Synthesis of Mixed Arylalkyl Tertiary Phosphines via the Grignard Approach

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Supporting Information

Experimental

*Ethyldiphenylphosphine (**3**)*

Dichlorophenylphosphine (250 mg, 1.397 mmol), phenylmagnesium bromide (1.4 mL, 1.397 mmol, 1 M solution in THF) and ethylmagnesium bromide (1.4 mL, 1.397 mmol, 1 M solution in THF) were reacted by following method C to yield product (**3**) as a colorless liquid (78 mg, 26 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 4H), 7.38 – 7.28 (m, 6H), 2.06 (q, J = 7.6 Hz, 2H), 1.10 (dt, J = 17.1, 7.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.82 (d, J = 2.1 Hz), 138.72, 132.82, 132.67, 128.49, 128.42, 128.36, 20.66 (d, J = 10.2 Hz), 10.13 (d, J = 16.4 Hz)

*Isopropyldiphenylphosphine (**4**)*

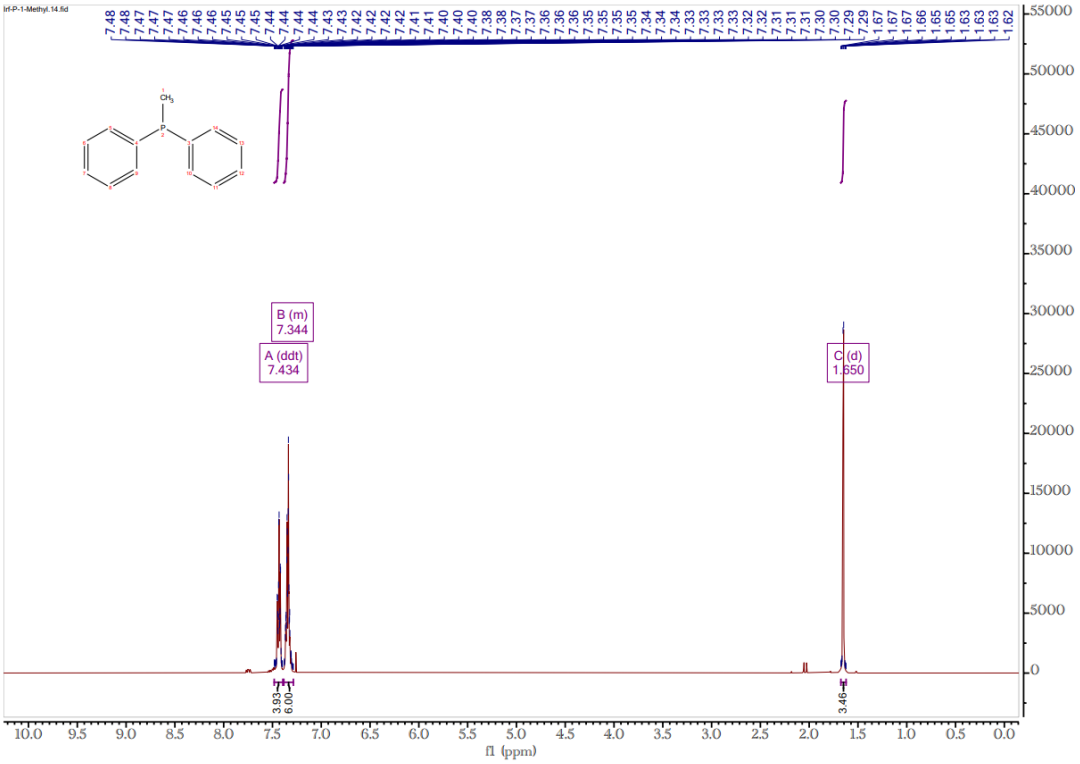
Dichlorophenyl phosphine (200 mg, 1.117 mmol), phenylmagnesium bromide (2.2 mL, 1.117 mmol, 1 M solution in THF) and isopropylmagnesium chloride (2.2 mL, 1.117 mmol, 1 M solution in THF) were reacted following method C to yield product as a colorless liquid (58 mg, 23 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dddd, J = 9.6, 6.0, 3.0, 1.3 Hz, 4H), 7.37 – 7.31 (m, 6H), 2.55 – 2.46 (m, 1H), 1.11 (d, J = 6.9 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H), 13C NMR (126 MHz, CDCl3) δ 133.65, 133.50, 131.54 (d, J = 2.7 Hz), 131.11, 131.04, 128.63, 128.54, 128.46, 128.40, 24.88, 19.39, 15.28

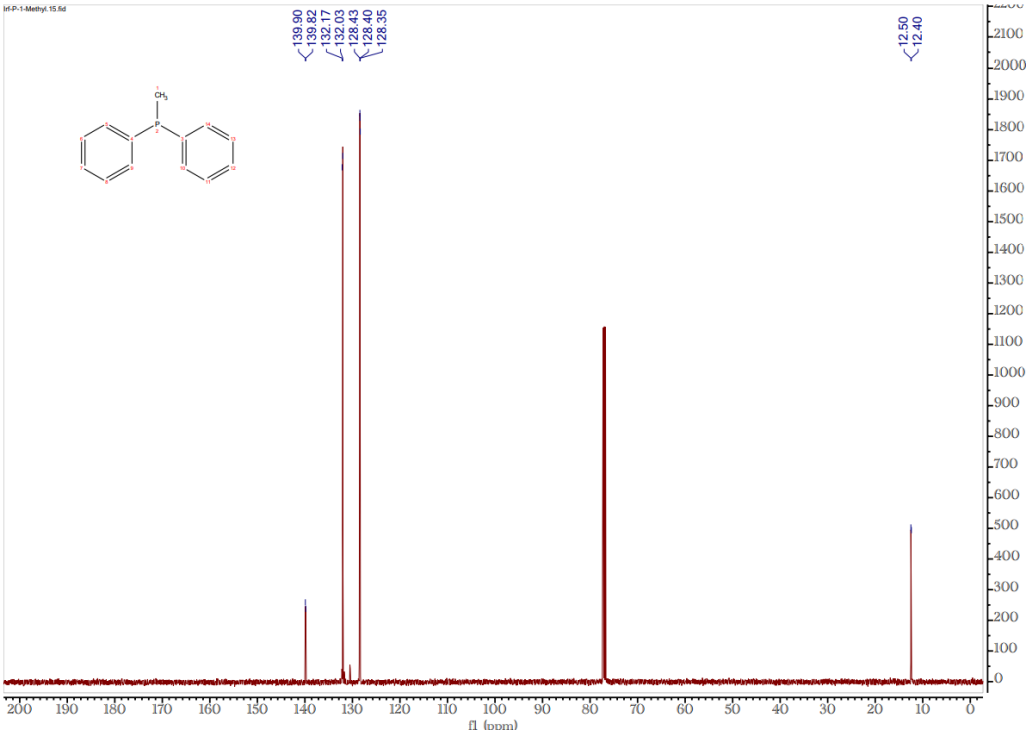
*Isopentyldiphenylphosphine (**5**)*

Dichlorophenylphosphine (300 mg, 1.676 mmol) in THF (10 mL), phenylmagnesium bromide (1.7 mL, 1.676 mmol, 2 M solution in THF) and isopentylmagnesium bromide (0.85 mL, 1.676 mmol, 1 M solution in ether) were reacted by following method C to yield product (**5**) as a colorless liquid (78 mg, 18 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (ddq, J = 8.6, 6.3, 2.3 Hz, 4H), 7.39 – 7.29 (m, 6H), 2.09 – 2.02 (m, 2H), 1.67 (dtd, J = 13.2, 6.6, 0.9 Hz, 1H), 1.41 – 1.29 (m, 2H), 0.91 (d, J = 6.7 Hz, 6H), ^{13}C NMR (126 MHz, CDCl3) δ 138.91, 138.81, 132.74, 132.60, 128.43, 128.36, 128.31, 34.80, 29.38, 25.75, 22.24.

(4-Methoxyphenyl)diphenylphosphine (7)

Dichlorophenyl phosphine (200 mg, 1.117 mmol), phenylmagnesium bromide (1.1 mL, 1.117 mmol, 1 M solution in THF) and 4-methoxyphenylmagnesium bromide (1.05 mL, 1.117 mmol, 1 M solution in THF) were reacted by following method B to yield product (**7**) as colorless liquid (108 mg, 33 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 13H), 6.91 – 6.86 (m, 2H), 3.80 (s, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.36, 137.91, 137.83, 135.68, 135.51, 133.48, 133.32, 128.46, 128.43, 128.37, 127.63, 127.56, 114.26, 114.19, 55.17.


lrf-P-1-Methyl. 14.fid
B (m)
7.344
A (ddt)
7.434
C (d)
1.550
3.93
6.00
3.46
f1 (ppm)


lrf-P-1-Methyl. 15.fid
139.90
139.82
132.17
132.03
128.43
128.40
128.35
12.50
12.40
f1 (ppm)

