Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information for:

Synthesis and rhodium complexes of macrocyclic PNP and PONOP pincer ligands

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1. Selected NMR and HR ESI-MS spectra

1.1. Diethylamino-tert-butyl-octen-7-yl-phosphine (2)

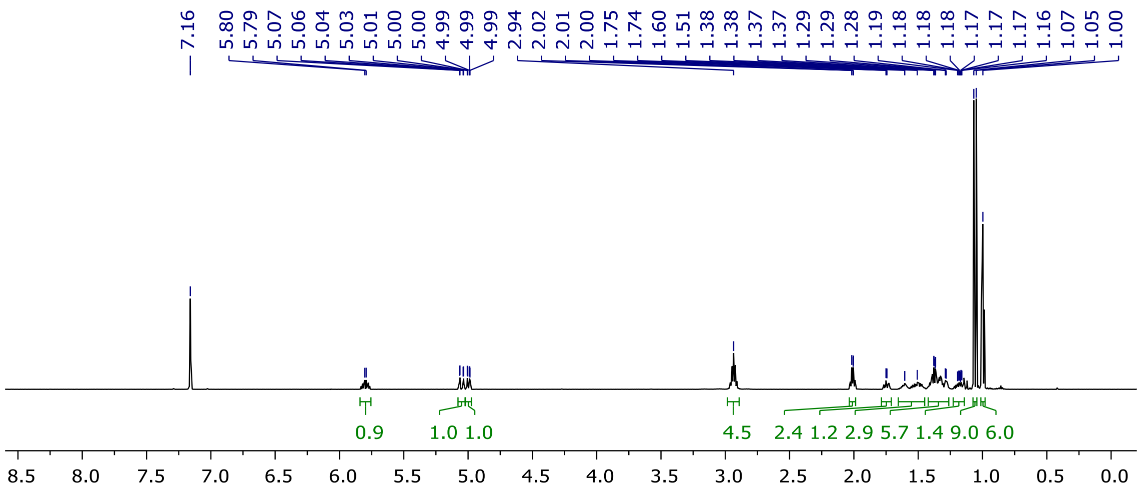

Figure S1. ^{1}H NMR spectrum of **2** (C_6D_6, 600 MHz).

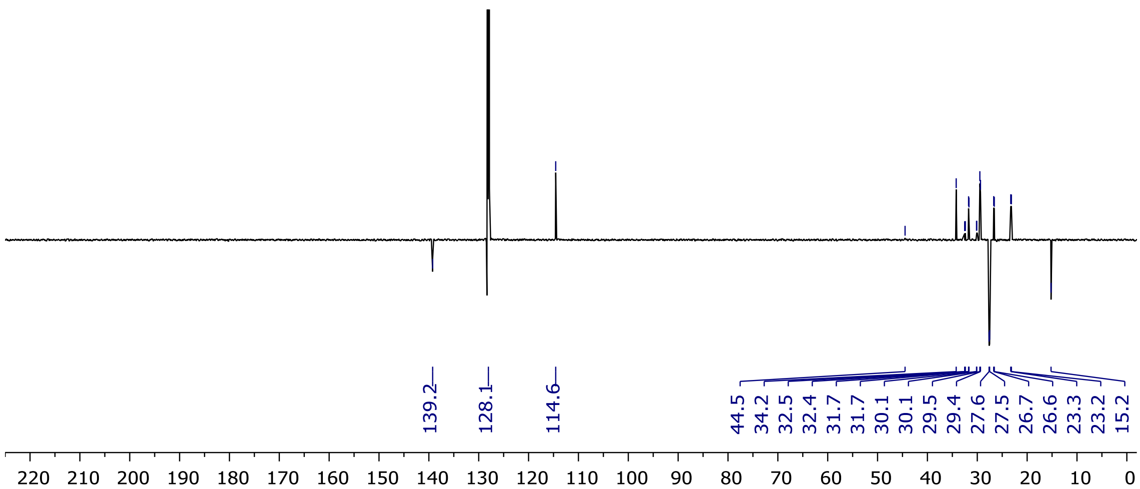

Figure S2. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2** (C_6D_6, 151 MHz).

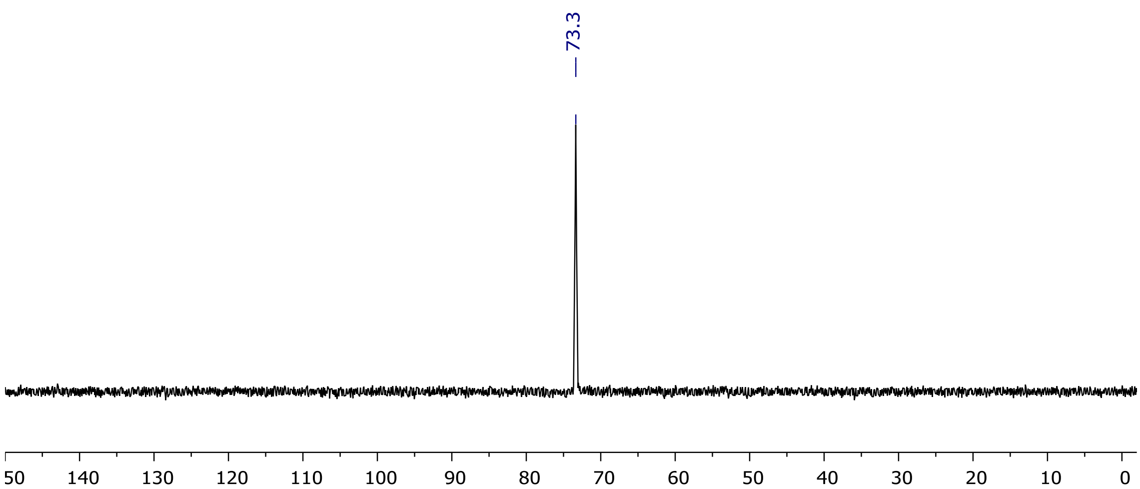

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (C_6D_6, 243 MHz).

1.2. Chloro-*tert*-butyl-octen-7-yl-phosphine (3)

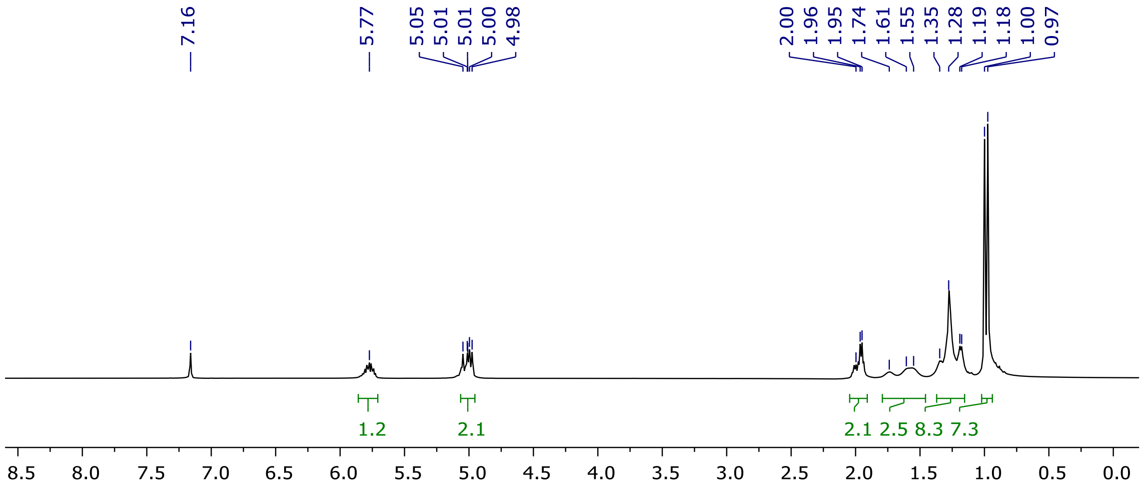

Figure S4. ^{1}H NMR spectrum of **3** (C_6D_6, 500 MHz).

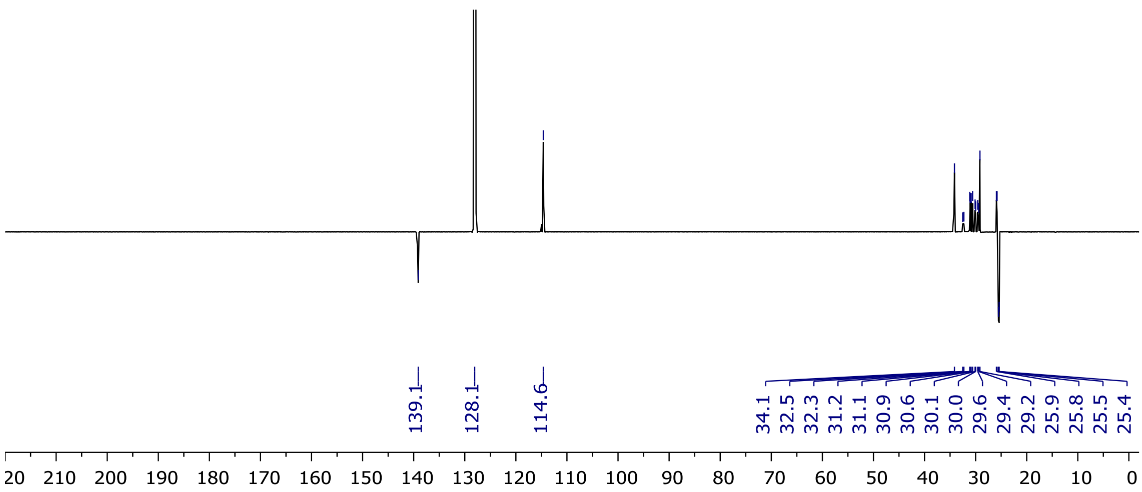

Figure S5. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3** (C_6D_6, 126 MHz).

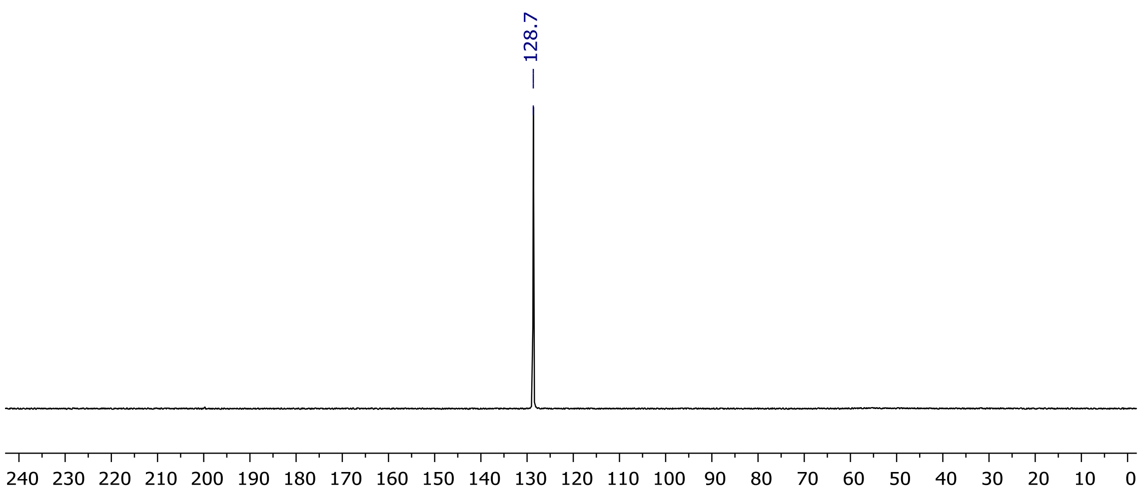

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **3** (C_6D_6, 162 MHz).

1.3. Chloro-*tert*-butyl-octen-7-yl-phosphonium chloride (3·HCl)

Experimental procedure: HCl in Et_2O (1 M, 3 equivalents) was added to a solution of **3** in hexane at 0 °C, which was then stirred at room temperature for 2 h. The resulting suspension was filtered and volatiles removed *in vacuo* to afford the product as a colourless oil.

^{1}H NMR (600 MHz, C_6D_6): δ 6.24 (dd, $^1J_{PH}$ = 427.9, $^3J_{HH}$ = 7.0, 1H), 5.78 (ddt, $^3J_{HH}$ = 16.9, $^3J_{HH}$ = 10.2, $^3J_{HH}$ = 6.7, 1H, C<u>H</u>=CH_2), 5.02 – 5.07 (m, 1H, CH=C<u>H</u>$_2$), 4.98 – 5.02 (m, 1H, CH=C<u>H</u>$_2$),1.93 – 1.99 (m, 2H, C<u>H</u>$_2$CH=CH_2), 1.64 – 1.75 (m, 1H, CH_2), 1.06 – 1.53 (m, 9H, CH_2), 0.88 (d, $^3J_{PH}$ = 15.6, 9H, *t*Bu).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 139.1 (s, <u>C</u>H=CH_2), 114.7 (s, CH=<u>C</u>H_2), 34.1 (s, <u>C</u>H_2CH=CH_2), 30.9 (d, J_{PC} = 12, CH_2), 30.8 (d, $^1J_{PC}$ = 67, *t*Bu{C}), 29.1 (2×CH_2), 24.3 (d, $^1J_{PC}$ = 61, CH_2), 23.7 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 23.0 (d, J_{PC} = 4, CH_2).

^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ 46.9 (s).

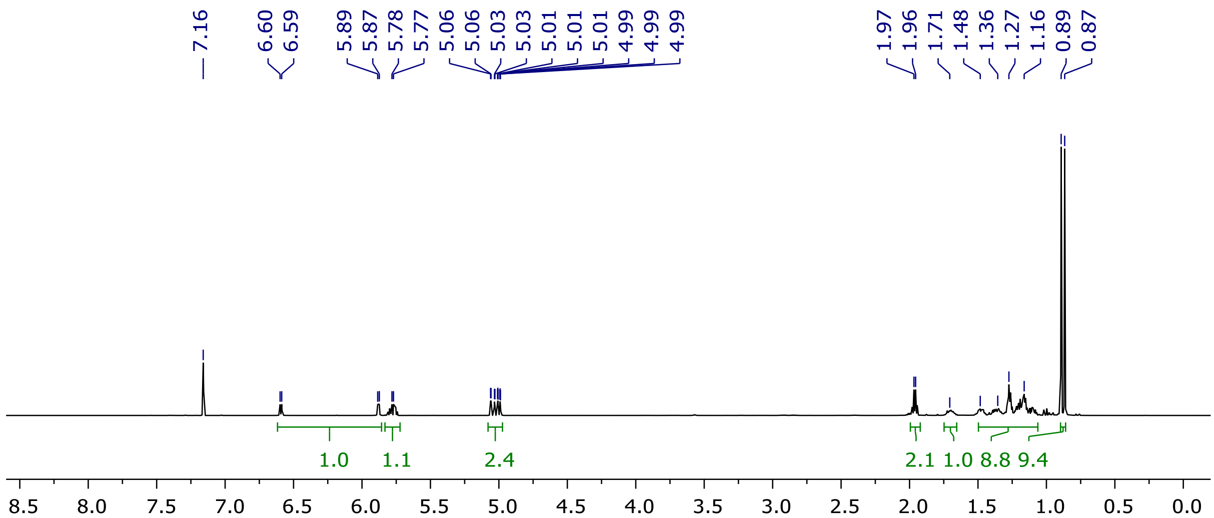

Figure S7. ^{1}H NMR spectrum of **3**·HCl (C_6D_6, 600 MHz).

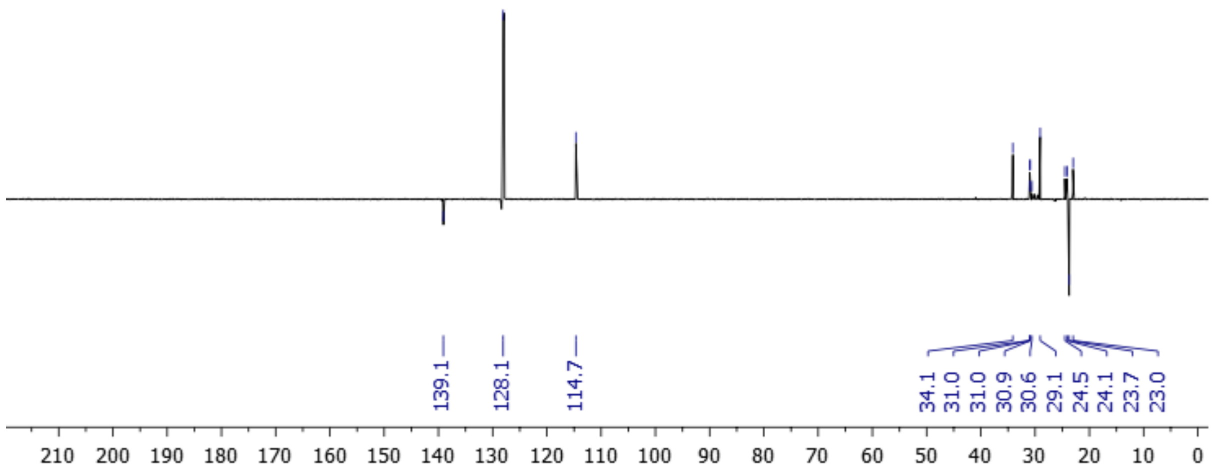

Figure S8. ^{13}C{^{1}H} APT NMR spectrum of **3**·HCl (C_6D_6, 151 MHz).

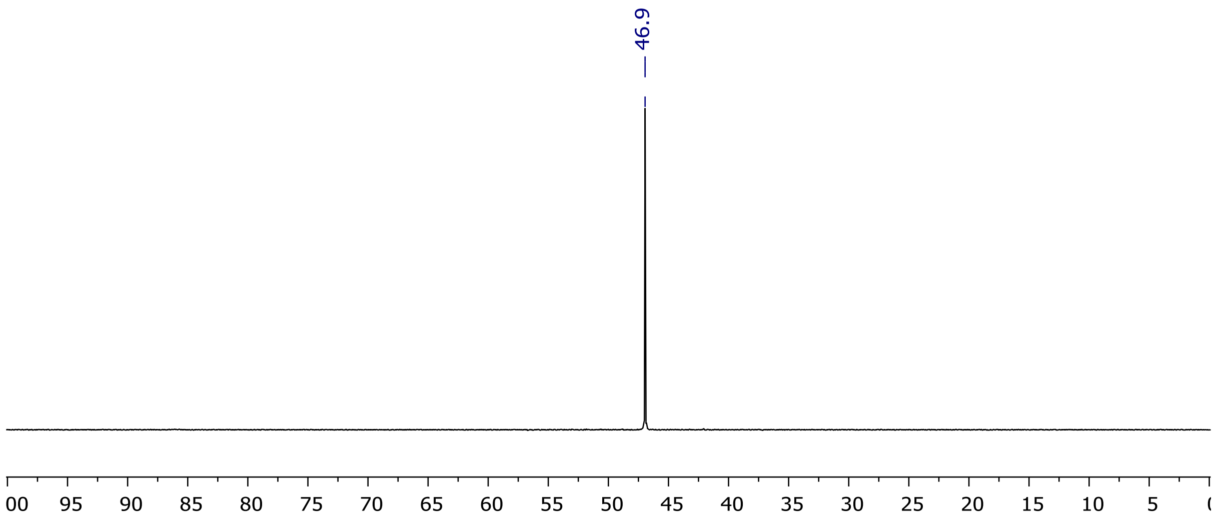

Figure S9. $^{31}P\{^1H\}$ NMR spectrum of **3**·HCl (C_6D_6, 243 MHz).

1.4. Intermediate 4a

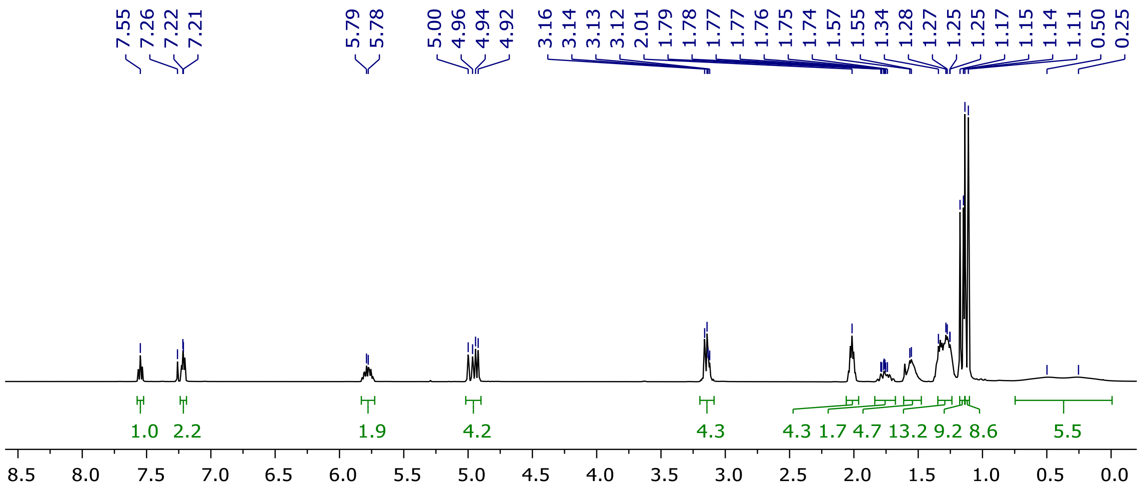

Figure S10. ^1H NMR spectrum of **4a** ($CDCl_3$, 500 MHz).

