

## **Supporting Information**

**to**

**“From Simple Diols to Carbohydrate Derivatives of Phenylarsonic Acid”**

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## Experimental Section

Phenylarsonic acid, *meso*-2,3-butanediol, *alpha*-hydroxycyclopropanecarboxylic acid (all Acros), ethane-1,2-diol, 1,2-dihydroxybenzene, (*rac*)-*trans*-1,2-cyclohexanediol, *cis*-1,2-cyclohexanediol, methyl  $\alpha$ -D-mannopyranoside (all Fluka), perfluoropinacol (ABCR), naphthalene-2,3-diol (Merck), *o*-aminophenol (EGA), *cis*-1,2-cyclopentanediol and pinacol (Aldrich) were obtained commercially and used as supplied without further purification. Anhydroerythritol [1], 1,1'-bicyclohexyl-1,1'-diol [2] and *exo-cis*-2,3-norbornanediol [3] were synthesized according to standard procedures. Benzene and toluene (both Fluka) were dried over molecular sieves prior to use. The same holds true for the deuterated solvents ( $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , both Aldrich) applied for NMR measurements. The synthesis of phenyl-substituted *spiro*-arsoranes derived from ethane-1,2-diol (Etg) [4], pinacole (Pina) [5], 1,2-dihydroxybenzene (Cat) [6], naphthalene-2,3-diol (Nptd) [4] and *o*-aminophenol (oAmph) [6] was conducted according to published procedures.

NMR spectra were recorded on a JEOL Eclipse 270, a JEOL Eclipse 400 and a JEOL EX-400 spectrometer. Data were processed using the Delta software (by JEOL).  $^1\text{H}$ - and  $^{13}\text{C}$  signal shifts were referenced towards TMS as primary internal or the solvent signal as secondary internal standard,  $\text{CFCl}_3$  served as external reference for the shifts of  $^{19}\text{F}$  signals. All measurements were performed at room temperature. Mass spectra were obtained on a JEOL JMS-700 apparatus and a Finnigan MAT 95 apparatus (HRMS). IR-spectra were taken on a Perkin Elmer Spectrum BX FT-IR spectrometer. Raman spectra were done on a Perkin Elmer 2000 NIR FT-spectrometer. UV/Vis-spectra were recorded on a Varian CARY 50 BIO UV-visible spectrometer applying cuvettes made of quartz glass. Air was admitted in between the laser, the sample and the detector. Scanning was conducted between 1100 nm and 190 nm. Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Until otherwise stated all manipulations and reactions were conducted without special precautions to exclude oxygen or moisture.

Elemental analysis were precluded by technical problems arising from arsenic in the sample resulting in severe damage to the analytical apparatus.

The application of benzene as the solvent during synthesis procedures is not mandatory but can also be substituted for toluene or cyclohexane.

**PhAs(*meso*-ButdH<sub>2</sub>)<sub>2</sub> (1):** Phenylarsonic acid (1.01 g, 5 mmol) and *meso*-2,3-butanediol (0.90 g, 10.0 mmol) were suspended in benzene (50 mL) and heated under reflux for four

hours. The water liberated during the reaction was removed by azeotropic distillation and collected in a Dean-Stark-trap. The solvent was removed entirely from the clear reaction mixture under reduced pressure and the oily residue was stored at ambient temperature. In the course of two months the oil completely crystallized yielding large colourless platelets with a slightly sweet odour (1.56 g, 4.75 mmol, 95.0% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.8 MHz, 22 °C):  $\delta$  = 8.24–8.22 (m,  $\text{H}_{\text{ar}}$ ), 8.08–8.05 (m,  $\text{H}_{\text{ar}}$ ), 7.97–7.93 (m,  $\text{H}_{\text{ar}}$ ), 7.56–7.45 (m,  $\text{H}_{\text{ar}}$ ), 4.24–4.14 (m,  $\text{HCO}$ ), 3.91–3.77 (m,  $\text{HCO}$ ), 3.62–3.57 (m,  $\text{HCO}$ ), 1.21–1.18 (m,  $\text{CH}_3$ ), 1.06–1.04 (m,  $\text{CH}_3$ ), 1.00–0.99 (m,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.5 MHz, 24 °C):  $\delta$  = 138.8 ( $\text{C}_{\text{ar}}$ ), 137.8 ( $\text{C}_{\text{ar}}$ ), 135.5 ( $\text{C}_{\text{ar}}$ ), 133.5 ( $\text{C}_{\text{ar}}$ ), 132.4 ( $\text{C}_{\text{ar}}$ ), 132.2 ( $\text{C}_{\text{ar}}$ ), 132.1 ( $\text{C}_{\text{ar}}$ ), 131.6 ( $\text{C}_{\text{ar}}$ ), 129.2 ( $\text{C}_{\text{ar}}$ ), 129.1 ( $\text{C}_{\text{ar}}$ ), 129.0 ( $\text{C}_{\text{ar}}$ ), 128.9 ( $\text{C}_{\text{ar}}$ ), 70.4 ( $\text{HCO}$ ), 70.3 ( $\text{HCO}$ ), 69.2 ( $\text{HCO}$ ), 69.1 ( $\text{HCO}$ ), 16.5 ( $\text{CH}_3$ ), 16.1 ( $\text{CH}_3$ ) ppm. MS- $\text{EI}^+$  (intensity):  $m/z$  = 328 (0.5,  $[\text{M}]^+$ ), 152 (98,  $[\text{M}-\text{C}_4\text{H}_8\text{O}_2-\text{C}_4\text{H}_8\text{O}_2]^+$ ). HRMS- $\text{DEI}^+$ : calculated for  $\text{C}_{14}\text{H}_{21}\text{AsO}_4^+$  ( $\text{M}^+$ ): 328.0656; found: 328.0647. IR absorptions (neat):  $\nu_{\text{bar}}$  = 3059 (w), 2982 (w), 2972 (w), 2920 (w), 2873 (w), 1455 (w), 1437 (m), 1375 (m), 1354 (w), 1344 (w), 1305 (w), 1287 (w), 1261 (w), 1166 (w), 1111 (w), 1075 (s), 1013 (s), 995 (m), 938 (m), 920 (s), 910 (s), 887 (w), 791 (s), 752 (s), 706 (s), 696 (s), 680 (s), 665 (s), 634 (s)  $\text{cm}^{-1}$ . Raman frequencies (100 mW, 100 scans) (intensity): 3062 (57), 2986 (44), 2973 (33), 2938 (52), 2920 (77), 2874 (27), 1578 (19), 1461 (10), 1445 (19), 1350 (7), 1323 (9), 1291 (12), 1172 (14), 1160 (17), 1142 (7), 1113 (9), 1089 (10), 1017 (18), 1000 (71), 795 (12), 689 (11), 666 (100), 638 (7), 615 (13), 599 (14), 521 (9), 432 (10), 342 (51), 283 (14), 245 (22). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.1, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 258.0, 264.0, 270.5. Melting point: 60.9–64.9 °C.

**PhAs(*exo-cis*-2,3-NorbornH<sub>2</sub>)<sub>2</sub> (2):** This compound was prepared according to the procedure used for the preparation of **3** from phenylarsonic acid (0.505 g, 2.50 mmol) and *exo-cis*-2,3-norbornanediol (0.641 g, 5.00 mmol) with a heating period of five hours. Stripping the clear reaction mixture of the solvent under reduced pressure yielded a colourless solid which was recrystallized from boiling toluene (4 mL). After cooling to room temperature medium-sized colourless platelets with a pleasant sweet smell are obtained overnight (1.01 g, 2.50 mmol, 100% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270.2 MHz, 23 °C):  $\delta$  = 7.97–7.94 (m,  $\text{H}_{\text{ar}}$ ), 7.85–7.80 (m,  $\text{H}_{\text{ar}}$ ), 7.57–7.44 (m,  $\text{H}_{\text{ar}}$ ), 4.064–4.058 (m,  $\text{HCO}$ ), 3.612–3.606 (m,  $\text{HCO}$ ), 3.484–3.478 (m,  $\text{HCO}$ ), 2.36–2.34 (m,  $\text{CH}$ ), 2.29–2.28 (m,  $\text{CH}$ ), 2.14–2.12 (m,  $\text{CH}$ ), 1.75–1.71 (m,  $\text{CH}_2$ ), 1.52–1.36 (m,  $\text{CH}_2$ ), 1.14–0.96 (m,  $\text{CH}_2$ ), 0.80–0.68 (m,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz, 25 °C):  $\delta$  = 135.1 ( $\text{C}_{\text{ar}}$ ), 132.20 ( $\text{C}_{\text{ar}}$ ), 132.19 ( $\text{C}_{\text{ar}}$ ), 132.1 ( $\text{C}_{\text{ar}}$ ), 131.3 ( $\text{C}_{\text{ar}}$ ), 129.2 ( $\text{C}_{\text{ar}}$ ), 129.0 ( $\text{C}_{\text{ar}}$ ), 76.4 ( $\text{HCO}$ ), 74.3 ( $\text{HCO}$ ), 74.2 ( $\text{HCO}$ ), 41.9 ( $\text{CH}$ ), 41.8 ( $\text{CH}$ ), 41.7 ( $\text{CH}$ ), 31.7 ( $\text{CH}_2$ ), 31.2 ( $\text{CH}_2$ ), 31.1 ( $\text{CH}_2$ ), 24.4 ( $\text{CH}_2$ ), 24.2 ( $\text{CH}_2$ ) ppm. MS- $\text{DEI}^+$

