# Supporting Information

## Hydrophosphination of alkenes and alkynes with primary phosphine catalyzed by zirconium complexes bearing aminophenolato ligands

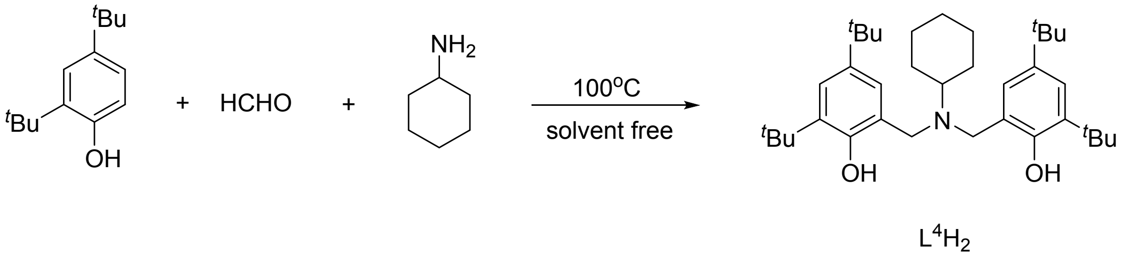
**Yu Zhang, Xinxin Wang, Yaorong Wang, Dan Yuan*, and Yingming Yao***

†Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

*To whom correspondence should be addressed. Email: yuandan@suda.edu.cn; yaoym@suda.edu.cn

**Content**

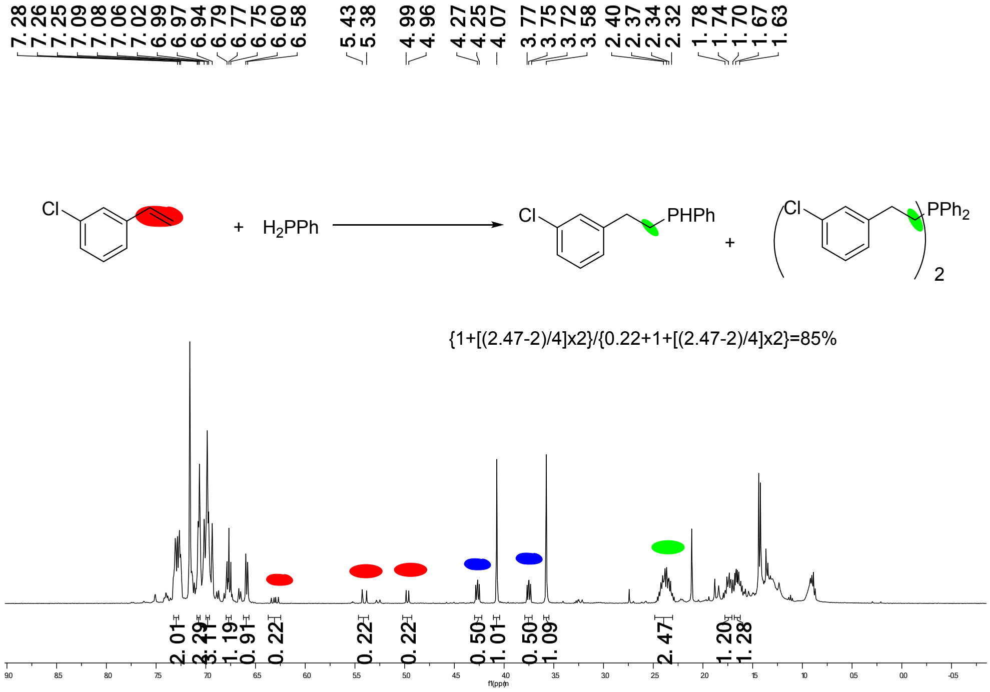
**Preparation of ligand precursor $L^4H_2$**



2,4-di-*tert*-butylphenol (100 mmol, 20.63 g), paraformaldehyde (100 mmol, 3.00 g) and cyclohexanamine (50 mmol, 5.72 g) were mixed in a 250 mL round bottom flask. The resulting mixture was heat to 100 °C and stirred for 12 hours. After that, the pure product was isolated by silica gel chromatography. Yield 17.40 g, 65%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.22 (s, 2H, ArH), 6.92 (s, 2H, ArH), 3.77 (d, 4H, $NCH_2$), 2.73 (t, 1H, NCH), 1.94 (m, 2H, $CH_2$), 1.81 (m, 2H, $CH_2$), 1.62 (m, 2H, $CH_2$), 1.42 (d, 18H, J = 6.05 Hz, $C(CH_3)_3$), 1.29 (d, 18H, J = 5.63 Hz, $C(CH_3)_3$), 1.28 (m, 4H, $CCH_2$). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): 152.8, 141.6, 136.3, 125.3, 123.6, 122.0 (Ar-C), 57.6 (Ar-$CH_2$N), 52.7 (Ar-$CH_2$N), 36.1 (NCH), 34.4 ($\mathit{C}(CH_3)_3$), 34.5 ($\mathit{C}(CH_3)_3$), 32.1 ($C(\mathit{C}H_3)_3$), 29.9 ($C(\mathit{C}H_3)_3$), 27.7 ($\mathit{C}H_2$) , 26.4 ($\mathit{C}H_2$) , 26.0 ($\mathit{C}H_2$). MS calcd m/z 536.4468 for $C_{36}H_{58}NO_2$ $[M + H]^+$, Found: 536.4485.

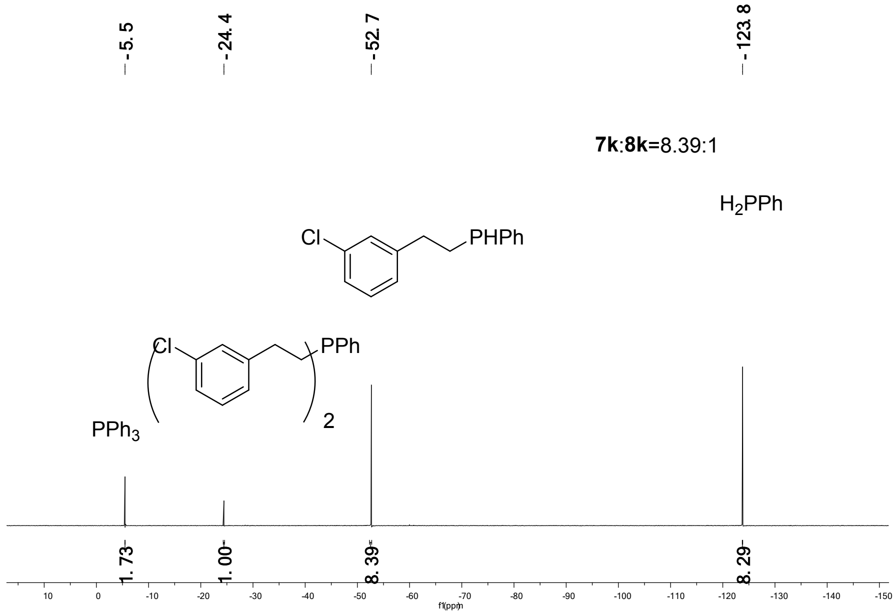
**Characterizations of hydrophosphination products**

The conversion was determined by comparison of the integration of remaining styrene and the new product. The ratio of **7** and **8** was determined by $^{31}$P NMR. Taking substrate **5k** as an example (see below):



{1+[(2.47-2)/4]x2}/{0.22+1+[(2.47-2)/4]x2}=85%

Fig. S1 $^1$H NMR of the conversion of substrate **5k**



**7k**:**8k**=8.39:1

Fig. S2 $^{31}$P NMR of the conversion of substrate **5k**

## Parameters for quantitative $^{31}$P NMR experiment

| | | |
|---|---|---|
| General | | |
| PULPROG | zgig30 | |
| TD | 65536 | |
| SWH [Hz, ppm] | 49019.61 | 302.654 |
| AQ [sec] | 0.6684672 | |
| RG | 203 | |
| DW [μsec] | 10.200 | |
| DE [μsec] | 6.50 | |
| D1 | 10.00000000 | |
| d11 | 0.03000000 | |
| DS | 4 | |
| NS | 16 | |
| TD0 | 1 | |
| Channel f1 | | |
| SFO1 [MHz] | 161.9658745 | |
| O1 [Hz, ppm] | -9718.54 | -60 |
| NUC1 | 31P | |
| P1 [μsec] | 7.10 | |
| PLW1 [W, -dBW] | 75 | -18.75 |
| Channel f2 | | |
| SFO2 [MHz] | 400.1316005 | |
| O2 [Hz, ppm] | 1600.50 | 4.000 |
| NUC2 | 1H | |
| CPDPRG 2 | Waltz16 | |
| PCPD2 [μsec] | 90.00 | |
| PLW2 [W, -dBW] | 21.979 | -13.42 |
| PLW12 [W, -dBW] | 0.27134 | 5.66 |

## phenethyl(phenyl)phosphine (7a)[1a]

**7a** was prepared from **5a** (57 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.36−7.33 (m, 2H, ArH), 7.12 (t, 3H, ArH), 7.08−7.03 (m, 3H, ArH), 6.94 (d, ArH, 2H, J = 7.76 Hz), 4.36 (dt, J = 206.12 Hz and $^2$J = 14.17 Hz, PH), 2.67−2.54 (m, 2H, $CH_2$), 1.98−1.90 (m, 1H, $CH_2$), 1.86−1.79 (m, 1H, $CH_2$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): -52.9.

**(2-methylphenethyl)(phenyl)phosphine (7b)**

**7b** was prepared from **5b** (64 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). Crude product was dissolved in anhydrous hexane (5 mL), and filtered. The solvent was removed in vacuo, and the resulting mixture was purified by passing through a short plug of silica gel (petroleum ether as eluent) under inert conditions, which gave the pure product in 90 mg (0.39 mol, 79% yield). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.37−7.33 (m, 2H, ArH), 7.07−7.02 (m, 5H, ArH), 7.00-6.94 (m, ArH, 2H), 4.39 (dt, J = 206.16 Hz and $^2$J = 13.74 Hz, PH), 2.67−2.50 (m, 2H, $CH_2$), 1.96 (s, 3H, $CH_3$), 1.92−1.76 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -51.6. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): 141.1 (d, J = 8.62 Hz, $C_6H_4$), 136.5 (d, J = 11.88 Hz, Ar-C), 134.4 (d, J = 15.36 Hz, Ar-C), 130.9 (s, Ar-C), 129.1 (d, J = 5.63 Hz, Ar-C), 126.8 (d, J = 9.87 Hz, Ar-C), 126.8 (s, Ar-C), 32.7 (d, J = 8.28 Hz, $CH_2$), 24.8 (d, J = 12.56 Hz, $CH_2$), 19.4 (s, $CH_3$). MS calcd m/z 267.0915 for $C_{15}H_{17}OP$ $[M + Na]^+$, Found: 267.0929. Phosphines (in small amount for MS spectrometry measurement) are oxidized when waiting for measurement.

**(3-methylphenethyl)(phenyl)phosphine (7c)**

**7c** was prepared from **5c** (66 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). Crude product was dissolved in anhydrous hexane (5 mL), and filtered. The solvent was removed in vacuo, and the resulting mixture was purified by passing through a short plug of silica gel (petroleum ether as eluent) under inert conditions, which gave the pure product in 91 mg (0.4 mol, 80% yield). $^1$H

NMR (400 MHz, $C_6D_6$):$\delta$ 7.38−7.34 (m, 2H, ArH), 7.10-7.03 (m, 4H, ArH), 6.90−6.78 (m, 3H, ArH), 4.39 (dt, J = 206.22 Hz and $^2$J = 13.57 Hz, PH), 2.68−2.53 (m, 2H, $CH_2$), 2.12 (s, 3H, $CH_3$), 2.02−1.81 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -52.7. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): δ 142.9 (d, J = 7.39 Hz, Ar-C), 138.3 (s, Ar-C), 134.3 (d, J = 14.30 Hz, Ar-C), 129.7 (s, Ar-C), 129.1 (d, J = 5.53 Hz, Ar-C), 127.4 (s, Ar-C), 126.0 (s, Ar-C), 35.2 (d, J = 8.25 Hz, $CH_2$), 26.1 (d, J = 13.41 Hz, $CH_2$), 21.7 (s, $CH_3$). MS calcd m/z 245.1095 for $C_{15}H_{17}OP$ $[M + H]^+$, Found: 245.1097. Phosphines (in small amount for MS spectrometry measurement) are oxidized when waiting for measurement.

**(4-methylphenethyl)(phenyl)phosphine (7d)**[1a]

**7d** was prepared from **5d** (66 µL, 0.5 mmol) and **7** (82 µL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.38−7.34 (m, 2H, ArH), 7.08-7.06 (m, 2H, ArH), 6.98−6.95 (m, 3H, ArH), 6.90 (d, ArH, 2H, J = 7.81 Hz), 4.38 (dt, J = 207.15 Hz and $^2$J = 14.81 Hz, PH), 2.70−2.55 (m, 2H, $CH_2$), 2.13 (s, 3H, $CH_3$), 2.02−1.92 (m, 1H, $CH_2$), 1.86−1.82 (m, 1H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -53.0.

**(4-(*tert*-butyl)phenethyl)(phenyl)phosphine (7e)**[1b]

**7e** was prepared from **5e** (92 µL, 0.5 mmol) and **7** (82 µL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.37−7.34 (m, 2H, ArH), 7.28-7.22 (m, 3H, ArH), 7.08-7.06 (m, 2H, ArH), 6.98 (d, ArH, 2H, J = 7.70 Hz), 4.40 (dt, J = 205.42 Hz and $^2$J = 15.68 Hz, PH), 2.73−2.61 (m, 2H, $CH_2$), 2.05−1.97 (m, 1H, $CH_2$), 1.93−1.84 (m, 1H, $CH_2$), 1.24 (d, $C(CH_3)_3$, 9H, J = 3.92 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -52.9.

**(4-methoxyphenethyl)(phenyl)phosphine (7f)**[1a]

**7f** was prepared from **5f** (66 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1H$ NMR (400 MHz, $C_6D_6$): *δ* 7.38−7.35 (m, 2H, ArH), 7.11-7.05 (m, 3H, ArH), 6.87 (d, ArH, 2H, J = 7.78 Hz), 6.79 (d, ArH, 2H, J = 9.18 Hz), 4.39 (dt, J = 206.00 Hz and $^2J$ = 13.03 Hz, PH), 3.32 (s, 3H, $CH_3$), 2.70−2.55 (m, 2H, $CH_2$), 1.99−1.95 (m, 1H, $CH_2$), 1.85−1.83 (m, 1H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -53.4.

**(2-fluorophenethyl)(phenyl)phosphine (7g)**

**7g** was prepared from **5g** (60 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). Crude product was dissolved in anhydrous hexane (5 mL), and filtered. The solvent was removed in vacuo, and the resulting mixture was purified by passing through a short plug of silica gel (petroleum ether as eluent) under inert conditions, which gave the pure product in 95 mg (0.41 mol, 82% yield). $^1H$ NMR (400 MHz, $C_6D_6$): *δ* 7.35−7.31 (m, 2H, ArH), 7.08−7.02 (m, 3H, ArH), 6.83−6.73 (m, 4H, ArH), 4.35 (dt, J = 206.09 Hz and $^2J$ = 13.93 Hz, PH), 2.74 −2.58 (m, 2H, $CH_2$), 2.00−1.80 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -53.2. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): δ 163.1 (s, Ar-C), 160.6 (s, Ar-C), 137.2 (d, J = 15.11 Hz, Ar-C), 132.0 (d, J = 5.11 Hz, Ar-C), 129.1 (d, J = 5.71 Hz, Ar-C), 124.5 (d, J = 3.31 Hz, Ar-C), 115.9 (d, J = 22.14 Hz, Ar-C), 29.4 (d, J = 8.05 Hz, $CH_2$), 24.0 (d, J = 13.76 Hz, $CH_2$). MS calcd m/z 249.0845 for

$C_{14}H_{15}FOP$ [M + H]$^+$. Found: 249.0853. Phosphines (in small amount for MS spectrometry measurement) are oxidized when waiting for measurement.

**(2-chlorophenethyl)(phenyl)phosphine (7h)**[1c]

**7h** was prepared from **5h** (64 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1H$ NMR (400 MHz, $C_6D_6$): *δ* 7.38−7.34 (m, 2H, ArH), 7.09−7.06 (m, 2H, ArH), 7.97−7.00 (m, 3H, ArH), 6.85−6.78 (m, 2H, ArH), 4.38 (dt, J = 206.74 Hz and $^2J$ = 13.96 Hz, PH), 2.83−2.70 (m, 2H, $CH_2$), 1.98−1.93 (m, 1H, $CH_2$), 1.89−1.83 (m, 1H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -51.8.

**(2-bromophenethyl)(phenyl)phosphine (7i)**

**7i** was prepared from **5i** (63 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). Crude product was dissolved in anhydrous hexane (5 mL), and filtered. The solvent was removed in vacuo, and the resulting mixture was purified by passing through a short plug of silica gel (petroleum ether as eluent) under inert conditions, which gave the pure product in 117 mg (0.40 mol, 80% yield). $^1H$ NMR (400 MHz, $C_6D_6$): *δ* 7.38−7.32 (m, 2H, ArH), 7.08−7.06 (m, 2H, ArH), 7.01−6.96 (m, 2H, ArH), 6.85−6.84 (m, 1H, ArH), 6.77−6.75 (m, 1H, ArH), 6.66−6.61 (m, 1H, ArH), 4.40 (dt, J = 206.85 Hz and $^2J$ = 13.6 Hz, PH), 2.82 −2.68 (m, 2H, $CH_2$), 1.97−1.80 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -51.7. $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$): 134.4 (d, J = 16.56 Hz, Ar-C), 133.4 (s, Ar-C), 130.8 (s, Ar-C), 129.1 (d, J = 5.67 Hz, Ar-C), 127.9 (s, Ar-C), 124.9 (s, Ar-C), 35.7 (d, J = 8.45 Hz, $CH_2$), 24.2 (d, J = 14.32 Hz, $CH_2$). MS calcd m/z 330.9863 for $C_{14}H_{14}BrOP$ [M + Na]$^+$. Found: 330.9881. Phosphines (in small amount for MS spectrometry measurement) are oxidized when waiting for measurement.

**(3-fluorophenethyl)(phenyl)phosphine (7j)**

**7j** was prepared from **5j** (60 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). Crude product was dissolved in anhydrous hexane (5 mL), and filtered. The solvent was removed in vacuo, and the resulting mixture was purified by passing through a short plug of silica gel (petroleum ether as eluent) under inert conditions, which gave the pure product in 74 mg (0.32 mol, 64% yield). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.33−7.29 (m, 2H, ArH), 7.09−7.05 (m, 3H, ArH), 6.87 −6.54 (m, 4H, ArH), 4.28 (dt, J = 206.34 Hz and $^2$J = 13.03 Hz, PH), 2.51 −2.34 (m, 2H, $CH_2$), 1.84−1.65 (m, 2H, $CH_2$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): -52.9. $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$): δ 165.0 (s, Ar-C), 162.6 (s, Ar-C), 134.3 (d, J = 15.22 Hz, Ar-C), 130.4 (d, J = 7.96 Hz, Ar-C), 129.1 (d, J = 6.39 Hz, Ar-C), 124.5 (d, J = 2.97 Hz, Ar-C), 115.8 (d, J = 20.36 Hz, Ar-C), 113.5 (d, J = 20.36, Ar-C), 34.6 (d, J = 7.62 Hz, $CH_2$), 25.3 (d, J = 14.37 Hz, $CH_2$). MS calcd m/z 249.0845 for $C_{14}H_{15}FOP$ $[M + H]^+$. Found: 249.0835. Phosphines (in small amount for MS spectrometry measurement) are oxidized when waiting for measurement.

**(3-chlorophenethyl)(phenyl)phosphine (7k)**[1c]

**7k** was prepared from **5k** (64 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.30−7.28 (m, 2H, ArH), 7.09−7.06 (m, 2H, ArH), 7.97−7.99 (m, 3H, ArH), 6.79−6.65 (m, 1H, ArH), 6.60 (d, ArH, 1H, J = 7.61

Hz), 4.28 (dt, J = 206.43 Hz and ${}^2$J = 14.19 Hz, PH), 2.46 −2.32 (m, 2H, $CH_2$), 1.78−1.70 (m, 1H, $CH_2$), 1.67−1.63 (m, 1H, $CH_2$). ${}^{31}P\{{}^1H\}$ NMR (162 MHz, $C_6D_6$): -52.7.

**(3-bromophenethyl)(phenyl)phosphine (7l)**[1a]

**7l** was prepared from **5l** (65 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). ${}^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.30−7.25 (m, 2H, ArH), 7.10−7.06 (m, 2H, ArH), 7.02−6.96 (m, 3H, ArH), 6.71−6.60 (m, 2H, ArH), 4.28 (dt, J = 206.64 Hz and ${}^2$J = 13.89 Hz, PH), 2.41 −2.28 (m, 2H, $CH_2$), 1.78−1.70 (m, 1H, $CH_2$), 1.66−1.59 (m, 1H, $CH_2$). ${}^{31}P\{{}^1H\}$ NMR (162 MHz, $C_6D_6$): -52.6.

**(4-fluorophenethyl)(phenyl)phosphine (7m)**[1b]

**7m** was prepared from **5m** (60 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). ${}^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.35−7.25 (m, 2H, ArH), 7.09−7.06 (m, 2H, ArH), 6.97−6.95 (m, 3H, ArH), 6.65−6.62 (m, 2H, ArH), 4.30 (dt, J = 205.91 Hz and ${}^2$J = 13.41 Hz, PH), 2.50 −2.39 (m, 2H, $CH_2$), 1.85−1.79 (m, 1H, $CH_2$), 1.74−1.69 (m, 1H, $CH_2$). ${}^{31}P\{{}^1H\}$ NMR (162 MHz, $C_6D_6$): -52.5.

**(4-chlorophenethyl)(phenyl)phosphine (7n)**[1b]

**7n** was prepared from **5n** (60 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). ${}^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.34−7.31 (m, 2H, ArH), 7.10−7.05 (m, 3H, ArH), 6.99−6.97 (m, 2H, ArH), 6.59 (d, ArH, 2H, J = 8.59 Hz), 4.30 (dt, J = 206.59 Hz and ${}^2$J = 14.61 Hz, PH), 2.46 −2.34 (m, 2H, $CH_2$), 1.83−1.73 (m, 1H, $CH_2$), 1.70−1.64 (m, 1H, $CH_2$). ${}^{31}P\{{}^1H\}$ NMR (162MHz, $C_6D_6$): -53.0.

**(4-bromophenethyl)(phenyl)phosphine (7o)**[1b]

**7o** was prepared from **5p** (65 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.32−7.30 (m, 2H, ArH), 7.09−7.07 (m, 3H, ArH), 7.00−6.96 (m, 2H, ArH), 6.51 (d, ArH, 2H, J = 8.83 Hz), 4.29 (dt, J = 205.02 Hz and $^2$J = 15.71 Hz, PH), 2.43 −2.31 (m, 2H, $CH_2$), 1.81−1.73 (m, 1H, $CH_2$), 1.69−1.63 (m, 1H, $CH_2$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): -53.0.

**phenyl(2-phenylpropyl)phosphine (7p)**[1c]

**7p** was prepared from **5p** (66 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 7.37−7.35 (m, 3H, ArH), 7.14-7.10 (m, 2H, ArH), 7.03−7.05 (m, 3H, ArH), 6.99−6.97 (m, ArH, 2H), 4.33 (dm, J = 207.39 Hz, PH), 2.74 (m, 1H, CH), 2.03 (dm, J = 89.94 Hz, $CH_2$), 1.18 (dd, 3H, $CH_3$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): -48.8.

**2-(2-(phenylphosphinyl)ethyl)pyridine (7q)**[1a]

**7q** was prepared from **5q** (54 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 8.60−8.59 (m, 1H, ArH), 7.43−7.39 (m, 2H, ArH), 7.18−7.17 (m, 1H, ArH), 7.09−7.07 (m, 3H, ArH), 6.83−6.82 (m, 1H, ArH), 6.60 (d, ArH, 1H, J = 5.66 Hz), 4.37 (dt, J = 206.68 Hz and $^2$J = 14.05 Hz, PH), 2.46 −2.35 (m, 2H, $CH_2$), 1.85−1.79 (m, 1H, $CH_2$), 1.86−1.74 (m, 2H, $CH_2$). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): -52.5.

**4-(2-(phenylphosphinyl)ethyl)pyridine (7r)**[1a]

**7r** was prepared from **5r** (53 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): *δ* 8.48−8.46 (m, 1H, ArH), 7.40−7.36 (m, 2H, ArH), 7.06−7.05 (m, 1H, ArH), 7.00−7.97 (m, 3H, ArH), 6.60−6.57 (m, 2H, ArH), 4.41 (dt, J = 206.78 Hz and $^2$J = 13.73 Hz, PH), 2.88 −2.79 (m, 2H, $CH_2$), 2.29−2.17 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -52.5.

**methyl 3-(phenylphosphinyl)propanoate (7s)**[1a]

**7s** was prepared from **5s** (45 μL, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): 4.30 (dt, J = 208.19 Hz and $^2$J = 14.43 Hz, PH), 3.26 (s, 3H, $CH_3$), 2.20−2.13 (m, 2H, $CH_2$), 1.87−1.82 (m, 2H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): -51.4.

**bicyclo[2.2.1]heptan-2-yl(phenyl)phosphine (7t)**[1c]

**7t** was prepared from **5t** (47 mg, 0.5 mmol) and **7** (82 μL, 0.75 mmol). $^1$H NMR (400 MHz, $C_6D_6$): δ 7.45 (m, $C_6H_5$, 2 H), 7.07 (m, $C_6H_5$, 3H), 4.42 (dd, J = 203.40 Hz and $^2$J = 8.17 Hz, PH), 4.22 (dd, J = 207.01 Hz and $^2$J = 7.22 Hz, PH), 3.27 (m, $CH_2$, 1H), 2.13 (s, CH, 1H), 2.05 (t, $CH_2$, 1H), 1.88 (m, $CH_2$, 2 H), 1.58−1.48 (m, $CH_2$, 2H), 1.35−1.29 (m, $CH_2$, 2H), 1.09 (t, CH, 1 H), 1.13−0.99 (m, $CH_2$, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): δ −37.6, −39.4.

**(Z)-(1,2-diphenylvinyl)(phenyl)phosphine (7u)**[1d]

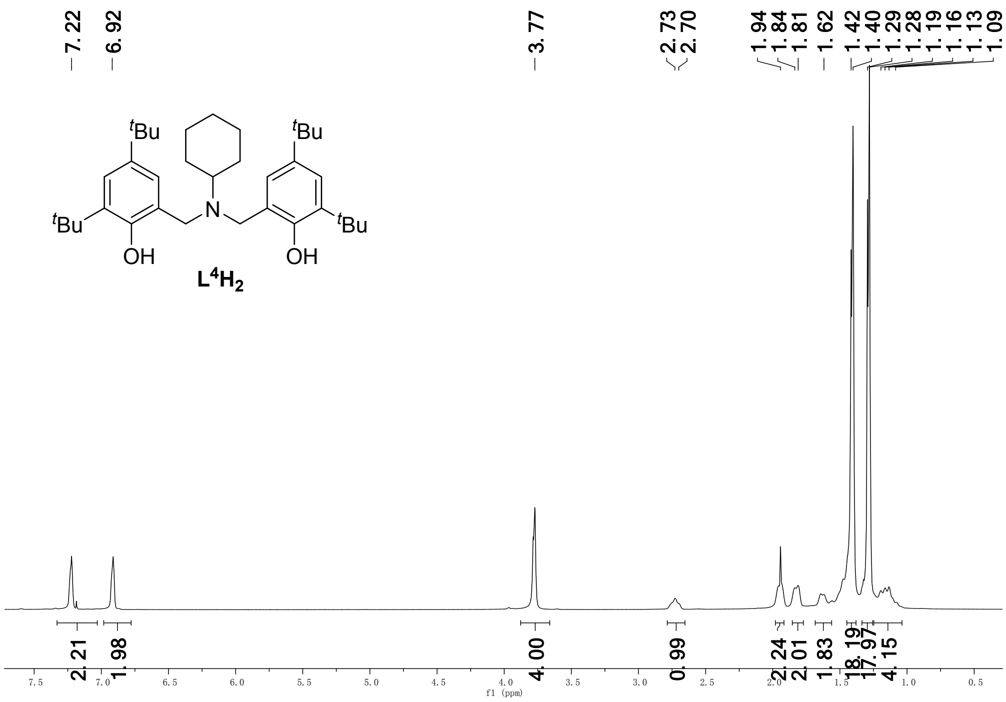
**7u** was prepared from **5u** (0.089 g, 0.5 mmol) and **7** (55 μL, 0.5 mmol). $^1$H NMR (400 MHz, $C_6D_6$): δ 7.81-7.15 (m, $C_6H_5$, 10H), 7.24 (d, J = 1.65Hz, CH), 5.25 (d, J = 223.83 Hz, PH). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): δ −54.0.

