

# Supporting Information

## Expanding the Phosphorus-Carbon Analogy: Formation of an Unprecedented 5- Phosphasemibullvalene Derivative

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### General remarks:

Unless otherwise stated, all the experiments were performed under an inert argon atmosphere using modified Schlenk techniques or in a MBraun dry box. All common chemicals were commercially available and were used as received. Dry or deoxygenated solvents were prepared using standard techniques or used from a MBraun solvent purification system.

The NMR spectra were recorded on a JEOL ECX400 (400 MHz) spectrometer and chemical shifts are reported relative to the residual resonance in the deuterated solvents. IR spectra were measured on a Nicolet iS10 FTIR-ATR spectrometer by Thermo Scientific in the solid state. For reactions under UV irradiation, a UVP High intensity 100 Watt B-100AP Mercury Vapor Lamp without filter was used. HPLC equipment consisted of a Shimadzu LC-20 AD pump, a Shimadzu SPD-20 A UV/Vis detector and a Shimadzu CTO-20AC oven with column selector. Column and analysis specifications: Chiralpak IA (250x4.6 mm, particle size = 5  $\mu\text{m}$ , purchased from Daicel), eluent = 2-propanol, column temperature = 25°C, flow rate = 0.5 mL/min,  $\lambda=254$  nm (UV detector), injection volume = 10  $\mu\text{L}$ . The mass characterizations have been performed on an Agilent 6210 ESI-TOF instrument by Agilent Technologies, Santa Clara, CA, USA with standard settings of 5 L/min, 4 kV and 15 psi. Phosphabarrelene **6** was synthesized according to literature.<sup>S1</sup>

### Compound 11:

A solution of **6** (30 mg, 0.075 mmol) in THF (or DCM alternatively) in an NMR tube was exposed to UV light for 15 h, shaking the sample from time to time. The solution turned from colourless to light-yellow. Afterwards the volatiles were removed, yielding the product as a pale yellow solid in quantitative yield.

The <sup>13</sup>C NMR spectrum was recorded in benzene-d<sub>6</sub> as the resonances of the three sp<sup>3</sup>-hybridized C-atoms could only be detected in this solvent (Figure 5).

<sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz):  $\delta$  = 4.20 (m, 1H), 6.47 (dd,  $J$  = 7.4, 3.4 Hz, 1H), 6.75 (m, 1H), 6.98-7.35 (m, 15H), 7.43 (m, 1H), 7.61 (d,  $J$  = 8.3 Hz, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz):  $\delta$  = 47.82 (d,  $J$  = 3.5 Hz), 60.43 (d,  $J$  = 8.9 Hz), 63.68 (d,  $J$  = 2.1 Hz), 124.16 (d,  $J$  = 1.7 Hz), 124.63

(s), 124.71 (s), 124.78 (s), 124.95-125.04 (m), 125.10 (s), 125.34 (d,  $J = 1.3$  Hz), 125.39 (s), 125.74 (d,  $J = 2.1$  Hz), 125.84 (s), 125.92 (s), 126.04 (s), 126.11 (s), 126.41(s), 129.40 (s), 133.80 (d,  $J = 18$  Hz), 136.32 (d,  $J = 23.2$  Hz), 136.96(s), 143.84 (d,  $J = 15.6$  Hz), 146.63 (d,  $J = 3.1$  Hz), 147.60 (d,  $J = 21.5$  Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ , 162 MHz):  $\delta = 33.1$  (s) ppm. ESI-TOF (m/z): 801.2885 g/mol (calc.: 801.2840 g/mol)  $[2\text{M} + \text{H}]^+$ .

### Compound 12:

The compound could be obtained in two different ways:

*Method A:* To a solution of **11** (30 mg, 0.075 mmol) in toluene (0.7 mL), an excess of grey selenium was added and the solution was heated at reflux for overnight. Afterwards the solution was filtered over celite and the solvent was removed in vacuo, yielding the product as an off-white powder (35 mg, 97%).

*Method B:* A solution of **13** (35.9 mg, 0.075 mmol) in THF (0.7 mL) in an NMR tube was exposed to UV light for 1.5 h. The solution turned from colourless to pale-yellow. Afterwards the volatiles were removed, yielding the product as an off-white powder in quantitative yield.

$^1\text{H}$  NMR (THF- $d_8$ , 400 MHz):  $\delta = 4.46$  (dd,  $J = 9.3, 4.1$  Hz, 1H), 6.63 (dd,  $J = 38.0, 4.0$  Hz, 1H), 6.87 (m, 1H), 7.04-7.44 (m, 15H), 7.65 (dd,  $J = 10.9, 6.9$  Hz, 1H), 7.76 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 101 MHz):  $\delta = 48.11$  (d,  $J = 7.9$  Hz), 64.67 (d,  $J = 62.0$  Hz), 65.21 (d,  $J = 4.2$  Hz), 126.58 (d,  $J = 10.6$  Hz), 128.47 (d,  $J = 2.1$  Hz), 128.58 (m), 128.70 (m), 128.85 (s), 129.06 (s), 129.17 (s), 131.18 (d,  $J = 4.5$  Hz), 132.12 (m), 132.57 (d,  $J = 19.5$  Hz), 133.30 (d,  $J = 5.5$  Hz), 133.99 (d,  $J = 11.8$  Hz), 138.56 (d,  $J = 1.6$  Hz), 141.01 (d,  $J = 73.6$  Hz), 143.54 (d,  $J = 61.6$  Hz), 145.27 (d,  $J = 17.2$  Hz) ppm.  $^{31}\text{P}$  NMR (THF- $d_8$ , 162 MHz):  $\delta = 57.2$  (s, with  $^{77}\text{Se}$  satellites,  $^1J_{\text{P-Se}} = 824.9$  Hz) ppm. ESI-TOF (m/z): 503.0485 g/mol (calc.: 503.0444 g/mol)  $[\text{M} + \text{Na}]^+$ .

### General procedure for the synthesis of $[\text{LNi}(\text{CO})_3]$ complexes:

Caution:  $\text{Ni}(\text{CO})_4$  is highly toxic and potentially carcinogenic. It can be absorbed through the skin or inhaled due to its high volatility. Vapors of  $\text{Ni}(\text{CO})_4$  can autoignite. All manipulations must be done with extreme care in a well-ventilated fumehood.

Under vacuum 0.6 mL of THF were condensed in a Young NMR tube containing the appropriate ligand (0.075 mmol). Afterwards, roughly 2 equivalents of  $\text{Ni}(\text{CO})_4$  were condensed in the same tube using a condensation line. The tube was slowly heated up to room temperature. The reaction progress was monitored by  $^{31}\text{P}$ NMR and the tube was degassed until full conversion. The volatiles were removed in vacuo, yielding the product quantitatively. IR spectra were measured in DCM.

