Electronic Supplementary Material (ESI) for Dalton Transactions


# Synthesis of Biphenyl-Based Arsine Ligands by Suzuki-Miyaura Coupling and their Application to Pd-Catalyzed Arsination

Paula M. Uberman, Mario N. Lanteri, Sol C. Parajón Puenzo and Sandra E. Martín*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5000, Córdoba, Argentina

**Supplementary Material**

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## 1. Experimental Section

### *1.1 General Methods*

Gas chromatographic analyses were performed on a gas chromatograph with a flame ionization detector, and equipped with the following columns: HP-1 25 m x 0.20 mm x 0.25 μm column. $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR were conducted on a High Resolution Spectrometer Bruker Advance 400, in $CDCl_3$ as solvent. Gas Chromatographic/Mass Spectrometer analysis were carried out on a GC/MS QP 5050 spectrometer equipped with a VF-5ms, 30 m x 0.25 mm x 0.25 μm column. Melting points were performed with an electrical instrument. The HRMS were recorded at the UCR Mass Spectrometry Facility, University of California, USA. The Elemental Analyses were carried out on an EXETER CE 440 at the UMYMFOR – FCEN, University of Buenos Aires, Argentina.

The $AsPh_3$, $PPh_3$, (*o*-bph)$PCy_2$, (*o*-bph)$P^tBu_2$, $PCy_3$, *n*-$Bu_3SnCl$, $(PPh_3)_2PdCl_2$, $Pd(OAc)_2$, $Pd(dba)_2$, CuI, $R_fI$, $ArB(OH)_2$, $K_3PO_4$, $Cs_2CO_3$, $Ba(OH)_2$, NaOH, $Na_2SO_4$ and ArI were commercially available and used as received. (2-bromophenyl)diphenylarsine (**2**) was prepared as previously reported from the corresponding 2-bromoiodobenzene.[1] CsF was dried under vacuum at 120°C. All solvents were analytical grade and distillated before use. Toluene was distilled under nitrogen with Na-benzophenone and dioxane was distilled under nitrogen. All reactions were carried out under atmosphere of nitrogen. Silica gel (0.063-0.200 mm) was used in column chromatography.

***1.2 General Procedure for the preparation of n-$Bu_3SnAsPh_2$.*** A typical procedure involves the formation of $Ph_2As^-$ ions from $Ph_3As$ and Na metal in liquid ammonia, followed by addition of *n*-$Bu_3SnCl$ to obtain the *n*-$Bu_3SnAsPh_2$. Into a three-necked, 500 mL, round-bottomed flask equipped with a cold finger condenser charged with dry ice-ethanol, a nitrogen inlet, and a magnetic stirrer, approximately 400 mL of ammonia previously dried with Na metal under nitrogen was condensed. $AsPh_3$ (1.0 mmol) and then 2 equivalents of Na metal (2 mmol) in small pieces were added, with a pause for bleaching between each addition. At 20-30 min of the last addition, $Ph_2As^-$ anion was formed (clear orange-red solution), and *n*-$Bu_3SnCl$ (1 mmol) was added slowly. The mixture was then stirred for 5 min and the liquid ammonia allowed to evaporate. The evaporation left a white solid residue which was dissolved in dry organic solvent (12 mL). Reagent **1** was formed in almost quantitative yield. This stannane solution without purification was used for the cross-coupling Pd-catalyzed arsinations.

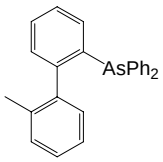
***1.3 Representative Procedure for Pd-Catalyzed Cross-Coupling Suzuki-Miyaura Reaction.*** The following procedure of the reaction is representative of all cross-coupling Suzuki-Miyaura reactions. Into a 25 mL Schlenk tube with Teflon screw-cap septum equipped with a magnetic stirrer and a nitrogen inlet, $Pd(OAc)_2$ (1 mol%, 0.01 mmol), $PPh_3$ (Pd:L 1:4, 0.04 mmol) (2-bromophenyl)diphenylarsine (**2**) (1 mmol), arylboronic acid (**3a-g**) (1.5 mmol), $K_3PO_4$ (2 mmol) were added, and then dioxane (5 mL) and water (2.5 mL) were added. The reaction mixture was heated for 24 h in an oil bath at 100°C. The solvent condensation took place on the walls of Schlenk tube. After being cooled to room temperature, the mixture was open to the air and diluted with water and then extracted three times with $CH_2Cl_2$ (30 mL each). The biarylarsine product was purified in an open atmosphere by silica-gel column chromatography after being dried with anhydrous $Na_2SO_4$. These reactions were scaled up to 5 mmol of (2-bromophenyl)diphenylarsine (**2**) at most.

***1.4 Representative Procedure for Pd-Catalyzed Arsination Reaction with n-$Bu_3SnAsPh_2$ and Perfluoroalkyl Iodides ($R_fI$).*** The following procedure of the reaction of n-$Bu_3SnAsPh_2$ (**1**) with perfluorooctyl iodide (**4a**) is representative of all these reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a cold finger condenser charged with dry ice-ethanol, a nitrogen inlet, and a magnetic stirrer, approximately 400 mL of ammonia previously dried with Na metal under nitrogen was condensed. The $AsPh_3$ (1.0 mmol) was added followed by 2 equivalents of Na metal (2 mmol) in small pieces, waiting for bleaching between each addition. After 20-30 min of the last addition, $Ph_2As^-$ anion was formed (clear orange-red solution), and *n*-$Bu_3SnCl$ (1 mmol) was added slowly. The mixture was stirred for 5 min and the liquid ammonia was then allowed to evaporate. Evaporation left a solid white residue which was dissolved in dry toluene (12 mL). This solution was added via cannula and syringe into a Schlenk tube. In the tube, CsF (3 eq.) was previously dried under vacuum at 120°C for 3 h; after cooling the tube at room temperature, $(PPh_3)_2PdCl_2$ (10 mol%), ligand (40 mol%), substrate **4a** (0.7 mmol) and toluene (3 mL) were added. When the solution of stannane **1** was added, the reaction mixture turned deep brown. The reaction mixture was heated for 24 h in an oil bath at reflux. Water was added to the cooled reaction mixture and then extracted three

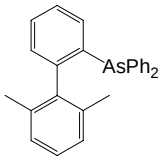
times with $CH_2Cl_2$ (30 mL each). After being dried with anhydrous $Na_2SO_4$, product **5** was quantified by CG using the internal standard method.

The products were characterized by $^1$H NMR, $^{13}$C NMR, GC-MS and HRMS. All these spectroscopic data agreed with those previously reported for compounds **L1**[1] and **5-8**.[2]

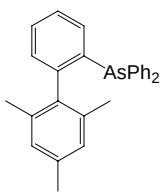
**2. Characterizations Data**




***2-Diphenylarsino-2'-methylbiphenyl (L2)***. Compound **L2** was obtained according to the general procedure. Product **L2** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether) obtaining 0.3488 g of **L2** (88 % yield). After crystallization from $CH_3CN$ cubic crystals were obtained (mp 74.3-75.7 °C). **$^1$H-NMR ($CDCl_3$):** δ 7.42-7.18 (16 H, m); 7.08-7.04 (1 H, m); 6.91 (1 H, d, $^3J$ = 8 Hz); 2.05 (3 H, s). **$^{13}$C-NMR ($CDCl_3$):** δ 147.45; 141.61; 139.95; 139.90; 139.69; 136.03; 134.00; 133.94; 133.84; 130.43; 129.80; 129.62; 128.51; 127.74; 127.57; 125.05; 20.51. **NMR 2D** (COSY-45) $\delta_H$ /$\delta_H$: 2.05 / 6.91; 2.05 / 7.09; 2.05 / 7.23; 6.91 / 7.09; 6.91 / 7.26. **NMR 2D** (HSQC) $\delta_H$ /$\delta_C$: 2.05 / 20.51; 6.90 /129.80; 7.04 / 125.05; 7.23 / 133.78; 7.38 / 128.51. **MS: m/z (%):** 396 (89), 381 (74), 303 (12), 241 (84), 227 (100), 165 (88), 152 (50), 139 (6), 115 (6), 91 (8), 78 (9), 51 (6). **HRMS (EI):** calcd. for $C_{25}H_{22}As$ 397.0932, found $[M+H]^+$ 397.0937. **Elemental Analysis (%)** calc. for $C_{25}H_{21}As$: C, 75.76; H, 5.34; As, 18.90. Found: C, 75.53; H, 5.28.

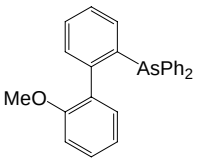



***2-Diphenylarsino-2',6'-dimethylbiphenyl (L3)***. Compound **L3** was obtained according to the general procedure. Product **L3** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether), yielding 0.2914 g of the product (71 % yield). After crystallization from $CH_3CN$ cubic crystals were obtained (mp 92.5-93.3 °C). **$^1$H-NMR ($CDCl_3$):** δ 7.40-7.37 (1 H, m); 7.29-7.17 (13 H, m); 7.10 (1 H, d, $^3J$ = 7.6 Hz); 7.03 (2 H, d, $^3J$ = 7.6 Hz); 1.79 (6 H, s). **$^{13}$C-NMR ($CDCl_3$):** δ 146.60; 141.35; 139.89; 139.72; 136.39; 134.27; 133.80; 129.22; 129.05; 128.50; 128.22; 127.51; 127.34; 127.10; 20.77. **NMR 2D** (COSY-45) $\delta_H$ /$\delta_H$: 1 / 6.82; 7.04 / 7.19; 7.11 / 7.40; 7.29 / 7.40. **NMR 2D** (HSQC) $\delta_H$ /$\delta_C$: 1.79 / 20.77; 7.03 / 127.10; 7.10 / 129.22; 7.19 / 127.47; 7.24 / 133.76; 7.38 / 129.05. **NMR 2D** (HMBC) $\delta_H$ /$\delta_C$: 1.79 / 127.10; 1.79 / 136.39; 1.79 / 141.35; 7.04 / 20.77. **MS: m/z (%):** 410 (77), 395 (60), 317 (8), 255 (31), 241 (100), 227 (17), 179 (37), 165 (64), 152 (32), 91 (14), 77 (14), 51 (12). **HRMS (EI):** calcd. for $C_{26}H_{24}As$ 411.1088, found $[M-H]^+$ 411.1099. **Elemental Analysis (%)** calc. for $C_{26}H_{23}As$: C, 76.09; H, 5.65; As, 18.26. Found: C, 75.75; H, 5.72. 76.09; H, 5.65; As, 18.26. Found: C, 75.75; H, 5.72.

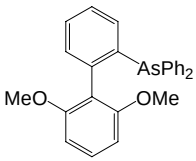



***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)***. Compound **L4** was obtained according to the general procedure. Product **L4** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether), yielding 0.3607 g of the product (85 % yield). After crystallization from $CH_3CN$ needle-shaped crystals

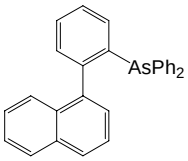
were obtained (mp 118.9-119.5 °C). **$^{1}$H-NMR ($CDCl_3$):** δ 7.39-7.36 (1 H, m); 7.29-7.22 (13 H, m); 7.09 (1H, d, $^{3}J$ = 7.6); 6.87 (2 H, s); 2.33 (3 H, s); 1.77 (6 H, s). **$^{13}$C-NMR ($CDCl_3$):** δ 146.72; 140.05; 139.87; 138.55; 137.00; 136.17; 134.29; 133.77; 129.52; 129.03; 128.48; 128.18; 127.91; 127.25; 21.22; 20.70. **NMR 2D** (COSY-45) $\delta_H/\delta_H$: 1.77 / 2.33; 1.77 / 6.87; 2.33 / 6.87; 7.09 / 7.39; 7.26 / 7.09; 7.27 / 7.38. **NMR 2D** (HSQC) $\delta_H/\delta_C$: 1.77 / 20.70; 2.33 / 21.22; 6.87 / 127.91; 7.09 / 129.52; 7.26 / 127.25; 7.38 / 129.03. **NMR 2D** (HMBC) $\delta_H/\delta_C$: 1.77 / 127.91; 1.77 / 136.17; 1.77 / 138.55; 2.33 / 127.91; 2.33 / 137.00; 6.87 / 127.91; 6.87 / 138.55; 7.09 / 127.25; 7.09 / 140.05; 7.38 / 134.29. **MS: m/z (%):** 425 (29), 424 (84), 410 (18), 409 (75), 270 (19), 269 (37), 255 (100), 227 (13), 194 (22), 193 (27), 179 (44), 178 (31), 165 (22), 152 (20), 91 (9). **HRMS (EI):** calcd. for $C_{27}H_{26}As$ 425.1245, found $[M-H]^+$ 425.1235. **Elemental Analysis (%)** calc. for $C_{27}H_{25}As$: C, 76.41; H, 5.94; As, 17.65. Found: C, 76.15; H, 6.02.




***2-Diphenylarsino-2'-methoxybiphenyl (L5)***. Compound **L5** was obtained according to the general procedure. Product **L5** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether), yielding 0.3629 g (88 % yield) of the product as an amorphous white solid (mp 87.6-89 ºC). **$^{1}$H-NMR ($CDCl_3$):** δ 7.38 (1 H, td; $^{3}J$ = 7.5 Hz; $^{4}J$ = 1.4 Hz); 7.32-7.16 (14 H, m); 7.09 (1 H, dd, $^{3}J$ = 7.5 Hz; $^{4}J$ = 1.6 Hz); 6.91 (1 H, td, $^{3}J$ = 7.4 Hz; $^{4}J$ = 1.0 Hz); 6.82 (1 H, d, $^{3}J$ = 8 Hz); 3.40 (3 H, s). **$^{13}$C-NMR ($CDCl_3$):** δ 156.58; 144.66; 140.96; 140.29; 140.10; 134.20; 133.74; 131.45; 130.99; 130.21; 129.09; 128.53; 128.44; 128.35; 128.06; 127.94; 127.49; 120.10; 110.26; 54.80. **NMR 2D** (COSY-45) $\delta_H/\delta_H$: 3.40 / 6.83; 6.82 / 7.30; 6.91 / 7.08; 6.91 / 7.30; 7.10 / 7.30. **NMR 2D** (HSQC) $\delta_H/\delta_C$: 3.40 / 54.8; 6.82 / 110.27; 6.91 / 120.10; 7.08 / 131.45. **NMR 2D** (HMBC) $\delta_H/\delta_C$: 3.40 / 156.58; 6.82 / 120.1; 7.09 / 156.59. **MS: m/z (%):** 412 (9), 382 (30), 381 (100), 303 (6), 257 (24), 243 (11), 228 (10), 227 (23), 213 (13), 168 (11), 152 (16), 151 (9), 139 (9), 78 (4), 51 (5). **HRMS (EI):** calcd. for $C_{25}H_{22}AsO$ 413.0881, found $[M-H]^+$ 413.0888. **Elemental Analysis (%)** calc. for $C_{25}H_{21}AsO$: C, 72.82; H, 5.13; As, 18.17; O, 3.88. Found: C, 72.95; H, 5.35.



