

Supporting Information for:

Visible-Light and Thermal Driven Double Hydrophosphination of
Terminal Alkynes Catalyzed by a Commercially Available Iron
Compound

Brandon J. Ackley, Justin K. Pagano[‡], and Rory Waterman*

University of Vermont, Department of Chemistry, Discovery Hall, Burlington, VT 05401

[‡]Current address: Chemistry Division, Los Alamos National Laboratory, Mail Stop J-514, Los
Alamos, NM, 87545

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General considerations: All manipulations were performed under an inert atmosphere of N₂ using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer and were referenced to residual solvent impurities ($\delta = 7.16$ for C₆D₆ and 7.26 for CDCl₃) for ¹H NMR experiments and to an external reference of 85% H₃PO₄ in H₂O for ³¹P NMR experiments ($\delta = 0$). Ph₂PH was prepared by a modified literature procedure and was stored under an inert atmosphere of N₂ prior to use. All other reagents were obtained from commercial suppliers and dried by conventional means as necessary. A commercially available GE LED Lamp A19 bulb with an operating power of 13 W and output of 800 lumens was used for light catalyzed procedures.

General procedure for visible-light double hydrophosphination reactions: A PTFE-sealed NMR tube was charged with [CpFe(CO)₂]₂ (10.0 mg, 0.028 mmol), terminal alkyne (0.56 mmol), and Ph₂PH (0.20 mL, 1.12 mmol) in a N₂-filled glovebox. The reaction was irradiated with visible light for 20 hours, after which ³¹P NMR revealed a complete reaction for phenylacetylene and 4-tolylacetylene. In the case of all other alkynes, the reaction was brought back into the glovebox and THF (1 mL) was added to solubilize the reaction mixture, which was then further irradiated with visible light for 20–36 hours to ensure a complete reaction as evidenced by ³¹P NMR spectroscopy.

General procedure for thermal double hydrophosphination reactions: A PTFE-sealed NMR tube was charged with [CpFe(CO)₂]₂ (10.0 mg, 0.028 mmol), terminal alkyne (0.56 mmol), and Ph₂PH (0.20 mL, 1.12 mmol) in a N₂-filled glovebox. The reaction was heated to 110 °C for 1–16 hours, after which the reaction was allowed to cool to ambient temperature and volatiles were removed under reduced pressure. The reaction was then brought back into the glovebox and was worked up as described for each individual substrate.

Double hydrophosphination of phenylacetylene: Reaction time: 2 hours. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with 1:1 hexanes:DCM (4 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The now white residue was dried under reduced pressure to give pure 1,2-bis(diphenylphosphino)-1-phenylethane as a fluffy white powder. Final purified yield = 255 mg (96 %). NMR data are consistent with literature values.¹

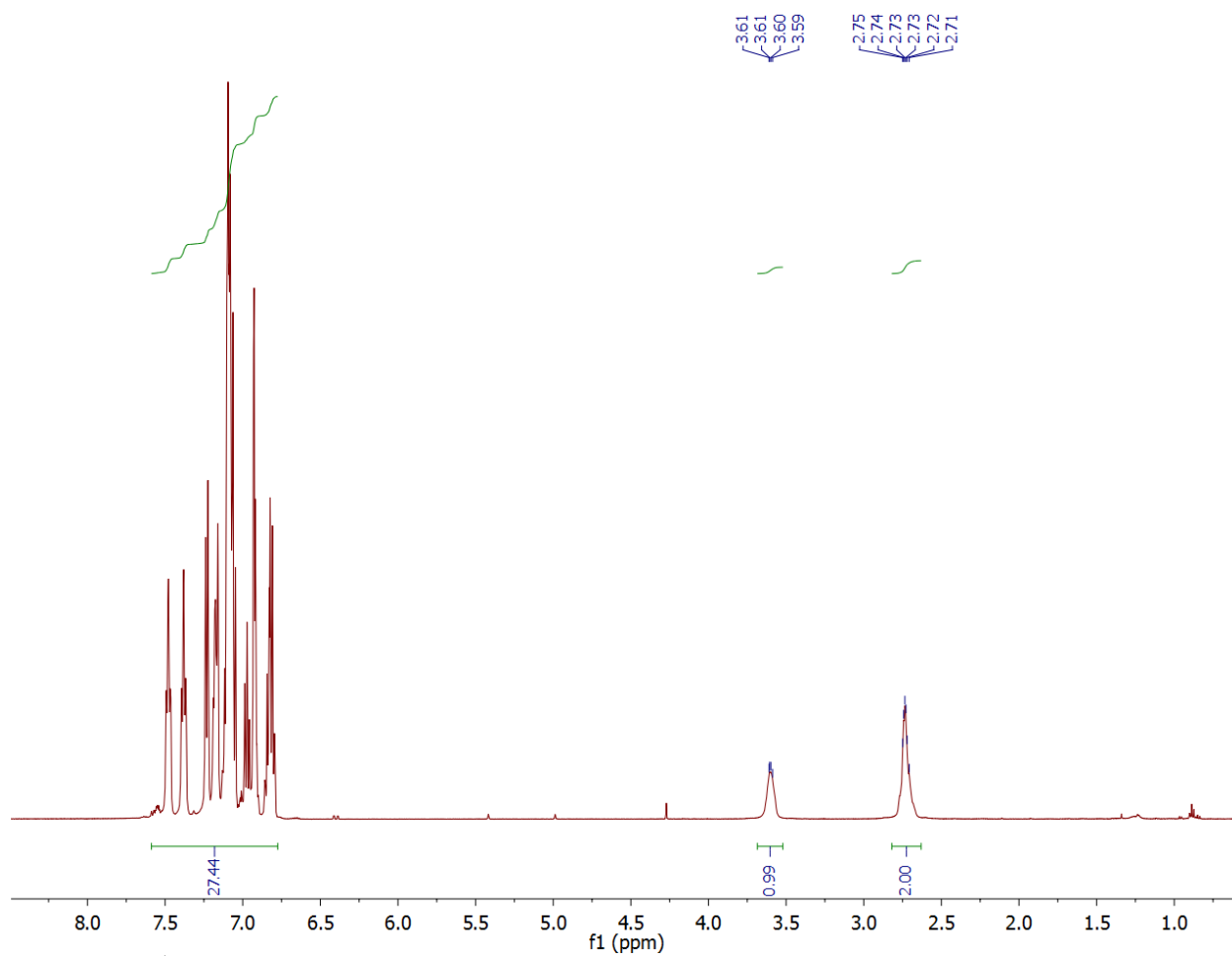


Figure S.1: ^1H NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-phenylethane.

JP_5_73

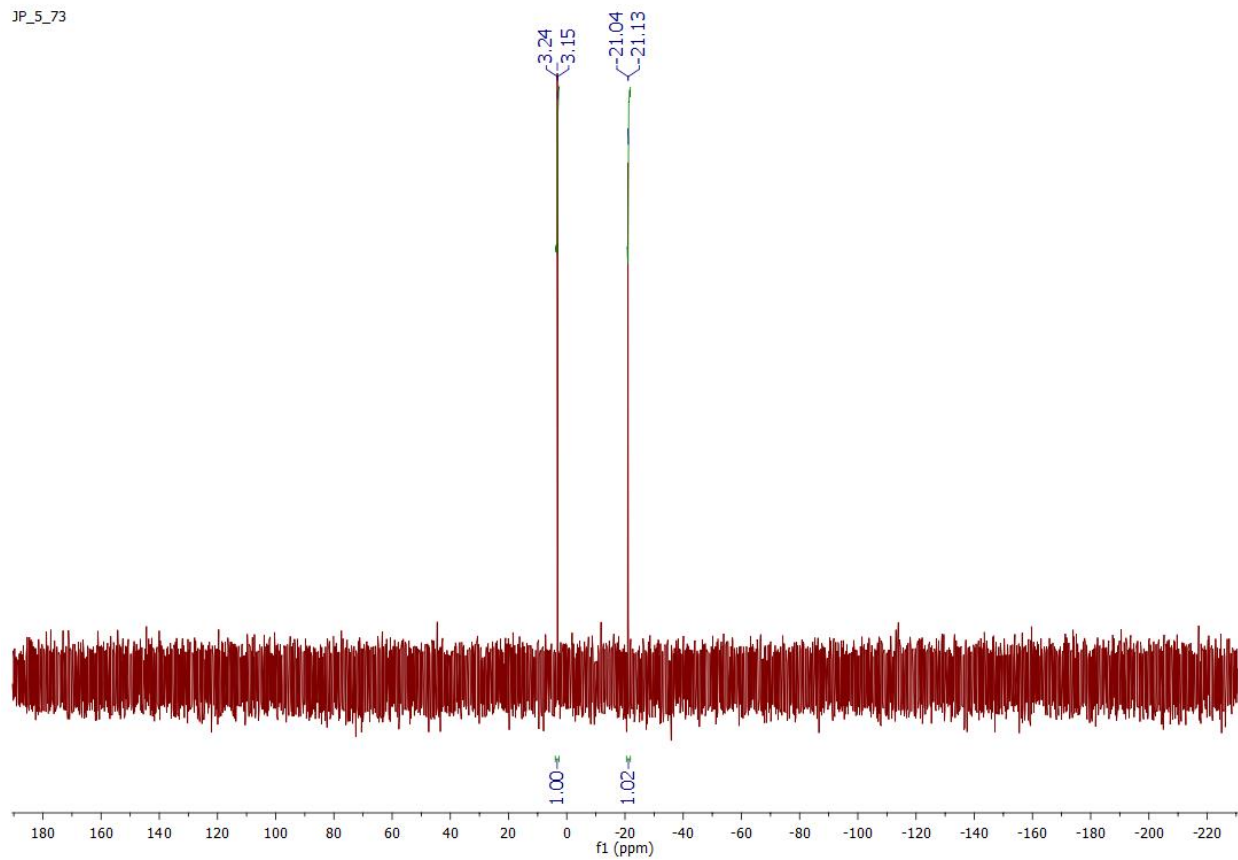


Figure S.2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-phenylethane.

Double hydrophosphination of *p*-tolylacetylene: Reaction time: 2 hours. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with 1:1 hexanes:DCM (4 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The now white residue was dried under reduced pressure to give pure 1,2-bis(diphenylphosphino)-1-(*p*-tolyl)ethane as a fluffy white powder. Final purified yield = 254 mg (93 %). NMR data are consistent with literature values.¹

JP_5_63

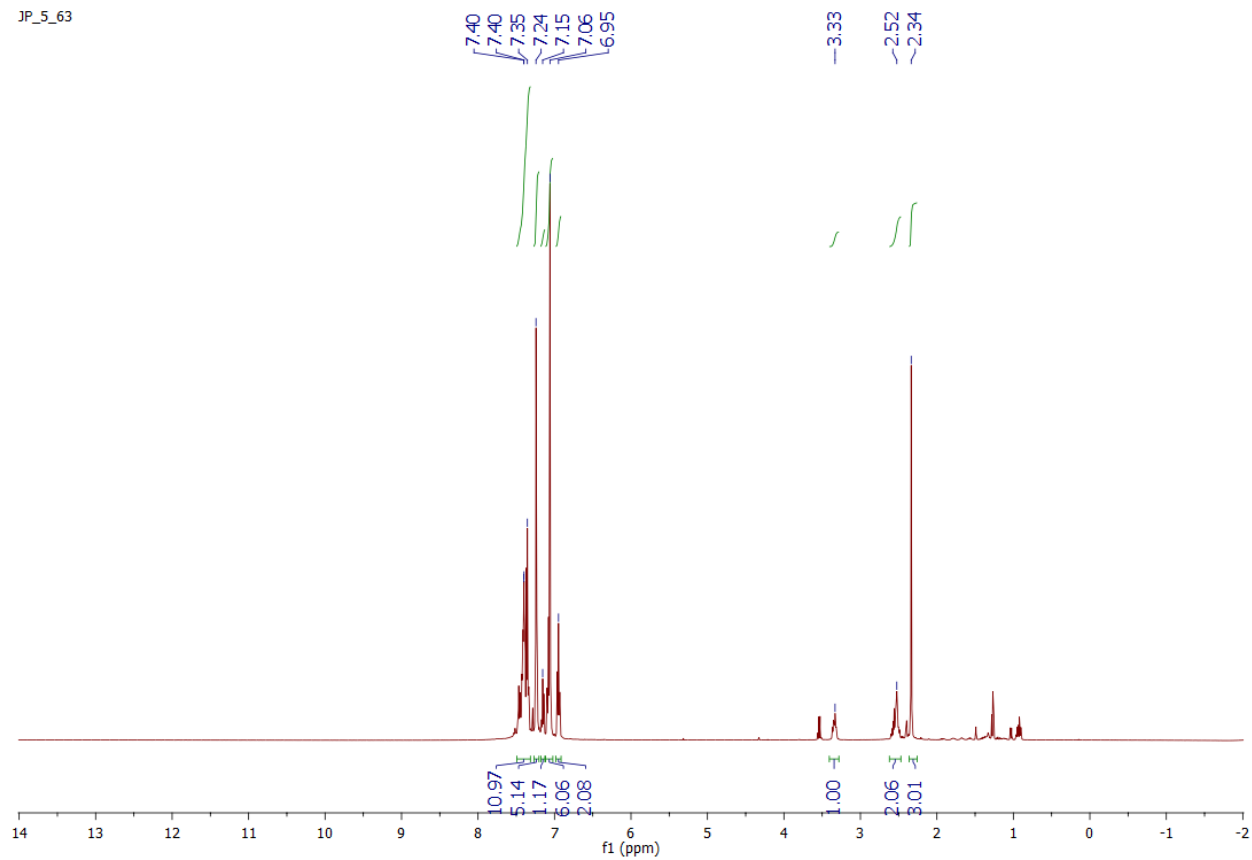


Figure S.3: ^1H NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-*p*-tolylethane.

