The Hendrickson reagent and the Mitsunobu reaction – a mechanistic study

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Electronic Supplementary Information

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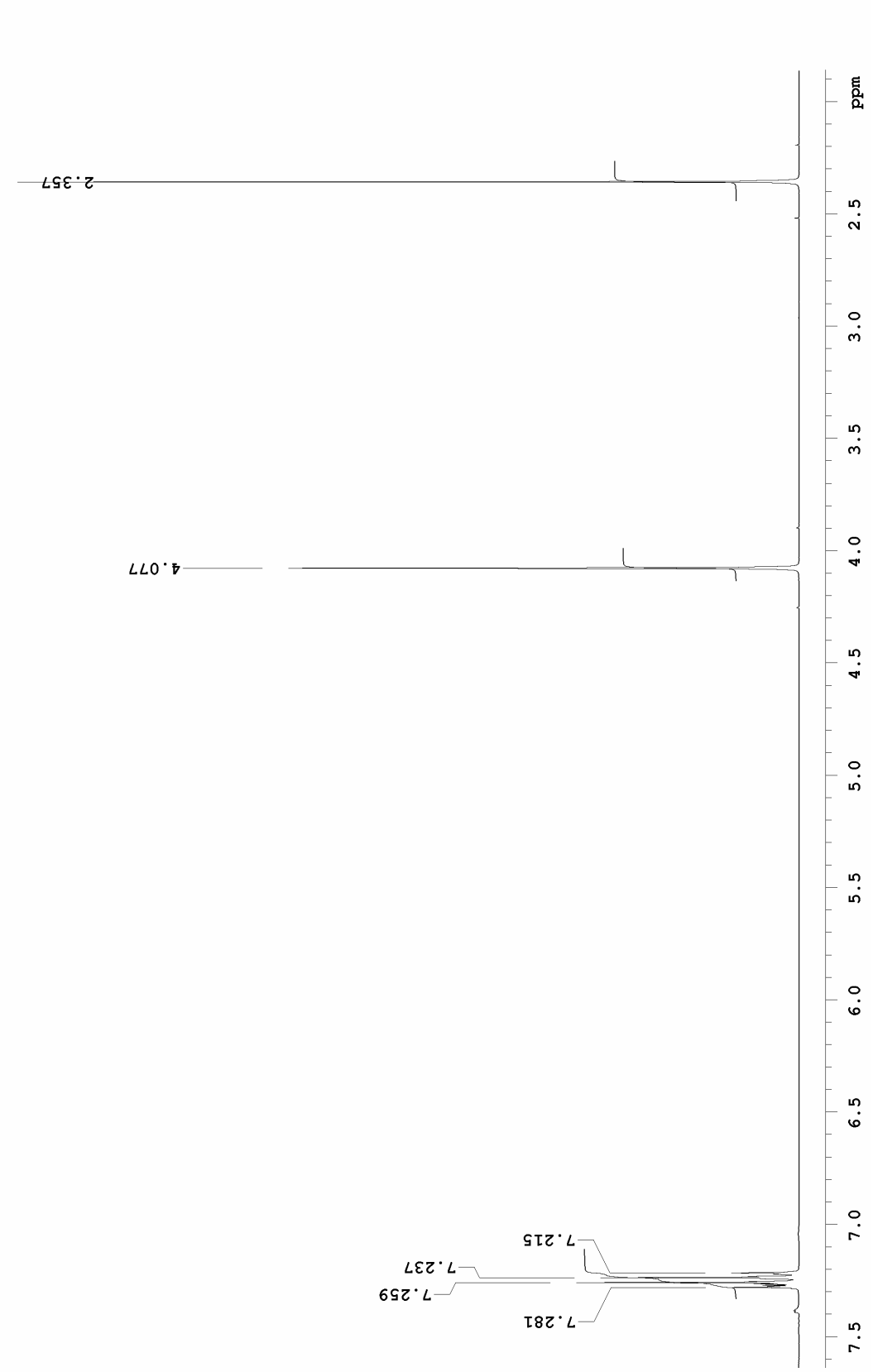

FIGURE S1. 4-Chlorobenzylthioacetate **3**, ^{1}H NMR spectrum.