### Compound 14:

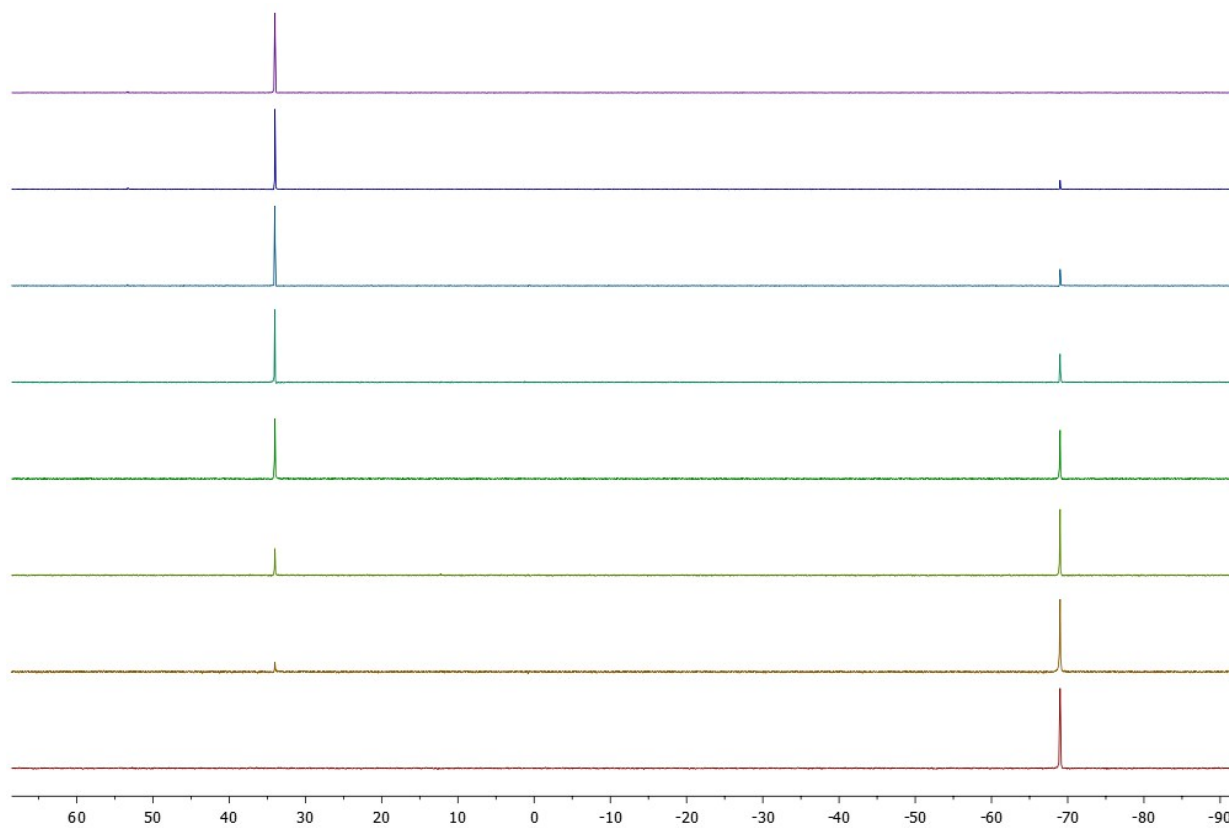
$^1\text{H}$  NMR (THF- $d_8$ , 400 MHz):  $\delta = 4.37$ (dd,  $J = 6.1, 3.6$  Hz, 1H), 6.42 (dd,  $J = 19.4, 3.5$  Hz, 1H), 6.91 (m), 7.04 - 7.34 (m, 13H), 7.43 (m, 4H), 7.63 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 101 MHz):  $\delta = 50.42$  (s), 65.22 (s), 65.61 (d,  $J = 28.2$  Hz), 126.19 (s), 126.36 (s), 127.04 (s), 127.14 (m), 127.40 (s), 127.52 (d,  $J = 5.6$  Hz), 127.72 (d,  $J = 3.5$  Hz), 127.88 (m), 135.09 (d,  $J = 15.1$  Hz), 135.99 (d,  $J = 14.5$  Hz), 138.08 (s), 144.04 (d,  $J = 26.7$  Hz), 146.64 (d,  $J = 17.8$  Hz), 147.03 (d,  $J =$

2.7 Hz), 195.04 (s, CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ , 162 MHz):  $\delta = 73.9$  (s) ppm. IR (DCM): 2074 (m), 2001 (bs)  $\text{cm}^{-1}$ .

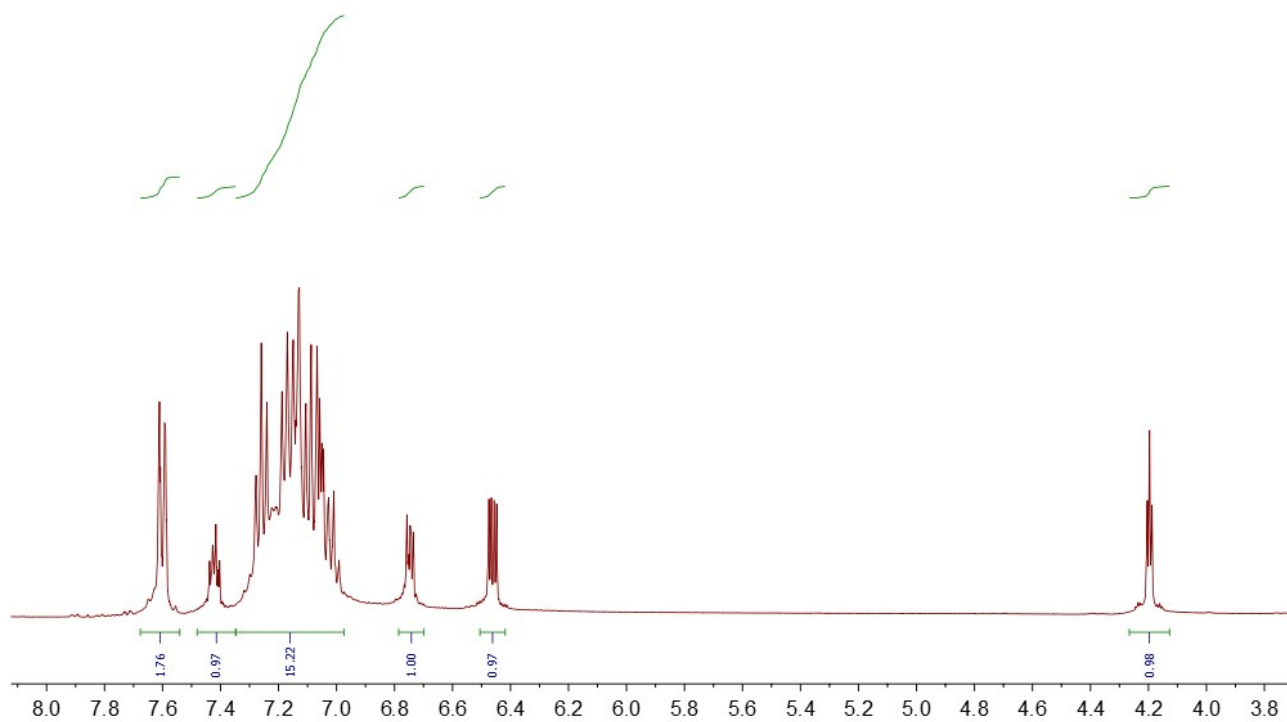
**Compound 15:** IR (DCM): 2075 (m), 2001 (bs)  $\text{cm}^{-1}$ .