(intensities):  $m/z = 404$  (0.1,  $[M]^+$ ), 278 (100,  $[M-C_7H_{10}O_2]^+$ ), 152 (42,  $[M-C_7H_{10}O_2-C_7H_{10}O_2]^+$ ). HRMS-DEI<sup>+</sup>: calculated for  $C_{20}H_{25}AsO_4^+$  ( $M^+$ ): 404.0969; found: 404.0976. IR absorptions (neat):  $\bar{\nu} = 2966$  (s), 2946 (m), 2930 (m), 2920 (m), 2904 (s), 2868 (m), 1465 (m), 1439 (m), 1393 (w), 1339 (m), 1313 (w), 1305 (w), 1290 (w), 1282 (w), 1261 (m), 1225 (w), 1223 (w), 1184 (w), 1163 (w), 1137 (m), 1093 (m), 1068 (m), 1026 (s), 956 (w), 944 (w), 931 (w), 920 (m), 887 (w), 871 (m), 840 (m), 825 (m), 794 (m), 765 (w), 758 (w), 750 (m), 693 (m), 685 (m), 657 (m), 613 (w)  $cm^{-1}$ . Raman frequencies (100 mW, 100 scans) (intensity): 3059 (40), 2981 (100), 2946 (36), 2919 (41), 2909 (54), 2868 (21), 1583 (17), 1472 (8), 1447 (25), 1343 (10), 1315 (8), 1291 (14), 1283 (9), 1218 (13), 1207 (9), 1187 (8), 1164 (11), 1117 (18), 1094 (14), 1066 (12), 1043 (22), 1012 (14), 998 (53), 959 (13), 944 (15), 922 (39), 889 (24), 845 (15), 803 (8), 770 (10), 695 (9), 668 (68), 615 (13), 567 (12), 492 (9), 451 (14), 369 (10), 359 (9), 299 (11), 261 (30), 200 (36). UV/Vis (acetonitrile):  $\lambda_{max}/nm = 256.9, 262.4, 268.4$ , UV/Vis (cyclohexane):  $\lambda_{max}/nm = 252.1, 263.5, 269.5$ . Melting point: 230.3–232.1 °C (decomposition).

**PhAs(*cis*-1,2-CptdH<sub>2</sub>)<sub>2</sub> (3):** Phenylarsonic acid (1.01 g, 5 mmol) and *cis*-1,2-cyclopentanediol (1.02 g, 10.0 mmol) were suspended in benzene (50 mL) and heated under reflux for five hours. The water liberated during the reaction was removed by azeotropic distillation and collected in a Dean-Stark-trap. A little amount of undissolved solid was removed by filtering the reaction mixture through a coarse-sintered glass-disk. The solvent was removed under reduced pressure and the pale yellow powder recrystallized from boiling toluene (5 mL). After cooling to room temperature the flask was stored at –25 °C upon which small colourless platelets with a slightly sweet odour are obtained in the course of two months (0.24 g, 0.68 mmol, 13.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270.2 MHz, 23 °C):  $\delta = 8.04$ – $8.00$  (m, H<sub>ar</sub>), 7.95–7.91 (m, H<sub>ar</sub>), 7.87–7.84 (m, H<sub>ar</sub>), 7.57–7.41 (m, H<sub>ar</sub>), 4.52–4.48 (m, HCO), 4.15–4.14 (m, HCO), 4.04–4.03 (m, HCO), 1.93–1.59 (m, CH<sub>2</sub>), 1.54–1.44 (m, CH<sub>2</sub>), 1.25–1.11 (m, CH<sub>2</sub>), 1.01–0.84 (m, CH<sub>2</sub>) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 67.9 MHz, 26 °C):  $\delta = 136.6$  (C<sub>ar</sub>), 135.3 (C<sub>ar</sub>), 132.1 (C<sub>ar</sub>), 132.0 (C<sub>ar</sub>), 131.9 (C<sub>ar</sub>), 131.8 (C<sub>ar</sub>), 131.5 (C<sub>ar</sub>), 131.3 (C<sub>ar</sub>), 129.2 (C<sub>ar</sub>), 128.9 (C<sub>ar</sub>), 128.5 (C<sub>ar</sub>), 74.1 (HCO), 73.7 (HCO), 72.8 (HCO), 72.4 (HCO), 34.41 (CH<sub>2</sub>), 34.39 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 21.55 (CH<sub>2</sub>), 21.49 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>) ppm. MS-Cl<sup>+</sup> (NH<sub>3</sub>):  $m/z = 352$  ( $[M]^+$ ), 252 ( $[M-C_5H_8O_2]^+$ ), 152 ( $[M-C_5H_8O_2-C_5H_8O_2]^+$ ). HRMS-DEI<sup>+</sup>: calculated for  $C_{16}H_{21}AsO_4^+$  ( $M^+$ ): 352.0656; found: 352.0637. IR absorptions (neat):  $\bar{\nu} = 2956$  (m), 2930 (m), 2884 (w), 1331 (w), 1261 (m), 1212 (w), 1104 (m), 1088 (s), 1021 (s), 980 (s), 933 (w), 863 (w), 794 (s), 755 (m), 719 (w), 693 (m), 680 (m), 649 (m)

cm<sup>-1</sup>. Raman frequencies (100 mW, 100 scans) (intensity): 3062 (62), 2955 (73), 2930 (65), 1586 (31), 1440 (37), 1306 (27), 1286 (23), 1219 (21), 1189 (21), 1091 (25), 1043 (28), 1027 (31), 1001 (100), 902 (42), 835 (26), 684 (34), 666 (59), 615 (35), 310 (65), 257 (35), 193 (35). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 262.4, 269.1, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.5. Melting point: 101.1–112.3 °C.

**PhAs(AnErytH-<sub>2</sub>)<sub>2</sub> (4):** **4** was prepared according to the procedure used for the preparation of **3** from phenylarsonic acid (1.01 g, 5 mmol) and anhydroerythritol (0.75 mL, 1.04 g, 10.0 mmol) with a heating period of five hours. After filtration and solvent removal the colourless powder was recrystallized from boiling toluene (6 mL). After cooling to room temperature medium-sized colour- and odourless platelets and blocks are obtained in the course of two days (1.32 g, 3.71 mmol, 74.2% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270.2 MHz, 23 °C):  $\delta$  = 7.92–7.79 (m, H<sub>ar</sub>), 7.60–7.39 (m, H<sub>ar</sub>), 7.23–7.13 (m, H<sub>ar</sub>), 4.63–4.60 (m, CH), 4.26–4.22 (m, CH), 4.00–3.95 (m, CH), 3.74–3.60 (m, CH), 3.49–3.44 (m, CH) ppm. <sup>13</sup>C {<sup>1</sup>H}NMR (CDCl<sub>3</sub>, 67.9 MHz, 24 °C):  $\delta$  = 136.3 (C<sub>ar</sub>), 134.9 (C<sub>ar</sub>), 134.2 (C<sub>ar</sub>), 132.7 (C<sub>ar</sub>), 132.5 (C<sub>ar</sub>), 132.2 (C<sub>ar</sub>), 131.2 (C<sub>ar</sub>), 131.0 (C<sub>ar</sub>), 129.6 (C<sub>ar</sub>), 129.1 (C<sub>ar</sub>), 128.5 (C<sub>ar</sub>), 128.2 (C<sub>ar</sub>), 75.0 (CH<sub>2</sub>), 74.9 (CH<sub>2</sub>), 74.8 (CH<sub>2</sub>), 74.7 (CH<sub>2</sub>), 72.4 (HCO), 72.2 (HCO), 71.34 (HCO), 71.33 (HCO) ppm. MS-DEI<sup>+</sup> (intensities):  $m/z$  = 356 (1, [M]<sup>+</sup>), 254 (88, [M–C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>]<sup>+</sup>), 152 (100, [M–C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>–C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>]<sup>+</sup>). HRMS-DEI<sup>+</sup>: calculated for C<sub>14</sub>H<sub>17</sub>AsO<sub>6</sub><sup>+</sup> (M<sup>+</sup>): 356.0241; found: 356.0228. IR absorptions (neat):  $\nu_{\text{bar}}$  = 2966 (m), 2956 (m), 2941 (m), 2868 (m), 1481 (w), 1470 (w), 1455 (w), 1439 (m), 1367 (w), 1339 (w), 1310 (w), 1290 (w), 1279 (w), 1266 (w), 1212 (w), 1122 (w), 1109 (s), 1083 (m), 1068 (s), 1029 (s), 1000 (m), 928 (s), 910 (m), 902 (m), 851 (m), 830 (s), 745 (m), 732 (m), 693 (m), 685 (m), 683 (m), 646 (s), 610 (m) cm<sup>-1</sup>. Raman frequencies (100 mW, 100 scans) (intensity): 3073 (39), 3007 (26), 2973 (34), 2955 (48), 2942 (42), 2871 (26), 1579 (19), 1463 (14), 1289 (12), 1228 (12), 1183 (9), 1160 (10), 1083 (10), 1064 (10), 1044 (20), 1025 (18), 1003 (47), 937 (20), 913 (12), 850 (18), 730 (9), 681 (7), 649 (100), 614 (12), 505 (12), 472 (12), 427 (13), 342 (31), 302 (14), 276 (29), 218 (13), 202 (18). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.5, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 263.5. Melting point: 134.1–160.5 °C (decomposition becomes apparent by partial solidification).

