Supporting Information for:

A Phosphine-Mediated, Stereocontrolled Synthesis of Z-Enediynes by a Vicinal Dialkynylation of Ethynylphosphonium Salts

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I. General Experimental

All reactions were carried out under an N₂ atmosphere using dry glassware and standard Schlenk techniques. Column chromatography was performed using 230-400 mesh silica gel purchased from Silicycle as the stationary phase. All NMR spectra were obtained in CDCl₃ using a Bruker DPX-300 spectrometer for ¹H spectra and a Bruker AV-360 spectrometer for ¹³C{¹H} and ³¹P{¹H} spectra. ¹H spectra were referenced to an internal TMS standard, ¹³C spectra to the internal solvent peak (δ = 77.16 ppm) and ³¹P spectra to an external sample of 85% H₃PO₄. High resolution EI and ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the School of Chemical Sciences, University of Illinois at Urbana-Champaign.

All reagents were purchased through Sigma-Aldrich, Alfa Aesar, or Oakwood Chemical, and used as received unless otherwise noted. Tetrahydrofuran and toluene were purified under argon using a Glass Contour Solvent Purification System. *n*BuLi was titrated prior to use using diphenylacetic acid as indicator.¹ Phenylacetylene and 4-ethynyltoluene were obtained from Alfa Aesar and distilled prior to use. Phenylacetylene-*d* (95% D) was prepared by quenching of lithium phenylacetylide with D₂O (99.9% D).² The alkynes 3-ethynyl- α , α , α -trifluorotoluene, 4-ethynyl- α , α , α -trifluorotoluene, and 2-ethynylnaphthalene were prepared according to literature precedent using Corey-Fuchs methodology.³ 2-Ethynyltoluene,⁴ 1-chloro-4-ethynylbenzene,⁵ 1-bromo-4-ethynylbenzene,⁶ 1-ethynyl-4-vinylbenzene,⁷ and 1-(3,3-dimethylbut-1-yn-1-yl)-4-ethynylbenzene⁸ were prepared by Sonagashira methodology. The corresponding bromoalkynes were prepared according to literature precedent using silver nitrate/*N*-bromosuccinimide.⁹ Tri(4-methoxyphenyl)phosphine was prepared from PCl₃ and the corresponding aryl Grignard reagent.¹⁰

II. Synthetic Procedures



tri(4-methoxyphenyl)(phenylethynyl)phosphonium bromide: A solution of tri(4-methoxyphenyl)phosphine (0.856g, 2.4 mmol) in toluene (20 mL) was prepared and cooled to -78 °C. Freshly distilled 1-bromo-2-phenylacetylene (0.510 g, 2.8 mmol) was added neat via syringe, following which the solution was warmed to room temperature and stirred for 1.5 days to yield a yellow oil. The supernatant toluene was removed, and the oil dissolved in ~5 mL of dichloromethane. Pentane was added to produce a solid,

which was collected in a glove box to yield the desired product as a pale yellow solid (0.981 g, 1.8 mmol, 76%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.98$ (s, 9H, OCH₃), 7.26-7.34 (m, 6H, Ar), 7.49-7.56 (m, 2H, Ar), 7.59-7.74 (m, 7H, Ar), 7.77-7.82 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.3, 70.7 (d, ¹*J*_{P-C} = 183 Hz), 108.6 (d, ¹*J*_{P-C} = 109 Hz), 116.2 (d, ²*J*_{P-C} = 32 Hz), 116.6 (d, *J*_{P-C} = 15.6 Hz), 117.1 (d, *J*_{P-C} = 4.6 Hz), 129.1, 132.9, 133.4 (d, *J*_{P-C} = 2.1 Hz), 135.1 (d, *J*_{P-C} = 14.3 Hz), 165.4 (d, *J*_{P-C} = 3.1 Hz); ³¹P NMR (CDCl₃, 146 MHz): +5.3 ppm; HRMS (Positive ESI) Calcd. For C₂₉H₂₆O₃P⁺: 453.1620, Found: 453.1609.



bis(2-methoxyphenyl)phenylphosphine: A solution of 2-bromoanisole (8.06g, 43 mmol) in THF (80 mL) was prepared, and ca. 5 mL was added via cannula to a three necked flask containing magnesium turnings (1.41g, 58 mmol). The mixture was heated gently under vigorous stirring until an

exothermic reaction was observed, following which the remainder of the 2-bromoanisole solution was added dropwise. Upon complete addition, the Grignard solution was heated to 60 °C for 1 h then cooled to room temperature and added dropwise to a solution of dichlorophenylphosphine (2.8 mL, 21 mmol) in THF (60 mL) cooled to -78 °C. After addition the cooling bath was removed and the reaction stirred for 3 h at room temperature, during which time the phosphine precipitated from solution. Water was then added to quench the reaction, and the aqueous layer was extracted with DCM. The combined organic layers were dried over MgSO₄ and concentrated to yield an off white solid. Washing this solid with hexanes, followed by filtration over a plug of silica gel using DCM as eluent, afforded the phosphine as a white solid (5.2g, 16 mmol, 75%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.72$ (s, 6H, OCH₃), 6.63-6.70 (m,

2H, Ar), 6.79-6.91 (m, 4H, Ar), 7.23-7.38 (m, 7H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 55.8, 110.2 (d, $J_{P-C} = 1.5$ Hz), 121.0, 125.2 (d, $J_{P-C} = 12.5$ Hz), 128.3 (d, $J_{P-C} = 7.3$ Hz), 128.6, 130.2, 133.8, 134.1 (d, $J_{P-C} = 20.7$ Hz), 136.5 (d, $J_{P-C} = 10.4$ Hz), 161.4 (d, $J_{P-C} = 15.9$ Hz); ³¹P NMR (CDCl₃, 146 MHz): -27.6 ppm.



1-bromo-2,4-diphenylbut-1-en-3-yne:¹¹ A suspension of (bromomethyl) triphenylphosphonium bromide (9.36g, 21 mmol) in THF (150 mL) was cooled to -78 °C, and LiHMDS (1.0 M in THF, 26 mL) was added dropwise. After stirring for an additional 0.75 h at this temperature, a solution of 1,3-diphenylprop-2-yn-1-one¹² (4.2g, 20 mmol) in THF (10 mL) was added dropwise and the resulting mixture warmed to room temperature overnight.

The resulting dark solution was quenched with NH₄Cl (aq.), and the aqueous layer extracted with diethyl ether. The combined organic layers were dried over MgSO₄ and concentrated. Column chromatography (silica gel, hexanes) yielded the desired product as a pale yellow oil (3.7g, 13 mmol, 64%). Isomer ratio approximately 1.5:1.



(Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium

bromide (Z-10): Following literature precedent,¹³ a mixture of vinyl bromide (0.98g, 3.5 mmol), triphenylphosphine (0.89 g, 3.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.170 g, 0.14 mmol) was dissolved in toluene (15 mL) and stirred at 110 °C for 24 h. After cooling to room temperature the resulting solid was collected by

filtration, and washed with toluene and diethyl ether to afford essentially pure (*Z*)-isomer as a white solid (0.440g, 0.81 mmol, 24%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.81-6.87$ (m, 2H, Ar), 7.23-7.30 (m, 2H, Ar), 7.34-7.44 (m, 2H, Ar), 7.52-7.57 (m, 3H, Ar), 7.69-7.87 (m, 15H, Ar), 8.14-8.20 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 86.1 (d, *J*_{P-C} = 11.7 Hz), 107.7 (d, *J*_{P-C} = 94 Hz), 108.2 (d, *J*_{P-C} = 1.1 Hz), 118.7 (d, *J*_{P-C} = 92 Hz), 119.5, 127.9, 128.5, 129.1, 130.7, 130.5 (d, *J*_{P-C} = 13.2 Hz), 131.3, 132.2, 133.6 (d, *J*_{P-C} = 10.6 Hz), 135.0, 135.1 (d, *J*_{P-C} = 3.2 Hz), 149.0; ³¹P NMR (CDCl₃, 146 MHz): +16.0 ppm; HRMS (Positive ESI) Calcd. For C₃₄H₂₆P⁺: 465.1772, Found: 465.1765. The [BF₄] salt was prepared via anion exchange in dichloromethane with aqueous NaBF₄, and X-ray quality crystals were prepared via slow diffusion of hexanes into a 1,2-dichloroethane solution of the phosphonium salt.

Photoisomerization of (Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium bromide

A solution of (*Z*)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium bromide (0.350g, 0.64 mmol) in acetonitrile (7 mL) was placed into several standard NMR tubes and irradiated with a 300W incandescent bulb for 6 h. Removal of solvent and 31P NMR indicated an ~1.1:1 *Z:E* ratio. Storage overnight in the dark in CD₃CN resulted in no change in the isomer ratio. Replacement of the bromide counterion with tetrafluoroborate did not affect the photoisomerization. The identity of the new species was determined by X-ray analysis (slow diffusion of hexanes into a 1,2-dichloroethane solution of the phosphonium tetrafluoroborate isomers). The (*E*) isomer crystallized first as colorless blocks. ³¹P NMR (CDCl₃, 146 MHz): +15.9 (*Z*), +14.0 (*E*) ppm.

General Synthesis of Bis(2-methoxyphenyl)(phenyl)(ethynyl)phosphonium Salts

To a solution of bis(2-methoxyphenyl)phenylphosphine (~3 mmol) in toluene (40 mL) was added bromoalkyne (1.2 eq., neat or as a solution in ~5 mL toluene), and the resulting solution was warmed to ~50 °C and stirred for 3-4 days. After cooling, the solid which formed was collected via filtration, and washed with toluene and ether to yield the desired alkynylphosphonium salt as a white solid. No additional purification was attempted unless otherwise noted.



R	Phosphine Mass (g)	Bromoalkyne Mass (g)	Temperature (°C)	Time (days)	Phosphonium Mass (g) Yield (%) ^a
Jaa Jaa	2.10	1.30	45	3	2.18 (66)
3b	0.988	0.66	50	3	0.67 (42)
3c	1.14	0.80	50	3.5	1.03 (56)
F ₃ C	0.630	0.60	45	3	0.92 (82)
F ₃ C 3e	0.938	0.945	50	3.5	1.13 (68)
CI 3f	0.967	0.774	45	3	1.30 (80)
Br 3g	0.910	0.866	45	3	1.45 (88)

3h	0.989	0.843	45	4	1.37 (81)
3i	1.03	0.770	45	3.5	1.15 (68)
3j	1.01	0.970	50	4	0.733 (40)
× <u> </u>					

^alsolated Yields.



bis(2-methoxyphenyl)(phenyl)(phenylethynyl)phosphonium bromide (3a): ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.84$ (s, 6H, OCH₃), 7.22-7.32 (m, 2H, Ar), 7.33-7.46 (m, 4H, Ar), 7.47-7.57 (m, 2H, Ar), 7.57-7.66 (m, 1H, Ar), 7.68-7.80 (m, 6H, Ar), 7.81-7.87 (m, 1H, Ar), 7.87-7.97 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.7, 69.7 (d, ¹*J*_{P-C} = 194 Hz), 104.8 (d, ¹*J*_{P-C} = 107 Hz), 113.4 (d, *J*_{P-C} = 6.9 Hz), 113.7 (d, ²*J*_{P-C} = 33 Hz), 117.5 (d, *J*_{P-C} = 4.7

Hz), 118.9 (d, ${}^{1}J_{P-C} = 106$ Hz), 122.3 (d, $J_{P-C} = 14.6$ Hz), 129.0, 129.9 (d, $J_{P-C} = 14.7$ Hz), 132.1 (d, $J_{P-C} = 12.8$ Hz), 132.4, 132.9 (d, $J_{P-C} = 2.0$ Hz), 134.4 (d, $J_{P-C} = 10.7$ Hz), 134.7 (d, $J_{P-C} = 3.1$ Hz), 138.5, 161.8 (d, $J_{P-C} = 2.3$ Hz); 31 P NMR (CDCl₃, 146 MHz): +1.3 ppm; HRMS (Positive ESI) Calcd. For C₂₈H₂₄O₂P⁺: 423.1514, Found: 423.1513. The [BF₄] salt was prepared via anion exchange in dichloromethane with aqueous NaBF₄, and X-ray quality crystals were prepared via slow diffusion of hexanes into a 1,2-dichloroethane solution of the phosphonium salt.



bis(2-methoxyphenyl)(phenyl)((*p***-tolylethynyl)phosphonium bromide** (**3b**): ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.44$ (s, 3H, CH₃), 3.84 (s, 6H, OCH₃), 7.20-7.47 (m, 8H, Ar), 7.60 (d, *J* = 7.9 Hz, 2H, Ar), 7.68-7.80 (m, 4H, Ar), 7.80-7.87 (m, 1H, Ar), 7.87-7.96 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 21.8, 56.6, 69.0 (d, ¹*J*_{P-C} = 195 Hz), 105.0 (d, ¹*J*_{P-C} = 107 Hz), 113.3 (d, *J*_{P-C} = 7.0 Hz), 114.4 (d, *J*_{P-C} = 4.9 Hz), 114.4 (d, ²*J*_{P-C} = 33 Hz), 119.1 (d, ¹*J*_{P-C} = 106 Hz), 122.2 (d, *J*_{P-C} = 14.6 Hz), 129.7, 129.9 (d, right peak

obscured, $J_{P-C} \sim 14.6$ Hz), 132.1 (d, $J_{P-C} = 12.9$ Hz), 132.8 (d, $J_{P-C} = 2.2$ Hz), 134.4 (d, $J_{P-C} = 10.6$ Hz), 134.6 (d, $J_{P-C} = 3.3$ Hz), 138.4 (d, $J_{P-C} = 2.0$ Hz), 143.5, 161.8 (d, $J_{P-C} = 2.4$ Hz); ³¹P

NMR (CDCl₃, 146 MHz): +1.2 ppm; HRMS (Positive ESI) Calcd. For C₂₉H₂₆O₂P⁺: 437.1670, Found: 437.1663.



bis(2-methoxyphenyl)(phenyl)((*o***-tolylethynyl)phosphonium bromide** (**3c**): ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.50$ (s, 3H, CH₃), 3.84 (s, 6H, OCH₃), 7.21-7.54 (m, 9H, Ar), 7.67 (d, *J* = 7.6 Hz, 1H, Ar), 7.69-7.81 (m, 4H, Ar), 7.81-7.88 (m, 1H, Ar), 7.88-7.98 (m, 2H, Ar);¹³C NMR (CDCl₃, 90 MHz): 20.4, 56.7, 73.3 (d, ¹*J*_{P-C} = 194 Hz), 104.9 (d, ¹*J*_{P-C} = 107 Hz), 113.0 (d, left peak obscured, ²*J*_{P-C} ~33 Hz), 113.4 (d, *J*_{P-C} = 6.8 Hz), 117.6 (d, *J*_{P-C} = 4.7 Hz), 119.1 (d, ¹*J*_{P-C} = 106 Hz), 122.4 (d, *J*_{P-C} = 14.6 Hz), 126.3, 130.9 (d, *J*_{P-C}

= 14.6 Hz), 130.2, 132.2 (d, J_{P-C} = 12.8 Hz), 132.5, 133.5 (d, J_{P-C} = 2.2 Hz), 134.5 (d, J_{P-C} = 10.7 Hz), 134.8 (d, J_{P-C} = 3.1 Hz), 138.6 (d, J_{P-C} = 1.9 Hz), 142.5 (d, J_{P-C} = 1.9 Hz), 161.8 (d, J_{P-C} = 2.5 Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.1 ppm; HRMS (Positive ESI) Calcd. For C₂₉H₂₆O₂P⁺: 437.1670, Found: 437.1673.



bis(2-methoxyphenyl)(phenyl)((3-(trifluoromethyl)phenyl)ethynyl) phosphonium bromide (3d): ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.87$ (s, 6H, OCH₃), 7.25-7.34 (m, 2H, Ar), 7.34-7.46 (m, 4H, Ar), 7.70-8.00 (m, 10H, Ar), 8.03-8.10 (m, 1H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.6, 71.4 (d, ¹*J*_{P-C} = 190 Hz), 104.0 (d, ¹*J*_{P-C} = 107 Hz), 110.6 (d, ²*J*_{P-C} = 32 Hz), 113.2 (d, *J*_{P-C} = 6.9 Hz), 118.1 (d, ¹*J*_{P-C} = 106 Hz), 118.4 (d, *J*_{P-C} = 4.7 Hz), 122.3 (d, *J*_{P-C} = 14.7 Hz), 122.7 (q, *J*_{F-C} = 273 Hz), 128.6 (q, *J*_{F-C} = 3.5 Hz), 129.0 (dq, *J*

unresolved), 129.9 (d, $J_{P-C} = 14.7$ Hz), 130.2, 131.0 (q, $J_{F-C} = 33$ Hz), 132.0 (d, $J_{P-C} = 12.8$ Hz), 134.4 (d, $J_{P-C} = 10.7$ Hz), 134.8 (d, $J_{P-C} = 3.1$ Hz), 136.5, 138.6 (d, $J_{P-C} = 1.9$ Hz), 161.7 (d, $J_{P-C} = 2.5$ Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.4 ppm; HRMS (Positive ESI) Calcd. For C₂₉H₂₃O₂F₃P⁺: 491.1388, Found: 491.1376.



bis(2-methoxyphenyl)(phenyl)((4-(trifluoromethyl)phenyl)ethynyl) phosphonium bromide (3e): ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.87$ (s, 6H, OCH₃), 7.25-7.34 (m, 2H, Ar), 7.34-7.46 (m, 4H, Ar), 7.71-7.82 (m, 6H, Ar), 7.83-7.89 (m, 1H, Ar), 7.89-8.00 (m, 4H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.5, 71.8 (d, ¹*J*_{P-C} = 190 Hz), 103.9 (d, ¹*J*_{P-C} = 107 Hz), 110.5 (d, ²*J*_{P-C} = 32 Hz), 113.1 (d, *J*_{P-C} = 6.8 Hz), 118.0 (d, ¹*J*_{P-C} = 106 Hz), 121.1 (dq, *J* unresolved), 122.2 (d, *J*_{P-C} = 14.8 Hz), 122.8 (q, *J*_{F-C} = 273 Hz), 125.6 (q, *J*_{F-C} = 3.6 Hz), 129.8 (d, J_{P-C} = 14.7 Hz), 131.9 (d, J_{P-C} = 12.9 Hz), 133.0 (q, J_{F-C} = 33 Hz), 133.4 (d, J_{P-C} = 2.2 Hz), 134.3 (d, J_{P-C} = 10.8 Hz), 134.6 (d, J_{P-C} = 3.1 Hz), 138.4 (d, J_{P-C} = 2.0 Hz), 161.6 (d, J_{P-C} = 2.3 Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.4 ppm; HRMS (Positive ESI) Calcd. For C₂₉H₂₃O₂F₃P⁺: 491.1388, Found: 491.1395.

