Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Phosphorus-nitrogen compounds: Part 71. Novel unsymmetrically-substituted dispiro-cyclotriphosphazenes: Synthesis, characterization, antituberculosis activity and phototunable charge storage studies

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Supporting Information

Electrochemical measurements

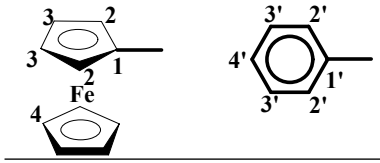
Cyclic Voltamogram experiments were performed with a Gamry Reference 3000 electrochemical analyzer with a C3 stand containing a three-electrode system. A Pt wire, an Ag/AgCl electrode, and a glassy carbon electrode served as auxiliary, reference and working electrodes, respectively. Cyclic voltammetry measurements were made in dichloromethane solution using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a support.

Antituberculosis Activity

The antituberculosis activities of the compounds (**6a**, **6b**, **10a** and **10b**) were tested against the reference strain *Mycobacterium tuberculosis* H37Rv (ATCC 27294) with the “Agar proportion method” in agar-based Middlebrook 7H10 medium in accordance with Clinical and Laboratory Standards Institute (CLSI) recommendations.[1] The final concentration of each compound in the medium was set to be 5, 10, 20, 40 and 80 µg / mL, respectively. The compounds were sterilized after dissolving in dimethyl sulfoxide (DMSO) by passing through a 0.2 µm diameter filter.

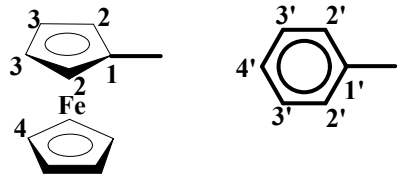
Middle Brook 7H10 medium was prepared according to the instructions and autoclaved at 121°C for 10 minutes. After the medium was cooled to 45-55°C, OADC and solutions of the prepared compounds were added to the medium. It was then mixed well and poured into sterilized plates. After sterility control of the whole medium, the antituberculosis activities of the compounds were tested using the *M. tuberculosis* H37Rv reference strain (susceptible to all anti-tuberculosis drugs). After the plates were incubated at 37 °C for 21 days, the results were evaluated. The concentration of which compounds were found effective were readjusted; *M. tuberculosis* H37Rv strain was susceptible to compounds **6b** and **10a** at a concentration of 40 µg / mL; to test whether the MIC values of these compounds are <40 µg / mL, the concentrations of these compounds were readjusted to 40, 35, 30, 25 and 20 µg / mL, respectively. Likewise, *M. tuberculosis* H37Rv strain was found to be susceptible to compound **6a** at a concentration of 20 µg/mL. Again, to determine whether the MIC value of this compound is <20 µg / mL, the concentration was adjusted to 20, 18, 16, 14 and 12 µg / mL, respectively.

Table S1. ^{13}C (decoupled) NMR spectral data of the unsymmetrical dispirocyclotriphosphazenes. [Chemical shifts (δ) reported in ppm and *J* values in Hz].



	$\underline{C}H_3$	$NCH_2\underline{C}H_2$	$N\underline{C}H_2CH_3$	$N\underline{C}H_2$	$CH_3N\underline{C}H_2$	$C_2H_5N\underline{C}H_2$	$Fc\underline{C}H_2$	C4	C3	C2	C1	$Ph\underline{C}H_2$	C4'	C3'	C2'	C1'
6a	31.54 $^2J_{PC}$=3.8 31.25 $^2J_{PC}$=3.9	-	-	47.31 $^2J_{PC}$=12.2 47.13 $^2J_{PC}$=12.2	43.49 $^2J_{PC}$=12.8 44.12 $^2J_{PC}$=12.9	-	44.21 $^2J_{PC}$=3.8	68.44	68.47 68.08	69.79 69.54	83.20 $^3J_{PC}$=7.7	48.68 $^2J_{PC}$=5.7	127.35	128.10	128.48	137.70 $^3J_{PC}$=6.4
6b	31.34 $^2J_{PC}$=4.0 31.23 $^2J_{PC}$=4.1	-	-	47.73 $^2J_{PC}$=12.8 47.13 $^2J_{PC}$=12.7	43.62 $^2J_{PC}$=13.1 44.16 $^2J_{PC}$=13.0	-	44.17	68.32	68.37 67.93	69.62 69.42	83.05 $^3J_{PC}$=8.0	48.75 $^2J_{PC}$=5.5	127.50	127.88	128.65	137.66 $^3J_{PC}$=6.2
7a	13.66 31.58	-	39.34 $^2J_{PC}$=4.5	47.32 $^2J_{PC}$=12.2 44.20 $^2J_{PC}$=13.5	43.56 $^2J_{PC}$=13.1	43.53 $^2J_{PC}$=14.6	44.14 $^2J_{PC}$=4.6	68.44	68.08	69.84 69.55	83.21	48.67 $^2J_{PC}$=5.8	127.32	128.07	128.47	137.72 $^3J_{PC}$=7.1
7b	13.78 $^3J_{PC}$=5.8 31.29 $^2J_{PC}$=3.8	-	39.92 $^2J_{PC}$=4.5	47.25 $^2J_{PC}$=12.2 44.25 $^2J_{PC}$=12.8	44.18 $^2J_{PC}$=13.4	43.61 $^2J_{PC}$=13.3	44.08 $^2J_{PC}$=5.7	68.35	67.96	69.69 69.47	83.08 $^3J_{PC}$=8.1	48.80 $^2J_{PC}$=6.4	127.49	127.85	128.64	137.66 $^3J_{PC}$=7.1
8b	13.80 $^3J_{PC}$=3.8 30.33	-	39.18 $^2J_{PC}$=3.8	47.13 $^2J_{PC}$=10.1 47.16 $^2J_{PC}$=10.8	43.80 $^2J_{PC}$=12.6	43.59 $^2J_{PC}$=12.6	44.23 $^2J_{PC}$=6.3	68.33	67.99 67.91	69.65 69.45	83.10	48.73 $^2J_{PC}$=2.5	127.48	127.92	128.64	137.69 $^3J_{PC}$=6.3
10a	31.58 $^2J_{PC}$=3.9 35.79	24.83 $^3J_{PC}$=1.9	-	50.49 47.30 $^2J_{PC}$=12.8	43.63 $^2J_{PC}$=12.8 45.76	-	44.54 $^2J_{PC}$=5.8	68.36 68.08	68.46	69.87 69.42	83.27 $^2J_{PC}$=7.7	50.60 $^2J_{PC}$=2.7	127.23	128.27	128.37	138.01 $^3J_{PC}$=9.0
10b	31.77 $^2J_{PC}$=4.5 35.69	24.89 $^3J_{PC}$=2.0	-	50.48 47.14 $^2J_{PC}$=12.9	43.69 $^2J_{PC}$=12.8 45.76	-	44.22 $^2J_{PC}$=5.8	67.89	68.33 67.89	69.58 69.24	83.15 $^2J_{PC}$=7.7	50.76 $^2J_{PC}$=3.2	127.44	128.25	128.55	138.01 $^3J_{PC}$=8.4
11a	13.60 $^3J_{PC}$=5.5 35.84	24.63	39.21 $^2J_{PC}$=4.4	45.68 43.71 $^2J_{PC}$=13.0	44.53 $^2J_{PC}$=5.4	43.66 $^2J_{PC}$=13.3	50.52	68.51	68.36 68.11	69.96 69.49	83.40 $^3J_{PC}$=8.2	50.55	127.19	128.14	128.37	138.12 $^3J_{PC}$=9.4
11b	13.75 $^3J_{PC}$=5.7 35.60	24.79	39.38 $^2J_{PC}$=4.5	45.76 43.77 $^2J_{PC}$=13.3	44.21 $^2J_{PC}$=5.5	43.70 $^2J_{PC}$=12.9	50.42	68.41	67.91	69.66 69.32	83.50	50.86	127.45	128.29	128.56	138.62 $^3J_{PC}$=9.0

Table S2. ^{1}H NMR spectral data of the unsymmetrical dispirocyclotriphosphazenes. [Chemical shifts (δ) reported in ppm and *J* values in Hz].
[s: singlet, d: doublet, dd: doublets of doublet, m: multiplet and bp: broad peak]



	C<u>*H*</u>$_3$	NCH$_2$C<u>*H*</u>$_2$	CH$_3$C<u>*H*</u>$_2$	NC<u>*H*</u>$_2$	CH$_3$NC<u>*H*</u>$_2$	C$_2$H$_5$NC<u>*H*</u>$_2$	FcC<u>*H*</u>$_2$	H2	H3	H4	PhC<u>*H*</u>$_2$	H2’	H3’	H4’
6a	2.43 (d, 3H) $^{3}J_{PH}$=12.0 2.73 (d, 3H) $^{3}J_{PH}$=12.0	-	-	3.02-3.21 (m, 4H)	3.02-3.21 (m, 4H)	-	3.93 (dd, 1H) $^{3}J_{PH}$=7.6 $^{2}J_{HH}$=14.0 3.79 (dd, 1H) $^{3}J_{PH}$=9.6 $^{2}J_{HH}$=14.0	4.36 4.18 (m, 2H)	4.11 (m, 2H)	4.09 (m, 5H)	4.02 (dd, 1H) $^{3}J_{PH}$=9.2 $^{2}J_{HH}$=15.2 4.05 (dd,.1H) $^{3}J_{PH}$=7.8 $^{2}J_{HH}$=15.2	7.42 (d, 2H) $^{3}J_{HH}$=6.8	7.32 (d, 2H) $^{3}J_{HH}$=7.6 $^{3}J_{HH}$=6.8	7.27 (d, 2H) $^{3}J_{HH}$=7.6
6b	2.61 (d, 3H) $^{3}J_{PH}$=11.6 2.66 (d, 3H) $^{3}J_{PH}$=11.7	-	-	3.05-3.23 (m, 4H)	3.05-3.23 (m, 4H)	-	3.81 (dd, 1H) $^{3}J_{PH}$=7.7 $^{2}J_{HH}$=13.7 3.59 (dd, 1H) $^{3}J_{PH}$=8.8 $^{2}J_{HH}$=13.7	4.27 4.06 (2H)	4.01 (2H)	3.85 (m, 5H)	4.15 (dd, 1H) $^{3}J_{PH}$=7.4 $^{2}J_{HH}$=15.3 4.23 (dd,.1H) $^{3}J_{PH}$=7.7 $^{2}J_{HH}$=15.3	7.53 (d, 2H) $^{3}J_{HH}$=7.1	7.39 (d, 2H) $^{3}J_{HH}$=7.0 $^{3}J_{HH}$=7.1	7.31 (d, 2H) $^{3}J_{HH}$=7.1
7a	1.04 (t, 3H) $^{3}J_{HH}$=7.2 2.73 (d, 3H) $^{3}J_{PH}$=11.6	-	2.82 (m, 2H) $^{3}J_{HH}$=7.2 $^{3}J_{PH}$=7.2	3.02-3.26 (m, 4H)	3.02-3.26 (m, 2H)	3.02-3.26 (m, 2H)	3.92 (dd, 1H) $^{3}J_{PH}$=7.6 $^{2}J_{HH}$=14.4 3.78 (dd, 1H) $^{3}J_{PH}$=9.0 $^{2}J_{HH}$=14.4	4.36 4.18 (2H)	4.12 (2H)	4.09 (5H)	4.03 (dd, 1H) $^{3}J_{PH}$=8.4 $^{2}J_{HH}$=16.8 4.06 (dd, 1H) $^{3}J_{PH}$=8.4 $^{2}J_{HH}$=16.8	7.43 (d, 2H) $^{3}J_{HH}$=7.2	7.33 (d, 2H) $^{3}J_{HH}$=7.2 $^{3}J_{HH}$=7.6	7.28 (d, 2H) $^{3}J_{HH}$=7.6