**PhAs(*cis*-1,2-ChxdH-<sub>2</sub>)<sub>2</sub> (5):** Phenylarsonic acid (1.01 g, 5 mmol) and *cis*-1,2-cyclohexanediol (1.16 g, 10.0 mmol) were suspended in benzene (50 mL) and heated under reflux for five hours. A little amount of undissolved solid was removed by filtering the reaction mixture through a coarse-sintered glass-disk. The solvent was removed under reduced pressure and the obtained foam-like solid was triturated with *n*-pentane (10 mL)

upon which a colourless powder was formed. Recrystallization from boiling toluene (5 mL) and storage at 4 °C afforded medium-sized colour- and odourless platelets and crystal blocks in the course of twelve weeks (0.32 g, 0.84 mmol, 16.8% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.8 MHz, 23 °C):  $\delta$  = 8.38–8.35 (m,  $\text{H}_{\text{ar}}$ ), 8.15–8.12 (m,  $\text{H}_{\text{ar}}$ ), 7.96–7.93 (m,  $\text{H}_{\text{ar}}$ ), 7.58–7.45 (m,  $\text{H}_{\text{ar}}$ ), 4.11–4.03 (m, HCO), 3.77–3.73 (m, HCO), 1.88–1.55 (m,  $\text{CH}_2$ ), 1.49–1.16 (m,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.5 MHz, 24 °C):  $\delta$  = 138.1 ( $\text{C}_{\text{ar}}$ ), 135.8 ( $\text{C}_{\text{ar}}$ ), 134.6 ( $\text{C}_{\text{ar}}$ ), 132.9 ( $\text{C}_{\text{ar}}$ ), 132.5 ( $\text{C}_{\text{ar}}$ ), 132.1 ( $\text{C}_{\text{ar}}$ ), 131.9 ( $\text{C}_{\text{ar}}$ ), 131.5 ( $\text{C}_{\text{ar}}$ ), 129.11 ( $\text{C}_{\text{ar}}$ ), 129.07 ( $\text{C}_{\text{ar}}$ ), 129.0 ( $\text{C}_{\text{ar}}$ ), 128.3 ( $\text{C}_{\text{ar}}$ ), 70.8 (HCO), 70.7 (HCO), 69.6 (HCO), 69.4 (HCO), 30.2 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 29.8 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 21.40 ( $\text{CH}_2$ ), 21.37 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_2$ ) ppm. MS- $\text{DCI}^+$  ( $\text{NH}_3$ ):  $m/z$  = 381 ( $[\text{M}+\text{H}^+]^+$ ), 266 ( $[\text{M}-\text{C}_6\text{H}_{10}\text{O}_2]^+$ ), 152 ( $[\text{M}-\text{C}_6\text{H}_{10}\text{O}_2-\text{C}_6\text{H}_{10}\text{O}_2]^+$ ). HRMS- $\text{DEI}^+$ : calculated for  $\text{C}_{18}\text{H}_{25}\text{AsO}_4^+$  ( $\text{M}^+$ ): 380.0969; found: 380.0955. IR absorptions (neat):  $\nu_{\text{bar}}$  = 3049 (w), 2938 (s), 2927 (s), 2905 (s), 2858 (s), 1708 (w), 1481 (w), 1461 (w), 1440 (m), 1405 (w), 1371 (m), 1364 (m), 1339 (w), 1310 (w), 1249 (w), 1185 (w), 1150 (w), 1122 (w), 1089 (m), 1062 (w), 1052 (m), 1045 (m), 1034 (s), 980 (s), 917 (m), 897 (m), 857 (m), 824 (m), 778 (m), 748 (m), 694 (s)  $\text{cm}^{-1}$ . Raman frequencies (100 mW, 100 scans) (intensity): 3066 (61), 2941 (100), 2904 (77), 2856 (47), 1585 (29), 1576 (23), 1449 (26), 1434 (21), 1373 (12), 1355 (13), 1339 (15), 1316 (16), 1257 (28), 1199 (14), 1186 (15), 1162 (14), 1148 (13), 1126 (10), 1092 (13), 1065 (23), 1037 (24), 1001 (81), 958 (10), 917 (10), 857 (22), 822 (9), 782 (55), 702 (26), 675 (59), 624 (78), 605 (10), 573 (16), 470 (15), 453 (15), 399 (19), 343 (35), 253 (39), 233 (71), 177 (26). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.1, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 259.0, 263.5, 270.0. Melting point: 110.1–121.0 °C.

***rac*-PhAs(*trans*-1,2-ChxdH<sub>2</sub>)<sub>2</sub> (6):** This compound was prepared according to the procedure used for the preparation of **3** from phenylarsonic acid (1.01 g, 5 mmol) and (*rac.*)-*trans*-1,2-cyclohexanediol (1.16 g, 10.0 mmol) with a heating period of five hours. After filtration and solvent removal the colourless powder was recrystallized from boiling toluene (5 mL). After cooling to room temperature medium-sized colourless platelets and crystal blocks with plasticine-like smell are obtained overnight (1.52 g, 4.00 mmol, 80.0% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270.2 MHz, 23 °C):  $\delta$  = 8.09–8.01 (m,  $\text{H}_{\text{ar}}$ ), 7.60–7.47 (m,  $\text{H}_{\text{ar}}$ ), 3.53–3.41 (m,  $\text{CH}_2$ ), 3.08–2.95 (m,  $\text{CH}_2$ ), 2.21–2.01 (m,  $\text{CH}_2$ ), 1.76–1.70 (m,  $\text{CH}_2$ ), 1.60–1.18 (m,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz, 25 °C):  $\delta$  = 136.2 ( $\text{C}_{\text{ar}}$ ), 135.8 ( $\text{C}_{\text{ar}}$ ), 132.5 ( $\text{C}_{\text{ar}}$ ), 132.3 ( $\text{C}_{\text{ar}}$ ), 132.2 ( $\text{C}_{\text{ar}}$ ), 129.2 ( $\text{C}_{\text{ar}}$ ), 129.1 ( $\text{C}_{\text{ar}}$ ), 129.0 ( $\text{C}_{\text{ar}}$ ), 128.2 ( $\text{C}_{\text{ar}}$ ), 77.8 (HCO), 77.6 (HCO), 76.9 (HCO), 76.5 (HCO), 30.3 ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_2$ ), 29.97 ( $\text{CH}_2$ ), 29.95 ( $\text{CH}_2$ ), 24.39 ( $\text{CH}_2$ ), 24.37 ( $\text{CH}_2$ ), 24.36 ( $\text{CH}_2$ ) ppm. MS- $\text{EI}^+$  (intensity):  $m/z$  = 380 (0.4,  $[\text{M}]^+$ ), 266 (100,  $[\text{M}-\text{C}_6\text{H}_{10}\text{O}_2]^+$ ), 152 (72,  $[\text{M}-\text{C}_6\text{H}_{10}\text{O}_2-\text{C}_6\text{H}_{10}\text{O}_2]^+$ ). HRMS- $\text{DEI}^+$ : calculated for

$\text{C}_{18}\text{H}_{25}\text{AsO}_4^+ (\text{M}^+)$ : 380.0969; found: 380.0956. IR absorptions (neat):  $\bar{\nu}$  = 2946 (s), 2930 (s), 2863 (s), 1357 (m), 1339 (w), 1318 (w), 1307 (w), 1287 (w), 1260 (w), 1233 (w), 1202 (w), 1168 (w), 1150 (w), 1140 (w), 1099 (s), 1077 (m), 1068 (m), 1031 (s), 998 (w), 946 (m), 931 (w), 884 (m), 856 (m), 835 (w), 791 (w), 747 (m), 693 (s), 667 (w), 641 (m), 616 (m), 605 (s)  $\text{cm}^{-1}$ . Raman frequencies (100 mW, 100 scans) (intensity): 3094 (14), 3021 (15), 3062 (61), 2971 (34), 2954 (84), 2903 (26), 2863 (61), 1583 (32), 1460 (15), 1451 (23), 1441 (20), 1371 (29), 1340 (10), 1318 (11), 1288 (10), 1241 (22), 1206 (19), 1187 (20), 1169 (17), 1140 (29), 1098 (8), 1077 (14), 1060 (33), 1043 (13), 1026 (23), 1000 (78), 946 (15), 838 (28), 796 (33), 693 (23), 668 (90), 614 (18), 576 (37), 453 (13), 289 (18), 280 (25), 246 (100), 203 (14), 191 (16), 148 (8).. UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.1, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 263.5. Melting point: 216.2–217.6 °C.

