Electronic Supporting Information

Mechanism of Generation of *closo*-Decaborato Amidrazones. Intramolecular Non-covalent B–H•••π(Ph) Interaction Determines Stabilization of the Configuration around the Amidrazone C=N Bond

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Analytical and spectroscopic data for (Ph_3PCH_2Ph)[3a–g]

Clusters (Ph_3PCH_2Ph)[**3a**–**g**] give satisfactory ICPMS-based B elemental analysis for the proposed formulas. These species were also characterized by HRESI$^-$-MS, IR, $^1H\{^{11}B\}$, and $^{11}B\{^1H\}$ NMR spectroscopies, molar conductivity and by single-crystal X-ray diffraction. (Ph_3PCH_2Ph)[**3a**–**d**] and (Ph_3PCH_2Ph)[**3g**] were additionally characterized by $^{13}C\{^1H\}$ NMR spectroscopy (**Figures 2S**–**35S**). Molar conductivities of (Ph_3PCH_2Ph)[**3a**–**g**] in MeCN are in the range 77.7–110.3 S cm^2 mol^{-1}, which is somehow lower than that expected for 1:1 electrolytes (120–160 S cm^2 mol^{-1} in MeCN[1]). However, the obtained range of conductivities is typical for 2-substituted *closo*-decaborates.[2]

Although compounds (Ph_3PCH_2Ph)[**3a**–**g**] are stable in the solid state at RT, they decompose at 142–238 °C. The negative mode HRESI mass spectra of (Ph_3PCH_2Ph)[**3a**–**g**] exhibit sets of peaks corresponding to the $[M]^-$, $[2M + Na]^-$, and $[M – R^1R^2CN]^{\bullet-}$ ions. The $[M – R^1R^2CN]^{\bullet-}$ ion is likely generated via the homolytic fragmentation of the N–N bond. Similar sets of peaks were previously observed for the oxime derived 2-iminium *closo*-decaborates.[2a, b]

In the IR spectra of (Ph_3PCH_2Ph)[**3a**–**g**], medium to weak bands were observed at the 3598–3300 and 3061–2912 cm^{-1} intervals, which are related to the N–H and C–H stretching vibrations, respectively.[3] The spectra also exhibit one strong band at 2474–2458 cm^{-1} from ν(B–H) of the *closo*-decaborate cluster,[2a, 4] and strong bands at 1652–1600 cm^{-1}, which is characteristic for ν(C=N).[3]

The $^1H\{^{11}B\}$ and $^{11}B\{^1H\}$ NMR spectra of (Ph_3PCH_2Ph)[**3a**–**f**], and $^{13}C\{^1H\}$ NMR spectra of (Ph_3PCH_2Ph)[**3a**–**d**], display double set of signals of the corresponding anions due to the existence of the compounds in the (*E*)- and (*Z*)-forms at the iminium C=N bond, respectively. The (*E*/*Z*)-ratio varies for different products and ranges from 45/55 to 85/15. The benzophenone hydrazone derivative (Ph_3PCH_2Ph)[**3g**] exists exclusively in the (*Z*)-form, because of the availability of attractive non-covalent interactions B–H•••Ph (see later). A characteristic feature of the $^1H\{^{11}B\}$ NMR spectra is the presence of a low-field broad singlet at δ 10.74–7.66 ppm due to

the $N_{imine}H$ hydrogen. For the substances (Ph_3PCH_2Ph)[**3c**–**f**] a broad signal of the NH_2 moiety at δ 5.86–5.65 ppm was observed. Another characteristic feature of the $^1H\{^{11}B\}$ NMR spectra is the presence of two broad singlets of one H each at δ 3.52–3.11 ppm, assignable to the axial hydrides B(10)H and B(1)H of the *closo*-decaborate cluster. The signals of the residual hydrides are located at δ 0.94–0.82, 0.46–0.39, 0.25–0.14 ppm (broad singlets, each with integral intensity of 2H from the B(3)H and B(5)H, B(6)H and B(9)H, B(7)H and B(8)H), and δ 0.21–0.01 ppm (broad singlet of 1H from the B(4)H). In the $^1H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3g**], the signal of B(10)H is located at δ 2.59, whereas the other peaks of the hydrides are located at δ 0.38, 0.26, 0.03, and –0.10 ppm; this high-field shift of the cluster hydrides is associated with the shielding effect of one of the phenyl rings. The $^{11}B\{H\}$ NMR spectra of (Ph_3PCH_2Ph)[**3a**–**g**] are typical for 2-substituted *closo*-decaborates.[2a, 5] Sets of doublets observed in the $^{13}C\{^1H\}$ NMR spectra at δ 135.32–117.46 and 29.88–29.85 ppm are typical for $(Ph_3PCH_2Ph)^+$ species.[2a] Two singlets at δ 172.26–151.51 ppm are specific for the quaternary carbon of the imine moiety of the (*E*/*Z*)-isomers of (Ph_3PCH_2Ph)[**3a**–**f**]. In the high-field region, two singlets at δ 29.90–19.92 and 11.47–9.72 ppm, respectively, were observed from the ethyl moiety.

Structure Analysis. *(i) X-ray Structure Determination.* Compounds (Ph_3PCH_2Ph)[**3a**–**g**] crystallize from MeCN solutions as (*E*)-(Ph_3PCH_2Ph)[**3a**]•MeCN, (*Z*)-(Ph_3PCH_2Ph)[**3b**]•MeCN, (*Z*)-(Ph_3PCH_2Ph)[**3c**], (*E*)-(Ph_3PCH_2Ph)[**3d**]•MeCN, (*E*)-(Ph_3PCH_2Ph)[**3e**], (*E*)-(Ph_3PCH_2Ph)[**3f**], and (*Z*)-(Ph_3PCH_2Ph)[**3g**]•MeCN. In the molecular structures, the *closo*-decaborate cluster exhibits the usual bicapped square bipyramidal geometry (**Figure 1**). The N(1)–B(2) bond lengths (1.516(3)–1.527(16) Å) are typical for *closo*-decaborate bound imines.[2] The N(1)–C(1) and N(2)–C(1) bonds have intermediate order between single and double bonds (1.2993(15)–1.316(2) and 1.326(2)–1.3490(15) Å, respectively), whereas the N(2)–N(3) distances (1.364(3)–1.414(2) Å) are normal single bonds.[6] The $Ph_3PCH_2Ph^+$ cation exhibits usual bond distances and angles.[7]

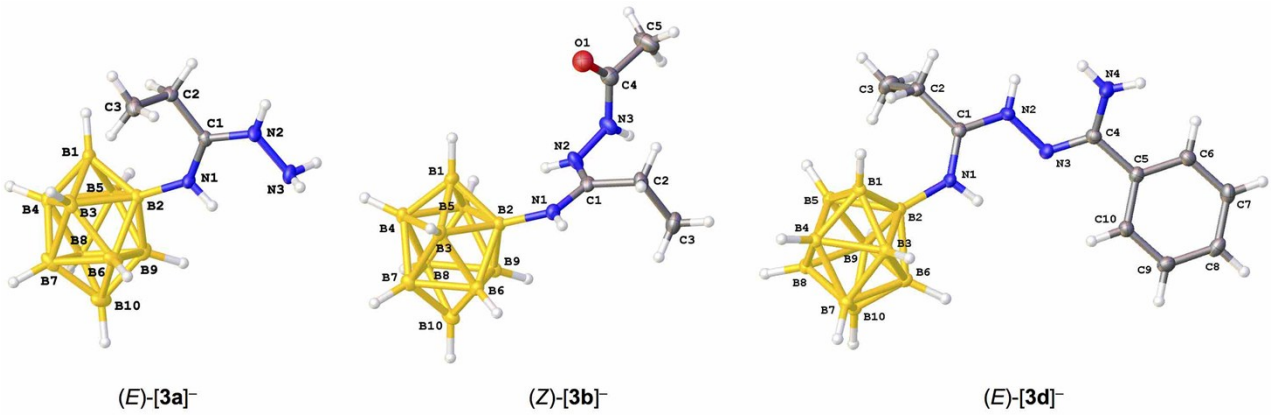
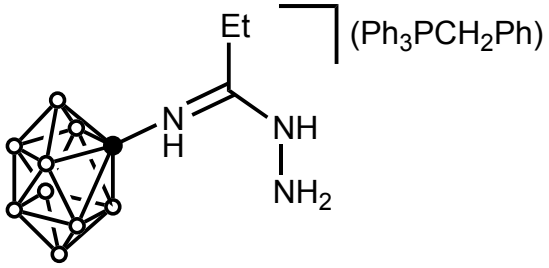


Figure 1S. Molecular structures of (*E*)-[**3a**]$^-$ (left), (*Z*)-[**3b**]$^-$ (center), and (*E*)-[**3d**]$^-$ (right) showing the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level.

Synthesis and Characterization of (Ph_3PCH_2Ph)[3a–g]

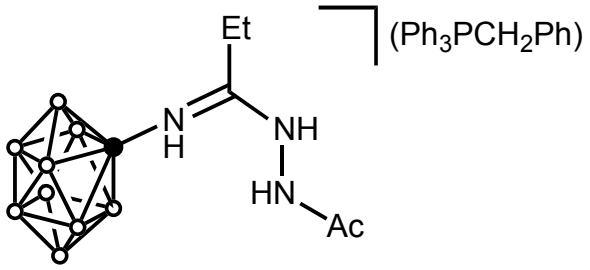
*Preparation of (Ph_3PCH_2Ph)[**3a**].* A solid (Ph_3PCH_2Ph)[**1**] (190 μmol) was dissolved in CH_2Cl_2 (750 μL) under ultrasound treatment at RT. A solution of **2a** in THF (190 μmol) was added to the solution of (Ph_3PCH_2Ph)[**1**]. The mixture was kept stirring at RT for 10 min, and a colorless precipitate appears in the range of 1–2 min. The solid was filtered off, washed with five 1-mL portions of Et_2O, and dried at RT for 12 h.



(Ph_3PCH_2Ph)[**3a**]. Yield: 92% (98 mg). *E*:*Z* = 45:55. mp: 204–207 °C (dec). Anal. Calcd for $C_{28}H_{40}B_{10}N_3P$: B, 19.38. Found: B, 19.39. HRESI$^-$-MS (*m/z*): 204.2515 ([M]$^-$, calcd 204.2511). Λ_M (CH_3CN, 7 × 10^{-4} *M*): 93.0 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3315(m) ν(N–H), 3058(w), 2930(w) ν(C–H), 2464(s) ν(B–H), 1652(s) ν(C=N). $^1H\{^{11}B\}$ NMR (*δ*): 9.23 (s, 1H, NH; *E*), 7.90 (t, *J* = 7.9 Hz, 3H, *Ph*$_3$PCH$_2$Ph), 7.75–7.67 (m, 6H, *Ph*$_3$PCH$_2$Ph), 7.66 (s, 1H, NH; *Z*), 7.64–7.56 (m, 6H, *Ph*$_3$PCH$_2$Ph), 7.35 (t, *J* = 7.6 Hz, 1H, Ph$_3$PCH$_2$*Ph*), 7.24 (t, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 7.00 (d, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 6.93 (s, br, 1H, N*H*NH$_2$; *Z*), 5.95 (s, br, 1H, N*H*NH$_2$; *E*), 4.72 (d, *J* = 14.8 Hz, 2H, Ph$_3$PC*H*$_2$Ph), 4.25 (s, 2H, NHN*H*$_2$; *E*), 3.85 (s, 2H, NHN*H*$_2$; *Z*), 3.43, 3.32 (s, 1H, B(1)H*; Z* and *E*), 3.14 (s, br, 1H, B(10)H), 2.75 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$; *Z*), 2.44 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$*; E*), 1.14 (t, *J* = 7.6 Hz, 3H, CH$_3$; *Z*), 1.05 (t, *J* = 7.6 Hz, 3H, CH$_3$*; E*), 0.87, 0.82 (s, 1H, B(3)H and B(5)H; *Z* and *E*), 0.42 (s, br, 2H, B(6)H and B(9)H), 0.16, 0.03 (s, br, 1H, B(7)H, B(8)H and B(4)H; *Z* and *E*). $^{11}B\{^1H\}$ NMR (*δ*): –6.11, –3.91, –0.66, 0.97 (B(1) and B(10); *Z* and *E*), –15.04, –16.84 (B(2); *Z* and *E*), –25.41 (B(6), B(9), B(3), B(5)), –28.48, –29.83 (B(7), B(8) and (B(4)). $^{13}C\{^1H\}$ NMR (*δ*): 171.89, 169.68 (NH*C*(Et)NH; *E* and *Z*), 135.30 (d, *J* = 5.5 Hz, *Ph*$_3$PCH$_2$Ph), 134.23 (d, *J* = 12.6 Hz, *Ph*$_3$PCH$_2$Ph), 131.00 (d, *J* = 3.2 Hz, Ph$_3$PCH$_2$*Ph*), 130.16 (d, *J* = 3.8 Hz, *Ph*$_3$PCH$_2$Ph), 128.99 (d, *J* = 3.2 Hz, Ph$_3$PCH$_2$*Ph*), 128.72 (d, *J* = 3.8 Hz, Ph$_3$PCH$_2$*Ph*),

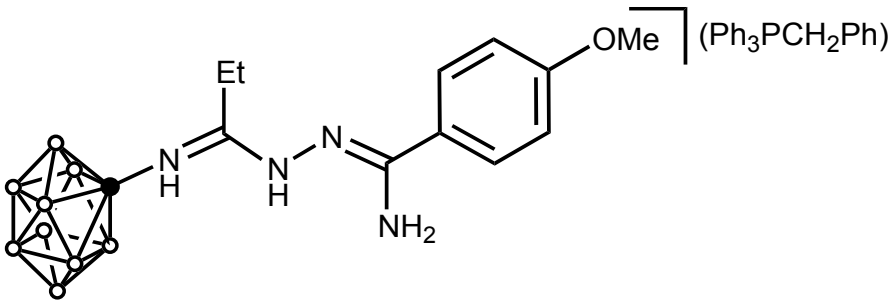
127.31 (d, J = 8.4 Hz, Ph_3PCH_2Ph), 117.51 (d, J = 86.2 Hz, Ph_3PCH_2Ph), 29.88 (Ph_3PCH_2Ph), 24.02, 21.80 (CH_2CH_3; *E* and *Z*), 10.86, 10.01 (CH_3; *E* and *Z*). Crystals of (*E*)-(Ph_3PCH_2Ph)[**3a**]•MeCN suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.

*Preparation of (Ph₃PCH₂Ph)[**3b**–**g**].* A mixture of any one of solid **2b**–**g** (95.2 μmol) and solid (Ph_3PCH_2Ph)[**1**] (95.2 μmol) was dissolved in MeCN (1 mL) under ultrasound treatment at RT. Then colorless ((Ph_3PCH_2Ph)[**3b**–**f**]) or yellow ((Ph_3PCH_2Ph)**[3g**]) crystals were obtained by slow evaporation of MeCN solution at RT in air. The crystals were washed by three 1 mL-portions of Et_2O and dried at RT in air.



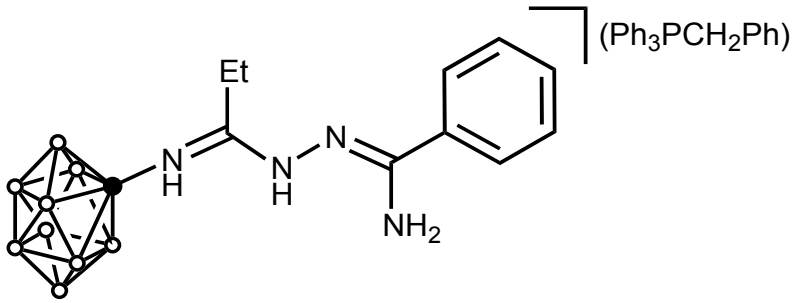
(Ph_3PCH_2Ph)[**3b**]. Yield: 75% (43 mg). *E*:*Z* = 85:15. mp: 236–238 °C (dec). Anal. Calcd for $C_{30}H_{42}B_{10}N_3OP$: B, 18.03. Found: B, 18.17. HRESI$^-$-MS (*m/z*): 187.2248 ([M – AcNH]$^{\bullet-}$, calcd 187.2246), 246.2623 ([M]$^-$, calcd 246.2618), 515.5127 ([2M + Na]$^-$, calcd 515.5129). Λ_M (CH_3CN, 7×10^{-4} *M*): 100.7 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3306(m) ν(N–H), 3050(w), 2933(w) ν(C–H), 2474(s) ν(B–H), 1637(s) ν(C=N). $^1H\{^{11}B\}$ NMR (δ): 9.44 (s, br, 1H, NH), 8.44 (s, br, 1H, NH), 7.90 (t, J = 7.1 Hz, 3H, Ph_3PCH_2Ph), 7.74–7.68(m, 6H, Ph_3PCH_2Ph), 7.62–7.58 (m, 6H, Ph_3PCH_2Ph), 7.36 (t, J = 7.5 Hz, 1H, Ph_3PCH_2Ph), 7.25 (t, J = 7.5 Hz, 2H, Ph_3PCH_2Ph), 6.98 (d, J = 7.5 Hz, 2H, Ph_3PCH_2Ph), 6.60 (s, br, 1H, NH; *E*), 6.47 (s, br, 1H, NH; *Z*), 4.68 (d, J = 11.6 Hz, 2H, Ph_3PCH_2Ph), 3.44 (s, br, 1H, B(1)H; *E*), 3.31 (s, br, 1H, B(1)H; *Z*), 3.15 (s, br, 1H, B(10)H; *E*), 3.11 (s, br, 1H, B(10)H; *Z*), 2.87 (q, J = 7.6 Hz, 2H, CH_2CH_3; *Z*), 2.26 (q, J = 7.6 Hz, 2H, CH_2CH_3; *E*), 1.99 (s, 3H, OCH_3; *E*), 1.93 (s, 3H, OCH_3; *Z*), 1.24 (t, J = 7.6 Hz, 3H, CH_2CH_3; *Z*), 2.24 (t, J = 7.6 Hz, 3H, CH_2CH_3; *E*), 0.86 (s, br, 2H, B(3)H and B(5)H; *Z*), 0.82 (s, br, 2H,

B(3)H and B(5)H; *E*), 0.40 (s, br, 2H, B(6)H and B(9)H), 0.18 (s, br, 2H, B(7)H and B(8)H), 0.14 (s, br, 1H, B(4)H; *E*), 0.04 (s, br, B(4)H; *Z*). $^{11}B\{^1H\}$ NMR (δ): 1.25, 0.45, 3.82, 6.09, (B(1) and B(10); *E* and *Z*), –14.68 (B(2); *Z*), –16.74 (B(2)*; E*), –25.57 (B(3), B(5), B(6) and B(9)), –28.77 (B(7), (B(8) and (B(4)). $^{13}C\{^1H\}$ NMR (δ): 172.26 (NH*C*(Et)NH), 169.82 (*C*(O)CH_3), 135.32 (d, *J* = 3.0 Hz, *Ph*$_3$PCH$_2$Ph), 134.21 (d, *J* = 9.7 Hz, *Ph*$_3$PCH$_2$Ph), 130.95 (d, *J* = 5.4 Hz, Ph$_3$PCH$_2$*Ph*), 130.16 (d, *J* = 12.1 Hz, *Ph*$_3$PCH$_2$Ph), 129.03 (d, *J* = 3.2 Hz, Ph$_3$PCH$_2$*Ph*), 128.76 (d, *J* = 3.7 Hz, Ph$_3$PCH$_2$*Ph*), 127.26 (d, *J* = 8.4 Hz, Ph$_3$PCH$_2$*Ph*), 117.49 (d, *J* = 86.2 Hz, *Ph*$_3$PCH$_2$Ph), 29.85 (d, *J* = 48.7 Hz Ph$_3$P*C*H$_2$Ph), 23.68 (s, C(O)*C*H$_3$), 19.92 (s, *C*H$_2$CH$_3$), 9.73 (s, CH$_2$*C*H$_3$). Crystals of (*Z*)-(Ph$_3$PCH$_2$Ph)[**3b**]•MeCN suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.



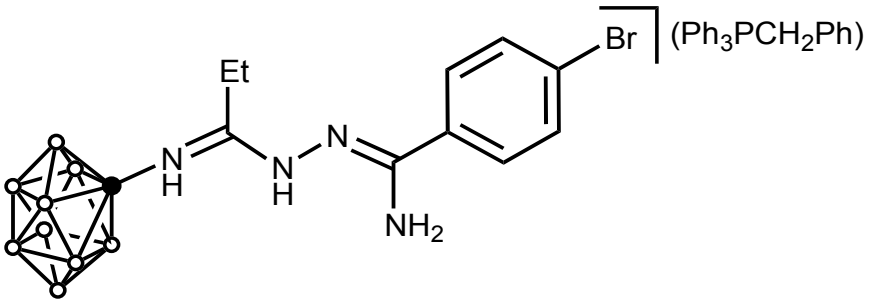
(Ph$_3$PCH$_2$Ph)[**3c**]. Yield: 58% (38 mg). *E*:*Z* = 75:25. mp: 177–178 °C (dec). Anal. Calcd for $C_{36}H_{47}B_{10}N_4OP$: B, 15.65. Found: B, 15.63. HRESI$^-$-MS (*m/z*): 188.2313 ([M – MeOC$_6$H$_4$C(NH$_2$)N]$^{\bullet-}$, calcd 188.2317), 337.3042 ([M]$^-$, calcd 337.3042). Λ_M (CH_3CN, 7×10^{-4} *M*): 88.9 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3449(m), 3316(m) ν(N–H), 3061(w), 2912(w) ν(C–H), 2462(s) ν(B–H), 1610(s) ν(C=N). $^1H\{^{11}B\}$ NMR (δ): 10.38 (s, 1H, NH; *E*), 8.39 (s, 1H, NH; *Z*), 7.90 (t, *J* = 7.6 Hz, 3H, *Ph*$_3$PCH$_2$Ph), 7.77 (d, *J* = 8.8 Hz, 2H, *p*-CH$_3$OC$_6$*H*$_4$; *E*), 7.74–7.67 (m, 6H, *Ph*$_3$PCH$_2$Ph), 7.65 (d, *J* = 8.8 Hz, 2H, *p*-CH$_3$OC$_6$*H*$_4$; *Z*), 7.62–7.54 (m, 6H, *Ph*$_3$PCH$_2$Ph), 7.36 (t, *J* = 7.6 Hz, 1H, Ph$_3$PCH$_2$*Ph*), 7.25 (t, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 7.04–6.95 (m, 4H, Ph$_3$PCH$_2$*Ph* and *p*-CH$_3$O*Ph*; *Z* and *E*), 6.88 (s, 1H, *p*-CH$_3$OC$_6$*H*$_4$C(NH$_2$)NN*H*; *Z*), 6.21 (s, 1H, *p*-CH$_3$OC$_6$*H*$_4$C(NH$_2$)NN*H; E*), 5.65 (s, 2H, *p*-CH$_3$OC$_6$*H*$_4$C(N*H*$_2$)NNH), 4.67 (d, *J* = 14.4 Hz, 2H, Ph$_3$PC*H*$_2$Ph), 3.86 (s, 3H, *p*-C*H*$_3$OC$_6$*H*$_4$C(NH$_2$)NNH*; E*), 3.84 (s, 3H, *p*-C*H*$_3$OC$_6$*H*$_4$C(NH$_2$)NNH; *Z*), 3.50 (s, 1H, B(1)H*; E*), 3.30 (s, 1H, B(1)H; Z), 3.25 (s, 1H, B(10)H;

Z), 3.15 (s, 1H, B(10)H*; E*), 2.93 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$; *Z*), 2.55 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$; *E*), 1.30 (t, *J* = 7.6 Hz, 3H, CH$_2$C*H*$_3$; *Z*), 1.11 (t, *J* = 7.6 Hz, 3H, CH$_2$C*H*$_3$*; E*), 0.92 (s, 2H, B(3)H and B(5)H; *E*), 0.88 (s, 2H, B(3)H and B(5)H; *Z*), 0.45 (s, 2H, B(6)H and B(9)H; *E*), 0.41 (s, 2H, B(6)H and B(9)H; *E*), 0.25 (s, 2H, B(7)H and B(8)H; *E*), 0.21 (s, 1H, B(4)H; *E*), 0.15 (s, 2H, B(7)H and B(8)H; *Z*), 0.03 (s, 1H, B(4)H; *Z*).^{11}B {^{1}H} (*δ*): 1.58, –0.62, –4.03, –6.41 (s, B(1) and B(10); *E* and *Z*), –15.05 (s, B(2); *Z*), –16.72 (s, B(2); *E*), –25.36 (s, B(3), B(5), B(6) and B(9)), –28.65 (s, B(7), B(8) and B(4)). ^{13}C {^{1}H} NMR (*δ*): 167.11, 165.44, 161.81, 161.61, 153.73, 151.51 (NH*C*(Et)NH, N*C*(NH$_2$)C$_6$H$_4$ and C$_6$H$_4$; *E* and *Z*), 135.31 (d, *J* = 2.4 Hz, *Ph*$_3$PCH$_2$Ph), 134.19 (d, *J* = 9.4 Hz, *Ph*$_3$PCH$_2$Ph), 130.93 (d, *J* = 5.2 Hz, Ph$_3$PCH$_2$*Ph*), 130.14 (d, *J* = 12.6 Hz, *Ph*$_3$PCH$_2$Ph), 129.03 (d, , *J* = 3.2 Hz, Ph$_3$PCH$_2$*Ph*), 128.75 (d, *J* = 3.8 Hz, Ph$_3$PCH$_2$*Ph*), 128.14, 128.05 (C$_6$H$_4$; *Z* and *E*), 127.23 (d, *J* = 8.4 Hz, Ph$_3$PCH$_2$*Ph*), 125.50 (C$_6$H$_4$), 117.46 (d, *J* = 86.2 Hz, *Ph*$_3$PCH$_2$Ph), 113.86, 113.79 (C$_6$H$_4$; *Z* and *E*), 55.15 (OCH$_3$); 29.87 (d, *J* = 48.7 Hz, Ph$_3$P*C*H$_2$Ph), 24.50, 22.13 (CH$_2$; *E* and *Z*), 11.47, 9.72 (CH$_2$*C*H$_3$; *Z* and *E*). Crystals of (*Z*)-(Ph$_3$PCH$_2$Ph)[**3c**] suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.



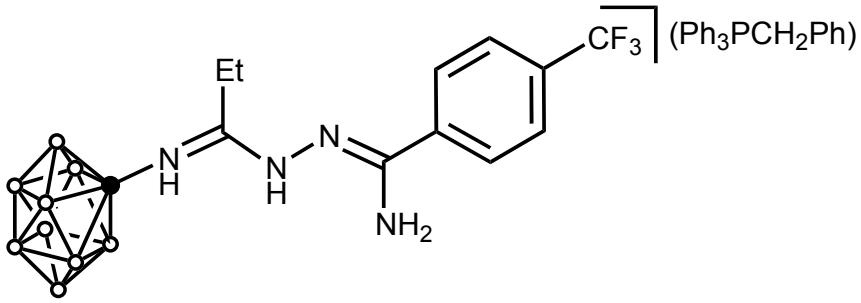
(Ph$_3$PCH$_2$Ph)[**3d**]. Yield: 84% (53 mg). *E*:*Z* = 80:20. mp: 159–162 °C (dec). Anal. Calcd for C$_{37}$H$_{48}$B$_{10}$N$_5$P: B, 15.40. Found: B, 15.36 ((Ph$_3$PCH$_2$Ph)[**3d**]•MeCN). HRESI$^-$-MS (*m/z*): 307.2939 ([M]$^-$, calcd 307.2936). Λ_M (CH$_3$CN, 7 × 10^{-4} *M*): 77.7 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3485(m), 3356(m), 3250(m) ν(N–H); 3050(w), 2930(m) ν(C–H); 2465(s) ν(B–H); 1622(s), 1597(s) ν(C=N). ^{1}H{^{11}B} NMR (*δ*): 10.43 (s, 1H, NH; *E*), 8.63 (s, 1H, NH; *Z*), 7.90 (t, *J* = 7.5 Hz, 3H, *Ph*$_3$PCH$_2$Ph), 7.83 (d, *J* = 6.8 Hz, 2H, Ph; *E*), 7.74–7.67 (m, 6H, *Ph*$_3$PCH$_2$Ph and Ph; *Z*), 7.63–7.54 (m, 6H, *Ph*$_3$PCH$_2$Ph), 7.54–7.44 (m, 3H, Ph), 7.37 (t, *J* = 7.6 Hz, 1H, Ph$_3$PCH$_2$*Ph*), 7.25 (t, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 6.97 (d, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 6.29 (s, br, 1H, PhC(NH$_2$)NN*H*),

5.78 (s, 2H, PhC(NH_2)NNH; *Z*), 5.74 (s, 2H, PhC(NH_2)NNH; *E*), 4.66 (d, 2H, Ph_3PCH_2Ph), 3.50 (s, 1H, B(1)H; *E*), 3.28 (s, 1H, B(1)H; *Z*), 3.25 (s, 1H, B(10)H; *E*), 3.14 (s, 1H, B(10)H; *Z*), 2.95 (q, *J* = 7.6 Hz, 2H, CH_2CH_3; *Z*), 2.58 (q, *J* = 7.6 Hz, 2H, CH_2CH_3; *E*), 1.31 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 1.13 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 0.92 (s, 2H, B(3)H and B(5)H; *E*), 0.86 (s, 2H, B(3)H and B(5)H; *Z*), 0.44 (s, 2H, B(6)H and B(9)H; *E*), 0.39 (s, 2H, B(6)H and B(9)H; *Z*), 0.24 (s, 2H, B(7)H and B(8)H; *E*), 0.21 (s, 1H, B(4)H; *E*), 0.13 (s, 2H, B(7)H and B(8)H; *Z*), 0.01 (s, 1H, B(4)H; *Z*). $^{11}B\{^1H\}$ NMR (δ): –1.57, –0.46, –3.97, –6.39 (B(1) and B(10)), –14.91 (B(2); *Z*), –16.65 (B(2); *E*), –25.35 (B(3), B(5), B(6) and B(9)), –28.59 (B(4), B(7) and B(8)). $^{13}C\{^1H\}$ NMR (δ): 167.30, 151.52 (NH*C*(Et)NH and N*C*(NH_2)Ph), 135.31 (d, *J* = 3.1 Hz, Ph_3PCH_2Ph), 135.18 (d, *J* = 79.0 Hz, Ph_3PCH_2Ph), 133.37 (NC(NH_2)*Ph*), 130.91 (d, *J* = 5.4 Hz, Ph_3PCH_2Ph), 130.50 (NC(NH_2)*Ph*), 130.14 (d, *J* = 12.6 Hz, Ph_3PCH_2Ph), 129.03 (d, *J* = 3.2 Hz, Ph_3PCH_2Ph), 128.77 (d, *J* = 3.7 Hz, Ph_3PCH_2Ph), 128.57, 128.50 (NC(NH_2)*Ph*; *Z* and *E*), 127.21 (d, *J* = 8.4 Hz, Ph_3PCH_2Ph), 126.52 NC(NH_2)*Ph*), 117.46 (d, *J* = 86.2 Hz, Ph_3PCH_2Ph), 29.86 (d, Ph_3PCH_2Ph), 29.88, 24.51 (CH_2CH_3; *Z* and *E*), 9.73 (CH_3; *Z* and *E*). Crystals of (*E*)-(Ph_3PCH_2Ph)[**3d**]•MeCN suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.



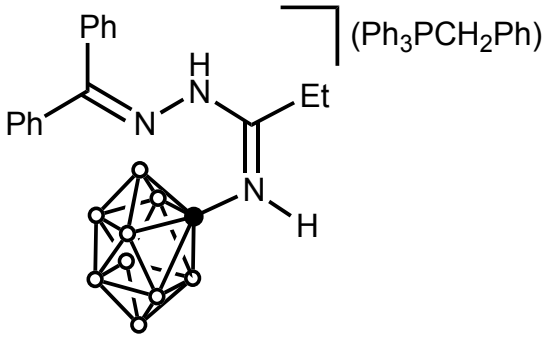
(Ph_3PCH_2Ph)[**3e**]. Yield: 68% (48 mg). *E*:*Z* = 80:20. mp: 164 °C (dec). Anal. Calcd for $C_{35}H_{44}B_{10}BrN_4P$: B, 14.61. Found: B, 14.60. HRESI$^-$-MS (*m/z*): 386.2025 ([M]$^-$, calcd 386.2027). Λ_M (CH_3CN, 7×10^{-4} *M*): 110.3 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3447(m), 3352(m) ν(N–H), 3059(w), 2927(w) ν(C–H), 2464(s) ν(B–H), 1600(s) ν(C=N). $^1H\{^{11}B\}$ NMR (δ): 10.45 (s, 1H, N*H*; *E*), 8.51 (s, 1H, NH; *Z*), 7.90 (t, *J* = 7.5 Hz, 3H, Ph_3PCH_2Ph), 7.77–7.55 (m, 16H, Ph_3PCH_2Ph and *p*-BrC_6H_4C(NH_2)NNH), 7.36 (t, *J* = 7.5 Hz, 1H, Ph_3PCH_2Ph), 7.25 (t, *J* = 7.7 Hz, 2H, Ph_3PCH_2Ph), 6.98 (dd, 2H, Ph_3PCH_2Ph), 6.91 (s, 1H, *p*-BrC_6H_4C(NH_2)NN*H*; *Z*) 6.33 (s, 1H, *p*-

$BrC_6H_4C(NH_2)NNH$; *E*), 5.73 (s, 2H, *p*-$BrC_6H_4C(NH_2)NNH$; *Z* and *E*), 4.65 (d, *J* = 14.8 Hz, 2H, Ph_3PCH_2Ph), 3.50 (s, 1H, B(1)H; *E*), 3.28 (s, 1H, B(1)H; *Z*), 3.24 (s, 1H, B(10)H; *E*), 3.14 (s, 1H,B(10)H; *Z*), 2.95 (q, *J* = 7.5 Hz, 2H, CH_2CH_3; *Z*), 2.57 (q, *J* = 7.5 Hz, 2H, CH_2CH_3; *E*), 1.31 (t, *J* = 7.5 Hz, 3H, CH_2CH_3; *Z*), 1.12 (t, *J* = 7.5 Hz, 3H, CH_2CH_3; *E*), 0.91 (s, 2H, B(3)H and B(5)H; *E*), 0.86 (s, 1H, B(3)H and B(5)H; *Z*), 0.43 (s, 1H, B(6)H and B(9)H; *E*), 0.39 (s, 1H, B(6)H and B(9)H; *Z*), 0.24 (s, 1H, B(7)H and B(8)H; *E*), 0.21 (s, 1H, B(4)H; *E*), 0.14 (s, 1H, B(7)H and B(8)H; *Z*), 0.01 (s, 1H, B(4)H; *Z*). $^{11}B\{^1H\}$ NMR (*δ*): 1.55, –0.57, –3.97, –6.49 (B(1) and B(10); *E* and *Z*), –14.94 (B(2); *Z*), –16.69 (B(2); *E*), –25.41 (B(6), B(9), B(3) and (B(5)), –28.67 (B(4), B(7) and B(8). $^{13}C\{^1H\}$ NMR spectrum was not measured due to poor solubility of (Ph_3PCH_2Ph)[**3e**] in MeCN. Crystals of (*E*)-(Ph_3PCH_2Ph)[**3e**] suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.