**Compound 16:** IR (DCM): 2079 (s), 2011 (s)  $\text{cm}^{-1}$ .

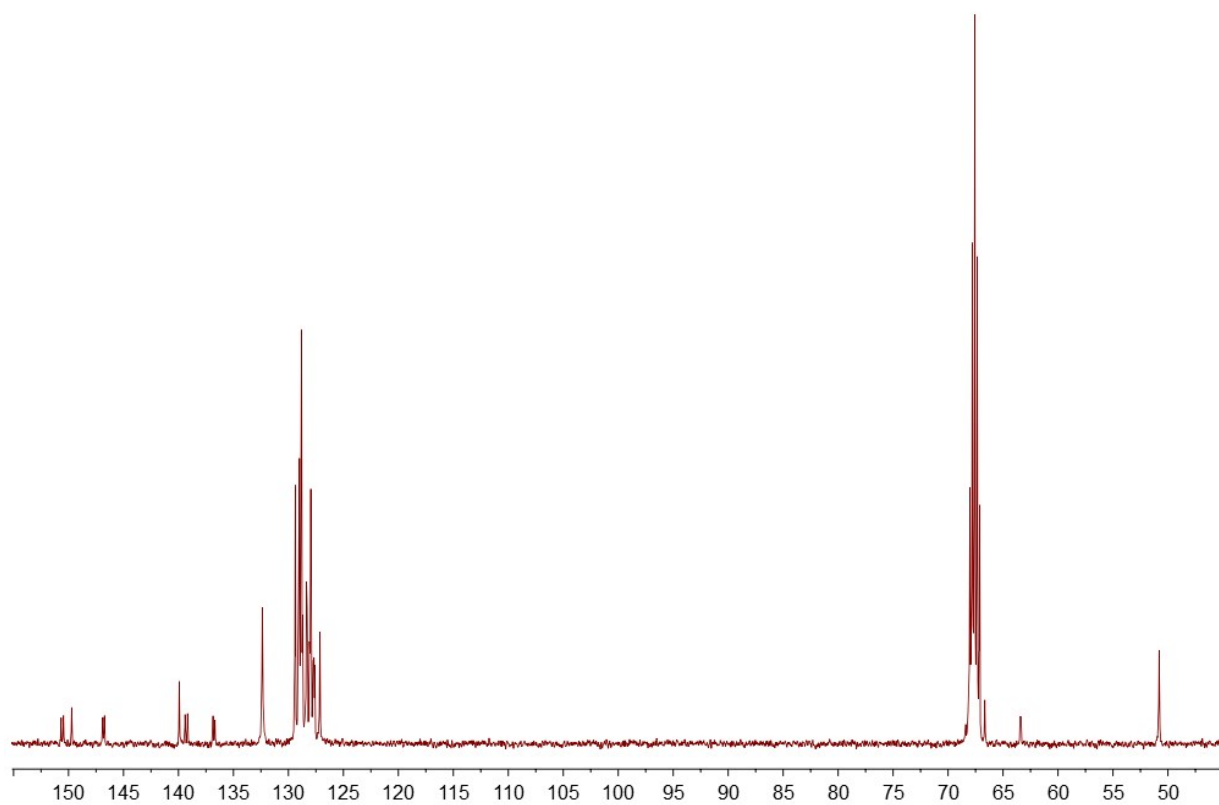
**NMR spectra:**



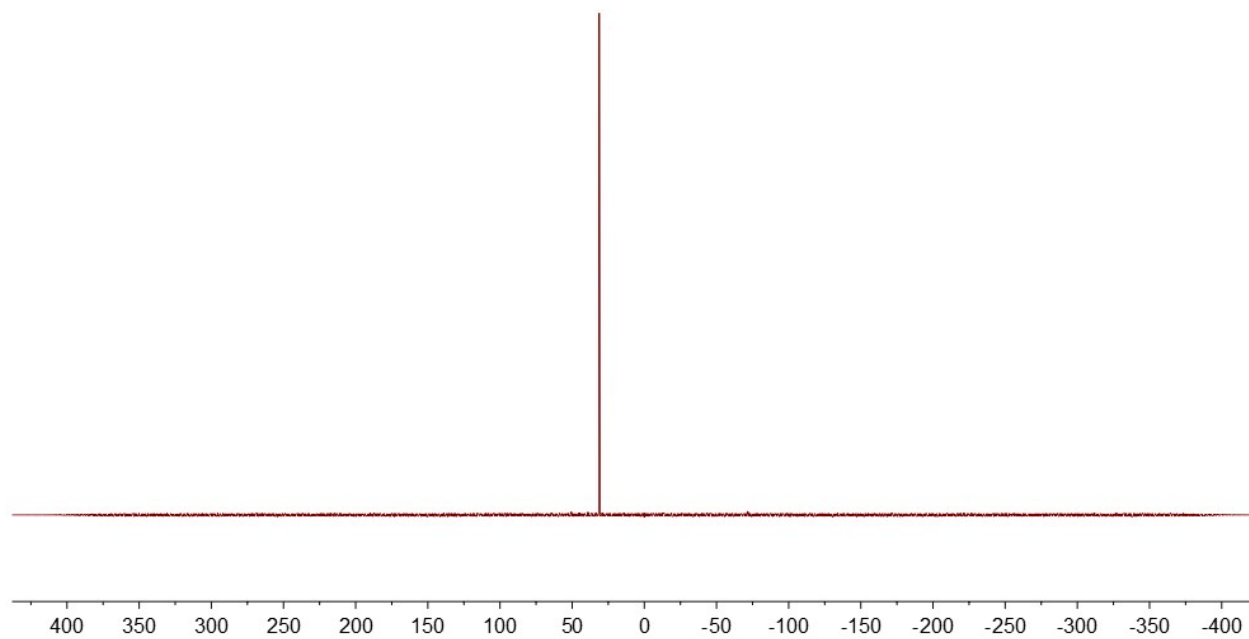
**Figure 1.** Time dependent  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound 11.