JP_5_63

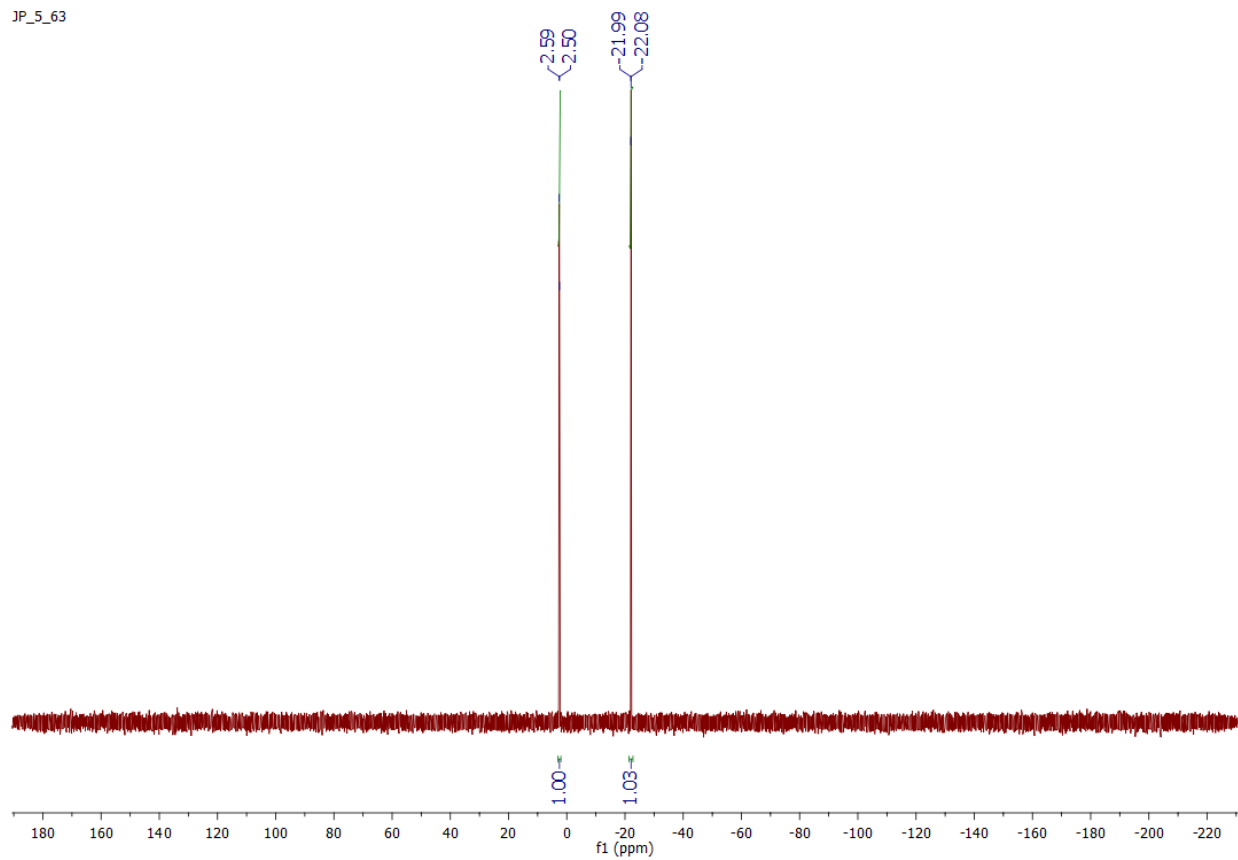


Figure S.4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1,2-bis(diphenylphosphino)-1-*p*-tolylethane.

Double hydrophosphination of 4-*tert*-butylphenylacetylene: Reaction time: 3 hours. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9” borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with DCM (5 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The now white residue was dried under reduced pressure to give pure 1,2-bis(diphenylphosphino)-1-(4-*tert*-butylphenyl)ethane as a fluffy white powder. Final purified yield = 279 mg (94 %) NMR data are consistent with literature values.¹

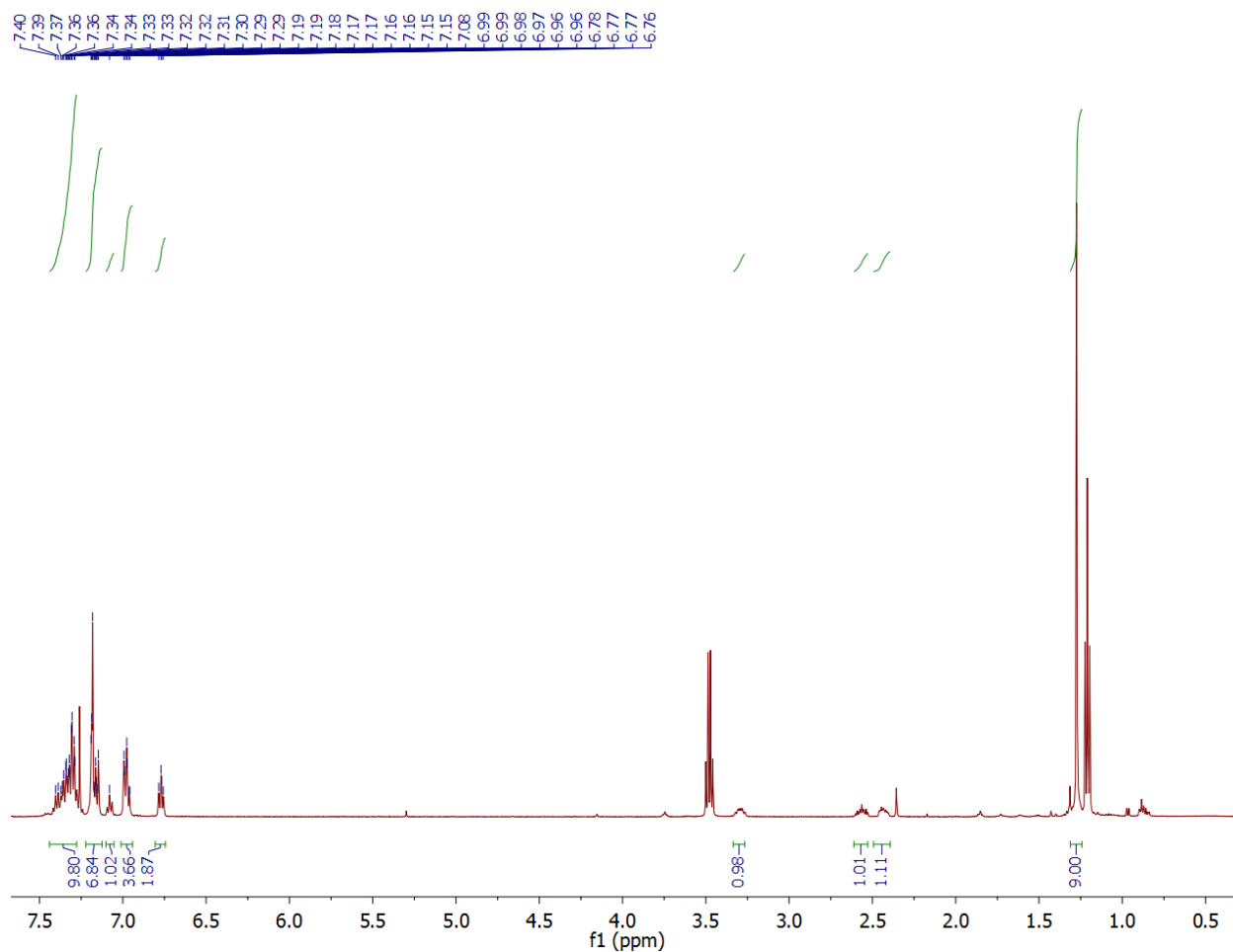


Figure S.5: ^1H NMR spectrum (CDCl_3) of 1,2-bis(diphenylphosphino)-1-(4-*tert*-butylphenyl)ethane.

JP_5_73

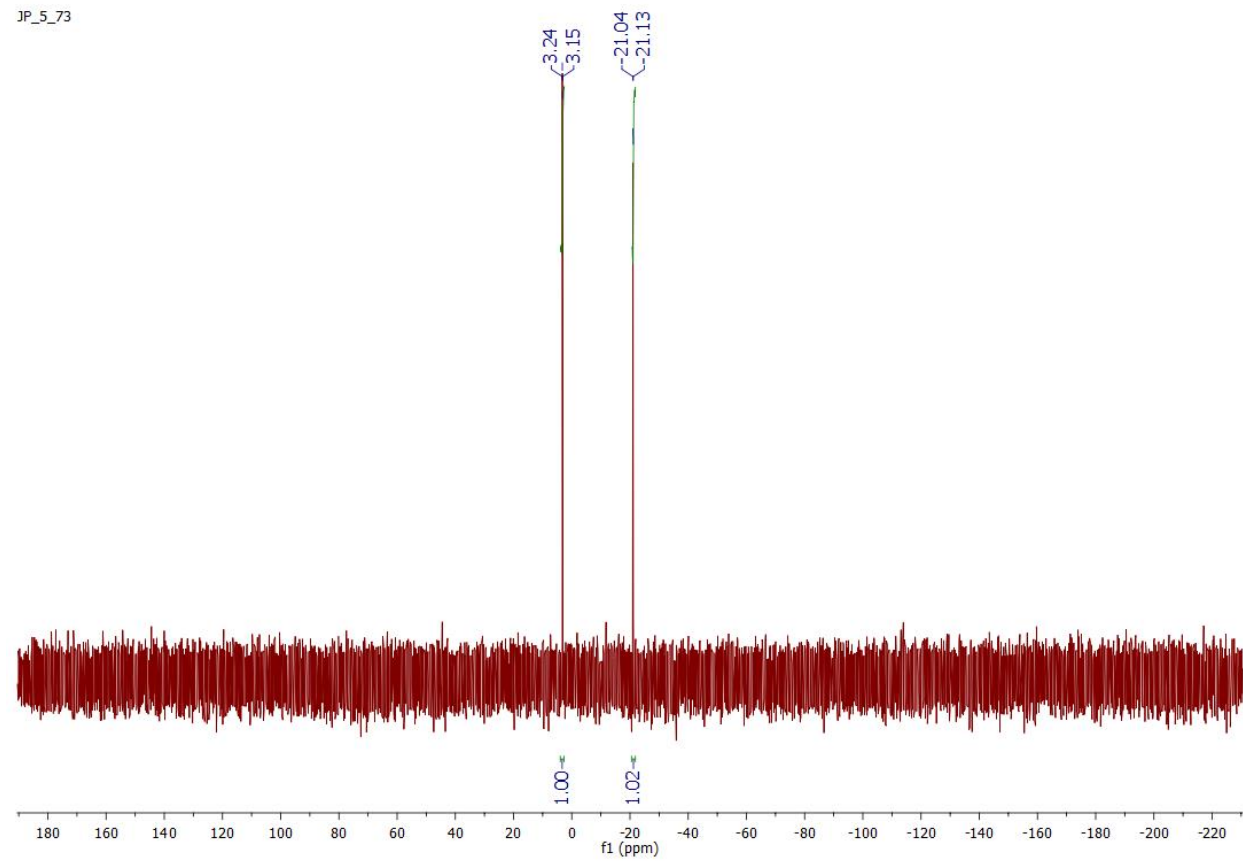


Figure S.6: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of 1,2-bis(diphenylphosphino)-1-(4-*tert*-butylphenyl)ethane.

Double hydrophosphination of 4-ethynylanisole: Reaction time: 4 hours. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (2 mL), 1:1 hexanes:DCM (4 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The now white residue was dried under reduced pressure, then was dissolved in minimal DCM (0.5 mL) that was layered with hexanes (10 mL) and cooled to $-30\text{ }^{\circ}\text{C}$ for 24 hours, which resulted in the deposition of pure 1,2-bis(diphenylphosphino)-1-(4-methoxyphenyl)ethane as a fluffy white powder. Final purified yield = 251 mg (89 %) NMR data are consistent with literature values.¹

JP_5_111

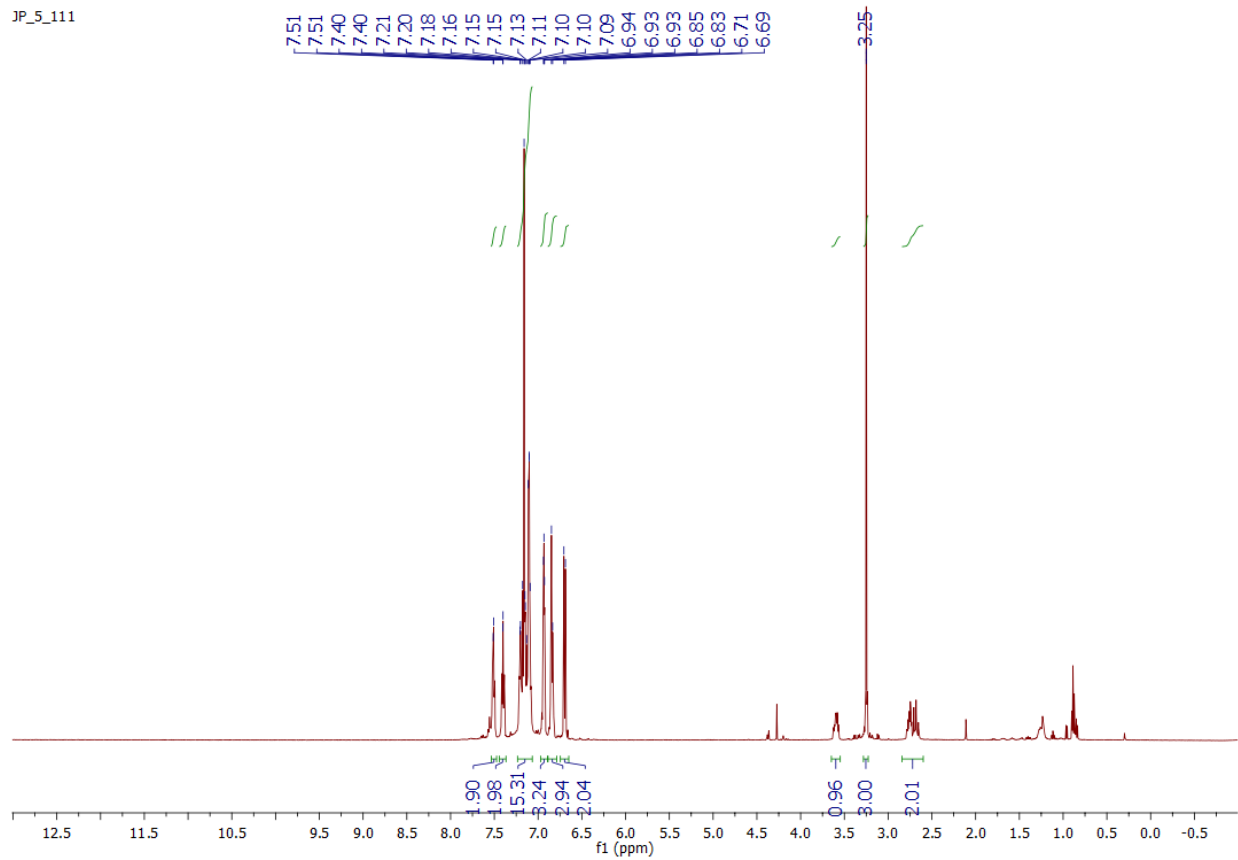


Figure S.7: ^1H NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(4-methoxyphenyl)ethane