**{PhAs(BchxdH<sub>2</sub>)O}<sub>2</sub> (7):** Phenylarsonic acid (1.01 g, 5.00 mmol) and 1,1'-bicyclohexyl-1,1'-diol (0.99 g, 5.00 mmol) were suspended in benzene (50 mL) and heated under reflux for four hours. The water liberated during the reaction was removed by azeotropic distillation and collected in a Dean-Stark-trap. The turbid reaction mixture is filtered while still being hot and the colourless filtrate is left for free evaporation of the solvent at room temperature. Small colourless platelets without a characteristic smell are obtained (0.49 g, 0.67 mmol, 13.4% yield). <sup>1</sup>H NMR and <sup>13</sup>C NMR precluded by low solubility in common deuterated solvents. MS-DCI<sup>+</sup> (isobutane):  $m/z$  = 7209 ([M+H]<sup>+</sup>), 728 ([M]<sup>+</sup>), 532 (1, [M-C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>]<sup>+</sup>). HRMS-DEI<sup>+</sup>: calculated for  $\text{C}_{36}\text{H}_{50}\text{As}_2\text{O}_6^+ (\text{M}^+)$ : 728.2039; found: 728.1961. IR absorptions (neat):  $\bar{\nu}$  = 3068 (w), 2980 (w), 2957 (m), 2928 (s), 2890 (m), 2858 (m), 2847 (m), 1484 (w), 1444 (m), 1364 (w), 1349 (w), 1337 (w), 1316 (w), 1284 (w), 1256 (w), 1204 (w), 1189 (w), 1149 (w), 1126 (w), 1086 (m), 1074 (w), 1063 (w), 1041 (w), 1023 (w), 1001 (w), 962 (m), 945 (s), 922 (w), 912 (m), 871 (w), 854 (m), 842 (m), 824 (m), 768 (s), 754 (s), 716 (s), 695 (m), 679 (m), 663 (w)  $\text{cm}^{-1}$ . Raman frequencies (100 mW, 100 scans) (intensity): 3148 (3), 3071 (80), 3056 (43), 2980 (26), 2931 (100), 2894 (51), 2858 (39), 1585 (30), 1482 (4), 1444 (32), 1429 (20), 1350 (10), 1279 (30), 1257 (8), 1237 (10), 1205 (8), 1191 (12), 1168 (8), 1152 (14), 1126 (7), 1087 (16), 1076 (15), 1064 (12), 1046 (23), 1032 (25), 1002 (93), 952 (12), 916 (7), 844 (31), 826 (7), 784 (24), 752 (17), 726 (5), 682 (16), 666 (75), 615 (16), 592 (5), 523 (6), 500 (10), 487 (8), 468 (19), 425 (12), 353 (7), 316 (13), 299 (18), 274 (18), 242 (23), 231 (25), 222 (27), 203 (52), 162 (11), 140 (11).. UV/Vis (acetonitrile): no distinct absorption maxima in the range from 190.0–1100.0, UV/Vis (cyclohexane): no distinct absorption maxima in the range from 190.0–1100.0. Melting point: 248.9–250.0 (decomposition) °C.

**{PhAs(FpinH<sub>2</sub>)O}<sub>2</sub> (8):** Phenylarsonic acid (1.01 g, 5.00 mmol) and perfluoropinacol (1.67 g, 5.00 mmol) were suspended in benzene (50 mL) and heated under reflux for two hours. The water liberated during the reaction was removed by azeotropic distillation and collected in a Dean-Stark-trap. After cooling to room temperature large colourless platelets settled out from the reaction mixture (1.85 g, 1.85 mmol, 92.5% yield). <sup>1</sup>H, <sup>13</sup>C und <sup>19</sup>F NMR precluded by low solubility in common deuterated solvents. MS-DEI<sup>+</sup> (intensity): *m/z* = 1000 (0.7, [M]<sup>+</sup>), 931 (79, [M-CF<sub>3</sub>]<sup>+</sup>). HRMS-DEI<sup>+</sup>: calculated for C<sub>24</sub>H<sub>10</sub>As<sub>2</sub>F<sub>24</sub>O<sub>6</sub><sup>+</sup> (M<sup>+</sup>): 999.8526; found: 999.8511. IR absorptions (neat):  $\bar{\nu}$  = 1483 (w), 1447 (w), 1257 (m), 1228 (s), 1208 (s), 1189 (m), 1176 (m), 1165 (m), 1130 (m), 1098 (m), 1078 (m), 1027 (w), 996 (w), 957 (m), 935 (w), 882 (m), 772 (w), 748 (m), 740 (w), 716 (w), 685 (m), 660 (m) cm<sup>-1</sup>. Raman frequencies (100 mW, 100 scans) (intensity): 3071 (39), 1584 (41), 1286 (21), 1271 (21), 1187 (24), 1167 (24), 1098 (23), 1080 (22), 1028 (38), 1000 (100), 774 (43), 739 (29), 707 (24), 685 (42), 679 (42), 627 (31), 615 (31), 341 (31), 328 (36), 307 (42), 276 (29), 260 (34), 223 (39), 202 (27). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.6, 263.1, 269.1, UV/Vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  = 263.5. Melting point: 200.6–202.0 °C (decomposition becomes apparent by partial solidification).

**PhAs(Me-a-D-Manp-2,3H<sub>2</sub>)<sub>2</sub> (9):** Phenylarsonic acid (1.01 g, 5.00 mmol) and methyl  $\alpha$ -D-mannopyranoside (1.94 g, 10.0 mmol) were suspended in dioxane (70 mL) and heated under reflux for two hours. The water liberated during the reaction was removed by azeotropic distillation and collected in a Dean-Stark-trap. After one hour the water trap is emptied and an equal volume of fresh dioxane is added to the reaction mixture. Towards the end of the heating period the amount of solvent is reduced by periodic emptying of the water trap to about 30 mL. The remaining dioxane is removed entirely on a rotary evaporator upon which a colourless foam-like solid is obtained which is triturated with *n*-pentane (25 mL) at room temperature for one hour. The hydrocarbon is then removed entirely under reduced pressure and the white powder is recrystallized from boiling acetonitrile (20 mL). Storage at room temperature yielded white crystals (2.61 g, 4.87 mmol, 97.4% yield). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 399.8 MHz, 20 °C)  $\delta$  = 8.27–8.25 (m, H<sub>ar</sub>), 8.10–8.08 (m, H<sub>ar</sub>), 7.87–7.85 (m, H<sub>ar</sub>), 7.80–7.77 (m, H<sub>ar</sub>), 7.76–7.71 (m, H<sub>ar</sub>), 7.65–7.57 (m, H<sub>ar</sub>), 7.55–7.47 (m, H<sub>ar</sub>), 4.96 (s, CH), 4.88 (s, CH), 4.86 (s, CH), 4.11–4.03 (m, CH), 3.95–3.92 (m, CH), 3.83–3.76 (m, CH), 3.73–3.42 (m, CH), 3.37–3.36 (m, CH), 3.32–3.24 (m, CH), 1.978–1.976 (m, OCH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100.5 MHz, 22 °C)  $\delta$  = 136.8 (C<sub>ar</sub>), 136.7 (C<sub>ar</sub>), 136.4 (C<sub>ar</sub>), 135.7 (C<sub>ar</sub>), 135.2 (C<sub>ar</sub>), 135.1 (C<sub>ar</sub>), 134.8 (C<sub>ar</sub>), 134.5 (C<sub>ar</sub>), 134.2 (C<sub>ar</sub>), 132.7 (C<sub>ar</sub>), 132.0 (C<sub>ar</sub>), 131.2 (C<sub>ar</sub>), 130.8 (C<sub>ar</sub>), 130.7 (C<sub>ar</sub>), 130.6 (C<sub>ar</sub>), 100.7 (HCO), 100.4 (HCO), 100.1 (HCO), 100.0 (HCO), 76.13 (HC),



76.10 (HC), 74.7 (HC), 74.5 (HC), 72.9 (HC), 72.6 (HC), 72.15 (HC), 71.9 (HC), 71.85 (HC), 71.82 (HC), 70.8 (HC), 69.9 (HC), 69.6 (HC), 69.4 (HC), 68.1 (HC), 62.5 (HC), 62.3 (HC), 55.22 (OCH<sub>3</sub>), 55.15 (OCH<sub>3</sub>). MS-DCI<sup>+</sup> (isobutane):  $m/z$  = 537 ([M+H]<sup>+</sup>). HRMS-DEI<sup>+</sup>: calculated for C<sub>20</sub>H<sub>28</sub>AsO<sub>12</sub><sup>+</sup> (M-H<sup>+</sup>): 535.0797; found: 535.0452. IR absorptions (neat):  $\nu_{\text{bar}}$  = 3524 (w), 2938 (w), 2904 (w), 2364 (w), 2324 (w), 1559 (m), 1507 (m), 1318 (m), 1258 (m), 1204 (m), 1188 (m), 1145 (s), 1136 (s), 1114 (s), 1091 (s), 1062 (s), 1030 (s), 1012 (s), 993 (s), 966 (s), 908 (s), 872 (s), 851 (s), 824 (s), 750 (s), 729 (s), 683 (s), 667 (s), 653 (s), 645 (s) cm<sup>-1</sup>. Raman frequencies (100 mW, 100 scans) (intensity): 3101 (15), 3064 (56), 2999 (25), 2952 (61), 2941 (69), 2920 (38), 2907 (43), 2254 (17), 1579 (45), 1455 (25), 1407 (14), 1388 (16), 1376 (15), 1316 (28), 1280 (13), 1257 (15), 1189 (18), 1171 (15), 1142 (13), 1110 (15), 1072 (26), 1024 (40), 999 (100), 970 (19), 910 (24), 857 (17), 789 (5), 724 (17), 676 (70), 654 (51), 619 (35), 508 (17), 456 (19), 432 (17), 381 (23), 326 (16), 293 (36), 246 (62), 226 (40), 183 (19). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 259.6, 265.1, 272.0, UV/Vis (cyclohexane): no distinct absorption maxima between 195.0 and 1100.0 nm. Melting point: 130.4–137.1 °C.

### Resynthesized compounds:

**PhAs(EtgH<sub>2</sub>)<sub>2</sub>:** In a 100-mL round-bottomed flask phenylarsonic acid (1.01 g, 5.00 mmol) and ethane-1,2-diol (0.56 mL, 0.62 g, 10.0 mmol) are suspended in of benzene (50 mL). The mixture is heated under reflux for two hours. The water liberated during the reaction is removed by azeotropic distillation and collected in a Dean-Stark trap.