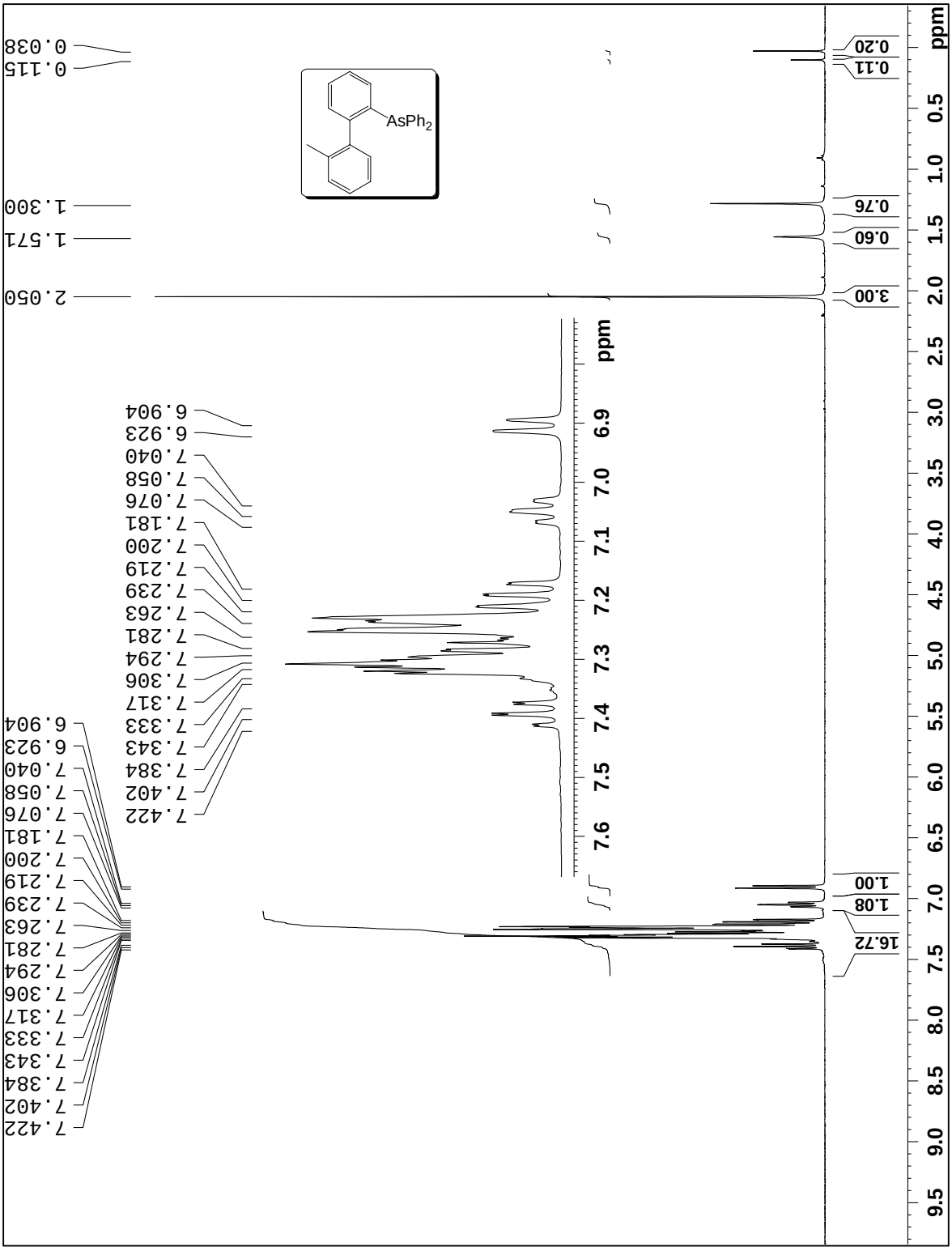

***2-Diphenylarsino-2',6'-dimethoxybiphenyl (L6)***. Compound **L6** was obtained according to the general procedure. Product **L6** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether), yielding 0.4203 g of the product (95 % yield). After crystallization from $CH_3CN$ cubic crystals were obtained (mp 133.0-133.8 °C). **$^{1}$H-NMR ($CDCl_3$):** δ 7.41-7.39 (1 H, m); 7.29-7.22 (13 H, m); 7.18-7.16 (1 H, m); 6.53 (2 H, d, $^{3}J$ = 8.8 Hz); 3.46 (6 H, s). **$^{13}$C-NMR ($CDCl_3$):** δ 157.83; 140.80; 140.63; 133.97; 133.74; 130.81; 129.20; 128.45; 128.24; 127.83; 127.37; 119.30; 103.57; 55.39. **NMR 2D** (COSY-45) $\delta_H/\delta_H$: 3.46 / 6.52; 3.46 / 7.26; 6.52 / 7.28; 7.17 / 7.25; 7.17 / 7.40; 7.25 / 7.40. **NMR 2D** (HSQC) $\delta_H/\delta_C$: 3.46 / 55.39; 6.56 / 103.57; 7.17 / 133.97; 7.40 / 129.20. **MS: m/z (%):** 442 (8), 411 (100), 396 (8), 273 (8), 257 (8), 227 (12), 214 (10), 152 (7), 77 (5), 51 (6). **HRMS (EI):** calcd. for $C_{26}H_{24}AsO_2$ 443.0987, found $[M-H]^+$ 443.0998. **Elemental Analysis (%)** calc. for $C_{26}H_{23}AsO_2$: C, 70.59; H, 5.24; As, 16.94; O, 7.23. Found: C, 70.65; H, 5.13.



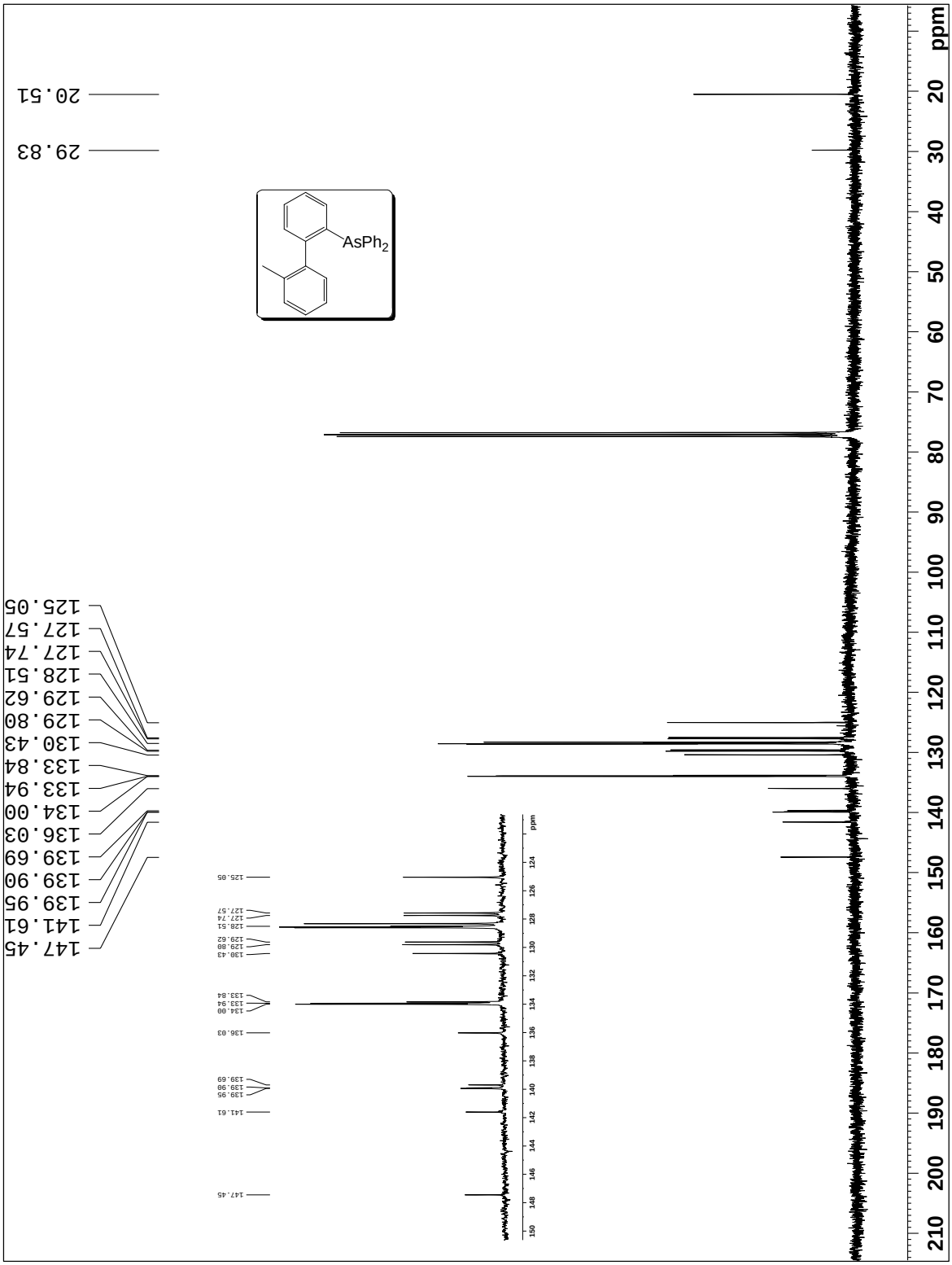

***1-(2-Diphenylarsinophenyl)naphthalene (L7)***. Compound **L7** was obtained according to the general procedure. Product **L7** was isolated from the reaction mixture by silica-gel column chromatography (petroleum ether), obtaining 0.3026 g of the product (70 % yield). After extensive drying with vacuum pump, **L7** was obtained as an amorphous white solid (mp 50-53 °C). **$^{1}$H-NMR ($CDCl_3$):** δ 7.87-7.81 (2 H, m); 7.46-7.10 (20 H, m). **$^{13}$C-NMR ($CDCl_3$):** δ 145.99; 140.67; 140.30; 139.98; 139.57; 133.99; 133.76; 133.72; 133.35; 132.35; 130.62; 128.51; 128.36; 128.26; 128.20; 128.06; 127.89; 127.86; 127.81; 126.38; 125.83; 125.66; 124.68. **MS: m/z (%):** 433 (15), 432 (51), 354 (10), 279 (14), 278 (45), 277 (100), 202 (75), 177 (14). **HRMS (EI):** calcd. for $C_{28}H_{22}As$ 433.0932, found $[M-H]^+$ 433.0918. **Elemental Analysis (%)** calc. for $C_{28}H_{21}As$: C, 77.78; H, 4.90; As, 17.33. Found: C, 77.86; H, 4.72.

### 3. NMR Spectroscopy

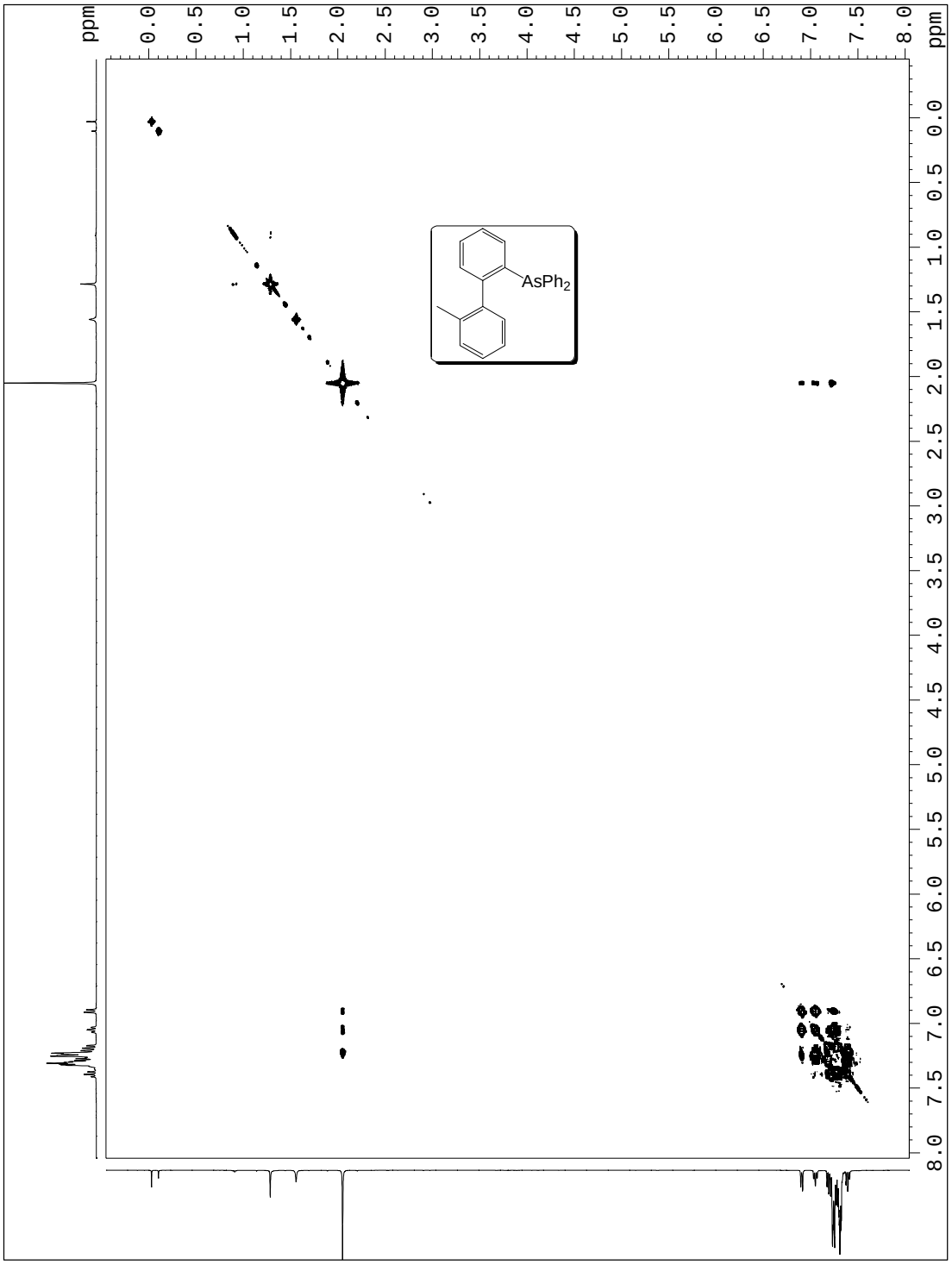
***2-Diphenylarsino-2'-methylbiphenyl (L2)*** $^{1}$H NMR ($CDCl_3$).



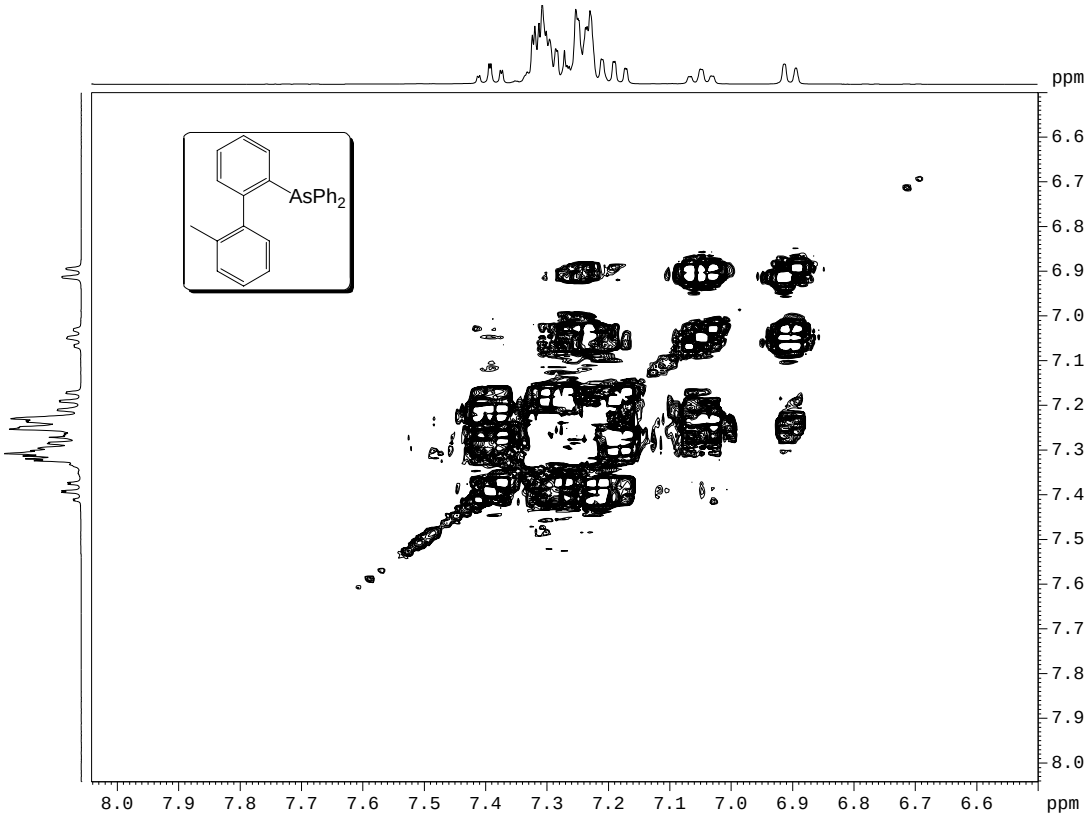
***2-Diphenylarsino-2'-methylbiphenyl (L2)*** $^{13}$C NMR ($CDCl_3$).