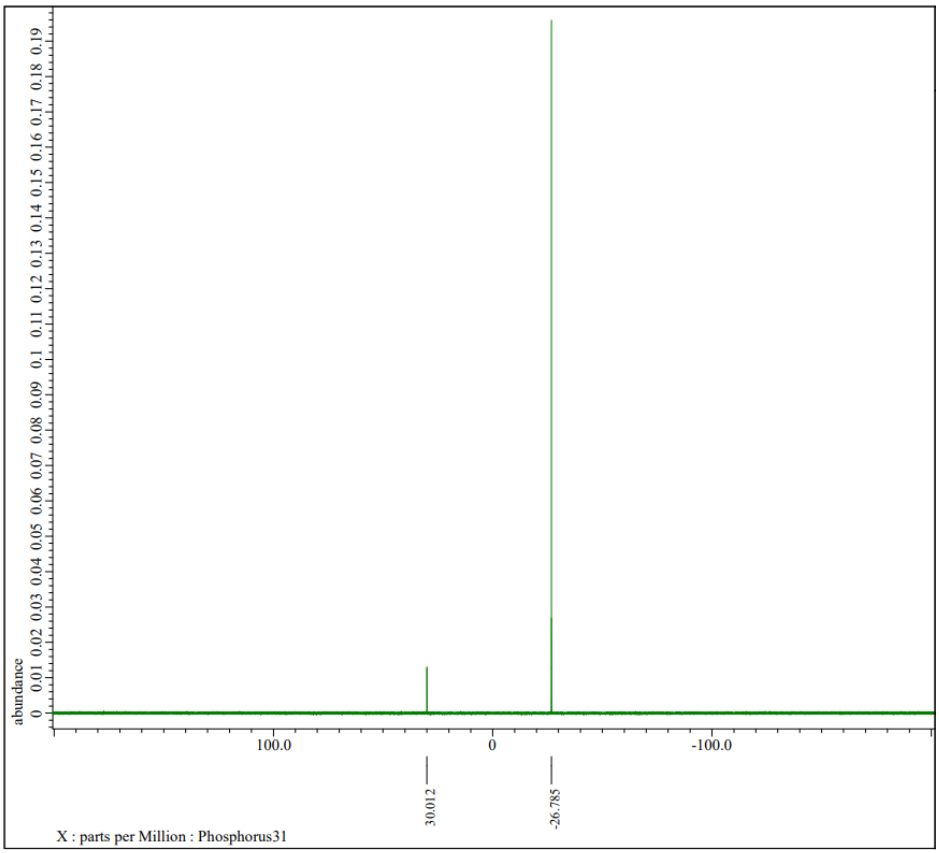
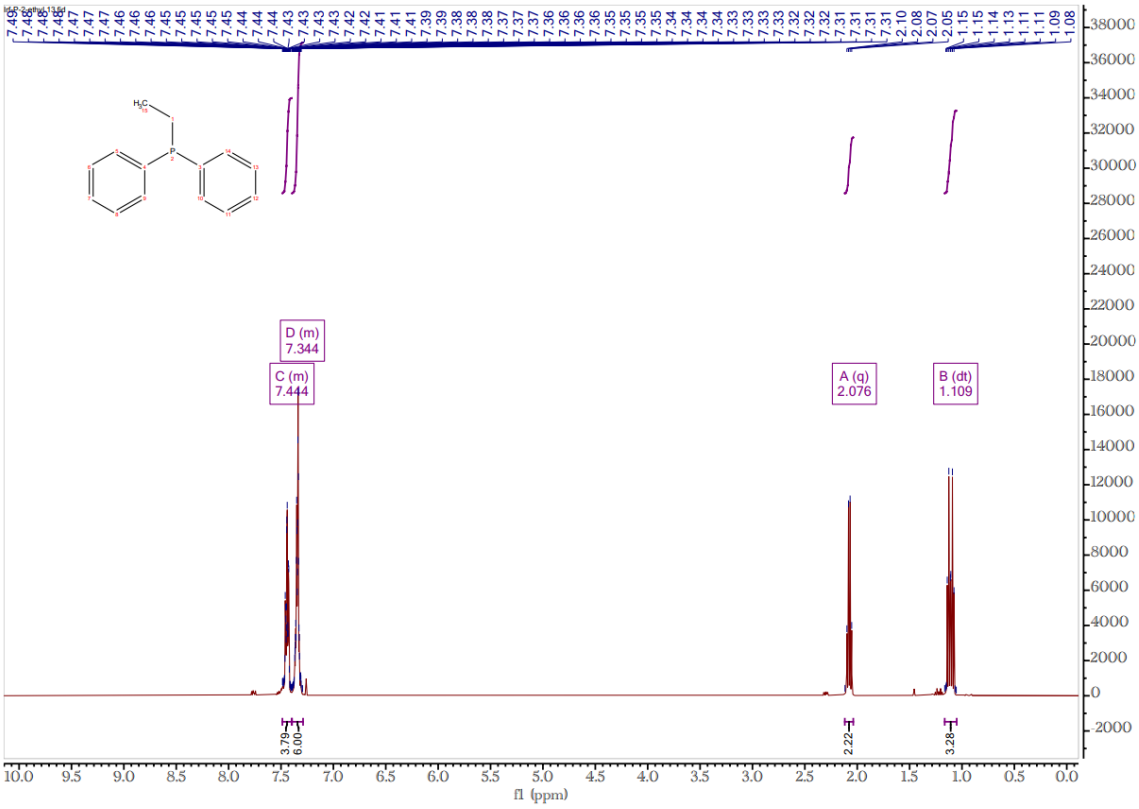
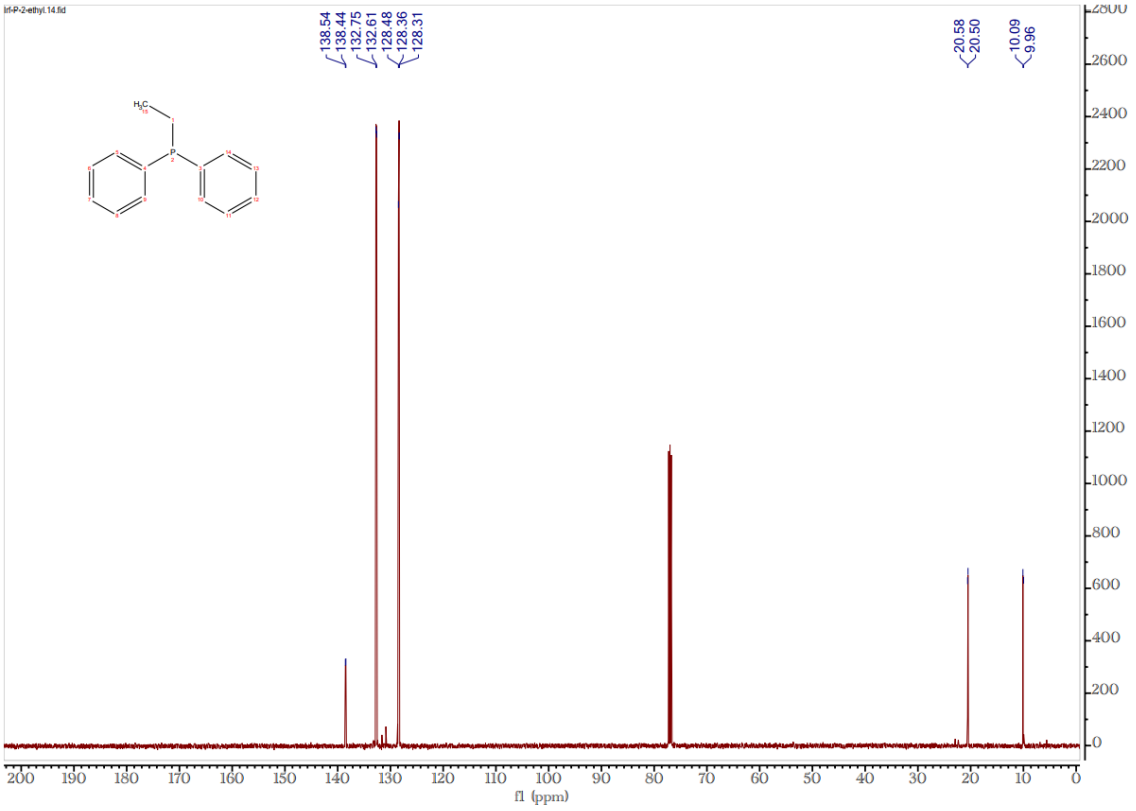


Figure S1. ^{1}H-NMR, ^{13}C-NMR AND ^{31}P-NMR spectra of (**2**) obtained by method A.


D (m)
7.344
C (m)
7.444
A (q)
2.076
B (dt)
1.109
3.79
6.00
2.22
3.28
f1 (ppm)


138.54
138.44
132.75
132.61
128.48
128.36
128.31
20.58
20.50
10.09
9.96
f1 (ppm)

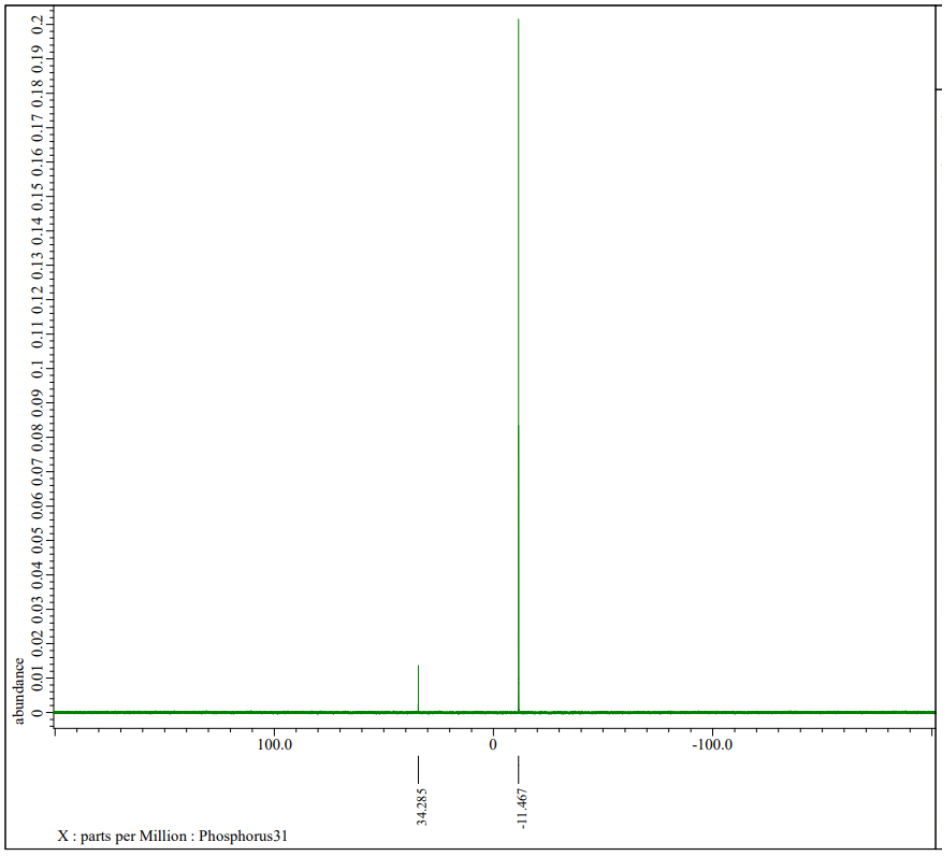
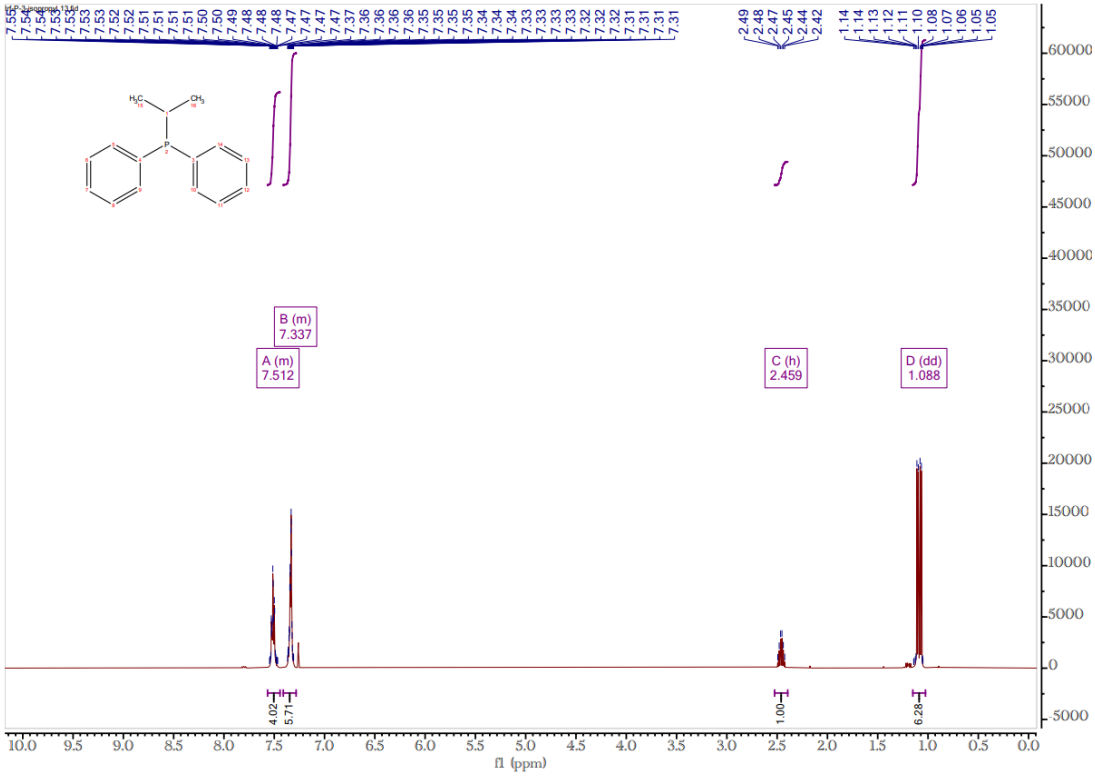
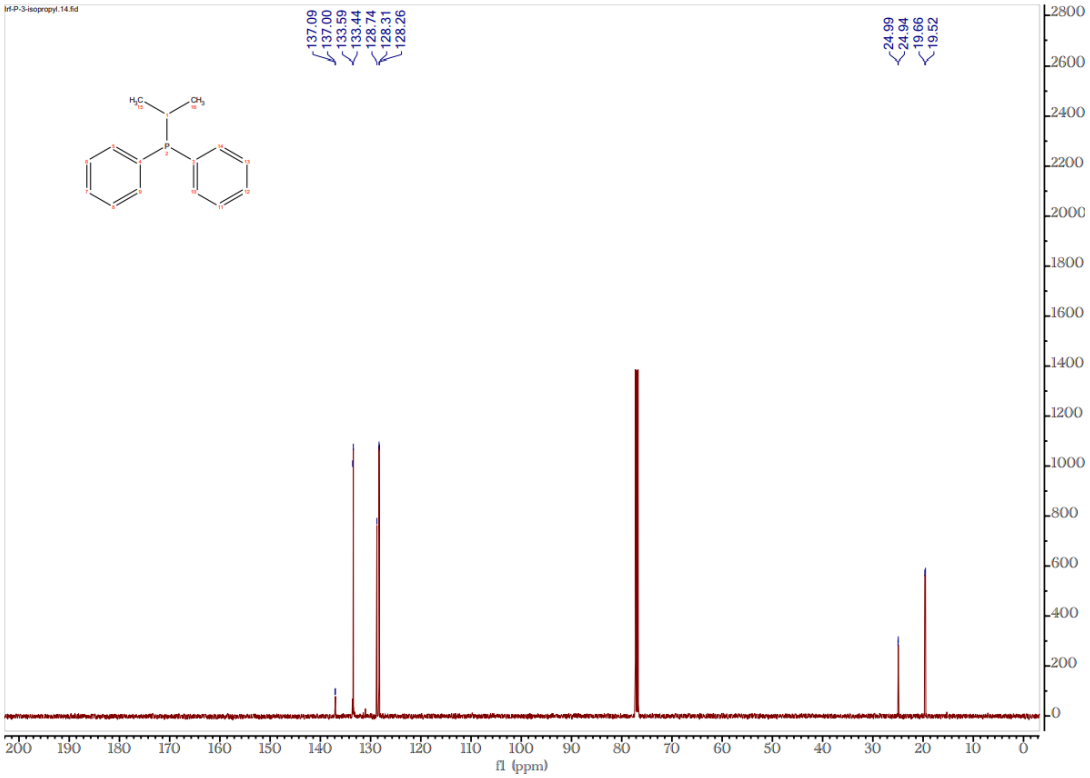


