

Supplementary data

Unprecedented Asymmetric Induction through Configurationally Stable Lithium *N*-(α - Methylbenzyl)phosphinamides. A New Entry to enantiomerically pure gamma aminophosphinic acids and esters

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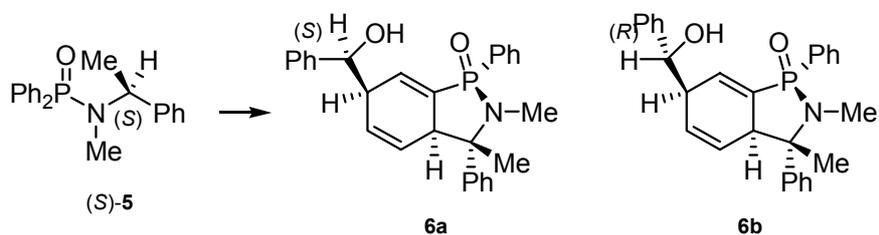
- Optimization of the reaction times in the anionic dearomatising cyclization reaction (Table S1).
- Synthetic procedures and NMR data of **6a-c**, **7c**, **10**, **11**, and **12**.
- Phase sensitive 2D gNOESY spectra and rows extracted from the 2D gNOESY of **10** and **11** respectively (Figures S1a, S1b, S2a, S2b).
- ¹H and ¹H{³¹P} NMR spectra of **12** and **13** (Figure S3 and S4).

Optimization of the reaction times

Table S1 Optimization of the reaction times for the lithiation of (S)-**5** and subsequent trapping of the dearomatised products with benzaldehyde.

t_1	t_2	Ratio (%)		Yield (%)	5 (%)
		6a	6b		
1 sec	1 sec	88	12	73	10
5 sec	5 sec	89	11	71	12
10 sec	1 sec	88	12	82	7
30 sec	1 sec	89	11	86	6
30 sec	30 sec	86	14	90	6
1 min	1 sec	90	10	93	-
1 min	1 min	88	12	98	-
1 min ^b	1 min		6	6	32
1 min	12 h	66	34	98	-
30 min	12 h	66	34	98	-

^a All reaction were carried in a 20 mM scale using HMPA as cosolvent. ^b DMPU was used instead of HMPA.



Synthetic procedures

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. THF was distilled from sodium/benzophenone immediately prior to use. HMPA and DMPU was distilled from KOH and CaH₂, respectively, under reduced pressure and stored over molecular sieves (3Å). Commercial reagents were purchased from Sigma-Aldrich Química S.A. and were distilled prior to their use, except *t*-BuLi. TLC was performed on Merck plates with aluminum backing and silica gel 60 F₂₅₄. For column chromatography silica gel 60 (40-63 μm) from Scharlau was used. NMR spectra were recorded on Bruker Avance 300 and 500 spectrometers using CDCl₃ as solvent. Chemical shifts are referred to internal tetramethylsilane for ¹H and ¹³C, internal CFCl₃ for ¹⁹F, and to external 85% H₃PO₄ for ³¹P. 2D NMR Correlation spectra (gCOSY, gTOCSY, gNOESY, gHMQC and gHMBC), and selective 1D gTOCSY and gNOESY were acquired using standard Bruker software and processing routines. Chiral HPLC separations were performed on a HP1100 apparatus equipped with a diode array detector using a Chiracel OD-H column. The eluents used were mixtures of hexane:alcohol (EtOH, or *i*-PrOH) in a ratio ranging from 97:3 to 98:2. The flux was set to 0.3-0.4 mL min⁻¹ and the volumen of injection was 20 μL.

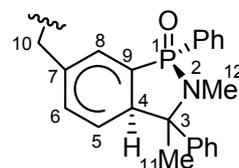
General procedure for the synthesis of tetrahydrobenzo[*c*][1,2]-1λ⁵-azaphospholes 6-7. To a solution of the appropriate phosphinamide **5** (0.597 mmol) and HMPA (3.58 mmol) in THF (30 mL) was added a solution of *t*-BuLi (0.9 mL of a 1.7 M solution in cyclohexane, 1.49 mmol) at -90 °C. After *t*₁ (specified in table S1) of metalation was added the corresponding electrophile (1.49 mmol). The reaction mixture was stirred at -90 °C for *t*₂ min. Then the reaction mixture was poured into ice water and extracted with ethyl acetate (3x15 mL). The organic layers were dried over Na₂SO₄ and concentrated in vacuo. ¹H, ¹H{³¹P}, and ³¹P NMR spectra of the crude reaction were measured in order to determine the stereoselectivity of the process. The reaction mixture was then purified by flash column chromatography using different mixtures of ethyl acetate:hexane as eluent. The same procedure was applied when the reaction was carried out in the presence of DMPU (3.58 mmol) as cosolvent.

General procedure for conversion from azaphospholes **6b and *ent*-**6b** to esters **9** and **10** respectively.** To a solution of the azaphosphole **6b** or *ent*-**6b** (0.09 mmol) in CH₂Cl₂ (3.6 mL) was added (2*R*)-2-methoxy-2-(trifluoromethyl)phenylacetic acid (Mosher's acid) (0.22 mmol), DCC (0.23 mmol) and some crystals of DMAP (~1 mg) at 0 °C. After stirring for 5 min at 0 °C and for a further 6 h at room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (3x10 mL). The organic layers were dried over Na₂SO₄. Removal of the solvent from ethyl acetate under reduced pressure gave a crude product, which was purified by flash column chromatography (ethyl acetate:hexane, 1:1 to 4:1) to furnish compound **9** or **10** as a white oils.

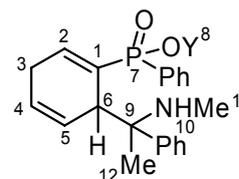
General procedure for the preparation of γ -*N*-methylaminophosphinic acid **11.** To a solution of the phosphole **6b** (0.60 mmol) in acetone (10 mL) was added 2N HCl (1mL) at room temperature and the mixture was stirred for 30 min. Then, the pH was set to neutral by adding 1N NaOH and the reaction was extracted with ethyl acetate (3x15 mL). The organic layers were dried over Na₂SO₄ and concentrated in vacuo affording a white solid that was washed with diethyl ether.