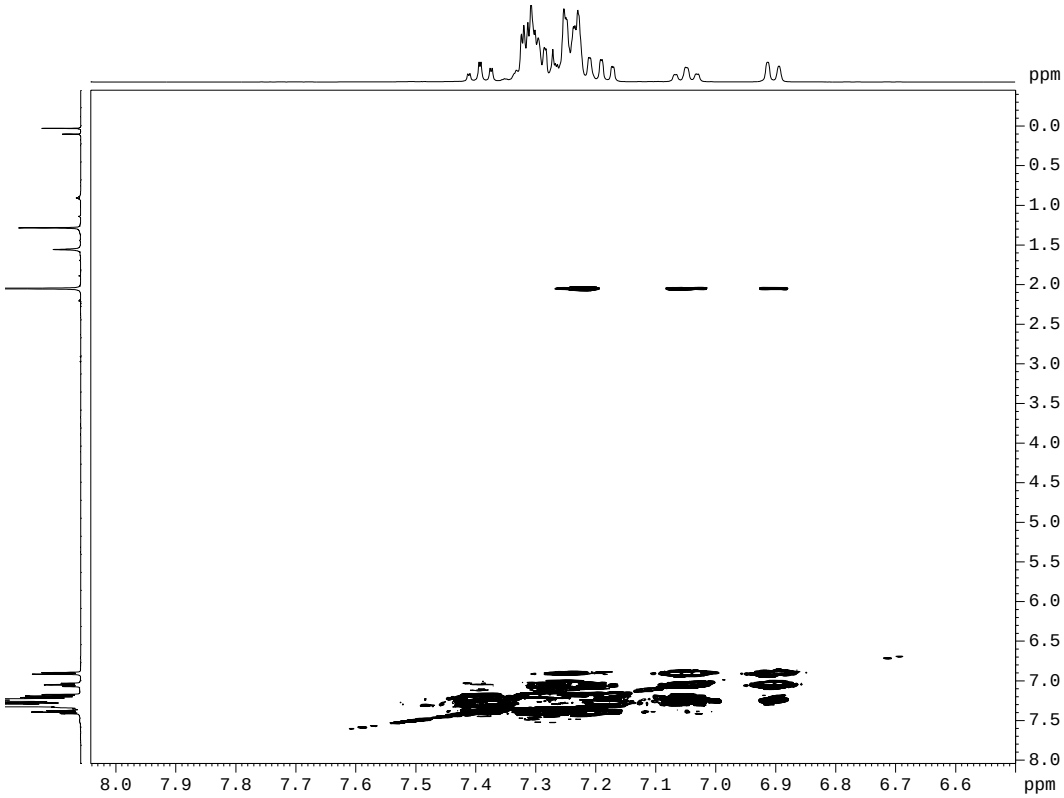


***2-Diphenylarsino-2'-methylbiphenyl (L2)*** NMR 2D (COSY-45) ($CDCl_3$).

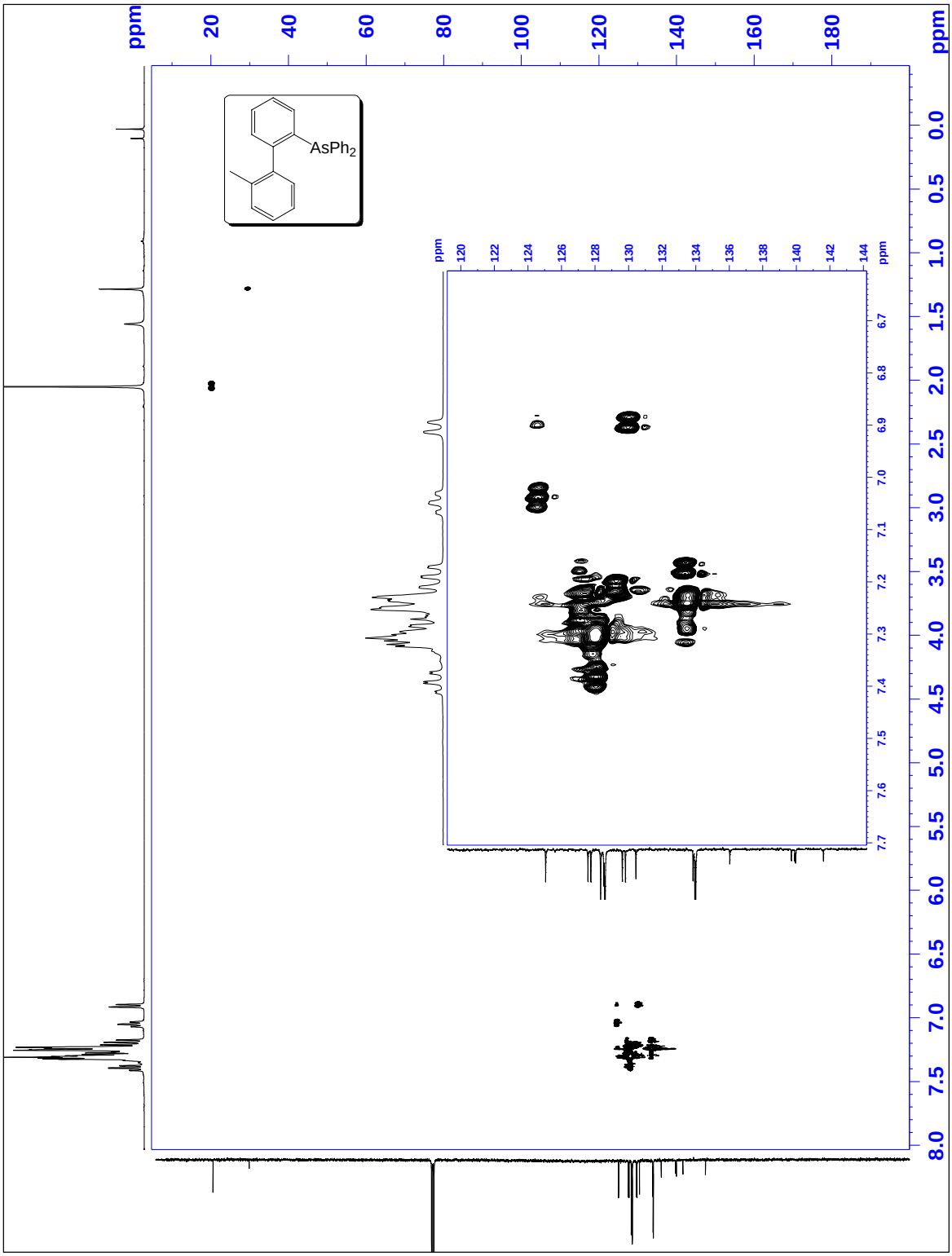


***2-Diphenylarsino-2'-methylbiphenyl (L2)*** NMR 2D (COSY-45) ($CDCl_3$).

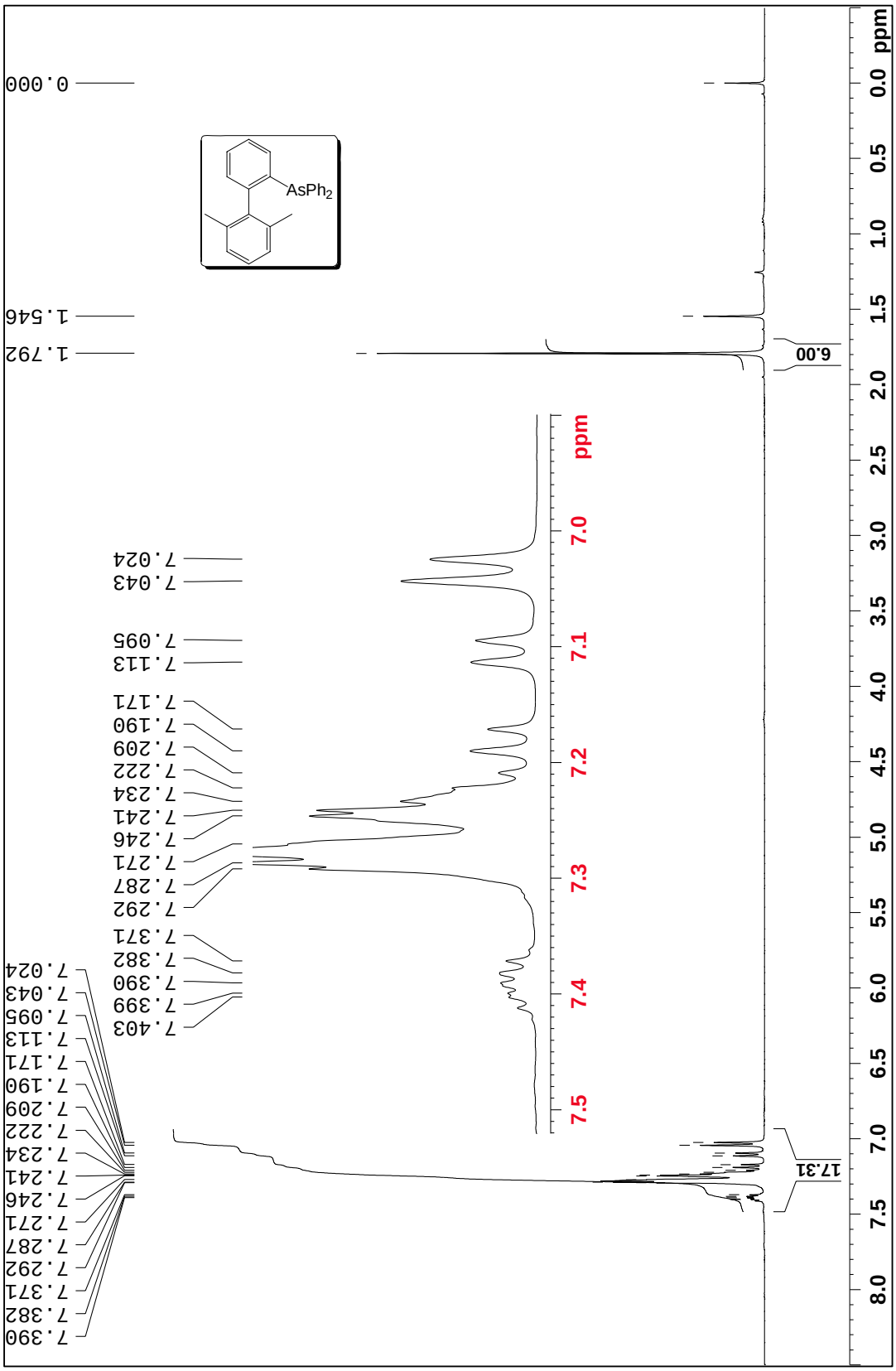


***2-Diphenylarsino-2'-methylbiphenyl (L2)*** NMR 2D (HSQC) ($CDCl_3$).



***2-Diphenylarsino-2',6'-dimethylbiphenyl (L3)*** $^{1}$H NMR ($CDCl_3$).



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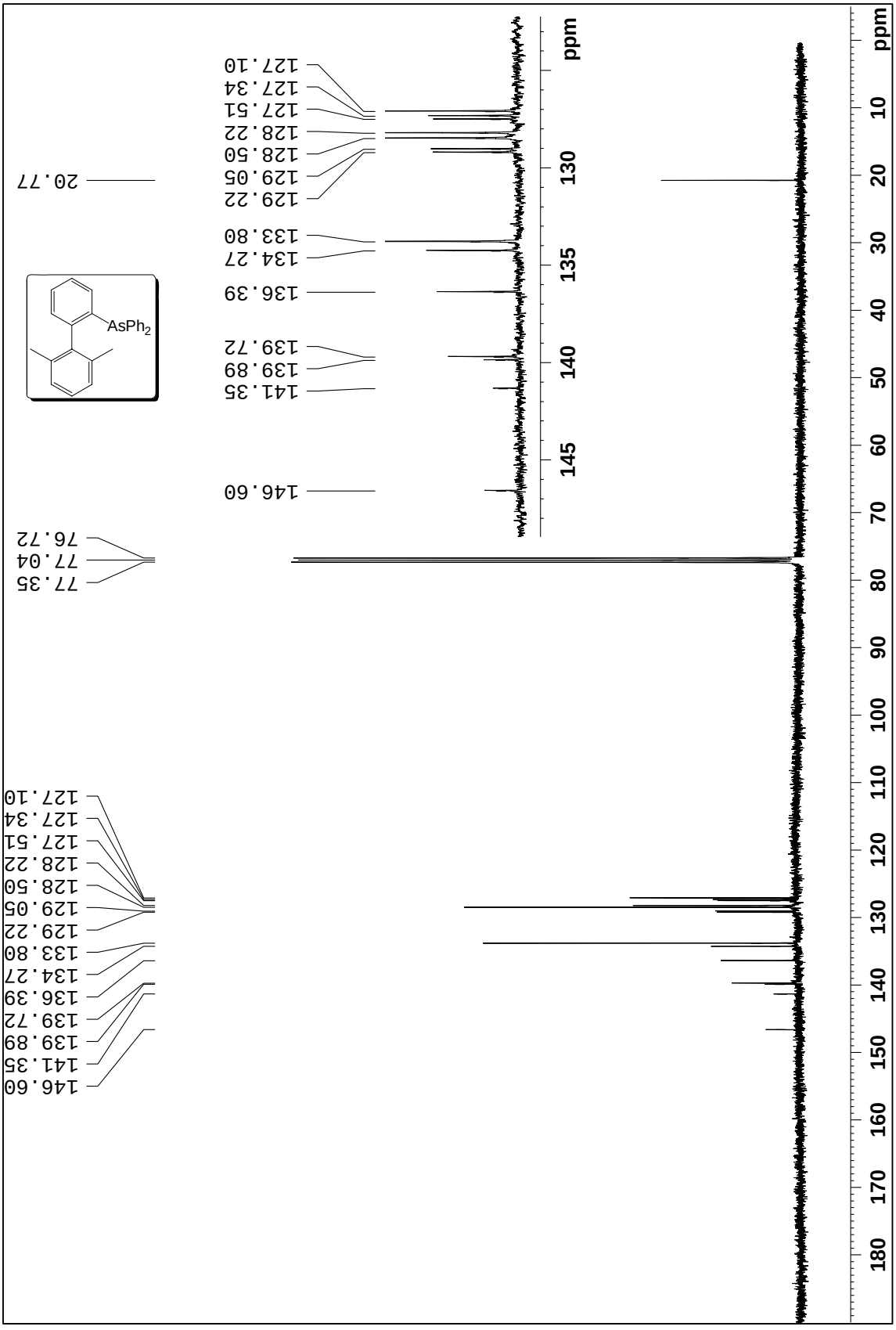
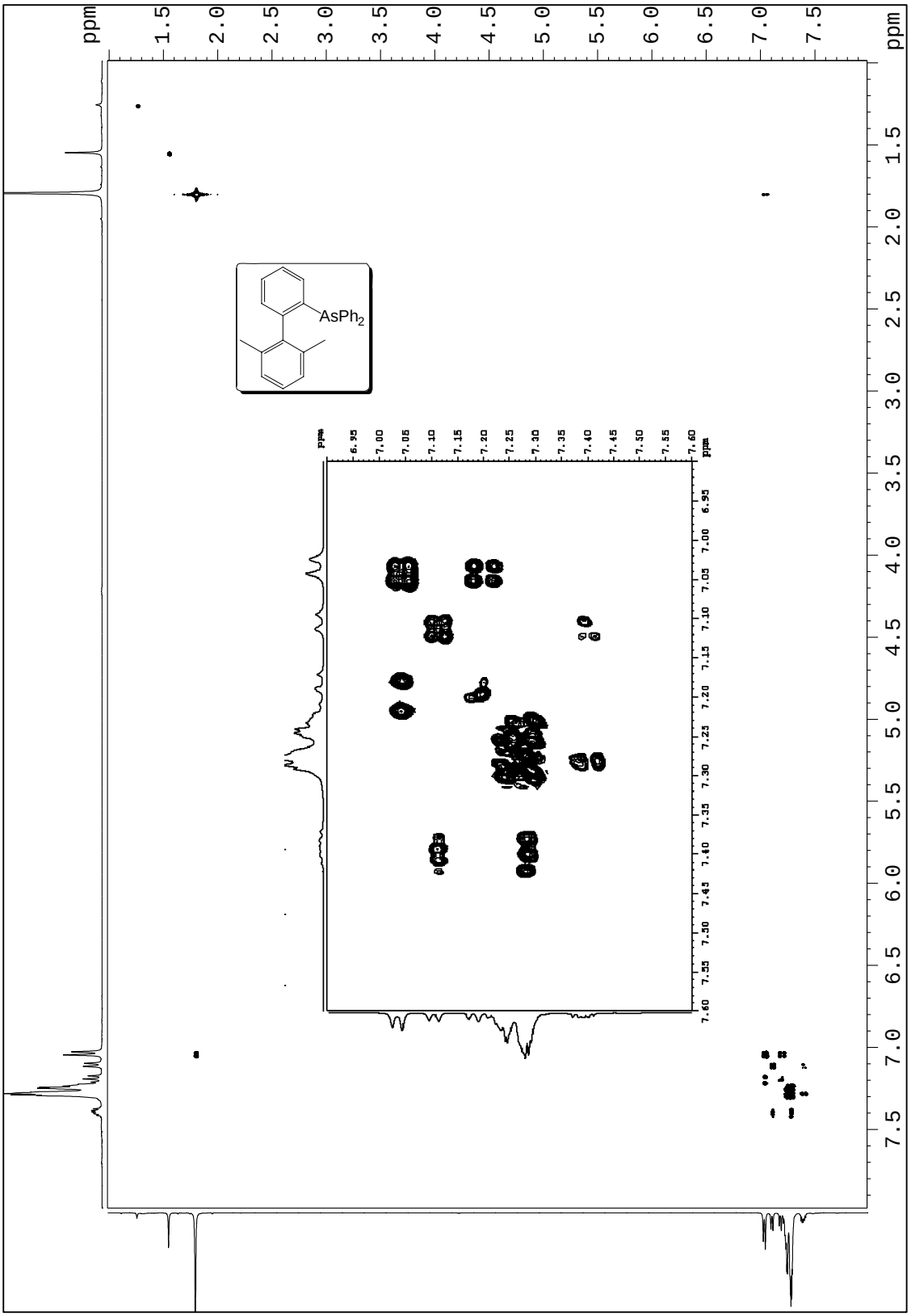
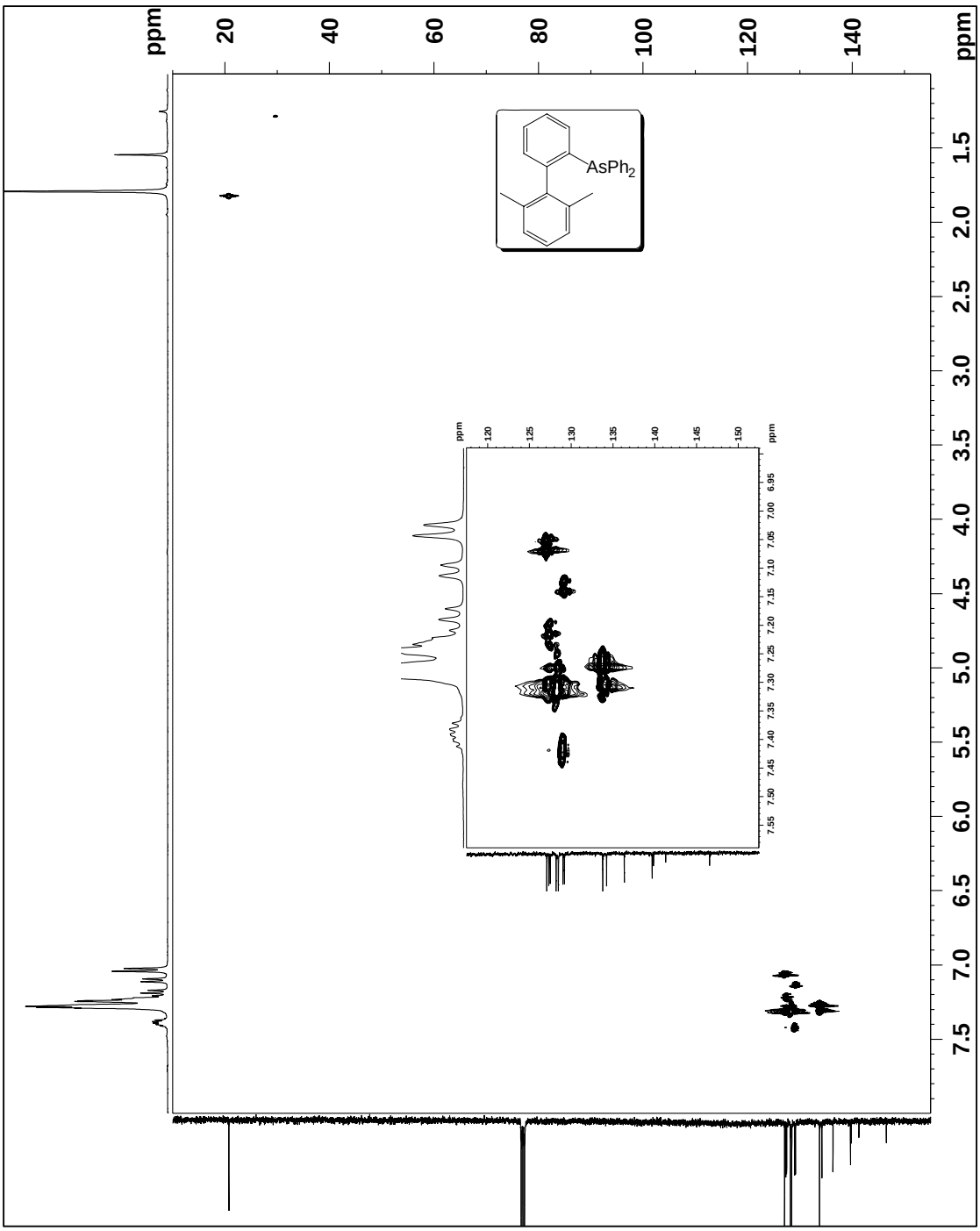