Figure S2. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of **(3)** obtained by method A.


B (m)
7.337
A (m)
7.512
C (h)
2.459
D (dd)
1.088
4.02
5.71
1.00
6.28
f1 (ppm)


137.09
137.00
133.59
133.44
128.74
128.31
128.26
24.99
24.94
19.66
19.52
f1 (ppm)

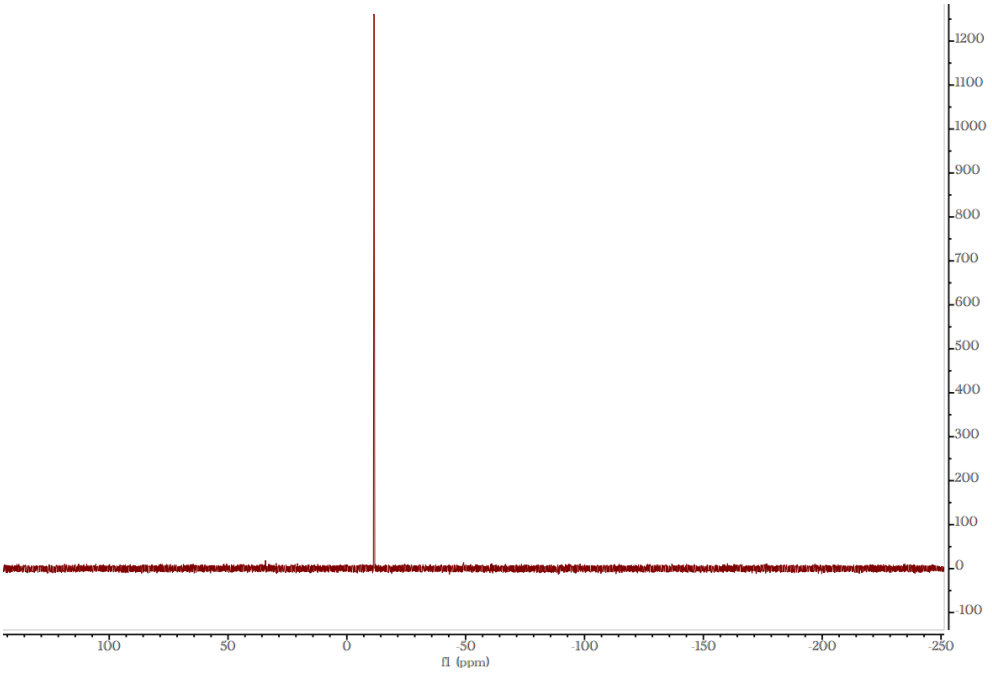
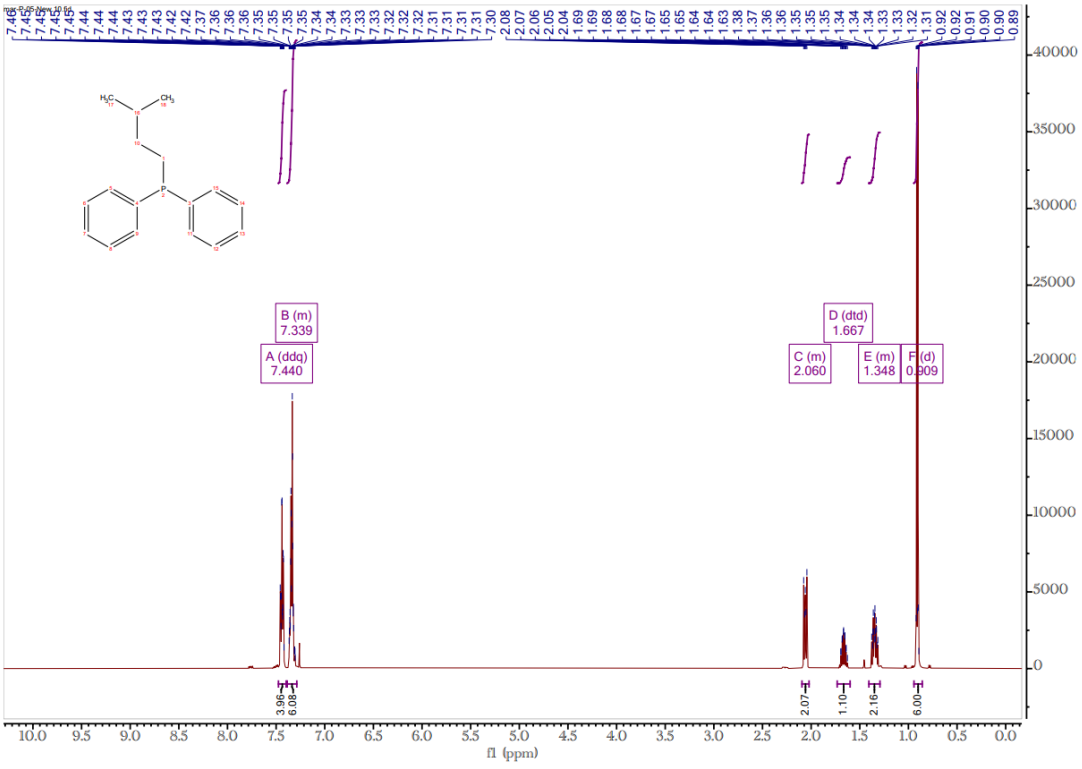
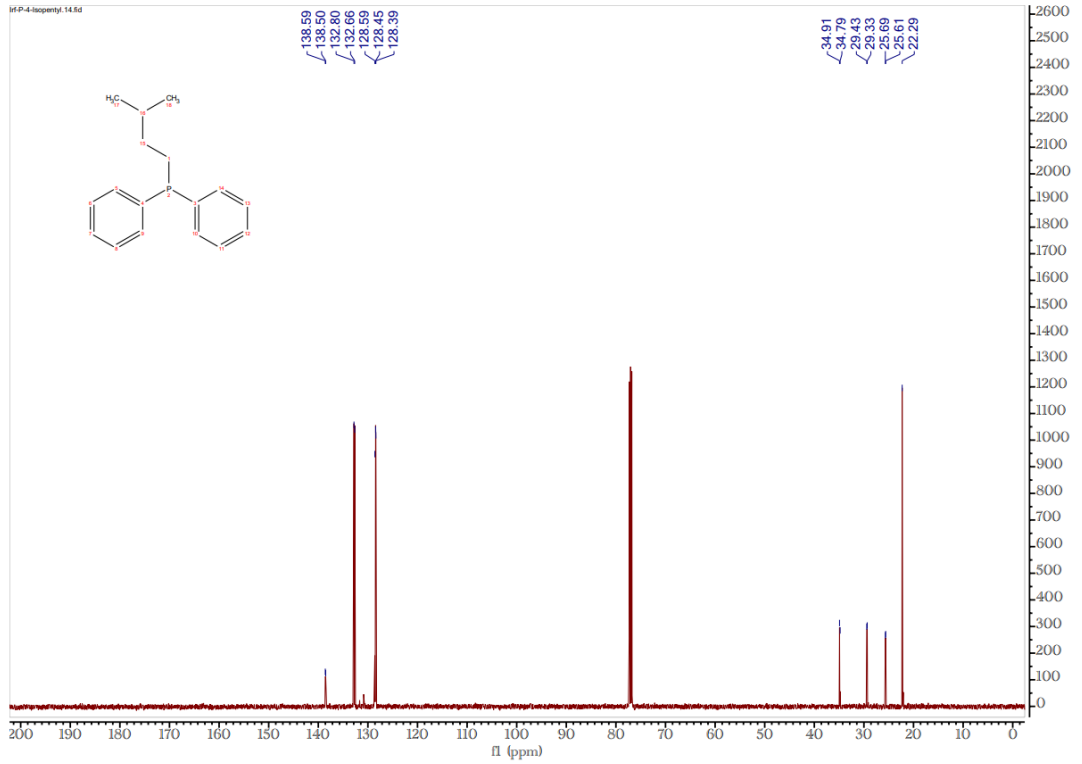


Figure S3. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of **(4)** obtained by method A.