General procedure for the preparation of γ -*N*-methylaminophosphinic ester **12.** To a solution of the phosphole **6b** (0.60 mmol) in dry methanol (10 mL) was added a methanolic solution of HCl (1mL) at room temperature and the mixture was stirred for 30 min. Then, the pH was set to neutral by adding 1N NaOH and the reaction was extracted with ethyl acetate (3x15 mL). The organic layers were dried over Na₂SO₄ and concentrated in vacuo affording a white solid that was washed with diethyl ether.

NMR characterization:



Scheme numbering used for the basic skeleton:



NMR data for **6a**. ^1H NMR (300.13 MHz): δ 1.41 (s, H-11), 2.27 (d, 3H, $^3J_{\text{PH}}$ 9.2 Hz, H-12), 2.98 (dddd, 1H, $^3J_{\text{PH}}$ 2.2, $^5J_{\text{HH}}$ 11.4 $^3J_{\text{HH}}$ 4.0, $^3J_{\text{HH}}$ 3.9, $^4J_{\text{HH}}$ 1.8 Hz, H-7), 3.40 (ddd, 1H, $^5J_{\text{HH}}$ 11.4, $^4J_{\text{HH}}$ 4.4, $^3J_{\text{HH}}$ 2.2 Hz, H-4), 3.84 (bs, OH, H-13), 4.98 (d, 1H, $^3J_{\text{HH}}$ 3.9 Hz, H-10), 5.49 (ddt, 1H, $^4J_{\text{PH}}$ 4.4, $^3J_{\text{HH}}$ 10.4, $^3J_{\text{HH}}$ 2.2 Hz, H-5), 5.75 (m, 1H, $^3J_{\text{HH}}$ 10.4, $^4J_{\text{HH}}$ 4.0, $^3J_{\text{HH}}$ 2.2 Hz, H-6), 6.79 (ddd, 1H, $^3J_{\text{PH}}$ 17.2, $^3J_{\text{HH}}$ 4.0, $^4J_{\text{HH}}$ 1.8 Hz, H-8), 7.63-7.22 (m, 8H, ArH), 7.92 (m, 2H, H-15). ^{13}C NMR (75.47 MHz): δ 18.35 (C-11), 25.26 (d, $^2J_{\text{PC}}$ 3.0 Hz, C-12), 44.75 (d, $^3J_{\text{PC}}$ 12.0 Hz, C-7), 52.46 (d, $^2J_{\text{PC}}$ 13.8 Hz, C-4), 66.84 (d, $^2J_{\text{PC}}$ 10.2 Hz, C-3), 75.70 (C-10), 123.41 (d, $^3J_{\text{PC}}$ 6.6 Hz, C-5), 126.51 (d, $^4J_{\text{PC}}$ 1.8 Hz, C-6), 128.61-126.48 (12CAr), 131.71 (d, $^4J_{\text{PC}}$ 3.0 Hz, C-17), 131.83 (d, $^2J_{\text{PC}}$ 10.2 Hz, C-15), 132.88 (d, $^1J_{\text{PC}}$ 134.6 Hz, C-14), 134.49 (d, $^1J_{\text{PC}}$ 120.1 Hz, C-9), 137.53 (d, $^2J_{\text{PC}}$ 9.6 Hz, C-8), 141.65 (C-18), 142.83 (d, $^3J_{\text{PC}}$ 8.4 Hz, C-22). ^{31}P NMR (121.50 MHz): δ 29.12.

NMR data of **6b**. ^1H NMR (300.13 MHz): δ 1.49 (s, H-11), 2.29 (d, 3H, $^3J_{\text{PH}}$ 9.1 Hz, H-12), 3.42 (m, 2H, H-4, -7), 4.05 (d, OH, $^3J_{\text{HH}}$ 4.4 Hz, H-13), 4.91 (m, 1H, H-10), 5.54 (dd, 1H, $^4J_{\text{PH}}$ 4.4, $^3J_{\text{HH}}$ 10.3 Hz, H-5), 5.88 (dd, 1H, $^3J_{\text{HH}}$ 10.3, $^3J_{\text{HH}}$ 1.1 Hz, H-6), 6.34 (dd, 1H, $^3J_{\text{HH}}$ 3.3, $^3J_{\text{HH}}$ 1.8 Hz, H-20), 6.41 (d, 1H, $^3J_{\text{HH}}$ 3.3 Hz, H-19), 6.74 (dd, 1H, $^3J_{\text{PH}}$ 18.7, $^4J_{\text{HH}}$ 1.5 Hz, H-8), 7.59-7.28 (m, 8H, ArH), 7.43 (d, 1H, $^3J_{\text{HH}}$ 1.8 Hz, H-21), 7.94 (m, 2H, H-15). ^{13}C NMR (75.47 MHz): δ 18.54 (C-11), 25.28 (d, $^2J_{\text{PC}}$ 3.0 Hz, C-12), 42.74 (d, $^3J_{\text{PC}}$ 12.0 Hz, C-7), 52.47 (d, $^2J_{\text{PC}}$ 13.8 Hz, C-4), 66.89 (d, $^2J_{\text{PC}}$ 10.2 Hz, C-3), 69.98 (C-10), 107.38 (C-19), 110.33 (C-20), 123.60 (d, $^3J_{\text{PC}}$ 6.6 Hz, C-5), 126.60 (d, $^4J_{\text{PC}}$ 1.8 Hz, C-6), 128.64-126.74 (7CAr), 131.75 (d, $^4J_{\text{PC}}$ 3.0 Hz, C-17), 131.91 (d, $^2J_{\text{PC}}$ 10.2 Hz, C-15), 132.76 (d, $^1J_{\text{PC}}$ 135.2 Hz, C-14), 134.38 (d, $^1J_{\text{PC}}$ 119.5 Hz, C-9), 141.66 (C-21), 142.84 (d, $^3J_{\text{PC}}$ 8.4 Hz, C-22), 154.66 (C-18). ^{31}P NMR (121.50 MHz): δ 29.00.

