Supplementary Material for Chemical Communications

Supporting Information

Alkali-Metal-Catalyzed Addition of Primary and Secondary Phosphines to Carbodiimides. A General and Efficient Route to Substituted Phosphaguanidines

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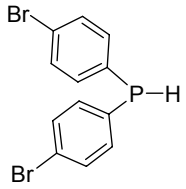
Experimental Section

General Methods. All reactions were carried out under a dry and inert atmosphere using either standard Schlenk techniques or a N_2-filled glovebox. Solvents were distilled from sodium/benzophenone ketyl, and dried over fresh Na. Benzene-d_6, toluene-d_8 and THF-d_8 (all 99+atom % D) were obtained from Acros Organics, which were dried over fresh Na chips for NMR reactions. $(Me_3Si)_2NNa$ and *n*-BuLi were purchased from TCI. $(Me_3Si)_2NLi$, $(Me_3Si)_2NK$, and Me_3SiCH_2Li were purchased from Aldrich. Ph_2PH, $PhPH_2$, and $CyPH_2$ were purchased from TCI. $(4\text{-}MeC_6H_4)_2PH$ and $(3,5\text{-}Me_2C_6H_3)_2PH$ were purchased from Strem. Others phosphines were prepared according to literature.[1,2] $(4\text{-}BrC_6H_4)_2PH$ (new compound) was synthesized analogously.[1] Phosphaguanidines **1a**,[3] **1b**[3] and **1e**[4] are known compounds. All other phosphaguanidines reported in this paper are new compounds.

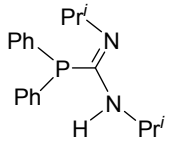
IR spectra were obtained on a Shimadzu IRPrestige-21 spectrophotometer using Nujol mulls between KBr disks. HRMS were recorded on a JEOL JMS-700 instrument operated in EF-FAB$^+$ mode. Samples for NMR spectroscopic measurements were prepared under a dry and oxygen-free argon atmosphere by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a JEOL-AL400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C; 160 MHz for ^{31}P) or a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C). Phosphorus chemical shifts were measured relative to an external 85% aqueous solution of H_3PO_4.

(1) C. A. Busacca, J. C. Lorenz, N.Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.* 2005, **7**, 4277–4280.
(2) Z. Herseczki, I. Gergely, C. Hegedüs, Á. Szöllősy and J. Bakos, *Tetrahedron*: *Asymmetry* 2004, **15**, 1673–1676.
(3) J. Grundy, M. P. Coles and P. B. Hitchcock, *Dalton Trans.* 2003, **25**73–2577.
(4) D. H. M. W. Thewissen and H. P. M. M. Ambrosius, *Recl. Trav. Chim. Pays-Bas* 1980, **99**, 344–346.

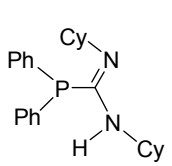


Bis(4-bromophenyl)-phosphine was prepared according to literature[1] via reduction of $(4\text{-}BrC_6H_4)_2POH$ by use of 3eq. DIBAL-H/THF. Colorless solid, isolated yield, 86%. ^{1}H NMR (300 MHz, C_6D_6): δ 4.80 (d, $^1J_{PH}$ = 216.9 Hz, 1H, PH), 6.82–6.87 (m, 4H, C_6H_4), 7.11–7.14 (m, 4H, C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 123.6, 132.0 (d, $^3J_{PC}$ = 6.2 Hz), 133.6 (d, $^1J_{PC}$ = 11.7 Hz), 135.6 (d, $^2J_{PC}$ = 17.9 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –43.5. HRMS Calcd for $[M+H]^+$ $C_{12}H_{10}{}^{79}Br_2P$ 342.8887, Found 342.8895.

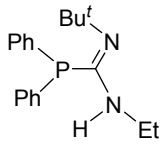
Typical Procedures for Catalytic Addition Reaction of Phosphines to Carbodiimides:
(i) NMR Tube Reaction by Use of $(Me_3Si)_2NK$ as a Catalyst. Under a dry and oxygen-free argon atmosphere, a J. Young valve NMR tube was charged with $(Me_3Si)_2NK$ (3.6 mg, 0.018 mmol), THF-d_8 (0.45 mL), diphenylphosphine (112 mg, 0.60 mmol), N,N'-diisopropylcarbodiimide (76 mg, 0.60 mmol). Formation of **1a** and disappearance of diphenylphosphine were easily monitored by ^{31}P NMR. The conversion of diphenylphosphine was determined by ^{31}P NMR. The reaction was completed within 5 min. No other coupling products were observed.
(ii) Preparative Scale Reaction by Use of $(Me_3Si)_2NK$ as a Catalyst. Under a dry and oxygen-free argon atmosphere, a THF solution (3 mL) of diphenylphosphine (376 mg, 2.02 mmol) was added to a THF solution (2 mL) of $(Me_3Si)_2NK$ (4 mg, 0.02 mmol) in a Schlenk tube. Then N,N'-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. After 5 min of stirring, the solvent was removed under reduced pressure. The residue was extracted with hexane and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in hexane to provide a colorless solid **1a**. It should be noted that this type of phosphaguanidines are very sensitive to oxygen, and must be stored under an inert atmosphere.
(iii) Larger-scale and solvent-free catalytic preparation of 1a. Under a dry and oxygen-free argon atmosphere, $(Me_3Si)_2NK$ (199 mg, 1 mmol) was added to diphenylphosphine (9.31 g, 50 mmol) in a Schlenk tube. After about 10 min of rigorous stirring at room temperature, the mixture became orange that showed the formation of lithium diphenylphosphide. Then N,N'-diisopropylcarbodiimide (6.31 g, 50 mmol) was added to the above reaction mixture. After 0.5 h of rigorous stirring at room temperature, the reaction mixture was directly determined by ^{1}H NMR and ^{31}P NMR, which showed the purity of **1a** was ≥99%. Yield, ≥99%.



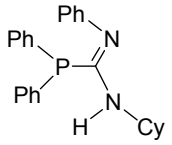
(*Z*)-*N*,*N*′-diisopropyl(diphenylphosphino)formamidine (1a): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3431 (N–H), 1599 (C=N), 1462, 1377, 1173, 1026, 743, 696. ^{1}H NMR (300 MHz, C_6D_6): δ 0.94 (d, J = 6.6 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.23 (d, J = 6.3 Hz, 6H, $CH(C\underline{H}_3)_2$), 3.63 (d, ^3J = 6.3 Hz, 1H, NH), 4.28–4.43 (m, 2H, CH), 7.03–7.05 (m, 6H, C_6H_5), 7.42–7.47 (m, 4H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6): δ 22.5, 25.3, 42.9, 52.2 (d, $^3J_{PC}$ = 35.3 Hz), 129.0 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.3 (d, $^2J_{PC}$ = 19.8 Hz), 135.5 (d, $^1J_{PC}$ = 13.7 Hz), 152.4 (d, $^1J_{PC}$ = 31.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –18.5. HRMS Calcd for $[M+H]^+$ $C_{19}H_{26}N_2P$ 313.1834, Found 313.1853.



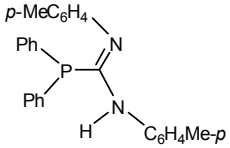
(*Z*)-*N*,*N*′-dicyclohexyl(diphenylphosphino)formamidine (1b): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3431 (N–H), 1599 (C=N), 1461, 1377, 1153, 1027, 742, 695. ^{1}H NMR (300 MHz, C_6D_6): δ 0.92–1.93 (m, 20H, Cy), 3.81 (d, ^3J = 6.9 Hz, 1H, NH), 4.05–4.19 (m, 2H, CH), 7.02–7.13 (m, 6H, C_6H_5), 7.48–7.53 (m, 4H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6): δ 24.6, 25.2, 26.2, 26.3, 32.5, 35.7, 49.1, 60.3 (d, $^3J_{PC}$ = 33.4 Hz), 129.0 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.2 (d, $^2J_{PC}$ = 19.2 Hz), 135.7 (d, $^1J_{PC}$ = 14.9 Hz), 152.4 (d, $^1J_{PC}$ = 31.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –18.1. HRMS Calcd for $[M+H]^+$ $C_{25}H_{34}N_2P$ 393.2460, Found 393.2455.



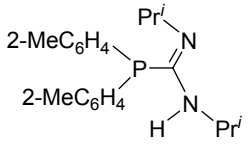
(*Z*)-*N′*-tert-butyl-*N*-ethyl(diphenylphosphino)formamidine (1c): colorless solid, isolated yield, 98%. IR (Nujol, cm^{-1}): ν = 3433 (N–H), 1609 (C=N), 1462, 1377, 1219, 1028, 743, 696. ^{1}H NMR (300 MHz, C_6D_6): δ 1.27 (t, J = 7.2 Hz, 3H, $CH_2C\underline{H}_3$), 1.33 (s, 9H, $C(CH_3)_3$), 3.72–3.80 (m, 3H, NH and $C\underline{H}_2CH_3$), 6.99–7.07 (m, 6H, C_6H_5), 7.42–7.47 (m, 4H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6): δ 17.7, 28.7, 46.9 (d, $^3J_{PC}$ = 36.5 Hz), 52.1, 129.1 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.3 (d, $^2J_{PC}$ = 19.2 Hz), 135.4 (d, $^1J_{PC}$ = 14.3 Hz), 153.8 (d, $^1J_{PC}$ = 33.4 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –16.0. HRMS Calcd for $[M+H]^+$ $C_{19}H_{26}N_2P$ 313.1834, Found 313.1840.



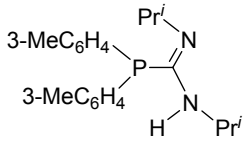
(*Z*)-*N*-cyclohexyl-*N′*-phenyl(diphenylphosphino)formamidine (1d): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3405 (N–H), 1578 (C=N), 1500, 1485, 1458, 1377, 1166, 761, 694. ^{1}H NMR (400 MHz, C_6D_6): δ 0.87–1.94 (m, 10H, Cy), 4.19–4.25 (m, 1H, CH), 4.38 (d, ^3J = 7.2 Hz, 1H, NH), 6.83 (t, J = 7.2 Hz, 1H, C_6H_5), 7.03–7.10 (m, 10H, C_6H_5), 7.44 (t, J = 7.2 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 24.8, 26.2, 32.7, 50.0, 122.2, 123.3 (d, $^4J_{PC}$ = 2.5 Hz), 128.5, 129.0 (d, $^3J_{PC}$ = 6.6 Hz), 129.4, 134.4 (d, $^2J_{PC}$ = 20.6 Hz), 135.2 (d, $^1J_{PC}$ = 15.7 Hz), 151.9 (d, $^3J_{PC}$ = 12.4 Hz), 156.2 (d, $^1J_{PC}$ = 36.3 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –14.5. HRMS Calcd for $[M+H]^+$ $C_{25}H_{28}N_2P$ 387.1990, Found 387.1998.



(*Z*)-(diphenylphosphino)-*N*,*N′*-di-*p*-tolylformamidine (1e): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3410 (N–H), 1615 (C=N), 1602, 1511, 1500, 1464, 1433, 1377, 1306, 1135, 821, 740, 699. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 6.16 (s, 1H, NH), 6.58 (d, J = 7.6 Hz, 2H, C_6H_4), 6.87 (d, J = 8.4 Hz, 2H, C_6H_4), 6.99 (d, J = 8.4 Hz, 2H, C_6H_4), 7.30–7.41 (m, 10H, C_6H_5 and 2H, C_6H_4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 20.9, 118.7, 121.9 (d, $^4J_{PC}$ = 2.5 Hz), 128.7, 128.9 (d, $^3J_{PC}$ = 7.5 Hz), 129.1, 129.5, 131.6, 132.2, 133.82, 133.84 (d, $^1J_{PC}$ = 16.5 Hz), 133.9 (d, $^2J_{PC}$ = 20.6 Hz), 137.6, 147.5 (d, $^3J_{PC}$ = 13.2 Hz), 154.8 (d, $^1J_{PC}$ = 38.7 Hz); ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$): δ –12.6. HRMS Calcd for $[M+H]^+$ $C_{27}H_{26}N_2P$ 409.1834, Found 409.1840.

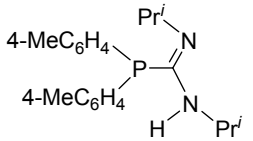


(*Z*)-*N*,*N′*-diisopropyl(di-*o*-tolylphosphino)formamidine (1f): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3443 (N–H), 1594 (C=N), 1455, 1377, 1168, 1088, 966, 763. ^{1}H NMR (300 MHz, C_6D_6): δ 0.93 (d, J = 6.6 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.29 (d, J = 6.0 Hz, 6H, $CH(C\underline{H}_3)_2$), 2.41 (s, 6H, Me), 3.70 (d, ^3J = 6.6 Hz, 1H, NH), 4.32–4.43 (m, 2H, CH), 6.94–7.09 (m, 8H, C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 21.1 (d, $^3J_{PC}$ = 21.7 Hz), 22.4, 25.5, 42.7, 52.8 (d, $^3J_{PC}$ = 37.1 Hz), 126.8, 129.6, 130.6 (d, $^3J_{PC}$ = 4.3 Hz), 133.3, 142.9 (d, $^1J_{PC}$ or $^2J_{PC}$ = 26.0 Hz, 2C), 151.9 (d, $^1J_{PC}$ = 30.3 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –33.5. HRMS Calcd for $[M+H]^+$ $C_{21}H_{30}N_2P$ 341.2147, Found 341.2153.

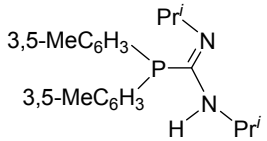


(*Z*)-*N*,*N′*-diisopropyl(di-*m*-tolylphosphino)formamidine (1g): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3429 (N–H), 1599 (C=N), 1462, 1377, 1175, 1119, 777, 696. ^{1}H NMR (400 MHz, C_6D_6): δ 0.85 (d, J =

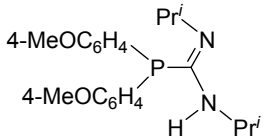
6.4 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.12 (d, J = 6.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.90 (s, 6H, Me), 3.63 (d, J = 6.4 Hz, 1H, NH), 4.16–4.33 (m, 2H, CH), 6.80 (d, J = 7.6 Hz, 2H, C_6H_4), 6.93 (dd, J = 7.6 Hz, J = 7.6 Hz, 2H, C_6H_4), 7.18–7.26 (m, 4H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 21.5, 22.8, 25.6, 43.0, 52.3 (d, $^3J_{PC}$ = 35.5 Hz), 129.0 (d, $^3J_{PC}$ = 6.6 Hz), 130.2, 131.3 (d, $^2J_{PC}$ = 17.3 Hz), 135.0 (d, $^2J_{PC}$ = 23.1 Hz), 135.5 (d, $^1J_{PC}$ = 14.0 Hz), 138.5 (d, $^3J_{PC}$ = 7.4 Hz), 152.6 (d, $^1J_{PC}$ = 32.1 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −18.3. HRMS Calcd for $[M+H]^+$ $C_{21}H_{30}N_2P$ 341.2147, Found 341.2150.



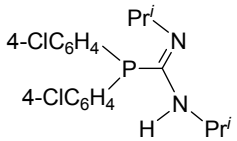
(*Z*)-*N*,*N*′-diisopropyl(di-*p*-tolylphosphino)formamidine (1h): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3429 (N–H), 1599 (C=N), 1460, 1377, 1175, 1020, 806, 721. ^{1}H NMR (300 MHz, C_6D_6): δ 0.89 (d, J = 6.3 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.16 (d, J = 6.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.94 (s, 6H, Me), 3.67 (d, J = 6.0 Hz, 1H, NH), 4.23–4.35 (m, 2H, CH), 6.85 (d, J = 7.5 Hz, 4H, C_6H_4), 7.33 (dd, J = 7.5 Hz, J = 7.8 Hz, 4H, C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 21.2, 22.6, 25.4, 42.8, 52.0 (d, $^3J_{PC}$ = 34.6 Hz), 129.9 (d, $^3J_{PC}$ = 6.8 Hz), 132.3 (d, $^1J_{PC}$ = 12.4 Hz), 134.4 (d, $^2J_{PC}$ = 19.2 Hz), 139.3, 153.0 (d, $^1J_{PC}$ = 31.5 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −20.0. HRMS Calcd for $[M+H]^+$ $C_{21}H_{30}N_2P$ 341.2147, Found 341.2173.



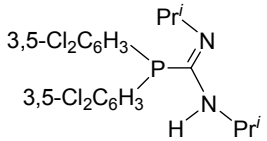
(*Z*)-(bis(3,5-dimethylphenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1i): colorless solid, isolated yield, 98%. IR (Nujol, cm^{-1}): ν = 3428 (N–H), 1599 (C=N), 1462, 1377, 1175, 1123, 847, 692. ^{1}H NMR (400 MHz, C_6D_6): δ 1.02 (d, J = 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.30 (d, J = 6.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 2.04 (s, 12H, Me), 3.89 (d, J = 6.8 Hz, 1H, NH), 4.34–4.50 (m, 2H, CH), 6.75 (s, 2H, C_6H_3), 7.26 (d, J = 8.0 Hz, 4H, C_6H_3); ^{13}C NMR (100 MHz, C_6D_6): δ 21.4, 22.8, 25.6, 43.0, 52.2 (d, $^3J_{PC}$ = 34.6 Hz), 131.2, 132.1 (d, $^2J_{PC}$ = 19.8 Hz), 135.4 (d, $^1J_{PC}$ = 14.0 Hz), 138.4 (d, $^3J_{PC}$ = 7.4 Hz), 153.0 (d, $^1J_{PC}$ = 33.0 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −18.0. HRMS Calcd for $[M+H]^+$ $C_{23}H_{34}N_2P$ 369.2460, Found 369.2453.