7b	1.19 (t, 3H) $^3J_{HH}$=7.2 2.63 (d, 3H) $^3J_{PH}$=11.6	-	2.82 (m, 2H) $^3J_{HH}$=7.2 $^3J_{PH}$=7.6	3.00-3.25 (m, 4H)	3.00-3.25 (m, 2H)	3.00-3.25 (m, 2H)	3.78 (dd, 1H) $^3J_{PH}$=7.6 $^2J_{HH}$=14.2 3.57 (dd, 1H) $^3J_{PH}$=8.6 $^2J_{HH}$=14.2	4.24 4.04 (2H)	3.99 (2H)	3.81 (5H)	4.20 (dd, 1H) $^3J_{PH}$=7.6 $^2J_{HH}$=15.3 4.11 (dd, 1H) $^3J_{PH}$=7.4 $^2J_{HH}$=15.3	7.51 (d, 2H) $^3J_{HH}$=7.2	7.36 (d, 2H) $^3J_{HH}$=7.2 $^3J_{HH}$=7.6	7.28 (d, 2H) $^3J_{HH}$=7.6
8b	1.27 (t, 3H) $^3J_{HH}$=6.8 2.60 (d, 3H) $^3J_{PH}$=10.0	-	3.04-3.28 (m, 4H)	3.04-3.28 (m, 4H)	3.04-3.28 (m, 2H)	3.04-3.28 (m, 2H)	3.77 (dd, 1H) $^3J_{PH}$=8.0 $^2J_{HH}$=15.0 3.59 (dd, 1H) $^3J_{PH}$=8.2 $^2J_{HH}$=15.0	4.28 4.06 (2H)	4.02 4.00 (2H)	3.85 (bp,5H)	4.02 (dd, 1H) $^3J_{PH}$=8.4 $^2J_{HH}$=16.8 4.06 (dd, 1H) $^3J_{PH}$=8.4 $^2J_{HH}$=16.8	7.53 (d, 2H) $^3J_{HH}$=7.5	7.39 (d, 2H) $^3J_{HH}$=7.5 $^3J_{HH}$=7.4	7.31 (d, 2H) $^3J_{HH}$=7.6
10a	2.77 (d, 3H) $^3J_{PH}$=13.6 2.40 (d, 3H) $^3J_{PH}$=12.0	1.84 (m, 2H)	-	2.97-3.19 (m, 4H)	2.97-3.19 (m, 4H)	-	3.92 (dd, 1H) $^3J_{PH}$=9.6 $^2J_{HH}$=14.0 3.83 (dd, 1H) $^3J_{PH}$=7.2 $^2J_{HH}$=14.0	4.35 (2H)	4.17 (2H)	4.08 (bp, 5H)	4.02 (bp, 2H)	7.40 (d, 2H) $^3J_{HH}$=7.2	7.31 (dd, 2H) $^3J_{HH}$=7.2 $^3J_{HH}$=6.8	7.26 (d, 1H) $^3J_{HH}$=6.8
10b	2.67 (d, 3H) $^3J_{PH}$=13.6 2.59 (d, 3H) $^3J_{PH}$=12.0	1.81 (m, 2H)	-	2.96-3.17 (m, 4H)	2.96-3.17 (m, 4H)	-	3.81 (dd, 1H) $^3J_{PH}$=7.8 $^2J_{HH}$=14.3 3.58 (dd, 1H) $^3J_{PH}$=8.8 $^2J_{HH}$=14.3	4.25 4.04 (2H)	3.99 3.94 (2H)	3.88 (bp, 5H)	4.20 (dd, 1H) $^3J_{PH}$=7.4 $^2J_{HH}$=14.8 4.14 (dd, 1H) $^3J_{PH}$=8.8 $^2J_{HH}$=14.8	7.48 (d, 2H) $^3J_{HH}$=7.2	7.35 (dd, 2H) $^3J_{HH}$=7.6 $^3J_{HH}$=7.2	7.28 (d, 1H) $^3J_{HH}$=7.6
11a	0.99 (t, 3H) $^3J_{HH}$=7.0 2.80 (d, 3H)	1.86 (m, 2H)	3.00-3.18 (m, 2H)	3.00-3.18 (m, 4H)	3.00-3.18 (m, 2H)	3.00-3.18 (m, 2H)	3.92 (dd, 1H) $^3J_{PH}$=8.7	4.38 (2H)	4.27 (2H)	4.11 (bp, 5H)	4.19 (dd, 1H) $^3J_{PH}$=7.7	7.42 (d, 2H) $^3J_{HH}$=7.2	7.34 (dd, 2H) $^3J_{HH}$=7.2	7.28 (d, 1H) $^3J_{HH}$=7.3

	$^3J_{PH}$=13.2						$^2J_{HH}$=13.8 3.84 (dd, 1H) $^3J_{PH}$=6.8 $^2J_{HH}$=13.8				$^2J_{HH}$=15.1 4.05 (dd, 1H) $^3J_{PH}$=8.4 $^2J_{HH}$=15.1		$^3J_{HH}$=7.3	
11b	1.19 (t, 3H) $^3J_{HH}$=7.2 2.68 (d, 3H) $^3J_{PH}$=13.4	1.83 (m, 2H)	2.94-3.14 (m, 2H)	2.94-3.14 (m, 4H)	2.94-3.14 (m, 2H)	2.94-3.14 (m, 2H)	3.84 (dd, 1H) $^3J_{PH}$=8.5 $^2J_{HH}$=14.2 3.60 (dd, 1H) $^3J_{PH}$=7.5 $^2J_{HH}$=14.2	4.28 4.07 (2H)	4.03 3.98 (2H)	3.90 (bp, 5H)	4.24 (dd, 1H) $^3J_{PH}$=7.7 $^2J_{HH}$=14.8 4.16 (dd, 1H) $^3J_{PH}$=8.9 $^2J_{HH}$=14.8	7.51 (d, 2H) $^3J_{HH}$=7.4	7.38 (dd, 2H) $^3J_{HH}$=7.4 $^3J_{HH}$=7.7	7.30 (d, 1H) $^3J_{HH}$=7.4

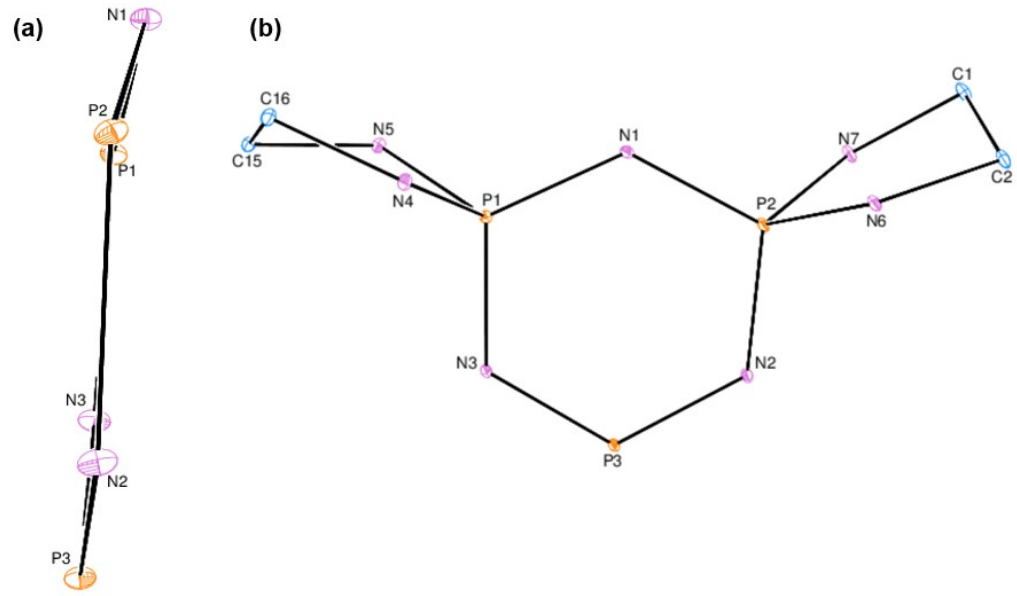


Fig. S1. The conformations of (a) the phosphazene ring and (b) the five-membered spiro-rings of **6b**.

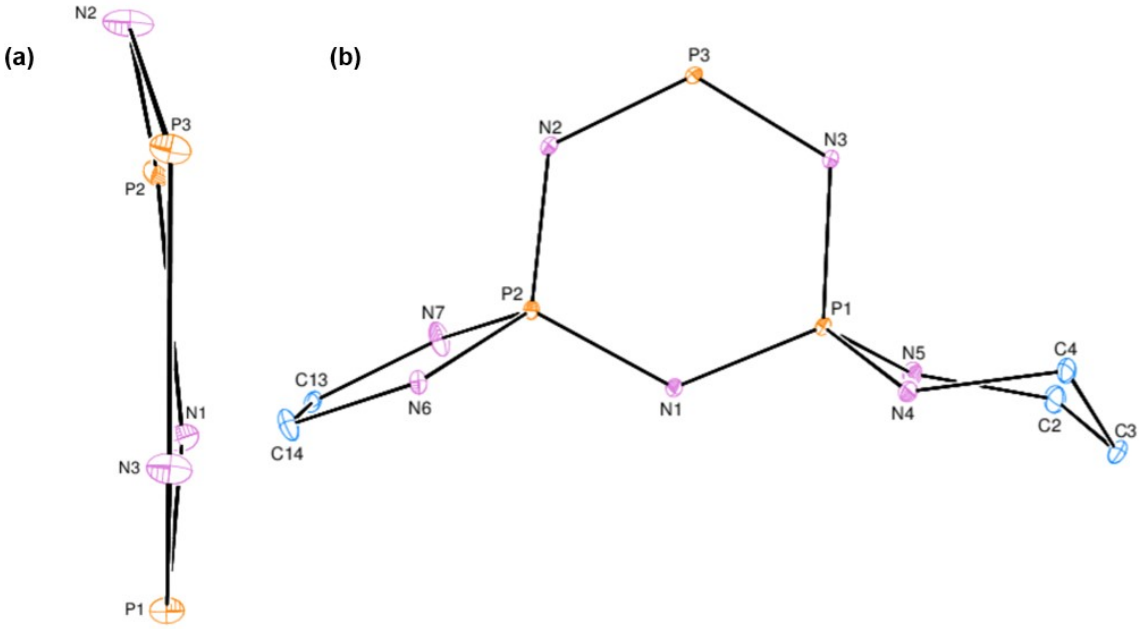


Fig. S2. The conformations of (a) the phosphazene ring and (b) the five- and six-membered spiro-rings of **10b**.

