Solvent- and Catalyst-free Regioselective Hydrophosphanation of Alkenes

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Supplementary Information

General

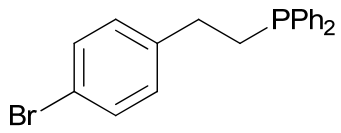
Diphenylphosphane (Aldrich) and all the starting alkenes were commercially available of the best grade (Aldrich, Acros, Alfa Aesar) and were used without further purification. Infrared analysis was performed with a FT-IR-4100 (ATR) spectrophotometer; wavenumbers are given in cm^{-1}. NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers (300 and 400 MHz for ^{1}H NMR; 75 and 101 MHz for ^{13}C NMR; 162 MHz for ^{31}P MNR); chemical shifts are given in (δ) parts per million and coupling constants (J) in hertz. Mass spectra (EI) were obtained at 70 eV on an Agilent 5973 spectrometer; fragment ions in *m/z* with relative intensities (%) in parenthesis. HRMS analyses were carried out on a Finnigan MAT95S spectrometer. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with a Hewlett Packard HP-6890 instrument equipped with a flame ionization detector and a 30 m capillary column (0.32 mm diameter, 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{injector}$ = 270 ºC, T_{column} = 60 ºC (3 min) and 60–270 ºC (15 ºC/min); retention times (t_r) are given in min. Thin layer chromatography was carried out on TLC plastic sheets with silica gel 60 F_{254} (Merck). Column chromatography was performed using silica gel 60 of 40–60 microns (hexane/EtOAc as eluent).

General procedure for the hydrophosphanation of alkenes

All reactions were performed using tubes in a multi-reactor system under argon. Diphenylphosphane (0.5 mmol, 87 μL) and the alkyne (0.5 mmol) were stirred during the specified time at 70 ºC or room temperature (see Table 2). The progress of the reaction was monitored by TLC and GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent in vacuo. The reaction crude absorbed on silicagel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure phosphanes **2**.

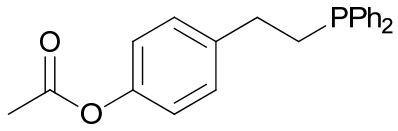
Characterisation of new compounds 2

Compounds **2a**,[1] **2b**,[1] **2d**,[1] **2f**,[2] **2g**,[3] **2j**,[4] **2m**,[5] **2o**,[2] and **2p**,[2] were characterised by comparison of their physical and spectroscopic data with those described in the literature. Data for the new compounds, follow:



(4-Bromophenethyl)diphenylphosphane (2c)

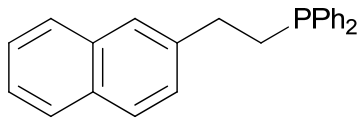
Colourless oil; t_r 16.59 min; R_f 0.63 (hexane). IR (neat) ν = 3069, 2926, 1489, 1432, 1092, 1014, 803, 735, 694, 646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.29–2.39 (m, 2H), 2.62–2.74 (m, 2H), 7.04 (d, J = 8.4 Hz, 2H), 7.31–7.49 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.2 (d, J = 12.9 Hz, CH_2CH_2P), 31.8 (d, J = 18.1 Hz, CH_2P), 119.9, 128.6, 128.7 (d, J = 23.6 Hz, *C*HCHCP), 130.1, 131.6, 132.8 (d, J = 18.5 Hz, *C*HCP), 138.4 (d, J = 12.7 Hz, CCH_2), 141.6 (d, J = 13.0 Hz, *C*P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –16.2. GC-MS (EI): *m/z* (%) = 370 (34) $[M^+$+2], 369 (56) $[M^+$+1], 368 (35) $[M]^+$, 367 (51), 342 (28), 340 (29), 200 (10), 199 (71), 186 (49), 184 (10), 183 (54), 165 (11), 152 (10), 121 (100), 109 (12), 108 (56), 107 (22), 104 (10), 91 (11), 78 (12), 77 (24), 51 (10). HRMS (EI): *m/z* calcd. for $C_{20}H_{18}BrP$ 368.0329, found 368.0336.



4-[2-(Diphenylphosphanyl)ethyl]phenyl acetate (2e)

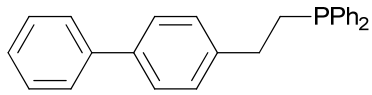
Colourless oil; t_r 17.72 min; R_f 0.32 (hexane/EtOAc 9:1). IR (neat) ν = 3051, 2915, 1760, 1506, 1432, 1367, 1213, 1192, 1164, 1016, 909, 736, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 2.31–2.38 (m, 2H), 2.64–2.75 (m, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.28–7.37 (m, 6H), 7.40–7.47 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.2. 30.2 (d, J = 12.9

Hz, CH_2CH_2P), 31.7 (d, J = 18.2 Hz, CH_2P), 121.5, 128.6, 128.7 (d, J = 20.8 Hz, CHCHCP), 129.2, 132.8 (d, J = 18.5 Hz, CHCP), 138.5 (d, J = 12.9 Hz, CCH_2), 140.3 (d, J = 13.4 Hz, CP), 148.9, 169.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.9. GC-MS (EI): *m/z* (%) = 349 (13) [M^++1], 348 (61) [M^+], 347 (96), 320 (27), 305 (22), 278 (19), 200 (10), 199 (64), 186 (42), 183 (42), 165 (10), 121 (100), 108 (44), 107 (18), 91 (14), 77 (16). HRMS (EI): *m/z* calcd. for $C_{22}H_{21}O_2P$ 348.1271, found 348.1279.



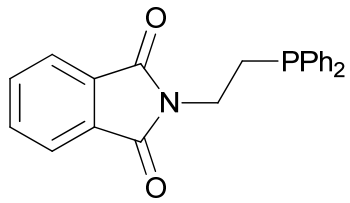
[2-(Naphthalen-2-yl)ethyl]diphenylphosphane (2h)

Yellow oil; t_r 20.90 min; R_f 0.44 (hexane). IR (neat) ν = 3052, 1435, 1178, 1121, 818, 693, 740, 724, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40–2.47 (m, 2H), 2.82–2.92 (m, 2H), 7.28–7.36 (m, 7H), 7.39–7.49 (m, 6H), 7.58 (br s, 1H), 7.73–7.78 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.2 (d, J = 13.0 Hz, CH$_2$CH$_2$P), 32.5 (d, J = 17.8 Hz, CH_2P), 125.4, 126.1, 126.2, 127.2, 127.6, 127.8, 128.2, 128.6, 128.7 (d, J = 19.4 Hz, CHCHCP), 132.2, 132.9 (d, J = 18.5 Hz, CHCP), 133.8, 138.6 (d, J = 13.0 Hz, CCH_2), 140.2 (d, J = 13.3 Hz, CP). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.7. GC-MS (EI): *m/z* (%) = 341 (15) [M^++1], 340 (72) [M^+], 339 (100), 312 (37), 199 (31), 186 (18), 183 (22), 154 (17), 153 (13), 152 (11), 121 (55), 115 (11), 108 (25). HRMS (EI): *m/z* calcd. for $C_{24}H_{21}O_2P$, 340.1381, found 340.1376.