((4-chlorophenyl)ethynyl)bis(2-methoxyphenyl)(phenyl)phosphonium bromide (3f): ¹H NMR (CDCl₃, 300 MHz): δ = 3.85 (s, 6H, OCH₃), 7.24-7.32 (m, 2H, Ar), 7.34-7.45 (m, 4H, Ar), 7.51 (d, *J* = 8.6 Hz, 2H, Ar), 7.68-7.80 (m, 6H, Ar), 7.81-7.88 (m, 1H, Ar), 7.88-7.96 (m, 2H, Ar);¹³C NMR (CDCl₃, 90 MHz): 56.4, 70.5 (d, ¹*J*_{P-C} = 192 Hz), 104.2 (d, ¹*J*_{P-C} = 107 Hz), 111.8 (d, ²*J*_{P-C} = 33 Hz), 113.0 (d, *J*_{P-C} = 6.9 Hz), 115.7 (d, *J*_{P-C} = 4.7 Hz), 118.3 (d, ¹*J*_{P-C} = 106 Hz), 122.1 (d, *J*_{P-C} = 14.6 Hz), 129.2, 129.7 (d, *J*_{P-C} =

14.7 Hz), 131.9 (d, $J_{P-C} = 12.8$ Hz), 134.1 (d, $J_{P-C} = 2.3$ Hz), 134.2 (d, $J_{P-C} = 10.8$ Hz), 134.5 (d, $J_{P-C} = 2.9$ Hz), 138.2 (d, $J_{P-C} = 1.7$ Hz), 138.4, 161.5 (d, $J_{P-C} = 2.4$ Hz); ³¹P NMR (CDCl₃, 146 MHz): 1.3 ppm; HRMS (Positive ESI) Calcd. For C₂₈H₂₃ClO₂P⁺: 457.1124, Found: 457.1120.



Br⁻

OMe

OMe

((4-bromophenyl)ethynyl)bis(2-methoxyphenyl)(phenyl)phosphonium bromide (3g): ¹H NMR (CDCl₃, 300 MHz): δ = 3.85 (s, 6H, OCH₃), 7.24-7.33 (m, 2H, Ar), 7.34-7.45 (m, 4H, Ar), 7.67 (s, 4H, Ar), 7.70-7.80 (m, 4H, Ar), 7.81-7.88 (m, 1H, Ar), 7.88-7.98 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.9, 71.1 (d, ¹*J*_{P-C} = 192 Hz), 104.7 (d, ¹*J*_{P-C} = 107 Hz), 112.4 (d, ²*J*_{P-C} $_{\rm C}$ = 33 Hz), 113.5 (d, *J*_{P-C} = 6.8 Hz), 116.6 (d, *J*_{P-C} = 4.8 Hz), 118.8 (d, ¹*J*_{P-C} = 106 Hz), 122.6 (d, *J*_{P-C} = 14.6 Hz), 127.6, 130.1 (d, *J*_{P-C} = 14.7 Hz), 132.4

(d, $J_{P-C} = 12.8$ Hz), 132.6, 134.5 (d, $J_{P-C} = 2.1$ Hz), 134.7 (d, $J_{P-C} = 10.7$ Hz), 135.0 (d, $J_{P-C} = 2.9$ Hz), 138.7 (d, $J_{P-C} = 1.7$ Hz), 162.0 (d, $J_{P-C} = 2.4$ Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.3 ppm; HRMS (Positive ESI) Calcd. For C₂₈H₂₃BrO₂P⁺: 501.0619, Found: 501.0612.



bis(2-methoxyphenyl)(naphthalen-2-ylethynyl)(phenyl)phosphonium bromide (3h): ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.87$ (s, 6H, OCH₃), 7.25-7.34 (m, 2H, Ar), 7.34-7.51 (m, 4H, Ar), 7.56-7.70 (m, 3H, Ar), 7.72-8.01 (m, 10H, Ar), 8.35 (s, 1H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.8, 69.8 (d, ¹*J*_{P-C} = 194 Hz), 104.9 (d, ¹*J*_{P-C} = 107 Hz), 113.4 (d, *J*_{P-C} = 7.0 Hz), 114.3 (d, ²*J*_{P-C} = 33 Hz), 114.6 (d, *J*_{P-C} = 4.9 Hz), 119.0 (d, ¹*J*_{P-C} = 106 Hz), 122.4 (d, *J*_{P-C} = 14.6 Hz), 127.2 (d, *J*_{P-C} = 2.3 Hz), 127.5, 127.9, 128.4, 128.9, 129.1, 130.0 (d,

 $J_{P-C} = 14.7 \text{ Hz}$), 132.2 (d, $J_{P-C} = 12.8 \text{ Hz}$), 132.2, 134.4, 134.6 (d, $J_{P-C} = 10.7 \text{ Hz}$), 134.8 (d, J_{P-C} = 10.7 \text{ Hz}), 134.8 (d, J_{P-C} = 10.7 \text{ Hz} = 3.2 Hz), 135.0 (d, J_{P-C} = 2.5 Hz), 138.6 (d, J_{P-C} = 2.0 Hz), 161.9 (d, J_{P-C} = 2.2 Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.3 ppm; HRMS (Positive ESI) Calcd. For C₃₂H₂₆O₂P⁺: 473.1670, Found: 473.1667.



Br⁻

OMe

bis(2-methoxyphenyl)(phenyl)((4-vinylphenyl)ethynyl)phosphonium **bromide (3i):** ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.86$ (s, 6H, OCH₃), 5.44 (d, J = 10.8 Hz, 1H, CH), 5.91 (d, J = 17.6 Hz, 1H, CH), 6.75 (dd, J = 10.9, 17.5 Hz, 1H, CH), 7.23-7.33 (m, 2H, Ar), 7.34-7.48 (m, 4H, Ar), 7.51-7.59 (m, 2H, Ar), 7.66-7.81 (m, 6H, Ar), 7.81-7.88 (m, 1H, Ar), 7.88-7.98 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 56.6, 70.0 (d, ${}^{1}J_{P-C} = 194$ Hz), 104.8 (d, {}^{1}J_{P-C} = 194 Hz), 104 $_{\rm C} = 107$ Hz), 113.3 (d, $J_{\rm P-C} = 7.0$ Hz), 113.8 (d, ${}^{2}J_{\rm P-C} = 33$ Hz), 116.3 (d, $J_{\rm P-C} = 33$ Hz), 116.3 (d, J_{\rm P-C} = 33 Hz), 116.3 (d, J_{\rm P-C} = 5.2 Hz), 117.5, 118.9 (d, ${}^{1}J_{P-C} = 106$ Hz), 122.2 (d, $J_{P-C} = 14.6$ Hz), 126.6,

129.8 (d, $J_{P-C} = 14.8$ Hz), 132.1 (d, $J_{P-C} = 12.9$ Hz), 133.2 (d, $J_{P-C} = 2.3$ Hz), 134.4 (d, $J_{P-C} = 10.7$ Hz), 134.6 (d, $J_{P-C} = 3.1$ Hz), 135.2, 138.4 (d, $J_{P-C} = 2.0$ Hz), 141.3, 161.7 (d, $J_{P-C} = 2.6$ Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.1 ppm; HRMS (Positive ESI) Calcd. For C₃₀H₂₆O₂P⁺: 449.1670, Found: 449.1670.

((4-(3,3-dimethylbut-1-yn-1-yl)phenyl)ethynyl)bis(2methoxyphenyl)(phenyl)phosphonium bromide (3j): ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.32 \text{ (s, 9H, CH_3)}, 3.85 \text{ (s, 6H, OCH_3)}, 7.24-7.33 \text{ (m, 2H, Ar)},$ 7.34-7.46 (m, 4H, Ar), 7.49 (d, *J* = 8.2 Hz, 2H, Ar), 7.65 (d, *J* = 8.2 Hz, 2H, Ar), 7.69-7.80 (m, 4H, Ar), 7.81-7.88 (m, 1H, Ar), 7.88-7.97 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 27.9, 30.5, 56.6, 70.7 (d, ${}^{1}J_{P-C} = 193$ Hz), 78.1, OMe 103.6, 104.6 (d, ${}^{1}J_{P-C} = 107$ Hz), 113.2 (d, ${}^{2}J_{P-C} = 33$ Hz), 113.3 (d, $J_{P-C} = 6.8$ Hz), 115.9 (d, $J_{P-C} = 4.6$ Hz), 118.8 (d, ${}^{1}J_{P-C} = 106$ Hz), 122.3 (d, $J_{P-C} = 14.6$ Hz), 128.5, 129.9 (d, $J_{P-C} = 14.7$ Hz), 131.8, 132.1 (d, $J_{P-C} = 12.7$ Hz), 132.6 (d, $J_{P-C} = 2.1$ Hz), 134.4 (d, $J_{P-C} = 10.7$ Hz), 134.7 (d, $J_{P-C} = 3.2$ Hz), 138.5 (d, $J_{P-C} = 2.0$ Hz),

161.8 (d, $J_{P-C} = 2.6$ Hz); ³¹P NMR (CDCl₃, 146 MHz): +1.2 ppm (Note: Impurities at +20.5 and -10.9 ppm could not be removed despite several recrystallization attempts.); HRMS (Positive ESI) Calcd. For C₃₄H₃₂O₂P⁺: 503.2140, Found: 503.2139.

General Procedure for the Synthesis of *cis*-Enediynes via Alkynylphosphonium Salts

To a THF (9 mL) suspension of alkynylphosphonium salt (0.5 mmol) at ambient temperature was added the corresponding arylacetylene (1.0 mmol, 2 eq.), followed by lithium arylacetylide (1.1 eq., prepared by addition of 1.0 eq. of *n*BuLi or LiHMDS to a THF solution (0.5-1.0 M) of arylacetylene at -78 °C). The reaction was stirred for 0.5 h at ambient temperature, during which time the mixture became homogeneous and yellow to dark yellow in color. Aqueous NH₄Cl solution (1-2 drops) was added to quench the reaction, which was concentrated *in vacuo* and adsorbed onto silica gel. Purification by column chromatography afforded the endiyne.



R	Phosphonium Mass (g)	Eluting Solvent	Enediyne Mass (g) (% Yield) ^a	Diyne Mass (g) (% Yield) ^a	Recovered PR ₃ Mass (g) (% Recovery) ^a
4a	0.251	Hexanes to 95:5 hexanes:ether	0.121 (80)	0.012 (12)	0.144 (90)
4b	0.257	Hexanes to 95:5 hexanes:ether	0.123 (71)	0.018 (16)	0.148 (92)
4c	0.257	Hexanes to 95:5 hexanes:ether	0.079 (46)	0.042 (37)	0.133 (83)
F ₃ C 4d	0.286	Hexanes to 95:5 hexanes:ether	0.176 (69)	0.008 (5)	0.113 (70)
F ₃ C 4e	0.283	Hexanes to 95:5 hexanes:ether	0.171 (68)	0.018 (11)	0.147 (92)

	0.270	Hexanes to 4:1 hexanes:DCM	0.160 (78)	_b	<u>_</u> b
Br 4g	0.292	Hexanes to 4:1 hexanes:DCM	0.214 (79) ^c	_b	_b
4h	0.274	Hexanes to 4:1 hexanes:DCM	0.144 (64)	0.018 (12)	0.125 (78)
4i	0.260	Hexanes to 95:5 hexanes:ether	0.146 (78) ^c	0.017 (14)	0.146 (92)
4j	0.290	Hexanes to 97:3 hexanes:ether	0.152 (56) ^c	_b	_b
1					

^aIsolated Yields. ^bDiyne inseparable from acetylene. Phosphine not recovered. ^cLiHMDS used to generate lithium acetylide.



(Z)-hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (4a): Orange solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.56$ (s, 1H, CH), 7.29-7.42 (m, 9H, Ar), 7.50-7.55 (m, 2H, Ar), 7.57-7.63 (m, 2H, Ar), 7.70-7.77 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 87.7, 89.2, 98.5, 98.6, 113.8, 123.2, 123.5, 126.2, 128.5 (2), 128.6, 128.7, 128.9, 129.0, 131.7, 131.8, 133.5, 136.8; HRMS (EI) Calcd. For C₂₄H₁₆: 304.1252, Found: 304.1248. X-ray

quality crystals were prepared via slow evaporation of a hexanes solution of the enediyne.



(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(methylbenzene) (4b): Yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.35$ (s, 3H, ArCH₃), 2.37 (s, 6H, ArCH₃), 6.50 (s, 1H, CH), 7.11-7.21 (m, 6H, Ar), 7.42 (d, J = 8.1 Hz, 2H, Ar), 7.49 (d, J = 8.1 Hz, 2H, Ar), 7.62 (d, J = 8.2 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 21.4, 21.7 (2), 87.4, 88.8, 98.4, 98.5, 112.7, 120.3, 120.7, 126.1, 129.30, 129.32, 129.4, 131.6, 131.8, 133.2, 134.2, 138.7, 138.9, 139.0; HRMS (EI) Calcd. For C₂₇H₂₂: 346.1722, Found:

346.1724. X-ray quality crystals were prepared via slow evaporation of a hexanes solution of the enediyne.



(Z)-2,2',2''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(methylbenzene) (4c): Yellow oil. ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.43$ (s, 3H, ArCH₃), 2.48 (s, 3H, ArCH₃), 2.54 (s, 3H, ArCH₃), 6.20 (s, 1H, CH), 7.08-7.29 (m, 9H, Ar), 7.35-7.40 (m, 1H, Ar), 7.42-7.51 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 20.7, 21.0 (2), 92.1, 92.4, 96.5, 97.5, 118.1, 123.1, 123.2, 125.6, 125.7, 126.1, 128.4, 128.7 (2), 129.0, 129.6 (2), 130.8, 132.2, 134.2,

136.0, 138.8, 140.5, 140.6 (one resonance is unresolved); HRMS (EI) Calcd. For $C_{27}H_{22}$: 346.1722, Found: 346.1727.



