

## Supporting Information

### Typical procedure (Table 1, entry 2):

To a THF (10 ml) solution of perylithium (1.58 M cyclohexane-ether solution, 0.79 mL, 1.24 mmol) was added **1a** (200 mg, 0.54 mmol) at  $-78\text{ }^{\circ}\text{C}$ . After stirring for 25 min at  $-78\text{ }^{\circ}\text{C}$ , the reaction was successively quenched with MeOH (1.0 ml) and satd  $\text{NH}_4\text{Cl}$  (20 mL), and extracted with EtOAc (30 mL). The extract was washed with satd NaCl and dried over  $\text{Na}_2\text{SO}_4$ . Concentration followed by silica gel column chromatography (EtOAc-MeOH = 95 : 5) gave *trans*-**3a** (n = 6, R = Ph, 154 mg, 64%), *cis*-**3a** (n = 6, R = Ph, 21 mg, 9%) and **5a** (n = 6, 24 mg, 12%).

*trans*-**3a** (n = 6, R = Ph): Colorless oil, Rf = 0.61 (EtOAc/MeOH = 9/1).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.85, 1.23, 1.32 and 1.33 (each 3H, t,  $J = 7.0$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 1.20-1.30 (1H, m, H5), 1.32-1.45 (2H, m, H3 and H4), 1.76 (1H, m, H4), 1.83 (1H, m, H3), 1.85 (1H, ddd,  $J = 18.3$  (HA-P), 15.2 (HA-HB), 9.1 (HA-H6) Hz,  $\text{H}^{\text{A7}}$ ), 2.15-2.30 (1H, m, H6), 2.22 (1H, ddd,  $J = 19.3$  (H1-P), 10.9 (H1-H6), 10.4 (H1-H2) Hz, H1) 2.40 (1H, m, H5), 2.83 (1H, ddd,  $J = 10.7$  (H2-H3), 10.4 (H2-H1), 4.2 (H2-H3) Hz, H2), 3.04 (1H, ddd,  $J = 21.0$  (HB-P), 15.2 (HB-HA), 1.9 (HB-H6) Hz,  $\text{H}^{\text{B7}}$ ), 3.26 (1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.67 (1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.92 (2H, m,  $\text{POCH}_2\text{CH}_3$ ), 4.05-4.15 (4H, m,  $\text{POCH}_2\text{CH}_3$ ), 7.13-7.28 (5H, m, Ph).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 15.8, 16.3, 16.4 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 24.9 (s, C4), 31.2 (d,  $J = 136.5$  Hz, C7), 32.6 (dd,  $J = 2.0, 2.0$  Hz, C6), 33.5 (d,  $J = 14.5$  Hz, C5), 36.8 (d,  $J = 14.5$  Hz, C3), 44.5 (d,  $J = 2.0$  Hz, C2), 45.0 (dd,  $J = 134.4, 16.6$  Hz, C1), 60.8, 61.0, 61.2, 61.3 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 125.8, 127.3, 128.1, 146.7 (each s, Ph).

$^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 30.9, 31.8.

IR (neat): 1220 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 446 ( $\text{M}^+$ ), 309 ( $\text{M-PO(OEt)}_2$ ). Anal. Calcd. for  $\text{C}_{21}\text{H}_{36}\text{O}_6\text{P}_2$ : C, 56.50; H, 8.13. Found C, 56.23; H, 7.96.

*cis*-**3a** (n = 6, R = Ph): Colorless oil, Rf = 0.59 (EtOAc/MeOH = 9/1).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.93, 1.21, 1.330, 1.332 (each 3H, t,  $J = 7.0$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 1.47-1.59 (2H, m, H3 and H5), 1.60-1.70 (2H, m,  $\text{H}_2\text{4}$ ), 1.83-1.90 (1H, m, H3), 2.18 (1H, ddd,  $J = 18.3, 15.6, 12.2$  Hz,  $\text{H}^{\text{A7}}$ ), 2.20-2.30 (1H, m, H5), 2.29 (1H, dddd,  $J = 16.5$  (H1-P1), 11.6 (H1-H2), 4.6 (H1-P7), 3.9 (H1-H6) Hz, H1), 2.42 (1H, ddd,  $J = 21.1, 15.6, 2.2$  Hz,  $\text{H}^{\text{B7}}$ ), 2.75-2.85 (1H, m, H6), 2.90 (1H, dddd,  $J = 11.9$  (H2-H3), 11.6 (H2-H1), 5.2 (H2-P1), 4.2 (H2-H3) Hz, H2), 3.01 and 3.53 (each 1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.90 (2H, m,  $\text{POCH}_2\text{CH}_3$ ), 4.11 (4H, m,  $\text{POCH}_2\text{CH}_3$ ), 7.15-7.19 (1H, m, Ph), 7.25-7.29 (4H, m, Ph).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 16.07, 16.12, 16.3 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 20.0 (s, C4), 23.9 (d,  $J = 138.5$  Hz, C7), 29.4 (d,  $J = 13.4$  Hz, C5), 29.8 (dd,  $J = 2.0, 2.0$  Hz, C6), 35.7 (d,  $J = 14.6$  Hz, C3), 39.5 (d,  $J = 2.1$  Hz, C2), 45.6 (dd,  $J = 140.7, 18.7$  Hz, C1), 60.6, 60.8, 61.2, 61.4

(each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 126.4, 128.0, 128.2, 144.2 (each s, Ph).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 29.2, 31.9. IR (neat): 1220 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 446 ( $\text{M}^+$ ), 309 (M-PO(OEt)<sub>2</sub>). Anal. Calcd. for  $\text{C}_{21}\text{H}_{36}\text{O}_6\text{P}_2$ : C, 56.50; H, 8.13. Found C, 56.47; H, 7.23.

**5a**: Colorless oil,  $R_f = 0.35$  (EtOAc/MeOH = 9/1).

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.33 (9H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.34 (3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.65 (3H, m, H<sub>24</sub> and H<sub>3</sub>), 1.76 (1H, ddd,  $J = 15.9, 11.9, 11.9$  Hz, HA<sub>7</sub>), 2.04-2.25 (3H, m, H<sub>25</sub>, H<sub>3</sub>), 2.43 (1H, ddd,  $J = 20.1, 15.9, 1.8$  Hz, HB<sub>7</sub>), 2.81 (1H, m, H<sub>6</sub>), 4.08 (8H, m,  $\text{OCH}_2\text{CH}_3$ ), 6.81 (1H, ddd,  $J = 22.3, 4.0, 4.0$  Hz, H<sub>2</sub>).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 16.22 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 16.24 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 16.3 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 16.6 (s, C<sub>4</sub>), 25.9 (d,  $J = 17.6$  Hz, C<sub>5</sub>), 26.3 (d,  $J = 9.3$  Hz, C<sub>3</sub>), 28.5 (dd,  $J = 2.1, 9.3$  Hz, C<sub>6</sub>), 28.6 (d,  $J = 136.6$  Hz, C<sub>7</sub>), 61.1, 61.4, 61.45, 61.50 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 130.9 (dd,  $J = 179.0, 20.7$  Hz, C<sub>1</sub>), 144.8 (d,  $J = 9.3$  Hz, C<sub>2</sub>).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 19.9, 30.4.

IR (neat): 1230 (P=O), 1630 (C=C)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 368 ( $\text{M}^+$ ), 231 (M-PO(OEt)<sub>2</sub>). Anal. Calcd. for  $\text{C}_{15}\text{H}_{30}\text{O}_6\text{P}_2$ : C, 48.91; H, 8.21. Found C, 49.18; H, 8.08.