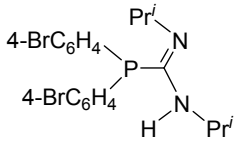
(*Z*)-(bis(4-methoxyphenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1j): colorless solid, isolated yield, 99%. IR (Nujol, cm^{-1}): ν = 3427 (N–H), 1597 (C=N), 1498, 1459, 1377, 1285, 1249, 1177, 1092, 1035, 827, 798. ^{1}H NMR (300 MHz, C_6D_6): δ 1.01 (d, J = 6.6 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.24 (d, J = 6.3 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 3.26 (s, 6H, CH_3O), 3.79 (d, J = 6.6 Hz, 1H, NH), 4.30–4.49 (m, 2H, CH), 6.73 (d, J = 8.7 Hz, 4H, C_6H_4), 7.43 (dd, J = 8.1 Hz, J = 7.5 Hz, 4H, C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 22.6, 25.4, 42.8, 51.8 (d, $^3J_{PC}$ = 34.1 Hz), 54.7, 114.8 (d, $^3J_{PC}$ = 8.0 Hz), 126.4 (d, $^1J_{PC}$ = 11.2 Hz), 135.9 (d, $^2J_{PC}$ = 21.1 Hz), 153.6 (d, $^1J_{PC}$ = 33.0 Hz), 161.1; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −21.2. HRMS Calcd for $[M+H]^+$ $C_{21}H_{30}N_2O_2P$ 373.2045, Found 373.2050.



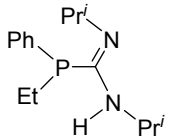
(*Z*)-(bis(4-chlorophenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1k): colorless solid, isolated yield, 98%. IR (Nujol, cm^{-1}): ν = 3431 (N–H), 1599 (C=N), 1479, 1383, 1173, 1099, 1015, 818, 743. ^{1}H NMR (400 MHz, C_6D_6): δ 0.91 (d, J = 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.23 (d, J = 6.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 3.43 (d, J = 5.6 Hz, 1H, NH), 4.24–4.29 (m, 2H, CH), 7.00 (d, J = 8.0 Hz, 4H, C_6H_4), 7.09 (dd, J = 8.0 Hz, J = 7.6 Hz, 4H, C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ 22.3, 25.3, 43.0, 52.3 (d, $^3J_{PC}$ = 35.3 Hz), 129.4 (d, $^3J_{PC}$ = 6.8 Hz), 133.5 (d, $^1J_{PC}$ = 15.5 Hz), 135.4 (d, $^2J_{PC}$ = 20.4 Hz), 136.1, 151.3 (d, $^1J_{PC}$ = 31.5 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −21.1. HRMS Calcd for $[M+H]^+$ $C_{19}H_{24}Cl_2N_2P$ 381.1054, Found 381.1050.



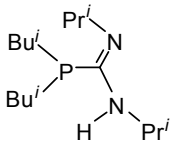
(*Z*)-(bis(3,5-dichlorophenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1l): colorless solid, isolated yield, 98%. IR (Nujol, cm^{-1}): ν = 3436 (N–H), 1604 (C=N), 1555, 1457, 1378, 1135, 860, 799, 676. ^{1}H NMR (300 MHz, C_6D_6): δ 0.86 (d, J = 6.6 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.16 (d, J = 6.0 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 3.37 (d, J = 6.3 Hz, 1H, NH), 4.08–4.16 (m, 2H, CH), 7.01 (s, 2H, C_6H_3), 7.21 (d, J = 7.8 Hz, 4H, C_6H_3); ^{13}C NMR (75 MHz, C_6D_6): δ 22.1, 25.1, 43.3, 52.7 (d, $^3J_{PC}$ = 37.1 Hz), 130.1, 131.7 (d, $^2J_{PC}$ = 20.4 Hz), 136.2 (d, $^3J_{PC}$ = 7.4 Hz), 138.4 (d, $^1J_{PC}$ = 21.6 Hz), 149.2 (d, $^1J_{PC}$ = 32.8 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −18.1. HRMS Calcd for $[M+H]^+$ $C_{19}H_{22}Cl_4N_2P$ 449.0275, Found 449.0283.



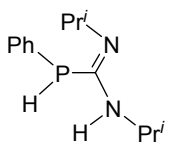
(*Z*)-(bis(4-bromophenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1m): colorless solid, isolated yield, 97%. IR (Nujol, cm^{-1}): ν = 3421 (N–H), 1601 (C=N), 1462, 1378, 1173, 1068, 1010, 814, 725. ^{1}H NMR (400 MHz, C_6D_6): δ 0.90 (d, J = 6.0 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.22 (d, J = 6.4 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 3.42 (d, J = 6.8 Hz, 1H, NH), 4.23–4.29 (m, 2H, CH), 7.01 (dd, J = 8.4 Hz, J = 6.8 Hz, 4H, C_6H_4), 7.15 (d, J = 8.4 Hz, 4H, C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ 22.5, 25.5, 43.2, 52.5 (d, $^3J_{PC}$ = 36.3 Hz), 124.4, 132.3 (d, $^3J_{PC}$ = 6.6 Hz), 134.0 (d, $^1J_{PC}$ = 15.7 Hz), 135.5 (d, $^2J_{PC}$ = 20.6 Hz), 151.1 (d, $^1J_{PC}$ = 32.1 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −21.2. HRMS Calcd for $[M+H]^+$ $C_{19}H_{24}{}^{79}Br_2N_2P$ 469.0044, Found 469.0052.



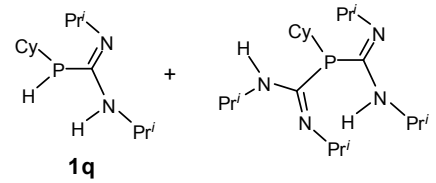
(*Z*)-(ethyl(phenyl)phosphino)-*N*,*N*′-diisopropylformamidine (1n): colorless liquid, isolated yield, 96%. IR (Nujol, cm^{-1}): ν = 3432 (N–H), 1598 (C=N), 1464, 1377, 1174, 1118, 1028, 742, 697. ^{1}H NMR (400 MHz, C_6D_6): δ 0.94 (d, J = 6.4 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.99 (d, J = 6.8 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.01–1.17 (m, 3H, CH$_2$C$\underline{H}_3$), 1.27 (d, J = 6.0 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.36 (d, J = 6.0 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.70–1.79 (m, 2H, C$\underline{H}_2$CH$_3$), 3.54 (d, J = 6.4 Hz, 1H, NH), 4.25–4.30 (m, 1H, CH), 4.51–4.56 (m, 1H, CH), 7.05–7.15 (m, 3H, C_6H_5), 7.39–7.43 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 10.7 (d, $^2J_{PC}$ = 16.5 Hz), 18.6 (d, $^1J_{PC}$ = 14.0 Hz), 22.5, 22.8, 25.8, 26.0, 42.6, 52.0 (d, $^3J_{PC}$ = 36.3 Hz), 128.8 (d, $^3J_{PC}$ = 8.2 Hz), 128.9, 132.7 (d, $^2J_{PC}$ = 18.1 Hz), 137.0 (d, $^1J_{PC}$ = 17.3 Hz), 154.4 (d, $^1J_{PC}$ = 34.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −29.0. HRMS Calcd for $[M+H]^+$ $C_{15}H_{26}N_2P$ 265.1834, Found 265.1840.



(*Z*)-1,1-diisobutyl-*N*,*N*′-diisopropylphosphinecarboximidamide (1o): colorless liquid, isolated yield, 95%. IR (Nujol, cm^{-1}): ν = 3447 (N–H), 1595 (C=N), 1462, 1380, 1366, 1173. ^{1}H NMR (300 MHz, C_6D_6): δ 0.93 (d, J = 6.6 Hz, 6H, CH_3), 0.98 (d, J = 6.6 Hz, 6H, CH_3), 1.04 (d, J = 6.3 Hz, 6H, CH_3), 1.12–1.24 (m, 4H, CH_2), 1.26 (d, J = 6.0 Hz, 6H, CH_3), 1.39–1.70 (m, 2H, CH), 3.53 (d, J = 6.9 Hz, 1H, NH), 4.23–4.29 (m, 1H, CH), 4.52–4.59 (m, 1H, CH); ^{13}C NMR (75 MHz, C_6D_6): δ 22.7, 24.0 (d, $^3J_{PC}$ = 9.9 Hz), 24.5 (d, $^3J_{PC}$ = 8.0 Hz), 25.9, 27.1 (d, $^2J_{PC}$ = 14.2 Hz), 37.7 (d, $^1J_{PC}$ = 16.7 Hz), 41.9, 51.4 (d, $^3J_{PC}$ = 38.9 Hz), 156.1 (d, $^1J_{PC}$ = 36.5 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ −56.9. HRMS Calcd for $[M+H]^+$ $C_{15}H_{34}N_2P$ 273.2460, Found 273.2472.

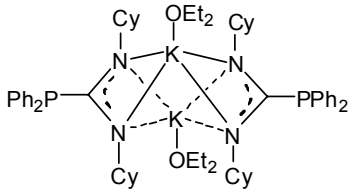


^{i}PrN=C(PHPh)(NH^{i}Pr) (1p): colorless liquid, isolated yield, 97%. IR (Nujol, cm^{-1}): ν = 3414 (N–H), 1601 (C=N), 1462, 1377, 721. ^{1}H NMR (400 MHz, C_6D_6): δ 0.97 (d, J = 6.4 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.08 (d, J = 6.4 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.24 (d, J = 6.4 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.36 (d, J = 6.4 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 4.28–4.39 (m, 4H, PH, NH and CH), 6.99–7.06 (m, 3H, C_6H_5), 7.51–7.55 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 22.6, 25.6 (d, $^{4}J_{PC}$ = 8.2 Hz), 43.1, 52.9 (d, $^{3}J_{PC}$ = 37.1 Hz), 129.3 (d, $^{3}J_{PC}$ = 6.6 Hz), 129.6, 133.4 (d, $^{1}J_{PC}$ = 18.1 Hz), 134.1 (d, $^{2}J_{PC}$ = 19.0 Hz), 151.5 (d, $^{1}J_{PC}$ = 36.2 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –35.0. HRMS Calcd for $[M+H]^+$ $C_{13}H_{22}N_2P$ 237.1521, Found 237.1526.



1q

^{i}PrN=C(PHCy)(NH^{i}Pr) (**1q**) and **(^{i}PrN=CNH^{i}Pr)$_2$(PCy):** colorless liquid. The reaction products were not isolated. The yield of **1q** (80%) was determined by ^{31}P NMR. The bis-addition product (^{i}PrN=CNH^{i}Pr)$_2$(PCy) (15%) was also formed. **1q**: HRMS Calcd for $[M+H]^+$ $C_{13}H_{28}N_2P$ 243.1990, Found 243.1999. (^{i}PrN=CNH^{i}Pr)$_2$(PCy): HRMS Calcd for $[M+H]^+$ $C_{20}H_{42}N_4P$ 369.3147, Found 369.31485. ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –46.4, –47.2.



Isolation of the potassium phosphaguanidinate [Ph$_2$PC(NCy)$_2$K(OEt$_2$)]$_2$ (2)
Under a dry and oxygen-free argon atmosphere, a THF solution (3 mL) of diphenylphosphine (372 mg, 2.00 mmol) was added to a THF solution (5 mL) of $(Me_3Si)_2NK$ (399 mg, 2.00 mmol) in a Schlenk tube. Then N,N'-dicyclohexylcarbodiimide (413 mg, 2.00 mmol) was added to the above reaction mixture. After 1 h of stirring, the solvent was removed under reduced pressure. The residue was extracted with ether and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **2** as light yellow crystalline powder (969 mg, 0.96 mmol, 96% yield). Single crystals of **2** suitable for X-ray analysis were grown in ether at room temperature overnight. IR (Nujol, cm^{-1}): ν = 2122, 1582, 1471, 1377, 1339, 1076, 979, 740. ^{1}H NMR (400 MHz, C_6D_6): δ 1.01 (t, J = 7.2 Hz, 12H, (C$\underline{H}_3$CH$_2$)$_2$O), 1.21–1.86 (br, 40H, CH$_2$(Cy)), 3.11–3.16 (m, 4H, CH(Cy)), 3.28 (q, J = 7.2 Hz, 8H, (CH$_3$C$\underline{H}_2$)$_2$O), 6.76–6.80 (m, 4H, C_6H_5), 7.03–7.09 (m, 8H, C_6H_5), 7.65 (br, 8H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ 15.8, 25.0, 26.0, 35.5, 55.8, 66.0, 129.0 (d, $^{3}J_{PC}$ = 6.6 Hz), 129.3, 134.3 (d, $^{1}J_{PC}$ = 18.9 Hz), 135.9 (d, $^{2}J_{PC}$ = 16.5 Hz), 139.8 (d, $^{1}J_{PC}$ = 34.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): δ –14.8, –18.0, –20.6. Anal. Calcd for $C_{58}H_{84}K_2N_4O_2P_2$: C, 69.01; H, 8.39; N, 5.55. Found: C, 68.96; H, 8.18; N, 5.38.

NMR tube reaction of the potassium phosphaguanidinate [Ph$_2$PC(NCy)$_2$K(OEt$_2$)]$_2$ (2) with Ph$_2$PH: A mixture of **2** (101 mg, 0.1 mmol) and diphenylphosphine (37 mg, 0.2 mmol) in THF-d_8 was added to an NMR tube under a dry and oxygen-free argon atmosphere. The reaction was monitored immediately by ^{31}P NMR spectroscopy. The ^{31}P NMR shift for diphenylphosphine disappeared completely, and CyN=C(PPh$_2$)(NHCy) (**1b**) and KPPh$_2$ were formed almost quantitatively.

X-ray Crystallographic Study
Single crystals of **2** suitable for X-ray analysis were grown in ether at room temperature overnight. The crystal for X-ray analysis was manipulated in the glovebox under a microscope and was sealed in a thin-walled glass capillary. Data collection was performed at –110 °C on a Bruker CCD APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structure was solved by use of SHELXTL program. The methylene carbon atoms in the OEt$_2$ ligand are disordered, and are treated with 50% occupancy. Due to this disorder problem, the hydrogen atoms of the ether molecule could not be placed at the calculated positions. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms except ether H atoms were placed at the calculated positions and were included in

the structure calculation without further refinement of the parameters. CCDC-606651 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data, processing parameters, and structural data of **2** are given below.

STable 1. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	C58 H84 K2 N4 O2 P2	
Formula weight	1009.43	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.1009(12) Å	α= 90°.
	b = 19.529(2) Å	β= 112.539(2)°.
	c = 14.3917(15) Å	γ = 90°.
Volume	2881.6(5) $Å^3$	
Z	2	
Density (calculated)	1.163 Mg/m^3	
Absorption coefficient	0.263 mm^{-1}	
F(000)	1088	
Crystal size	0.55 x 0.45 x 0.3 mm^3	
Theta range for data collection	1.85 to 25.05°.	
Index ranges	-13<=h<=7, -23<=k<=22, -17<=l<=17	
Reflections collected	14823	
Independent reflections	5091 [R(int) = 0.0259]	
Completeness to theta = 25.05°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.92 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5091 / 0 / 305	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1626	
R indices (all data)	R1 = 0.0689, wR2 = 0.1716	
Largest diff. peak and hole	0.801 and -0.474 e.$Å^{-3}$	

STable 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	761(1)	679(1)	-122(1)	44(1)
P(1)	1234(1)	729(1)	3273(1)	34(1)
N(1)	-490(2)	532(1)	1298(2)	40(1)
N(2)	1374(2)	-71(1)	1624(1)	41(1)
O(1)	1664(6)	1823(2)	-652(3)	167(2)
C(1)	674(2)	336(1)	1952(2)	33(1)
C(2)	-1377(2)	965(1)	1561(2)	37(1)
C(3)	-1329(3)	1705(1)	1243(2)	51(1)
C(4)	-2338(3)	2153(2)	1435(3)	63(1)
C(5)	-3691(3)	1872(2)	913(3)	58(1)
C(6)	-3769(3)	1143(2)	1249(3)	55(1)
C(7)	-2757(3)	694(1)	1058(2)	47(1)
C(8)	2618(2)	-370(1)	2243(2)	35(1)
C(9)	2548(3)	-1145(1)	2048(2)	43(1)
C(10)	3827(3)	-1509(1)	2603(2)	50(1)
C(11)	4924(3)	-1200(2)	2368(2)	53(1)
C(12)	5020(3)	-427(2)	2555(2)	47(1)
C(13)	3723(3)	-75(1)	1984(2)	40(1)
C(14)	1410(2)	9(1)	4130(2)	36(1)
C(15)	1768(3)	150(2)	5156(2)	43(1)
C(16)	1750(3)	-355(2)	5822(2)	49(1)
C(17)	1357(3)	-1005(2)	5482(2)	52(1)
C(18)	993(3)	-1154(2)	4473(2)	53(1)
C(19)	1027(3)	-650(1)	3804(2)	43(1)
C(20)	2891(2)	1020(1)	3501(2)	35(1)
C(21)	2998(3)	1542(1)	2875(2)	45(1)
C(22)	4190(3)	1835(1)	3022(2)	52(1)
C(23)	5311(3)	1618(2)	3797(2)	54(1)
C(24)	5224(3)	1103(2)	4427(2)	49(1)
C(25)	4028(3)	809(1)	4285(2)	41(1)
C(26)	2801(9)	1525(4)	-1061(7)	79(2)
C(27)	1983(5)	1262(4)	-1951(4)	133(2)
C(28)	2474(12)	2421(7)	-14(10)	128(4)
C(29)	1693(7)	2709(3)	385(4)	137(2)
C(30)	1583(11)	1904(6)	-1658(8)	108(3)
C(31)	933(10)	2485(5)	-510(8)	102(3)
H(2)	-1127	952	2292	45
H(3A)	-1486	1718	532	62
H(3B)	-465	1889	1611	62
H(4A)	-2132	2178	2153	76
H(4B)	-2301	2613	1194	76
H(5A)	-3925	1880	191	70
H(5B)	-4308	2156	1066	70
H(6A)	-4636	962	882	66
H(6B)	-3611	1139	1960	66
H(7A)	-2795	235	1304	56
H(7B)	-2976	664	339	56
H(8)	2794	-285	2954	42
H(9A)	1883	-1341	2250	51
H(9B)	2286	-1225	1332	51
H(10A)	4038	-1481	3322	60
H(10B)	3737	-1989	2416	60
H(11A)	4778	-1289	1670	64
H(11B)	5741	-1414	2785	64
H(12A)	5283	-340	3269	56
H(12B)	5681	-237	2343	56