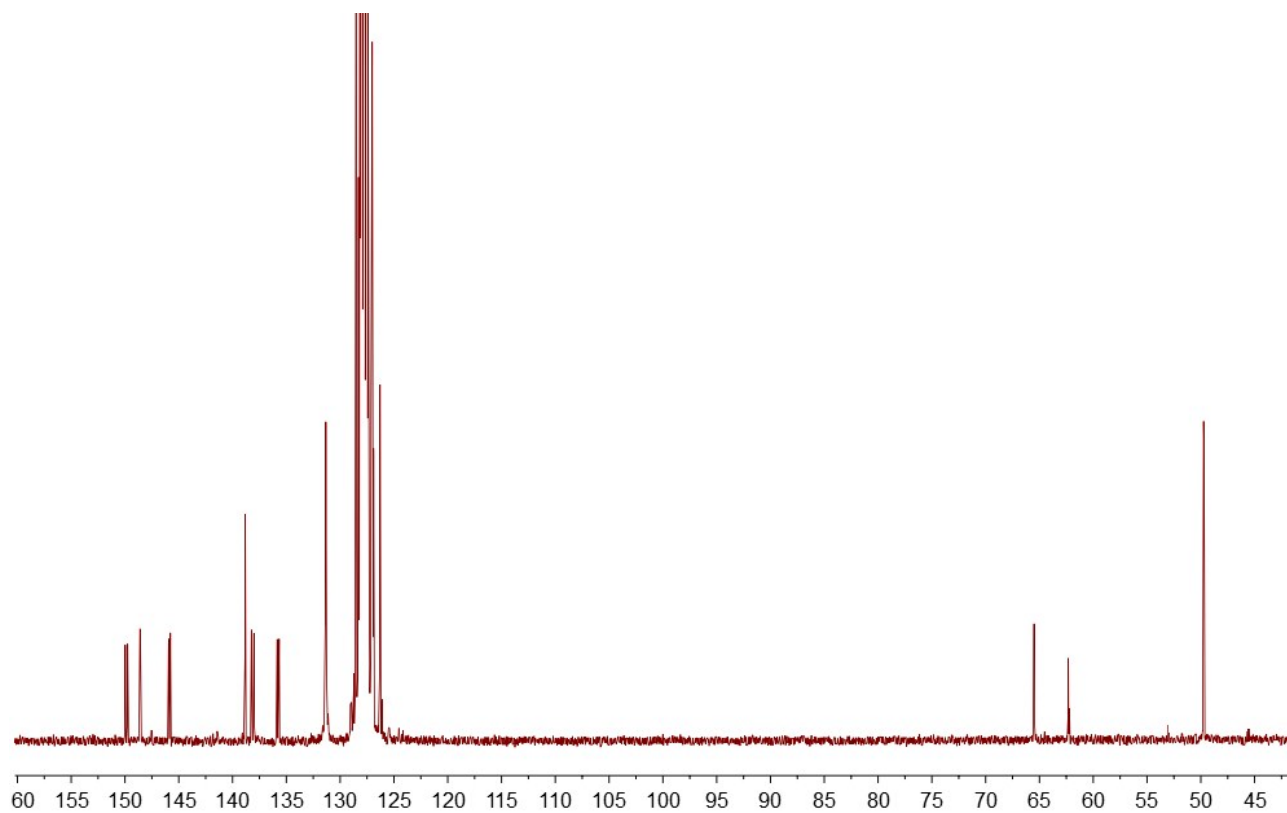
**Figure 2.**  $^1\text{H}$  NMR spectrum of compound **11** in  $\text{THF-d}_8$ .



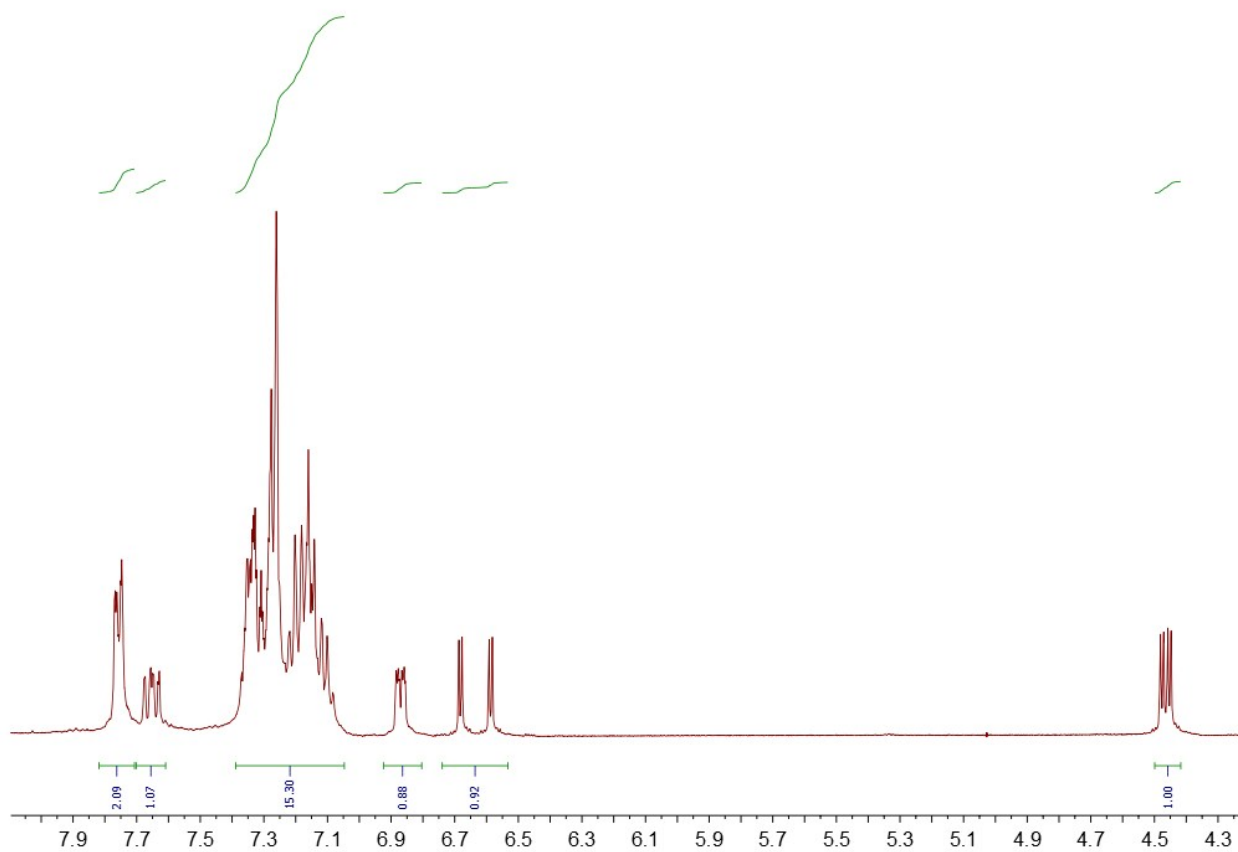
**Figure 3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **11** in  $\text{THF-d}_8$ .