***2-Diphenylarsino-2',6'-dimethylbiphenyl (L3)*** NMR 2D (COSY-45) ($CDCl_3$).



***2-Diphenylarsino-2',6'-dimethylbiphenyl (L3)*** NMR 2D (HSQC) ($CDCl_3$).



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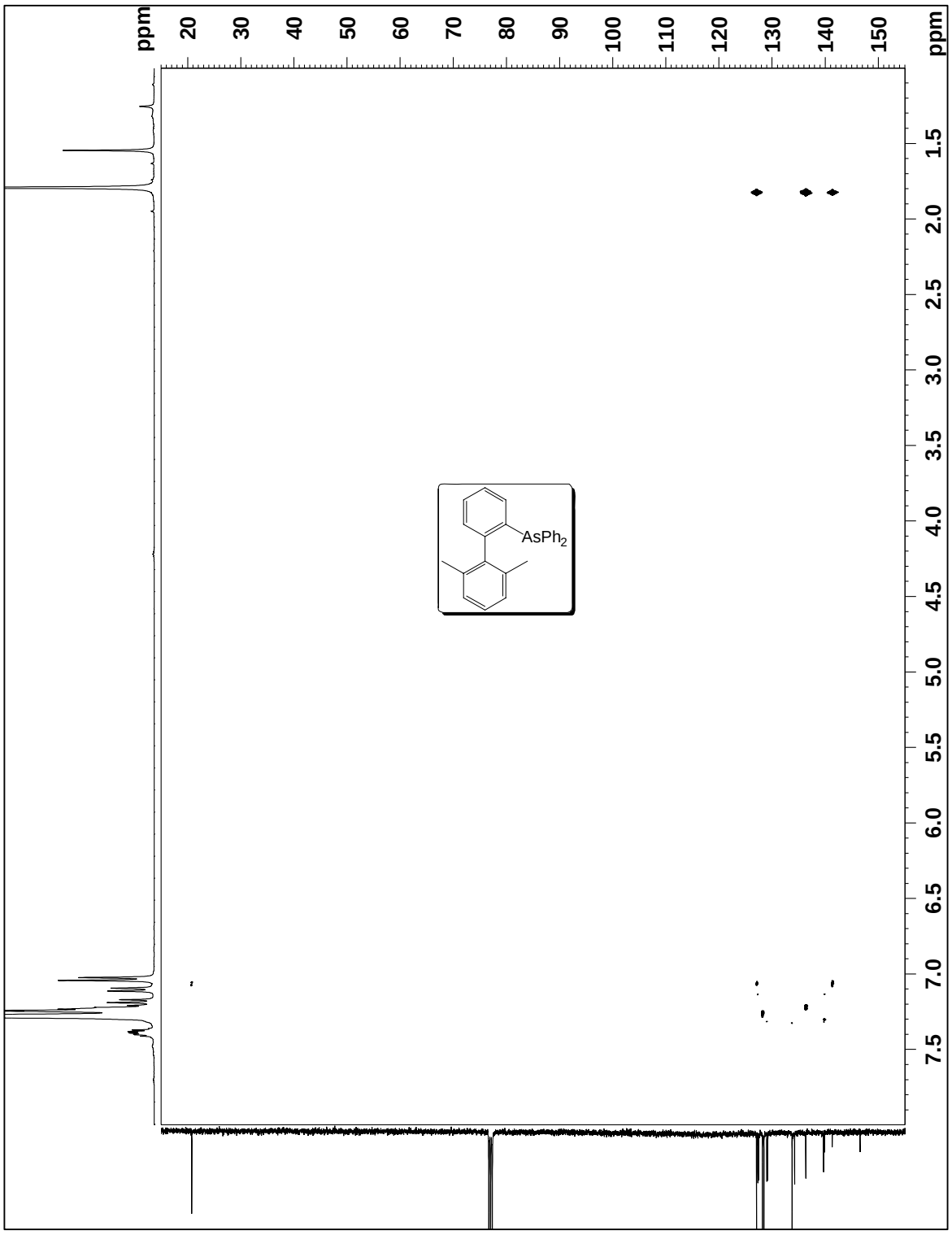
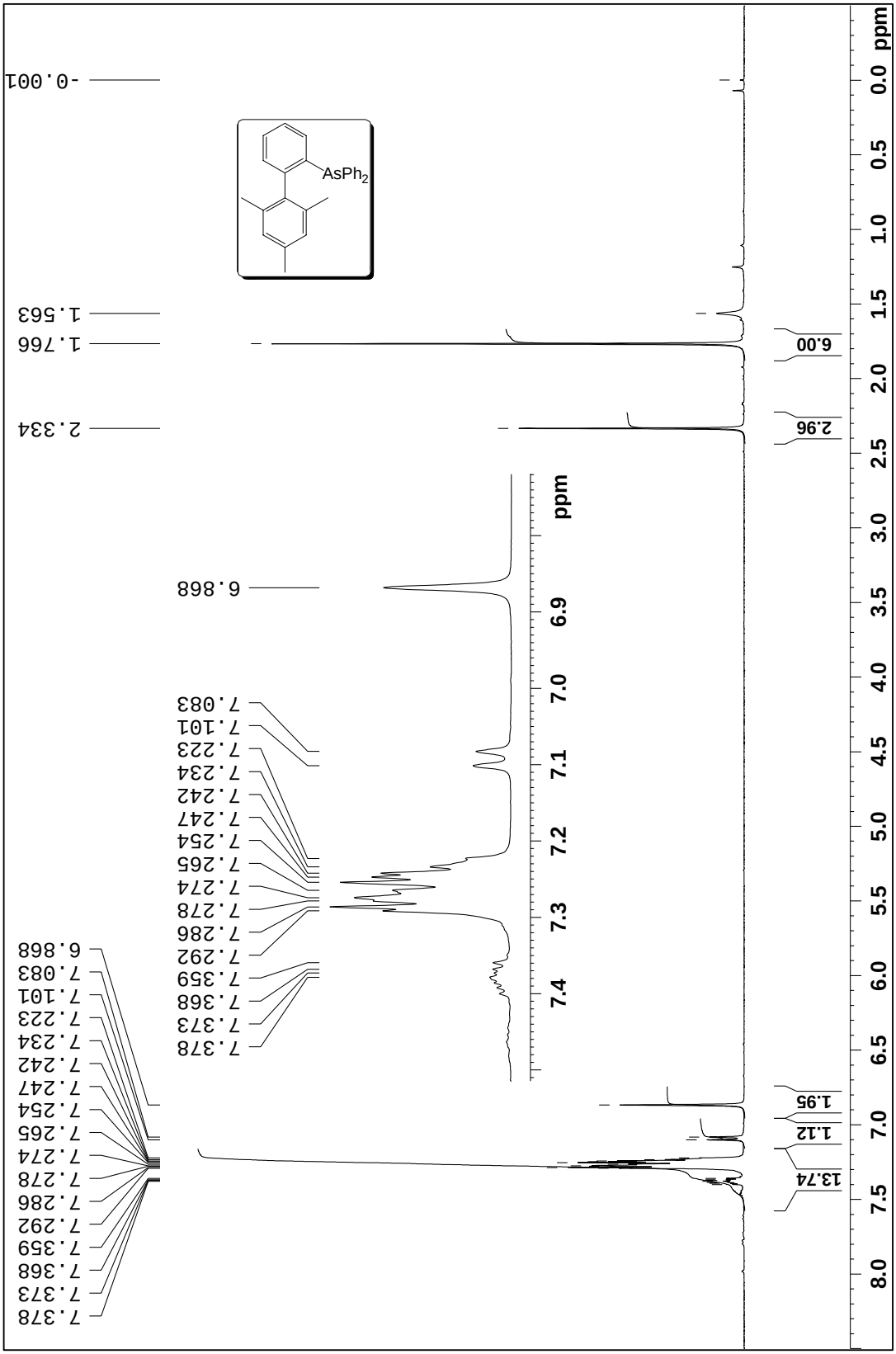
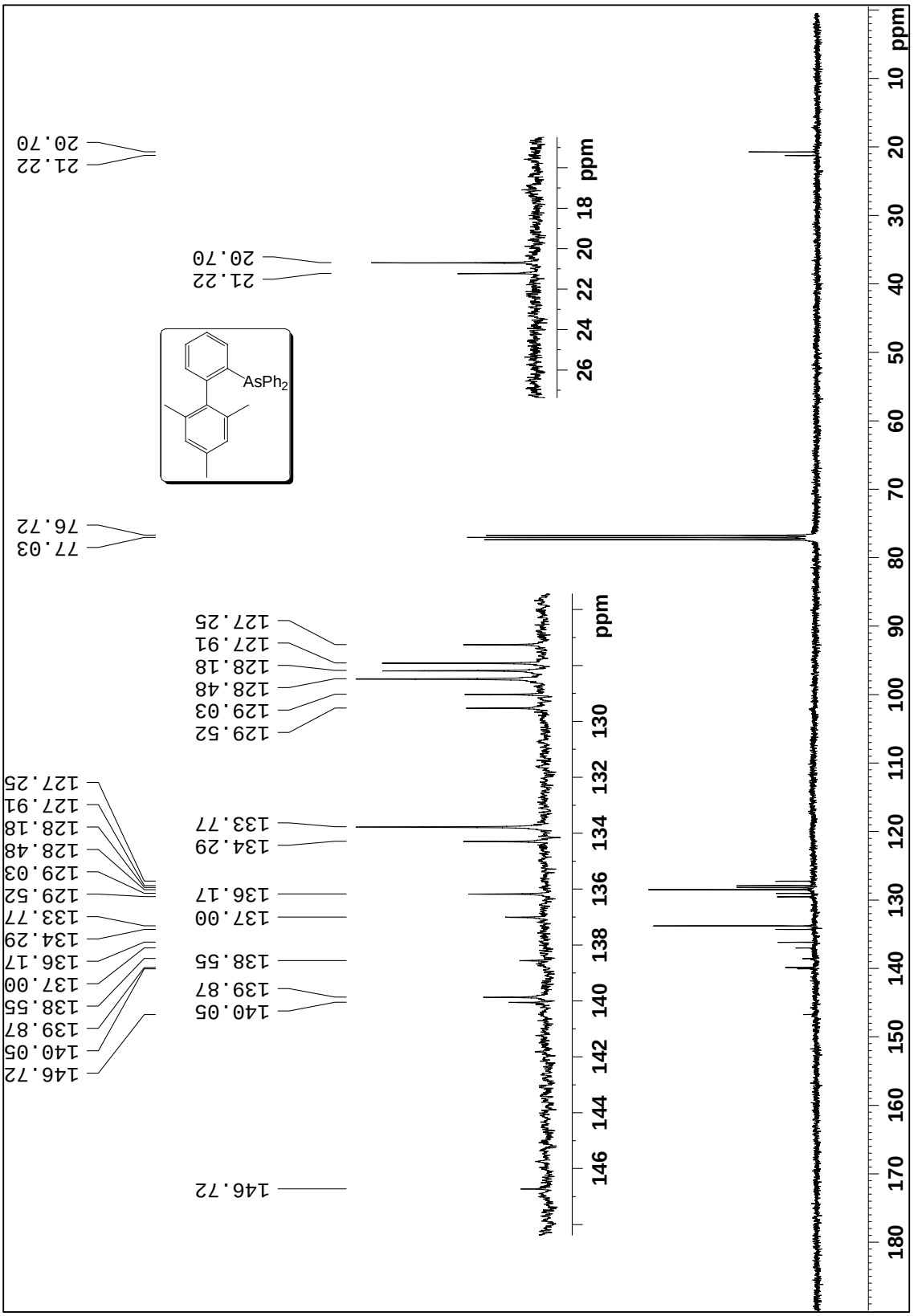


