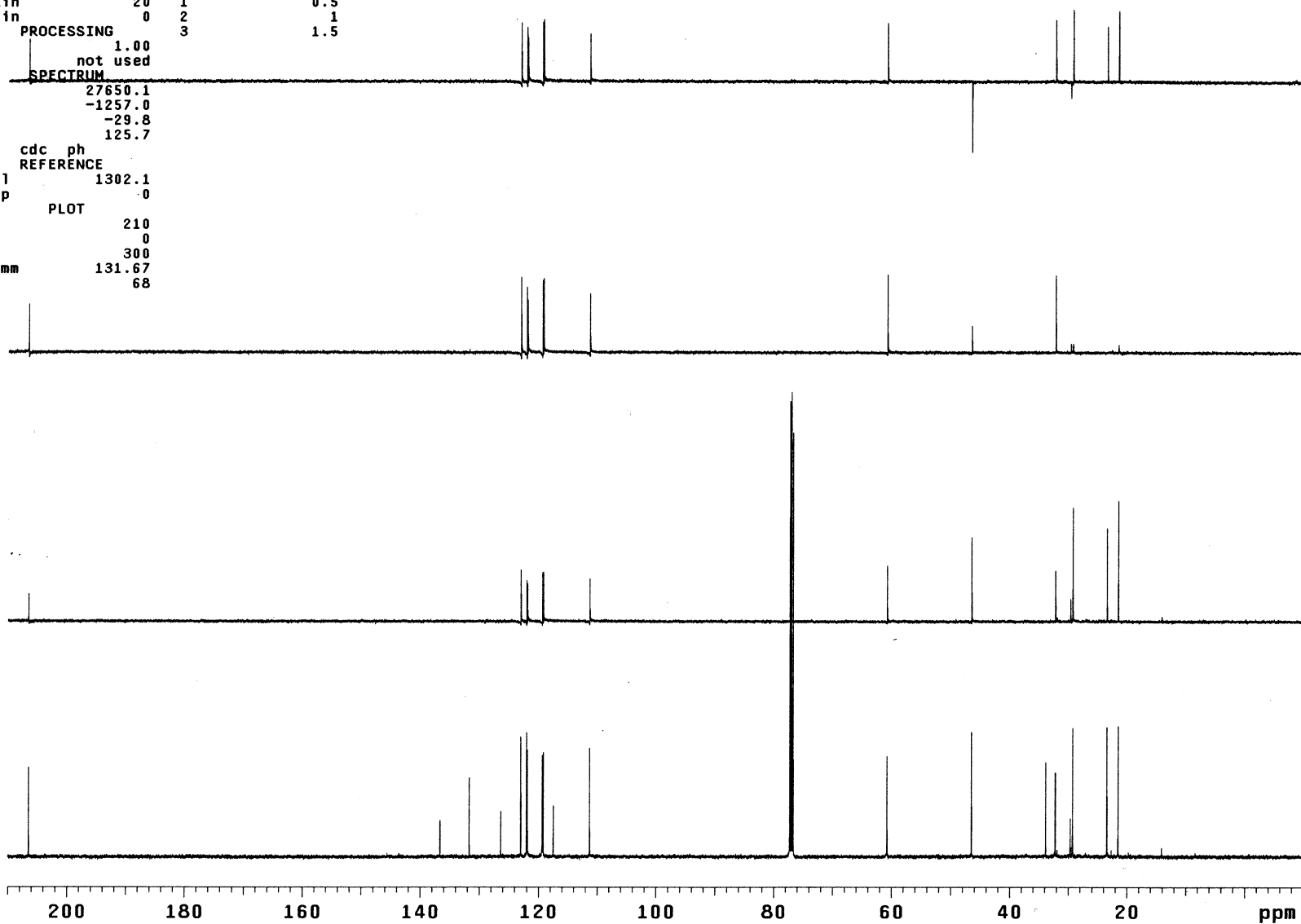




Fig S17. HSQC of compound 4a.

NSD-09-68-F1

exp8 gHSQC

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date	Aug 1 2013	hs	n	array
solvent	cdc13	sspul	y	arraydim
sample	undefined	PFGflg	y	phase
ACQUISITION		hsglv1	1006	phase
sw	5497.5	SPECIAL	1	1
at	0.186	temp	not used	2
np	2048	gain	60	
fb	not used	spin	0	
ss	32	GRADIENTS		
d1	1.000	gzlv11	1006	
nt	8	gt1	0.002000	
2D ACQUISITION		gzlv13	506	
sw1	21367.5	gt3	0.001000	
n1	128	gstab	0.000500	
phase	arrayed	F2 PROCESSING		
TRANSMITTER		gf	0.086	
tn	H1	gfs	not used	
sfrq	499.833	fn	2048	
tof	249.8	F1 PROCESSING		
tpwr	61	gf1	0.006	
pw	12.000	gfs1	not used	
DECOUPLER		proc1	1p	
dn	C13	fn1	2048	
dof	-2515.1	DISPLAY		
dm	nny	sp	268.5	
dmm	ccp	wp	4235.9	
dmf	32258	sp1	1233.1	
dpwr	41	wp1	15086.6	
pwxlvl	57	rfl	1331.6	
pw	13.600	rflp	1315.6	
HSQC		rfl1	8929.1	
j1xh	140.0	rflp1	7637.3	
nullflg	y	PLOT		
mult	2	wc	150.0	
		sc	6.2	
		wc2	116.2	
		sc2	0	
		vs	100	
		th	4	
		ai	cdc	ph

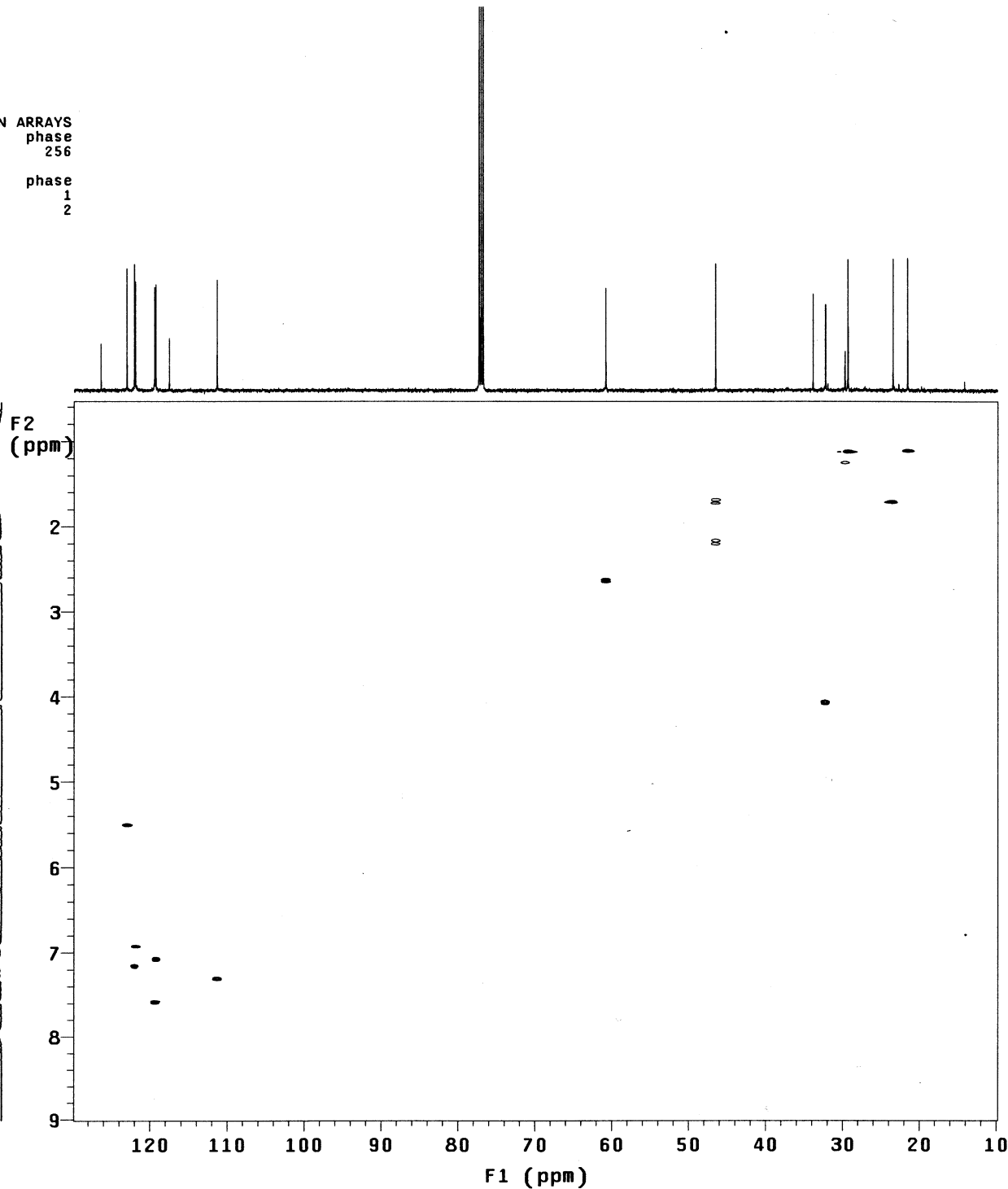


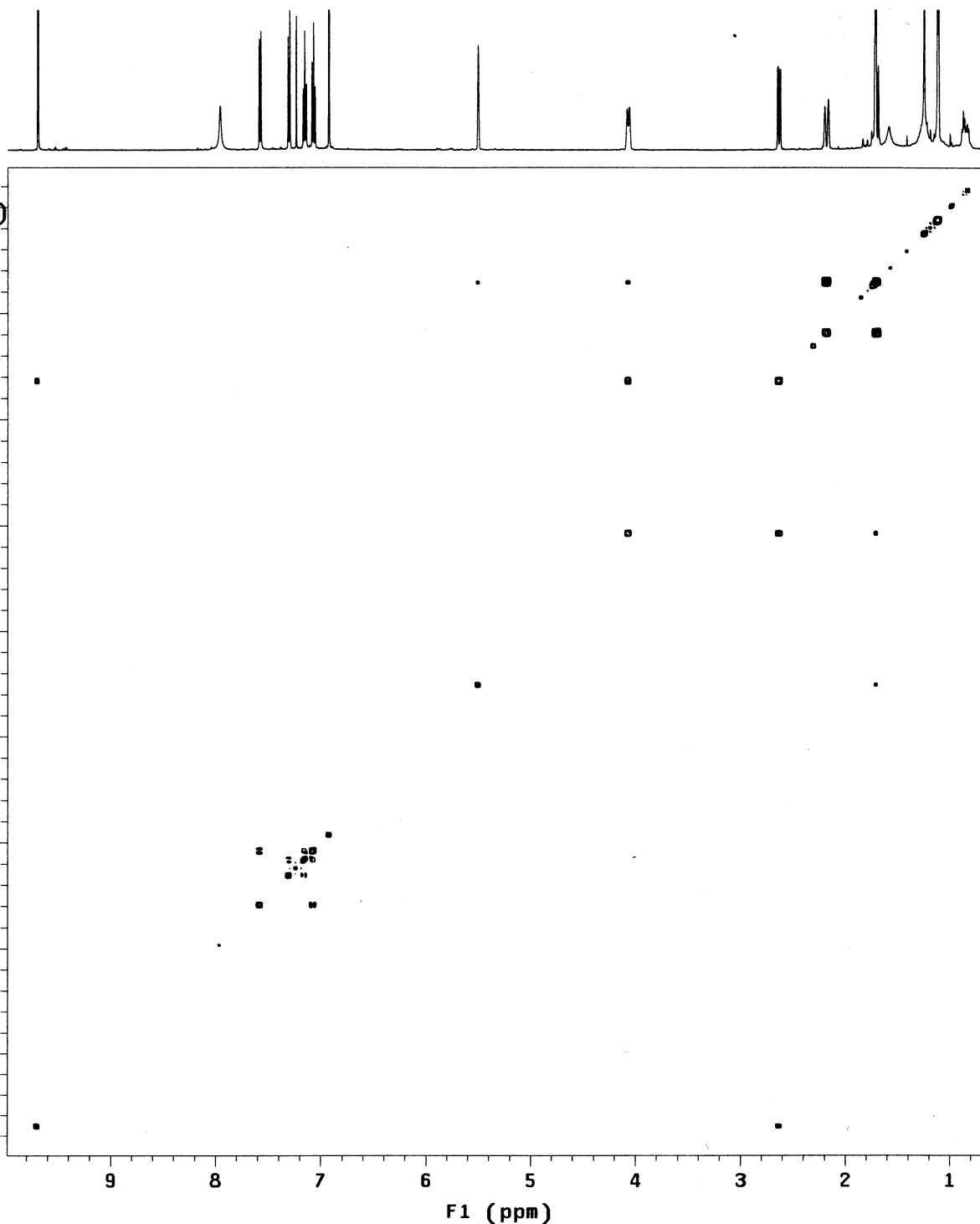
Fig S18. COSY of compound 4a.

NSD-09-68-F1

exp6 gCOSY

SAMPLE		FLAGS	
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solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1006
ACQUISITION		SPECIAL	
sw	5497.5	temp	not used
at	0.186	gain	54
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.093
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	5497.5	sb1	-0.023
n1	128	sbs1	not used
TRANSMITTER		PROC1	
tn	H1	fn1	2048
sfrq	499.833	DISPLAY	
tof	249.8	sp	310.9
tpwr	61	wp	4681.5
pw	12.000	sp1	312.3
GRADIENTS		wp1	4676.1
gzlv11	1006	rfl	2767.6
gt1	0.001000	rfp	2751.1
gstab	0.000500	rfl1	2766.2
DECOUPLER		rfl1	2751.1
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	100
		th	9
		ai	cdc av

F2 (ppm)



F1 (ppm)

Fig S19. NOESY of compound 4a.

NSD-09-68-F1

exp9 NOESY

SAMPLE		FLAGS	n
date	Aug 1 2013	hs	y
solvent	cdc13	sspul	y
sample	undefined	PFgflg	y
ACQUISITION		hsglvi	1006
sw	5497.5	SPECIAL	
at	0.186	temp	not used
np	2048	gain	28
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.086
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	5497.5	F1 PROCESSING	
ni	200	gf1	0.034
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.833	fn1	2048
tof	249.8	DISPLAY	
tpwr	61	sp	273.2
pw	12.000	wp	4719.1
NOESY		sp1	263.5
mix	0.600	wp1	4724.4
PRESATURATION		rfl	2767.8
satmode	nnnn	rfp	2751.1
satpwr	0	rfl1	2766.7
satdly	0	rfp1	2751.1
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	205
		th	1
		ai	ph

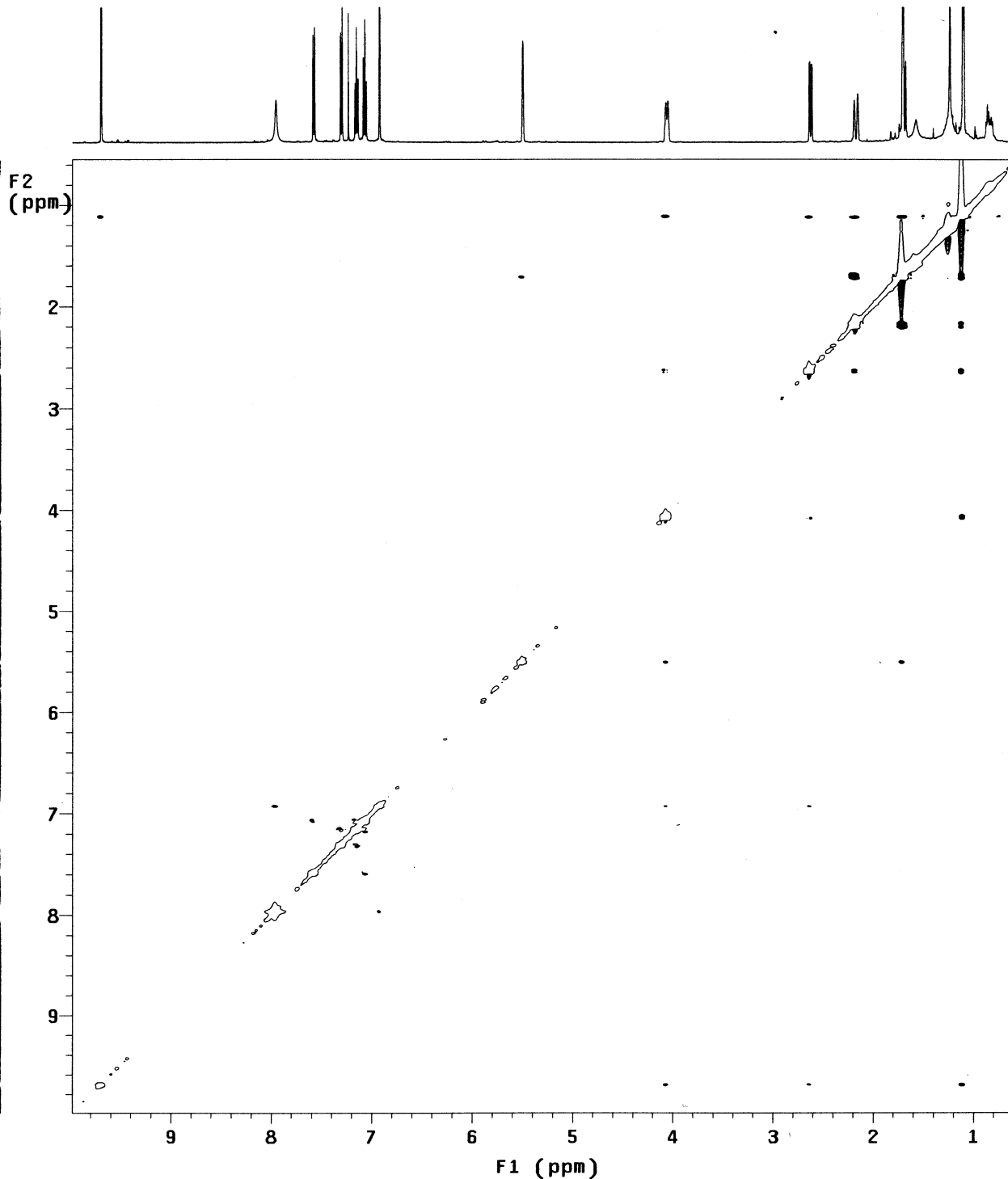
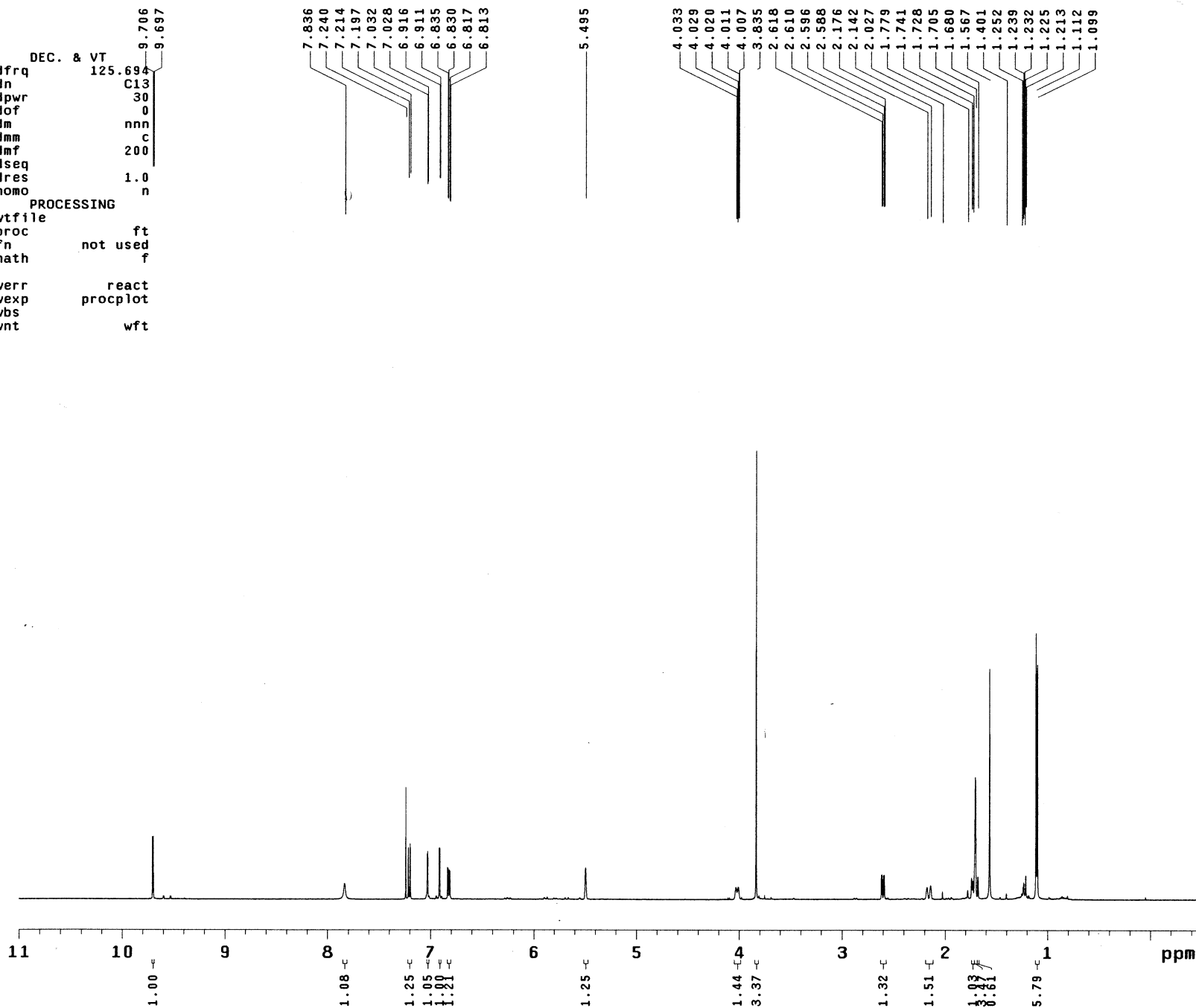


Fig S20. 1H NMR (CDCl3, 500 MHz) of compound 4b.

NSD-09-169-f1

exp70 s2pu1

SAMPLE		DEC. & VT	9.706
date	Feb 15 2014	dfrq	125.694
solvent	cdc13	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.833	dm	nnn
tn	Hi	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	61	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	80		
sc	0		
wc	210		
hzmm	27.37		
is	33.57		
rfl	4636.0		
rfp	3618.8		
th	2		
ins	1.000		
nm	cdc ph		



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NSD-09-169-f1
exp71 s2pu1

SAMPLE
date Feb 15 2014 dfrq 499.833
solvent cdc13 dn H1
file exp dpwr 44
ACQUISITION dof 0
sfrq 125.697 dm yyy
tn C13 dmm w
at 1.000 dmf 10870
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16
ss 2
tpwr 60
pw 4.0
d1 1.000
tof 2512.2
nt 6000
ct 6000
alock y
gain not used
FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -1257.0
wp 28906.3
vs 400
sc 0
wc 210
hzmm 137.65
is 500.00
rfl 10980.6
rfp 9677.5
th 6
ins 100.000
nm cdc ph

DEC. & VT
206.471
153.632
131.817
131.756
126.769
122.906
122.700
117.156
111.903
111.842
101.572
77.252
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33.828
32.102
29.277
23.436
21.527

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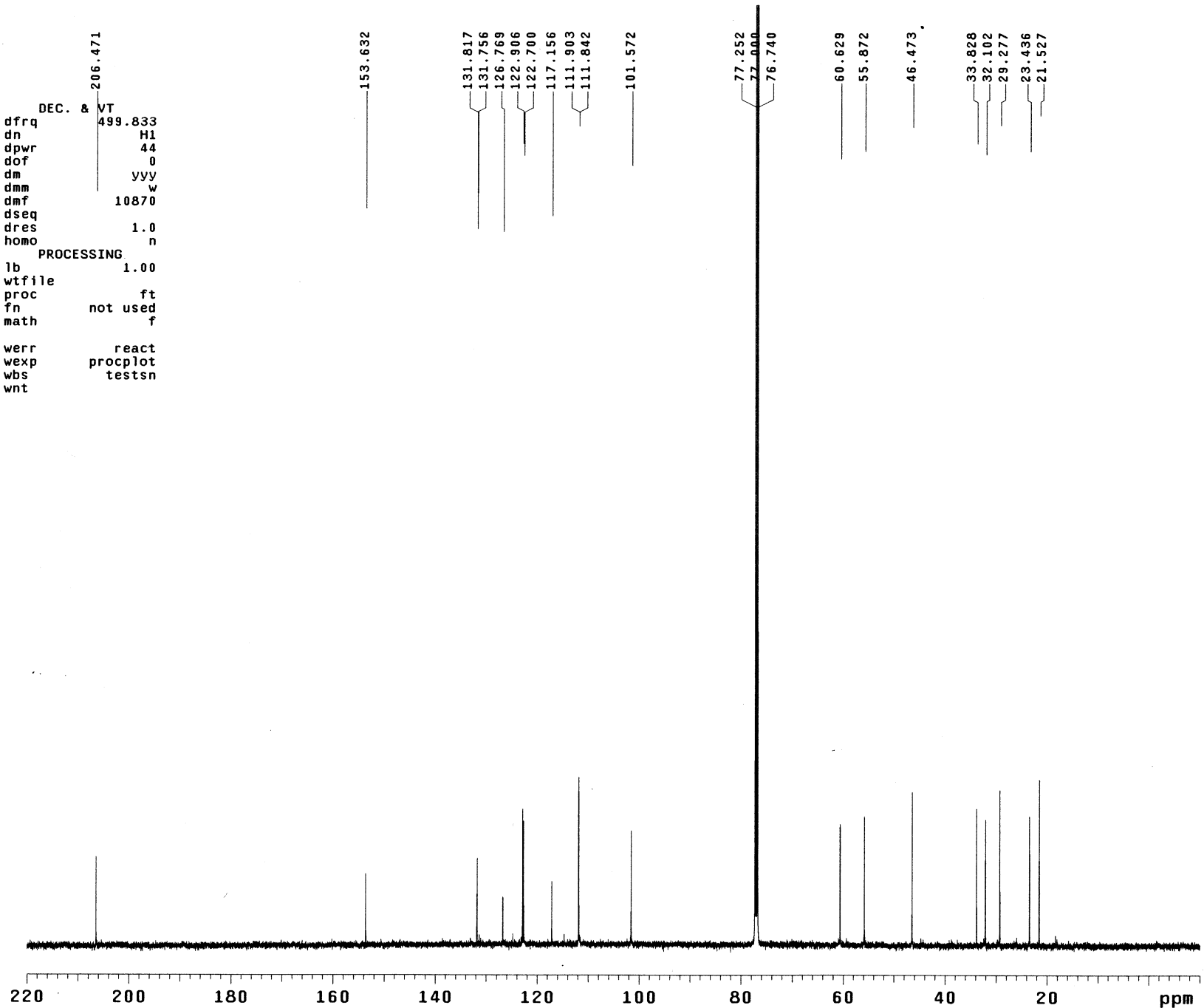
Fig S21. 13C NMR (CDCl<sub>3</sub>, 125 MHz) of compound 4b.

Fig S22. DEPT of compound 4b.

NSD-09-169-f1

exp72 DEPT

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sample	undefined	SPECIAL		not used	i	mult
sw	ACQUISITION	temp	not used		1	0.5
at	31446.5	gain	34	1	2	1
np	1.000	spin	0	2	3	1.5
bs	62894	PROCESSING		1.00		
ss	16	lb	1.00			
d1	-4	fn	not used			
nt	1.000	SPECTRUM				
ct	3000	wp	28906.3			
tn	3000	sp	-1257.0			
tof	TRANSMITTER	rp	-0.9			
tpwr	C13	lp	87.8			
pw	2512.2	ai	cdc ph			
dn	60	REFERENCE				
dof	10.400	rfl	1303.0			
dpwr	DECOUPLER	rfp	0			
dm	H1	PLOT				
dmm	0	wc	210			
dmf	44	sc	0			
pp1v1	nny	vs	600			
pp	61	ccw	137.65			
	14.600	th	68			

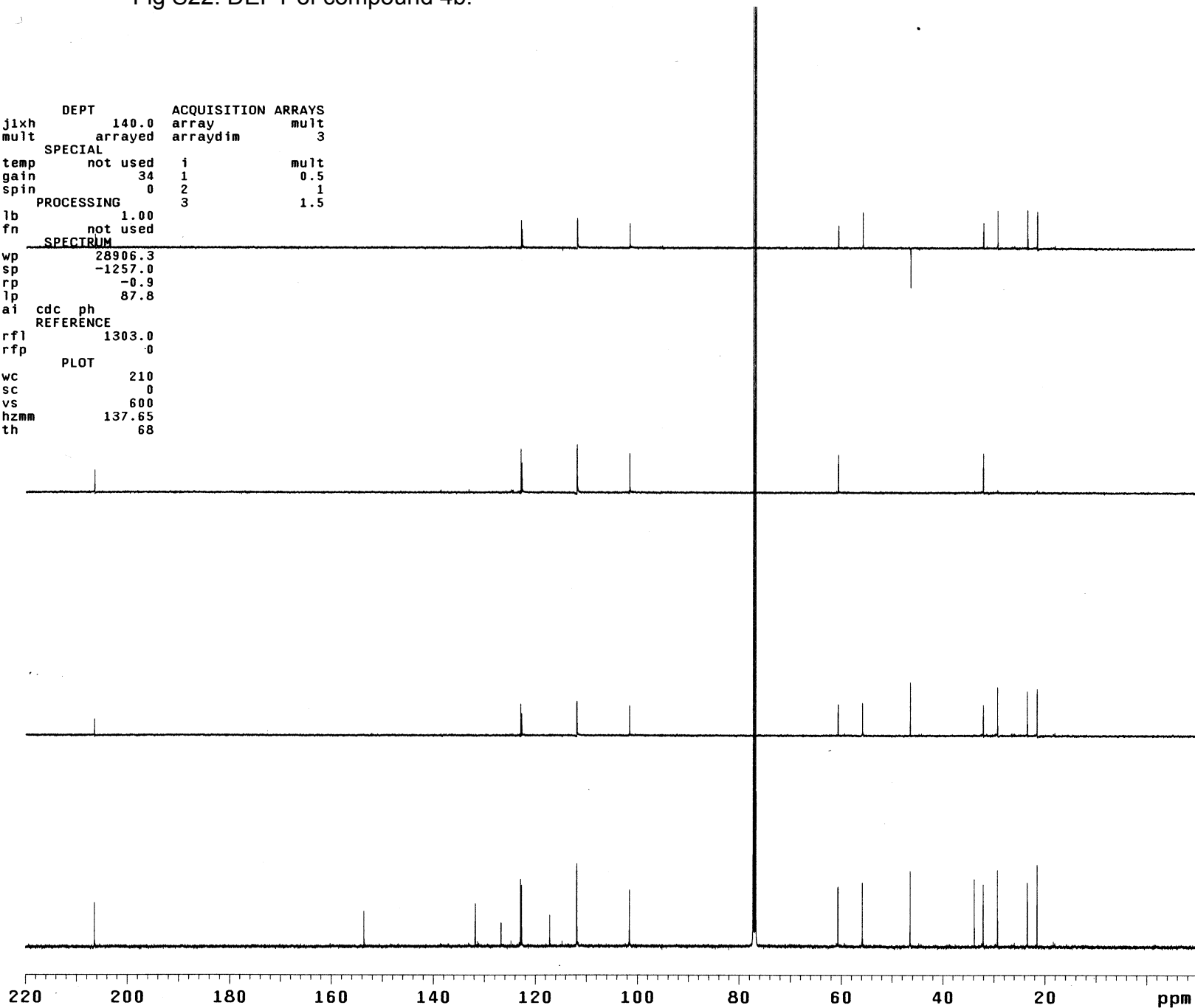


Fig S23. HMQC of compound 4b.

NSD-09-169-f1

exp75 gHMQC

SAMPLE		FLAGS		ACQUISITION		ARRAYS	
date	Feb 15 2014	hs	n	array	phase		
solvent	cdcl3	sspul	y	arraydim	256		
sample	undefined	PFGflg	y				
ACQUISITION		hsglv1	1009	i	phase		
sw	5006.3	SPECIAL	1	1	1		
at	0.205	temp	not used	2	2		
np	2048	gain	54				
fb	not used	spin	0				
ss	32	GRADIENTS					
d1	1.000	gzlv11	1009				
nt	8	gt1	0.001000				
2D ACQUISITION		gzlv13	508				
sw1	21367.5	gt3	0.001000				
ni	128	gstab	0.000500				
phase	arrayed	F2 PROCESSING					
TRANSMITTER		gf	0.094				
tn	H1	gfs	not used				
sfrq	499.833	fn	2048				
tof	-0.1	F1 PROCESSING					
tpwr	61	gf1	0.006				
pw	12.900	gfs1	not used				
DECOUPLER		proci	1p				
dn	C13	fn1	2048				
dof	-2515.1	DISPLAY					
dm	nny	sp	401.4				
dmm	ccp	wp	3324.5				
dmf	32258	sp1	1859.3				
dpwr	42	wp1	13897.2				
pwxlvl	59	rfl	1935.9				
pw	12.200	rflp	1916.8				
HMQC		rfl1	8313.7				
j1xh	140.0	rflp1	7022.1				
nullflg	y	PLOT					
		wc	150.0				
		sc	6.2				
		wc2	116.2				
		sc2	0				
		vs	475				
		th	5				
		ai	cdc ph				

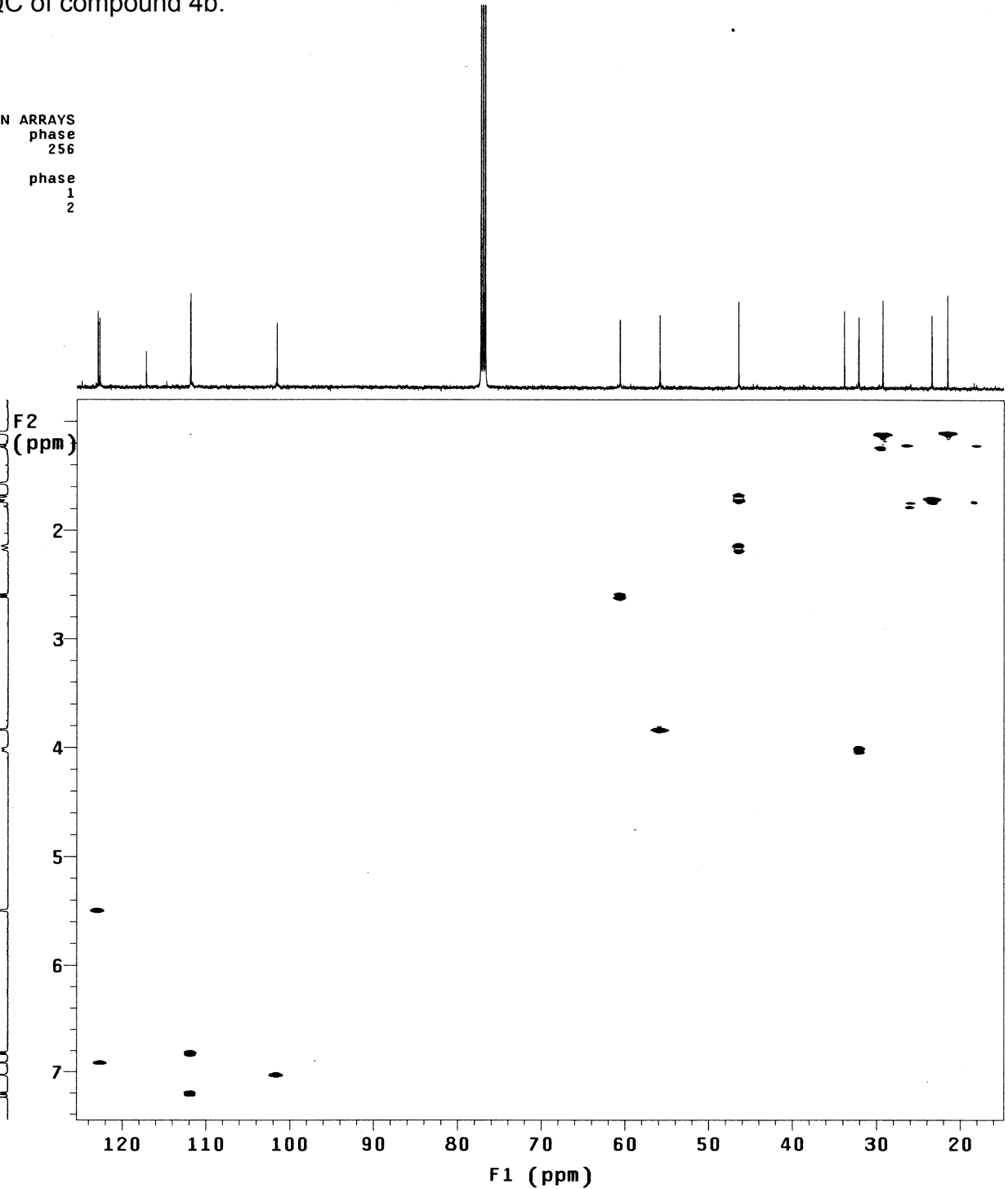


Fig S24. COSY of compound 4b.

NSD-09-169-f1

exp73 gCOSY

SAMPLE		FLAGS	
date	Feb 15 2014	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1009
ACQUISITION		SPECIAL	
sw	5006.3	temp	not used
at	0.205	gain	24
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.102
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	5006.3	sb1	-0.026
ni	128	sbs1	not used
TRANSMITTER		PROC1	
tn	H1	lp	2048
sfrq	499.833	DISPLAY	
tof	-0.1	sp	311.8
tpwr	61	wp	4595.6
pw	12.900	sp1	312.5
GRADIENTS		wp1	4595.6
gzlv11	1009	rfl	2767.2
gt1	0.001000	rfp	2746.6
gstab	0.000500	rfl1	2766.5
DECOUPLER		rfp1	2746.6
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	475
		th	6
		ai	cdc av

F2 (ppm)

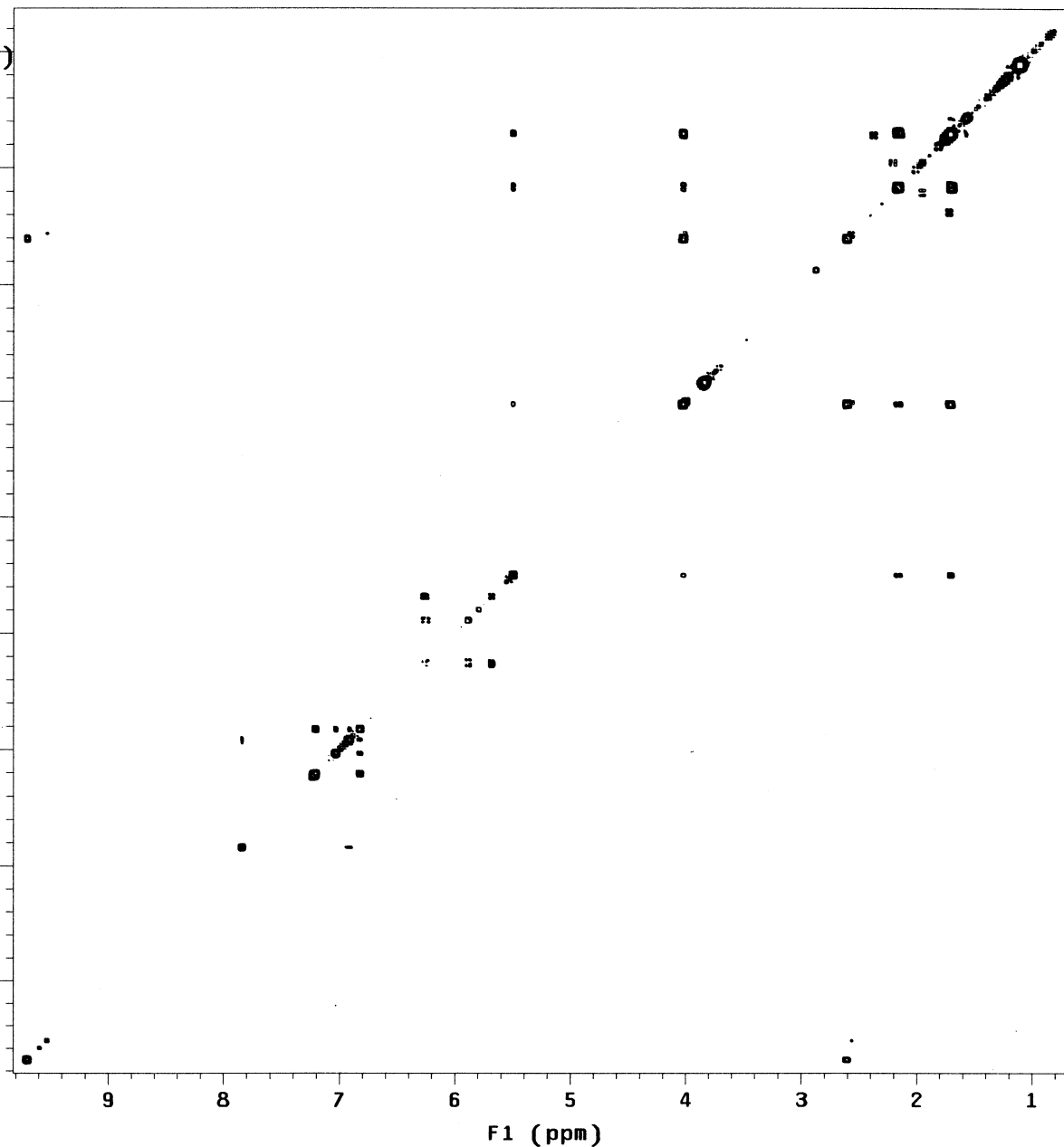




Fig S25. NOESY of compound 4b.