B (m)
7.339
A (ddq)
7.440
D (dtd)
1.667
C (m)
2.060
E (m)
1.348
F (d)
0.909
3.96
6.08
2.07
1.10
2.16
6.00
f1 (ppm)


138.59
138.50
132.80
132.66
128.59
128.45
128.39
34.91
34.79
29.43
29.33
25.69
25.61
22.29
f1 (ppm)

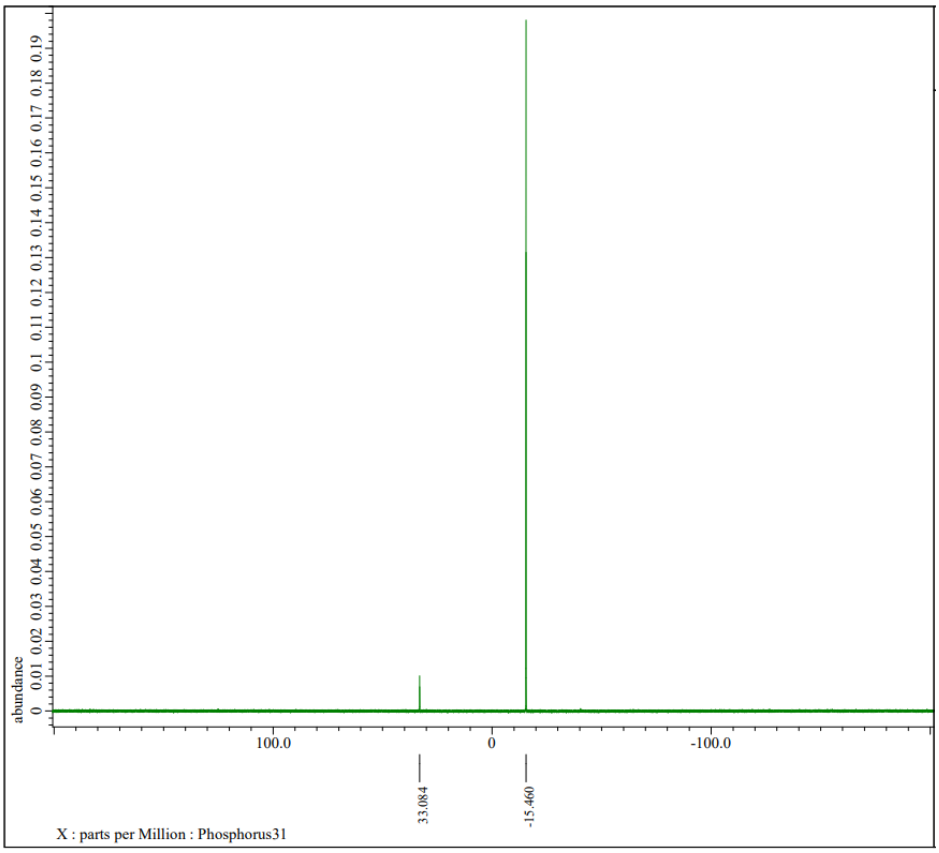
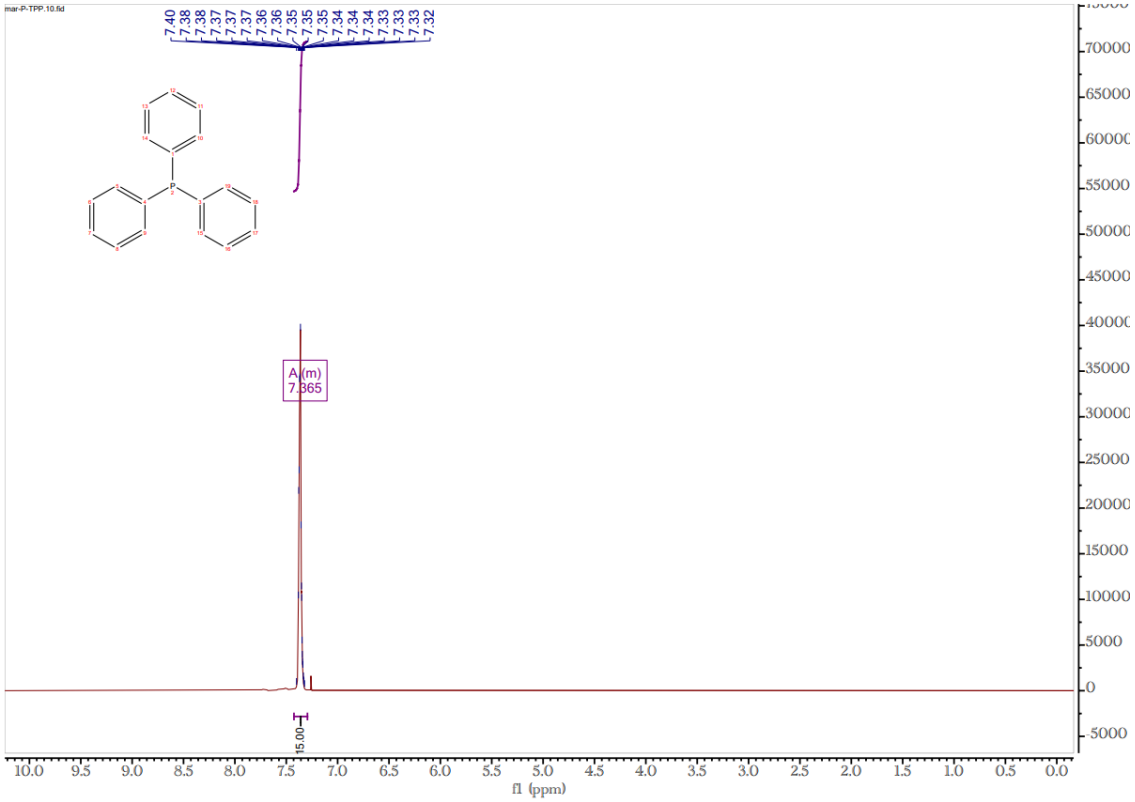
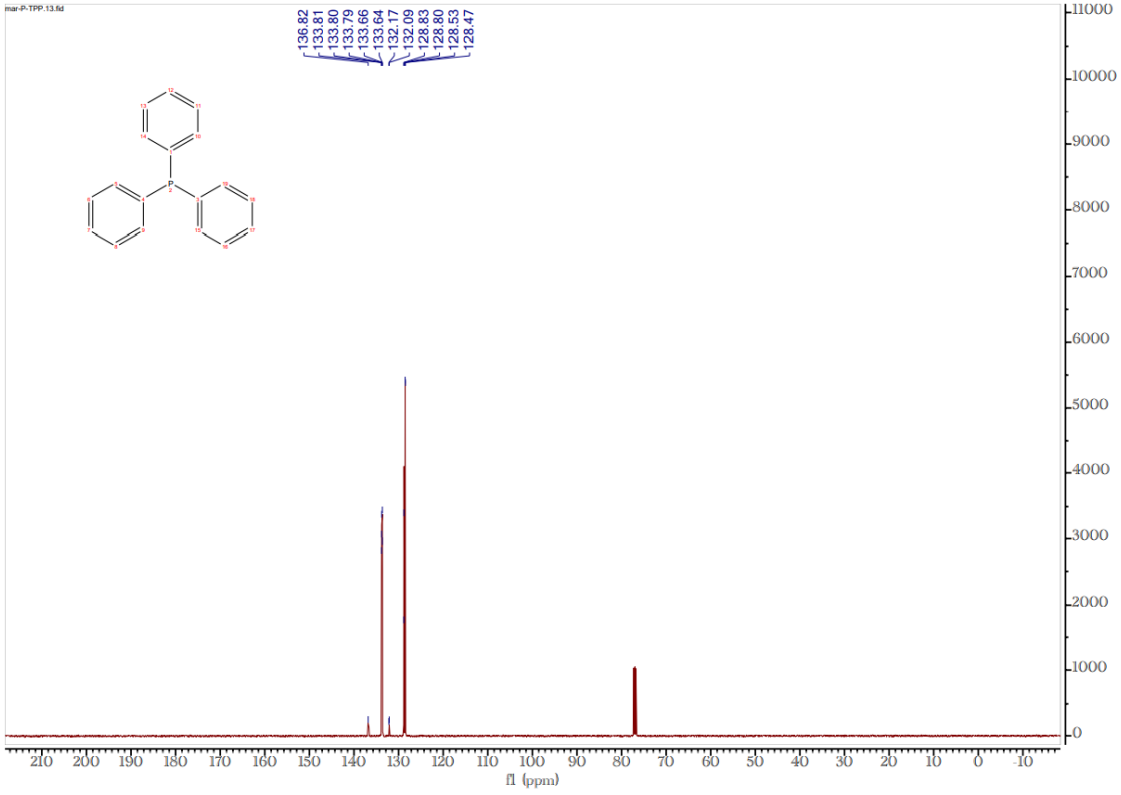


Figure S4. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of (**5**) obtained by method A.


mar-P-TPP.10.fid
7.40
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.32
A(m)
7.365
15.00
f1 (ppm)


mar-P-TPP.13.fid
136.82
133.81
133.80
133.79
133.66
133.64
132.17
132.09
128.83
128.80
128.53
128.47
f1 (ppm)