(Z)-3,3',3''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris ((trifluoromethyl)benzene) (4d): Orange oil which darkens over time. Aged samples displayed decomposition. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.63$ (s, 1H, CH), 7.43-7.70 (m, 7H, Ar), 7.72-7.78 (m, 2H, Ar), 7.83 (s, 1H, Ar), 7.85-7.91 (m, 1H, Ar), 7.95 (s, 1H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 88.2, 89.9, 97.6, 98.2, 115.5, 122.9 (q, $J_{F-C} = 3.8$ Hz), 123.7, 123.8 (q, $J_{F-C} = 272$ Hz) (2), 124.1,

124.1 (q, $J_{F-C} = 272$ Hz), 125.6 (q, $J_{F-C} = 3.7$ Hz), 125.9 (m, 2 overlapping quartets, $J_{F-C} \sim 3.7$ Hz), 128.6 (m, 2 overlapping quartets, $J_{F-C} \sim 3.8$ Hz), 129.2, 129.3, 129.4, 129.5, 131.4 (q, $J_{F-C} = 32.8$ Hz), 131.4 (q, $J_{F-C} = 33.0$ Hz), 131.5 (q, $J_{F-C} = 32.8$ Hz), 132.6, 134.7, 134.9, 137.0; HRMS (EI) Calcd. For C₂₇H₁₃F₉: 508.0873, Found: 508.0882.



(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris((trifluoromethyl) benzene) (4e): Orange solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.65$ (s, 1H, CH), 7.56-7.68 (m, 10H, Ar), 7.80 (d, J = 8.2 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 88.9, 90.5, 97.7, 98.5, 116.1, 124.0 (q, $J_{F-C} =$ 272 Hz) (2), 124.1 (q, $J_{F-C} = 272$ Hz), 125.7 (m, 2 overlapping quartets, $J_{F-C} \sim 3.7$ Hz), 125.9 (q, $J_{F-C} = 3.7$ Hz), 126.4, 126.6, 126.8, 130.8 (q, $J_{F-C} = 32.8$ Hz), 131.0 (q, $J_{F-C} = 32.8$ Hz), 131.2 (q, $J_{F-C} = 32.8$ Hz),

132.0, 132.1, 132.8, 139.6; HRMS (EI) Calcd. For C₂₇H₁₃F₉: 508.0873, Found: 508.0870.







(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(chlorobenzene) (4f): Yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.52$ (s, 1H, CH), 7.29-7.44 (m, 8H, Ar), 7.49 (d, J = 8.6 Hz, 2H, Ar), 7.63 (d, J = 8.6Hz, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 88.1, 89.7, 97.6, 98.0, 114.1, 121.4, 121.8, 127.4, 129.0 (2), 129.1, 132.4, 132.9, 133.0, 135.0 (2) 135.2, 135.3; HRMS (EI) Calcd. For C₂₄H₁₃: 406.0083, Found: 406.0085.

(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(bromobenzene) (4g): Yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.53$ (s, 1H, CH), 7.35 (d, J = 8.4 Hz, 2H, Ar), 7.42 (d, J = 8.5 Hz, 2H, Ar), 7.45-7.61 (m, 8H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 88.2, 89.9, 97.7, 98.2, 114.2, 121.8, 122.2, 123.2, 123.4, 123.5, 127.7, 132.0 (2), 132.5, 133.1, 133.2, 135.4 (one resonance is unresolved); HRMS (EI) Calcd. For C₂₄H₁₃Br₃: 537.8567, Found: 537.8567.

(Z)-2,2',2''-(hexa-3-en-1,5-diyne-1,3,6-triyl)trinaphthalene (4h): Yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.80$ (s, 1H, CH), 7.45-7.57 (m, 6H, Ar), 7.58-7.66 (m, 1H, Ar), 7.71-7.78 (m, 2H, Ar), 7.78-7.92 (m, 8H, Ar), 7.92-7.99 (m, 1H, Ar), 8.12 (s, 1H, Ar), 8.24 (s, 1H, Ar), 8.31 (s, 1H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 88.3, 90.0, 99.2, 99.7, 114.3, 120.6, 121.0, 123.3, 126.4, 126.7, 126.8 (2), 126.9, 127.0, 127.1, 127.8, 128.0 (2), 128.1, 128.3, 128.4, 128.5, 128.6, 128.8, 131.8, 132.1, 133.2 (2), 133.3, 133.5, 133.7, 133.8, 134.1

(three resonances are unresolved); HRMS (EI) Calcd. For C₃₆H₂₂: 454.1722, Found: 454.1721.



(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(vinylbenzene) (4i): Yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 5.29$ (d, J = 10.7 Hz, 1H, CH), 5.30 (d, J = 10.9 Hz, 1H, CH), 5.32 (d, J = 10.7 Hz, 1H, CH), 5.78 (d, J = 17.6 Hz, 1H, CH), 5.79 (d, J = 17.5 Hz, 1H, CH), 5.80 (d, J = 17.6 Hz, 1H, CH), 6.57 (s, 1H, CH), 6.63-6.79 (m, 3H, CH), 7.34-7.52 (m, 8H, Ar), 7.56 (d, J = 8.2 Hz, 2H, Ar), 7.70 (d, J = 8.3 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz):

88.4, 90.2, 98.6, 99.1, 113.4, 114.8, 115.1, 115.2, 122.4, 122.8, 126.4 (3), 126.6, 131.9, 132.1,

133.0, 136.1, 136.31, 136.33, 137.8, 138.0, 138.2 (1 peak is overlapped); HRMS (EI) Calcd. For C₃₀H₂₂: 382.1722, Found: 382.1717.



(Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(3,3dimethylbut-1-yn-1-yl)benzene) (4j): Orange solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.32$ (s, 9H, CH₃), 1.33 (s, 18H, CH₃), 6.55 (s, 1H, CH), 7.30-7.45 (m, 8H, Ar), 7.49 (d, J = 8.2 Hz, 2H, Ar), 7.63 (d, J = 8.4 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 28.2 (2), 31.1 (2), 79.0 (3), 88.8, 90.6, 98.6, 99.1, 100.5, 101.1, 101.2, 113.8, 122.0, 122.4, 124.5, 124.8, 124.9, 125.9, 131.5, 131.6, 131.8 (2), 131.9, 133.0, 135.5 (two alkyl resonances are unresolved); HRMS (EI) Calcd. For C₄₂H₄₀: 544.3130, Found: 544.3138.



 $(4-{}^{2}\text{H})(\text{Z})$ -hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (4a-*d*): Orange solid. D Content: 93% ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.57$ (s, 0.07H, CH), 7.29-7.43 (m, 9H, Ar), 7.50-7.56 (m, 2H, Ar), 7.57-7.64 (m, 2H, Ar), 7.70-7.77 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 87.7, 89.1, 98.5, 98.6, 113.5 (t, ${}^{1}J_{\text{CD}} = 24.9$ Hz), 123.2, 123.6, 126.2, 128.5, 128.6, 128.7 (2), 128.9, 129.0, 131.8, 131.9, 133.4, 136.8; HRMS (EI) Calcd. For

C₂₄H₁₅²H: 305.1315, Found: 305.1310.

Procedure for the Gram Scale, One-Pot Synthesis of (Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(bromobenzene) 4g (cf. Figure 2)



To a solution of bis(2-methoxyphenyl)phenylphosphine (3.23g, 10.0 mmol) in toluene (60 mL) was added a solution of 1-bromo-4-(2-bromoethynyl)benzene (2.59g, 10.0 mmol) in toluene (40 mL) and the resulting mixture stirred at 45 °C for 72 h to yield a fine suspension of phosphonium salt. This mixture was cooled to ambient temperature, then a solution of 1-bromo-4-ethynylbenzene (3.66g, 20.2 mmol) in THF (80 mL) was added, followed by the addition of lithium acetylide solution (prepared from 1-bromo-4-ethynylbenzene (2.00g, 11 mmol) and LiHMDS (1.0 M, 11 mL) in THF (10 mL)). The reaction was quenched with a small amount of water after 1 h of stirring to yield a dark yellow, homogeneous solution, which was stripped of solvent and adsorbed onto silica gel. Column chromatography (silica gel, hexanes to 80:20 hexanes:DCM) afforded the desired product **4g** as a yellow solid (3.80g, 7.0 mmol, 70%). ¹H NMR data were identical to samples previously prepared on 0.5 mmol scale.

Procedure for the Treatment of (2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium Bromide with Lithium Phenylacetylide and Phenylacetylene (cf. Figure 4b)



To THF mL) suspension of (Z)-(2,4-diphenylbut-1-en-3-yn-1a (3 yl)triphenylphosphonium bromide (0.062g, 0.1 mmol) at ambient temperature was added phenylacetylene (0.01 mL, ~1 eq.), followed by lithium phenylacetylide (1.1 eq., prepared by addition of 1.0 eq. of *n*BuLi to a THF solution (1.0 M) of phenylacetylene at -78 °C). The reaction was stirred for 0.5 h at ambient temperature, then quenched with aqueous NH₄Cl solution (1-2 drops). Removal of volatiles in vacuo and NMR analysis indicated essentially quantitative conversion to the *cis*-enediyne **4a** and triphenylphosphine. Repeating this procedure with an ~1.1:1 Z:E mixture of the vinylphosphonium salt again resulted in nearly quantitative conversion to the *cis*-enediyne **4a** $(1:0.04 \text{ cis:trans ratio}^{14})$.

III. Experimental Observations Regarding the Preparation of Differentially Substituted Enediynes

We have investigated the possibility of preparing differentially substituted enediynes via the described methodology. The results of these investigations are described below.

Attempts to Prepare Differentially Aryl-Substituted Enediynes

We have found that alkynylation of vinyl phosphonium salts (in analogy to the reaction in Figure 4b) permits the regioselective synthesis of differentially substituted enediynes. Specifically, starting from vinyl phosphonium (*Z*)-**10**, reaction with lithium (*p*-tolyl)acetylide and (*p*-tolyl)acetylene in THF solution (Eq. S1) proceeds to give the mixed enediyne **S1** in 62% isolated yield.



Mixed enediyne **S1.** To a suspension of phosphonium salt (*Z*)-**10** (91 mg, 0.17 mmol) and HC=C(*p*-Tol) (0.02 mL, 0.17 mmol) in THF (2 mL) was added LiC=C(*p*-Tol) (1.1 eq, 0.38 mL, 0.48 M in THF). The mixture was stirred at rt for 0.5 h. Removal of solvent and NMR analysis of the crude reaction mixture indicated nearly complete conversion to the *cis*-enediyne (Z)-**S1**. The crude residue was treated with iodomethane (ca. 1

mL) and stirred for 1h, at which time (methyl)triphenylphosphonium iodide precipitated. The crude mixture was adsorbed onto silica gel and applied to a silica gel column. Elution (hexanes to 10:1 hexanes:ether) furnished enediyne (Z)-**S1** as a yellow solid (33 mg, 62 % yield). ¹H NMR (CDCl₃, 300 MHz): $\delta = 2.36$ (s, 3H, ArCH₃), 6.57 (s, 1H, CH), 7.14 (d, J = 7.8 Hz, 2H, Ar), 7.31-7.45 (m, 8H, Ar), 7.58-7.63 (m, 2H, Ar), 7.70-7.76 (m, 2H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 21.7, 87.8, 88.6, 98.3, 99.0, 114.0, 120.5, 123.3, 126.2, 128.6, 128.7, 128.8, 128.9, 129.4, 131.7, 131.9, 133.0, 136.9, 138.9; HRMS (EI) Calcd. For C₂₅H₁₈: 318.1409 Found: 318.1394.

By contrast, attempts to prepare mixed enediynes by alkynylation of ethynylphosphonium salts have resulted in the formation of compositionally diverse enediyne products. For instance, treatment of alkynylphosphonium **3a** with lithium (*p*-tolyl)acetylide and (*p*-tolyl)acetylene provides a mixture of enediynes (as assessed by the presence of multiple vinylic singlets in ¹H NMR) in 81% combined yield. On the basis of spectral comparison with an authentic sample, the major enediyne product formed was assigned as tri-tolyl enediyne **4b** (eq. S2). In a complementary experiment, tolyl(ethynyl)phosphonium **3b** was treated with lithium phenylacetylide and phenylacetylene. Again, a mixture of enediynes was isolated (56% combined yield) from which the symmetric phenyl-substituted enediyne **4a** was determined to be the major component (eq. S3). Although we have not been able to separate and rigorously characterize each of the minor enediyne products from these reactions, we posit the formation of mixed enediynes in ratios roughly statistical with respect to the starting alkynyl units.



Taken together, these results implicate a dynamic exchange process that competes kinetically with the described bond forming chemistry. We speculate that an acetylide exchange process of the alkynylphosphonium starting material proceeding via dialkynyl phosphorane intermediates could account for the observed compositional scrambling. Consequently, selective formation of differentially aryl-substituted enediynes may not be achieved under these reaction conditions.

Attempts to Prepare Aliphatic-Substituted Enediynes

Our attempts to prepare aliphatic-substituted enediynes has been unsuccessful to date. For instance, treatment of phosphonium 3a with 1-lithiohexyne and 1-hexyne (in accord with the general enediyne procedure) results only in a complex reaction mixture with no observable enediyne product as judged by ¹H NMR (eq. S4).



In view of the potential for competing ylidic pathways arising from deprotonation of the propargylic C–H bonds, we prepared *tert*-butyl substituted phosphonium **S2**. However, upon treatment of **S2** with 1-lithio-3,3-dimethylbutyne and 3,3-dimethyl-1-butyne according to the general procedure, no enediyne product was observed. Instead, if the reaction was quenched at ambient temperature by the addition of aqueous triflic acid, the colorless vinylphosphonium **S3** was obtained in nearly quantitative yield based on ¹H NMR (eq S5). This result contrasts with the chemistry of the aryl-substituted analogues, where the proposed vinylphosphonium intermediates have not been directly observed, but instead continue on to enediyne product in situ.



While the origin of the decreased reactivity of the aliphatic-substituted compounds remains to be verified, at this juncture aliphatic alkyne derivatives do not appear to be viable substrates for enediyne formation.



Ethynylphosphonium S2. Following literature precedent,¹⁵ a solution of bis(2-methoxyphenyl)phenylphosphine (0.682g, 2.1 mmol) in DCM (20 mL) was added slowly to a solution of 3,3-dimethyl-1-butynyl(phenyl)iodonium triflate (0.871g, 2.0 mmol) in DCM (60 mL) at -78 °C, and the mixture warmed to room temperature overnight. Concentration *in vacuo*, followed by the addition of diethyl ether afforded a white solid, which was collected by

filtration and washed with ether to afford the phosphonium salt as a white solid (1.02g, 1.8 mmol, 92%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.42$ (s, 9H, CH₃), 3.78 (s, 6H, OCH₃), 7.17-7.37 (m, 6H, Ar), 7.58-7.74 (m, 4H, Ar), 7.76-7.92 (m, 3H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 29.4 (d, $J_{P-C} = 3.2$ Hz), 29.5 (d, $J_{P-C} = 1.6$ Hz), 56.3, 60.9 (d, $J_{P-C} = 195$ Hz), 105.3 (d, $J_{P-C} = 107$ Hz), 113.2 (d, $J_{P-C} = 6.9$ Hz), 119.4 (d, $J_{P-C} = 106$ Hz), 121.0 (q, $J_{F-C} = 321$ Hz), 122.4 (d, $J_{P-C} = 14.6$ Hz), 125.9 (d, $J_{P-C} = 30.6$ Hz), 129.9 (d, $J_{P-C} = 14.6$ Hz), 132.2 (d, $J_{P-C} = 12.8$ Hz), 134.6 (d, $J_{P-C} = 10.7$ Hz), 134.7 (d, $J_{P-C} = 3.2$ Hz), 138.4 (d, $J_{P-C} = 1.8$ Hz), 161.9 (d, $J_{P-C} = 2.4$ Hz); ³¹P NMR (CDCl₃, 146 MHz): - 0.36 ppm; HRMS (Positive ESI) Calcd. For C₂₆H₂₈O₂P⁺: 403.1827, Found: 403.1819.