NSD-09-169-f1

exp76 NOESY

SAMPLE		FLAGS	
date	Feb 17 2014	hs	n
solvent	cdc13	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1009
sw	5006.3	SPECIAL	
at	0.205	temp	not used
np	2048	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.094
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	5006.3	F1 PROCESSING	
n1	200	gf1	0.037
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.833	fn1	2048
tof	-0.1	DISPLAY	
tpwr	61	sp	330.8
pw	12.900	wp	4561.4
NOESY		sp1	329.2
mix	0.600	wp1	4561.4
PRESATURATION		rfl	3937.9
satmode	nnnn	rfp	3916.7
satpwr	0	rfl1	3939.5
satdly	0	rfl1	3916.7
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	113
		th	1
		ai	ph

F2 (ppm)

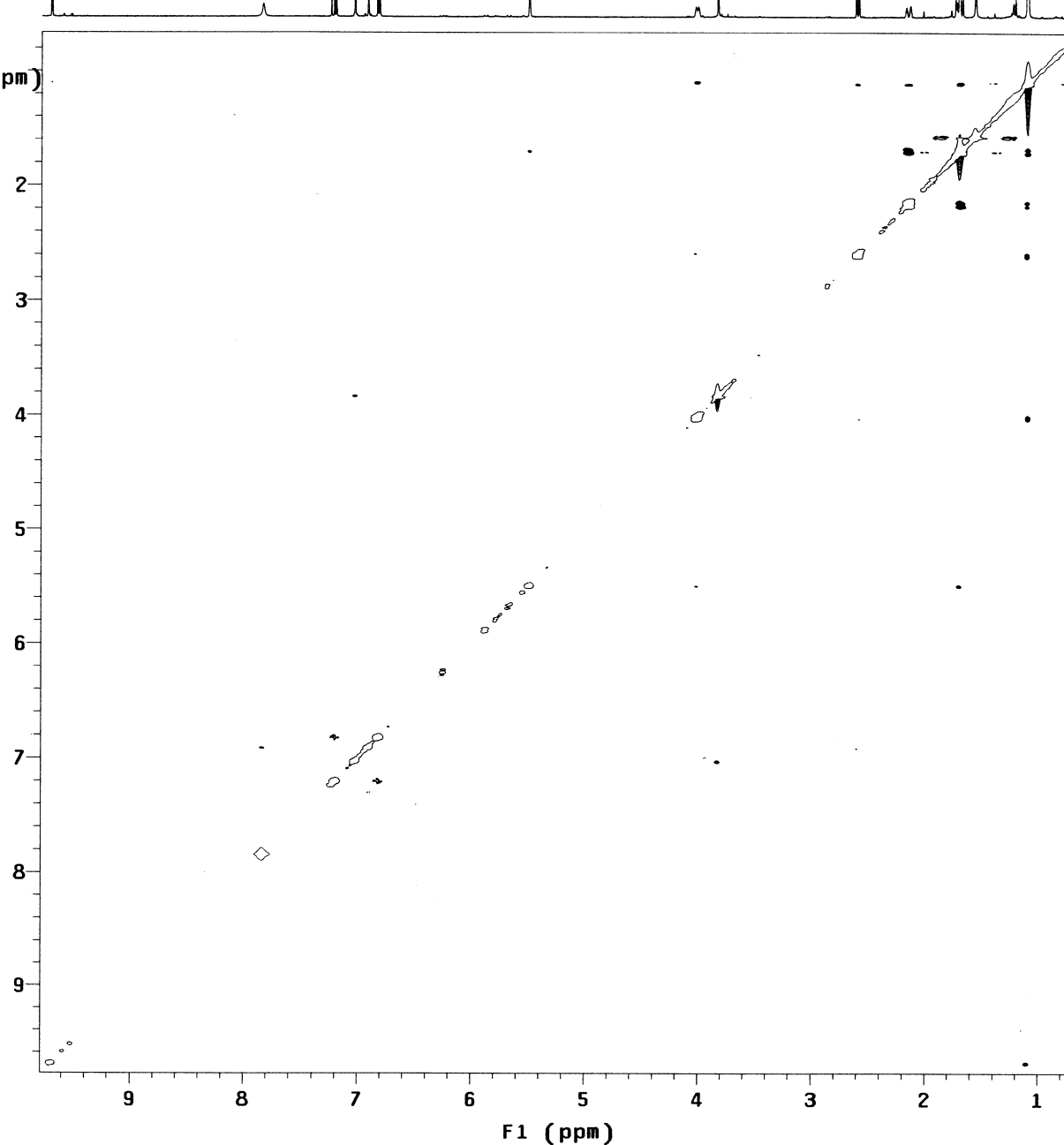
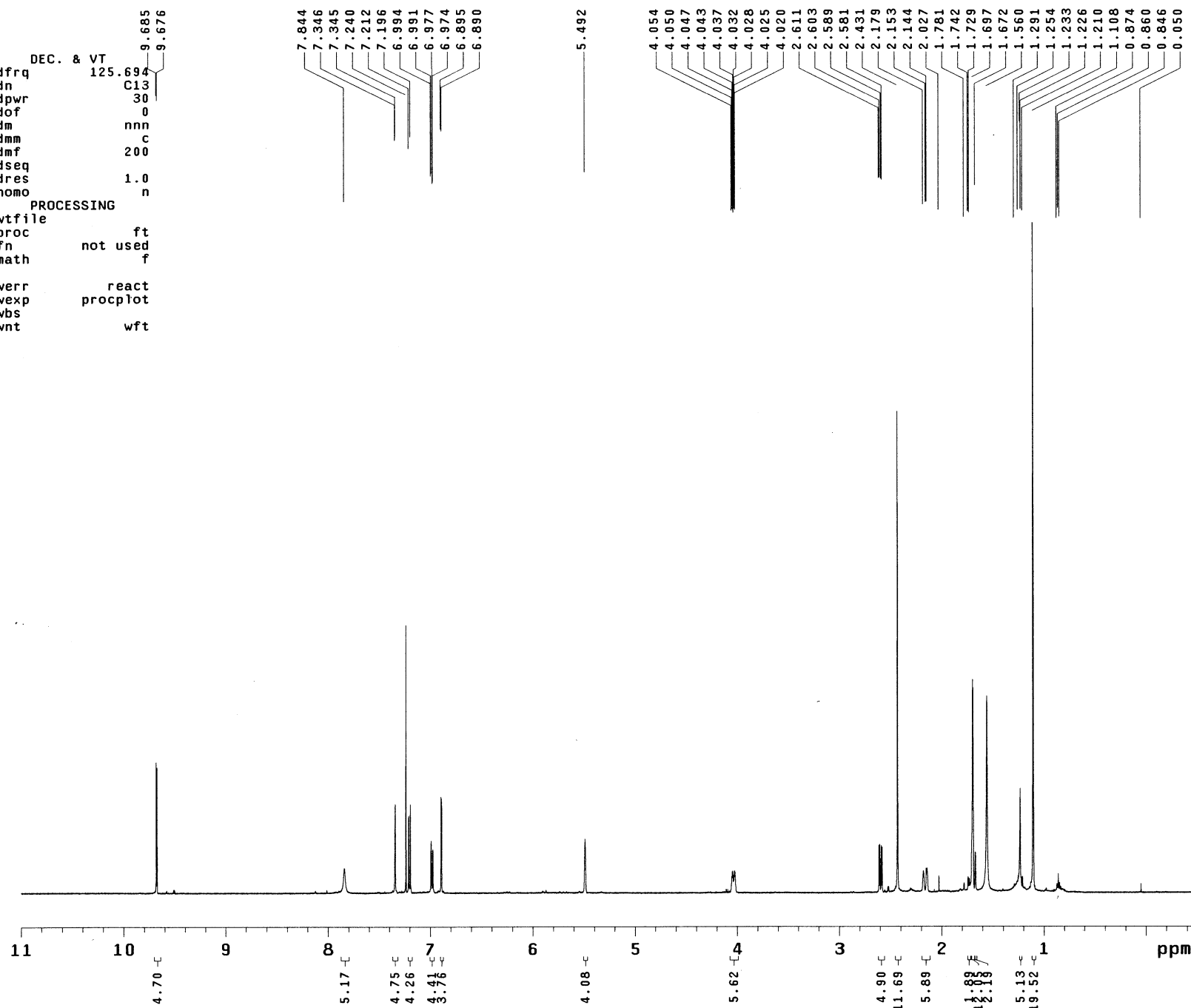


Fig S26. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of compound 4c.

NSD-09-175-F1

exp93 s2pu1

SAMPLE		DEC. & VT	
date	Mar 21 2014	dfrq	125.694
solvent	cdc13	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.833	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	61	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	120		
sc	0		
wc	210		
hzmm	27.37		
is	33.57		
rfl	4636.0		
rfp	3618.8		
th	3		
ins	100.000		
nm	cdc ph		



```

NSD-09-175-F1
exp94 s2pu1

SAMPLE
date Mar 21 2014 dfrq 499.833
solvent cdc13 dn H1
file exp dpwr 44
ACQUISITION dof 0
sfrq 125.697 dm yvy
tn C13 dmm w
at 1.000 dmf 10870
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16
ss 2 PROCESSING
tpwr 60 wtfile
pw 4.0 proc ft
dl 1.000 fn not used
tof 2512.2 math f
nt 2048
ct 2048 werr react
alock y wexp procplot
gain not used wbs testsn
wnt

FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -1257.0
wp 28906.3
vs 800
sc 0
wc 210
hzmm 137.65
is 500.00
rf1 10979.6
rfp 9677.5
th 6
ins 100.000
nm cdc ph

```

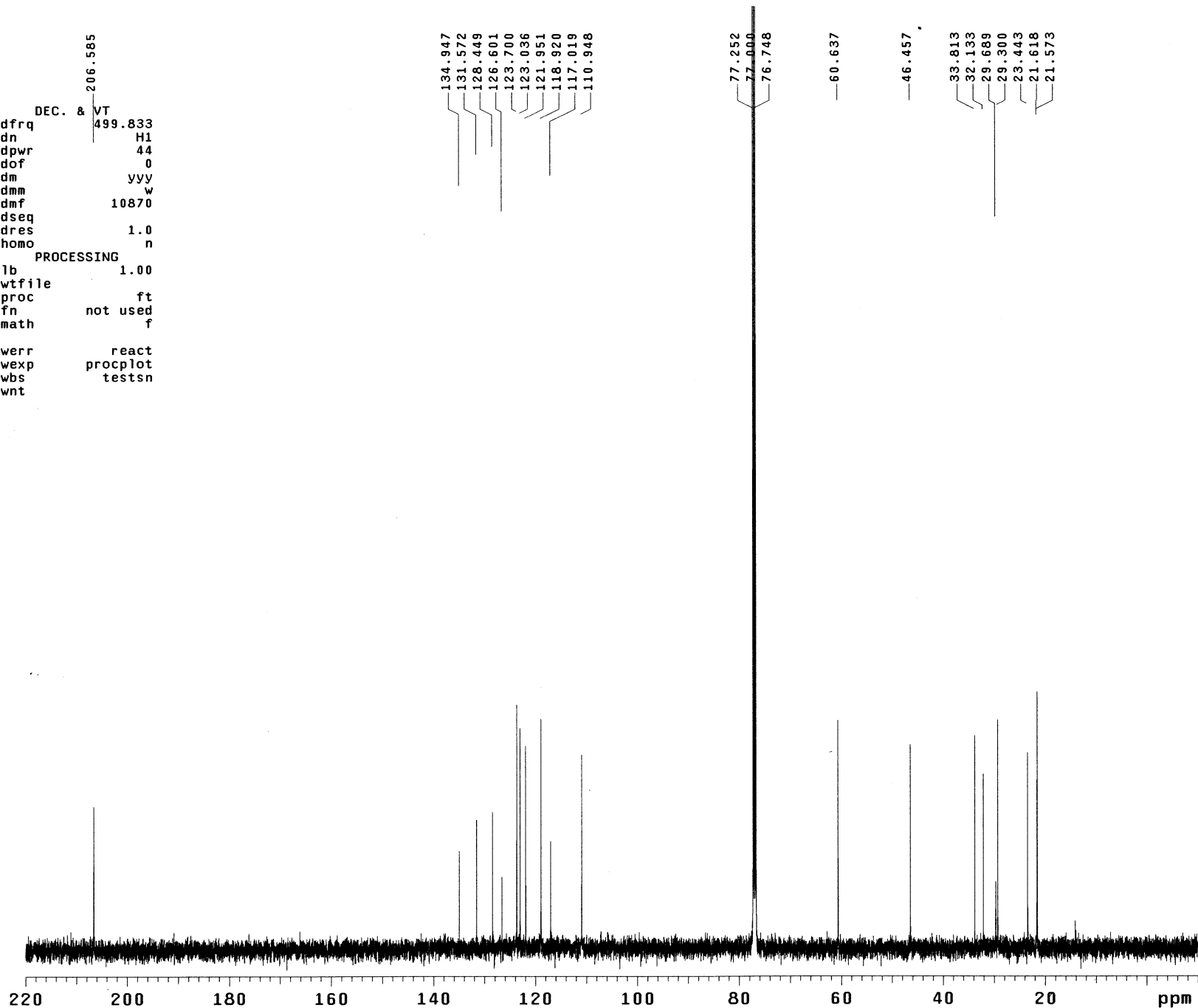


Fig S27.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of compound 4c.

Fig S28. DEPT of compound 4c.

NSD-09-175-F1

exp95 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Mar 21 2014	j1xh 140.0	array	mult
solvent	cdcl3	mult arrayed	arraydim	3
sample	undefined	SPECIAL		
ACQUISITION		temp not used	i	mult
sw	31446.5	gain 54	1	0.5
at	1.000	spin 0	2	1
np	62894	PROCESSING		3 1.5
bs	16	lb 1.00		
ss	-4	fn not used		
d1	1.000	SPECTRUM		
nt	1536	wp 28906.3		
ct	1536	sp -1257.0		
TRANSMITTER		rp -26.8		
tn	C13	lp 141.5		
tof	2512.2	ai cdc ph		
tpwr	60	REFERENCE		
pw	10.400	rfl 1302.1		
DECOUPLER		rfp 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	44	sc 0		
dm	nny	vs 1000		
dmm	ccw	hzmm 137.65		
dmf	10870	th 68		
pp1v1	61			
pp	14.600			

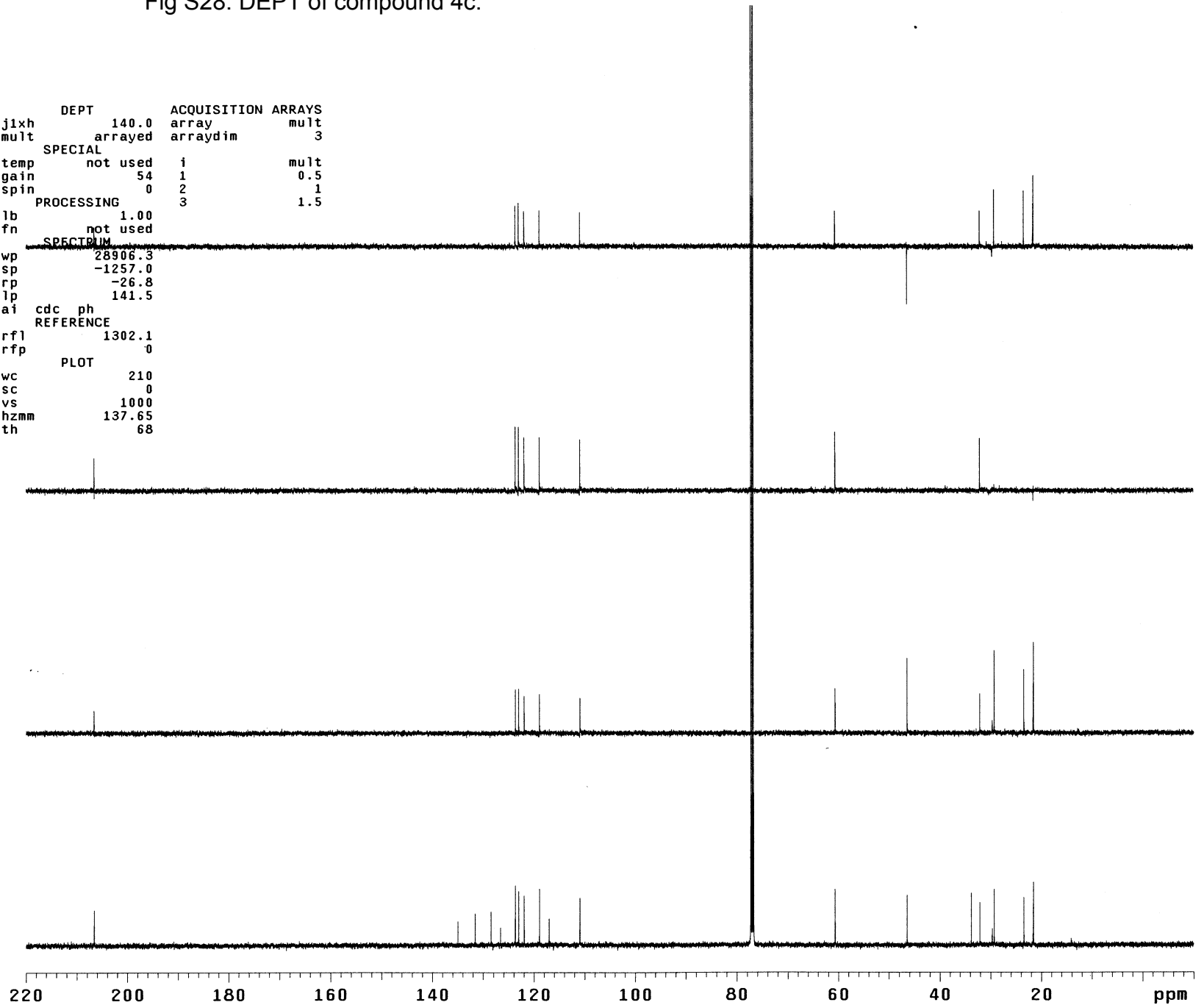


Fig S29. HSQC of compound 4c.

NSD-09-175-F1

exp98 gHSQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date Mar 21 2014	hs	n	phase
solvent cdc13	sspul	y	arraydim 256
sample undefined	PFGflg	y	
ACQUISITION	hsglv1	1009	phase
sw 6000.6	SPECIAL	i	1
at 0.171	temp	not used	2
np 2048	gain	54	
fb not used	spin	0	
ss 32	GRADIENTS		
d1 1.000	gzlv11	1009	
nt 8	gt1	0.002000	
2D ACQUISITION	gzlv13	508	
sw1 21367.5	gt3	0.001000	
ni 128	gstab	0.000500	
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf	0.079	
tn H1	gfs	not used	
sfrq 499.833	fn	2048	
tof -0.1	F1 PROCESSING		
tpwr 61	gf1	0.006	
pw 12.900	gfs1	not used	
DECOUPLER	proc1	1p	
dn C13	fn1	2048	
dof -2515.1	DISPLAY		
dm nny	sp	351.3	
dmm ccp	wp	3539.4	
dmf 32258	sp1	2318.3	
dpwr 42	wp1	13667.7	
pxlv1 59	rfl	3261.1	
pxw 12.200	rfp	2745.1	
HSQC	rfl1	16755.1	
j1xh 140.0	rfp1	15463.5	
nullflg y	PLOT		
mult 2	wc	150.0	
	sc	6.2	
	wc2	116.2	
	sc2	0	
	vs	100	
	th	6	
	ai	cdc	ph

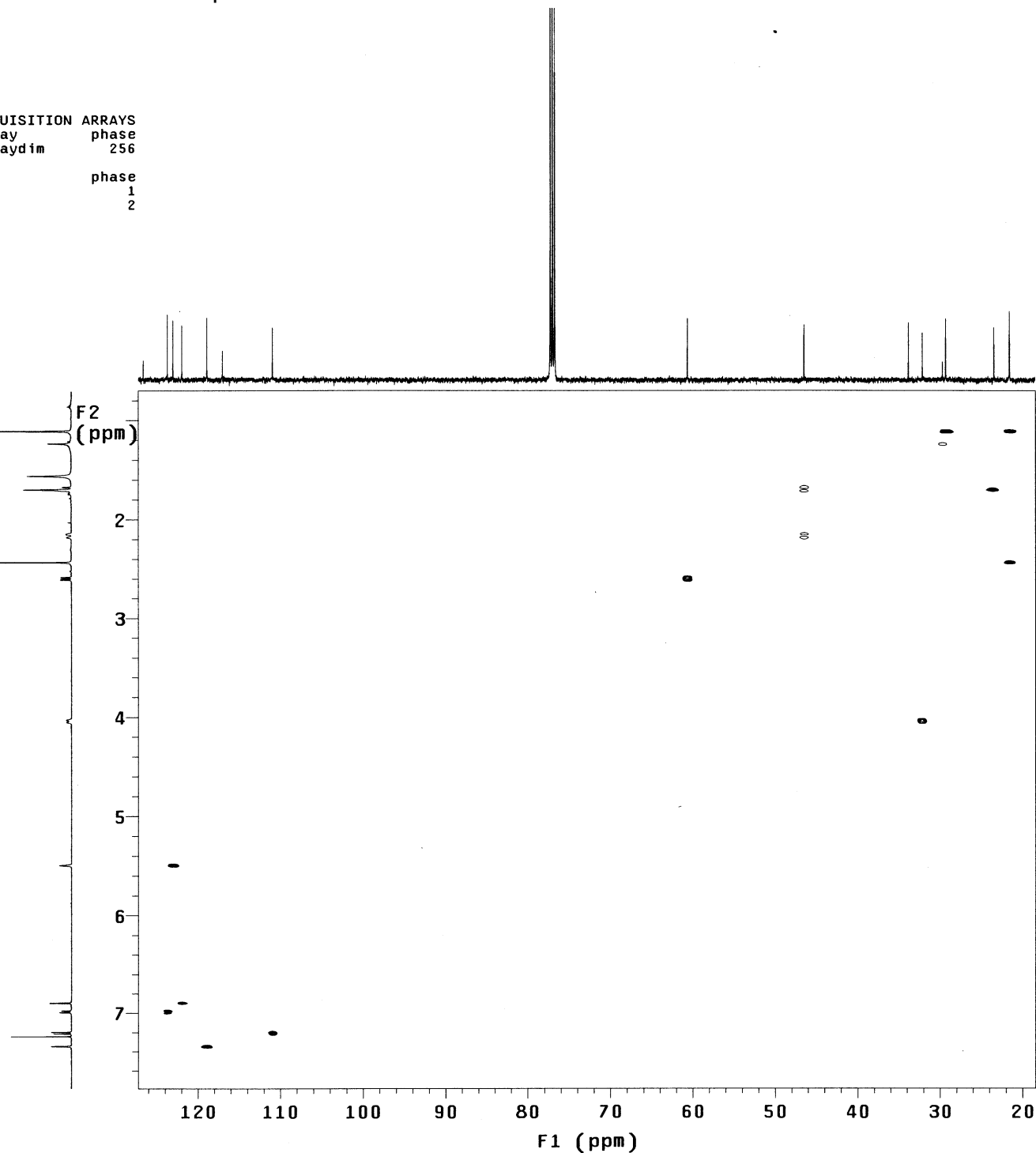


Fig S30. COSY of compound 4c.

NSD-09-175-F1

exp96 gCOSY

SAMPLE		FLAGS	
date	Mar 21 2014	hs	nn
solvent	cdc13	sspul	n
sample	undefined	hsglv1	1009
ACQUISITION		SPECIAL	
sw	6000.6	temp	not used
at	0.171	gain	34
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.085
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	6000.6	sb1	-0.021
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.833	DISPLAY	
tof	-0.1	sp	324.9
tpwr	61	wp	4629.4
pw	12.900	sp1	325.3
GRADIENTS		wp1	4629.4
gzlv11	1009	rfl	3264.0
gt1	0.001000	rfp	2745.1
gstab	0.000500	rfl1	3263.6
DECOUPLER		rfp1	2745.1
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	100
		th	6
		ai	cdc av

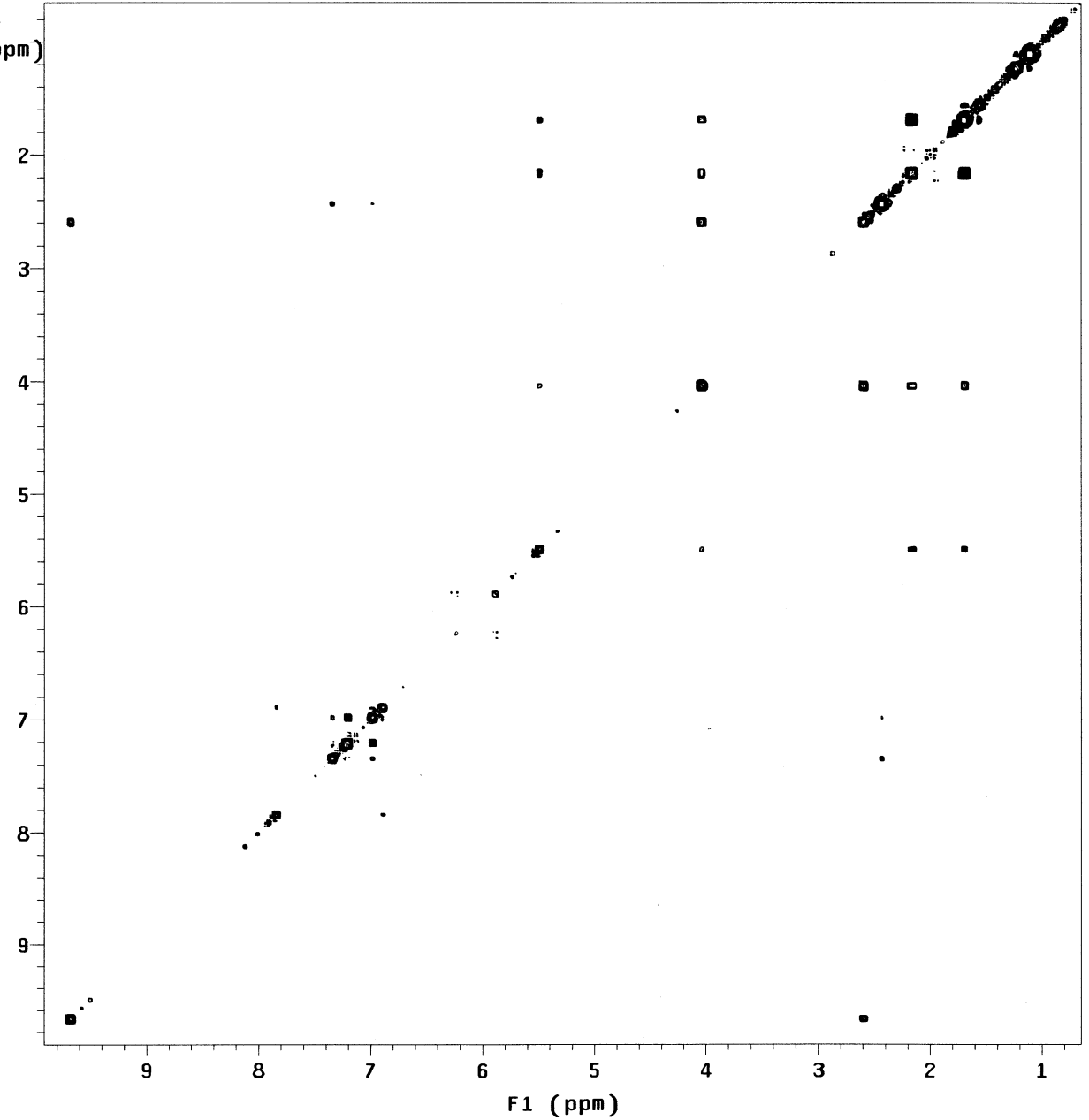
F2  
(ppm)

Fig S31. NOESY of compound 4c.

NSD-09-175-F1

exp97 NOESY

SAMPLE		FLAGS	n
date	Mar 21 2014	hs	y
solvent	cdc13	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1009
sw	6000.6	SPECIAL	
at	0.171	temp	not used
np	2048	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.079
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	6000.6	F1 PROCESSING	
ni	200	gf1	0.031
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	499.833	fn1	2048
tof	-0.1	DISPLAY	
tpwr	61	sp	220.1
pw	12.900	wp	4711.4
NOESY		sp1	210.7
mix	0.600	wp1	4717.3
PRESATURATION		rfl	3263.3
satmode	nnnn	rfp	2745.1
satpwr	0	rfl1	3261.0
satdly	0	rfp1	2745.1
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	100
		th	1
		ai	ph

F2 (ppm)

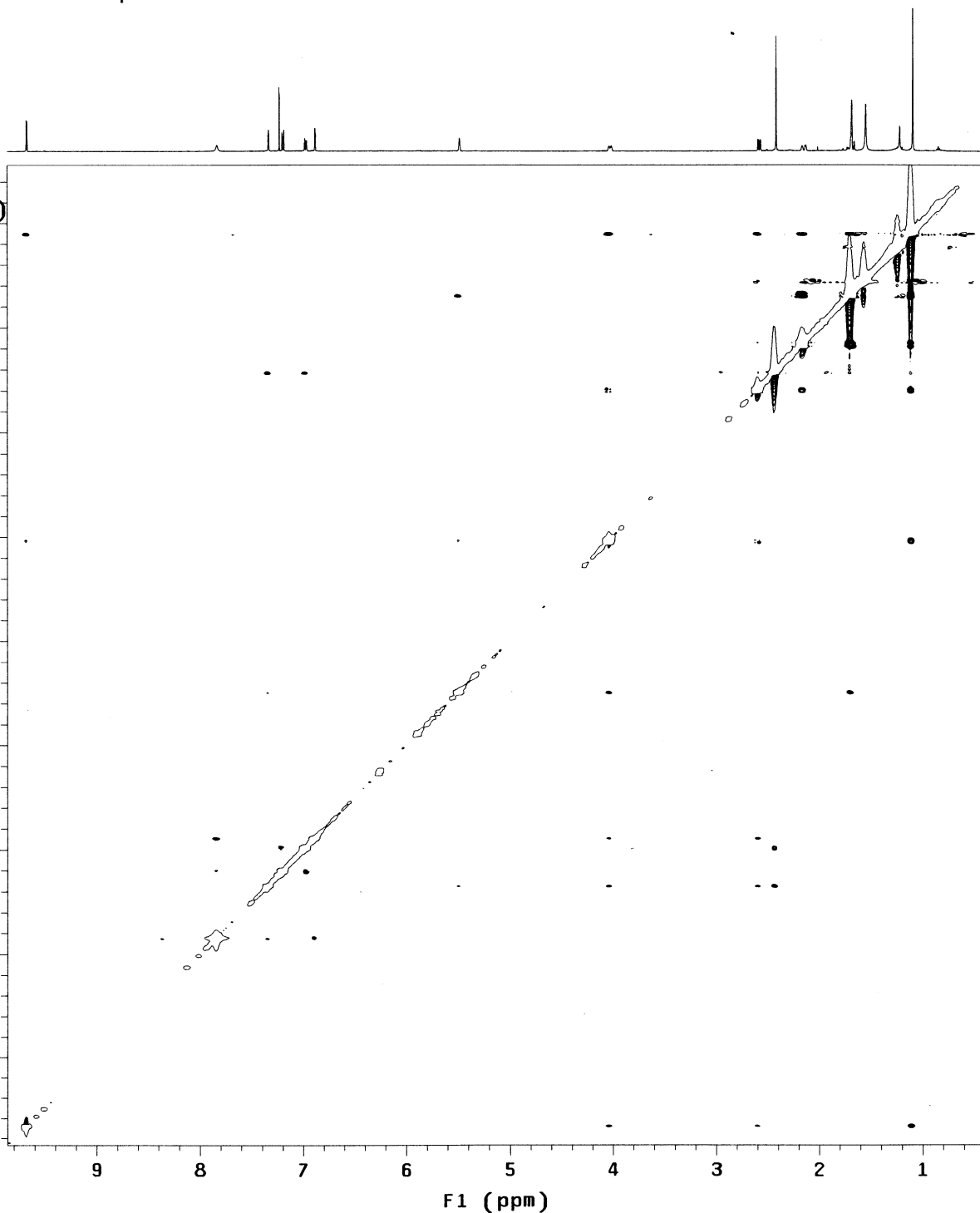
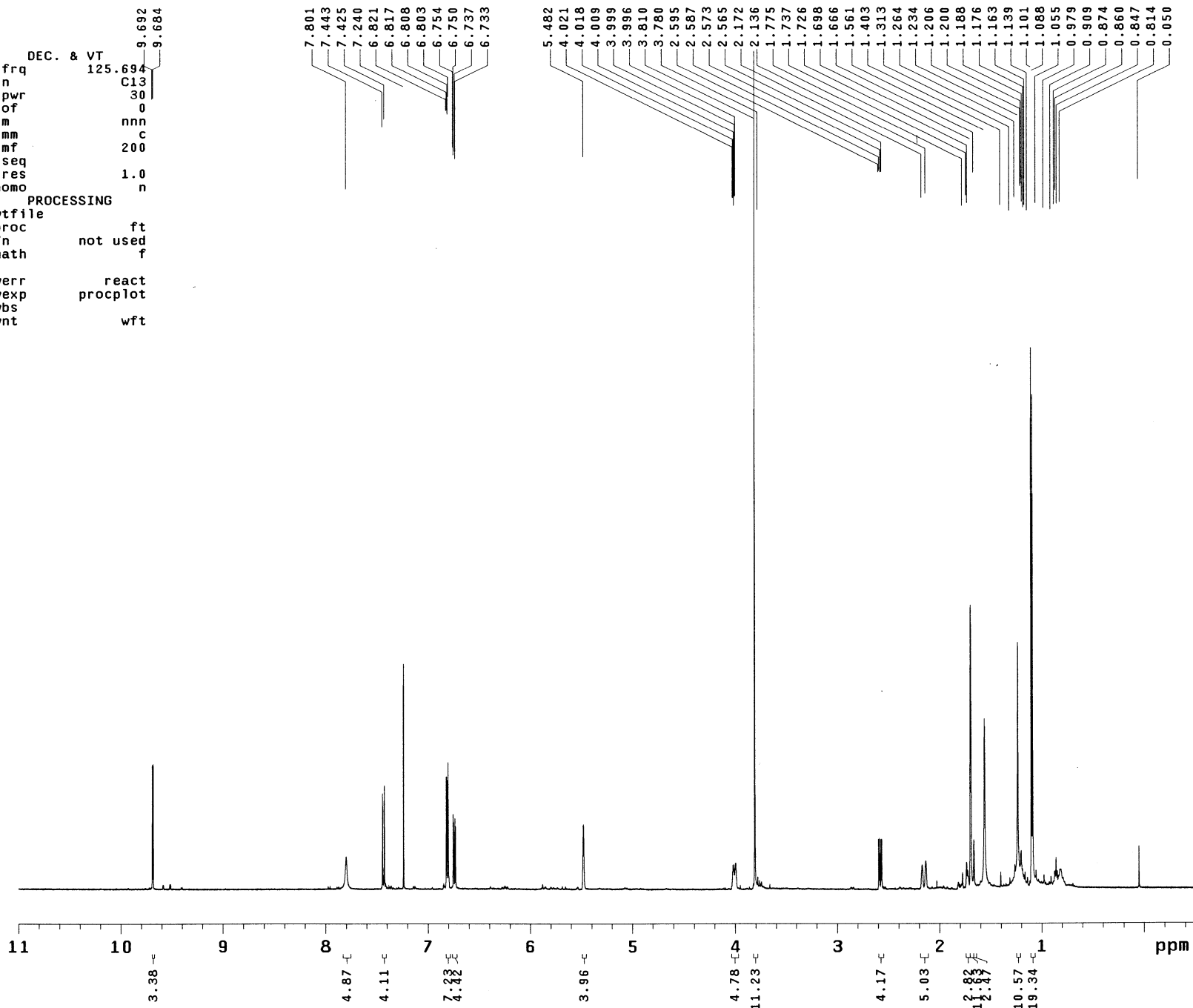


Fig S32. 1H NMR (CDCl3, 500 MHz) of compound 4d.

NSD-09-186-f1

exp60 s2pu1

SAMPLE		DEC. & VT	
date	Mar 27 2014	dfrq	125.694
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.833	dm	nnn
tn	H1	dmm	c
at	3.000	dmf	200
np	48000	dseq	
sw	8000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	61	wtfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	150		
sc	0		
wc	210		
hzmm	27.37		
is	33.57		
rfl	4635.7		
rfp	3618.8		
th	3		
ins	100.000		
nm	cdc ph		





```

NSD-09-186-f1
exp61 s2pu1
SAMPLE DEC. & VT
date Mar 27 2014 dfrq 499.833
solvent cdc13 dn H1
file exp dpwr 44
ACQUISITION dof 0
sfrq 125.697 dm yyy
tn C13 dmm w
at 1.000 dmf 10870
np 62894 dseq
sw 31446.5 dres 1.0
fb not used homo n
bs 16 PROCESSING
ss 2 lb 1.00
tpwr 60 wtfile
pw 4.0 proc ft
d1 1.000 fn not used
tof 2512.2 math f
nt 6000
ct 6000 werr react
alock y wexp procplot
gain not used wbs testsn
FLAGS wnt
il n
in n
dp y
hs nn
DISPLAY
sp -1257.0
wp 28906.3
vs 1000
sc 0
wc 210
hzmm 137.65
is 500.00
rfl 10979.6
rfp 9677.5
th 6
ins 100.000
nm cdc ph

```

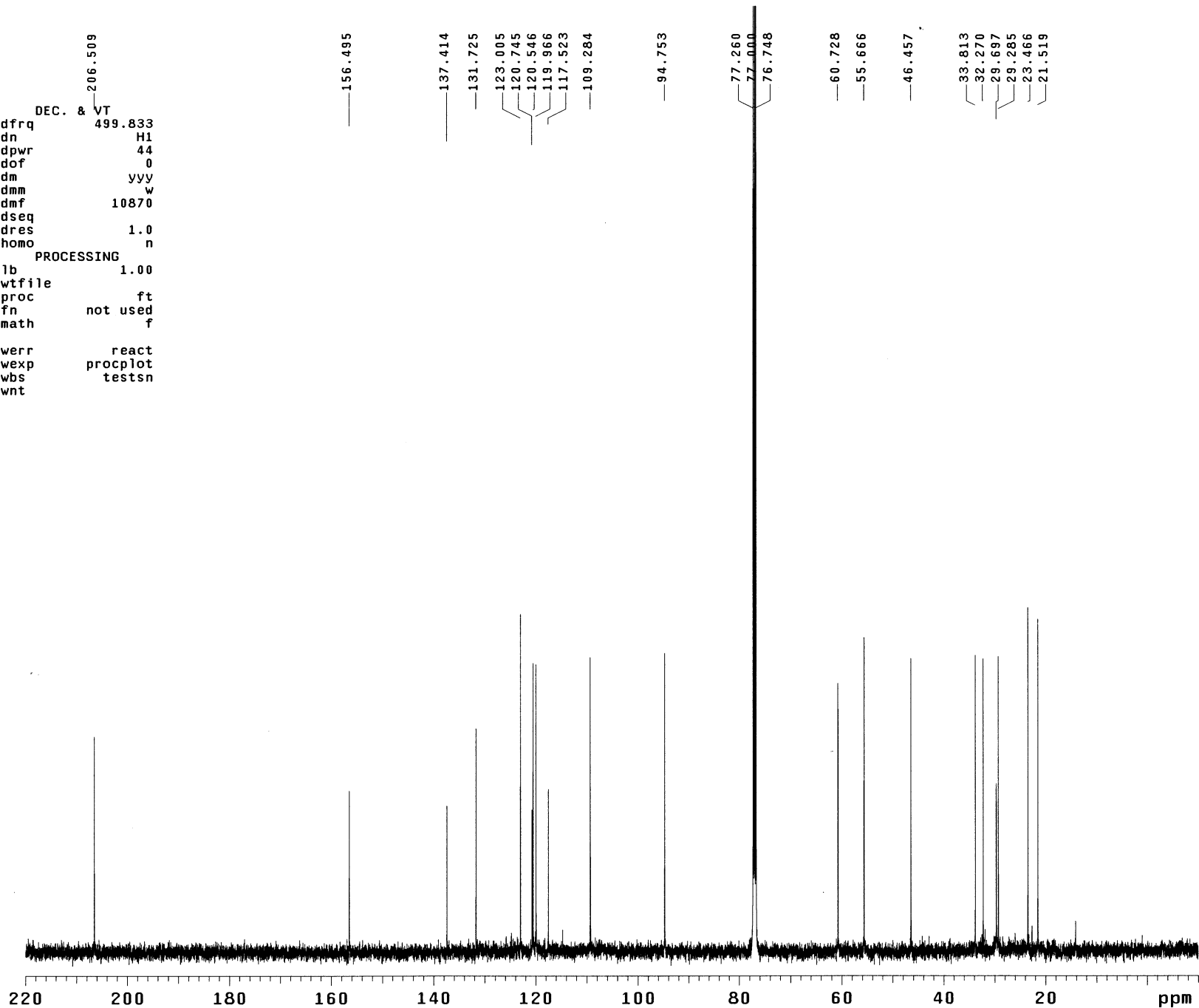
Fig S33. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) of compound 4d.

Fig S34. DEPT of compound 4d.

NSD-09-186-f1

exp62 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS	
date	Mar 27 2014	j1xh	140.0	array
solvent	cdcl3	mult	arrayed	mult
sample	undefined		arraydim	3
ACQUISITION		SPECIAL	temp	not used
sw	31446.5	gain	34	1
at	1.000	spin	0	2
np	62894	PROCESSING	3	3
bs	16	lb	1.00	1.5
ss	-4	fn	not used	
d1	1.000	SPECTRUM		
nt	3000	wp	28906.3	
ct	3000	sp	-1257.0	
TRANSMITTER		rp	6.1	
tn	C13	lp	91.5	
tof	2512.2	ai	cdc ph	
tpwr	60	REFERENCE		
pw	10.400	rfl	1302.1	
DECOUPLER		rfp	0	
dn	H1	PLOT		
dof	0	wc	210	
dpwr	44	sc	0	
dm	nny	vs	1000	
dmm	ccw	hzmm	137.65	
dmf	10870	th	68	
pp1v1	61			
pp	14.600			

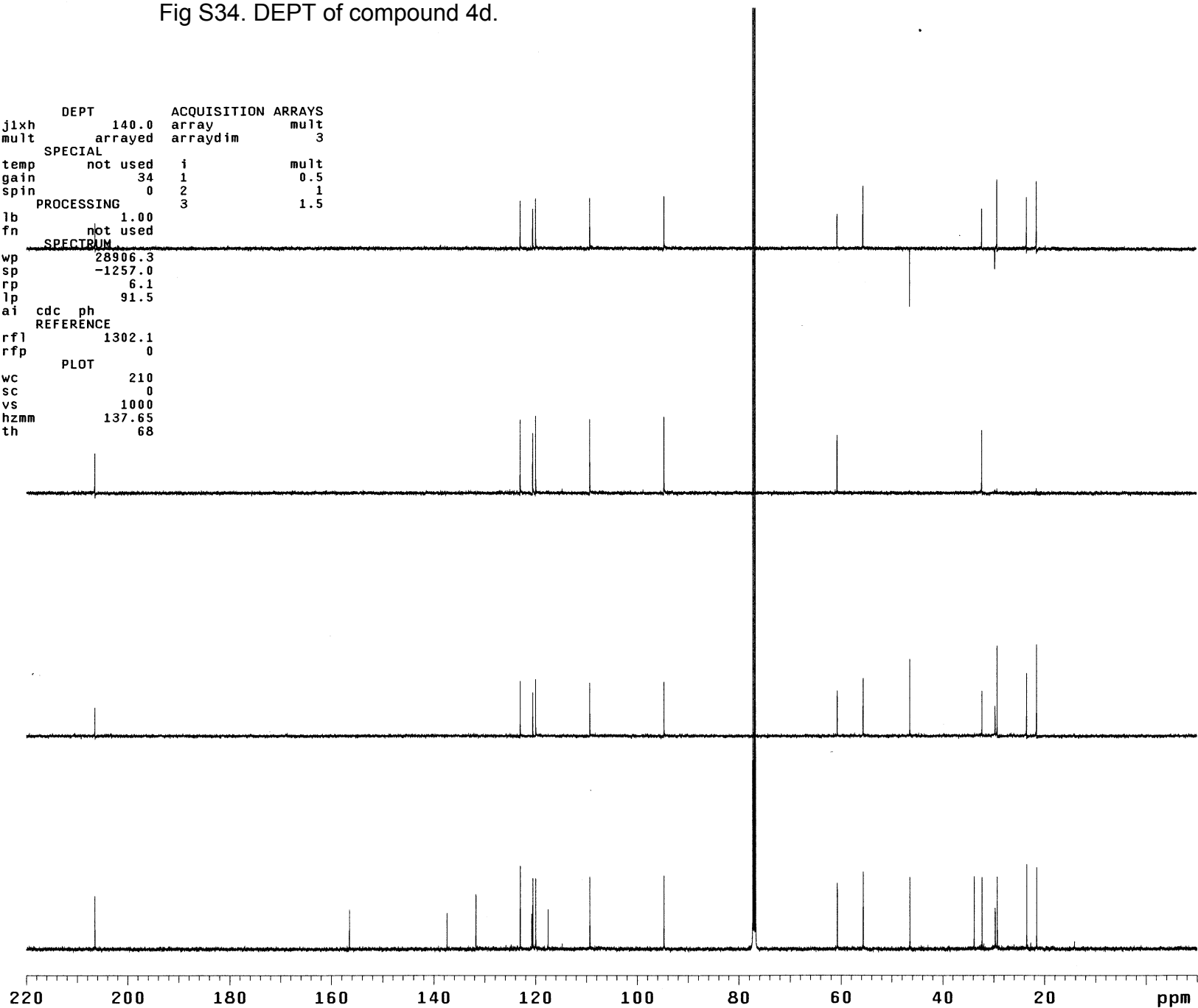


Fig S35. HSQC of compound 4d.