NMR data of **6c**. ^1H NMR (300.13 MHz): δ 0.75 (d, 3H, $^3J_{\text{HH}}$ 6.6 Hz, H-19), 0.85 (d, 3H, $^3J_{\text{HH}}$ 6.6 Hz, H-20), 1.43 (s, H-11), 1.73 (dsp, 1H, $^3J_{\text{HH}}$ 7.0 $^3J_{\text{HH}}$ 6.6 Hz, H-18), 2.12 (d, 3H, $^3J_{\text{PH}}$ 9.2 Hz, H-12), 2.90 (m, 1H, $^3J_{\text{HH}}$ 13.2 $^3J_{\text{HH}}$ 7.0, $^3J_{\text{HH}}$ 4.4 Hz, H-7), 3.24 (m, 1H, $^3J_{\text{PH}}$ 12.8, $^4J_{\text{HH}}$ 2.5 Hz, H-4), 3.26 (dd, 1H, $^3J_{\text{HH}}$ 7.0, $^3J_{\text{HH}}$

4.4 Hz, H-10), 5.36 (ddt, 1H, $^3J_{HH}$ 10.3, $^3J_{HH}$ 4.4, $^4J_{HH}$ 2.2 Hz, H-5), 5.72 (d, 1H, $^3J_{HH}$ 10.3, H-6), 6.53 (ddd, 1H, $^3J_{PH}$ 17.4, $^3J_{HH}$ 4.4, $^4J_{HH}$ 2.5 Hz, H-8), 7.42-7.10 (m, 8H, ArH), 7.78 (m, 2H, H-15). ^{13}C NMR (75.47 MHz): δ 18.45 (C-11), 18.62 (C-20), 19.51 (C-19), 25.06 (d, $^2J_{PC}$ 3.0 Hz, C-12), 30.43 (C-18), 41.16 (d, $^3J_{PC}$ 11.9 Hz, C-7), 52.27 (d, $^2J_{PC}$ 13.7 Hz, C-4), 66.88 (d, $^2J_{PC}$ 10.1 Hz, C-3), 78.43 (C-10), 122.87 (d, $^3J_{PC}$ 6.8 Hz, C-5), 128.51-126.53 (7CAr), 127.03 (d, $^4J_{PC}$ 1.6 Hz, C-6), 131.69 (d, $^2J_{PC}$ 10.4 Hz, C-15), 131.66 (d, $^4J_{PC}$ 3.1 Hz, C-17), 132.52 (d, $^1J_{PC}$ 132.5 Hz, C-14), 133.18 (d, $^1J_{PC}$ 120.3 Hz, C-9), 139.78 (d, $^2J_{PC}$ 9.3 Hz, C-8), 142.69 (d, $^3J_{PC}$ 8.3 Hz, C-21). ^{31}P NMR (121.50 MHz): δ 28.19.

NMR data of **7c**. ^1H NMR (300.13 MHz): δ 0.77 (d, 3H, $^3J_{HH}$ 6.6 Hz, H-19), 0.83 (d, 3H, $^3J_{HH}$ 6.6 Hz, H-20), 1.42 (s, H-11), 1.73 (m, 1H, $^3J_{HH}$ 5.0, H-18), 2.12 (d, 3H, $^3J_{PH}$ 9.2 Hz, H-12), 2.89 (m, $^3J_{HH}$ 4.4 Hz 1H, H-7), 3.22 (m, 1H, $^3J_{PH}$ 12.8 Hz, H-4), 3.19 (dd, 1H, $^3J_{HH}$ 5.5, $^3J_{HH}$ 5.0 Hz, H-10), 5.36 (m, 1H, $^3J_{HH}$ 11.0, $^3J_{HH}$ 4.4 Hz, H-5), 5.66 (d, 1H, $^3J_{HH}$ 11.0, H-6), 6.65 (d, 1H, $^3J_{PH}$ 17.4 Hz, H-8), 7.42-7.10 (m, 8H, ArH), 7.78 (m, 2H, H-15). ^{13}C NMR (75.47 MHz): δ 17.82 (C-20), 18.47 (C-11), 19.84 (C-19), 25.08 (d, $^2J_{PC}$ 3.0 Hz, C-12), 30.48 (C-18), 41.40 (d, $^3J_{PC}$ 11.9 Hz, C-7), 52.31 (d, $^2J_{PC}$ 14.0 Hz, C-4), 66.82 (d, $^2J_{PC}$ 10.2 Hz, C-3), 78.49 (C-10), 122.57 (d, $^3J_{PC}$ 6.8 Hz, C-5), 128.51-126.53 (7CAr), 129.15 (d, $^4J_{PC}$ 1.6 Hz, C-6), 131.71 (d, $^2J_{PC}$ 10.2 Hz, C-15), 131.66 (d, $^4J_{PC}$ 3.1 Hz, C-17), 132.58 (d, $^1J_{PC}$ 135.6 Hz, C-14), 133.27 (d, $^1J_{PC}$ 120.4 Hz, C-9), 137.74 (d, $^2J_{PC}$ 9.3 Hz, C-8), 142.68 (d, $^3J_{PC}$ 8.3 Hz, C-21). ^{31}P NMR (121.50 MHz): δ 28.22