MeOD quench gave **11**, **14**, and **16**.

**11**: Colorless oil,  $R_f = 0.61$  (EtOAc/MeOH = 9/1).

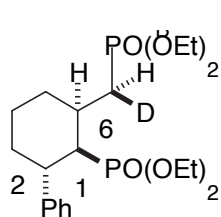
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.85, 1.23, 1.32 and 1.33 (each 3H, t,  $J = 7.0$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 1.20-1.30 (1H, m, H<sub>5</sub>), 1.32-1.45 (2H, m, H<sub>3</sub> and H<sub>4</sub>), 1.77 (1H, m, H<sub>4</sub>), 1.84 (1H, m, H<sub>3</sub>), 2.15-2.30 (1H, m, H<sub>6</sub>), 2.22 (1H, ddd,  $J = 20.0$  (H<sub>1</sub>-P), 10.9 (H<sub>1</sub>-H<sub>6</sub>), 10.4 (H<sub>1</sub>-H<sub>2</sub>) Hz, H<sub>1</sub>), 2.39 (1H, m, H<sub>5</sub>), 2.83 (1H, dddd,  $J = 16.2$  (H<sub>2</sub>-P), 11.3 (H<sub>2</sub>-H<sub>3</sub>), 10.4 (H<sub>2</sub>-H<sub>1</sub>), 4.2 (H<sub>2</sub>-H<sub>3</sub>) Hz, H<sub>2</sub>), 3.00 (1H, dd,  $J = 20.4$  (HB-P), 1.0 (HB-H<sub>6</sub>) Hz, HB<sub>7</sub>), 3.27 (1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.67 (1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.92 (2H, m,  $\text{POCH}_2\text{CH}_3$ ), 4.05-4.15 (4H, m,  $\text{POCH}_2\text{CH}_3$ ), 7.13-7.28 (5H, m, Ph).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 15.8, 16.2, 16.3 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 24.9 (s, C<sub>4</sub>), 31.5 (m, C<sub>7</sub>), 32.5 (dd,  $J = 2.0, 2.0$  Hz, C<sub>6</sub>), 33.4 (d,  $J = 13.4$  Hz, C<sub>5</sub>), 36.8 (d,  $J = 13.4$  Hz, C<sub>3</sub>), 44.5 (d,  $J = 2.0$  Hz, C<sub>2</sub>), 44.8 (dd,  $J = 134.4, 16.5$  Hz, C<sub>1</sub>), 60.8, 61.0, 61.1, 61.3 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 125.8, 127.3, 128.0, 146.7 (each s, Ph).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 30.9, 31.9.

IR (neat): 1220 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 447 ( $\text{M}^+$ ), 310 (M-PO(OEt)<sub>2</sub>). Anal. Calcd. for  $\text{C}_{21}\text{H}_{35}\text{DO}_6\text{P}_2$ : C, 56.37; H, 8.33. Found C, 56.44; H, 8.12.

**14**: Colorless oil,  $R_f = 0.59$  (EtOAc/MeOH = 9/1).

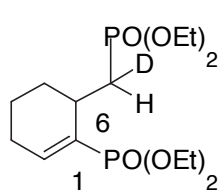


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.94 and 1.20 (each 3H, t,  $J = 7.0$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 1.330 (6H, t,  $J = 7.0$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 1.47-1.59 (2H, m, H3 and H5), 1.60-1.70 (2H, m, H<sub>2</sub>4), 1.80-1.90 (1H, m, H3), 2.20-2.30 (1H, m, H5), 2.29 (1H, dddd,  $J = 16.5$  (H1-P1), 11.6 (H1-H2), 4.6 (H1-P7), 3.9 (H1-H6) Hz, H1), 2.42 (1H, d,  $J = 21.4$ , H<sup>B7</sup>), 2.75-2.85 (1H, m, H6), 2.90 (1H, dddd,  $J = 11.9$  (H2-H3), 11.6 (H2-H1), 5.2 (H2-P1), 4.2 (H2-H3) Hz, H2), 3.01 and 3.53 (each 1H, m,  $\text{POCH}_2\text{CH}_3$ ), 3.90 (2H, m,  $\text{POCH}_2\text{CH}_3$ ), 4.11 (4H, m,  $\text{POCH}_2\text{CH}_3$ ), 7.15-7.19 (1H, m, Ph), 7.25-7.29 (4H, m, Ph).

$^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 29.3, 31.9.

IR (neat): 1220 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 447 ( $\text{M}^+$ ), 310 ( $\text{M-PO(OEt)}_2$ ). HRMS Calcd. for  $\text{C}_{21}\text{H}_{35}\text{DO}_6\text{P}_2$ : 447.2049. Found 447.2055.

**16**: Colorless oil,  $R_f = 0.35$  (EtOAc/MeOH = 9/1).



$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.33 (9H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.34 (3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.65 (3H, m, H<sub>2</sub>4 and H3), 2.04-2.25 (3H, m, H<sub>2</sub>5, H3), 2.43 (1H, d,  $J = 20.5$  Hz, H<sup>B7</sup>), 2.81 (1H, m, H6), 4.08 (8H, m,  $\text{OCH}_2\text{CH}_3$ ), 6.81 (1H, ddd,  $J = 22.3, 4.0, 4.0$  Hz, H2).

$^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 19.9, 30.4.

IR (neat): 1230 (P=O), 1630 (C=C)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 369 ( $\text{M}^+$ ), 232 ( $\text{M-PO(OEt)}_2$ ). HRMS Calcd. for  $\text{C}_{15}\text{H}_{29}\text{DO}_6\text{P}_2$ : 369.1579. Found: 369.1574.

### Characterization of **3**, **5**, **7**, **8**

**7**: Colorless oil,  $R_f = 0.75$  (EtOAc/MeOH = 95/5).



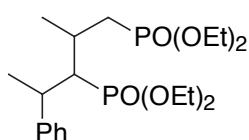
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.21 (3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.25 (3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.39 (3H, d,  $J = 7.3$  Hz, CH<sub>3</sub>), 2.03 (1H, ddd,  $J = 7.9, 15.3, 17.7$  Hz, PCH<sub>2</sub>), 2.11 (1H, ddd,  $J = 6.1, 15.3, 18.3$  Hz, PCH<sub>2</sub>), 3.21 (1H, m, CH), 3.85-4.05 (4H, m,  $\text{OCH}_2\text{CH}_3$ ), 7.18-7.24 (3H, m, Ph), 7.26-7.32 (2H, m, Ph).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 16.3 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 23.5 (d,  $J = 8.3$  Hz, CH<sub>3</sub>), 34.2 (d,  $J = 120.0$  Hz, PCH<sub>2</sub>), 34.7 (d,  $J = 22.0$  Hz, CH), 61.2 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 126.4, 126.6, 128.5, 146.6 (Ph).

IR (neat): 1220 (P=O)  $\text{cm}^{-1}$ . FABMS  $m/z$ : 257 ( $\text{M}^+\text{H}^+$ ), 211 ( $\text{M-OEt}$ ). HRMS Calcd. for  $\text{C}_{13}\text{H}_{22}\text{O}_3\text{P}$ : 257.1306. Found 257.1316.