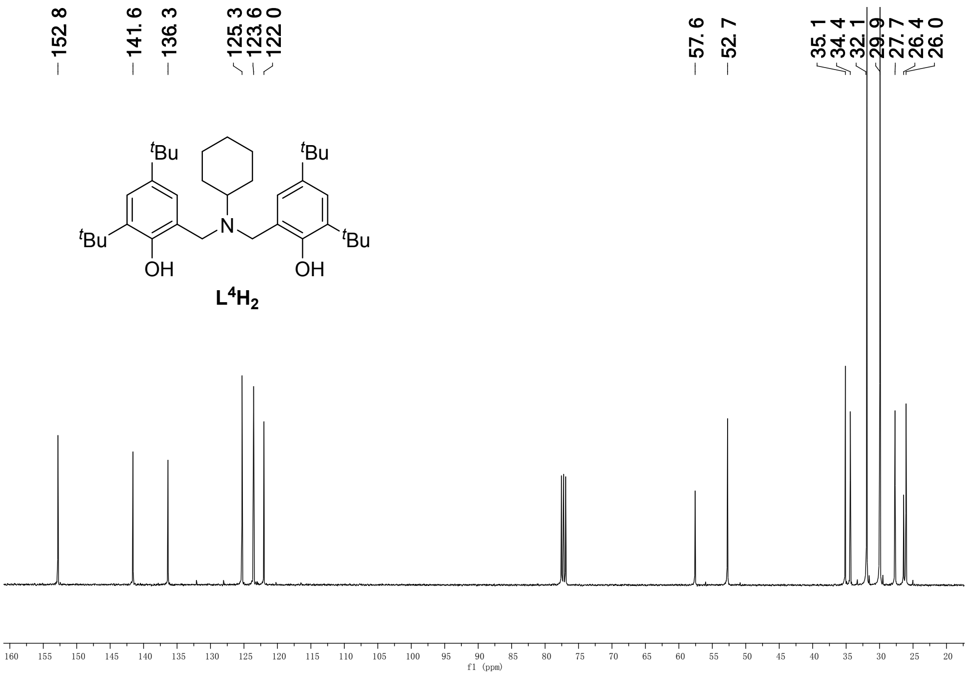
**(Z)-phenyl(1-phenylprop-1-en-2-yl)phosphine (7v)**[1d]

**7v** was prepared from **5v** (63 μL, 0.5 mmol) and **7** (55 μL, 0.5 mmol). $^1$H NMR (400 MHz, $C_6D_6$): δ 7.49-6.97 (m, $C_6H_5$, 10H), 6.96 (d, J = 5.12 Hz, CH), 4.62 (d, J =

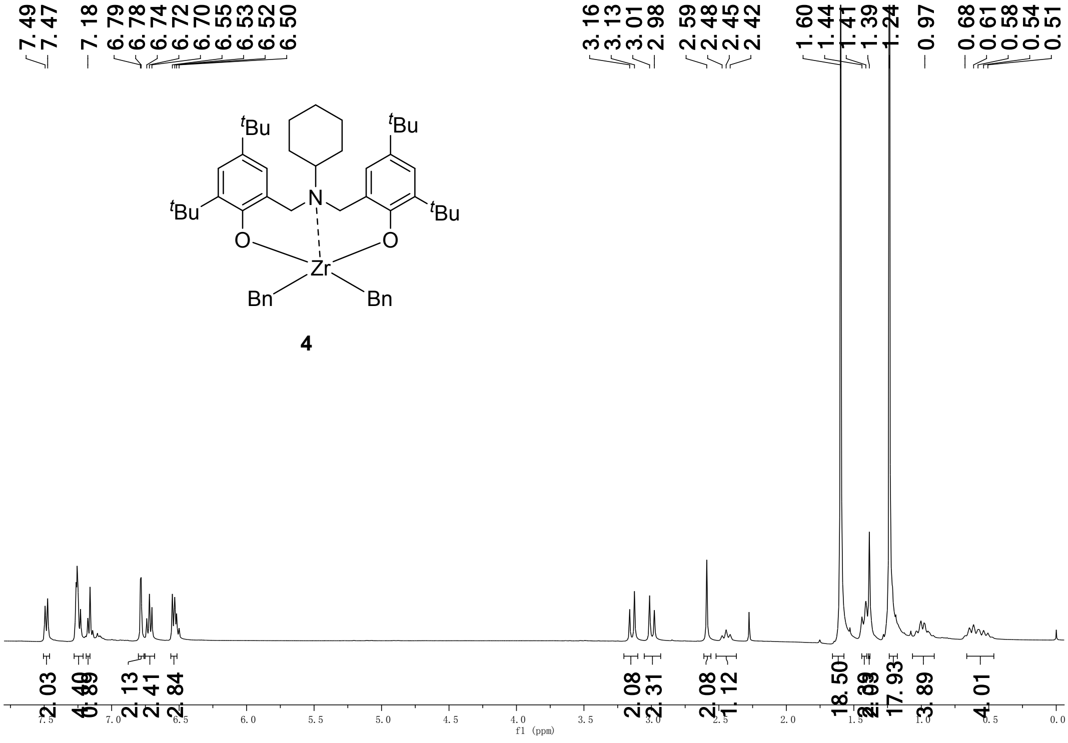
220.31 Hz, PH). 1.88 (d, J = 4.74 Hz, J = 1.35 Hz, $CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $C_6D_6$): δ −52.5.

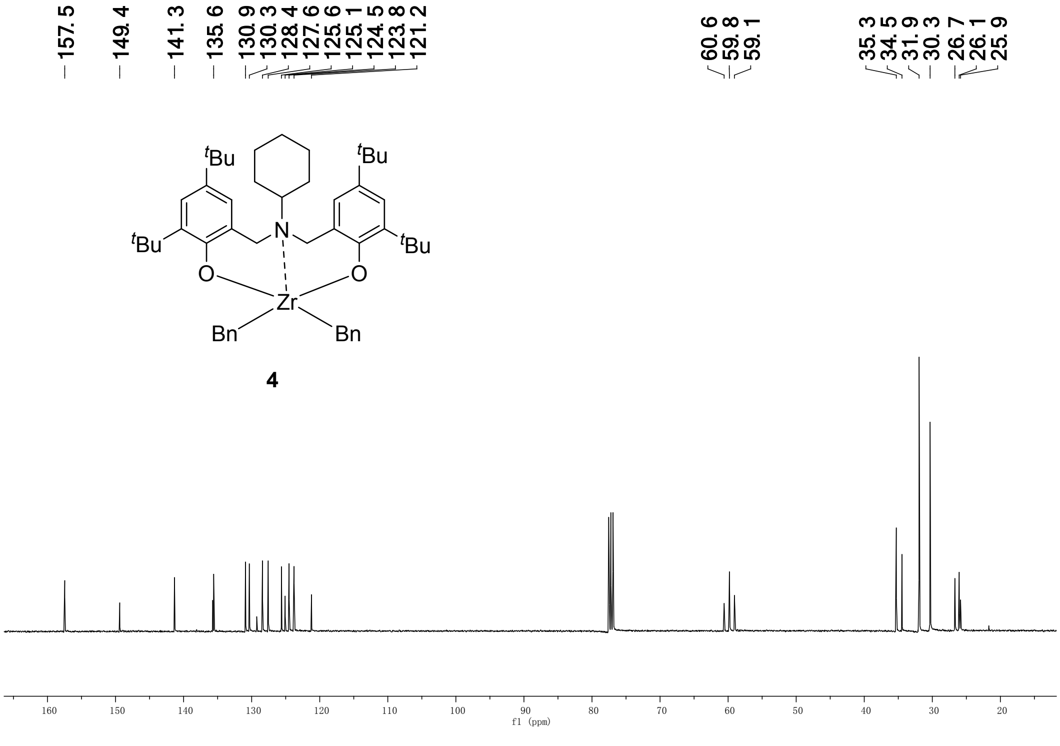
## $^1H$ and $^{13}C$ NMR spectra of ligand precursor $L^4H_2$





## $^1$H and $^{13}$C NMR spectra of complex 4

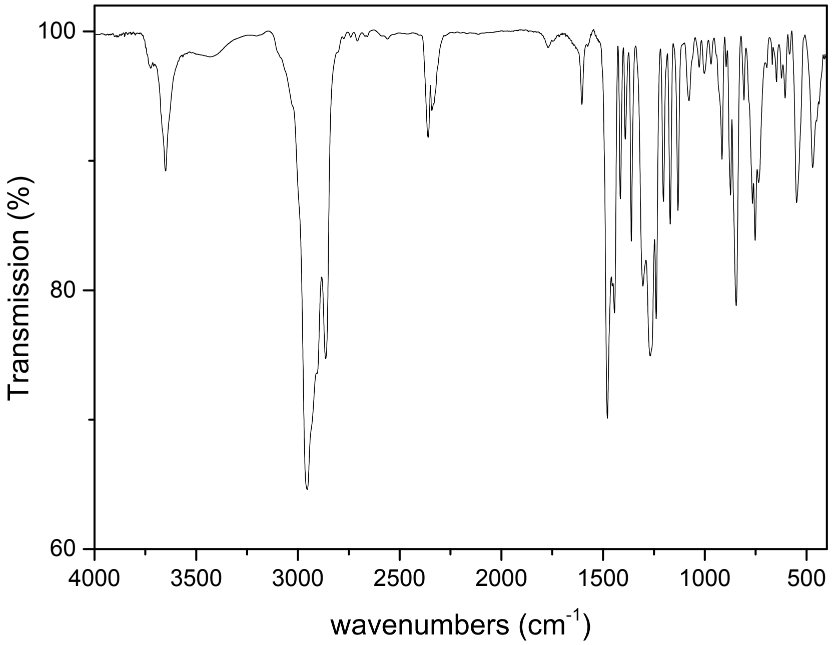




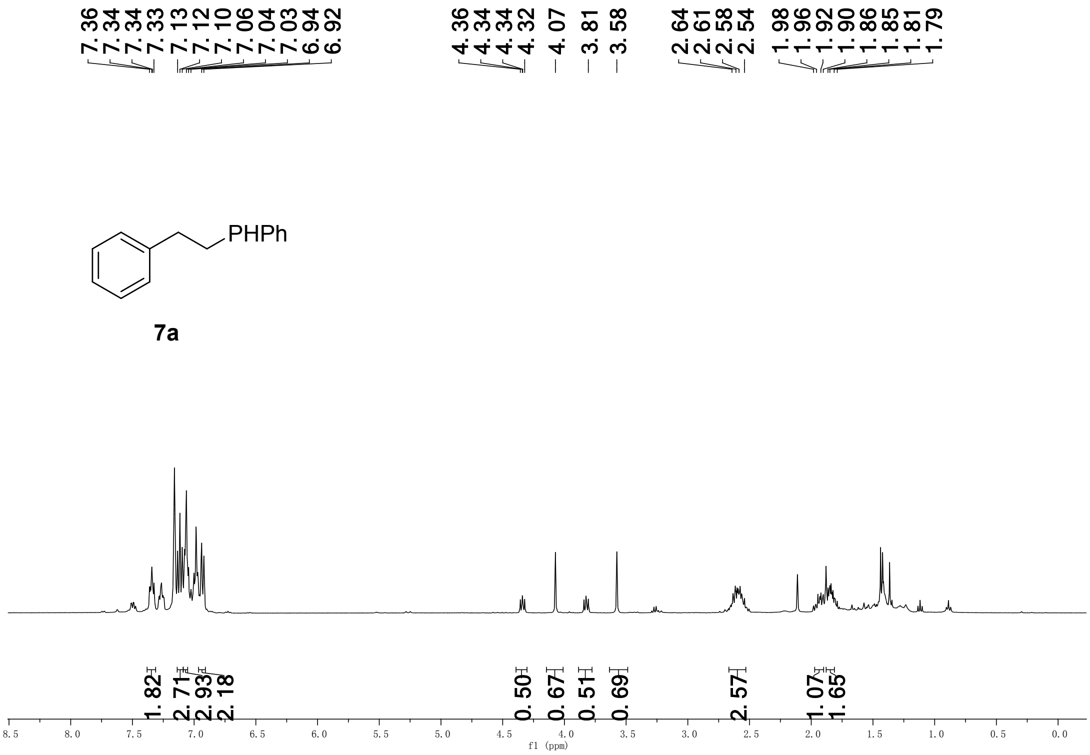
**IR spectrum of complex 4**

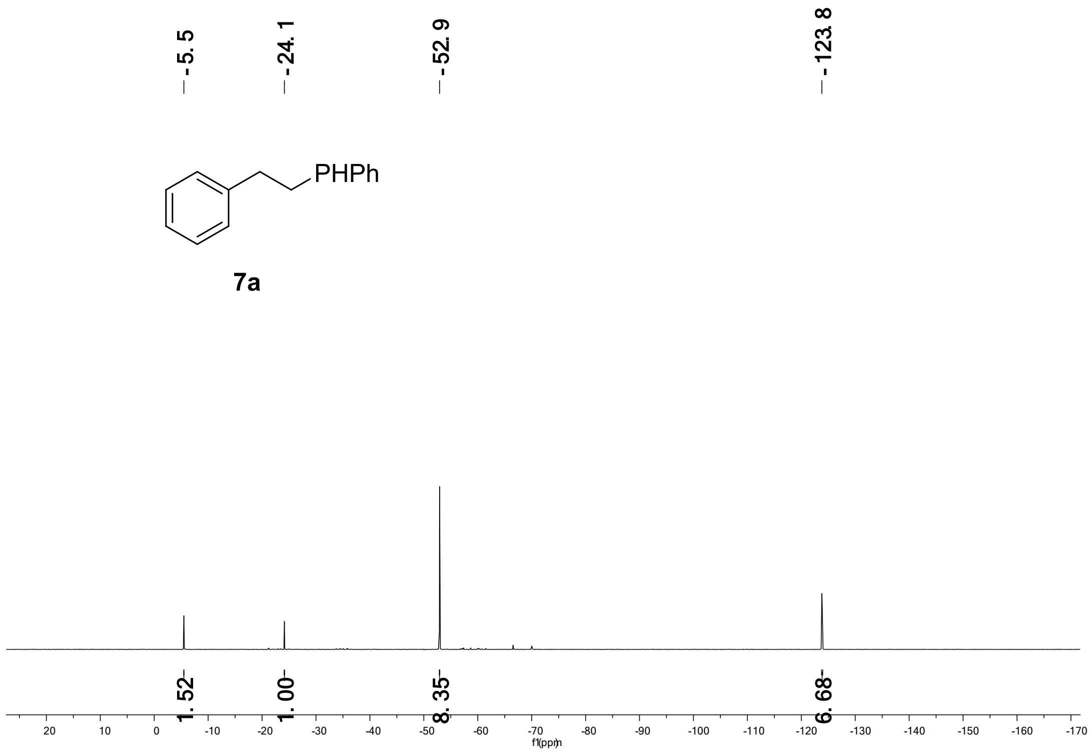
The strong absorptions at 2954 and 2863 cm$^{-1}$ are assigned to the stretching vibration of –$CH_3$ and -$CH_2$- groups. The absorptions at 1444-1604 cm$^{-1}$ are assigned to the stretching vibration of benzene ring. The stretching vibration of C-O bond is observed at 1239 cm$^{-1}$.

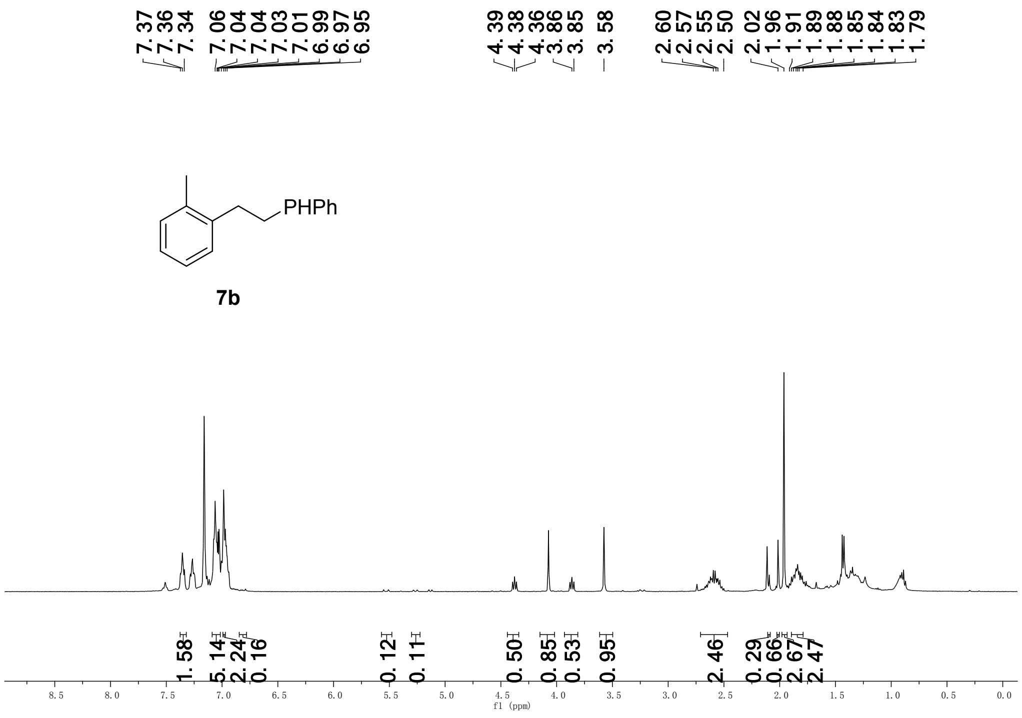
IR: 3651m, 2954vs, 2863s, 2360m, 2342m, 1604m, 1479s, 1444s, 1415m, 1391m, 1361m, 1268w, 1239m, 1203m, 1170m, 1131m, 1078m, 915m, 873m, 845m, 807m, 765m, 752m, 729m, 694W, 648W, 623W, 605W, 549m, 465m.



# $^1H$ and $^{31}P$ NMR spectra of reaction mixtures



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7.04
7.03
7.01
6.99
6.97
6.95
4.39
4.38
4.36
3.86
3.85
3.58
2.60
2.57
2.55
2.50
2.02
1.96
1.91
1.89
1.88
1.85
1.84
1.83
1.79
PHPh
1.58
5.14
2.24
0.16
0.12
0.11
0.50
0.85
0.53
0.95
2.46
0.29
0.66
2.67
2.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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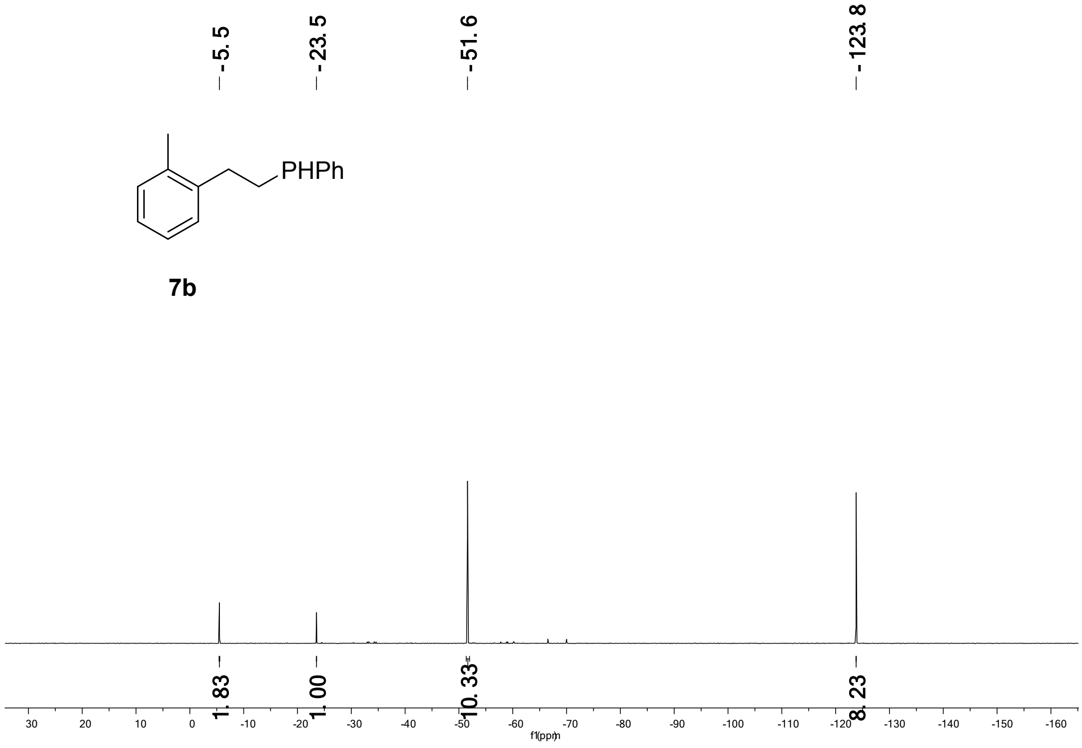
0.5
0.0
f1 (ppm)

**7b**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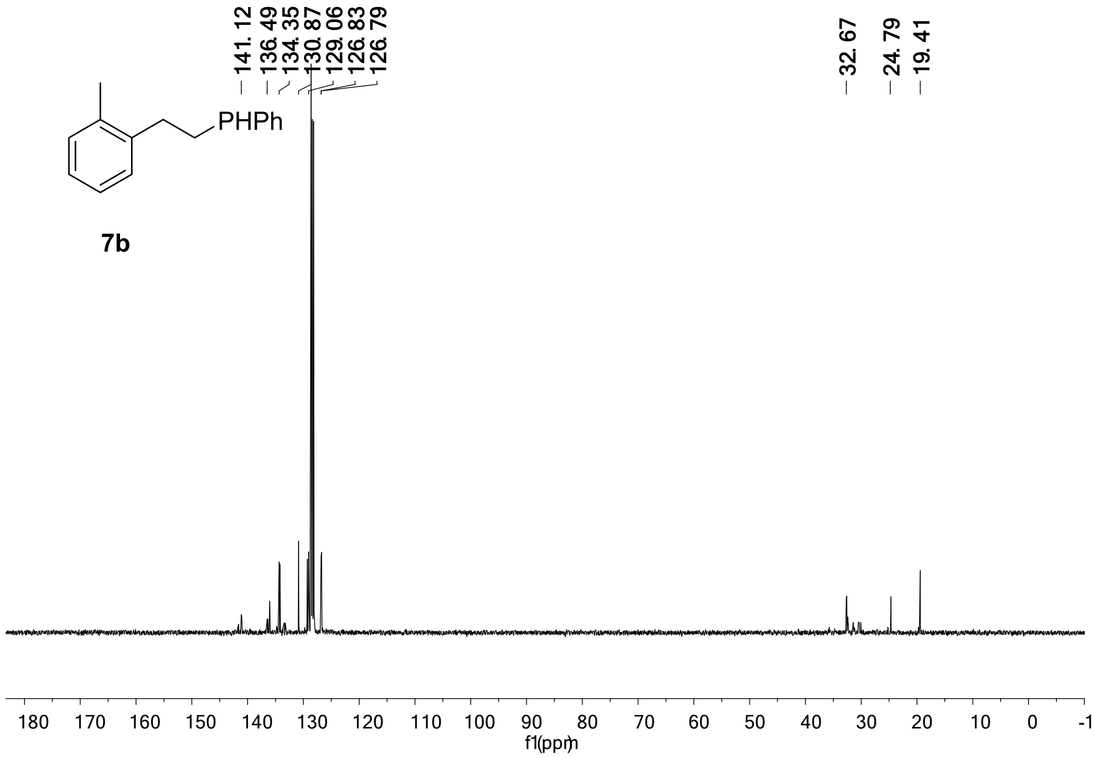
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1(ppm)

**7b**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126.79
32.67
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19.41
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7b
180
170
160
150
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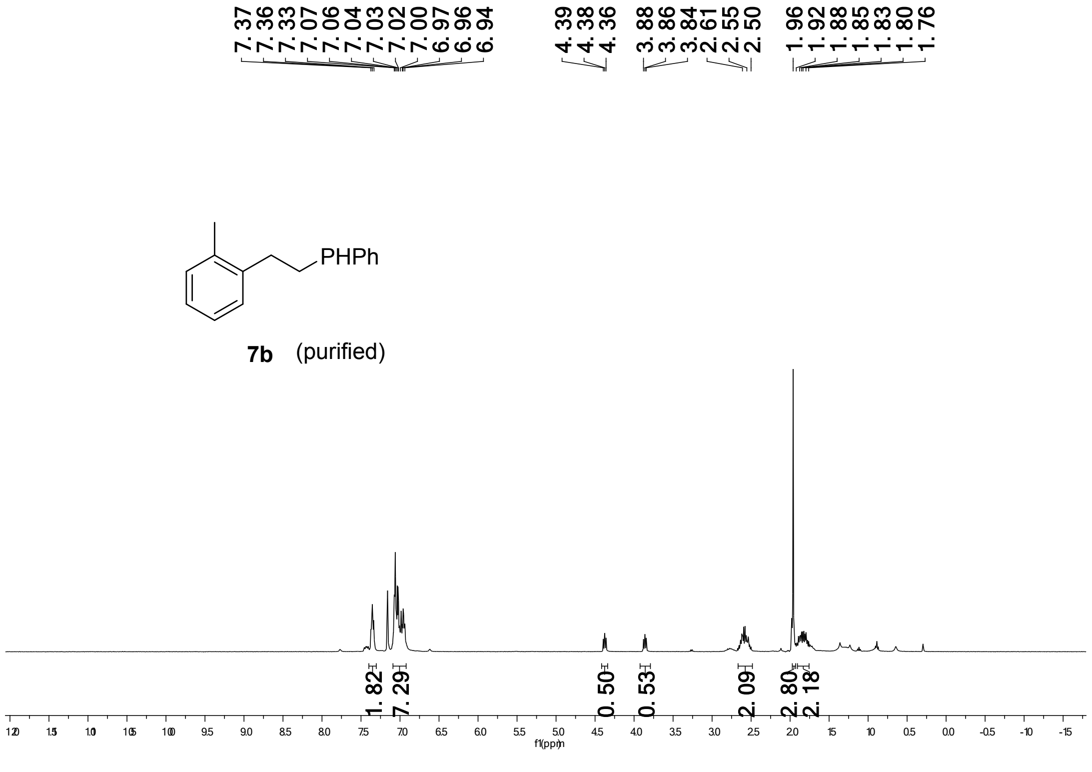
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.03
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6.96
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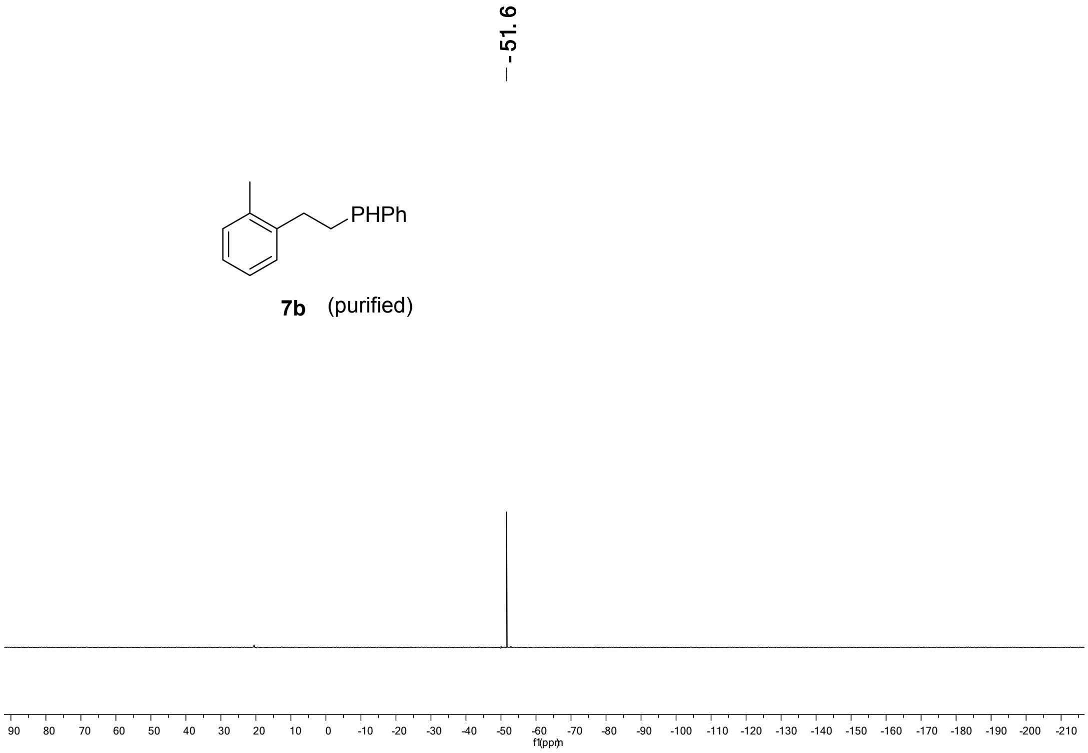
4.39
4.38
4.36
3.88
3.86
3.84
2.61
2.55
2.50
1.96
1.92
1.88
1.85
1.83
1.80
1.76
PHPh
7b (purified)
1.82
7.29
0.50
0.53
2.09
2.80
2.18
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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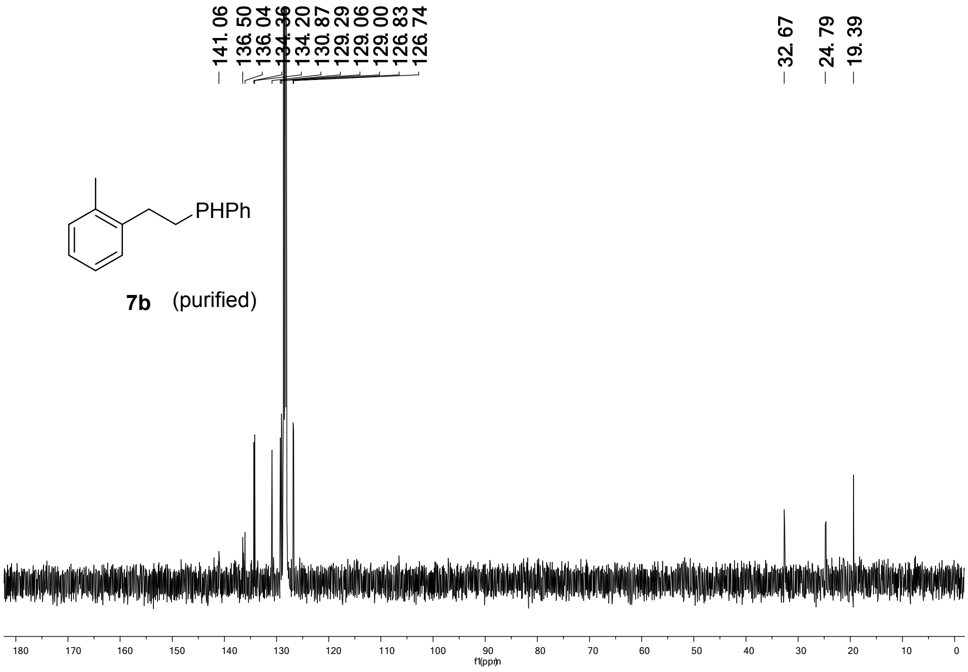
PHPh
7b (purified)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1(ppm)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130.87
129.29
129.06
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126.83
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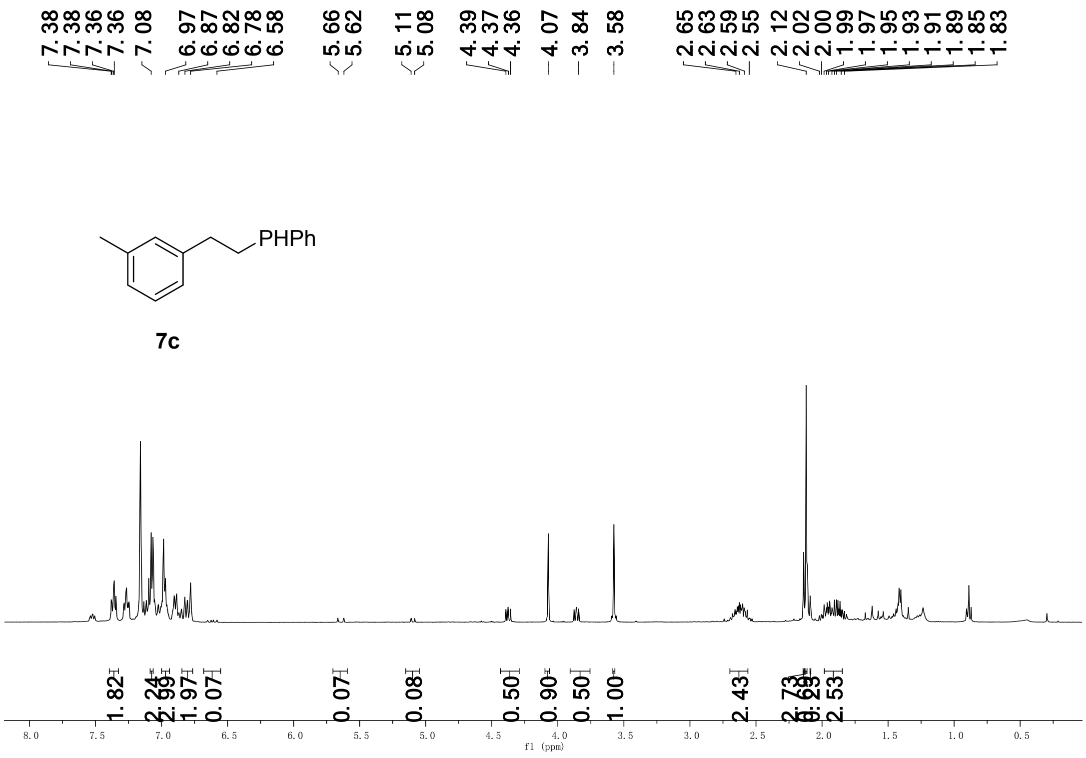
32.67
24.79
19.39
PHPh
7b (purified)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)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5.11
5.08
4.39
4.37
4.36
4.07
3.84
3.58
2.65
2.63
2.59
2.55
2.12
2.02
2.00
1.99
1.97
1.95
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1.91
1.89
1.85
1.83
PHPh
1.82
2.24
2.99
1.97
0.07
0.07
0.08
0.50
0.90
0.50
1.00
2.43
2.73
2.53
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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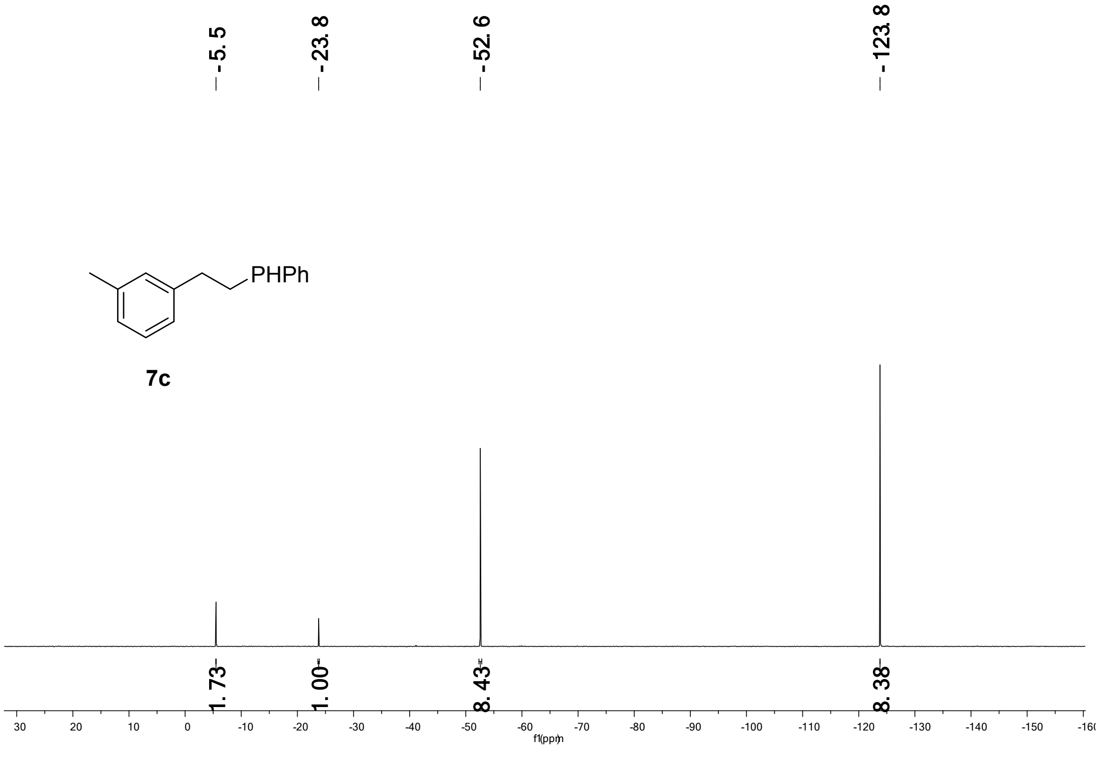
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