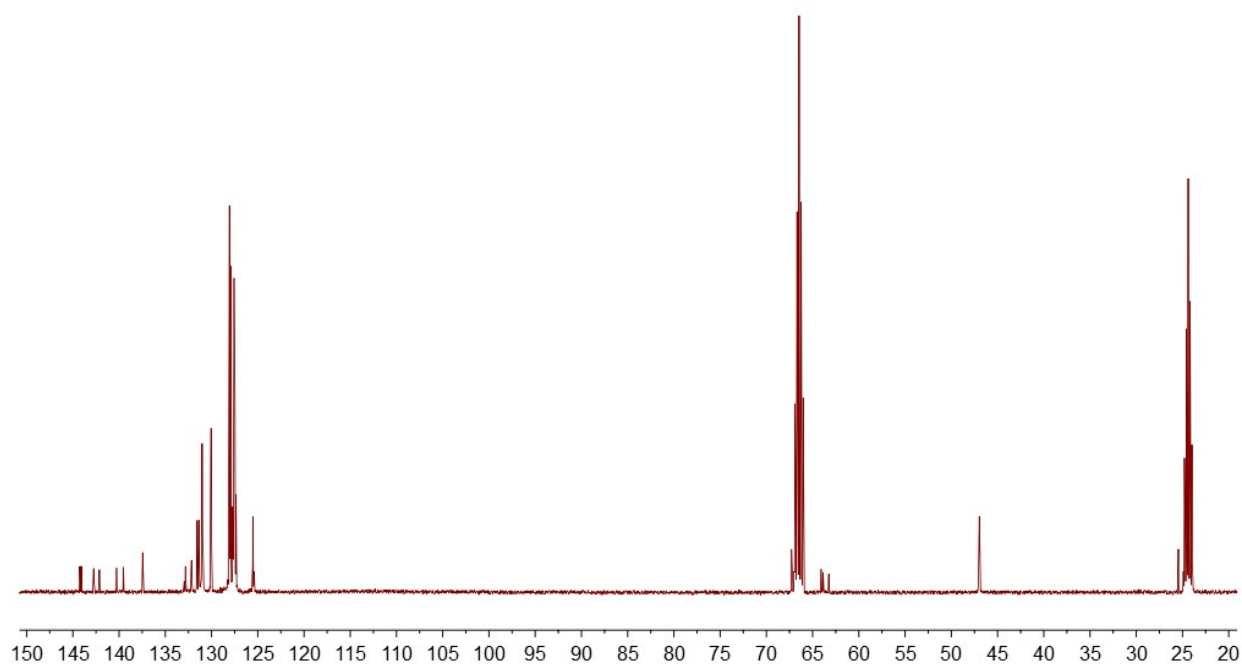
**Figure 4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound **11** in THF- $\text{d}_8$ .



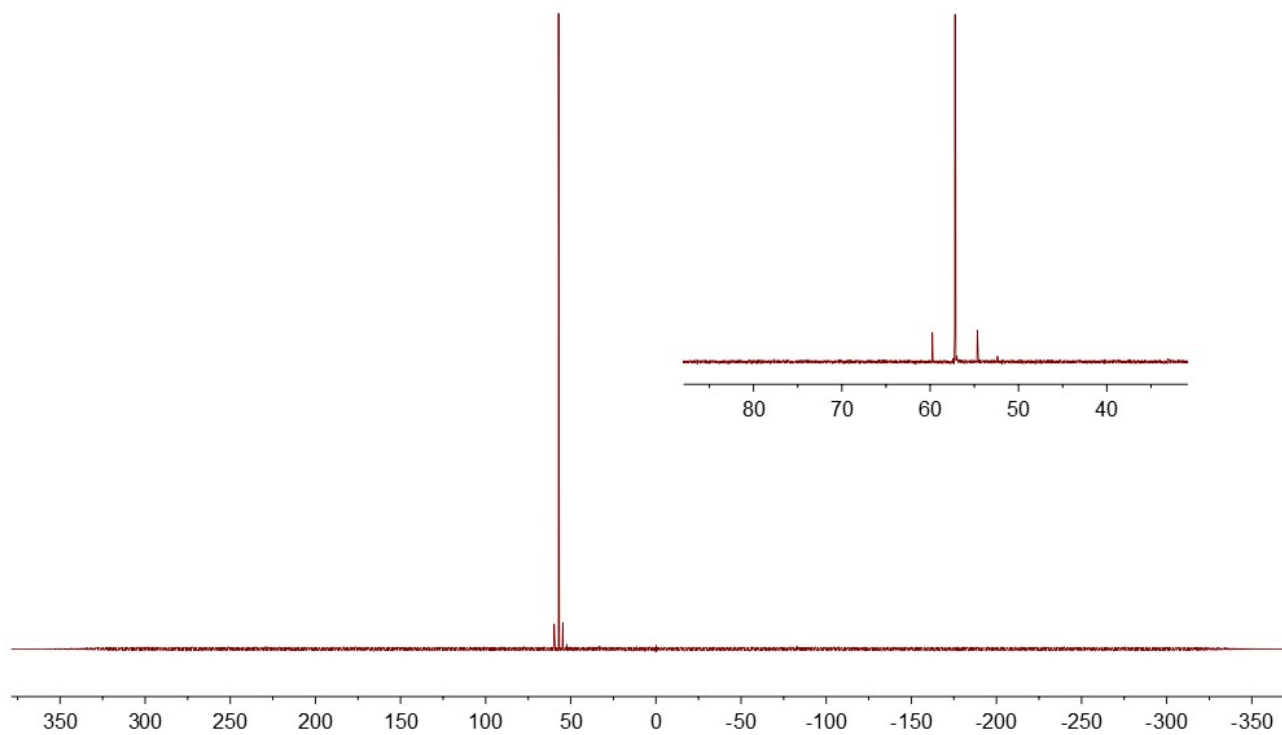
**Figure 5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **11** in benzene- $\text{d}_6$ .