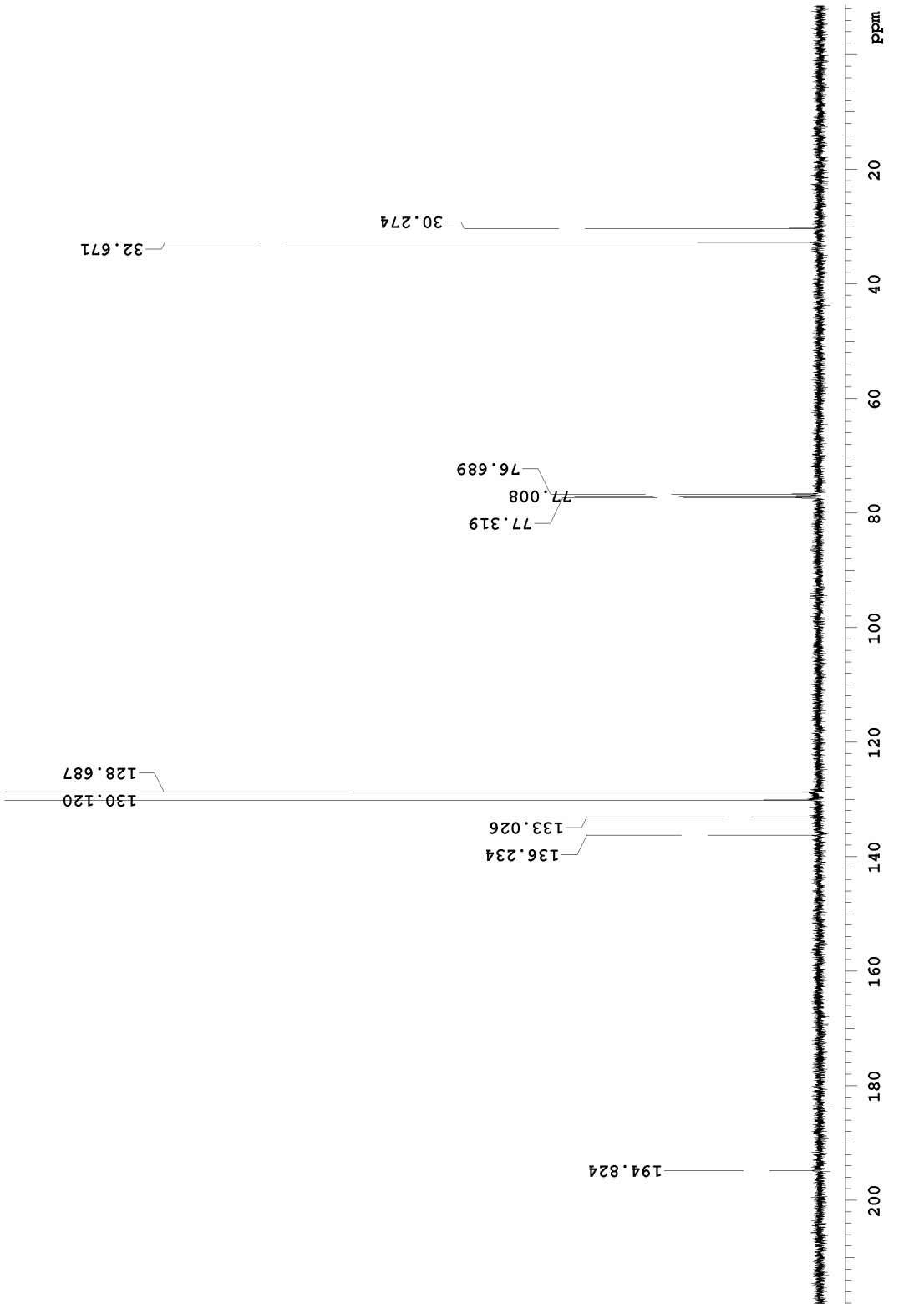

FIGURE S2. 4-Chlorobenzylthioacetate **3**, ^{13}C NMR spectrum.