JP_5_111

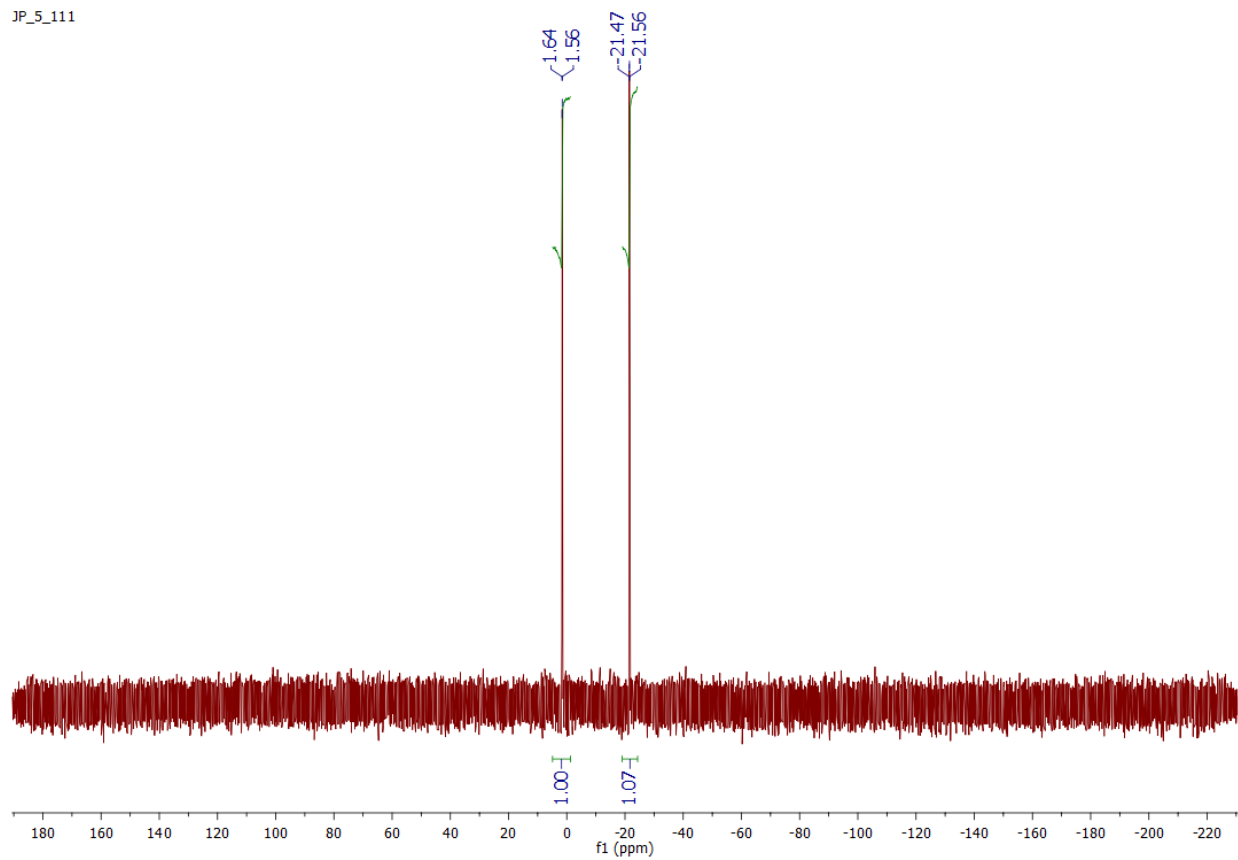


Figure S.8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1,2-bis(diphenylphosphino)-1-(4-methoxyphenyl)ethane.

Double hydrophosphination of 4-fluorophenylacetylene: Reaction time: 4 hours. Workup: A THF solution (1.5 mL) of the crude reaction mixture was layered with pentanes (4 mL), precipitating an off-white solid. The red solution was filtered through a medium porosity fritted funnel and the solid was collected. The solid was then washed with pentane (2x2 mL) until the washings ran clear, which yielded pure 1,2-bis(diphenylphosphino)-1-(4-fluorophenyl)ethane as a fluffy white powder. Final purified yield = 273 mg (99%) NMR data are consistent with literature values.¹

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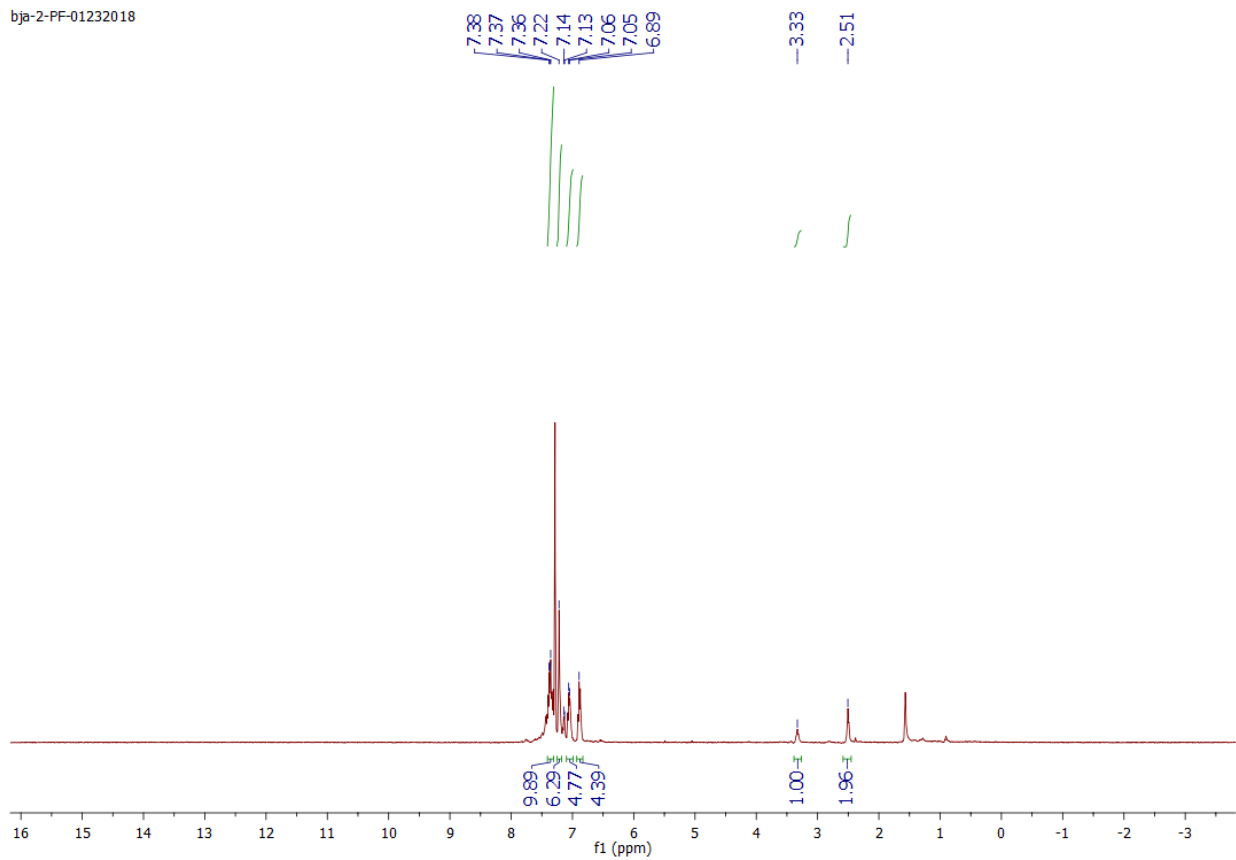


Figure S.9: ^1H NMR spectrum (CDCl_3) of 1,2-bis(diphenylphosphino)-1-(4-fluorophenyl)ethane

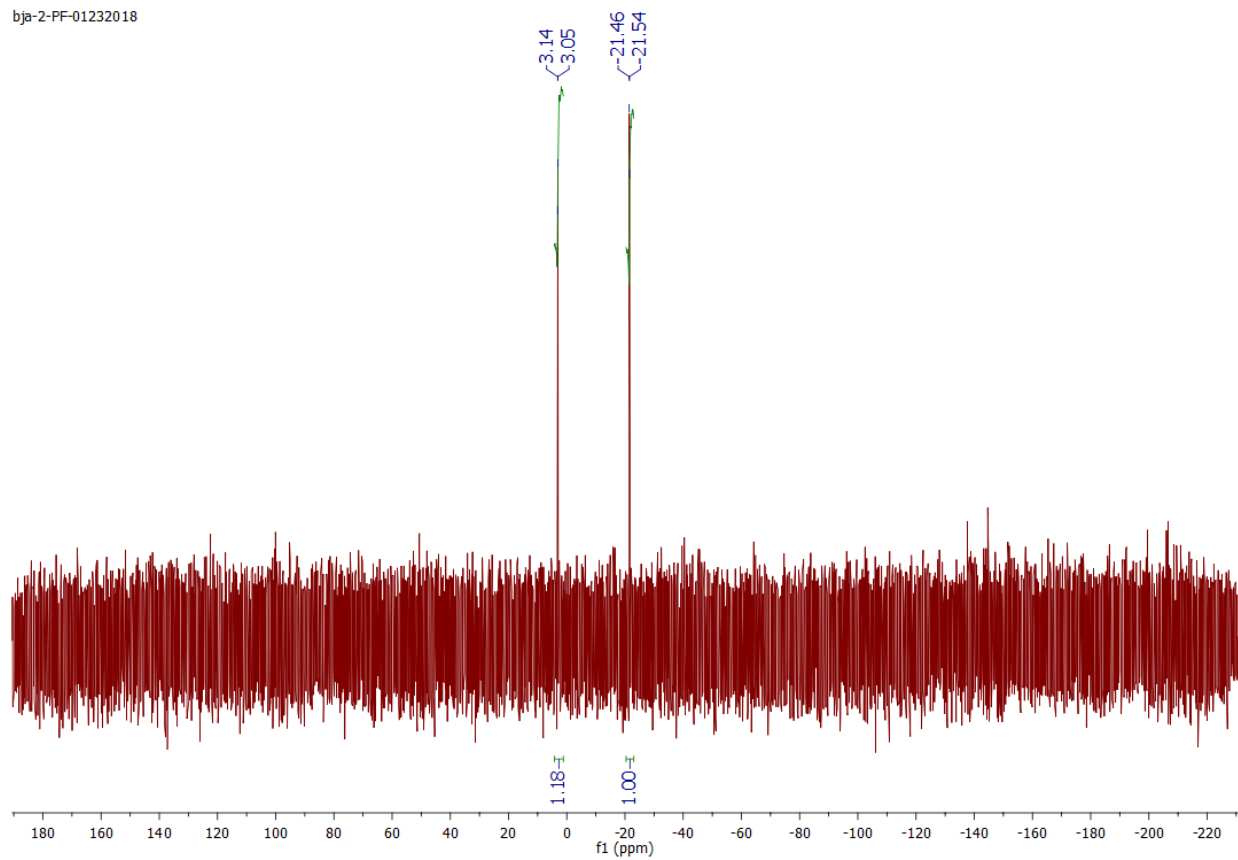


Figure S.10: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) of 1,2-bis(diphenylphosphino)-1-(4-fluorophenyl)ethane

Double hydrophosphination of 4-(trifluoromethyl)phenylacetylene: Reaction time: 6 hrs. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), 1:1 hexanes:DCM (2 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The product was a white crystalline powder, final yield post purification was 218 mg (72%). NMR data are consistent with literature values.²

bja-2-CF3-01232018

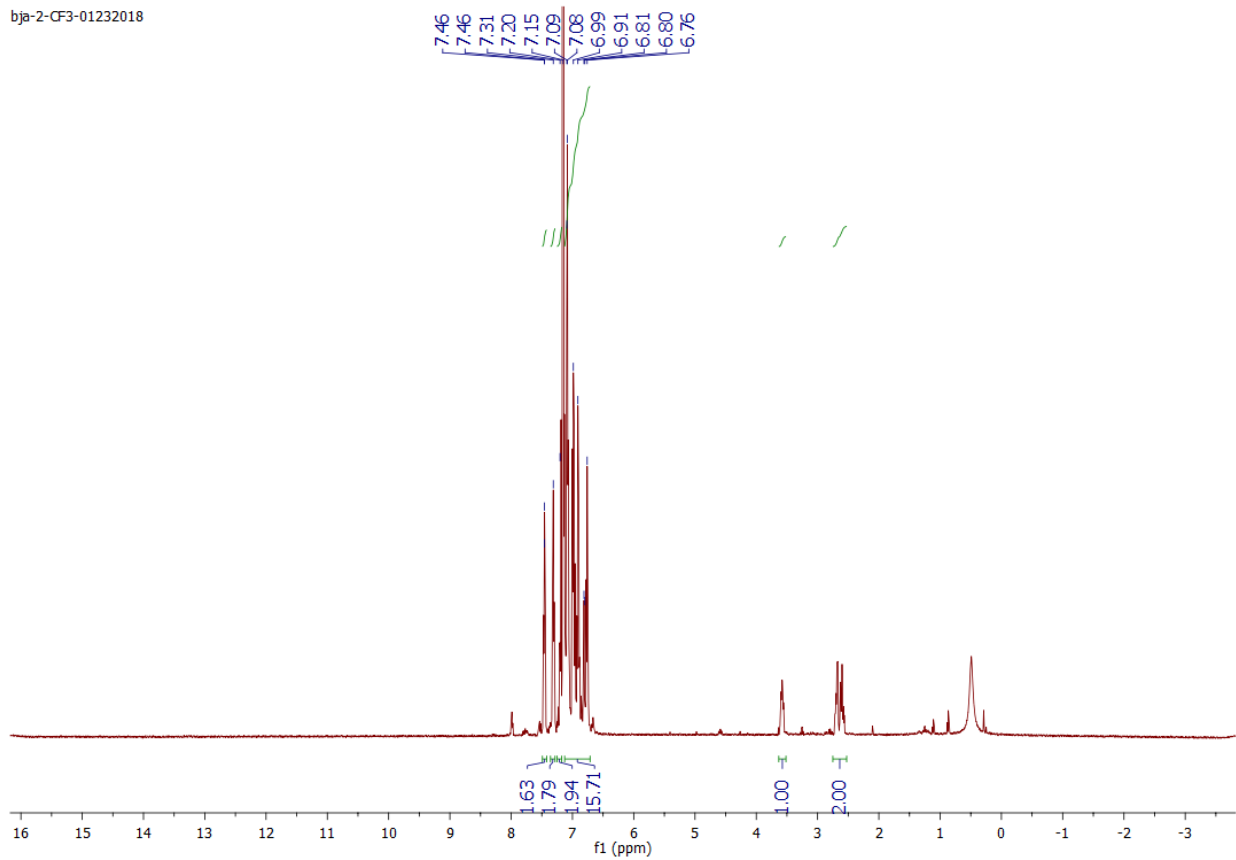


Figure S.11: ^1H NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(4-trifluoromethylphenyl)ethane