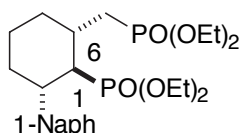
**8**: Colorless oil,  $R_f = 0.55$  (EtOAc/MeOH = 95/5). Mixture of diastereomer.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.04-1.41 (18H, m,  $\gamma\text{CH}_3 \times 2$  and  $\text{OCH}_2\text{CH}_3 \times 4$ ), 1.77-1.94 (2H,



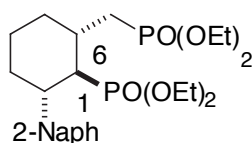
m, PCH<sub>2</sub>), 2.33-2.63 (2H, m, PCH, CH), 3.05 (0.6H, m, PhCH), 3.27 (0.4H, m, PhCH), 3.80-4.24 (8H, m, OCH<sub>2</sub>CH<sub>3</sub>), 7.18-7.31 (5H, m, Ph).  
 IR (neat): 1220 (P=O) cm<sup>-1</sup>. FABMS *m/z*: 435 (M+H<sup>+</sup>), 255 (CH<sub>3</sub>CH(Ph)CHPO(OEt)<sub>2</sub>), 179 (CH<sub>3</sub>CHCH<sub>2</sub>PO(OEt)<sub>2</sub>). HRMS Calcd. for C<sub>20</sub>H<sub>37</sub>O<sub>6</sub>P<sub>2</sub>: 435.2065. Found 435.2059.

*trans*-**3** (n = 6, R = 1-Naph): Colorless oil, R<sub>f</sub> = 0.39 (EtOAc/MeOH = 9/1).



<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz) δ: 0.50, 1.09, 1.33 and 1.35 (each 3H, t, *J* = 7.0 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 1.30-1.50 (2H, m, H3 and H5), 1.48-1.52 (1H, m, H4), 1.81 (1H, m, H4), 1.93 (1H, m, H3), 1.94 (1H, ddd, *J* = 18.0 (HA-P), 15.6 (HA-HB), 9.2 (HA-H6) Hz, H<sup>A</sup>7), 2.25-2.35 (1H, m, H6), 2.37 (1H, ddd, *J* = 20.1 (H1-P), 11.1 (H1-H6), 10.6 (H1-H2) Hz, H1), 2.49 (2H, m, H2 and H5), 2.98 (1H, m, POCH<sub>2</sub>CH<sub>3</sub>), 3.04 (1H, ddd, *J* = 19.8 (HB-P), 15.6 (HB-HA), 0.9 (HB-H6) Hz, H<sup>B</sup>7), 3.98 (1H, m, POCH<sub>2</sub>CH<sub>3</sub>), 3.50 (2H, m, POCH<sub>2</sub>CH<sub>3</sub>), 4.13 (4H, m, POCH<sub>2</sub>CH<sub>3</sub>), 7.46 (4H, m, Naph), 7.67 (1H, d, *J* = 7.9 Hz, Naph), 7.83 (1H, d, *J* = 8.0 Hz, Naph), 8.17 (1H, d, *J* = 8.5 Hz, Naph).  
<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125.7 MHz) δ: 15.3, 16.1, 16.4 (each d, *J* = 6.2 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 25.2 (s, C4), 31.3 (d, *J* = 136.5 Hz, C7), 33.0 (s, C6), 33.5 (d, *J* = 14.4 Hz, C5), 36.6 (bs, C3), 44.5 (d, *J* = 2.0 Hz, C2), 44.8 (dd, *J* = 141.1, 15.8 Hz, C1), 60.8, 61.0, 61.2, 61.3 (each d, *J* = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>x4), 123.0, 125.3, 125.5, 126.0, 128.7, 131.2, 133.9, 143.5 (Naph).  
<sup>31</sup>P-NMR (CDCl<sub>3</sub>, 202.4 MHz) δ: 30.8, 31.7.  
 IR (neat): 1230 (P=O) cm<sup>-1</sup>. EIMS *m/z*: 496 (M<sup>+</sup>), 359 (M-PO(OEt)<sub>2</sub>). Anal. Calcd. for C<sub>25</sub>H<sub>38</sub>O<sub>6</sub>P<sub>2</sub>: C, 60.48; H, 7.71. Found C, 60.18; H, 7.65.

*trans*-**3** (n = 6, R = 2-Naph): Colorless oil, R<sub>f</sub> = 0.39 (EtOAc/MeOH = 9/1).



<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz) δ: 0.62 and 1.18 (each 3H, t, *J* = 7.0 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 1.25-1.35 (1H, m, H5), 1.33 (6H, m, POCH<sub>2</sub>CH<sub>3</sub>), 1.40-1.52 (2H, m, H3 and H4), 1.80 (1H, m, H4), 1.85-1.90 (1H, m, H3), 1.91 (1H, ddd, *J* = 18.0 (HA-P), 15.6 (HA-HB), 9.8 (HA-H6) Hz, H<sup>A</sup>7), 2.25-2.30 (1H, m, H6), 2.36 (1H, ddd, *J* = 17.1 (H1-P), 11.0 (H1-H6), 10.4 (H1-H2) Hz, H1), 2.40-2.48 (1H, m, H5), 3.01 (1H, ddd, *J* = 20.2 (H2-P), 10.4 (H2-H1), 4.2 (H2-H3) Hz, H2), 3.06 (1H, ddd, *J* = 21.1 (HB-P), 15.6 (HB-HA), 2.1 (HB-H6) Hz, H<sup>B</sup>7), 3.21 (1H, m, POCH<sub>2</sub>CH<sub>3</sub>), 3.59 (1H, m, POCH<sub>2</sub>CH<sub>3</sub>), 3.90 (2H, m, POCH<sub>2</sub>CH<sub>3</sub>), 4.11 (4H, m, POCH<sub>2</sub>CH<sub>3</sub>), 7.32-7.45 (3H, m, Naph), 7.60-7.80 (4H, m, Naph).  
<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125.7 MHz) δ: 15.5, 16.2, 16.4 (each d, *J* = 6.2 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 24.9 (s, C4),

31.2 (d,  $J = 136.3$  Hz, C7), 32.6 (dd,  $J = 3.1, 3.1$  Hz, C6), 33.5 (d,  $J = 15.6$  Hz, C5), 36.6 (d,  $J = 13.4$  Hz, C3), 44.6 (d,  $J = 4.1$  Hz, C2), 44.9 (dd,  $J = 134.4, 15.6$  Hz, C1), 60.9, 61.1, 61.2, 61.3 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 125.0, 125.4, 125.7, 126.2, 127.7, 132.0, 133.4, 144.0 (Naph).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 30.8, 31.8.

IR (neat): 1230 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 496 ( $\text{M}^+$ ), 359 (M-PO(OEt) 2), 220. Anal. Calcd. for  $\text{C}_{25}\text{H}_{38}\text{O}_6\text{P}_2$ : C, 60.48; H, 7.71. Found C, 60.50; H, 4.59.

*trans*-**3** (n = 6, R = Bu): Colorless oil,  $R_f = 0.47$  (EtOAc/MeOH = 9/1).

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.89 (3H, t,  $J = 7.1$  Hz,  $(\text{CH}_2)_3\text{CH}_3$ ), 1.15-1.70 (6H, m,  $(\text{CH}_2)_3\text{CH}_3$ ), 1.20-1.25 (1H, m, H3), 1.25-1.35 (14H, m,  $\text{OCH}_2\text{CH}_3 \times 4$ , H3 and H5), 1.35-1.45 (1H, m, H4), 1.60-1.70 (1H, m, H4), 1.75-1.88 (5H, m, H1, H2, H3 and H7), 2.10-2.20 (1H, m, H5), 2.25-2.40 (1H, m, H6), 2.46 (1H, ddd,  $J = 3.9, 15.2, 20.5$  Hz, H7), 4.05-4.14 (8H, m,  $\text{OCH}_2\text{CH}_3$ ).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 14.1 (s,  $(\text{CH}_2)_3\text{CH}_3$ ), 16.4 and 16.5 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 19.9 (s, C4), 22.8 (s,  $(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ), 28.8 (d,  $J = 7.5$  Hz, C5), 29.5 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 30.9 (dd,  $J = 4.0$  Hz, C6), 31.0 (d,  $J = 3.8$  Hz, C3), 32.3 (dd,  $J = 137.5, 9.2$  Hz, C7), 34.4 (d,  $J = 3.1$  Hz, C2), 35.8 (d,  $J = 9.2$  Hz,  $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ), 43.2 (dd,  $J = 132.5, 13.4$ , C1), 61.3, 61.4, 61.45, 61.50 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 31.5, 33.5.