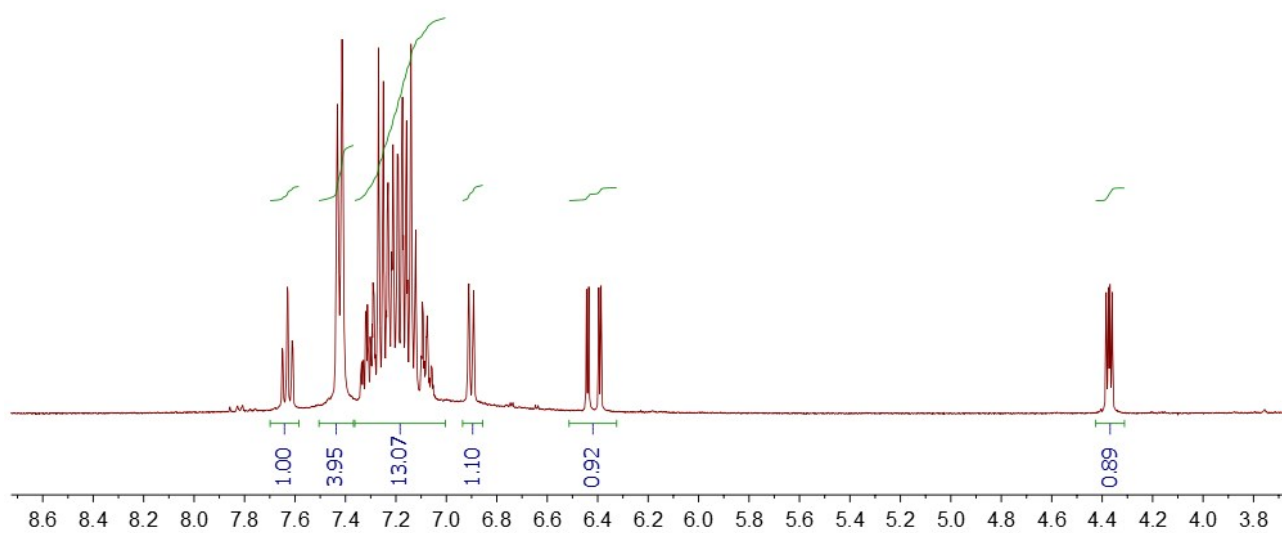
**Figure 6.**  $^1\text{H}$  NMR spectrum of compound **12**.



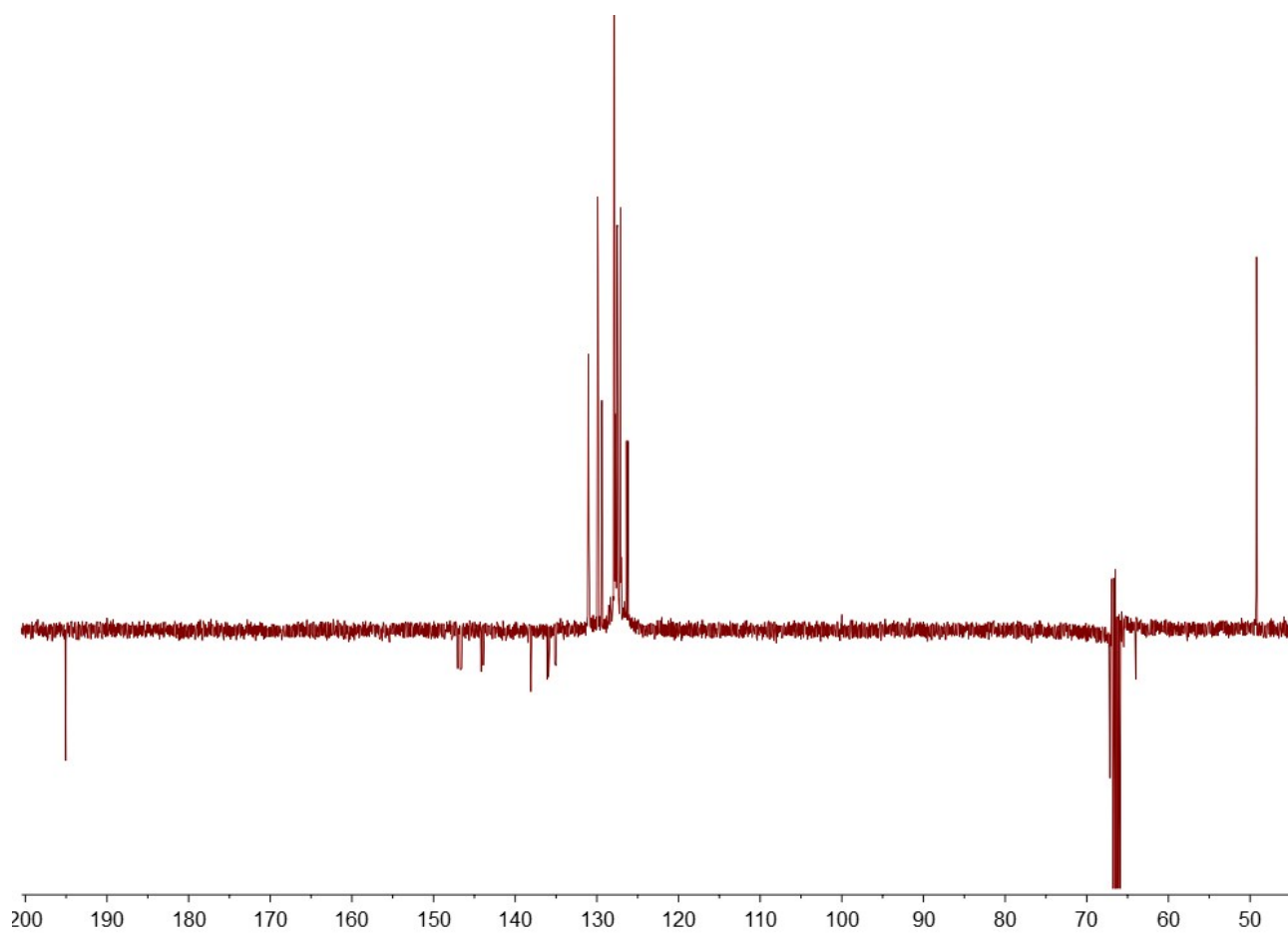
**Figure 7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **12**.