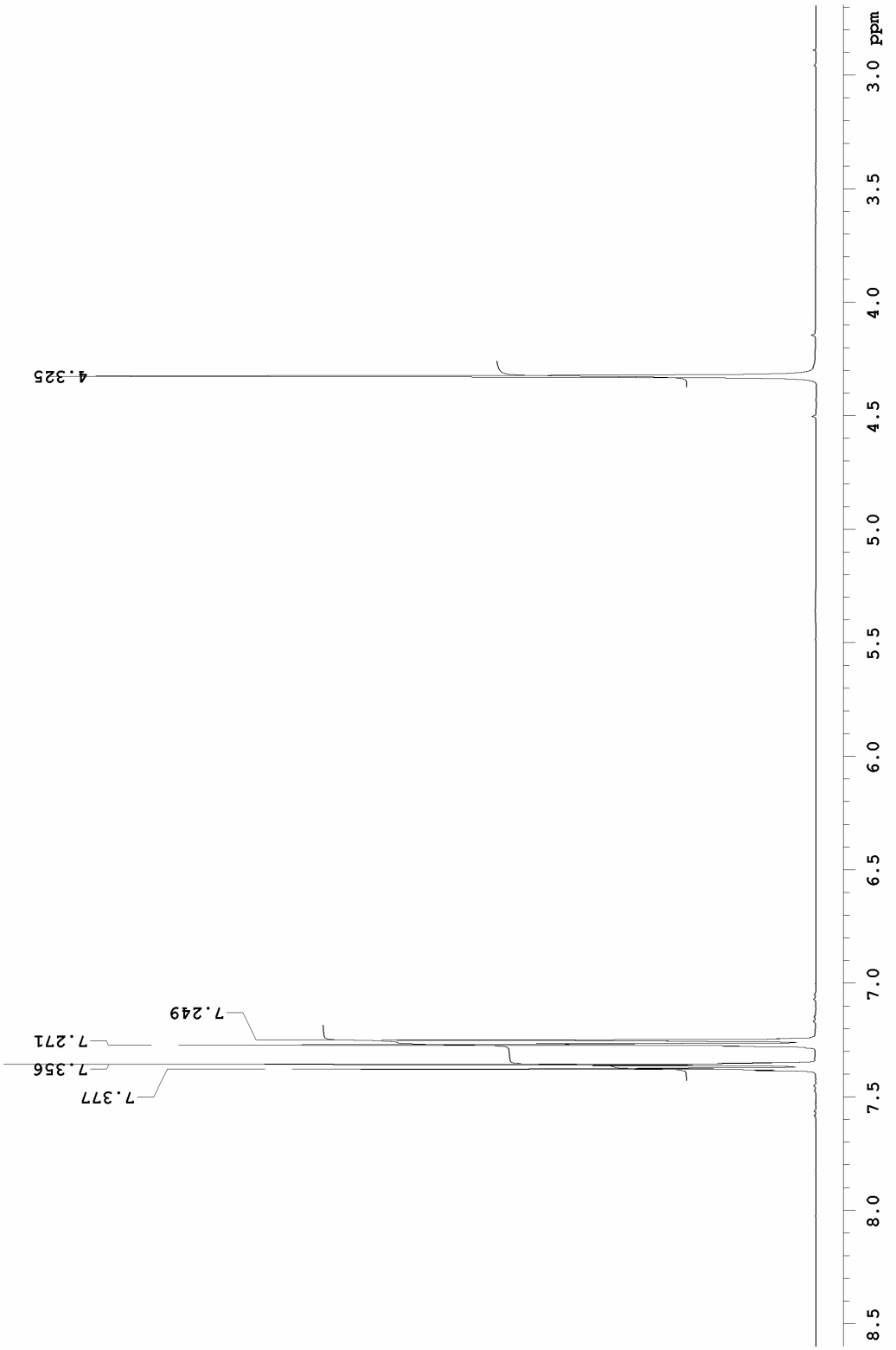

FIGURE S3. 4-Chlorobenzylazide **4**, ^{1}H NMR spectrum.

