Supporting Information

Water-Enhanced Electrochemical Hydrogenolysis of Aryl C–O Bonds

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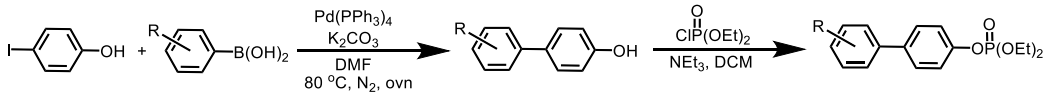
I. General Information

Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qindao Puke Co., China. All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using anhydrous solvents. Anhydrous solvents were purchased from Energy Chemicals Inc. and used as received. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were collected on a Bruker AV 300 MHz, 400 MHz, or 600 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: tetramethylsilane at 0 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm and DMSO-d_6 at 39.5 ppm). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz), and integration. High resolution mass spectra were recorded on a SCIEX X500R QTOF.

II. Synthesis of Substrate

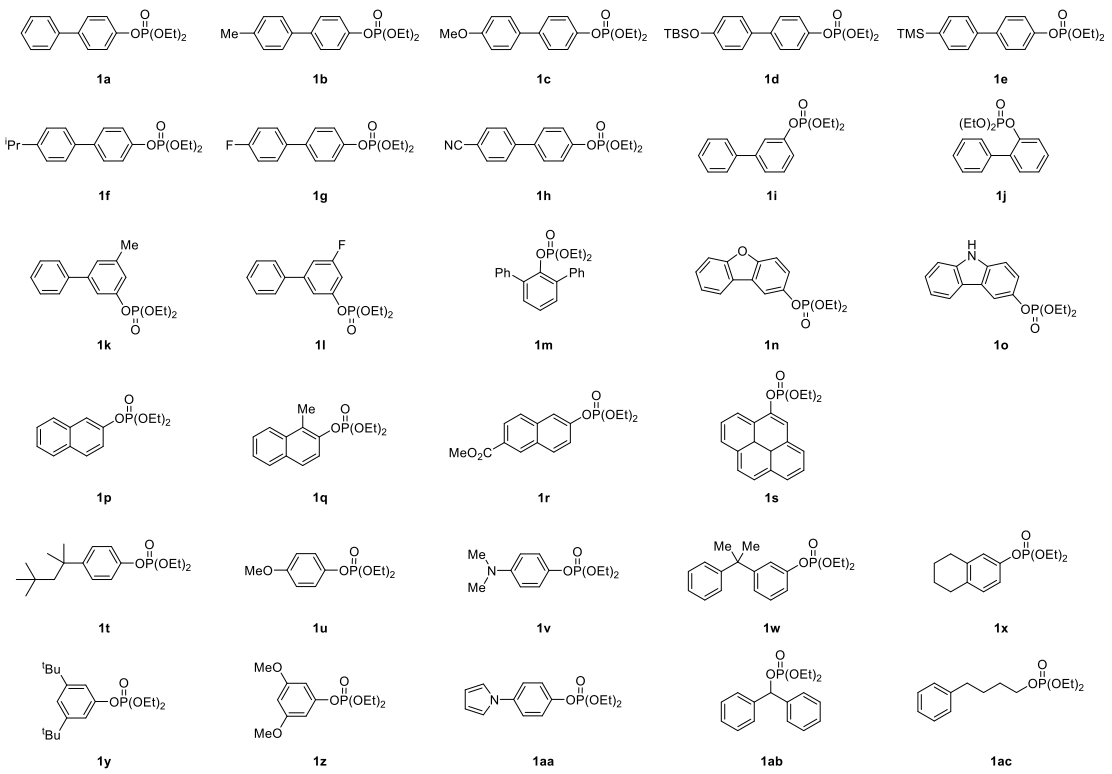
General procedure for the Synthesis of 1a-1l.



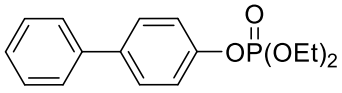
Known procedures were used for the preparation of **1a-l** with slight modification.[1] To a 200-mL Schlenk flask was added 4-iodophenol (10 mmol, 1.00 equiv), aryl boronic acid (15 mmol, 1.50 equiv), $Pd(PPh_3)_4$ (0.5 mmol, 5 mol%), and K_2CO_3 (30 mmol, 3.00 equiv). Then, the mixture was subjected to vacuum for 15 min and filled with Nitrogen gas, followed by injecting anhydrous DMF (50 mL) as solvent. The reaction mixture was stirred at 80 ˚C overnight and then poured into water. The aqueous phase was extracted with ethyl acetate (50 mL × 3) and the combined organic phases was washed with brine, dried over anhyfrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was subjected to silica gel flash chromatography to afford the phenol.

Under N_2 at 0 ˚C, to a solution of the above phenol in dichloromethane (20 mL) was added NEt_3 (3.00 equiv) and the solution was stired for 10 min. Then, diethyl phosphorochloridate (1.30 equiv) was added to the above solution dropwise and the reaction mixture was stirred overnight. The reaction mixture was poured into water and extracted by DCM three times. The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was subjected to silica gel flash chromatography to afford the phosphates with an overall yield range from 50-90%.

For substrate 1m-1ac, the corresponding phenols are commercially purchased, and the second step is same as above.



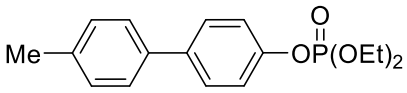
Characterization Data of Substrates



1a

[1,1'-Biphenyl]-4-yl diethyl phosphate (1a) was obtained as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 4H), 7.48 – 7.39 (m, 2H), 7.39 – 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 4.31 – 4.19 (m, 4H), 1.42 – 1.34 (m, 6H) ppm. The analytical data are in accordance with these reported in the literature.[2]



1b

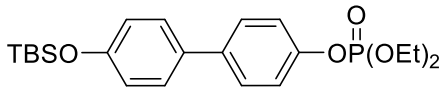
Diethyl (4'-methyl-[1,1'-biphenyl]-4-yl) phosphate (1b) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 4.29 – 4.18 (m, 4H), 2.39 (s, 3H), 1.37 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz), 138.0, 137.4, 137.1, 129.5, 128.1, 126.8, 120.2 (d, $^{3}J_{C\text{-}P}$ = 4.9 Hz), 64.6 (d, $^{2}J_{C\text{-}P}$= 6.1 Hz), 21.1, 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.2 ppm.

HR-MS (ESI) *m/z* calc. for $C_{17}H_{22}O_4P^+$ $[M+H]^+$ 321.1250, found 321.1246.



1d

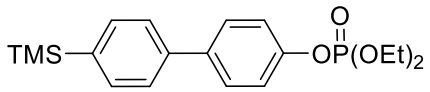
4'-((*tert*-Butyldimethylsilyl)oxy)-[1,1'-biphenyl]-4-yl diethyl phosphate (1d) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.44 – 7.34 (m, 2H), 7.29 – 7.17 (m, 2H), 6.93 – 6.81 (m, 2H), 4.32 – 4.13 (m, 4H), 1.41 – 1.29 (m, 6H), 1.00 (s, 9H), 0.22 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 149.7 (d, $^{2}J_{C\text{-}P}$ = 6.9 Hz), 137.8, 133.3, 128.0, 127.9, 120.4, 120.1 (d, $^{3}J_{C\text{-}P}$ = 4.8 Hz), 64.6 (d, $^{2}J_{C\text{-}P}$ = 6.1 Hz), 25.7, 18.2, 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.6 Hz), -4.4 ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.2 ppm.

HR-MS (ESI) *m/z* calc. For $C_{22}H_{34}O_5PSi^+$ $[M+H]^+$ 437.1908, found 437.1902.



1e

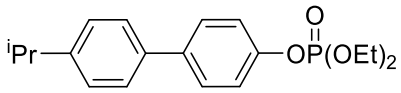
Diethyl (4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl) phosphate (1e) was obtained as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 6H), 7.33 – 7.26 (m, 2H), 4.32 – 4.17 (m, 4H), 1.44 – 1.31 (m, 6H), 0.30 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3 (d, $^2J_{C\text{-}P}$ = 6.9 Hz), 140.6, 139.3, 138.0, 133.8, 128.4, 126.3, 120.2 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 64.6 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 16.1 (d, $^3J_{C\text{-}P}$ = 6.6 Hz), -1.1 ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.2 ppm.

HR-MS (ESI) *m/z* calc. For $C_{19}H_{28}O_4PSi^+$ $[M+H]^+$ 379.1489, found 379.1484.



1f

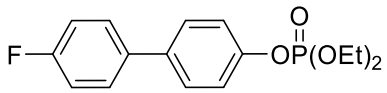
Diethyl (4'-isopropyl-[1,1'-biphenyl]-4-yl) phosphate (1f) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 14.1, 8.1 Hz, 4H), 4.29 – 4.18 (m, 4H), 3.06 – 2.83 (m, 1H), 1.48 – 1.32 (m, 6H), 1.28 (d, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0 (d, $^2J_{C\text{-}P}$ = 7.0 Hz), 148.0, 138.0, 137.7, 128.1, 126.9, 126.8, 120.1 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 64.6 (d, $^2J_{C\text{-}P}$ = 6.1 Hz) , 33.7, 23.9, 16.1 (d, $^3J_{C\text{-}P}$ = 6.5 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.2 ppm.

HR-MS (ESI) *m/z* calc. For $C_{19}H_{26}O_4P^+$ $[M+H]^+$ 349.1563, found 349.1560.



1g

Diethyl (4'-fluoro-[1,1'-biphenyl]-4-yl) phosphate (1g) was obtained as a colorless oil.

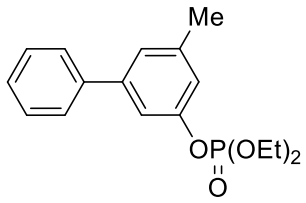
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 4H), 7.31 – 7.25 (m, 2H), 7.15 – 7.06 (m, 2H), 4.31 – 4.18 (m, 4H), 1.40 – 1.34 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 150.2 (d, $^2J_{C\text{-}P}$ = 6.9 Hz), 137.1, 136.4 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.6 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 128.3, 120.3 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 64.7 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 16.1 (d, $^3J_{C\text{-}P}$ = 6.6 Hz) ppm.

^{31}P NMR (121 MHz, $CDCl_3$) δ -6.2 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.6 ppm.

HR-MS (ESI) *m/z* calc. For $C_{16}H_{19}FO_4P^+$ $[M+H]^+$ 325.1000, found 325.0998.



1k

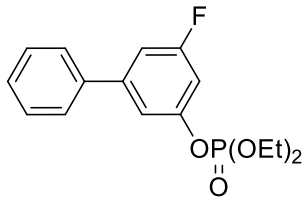
Diethyl (5-methyl-[1,1'-biphenyl]-3-yl) phosphate (1k) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.26 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 2.6 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.32 – 4.18 (m, 4H), 2.25 (s, 3H), 1.41 – 1.37 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.7 (d, $^2J_{C\text{-}P}$ = 6.7 Hz), 141.0, 138.8, 137.2, 130.9, 129.2, 128.1, 126.9, 121.4 (d, $^3J_{C\text{-}P}$ = 4.9 Hz), 117.1 (d, $^3J_{C\text{-}P}$ = 4.7 Hz), 64.5 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 20.6, 16.1 (d, $^3J_{C\text{-}P}$ = 6.6 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.1 ppm.

HR-MS (ESI) *m/z* calc. For $C_{17}H_{22}O_4P^+$ $[M+H]^+$ 321.1250, found 321.1248.



1l

Diethyl (5-fluoro-[1,1'-biphenyl]-3-yl) phosphate (1l) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9, 2.9 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.41 – 7.34 (m, 1H), 7.26 (s, 1H), 7.12 (d, *J* = 9.9 Hz, 1H), 7.01 – 6.91 (m, 1H), 4.29 – 4.20

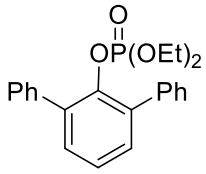
(m, 4H), 1.41 – 1.30 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) 163.2 (d, $^1J_{C-F}$ = 247.0 Hz), 151.8 (dd, $^3J_{C-F}$ = 12.0, $^2J_{C-P}$ =6.7 Hz), 144.3 (d, $^3J_{C-F}$ = 9.4 Hz), 139.0, 128.9, 128.3, 127.0, 114.5 (dd, $^3J_{C-P}$ = 5.4, $^4J_{C-F}$=3.1 Hz), 110.7 (d, $^2J_{C-F}$ = 22.0 Hz), 106.5 (dd, $^2J_{C-F}$ = 25.2, $^3J_{C-P}$=4.9 Hz), 64.8 (d, $^2J_{C-P}$ = 6.1 Hz), 16.1 (d, $^3J_{C-P}$ = 6.5 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.5 ppm

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.4 ppm.

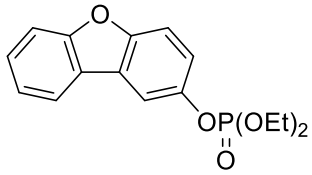
HR-MS (ESI) *m/z* calc. For $C_{16}H_{19}FO_4P^+$ $[M+H]^+$ 325.1000, found 325.0998.



1m

[1,1':3',1''-Terphenyl]-2'-yl diethyl phosphate (1m) was obtained as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$ δ 7.61 – 7.56 (m, 4H), 7.46 – 7.40 (m, 4H), 7.37 – 7.32 (m, 4H), 7.32 – 7.28 (m, 1H), 3.49 – 3.09 (m, 4H), 0.89 – 0.84 (m, 6H) ppm. The analytical data are in accordance with these reported in the literature.[3]



1n

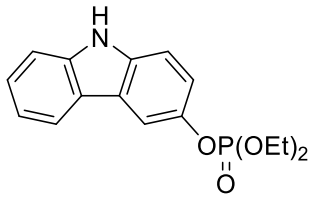
Dibenzo*[b,d]*furan-2-yl diethyl phosphate (1n) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.83 (dd, *J* = 2.6, 1.4 Hz, 1H), 7.62 – 7.40 (m, 3H), 7.40 – 7.28 (m, 2H), 4.33 – 4.13 (m, 4H), 1.37 (td, *J* = 7.1, 1.0 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 153.1, 146.4 (d, $^2J_{C-P}$ = 7.0 Hz), 127.7, 125.1, 124.0, 122.8, 120.9, 119.4 (d, $^3J_{C-P}$ = 4.9 Hz), 112.2, 112.0 (d, $^3J_{C-P}$ = 4.6 Hz), 111.8, 64.7 (d, $^2J_{C-P}$ = 6.1 Hz), 16.1 (d, $^3J_{C-P}$ = 6.7 Hz) ppm

^{31}P NMR (243 MHz, $CDCl_3$) δ -5.8 ppm.

HR-MS (ESI) *m/z* calc. For $C_{16}H_{18}O_5P^+$ $[M+H]^+$ 321.0886, found 321.0883.



1o

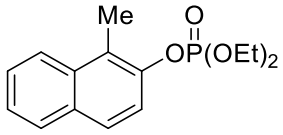
9*H*-Carbazol-3-yl diethyl phosphate (1o) was obtained as a yellow-brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.27 – 7.16 (m, 3H), 7.12 (dd, J = 7.7, 1.3 Hz, 1H), 4.35 – 4.21 (m, 4H), 1.38 – 1.27 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz), 141.4, 139.3, 126.0, 125.7, 122.7, 121.1, 119.5, 114.5 (d, $^{3}J_{C\text{-}P}$ = 8.3 Hz), 110.5, 109.1 (d, $^{3}J_{C\text{-}P}$ = 2.5 Hz), 107.4, 64.7 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz), 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.0 ppm.

HR-MS (ESI) *m/z* calc. For $C_{16}H_{19}NO_4P^+$ $[M+H]^+$ 321.1046, found 321.1048.



1q

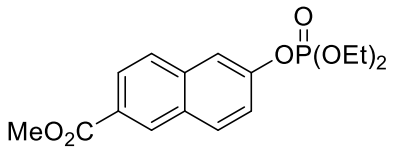
Diethyl (1-methylnaphthalen-2-yl) phosphate (1q) was obtained as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.5, 1.2 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.47 – 7.41 (m, 1H), 7.30 (d, J = 8.4 Hz, 1H), 4.28 – 4.12 (m, 4H), 2.55 (d, J = 1.7 Hz, 3H), 1.32 – 1.27 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.2 (d, $^{2}J_{C\text{-}P}$ = 8.7 Hz), 133.3, 129.1 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 127.5, 127.4 (d, $^{3}J_{C\text{-}P}$ = 2.7 Hz), 126.18, 126.16, 125.5, 125.1 (d, $^{3}J_{C\text{-}P}$ = 2.2 Hz), 122.2, 64.6 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz), 17.1, 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -5.4 ppm.

HR-MS (ESI) *m/z* calc. For $C_{15}H_{20}O_4P^+$ $[M+H]^+$ 295.1094, found 295.1098.



1r

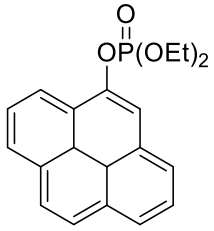
Methyl 6-((diethoxyphosphoryl)oxy)-2-naphthoate (1r) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 – 8.52 (m, 1H), 8.10 – 8.00 (m, 1H), 7.98 – 7.88 (m, 1H), 7.87 – 7.78 (m, 1H), 7.76 – 7.68 (m, 1H), 7.46 – 7.36 (m, 1H), 4.33 – 4.19 (m, 4H), 4.02 – 3.92 (m, 3H), 1.41 – 1.33 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 150.2 (d, $^2J_{C-P}$ = 6.6 Hz), 136.2, 131.4, 130.8, 129.9, 127.8, 127.1, 126.1, 120.9 (d, $^3J_{C-P}$ = 5.5 Hz), 116.3, 64.8 (d, $^2J_{C-P}$ = 6.1 Hz) , 52.2, 16.1 (d, $^3J_{C-P}$ = 6.6 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.4 ppm.

HR-MS (ESI) *m/z* calc. For $C_{16}H_{20}O_6P^+$ $[M+H]^+$ 339.0992, found 339.0991.



1s

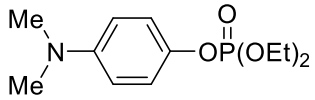
Diethyl pyren-1-yl phosphate (1s) was obtained as an orange oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.1 Hz, 1H), 8.16 – 8.12 (m, 2H), 8.11 – 8.08 (m, 2H), 8.06 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.99 – 7.96 (m, 3H), 4.36 – 4.22 (m, 4H), 1.37 – 1.31 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) 144.3 (d, $^2J_{C-P}$ = 7.4 Hz), 131.1, 131.0, 128.4, 127.8, 126.9, 126.7, 126.3, 125.6, 125.3, 125.1, 125.0, 124.4, 122.3 (d, $^3J_{C-P}$ = 6.7 Hz), 120.5, 117.3 (d, $^3J_{C-P}$= 2.6 Hz), 64.8 (d, $^2J_{C-P}$ = 6.0 Hz) 16.1 (d, $^3J_{C-P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -5.7 ppm.

HR-MS (ESI) *m/z* calc. For $C_{20}H_{20}O_4P^+$ $[M+H]^+$ 355.1094, found 355.1093.



1v

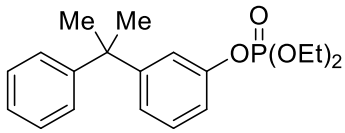
4-(Dimethylamino)phenyl diethyl phosphate (1v) was obtained as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 6.96 (m, 2H), 6.73 – 6.54 (m, 2H), 4.29 – 4.06 (m, 4H), 2.98 – 2.77 (m, 6H), 1.39 – 1.22 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 141.6 (d, J = 7.3 Hz) , 120.3 (d, $^2J_{C\text{-}P}$ = 4.5 Hz), 113.2, 64.2 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 40.8, 16.0 (d, $^2J_{C\text{-}P}$ = 6.1 Hz) ppm.

^{31}P NMR (121 MHz, $CDCl_3$) δ -5.5 ppm.

HR-MS (ESI) *m/z* calc. For $C_{12}H_{21}NO_4P^+$ $[M+H]^+$ 274.1203, found 274.1202.



1w

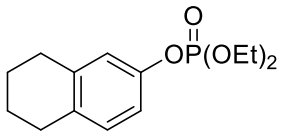
Diethyl (3-(2-phenylpropan-2-yl)phenyl) phosphate (1w) was obtained as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.23 – 7.19 (m, 2H), 7.19 – 7.15 (m, 3H), 7.12 – 7.07 (m, 2H), 4.26 – 4.15 (m, 4H), 1.66 (s, 6H), 1.37 – 1.32 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 148.6 (d, $^2J_{C\text{-}P}$ = 6.9 Hz), 148.5, 147.4, 128.04 (d, $^3J_{C\text{-}P}$ = 7.2 Hz), 127.99, 126.7, 125.7, 119.29, 119.26, 64.5 (d, $^2J_{C\text{-}P}$ = 6.1 Hz) , 42.6, 30.8, 16.0 (d, $^3J_{C\text{-}P}$ = 6.8 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.1 ppm.

HR-MS (ESI) *m/z* calc. For $C_{19}H_{26}O_4P^+$ $[M+H]^+$ 349.1563, found 349.1560.



1x

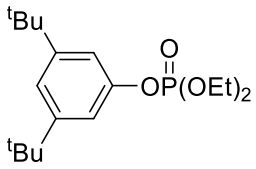
Diethyl (5,6,7,8-tetrahydronaphthalen-2-yl) phosphate (1x) was obtained as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 – 6.97 (m, 1H), 6.94 – 6.90 (m, 2H), 4.28 – 4.13 (m, 4H), 2.78 – 2.67 (m, 4H), 1.82 – 1.72 (m, 4H), 1.41 – 1.30 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3 (d, $^{2}J_{C\text{-}P}$ = 7.1 Hz), 138.6, 133.7, 130.0, 119.9 (d, $^{3}J_{C\text{-}P}$ = 4.9 Hz), 117.0 (d, $^{3}J_{C\text{-}P}$ = 4.8 Hz), 64.4 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz), 29.4, 28.7, 23.0, 22.8, 16.0 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.0 ppm.

HR-MS (ESI) *m/z* calc. For $C_{14}H_{22}O_4P^+$ $[M+H]^+$ 285.1250, found 285.1250.



1y

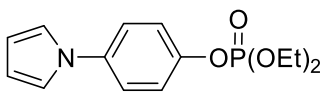
3,5-Di-*tert*-butylphenyl diethyl phosphate (1y) was obtained as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.04 (s, 2H), 4.28 – 4.16 (m, 4H), 1.38 – 1.33 (m, 6H), 1.31 (s, 18H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 150.4 (d, $^{2}J_{C\text{-}P}$ = 7.1 Hz), 118.8, 114.2 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz) , 64.4 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz), 34.9, 31.3, 16.1 (d, $^{3}J_{C\text{-}P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.3 ppm.

HR-MS (ESI) *m/z* calc. For $C_{18}H_{32}O_4P^+$ $[M+H]^+$ 343.2033, found 343.2031.



1aa

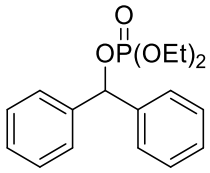
4-(1*H*-pyrrol-1-yl)phenyl diethyl phosphate (1aa) was obtained as brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 4H), 7.07 – 6.96 (m, 2H), 6.39 – 6.28 (m, 2H), 4.33 – 4.14 (m, 4H), 1.47 – 1.28 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3 (d, $^{2}J_{C-P}$ = 7.1 Hz), 137.8, 121.7, 121.0, 119.4 (d, $^{3}J_{C-P}$ = 4.9 Hz), 110.4, 64.7 (d, $^{2}J_{C-P}$ = 6.0 Hz), 16.0 (d, $^{3}J_{C-P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -6.1 pm.

HR-MS (ESI) *m/z* calc. For $C_{14}H_{19}NO_4P^+$ $[M+H]^+$ 296.1046, found 296.1050



1ab

Benzhydryl diethyl phosphate (1ab) was obtained as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.18 (m, 10H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.09 – 3.78 (m, 4H), 1.22 – 1.06 (m, 6H) ppm.

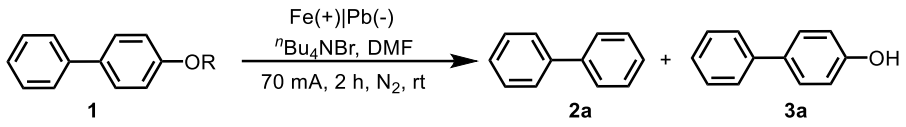
^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (d, $^{3}J_{C-P}$ = 5.0 Hz), 128.4, 128.0, 126.8, 80.8 (d, $^{2}J_{C-P}$ = 5.2 Hz), 63.6 (d, $^{2}J_{C-P}$ = 5.7 Hz), 15.8 (d, $^{3}J_{C-P}$ = 7.2 Hz) ppm.

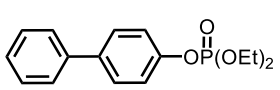
^{31}P NMR (121 MHz, $CDCl_3$) δ -1.6 ppm.

HR-MS (ESI) *m/z* calc. For $C_{19}H_{26}O_4P^+$ $[M+H]^+$ 349.1563, found 349.1560.

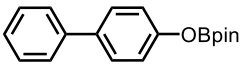
III. Optimization of Reaction Conditions

Table S1. Evaluation of different activating groups[a]

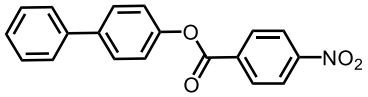




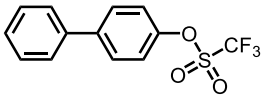
(**2a**:**3a**=64%:nd)



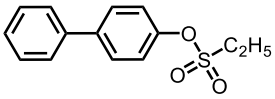
(**2a**:**3a**=nd: 76%)



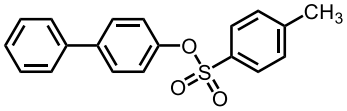
(**2a**:**3a**=nd:78%)



(**2a**:**3a**=2%:83%)



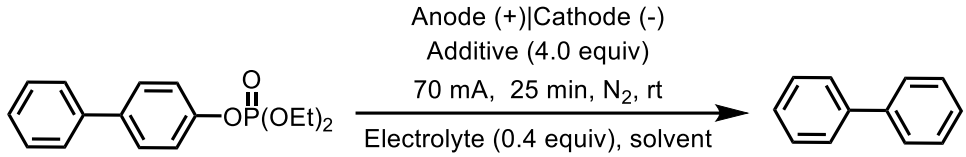
(**2a**:**3a**=nd:100%)



(**2a**:**3a**=nd:95%)

[a]Reaction Conditions: **1** (0.20 mmol), $^{n}Bu_4NBr$ (1.0 equiv, 0.20 mmol), Fe electrode (10 × 10 × 0.2 mm), Pb electrode (10 × 10 × 0.2 mm), DMF (4 mL), room temperature, 70 mA, 25 min (5 F mol^{-1}), yields were determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Table S2. Preliminary exploration of various parameters[a]



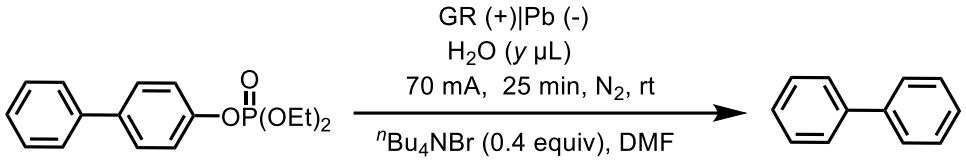
1a 2a

Entry	Electrodes	Electrolyte	Sacrificial Reductant	Solvent	Yield (%)
1	Mg(+)|GF(-)	$^{n}Bu_4NBr$	—	DMF	76
2	Pt(+)|GF(-)	$^{n}Bu_4NBr$	—	DMF	21
3	Pt(+)|GF(-)	$^{n}Bu_4NBr$	NEt_3	DMF	29
4	Pt(+)|GF(-)	$^{n}Bu_4NBr$	DABCO	DMF	18
5	Pt(+)|GF(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	32
6	Pt(+)|GF(-)	$^{n}Bu_4NBr$	DIPEA	DMF	26
7	Pt(+)|Pb(-)	$^{n}Bu_4NBr$	—	DMF	52
8	Pt(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	77
9	Pt(+)|Cu(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	57
10	Pt(+)|Zn(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	56
11	Pt(+)|Fe(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	50
12	Pt(+)|Al(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	32
13	Pt(+)|Sn(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	53
14	Pt(+)|Ti(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	48
15	GF(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	76
16	GR(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMF	80
17	GR(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMA	58
18	GR(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	NMP	41
19	GR(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	DMSO	76
20	GR(+)|Pb(-)	$^{n}Bu_4NBr$	$NHEt_2$	MeCN	37
21	GR(+)|Pb(-)	$^{n}Bu_4NI$	$NHEt_2$	DMF	55
22	GR(+)|Pb(-)	$^{n}Bu_4NOAc$	$NHEt_2$	DMF	61

23	GR(+)|Pb(-)	$^{n}Bu_4NBF_4$	$NHEt_2$	DMF	66
24	GR(+)|Pb(-)	$^{n}Bu_4NPF_6$	$NHEt_2$	DMF	69
25	GR(+)|Pb(-)	NaBr	$NHEt_2$	DMF	76
26	GR(+)|Pb(-)	KBr	$NHEt_2$	DMF	30
27	GR(+)|Pb(-)	KI	$NHEt_2$	DMF	43
28[b]	GR(+)|Pb(-)	$^{n}Bu_4NBr$	—	DMF	70

[a]Reaction Condition: [a] **1a** (0.20 mmol), electrolyte (0.40 equiv, 0.08 mmol), Sacrificial Reductant (4.00 eq, 0.80 mmol), Solvent (4 mL), room temperature, 5 F mol^{-1}, 70 mA, 25 min, all electrode posses the same length and width (10 × 10 mm), thickness (Pt, Mg, Pb, Zn, Cu, Sn, Al, Ti are 0.2 mm, GR is 0.5 mm, GF is 10 mm), yields were determined by ^1H NMR using CH_2Br_2 as internal standard. [b] H_2O (150 μL) as additive. GF, graphite felt; GR, graphite carbon plate.

Table S3. Evaluation of water equivalents[a]

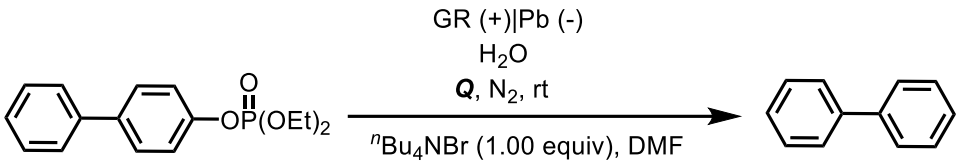


1a **2a**

Entry	H_2O (μL)	2a Yield (%)
1	75	67
2	150	70
3	225	86
4	300	90
5	375	77
6	750	76

[a]Reaction Condition: **1a** (0.20 mmol), ^{n}Bu$_4$NBr (0.40 equiv, 0.08 mmol), graphite carbon anode (10 × 10 × 0.5 mm), Pb electrode (10 × 10 × 0.2 mm), DMF (4 mL), room temperature, 70 mA, 25 min (5 F mol^{-1}), yields were determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Table S4. Evaluation of current and electricity amount[a]



1a **2a**

Entry	I/mA	t/min	2a Yield (%)
1	70	5	54
2	70	10	79
3	70	15	87
4	70	20	94
5	70	25	93
6	40	35	86
7	25	56	87
8	10	140	62

[a]Reaction Condition: **1a** (0.20 mmol), $^{n}Bu_4NBr$ (0.40 equiv, 0.08 mmol), graphite carbon anode (10 × 10 × 0.5 mm), Pb electrode (10 × 10 × 0.2 mm), H_2O (0.35 mL), DMF (4 mL), room temperature, yields were determined by ^1H NMR using CH_2Br_2 as internal standard.

IV. Electrochemical hydrogenolysis processes

General Procedure A (Standard Condition 1): Electrochemical hydrogenolysis of 1a-o.

The electrolysis was carried out in an undivided cell (10 mL) equipped with a graphite carbon plate anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (10 mm × 10 mm × 0.5 mm). $^{n}Bu_4NBr$ (129 mg, 0.40 mmol), biphenyl-based phosphates (0.40 mmol), DMF (4.0 mL) and H_2O (0.35 mL) were successively added. The electrolysis was performed at 70 mA and stirred at ambient temperature for 40-60 min (4.0–6.0 F mol^{-1}). Upon completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture was purified by silica gel column chromatography (eluent: *n*-hexane/DCM) to yield the desired product.

General Procedure B (Standard Condition 2): Electrochemical hydrogenolysis of 1p-s.

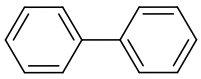
The electrolysis was carried out in an undivided cell (10 mL) equipped with a graphite carbon plate anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (20 mm × 10 mm × 0.5 mm). $^{n}Bu_4NBr$ (129 mg, 0.40 mmol), naphthyl-based phosphates (0.40 mmol), and DMF (4.0 mL) were successively added. The electrolysis was performed at 20 mA and stirred at 50 °C for 4 h (7.0 F mol^{-1}). Upon completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture was purified by silica gel column chromatography (eluent: *n*-hexane/DCM) to yield the desired product.

General Procedure C (Modified Condition): Electrochemical hydrogenolysis of 1t-

ac.

The electrolysis was carried out in an undivided cell (10 mL) equipped with a Fe anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (10 mm × 10mm × 0.5 mm). $^{n}Bu_4NBr$ (129 mg, 0.40 mmol), phosphates (0.40 mmol), and DMF (4.0 mL) were successively added. The electrolysis was performed at 20.0 mA and stirred at ambient temperature for 2 h (12 F mol^{-1}). After completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture was purified by silica gel column chromatography (eluent: *n*-hexane/DCM) to yield the desired product.

V. Characterization Data of Products

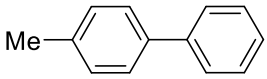


2a

1,1'-biphenyl (2a): The general procedure **A** was followed using [1,1'-Biphenyl]-4-yl diethyl phosphate (**1a**) (122.5 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2a** (52.4 mg, 85%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.47 – 7.41 (m, 4H), 7.37 – 7.32 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 128.7, 127.2, 127.1 ppm. The analytical data are in accordance with these reported in the literature.[4]

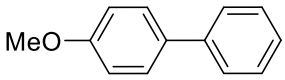


2b

4-methyl-1,1'-biphenyl (2b): The general procedure A was followed using diethyl (4'-methyl-[1,1'-biphenyl]-4-yl) phosphate (**1b**) (128.1 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (n-hexane/DCM): 20/1) yielded **2b** (51.7 mg, 77%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 7.34 – 7.29 (m, 1H), 7.26 – 7.22 (m, 2H), 2.39 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 138.3, 137.0, 129.5, 128.7, 126.97, 126.95, 126.94, 21.1 ppm. The analytical data are in accordance with these reported in the literature.[5]

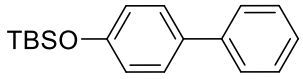


2c

4-methoxy-1,1'-biphenyl (2c): The general procedure **A** was followed using diethyl (4'-methoxy-[1,1'-biphenyl]-4-yl) phosphate (**1c**) (134.5 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2c** (52.3 mg, 71%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.45 – 7.38 (m, 2H), 7.33 – 7.27 (m, 1H), 7.01 – 6.94 (m, 2H), 3.85 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm. The analytical data are in accordance with these reported in the literature.[6]

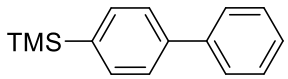


2d

([1,1'-Biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (2d): The general procedure **A** was followed using 4'-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-4-yl diethyl phosphate (**1d**) (174.6 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 10/1) yielded **2d** (76.3 mg, 67%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.31 – 7.26 (m, 1H), 6.90 (d, 2H), 1.00 (s, 9H), 0.23 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 140.9, 134.3, 128.7, 128.1, 126.7, 126.6, 120.3, 25.7, 18.2, -4.4 ppm. The analytical data are in accordance with these reported in the literature. [7]



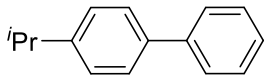
2e

[1,1'-Biphenyl]-4-yltrimethylsilane (2e): The general procedure **A** was followed using diethyl (4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl) phosphate (**1e**) (151.4 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2e** (58.9 mg, 65%) as a

white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 6H), 7.47 – 7.39 (m, 2H), 7.37 – 7.29 (m, 1H), 0.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 141.1, 139.2, 133.8, 128.7, 127.3, 127.2, 126.5, -1.1 ppm. The analytical data are in accordance with these reported in the literature.[8]

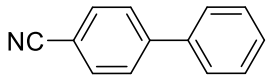


2f

4-Isopropyl-1,1'-biphenyl (2f): The general procedure **A** was followed using diethyl diethyl (4'-isopropyl-[1,1'-biphenyl]-4-yl) phosphate (**1f**) (139.4 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2f** (62.8 mg, 80%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 4H), 7.46 – 7.35 (m, 2H), 7.31 (dd, J = 7.9, 6.6 Hz, 3H), 3.03 – 2.86 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 141.1, 138.7, 128.7, 127.1, 127.0, 126.93, 126.82, 33.8, 24.0 ppm. The analytical data are in accordance with these reported in the literature.[9]

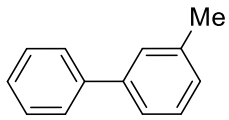


2h

[1,1'-Biphenyl]-4-carbonitrile (2h): The general procedure **A** was followed using 4'-cyano-[1,1'-biphenyl]-4-yl diethyl phosphate (**1h**) (132.5 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 10/1) yielded **2h** (37.3 mg, 52%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (q, J = 8.5 Hz, 4H), 7.63 – 7.55 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 139.1, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.8 ppm. The analytical data are in accordance with these reported in the literature.[10]

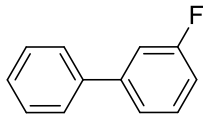


2k

3-Methyl-1,1'-biphenyl (2k): The general procedure **A** was followed using 4'-cyano-[1,1'-biphenyl]-4-yl diethyl phosphate (**1k**) (128.1 mg, 0.40 mmol) as substrate and electrolyzed for 1 h (6 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2k** (42.4 mg, 63%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.29 (m, 3H), 7.29 – 7.20 (m, 4H), 2.27 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4 ppm. The analytical data are in accordance with these reported in the literature.[11]



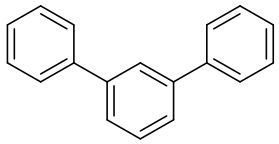
2l

3-fluoro-1,1'-biphenyl (2l): The general procedure **A** was followed using diethyl (5-fluoro-[1,1'-biphenyl]-3-yl) phosphate (**1l**) (129.7 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2l** (44.9 mg, 65%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.43 (dd, J = 8.4, 6.9 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.30 – 7.25 (m, 1H), 7.05 – 6.99 (m, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2 (d, $^{1}J_{C\text{-}F}$ = 245.6 Hz), 143.5 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 139.9 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 128.9, 127.8, 127.1, 122.7 (d, J = 2.7 Hz), 114.00 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 113.99 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz) ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.1 ppm. The analytical data are in accordance with these reported in the literature. [12]

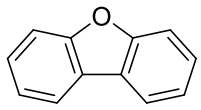


2m

1,1':3',1''-Terphenyl (2m): The general procedure **A** was followed using [1,1':3',1''-terphenyl]-2'-yl diethyl phosphate (**1m**) (153.0 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2m** (80.2 mg, 87%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.68 – 7.61 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.41 (m, 4H), 7.39 – 7.32 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.1, 129.2, 128.8, 127.4, 127.2, 126.1, 126.1 ppm. The analytical data are in accordance with these reported in the literature.[13]

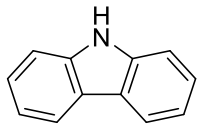


2n

Dibenzo[*b*,*d*]furan (2n): The general procedure **A** was followed using dibenzo[*b*,*d*]furan-2-yl diethyl phosphate (**1n**) (128.1 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2n** (39.8 mg, 59%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.6, 1.4 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.51 – 7.39 (m, 2H), 7.39 – 7.29 (m, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 127.2, 124.2, 122.7, 120.7, 111.7 ppm. The analytical data are in accordance with these reported in the literature.[14]



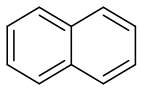
2o

9*H*-Carbazole (2o): The general procedure **A** was followed using 9*H*-carbazol-3-yl

diethyl phosphate (**1o**) (127.7 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 10/1) yielded **2o** (40.3 mg, 60%) as a yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.85 (dd, J = 7.8, 1.2 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.16 – 7.09 (m, 2H), 6.92 – 6.87 (m, 2H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6) δ 139.7, 125.5, 122.4, 120.1, 118.4, 110.9 ppm. The analytical data are in accordance with these reported in the literature. [15]

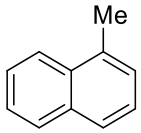


2p

Naphthalene (2p): The general procedure **B** was followed using diethyl naphthalen-1-yl phosphate (**1p**) (112.1 mg, 0.40 mmol) as substrate and electrolyzed for 4 h (7 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2p** (36.0 mg, 70%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 4H), 7.55 – 7.43 (m, 4H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.5, 127.9, 125.8 ppm. The analytical data are in accordance with these reported in the literature.[16]