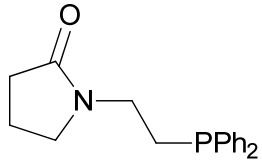
{2-[(1,1'-Biphenyl)-4-yl]ethyl}diphenylphosphane (2i)

Colourless oil; t_r 27.02 min; R_f 0.63 (hexane/EtOAc 9:1). IR (neat) ν = 3051, 3025, 2925, 1483, 1432, 820, 738, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.27–2.35 (m, 2H), 2.64–2.72 (m, 2H), 7.13–7.17 (m, 2H), 7.23–7.26 (m, 6H), 7.30–7.43 (m, 9H), 7.45–7.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.3 (d, J = 13.0 Hz, CH$_2$CH$_2$P), 32.0 (d, J = 17.9 Hz, CH_2P), 127.1, 127.2, 127.3, 128.5, 128.6, 128.7 (d, J = 19.8 Hz, CHCHCP), 128.9, 132.9 (d, J = 18.5 Hz, CHCP), 138.6 (d, J = 13.1 Hz, CP), 139.1, 141.2, 141.8 (d, J = 13.2 Hz, CCH_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.8. GC-MS (EI): *m/z* (%) = 367 (12) [M^++1], 366 (56) [M^+], 365 (100), 339 (12), 338 (48), 199 (40), 186 (29), 183 (30), 180 (19), 166 (11), 165 (25), 152 (13), 121 (66), 108 (30), 77 (12). HRMS (EI): *m/z* calcd. for $C_{26}H_{23}P$ 366.1537, found 366.1547.



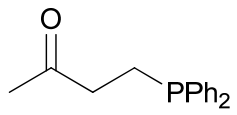
_N_-[2-(Diphenylphosphanyl)ethyl]phthalimide (2k)

Pale yellow oil; t_r 22.11 min; R_f 0.62 (hexane/EtOAc 7:3). IR (neat) ν = 3057, 2911, 1764, 1700, 1432, 1392, 1359, 1315, 1119, 1066, 946, 822, 714, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38–2.44 (m, 2H), 3.80 (dt, *J* = 15.7, 8.5 Hz, 2H), 7.19–7.26 (m, 6H), 7.36–7.41 (m, 4H), 7.58–7.63 (m, 2H), 7.66–7.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 27.5 (d, *J* = 14.8 Hz, CH_2P), 35.5 (d, *J* = 23.1 Hz, CH_2CH_2P), 123.3, 128.6, 128.8 (d, *J* = 19.2 Hz, *C*HCHCP), 132.8 (d, *J* = 19.0 Hz, *C*HCP), 134.0, 137.5, 137.5 (d, *J* = 12.1 Hz, CP), 168.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –21.5. GC-MS (EI): *m/z* (%) = 360 (25) [M^++1], 359 (100) [M^+], 201 (50), 199 (30), 186 (15), 183 (36), 179 (10), 130 (21), 121 (43), 108 (25), 107 (13), 77 (19). HRMS (EI): *m/z* calcd. for $C_{22}H_{18}NO_2P$ 359.1075, found 359.1072.



_N_-[2-(Diphenylphosphanyl)ethyl]pyrrolidin-2-one (2l)

Yellow oil; t_r 19.57 min; R_f 0.37 (EtOAc). IR (neat) ν = 3050, 2914, 2873, 2360, 2341, 1677, 1432, 1285, 739, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.83–1.92 (m, 2H), 2.24–2.34 (m, 4H), 3.34 (t, *J* = 7.0 Hz, 2H), 3.39–3.45 (m, 2H), 7.28–7.37 (m 6H), 7.39–7.45 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 17.9, 26.6 (d, *J* = 14.3 Hz, CH_2P), 31.0, 40.2 (d, *J* = 22.3 Hz, CH_2CH_2P), 47.6, 128.7 (d, *J* = 22.4 Hz, *C*HCHCP), 128.9, 132.8 (d, *J* = 19.0 Hz, *C*HCP), 137.9 (d, *J* = 12.2 Hz, CP), 174.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –20.7. GC-MS (EI): *m/z* (%) = 297 (40) [M^+], 269 (26), 241 (12), 220 (65), 213 (24), 212 (70), 211 (20), 199 (22), 197 (11), 186 (22), 185 (17), 184 (11), 183 (73), 172 (100), 165 (11), 152 (13), 145 (13), 134 (34), 133 (18), 121 (73), 109 (18), 108 (87), 107 (32), 98 (13), 91 (21), 77 (20), 70 (12), 69 (18), 68 (13), 56 (10). HRMS (EI): *m/z* calcd. for $C_{18}H_{20}NOP$ 297.1283, found 297.1273.



4-(Diphenylphosphanyl)butan-2-one (2n)

Colourless oil; t_r 15.18 min; R_f 0.50 (hexane/EtOAc 8:2). IR (neat) ν = 3051, 2914, 1714, 1432, 1385, 740, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.24–2.33 (m, 2H), 2.44–2.56 (m, 2H), 7.29–7.36 (m, 6H), 7.40–7.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.4 (d, *J* = 11.2 Hz, CH_2P), 29.9, 39.9 (d, *J* = 39.9 Hz, *C*H_2CH_2P), 128.6, 128.8 (d, *J* = 22.9 Hz, *C*HCHCP), 132.8 (d, *J* = 18.6 Hz, *C*HCP), 138.1 (d, *J* = 12.5 Hz, CP), 200.7 (d, *J* = 12.5 Hz, CO). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.6. GC-MS (EI): *m/z* (%) = 256 (56) [M^+], 255 (98), 217 (12), 215 (11), 213 (12), 202 (10), 201 (63), 185 (21), 184 (13), 183 (100), 152 (14), 141 (37), 131 (11), 121 (21), 108 (22), 107 (21). HRMS (EI): *m/z* calcd. for $C_{16}H_{17}OP$ 256.1017, found 256.1007.

