Supporting Information

Silyl alkynylphosphine-boranes: key-precursors of triazolylphosphines via tandem desilylation-Click chemistry

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1. General Information

Toluene, diethyl ether, dichloromethane and THF were purified by an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves) and degassed. Alkynylphosphine-boranes **4a-d**[1,2] and benzyl azide **5a**[3] were prepared according to literature procedures. All other reagents were used as supplied.

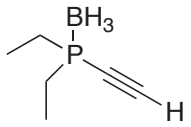
Chromatographic purifications were conducted using Merck silica gel Si 60 (40-63 μm) and TLC were performed on silica gel 60-F_{254} plates (0.1 mm) with UV or $KMnO_4$ detection. ^{1}H, ^{13}C, ^{31}P, ^{11}B ^{19}F NMR spectra were recorded on a BRUKER AVANCE III 400 or 500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm using the residual peak of chloroform-*d* (7.26 and 77.16 ppm) or dichloromethane-d_2 (5.32 and 53.84 ppm) as internal standard. ^{31}P, ^{19}F and ^{11}B NMR chemical shifts are reported relative to respectively H_3PO_4 (85%), $CFCl_3$ and $BF_3.Et_2O$ used as external references. Coupling constants *J* are reported in Hertz (Hz). Abbreviations are used as follows: s = singulet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet, br = broad. High Resolution Mass Spectrometry (HRMS) was performed on a QTOF Micro WATERS spectrometer. IR spectra were recorded a Perkin Elmer Spectrum One FTIR spectrometer equipped with an ATR device, and only the strongest or structurally most important peaks are listed. Melting points (Mp) were measured with an Electrotherma IA 9200 instrument. Elemental analysis (Anal.) was obtained from a ThermoQuest NA 2500 CHNS-O device.

Optical rotations were recorded on a JASCO P-2000 polarimeter at 589 nm and reported as follows: $[\alpha]_D^{20}$, concentration (*c* in g/100 mL), and solvent.

X-Ray diffraction analysis was performed on a Bruker APEXII Kappa CCD diffractometer (MoKα λ=0,71073 Å; graphite monochromator).

2. Experimental procedure and characterization data

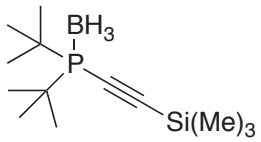
Diethyl-ethynylphosphine-borane (3a): To a solution of (triisopropylsilyl)ethynyl-diethylphosphine-borane **4a**[1] (2.5 g, 8.8 mmol, 1 equiv.) in THF (30 mL) at 0 °C under N_2 atmosphere were successively added H_2O (0.75 mL) and TBAF (1M in THF, 18.5 mL, 18.5 mmol, 2.1 equiv.). The reaction mixture was stirred at 25−30 °C for 2.5 h, then hydrolysed and washed with brine. The aqueous layer was extracted with Et_2O and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with pentane/Et_2O (9:1) as eluent to afford **3a** as a colourless oil (1.08 g, 96%).



$C_6H_{14}BP$
M= 127.96 g.mol^{-1}
R_f = 0.4 (Pentane/Et_2O: 9/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (d, J_{HP} = 7.4 Hz, 1H), 1.81 (m, 4H), 1.25 (dt, J_{HP} = 17.6 Hz, J_{HH} = 7.6 Hz, 6 H), 0.95-0.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.1 (d, J_{CP} = 10.1 Hz), 75.3 (d, J_{CP} = 82.8 Hz), 18.4 (d, J_{CP} = 39.9 Hz), 7.2 (d, J_{CP} = 3.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.9 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.2 (qd, J_{BH} = 97.6 Hz, J_{BP} = 54.1 Hz). IR (ATR, cm^{-1}) ν 3252, 2977, 2379, 2341, 2060, 1458, 1068, 1036, 1021, 758.

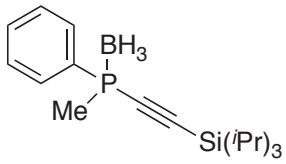
Di-*t*-butyl-(trimethylsilyl)ethynylphosphine-borane (4b): To an ice-bath cooled solution of trimethylsilylacetylene (0.77 g, 7.8 mmol, 1.1 equiv.) in Et_2O (20 mL) under N_2 was added dropwise a solution of *n*-BuLi (1.7 M in hexane, 5.1 mL, 8.7 mmol, 1.2 equiv.). After stirring at 0 °C for 1 h, the reaction medium was cooled to −78 °C and a solution of di-*t*-butylchlorophosphine (1.26 g, 7.0 mmol, 1 equiv.) in Et_2O (10 mL) was slowly added. The reaction mixture was warmed up to rt and stirred overnight. After cooling to 0 °C, BH_3•SMe_2 (1 mL, 10.5 mmol, 1.5 equiv.) was added dropwise. After 1 h of stirring at rt, the reaction mixture was hydrolysed at 0 °C with H_2O (20 mL) and extracted with Et_2O. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$ and finally concentrated under reduced pressure. The residue was purified by silica gel column chromatography with pentane/Et_2O (9:1) as the eluent to afford **4b** as a colourless oil (1.34 g, 75% yield).



$C_{13}H_{30}BPSi$
M= 256.25 g.mol^{-1}
R_f = 0.5 (Pentane/Et_2O: 19/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, J_{HP} = 14.0 Hz, 18H), 1.05−0.70 (m, 3H), 0.23 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.7 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ −40.3 (m). HRMS (ESI) Calcd for $C_{13}H_{30}BNaPSi$ $[M+Na]^+$: 279.1845. Found: 279.1833.

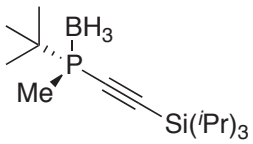
(Triisopropylsilyl)ethynyl-methylphenylphosphine-borane (4c): In a Schlenk tube, flushed with nitrogen, CuI (28 mg, 0.15 mmol, 10 mol%), 1,10-phenanthroline (27 mg, 0.15 mmol, 10 mol%) and degassed dry toluene (5 mL) were introduced. After 20 min of stirring at rt, methylphenylphosphine-borane[4] (200 mg, 1.45 mmol, 1 equiv.), K_3PO_4 (616 mg, 2.9 mmol, 2 equiv.), 1-bromo-(triisopropylsilyl)ethyne **7** (416 mg, 1.60 mmol, 1.1 equiv.) and degassed dry toluene (15 mL) were successively added. The reaction mixture was flushed with nitrogen prior to thermal heating at 60 °C overnight. After cooling to rt, the reaction mixture was filtered over celite with toluene as the eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with pentane/toluene (3:2) as the eluent to afford **4c** as a colourless oil (251 mg, 54% yield).



$C_{18}H_{32}BPSi$
M= 318.32 g.mol^{-1}
R_f = 0.4 (Pentane/Toluene: 3/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.83 (m, 2H), 7.53−7.46 (m, 3H), 1.73 (d, J_{HP} = 10.4 Hz, 3H), 1.13−1.08 (m, 21H), 1.40−0.50 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.6 (d, J_{CP} = 2.5 Hz), 131.5 (d, J_{CP} = 10.8 Hz), 129.4 (d, J_{CP} = 62.1 Hz), 129.1 (d, J_{CP} = 11.5 Hz), 115.1 (d, J_{CP} = 6.6 Hz), 98.6 (d, J_{CP} = 87.3 Hz) 18.6 (s), 16.2 (d, J_{CP} = 43.3 Hz), 11.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −4.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −36.8 (qd, J_{BH} = 96.5 Hz, J_{BP} = 54.4 Hz). IR (ATR, cm^{-1}) ν 2944, 2866, 2373, 1462, 1057, 896, 882, 800, 677. HRMS (ESI) Calcd for $C_{18}H_{32}BNaPSi$ $[M+Na]^+$: 341.2002. Found: 341.2018.

(*R*)-(Triisopropylsilyl)ethynylmethyl-*t*-butylphosphine borane (8): In a Schlenk tube, flushed with nitrogen, CuI (7.2 mg, 0.04 mmol, 10 mol%), 1,10-phenanthroline (6.8 mg, 0.04 mmol, 10 mol%) and degassed dry toluene (2 mL) were introduced. After 20 min of stirring at rt, (*S*)-*tert*-butylmethylphosphine-borane (**6**)[5] (44 mg, 0.37 mmol), K_2CO_3 (104 mg, 0.75 mmol, 2 equiv.), 1-bromo-(triisopropylsilyl)ethyne **7** (105 mg, 0.37 mmol, 1 equiv.) and degassed dry toluene (3 mL) were successively added. The reaction mixture was flushed with nitrogen prior to thermal heating at 60 °C overnight. After cooling to rt, the reaction mixture was filtered over celite with CH_2Cl_2 as the eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with pentane/Et_2O (9:1) as the eluent to afford **8** as a white solid (80 mg, 72% yield).

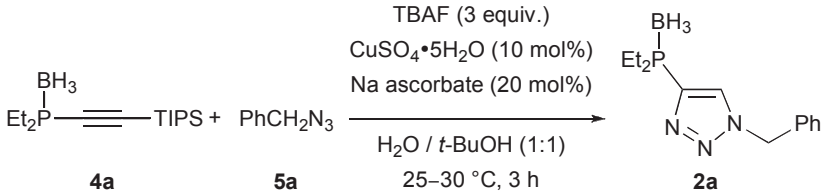


$C_{16}H_{36}BPSi$
M= 298.33 g.mol^{-1}
Mp < 20 °C
R_f = 0.5 (Pentane/Et_2O: 19/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, J_{HP} = 10.0 Hz, 3H), 1.24 (d, J_{HP} = 15.2 Hz, 9H), 1.10−1.05 (m, 21H), 0.90−0.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.4 (d, J_{CP} = 3.4 Hz), 98.3 (d, J_{CP} = 77.6 Hz), 28.7 (d, J_{CP} = 37.5 Hz), 24.9 (d, J_{CP} = 3.5 Hz), 18.5 (s), 11.0, 8.5 (d, J_{CP} = 39.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.9 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ −38.9 (m). HRMS (ESI) Calcd for $C_{16}H_{36}BNaSiP$ $[M+Na]^+$: 321.2315. Found: 321.2331.

Typical procedure for the synthesis of triazolylphosphine-boranes 2: Synthesis of triazolylphosphine-borane 2a (Scheme 4): TBAF (965 mg, 3.69 mmol, 3 equiv.) was added to a solution of TIPS-ethynyldiethylphosphine-borane (**4a**, 350 mg, 1.23 mmol, 1 equiv.) in *tert*-butanol (2 mL). After 5 min of stirring at rt, benzyl azide (**5a**, 170 µL, 1.29 mmol, 1.05 equiv.) and a solution of $CuSO_4$•$5H_2O$ (31 mg, 0.12 mmol, 10 mol%) with L(+)-ascorbic acid sodium salt (48 mg, 0.24 mmol, 20 mol%) in H_2O (2 mL) were successively added. After 3 h of stirring at rt, the reaction mixture was washed with H_2O, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with a (8:2) pentane/EtOAc mixture as eluent. 1-Benzyl-4-(diethylphosphino-borane)-1*H*-1,2,3-triazole (**2a**) was isolated as a white solid (295 mg , 1.13 mmol) in 92% yield.

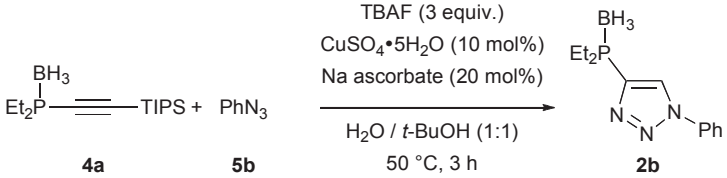
1-Benzyl-4-(diethylphosphino-borane)-1*H*-1,2,3-triazole (2a)



$C_{13}H_{21}BN_3P$
M= 261.11 g.mol^{-1}
Mp = 45−46 °C
R_f = 0.35
(Pentane/EtOAc: 8/2)

Yield: 99% (1.83 g), obtained from **4a** (2.00 g, 7.04 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.40–7.37 (m, 3H), 7.29–7.26 (m, 2H), 5.56 (s, 2H), 2.10−1.87 (m, 4H), 1.08 (dt, J_{HP} = 17.2 Hz, J_{HH} = 7.6 Hz, 6H), 0.96–0.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (d, J_{CP} = 70.7 Hz), 134.0, 131.3 (d, J_{CP} = 27.1 Hz), 129.4, 129.2, 128.3, 54.4, 17.6 (d, J_{CP} = 38.9 Hz), 7.0 (d, J_{CP} = 2.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.6 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −41.9 (qd, J_{BH} = 94.4 Hz, J_{BP} = 57.4 Hz). IR (ATR, cm^{-1}) ν 3131, 2966, 2923, 2375, 1453, 1212, 1020, 717. HRMS (ESI) Calcd for $C_{13}H_{21}BN_3NaP$ $[M+Na]^+$: 284.1464. Found: 284.1467.

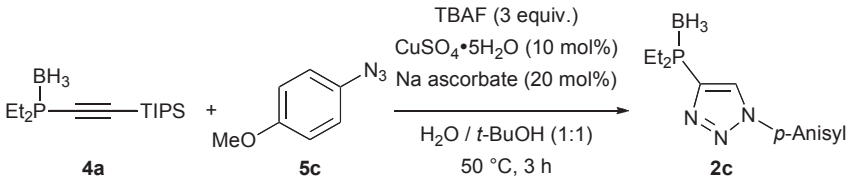
4-(Diethylphosphino-borane)-1-phenyl-1*H*-1,2,3-triazole (2b)



$C_{12}H_{19}BN_3P$
M= 247.08 g.mol^{-1}
White solid
Mp = 91−92 °C
R_f = 0.40
(Pentane/EtOAc: 8/2)

Yield: 65% (21 mg), obtained from **4a** (37 mg, 0.13 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.78–7.75 (m, 2H), 7.57–7.53 (m, 2H), 7.50–7.47 (m, 1H), 2.19–1.94 (m, 4H), 1.15 (dt, J_{HP} = 17.3 Hz, J_{HH} = 7.6 Hz, 6H), 1.10–0.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (d, J_{CP} = 69.3 Hz), 136.6, 130.0, 129.6 (d, J_{CP} = 26.9 Hz), 129.4, 120.8, 17.6 (d, J_{CP} = 38.8 Hz), 7.1 (d, J_{CP} = 2.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.2 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −41.9 (qd, J_{BH} = 95.0 Hz, J_{BP} = 57.1 Hz). IR (ATR, cm^{-1}) ν 3149, 2976, 2939, 2378, 2359, 1502, 1222, 1033, 750. HRMS (ESI) Calcd for $C_{12}H_{19}BN_3NaP$ $[M+Na]^+$: 270.1307. Found: 270.1298.

4-(Diethylphosphino-borane)-1-(4-anisyl)-1*H*-1,2,3-triazole (2c)

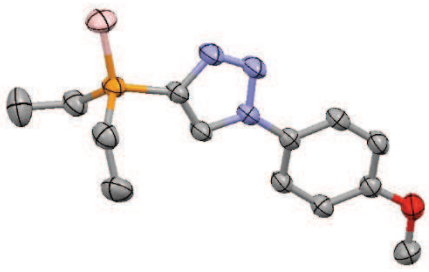


4a **5c** **2c**

$C_{13}H_{21}BN_3OP$
M= 277.11 g.mol^{-1}
Orange solid
Mp = 65–66 °C
R_f = 0.36
(Pentane/AcOEt: 8/2)

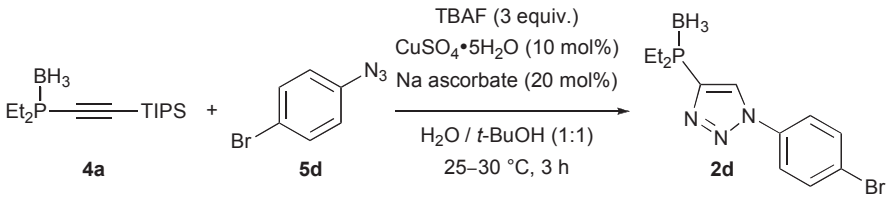
Yield: 55% (242 mg), obtained from **4a** (600 mg, 2.11 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.65 (d, J_{HH} = 8.8 Hz, 2H), 7.03 (d, J_{HH} = 8.8 Hz, 2H), 3.87 (s, 3H), 2.17–1.93 (m, 4H), 1.14 (dt, J_{HP} = 17.3 Hz, J_{HH} = 7.6 Hz, 6H), 0.95–0.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 137.8 (d, J_{CP} = 70.4 Hz), 130.0, 129.7 (d, J_{CP} = 27.2 Hz), 122.5, 115.0, 55.8, 17.7 (d, J_{CP} = 39.2 Hz), 7.1 (d, J_{CP} = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.9 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −41.8 (qd, J_{BH} = 95.0 Hz, J_{BP} = 56.8 Hz). IR (ATR, cm^{-1}) ν 2971, 2380, 2348, 2331, 1518, 1440, 1247, 1034, 847, 818, 763. HRMS (ESI) Calcd for $C_{13}H_{21}BN_3ONaP$ $[M+Na]^+$: 300.1413. Found: 300.1408.

Recrystallisation at −20 °C from CH_2Cl_2/pentane gave orange single crystals.



Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 291(2) K. Formula $C_{13}H_{21}BN_3OP$, formula weight 277.11, crystal system monoclinic, space group *P*2(1)/c, crystal dimensions 0.40 x 0.32 x 0.10 mm^3, *a* = 15.8190(3), *b* = 7.2629(1), *c* = 13.1199(2) Å, α = γ = 90.00, β = 94.554(1)°, *V* = 1502.61(4) Å^3, Z = 4, ρ_{calcd} = 1.225 Mgm^{-3}, μ = 0.178 mm^{-1}, $2\theta_{max}$ = 60.06 °, 28283 measured reflections, 4391 independent reflections (R_{int}= 0.0268), *R*1 [I>2σ(I)] = 0.0434, *wR*2 [I>2σ(I)] = 0.1236, GOF = 1.047, 234 parameters, final difference map within 0.295 and −0.260 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C1 1.7963(14), P1-C12 1.8116(17), P1-C10 1.8191(18), P1-B1 1.9159(19), C1-N3 1.3607(17), N1-C2 1.3470(17), N1-N2 1.3483(16), N1-C3 1.4287(18), N3-N2 1.3049(19), C1-P1-C12 103.76(7), C1-P1-C10 107.07(7), C12-P1-C10 107.22(9), C1-P1-B1 112.21(8), C12-P1-B1 114.98(10), C10-P1-B1 111.04(10).

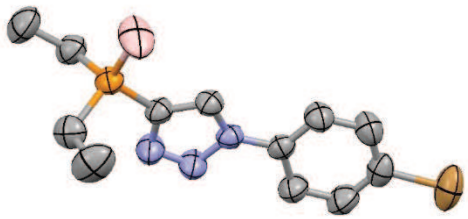
1-(4-Bromophenyl)-4-(diethylphosphino-borane)-1*H*-1,2,3-triazole (2d)



$C_{12}H_{18}BBrN_3P$
M= 325.98 g.mol^{-1}
White solid
Mp = 48–49 °C
R_f = 0.35
(Pentane/EtOAc: 8/2)

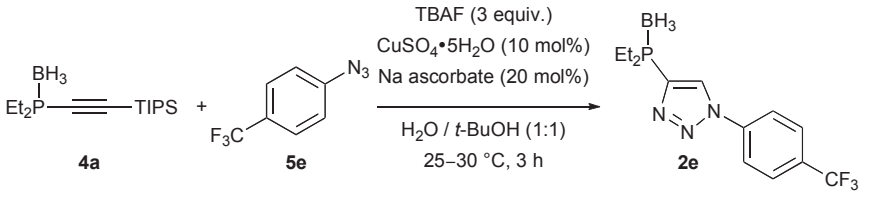
Yield: 95% (40 mg), obtained from **4a** (37 mg, 0.13 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.68–7.66 (m, 4H), 2.19–1.92 (m, 4H), 1.14 (dt, J_{HP} = 17.3 Hz, J_{HH} = 7.6 Hz, 6H), 0.90–0.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (d, J_{CP} = 69.0 Hz), 135.5, 133.2, 129.5 (d, J_{CP} = 27.1 Hz), 123.2, 122.2, 17.6 (d, J_{CP} = 38.8 Hz), 7.1 (d, J_{CP} = 2.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.4 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −41.9 (qd, J_{BH} = 93.8 Hz, J_{BP} = 55.0 Hz). IR (ATR, cm^{-1}) ν 2922, 2854, 2351, 1497, 1455, 1225, 1033, 1010, 982, 822, 742. HRMS (ESI) Calcd for $C_{12}H_{18}BBrN_3NaP$ $[M+Na]^+$: 348.0412. Found: 348.0406.

Recrystallisation at −20 °C from CH_2Cl_2/pentane gave colorless single crystals.



Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; T = 291(2) K. Formula $C_{12}H_{18}BBrN_3P$, formula weight 325.98, crystal system triclinic, space group P-1, crystal dimensions 0.29 x 0.24 x 0.22 mm^3, a = 7.6993(2), b = 10.2355(3), c = 11.5727(5) Å, α = 105.331(2), β = 104.973(2), γ = 107.292(2)°, V = 781.55(5) Å^3, Z = 2, ρ_{calcd} = 1.385 Mgm^{-3}, μ = 2.719 mm^{-1}, $2\theta_{max}$ = 53.46 °, 9184 measured reflections, 2422 independent reflections (R_{int} = 0.0280), $R1$ [I>2σ(I)] = 0.0429, $wR2$ [I>2σ(I)] = 0.1126, GOF = 1.008, 166 parameters, final difference map within 0.551 and −0.688 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986148 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Br1-C6 1.891(3), P1-C2 1.794(3), P1-C9 1.815(4), P1-C11 1.810(4), P1-B1 1.904(4), N3-C2 1.363(4), N3-N2 1.293(4), N2-N1 1.354(3), N1-C1 1.349(3), C1-C2 1.349(4), C3-N1 1.422(4), C2-P1-C9 104.82(14), C2-P1-C11 104.84(16), C9-P1-C11 104.40(17), C2-P1-B1 110.7(2), C9-P1-B1 115.3(3), C11-P1-B1 115.7(3).

4-(Diethylphosphino-borane)-1-(4-trifluoromethylphenyl)-1*H*-1,2,3-triazole (2e)

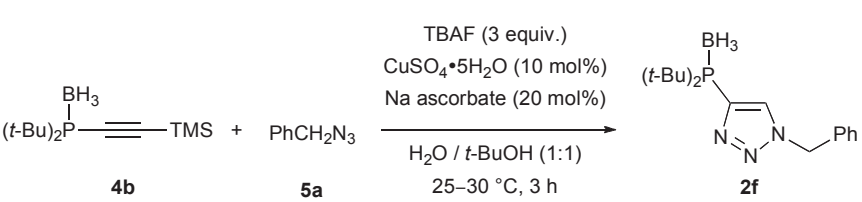


4a 5e 2e

$C_{13}H_{18}BF_3N_3P$
M= 315.08 g.mol^{-1}
White solid
Mp = 97–98 °C
R_f = 0.40
(Pentane/EtOAc: 9/1)

Yield: 98% (483 mg) obtained from **4a** (446 mg, 1.57 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.94 (d, J_{HH} = 8.4 Hz, 2H), 7.83 (d, J_{HH} = 8.4 Hz, 2H), 2.18–1.95 (m, 4H), 1.14 (dt, J_{HP} = 17.6 Hz, J_{HH} = 7.6 Hz, 6H), 1.10–0.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (d, J_{CP} = 68 Hz), 138.8, 131.3 (q, J_{CF} = 33 Hz), 129.5 (d, J_{CP} = 27 Hz), 127.3 (q, J_{CF} = 4 Hz), 123.5 (q, J_{CF} = 270 Hz), 120.8, 17.5 (d, J_{CP} = 39 Hz), 7.0 (d, J_{CP} = 2.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.7 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ –41.9 (qd, J_{BH} = 94.7 Hz, J_{BP} = 59.4 Hz). IR (ATR, cm^{-1}) ν 3128, 2983, 2381, 1618, 1525, 1499, 1441, 1406, 1325, 1227, 1158, 1121, 1070, 1018, 981, 843, 760. HRMS (ESI) Calcd for $C_{13}H_{18}BN_3F_3NaP$ $[M+Na]^+$: 338.1181. Found: 338.1180.

1-Benzyl-4-(di-*tert*-butylphosphino-borane)-1*H*-1,2,3-triazole (2f)

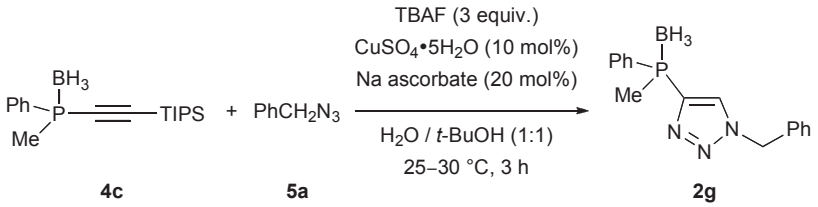


4b 5a 2f

$C_{17}H_{29}BN_3P$
M = 317.22 g.mol^{-1}
White solid
Mp = 102–103 °C
R_f = 0.75
(Pentane/EtOAc: 4/1)

Yield: 76% (690 mg), obtained from **4b** (730 mg, 2.85 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.39–7.35 (m, 3H), 7.27–7.22 (m, 2H), 5.57 (s, 2H), 1.31 (d, J_{HP} = 13.6 Hz, 18H), 0.95–0.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (d, $^1J_{CP}$ = 64.4 Hz), 134.2, 133.0 (d, J_{CP} = 24.0 Hz), 129.3, 128.9, 127.9, 54.1, 33.0 (d, $^1J_{CP}$ = 29.2 Hz), 28.3 (d, J_{CP} = 2.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ −41.6 (m). IR (ATR, cm^{-1}) ν 3133, 2965, 2385, 1497, 1475, 1457, 1393, 1368, 1211, 1076, 1045, 814, 719. HRMS (ESI) Calcd for $C_{17}H_{29}BN_3NaP$ $[M+Na]^+$: 340.2090. Found: 340.2083.

1-Benzyl-4- (methylphenylphosphino-borane)-1*H*-1,2,3-triazole (2g)



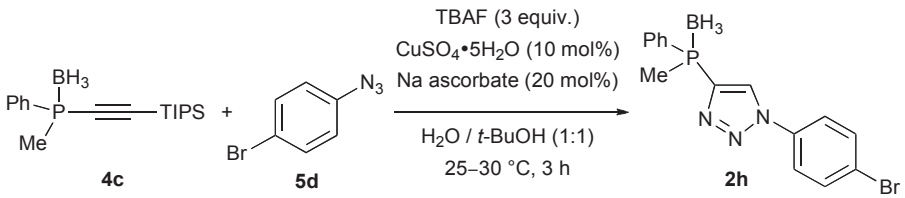
4c 5a 2g

$C_{16}H_{19}BN_3P$
M= 295.13 g.mol^{-1}
White solid
Mp = 123–124 °C
R_f = 0.33
(Pentane/EtOAc: 8/2)

Yield: 88% (42 mg), obtained from **4c** (52 mg, 0.16 mmol) according to the typical procedure with 1.2 equiv. of benzyl azide (**5a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.84–7.77 (m, 2H), 7.36–7.16 (m, 8H), 5.45 and 5.43 (AB, J_{HH} = 15.0 Hz, 2H), 1.84 (d, J_{HP} = 10.8 Hz,

3H), 1.40–0.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (d, J_{CP} = 77.9 Hz), 133.8, 132.1 (d, J_{CP} = 10.2 Hz), 131.6 (d, J_{CP} = 2.5 Hz), 130.2 (d, J_{CP} = 30.0 Hz), 129.3 (d, J_{CP} = 59.1 Hz), 129.3, 129.1, 128.8 (d, J_{CP} = 10.1 Hz), 128.4, 54.4, 12.3 (d, J_{CP} = 43.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ –6.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.3 (qd, J_{BH} = 90.9 Hz, J_{BP} = 53.4 Hz). IR (ATR, cm^{-1}) ν 3127, 2922, 2380, 1496, 1438, 1116, 1060, 887, 732, 690. HRMS (ESI) Calcd for $C_{16}H_{19}BN_3NaP$ $[M+Na]^+$: 318.1307. Found: 318.1301.

1-(4-Bromophenyl)-4-(methylphenylphosphino-borane)-1*H*-1,2,3-triazole (2h)

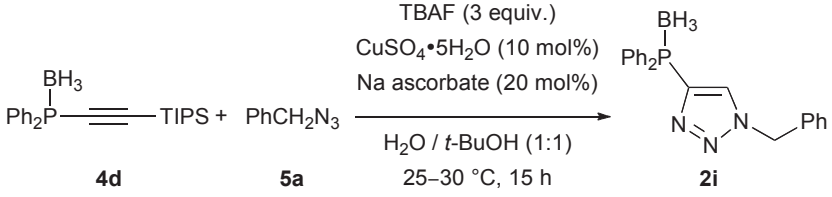


4c 5d 2h

$C_{15}H_{16}BBrN_3P$
M= 359.04 g.mol^{-1}
White solid
Mp = 101–102 °C
R_f = 0.25
(Pentane/EtOAc 8/2)

Yield: 76% (36 mg), obtained from **4c** (41 mg, 0.13 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.98–7.92 (m, 2H), 7.68–7.62 (m, 4H), 7.51–7.44 (m, 3H), 2.00 (d, J_{HP} = 10.6 Hz, 3H), 1.30–0.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (d, J_{CP} = 75.8 Hz), 135.5, 133.2, 132.2 (d, J_{CP} = 10.2 Hz), 131.8 (d, J_{CP} = 2.5 Hz), 129.0 (d, J_{CP} = 10.5 Hz), 129.0 (d, J_{CP} = 74.6 Hz), 128.4 (d, J_{CP} = 29.9 Hz), 123.3, 122.3, 12.2 (d, J_{CP} = 42.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −5.6 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.3 (qd, J_{BH} = 102.2 Hz, J_{BP} = 49.0 Hz). IR (ATR, cm^{-1}) ν 3127, 2374, 1500, 1225, 1072, 1037, 895, 823, 744. HRMS (ESI) Calcd for $C_{15}H_{14}BrN_3P$ $[(M-BH_3)+H]^+$: 346.0109. Found: 346.0113.

1-Benzyl-4-(diphenylphosphino-borane)-1*H*-1,2,3-triazole (2i)

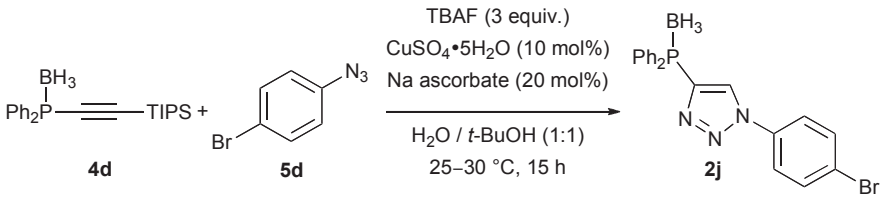


4d 5a 2i

$C_{21}H_{21}BN_3P$
M= 357.02 g.mol^{-1}
White solid
Mp = 119–120 °C
R_f = 0.36
(Pentane/EtOAc: 8/2)

Yield: 60% (337 mg), obtained from **4d** (604 mg, 1.58 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.87–7.81 (m, 4H), 7.46–7.37 (m, 9H), 7.32–7.29 (m, 2H), 5.57 (s, 2H), 1.70–0.70 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2 (d, J_{CP} = 80.1 Hz), 133.8, 133.1 (d, J_{CP} = 10.2 Hz), 131.7 (d, J_{CP} = 26.5 Hz), 131.5 (d, J_{CP} = 2.5 Hz), 129.4, 129.2, 128.8 (d, J_{CP} = 9.0 Hz), 128.7 (d, J_{CP} = 62.3 Hz), 128.5, 54.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 0.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.0 (m). IR (ATR, cm^{-1}) ν 3150, 2926, 2395, 1495, 1457, 1436, 1107, 1052, 1061, 731, 692. HRMS (ESI) Calcd for $C_{21}H_{21}BN_3NaP$ $[M+Na]^+$: 380.1464. Found: 380.1465.

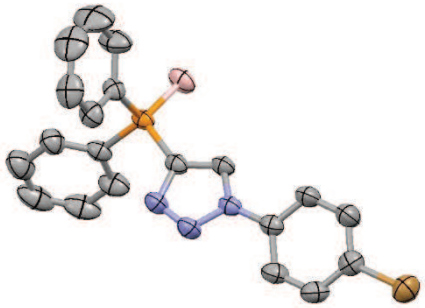
1-(4-Bromophenyl)-4-(diphenylphosphino-borane)-1*H*-1,2,3-triazole (2j)



$C_{20}H_{18}BBrN_3P$
M= 422.07 g.mol^{-1}
White solid
Mp = 119–120 °C
R_f = 0.65
(Pentane/EtOAc: 8/2)

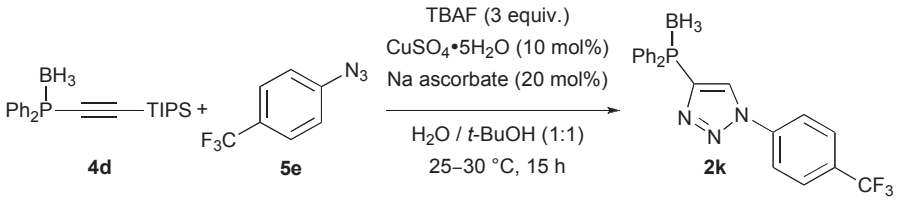
Yield: 55% (61 mg), obtained from **4d** (100 mg, 0.26 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.91–7.86 (m, 4H), 7.70–7.64 (m, 4H), 7.52–7.43 (m, 6H), 1.70–0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J_{CP} = 78.0 Hz), 135.4, 133.1, 133.0 (d, J_{CP} = 10.6 Hz), 131.6 (d, J_{CP} = 2.5 Hz), 129.6 (d, J_{CP} = 30.5 Hz), 128.9 (d, J_{CP} = 10.8 Hz), 128.2 (d, J_{CP} = 62.2 Hz), 123.2, 122.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 0.6 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ –41.9 (qd, J_{BH} = 94.7 Hz, J_{BP} = 59.4 Hz). IR (ATR, cm^{-1}) ν 3143, 3059, 2389, 2338, 1501, 1437, 1225, 1107, 1059, 1035, 983, 738, 692. HRMS (ESI) Calcd for $C_{20}H_{18}BBrN_3NaP$ $[M+Na]^+$: 444.0412. Found: 444.0424.

Recrystallisation at rt from CH_2Cl_2/pentane gave colorless single crystals.



Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 291(2) K. Formula $C_{20}H_{18}BBrN_3P$, formula weight 422.06, crystal system monoclinic, space group *C*2/c, crystal dimensions 0.42 x 0.41 x 0.35 mm^3, *a* = 11.4175(3), *b* = 15.1163(4), *c* = 23.4211(7) Å, α = γ = 90.00°, β = 98.935(2), *V* = 3993.20(19) Å^3, Z = 8, ρ_{calcd} = 1.404 Mgm^{-3}, μ = 2.147 mm^{-1}, $2\theta_{max}$ = 56.68 °, 13208 measured reflections, 5129 independent reflections (R_{int} = 0.0186), *R*1 [$I>2\sigma(I)$] = 0.0385, *wR*2 [$I>2\sigma(I)$] = 0.0936, GOF = 1.023, 236 parameters, final difference map within 0.700 and −0.663 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): Br1-C1 1.895(2), P1-C6 1.795(2), P1-C7 1.808(2), P1-C11 1.807(2), P1-B1 1.911(2), N1-C5 1.350(3), C5-C6 1.362(3), C6-N2 1.368(3), N2-N3 1.302(3), N3-N1 1.356(2), C4-N1 1.422(4), C6-P1-C11 104.19(9), C6-P1-C7 104.61(10), C11-P1-C7 107.45(10).

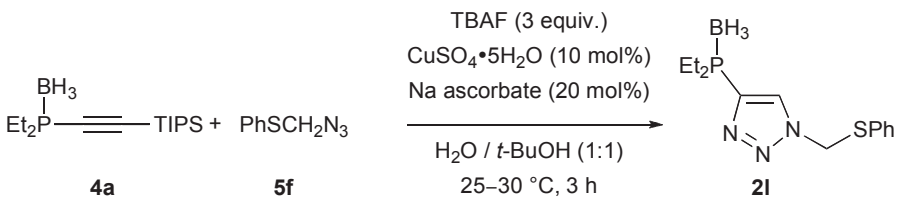
1-(4-Trifluoromethylphenyl)-4-(diphenylphosphino-borane)-1*H*-1,2,3-triazole (2k)



$C_{21}H_{18}BF_3N_3P$
M= 411.17 g.mol^{-1}
White solid
Mp = 131–133 °C
R_f = 0.36
(Pentane/EtOAc 8/2)

Yield: 53% (218 mg), obtained from **4d** (380 mg, 1 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.92–7.81 (m, 8H), 7.53–7.44 (m, 6H), 1.85–0.84 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8 (d, J_{CP} = 78.0 Hz), 138.9, 133.2 (d, J_{CP} = 10.4 Hz), 131.8 (d, J_{CP} = 2.5 Hz), 131.5 (q, J_{CF} = 33.3 Hz), 129.8 (d, J_{CP} = 30.5 Hz), 129.0 (d, J_{CP} = 11.0 Hz), 128.1 (d, J_{CP} = 62.7 Hz), 127.4 (q, J_{CF} = 3.7 Hz), 123.5 (q, J_{CF} = 272.4 Hz), 120.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 0.7 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ −39.5 (m). IR (ATR, cm^{-1}) ν 3133, 3059, 2378, 1618, 1524, 1437, 1322, 1223, 1162, 1126, 1107, 1067, 842, 735. HRMS (ESI) Calcd for $C_{21}H_{18}BF_3N_3NaP$ $[M+Na]^+$: 434.1181. Found: 434.1165. Anal. Calcd for $C_{21}H_{18}BF_3N_3P$: C, 61.34; H, 4.41; N, 10.22. Found: C, 61.11; H, 4.61; N, 10.12.