After cooling to room temperature the solvent is removed under reduced pressure. A colour- and odourless crystalline solid is obtained (1.16 g, 4.26 mmol, 85.2% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270.2 MHz, 23 °C)  $\delta$  = 7.96–7.92 (m, H<sub>ar</sub>), 7.60–7.47 (m, H<sub>ar</sub>), 4.05–3.93 (m, CH<sub>2</sub>), 3.78–3.66 (m, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz, 26 °C)  $\delta$  = 134.8 (C<sub>ar</sub>), 132.4 (C<sub>ar</sub>), 131.8 (C<sub>ar</sub>), 129.3 (C<sub>ar</sub>), 60.2 (CH<sub>2</sub>). MS-DCI<sup>+</sup> (isobutane)  $m/z$ : 273 ([M+H]<sup>+</sup>), 212 ([M-C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>]<sup>+</sup>). IR absorptions (neat):  $\nu_{\text{bar}}$  = 2973 (w), 2939 (w), 2875 (w), 1440 (m), 1228 (w), 1181 (w), 1122 (w), 1093 (w), 1031 (s), 999 (m), 978 (w), 930 (m), 910 (s), 850 (m), 803 (m), 773 (m), 742 (s), 687 (s), 663 (s), 642 (s), 610 (m). Raman frequencies (100 mW, 100 scans) (intensity): 3070 (51), 2976 (39), 2878 (40), 1579 (23), 1524 (7), 1469 (18), 1343 (7), 1242 (16), 1181 (12), 1162 (8), 1090 (11), 1027 (24), 1001 (100), 931 (22), 685 (20), 647 (76), 614 (15), 500 (11), 431 (32), 363 (30), 294 (13), 259 (38), 195 (13), 164 (9). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm}$  = 257.0, 263.0, 269.0, UV/Vis (cyclohexane): 264.0.

**PhAs(PinaH<sub>2</sub>)<sub>2</sub>:** In a 100-mL round-bottomed flask phenylarsonic acid (1.01 g, 5.00 mmol) and pinacol (1.18, 10.0 mmol) are suspended in of benzene (50 mL). The mixture is heated under reflux for two hours. The water liberated during the reaction is removed by azeotropic distillation and collected in a Dean-Stark trap.

After cooling to room temperature the solvent is removed under reduced pressure. A colourless crystalline solid is obtained (1.85 g, 4.81 mmol, 96.2% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.8 MHz, 22 °C) δ = 8.15–8.12 (m, H<sub>ar</sub>), 7.51–7.41 (m, H<sub>ar</sub>), 1.30 (s, CH<sub>3</sub>), 1.02 (s, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.5 MHz, 24 °C) δ = 140.6 (C<sub>ar</sub>), 132.6 (C<sub>ar</sub>), 131.6 (C<sub>ar</sub>), 128.6 (C<sub>ar</sub>), 24.9 (CH<sub>3</sub>), 24.0 (CH<sub>3</sub>). MS-DCI<sup>+</sup> (isobutane) *m/z*: 385 ([M+H]<sup>+</sup>), 285 ([M–C<sub>6</sub>H<sub>12</sub>O+H]<sup>+</sup>). IR absorptions (neat): ν<sub>bar</sub> = 3063 (w), 2980 (w), 2932 (w), 1374 (w), 1364 (w), 1338 (w), 1214 (w), 1158 (m), 1140 (m), 1077 (m), 1027 (w), 1006 (w), 953 (m), 924 (w), 883 (s), 849 (w), 739 (s), 687 (m), 675 (s), 648 (m), 623 (m), 614 (m), 602 (m). Raman frequencies (100 mW, 100 scans) (intensity): 3067 (58), 2990 (74), 2981 (76), 2930 (57), 1584 (29), 1467 (14), 1438 (34), 1267 (10), 1234 (24), 1213 (16), 1181 (10), 1156 (9), 1077 (7), 1030 (24), 1000 (84), 950 (9), 931 (9), 902 (5), 734 (9), 663 (39), 639 (100), 614 (9), 544 (9), 522 (8), 450 (32), 371 (21), 247 (78). UV/Vis (acetonitrile): λ<sub>max</sub>/nm = 258.0, 264.0, 270.6, UV/Vis (cyclohexane): 258.9, 264.4, 271.0.

**PhAs(CatH<sub>2</sub>)<sub>2</sub>:** In a 100-mL round-bottomed flask phenylarsonic acid (1.01 g, 5.00 mmol) and 1,2-dihydroxybenzene (1.10 g, 10.0 mmol) are suspended in of benzene (50 mL). The mixture is heated under reflux for three hours. The water liberated during the reaction is removed by azeotropic distillation and collected in a Dean-Stark trap.

After cooling to room temperature the solvent is removed under reduced pressure. A bright yellow crystalline solid from candylike smell is obtained (1.76 g, 4.78 mmol, 95.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.8 MHz, 23 °C) δ = 7.92–7.89 (m, H<sub>ar</sub>), 7.62–7.58 (m, H<sub>ar</sub>), 7.53–7.49 (m, H<sub>ar</sub>), 7.11–7.06 (m, H<sub>ar</sub>), 6.89–6.85 (m, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.5 MHz, 24 °C) δ = 144.1 (C<sub>ar</sub>), 134.0 (C<sub>ar</sub>), 132.6 (C<sub>ar</sub>), 131.5 (C<sub>ar</sub>), 129.9 (C<sub>ar</sub>), 128.3 (C<sub>ar</sub>), 121.4 (C<sub>ar</sub>), 111.6 (C<sub>ar</sub>). MS-DCI<sup>+</sup> (isobutane) *m/z*: 369 ([M+H]<sup>+</sup>), 368 ([M]<sup>+</sup>), 260 ([M–C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>]<sup>+</sup>). IR absorptions (neat): ν<sub>bar</sub> = 3065 (w), 3026 (w), 1594 (w), 1507 (w), 1473 (s), 1439 (m), 1420 (w), 1330 (m), 1310 (w), 1279 (w), 1256 (m), 1238 (s), 1207 (m), 1183 (w), 1160 (w), 1148 (w), 1129 (w), 1105 (w), 1089 (m), 1066 (w), 1015 (m), 967 (w), 930 (w), 884 (w), 822 (m), 797 (s), 759 (m), 748 (s), 738 (s), 687 (s), 622 (w). Raman frequencies (100 mW, 100 scans) (intensity): 3058 (44), 2986 (34), 1603 (26), 1590 (23), 1482 (22), 1460 (11), 1332 (31), 1255 (74), 1185 (15), 1150 (17), 1086 (11), 1018 (56), 999 (65), 824 (24), 757 (9), 744 (10), 694 (31), 673 (100), 611 (9), 589 (11), 557 (10), 433 (11), 401 (12), 386 (13), 325 (23), 317 (29),

268 (83), 224 (19), 129 (7). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm} = 267.4$ , UV/Vis (cyclohexane): 267.4, 273.6.

**PhAs(NptdH<sub>2</sub>)<sub>2</sub>:** In a 100-mL round-bottomed flask phenylarsonic acid (1.01 g, 5.00 mmol) and naphthalene-2,3-diol (1.60 g, 10.0 mmol) are suspended in of benzene (50 mL). The mixture is heated under reflux for three hours. The water liberated during the reaction is removed by azeotropic distillation and collected in a Dean-Stark trap.