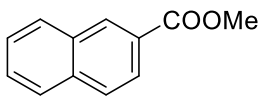
2q

1-Methylnaphthalene (2q): The general procedure **B** was followed using diethyl (1-methylnaphthalen-2-yl) phosphate (**1q**) (117.7 mg, 0.40 mmol) as substrate and electrolyzed for 4 h (7 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2q** (19.2 mg, 33%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.69 (m, 3H), 7.69 – 7.56 (m, 1H), 7.55 – 7.37 (m, 2H), 7.37 – 7.27 (m, 1H), 2.63 – 2.46 (m, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 133.7, 131.7, 128.1, 127.7, 127.6, 127.2, 126.8,

125.8, 124.9, 21.7 ppm. The analytical data are in accordance with these reported in the literature.[17]

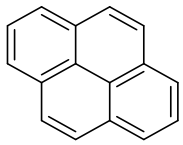


2r

Methyl 2-naphthoate (2r): The general procedure **B** was followed using methyl 6-((diethoxyphosphoryl)oxy)-2-naphthoate (**1r**) (117.7 mg, 0.40 mmol) as substrate and electrolyzed for 4 h (7 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 20/1) yielded **2r** (23.1 mg, 31%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (t, *J* = 1.2 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.92 – 7.85 (m, 2H), 7.64 – 7.51 (m, 2H), 3.99 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.26, 135.51, 132.49, 131.05, 129.34, 128.21, 128.13, 127.74, 127.39, 126.62, 125.21, 52.2 ppm. The analytical data are in accordance with these reported in the literature.[18]

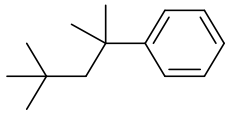


2s

Pyrene (2s): The general procedure **B** was followed using diethyl pyren-1-yl phosphate (**1s**) (141.7 mg, 0.40 mmol) as substrate and electrolyzed for 4 h (7 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2s** (40.2 mg, 50%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 4H), 8.05 (s, 4H), 7.98 (dd, *J* = 8.1, 7.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1, 127.4, 125.8, 124.9, 124.6 ppm. The analytical data are in accordance with these reported in the literature.[19]

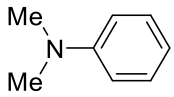


2t

(2,4,4-Trimethylpentan-2-yl)benzene (2t): The general procedure **C** was followed using diethyl (4-(2,4,4-trimethylpentan-2-yl)phenyl) phosphate (**1t**) (137 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2t** (49.2 mg, 64%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.18 – 7.11 (m, 1H), 1.74 (s, 2H), 1.37 (s, 6H), 0.71 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 127.7, 126.1, 125.2, 57.0, 38.5, 32.3, 31.7, 31.5 ppm. The analytical data are in accordance with these reported in the literature.[20]

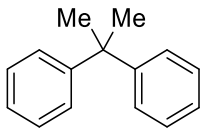


2v

***N, N*-Dimethylaniline (2v)**: The general procedure **C** was followed using 4-(dimethylamino)phenyl diethyl phosphate (**1v**) (109.3 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 10/1) yielded **2v** (35.2 mg, 72%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 2H), 6.80 – 6.66 (m, 3H), 2.93 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 129.0, 116.6, 112.6, 40.6 ppm. The analytical data are in accordance with these reported in the literature.[21]



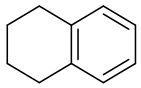
2w

Propane-2,2-diyldibenzene (2w): The general procedure **C** was followed using diethyl (3-(2-phenylpropan-2-yl)phenyl) phosphate (**1w**) (139.4 mg, 0.40 mmol) as substrate

and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2w** (56.1 mg, 71%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.02 (m, 10H), 1.68 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 128.0, 126.8, 125.6, 42.9, 30.7 ppm. The analytical data are in accordance with these reported in the literature.[22]

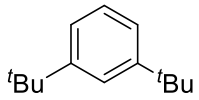


2x

1,2,3,4-Tetrahydronaphthalene (2x): The general procedure **C** was followed using diethyl (5,6,7,8-tetrahydronaphthalen-2-yl) phosphate (**1x**) (113.7 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2x** (37.5 mg, 71%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.00 (m, 4H), 2.82 – 2.72 (m, 4H), 1.88 – 1.74 (m, 4H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 129.1, 125.4, 29.4, 23.2 ppm. The analytical data are in accordance with these reported in the literature.[23]

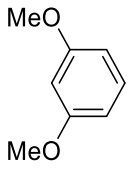


2y

1,3-Di-tert-butylbenzene (2y): The general procedure **C** was followed using diethyl 3,5-di-*tert*-butylphenyl diethyl phosphate (**1y**) (137.0 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/DCM: 20/1) yielded **2y** (46.1 mg, 60%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.28 – 7.17 (m, 3H), 1.33 (s, 18H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 127.7, 122.4, 122.3, 34.9, 31.6 ppm. The analytical data are in accordance with these reported in the literature.[24]

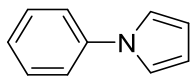


2z

1,3-Dimethoxybenzene (2z): The general procedure **C** was followed using 3,5-dimethoxyphenyl diethyl phosphate (**1z**) (116.1 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 10/1) yielded **2z** (39.2 mg, 71%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 1H), 6.51 (dd, *J* = 8.2, 2.4 Hz, 2H), 6.48 – 6.45 (m, 1H), 3.79 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 129.9, 106.1, 100.5, 55.2 ppm. The analytical data are in accordance with these reported in the literature.[25]

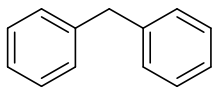


2aa

1-Phenyl-1*H*-pyrrole (2aa): The general procedure **C** was followed using 1-phenyl-1*H*-pyrrole (**1aa**) (118.1 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 10/1) yielded **2aa** (33.2 mg, 58%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 4H), 7.27 – 7.21 (m, 1H), 7.14 – 7.06 (m, 2H), 6.39 – 6.31 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 129.5, 125.6, 120.5, 119.3, 110.4 ppm. The analytical data are in accordance with these reported in the literature.[26]



2ab

Diphenylmethane (2ab): The general procedure **C** was followed using benzhydryl diethyl phosphate (**1ab**) (128.1 mg, 0.40 mmol) as substrate and electrolyzed for 2 h

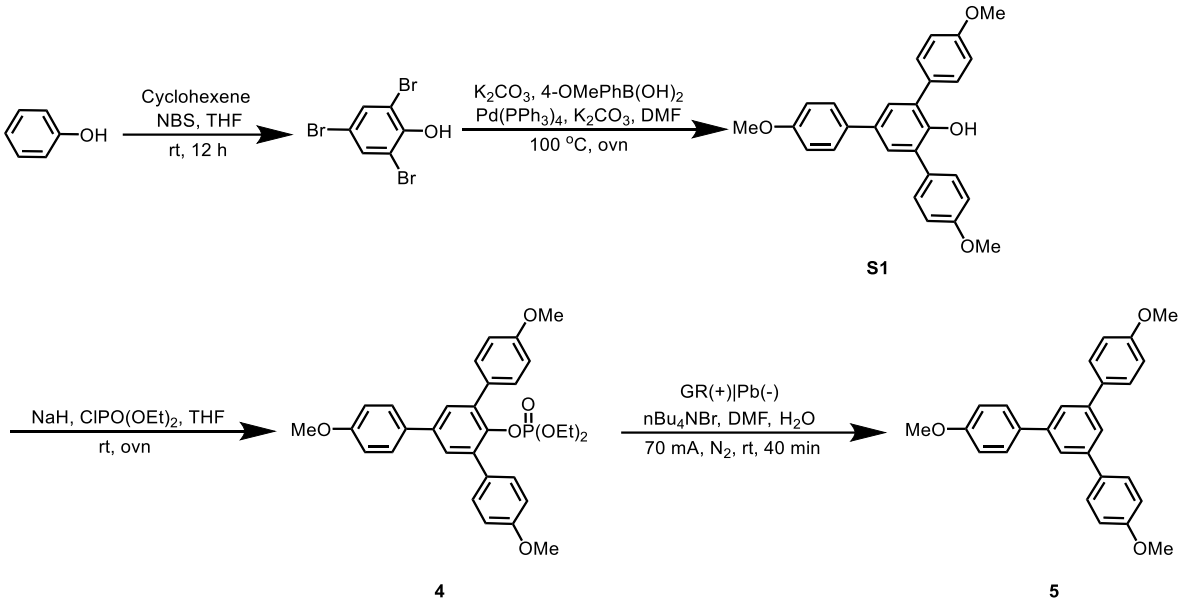
(12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EA: 10/1) yielded **2ab** (40.6 mg, 60%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 4H), 7.18 (d, *J* = 7.7 Hz, 6H), 3.97 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 128.9, 128.4, 126.0, 41.9 ppm. The analytical data are in accordance with these reported in the literature.[27]

VI. Applications and Derivatizations

Application 1: Synthesis of 5



Tribromophenol was synthesized according to the literature procedure[28], followed by the cross-coupling reaction same as the first step of preparation of **1a**. **S1** was obtained by silica gel column chromatography (eluent: n-hexane/EtOAc=10:1 to 5:1). Under N_2 at 0 °C, to the suspended solution of NaH (300 mg, 7.5 mmol, 1.50 equiv, 60 wt% in paraffin) in THF (10 mL) was added **S1** solution (2.1 g, 5 mmol, 0.3 M in THF) dropwise. After stirring for 30 min, diethyl phosphorochloridate (1.12 g, 1.30 equiv) was added to the above solution dropwise. The suspension was stirred at room temperature overnight. Upon completion, the reaction mixture was poured into water and extracted by EtOAc (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was subjected to silica gel flash chromatography to afford **4** (2.3 g, 85% yield) as a viscous liquid.

4,4''-Dimethoxy-5'-(4-methoxyphenyl)-[1,1':3',1''-terphenyl]-4'-yl diethyl phosphate (4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 6H), 7.45 (s, 2H), 7.02 – 6.93 (m, 6H), 3.85 (s, 6H), 3.84 (s, 3H), 3.61 – 3.47 (m, 2H), 3.32 – 3.19 (m, 2H), 0.96 – 0.89 (m, 6H)

ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 159.0, 144.2 (d, $^2J_{C-P}$ = 8.3 Hz), 144.1, 138.1, 135.5 (d, $^3J_{C-P}$ = 3.3 Hz), 132.7, 131.0, 128.4 (d, $^3J_{C-P}$ = 2.1 Hz), 128.1, 114.2, 113.6, 63.3 (d, $^2J_{C-P}$ = 5.8 Hz), 55.3, 15.8 (d, $^3J_{C-P}$ = 7.7 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.7 ppm.

HR-MS (ESI) *m/z* calc. For $C_{31}H_{34}O_7P^+$ $[M+H]^+$ 549.2037, found 549.2034.

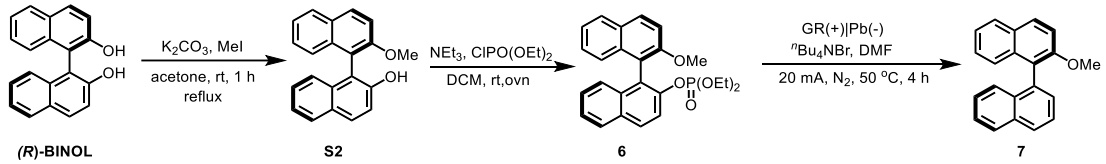
Electrochemical hydrogenolysis of 4 to prepare 5:

4,4''-Dimethoxy-5'-(4-methoxyphenyl)-1,1':3',1''-terphenyl (5): The general procedure **A** was followed using 4,4''-Dimethoxy-5'-(4-methoxyphenyl)-[1,1':3',1''-terphenyl]-4'-yl diethyl phosphate (**4**) (219.4 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **5** (136.4 mg, 86%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 3H), 7.63 – 7.57 (m, 6H), 7.02 – 6.94 (m, 6H), 3.83 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 141.8, 133.8, 128.3, 123.8, 114.2, 55.3 ppm. The analytical data are in accordance with these reported in the literature.[29]

Application 2: preparation of 7.



S2 was synthesized according to a literature procedure.[30] Under N_2 atmosphere, to a 100-mL oven-dried rould bottom flask was successively added (*R*)-BINOL (2.86 g, 10 mmol, 1.00 equiv), K_2CO_3 (1.66 g, 12.0 mmol, 1.20 equiv) and acetone (20 mL). Then, MeI (1.42 g, 10 mmol, 1.00 equiv) was added dropwise to the mixture. The mixture was stirred for 1 h at room temperature, and refluxed until complete conversion of (*R*)-BINOL (TLC monitor). The reaction was cooled to room temperature and filtered and concentrated. The crude product was purified via column chromatography, yielding **S2** as a white solid (2.6 g, 85% yield). Compound **6** was prepared following the same

procedure as preparation of **1a** (3.4 g, 92% yield).

Diethyl (2'-methoxy-[1,1'-binaphthalen]-2-yl) phosphate (6)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 9.2, 4.1 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.34 – 7.21 (m, 4H), 7.15 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 3H), 3.71 – 3.57 (m, 2H), 3.56 – 3.46 (m, 2H), 1.05 – 0.98 (m, 3H), 0.90 – 0.83 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.03, 146.5 (d, $^2J_{C-P}$ = 6.6 Hz), 133.8 (d, $^4J_{C-P}$ = 2.8 Hz), 131.0, 129.8, 129.5, 128.9, 128.0, 127.7, 126.6 (d, $^3J_{C-P}$ = 5.6 Hz), 126.5, 125.9, 125.4, 125.1, 123.6, 123.21 (d, $^3J_{C-P}$ = 8.0 Hz), 123.16, 119.4, 117.9, 113.6, 64.11 (d, $^2J_{C-P}$ = 6.6 Hz), 64.0 (d, $^2J_{C-P}$ = 6.5 Hz), 56.6, 15.70 (d, $^3J_{C-P}$ = 6.8 Hz), 15.55 (d, $^3J_{C-P}$ = 6.7 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -7.3 ppm.

HR-MS (ESI) *m/z* calc. For $C_{25}H_{26}O_5P^+$ $[M+H]^+$ 437.1512, found 437.1504.

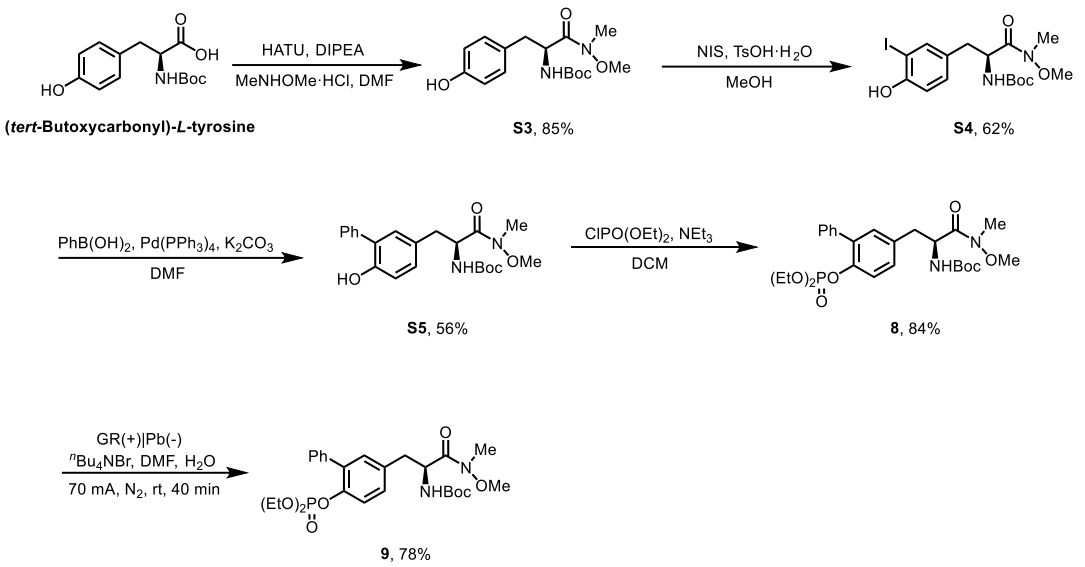
Electrochemical hydrogenolysis of 6 to prepare 7:

2-Methoxy-1,1'-binaphthalene (7). The general procedure **B** was followed using diethyl (2'-methoxy-[1,1'-binaphthalen]-2-yl) phosphate (**6**) (174.6 mg, 0.40 mmol) as substrate and electrolyzed for 4 h (7 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1) yielded **7** (86.7 mg, 76%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 3H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.47 – 7.39 (m, 3H), 7.35 – 7.27 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 134.5, 134.2, 133.7, 132.9, 129.4, 129.0, 128.4, 128.2, 127.8, 127.7, 126.4, 126.2, 125.8, 125.7, 125.54, 125.47, 123.5, 123.2, 113.8, 56.7 ppm. The analytical data are in accordance with these reported in the literature.[31]

Application 3: preparation of unnatural amino acid 9.



(*tert*-Butoxycarbonyl)-*L*-tyrosine

S3, 85%

S4, 62%

S5, 56%

8, 84%

9, 78%

To a 250-mL oven-dried round-bottom flask was successively added (*tert*-Butoxycarbonyl)-*L*-tyrosine (5.6 g, 20 mmol, 1.00 equiv), MeNHOMe·HCl (3.9 g, 40 mmol, 2.00 equiv), DMF (50 mL) and DIPEA (10.6 mL, 60 mmol, 3.00 equiv). After stiring for 10 min, HATU (10.4 g, 30 mmol, 1.50 eqiuiv) was added. The reaction was monitored by TLC until complete conversion of starting material. The reaction mixture was poured into water (200 mL) and extracted with EA (30 mL × 3). The combined organic phase was dried with Na_2SO_4, filtered and concentrated. Upon addition of EtOAc/Hexane (20/1) to the crude product, a precipitation was formed and filtered. The obtained solid **S3** (5.5 g, 85% yield) was pure enough for the next step.

To a solution of **S3** in MeOH (170 mL, 0.1 M) was added TsOH·H_2O (0.32 g, 10 mol%). Then, NIS (3.8 g, 17 mmol, 1.00 equiv) in MeOH (170 mL, 0.1 M) was added slowly in 1 h using micro-injection pump. The reaction was stirred for 10 min before quenched by 1 M $Na_2S_2O_3$ aqueous solution. The reaction solution was concentrated in *vacuo* and the crude product was purified via column chromatography (eluent: EtOAc/hexane=1/2 to EtOAc/DCM=1/10) to provide **S4** as a white solid (4.73 g, 10.5 mmol, 62% yield).

***tert*-Butyl(*S*)-(3-(4-hydroxy-3-iodophenyl)-1-(methoxy(methyl)amino)-1-oxopropan-2-yl)carbamate (S4):**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.36 (m, 2H), 7.02 – 6.92 (m, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 5.35 (d, *J* = 9.2 Hz, 1H), 4.88 (q, *J* = 7.4 Hz, 1H), 3.72 (s, 3H), 3.20 (s, 3H), 3.00 – 2.91 (m, 1H), 2.82 – 2.72 (m, 1H), 1.41 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 155.3, 154.5, 139.3, 130.6, 129.7, 114.9, 84.3, 80.0, 61.7, 51.5, 37.2, 32.1, 28.2 ppm.

HR-MS (ESI) *m/z* calc. For $C_{16}H_{24}IN_2O_5^+$ $[M+H]^+$ 451.0724, found 451.0729.

Under Nitrogen atmosphere, **S4** (4.73 g, 10.5 mmol), K_2CO_3 (4.4 g, 31.5 mmol), $PhB(OH)_2$ (1.7 g, 14 mmol), $Pd(PPh_3)_4$ (0.6 g 5 mol%) and DMF (40 mL) were added to a round-bottom flask. The suspension was vacuumized and filled with nitrogen for three times. Then, the mixture was stirred overnight at 100 ºC. The mixture was extracted with EtOAc (50 mL×3) and the combined organic phase was washed by brine (50 mL×3). The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel flash chromatography (eluent: EtOAc/Hexane=1:5 to 1:2) to get **S5** as a colorless solid (2.35 g, 5.88 mmol, 56% yield).

***tert*-Butyl(*S*)-(3-(6-hydroxy-[1,1'-biphenyl]-3-yl)-1-(methoxy(methyl)amino)-1-oxopropan-2-yl) carbamate(S5)**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 7.04 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.88 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.30 (d, *J* = 9.1 Hz, 1H), 4.99 – 4.83 (m, 1H), 3.61 (s, 3H), 3.15 (s, 3H), 3.00 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.82 (dd, *J* = 13.9, 7.2 Hz, 1H), 1.38 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 155.3, 152.0, 137.8, 131.4, 130.2, 129.5, 129.1, 128.4, 127.94, 127.0, 115.9, 79.7, 61.4, 51.6, 37.6, 32.0, 28.2 ppm.

HR-MS (ESI) *m/z* calc. For $C_{22}H_{29}N_2O_5^+$ $[M+H]^+$ 401.2071, found 401.2066.

The phenol **S5** (2.35 g, 5.88 mmol) was transformed into phosphate **8** following the same procedure as preparation of **1a** (2.65 g, 84%).

***tert*-Butyl(*S*)-(3-(6-((diethoxyphosphoryl)oxy)-[1,1'-biphenyl]-3-yl)-1-(methoxy(methyl)amino)-1-oxopropan-2-yl)carbamate (8)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.44 – 7.32 (m, 4H), 7.22 – 7.10 (m, 2H), 5.22 (d, *J* = 9.2 Hz, 1H), 5.03 – 4.90 (m, 1H), 4.04 – 3.83 (m, 4H), 3.70 (s, 3H), 3.18 (s, 3H), 3.08 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.91 (dd, *J* = 13.9, 7.2 Hz, 1H), 1.40

(s, 9H), 1.22 – 1.17 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 155.1, 146.5 (d, $^2J_{C-P}$ = 6.9 Hz), 137.4, 133.5, 133.3 (d, $^3J_{C-P}$ = 18.8 Hz), 132.2, 129.6, 129.5, 128.0, 127.3, 120.3, 80.0, 64.3 (d, $^2J_{C-P}$ = 6.2 Hz), 61.6, 51.4, 38.0, 32.1, 28.3, 15.9 (d, $^3J_{C-P}$ = 6.9 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.9 ppm.

HR-MS (ESI) *m/z* calc. For $C_{26}H_{38}N_2O_8P^+$ $[M+H]^+$ 537.2360, found 537.2351.

Electrochemical hydrogenolysis of 8 to prepare 9:

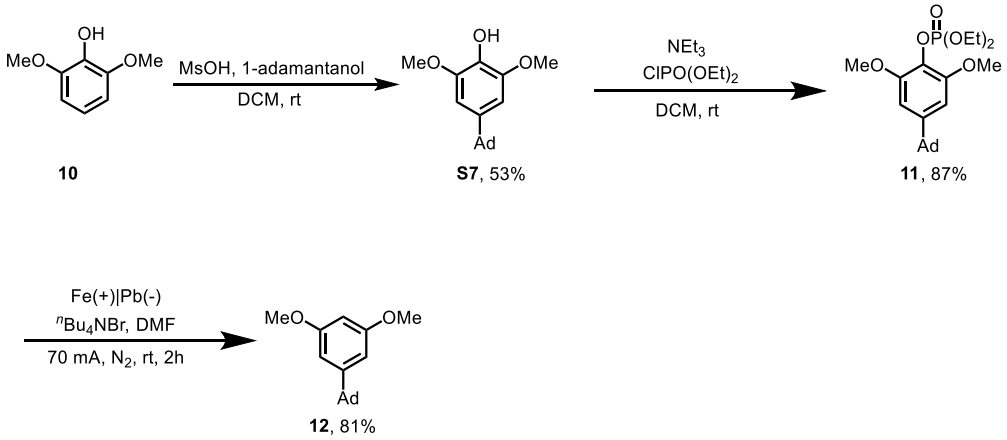
***tert*-butyl (*S*)-(3-([1,1'-biphenyl]-3-yl)-1-(methylamino)-1-oxopropan-2-yl)carbamate (9).** The general procedure **A** was followed using *tert*-Butyl(*S*)-(3-(6-((diethoxyphosphoryl)oxy)-[1,1'-biphenyl]-3-yl)-1-(methoxy(methyl)amino)-1-oxopropan-2-yl)carbamate (**8**) (214.6 mg, 0.40 mmol) as substrate and electrolyzed for 40 min (4 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1 to 5/1) yielded **9** (113.6 mg, 78%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.51 – 7.30 (m, 6H), 7.18 (d, *J* = 7.5 Hz, 1H), 5.75 (s, 1H), 5.05 (s, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 7.1 Hz, 2H), 2.74 (d, *J* = 4.9 Hz, 3H), 1.39 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 155.5, 141.4, 140.8, 137.3, 129.0, 128.7, 128.1, 128.1, 127.3, 127.1, 125.6, 80.1, 55.9, 38.8, 28.2, 26.1 ppm.

HR-MS (ESI) *m/z* calc. For $C_{21}H_{27}O_3N_2^+$ $[M+H]^+$ 355.2016, found 355.2015.

Application 4: preparation of 12



10 **S7**, 53% **11**, 87%

12, 81%

Compound **S7** was prepared according to previous reference.[32] 1-Adamantanaol (3.35 g, 22 mmol, 1.10 equiv) was dissolved in methanesulfonic acid (15 mL). Subsequently, a 20 mL DCM solution of **10** (20 mmol, 1.00 equiv) was slowly added over 1 h and the reaction was stirred at room temperature overnight. Upon completion, the reaction was diluted with 40 mL of DCM, stirred for another 10 minutes, and poured into ice-water. The organic layer was separated and the aqueous phase was extracted with DCM (50 mL × 3). The combined organic phase was washed with saturated $NaHCO_3$ three times. Next the organic phase was concentrated under vacuum and redissolved in EA. The organic solution was extracted with NaOH solution (2 M). Then, aqueous phase was neutralized by 2 M HCl and re-extracted by EtOAc. The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The pure **S7** was obtained without further purification for the next step (2.9 g, 53% yield).

Compound **11** was obtained from **S7** using the same procedure as preparation of **1a**.

4-((3r,5r,7r)-Adamantan-1-yl)-2,6-dimethoxyphenyl diethyl phosphate (11)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.35 – 4.26 (m, 4H), 3.86 (s, 6H), 2.12 – 2.06 (m, 3H), 1.87 (d, J = 2.9 Hz, 6H), 1.83 – 1.70 (m, 6H), 1.43 – 1.35 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3 (d, $^3J_{C\text{-}P}$ = 3.4 Hz), 148.7 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 127.5 (d, $^2J_{C\text{-}P}$ = 7.8 Hz), 102.2, 64.14 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 56.08, 43.25, 36.71, 36.48, 28.92, 16.08 (d, $^3J_{C\text{-}P}$ = 7.4 Hz) ppm.

^{31}P NMR (243 MHz, $CDCl_3$) δ -5.3 ppm.

HR-MS (ESI) *m/z* calc. For $C_{22}H_{34}O_6P^+$ $[M+H]^+$ 425.2088, found 425.2083.

Electrochemical hydrogenolysis of 11 to prepare 12:

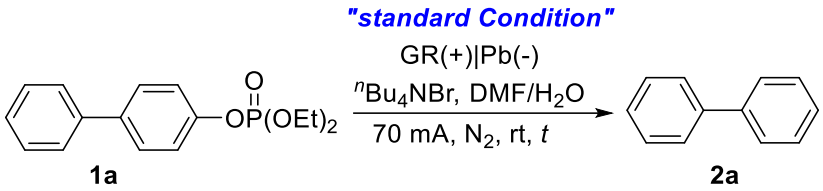
(3*r*,5*r*,7*r*)-1-(3,5-Dimethoxyphenyl)adamantane (12). The general procedure **C** was followed using 4-((3r,5r,7r)-Adamantan-1-yl)-2,6-dimethoxyphenyl diethyl phosphate (**11**) (169.8 mg, 0.40 mmol) as substrate and electrolyzed for 2 h (12 F/mol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **12** (88.5 mg, 81%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, J = 2.3 Hz, 2H), 6.30 (t, J = 2.3 Hz, 1H), 3.78

(s, 6H), 2.11 – 2.02 (m, 3H), 1.89 (t, J = 3.2, 1.9 Hz, 6H), 1.81 – 1.71 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 154.0, 103.5, 96.9, 55.1, 43.1, 36.8, 36.4, 28.9 ppm. The analytical data are in accordance with these reported in the literature.[32]

VII. Mechanism Studies

Reaction profiles of 1a under standard conditions



Under nitrogen atmosphere, to an oven-dried 10-mL vial equipped with GR as anode and Pb as cathode were added **1a** (306 mg, 1 mmol), ^{n}Bu$_4$NBr (322 mg, 1 mmol) and DMF/H$_2$O (4: 0.35 mL). The vial was sealed, stirred and electrolyzed under 70 mA. During the electrolysis, aliquots of 200 μL reaction solution were taken by microsyringe at 0.6, 0.8, 1, 2, 3, 4 and 5 F/mol, respectively. Each portionwise solution was mixed with water (1 mL) and extracted with EA (1 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. Yields were determined by ^{1}H NMR using CH_2Br_2 as internal standard.

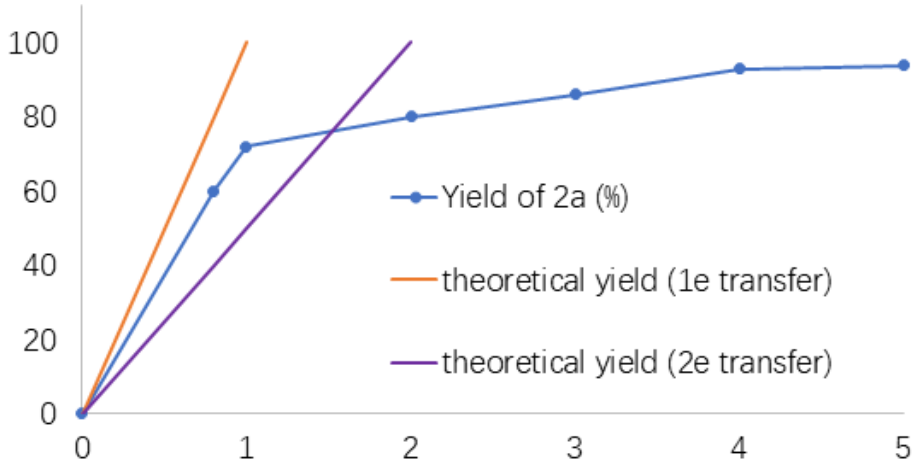
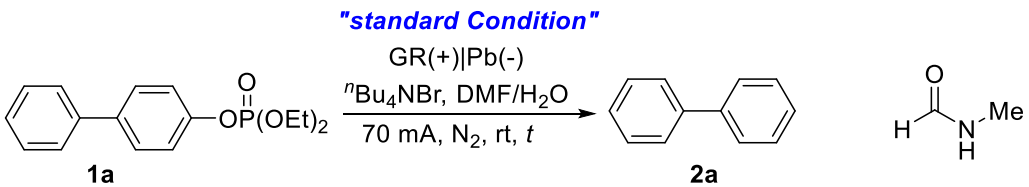


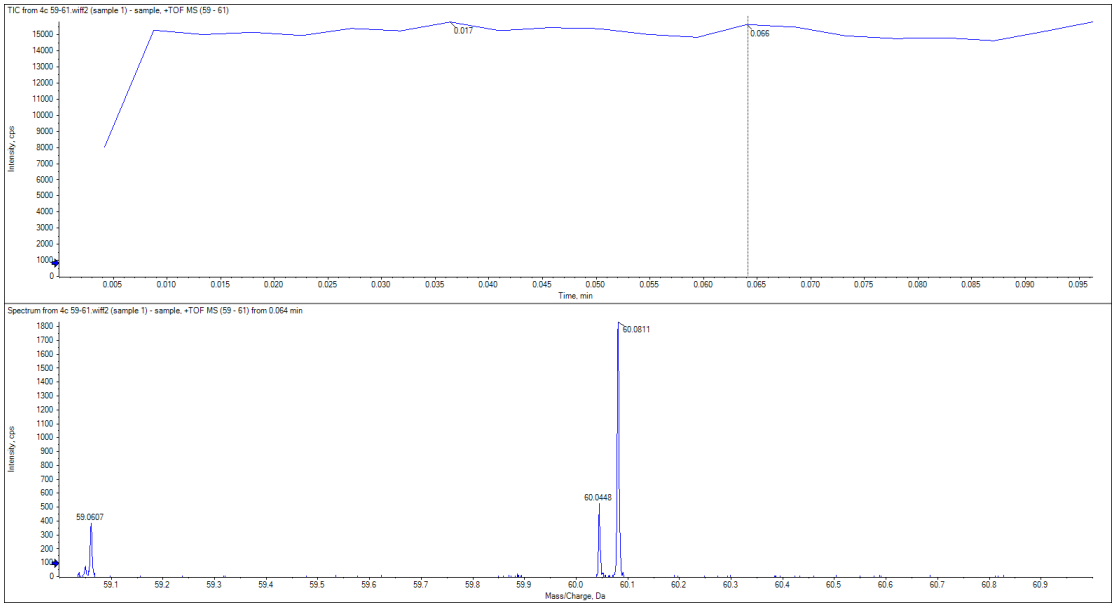
Figure S1. Reaction profile of 1a.

Detection of DMF hydrolysis product-N-Methylformamide.

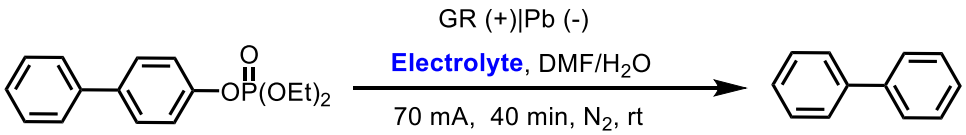


calc. $[M+H]^+$: 60.0444
found: 60.0449

The reaction mixture of **1a** under standard condition was subjected to HR-MS analysis directly, revealing the existence of the DMF hydrolysis product N-Methylformamide.



Comparison of electrolytes in electrolysis



0.40 mmol

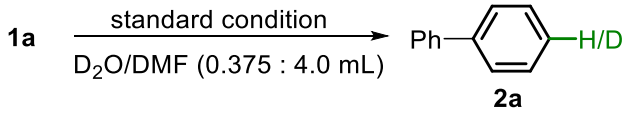
1a **2a**

The electrolysis was carried out in three parallel undivided cells (10 mL), each was equipped with a graphite carbon plate anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (10 mm × 10 mm × 0.5 mm). In all cells were added **1a** (122 mg, 0.40 mmol), DMF (4.0 mL) and H_2O (0.35 mL). The only difference is the electrolytes, which are indicated in the following table. The electrolysis was performed at 70 mA and stirred at ambient temperature for 40min (4.0 F mol^{-1}). Upon completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. Yields were determined by ^1H NMR

using CH_2Br_2 as internal standard and the results are shown in the following table.

Entry	Electrolyte	**2a** (%)	Conversion of **1a** (%)
1	$^nBu_4NBr$	87	>99
2	$^nBu_4NBF_4$	42	69
3	$^nBu_4NBF_4$+20 mol% $^nBu_4NBr$	60	63

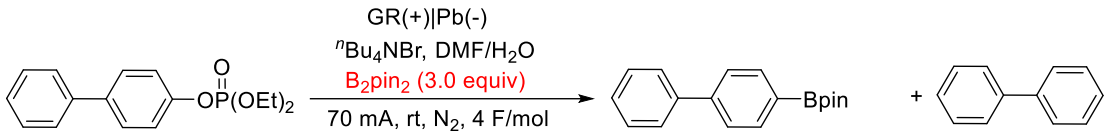
Isotope Experiment



The electrolysis was carried out in three parallel undivided cells (10 mL), each was equipped with a graphite carbon plate anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (10 mm × 10 mm × 0.5 mm). In all cells were added **1a** (122 mg, 0.40 mmol), $^nBu_4NBr$ (128 mg, 0.40 mmol), DMF (4.0 mL) and D_2O (0.35 mL). The electrolysis was performed at 20, 70 and 200 mA, respectively, with a total charge of 4.0 F mol^{-1}. Upon completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography. The deuterium ratio was determined by ^1H NMR and the results are shown in the following table.

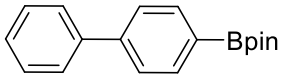
Entry	Current (mA)	Time (min)	Yield (%)	Deuterated Ratio (%)
1	20	140	70	18
2	70	40	87	23
3	200	14	72	40

Trapping aryl radical by B_2pin_2 reagent Experiment



1a **13**, 27% **2a**

The electrolysis was carried out in an undivided cell (10 mL) equipped with a graphite carbon plate anode (10 mm × 10 mm × 0.5 mm) and a lead cathode (10 mm × 10 mm × 0.5 mm). To the cell were added **1a** (122 mg, 0.40 mmol), $^{n}Bu_4NBr$ (128 mg, 0.40 mmol), B_2pin_2 (304.8 mg, 1.20 mmol) and DMF (4.0 mL). The electrolysis was performed at 20 mA for 4 h at 60 ˚C. Upon completion, the reaction mixture was transferred into a separatory funnel and the electrodes were rinsed with EtOAc (10 mL). A saturated aqueous NaCl solution (10 mL) was added slowly and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography to yield **13** (22.7 mg, 27% yield) as a white solid.



13

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.65 – 7.57 (m, 4H), 7.48 – 7.40 (m, 2H), 7.38 – 7.32 (m, 1H), 1.36 (s, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.0, 135.2, 128.8, 127.5, 127.2, 126.5, 83.8, 24.9 ppm. The carbon signal attached to B atom was not observed due to low intensity.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.19 ppm. The analytical data are in accordance with these reported in the literature [33].

Cyclic voltammograms experiments

Cyclic voltammograms (CVs) were recorded using a CHI600E potentiostat and a 3-electrodes cell equipped with a glassy carbon disk (3 mm diameter) working electrode, a platinum wire counter electrode and a SCE electrode. The measurements were

performed in dry $TBABF_4$/MeCN or $TBABF_4$/DMF (0.1 M, 5 mL) solutions purged of air with nitrogen. Unless specified, a scan rate of 100 mV s^{-1} was used.

Oxidation potential of substrates

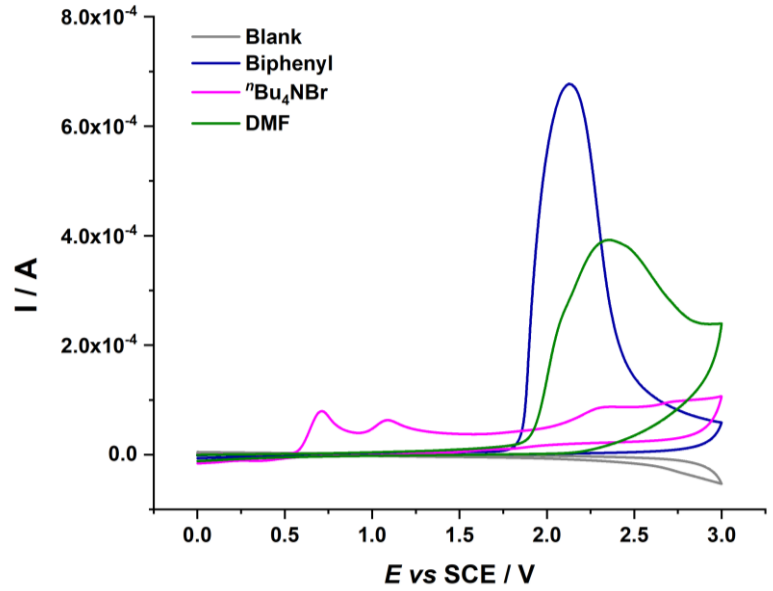
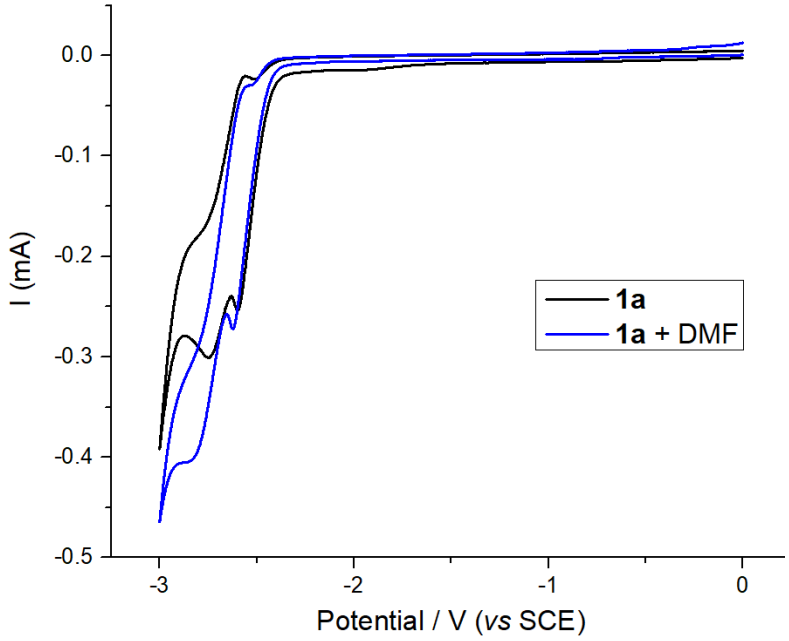


Figure S2. CV measurements in MeCN with 0.1 M $^{n}Bu_4NBF_4$ and 5 mM substrate at room temperature with the scan mode of positive direction from 0 V to 3.0 V.