**7c**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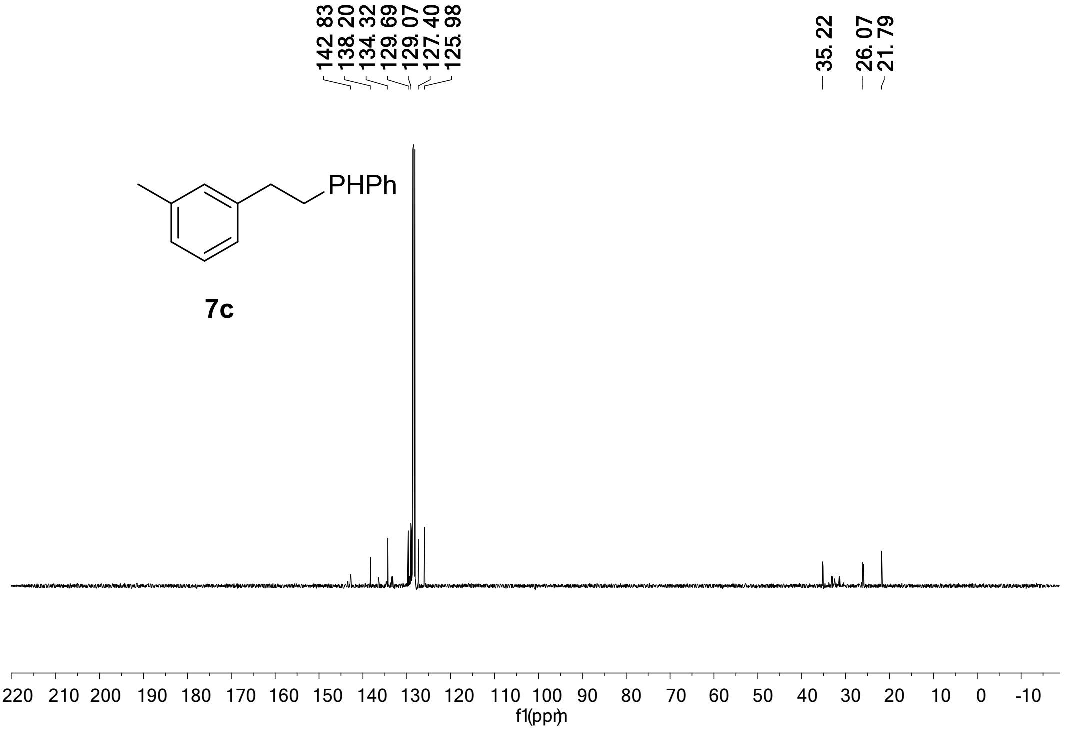
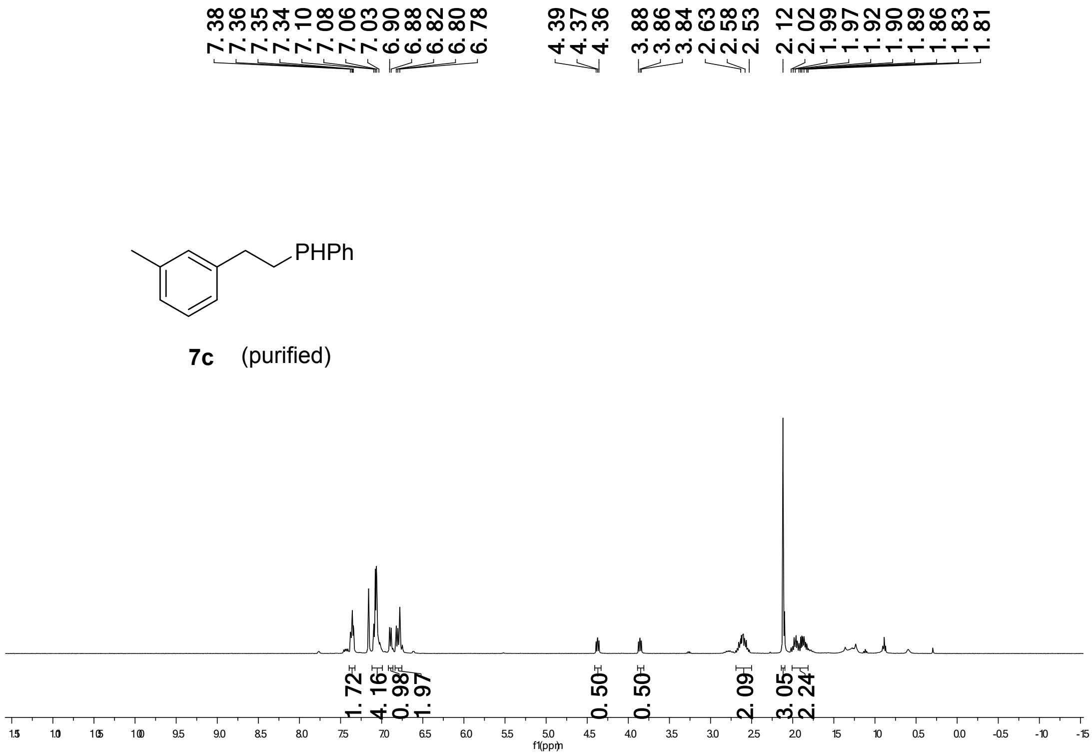
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-16
f1(ppm)

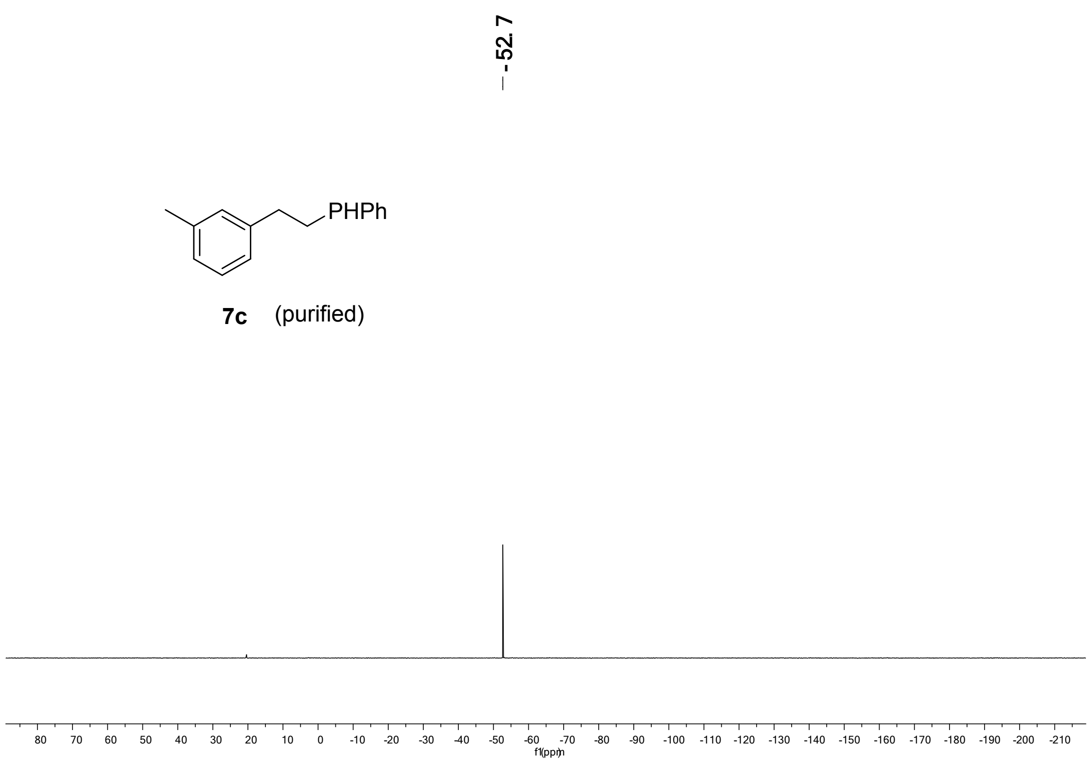
**7c**



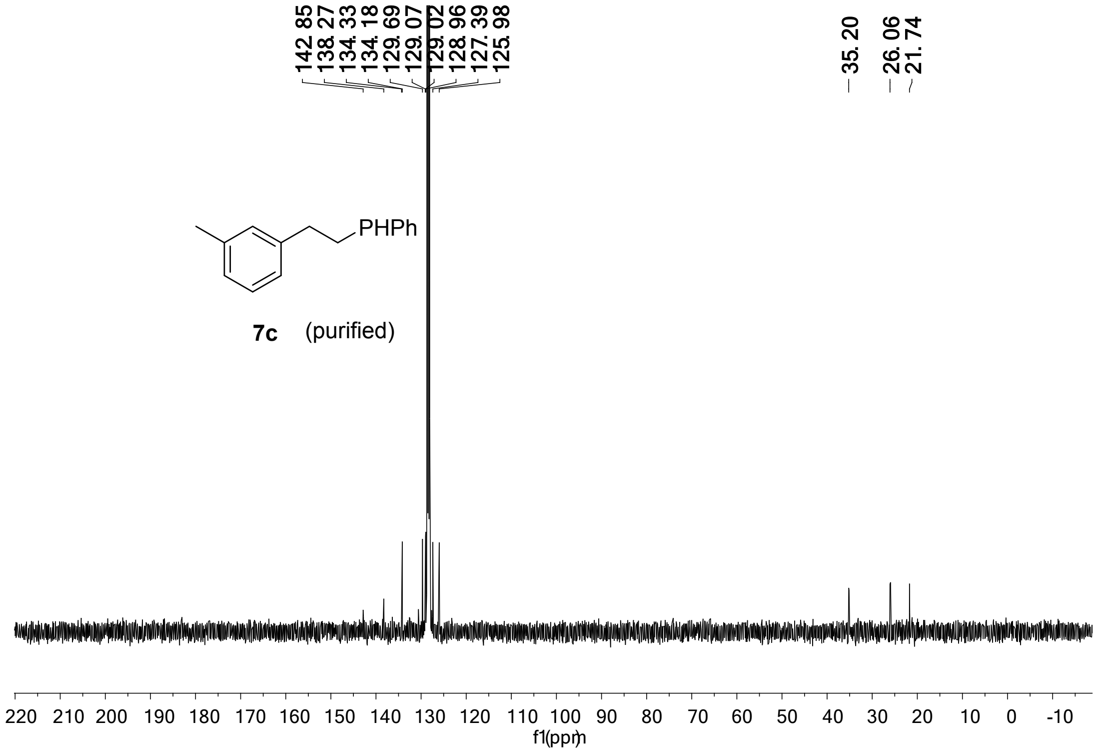
**7c**



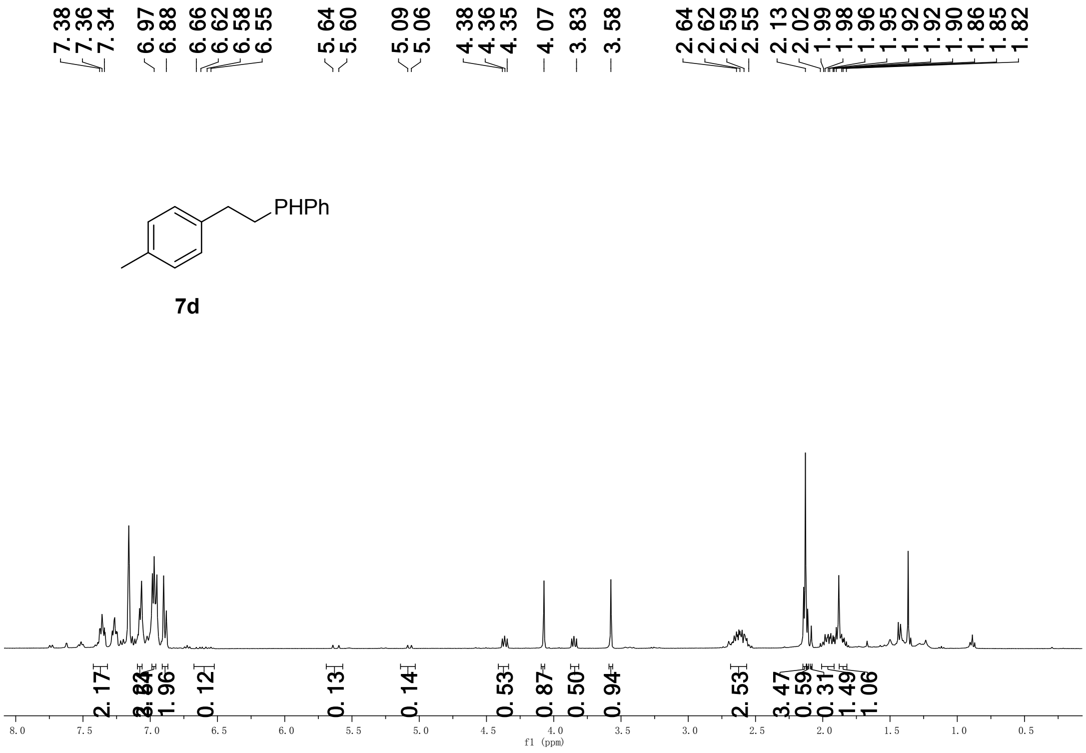
**7c** (purified)