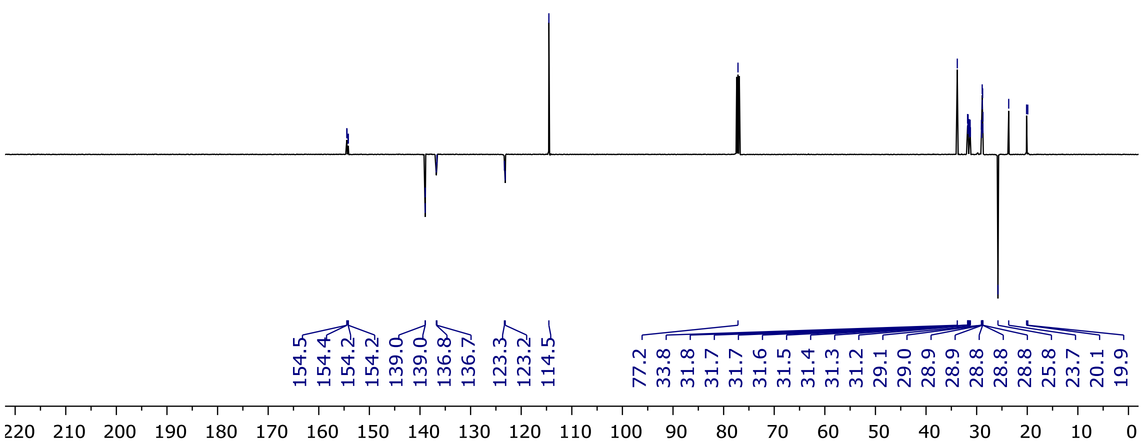

Figure S11. $^{13}C\{^1H\}$ APT NMR spectrum of **4a** ($CDCl_3$, 126 MHz).

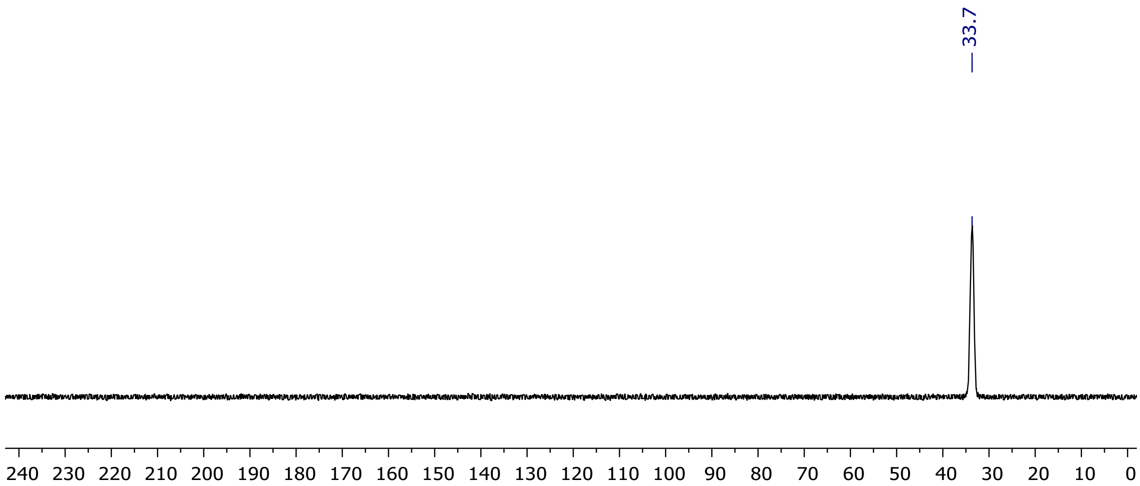

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **4a** ($CDCl_3$, 162 MHz).

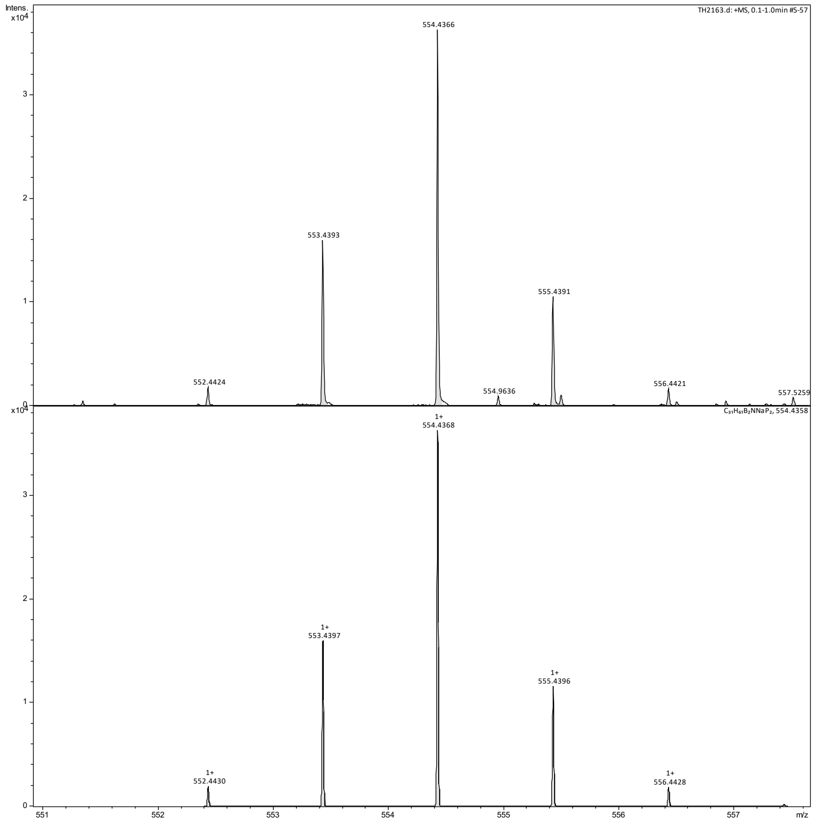

Figure S13. HR ESI-MS of **4a**.

1.5. Intermediate 4b

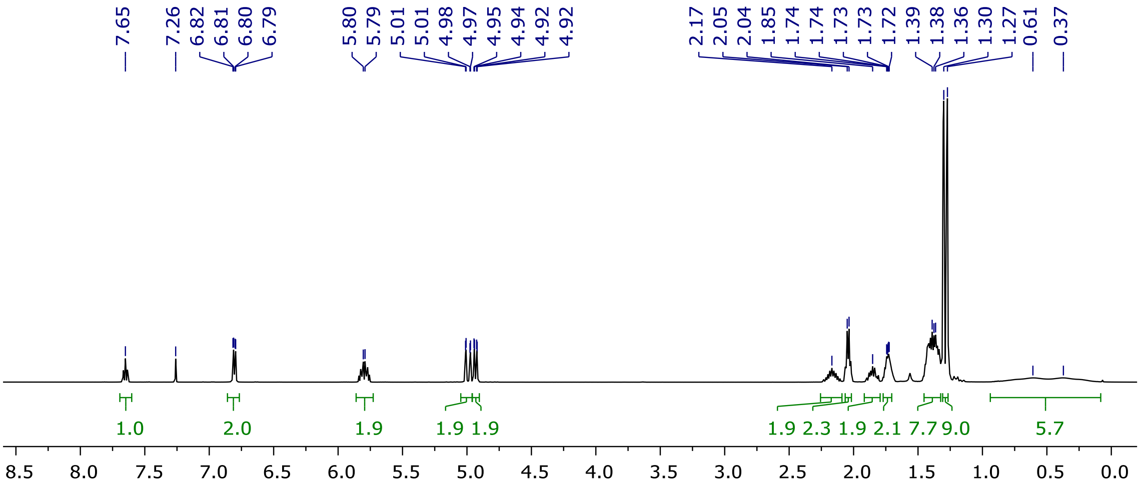

Figure S14. ^{1}H NMR spectrum of **4b** ($CDCl_3$, 500 MHz).

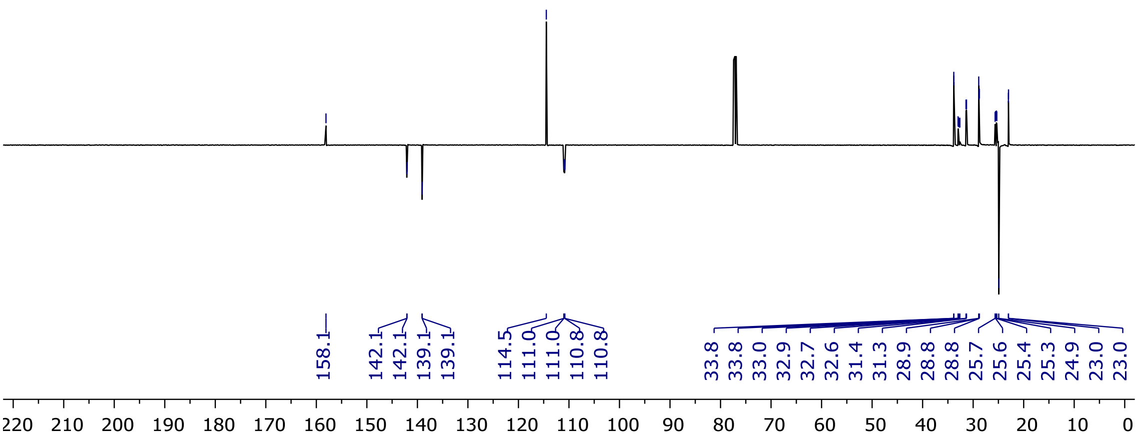

Figure S15. ^{13}C{^{1}H} APT NMR spectrum of **4b** ($CDCl_3$, 126 MHz).

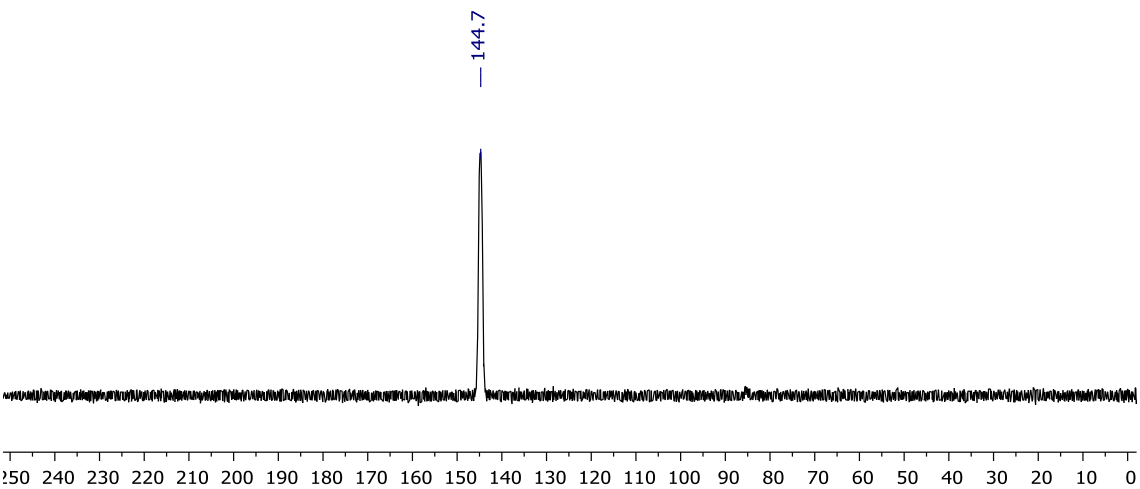

Figure S16. ^{31}P{^{1}H} NMR spectrum of **4b** ($CDCl_3$, 162 MHz).

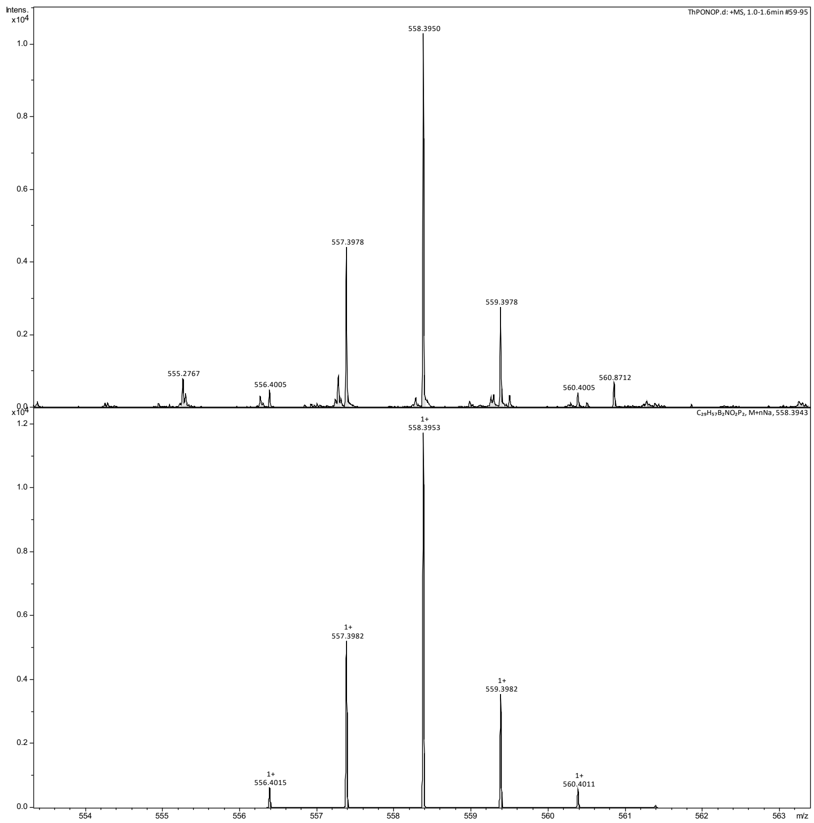

Figure S17. HR ESI-MS of **4b**.

1.6. Intermediate *cis*-5a

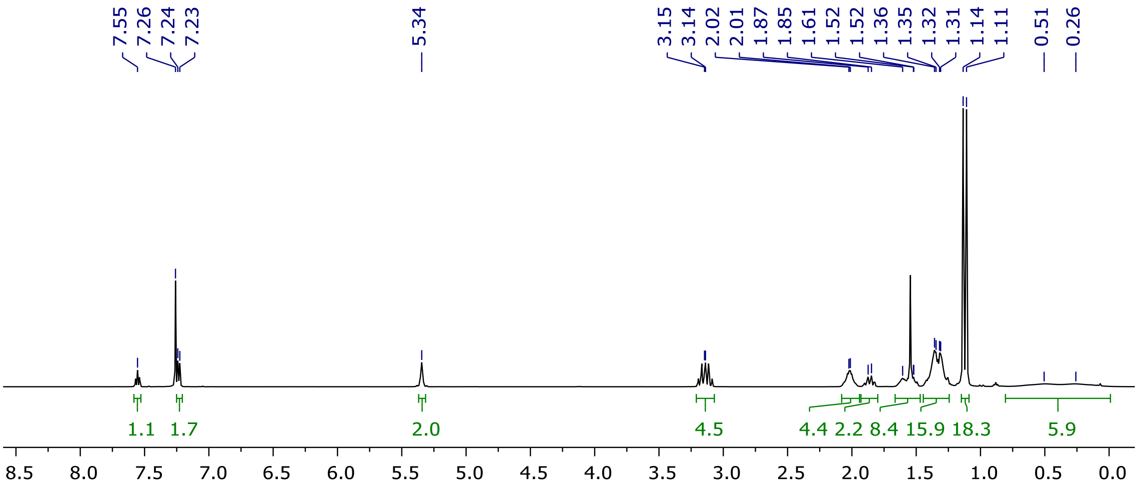

Figure S18. ^{1}H NMR spectrum of *cis*-**5a** ($CDCl_3$, 500 MHz).

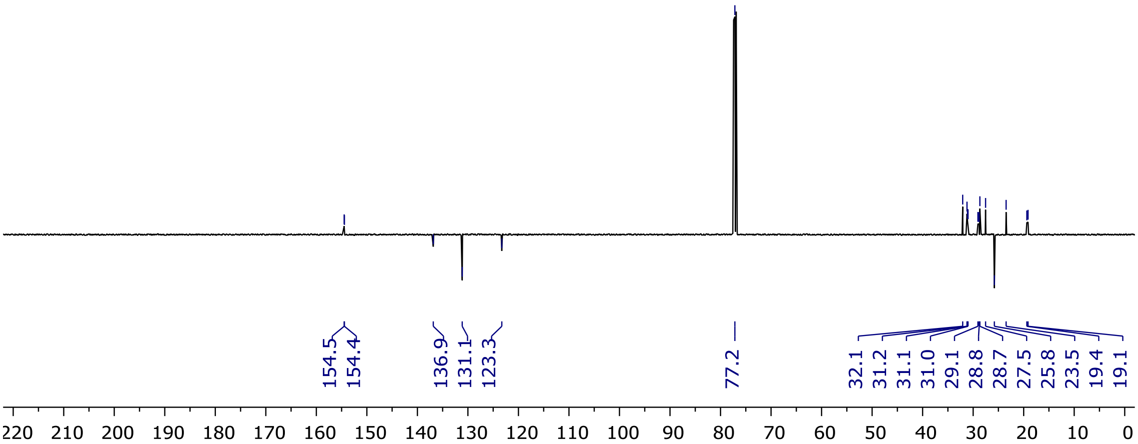

Figure S19. $^{13}C\{^{1}H\}$ APT NMR spectrum of *cis*-**5a** ($CDCl_3$, 126 MHz).

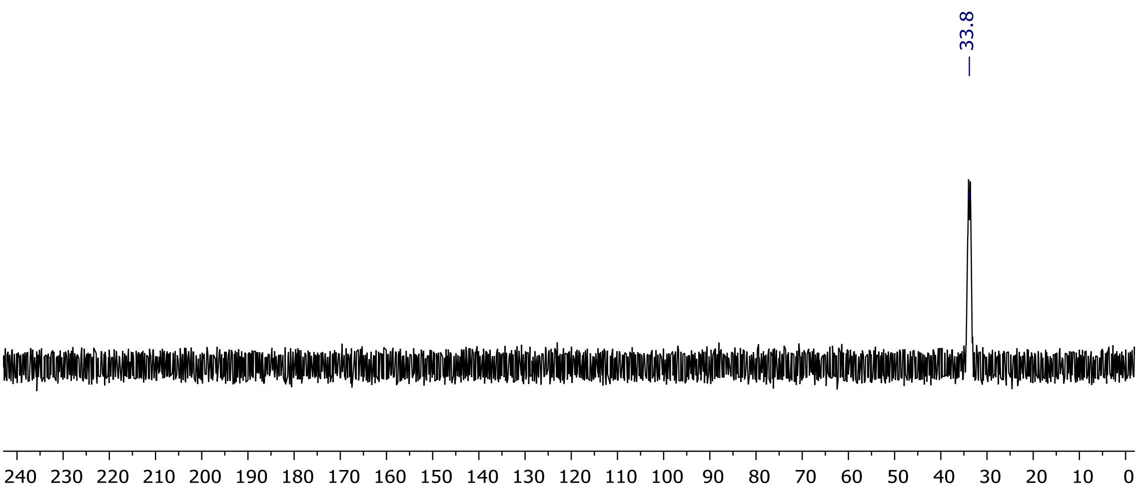

Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**5a** ($CDCl_3$, 162 MHz).

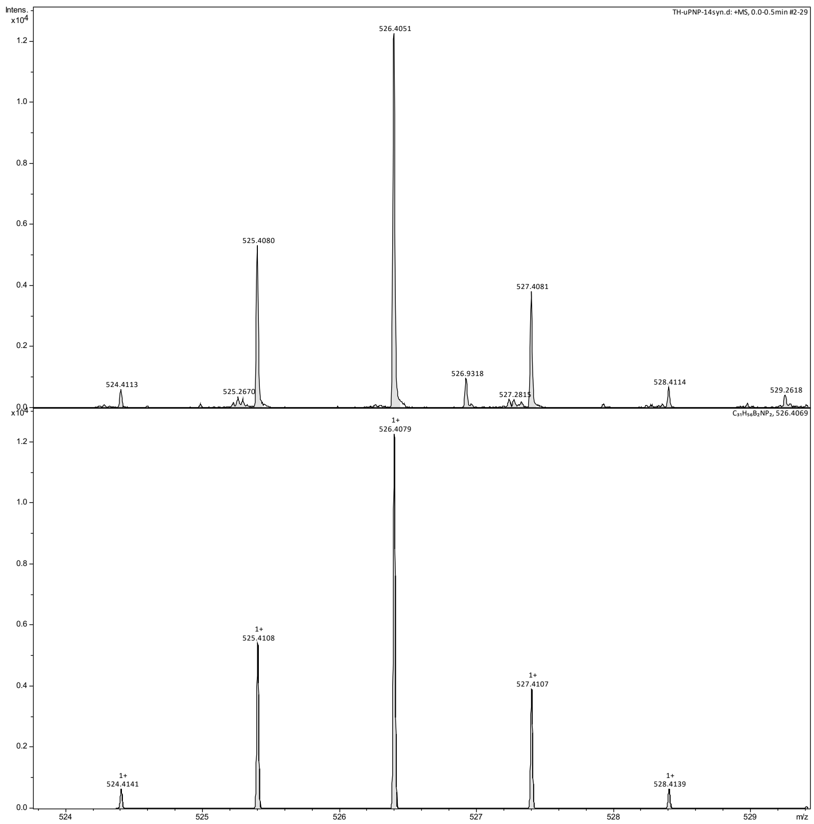

Figure S21. HR ESI-MS of *cis*-**5a**.