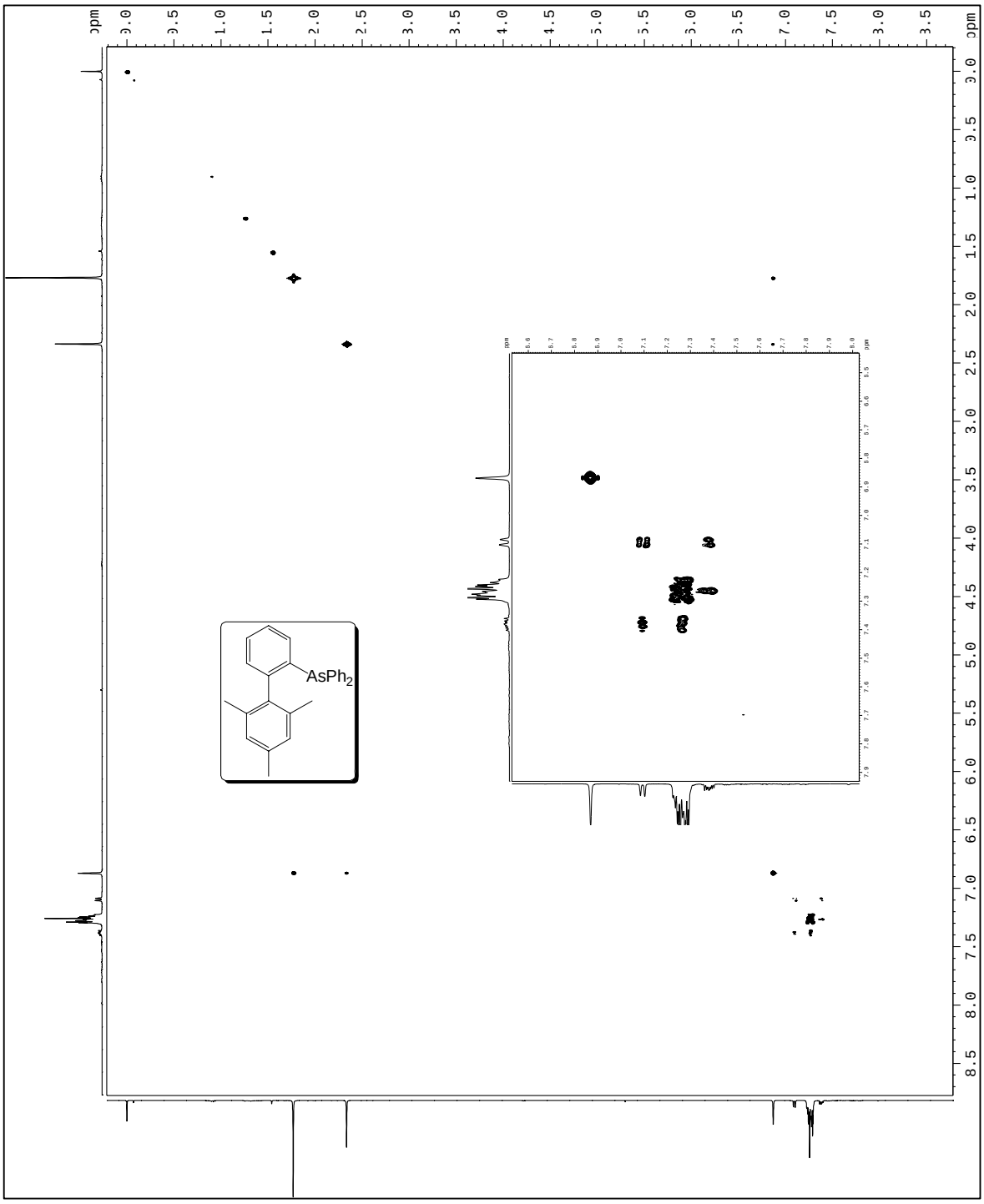
***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)*** $^{1}$H NMR ($CDCl_3$).



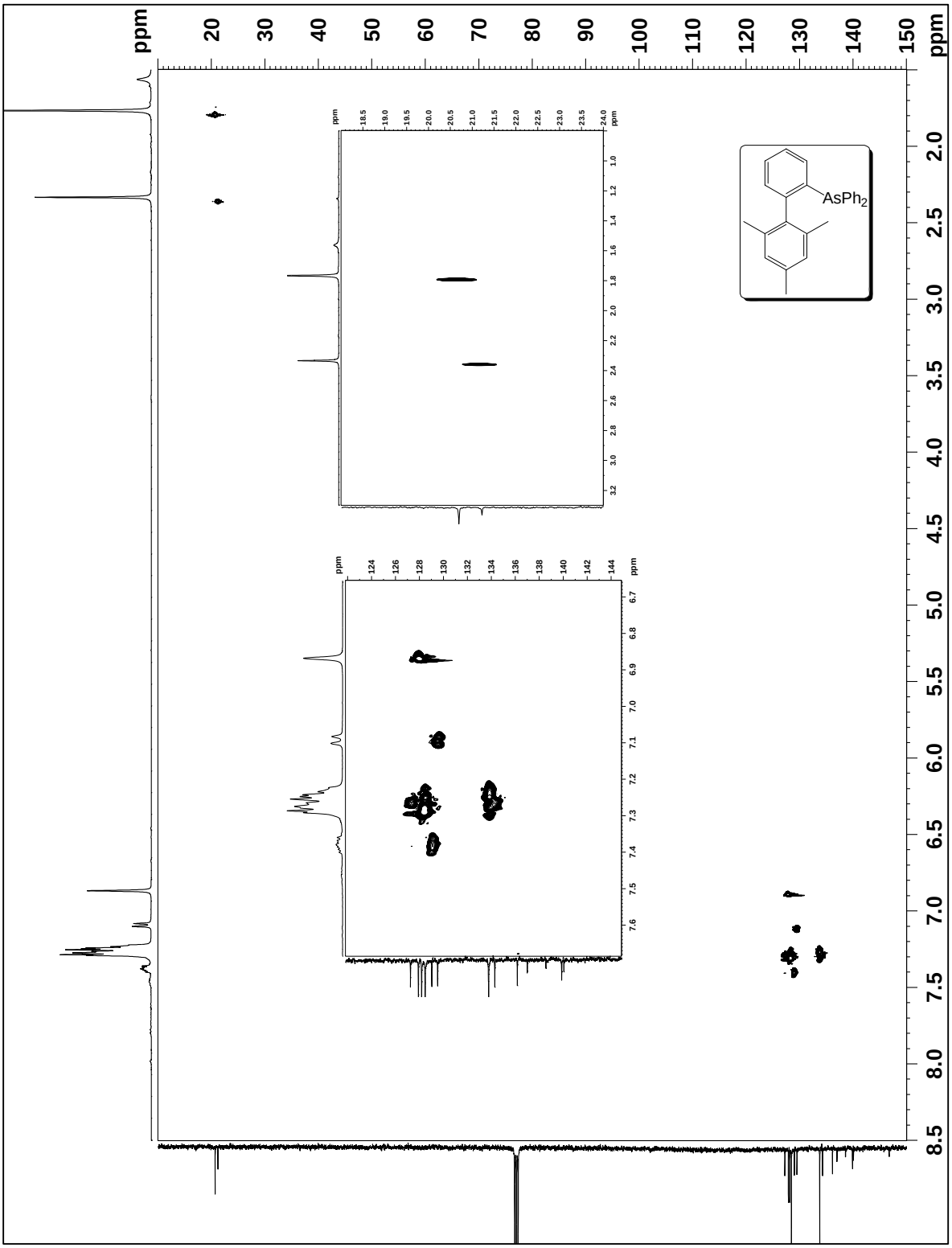
***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)*** $^{13}$C NMR ($CDCl_3$).



***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)*** NMR 2D (COSY-45) ($CDCl_3$).



***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)*** NMR 2D (HSQC) ($CDCl_3$).



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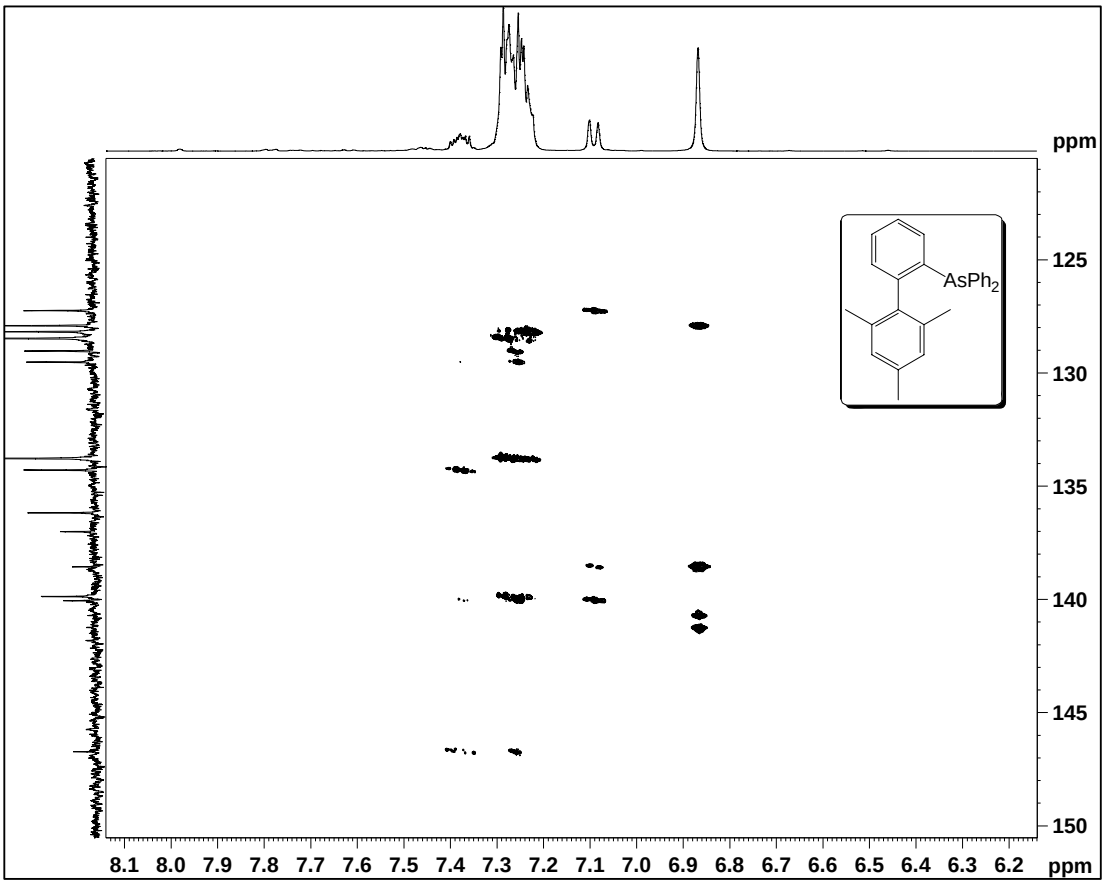
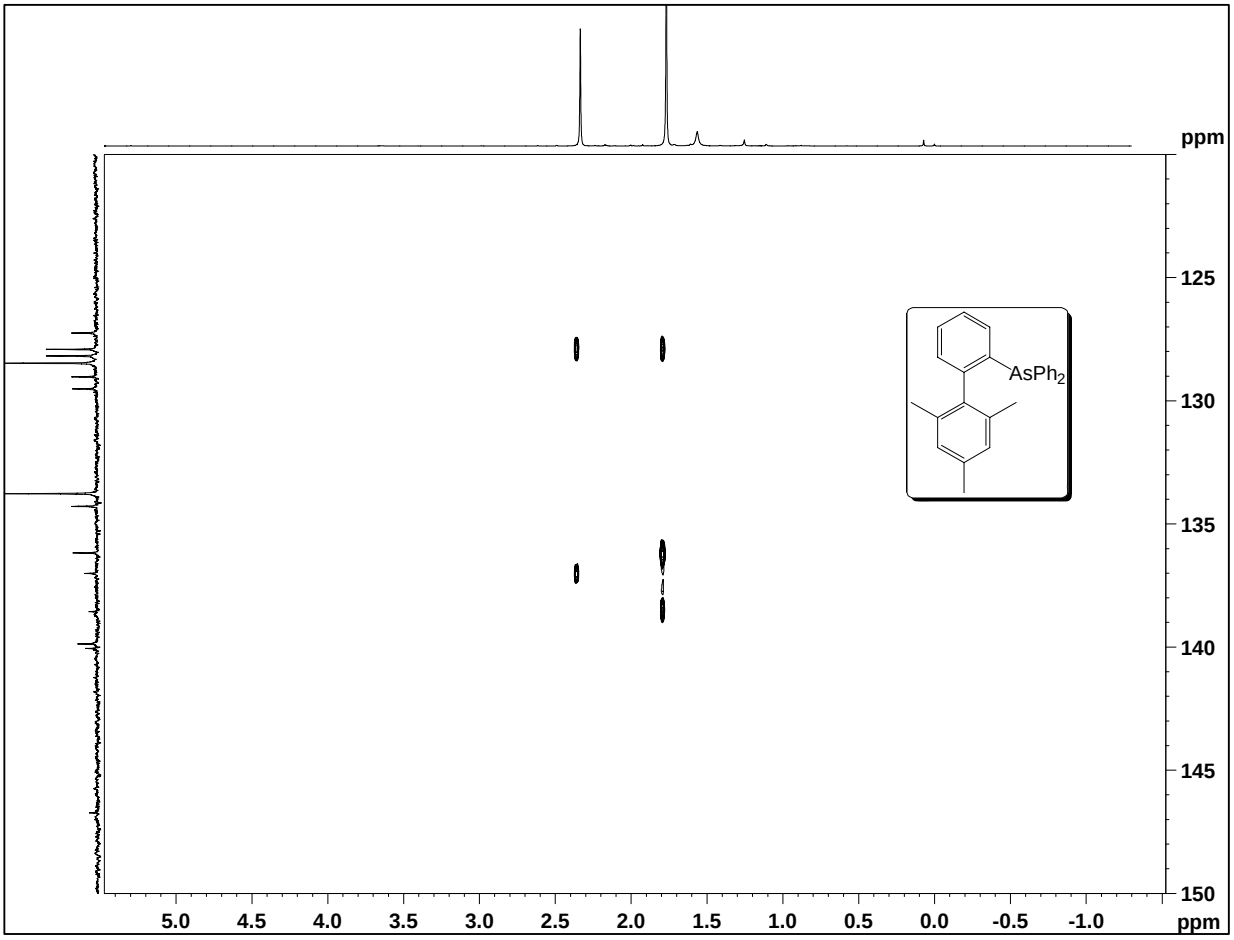
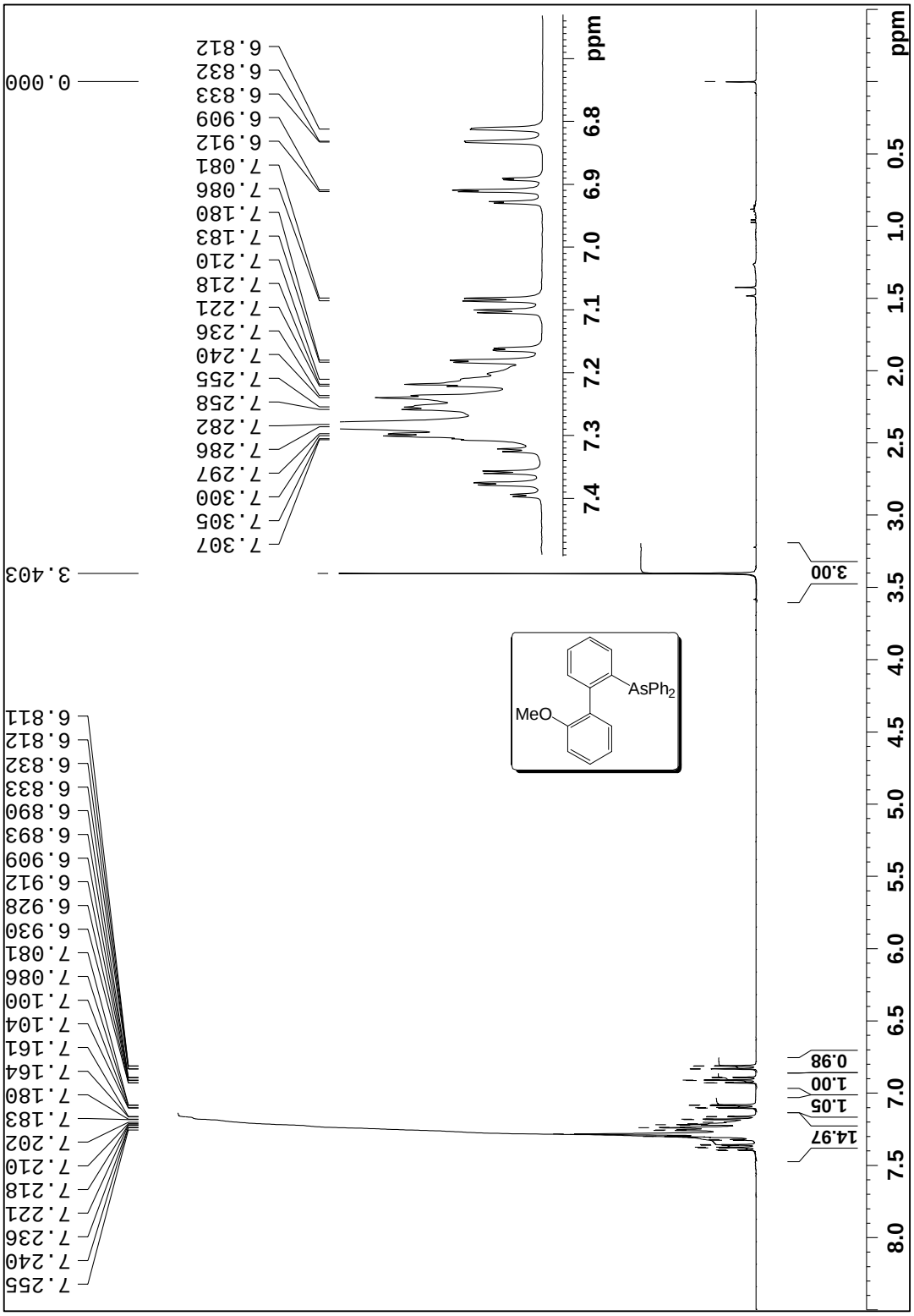