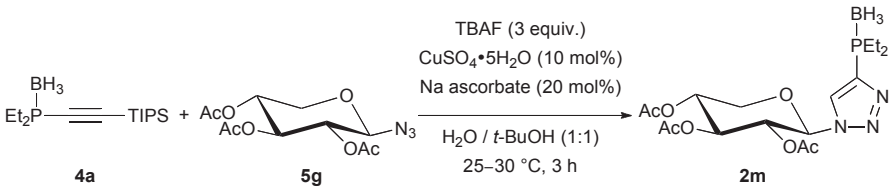
4-(Diethylphosphino-borane)-1-(phenylthiomethyl)-1*H*-1,2,3-triazole (2l)



$C_{13}H_{21}BN_3PS$
M= 293.18 g.mol^{-1}
White solid
Mp = 69–70 °C
R_f = 0.30
(Pentane/EtOAc 8/2)

Yield: 76% (29 mg), obtained from **4a** (37 mg, 0.13 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.35–7.31 (m, 5H), 5.64 (s, 2H), 2.10−1.85 (m, 4H), 1.06 (dt, J_{HP} = 17.4 Hz, J_{HH} = 7.7 Hz, 6H), 0.83–0.06 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (d, J_{CP} = 69.8 Hz), 133.2, 131.4 (d, J_{CP} = 27.0 Hz), 131.2, 129.7, 129.4, 54.4, 17.6 (d, J_{CP} = 38.8 Hz), 6.98 (d, J_{CP} = 2.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.1 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −42.0 (qd, J_{BH} = 94.1 Hz, J_{BP} = 56.8 Hz). IR (ATR, cm^{-1}) ν 3130, 2973, 2937, 2386, 2363, 1439, 1210, 1070, 1039, 747, 690. HRMS (ESI) Calcd for $C_{13}H_{21}BN_3NaPS$ $[M+Na]^+$: 316.1185. Found: 316.1174.

4-(Diethylphosphino-borane)-1-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-1*H*-1,2,3-triazole (2m)

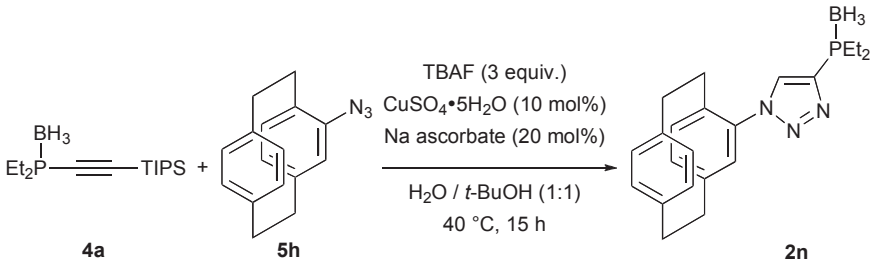


4a **5g** **2m**

$C_{17}H_{29}BN_3O_7P$
M= 429.21 g.mol^{-1}
White solid
Mp = 119–120 °C
R_f = 0.33
(Pentane/EtOAc: 6/4)

Yield: 75% (96 mg), obtained from **4a** (85 mg, 0.30 mmol) according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 5.80 (d, J_{HH} = 8.8 Hz, 1H), 5.44 (dd, J_{HH} = 9.4 Hz, J_{HH} = 9.3 Hz, 1H), 5.35 (dd, J_{HH} = 9.4 Hz, J_{HH} = 8.9 Hz, 1H), 5.16 (ddd, J_{HH} = 10.3 Hz, J_{HH} = 9.3 Hz, J_{HH} = 5.6 Hz, 1H), 4.34 (dd, J_{HH} = 11.6 Hz, J_{HH} = 5.6 Hz, 1H), 3.61 (dd, J_{HH} = 11.6 Hz, J_{HH} = 10.3 Hz, 1H), 2.15–1.84 (m, 4H), 2.07 (s, 3H), 2.04 (s, 3H), 1.86 (s, 3H), 1.08 (dt, J_{HP} = 17.2 Hz, J_{HH} = 7.6 Hz, 3H), 1.04 (dt, J_{HP} = 17.2 Hz, J_{HH} = 7.6 Hz, 3H), 1.10–0.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.7, 168.6, 138.0 (d, J_{CP} = 68.4 Hz), 130.4 (d, J_{CP} = 26.7 Hz), 86.5, 71.7, 70.8, 68.3, 65.7, 20.7, 20.6, 20.1, 17.8 (d, J_{CP} = 38.5 Hz), 17.3 (d, J_{CP} = 38.8 Hz), 6.9 (d, J_{CP} = 1.9 Hz), 6.7 (d, J_{CP} = 2.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.0 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ −42.3 (m). IR (ATR, cm^{-1}) ν 3162, 2979, 2945, 2381, 1761, 1742, 1376, 1246, 1208, 1034. HRMS (ESI) Calcd for $C_{17}H_{29}BN_3O_7NaP$ $[M+Na]^+$: 452.1734. Found: 452.1720.

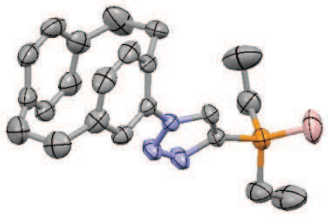
4-(Diethylphosphino-borane)-1-([2.2]-paracyclophan-4-yl)-1*H*-1,2,3-triazole (2n)



$C_{22}H_{29}BN_3P$
M= 377.27 g.mol^{-1}
Pale yellow solid
Mp = 140–141 °C
R_f = 0.40
(Pentane/EtOAc: 9/1)

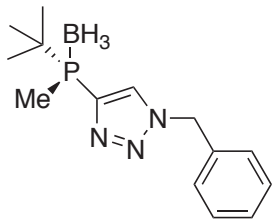
Yield: 77% (287 mg) obtained from **4a** (284 mg, 1.00 mmol), according to the typical procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 6.75–6.50 (m, 7H), 3.30–2.86 (m, 7H), 2.65–2.53 (m, 1H), 2.27–1.95 (m, 4H), 1.27–1.12 (m, 6H), 1.05–0.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.4, 139.0, 137.0 (d, J_{CP} = 70.1 Hz), 136.8, 135.8 134.5, 133.1, 133.0, 132.8, 132.6, 132.3 (d, J_{CP} = 27 Hz), 130.5, 127.4, 35.3, 34.9, 34.7, 32.8, 17.8 (d, J_{CP} = 8.6 Hz), 17.4 (d, J_{CP} = 8.6 Hz), 7.10 (d, J_{CP} = 2.3 Hz), 7.06 (d, J_{CP} = 2.3 Hz). ^{31}P NMR (162MHz, $CDCl_3$) δ 7.9 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ −41.8 (m). IR (ATR, cm^{-1}) ν 3130, 2970, 2935, 2383, 2365, 1455, 1501, 1225, 1034, 777, 721. HRMS (ESI) Calcd for $C_{22}H_{29}BN_3NaP$ $[M+Na]^+$: 400.2090. Found: 400.2071.

Recrystallisation at rt by slow diffusion of pentane into a $CHCl_3$ solution gave colourless single crystals.



Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; T = 291(2) K. Formula $C_{22}H_{29}BN_3P$, formula weight 377.26, crystal system orthorhombic, space group *P*ca2(1), crystal dimensions 0.47 x 0.45 x 0.31 mm^3, a = 11.0128(2), b = 7.8943(2), c = 24.9976(5) Å, α = γ = β =90.00°, V = 2173.25(8) Å^3, Z = 4, ρ_{calcd} = 1.153 Mgm^{-3}, μ = 0.137 mm^{-1}, $2\theta_{max}$ = 59.20°, 34410 measured reflections, 6342 independent reflections (R_{int}= 0.0246), *R*1 [I>2σ(I)] = 0.0431, *wR*2 [I>2σ(I)] = 0.1136, GOF = 1.058, 247 parameters, final difference map within 0.233 and −0.197 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986150 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C18 1.7878(15), P1-C19 1.816(2), P1-C21 1.808(2), P1-B1 1.908(2), N1-C17 1.3440(18), C17-C18 1.368(2), C18-N3 1.3615(19), N3-N2 1.2983(19), N2-N1 1.3536(17), N1-C4 1.4257(18), C18-P1-C21 104.30(9), C18-P1-C19 103.80(8).

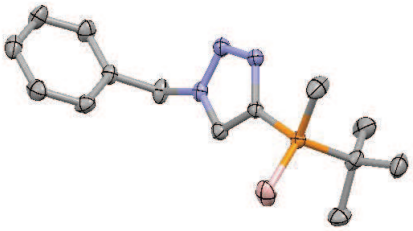
(*R*)-1-Benzyl-4-(methyl-*tert*-butylphosphino-borane)-1*H*-1,2,3-triazole (9)



$C_{14}H_{23}BN_3P$
M = 275.14 g.mol^{-1}
White solid
Mp = 125–126 °C
R_f = 0.4 (Pentane/Et_2O: 3/1)

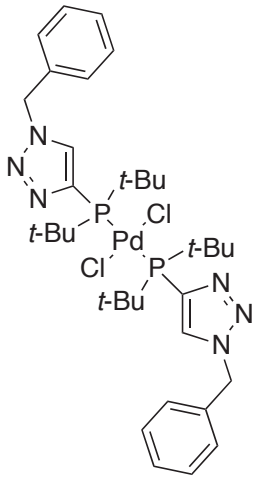
Yield: 80% (176 mg), obtained from **8** (240 mg, 0.8 mmol) after 3 h of stirring at 25-30 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.40–7.37 (m, 3H), 7.29–7.26 (m, 2H), 5.57 (s, 2H), 1.64 (d, J_{HP} = 10.0 Hz, 3H), 1.16 (d, J_{HP} = 14.8 Hz, 9H), 0.90–0.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7 (d, J_{CP} = 69.5 Hz), 133.9, 131.3 (d, J_{CP} = 26.9 Hz), 129.3, 129.1, 128.1, 54.3, 28.5 (d, J_{CP} = 35.5 Hz), 25.2 (d, J_{CP} = 3.0 Hz), 5.5 (d, J_{CP} = 39.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.4 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ −40.7 (m). IR (ATR, cm^{-1}) ν 3117, 2923, 2854, 2377, 1498, 1460, 1417, 1365, 1214, 1104, 1067, 905, 889, 722. HRMS (ESI) Calcd for $C_{14}H_{23}BN_3NaP$ $[M+Na]^+$: 298.1620 Found: 298.1624. $[\alpha]_D$ –21 (c 0.01, $CHCl_3$), 98.8% ee (*R*). The ee value was determined by HPLC analysis (Daicel Chiralpak IC 4, *n*-heptane/propan-2-ol = 90/10, flow rate = 1.0 mL.min^{-1}, 210 nm, t_R = 9.71 min (*S*), t_R = 12.92 min (*R*)).

Recrystallisation at 4 °C from CH_2Cl_2/pentane gave colourless single crystals.



Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 150(2) K. Formula $C_{14}H_{23}BN_3P$, formula weight 275.13, crystal system orthorhombic, space group *P*2(1)2(1)2(1), crystal dimensions 0.32 x 0.32 x 0.28 mm^3, *a* = 9.8500(2), *b* = 11.1410(2), *c* = 14.4209(3) Å, α = γ = β =90.00°, *V* = 1582.53(5) Å^3, Z = 4, ρ_{calcd} = 1.155 Mgm^{-3}, μ = 0.164 mm^{-1}, $2\theta_{max}$ = 68.98° , 32222 measured reflections, 6676 independent reflections (R_{int}= 0.0252), *R*1 [*I*>2σ(*I*)] = 0.0338, *wR*2 [*I*>2σ(*I*)] = 0.0799, GOF = 1.076, 219 parameters, final difference map within 0.315 and −0.214 eÅ^{-3}. Flack parameter = 0.01(5). The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986151 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C1 1.7974(9), P1-C10 1.8491(10), P1-C14 1.7956(11), P1-B1 1.9137(14), C1-C2 1.3772(12), C2-N3 1.3494(13), N3-N2 1.3476(12), N2-N1 1.3116(12), N1-C1 1.3699(12), N3-C3 1.4656(12), C1-P1-C14 102.83(5), C1-P1-C10 106.64(4), C14-P1-C10 107.51(6).

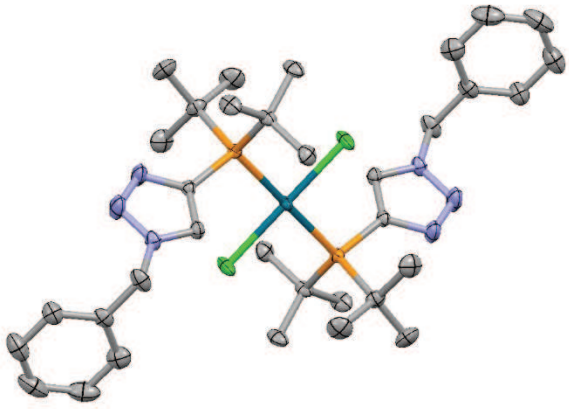
Dichlorobis[1-benzyl-4-(di-*tert*-butylphosphino)-1*H*-1,2,3-triazole]palladium(II) (10): A mixture of triazolylphosphine-borane **2f** (300 mg, 0.95 mmol, 1 equiv.) and DABCO (531 mg, 4.73 mmol, 5 equiv.) in THF (5 mL) was heated at 70 °C under an argon atmosphere for 3 h and then concentrated under reduced pressure. The residue was next filtered on silica gel using degassed Et_2O (100 mL) as the eluent directly into a round bottomed flask containing a suspension of $PdCl_2(PhCN)_2$ (181 mg, 0.47 mmol, 0.5 equiv.) in Et_2O (5 mL). The resulting yellow solution was stirred for 30 min at rt and then concentrated under reduced pressure. The residual yellow solid was washed with pentane to afford the desired product as a yellow solid (343 mg, 93% yield).



$C_{34}H_{52}Cl_2N_6P_2Pd$
M = 784.09 g.mol^{-1}
Yellow solid
Decomposition at 215−220 °C

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.76 (s, 2H), 7.36–7.34 (m, 6H), 7.22–7.20 (m, 4H), 5.59 (s, 4H), 1.56–1.51 (m, 36H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 136.5 (t_{app}, J_{CP} = 25 Hz), 135.1, 133.1 (t_{app}, J_{CP} = 12 Hz), 128.9, 128.4, 127.4, 53.6, 38.2 (t_{app}, J_{CP} = 8.5 Hz), 30.6 (t_{app}, J_{CP} = 2.5 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 33.8. IR (ATR, cm^{-1}) ν 3144, 2963, 2898, 1498, 1497, 1476, 1456, 1441, 1391, 1363, 1203, 1174, 1107, 1048, 1024, 930, 811, 716, 702 cm^{-1}. HRMS (ESI) Calcd for $C_{34}H_{52}ClN_6P_2Pd$ $[M\text{-}Cl]^+$: 747.2452. Found: 747.2436.

Recrystallisation at rt from CH_2Cl_2/Et_2O gave yellow single crystals.

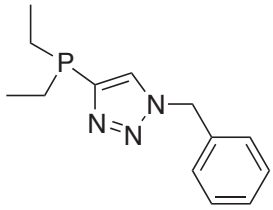


Crystallographic data: Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 150(2) K. Formula $C_{34}H_{52}BCl_2N_6P_2Pd$, formula weight 784.06, crystal system monoclinic, space group *P*2(1)/c, crystal dimensions 0.48 x 0.41 x 0.38 mm^3, *a*

= 10.2656(5), b = 20.6740(10), c = 9.0479(4) Å, α = γ = 90.00°, β =100.041(2)°, V = 1890.83(15) Å^3, Z = 2, ρ_{calcd} = 1.377 Mgm^{-3}, μ = 0.749 mm^{-1}, $2\theta_{max}$ = 71.04° , 39732 measured reflections, 5081 independent reflections (R_{int}= 0.0289), $R1$ [I>2σ(I)] = 0.0196, $wR2$ [I>2σ(I)] = 0.0508, GOF = 1.053, 211 parameters, final difference map within 0.315 and −0.214 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986152 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-Pd1 2.3756(3), P1-C1 1.8104(11), P1-C10 1.8767(12), P1-C14 1.8982(12), Pd1-Cl1 2.2961(3), C1-C2 1.3730(16), C2-N3 1.3381(14), N3-N2 1.3402(15), N2-N1 1.3130(16), N1-C1 1.3639(15), N3-C3 1.4661(15), C1-P1-C14 100.01(5), C1-P1-C10 105.02(5), C14-P1-C10 112.98(6), Cl1-Pd1-P1 89.894(11), Cl1a-Pd1-P1a 90.107(11).

General procedure for borane decomplexation of triazolylphosphine-boranes 2:
A mixture of triazolylphosphine-borane **2** (1 equiv.) and DABCO (2 equiv. or 3 equiv. with dialkylphosphino derivatives) in THF was heated at 70 °C under a nitrogen atmosphere for 3 h. After removal of solvent the residue was purified by silica gel column chromatography with pentane/EtOAc as eluent (diphenylphosphino compounds) or was filtered through a neutral alumina column using degassed EtOAc/pentane (2/8) as eluent (diethyl/phenyl-methylphosphino compounds).

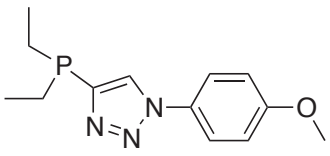
1-Benzyl-4-(diethylphosphino)-1*H*-1,2,3-triazole (1a)



$C_{13}H_{18}N_3P$
M = 247.28 g.mol^{-1}
White solid
Mp = 52–53 °C

Yield: 74% (77 mg) obtained from **2a** (110 mg, 0.42 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.32–7.27 (m, 3H), 7.20–7.16 (m, 2H), 5.48 (s, 2H), 1.86-1.61 (m, 4H), 0.97 (dt, J_{HP} = 15.8 Hz, J_{HH} = 7.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2 (d, J_{CP} = 15.6 Hz), 134.7, 129.1, 128.7, 128.4 (d, $^2J_{CP}$ = 30.7 Hz), 128.0, 53.9, 19.2 (d, J_{CP} = 6.7 Hz), 10.0 (d, J_{CP} = 13.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −39.1. HRMS (ESI) Calcd for $C_{13}H_{19}N_3P$ $[M+H]^+$: 248.1317. Found: 248.1315.

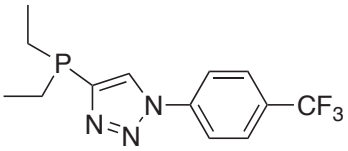
1-(4-Anisyl)-4-(diethylphosphino)-1*H*-1,2,3-triazole (1c)



$C_{13}H_{18}N_3PO$
M = 263.28 g.mol^{-1}
White solid
Mp = 155–157 °C

Yield: 61% (58 mg) obtained from **2c** (100 mg, 0.36 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.62 (d, J_{HH} = 9.2 Hz, 2H), 6.99 (d, J_{HH} = 9.2 Hz, 2H), 3.84 (s, 3H), 1.97–1.75 (m, 4 H), 1.06 (dt, J_{HP} = 16.0 Hz, J_{HH} = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.4 (d, J_{CP} = 17.1 Hz), 130.5, 126.7 (d, J_{CP} = 31.2 Hz), 122.2, 114.8, 55.7 (d, J_{CP} = 2.0 Hz), 19.3 (d, J_{CP} = 6.0 Hz), 10.0 (d, J_{CP} = 13.1 Hz,). ^{31}P NMR (162 MHz, $CDCl_3$) δ –39.1. HRMS (ESI) Calcd for $C_{13}H_{19}N_3OP$ $[M+H]^+$: 264.1266. Found: 264.1264.

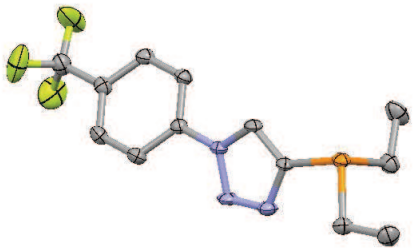
4-(Diethylphosphino)-1-(4-trifluoromethylphenyl)-1*H*-1,2,3-triazole (1e)



$C_{13}H_{15}F_3N_3P$
M = 301.25 g.mol^{-1}
White solid
Mp = 62–63 °C

Yield: 88% (189 mg) obtained from **2e** (225 mg, 0.71 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.91 (d, J_{HH} = 8.8 Hz, 2H), 7.80 (d, J_{HH} = 8.8 Hz, 2H), 2.00–1.78 (m, 4H), 1.08 (dt, J_{HP} = 16.0 Hz, J_{HH} = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6 (d, J_{CP} = 19.1 Hz), 139.3, 130.6 (q, J_{CF} = 33.2 Hz), 127.1 (q, J_{CF} = 4.0 Hz), 126.4 (d, J_{CP} = 31.2 Hz), 123.6 (q, J_{CF} = 271.6 Hz), 120.8, 19.1 (d, J_{CP} = 7.0 Hz), 9.9 (d, J_{CP} = 13.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ –38.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.6. HRMS (ESI) Calcd for $C_{13}H_{16}N_3F_3P$ $[M+H]^+$: 302.1034. Found: 302.1037.

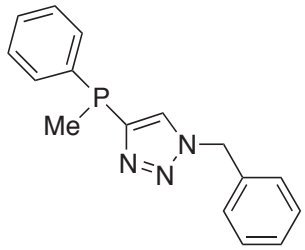
Recrystallisation at rt by slow diffusion of pentane into a $CHCl_3$ solution gave colourless single crystals.



Crystallographic data : Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ=0.71073 Å; graphite monochromator; *T*=140(2) K. Formula $C_{13}H_{15}F_3N_3P$, formula weight 301.25, crystal system monoclinic, space group *P*2(1), crystal dimensions 0.35 x 0.29 x 0.15 mm^3, *a*=5.4783(5), *b*=6.9229(6), *c*=18.7771(17) Å, α=γ=90.00°, β=95.059(3)°, *V*=709.36(11) Å^3, *Z*=2, ρ_{calcd}=1.410 Mgm^{-3}, μ=0.221 mm^{-1}, $2\theta_{max}$=59.12°, 8283 measured reflections, 3679 independent reflections (R_{int}= 0.0343), *R*1 [$I>2\sigma(I)$]=0.0427, *wR*2 [$I>2\sigma(I)$]= 0.0979, GOF=1.111, 183 parameters, final difference map within 0.414 and -0.392 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986144 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C1 1.817(2), P1-C12 1.846(2), P1-C10 1.850(2), C3-N1 1.424(3), C2-N1 1.358(3), N1-N2

1.358(3), N2-N3 1.302(3), N3-C1 1.380(3), C1-C2 1.376(3), C1-P1-C12 99.16(10), C1-P1-C10 98.71(10), N1-C2-C1 105.63(18), C2-C1-N3 107.06(19), N2-N1-C2 110.00(17), N2-N3-C1 109.70(18), N3-N2-N1 107.61(17).

1-Benzyl-4-(phenylmethylphosphino)-1*H*-1,2,3-triazole (1g)

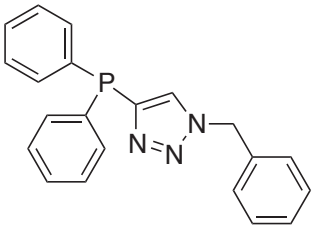


$C_{16}H_{16}N_3P$

M = 281.29 g.mol^{-1}
White solid
Mp = 155–157 °C

Yield: 71% (204 mg) obtained from **2g** (300 mg, 1.01 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.41 (s, 1H), 7.37–7.24 (m, 8H), 5.54 and 5.49 (AB, J_{AB} = 14.8 Hz, 2H), 1.72 (d, J_{HP} = 3.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4 (d, J_{CP} = 9.3 Hz), 138.7 (d, J_{CP} = 9.2 Hz), 134.6, 132.1 (d, J_{CP} = 19.6 Hz), 129.1, 128.8, 128.6 (d, J_{CP} = 33.4 Hz), 128.4, 128.1, 127.8 (d, J_{CP} = 29.2 Hz), 54.0, 11.8 (d, J_{CP} = 8.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ –51.3. HRMS (ESI) Calcd for $C_{16}H_{17}N_3P$ $[M+H]^+$: 282.1160. Found: 282.1152.

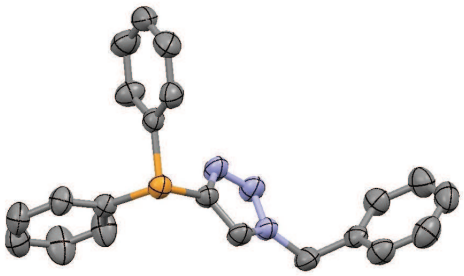
1-Benzyl-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1i)



$C_{21}H_{18}N_3P$
M = 343.36 g.mol^{-1}
White solid
Mp = 97–99 °C

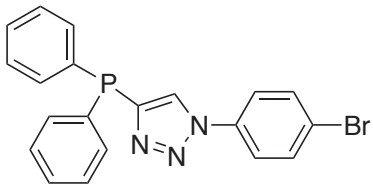
Yield: 92% (230 mg) obtained from **2i** (261 mg, 0.73 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.32 (m, 4H), 7.29–7.19 (m, 10H), 7.15–7.13 (m, 2H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (d, J_{CP} = 5.8 Hz), 136.5 (d, J_{CP} = 6.8 Hz), 134.6, 133.6 (d, J_{CP} = 20.0 Hz), 129.4 (d, $^{2}J_{CP}$ = 25.6 Hz), 129.2, 129.0, 128.8, 128.6 (d, J_{CP} = 7.3 Hz), 128.1, 54.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ –31.9. HRMS (ESI) Calcd for $C_{21}H_{19}N_3P$ $[M+H]^+$: 344.1317. Found: 344.1306.

Recrystallisation at −20 °C from CH_2Cl_2/pentane gave colourless single crystals.



Crystallographic data : Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 291(2) K. Formula $C_{21}H_{18}N_3P$, formula weight 343.35, crystal system monoclinic, space group *P*2(1)/c, crystal dimensions 0.51 x 0.32 x 0.21 mm^3, *a*=10.0928(3), *b*=10.6178(3), *c*=17.3125(5) Å, α=γ=90.00°, β=98.415(2)°, *V*=1835.29(9) $Å^3$, Z=4, ρ_{calcd}=1.243 Mgm^{-3}, μ=0.157 mm^{-1}, $2\theta_{max}$=52.76°, 43181 measured reflections, 4717 independent reflections (R_{int}= 0.0272), *R*1 [*I*>2σ(*I*)]=0.0375, *wR*2 [*I*>2σ(*I*)]= 0.0942, GOF=1.039, 298 parameters, final difference map within 0.202 and -0.211 $eÅ^{-3}$. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986145 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C1 1.8147(13), P1-C10 1.8325(14), P1-C16 1.8315(13), C1-C2 1.3713(18), C2-N3 1.3382(17), N3-N2 1.3420(15), N2-N1 1.3108(17), C1-P1-C16 102.25(6), C1-P1-C10 103.00(6), C16-P1-C10 101.78(6).

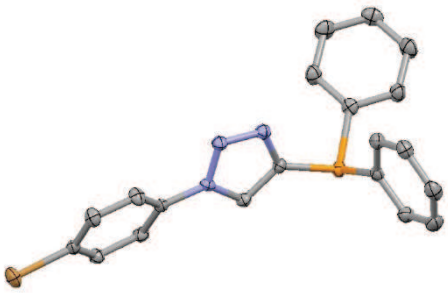
1-(4-Bromophenyl)-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1j)



$C_{20}H_{15}BrN_3P$
M = 408.23 $g.mol^{-1}$
White solid
Mp = 166–168 °C

Yield: 91% (220 mg) obtained from **2j** (250 mg, 0.59 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.64–7.57 (m, 4H), 7.53–7.48 (m, 4H), 7.37–7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (d, J_{CP} = 7.7 Hz), 136.0 (d, J_{CP} = 6.9 Hz), 135.9, 133.6 (d, J_{CP} = 20.1 Hz), 133.0, 129.3, 128.8 (d, J_{CP} = 7.3 Hz), 127.1 (d, J_{CP} = 23.8 Hz), 122.6, 122.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ −31.8. HRMS (ESI) Calcd for $C_{20}H_{16}BrN_3P$ $[M+H]^+$: 408.0265. Found: 408.0257.

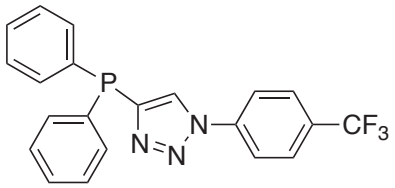
Recrystallisation at −20 °C from CH_2Cl_2/pentane gave colorless single crystals.



Crystallographic data : Bruker Kappa APEXII CCD diffractometer ($Mo_{K\alpha}$ λ = 0.71073 Å; graphite monochromator; *T* = 150(2) K. Formula $C_{20}H_{15}BrN_3P$, formula weight 408.23, crystal system triclinic, space group *P*-1, crystal dimensions 0.41 x 0.13 x 0.06 mm^3, *a* = 5.7216(2), *b* = 12.5095(5), *c* = 12.5281(5) Å, α = 86.643(2)°, β =79.834(2)°, γ = 82.749(6), *V* = 874.95(6) $Å^3$, Z = 2, ρ_{calcd} = 1.550 Mgm^{-3}, μ = 2.448 mm^{-1}, $2\theta_{max}$ = 64.10° , 11222 measured reflections, 4448 independent reflections (R_{int}= 0.0228), *R*1 [*I*>2σ(*I*)] = 0.0271,

*wR*2 [$I>2\sigma(I)$] = 0.0597, GOF = 1.033, 226 parameters, final difference map within 0.315 and −0.214 eÅ^{-3}. The structure was solved using direct methods and refined by full-matrix least-squares analysis on F^2. CCDC 986146 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths (Å) and angles (deg): P1-C6 1.8174(16), P1-C7 1.8352(17), P1-C13 1.8350(17), C5-C6 1.375(2), C6-N3 1.375(2), N3-N2 1.3086(19), N2-N1 1.3596(18), N1-C5 1.351(2), C6-P1-C7 102.68(7), C6-P1-C13 101.05(7), C7-P1-C13 101.87(7).

1-(4-Trifluoromethylphenyl)-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1k)



$C_{21}H_{15}F_3N_3P$
M = 397.33 g.mol^{-1}
White solid
Mp = 155−157 °C

Yield: 97% (65 mg) obtained from **2k** (70 mg, 0.17 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J_{HH} = 8.4 Hz, 2H), 7.85 (s, 1H), 7.78 (d, J_{HH} = 8.4 Hz, 2H), 7.54−7.49 (m, 4H), 7.40−7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6 (d, J_{CP} = 9.0 Hz), 139.3, 135.9 (d, J_{CP} = 7.0 Hz), 133.7 (d, J_{CP} = 20.1 Hz), 130.9 (q, J_{CF} = 33.2 Hz), 129.4, 128.8 (d, J_{CP} = 7.0 Hz), 127.2 (q, J_{CF} = 3 Hz), 127.0, 123.6 (q, J_{CF} = 271.6 Hz), 120.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ −31.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7. IR (ATR, cm^{-1}) ν 3146, 1615, 1523, 1434, 1321, 1164, 1123, 1109, 1067, 1031, 845, 744, 695. HRMS (ESI) Calcd for $C_{21}H_{15}N_3F_3NaP$ $[M+Na]^+$: 420.0853. Found: 420.0838.

General procedure for the Suzuki-Miyaura cross-coupling reactions: A Schlenk tube was charged with boronic acid **12** (1.5 mmol, 1.5 equiv.), K_3PO_4 (2 mmol, 2 equiv.) and Pd(II)-complex **10** (1 or 0.1 mol%). The flask was evacuated and backfilled with argon three times. Toluene (3 mL) and aryl chloride **11** (1 mmol) were subsequently added. The reaction mixture was stirred at 100 °C under argon atmosphere for 12 hours then cooled to rt, extracted with EtOAc, washed with H_2O and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was finally purified by flash colum chromatography on silica gel with Pentane/CH_2Cl_2 (19:1) as eluent to afford bis-arenes **13**.

^{1}H and ^{13}C NMR data for compounds **13a**,[6] **13b**,[7] and **13c**[8] were in good agreement with the literature data.

References:

1 E. Bernoud, C. Alayrac, O. Delacroix and A.-C. Gaumont, *Chem. Commun.*, 2011, **47**, 3239–3241.
2 X. Zhao, A. J. Lough and D. W. Stephan, *Chem. Eur. J.*, 2011, **17**, 6731–6743.
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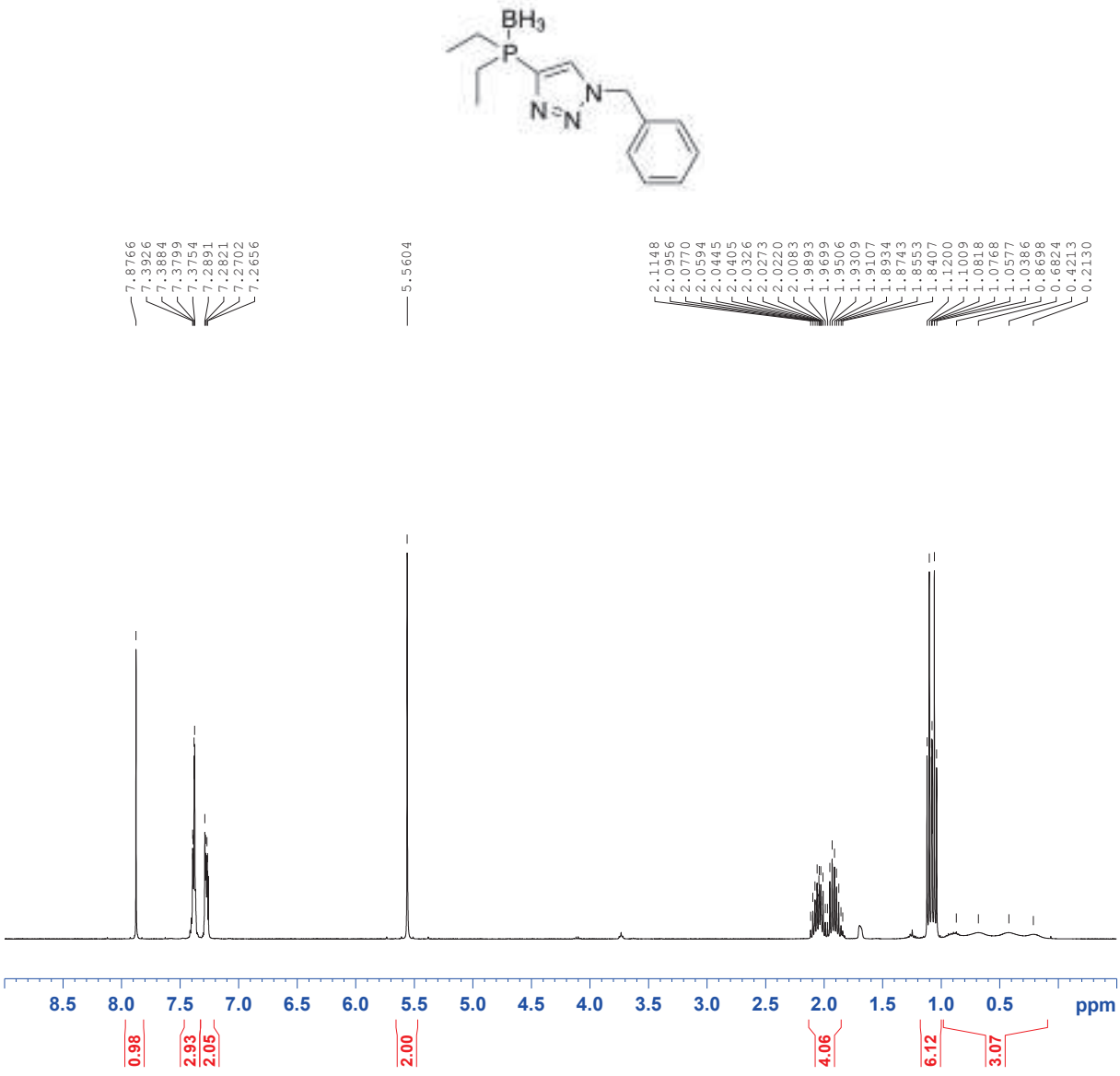
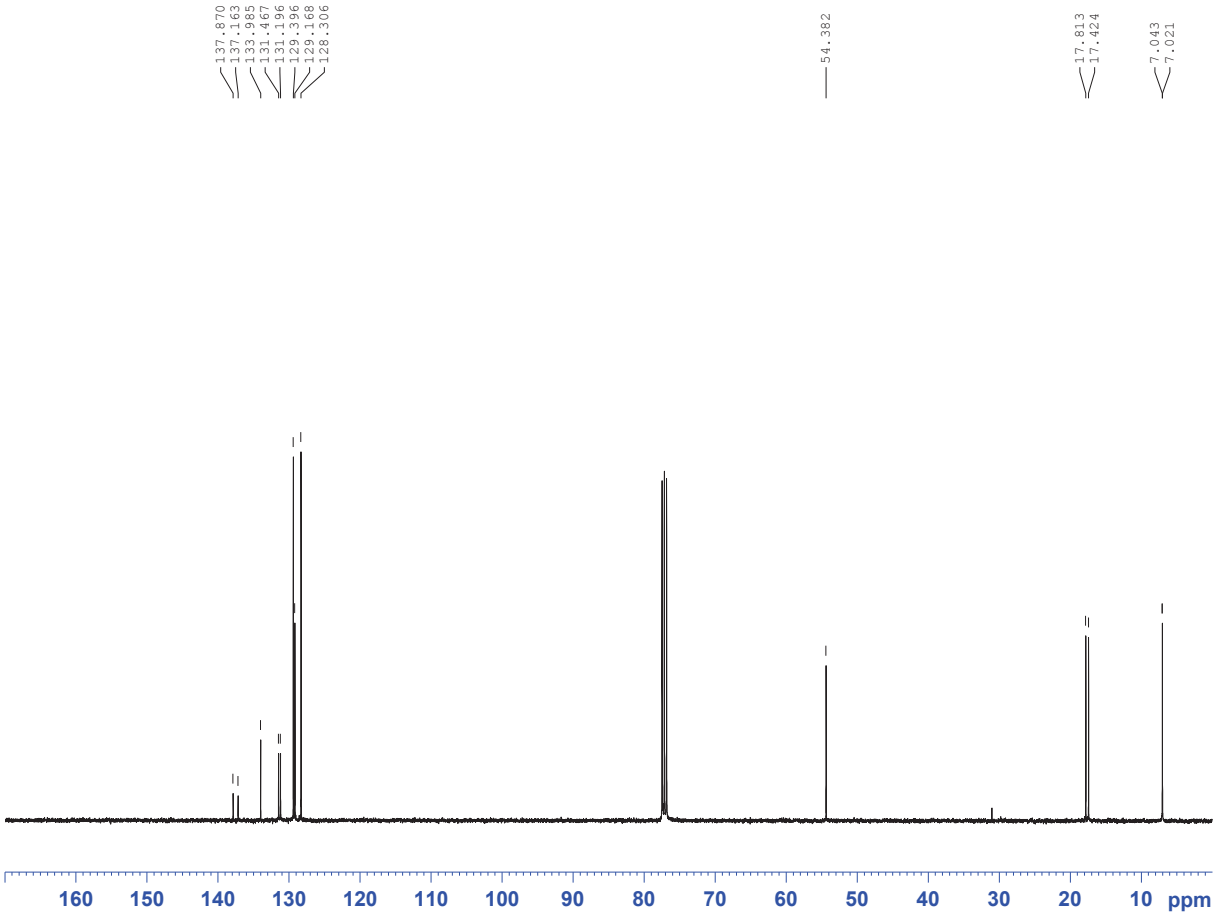
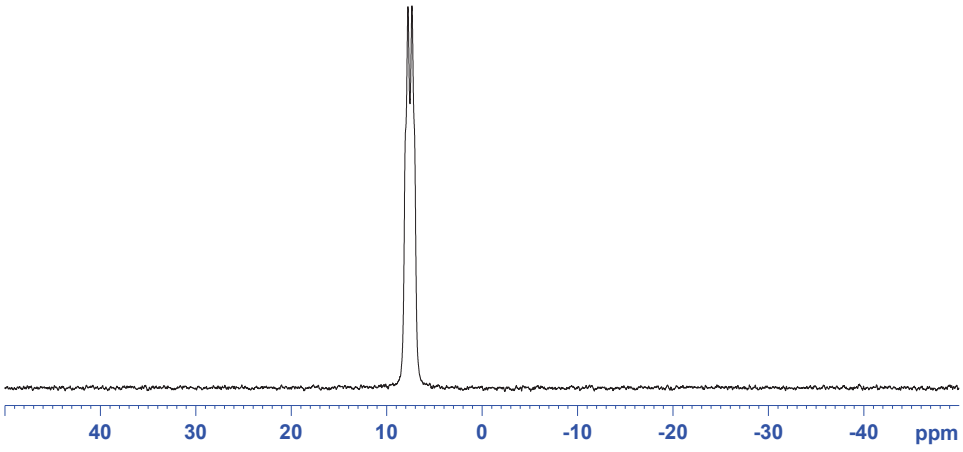
5 K. Nagata, S. Matsukawa and T. Imamoto, *J. Org. Chem.,* 2000, **65**, 4185–4188.
6 D. Liu, W. Gao, Q. Dai and X. Zhang, *Org. Lett.,* 2005, **7**, 4907–4910.
7 Z. Zhang and Z. Wang, *J. Org. Chem.,* 2006, **71**, 7485–7487.
8 I. J. S. Fairlamb, A. R. Kapdi and A. F. Lee, *Org. Lett.*, 2004, **6**, 4435–4438.