H(13A)	3506	-123	1267	47
H(13B)	3808	410	2142	47
H(15)	2022	591	5392	51
H(16)	2004	-253	6502	59
H(17)	1336	-1345	5929	62
H(18)	724	-1595	4241	64
H(19)	788	-757	3127	52
H(21)	2254	1696	2350	54
H(22)	4238	2182	2594	63
H(23)	6112	1816	3894	65
H(24)	5973	951	4949	58
H(25)	3984	467	4720	49

STable 3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	49(1)	47(1)	39(1)	-2(1)	21(1)	-8(1)
P(1)	33(1)	40(1)	28(1)	-3(1)	12(1)	2(1)
N(1)	34(1)	55(1)	30(1)	-5(1)	11(1)	9(1)
N(2)	38(1)	53(1)	30(1)	-4(1)	12(1)	10(1)
O(1)	353(7)	50(2)	157(3)	-25(2)	162(4)	-46(3)
C(1)	35(1)	38(1)	27(1)	-2(1)	13(1)	0(1)
C(2)	34(1)	50(2)	29(1)	-2(1)	13(1)	7(1)
C(3)	45(2)	49(2)	64(2)	-5(1)	26(2)	-1(1)
C(4)	59(2)	49(2)	85(2)	-5(2)	31(2)	7(2)
C(5)	48(2)	59(2)	64(2)	-1(2)	19(2)	17(2)
C(6)	35(2)	64(2)	67(2)	-4(2)	21(1)	6(1)
C(7)	37(2)	48(2)	56(2)	-2(1)	18(1)	4(1)
C(8)	35(1)	40(1)	31(1)	-4(1)	14(1)	4(1)
C(9)	42(2)	43(2)	48(2)	-8(1)	23(1)	-2(1)
C(10)	52(2)	42(2)	60(2)	3(1)	26(2)	10(1)
C(11)	45(2)	53(2)	63(2)	0(1)	23(2)	14(1)
C(12)	36(2)	54(2)	53(2)	-3(1)	19(1)	1(1)
C(13)	43(2)	41(1)	38(1)	-1(1)	20(1)	3(1)
C(14)	29(1)	48(2)	33(1)	0(1)	16(1)	3(1)
C(15)	36(1)	58(2)	35(1)	-2(1)	14(1)	-4(1)
C(16)	38(2)	76(2)	34(1)	7(1)	13(1)	-4(1)
C(17)	46(2)	66(2)	52(2)	18(2)	28(1)	1(2)
C(18)	56(2)	49(2)	67(2)	1(1)	37(2)	-6(1)
C(19)	45(2)	49(2)	42(2)	-6(1)	24(1)	-5(1)
C(20)	37(1)	36(1)	33(1)	-5(1)	15(1)	1(1)
C(21)	44(2)	43(2)	47(2)	5(1)	16(1)	3(1)
C(22)	58(2)	41(2)	64(2)	8(1)	29(2)	-2(1)
C(23)	42(2)	53(2)	69(2)	-8(2)	22(2)	-10(1)
C(24)	35(2)	58(2)	49(2)	-6(1)	11(1)	-1(1)
C(25)	39(2)	48(2)	36(1)	-1(1)	15(1)	-1(1)
C(27)	93(4)	207(7)	124(4)	-8(4)	68(4)	-19(4)
C(29)	195(6)	120(4)	104(4)	13(3)	66(4)	66(4)

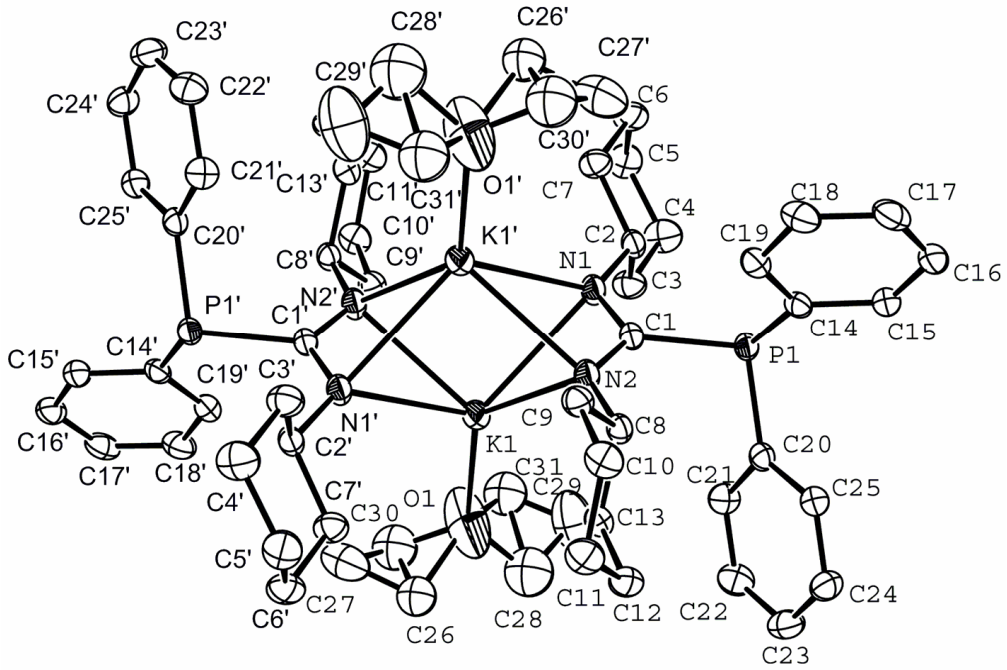
STable 4. Bond lengths [Å] and angles [°] for **2**.

K(1)-O(1)	2.676(3)	K(1)-N(1)	2.891(2)
K(1)-N(2)	2.759(2)	K(1)-C(1)	3.095(2)
K(1)-N(2)#1	2.788(2)	K(1)-C(1)#1	3.192(2)
K(1)-N(1)#1	2.857(2)	K(1)-K(1)#1	3.2357(12)

P(1)-C(14)	1.831(3)	N(2)-K(1)-C(1)#1	106.98(6)
P(1)-C(20)	1.831(3)	N(2)#1-K(1)-C(1)#1	24.29(6)
P(1)-C(1)	1.921(2)	N(1)#1-K(1)-C(1)#1	24.62(6)
N(1)-C(1)	1.331(3)	N(1)-K(1)-C(1)#1	107.34(6)
N(1)-C(2)	1.454(3)	C(1)-K(1)-C(1)#1	118.08(5)
N(1)-K(1)#1	2.857(2)	O(1)-K(1)-K(1)#1	169.53(12)
N(2)-C(1)	1.319(3)	N(2)-K(1)-K(1)#1	54.73(5)
N(2)-C(8)	1.448(3)	N(2)#1-K(1)-K(1)#1	53.91(5)
N(2)-K(1)#1	2.788(2)	N(1)#1-K(1)-K(1)#1	56.23(5)
O(1)-C(30)	1.424(11)	N(1)-K(1)-K(1)#1	55.25(5)
O(1)-C(28)	1.544(13)	C(1)-K(1)-K(1)#1	60.51(5)
O(1)-C(31)	1.580(11)	C(1)#1-K(1)-K(1)#1	57.56(5)
O(1)-C(26)	1.688(9)	C(14)-P(1)-C(20)	106.11(11)
C(1)-K(1)#1	3.192(2)	C(14)-P(1)-C(1)	105.68(11)
C(2)-C(7)	1.516(4)	C(20)-P(1)-C(1)	102.84(11)
C(2)-C(3)	1.523(4)	C(1)-N(1)-C(2)	123.6(2)
C(3)-C(4)	1.527(4)	C(1)-N(1)-K(1)#1	91.95(14)
C(4)-C(5)	1.503(5)	C(2)-N(1)-K(1)#1	135.09(16)
C(5)-C(6)	1.515(4)	C(1)-N(1)-K(1)	85.93(14)
C(6)-C(7)	1.532(4)	C(2)-N(1)-K(1)	133.07(16)
C(8)-C(13)	1.524(3)	K(1)#1-N(1)-K(1)	68.52(5)
C(8)-C(9)	1.537(4)	C(1)-N(2)-C(8)	125.2(2)
C(9)-C(10)	1.514(4)	C(1)-N(2)-K(1)	91.79(14)
C(10)-C(11)	1.510(4)	C(8)-N(2)-K(1)	128.15(15)
C(11)-C(12)	1.529(4)	C(1)-N(2)-K(1)#1	95.30(15)
C(12)-C(13)	1.521(4)	C(8)-N(2)-K(1)#1	129.21(15)
C(14)-C(19)	1.380(4)	K(1)-N(2)-K(1)#1	71.36(5)
C(14)-C(15)	1.400(3)	C(30)-O(1)-C(28)	108.4(7)
C(15)-C(16)	1.380(4)	C(30)-O(1)-C(31)	101.8(7)
C(16)-C(17)	1.372(4)	C(28)-O(1)-C(31)	61.0(6)
C(17)-C(18)	1.380(4)	C(30)-O(1)-C(26)	56.5(5)
C(18)-C(19)	1.388(4)	C(28)-O(1)-C(26)	97.2(7)
C(20)-C(25)	1.394(3)	C(31)-O(1)-C(26)	144.7(5)
C(20)-C(21)	1.395(4)	C(30)-O(1)-K(1)	119.9(5)
C(21)-C(22)	1.381(4)	C(28)-O(1)-K(1)	131.2(5)
C(22)-C(23)	1.382(4)	C(31)-O(1)-K(1)	112.2(4)
C(23)-C(24)	1.382(4)	C(26)-O(1)-K(1)	103.0(3)
C(24)-C(25)	1.387(4)	N(2)-C(1)-N(1)	117.8(2)
C(26)-C(27)	1.355(10)	N(2)-C(1)-P(1)	125.74(18)
C(26)-C(30)	1.491(13)	N(1)-C(1)-P(1)	116.32(17)
C(27)-C(30)	1.445(12)	N(2)-C(1)-K(1)	63.00(12)
C(28)-C(29)	1.334(13)	N(1)-C(1)-K(1)	68.68(13)
C(28)-C(31)	1.586(15)	P(1)-C(1)-K(1)	138.61(11)
C(29)-C(31)	1.315(11)	N(2)-C(1)-K(1)#1	60.41(13)
		N(1)-C(1)-K(1)#1	63.43(13)
O(1)-K(1)-N(2)	135.61(12)	P(1)-C(1)-K(1)#1	159.29(11)
O(1)-K(1)-N(2)#1	115.72(12)	K(1)-C(1)-K(1)#1	61.92(5)
N(2)-K(1)-N(2)#1	108.64(5)	N(1)-C(2)-C(7)	109.5(2)
O(1)-K(1)-N(1)#1	119.18(9)	N(1)-C(2)-C(3)	111.6(2)
N(2)-K(1)-N(1)#1	91.86(6)	C(7)-C(2)-C(3)	109.4(2)
N(2)#1-K(1)-N(1)#1	47.37(6)	C(2)-C(3)-C(4)	112.1(2)
O(1)-K(1)-N(1)	128.24(9)	C(5)-C(4)-C(3)	111.2(3)
N(2)-K(1)-N(1)	47.27(6)	C(4)-C(5)-C(6)	110.6(3)
N(2)#1-K(1)-N(1)	90.57(6)	C(5)-C(6)-C(7)	110.2(3)
N(1)#1-K(1)-N(1)	111.48(5)	C(2)-C(7)-C(6)	113.0(2)
O(1)-K(1)-C(1)	127.55(9)	N(2)-C(8)-C(13)	111.4(2)
N(2)-K(1)-C(1)	25.20(6)	N(2)-C(8)-C(9)	108.3(2)
N(2)#1-K(1)-C(1)	108.92(7)	C(13)-C(8)-C(9)	108.51(19)
N(1)#1-K(1)-C(1)	110.89(7)	C(10)-C(9)-C(8)	113.2(2)
N(1)-K(1)-C(1)	25.39(6)	C(11)-C(10)-C(9)	111.6(2)
O(1)-K(1)-C(1)#1	113.94(10)	C(10)-C(11)-C(12)	111.3(2)

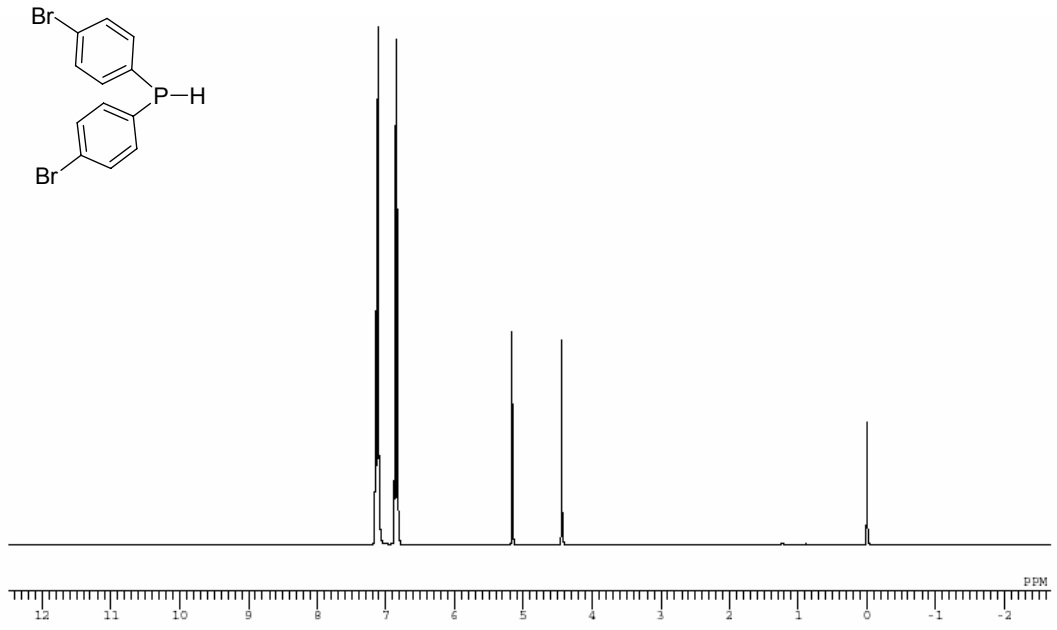
C(13)-C(12)-C(11)	111.3(2)	C(23)-C(24)-C(25)	120.5(3)
C(12)-C(13)-C(8)	112.4(2)	C(24)-C(25)-C(20)	121.0(3)
C(19)-C(14)-C(15)	117.9(2)	C(27)-C(26)-C(30)	60.8(6)
C(19)-C(14)-P(1)	123.20(19)	C(27)-C(26)-O(1)	98.1(6)
C(15)-C(14)-P(1)	118.3(2)	C(30)-C(26)-O(1)	52.8(5)
C(16)-C(15)-C(14)	121.2(3)	C(26)-C(27)-C(30)	64.2(6)
C(17)-C(16)-C(15)	120.0(3)	C(29)-C(28)-O(1)	104.3(9)
C(16)-C(17)-C(18)	119.7(3)	C(29)-C(28)-C(31)	52.7(6)
C(17)-C(18)-C(19)	120.4(3)	O(1)-C(28)-C(31)	60.6(6)
C(14)-C(19)-C(18)	120.8(3)	C(31)-C(29)-C(28)	73.5(7)
C(25)-C(20)-C(21)	117.6(2)	O(1)-C(30)-C(27)	107.1(8)
C(25)-C(20)-P(1)	126.0(2)	O(1)-C(30)-C(26)	70.7(6)
C(21)-C(20)-P(1)	116.1(2)	C(27)-C(30)-C(26)	55.0(6)
C(22)-C(21)-C(20)	121.1(3)	C(29)-C(31)-O(1)	103.3(7)
C(21)-C(22)-C(23)	120.7(3)	C(29)-C(31)-C(28)	53.8(6)
C(24)-C(23)-C(22)	119.0(3)	O(1)-C(31)-C(28)	58.4(6)

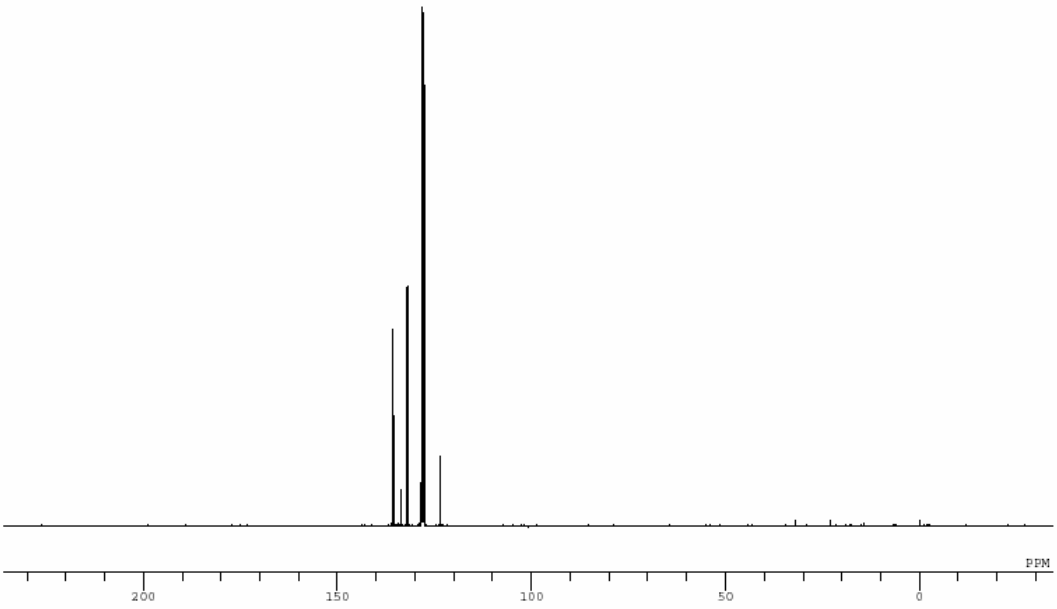
Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