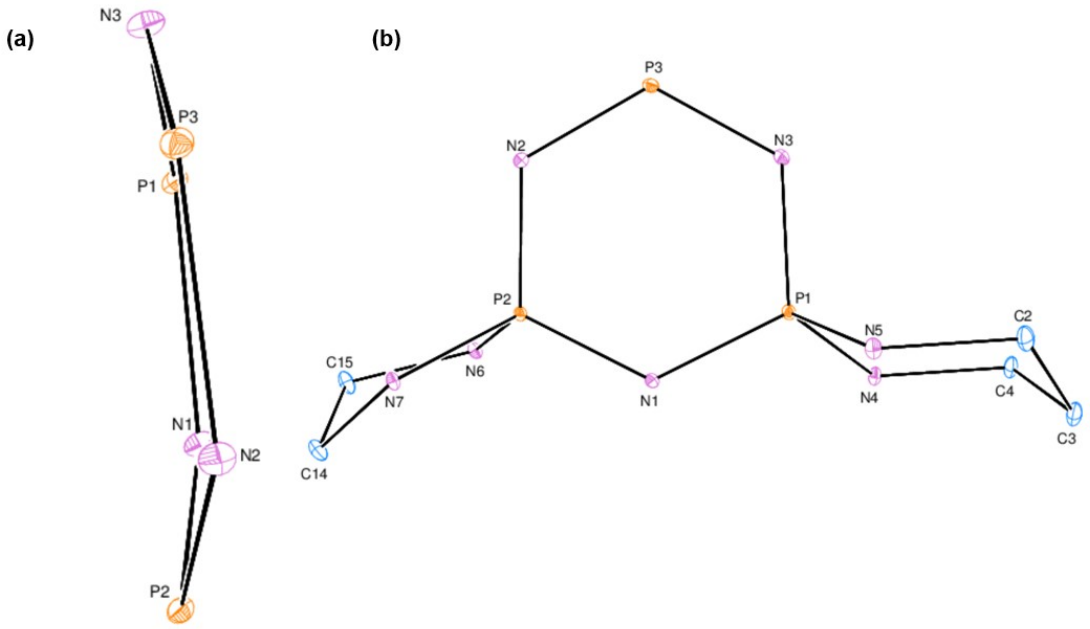


Fig. S3. The conformations of (a) the phosphazene ring and (b) the five- and six-membered spiro-rings of **11b**.

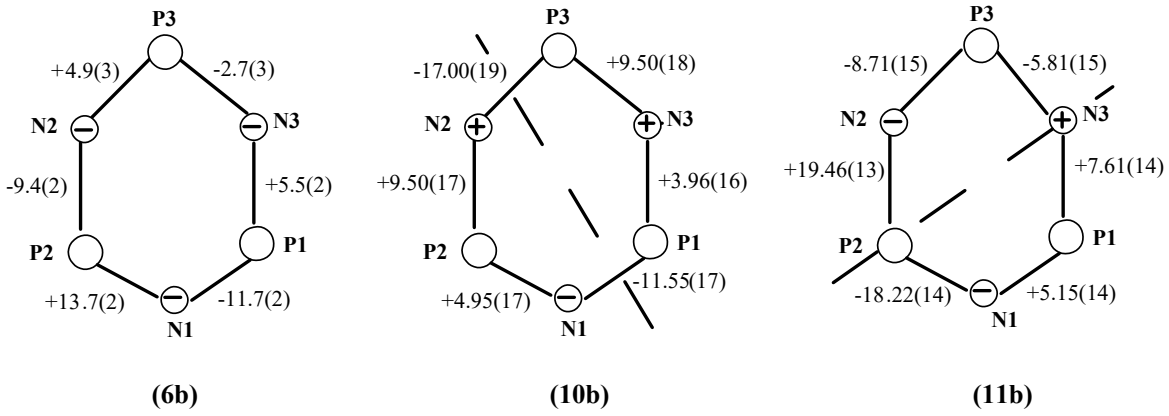
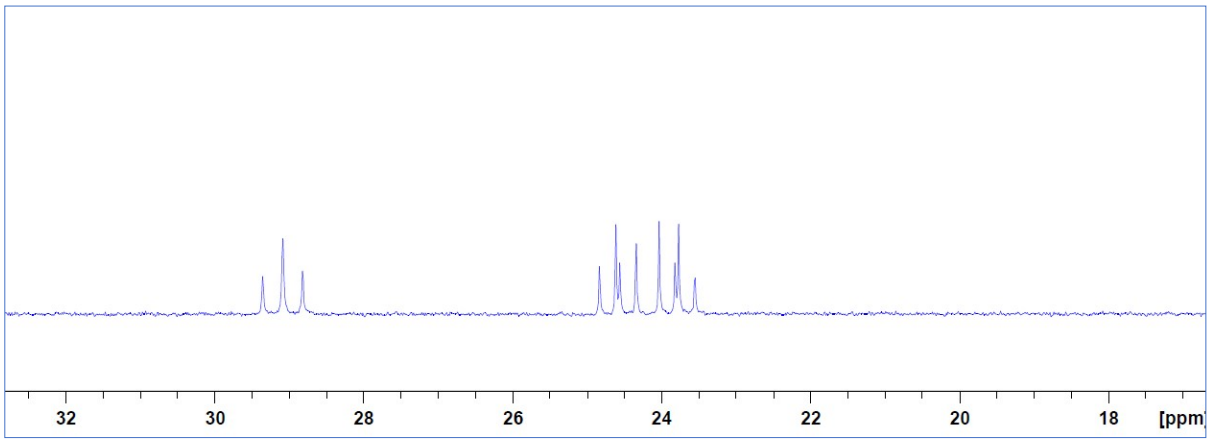


Fig. S4. The shapes of the phosphazene rings in cis-dispirophosphazenes (**6b**, **10b** and **11b**) with torsion angles (deg).

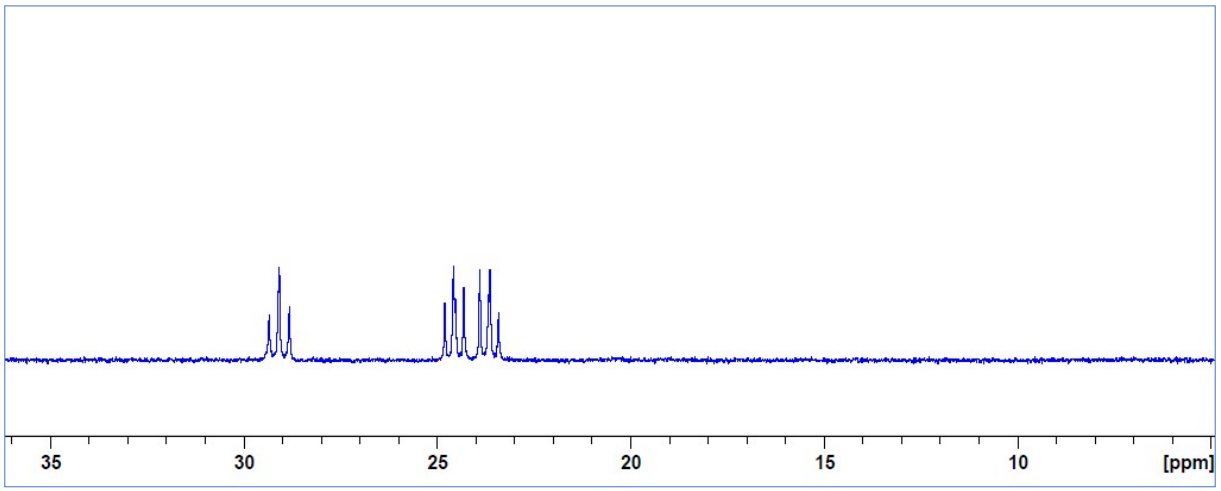
Reference:

1. C. F. Mackenzie, P. R. Spackman, D. Jayatilaka, M. A. Spackman, *IUCrJ* **2017**, *4*, 575.

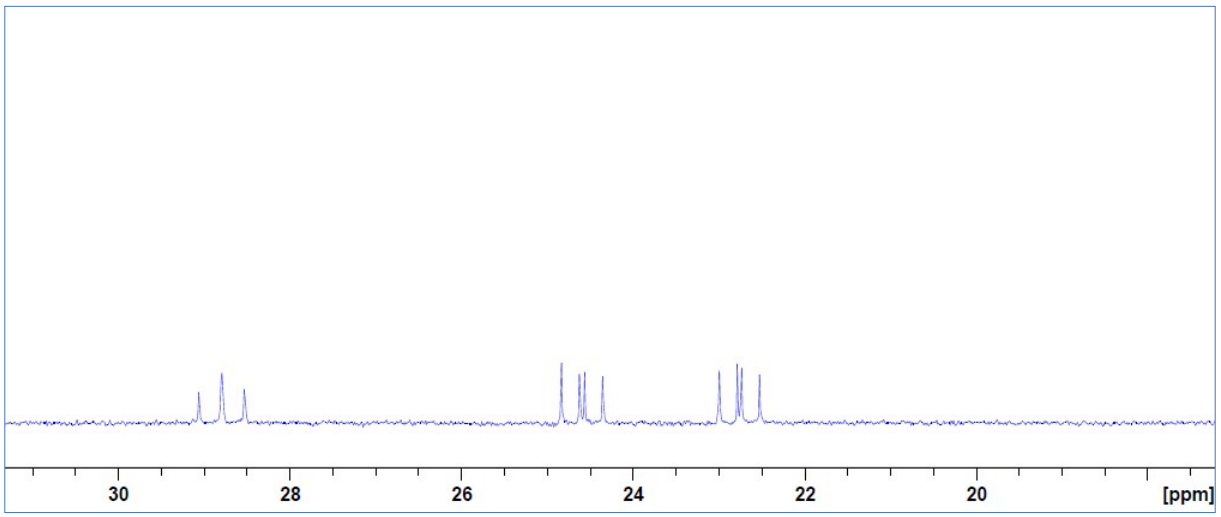
The ^{31}P NMR spectra of the phosphazenes