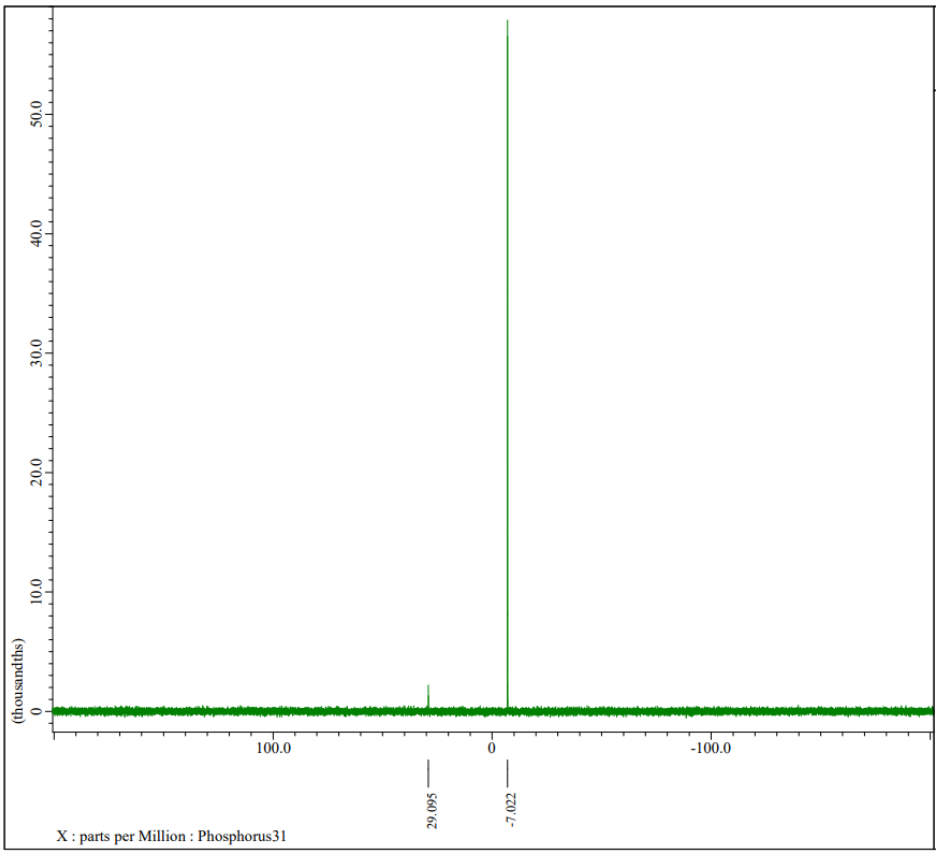
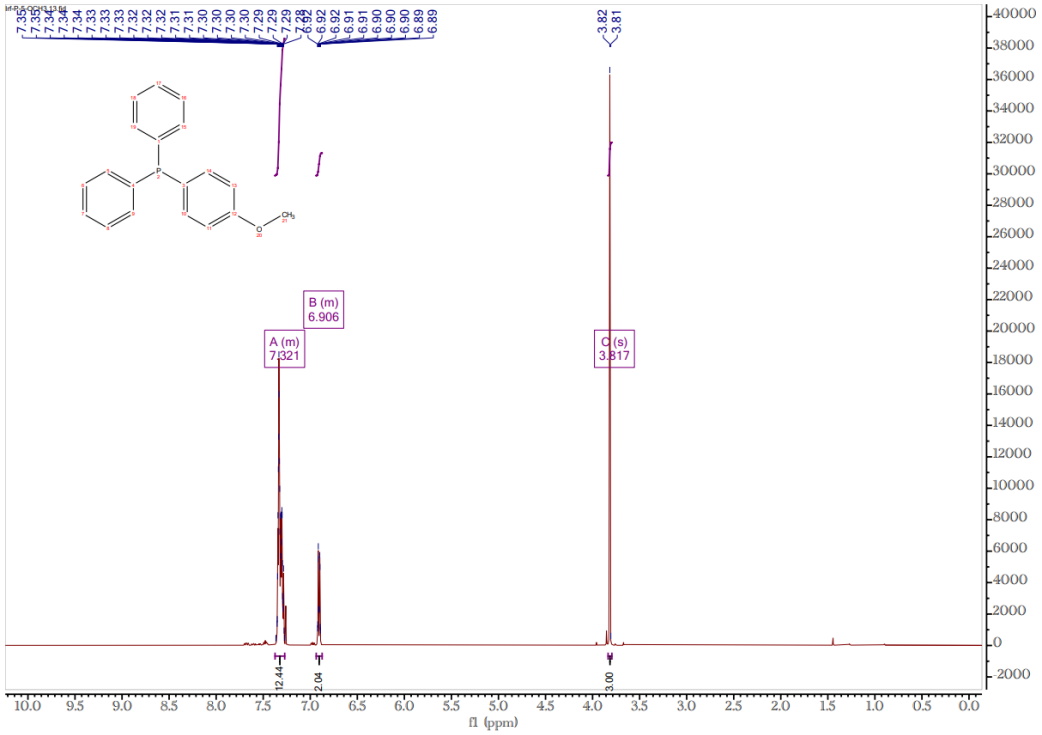
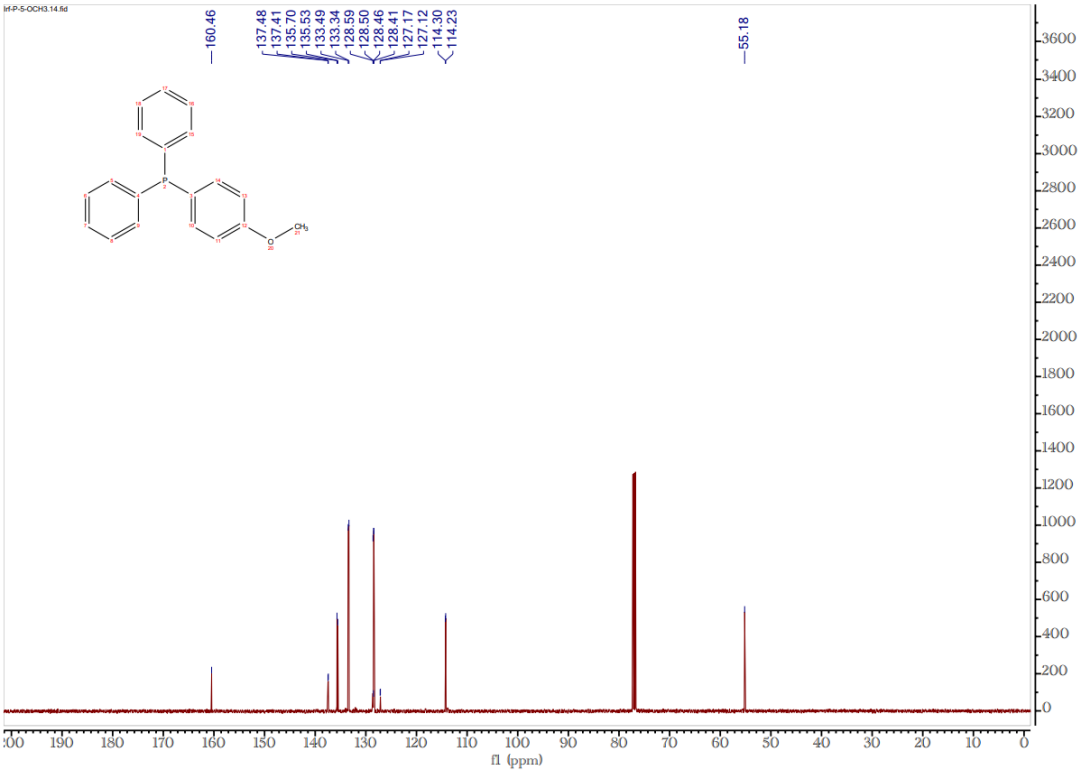


Figure S5. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of **(6)** obtained by method A.


B (m)
6.906
A (m)
7.321
C (s)
3.817
12.44
2.04
3.00
f1 (ppm)


160.46
137.48
137.41
135.70
135.53
133.49
133.34
128.59
128.50
128.46
128.41
127.17
127.12
114.30
114.23
55.18
f1 (ppm)

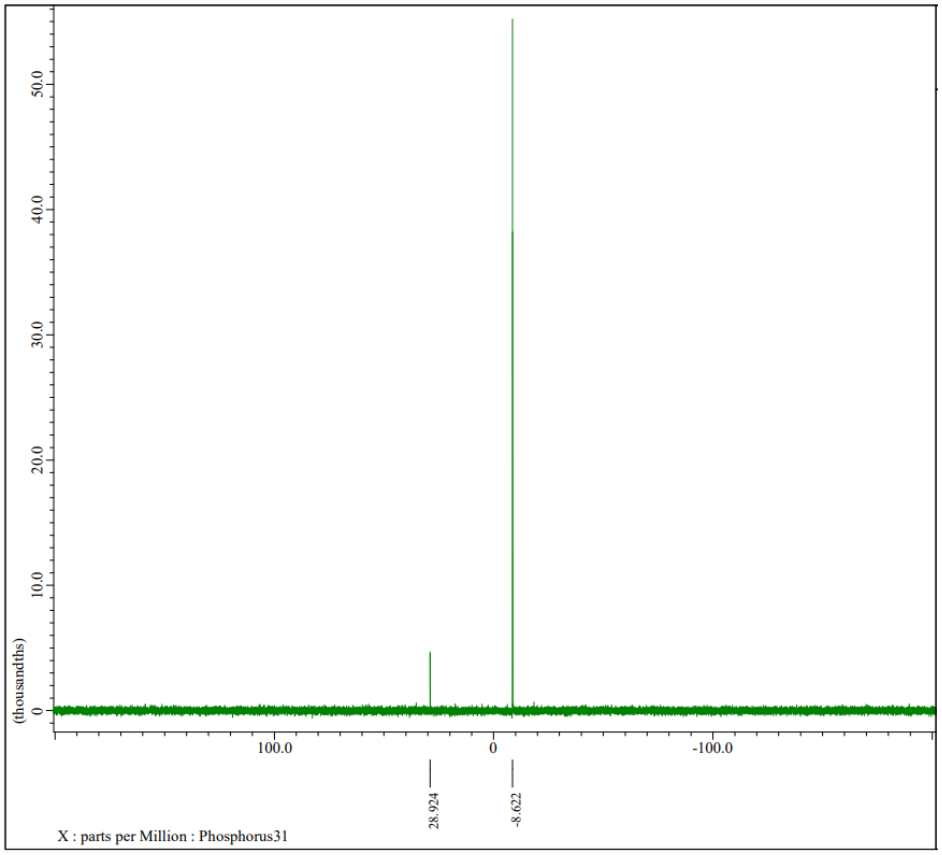


Figure S6. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of **(7)** obtained by method A.