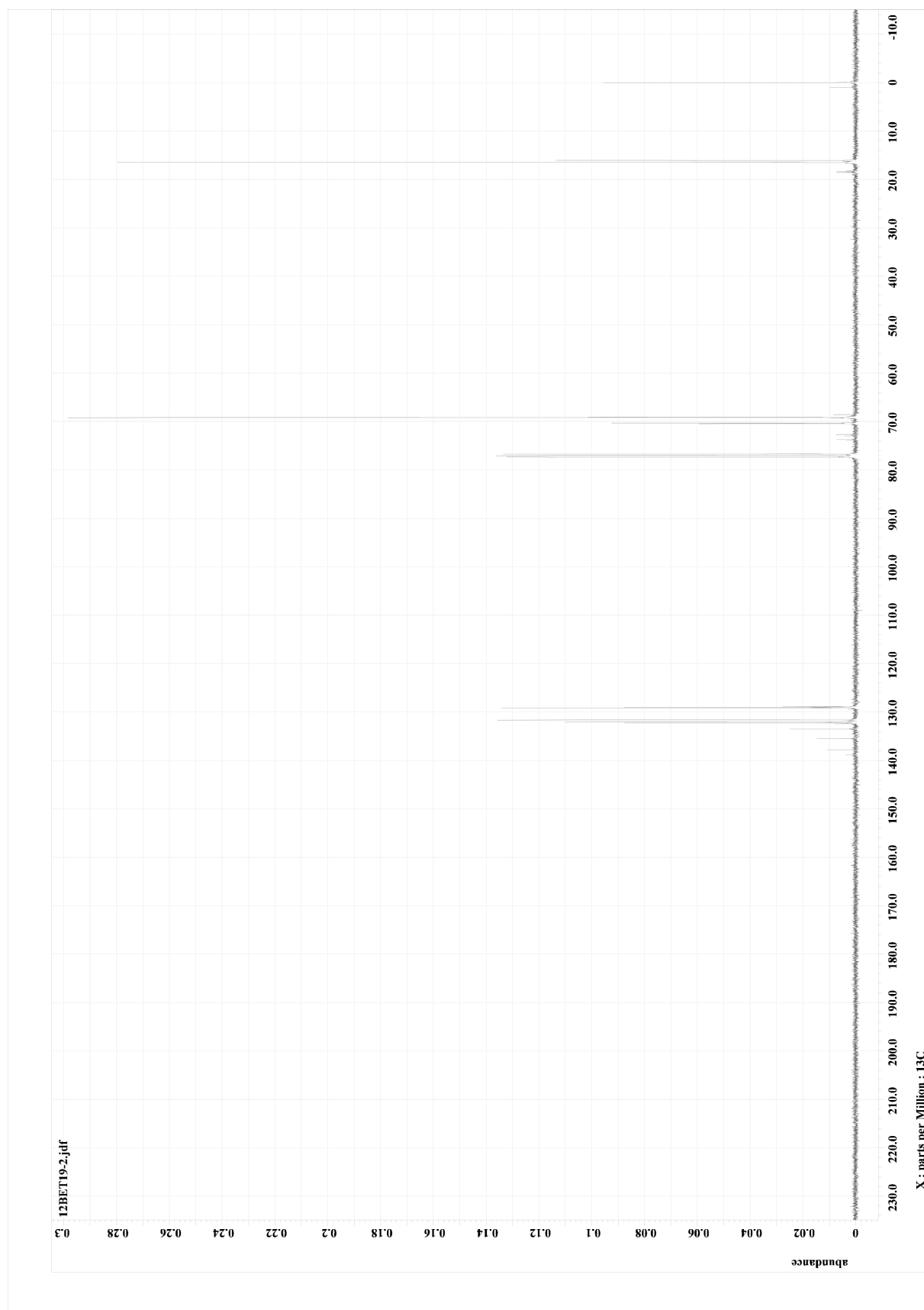
After cooling to room temperature the solvent is removed under reduced pressure. A faint yellow crystalline solid from yeastlike smell is obtained (2.25 g, 4.80 mmol, 96.0% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 399.8 MHz, 23 °C)  $\delta$  = 7.94–7.91 (m, H<sub>ar</sub>), 7.73–7.70 (m, H<sub>ar</sub>), 7.61–7.57 (m, H<sub>ar</sub>), 7.51–7.47 (m, H<sub>ar</sub>), 7.46–7.45 (m, H<sub>ar</sub>), 7.38–7.34 (m, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.5 MHz, 24 °C)  $\delta$  = 143.7 (C<sub>ar</sub>), 134.3 (C<sub>ar</sub>), 132.1 (C<sub>ar</sub>), 131.4 (C<sub>ar</sub>), 130.1 (C<sub>ar</sub>), 129.7 (C<sub>ar</sub>), 127.0 (C<sub>ar</sub>), 124.7 (C<sub>ar</sub>), 107.0 (C<sub>ar</sub>). MS-DCI<sup>+</sup> (isobutane)  $m/z$ : 469 ([M+H]<sup>+</sup>), 468 ([M]<sup>+</sup>), 311 ([M–C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>+H]<sup>+</sup>), 310 ([M–C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>]<sup>+</sup>). IR absorptions (neat):  $\nu_{\text{bar}}$  = 3060 (w), 3031 (w), 1506 (w), 1450 (m), 1404 (w), 1236 (m), 1156 (m), 1094 (m), 1064 (w), 1020 (w), 950 (m), 921 (w), 861 (s), 835 (m), 744 (s), 710 (m), 686 (s), 670 (s), 607 (m). Raman frequencies (100 mW, 100 scans) (intensity): 3057 (33), 3031 (14), 1632 (10), 1590 (33), 1502 (12), 1471 (100), 1408 (24), 1388 (18), 1359 (94), 1254 (13), 1216 (12), 1185 (13), 1165 (27), 1096 (12), 1019 (35), 1002 (38), 883 (12), 760 (97), 696 (13), 672 (55), 611 (13), 512 (14), 462 (11), 416 (22), 370 (12), 332 (12), 287 (12), 248 (29), 203 (61), 170 (14). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm} = 222.5, 301.5, 314.9$ , UV/Vis (cyclohexane): no distinct absorption maxima in the range from 195.0 nm to 1100.0 nm.

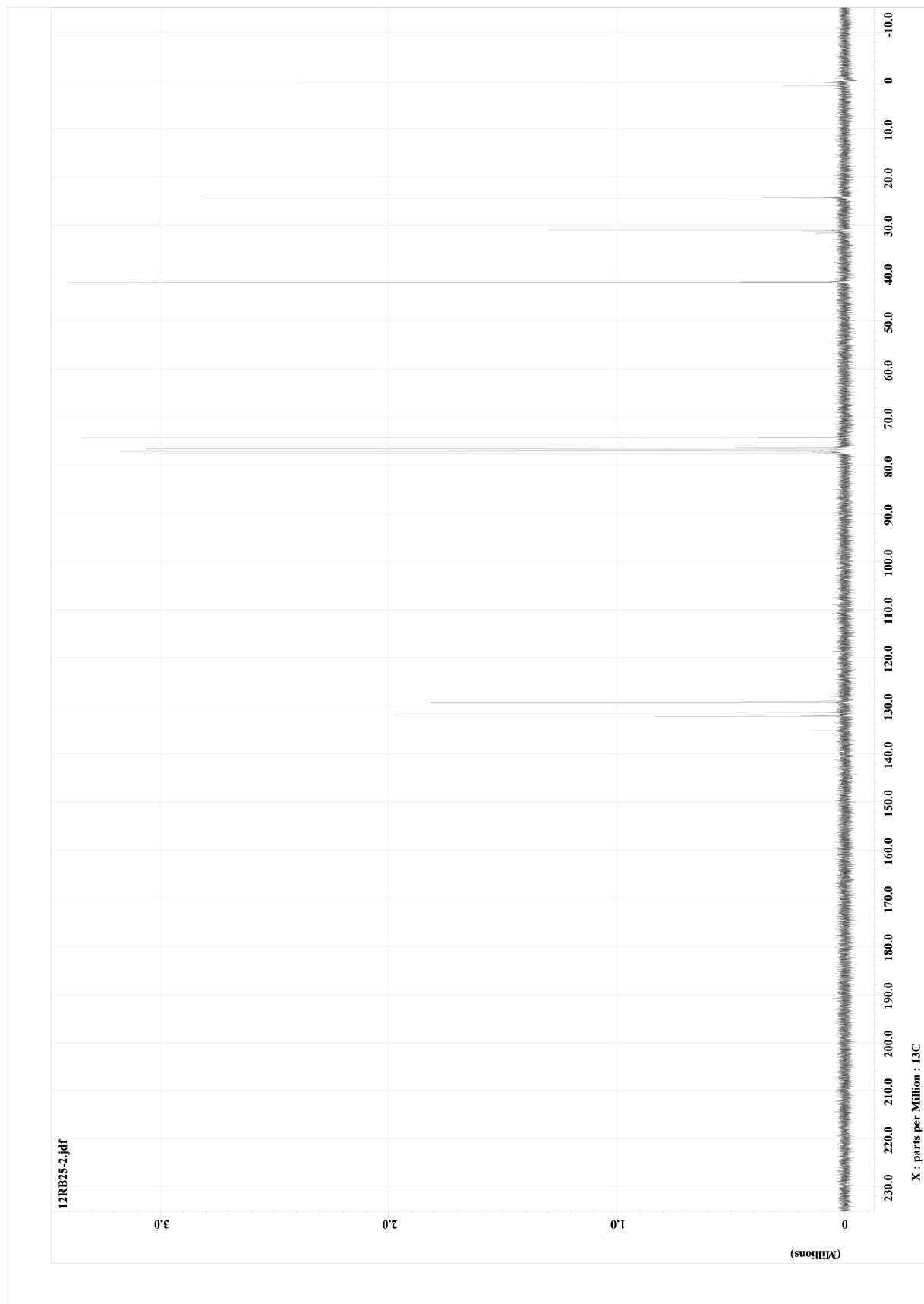
**PhAs(oAmphH<sub>2</sub>)<sub>2</sub>:** In a 100-mL round-bottomed flask phenylarsonic acid (1.01 g, 5.00 mmol) and *o*-aminophenol (1.09 g, 10.0 mmol) are suspended in of benzene (50 mL). The mixture is heated under reflux for three hours. The water liberated during the reaction is removed by azeotropic distillation and collected in a Dean-Stark trap.

After cooling to room temperature the solvent is removed under reduced pressure. A yellow-brown crystalline solid without a characteristic smell is obtained (1.64 g, 4.48 mmol, 89.6% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 399.8 MHz, 23 °C)  $\delta$  = 8.28 (s, NH), 7.72–7.69 (m, H<sub>ar</sub>), 7.58–7.53 (m, H<sub>ar</sub>), 6.82–6.77 (m, H<sub>ar</sub>), 6.75–6.71 (m, H<sub>ar</sub>), 6.65–6.57 (m, H<sub>ar</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100.5 MHz, 24 °C)  $\delta$  = 148.0 (C<sub>ar</sub>), 139.0 (C<sub>ar</sub>), 132.9 (C<sub>ar</sub>), 132.7 (C<sub>ar</sub>), 132.0 (C<sub>ar</sub>), 130.0 (C<sub>ar</sub>), 129.7 (C<sub>ar</sub>), 129.4 (C<sub>ar</sub>), 128.3 (C<sub>ar</sub>), 119.0 (C<sub>ar</sub>), 118.6 (C<sub>ar</sub>), 110.7 (C<sub>ar</sub>), 110.2 (C<sub>ar</sub>). MS-DCI<sup>+</sup> (isobutane)  $m/z$ : 366 ([M]<sup>+</sup>), 259 ([M–C<sub>6</sub>H<sub>5</sub>NO]<sup>+</sup>), 258 ([M–C<sub>6</sub>H<sub>5</sub>NO–H]<sup>+</sup>). IR absorptions (neat):  $\nu_{\text{bar}}$  = 3375 (w), 3302 (w), 3064 (w), 3048 (w), 3031 (w), 1481 (s), 1463 (m), 1439 (m), 1419 (w), 1398 (w), 1356 (m), 1308 (w), 1263 (m), 1246 (s), 1224 (m), 1203

(s), 1180 (m) 1160 (w), 1100 (w), 1091 (w), 1022 (m), 999 (w), 972 (w), 954 (w), 919 (w), 905 (w), 879 (w), 869 (w), 843 (w), 800 (s), 766 (w), 741 (s), 731 (w), 687 (m), 644 (s), 632 (s), 617 (m), 605 (m). Raman frequencies (100 mW, 100 scans) (intensity): 3060 (61), 1599 (57), 1581 (37), 1491 (32), 1464 (24), 1362 (49), 1264 (79), 1207 (19), 1181 (23), 1160 (31), 1092 (28), 1022 (86), 999 (81), 813 (37), 766 (48), 731 (29), 681 (49), 441 (31), 397 (31), 320 (49), 256 (100). UV/Vis (acetonitrile):  $\lambda_{\text{max}}/\text{nm} = 282.0$ , UV/Vis (cyclohexane): 226.4, 280.9.