Vinylphosphonium S3. To a suspension of phosphonium salt S2 (108 mg, 0.20 mmol) and 3,3-dimethyl-1-butyne (0.05 mL, 0.40 mmol, 2 eq.)
^{f⁻} and THF (2 mL) was added LiC≡CtBu (0.26 mL, 0.9 M in THF, 1.2 eq.). The mixture was stirred for 0.5 h at ambient temperature, during

which time the mixture became orange and homogeneous. Aqueous triflic acid (~0.5M) was added until the orange color was discharged, and then the crude mixture was concentrated by rotary evaporation. The crude residue was recrystallized from CH₂Cl₂:Et₂O to give vinylphosphonium **S3** (112 mg, 90 %) as a white solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.84$ (s, 9H, CH₃), 1.27 (s, 9H, CH₃), 3.73 (s, 6H, OCH₃), 6.33 (d, $J_{C-P} = 20$ Hz, 1H, CH), 7.06-7.32 (m, 6H, Ar), 7.50-7.70 (m, 4H, Ar), 7.73-7.89 (m, 3H, Ar); ¹³C NMR (CDCl₃, 90 MHz): 28.1, 28.9, 29.6, 40.5 (d, $J_{P-C} = 13.2$ Hz), 56.3, 76.0 (d, $J_{P-C} = 13.0$ Hz), 106.1 (d, $J_{P-C} = 96.8$ Hz), 108.0 (d, $J_{P-C} = 94.9$ Hz), 113.0 (d, $J_{P-C} = 6.6$ Hz), 116.7, 119.4 (d, $J_{P-C} = 94.9$ Hz), 120.9 (q, $J_{F-C} = 321$ Hz), 122.0 (d, $J_{P-C} = 13.3$ Hz), 129.6 (d, $J_{P-C} = 13.3$ Hz), 132.8 (d, $J_{P-C} = 10.8$ Hz), 134.2 (d, $J_{P-C} = 2.9$ Hz), 135.2 (d, $J_{P-C} = 9.1$ Hz), 137.6 (d, $J_{P-C} = 1.8$ Hz), 159.9 (d, $J_{P-C} = 3.7$ Hz), 161.6 (d, $J_{P-C} = 2.0$ Hz); ³¹P NMR (CDCl₃, 146 MHz): +11.4 ppm; HRMS (Positive ESI) Calcd. For C₃₂H₃₈O₂P⁺: 485.2609, Found: 485.2598.

IV. Crystallographic Data



Figure S1. Thermal ellipsoid plot (50%) of (Z)-hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (**4a**). Hydrogen atoms omitted for clarity.

Crystal information for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1000561). A yellow rod shaped crystal with approximate dimensions 0.07 x 0.07 x 0.18 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1650 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 9843 reflections to a maximum θ angle of 28.39° (0.90 Å resolution), of which 3880 were independent, completeness = 97.5%, $R_{int} = 0.0369$, $R_{sig} = 0.0471$ and 1607 were greater than $2\sigma(I)$. The final cell constants: a = 17.56(3)Å, b = 17.03(3)Å, c = 5.895(10)Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, volume = 1762(5)Å³, are based upon the refinement of the XYZ-centroids of 1029 reflections above $20\sigma(I)$ with 2.390° corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.3186. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Pna2(1), with Z = 4 for the formula unit, C24 H16. The final anisotropic full-matrix least-squares refinement on F^2 with 217 variables converged at R1 = 6.73%, for the observed data and wR2 = 22.41% for all data. The goodness-of-fit was 0.982. The largest peak on the final difference map was 0.224 e⁻/Å³ and the largest hole was -0.095 e⁻/Å³. Based on the final model, the calculated density of the crystal is 1.147 g/cm³ and F(000) amounts to 640 electrons.

Crystallization method	slow evaporation of	slow evaporation of hexanes	
Empirical formula	C24 H16		
Formula weight	304.37		
Temperature	298(2) K		
Wavelength	0.71073 Å	0.71073 Å	
Crystal size 0.18 x 0.07 x 0.07 mm		nm	
Crystal habit	yellow rod		
Crystal system	Orthorhombic		
Space group	Pna2(1)		
Unit cell dimensions	a = 17.56(3) Å	$\alpha = 90^{\circ}$	
	b = 17.03(3) Å	$\beta = 90^{\circ}$	
	c = 5.895(10) Å	$\gamma = 90^{\circ}$	
Volume	1762(5) Å ³		
Z	4		
Density (calculated)	1.147 g/cm ³		
Absorption coefficient	0.065 mm ⁻¹		
F(000)	640		

Table S1. Sample and crystal data for (Z)-hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (4a).

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters $(Å^2)$ for (Z)-hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (4a). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	Х	У	Z	U(eq)
<u>C1</u>	0.3869(2)	0.1222(2)	0.2409(8)	0.0918(12)
C2	0.3738(2)	0.0496(2)	0.3728(8)	0.0835(11)
C3	0.4108(2)	0.0362(3)	0.5755(9)	0.1037(14)
C4	0.4005(3)	-0.0314(3)	0.6964(10)	0.1156(15)
C5	0.3522(3)	-0.0860(3)	0.6199(12)	0.1180(17)
C6	0.3136(3)	-0.0763(3)	0.4235(11)	0.1117(15)
C7	0.3237(2)	-0.0098(3)	0.2998(9)	0.1029(13)
C8	0.4489(2)	0.1739(2)	0.3165(8)	0.0935(11)
C9	0.5004(2)	0.2140(2)	0.3793(9)	0.0954(12)
C10	0.56062(19)	0.2611(2)	0.4522(8)	0.0855(11)
C11	0.5962(3)	0.2470(2)	0.6605(9)	0.1128(15)
C12	0.6596(3)	0.2895(3)	0.7183(10)	0.1216(16)
C13	0.6860(3)	0.3459(3)	0.5817(12)	0.1186(16)
C14	0.6521(3)	0.3603(3)	0.3887(12)	0.142(2)
C15	0.5904(3)	0.3193(3)	0.3209(10)	0.1298(17)
C16	0.3470(2)	0.1453(3)	0.0596(8)	0.1036(14)
C17	0.3564(2)	0.2139(3)	-0.0718(10)	0.1018(13)
C18	0.3668(3)	0.2697(3)	-0.1807(8)	0.1042(14)
C19	0.3757(2)	0.3399(3)	-0.3115(8)	0.0925(12)
C20	0.4229(2)	0.3991(3)	-0.2451(9)	0.1115(14)
C21	0.4311(3)	0.4654(3)	-0.3689(14)	0.1410(19)
C22	0.3924(3)	0.4757(3)	-0.5634(12)	0.1273(18)
C23	0.3453(3)	0.4166(4)	-0.6368(10)	0.1334(19)
C24	0.3374(3)	0.3492(3)	-0.5134(9)	0.1187(15)

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Figure S2. Thermal ellipsoid plot (50%) of (Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(methylbenzene) (4b). Hydrogen atoms omitted for clarity.

Crystal information for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1000562). A yellowish needle shaped crystal with approximate dimensions 0.02 x 0.03 x 0.11 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 40 seconds/frame. The total data collection time was about 20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 15340 reflections to a maximum θ angle of 28.31° (0.90 Å resolution), of which 4859 were independent, completeness = 97.9%, R_{int} = 0.1079, R_{sig} = 0.1220 and 1965 were greater than 2 σ (I). The final cell constants: a = 18.887(6)Å, b = 14.683(4)Å, c = 7.344(2)Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, volume = 2036.8(11)Å³, are based upon the refinement of the XYZ-centroids of 981 reflections above $20\sigma(I)$ with 2.774° < θ <27.540°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.1040. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Pna2(1), with Z = 4 for the formula unit, C27 H22. All the hydrogens were placed at geometrical positions and rode their parent atom. The final anisotropic full-matrix least-squares refinement on F² with 247 variables converged at R1 = 11.46%, for the observed data and wR2 = 25.84% for all data. The goodness-of-fit was 1.048. The largest peak on the final difference map was 0.226 e⁻/Å³ and the largest hole was -0.161 e⁻/Å³. Based on the final model, the calculated density of the crystal is 1.130 g/cm³ and F(000) amounts to 736 electrons.

Crystallization method	slow evaporation of hexanes
Empirical formula	C27 H22
Formula weight	346.45
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal size	0.11 x 0.03 x 0.02 mm
Crystal habit	yellow needle
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	$a = 18.887(6) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 14.683(4) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 7.344(2) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	2036.8(11) Å ³
Z	4
Density (calculated)	1.130 g/cm ³
Absorption coefficient	0.064 mm ⁻¹
F(000)	736

Table S3. Sai	mple and c	erystal data fo	or (Z)-4,4',4	''-(hexa-3-en-1,5-	-diyne-1,3,6-
		triyl)tris(met	hylbenzene)) (4b).	

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for (Z)-4,4',4''-(hexa-3-en-1,5-diyne-1,3,6-triyl)tris(methylbenzene) (4b). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	Х	у	Z	U(eq)
<u>C1</u>	0.8636(5)	0.7656(4)	0.1058(13)	0.121(3)
C2	0.8827(4)	0.6634(4)	0.1168(9)	0.0725(16)
C3	0.9464(3)	0.6398(4)	0.1962(9)	0.0752(18)
C4	0.9664(3)	0.5481(4)	0.2085(8)	0.0666(16)
C5	0.9213(3)	0.4804(4)	0.1463(7)	0.0507(13)
C6	0.8578(3)	0.5065(4)	0.0682(7)	0.0625(16)
C7	0.8402(3)	0.5970(4)	0.0502(8)	0.0724(17)
C8	0.9402(3)	0.3828(3)	0.1517(7)	0.0566(14)
C9	0.8872(3)	0.3153(4)	0.1334(8)	0.0544(14)
C10	0.8463(3)	0.2538(4)	0.1244(9)	0.0627(15)
C11	0.8005(3)	0.1749(3)	0.1176(8)	0.0527(13)
C12	0.8284(3)	0.0924(4)	0.1844(7)	0.0578(15)
C13	0.7893(3)	0.0136(4)	0.1753(8)	0.0624(15)
C14	0.7215(3)	0.0141(4)	0.1009(8)	0.0624(15)
C15	0.6793(3)	-0.0724(4)	0.0853(9)	0.087(2)
C16	0.6943(3)	0.0952(5)	0.0388(8)	0.0660(16)
C17	0.7338(3)	0.1751(4)	0.0522(8)	0.0610(15)
C18	1.0083(3)	0.3556(4)	0.1771(8)	0.0693(17)
C19	1.0307(3)	0.2629(4)	0.1653(9)	0.0701(17)
C20	1.0496(3)	0.1862(4)	0.1480(10)	0.0684(17)
C21	1.0688(3)	0.0921(4)	0.1368(8)	0.0641(15)
C22	1.1335(3)	0.0608(4)	0.2054(8)	0.0671(17)
C23	1.1499(3)	-0.0305(4)	0.2010(8)	0.0651(16)
C24	1.1042(3)	-0.0933(4)	0.1292(8)	0.0654(15)
C25	1.0393(3)	-0.0634(4)	0.0600(8)	0.0724(18)
C26	1.0231(3)	0.0280(5)	0.0622(8)	0.0698(17)
<u>C27</u>	1.1224(4)	-0.1940(3)	0.1288(11)	0.098(2)



Figure S3. Thermal ellipsoid plot (50%) of (*Z*)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium tetrafluoroborate ((*Z*)-10-BF₄). Hydrogen atoms and $[BF_4]^-$ counterion omitted for clarity.

Crystal information for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1000563). A colorless rod shaped crystal with approximate dimensions 0.07 x 0.08 x 0.28 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1550 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 seconds/frame. The total data collection time was about 13 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 12224 reflections to a maximum θ angle of 25.00° (0.90 Å resolution), of which 4982 were independent, completeness = 98.6%, R_{int} = 0.0694, R_{sig} = 0.1024 and 2647 were greater than $2\sigma(I)$. The final cell constants: a = 10.743(6)Å, b = 10.216(5)Å, c = 26.175(16)Å, $\alpha = 90^{\circ}$, $\beta = 94.556(10)^{\circ}$, $\gamma = 90^{\circ}$, volume = 2864(3)Å³, are based upon the refinement of the XYZ-centroids of 1857 reflections above $20\sigma(I)$ with $2.271^{\circ} < \theta < 24.342^{\circ}$. Analysis of the data showed negligible decay during data

collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.5620. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/n, with Z = 4 for the formula unit, C34 H26 B F4 P. They hydrogen atoms were placed geometrically and refined as riding atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 398 variables converged at R1 = 10.84%, for the observed data and wR2 = 29.79% for all data. The goodness-of-fit was 1.086. The largest peak on the final difference map was 0.247 e⁻/Å³ and the largest hole was -0.410 e⁻/Å³. Based on the final model, the calculated density of the crystal is 1.281 g/cm³ and F(000) amounts to 1144 electrons.

Crystallization method	slow diffusion of he	exanes into 1,2-dichloroethane	
Empirical formula	C34 H26 B F4 P		
Formula weight	552.33		
Temperature	298(2) K		
Wavelength	0.71073 Å	0.71073 Å	
Crystal size	0.28 x 0.08 x 0.07 n	nm	
Crystal habit	colorless rod		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	a = 10.743(6) Å	$\alpha = 90^{\circ}$	
	b = 10.216(5) Å	$\beta = 94.556(10)^{\circ}$	
	c = 26.175(16) Å	$\gamma = 90^{\circ}$	
Volume	2864(3) Å ³		
Z	4		
Density (calculated)	1.281 g/cm ³		
Absorption coefficient	0.144 mm ⁻¹		
F(000)	1144		

Table S5. Sample and crystal data for (*Z*)-(2,4-diphenylbut-1-en-3-yn-1yl)triphenylphosphonium tetrafluoroborate ((*Z*)-10-BF₄).

Table S6. Atomic coordinates and equivalent isotropic atomic displacement parameters $(Å^2)$ for (Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium tetrafluoroborate ((Z)-
10-BF4).

	х	у	Z	U(eq)
<u>C1</u>	0.7627(6)	0.1617(7)	0.6374(2)	0.0571(17)
C2	0.6583(5)	0.0886(6)	0.6358(2)	0.0469(15)
C3	0.6443(6)	-0.0288(6)	0.6681(2)	0.0522(16)
C4	0.5250(7)	-0.0688(7)	0.6782(2)	0.0649(19)
C5	0.2968(9)	0.2048(8)	0.4442(3)	0.084(2)
C6	0.3933(7)	0.1836(8)	0.4810(3)	0.074(2)
C7	0.3683(6)	0.1698(6)	0.5319(2)	0.0555(16)
C8	0.2470(7)	0.1771(8)	0.5447(3)	0.079(2)
C9	0.1529(8)	0.1989(10)	0.5073(4)	0.101(3)
C10	0.5532(6)	0.1214(6)	0.6012(3)	0.0532(16)
C12	0.8022(5)	0.2973(6)	0.5399(2)	0.0500(16)
C13	0.7812(7)	0.1823(8)	0.5140(3)	0.067(2)
C14	0.8009(7)	0.1778(8)	0.4627(3)	0.076(2)
C15	0.8396(6)	0.2837(9)	0.4370(3)	0.069(2)
C16	0.8598(6)	0.3988(8)	0.4628(3)	0.0652(19)
C17	0.9084(6)	0.3948(7)	0.6384(2)	0.0580(18)
C18	0.9022(7)	0.5228(8)	0.6555(3)	0.070(2)
C20	0.5744(6)	0.4739(7)	0.5734(2)	0.0639(19)
C21	0.4662(7)	0.5419(9)	0.5813(3)	0.083(2)
C22	0.4220(7)	0.5444(9)	0.6289(3)	0.081(2)
C23	0.4828(7)	0.4798(8)	0.6682(3)	0.075(2)
C24	0.7461(7)	-0.0982(7)	0.6890(2)	0.0622(19)
C25	0.6105(10)	-0.2458(8)	0.7285(3)	0.083(3)
C26	0.7292(9)	-0.2069(8)	0.7193(3)	0.074(2)
C27	0.5085(9)	-0.1744(8)	0.7088(3)	0.081(2)
C28	0.1784(10)	0.2099(9)	0.4566(4)	0.097(3)
C29	0.6400(6)	0.4074(6)	0.6140(2)	0.0510(16)
C30	0.8410(6)	0.4077(7)	0.5139(2)	0.0570(17)
C31	0.4680(7)	0.1430(7)	0.5703(3)	0.0594(18)
C32	0.5910(6)	0.4138(7)	0.6610(2)	0.0641(19)
C33	1.0217(7)	0.3271(8)	0.6457(3)	0.067(2)
C34	1.0054(8)	0.5801(9)	0.6798(3)	0.079(2)
C35	1.1144(8)	0.5128(10)	0.6876(3)	0.080(2)
C36	1.1223(7)	0.3884(10)	0.6707(3)	0.083(2)
B1	0.8718(10)	0.0269(12)	0.3230(4)	0.074(3)
F1	0.7842(11)	-0.0502(16)	0.3390(8)	0.153(7)
F2	0.9391(18)	-0.0370(17)	0.2908(4)	0.149(7)
F3	0.9470(18)	0.034(3)	0.3666(6)	0.188(11)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

F4	0.8277(19)	0.1419(11)	0.3096(10)	0.174(11)
F1B	0.829(4)	-0.064(2)	0.2866(12)	0.168(15)
F2B	0.971(2)	-0.004(4)	0.354(2)	0.18(2)
F3B	0.925(4)	0.099(4)	0.2940(15)	0.217(17)
F4B	0.781(4)	0.077(10)	0.3372(19)	0.33(4)
P1	0.77646(15)	0.31410(17)	0.60648(6)	0.0512(5)



Figure S4. Thermal ellipsoid plot (50%) of (*E*)-(2,4-diphenylbut-1-en-3-yn-1yl)triphenylphosphonium tetrafluoroborate ((*E*)-10-BF₄). Hydrogen atoms and $[BF_4]^-$ counterion omitted for clarity.