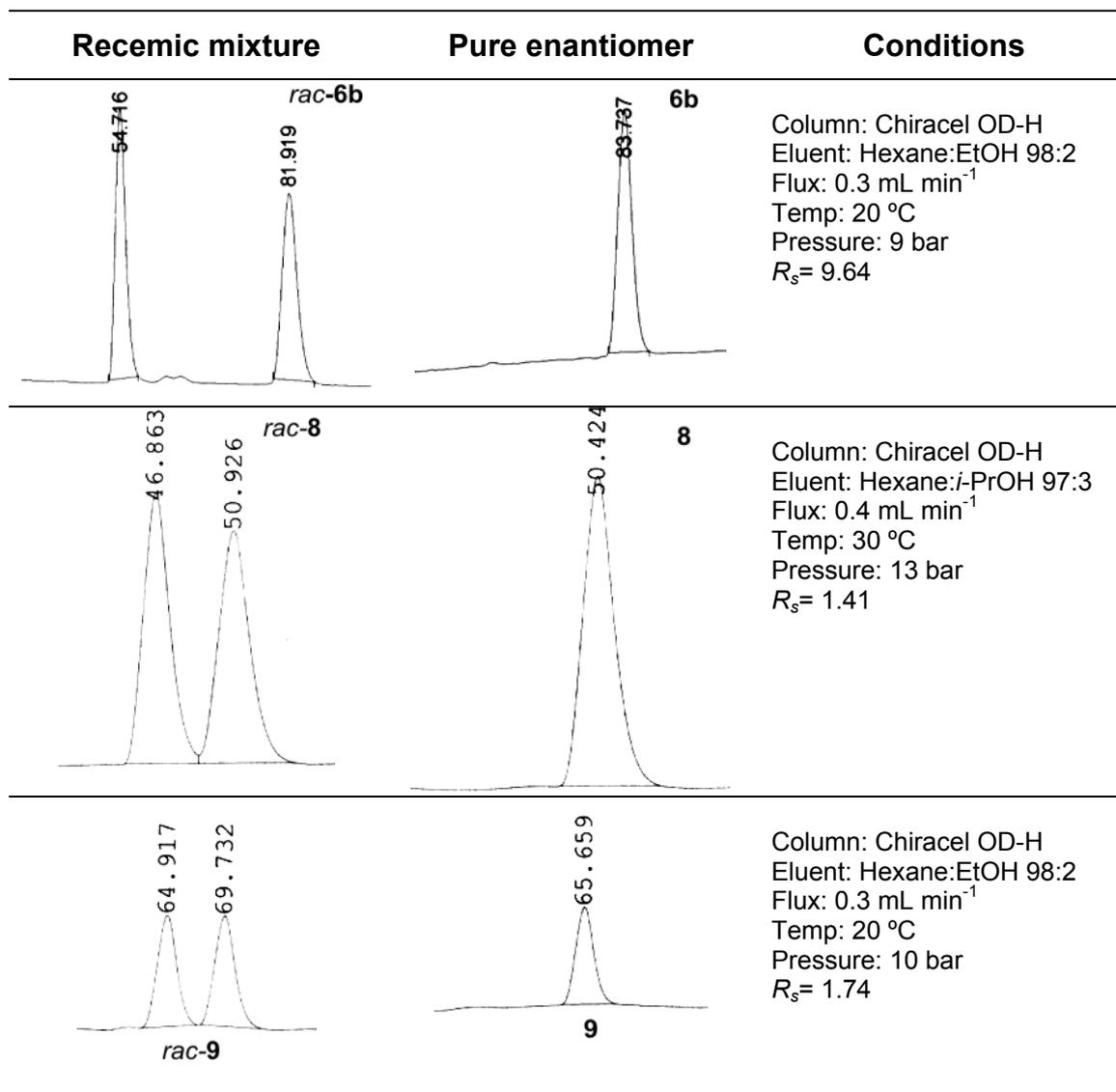
NMR data of **10**. ^1H NMR (500.13 MHz): δ 1.50 (s, 3H, H-11), 2.31 (d, 3H, $^3J_{PH}$ 9.1 Hz, H-12), 3.40 (dq, 1H, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5, $^5J_{HH}$ 11.9 Hz, H-4), 3.47 (c, 3H, $^5J_{FH}$ 0.9 Hz, H-16), 3.58 (m, 1H, $^3J_{HH}$ 8.2, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5, $^5J_{HH}$ 11.9 Hz, H-7), 5.54 (ddt, 1H, $^4J_{PH}$ 4.0, $^3J_{HH}$ 10.3, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5 Hz, H-5), 5.67 (dq, 1H, $^3J_{HH}$ 10.3, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5 Hz, H-6), 6.04 (d, 1H, $^3J_{HH}$ 8.2 Hz, H-10), 6.40 (dd, 1H, $^3J_{HH}$ 3.6, $^3J_{HH}$ 1.9 Hz, H-24), 6.42 (dq, $^3J_{PH}$ 15.5, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5 Hz, H-8), 6.58 (dd, 1H, $^3J_{HH}$ 3.6, $^4J_{HH}$ 0.8 Hz, H-23), 7.43-7.29 (m, 6H, ArH), 7.44 (dd, 1H, $^3J_{HH}$ 1.9, $^4J_{HH}$ 0.8 Hz, H-25), 7.48-7.45 (m, 4H, ArH), 7.61-7.52 (m, 3H, ArH), 7.93 (m, 2H, $^3J_{PH}$ 12.8 Hz, H-19). ^{13}C NMR (125.76 MHz): δ 18.76 (C-11), 25.37 (d, $^2J_{PC}$ 3.0 Hz, C-12), 39.71 (d, $^3J_{PC}$ 12.7 Hz, C-7), 52.57 (d, $^2J_{PC}$ 13.6 Hz, C-4), 55.46 (q, $^4J_{FC}$ 1.3 Hz, C-16), 66.74 (d, $^2J_{PC}$ 9.3 Hz, C-3), 72.17 (C-10), 84.45 (q, $^2J_{FC}$ 27.8 Hz, C-15), 110.78 (C-24), 112.03 (C-23), 123.26 (q, $^1J_{FC}$ 286.5 Hz, C-17), 124.43 (d, $^3J_{PC}$ 6.8 Hz, C-5), 125.37 (d, $^4J_{PC}$ 1.3 Hz, C-6), 128.37-126.77 (4CAr), 128.60 (d, $^3J_{PC}$ 13.2 Hz, C-20), 128.78 (CAr), 129.57 (CAr), 131.85 (d, $^4J_{PC}$ 3.0 Hz, C-21), 131.95 (d, $^2J_{PC}$ 10.2 Hz, C-19), 132.16 (C-26), 132.90 (d, $^1J_{PC}$ 134.8 Hz, C-18), 133.80 (d, $^2J_{PC}$ 10.6 Hz, C-8), 135.68 (d, $^1J_{PC}$ 119.9 Hz, C-9), 142.62 (d, $^3J_{PC}$ 8.1 Hz, C-30), 143.13 (C-25), 148.72 (C-22), 165.70 (C-14). ^{31}P NMR (202.46 MHz): δ 27.65. ^{19}F NMR (282.40 MHz): δ -71.69.