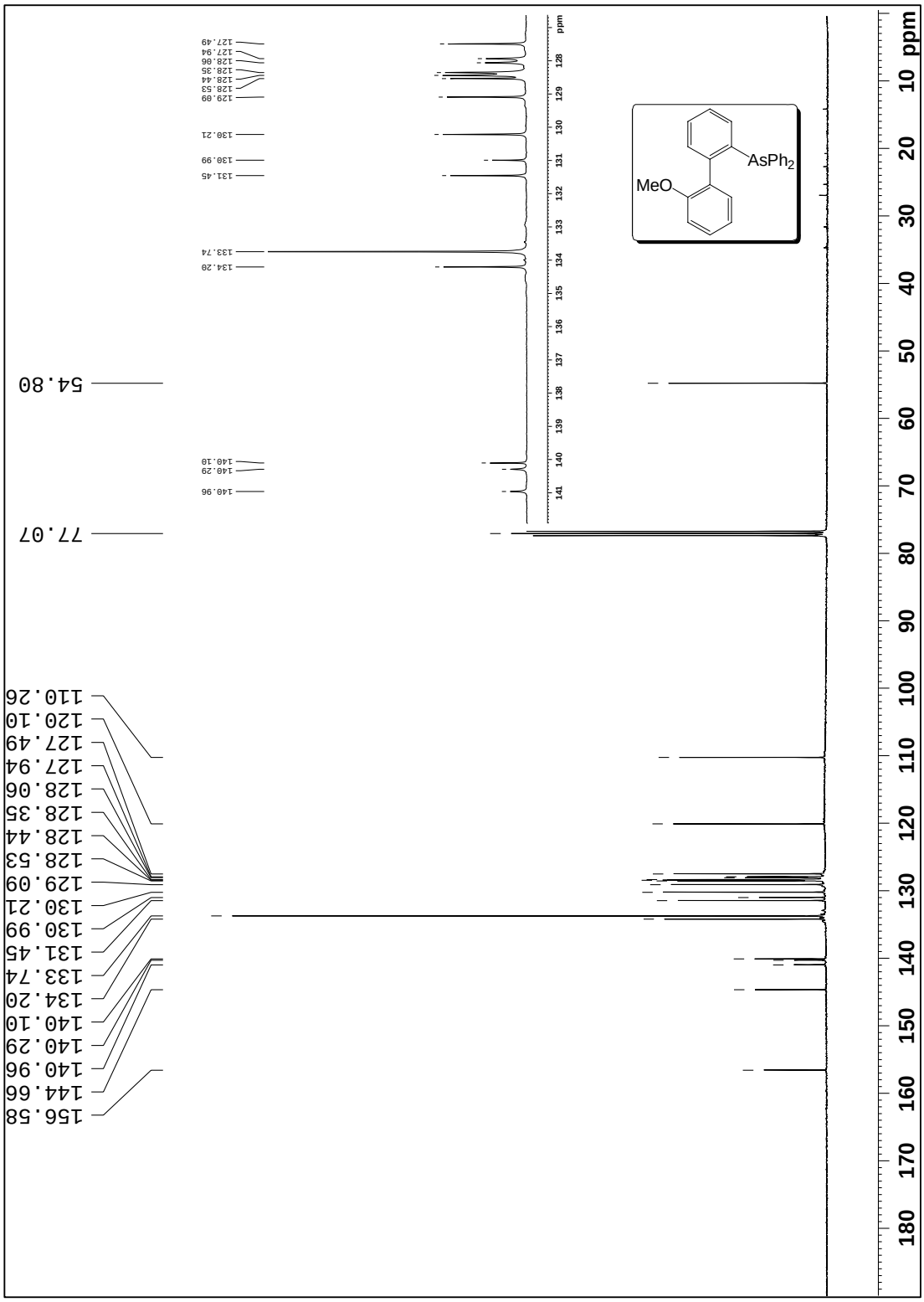
***2-Diphenylarsino-2',4',6'-trimethylbiphenyl (L4)*** NMR 2D (HMBC) ($CDCl_3$).



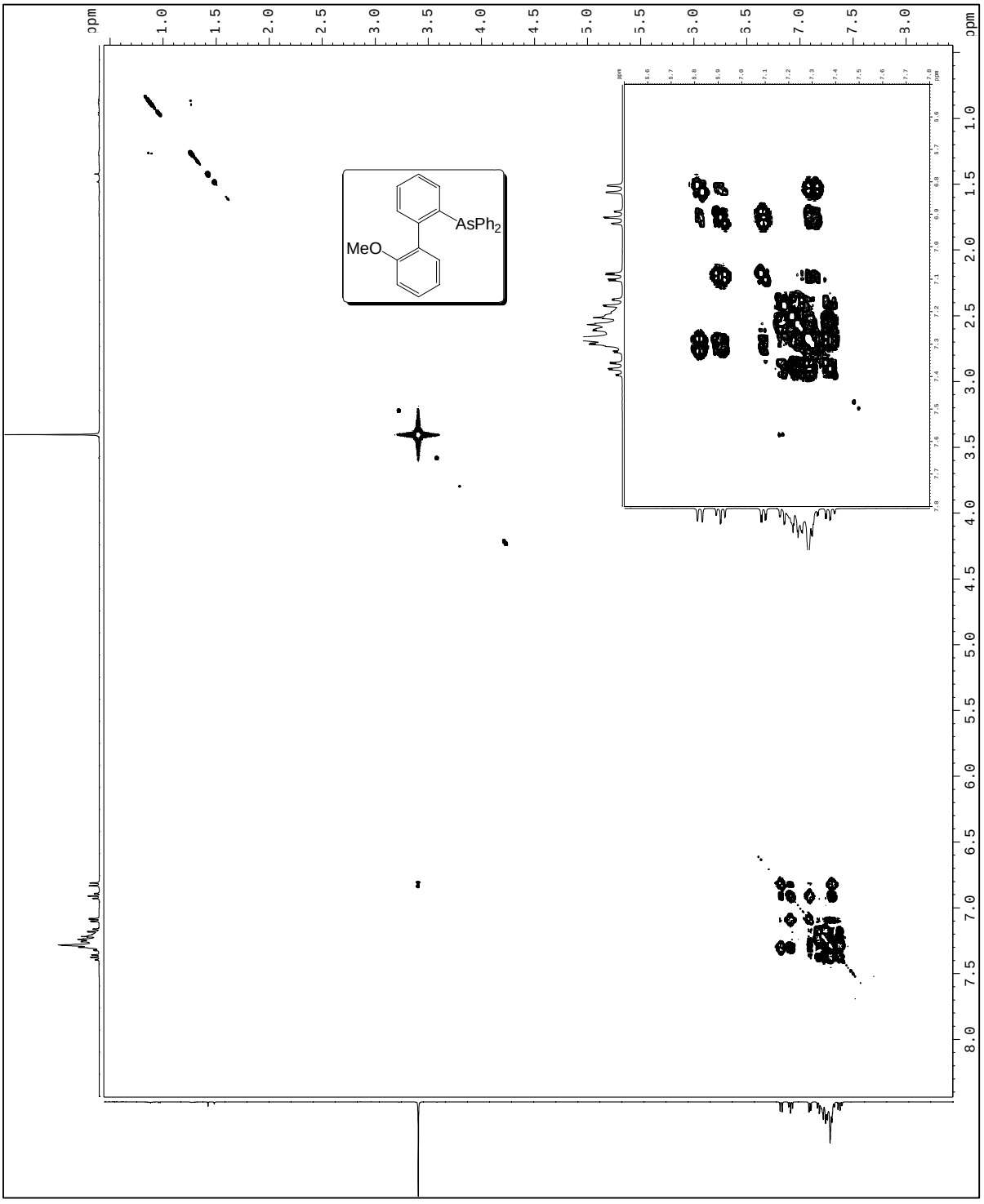
***2-Diphenylarsino-2'-methoxybiphenyl (L5)*** $^{1}$H NMR ($CDCl_3$).



***2-Diphenylarsino-2'-methoxybiphenyl (L5)*** $^{13}$C NMR ($CDCl_3$).



***2-Diphenylarsino-2'-methoxybiphenyl (L5)*** NMR 2D (COSY-45) ($CDCl_3$).



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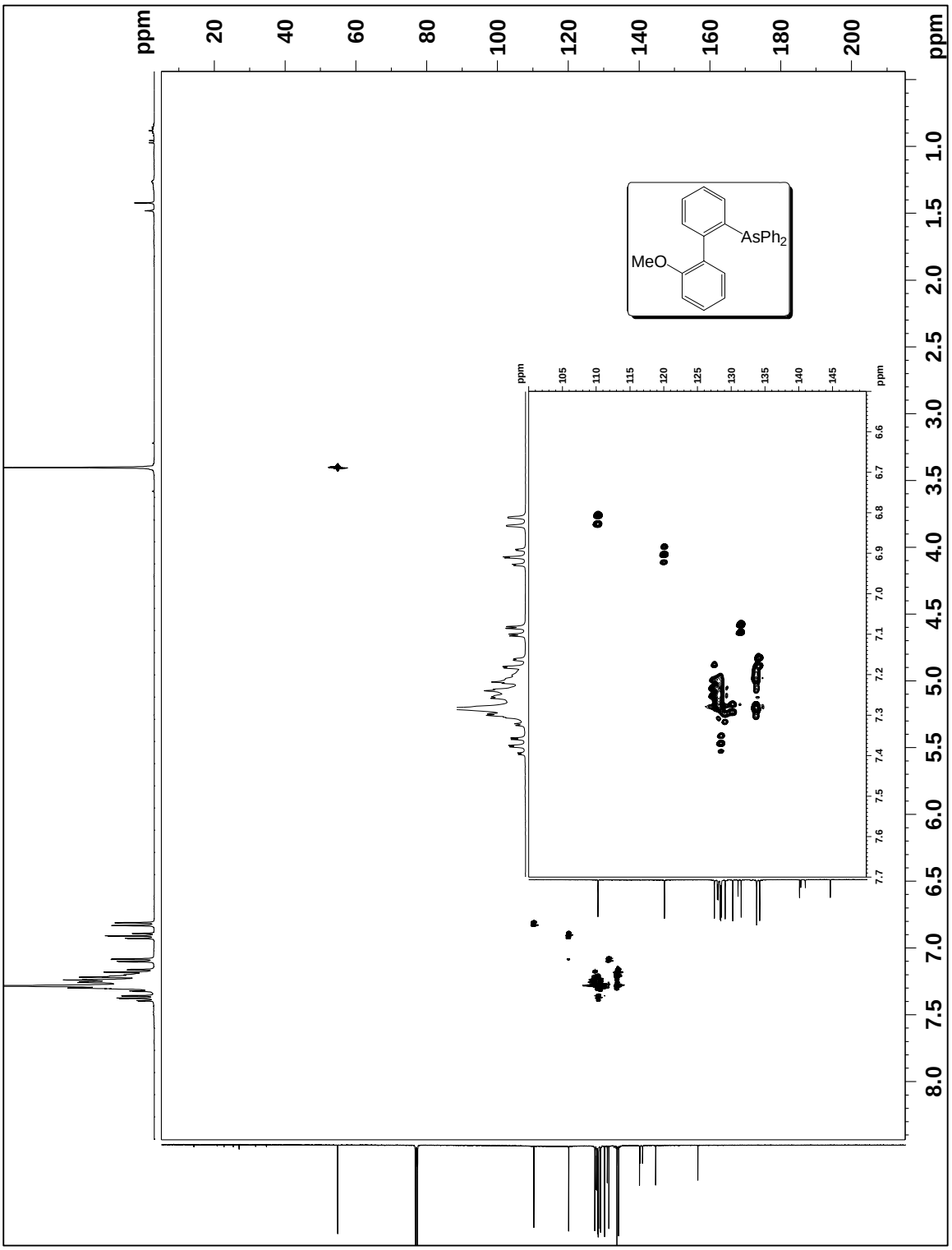
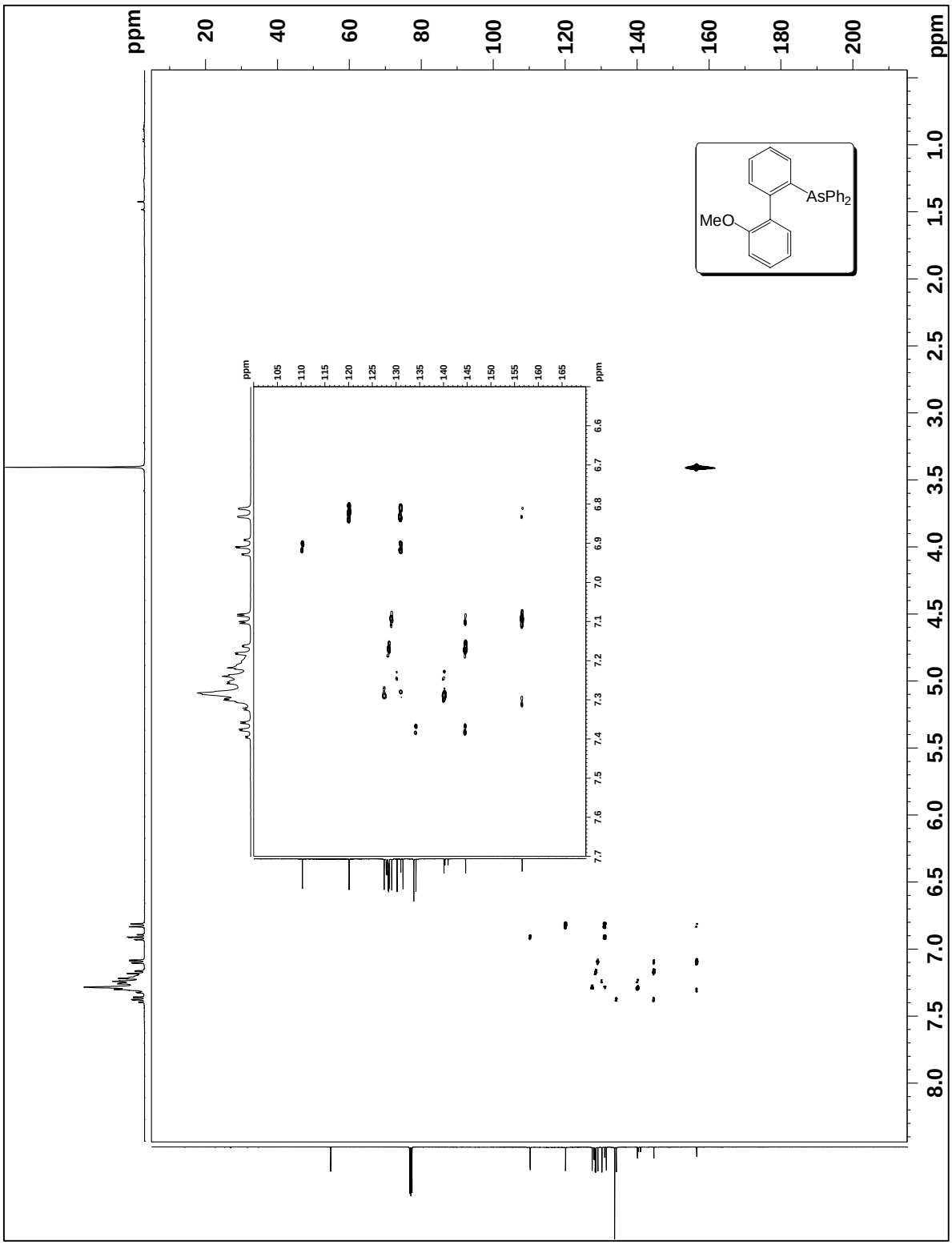
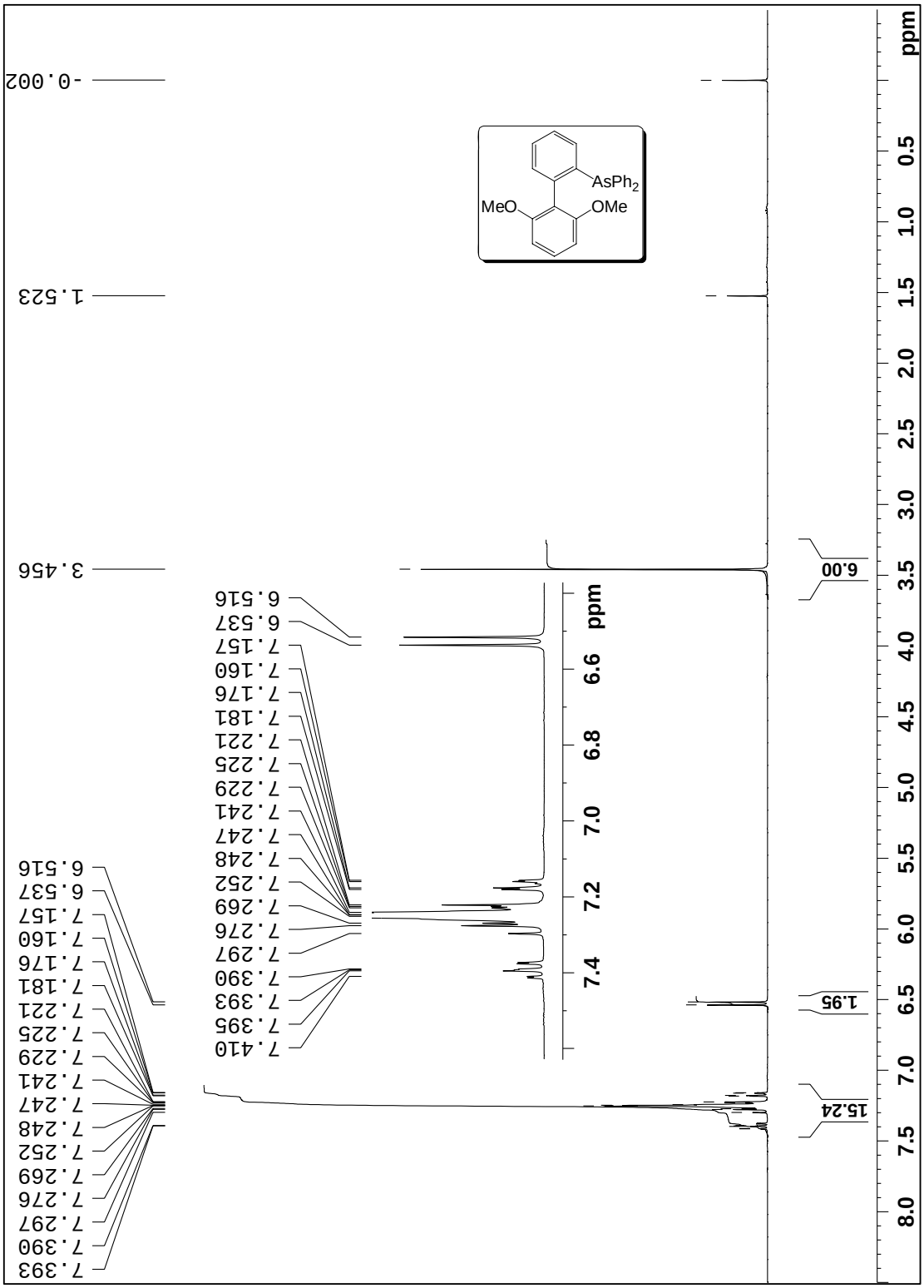