NSD-09-186-f1

exp65 gHSQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date Mar 27 2014	hs	n	array
solvent cdc13	sspul	y	arraydim
sample undefined	PFGflg	y	phase
ACQUISITION	hsglv1	1009	i
sw 5006.3	SPECIAL	1	phase
at 0.205	temp	not used	2
np 2048	gain	54	
fb not used	spin	0	
ss 32	GRADIENTS		
d1 1.000	gzlv11	1009	
nt 8	gt1	0.002000	
2D ACQUISITION	gzlv13	508	
sw1 21367.5	gt3	0.001000	
n1 128	gstab	0.000500	
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf	0.094	
tn H1	gfs	not used	
sfrq 499.833	fn	2048	
tof -0.1	F1 PROCESSING		
tpwr 61	gf1	0.006	
pw 12.900	gfs1	not used	
DECOUPLER	procl	1p	
dn C13	fn1	2048	
dof -2515.1	DISPLAY		
dm nny	sp	403.6	
dmm ccp	wp	3441.8	
dmf 32258	sp1	2429.9	
dpwr 42	wp1	13292.1	
pwxlvl 59	rfl	2756.9	
pw 12.200	rfp	2740.1	
HSQC	rfl1	16743.9	
j1xh 140.0	rfl1	15459.6	
nullflg y	PLOT		
mult 2	wc	150.0	
	sc	6.2	
	wc2	116.2	
	sc2	0	
	vs	331	
	th	5	
	ai	cdc	ph

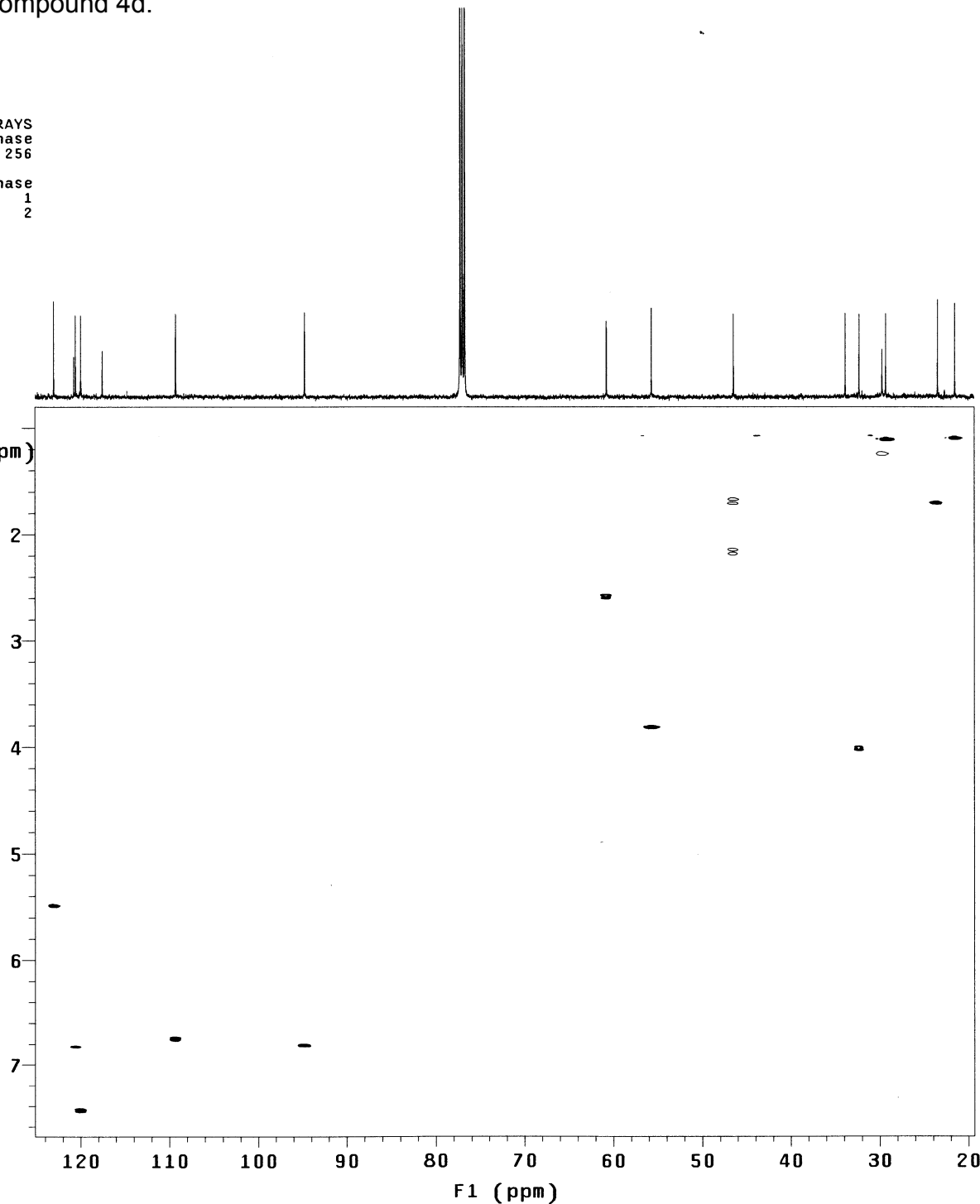
F2  
(ppm)

Fig S36. COSY of compound 4d.

NSD-09-186-f1

exp63 gCOSY

SAMPLE		FLAGS	
date	Mar 27 2014	hs	nn
solvent	cdc13	sspul	n
sample	undefined	hsglv1	1009
ACQUISITION		SPECIAL	
sw	5006.3	temp	not used
at	0.205	gain	34
np	2048	spin	n
fb	not used	F2 PROCESSING	
ss	16	sb	-0.102
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	5006.3	sb1	-0.026
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.833	DISPLAY	
tof	-0.1	sp	210.0
tpwr	61	wp	4717.8
pw	12.900	sp1	205.6
GRADIENTS		wp1	4722.7
gzlv11	1009	rfl	2759.8
gt1	0.001000	rfp	2740.1
gstab	0.000500	rfl1	2759.3
DECOUPLER		rfp1	2740.1
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	331
		th	6
		ai	cdc av

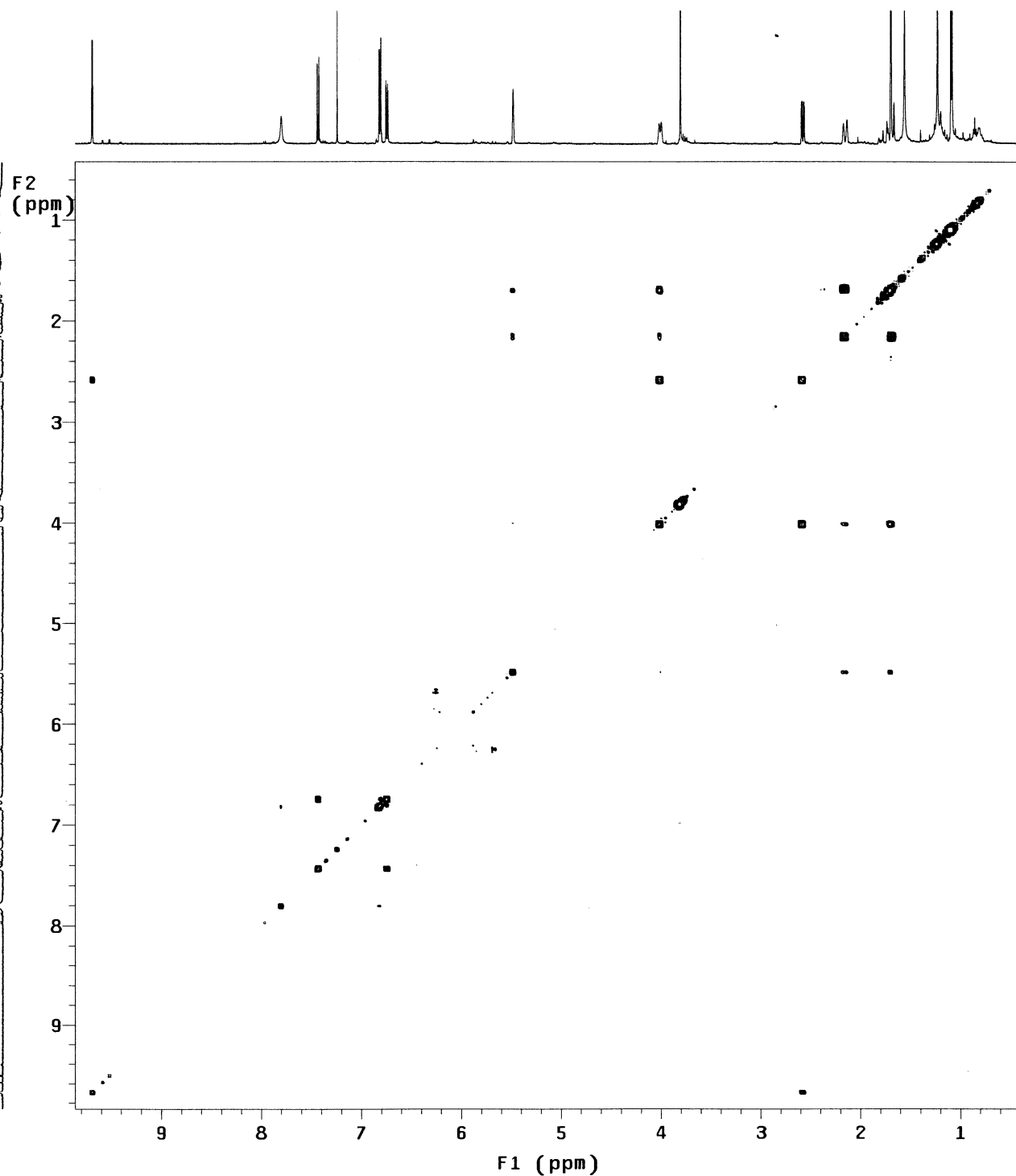


Fig S37. NOESY of compound 4d.

NSD-09-186-f1

exp64 NOESY

SAMPLE		FLAGS	
date	Mar 27 2014	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv	1009
sw	5006.3	SPECIAL	
at	0.205	temp	not used
np	2048	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.094
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	5006.3	F1 PROCESSING	
ni	200	gf1	0.037
TRANSMITTER		gfs1	not used
tn	H1	procl	lp
sfrq	499.833	fn1	2048
tof	-0.1	DISPLAY	
tpwr	61	sp	263.7
pw	12.900	wp	4649.4
NOESY		sp1	259.3
mix	0.600	wp1	4649.4
PRESATURATION		rfl	2760.0
satmode	nnnn	rfp	2740.1
satpwr	0	rfl1	2759.4
satdly	0	rfp1	2740.1
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	331
		th	1
		ai	ph

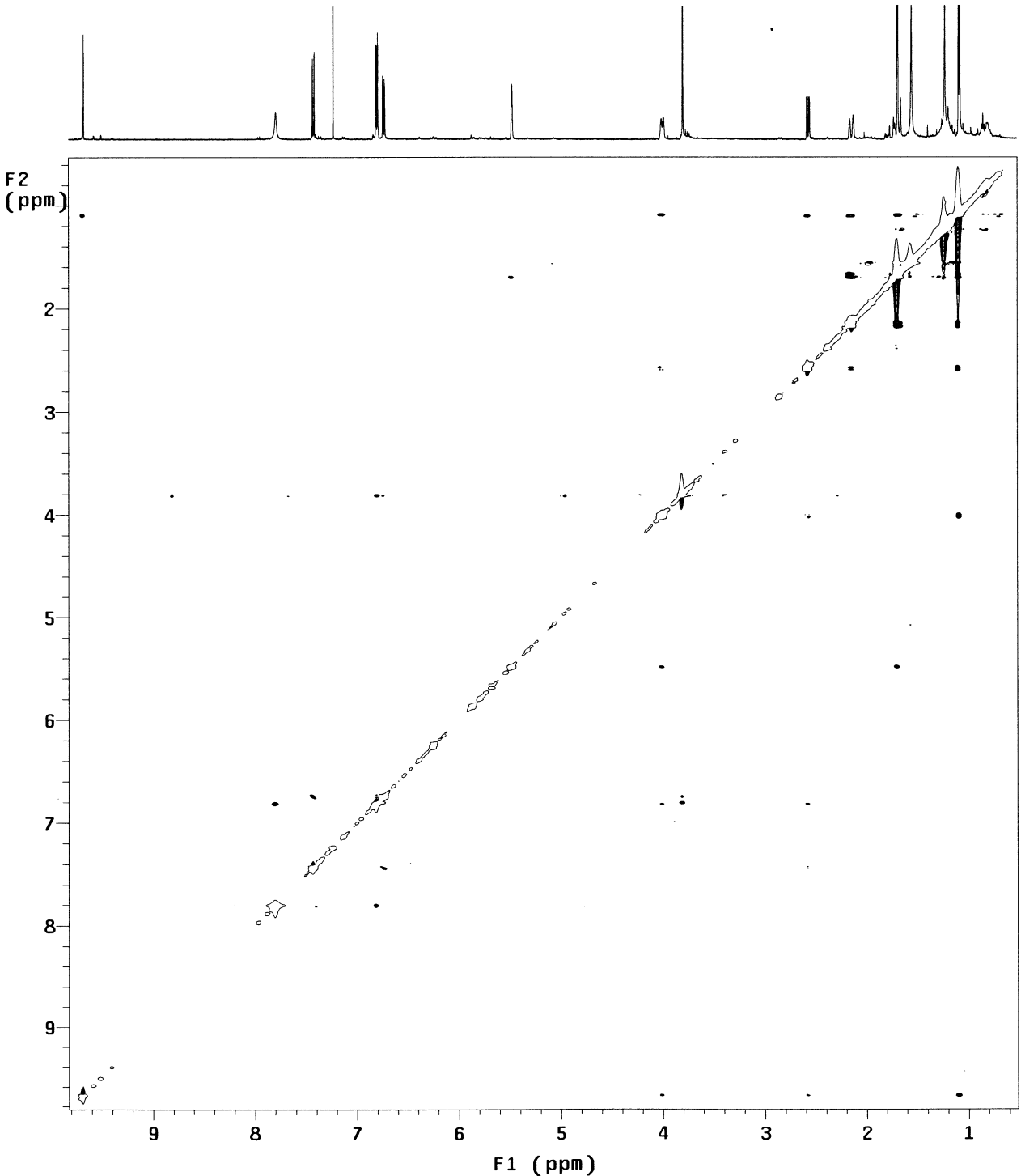
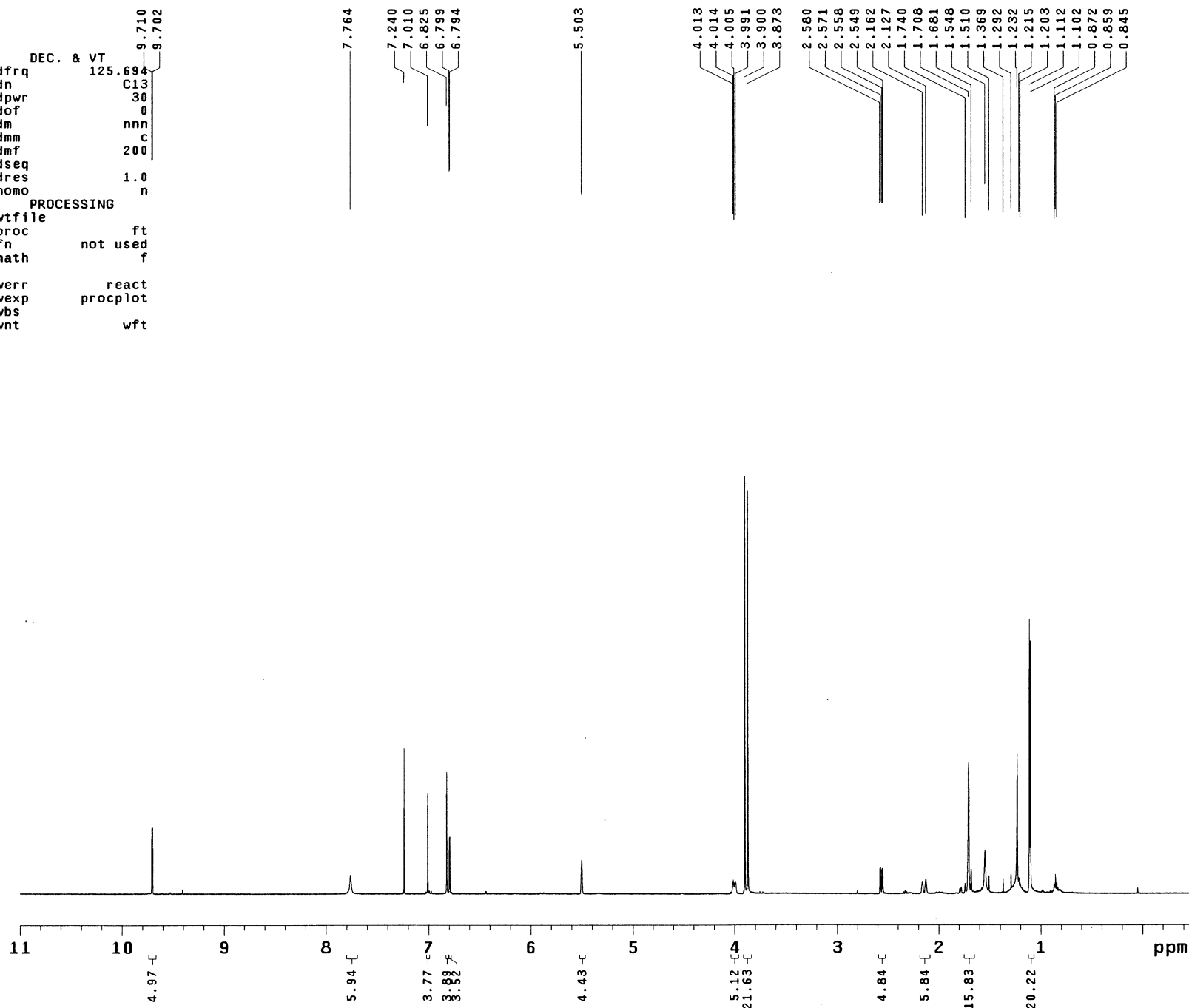


Fig S38. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of compound 4e.

NSD-09-184-f1

exp40 s2pu1

date	May 24 2014	dfrq	125.694
solvent	cdcl3	dn	C13
file	exp	dpwr	30
ACQUISITION			
sfrq	499.833	dof	0
tn	H1	dm	nnn
at	3.000	dmm	c
np	48000	dmf	200
sw	8000.0	dseq	1.0
fb	not used	dres	n
bs	4	homo	n
PROCESSING			
tpwr	61	wfile	
pw	4.8	proc	ft
d1	1.000	fn	not used
tof	499.7	math	f
nt	4		
ct	4	werr	react
alock	y	wexp	procplot
gain	not used	wbs	
FLAGS			
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5748.0		
vs	75		
sc	0		
wc	210		
hzmm	27.37		
is	33.57		
rfl	4636.2		
rfp	3618.8		
th	2		
ins	100.000		
nm	cdc	ph	



NSD-09-184-f1

exp41 s2pul

```

SAMPLE
date May 24 2014 dfrq 499.833
solvent cdc13 dn H1
file exp dpwr 44
ACQUISITION dof 0
sfrq 125.696 dm vvy
tn C13 dmm w
at 1.000 dmf 10870
np 60332 dseq
sw 30165.9 dres 1.0
fb not used homo n
bs 4
tpwr 60 lb 1.00
pw 4.8 wtfile
d1 1.000 proc ft
tof 1883.7 fn 131072
nt 6000 math f
ct 6000
alock y werr react
gain not used wexp procplot
FLAGS wbs testsn
il n wnt
in n
dp y
hs nn
DISPLAY
sp -1257.2
wp 28906.5
vs 600
sc 0
wc 210
hzmm 137.65
is 33.57
rf1 10967.9
rfp 9677.5
th 6
ins 100.000
nm cdc ph

```

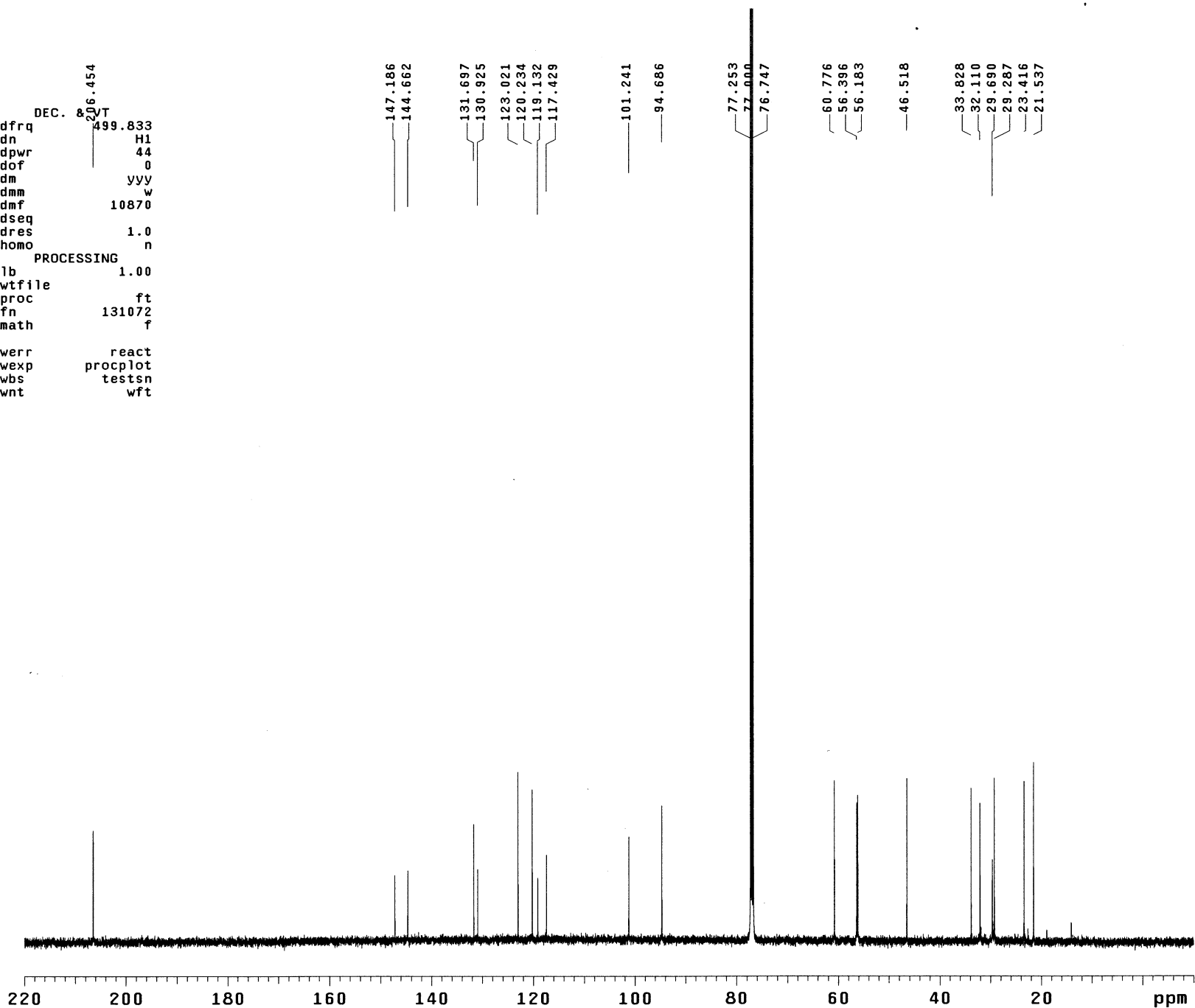
Fig S39. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) of compound 4e.

Fig S40. DEPT of compound 4e.

NSD-09-184-f1

exp42 DEPT

date	May 24 2014	j1xh	DEPT	140.0	array	mult
solvent	cdcl3	mult	arrayed		arraydim	3
sample	undefined	SPECIAL				
ACQUISITION		temp	not used	i	mult	
sw	30165.9	gain	52	1	0.5	
at	1.000	spin	0	2	1	
np	60332	PROCESSING		3	1.5	
bs	4	lb	1.00			
ss	-4	fn	131072			
d1	1.000	SPECTRUM				
nt	3000	wp	28906.5			
ct	3000	sp	-1257.2			
TRANSMITTER		rp	-72.0			
tn	C13	lp	71.5			
tof	1883.7	ai	cdc ph			
tpwr	60	REFERENCE				
pw	10.400	rfl	1290.4			
DECOUPLER		rfp	0			
dn	H1	PLOT				
dof	0	wc	210			
dpwr	44	sc	0			
dm	nny	vs	1400			
dmm	ccw	hzmm	137.65			
dmf	10870	th	7			
pplvl	61					
pp	14.600					

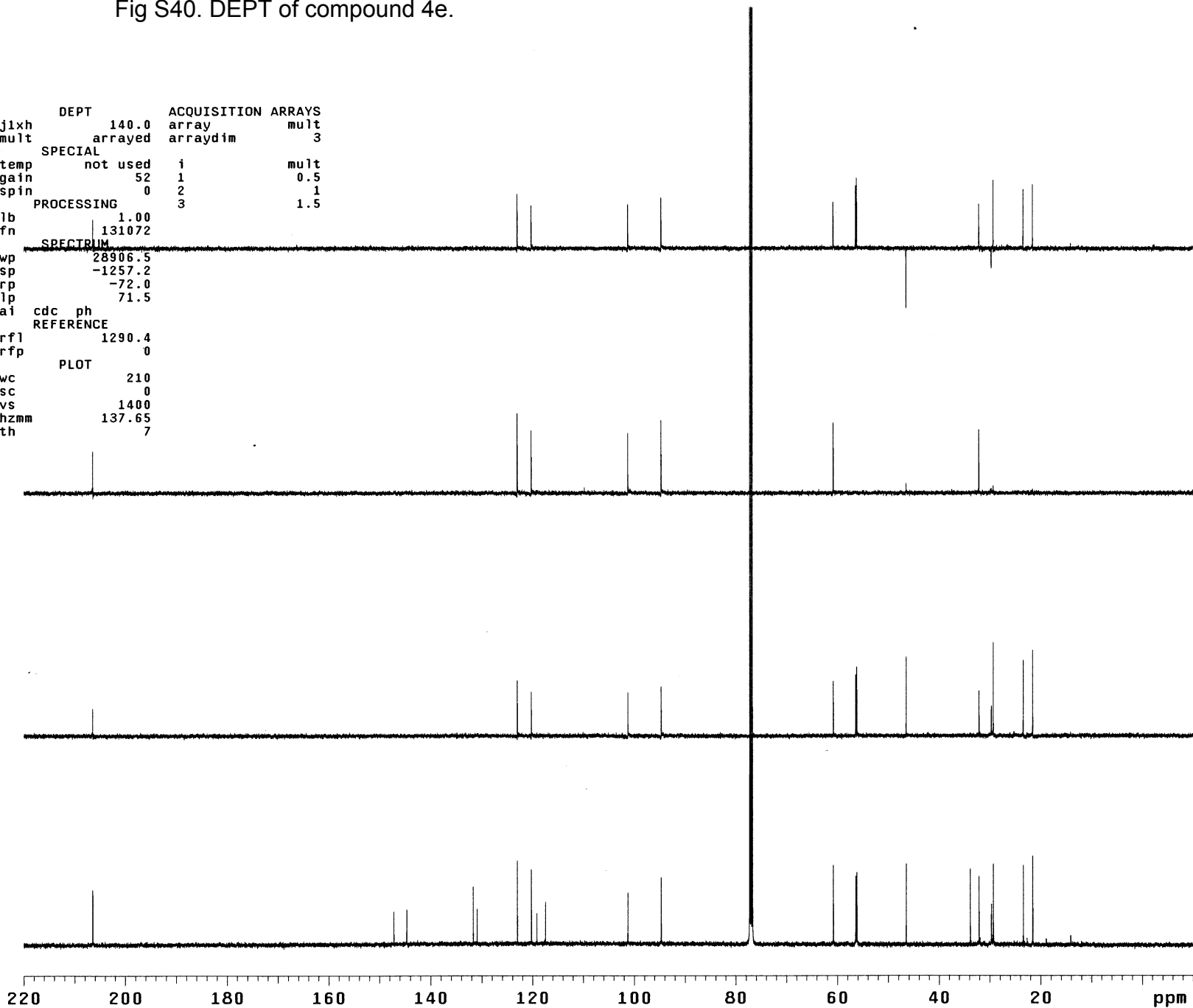




Fig S41. HMQC of compound 4e.

NSD-09-184-f1

exp45 gHMQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date May 26 2014	hs	n	array phase
solvent cdc13	sspul	y	arraydim 256
sample undefined	PFGflg	y	
ACQUISITION	hsglv1	1009	phase
sw 5006.3	SPECIAL	i	1
at 0.205	temp not used	2	2
np 2048	gain 54		
fb not used	spin 0		
ss 32	GRADIENTS		
d1 1.000	gzlv11 1009		
nt 8	gt1 0.001000		
2D ACQUISITION	gzlv13 508		
sw1 21367.5	gt3 0.001000		
ni 128	gstab 0.000500		
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf 0.094		
tn H1	gfs not used		
sfrq 499.833	fn 2048		
tof -0.1	F1 PROCESSING		
tpwr 61	gf1 0.006		
pw 12.900	gfs1 not used		
DECOUPLER	proc1 1p		
dn C13	fn1 2048		
dof -2515.1	DISPLAY		
dm nny	sp 402.1		
dmm ccp	wp 3275.6		
dmf 32258	sp1 2317.8		
dpwr 42	wp1 13542.5		
pxlv1 59	rfl 2768.9		
pxw 12.200	rfp 2750.6		
HMQC	rfl1 16753.7		
j1xh 140.0	rfp1 15461.6		
nullflg y	PLOT		
	wc 150.0		
	sc 6.2		
	wc2 116.2		
	sc2 0		
	vs 214		
	th 5		
	ai cdc ph		

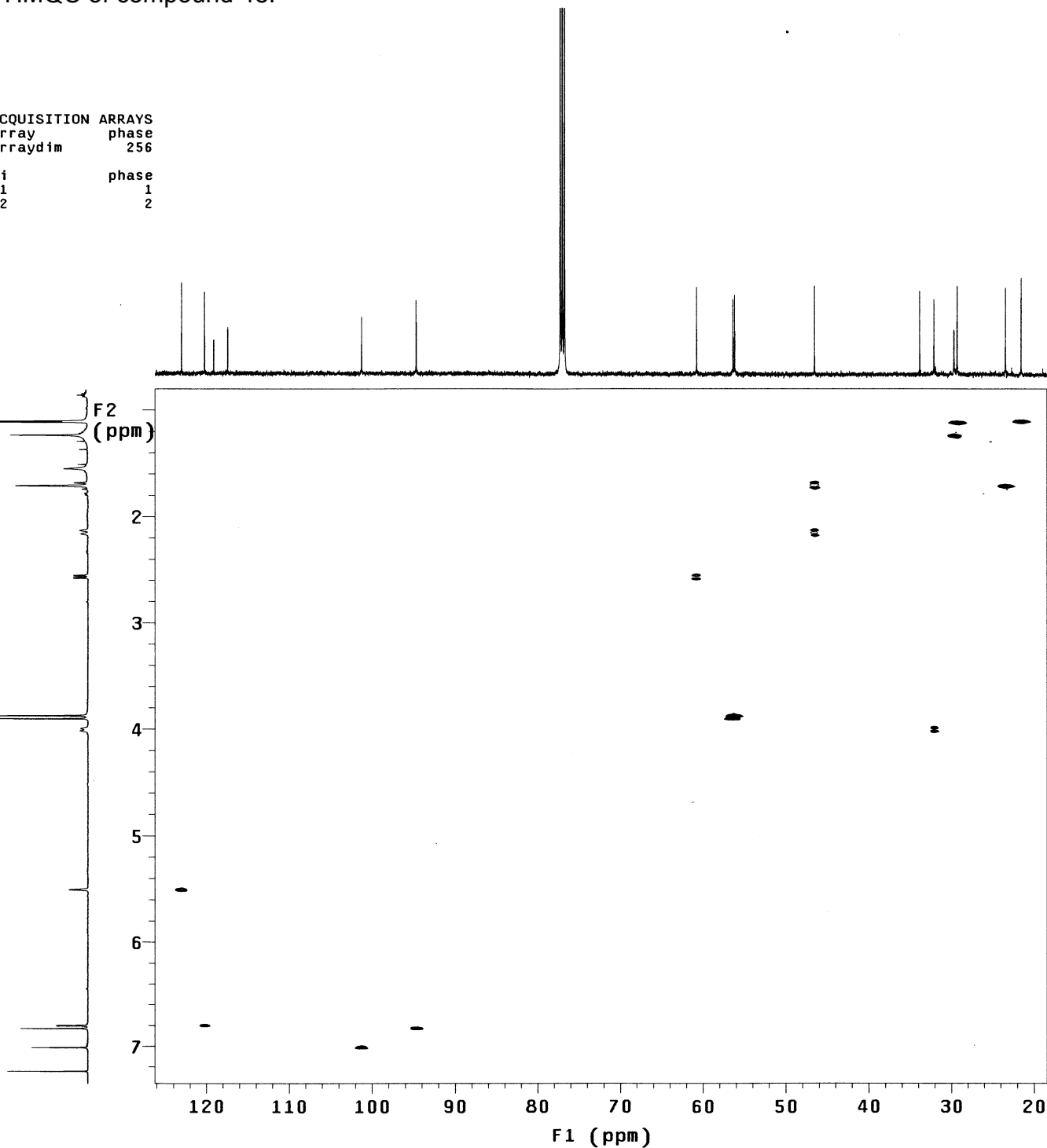


Fig S42. COSY of compound 4e.

NSD-09-184-f1

exp43 gCOSY

SAMPLE		FLAGS	
date	May 24 2014	hs	nn
solvent	cdcl3	sspul	n
sample	undefined	hsglv1	1009
ACQUISITION		SPECIAL	
sw	5006.3	temp	not used
at	0.205	gain	34
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.102
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	5006.3	sb1	-0.026
ni	128	sbs1	not used
TRANSMITTER		proc1	
tn	H1	fn1	2048
sfrq	499.833	DISPLAY	
tof	-0.1	sp	299.4
tpwr	61	wp	4615.1
pw	12.900	sp1	299.4
GRADIENTS		wp1	4620.0
gzlv11	1009	rfl	2768.9
gt1	0.001000	rfp	2750.6
gstab	0.000500	rfl1	2768.9
		rfp1	2750.6
DECOUPLER		PLOT	
dn	C13	wc	155.0
dm	nnn	sc	10.0
		wc2	155.0
		sc2	0
		vs	148
		th	6
		ai	cdc av

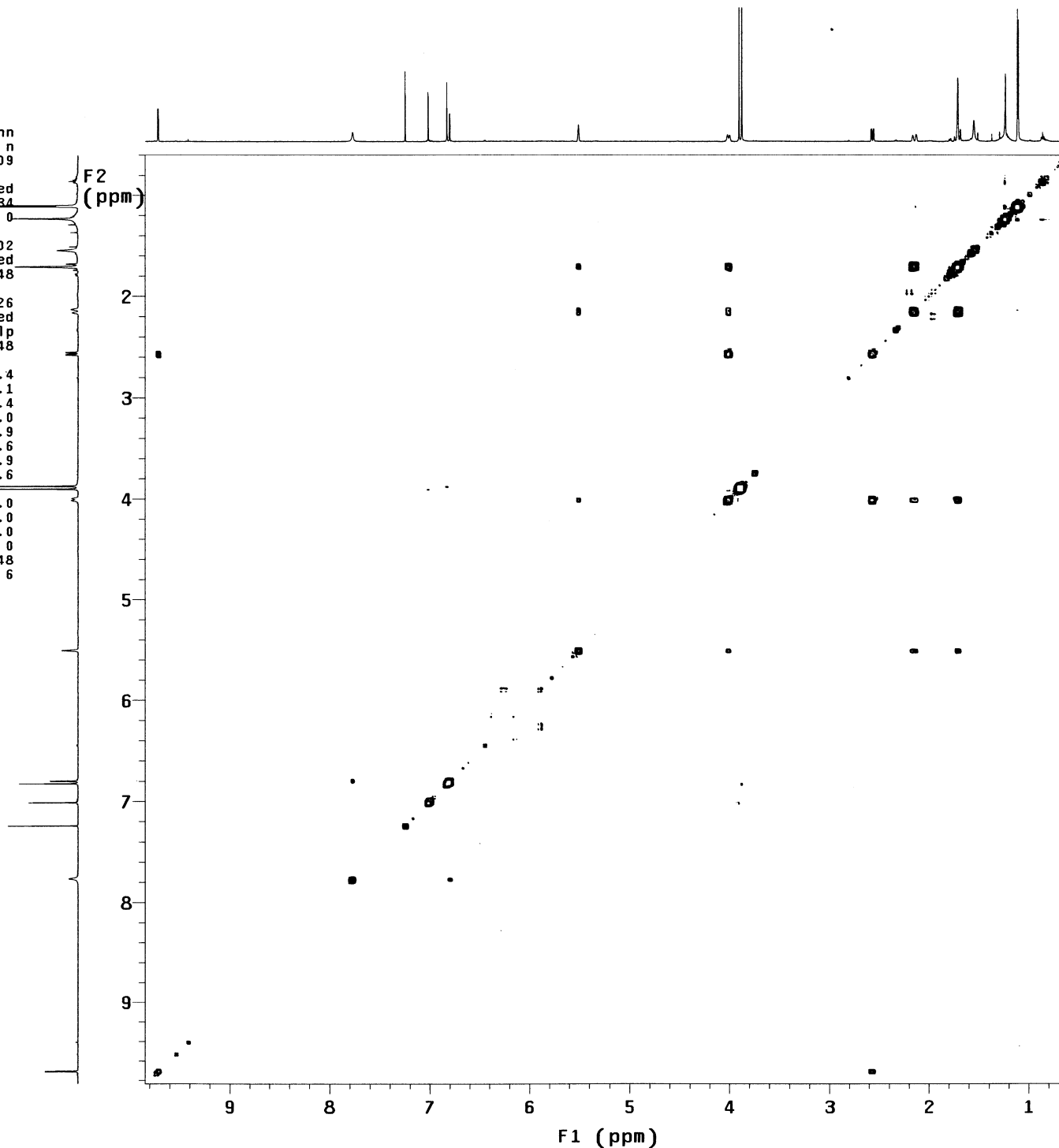


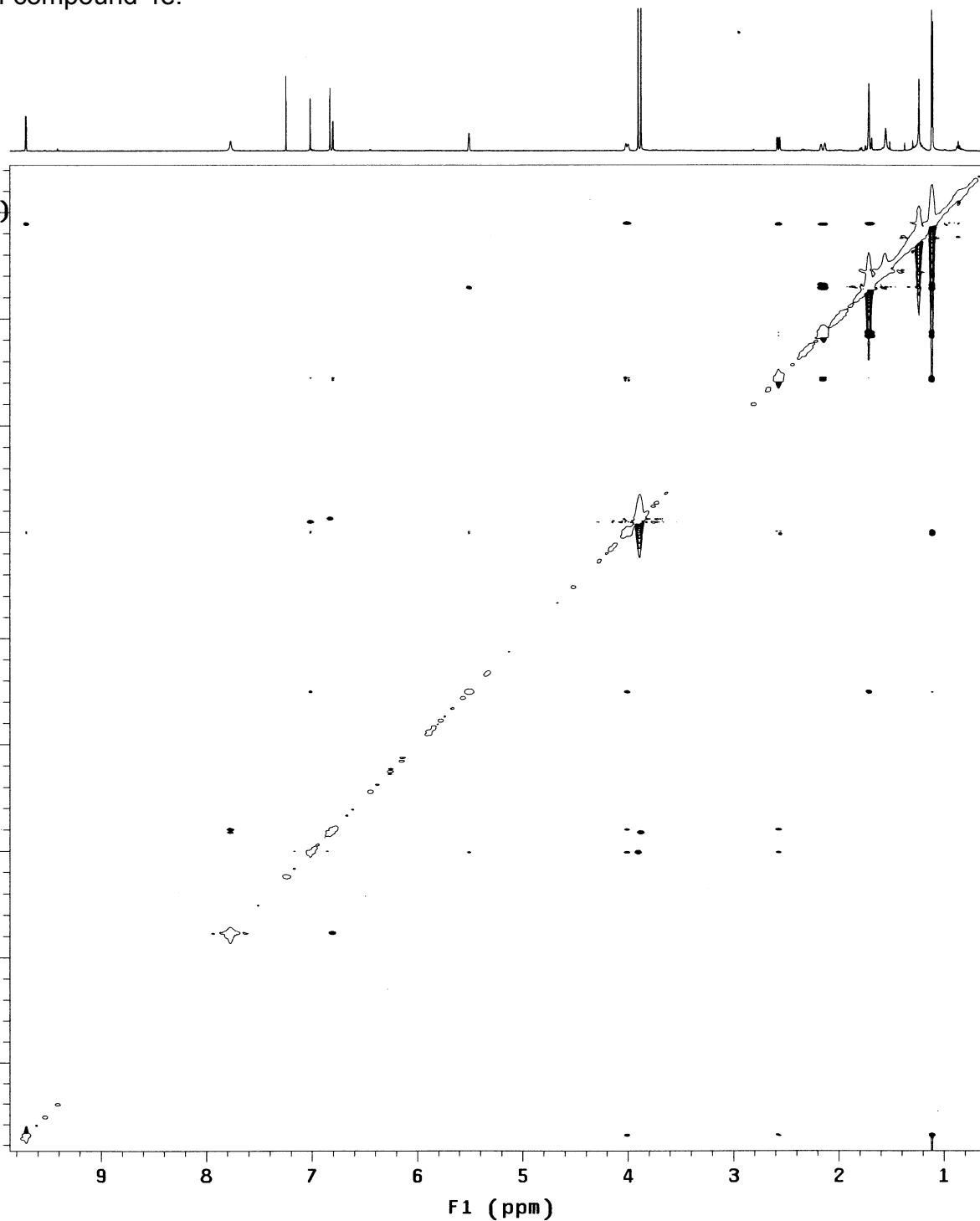
Fig S43. NOESY of compound 4e.