Crystal information for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1000560). A colorless block shaped crystal with approximate dimensions 0.17 x 0.26 x 0.29 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. For the Orthorhombic crystal, a total of 1250 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 seconds/frame. The total data collection time was about 5 hours.

The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 31645 reflections to a maximum θ angle of 28.34° (0.90 Å resolution), of which 11499 were independent, completeness = 99.7%, $R_{int} = 0.0346$, $R_{sig} = 0.0459$ and 8569 were greater than $2\sigma(I)$. The final cell constants: a = 20.732(3)Å, b = 19.775(3)Å, c = 13.7739(19)Å, $\alpha = 90^{\circ}$, $\beta = 10.775(3)$ Å, c = 13.7739(19)Å, $\alpha = 90^{\circ}$, $\beta = 10.775(3)$ Å, c = 13.7739(19)Å, $\alpha = 90^{\circ}$, $\beta = 10.775(3)$ Å, c = 13.7739(19)Å, $\alpha = 10.775(3)$ Å, $\alpha = 10.775(3)$ Å 90°, $\gamma = 90^{\circ}$, volume = 5646.9(13)Å³, are based upon the refinement of the XYZ-centroids of 6504 reflections above $20\sigma(I)$ with $2.283^{\circ} < \theta < 23.735^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.7406. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group Pca2(1), with Z = 8 for the formula unit, C34 H26 B F4 P. The hydrogen atoms were placed geometrically, and the final anisotropic full-matrix least-squares refinement on F^2 with 757 variables converged at R1 = 5.40%, for the observed data and wR2 = 13.66% for all data. The goodness-of-fit was 1.019. The largest peak on the final difference map was 0.442 e^{-}/A^{3} and the largest hole was -0.252 e^{-}/A^{3} . Based on the final model, the calculated density of the crystal is 1.299 g/cm^3 and F(000) amounts to 2288 electrons.

Crystallization method	slow diffusion of hexanes into 1,2-dichloroethane
Empirical formula	C34 H26 B F4 P
Formula weight	552.33
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal size	0.29 x 0.26 x 0.17 mm
Crystal habit	colorless block
Crystal system	Orthorhombic
Space group	Pca2(1)
Unit cell dimensions	$a = 20.732(3) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 19.775(3) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 13.7739(19) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	5646.9(13) Å ³

Table S7. Sample and crystal data for (*E*)-(2,4-diphenylbut-1-en-3-yn-1yl)triphenylphosphonium tetrafluoroborate ((*E*)-10-BF₄).

Z	8
Density (calculated)	1.299 g/cm ³
Absorption coefficient	0.146 mm ⁻¹
F(000)	2288

Table S8. Atomic coordinates and equivalent isotropic atomic displacement parameters $(Å^2)$ for (E)-(2,4-diphenylbut-1-en-3-yn-1-yl)triphenylphosphonium tetrafluoroborate ((E)-
10-BF₄).

	Х	у	Z	U(eq)
B1	0.6228(2)	0.2522(2)	0.3091(3)	0.0624(11)
B2	0.2571(2)	0.2681(2)	0.8603(5)	0.0729(13)
C1	0.61546(12)	0.34752(13)	0.6311(2)	0.0375(6)
C2	0.62230(14)	0.28605(14)	0.5826(2)	0.0494(7)
C3	0.66150(17)	0.23650(16)	0.6210(3)	0.0623(9)
C4	0.69346(17)	0.24734(19)	0.7058(3)	0.0701(11)
C5	0.68572(16)	0.30707(19)	0.7564(3)	0.0652(9)
C6	0.64619(14)	0.35707(16)	0.7189(2)	0.0515(7)
C7	0.48477(12)	0.37934(12)	0.5805(2)	0.0378(6)
C8	0.45443(15)	0.35698(14)	0.4971(3)	0.0486(7)
C9	0.39536(15)	0.32505(16)	0.5025(3)	0.0563(9)
C10	0.36672(15)	0.31608(15)	0.5906(3)	0.0597(9)
C11	0.39654(15)	0.33833(16)	0.6745(3)	0.0531(8)
C12	0.45596(14)	0.36925(15)	0.6701(2)	0.0441(7)
C13	0.57616(13)	0.49023(13)	0.6364(2)	0.0396(6)
C14	0.63886(16)	0.51435(16)	0.6487(3)	0.0562(8)
C15	0.6478(2)	0.5760(2)	0.6934(3)	0.0724(11)
C16	0.5966(2)	0.61363(19)	0.7234(3)	0.0754(11)
C17	0.5347(2)	0.59044(16)	0.7100(3)	0.0657(10)
C18	0.52391(16)	0.52795(14)	0.6663(2)	0.0494(7)
C19	0.59320(12)	0.41582(13)	0.4533(2)	0.0368(6)
C20	0.59036(12)	0.46955(14)	0.39273(19)	0.0356(6)
C21	0.55599(13)	0.53429(14)	0.4144(2)	0.0394(6)
C22	0.49006(15)	0.53586(16)	0.4239(3)	0.0512(7)
C23	0.45927(18)	0.59650(19)	0.4442(3)	0.0676(10)
C24	0.4953(2)	0.65409(19)	0.4556(3)	0.0809(12)
C25	0.5608(2)	0.65263(19)	0.4468(3)	0.0774(12)
C26	0.59124(17)	0.59327(15)	0.4248(3)	0.0550(8)
C27	0.62187(13)	0.46537(14)	0.3005(2)	0.0411(6)
C28	0.64673(13)	0.46177(15)	0.2230(2)	0.0440(7)
C29	0.67707(12)	0.45636(14)	0.1291(2)	0.0411(6)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C30	0.68025(17)	0.51173(17)	0.0678(3)	0.0645(9)
C31	0.70922(19)	0.5067(2)	-0.0217(3)	0.0721(10)
C32	0.73442(16)	0.44601(19)	-0.0509(3)	0.0634(9)
C33	0.73128(14)	0.39120(17)	0.0081(3)	0.0537(8)
C34	0.70253(13)	0.39532(15)	0.0985(2)	0.0453(7)
C35	0.49915(12)	0.10907(13)	0.1263(2)	0.0387(6)
C36	0.46857(14)	0.13122(14)	0.0415(2)	0.0450(7)
C37	0.41776(16)	0.17496(15)	0.0475(3)	0.0529(8)
C38	0.39718(16)	0.19726(16)	0.1368(3)	0.0627(10)
C39	0.42689(17)	0.17634(19)	0.2201(3)	0.0686(10)
C40	0.47790(16)	0.13210(16)	0.2151(3)	0.0554(8)
C41	0.62650(13)	0.10152(14)	0.0443(2)	0.0407(6)
C42	0.67109(18)	0.06998(17)	-0.0152(3)	0.0742(12)
C43	0.71708(18)	0.1086(2)	-0.0612(3)	0.0831(13)
C44	0.71820(17)	0.1771(2)	-0.0520(3)	0.0661(10)
C45	0.6720(2)	0.2083(2)	0.0031(4)	0.0939(15)
C46	0.6264(2)	0.17107(18)	0.0512(3)	0.0775(12)
C47	0.54941(13)	-0.02389(12)	0.0598(2)	0.0377(6)
C48	0.59794(15)	-0.07278(15)	0.0520(3)	0.0533(8)
C49	0.58377(19)	-0.13457(17)	0.0103(3)	0.0655(10)
C50	0.52272(18)	-0.14851(16)	-0.0217(3)	0.0606(9)
C51	0.47546(17)	-0.10130(16)	-0.0130(3)	0.0587(9)
C52	0.48825(15)	-0.03853(15)	0.0276(2)	0.0497(8)
C53	0.60592(13)	0.04303(13)	0.2313(2)	0.0393(6)
C54	0.59885(12)	-0.00901(13)	0.2922(2)	0.0381(6)
C55	0.55143(13)	-0.06548(14)	0.2836(2)	0.0409(6)
C56	0.57364(16)	-0.13224(15)	0.2865(3)	0.0536(8)
C57	0.5303(2)	-0.18525(18)	0.2825(3)	0.0701(10)
C58	0.4659(2)	-0.1731(2)	0.2789(3)	0.0766(12)
C59	0.44346(17)	-0.1080(2)	0.2773(3)	0.0756(12)
C60	0.48625(15)	-0.05374(17)	0.2794(3)	0.0568(8)
C61	0.63857(13)	-0.01380(14)	0.3766(2)	0.0408(6)
C62	0.66636(14)	-0.02614(15)	0.4518(2)	0.0454(7)
C63	0.69565(14)	-0.04340(17)	0.5429(2)	0.0499(7)
C64	0.72763(15)	-0.10432(19)	0.5526(3)	0.0638(9)
C65	0.7500(2)	-0.1242(2)	0.6431(4)	0.0826(13)
C66	0.7410(2)	-0.0837(3)	0.7213(4)	0.0979(16)
C67	0.7109(3)	-0.0238(3)	0.7130(4)	0.1087(17)
C68	0.6880(2)	-0.0021(2)	0.6212(3)	0.0905(13)
F1	0.67004(9)	0.28967(10)	0.35362(17)	0.0709(6)
F2	0.61271(19)	0.27737(18)	0.2167(2)	0.1383(12)
F3	0.6384(2)	0.18862(13)	0.3061(4)	0.1775(19)
F4	0.56530(12)	0.26304(17)	0.3563(3)	0.1205(11)
F5	0.30897(14)	0.23500(17)	0.8365(3)	0.1423(14)
F6B	0.247(2)	0.3213(18)	0.905(4)	0.13(3)
F6A	0.2037(3)	0.2344(4)	0.8659(7)	0.205(4)

F7A	0.2425(8)	0.3098(11)	0.8022(19)	0.298(12)
F7B	0.2737(5)	0.2800(8)	0.9584(8)	0.170(4)
F8A	0.2629(5)	0.3332(5)	0.8715(13)	0.132(5)
F8B	0.2252(11)	0.2330(8)	0.9242(19)	0.160(13)
F8C	0.2453(13)	0.2700(8)	0.7572(13)	0.148(9)
P1	0.56581(3)	0.41104(3)	0.57516(5)	0.03350(15)
P2	0.56836(3)	0.05557(3)	0.11584(5)	0.03556(15)



Figure S5. Thermal ellipsoid plot (50%) of bis(2-methoxyphenyl)(phenyl) (phenylethynyl)phosphonium tetrafluoroborate (**3a-BF**₄). Hydrogen atoms and [BF₄]⁻ counterion omitted for clarity.

Crystal information for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1000559). A colorless block shaped crystal with approximate dimensions 0.15 x 0.16 x 0.18 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A

total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 seconds/frame.The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 12288 reflections to a maximum θ angle of 28.37° (0.90 Å resolution), of which 6326 were independent, completeness = 97.3%, R_{int} = 0.0094, $R_{sig} = 0.0152$ and 5327 were greater than $2\sigma(I)$. The final cell constants: a = 9.794(5)Å, b = 11.579(5)Å, c = 12.366(6)Å, α = 72.176(9)°, β = 86.868(9)°, γ = 76.456(9)°, volume = 1297.8(10)Å³, are based upon the refinement of the XYZ-centroids of 5467 reflections above $20\sigma(I)$ with $2.514^{\circ} < \theta < 27.545^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.6306. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, C28 H24 B F4 O2 P. Hydrogen atoms were placed geometrically and rode the parent atom during refinement. The final anisotropic fullmatrix least-squares refinement on F^2 with 365 variables converged at R1 = 5.00%, for the observed data and wR2 = 15.09% for all data. The goodness-of-fit was 1.031. The largest peak on the final difference map was 0.353 $e^{-}/Å^{3}$ and the largest hole was -0.190 $e^{-}/Å^{3}$. Based on the final model, the calculated density of the crystal is 1.306 g/cm^3 and F(000) amounts to 528 electrons.

Crystallization method	slow diffusion of hexanes into 1,2-dichloroethane
Empirical formula	C28 H24 B F4 O2 P
Formula weight	510.25
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal size	0.18 x 0.16 x 0.15 mm
Crystal habit	colorless block
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 9.794(5) \text{ Å}$ $\alpha = 72.176(9)^{\circ}$

Table S9. Sample and crystal data for bis(2-methoxyphenyl)(phenyl)(phenylethynyl)phosphonium tetrafluoroborate (3a-BF4)
	b = 11.579(5) Å	$\beta = 86.868(9)^{\circ}$
	c = 12.366(6) Å	$\gamma = 76.456(9)^{\circ}$
Volume	1297.8(10) Å ³	
Z	2	
Density (calculated)	1.306 g/cm ³	
Absorption coefficient	0.158 mm ⁻¹	
F(000)	528	

$\label{eq:stables} \begin{array}{l} \mbox{Table S10. Atomic coordinates and equivalent isotropic atomic displacement} \\ \mbox{parameters (\AA^2) for bis(2-methoxyphenyl)(phenyl)(phenylethynyl)phosphonium} \\ \mbox{tetrafluoroborate (3a-BF_4).} \end{array}$

 $U(\mbox{eq})$ is defined as one third of the trace of the orthogonalized $U_{\mbox{ij}}$ tensor.

	Х	у	Z	U(eq)
B1	0.8789(3)	0.2201(4)	0.2263(3)	0.1027(10)
C1	0.58857(16)	0.58065(15)	0.25560(13)	0.0560(3)
C2	0.52965(15)	0.51845(15)	0.22277(13)	0.0555(3)
C3	0.45509(16)	0.44238(15)	0.18879(13)	0.0553(3)
C4	0.3510(2)	0.4966(2)	0.10569(19)	0.0800(5)
C5	0.2745(3)	0.4220(3)	0.0797(2)	0.1035(8)
C6	0.3010(3)	0.2981(3)	0.1339(3)	0.1027(8)
C7	0.4067(3)	0.2437(2)	0.2138(2)	0.0926(7)
C8	0.4851(2)	0.31578(18)	0.24148(16)	0.0702(4)
C9	0.78421(14)	0.73503(14)	0.21471(11)	0.0497(3)
C10	0.81367(19)	0.84750(16)	0.20769(15)	0.0665(4)
C11	0.9175(2)	0.8883(2)	0.13445(19)	0.0864(6)
C12	0.9861(2)	0.8183(2)	0.06839(17)	0.0869(7)
C13	0.95556(19)	0.7083(2)	0.07335(15)	0.0788(6)
C14	0.85511(16)	0.66394(19)	0.14805(13)	0.0640(4)
C15	0.73165(14)	0.58064(13)	0.44575(11)	0.0484(3)
C16	0.71983(18)	0.45784(15)	0.48896(15)	0.0644(4)
C17	0.7812(2)	0.38469(19)	0.59180(18)	0.0821(6)
C18	0.8547(2)	0.4336(2)	0.65116(16)	0.0818(6)
C19	0.86941(19)	0.5546(2)	0.61070(14)	0.0705(5)
C20	0.80710(15)	0.62953(15)	0.50717(12)	0.0541(3)
C21	0.8942(3)	0.8049(2)	0.5101(2)	0.1042(8)
C22	0.51018(15)	0.79513(13)	0.32541(12)	0.0510(3)
C23	0.46934(18)	0.80853(17)	0.43078(15)	0.0660(4)
C24	0.3436(2)	0.8886(2)	0.4409(2)	0.0846(6)
C25	0.2607(2)	0.95448(18)	0.3459(2)	0.0833(6)

C26	0.29952(18)	0.94427(16)	0.24080(18)	0.0702(5)
C27	0.42526(16)	0.86490(14)	0.22910(14)	0.0566(3)
C28	0.3827(3)	0.8877(3)	0.0340(2)	0.1071(8)
F1A	0.8354(13)	0.2955(12)	0.2851(13)	0.192(7)
F1B	0.9010(10)	0.3418(5)	0.1870(10)	0.231(4)
F2A	0.8292(7)	0.2165(11)	0.3242(4)	0.136(4)
F2B	0.8391(11)	0.1183(7)	0.3083(8)	0.284(5)
F3A	1.0028(7)	0.1523(7)	0.2156(7)	0.155(3)
F3B	1.0121(7)	0.1821(14)	0.2088(8)	0.173(5)
F4A	0.7993(6)	0.2609(11)	0.1326(3)	0.153(4)
F4B	0.7991(10)	0.1845(19)	0.1635(16)	0.179(6)
01	0.80943(14)	0.75002(12)	0.45869(11)	0.0723(3)
O2	0.47504(12)	0.84647(12)	0.13019(10)	0.0703(3)
P1	0.65569(3)	0.67565(3)	0.31076(3)	0.04385(12)

Note: The small molecule crystallographic facility was established using funds from an NSF Chemistry Research Instrumentation and Facilities grant CHE-0131112.