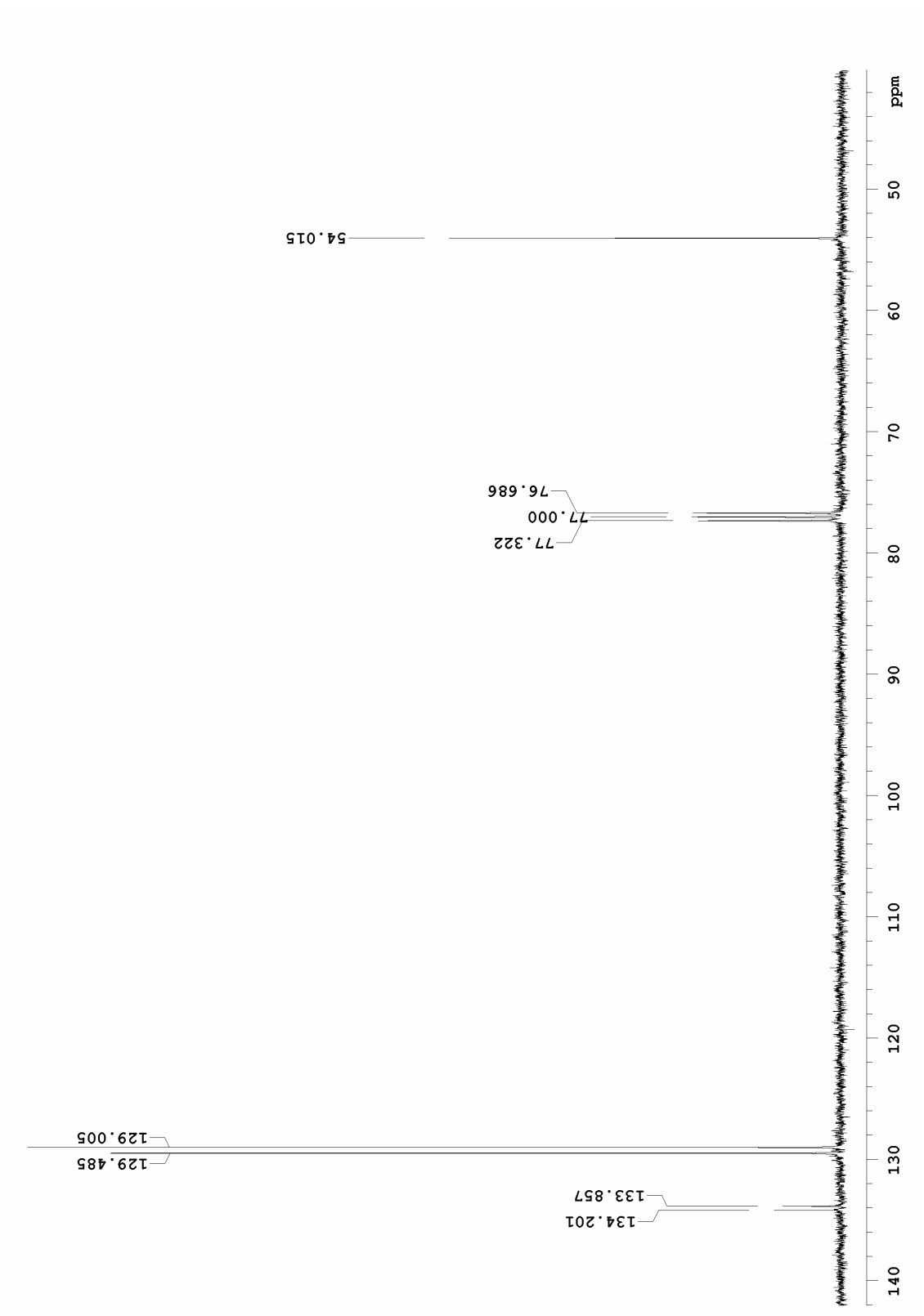

FIGURE S4. 4-Chlorobenzylazide **4**, ^{13}C NMR spectrum.