IR (neat): 1225 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 426 ( $\text{M}^+$ ), 289 (M-PO(OEt) 2). Anal. Calcd. for  $\text{C}_{19}\text{H}_{40}\text{O}_6\text{P}_2$ : C, 53.51; H, 9.45. Found C, 53.44; H, 9.29.

*trans*-**3** (n = 5, R = Ph): Colorless oil,  $R_f = 0.55$  (EtOAc/MeOH = 4/1).

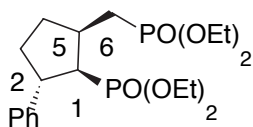
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.12 and 1.16 (each 3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.34 (6H, m,  $\text{OCH}_2\text{CH}_3$ ), 1.78-1.83 (2H, m, H3 and H4), 1.85 (1H, ddd,  $J = 17.4, 15.3, 11.0$  Hz, H6), 2.09 (1H, ddd,  $J = 16.1, 9.5, 9.5$  Hz, H1), 2.13 (1H, m, H4), 2.20 (1H, m, H3), 2.46 (1H, ddd,  $J = 19.2, 15.3, 3.1$  Hz, H6), 2.65 (1H, m, H5), 3.35 (1H, dq,  $J = 16.5, 8.5$  Hz, H2), 3.83 (1H, m,  $\text{OCH}_2\text{CH}_3$ ), 3.94 (3H, m,  $\text{OCH}_2\text{CH}_3$ ), 4.10 (4H, m,  $\text{OCH}_2\text{CH}_3$ ), 7.17-7.30 (5H, m, Ph).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 16.1, 16.2, 16.4 (each d,  $J = 6.2$  Hz,  $\text{POCH}_2\text{CH}_3$ ), 31.2 (d,  $J = 138.6$  Hz, C6), 35.2 (d,  $J = 14.4$  Hz, C4), 36.3 (d,  $J = 3.1$  Hz, C5), 46.8 (s, C2), 50.6 (dd,  $J = 142.6, 17.6$  Hz, C1), 61.2, 61.3, 61.5, 61.6 (each d,  $J = 6.3$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 126.2, 127.2, 128.3, 144.7 (Ph).

$^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 30.1, 31.9.

IR (neat): 1225 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 432 ( $\text{M}^+$ ), 295 ( $\text{M-PO(OEt)}_2$ ), 91. Anal. Calcd. for  $\text{C}_{20}\text{H}_{34}\text{O}_6\text{P}_2$ : C, 55.55; H, 7.93. Found C, 55.31; H, 7.92.

*cis*-**3** ( $n = 5$ , R = Ph): Colorless oil,  $R_f = 0.57$  (EtOAc/MeOH = 4/1).

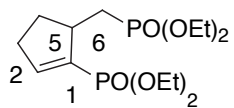


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.11 and 1.17 (each 3H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.34 (6H, m,  $\text{OCH}_2\text{CH}_3$ ), 1.74-1.76 (1H, m, H3), 1.76-1.77 (1H, m, H4), 1.85 (1H, ddd,  $J = 19.3, 15.3, 10.1$  Hz, H6), 2.09 (1H, ddd,  $J = 18.9, 8.9, 8.9$  Hz, H1), 2.15 (1H, m, H4), 2.23 (1H, m, H3), 2.50 (1H, ddd,  $J = 20.1, 15.3, 2.5$  Hz, H6), 2.83 (1H, m, H5), 3.44 (1H, m, H2), 3.80-3.85 (1H, m,  $\text{OCH}_2\text{CH}_3$ ), 3.90-3.40 (3H, m,  $\text{OCH}_2\text{CH}_3$ ), 4.05-4.15 (4H, m,  $\text{OCH}_2\text{CH}_3$ ), 7.17-7.30 (5H, m, Ph).

$^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 30.8, 31.5.

IR (neat): 1225 (P=O)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 432 ( $\text{M}^+$ ), 295 ( $\text{M-PO(OEt)}_2$ ), 91. HRMS Calcd. for  $\text{C}_{20}\text{H}_{34}\text{O}_6\text{P}_2$ : 432.1831. Found 432.1852.

**5b**: Colorless oil,  $R_f = 0.40$  (EtOAc/MeOH = 4/1).



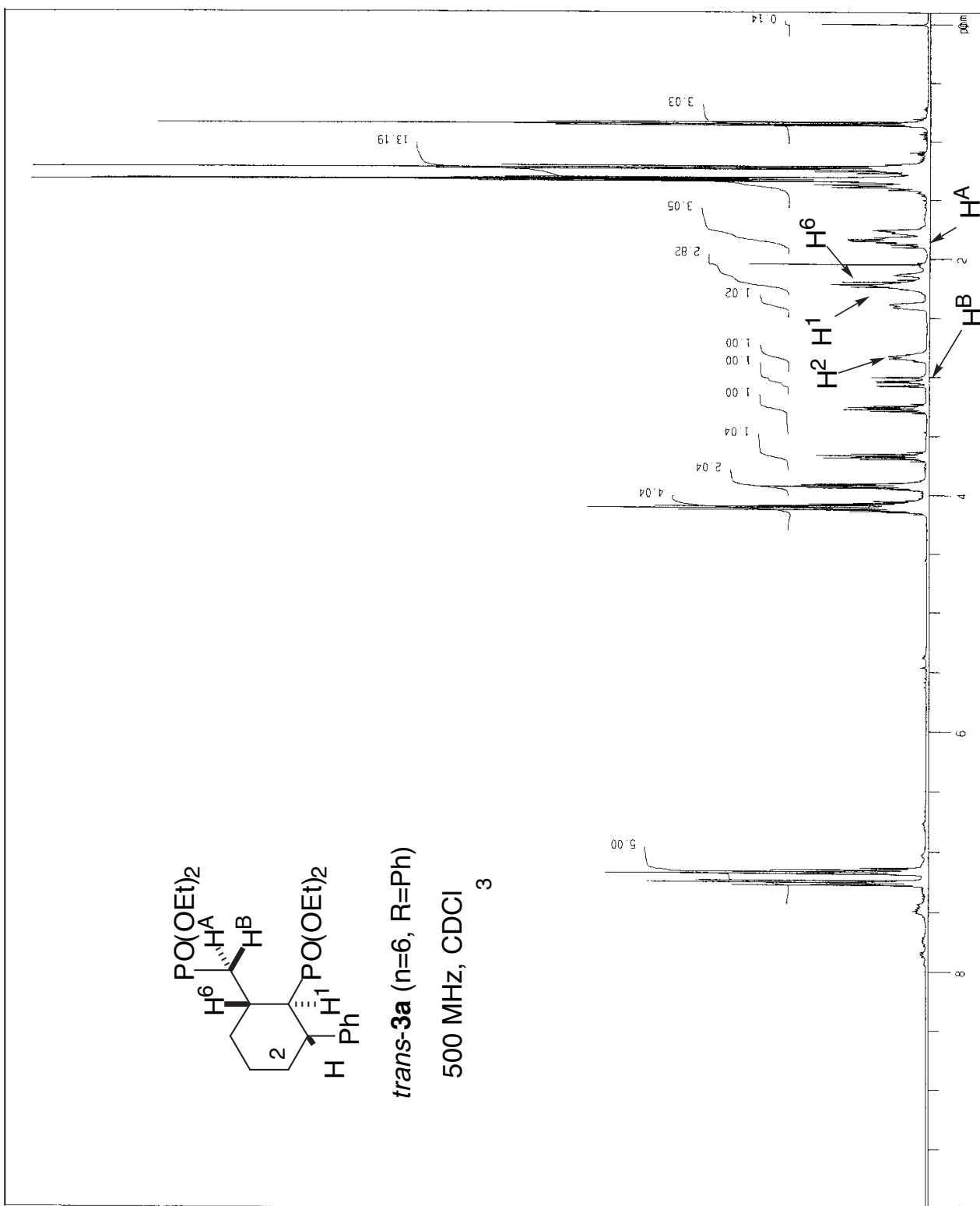
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.26 (12H, t,  $J = 7.0$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.55 (1H, m, H6), 1.80-1.85 (1H, m, H3), 2.26-2.35 (1H, m, H4), 2.40-2.55 (3H, m, H3, H4 and H6), 3.15-3.25 (1H, m, H5), 4.00-4.20 (8H, m,  $\text{OCH}_2\text{CH}_3$ ).