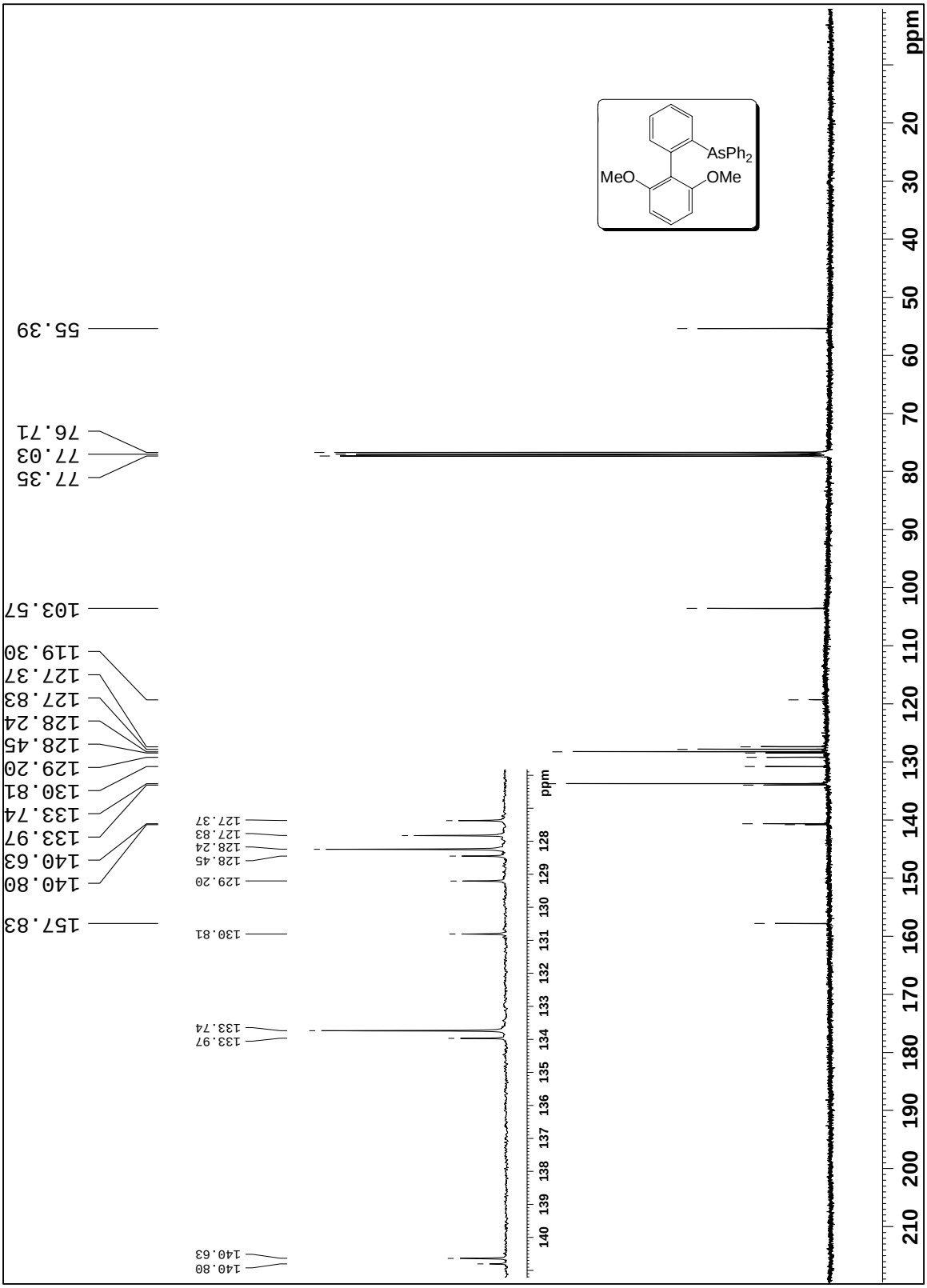
***2-Diphenylarsino-2'-methoxybiphenyl (L5)*** NMR 2D (HMBC) ($CDCl_3$).



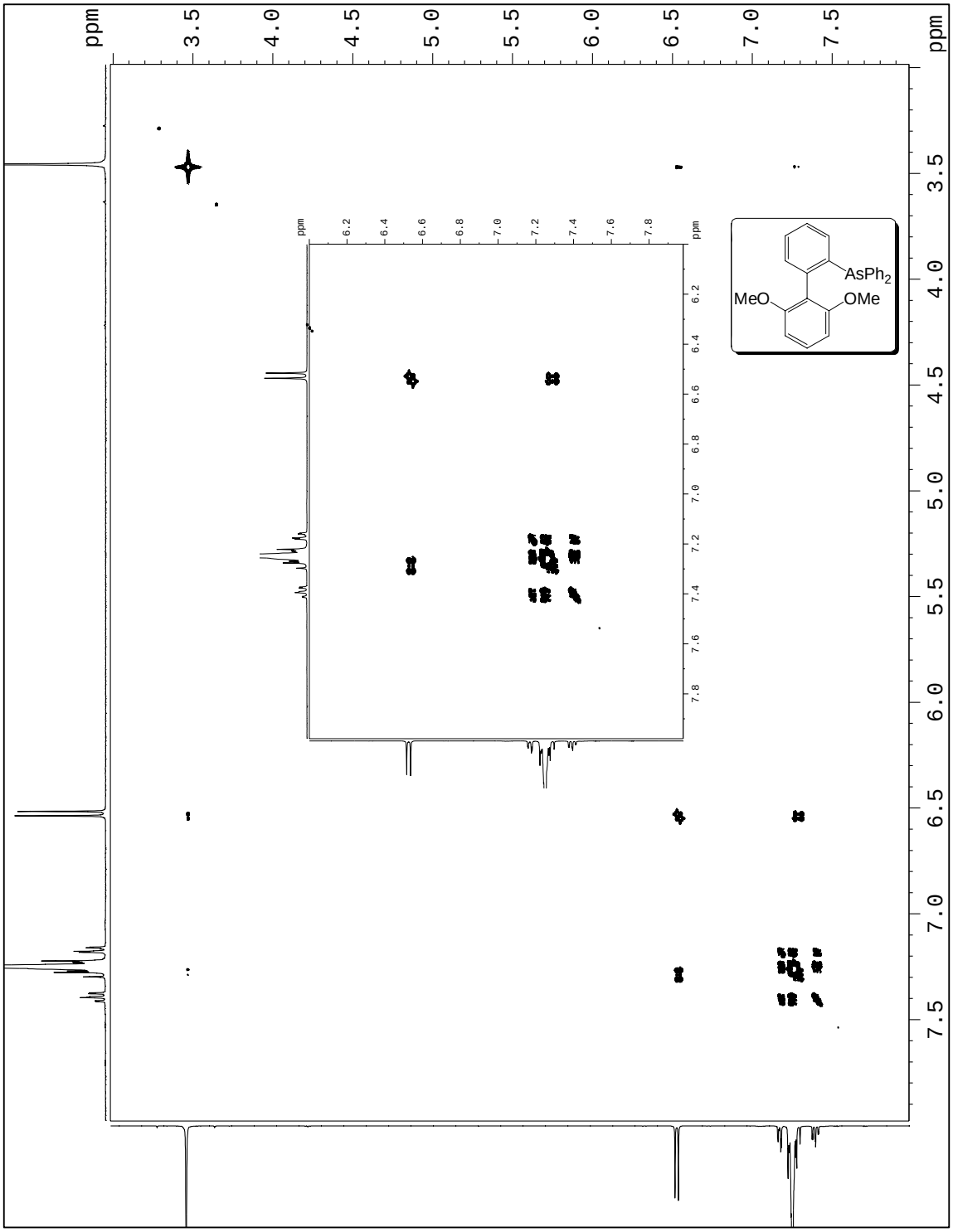
***2-Diphenylarsino-2',6'-dimethoxybiphenyl (L6)*** $^{1}$H NMR ($CDCl_3$).



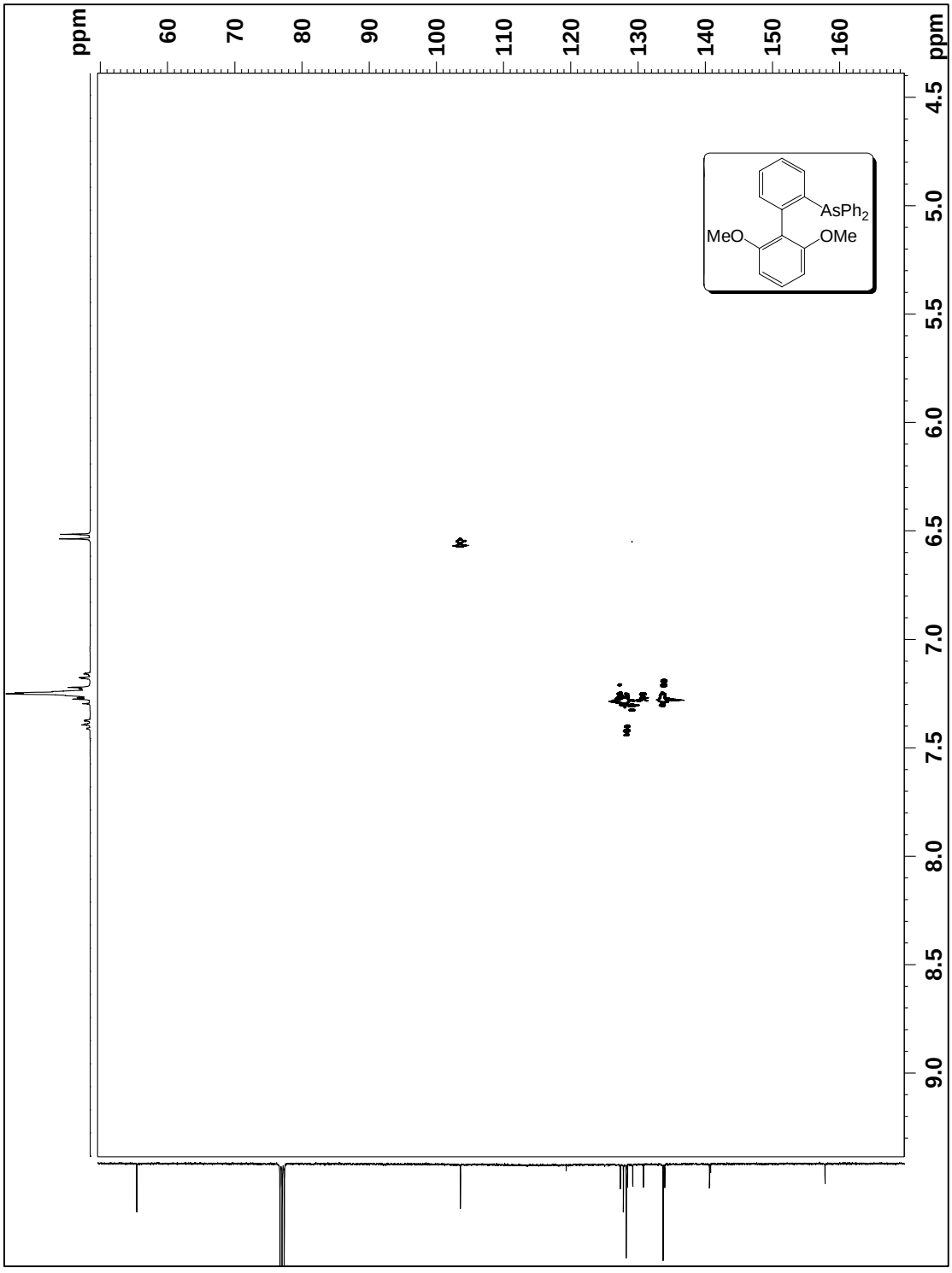
***2-Diphenylarsino-2',6'-dimethoxybiphenyl (L6)*** $^{13}$C NMR ($CDCl_3$).