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		cers							Hz	Hz	ספר	USEC	usec	¥	sec			USEC	dB	MHZ	S		MHZ			Hz				EO	mdd	Hz	mqq	HZ	ppm/cm	Hz/cm	
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G788.8 -6.6732 6.6824 6.6883 -\$E18.8 8858.8 6.8823 7.2753 7.2823 7.2907 7.2930 8865.7 -7.3024 290E.T ETIE.T 7.3237 7.3203



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BRAME Current Data Parameters NAME EXPNO FROCNO 1	F2 - Acquisition Parameters Date_ 20130716 Time 20130716 Time 200.48 INSTRUM 5 mm BBO BB-1H PULPROG 5 mm BBO BB-1H PULPROG 5 mm BBO BB-1H CDC13 NS COLVENT 299930 65536 SOLVENT 299336 SOLVENT 20013 NS 58139.535 Hz CDC13 NS 58139.535 Hz CDC13 NS 58139.535 Hz CDC13 NS 50 0.887139 Hz CDC13 NS 50 0.887139 Hz CDC13 NS 50 0.887139 Hz CD23 NS 50 D1 0.03000000 Sec D1 0.03000000 Sec D11 0.03000000 Sec D11 0.03000000 Sec D11 0.03000000 Sec D11 0.03000000 Sec D11 0.03000000 Sec	======= CHANNEL f1 ======= NUC1 31P P1 5.80 usec PL1 145.7832960 MHz SF01 145.7832960 MHz ======= CHANNEL f2 ======= CPDPRG2 waltz16	PCPD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 20.23 dB SFO2 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 145.7832311 MHz WDW 0 SSB 0.00 Hz GB 0.00 Hz GB 1.40
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	<pre>rrent Data Parameters ME xPR3 13C PNO 6 CONO 1 - Acquisition Parameters te_ 20130716 me 200.22 STRUM 5 mm BBO BB-1H LPROG 55536 LVENT 65536 LVENT 400 LPROG 5536 1.5139316 sec 1 15139316 sec 1 15139316 sec 1 1.8999998 sec 1 TA 1.8999998 sec 1 </pre>	====== CHANNEL fl ========= C1 13C 7.40 usec 1 90.5638160 MHz	===== CHANNEL f2 ======== DPRG2 waltz16 C2 1H PD2 110.00 usec 2 0.00 dB 12 19.70 dB 13 360.1314405 MHz 02 360.1314405 MHz	- Processing parameters 32768 90.5547560 MHz W	0.50 Hz 1.40
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Data Parameters kdrinitialPR3 5	turisition Paramet 20130731 20130731 20130731 5 mm Multinu 20330 65536 65536 65536 65536 65536 65366 65366 653666 5,3084660 5,308460 5,30840 5,000 5,308460 5,30840 5,000 5,30840 5,000 5,30840 5,000 5,308000 5,308000 5,308000 5,0000000 5,000000000 5,0000000000	===== CHANNEL f1 1H 10.10 -6.00 300.1318534	32768 32768 32768 3200.1299785 0 0.00 0.00 1.00	olot parameters 20.00 20.000 3001.30 -1.000 -300.13 0.55000 165.07149
Current NAME EXPNO PROCNO	F2 - Acr Date INSTRUM PROBHD PULPHOG PULPHOG PULPHOG SOLVENT SOLVENT SOLVENT FIDRES SWH FIDRES SWH FIDRES DM DM DM	NUC1 PL1 PL1 SF01	S S S S S S S S S S S S S S S S S S S	10 NMA CX F1 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2

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Data Parameters kdr-initial PR3 31P 1 1	uisition Parameters 20130731 15.41 5 mm BBO BB-1H 29pg30 65536 CDC13 25 25	58139.535 Hz 0.887139 Hz 0.5636596 sec 20642.5 sec 8.600 usec 6.00 usec 6.00 usec 1.89999998 sec 1.89999998 sec	CHANNEL fl ======= 31P 5.80 usec -3.00 dB 145.7832960 MHz	CHANNEL f2 ======= waltz16 1H 110.00 usec 0.00 dB 19.70 dB 19.70 dB 19.70 dB 360.1314405 MHz	cessing parameters 32768 145.7832311 MHz EM 0 1.00 Hz 1.40
Current NAME EXPNO PROCNO	F2 - Acq Date_ Time INSTRUM PROBHD PULPROG FULPROG SOLVENT NS	DS SWH FIDRES AQ DW DE DE d11 d11 DELTA TD0	======= NUC1 P1 PL1 SF01	======================================	FZ - Pro SI WDW SSB SSB LB CB PC



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	urrent Data Parameters AME kdr-initialPR3 13C XPNO 2 ROCNO 1 2 - Acquisition Parameters ate 20130731 ime 20.48 NSTRUM spect ROBHD 5 mm BBO BB-1H ULPROG 290330 0 65536	DIVENT CDC13 S 1700 S 1700 S 21645.021 Hz 0.330277 Hz 0.330277 Hz 1.5139316 sec 3 11585.2 6.00 usec 6.00 usec 1 23.100 usec 1 2000000 sec 11 0.0300000 sec 11 0.0300000 sec 11 0.0300000 sec 11 1.8999998 sec	===== CHANNEL fl ======= UC1 13C 1 7.40 usec L1 90.5638160 MHz	====== CHANNEL f2 ======== PDPRG2 waltz16 1H CC2 110.00 usec 10.00 dB L12 19.70 dB L13 360.1314405 MHz	2 - Processing parameters I 32768 F 90.5547686 MHz DW 0.5547686 MHz B 0.50 Hz	1.40
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Data Parameters kdr-vinylPPh3 1	uisition Paramet	20130720	19.06	Spect	DED4	65536	CDC13	8	2	6172.839	0.094190	5,3084660	181	81.000	5.00	300.0	1.0000000	==== CHANNEL f1	H	10.10	-6.00	300.1318534	tones animos	usice furger	CC/6621.005	2	0	0.00	0	1.00	lot parameters	20.00	10.000	3001.30	-1.000	-300.13	0.55000	165.07149	
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Ľ	ers 3 31P 1	mmeters 720 - 45 - 14 -14 -14 -11 -11 -13 5336 5336 513 513	4 1335 Hz 1395 Hz 1396 Sec 500 usec 100 usec 13.4 K 14 K 14 K 100 sec 1385 Sec	======== 31P .80 usec .00 dB 960 MHz	216 216 1H 00 usec 00 dB 70 dB 23 dB	neters 768 311 MHz 0 0 Hz 0 .00 Hz .40
	bata Paramete kdrvinylPPh3	uisition Para 201307 18, 18, 5 mm BBO BB- 50 2909 659 659	58139. 0.56369 2.0642 8.6 0.0000000 1.8999999999999999999999999999999999999	CHANNEL fl = 5. -3. 145.78329	CHANNEL f2 = walt2 walt2 110 190 360.1314(cessing paran 327 145.78323 0.
	Current NAME EXPNO PROCNO	F2 - Acq Date_ Time_ INSTRUM PROBHD PULPROG TD SOLVENT NS	DS SWH AQ AQ DW DE DE TTE C11 A11 DELTA TD0 TD0	======= NUC1 P1 PL1 SF01	====== CPDPRG2 NUC2 PCPD2 PL2 PL12 PL13 PL13 PL13 SF02	F2 - Pro SI SF WDW SSB LB CG FC



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Data Parameters kdrvinylPPh3 13C 2 1	<pre>fuisition Parameters 20130720 17.35 spect spect zgpg30 65536 CDC13 CDC13 </pre>	$\begin{array}{c} 21645.021 \ \text{Hz} \\ 0.330277 \ \text{Hz} \\ 1.5139316 \ \text{sec} \\ 16384 \ \text{sec} \\ 23.100 \ \text{usec} \\ 6.00 \ \text{usec} \\ 6.00 \ \text{usec} \\ 23.000000 \ \text{sec} \\ 1.89999998 \ \text{sec} \\ 1.89999998 \ \text{sec} \end{array}$: CHANNEL fl ======= 13C 7.40 usec -3.00 dB 90.5638160 MHz	: CHANNEL f2 ======== waltz16 1H 110.00 usec 0.00 dB 19.70 dB 20.23 dB 360.1314405 MHz	cessing parameters 32768 90.5547741 MHz EM 0 0.50 Hz 1.40
Current NAME EXPNO PROCNO	F2 - Acc Date_ Time_ INSTRUM PROBHD PULPROG TD SOLVENT NS	DS SWH SWH AQ DW DE DE TT C1 C1 DELTA DELTA TDO	NUC1 P1 PL1 SF01	======= CPDPRG2 NUC2 PCPD2 PL2 PL13 PL13 SF02 SF02	FF2 - Pro SF WDW SSB LB GB PC

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waltz16 1H 110.00 usec 0.00 dB 19.70 dB 20.23 dB 360.1314405 MHz 58139.535 Hz 0.887139 Hz 0.5636596 sec 20642.5 8.600 usec 6.00 msec 294.0 K 2.00000000 sec 0.03000000 sec 1.89999998 sec F2 - Processing parameters SI 32768 SF 145.7832560 MHz WDW EM SSB 0 LB 1.00 Hz GB 1.40 PC 1.40 ====== CHANNEL f2 ======== CPDPRG2 waltz16 NUC2 1H CHANNEL f1 ======== 31P 5.80 usec -3.00 dB 145.7832960 MHz P Current Data Parameters NAME kdrcc-288 EXPNO PROCNO PCPD2 PL2 PL12 PL13 SF02 NUC1 P1 PL1 SF01 11



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Current Data Parameters NAME kdrcc-122p EXPNO 6 PROCNO 1 F2 - Acquisition Parameters Date_ 20130808 1.1me 19.49 INSTRUM 5 mm GNP 1H/1 PULPROG 5536 SOLVENI 5 mm GNP 1H/1 PULPROG 5536 SOLVENI 5 mm GNP 1H/1 PULPROG 55536 SOLVENI 6172.839 Hz FIDRES 0.094190 Hz M 5.3084660 sec	DW B1.000 usec DE 6.00 usec TE 300.0 K D1 1.0000000 sec ======= CHANNEL f1 NUC1 14 P1 12.10 usec PL1 299.8718518 MHz	F2 - Processing parameters SI 32768 SF 299.8699923 MHz WDW no SSB 0 0 LB 0.00 Hz GB 0.00 Hz GB 1.00 PC 1.00	CX 20.00 cm F1P 10.000 ppm F1 2998.70 Hz F2P -1.000 ppm F2 -299.87 Hz PPMCM 0.55000 ppm/cm H2CM 164.92850 Hz/cm	
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Data Parameters kdrcc-122p 31P 2 1	<pre>guisition Parameters 20130610 12.50 spect spect cord3 cor</pre>	58139.535 Hz 0.887139 Hz 0.5636596 sec 20642.5 8.600 usec 6.00 usec 6.00 usec 0.03000000 sec 0.03000000 sec 1.89999998 sec	<pre>= CHANNEL f1 ======== 31P 10.25 usec -3.00 dB 145.7832960 MHz</pre>	<pre>= CHANNEL f2 ======== waltz16 1H 110.00 usec -1.00 dB 15.00 dB 15.00 dB 15.00 dB 360.1314405 MHz</pre>	ocessing parameters 32768 145.7832311 MHz no 0.00 Hz 1.40
Current NAME EXPNO PROCNO	F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS	DS SWH AQ AQ DW DM D1 d11 d11 TD0 TD0 TD0	nuc1 P1 PL1 SF01	EEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE	F2 - Prc SI WDW WDW SSB SSB LLB CGB



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BRUKER	Current Data Parameters NAME kdrcc-122p 31P EXPNO 1 PROCNO 1	F2 - Acquisition Parameters Date20130513 Time19.20 INSTRUM spect PROBHD 5 mm QNP 1H/15 PULPROG 229P930 TD 65536 SOLVENT CDC13 NS 1900	DS 4 SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec RG 1.5139316 sec RG 23.100 usec DF 6.00 wsec DE 2.0000000 sec D1 0.03000000 sec DELTA 1.8999998 sec TD0 1.8999998 sec	====== CHANNEL fl ======== NUC1 13C 6.50 usec Pl -3.00 dB PL1 90.5638160 MHz	====== CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 -1.00 dB PL12 15.00 dB PL13 16.10 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547765 MHz WDW EM SSB 1.00 Hz GB 1.40 PC 1.40
		OMe P+ OMe	3			40 20 0 ppm

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	ata Parameters kdrcc-123p 31P 2	iisition Parameters 20130713 15.19 spect spect 65536 CDC13 65236 CDC13 58139.535 Hz	0.01391333 Hz 0.5535395 Sec 20642.5 8.600 usec 6.00 usec 0.03000000 sec 1.8999998 sec 1	CHANNEL f1 ======= 31P 5.80 usec -3.00 dB 145.7832960 MHz	CHANNEL f2 ======== waltz16 1H 110.00 usec 0.00 dB 19.70 dB 20.23 dB 360.1314405 MHz	:essing parameters 32768 145.7832311 MHz EM 0 50 H7	1.40
	Current I NAME EXPNO PROCNO	F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS SOLVENT SSU	FIDRES AQ DW DW DE TE d11 DELTA TD0	NUC1 P1 PL1 SF01	====== CPDPRG2 NUC2 PCPD2 PL12 PL13 PL13 SF02	F2 - Proc SI SF WDW SSB I.B	PC BB
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256.60 251.75 252.70 256.60 252.7	====== CHANNEL f1 ======== NUC1 13C P1 7.40 usec PL1 90.5638160 MHz									
26.60 2013011 2133 25336 2553 25536 2553 25536 2553 2553 25536 2553 25536 2553 25536 2553 25536 2553 2553 25536 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 2553 255 25 255 255 255 255	DS 1.80 SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec AQ 1.5139316 sec AQ 1.5139316 sec AQ 1.5139316 sec AQ 2.100 usec DE 2.0000000 sec d11 0.03000000 sec DELTA 1.89999998 sec TD0 1	×								
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2020 2020	Current Data Parameters NAME kdrcc-123p 13C EXPNO 1 PROCNO 1									
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	ن ع	HZ HZ Sec Sec Sec	usec dB MHz srs MHz	μz	cm ppm Hz pp <i>m</i> Hz Hz/cm Hz/cm
ta Parameters kdrcc-133p 1	sition Paramet 20130609 16.13 spect 5 mm Multinu 2930 65536 8 8 8 220213 2 2	6172.835 0.094190 5.3084660 5.3084660 203.2 81.000 6.00 1.0000000	<pre>~= CHANNEL f1 1H 10.10 -00.10 300.1318534 300.1318534 32768 32768 32768</pre>	1.00 1.00 1.00 1.00 1.00	20.00 10.000 3001.30 -1.000 -300.13 -300.13 0.55000 165.07149
Current Da NAME EXPNO PROCNO	F2 - Acqui Date_ ITime PROBHD PULPROG PULPROG SOLVENT SOLVENT SOLVENT SOLVENT SOLVENT	FIDRES AQ DW DE D1 D1	NUC1 P1 PL1 SF01 F2 - Proce S1 SF	PC MDW SSB GGB PC MM D10	F1P F1 F2P F2P F2CM HZCM