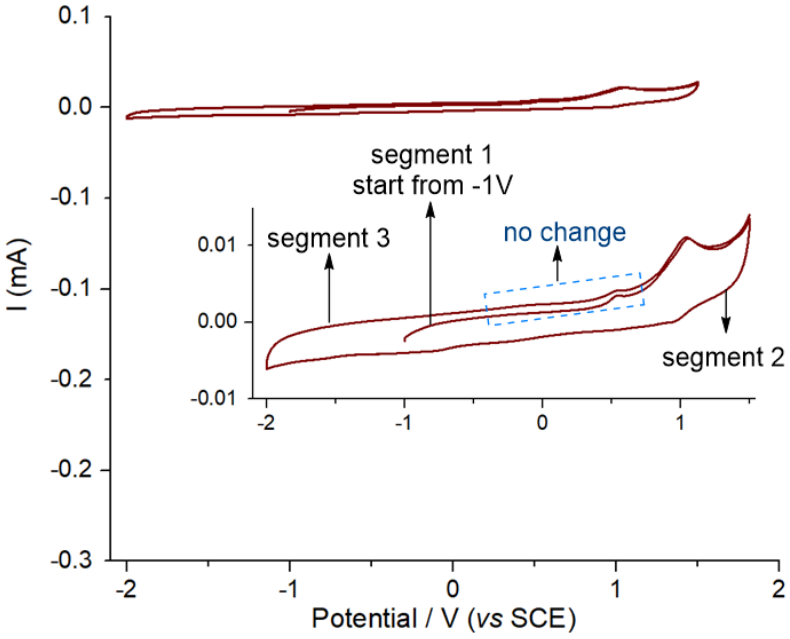
The interaction between 1a and DMF in MeCN



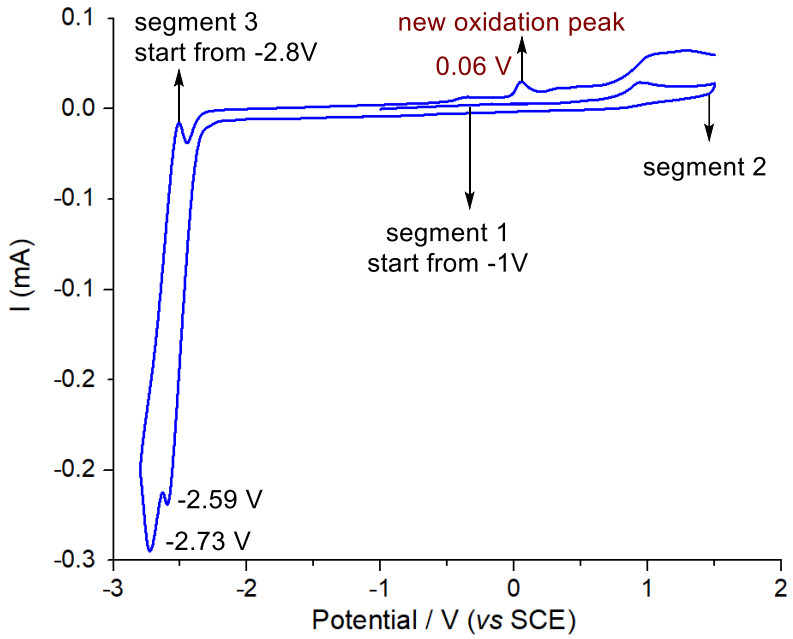
CV of **1a** (black) and **1a** + DMF (blue). CV measurements in MeCN with 0.1 M

$^{n}Bu_4NBF_4$ and 5 mM **1a** or 5 mM **1a** + DMF at room temperature with the scan mode of negative direction from 0 V to -3 V.

The redox behavior of 1a in DMF



CV of **1a** in DMF. CV measurements in DMF with 0.1 M $^{n}Bu_4NBF_4$ and 5 mM **1a** at room temperature with the scan mode of positive direction from -1 V to +1.5 V (segment 1), then from +1.5 V to -2 V (segment 2), finally from -2 V to +1.5 V (segment 3).



CV of **1a** in DMF. CV measurements in DMF with 0.1 M $^{n}Bu_4NBF_4$ and 5 mM **1a** at room temperature with the scan mode of positive direction from -1 V to +1.5 V (segment 1), then from +1.5 V to -2.8 V (segment 2), finally from -2.8 V to +1.5 V (segment 3).

VIII. References

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3477.
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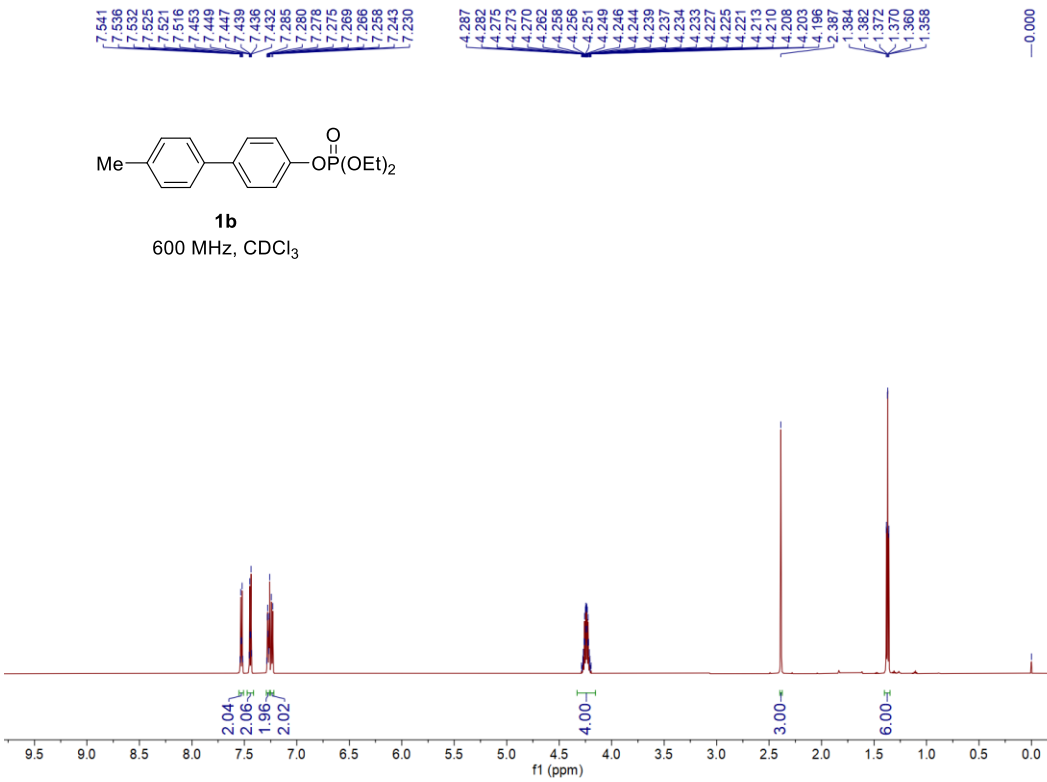
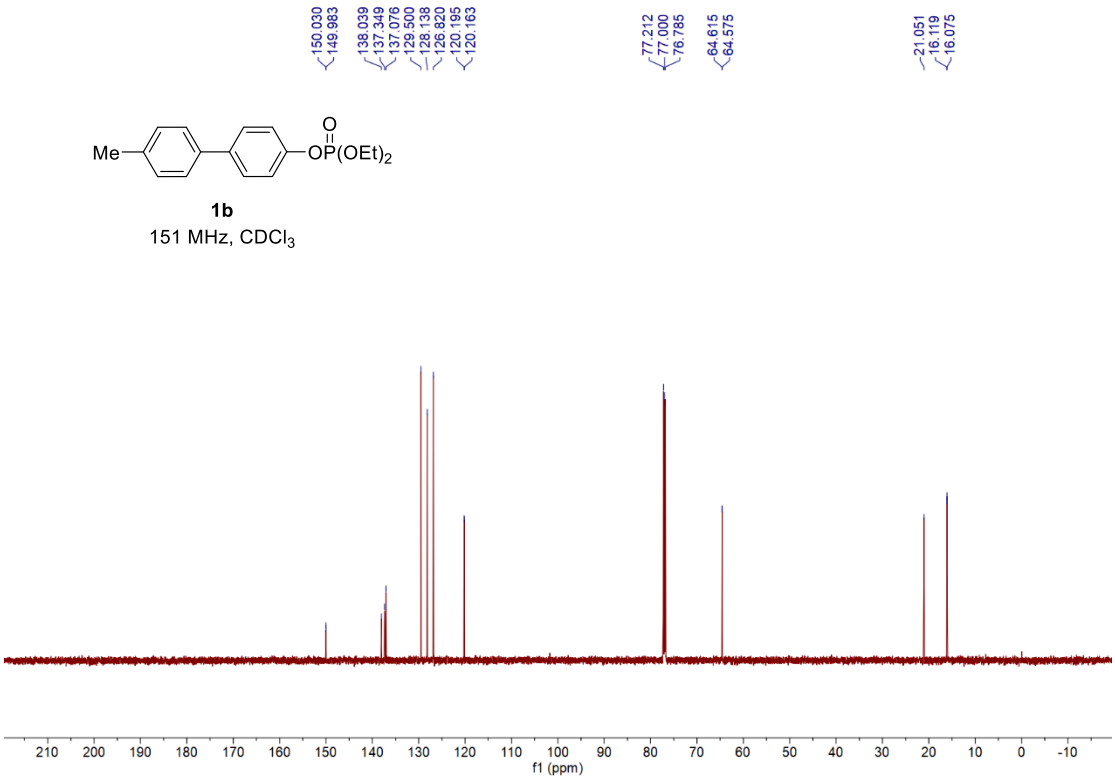
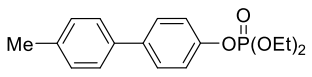
IX. NMR Spectra

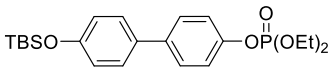






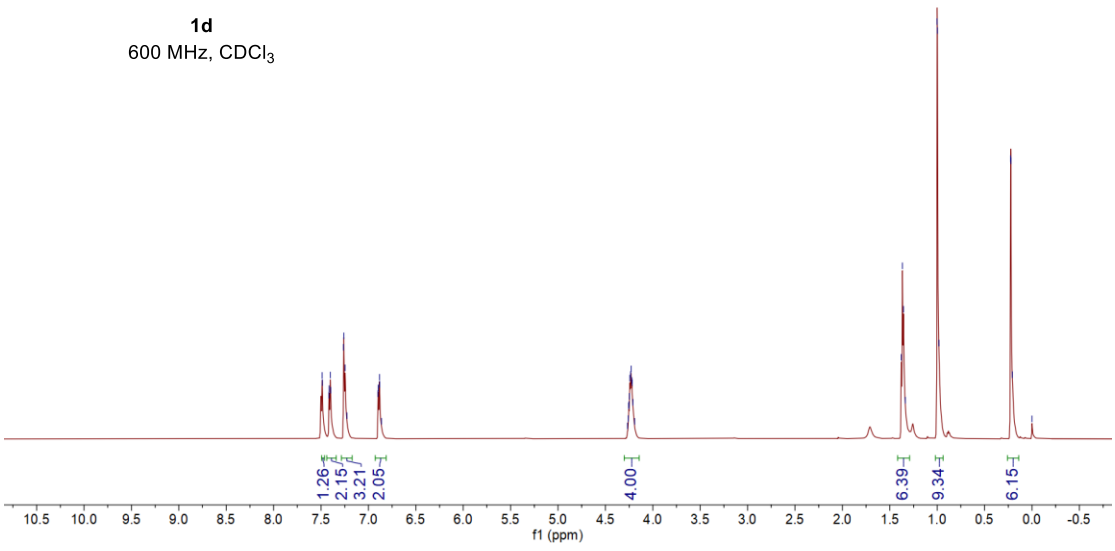
1b

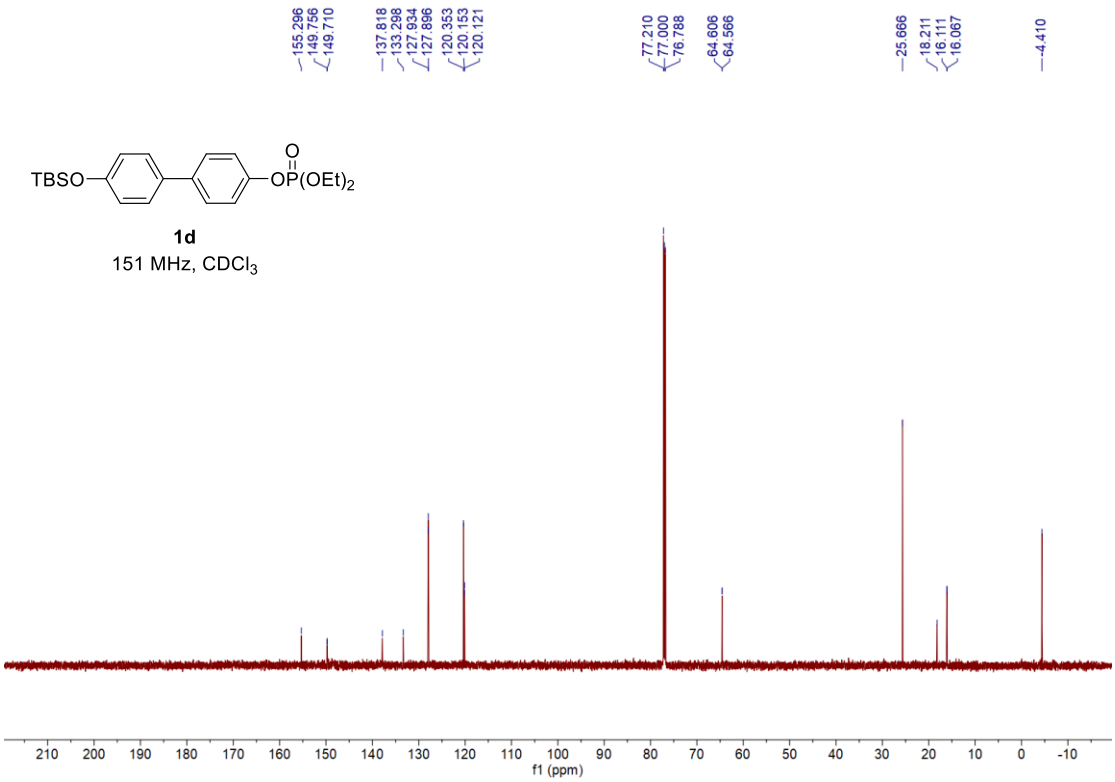
243 MHz, $CDCl_3$



1d

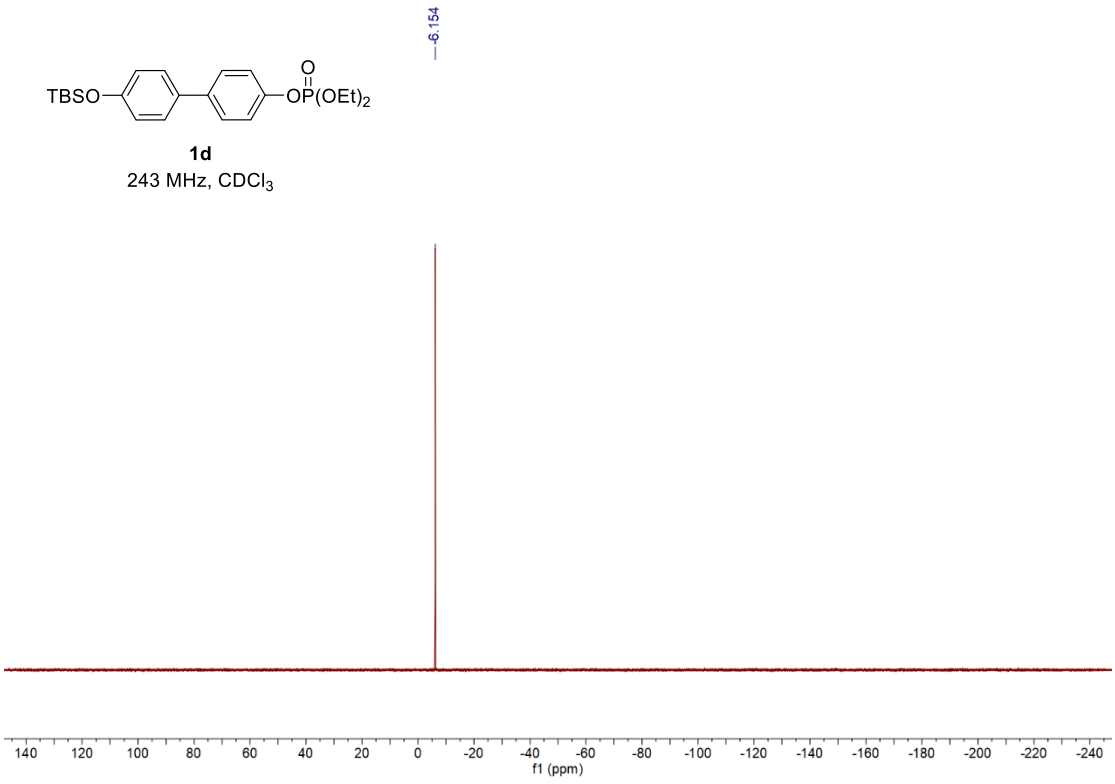
600 MHz, $CDCl_3$





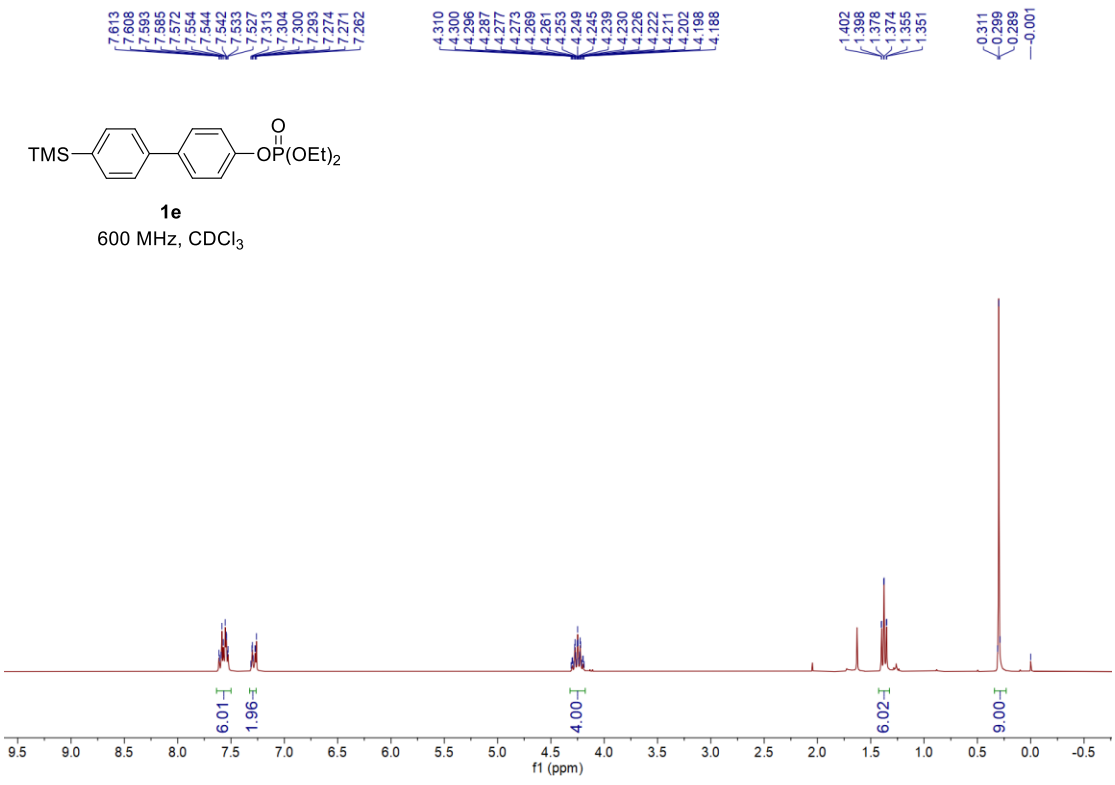
1d

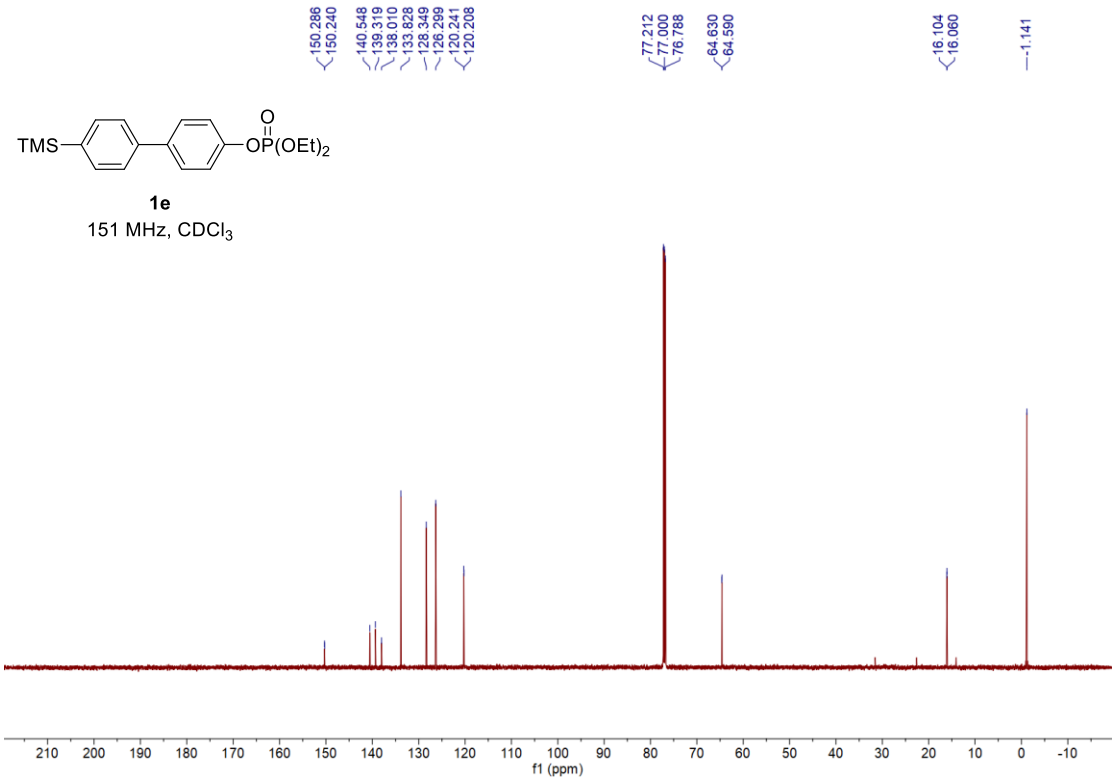
151 MHz, $CDCl_3$

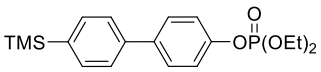


1d

243 MHz, $CDCl_3$

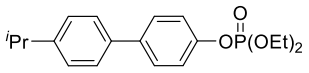

7.613
7.608
7.593
7.585
7.572
7.554
7.544
7.542
7.533
7.527
7.313
7.304
7.300
7.293
7.274
7.271
7.262
4.310
4.300
4.296
4.287
4.277
4.273
4.269
4.261
4.253
4.249
4.245
4.239
4.230
4.226
4.222
4.211
4.202
4.198
4.188
1.402
1.398
1.378
1.374
1.355
1.351
0.311
0.299
0.289
-0.001
TMS
OP(OEt)2
O
1e
600 MHz, CDCl3
6.01
1.96
4.00
6.02
9.00
f1 (ppm)


150.286
150.240
140.548
139.319
138.010
133.828
128.349
126.299
120.241
120.208
77.212
77.000
76.788
64.630
64.590
16.104
16.060
-1.141
TMS
OP(OEt)2
O
1e
151 MHz, CDCl3
f1 (ppm)



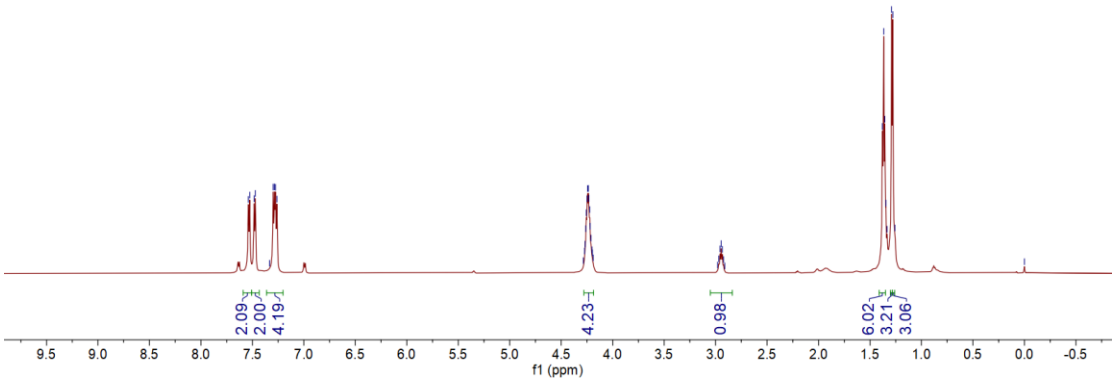
1e

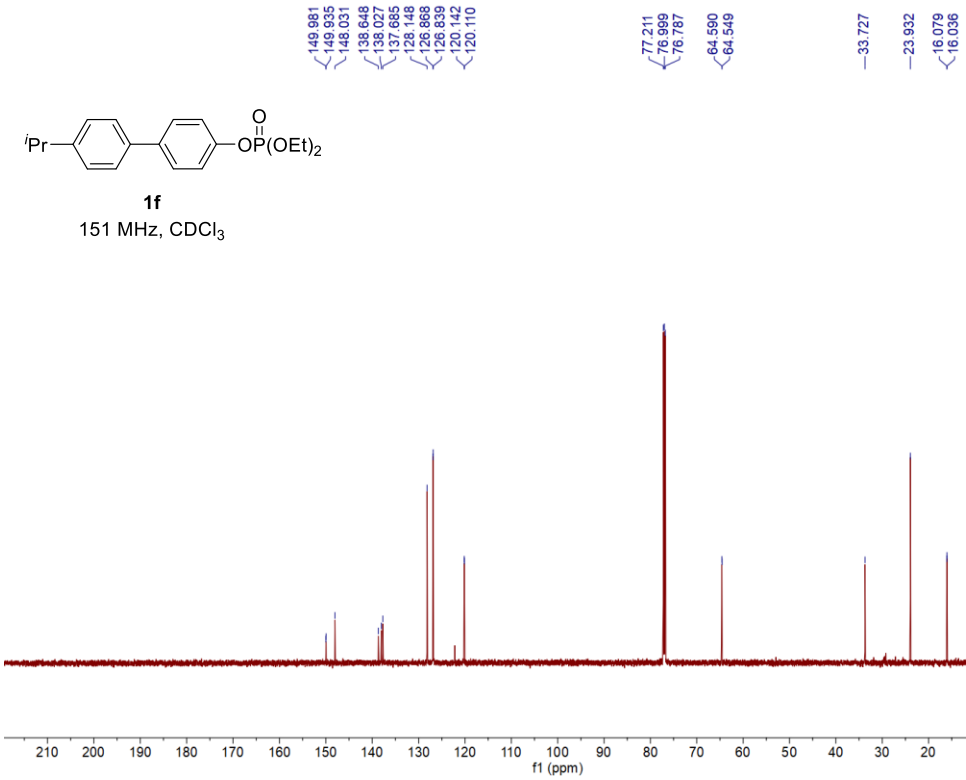
243 MHz, $CDCl_3$



1f

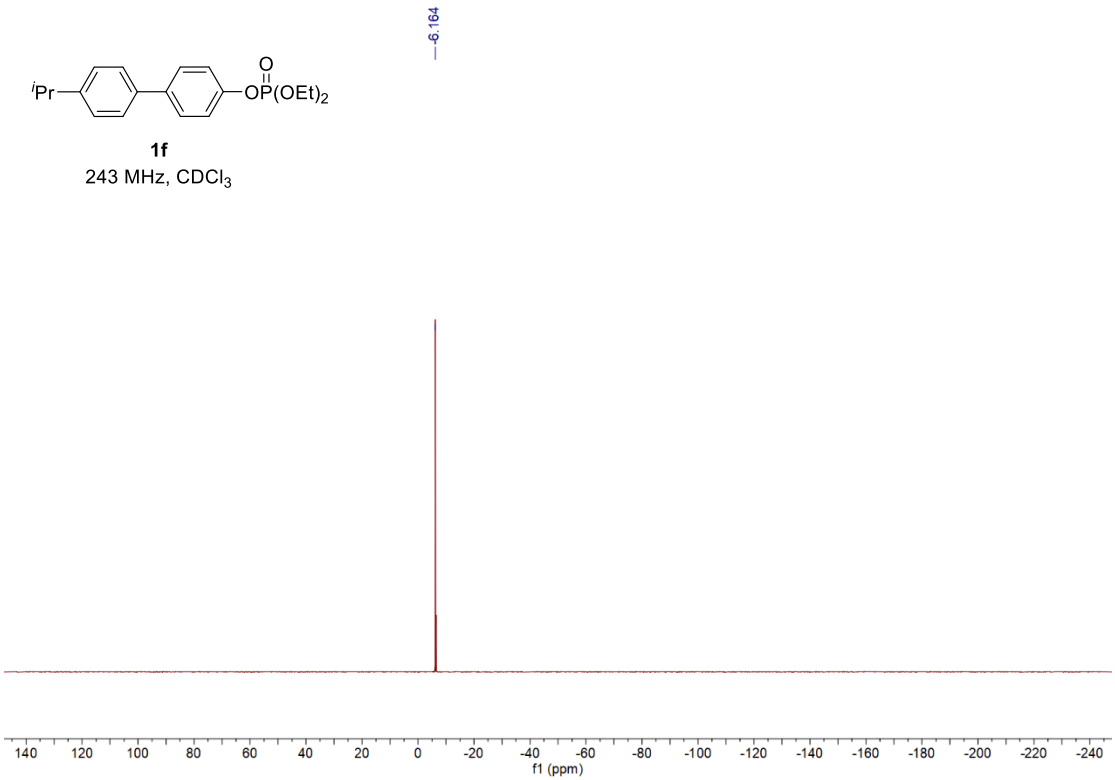
600 MHz, $CDCl_3$





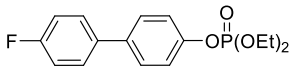
1f

151 MHz, $CDCl_3$



1f

243 MHz, $CDCl_3$



1g

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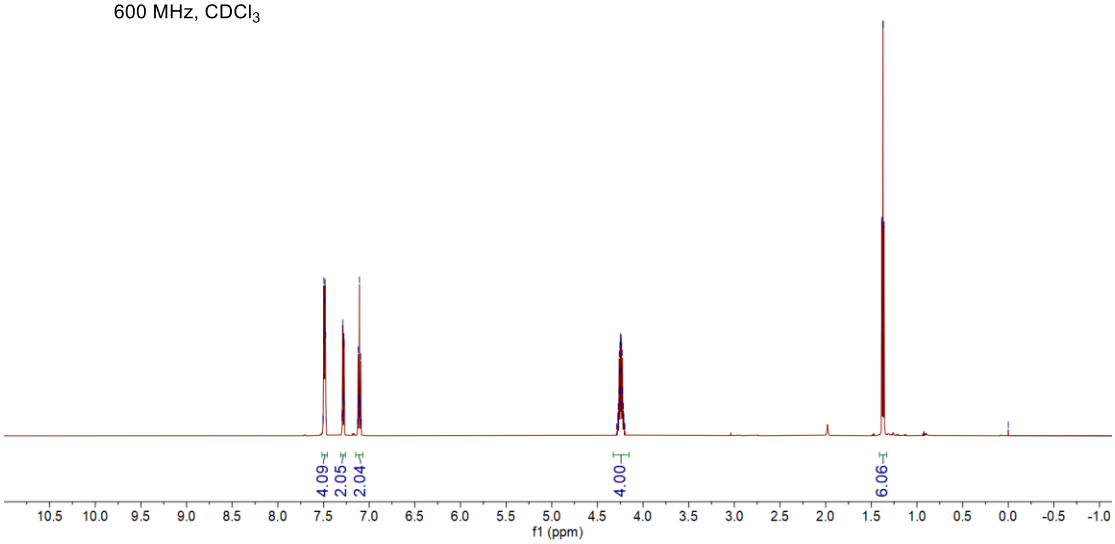
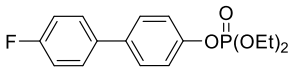
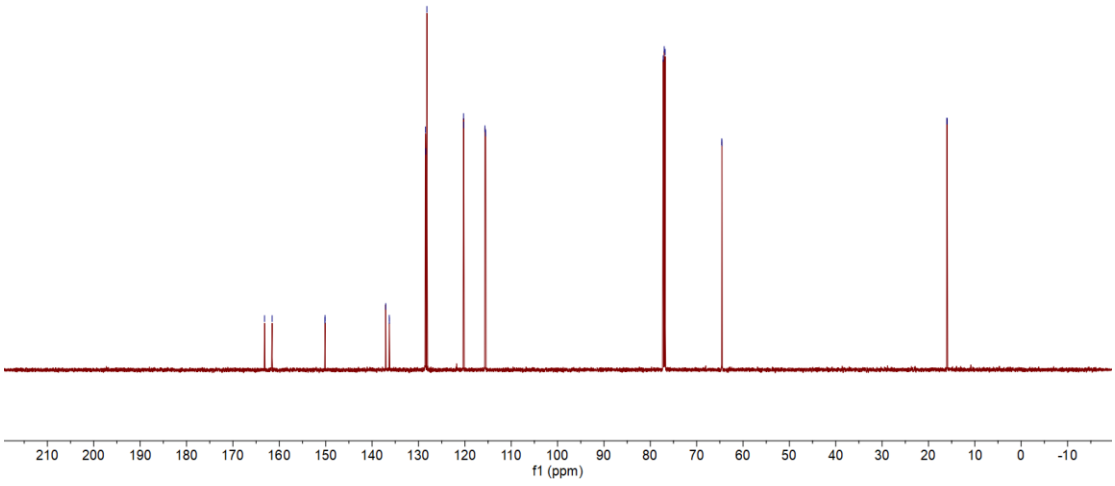
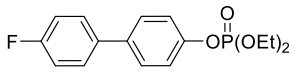




1g

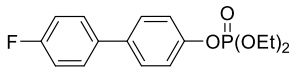
151 MHz, $CDCl_3$





1g

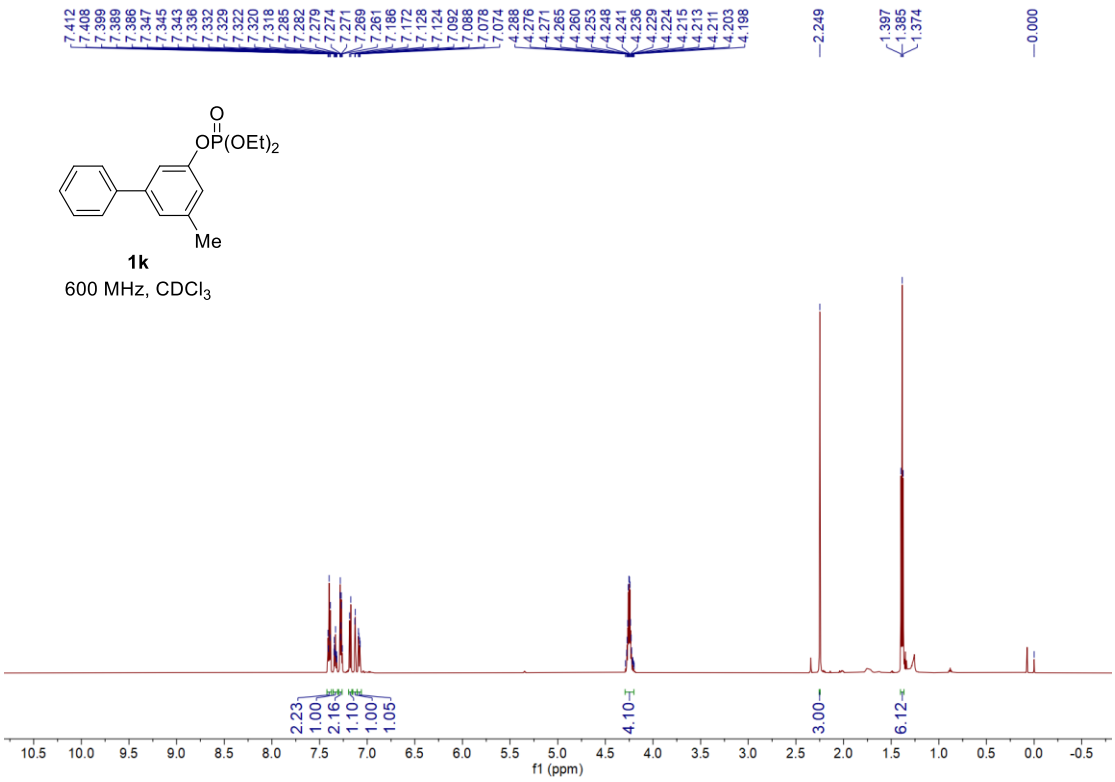
243 MHz, $CDCl_3$

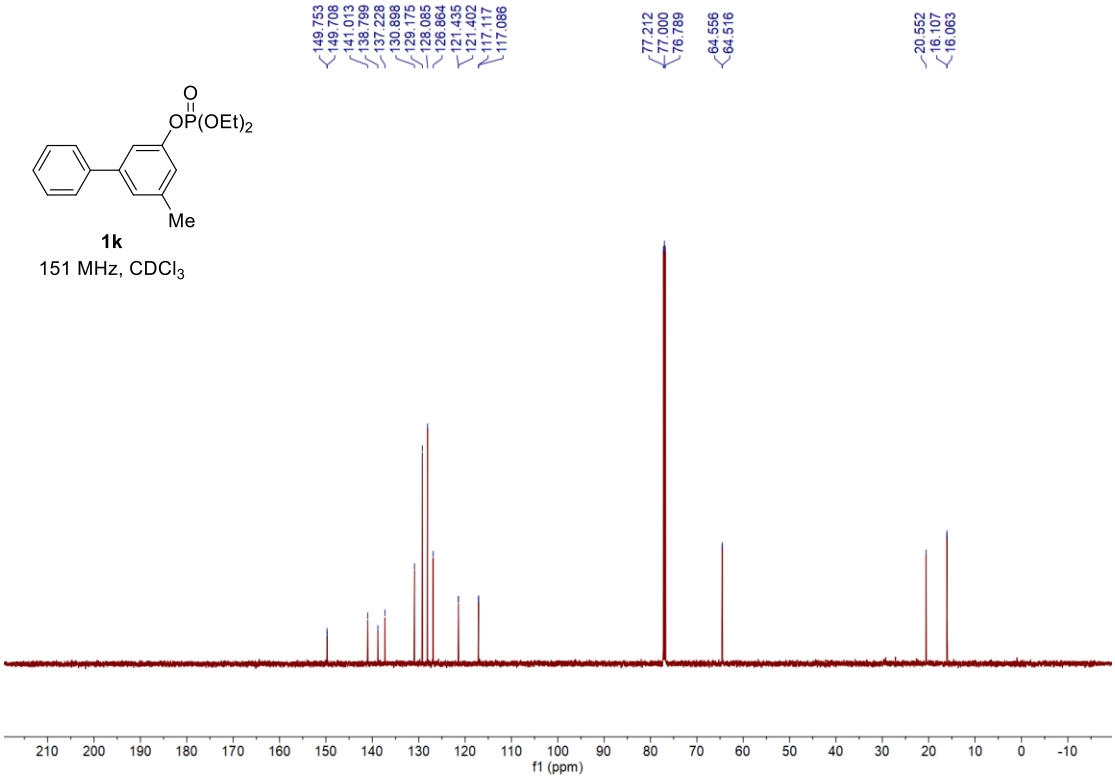


1g

565 MHz, $CDCl_3$

S


7.412
7.408
7.399
7.389
7.386
7.347
7.345
7.343
7.336
7.332
7.329
7.322
7.320
7.318
7.285
7.282
7.279
7.274
7.271
7.269
7.261
7.186
7.172
7.128
7.124
7.092
7.088
7.078
7.074
4.288
4.276
4.271
4.265
4.260
4.253
4.248
4.241
4.236
4.229
4.224
4.215
4.213
4.211
4.203
4.198
2.249
1.397
1.385
1.374
0.000
O
OP(OEt)2
Me
1k
600 MHz, CDCl3
2.23
1.00
2.16
1.10
1.00
1.05
4.10
3.00
6.12
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)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137.228
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128.085
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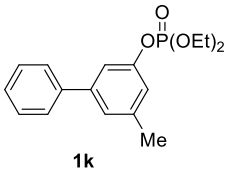
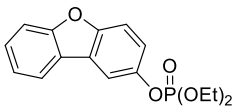
121.435
121.402
117.117
117.086
77.212
77.000
76.789
64.556
64.516
20.552
16.107
16.063
O
OP(OEt)2
Me
1k
151 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