References

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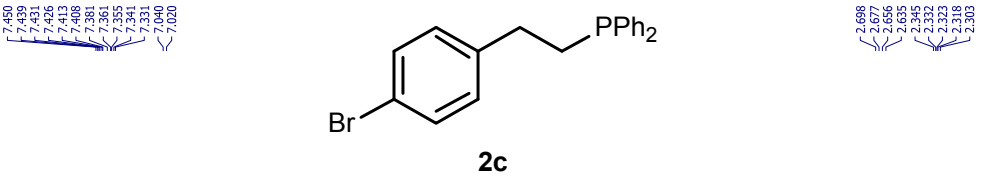
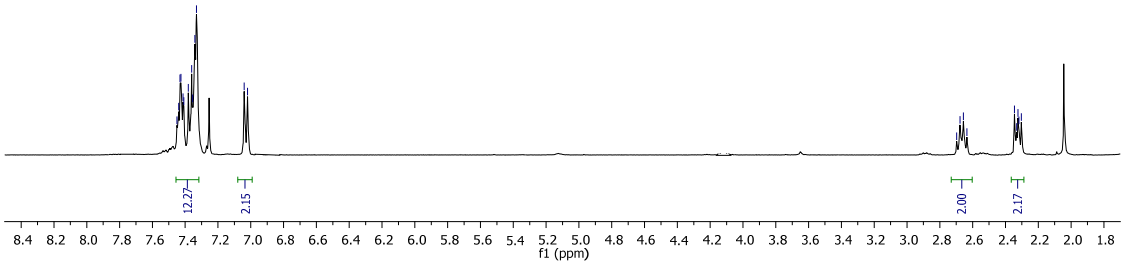
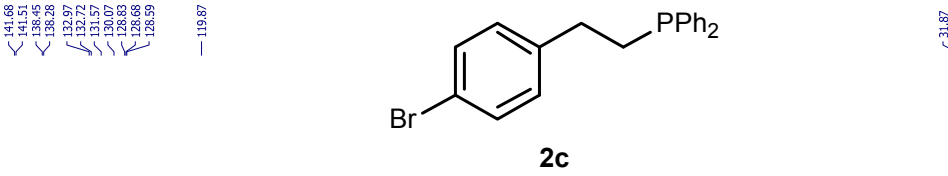
NMR spectra of new compounds 2



2c





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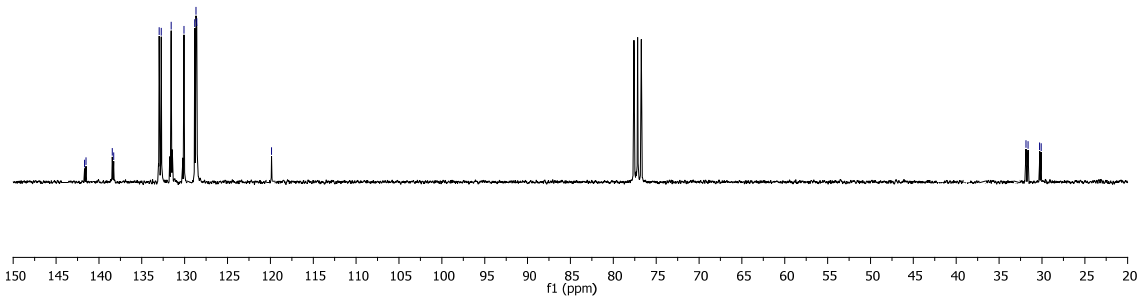
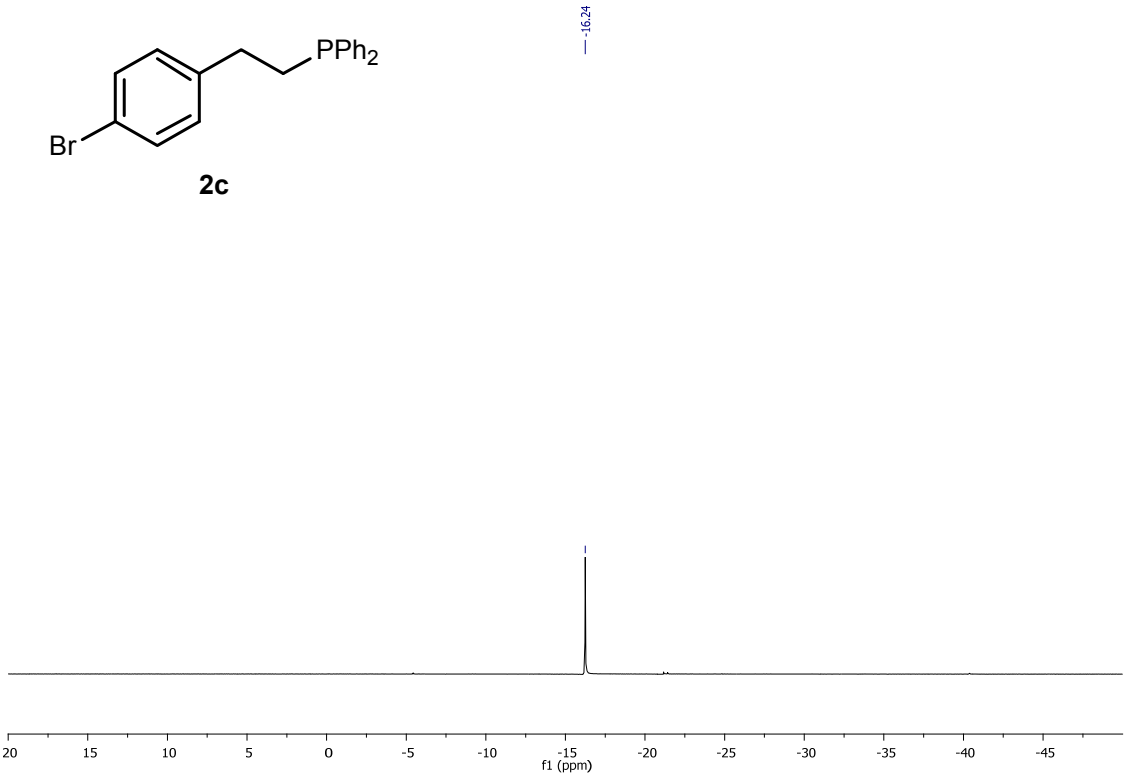