NMR data of **11**. ^1H NMR (500.13 MHz): δ 1.48 (s, 3H, H-11), 2.32 (d, 3H, $^3J_{PH}$ 9.1 Hz, H-12), 3.43 (dq, 1H, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5, $^5J_{HH}$ 12.0 Hz, H-4), 3.51 (c, 3H, $^5J_{FH}$ 1.0 Hz, H-16), 3.61 (m, 1H, $^3J_{HH}$ 7.4, $^3J_{HH}$ 4.8, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5, $^5J_{HH}$ 12.0 Hz, H-7), 5.54 (ddt, 1H, $^4J_{PH}$ 4.1, $^3J_{HH}$ 10.2, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5 Hz, H-5), 5.67 (m, 1H, $^5J_{PH}$ 0.9, $^3J_{HH}$ 10.2, $^3J_{HH}$ 2.5, $^4J_{HH}$ 2.5 Hz, H-6), 6.06 (d, 1H, $^3J_{HH}$ 7.4 Hz, H-10), 6.37 (dd, 1H, $^3J_{HH}$ 3.4, $^3J_{HH}$ 1.8 Hz, H-24), 6.48 (dd, 1H, $^3J_{HH}$ 3.4, $^4J_{HH}$ 0.8 Hz, H-23), 6.55 (m, $^3J_{PH}$ 16.9, $^3J_{HH}$ 4.8, $^4J_{HH}$ 2.5 Hz, H-8), 7.37-7.34 (m, 1H,

ArH), 7.37 (dd, 1H, $^3J_{\text{HH}}$ 1.8, $^4J_{\text{HH}}$ 0.8 Hz, H-25), 7.38 (m, 4H, ArH), 7.49-7.43 (m, 5H, ArH), 7.61-7.53 (m, 3H, ArH), 7.96 (m, 2H, $^3J_{\text{PH}}$ 12.5 Hz, H-19). ^{13}C NMR (125.76 MHz): δ 18.72 (C-11), 25.38 (d, $^2J_{\text{PC}}$ 3.0 Hz, C-12), 40.00 (d, $^3J_{\text{PC}}$ 12.6 Hz, C-7), 52.61 (d, $^2J_{\text{PC}}$ 13.4 Hz, C-4), 55.58 (q, $^4J_{\text{FC}}$ 1.4 Hz, C-16), 66.82 (d, $^2J_{\text{PC}}$ 9.6 Hz, C-3), 72.79 (C-10), 84.87 (q, $^2J_{\text{FC}}$ 27.9 Hz, C-15), 110.58 (C-24), 111.35 (C-23), 123.19 (q, $^1J_{\text{FC}}$ 288.7 Hz, C-17), 124.57 (d, $^3J_{\text{PC}}$ 6.9 Hz, C-5), 125.34 (d, $^4J_{\text{PC}}$ 1.1 Hz, C-6), 128.43-126.79 (4CAr), 128.65 (d, $^3J_{\text{PC}}$ 13.4 Hz, C-20), 128.80 (CAr), 129.60 (CAr), 131.68 (C-26), 131.93 (d, $^4J_{\text{PC}}$ 2.8 Hz, C-21), 131.96 (d, $^2J_{\text{PC}}$ 10.3 Hz, C-19), 132.89 (d, $^1J_{\text{PC}}$ 135.4 Hz, C-18), 134.18 (d, $^2J_{\text{PC}}$ 10.3 Hz, C-8), 135.67 (d, $^1J_{\text{PC}}$ 119.3 Hz, C-9), 142.64 (d, $^3J_{\text{PC}}$ 8.0 Hz, C-30), 142.98 (C-25), 148.82 (C-22), 165.78 (C-14). ^{31}P NMR (202.46 MHz): δ 27.74. ^{19}F NMR (282.40 MHz): δ -71.91.

NMR data of **12**. ^1H NMR (300.13 MHz): δ 1.62 (s, 3H, H-12), 2.18 (s, 3H, H-11), 3.09 (m, 1H, H-6), 4.45 (m, 1H, $^4J_{\text{PH}}$ 4.9 Hz, H-3), 4.48 (d, 1H, $^3J_{\text{HH}}$ 7.0 Hz, H-13), 4.86 (ddd, 1H, $^4J_{\text{PH}}$ 4.9, $^3J_{\text{HH}}$ 10.3, $^3J_{\text{HH}}$ 3.3 Hz, H-5), 5.52 (dd, 1H, $^3J_{\text{PH}}$ 22.2, $^3J_{\text{HH}}$ 3.2 Hz, H-2), 5.67 (d, 1H, $^3J_{\text{HH}}$ 10.3 Hz, H-4), 6.12 (d, 1H, $^3J_{\text{HH}}$ 3.1 Hz, H-20), 6.24 (dd, 1H, $^3J_{\text{HH}}$ 3.1, $^3J_{\text{HH}}$ 1.8 Hz, H-21), 7.24 (d, 1H, $^3J_{\text{HH}}$ 1.8 Hz, H-22), 7.30-7.45 (m, 8H, ArH), 7.86 (m, 2H, H-16), 10.80 (bs, OH, H-8), 12.85 (bs, NH, H-10). ^{13}C NMR (75.47 MHz): δ 16.33 (C-12), 26.48 (C-11), 43.05 (d, $^2J_{\text{PC}}$ 13.6 Hz, C-6), 45.30 (d, $^3J_{\text{PC}}$ 8.7 Hz, C-3), 65.41 (C-9), 71.20 (C-13), 106.69 (C-20), 110.01 (C-21), 126.08 (C-4), 127.64 (d, $^3J_{\text{PC}}$ 12.4 Hz, C-5), 128.83-127.48 (7 CAr), 130.31 (d, $^4J_{\text{PC}}$ 2.5 Hz, C-18), 132.54 (d, $^2J_{\text{PC}}$ 9.1 Hz, C-16), 135.21 (d, $^1J_{\text{PC}}$ 136.9 Hz, C-15), 136.96 (d, $^2J_{\text{PC}}$ 12.8, C-2), 137.63 (d, $^1J_{\text{PC}}$ 119.5 Hz, C-1), 138.85 (C-23), 141.83 (C-22), 154.51 (C-19). ^{31}P NMR (121.50 MHz): δ 30.80.

HPLC characterisation:



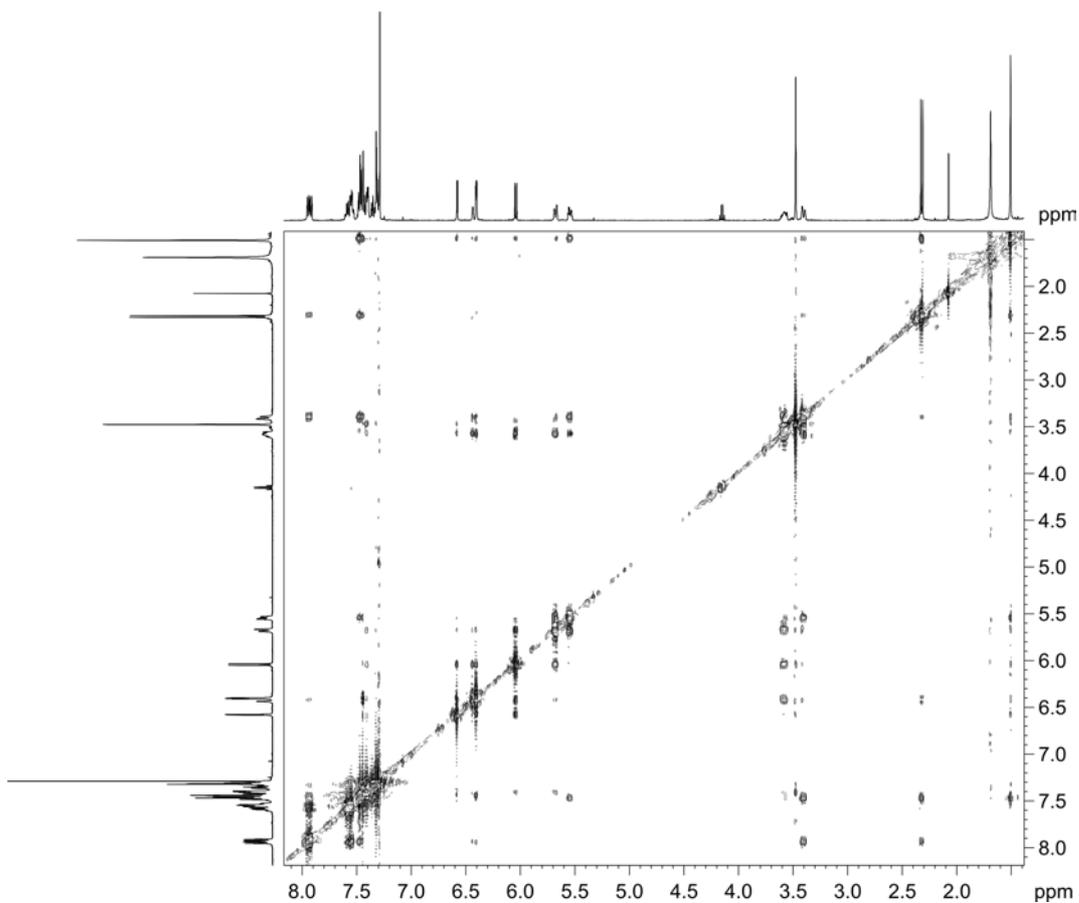


Figure S1a. Phase sensitive 2D gNOESY spectrum (500.13 MHz, (mixing time of 500 ms) of **10**.

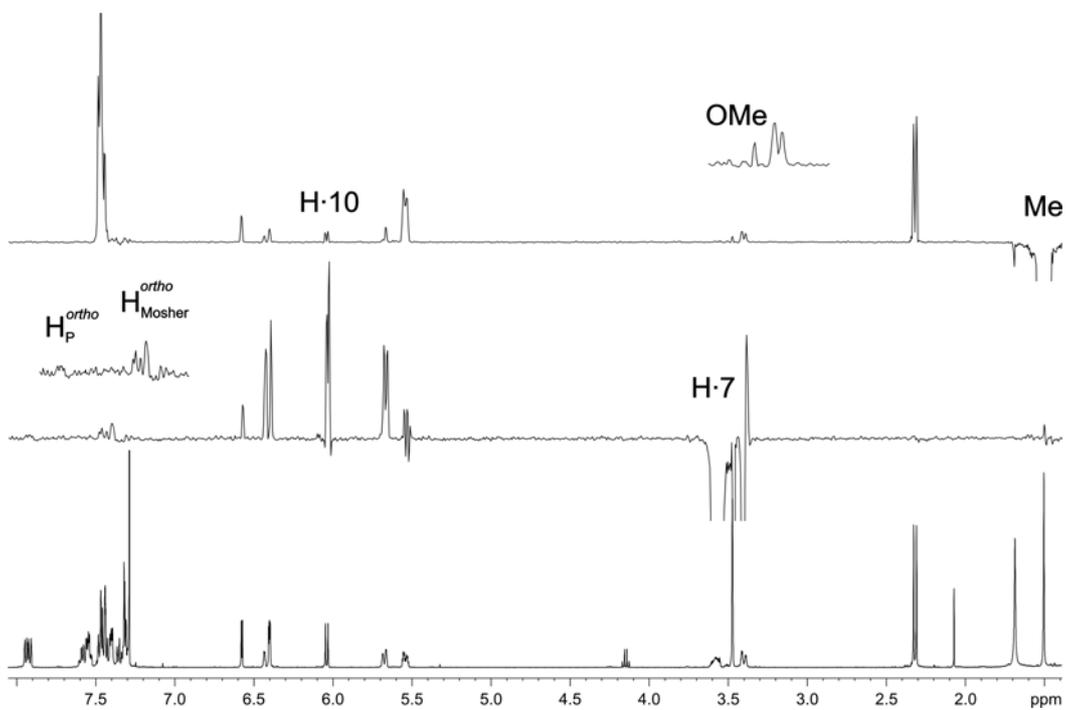


Figure S1b. ^1H NMR reference spectrum (500.13 MHz) and rows extracted from the 2D gNOESY (mixing time of 500 ms) spectrum of **10**.