(Ph_3PCH_2Ph)[**3f**]. Yield: 59% (41 mg). *E*:*Z* = 70:30. mp: 211–212 °C (dec). Anal. Calcd for $C_{36}H_{44}B_{10}F_3N_4P$: B, 14.83. Found: B, 14.49. HRESI$^-$-MS (*m/z*): 375.2814 ([M]$^-$, cacld 375.2811). Λ_M (CH_3CN, 7×10^{-4} *M*): 93.9 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3458(m), 3352(m) ν(N–H), 3036(w), 2930(w) ν(C–H), 2463(s) ν(B–H), 1602(s) ν(C=N). $^1H\{^{11}B\}$ NMR (*δ*): 10.51 (s, 1H, NH; *E*), 8.64 (s, 1H, NH; *Z*), 8.00 (d, *J* = 8.4 Hz, 2H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *E*), 7.90 (t, 3H, Ph_3PCH_2Ph), 7.87 (d, 2H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *Z*), 7.79 (d, *J* = 8.4 Hz, 2H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *E*), 7.76 (d, *J* = 8.4 Hz, 2H, *p*-$CF_3C_6H_4hC(NH_2)NNH$; *Z*), 7.74–7.67 (m, 6H, Ph_3PCH_2Ph), 7.64–7.54 (m, 6H, Ph_3PCH_2Ph), 7.36 (t, *J* = 7.5 Hz, 1H, Ph_3PCH_2Ph), 7.24 (t, *J* = 7.5 Hz, 2H, Ph_3PCH_2Ph), 6.98 (d, *J* = 7.5 Hz, 2H, Ph_3PCH_2Ph), 6.39 (s, 1H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *E*), 5.86 (s, 2H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *Z*), 5.80 (s, 2H, *p*-$CF_3C_6H_4C(NH_2)NNH$; *E*), 4.68 (d, *J* = 14.8 Hz, 2H, Ph_3PCH_2Ph), 3.52 (s, 1H, B(1)H; *E*), 3.31 (s,

1H, B(1)H; *Z*), 3.26 (s, 1H, B(10)H; *E*), 3.16 (s, 1H, B(10)H; *Z*), 2.95 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$; *Z*), 2.59 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$; *E*), 1.31 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$; *Z*), 1.13 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$; *E*), 0.94 (s, 2H, B(3)H and B(5)H; *E*), 0.89 (s, 2H, B(3)H and B(5)H; *Z*), 0.46 (s, 2H, B(6)H and B(9)H; *E*), 0.42 (s, 2H, B(6)H and B(9)H; *Z*), 0.26 (s, 2H, B(7)H, B(8)H and B(4)H; *E*), 0.17 (s, 2H, B(7)H and B(8)H; *Z*), 0.04 (s, 2H, B(4)H; *Z*). ^{11}B{^{1}H} NMR (*δ*): 1.63, –0.49, –3.92, –6.42 (s, B(1) and B(10); *E* and *Z*), –14.92 (s, B(2); *Z*), –16.68 (s, B(2); *E*), –25.35 (s, B(6), B(9), B(3) and B(5)), –28.64 (s, B(7), B(8) and B(4)).^{13}C{^{1}H} NMR spectrum was not measured due to poor solubility of (Ph$_3$PCH$_2$Ph)[**3f**] in MeCN. Crystals of (*E*)-(Ph$_3$PCH$_2$Ph)[**3f**] suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.

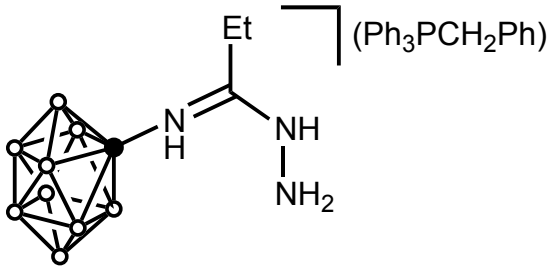


(*Z*)-(Ph$_3$PCH$_2$Ph)[**3g**]. Yield: 78% (54 mg). mp: 136–139 °C (dec). Anal. Calcd for C$_{43}$H$_{51}$B$_{10}$N$_4$P: B, 14.17. Found: B, 14.07. HRESI$^-$-MS (*m/z*): 368.3139 ([M]$^-$, calcd 368.3143). Λ_M (CH$_3$CN, 7 × 10^{-4} *M*): 78.4 S cm^2 mol^{-1}. IR (KBr, selected bonds, cm^{-1}): 3598(m), 3300(m) ν(N–H), 3059(w), 2936(w) ν(C–H), 2458(s) ν(B–H), 1641(s) ν(C=N). ^{1}H{^{11}B} NMR (*δ*): 10.74 (s, 1H, NH), 7.90 (t, *J* = 7.5 Hz, 3H, *Ph*$_3$PCH$_2$Ph), 7.74–7.54 (m, 17H, *Ph*$_3$PCH$_2$Ph and *Ph*$_2$CNNH), 7.48–7.39 (m, 6H, *Ph*$_2$CNNH and Ph$_3$PCH$_2$*Ph*), 7.36 (t, 1H, Ph$_3$PCH$_2$*Ph*), 7.25 (t, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 7.00 (d, *J* = 7.6 Hz, 2H, Ph$_3$PCH$_2$*Ph*), 6.74 (s, 1H, N*H*NCPh$_2$), 4.67 (d, *J* = 14.4 Hz, 2H, Ph$_3$PC*H*$_2$Ph), 3.32 (s, br, 1H, B(1)*H*), 2.78 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.59 (s, br, 1H, B(10)*H*), 1.22 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$), 0.38 (s, br, 2H, B(3)H and B(5)H), 0.26 (s, br, 2H, B(6)H and B(9)H), 0.03 (s, br, 2H, B(7)H and B(8)H), −0.10 (s, br, 1H, B(4)H). ^{11}B{^{1}H} NMR (*δ*): 0.80 (B(1)), –5.72 (B(10)), –17.07 (B(3) and B(5)), –25.48 (B(6) and B(9)), –26.07 (B(7) and B(8)), –28.78 (B(4)).^{13}C{^{1}H} NMR (*δ*): 168.72, 155.02 (NH*C*(Et)NH and NHN*C*Ph$_2$), 137.47 (NHNC*Ph*$_2$),

135.32 (d, J = 3.0 Hz, *Ph*$_3$PCH$_2$Ph), 134.19 (d, J = 9.7 Hz, *Ph*$_3$PCH$_2$Ph), 131.86 (NHNC*Ph*$_2$), 130.93 (d, J = 5.5 Hz, Ph$_3$PCH$_2$*Ph*), 130.15 (d, J = 12.6 Hz, *Ph*$_3$PCH$_2$Ph), 130.06, 130.02, 129.85 (NHNC*Ph*$_2$), 129.03 (d, J = 3.2 Hz, Ph$_3$PCH$_2$*Ph*), 129.01 (NHNC*Ph*$_2$), 128.76 (d, J = 3.8 Hz, Ph$_3$PCH$_2$*Ph*), 128.42, 127.70 (NHNC*Ph*$_2$), 127.23 (d, J = 8.5 Hz, Ph$_3$PCH$_2$*Ph*), 117.47 (d, J = 86.2 Hz, *Ph*$_3$PCH$_2$Ph), 29.87 (d, J = 48.7 Hz, Ph$_3$P*C*H$_2$Ph), 25.90 (*C*H$_2$CH$_3$), 10.26 (CH$_3$). Crystals of (*Z*)-(Ph$_3$PCH$_2$Ph)[**3g**]•MeCN suitable for X-ray diffraction were obtained by slow evaporation of MeCN solution.

Spectra of (Ph_3PCH_2Ph)[3a−g]

(Ph_3PCH_2Ph)**[3a]**



Acquisition Parameter

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Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

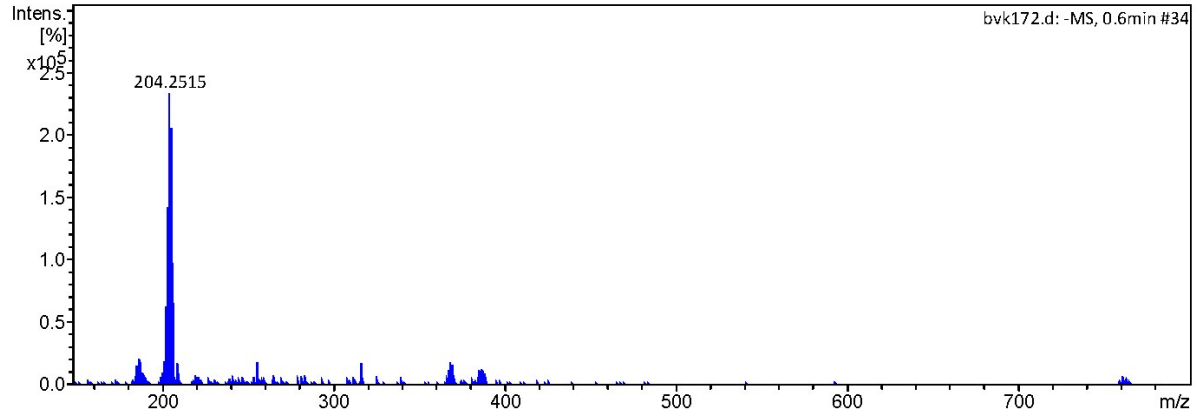


Figure 2S. HRESI⁻-mass spectrum of (Ph_3PCH_2Ph)[**3a**].

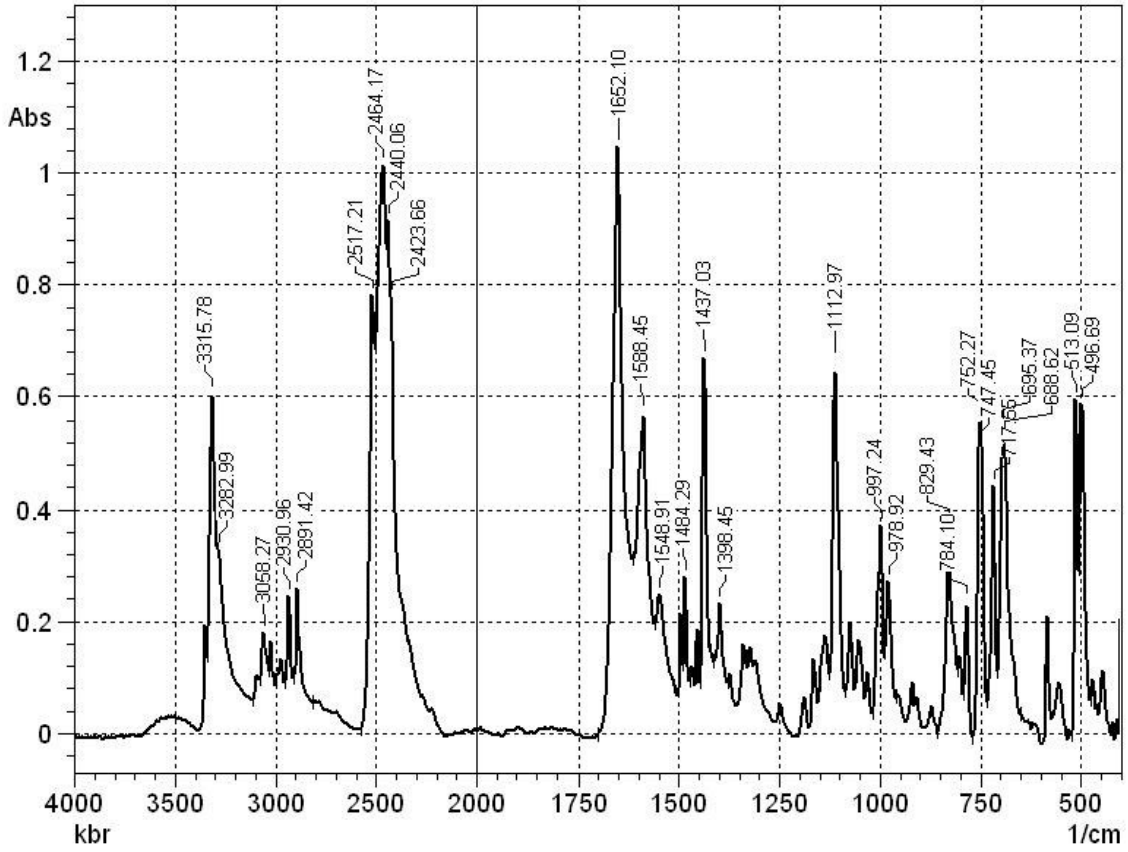


Figure 3S. IR spectrum of (Ph_3PCH_2Ph)[**3a**].

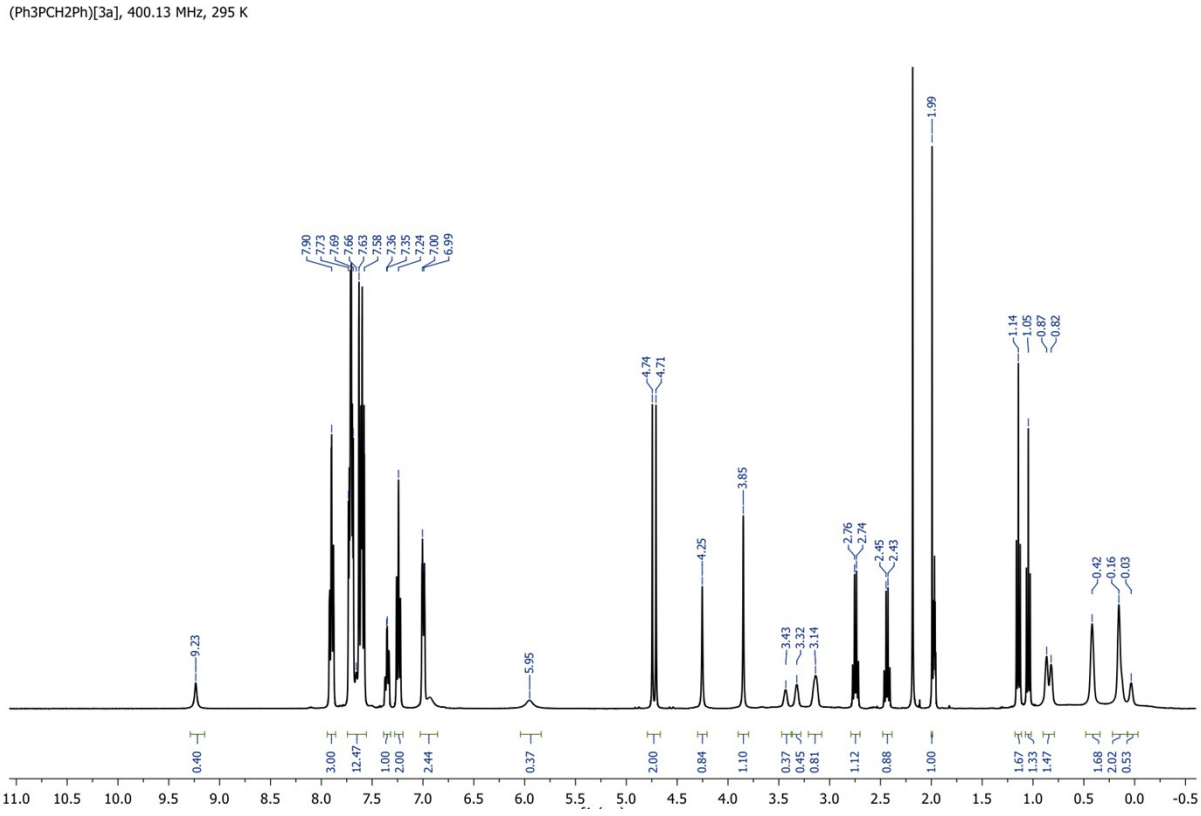


Figure 4S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3a**].

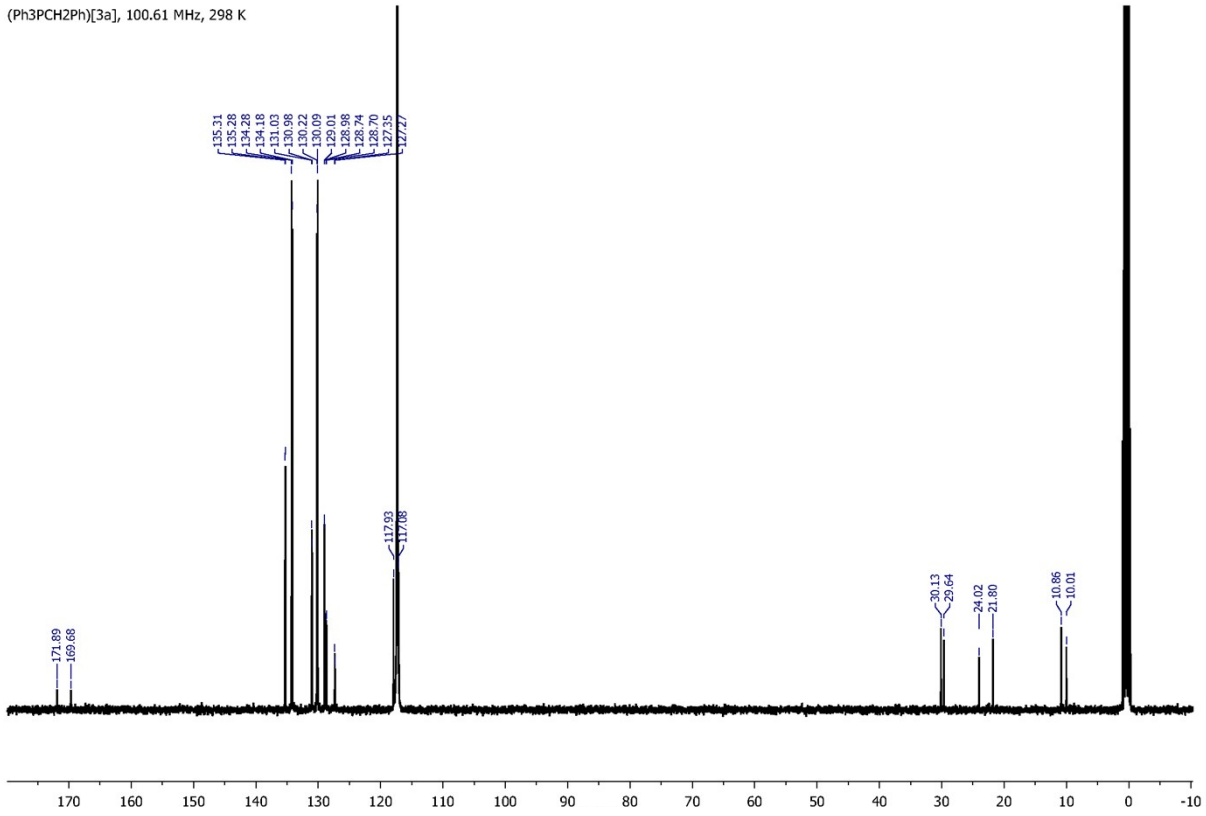


Figure 5S. $^{13}C\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3a**].

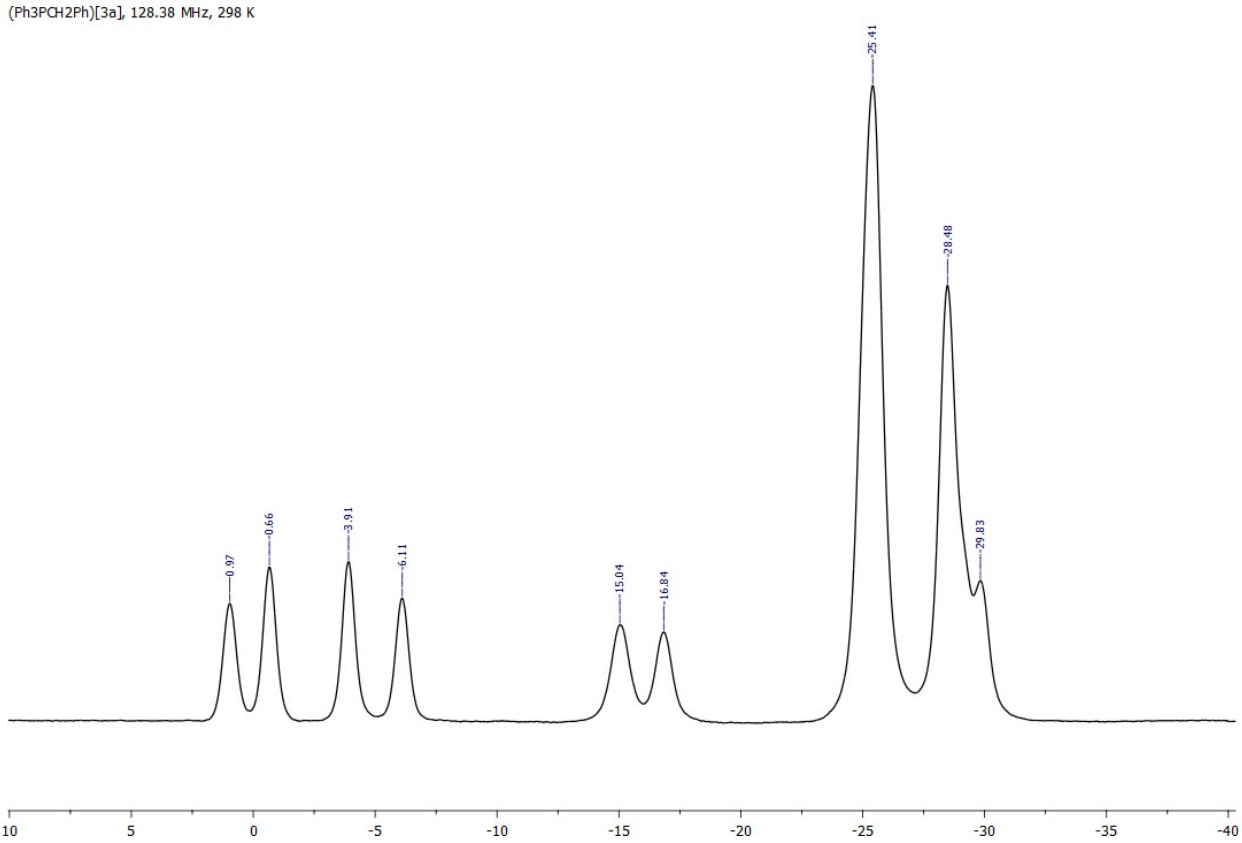


Figure 6S. $^{11}B\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3a**].

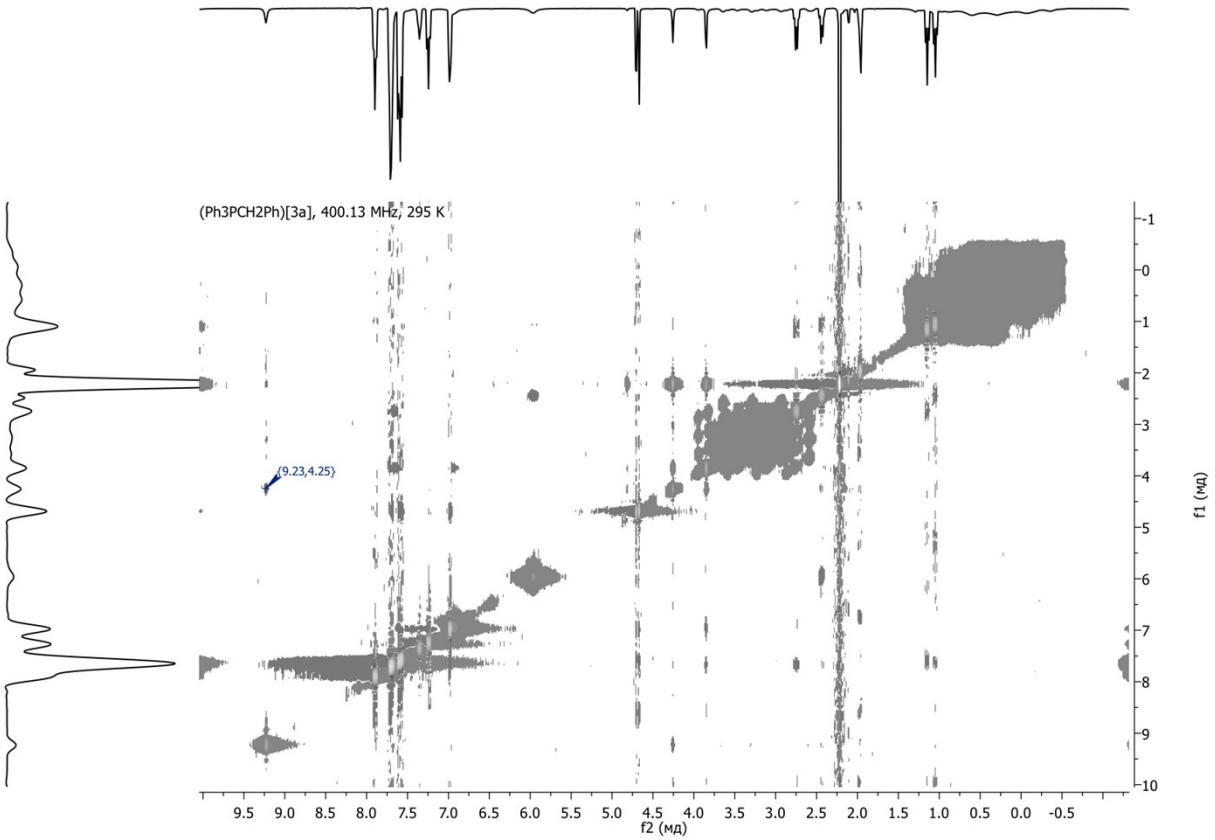
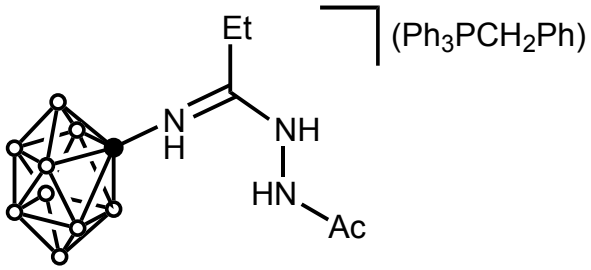


Figure 7S. NOESY-spectrum of (Ph_3PCH_2Ph)[**3a**].

(Ph_3PCH_2Ph)[**3b**]



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
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Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

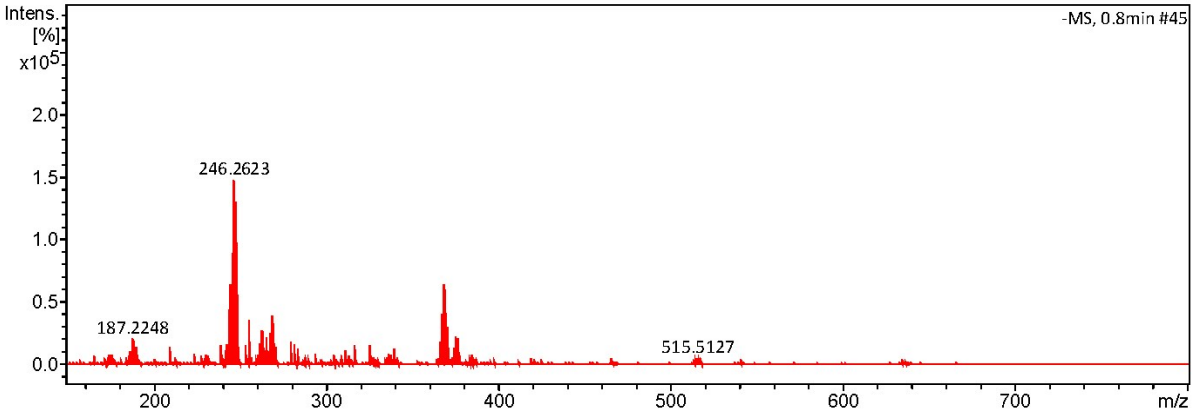


Figure 8S. HRESI⁻-mass spectrum of (Ph_3PCH_2Ph)[**3b**].

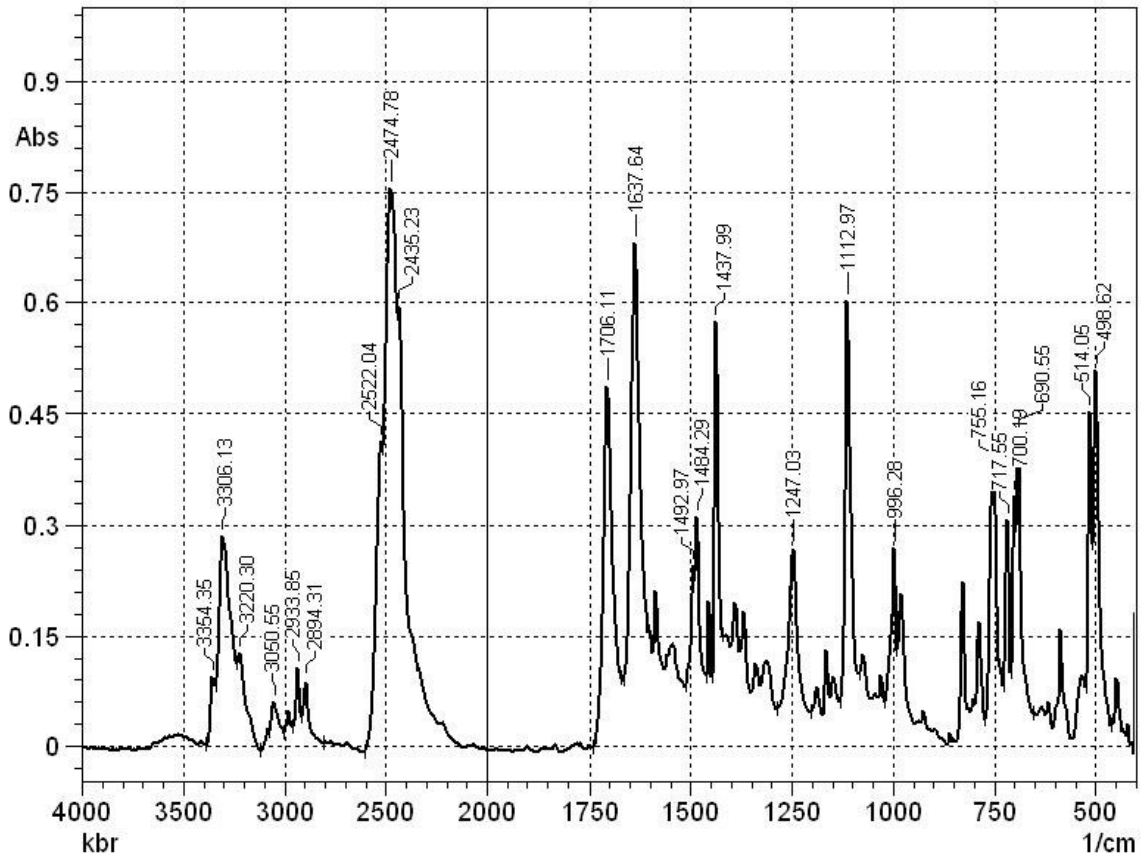


Figure 9S. IR spectrum of (Ph_3PCH_2Ph)[**3b**].

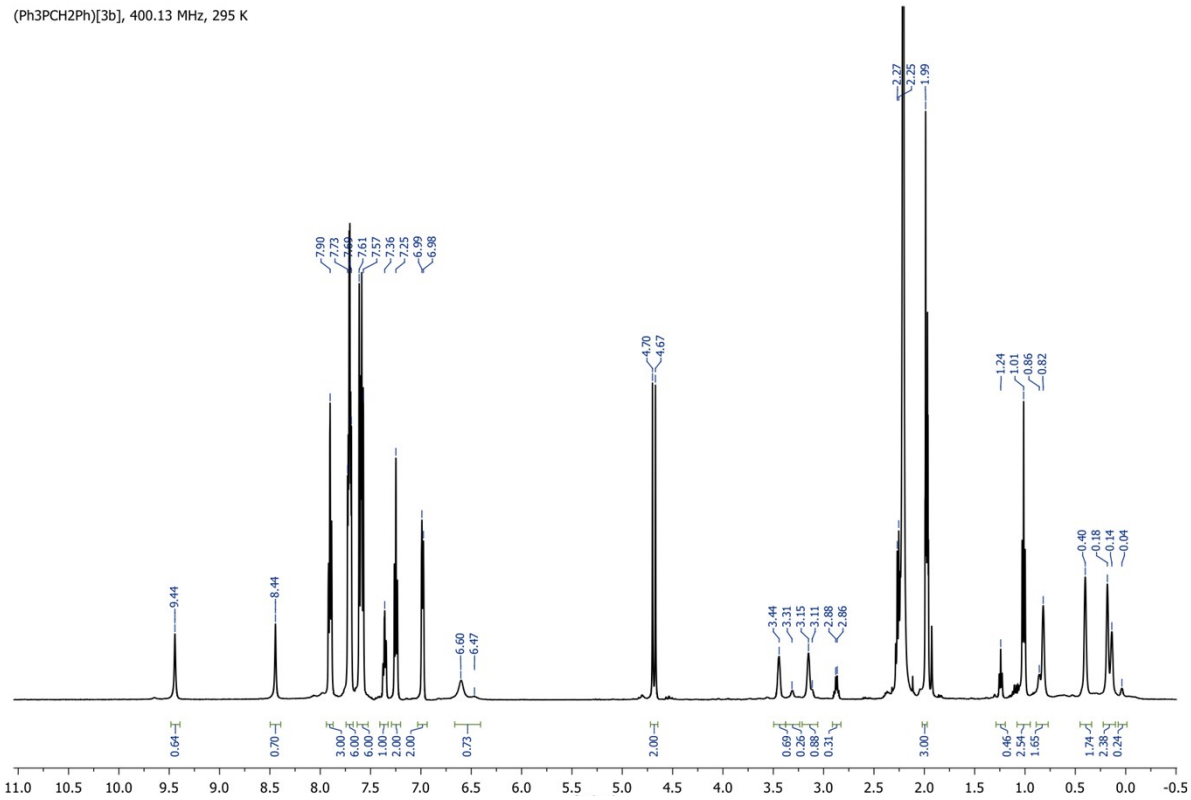


Figure 10S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3b**].

