Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Coupling of ortho-substituted Aryl Chlorides with Bulky Amides

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[‡] X-ray crystal structure determination

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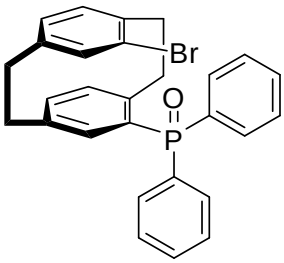
General Information

^{1}H-NMR spectra were recorded on a *Bruker* AC 250 (250 MHz), *Bruker* AM 400 (400 MHz) or a *Bruker* DRX 500 (500 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm), CD_3CN (1.94 ppm) as internal standards. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of dd, dt = doublet of triplets, etc. The spectra were analyzed according to first order. Aromatic protons of the [2.2]Paracyclophane moiety are labeled as H_{PC}. ^{13}C-NMR spectra were recorded on a *Bruker* AM 400 (100 MHz) or a *Bruker* DRX 500 (125 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CDCl_3$ (77.0 ppm) or to CD_3CN (1.24 ppm) as internal standards. ^{31}P-NMR spectra were recorded on a *Bruker* AC 250 (101 MHz), or a *Bruker* DRX 500 (202 MHz). Chemical shifts are expressed in parts per million (ppm, δ) downfield from phosphoric acid. MS (EI) (electron impact mass spectrometry): *Finnigan* MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the Molecule-Ion. IR (infrared spectroscopy): FT-IR *Bruker* IFS 88. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. The deposit of the absorption band is given in wave numbers $\tilde{\nu}$ in cm^{-1}.

Reactions under microwave conditions were performed in a *CEM Discover* microwave reactor. Routine monitoring of reactions were performed using Silica gel coated aluminum plates (Merck, silica gel 60, F_{254}), which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdato phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and/or $KMnO_4$-solution and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, ABCR and Acros. Tetrahydrofuran was distilled from sodium/potassium under argon prior to use. Dichloromethane was distilled from calcium hydride, toluene was

distilled from sodium. Anhydrous *t*-BuOH (Sure/Seal™) was purchased from Sigma-Aldrich and anhydrous 1,4-Dioxane (extra dry over moleucar sieves) was purchased from Acros. Cs_2CO_3 (ReagenPlus®) was purchased from Sigma-Aldrich and used under air. All other solvents, reagents and chemicals were used as purchased unless stated otherwise. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried glassware.

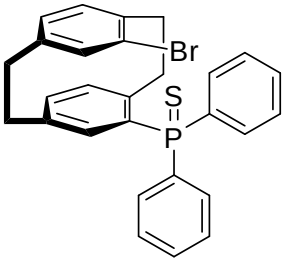
***rac*-*P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenylphosphine oxide (3)**



A solution of bromine (7.9 mL, 24.6 g, 154 mmol, 3.5 equiv.) in CCl_4 (50 mL) was prepared. A suspension of iron powder (246 mg, 4.4 mmol, 10 mol%) with 10 mL of this solution was stirred for 1 h. Then CH_2Cl_2 (350 mL) and *rac*-*P*-(4-[2.2]paracyclophanyl)-*P*,*P*-diphenylphosphine oxide (2) (18.0 g, 44.1 mmol, 1.0 equiv.) were added. The remaining Br_2/CCl_4 solution was added dropwise. The solution was stirred for 16 h. As no educt could be detected by TLC the reaction mixture was quenched by addition of aqueous sat. $Na_2S_2O_3$ (50 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The residue was washed with cold ethyl acetate (2 x 100 mL) to give **3** as a pale-yellow solid (17.4 g, 35.7 mmol, 81%). Analytical pure material was obtained after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 1:1 v/v). Crystals suitable for X-ray analysis were obtained from a solution of **3** in ethyl acetate. m.p. 182 °C (capillary); R_f (cyclohexane/ethyl acetate 1:1 v/v) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.69 (m, 2H, H_{Ar}), 7.53–7.48 (m, 1H, H_{Ar}), 7.45–7.41 (m, 2H, H_{Ar}), 7.38–7.33 (m, 1H, H_{Ar}), 7.27–7.23 (m, 2H, H_{Ar}), 7.17–7.12 (m, 2H, H_{Ar}), 6.75 (d, J = 7.6 Hz, 1H, H_{PC}), 6.61 (dd, J = 7.5 Hz, J = 1.6 Hz, 1H, H_{PC}), 6.59–4.54 (m, 2H, H_{PC}), 6.34 (d, J = 1.4 Hz, 1H, H_{PC}), 6.30 (dd, J = 15.0 Hz, J = 1.6