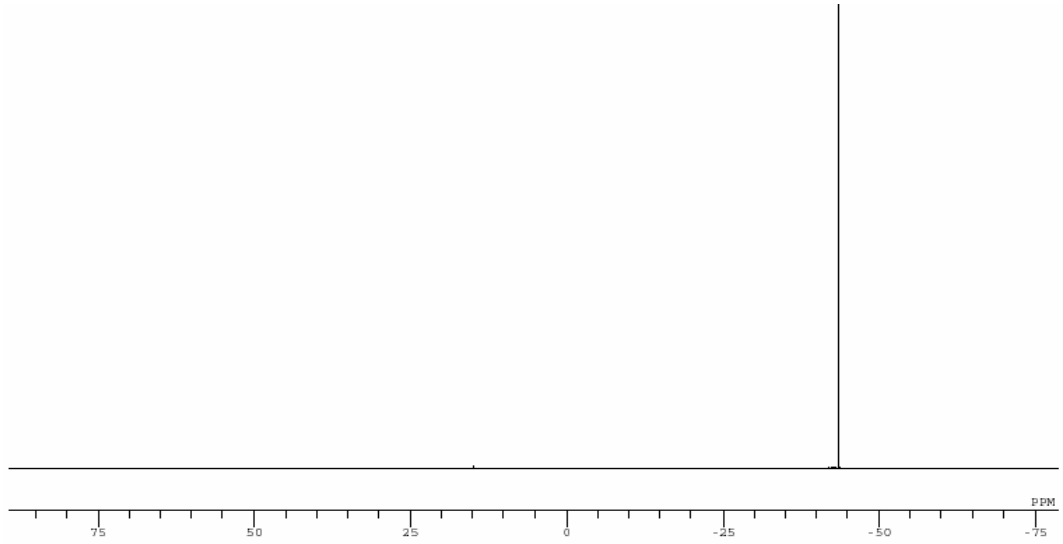


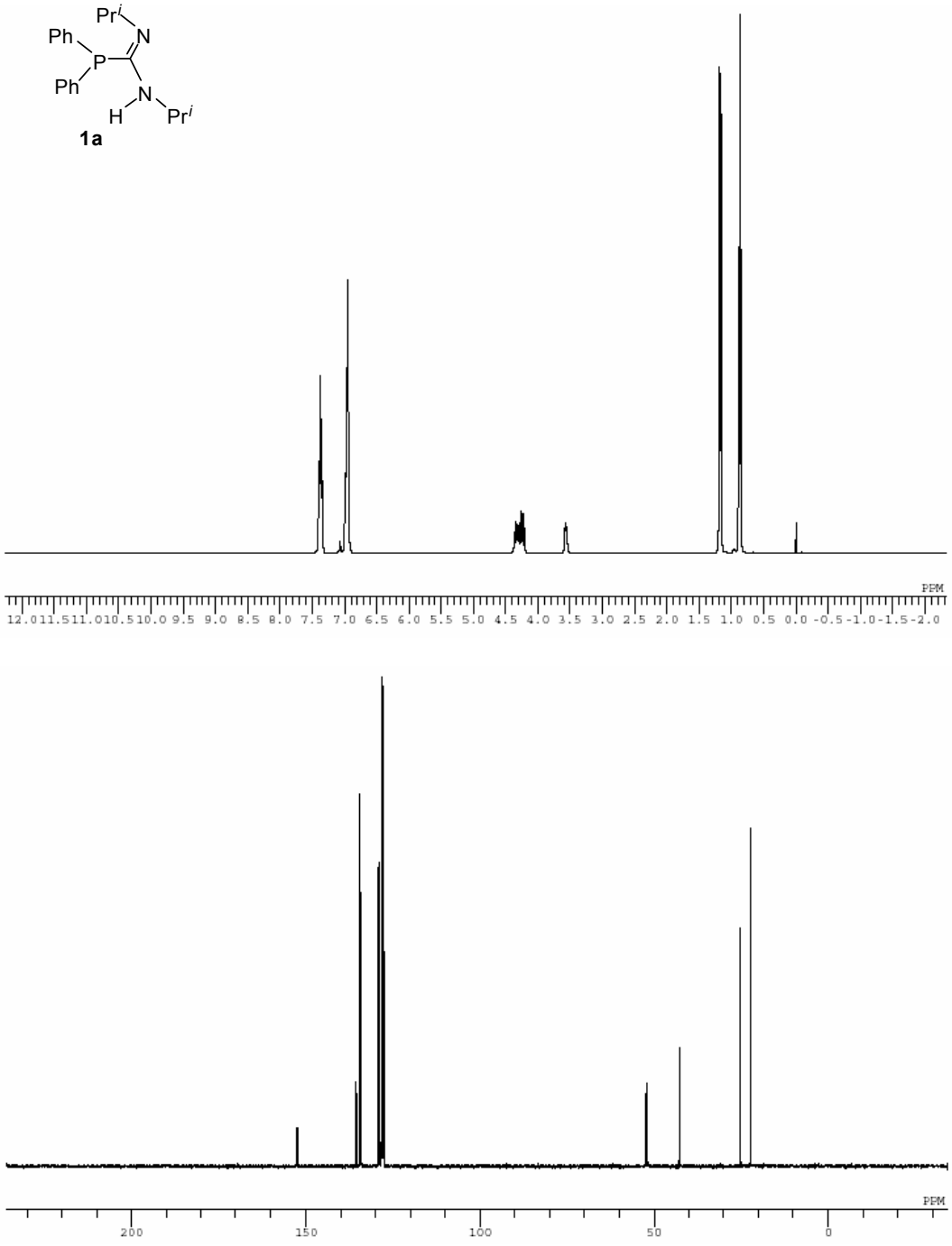
SFigure 1. ORTEP drawing of **2.**

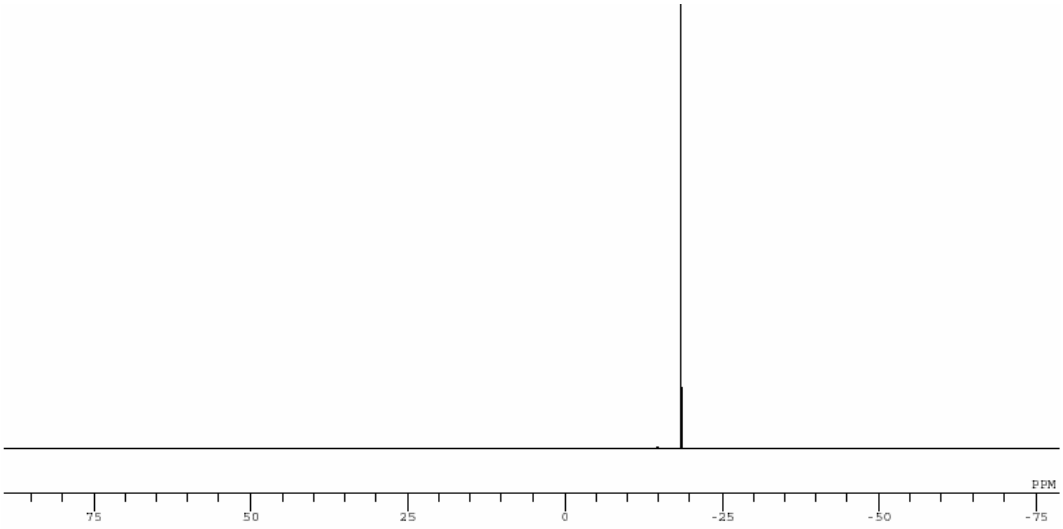
Scanned ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of all compounds:

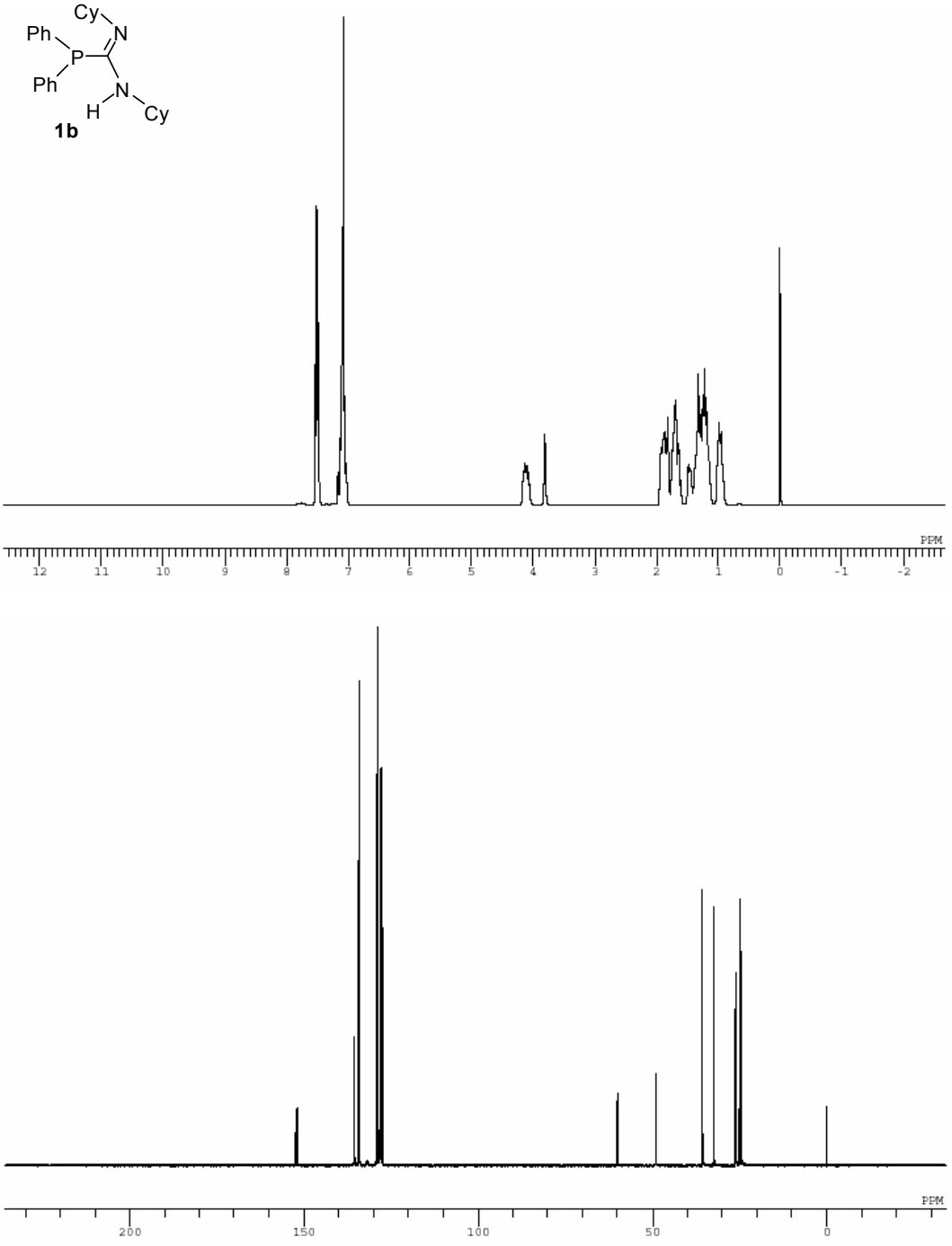


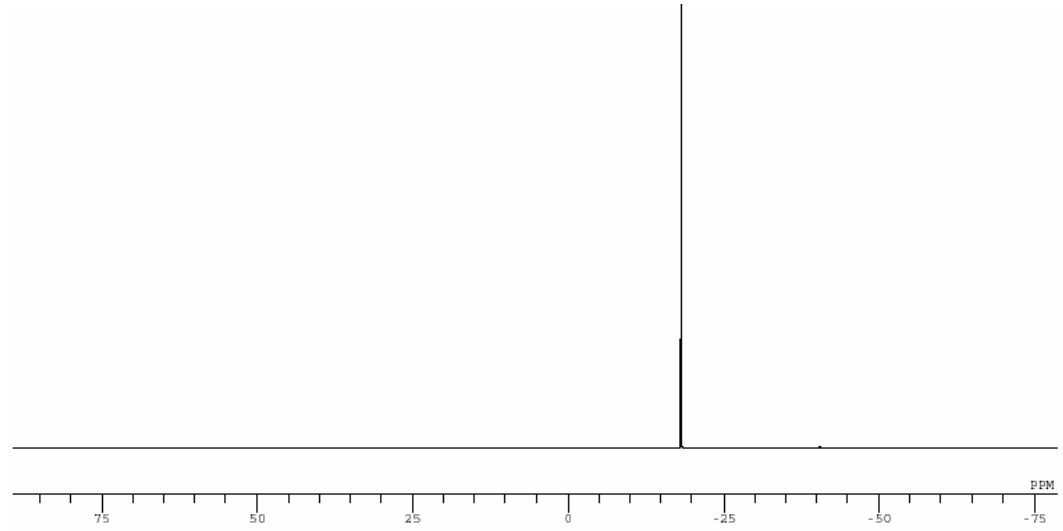


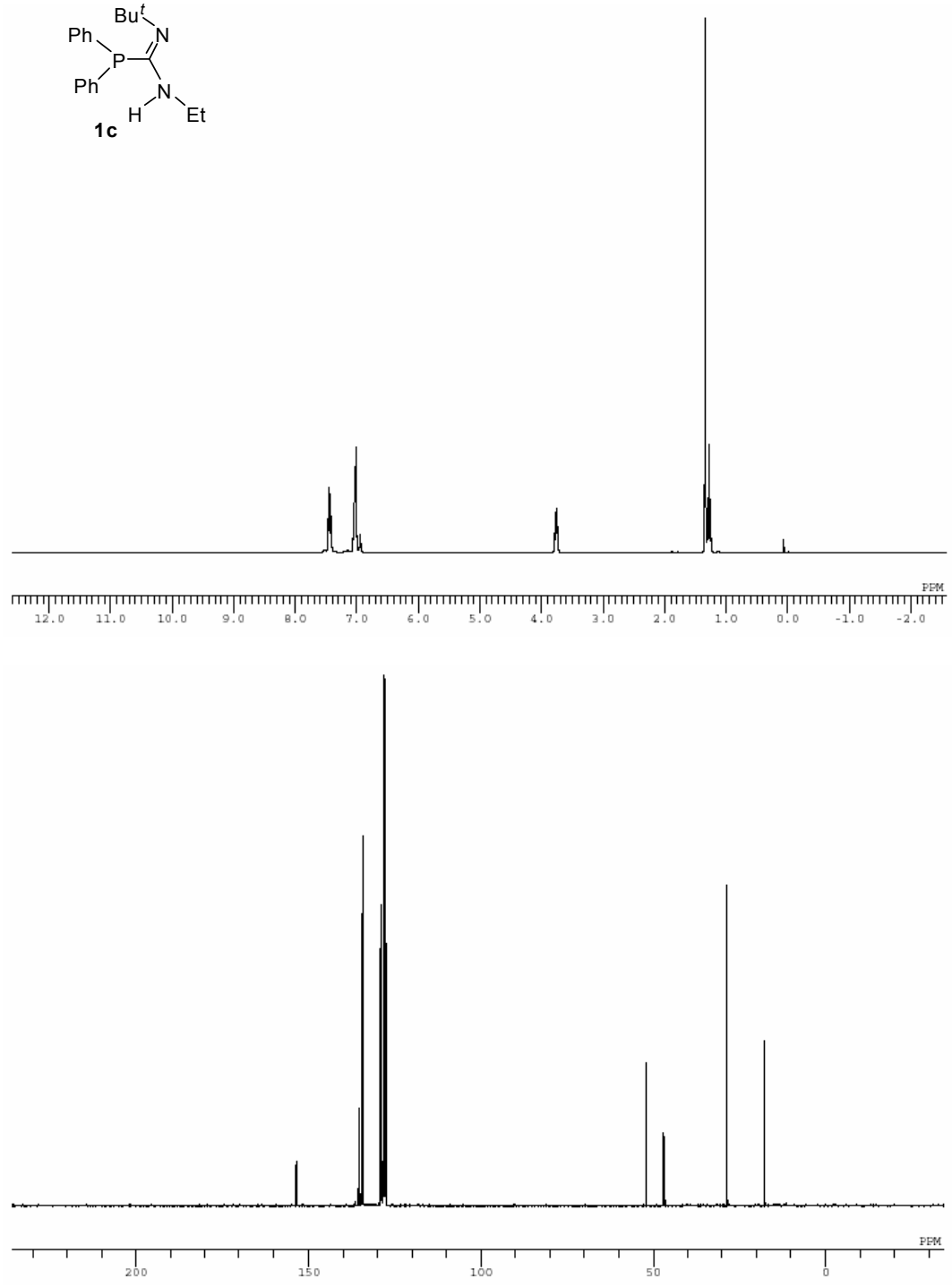


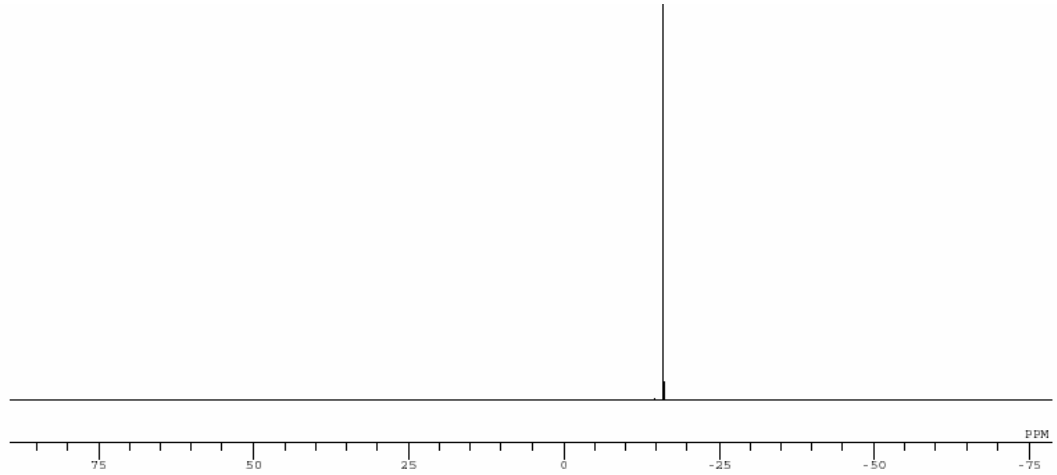


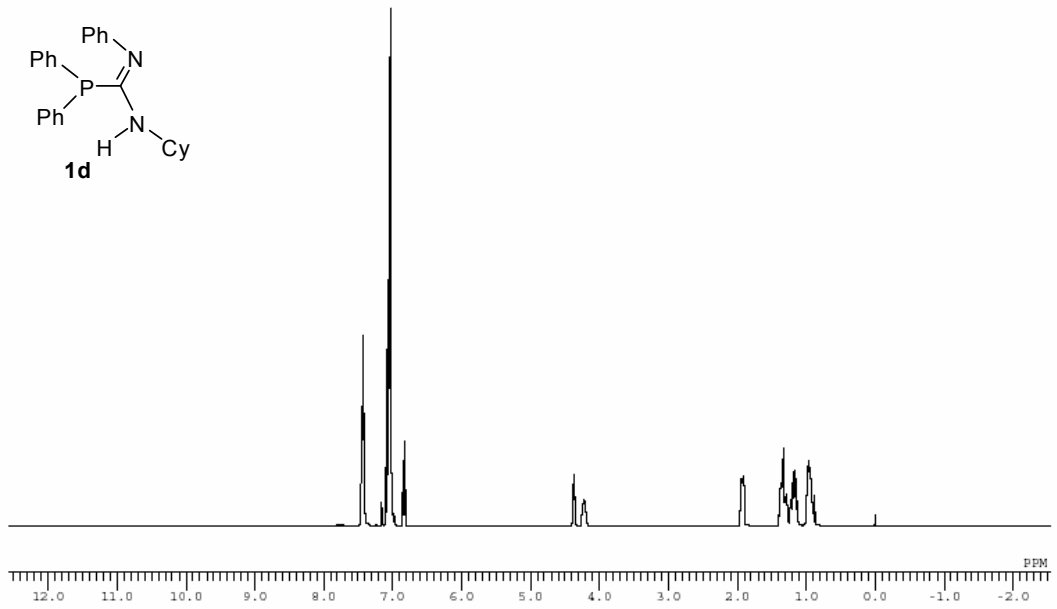


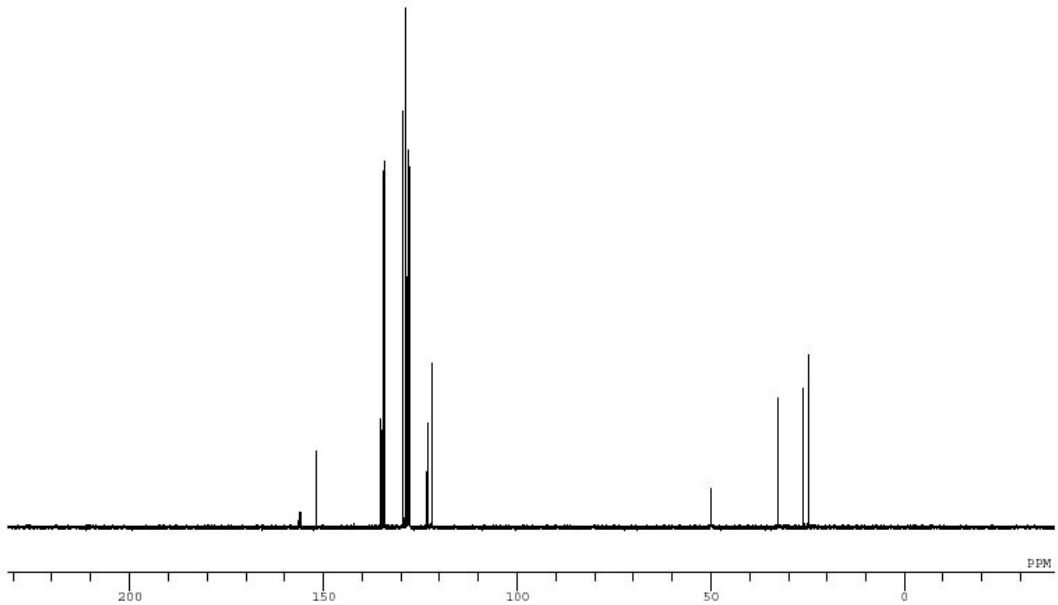


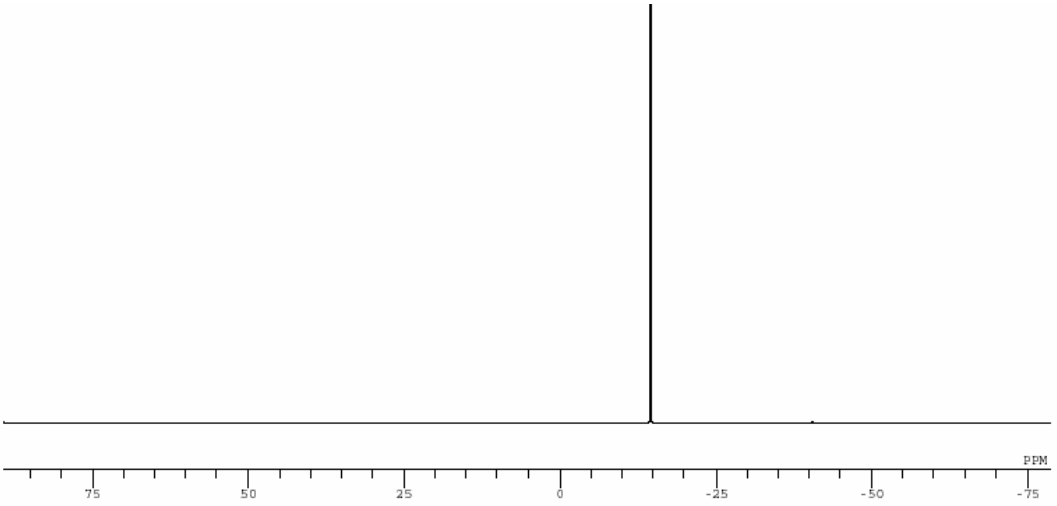


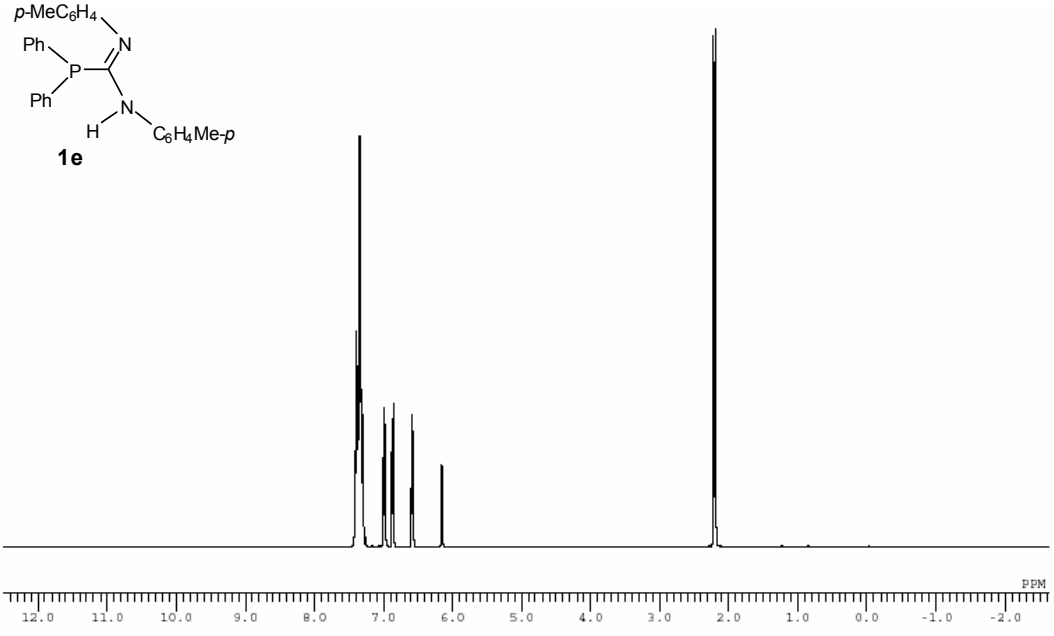


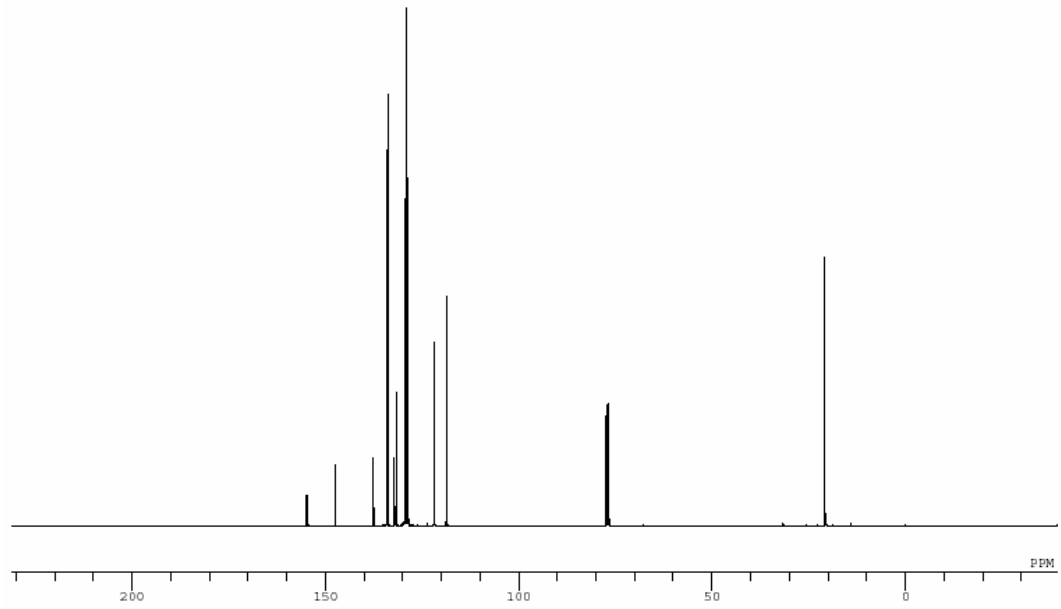


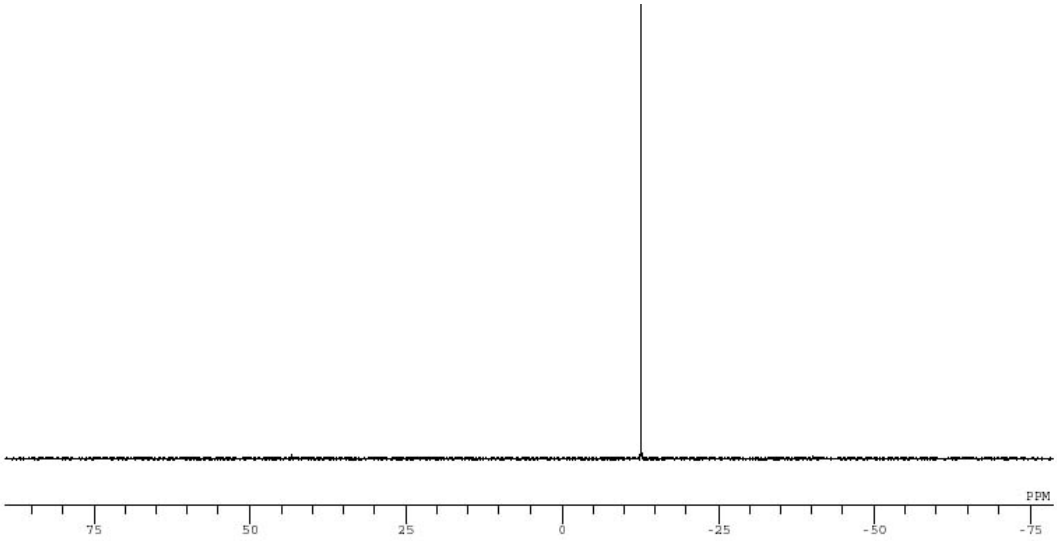


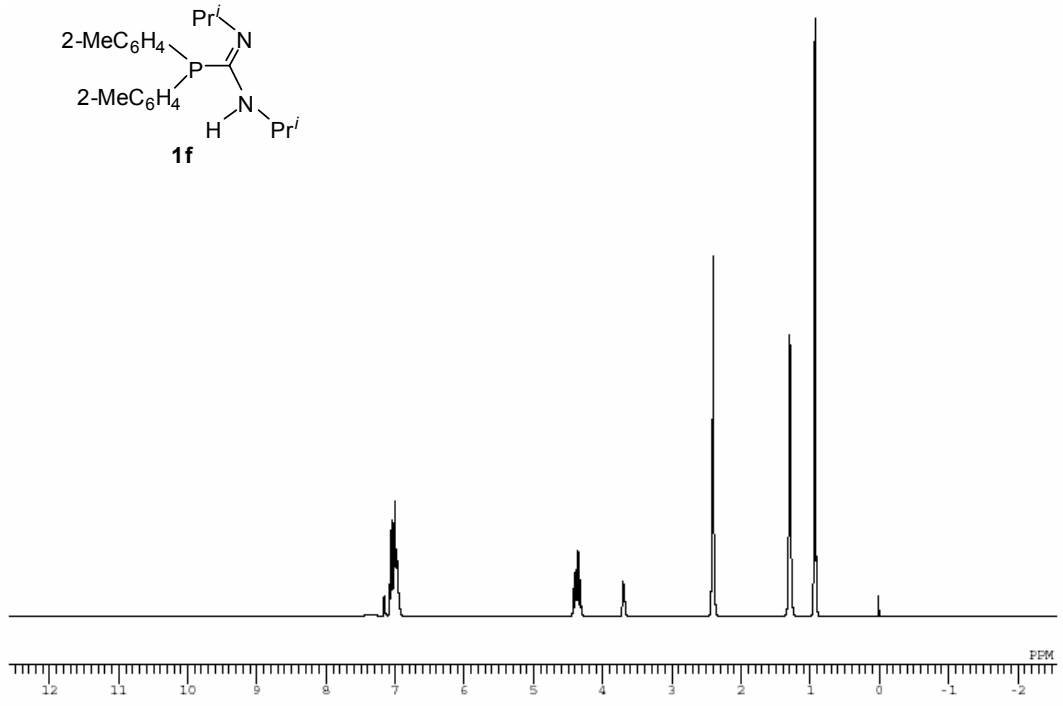












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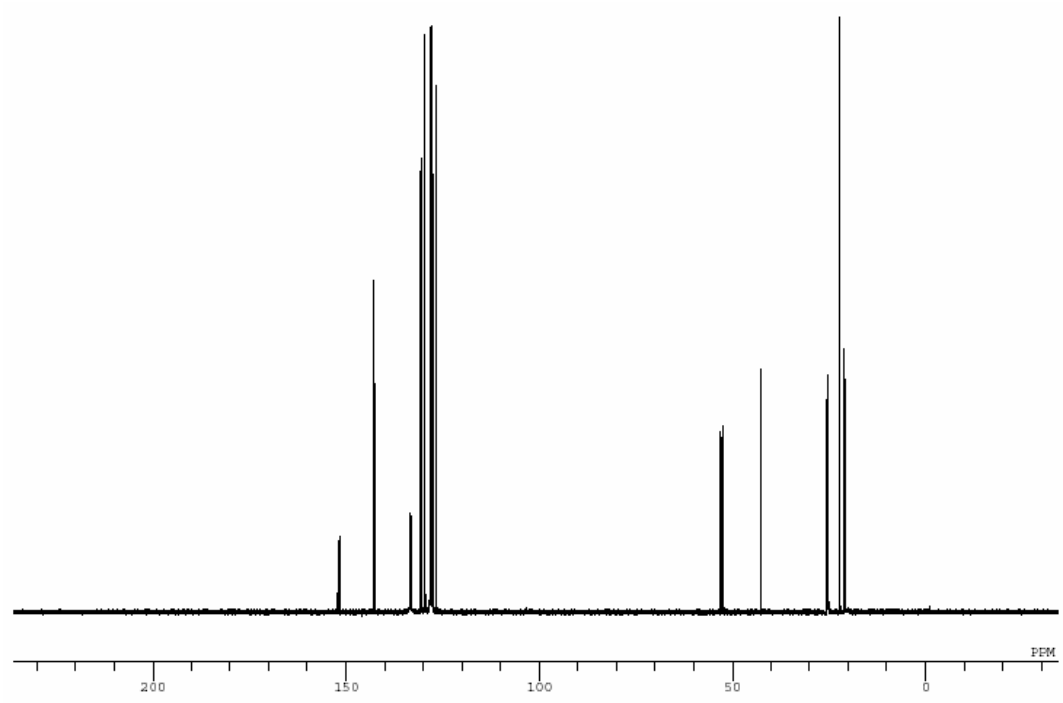