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BRUKER Current Data Parameters	NAME kårcc-133p 13C EXPNO 3 PROCNO 1 F2 - Acquisition Parameters Date 20130609 Time 17.36 INSTRUM spect PROBHD 5 mm QNP 1H/15 PULPROG 5 mm QNP 1H/15 PULPROG 5 mg 20130609 TD 5 mm QNP 1H/15 PULPROG 5 mm QNP 1H/15 PULPROG 2013060 SOLVENT 1800 DS 29536 SOLVENT 1800 DS 21645.021 Hz SWH 21645.021 Hz SWH 21645.021 Hz SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec RG 23.100 usec DE 6.00 usec DE 294.9 K D1 0.0300000 sec DE 294.9 K D1 0.0300000 sec	====== CHANNEL f1 ======= NUC1 13C 13C P1 6.50 usec PL1 90.5638160 MHz	====== CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 PL2 -1.00 PL12 15.00 PL13 16.10 PL13 360.1314405	F2 - Processing parameters SI 32768 SF 90.5547723 MHz WDW 0 SSB 0.00 Hz	- GB 0 PC 1.40
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BRACKO	F2 - Acquisition Parameters Date_ 20130713 Time 15.13 INSTRUM Spect PROBHD 5 mm BBO BB-1H PULPROG 229P930 TD 65536 SOLVENT CDC13 NS 50	DS 58139.535 4 SWH 58139.535 4 FIDRES 0.887139 Hz AQ 0.5636596 sec RG 8.600 usec DE 6.00 usec 0.0300000 sec d11 0.0300000 sec DELTA 1.8999998 sec TD0 1	Terrest channel fl ======= NUC1 31P NUC1 5.80 usec Pl -3.00 dB PL1 145.7832960 MHz	====== CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 20.23 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 145.7832311 MHz WDW 0 SSB 0.00 Hz GB 0.00 Hz GB 1.40
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Data Parameters kdrcc-132p 13C 1 1	Uuisition Parameters 20130713 13.56 spect 5 mm BBO BB-1H 299930 65536 65536 1200	21645.021 Hz 0.330277 Hz 1.5139316 sec 1.5139316 sec 23.100 usec 6.00 usec 6.00 usec 2.0000000 sec 0.03000000 sec 1.89999998 sec	: CHANNEL fl ======= 13C 7.40 usec -3.00 dB 90.5638160 MHz	<pre>CHANNEL f2 ======= waltz16 1H 110.00 usec 0.00 dB 19.70 dB 19.70 dB 20.23 dB 360.1314405 MHz</pre>	cessing parameters 32768 90.5547874 MHz EM 0 0.50 Hz 1.40
Current NAME EXPNO PROCNO	F2 - Acç Date_ Time_ INSTRUM PROBHD PULPROG PULPROG SOLVENT NS	DS SWH AQ DW DE DT D1 D1 D1 DELTA TD0 TD0 TD0	======= NUC1 P1 PL1 SF01	====== CPDPRG2 NUC2 PCPD2 PCPD2 PL13 PL13 PL13 SF02	FZ - Prc SS WDW SSB SSB SSB GB GB PC



PC 1.40	mdd	0 105	÷	115	120	125	130	135	140	145
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PL13 20.23 dB SF02 360.1314405 MHz										
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======= CHANNEL f2 ======= CPDPRG2 waltz16	Wattana						6			
P1 7.40 usec PL1 -3.00 dB SF01 90.5638160 MHz										
====== CHANNEL f1 ======= NUC1 13C										
D1 2.0000000 sec d11 0.03000000 sec DELTA 1.8999998 sec TD0 1									118 IV - 548 (* 549)	
RG 16384 DW 23.100 usec DE 6.00 usec										
EXECUTE 21645.021 Hz FIDRES 0.330277 Hz AO 1.5139316 sec		3d	Ŷ _							
PULPROG ZGPG30 TD 65536 SOLVENT CDC13 NS 1200 NS 1200	2									
F2 - Acquisition Parameters Date20130713 Time13.56 INSTRUMspect		Br'								
Current Data Parameters NAME kdrcc-132p 13C EXPNO 1 PROCNO 1			F ₃ C							
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Parameters kdrcc-138p 2 1	tion Paramet 20130711 230711 13.25 spect spect 5330 65536 65536 65536 6172.833 0.094190 5.3084660 5.3084660 5.3084660 6.00 6.00 1.0000000	CHANNEL f1 1H 10.10 -6.00 -6.00 -6.00 -300.1318534 300.1299685 300.1299685 0 0 0 0 1.00	parameters 20.000 10.0000 3001.30 -1.000 -300.13 0.55000 165.07149
Current Data NAME EXPNO PROCNO	Parter Date Time INSTRUM PROBHD PULPHOG PULPHOG TD SOLVENT SSUH SSUH FIDRES SWH FIDRES SWH FIDRES DD DE TE TE	NUC1 P1 F1 SF01 SF01 F2 - Process S1 S5 MDM S5 B0 GB GB GB	10 NMH Plot CX F1 F2 F2 F2 PPMCM H2CM
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	Current Data Parameters NAME kdrcc-138p 31P EXPNO 1 PROCNO 1	F2 - Acquisition Parameters Date_ 20130710 Time 18.44 INSTRUM Spect PROBHD 5 mm BBD BB-1H PULPROG 299930 TD 65536 SOLVENT CDC13 NS 65139,535 Hz NS 58139,535 Hz SWH 58139,535 Hz	AQ 0.5636596 sec RG 0.5636596 sec DW 8.600 usec 6.00 usec 6.00 usec 0.03000000 sec d11 2.0000000 sec DELTA 1.8999998 sec TD0 1	====== CHANNEL f1 ======= NUC1 31P P1 5.80 usec PL1 -3.00 dB PL1 145.7832960 MHz	====== CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 110.00 dB PL12 19.70 dB PL13 20.23 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 145.7832311 MHz WDW no 0	PC 1.40
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	Current Data Parameters NAME kdrcc-138p 13C EXPNO 3 PROCNO 1 1 F2 - Acquisition Parameters Date_ 19.55 INNTRUM 5 mm BBO BB-1H PROBHD 5 mm BBO B1 H PROBHD 5 mm BBO B5 1 H PROBHD 5 mm B5 1 H PROBHD 5 mm B5 1 H PROBHD 5 mm B5 1 H PROBHD 5 m B5 1 H PROBHD 5 M B5 1 H PROBHD 5 M B5 1 H PROBHD 5 M B5 1 H PROBHD 5 M B5 1 H PROBHD 5 H PROBH	D1 2.0000000 sec d11 0.03000000 sec DELTA 1.89999998 sec TD0 1.89999998 sec TD0 1.80999998 sec TD1 1.80099998 sec T01 1.800000 sec P1 1.800000 sec P1 7.40 usec P1 -3.00 dB SF01 90.5638160 MHz	======= CHANNEL f2 ======== CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 260.1314405 MHz SF02 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547938 MHz WDW EM SSB 0.50 Hz GB 0.50 Hz CB 1.40
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	Current Data Parameters NAME kdrcc-138p 13C EXPNO 3 PROCNO 1	F2 - Acquisition Parameters Date_ 20130711 Time 19.55 INSTRUM spect PROBHD 5 mm BBO BB-1H PULPROG 299930 TD 299930 SOLVENT 2021 H2 SOLVENT 2021 H2 1400 DS 21645.021 H2 SWH 21645.021 H2 SWH 21645.021 H2 SWH 2330277 H2 SWH 2330277 H2 SWH 2330277 H2 CO000000 552 CO000000 552 CO000000 552 d11 0.03300000 550 D1 0.03000000 550 D1 0.0300000 550 D1 0.0300000 550 D1 0.0300000 550 D1 0.0300000 550 D1 0.0300000 550 D1 0.0300000 550 D1 0.03000000 550 D1 0.0300000000000 550 D1 0.030000000 550 D1 0.030000000000000 550 D1 0.030000000 550 D1 0.030000000000000000000000000000000000	======= CHANNEL f1 ========= NUC1 13C P1 7.40 usec PL1 90.5638160 MHz	====== CHANNEL f2 ======== CPDFRG2 waltz16 NUC2 1H NUC2 110.00 usec PL12 119.70 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547938 MHz WDW EM SSB 0.50 Hz LB 0.50 Hz	GB 0 PC 1.40
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Current Data Parameters NAME kdrcc-144p EXPNO 1 PROCNO 1 PROCNO 1 PROCNO 1 F2 - Acquisition Parameters Date_ 20130609 Time 20130609 Time 20130609 Time 20306 SOLVENT 2030 B 65536 SOLVENT 2030 B 65536 SOLVENT 2030 B 8172.839 Hz FIDRES 0.094190 Hz AQ 5.3084660 Sec RG 203.2 SWH 6172.839 Hz FIDRES 0.094190 Hz AQ 5.3084660 Sec RG 203.2 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	U1 1.0000000 SEC F1 14 P1 10.10 USEC P1 -6.00 dB F2 - Processing parameters SF01 300.1318534 MHz F2 - Processing parameters SF 300.1318534 MHz PL -6.00 dB SF01 300.1318534 MHz PL -6.00 dB SF 300.1318534 MHz PL -6.00 dB SF 300.1299738 MHz MDM 0 D 0 SSB 0 O 0 PC 1.00 PC 1.00	F 1P 10.00 ppm F 1 3001.30 Hz F 2P -1.000 ppm F 2 -300.13 Hz PPMCM 0.55000 ppm/cm HZCM 165.07149 Hz/cm	
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	ata Parameters kdrcc-144p 31P 3	isition Parameters 20130609 18.21 spect spect 25336 CDC13 50	58139.535 Hz 0.887139 Hz 0.5636596 sec 10321.3 8.600 usec 6.00 usec 294.6 K 2.0000000 sec	1.89999998 sec 1 CHANNEL f1 ======= 10.25 usec -3.00 dB 145.7832960 MHz	CHANNEL f2 ======= waltz16 1H 110.00 usec -1.00 dB 15.00 dB 16.10 dB 360.1314405 MHz	essing parameters 32768 145.7832311 MHz 00 0.00 Hz	1.40
	Current D NAME EXPNO PROCNO	F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS	SWH FIDRES AQ RG DW DE D1 d11 d11	TD0 TD0 ====== NUC1 P1 P11 SF01	E===== CPDPRG2 NUC2 PCPD2 PL12 PL13 FL13 SF02 SF02	F2 - Proc SI SF WDW SSB LB	B PC
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	Current Data Parameters NAME kdrcc-144p 13C EXPNO 44 PROCNO 1	F2 - Acquisition Parameters Date20130708 Time18.56 INSTRUM 5 mm BBO BB-1H PROBHD 5 mm BBO BB-1H	PULPROG ZGPG30 TD 65536 SOLVENT CDC13 NS 600 DS 4	SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec 16384	DE 23.10 used TE 26.00 used 01 2.0000000 sec d11 0.03000000 sec DELTA 1.8999998 sec	PUC 1 ====== CHANNEL fl ===================================	SFO1 90.5638160 MHz ======= CHANNEL f2 ======= CPDFRG2 waltz16 14	PCCD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 20.23 dB SFO2 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547963 MHz	WDW EM	PC 1.40
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urrent Data Parameters AME kdrcc-167p 31P KPNO 1 ROCNO 1	2 - Acquisition Parameters ate20130615 ime20130615 ime20130615 ime20130615 spect sp	AH 58139.535 Hz WH 58139.535 Hz D0.887139 Hz 0.887136 56 0.5636596 sec 115855.2 0.5636596 sec 115855.2 200000000 sec 11 1.89999998 sec	CC CHANNEL F1 ======= JC1 31P 31P 10.25 usec L1 145.7832960 MHz	====== CHANNEL f2 ======== PDPRG2 waltz16 JC2 1H C2 1H0.00 usec -1.00 dB L12 15.00 dB L13 360.1314405 MHz	2 - Processing parameters 1 32768 32768 145.7832311 MHz 0 0 0 0 0 0 1.40 1.40
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====== CHANNEL f1 ======= NUC1 13C 7.40 usec P1 -3.00 dB PL1 90.5638160 MHz		
Current Data Parameters NAME kdrcc-167p 13C EXPNO 3 PROCNO 1 F2 - Acquisition Parameters Date 20130703 Time 19.57 INSTRUM 5 mm BBO BB-1H PULPROG 5 mm BBO BB-1H PULPROG 20130703 NS 201VENT 1000 DS 235555 SSMH 0.330277 Hz NS 1000 DS 23.1000 usec RG 1.5139316 sec RG 0.330277 Hz SWH 2.1645.021 Hz SWH 2.1645.021 Hz SWH 2.1645.021 Hz SWH 2.31000 sec d11 0.03000000 sec d11 0.03000000 sec DELTA 1.8999998 sec TD 0.0300000 sec DELTA 1.8999998 sec		
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BRUKER	Current Data Parameters NAME kdrcc-146p 31P EXPNO 3 PROCNO 1	F2 - Acquisition Parameters Date_ 20130606 Time 22.07 INSTRUM spect PROBHD 5 mm QNP 1H/15 PULPROG 2299330 TD 55536 SOLVENT CDC13 NS SOLVENT CDC13 NS 58139.535 Hz SWH 58139.535 Hz SWH 58139.535 Hz FIDRES 0.5636596 sec RG 2.0642.5 RG 2.0642.5 RG 2.0642.5	TE 294.6 K D1 2.0000000 sec d11 0.03000000 sec DELTA 1.8999998 sec TD0 1	======= CHANNEL f1 ======== NUC1 31P P1 10.25 usec P1 -3.00 dB PL1 145.7832960 MHz	======= CHANNEL f2 ======== CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 110.00 dB PL12 15.00 dB PL13 16.10 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 145.7832311 MHz WDW no	SSB 0.00 Hz LB 0.00 Hz GB 0 PC 1.40
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====== CHANNEL f1 ======== NUC1 13C 6.50 usec P1 -3.00 dB PL1 90.5638160 MHz										
Filme 20130606 Time 20130606 Time 20130606 FNSTRUM spect PFOBHD 5 mm QNP 1H/15 FULPROG 5536 FULPROG 5536 SULVENT 18.58 TD 5 mm QNP 1H/15 FULPROG 5536 SWH 0.0213 NS 21645.021 NS 1.5139316 SWH 0.330277 AQ 1.5139316 RG 1.5139316 RG 1.5139316 RG 1.5139316 RG 1.5139316 RG 1.5139316 PE 0.330277 RG 1.5139316 RG 1.89999998 RG 1.89999998 RG 1.89999998	3h 3h 3h									
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	t Data Parameters kdrcc-151p 31P 3	cquisition Parameters 20130609 14.05 14.05 14.05 14.05 55336 55336 55336 55336 55336 50 5139.535 Hz 0.887139 Hz 0.887139 Hz 0.5636596 sec 9195.2 8.600 usec 6.00 usec 0.03000000 sec 1.89999998 sec 1.89999998 sec	1 == CHANNEL fl ======== 31P 10.25 usec -3.00 dB 145.7832960 MHz	<pre>== CHANNEL f2 ========= 2</pre>	rocessing parameters 32768 145.7832311 MHz no 0.00 Hz	1.40
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BRUKER Current Data Parameters NAME	NAME KATCC-LDIP D3C EXPNO 3 FXONO 3 FXONO 3 FXONO 3 FXONO 20130609 Time 15.35 Time 15.35 Trime 15.35 PROBHD 5 mm QNP 1H/15 PULPROG 55536 SOLVENT 220536 NS 21645.021 Hz NS 1.5139316 sec NS 1.5139316 sec DW 0.330277 Hz DM 2.100 Usec DM 2.00000000 sec DI 0.03000000 sec DELTA 1.899999998 sec	======= CHANNEL f1 ======== NUC1 13C P1 6.50 usec PL1 90.5638160 MHz SF01 90.5638160 MHz	======= CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 15.00 dB PL12 15.00 dB PL13 360.1314405 MHz SF02 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547821 MHz WDW no SSB 0.00 Hz	GB PC 1.40
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==== CHANNEL f2 ===================================	CPDE CPDE PCPI PL12 PL12 SF02 SF02							
==== CHANNEL f1 ======== 31P 5.80 usec -3.00 dB 145.7832960 MHz	E=== NUC1 P1 PL1 SF01							
ent Data Parameters 1 kdrcc-174p 31P 1 2 1 2 1 15.20 RUM 20130723 15.20 RUM 25 mm BBO BB-1H ROG 65536 ENT 20130723 15.20 10.253555 12.20 12.22 12.22 12.22 13.23 15.20	Current Revealed to the second revealed to th							
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	BRUKER	urrent Data Parameters AME kdrcc-174p 13C XPNO 1 ROCNO 1	2 - Acquisition Parameters ime 20130723 ime 18.46 NSTRUM 5 mm BBO BB-1H ULPROG 5536 0LVENT 5 mm BBO BB-1H ULPROG 5536 0LVENT CDC13 500 55536 0LVENT 21645.021 Hz 0.330277 Hz 100 usec 6 1.5139316 sec 6 0.33027313 23.100 usec 6 0.00 usec 1 2.0000000 sec 1 2.0000000 sec ELTA 1.8999998 sec	====== CHANNEL f1 ======== UC1 13C 1 7.40 usec L1 90.5638160 MHz	====== CHANNEL f2 ======== PDPRG2 waltz16 UC2 1H UC2 110.00 usec L2 0.00 dB L12 19.70 dB L13 360.1314405 MHz	2 - Processing parameters I 32768 F 90.5547801 MHz DW n0 SB	B 0.00 Hz B 0 C 1.40
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Current Data Parameters NAME kdrcc-122 EXPNO 1 PROCNO 1 PROCNO 1 F2 - Acquisition Parameters Date20130227 Time 20130227 Time 20130227 Time 20130227 Time 20130227 Time 20130227 Time 20130227 Source 20130227 Time 20130227 Time 20130227 F2 - Acquisition Parameters Source 20130227 F10R55 0.00013 Source 4143.7 B 6172.839 Hz F10R55 0.0384660 sec 143.7 B 6172.839 Hz F1000 usec 6.00 usec F1000 usec F1 10.10 usec F2 - Processing parameters SFD 10.110 usec F2 - Processing parameters SFD 200.1310553 MHz F2 - Processing parameters SFD 0.1310553 MHz F2 - Processing parameters SFD 0.1310553 MHz F2 - Processing parameters SFD 0.1310553 MHz F1 10.000 pm SFD 0.000 pm	F1 3001.30 H2 F2P -1.022 ppm F2 -306.74 H2 PPMCN 0.55110 ppm/cm HZCM 165.40225 Hz/cm	
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ata Parameters kdrcc-122 13C 1	isition Parameters 20130227 21.01 spect spect 5 mm QNP 1H/15 5536 65536 65536 65536 400	21645.021 Hz 0.330277 Hz 1.5139316 sec 9195.2 23.100 usec 6.00 usec 25.9 K 2.000000 sec	1.89999998 sec 1 CHANNEL fl ======= 13C -3.00 dB 90.5638160 MHz	CHANNEL f2 ======== waltz16 110.00 usec -1.00 dB 15.00 dB 16.10 dB 360.1314405 MHz	essing parameters 32768 90.5547654 MHz no 0 0.00 Hz 1.40
Current D NAME EXPNO PROCNO	F2 - Acqu Date_ Time_ INSTRUM PROBHD PULPROG TD SOLVENT NS	SUS FIDRES AQ AQ DE DE DE CI A 1	DELTA TD0 ====== NUC1 P1 PL1 SF01	====== CPDFRG2 NUC2 PCPD2 PL12 PL13 PL13 SF02	F2 - Proc SI SF WDW SSB LLB LB LB CG B PC
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RUKER Fort Data Parameters kdrcc-123 13C	VO 1 ENO 1 CNO 1 CNO 100 Parameters - Acquisition Parameters - 20130228 19.58 FRUM 5 mm QNP 1H/15 SPECt 19.58 FRUM 5 mm QNP 1H/15 CDC13 CDC13 FRUT CDC13 CDC1	CA 0.03000000 sec 1.89999998 sec 1 1.89999998 sec 1 13C 6.50 usec -3.00 dB 1 90.5638160 MHz		- Processing parameters 32768 90.5547550 MHz EM 0.30 Hz 1.40
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	Current Data Parameters NAME kdrcc-133 13C EXPNO 2 PROCNO 1	F2 - Acquisition Parameters Date_ 20130805 Time 19.03 INSTRUM 5 mm BBO BB-1H PULPROG 290930 TD 65536 SOLVENT CDC13 NS 1000	DS 4 SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec RG 1.5139316 sec CG 23.100 usec DE 6.00 usec	TE 293.8 K D1 2.0000000 sec d11 0.0300000 sec DELTA 1.8999998 sec TD0 1	======= CHANNEL f1 ======== NUC1 13C P1 7.40 usec PL1 90.5638160 MHz SF01 90.5638160 MHz	CHANNEL f2 Energy CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 20.23 dB SF02 360.1314405 MHz	F2 - Processing parameters S1 32768 SF 90.5547550 MHz	WDW EM SSB 0.50 Hz	PC 1.40
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	SLa	HZ HZ Sec usec K, Sec Sec	usec dB MHz	S L Z H MHZ	cm ppm Hz ppm Hz Hz/cm Hz/cm
Jata Parameters kdrcc-132 1	uisition Paramet 20130311 19.51 spect 5 mm Multinu 2330 65536 65536	8 6172.839 0.094190 5.3084660 151.3 81.000 81.000 81.000 300.0	==== CHANNEL f1 1H 10.10 -6.00 300.1318534	cessing paramete 32768 300.1300145 00 0.00 1.00	lot parameters 20.00 10.040 3013.19 -0.910 -273.18 0.54749 164.31822
Current VAME EXPNO PROCNO	2 - Acq Date_ 13me NSTRUM NSTRUM NOSTRUM NOSTRUM OULPROG DULPROG SOLVENT	US SWH TIDRES 00 01 11 11	LC1 10C1 11 11 11 1501	- 2.5 - 7.0 - 7.0	I U NMH P XX XX 11 22 PMCM FZCM