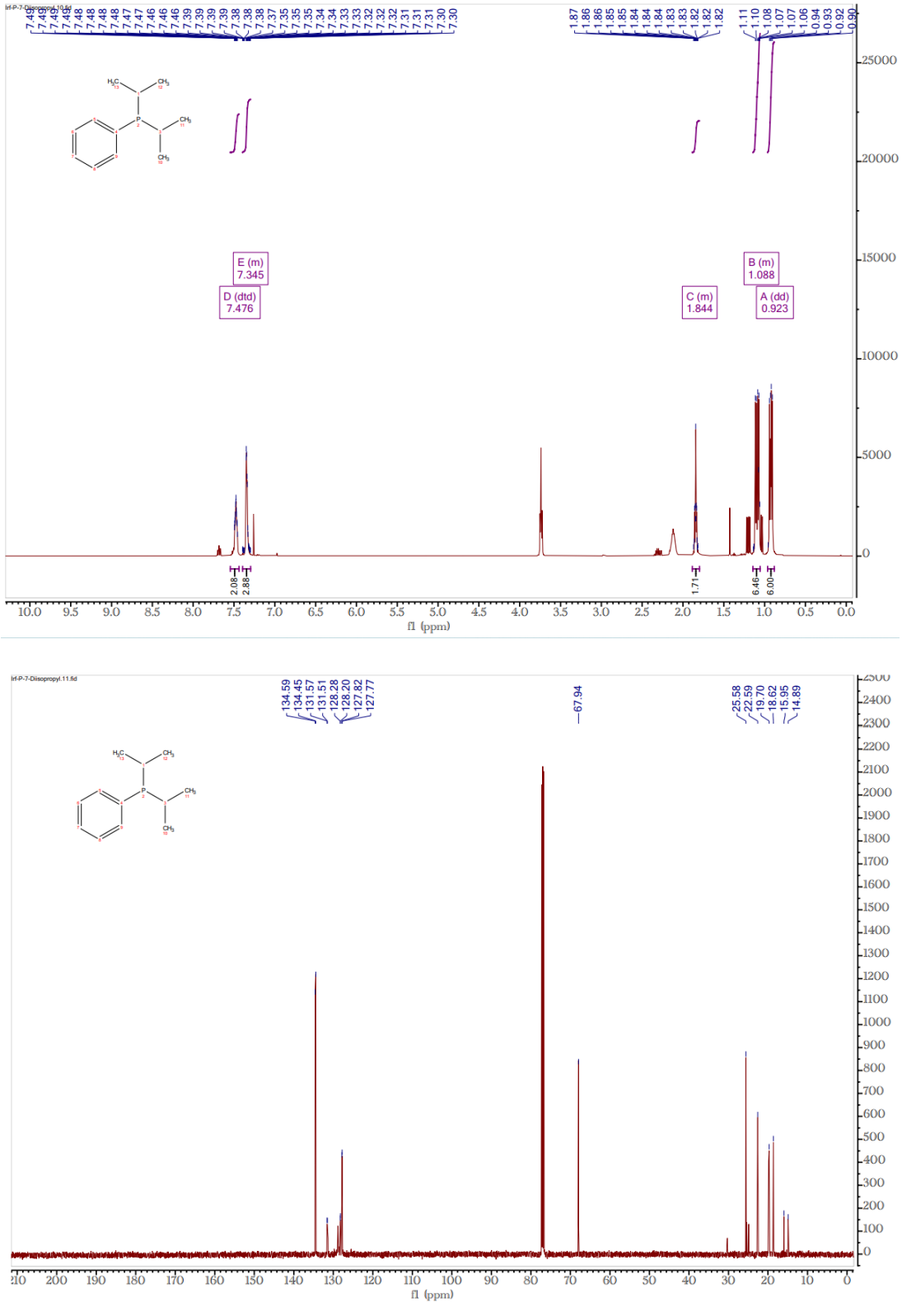
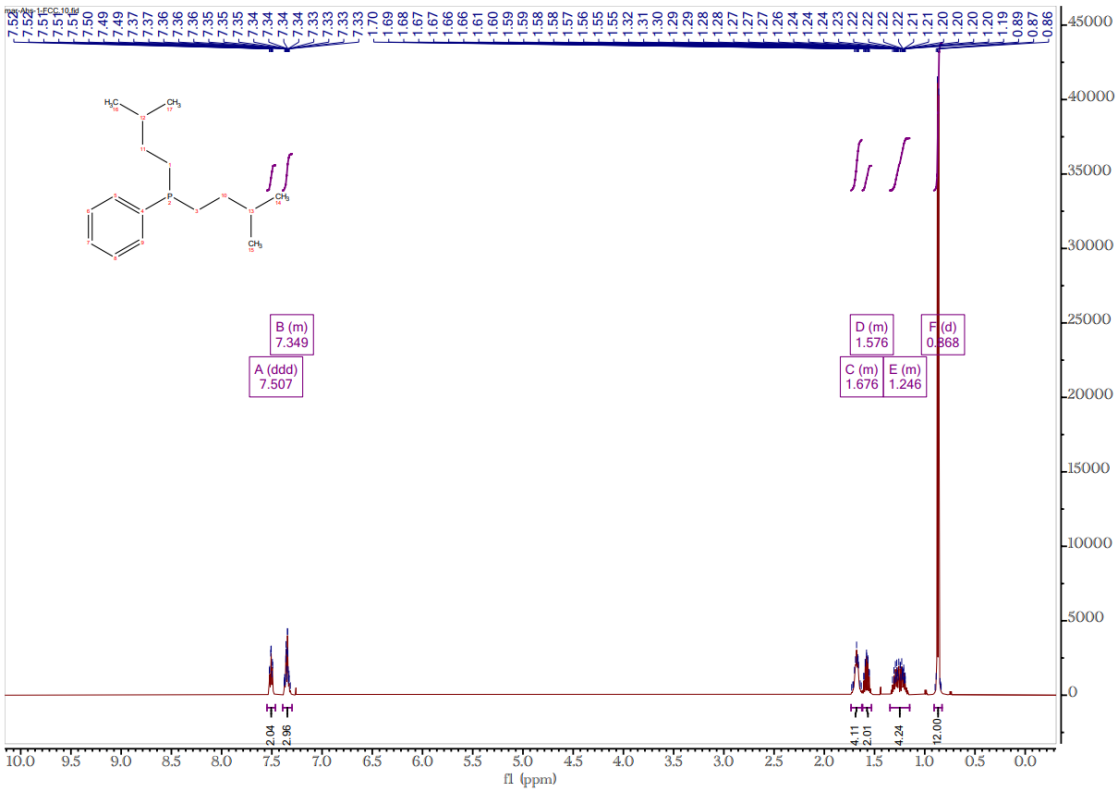
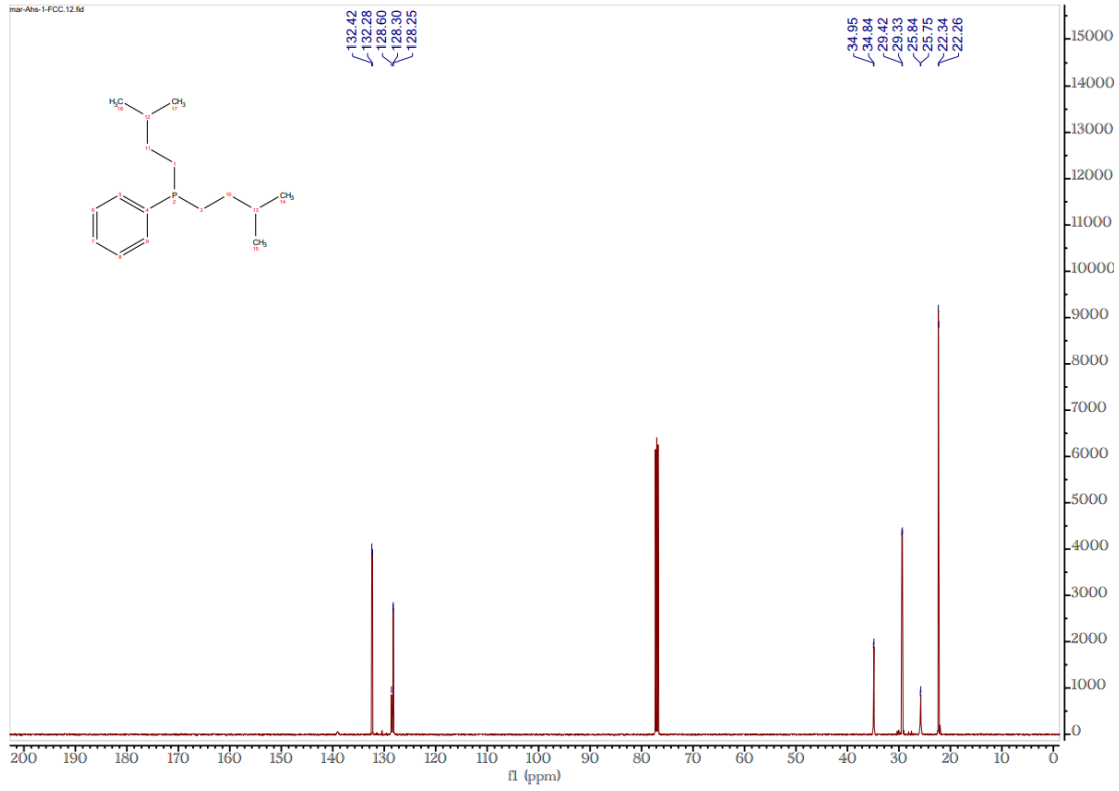


Figure S7. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra of (**9**) obtained by method B.


B (m)
7.349
A (ddd)
7.507
D (m)
1.576
F (d)
0.868
C (m)
1.676
E (m)
1.246
2.04
2.96
4.11
2.01
4.24
12.00
f1 (ppm)


mar-Ahs-1-FCC.12.fid
132.42
132.28
128.60
128.30
128.25
34.95
34.84
29.42
29.33
25.84
25.75
22.34
22.26
f1 (ppm)

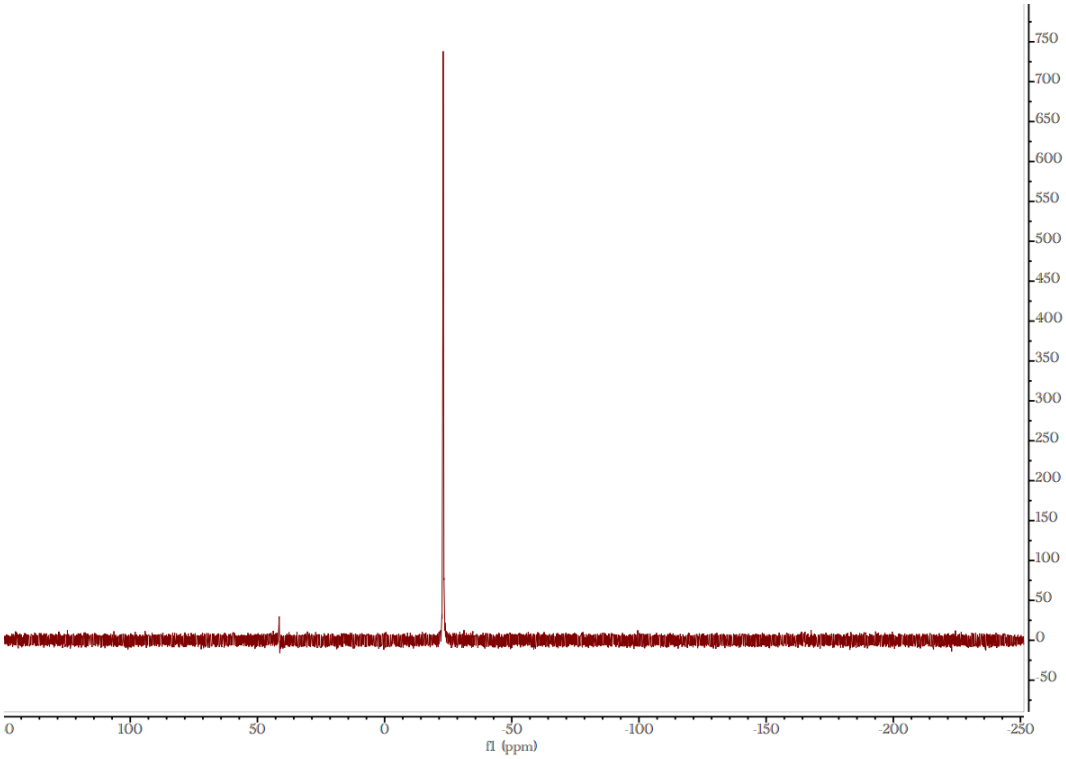


Figure S8. ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR spectra of (**10**) obtained by method B.