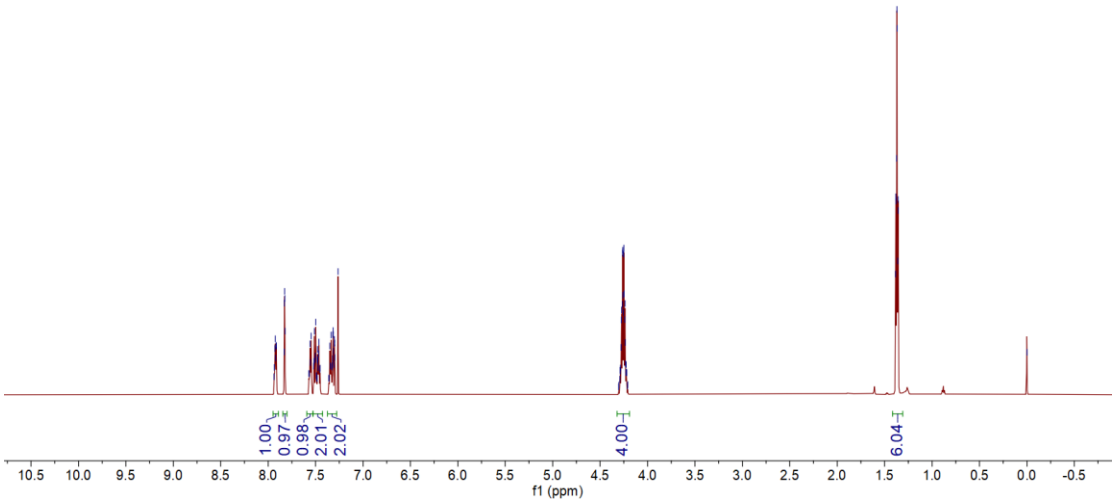
1k

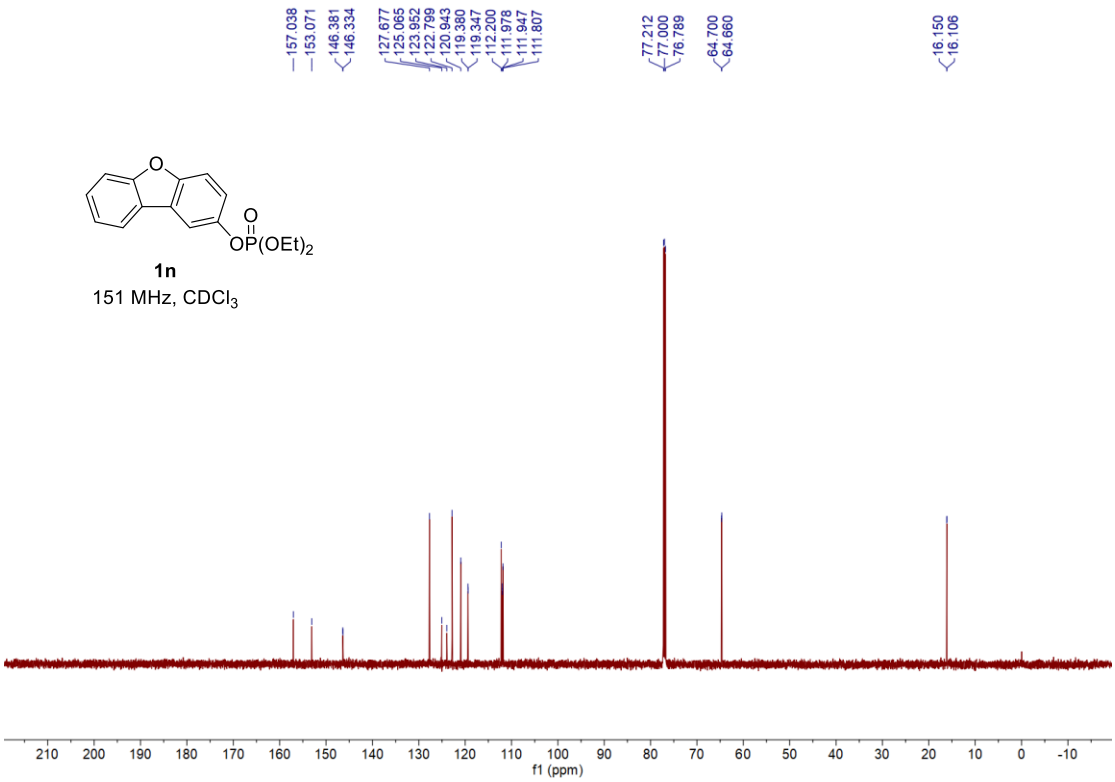
243 MHz, $CDCl_3$



1n

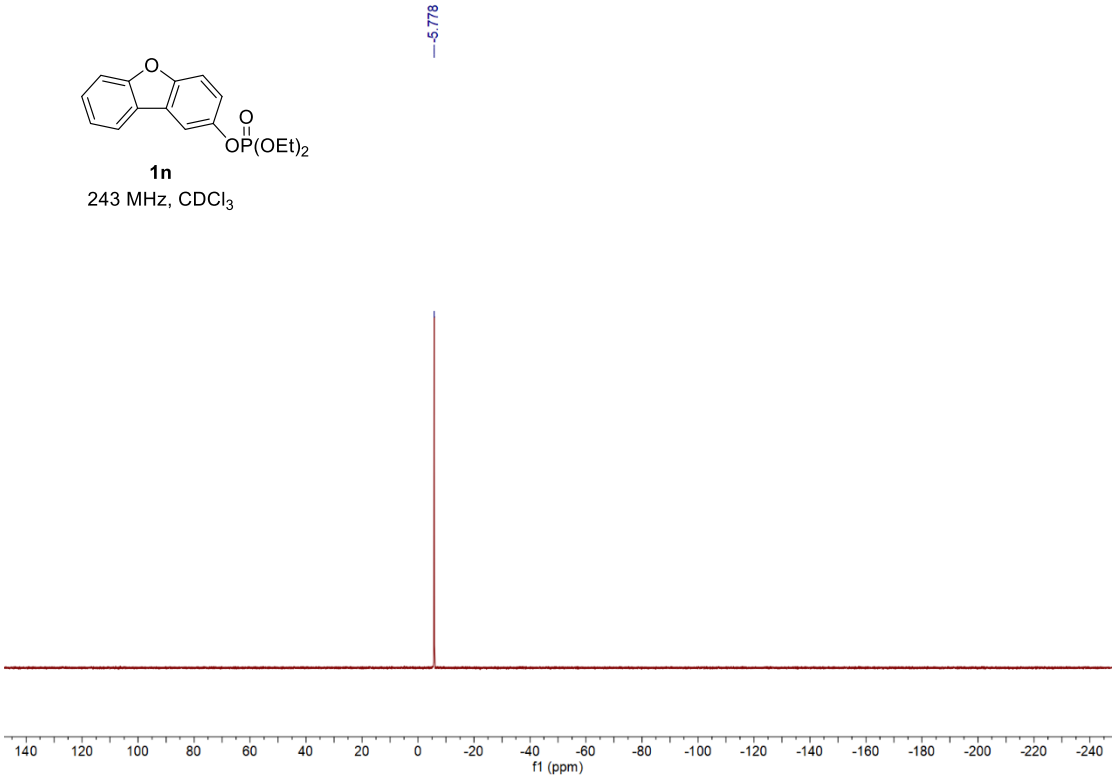
600 MHz, $CDCl_3$





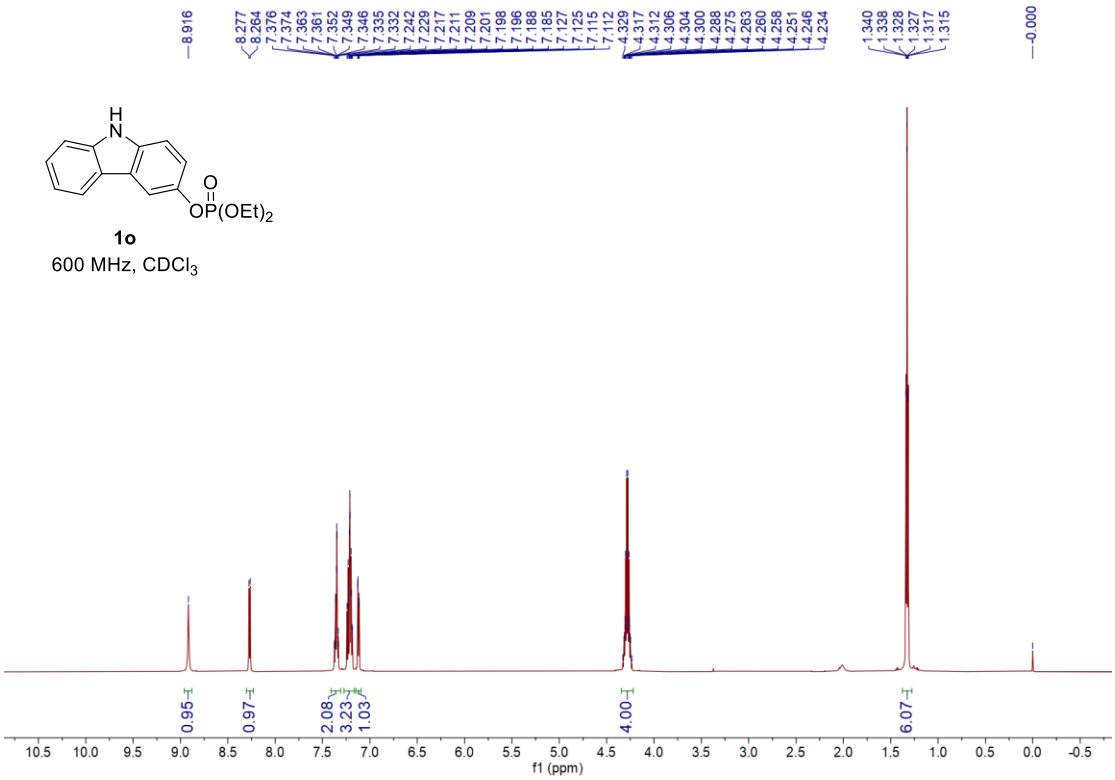
1n

151 MHz, $CDCl_3$



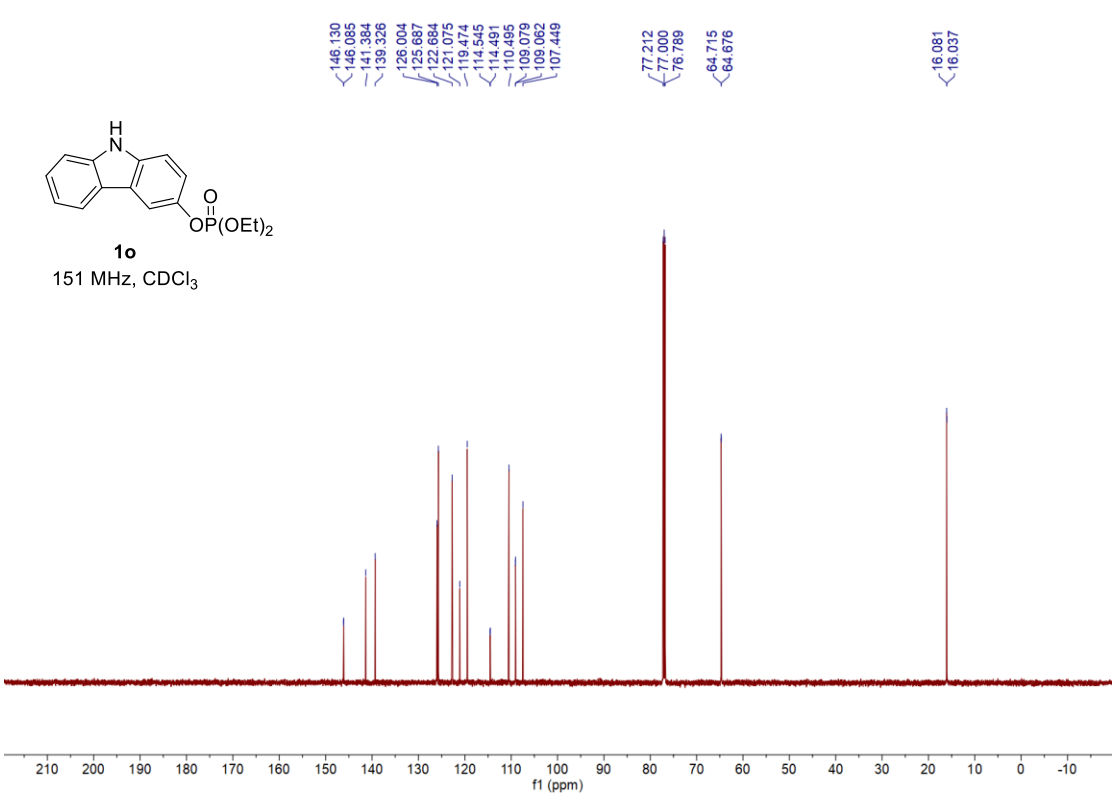
1n

243 MHz, $CDCl_3$



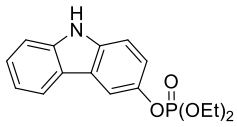
1o

600 MHz, $CDCl_3$



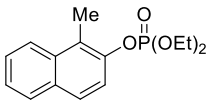
1o

151 MHz, $CDCl_3$



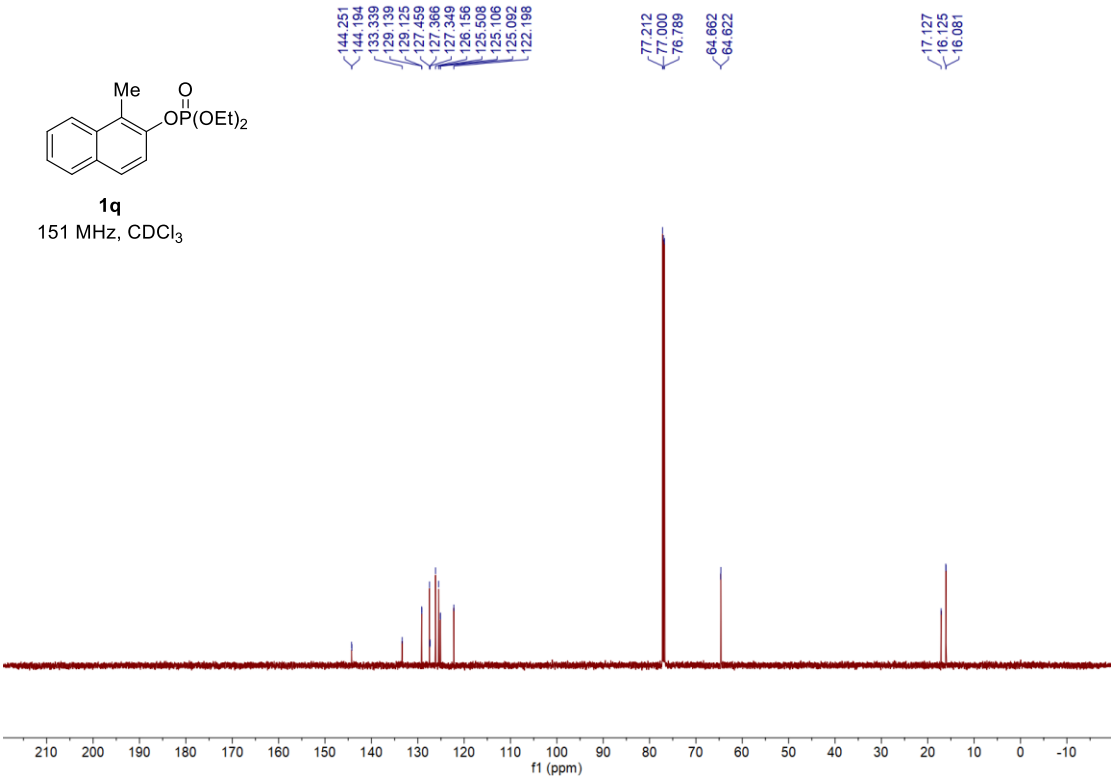
1o

243 MHz, $CDCl_3$



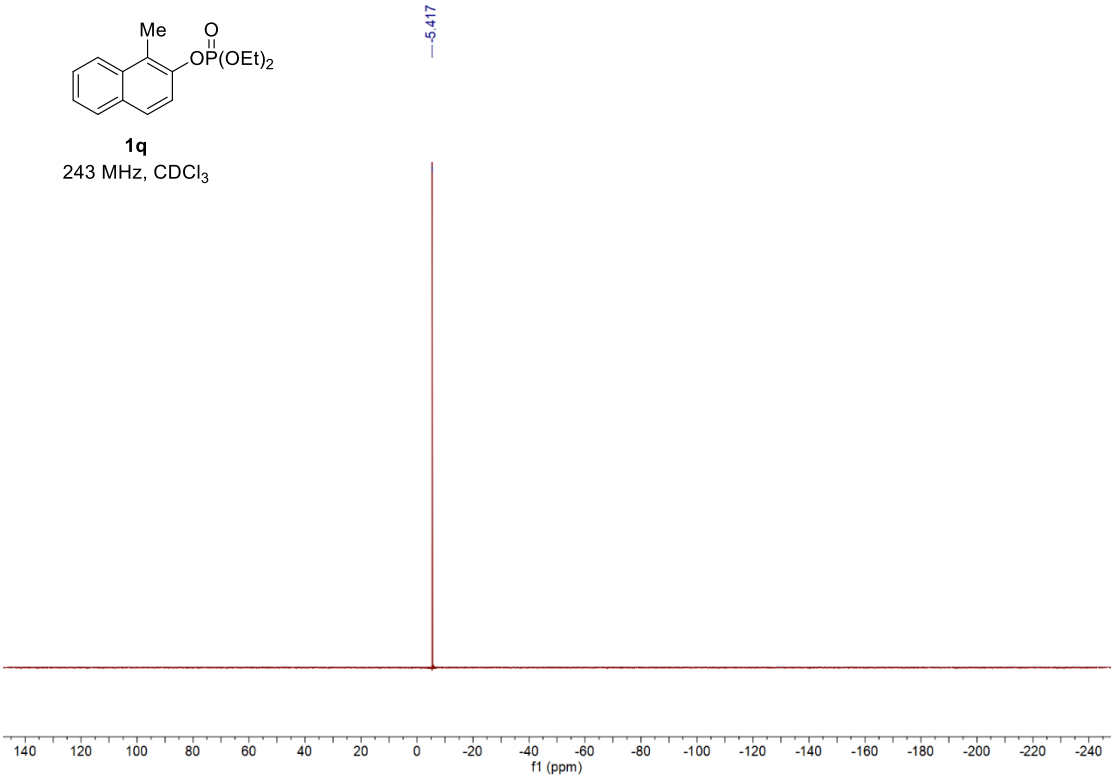
1q

600 MHz, $CDCl_3$



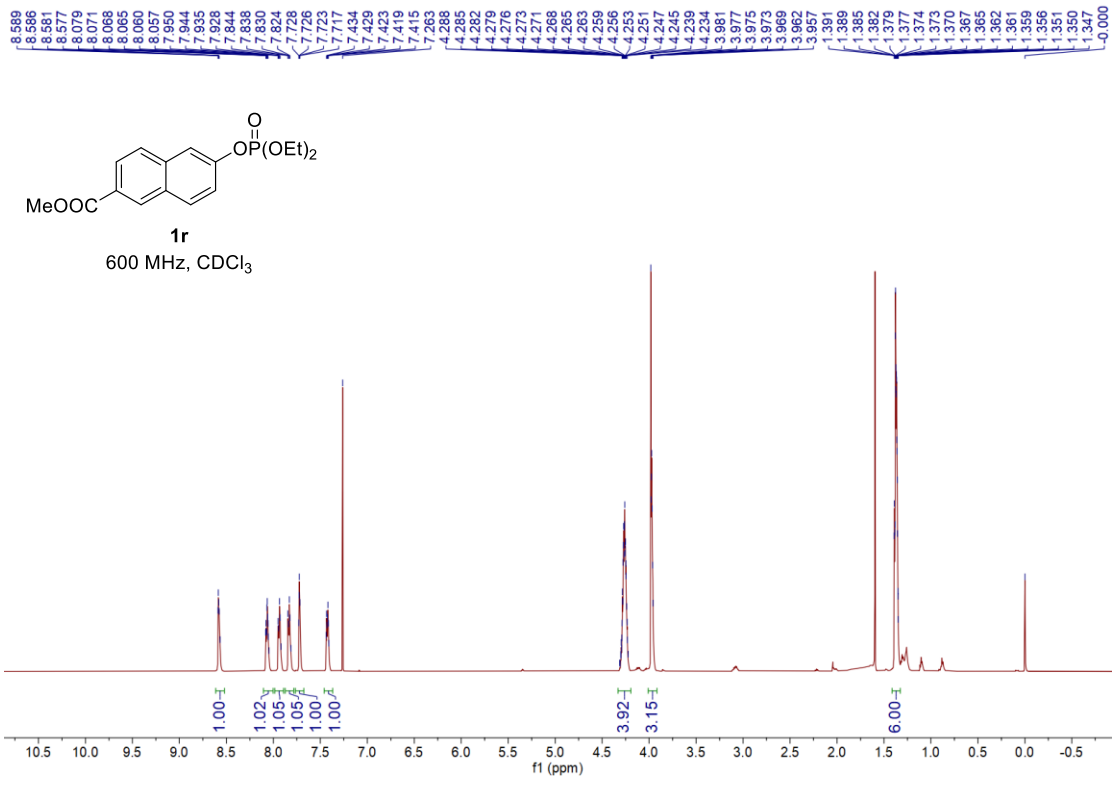
1q

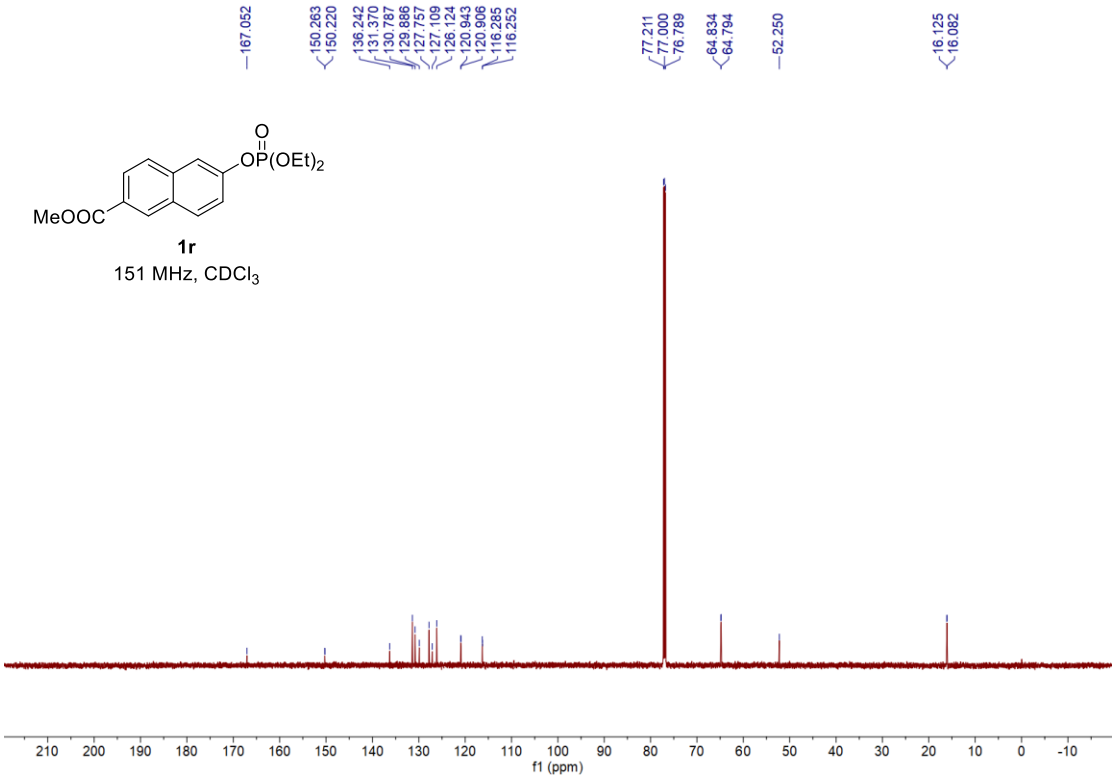
151 MHz, $CDCl_3$

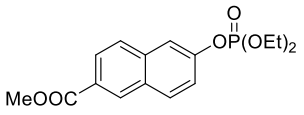


1q

243 MHz, $CDCl_3$

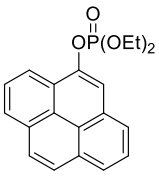

8.589
8.586
8.581
8.577
8.079
8.071
8.068
8.065
8.060
8.057
7.950
7.944
7.935
7.928
7.844
7.838
7.830
7.824
7.728
7.726
7.723
7.717
7.434
7.429
7.423
7.419
7.415
7.263
4.288
4.285
4.282
4.279
4.276
4.273
4.271
4.268
4.265
4.263
4.259
4.256
4.253
4.251
4.247
4.245
4.239
4.234
3.981
3.977
3.975
3.973
3.969
3.962
3.957
1.391
1.389
1.385
1.382
1.379
1.377
1.374
1.373
1.370
1.367
1.365
1.362
1.361
1.359
1.356
1.351
1.350
1.347
0.000
O
OP(OEt)2
MeOOC
1r
600 MHz, CDCl3
1.00
1.02
1.05
1.05
1.00
1.00
3.92
3.15
6.00
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)


167.052
150.263
150.220
136.242
131.370
130.787
129.886
127.757
127.109
126.124
120.943
120.906
116.285
116.252
77.211
77.000
76.789
64.834
64.794
52.250
16.125
16.082
O
OP(OEt)2
MeOOC
1r
151 MHz, CDCl3
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)