3. ^{1}H, ^{31}P and ^{13}C NMR Spectra

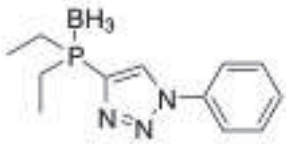
1-Benzyl-4-(diethylphosphino-borane)-1*H*-1,2,3-triazole (2a)

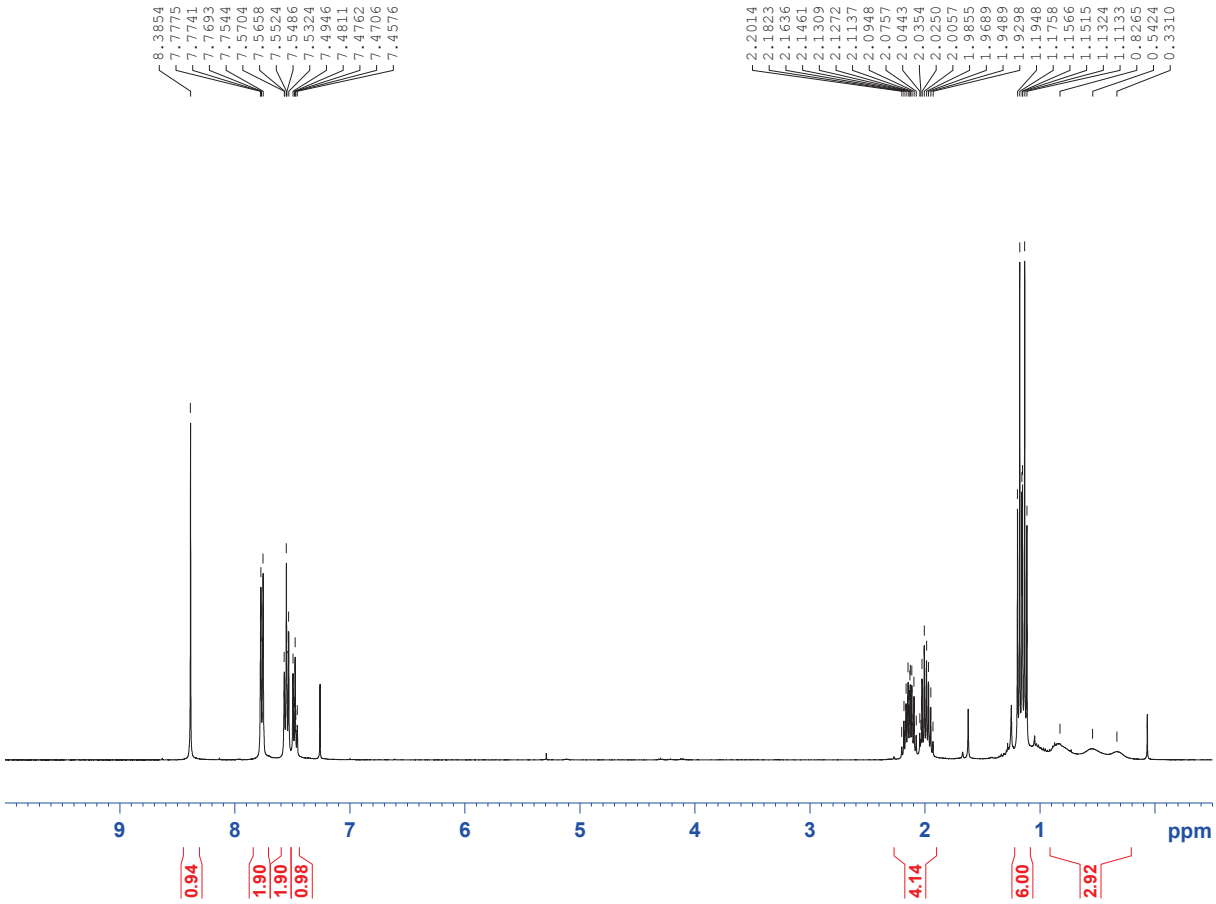


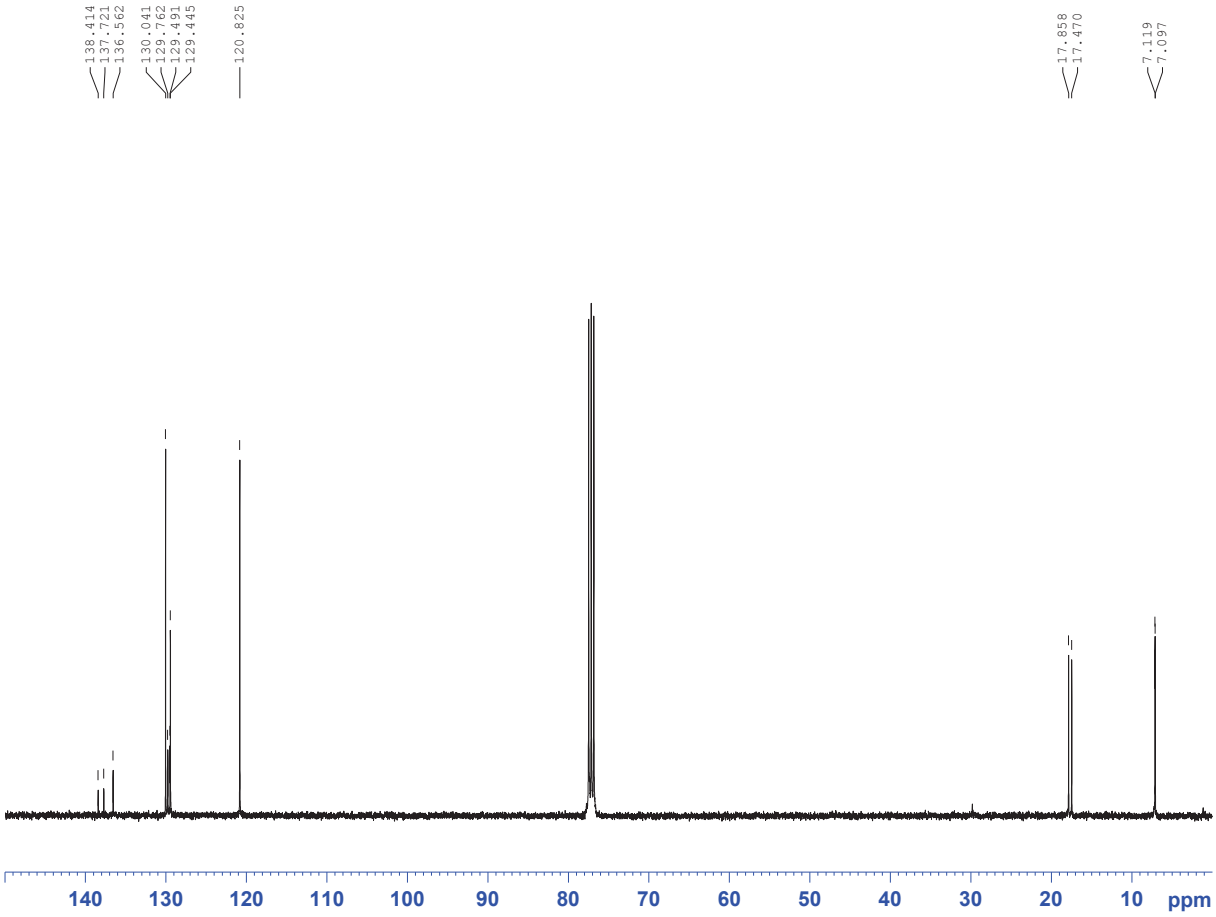

137.870
137.163
133.985
131.467
131.196
129.396
129.168
128.306
54.382
17.813
17.424
7.043
7.021
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

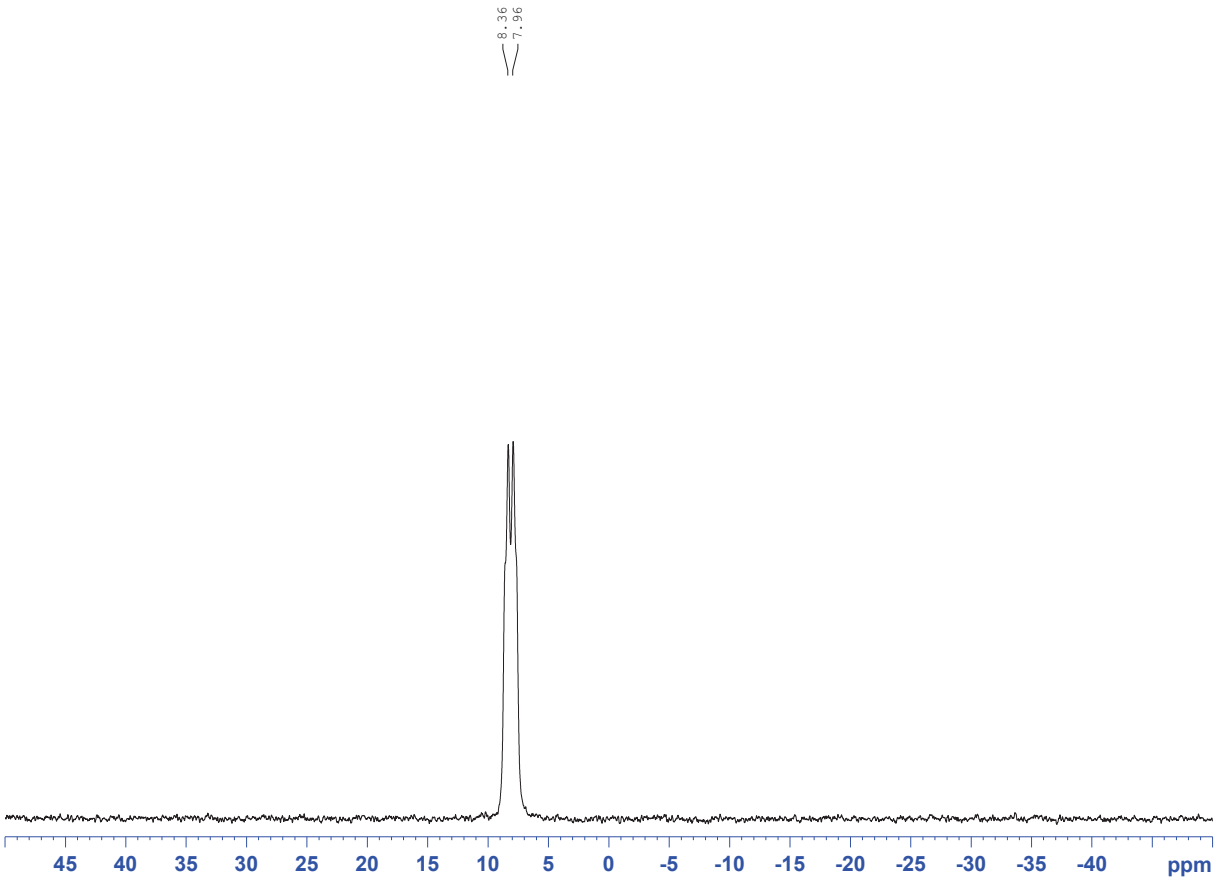

7.80
7.38
40
30
20
10
0
-10
-20
-30
-40
ppm

4-(Diethylphosphino-borane)-1-phenyl-1*H*-1,2,3-triazole (2b)

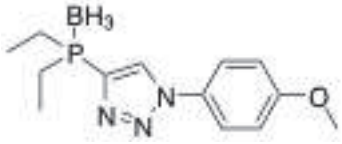


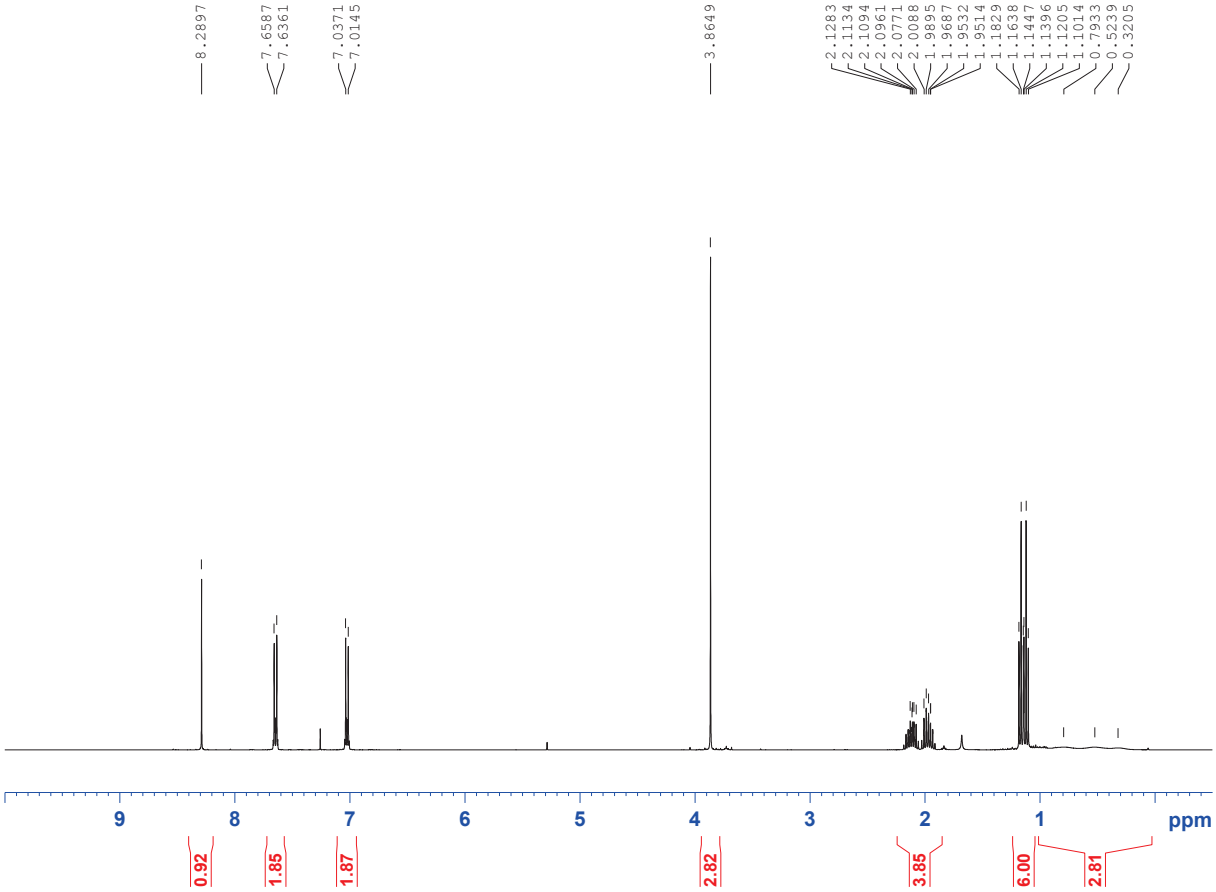


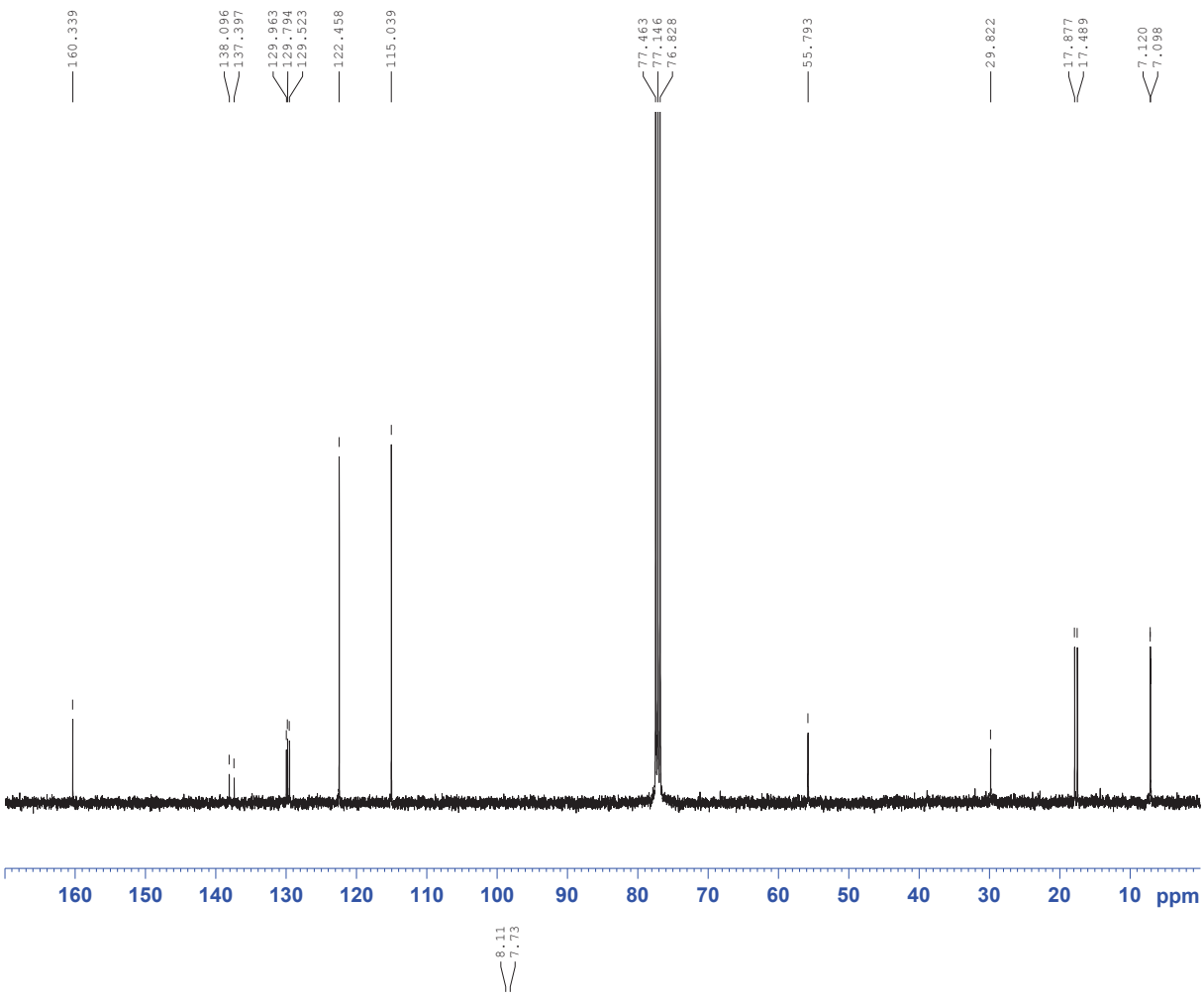

138.414
137.721
136.562
130.041
129.762
129.491
129.445
120.825
17.858
17.470
7.119
7.097
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

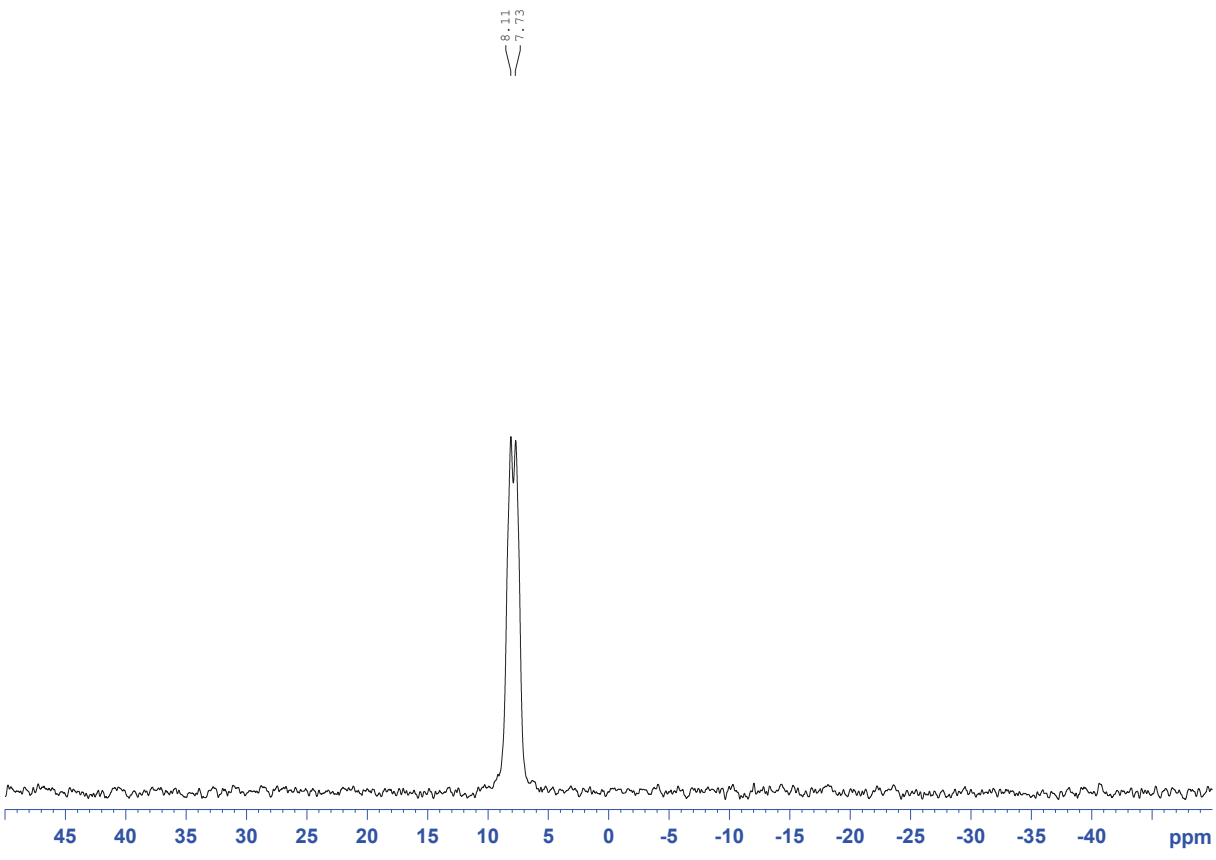

8.36
7.96
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

4-(Diethylphosphino-borane)-1-(4-anisyl)-1*H*-1,2,3-triazole (2c)

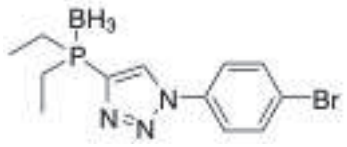


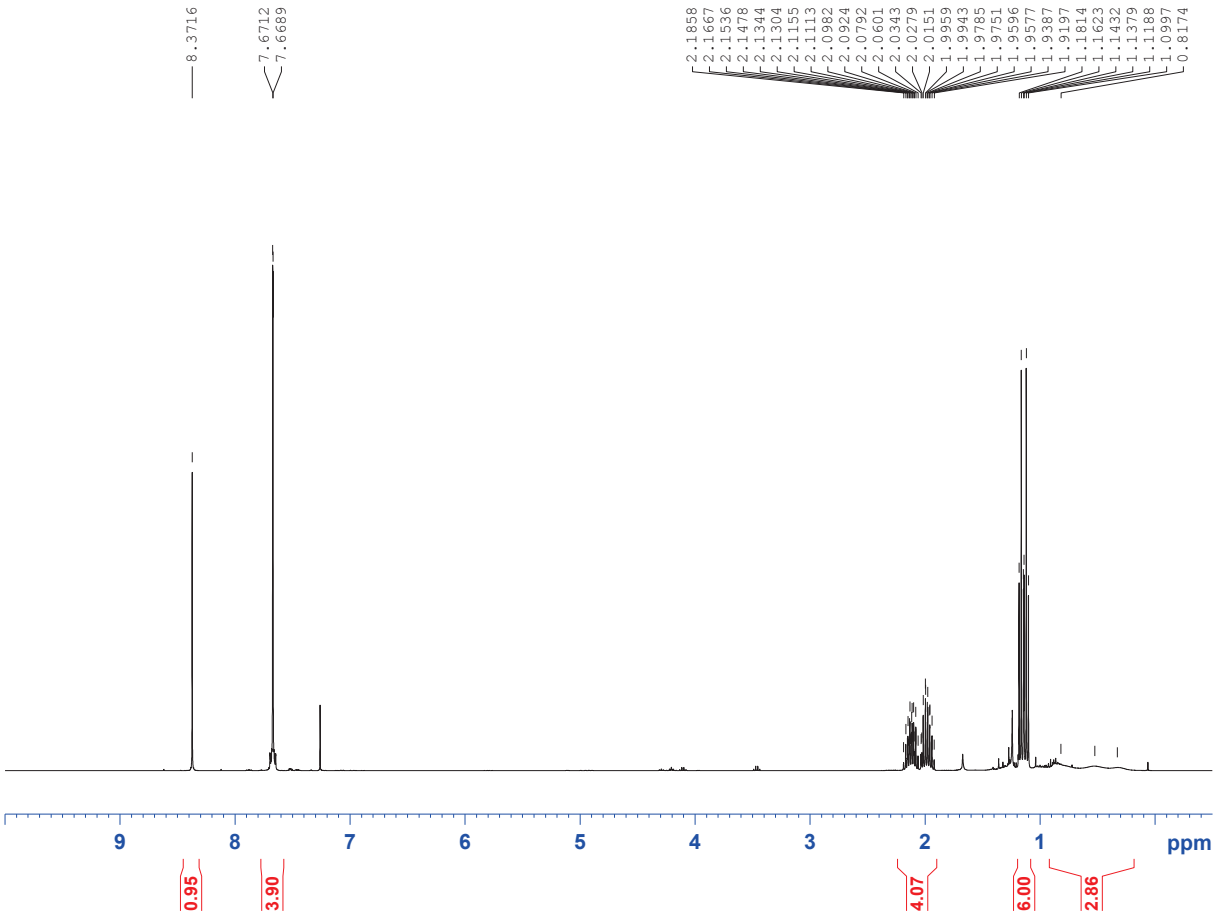


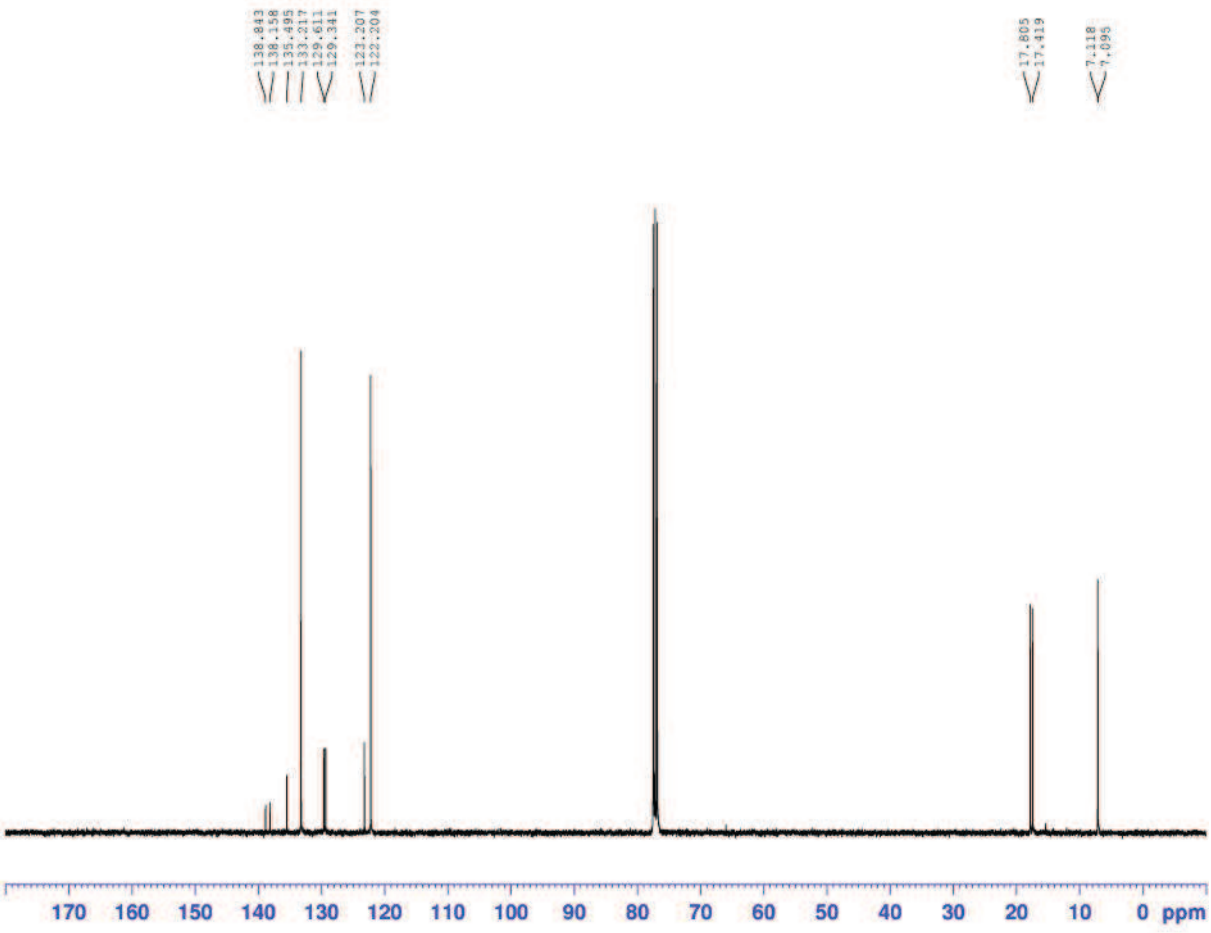

160.339
138.096
137.397
129.963
129.794
129.523
122.458
115.039
77.463
77.146
76.828
55.793
29.822
17.877
17.489
7.120
7.098
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

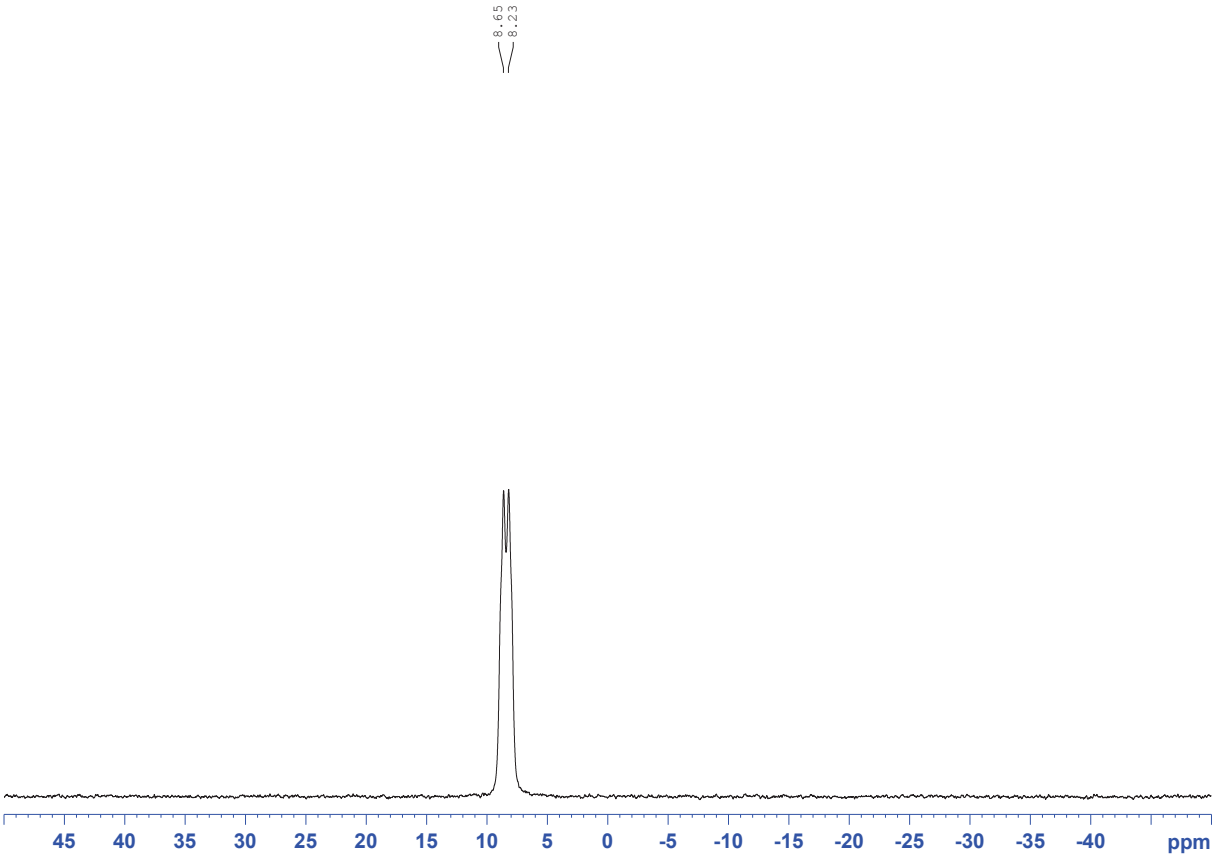

8.11
7.73
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 ppm

1-(4-Bromophenyl)-4-(diethylphosphino-borane)-1*H*-1,2,3-triazole (2d)