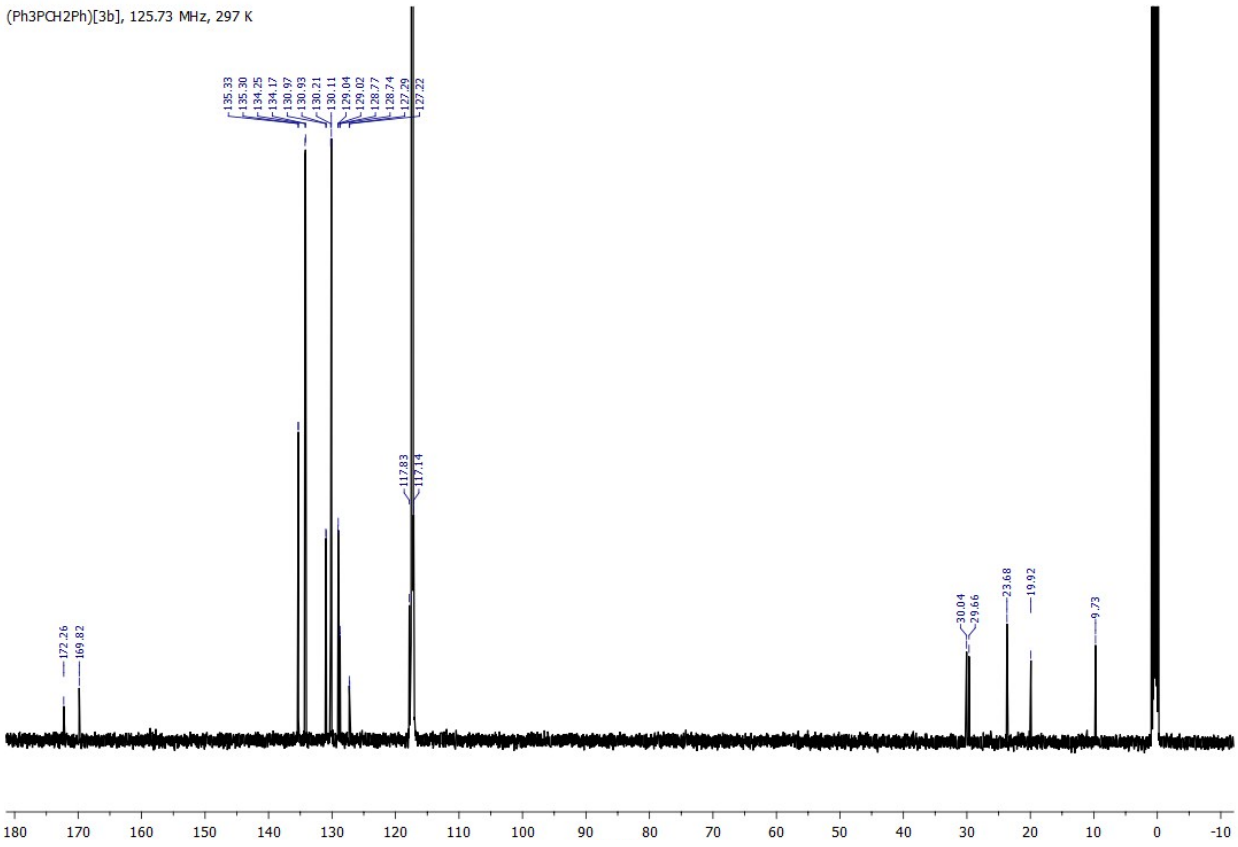


Figure 11S. $^{13}C\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3b**].

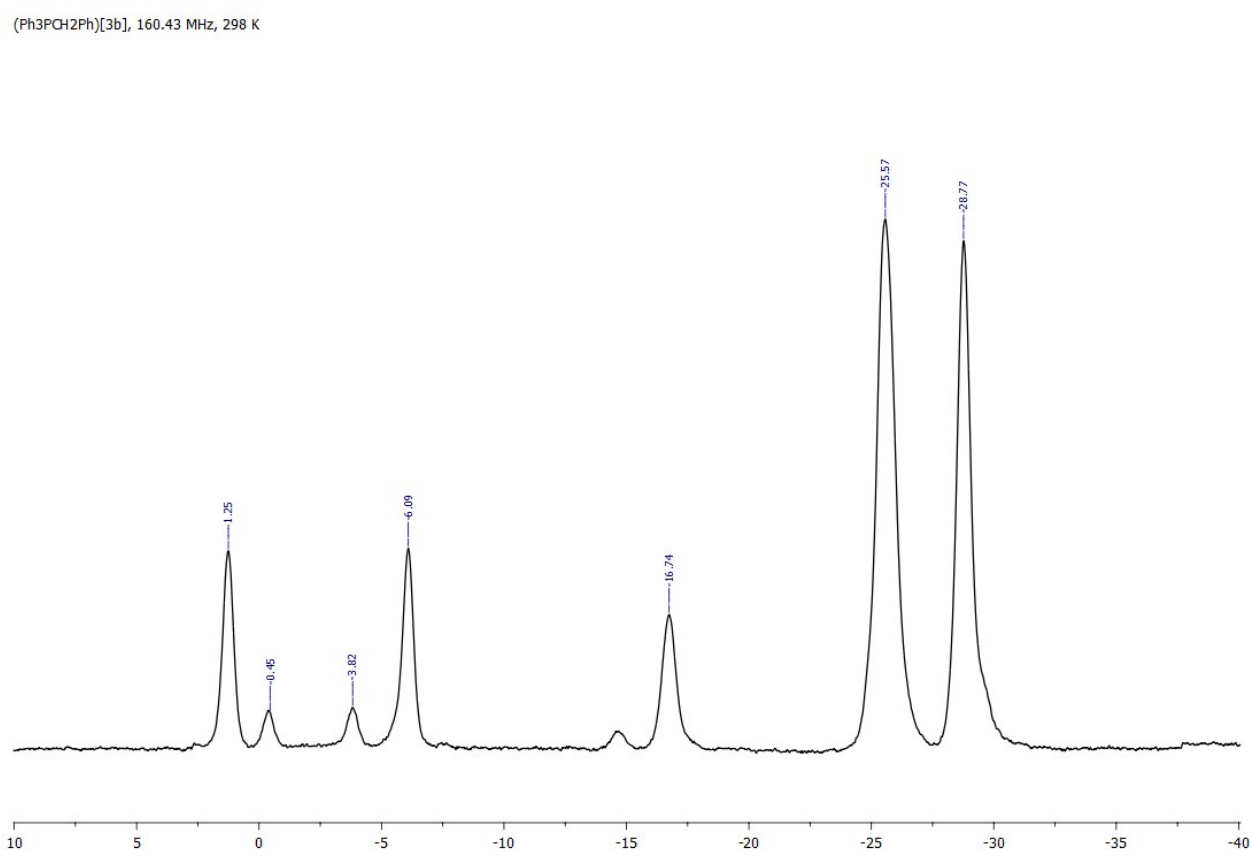
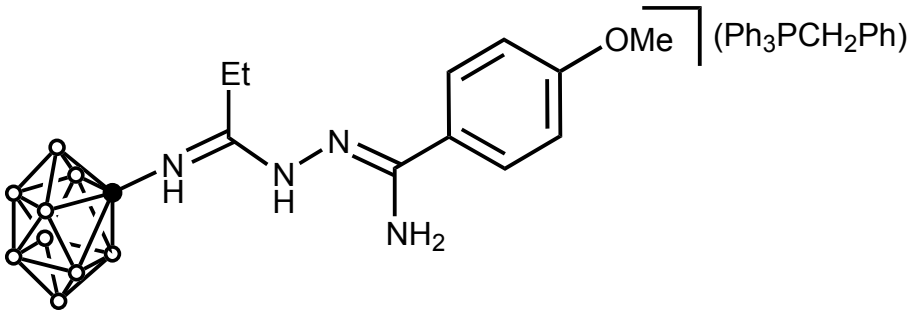


Figure 12S. $^{11}B\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3b**].

(Ph_3PCH_2Ph)[**3c**]



Acquisition Parameter

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Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

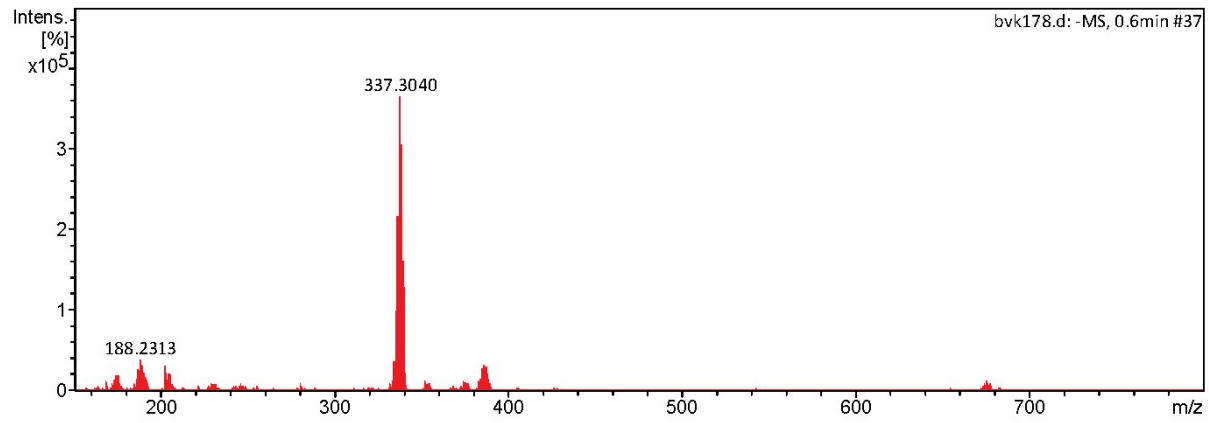


Figure 13S. HRESI⁻-mass spectrum of (Ph_3PCH_2Ph)[**3c**].

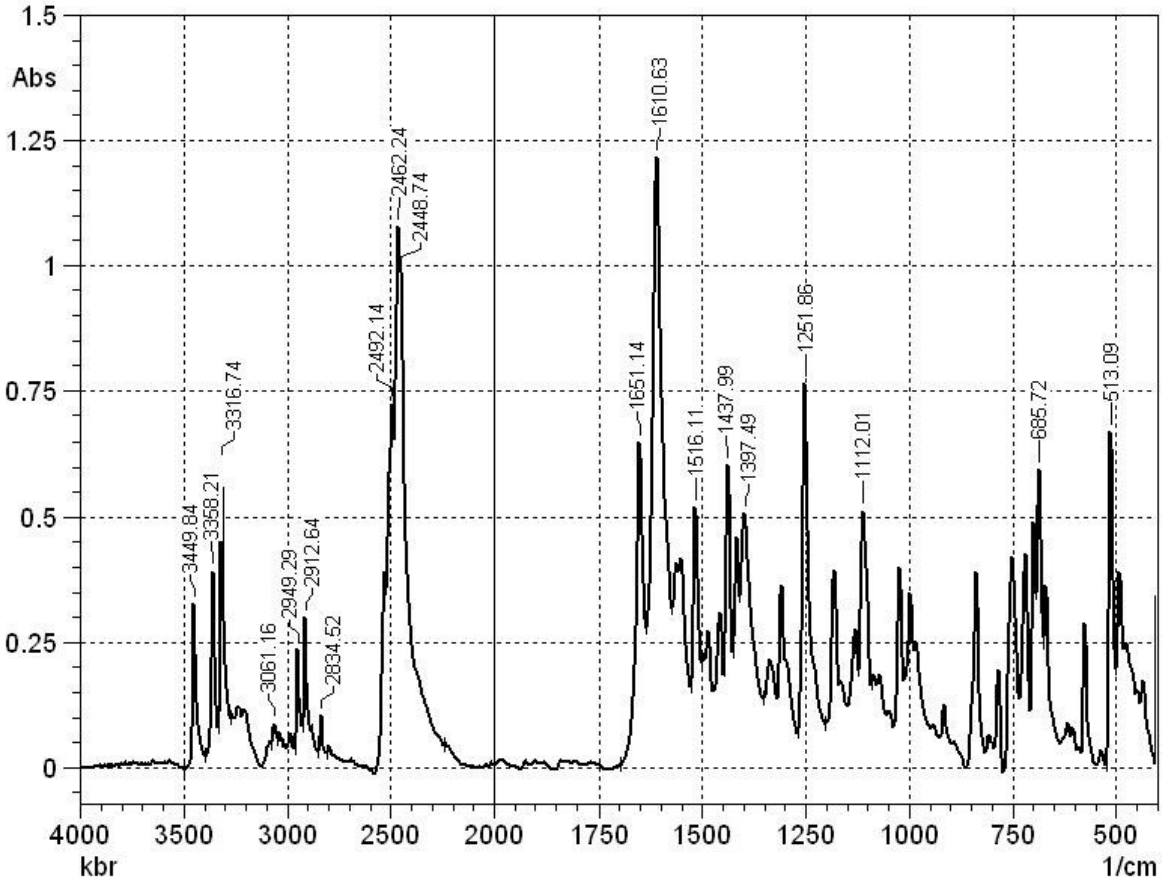


Figure 14S. IR spectrum of (Ph_3PCH_2Ph)[**3c**].

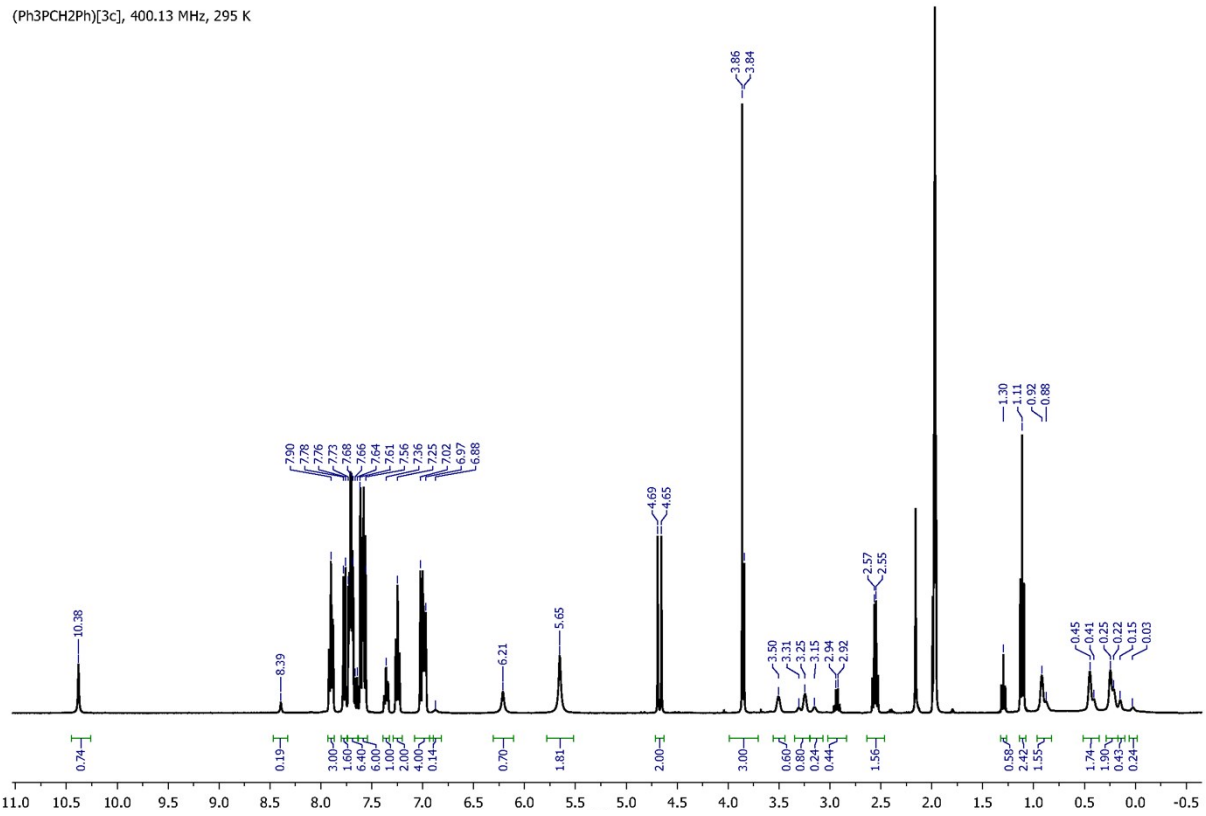


Figure 15S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3c**].

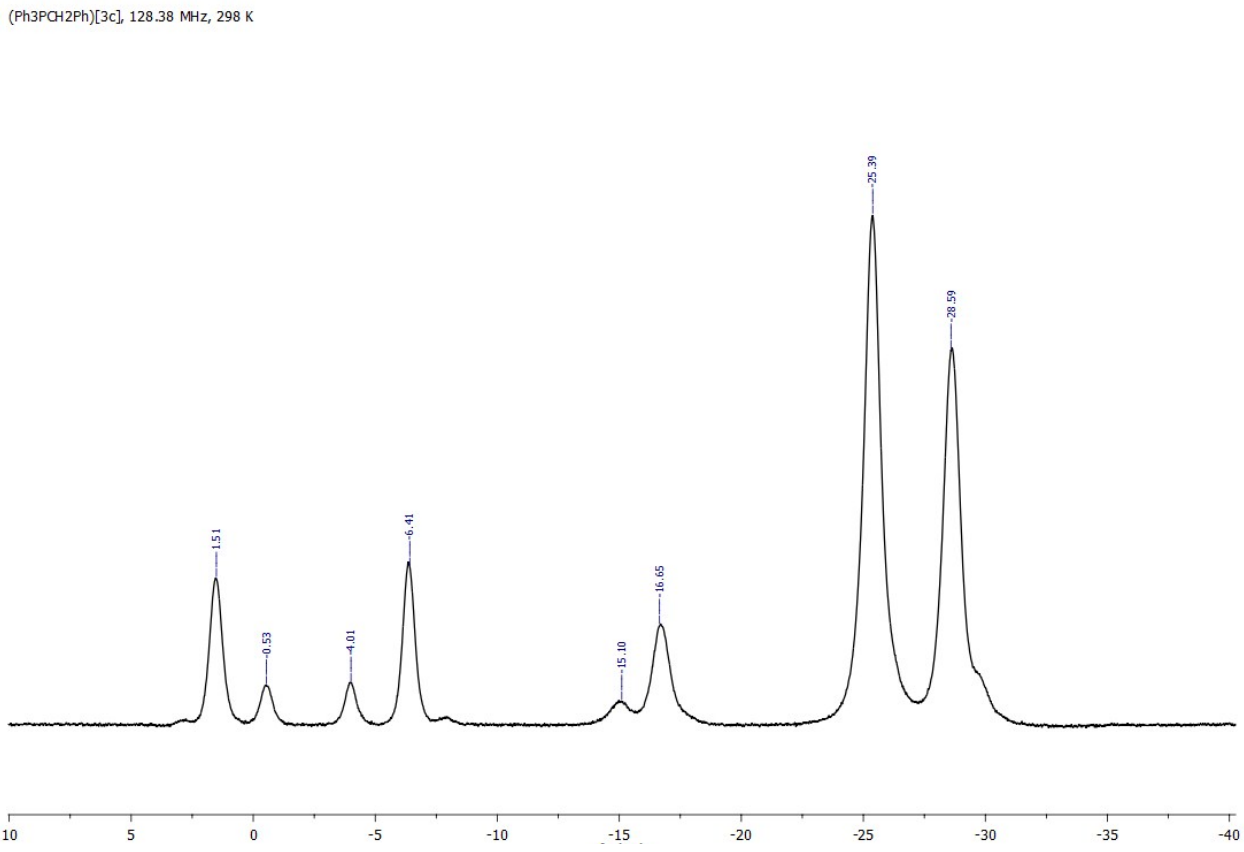


Figure 16S. $^{11}B\{^{1}H\}$ NMR spectrum of(Ph_3PCH_2Ph)[**3c**].

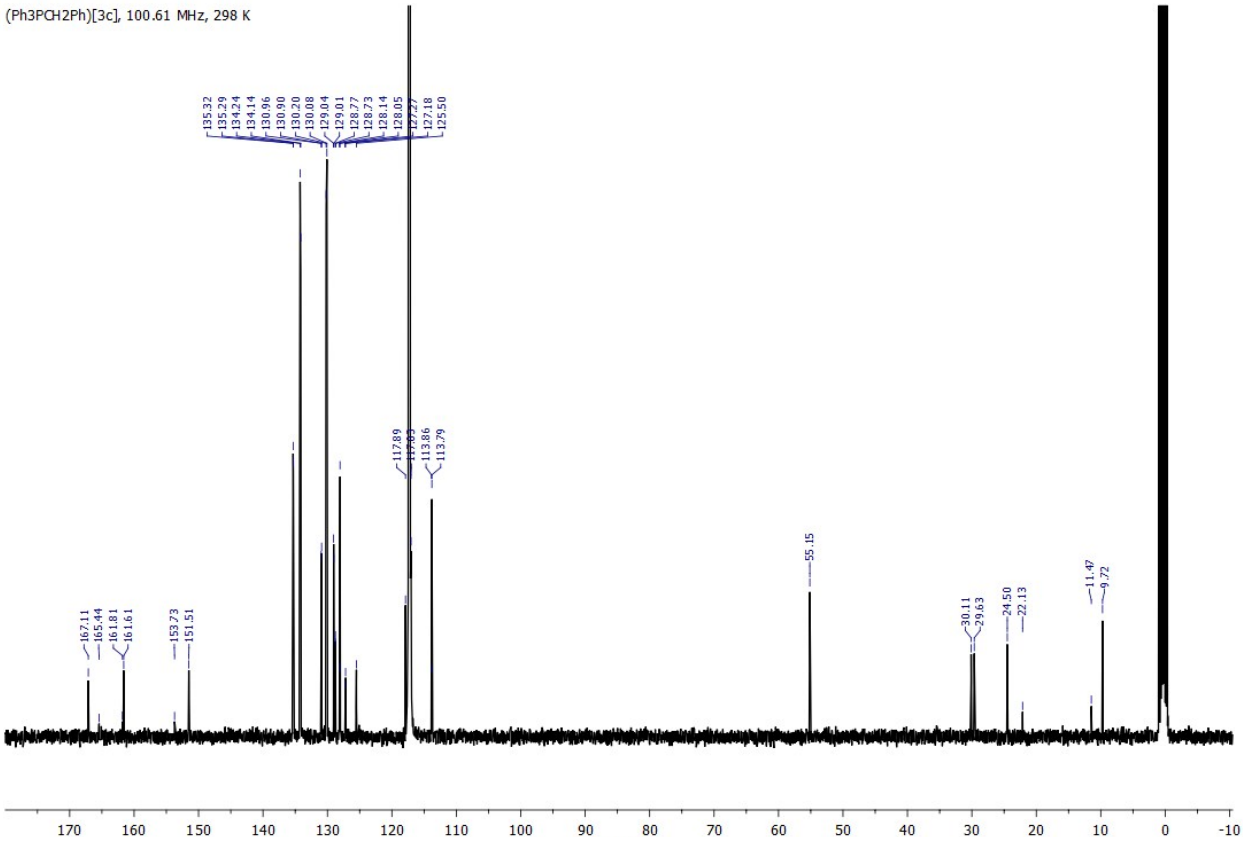
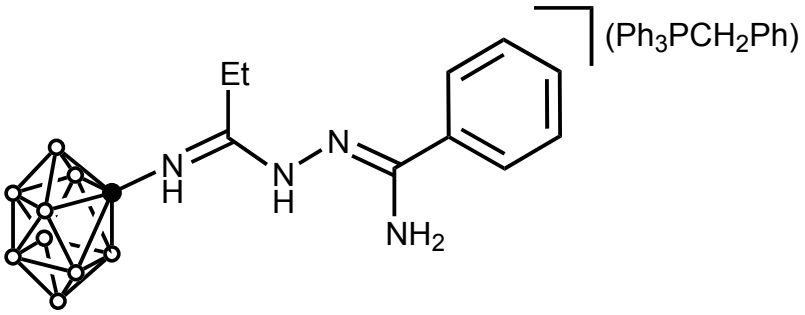


Figure 17S. $^{13}C\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3c**].

(Ph_3PCH_2Ph)[**3d**]



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

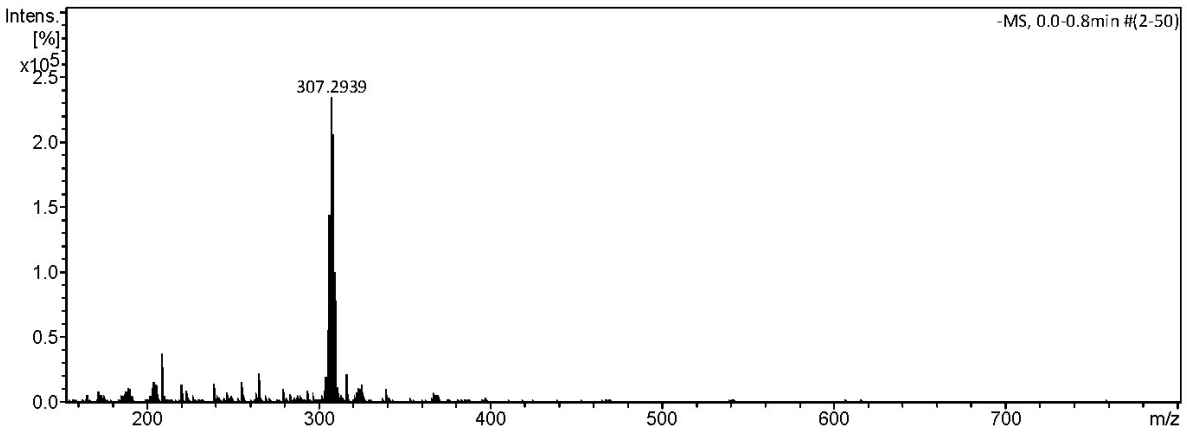


Figure 18S. HRESI$^-$-mass spectrum of (Ph_3PCH_2Ph)[**3d**].

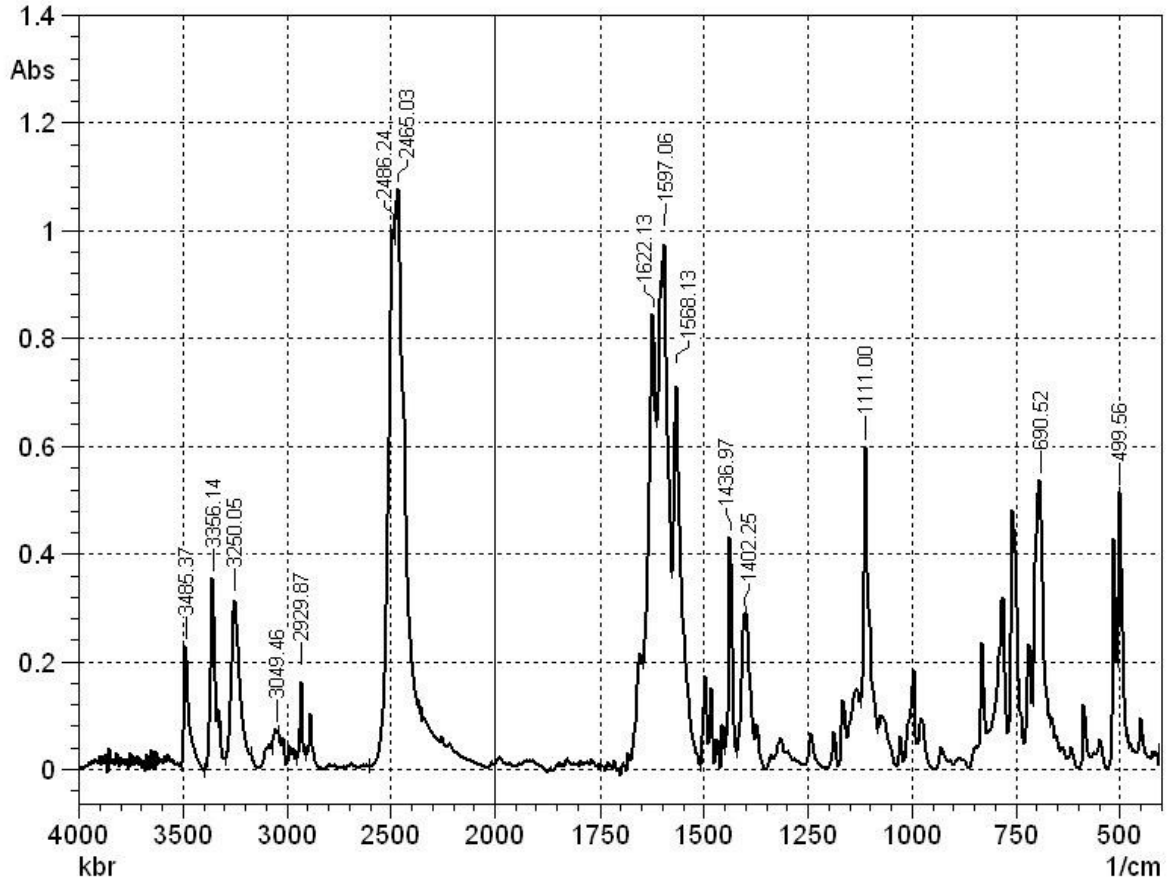


Figure 19S. IR spectrum of (Ph_3PCH_2Ph)[**3d**].

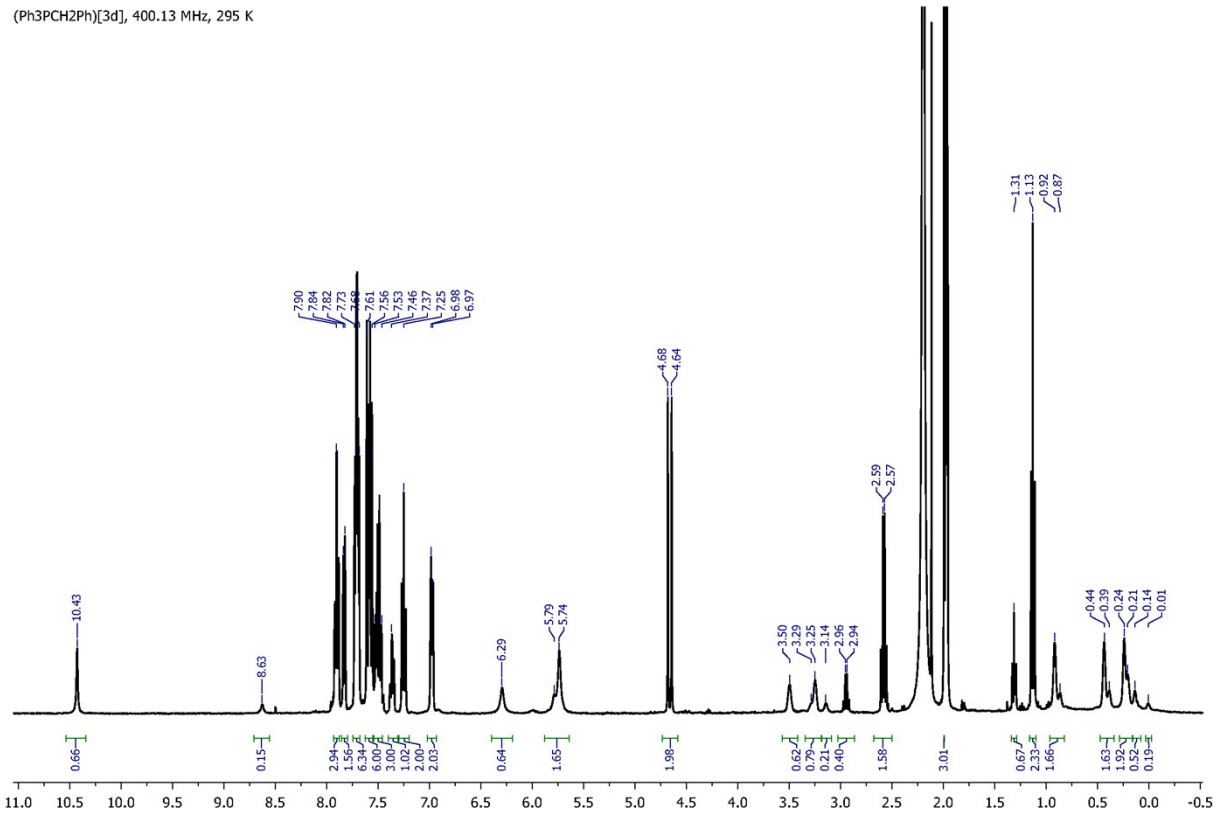


Figure 20S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3d**].

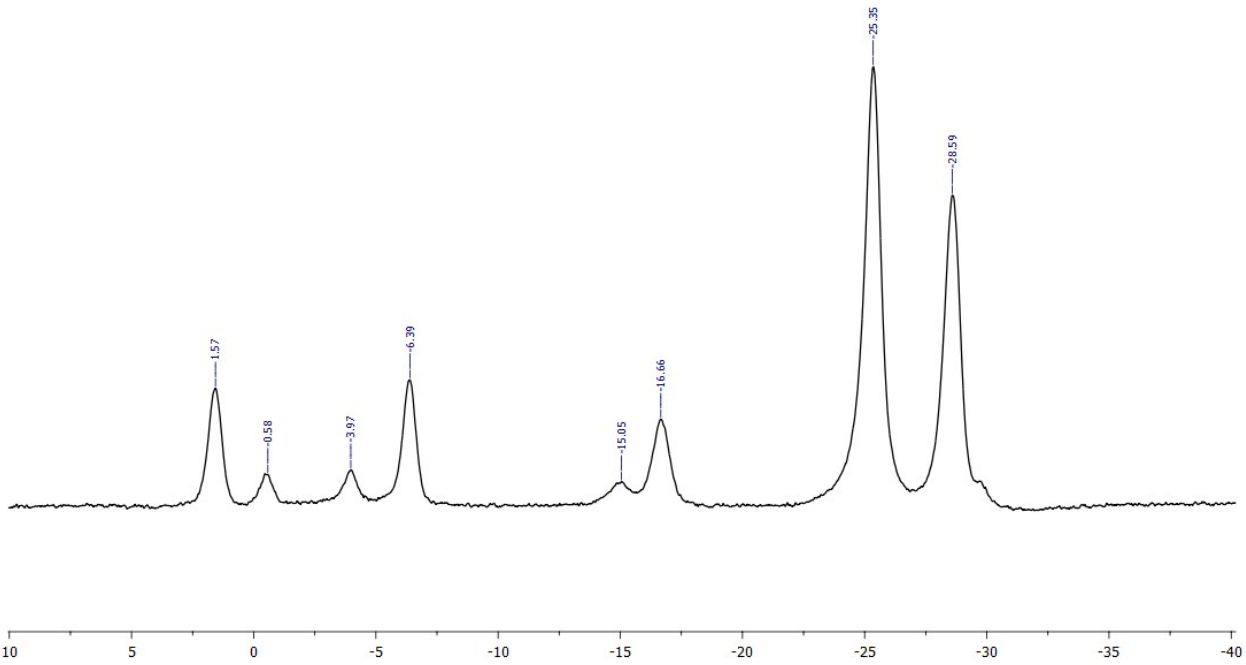


Figure 21S. $^{11}B\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3d**].