NSD-09-184-f1

exp44 NOESY

SAMPLE		FLAGS	
date	May 24 2014	hs	n
solvent	cdc13	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1009
sw	5006.3	SPECIAL	
at	0.205	temp	not used
np	2048	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.094
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	5006.3	F1 PROCESSING	
ni	200	gf1	0.037
TRANSMITTER		gfs1	not used
tn	H1	procl	lp
sfrq	499.833	fn1	2048
tof	-0.1	DISPLAY	
tpwr	61	sp	277.3
pw	12.900	wp	4649.4
NOESY		sp1	279.9
mix	0.600	wp1	4649.4
PRESATURATION		rfl	2771.5
satmode	nnnn	rfp	2750.6
satpwr	0	rfl1	2768.9
satdly	0	rfp1	2750.6
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	148
		th	1
		ai	ph

F2 (ppm)



F1 (ppm)

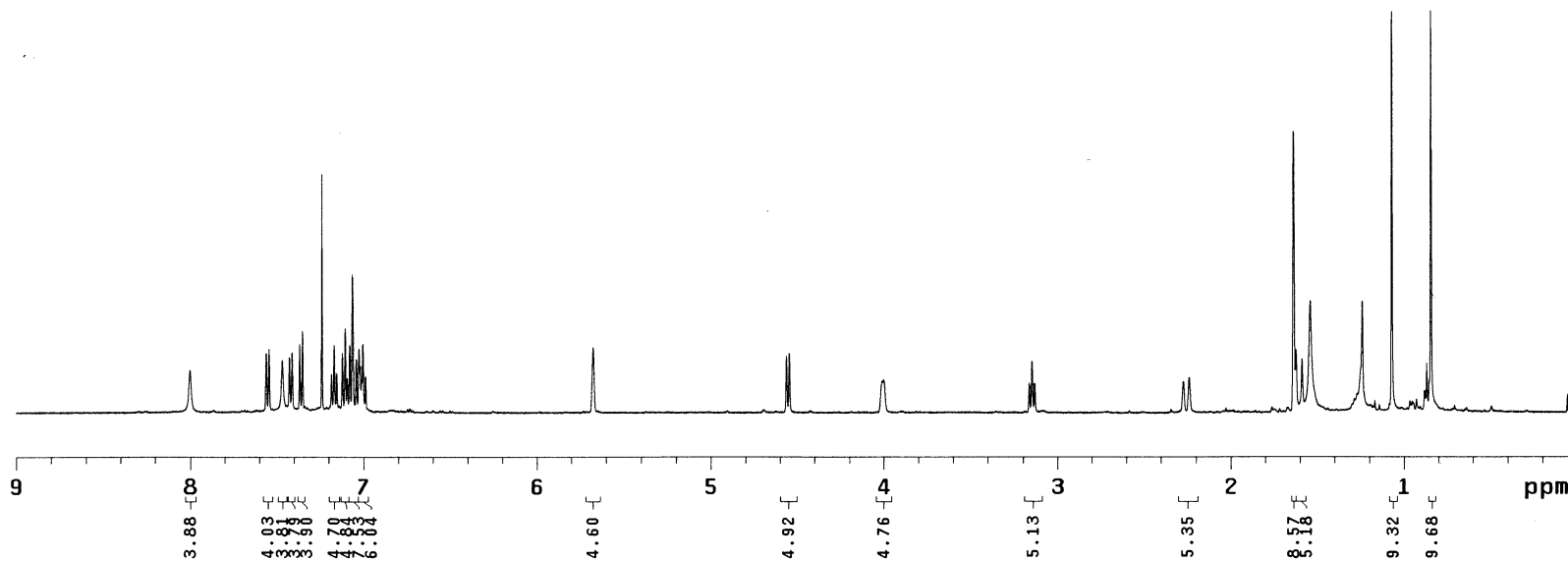
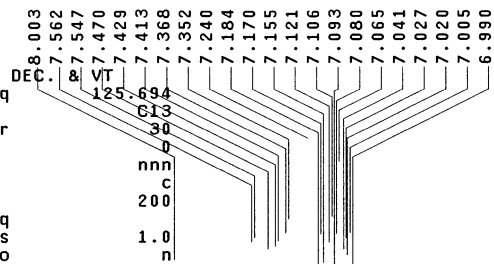
Fig S44. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of compound 1a.

NSD-10-024

exp50 s2pul

```

SAMPLE
date Jun 9 2014 dfrq
solvent cdc13 dn
file exp dpwr
ACQUISITION dof
sfrq 499.833 dm
tn H1 dmm
at 3.000 dmf
np 48000 dseq
sw 8000.0 dres
fb not used homo
bs 4
tpwr 61 wtfile
pw 4.8 proc
d1 1.000 fn
tof 499.7 math
nt 4
ct 4 werr
alock y wexp
gain not used wbs
FLAGS wnt
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 4498.3
vs 55
sc 0
wc 210
hzmm 21.42
is 33.57
rfl 4636.2
rfp 3618.8
th 4
ins 100.000
nm cdc ph
    
```



NSD-10-024

exp51 s2pu1

SAMPLE  
 date Jun 9 2014  
 solvent cdc13  
 file exp  
 ACQUISITION  
 sfrq 125.696  
 tn C13  
 at 1.000  
 np 60332  
 sw 30165.9  
 fb not used  
 bs 4  
 tpwr 60  
 pw 4.8  
 d1 1.000  
 tof 1883.7  
 nt 6000  
 ct 6000  
 alock y  
 gain not used  
 FLAGS  
 il n  
 in n  
 dp y  
 hs nn  
 DISPLAY  
 sp -0.2  
 wp 20108.9  
 vs 200  
 sc 0  
 wc 210  
 hzmm 95.76  
 is 33.57  
 rfl 10967.5  
 rfp 9677.5  
 th 6  
 ins 100.000  
 nm cdc ph

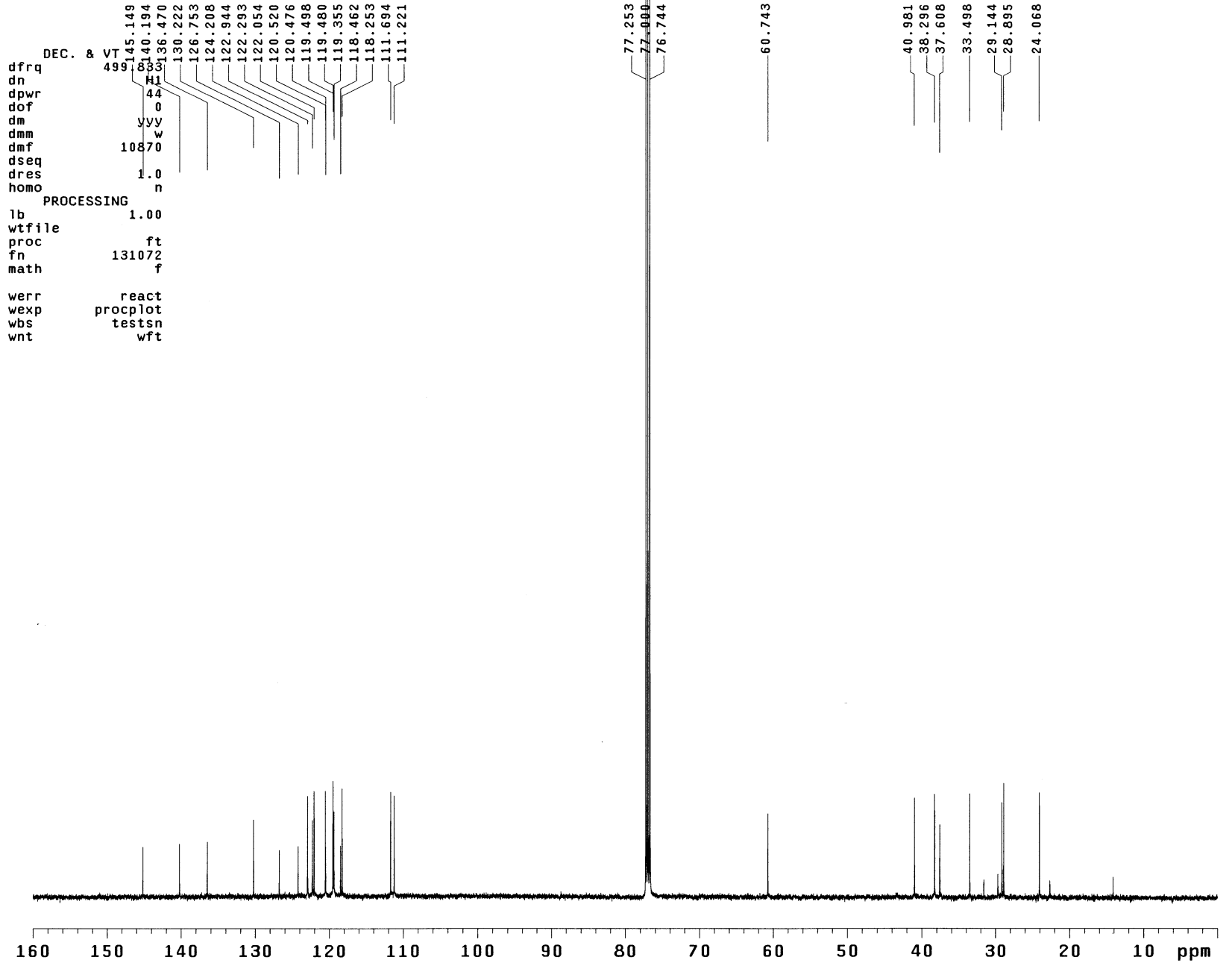
Fig S45. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) of compound 1a.

Fig S46. DEPT of compound 1a.

NSD-10-024

exp52 DEPT

SAMPLE		DEPT	ACQUISITION ARRAYS
date	Jun 9 2014	j1xh 140.0	array mult
solvent	cdc13	mult arrayed	arraydim 3
sample	undefined	SPECIAL	
ACQUISITION		temp not used	i mult
sw	30165.9	gain 34	1 0.5
at	1.000	spin 0	2 1
np	60332	PROCESSING	3 1.5
bs	4	lb 1.00	
ss	-4	fn 131072	
d1	1.000	SPECTRUM	
nt	3000	wp 20108.9	
ct	3000	sp -0.2	
TRANSMITTER		rp -120.4	
tn	C13	lp 227.9	
tof	1883.7	ai cdc ph	
tpwr	60	REFERENCE	
pw	10.400	rfl 1289.9	
DECOUPLER		rfp 0	
dn	H1	PLOT	
dof	0	wc 210	
dpwr	44	sc 0	
dm	nny	vs 800	
dmm	ccw	hzmm 95.76	
dmf	10870	th 7	
pp1v1	61		
pp	14.600		

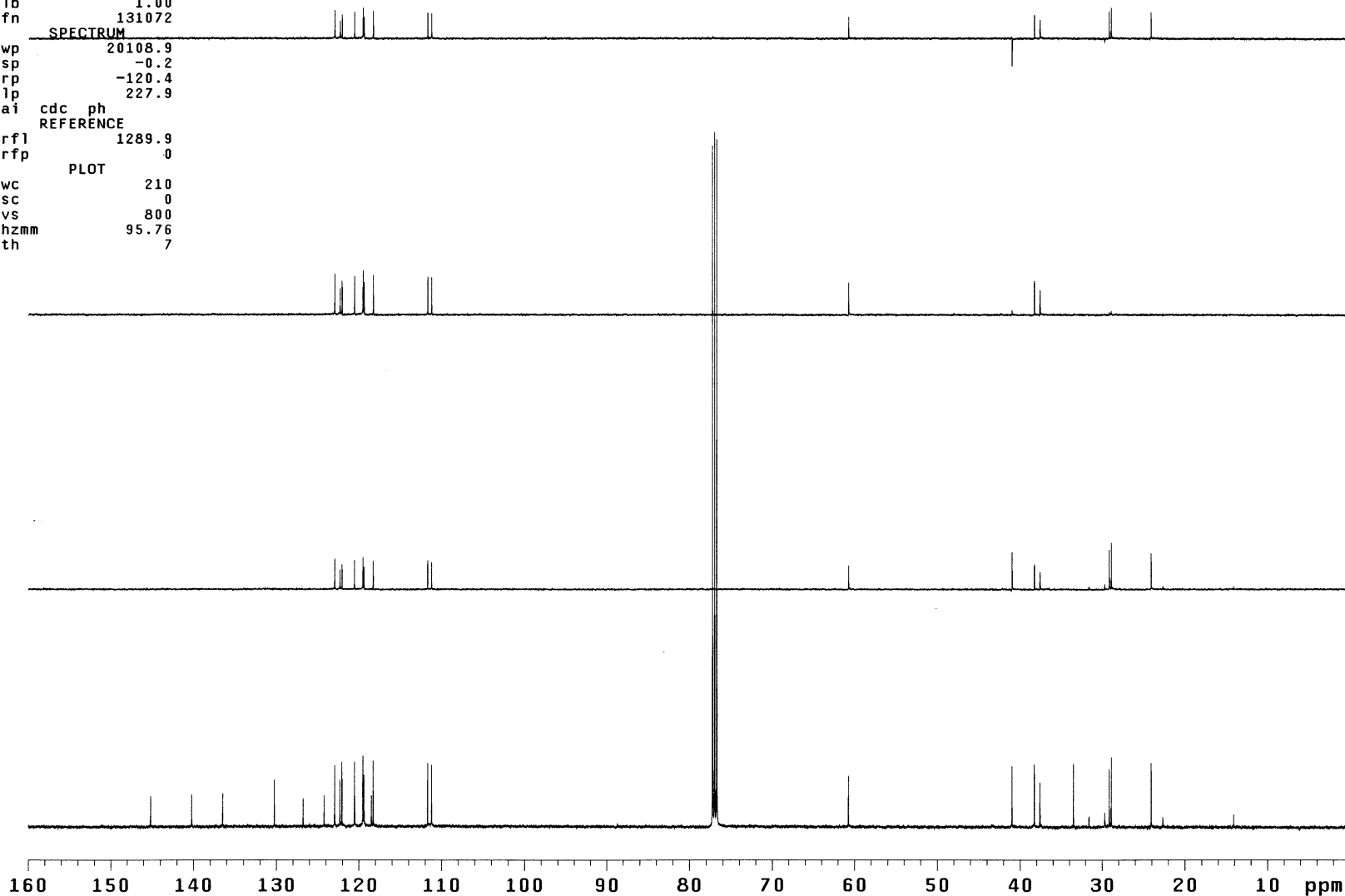


Fig S47. HSQC of compound 1a.

NSD-10-024

exp55 gHSQC

SAMPLE		FLAGS		ACQUISITION		ARRAYS	
date	Jun 9 2014	hs	n	array	phase		
solvent	cdcl3	sspu1	y	arraydim	256		
sample	undefined	PFGflg	y				
	ACQUISITION	hsglv1	1009	1	phase		
sw	4490.3	SPECIAL	1	1	1		
at	0.228	temp	not used	2	2		
np	2048	gain	54				
fb	not used	spin	0				
ss	32	GRADIENTS					
d1	1.000	gzlv11	1009				
nt	8	gt1	0.002000				
	2D ACQUISITION	gzlv13	508				
sw1	21367.5	gt3	0.001000				
ni	128	gstab	0.000500				
phase	arrayed	F2 PROCESSING					
	TRANSMITTER	gf	0.105				
tn	H1	gfs	not used				
sfrq	499.833	fn	2048				
tof	-250.0	F1 PROCESSING					
tpwr	61	gf1	0.006				
pw	12.900	gfs1	not used				
	DECOUPLER	proc1	ip				
dn	C13	fn1	2048				
dof	-2515.1	DISPLAY					
dm	nny	sp	326.2				
dmm	ccp	wp	3608.9				
dmf	32258	sp1	2797.6				
dpwr	42	wp1	12979.1				
pxlv1	59	rfl	2848.5				
pxw	12.200	rfp	2837.0				
	HSQC	rfl1	16723.3				
j1xh	140.0	rfpl	15451.9				
nullflg	y	PLOT					
mult	2	wc	150.0				
		sc	6.2				
		wc2	116.2				
		sc2	0				
		vs	55				
		th	6				
		ai	cdc ph				

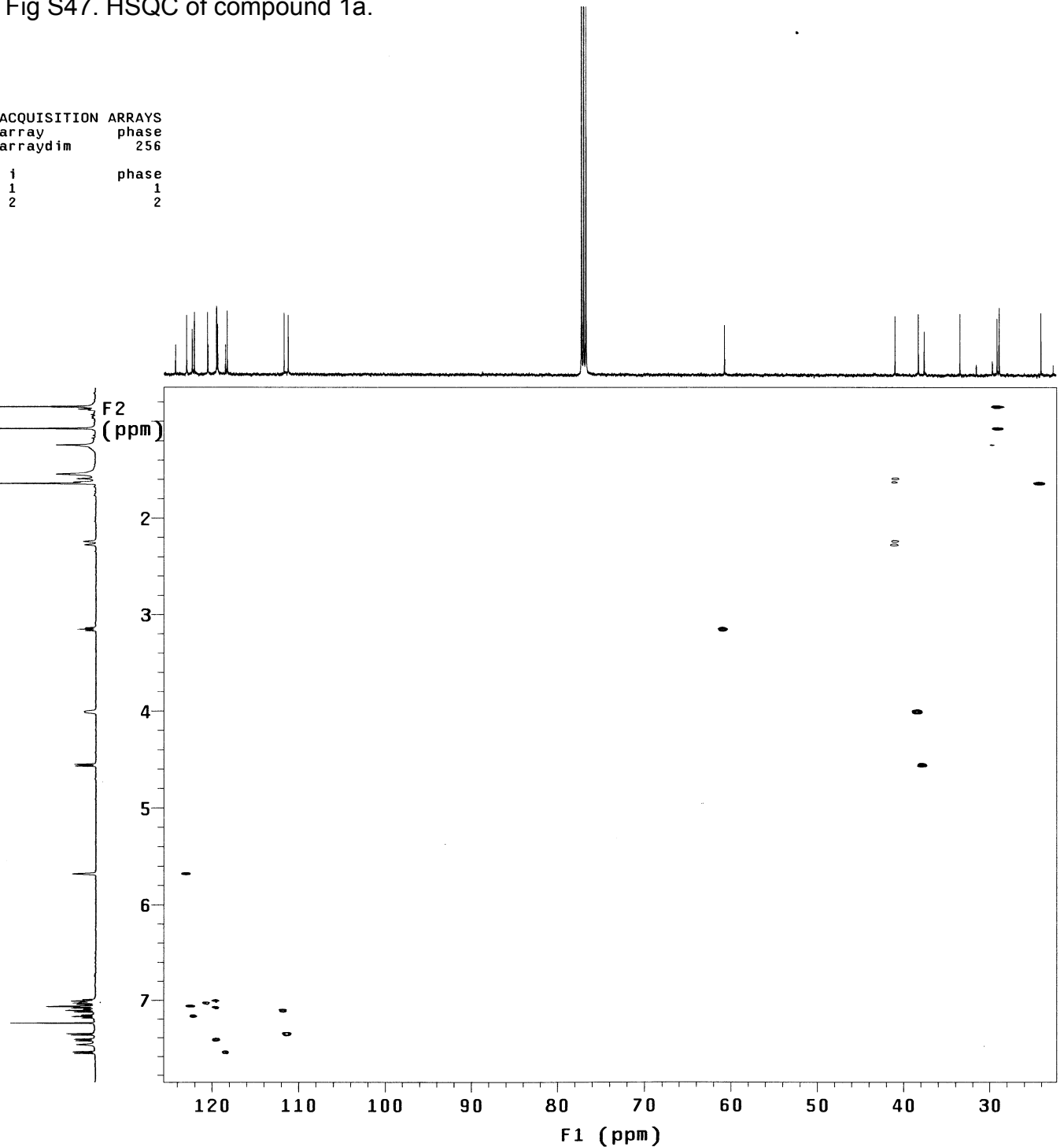


Fig S48. COSY of compound 1a.

NSD-10-024  
exp53 gCOSY

SAMPLE		FLAGS	
date	Jun 9 2014	hs	nn
solvent	cdc13	sspul	n
sample	undefined	hsglv1	1009
ACQUISITION		SPECIAL	
sw	4490.3	temp	not used
at	0.228	gain	34
np	2048	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.114
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4490.3	sb1	-0.029
ni	128	sbs1	not used
TRANSMITTER		PROC1	
tn	H1	fn1	2048
sfrq	499.833	DISPLAY	
tof	-250.0	sp	223.4
tpwr	61	wp	3841.4
pw	12.900	sp1	215.0
		wp1	3850.1
GRADIENTS		rfl	2850.4
gzlv11	1009	rfp	2837.0
gt1	0.001000	rf11	2850.0
gstab	0.000500	rfp1	2837.0
DECOUPLER		PLOT	
dn	C13	wc	155.0
dm	nnn	sc	10.0
		wc2	155.0
		sc2	0
		vs	55
		th	7
		ai	cdc av

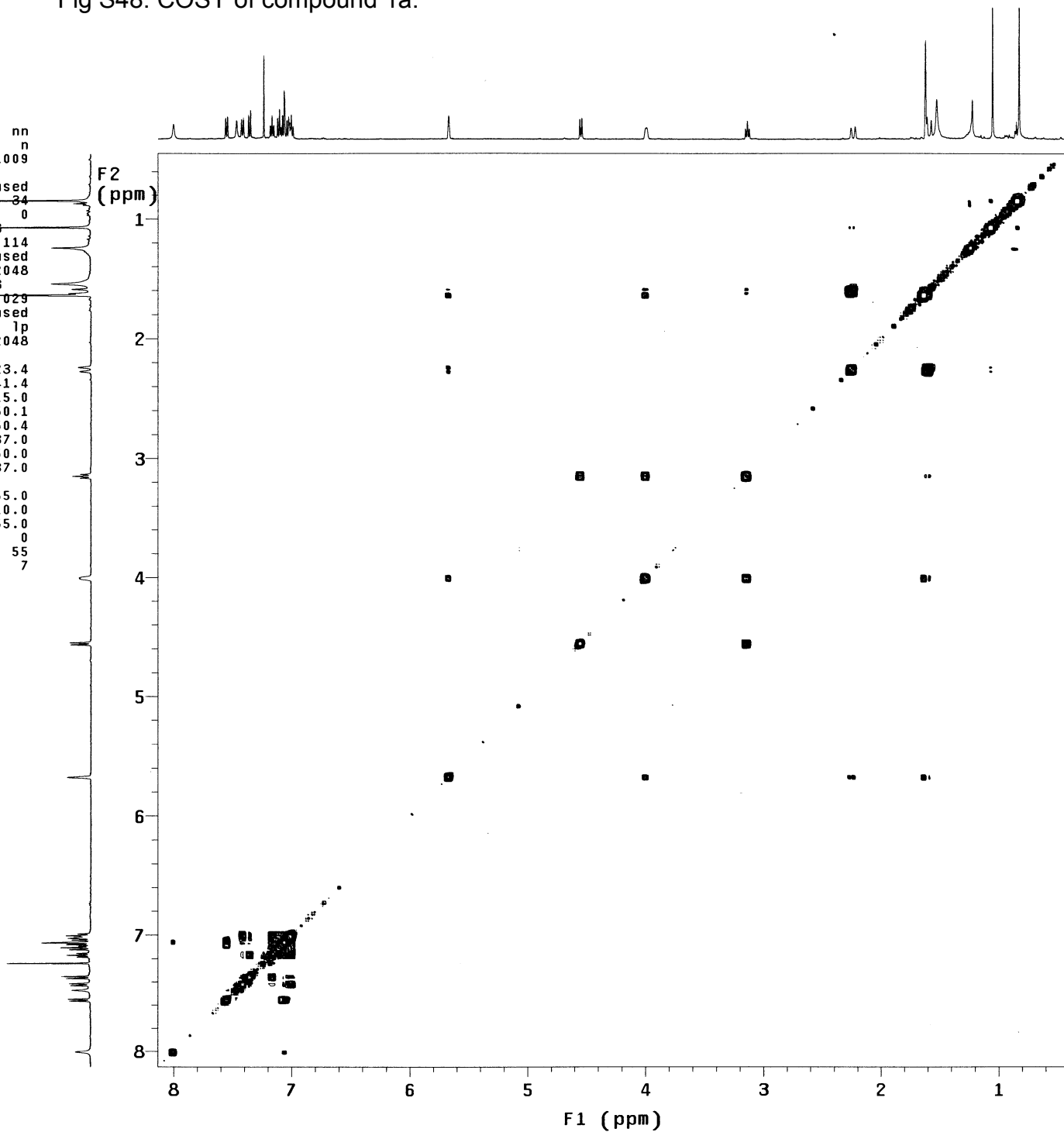




Fig S49. NOESY of compound 1a.

NSD-10-024

exp54 NOESY

SAMPLE		FLAGS	
date	Jun 9 2014	hs	n
solvent	cdcl3	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglvi	1009
sw	4490.3	SPECIAL	
at	0.228	temp	not used
np	2048	gain	34
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.105
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	4490.3	F1 PROCESSING	
ni	200	gf1	0.041
TRANSMITTER		gfs1	not used
tn	H1	procl	lp
sfrq	499.833	fn1	2048
tof	-250.0	DISPLAY	
tpwr	61	sp	131.8
pw	12.900	wp	4091.3
NOESY		sp1	132.0
mix	0.600	wp1	4086.9
PRESATURATION		rf1	2850.0
satmode	nnnn	rfl	2837.0
satpwr	0	rfl1	2849.8
satdly	0	rfl1	2837.0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	55
		th	1
		ai	ph

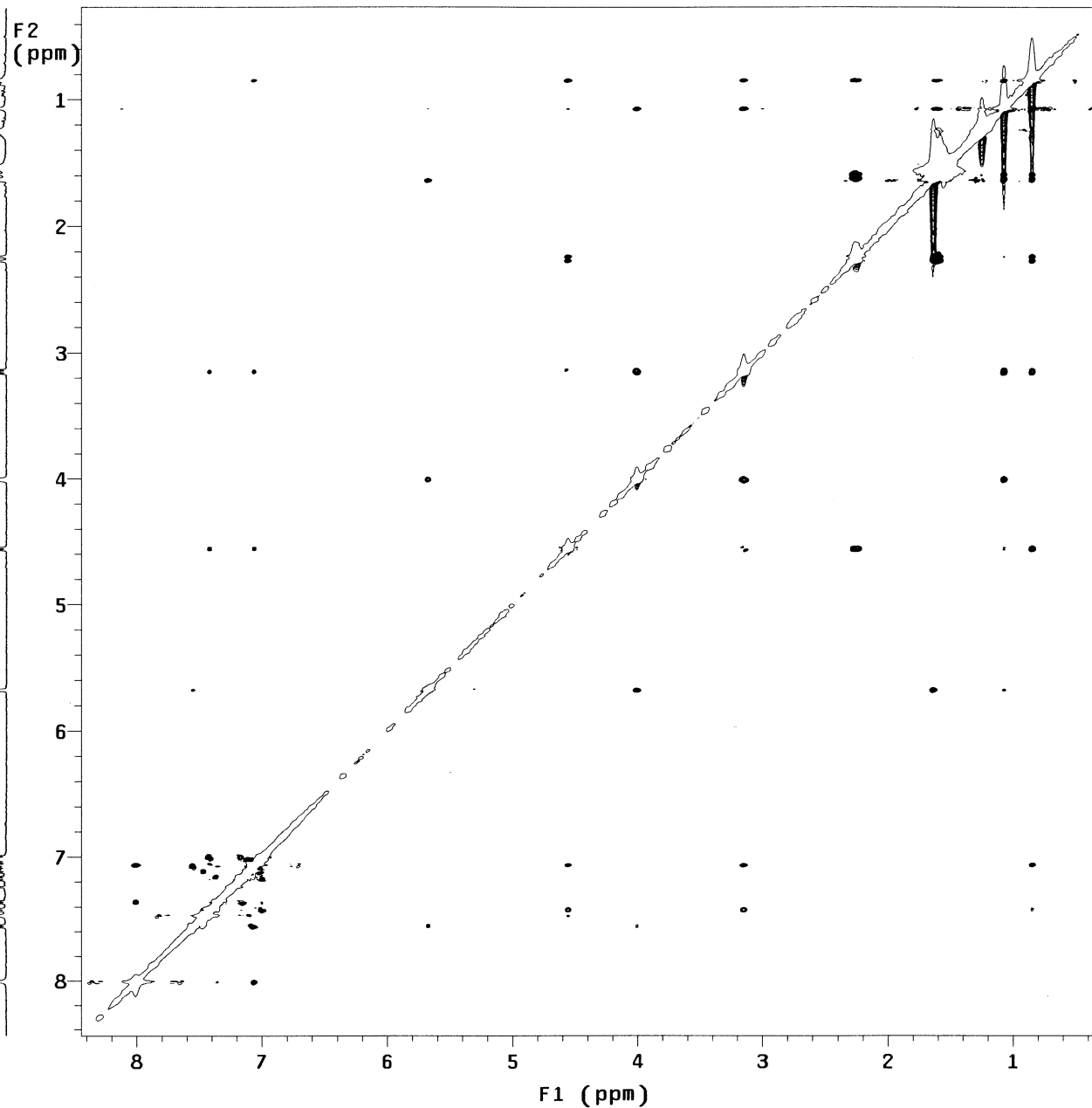


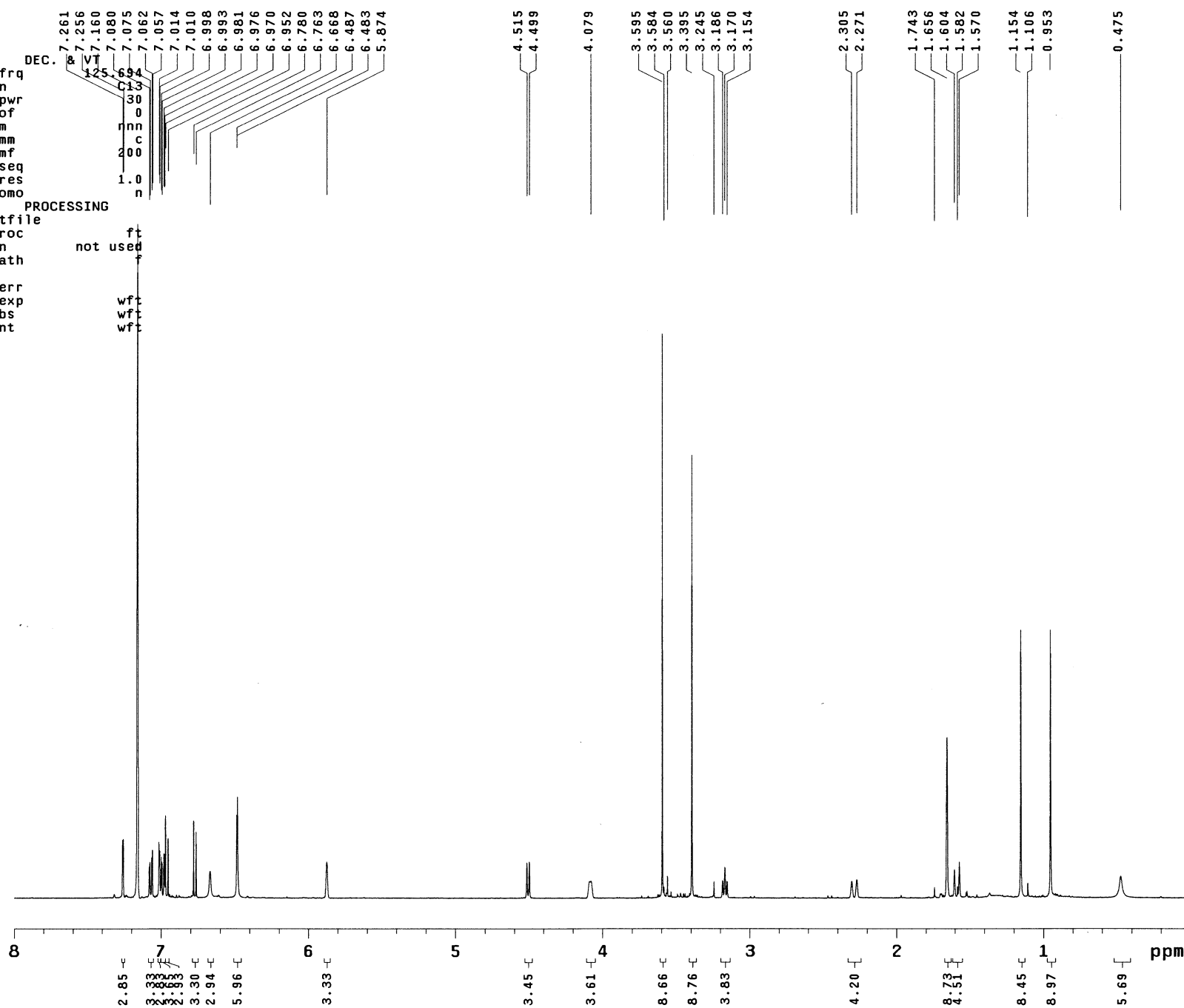
Fig S50. 1H NMR (C6D6, 500 MHz) of compound 1b.

NSD-10-018

exp50 s2pu1

```

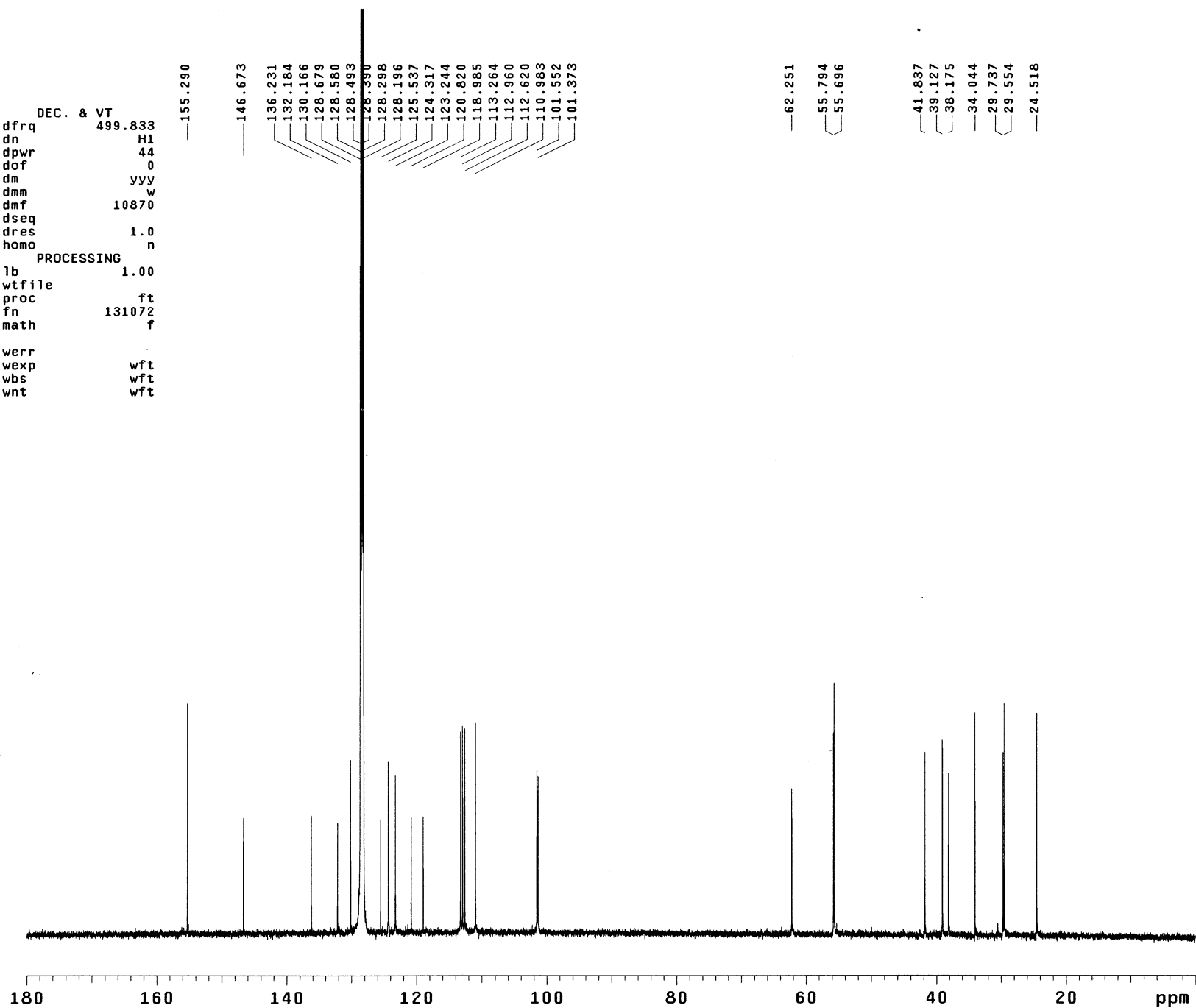
SAMPLE
date May 27 2014 dfrq
solvent Benzene dn
file exp dpwr
ACQUISITION dof
sfrq 499.833 dm
tn H1 dmm
at 3.000 dmf
np 48000 dseq
sw 8000.0 dres
bs not used homo
tpwr 61 wtfile
pw 4.8 proc
d1 1.000 fn
tof 499.7 math
nt 4
ct 4 werr
alock y wexp
gain not used wbs
FLAGS wnt
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 3998.5
vs 120
sc 0
wc 210
hzmm 19.04
is 33.57
rfl 4564.7
rfp 3578.8
th 2
ins 100.000
nm cdc ph
    
```



NSD-10-018

exp51 s2pu1

SAMPLE		DEC. & VT	
date	May 26 2014	dfrq	499.833
solvent	Benzene	dn	H1
file	exp	dpwr	44
ACQUISITION		dof	0
sfrq	125.696	dm	yyy
tn	C13	dmm	w
at	1.000	dmf	10870
np	60332	dseq	
sw	30165.9	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
tpwr	60	lb	1.00
pw	4.8	wtfile	
d1	1.000	proc	ft
tof	1883.7	fn	131072
nt	6000	math	f
ct	6000		
alock	y	werr	
gain	not used	wexp	wft
FLAGS		wbs	wft
		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-0.2		
wp	22622.6		
vs	2500		
sc	0		
wc	210		
hzmm	107.73		
is	33.57		
rfl	17334.7		
rfp	16136.4		
th	8		
ins	100.000		
nm	cdc ph		

Fig S51. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz) of compound 1b.

NSD-10-018

exp52 DEPT

SAMPLE	DEPT	ACQUISITION ARRAYS
date May 26 2014	j1xh 140.0	array mult
solvent Benzene	mult arrayed	arraydim 3
sample undefined	SPECIAL	
ACQUISITION	temp not used	i mult
sw 30165.9	gain 50	1 0.5
at 1.000	spin 0	2 1
np 60332	PROCESSING	3 1.5
bs 4	lb 1.00	
ss -4	fn 131072	
d1 1.000	SPECTRUM	
nt 3000	wp 22622.6	
ct 3000	sp -0.2	
TRANSMITTER	rp -104.3	
tn C13	lp 173.2	
tof 1883.7	ai cdc ph	
tpwr 60	REFERENCE	
pw 10.400	rfl 1198.4	
DECOUPLER	rfp 0	
dn H1	PLOT	
dof 0	wc 210	
dpwr 44	sc 0	
dm nny	vs 850	
dmm ccw	hzmm 107.73	
dmf 10870	th 7	
pp1v1 61		
pp 14.600		

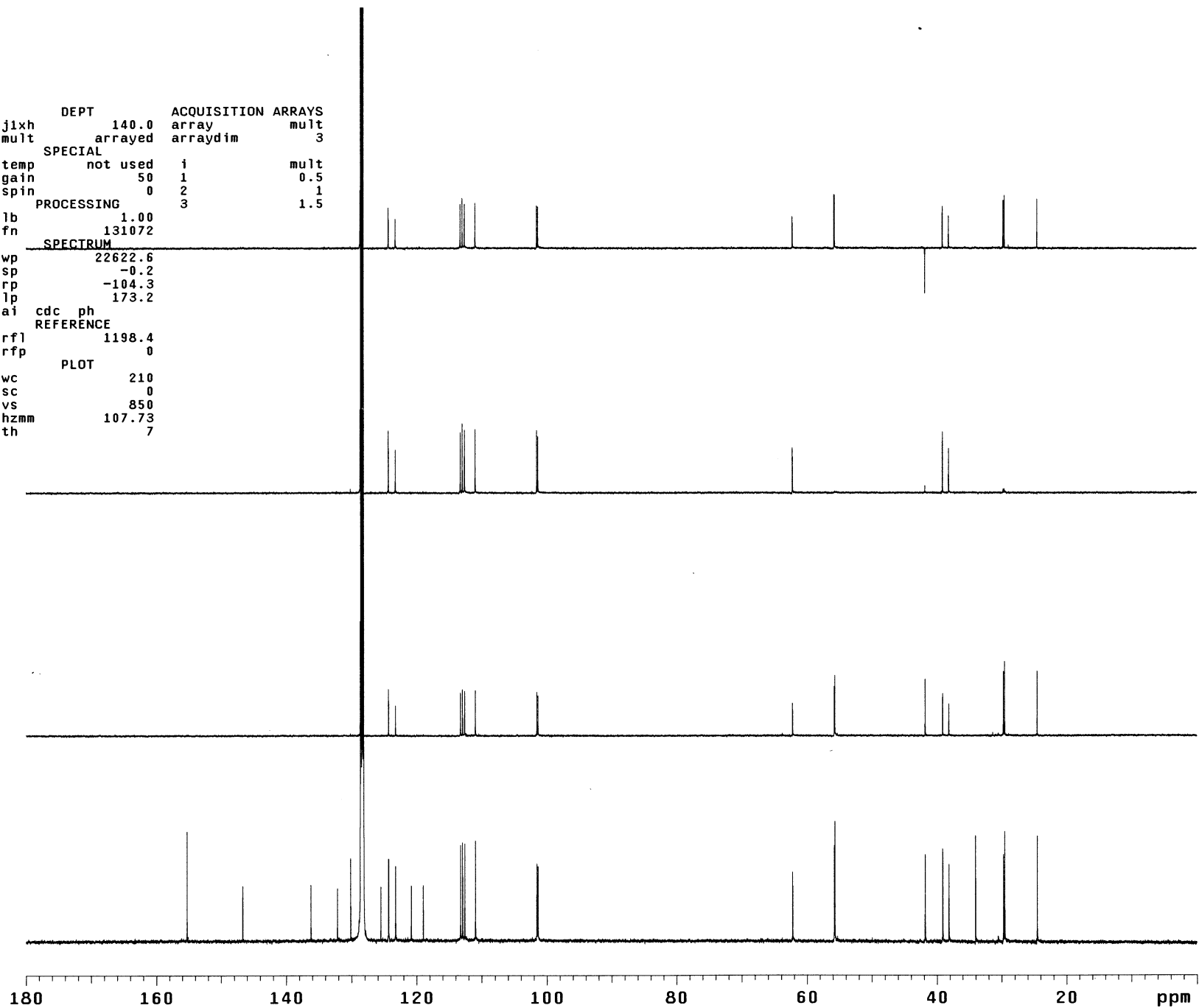


Fig S52. DEPT of compound 1b.

Fig S53. HMQC of compound 1b.