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125.7 MHz)  $\delta$ : 16.2 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 16.3 (d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 30.5 (d,  $J = 138.3$  Hz, C6), 31.8 (d,  $J = 21.7$  Hz, C4), 32.6 (d,  $J = 21.0$  Hz, C3), 41.0 (d,  $J = 10.3$  Hz, C5), 61.2, 61.3, 61.4, 61.6 (each d,  $J = 6.2$  Hz,  $\text{OCH}_2\text{CH}_3 \times 4$ ), 135.2 (dd,  $J = 180.0, 19.2$  Hz, C1), 149.0 (d,  $J = 13.4$  Hz, C2).

$^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ , 202.4 MHz)  $\delta$ : 16.3, 30.4.

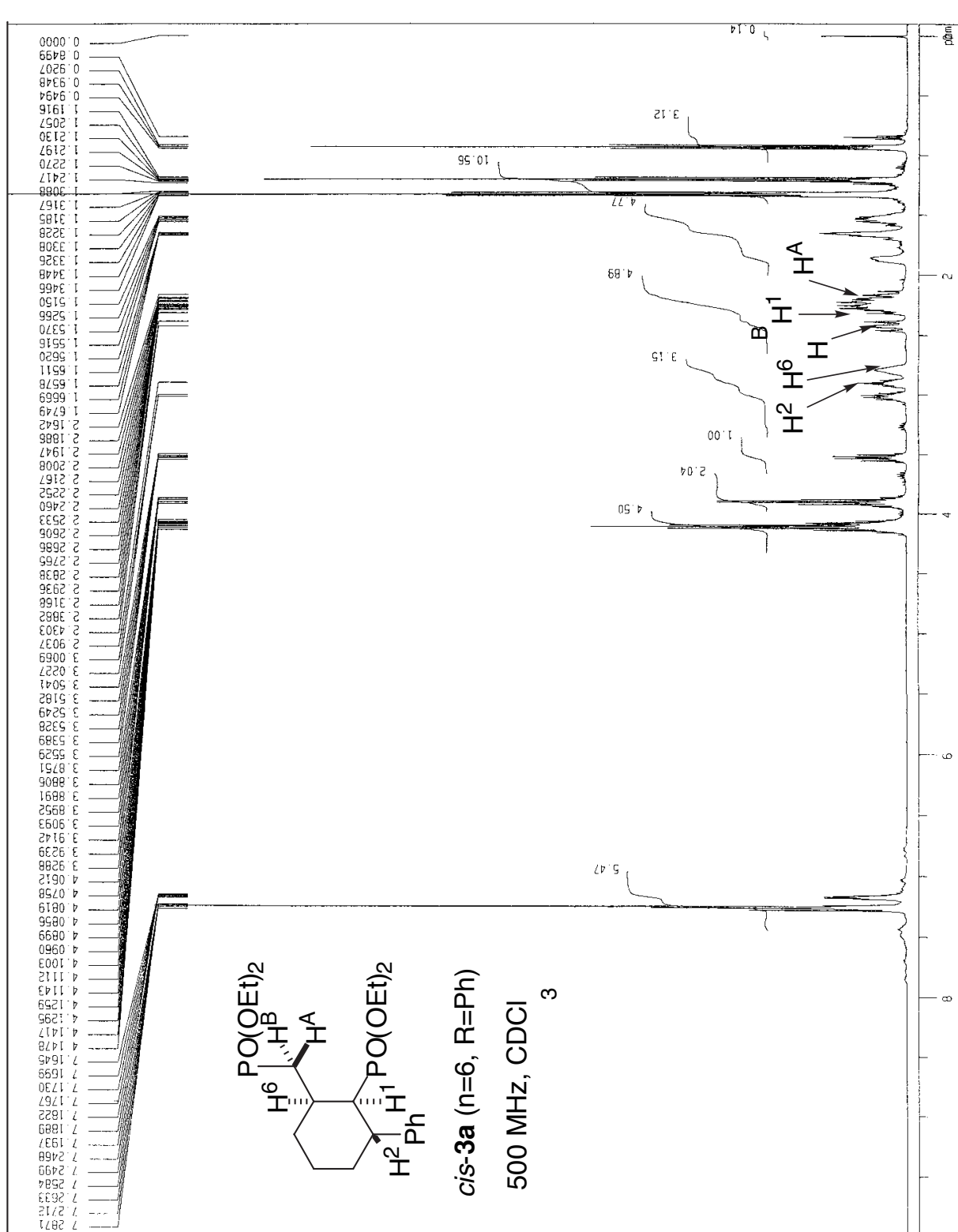
IR (neat): 1230 (P=O), 1630 (C=C)  $\text{cm}^{-1}$ . EIMS  $m/z$ : 354 ( $\text{M}^+$ ), 217 ( $\text{M-PO(OEt)}_2$ ). Anal. Calcd. for  $\text{C}_{14}\text{H}_{28}\text{O}_6\text{P}_2$ : C, 47.46; H, 7.97. Found C, 47.28; H, 8.01.