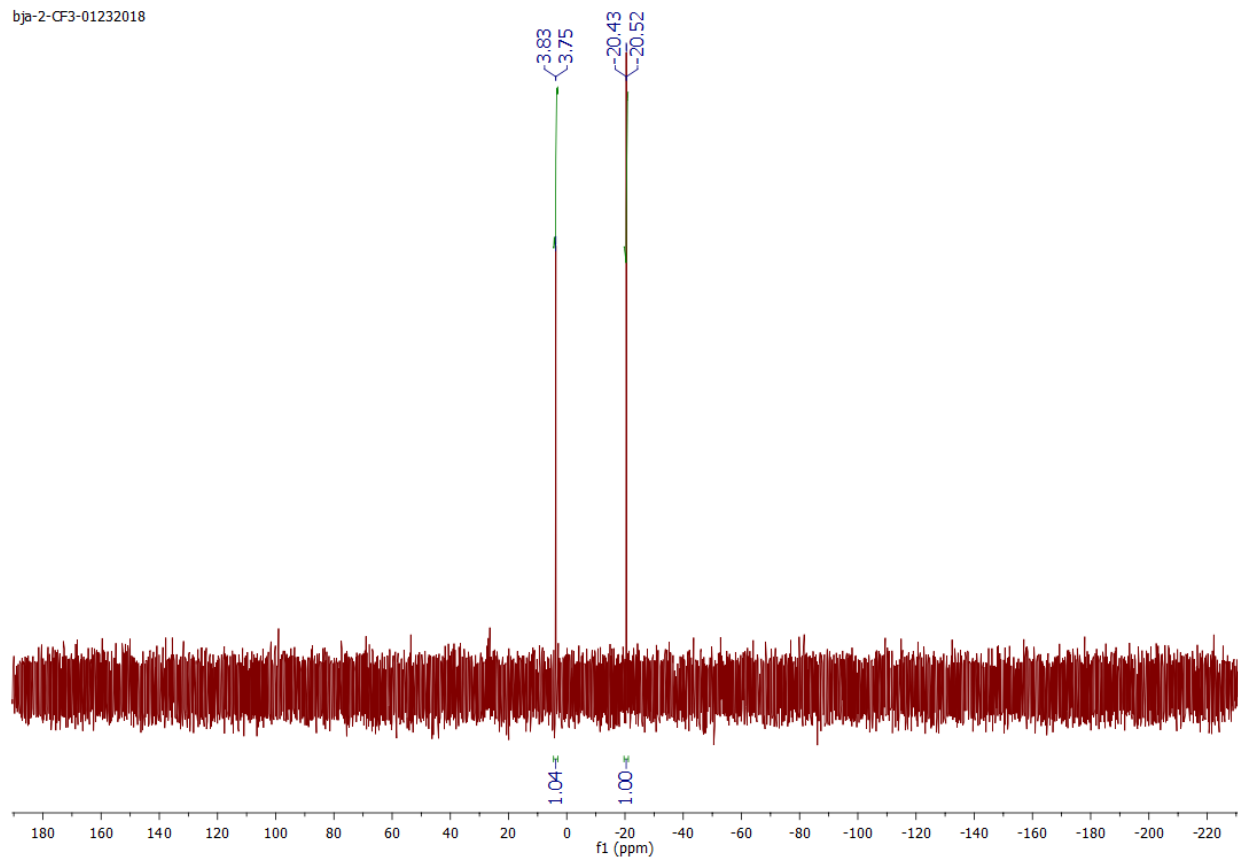


Figure S.12: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(4-trifluoromethylphenyl)ethane

Double hydrophosphination of 4-ethynyl-*N,N*-dimethylaniline: Reaction time: 16 hrs. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), 1:1 hexanes:DCM (2 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The product was a white crystalline powder, final yield post purification was 263 mg (93%).

^1H NMR (500 MHz, C_6D_6): δ 2.48 (s, 6H, NCH_3), 2.78 (s, 2H, CH_2), 3.63 (s, 1H, CH), 6.51 (m, 2H, Ph(H)), 6.86 (m, 3H, Ph(H)), 6.93 (m, 3H, Ph(H)), 7.11 (m, 6H, Ph(H)), 7.21–7.26 (m, 6H, Ph(H)), 7.43 (s, 2H, Ph(H)), 7.54 (s, 2H, Ph(H)). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): δ 34.11, 39.83, 41.22, 112.59, 128.14, 128.43, 128.91, 130.17, 132.15, 133.39, 134.39, 149.21. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ -21.32, 1.13. $m/z=516.5$

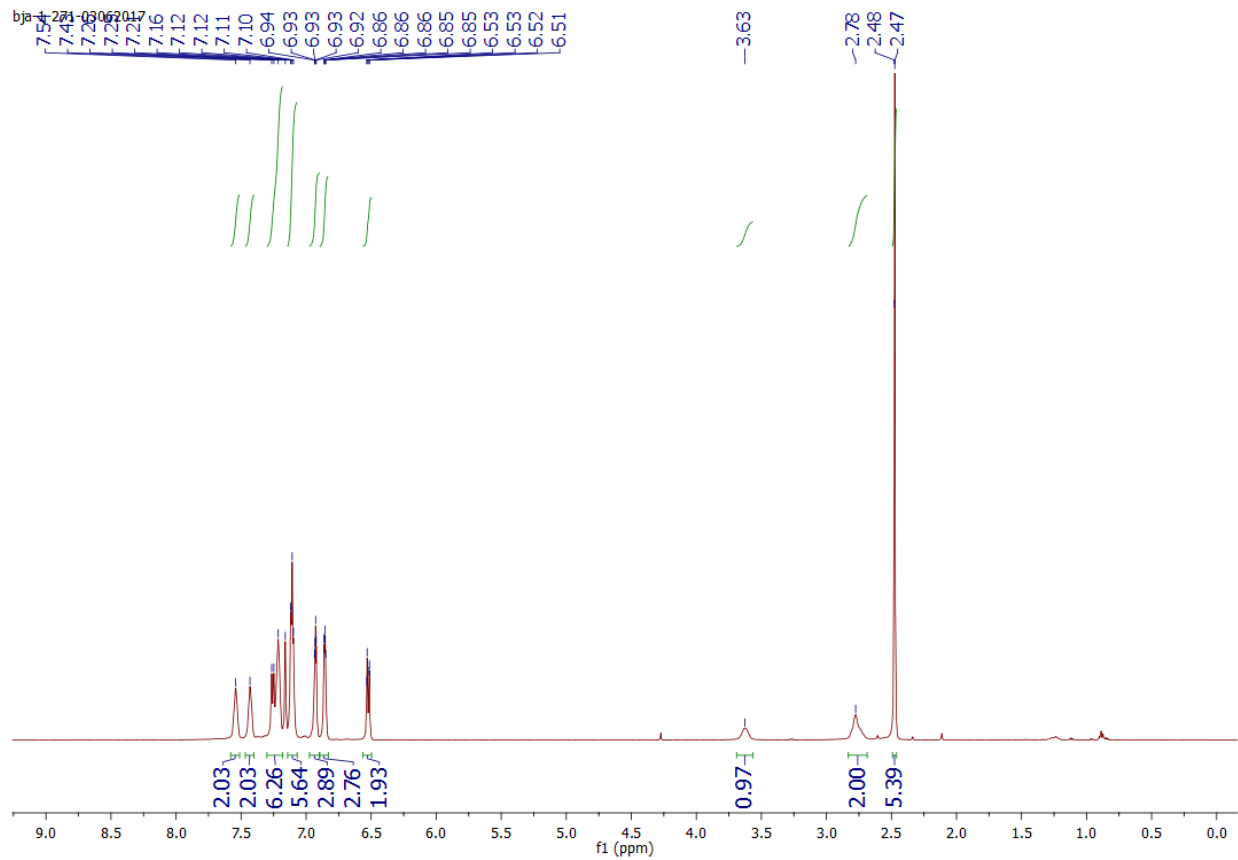


Figure S.13: ^1H NMR (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(4-*N,N*-dimethylaniline)ethane

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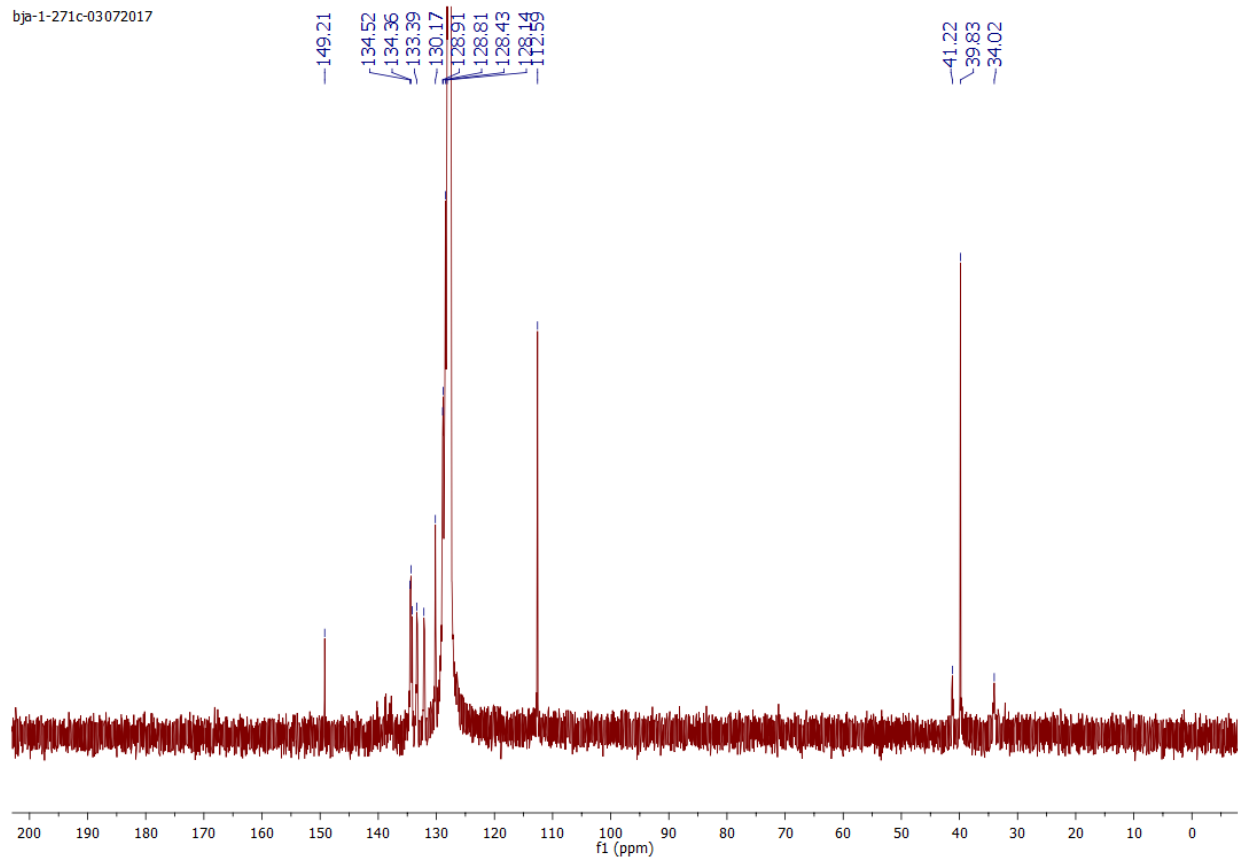


Figure S.14: $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(4-*N,N*-dimethylaniline)ethane

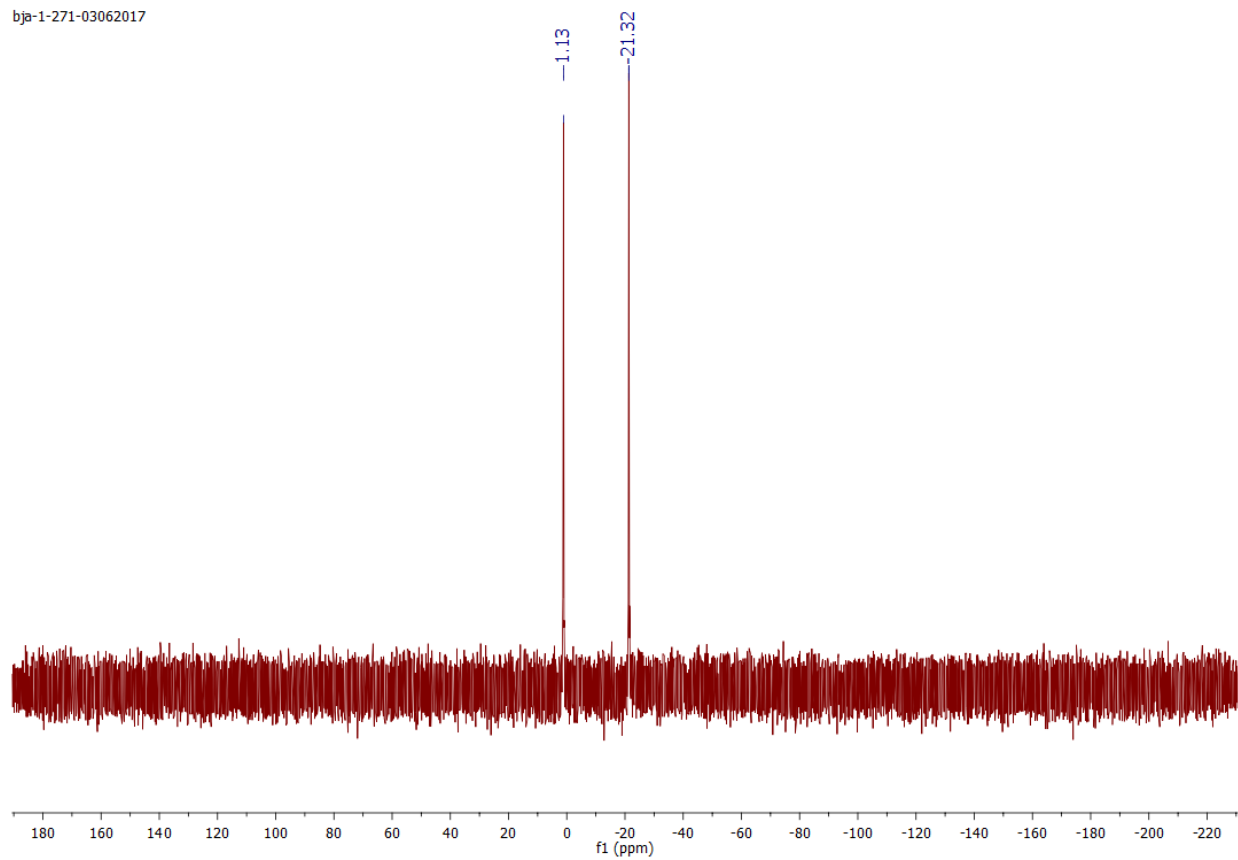


Figure S.15: $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6) NMR of 1,2-bis(diphenylphosphino)-1-(4-*N,N*-dimethylaniline)ethane