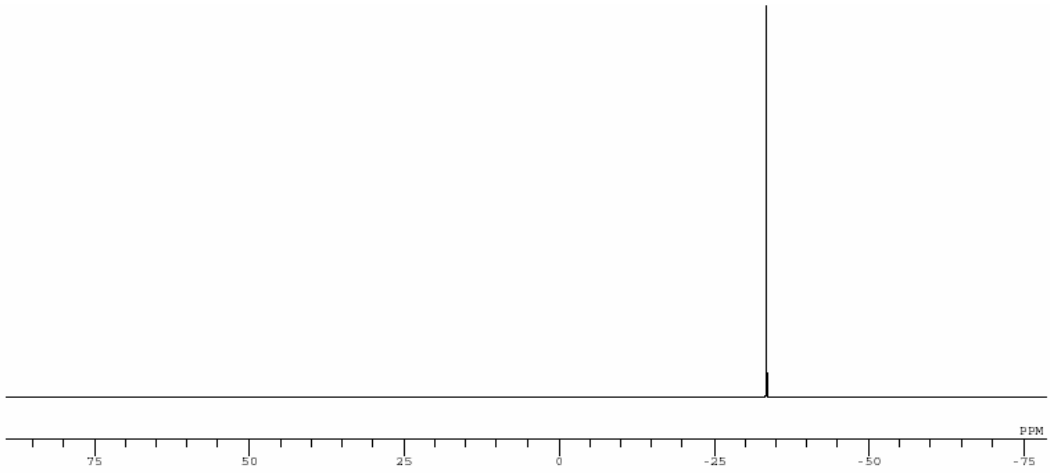

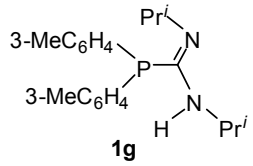

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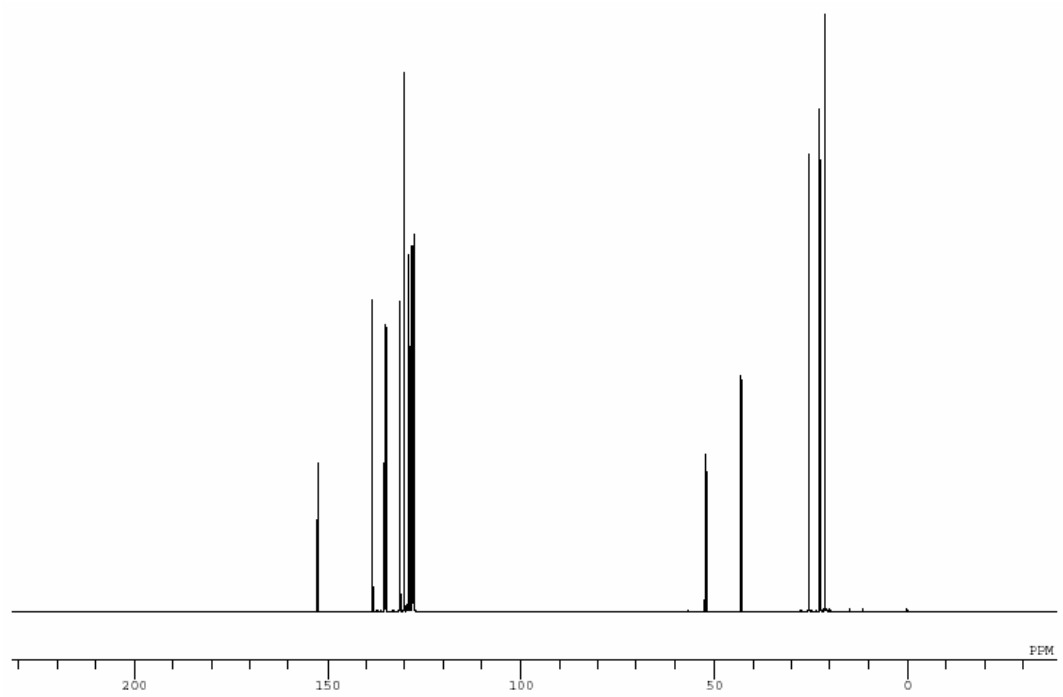

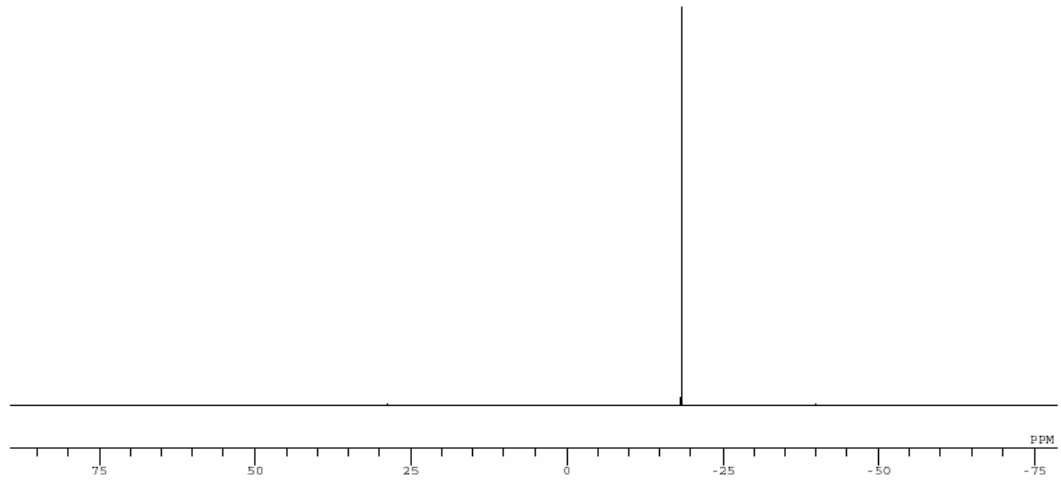

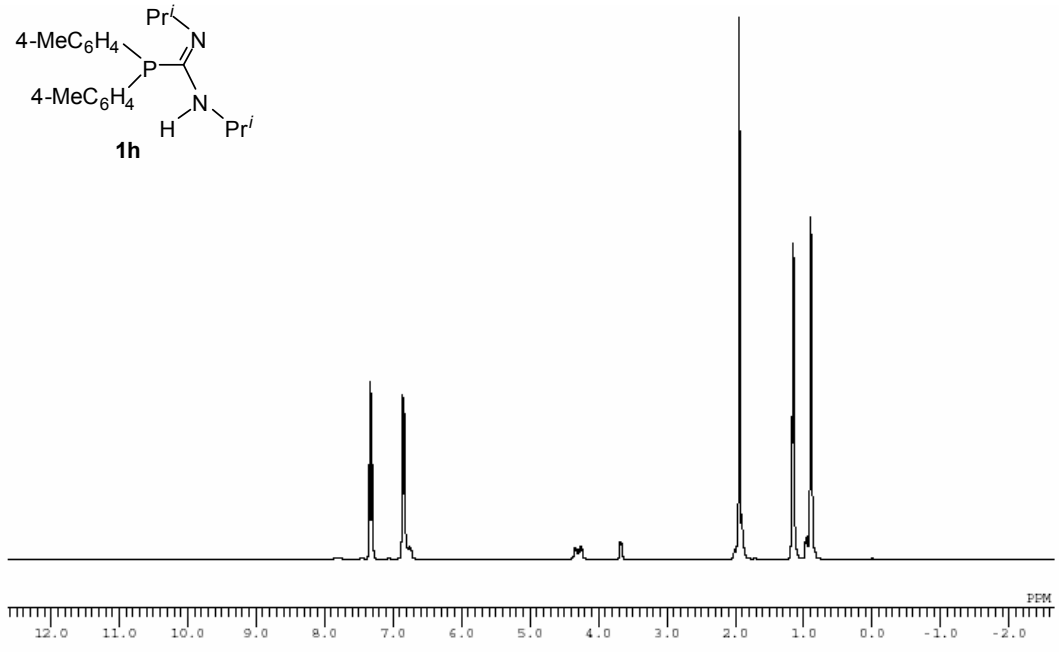
Pr^i
N
4-MeC$_6$H$_4$
P
4-MeC$_6$H$_4$
N
H
Pr^i
PPM
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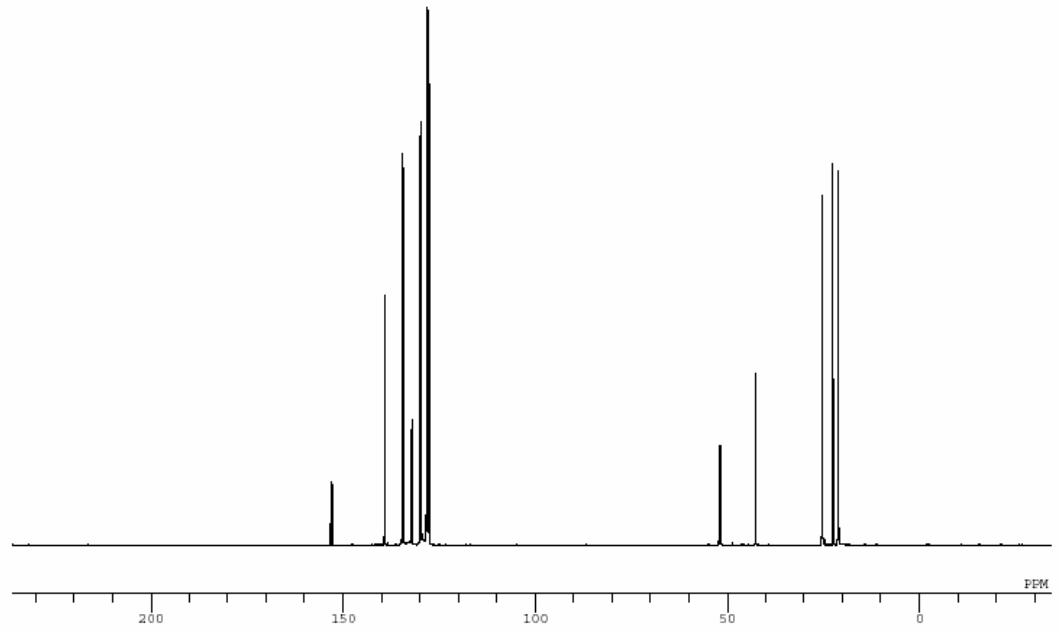
1h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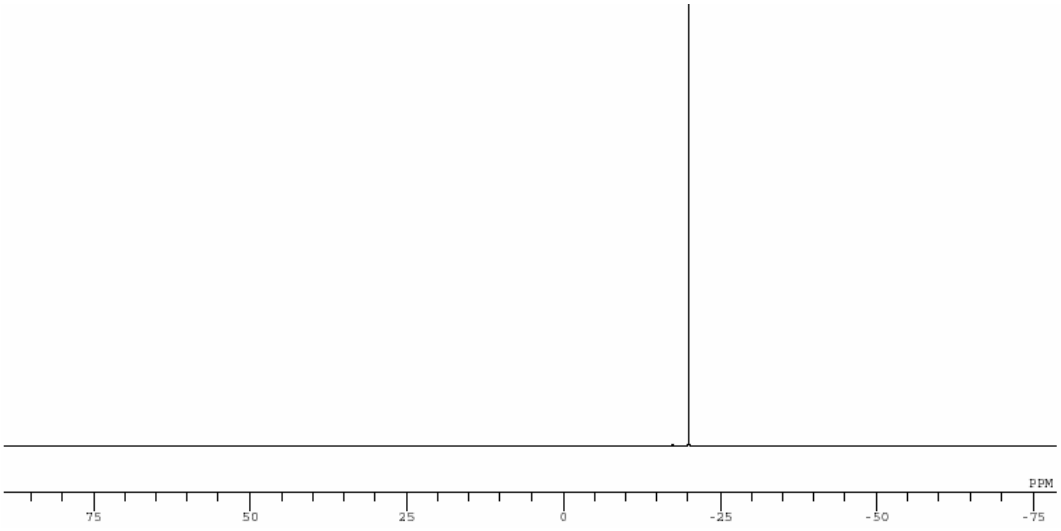
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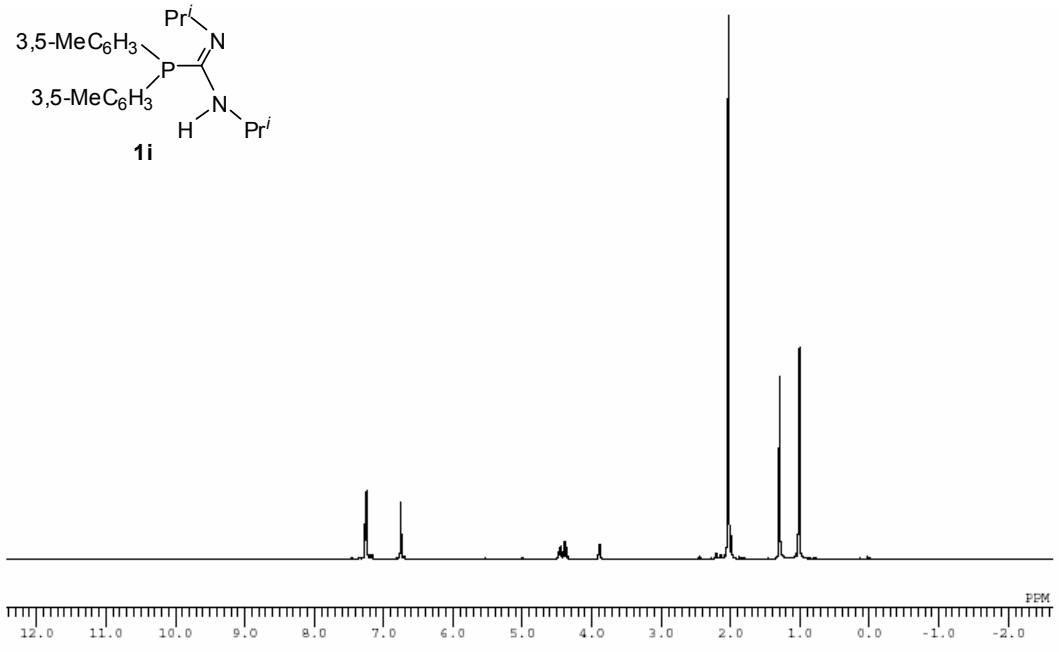

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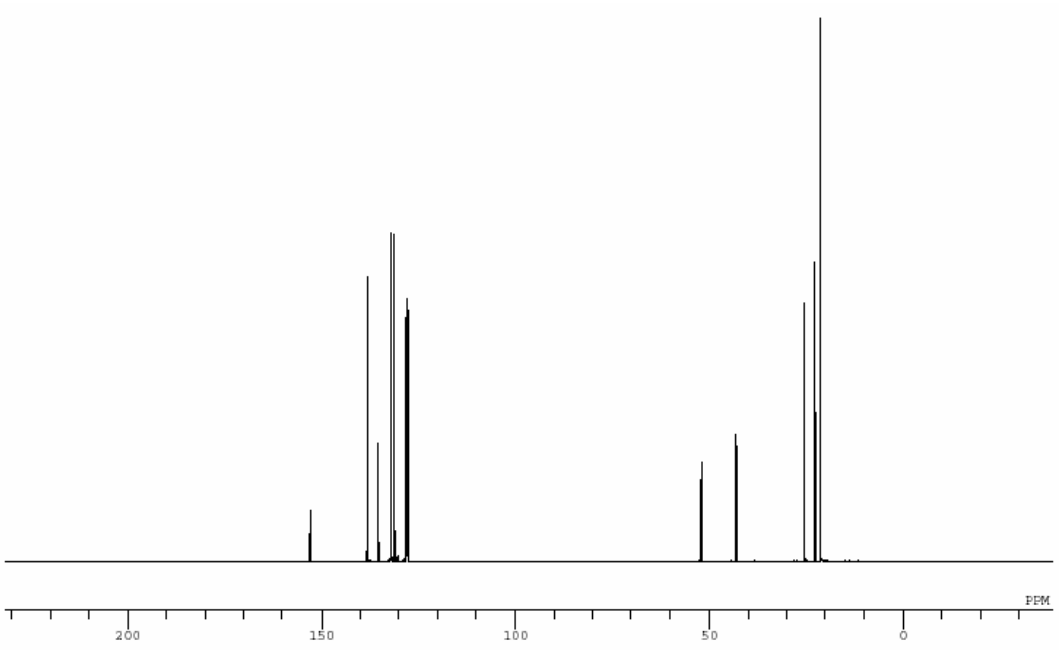