NSD-10-018

exp55 gHMQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date May 27 2014	hs	n	phase
solvent Benzene	sspul	y	arraydim 256
sample undefined	PFGflg	y	
ACQUISITION	hsglv1	1009	phase
sw 4001.6	SPECIAL	1	1
at 0.128	temp	not used	2
np 1024	gain	50	
fb not used	spin	0	
ss 32	GRADIENTS		
d1 1.000	gzlv11	1009	
nt 8	gt1	0.001000	
2D ACQUISITION	gzlv13	508	
sw1 21367.5	gt3	0.001000	
ni 128	gstab	0.000500	
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf	0.059	
tn H1	gfs	not used	
sfrq 499.832	fn	1024	
tof -500.0	F1 PROCESSING		
tpwr 61	gf1	0.006	
pw 12.900	gfs1	not used	
DECOUPLER	proc1	1	
dn C13	fn1	2048	
dof -2515.1	DISPLAY		
dm nny	sp	372.7	
dmm ccp	wp	3360.7	
dmf 32258	sp1	2669.7	
dpwr 42	wp1	13918.1	
pxlv1 59	rfl	2922.8	
pxw 12.200	rfp	2936.0	
HMQC	rfl1	16836.0	
j1xh 140.0	rfl1	15624.5	
nullfig y	PLOT		
	wc	150.0	
	sc	6.2	
	wc2	116.2	
	sc2	0	
	vs	86	
	th	5	
	ai cdc ph		

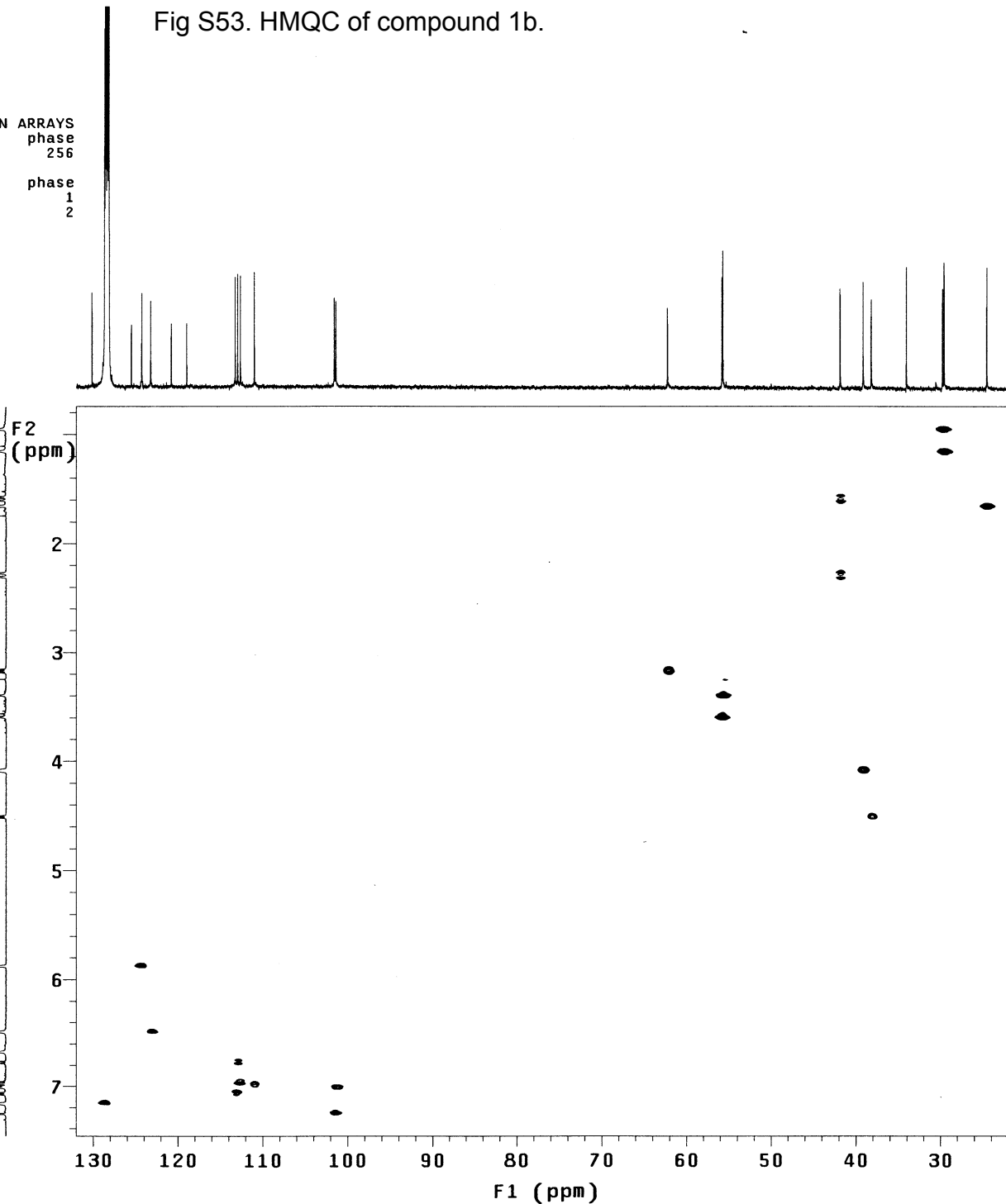


Fig S54. COSY of compound 1b.

NSD-10-018

exp53 gCOSY

SAMPLE		FLAGS	nn
date	May 27 2014	hs	n
solvent	Benzene	sspul	1009
sample	undefined	hsglv1	
ACQUISITION		SPECIAL	
sw	4001.6	temp	not used
at	0.128	gain	30
np	1024	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.064
d1	1.000	sbs	not used
nt	8	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	4001.6	sb1	-0.032
ni	128	sbs1	not used
TRANSMITTER		proc1	1p
tn	H1	fn1	1024
sfrq	499.832	DISPLAY	
tof	-500.0	sp	435.3
tpwr	61	wp	3235.7
pw	12.900	sp1	428.2
GRADIENTS		wp1	3235.7
gzlv11	1009	rfl	2922.8
gt1	0.001000	rfp	2936.0
gstab	0.000500	rfl1	2922.0
DECOUPLER		rfl1	2936.0
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	86
		th	6
		ai	cdc av

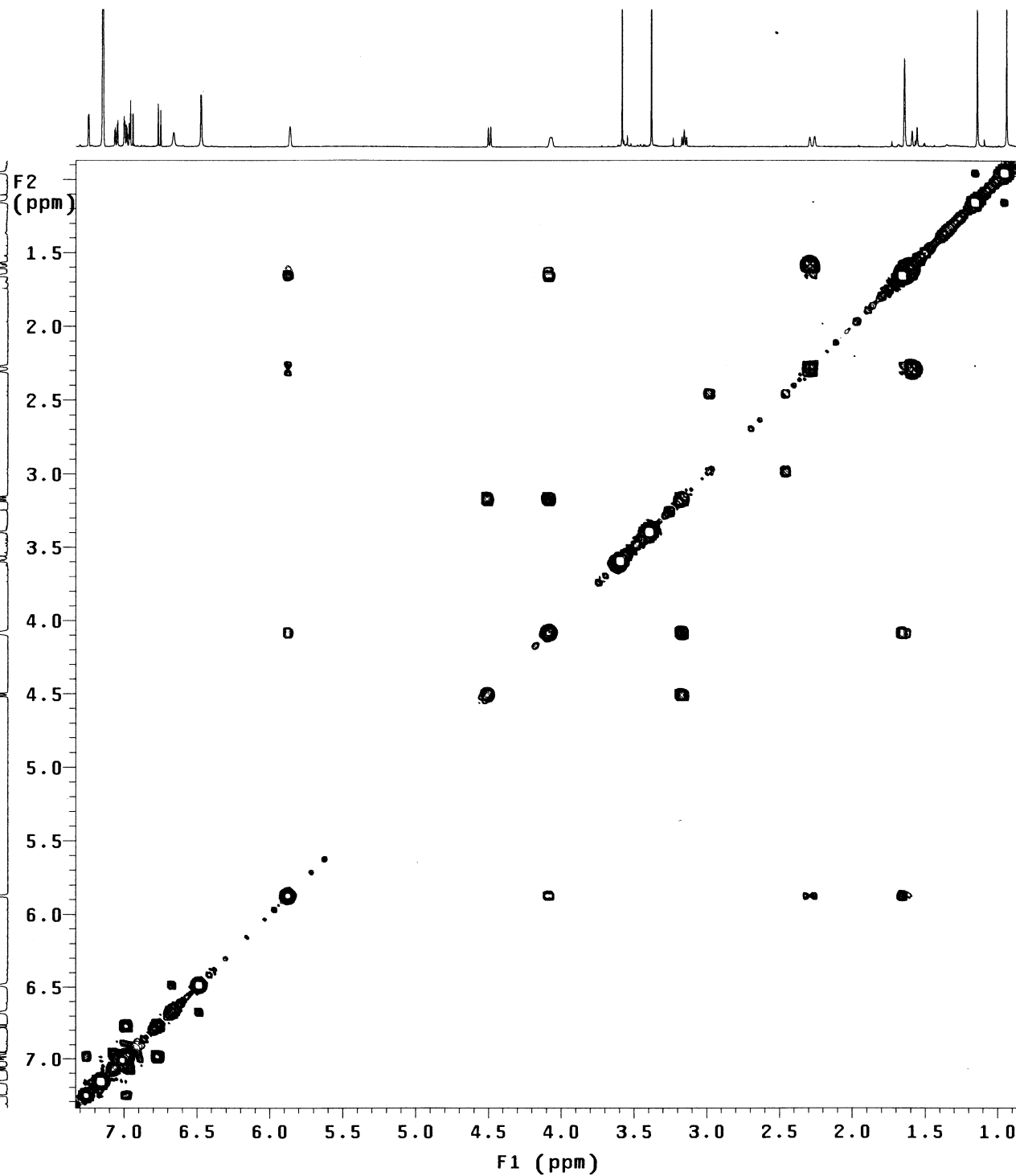


Fig S55. NOESY of compound 1b.

NSD-10-018

exp54 NOESY

SAMPLE		FLAGS	
date	May 27 2014	hs	n
solvent	Benzene	sspul	y
sample	undefined	PFGflg	y
ACQUISITION		hsglv1	1009
sw	4001.6	SPECIAL	
at	0.128	temp	not used
np	1024	gain	30
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.059
nt	16	gfs	not used
2D ACQUISITION		fn	1024
sw1	4001.6	F1 PROCESSING	
ni	200	gf1	0.046
TRANSMITTER		gfs1	not used
tn	H1	proc1	1p
sfrq	499.832	fn1	1024
tof	-500.0	DISPLAY	
tpwr	61	sp	154.2
pw	12.900	wp	3595.2
NOESY		sp1	162.2
mix	0.600	wp1	3595.2
PRESATURATION		rf1	2922.4
satmode	nnnn	rfp	2936.0
satpwr	0	rf11	2922.3
satdly	0	rfp1	2936.0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	86
		th	1
		ai	ph

F2 (ppm)

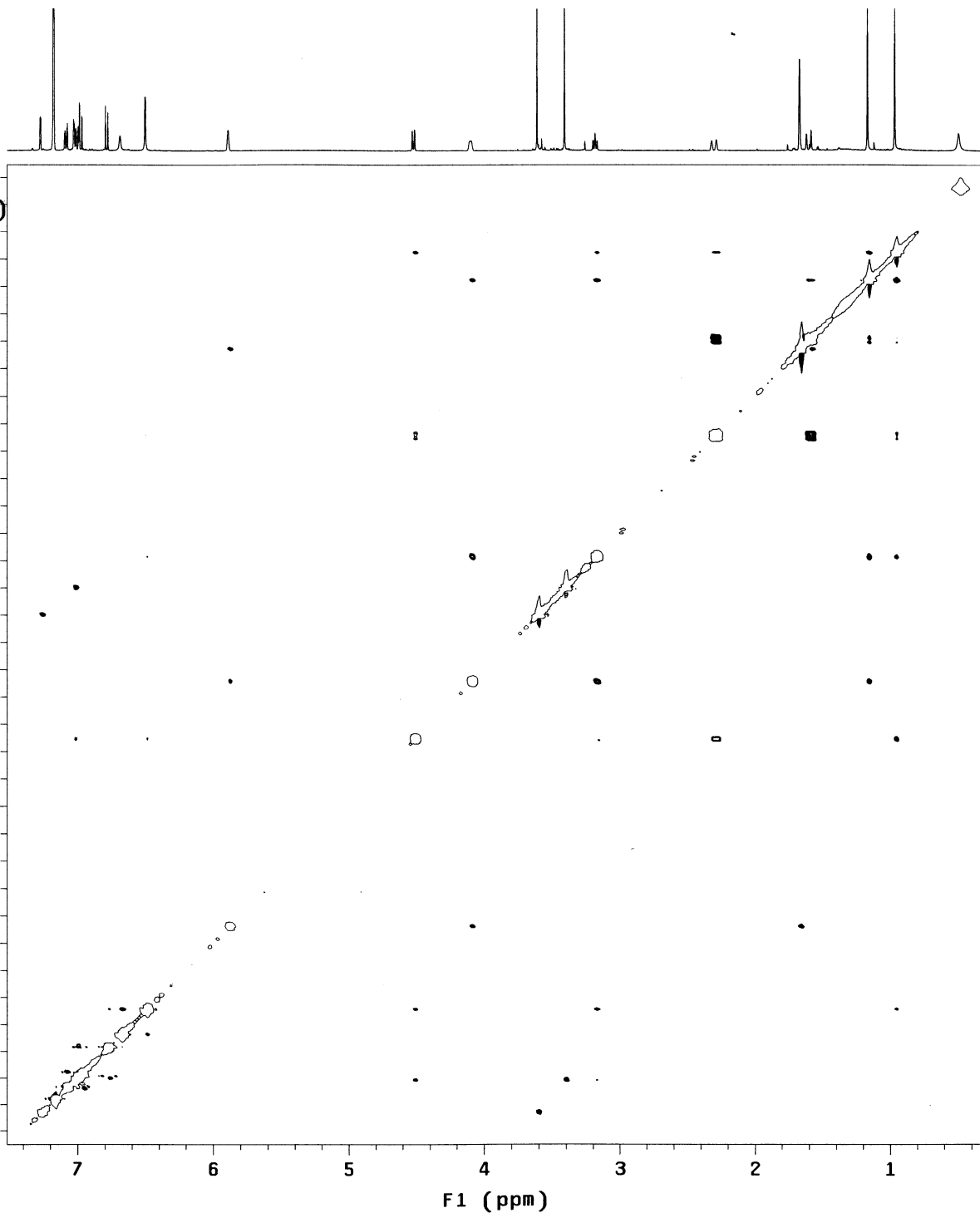
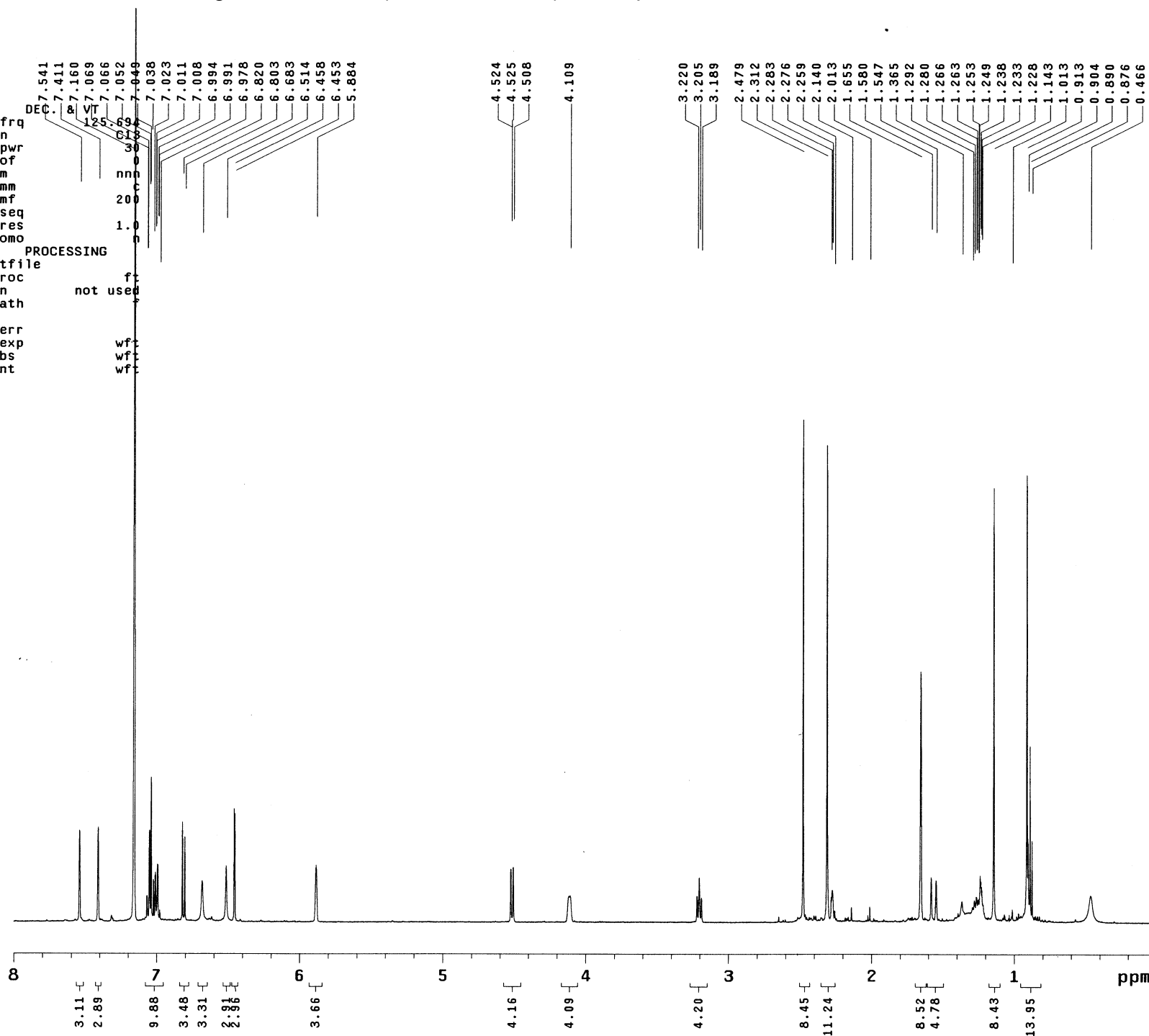


Fig S56. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) of compound 1c.

```

NSD-10-026
exp40 s2pu1
SAMPLE
date Jun 13 2014 dfrq
solvent Benzene dn
file exp dpwr
ACQUISITION dof
sfrq 499.833 dm
tn H1 dmm
at 3.000 dmf
np 48000 dseq
sw 8000.0 dres
fb not used homo
bs 4
tpwr 61 wtfile
pw 4.8 proc
d1 1.000 fn
tof 499.7 math
nt 4
ct 4 werr
alock y wexp
gain not used wbs
FLAGS wnt
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 3998.5
vs 200
sc 0
wc 210
hzmm 19.04
is 33.57
rfl 4564.9
rfp 3578.8
th 3
ins 100.000
nm cdc ph
    
```





NSD-10-026  
exp57 s2pu1

```

SAMPLE
date Jun 13 2014 dfrq
solvent Benzene dn
file /export/home/~ dpwr
vnmr1/vnmrsys/data~ dof
/NSD/NSD-10-026/ne~ dm
w/C13.fid dmm
ACQUISITION dmf
sfrq 125.696 dseq
tn C13 dres
at 1.000 homo
np 60332
sw 30165.9 lb
fb not used wtfile
bs 4 proc
tpwr 58 fn
pw 4.8 math
d1 1.000
tof 1883.7 werr
nt 8000 wexp
ct 8000 wbs
alock y wnt
gain not used

FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -0.2
wp 20108.9
vs 800
sc 0
wc 210
hzmm 95.76
is 33.57
rfl 17334.3
rfp 16136.4
th 22
ins 100.000
nm cdc ph

```

```

DEC.
146.112
139.568
135.521
130.075
129.251
128.928
128.683
128.584
128.496
128.390
128.302
128.196
125.555
124.493
124.380
122.647
122.633
120.314
119.436
119.135
118.919
112.107
111.635

```

```

PROCESSING
lb 1.00
ft
131072
f
wft
wft
wft

```

— 62.288

41.790  
39.138  
38.069  
34.047  
29.854  
29.532  
24.529  
22.203  
22.057

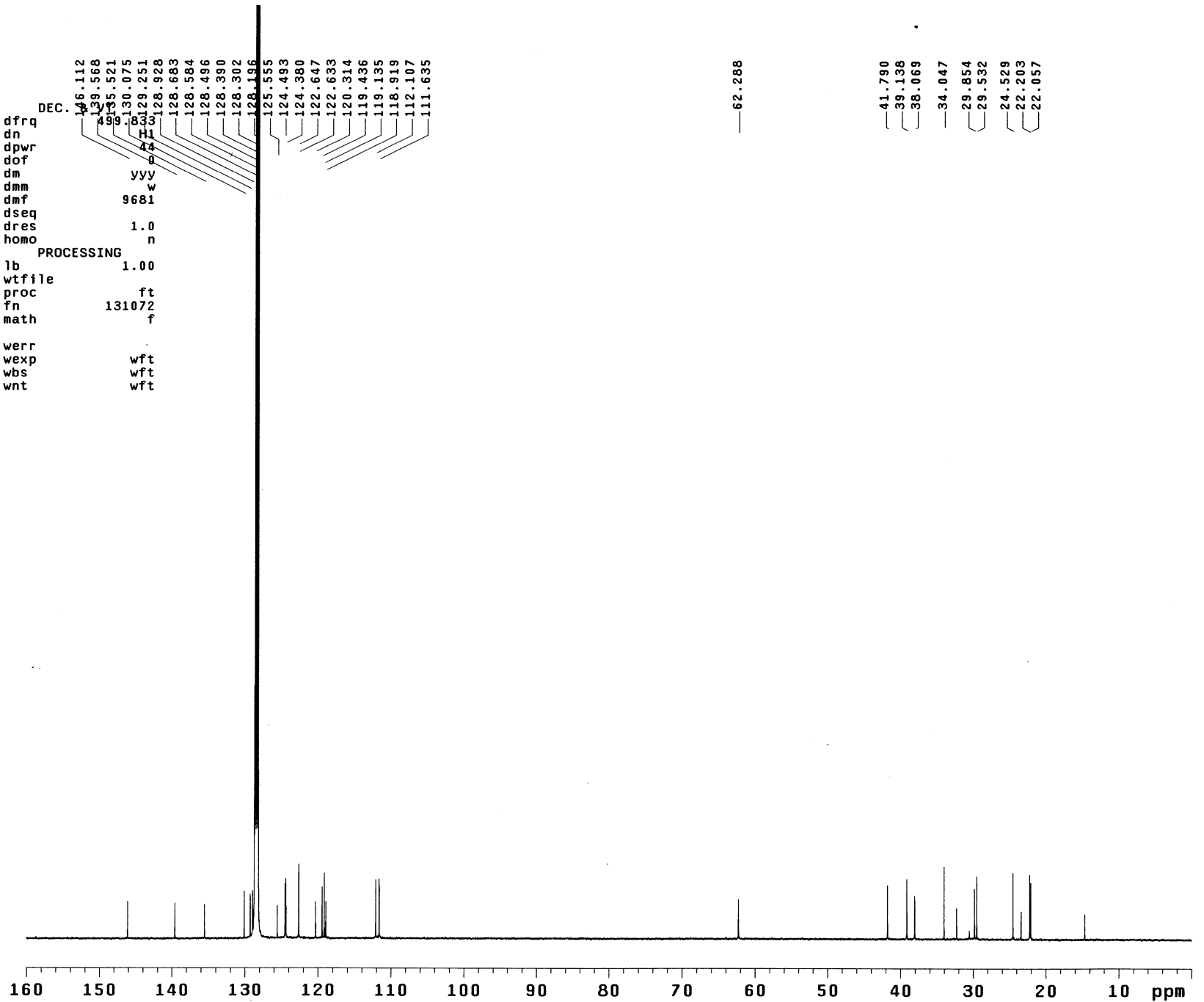


Fig S57. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz) of compound 1c.

Fig S58. DEPT of compound 1c.

NSD-10-026

exp42 DEPT

SAMPLE		DEPT	ACQUISITION	ARRAYS
date	Jun 13 2014	j1xh 140.0	array	mult
solvent	Benzene	mult arrayed	arraydim	3
sample	undefined	SPECIAL		
ACQUISITION		temp not used	i	mult
sw	30165.9	gain 30	1	0.5
at	1.000	spin 0	2	1
np	60332	PROCESSING	3	1.5
bs	4	lb 1.00		
ss	-4	fn 131072		
d1	1.000	SPECTRUM		
nt	4000	wp 20108.9		
ct	4000	sp -0.2		
TRANSMITTER		rp -145.5		
tn	C13	lp 232.8		
tof	1883.7	ai cdc ph		
tpwr	58	REFERENCE		
pw	13.800	rfl 1197.9		
DECOUPLER		rfp 0		
dn	H1	PLOT		
dof	0	wc 210		
dpwr	44	sc 0		
dm	nny	vs 600		
dmm	ccw	hzmm 95.76		
dmf	9681	th 7		
pp1v1	61			
pp	14.800			

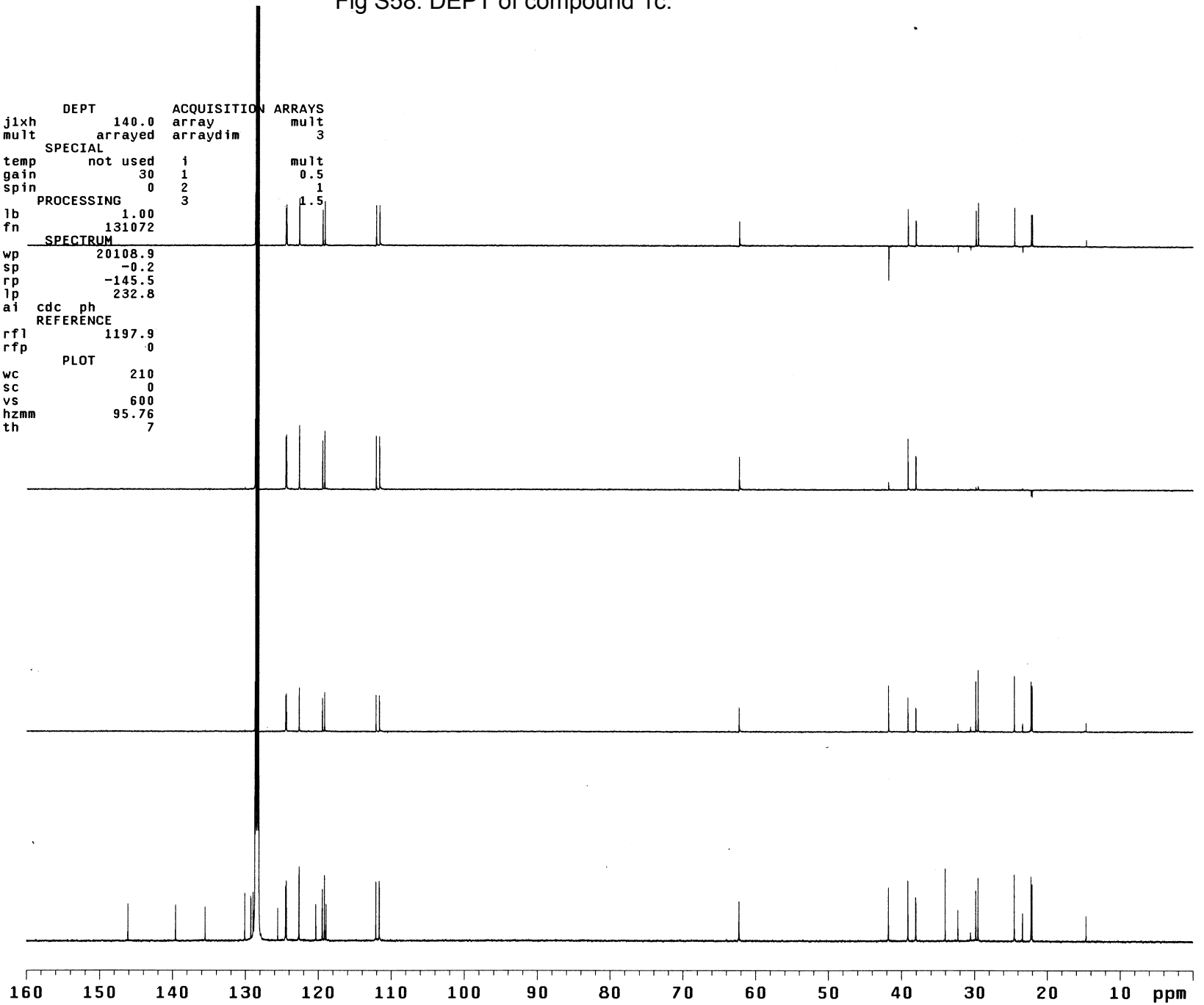
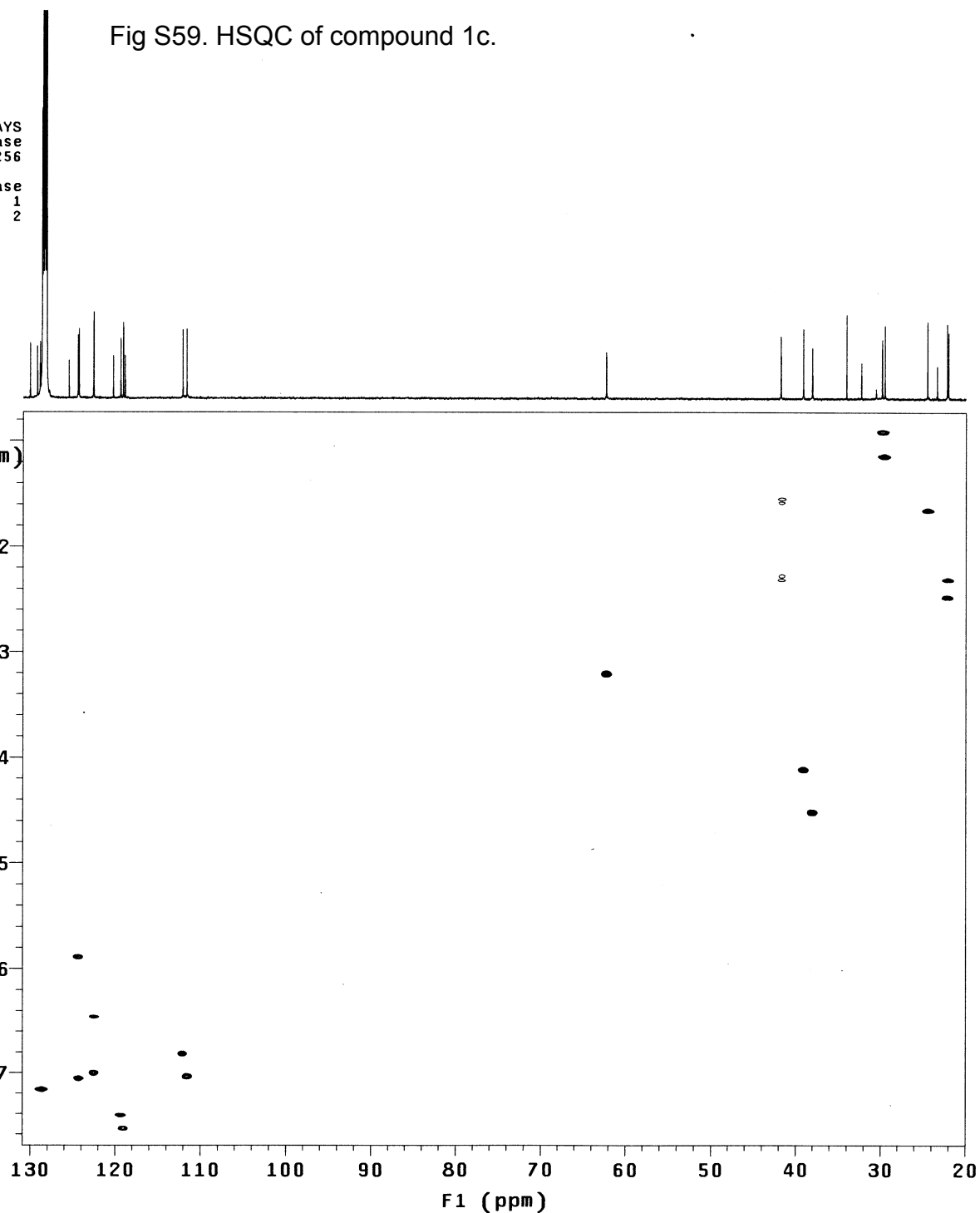


Fig S59. HSQC of compound 1c.

NSD-10-026

exp45 gHSQC

SAMPLE	FLAGS	ACQUISITION	ARRAYS
date Jun 13 2014	hs	n	phase
solvent Benzene	sspul	array	256
sample undefined	PFGflg	arraydim	
ACQUISITION	hsglv1	1009	phase
sw 4001.6	SPECIAL	i	1
at 0.128	temp	not used	2
np 1024	gain	50	
fb not used	spin	0	
ss 32	GRADIENTS		
d1 1.000	gzlv11	1009	
nt 8	gt1	0.002000	
2D ACQUISITION	gzlv13	507	
sw1 21367.5	gt3	0.001000	
ni 128	gstab	0.000500	
phase arrayed	F2 PROCESSING		
TRANSMITTER	gf	0.059	
tn H1	gfs	not used	
sfrq 499.832	fn	1024	
tof -500.0	F1 PROCESSING		
tpwr 61	gf1	0.006	
pw 13.900	gfs1	not used	
DECOUPLER	proc1	1p	
dn C13	fn1	2048	
dof -2515.1	DISPLAY		
dm nny	sp	366.0	
dmm ccp	wp	3485.8	
dmf 32258	sp1	2509.9	
dpwr 42	wp1	13939.0	
pwxlvl 60	rfl	2926.7	
pxw 10.700	rfl1	2941.0	
HSQC	rfl1	16836.7	
j1xh 140.0	rfpl	15632.4	
nullflg y	PLOT		
mult 2	wc	150.0	
	sc	6.2	
	wc2	116.2	
	sc2	0	
	vs	60	
	th	6	
	ai	cdc	ph

F2  
(ppm)

F1 (ppm)

Fig S60. COSY of compound 1c.

NSD-10-026

exp43 gCOSY

SAMPLE		FLAGS	nn
date	Jun 13 2014	hs	n
solvent	Benzene	sspul	1009
sample	undefined	hsglv	
ACQUISITION		SPECIAL	
sw	4001.6	temp	not used
at	0.128	gain	30
np	1024	spin	0
fb	not used	F2 PROCESSING	
ss	16	sb	-0.064
d1	1.000	sbs	not used
nt	8	fn	1024
2D ACQUISITION		F1 PROCESSING	
sw1	4001.6	sb1	-0.032
ni	128	sbs1	not used
TRANSMITTER		procl	lp
tn	H1	fn1	1024
sfrq	499.832	DISPLAY	
tof	-500.0	sp	139.8
tpwr	61	wp	3774.9
pw	13.900	sp1	140.5
GRADIENTS		wp1	3774.9
gzlv11	1009	rfl	2926.3
gt1	0.001000	rfl1	2941.0
gstab	0.000500	rfl1	2925.6
DECOUPLER		rfl1	2941.0
dn	C13	PLOT	
dm	nnn	wc	155.0
		sc	10.0
		wc2	155.0
		sc2	0
		vs	60
		th	6
		ai	cdc av

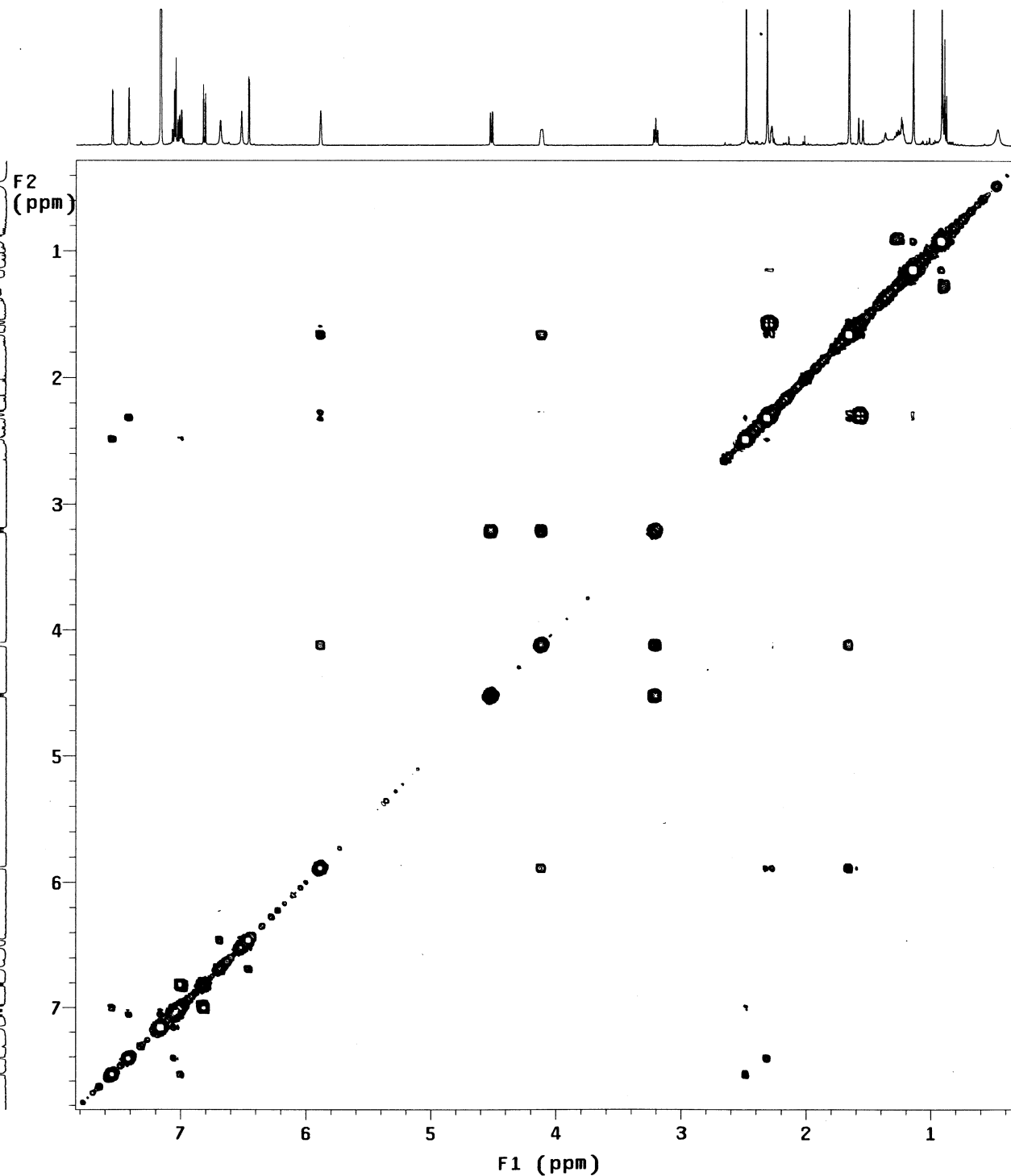


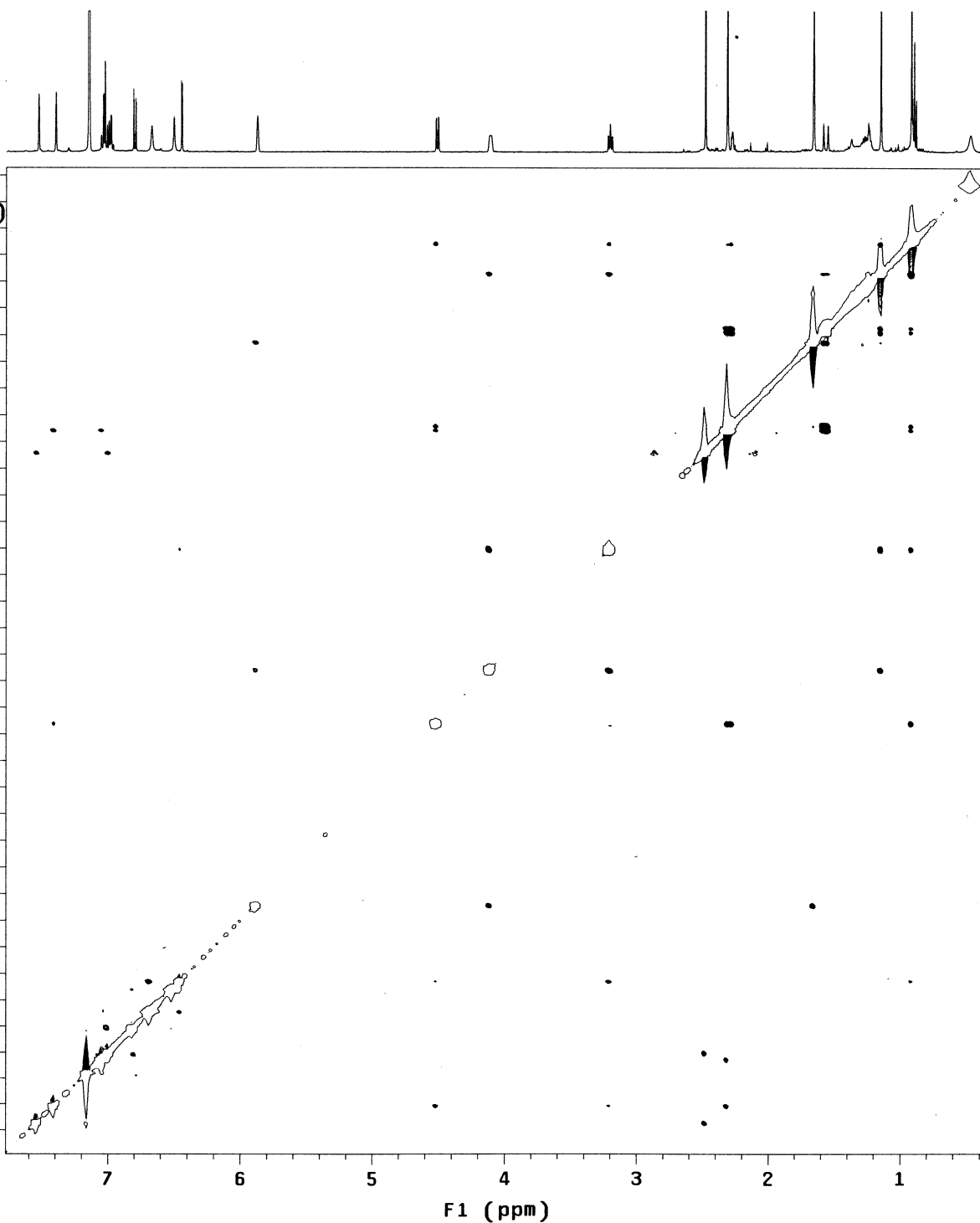
Fig S61. NOESY of compound 1c.