1.7. Intermediate *trans*-5a

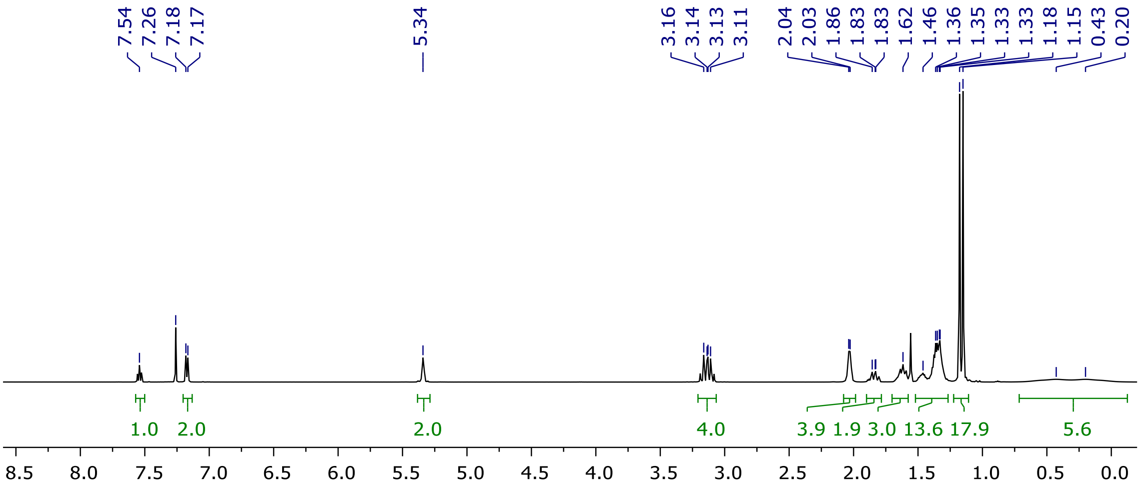

Figure S22. ^{1}H NMR spectrum of *trans*-**5a** ($CDCl_3$, 500 MHz).

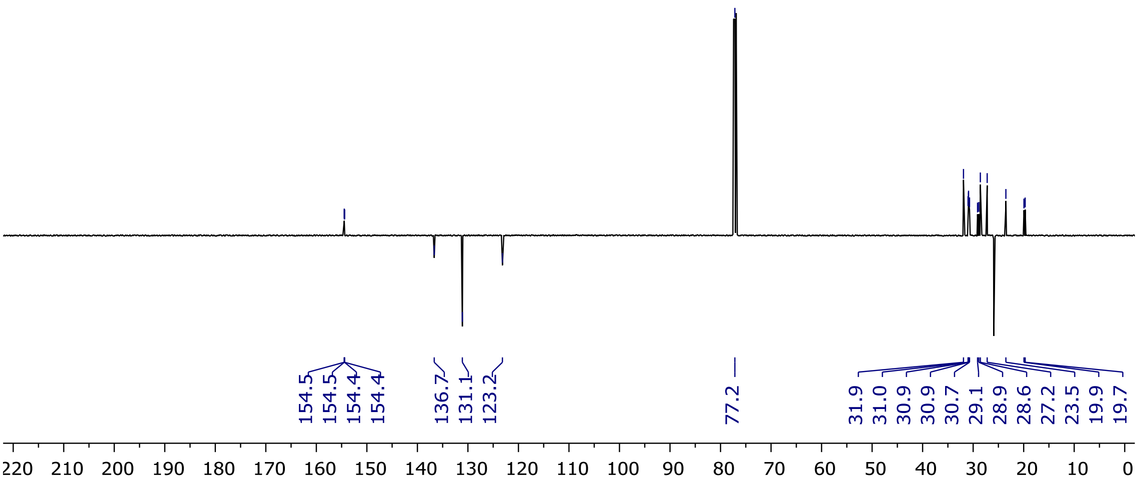

Figure S23. $^{13}C\{^{1}H\}$ APT NMR spectrum of *trans*-**5a** ($CDCl_3$, 126 MHz).

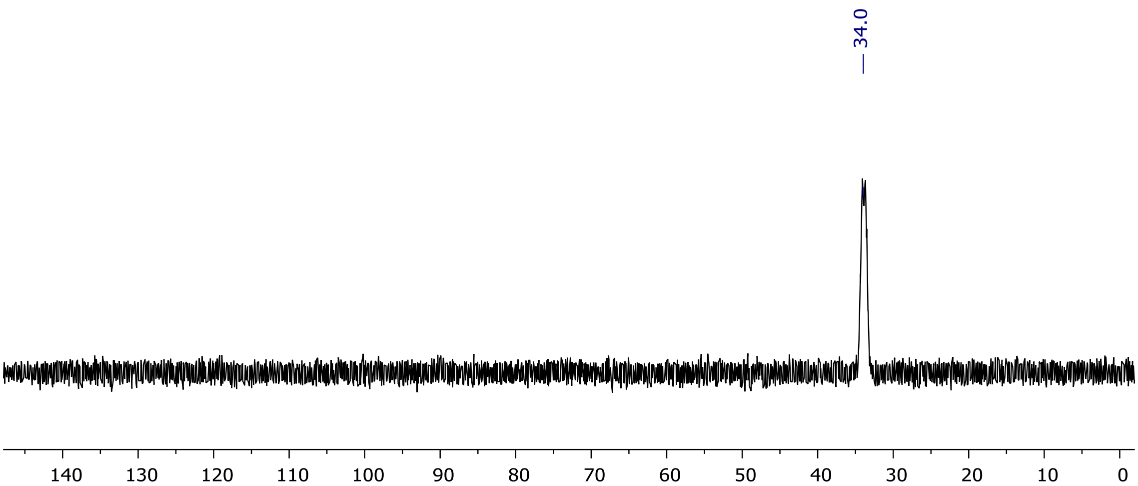

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**5a** ($CDCl_3$, 162 MHz).

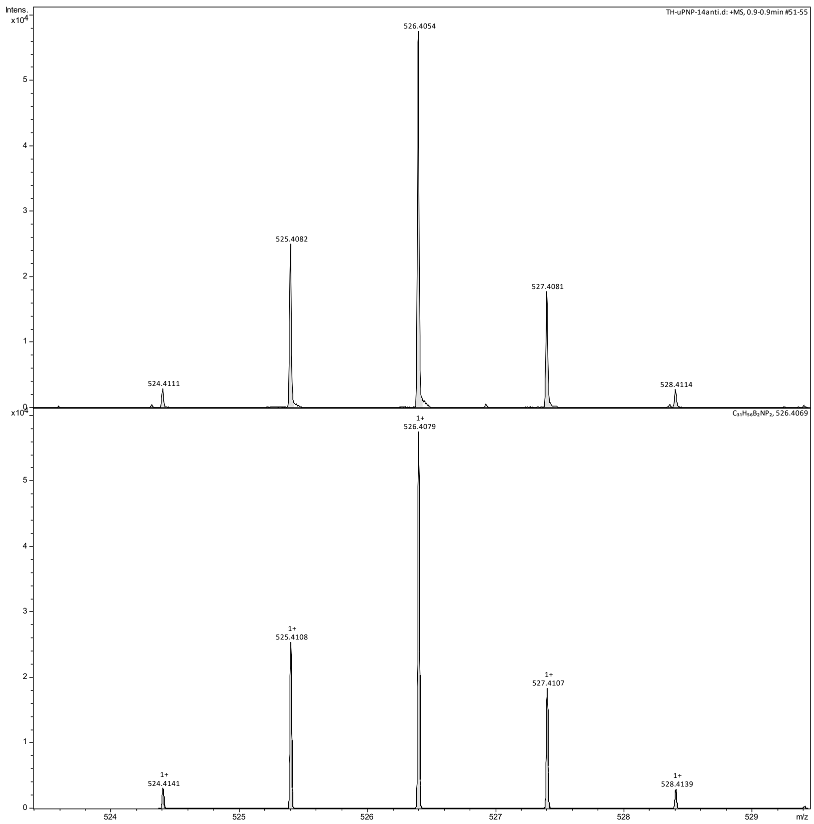

Figure S25. HR ESI-MS of *trans*-**5a**.

1.8. Intermediate *cis*-5b

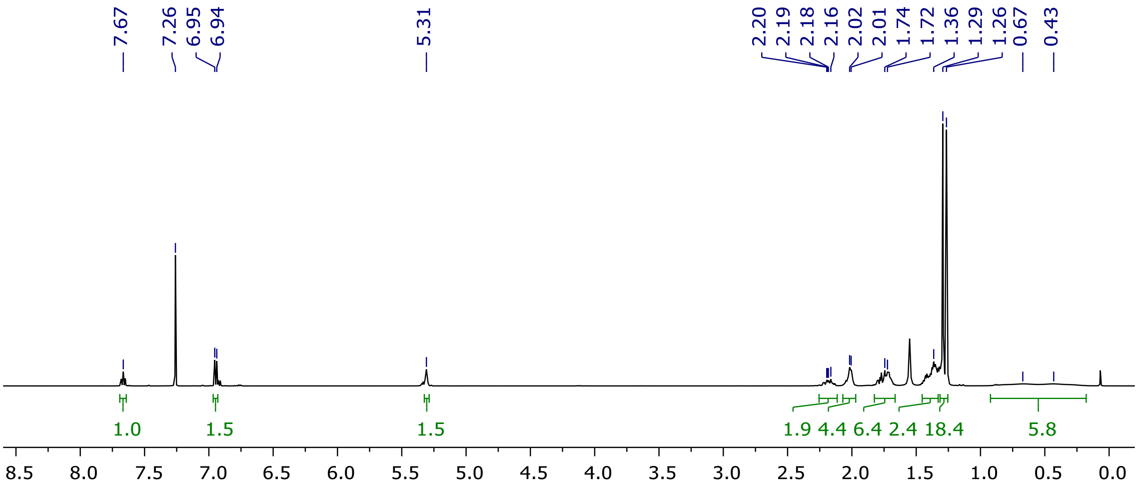

Figure S26. ^{1}H NMR spectrum of *cis*-**5b** ($CDCl_3$, 500 MHz).

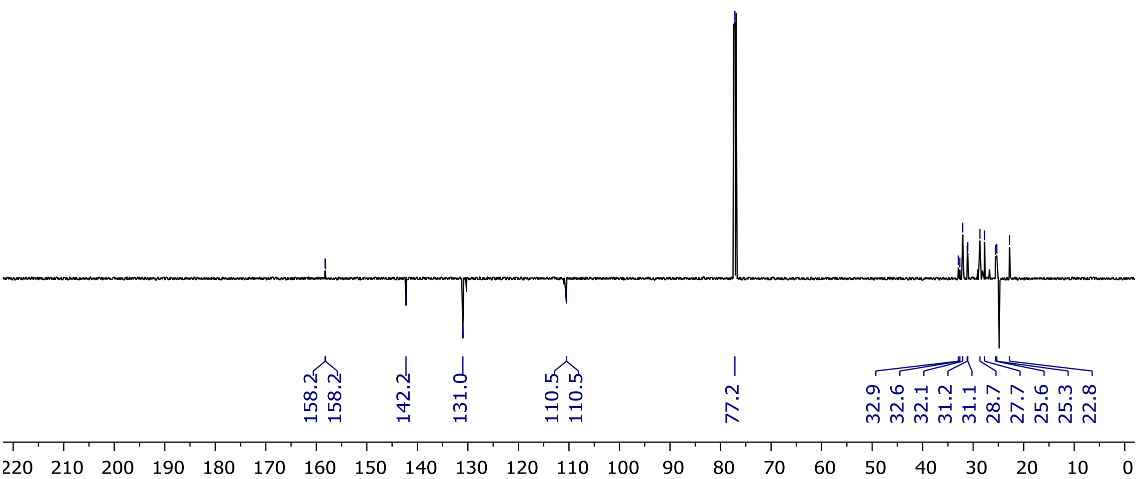

Figure S27. $^{13}C\{^{1}H\}$ APT NMR spectrum of *cis*-**5b** ($CDCl_3$, 126 MHz).

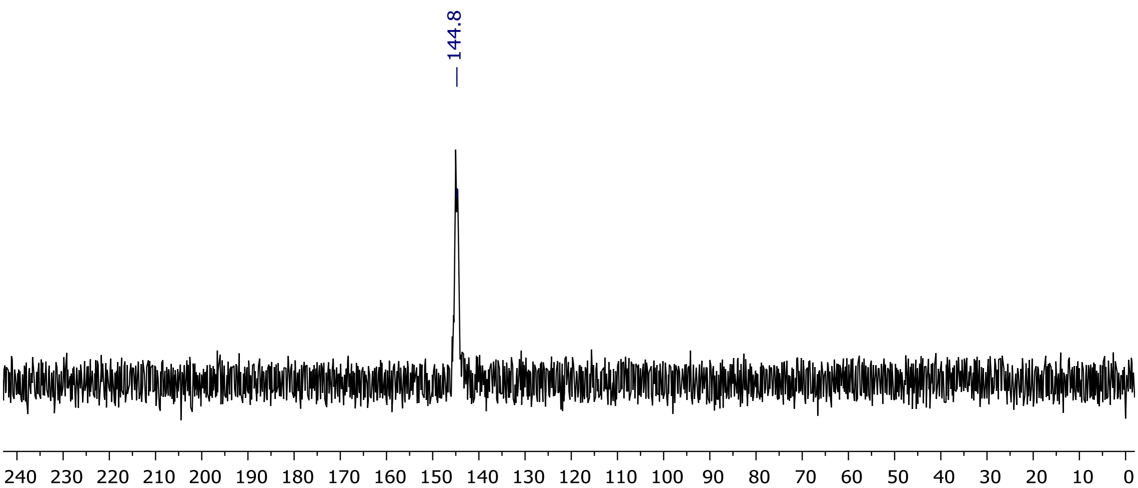

Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**5b** ($CDCl_3$, 162 MHz).

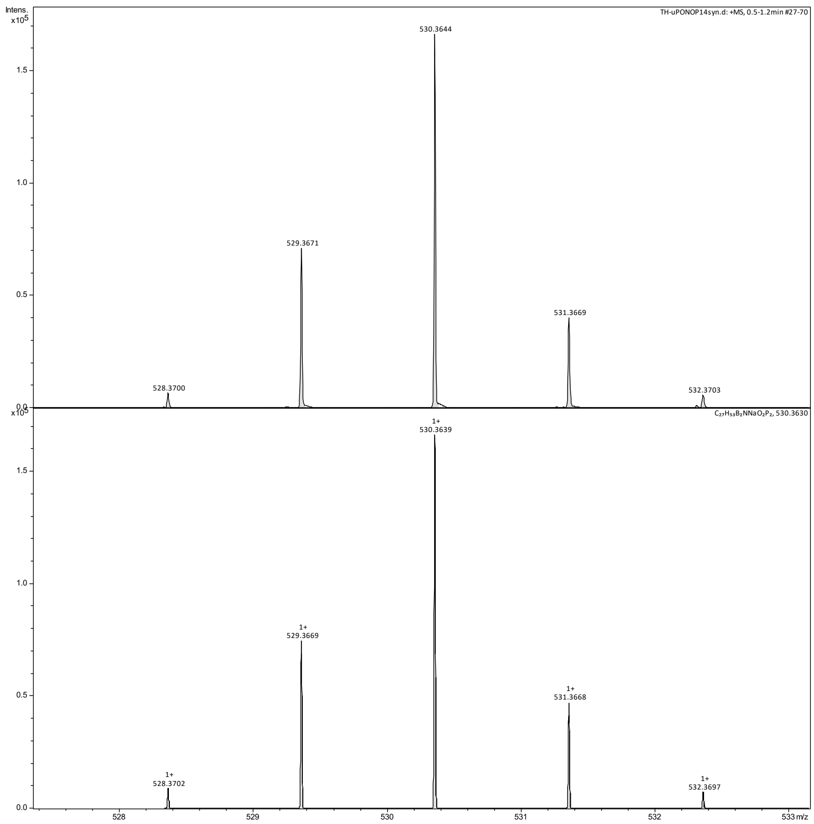

Figure S29. HR ESI-MS of *cis*-**5b**.

1.9. Intermediate *trans*-5b

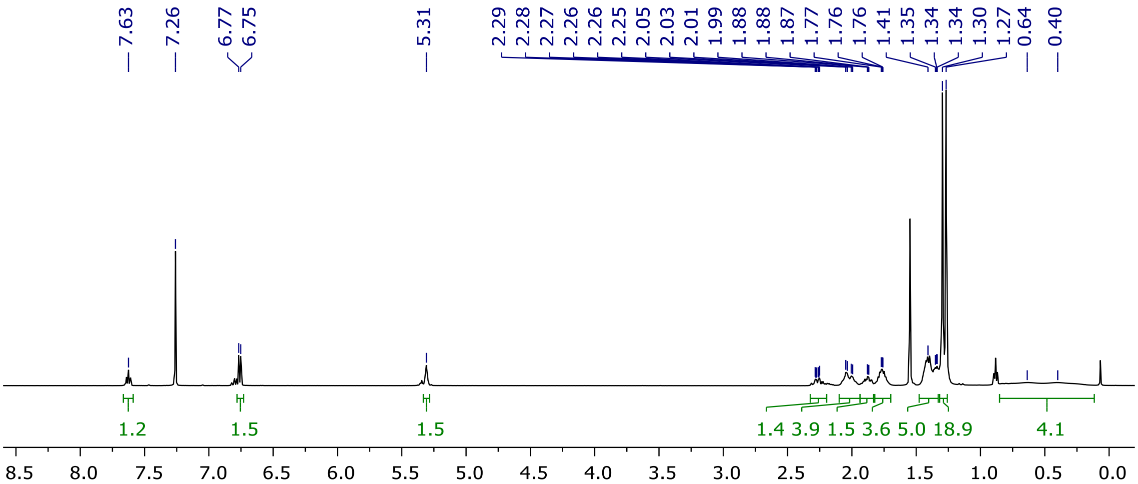

Figure S30. ^{1}H NMR spectrum of *trans*-**5b** ($CDCl_3$, 500 MHz).

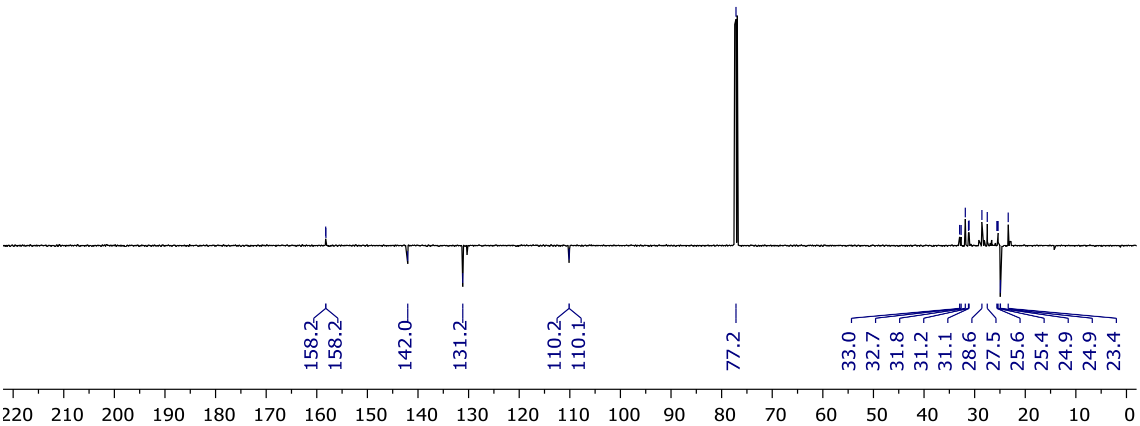

Figure S31. $^{13}C\{^{1}H\}$ APT NMR spectrum of *trans*-**5b** ($CDCl_3$, 126 MHz).

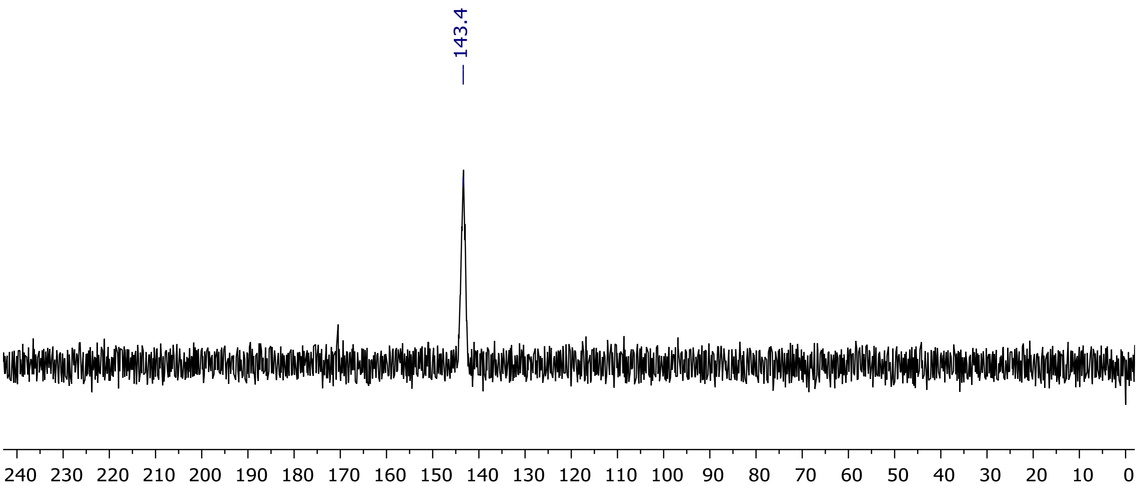

Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**5b** ($CDCl_3$, 162 MHz).