**7c** (purified)



**7c** (purified)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4.36
4.35
4.07
3.83
3.58
2.64
2.62
2.59
2.55
2.13
2.02
1.99
1.98
1.96
1.95
1.92
1.92
1.90
1.86
1.85
1.82
PHPh
7d
2.17
2.83
3.64
1.96
0.12
0.13
0.14
0.53
0.87
0.50
0.94
2.53
3.47
0.59
0.31
1.49
1.06
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7.5
7.0
6.5
6.0
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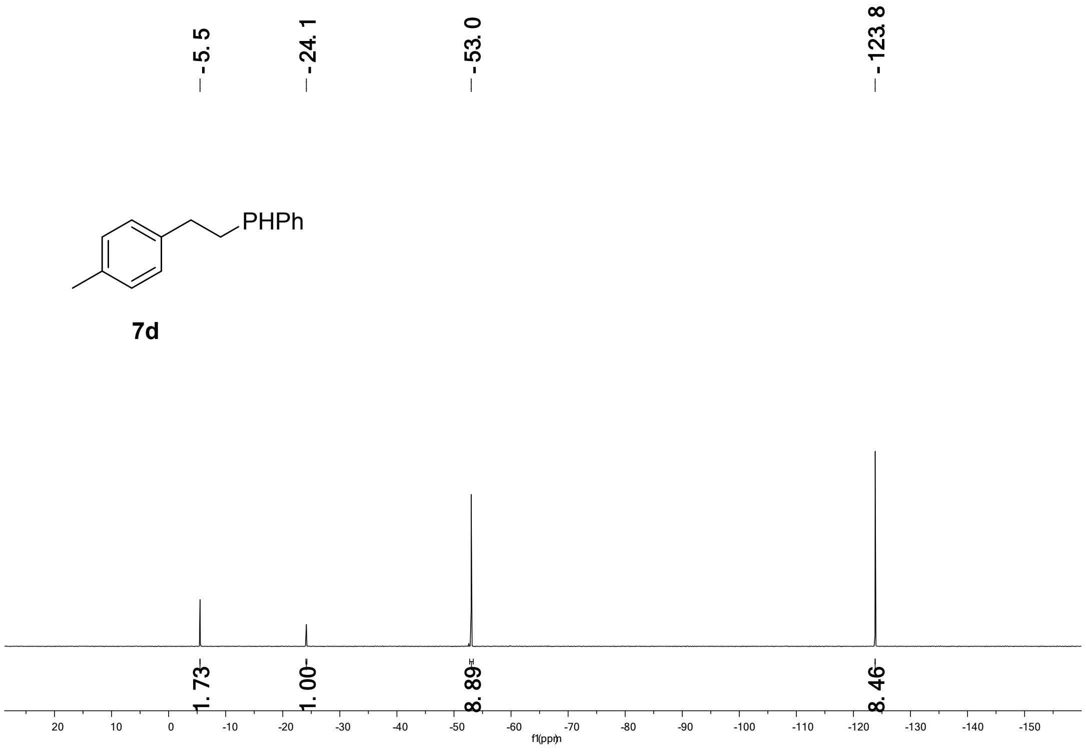
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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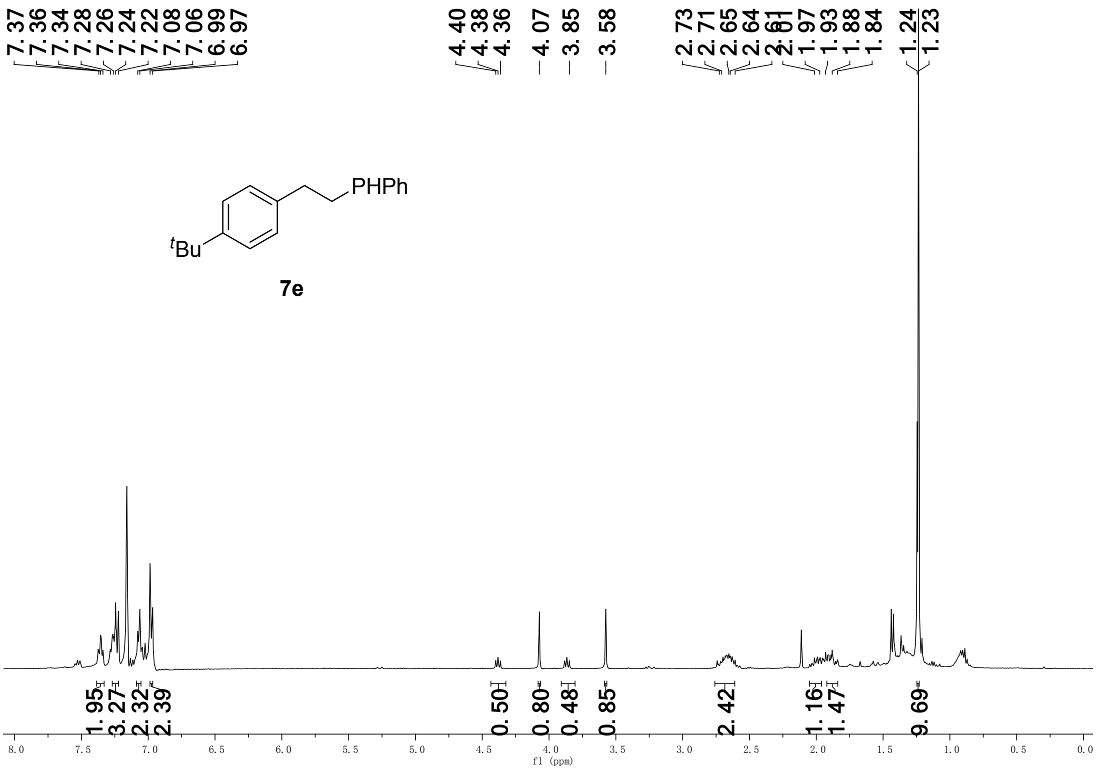
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1(ppm)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7.08
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6.99
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4.38
4.36
4.07
3.85
3.58
2.73
2.71
2.65
2.64
2.61
2.01
1.97
1.93
1.88
1.84
1.24
1.23
PHPh
$^t$Bu
7e
1.95
3.27
2.32
2.39
0.50
0.80
0.48
0.85
2.42
1.16
1.47
9.69
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7.0
6.5
6.0
5.5
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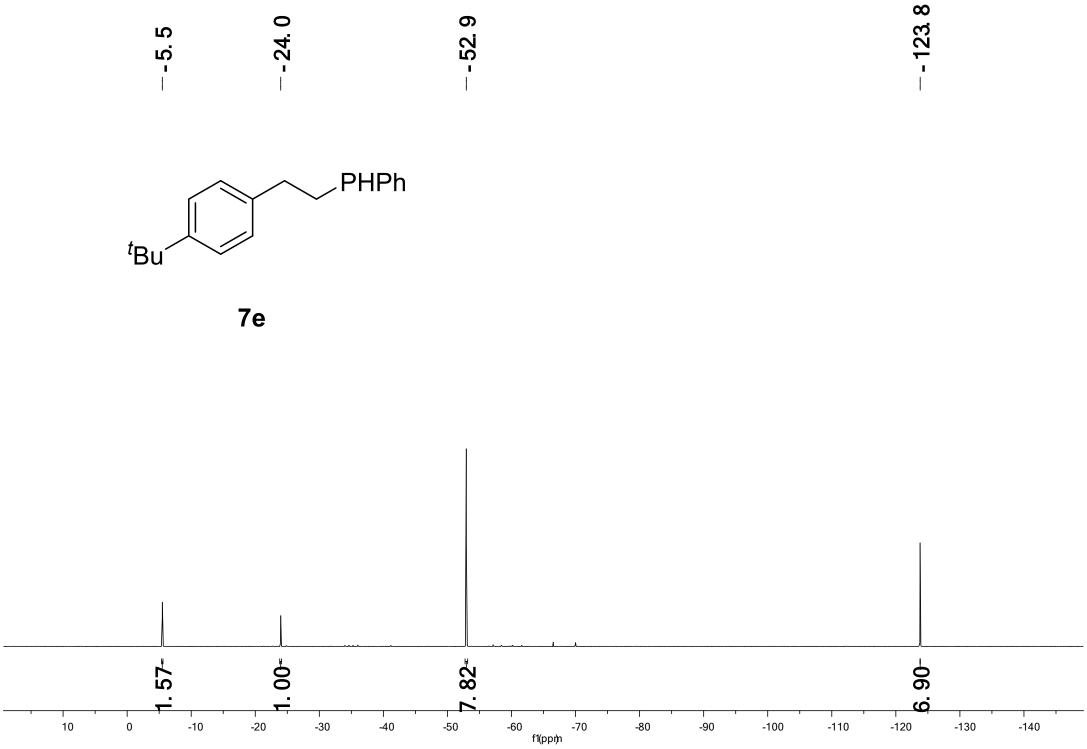
0.0
f1 (ppm)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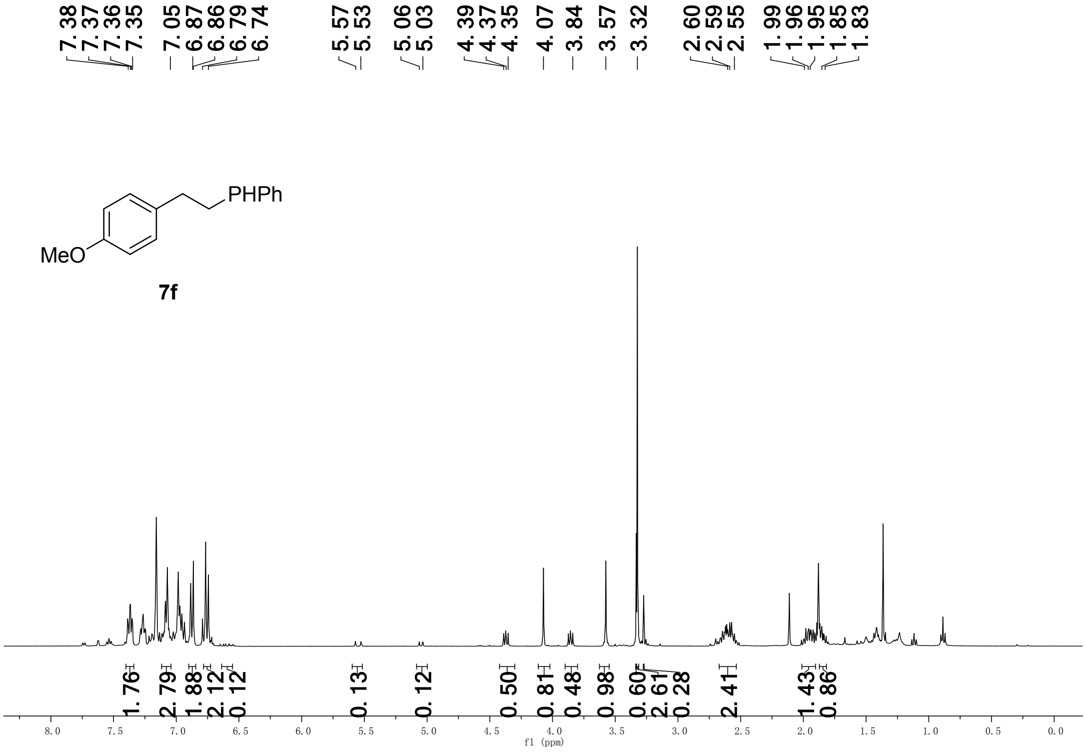
f1 (ppm)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4.37
4.35
4.07
3.84
3.57
3.32
2.60
2.59
2.55
1.99
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1.95
1.85
1.83
PHPh
MeO
7f
1.76
2.79
1.88
2.12
0.12
0.13
0.12
0.50
0.81
0.48
0.98
0.60
2.61
0.28
2.41
1.43
0.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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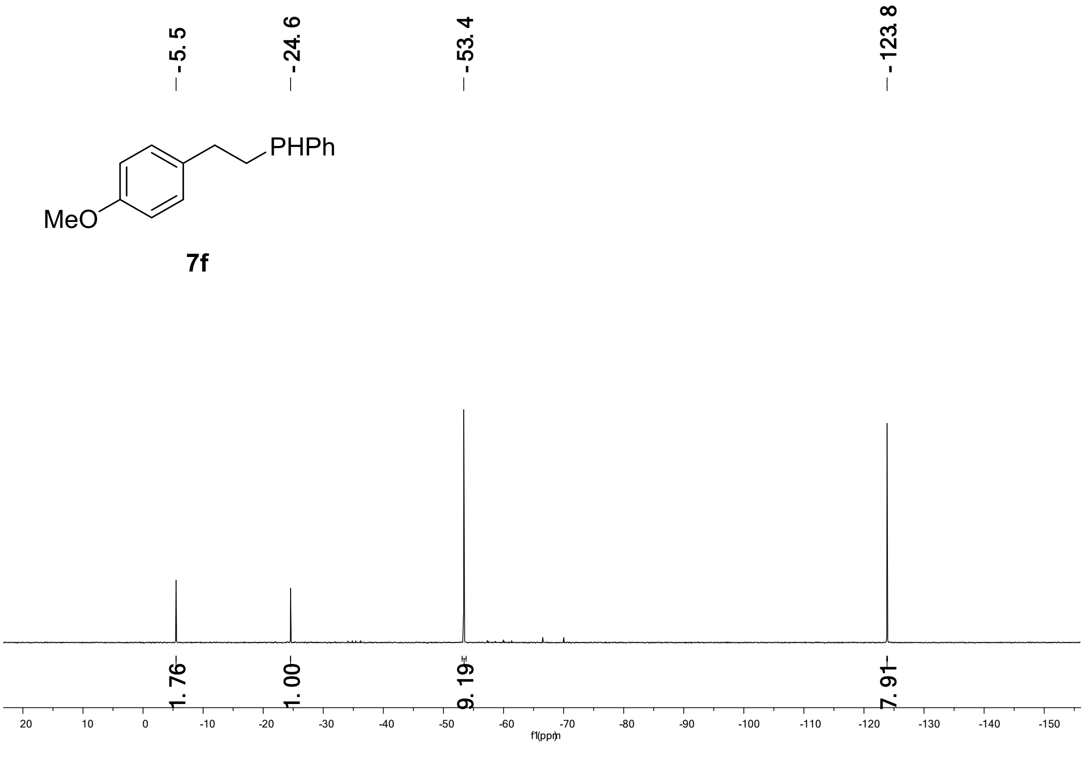
f1 (ppm)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10
0
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-80
-90
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-120
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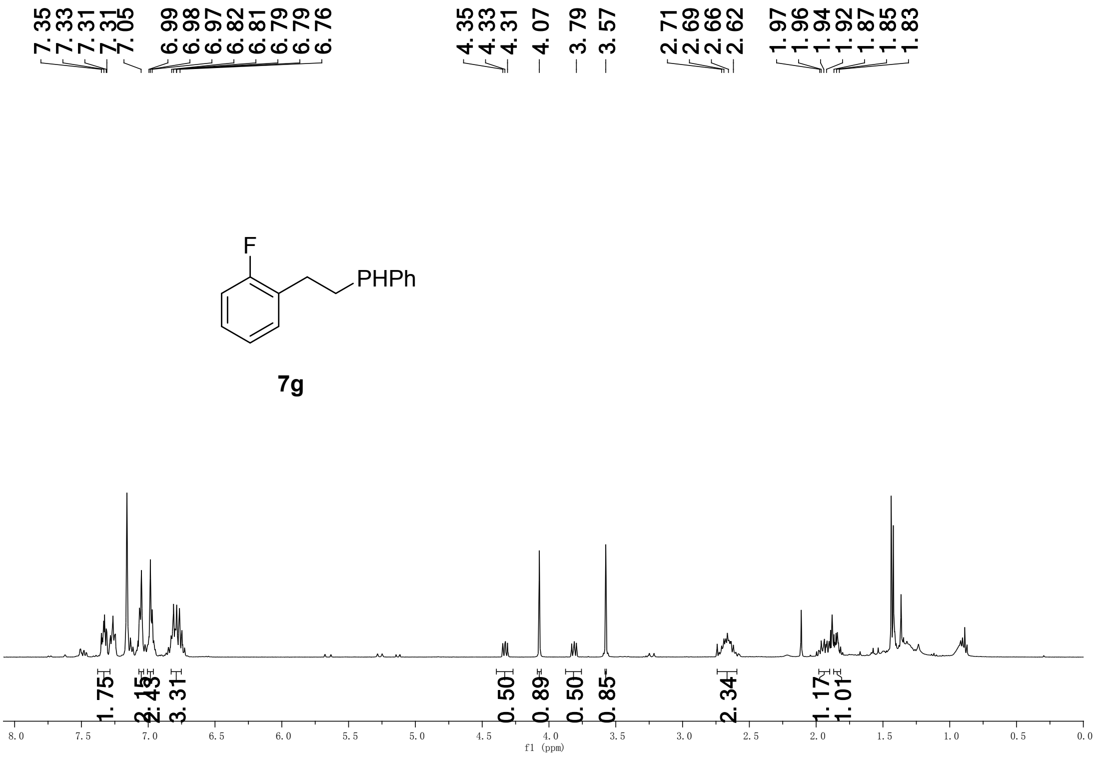
-150
f1(ppm)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6.76
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4.33
4.31
4.07
3.79
3.57
2.71
2.69
2.66
2.62
1.97
1.96
1.94
1.92
1.87
1.85
1.83
F
PHPh
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0.50
0.85
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1.17
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7.0
6.5
6.0
5.5
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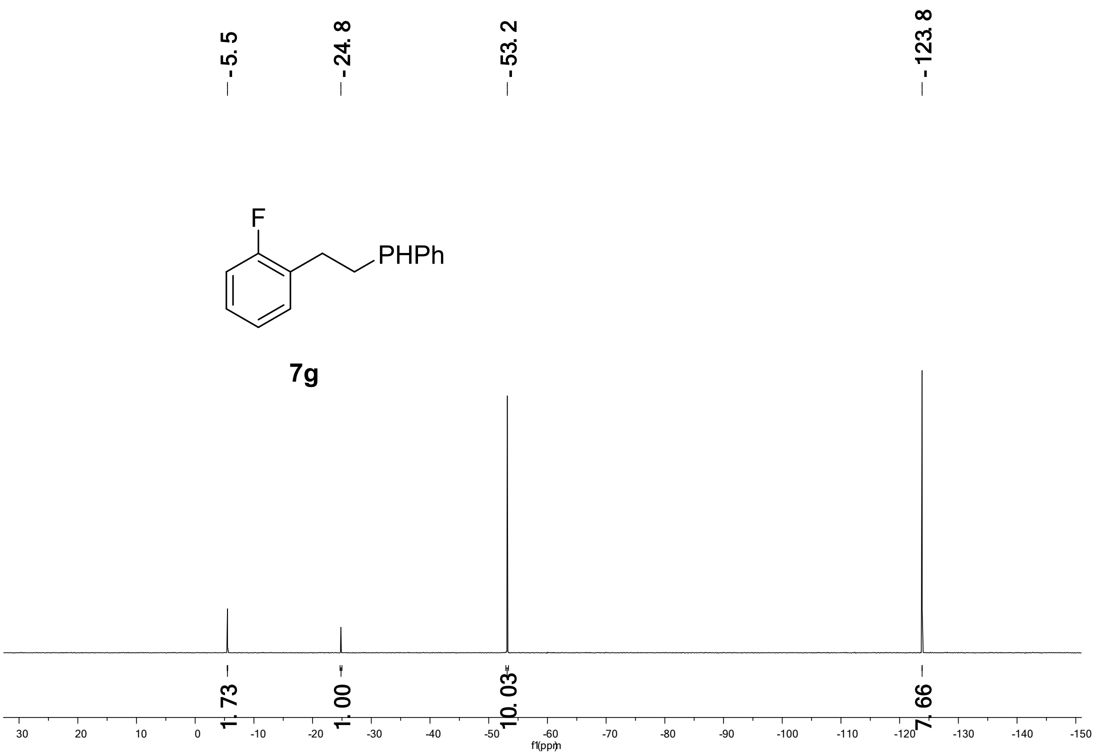
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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0
-10
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-50
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-80
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-100
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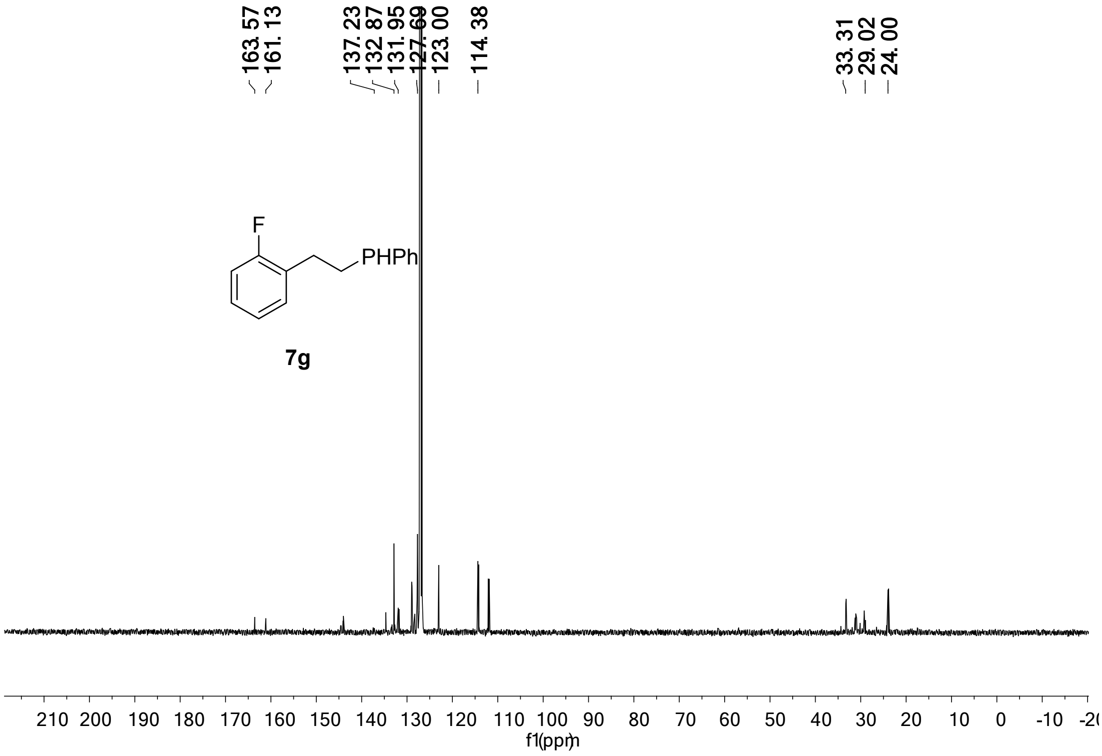
-120
-130
-140
-150
f1(ppm)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114.38
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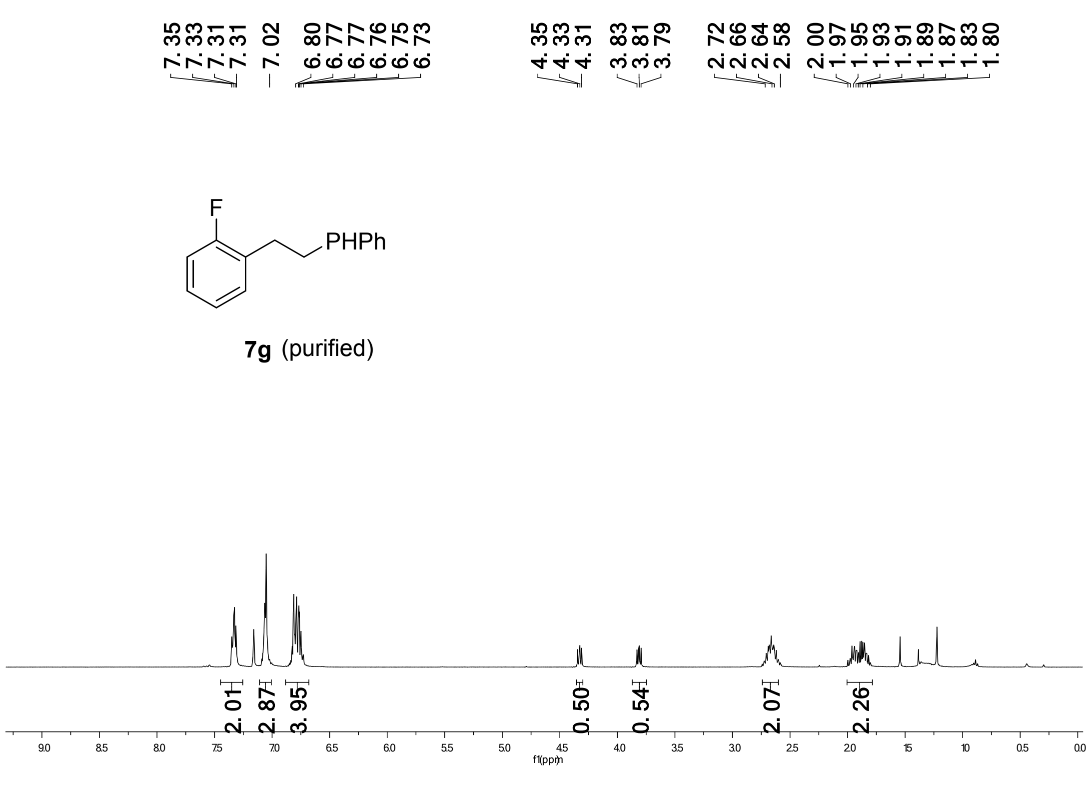
PHPh
7g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2(
f1(ppm)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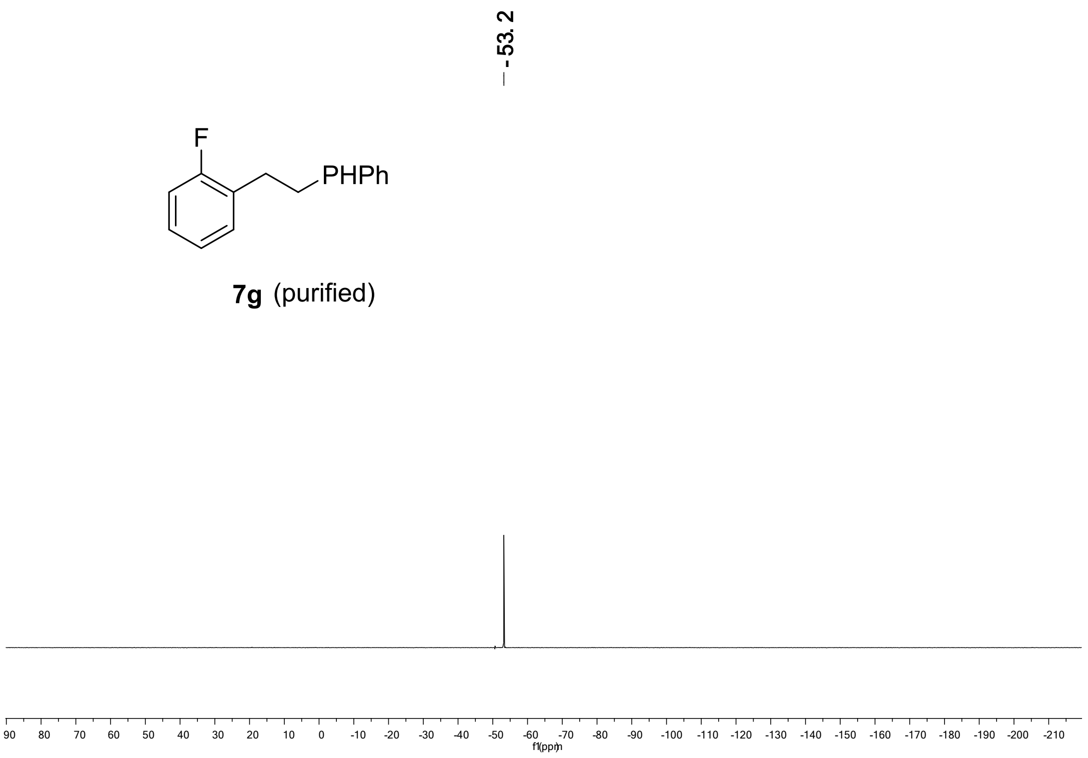
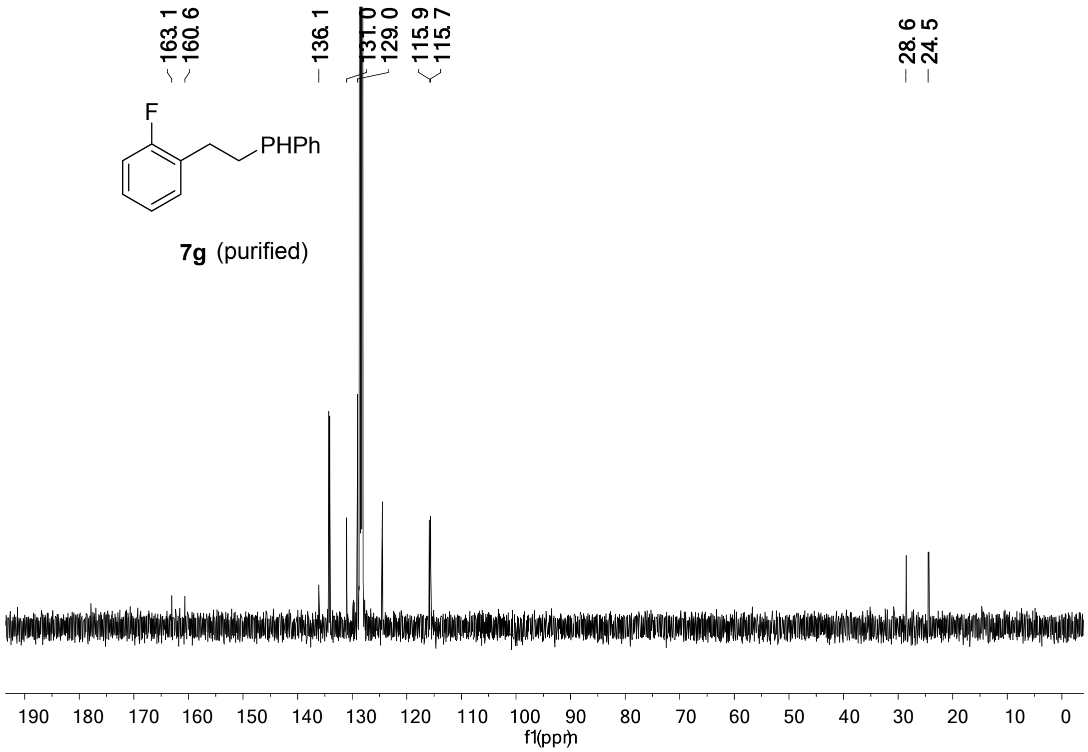
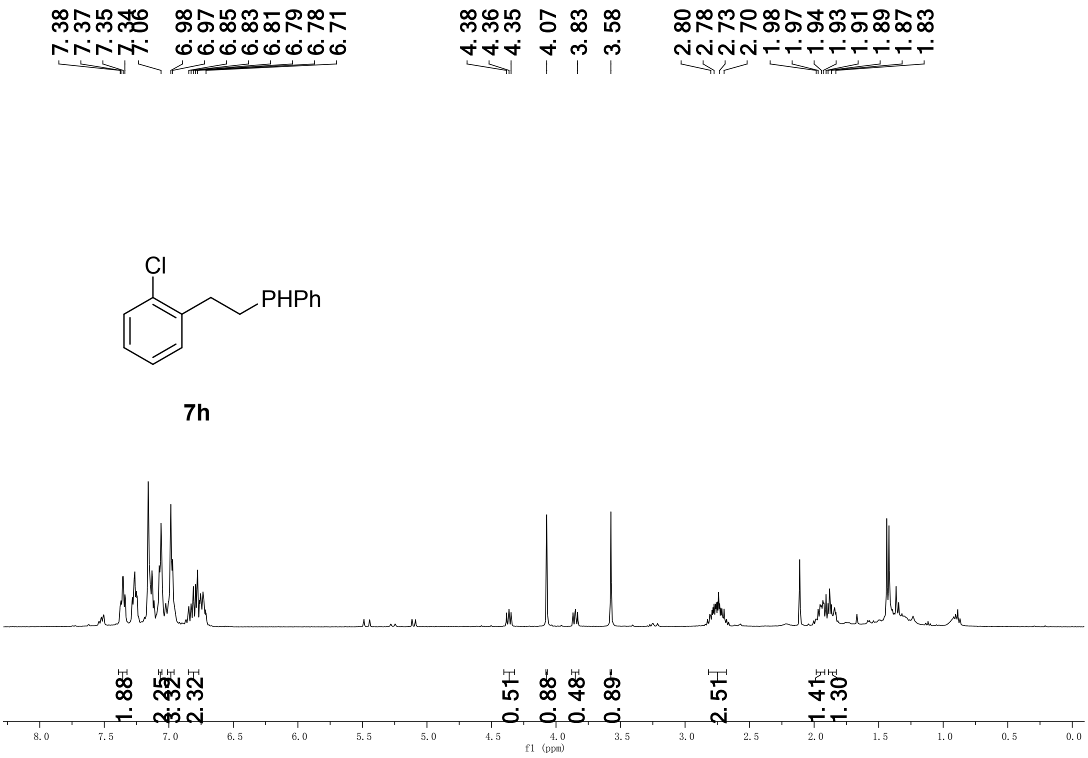
4.33
4.31
3.83
3.81
3.79
2.72
2.66
2.64
2.58
2.00
1.97
1.95
1.93
1.91
1.89
1.87
1.83
1.80
F
PHPh
7g (purified)
2.01
2.87
3.95
0.50
0.54
2.07
2.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1(ppm)



**7g** (purified)



**7g** (purified)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1.94
1.93
1.91
1.89
1.87
1.83
Cl
PHPh
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0.89
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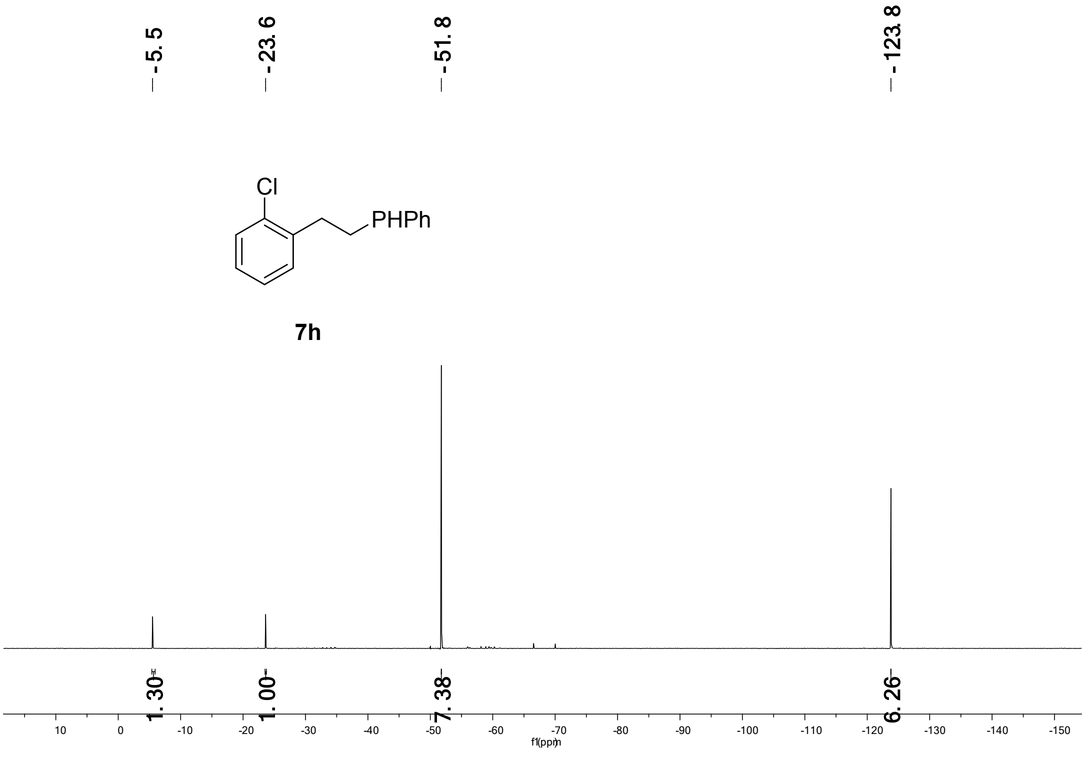
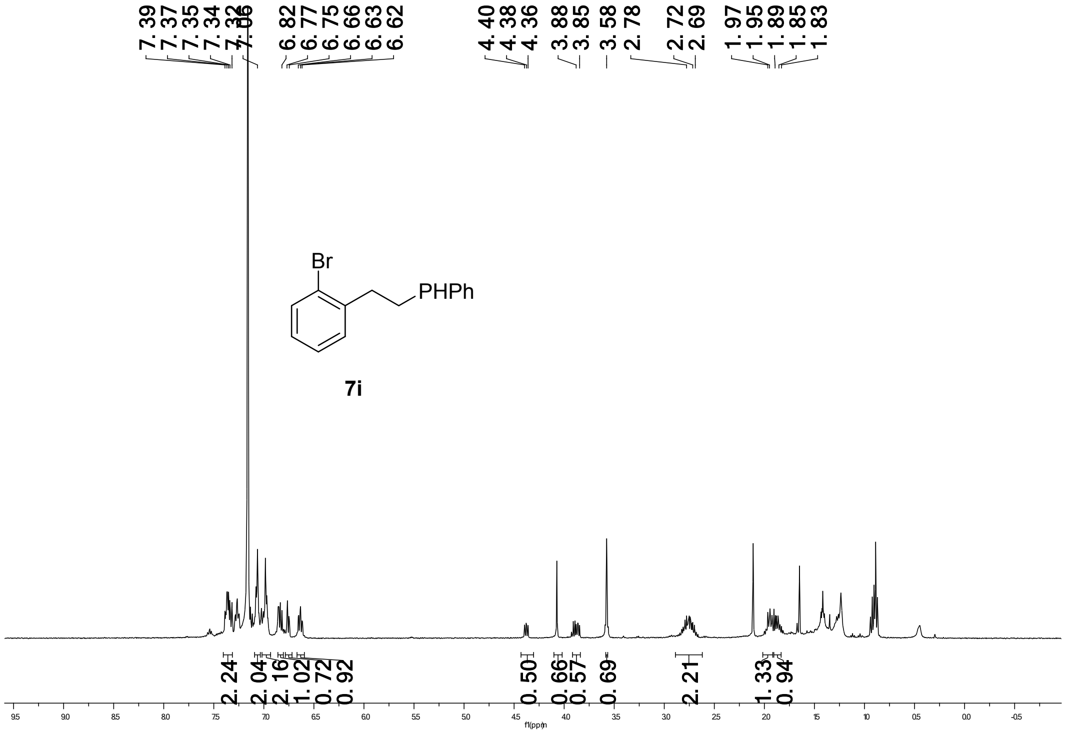
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

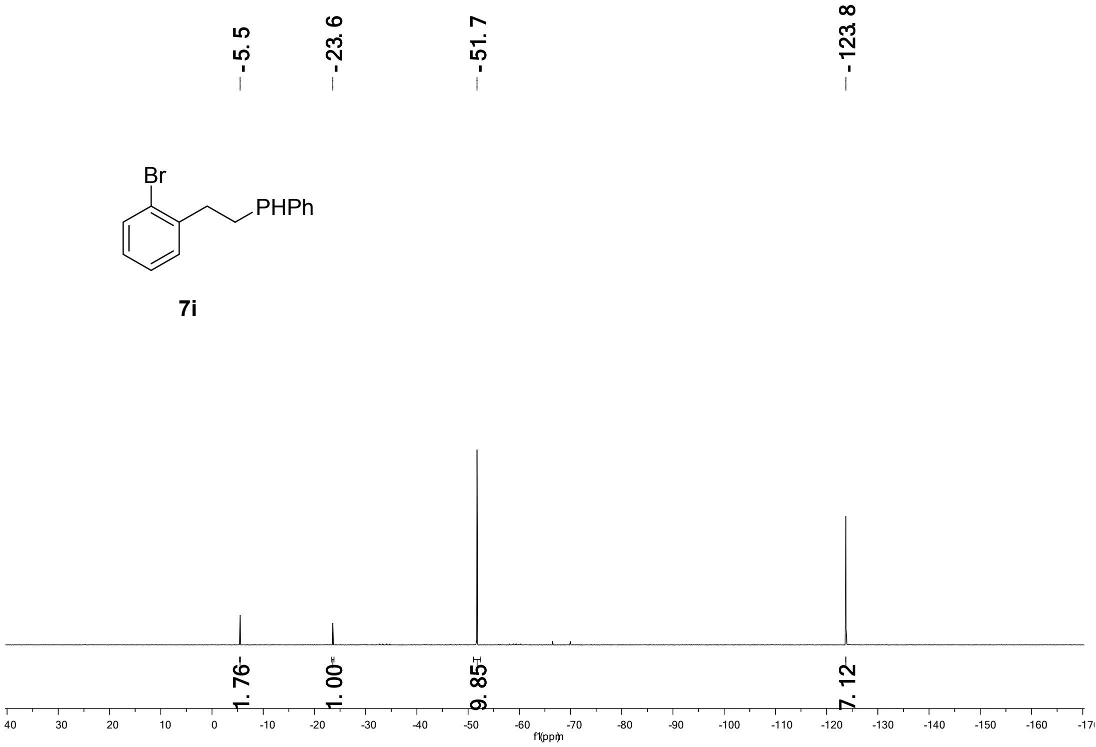
**7h**


-5.5
-23.6
-51.8
-123.8
Cl
PHPh
1.30
1.00
7.38
6.26
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1(ppm)