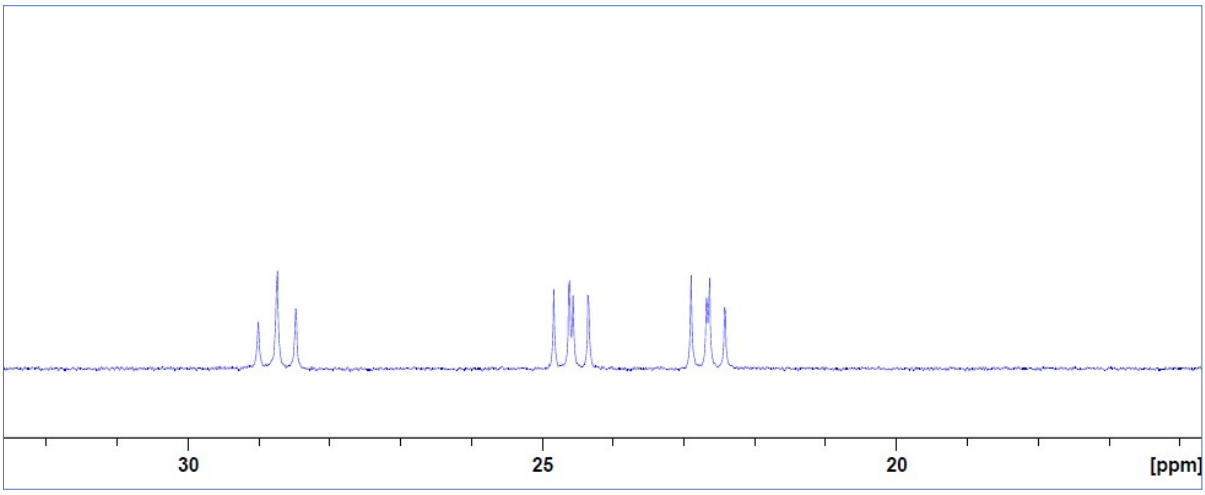
Compound trans-6a



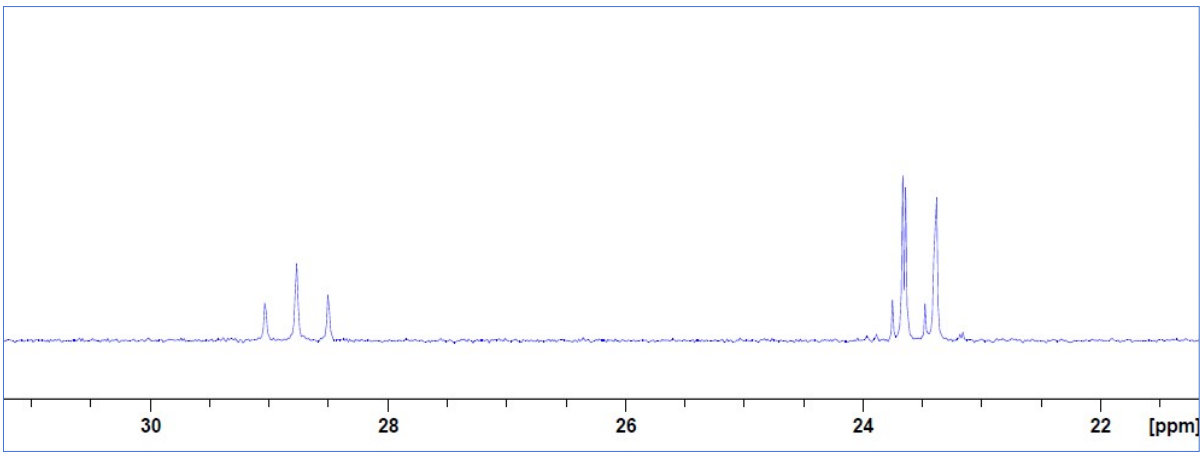
Compound cis-6b



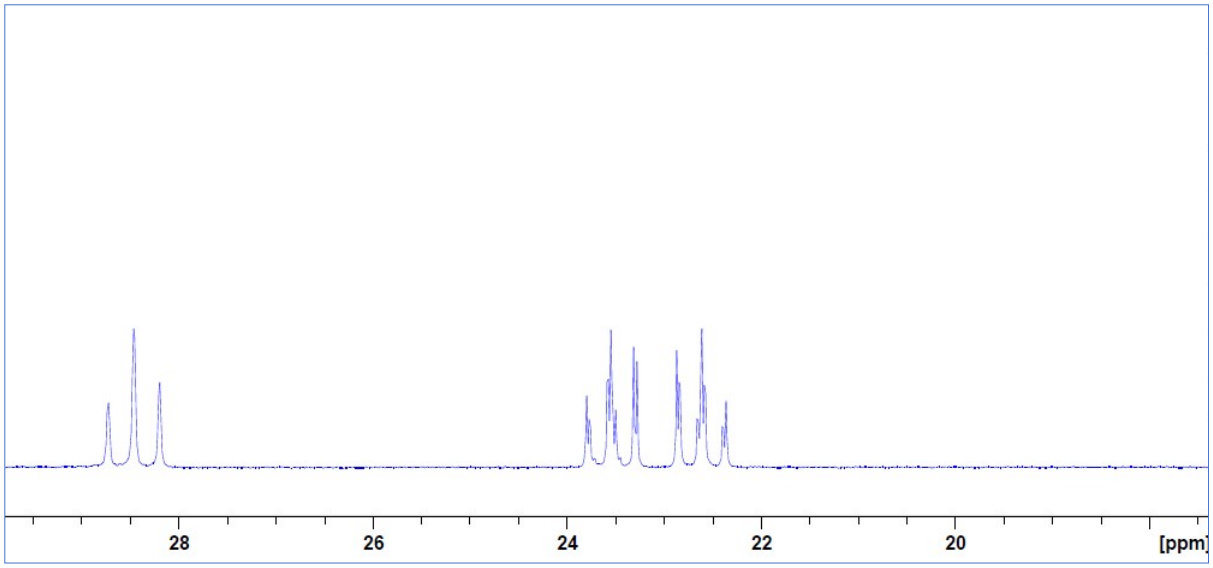
Compound trans-7a



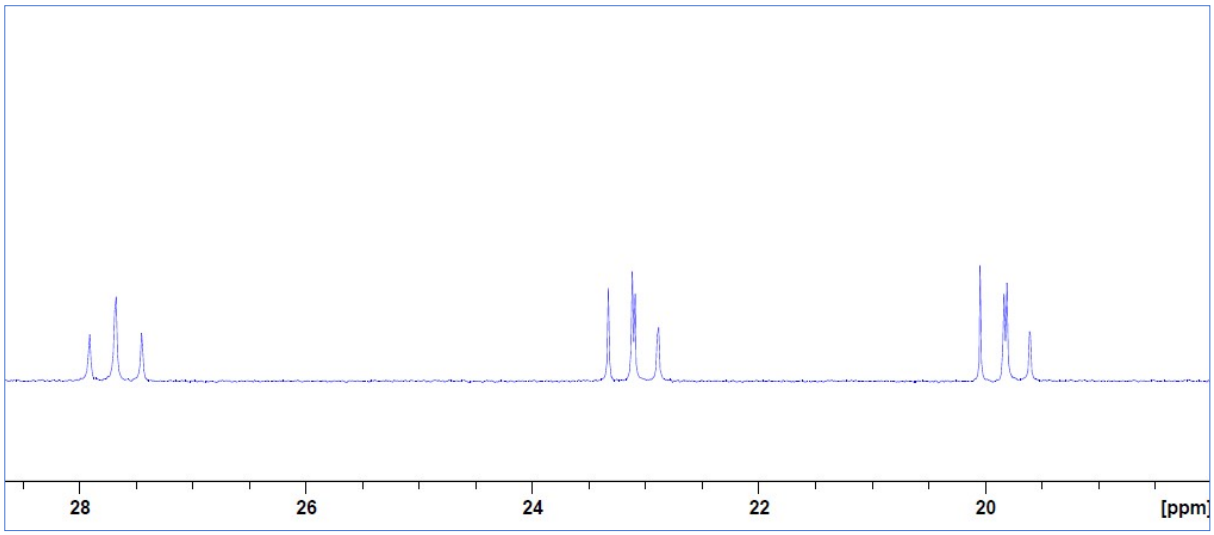
Compound cis-7b



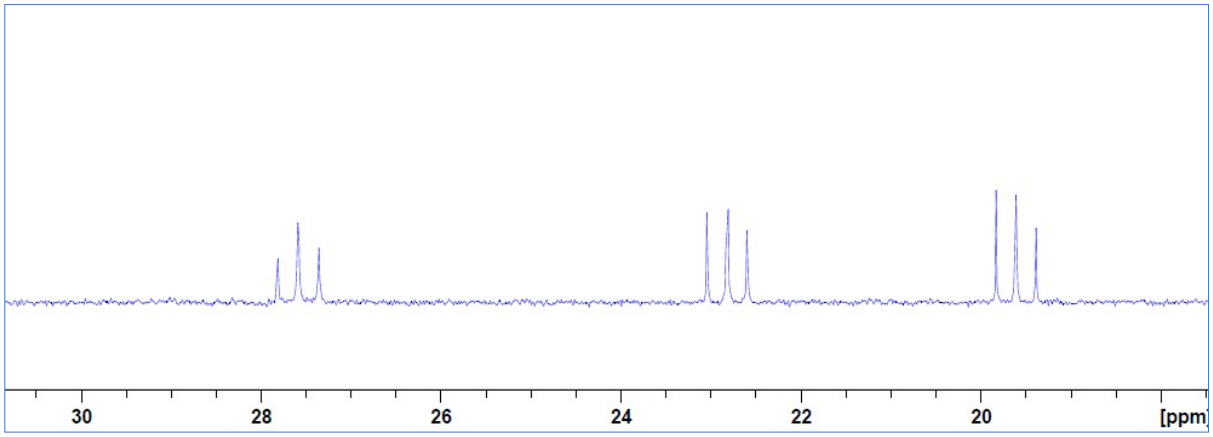
Compounds trans-8a and cis-8b



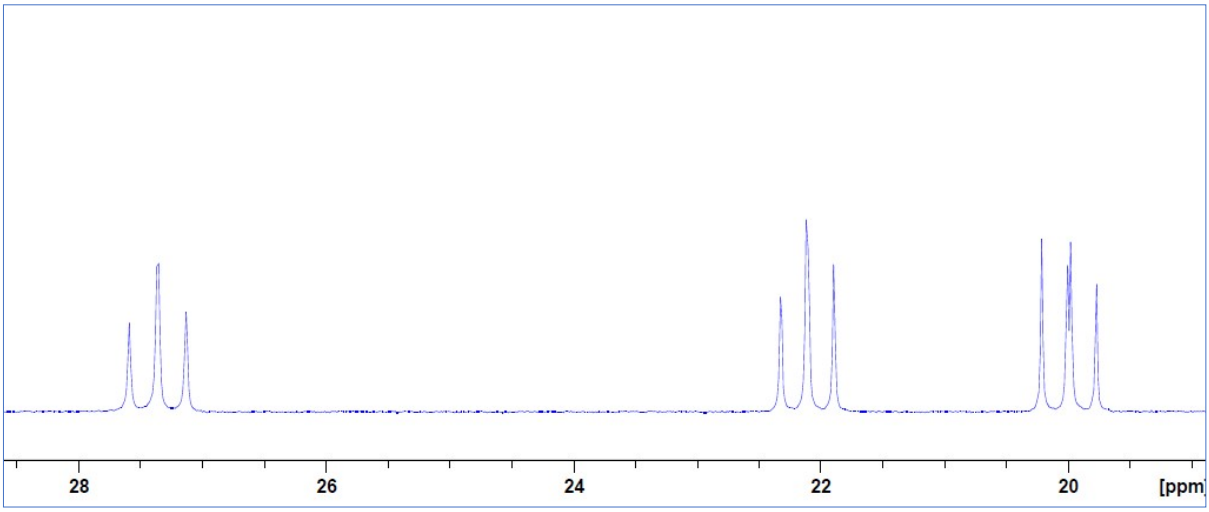
The mixture of compounds trans-9a and cis-9b