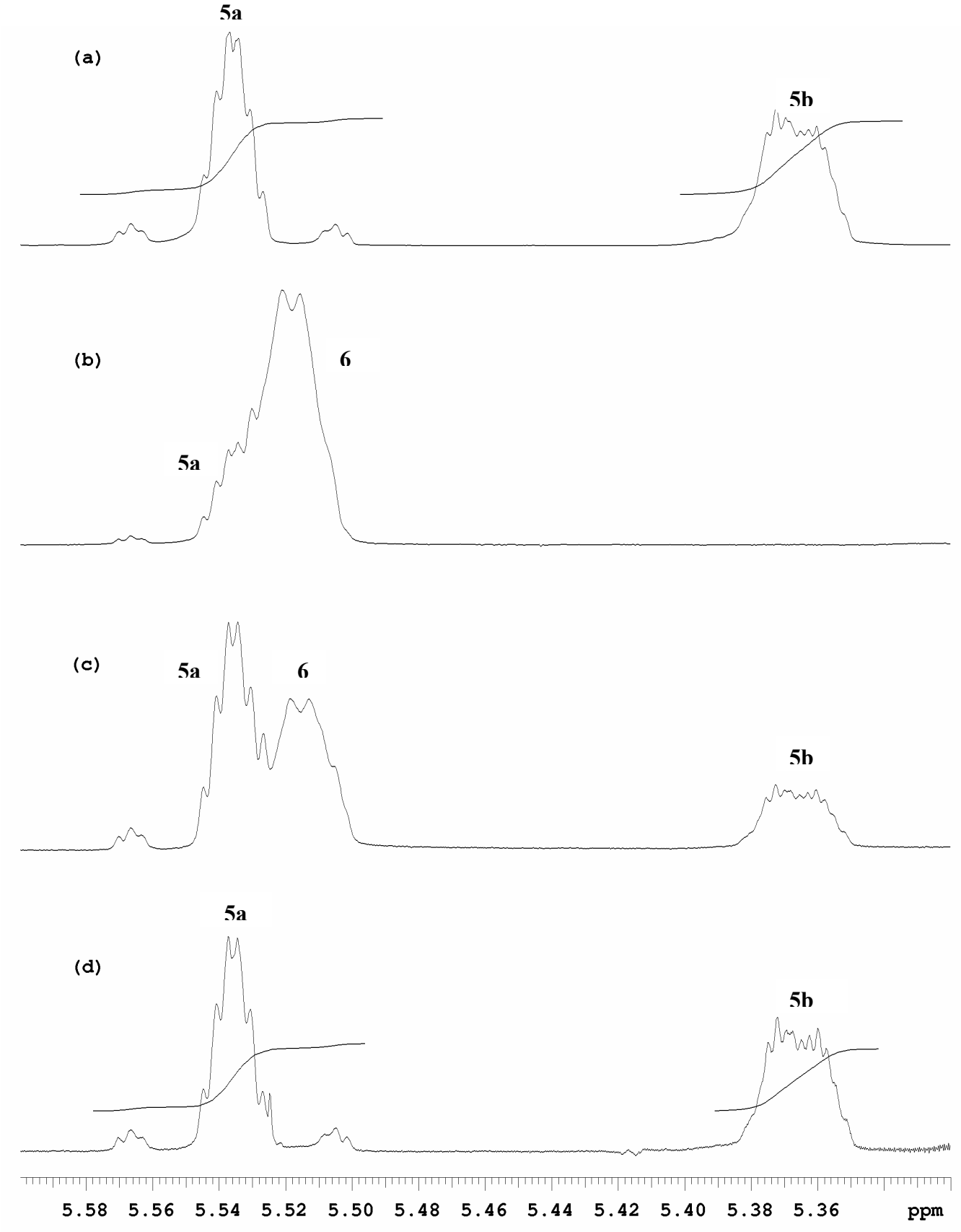

FIGURE S5. Menthenes **5a-5b** formed by (a) thermolysis of menthol diphenylphosphate ester[21]; (b) Mitsunobu reagents (Organic Syntheses conditions)[16]; (c) Hendrickson reagent (Table 1, entry 3) and (d) Hendrickson reagent (Table 1, entry 8).