NSD-10-026

exp44 NOESY

SAMPLE		FLAGS	n
date	Jun 13 2014	hs	y
solvent	Benzene	sspul	y
sample	undefined	PFgflg	y
ACQUISITION		hsglv1	1009
sw	4001.6	SPECIAL	
at	0.128	temp	not used
np	1024	gain	30
fb	not used	spin	0
ss	32	F2 PROCESSING	
d1	1.000	gf	0.059
nt	16	gfs	not used
2D ACQUISITION		fn	1024
sw1	4001.6	F1 PROCESSING	
ni	200	gf1	0.046
TRANSMITTER		gfs1	not used
tn	H1	proc1	1p
sfrq	499.832	fn1	1024
tof	-500.0	DISPLAY	
tpwr	61	sp	171.1
pw	13.900	wp	3720.2
NOESY		sp1	172.1
mix	0.600	wp1	3712.4
PRESATURATION		rfl	2926.2
satmode	nnnn	rfp	2941.0
satpwr	0	rfl1	2925.2
satdly	0	rfp1	2941.0
satfrq	0	PLOT	
DECOUPLER		wc	155.0
dn	C13	sc	10.0
dm	nnn	wc2	155.0
		sc2	0
		vs	60
		th	1
		ai	ph

F2 (ppm)



F1 (ppm)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/28 05:28 下午  
 Reported Date and Time: 2014/03/05 06:46 下午

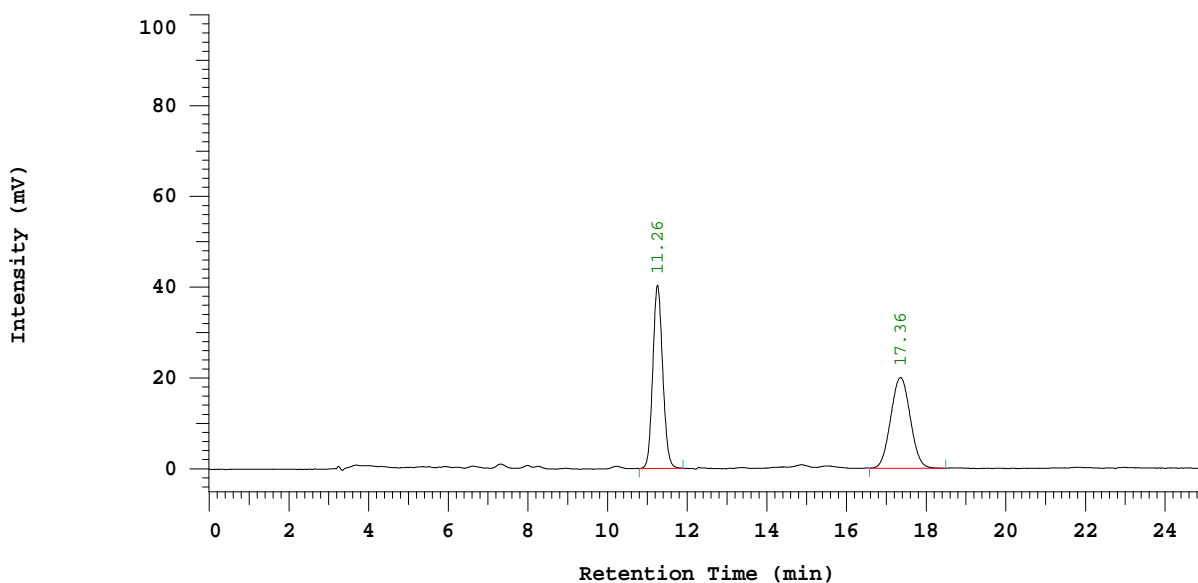
Processed Date and Time: 2014/03/05 06:45 下午

Data Path: D:\NITIN\DATA\0079\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0079  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-183 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.26	692724	40304	50.611
2	17.36	676005	19959	49.389
		1368729	60263	100.000

Peak rejection level: 200000

Fig S62. HPLC analysis of the racemic compound 4a, for comparison in Table 1.

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/09/17 01:16 下午  
 Reported Date and Time: 2013/09/17 02:54 下午

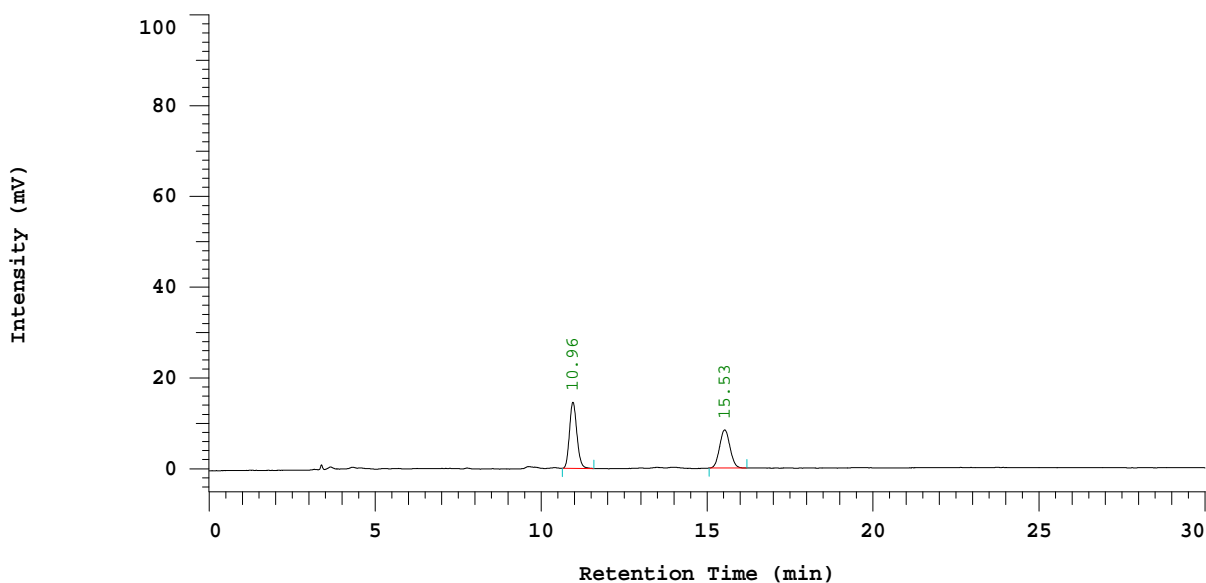
Processed Date and Time: 2013/09/17 02:52 下午

Data Path: D:\NITIN\DATA\0016\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0016  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-96 (Takemoto-NH2) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.96	223804	14601	55.473
2	15.53	179641	8373	44.527
		403445	22974	100.000

Peak rejection level: 100000

Fig S63. HPLC analysis of the compound 4a (Table 1, entry 1)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/09/19 02:34 下午  
 Reported Date and Time: 2013/09/19 03:26 下午

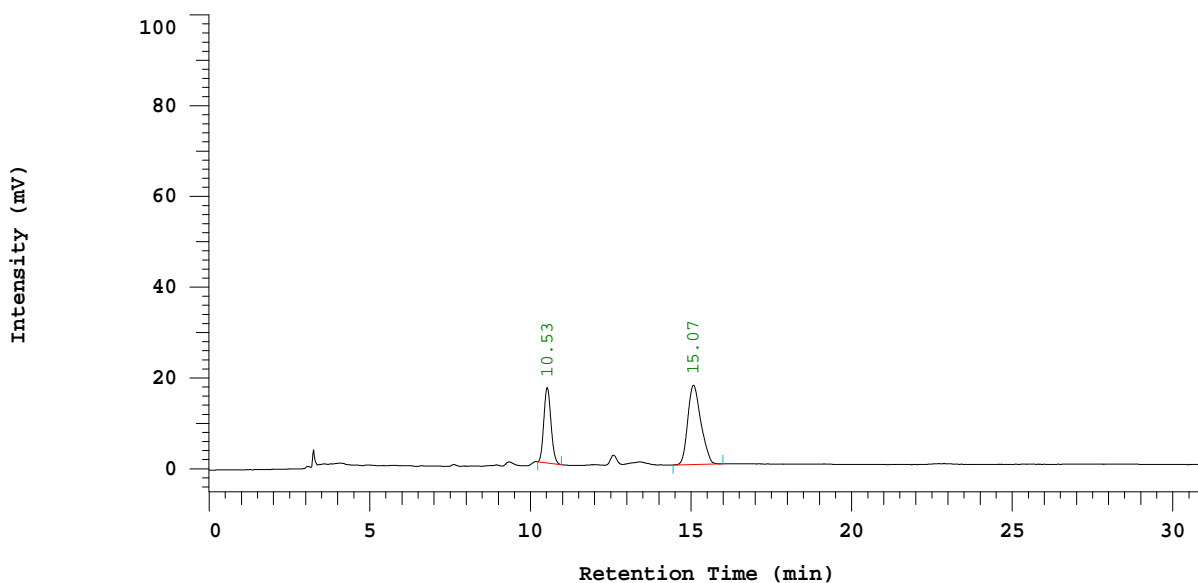
Processed Date and Time: 2013/09/19 03:25 下午

Data Path: D:\NITIN\DATA\0017\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0017  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-97 (Quinidine-NH2) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.53	253164	16569	34.057
2	15.07	490194	17416	65.943
		743358	33985	100.000

Peak rejection level: 200000

Fig S64. HPLC analysis of the compound 4a (Table 1, entry 3)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/09/13 11:37 上午  
 Reported Date and Time: 2013/09/13 01:51 下午

Processed Date and Time: 2013/09/13 01:50 下午

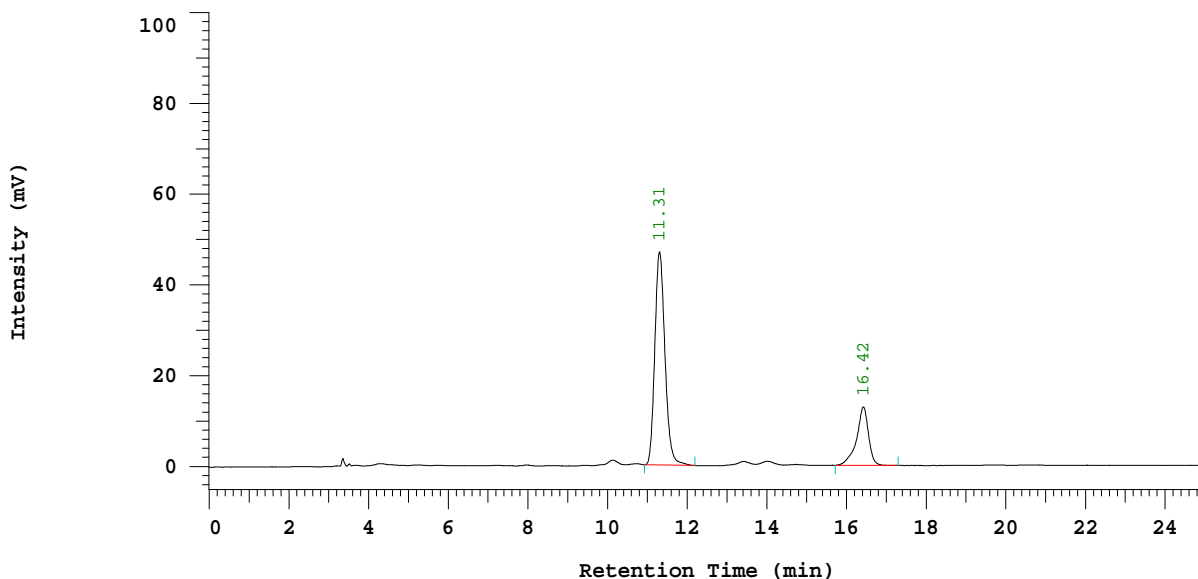
Data Path: D:\NITIN\DATA\0015\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0015  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-94 (Hydroquinine-NH2) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.31	824163	46937	75.636
2	16.42	265476	12857	24.364
		1089639	59794	100.000

Peak rejection level: 200000

Fig S65. HPLC analysis of the compound 4a (Table 1, entry 4)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/11/19 10:44 上午  
 Reported Date and Time: 2013/11/19 11:18 上午

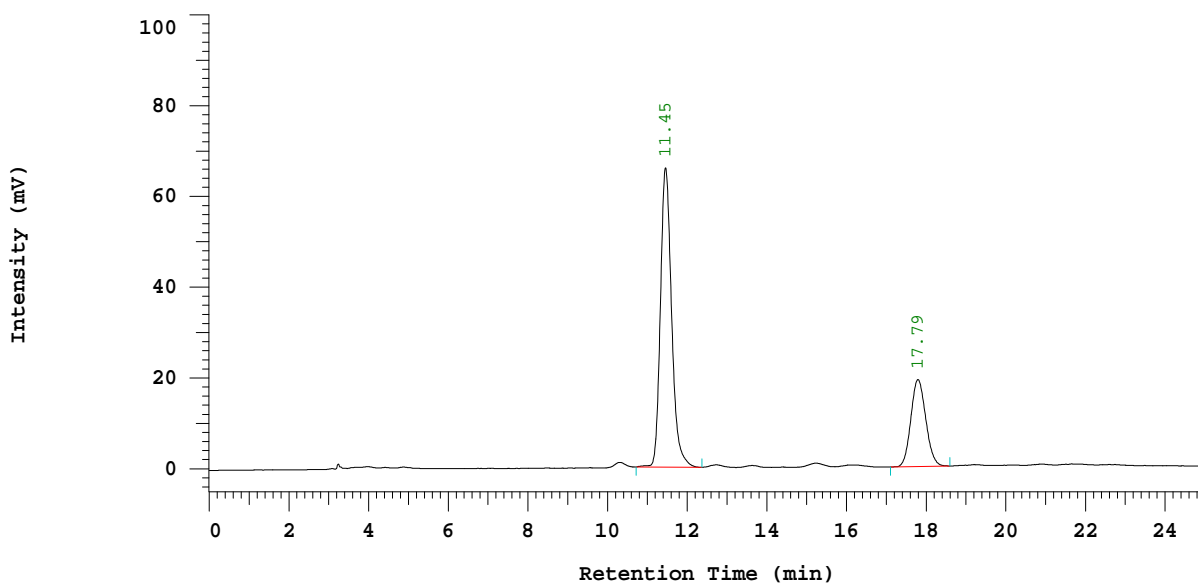
Processed Date and Time: 2013/11/19 11:16 上午

Data Path: D:\NITIN\DATA\0038\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0038  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-128(DHQ-TCA-CH2Cl2) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.45	1274655	65882	72.027
2	17.79	495024	19129	27.973
		1769679	85011	100.000

Peak rejection level: 200000

Fig S66. HPLC analysis of the compound 4a (Table 1, entry 6)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/11/06 01:17 下午  
 Reported Date and Time: 2013/11/06 12:50 下午

Processed Date and Time: 2013/11/06 12:50 下午

Data Path: D:\NITIN\DATA\0035\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1

Series: 0035

Application(data): NITIN

Vial Number: 1

Sample Name: NSD-09-119(DHQ-PentFBA-CH2Cl2)

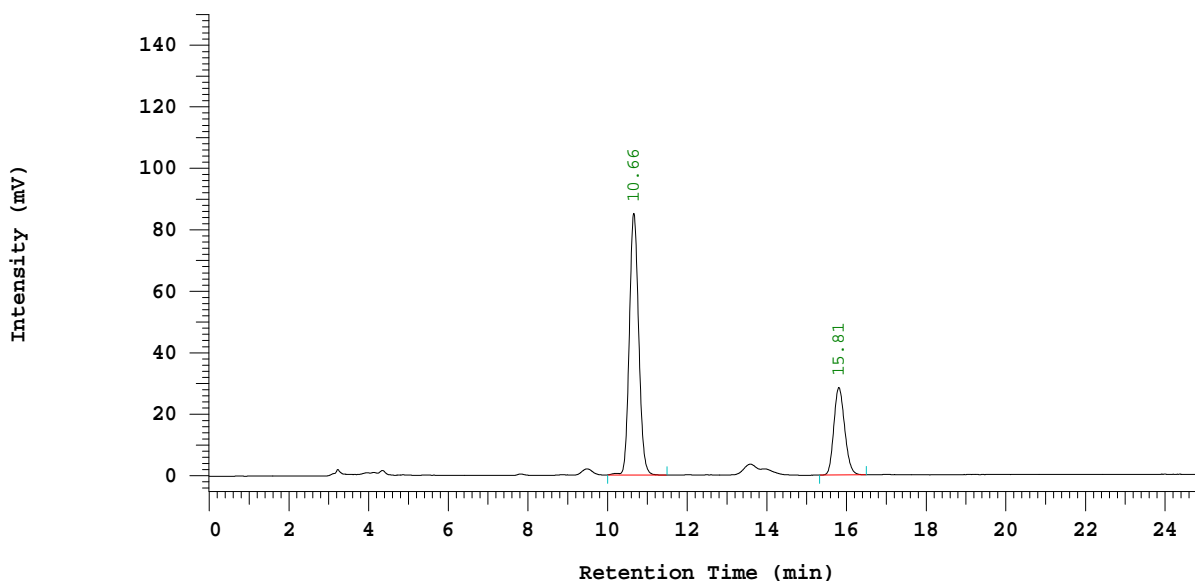
Vial Type: UNK

Volume: 20.0 ul

Injection from this vial: 1 of 1

Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.66	1374364	85043	71.975
2	15.81	535137	28438	28.025
		1909501	113481	100.000

Peak rejection level: 200000

Fig S67. HPLC analysis of the compound 4a (Table 1, entry 10)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/11/06 12:47 下午  
 Reported Date and Time: 2013/11/06 12:47 下午

Processed Date and Time: 2013/11/06 12:47 下午

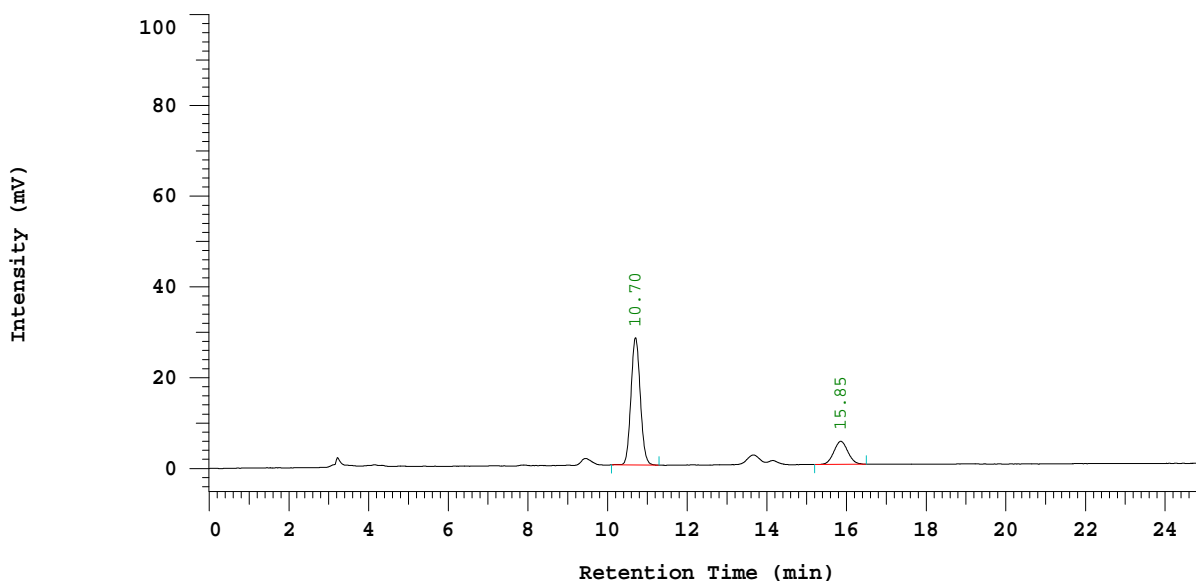
Data Path: D:\NITIN\DATA\0034\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0034  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-118(DHQ-2-NBA-CH2Cl2) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.70	453568	28017	78.770
2	15.85	122242	5060	21.230
		575810	33077	100.000

Peak rejection level: 100000

Fig S68. HPLC analysis of the compound 4a (Table 1, entry 11)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/29 01:04 下午  
 Reported Date and Time: 2013/10/29 12:39 下午

Processed Date and Time: 2013/10/29 12:38 下午

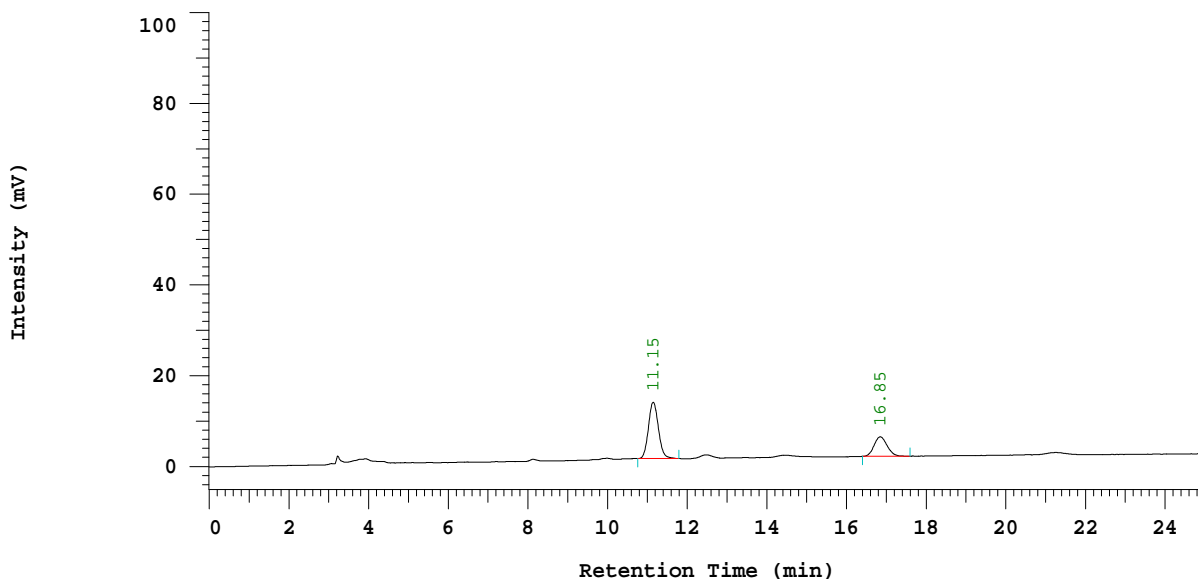
Data Path: D:\NITIN\DATA\0033\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0033  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-115(DHQ-R-CSA-CH2Cl2) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.15	216958	12413	68.984
2	16.85	97547	4311	31.016
		314505	16724	100.000

Peak rejection level: 50000

Fig S69. HPLC analysis of the compound 4a (Table 1, entry 14)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/23 11:07 上午  
 Reported Date and Time: 2013/10/23 11:57 上午

Processed Date and Time: 2013/10/23 11:57 上午

Data Path: D:\NITIN\DATA\0028\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1

Series: 0028

Application(data): NITIN

Vial Number: 1

Sample Name: NSD-09-114(DHQ-NH2-R-PACH2Cl2)

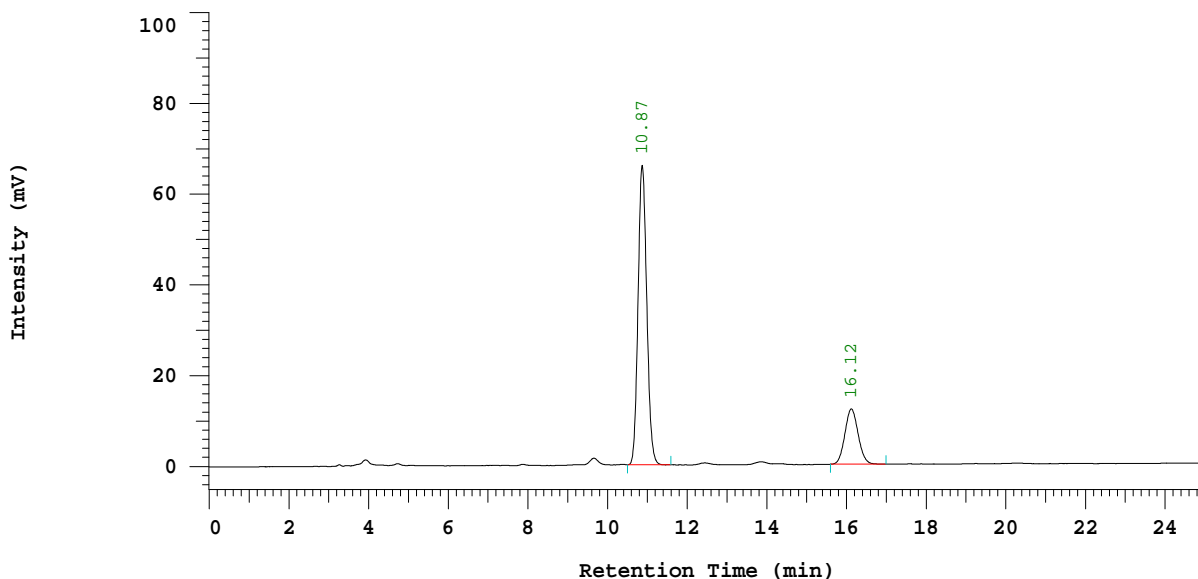
Vial Type: UNK

Volume: 20.0 ul

Injection from this vial: 1 of 1

Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.87	999878	65948	78.286
2	16.12	277333	12135	21.714
		1277211	78083	100.000

Peak rejection level: 200000

Fig S70. HPLC analysis of the compound 4a (Table 1, entry 15)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/23 10:38 上午  
 Reported Date and Time: 2013/10/23 11:54 上午

Processed Date and Time: 2013/10/23 11:52 上午

Data Path: D:\NITIN\DATA\0027\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1

Series: 0027

Application(data): NITIN

Vial Number: 1

Sample Name: NSD-09-113(DHQ-NH2-S-PACH2Cl2)

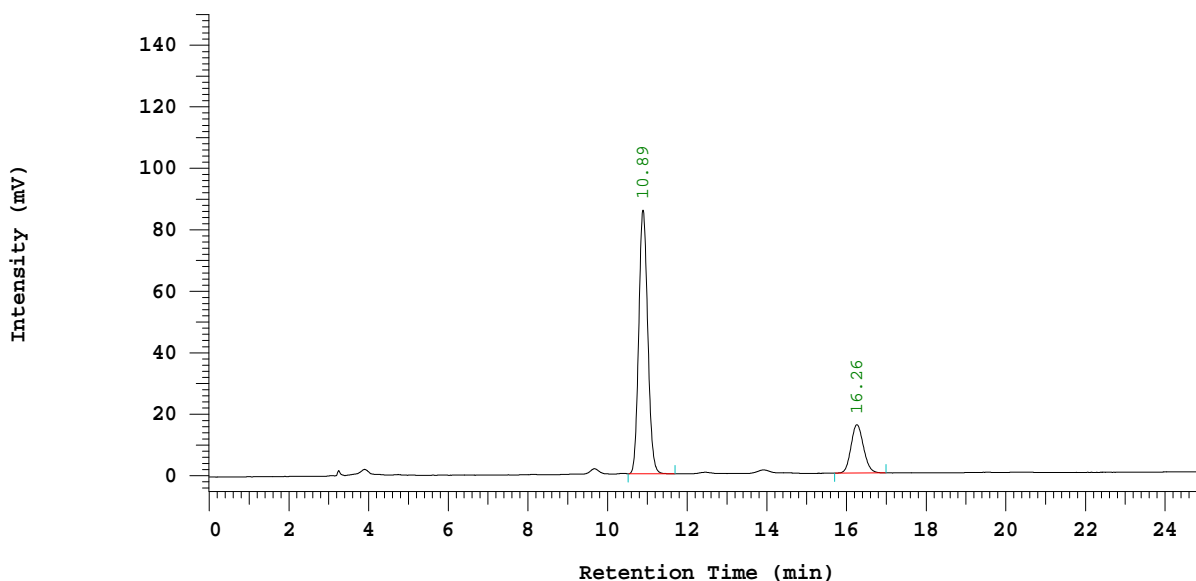
Vial Type: UNK

Volume: 20.0 ul

Injection from this vial: 1 of 1

Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.89	1338996	85661	79.793
2	16.26	339086	15715	20.207
		1678082	101376	100.000

Peak rejection level: 200000

Fig S71. HPLC analysis of the compound 4a (Table 1, entry 16)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/10 10:00 上午  
 Reported Date and Time: 2013/10/10 12:03 下午

Processed Date and Time: 2013/10/10 12:01 下午

Data Path: D:\NITIN\DATA\0023\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1

Series: 0023

Application(data): NITIN

Vial Number: 1

Sample Name: NSD-09-102(QuinineNH2-Toluene)

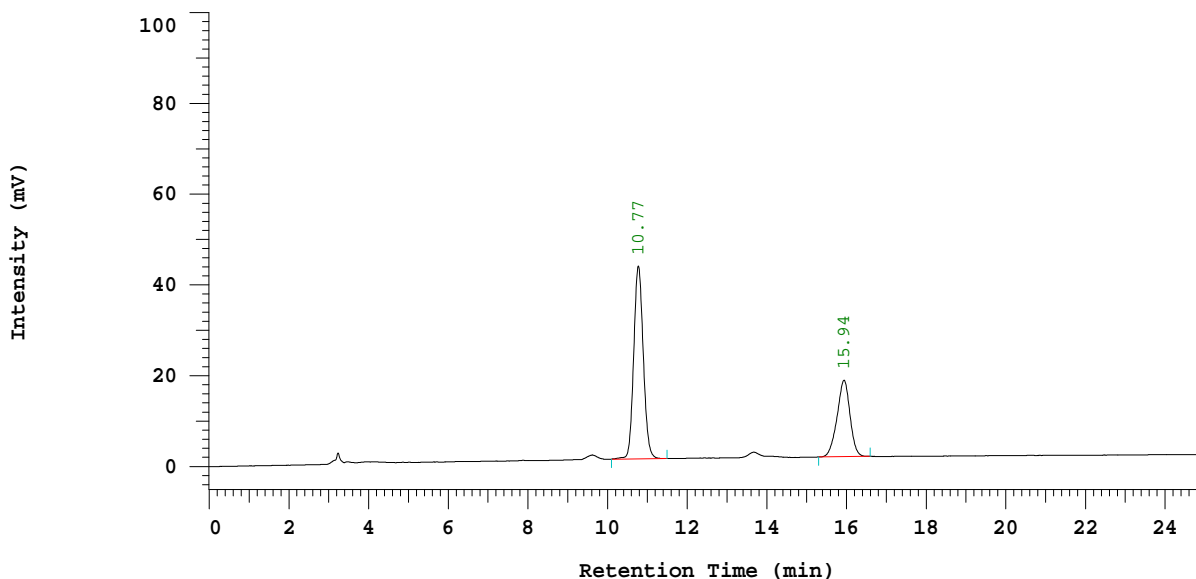
Vial Type: UNK

Volume: 20.0 ul

Injection from this vial: 1 of 1

Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.77	706987	42453	65.154
2	15.94	378121	16844	34.846
		1085108	59297	100.000

Peak rejection level: 200000

Fig S72. HPLC analysis of the compound 4a (Table 1, entry 19)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/09/26 11:49 上午  
 Reported Date and Time: 2013/09/26 12:25 下午

Processed Date and Time: 2013/09/26 12:23 下午

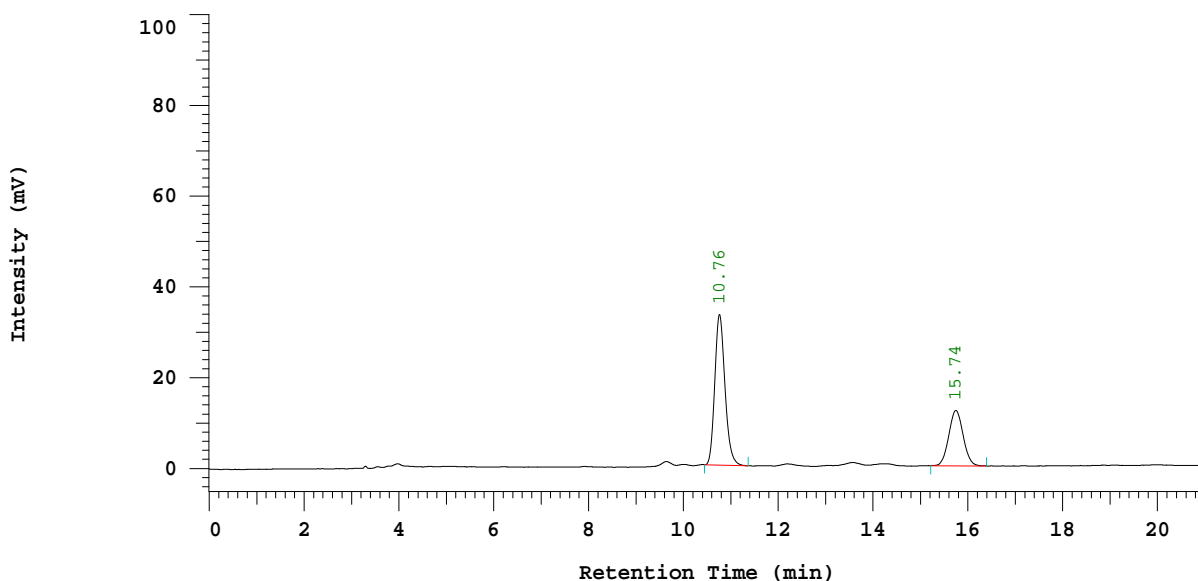
Data Path: D:\NITIN\DATA\0019\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0019  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-103 (Quinine-NH2-CHCl3) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.76	489623	33156	65.949
2	15.74	252803	12160	34.051
		742426	45316	100.000

Peak rejection level: 200000

Fig S73. HPLC analysis of the compound 4a (Table 1, entry 20)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/10 10:29 上午  
 Reported Date and Time: 2013/10/10 12:07 下午

Processed Date and Time: 2013/10/10 12:06 下午

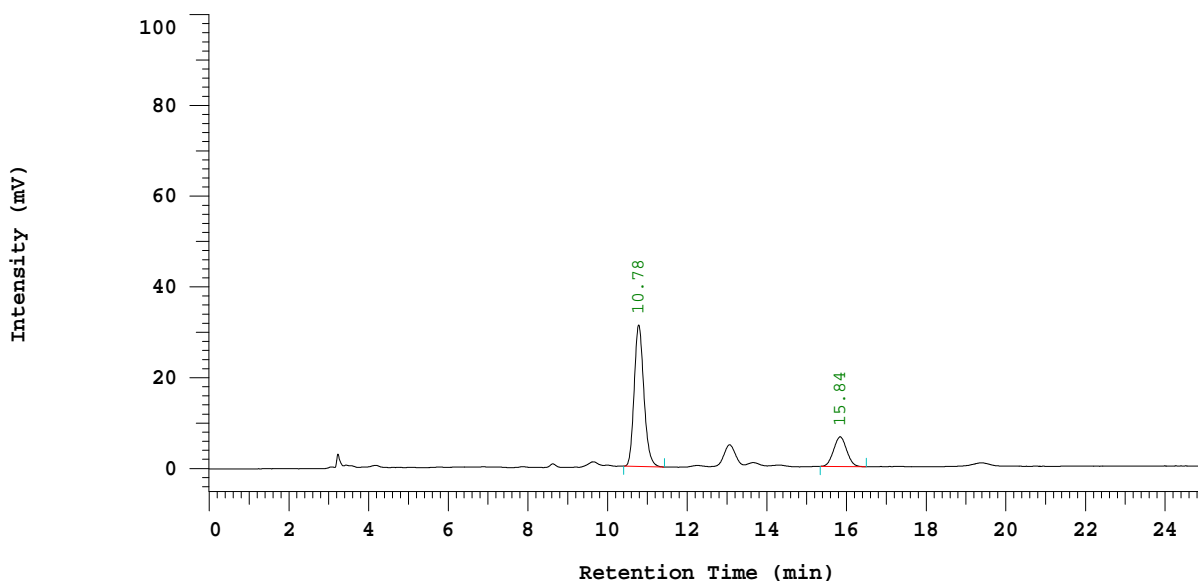
Data Path: D:\NITIN\DATA\0024\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0024  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-104(QuinineNH2-EtOAc) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.78	525161	31147	77.914
2	15.84	148861	6535	22.086
		674022	37682	100.000

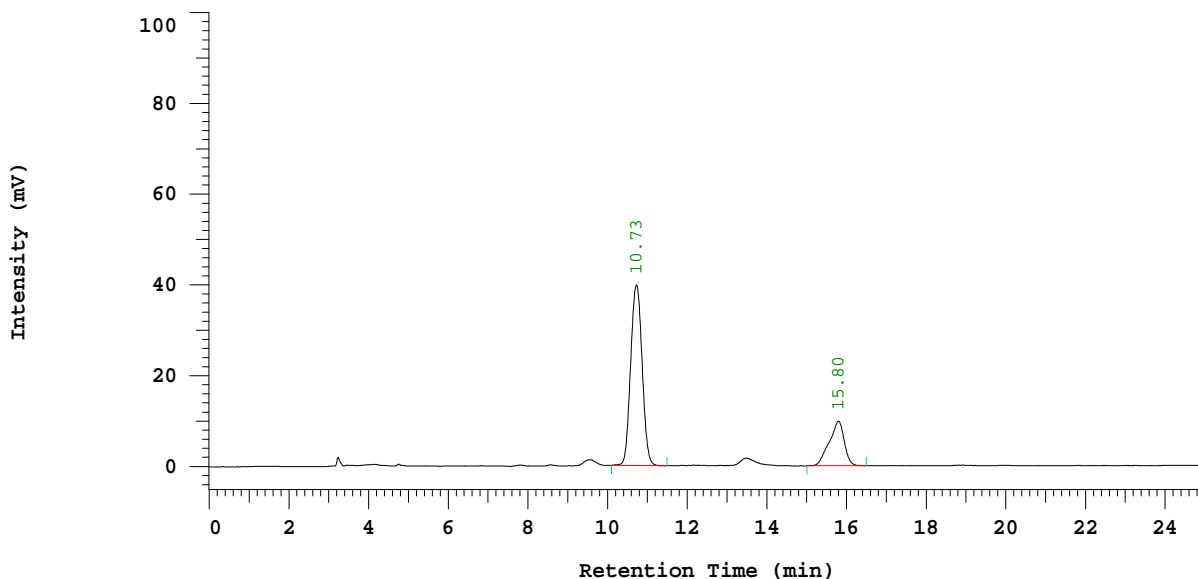
Peak rejection level: 100000

Fig S74. HPLC analysis of the compound 4a (Table 1, entry 21)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/10 11:04 上午  
 Reported Date and Time: 2013/10/10 12:11 下午  
 Processed Date and Time: 2013/10/10 12:10 下午  
 Data Path: D:\NITIN\DATA\0025\  
 Processing Method: Test-IPA/Hx-1  
 System (acquisition): Sys 1 Series: 0025  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-105(QuinineNH2-Dioxane) Vial Type: UNK  
 Volume: 20.0 ul  
 Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.73	791757	39731	75.604
2	15.80	255488	9795	24.396
		1047245	49526	100.000

Peak rejection level: 200000

Fig S75. HPLC analysis of the compound 4a (Table 1, entry 22)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/04 04:52 下午  
 Reported Date and Time: 2013/10/04 05:23 下午

Processed Date and Time: 2013/10/04 05:22 下午

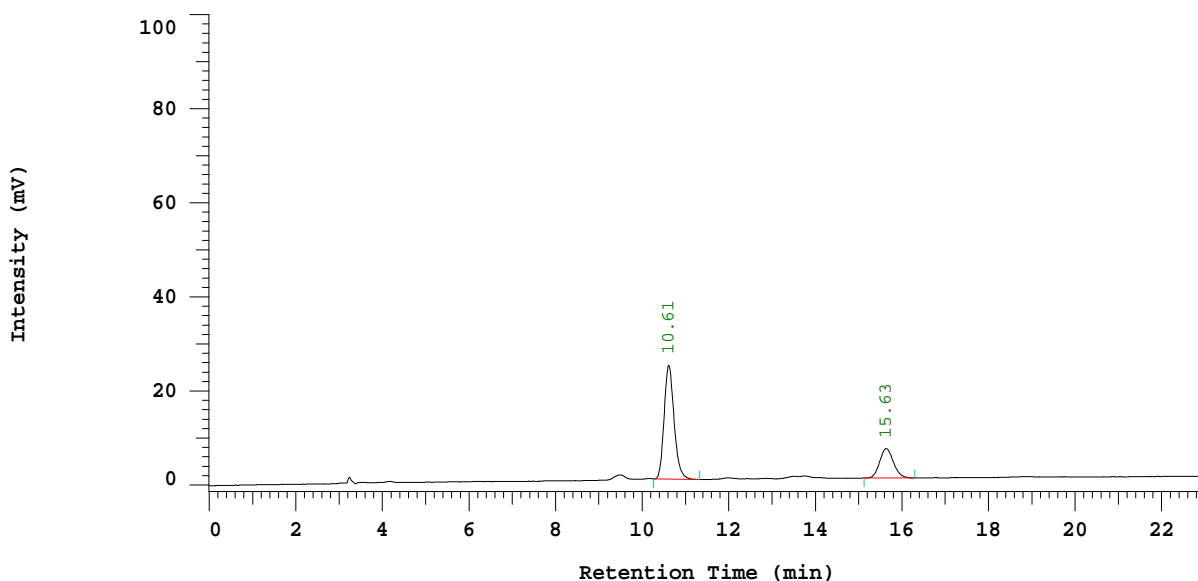
Data Path: D:\NITIN\DATA\0022\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0022  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-106 (Quinine-NH2-THF) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.61	385348	24162	73.762
2	15.63	137069	6249	26.238
		522417	30411	100.000

Peak rejection level: 100000

Fig S76. HPLC analysis of the compound 4a (Table 1, entry 23)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/10/10 11:32 上午  
 Reported Date and Time: 2013/10/10 12:14 下午

Processed Date and Time: 2013/10/10 12:12 下午

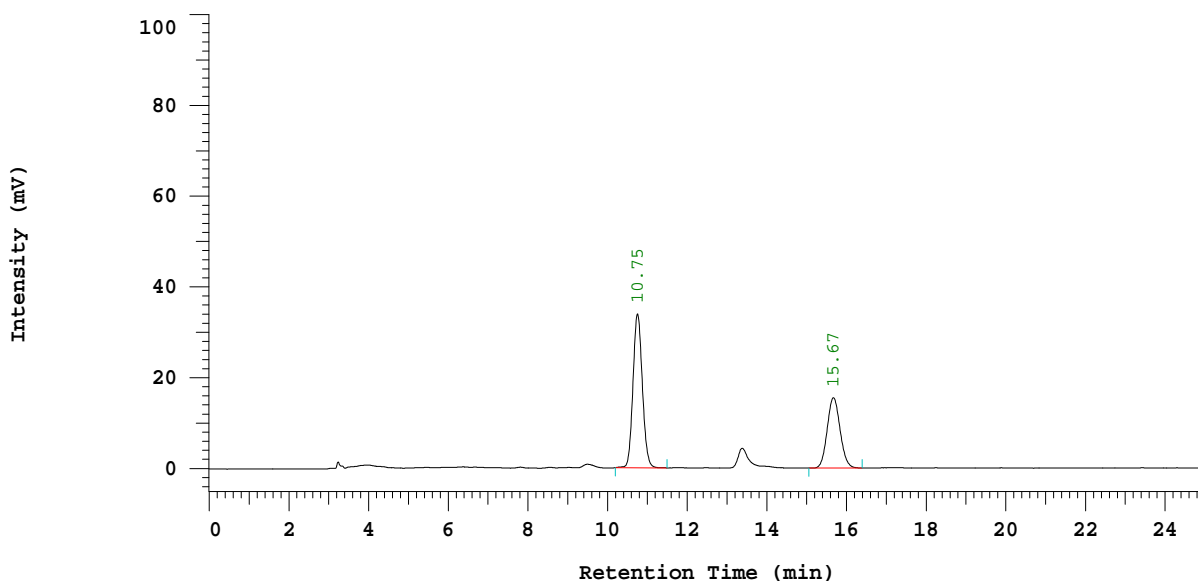
Data Path: D:\NITIN\DATA\0026\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0026  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-110 (QuinineNH2-DCE) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.75	550756	33883	61.378
2	15.67	346560	15491	38.622
		897316	49374	100.000

Peak rejection level: 200000

Fig S77. HPLC analysis of the compound 4a (Table 1, entry 24)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/12/06 11:04 上午  
 Reported Date and Time: 2013/12/06 01:40 下午