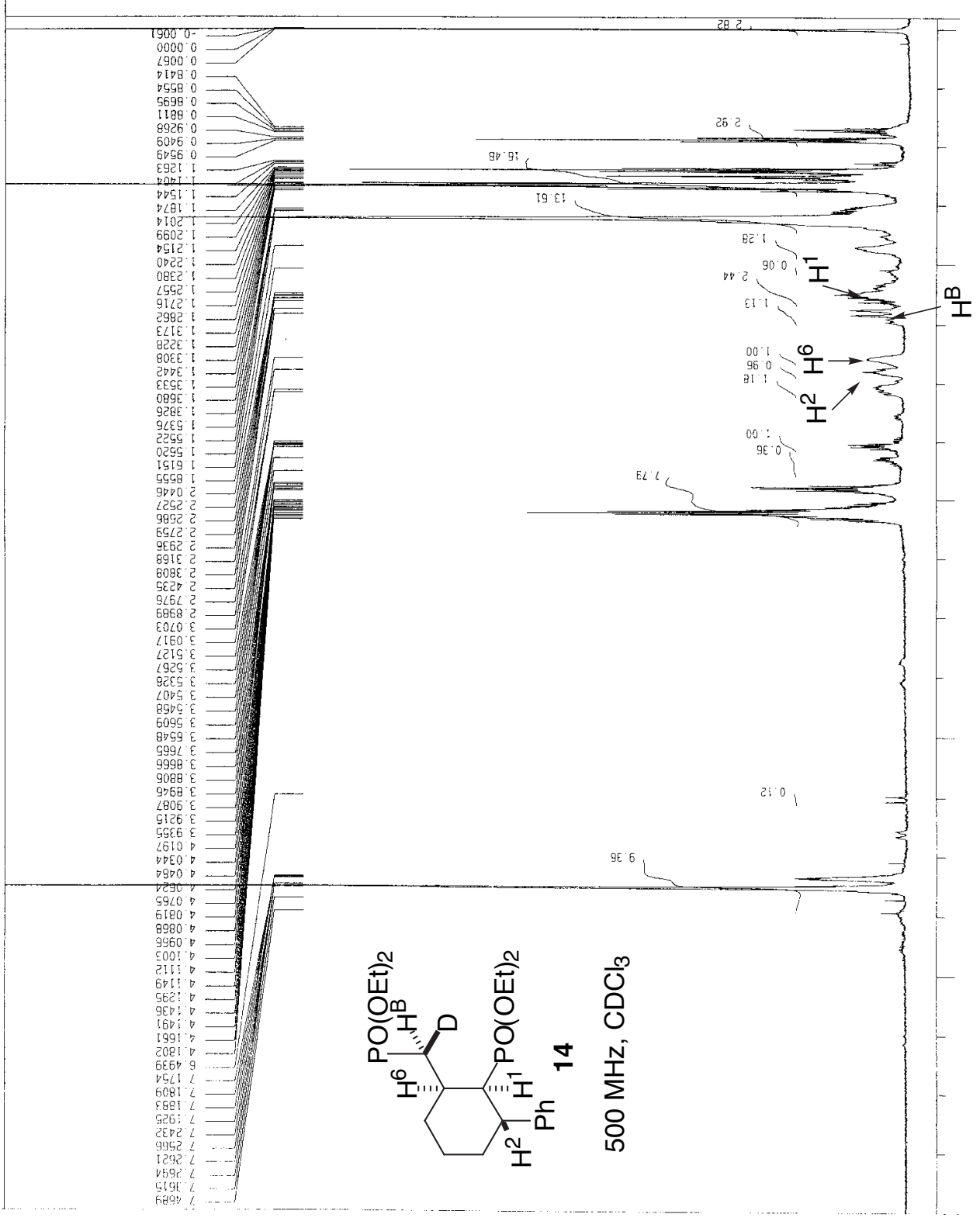
$^1\text{H}$  - and  $^{13}\text{C}$  -NMR spectra of **3a**, **5a**, **11**, **14** and **16**