PPh2
Br

2c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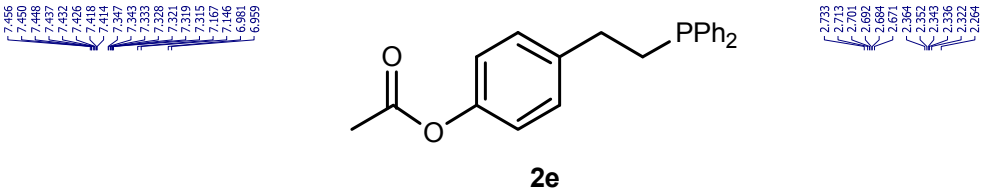
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)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2.713
2.701
2.692
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2.336
2.322
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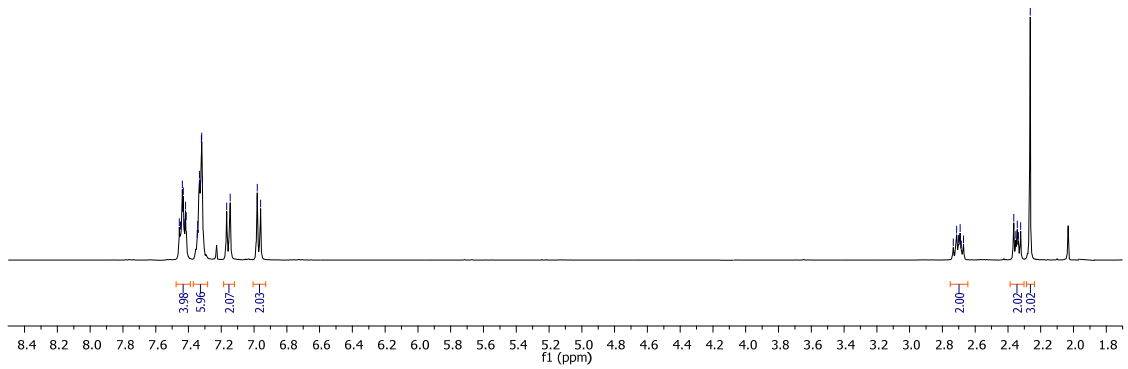
PPh2
O
O

2e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7.2
7.0
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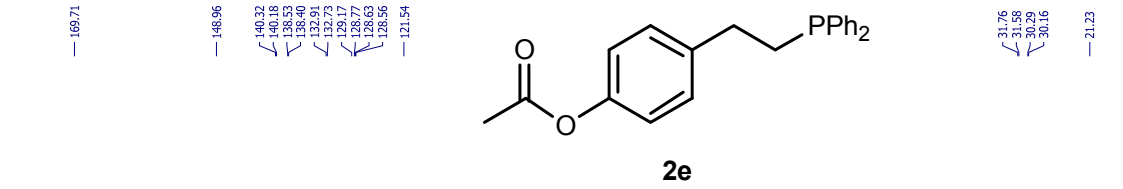
1.8
f1 (ppm)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132.73
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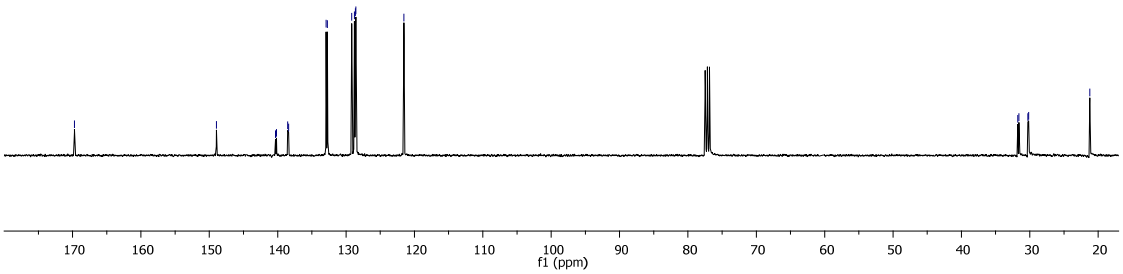
121.54
31.76
31.58
30.29
30.16
21.23
O
O
PPh2

2e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60
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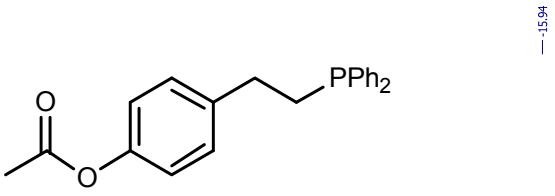
30
20
f1 (ppm)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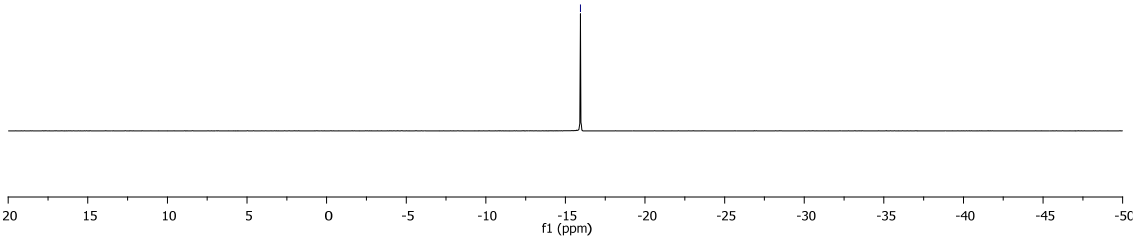
O
PPh2

2e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-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


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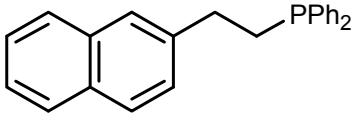
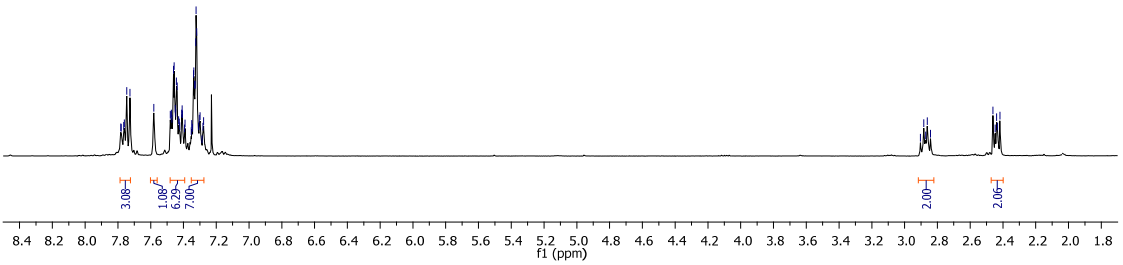

PPh2

2h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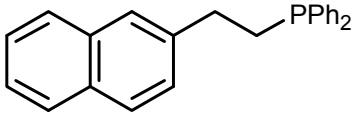
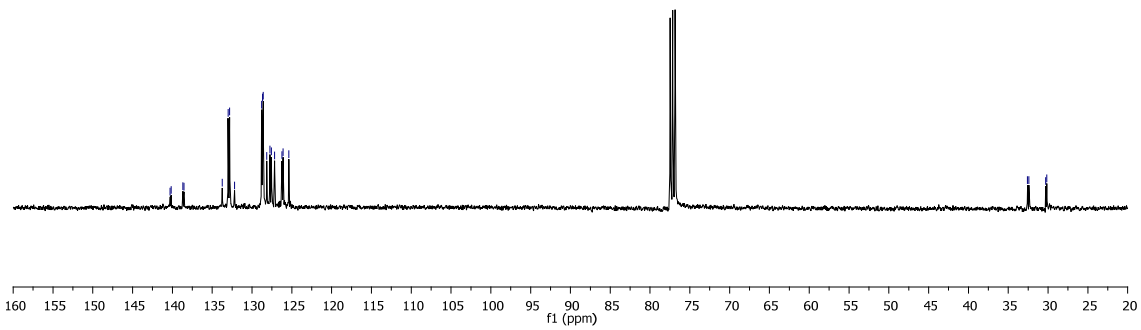
f1 (ppm)