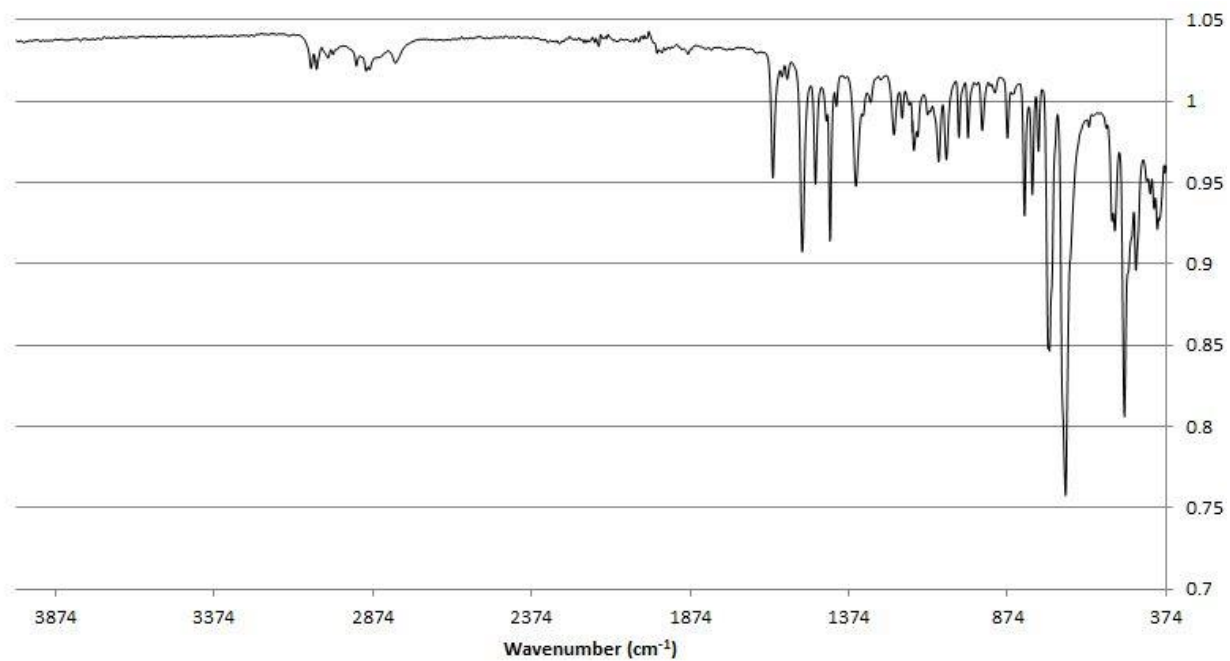


Figure S.16: IR spectrum of 1,2-bis(diphenylphosphino)-1-(4-*N,N*-dimethylaniline)ethane

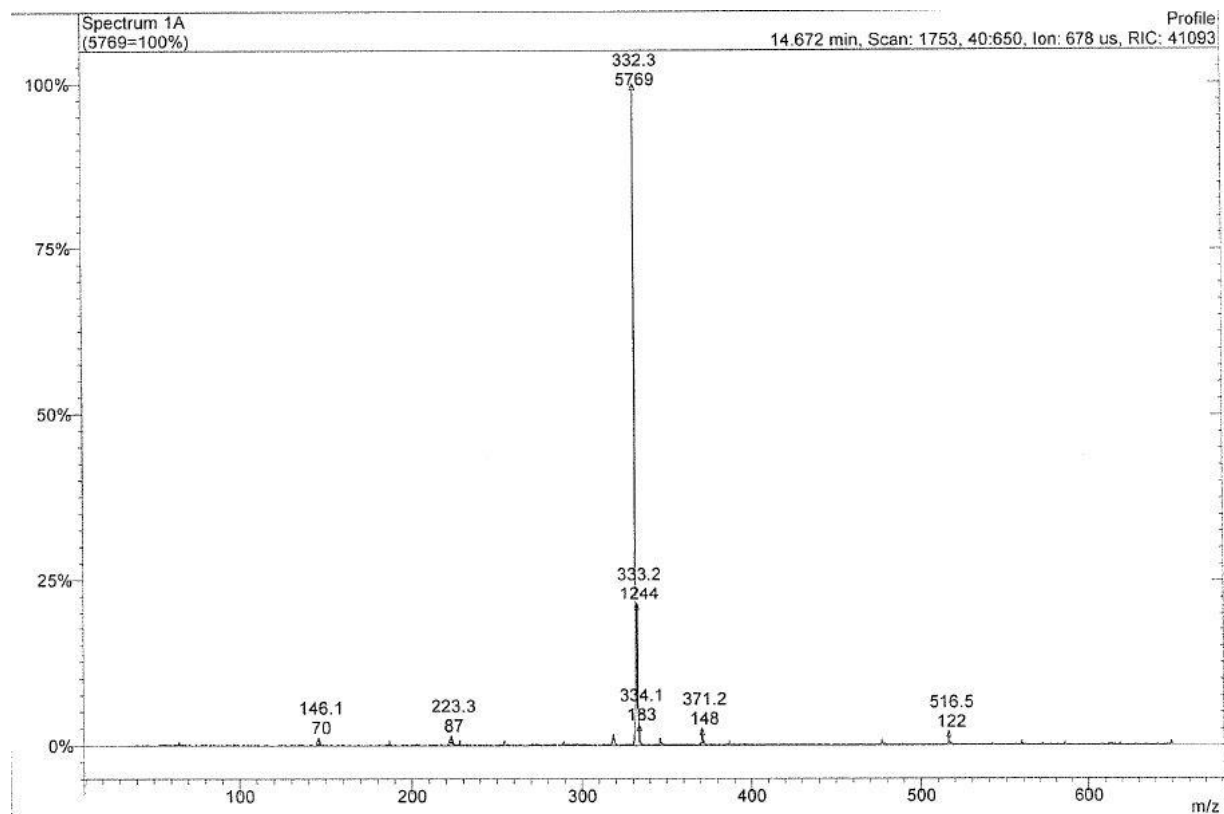


Figure S.17: Mass spectrum of 1,2-bis(diphenylphosphino)-1-(4-*N,N*-dimethylaniline)ethane

Double hydrophosphination of 2-ethynyl-2,4,6-trimethylbenzene: Reaction time: 16 hrs. Workup:

A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), 1:1 hexanes:DCM (3 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was recrystallized from a saturated hexanes solution. The product was a white crystalline powder, final yield post purification was 243 mg (84%).

^1H NMR (500 MHz, C_6D_6): δ 1.51 (s, 3H, PhCH₃), 2.13 (s, 3H, PhCH₃), 2.68 (m, 1H, PCH), 2.97 (s, 3H, PhCH₃), 3.11-4.29 (m, 2H, PCH₂), 6.54 (s, 1H, Ph(H)), 6.78-6.81 (m, 4H, Ph(H)), 6.89-6.92 (m, 5H, Ph(H)), 7.05 (m, 3H, Ph(H)), 7.10 (m, 3H, Ph(H)), 7.21 (m, 2H, Ph(H)), 7.79 (m, 2H, Ph(H)). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): δ 20.64, 21.23, 31.07, 36.72, 127.26, 128.07, 128.39, 128.77, 128.95, 129.60, 131.36, 131.64, 131.75, 131.90, 132.59, 132.72, 133.11, 134.03, 134.20, 134.47, 134.96, 135.13, 135.51, 135.74, 135.88, 137.60, 137.75, 137.90, 138.21, 138.35, 140.21, 140.34. $^{31}\text{P}\{^1\text{H}\}$ (202 MHz, C_6D_6): δ -18.96, -6.25. $m/z=517.5$

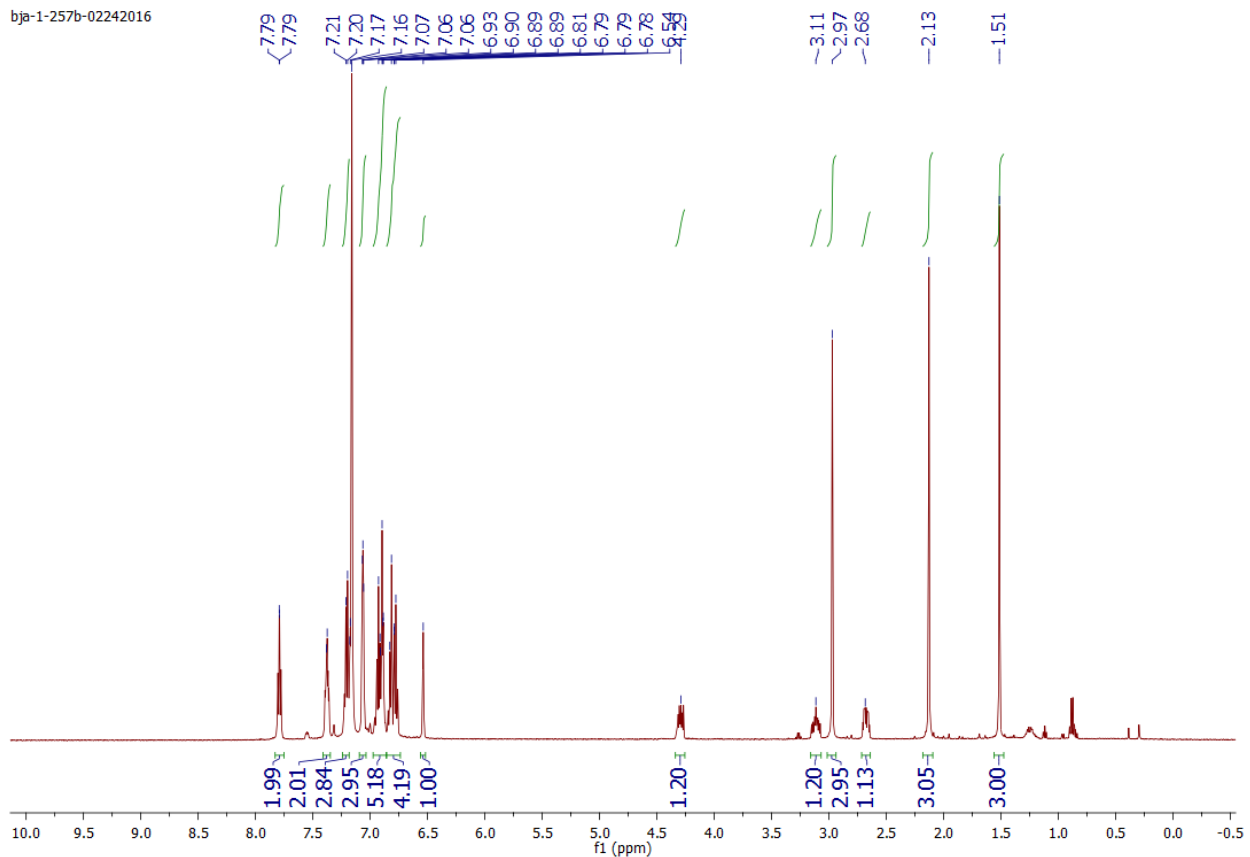


Figure S.18: ^1H NMR (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(2,4,6-trimethylphenyl)ethane

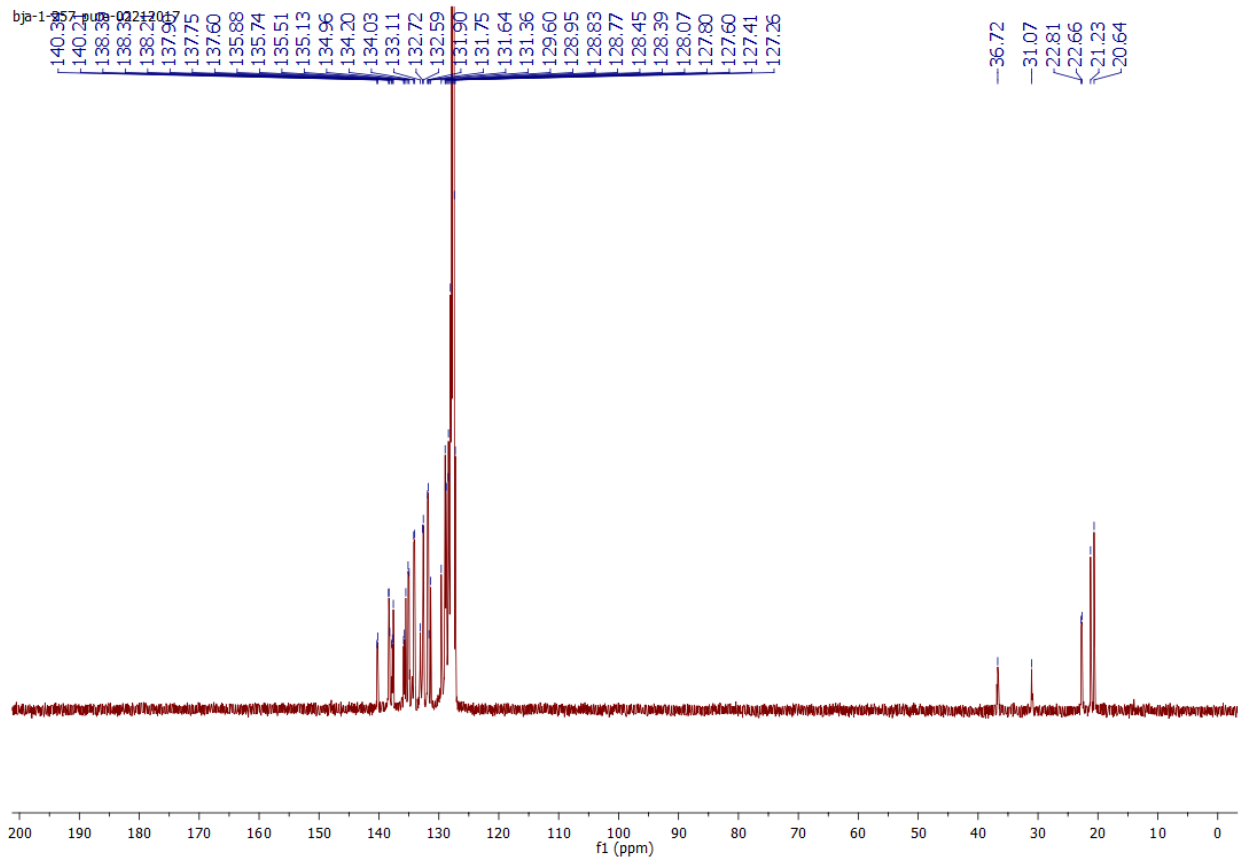


Figure S.19: ^{13}C NMR (C_6D_6) of 1,2-bis(diphenylphosphino)-1-(2,4,6-trimethylphenyl)ethane