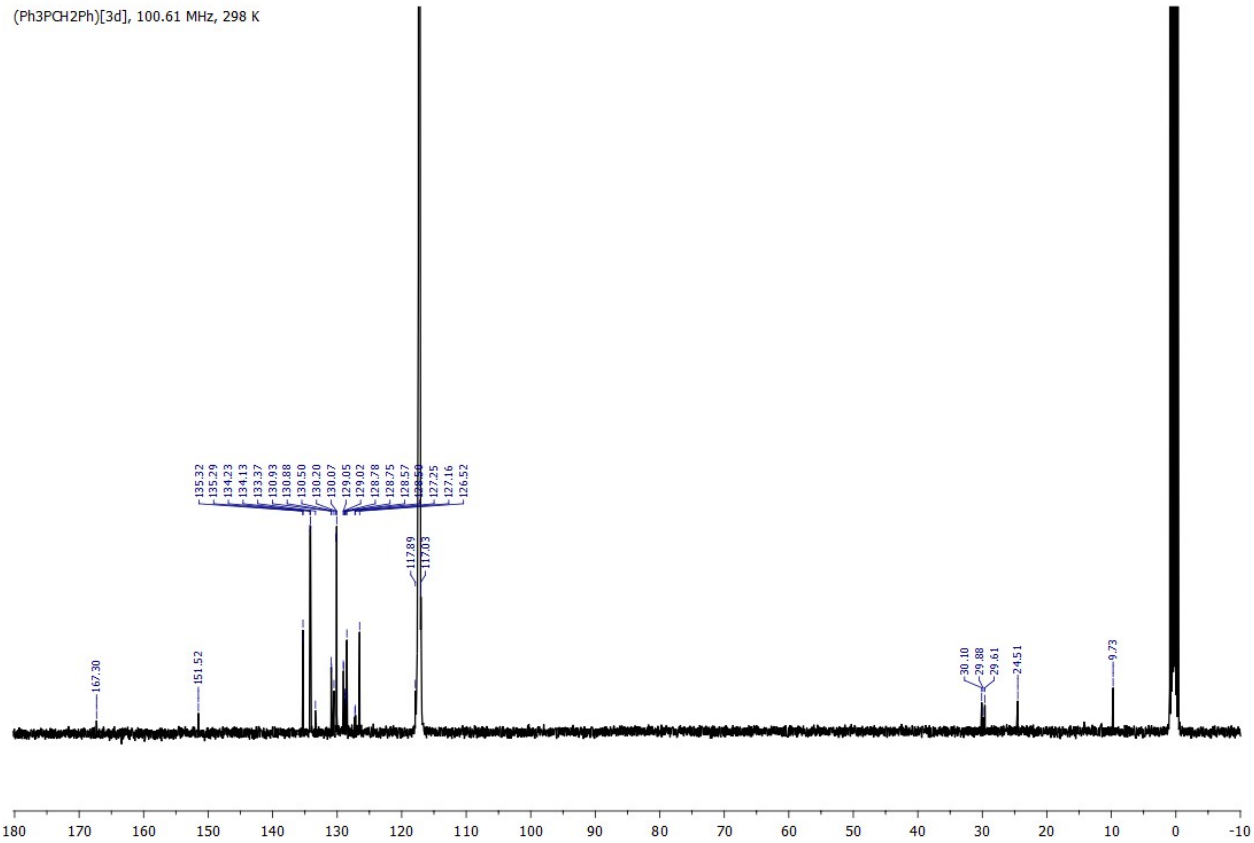
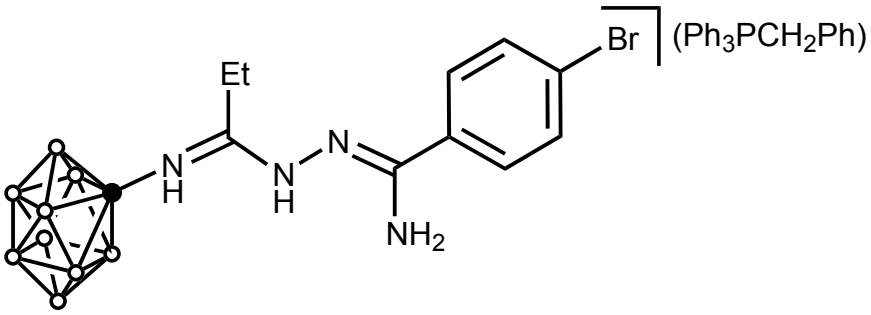


Figure 22S. $^{13}C\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3d**].

(Ph_3PCH_2Ph)[**3e**]



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

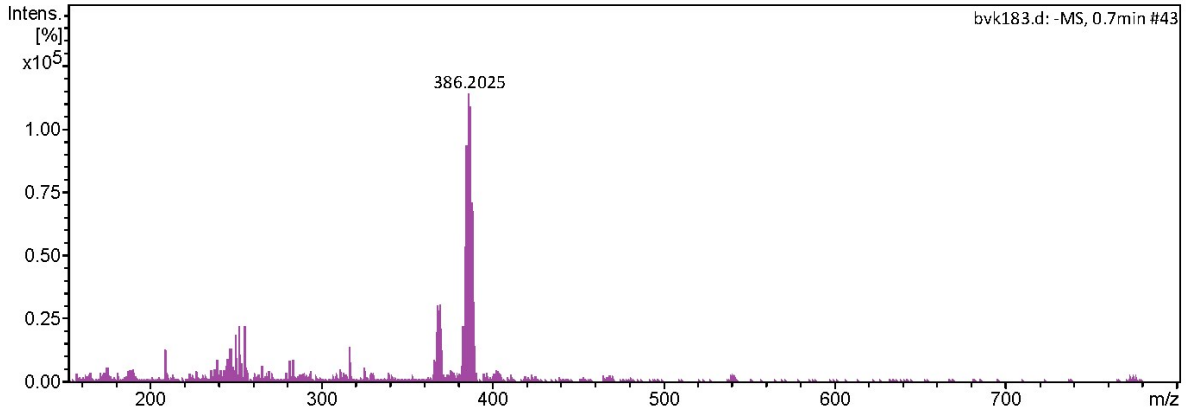


Figure 23S. HRESI$^-$-mass spectrum of (Ph_3PCH_2Ph)[**3e**].

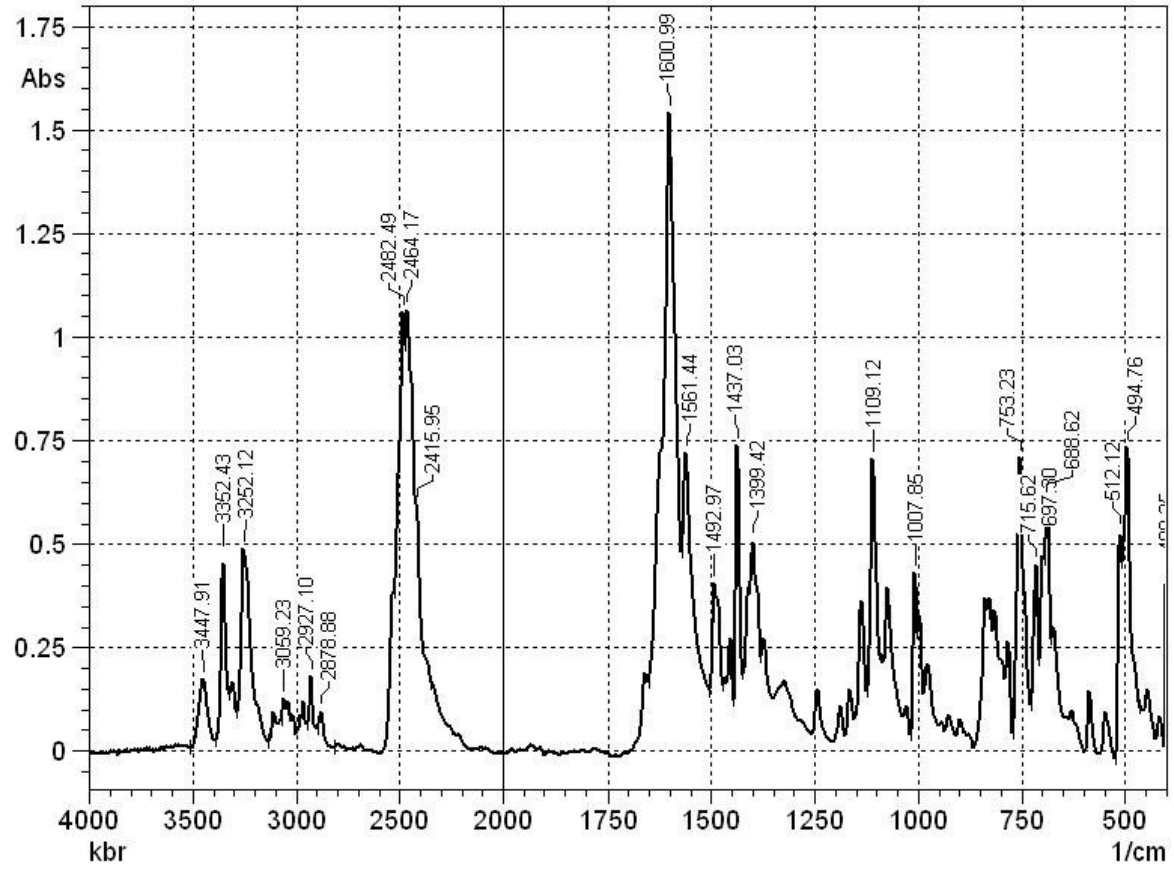


Figure 24S. IR spectrum of (Ph_3PCH_2Ph)[**3e**].

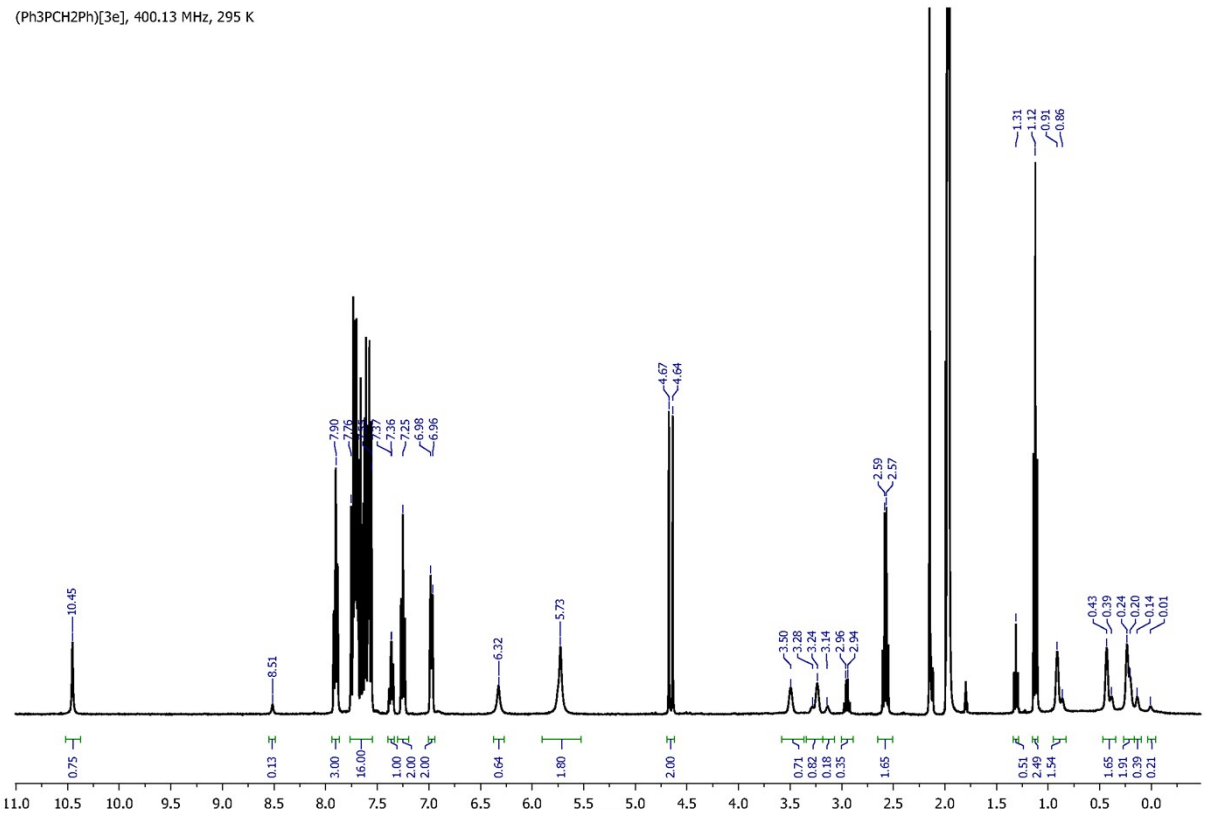


Figure 25S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3e**].

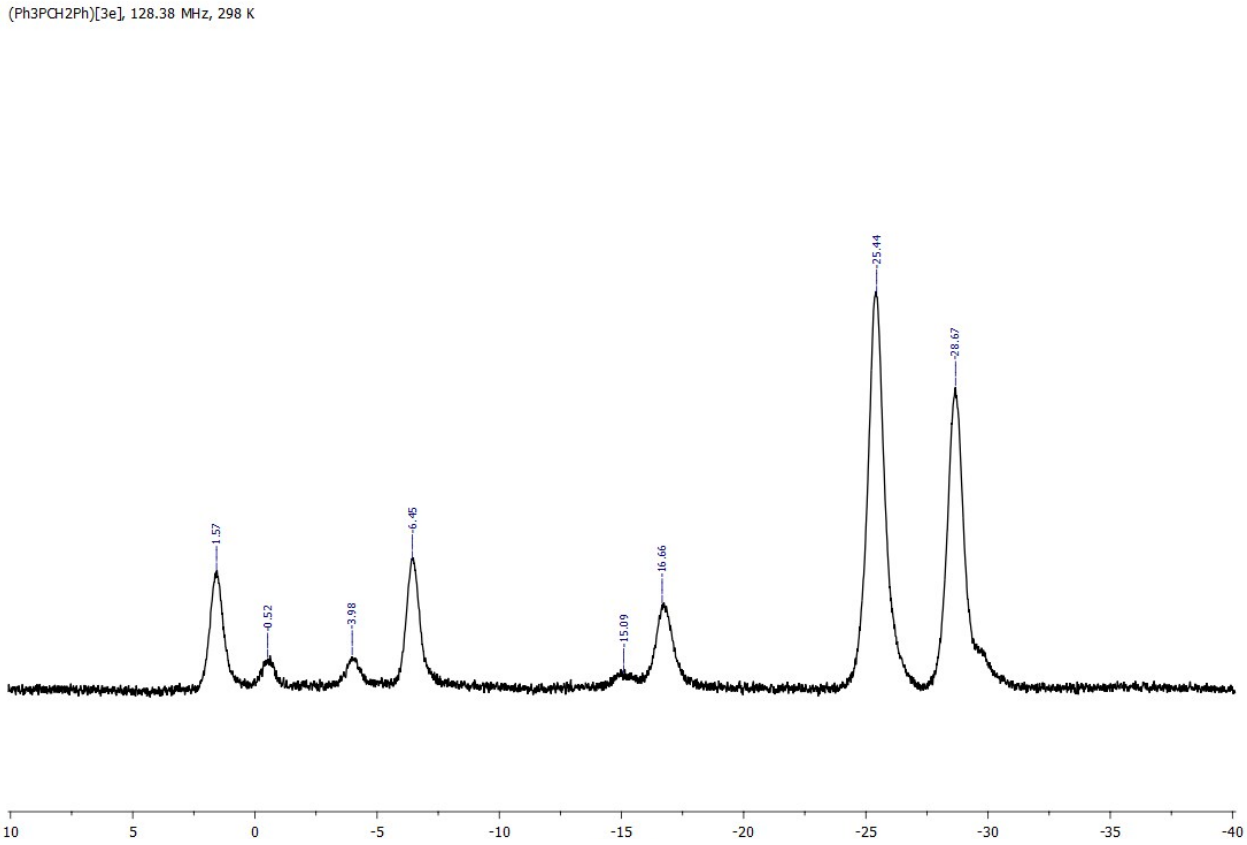
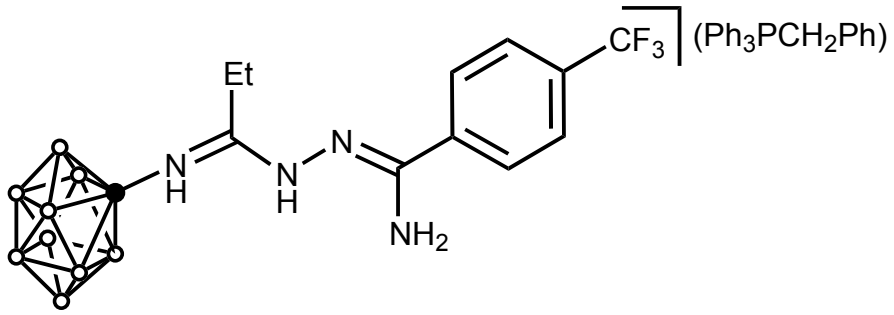


Figure 26S. $^{11}B\{^{1}H\}$ NMR spectrum of(Ph_3PCH_2Ph)[**3e**].

(Ph_3PCH_2Ph)[**3f**]



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

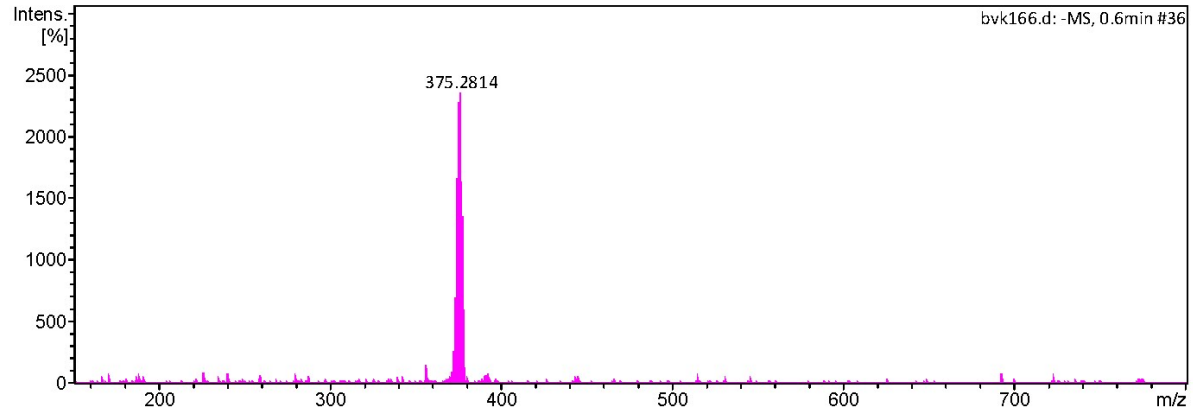


Figure 27S. HRESI⁻-mass spectrum of (Ph_3PCH_2Ph)[**3f**].

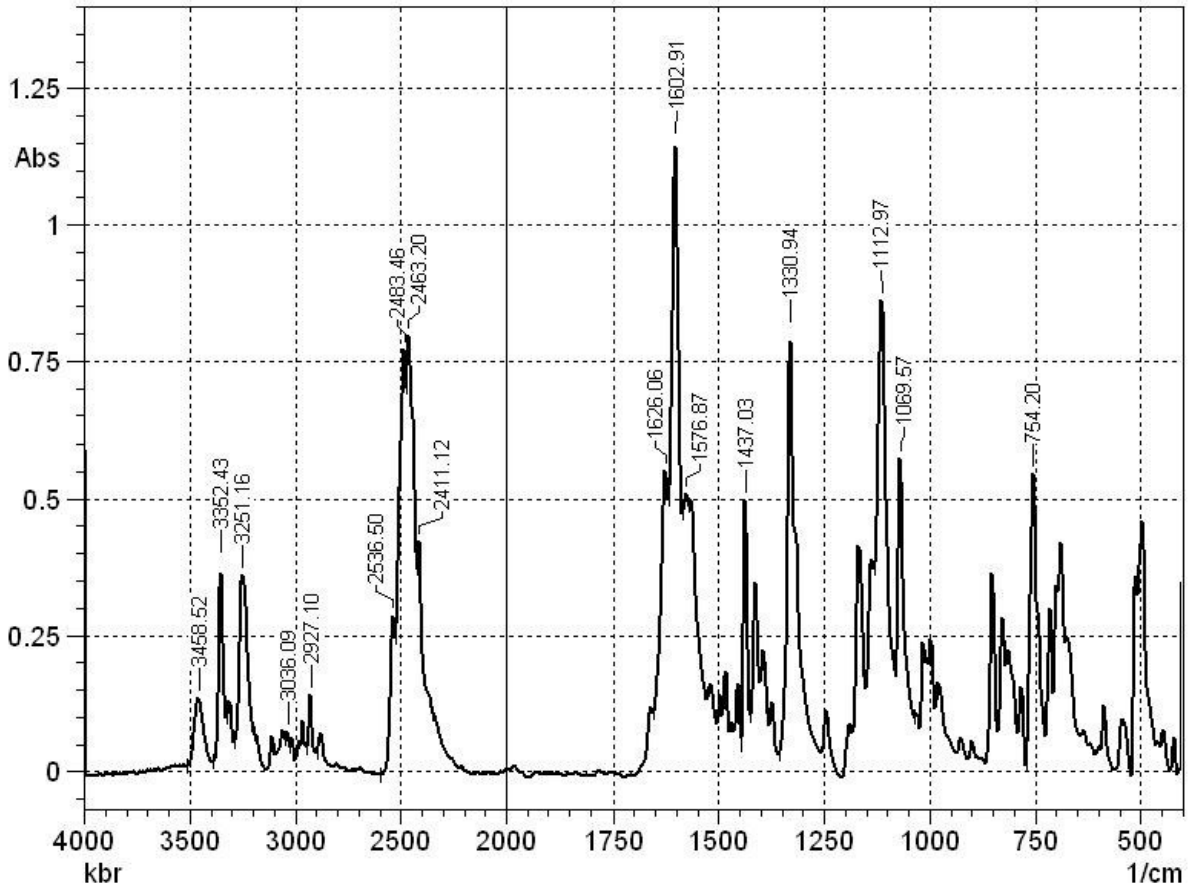


Figure 28S. IR spectrum of (Ph_3PCH_2Ph)[**3f].**

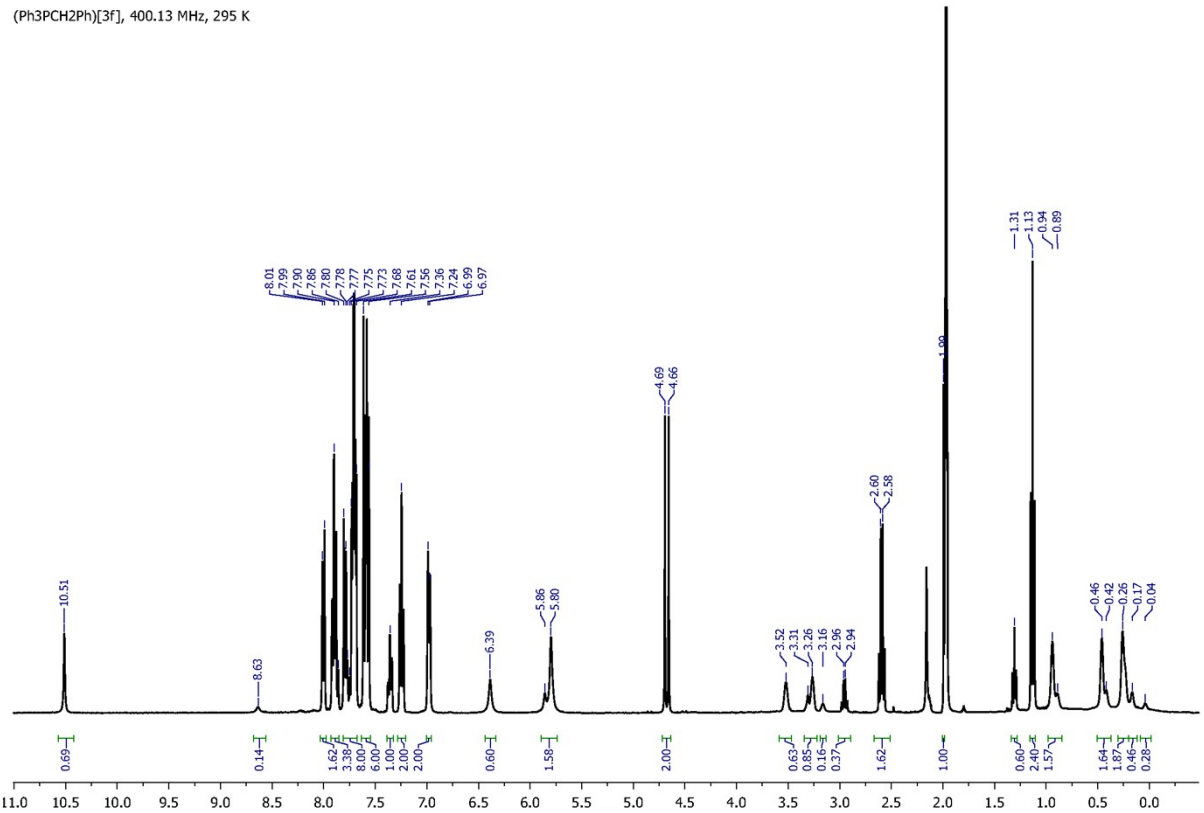


Figure 29S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3f**].

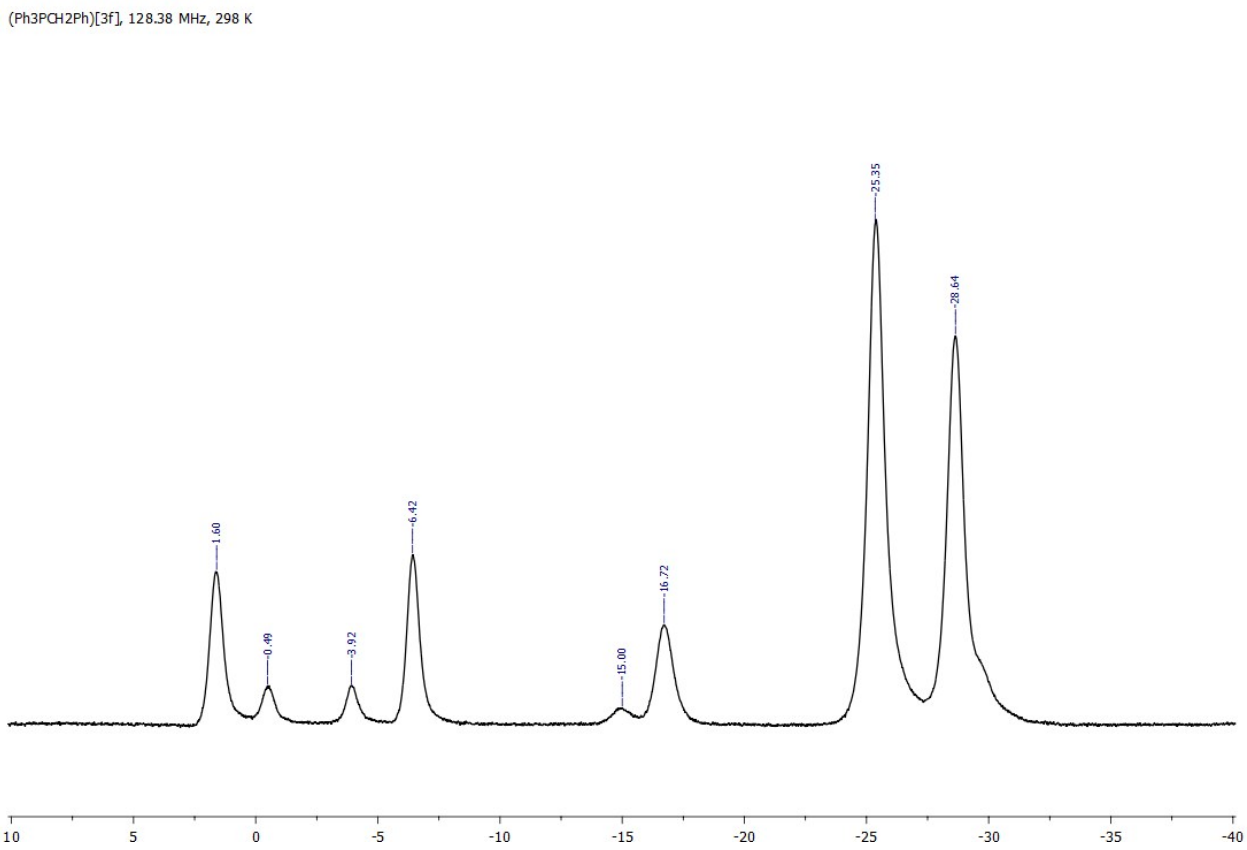
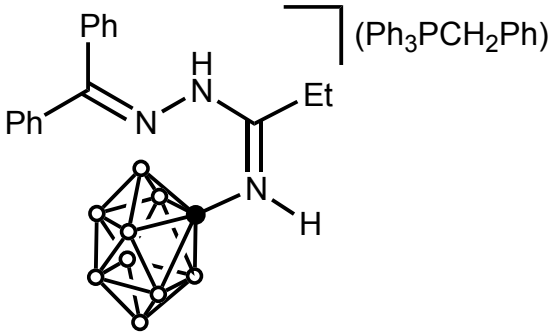


Figure 30S. $^{11}B\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3f**].

(Ph_3PCH_2Ph)[**3g**]



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

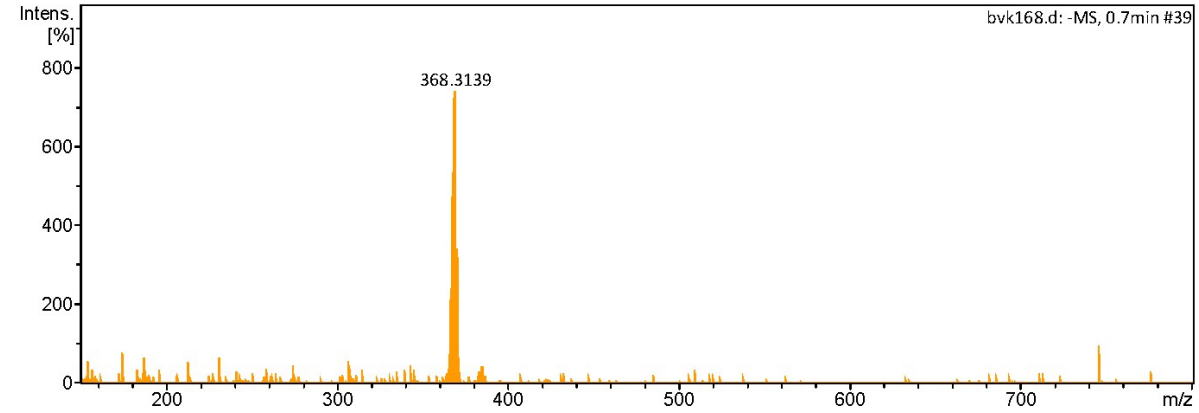


Figure 31S. HRESI$^-$-mass spectrum of (Ph_3PCH_2Ph)[**3g**].

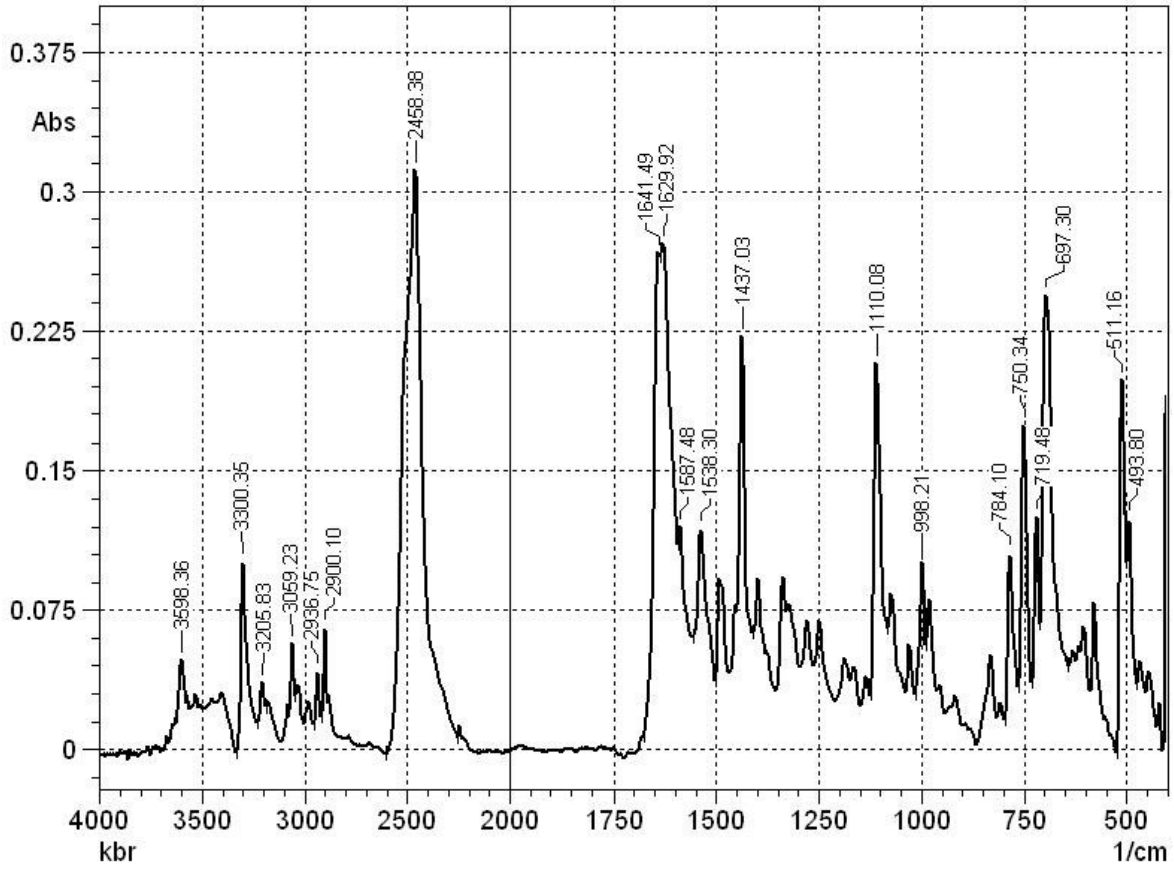


Figure 32S. IR spectrum of (Ph_3PCH_2Ph)[**3g].**

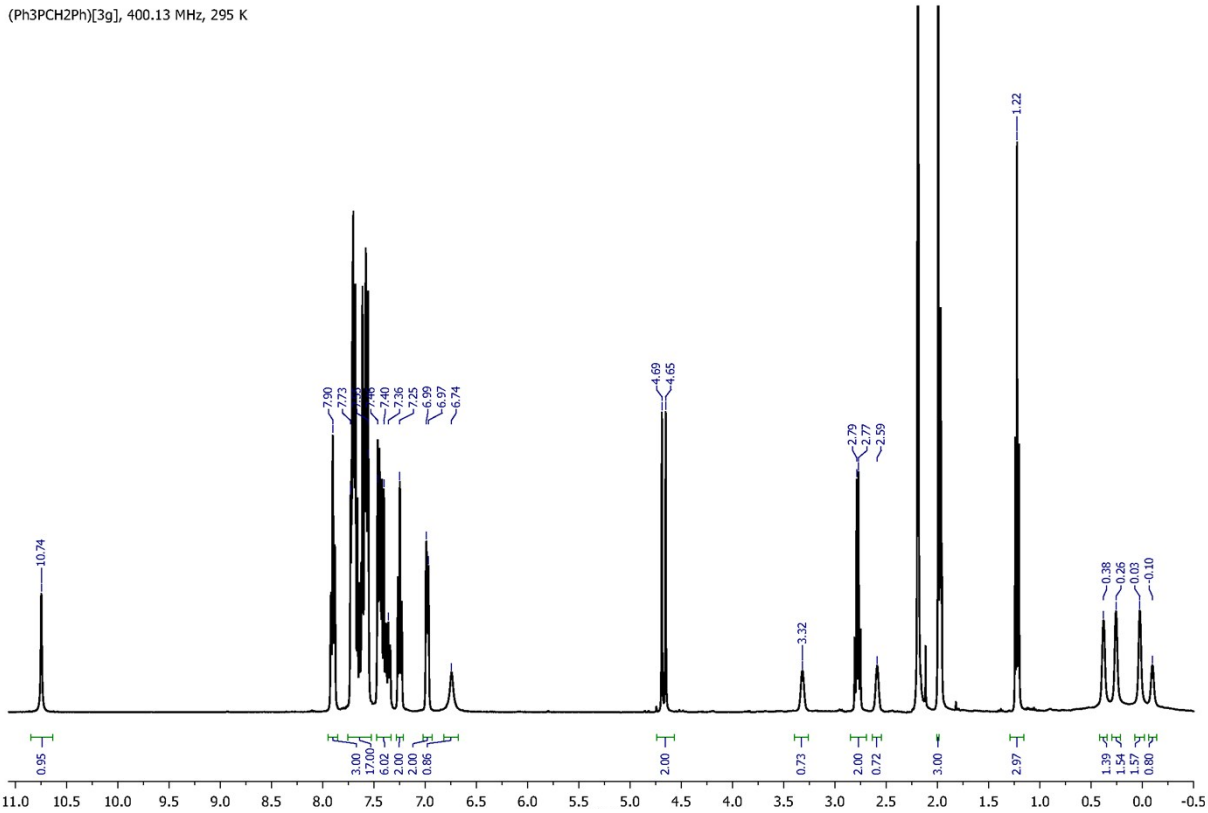


Figure 33S. $^{1}H\{^{11}B\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3g**].