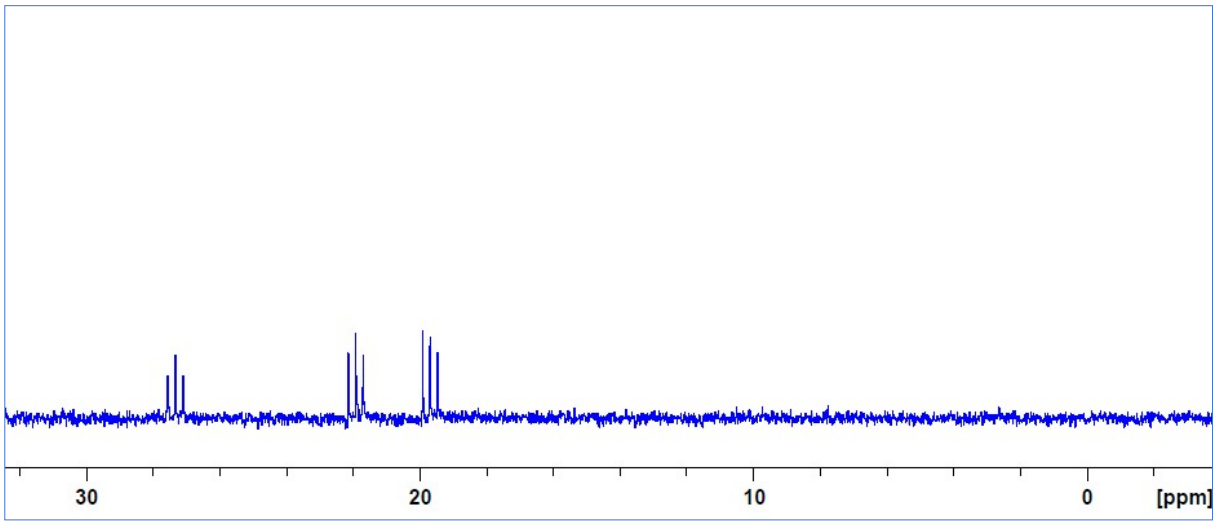
Compound trans-10a



Compound cis-10b

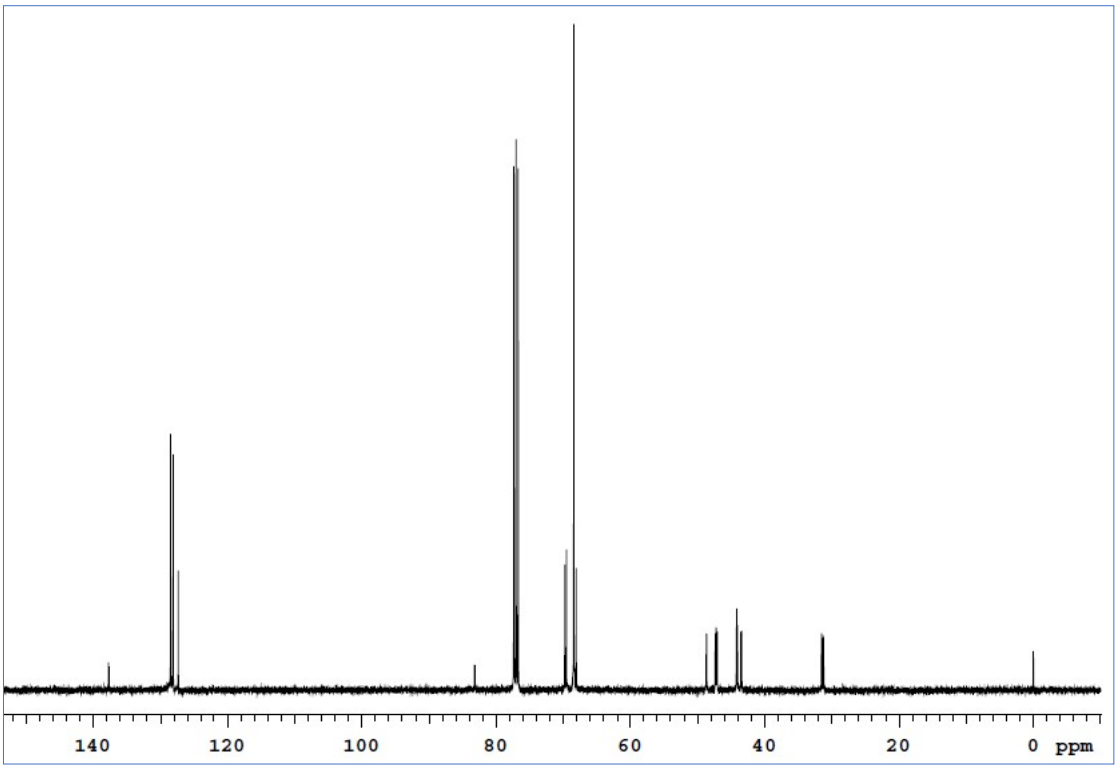


Compound trans-11a

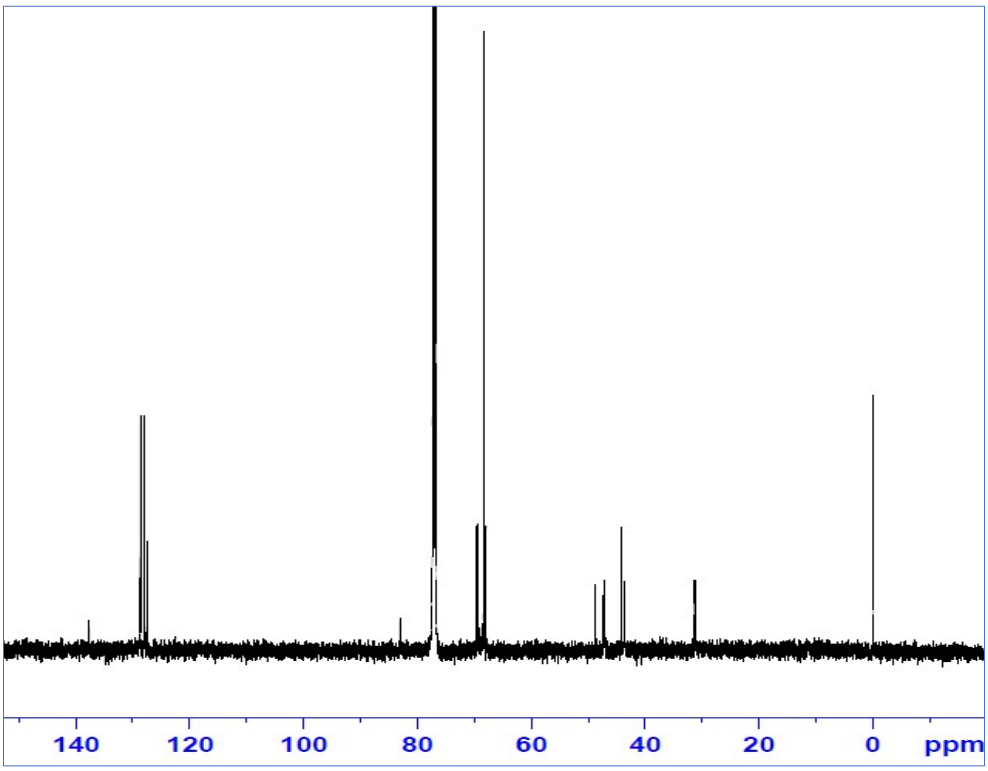


Compound cis-11b

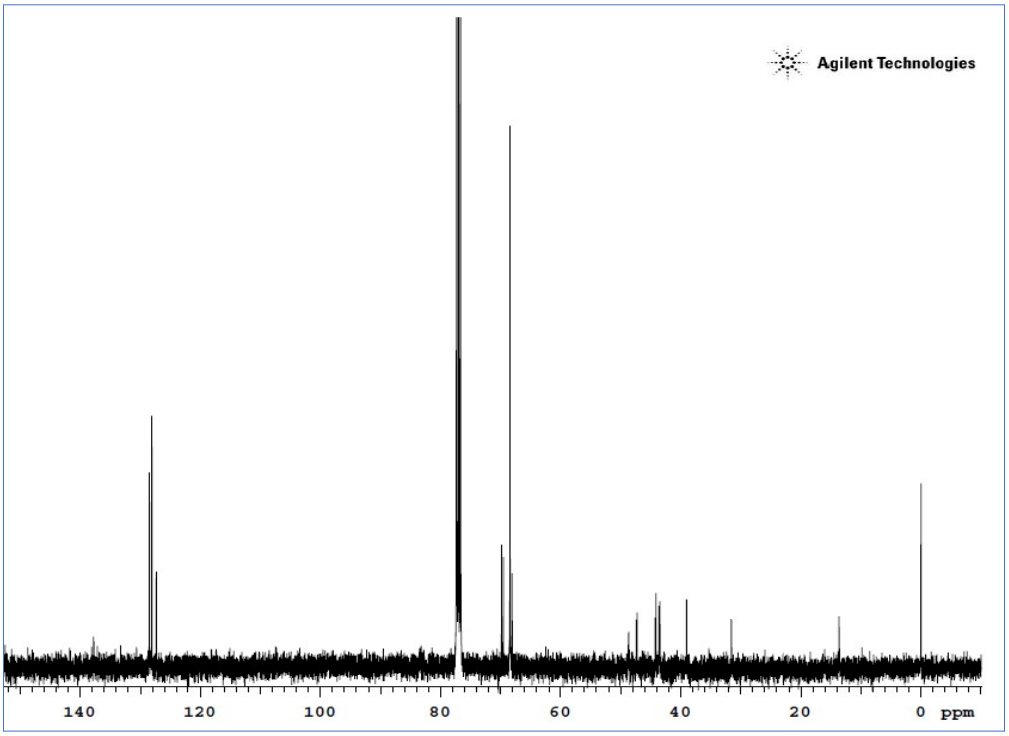
The ^{13}C NMR spectra of the phosphazenes