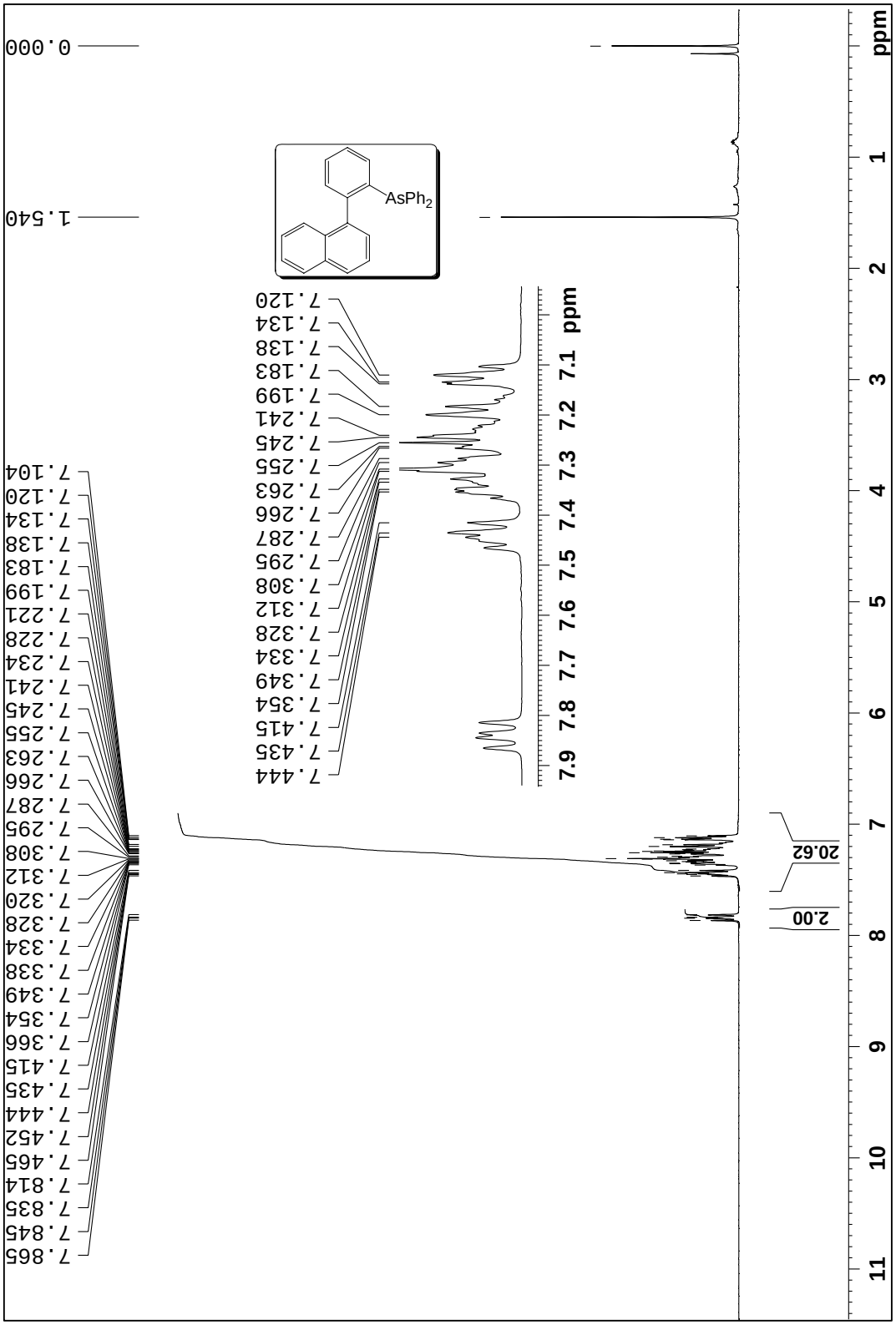
***2-Diphenylarsino-2',6'-dimethoxybiphenyl (L6)*** NMR 2D (COSY-45) ($CDCl_3$).



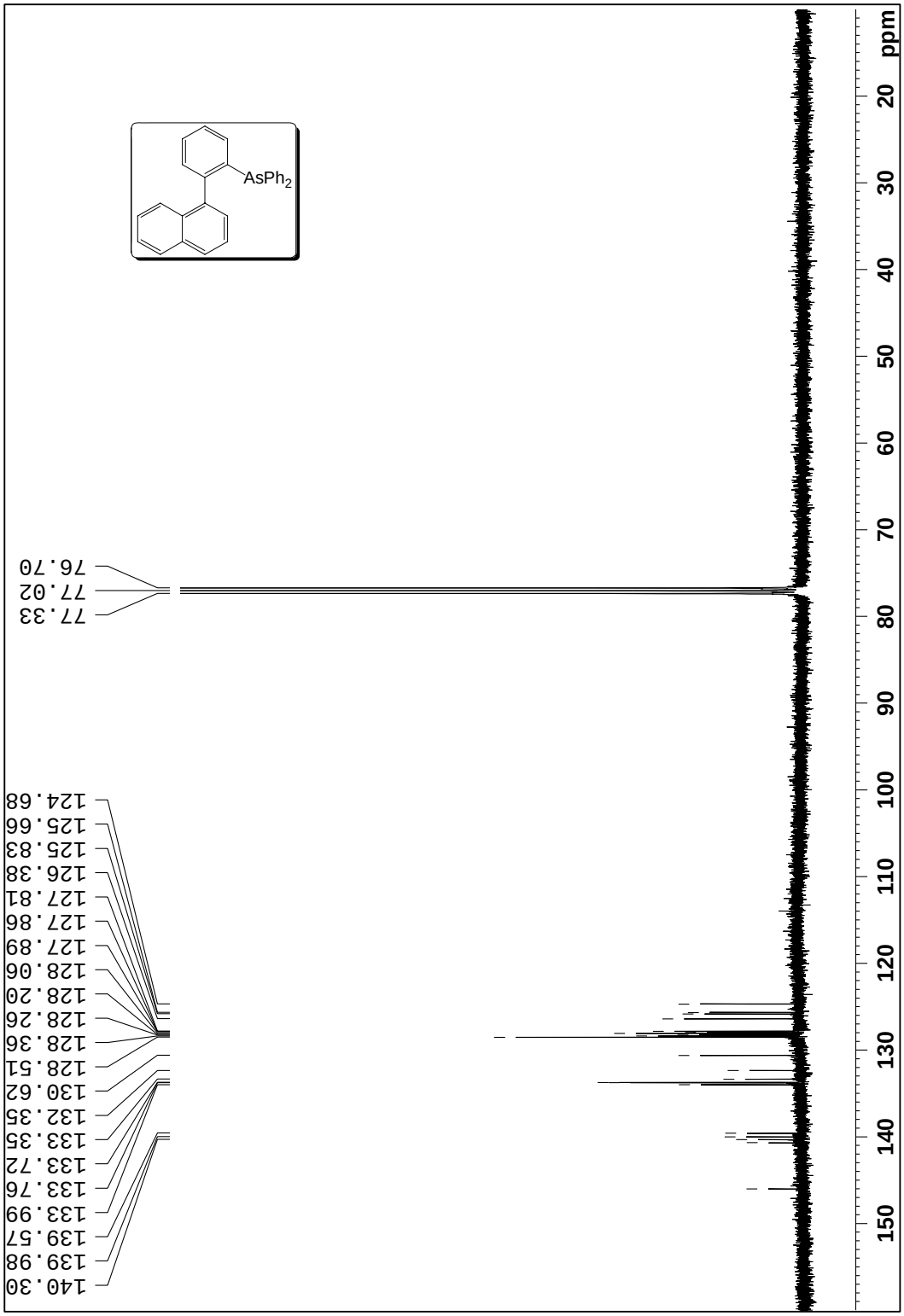
***2-Diphenylarsino-2',6'-dimethoxybiphenyl (L6)*** NMR 2D (HSQC) ($CDCl_3$).



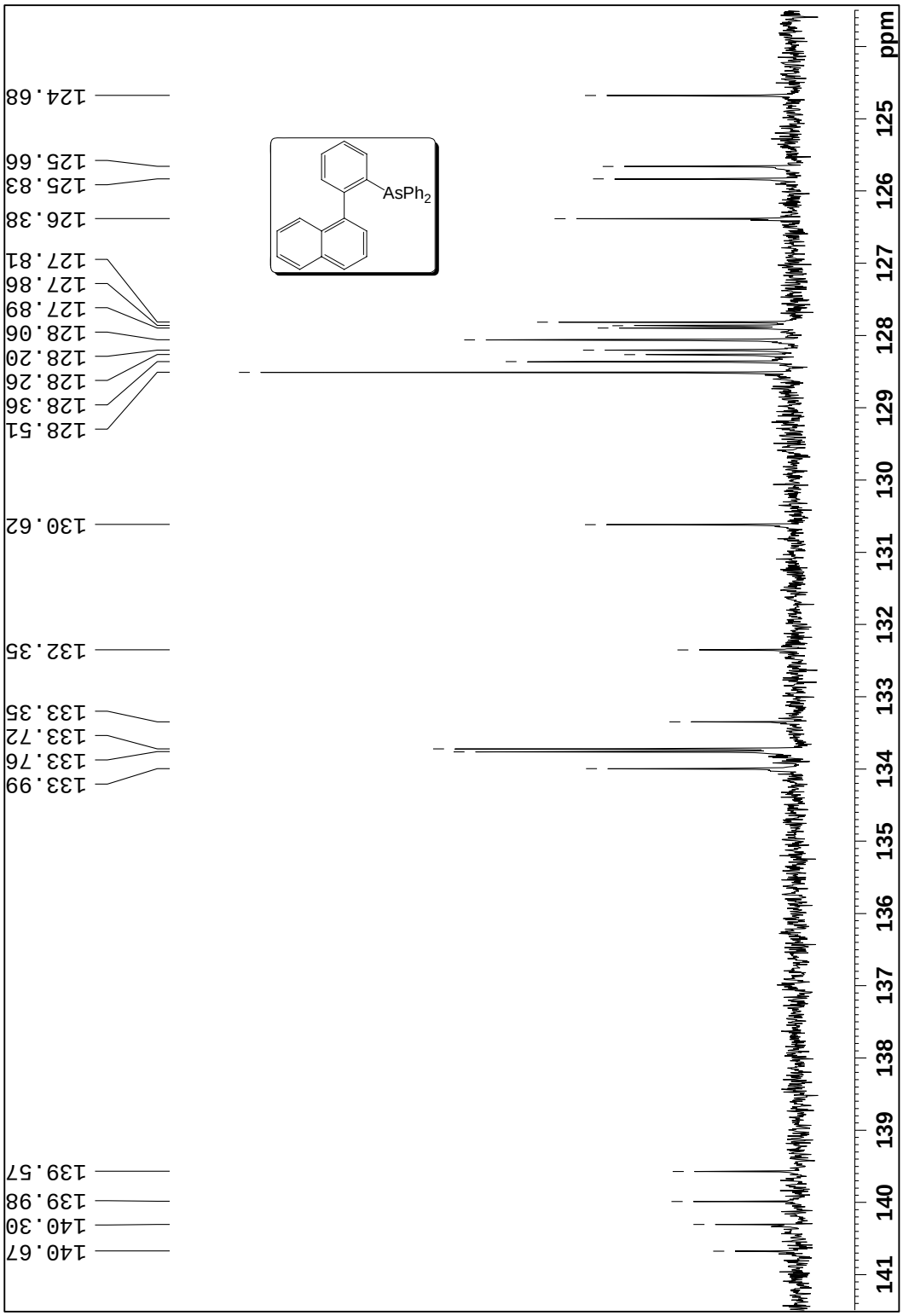
***1-(2-Diphenylarsinophenyl)naphthalene (L7)*** $^{1}$H NMR ($CDCl_3$).



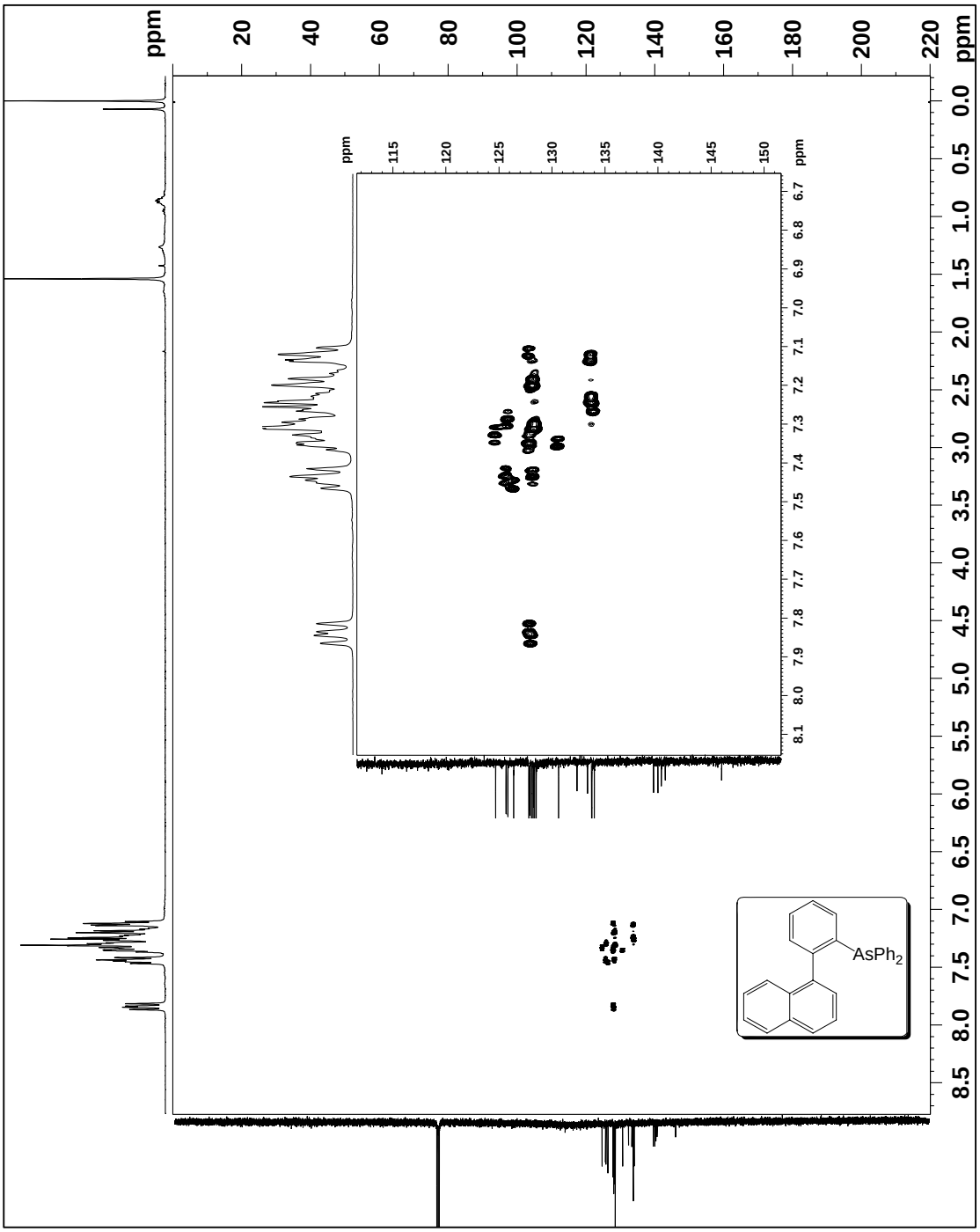
***1-(2-Diphenylarsinophenyl)naphthalene (L7)*** $^{13}$C NMR ($CDCl_3$).



***1-(2-Diphenylarsinophenyl)naphthalene (L7)*** $^{13}$C NMR ($CDCl_3$).



***1-(2-Diphenylarsinophenyl)naphthalene (L7)*** NMR 2D (HSQC) ($CDCl_3$).



**4. References**

1 Uberman, P. M.; Lanteri, M. N.; Martin, S. E. *Organometallics* **2009**, *28*, 6927-6934.

2 Lanteri, M. N.; Rossi, R. A.; Martín, S. E. *J. Organomet. Chem.*, **2009**, *694*, 3425-3430.