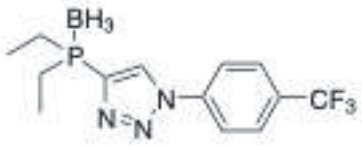


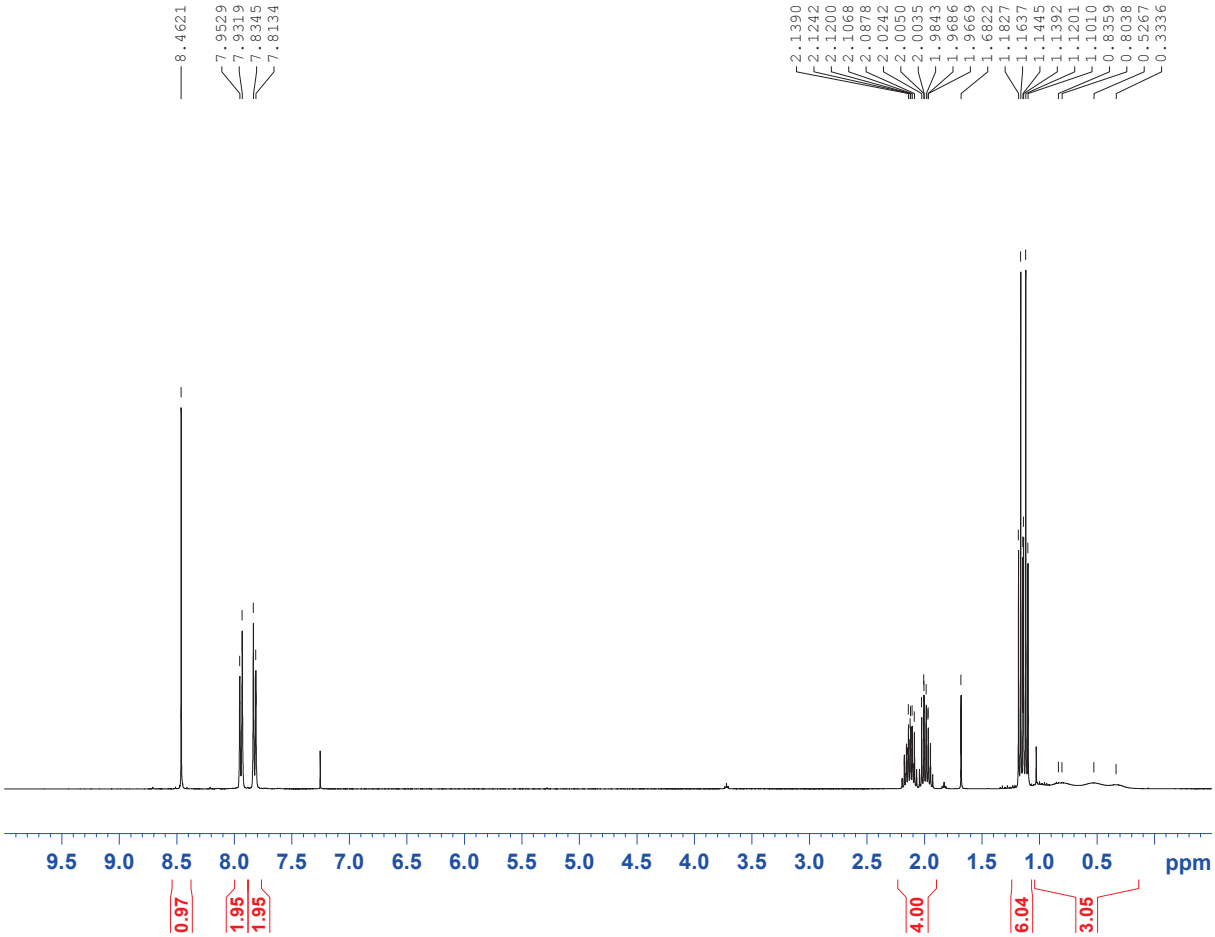


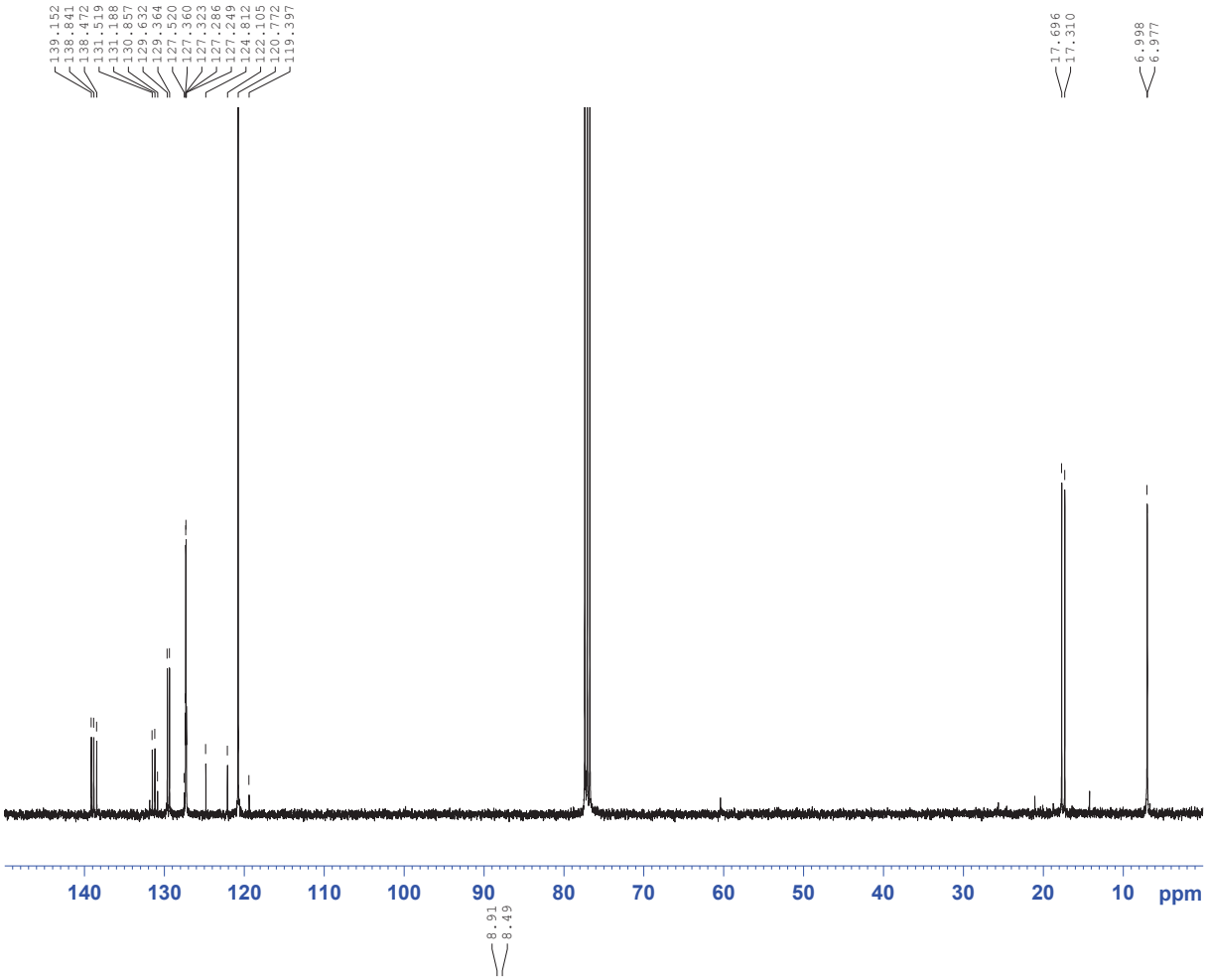

138.843
138.158
135.495
133.217
129.611
129.341
123.207
122.204
17.865
17.419
7.118
7.095
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

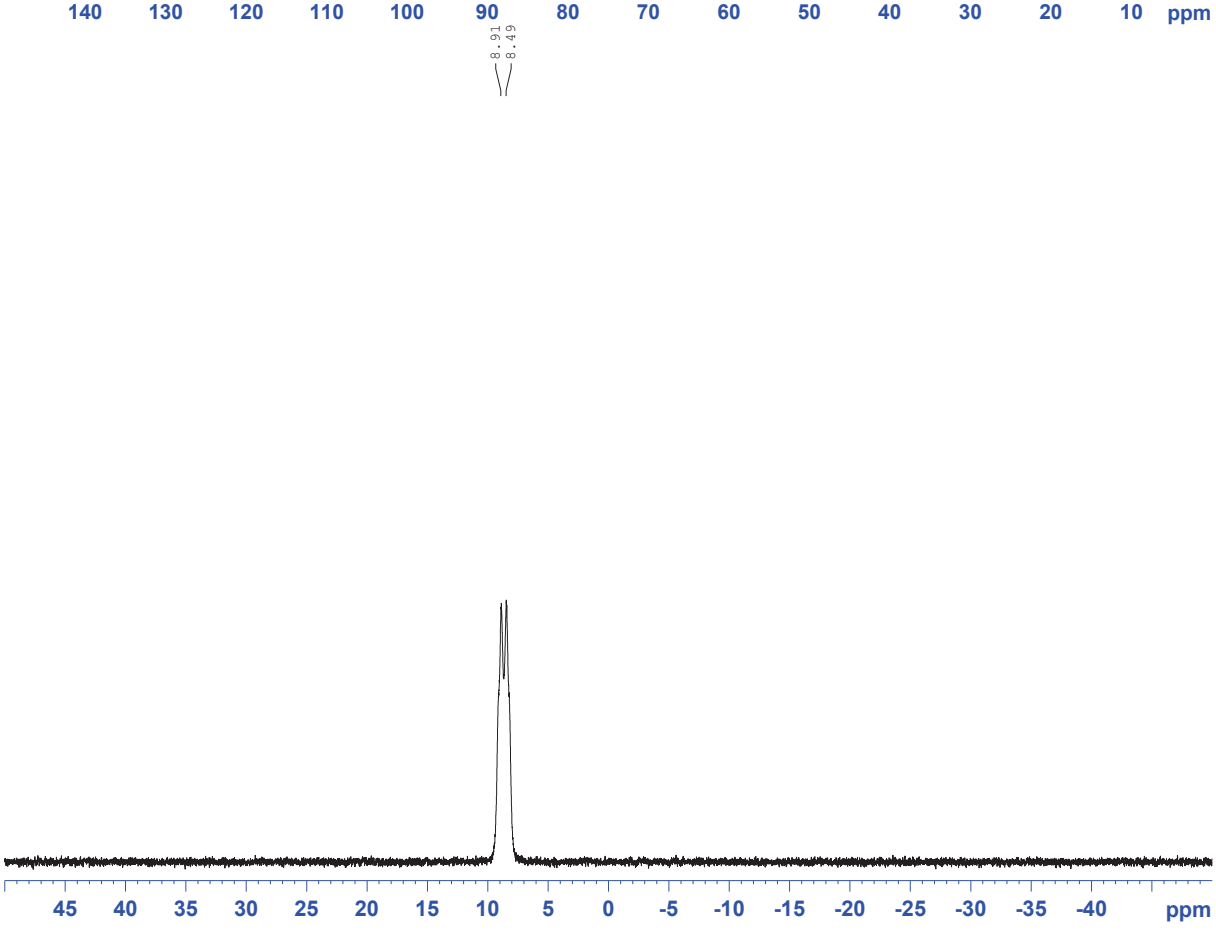

8.65
8.23
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 ppm

4-(Diethylphosphino-borane)-1-(4-trifluoromethylphenyl)-1*H*-1,2,3-triazole (2e)

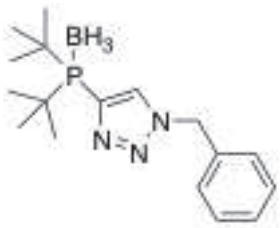


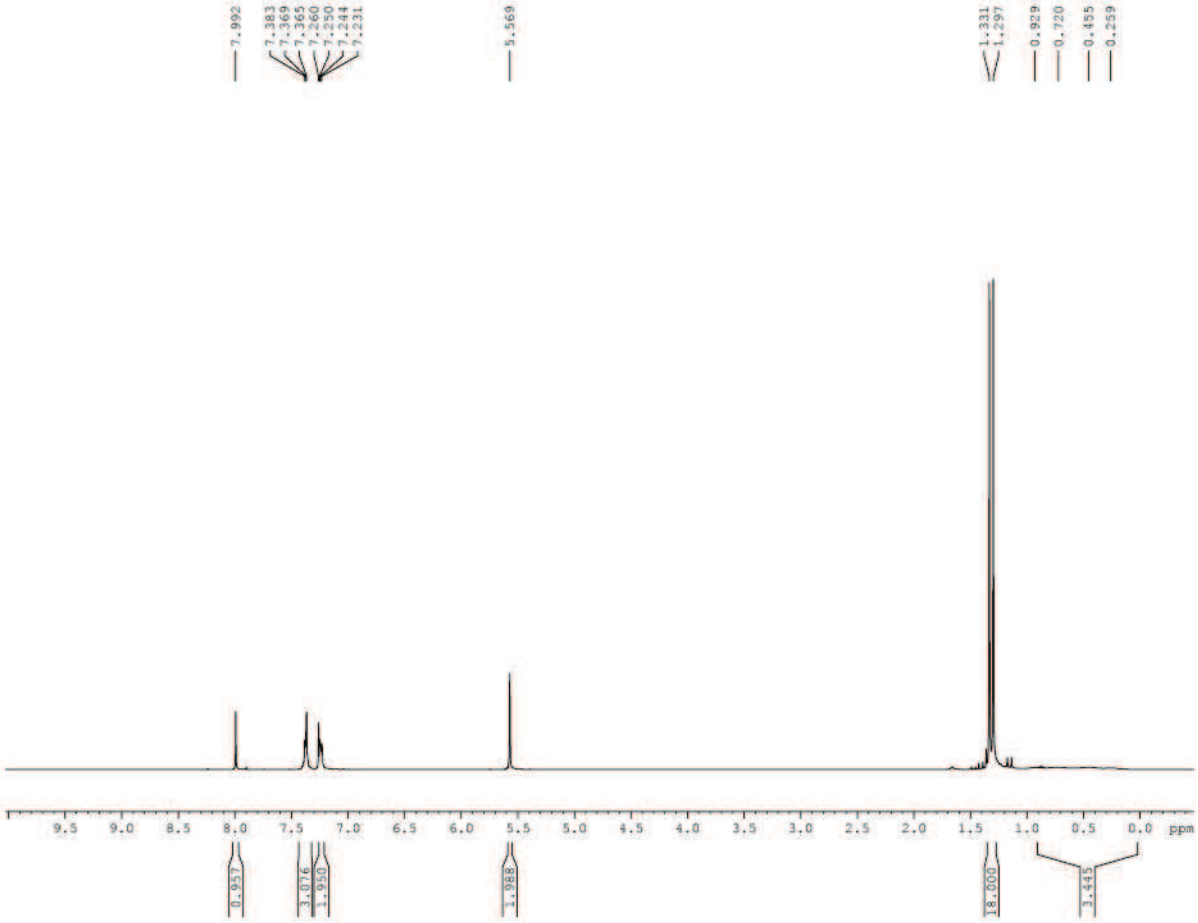


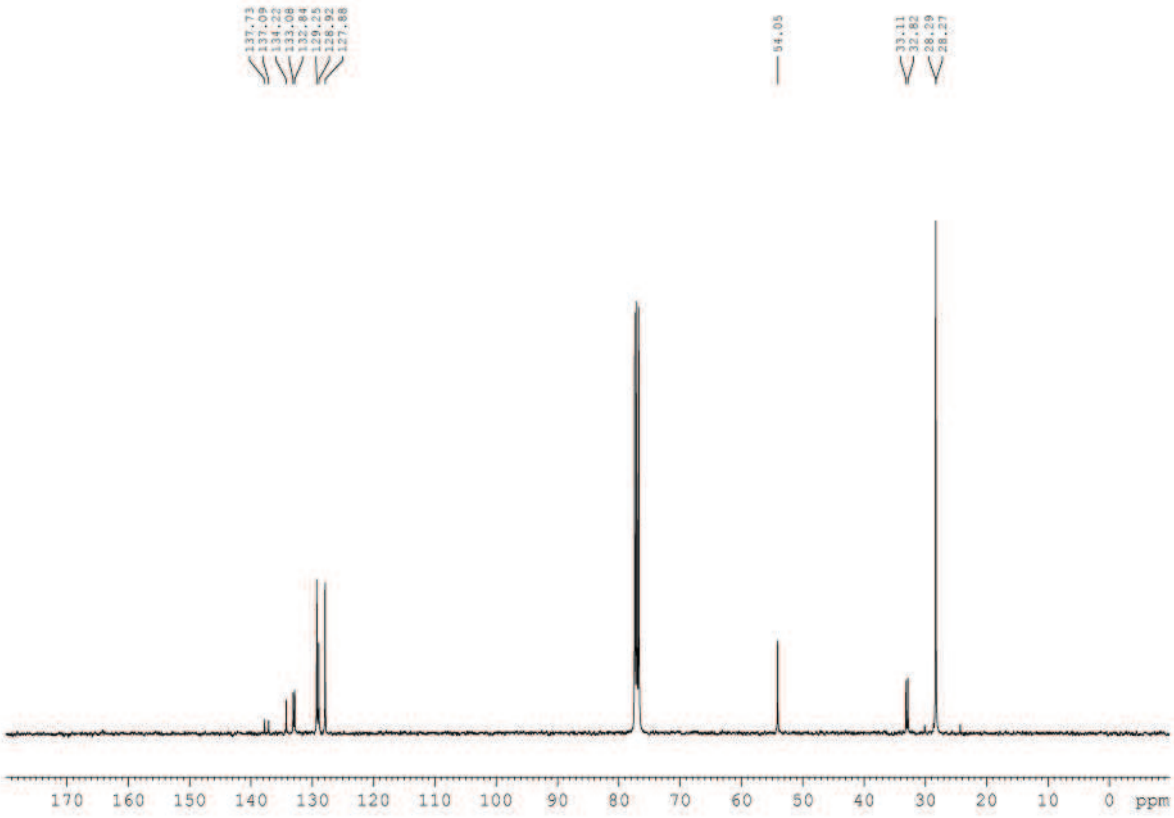

139.152
138.841
138.472
131.519
131.188
130.857
129.632
129.364
127.520
127.360
127.323
127.286
127.249
124.812
122.105
120.772
119.397
17.696
17.310
6.998
6.977
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

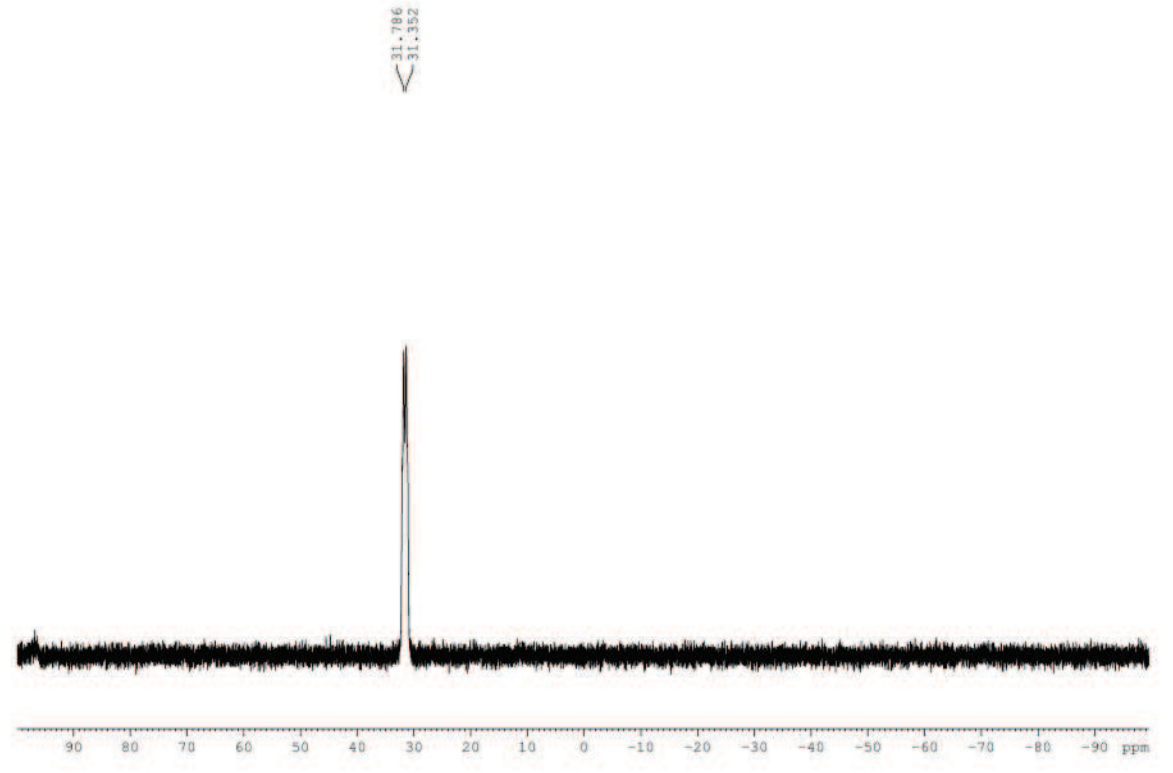

8.91
8.49
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

1-Benzyl-4-(di-*tert*-butylphosphino-borane)-1*H*-1,2,3-triazole (2f)

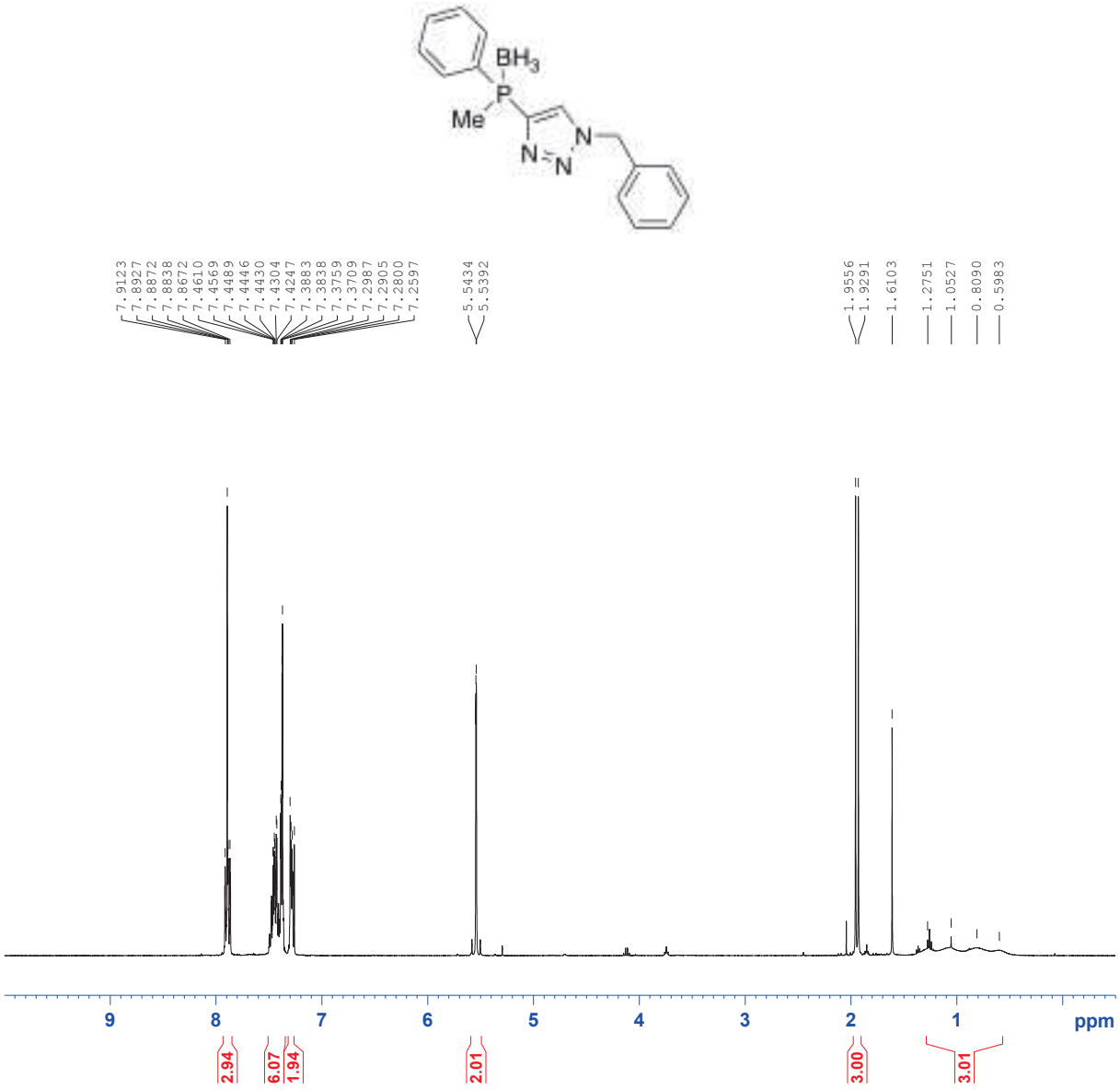


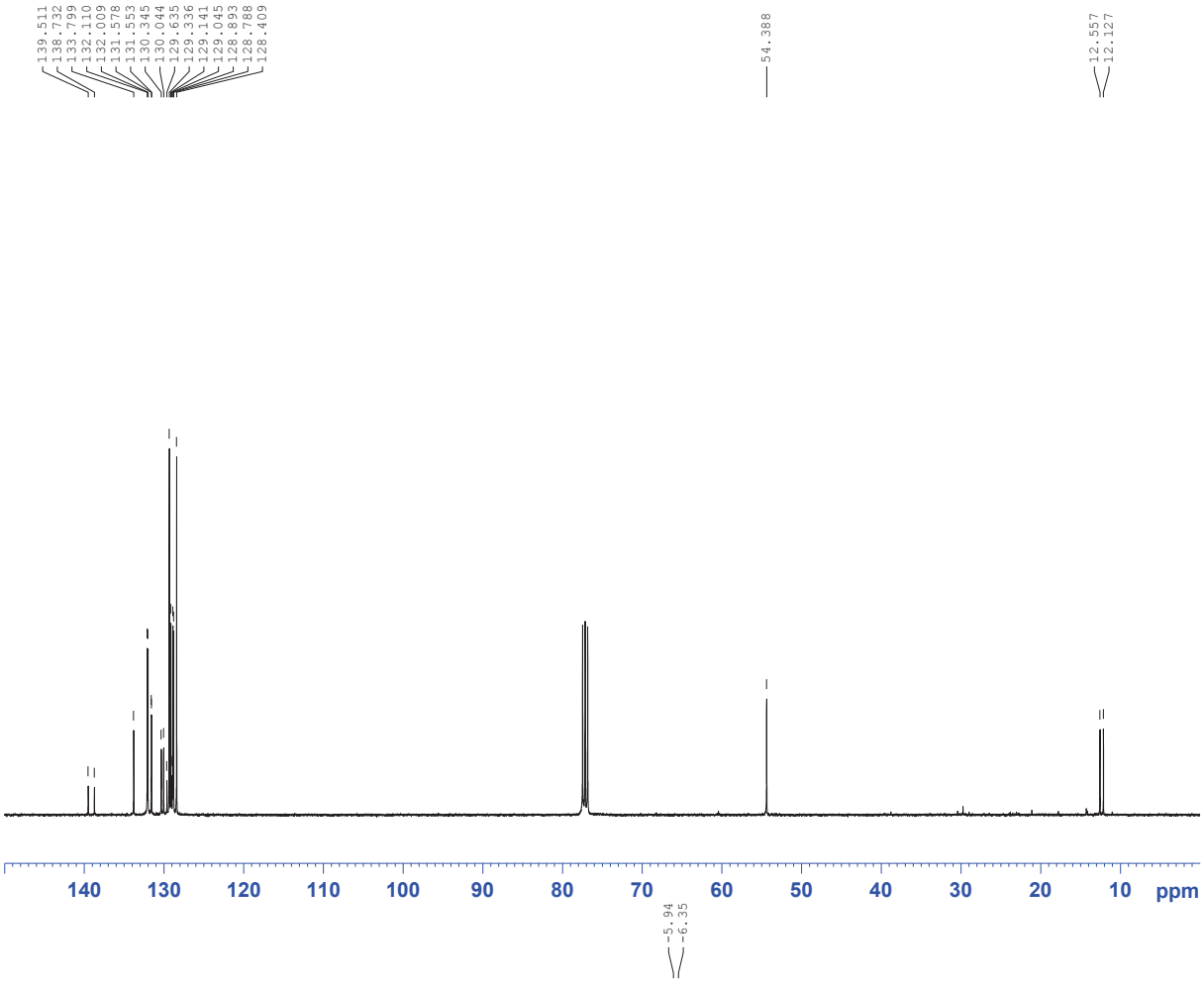


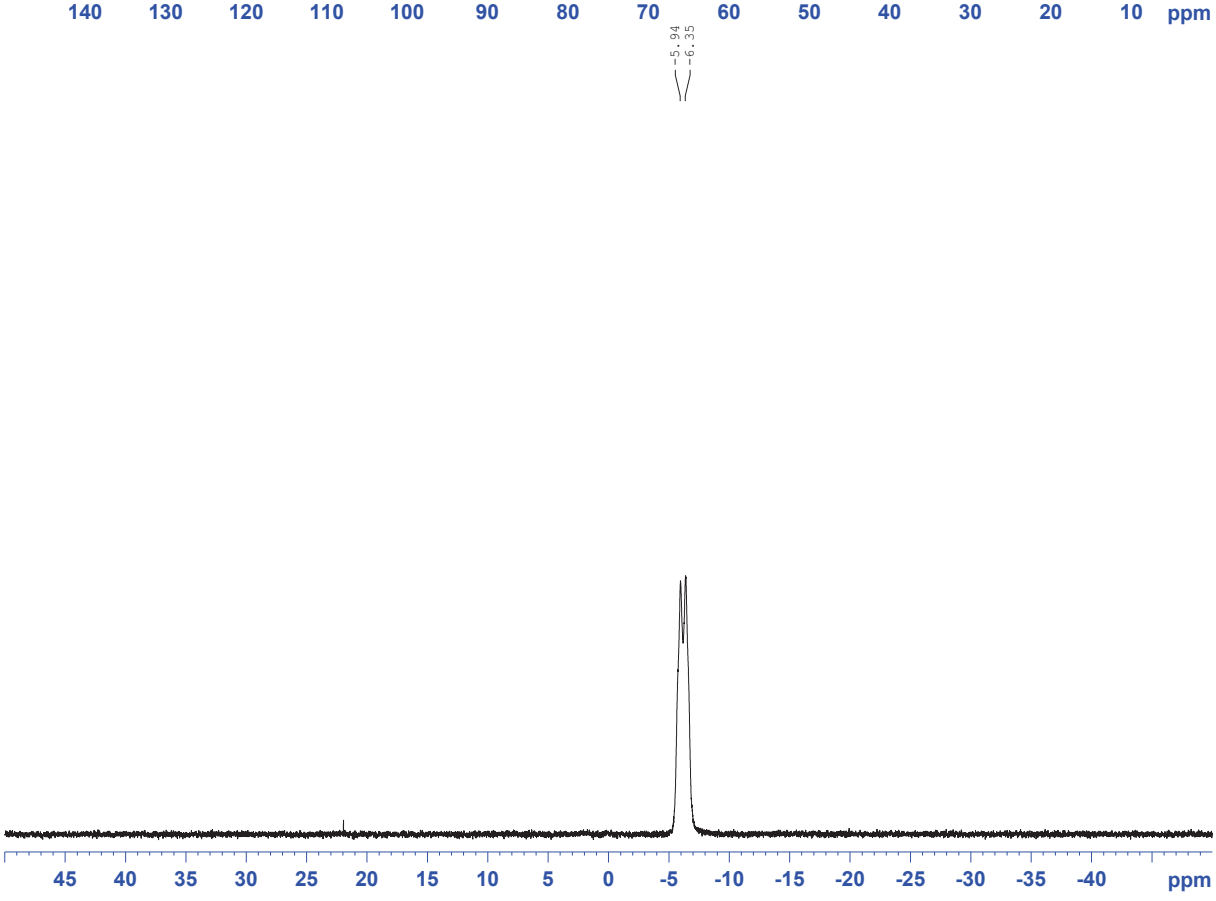

137.73
137.09
134.22
133.08
132.84
129.25
128.92
127.88
54.05
33.11
32.82
28.29
28.27
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


31.786
31.352
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

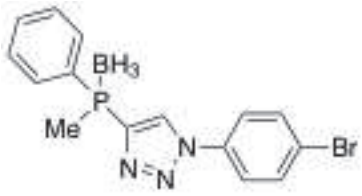
1-Benzyl-4-(methylphenylphosphino-borane)-1*H*-1,2,3-triazole (2g)

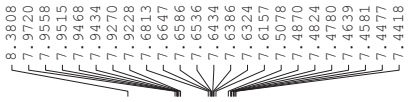


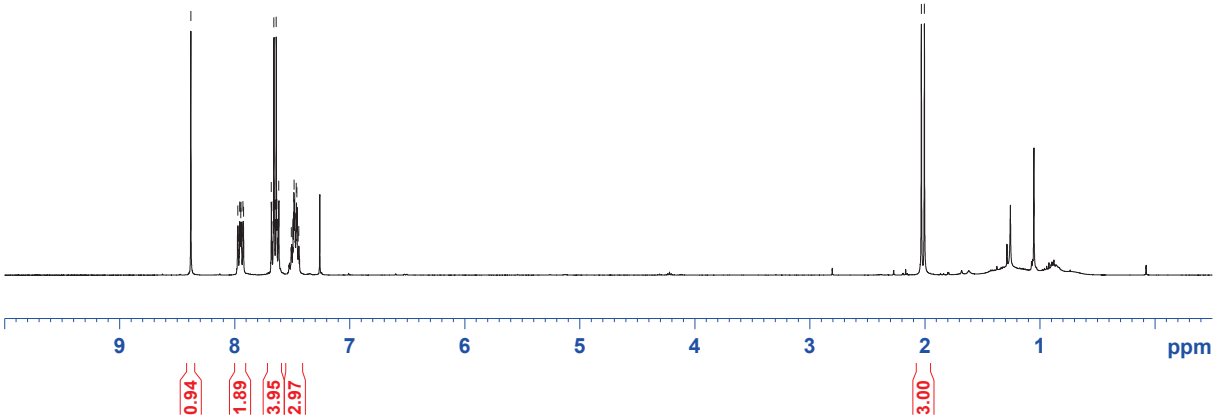

139.511
138.732
133.799
132.110
132.009
131.578
131.553
130.345
130.044
129.635
129.336
129.141
129.045
128.893
128.788
128.409
54.388
12.557
12.127
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

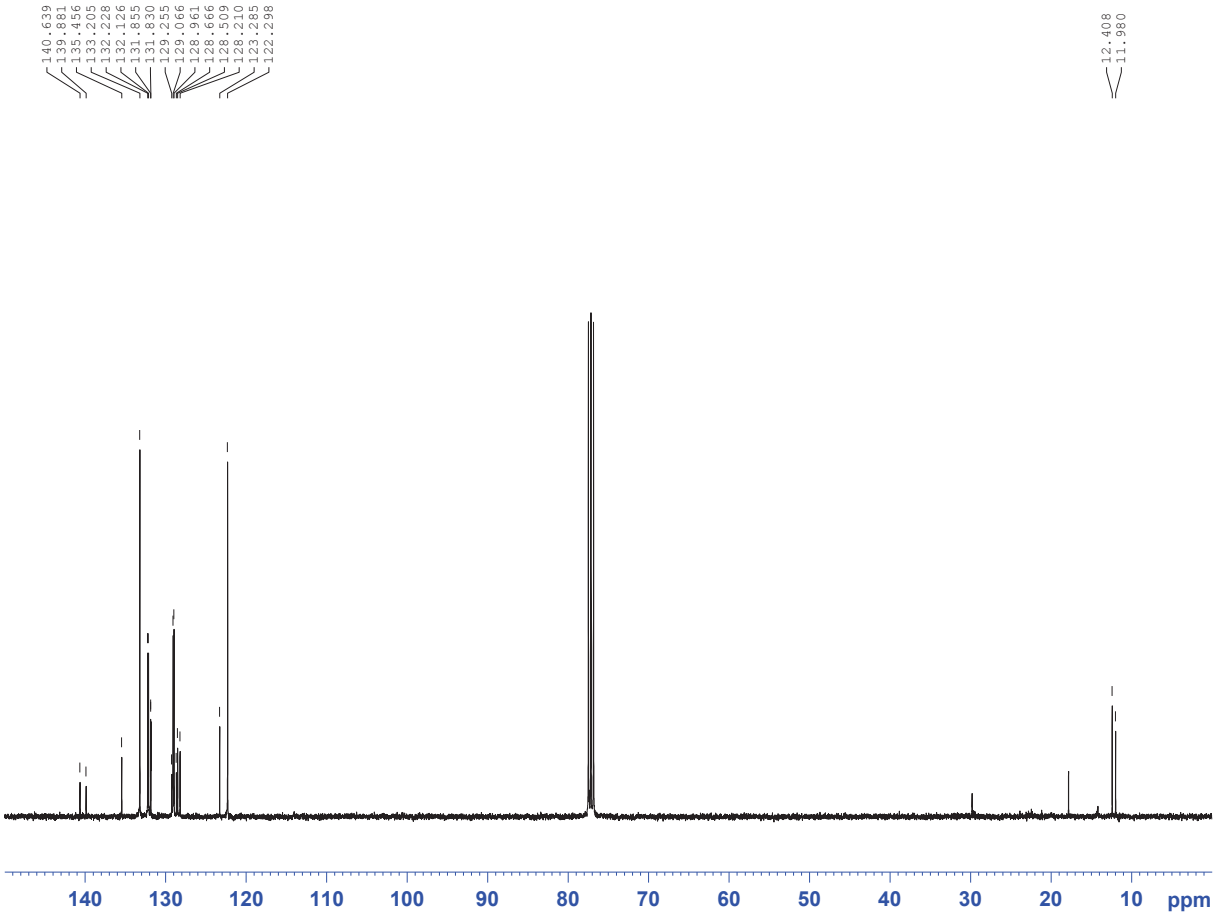

-5.94
-6.35
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

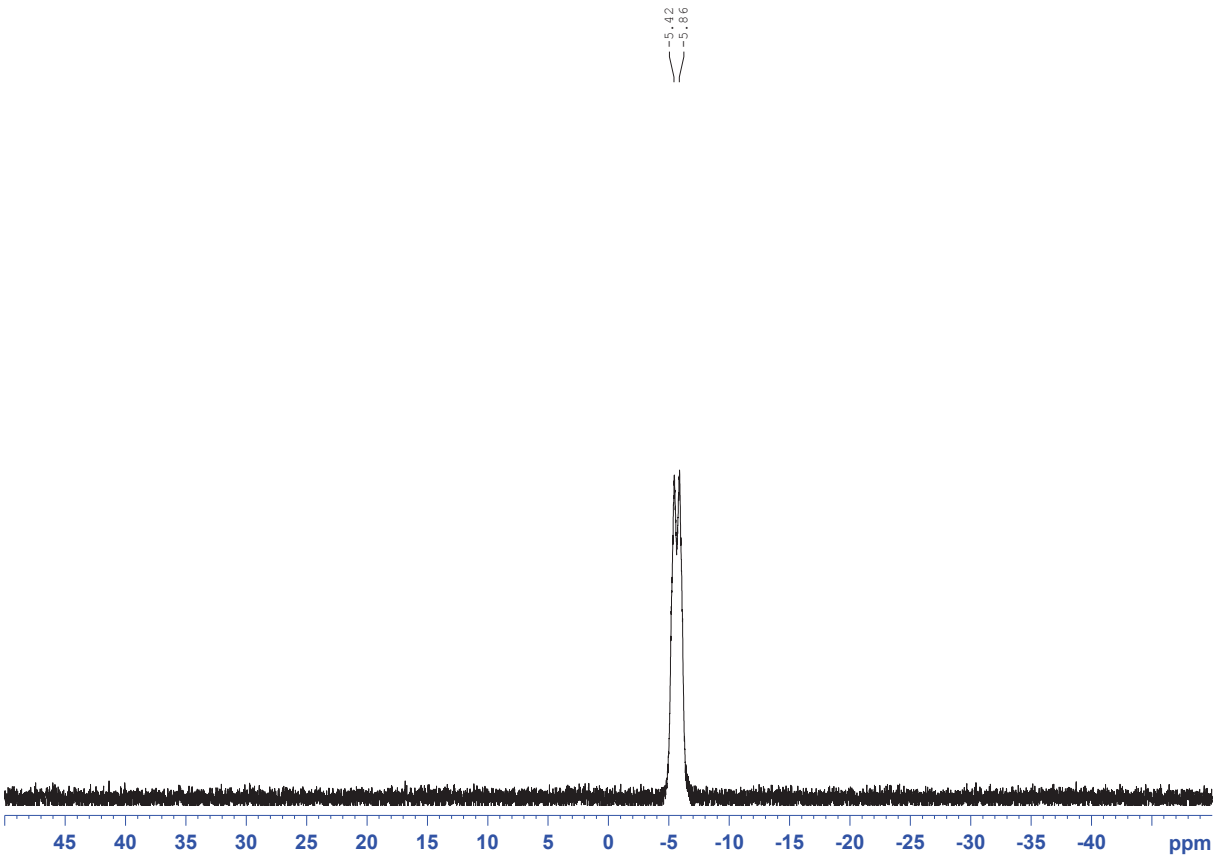
1-(4-Bromophenyl)-4-(methylphenylphosphino-borane)-1*H*-1,2,3-triazole (2h)