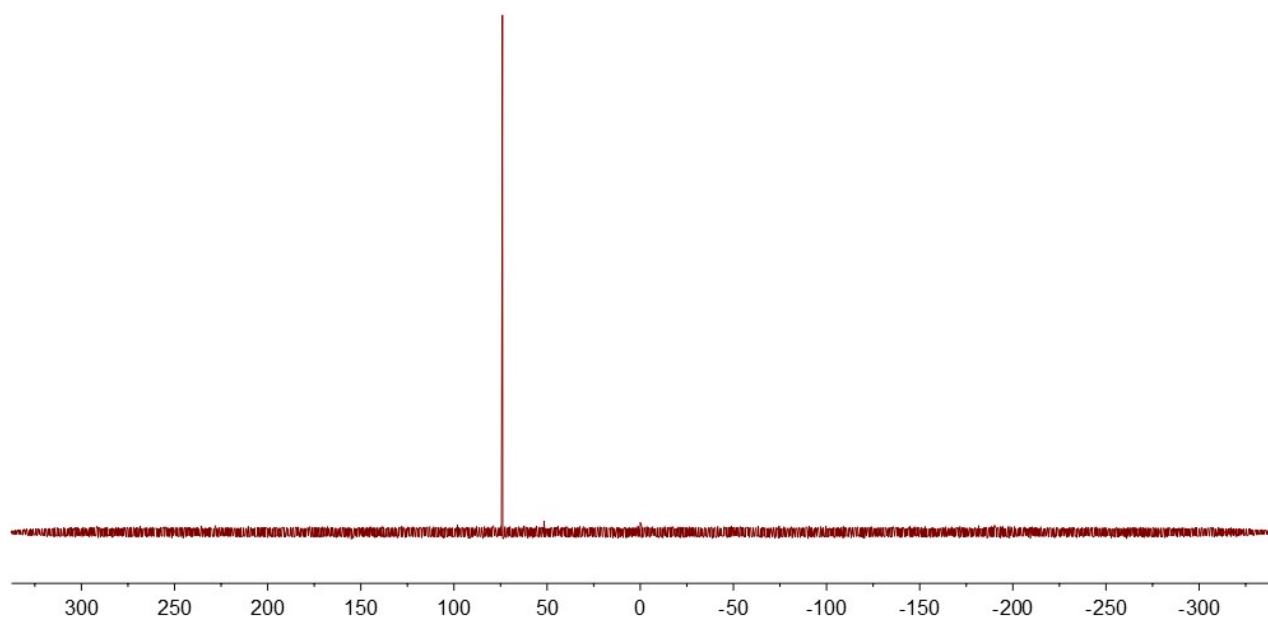
**Figure 8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound **12**.



**Figure 9.**  $^1\text{H}$  NMR spectrum of compound **14**.



**Figure 10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **14**.



**Figure 11.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of compound **14**.



### Enantiomeric resolution of *rac*-12 via HPLC:

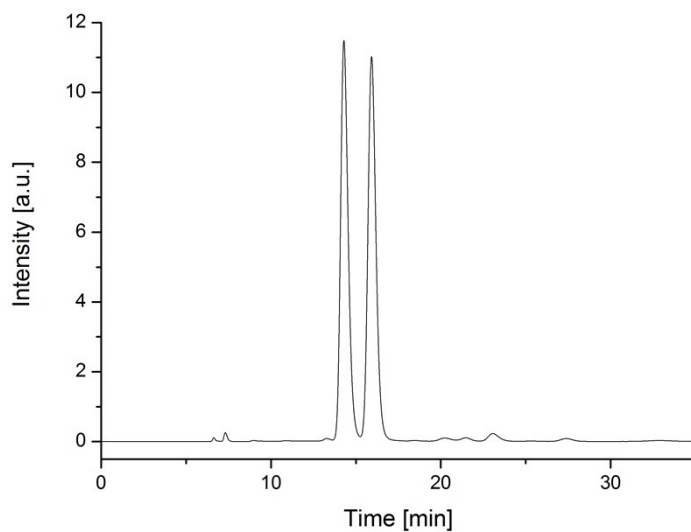


Figure 12. Enantiomeric resolution of *rac*-12: chromatogram.