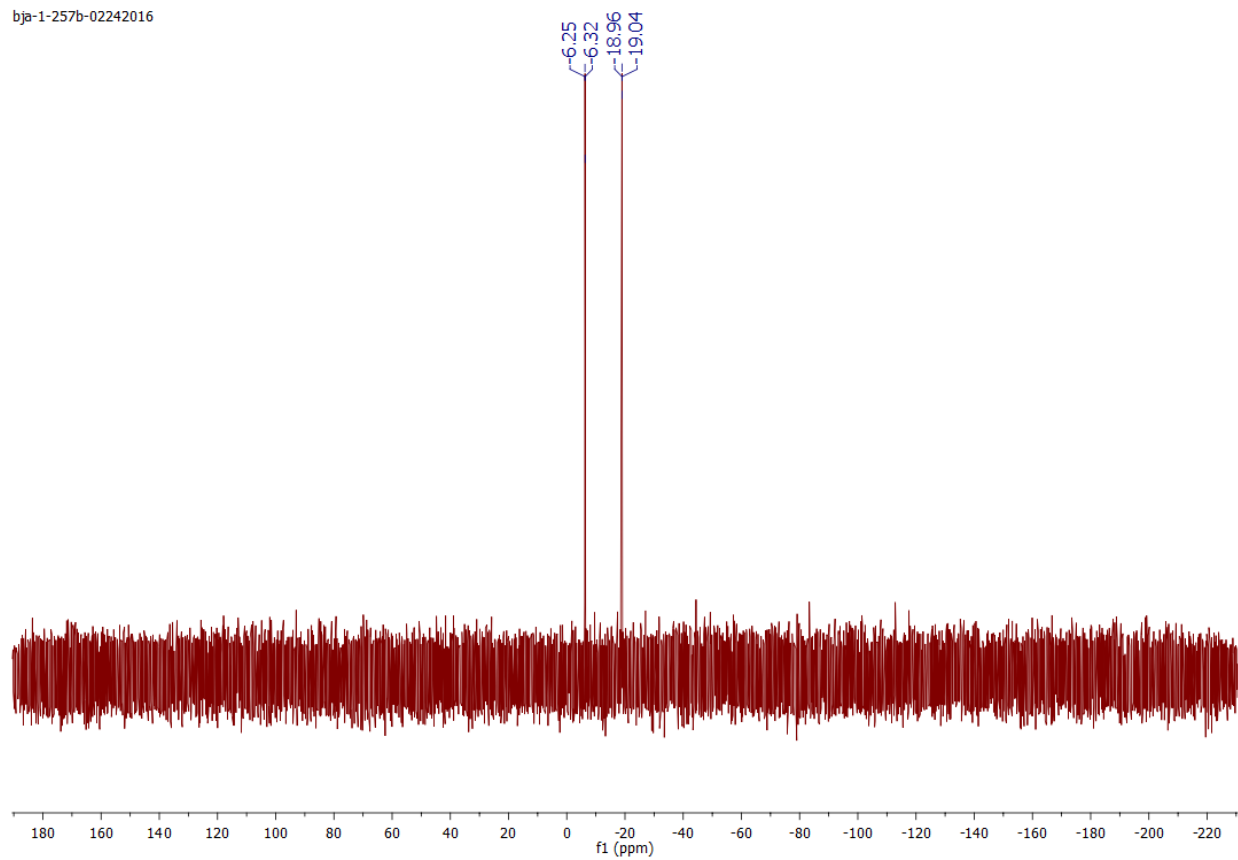


Figure S.20: $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6) NMR of 1,2-bis(diphenylphosphino)-1-(2,4,6-trimethylphenyl)ethane

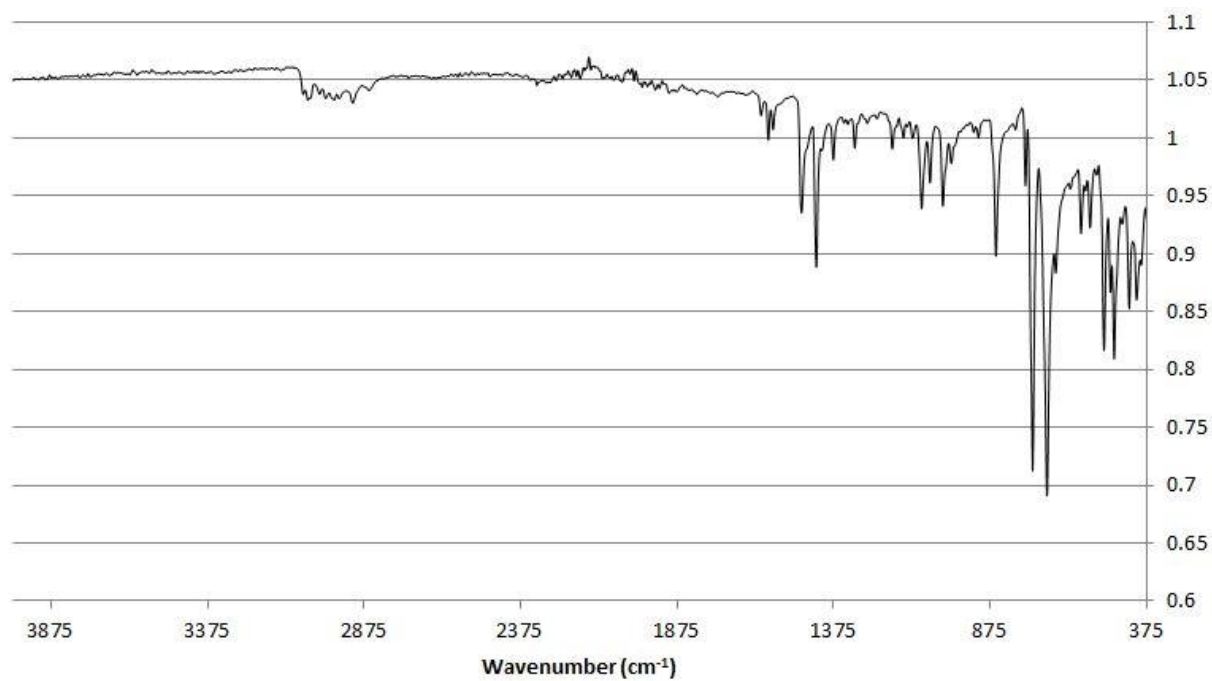


Figure S.21: IR spectrum of 1,2-bis(diphenylphosphino)-1-(2,4,6-trimethylphenyl)ethane

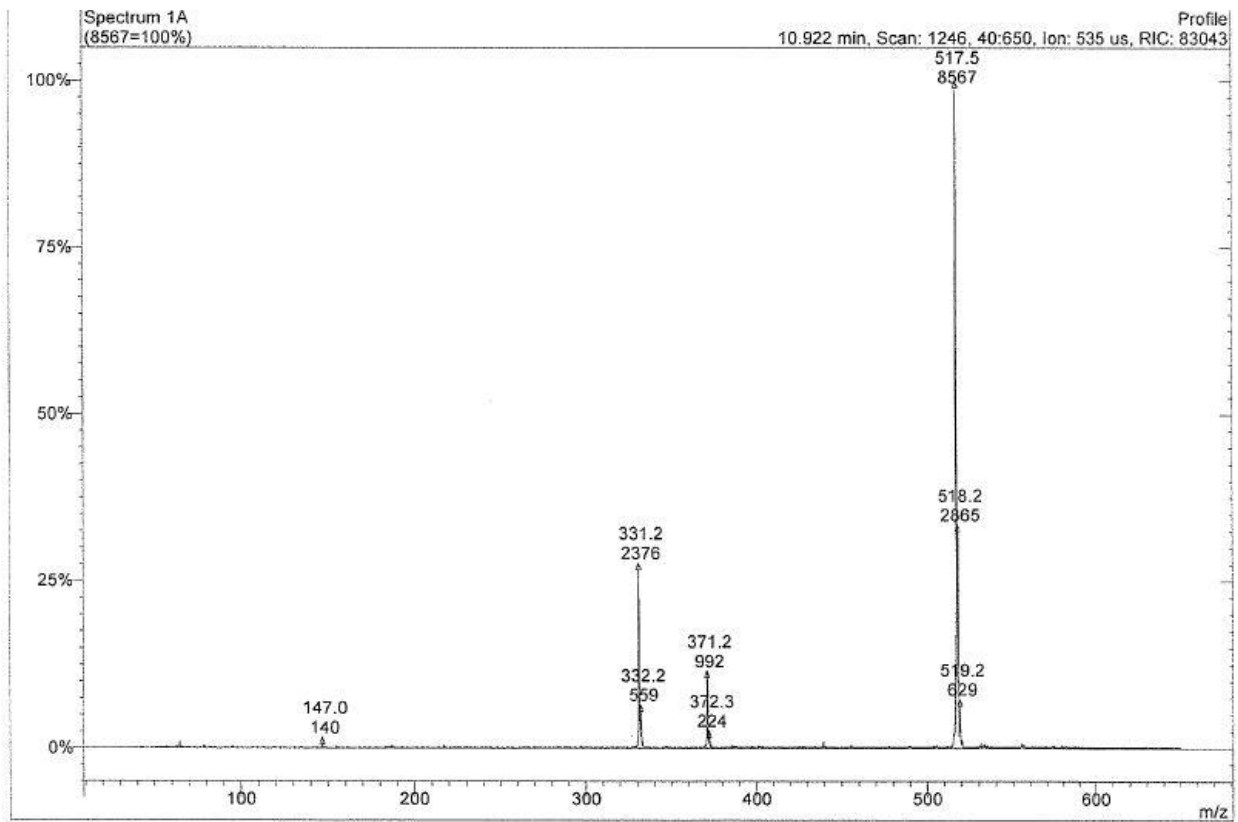


Figure S.22: Mass spectrum of 1,2-bis(diphenylphosphino)-1-(2,4,6-trimethylphenyl)ethane

Double hydrophosphination of 3-ethynyl thiophene: Reaction time: 4 hrs. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), 1:1 hexanes:DCM (2 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was washed with hexanes until the washings ran clear. The product was a white crystalline powder, final yield post purification was 268 mg. (99% yield). NMR data are consistent with literature values.¹

bja-2-35-01262018

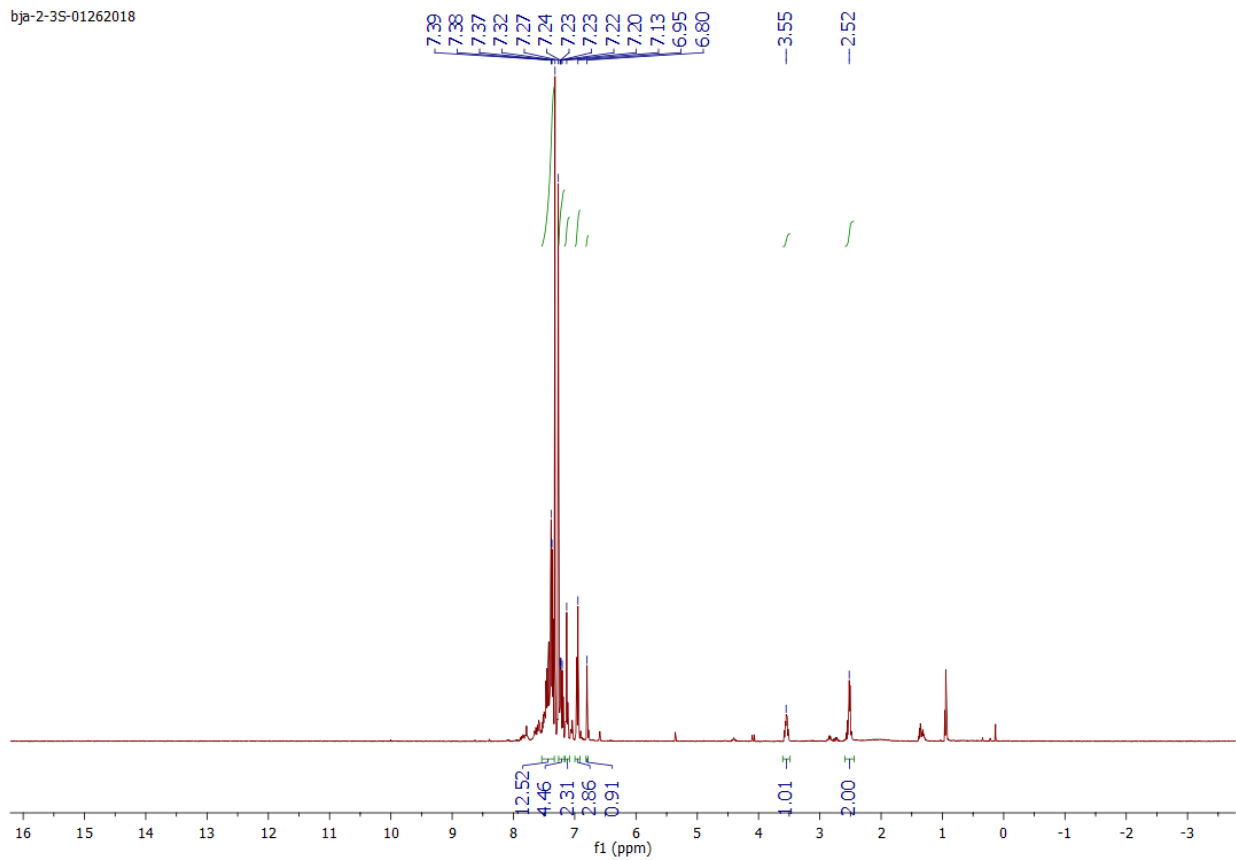


Figure S.23: ¹H NMR (CDCl₃) (of 1,1'-(1-(3-thienyl)-1,2-ethanediyl)bis(1,1-diphenyl-phosphine)