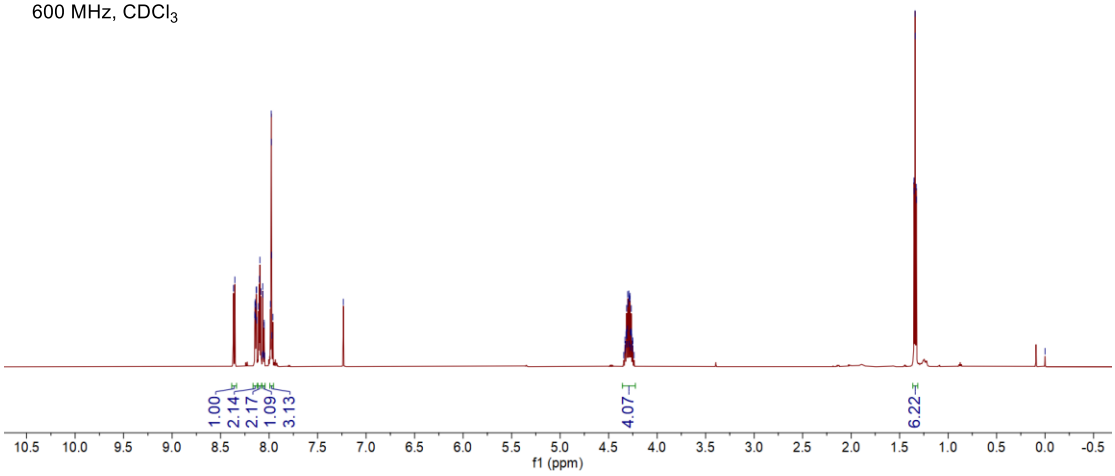
1r

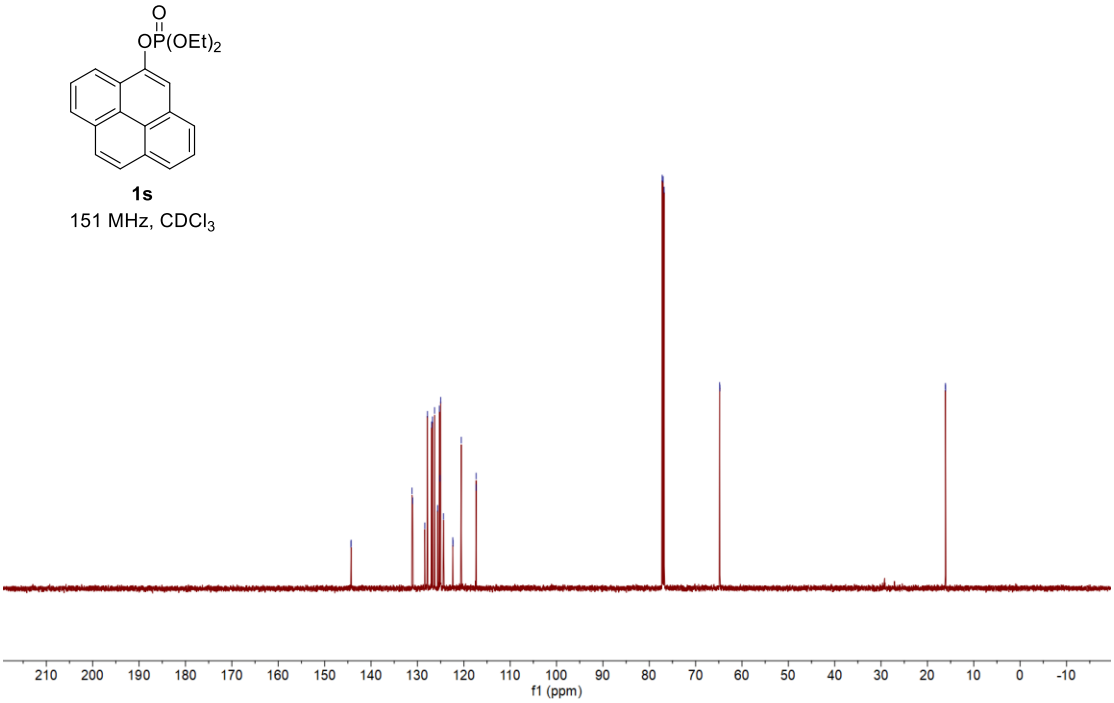
243 MHz, $CDCl_3$



1s

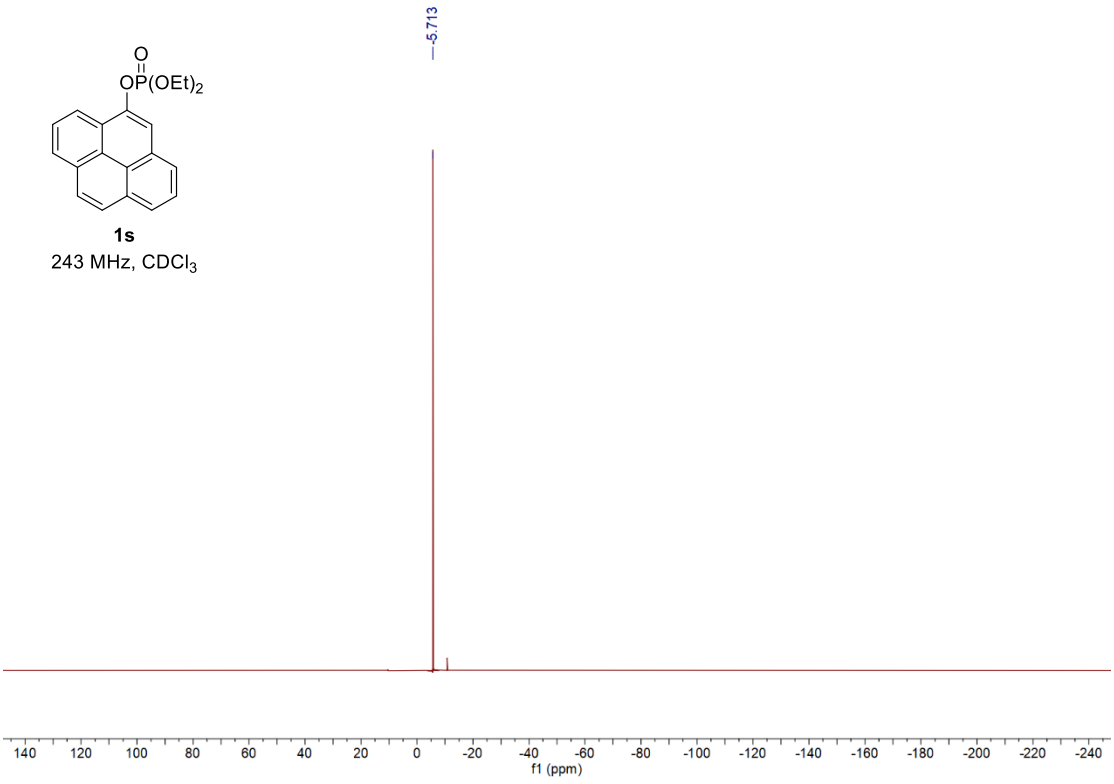
600 MHz, $CDCl_3$





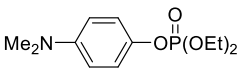
1s

151 MHz, $CDCl_3$



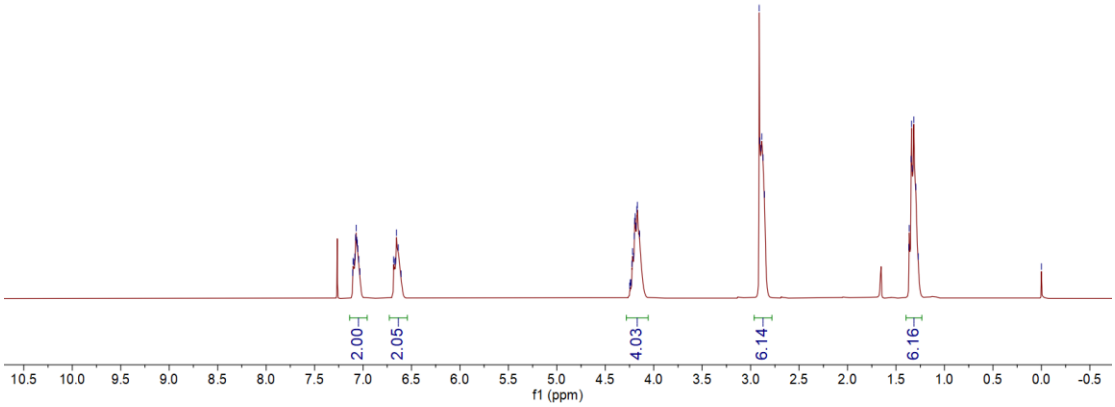
1s

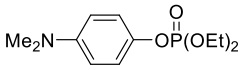
243 MHz, $CDCl_3$



1v

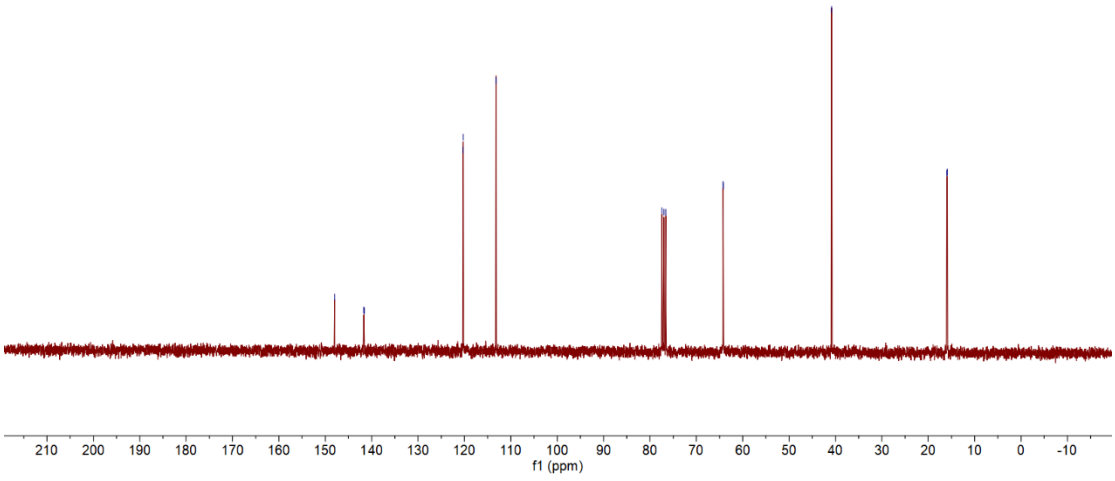
600 MHz, $CDCl_3$

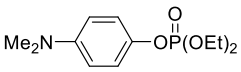




1v

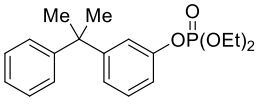
151 MHz, $CDCl_3$





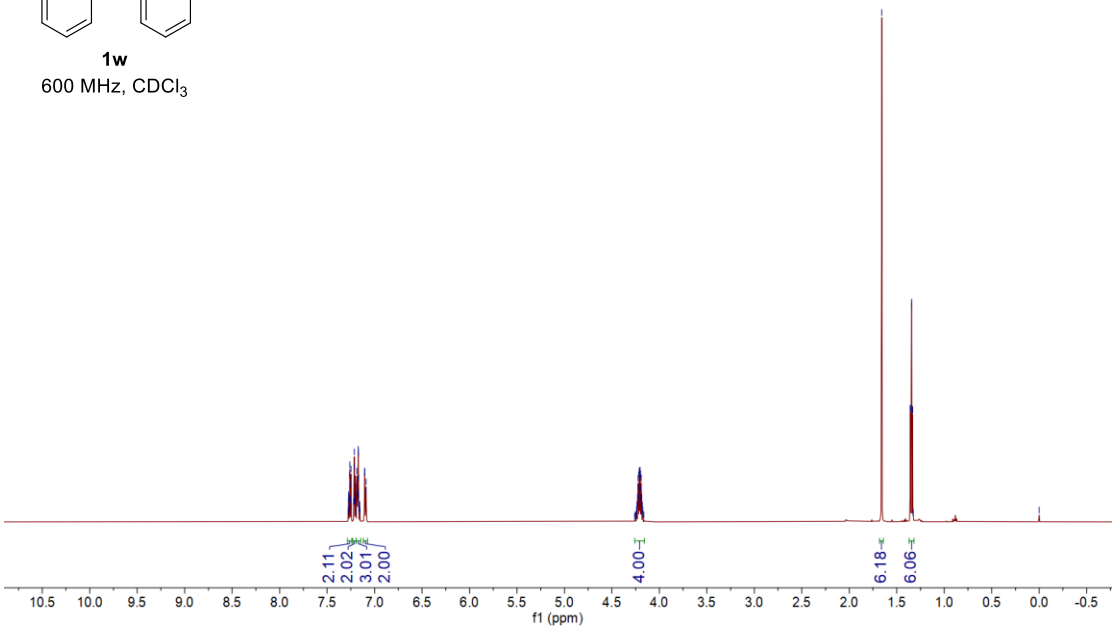
1v

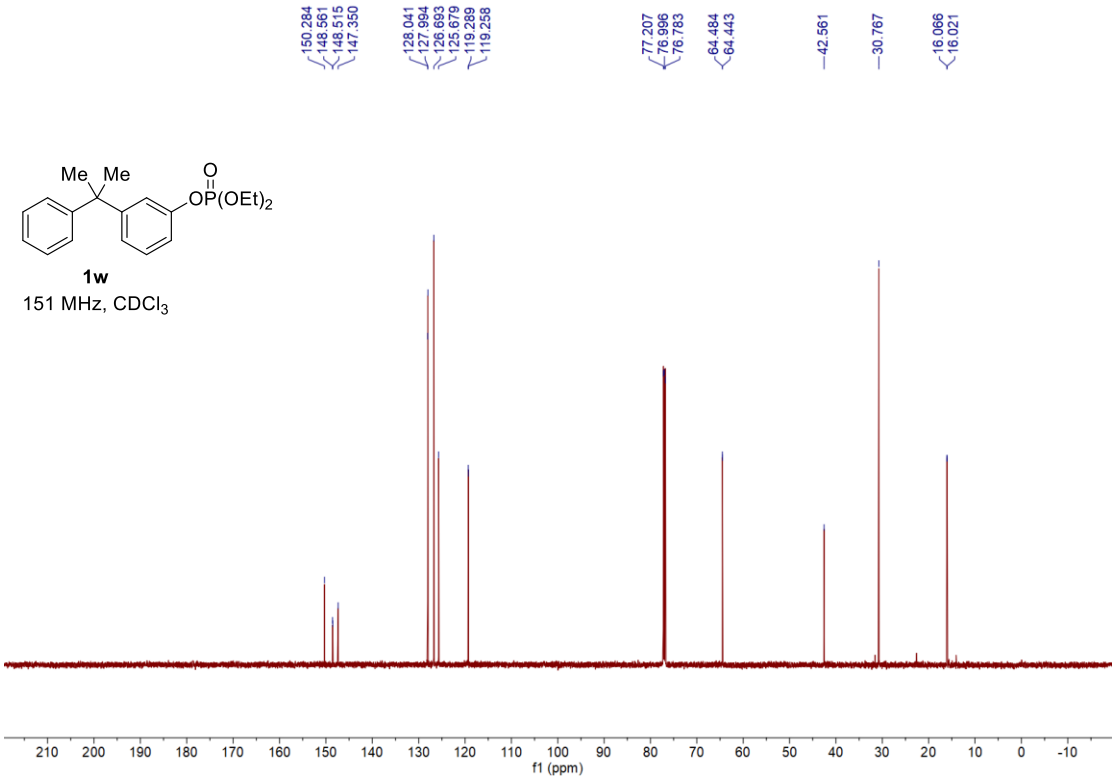
243 MHz, $CDCl_3$



1w

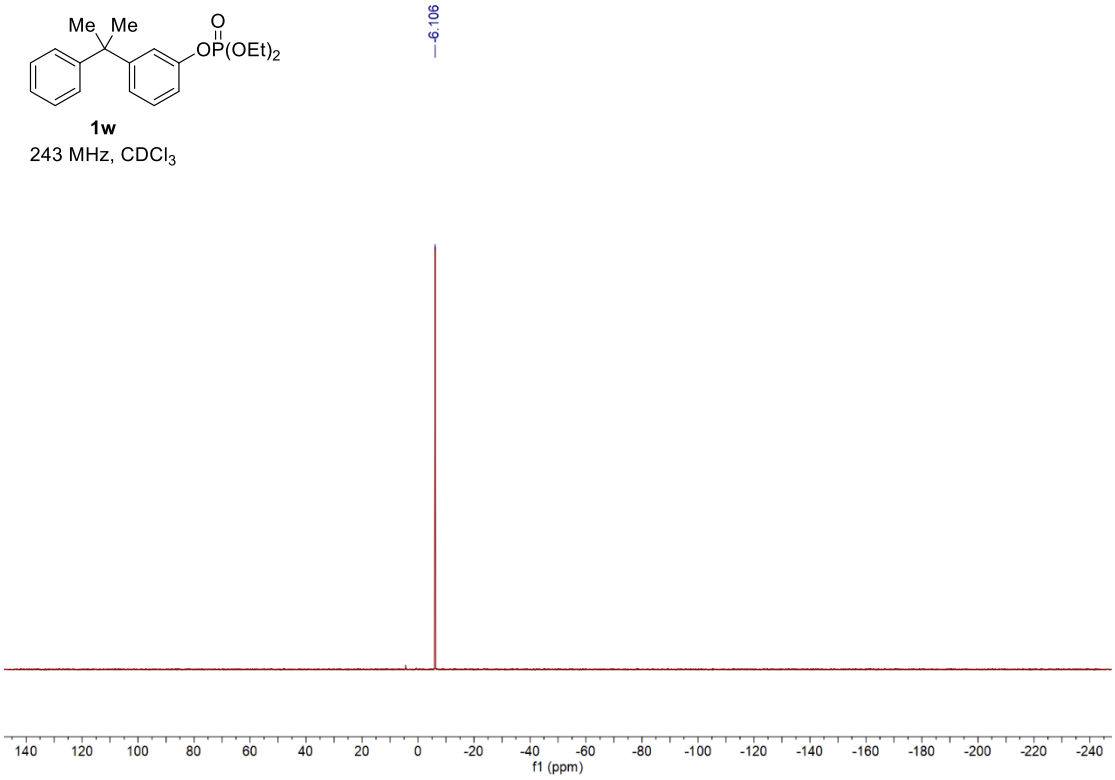
600 MHz, $CDCl_3$





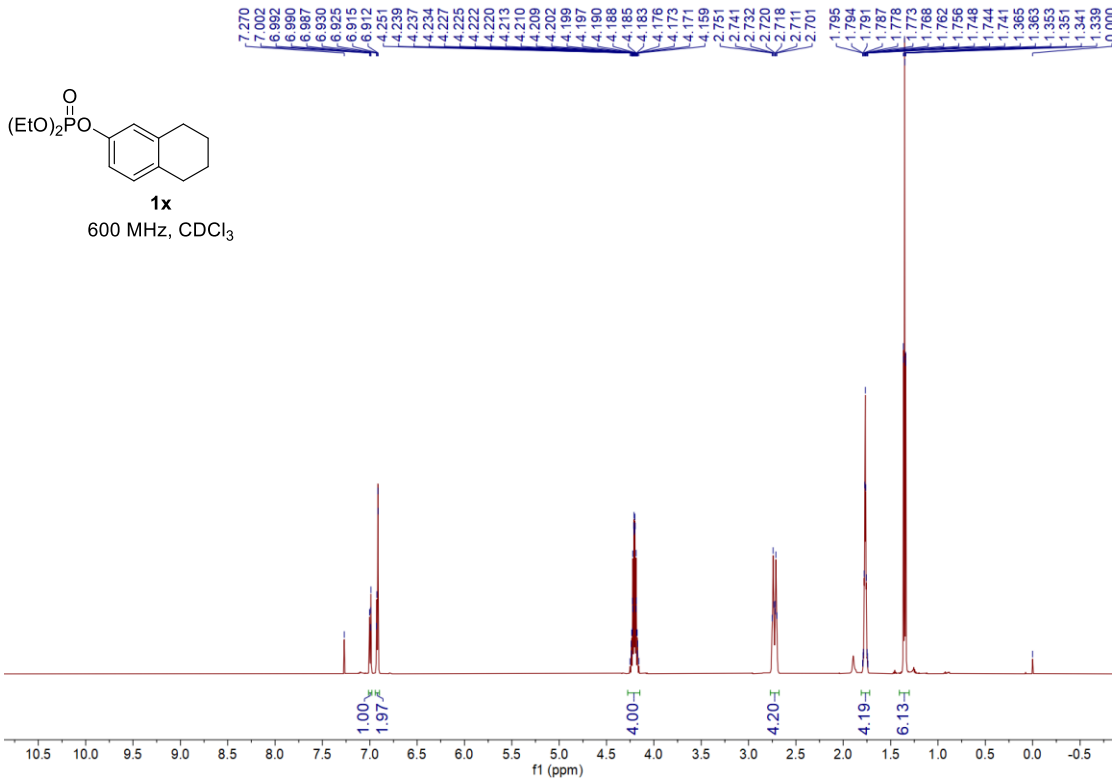
1w

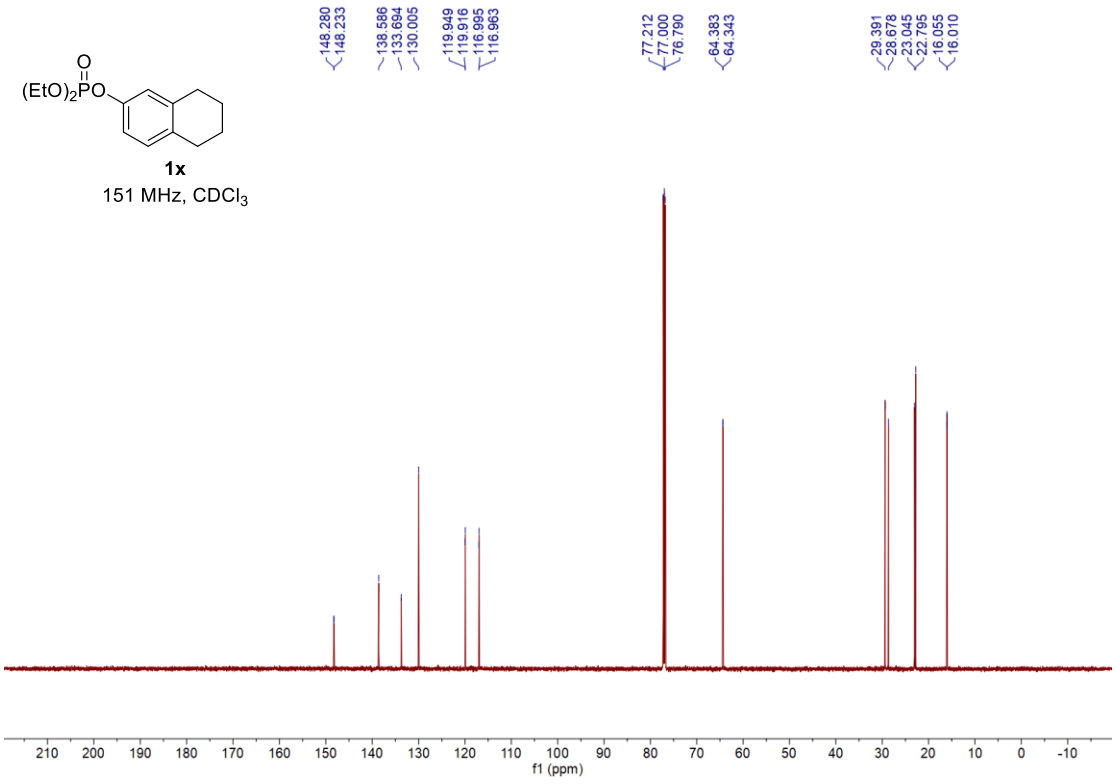
151 MHz, $CDCl_3$

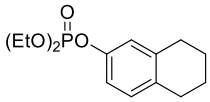


1w

243 MHz, $CDCl_3$

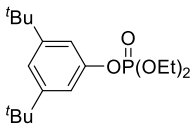

(EtO)2PO
1x
600 MHz, CDCl3
7.270
7.002
6.992
6.990
6.987
6.930
6.925
6.915
6.912
4.251
4.239
4.237
4.234
4.227
4.225
4.222
4.220
4.213
4.210
4.209
4.202
4.199
4.197
4.190
4.188
4.185
4.183
4.176
4.173
4.171
4.159
2.751
2.741
2.732
2.720
2.718
2.711
2.701
1.795
1.794
1.791
1.787
1.778
1.773
1.768
1.762
1.756
1.748
1.744
1.741
1.365
1.363
1.353
1.351
1.341
1.339
1.00
1.97
4.00
4.20
4.19
6.13
f1 (ppm)


(EtO)2PO
1x
151 MHz, CDCl3
148.280
148.233
138.586
133.694
130.005
119.949
119.816
116.995
116.963
77.212
77.000
76.790
64.383
64.343
29.391
28.678
23.045
22.795
16.055
16.010
f1 (ppm)



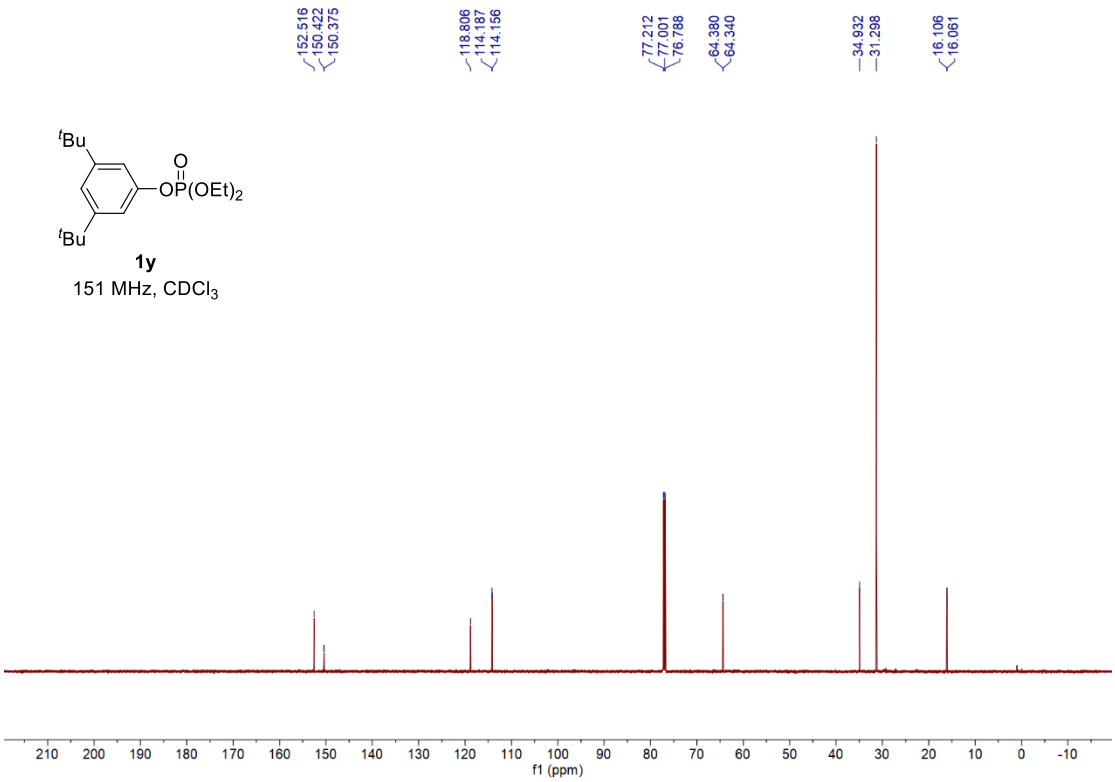
1x

243 MHz, $CDCl_3$



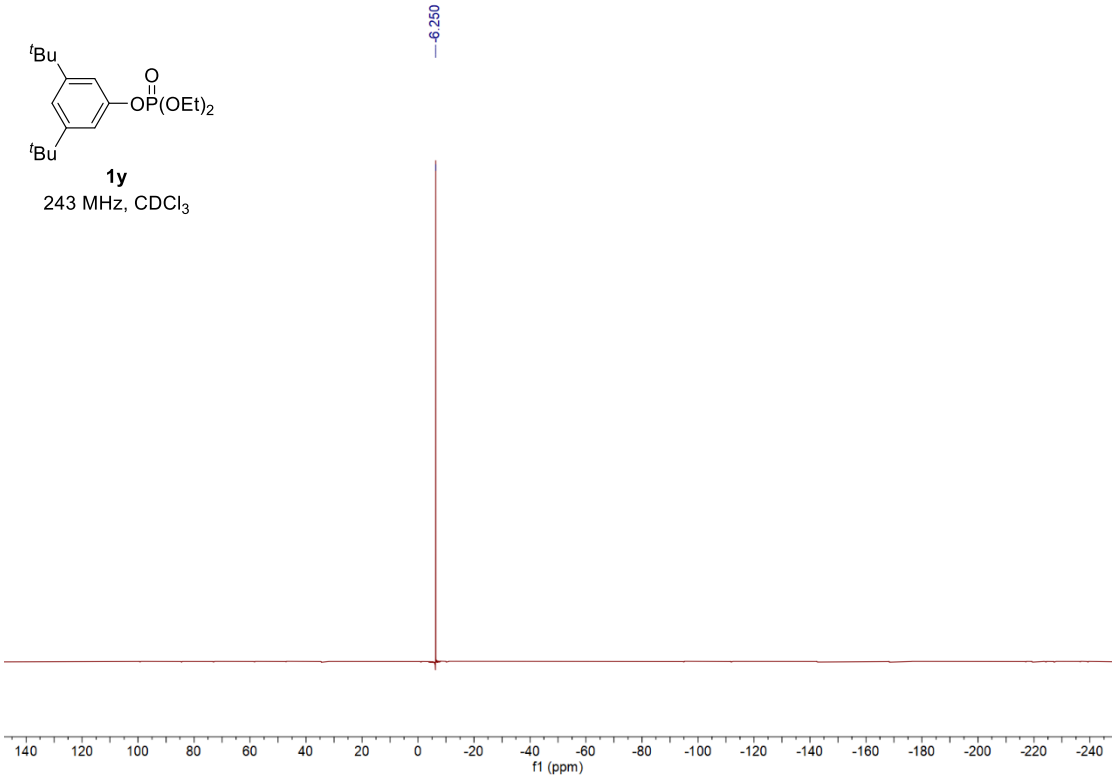
1y

600 MHz, $CDCl_3$



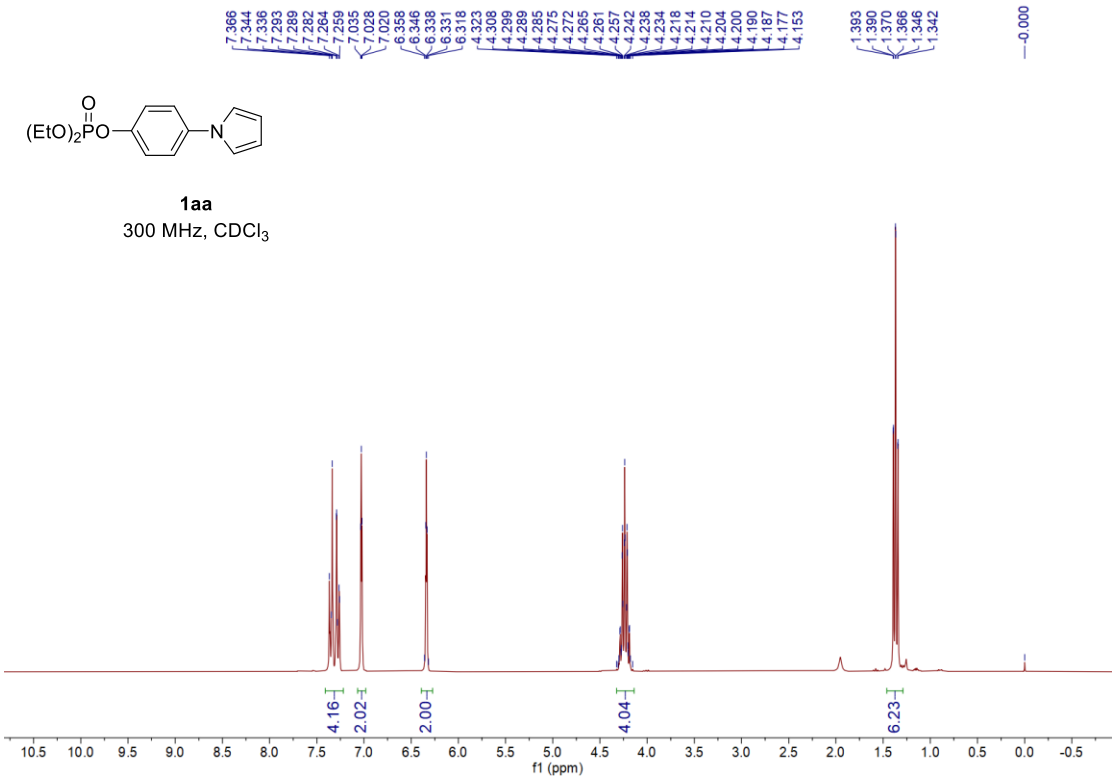
1y

151 MHz, $CDCl_3$



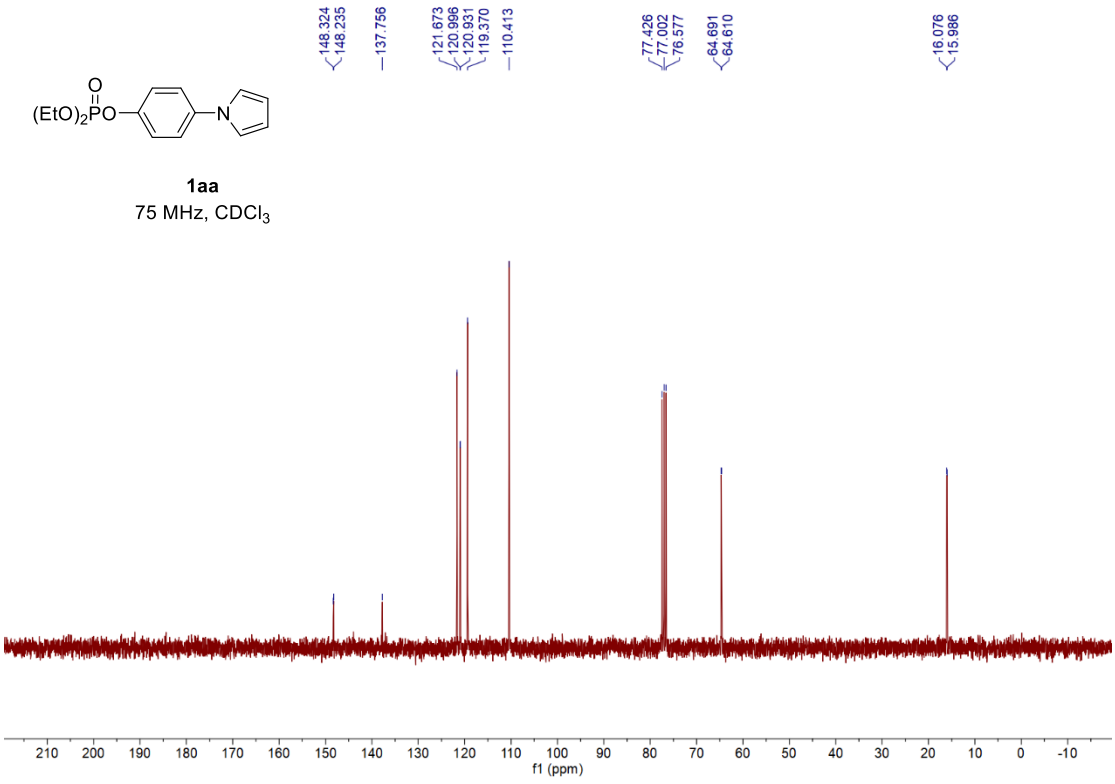
1y

243 MHz, $CDCl_3$



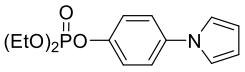
1aa

300 MHz, $CDCl_3$



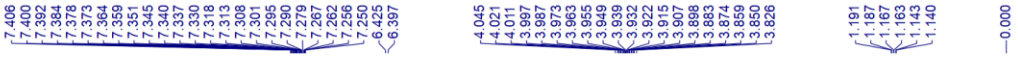
1aa

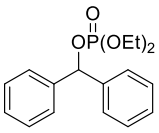
75 MHz, $CDCl_3$



1aa

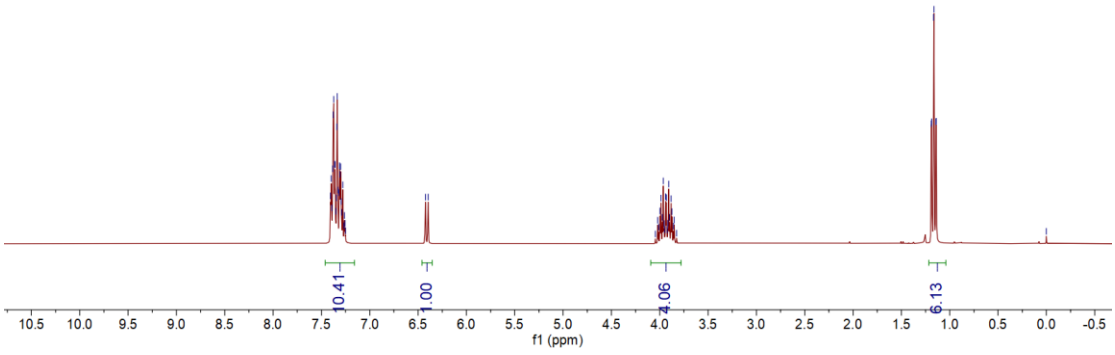
243 MHz, $CDCl_3$

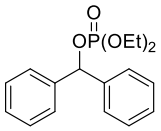




1ab

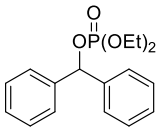
300 MHz, $CDCl_3$





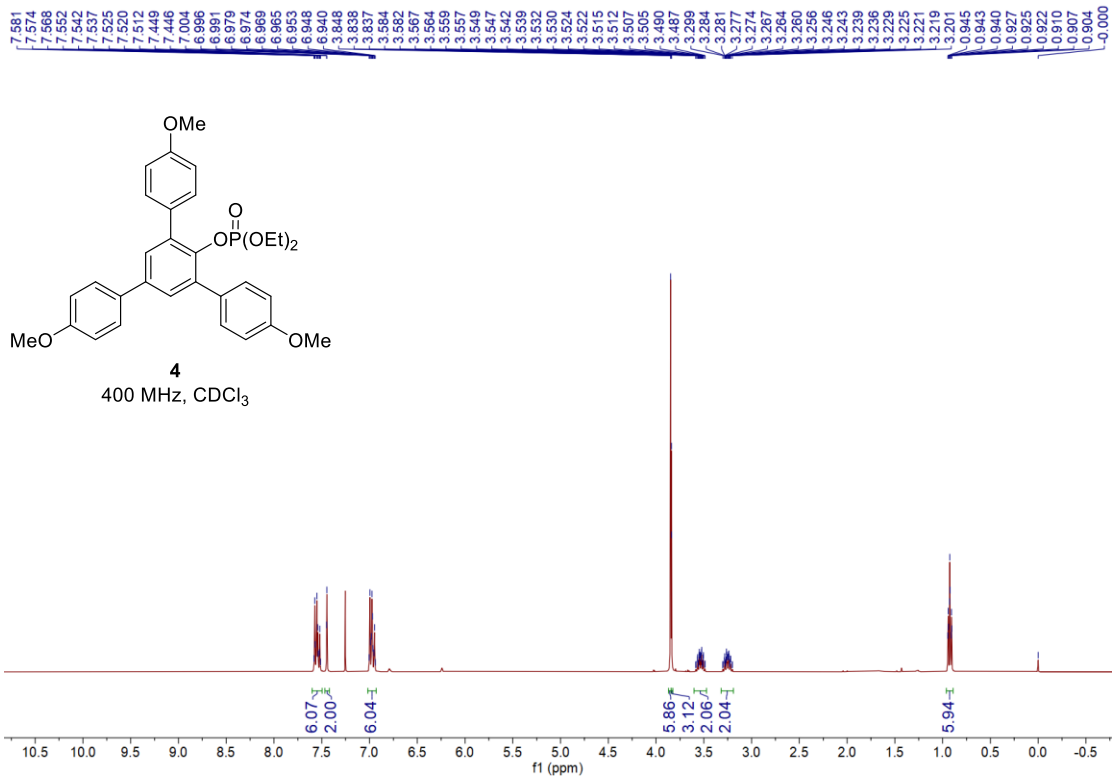
1ab

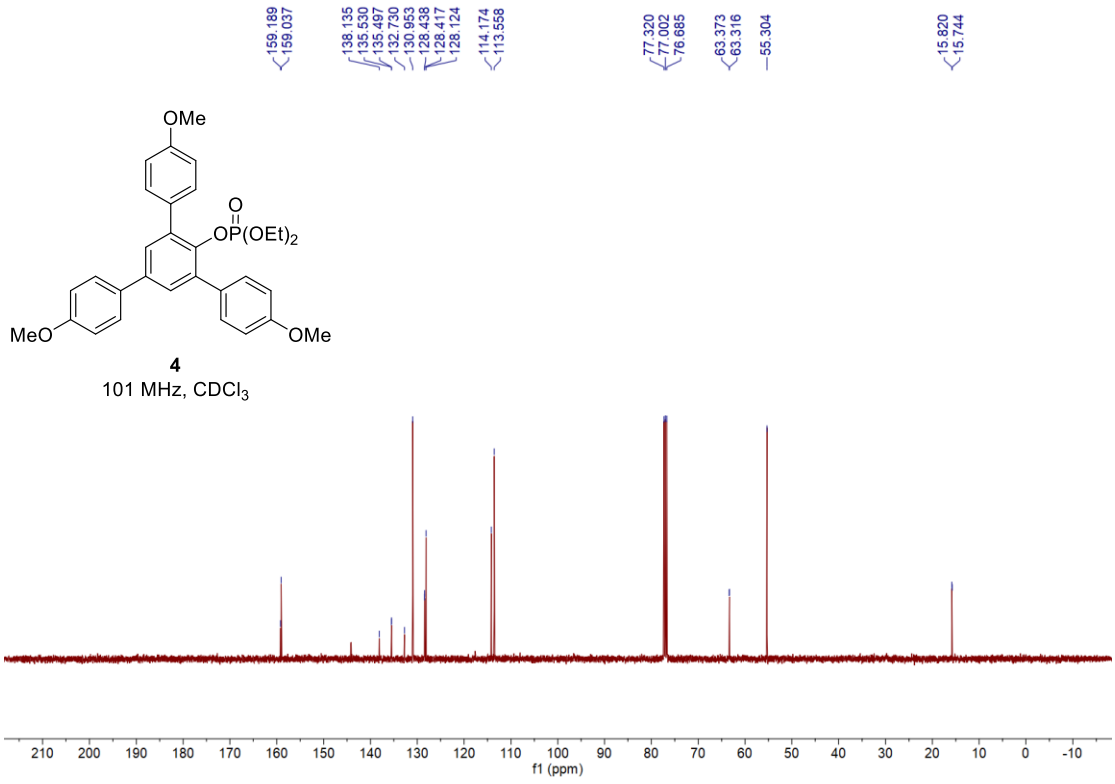
75 MHz, $CDCl_3$

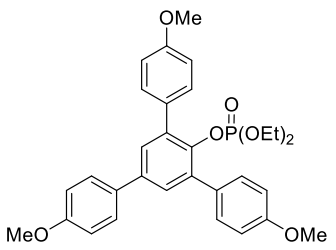


1ab

243 MHz, $CDCl_3$

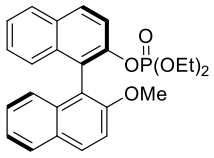

OMe
O
OP(OEt)2
MeO
OMe
4
400 MHz, CDCl3
6.07
2.00
6.04
5.86
3.12
2.06
2.04
5.94
f1 (ppm)


OMe
O
OP(OEt)2
MeO
OMe
4
101 MHz, CDCl3
f1 (ppm)



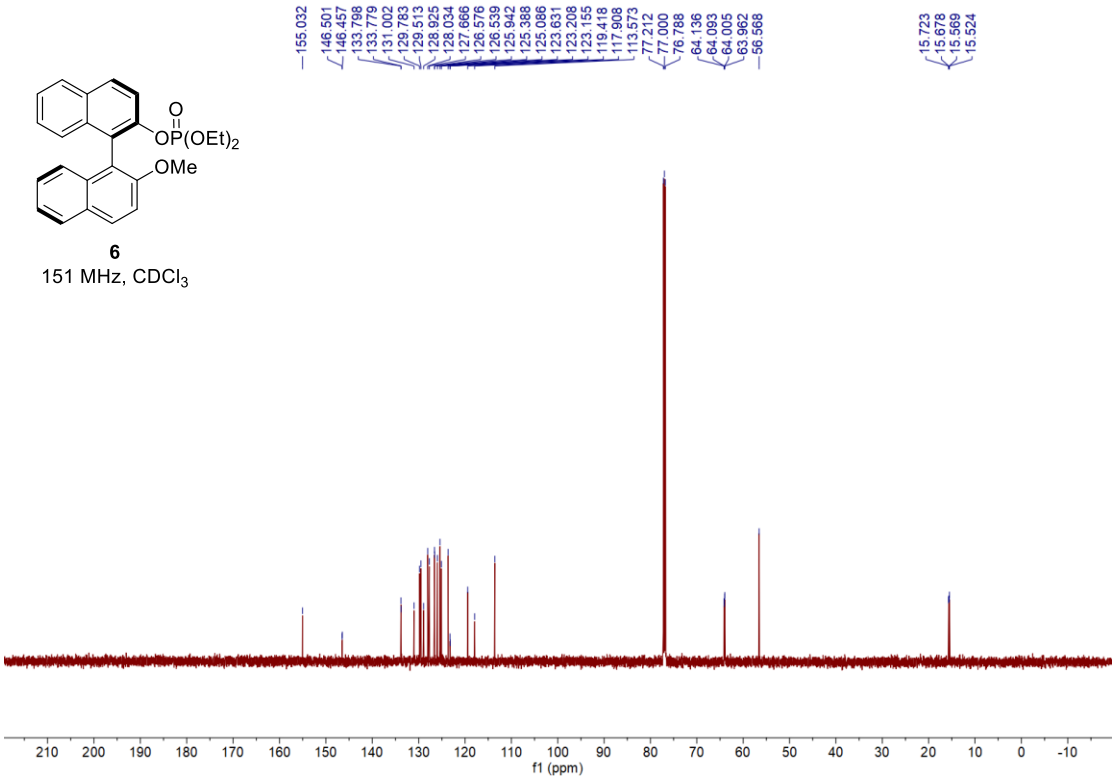
4

243 MHz, $CDCl_3$



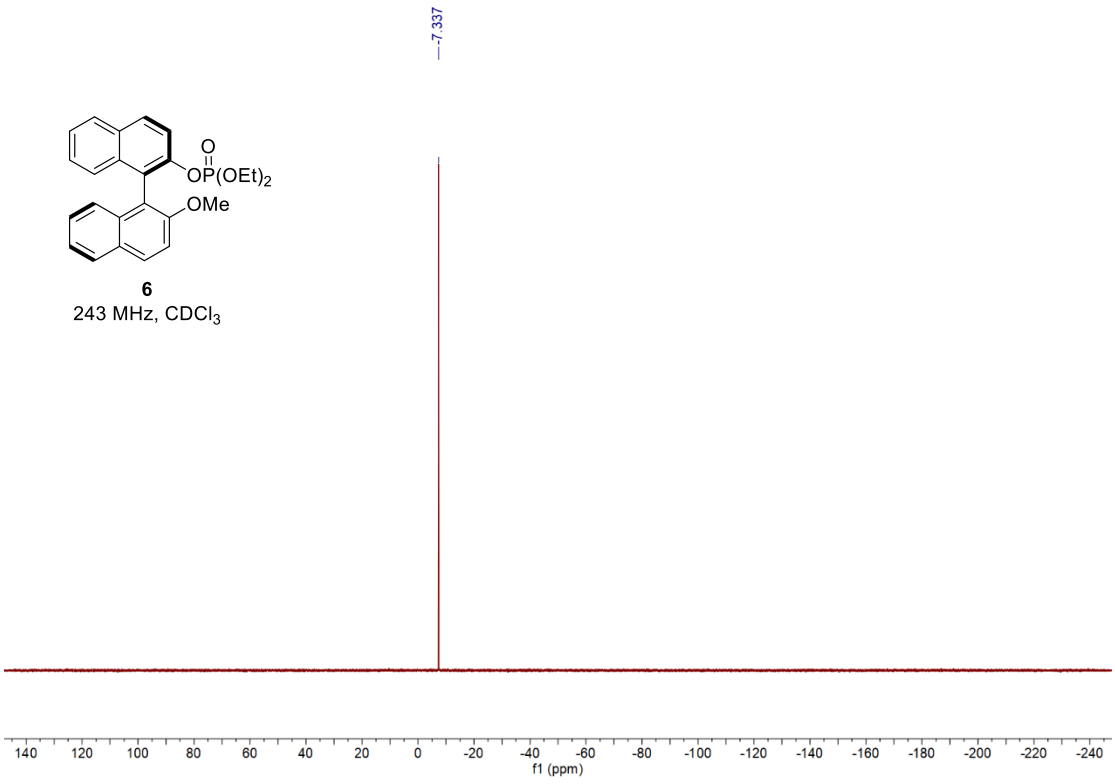
6

600 MHz, $CDCl_3$



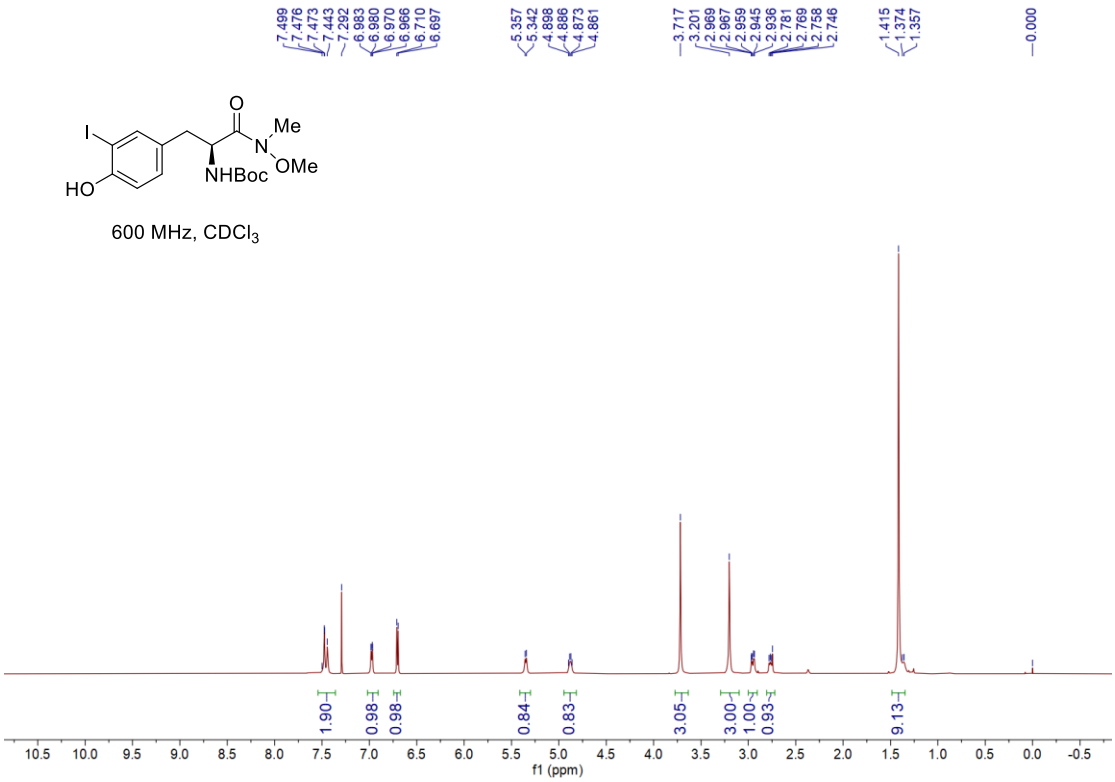
6

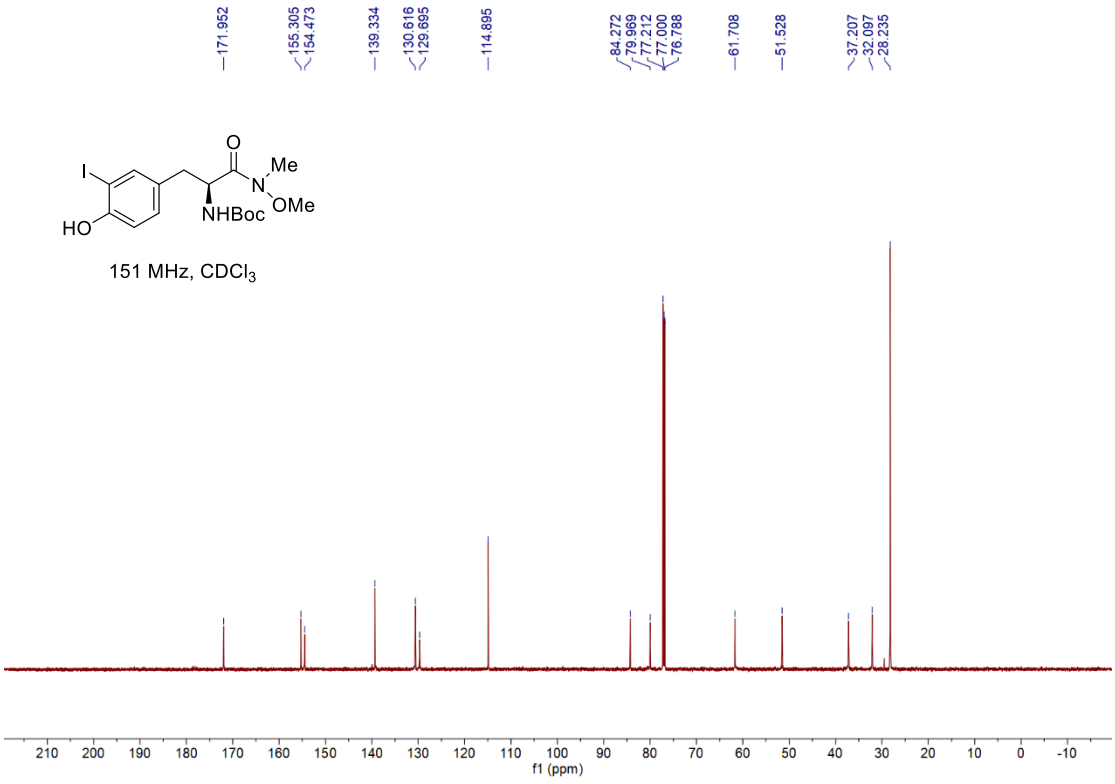
151 MHz, $CDCl_3$

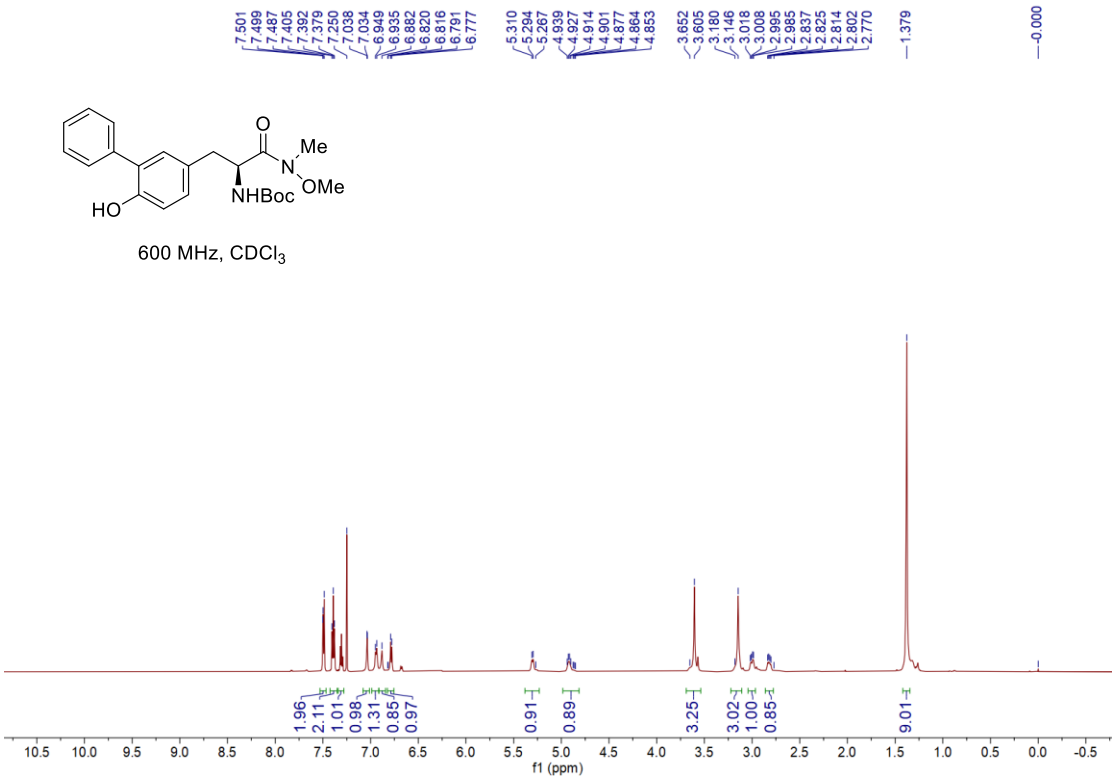


6

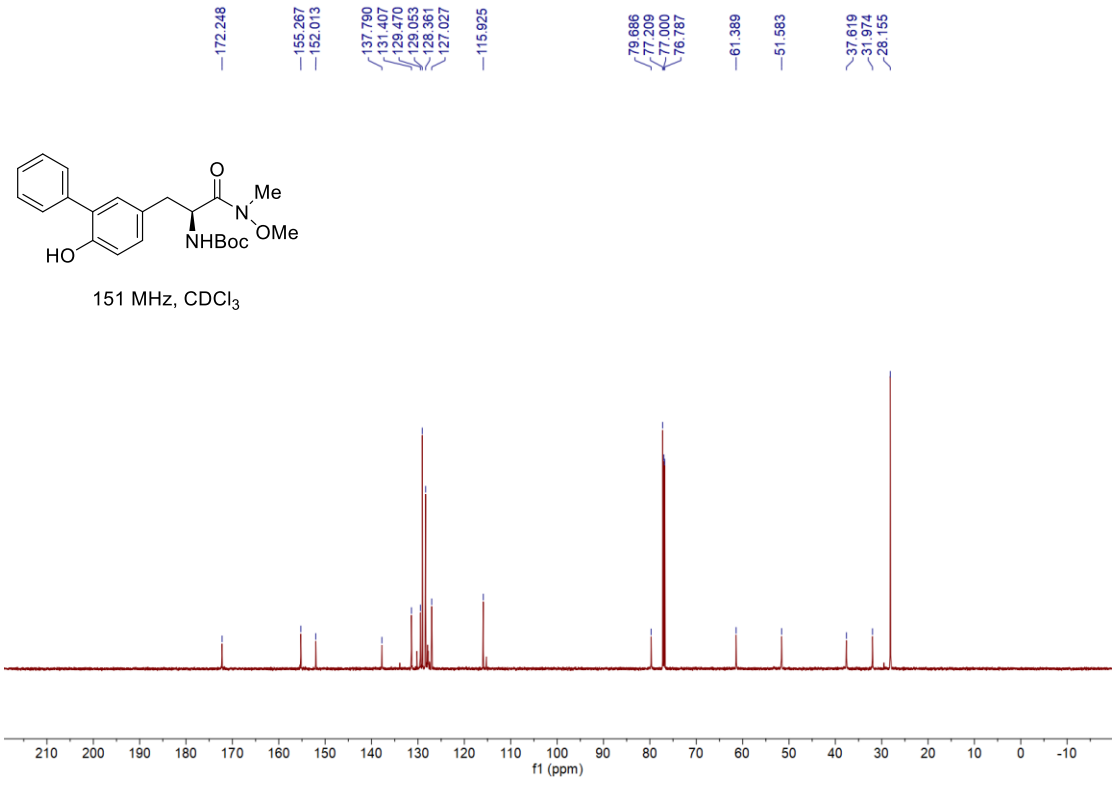
243 MHz, $CDCl_3$


7.499
7.476
7.473
7.443
7.292
6.983
6.980
6.970
6.966
6.710
6.697
5.357
5.342
4.888
4.886
4.873
4.861
3.717
3.201
2.969
2.967
2.959
2.945
2.936
2.781
2.769
2.758
2.746
1.415
1.374
1.357
0.000
I
HO
O
N
Me
OMe
NHBoc
600 MHz, CDCl3
1.90
0.98
0.98
0.84
0.83
3.05
3.00
1.00
0.93
9.13
f1 (ppm)