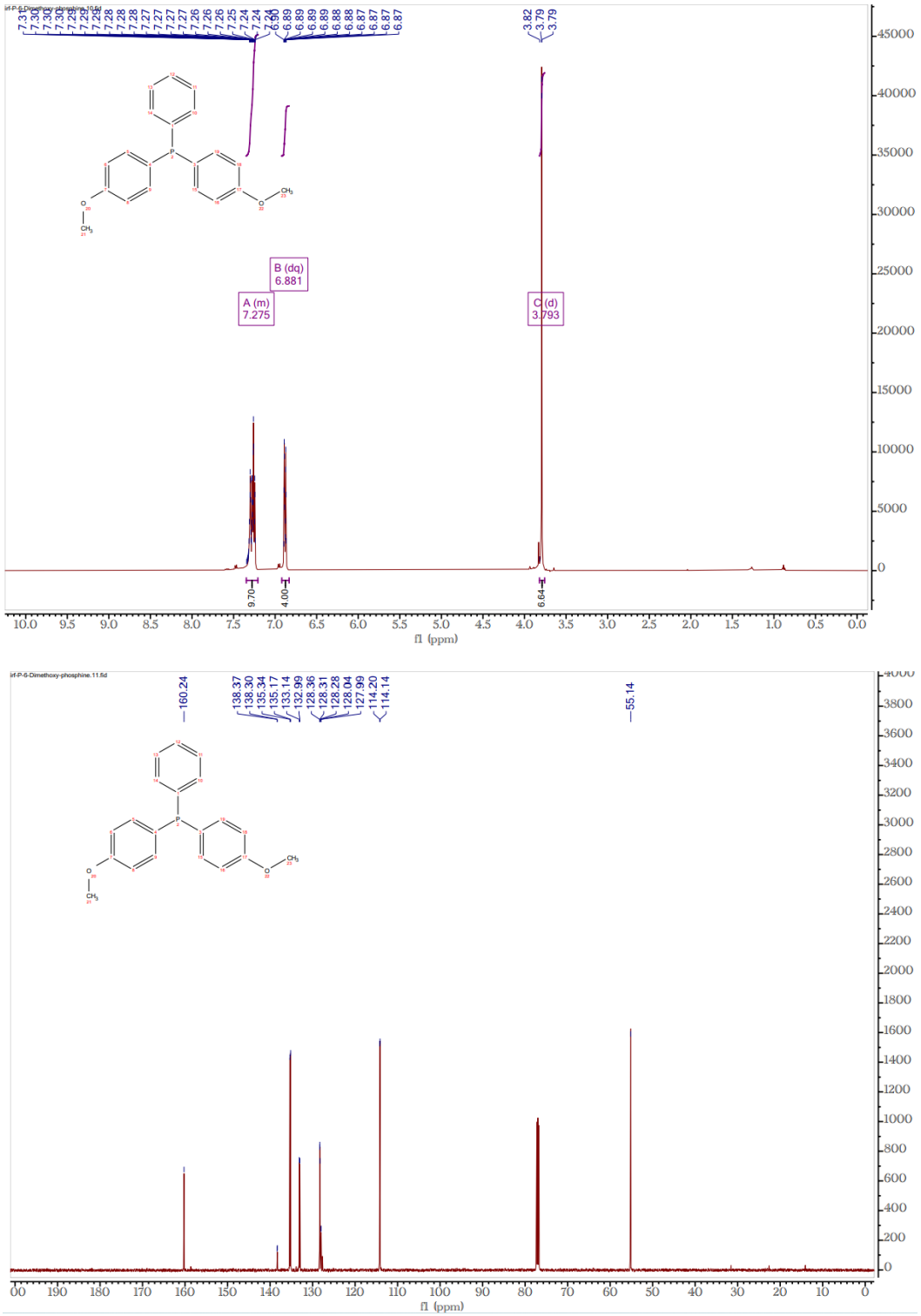
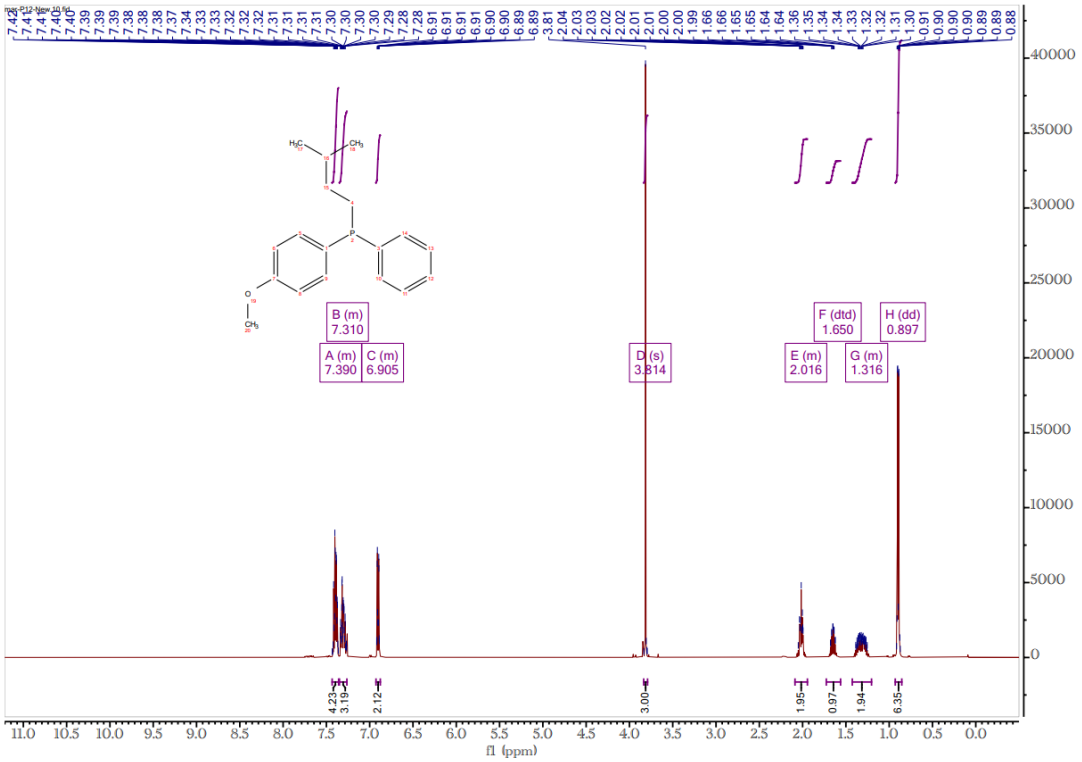
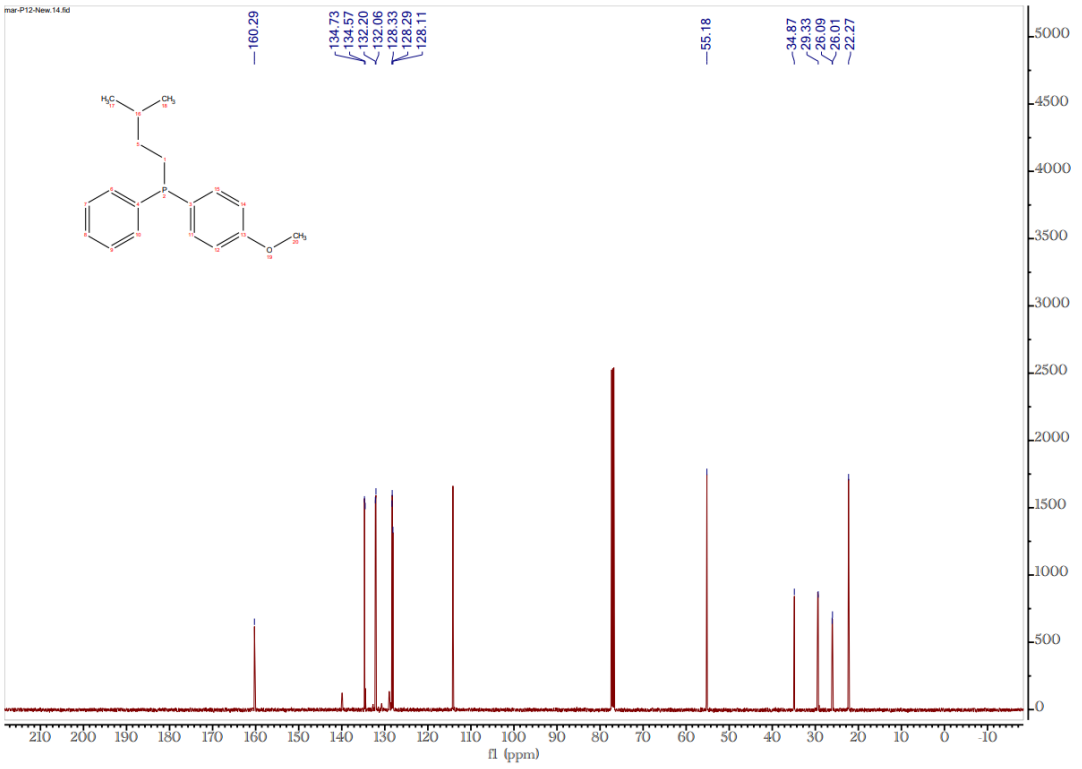


Figure S9. ^{1}H-NMR and ^{13}C-NMR spectra of **(11)** obtained by method B.


B (m)
7.310
A (m)
7.390
C (m)
6.905
D (s)
3.814
E (m)
2.016
F (dtd)
1.650
G (m)
1.316
H (dd)
0.897
4.23
3.19
2.12
3.00
1.95
0.97
1.94
6.35
f1 (ppm)


160.29
134.73
134.57
132.20
132.06
128.33
128.29
128.11
55.18
34.87
29.33
26.09
26.01
22.27
f1 (ppm)

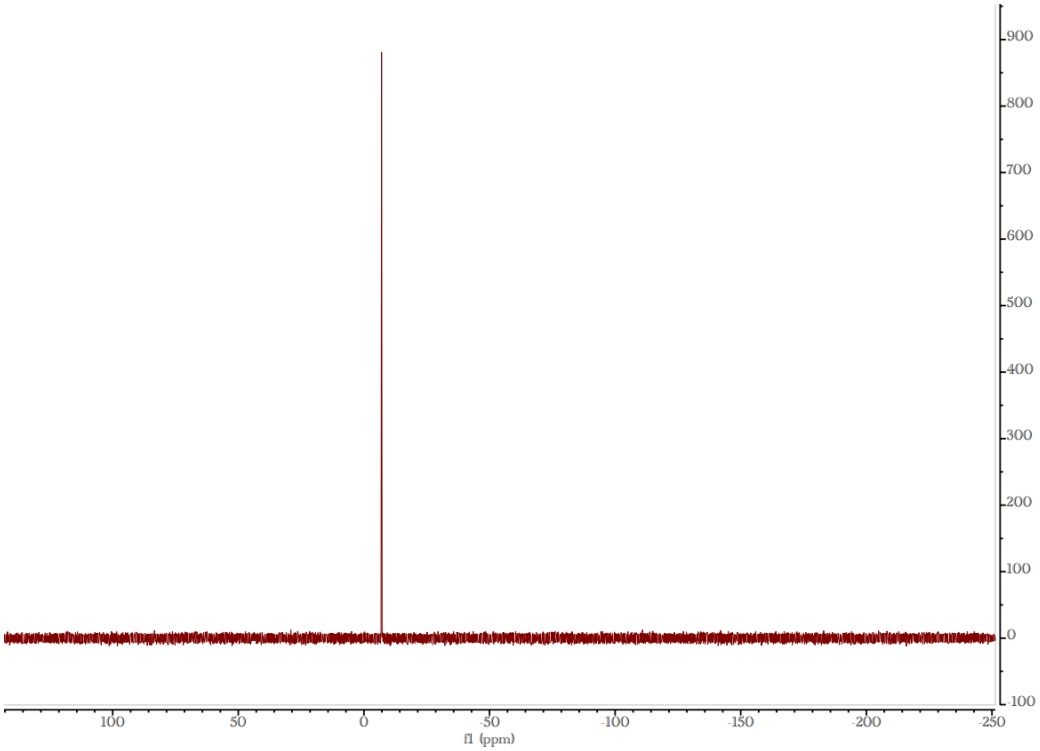


Figure S10. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR of **(12)** obtained by method C.