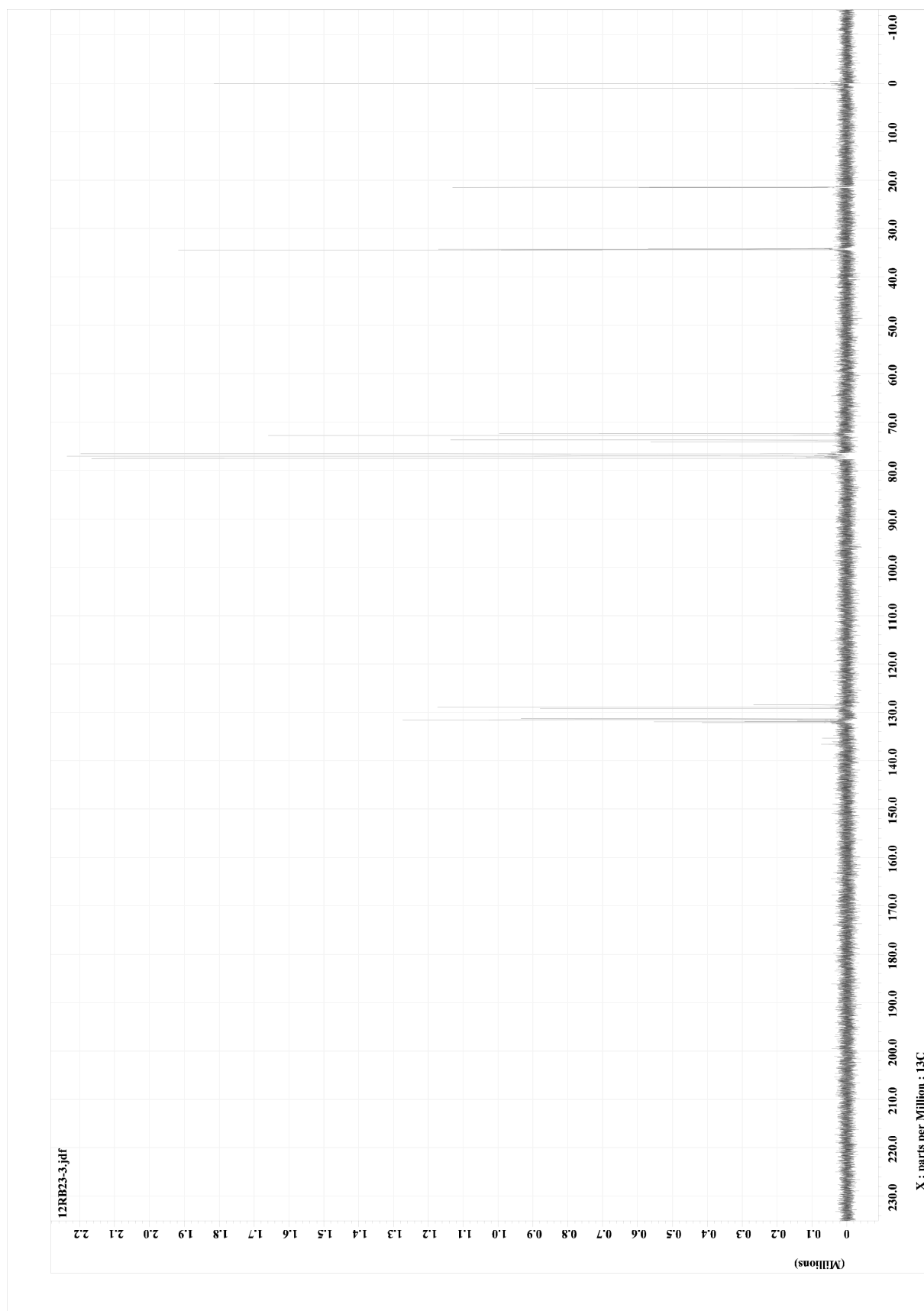
$^{13}\text{C}$  NMR of compound **1**



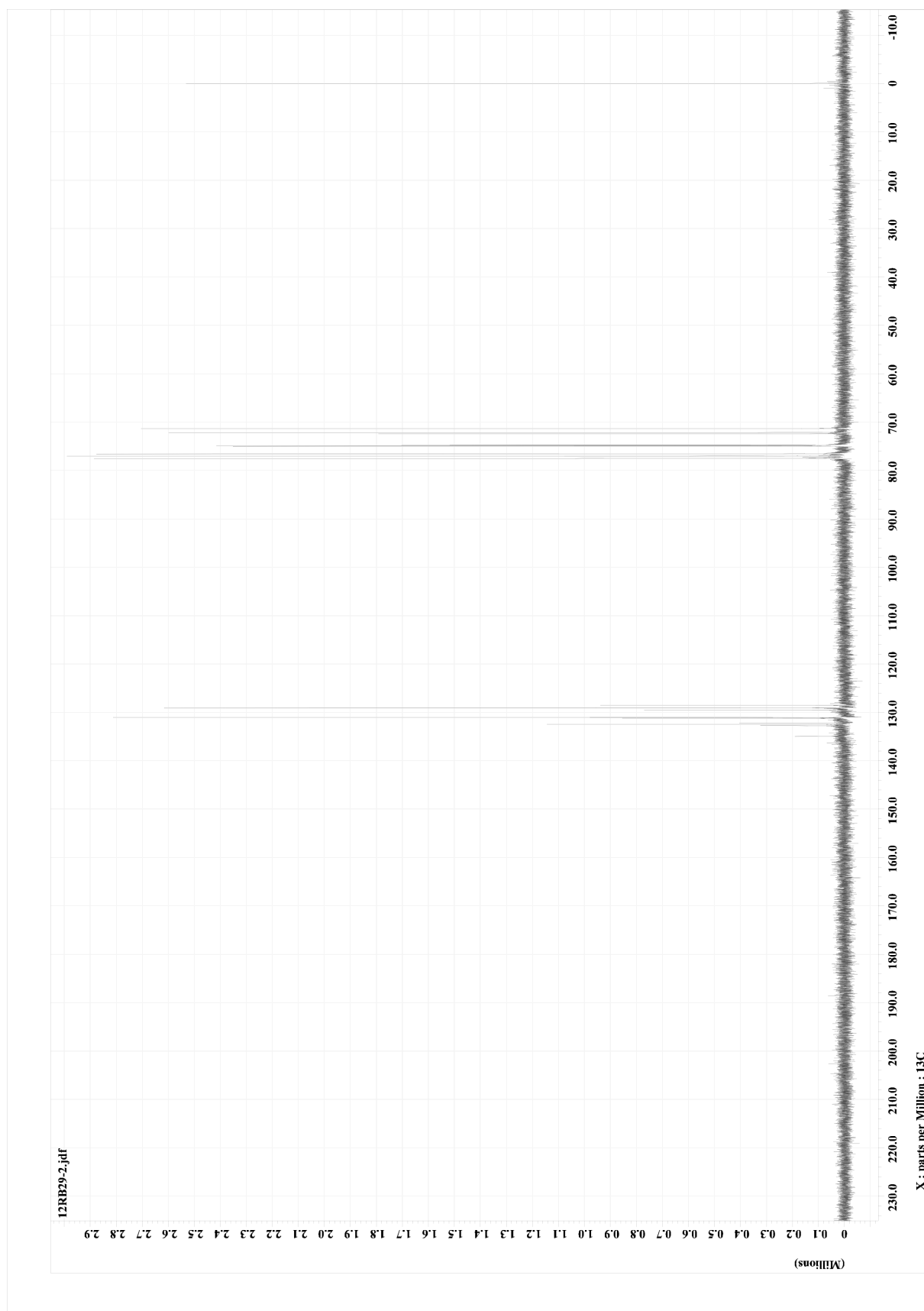


$^{13}\text{C}$  NMR of compound **2**

$^{13}\text{C}$  NMR of compound **3**

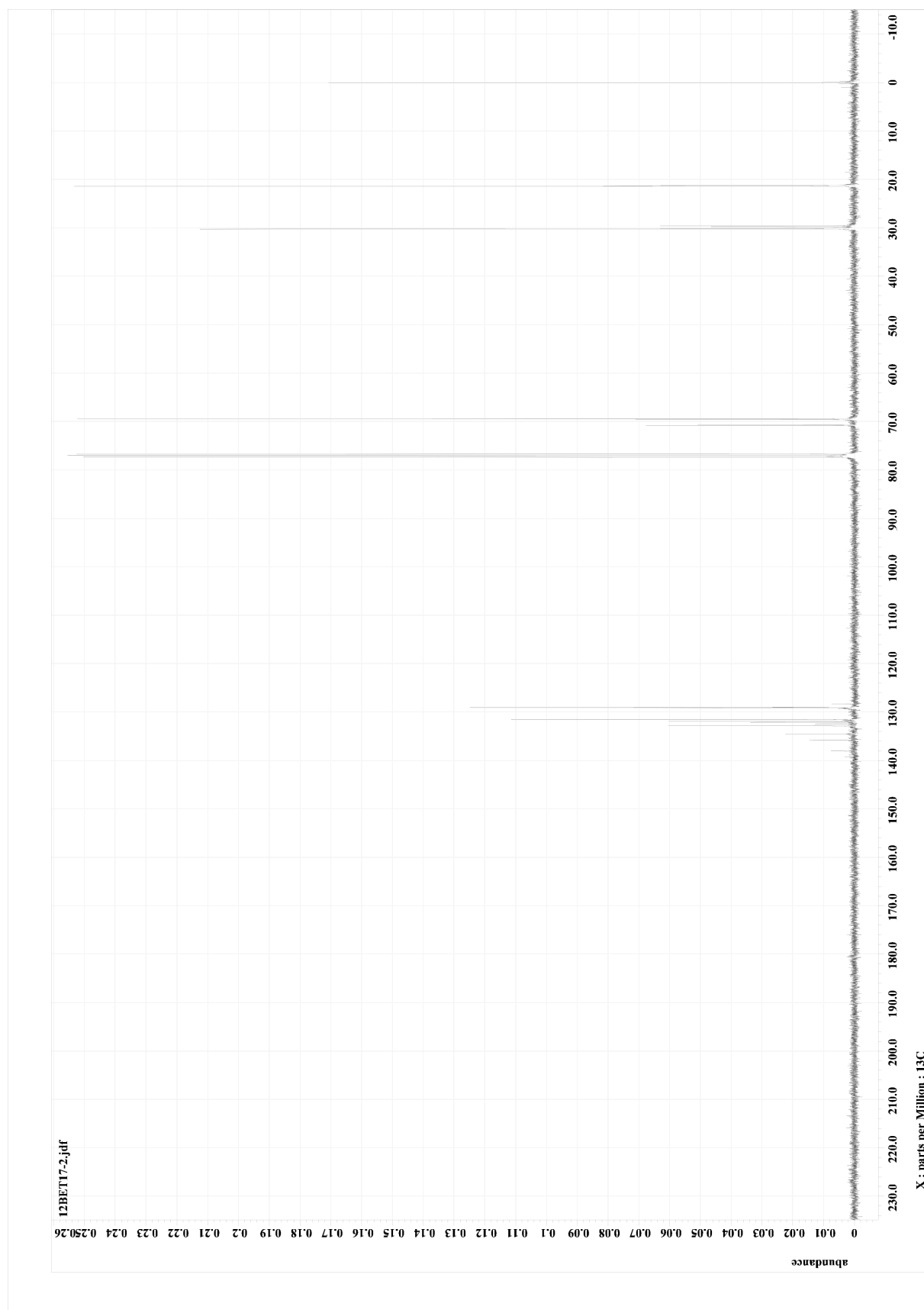


$^{13}\text{C}$  NMR of compound **4**



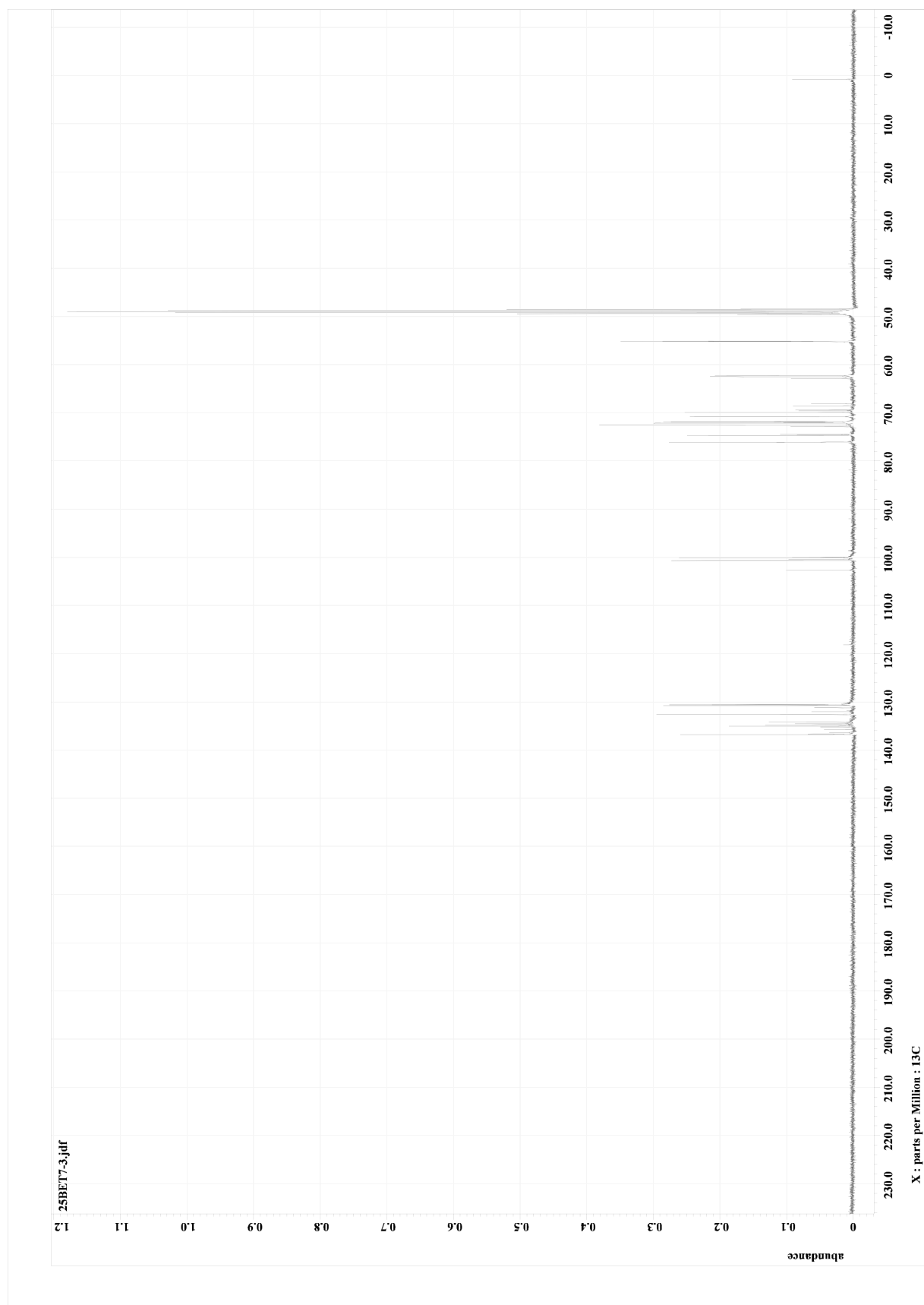


$^{13}\text{C}$  NMR of compound **5**

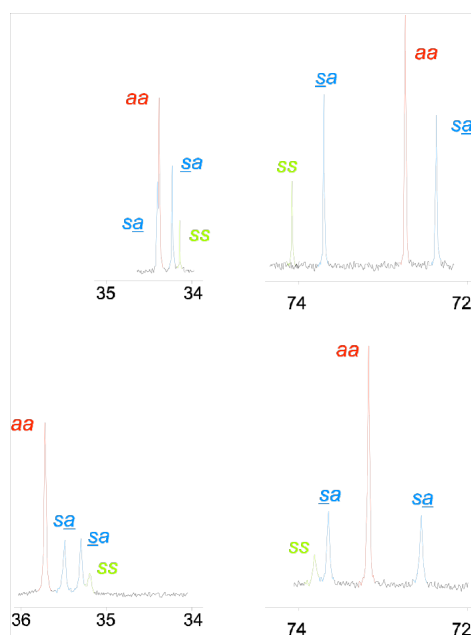




$^{13}\text{C}$  NMR of compound **10**



## syn/anti Isomerism



To illustrate the issue of *syn/anti* isomerism in both silicon and arsenic chemistry, a cutout of the  $^{13}\text{C}$  NMR spectra of  $\text{PhAs}(\text{CptdH-2})_2$  (**3**, top) and  $\text{PhSi}(\text{CptdH-2})_2$  (bottom) recorded at 67.9 MHz in  $\text{CDCl}_3$  at 26 °C (arsenic-containing compound) and 100.6 MHz in  $\text{CD}_3\text{OD}$  at 24 °C (silicon-containing compound).

Two of the *cis*-cyclopentanediol's carbon resonances showing a splitting in four signals are depicted. The analogy of observable *syn/anti* isomerism between pentacoordinate phenyl silicates and phenyl arsoranes is clearly visible.

- 1 Otey, F. H.; Mehlretter, C. L. *J. Org. Chem.* **1961**, *26*, 1673.
- 2 Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260–265.
- 3 Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822–2824.
- 4 Holmes, R. R.; Day, R. O.; Sau, A. C. *Organometallics* **1985**, *4*, 714–720.
- 5 Goldwhite, H.; Teller, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5357–5362.
- 6 Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R.; Deiters, J. A.; Devillers, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 2127–2132.