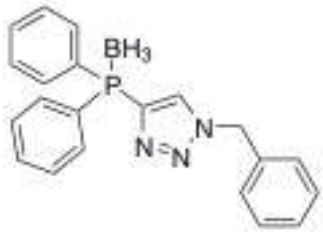


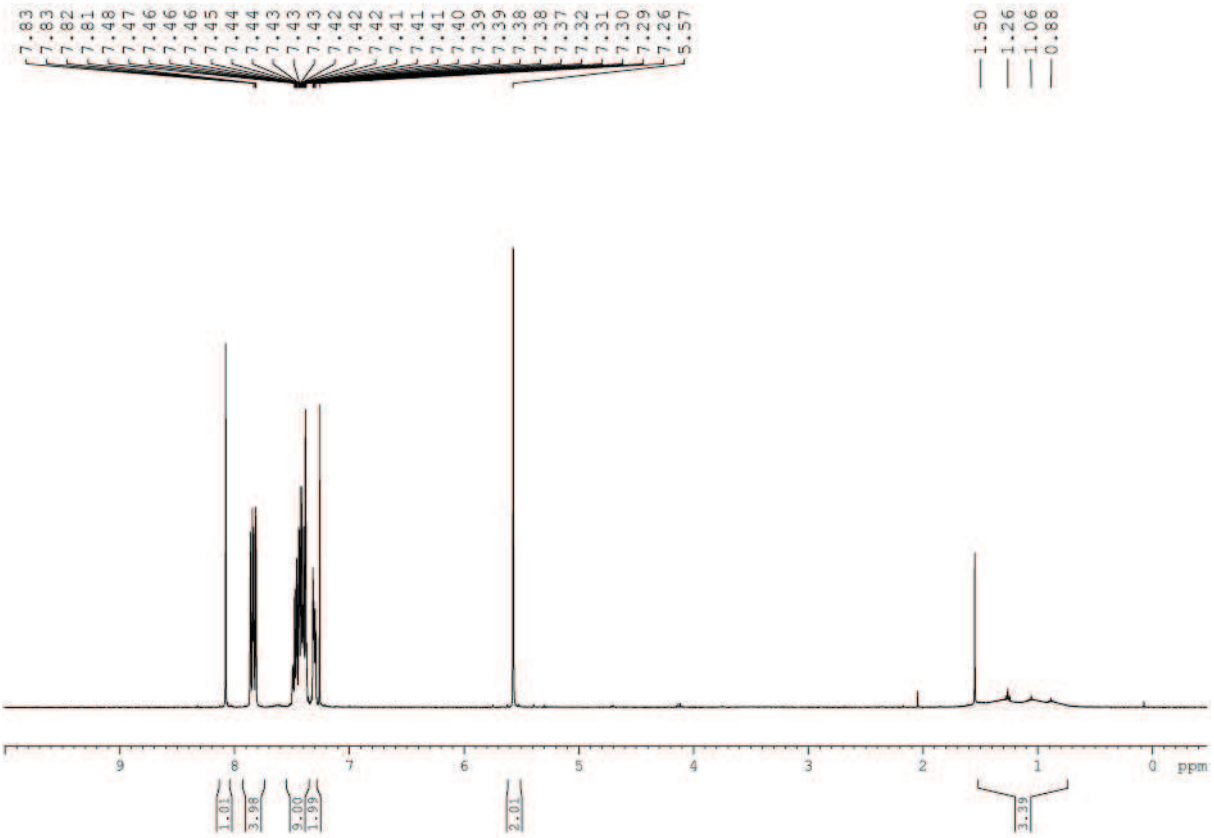


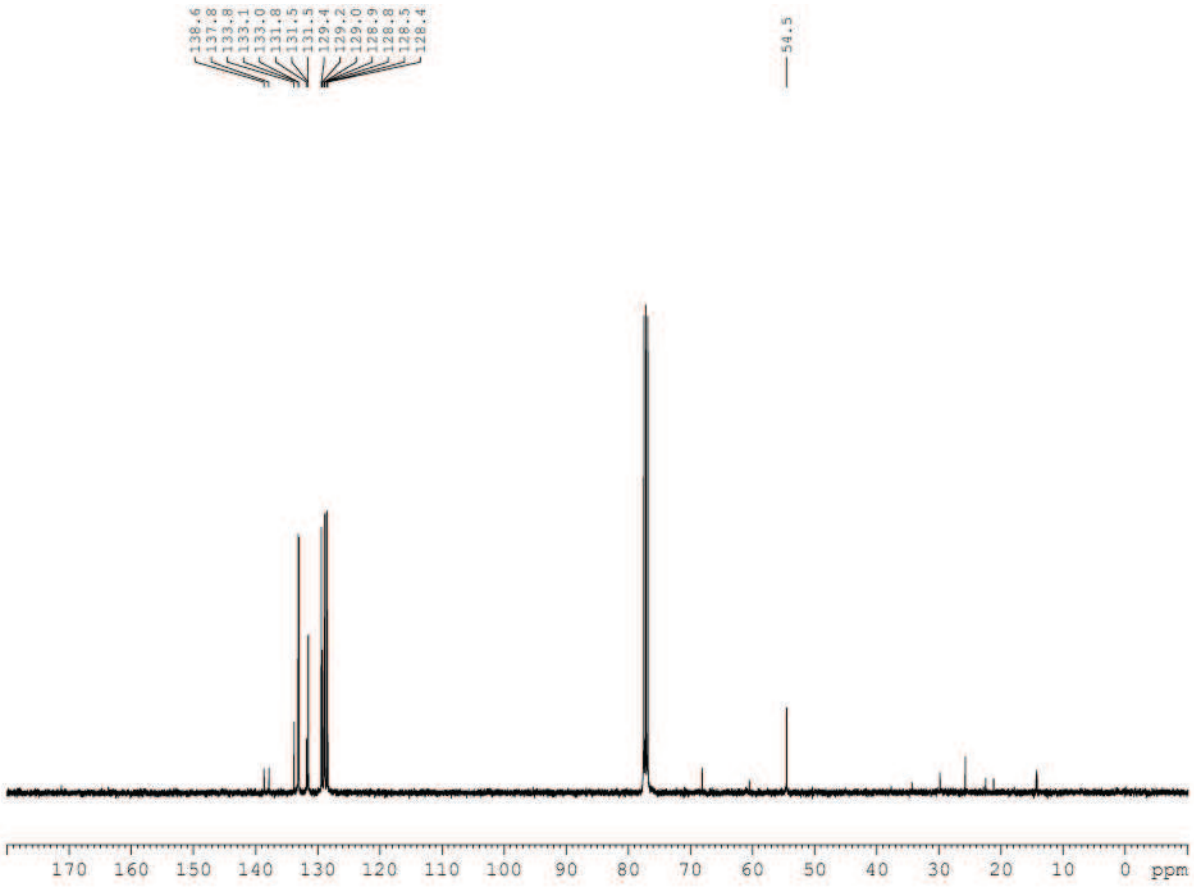

140.639
139.881
135.456
133.205
132.228
132.126
131.855
131.830
129.255
129.066
128.961
128.666
128.509
128.210
123.285
122.298
12.408
11.980
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

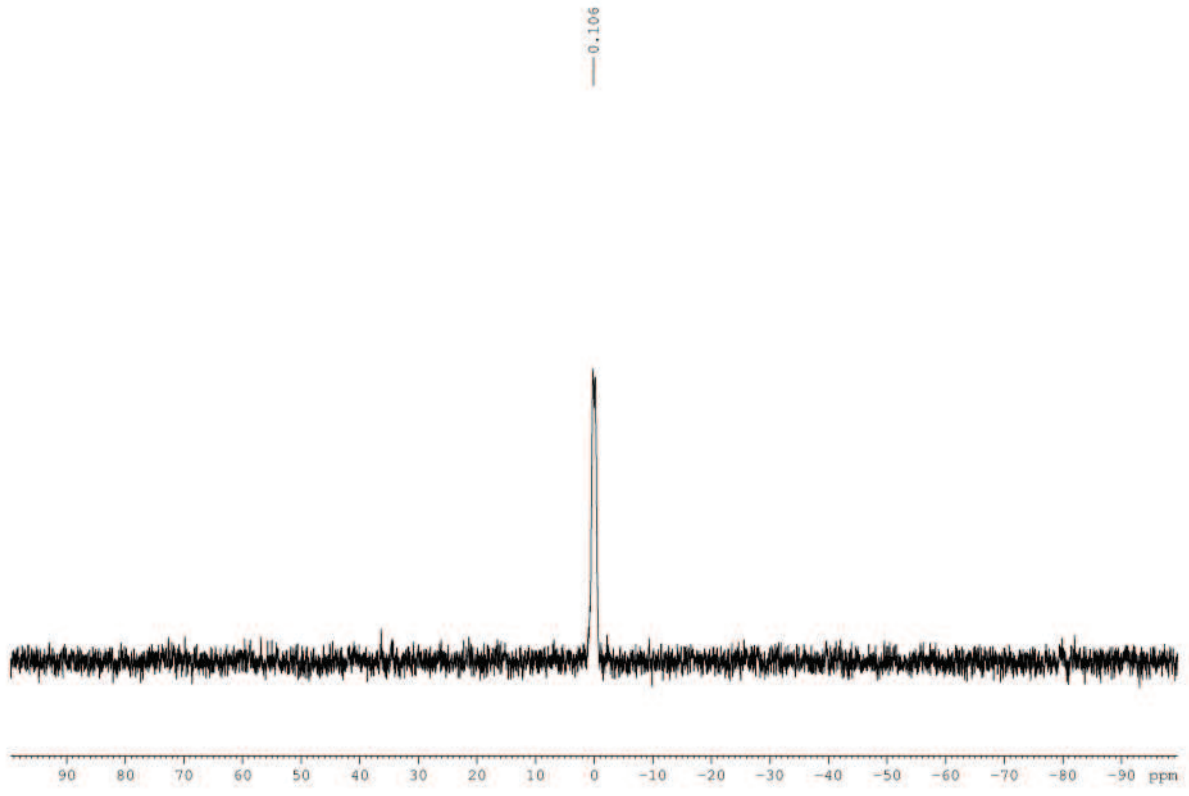

-5.42
-5.86
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

1-Benzyl-4-(diphenylphosphino-borane)-1*H*-1,2,3-triazole (2i)

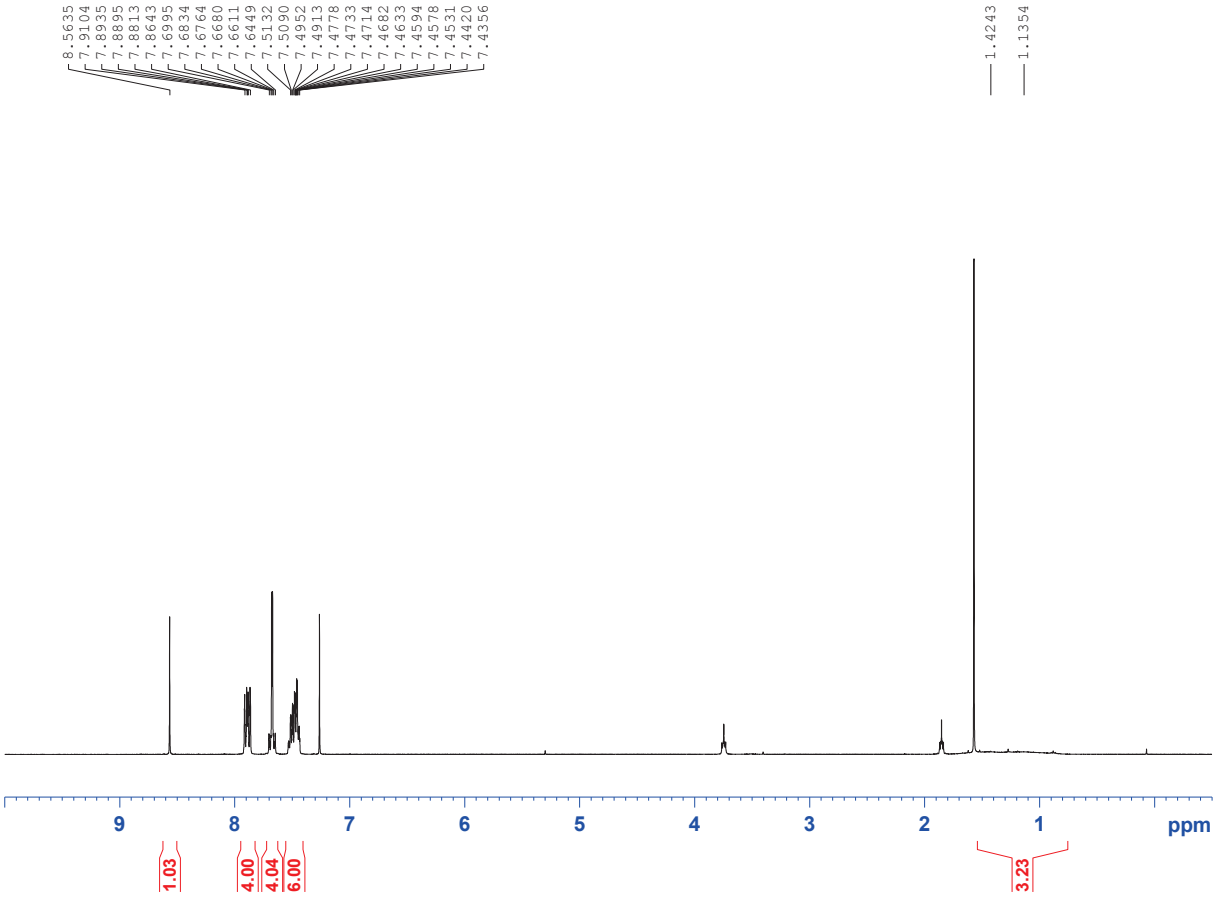


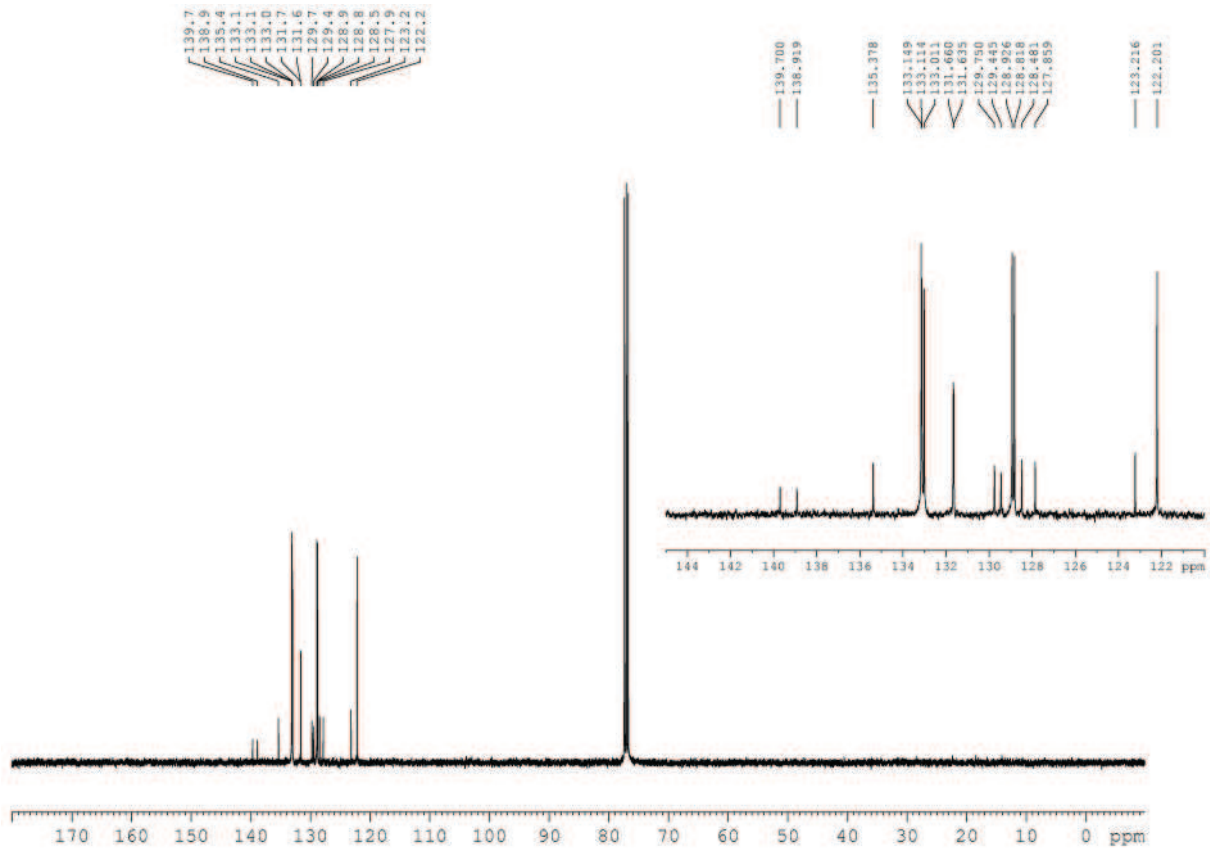


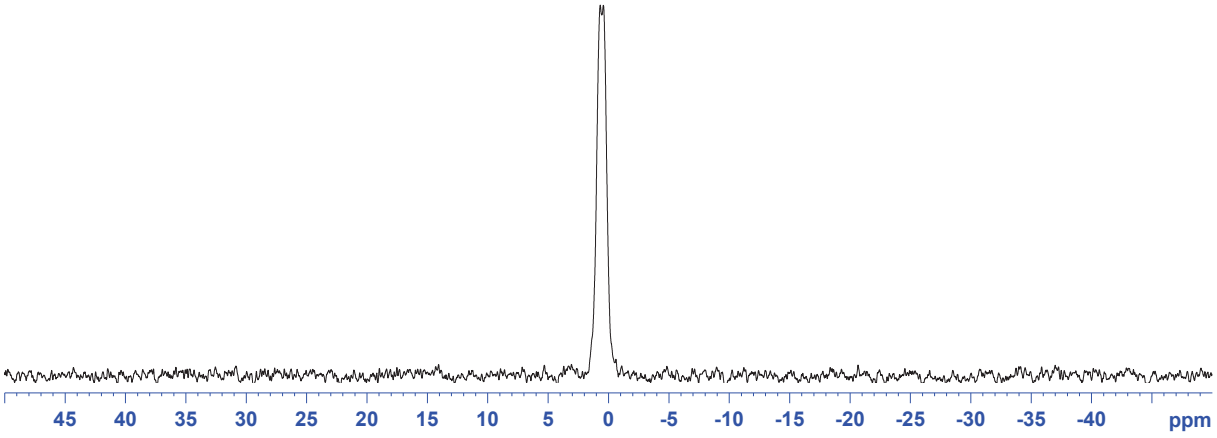

138.6
137.8
133.8
133.1
133.0
131.8
131.5
131.5
129.4
129.2
129.0
128.9
128.8
128.5
128.4
54.5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


0.106
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

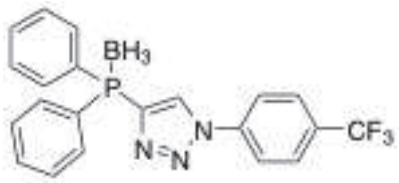
1-(4-Bromophenyl)-4-(diphenylphosphino-borane)-1H-1,2,3-triazole (2j)

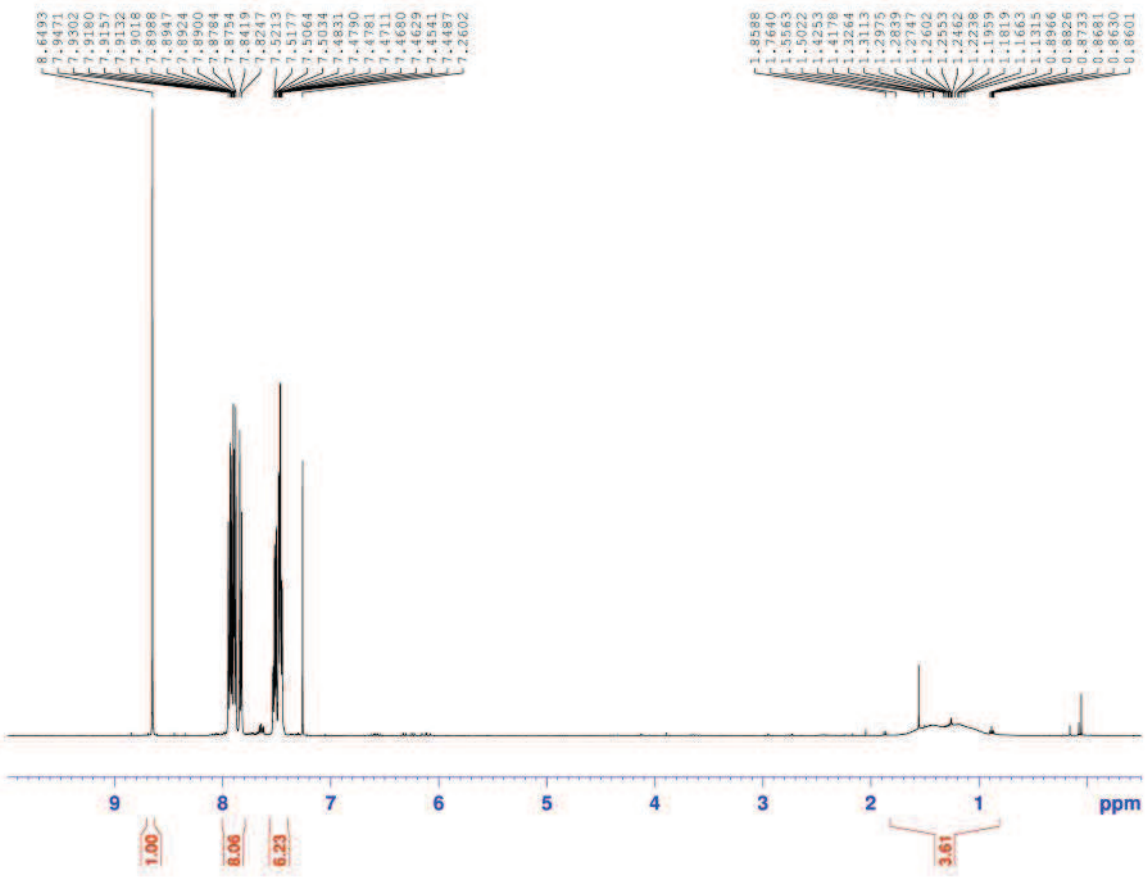


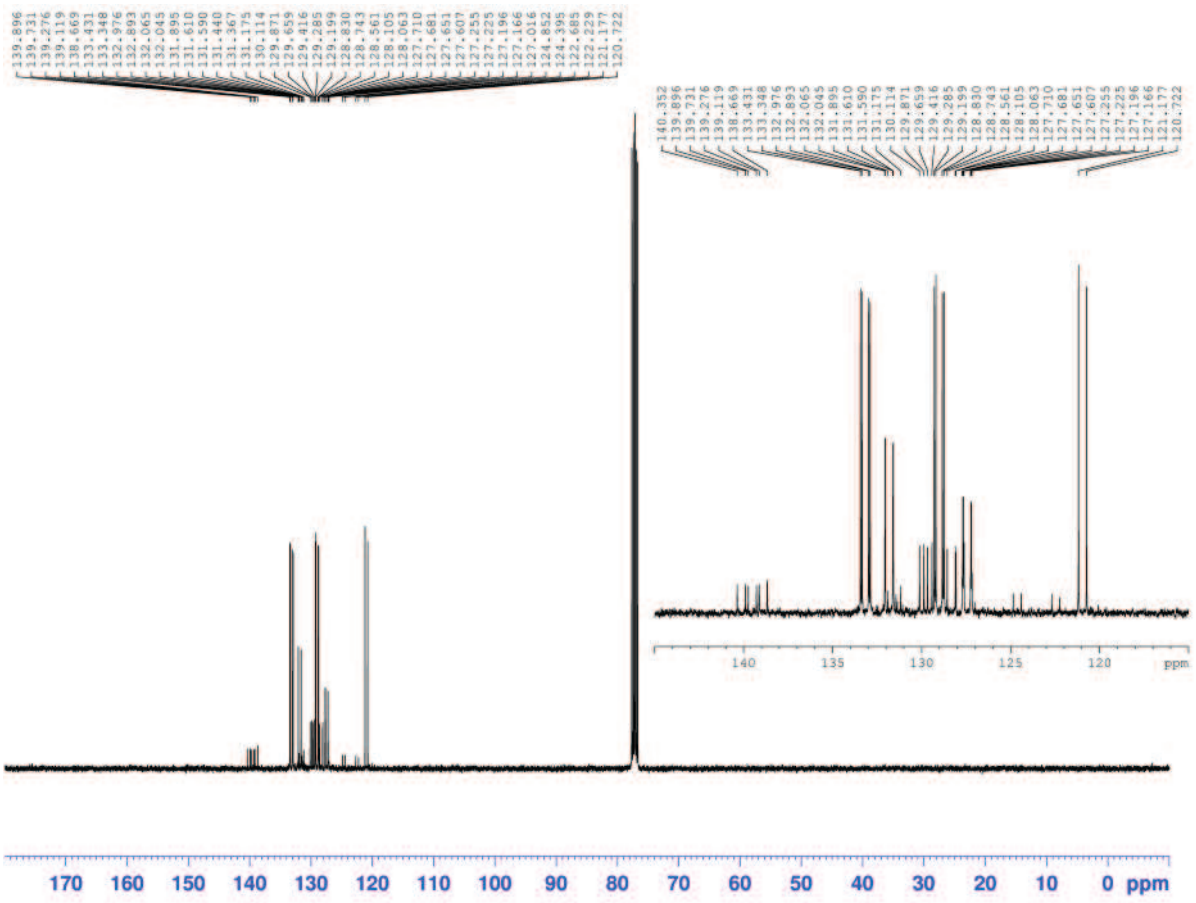

139.7
138.9
135.4
133.1
133.1
133.0
131.7
131.6
129.7
129.4
128.9
128.8
128.5
127.9
123.2
122.2
139.700
138.919
135.378
133.149
133.114
133.011
131.660
131.635
129.750
129.745
129.475
128.856
128.810
128.481
127.859
123.216
122.201
144 142 140 138 136 134 132 130 128 126 124 122 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

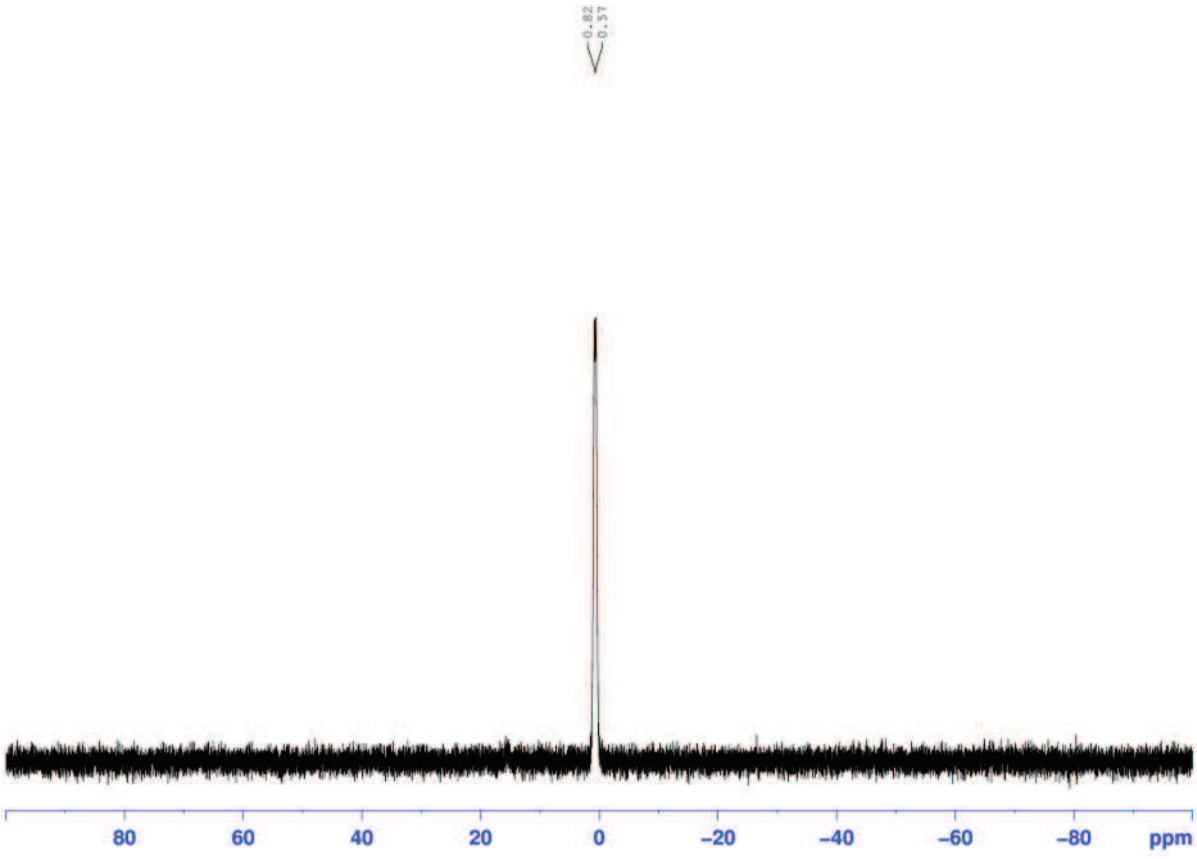

0.73
0.42
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 ppm

1-(4-Trifluoromethylphenyl)-4-(diphenylphosphino-borane)-1*H*-1,2,3-triazole (2k)

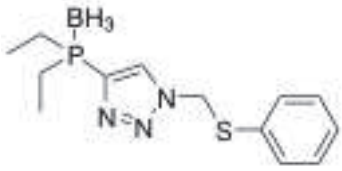


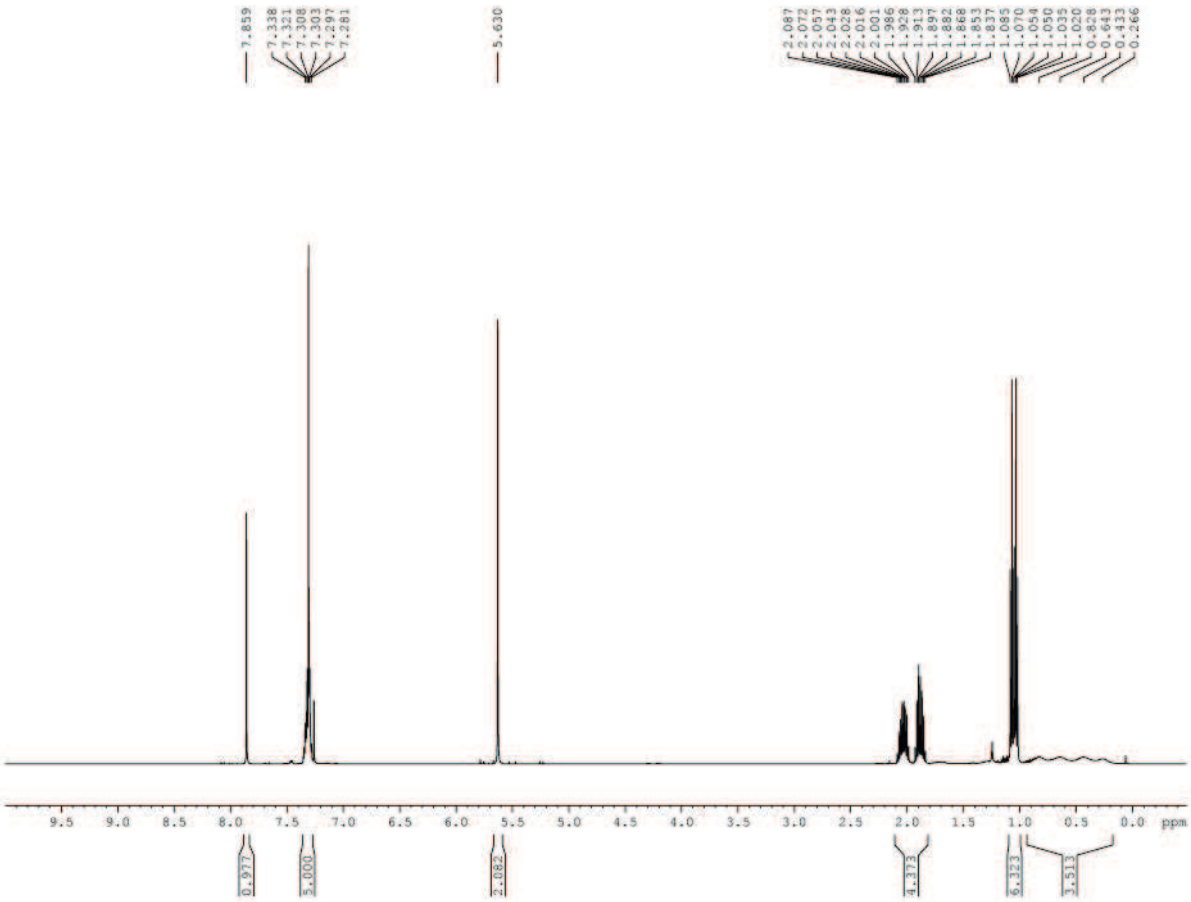


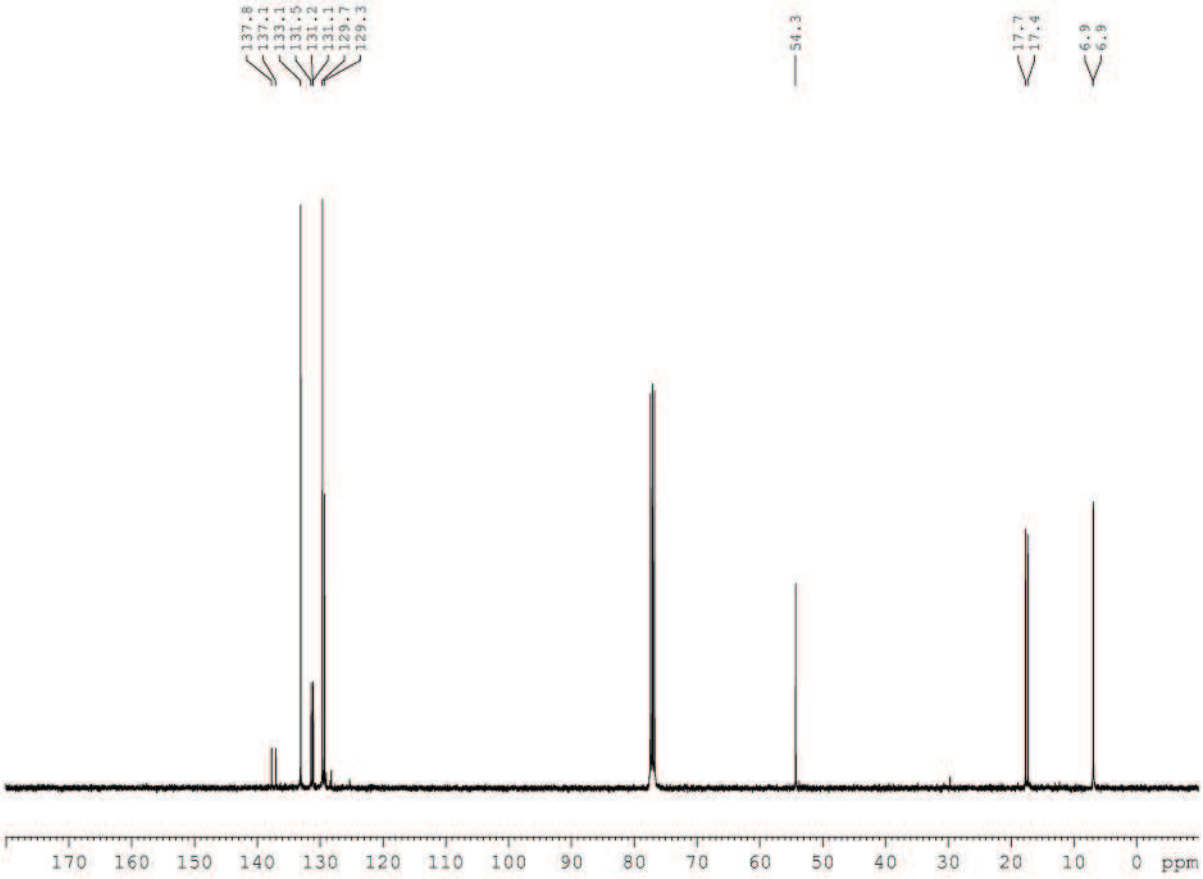

139.896
139.731
139.276
139.119
138.669
133.431
133.348
132.976
132.893
132.065
132.045
131.895
131.610
131.590
131.440
131.367
131.175
130.114
129.871
129.659
129.416
129.285
129.199
128.830
128.743
128.561
128.105
128.063
127.710
127.681
127.651
127.607
127.255
127.225
127.196
127.166
127.016
124.852
124.395
122.689
122.259
121.177
120.722
140.352
139.896
139.731
139.276
139.119
138.669
133.431
133.348
132.976
132.893
132.065
132.045
131.895
131.610
131.590
131.175
130.114
129.871
129.659
129.416
129.285
129.199
128.830
128.743
128.561
128.105
128.063
127.710
127.681
127.651
127.607
127.255
127.225
127.196
127.166
121.177
120.722
140
135
130
125
120
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

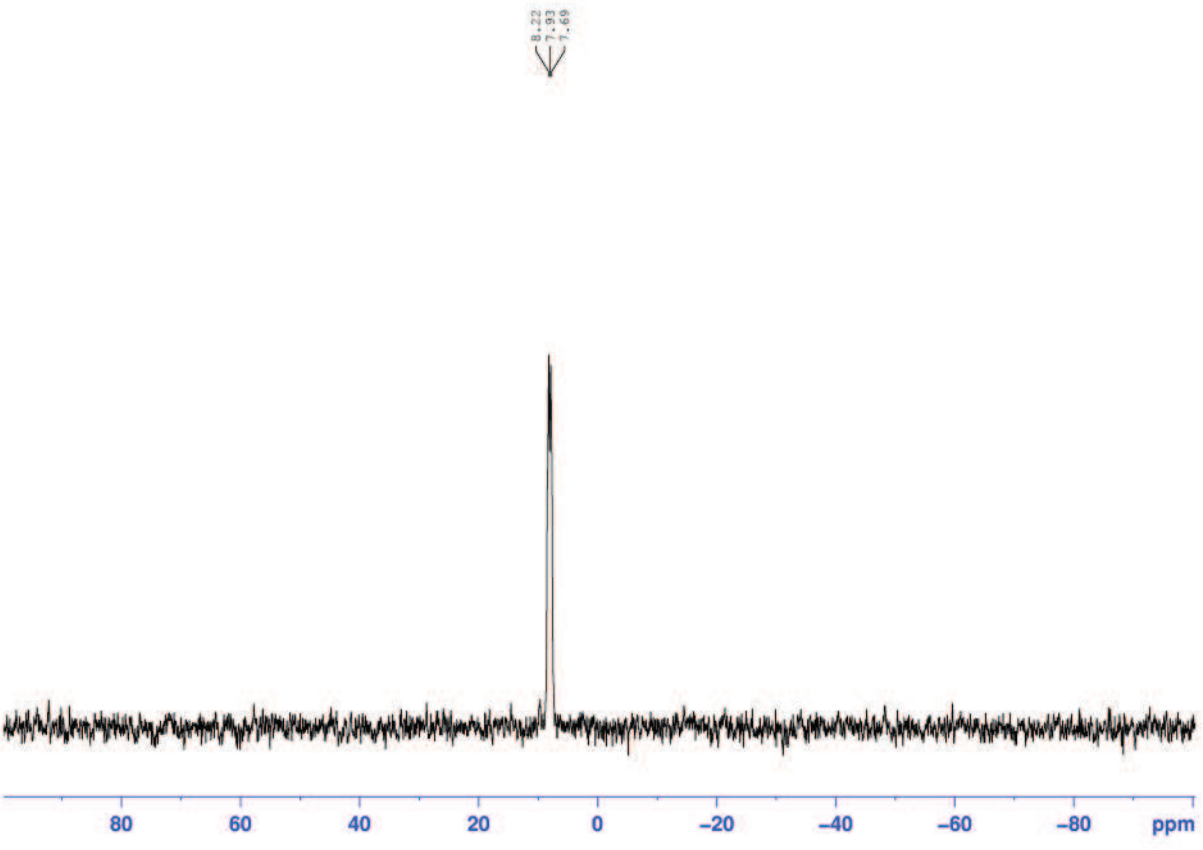

0.82
0.37
80
60
40
20
0
-20
-40
-60
-80
ppm

4-(Diethylphosphino-borane)-1-(phenylthiomethyl)-1*H*-1,2,3-triazole (2l)