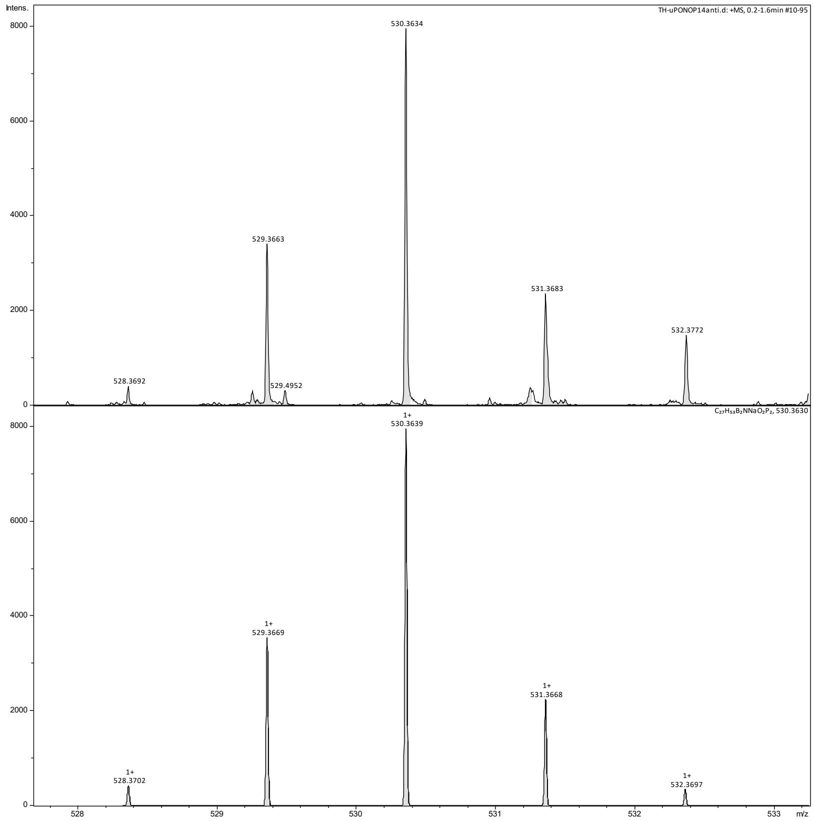

Figure S33. HR ESI-MS of *trans*-**5b**.

1.10. Borane protected ligand isomer *cis*-1a

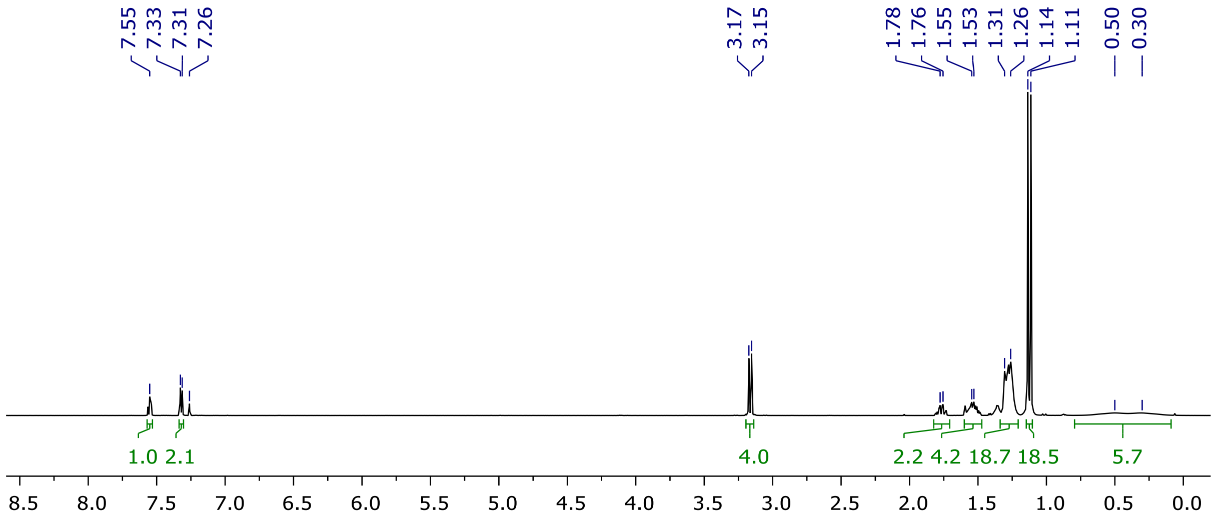

Figure S34. ^{1}H NMR spectrum of *cis*-**1a** ($CDCl_3$, 600 MHz).

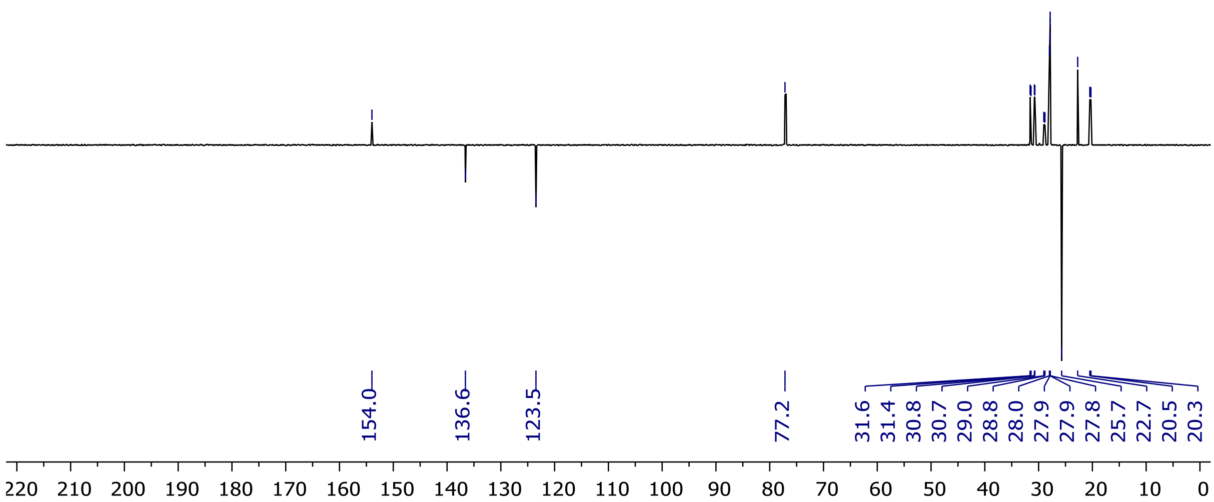

Figure S35. $^{13}C\{^{1}H\}$ APT NMR spectrum of *cis*-**1a** ($CDCl_3$, 151 MHz).

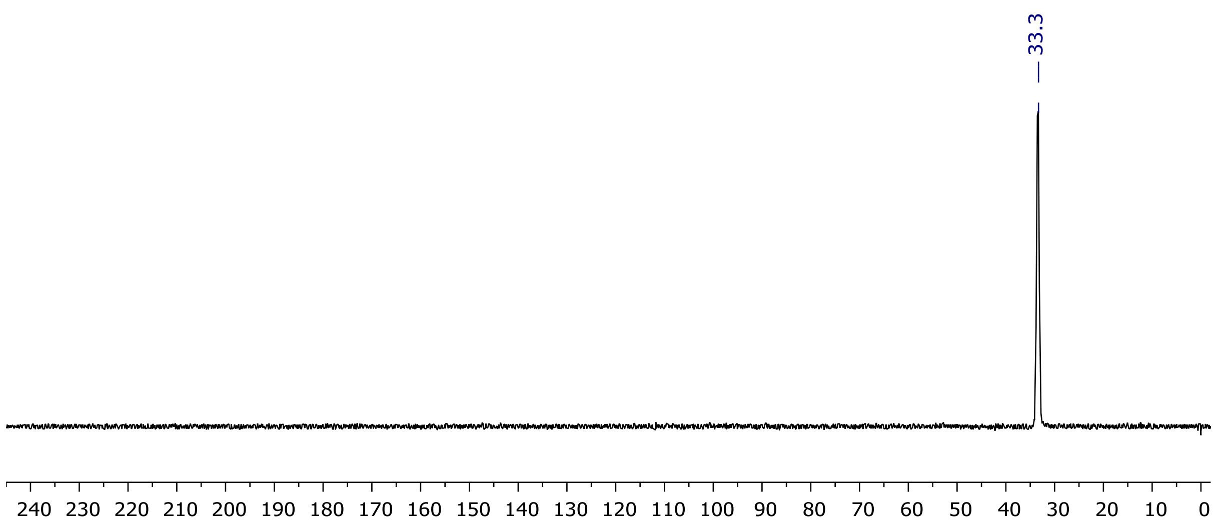

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**1a** ($CDCl_3$, 243 MHz).

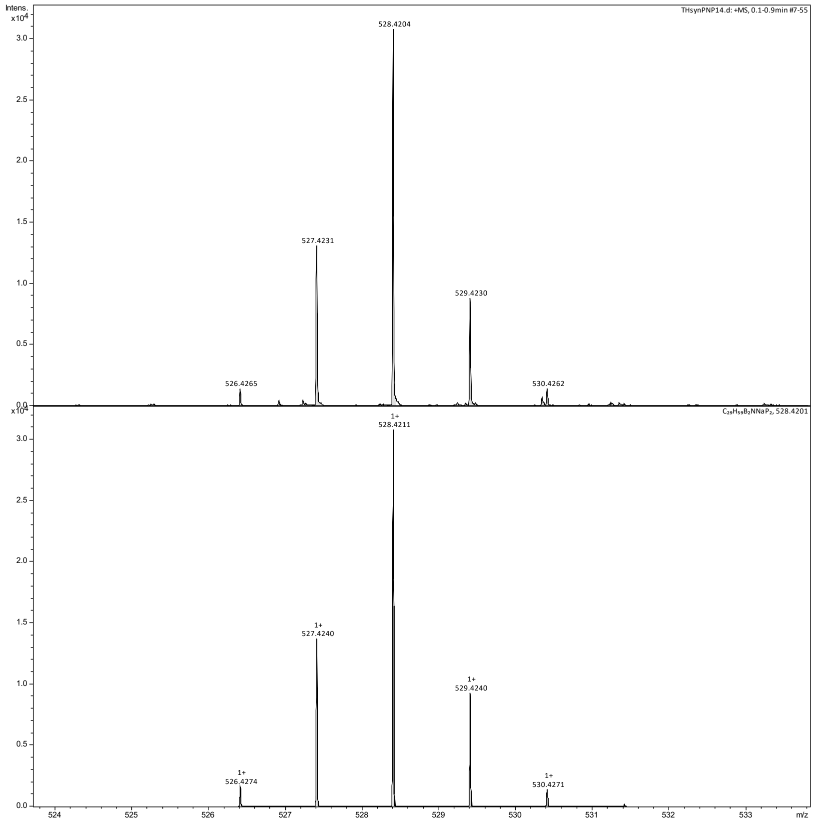

Figure S37. HR ESI-MS of *cis*-**1a**.

1.11. Borane protected ligand *trans*-1a

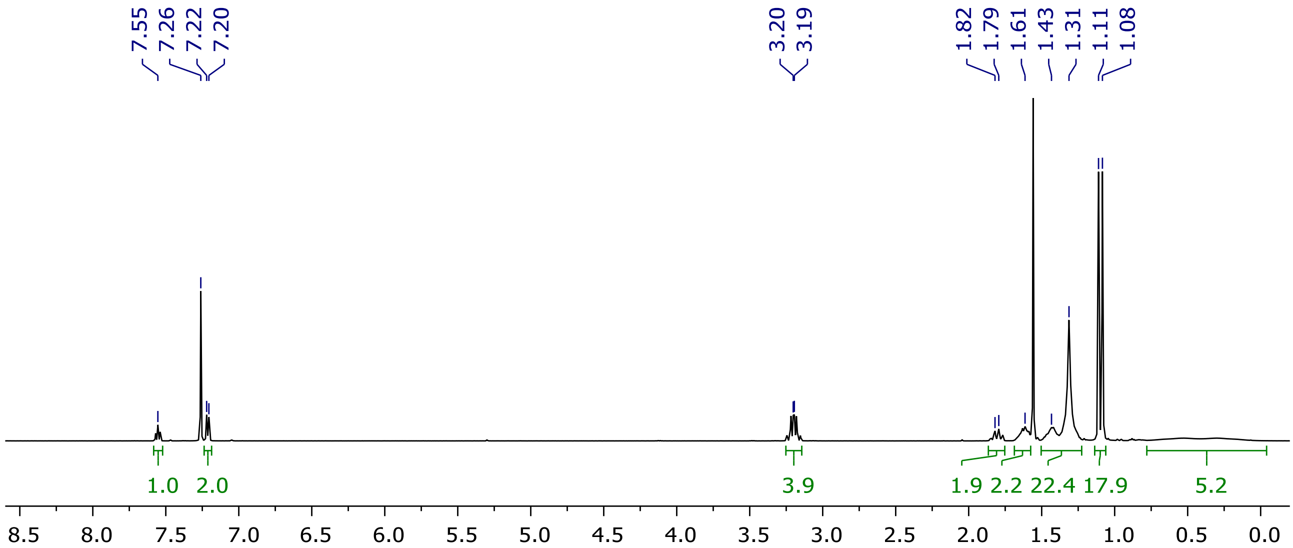

Figure S38. ^{1}H NMR spectrum of *trans*-**1a** ($CDCl_3$, 500 MHz).

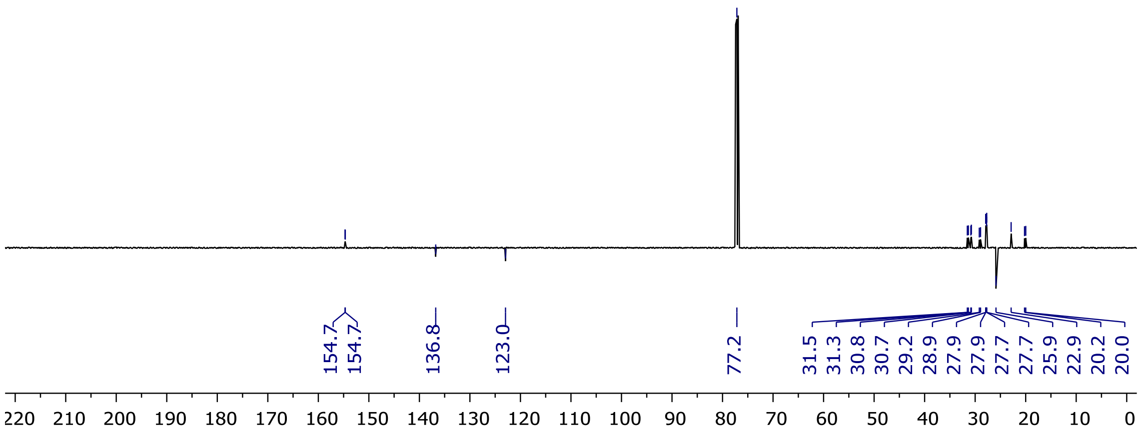

Figure S39. $^{13}C\{^{1}H\}$ APT NMR spectrum of *trans*-**1a** ($CDCl_3$, 126 MHz).

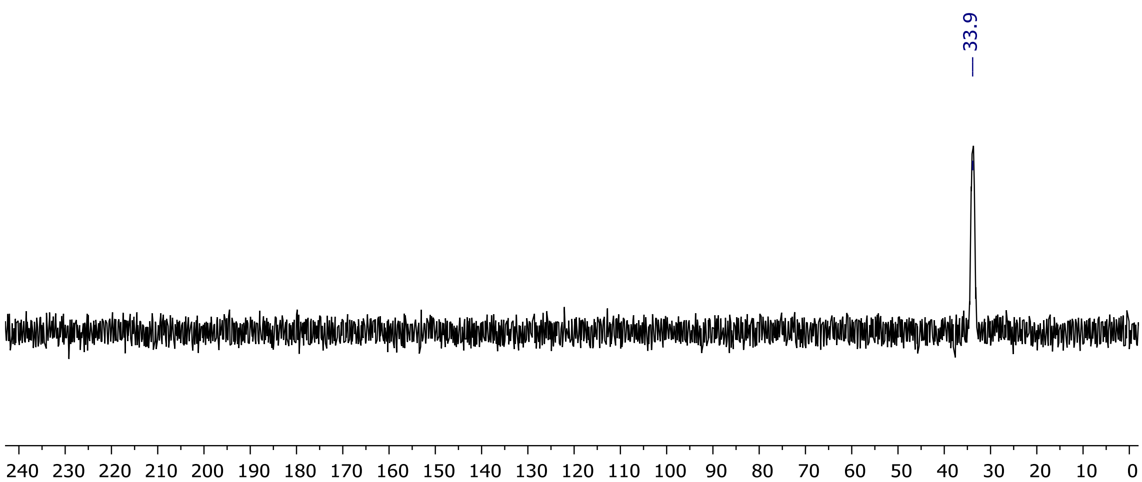

Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**1a** ($CDCl_3$, 162 MHz).

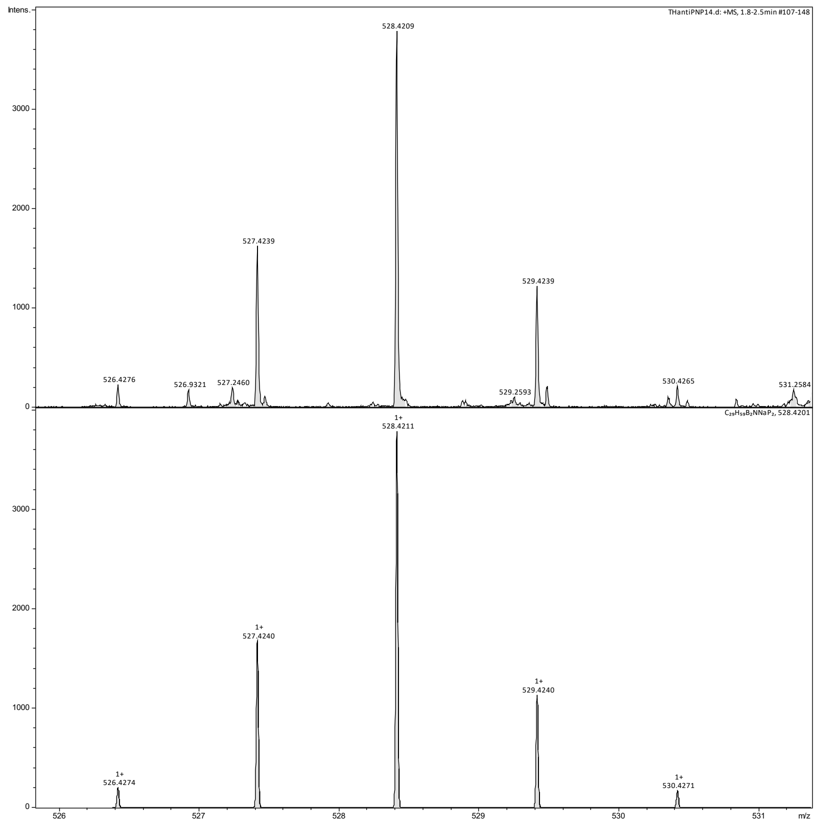

Figure S41. HR ESI of *trans*-**1a**.

1.12. Borane protected ligand isomer *cis*-1b

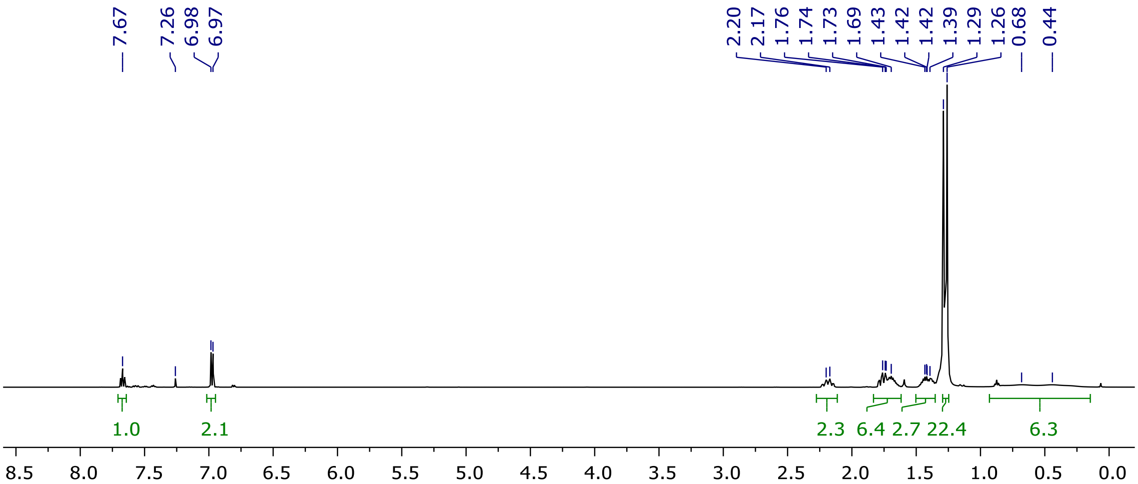

Figure S42. ^{1}H NMR spectrum of *cis*-**1b** ($CDCl_3$, 500 MHz).