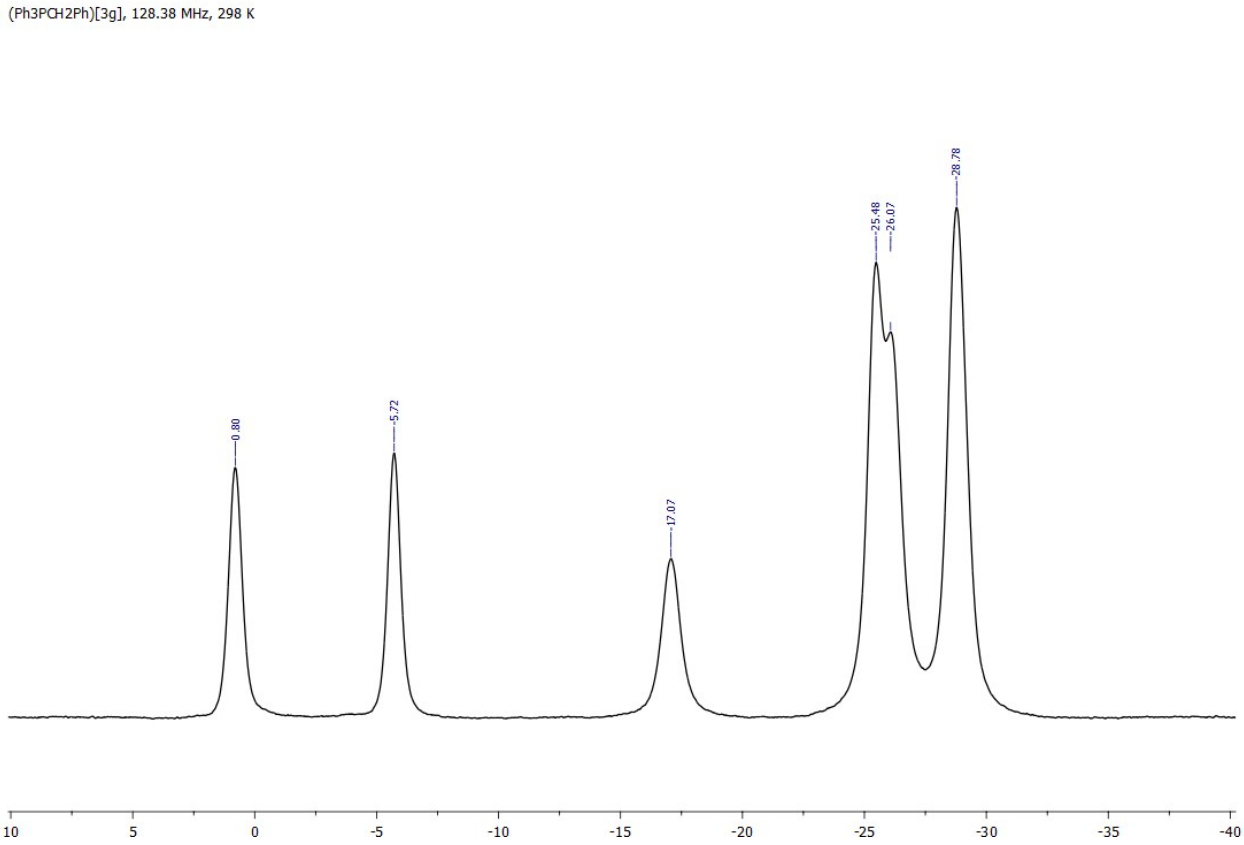


Figure 34S. $^{11}B\{^{1}H\}$ NMR spectrum of (Ph_3PCH_2Ph)[**3g**].

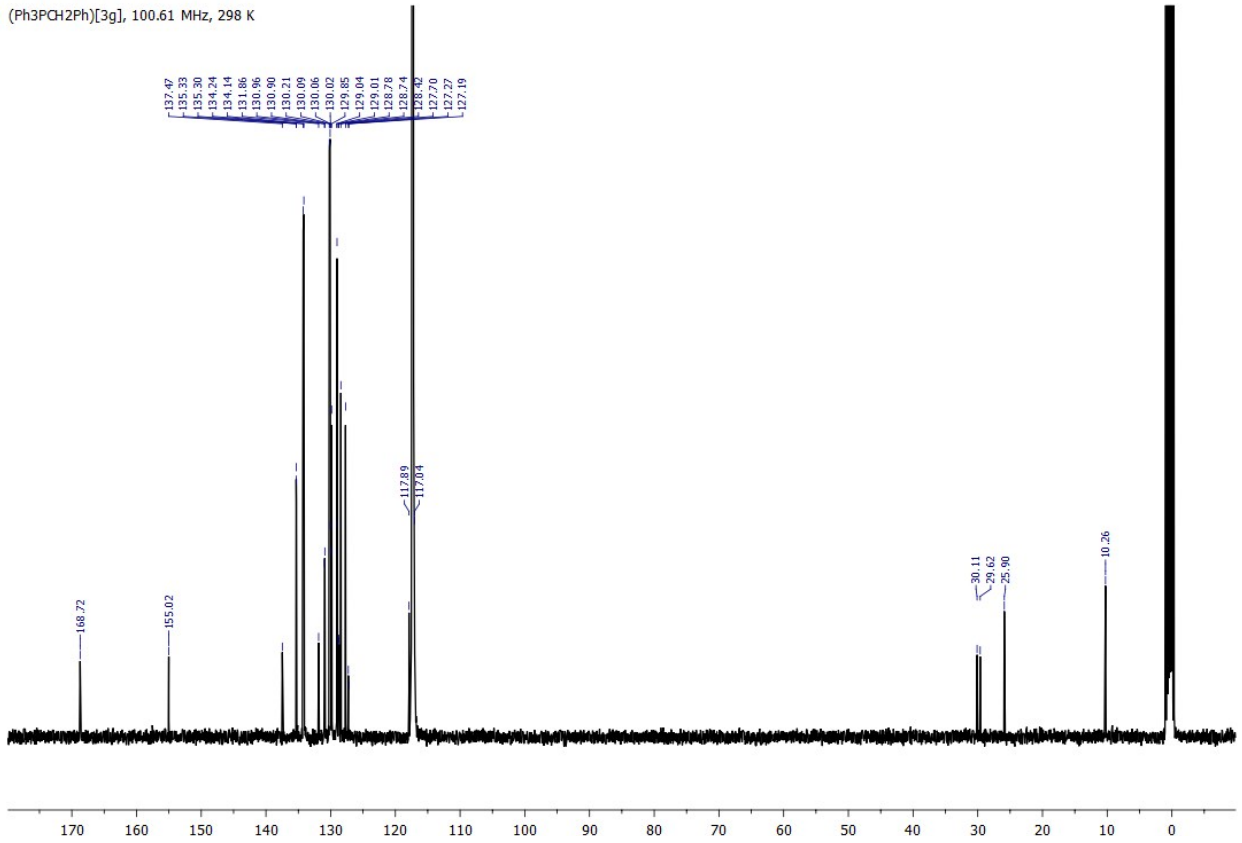
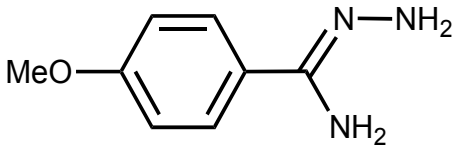


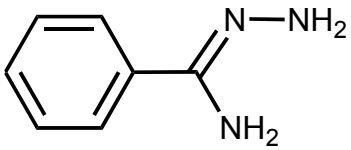
Figure 35S. $^{13}C\{^{1}H\}$ spectrum of (Ph_3PCH_2Ph)[**3g**].

Synthesis and Characterization of 2c–f

Dry gaseous HCl was bubbled through an ice-cooled vigorously stirred solution/suspension of corresponding benzonitrile (0.05 mol) in absolute MeOH (25 mL) for 3 h. The mixture was left stirring overnight and then poured into Et_2O (100 mL). Colorless crystals were collected and washed with two Et_2O 30-mL portions. The obtained iminoester hydrochloride was added to an ice-cooled stirred mixture of CH_2Cl_2 (80 mL) and saturated aqueous $NaHCO_3$ (80 mL). The organic layer was separated and aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined organic phases were dried over $CaCl_2$ and evaporated to dryness. Hydrazine hydrate (0.035 mol) was added dropwisely to an ice-cooled stirred solution of the resulted iminoester (0.03 mol) in ^{i}PrOH (50 mL). The mixture was stirred for 1 h under gradual cooling to RT and then at RT overnight. The residue after evaporation of volatiles was treated with Et_2O (50 mL) and cooled in ice. Crystals were filtered off and dried in *vacuo*.

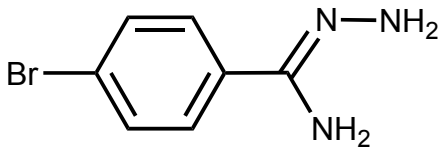


2c. Yield: 42%. Anal. Calcd for $C_8H_{11}N_3O$: C, 58.17; H, 6.71; N, 25.44. Found: C, 57.89; H, 6.75; N, 25.68. HRESI$^+$-MS (*m/z*): 166.0969 ([M + H]$^+$, calcd 166.09751). HRESI$^-$-MS (*m/z*): 164.0813 ([M – H]$^-$, calcd 164.0824). IR (KBr, selected bonds, cm^{-1}): 3396(m), 3269(m), 3176(m) ν(N–H); 2962(w) ν(C–H); 1642(s) ν(C=N); 1243(s) ν(C_{ar}–O–C). ^{1}H NMR (δ): 7.61 (d, J = 8.9 Hz, 2H, C_6H_4), 6.93 (d, J = 8.9 Hz, 2H, C_6H_4), 4.94 (s, br, 2H. NH_2), 4.39 (s, br, 2H, NH_2), 3.83 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (δ): 160.29 (NCN), 127.67, 126.88, 126.81, 113.49 (C_6H_4), 54.98 (OCH_3).

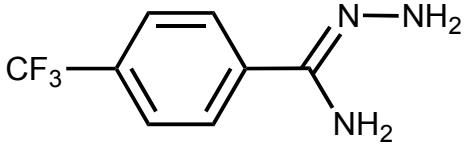


2d.Yield: 53%. Anal. Calcd for $C_7H_9N_3$: C, 62.20; H, 6.71; N, 31.09. Found: C, 62.03; H, 6.71; N, 31.17. HRESI$^+$-MS (*m/z*): 136.0877 ([M + H]$^+$, calcd 136.0869). HRESI$^-$-MS (*m/z*): 134.0706 ([M – H]$^-$, calcd 134.0718). IR (KBr, selected bonds, cm^{-1}): 3396(m), 3326(m), 3161(m) ν(N–H);

1640(s) ν(C=N). ^{1}H NMR (δ): 7.72–7.67 (m, 2H, Ph), 7.41–7.36 (m, 3H, Ph), 4.93 (s, br, 2H, NH_2), 4.56 (s, br, 2H, NH_2). $^{13}C\{^{1}H\}$ NMR (δ): 148.87 (NCN), 135.85, 129.23, 123.75, 125.86 (Ph).



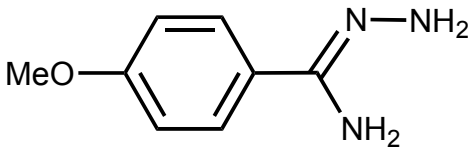
2e.Yield: 50%. Anal. Calcd for $C_7H_8BrN_3$: C, 39.28; H, 3.77; N, 19.63. Found: C, 38.99; H, 3.72; N, 19.85. HRESI^{+}-MS: no characteristic peaks were detected. HRESI^{-}-MS (*m/z*): 211.9821 ([M – H]$^{-}$, calcd 211.9823). IR (KBr, selected bonds, cm^{-1}): 3453(m), 3301(m), 3143(m) ν(N–H), 1634(s) ν(C=N). ^{1}H NMR (δ): 7.60 (d, J = 8.6 Hz, 2H, C_6H_4), 7.54 (d, J = 8.6 Hz, 2H, C_6H_4), 4.87 (s, br, 2H, NH_2), 4.58 (s, br, 2H, NH_2). $^{13}C\{^{1}H\}$ NMR (δ): 147.08 (NCN), 134.44, 131.17, 127.17, 122.08 (C_6H_4).



2f. Yield: 46%. HRESI^{+}-MS (*m/z*): 204.0744 ([M + H]$^{+}$, 204.0749), HRESI^{-}-MS (*m/z*): 202.0588 ([M – H]$^{-}$, 202.0592). IR (KBr, selected bonds, cm^{-1}): 3381(m), 3204(m) ν(N–H), 1649(m) ν(C=N), 1329(m), 1123(s), 1117(s) ν(C–F). ^{1}H NMR (δ): 7.86 (d, J = 8.2 Hz, 2H, C_6H_4), 7.69 (d, J = 8.2 Hz, 2H, C_6H_4), 4.94 (s, br, 2H, NH_2), 4.69 (s, br, 2H, NH_2). $^{13}C\{^{1}H\}$ NMR (δ): 146.39 (NCN), 138.95 (C_{gem}), 129.55 (q, J^{2}_{CF} = 32.1 Hz, CCF$_3$), 125.78 (C_{ortho}), 125.04 (q, J^{3}_{CF} = 3.9 Hz, C_{meta}), 124.44 (q, J^{1}_{CF} = 271.1 Hz, CF_3).

Spectra of 2c−f

2c



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

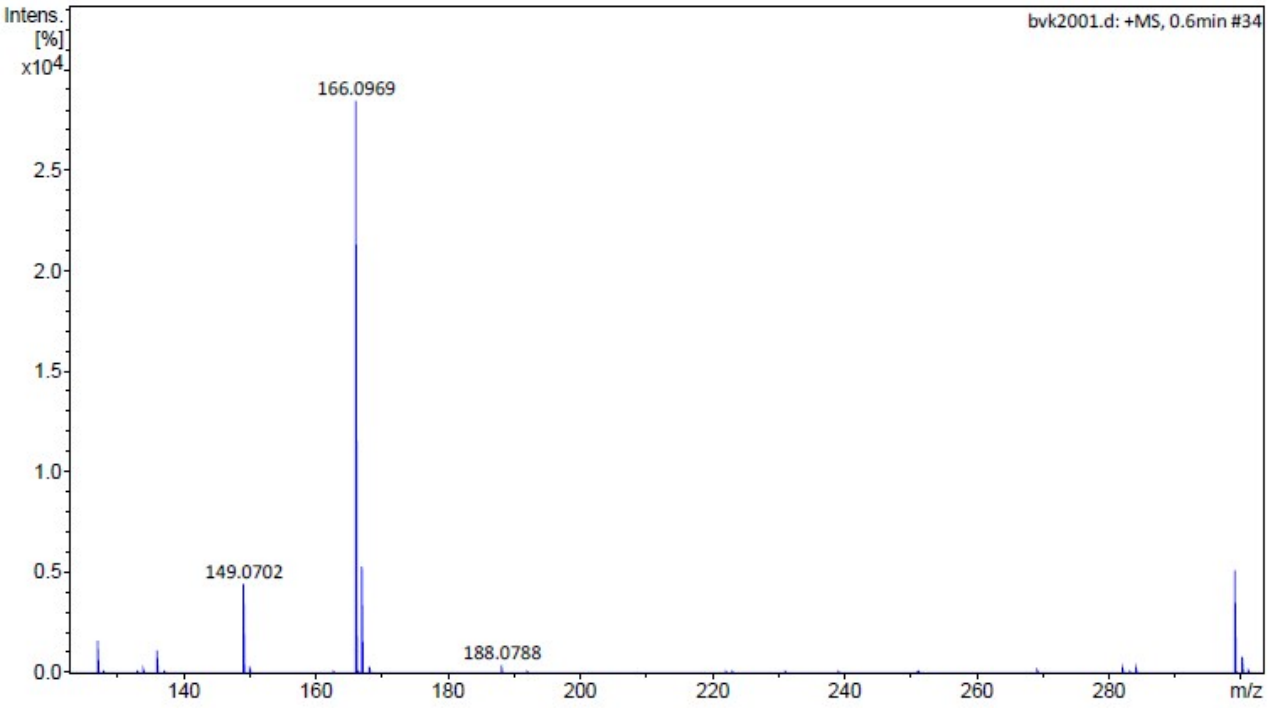


Figure 36S. HRESI$^+$-mass spectrum of **2c**.

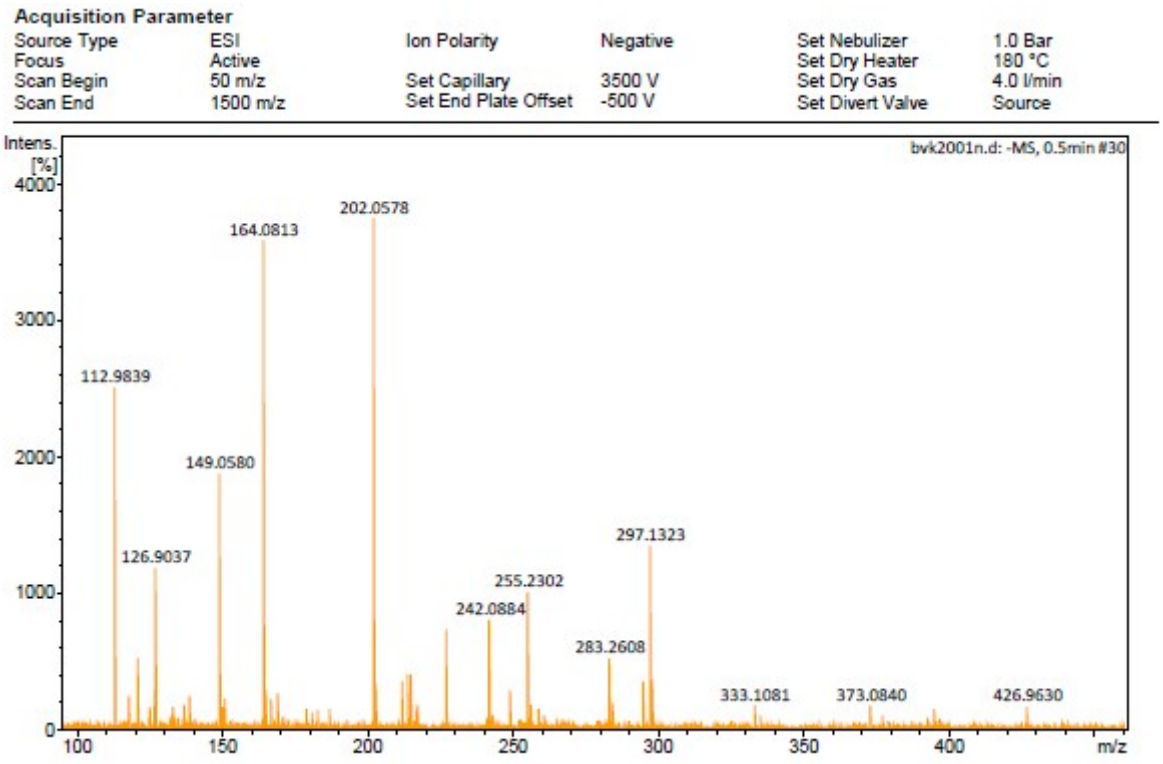


Figure 37S. HRESI⁻-mass spectrum of **2c**.

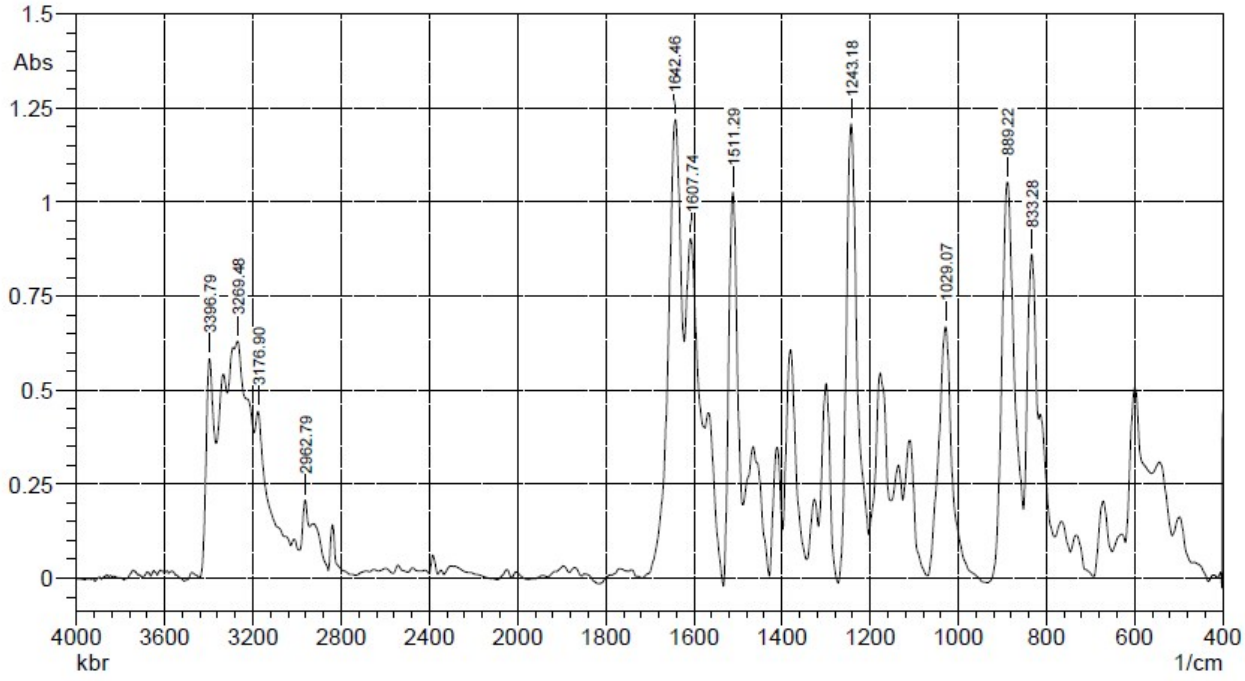


Figure 38S. IR spectrum of **2c**.

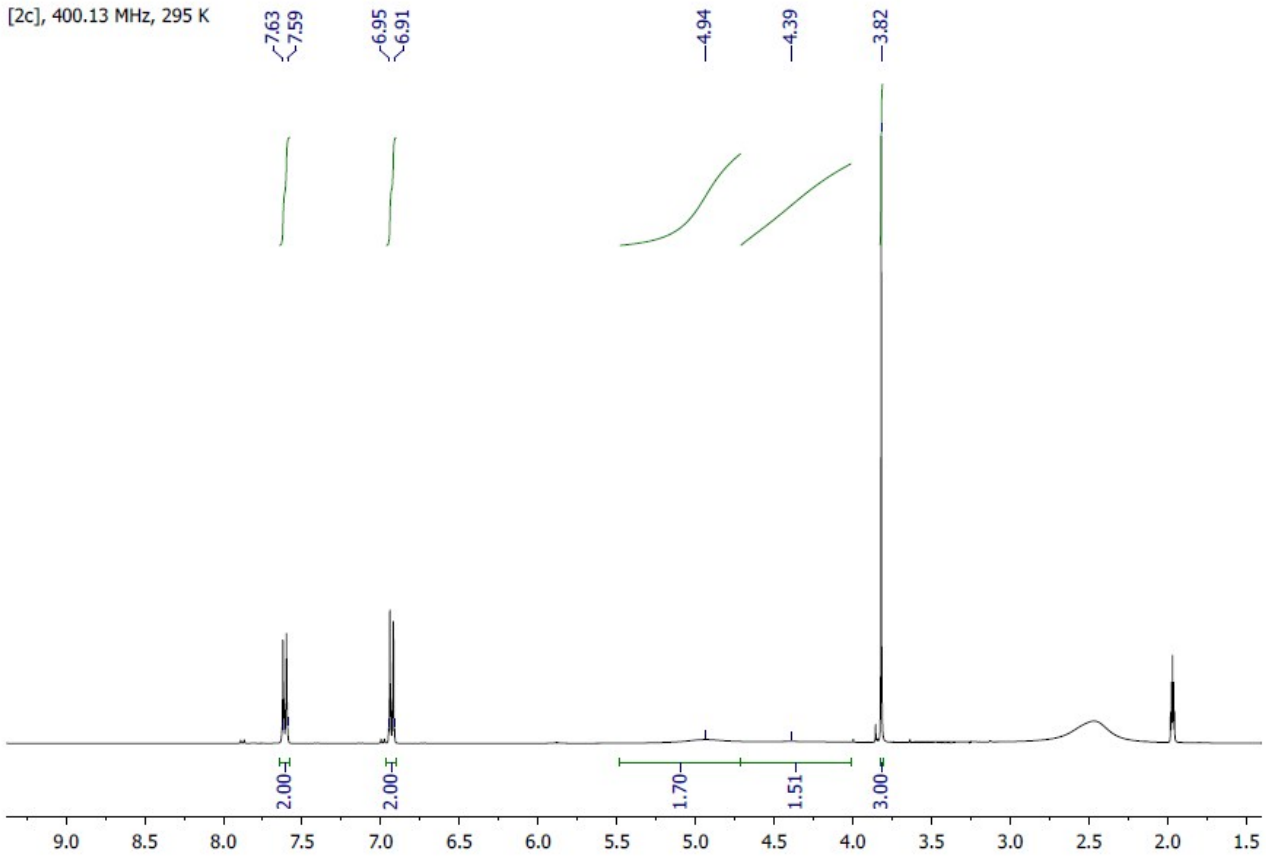


Figure 39S. ^{1}H NMR spectrum of **2c**.

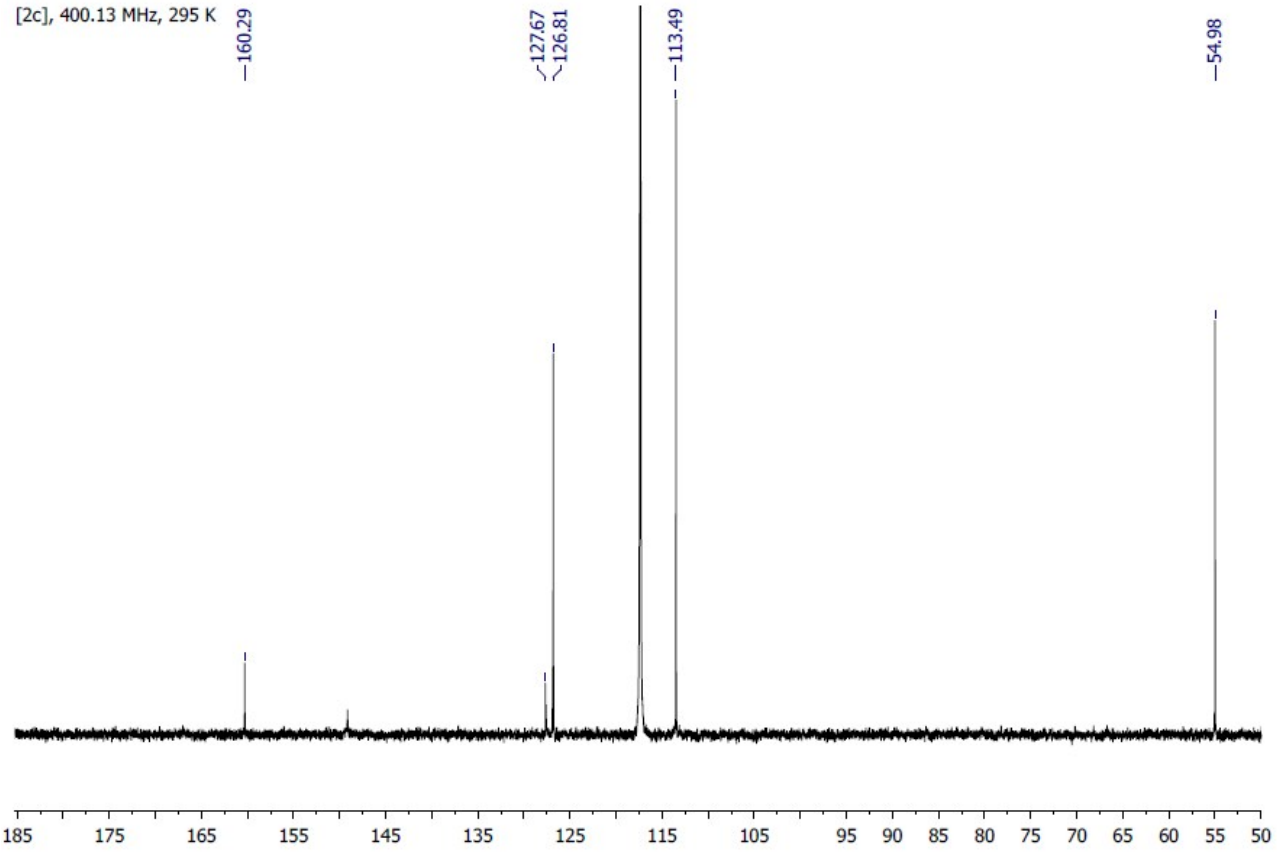
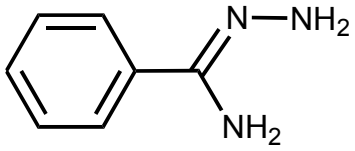


Figure 40S. ^{13}C NMR spectrum of **2c**.

2d



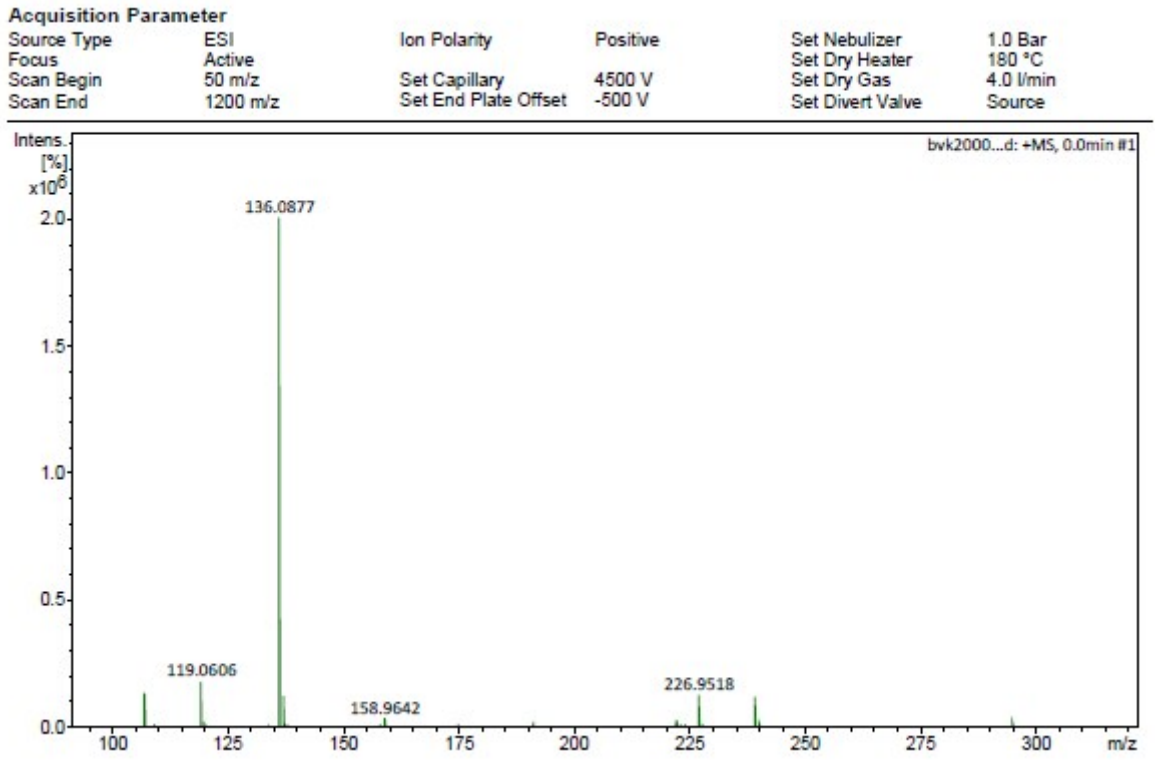


Figure 41S. HRESI^{+}-mass spectrum of **2d**.