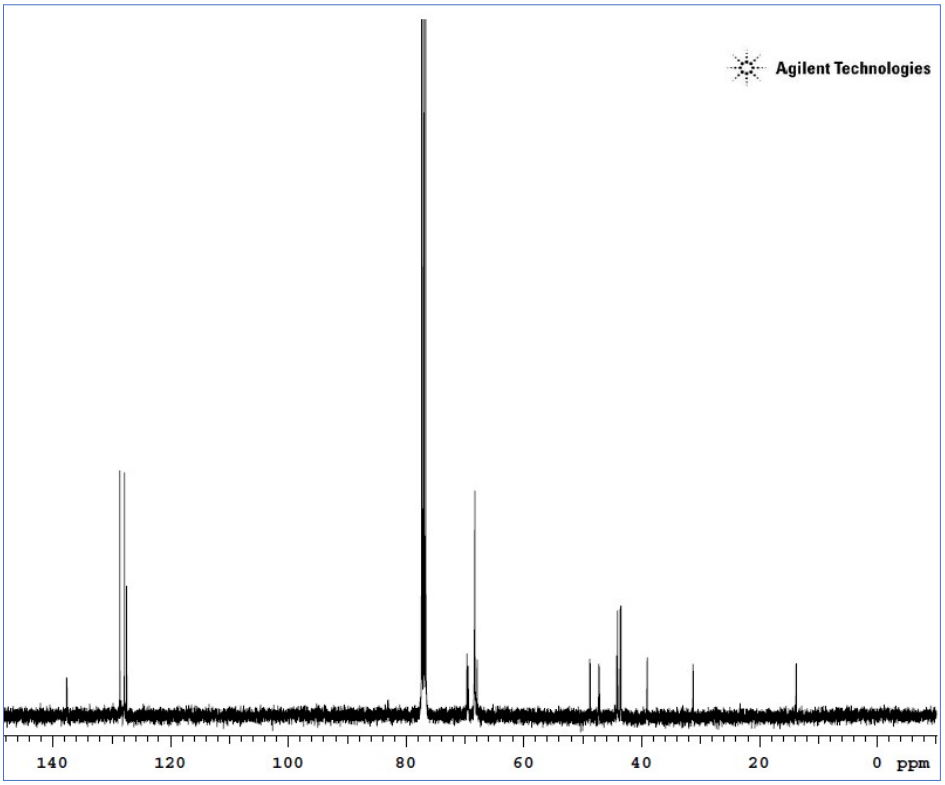
Compound trans-6a



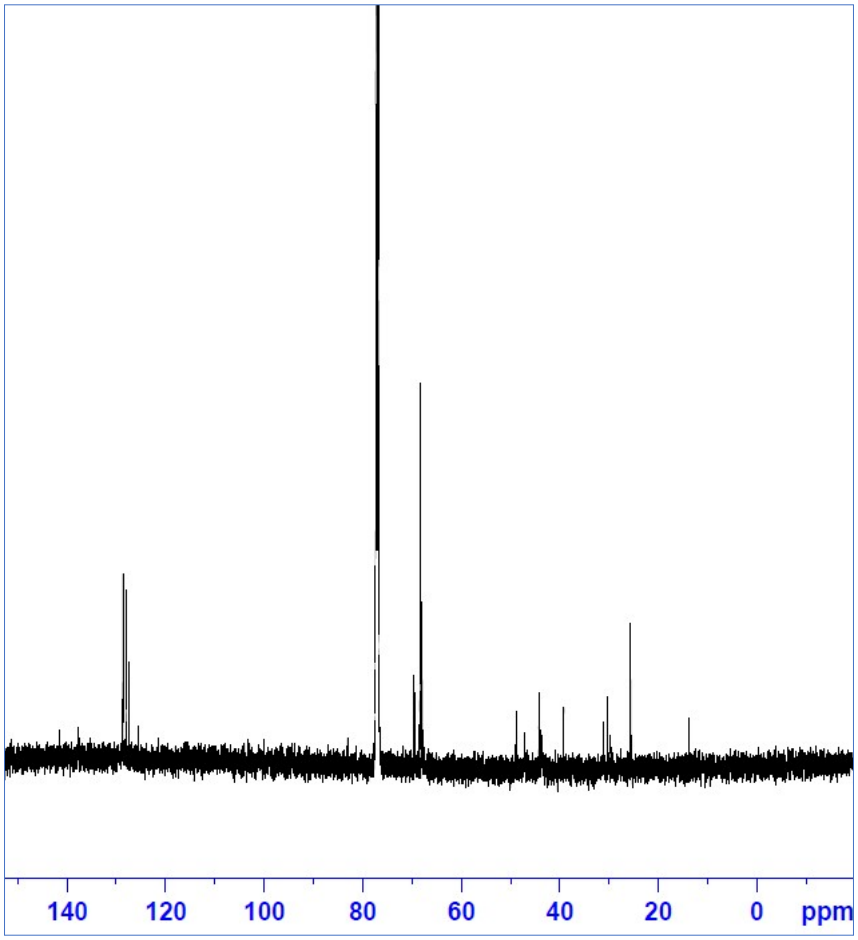
Compound cis-6b



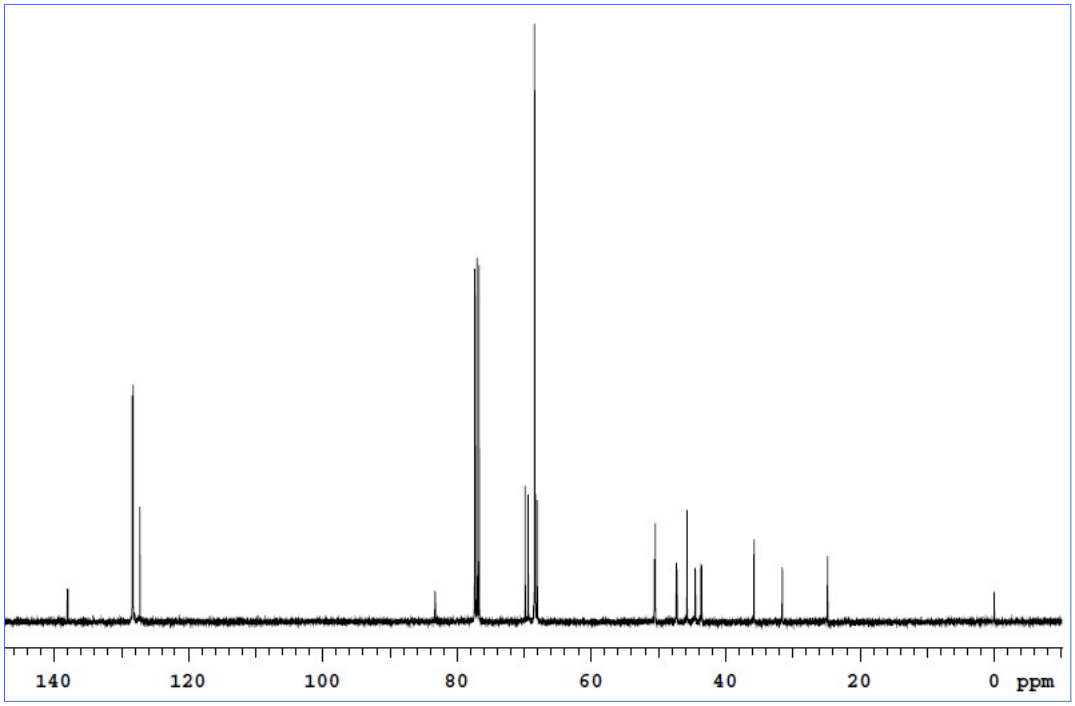
Compound trans-7a



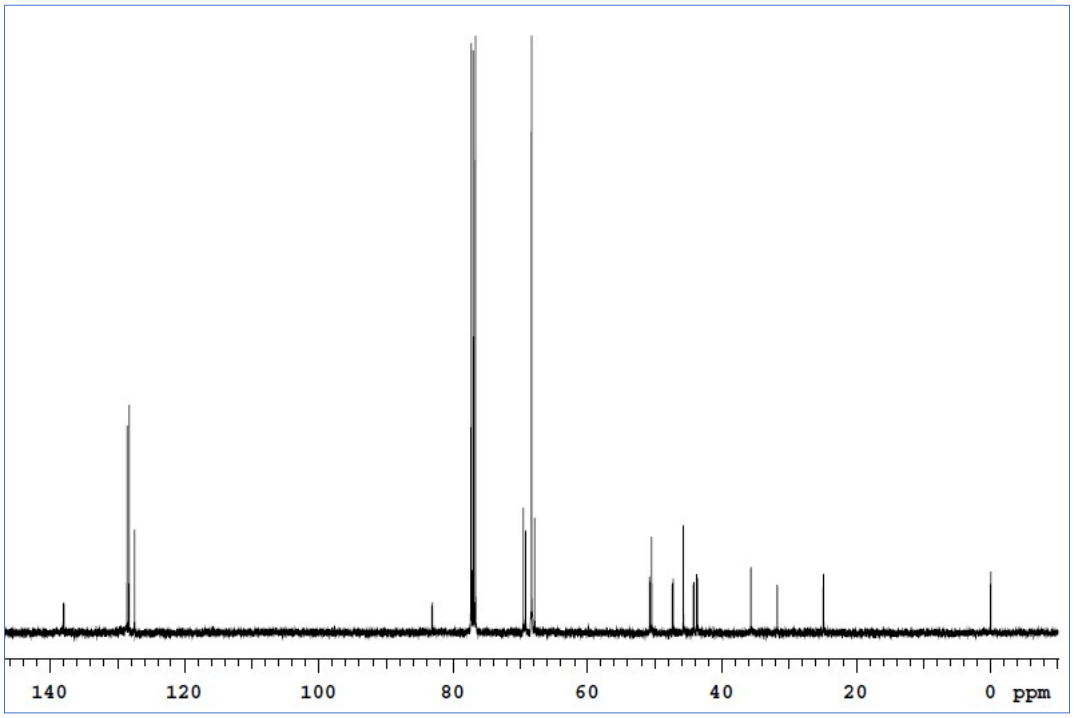
Compound cis-7b



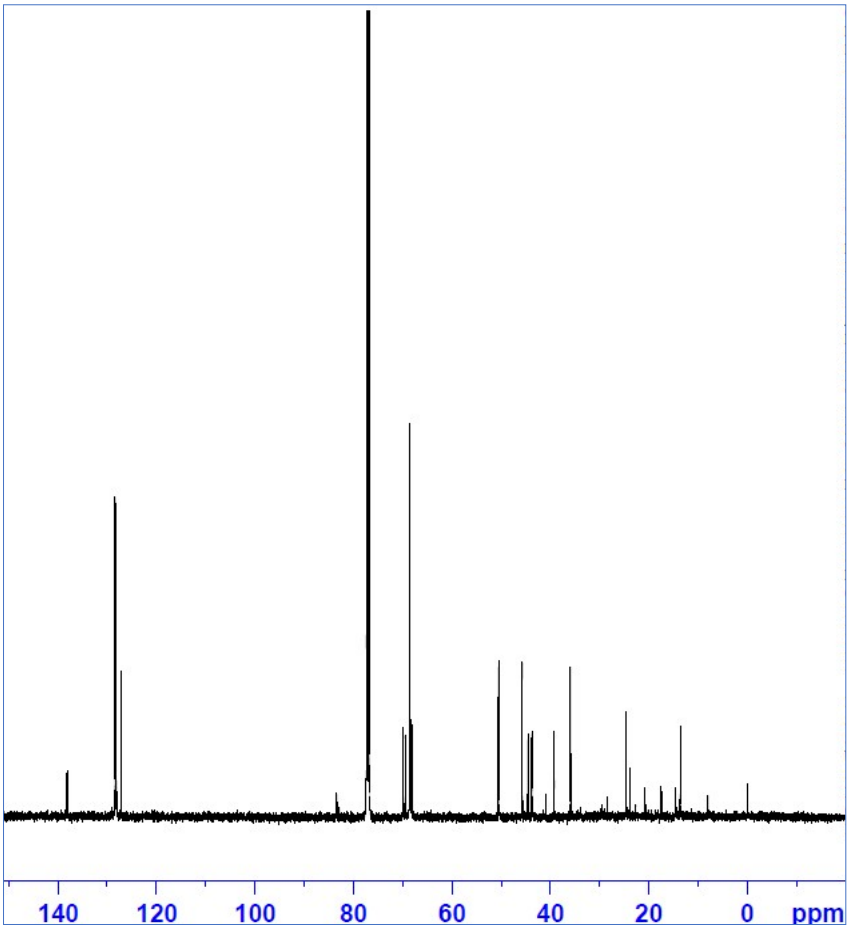
Compound cis-8b



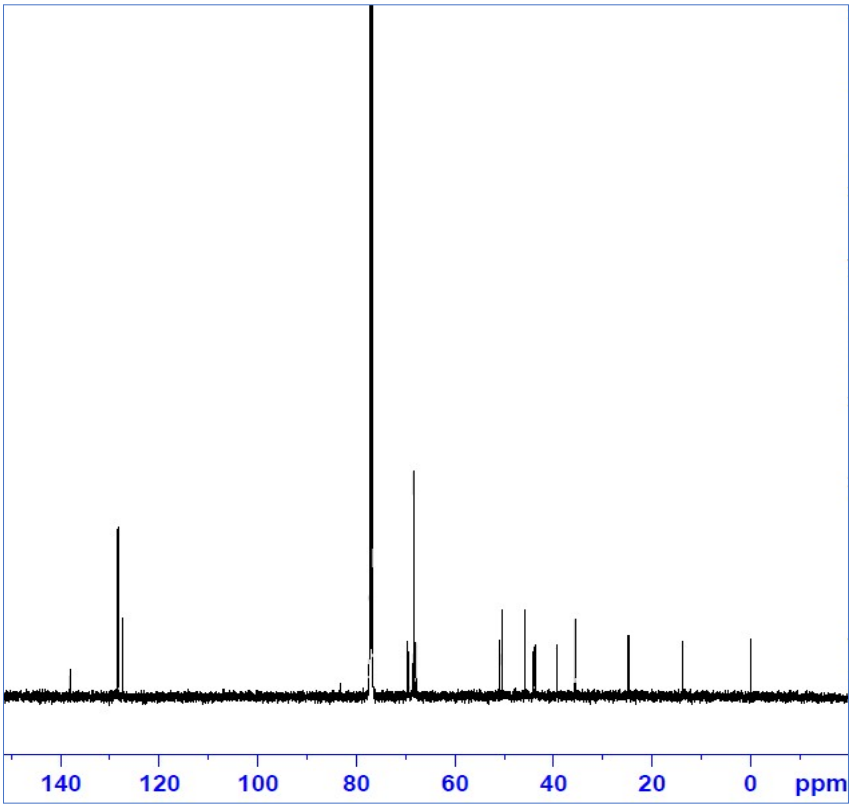
Compound trans-10a



Compound cis-10b