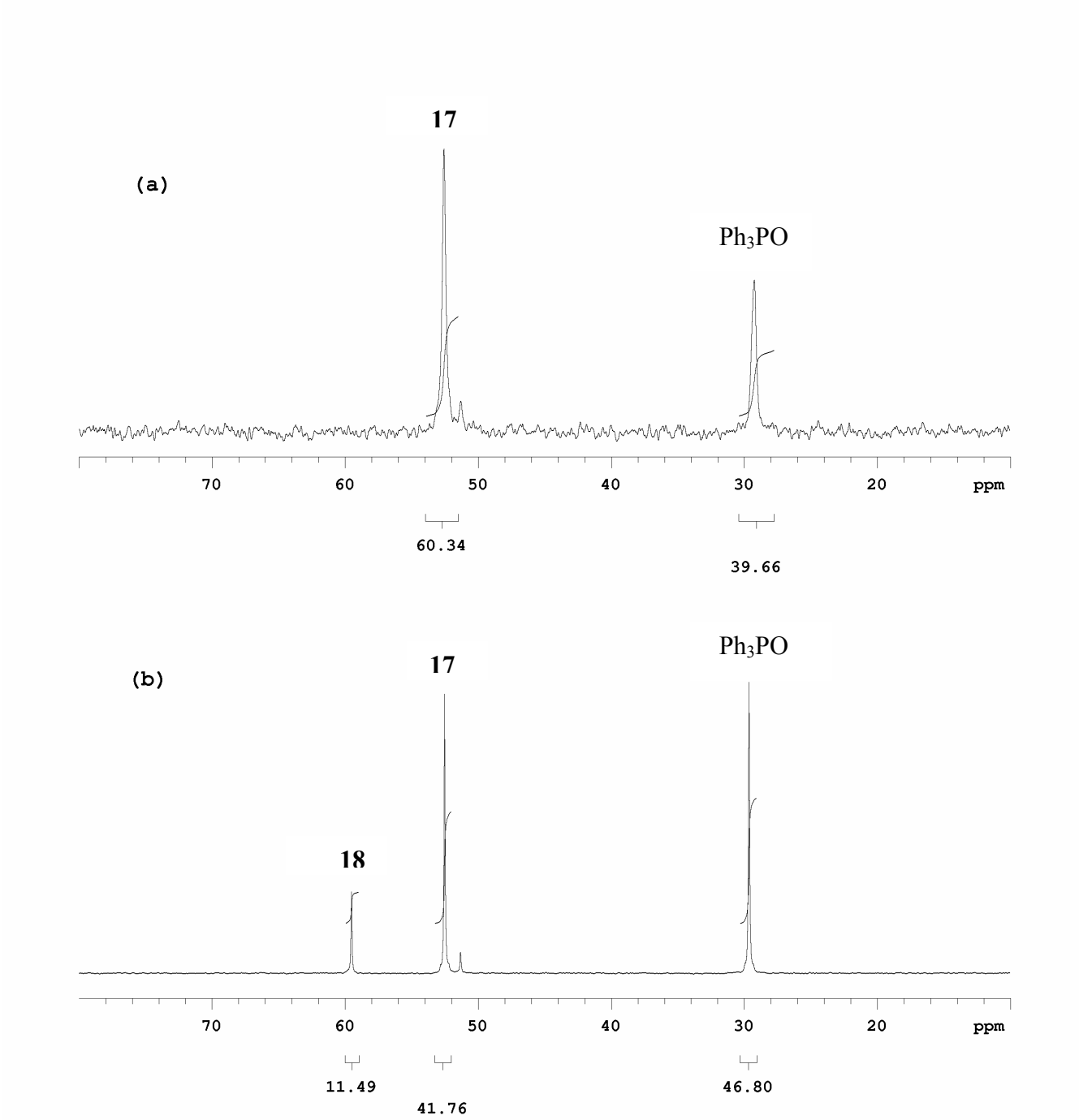

FIGURE S6. Mitsunobu reaction (PPh_3, DIAD, menthol and 4-nitrobenzoic acid in CD_2Cl_2) in the presence of diisopropylethylammonium triflate. (a) ^{31}P spectrum at 25°C following DIAD addition. (b) ^{31}P spectrum at 25°C after standing at room temperature for 24 hours.

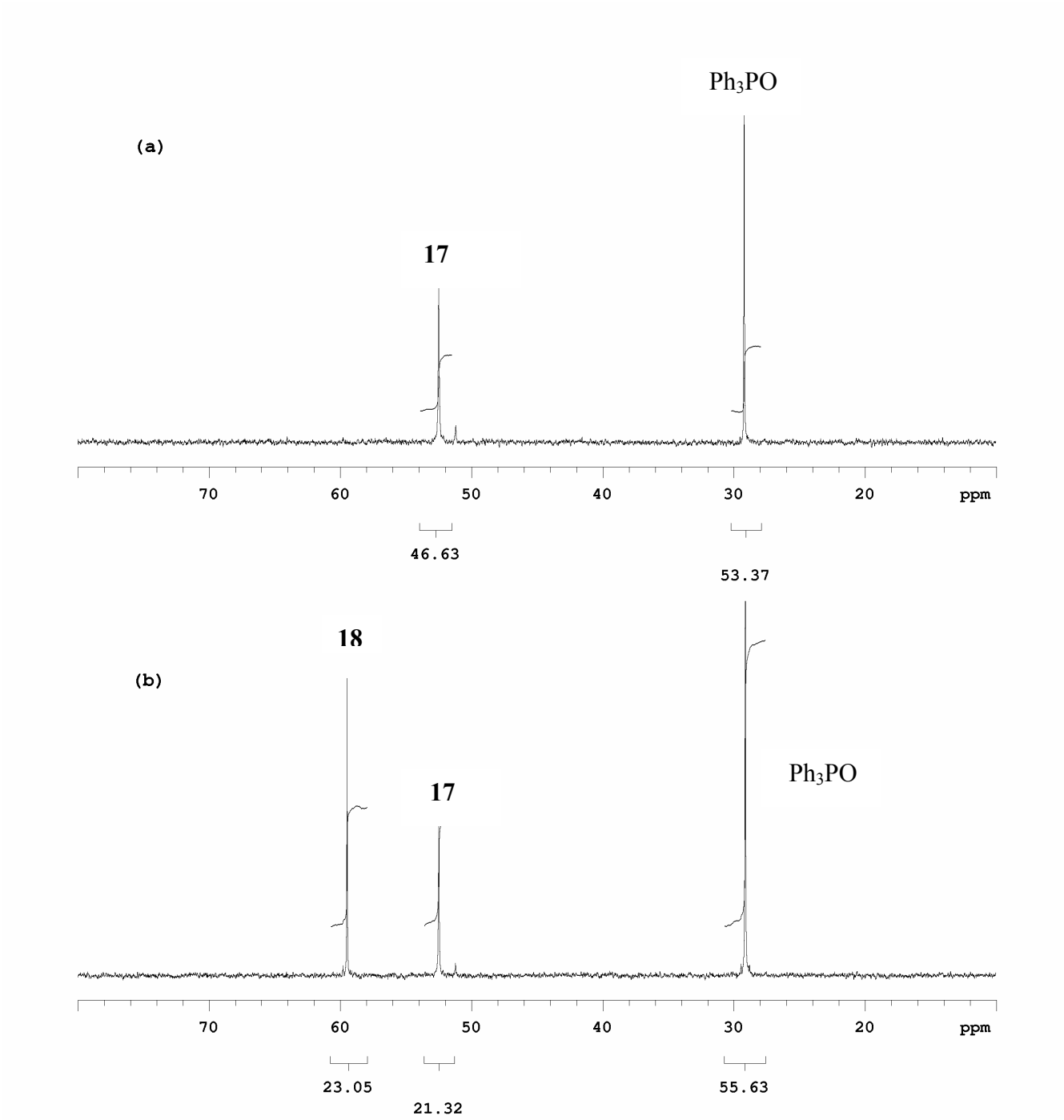

FIGURE S7. Mitsunobu reaction (PPh_3, DIAD, menthol and 4-nitrobenzoic acid in CD_2Cl_2) in the presence of diisopropylethylammonium triflate and diisopropylethylamine (2 eq). (a) ^{31}P spectrum at 25°C following DIAD addition. (b) ^{31}P spectrum at 25°C after standing at room temperature for 24 hours.