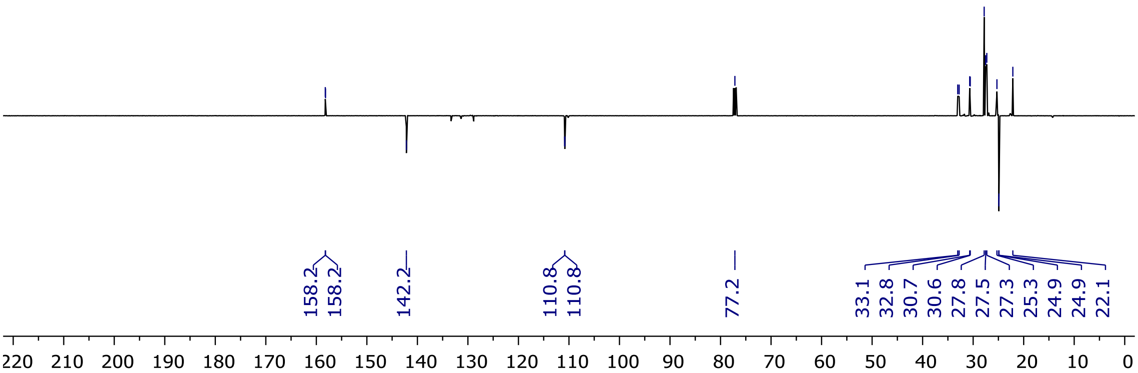

Figure S43. $^{13}C\{^{1}H\}$ APT NMR spectrum of *cis*-**1b** ($CDCl_3$, 126 MHz).

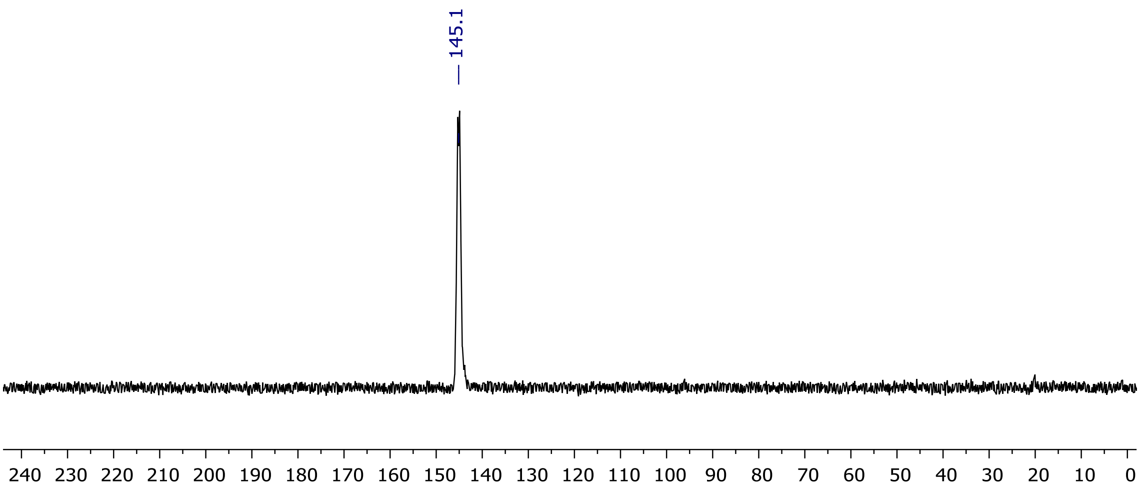

Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**1b** ($CDCl_3$, 162 MHz).

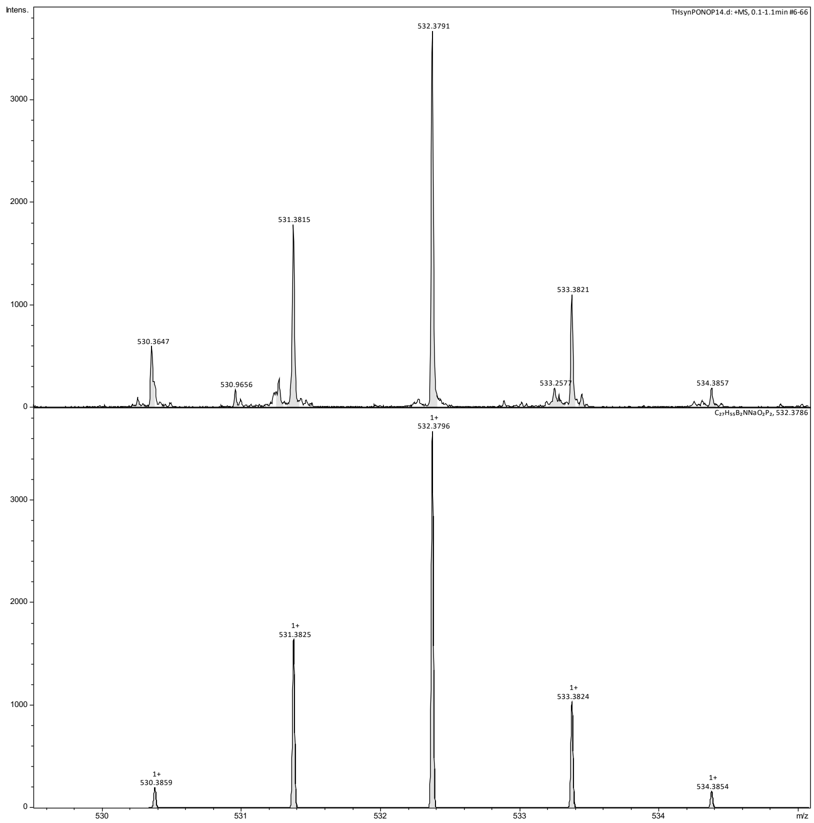

Figure S45. HR ESI-MS of *cis*-**1b**.

1.13. Borane protected ligand *trans*-1a

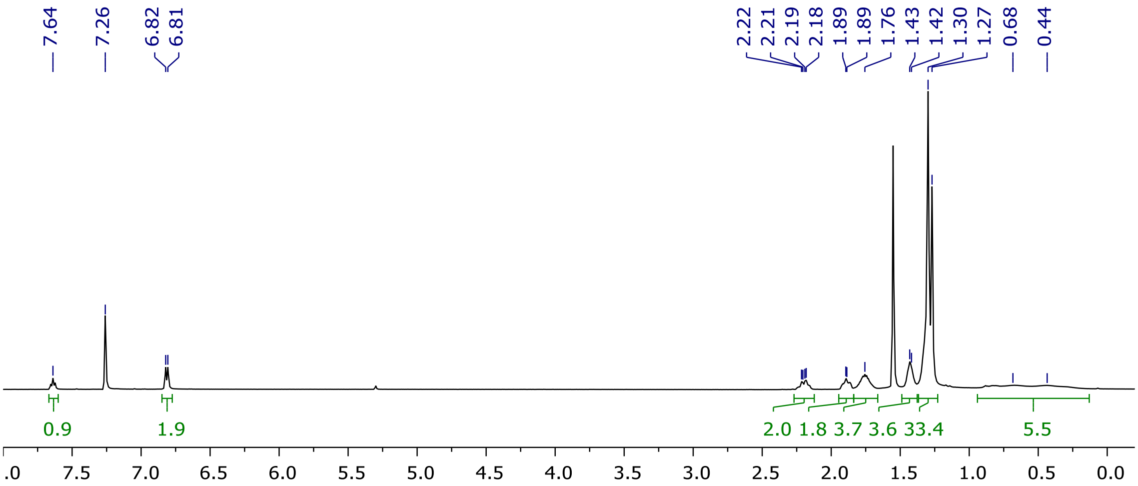

Figure S46. ^{1}H NMR spectrum of *trans*-**1b** ($CDCl_3$, 500 MHz).

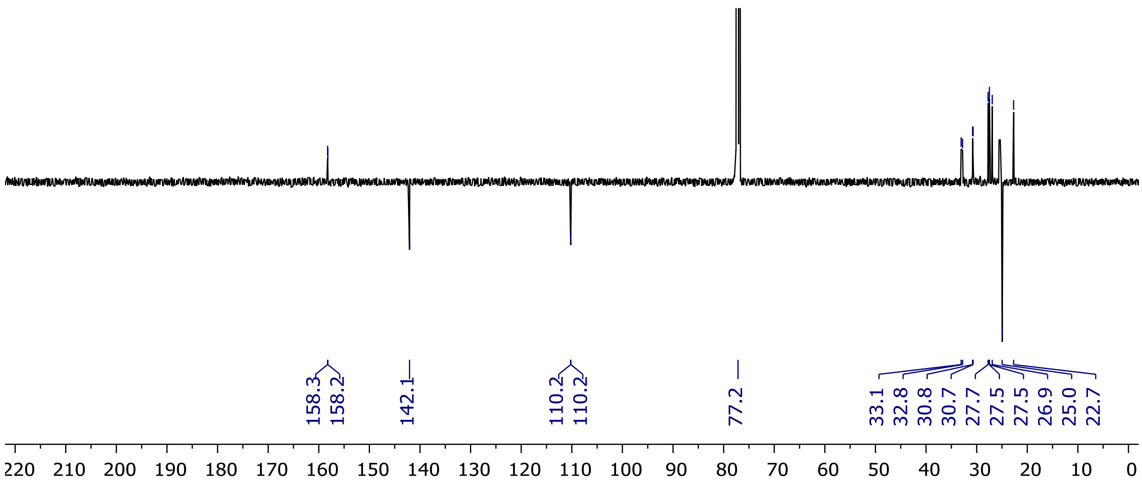

Figure S47. $^{13}C\{^{1}H\}$ APT NMR spectrum of *trans*-**1b** ($CDCl_3$, 126 MHz).

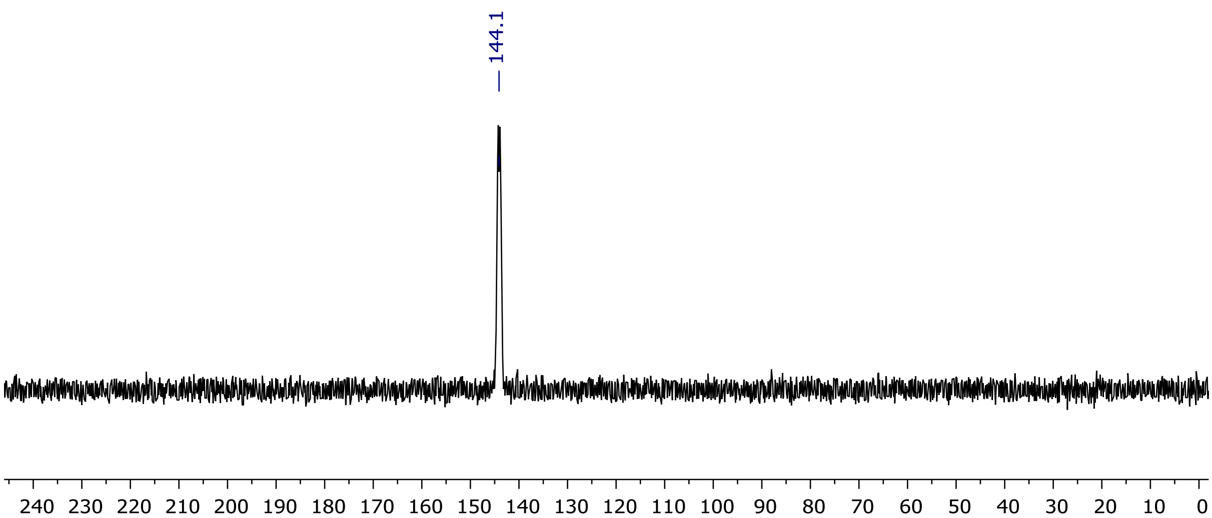

Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**1b** ($CDCl_3$, 162 MHz).

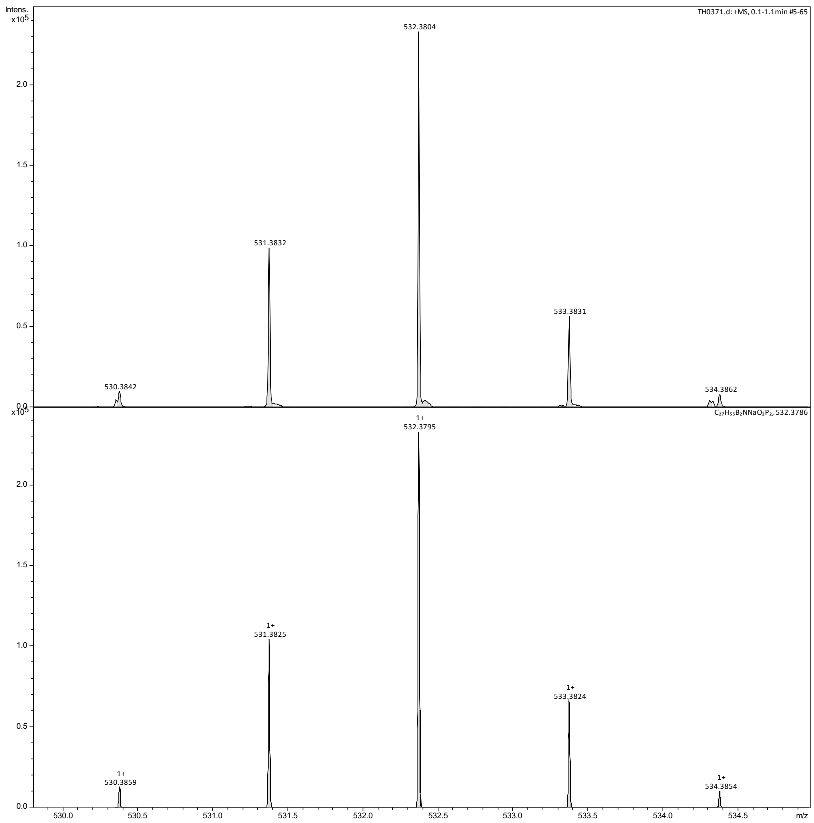

Figure S49. HR ESI-MS of *trans*-**1b**.

1.14. Isolated PNP-14

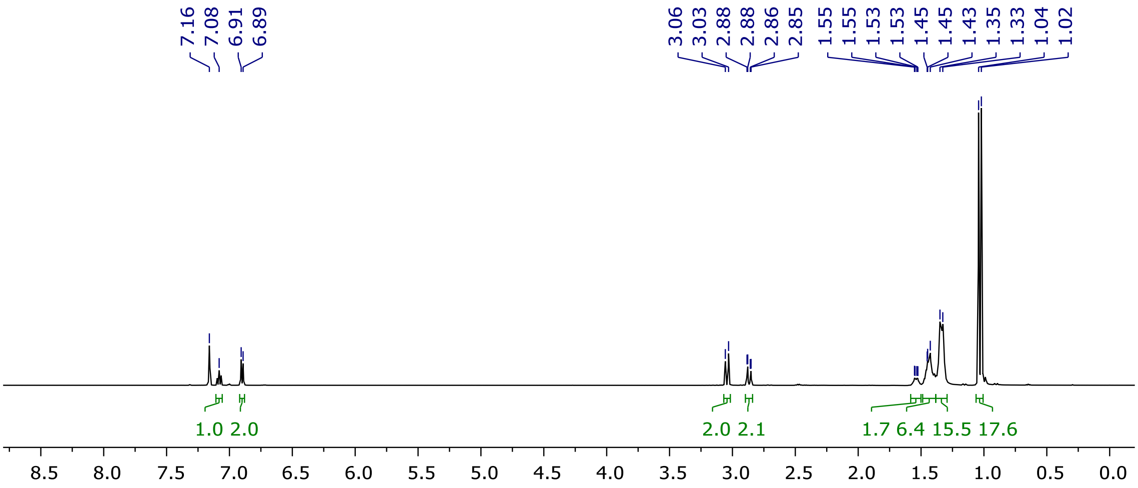

Figure S50. ^{1}H NMR spectrum of PNP-14 (C_6D_6, 500 MHz).

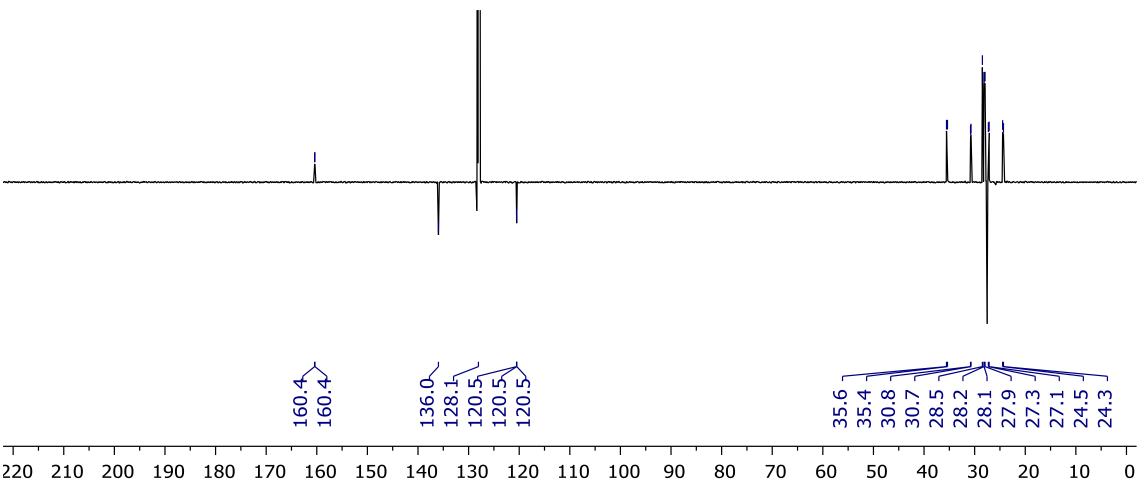

Figure S51. $^{13}C\{^{1}H\}$ APT NMR spectrum of PNP-14 (C_6D_6, 126 MHz).

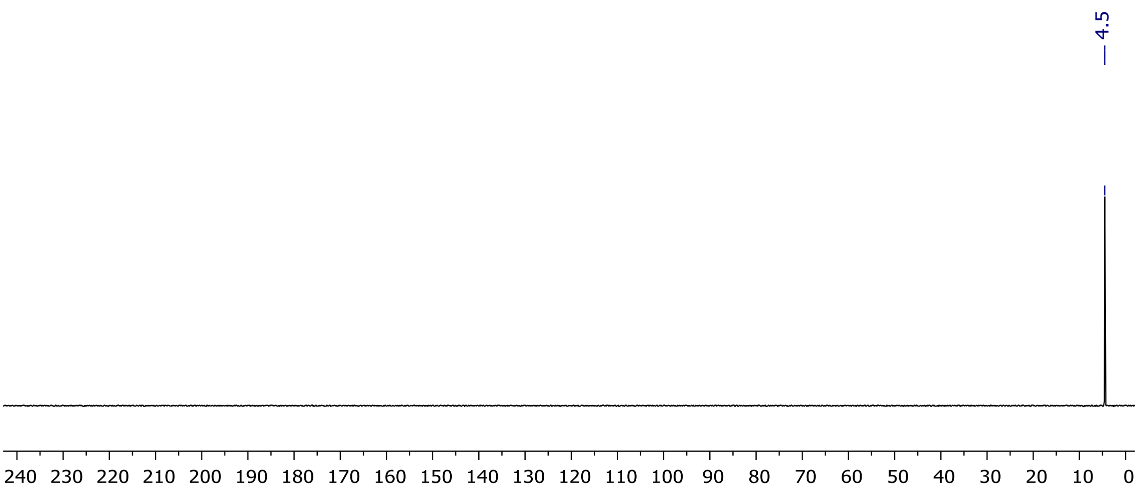

Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum of PNP-14 (C_6D_6, 162 MHz).

1.15. In situ generated PONOP-14

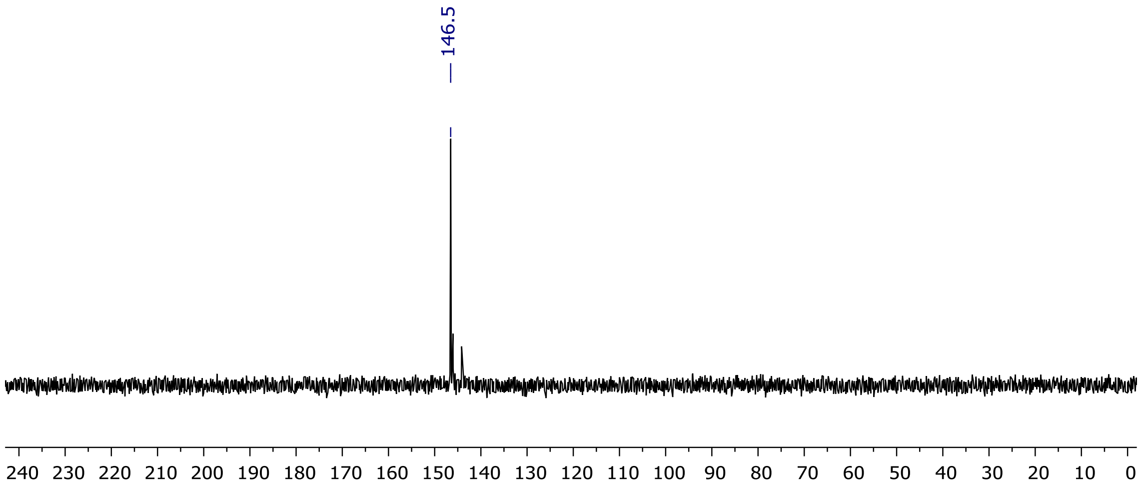

Figure S53. $^{31}P\{^1H\}$ NMR spectrum of PONOP-14 (THF:Et_2NH, 162 MHz).