140.29
140.15
138.66
138.55
133.75
133.00
132.82
132.20
128.79
128.66
128.60
128.15
127.76
127.58
127.16
126.24
126.10
125.37


PPh2

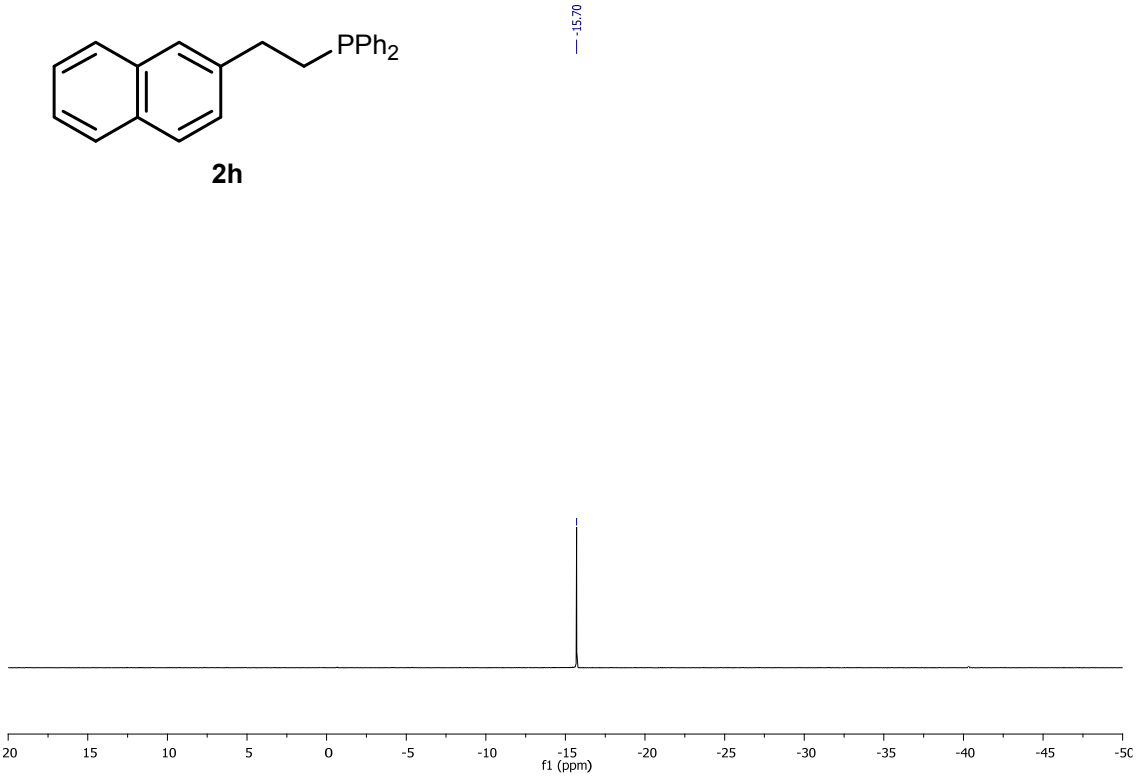

32.59
32.41
30.30
30.17

2h

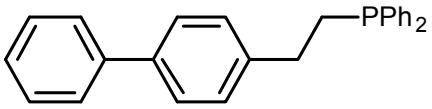

160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

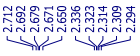
PPh2

2h

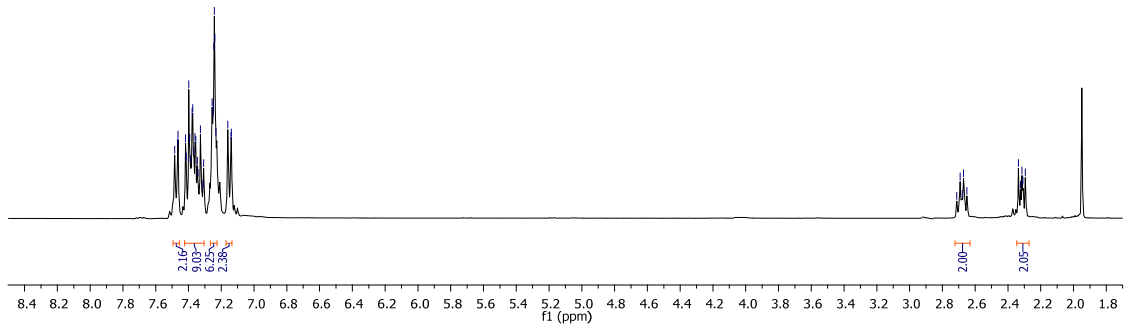

-15.70
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

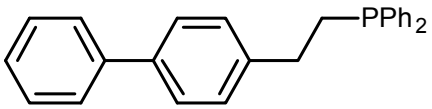

7.484
7.467
7.464
7.418
7.414
7.398
7.393
7.388
7.378
7.374
7.367
7.360
7.356
7.346
7.342
7.327
7.312
7.308
7.256
7.252
7.249
7.245
7.242
7.239
7.233
7.160
7.140
7.138


PPh2

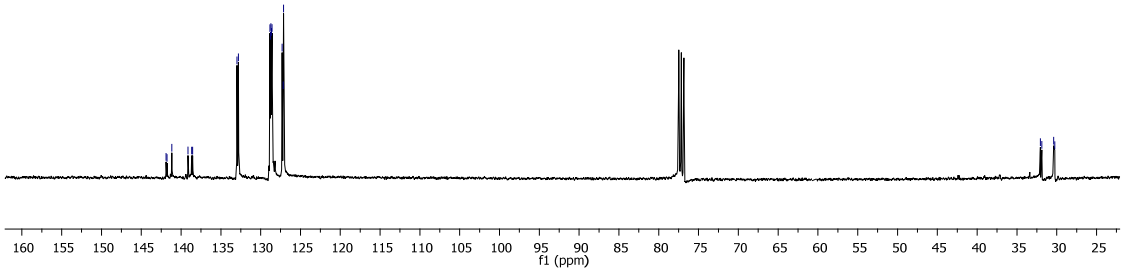

2.712
2.692
2.679
2.671
2.650
2.336
2.323
2.314
2.309
2.294

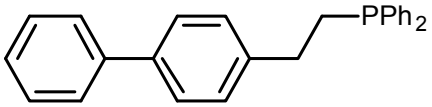
2i


2.16
9.03
6.25
2.38
2.00
2.05
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