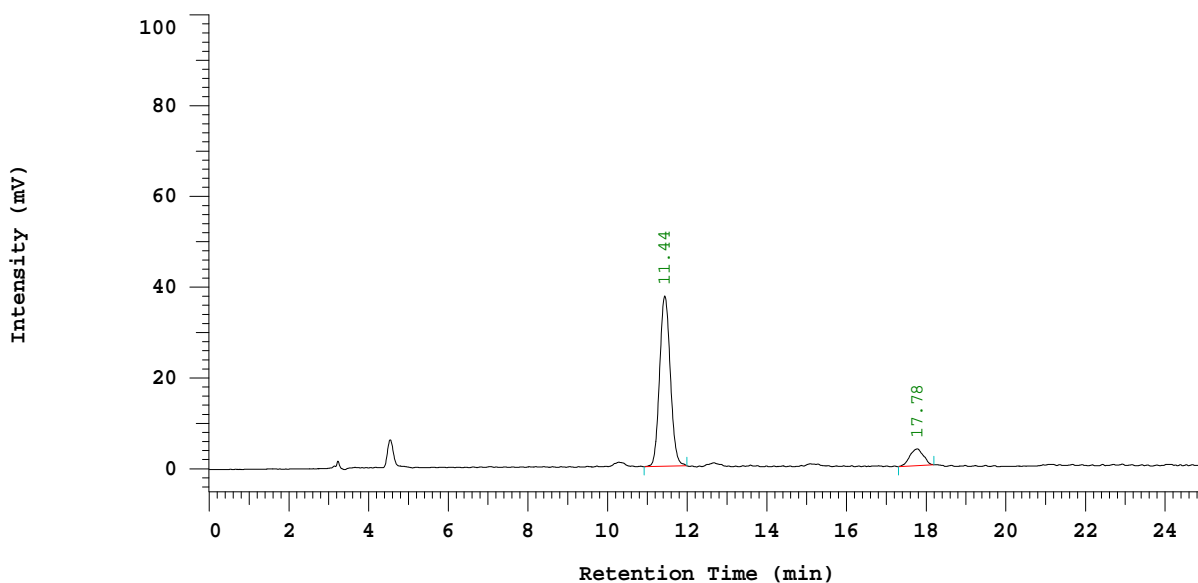
Processed Date and Time: 2013/12/06 01:38 下午

Data Path: D:\NITIN\DATA\0044\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0044  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-131(DHQ-DCM-EtOAc) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.44	693371	37478	88.935
2	17.78	86268	3659	11.065
		779639	41137	100.000

Peak rejection level: 50000

Fig S78. HPLC analysis of the compound 4a (Table 1, entry 26)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/28 06:01 下午  
 Reported Date and Time: 2014/03/05 06:50 下午

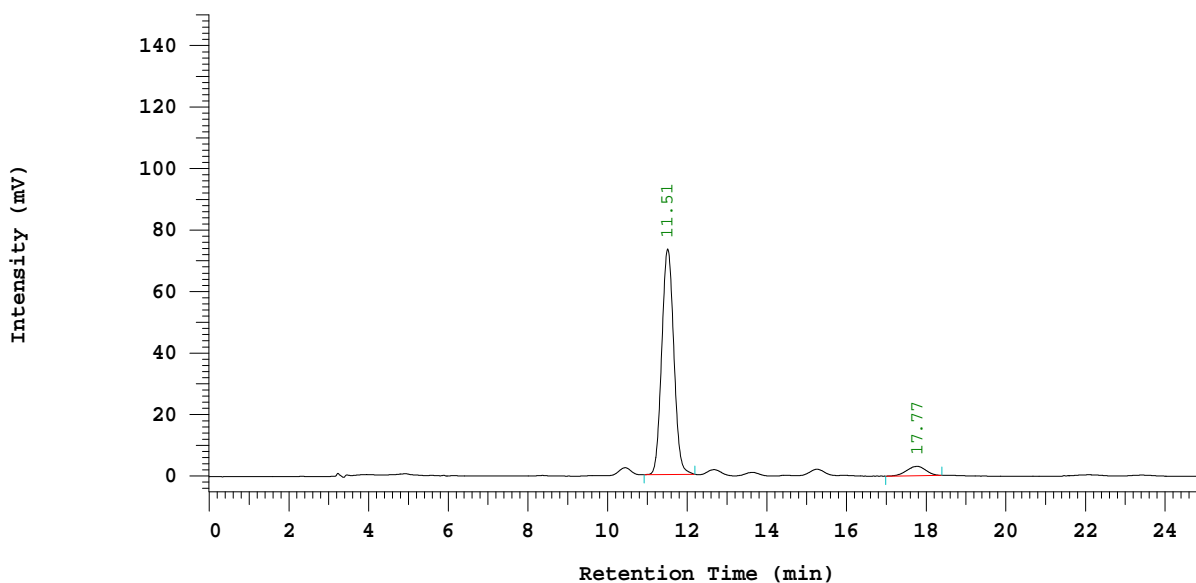
Processed Date and Time: 2014/03/05 06:49 下午

Data Path: D:\NITIN\DATA\0081\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0081  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-172-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3  
 Column Type: IC Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.51	1533021	73316	93.722
2	17.77	102695	3073	6.278
		1635716	76389	100.000

Peak rejection level: 50000

Fig S79. HPLC analysis of the compound 4a (Table 1, entry 27)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/12/06 01:34 下午  
 Reported Date and Time: 2013/12/06 02:48 下午

Processed Date and Time: 2013/12/06 02:47 下午

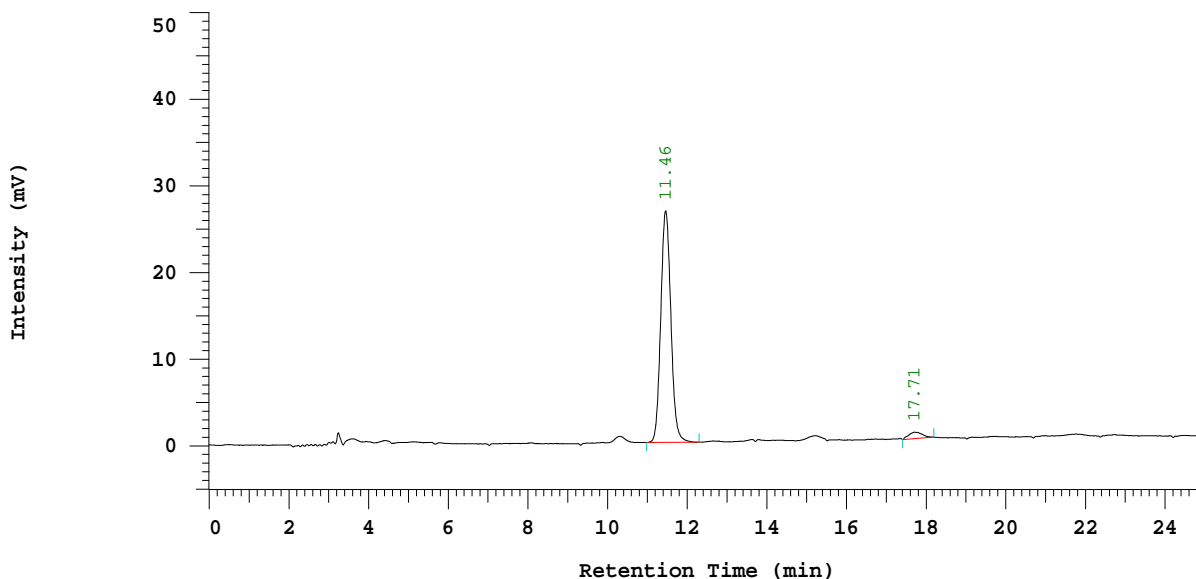
Data Path: D:\NITIN\DATA\0045\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0045  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-132(DHQ-CHCl3-EtOAc) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.46	467565	26696	96.358
2	17.71	17673	745	3.642
		485238	27441	100.000

Peak rejection level: 10000

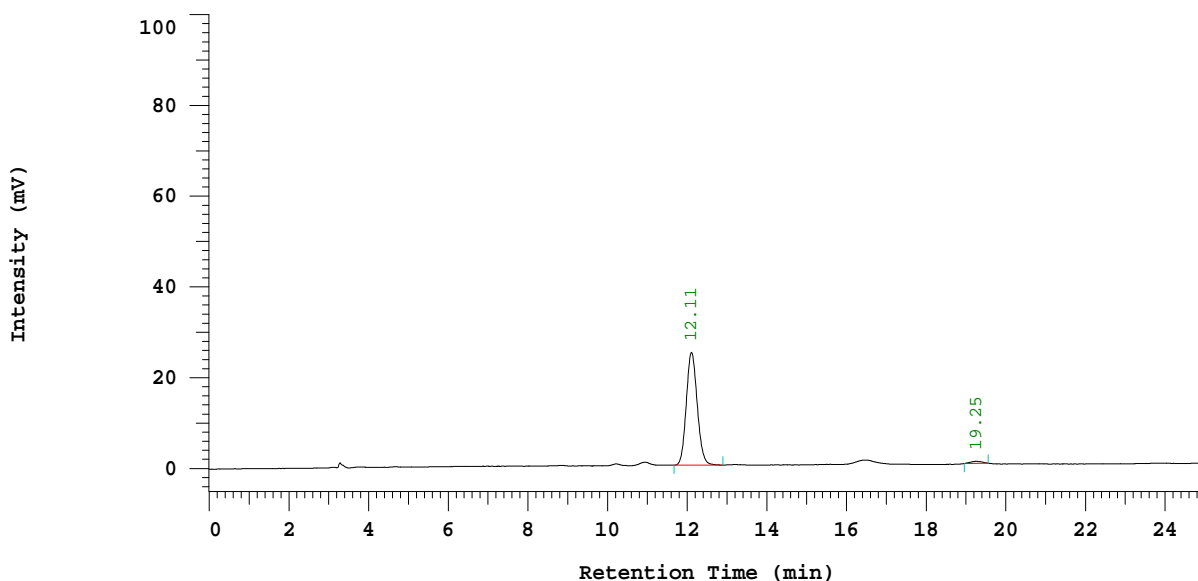
Fig S80. HPLC analysis of the compound 4a (Table 1, entry 28)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/12/31 02:15 下午  
 Reported Date and Time: 2013/12/31 04:45 下午  
 Processed Date and Time: 2013/12/31 04:44 下午  
 Data Path: D:\NITIN\DATA\0058\  
 Processing Method: Test-IPA/Hx-1  
 System (acquisition): Sys 1 Series: 0058  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-145(DHQ-CHCl3-EtOAc) Vial Type: UNK  
 Volume: 20.0 ul  
 Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	12.11	469252	24830	98.140
2	19.25	8893	445	1.860
		478145	25275	100.000

Peak rejection level: 5000

Fig S81. HPLC analysis of the compound 4a (Table 1, entry 29)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/01/09 02:16 下午  
 Reported Date and Time: 2014/01/16 02:21 下午

Processed Date and Time: 2014/01/16 02:20 下午

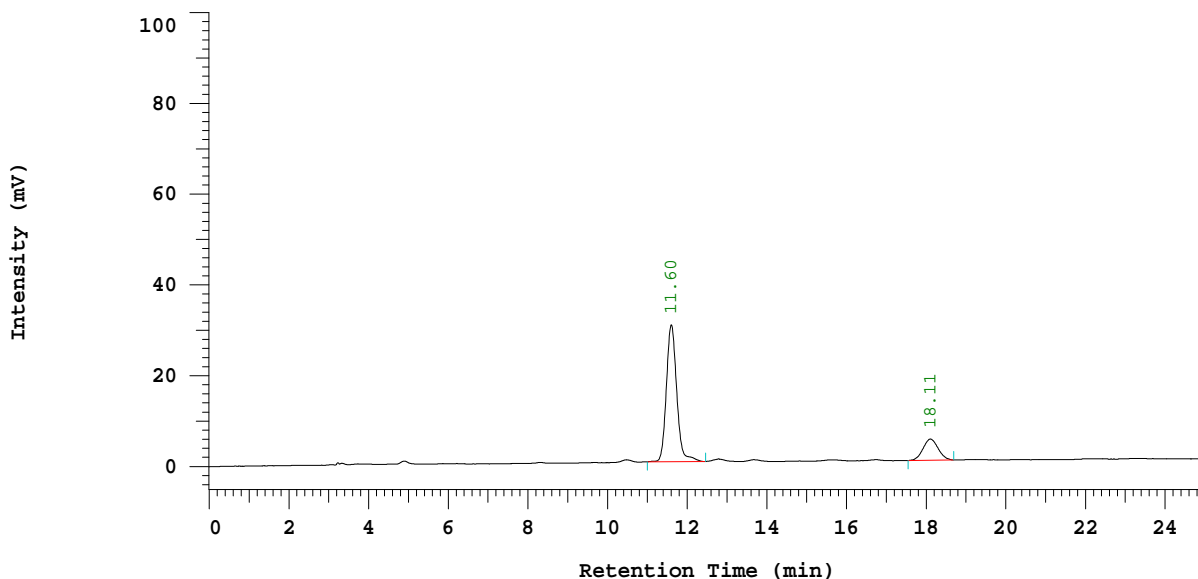
Data Path: D:\NITIN\DATA\0064\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0064  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-160(MicroW-CHCl3-EtOAc) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1 Method Developer: NSD  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.60	541879	30119	81.628
2	18.11	121956	4653	18.372
		663835	34772	100.000

Peak rejection level: 100000

Fig S82. HPLC analysis of the compound 4a (Table 1, entry 30)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/28 05:28 下午  
 Reported Date and Time: 2014/03/05 06:46 下午

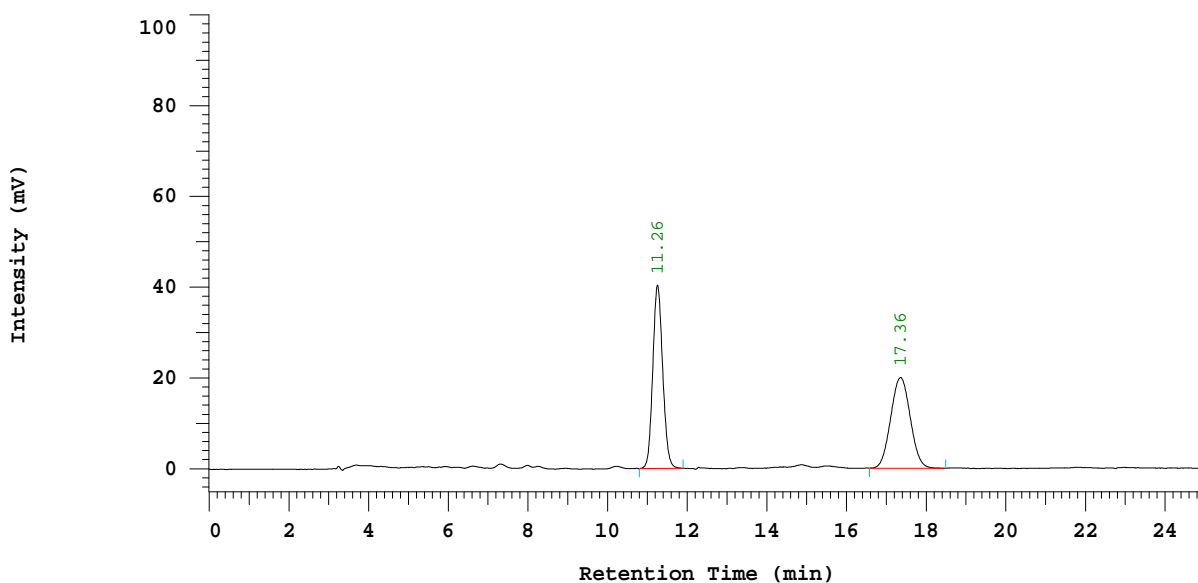
Processed Date and Time: 2014/03/05 06:45 下午

Data Path: D:\NITIN\DATA\0079\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0079  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-183 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.26	692724	40304	50.611
2	17.36	676005	19959	49.389
		1368729	60263	100.000

Peak rejection level: 200000

Fig S83. HPLC analysis of the racemic compound 4a, as a standard for comparison (Scheme 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/28 06:01 下午  
 Reported Date and Time: 2014/03/05 06:50 下午

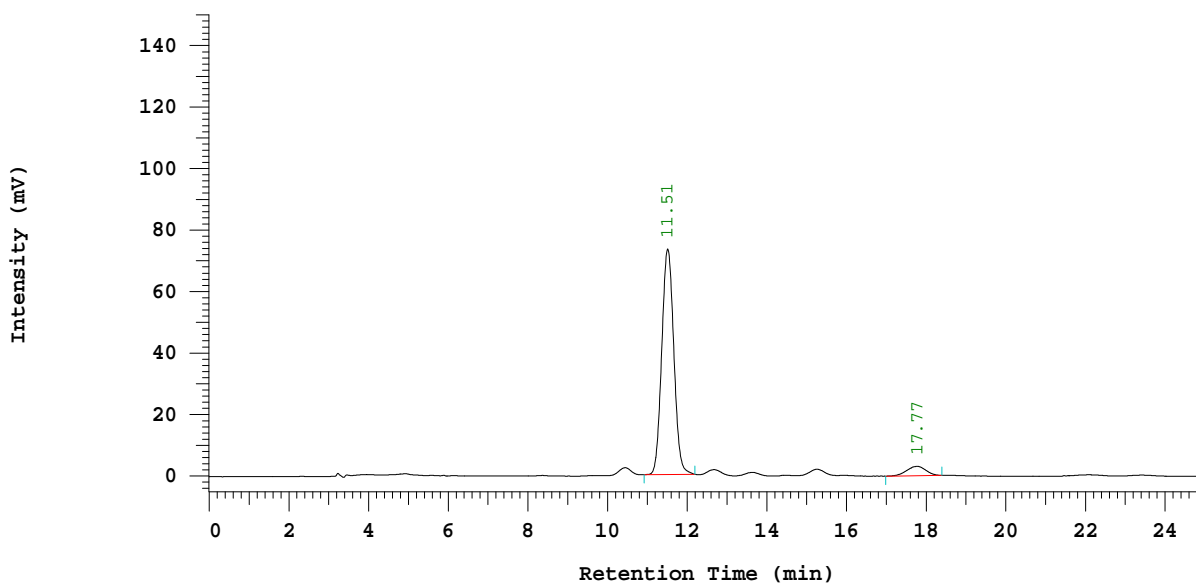
Processed Date and Time: 2014/03/05 06:49 下午

Data Path: D:\NITIN\DATA\0081\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0081  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-172-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3  
 Column Type: IC Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.51	1533021	73316	93.722
2	17.77	102695	3073	6.278
		1635716	76389	100.000

Peak rejection level: 50000

Fig S84. HPLC analysis of the compound 4a (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/28 04:27 下午  
 Reported Date and Time: 2014/03/05 05:52 下午

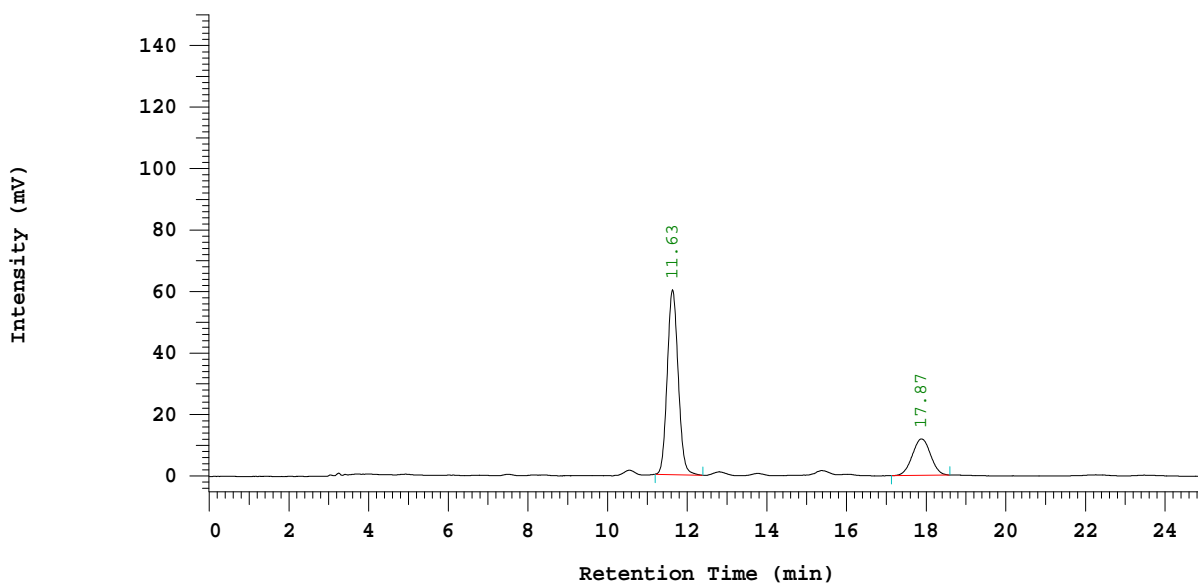
Processed Date and Time: 2014/03/05 05:52 下午

Data Path: D:\NITIN\DATA\0082\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0082  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-172-F1 (CO) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.63	1142080	60059	75.172
2	17.87	377213	11872	24.828
		1519293	71931	100.000

Peak rejection level: 200000

Fig S85. HPLC analysis of the mixture of chiral compound 4a and the racemic 4a, for comparison (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/07 11:22 上午  
 Reported Date and Time: 2014/03/07 12:02 下午

Processed Date and Time: 2014/03/07 12:01 下午

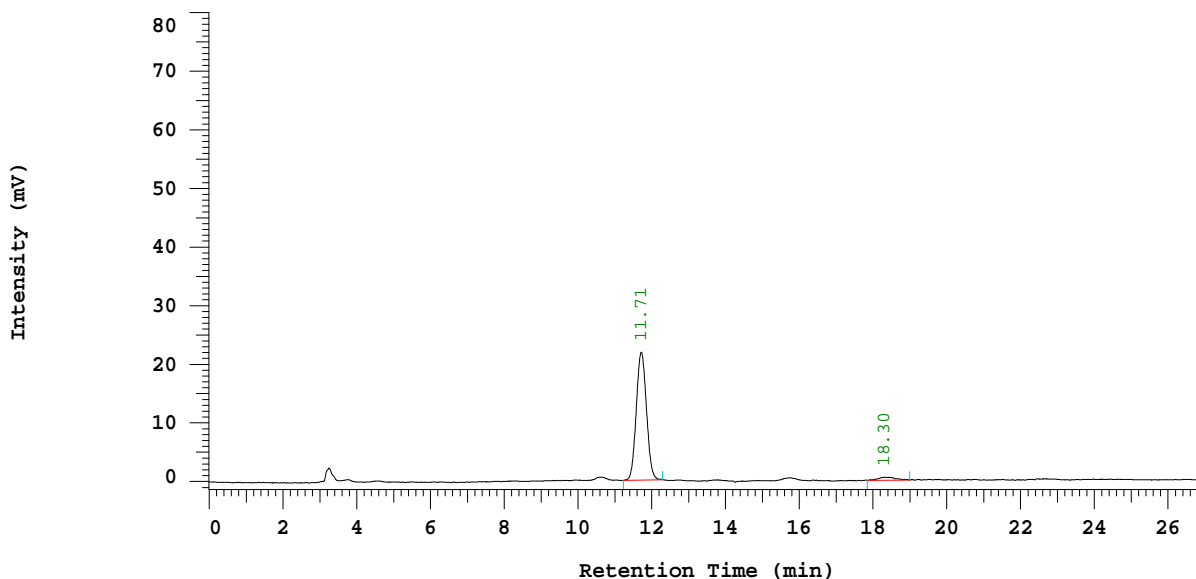
Data Path: D:\NITIN\DATA\0086\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0086  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-132(cat+acid1:1- Indole) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3 Method Developer: NITIN  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.71	416923	21789	96.081
2	18.30	17006	501	3.919
		433929	22290	100.000

Peak rejection level: 5000

Fig S86. HPLC analysis of the compound 4a (Scheme 2, Method B)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/17 10:22 上午  
 Reported Date and Time: 2014/02/17 11:48 上午

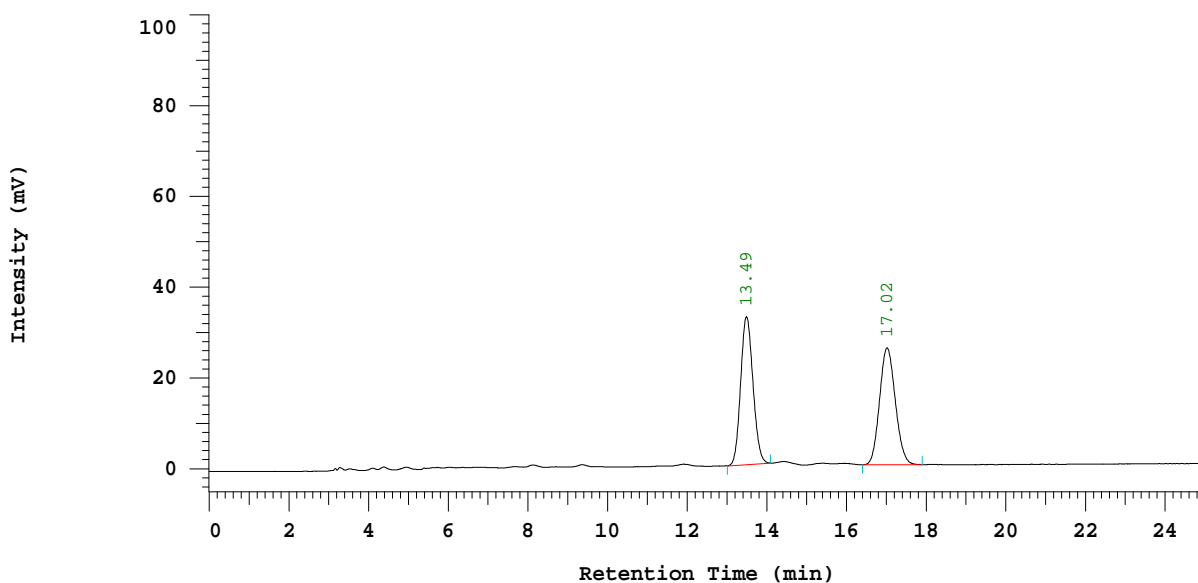
Processed Date and Time: 2014/02/17 11:47 上午

Data Path: D:\NITIN\DATA\0073\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0073  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-171 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	13.49	696417	32607	49.782
2	17.02	702508	25754	50.218
		1398925	58361	100.000

Peak rejection level: 200000

Fig S87. HPLC analysis of the racemic compound 4b, as a standard for comparison (Scheme 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/17 10:49 上午  
 Reported Date and Time: 2014/02/17 11:51 上午

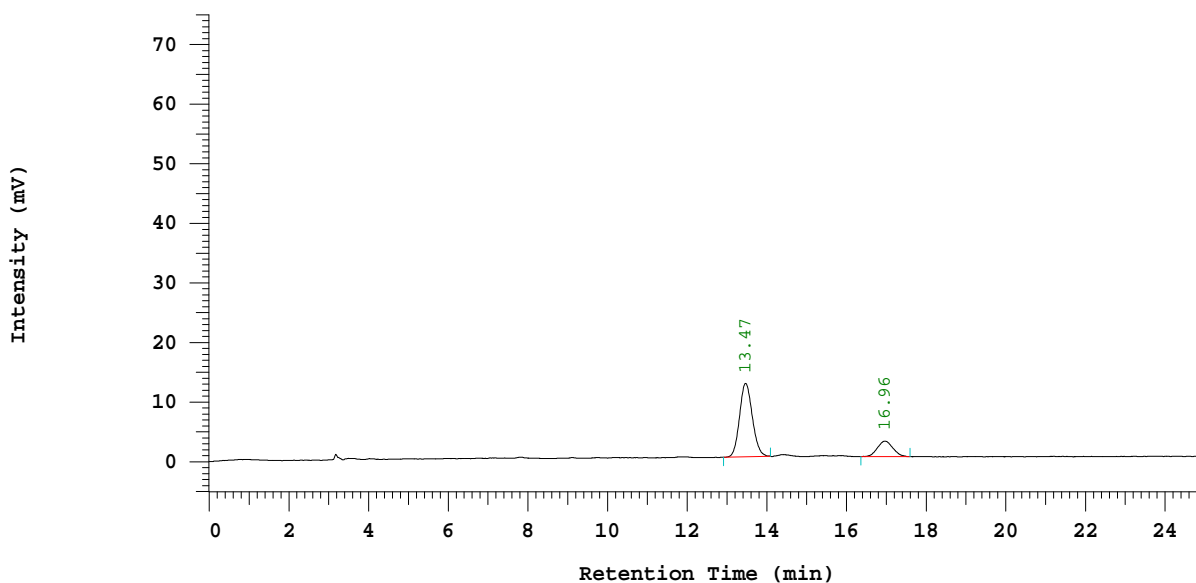
Processed Date and Time: 2014/02/17 11:50 上午

Data Path: D:\NITIN\DATA\0074\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0074  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-169-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	13.47	274210	12318	79.412
2	16.96	71090	2634	20.588
		345300	14952	100.000

Peak rejection level: 50000

Fig S88. HPLC analysis of the compound 4b (Scheme 2, Method A)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/02/17 11:15 上午  
 Reported Date and Time: 2014/02/17 11:53 上午

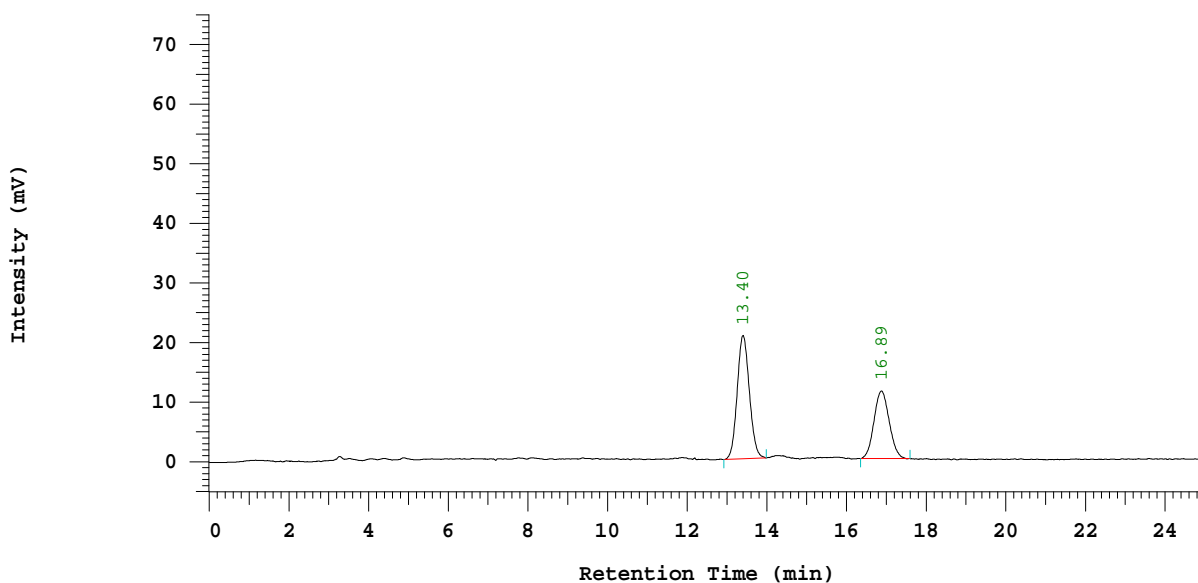
Processed Date and Time: 2014/02/17 11:52 上午

Data Path: D:\NITIN\DATA\0075\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0075  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-169-F1 (CO) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	13.40	438442	20697	59.344
2	16.89	300377	11350	40.656
		738819	32047	100.000

Peak rejection level: 50000

Fig S89. HPLC analysis of the mixture of chiral compound 4b and the racemic 4b, for comparison (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/07 10:37 上午  
 Reported Date and Time: 2014/03/07 11:09 上午

Processed Date and Time: 2014/03/07 11:07 上午

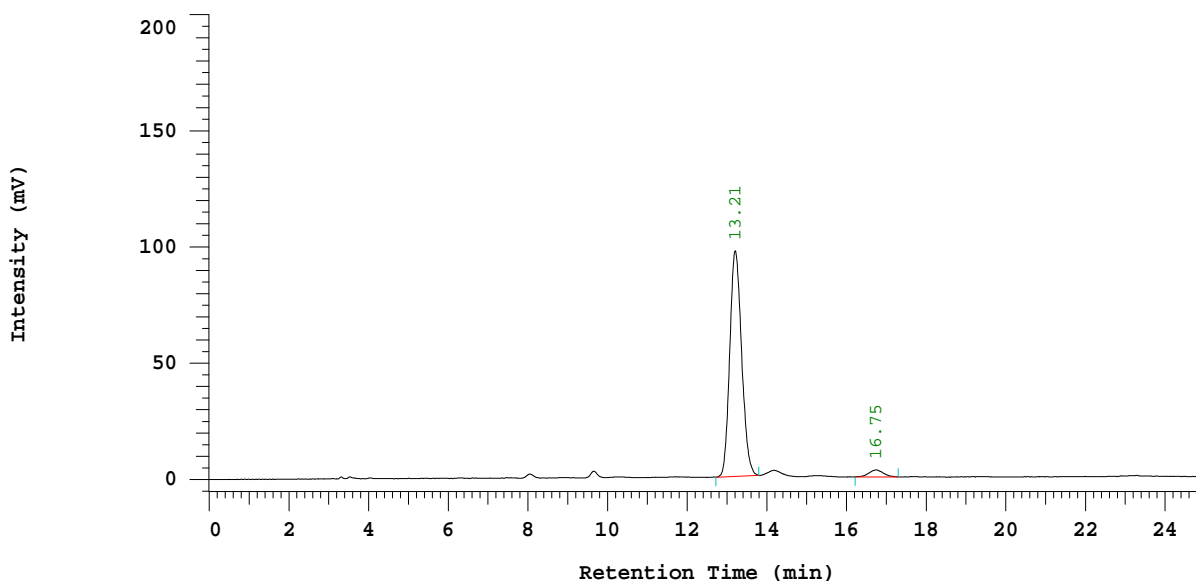
Data Path: D:\NITIN\DATA\0085\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0085  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-178(cat+acid-1:1-5 Vial Type: UNK  
 -OMe) Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 8%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3 Method Developer: NITIN  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	13.21	1996824	97014	96.365
2	16.75	75329	2975	3.635
		2072153	99989	100.000

Peak rejection level: 50000

Fig S90. HPLC analysis of the compound 4b (Scheme 2, Method B)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/11 10:28 上午  
 Reported Date and Time: 2014/03/11 12:07 下午

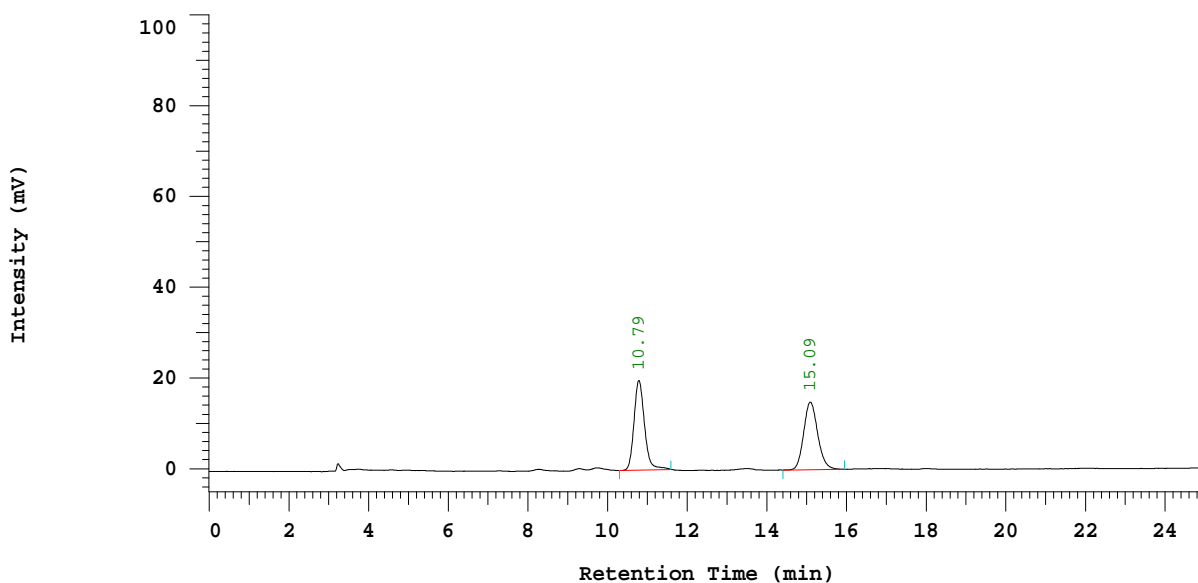
Processed Date and Time: 2014/03/11 12:05 下午

Data Path: D:\NITIN\DATA\0087\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0087  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-185-F1 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.79	361173	19723	49.633
2	15.09	366513	14909	50.367
		727686	34632	100.000

Peak rejection level: 200000

Fig S91. HPLC analysis of the racemic compound 4c, as a standard for comparison (Scheme 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/11 10:59 上午  
 Reported Date and Time: 2014/03/11 12:08 下午

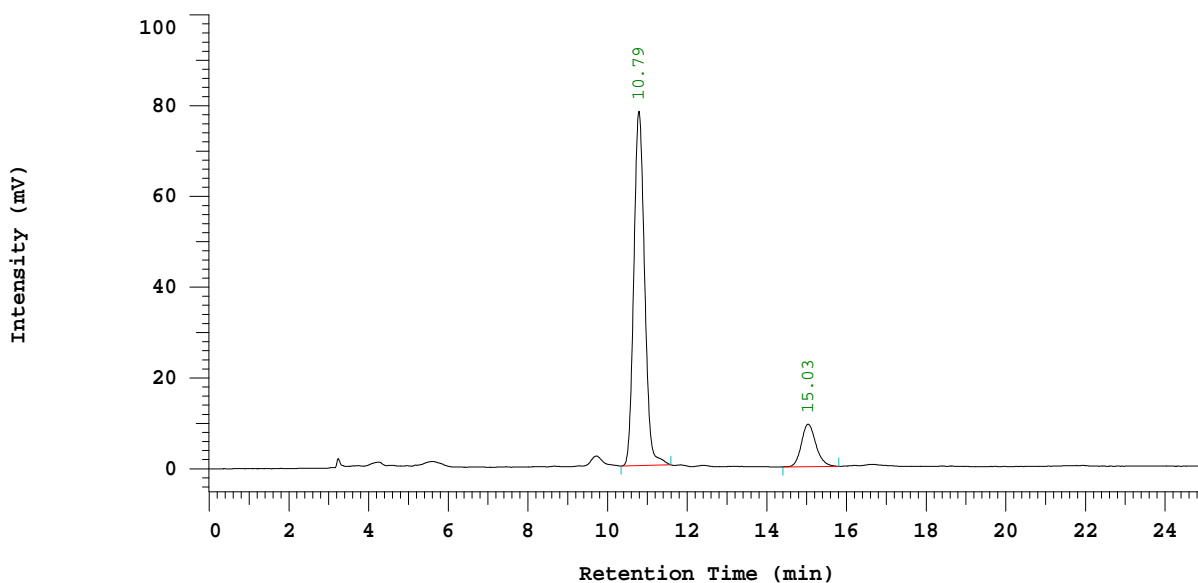
Processed Date and Time: 2014/03/11 12:07 下午

Data Path: D:\NITIN\DATA\0088\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0088  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-175-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.79	1460557	78016	86.058
2	15.03	236618	9340	13.942
		1697175	87356	100.000

Peak rejection level: 200000

Fig S92. HPLC analysis of the compound 4c (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/11 11:27 上午  
 Reported Date and Time: 2014/03/11 12:10 下午

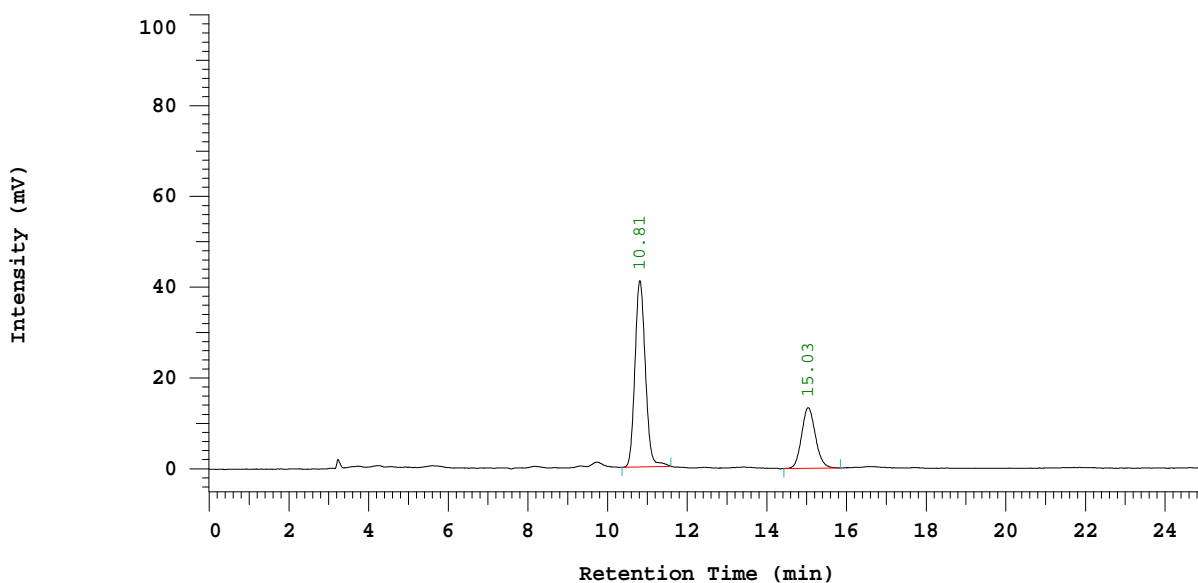
Processed Date and Time: 2014/03/11 12:09 下午

Data Path: D:\NITIN\DATA\0089\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0089  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-175-F1 (CO) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	10.81	744820	41036	69.671
2	15.03	324238	13368	30.329
		1069058	54404	100.000

Peak rejection level: 200000

Fig S93. HPLC analysis of the mixture of chiral compound 4c and the racemic 4c, for comparison (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/06/25 01:17 下午  
 Reported Date and Time: 2014/06/25 02:18 下午

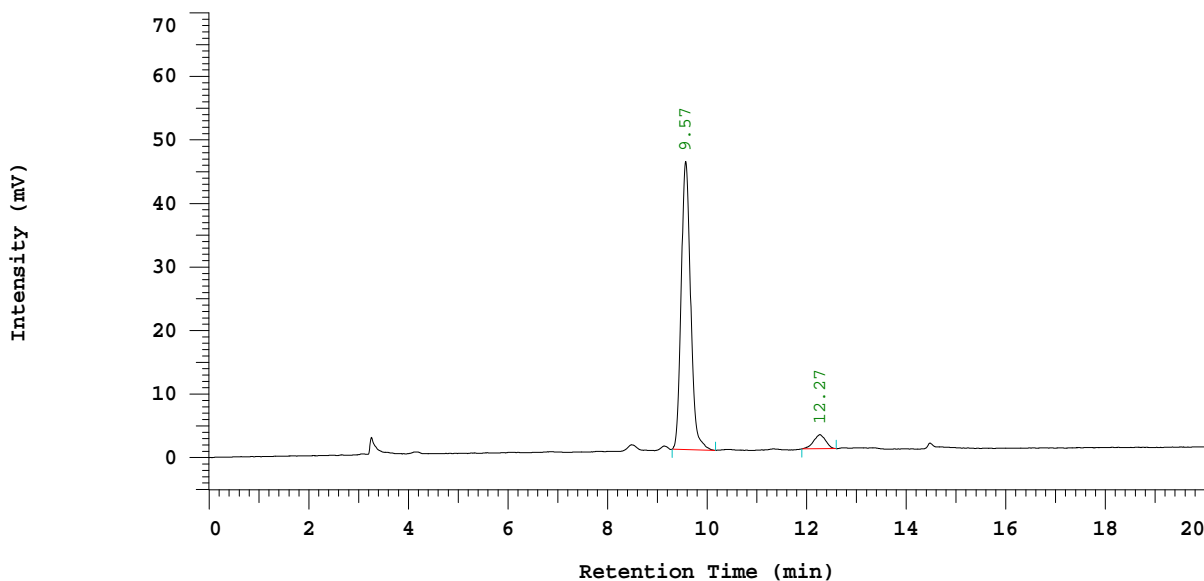
Processed Date and Time: 2014/06/25 02:16 下午