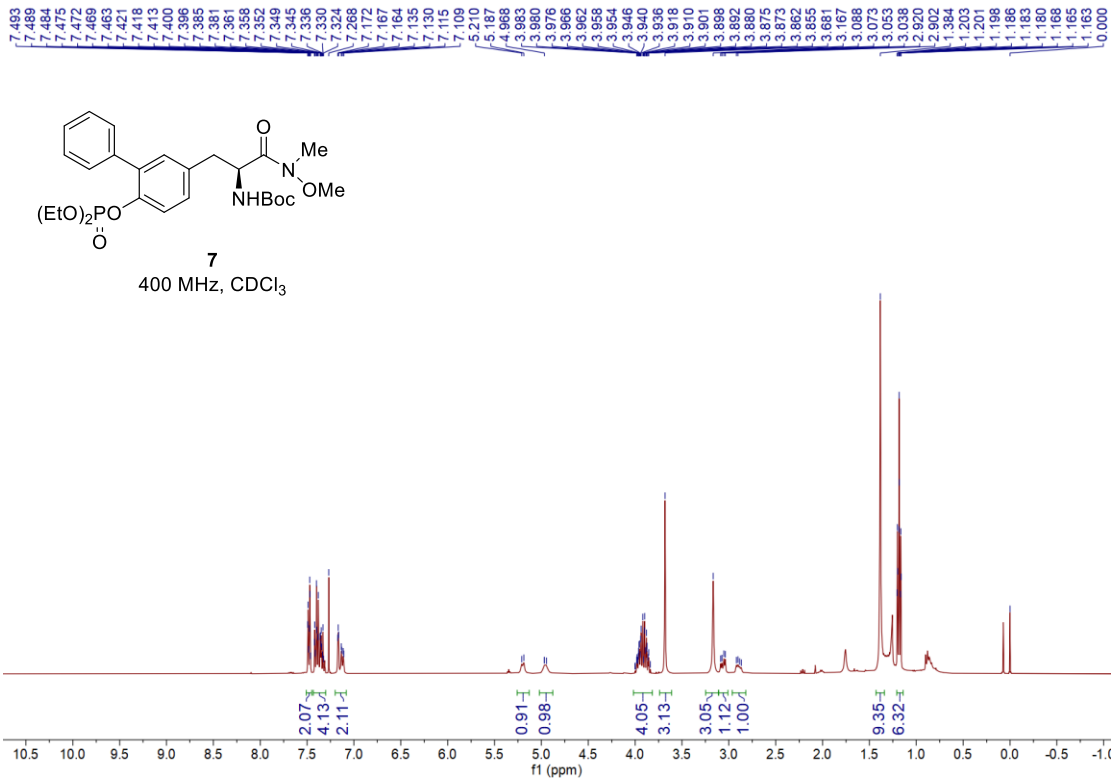

171.952
155.305
154.473
139.334
130.616
129.695
114.895
84.272
79.969
77.212
77.000
76.788
61.708
51.528
37.207
32.097
28.235
I
HO
O
N
Me
OMe
NHBoc
151 MHz, CDCl3
f1 (ppm)

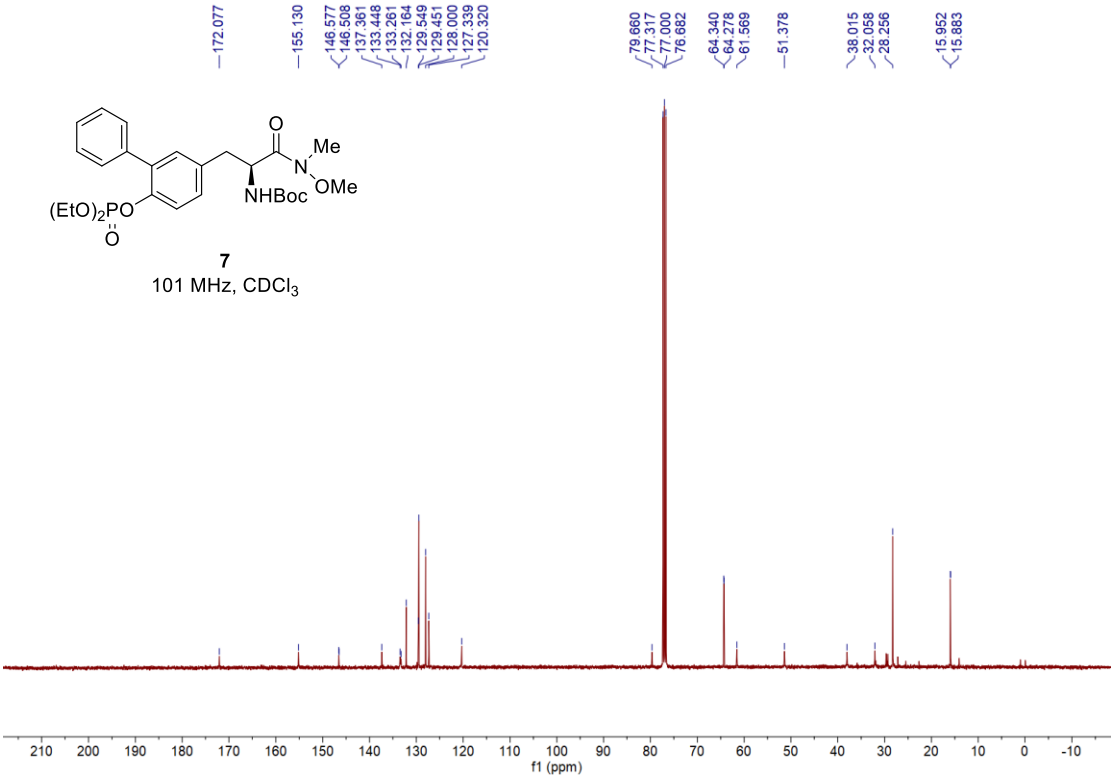


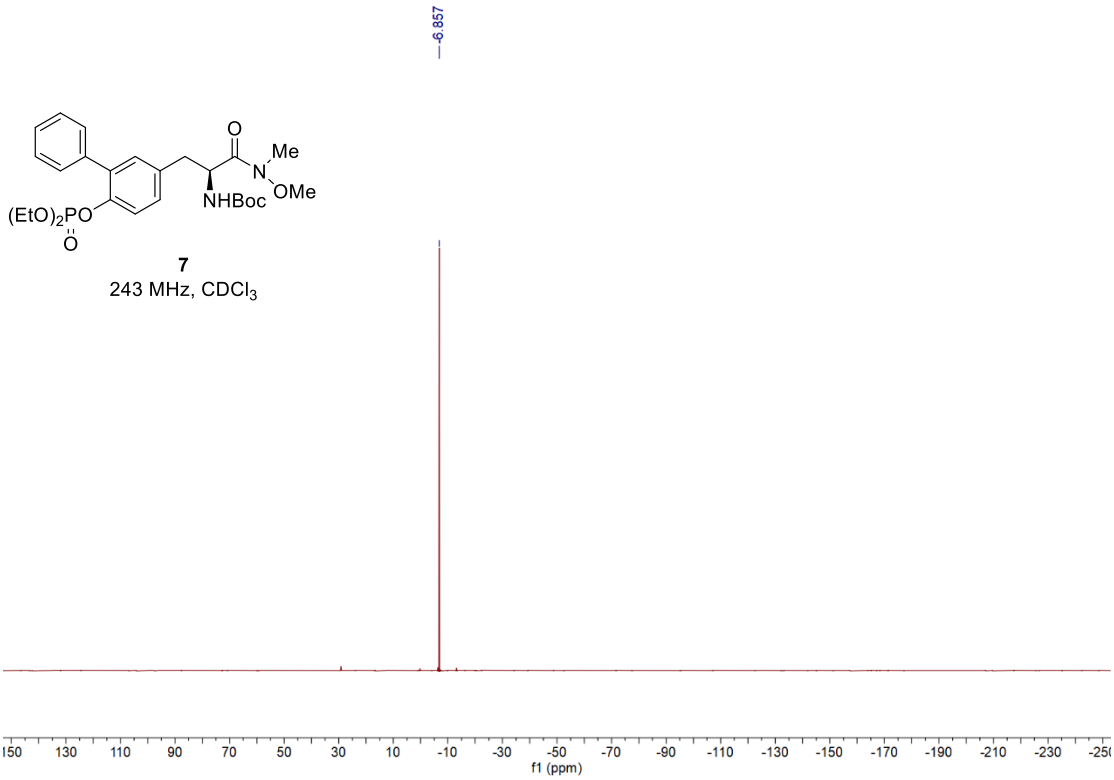
600 MHz, $CDCl_3$



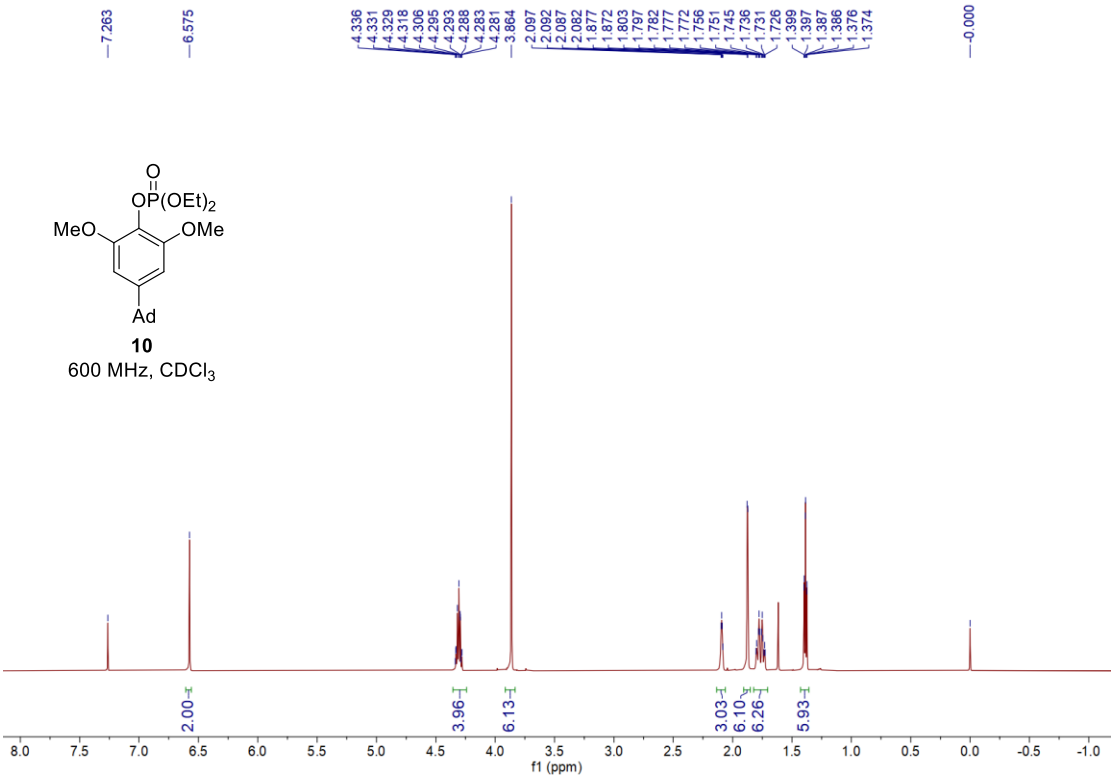
151 MHz, $CDCl_3$


7.493 7.489 7.484 7.475 7.472 7.469 7.463 7.421 7.418 7.413 7.400 7.396 7.385 7.381 7.361 7.358 7.352 7.349 7.345 7.336 7.330 7.324 7.268 7.172 7.167 7.164 7.135 7.130 7.115 7.109 5.210 5.187 4.968 3.983 3.980 3.976 3.966 3.962 3.958 3.954 3.946 3.940 3.936 3.918 3.910 3.901 3.898 3.892 3.880 3.875 3.873 3.862 3.855 3.681 3.167 3.088 3.073 3.053 3.038 2.920 2.902 1.384 1.203 1.201 1.198 1.186 1.183 1.180 1.168 1.165 1.163 0.000
O
Me
N
OMe
NHBoc
(EtO)2PO
O
7
400 MHz, CDCl3
2.07 4.13 2.11 0.91 0.98 4.05 3.13 3.05 1.12 1.00 9.35 6.32
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)

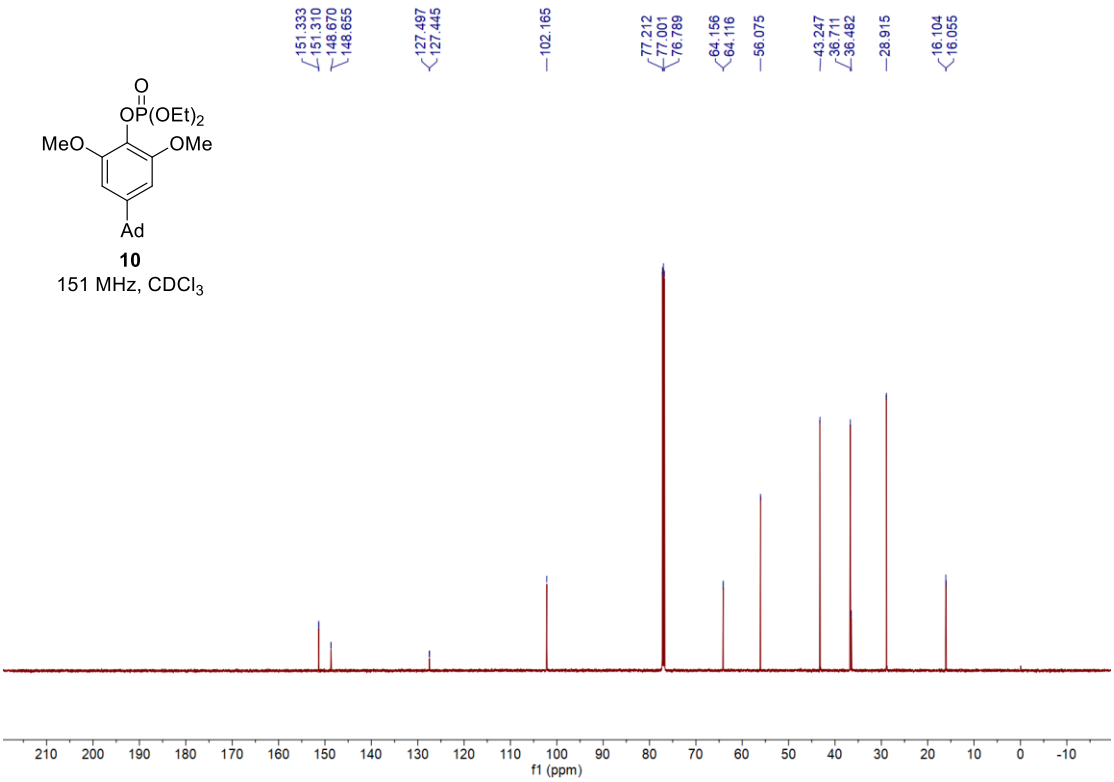

172.077 155.130 146.577 146.508 137.361 133.448 133.261 132.164 129.549 129.451 128.000 127.339 120.320 79.660 77.317 77.000 76.682 64.340 64.278 61.569 51.378 38.015 32.058 28.256 15.952 15.883
O
Me
N
OMe
NHBoc
(EtO)2PO
O
7
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7
243 MHz, $CDCl_3$