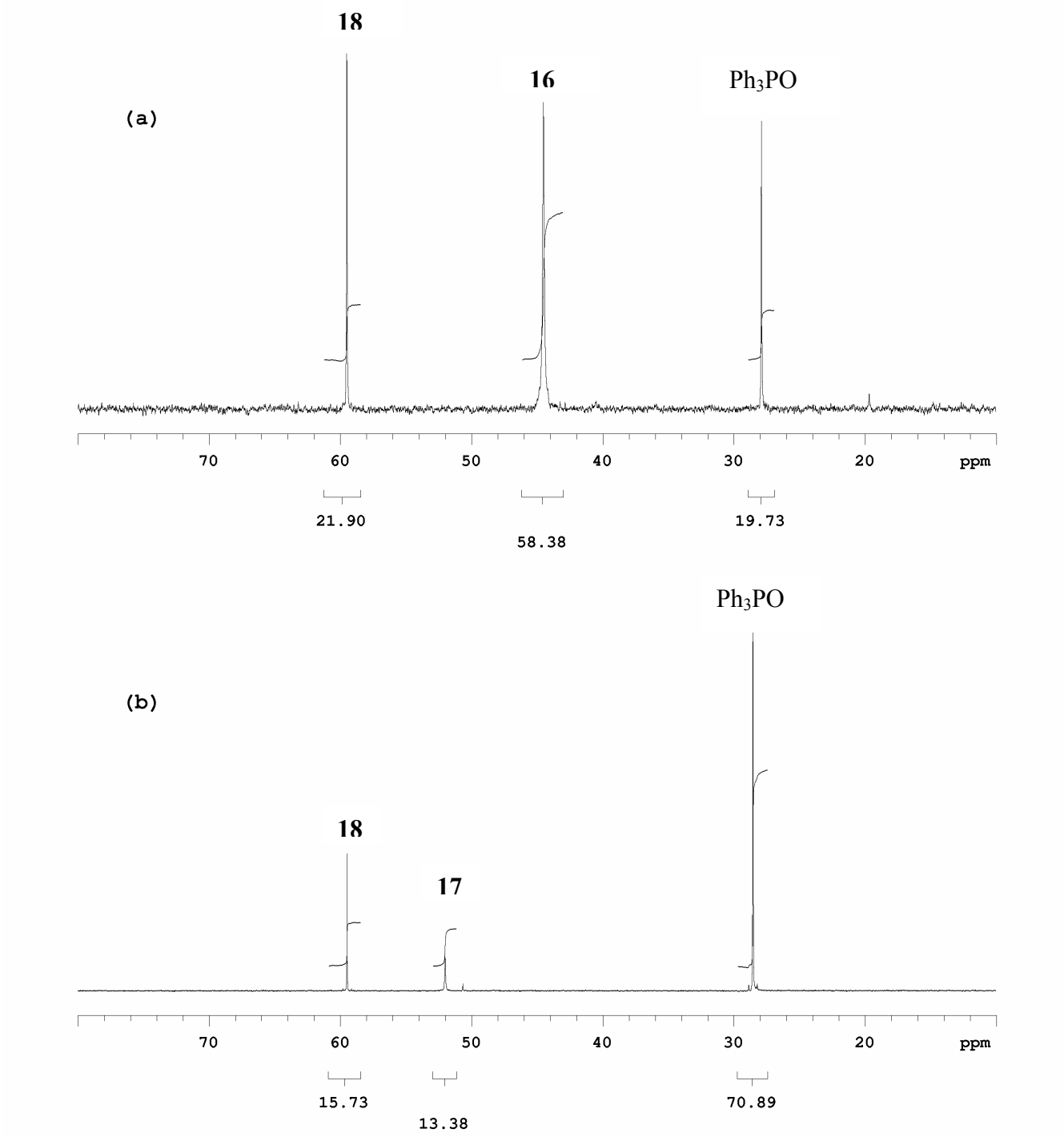

FIGURE S8. Mitsunobu reaction (PPh_3, DIAD, menthol and 4-nitrobenzoic acid in CD_2Cl_2) in the presence of tetrabutylammonium triflate (1 eq). (a) ^{31}P spectrum at 25°C following DIAD addition. (b) ^{31}P spectrum at 25°C after standing at room temperature for 24 hours.