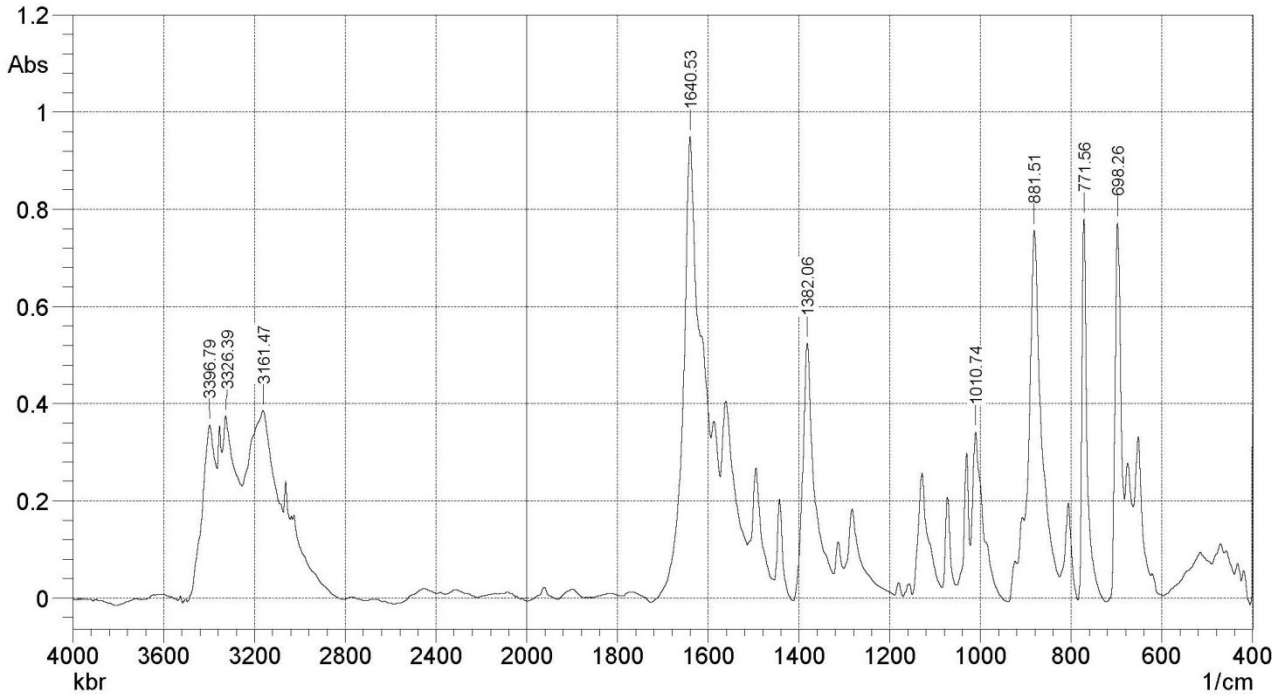


Figure 42S. IR spectrum of **2d** .

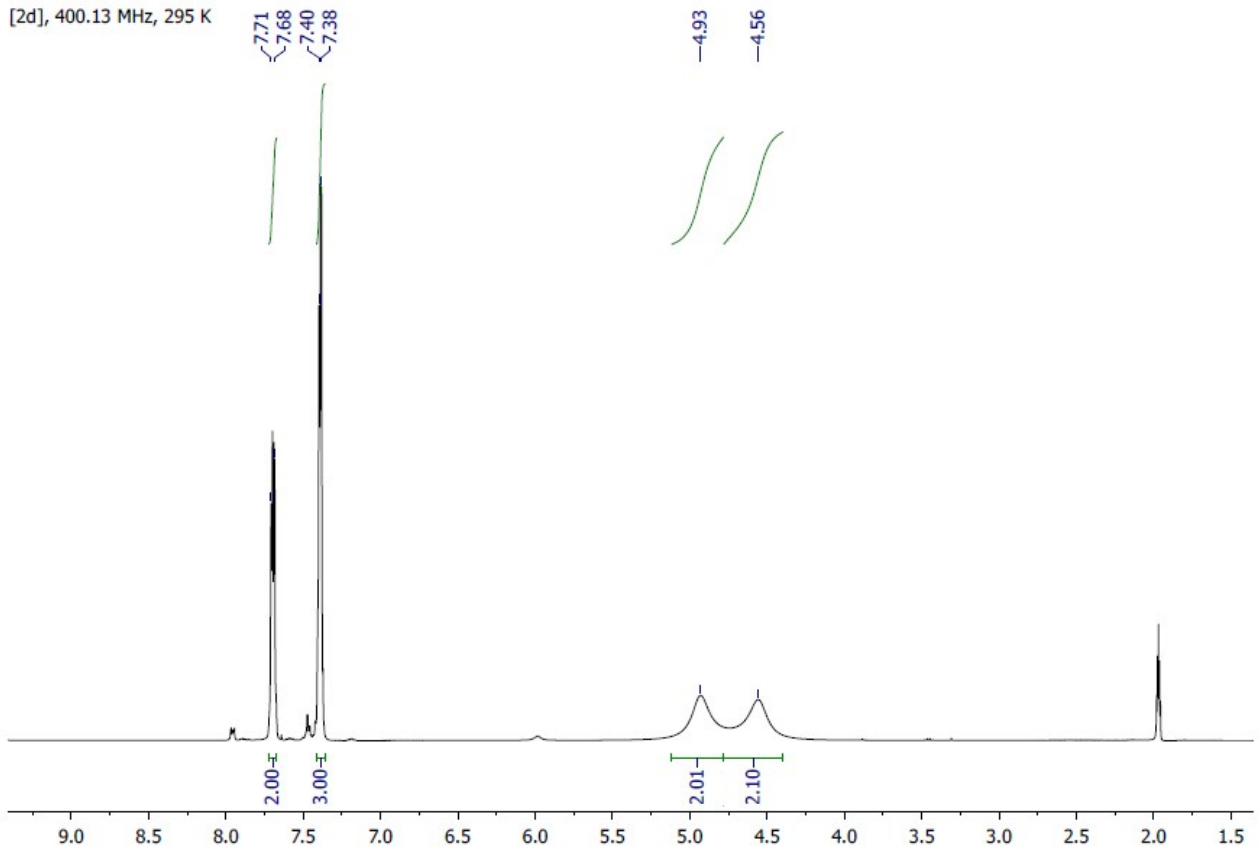


Figure 43S. ^{1}H NMR spectrum of **2d** .

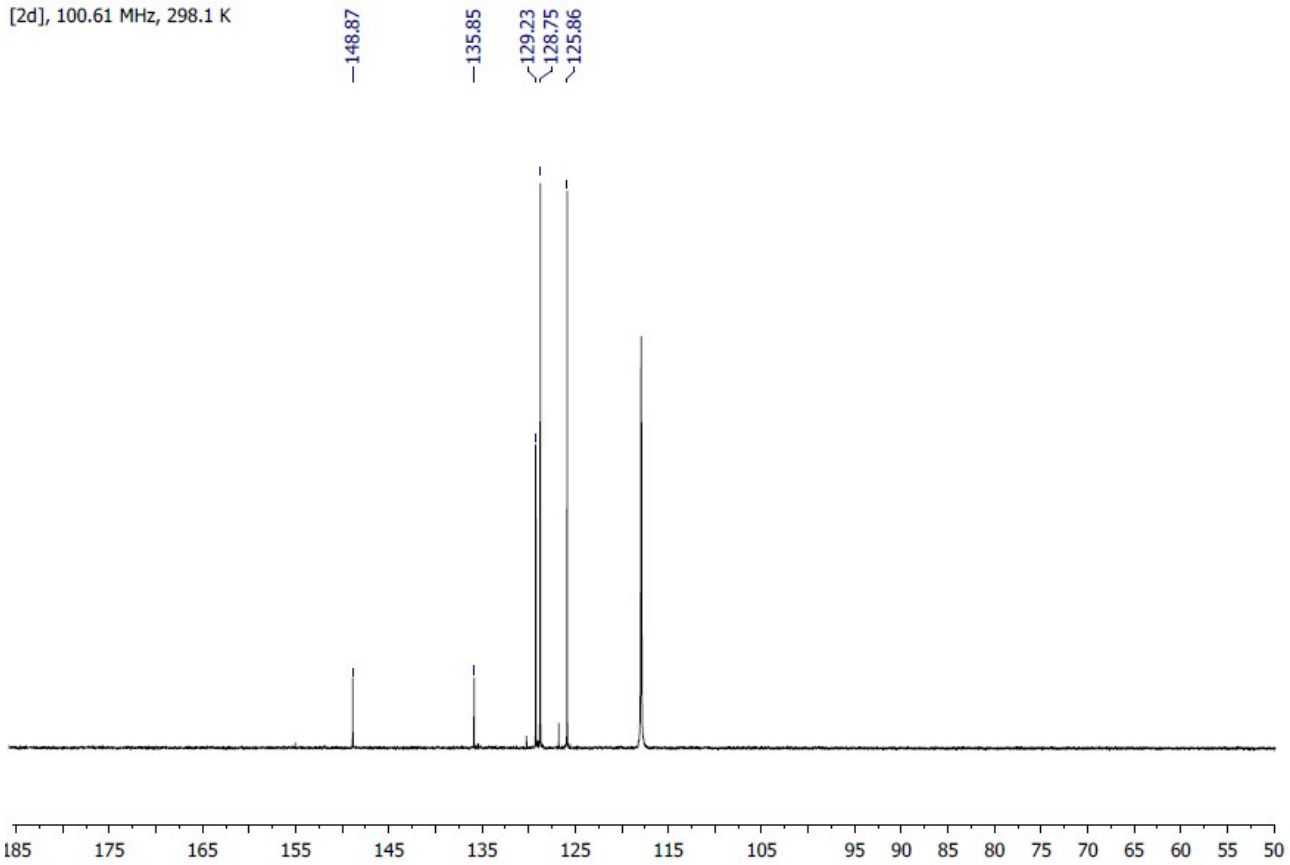
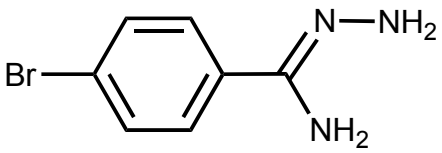


Figure 44S. ^{13}C NMR spectrum of **2d** .

2e



Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

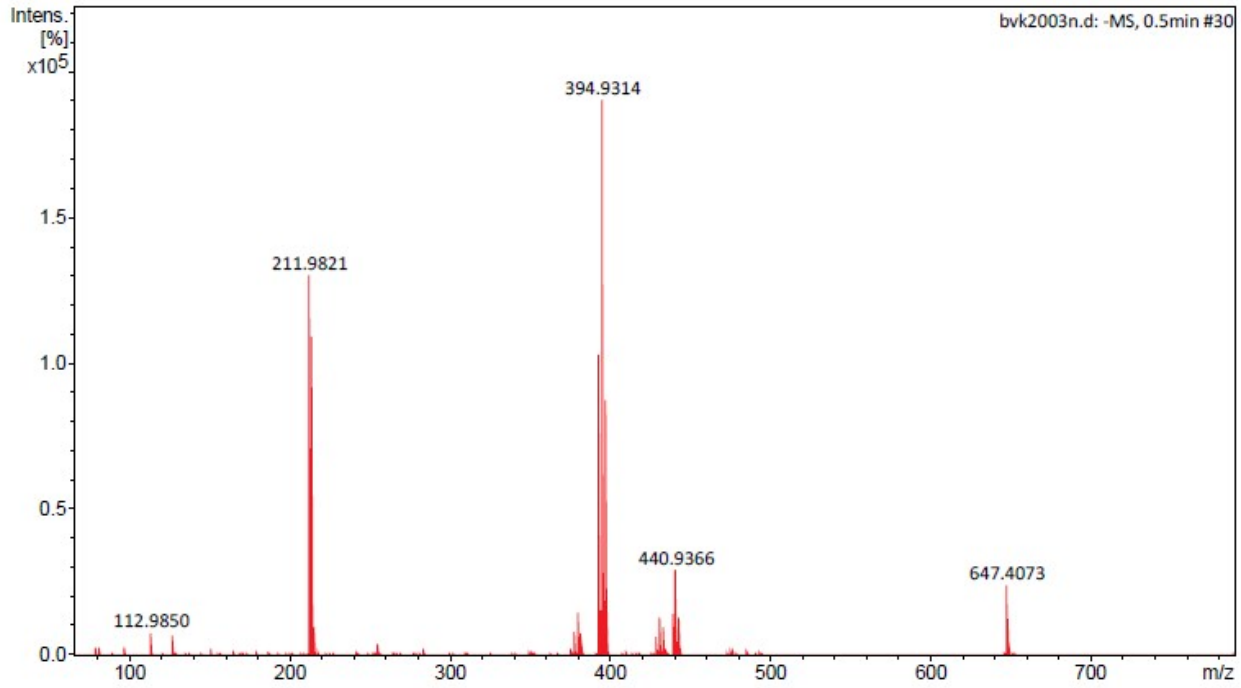


Figure 45S. HRESI⁻-mass spectrum of **2e** .

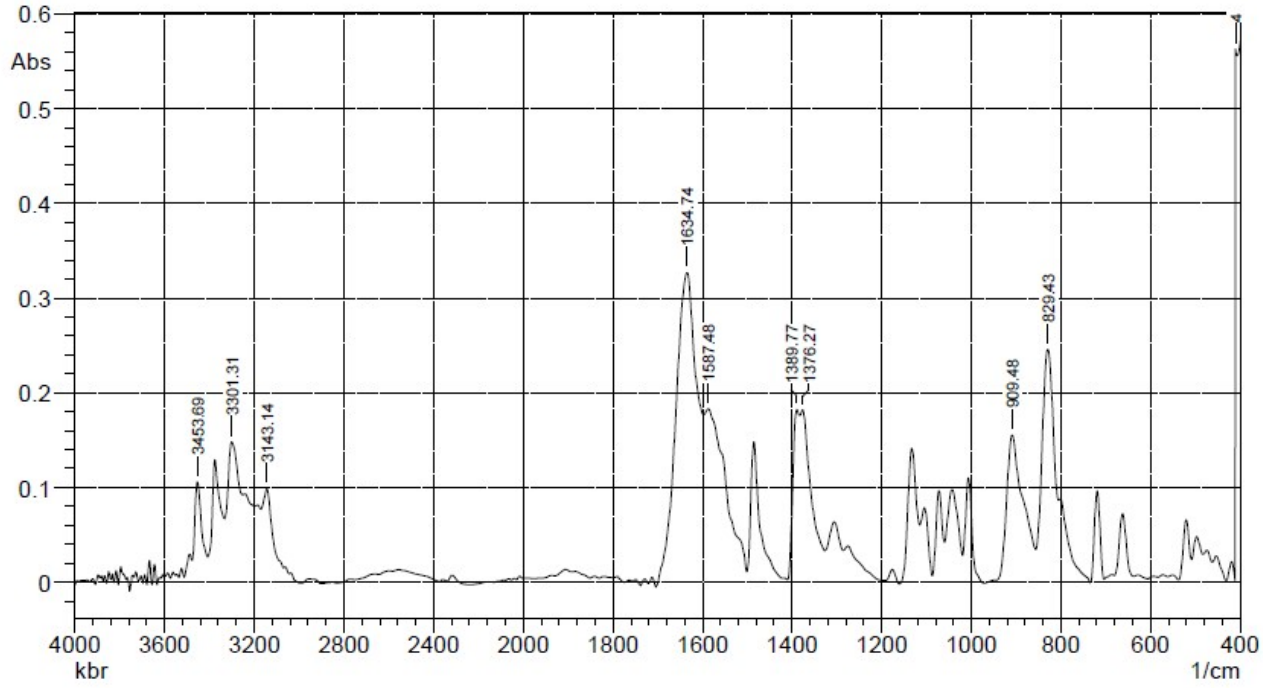


Figure 46S. IR spectrum of **2e** .

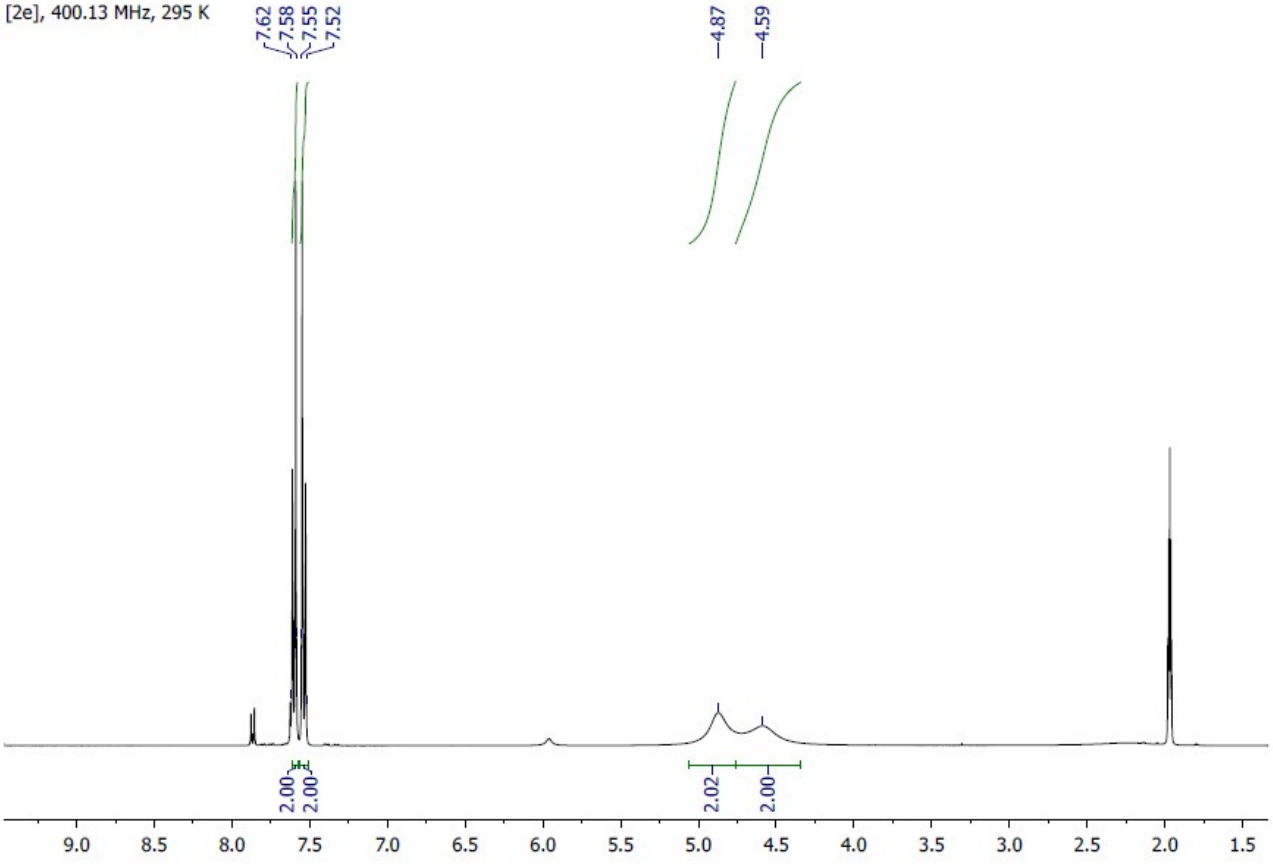


Figure 47S. ^{1}H NMR spectrum of **2e** .

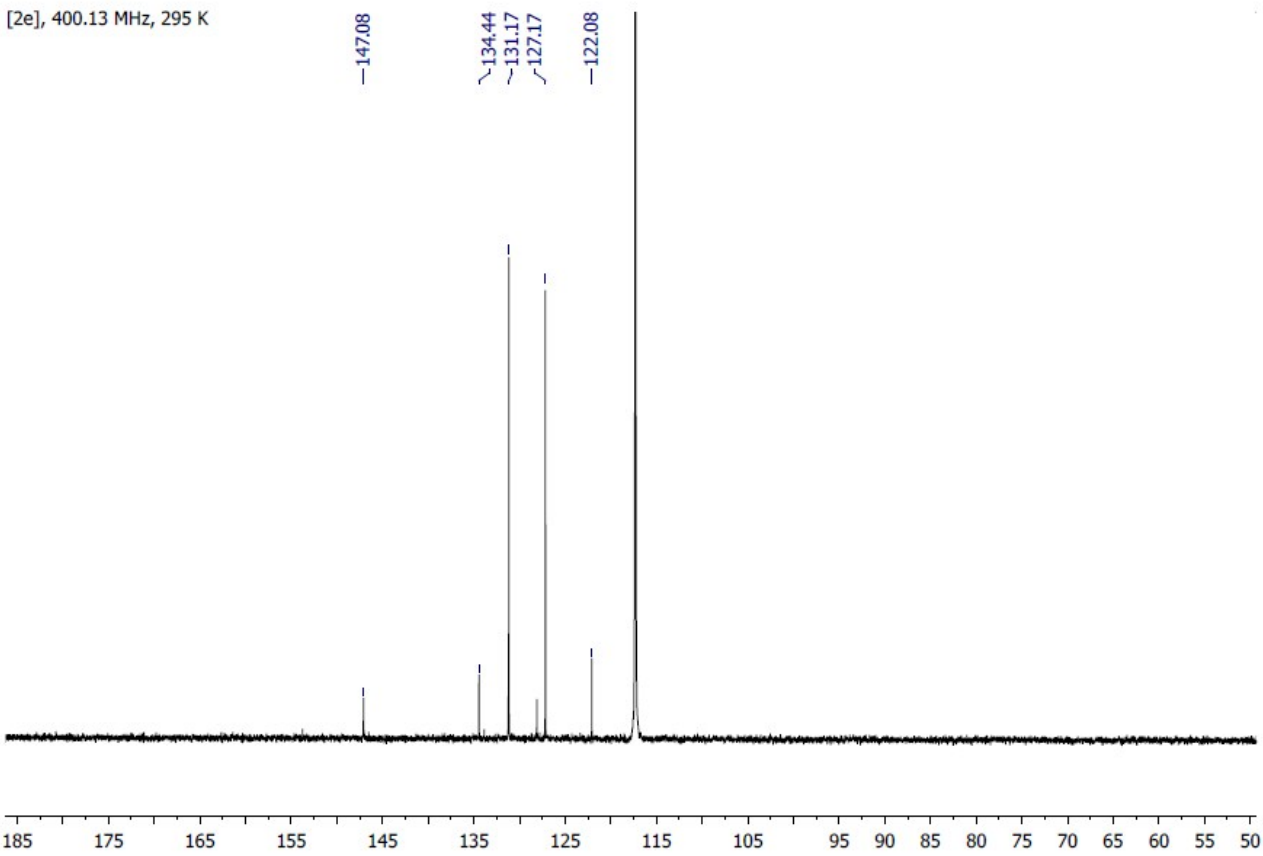
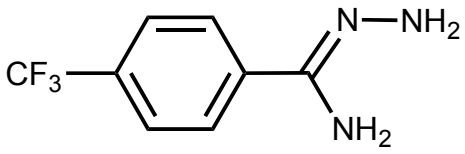


Figure 48S. ^{13}C NMR spectrum of **2e**.

2f



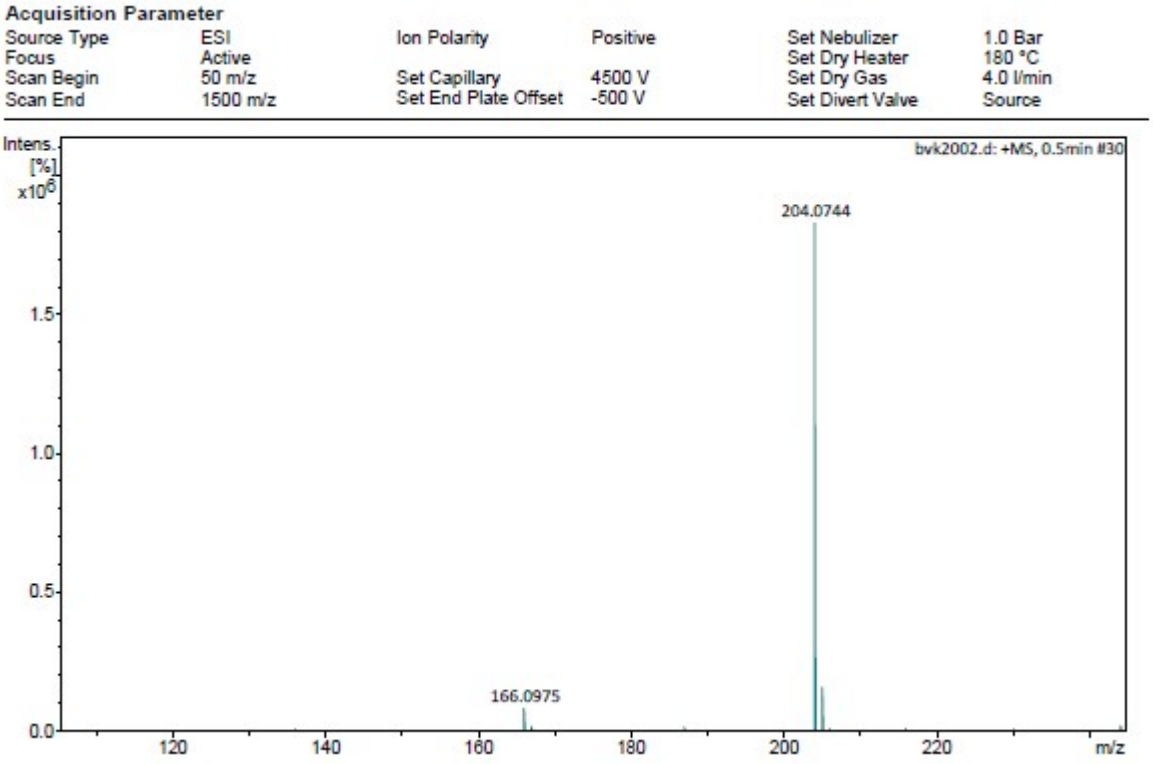


Figure 49S. HRESI^{+}-mass spectrum of **2f** .

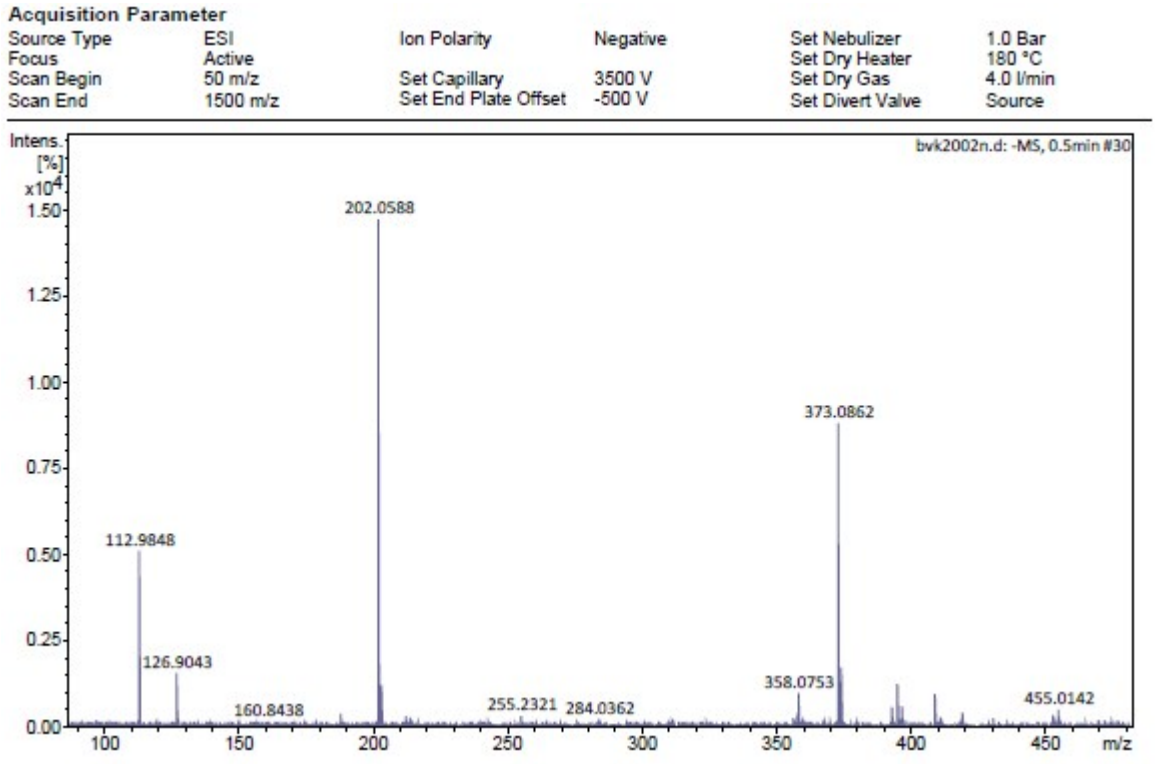


Figure 50S. HRESI^{-}-mass spectrum of **2f** .

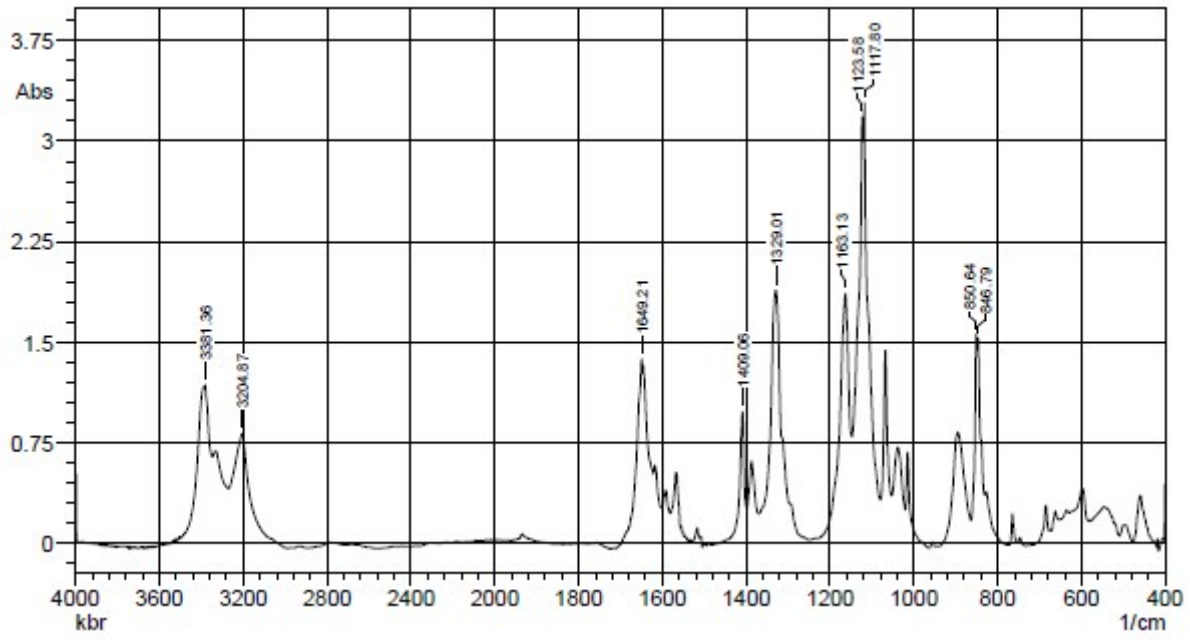


Figure 51S. IR spectrum of **2f** .

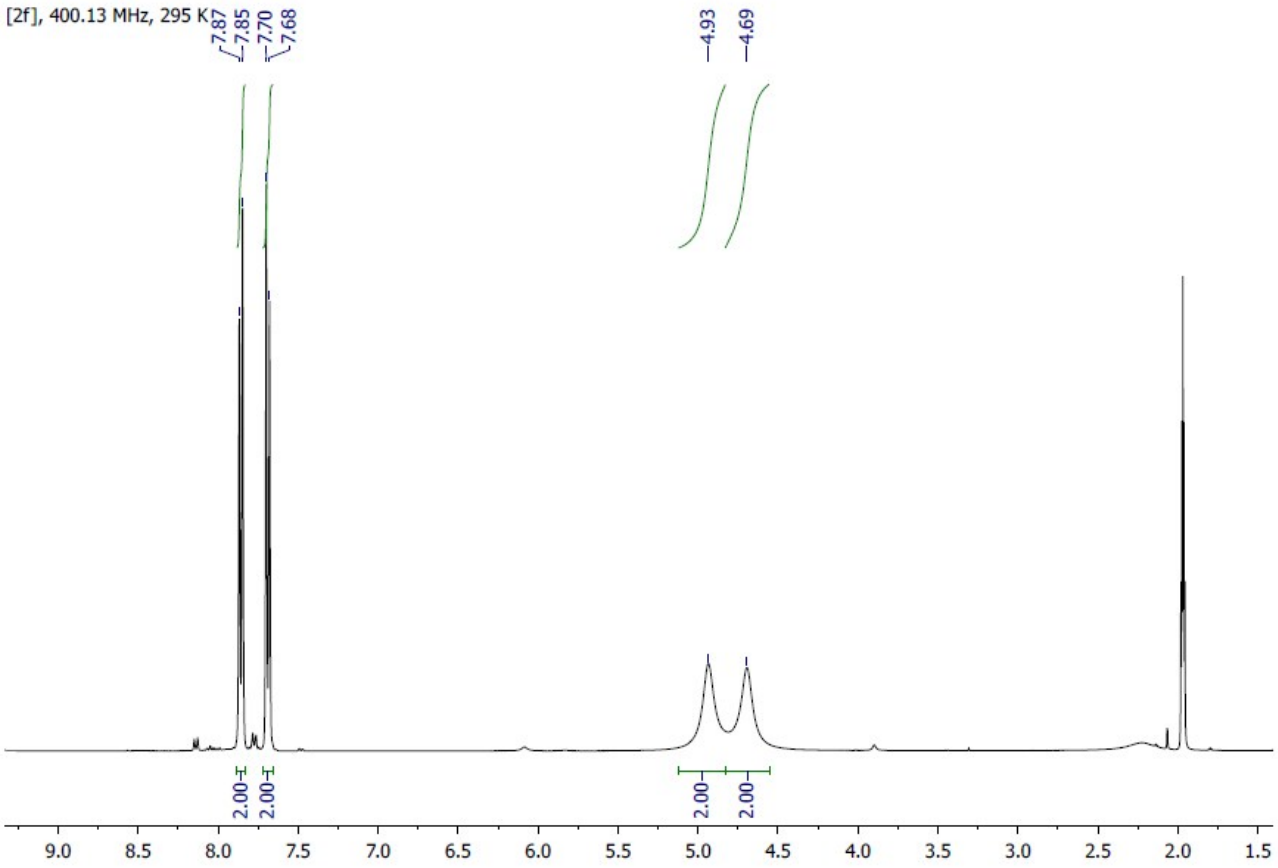


Figure 52S. ^{1}H NMR spectrum of **2f** .