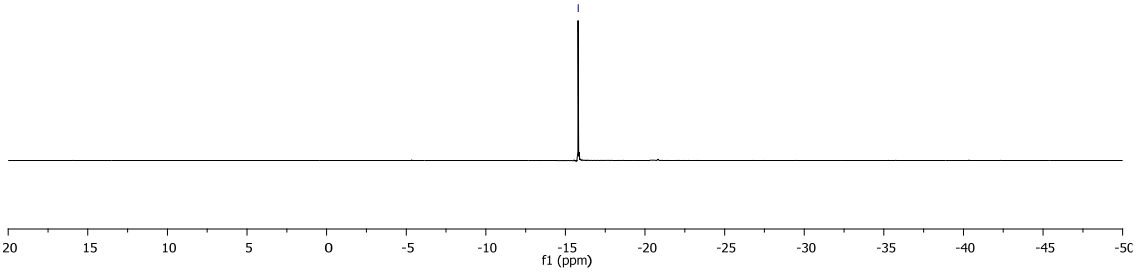


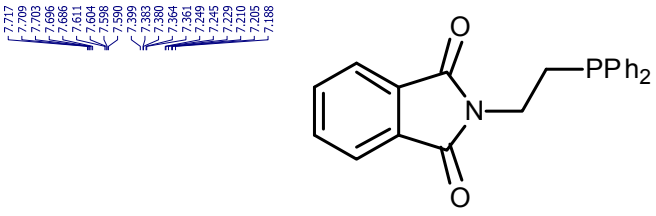
2i



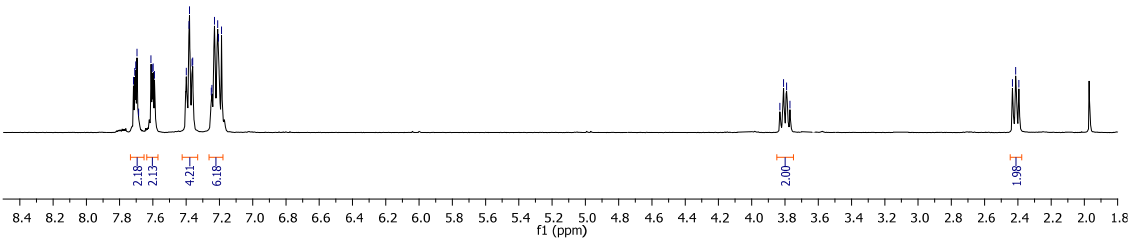


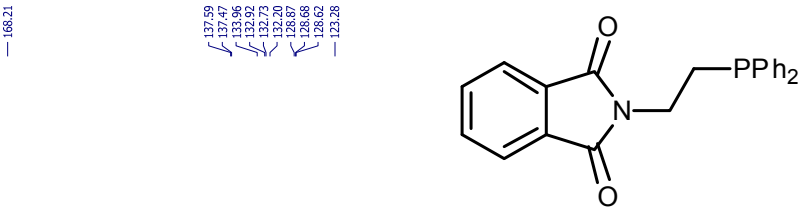
2i



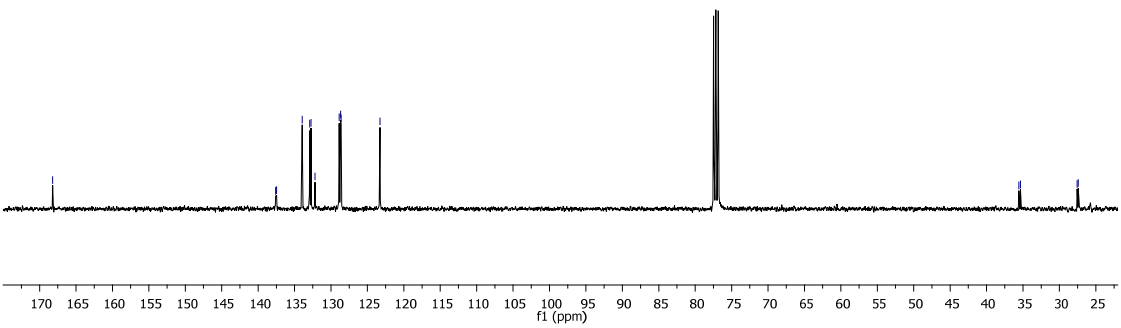

7.717
7.709
7.703
7.696
7.686
7.611
7.604
7.598
7.590
7.399
7.383
7.380
7.364
7.361
7.249
7.245
7.229
7.210
7.205
7.188
3.831
3.808
3.790
3.770
2.432
2.413
2.394
O
N
O
PPh2

2k


2.18
2.13
4.21
6.18
2.00
1.98
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