bja-2-72-09042017

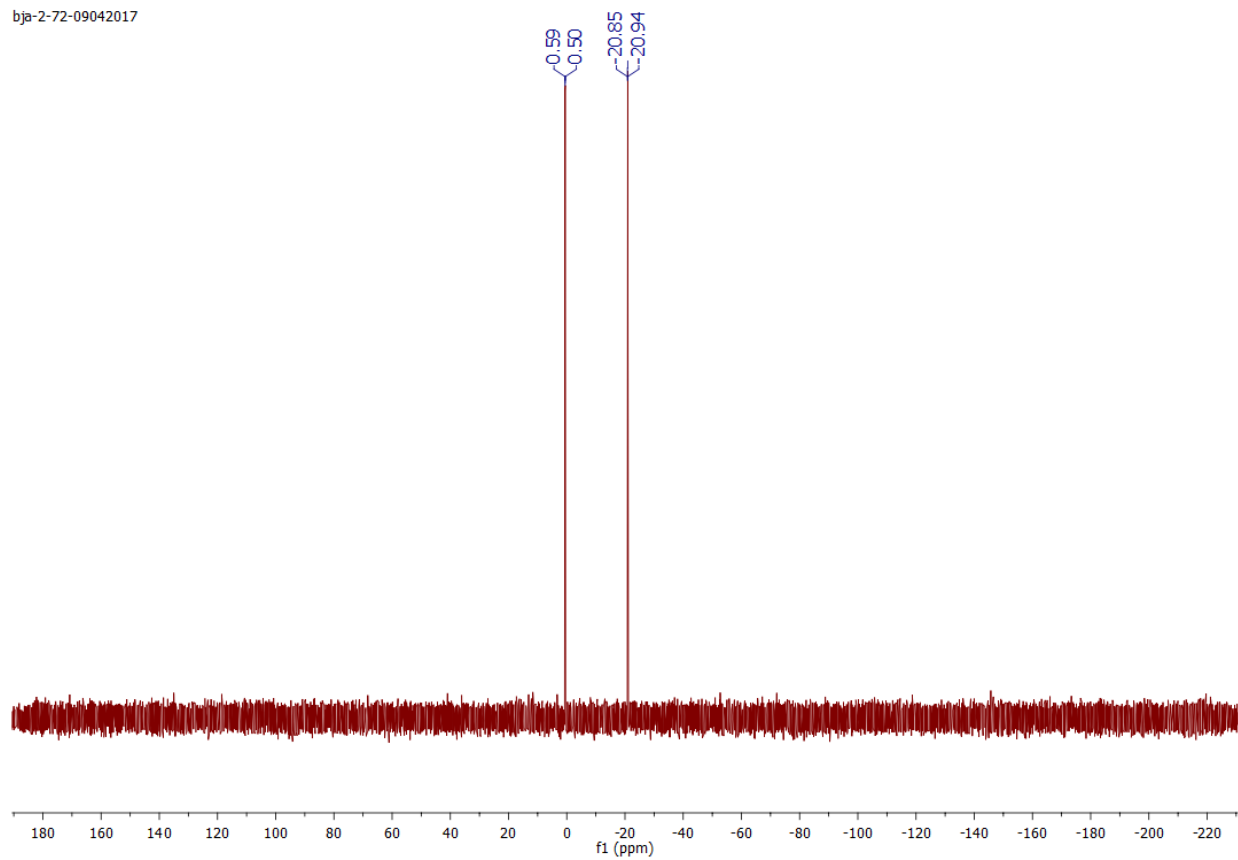


Figure S.24: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 1,1'-(1-(3-thienyl)-1,2-ethanediyl)bis(1,1-diphenylphosphine)

Double hydrophosphination of 2-ethynylpyridine: Reaction time: 16 hrs. Workup: A DCM solution of the crude reaction mixture (0.5 mL) was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), then DCM (10 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which was recrystallized from a saturated pentane solution. The product was a white crystalline powder, final yield post purification was 228 mg (86%). NMR spectra are consistent with literature values.¹

bja-2-2py-01292018

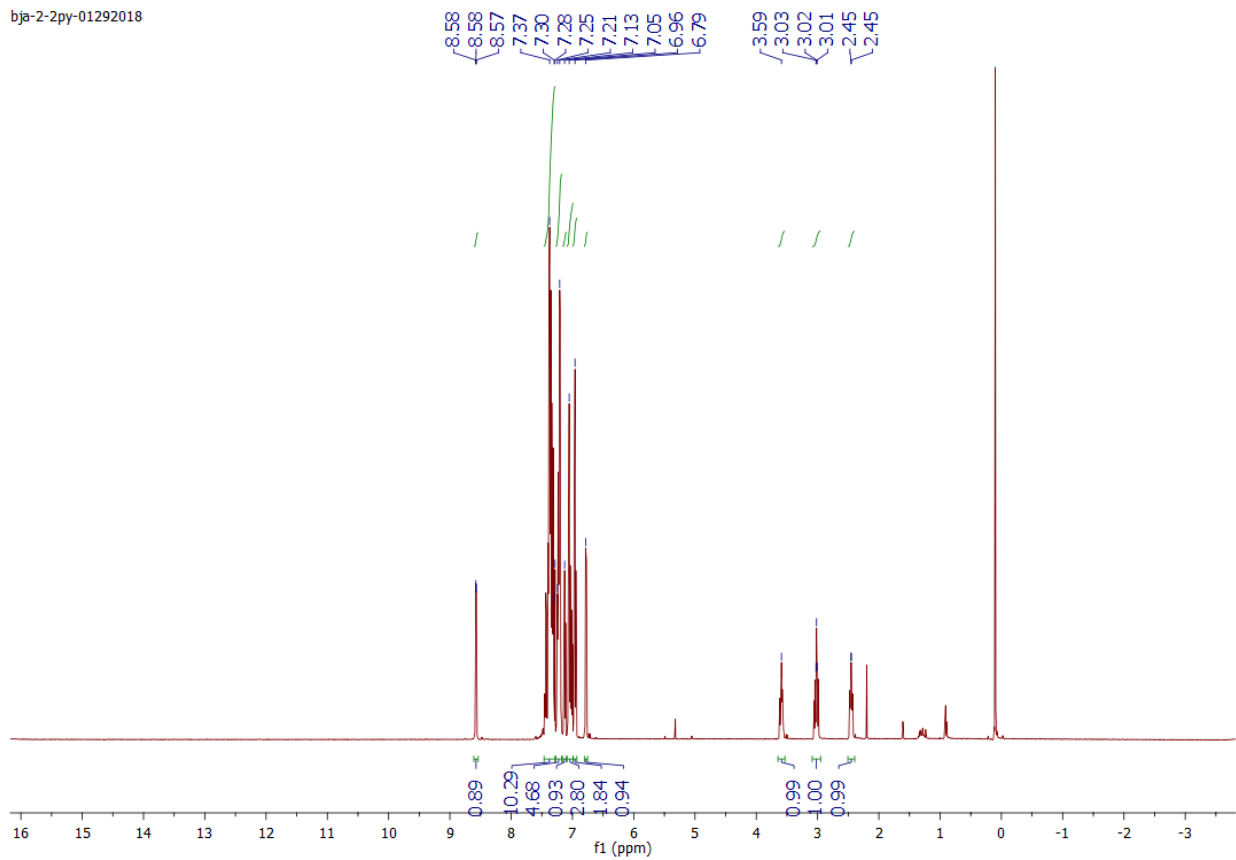


Figure S.25: ^1H NMR (CDCl_3) of 1,1'-[1-(2-pyridyl)-1,2-ethanediyl]bis(1,1-diphenyl-phosphine)

bja-2py-02192018

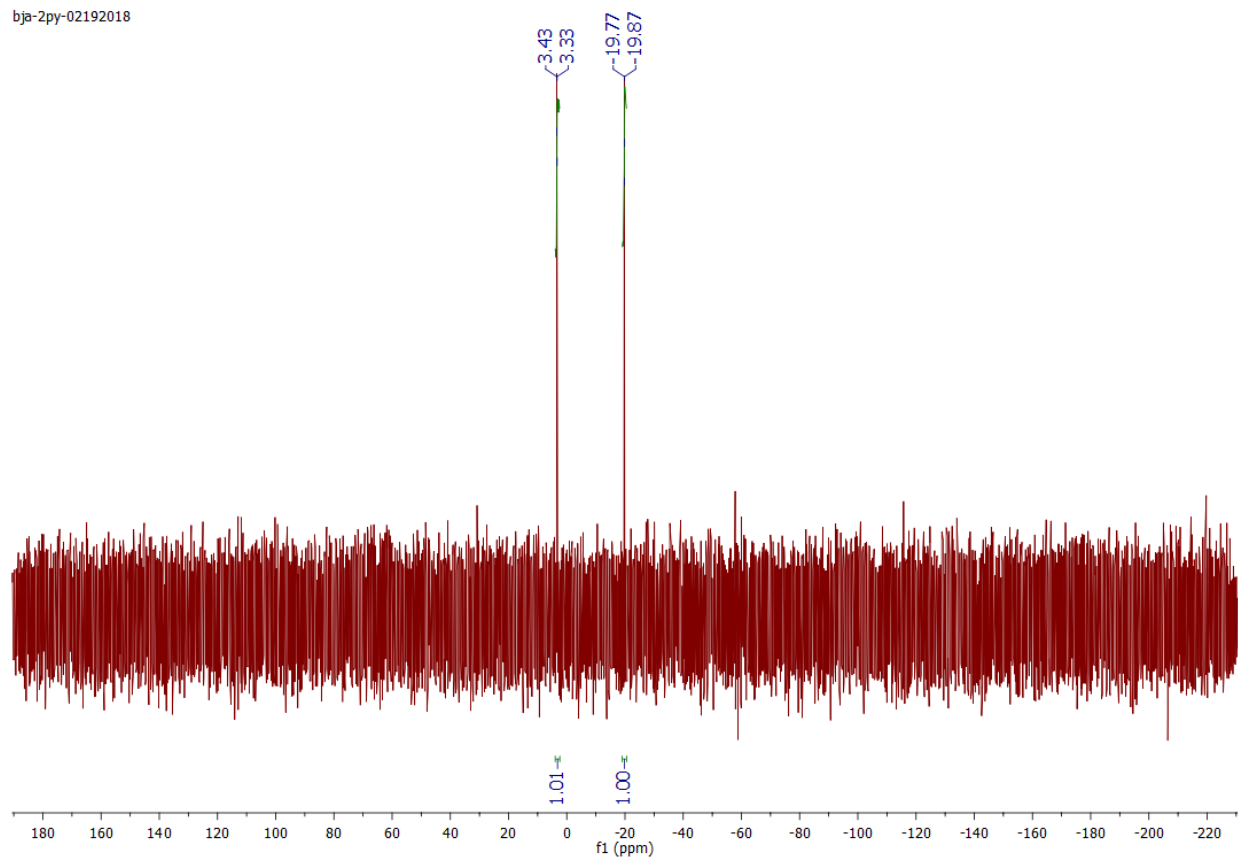


Figure S. 26: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 1,1'-[1-(2-pyridyl)-1,2-ethanediyl]bis(1,1-diphenylphosphine)

Double hydrophosphination of 3-ethynylpyridine: Reaction time: 16 hrs. Workup: A DCM solution (0.5 mL) of the crude reaction mixture was layered with pentanes (5 mL) precipitating an off-white crystallin solid. The product was loaded onto a fine porosity frit and washed hexanes (6 mL) until the washings ran clear, and the solid was collected, yielding pure 1,1'-[1-(3-pyridyl)-1,2-ethanediyl]bis(1,1-diphenyl-phosphine). Final yield of purified product was 194 mg (73%) NMR spectra are consistent with literature values.¹