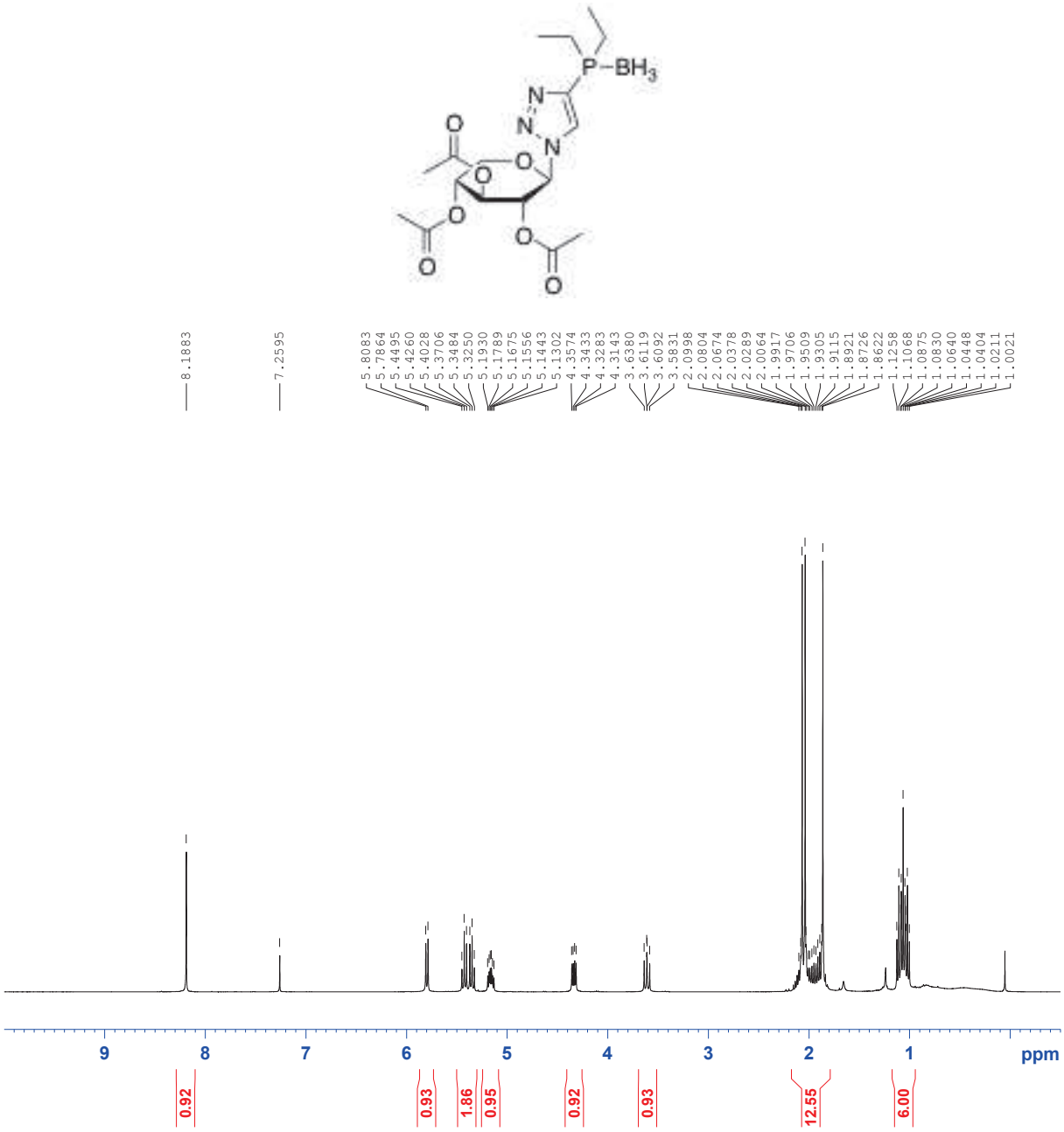


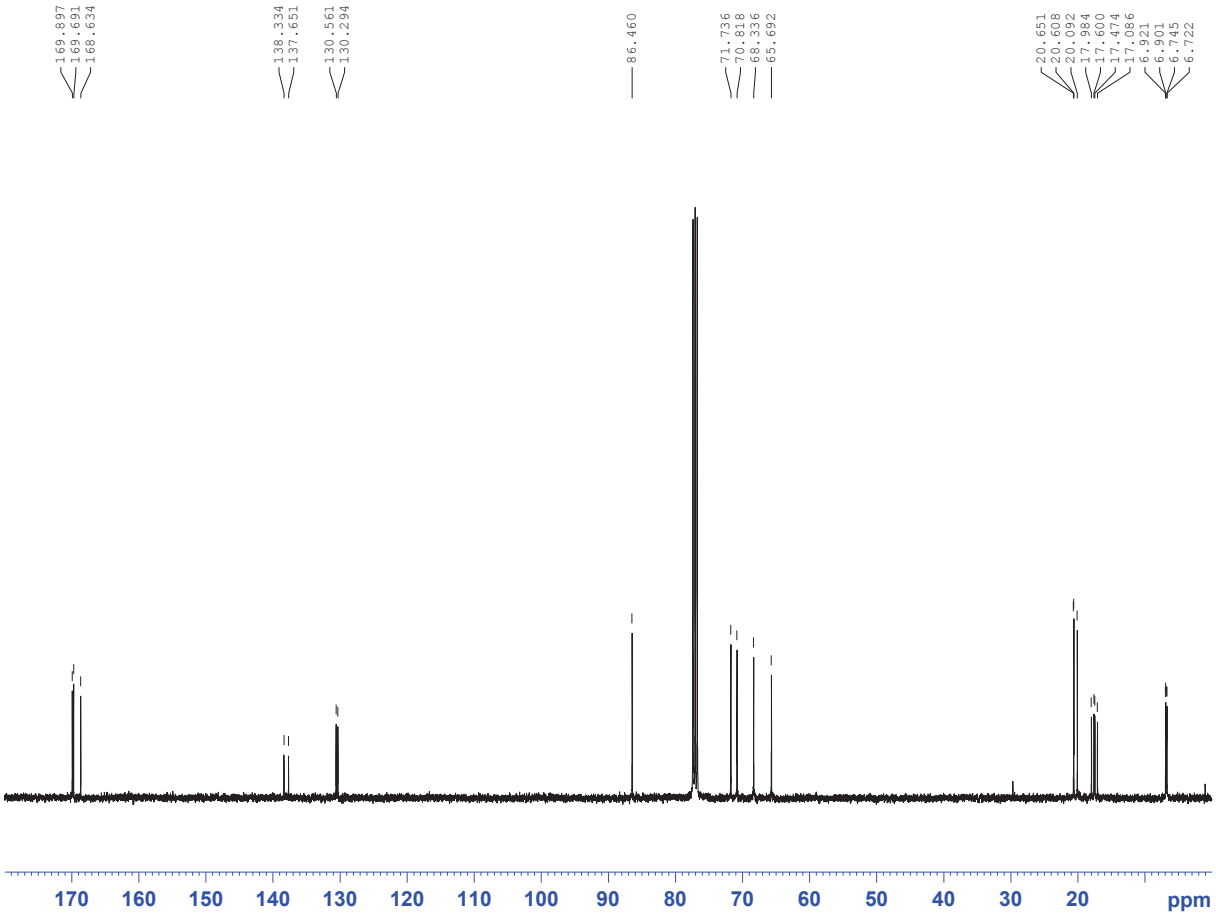


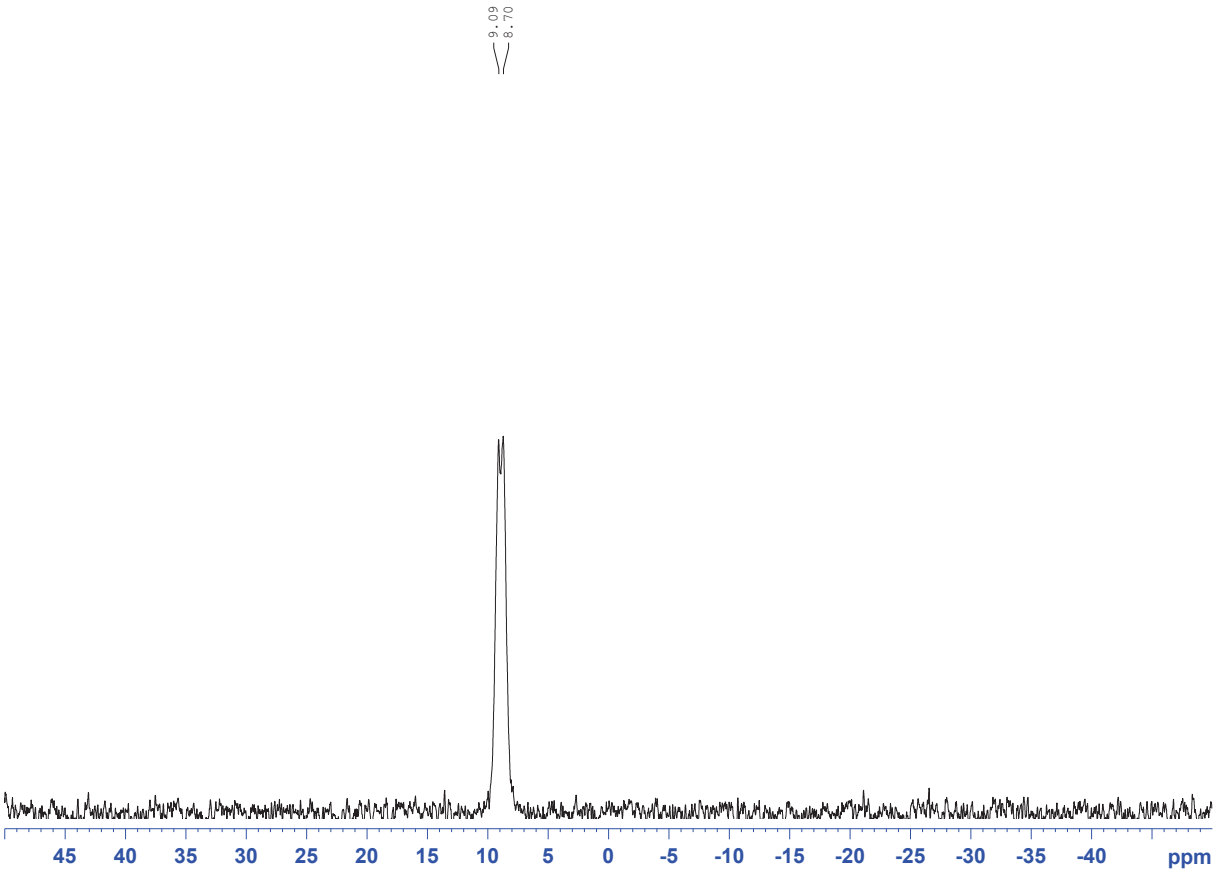

137.8
137.1
133.1
131.5
131.2
131.1
129.7
129.3
54.3
17.7
17.4
6.9
6.9
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.22
7.83
7.69
80 60 40 20 0 -20 -40 -60 -80 ppm

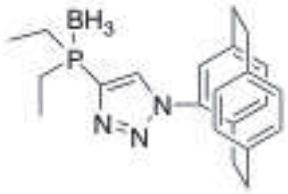
4-(Diethylphosphino-borane)-1-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-1*H*-1,2,3-triazole (2m)

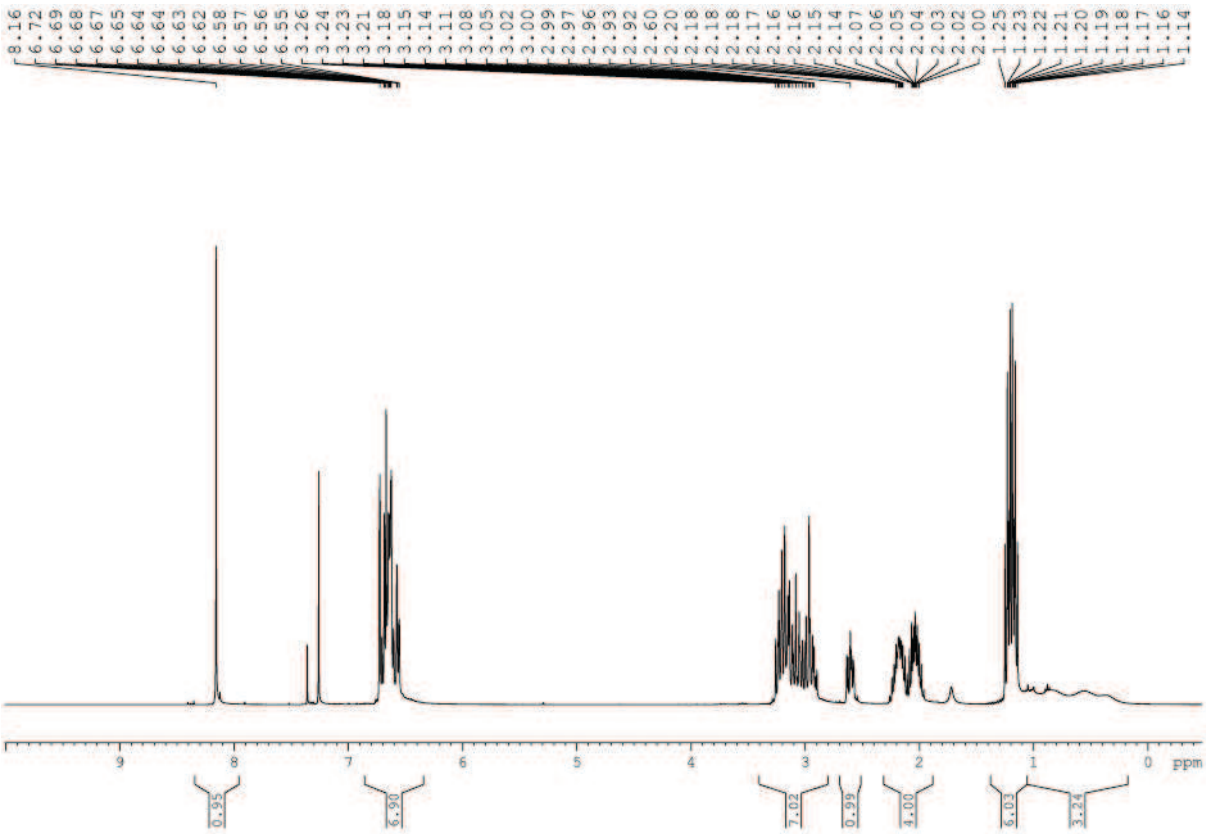


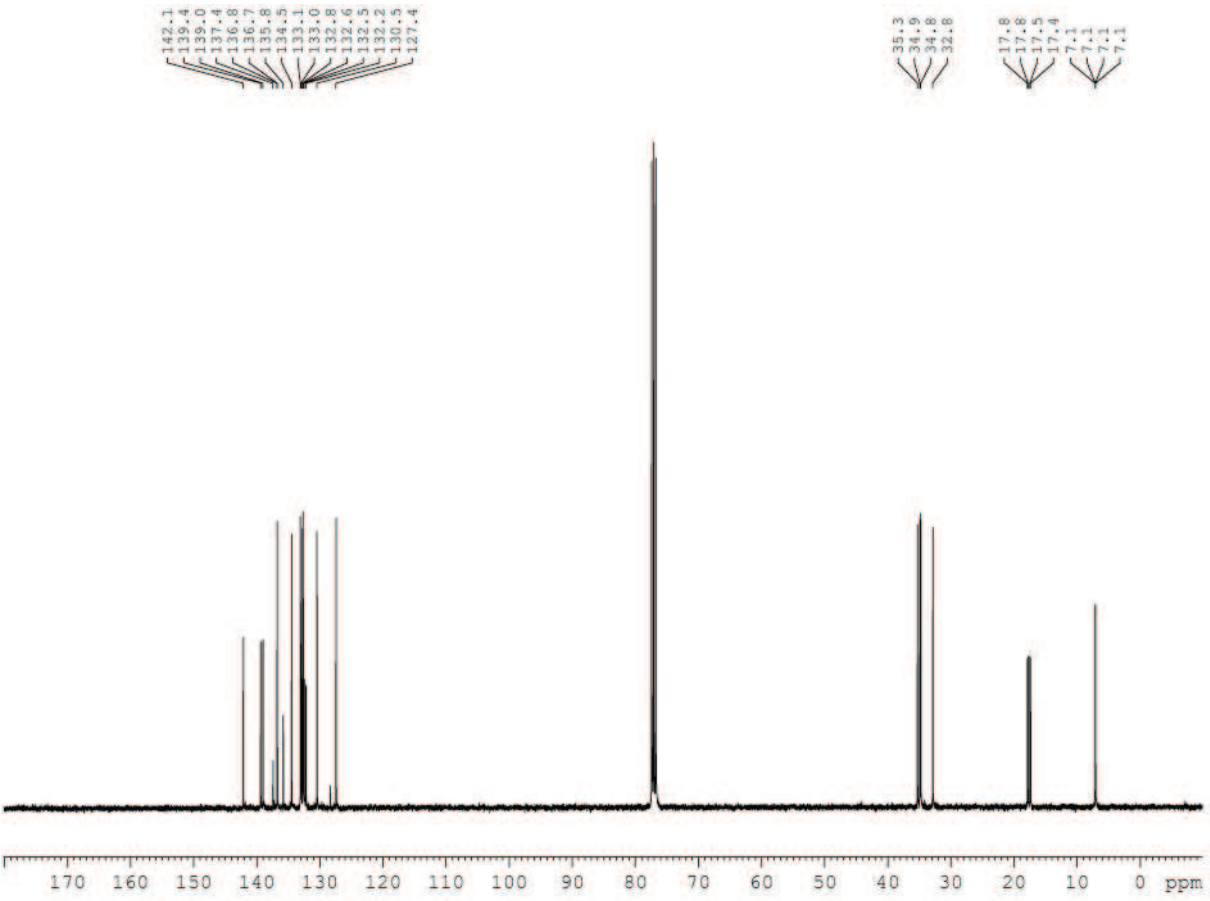

169.897
169.691
168.634
138.334
137.651
130.561
130.294
86.460
71.736
70.818
68.336
65.692
20.651
20.608
20.092
17.984
17.600
17.474
17.086
6.921
6.901
6.745
6.722
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

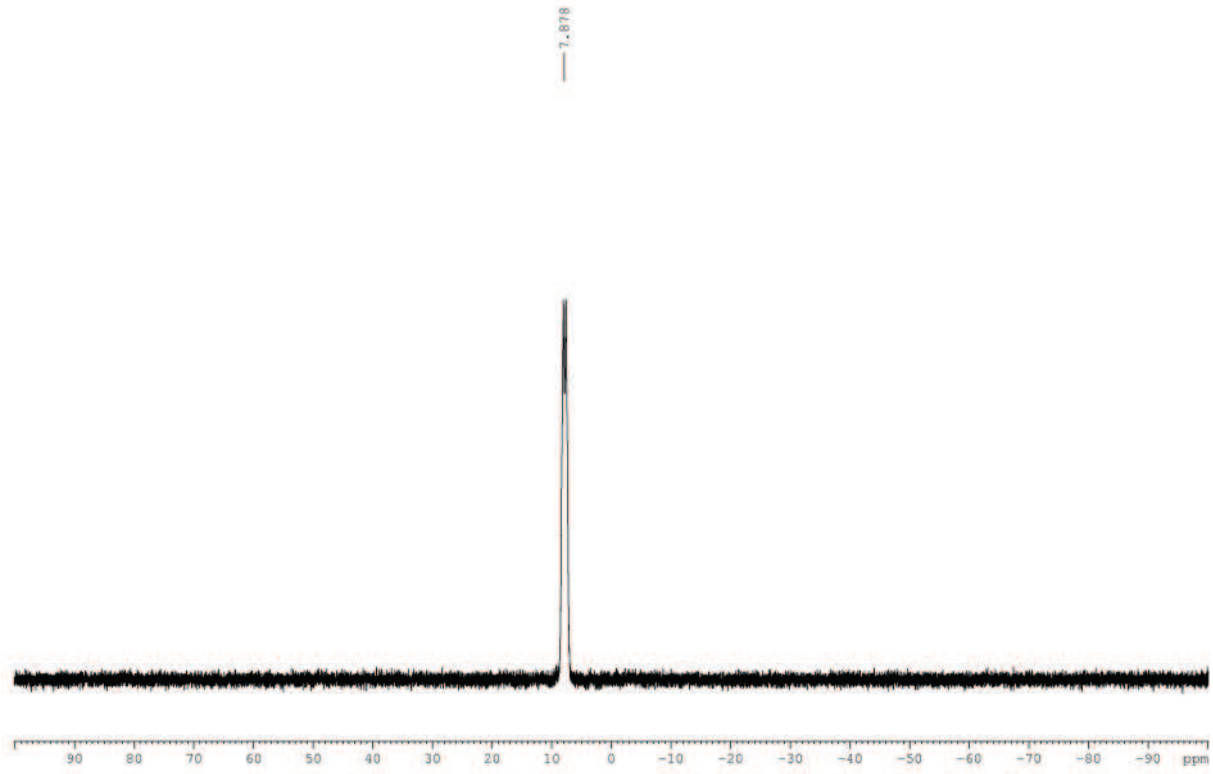

9.09
8.70
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 ppm

4-(Diethylphosphino-borane)-1-([2.2]-paracyclophan-4-yl)-1*H*-1,2,3-triazole (2n)

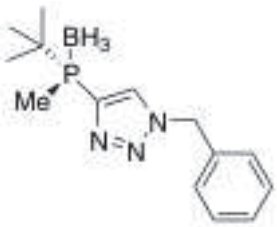


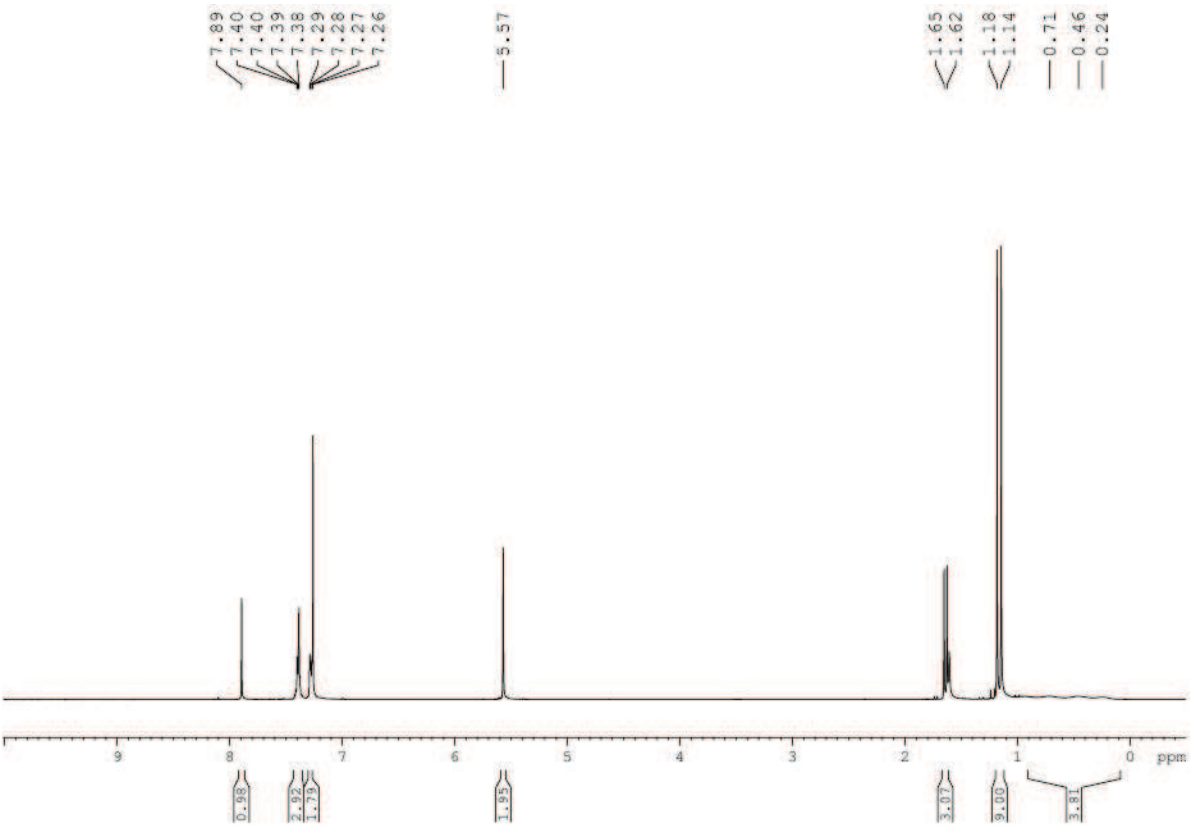


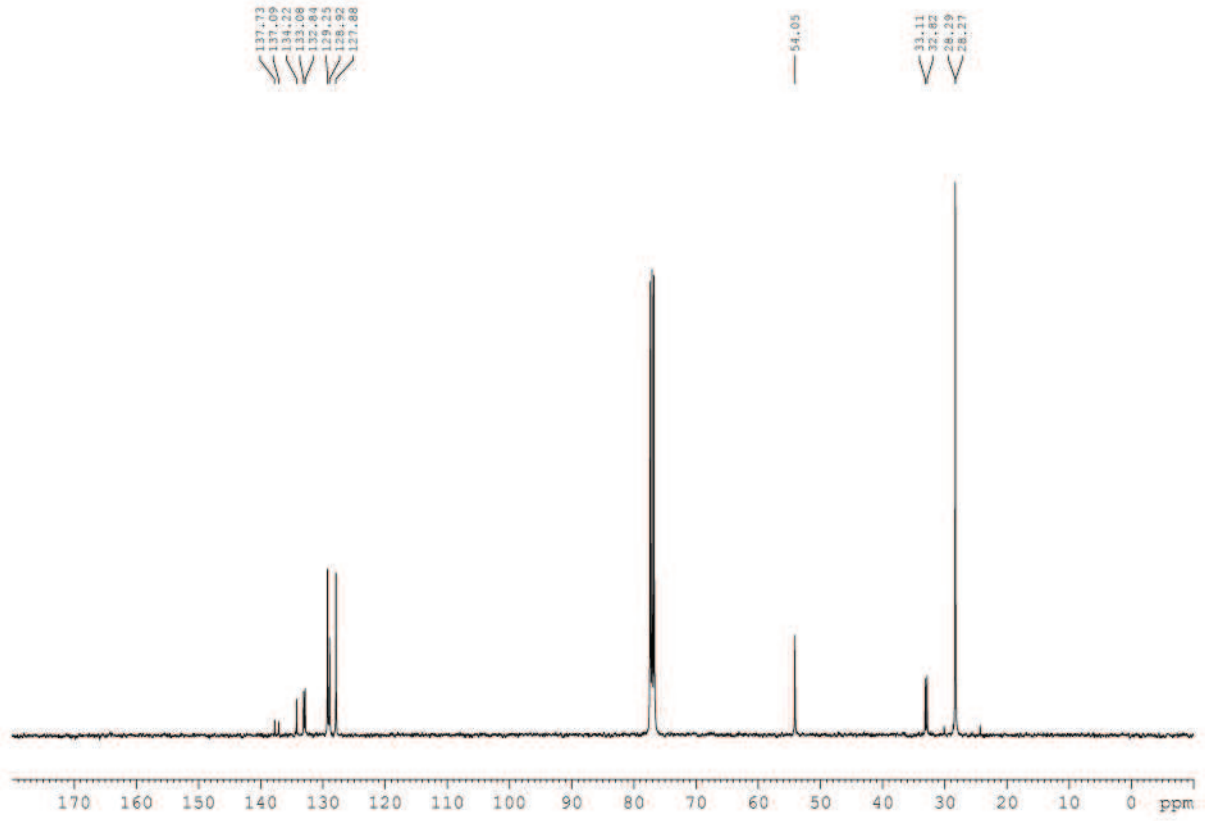

142.1
139.4
139.0
137.4
136.8
136.7
135.8
134.5
133.1
133.0
132.8
132.6
132.5
132.2
130.5
127.4
35.3
34.9
34.8
32.8
17.8
17.8
17.5
17.4
7.1
7.1
7.1
7.1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

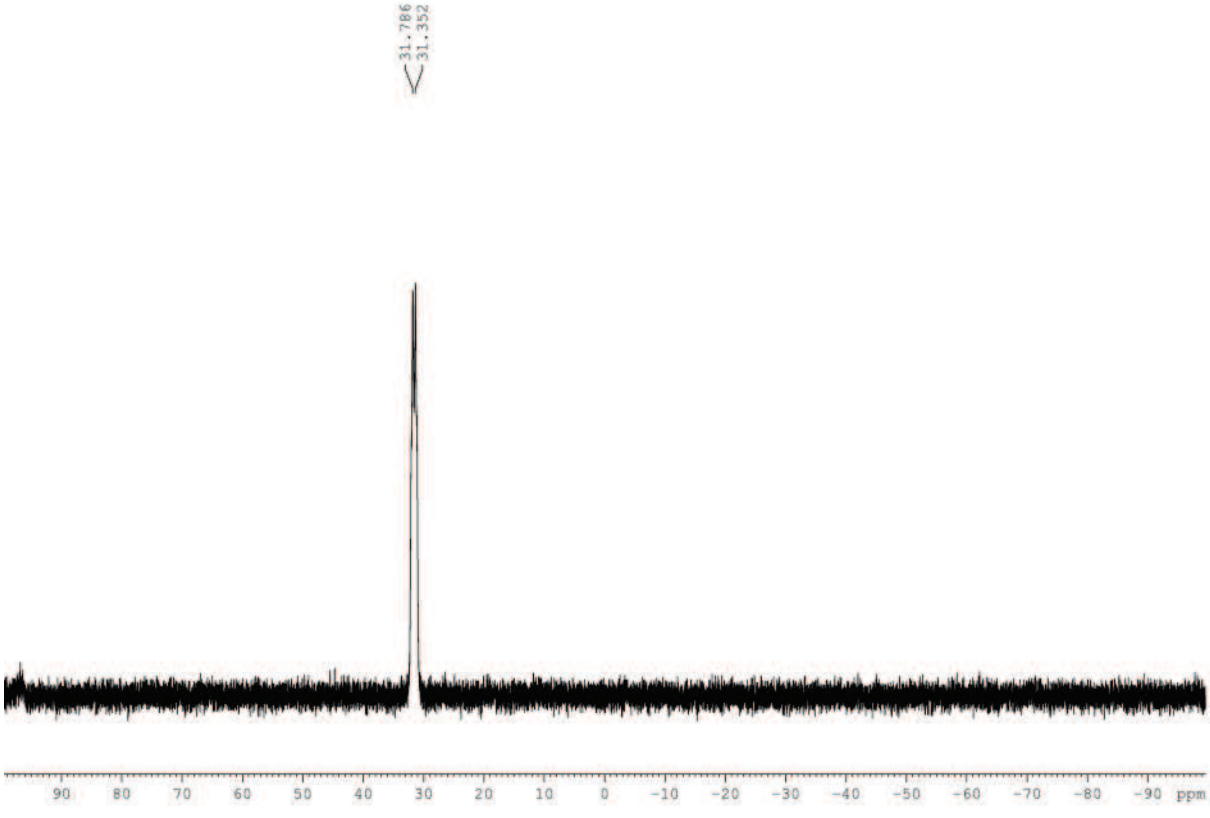

7.878
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

(*R*)-1-Benzyl-4-(methyl-*tert*-butylphosphino-borane)-1*H*-1,2,3-triazole (9)

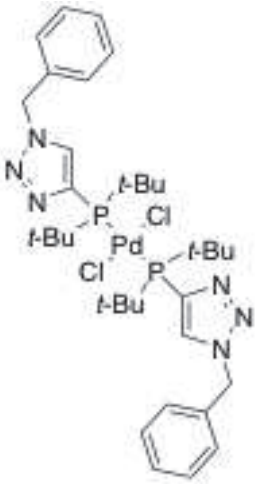


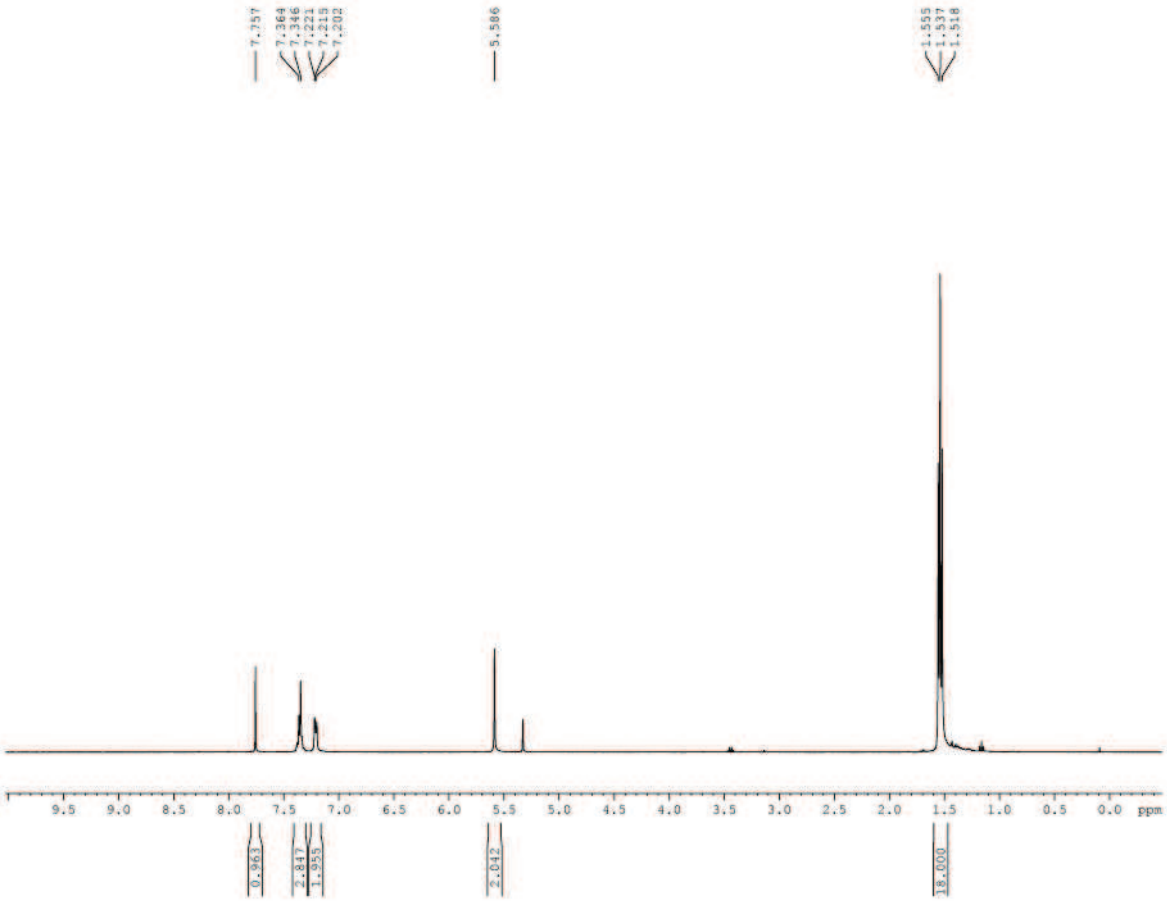


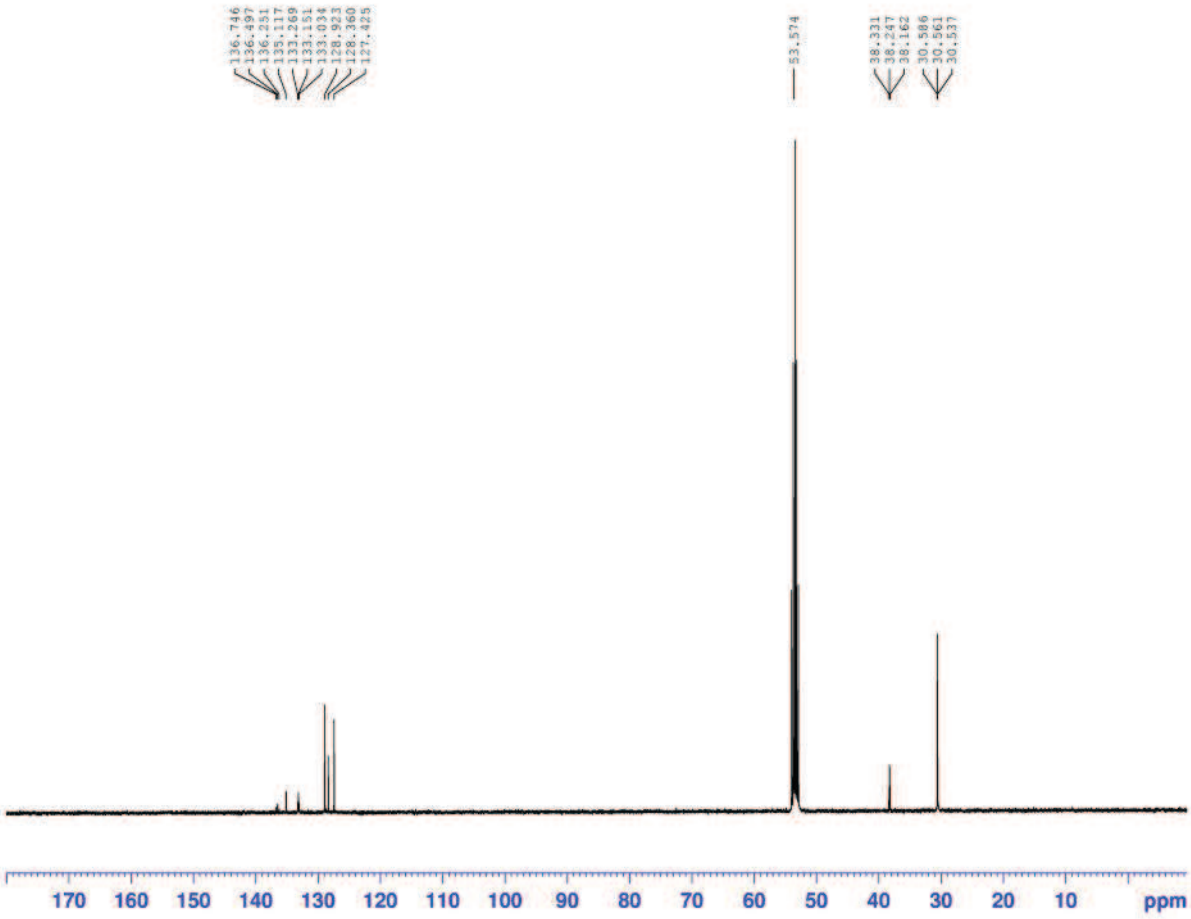

137.73
137.09
134.22
133.08
132.84
129.25
128.92
127.88
54.05
33.11
32.82
28.29
28.27
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