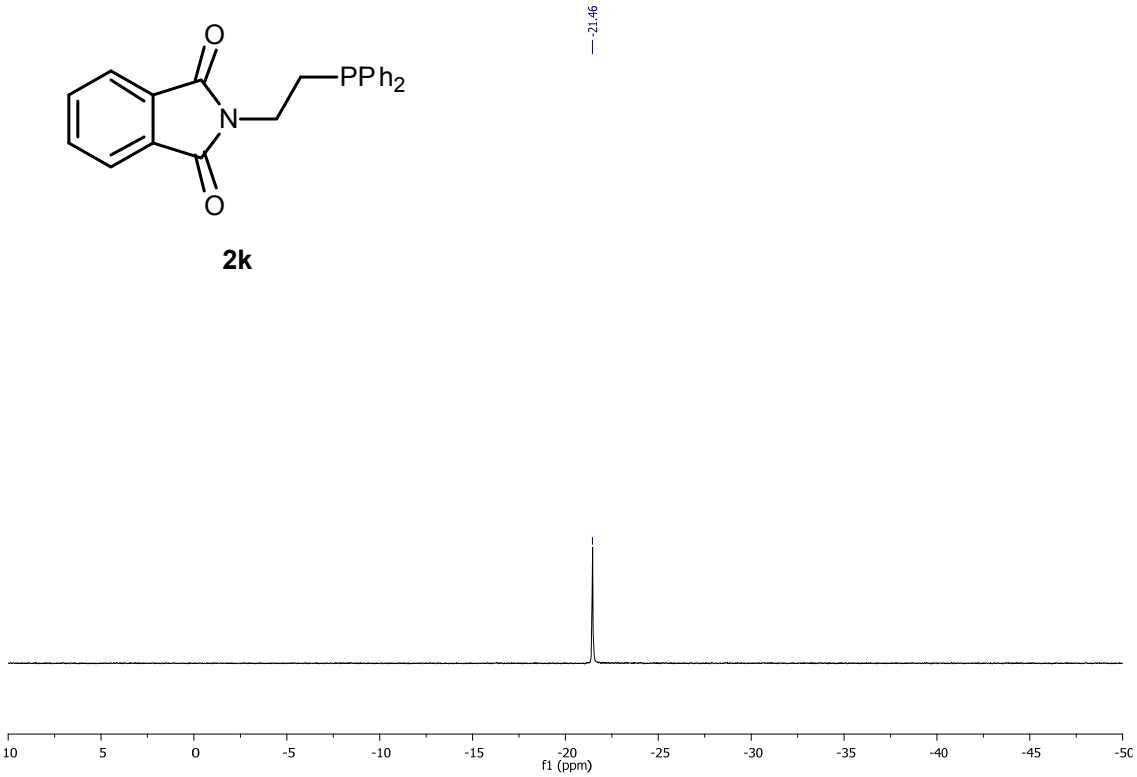

168.21
137.59
137.47
133.96
132.92
132.73
132.20
128.87
128.68
128.62
123.28
35.57
35.34
27.56
27.41
O
N
O
PPh2

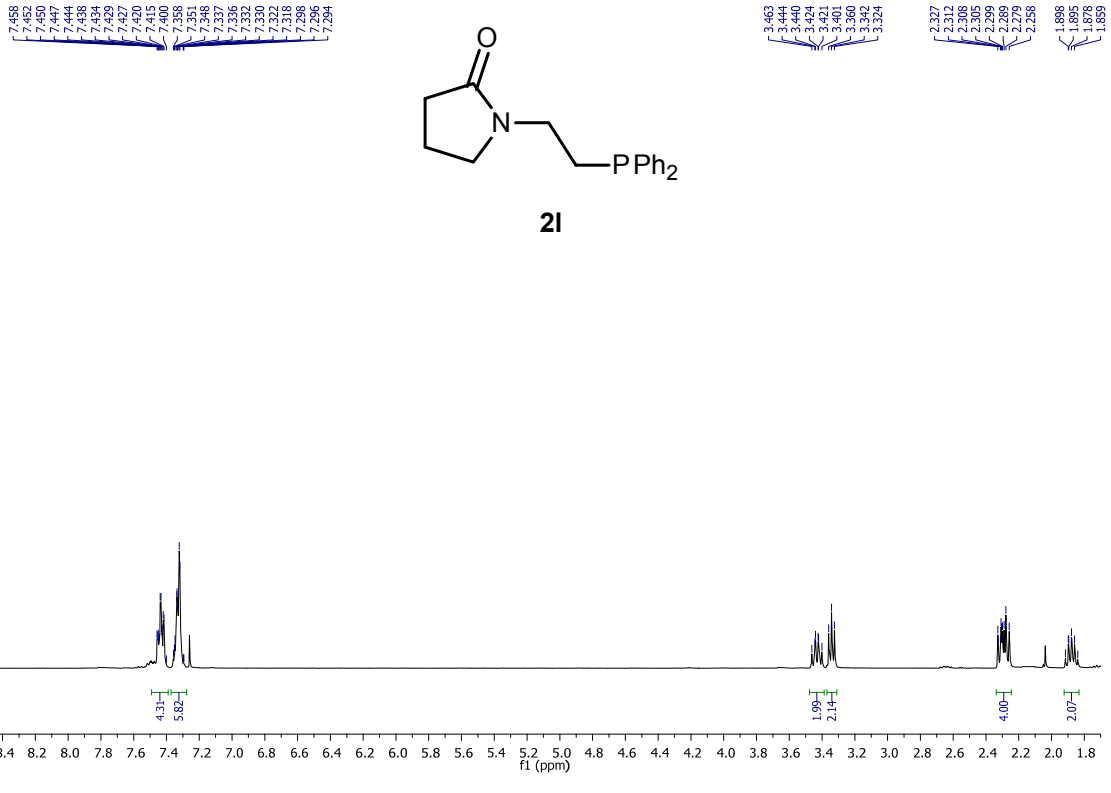
2k


170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

O
N
O
PPh2

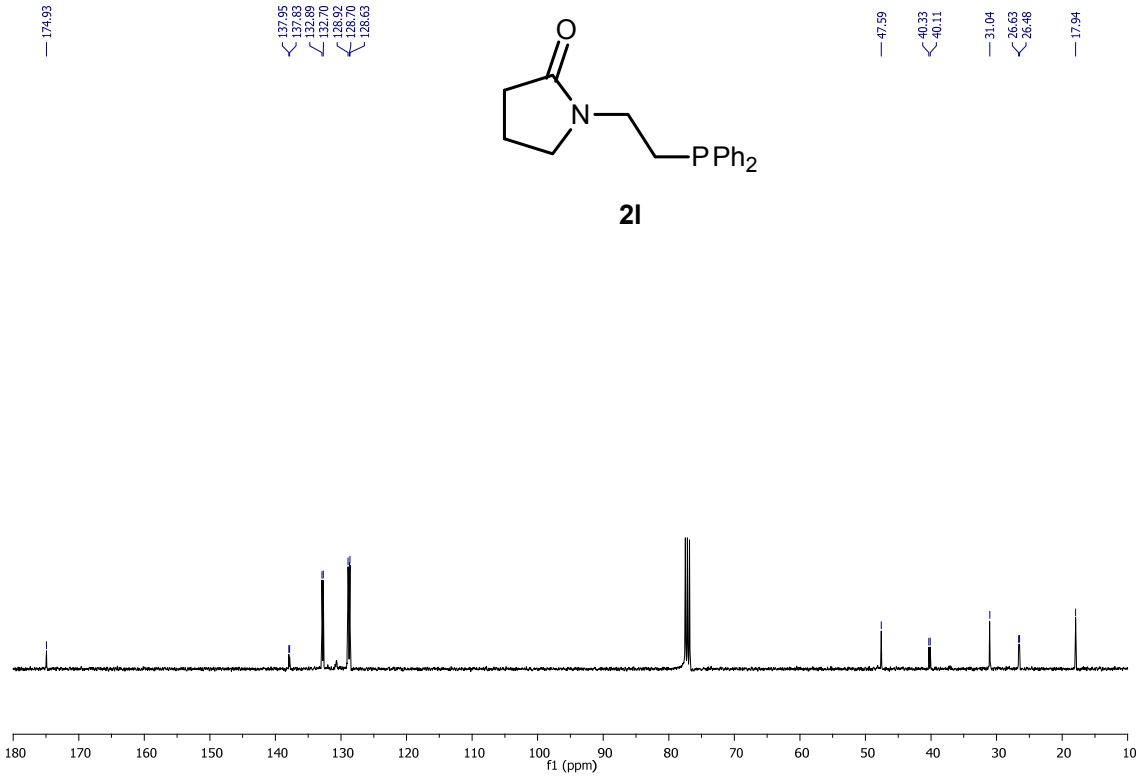
2k


-21.46
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

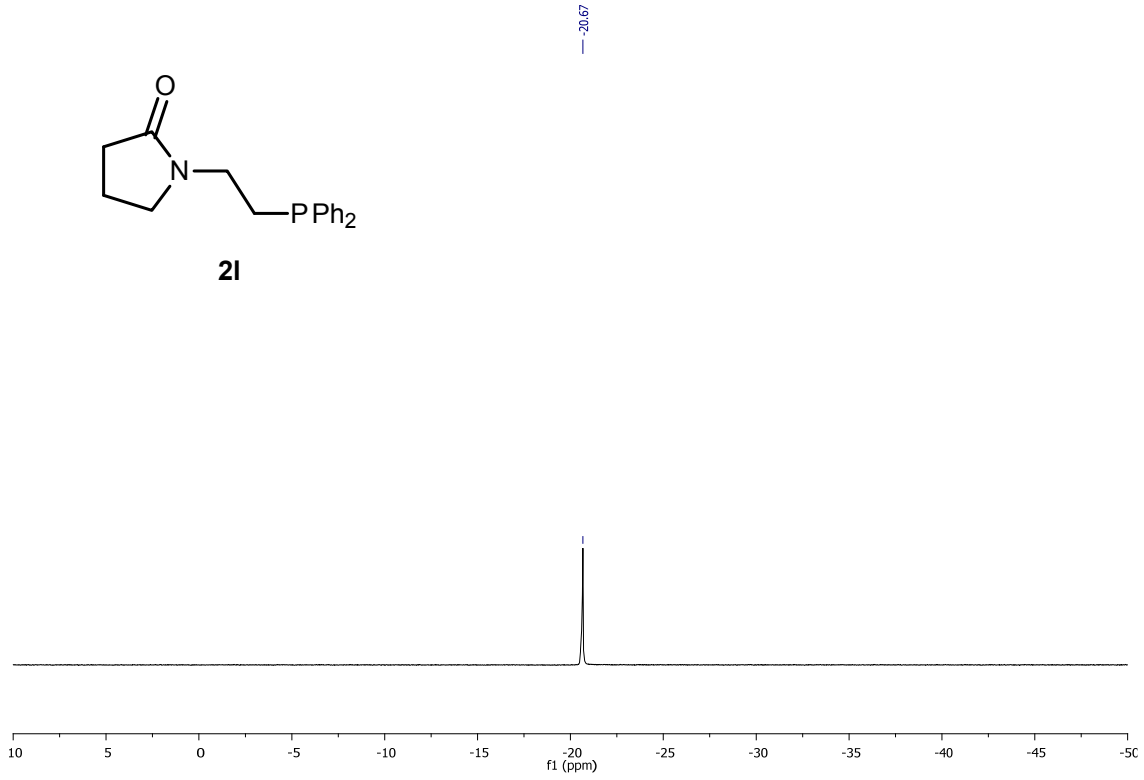

7.458
7.452
7.450
7.447
7.444
7.438
7.434
7.429
7.427
7.420
7.415
7.400
7.358
7.351
7.348
7.337
7.336
7.332
7.330
7.322
7.318
7.298
7.296
7.294
3.463
3.444
3.440
3.424
3.421
3.401
3.360
3.342
3.324
2.327
2.312
2.308
2.305
2.299
2.289
2.279
2.258
1.898
1.895
1.878
1.859
4.31
5.82
1.99
2.14
4.00
2.07
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

O
N