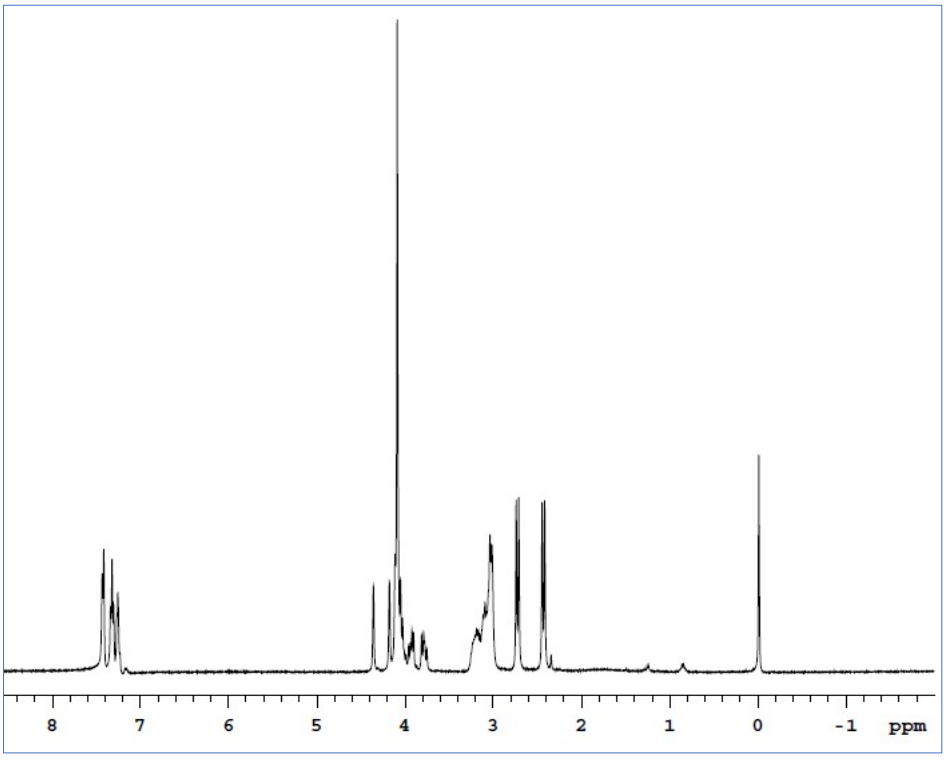


Compound trans-11a

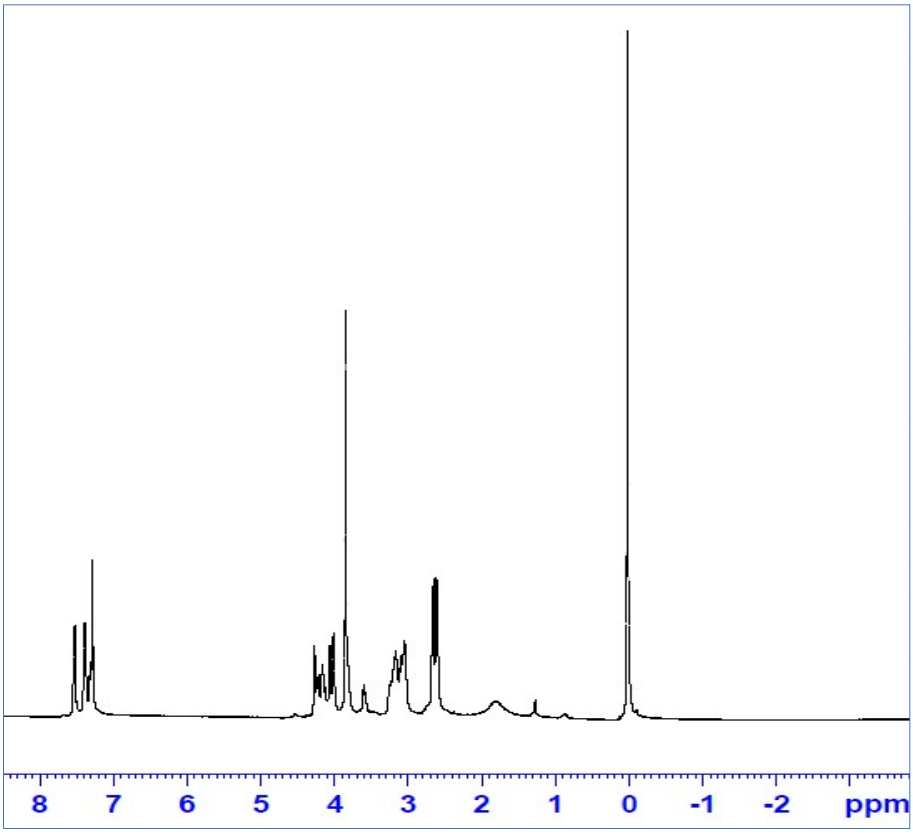


Compound cis-11b

The ^{1}H NMR spectra of the phosphazenes



Compound trans-6a



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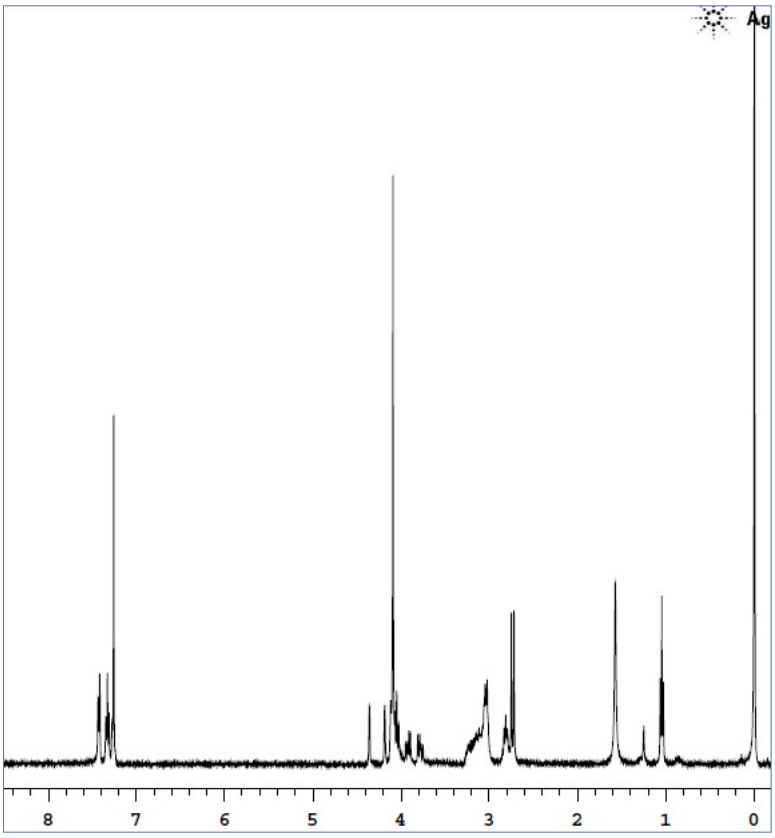

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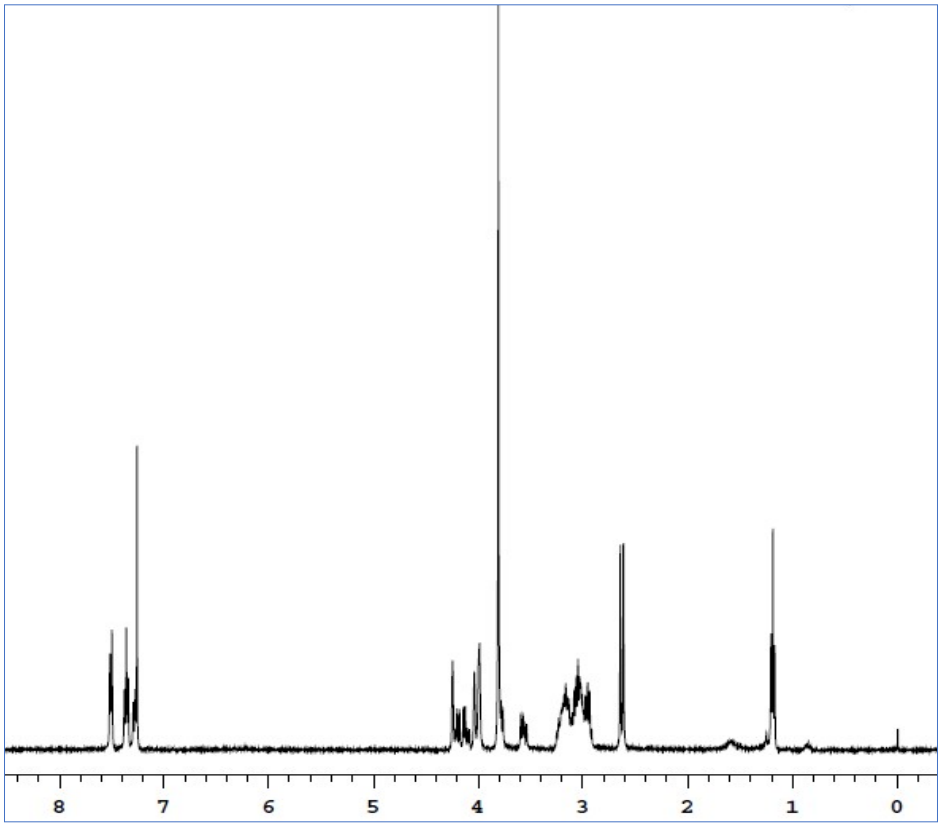