1.16. [Rh(PNP-14)(biph)][BAr$^F{}_4$] (6a)

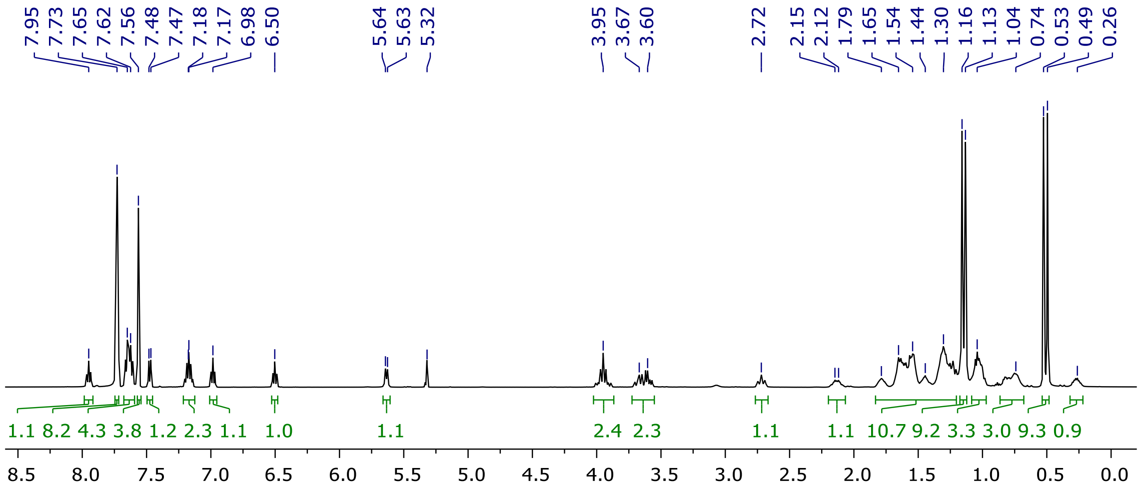

Figure S54. ^1H NMR spectrum of **6a** (CD_2Cl_2, 500 MHz).

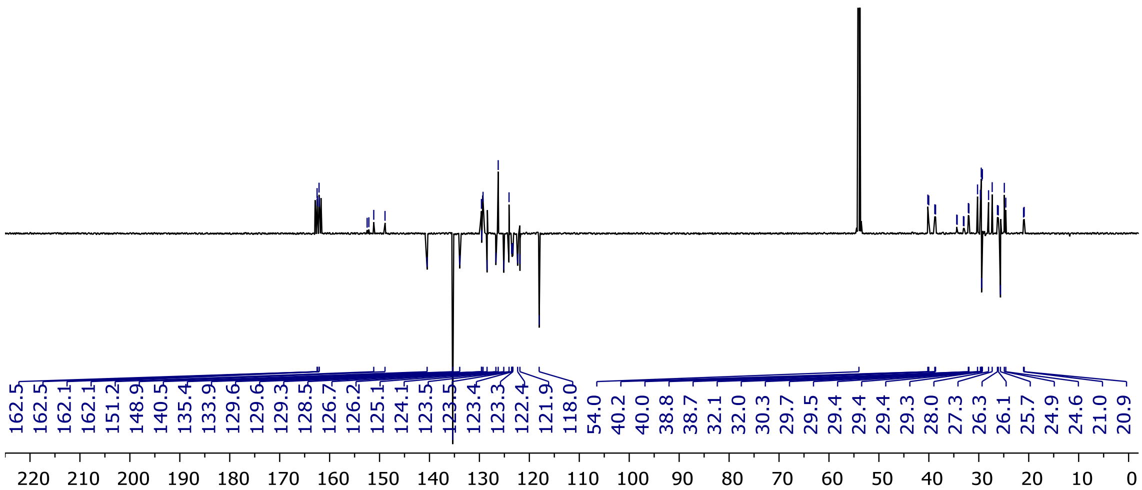

Figure S55. $^{13}C\{^1H\}$ APT NMR spectrum of **6a** (CD_2Cl_2, 126 MHz).

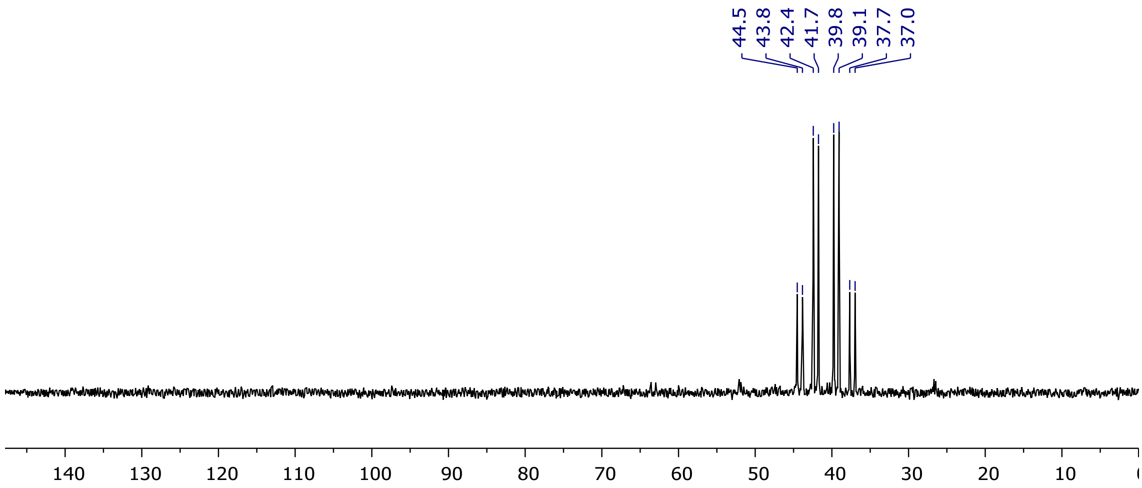

Figure S56. $^{31}P\{^{1}H\}$ NMR spectrum of **6a** (CD_2Cl_2, 162 MHz).

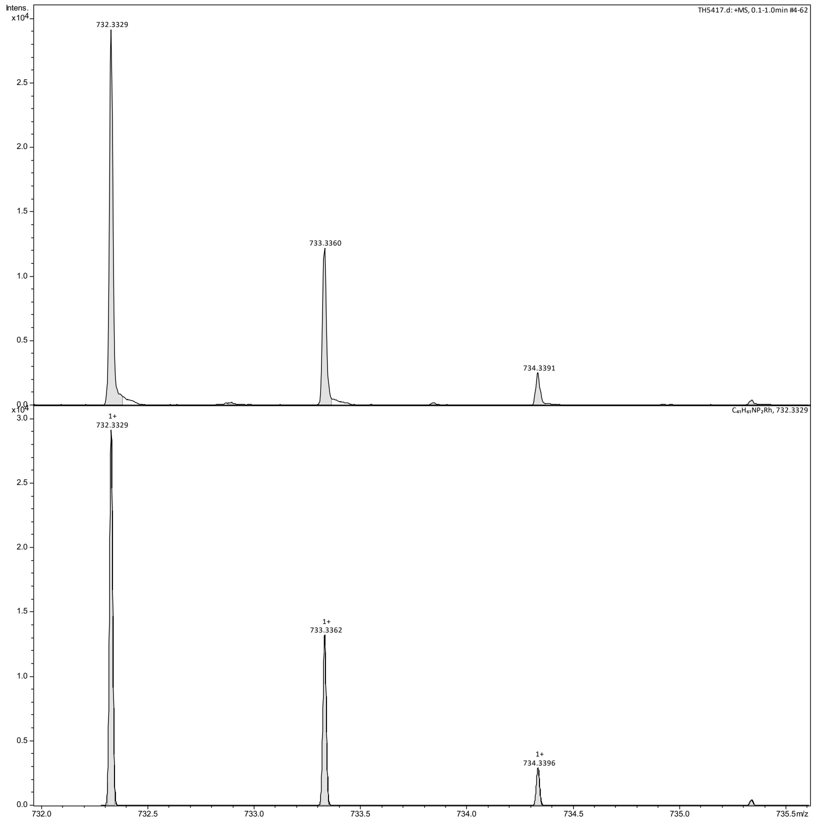

Figure S57. HR ESI-MS of **6a**.

1.17. [Rh(PONOP-14)(biph)][BAr$^F_4$] (6b)

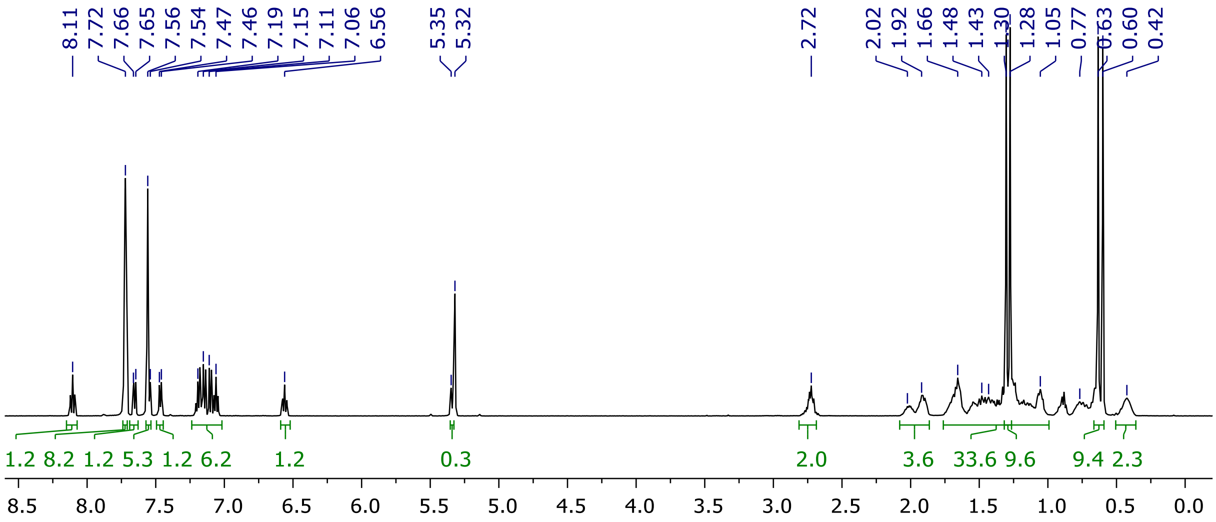

Figure S58. ^{1}H NMR spectrum of **6b** (CD_2Cl_2, 500 MHz).

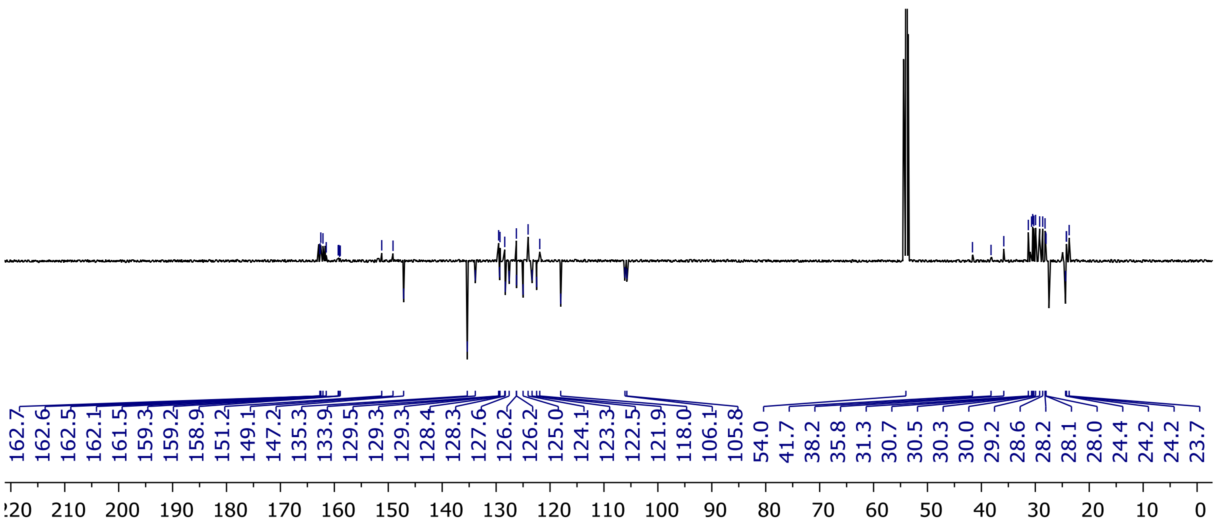

Figure S59. $^{13}C\{^1H\}$ APT NMR spectrum of **6b** (CD_2Cl_2, 126 MHz).

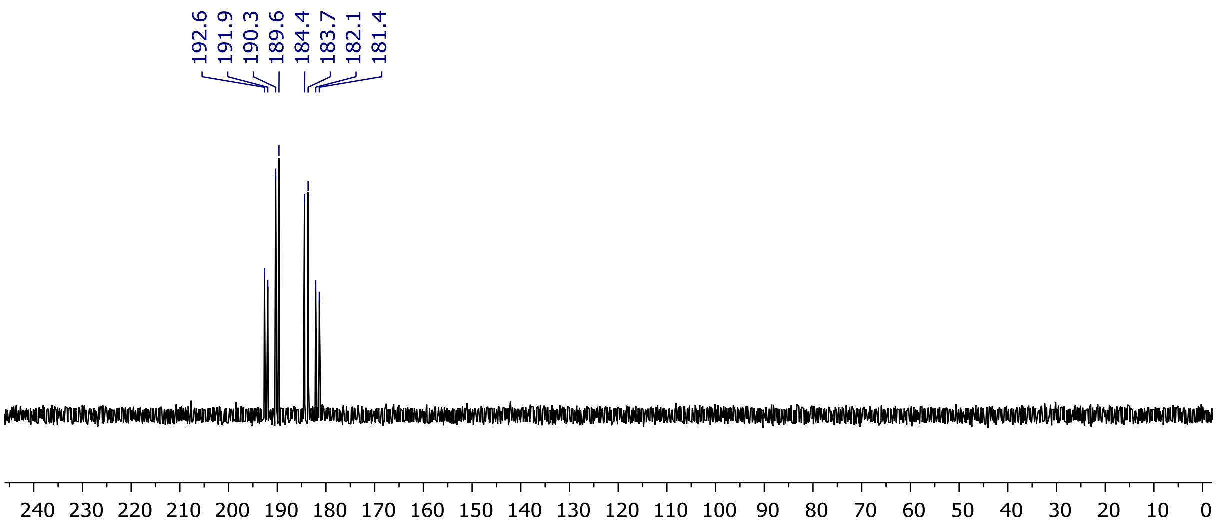

Figure S60. $^{31}P\{^1H\}$ NMR spectrum of **6b** (CD_2Cl_2, 162 MHz).

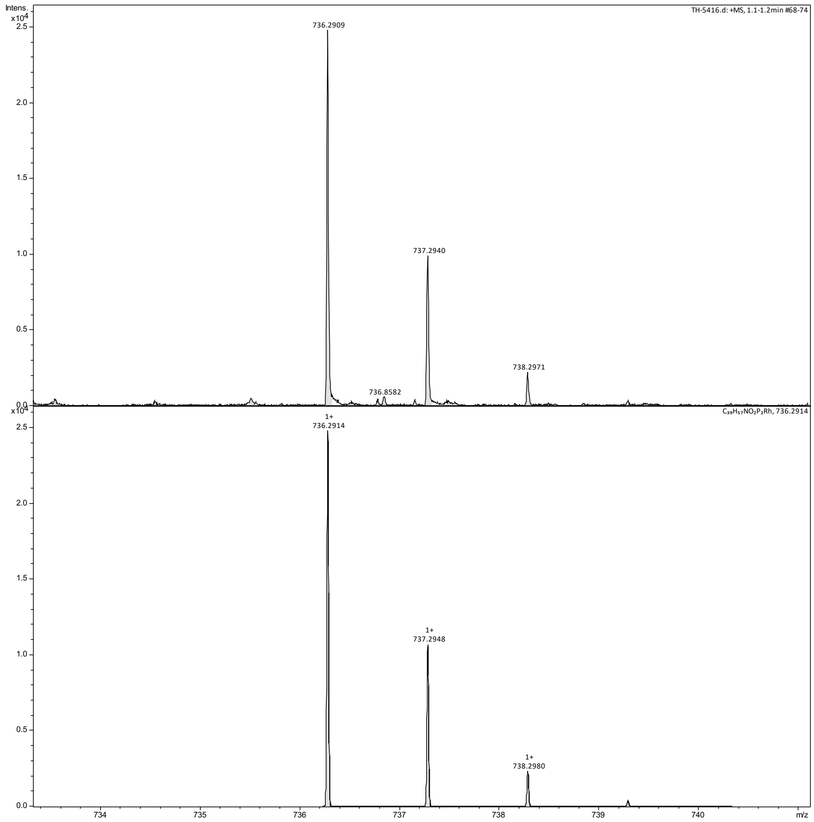

Figure S61. HR ESI-MS of **6b**.

1.18. [Rh(PNP-14)(H_2)][BAr$^F{}_4$] (7a)

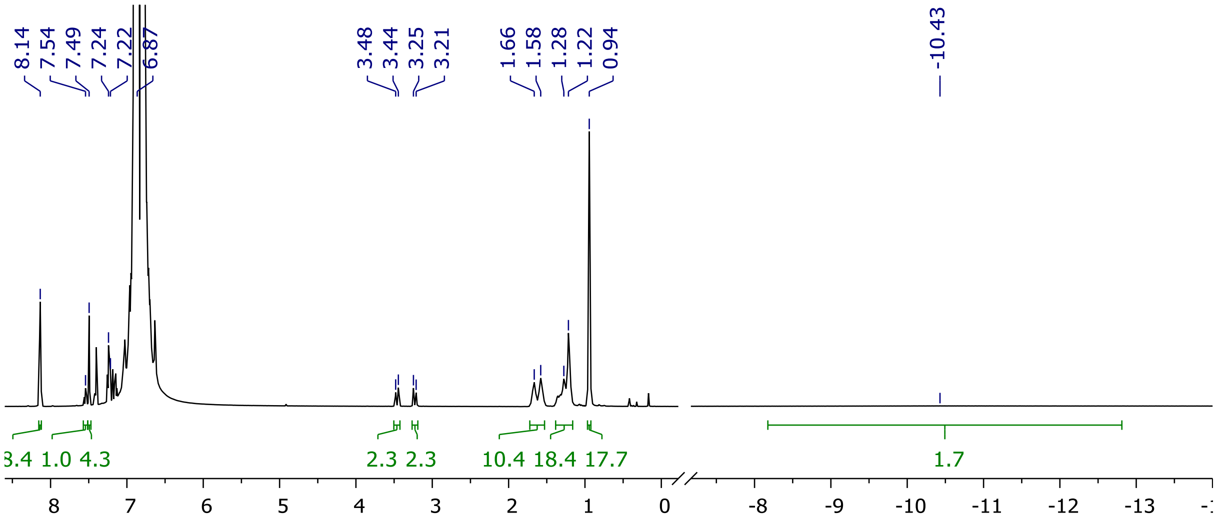

Figure S62. ^{1}H NMR spectrum of **7a** (DFB, 500 MHz).

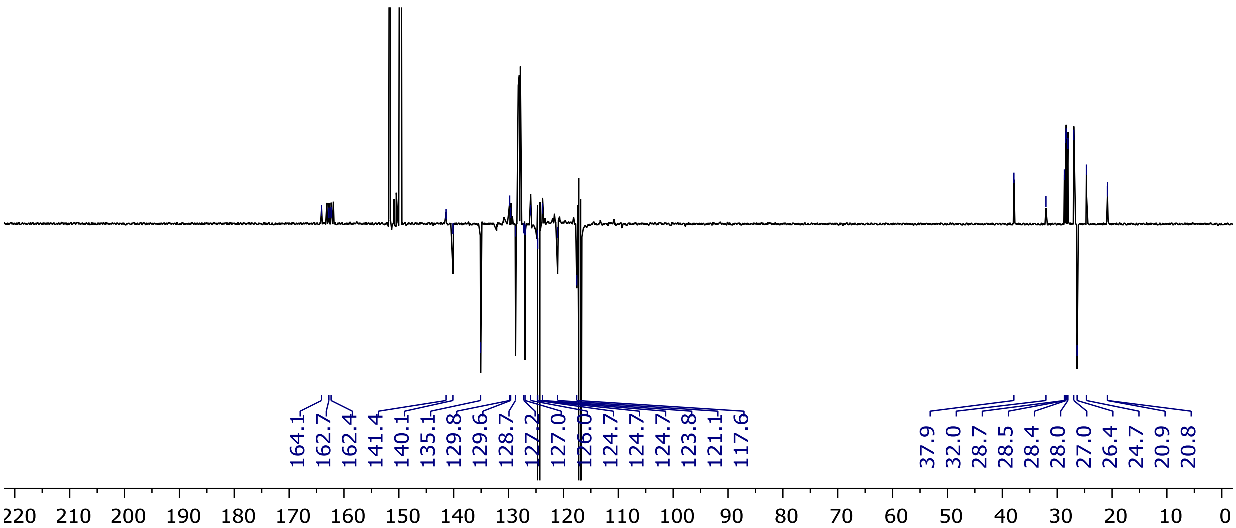

Figure S63. ^{13}C{^{1}H} APT NMR spectrum of **7a** (DFB, 126 MHz).