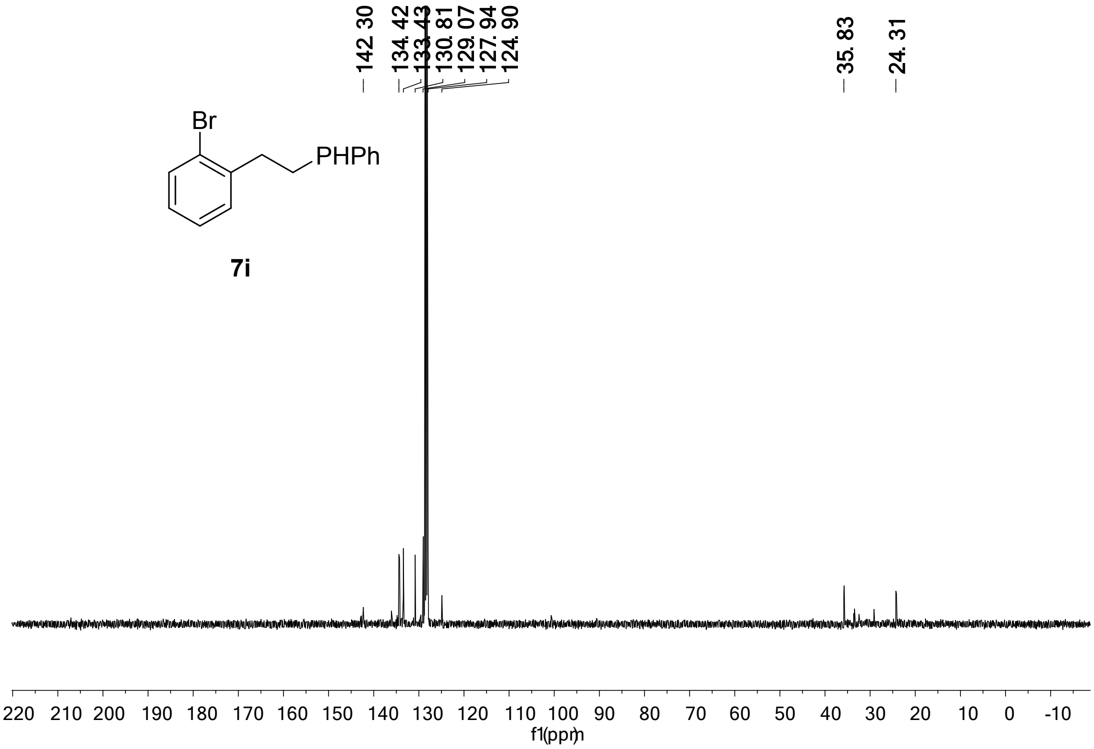
**7h**

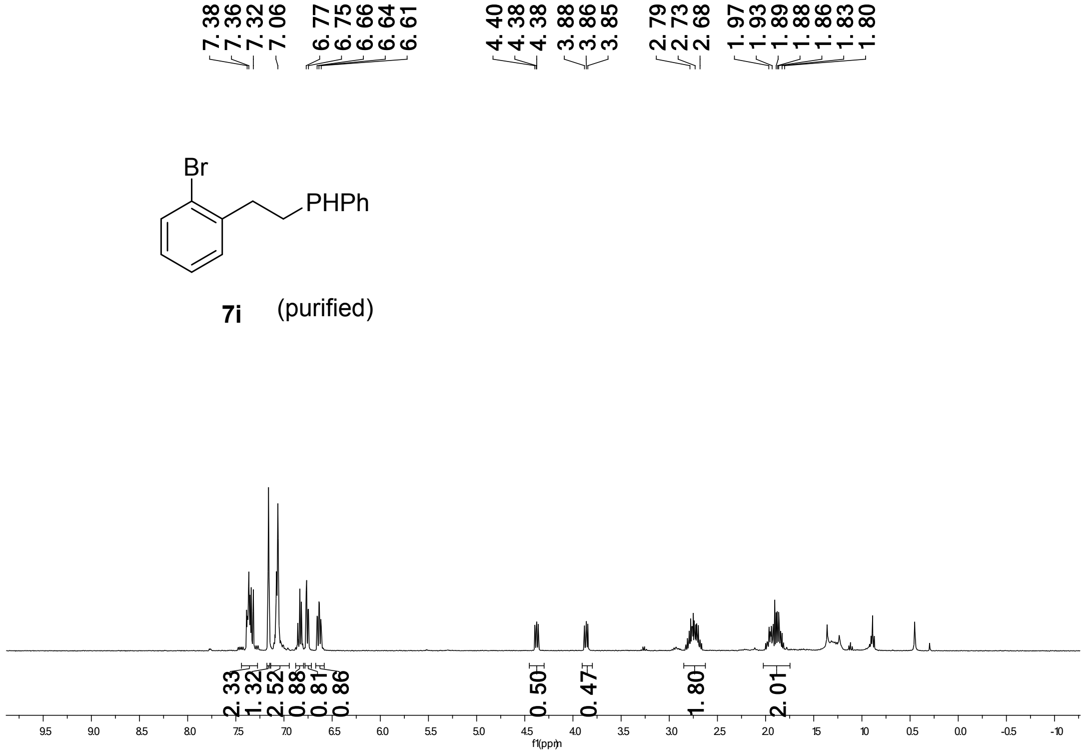

7.39
7.37
7.35
7.34
7.32
7.06
6.82
6.77
6.75
6.66
6.63
6.62
4.40
4.38
4.36
3.88
3.85
3.58
2.78
2.72
2.69
1.97
1.95
1.89
1.85
1.83
Br
PHPh
2.24
2.04
2.16
1.02
0.72
0.92
0.50
0.66
0.57
0.69
2.21
1.33
0.94
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
05
00
-05
f1(ppm)

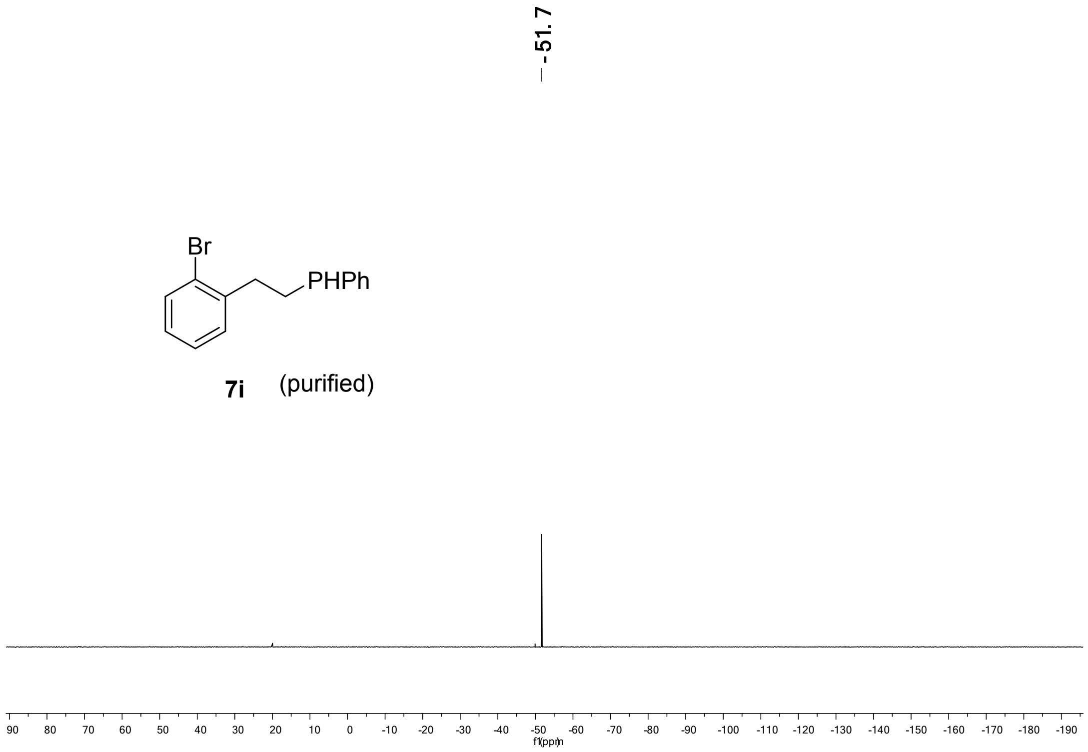
**7i**

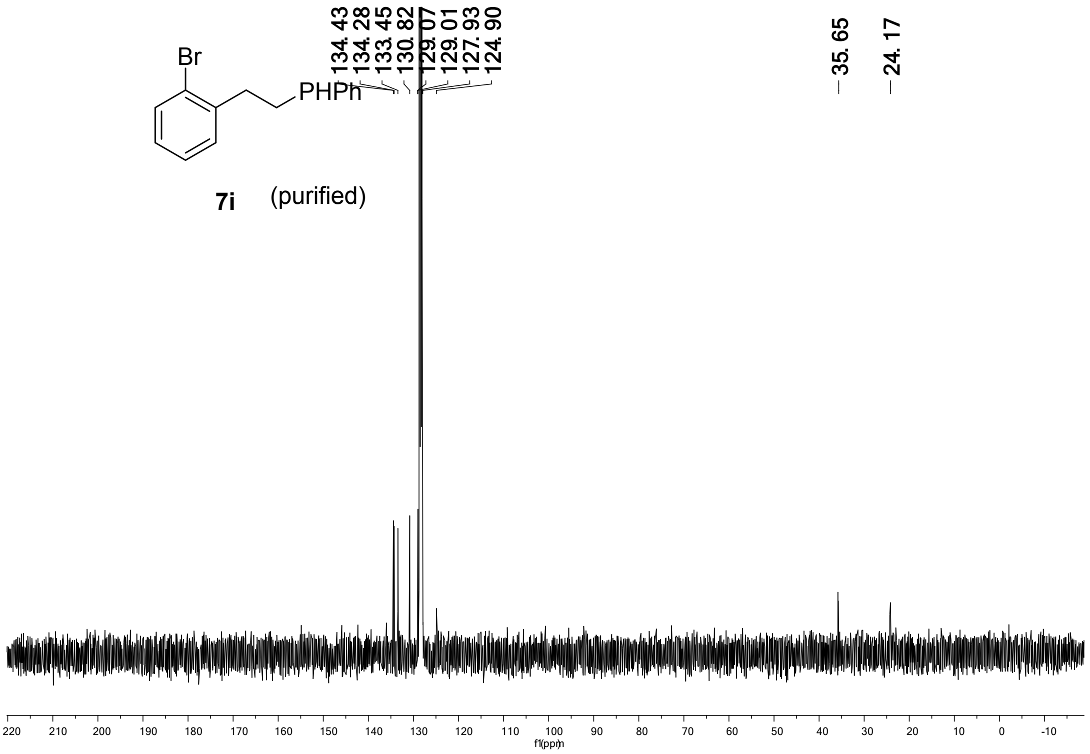

-5.5
-23.6
-51.7
-123.8
Br
PHPh
1.76
1.00
9.85
7.12
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1(ppm)

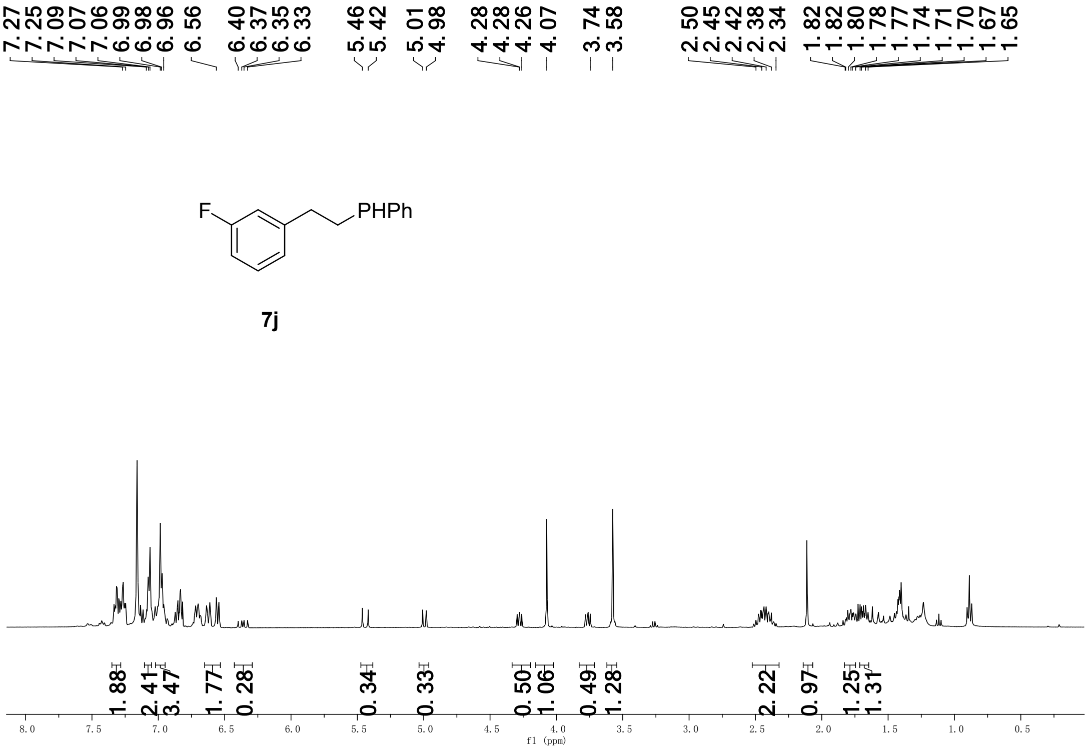
**7i**

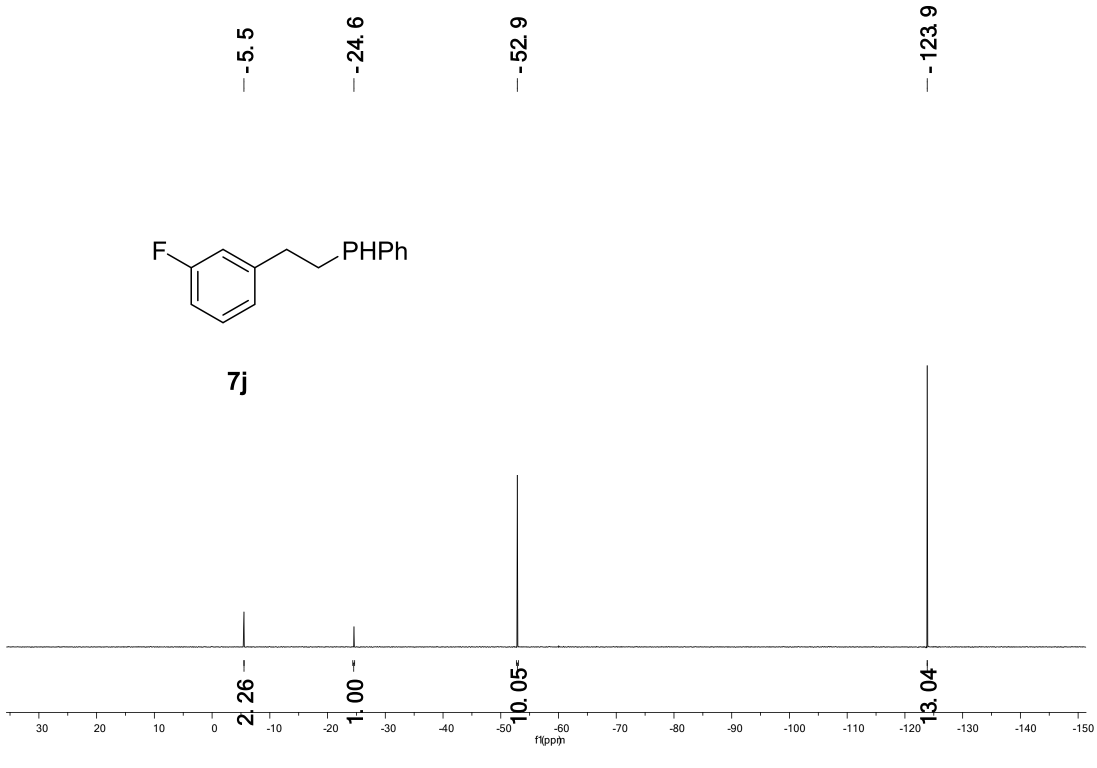

142.30
134.42
133.43
130.81
129.07
127.94
124.90
35.83
24.31
Br
PHPh
7i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

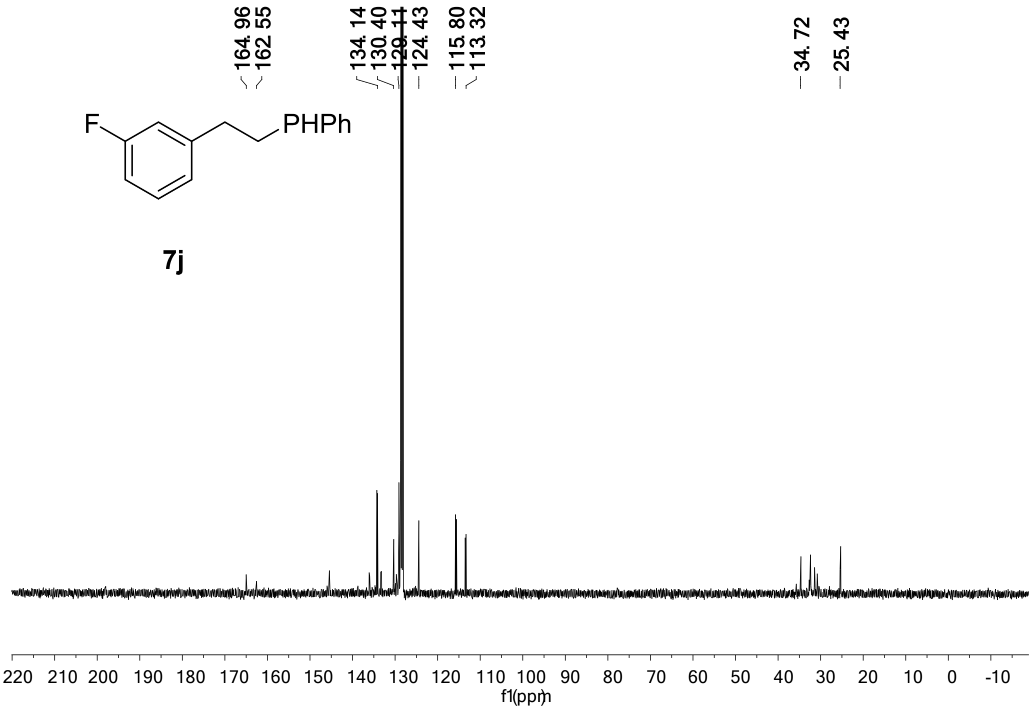

7.38
7.36
7.32
7.06
6.77
6.75
6.66
6.64
6.61
4.40
4.38
4.38
3.88
3.86
3.85
2.79
2.73
2.68
1.97
1.93
1.89
1.88
1.86
1.83
1.80
Br
PHPh
7i (purified)
2.33
1.32
2.52
0.88
0.81
0.86
0.50
0.47
1.80
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


**7i** (purified)

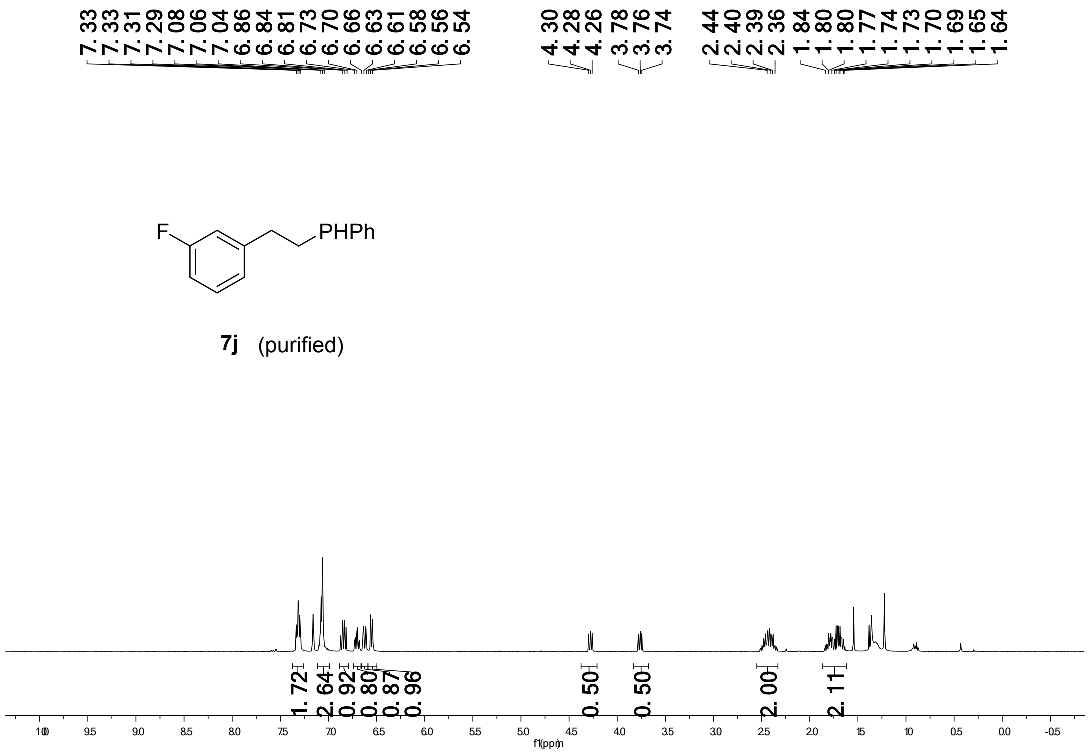

**7i** (purified)


7.27
7.25
7.09
7.07
7.06
6.99
6.98
6.96
6.56
6.40
6.37
6.35
6.33
5.46
5.42
5.01
4.98
4.28
4.28
4.26
4.07
3.74
3.58
2.50
2.45
2.42
2.38
2.34
1.82
1.82
1.80
1.78
1.77
1.74
1.71
1.70
1.67
1.65
F
PHPh
7j
1.88
2.41
3.47
1.77
0.28
0.34
0.33
0.50
1.06
0.49
1.28
2.22
0.97
1.25
1.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

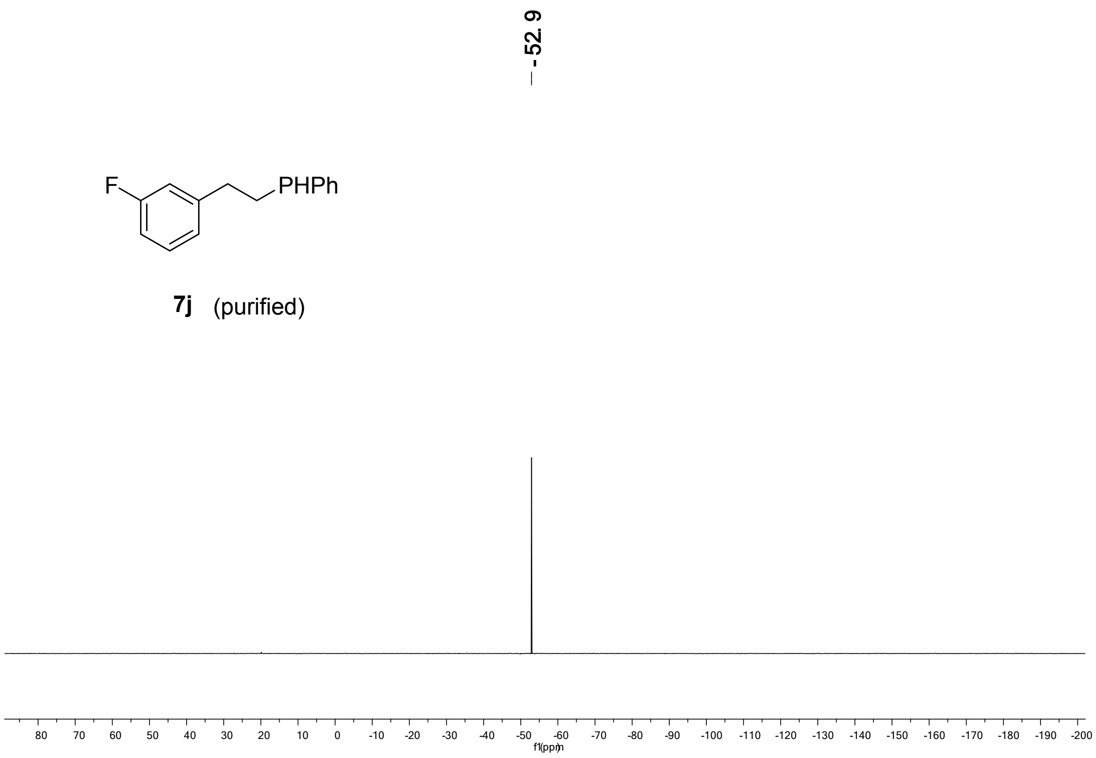

-5.5
-24.6
-52.9
-123.9
F
PHPh
7j
2.26
1.00
10.05
13.04
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1(ppm)



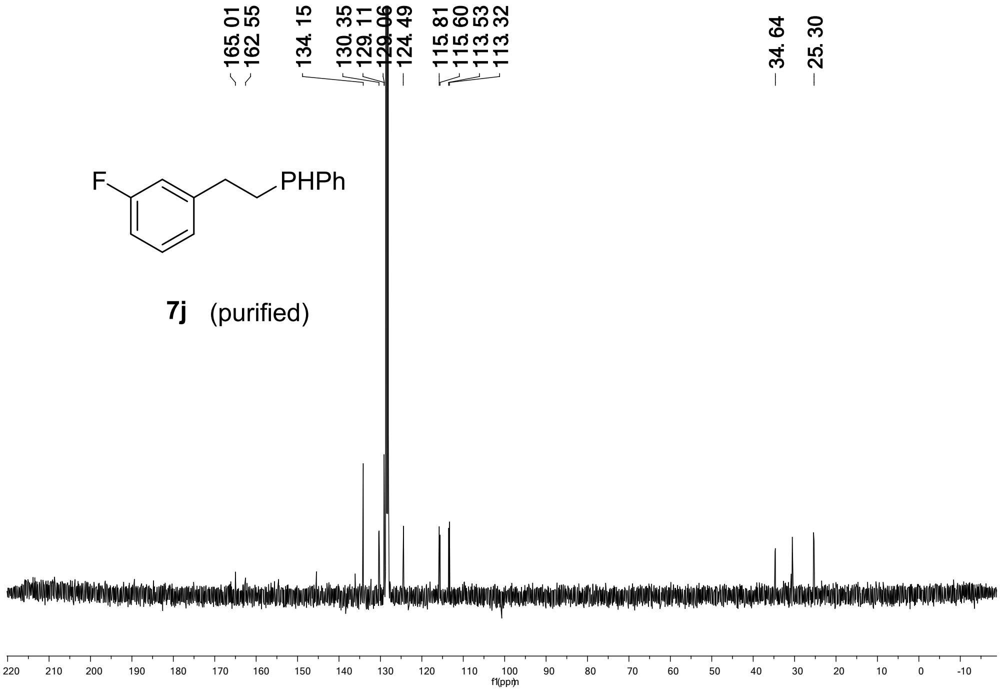
**7j**



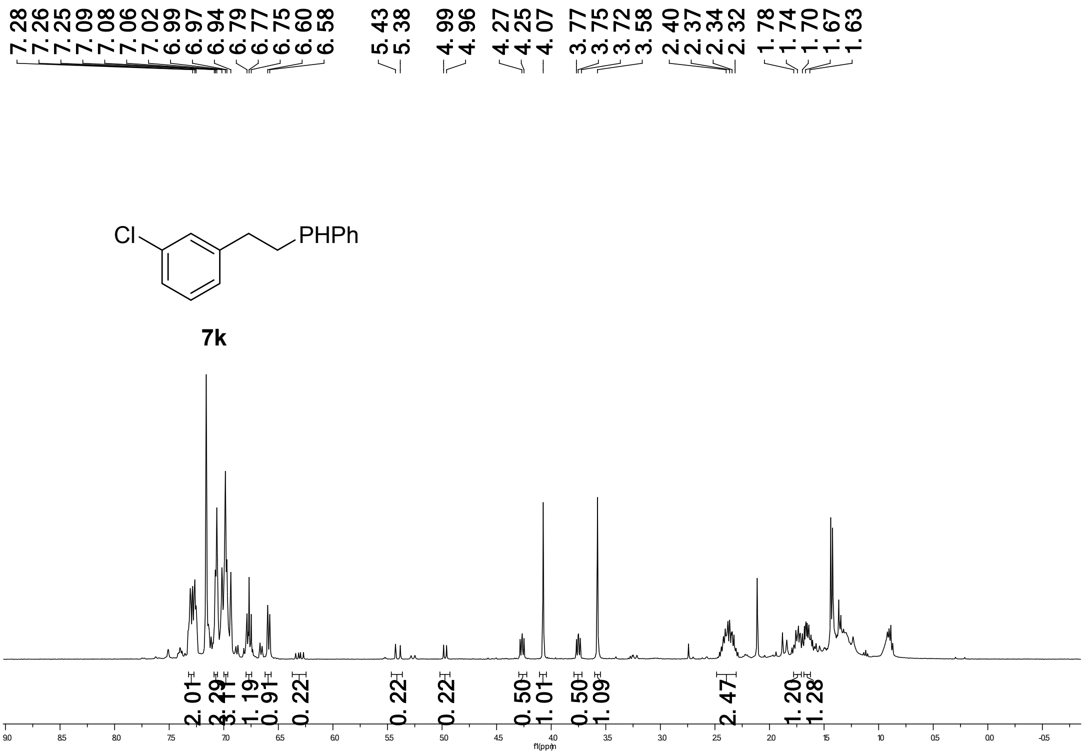
**7j** (purified)