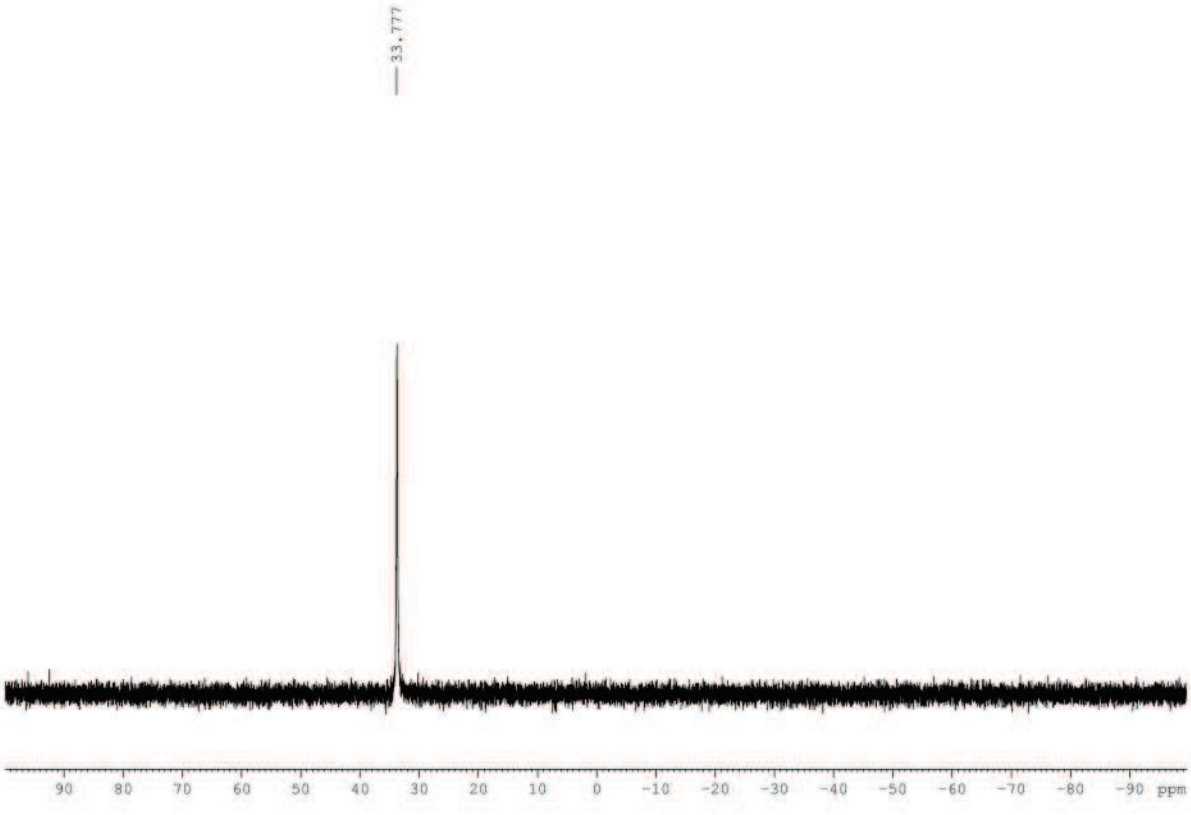

31.786
31.352
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

Dichlorobis[1-benzyl-4-(di-*tert*-butylphosphino)-1*H*-1,2,3-triazole]palladium(II) (10)

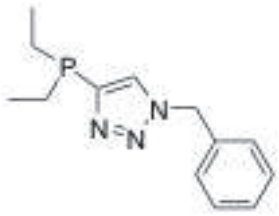


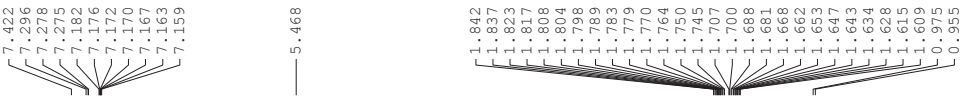


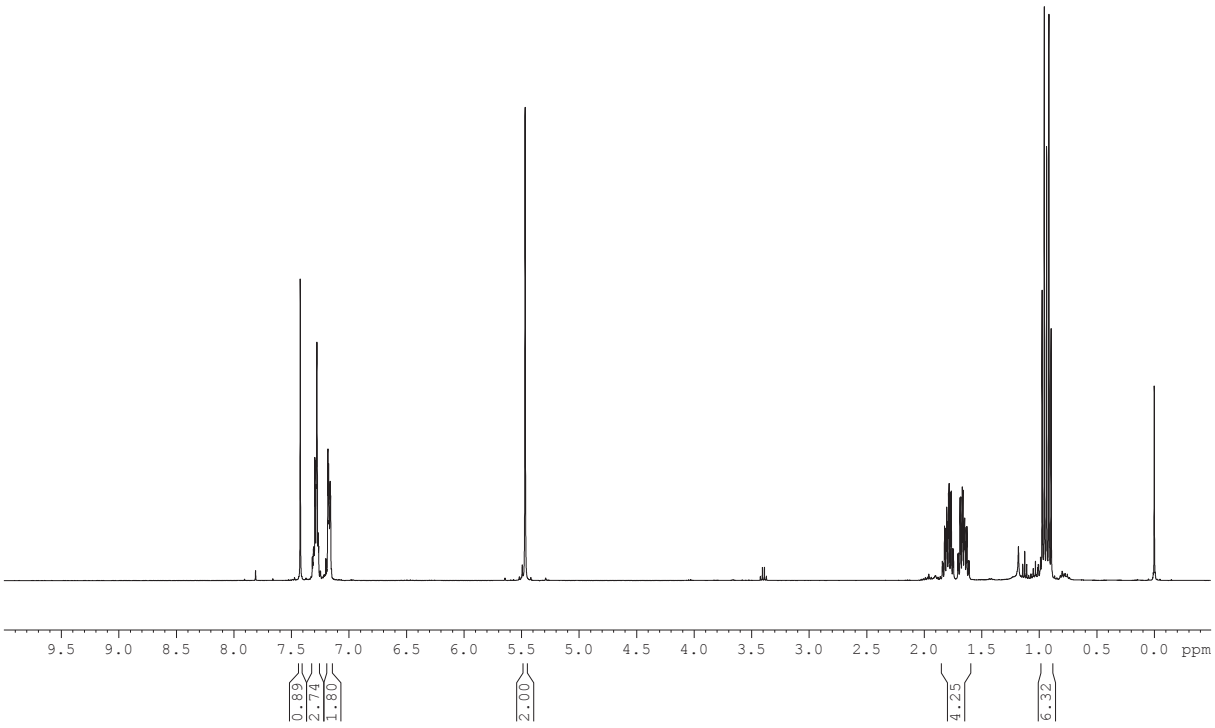

136.746
136.497
136.251
135.117
133.269
133.151
133.034
128.923
128.360
127.425
53.574
38.331
38.247
38.162
30.586
30.561
30.537
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

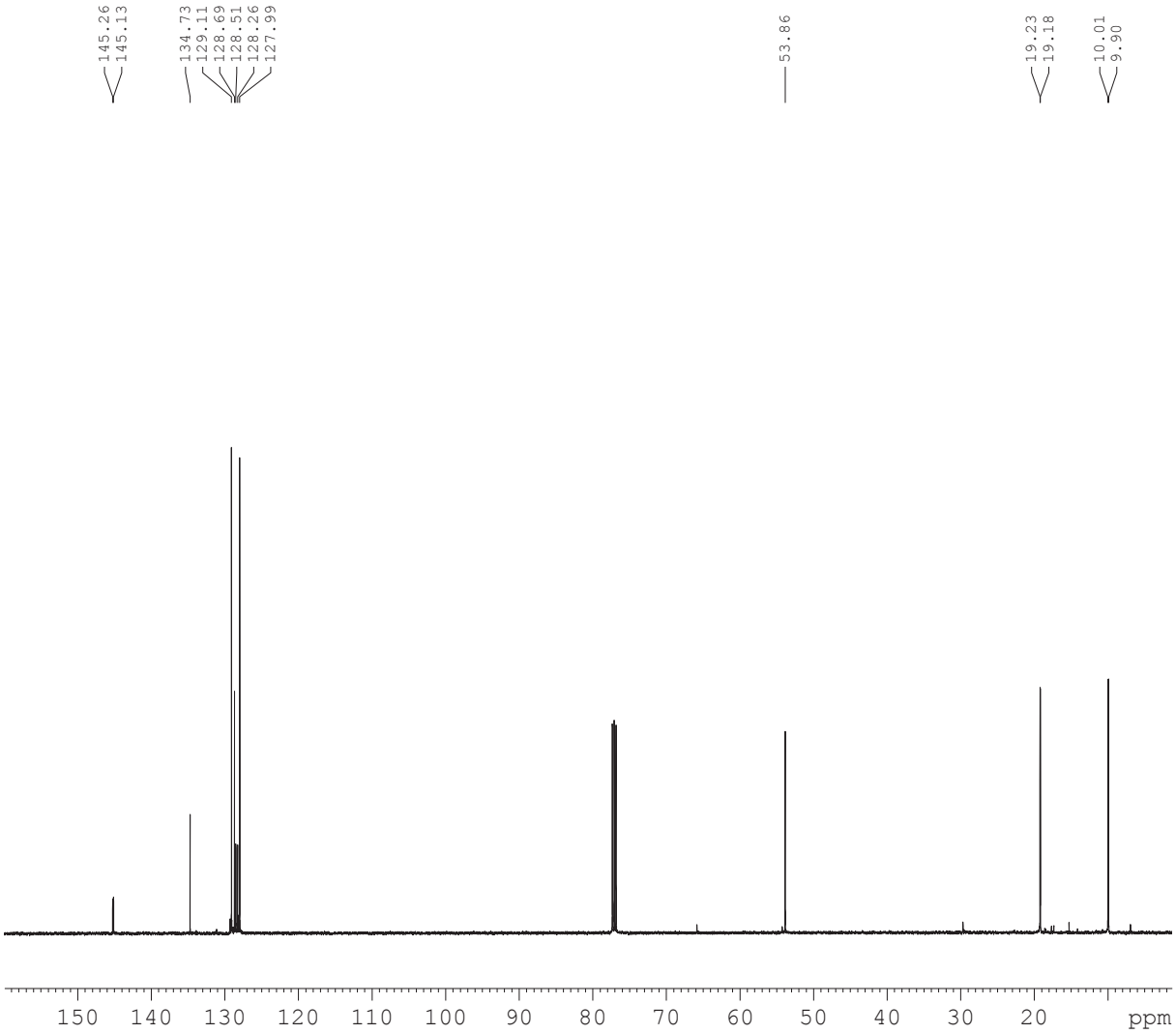

33.777
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm

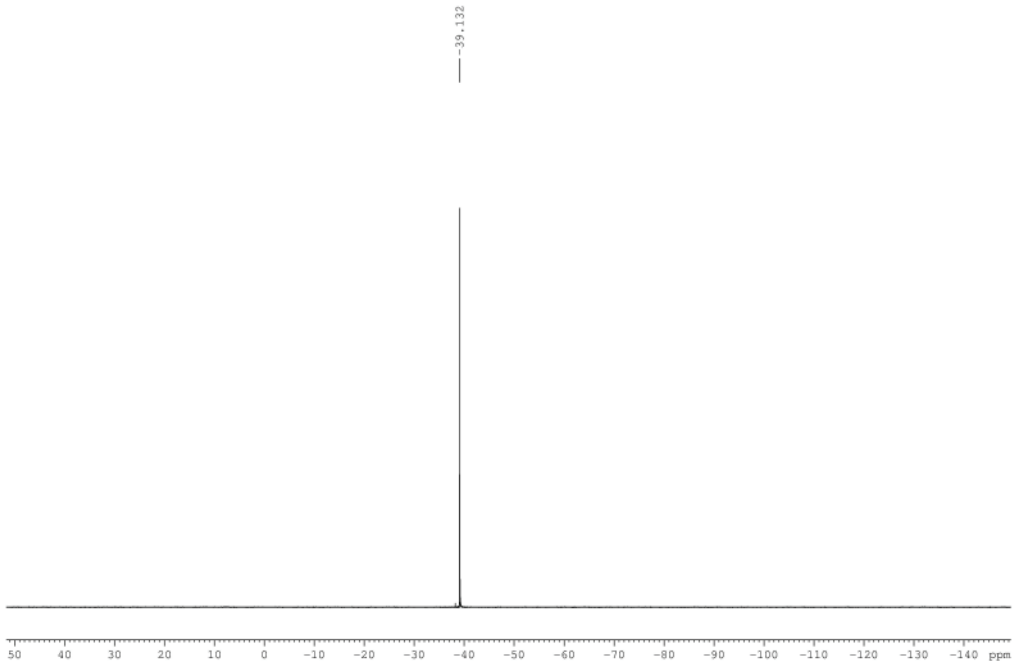
1-Benzyl-4-(diethylphosphino)-1*H*-1,2,3-triazole (1a)



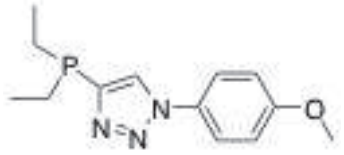


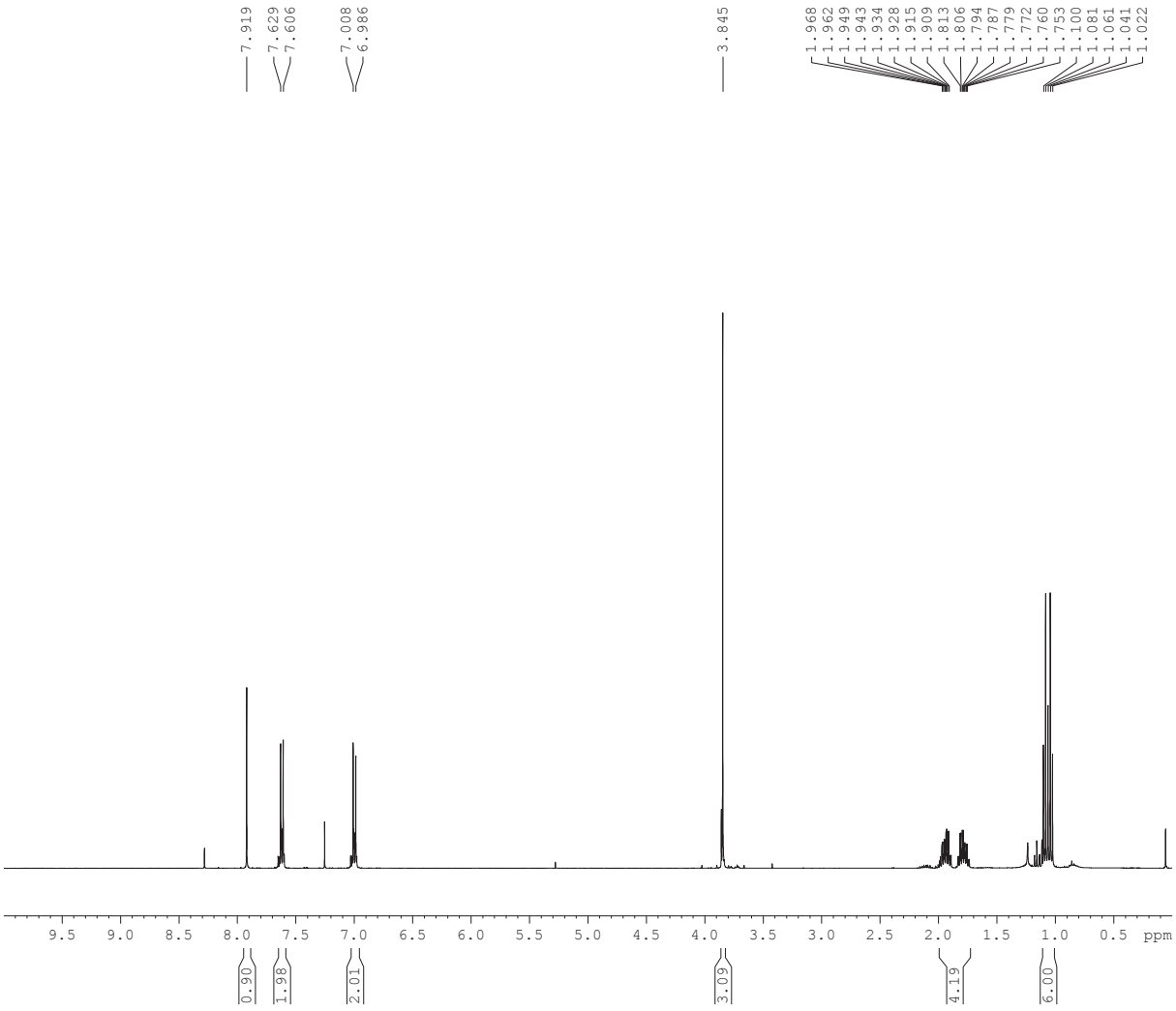


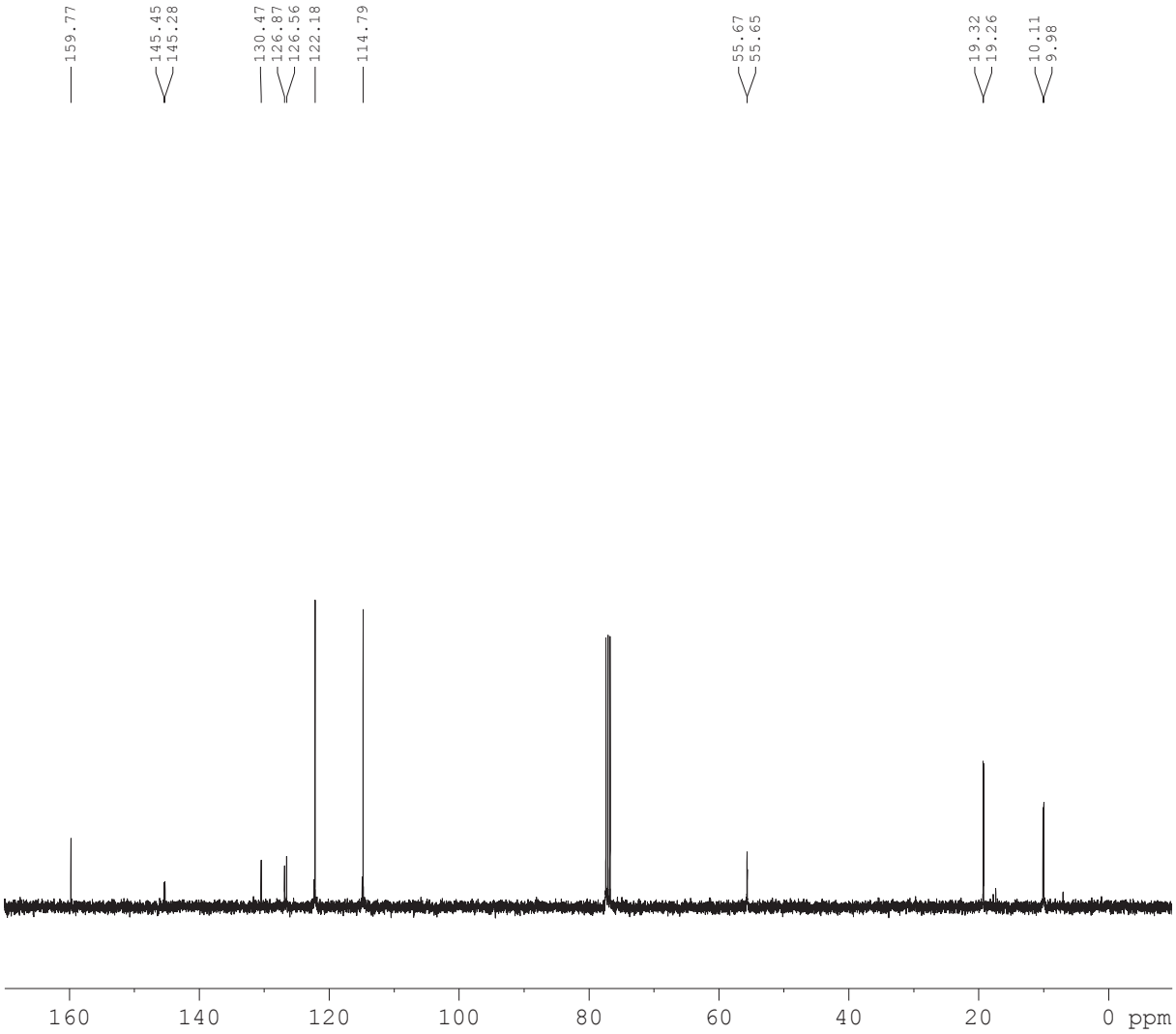

145.26
145.13
134.73
129.11
128.69
128.51
128.26
127.99
53.86
19.23
19.18
10.01
9.90
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

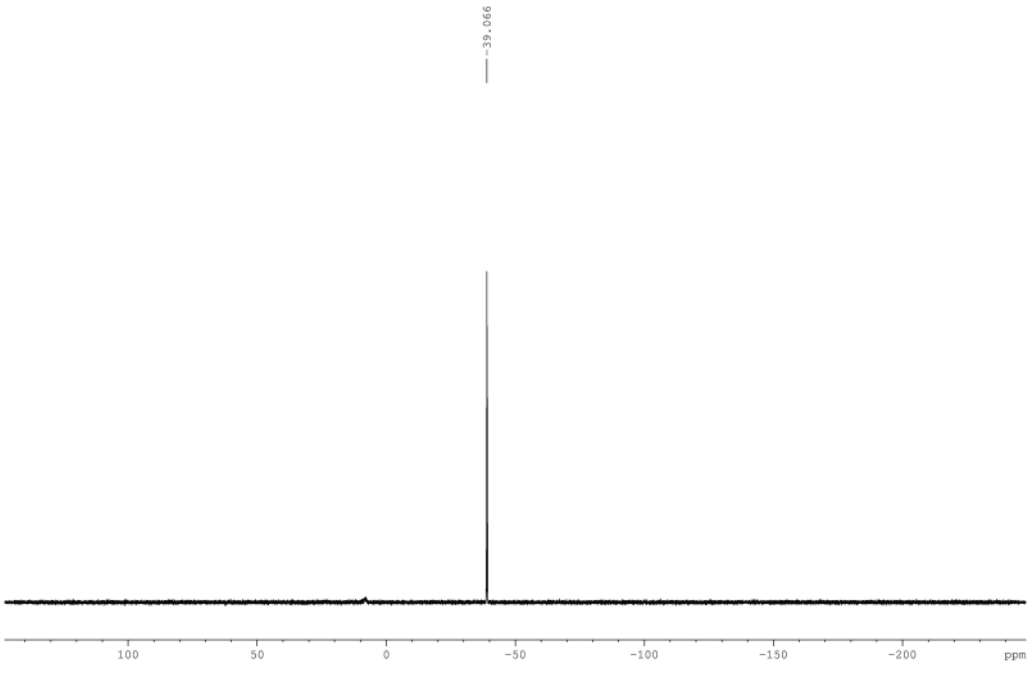

-39.132
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm

1-(4-Anisyl)-4-(diethylphosphino)-1*H*-1,2,3-triazole (1c)

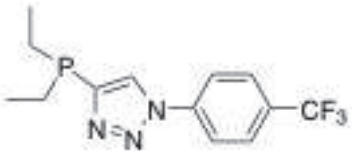


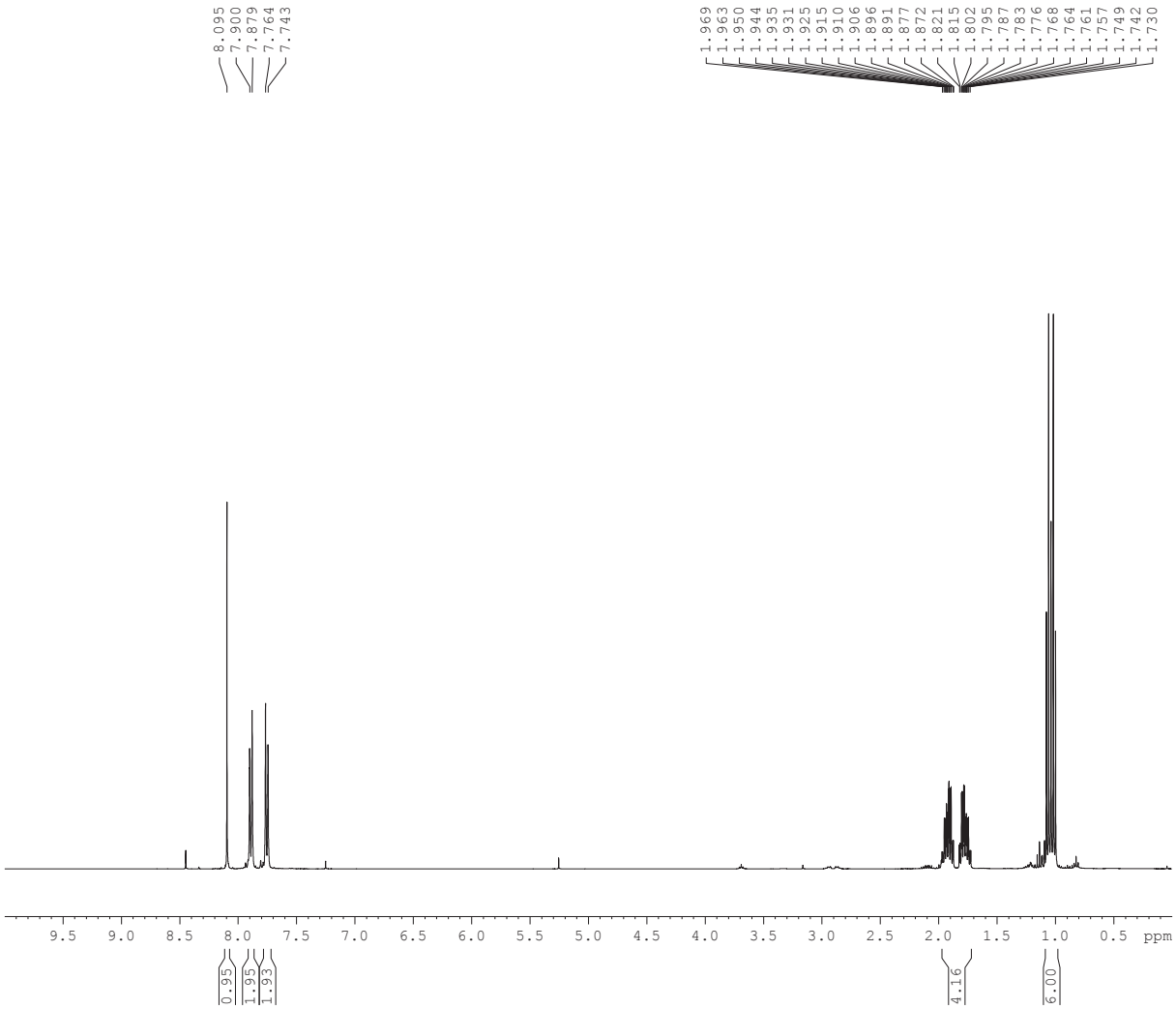


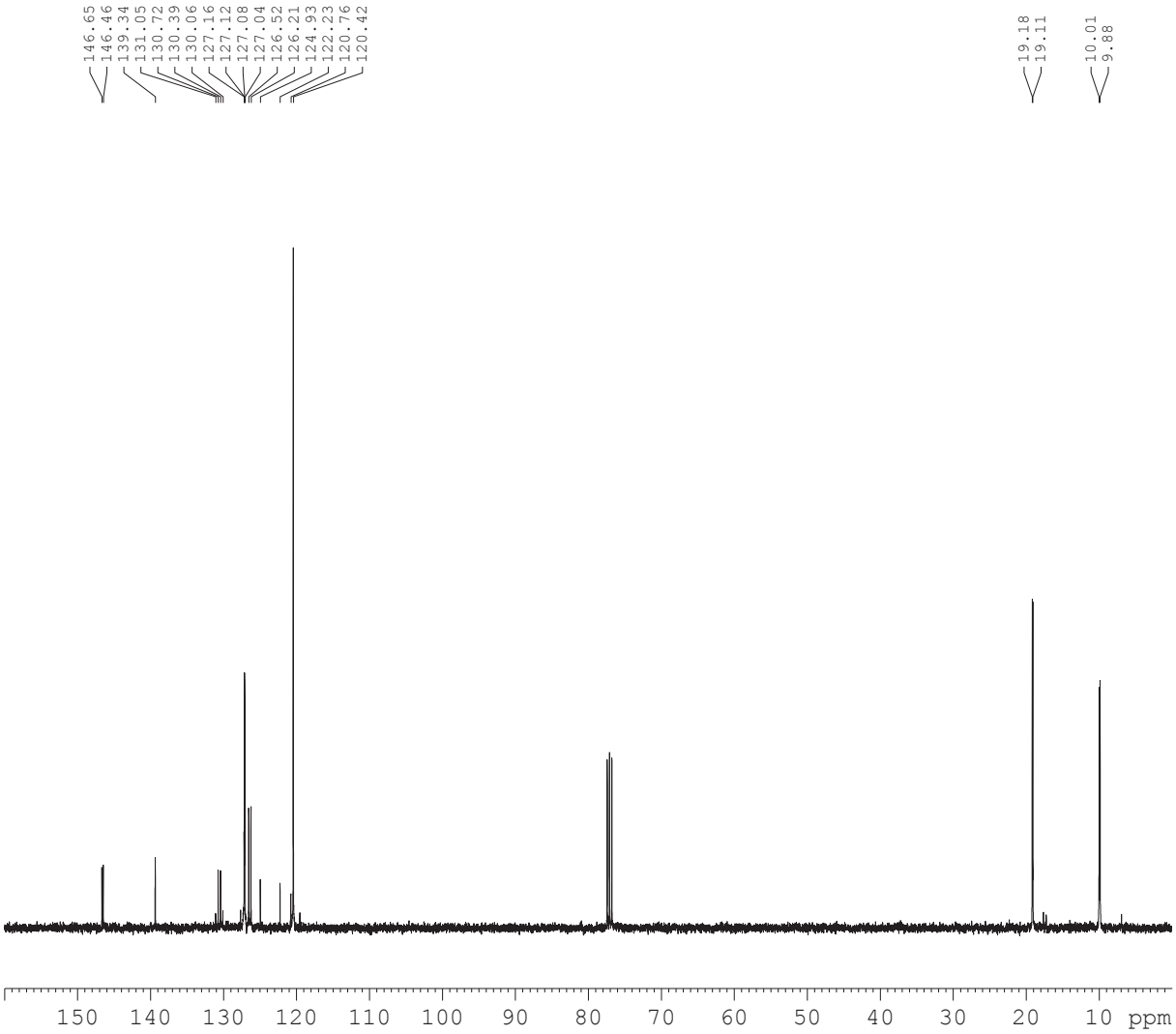

159.77
145.45
145.28
130.47
126.87
126.56
122.18
114.79
55.67
55.65
19.32
19.26
10.11
9.98
160
140
120
100
80
60
40
20
0 ppm

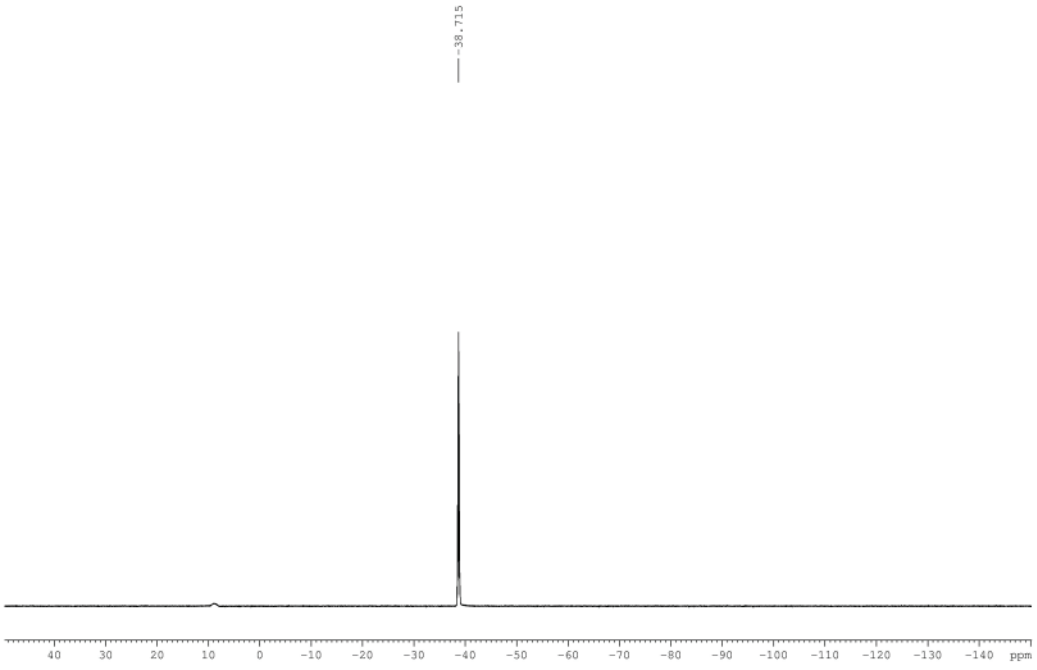

-39.066
100
50
0
-50
-100
-150
-200
ppm

4-(Diethylphosphino)-1-(4-trifluoromethylphenyl)-1*H*-1,2,3-triazole (1e)