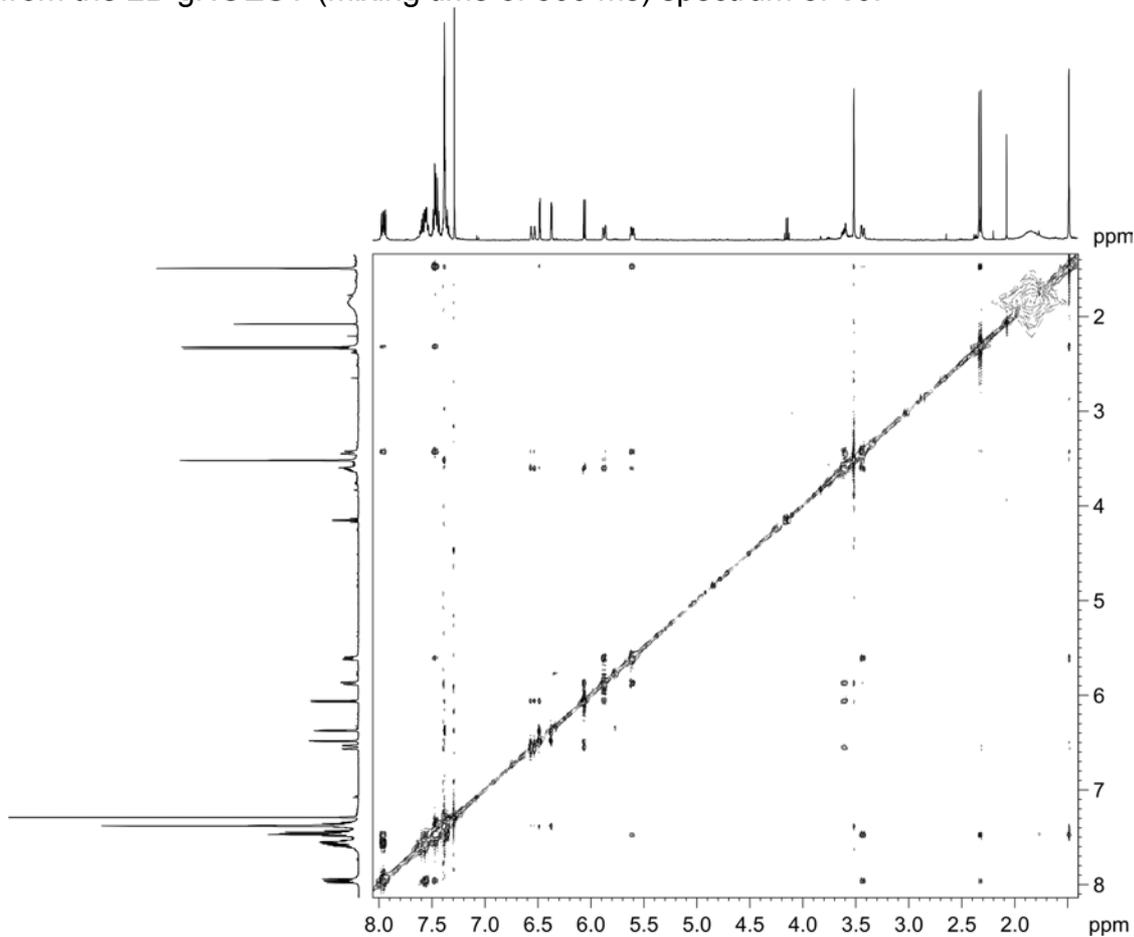


Figure S2a. Phase sensitive 2D gNOESY spectrum (500.13 MHz, mixing time of 500 ms) of **11**.

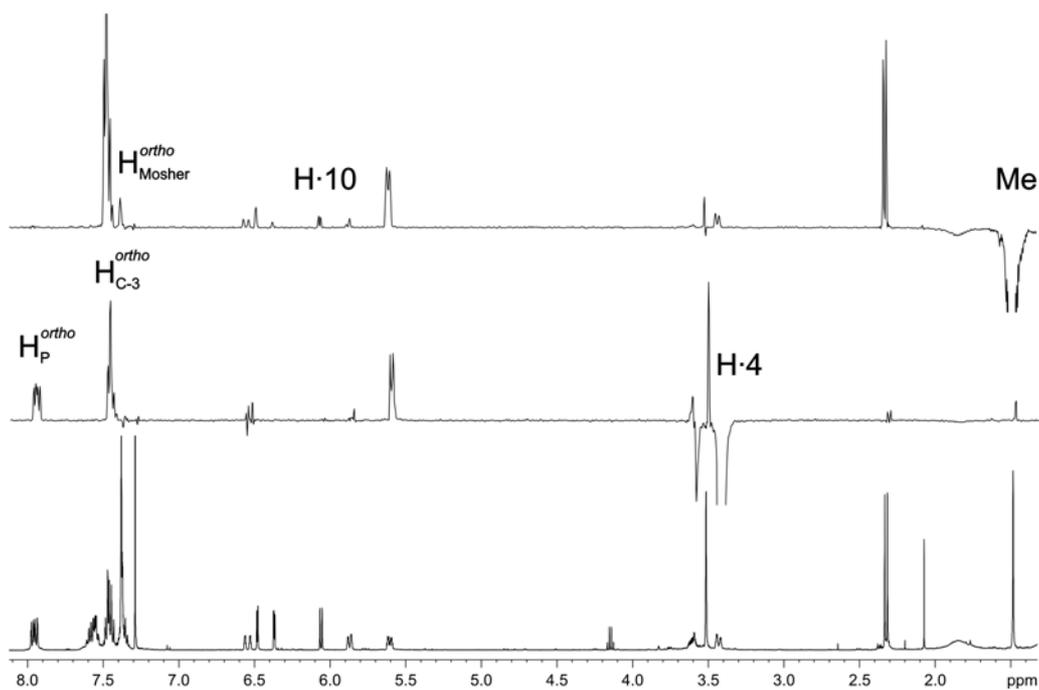


Figure S2b. ^1H NMR reference spectrum (500.13 MHz) and rows extracted from the 2D gNOESY spectrum of **11**.