**7j** (purified)



**7j** (purified)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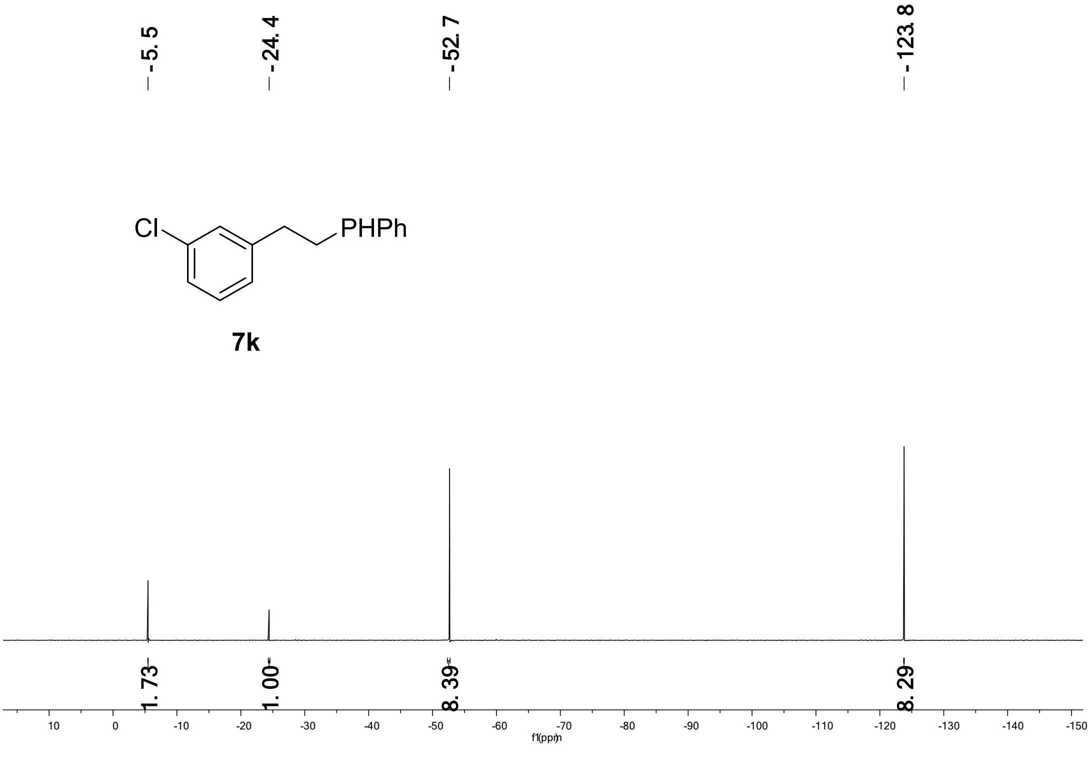
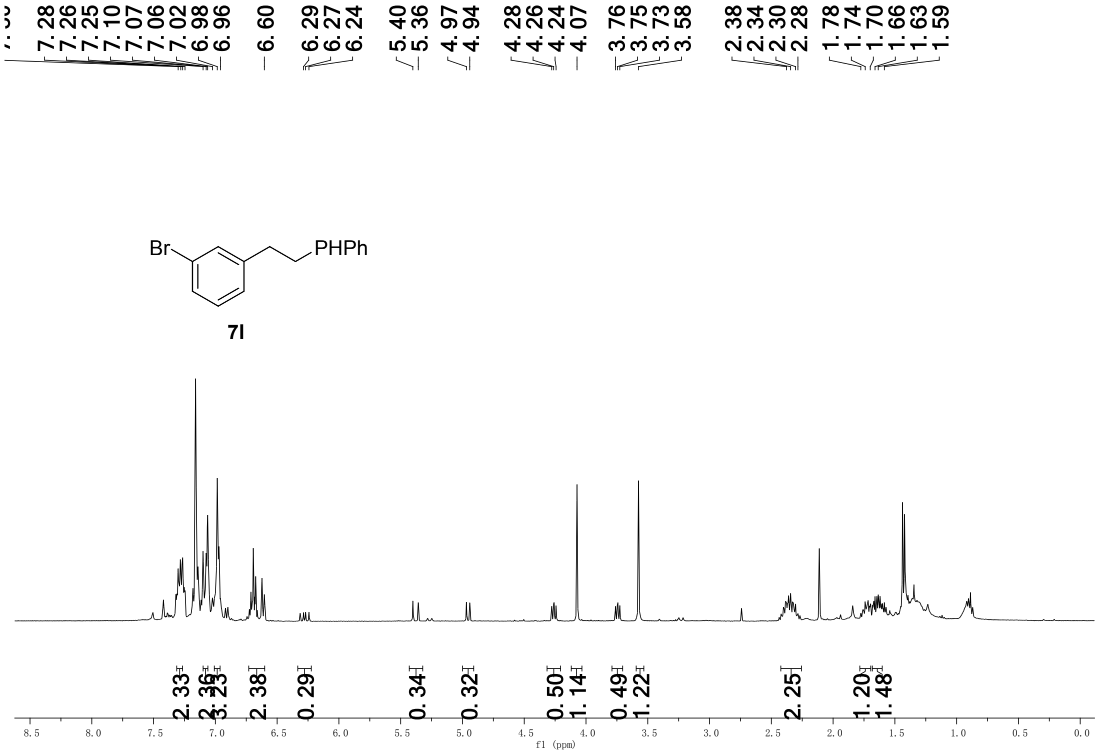
7.26
7.25
7.09
7.08
7.06
7.02
6.99
6.97
6.94
6.79
6.77
6.75
6.60
6.58
5.43
5.38
4.99
4.96
4.27
4.25
4.07
3.77
3.75
3.72
3.58
2.40
2.37
2.34
2.32
1.78
1.74
1.70
1.67
1.63
Cl
PHPh
2.01
2.29
3.11
1.19
0.91
0.22
0.22
0.22
0.50
1.01
0.50
1.09
2.47
1.20
1.28
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
05
00
-05
f1(ppm)

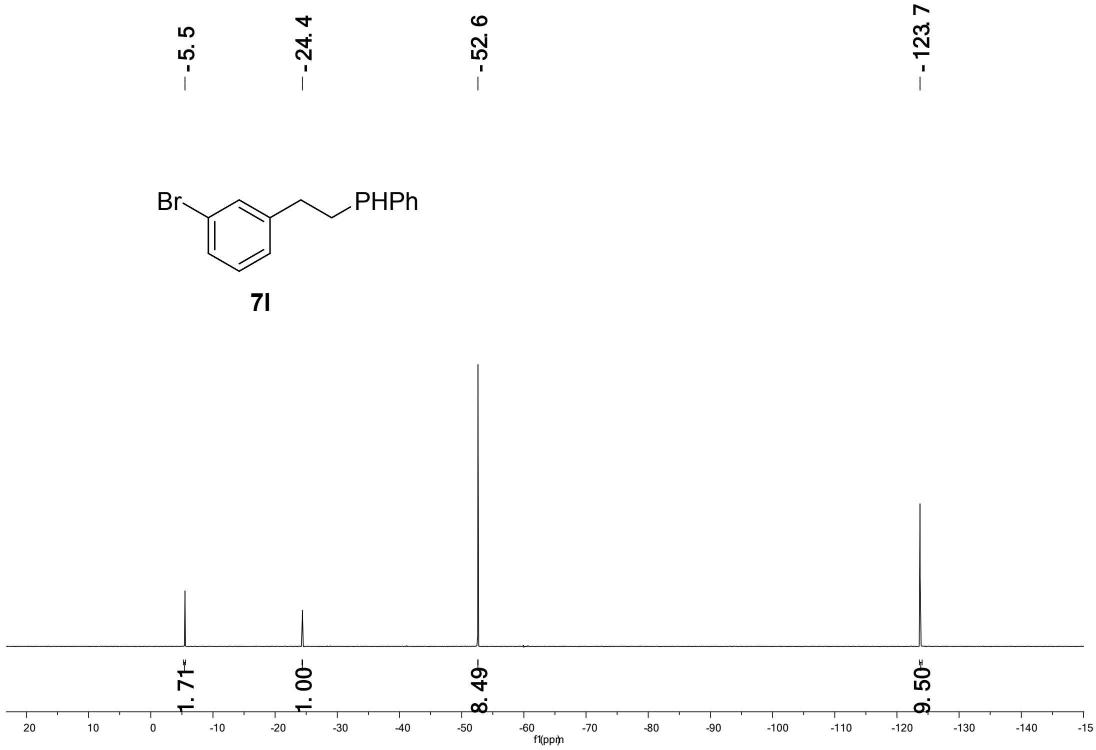
**7k**


-5.5
-24.4
-52.7
-123.8
Cl
PHPh
1.73
1.00
8.39
8.29
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1(ppm)

**7k**


7.28
7.26
7.25
7.10
7.07
7.06
7.02
6.98
6.96
6.60
6.29
6.27
6.24
5.40
5.36
4.97
4.94
4.28
4.26
4.24
4.07
3.76
3.75
3.73
3.58
2.38
2.34
2.30
2.28
1.78
1.74
1.70
1.66
1.63
1.59
Br
PHPh
2.33
2.36
3.23
2.38
0.29
0.34
0.32
0.50
1.14
0.49
1.22
2.25
1.20
1.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7l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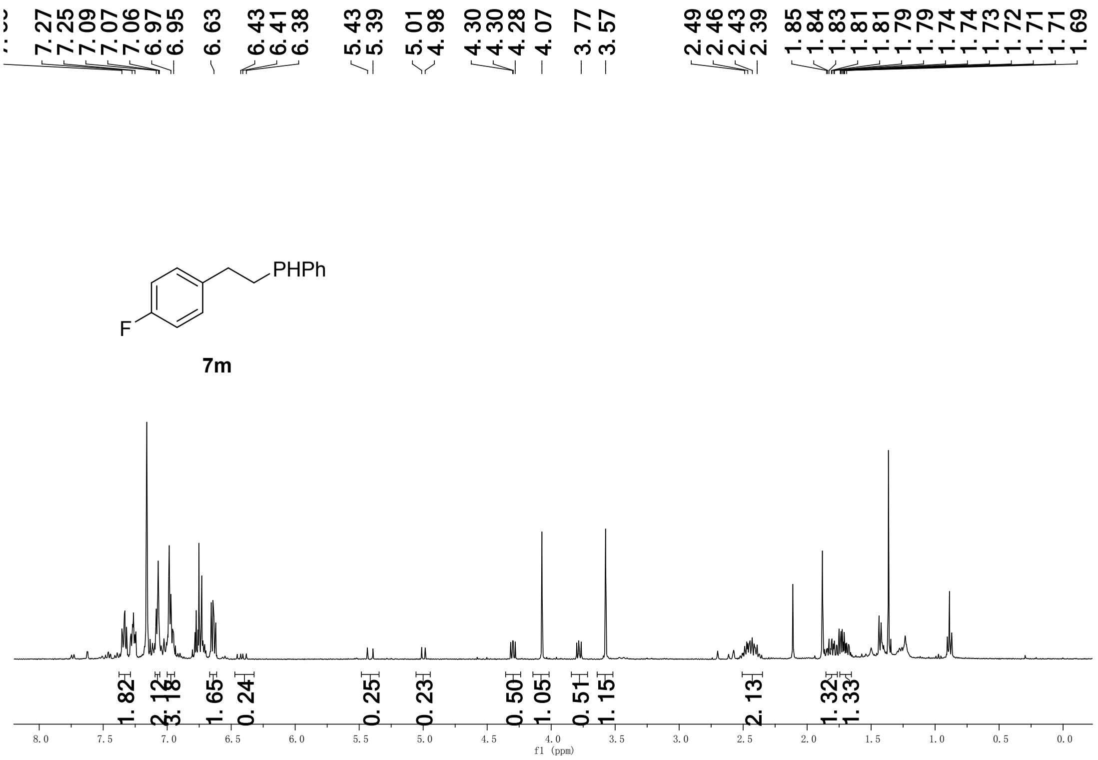
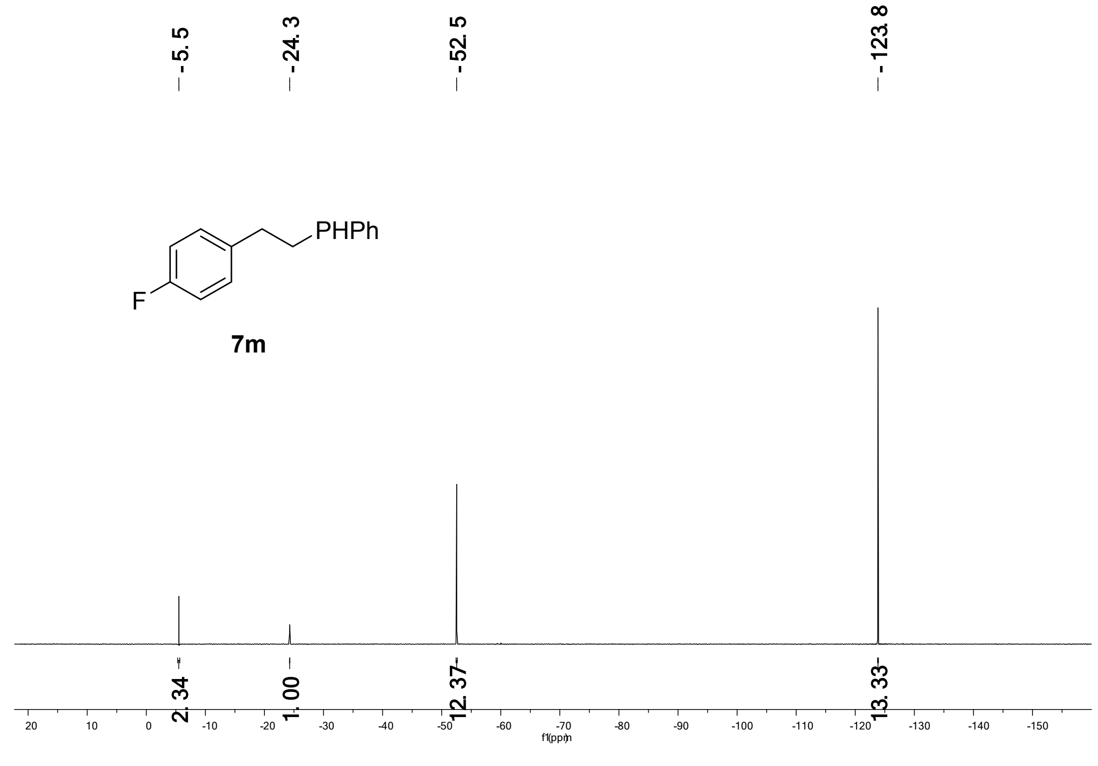
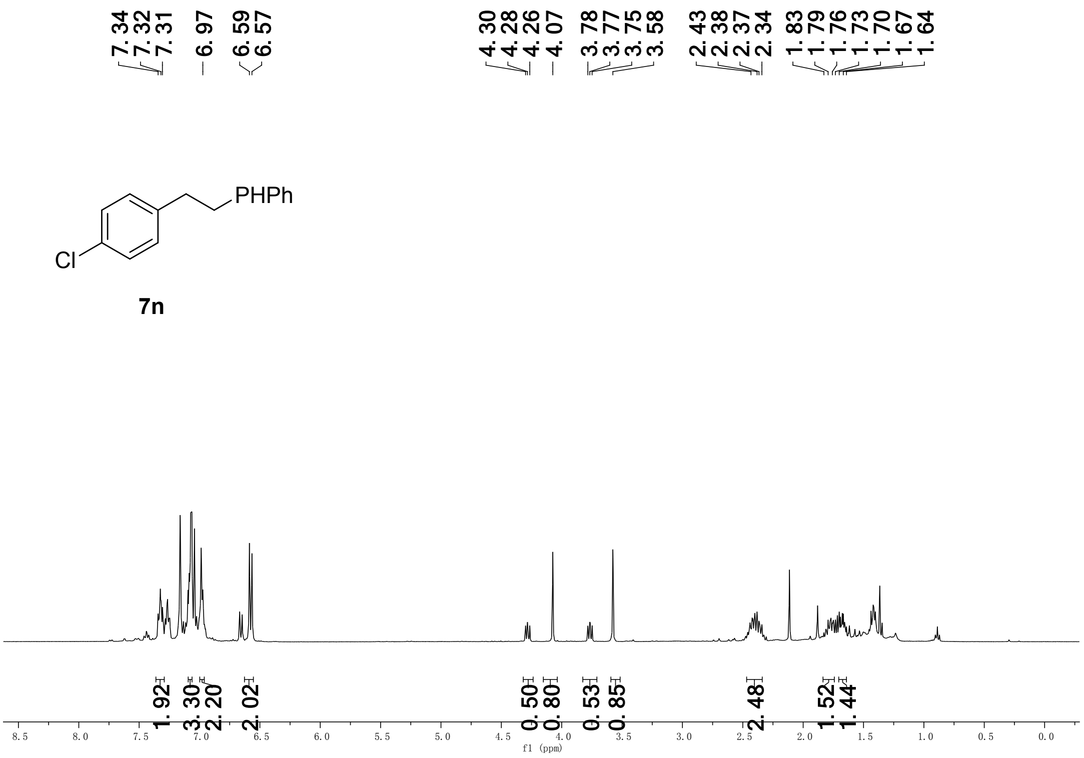
-24.4
-52.6
-123.7
Br
PHPh
1.71
1.00
8.49
9.50
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-15
f1(ppm)

7l


7.27
7.25
7.09
7.07
7.06
6.97
6.95
6.63
6.43
6.41
6.38
5.43
5.39
5.01
4.98
4.30
4.30
4.28
4.07
3.77
3.57
2.49
2.46
2.43
2.39
1.85
1.84
1.83
1.81
1.81
1.79
1.74
1.74
1.73
1.72
1.71
1.71
1.69
PHPh
F
7m
1.82
2.12
3.18
1.65
0.24
0.25
0.23
0.50
1.05
0.51
1.15
2.13
1.32
1.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-5.5
-24.3
-52.5
-123.8
PHPh
F
7m
2.34
1.00
12.37
13.33
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)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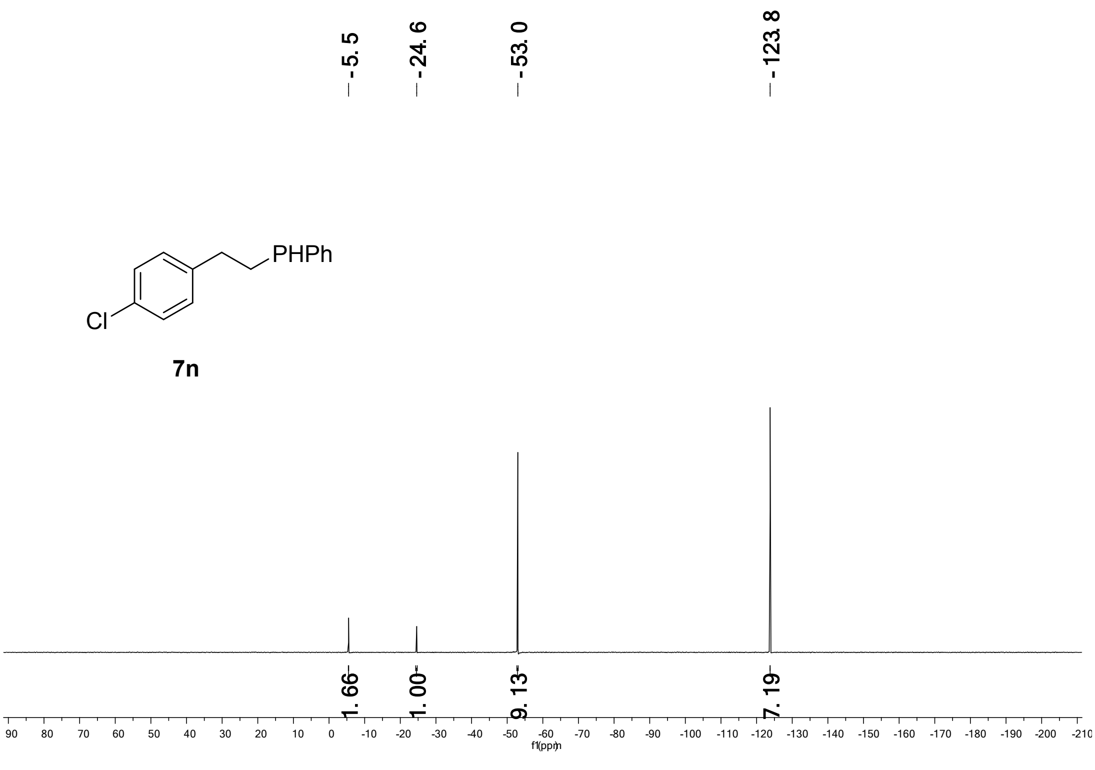
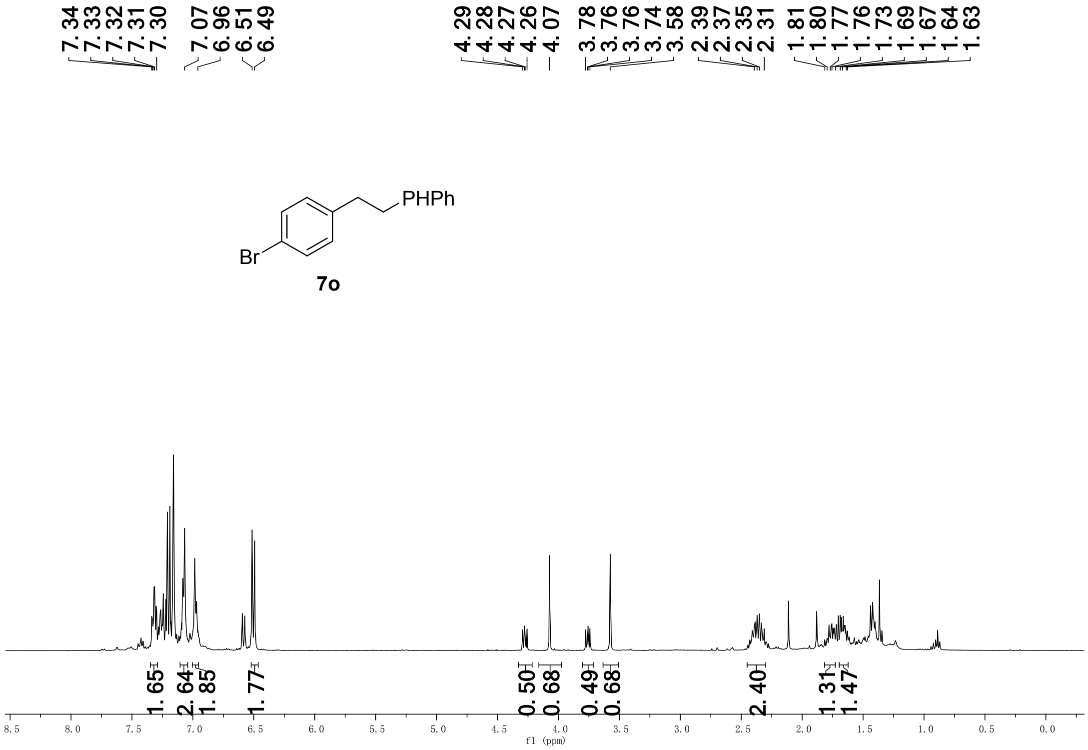
7.32
7.31
6.97
6.59
6.57
4.30
4.28
4.26
4.07
3.78
3.77
3.75
3.58
2.43
2.38
2.37
2.34
1.83
1.79
1.76
1.73
1.70
1.67
1.64
PHPh
Cl
7n
1.92
3.30
2.20
2.02
0.50
0.80
0.53
0.85
2.48
1.52
1.44
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-5.5
-24.6
-53.0
-123.8
PHPh
Cl
7n
1.66
1.00
9.13
7.19
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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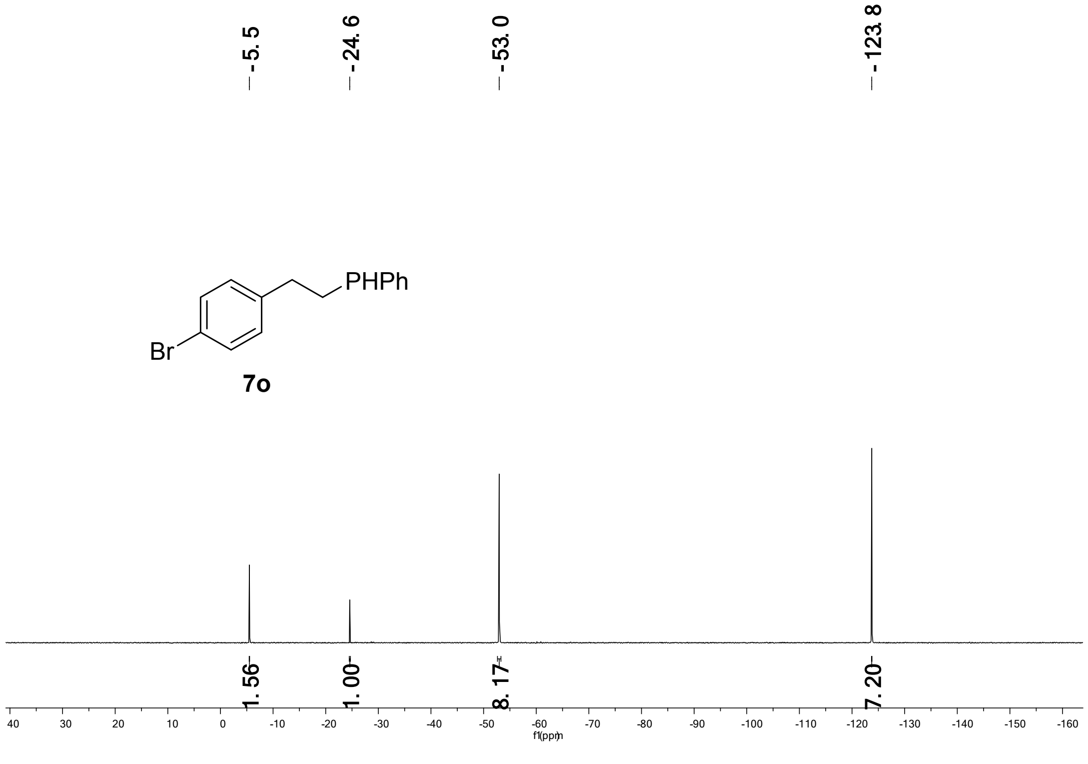
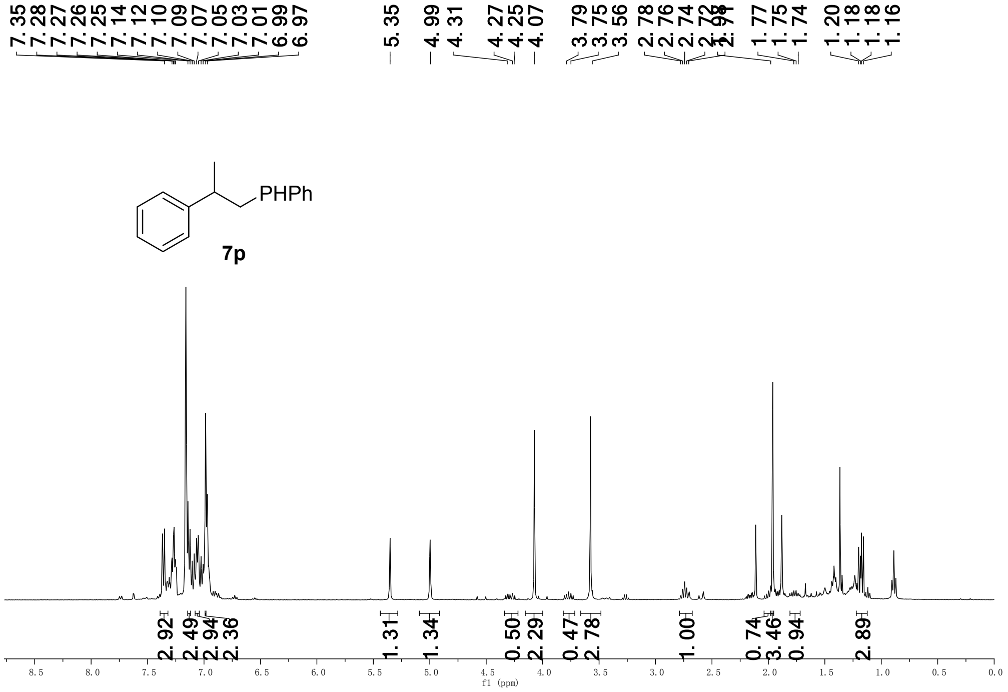
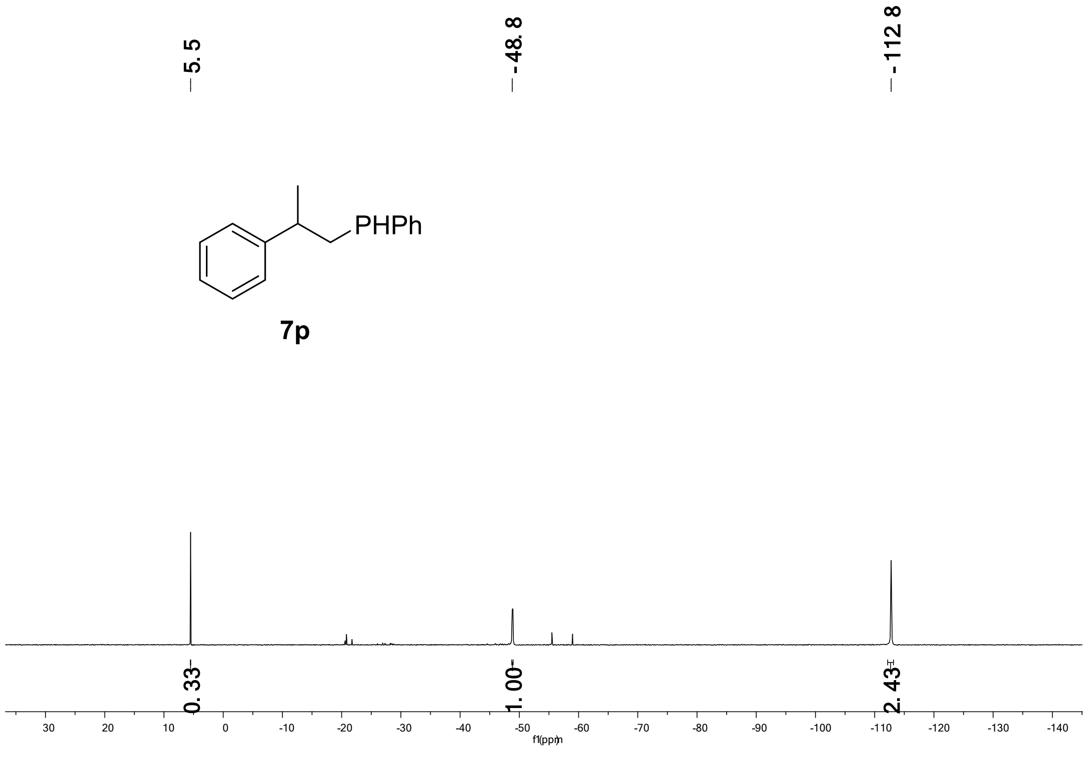
7.33
7.32
7.31
7.30
7.07
6.96
6.51
6.49
4.29
4.28
4.27
4.26
4.07
3.78
3.76
3.76
3.74
3.58
2.39
2.37
2.35
2.31
1.81
1.80
1.77
1.76
1.73
1.69
1.67
1.64
1.63
PHPh
Br
7o
1.65
2.64
1.85
1.77
0.50
0.68
0.49
0.68
2.40
1.31
1.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