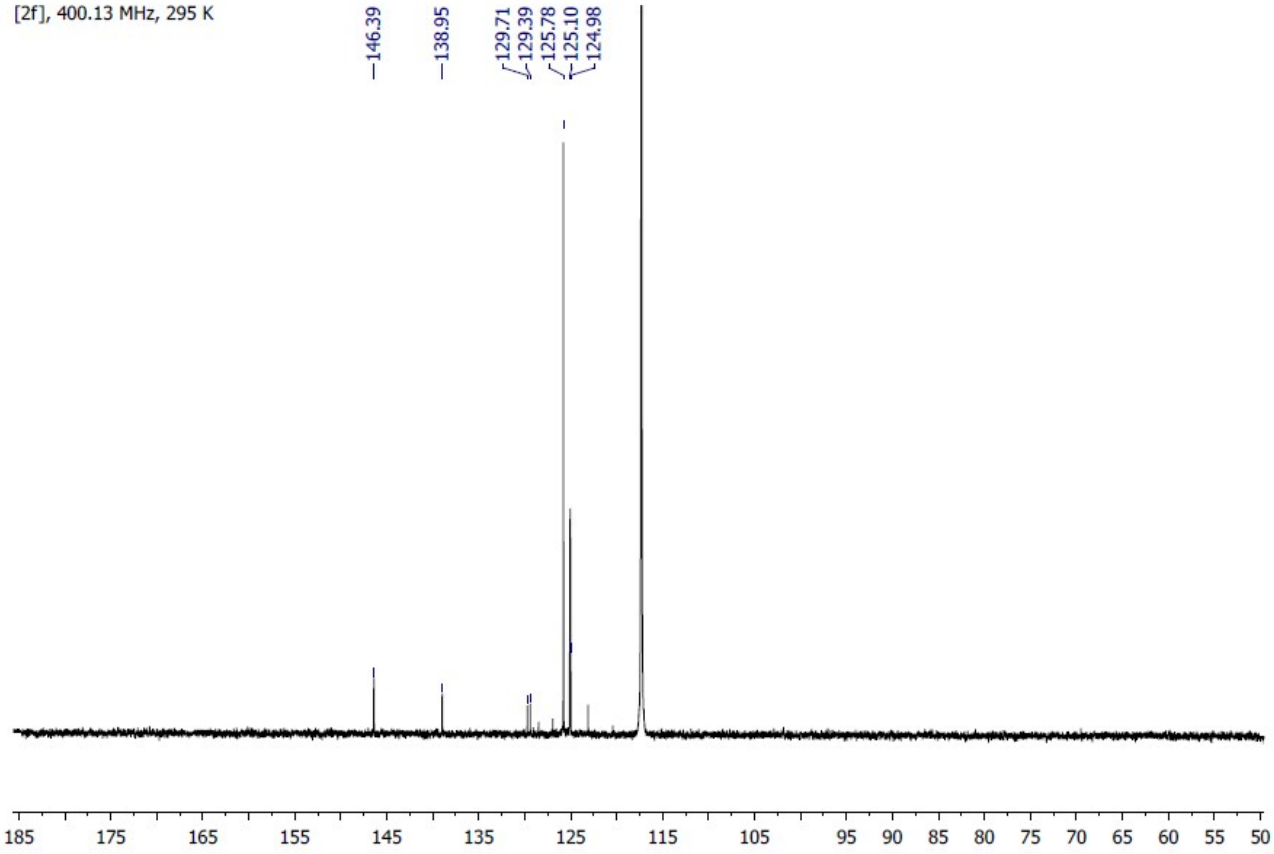


Figure 53S. ^{13}C NMR spectrum of **2f** .

IR identification of dimers of 2e

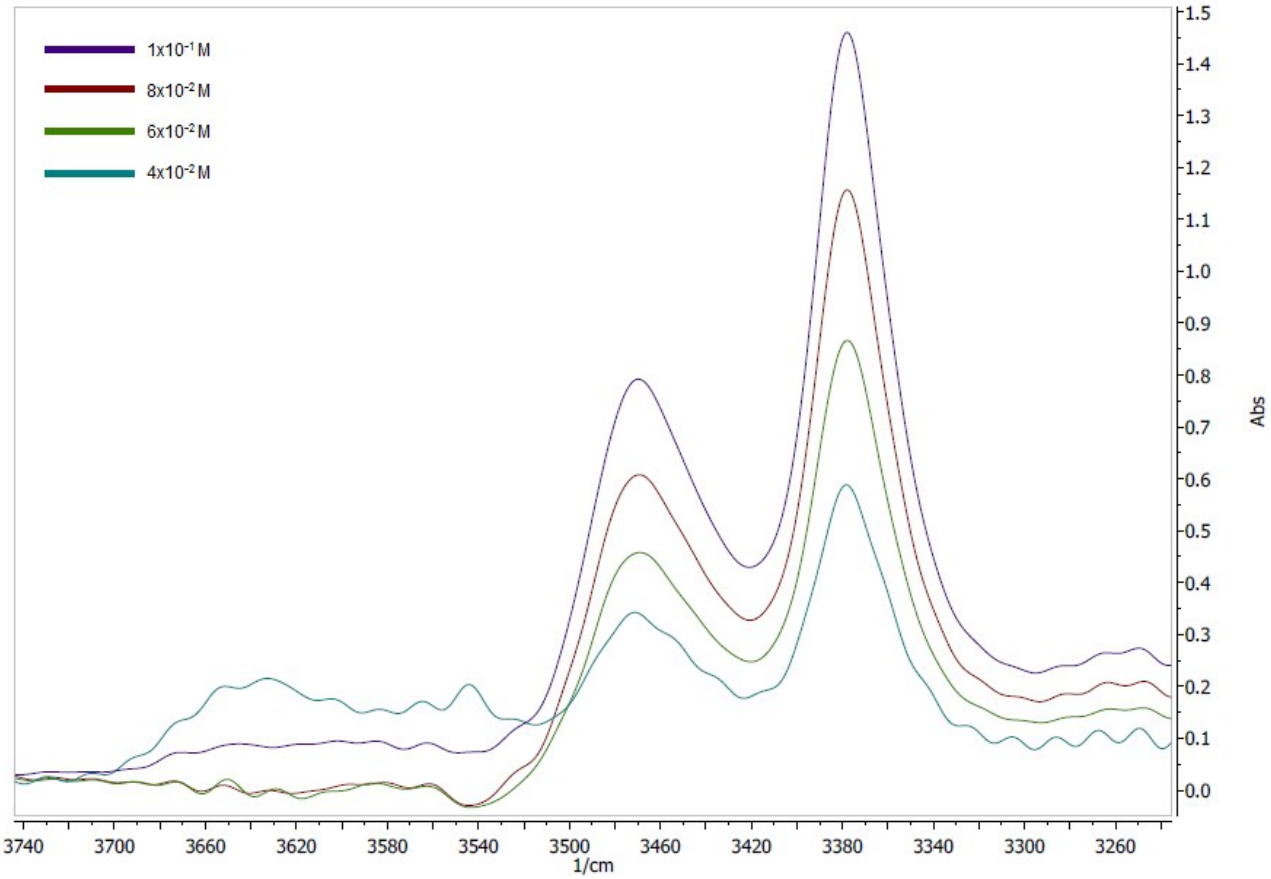


Figure 54S. Combined IR spectra of solution of **2e** in MeCN in the range of concentrations from 4×10^{-2} to 1×10^{-1} M.

Theoretical studies

Theoretical calculations of relative energies for different isomers of (Ph_3PCH_2Ph)[3a–g] in acetonitrile solution. Compounds (Ph_3PCH_2Ph)[**3a**–**g**] can exist as two isomers exhibiting different *E*/*Z* configurations of the oxime C=N bond. In order to determine the relative stability for these isomers, we carried out geometry optimization procedure in acetonitrile solution for model structures based on the experimental X-ray data. The most stable isomers in all cases are those for which crystal structures have been experimentally obtained (**Table 2S**). The calculated total electronic energies, enthalpies, Gibbs free energies and entropies for equilibrium structures of all model species in acetonitrile solution are presented in **Table 3S**.

Table 1S. Relative stability of different isomers of (Ph_3PCH_2Ph)[**3a–g**] in terms of total electronic energies (ΔE_s), enthalpies and Gibbs free energies (ΔH_s and ΔG_s) (in kcal/mol) in acetonitrile solution (M06-2X/6-311++G** level of theory).

Relative stability (*E*)→(*Z*)	**ΔE_s**	**ΔH_s**	**ΔG_s**
(Ph_3PCH_2Ph)[**3a**]	1.1	1.3	0.7
(Ph_3PCH_2Ph)[**3b**]	–3.6	–3.6	–3.6
(Ph_3PCH_2Ph)[**3c**]	–4.8	–4.7	–4.9
(Ph_3PCH_2Ph)[**3d**]	6.0	6.0	5.9
(Ph_3PCH_2Ph)[**3e**]	7.4	7.1	5.4
(Ph_3PCH_2Ph)[**3f**]	5.7	5.8	5.6
(Ph_3PCH_2Ph)[**3g**]	–4.9	–4.9	–4.0

Table 2S. Calculated total electronic energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) in acetonitrile solution (E_s, H_s, G_s, S_s) for different isomers of (Ph_3PCH_2Ph)[**3a**–**g**] (M06-2X/6-311++G** level of theory).

Compound	E_s	H_s	G_s	S_s
(*E*)-(Ph_3PCH_2Ph)[**3a**]	-538.164079	-537.881633	-537.937543	117.67
(*Z*)-(Ph_3PCH_2Ph)[**3a**]	-538.162312	-537.879541	-537.936376	119.62
(*E*)-(Ph_3PCH_2Ph)[**3b**]	-690.809101	-690.485867	-690.550606	136.26
(*Z*)-(Ph_3PCH_2Ph)[**3b**]	-690.814806	-690.491620	-690.556328	136.19
(*E*)-(Ph_3PCH_2Ph)[**3c**]	-977.158046	-976.730726	-976.808215	163.09
(*Z*)-(Ph_3PCH_2Ph)[**3c**]	-977.165741	-976.738171	-976.816095	164.00
(*E*)-(Ph_3PCH_2Ph)[**3d**]	-862.647585	-862.255796	-862.328569	153.16
(*Z*)-(Ph_3PCH_2Ph)[**3d**]	-862.637993	-862.246272	-862.319136	153.35
(*E*)-(Ph_3PCH_2Ph)[**3e**]	-3436.225092	-3435.841783	-3435.917974	160.36
(*Z*)-(Ph_3PCH_2Ph)[**3e**]	-3436.213333	-3435.830542	-3435.909420	166.01
(*E*)-(Ph_3PCH_2Ph)[**3f**]	-1199.703100	-1199.302922	-1199.383826	170.28
(*Z*)-(Ph_3PCH_2Ph)[**3f**]	-1199.694083	-1199.293632	-1199.374829	170.89
(*E*)-(Ph_3PCH_2Ph)[**3g**]	-1038.294371	-1037.835007	-1037.915564	169.55
(*Z*)-(Ph_3PCH_2Ph)[**3g**]	-1038.302251	-1037.842771	-1037.921943	166.63

Table 3S. Cartesian atomic coordinates for equilibrium structures of all model species in acetonitrile solution (unless otherwise specified). Nuclear charges of elements are shown in the second column.

Model structure	Charge	X	Y	Z
(*E*)-(Ph_3PCH_2Ph)[**3f**]				
	7	2.316320	0.416696	-0.146469
	1	1.423140	-0.072604	-0.138200
	7	-0.138489	1.461809	0.097787
	7	0.978030	2.275253	-0.020446
	1	0.920173	3.256040	0.244277
	7	-1.387857	3.225377	-0.844374
	1	-0.570743	3.725307	-1.169731
	1	-2.237308	3.436111	-1.349922
	6	-3.484455	-1.045488	-0.149952
	1	-3.401642	-2.124430	-0.219318
	6	-2.466096	1.139983	-0.195718
	6	2.194608	1.712346	-0.047159
	6	3.775967	2.745665	1.573137
	1	4.668163	3.368394	1.656341
	1	4.001356	1.763384	1.991524
	1	2.979785	3.202797	2.164983
	6	3.364795	2.633555	0.099003
	1	3.086631	3.614567	-0.291807
	1	4.189960	2.248352	-0.497830
	6	-1.242143	1.979291	-0.332685
	6	-4.724870	-0.445860	0.062834
	6	-2.356180	-0.251435	-0.274062

	1	-1.387205	-0.706199	-0.439263
	6	-3.712788	1.727965	0.013794
	1	-3.810050	2.804343	0.096764
	6	-4.847240	0.934314	0.145540
	1	-5.813050	1.393671	0.316302
	6	-5.937110	-1.321759	0.156743
	5	4.374954	-2.878647	1.158990
	1	4.246887	-3.733288	1.975192
	5	4.794968	-2.966382	-0.481967
	1	5.020720	-4.025042	-0.986202
	5	3.563732	-0.460165	-0.245914
	5	3.253359	-2.201569	0.083344
	1	2.110611	-2.551175	0.068526
	5	3.989756	-1.706543	-1.492225
	1	3.445013	-2.044872	-2.498988
	5	4.765925	-0.201869	-1.405123
	1	4.867137	0.661164	-2.216011
	5	4.184887	-1.200452	1.281049
	1	3.851978	-0.684708	2.305353
	5	5.729438	-1.957803	0.716636
	1	6.777198	-2.129141	1.263209
	5	5.308127	-0.276368	0.206137
	1	5.921904	0.634787	0.673402
	5	5.742289	-1.529813	-1.038749
	1	6.746222	-1.715119	-1.657552
	9	-6.283007	-1.830103	-1.044232
	9	-5.740319	-2.378696	0.965571

	9	-7.014119	-0.672276	0.621297
(*Z*)-(Ph_3PCH_2Ph)[**3f**]				
	7	3.490801	-0.345440	-0.519040
	7	0.948695	-1.524121	-0.033987
	7	2.174514	-2.096398	0.281872
	7	0.223570	-2.428300	2.010349
	6	-3.021638	-0.713858	-1.098361
	6	-1.336603	-1.264065	0.537386
	6	3.332117	-1.584009	-0.135233
	6	4.576700	-3.206257	-1.575521
	6	4.490912	-2.542336	-0.196968
	6	0.031915	-1.759106	0.848197
	6	-3.848424	-0.259994	-0.071248
	6	-1.766692	-1.213051	-0.791983
	6	-2.173162	-0.808410	1.555525
	6	-3.432955	-0.302516	1.252568
	6	-5.210817	0.251903	-0.430190
	5	2.532233	2.917094	1.803573
	5	2.846275	3.703608	0.332112
	5	2.730708	0.984803	-0.366484
	5	3.592160	2.112522	0.760453
	5	3.373270	2.570490	-0.970208
	5	2.074470	1.766781	-1.713278
	5	1.954671	1.443262	1.187668
	5	1.202004	3.038516	0.758857
	5	1.042593	1.642661	-0.372217
	5	1.686907	3.235415	-0.971950

	9	-5.161208	1.219471	-1.364626
	9	-5.990773	-0.721810	-0.944091
	9	-5.872606	0.759354	0.619009
	1	4.440718	-0.180300	-0.840303
	1	2.180586	-3.081474	0.541177
	1	1.153228	-2.483408	2.405691
	1	-0.541295	-2.519745	2.661764
	1	-3.357621	-0.679117	-2.128868
	1	5.404469	-3.916798	-1.590690
	1	4.747132	-2.462545	-2.356500
	1	3.655872	-3.747033	-1.804883
	1	4.360430	-3.301621	0.577287
	1	5.408052	-1.993871	0.023312
	1	-1.112528	-1.566119	-1.579151
	1	-1.844857	-0.815827	2.588680
	1	-4.076183	0.058747	2.045123
	1	2.673496	3.282607	2.926122
	1	3.283846	4.815062	0.327367
	1	4.690730	1.790324	1.102646
	1	4.347781	2.837882	-1.606214
	1	1.951843	1.374276	-2.828616
	1	1.631677	0.555479	1.921606
	1	0.195623	3.565877	1.127832
	1	-0.032458	1.142385	-0.480849
	1	1.173105	4.106341	-1.607171
(*E*)-(Ph_3PCH_2Ph)[**3d**]				
	7	0.735509	1.824747	-0.001646

	1	1.023407	2.772376	-0.236230
	7	-1.010270	0.341578	0.108770
	1	-0.265842	-0.349559	0.033502
	7	1.622037	0.774730	-0.211430
	6	3.812632	-0.107563	0.070411
	6	-0.577989	1.573169	0.055936
	6	5.173680	0.198047	0.000149
	1	5.513279	1.225305	0.073475
	7	3.209649	2.087088	0.927067
	1	2.515004	2.727965	1.286944
	1	4.067921	2.046776	1.457943
	6	-1.492562	2.757738	0.013667
	1	-0.967894	3.615328	0.439609
	1	-2.361842	2.545609	0.633636
	5	-2.572087	-1.958871	-0.147221
	1	-1.551617	-2.579871	-0.190503
	6	5.688839	-2.137187	-0.313267
	1	6.417873	-2.926008	-0.460033
	5	-3.863117	-2.299980	-1.191798
	1	-3.979288	-3.129162	-2.035549
	6	3.394992	-1.434964	-0.055566
	1	2.339016	-1.670656	0.004074
	6	2.804284	0.967429	0.281656
	6	4.331193	-2.444476	-0.242890
	1	4.000664	-3.473025	-0.330206
	6	6.106987	-0.815696	-0.194074
	1	7.160767	-0.569566	-0.255412

	5	-3.490684	0.293433	1.458881
	1	-3.349969	1.124091	2.297286
	5	-3.106612	-1.357203	1.471140
	1	-2.626631	-1.856911	2.443349
	5	-2.430677	-0.206679	0.240201
	5	-4.091372	0.414134	-0.128831
	1	-4.480159	1.463860	-0.543448
	5	-3.269329	-0.715915	-1.276986
	1	-2.857228	-0.259897	-2.301023
	6	-1.923852	3.061976	-1.426830
	1	-1.065170	3.349398	-2.037724
	1	-2.637440	3.887443	-1.426512
	1	-2.401995	2.194377	-1.884656
	5	-4.233268	-2.343530	0.462486
	1	-4.695032	-3.332395	0.947774
	5	-4.775956	-0.740754	1.099459
	1	-5.772610	-0.697874	1.755665
	5	-4.931839	-1.091822	-0.666373
	1	-6.008221	-0.979512	-1.171228
(*Z*)-(Ph_3PCH_2Ph)[**3d**]				
	7	0.351075	2.174555	-0.396052
	7	2.228684	0.973428	0.301649
	7	-0.581285	1.241194	0.028808
	6	-2.794856	0.407402	-0.134799
	6	1.643128	2.077898	-0.074827
	6	-3.714047	-0.155017	-1.023711
	7	-1.940215	2.095705	-1.687663

	6	2.422063	3.364836	-0.123171
	6	-4.806638	-1.282522	0.807501
	6	-2.889444	0.118538	1.229412
	6	-1.696224	1.281425	-0.625147
	6	-3.891859	-0.721830	1.697001
	6	-4.714559	-0.999202	-0.551885
	5	1.523052	-1.404480	1.655267
	5	3.042325	-1.781861	0.991109
	5	1.938321	-0.539932	0.264173
	5	0.560448	-1.718647	0.294284
	6	2.291745	4.134196	1.195736
	5	1.670723	-2.965328	1.020496
	1	0.014982	3.109123	-0.623227
	1	3.206169	1.138197	0.526203
	1	-3.638878	0.038393	-2.088108
	1	-1.165768	2.396259	-2.265432
	1	-2.828031	2.021939	-2.161908
	1	2.043301	3.970086	-0.950315
	1	3.467209	3.133048	-0.331722
	1	-5.587860	-1.939073	1.173448
	1	-2.175925	0.557865	1.916403
	1	-3.961211	-0.938063	2.756860
	1	-5.417734	-1.438977	-1.249819
	1	1.236050	-1.004131	2.737425
	1	4.027094	-1.669111	1.657487
	1	-0.622801	-1.596212	0.341599
	1	1.246407	4.366141	1.411144

	1	2.844003	5.072887	1.130934
	1	2.697530	3.553653	2.026592
	1	1.448159	-3.911577	1.714057
	5	3.160909	-1.391023	-0.765501
	5	2.465215	-2.568894	-1.760016
	5	1.410609	-1.335126	-1.261232
	5	2.967721	-3.107790	-0.230244
	5	1.213755	-3.056560	-0.725708
	1	4.102973	-0.746497	-1.118072
	1	2.760174	-2.938187	-2.850980
	1	0.835873	-0.659091	-2.063028
	1	3.748343	-4.007198	-0.139175
	1	0.450881	-3.909790	-1.067368
(*Z*)-(Ph_3PCH_2Ph)[**3c**]				
	7	2.736943	1.477472	-0.409373
	1	3.237327	2.350987	-0.530917
	8	-6.973009	0.019621	0.230690
	7	-0.718033	0.680304	-0.051067
	7	0.657679	0.548099	-0.187400
	1	1.110200	-0.327662	0.074858
	6	-1.384778	-0.385341	-0.357908
	6	-5.639095	-0.157906	0.103831
	6	-2.860200	-0.320441	-0.202636
	6	-4.892105	0.989723	-0.194980
	1	-5.409526	1.934823	-0.312103
	7	-0.839643	-1.567158	-0.758895
	1	0.101923	-1.574125	-1.131864

	1	-1.455481	-2.237366	-1.197965
	6	-3.521402	0.907573	-0.341193
	1	-2.949691	1.798128	-0.574359
	6	-3.610419	-1.456111	0.092154
	1	-3.124611	-2.416240	0.228630
	6	1.430227	1.613096	-0.383643
	6	-4.993090	-1.385724	0.250311
	1	-5.544228	-2.285116	0.490490
	6	0.800036	2.964866	-0.533055
	1	-0.091586	2.872332	-1.153457
	1	1.512440	3.612180	-1.046258
	5	4.720175	-0.628479	-1.336920
	1	5.061394	-0.394286	-2.455742
	5	4.920145	-1.744141	1.252501
	1	5.034607	-2.623189	2.051883
	5	5.321315	0.454371	-0.015350
	1	5.755365	1.520575	-0.335102
	5	3.558926	0.207869	-0.228988
	5	4.294649	-0.049739	1.400881
	1	3.832423	0.577266	2.305837
	5	3.260794	-1.340451	0.671091
	1	2.319114	-1.729387	1.295809
	5	3.167207	-1.234243	-1.026286
	1	2.269123	-1.483941	-1.765706
	5	5.949350	-0.396905	1.309593
	1	6.840992	-0.128757	2.048108
	5	5.949963	-1.237809	-0.164966

	1	6.972360	-1.670208	-0.603967
	6	0.435080	3.554087	0.834894
	1	-0.022617	4.535253	0.698751
	1	1.326086	3.674961	1.454388
	1	-0.272894	2.911312	1.359861
	5	4.432046	-2.182484	-0.433647
	1	4.521836	-3.324645	-0.767565
	6	-7.766998	-1.119318	0.542698
	1	-8.792638	-0.761113	0.601655
	1	-7.473512	-1.548291	1.504544
	1	-7.689350	-1.878458	-0.240565
(*E*)-(Ph_3PCH_2Ph)[**3c**]				
	7	2.437138	0.733674	-0.446004
	8	-7.179215	-1.204952	0.209333
	7	-1.090957	0.337720	-0.248713
	7	0.158639	0.948252	-0.328197
	6	-2.065215	1.151256	0.002641
	6	-5.988965	-0.569450	0.135620
	6	-3.430378	0.567719	0.050307
	6	-4.860818	-1.341451	0.445167
	7	-1.943597	2.497595	0.163074
	6	-3.600658	-0.779538	0.398910
	6	-4.556904	1.327342	-0.255469
	6	1.275060	0.236345	-0.111194
	6	-5.833978	0.770489	-0.219314
	6	1.152584	-1.119115	0.509660
	5	5.300981	0.533121	-1.299399

	5	3.852564	0.168566	-0.281547
	5	4.571653	-1.411533	0.228708
	5	4.470550	-0.943012	-1.400951
	6	0.965316	-2.193318	-0.569057
	5	6.038795	-1.048168	-0.786603
	6	-8.351754	-0.457616	-0.094257
	1	2.404463	1.650694	-0.887092
	1	0.240935	1.801376	-0.880941
	1	-4.999053	-2.379435	0.724584
	1	-1.034585	2.877504	0.393294
	1	-2.715208	2.985487	0.595707
	1	-2.733313	-1.381683	0.642888
	1	-4.459043	2.365866	-0.552967
	1	-6.686399	1.386193	-0.473687
	1	0.299820	-1.113902	1.187865
	1	2.055340	-1.315120	1.085637
	1	5.436959	1.209663	-2.273414
	1	4.078006	-2.436084	0.591520
	1	3.933555	-1.459782	-2.326426
	1	0.874687	-3.172095	-0.095089
	1	1.821791	-2.215592	-1.245236
	1	0.060876	-2.004804	-1.150546
	1	6.838904	-1.763209	-1.309767
	1	-9.184736	-1.145689	0.033325
	1	-8.329634	-0.097378	-1.126223
	1	-8.466736	0.386535	0.590917
	5	6.106480	-0.867505	1.010767

	5	5.070876	1.366276	0.287167
	5	4.556489	-0.000483	1.368673
	5	6.067572	0.752661	1.512457
	5	6.623723	0.506476	-0.071003
	1	6.726982	-1.674387	1.635356
	1	4.749253	2.516560	0.259403
	1	3.789645	-0.040708	2.283539
	1	6.578542	1.293182	2.439794
	1	7.699960	0.907762	-0.397651
(*E*)-(Ph_3PCH_2Ph)[**3a**]				
	7	0.951316	-0.620600	0.074446
	1	1.047501	-1.594283	0.357862
	7	3.223485	-0.805078	-0.173940
	1	4.101879	-0.375769	-0.442043
	6	2.099633	-0.090851	-0.256886
	7	3.197153	-2.125936	0.281647
	1	3.597768	-2.728677	-0.431976
	1	3.765180	-2.199172	1.121874
	6	2.259815	1.334530	-0.684966
	1	1.343511	1.660358	-1.172553
	1	3.073627	1.386366	-1.411339
	5	-0.473533	-0.073418	0.043570
	5	-1.571651	0.525864	1.363553
	1	-1.379378	0.754395	2.519517
	5	-1.645012	-1.196772	0.831601
	1	-1.178417	-2.018381	1.563200
	5	-2.605396	1.334823	0.108460

	1	-3.315333	2.293134	0.167551
	5	-2.989103	-1.544586	-0.141934
	1	-3.638175	-2.536353	-0.235511
	5	-1.605495	-1.048919	-0.982663
	1	-1.104006	-1.737789	-1.819926
	5	-1.508617	0.737618	-1.211206
	1	-1.259868	1.161868	-2.299399
	6	2.581746	2.220823	0.525552
	1	2.603003	3.267555	0.217717
	1	3.557661	1.964395	0.943162
	1	1.827840	2.108563	1.306540
	5	-0.928919	1.546911	0.169677
	1	-0.293885	2.544840	0.265579
	5	-3.112806	-0.049836	-0.933698
	1	-3.971560	0.133283	-1.743533
	5	-3.154817	-0.202628	0.881994
	1	-4.051447	-0.155343	1.669228
(*Z*)-(Ph_3PCH_2Ph)[**3a**]				
	7	-0.791627	-0.632159	-0.665496
	7	-1.976704	1.133184	0.188878
	6	-1.942518	-0.065840	-0.390722
	7	-3.134126	1.860456	0.491911
	6	-3.220091	-0.802667	-0.661079
	5	0.616700	-0.128418	-0.369853
	5	2.024639	0.190273	-1.460473
	5	2.710608	1.320445	-0.208850
	5	1.291278	1.000700	0.879313

	6	-3.688807	-1.557010	0.590399
	5	1.117861	1.439685	-0.758063
	5	1.911571	-1.359678	-0.531484
	5	2.944560	-1.406683	0.812097
	5	1.399211	-0.786889	1.119323
	5	2.887954	0.237550	1.228314
	5	3.403740	-0.337428	-0.423387
	1	-0.878608	-1.564072	-1.056746
	1	-1.104093	1.602847	0.402308
	1	-3.711990	1.339767	1.145714
	1	-3.668395	2.031053	-0.355680
	1	-3.031753	-1.509145	-1.470173
	1	-3.985014	-0.102776	-0.998801
	1	2.145751	0.128024	-2.645732
	1	3.441820	2.259208	-0.301621
	1	0.766293	1.652305	1.731383
	1	-4.602380	-2.107600	0.362234
	1	-3.897561	-0.879446	1.420586
	1	-2.927851	-2.270128	0.913813
	1	0.512169	2.334776	-1.252932
	1	1.636082	-2.347427	-1.143985
	1	3.528194	-2.315068	1.308828
	1	0.677192	-1.275477	1.935669
	1	3.507650	0.640067	2.165948
	1	4.477589	-0.441958	-0.934133
(*Z*)-(Ph_3PCH_2Ph)[**3b**]				
	8	2.976320	-1.504446	-1.146087

	7	2.687985	-0.359536	0.783086
	1	2.994506	-0.190012	1.733129
	7	1.371979	-0.075714	0.506029
	1	0.686742	-0.799579	0.711745
	6	4.768200	-1.551802	0.452996
	1	4.745992	-2.616878	0.695005
	1	5.055724	-0.990303	1.341433
	1	5.503074	-1.397035	-0.337066
	7	-0.203925	1.058415	-0.700522
	1	-0.375203	1.883900	-1.265727
	6	1.036389	0.928236	-0.318481
	5	-3.574736	-0.589297	1.255827
	1	-4.110642	-1.006548	2.237536
	6	2.075489	1.931837	-0.714338
	1	1.681076	2.505423	-1.553577
	1	2.968551	1.405413	-1.055029
	5	-2.461814	0.816853	0.993872
	1	-1.982796	1.632392	1.722635
	6	3.412269	-1.163126	-0.065148
	5	-4.096456	0.864112	0.552810
	1	-4.962975	1.613536	0.868505
	5	-3.004152	0.922746	-0.741377
	1	-2.995672	1.832970	-1.514669
	6	2.415375	2.862239	0.456003
	1	3.148980	3.600638	0.129607
	1	2.837192	2.307617	1.295940
	1	1.523886	3.390820	0.799392

	5	-1.413676	0.199563	-0.338874
	5	-4.118091	-0.481052	-0.482266
	1	-5.131819	-0.802891	-1.024091
	5	-1.383135	-1.487404	-0.451925
	1	-0.499068	-2.216076	-0.768660
	5	-1.799720	-0.863487	1.077837
	1	-1.163627	-1.171743	2.039873
	5	-2.571790	-0.713868	-1.382969
	1	-2.615937	-0.885868	-2.562358
	5	-2.972994	-1.780907	0.035716
	1	-3.374336	-2.902957	0.095491
(*E*)-(Ph_3PCH_2Ph)[**3b**]				
	8	3.645460	-1.770736	-0.426027
	7	3.413560	0.234902	0.595466
	7	2.180375	-0.075836	1.107633
	6	5.506401	-0.255755	-0.514193
	7	-0.088852	-0.269975	0.905965
	6	1.040122	0.157098	0.423086
	5	-3.723283	-0.066109	-1.308314
	6	1.106010	0.976422	-0.825729
	5	-2.071721	-0.790700	-1.128709
	6	4.123295	-0.696074	-0.123807
	5	-3.485778	-1.707249	-0.951815
	5	-2.565171	-1.523917	0.458815
	6	1.148005	2.471813	-0.486732
	5	-1.529551	-0.053708	0.420750
	5	-4.218891	-0.805364	0.282893

	5	-2.353078	1.368862	0.828389
	5	-2.331333	0.980126	-0.825168
	5	-3.030606	-0.068114	1.425317
	5	-3.854373	0.962155	0.173131
	1	3.856015	1.075260	0.946609
	1	2.161047	-0.674078	1.928905
	1	5.584524	-0.289776	-1.602052
	1	6.223670	-0.966617	-0.100144
	1	5.744426	0.747725	-0.163424
	1	-0.018918	-0.805198	1.770348
	1	-4.348643	0.254466	-2.273222
	1	0.230406	0.746827	-1.428412
	1	1.994388	0.691567	-1.390137
	1	-1.225288	-1.099930	-1.912200
	1	-3.847033	-2.686037	-1.520970
	1	-2.143279	-2.466275	1.059630
	1	1.166594	3.051634	-1.410573
	1	2.038687	2.721427	0.094280
	1	0.264875	2.763142	0.085243
	1	-5.281199	-1.135089	0.717199
	1	-1.960314	2.329708	1.406899
	1	-1.898294	1.757795	-1.620030
	1	-3.200955	-0.206765	2.598401
	1	-4.764054	1.731533	0.246218
(*E*)-(Ph_3PCH_2Ph)[**3e**]				
	35	6.213914	-1.481000	0.148921
	7	0.057069	1.492364	0.153940

	7	-2.377148	0.412084	-0.133998
	1	-1.477502	-0.063975	-0.098363
	7	-1.068825	2.290401	0.011354
	1	-1.030125	3.273641	0.269757
	7	1.286213	3.247210	-0.828384
	1	0.460395	3.737062	-1.146842
	1	2.123642	3.452233	-1.355746
	6	1.155455	2.009014	-0.293180
	6	4.653639	-0.396653	0.044736
	6	-2.275873	1.710585	-0.042614
	6	2.384704	1.179087	-0.161422
	6	-3.462678	2.616180	0.062212
	1	-4.266404	2.208856	-0.549065
	1	-3.189154	3.594848	-0.337474
	6	2.280080	-0.212884	-0.197145
	1	1.308528	-0.677057	-0.317274
	6	3.413174	-1.008202	-0.097825
	1	3.327496	-2.086673	-0.139811
	6	3.639650	1.769981	-0.010288
	1	3.742279	2.848192	0.042258
	5	-3.609595	-0.483926	-0.246611
	6	-3.912017	2.745729	1.523565
	1	-3.137620	3.224671	2.126916
	1	-4.132215	1.767037	1.953041
	1	-4.815601	3.355396	1.574886
	5	-3.279108	-2.217849	0.104591
	1	-2.131289	-2.550791	0.109967

	5	-4.242383	-1.217954	1.278499
	1	-3.931524	-0.686519	2.301760
	5	-4.406094	-2.899889	1.171584
	1	-4.277487	-3.744100	1.998496
	5	-3.999365	-1.749569	-1.486119
	1	-3.435271	-2.090545	-2.481218
	6	4.782346	0.984340	0.096552
	1	5.752584	1.449618	0.218387
	5	-5.760587	-1.594113	-1.059823
	1	-6.752073	-1.801449	-1.691530
	5	-4.801066	-3.010532	-0.474219
	1	-5.003716	-4.077732	-0.970176
	5	-4.798274	-0.255723	-1.425984
	1	-4.900719	0.596831	-2.247678
	5	-5.363313	-0.321532	0.177813
	1	-5.997527	0.585004	0.625903
	5	-5.767285	-2.003382	0.700336
	1	-6.820372	-2.184673	1.233336
(*Z*)-(Ph_3PCH_2Ph)[**3e**]				
	35	5.605097	0.368314	-0.517684
	7	-0.869727	-1.667513	0.016789
	7	-3.425056	-0.529462	-0.610679
	7	-2.113226	-2.192774	0.378917
	7	-0.331163	-1.810039	2.299435
	6	-0.043451	-1.557181	1.008896
	6	3.861057	-0.221764	-0.034297
	6	-3.254753	-1.738611	-0.132151