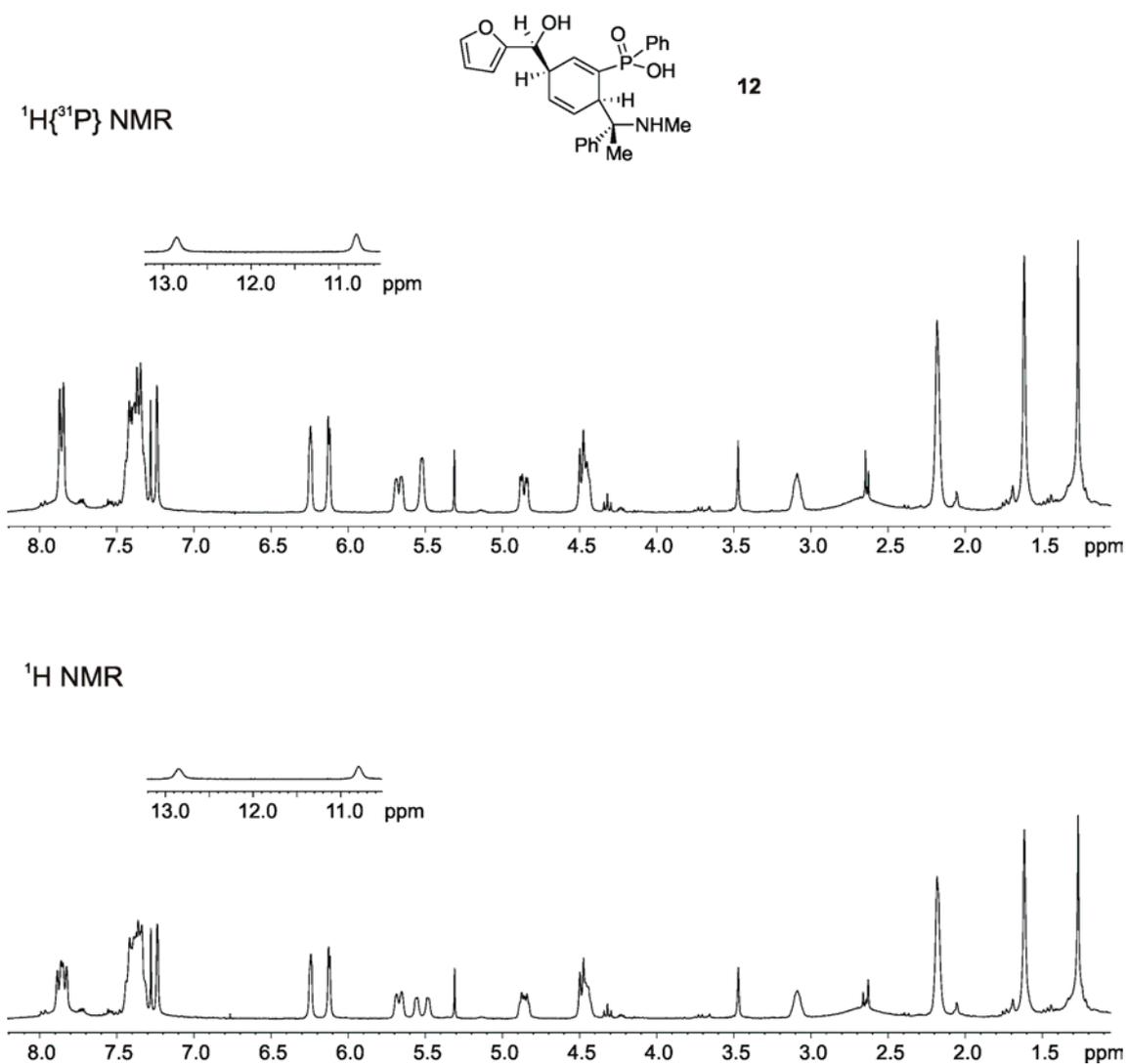


Figure S3. ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra (300.13 MHz) of **12**.

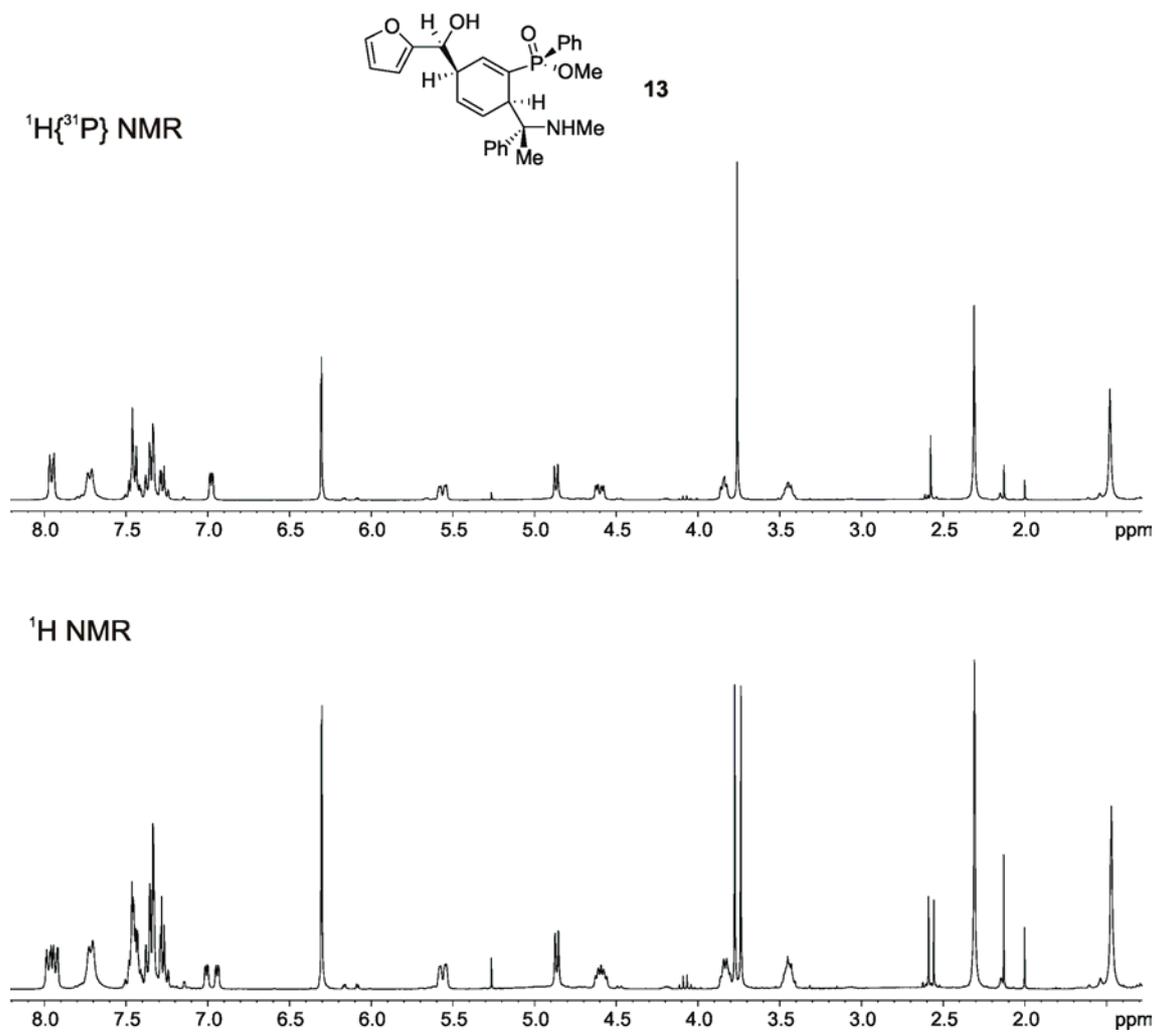


Figure S4. ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra (300.13 MHz) of **13**.