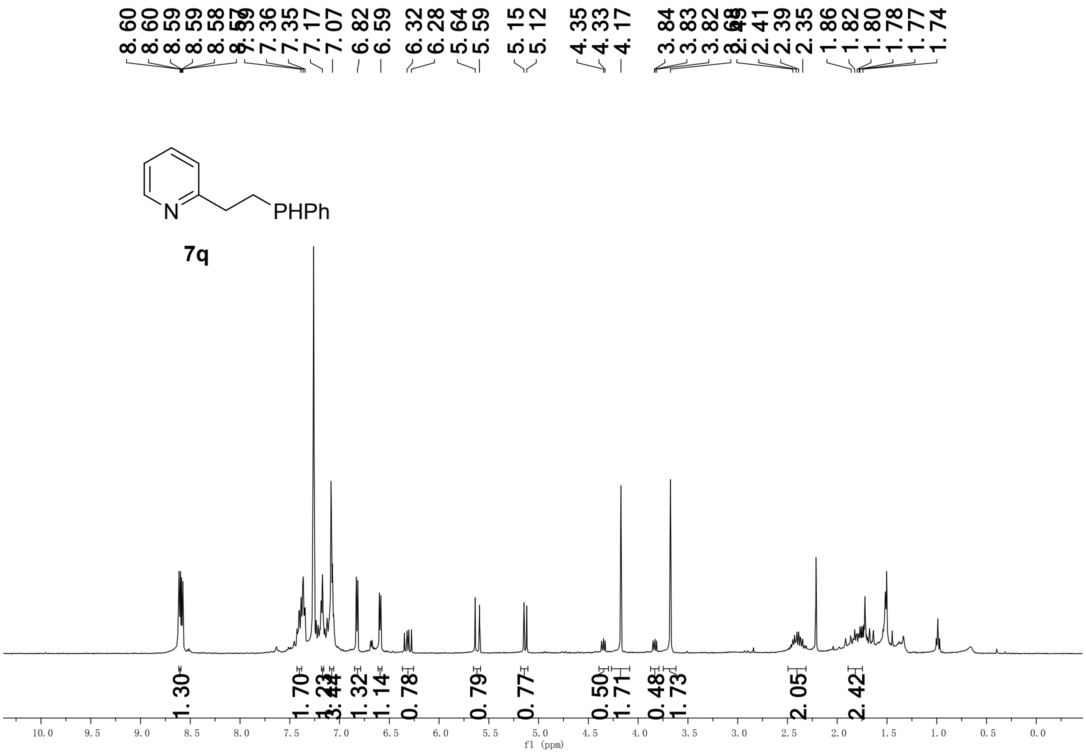

-5.5
-24.6
-53.0
-123.8
PHPh
Br
7o
1.56
1.00
8.17
7.20
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


7.35
7.28
7.27
7.26
7.25
7.14
7.12
7.10
7.09
7.07
7.05
7.03
7.01
6.99
6.97
5.35
4.99
4.31
4.27
4.25
4.07
3.79
3.75
3.56
2.78
2.76
2.74
2.72
2.71
1.77
1.75
1.74
1.20
1.18
1.18
1.16
PHPh
2.92
2.49
2.94
2.36
1.31
1.34
0.50
2.29
0.47
2.78
1.00
0.74
3.46
0.94
2.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**7p**

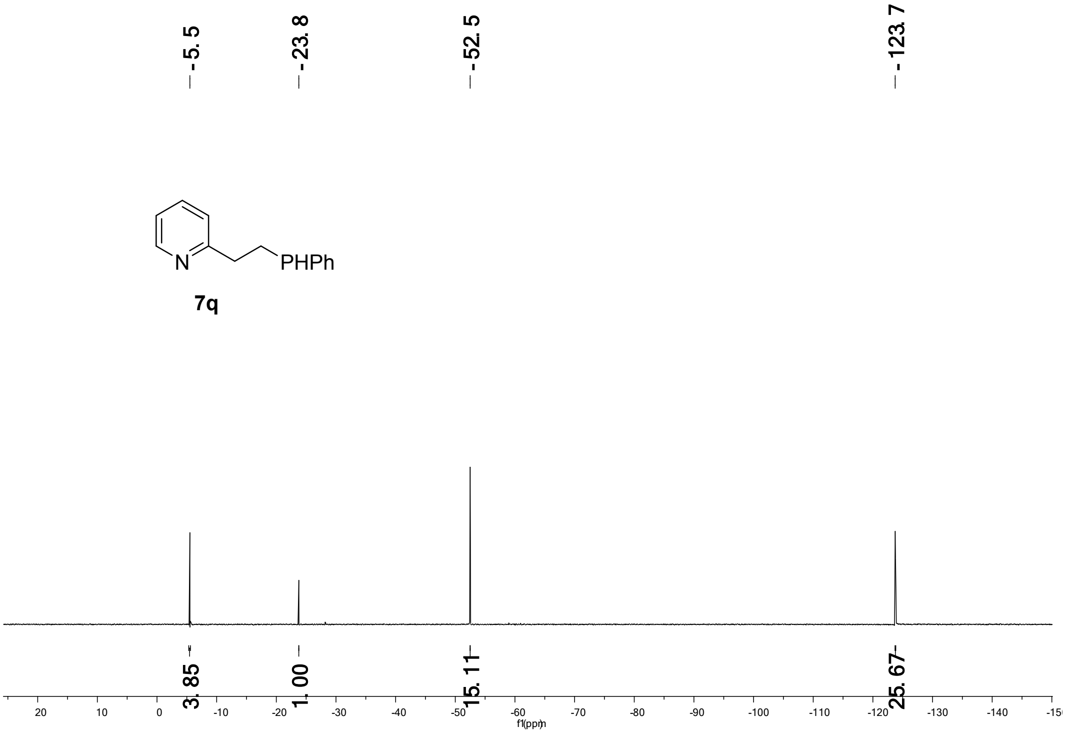

5.5
-48.8
-112.8
PHPh
0.33
1.00
2.43
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1(ppm)

**7p**



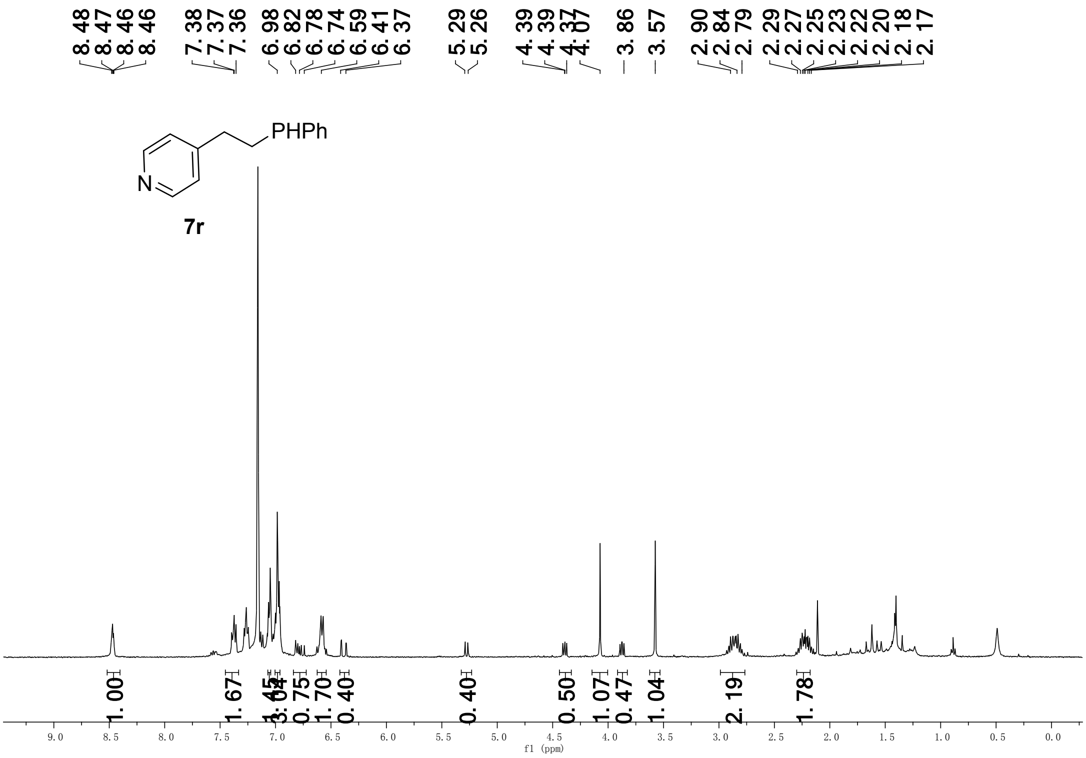
8.60
8.60
8.59
8.59
8.58
8.57
7.39
7.36
7.35
7.17
7.07
6.82
6.59
6.32
6.28
5.64
5.59
5.15
5.12
4.35
4.33
4.17
3.84
3.83
3.82
3.69
2.49
2.41
2.39
2.35
1.86
1.82
1.80
1.78
1.77
1.74
N
PHPh
1.30
1.70
1.23
3.44
1.32
1.14
0.78
0.79
0.77
0.50
1.71
0.48
1.73
2.05
2.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

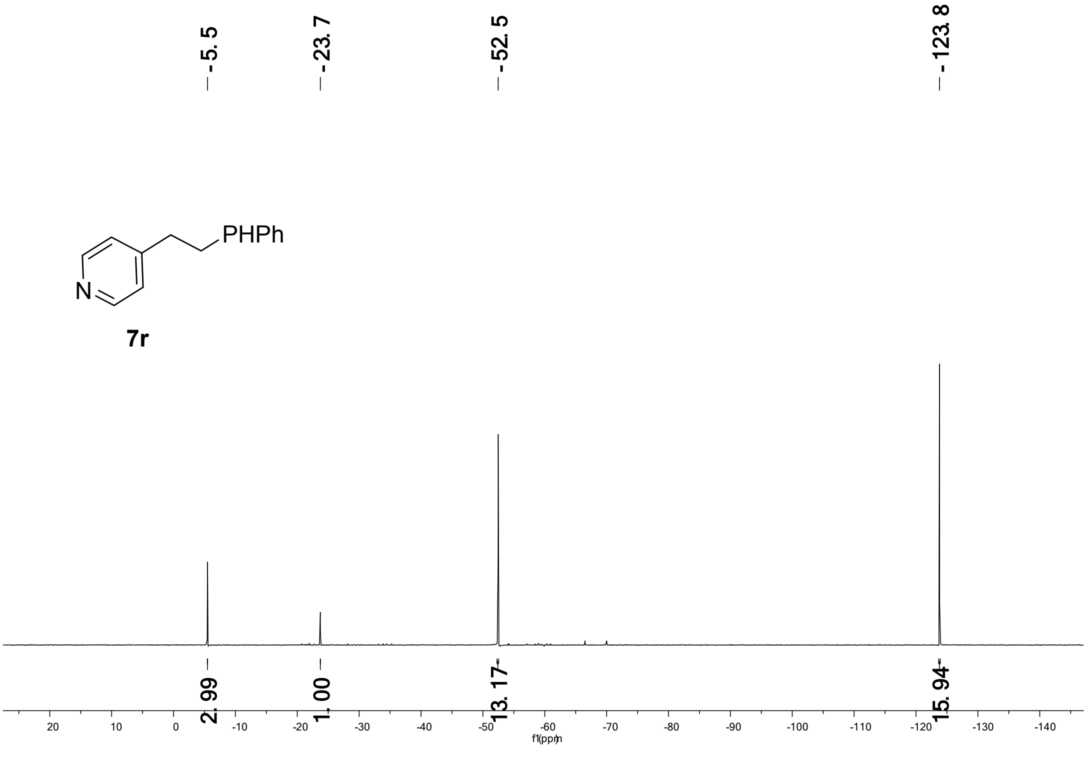
**7q**



-5.5
-23.8
-52.5
-123.7
N
PHPh
3.85
1.00
15.11
25.67
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

**7q**


8.48
8.47
8.46
8.46
7.38
7.37
7.36
6.98
6.82
6.78
6.74
6.59
6.41
6.37
5.29
5.26
4.39
4.39
4.37
4.07
3.86
3.57
2.90
2.84
2.79
2.29
2.27
2.25
2.23
2.22
2.20
2.18
2.17
PHPh
N
7r
1.00
1.67
1.45
3.04
0.75
1.70
0.40
0.40
0.50
1.07
0.47
1.04
2.19
1.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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15.94
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10
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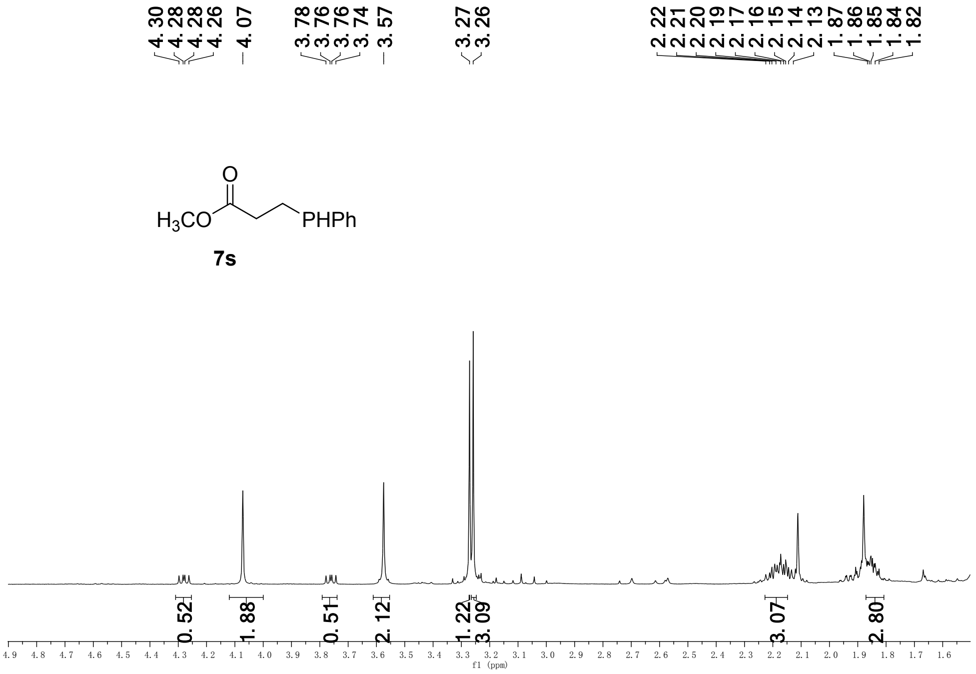
f1(ppm)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1.85
1.84
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O
H3CO
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7s
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1.88
0.51
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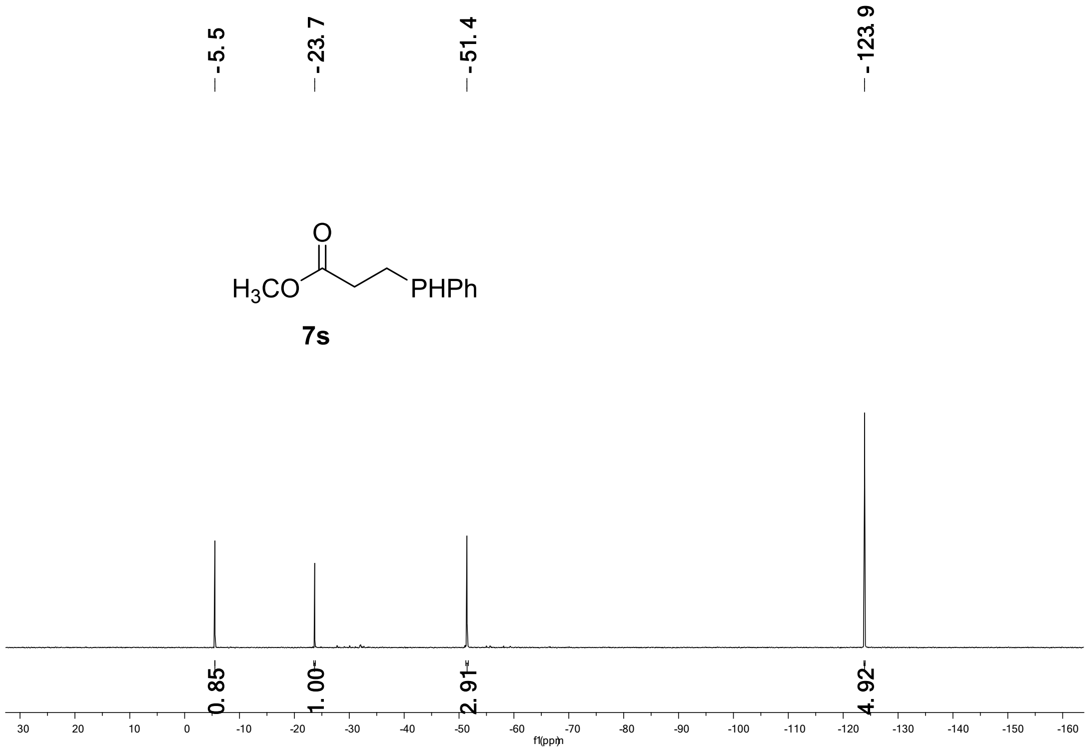
1.22
3.09
3.07
2.80
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)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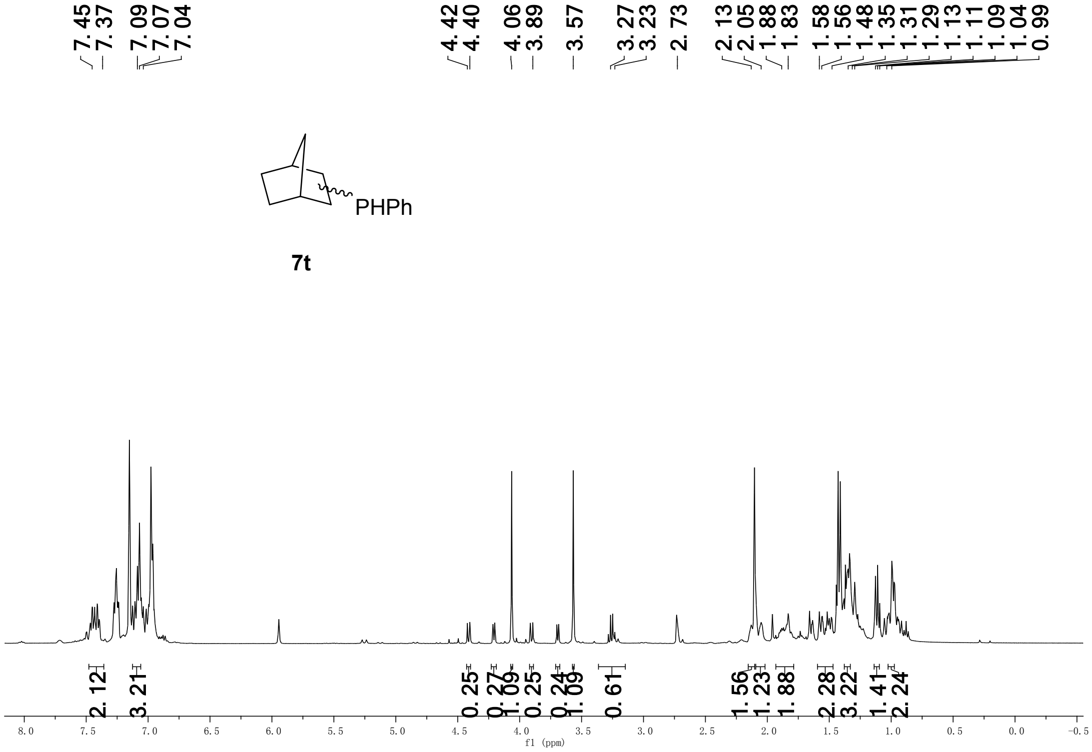
f1(ppm)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2.13
2.05
1.88
1.83
1.58
1.56
1.48
1.35
1.31
1.29
1.13
1.11
1.09
1.04
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7t
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0.25
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1.41
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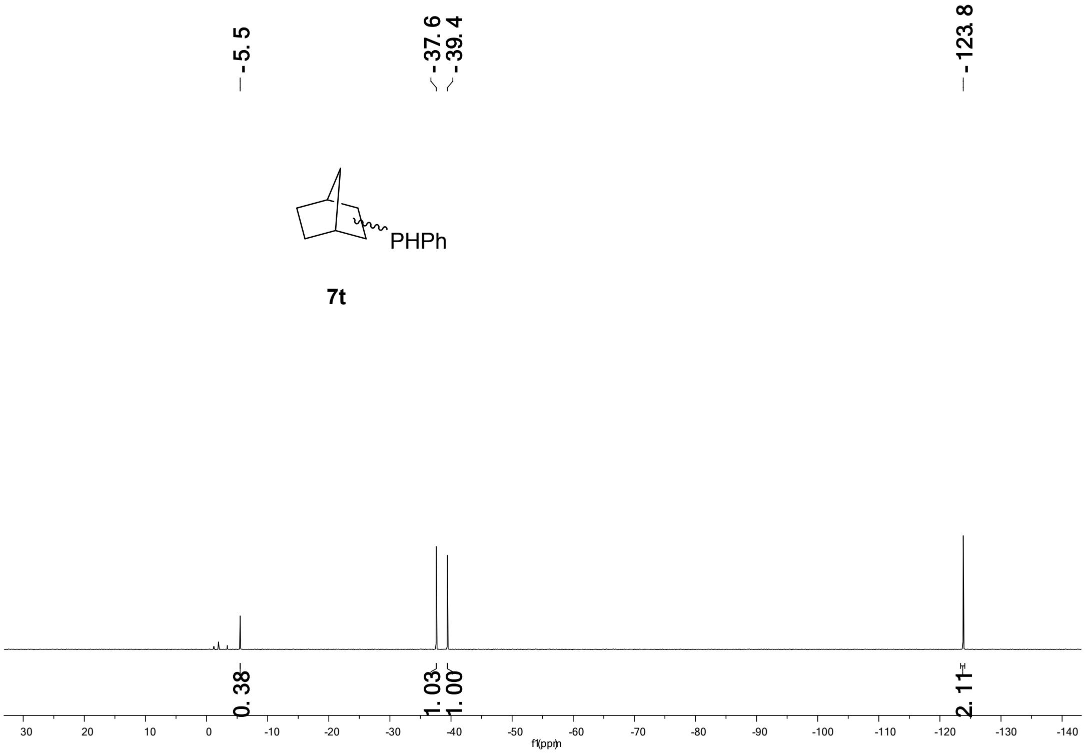
f1 (ppm)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-90
-100
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-120
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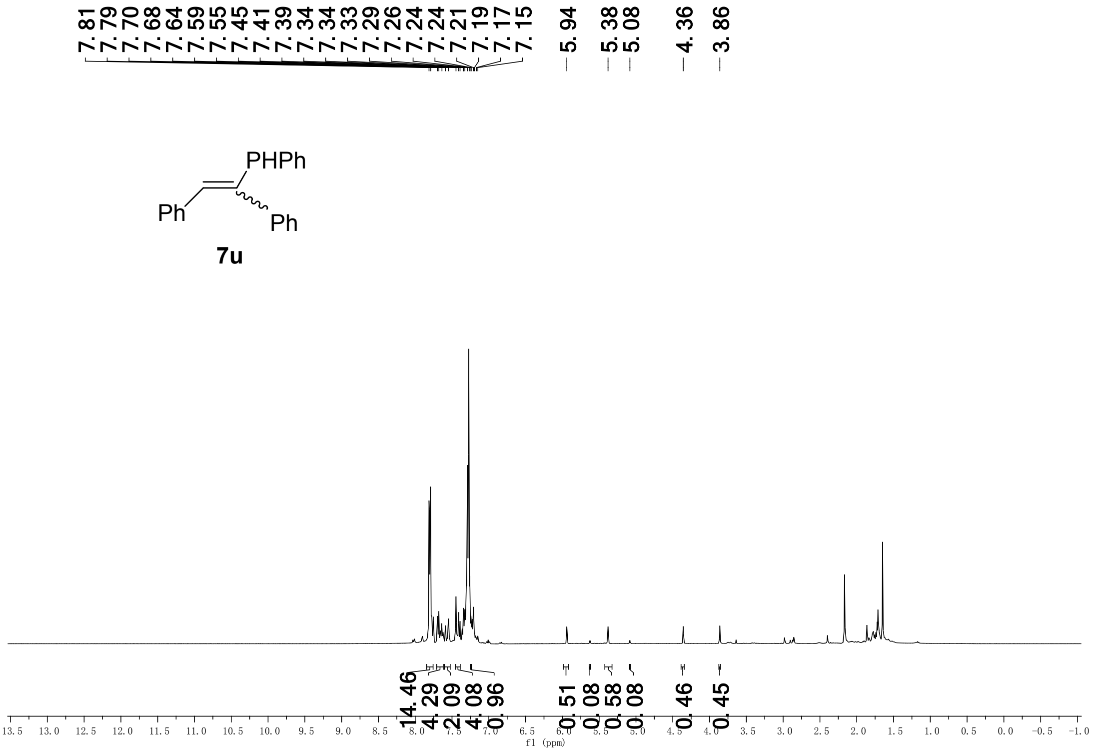
f1 (ppm)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4.36
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Ph
Ph
7u
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4.29
2.09
4.08
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0.51
0.08
0.58
0.08
0.46
0.45
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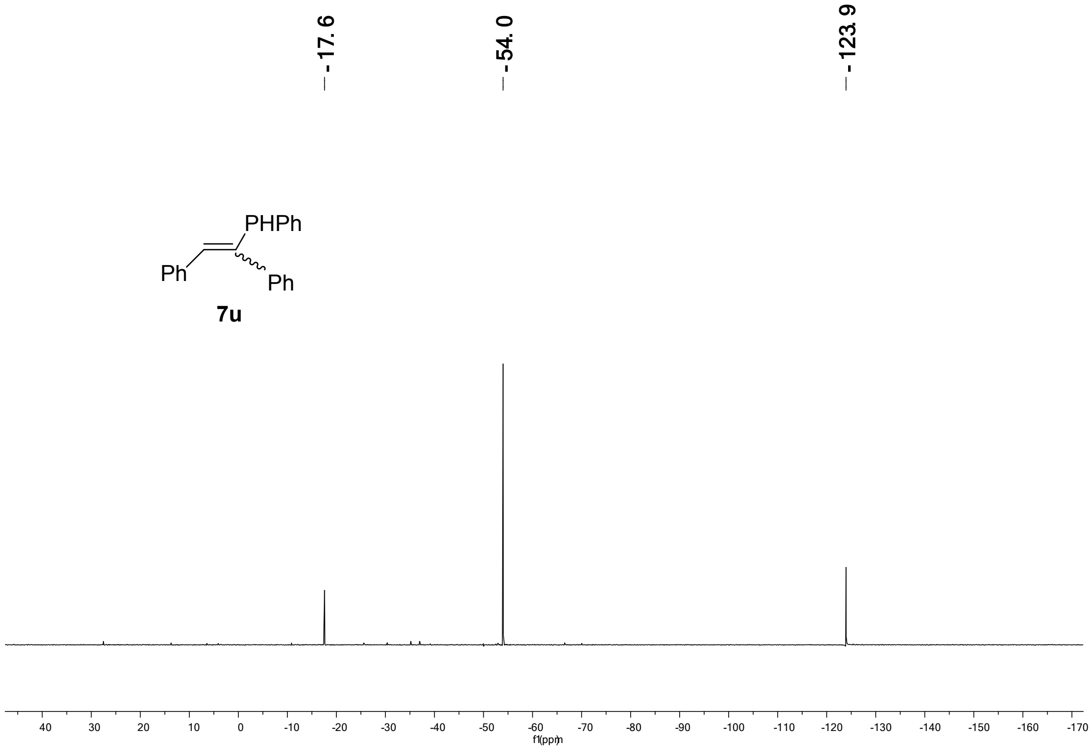
f1 (ppm)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PHPh
Ph
Ph
7u
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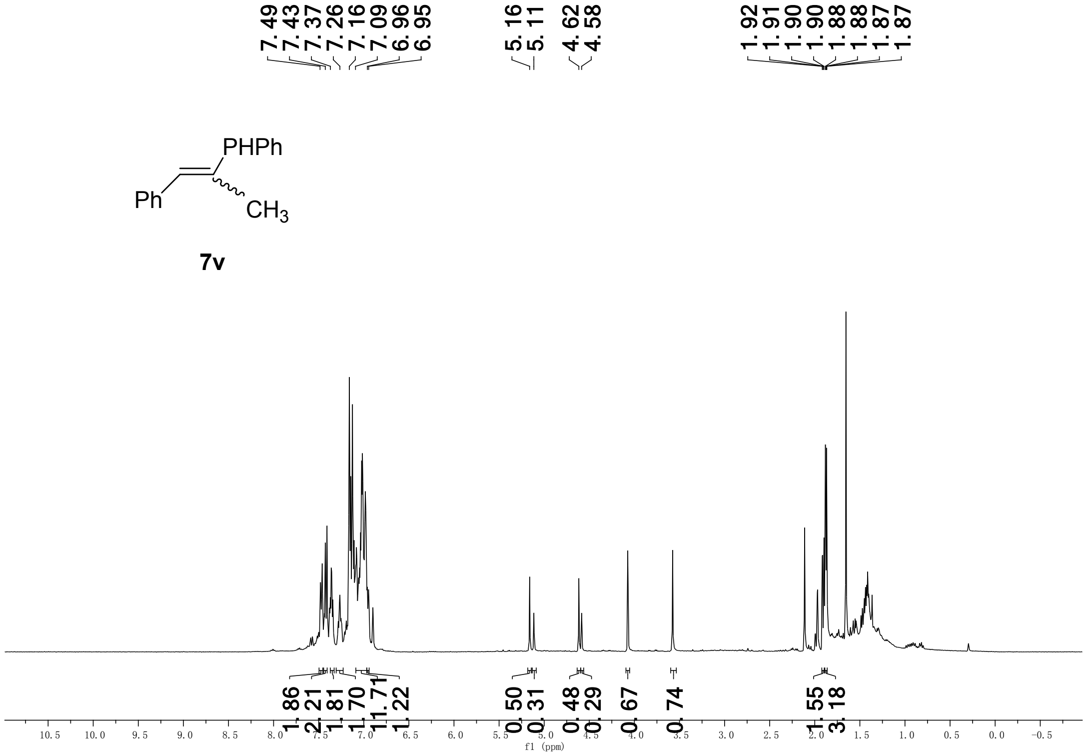
f1 (ppm)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1.88
1.88
1.87
1.87
PHPh
Ph
CH3
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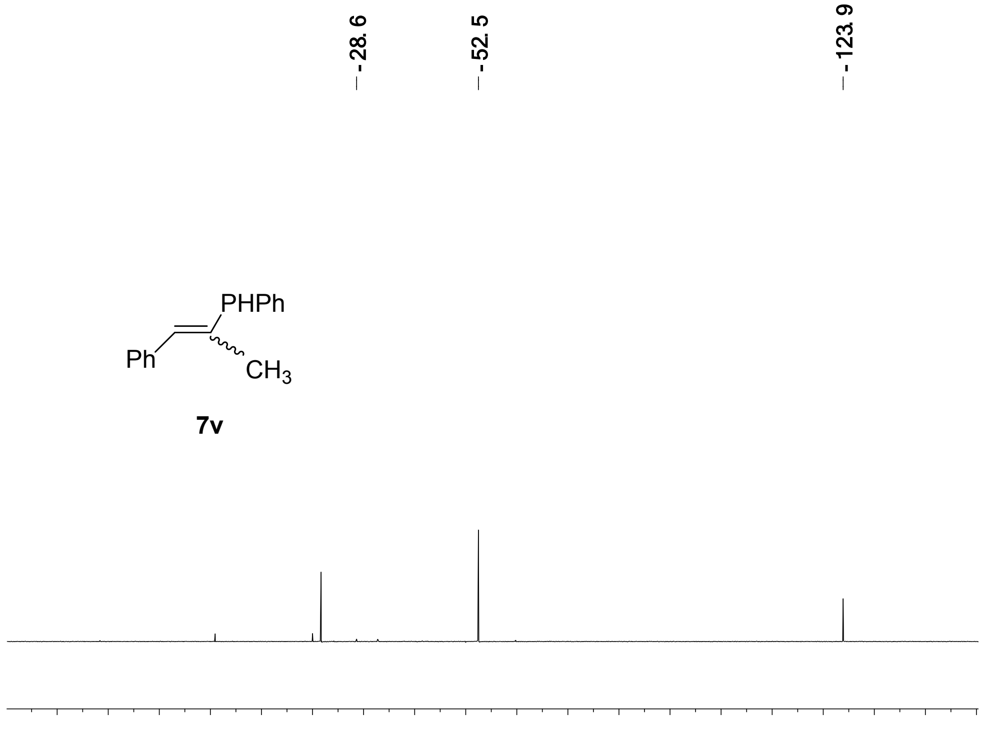
1.81
1.70
11.71
1.22
0.50
0.31
0.48
0.29
0.67
0.74
1.55
3.18
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