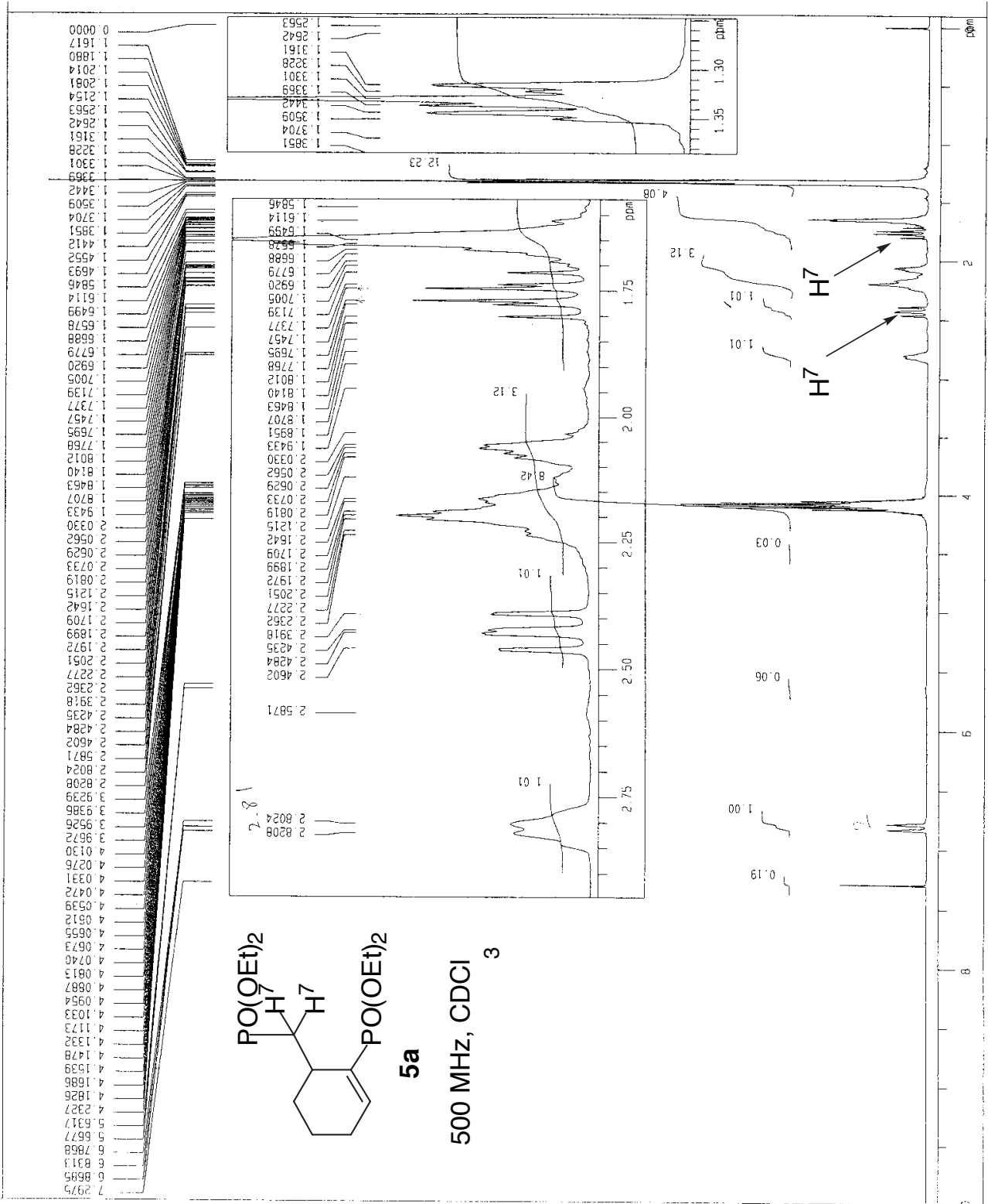




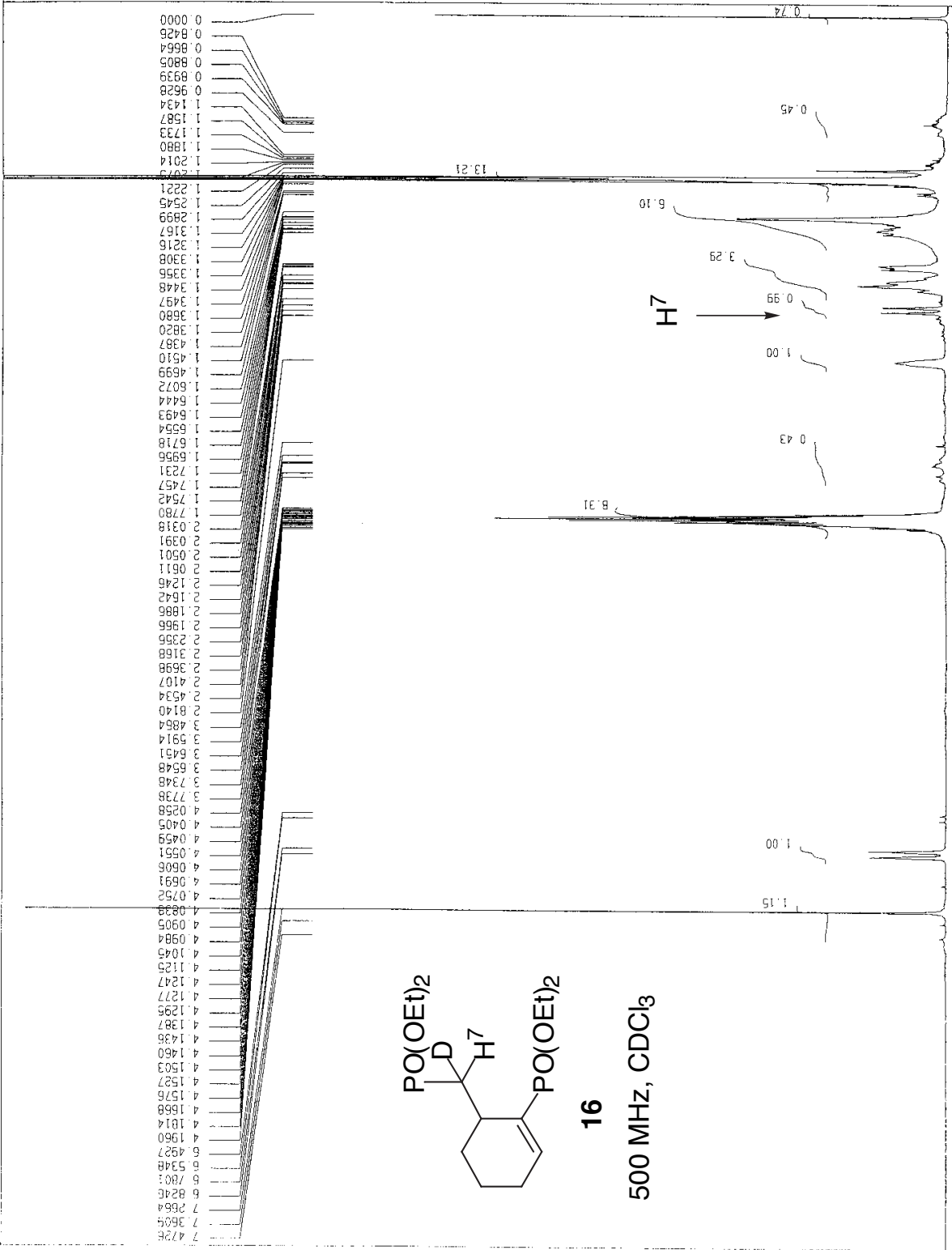




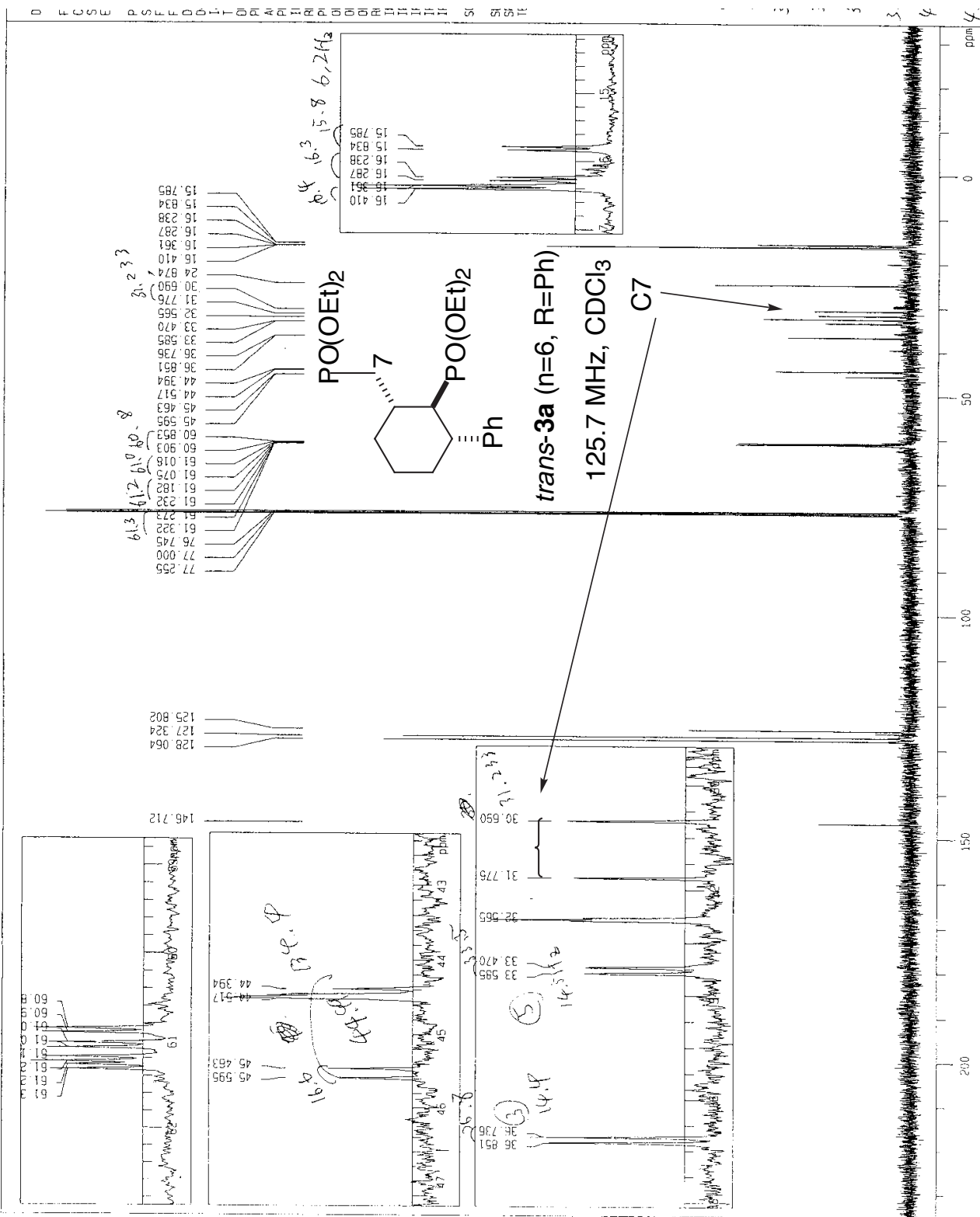




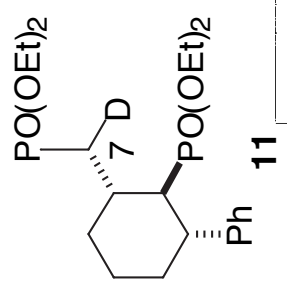
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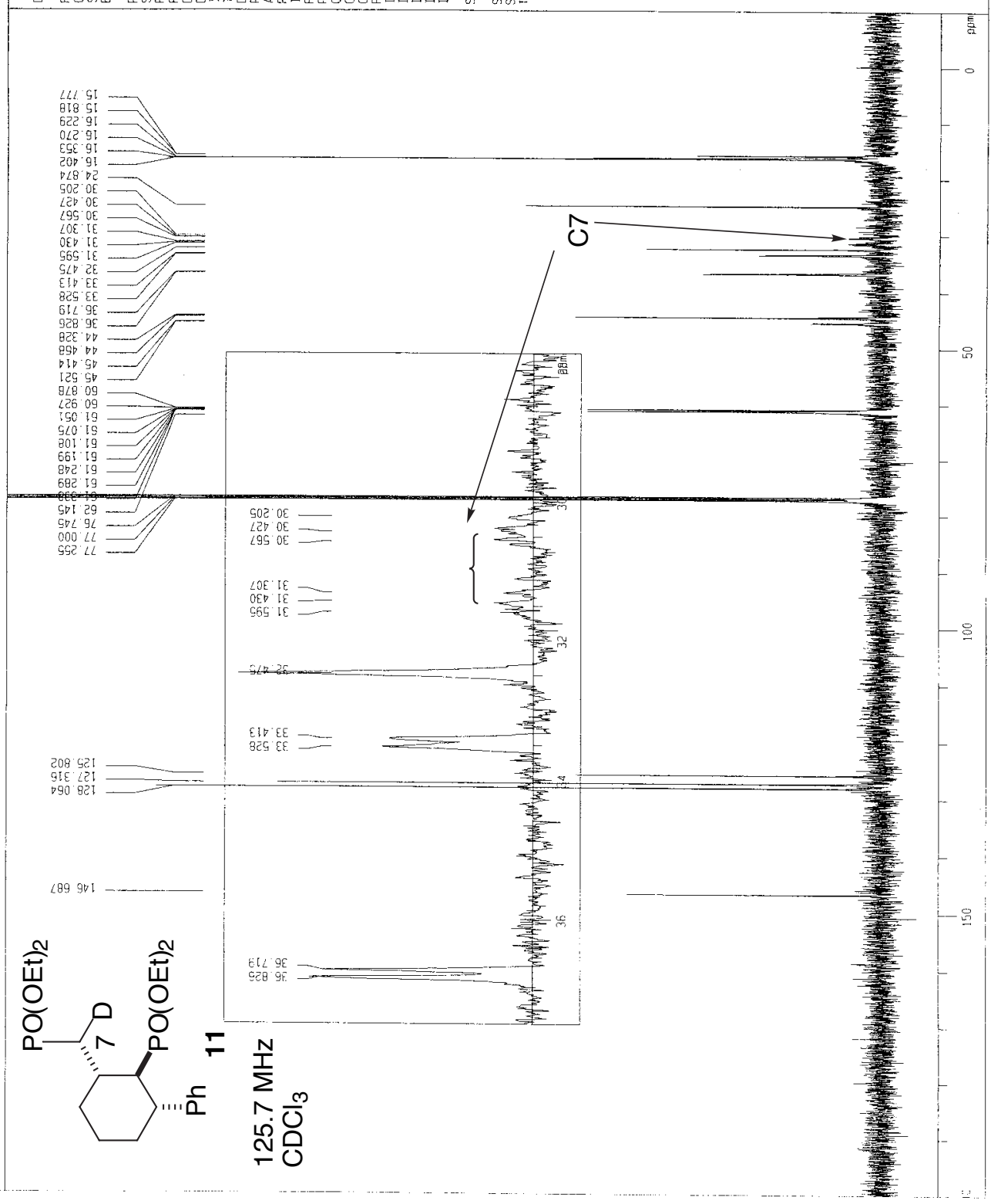