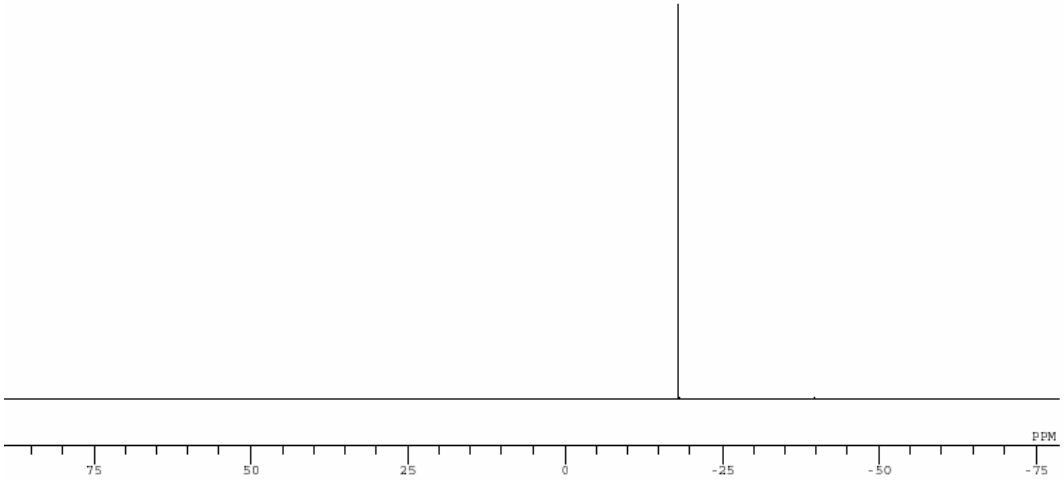

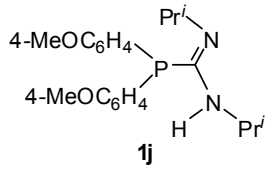

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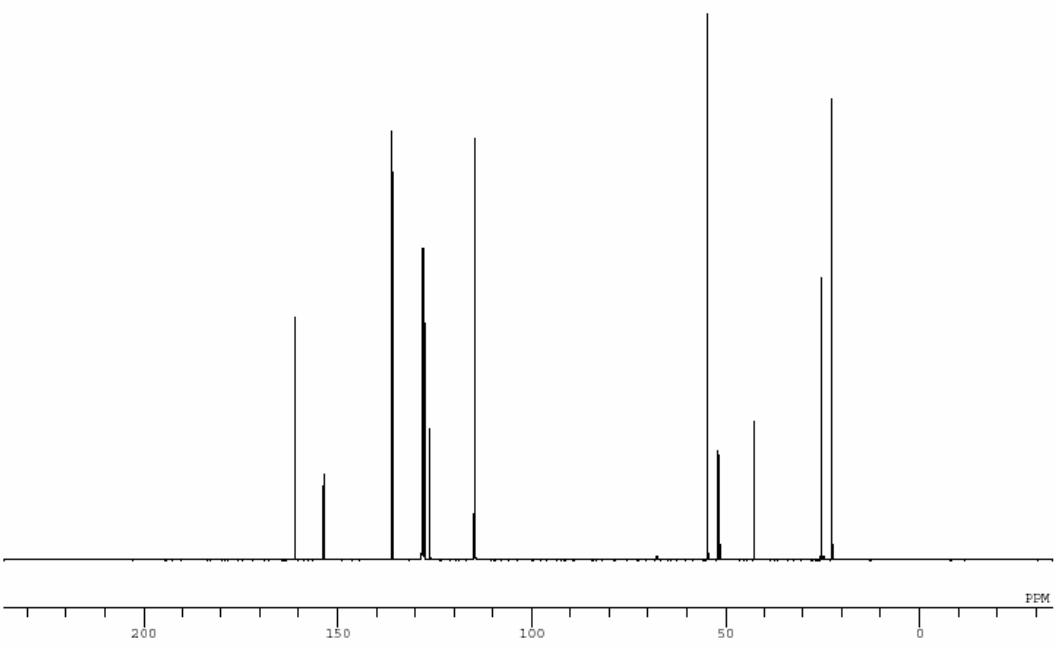

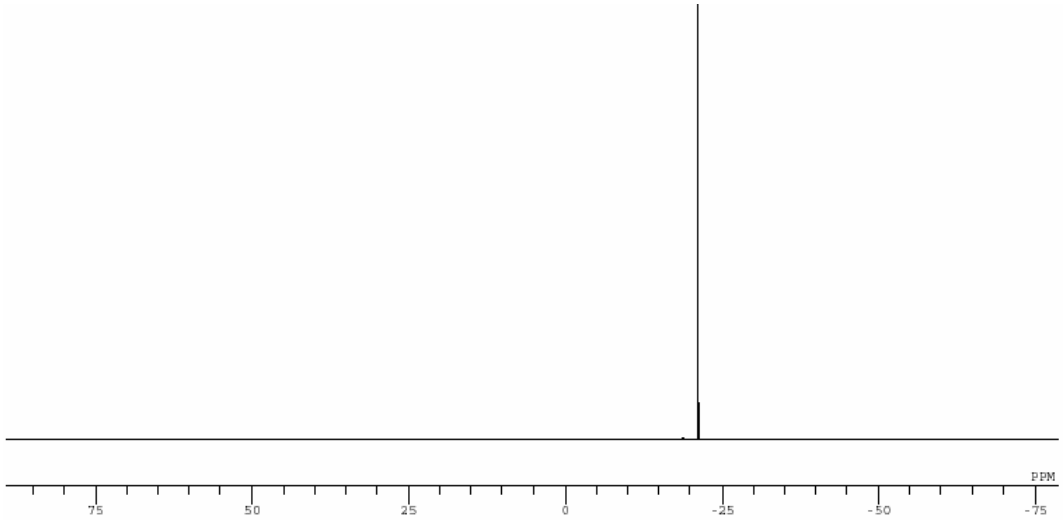

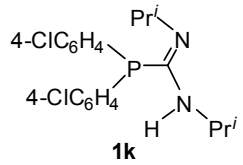

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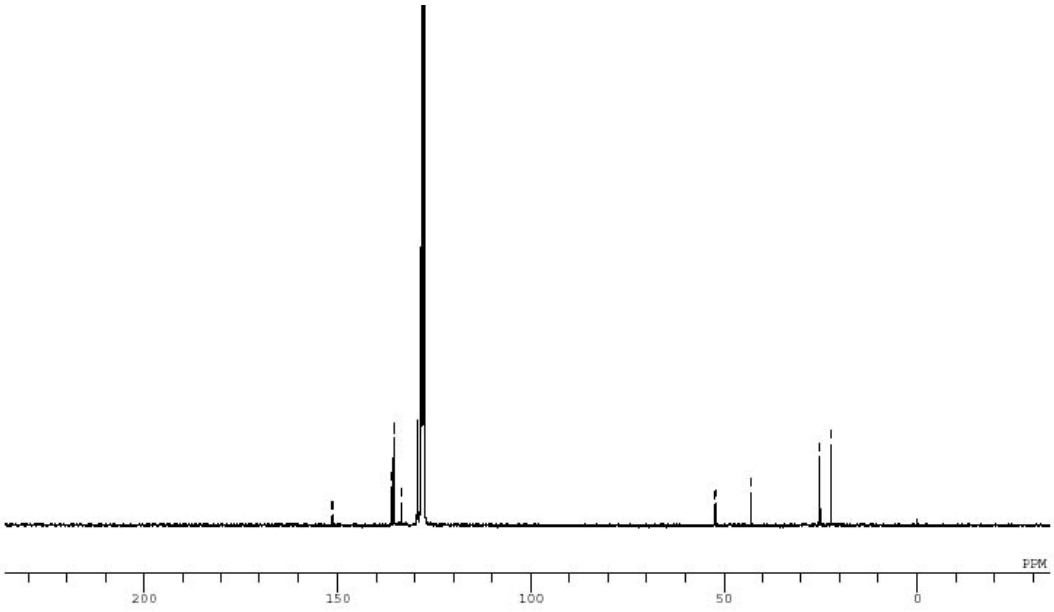

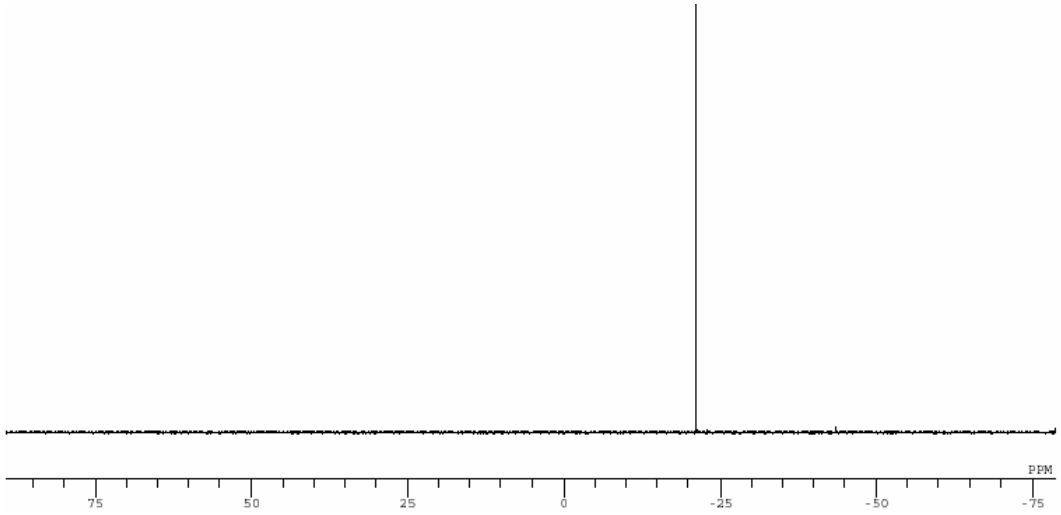

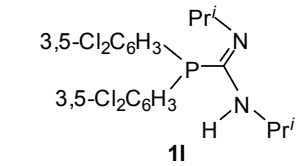

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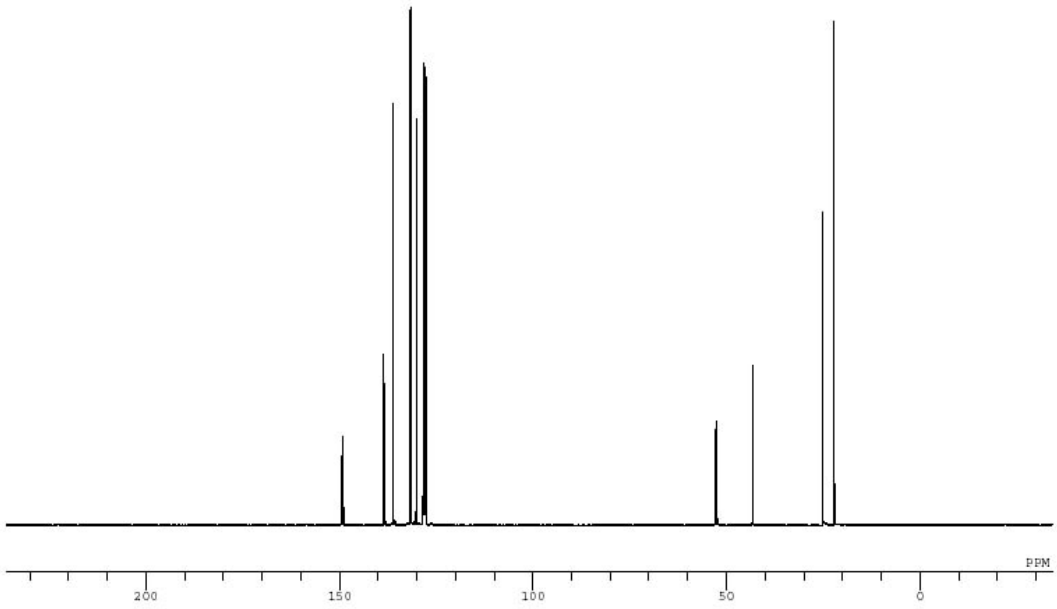

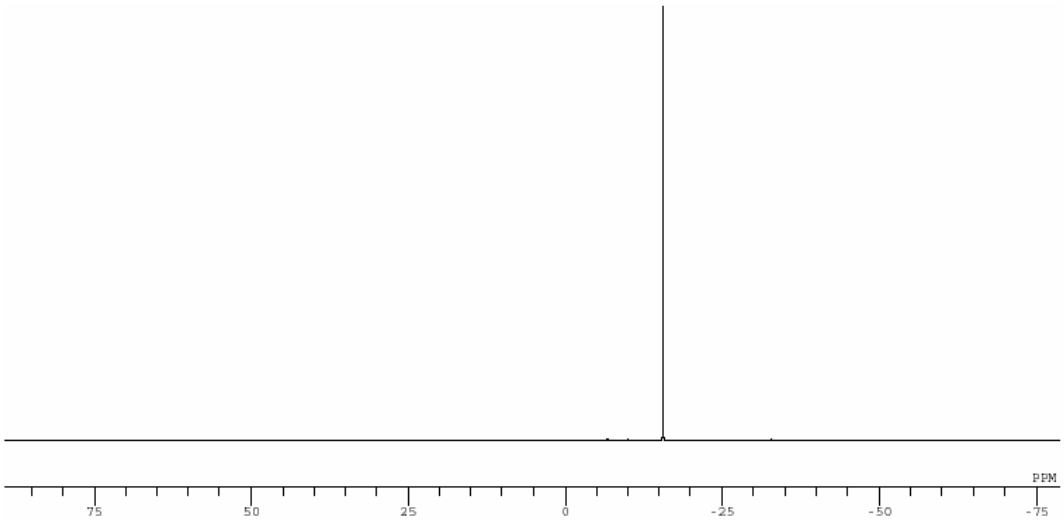

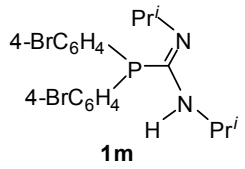

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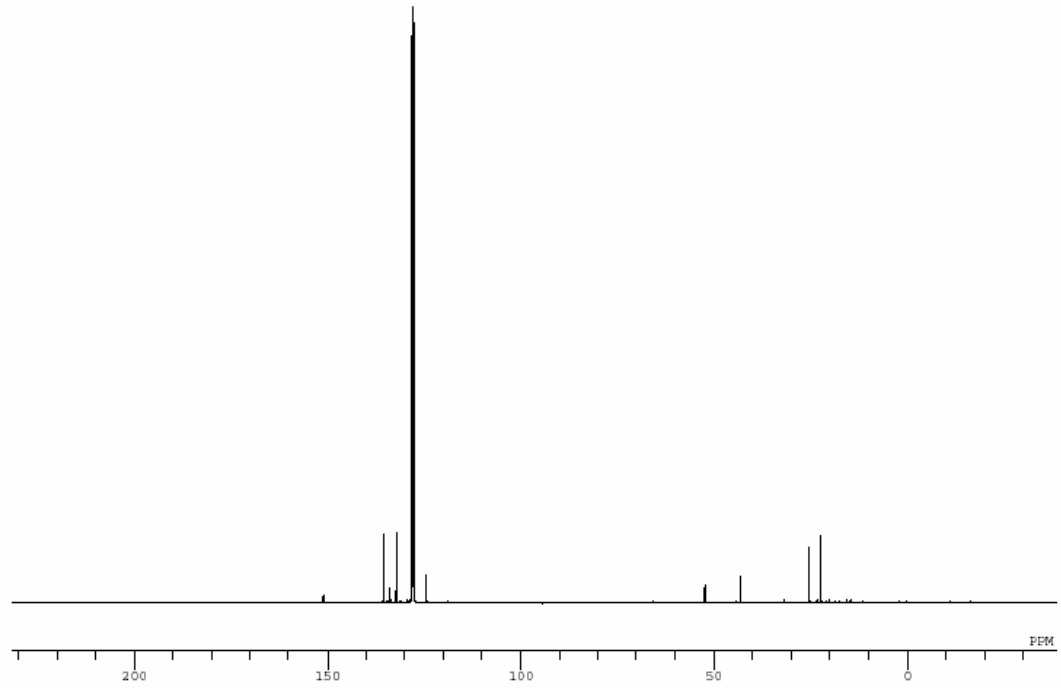