**7v**


-28.6
-52.5
-123.9
PHPh
Ph
CH3

**7v**

## Kinetic study

All manipulations were performed in glovebox under a nitrogen atmosphere. Complex **1** was mixed with styrene and phenylphosphine at room temperature and stirred for desired time. Amounts of catalyst and substrates are provided in captions of each plot. Reaction mixtures were taken after each interval and analyzed by NMR in $C_6D_6$. Conversions were determined by $^{31}P$ NMR.

Comparing to Fig.5, plot without origin:

If the rate-order of $H_2PPh$ is zero:

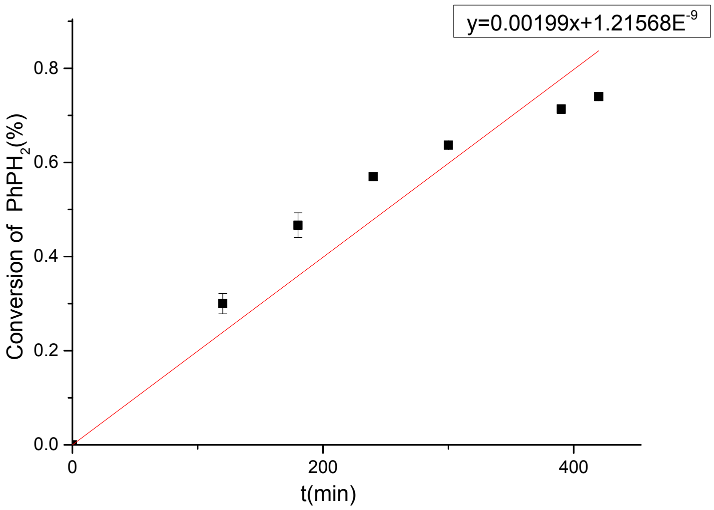


**Fig. S3** Plot of conversion of phenylphosphine versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (10 mol %), room temperature. $R^2 = 0.98703$.

If the rate-order of $H_2PPh$ is first:

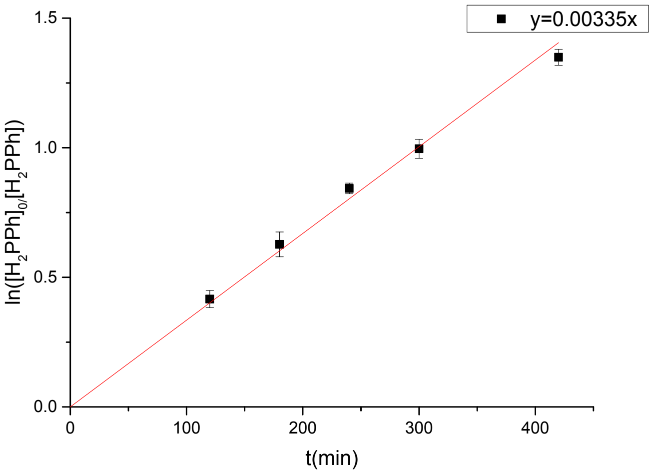


**Fig. S4** Plot of conversion of ln[phenylphosphine]$_0$/[phenylphosphine] versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (10 mol %), room temperature. $R^2 = 0.99796$.

Catalyst loading of 1 mol %:

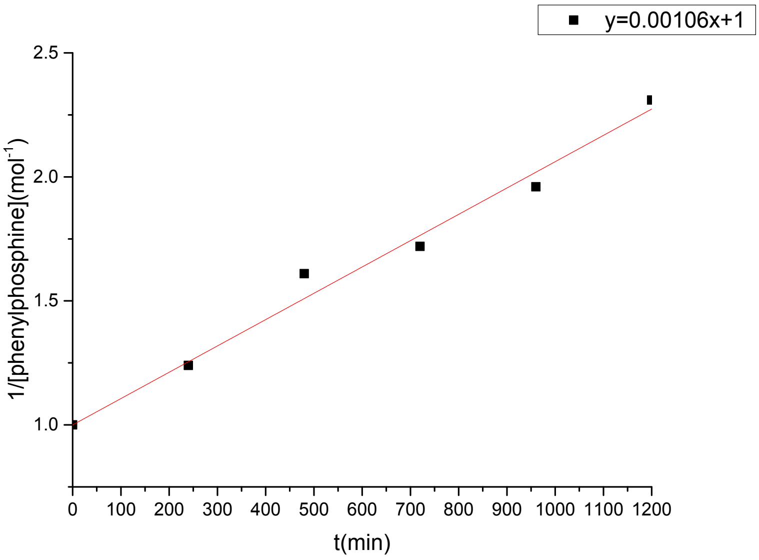


**Fig. S5** Plot of 1/[phenylphosphine] versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (1 mol %), room temperature. $R^2 = 0.99881$.

If the rate-order of $H_2PPh$ is first:

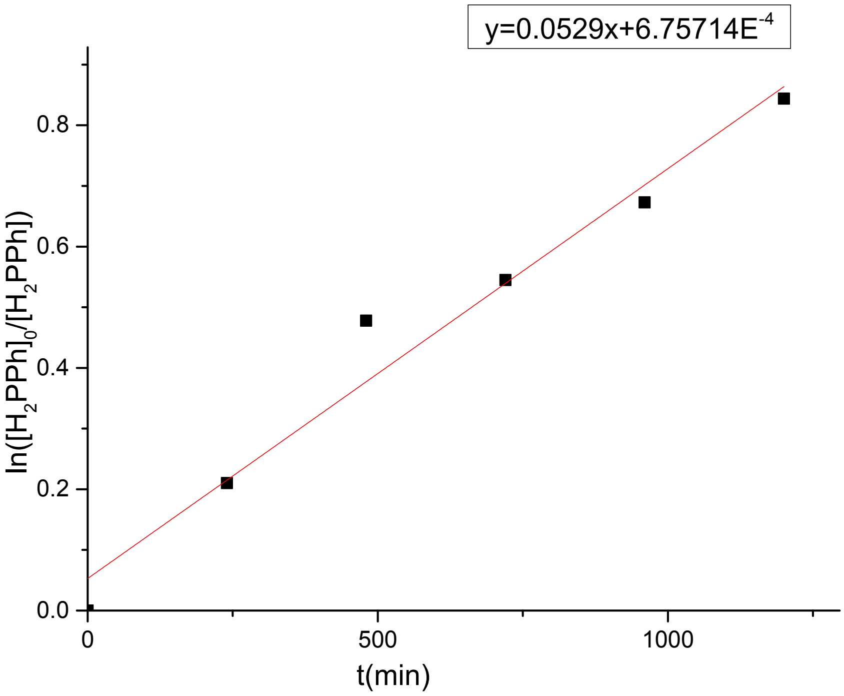


**Fig. S6** Plot of ln([phenylphosphine]$_0$/[phenylphosphine]) versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (1 mol %), room temperature. $R^2 = 0.96255$.

Catalyst loading of 3 mol %:

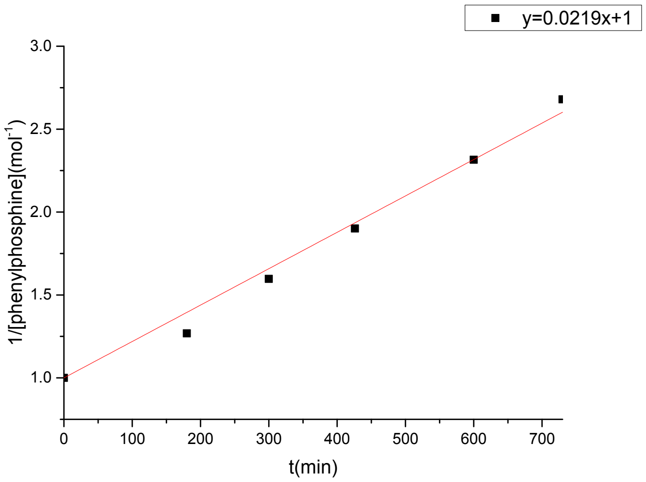


**Fig. S7** Plot of 1/[phenylphosphine] versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (3 mol %), room temperature. $R^2 = 0.99849$.

If the rate-order of $H_2PPh$ is first:

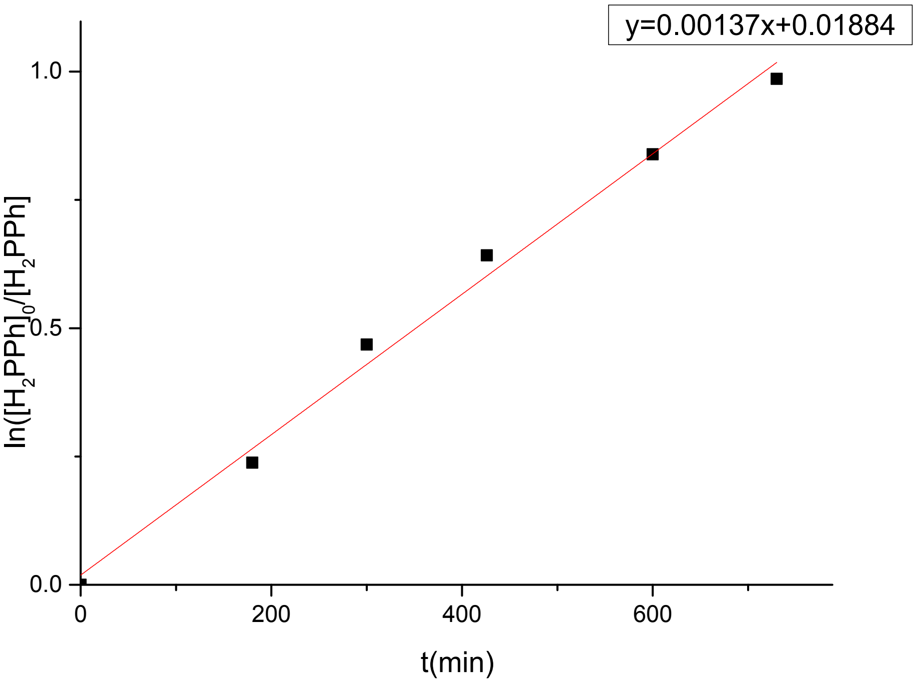


**Fig. S8** Plot of ln([phenylphosphine]$_0$/[phenylphosphine]) versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (3 mol %), room temperature. $R^2 = 0.9905$.

Catalyst loading of 5 mol %:

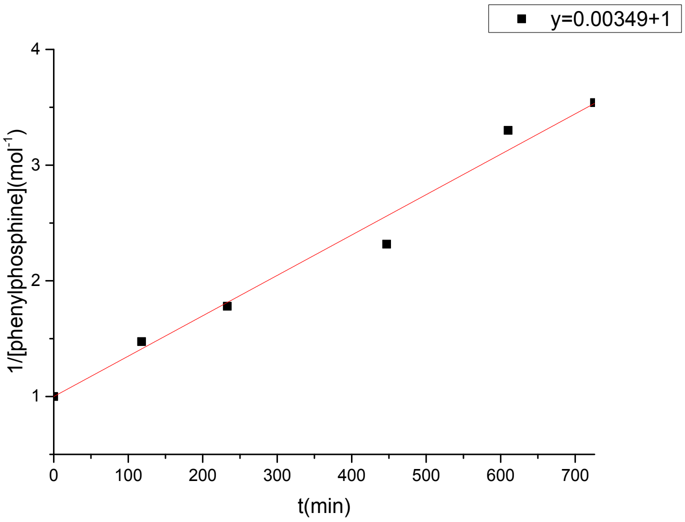


**Fig. S9** Plot of 1/[phenylphosphine] versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (5 mol %), room temperature. $R^2 = 0.99681$.

If the rate-order of $H_2PPh$ is first:

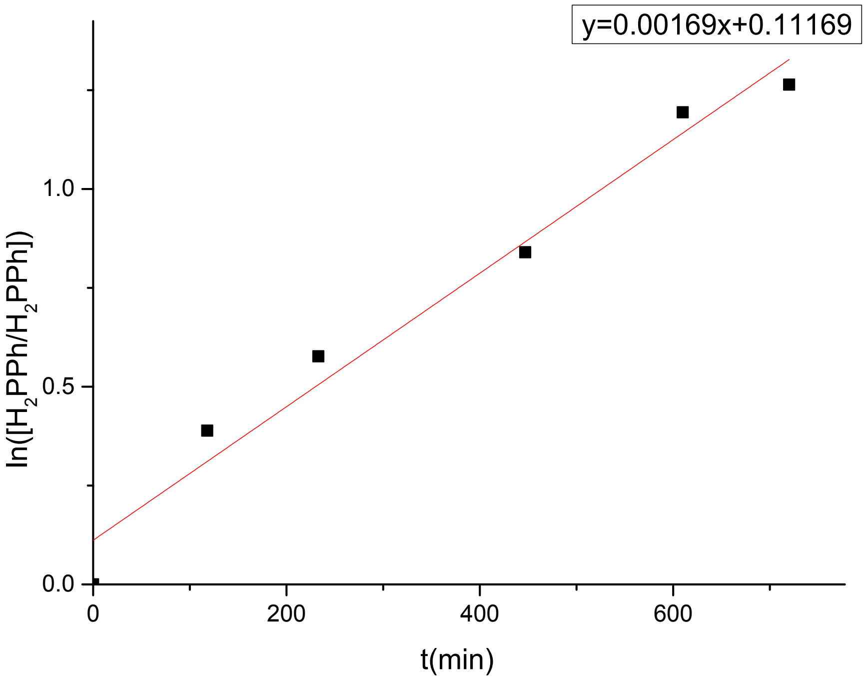


**Fig. S10** Plot of ln([phenylphosphine]$_0$/[phenylphosphine]) versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (5 mol %), room temperature. $R^2 = 0.96704$.

Catalyst loading of 7 mol %:

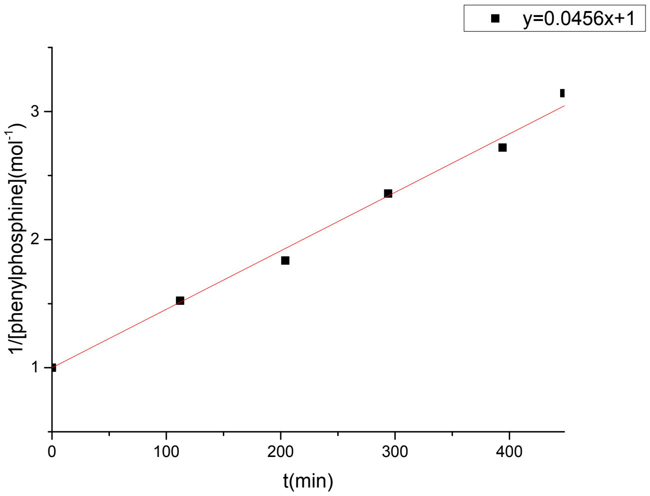


**Fig. S11** Plot of 1/[phenylphosphine] versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (7 mol %), room temperature. $R^2 = 0.99897$.

If the rate-order of $H_2PPh$ is first:

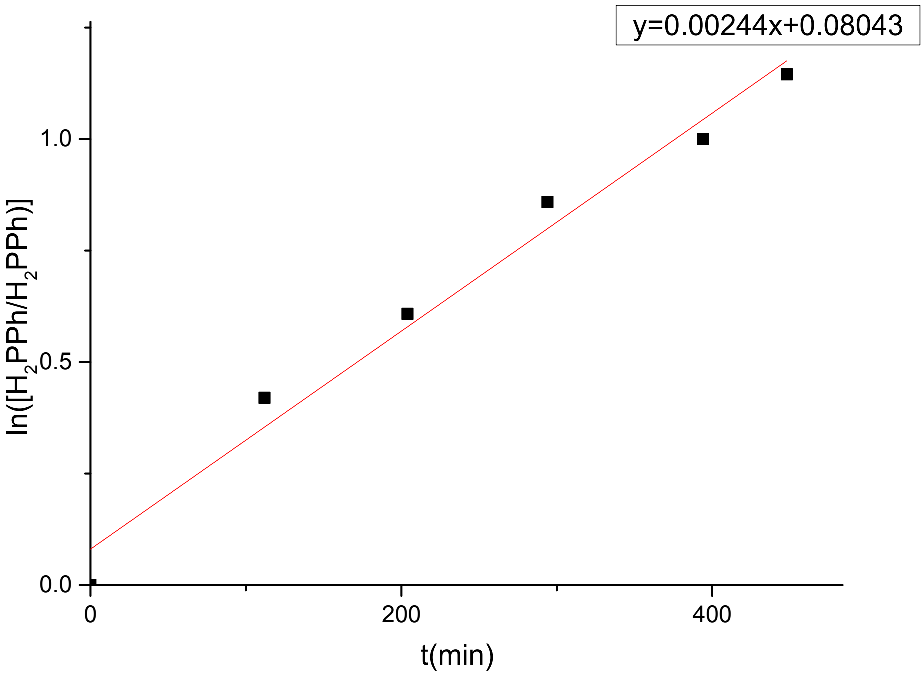


**Fig. S12** Plot of ln([phenylphosphine]$_0$/[phenylphosphine]) versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol), phenylphosphine (1 mmol), complex **1** (7 mol %), room temperature. $R^2 = 0.97499$.

As in the case of 10 mol% catalyst loading, the plots of 1st order and 2nd order dependence on $[H_2PPh]$ gave very similar $R^2$ values, half-life ($t_{1/2}$) study was conducted to further elucidate the rate order. Two parallel reactions were carried out with different initial concentration, and $t_{1/2}$ were determined.

It is assumed that the total volume of the mixture approximately equals to the initial volume of phenylphosphine plus the initial volume of styrene and did not change during the reaction. Thus, for the reaction plotted in Fig. 13, the initial concentration of phenylphosphine $[H_2PPh]_0$ = 1 mmol / (0.575 mL + 0.110 mL) = 1.46 mol/L, $t_{1/2}$ = 204 min. In Fig. S14, data are as follows: the initial concentration of phenylphosphine $[H_2PPh]_0$ = 1 mmol / (1.150 mL + 0.110 mL) = 0.79 mol/L, $t_{1/2}$ = 308 min. Therefore, the reaction order of phenylphosphine can be deduced as follows: $n = 1 + \ln(t_{1/2}/t'_{1/2})/\ln([H_2PPh]_0'/[H_2PPh]_0) = 1 + \ln(204/308)/\ln(0.79/1.46) = 1.7$.

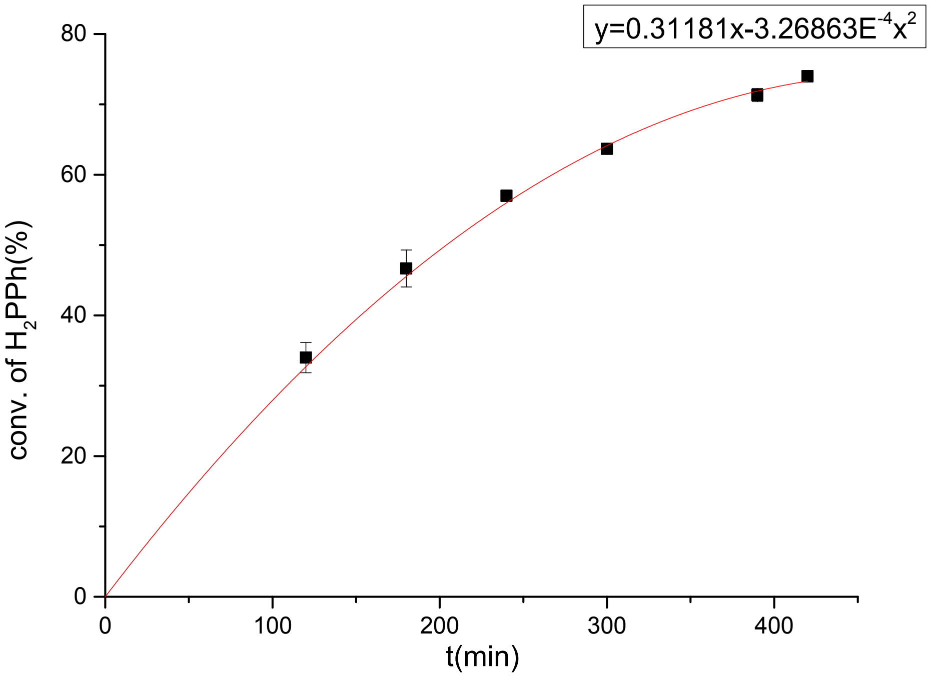


**Fig. S13** Plot of conversion of phenylphosphine versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol, 0.575 mL), phenylphosphine (1 mmol, 0.110 mL), complex **1** (10 mol %), room temperature. $R^2 = 0.99984$, $t_{1/2}$ = 204 min

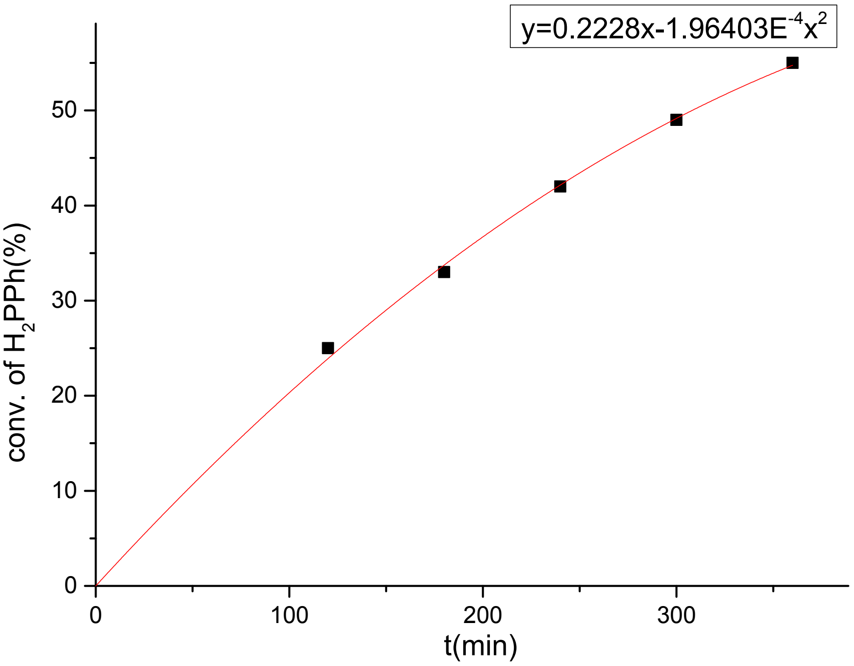


**Fig. S14** Plot of conversion of phenylphosphine versus time (min) for the hydrophosphination reaction of styrene (**5a**) and phenylphosphine (**6**) catalyzed by complex **1**. Conditions: styrene (5 mmol, 1.15 mL), phenylphosphine (1 mmol, 0.110 mL), complex **1** (10 mol %), room temperature. $R^2 = 0.99965$, $t_{1/2} = 308$ min

**Table S1. Experimental data of Fig. 3 (conversion of styrene)**

| t(min)<br>conv.<br>trial | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|
| 1 | 55 | 70 | 85 | 89 | 94 |
| 2 | 57 | 71 | 87 | 89 | 93 |
| 3 | 56 | 74 | 86 | 90 | 94 |

**Table S2. Experimental data of Fig. 4 (conversion of phenylphosphine)**

| t(min)<br>conv.<br>trial | 120 | 180 | 240 | 300 | 390 | 420 |
|---|---|---|---|---|---|---|
| 1 | 37 | 48 | 58 | 64 | 72 | 73 |
| 2 | 33 | 49 | 57 | 63 | 70 | 74 |
| 3 | 32 | 43 | 56 | 64 | 72 | 75 |

## X-Ray crystallographic structure determination

Suitable single crystal of complex **4** was sealed in a thin-walled glass capillary for determination the single-crystal structures. Intensity data were collected on an Agilent Xcalibur diffractometer equipped with MoKα radiation (graphite monochromated, λ = 0.71073 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data were given in Table S3.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

**Table S3. Crystallographic data of complex 4**

| compound | **4** |
|---|---|
| formula | $C_{50}H_{69}NO_2Zr$ |
| fw | 807.28 |
| Temp (K) | 223(2) |
| cryst syst | orthorhombic |
| color | colourless |
| cryst size(mm) | 0.50 × 0.30 × 0.20 mm |
| space group | P 21 21 21 |
| a (Å) | 11.1352 |
| b (Å) | 17.7158(8) |
| c (Å) | 23.1421(9) |
| α (deg) | 90 |
| β (deg) | 90 |
| γ (deg) | 90 |
| V ($Å_3$) | 4565.2(3) |
| Dcalcd (g $cm^{-3}$) | 1.175 |
| Z | 4 |
| radiation used | Mo Kα |
| μ ($mm^{-1}$) | 0.278 |
| F(000) | 1728 |
| $θ_{max}$ (deg) | 2.88-26.37 |
| final R indices (I > 2σ(I)) | $R_1$ =0.1054,<br>$wR_2$ =0.1765 |
| R indices (all data) | $R_1$ = 0.0677,<br>$wR_2$ = 0.1567 |
| goodness-of-fit on $F_2$ | 1.051 |
| Largest diff. peak, hole/e $Å^{-3}$ | 1.422, -1.032 |

# References:

1 a) K. J. Gallagher, M. Espinal-Viguri, M. F. Mahon, R. L. Webster, *Adv. Synth. Catal.* **2016**, *358*, 2460-2468; b) I. V. Basalov, B. Liu, T. Roisnel, A. V. Cherkasov, G. K. Fukin, J.-F. Carpentier, Y. Sarazin, A. A. Trifonov, *Organometallics* **2016**, *35*, 3261−3271; c) M. B. Ghebreab, C. A. Bange, R. Waterman, *J. Am. Chem. Soc.* **2014**, *136*, 9240−9243; d) C. A. Bange, R. Waterman, *ACS Catal.* **2016**, *6*, 6413−6416.