#1521r3



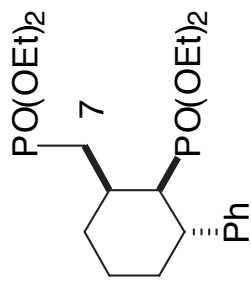
162-2



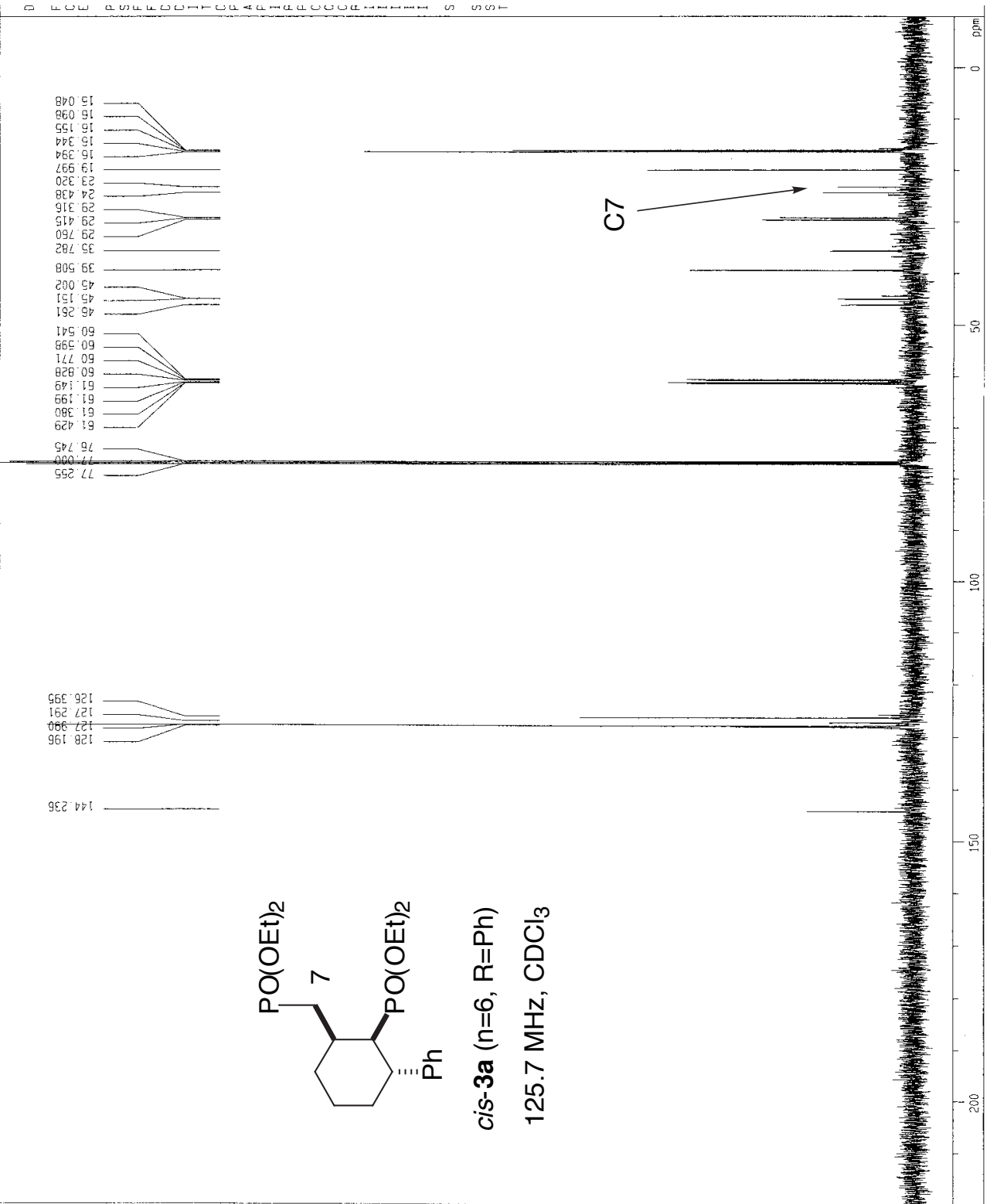
125.7 MHz  
CDCl<sub>3</sub>



#178Fr3bcm



*cis*-**3a** ( $n=6$ ,  $R=Ph$ )  
125.7 MHz,  $CDCl_3$



#151