Data Path: D:\NITIN\DATA\0140\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0140  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-27-F1 cat-acid(1:1) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	9.57	597009	45311	94.015
2	12.27	38005	2205	5.985
		635014	47516	100.000

Peak rejection level: 5000

Fig S94. HPLC analysis of the compound 4c (Scheme 2, Method B)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/27 11:00 上午  
 Reported Date and Time: 2014/03/27 12:50 下午

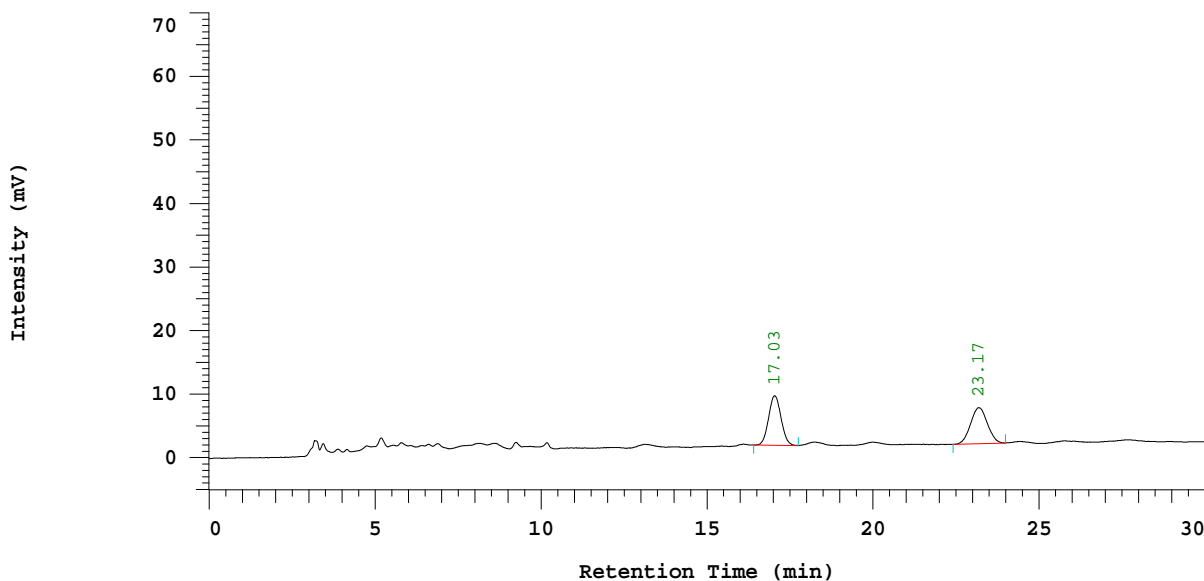
Processed Date and Time: 2014/03/27 12:48 下午

Data Path: D:\NITIN\DATA\0093\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0093  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-06-F1 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.03	202014	7800	50.320
2	23.17	199443	5659	49.680
		401457	13459	100.000

Peak rejection level: 50000

Fig S95. HPLC analysis of the racemic compound 4d, as a standard for comparison (Scheme 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/27 11:35 上午  
 Reported Date and Time: 2014/03/27 12:54 下午

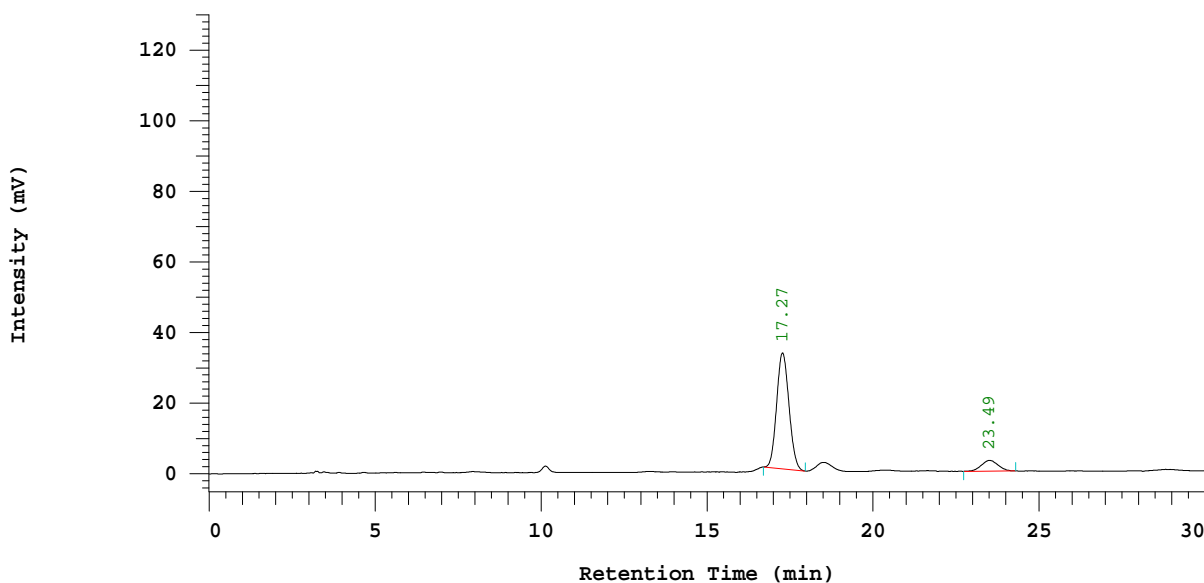
Processed Date and Time: 2014/03/27 12:53 下午

Data Path: D:\NITIN\DATA\0094\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0094  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-186-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.27	840037	32818	88.748
2	23.49	106506	3026	11.252
		946543	35844	100.000

Peak rejection level: 50000

Fig S96. HPLC analysis of the compound 4d (Scheme 2, Method A)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/03/27 12:06 下午  
 Reported Date and Time: 2014/03/27 12:55 下午

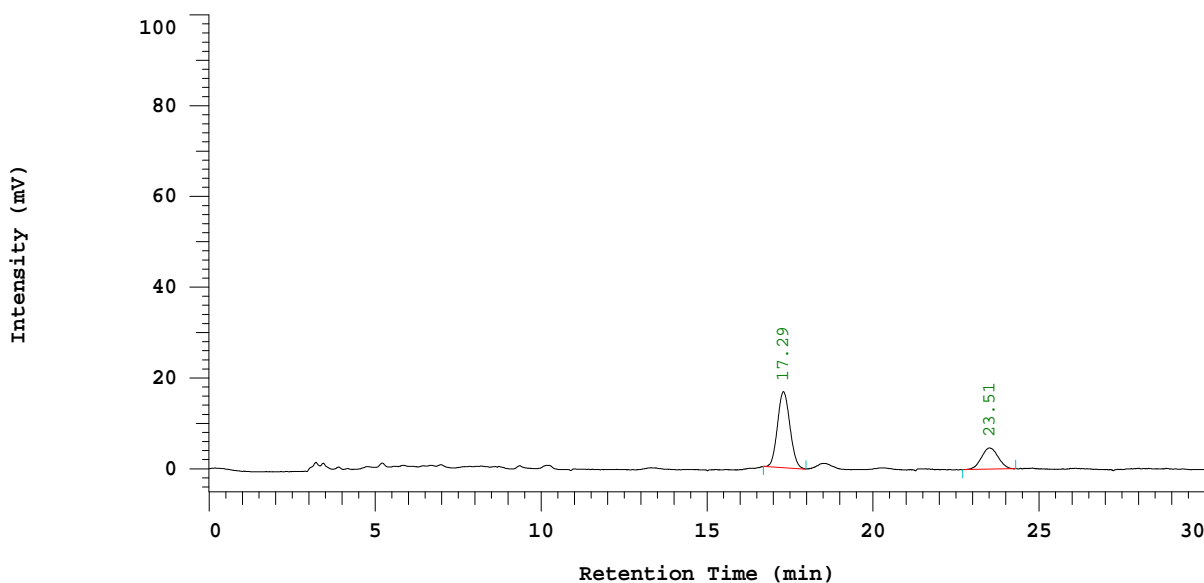
Processed Date and Time: 2014/03/27 12:55 下午

Data Path: D:\NITIN\DATA\0095\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0095  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-186-F1 (CO) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 8%IPA+HX 1mL/Min Col-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3

Column Type: IC

Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.29	432392	16734	72.585
2	23.51	163308	4666	27.415
		595700	21400	100.000

Peak rejection level: 50000

Fig S97. HPLC analysis of the mixture of chiral compound 4d and the racemic 4d, for comparison (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/04/04 04:23 下午  
 Reported Date and Time: 2014/04/04 05:04 下午

Processed Date and Time: 2014/04/04 05:03 下午

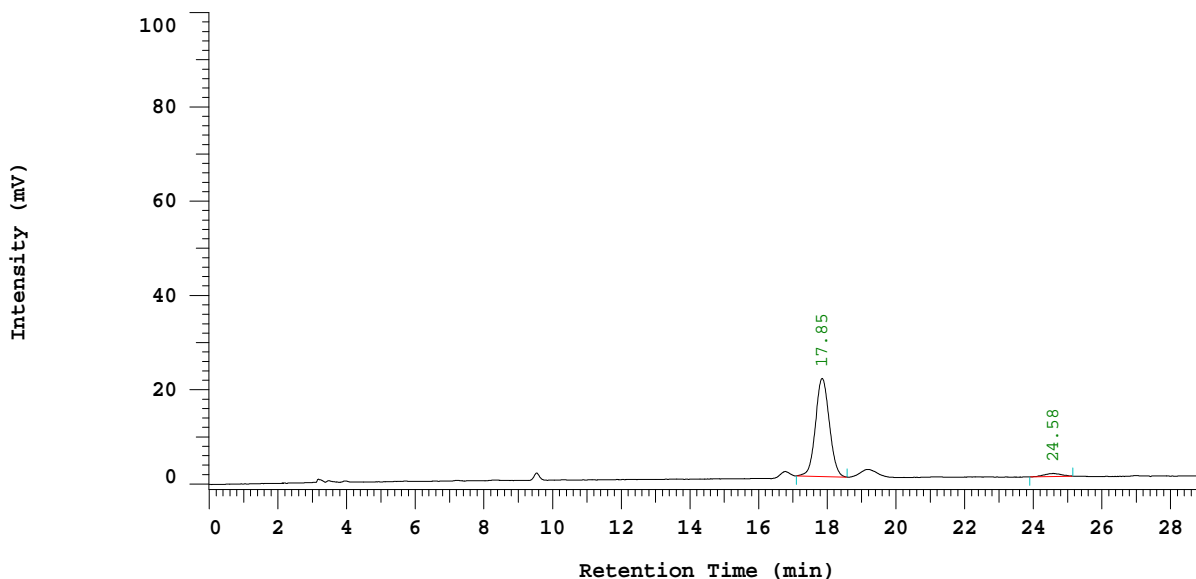
Data Path: D:\NITIN\DATA\0104\

Processing Method: test-IPA/Hx-3

System (acquisition): Sys 1 Series: 0104  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-04-F1 (acid-cat-1:1) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 8%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-3 Method Developer: NITIN  
 Column Type: IC  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.85	580047	20778	96.225
2	24.58	22755	652	3.775
		602802	21430	100.000

Peak rejection level: 5000

Fig S98. HPLC analysis of the compound 4d (Scheme 2, Method B)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/19 11:24 上午  
 Reported Date and Time: 2014/05/19 01:46 下午

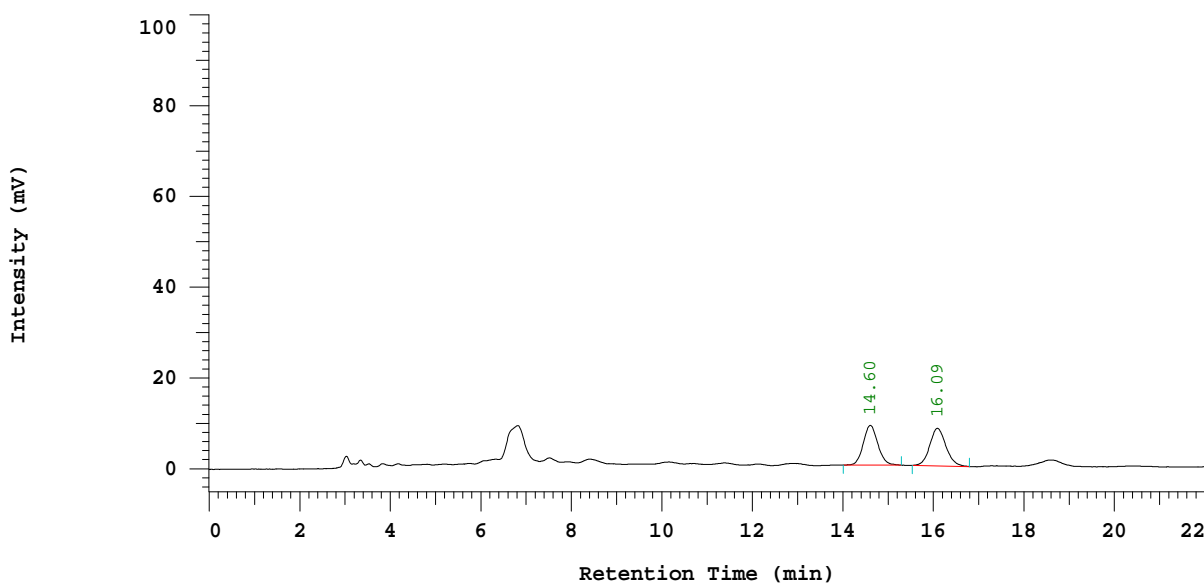
Processed Date and Time: 2014/05/19 01:45 下午

Data Path: D:\NITIN\DATA\0124\

Processing Method: Test-IPA/Hx-2

System (acquisition): Sys 1 Series: 0124  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-02-F1 (Racemic) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: Test-IPA/Hx-2

Column Type: IA

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.60	196429	8741	48.801
2	16.09	206085	8251	51.199
		402514	16992	100.000

Peak rejection level: 5000

Fig S99. HPLC analysis of the racemic compound 4e, as a standard for comparison (Scheme 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/19 11:54 上午  
 Reported Date and Time: 2014/05/19 01:47 下午

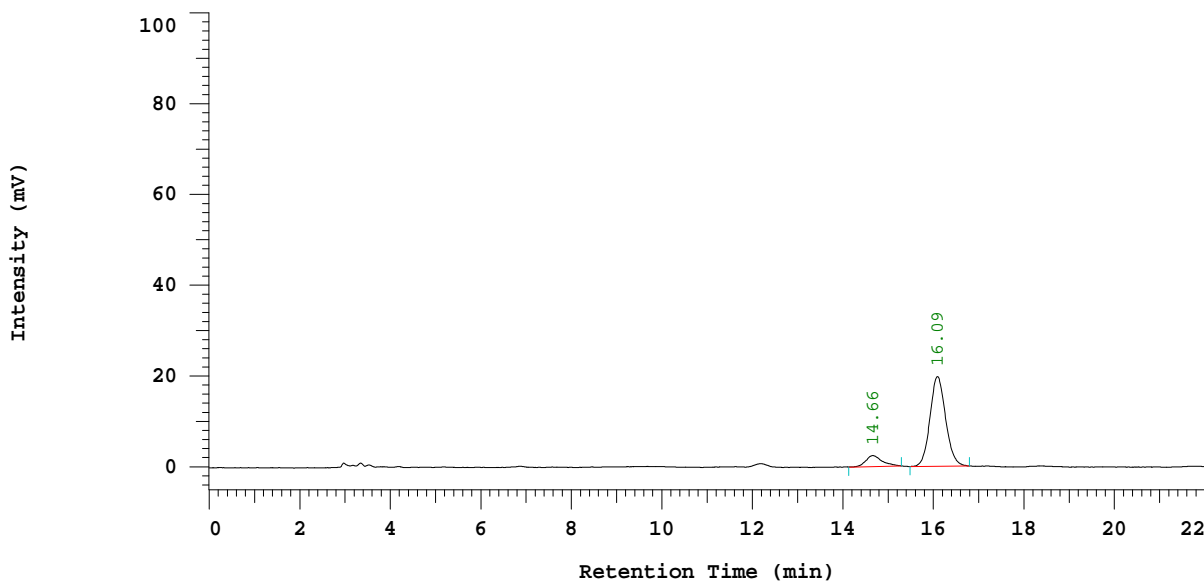
Processed Date and Time: 2014/05/19 01:46 下午

Data Path: D:\NITIN\DATA\0125\

Processing Method: Test-IPA/Hx-2

System (acquisition): Sys 1 Series: 0125  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-184-F1 (Chiral) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/Min Col-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: Test-IPA/Hx-2

Column Type: IA

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.66	60741	2395	11.357
2	16.09	474106	19745	88.643
		534847	22140	100.000

Peak rejection level: 5000

Fig S100. HPLC analysis of the compound 4e (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/19 12:18 下午  
 Reported Date and Time: 2014/05/19 01:48 下午

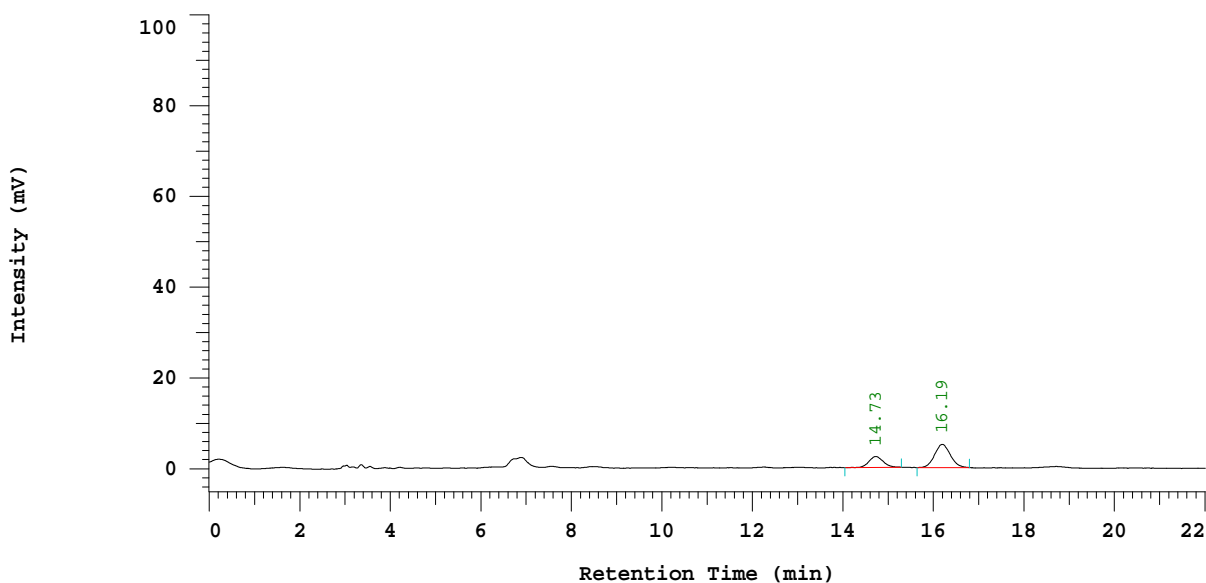
Processed Date and Time: 2014/05/19 01:48 下午

Data Path: D:\NITIN\DATA\0126\

Processing Method: Test-IPA/Hx-2

System (acquisition): Sys 1 Series: 0126  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-184-F1 (CO) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/Min Col-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: Test-IPA/Hx-2

Column Type: IA

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.73	52989	2388	30.104
2	16.19	123033	5105	69.896
		176022	7493	100.000

Peak rejection level: 5000

Fig S101. HPLC analysis of the mixture of chiral compound 4e and the racemic 4e, for comparison (Scheme 2, Method A)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/19 01:06 下午  
 Reported Date and Time: 2014/05/19 02:13 下午

Processed Date and Time: 2014/05/19 02:12 下午

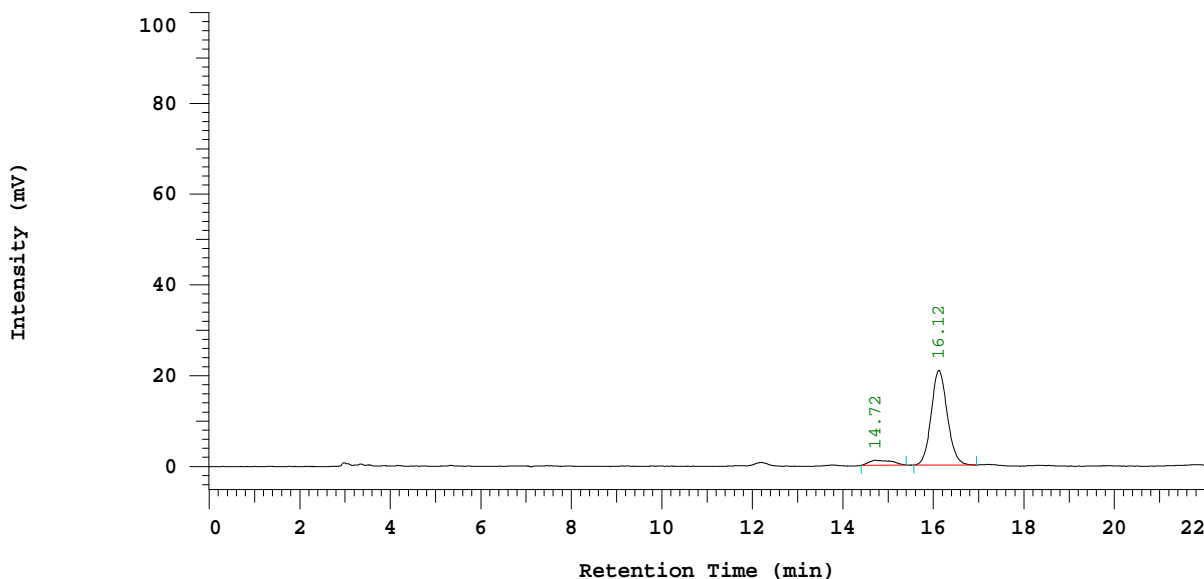
Data Path: D:\NITIN\DATA\0127\

Processing Method: Test-IPA/Hx-2

System (acquisition): Sys 1 Series: 0127  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-03-F1 (Chiral-C-A- Vial Type: UNK  
 1:1) Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 10%IPA+HX 1mL/Min Col-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: Test-IPA/Hx-2 Method Developer: NSD  
 Column Type: IA  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	14.72	38566	1089	6.964
2	16.12	515258	20859	93.036
		553824	21948	100.000

Peak rejection level: 5000

Fig S102. HPLC analysis of the compound 4e (Scheme 2, Method B)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/30 02:54 下午  
 Reported Date and Time: 2014/05/30 03:38 下午

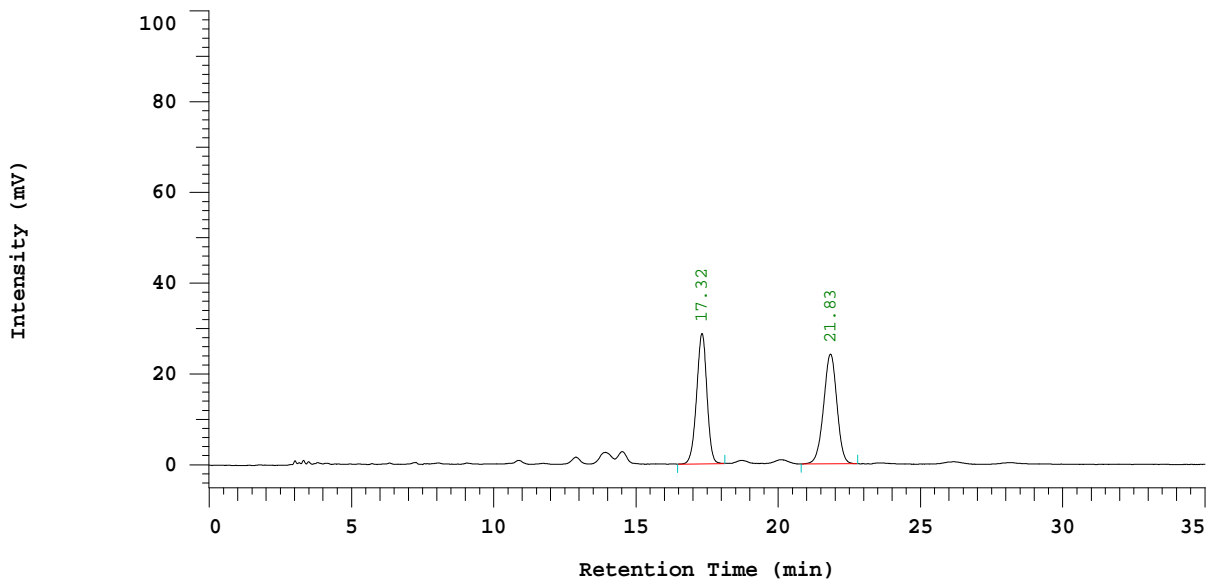
Processed Date and Time: 2014/05/30 03:38 下午

Data Path: D:\NITIN\DATA\0130\

Processing Method: test-IPA/Hx-2 (Final Compound)

System (acquisition): Sys 1 Series: 0130  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-147 (Final-CSA) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-2 (Final Compound)  
 Column Type: IA Method Developer: NITIN

Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.32	723156	28683	48.205
2	21.83	777024	24155	51.795
		1500180	52838	100.000

Peak rejection level: 200000

Fig S103. HPLC analysis of the compound 1a (Table 2, entry 1).

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/12/17 02:09 下午  
 Reported Date and Time: 2013/12/17 02:57 下午

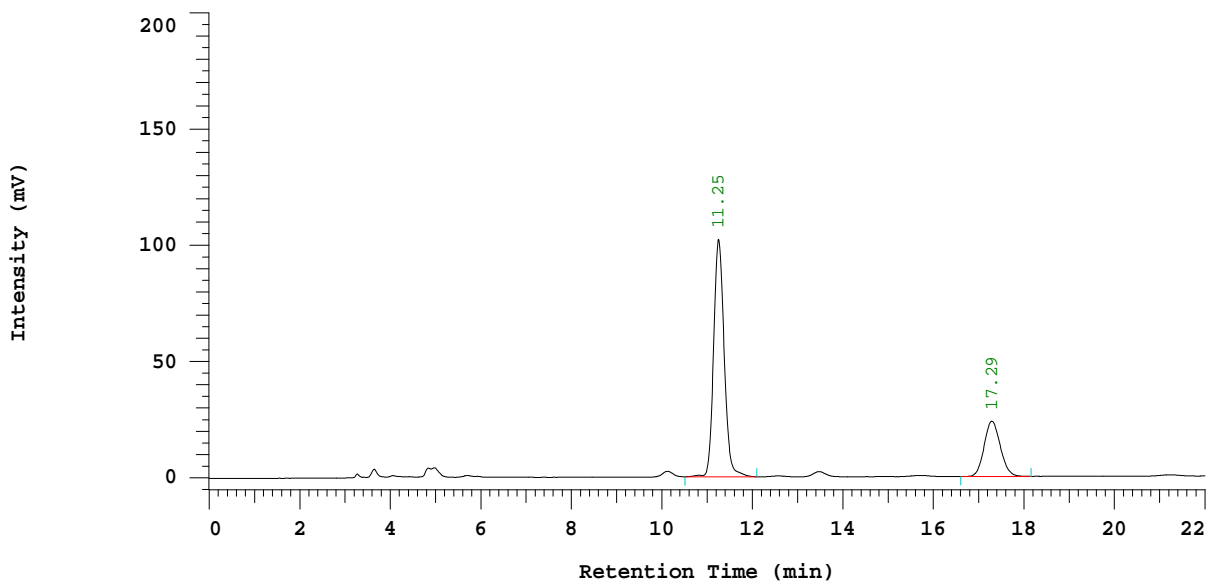
Processed Date and Time: 2013/12/17 02:56 下午

Data Path: D:\NITIN\DATA\0050\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0050  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-147 (Recovered MP) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1

Column Type: IC

Method Developer: NSD

Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA

Calculation Method: EXT-STD

Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.25	1654655	102039	73.627
2	17.29	592693	23754	26.373
		2247348	125793	100.000

Peak rejection level: 200000

Fig S104. HPLC analysis of the recovered compound 4a, (Table 2, entry 1)



### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/01/28 11:59 上午  
 Reported Date and Time: 2014/06/20 11:05 上午

Processed Date and Time: 2014/06/20 11:04 上午

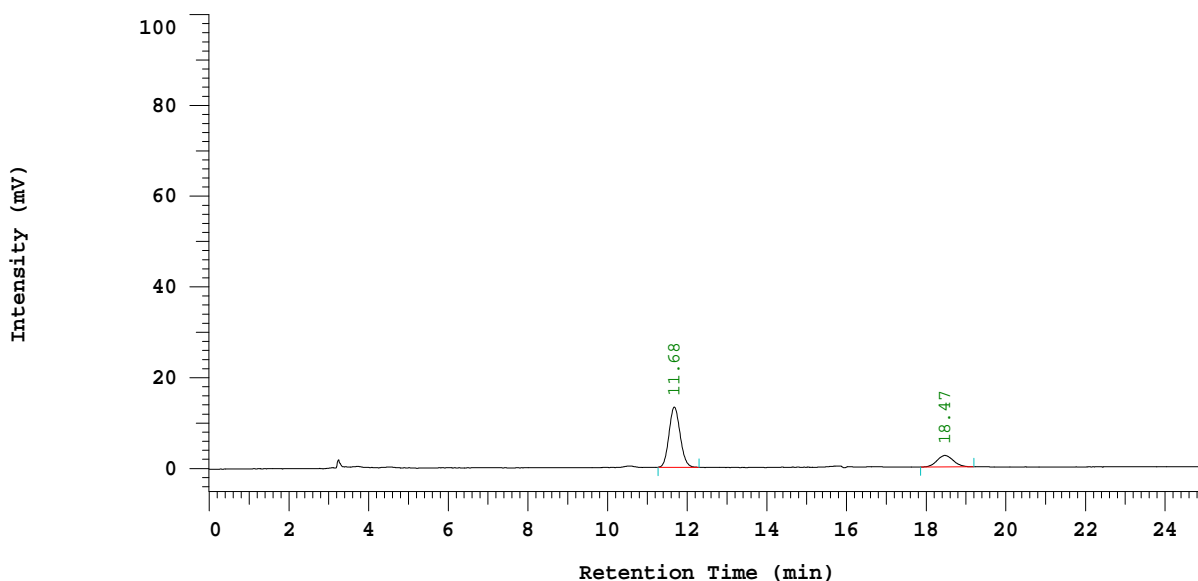
Data Path: D:\NITIN\DATA\0070\

Processing Method: Test-IPA/Hx-1

System (acquisition): Sys 1 Series: 0070  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-168 (MichaelP-CSA-6day) Vial Type: UNK  
 Volume: 20.0 ul

Injection from this vial: 1 of 1  
 Sample Description: 5%IPA+HX 1mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 275 nm



Processing Method: Test-IPA/Hx-1  
 Column Type: IC Method Developer: NSD  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 275 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	11.68	255937	13244	78.132
2	18.47	71631	2505	21.868
		327568	15749	100.000

Peak rejection level: 5000

Fig S105. HPLC analysis of the recovered compound 4a, (Table 2, entry 2)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/30 02:14 下午  
 Reported Date and Time: 2014/05/30 03:40 下午

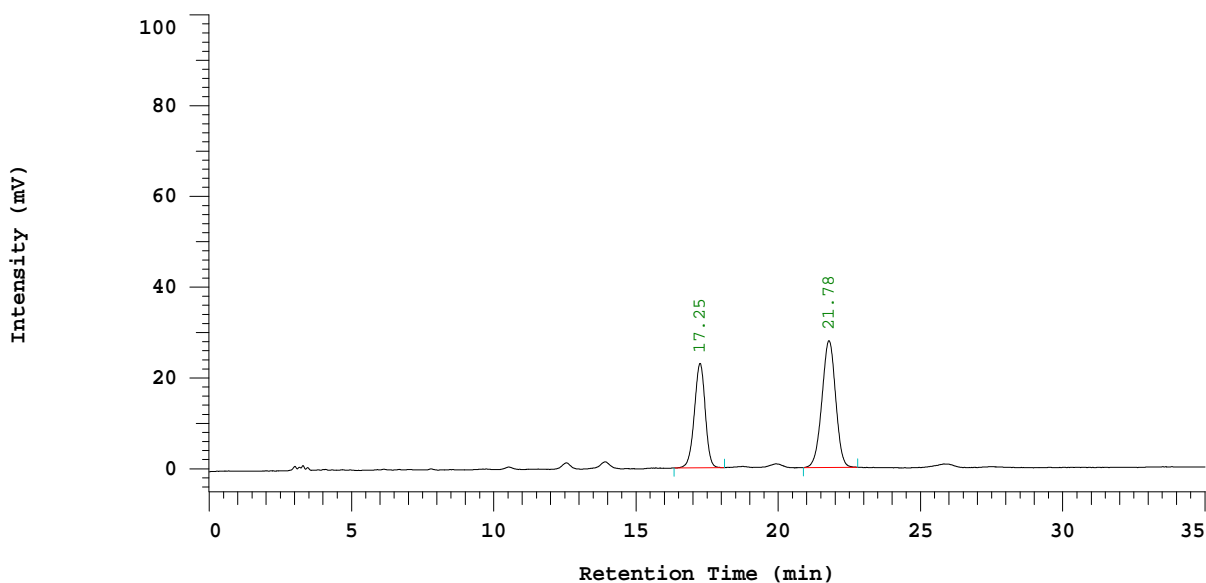
Processed Date and Time: 2014/05/30 03:39 下午

Data Path: D:\NITIN\DATA\0129\

Processing Method: test-IPA/Hx-2 (Final Compound)

System (acquisition): Sys 1 Series: 0129  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-15 Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-2 (Final Compound)  
 Column Type: IA Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.25	607459	22992	39.575
2	21.78	927482	27934	60.425
		1534941	50926	100.000

Peak rejection level: 200000

Fig S106. HPLC analysis of compound 1a, (Table 2, entry 3)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2014/05/30 12:34 下午  
 Reported Date and Time: 2014/05/30 12:29 下午

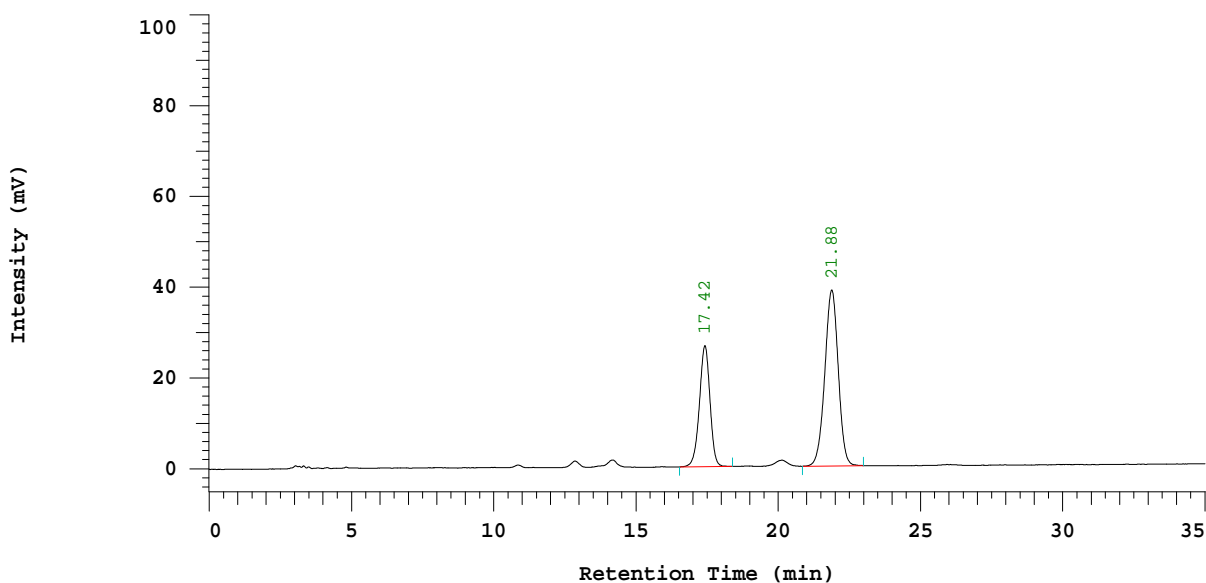
Processed Date and Time: 2014/05/30 12:28 下午

Data Path: D:\NITIN\DATA\0128\

Processing Method: test-IPA/Hx-2 (Final Compound)

System (acquisition): Sys 1 Series: 0128  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-10-21 Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-2 (Final Compound)  
 Column Type: IA Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	17.42	688054	26698	35.306
2	21.88	1260762	38718	64.694
		1948816	65416	100.000

Peak rejection level: 200000

Fig S107. HPLC analysis of compound 1a, (Table 2, entry 4)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/11/14 10:18 上午  
 Reported Date and Time: 2013/11/14 11:47 上午

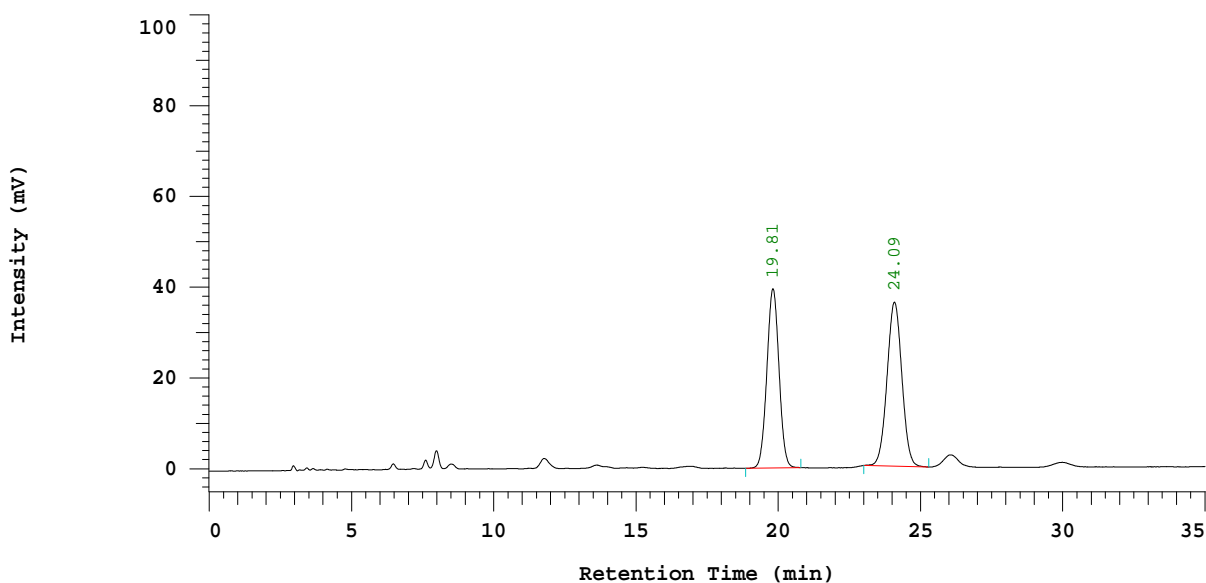
Processed Date and Time: 2013/11/14 11:45 上午

Data Path: D:\NITIN\DATA\0036\

Processing Method: test-IPA/Hx-2 (Final Compound)

System (acquisition): Sys 1 Series: 0036  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-124 (AKA-DCM) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-2 (Final Compound)  
 Column Type: IA Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	19.81	1155936	39478	47.185
2	24.09	1293857	36107	52.815
		2449793	75585	100.000

Peak rejection level: 200000

Fig S108. HPLC analysis of compound 1a, (Table 3, entry 1)

### D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2013/11/14 11:06 上午  
 Reported Date and Time: 2013/11/14 11:50 上午

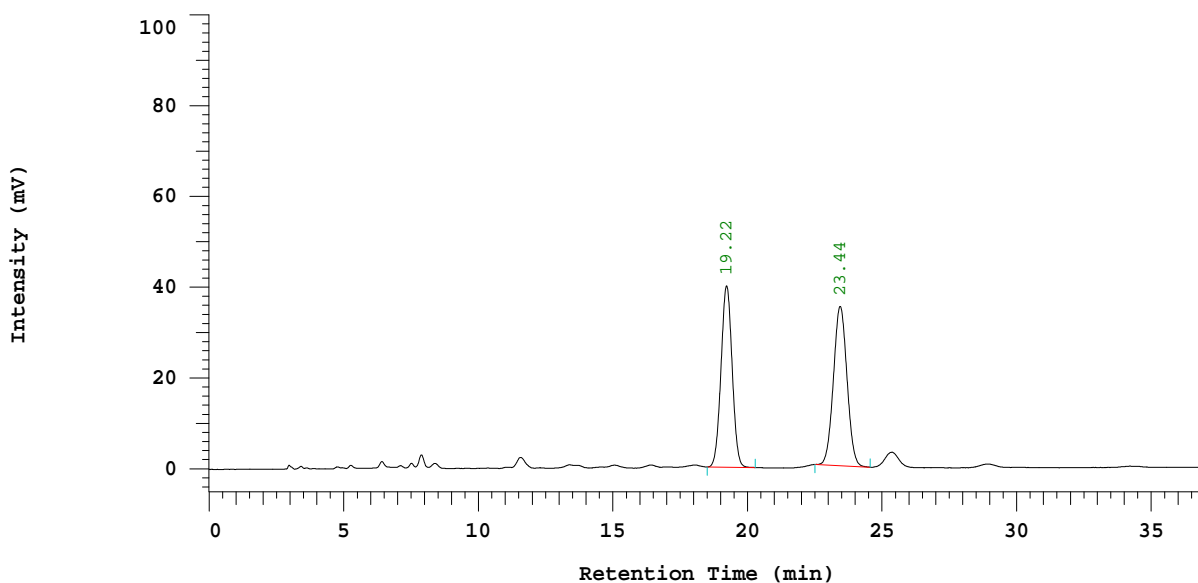
Processed Date and Time: 2013/11/14 11:49 上午

Data Path: D:\NITIN\DATA\0037\

Processing Method: test-IPA/Hx-2 (Final Compound)

System (acquisition): Sys 1 Series: 0037  
 Application(data): NITIN Vial Number: 1  
 Sample Name: NSD-09-125 (AKA-toluene) Vial Type: UNK  
 Injection from this vial: 1 of 1 Volume: 20.0 ul  
 Sample Description: 10%IPA+HX 1mL/MIN COL-IA

Chrom Type: Fixed WL Chromatogram, 280 nm



Processing Method: test-IPA/Hx-2 (Final Compound)  
 Column Type: IA Method Developer: NITIN  
 Method Description:

Chrom Type: Fixed WL Chromatogram, 280 nm

Peak Quantitation: AREA  
 Calculation Method: EXT-STD  
 Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	19.22	1133611	39948	48.246
2	23.44	1216012	35076	51.754
		2349623	75024	100.000

Peak rejection level: 200000

Fig S109. HPLC analysis of compound 1a, (Table 3, entry 2)