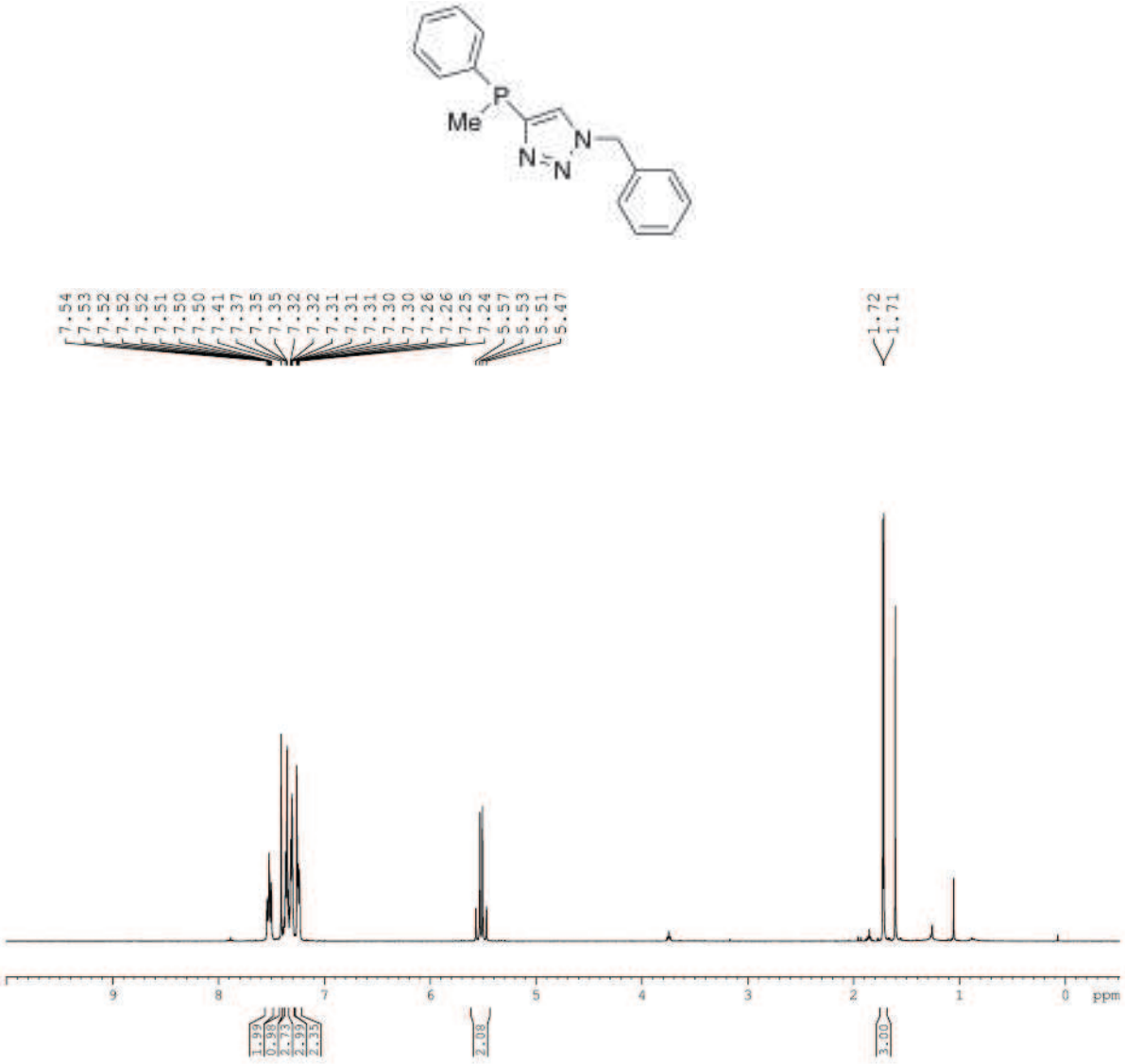


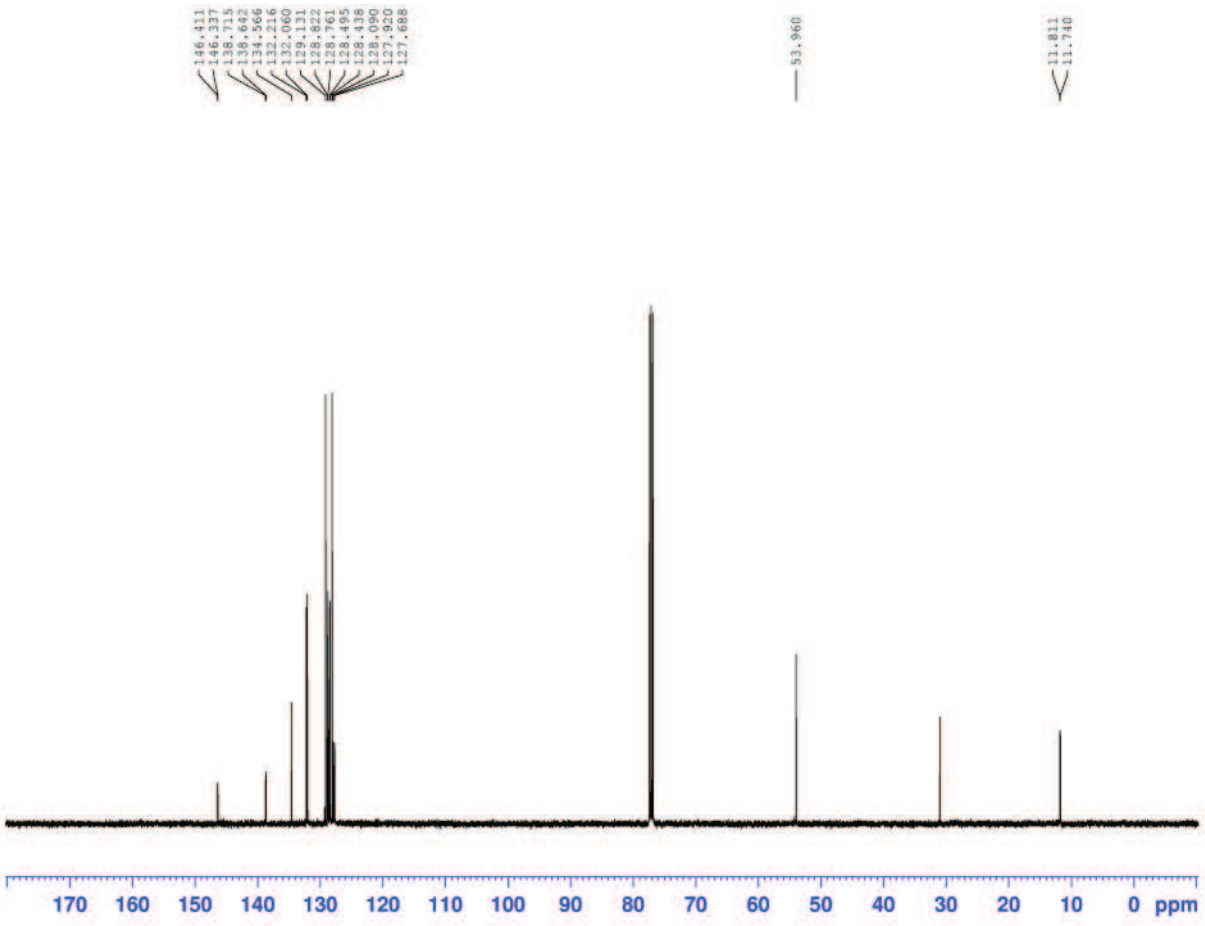


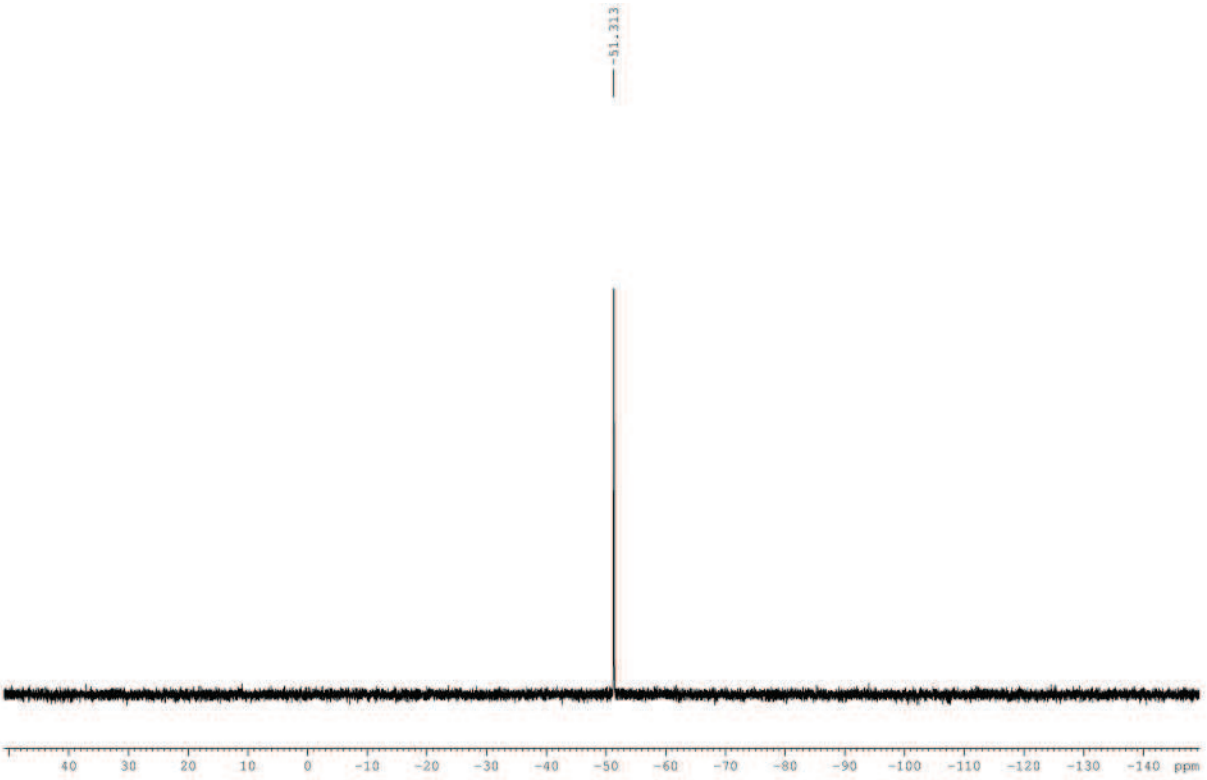

146.65
146.46
139.34
131.05
130.72
130.39
130.06
127.16
127.12
127.08
127.04
126.52
126.21
124.93
122.23
120.76
120.42
19.18
19.11
10.01
9.88
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


-38.715
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm

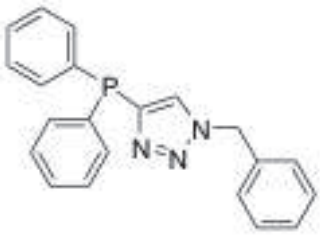
1-Benzyl-4-(phenylmethylphosphino)-1*H*-1,2,3-triazole (1g)

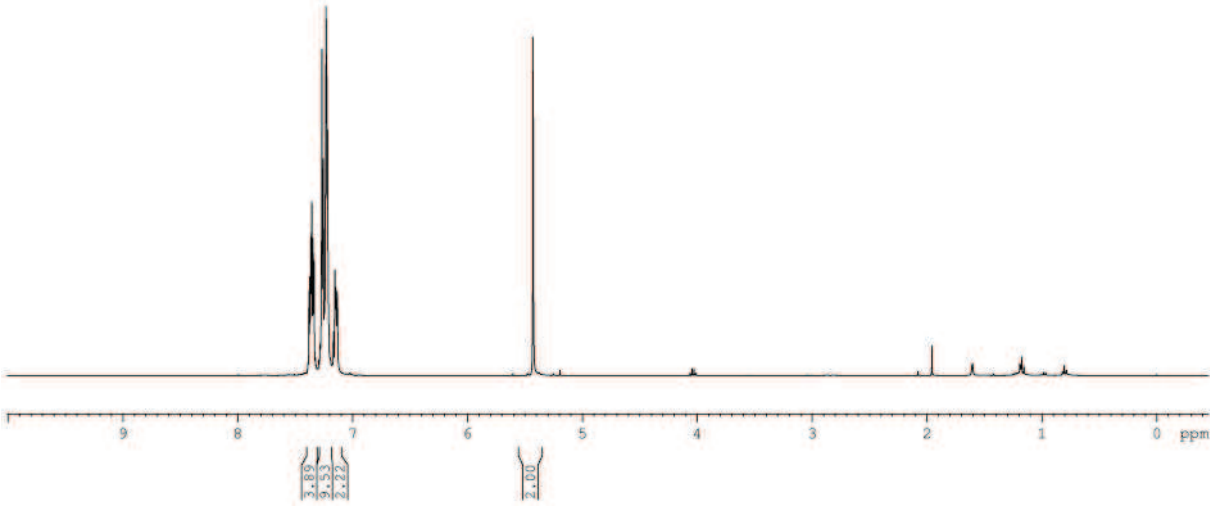


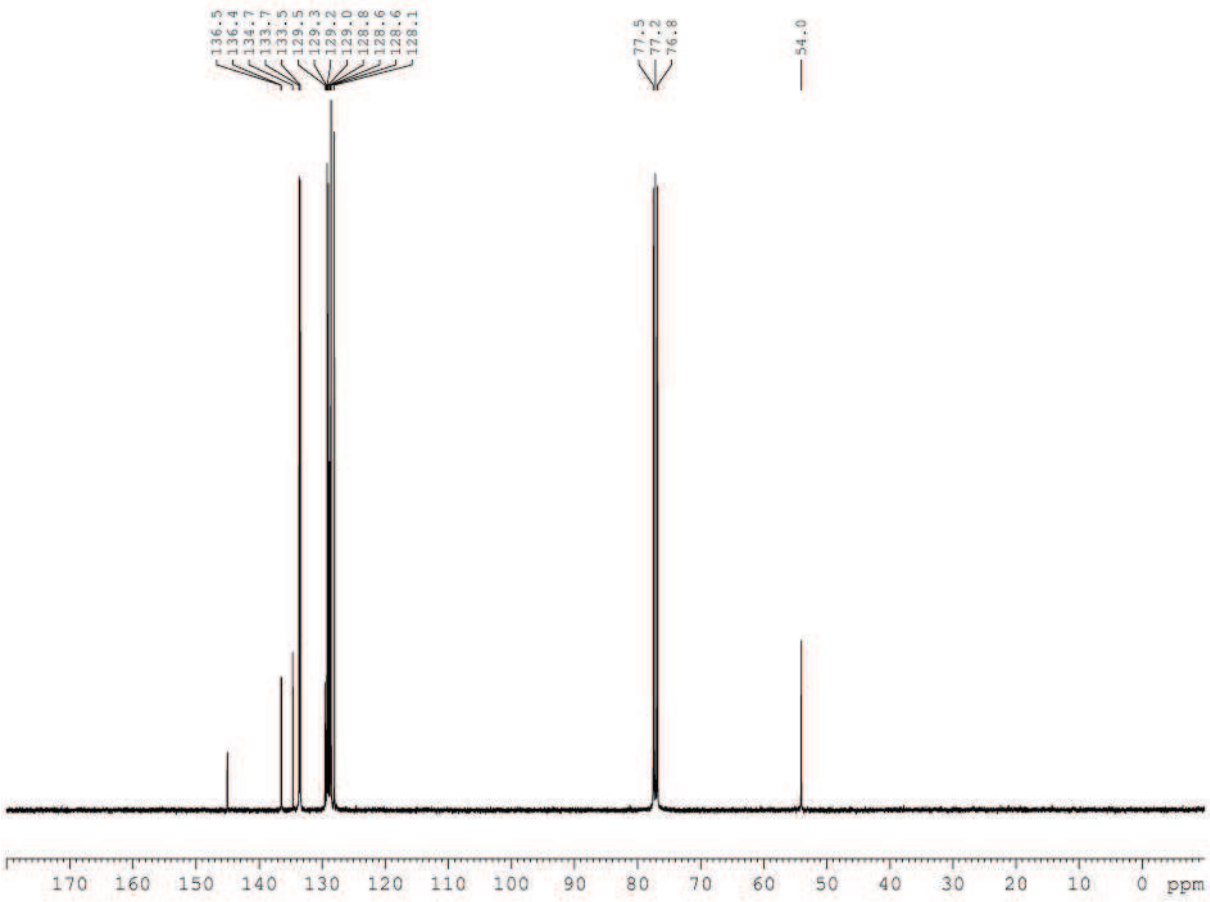

146.411
146.337
138.715
138.642
134.566
132.216
132.060
129.131
128.922
128.761
128.495
128.438
128.090
127.920
127.688
53.960
11.811
11.740
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

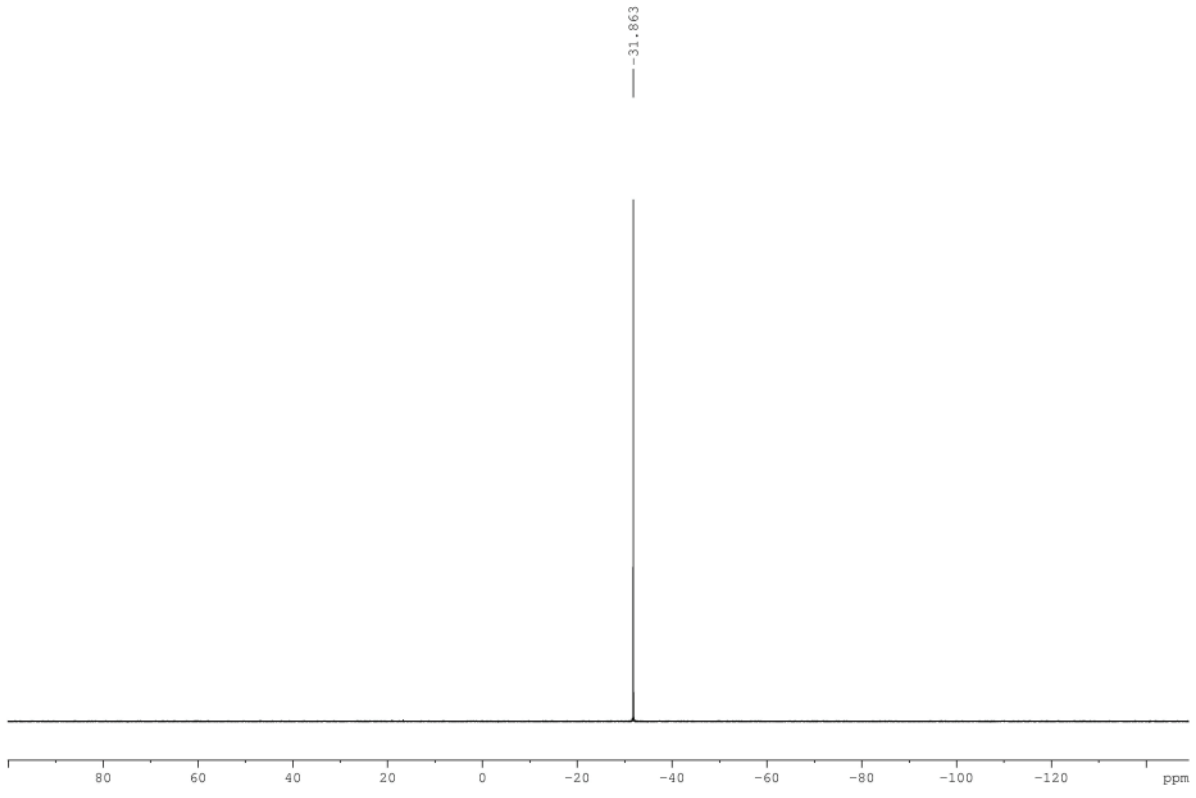

-51.313
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm

1-Benzyl-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1i)

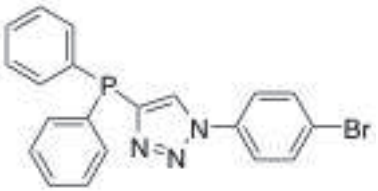


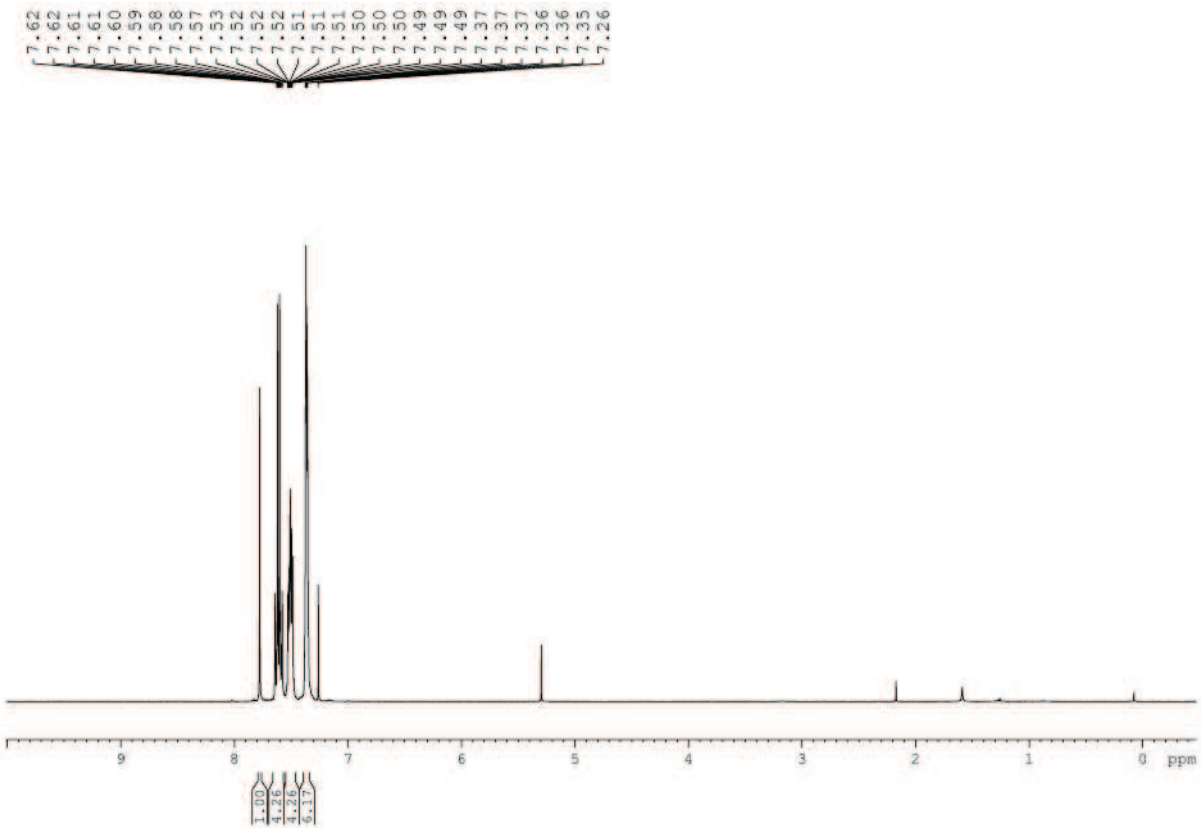


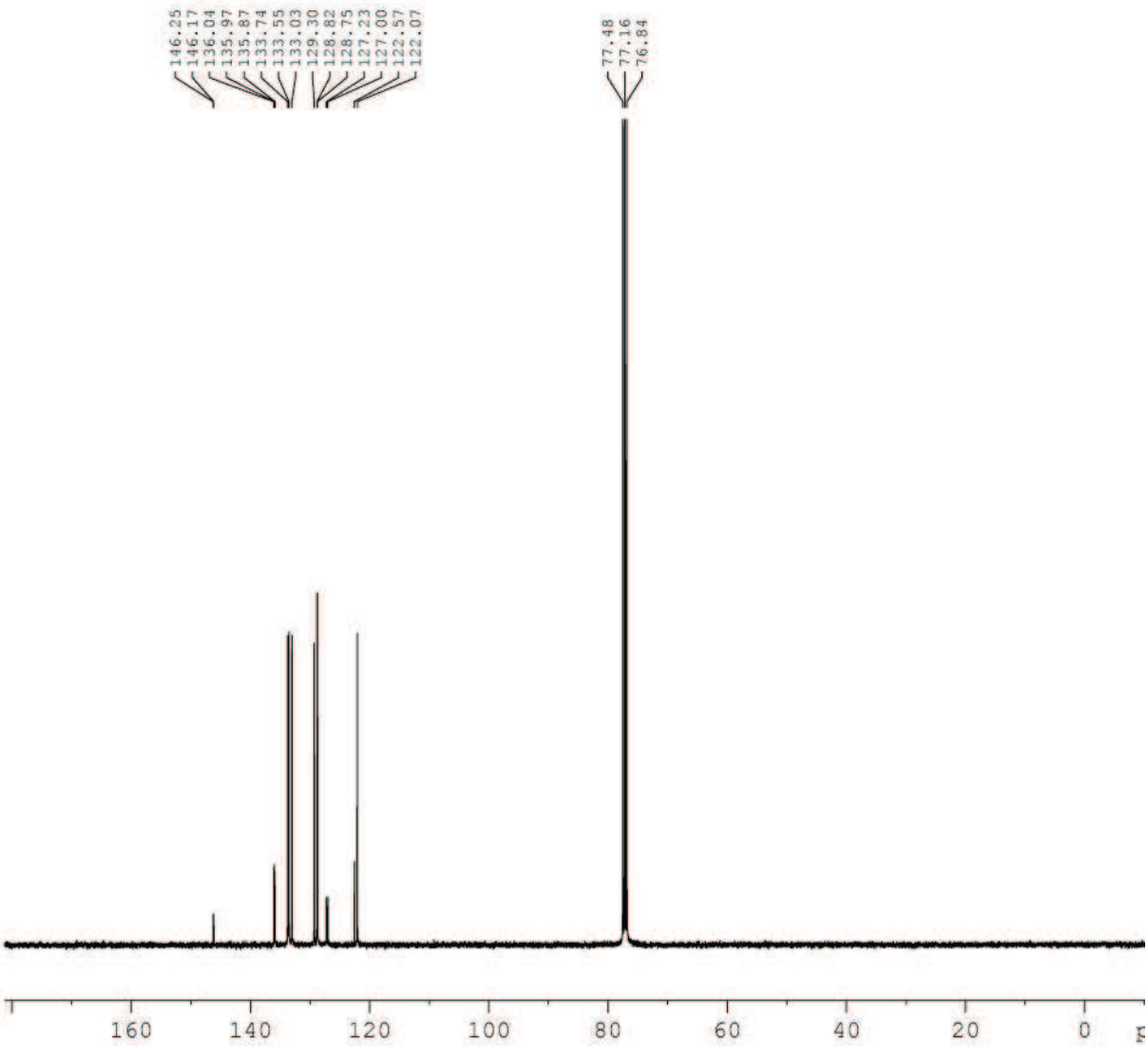

136.5
136.4
134.7
133.7
133.5
129.5
129.3
129.2
129.0
128.8
128.6
128.6
128.1
77.5
77.2
76.8
54.0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

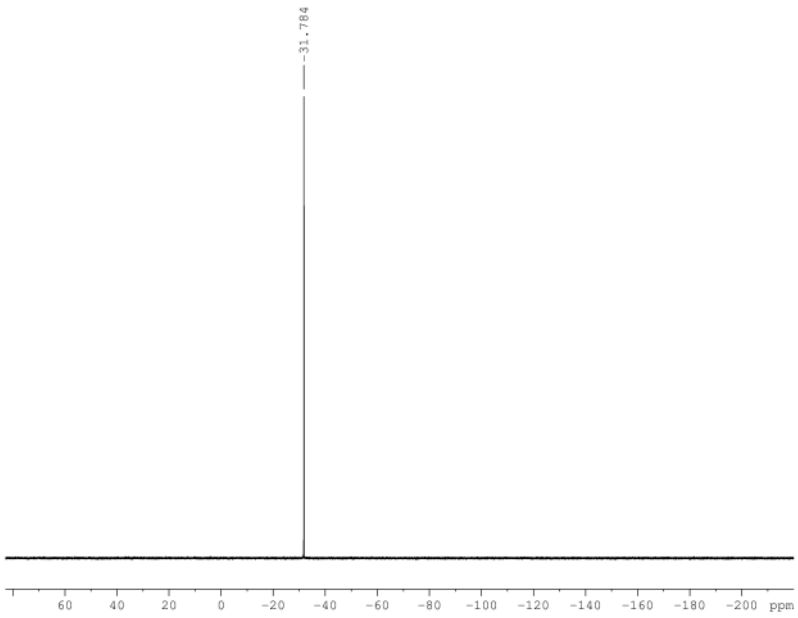

-31.863
80 60 40 20 0 -20 -40 -60 -80 -100 -120 ppm

1-(4-Bromophenyl)-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1j)

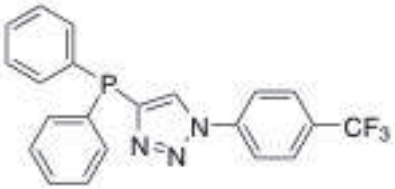


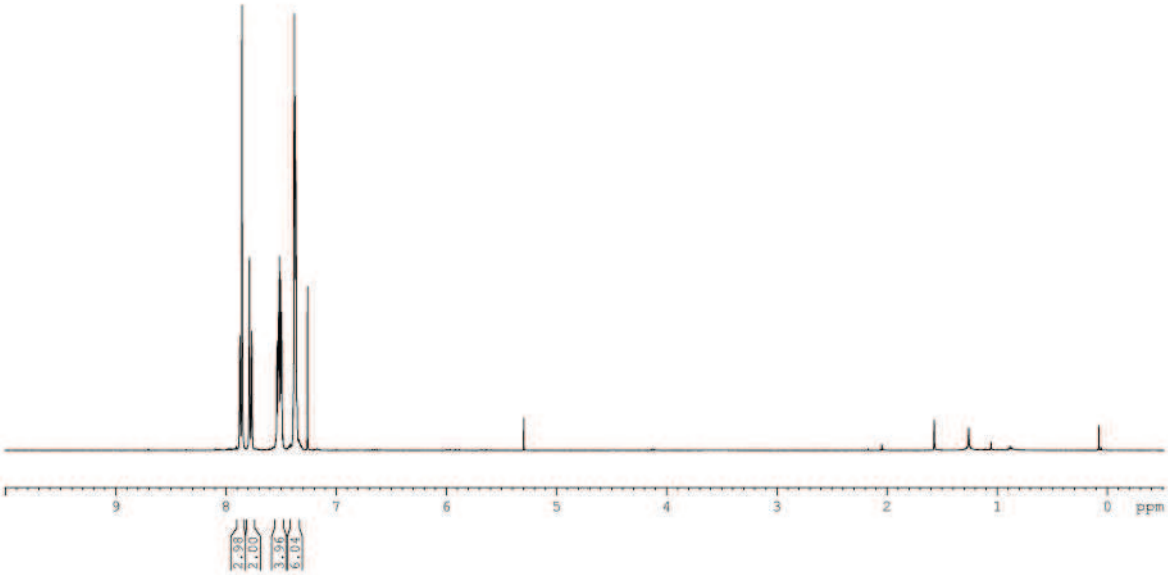


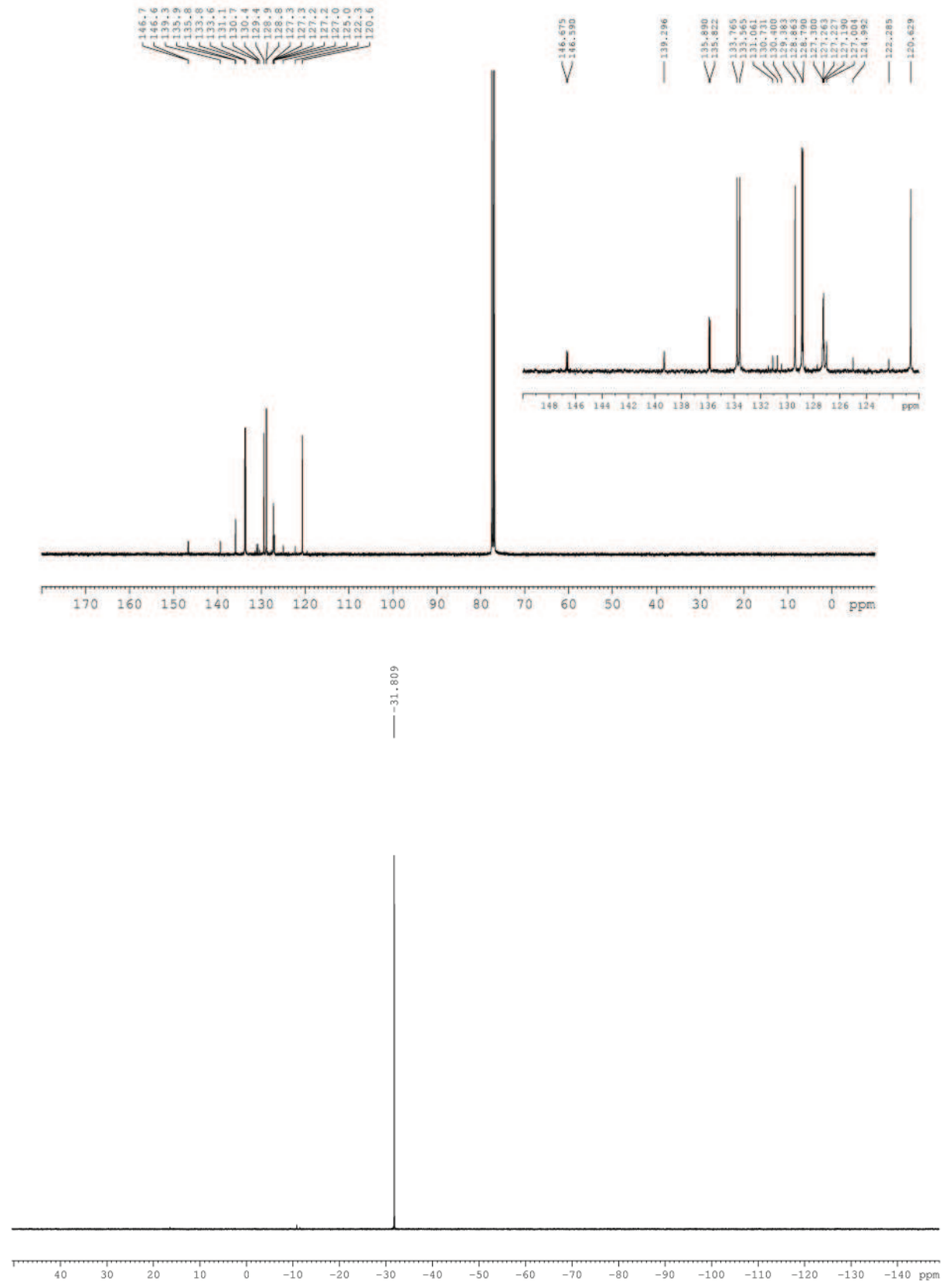

146.25
146.17
136.04
135.97
135.87
133.74
133.55
133.03
129.30
128.82
128.75
127.23
127.00
122.57
122.07
77.48
77.16
76.84
160
140
120
100
80
60
40
20
0


-31.784
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

1-(4-Trifluoromethylphenyl)-4-(diphenylphosphino)-1*H*-1,2,3-triazole (1k)







4. Chiral HPLC Analysis of 9

Empower software

RAPPORT HPLC

Reported by User: System

Project Name: IC_OBH_ASH_2013

RV421

Instrument Method: IC 1mL90%nhep10%prop_20dC

Stored: 1/9/2013 3:15:56 PM

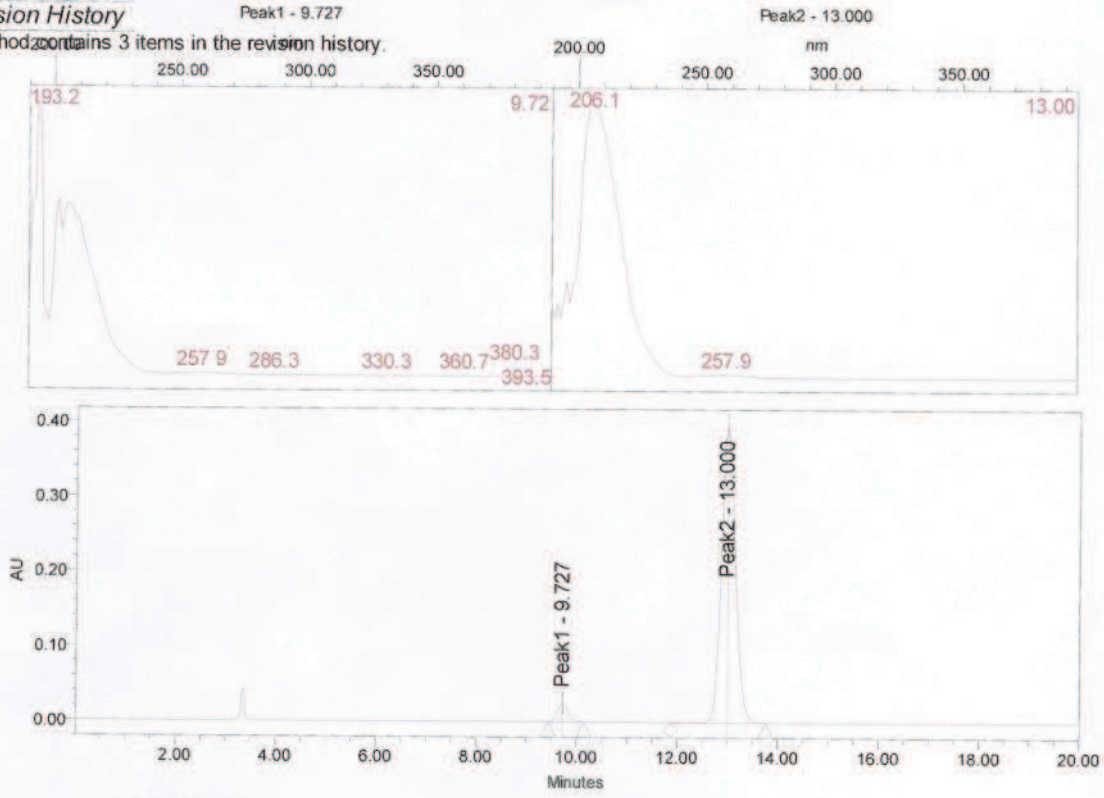
Method Information

Comments	Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C
Modified User	System
Locked	No
Method Id	1067
Method Version	1
Edit User	

Revision History

This method contains 3 items in the revision history.

Spectrum Index Plot



Peak Results

	Name	Retention Time (min)	Area (µV*sec)	% Area
1	Peak1	9.727	380315	4.66
2	Peak2	13.000	7778683	95.34

Processed Channel Descr. PDA 210.0 nm

Reported by User: System

Project Name: IC_OBH_ASH_2013

RV421-2

Instrument Method: IC 1mL90%nhep10%prop_20dC

Stored: 1/9/2013 3:15:56 PM

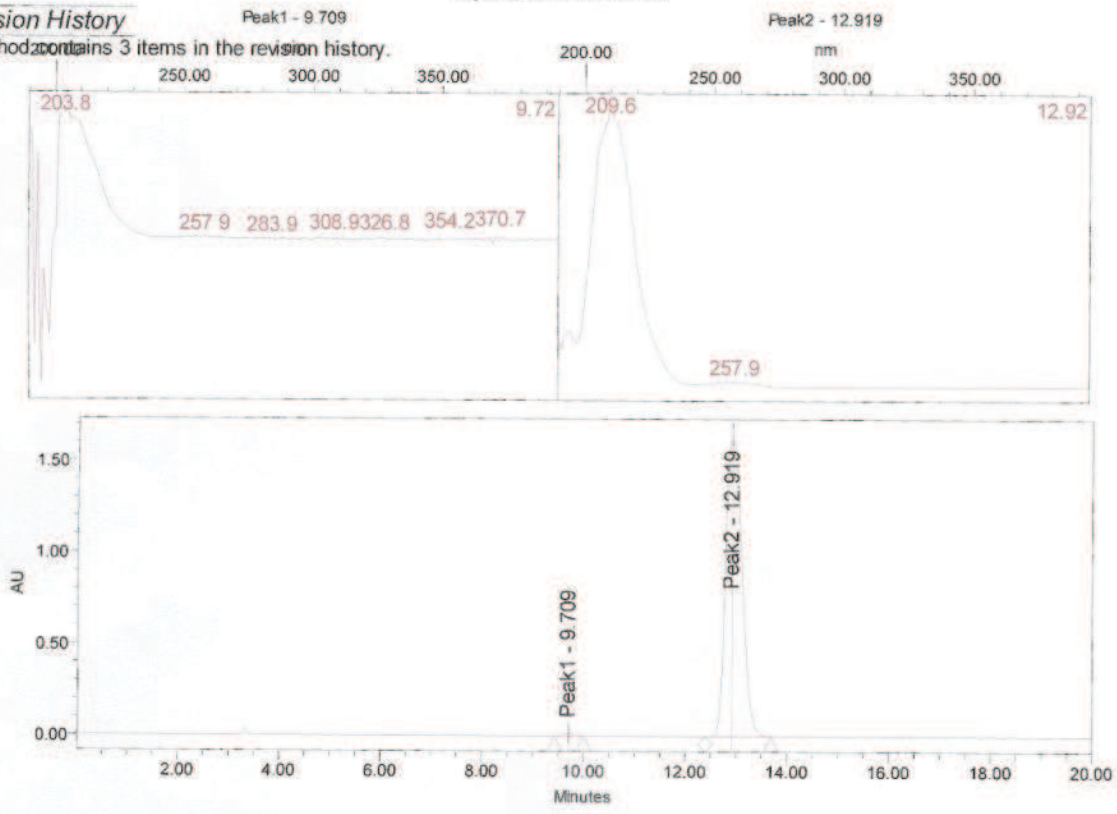
Method Information

Comments	Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 90%n-heptane10%propanol-2 éch.+col.à 20°C
Modified User	System
Locked	No
Method Id	1067
Method Version	1
Edit User	

Revision History

This method contains 3 items in the revision history.

Spectrum Index Plot



Peak Results

	Name	Retention Time (min)	Area (µV*sec)	% Area
1	Peak1	9.709	234799	0.63
2	Peak2	12.919	37252329	99.37

Processed Channel Descr. PDA 210.0 nm