	6	1.330748	-1.100643	0.667249
	6	-4.398218	-2.716037	-0.176100
	6	1.878283	-1.447397	-0.568677
	6	3.147489	-1.012845	-0.926426
	6	2.064732	-0.302336	1.545625
	5	-2.737070	0.838047	-0.420478
	6	-4.473534	-3.391846	-1.549886
	5	-3.988704	2.149206	-0.411483
	5	-3.161552	1.667645	1.135542
	5	-3.831276	3.206983	0.902014
	5	-2.614729	2.236643	-1.574172
	6	3.335719	0.143284	1.198042
	5	-1.307490	2.952353	-0.537306
	5	-2.976676	3.643901	-0.496189
	5	-1.262039	1.346556	-1.063923
	5	-1.437198	1.551997	0.616408
	5	-2.143515	3.158947	1.051252
	1	-4.371797	-0.415330	-0.960666
	1	-2.117966	-3.154100	0.713083
	1	-1.289967	-1.930895	2.593997
	1	0.372876	-1.719757	3.015676
	1	-5.324319	-2.180552	0.038795
	1	-4.254247	-3.466995	0.603398
	1	1.309549	-2.067033	-1.250815
	1	3.570785	-1.292068	-1.883188
	1	1.648006	0.004408	2.498789
	1	-3.543225	-3.917872	-1.775229

	1	-4.656813	-2.657477	-2.336864
	1	-5.289048	-4.116498	-1.559323
	1	-5.059915	1.854923	-0.854302
	1	-3.515902	0.971558	2.040348
	1	-4.656602	3.792368	1.526345
	1	-2.863576	2.333712	-2.737833
	1	3.898281	0.769240	1.879435
	1	-0.395907	3.679075	-0.796078
	1	-3.163900	4.707478	-1.005738
	1	-0.444404	0.759535	-1.695508
	1	-0.649006	1.069757	1.371014
	1	-1.594286	3.794912	1.900399
(*Z*)-(Ph_3PCH_2Ph)[**3g**]				
	6	-1.275277	-1.324799	0.035002
	6	-0.572645	4.024087	0.847593
	1	0.222936	4.163094	1.582676
	1	-1.301112	3.319198	1.251453
	1	-1.068535	4.983664	0.693610
	6	-0.696193	-3.243740	1.378555
	1	-0.751763	-3.781677	2.318031
	6	0.001649	3.524809	-0.483771
	1	-0.795403	3.384743	-1.214233
	1	0.712756	4.249037	-0.883235
	7	0.030140	1.089338	-0.156977
	1	0.524688	0.214933	0.023114
	6	-5.497516	1.300601	0.133069
	1	-6.006762	2.232867	0.349601

	6	-0.547523	-1.854905	-1.031925
	1	-0.488152	-1.307797	-1.967391
	6	0.728239	2.227511	-0.298955
	7	2.029940	2.189066	-0.225951
	1	2.477682	3.091281	-0.351427
	6	-3.441024	0.050860	-0.111843
	7	-1.332221	1.111344	-0.220483
	6	-1.355725	-2.027236	1.239576
	1	-1.927761	-1.615990	2.064839
	6	-6.235816	0.154267	-0.162202
	1	-7.319022	0.194889	-0.180023
	6	-5.577520	-1.042012	-0.426951
	1	-6.144463	-1.936828	-0.657283
	6	-1.956850	-0.003387	-0.105310
	6	-4.186667	-1.096957	-0.396904
	1	-3.681564	-2.033111	-0.606523
	6	-4.110734	1.251034	0.159505
	1	-3.536673	2.138735	0.398533
	6	0.105388	-3.076451	-0.890945
	1	0.674426	-3.481040	-1.720472
	6	0.034579	-3.768571	0.314333
	1	0.549008	-4.716369	0.426176
	5	4.634827	0.966931	0.681370
	1	5.375678	1.841068	1.012653
	5	4.456323	-0.855852	-1.600173
	1	4.826876	-1.310354	-2.633683
	5	4.344857	-0.714660	1.316215

	1	4.841999	-1.327048	2.211439
	5	2.907366	-0.396957	-1.090143
	1	1.962776	-0.480504	-1.815786
	5	4.316609	0.753242	-1.088101
	1	4.592801	1.665652	-1.806929
	5	2.642661	-0.668369	0.686285
	1	1.639789	-1.222481	1.027410
	5	3.899569	-1.618073	-0.189806
	1	3.834928	-2.809441	-0.134725
	5	5.312628	-0.462475	-0.189450
	1	6.491458	-0.642548	-0.136099
	5	3.298295	0.568007	1.649506
	1	2.903114	1.050232	2.660665
	5	2.946285	0.995581	0.048003
(*Z*)-(Ph_3PCH_2Ph)[**3g**]				
	6	2.629522	1.392085	-0.050358
	6	-1.077319	-2.208695	1.481689
	6	2.271797	3.510311	1.053689
	6	-1.133392	-1.948726	-0.030135
	7	0.201797	0.083427	-0.306326
	6	4.729170	-3.090274	-0.452885
	6	3.343404	2.042015	-1.059822
	6	-1.019734	-0.482803	-0.296987
	7	-2.068410	0.282144	-0.441443
	6	3.661462	-0.958405	-0.042527
	7	1.321553	-0.681236	-0.175850
	6	2.094157	2.130674	1.008033

	6	5.921333	-2.602950	0.082178
	6	5.983431	-1.295135	0.552165
	6	2.457179	-0.089723	-0.093857
	6	4.861569	-0.473416	0.486765
	6	3.607191	-2.275104	-0.516674
	6	3.507452	3.422245	-1.016848
	6	2.974733	4.156544	0.040393
	5	-4.897716	0.341719	-1.525790
	5	-5.889868	-0.994206	-0.791930
	5	-4.541507	-1.378997	0.367411
	5	-4.301496	-1.231548	-1.312223
	5	-3.562219	-0.046255	-0.363899
	1	-1.881660	-1.677445	1.995039
	1	-0.120820	-1.886135	1.898976
	1	-1.195823	-3.276643	1.670869
	1	1.862102	4.077868	1.881266
	1	-0.314819	-2.462129	-0.532324
	1	-2.076966	-2.300016	-0.440189
	1	0.283610	1.092725	-0.431988
	1	4.677354	-4.105652	-0.829003
	1	3.768055	1.465323	-1.874957
	1	-1.860681	1.273932	-0.543341
	1	1.549682	1.622124	1.797753
	1	6.797771	-3.239589	0.125811
	1	6.906541	-0.909622	0.969801
	1	4.919395	0.543151	0.859032
	1	2.684472	-2.649879	-0.943800

	1	4.054664	3.924295	-1.806486
	1	3.110480	5.231488	0.075678
	1	-4.891880	0.845598	-2.607526
	1	-6.765646	-1.670369	-1.239714
	1	-4.225669	-2.383940	0.928700
	1	-3.823799	-1.988957	-2.093169
	5	-5.725276	1.175620	1.153160
	5	-4.351762	0.189320	1.245177
	5	-4.595939	1.400346	-0.090763
	5	-6.003565	-0.483752	0.937391
	5	-6.251177	0.734246	-0.398160
	1	-6.178197	1.946354	1.936357
	1	-3.635890	0.202103	2.201027
	1	-4.089258	2.463946	-0.291401
	1	-6.770814	-1.061735	1.646816
	1	-7.235893	1.228525	-0.858670
(*Z*)-(Ph_3PCH_2Ph)[**3g**] (experimental X-ray geometry)				
	6	5.958932	1.627777	3.511440
	6	5.486494	6.977228	3.266705
	1	5.659189	7.205621	2.329590
	1	6.174747	6.355080	3.583047
	1	5.507877	7.792130	3.810456
	6	7.124657	0.400488	1.782183
	1	7.849948	0.326315	1.173593
	6	4.113760	6.322452	3.387042
	1	3.957843	6.050329	4.326187
	1	3.412726	6.975883	3.136350

	7	4.649030	3.979382	2.848163
	1	4.680480	3.292972	2.298456
	6	6.341660	3.446303	8.091432
	1	5.914806	3.916787	8.798566
	6	5.011612	0.608522	3.579121
	1	4.291604	0.670101	4.194886
	6	4.018145	5.118428	2.495273
	7	3.382666	5.168576	1.363101
	1	3.008046	5.941873	1.172240
	6	6.419630	2.777128	5.767663
	7	5.240935	3.918068	4.088220
	6	7.014243	1.519010	2.603293
	1	7.660615	2.213278	2.546170
	6	7.499091	2.710612	8.340634
	1	7.864992	2.685077	9.216836
	6	8.116273	2.016202	7.312285
	1	8.914094	1.529526	7.481488
	6	5.840524	2.821575	4.402667
	6	7.570096	2.028492	6.030537
	1	7.980274	1.527477	5.334638
	6	5.813046	3.490627	6.809278
	1	5.035653	4.008431	6.636826
	6	5.119532	-0.500518	2.743934
	1	4.467412	-1.189631	2.784408
	6	6.177276	-0.600871	1.853384
	1	6.250938	-1.361789	1.290005
	5	2.822292	4.187240	-1.458667

	1	2.729208	5.069707	-2.142789
	5	1.071732	2.165551	-0.250691
	1	0.083045	1.674040	-0.063620
	5	3.587751	2.539872	-1.701237
	1	4.106199	2.092995	-2.588132
	5	2.318190	2.576668	0.824358
	1	2.170156	2.342588	1.909966
	5	1.501192	3.813900	-0.262874
	1	0.700074	4.568480	-0.052791
	5	3.977873	2.438247	0.078916
	1	4.807267	1.921334	0.626729
	5	2.592653	1.482763	-0.608861
	1	2.663078	0.367321	-0.682227
	5	1.774752	2.727447	-1.702996
	1	1.191985	2.608779	-2.651752
	5	4.372415	3.795341	-0.876066
	1	5.361530	4.287499	-1.062596
	5	3.196833	4.071839	0.317019
(*Z*)-(Ph_3PCH_2Ph)[**3g**] (gas phase optimized geometry)				
	6	-1.234163	-1.347099	0.027444
	6	-0.649914	4.025118	0.866582
	1	0.136947	4.166470	1.609913
	1	-1.365866	3.302256	1.258961
	1	-1.161237	4.977967	0.717519
	6	-0.576727	-3.266835	1.329135
	1	-0.617259	-3.831275	2.253325
	6	-0.058235	3.527040	-0.457681

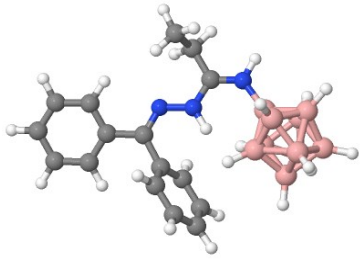
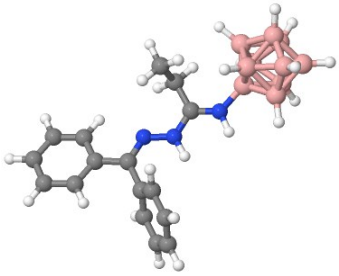
	1	-0.853265	3.359898	-1.185463
	1	0.630830	4.267191	-0.869407
	7	0.023906	1.095533	-0.085231
	1	0.561675	0.239461	0.097948
	6	-5.497308	1.241736	0.039809
	1	-6.015095	2.181939	0.192132
	6	-0.426900	-1.789392	-1.020351
	1	-0.341921	-1.192683	-1.921215
	6	0.704869	2.249421	-0.262658
	7	1.999537	2.223833	-0.210432
	1	2.459841	3.112682	-0.359817
	6	-3.423818	0.001519	-0.109642
	7	-1.327966	1.089551	-0.165682
	6	-1.317924	-2.099276	1.201029
	1	-1.940435	-1.750096	2.018175
	6	-6.224707	0.073975	-0.186930
	1	-7.307807	0.102504	-0.214777
	6	-5.550733	-1.126863	-0.371778
	1	-6.105569	-2.040747	-0.550121
	6	-1.939854	-0.038316	-0.084710
	6	-4.159977	-1.165338	-0.330922
	1	-3.639125	-2.104176	-0.478001
	6	-4.111861	1.206796	0.080159
	1	-3.541528	2.109749	0.260759
	6	0.323444	-2.951322	-0.884635
	1	1.004350	-3.244586	-1.674298
	6	0.251361	-3.687004	0.291420

	1	0.869412	-4.568335	0.413061
	5	4.598438	0.970602	0.671913
	1	5.351555	1.839805	0.990310
	5	4.345425	-0.839844	-1.622651
	1	4.686556	-1.294181	-2.666221
	5	4.264704	-0.707060	1.303486
	1	4.744215	-1.333002	2.197340
	5	2.813155	-0.348854	-1.095948
	1	1.861768	-0.386618	-1.822893
	5	4.255705	0.772621	-1.103211
	1	4.531060	1.687906	-1.824165
	5	2.561054	-0.619815	0.689590
	1	1.536760	-1.129797	1.046720
	5	3.778705	-1.596806	-0.207253
	1	3.673926	-2.786536	-0.155438
	5	5.226008	-0.475402	-0.214645
	1	6.398958	-0.684739	-0.172856
	5	3.253944	0.604275	1.655223
	1	2.860718	1.102205	2.661669
	5	2.916235	1.022154	0.053222
(*E*)-(Ph_3PCH_2Ph)[**3g**] (gas phase optimized geometry)				
	6	2.624126	1.398742	-0.048752
	6	-1.134874	-2.346716	1.210788
	6	2.247261	3.497840	1.090864
	6	-1.162856	-1.956800	-0.274714
	7	0.213158	0.095037	-0.382751
	6	4.682613	-3.134917	-0.243324

	6	3.278090	2.084094	-1.074392
	6	-1.038264	-0.476737	-0.416610
	7	-2.066872	0.293098	-0.507730
	6	3.656699	-0.955456	-0.024636
	7	1.319311	-0.658247	-0.251265
	6	2.110633	2.114378	1.035549
	6	5.903965	-2.614267	0.182893
	6	5.999531	-1.266266	0.504116
	6	2.460130	-0.084638	-0.116353
	6	4.884331	-0.439957	0.400096
	6	3.569713	-2.315669	-0.348646
	6	3.411910	3.466759	-1.018362
	6	2.896648	4.174841	0.063432
	5	-4.925566	0.524347	-1.419264
	5	-5.903205	-0.876013	-0.788063
	5	-4.500394	-1.432511	0.233176
	5	-4.355005	-1.086561	-1.434972
	5	-3.567114	-0.031507	-0.389670
	1	-1.950873	-1.849684	1.737983
	1	-0.179319	-2.078364	1.668438
	1	-1.276785	-3.424246	1.304773
	1	1.841760	4.044374	1.933856
	1	-0.342744	-2.431552	-0.814386
	1	-2.117095	-2.242759	-0.717259
	1	0.290063	1.108404	-0.387695
	1	4.600516	-4.185080	-0.498394
	1	3.680349	1.526674	-1.913534

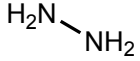
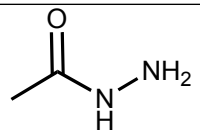
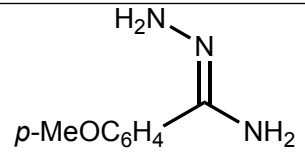
	1	-1.894861	1.295697	-0.550231
	1	1.602686	1.582382	1.833839
	1	6.772730	-3.257379	0.260917
	1	6.943072	-0.852889	0.841267
	1	4.966833	0.608806	0.661037
	1	2.618725	-2.713503	-0.680818
	1	3.914980	3.992040	-1.821802
	1	2.997586	5.252946	0.104045
	1	-4.941396	1.158128	-2.430068
	1	-6.816445	-1.478031	-1.262637
	1	-4.155242	-2.497847	0.653688
	1	-3.917571	-1.745863	-2.326073
	5	-5.559923	1.044903	1.395685
	5	-4.210456	0.025002	1.285836
	5	-4.509249	1.399468	0.116223
	5	-5.895183	-0.576024	1.002536
	5	-6.195237	0.801454	-0.163786
	1	-5.934801	1.723207	2.296697
	1	-3.420085	-0.080565	2.181429
	1	-3.955926	2.461563	0.005823
	1	-6.624453	-1.224499	1.688511
	1	-7.192165	1.364639	-0.497378

Table 4S. Calculated total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) (E, H, G, S) for two isomers of (Ph_3PCH_2Ph)[**3g**] (M06-2X/6-311++G** level of theory, optimization in gas phase).

Isomer	E	H	G	S
 (*Z*)-(Ph_3PCH_2Ph)[**3g**]	-1038.186703	-1037.727663	-1037.806072	165.03
 (*E*)-(Ph_3PCH_2Ph)[**3g**]	-1038.167566	-1037.709305	-1037.792369	174.82

Kinetic measurements

Table 5S. Observed pseudo first-order Rate constants for the six nucleophiles, **2a**–**c**; **2e**–**2g**; vary [Nu(H)]; Other details in Column 1.

Nucleophile	Conc, M	k_{obs} (Standard Deviation) (s^{-1})			
		35ºC	25ºC	15ºC	5ºC
 Chemical Formula: H_4N_2 Exact Mass: 32.04 Wavelength 335 nm (Ph_3PCH_2Ph)[**1**] = 5×10^{-4} M **2a**	0.003	-	0.000647 (0.000014)	-	-
	0.004	-	0.0009890 (0.000218)	-	-
	0.005	-	0.001465 (0.000036)	-	-
	0.006	-	0.002015 (0.000056)	-	-
	0.0075	-	0.003145 (0.000081)	-	-
	0.01	-	0.005343 (0.000167)	-	-
 Chemical Formula: $C_2H_6N_2O$ Exact Mass: 74.05 Wavelength 335 nm (Ph_3PCH_2Ph)[**1**] = 5×10^{-4} M **2b**	0.05	-	0.000489 (0.000014)	-	-
	0.06	-	0.000749 (0.000024)	0.000163 (0.000003)	-
	0.075	-	0.001088 (0.000031)	0.000224 (0.000007)	-
	0.09	-	0.001630 (0.000116)	0.000577 (0.000016)	-
	0.1	-	0.001930 (0.000032)	0.000718 (0.000012)	-
 Chemical Formula: $C_8H_{11}N_3O$ Exact Mass: 165.09 Wavelength 350 nm (Ph_3PCH_2Ph)[**1**]	0.00025	-	0.000715 (0.000008)	-	-
	0.0005	0.002340 (0.00002)	0.001532 (0.000026)	-	-
	0.001	0.006729 (0.000014)	0.004486 (0.000008)	0.004847 (0.000007)	-
	0.0015	0.016398 (0.000079)	0.011214 (0.000021)	0.009860 (0.000030)	-
	0.002	0.025030	0.019112	0.017223	-

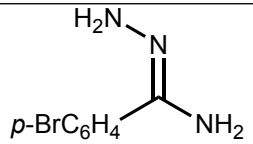
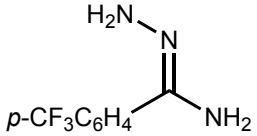
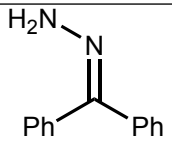
= 5 × 10^{-5} M **2c**		(0.000152)	(0.000056)	(0.000091)	
	0.0025	0.034918 (0.000373)	-	-	-
 Chemical Formula: $C_7H_8BrN_3$ Exact Mass: 212.99 Wavelength 360 nm (Ph_3PCH_2Ph)[**1**] = 5 × 10^{-5} M **2e**	0.00025	-	0.000196 (0.000001)	-	-
	0.0005	-	0.000470 (0.000004)	-	-
	0.00075	-	0.001380 (0.000016)	-	-
	0.001	0.0021812 (0.000002)	0.001711 (0.000001)	0.001579 (0.000011)	0.001426 (0.000005)
	0.002	0.0069203 (0.000012)	0.006142 (0.000007)	0.005544 (0.000077)	0.004065 (0.000012)
	0.003	0.018409 (0.000065)	0.013626 (0.000037)	0.012456 (0.000029)	0.011402 (0.000045)
	0.004	0.030796 (0.000241)	0.022034 (0.000107)	0.020261 (0.000114)	0.017673 (0.000099)
 Chemical Formula: $C_8H_8F_3N_3$ Exact Mass: 203.07 Wavelength 360 nm (Ph_3PCH_2Ph)[**1**] = 5 × 10^{-5} M **2f**	0.0005	-	0.000277 (0.000001)	-	-
	0.00075	-	0.000609 (0.000005)	-	-
	0.001	-	0.000836 (0.000001)	0.000849 (0.000009)	0.000748 (0.000001)
	0.002	-	0.004892 (0.000011)	0.003516 (0.00006)	0.002702 (0.000006)
	0.003	-	0.011421 (0.000084)	0.007606 (0.000037)	0.006429 (0.000023)
	0.004	-	-	0.013889 (0.000104)	0.009976 (0.000054)
 Chemical Formula: $C_{13}H_{12}N_2$ Exact Mass: 196.10 Wavelength 370 nm (Ph_3PCH_2Ph)[**1**] = 5 × 10^{-5} M **2g**	0.025	-	0.0000290 (0.000002)	-	-
	0.05	-	0.000121 (0.000002)	0.000140 (0.000104)	-
	0.075	-	0.000319 (0.000005)	0.000293 (0.000005)	-
	0.09	-	0.000449 (0.0000011)	-	-
	0.1	-	0.000539 (0.00017)	0.000505 (0.00002)	-

Table 6S. Data used to construct **Fig. 5**: *k*obs vs *k*obs_Calc for **2a**–**2c**; **2e**–**2g** at 25 ºC (details in **Table 5S**).

	2g		**2b**		**2a**		**2f**		**2e**		**2c**	
L	KOBS1	KOBS1_CALC	KOBS2	KOBS2_CALC	KOBS3	KOBS3_CALC	KOBS4	KOBS4_CALC	KOBS5	KOBS5_CALC	KOBS6	KOBS6_CALC
(M)	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})
0	0	0	0	0		0	0	0	0	0	0	0
0.00025		3.42E-09		1.23E-08		3.41E-06		7.86E-05	0.000196	8.86E-05		0.000301
0.0005							0.000278	0.000314	0.000471	0.000354	0.001532	0.001204
0.00075								0.000707	0.00138	0.000797		0.002709
0.001							0.000836	0.001257	0.001711	0.001418	0.004486	0.004816
0.0015								0.002828		0.00319	0.011215	0.010836
0.002							0.004892	0.005028	0.006143	0.00567	0.019112	0.019264
0.0025								0.007856		0.00886		0.030099
0.003					0.000648	0.000491	0.011421	0.011313	0.013627	0.012759		0.043343
0.004					0.000989	0.000874		0.020112	0.022034	0.022682		
0.005					0.001465	0.001365		0.031425		0.03544		
0.006					0.002015	0.001966						
0.0075					0.003145	0.003071						
0.01		5.47E-06		1.97E-05	0.005343	0.00546						
0.025	2.9E-05	3.42E-05		0.000123		0.034127						
0.05	0.000121	0.000137	0.00049	0.000491								
0.06		0.000197	0.000749	0.000708								
0.075	0.00032	0.000308	0.001089	0.001106								
0.09	0.00045	0.000443	0.00163	0.001592								
0.1	0.000539	0.000547	0.00193	0.001966								
0.115		0.000723		0.0026								

Table 7S. Observed pseudo first-order Rate constants for three nucleophiles [**Fig. 6**], **2c**; **2e** and **2f**; (Vary [B]).

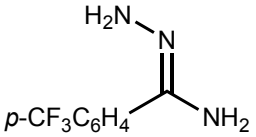
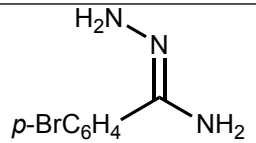
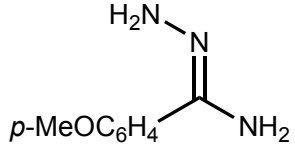
Nucleophile, [Nu] = 2.5 × 10^{-4} M	**Conc [B], M**	**k_{obs} (Standard Deviation) (s^{-1})**		
		35 ºC	25 ºC	15 ºC
 Chemical Formula: $C_8H_8F_3N_3$ Exact Mass: 203.07 **2f**	0.003	-	0.000797 (0.000013)	-
	0.004	-	0.000893 (0.000015)	-
	0.005	-	0.001041 (0.000029)	-
	0.01	-	0.001561 (0.000039)	-
 Chemical Formula: $C_7H_8BrN_3$ Exact Mass: 212.99 **2e**	0.003	0.001677 (0.000038)	0.001145 (0.000025)	0.000923 (0.000019)
	0.004	0.002125 (0.000053)	0.001385 (0.000036)	0.001098 (0.000027)
	0.005	0.002477 (0.000069)	0.001599 (0.000042)	0.001208 (0.000033)
	0.01	0.004047 (0.000162)	0.002531 (0.000096)	0.001401 (0.000049)
 Chemical Formula: $C_8H_{11}N_3O$ Exact Mass: 165.09 **2c**	0.003	-	0.003773 (0.000227)	-
	0.004	-	0.004592 (0.000317)	-
	0.005	-	0.004851 (0.000371)	-

Table 8S. Data from Global fit illustrated in **Fig. 7**: *k*obs vs *k*obs_Calc for 2e; 5–35 ºC (Details in **Table 5S**).

T	L	KOBS	KOBS_CALC
(ºC)	(M)	(s^{-1})	(s^{-1})
35	0		0
35	0.00025		0.000104
35	0.0005		0.000415
35	0.00063		0.000658
35	0.00075		0.000933
35	0.00088		0.001285
35	0.001	0.00218	0.001659
35	0.0015		0.003732
35	0.002	0.00692	0.006635
35	0.0025		0.010368
35	0.003	0.016031	0.014929
35	0.0033		0.018065
35	0.00365		0.0221
35	0.004	0.026675	0.026541
35	0.0042		0.029262
35	0.0046		0.035101
30	0.00063		0.00062
30	0.00075		0.000879
30	0.00088		0.001209
30	0.001	0.001695	0.001562
30	0.0015		0.003514
30	0.002	0.006864	0.006247
30	0.0025		0.009761
30	0.003		0.014056
30	0.0033		0.017008
30	0.00365		0.020807
30	0.004	0.024498	0.024989
30	0.0042		0.027551

30	0.0046		0.033048
30	0.0048		0.035984
25	0.00025	0.0002	9.17E-05
25	0.0005	0.00047	0.000367
25	0.00063		0.000583
25	0.00075	0.00138	0.000826
25	0.00088		0.001137
25	0.001	0.00171	0.001468
25	0.0015		0.003303
25	0.002	0.00614	0.005872
25	0.0025		0.009175
25	0.003	0.01363	0.013211
25	0.0033		0.015986
25	0.00365		0.019556
25	0.004	0.02203	0.023487
25	0.0042		0.025894
25	0.0046		0.031061
20	0.00063		0.000547
20	0.00075		0.000775
20	0.00088		0.001066
20	0.001	0.001658	0.001377
20	0.0015		0.003099
20	0.002	0.005914	0.005509
20	0.0025		0.008607
20	0.003	0.013174	0.012394
20	0.0033		0.014997
20	0.00365		0.018347
20	0.004	0.021534	0.022035
20	0.0042		0.024293
20	0.0046		0.029141
20	0.0048		0.03173
15	0.00025		8.06E-05
15	0.0005		0.000322

15	0.00063		0.000512
15	0.00075		0.000725
15	0.00088		0.000999
15	0.001	0.00158	0.00129
15	0.0015		0.002901
15	0.002	0.00554	0.005158
15	0.0025		0.00806
15	0.003	0.01246	0.011606
15	0.0033		0.014043
15	0.00365		0.01718
15	0.004	0.02026	0.020632
15	0.0042		0.022747
15	0.0046		0.027286
15	0.0048		0.029711
5	0.00063		0.000446
5	0.00075		0.000632
5	0.00088		0.00087
5	0.001	0.00143	0.001124
5	0.0015		0.002528
5	0.002	0.00407	0.004495
5	0.0025		0.007023
5	0.003	0.0114	0.010113
5	0.0033		0.012237
5	0.00365		0.014971
5	0.004	0.01767	0.017979
5	0.0042		0.019822
5	0.0046		0.023778

Table 9S. Reverse Rate constants for Nucleophiles **2**a–**2c**; **2e**–**2f** at 25 °C in MeCN; other details in Caption **Table 5S**.

Nucleophile	**Fig. 5** Eq. 5b[a)]	**Fig. 5** Eq. 4a[b)]	**Fig. 6** Eq. 6ab[c)]
	k_r	k_r	
2a	0.00017(18)	0.00017(18)	--
2b	0.000013(196)	-0.000004(196)	--
2c	0.00009(17)	0.00009(17)	0.0023(3)
2e	0.00034(12)	0.00033(12)	0.00059(11)
2f	-0.00017(16)	-0.00017(16)	0.00047(12)
2g	0.000004(171)	-0.000007(171)	--

[a)] Eq. 5b; Data in **Fig. 5**. [b)] Eq. 4a; Data in **Fig. 5**. [c)] Eq. 6ab; Data in **Fig. 6**

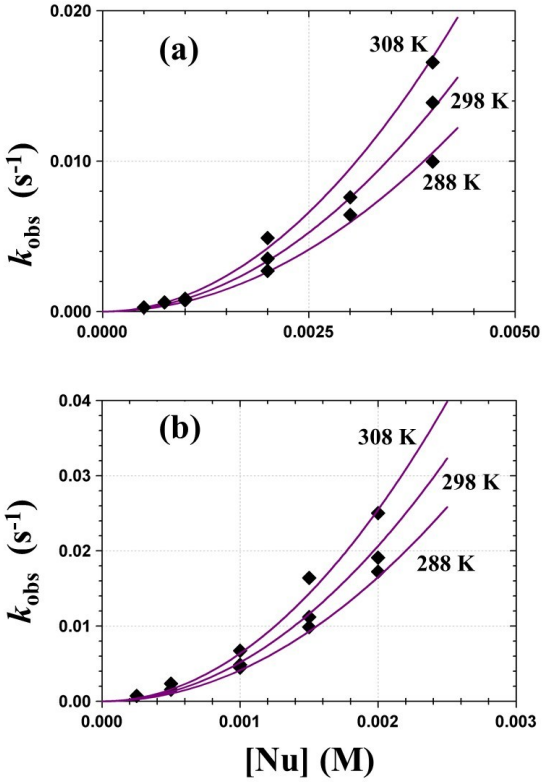


Figure 55S. Plots of k_{obs} *vs*. [Nu(H)] for the nucleophilic addition of (a) **2f** and (b) **2c** to **(**Ph_3PCH_2Ph)[**1**] at 25 °C in MeCN. Details in Experimental.

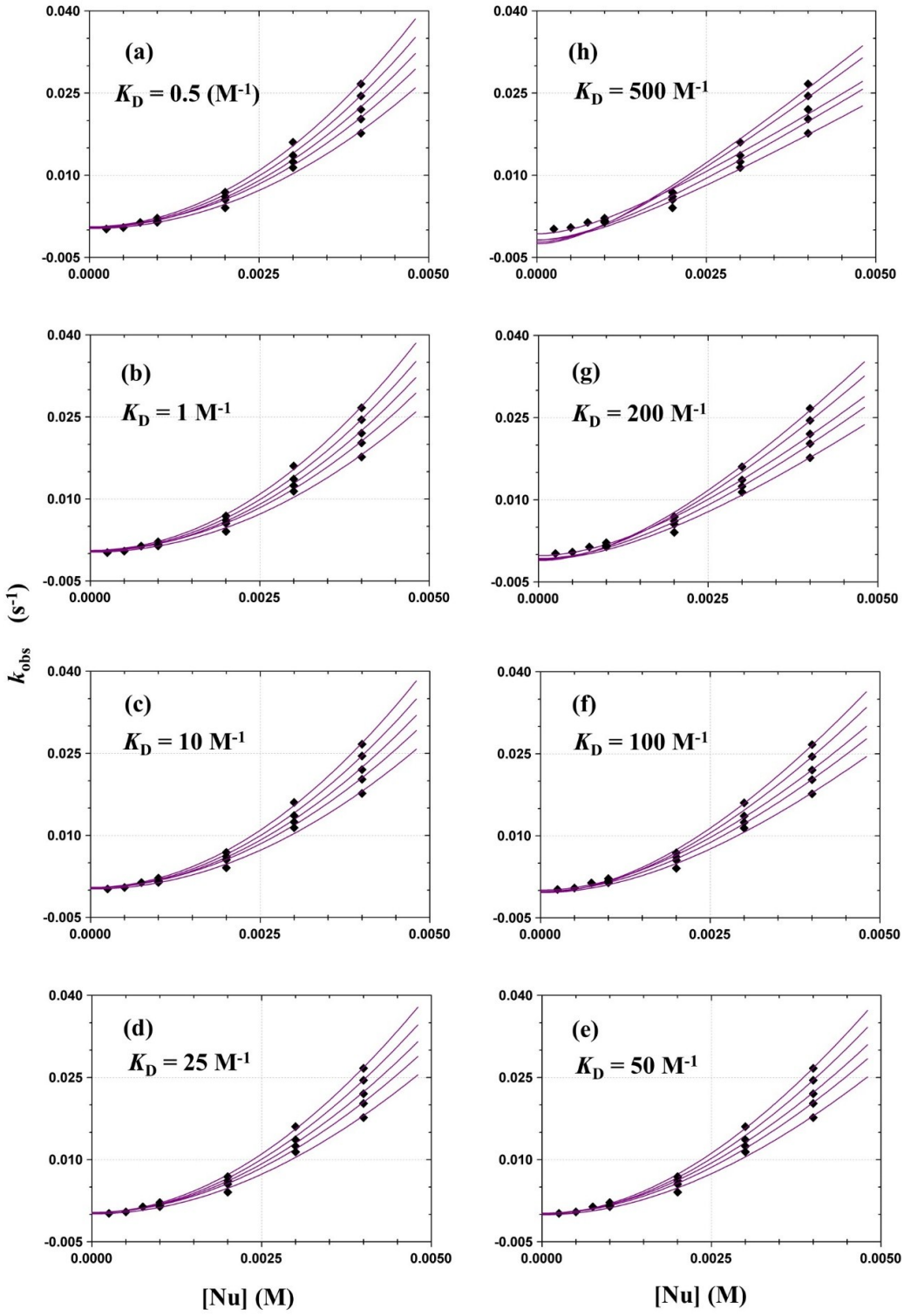


Figure 56S. Plots of k_{obs} *vs*. [Nu] in MeCN for the nucleophilic addition of **2e** to (Ph_3PCH_2Ph)[**1**] as a function of temperature to evaluate the magnitude and influence of K_D in Eq. 4a. A value of K_D=1 M^{-1} was selected for fits.

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