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	Current Data Parameters NAME kdrcc-132 13C EXPNO 2 PROCNO 1	F2 - Acquisition Parameters Date20130311 Time20.16 INSTRUM spect PROBHD 5 mm QNP 1H/15 PULPROG 29930 TD 65536 SOLVENT CDC13 NS	DS 21645.021 Hz SWH 21645.021 Hz 0.330277 Hz AQ 1.5139316 sec RG 14596.5 DW 23.100 usec	DE 6.00 usec TE 296.6 K D1 2.0000000 sec d11 0.03000000 sec DELTA 1.8999998 sec TD0 1	======= CHANNEL f1 ======== NUC1 13C P1 6.50 usec PL1 90.5638160 MHz SF01 90.5638160 MHz	====== CHANNEL f2 ======== CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 110.00 dB PL12 15.00 dB PL13 16.10 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547483 MHz WDW 5SB 0	LB 0.50 Hz GB 1.40 PC 1.40
02:88 85:80 19:20 85:80 19:20 85:80 10:20 85:80 10:20 85:80 10:20 85:80 10:20 85:80 10:20 85:80 10:20 85:821 10:20 85:821 10:20 85:821 10:20 11:1 10:20	CL	The second secon						200 180 160 140 120 100 80 60 40 20 ppm

	Current Data Parameters NAME kdrcc-132 13C EXPNO 2 PROCNO 1	F2 - Acquisition Parameters Date20130311 Time20.16 INSTRUM spect PROBHD 5 mm QNP 1H/15 PULPROG 29P930 TD 65536 SOLVENT CDC13 NG 1500	DS 21645.021 Hz SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec 14596.5 sec 23.100 usec DF 6.00 usec TE 296.6 K D1 2.0000000 sec d11 1.8999998 sec DELTA 1.8999998 sec	LUO L ====== CHANNEL f1 ======== NUC1 13C PL1 6.50 usec PL1 90.5638160 MHz	====== CHANNEL f2 ========= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 -1.00 dB PL12 15.00 dB PL13 16.10 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547483 MHz WDW SSB 0.5647481 LB 0.50 Hz	GB 0 PC 1.40
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Data Parameters kdrcc-138 1	uisition Parame ¹ 20130320 19.53 spect 5 mm Multinu 2536 65536 65536 65536 65536 6536 6536	==== CHANNEL f1 1H 10.10 -6.00 300.1318534 32768 32768 32768 32769 32769 0.00 0.00 0.00 0.00	10t parameters 20.00 10.034 3011.45 -1.026 -307.84 0.55297 165.96436
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	Current Data Parameters NAME kdrcc-138 13C EXPNO 1 PROCNO 1	F2 - Acquisition Parameters Date20130320 Time20.24 INSTRUM 5 mm 20.24 PROBHD 5 mm 20NP 1H/15 PULPROG 229Pg30 TD 65536 SOLVENT CDC13 NS 1800		D1 2.0000000 sec d11 0.03000000 sec DELTA 1.8999998 sec TD0 1	====== CHANNEL f1 ======= NUC1 13C P1 6.50 usec PL1 90.5638160 MHz SF01 90.5638160 MHz	======= CHANNEL f2 ======= CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 -1.00 dB PL12 15.00 dB PL13 15.00 dB PL13 860.1314405 MHz	F2 - Processing parameters S1 32768 SF 90.5547489 MHz WDW EM	SSB 0 LB 1.00 Hz 0 GB 0 PC 1.40
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	Data Parameters kdrcc-138 13C 1	guisition Parameters 20130320 20.24 spect 5 mm QNP 1H/15 65536 CDC13 1800	21645.021 Hz 0.330277 Hz 1.5139316 sec 13004 23.100 usec 6.00 usec 6.00 usec 295.9 K 2.0000000 sec 0.03000000 sec 1.89999998 sec	= CHANNEL fl ======== 13C 6.50 usec -3.00 dB 90.5638160 MHz	<pre>= CHANNEL f2 ======== waltz16 110.00 usec -1.00 dB 15.00 dB 15.00 dB 16.10 dB 360.1314405 MHz</pre>	ocessing parameters 32768 90.5547489 MHz EM 0 0	1.40
	Current NAME EXPNO PROCNO	F2 - Ac Date_ Time_ INSTRUM PROBHD PULPROG TD SOLVENT NS	DS SWH FIDRES AQ RG DW DE TE d1 DELTA TD0 TD0	NUC1 NUC1 P1 PL1 SF01	CFDFRG2 CFDFRG2 NUC2 PLC2 PL12 PL13 FL13 SF02 SF02	F2 - Pr SI SF MDW SSB TR	
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ata Parameters kdrcc-144 1 2	<pre>isition Paramet 20130326 20130326 19.56 spect 5 mm Multinu 2g30 65536 CDC13 8 8 6172.839 0.094190 0.094660 5.30084660</pre>	5.3U64050 512 512 6.00 6.00 300.0 1.0000000 1.0000000 1.000000 1.0000000 1.0000000 1.0000000 1.00000000	essing paramete 32768 300.1300075 0 0 0.00 1.00	ot parameters 20.00 10.000 3001.30 -1.000 -300.13 0.55000 165.07150
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Data Parameters kdrcc-144 C13 1 1	uisition Parameters 20130326 20.44 spect spect 299930 65536 65536 1500 1500	21645.021 Hz 0.330277 Hz 1.5139316 sec 9195.2 23.100 usec 6.00 usec 6.00 usec 0.03000000 sec 1.8999999 sec	CHANNEL f1 ======= 13C 6.50 usec -3.00 dB 90.5638160 MHz	CHANNEL f2 ======= waltz16 1H 110.00 usec -1.00 dB 15.00 dB 15.00 dB 16.10 dB 360.1314405 MHz	cessing parameters 32768 90.5547511 MHz EM 0 1.00 Hz 0 1.40
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a Parameters kdrcc-167 1	tion Paramet 20130629 15.51 15.51 spect 5 mm Multinu 2330 65536 CDC13 24	6172.833 0.094190 5.3084660 512 81.000 6.00 5.00 1.0000000	- CHANNEL f1 1H 10.10 10.10 6.00 300.1318534 ing paramet 32768 300.1300065 EM	0.30 0.100 1.00 10.083 20.00 10.083 3026,18 -1.121 -336.58 0.56022 158.13788
Current Data NAME EXPNO PROCND	F2 - Acquisi Date INSTRUM PROBHD PULPROG TD SOLVENT NS SOLVENT	SWH FIDRES AG DM DM D1 D1 D1	NUC1 Pl Pl SFL1 SF2 - Process SI SSB SSB	CB 68 10 NMA plot CX F1 F2 PPMCM H2CM H2CM







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Fent Data Parameters kdrcc-167 13C	CNO 1 CNO 1 CNO 1 - Acquisition Parameters e_ 20130701 e_ 18.55 TRUM 5 mm BBO BB-1H PROG 297930 VENT 2000 VENT 2000 VENT 2001 Hz RES 0.330277 Hz RES 0.330277 Hz	TA 1.4596.5 23.100 usec 6.00 usec 6.00 usec 0.0300000 sec 0.0300000 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.89999998 sec 1.890.300 dB	==== CHANNEL f2 ========= PRG2 waltz16 1H 02 110.00 usec 0.00 dB 19.70 dB 3 360.1314405 MHz	- Processing parameters 32768 90.5547516 MHz EM 1.00 Hz 1.40 1.40
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Parameters kdrcc-146 1	tion Parame 20130403 11.34 spect mm Multinu 2g30 65536 65536 65536 6172.839 0.094190 5.3084660 5.3084660 5.3084660 5.3084660 1.0000000 1.0000000	CHANNEL f1 1H 10.10 -6.00 300.1318534	ing paramet 32768 300.1300075 EM 0 0.30 0.30 0.30	parameters 20.00 9.976 2994.10 -0.995 -298.60 0.54855 164.63499
Current Data NAME EXPNO PROCNO	F2 - Acquisi Date - Time 5 PNCPRUM 5 PULPRDG 5 PULPRDG 5 PULPRDG 5 SULVENT 5 SULVENT 5 SULVENT 5 D 0 D 0 D 0 D 0 D 1 D 1 D 1 D 1 D 1 D 1 D 1 D 1 D 1 D 1	NUC1 P1 PL1 SF01	FF2 - Process SF WDW SSB CGB GB CGB FC	10 NMH Plot CX F1 F2 F2 PPMCM H2CM







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Parameters kdrcc-151 1	tion Paramet 20130410 23737 spect spect 5336 65536 65536 8	2 6172.839 0.094190 5.3084660 5.3084660 81.000 6.00 6.00 1.0000000	<pre>CHANNEL f1 1H 10.10 -6.00 -6.00 -5.00 300.1318534 300.1318534 32768 300.1300137 00 0 0 0 0</pre>	parameters 20.00 11.000 3301.43 -1.000 -1.000 -300.13 0.60000 180.07800
Current Data NAME EXPNO PROCNO	F2 - Acquisi Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS	DS SWH FIDRES AD DM DE D1 D1	NUC1 P1 PL1 SF01 ST S1 S5 S5 MDM MDM MDM MDM MDM HDM B8 S5 B8 S5 B9 C	1D NMR Plot CX F1 F2 F2 PPMCM HZCM







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	ى د ت	Hz Hz sec usec K* sec	«======= usec dB MHz sns MHz Hz	cm ppm hz hz Hz hz/cm Hz/cm
Parameters kdrcc-174 3	tion Paramet 20130703 13.06 spect spect mm Multinu 5536 65536 65536 8	6172.839 0.094190 5.3084660 81.000 6.00 6.00 1.0000000	CHANNEL f1 1H 10.10 -6.00 -6.00 -5.00 -5.00 -5.00 -5.00 -5.00 -0.00 -0.00 -1.00 -1.00	parameters 20.00 10.000 3001.30 -1.000 -300.13 0.55000 165.07150
Current Data NAME EXPNO PROCNO	F2 - Acquisi Date Time INSTRUM FROBHO 5 PHOBHO 5 PULPROG TD SOLVENT NS	DS SWH AQ DW DF D1 TE D1	NUC1 P1 SF01 SF01 S5 S5 S5 S5 S5 S5 S5 S5 S5 S5 B0 MDW S5 S5 S5 B0 B0 B0 C	10 NMR plat CX F1 F1 F2 F2 PPMCM HZCM



	Current Data Parameters NAME kdrcc-174 13C EXPNO 2 PROCNO 1	F2 - Acquisition Parameters Date20130702 Time23.46 INSTRUM Spect PROBHD 5 mm BBO BB-1H PULPROG 5396 SOLVENT CDC13 NS 1600	DS 4 SWH 21645.021 Hz FIDRES 0.330277 Hz AQ 1.5139316 sec RG 33.100 user DM 23.100 user	DE 6.00 usec TE 293.5 K D1 2.0000000 sec d11 0.0300000 sec DELTA 1.8999998 sec TD0 1	======= CHANNEL f1 ======== NUC1 13C P1 7.40 usec PL1 90.5638160 MHz SFO1 90.5638160 MHz	======= CHANNEL f2 ======== CPDPRG2 waltz16 NUC2 1H PCPD2 110.00 usec PL2 0.00 dB PL12 19.70 dB PL13 20.23 dB PL13 360.1314405 MHz	F2 - Processing parameters SI 32768 SF 90.5547505 MHz	WDW EM SSB 0 LB 0.50 Hz - GB 1.40 PC 1.40
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ta Parameters kdrcc-161 1	sition Paramet 20130603 20.11 spect 5 mm Multinu 2930 65536 65536 65536 65536 65536 65536 65536 0.094190 5.3084660 5.308460 5.308460 5.308460 5.308460 5.308400 5.308000000 5.308400000000000000000000000000000000000	== CHANNEL f1 1H 10.10 -6.00 300.1318534	ssing paramete 32768 300.1300199 0 0.00 0.00 1.00	t parameters 20.00 9.388 2817.58 -1.144 -343.39 0.52660 158.04854
Current Da NAME EXPNO PROCNO	F2 - Acqui Date - Time - INSTRUM PROBHD PULPROG PULPROG PULPROG SQLVENT SSUVENT SSUVENT SSUVENT SSUP DD DD DD DD DD DD DD DD DD DD DD	NUC1 P1 PL1 SF01	F2 - Proce SF WDW SSB SSB GB GB FC	10 NMR plo CX F1 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2 F2







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72 - Processing parameters 51 32768 5F 90.5547562 MHz 70W EM 70W 0 1.00 Hz 2B 1.00 Hz 3B 0	3B 0 PC 1.40
F2 - Processi	SI SF WDW SSB LB