PPh2

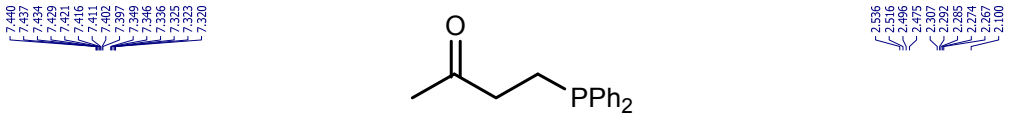
2l


174.93
137.95
137.83
132.89
132.70
128.92
128.70
128.63
47.59
40.33
40.11
31.04
26.63
26.48
17.94
O
N
PPh2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

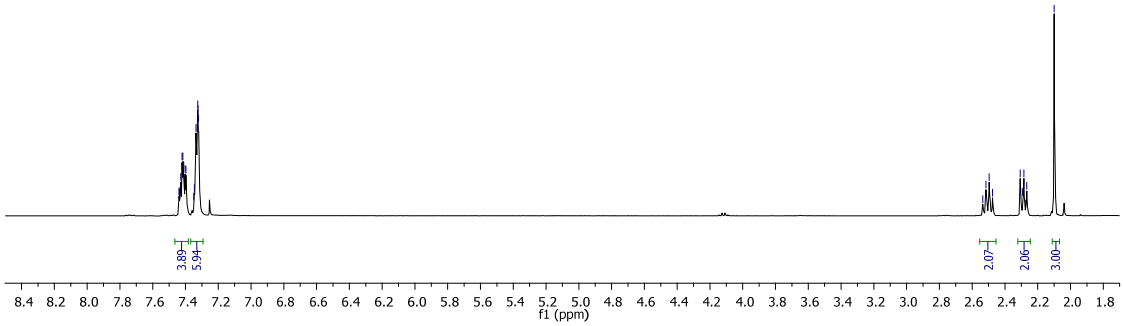
2l


20.67
O
N
PPh2
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

2l

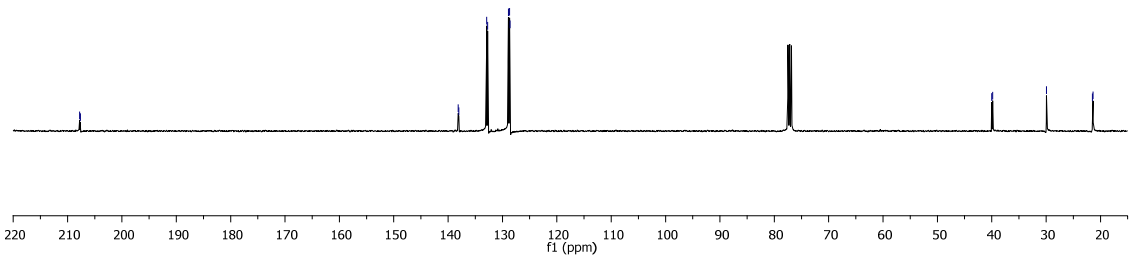

7.440
7.437
7.434
7.429
7.421
7.416
7.411
7.402
7.397
7.349
7.346
7.336
7.325
7.323
7.320
O
PPh2
2.536
2.516
2.496
2.475
2.307
2.292
2.285
2.274
2.267
2.100

2n


3.89
5.94
2.07
2.06
3.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)


207.77
207.65
O
PPh2
138.15
138.03
132.91
132.73
128.91
128.68
128.62
40.01
39.83
29.93
21.48
21.37

2n


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

2n