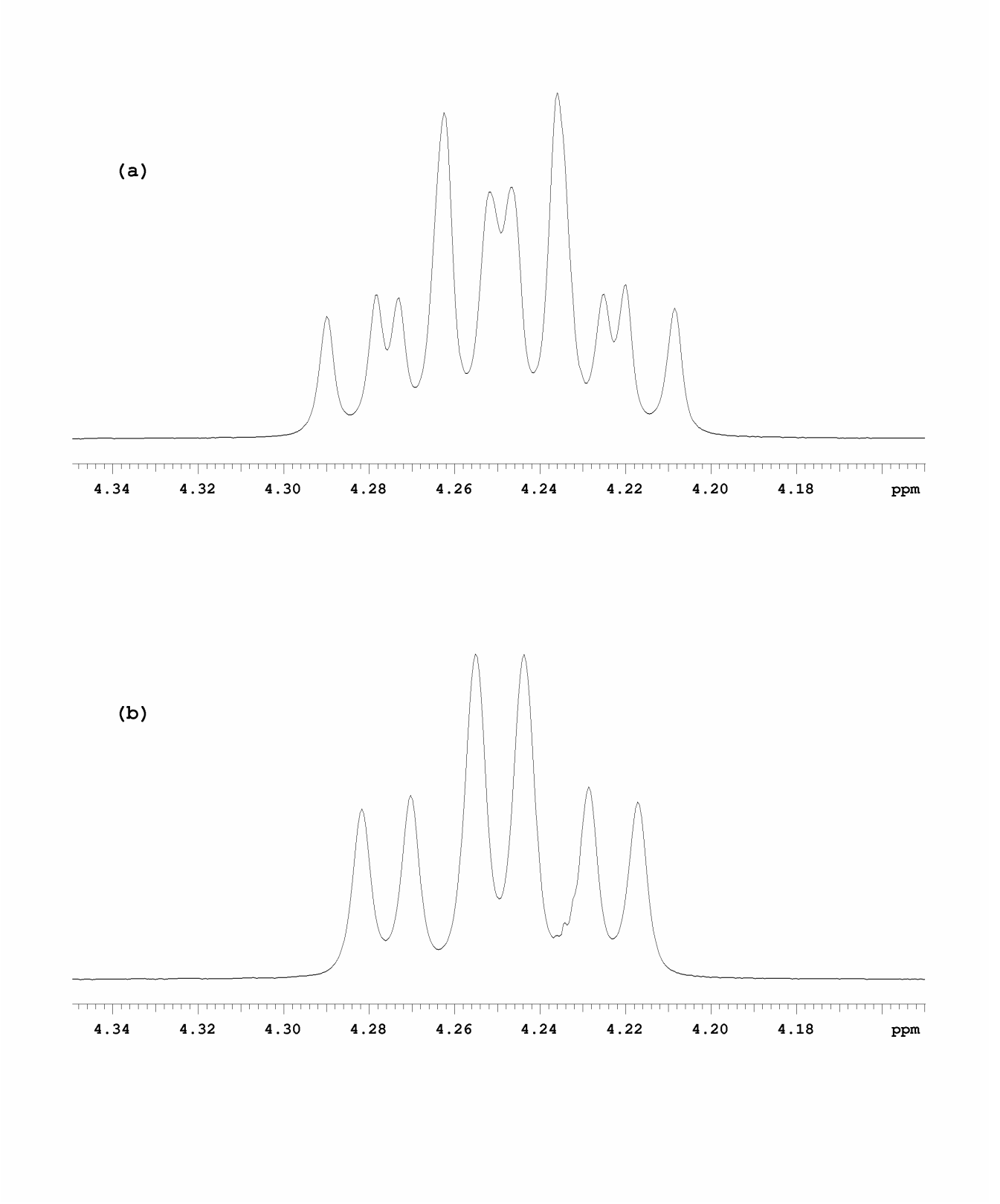

FIGURE S9. (-)-Menthoxytriphenylphosphonium triflate **11**, H3. (a) ^{1}H NMR spectrum. (b) $^{1}H\{^{31}P\}$ NMR spectrum.

TABLE 2. The effect of added tetrabutylammonium triflate on the outcome of the Mitsunobu reaction between *l*-(-)-menthol and 4-nitrobenzoic acid.[a]

Entry	Bu_4NOTf (eq)	GC analysis (%)			Elimination/ Substitution
		Menthol	2-Menthene **5a**	Ester **6**	
1	0	9.7	14.3	76.0	0.19
2	0.01	10.2	51.9	37.9	1.37
3	0.025	15.3	49.2	35.5	1.39
4	0.05	37.2	36.0	26.8	1.34
5	0.1	49.2	31.1	19.7	1.58
6	0.2	57.7	26.8	15.5	1.73
7	1	77.9	18.5	3.6	5.10
8	2	81.8	16.6	1.6	10.40

[a]Conditions: TPP (1.0 eq), DIAD (1.0 eq), *l*-(-)-menthol (0.85 eq), 4-nitrobenzoic acid (0.85 eq), n-Bu_4NOTf (0.01-2.0 eq) and DCM (8 mL); 24 hours at room temperature.