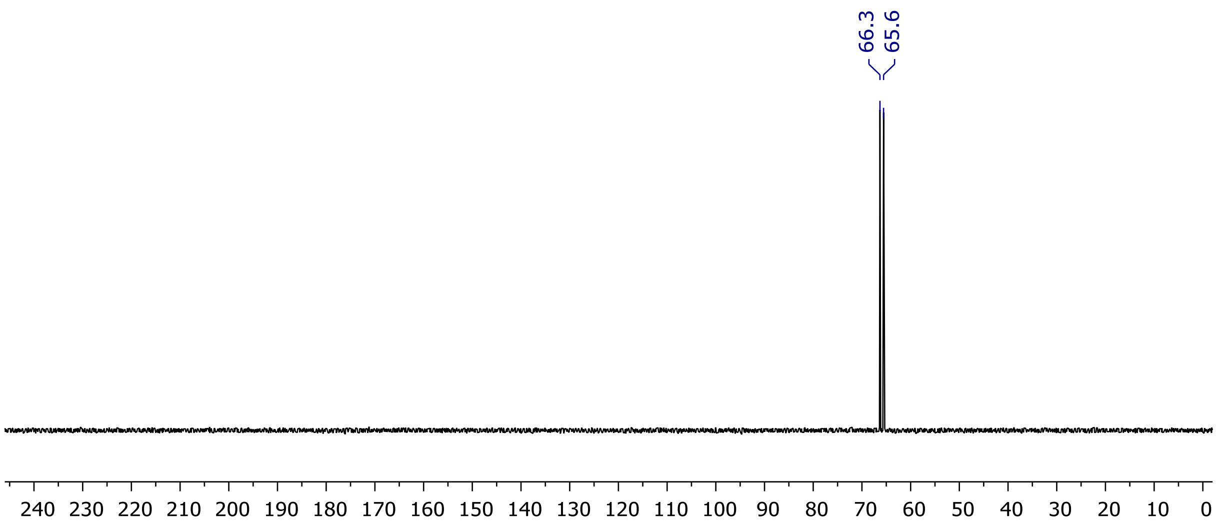

Figure S64. ^{31}P{^{1}H} NMR spectrum of **7a** (DFB, 162 MHz).

1.19. [Rh(PONOP-14)(H_2)][BAr$^F_4$] (7b)

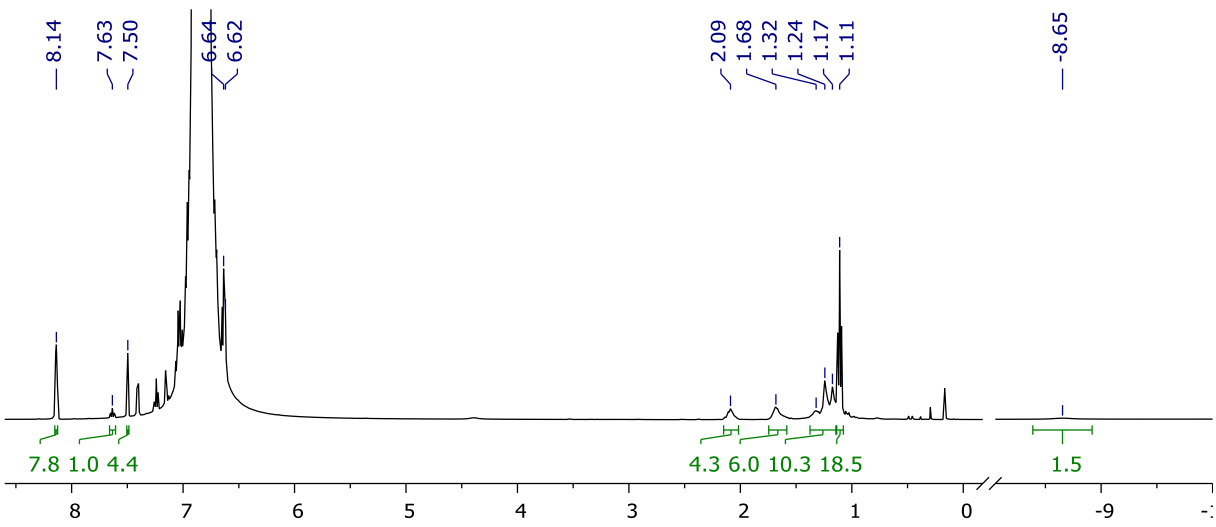

Figure S65. ^{1}H NMR spectrum of **7b** (DFB, 500 MHz).

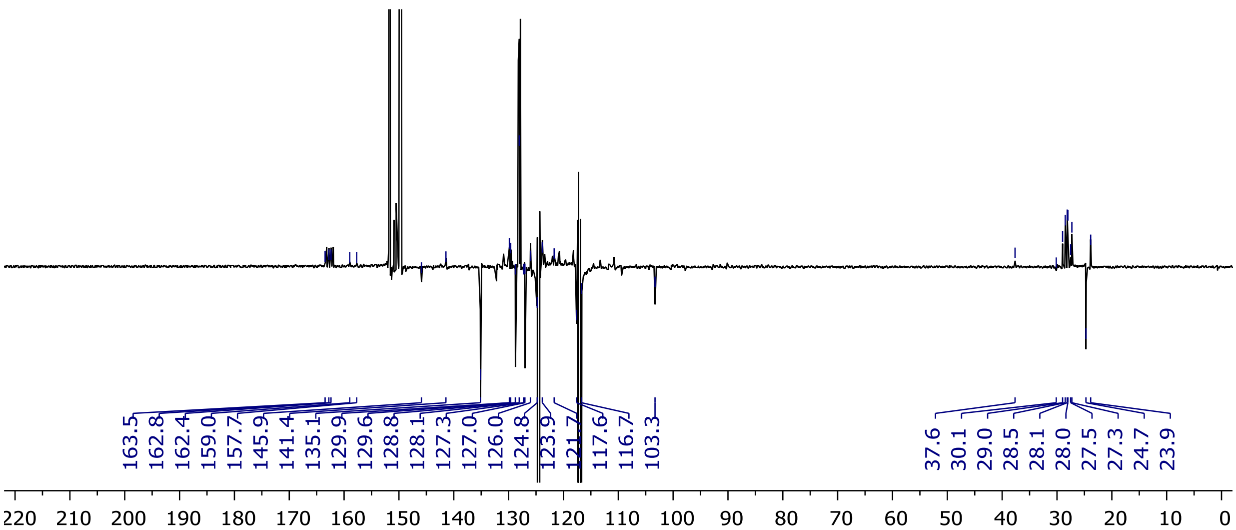

Figure S66. ^{13}C{^{1}H} APT NMR spectrum of **7b** (DFB, 126 MHz).

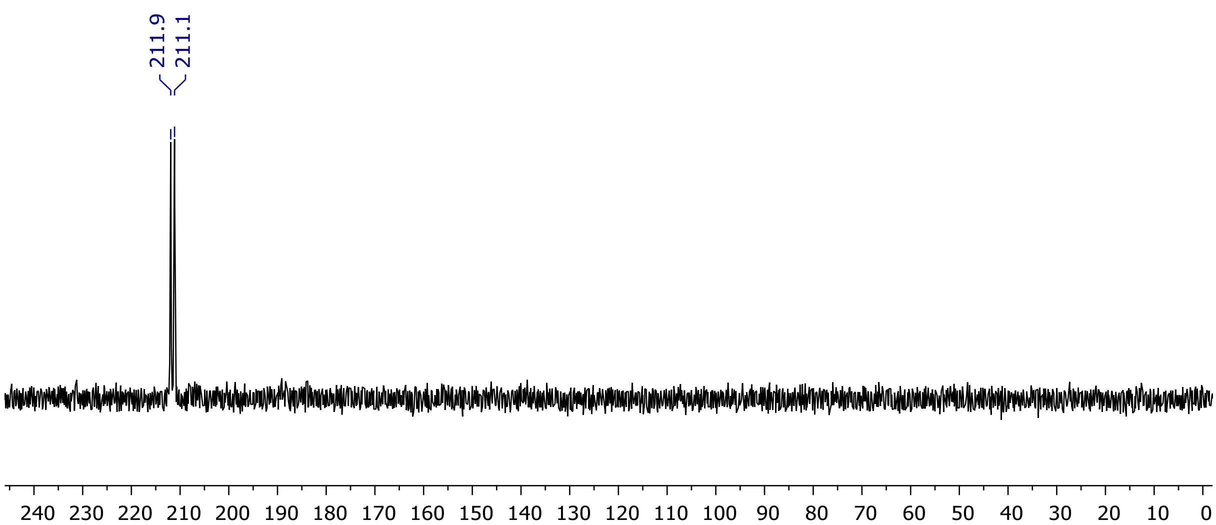

Figure S67. ^{31}P{^{1}H} NMR spectrum of **7b** (DFB, 162 MHz).

1.20. [Rh(PNP-14)(C_2H_4)][BAr$^F_4$] (8a)

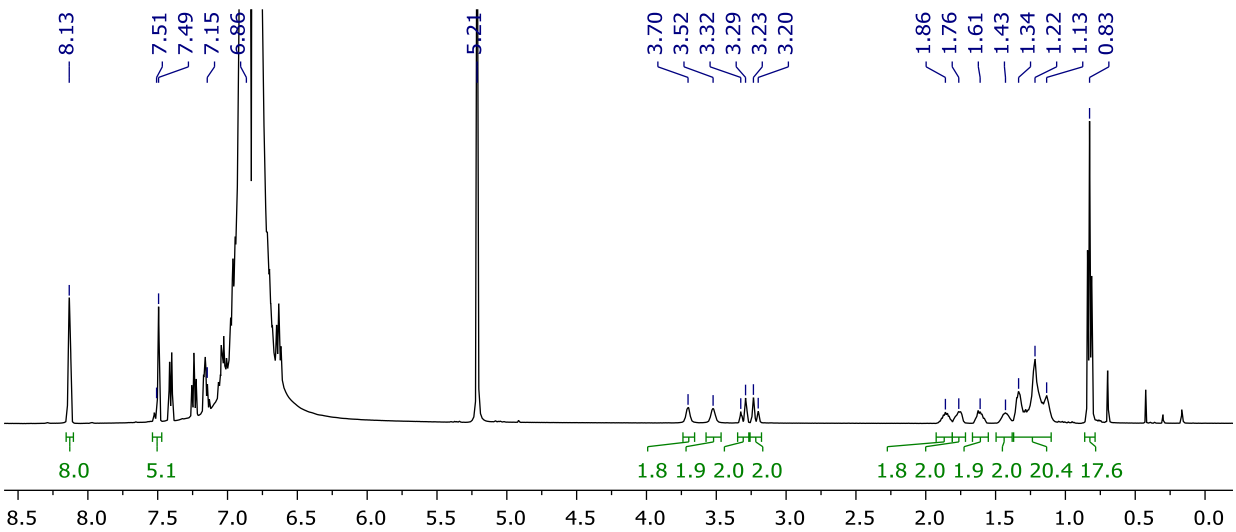

Figure S68. ^{1}H NMR spectrum of **8a** (DFB, 500 MHz).

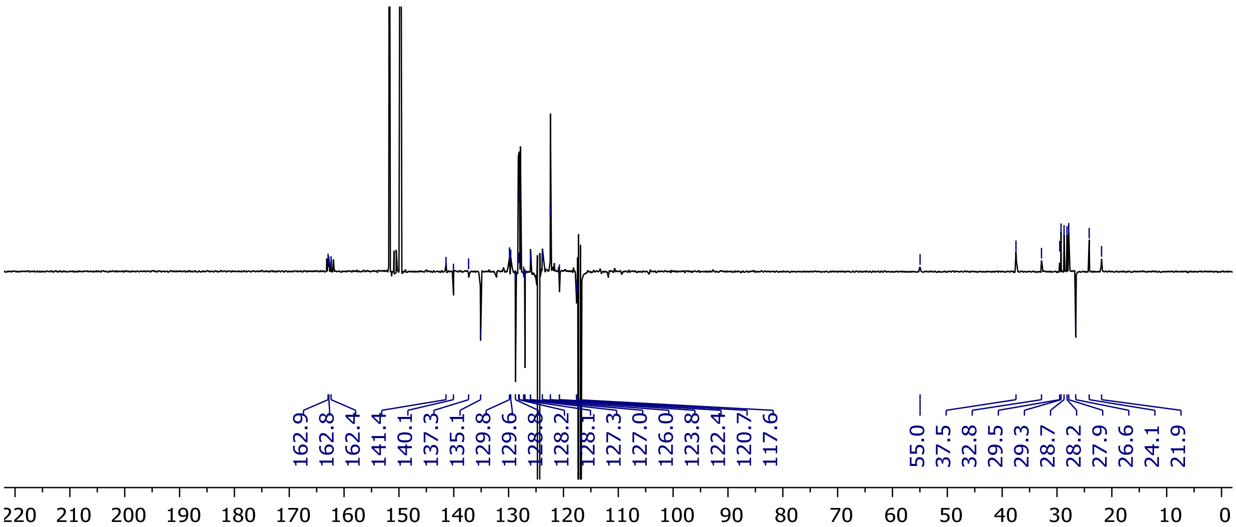

Figure S69. ^{13}C{^{1}H} APT NMR spectrum of **8a** (DFB, 126 MHz).

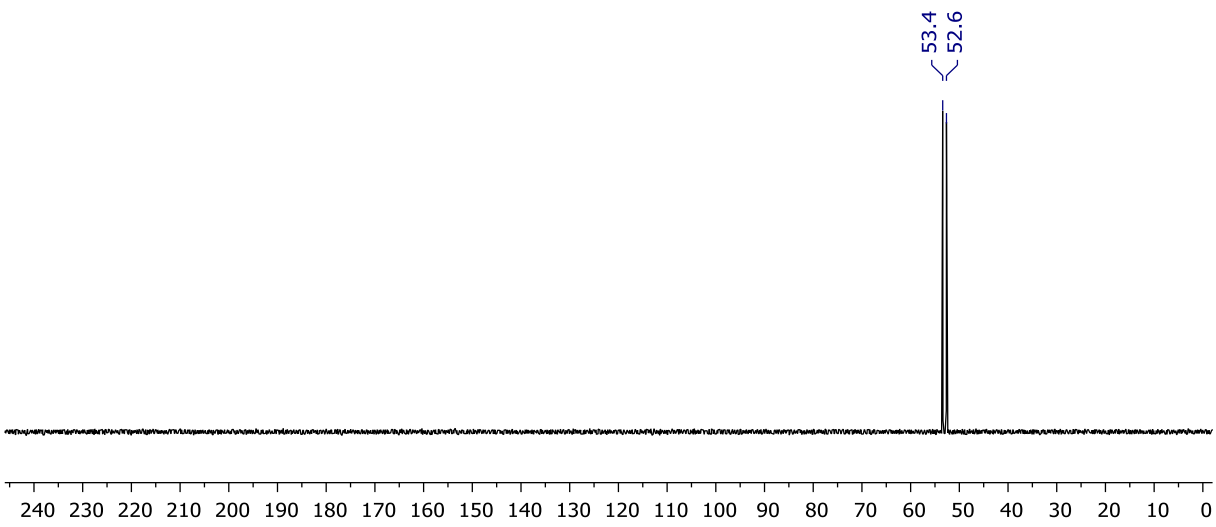

Figure S70. ^{31}P{^{1}H} NMR spectrum of **8a** (DFB, 162 MHz).

1.21. [Rh(PONOP-14)(C_2H_4)][BAr$^F_4$] (8b)

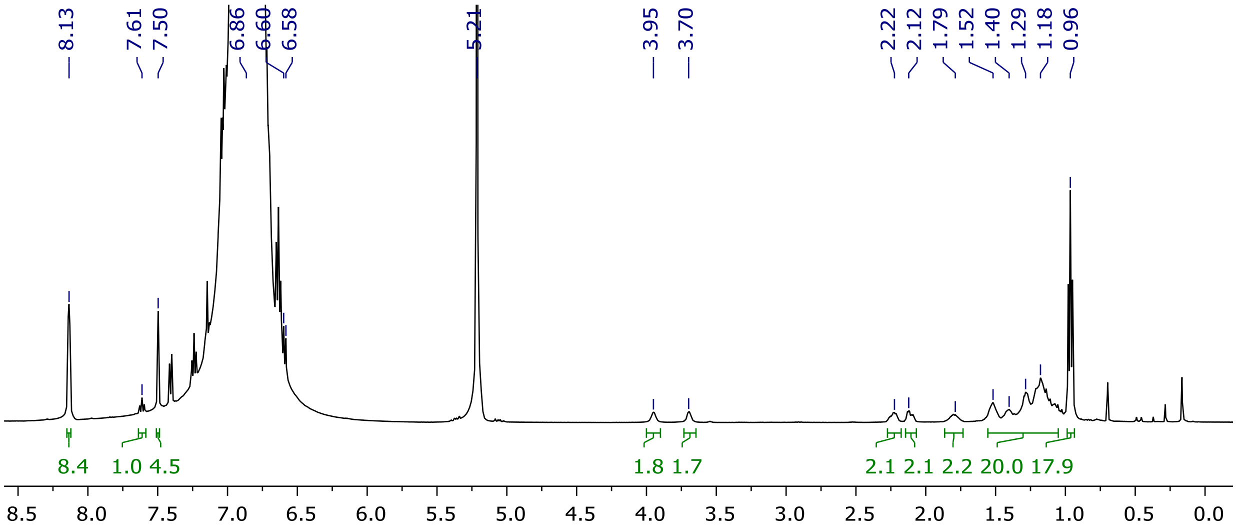

Figure S71. ^1H NMR spectrum of **8b** (DFB, 500 MHz).

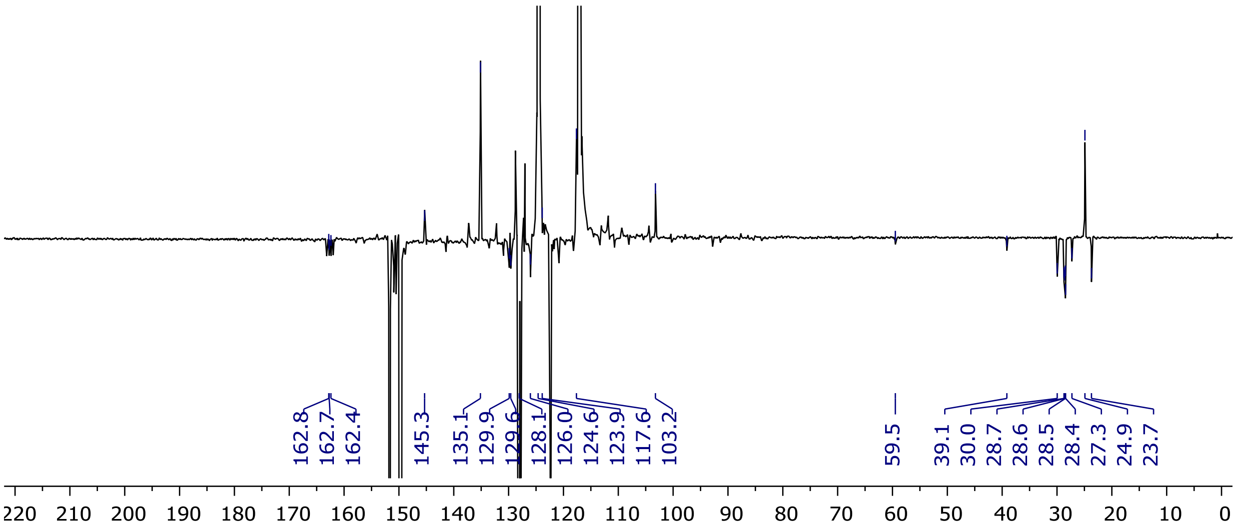

Figure S72. $^{13}C\{^1H\}$ APT NMR spectrum of **8b** (DFB, 126 MHz).

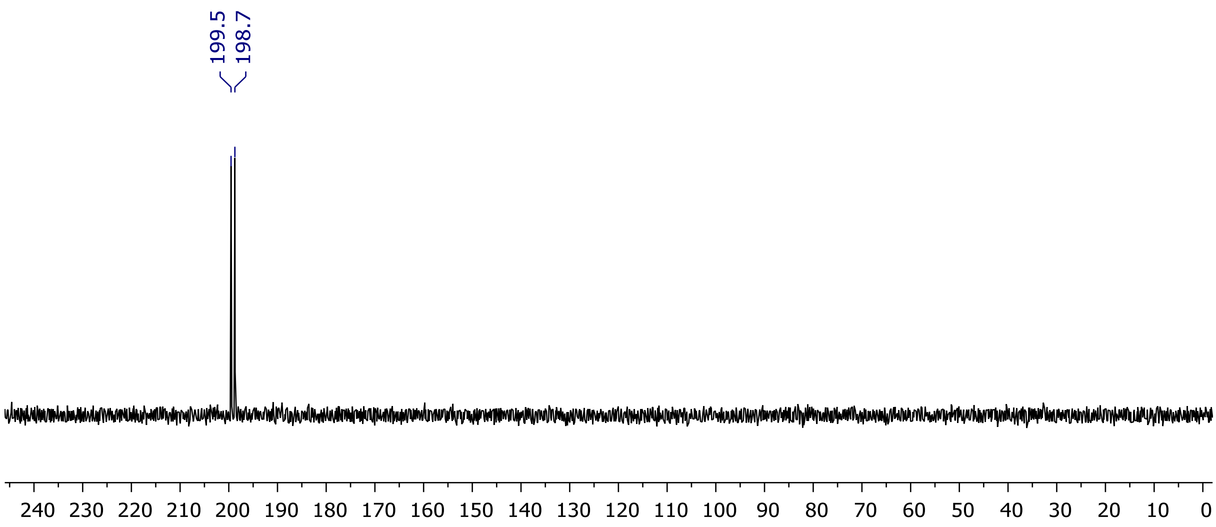

Figure S73. $^{31}P\{^1H\}$ NMR spectrum of **8b** (DFB, 162 MHz).