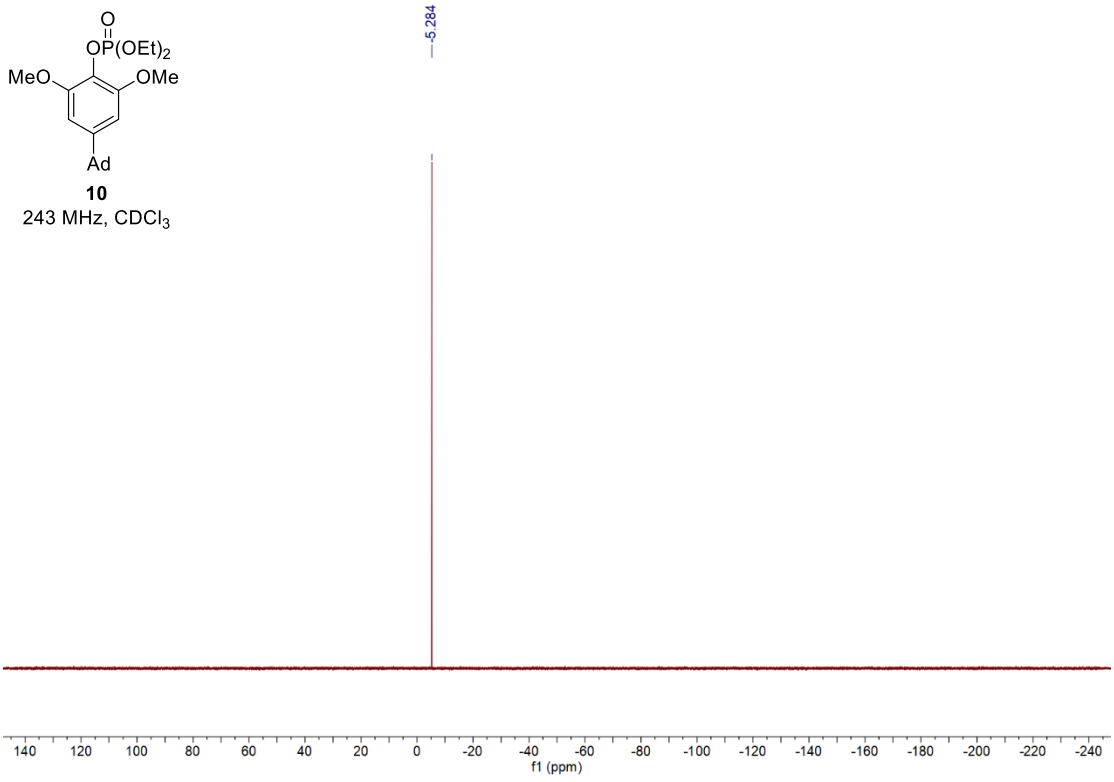


10
600 MHz, $CDCl_3$



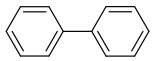
10

151 MHz, $CDCl_3$

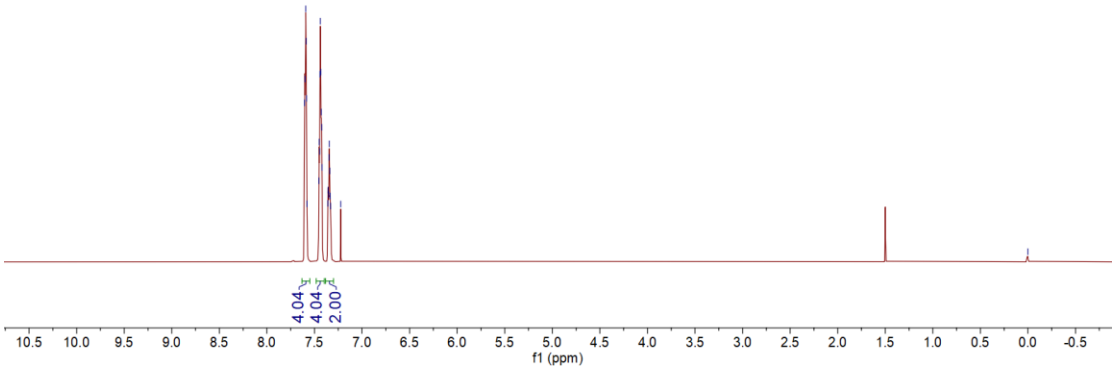


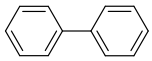
10

243 MHz, $CDCl_3$

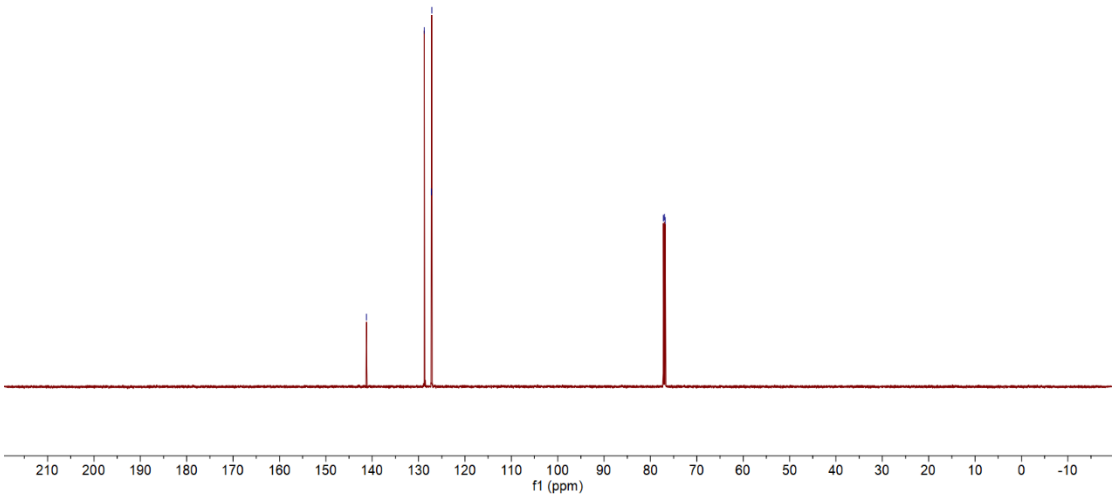


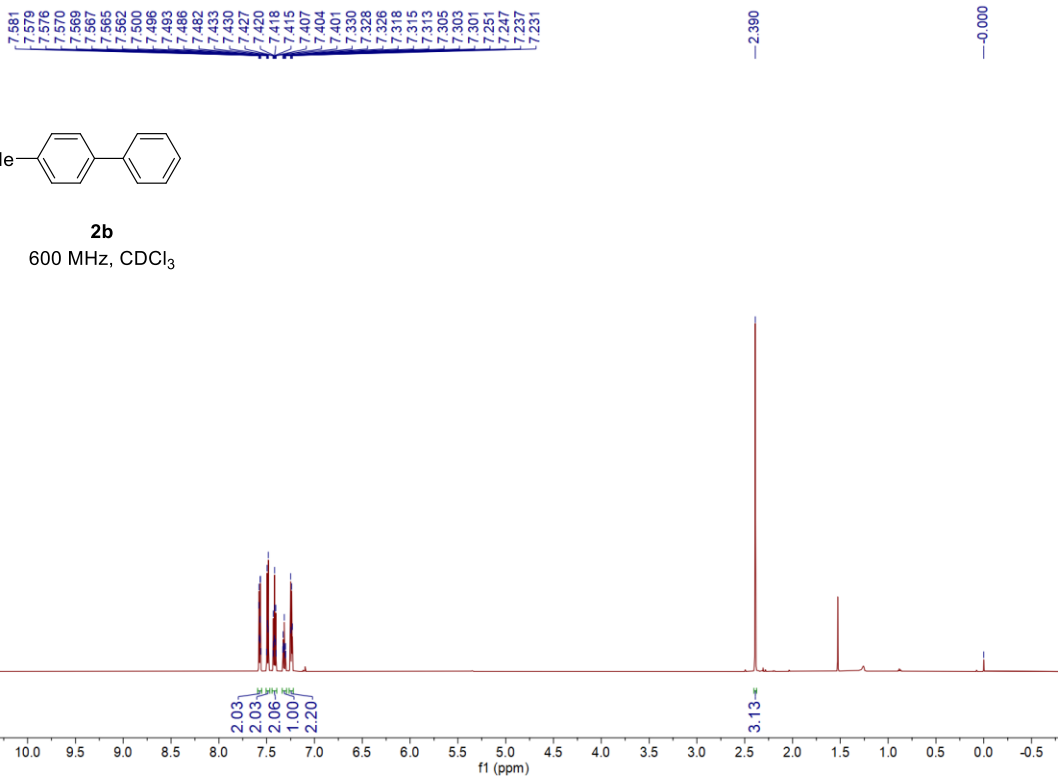
2a
600 MHz, $CDCl_3$



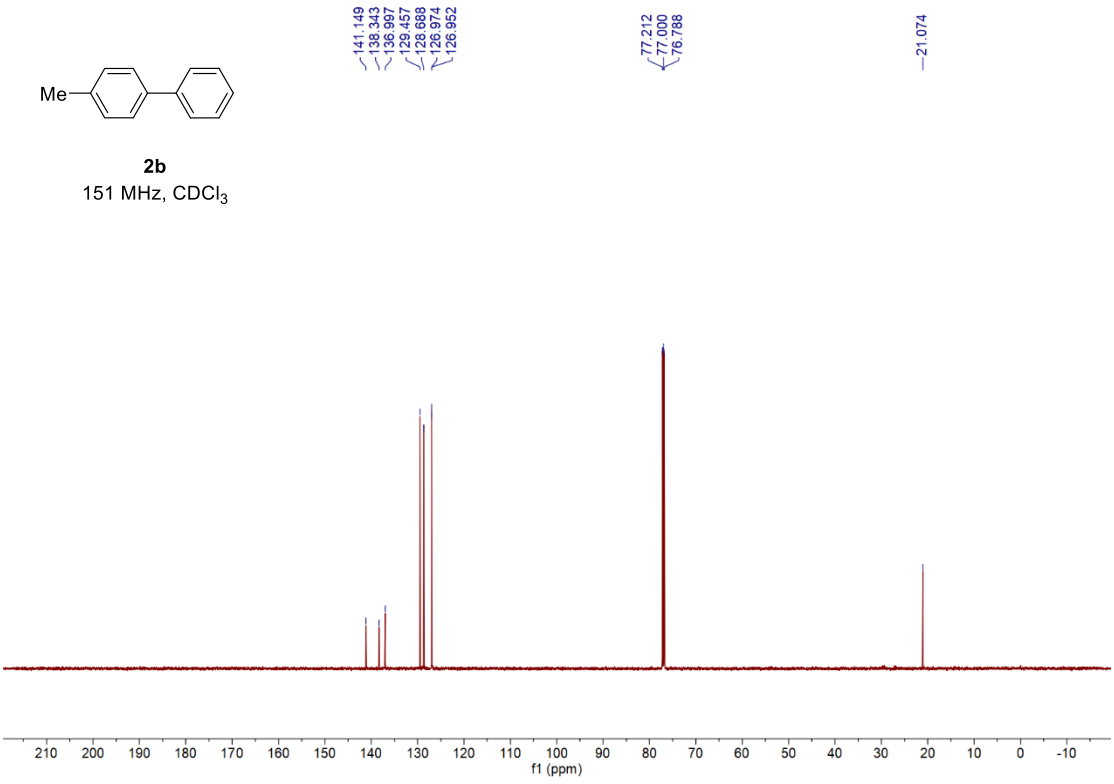


2a
151 MHz, $CDCl_3$

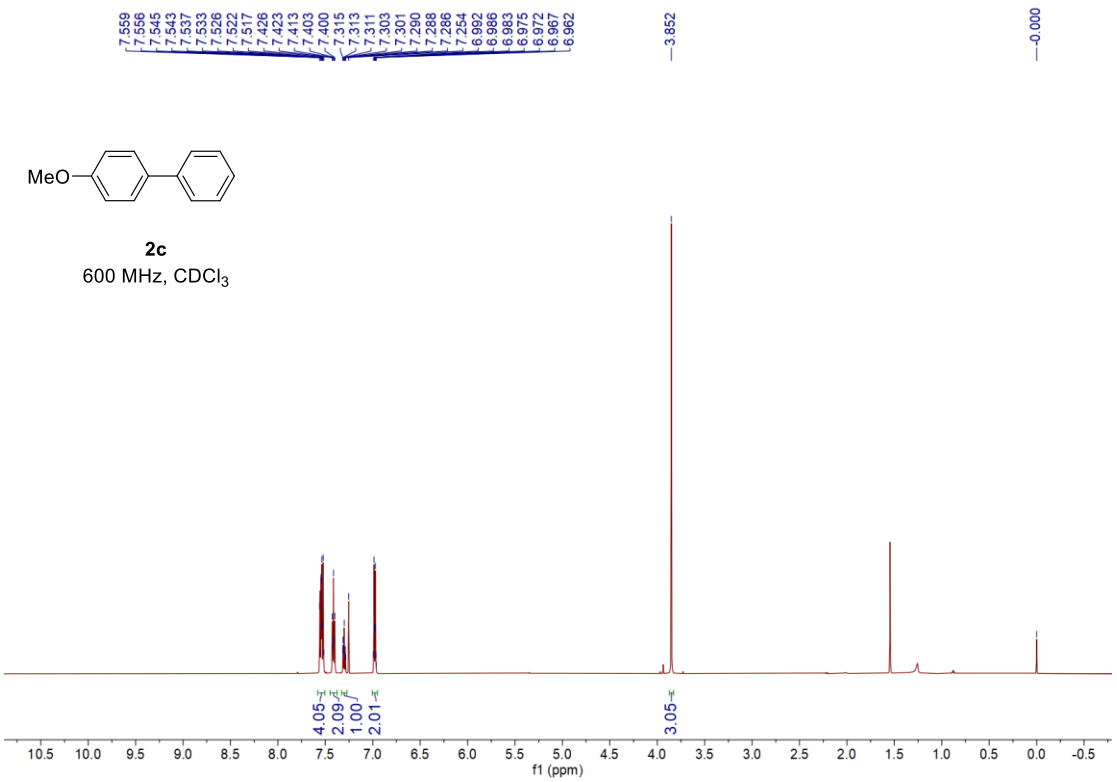




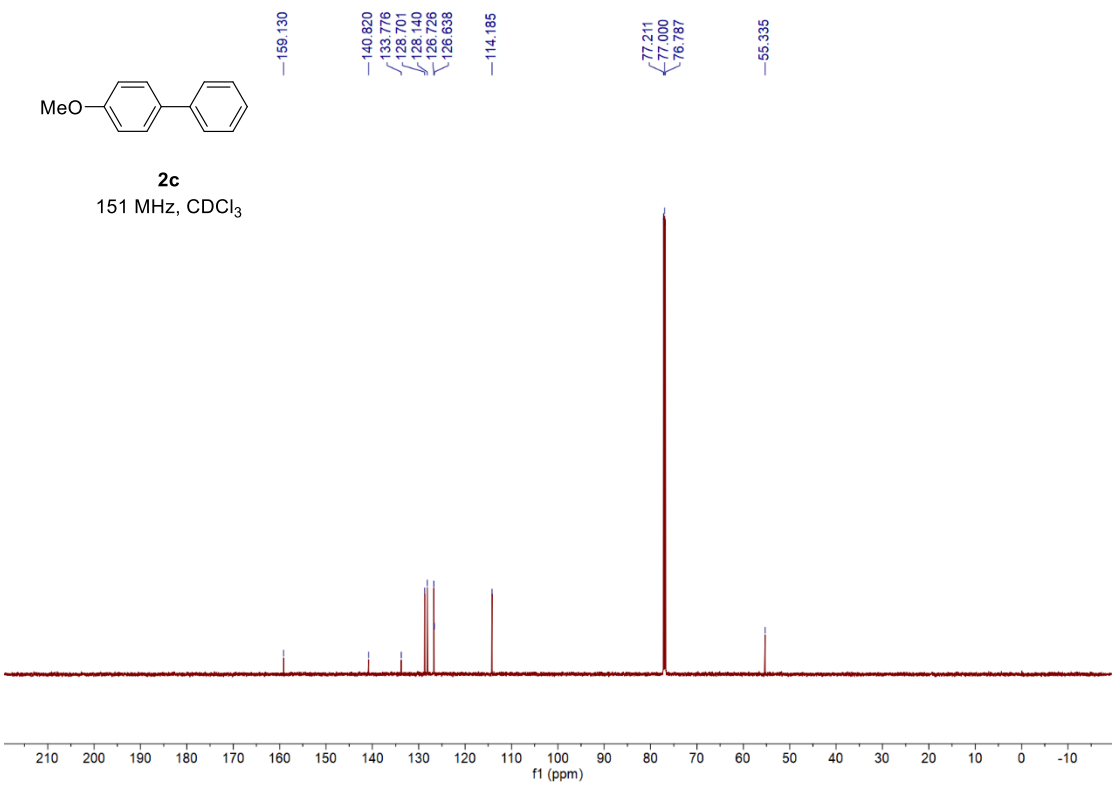
2b
600 MHz, $CDCl_3$



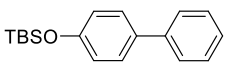
2b
151 MHz, $CDCl_3$



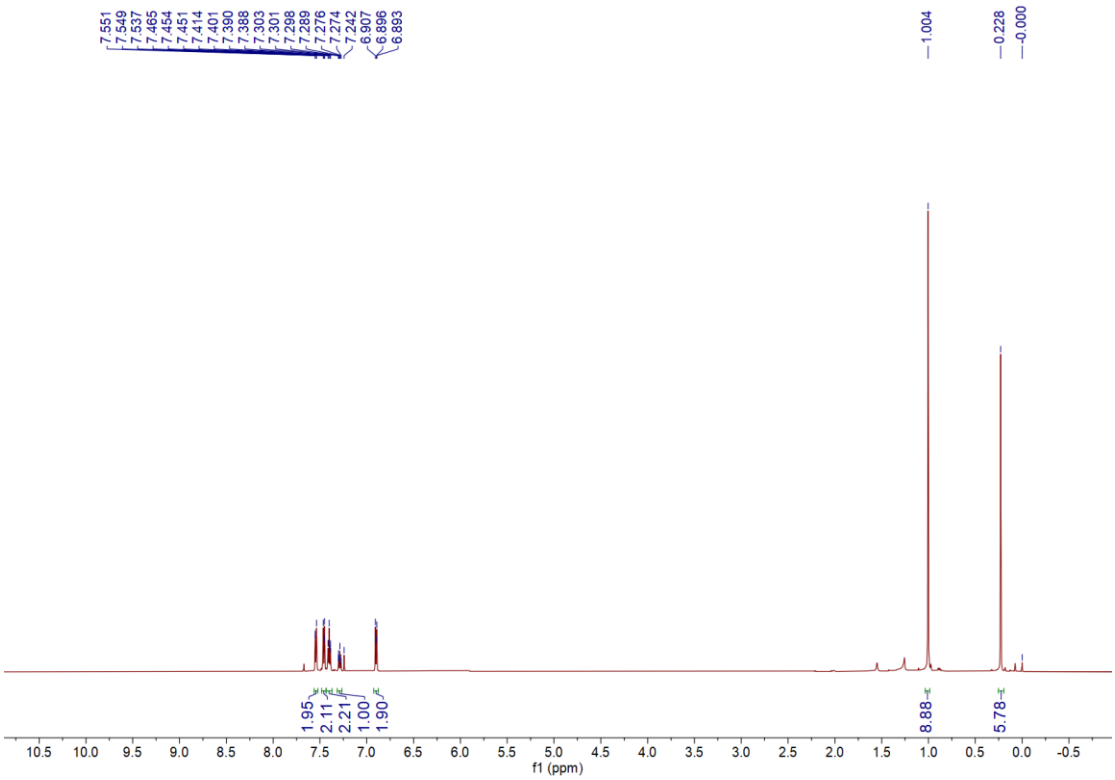
2c
600 MHz, $CDCl_3$

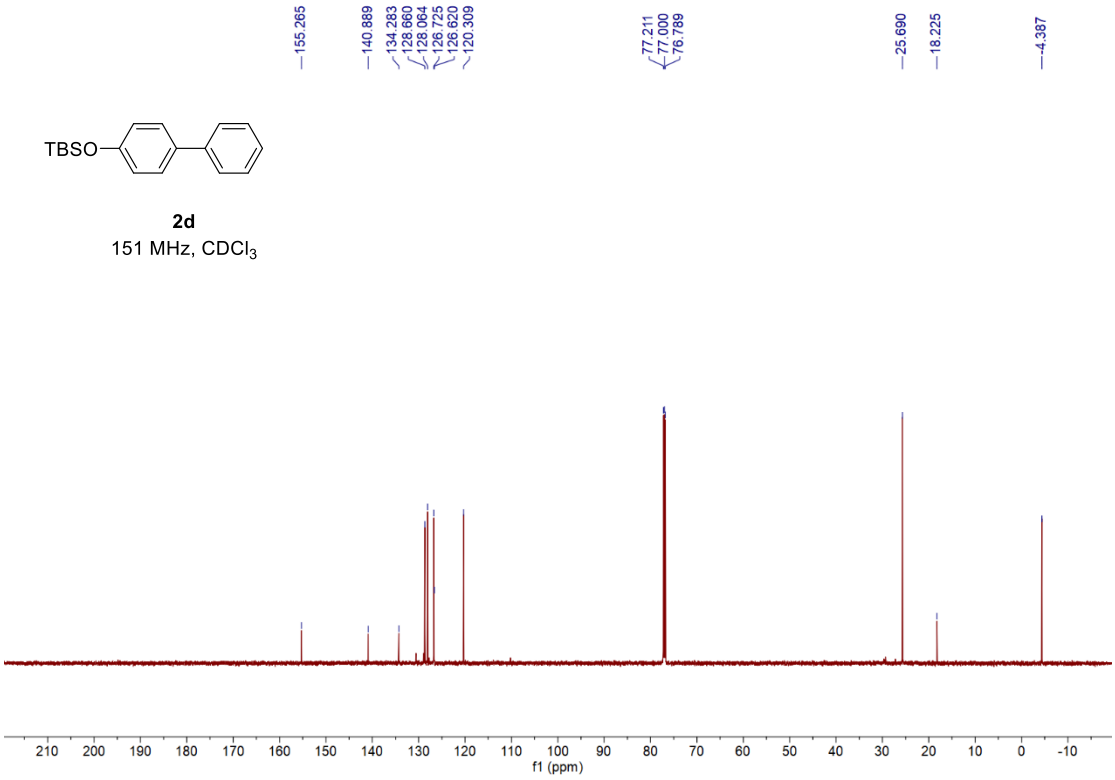


2c
151 MHz, $CDCl_3$



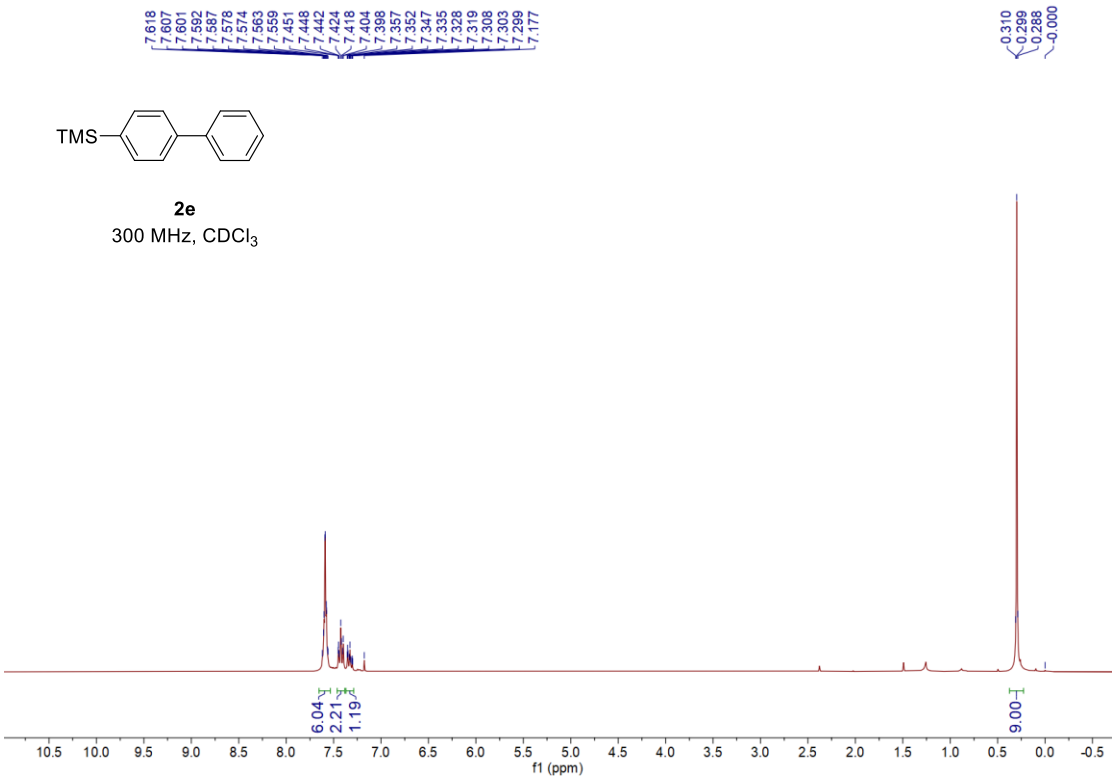
2d
600 MHz, $CDCl_3$





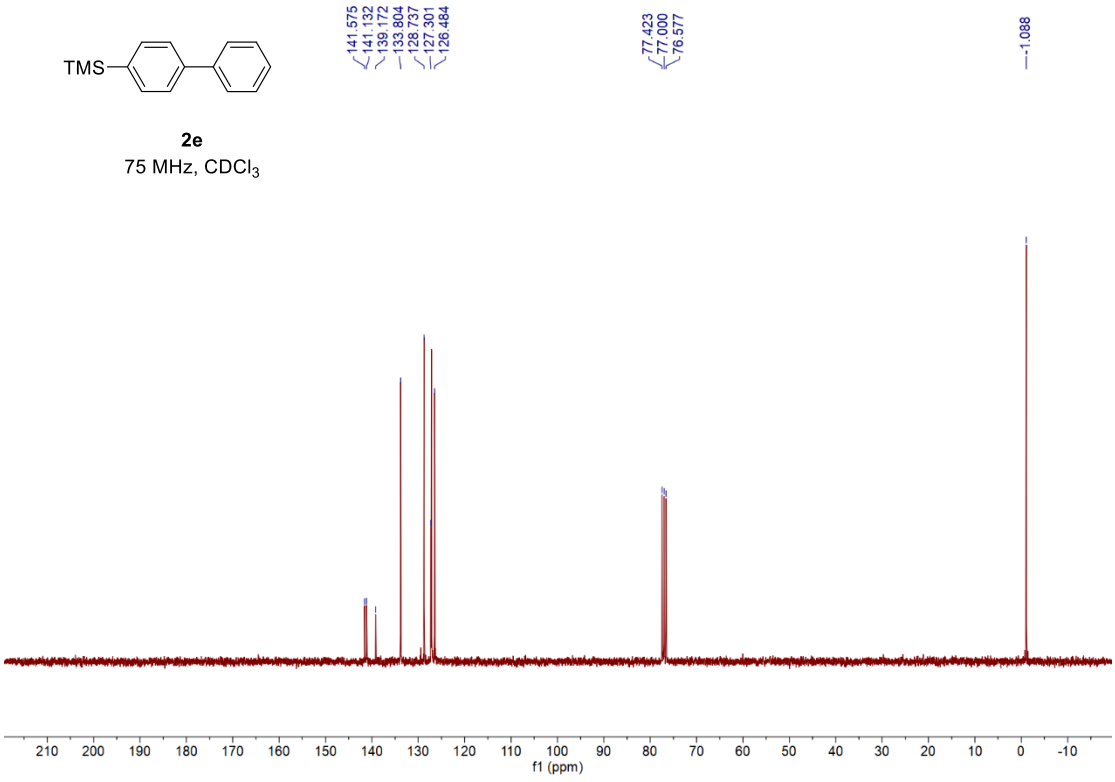
2d

151 MHz, $CDCl_3$



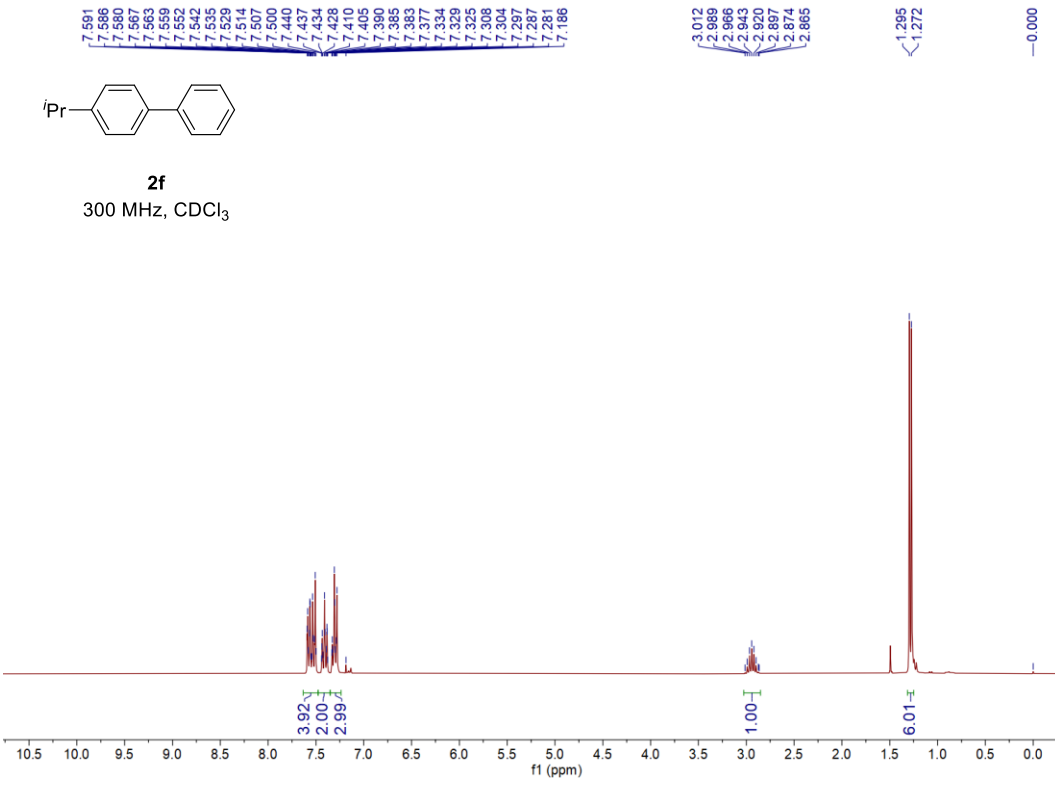
2e

300 MHz, $CDCl_3$

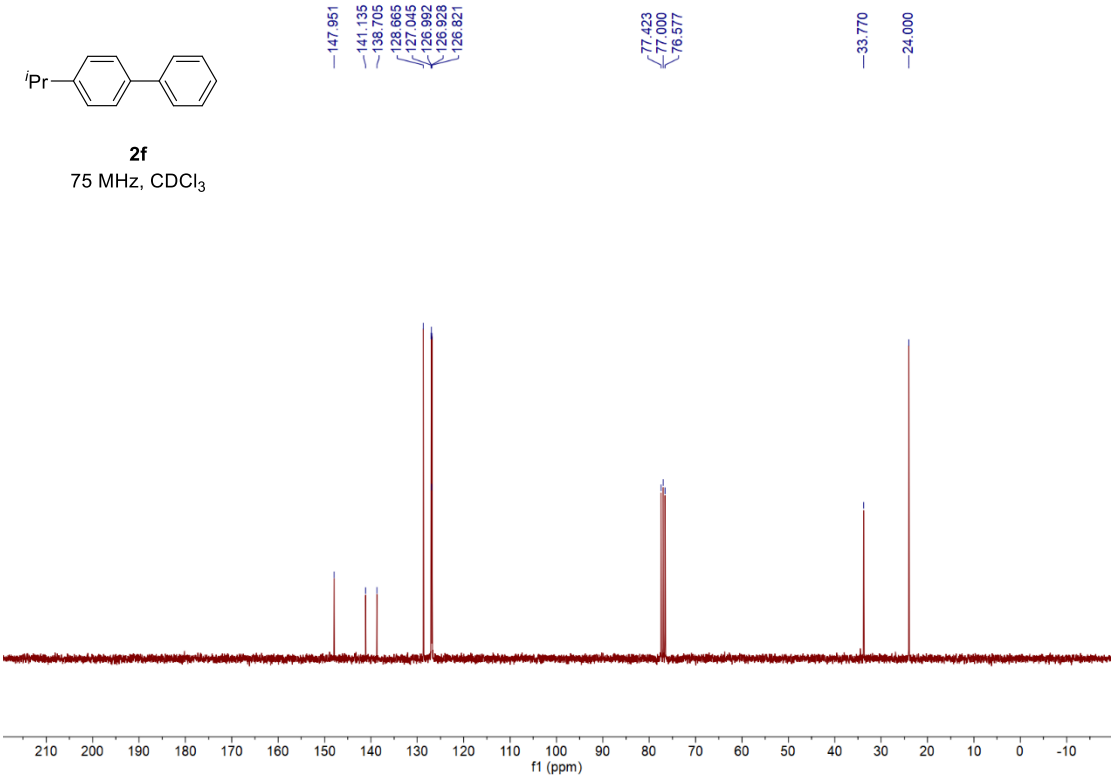


2e

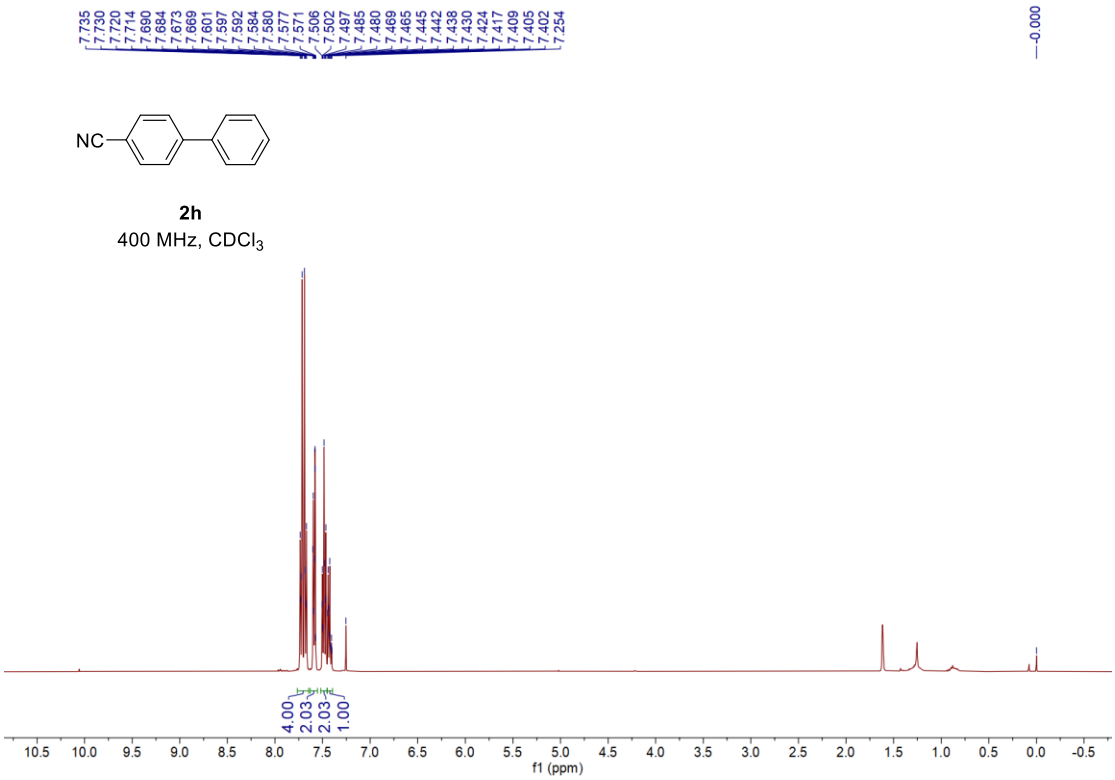
75 MHz, $CDCl_3$



2f
300 MHz, $CDCl_3$

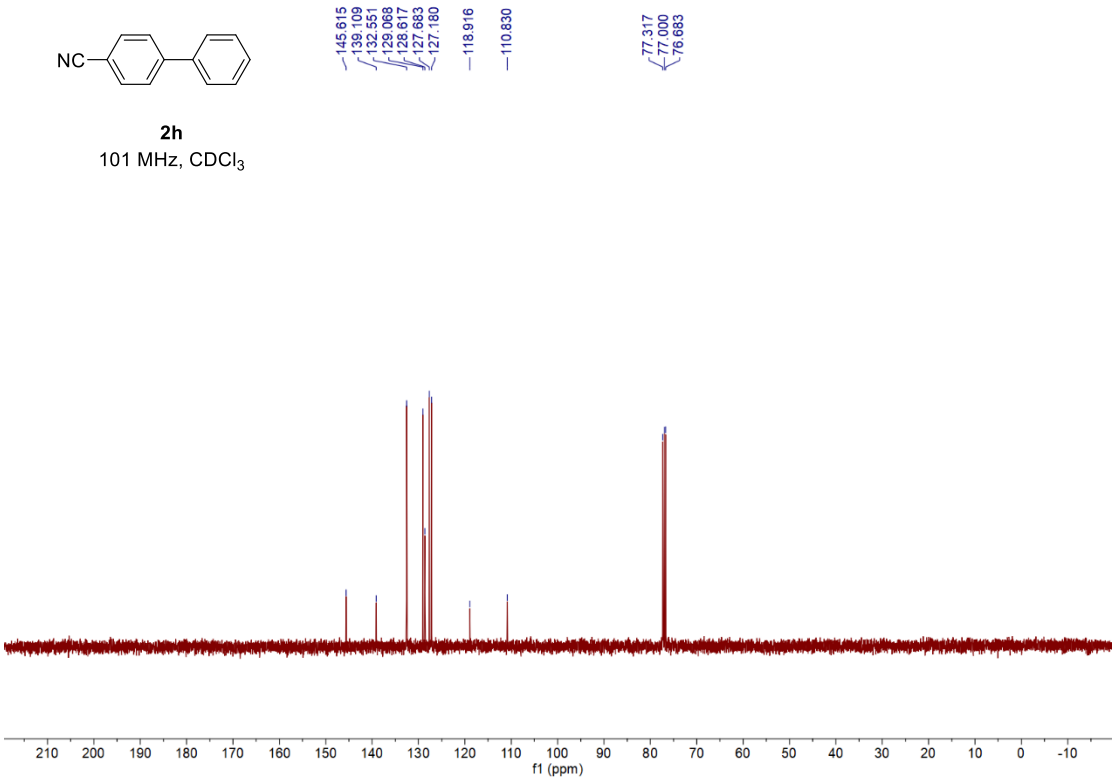


2f
75 MHz, $CDCl_3$



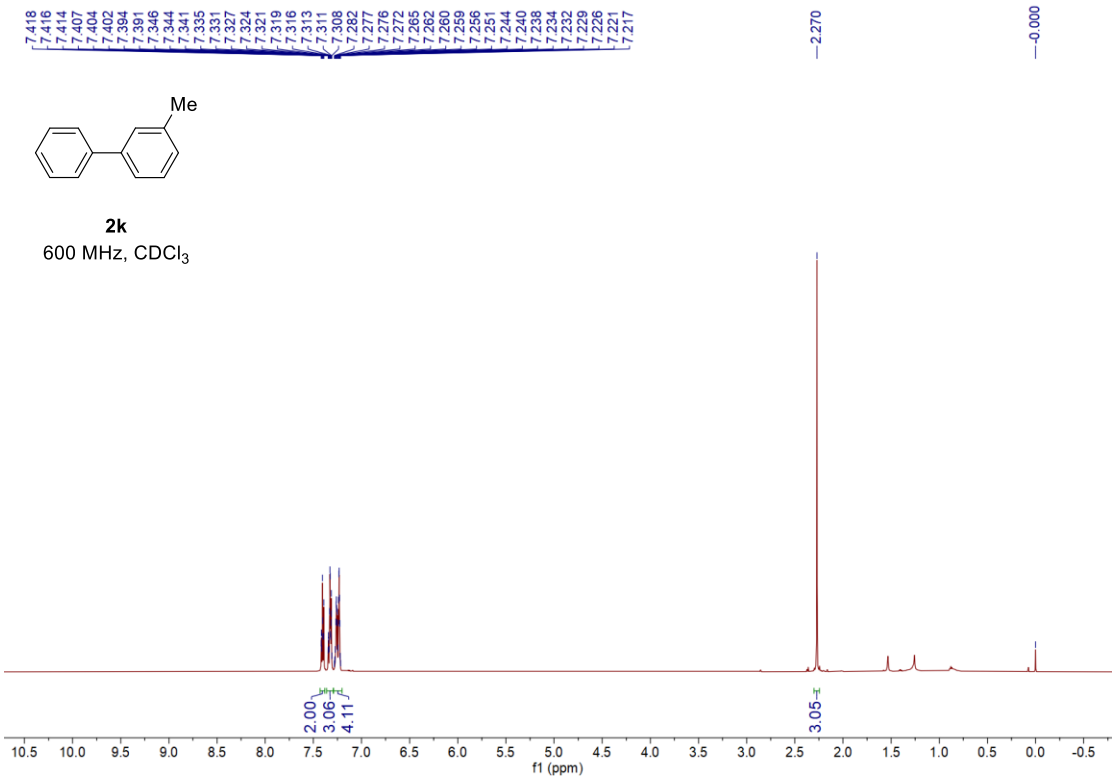
2h

400 MHz, $CDCl_3$

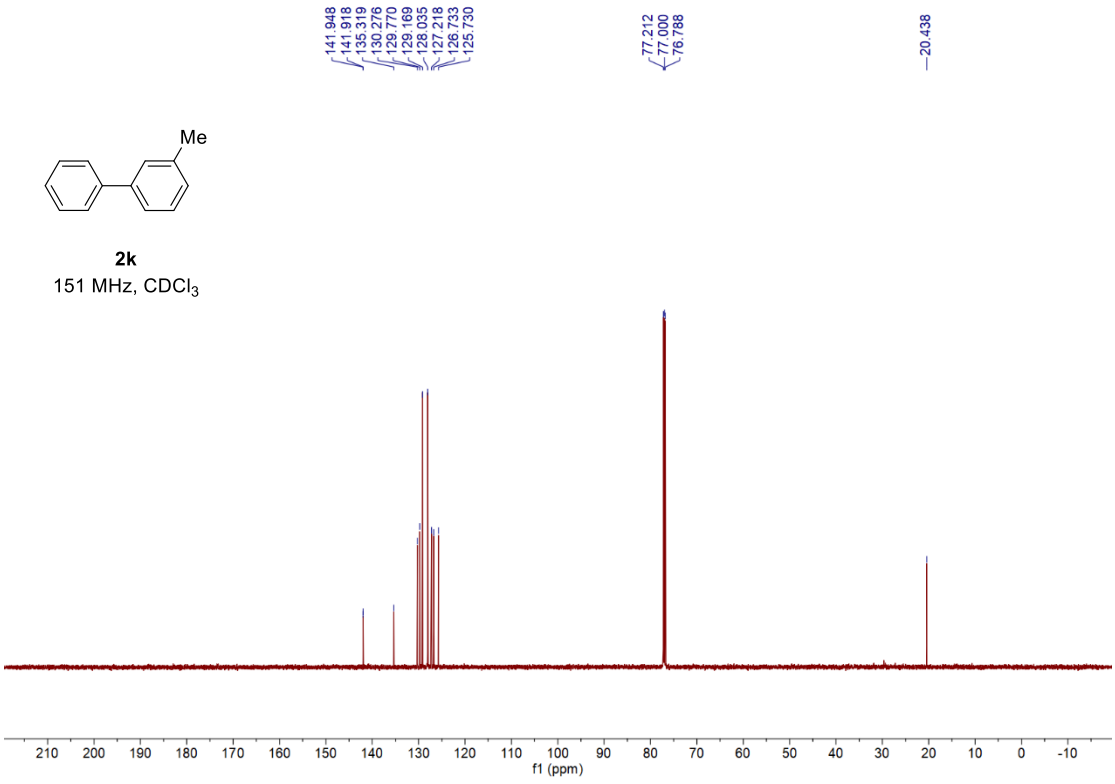


2h

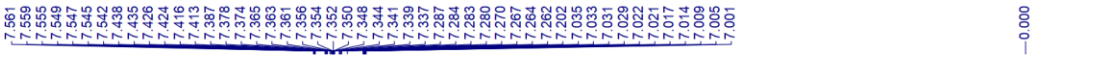
101 MHz, $CDCl_3$

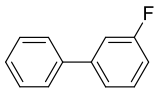


2k
600 MHz, $CDCl_3$



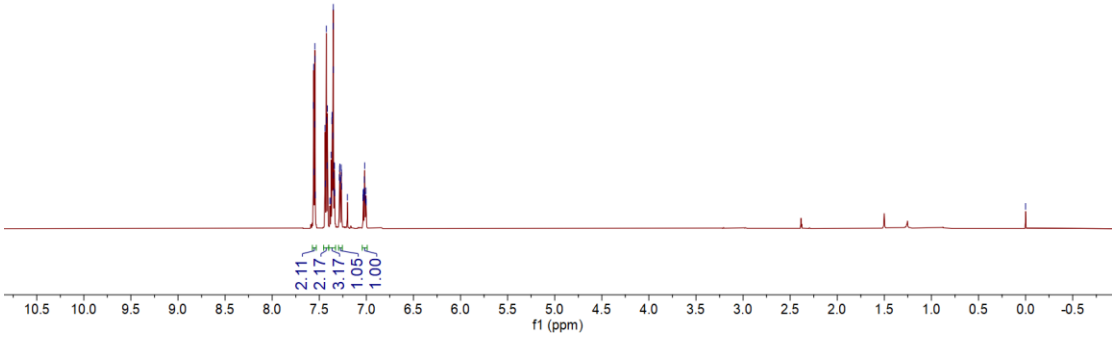
2k
151 MHz, $CDCl_3$

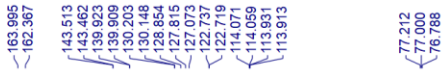


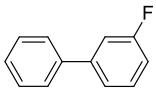


2l

600 MHz, $CDCl_3$

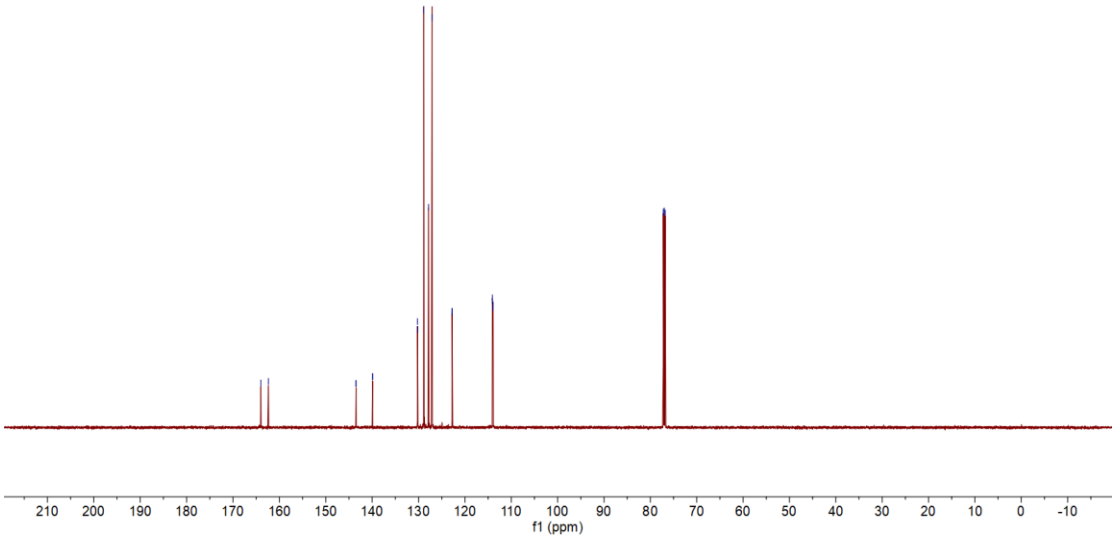


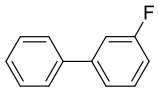




2l

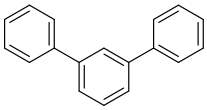
151 MHz, $CDCl_3$





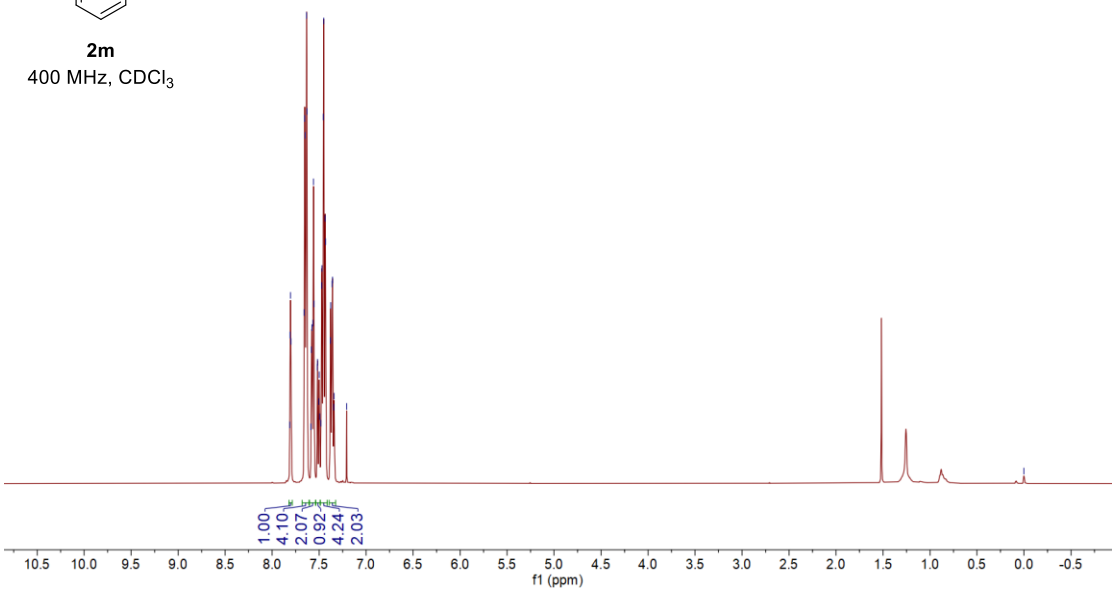
2l

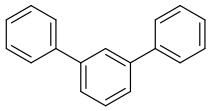
565 MHz, $CDCl_3$



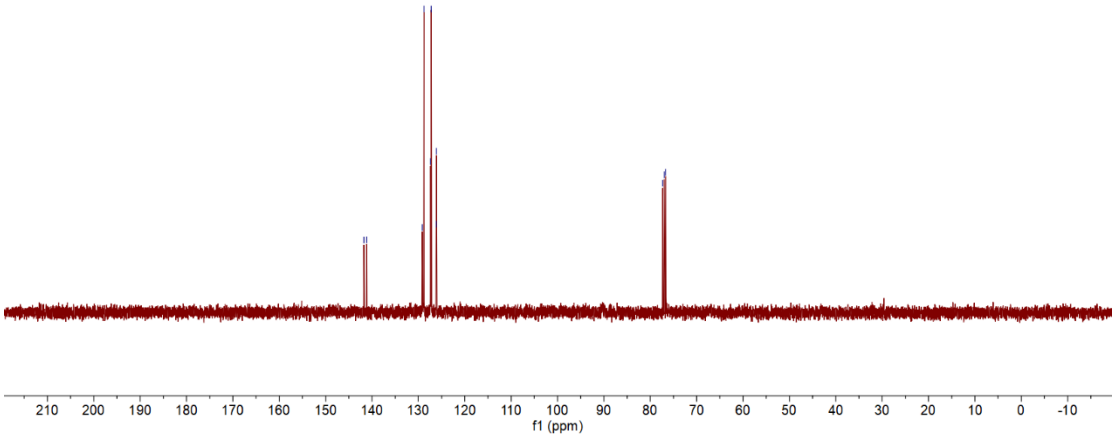
2m

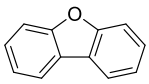
400 MHz, $CDCl_3$



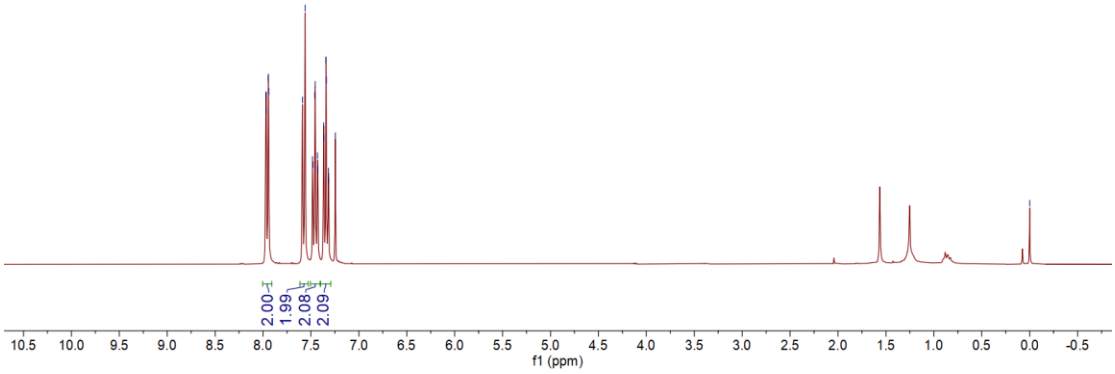


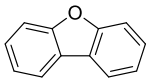
2m
101 MHz, $CDCl_3$





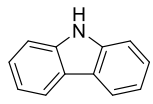
2n
300 MHz, $CDCl_3$





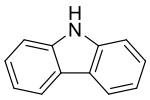
2n

75 MHz, $CDCl_3$



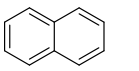
2o

600 MHz, DMSO-d_6



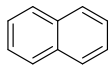
2o

151 MHz, DMSO-d_6

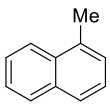


2p

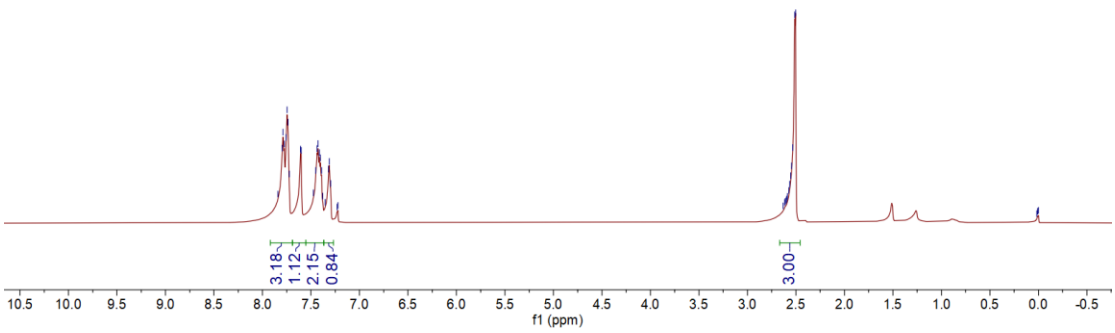