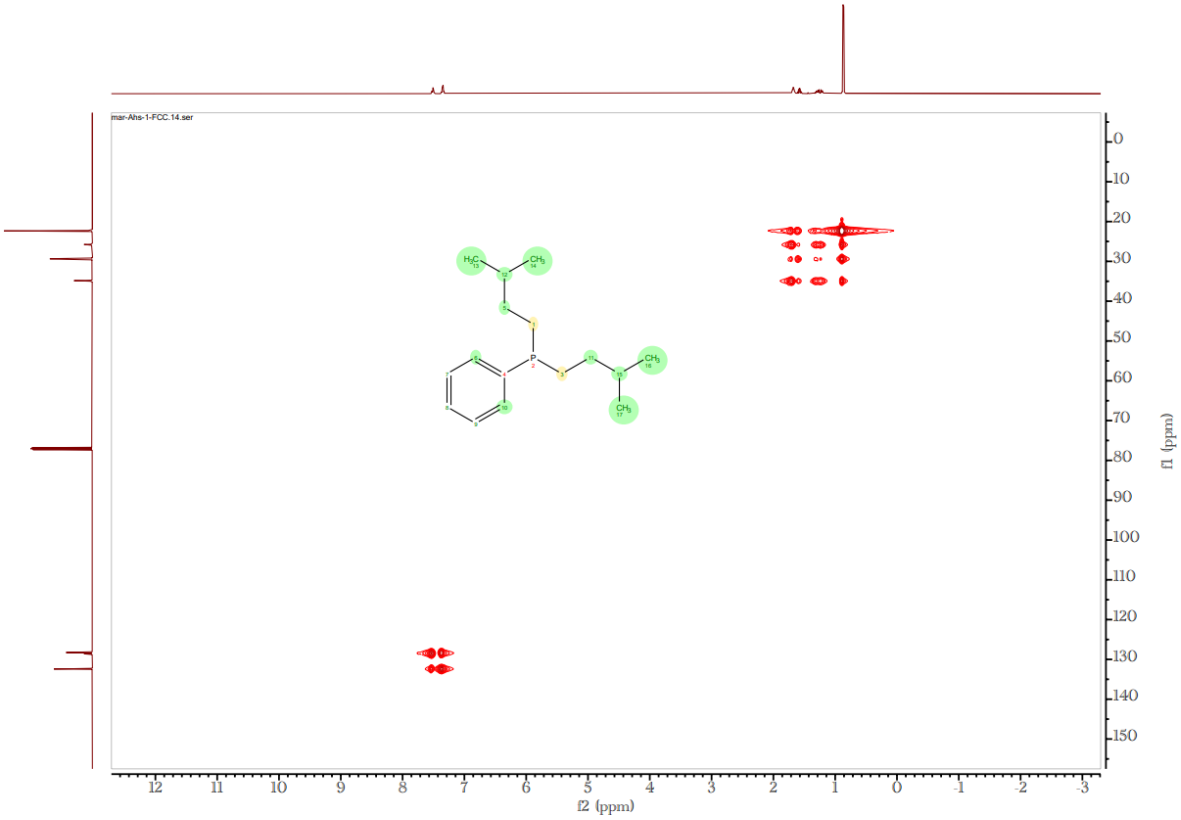


Figure S11. HMBC spectrum of compound **(10)** obtained by method B.

Table T1: Cartesian coordinates for the optimized structure of 5.

0 1

P	-0.27315200	-0.18579600	-0.58422600
C	-0.08598400	1.57986400	-0.22324800
C	1.05562400	2.30459700	-0.61843900
C	-1.17449500	2.26709600	0.34481300
C	1.11612200	3.67778800	-0.41189500
H	1.88415200	1.80320400	-1.10052000
C	-1.09554200	3.63724200	0.56693100
H	-2.06777400	1.71837500	0.61537000
C	0.04662300	4.34421000	0.18791900
H	1.99444700	4.23015300	-0.72438800
H	-1.92870900	4.15578400	1.02622000
H	0.09864800	5.41469700	0.34849900
C	-1.81591400	-0.87654200	-0.22233000
C	-2.72231300	-1.28300900	-1.28066100
C	-2.27415100	-1.05376200	1.15382900
C	-3.95233600	-1.81232100	-0.98470500
H	-2.42156600	-1.16845700	-2.31671100
C	-3.51916400	-1.58379300	1.40145400
H	-1.63402700	-0.77006500	1.98173700
C	-4.39189700	-1.97874200	0.36040800
H	-4.60376300	-2.10993500	-1.80127700
H	-3.83288400	-1.70529700	2.43507100
H	-5.36613000	-2.39486400	0.57957600
C	1.14997800	-1.18270800	0.06026200
H	1.02785500	-2.14207900	-0.44871500
H	0.89359700	-1.36052200	1.11368900
C	2.58367100	-0.65685000	-0.06483300
H	2.67063500	0.28879200	0.47643900
H	2.81787800	-0.44848100	-1.11544600
C	3.64226700	-1.63286900	0.49418700
H	3.34699900	-1.88894600	1.52031800
C	3.73298500	-2.93361600	-0.31569100
H	2.79177200	-3.48879900	-0.32002300
H	4.00531000	-2.72387100	-1.35592700
H	4.49802300	-3.59403000	0.10168000
C	5.01054300	-0.93958100	0.55774100
H	4.97167700	-0.03563800	1.17236900

H	5.76677100	-1.60418900	0.98456600
H	5.34827300	-0.65091700	-0.44358900

Table T2: Cartesian coordinates for the optimized structure of 10

0 1

P	0.07333500	-0.36561600	-0.39955600
C	-1.15961400	-1.54639200	-0.13199000
C	-1.88256500	-2.14281600	-1.24186400
C	-1.54354800	-1.96089200	1.21605100
C	-2.87250600	-3.06511000	-1.01731700
H	-1.63407400	-1.85795700	-2.25876000
C	-2.54269100	-2.88825700	1.39055800
H	-1.04167400	-1.54060100	2.08086800
C	-3.23422500	-3.47020400	0.29942700
H	-3.39016600	-3.49438100	-1.87046100
H	-2.80466900	-3.18049500	2.40428100
H	-4.01792800	-4.19795600	0.46229800
C	1.77499800	-0.85422500	0.11885300
H	1.98601900	-1.75881100	-0.45688000
H	1.68771200	-1.17086800	1.16694300
C	2.87822000	0.20008000	-0.04792200
H	2.64023100	1.07271600	0.56728200
H	2.90729700	0.54632000	-1.08817200
C	4.28255300	-0.30234100	0.35011200
H	4.21197400	-0.71022700	1.36722800
C	-0.24398900	1.35528900	0.19172000
H	-0.21835600	1.30788900	1.28940100
H	0.59949300	1.97300300	-0.12466000
C	-1.58526900	1.91919200	-0.29482300
H	-2.37618200	1.20245000	-0.05508500
H	-1.56796900	2.01030200	-1.38763200
C	-1.94981900	3.28569700	0.31880100
H	-1.91829700	3.17562800	1.41116200
C	5.27050700	0.87220100	0.38161500
H	4.94156700	1.65201500	1.07454900
H	6.26389200	0.54036500	0.69600800
H	5.36949200	1.32484800	-0.61099900
C	4.79486800	-1.41439200	-0.57560600
H	4.14893400	-2.29571000	-0.56530600
H	4.86160700	-1.05762400	-1.60930800

H	5.79346000	-1.73925100	-0.27079500
C	-3.38273800	3.67151800	-0.07354000
H	-4.10078200	2.90884400	0.24080900
H	-3.67403000	4.61934000	0.38772800
H	-3.47135800	3.78827400	-1.15912100
C	-0.96307100	4.39326100	-0.07665200
H	0.05513200	4.18022600	0.25886100
H	-0.93919300	4.52038700	-1.16467200
H	-1.25881500	5.34985700	0.36324400

Table T3: Cartesian coordinates for the optimized structure of PBu_3

0 1

P	-0.30308200	-0.44771100	0.61804900
C	-1.86259500	-1.06590800	-0.21664000
H	-1.91766200	-2.14017200	-0.00856600
H	-1.76457300	-0.95704800	-1.30368500
C	-3.14654900	-0.38488300	0.27474400
H	-3.08657300	0.69711300	0.10533200
H	-3.23682100	-0.51903300	1.35927100
C	-0.01675600	1.12829800	-0.36063800
H	0.31570900	0.86852400	-1.37300500
H	-0.99606700	1.60797800	-0.46441600
C	0.95636200	2.12170900	0.28977900
H	1.93776200	1.65408000	0.42814900
H	0.59661500	2.37373300	1.29446100
C	-5.69447500	-0.24747500	0.08722400
H	-5.67026900	0.83105900	-0.09810100
H	-6.57700000	-0.65152800	-0.41645000
H	-5.82840200	-0.39545500	1.16341100
C	2.08941700	4.41021000	0.13003300
H	3.08754000	3.97743000	0.25085100
H	2.19120600	5.31749200	-0.47189100
H	1.73521400	4.70690900	1.12227100
C	0.91446800	-1.62898900	-0.17734000
H	0.80648100	-1.58325000	-1.26797900
H	0.59876200	-2.63220200	0.13195800
C	2.38106500	-1.41656900	0.21979500
H	2.72260600	-0.43401600	-0.12485200
H	2.46775500	-1.40591100	1.31308200
C	3.31658900	-2.49204200	-0.34904300

H	3.22505300	-2.50783900	-1.44170100
H	2.98407900	-3.47701200	-0.00001000
C	4.78294400	-2.27979200	0.03839400
H	5.42257100	-3.06241100	-0.37894400
H	5.15306000	-1.31706700	-0.32810900
H	4.90951500	-2.29093900	1.12554200
C	-4.41175900	-0.92209400	-0.40767900
H	-4.47829400	-2.00369300	-0.23952600
H	-4.32136100	-0.78623500	-1.49203600
C	1.12949000	3.41145100	-0.52313000
H	0.14884900	3.88266500	-0.66163600
H	1.49127600	3.15898700	-1.52715200