Peak	Retention time (min)	Area (%)
1	14.29	50.15
2	15.92	49.85

### Mass spectra:

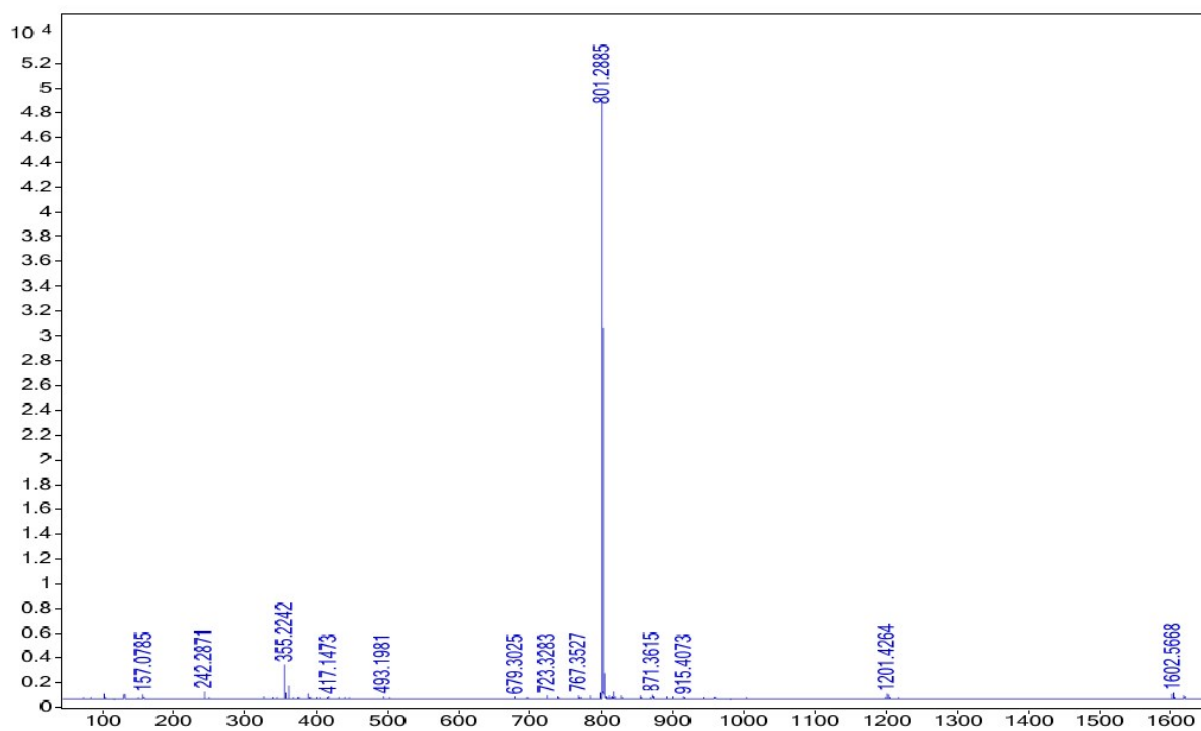
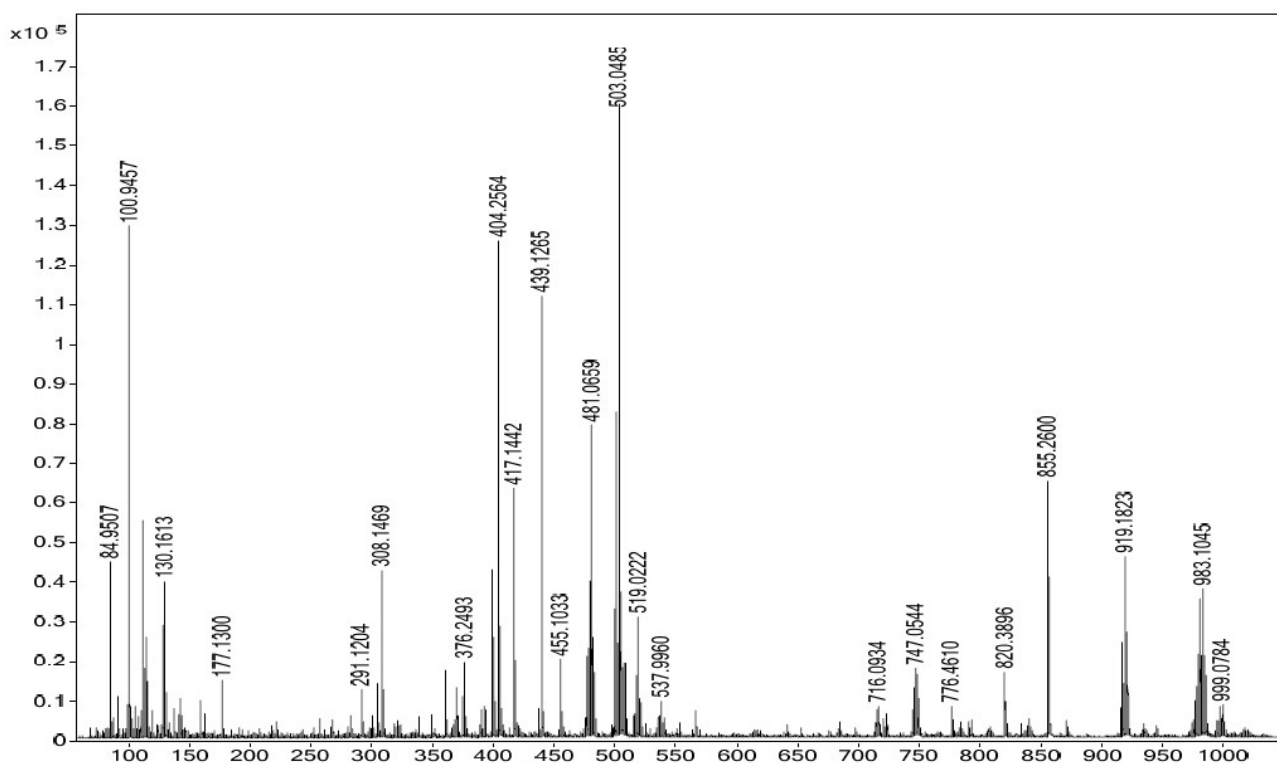


Figure 13. ESI spectrum of 11.



**Figure 14.** ESI spectrum of **12**.

### X-ray crystal structure determination of **12**:

Crystals suitable for X-ray diffraction were obtained from a saturated solution of **12** in toluene. *Crystallographic data*: C<sub>29</sub>H<sub>21</sub>PSe; *F*<sub>w</sub>=479.39; 0.38×0.20×0.07 mm<sup>3</sup>; colourless block, triclinic; P-1; *a*= 9.4639(2), *b*= 10.1522(2), *c*=14.1214(3) Å; α=77.6074(8)°, β=86.1247(9), γ=71.6074(7)°; *V*=1257.47(5) Å<sup>3</sup>; *Z*=2; *D*<sub>x</sub>=1.266 gcm<sup>-3</sup>; μ=1.569 mm<sup>-1</sup>. 23201 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation; λ = 0.71073 Å)<sup>S2</sup> up to a resolution of (sinθ/λ)<sub>max</sub> = 0.60 Å<sup>-1</sup> at a temperature of 100.0 K. 74381 reflections were unique (*R*<sub>int</sub> = 0.054). The structures were solved with SHELXS-2013 by using direct methods and refined with SHELXL-2013<sup>S3</sup> on *F*<sup>2</sup> for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 280 parameter were refined with one restraint. *R*<sub>1</sub>=0.033 for 4381 reflections with *I*>2σ(*I*) and *wR*<sub>2</sub>=0.076 for 5154 reflections, *S*=1.029, residual electron density was between -0.31 and 0.45 eÅ<sup>-3</sup>. Geometry calculations and checks for higher symmetry were performed with the PLATON program.<sup>S4</sup> The hkl were squeezed with the PLATON program, because the solvents were not identified.

CCDC - 1438074 contains the supplementary crystallographic data for this paper. 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).

SQUEEZE RESULTS (APPEND TO CIF)

Note: Data are Listed for all Voids in the P1 Unit Cell i.e. Centre of Gravity, Solvent Accessible Volume, Recovered number of Electrons in the Void and Details about the Squeezed Material

loop\_

```
_platon_squeeze_void_nr  
_platon_squeeze_void_average_x  
_platon_squeeze_void_average_y  
_platon_squeeze_void_average_z  
_platon_squeeze_void_volume  
_platon_squeeze_void_count_electrons  
_platon_squeeze_void_content  
1 0.000 0.500 0.500 200 47 ''
```

'The general procedure (based on a preliminary implementation of the technique) has been described in more detail as the 'BYPASS procedure'.<sup>S5</sup>

#### References:

- S1 a) G. Märkl, F. Lieb, C. Martin, *Tetrahedron Lett.*, 1971, **12**, 1249. b) E. Fuchs, M. Keller, B. Breit, *Chem. Eur. J.*, 2006, **12**, 6930.
- S2 Bruker (2010). APEX2, SAINT, SADABS and XSHLL. Bruker AXS Inc., Madison, Wisconsin, USA.
- S3 SHELX: G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122.
- S4 Platon: A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148–155.
- S5 P. van der Sluis, A.L. Spek; *Acta Cryst.* **1990**, *A46*, 194.