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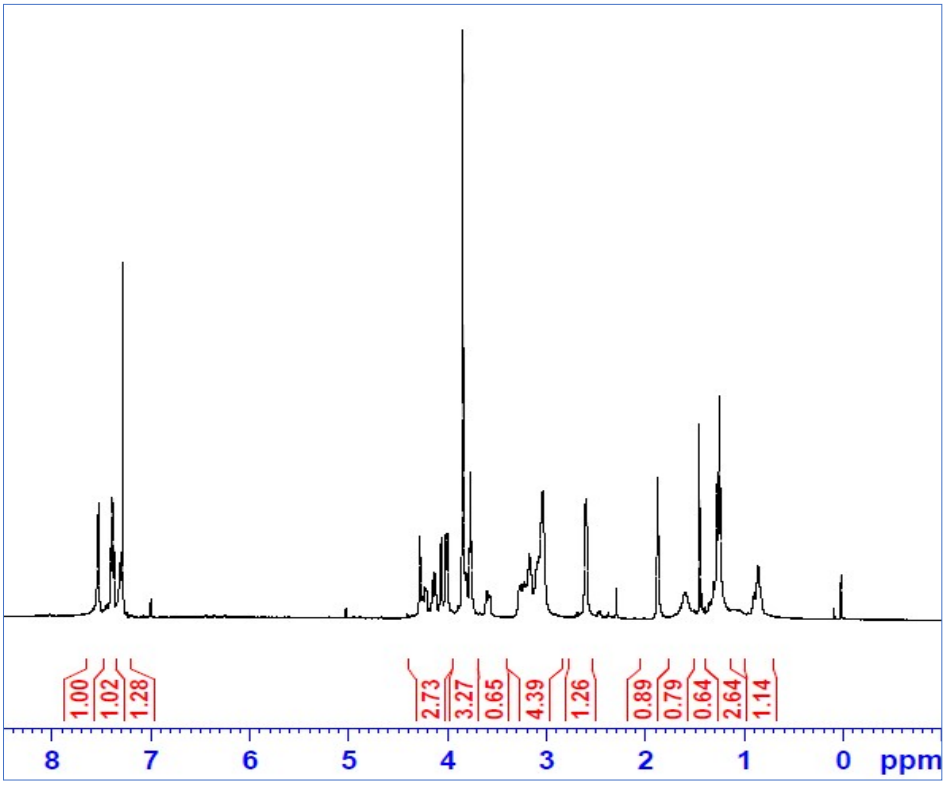
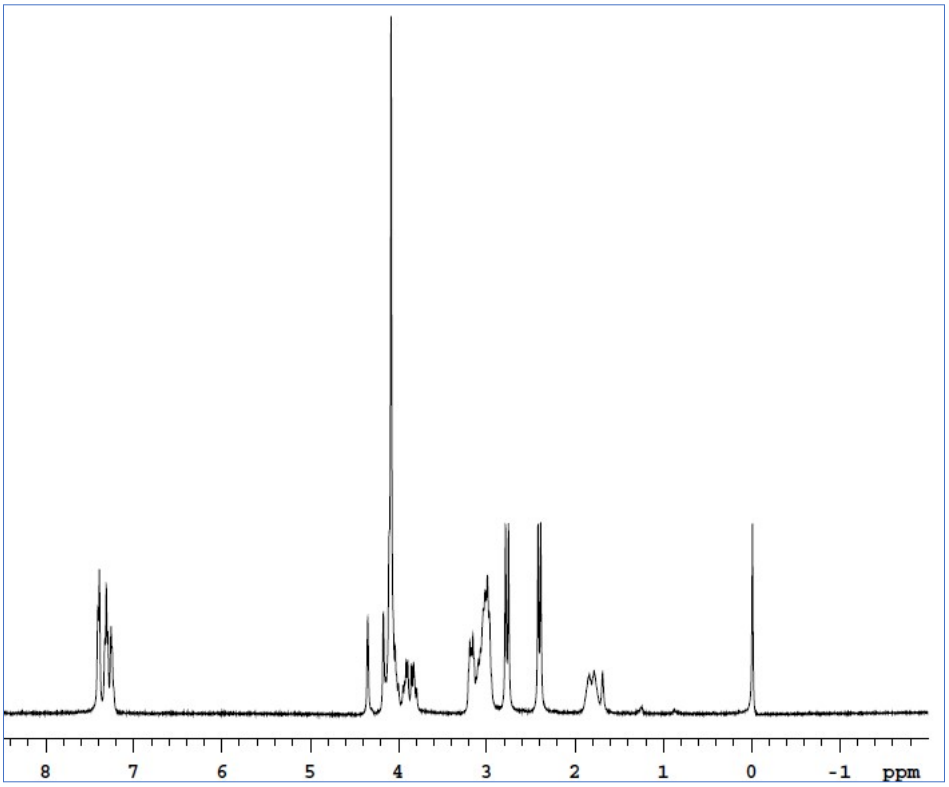
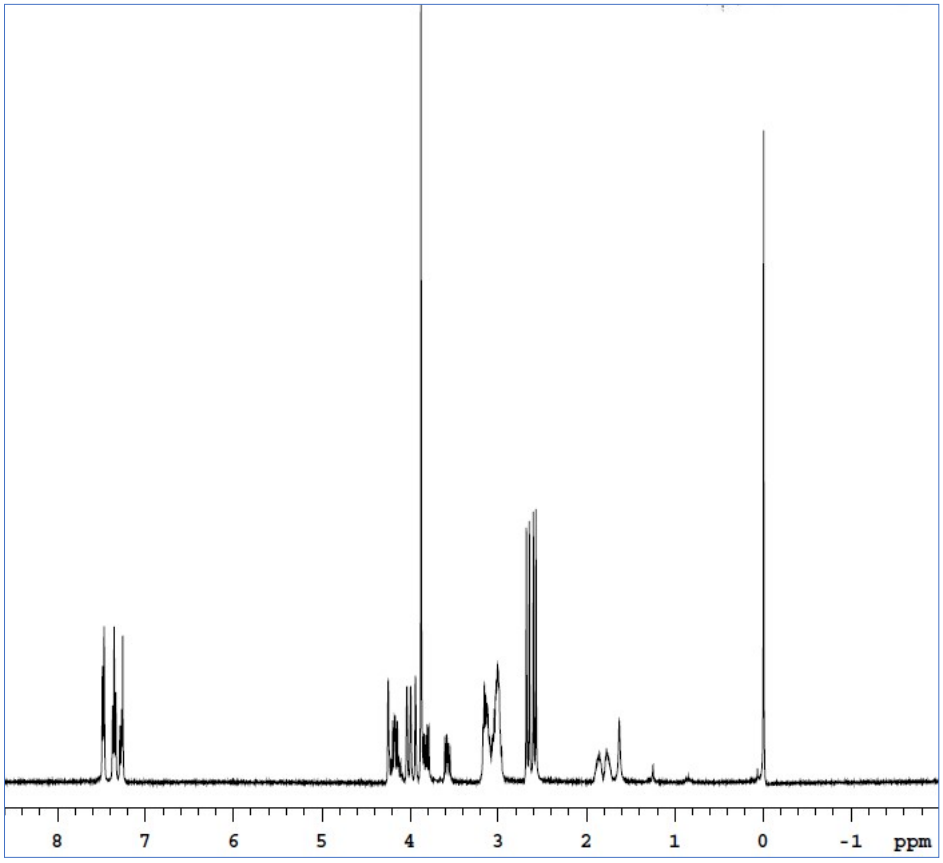


Compound cis-8b



Compound trans-10a



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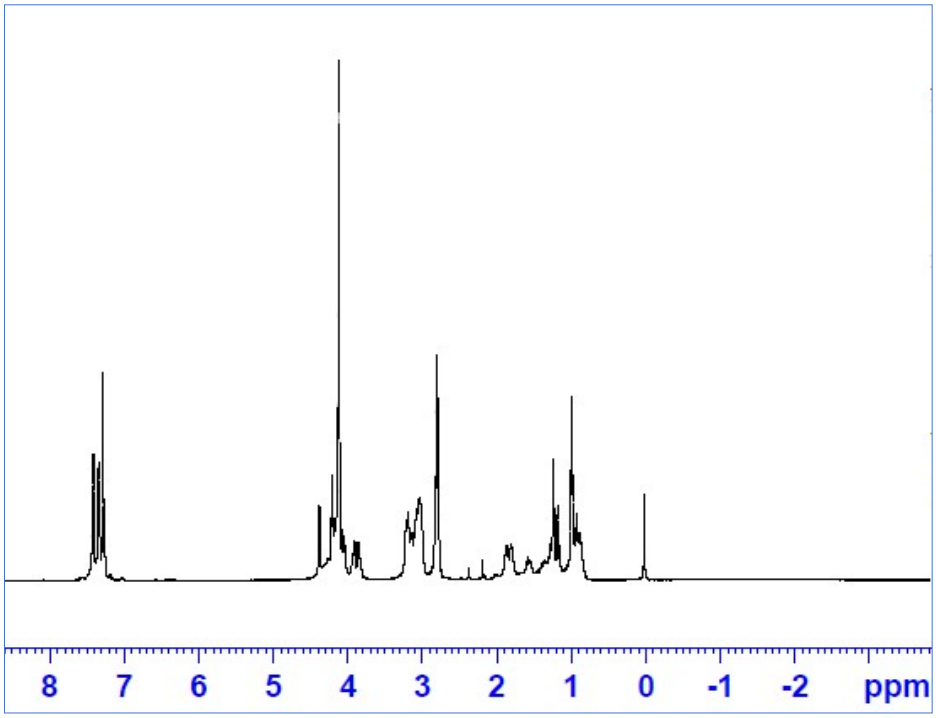
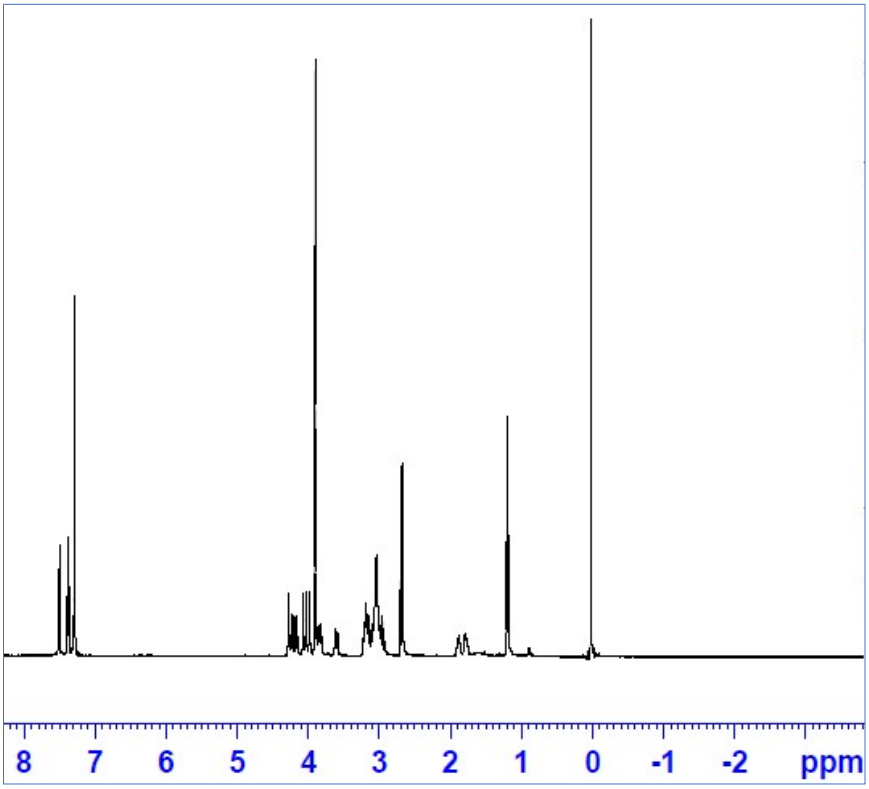


Compound trans-11a



Compound cis-11b