600 MHz, $CDCl_3$

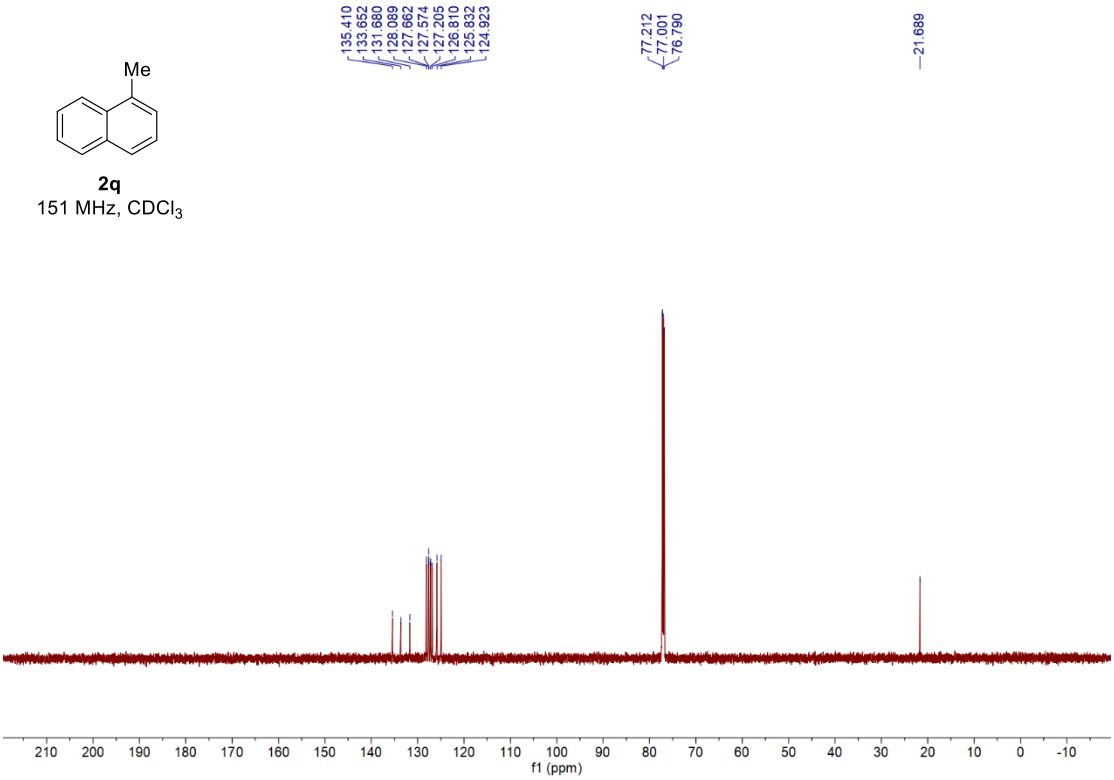


2p
151 MHz, $CDCl_3$

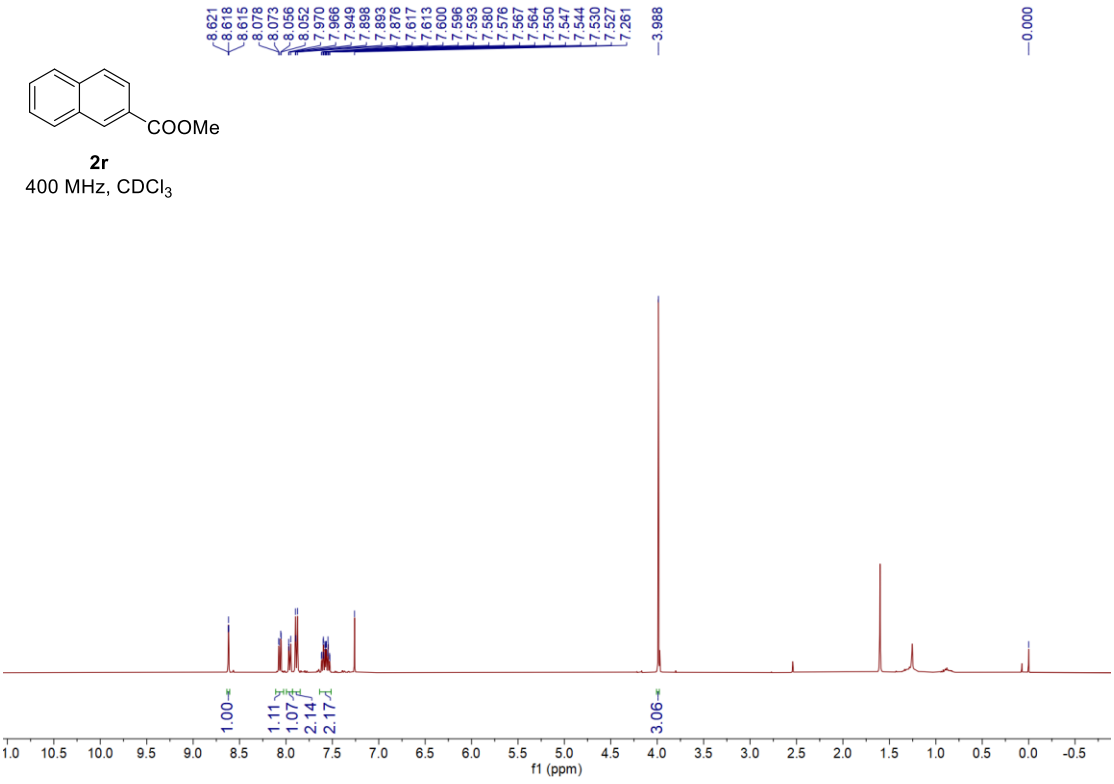


2q
600 MHz, $CDCl_3$

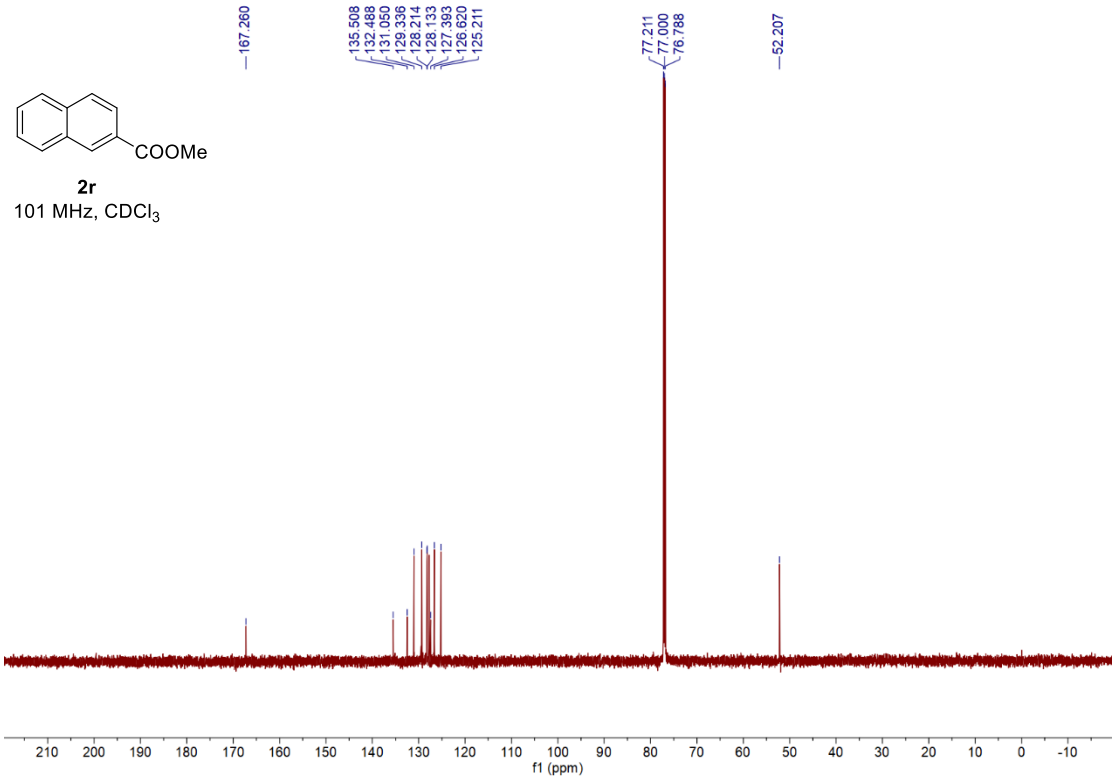




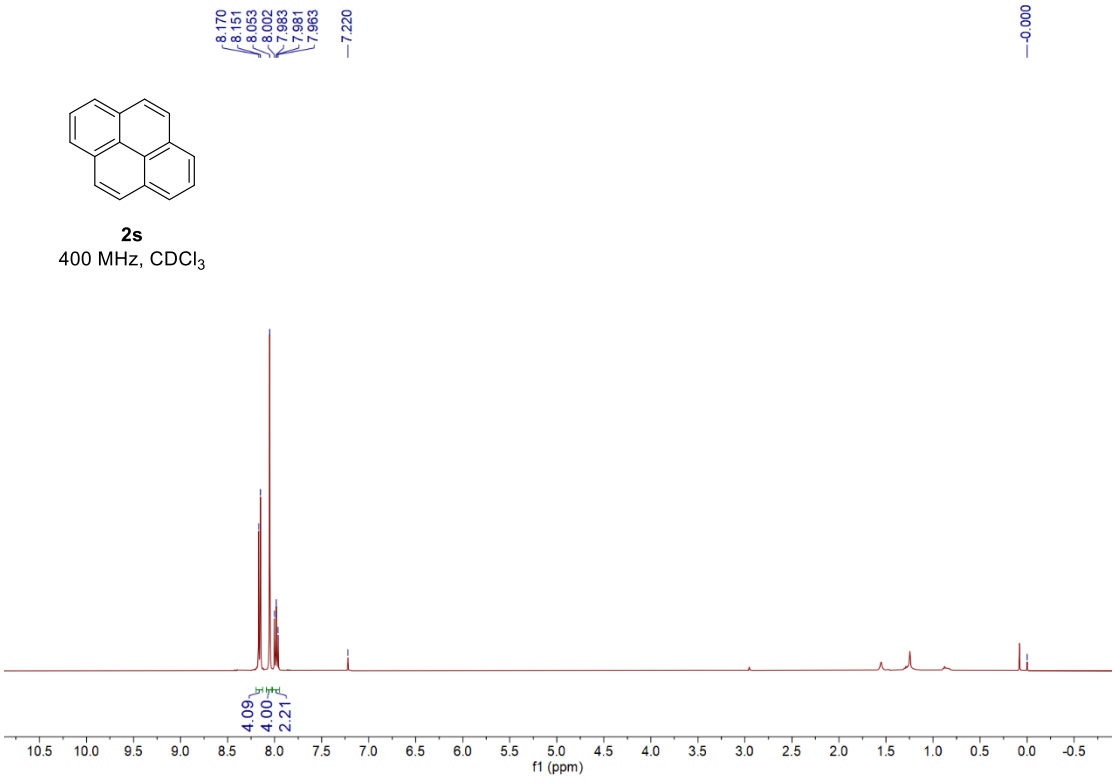
2q
151 MHz, $CDCl_3$



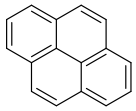
2r
400 MHz, $CDCl_3$



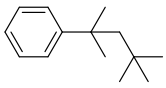
2r
101 MHz, $CDCl_3$



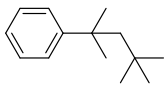
2s
400 MHz, $CDCl_3$



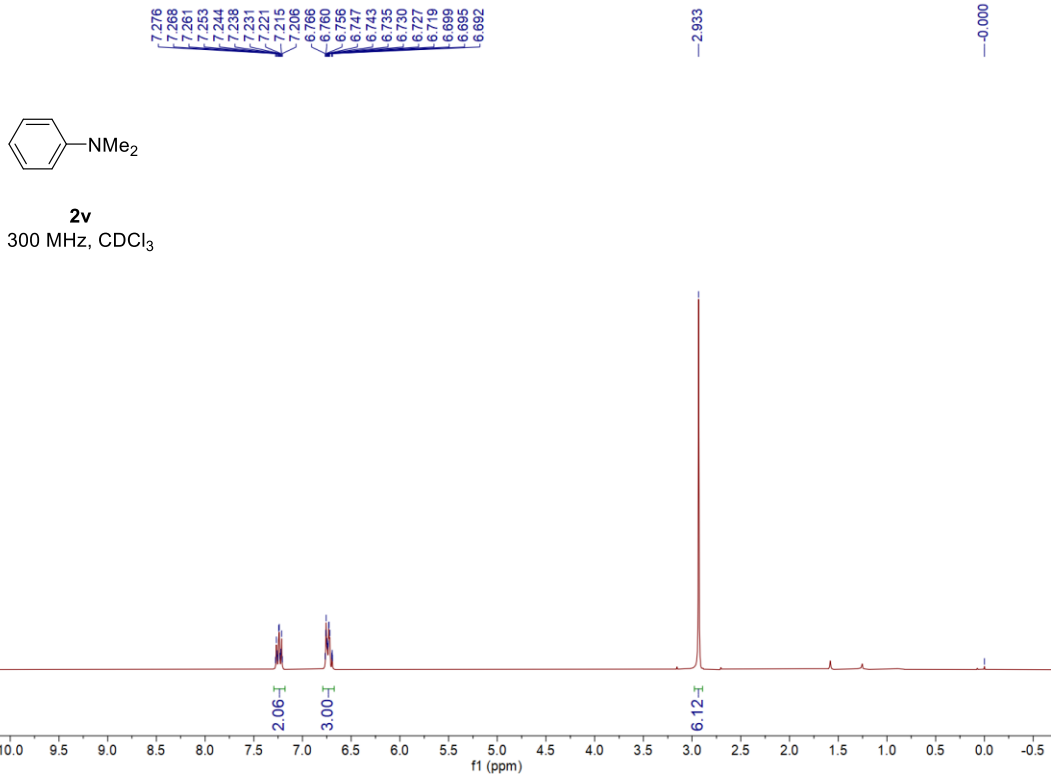
2s
101 MHz, $CDCl_3$



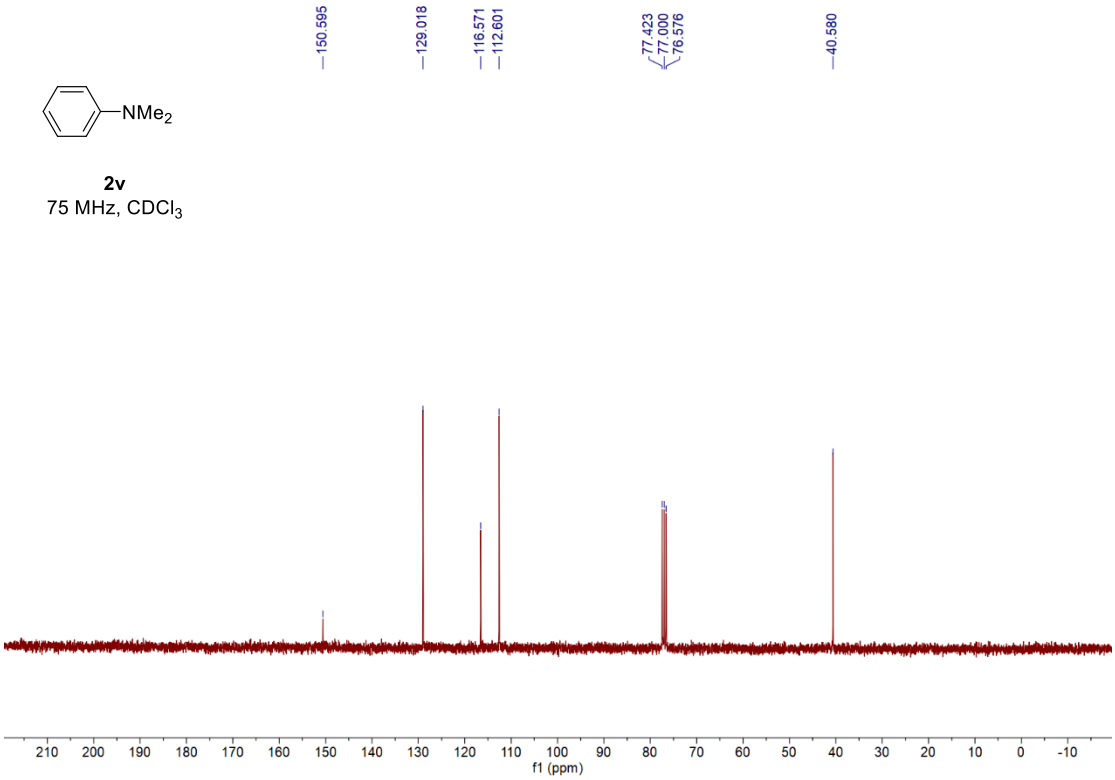
2t
600 MHz, $CDCl_3$



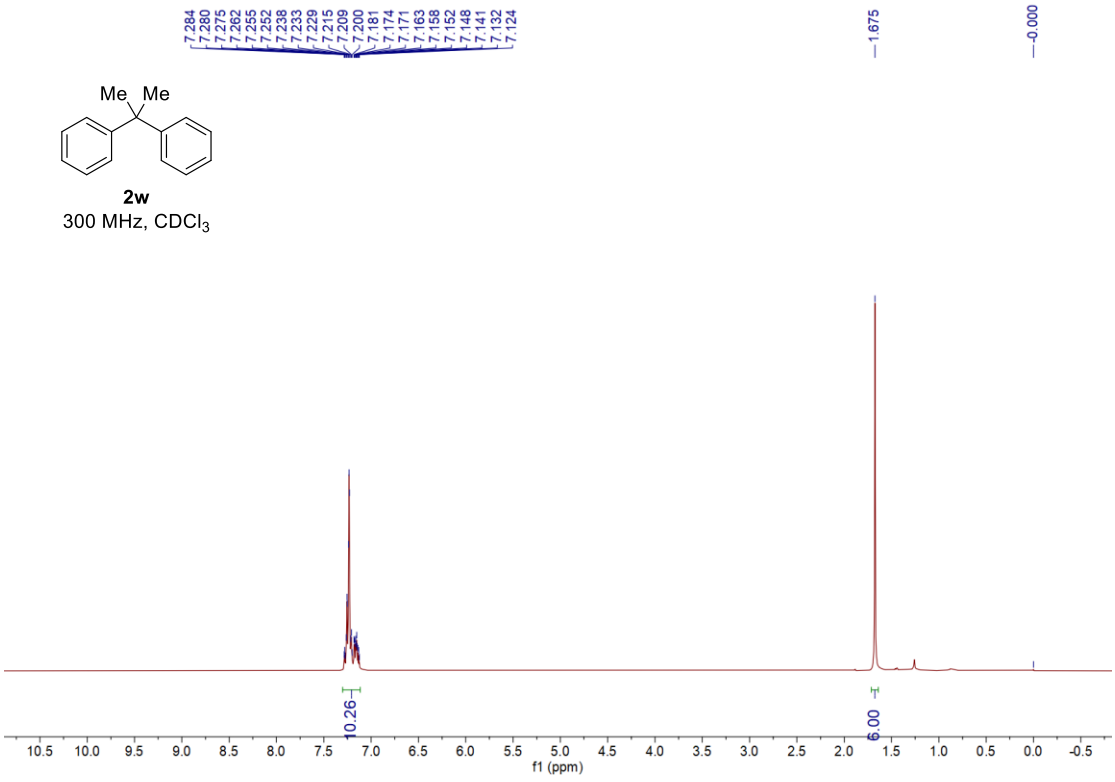
2t
151 MHz, $CDCl_3$



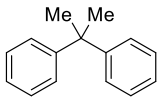
2v
300 MHz, $CDCl_3$



2v
75 MHz, $CDCl_3$

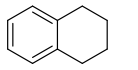


2w
300 MHz, $CDCl_3$



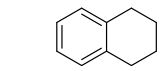
2w

75 MHz, $CDCl_3$



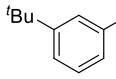
2x

600 MHz, $CDCl_3$



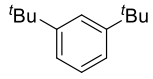
2x

151 MHz, $CDCl_3$



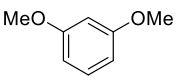
2y

600 MHz, $CDCl_3$



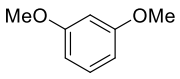
2y

151 MHz, $CDCl_3$



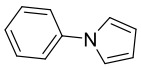
2z

600 MHz, $CDCl_3$



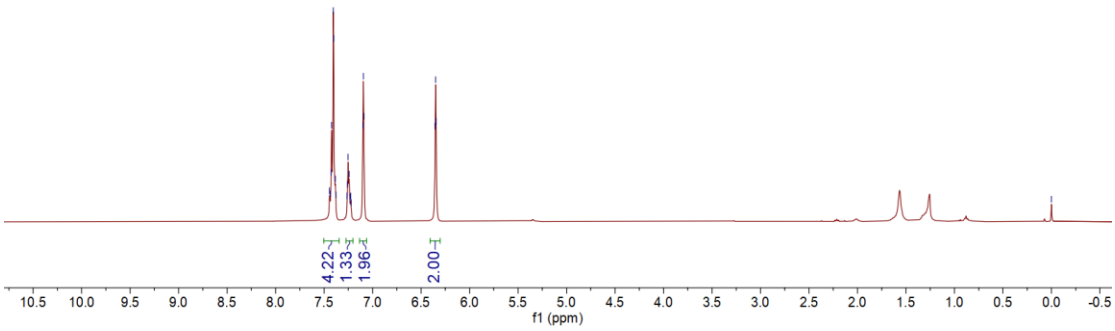
2z

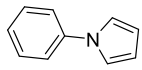
151 MHz, $CDCl_3$



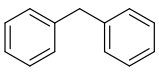
2aa

400 MHz, $CDCl_3$

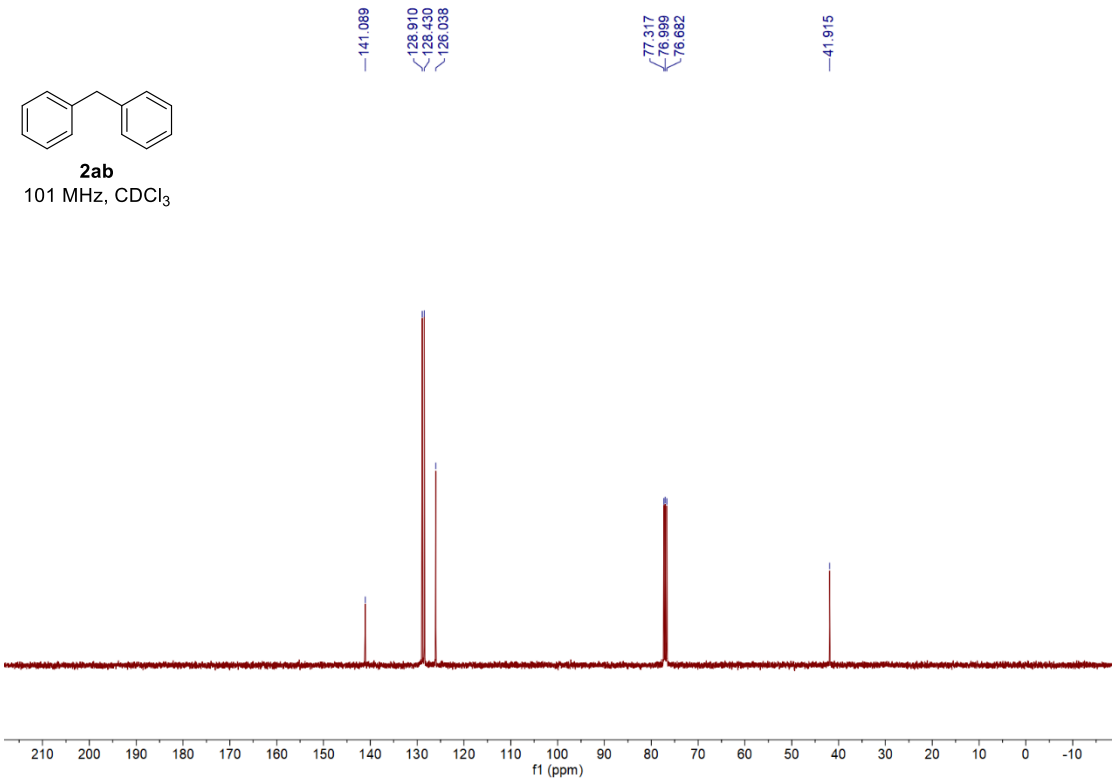




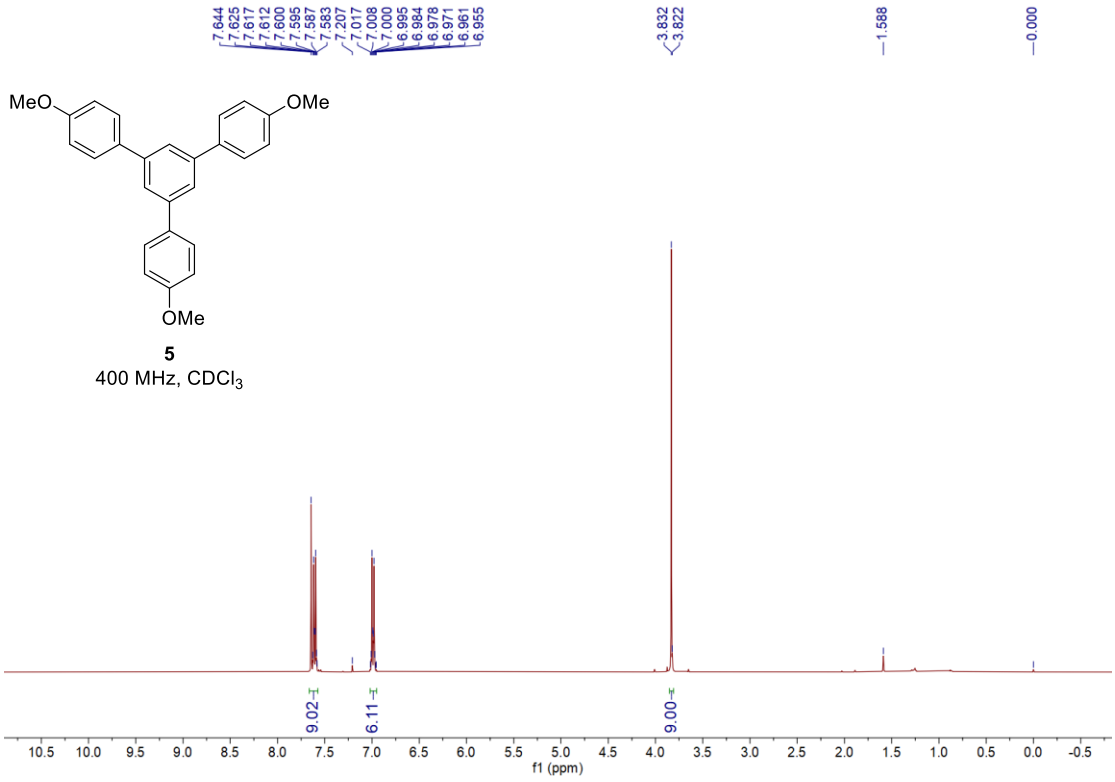
2aa
101 MHz, $CDCl_3$



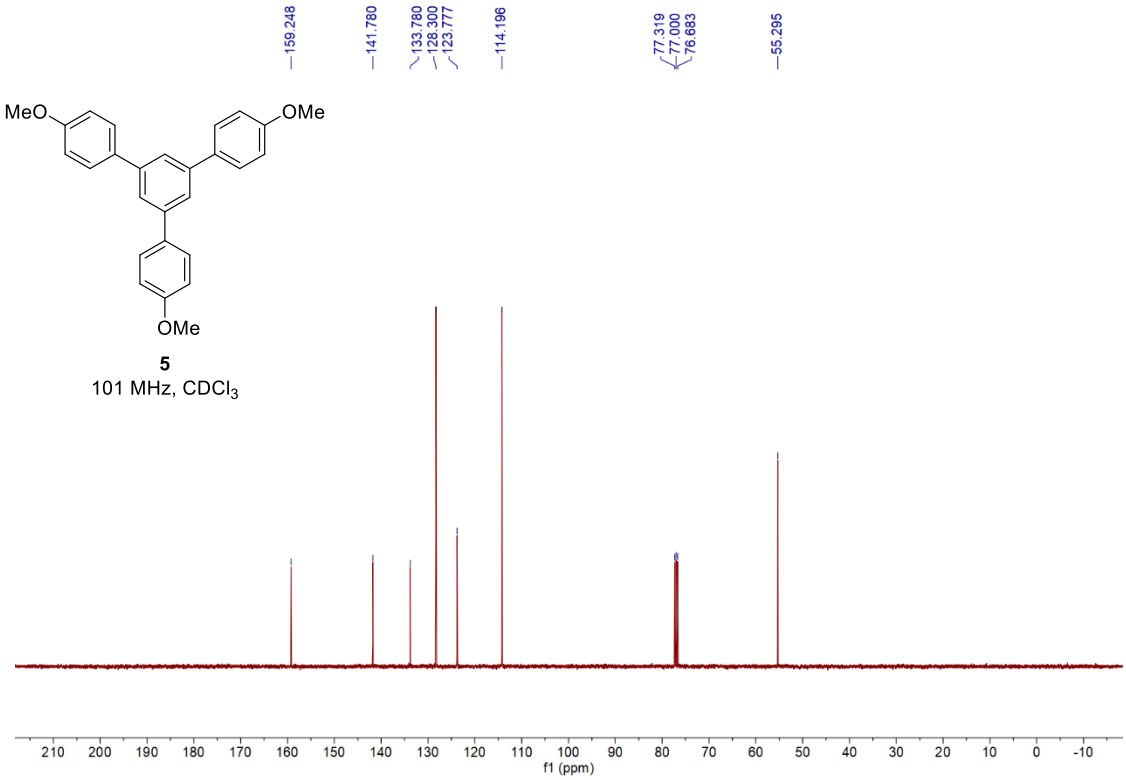
2ab
400 MHz, $CDCl_3$



2ab
101 MHz, $CDCl_3$

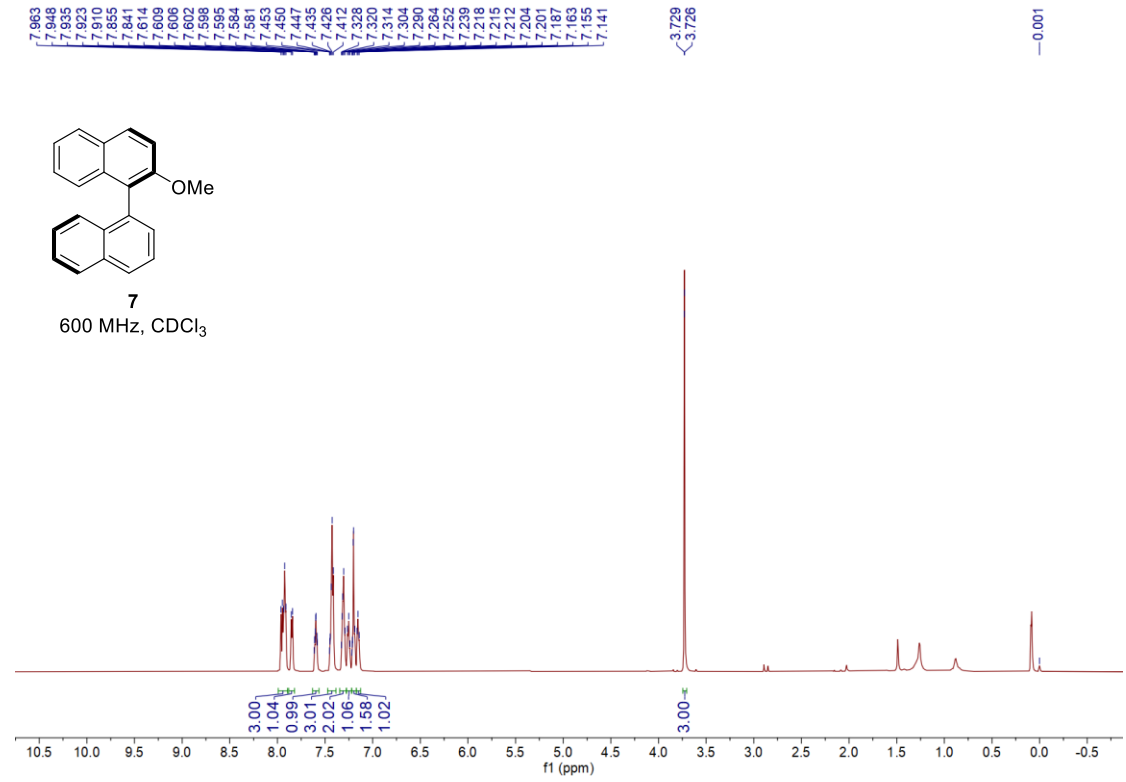


5
400 MHz, $CDCl_3$



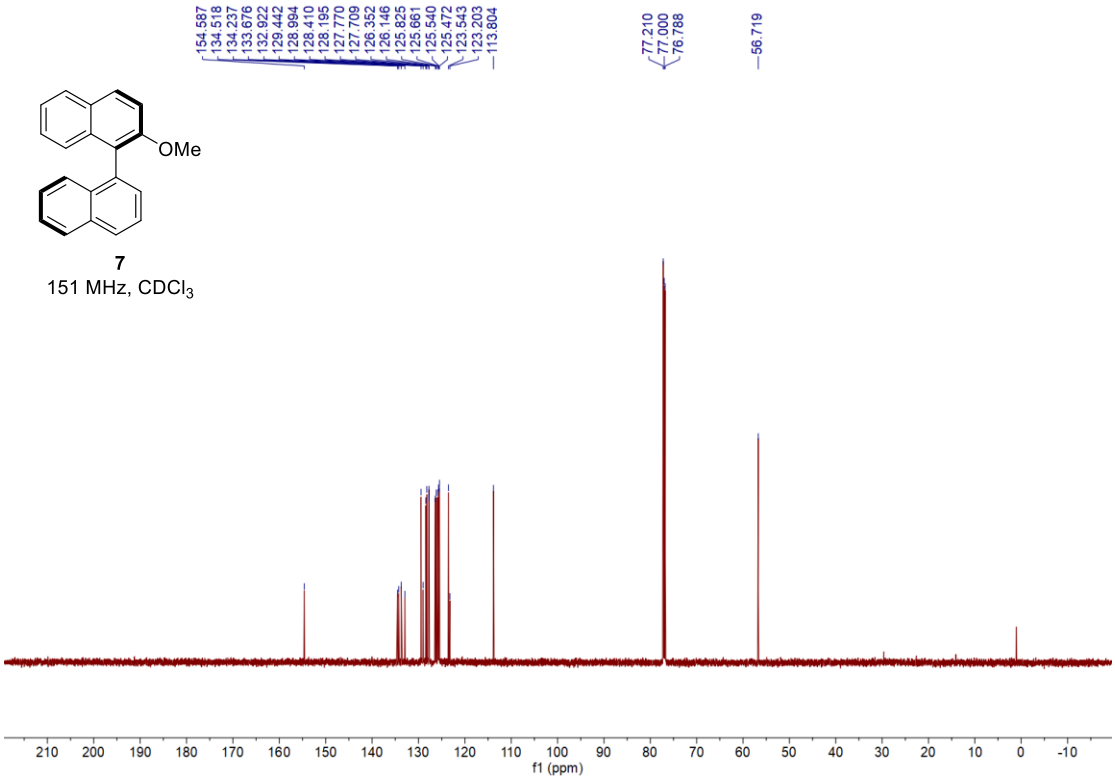
5

101 MHz, $CDCl_3$

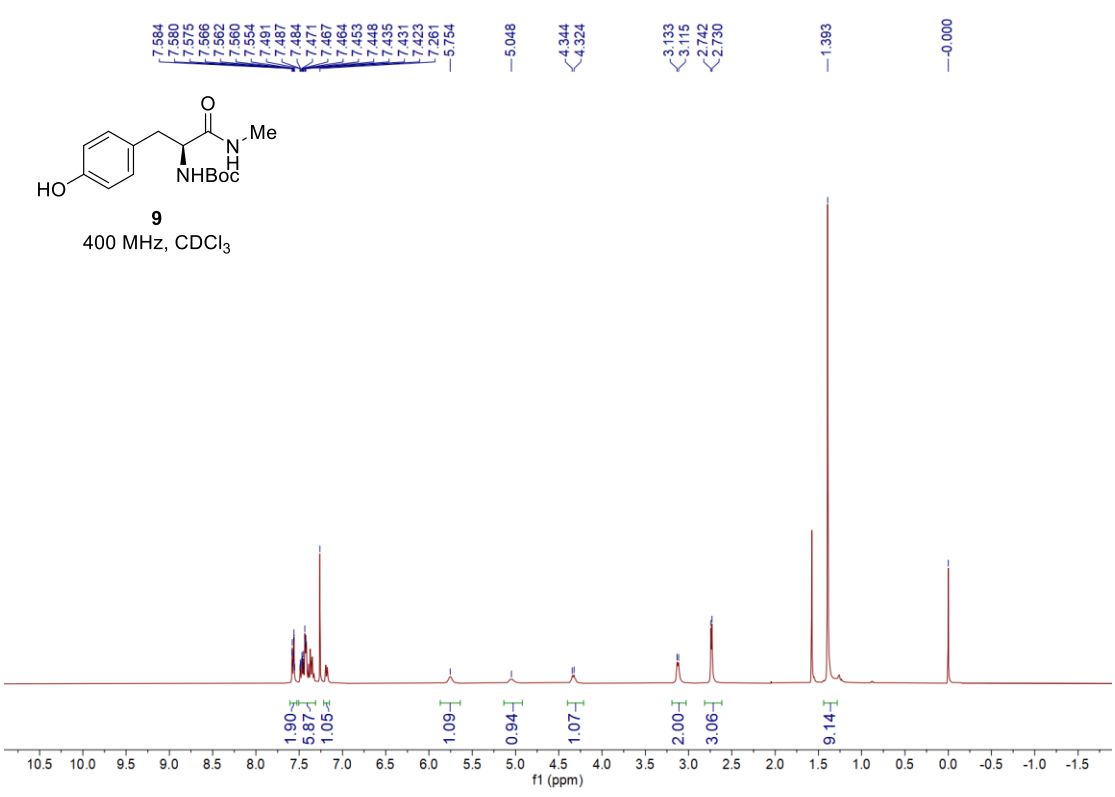


7

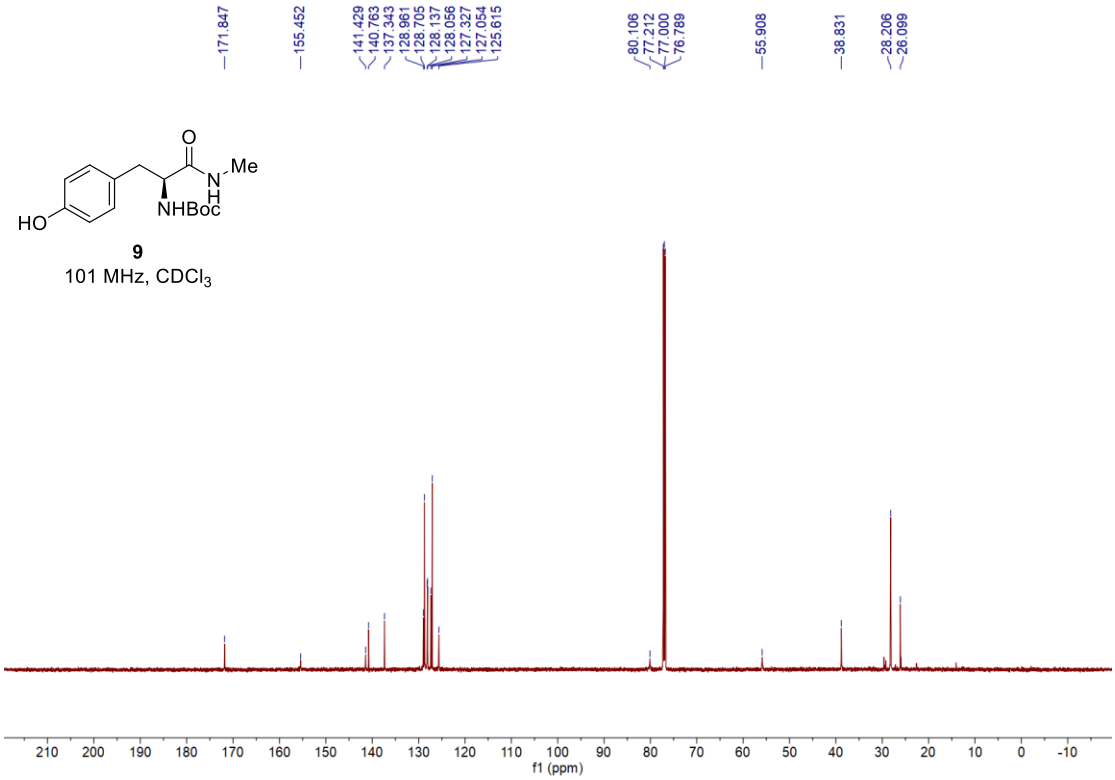
600 MHz, $CDCl_3$



7
151 MHz, $CDCl_3$

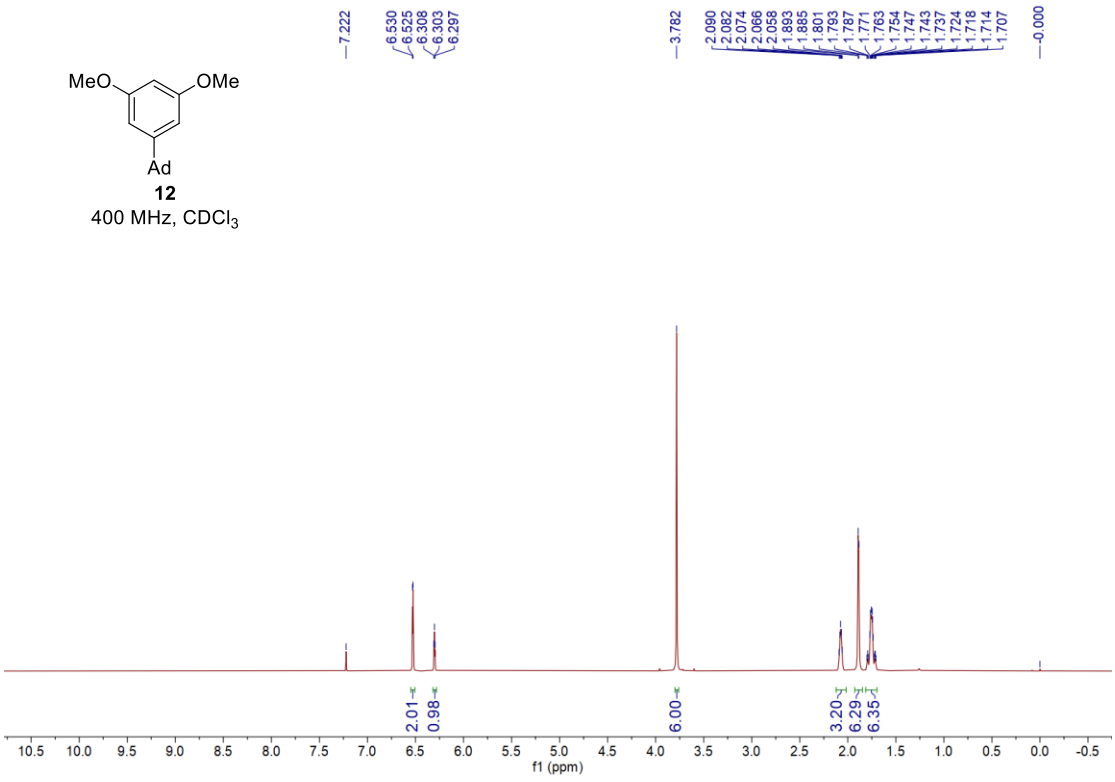


9
400 MHz, $CDCl_3$



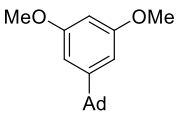
9

101 MHz, $CDCl_3$



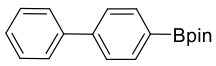
12

400 MHz, $CDCl_3$



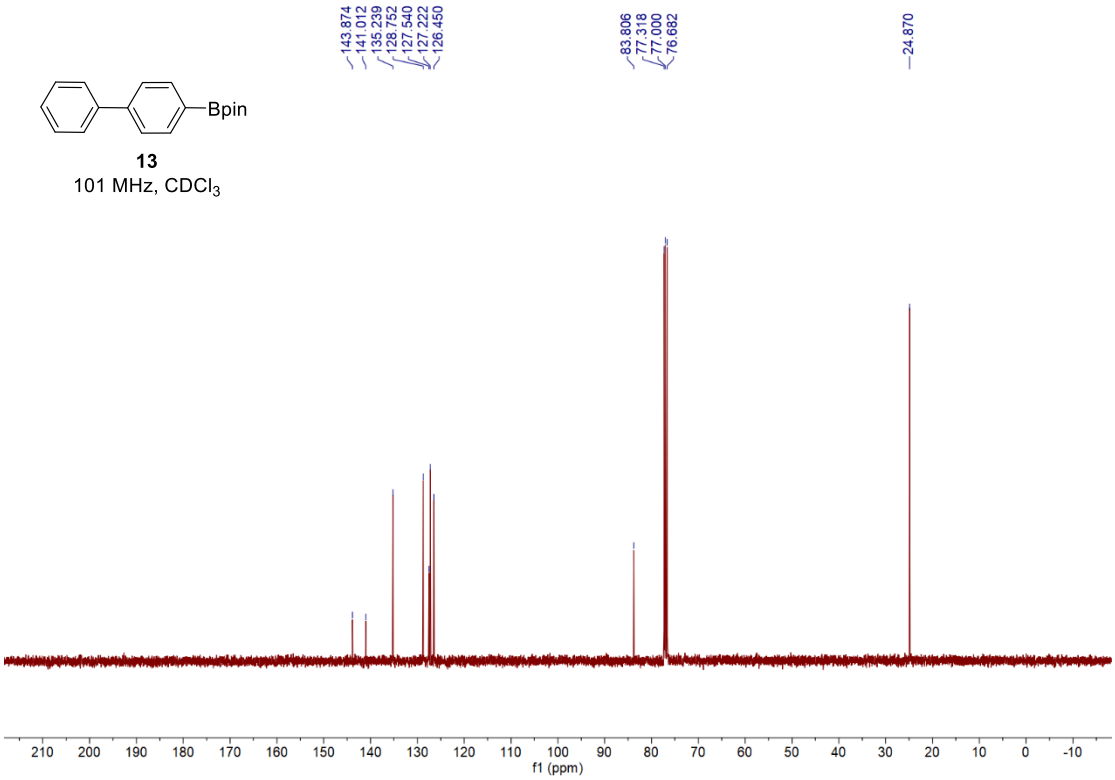
12

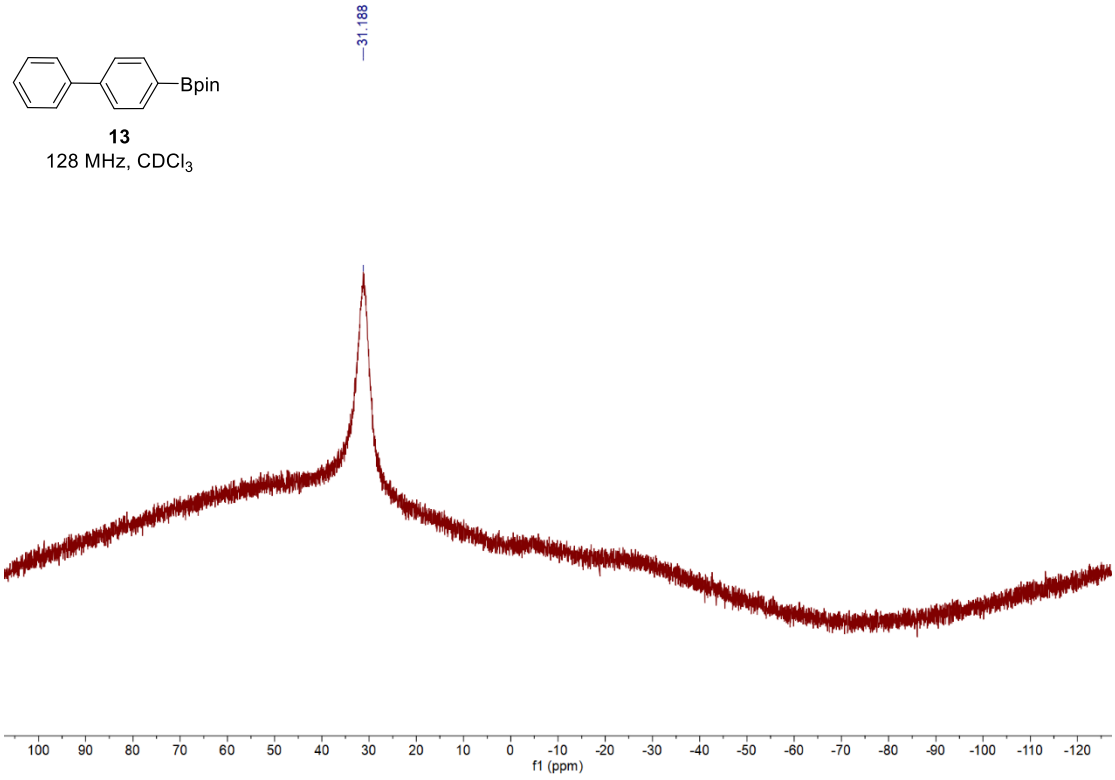
101 MHz, $CDCl_3$



13

400 MHz, $CDCl_3$


143.874
141.012
135.239
128.752
127.540
127.222
126.450
83.806
77.318
77.000
76.682
24.870
Bpin
13
101 MHz, CDCl3
f1 (ppm)


31.188
Bpin
13
128 MHz, CDCl3
f1 (ppm)