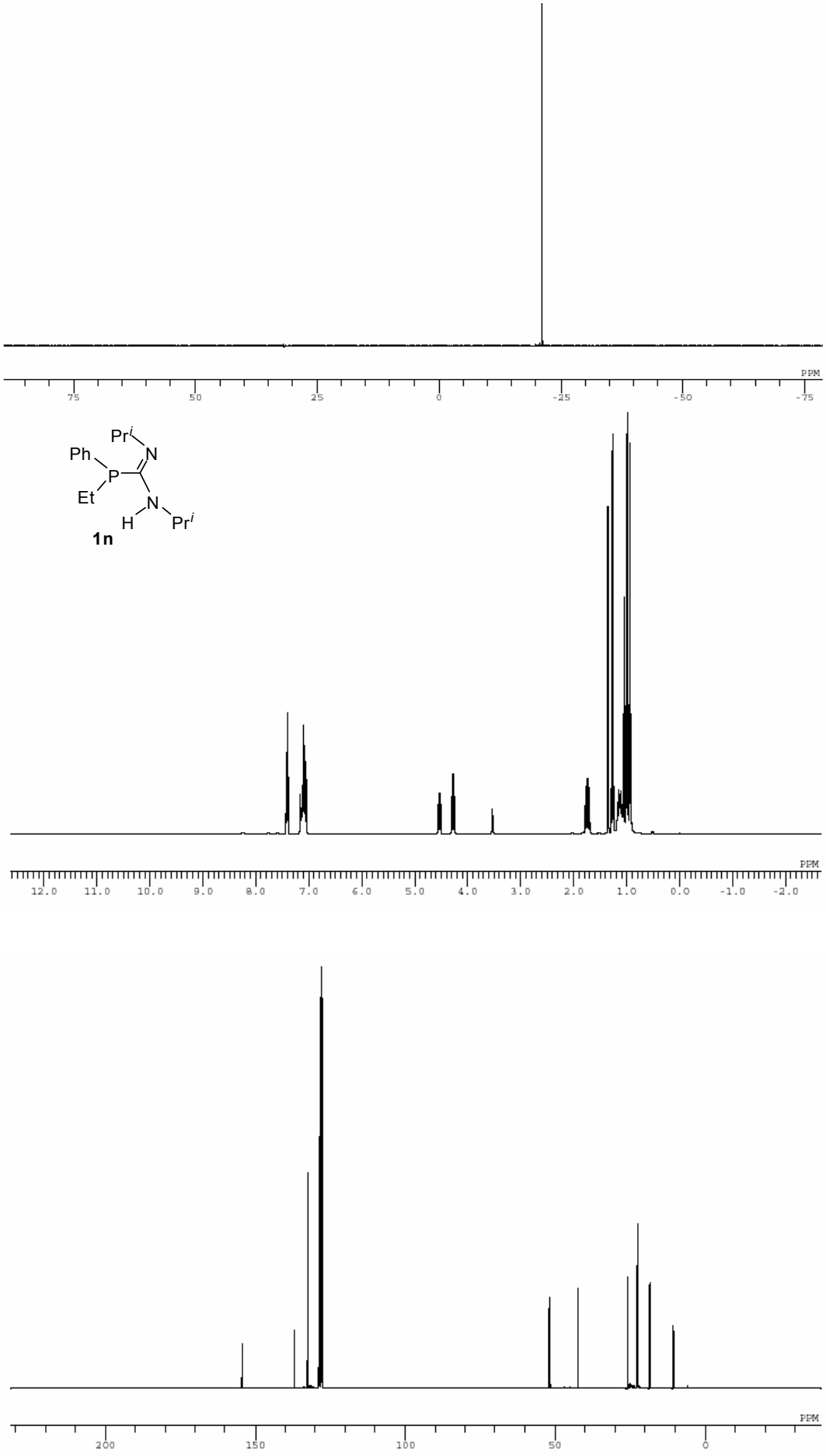

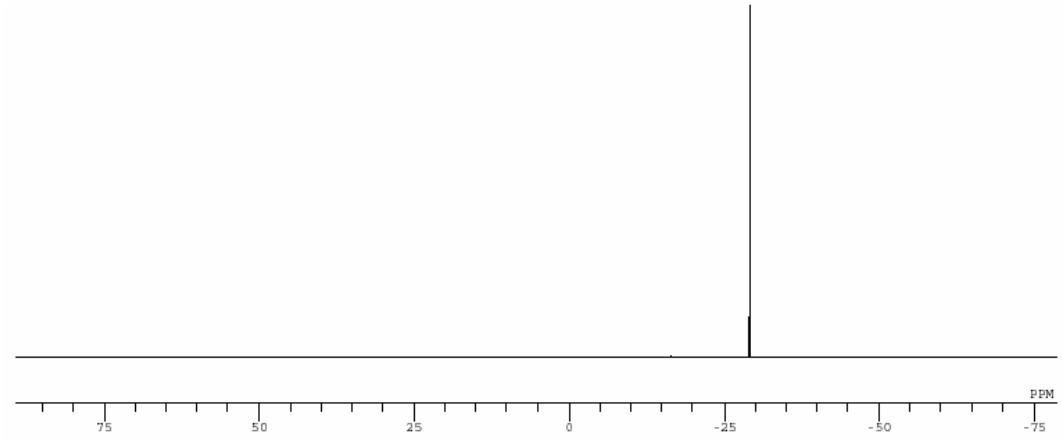

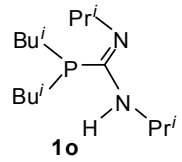

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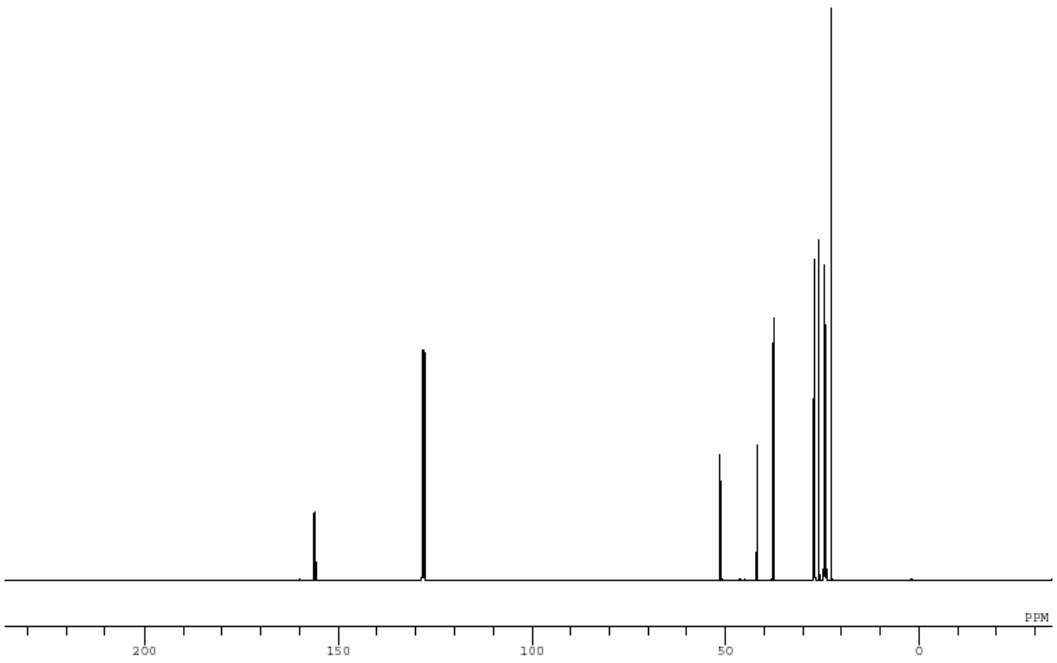

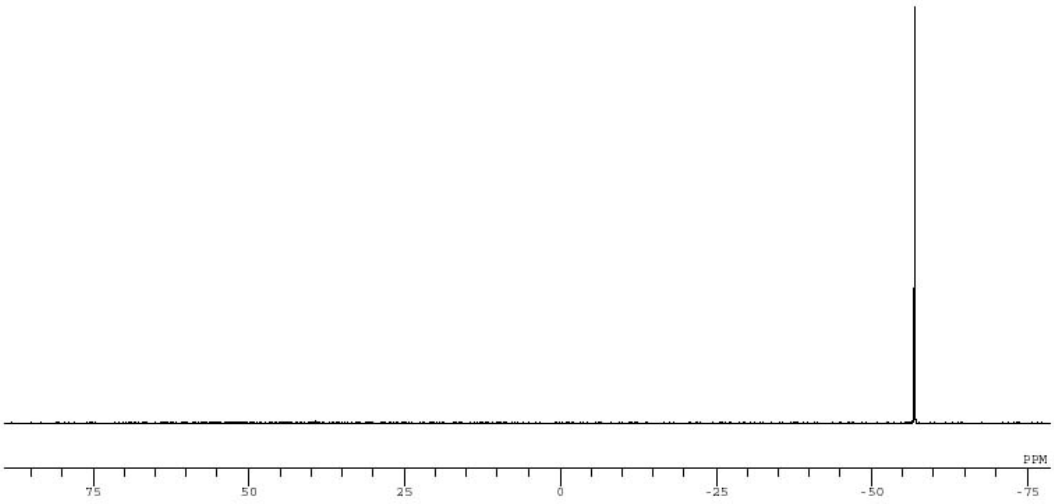

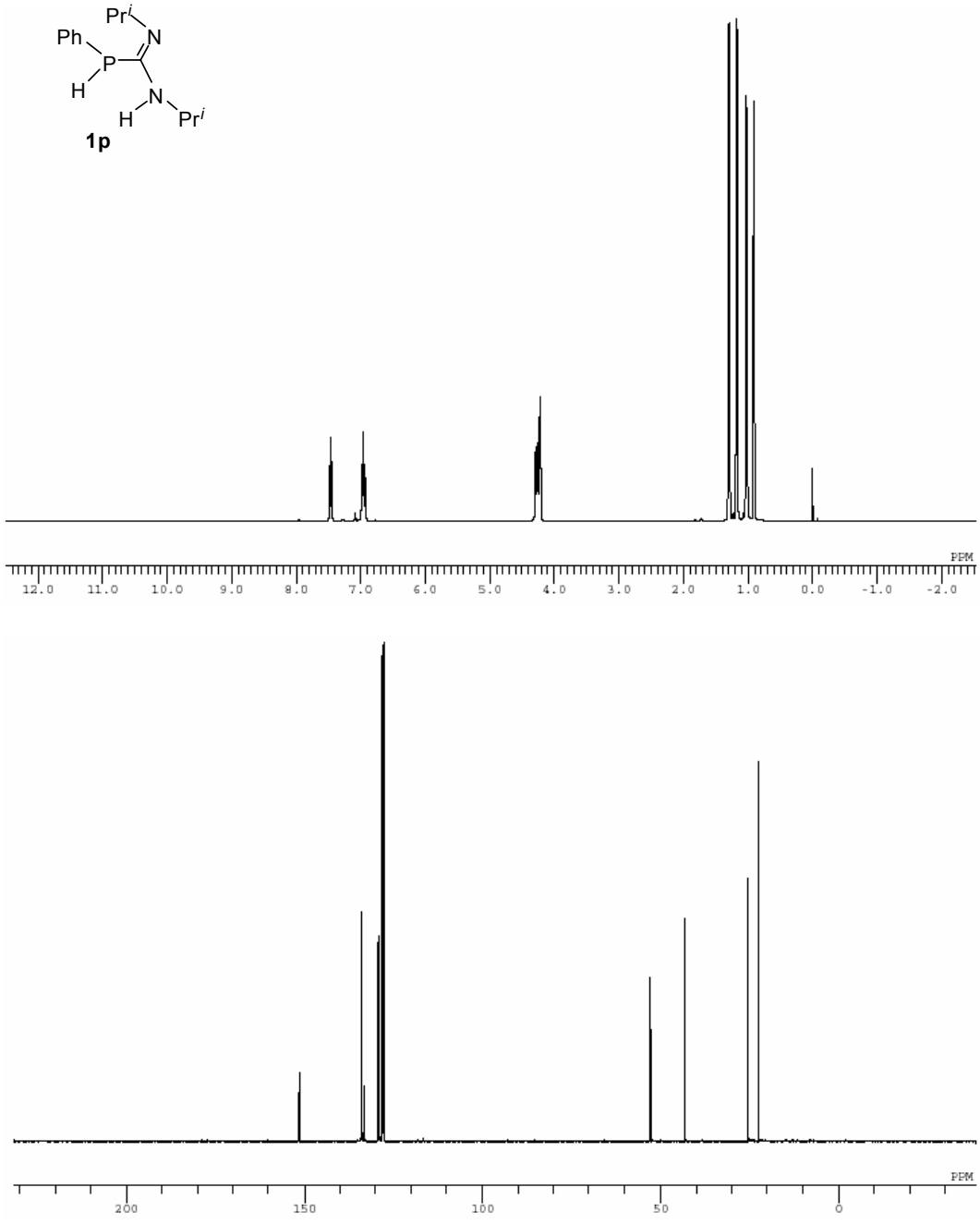

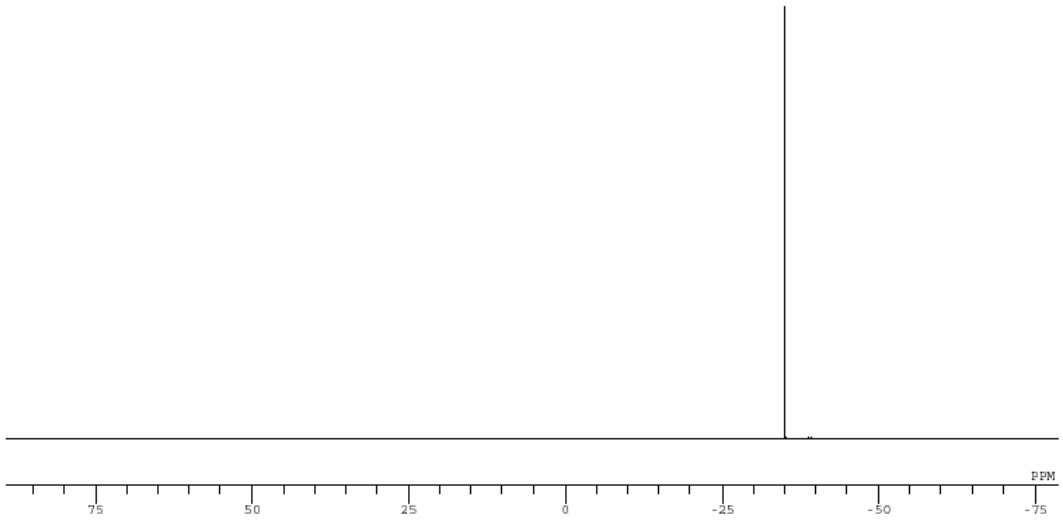

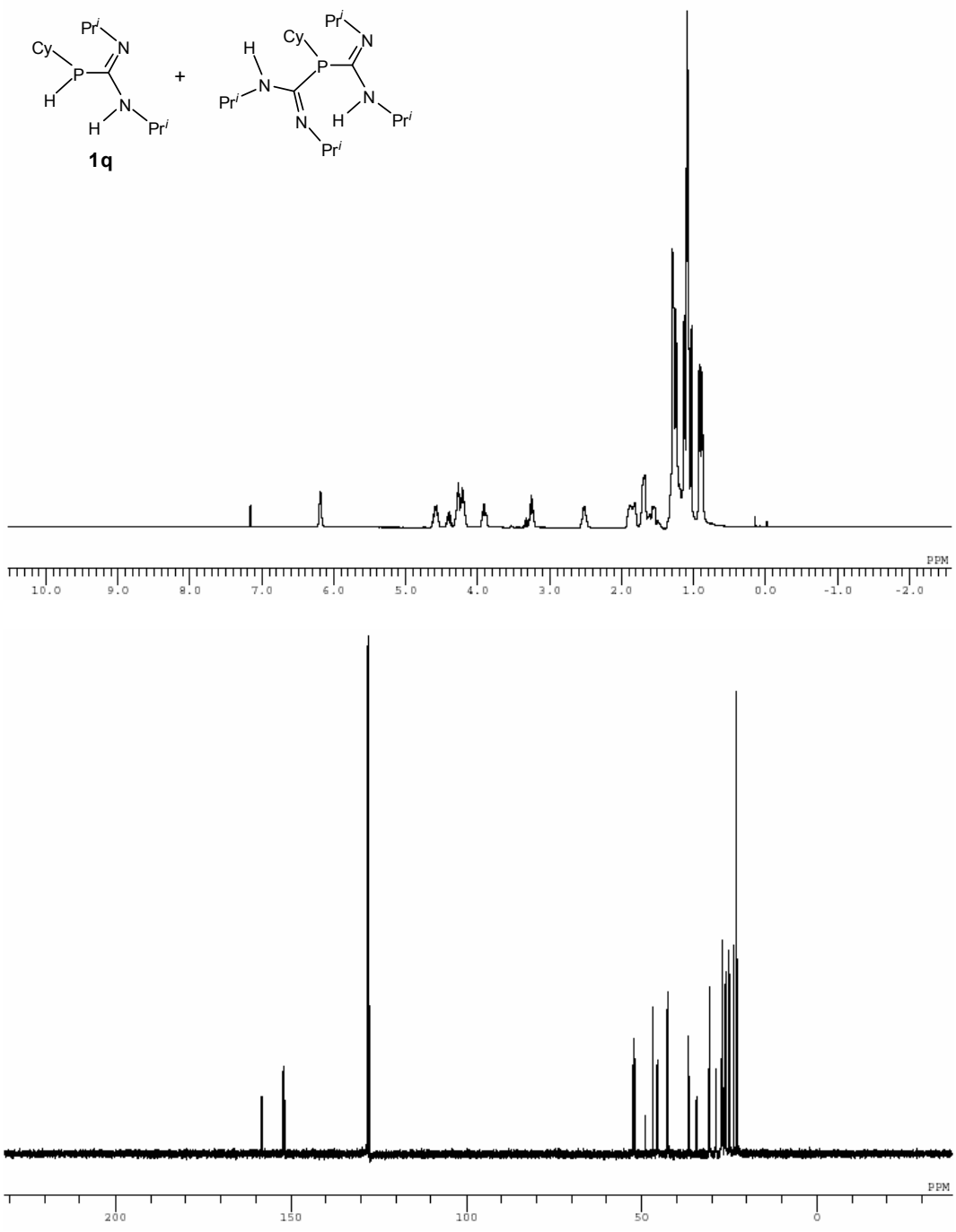

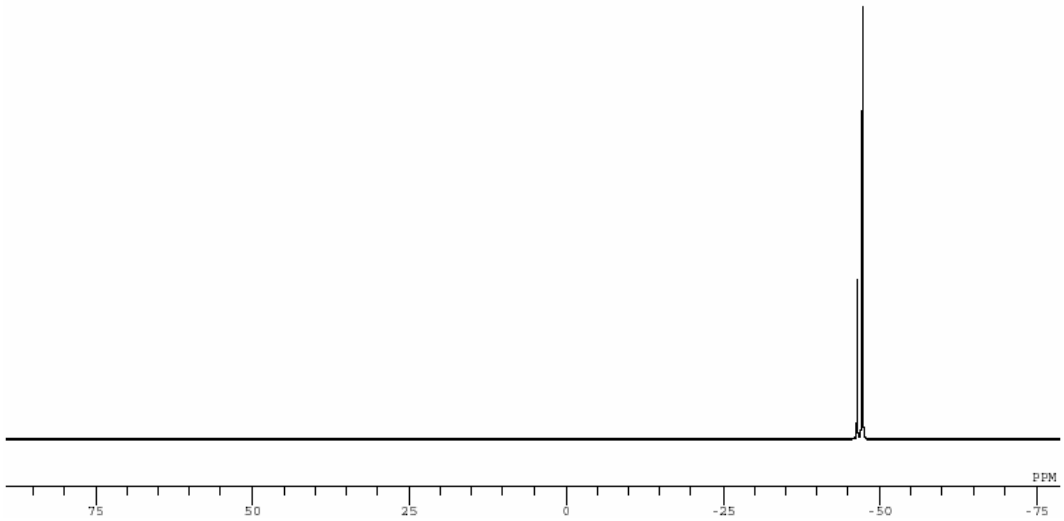

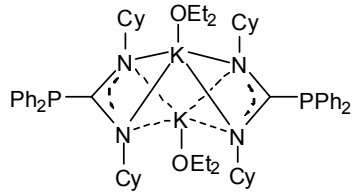

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