1.22. [Rh(PNP-14)(CO)][BAr^F_4] (9a)

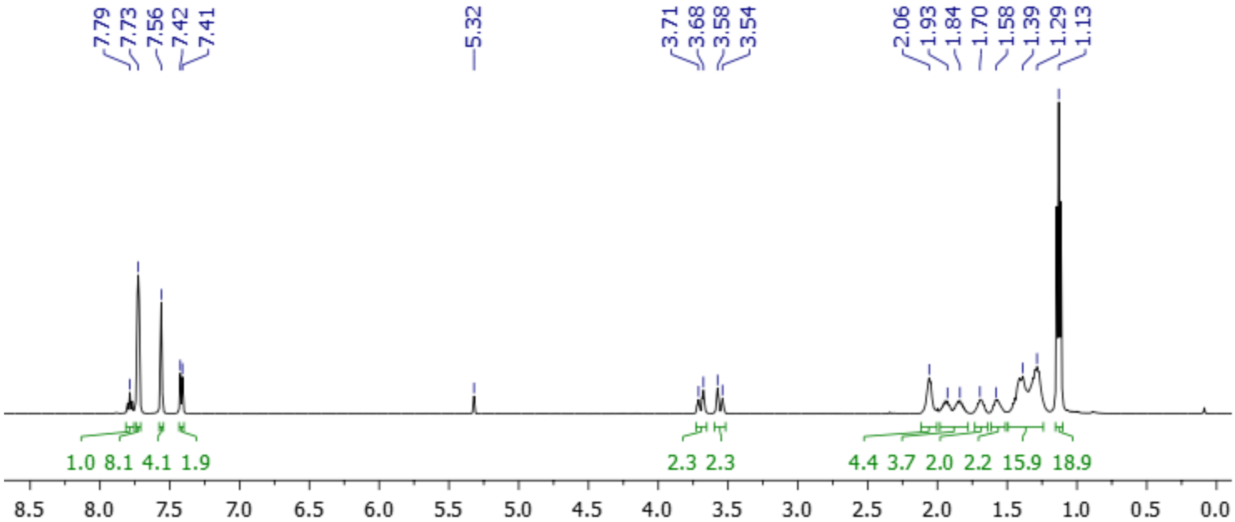

Figure S74. ^1H NMR spectrum of **9a** (CD_2Cl_2, 500 MHz).

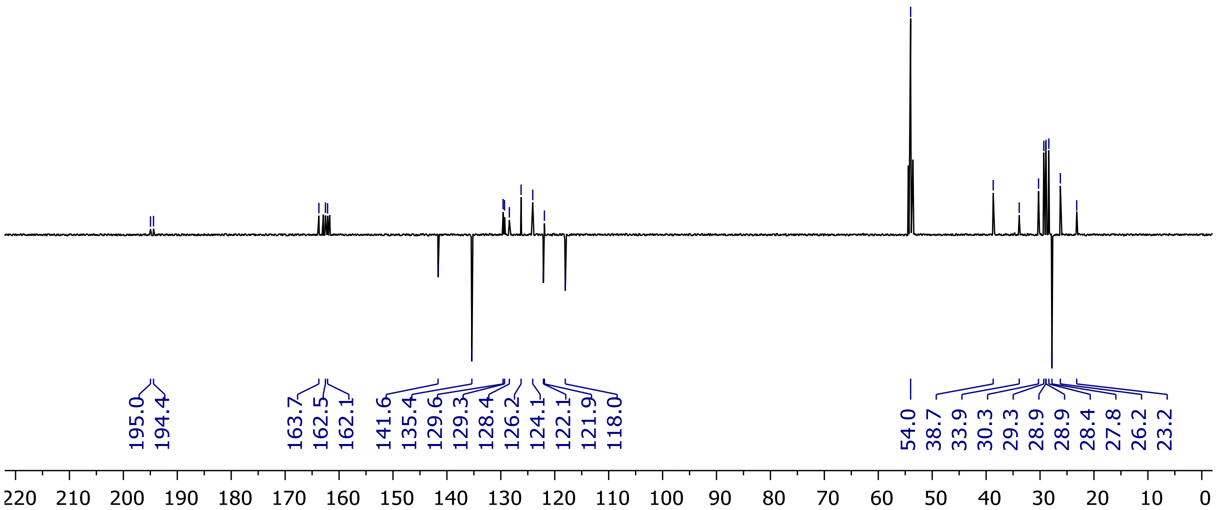

Figure S75. $^{13}C\{^1H\}$ APT NMR spectrum of **9a** (CD_2Cl_2, 126 MHz).

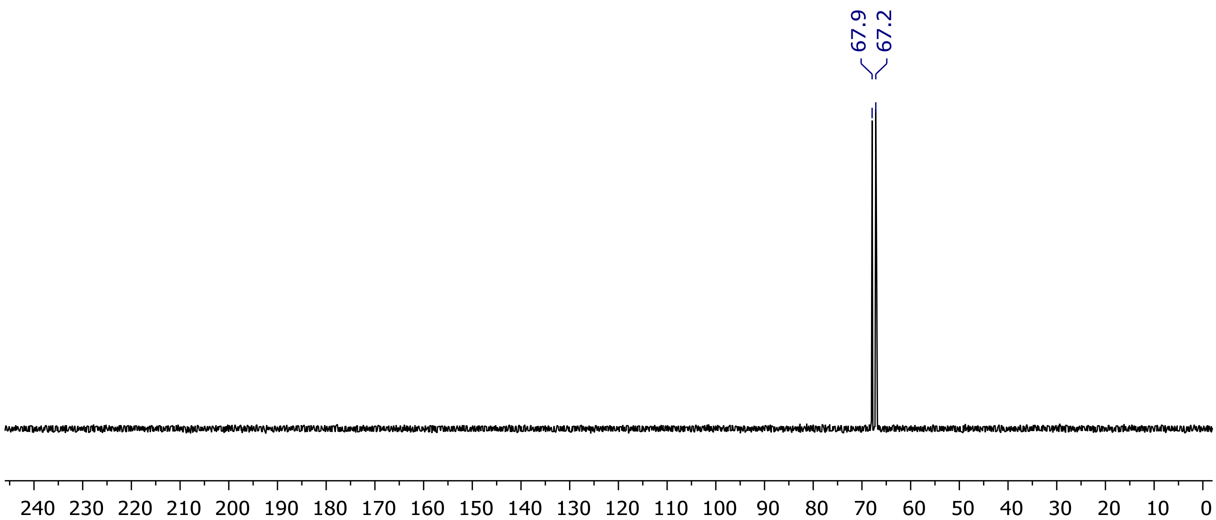

Figure S76. $^{31}P\{^1H\}$ NMR spectrum of **9a** (CD_2Cl_2, 162 MHz).

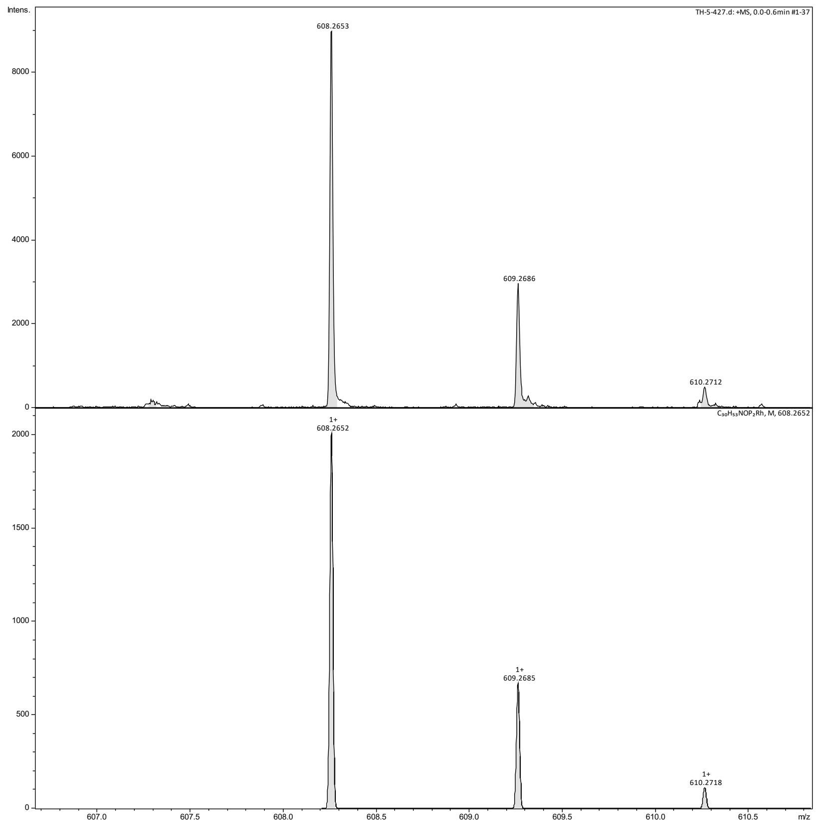

Figure S77. HR ESI-MS of **9a**.

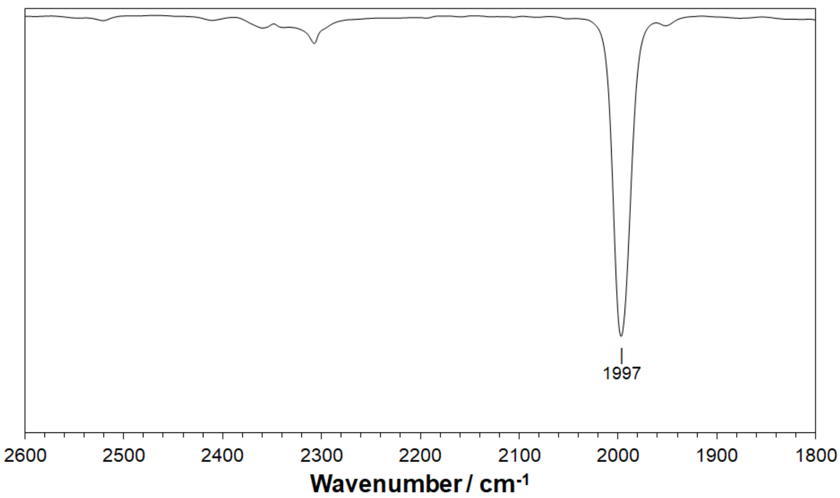

Figure S78. IR spectrum of **9a** recorded in CH_2Cl_2.

1.23. [Rh(PONOP-14)(CO)][BAr$^F_4$] (9b)

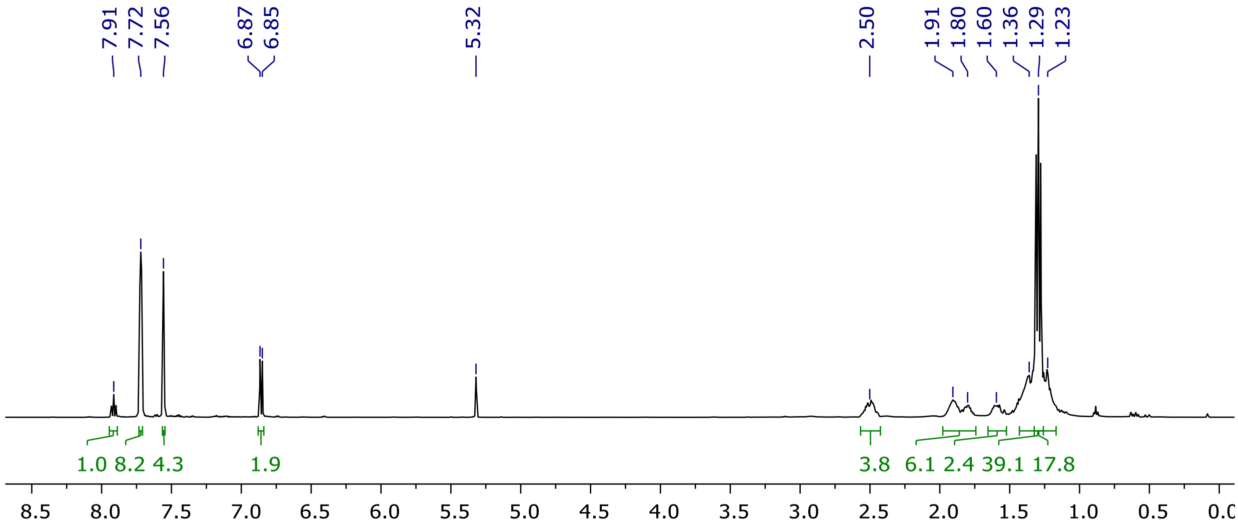

Figure S79. ^{1}H NMR spectrum of **9b** (CD_2Cl_2, 500 MHz).

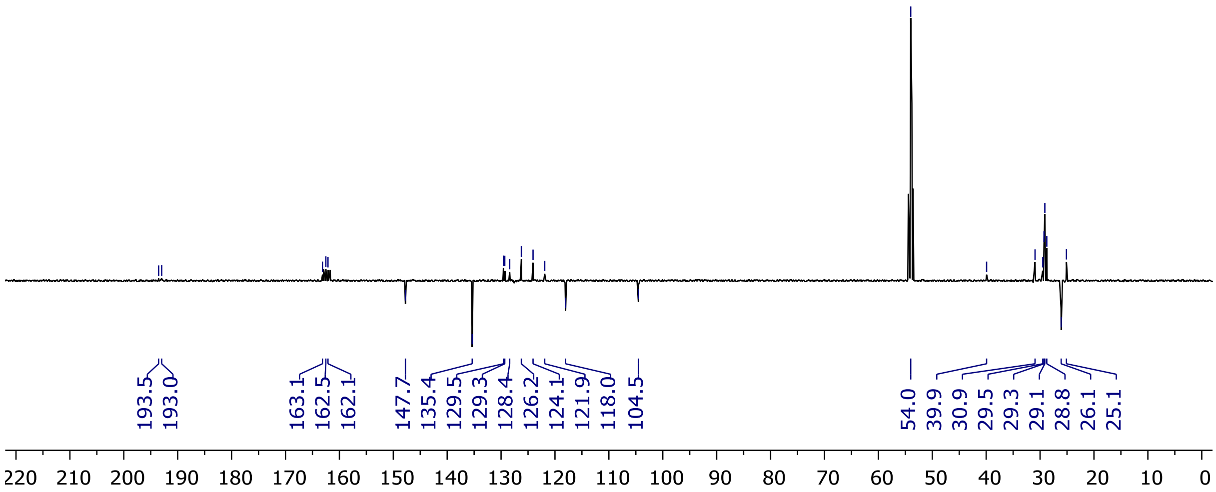

Figure S80. ^{13}C{^{1}H} APT NMR spectrum of **9b** (CD_2Cl_2, 126 MHz).

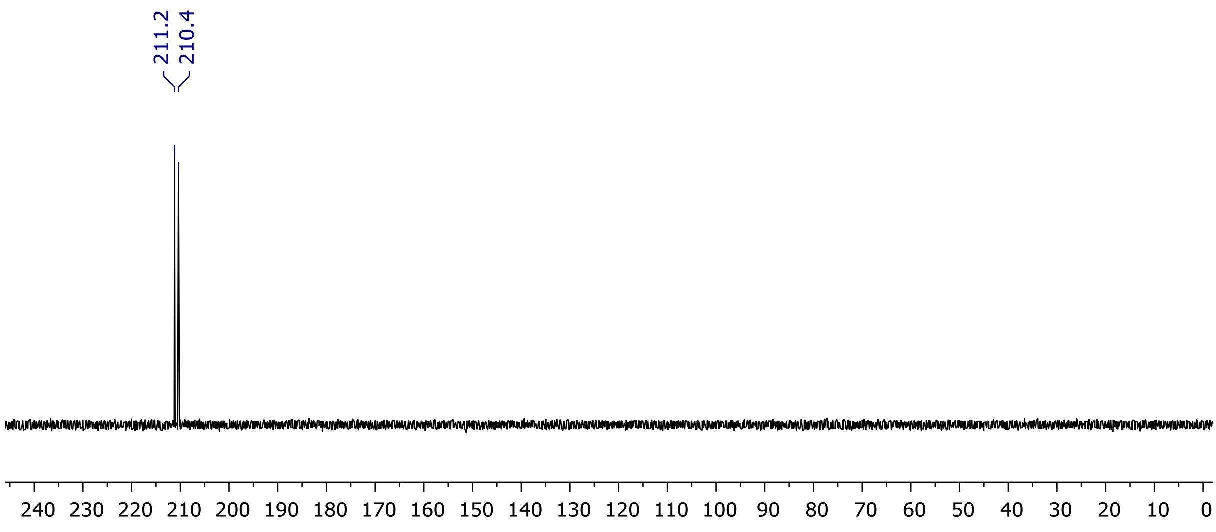

Figure S81. ^{31}P{^{1}H} NMR spectrum of **9b** (CD_2Cl_2, 162 MHz).

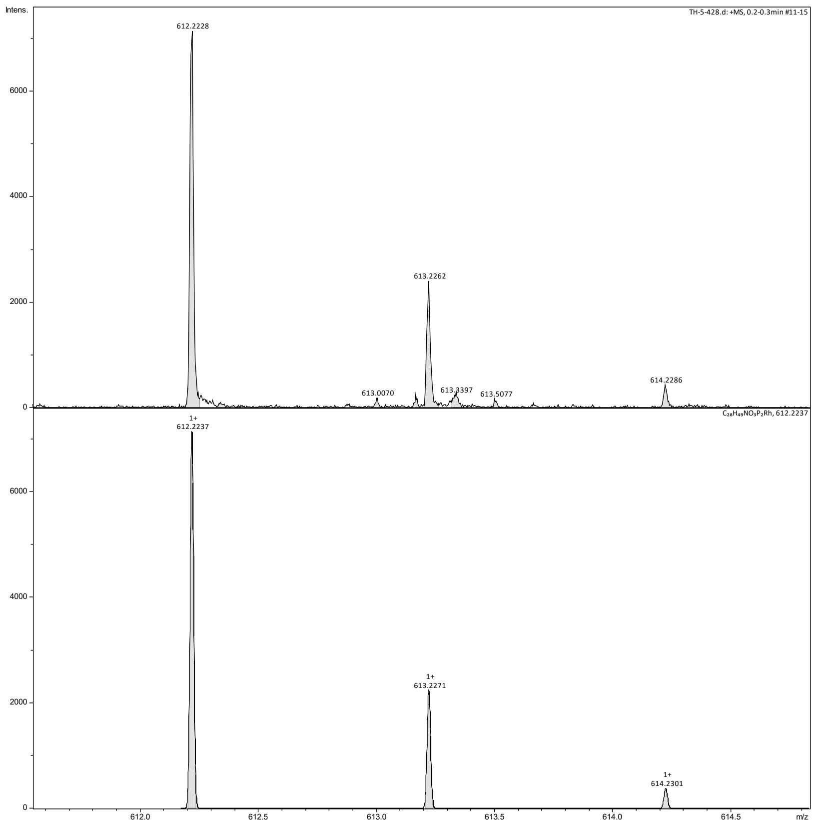

Figure S82. HR ESI-MS of **9b**.

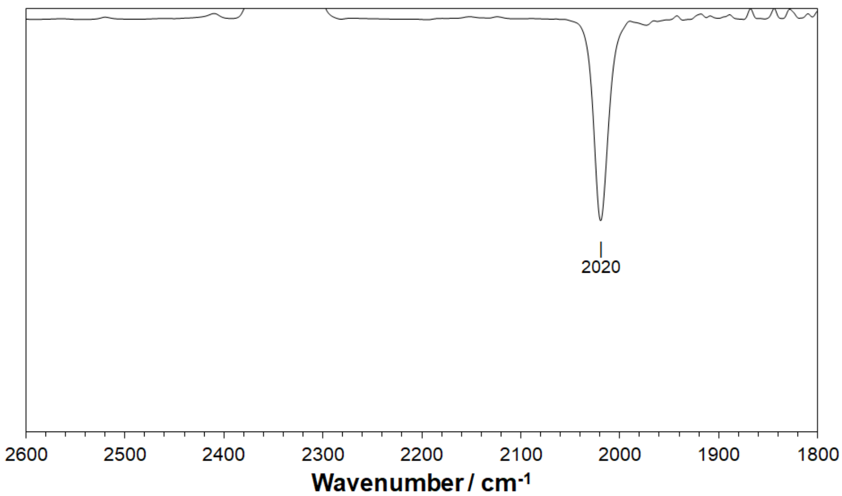

Figure S83. IR spectrum of **9b** recorded in CH_2Cl_2.

2. Deprotection optimisation

Table S1: Deprotection of *trans*-**1b**[a]

Conditions	Method reference	Purity (%)
Neat $HNEt_2$, 50 °C, 72 h	1	18
$HNEt_2$:THF (1:1), 19 ºC, 8 days	1	65 – 86
$HNEt_2$:THF (1:10), 19 ºC, 8 days	1	26
DABCO, C_6D_6, 45 °C, 2 weeks	2	2
4 Å sieves, THF:*t*BuOH (3:7), 70 °C, 7 days	3	29
PMe_3 (4 eq), C_7H_8, 50 °C, 4 weeks		5
HMP (20 eq), THF, 25 °C, 48 h		64[b]
Pyrdine-d$_5$, 50 °C, 7 days		22
IMes, C_6D_6, 80 °C, 3 weeks		22

[a] Reactions carried out in J Young's valve NMR tube using *trans*-**1b** (5.1 mg, 10 μmol), with purity determined by ^{31}P NMR spectroscopy. [b] Significant decomposition is observed upon work up

3. References

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2 K. Jouvin, R. Veillard, C. Theunissen, C. Alayrac, A.-C. Gaumont and G. Evano, *Org. Lett.*, 2013, **15**, 4592–4595.

3 M. Van Overschelde, E. Vervecken, S. G. Modha, S. Cogen, E. Van der Eycken and J. Van der Eycken, *Tetrahedron*, 2009, **65**, 6410–6415.