bja-2-3PY-01232018

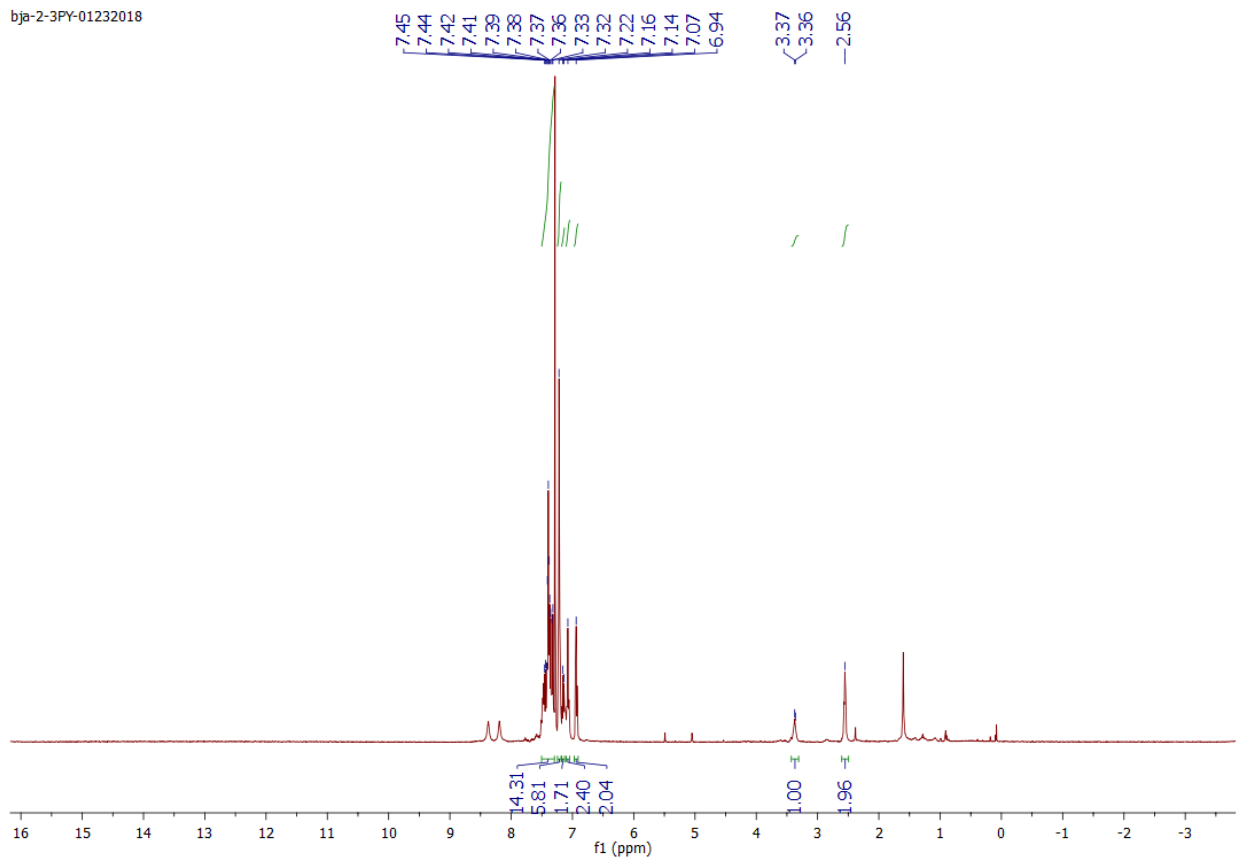


Figure S. 27: ^1H NMR (CDCl_3) of 1,1'-(1-(3-pyridyl)-1,2-ethanediyl)bis(1,1-diphenyl-phosphine)

bja-2-3py-02192018

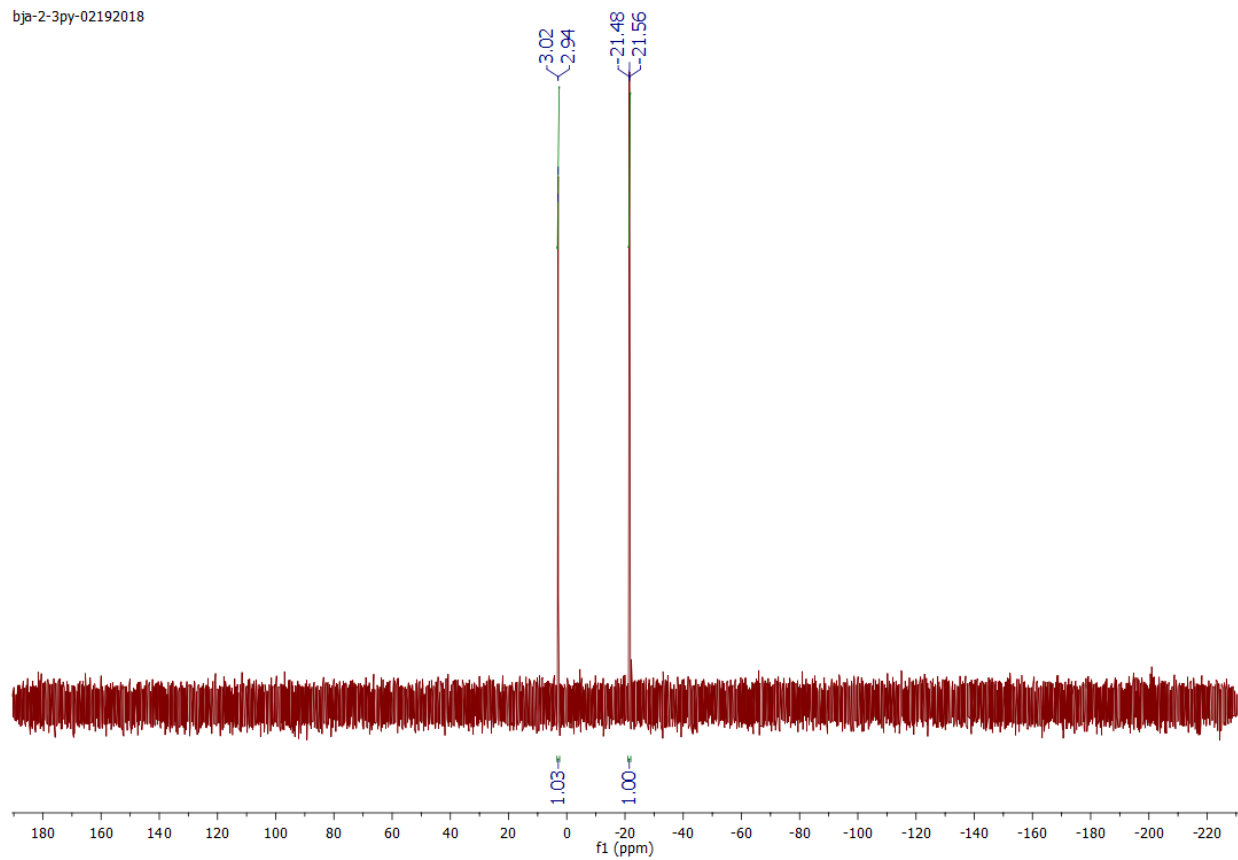


Figure S. 28: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 1,1'-(1-(3-pyridyl)-1,2-ethanediyl)bis(1,1-diphenylphosphine)

Double hydrophosphination of phenylacetylene with di-*p*-tolyl phosphine: A 10 mL schlenk flask fitted with a condenser was charged with $[\text{CpFe}(\text{CO})_2]_2$ (10.0 mg, 0.028 mmol), phenyl acetylene (0.06mL, 0.56 mmol), and (*p*-tol)₂PH (240 mg, 1.12 mmol) in a N₂-filled glovebox then was placed on a schlenk line under N₂. The reaction was heated to 110 °C for 16 hours, after which the reaction was allowed to cool to ambient temperature and volatiles were removed under reduced pressure. The reaction was then brought back into the glovebox and a DCM solution of the crude reaction mixture was loaded onto a silica gel column (9" borosilicate glass pipet approximately 60% full of silica packed with hexanes), which was eluted with hexanes (3 mL), 1:1 hexanes:DCM (2 mL), then DCM (2 mL). Volatiles were removed from the pale red eluent to give an off-red solid, which still possessed phosphine contaminants. Subsequent recrystallizations out of hexanes, pentane, DCM, and/or diethyl ether did not yield a pure product. Purification using preparatory TLC, using DCM and increasing fractions of methanol up to 100%, did not isolate the desired product, as a number of phosphine containing products moved identically across the column under the given conditions. NMR yield of the crude product = 32%.

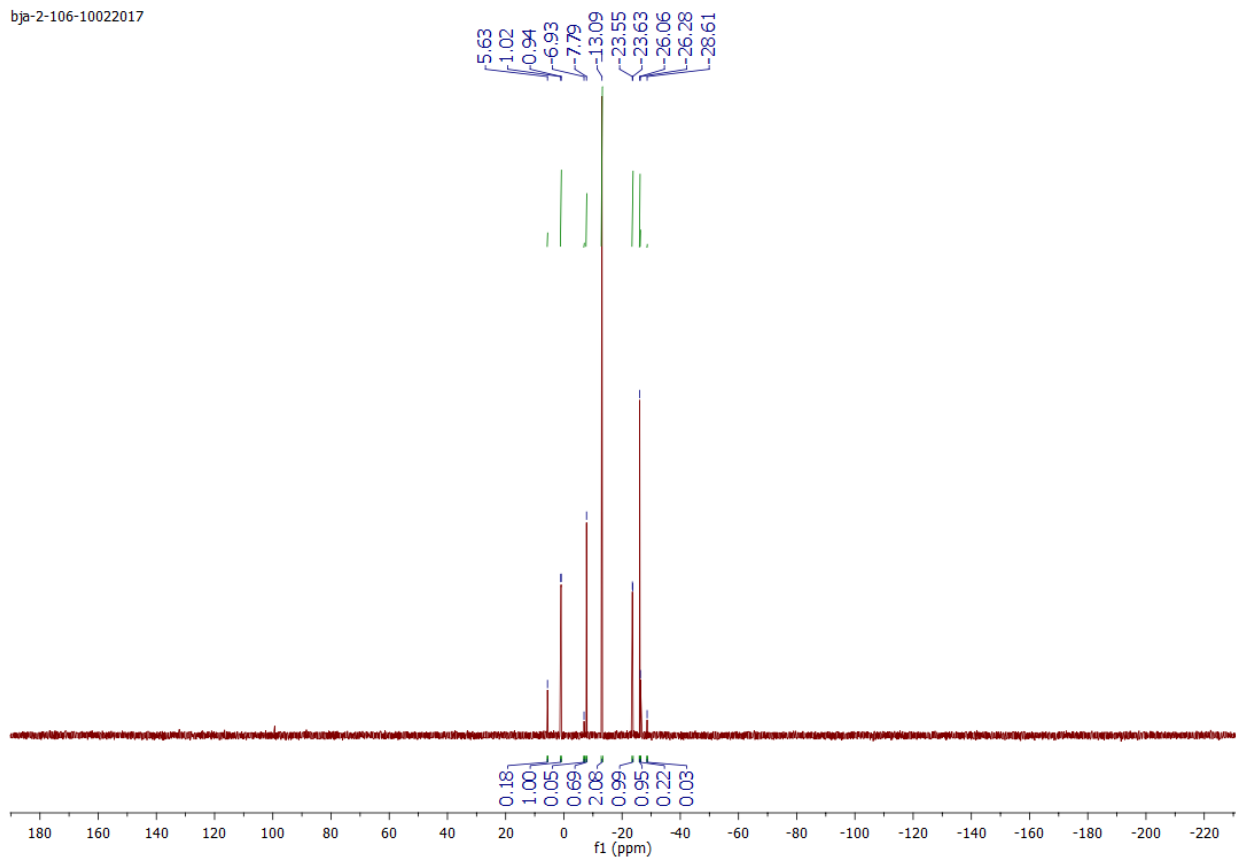


Figure S.29: Crude $^{31}\text{P}\{^1\text{H}\}$ NMR of 1,2-bis(di-*p*-tolyl-phosphino)-1-phenylethane

Product (ppm)	1,2-bis(di- <i>p</i> -tolyl-phosphino)-1-phenylethane (0.94, -23.63) ($J=16.77$ Hz) ¹	Tri(<i>p</i> -tolyl)phosphine (-7.79) ³	All others unknown*
%	32	11	57

*Although the peaks at 5.63 ppm and -13.09 ppm are unknown, they are likely to be the E and Z isomers of the vinyl phosphines as a result of a single addition across the alkyne, as these shifts are similar to those observed with diphenylphosphine, and account for 37%.⁴

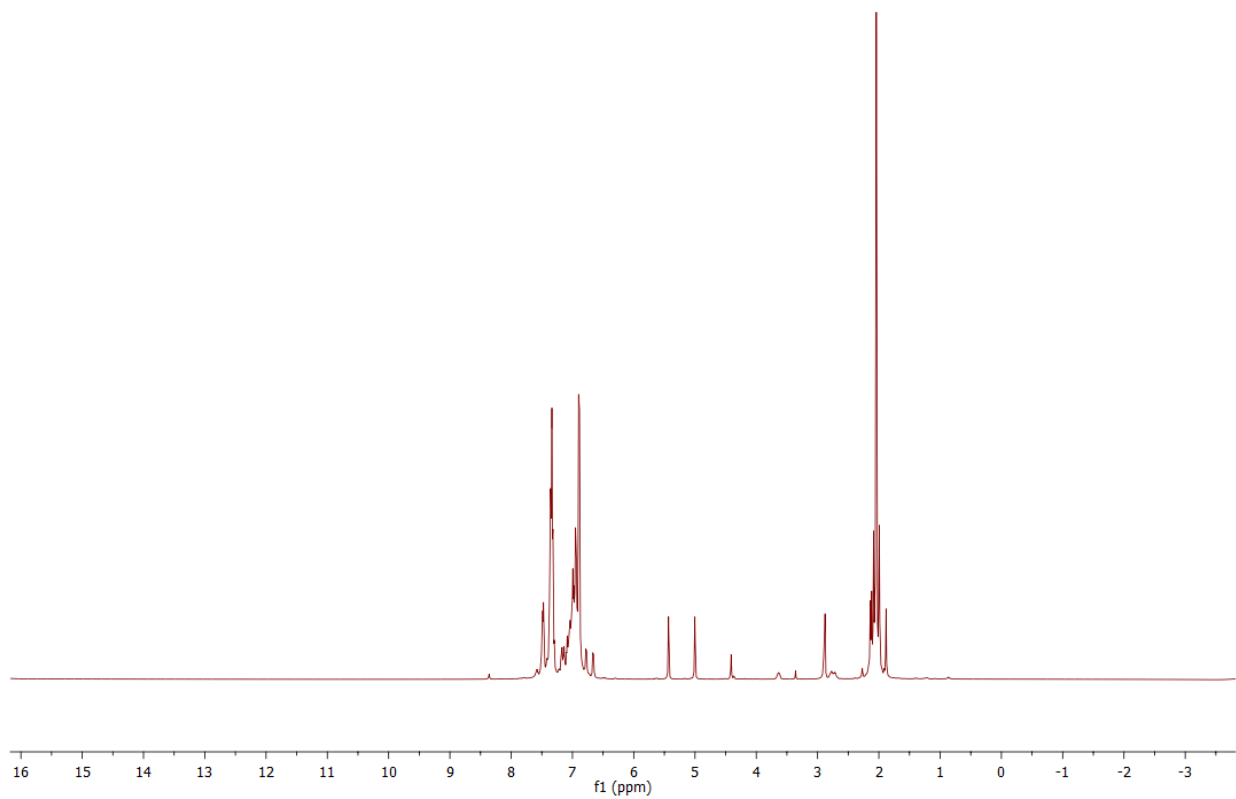


Figure S.30: Crude ^1H NMR of 1,2-bis(di-*p*-tolyl-phosphino)-1-phenylethane.

References

1. M. Kamitani, M. Itazaki, C. Tamiya and H. Nakazawa, *J. Am. Chem. Soc.*, 2012, **134**, 11932-11935.
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