Hz, 1H, H_{PC}), 4.23–4.17 (m, 1H, CH_2), 3.79–3.73 (m, 1H, CH_2), 3.16–3.09 (m, 1H, CH_2), 2.97–2.81 (m, 4H, CH_2), 2.72–2.65 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4 (d, *J* = 6.8 Hz, C), 140.7 (C), 139.1 (C), 137.9 (d, *J* = 13.2 Hz, C), 136.3 (d, *J* = 11.6 Hz, CH), 135.9 (d, *J* = 3.4 Hz, CH), 135.7 (CH), 135.7 (d, *J* = 104.6 Hz, C), 134.9 (d, *J* = 12.7 Hz, CH), 134.4 (CH), 132.7 (d, *J* = 9.4 Hz, 2 x CH), 132.6 (d, *J* = 103.1 Hz, C), 131.5 (d, *J* = 9.2 Hz, 2 x CH), 131.3 (d, *J* = 2.6 Hz, CH), 131.0 (d, *J* = 3.1 Hz, CH), 130.9 (CH), 129.3 (d, *J* = 106.7 Hz, C), 128.0 (d, *J* = 6.6 Hz, 2 x CH), 127.0 (d, *J* = 6.6 Hz, 2 x CH), 126.8 (C), 35.7 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 33.2 (d, *J* = 3.4 Hz, CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = 27.94 ppm; FTIR (KBr): $\tilde{\nu}$ = 3029 (w), 2929 (m), 2855 (w), 2062 (vw), 1913 (w), 1708 (s), 1584 (w), 1556 (w), 1537 (w), 1476 (w), 1435 (s), 1391 (m), 1309 (w), 1188 (s), 704 (m), cm^{-1}; MS (EI, 70 eV), m/z (%): 488.1 (9) $[M]^+$, 487.1 (3) $[M]^+$, 486.1 (9) $[M]^+$, 407.2 (5) $[M–Br]^+$, 304.1 (23) $[C_{20}H_{17}OP]^+$, 58.1 (55), 43.0 (100); HR-EIMS calcd for $C_{28}H_{24}BrPO$: 486.0748; found 486.0750 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{24}BrPO$: C 69.00, H 4.96; found: C 68.40, H 4.57.

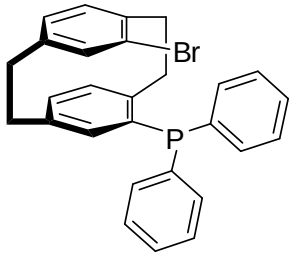
rac-P-13-(4-bromo-[2.2]paracyclophanylene)-_P_,_P_-diphenylphosphine sulfide (5)



To an oven-dried reaction vessel charged with *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenylphosphine oxide (3) (2.00 g, 4.10 mmol, 1.0 equiv.) and phosphorus pentasulfide (547 mg, 1.23 mmol, 0.3 equiv.) was added chlorobenzene (4 mL). The reaction mixture was stirred for 19 h at 90 °C. Afterwards it was allowed to cool to room temperature, and water (10 mL) was added to the mixture. After phase separation the aqueous layer was extracted with $CHCl_3$ (2 x 10 mL) and CH_2Cl_2 (2 x 10 mL). The combined organics were dried over $MgSO_4$, and filtrated. After rotary evaporation the residue was washed with cold ethyl acetate (2 x

15 mL) to give **5** as an off-white powder (1.88 g, 3.73 mmol, 91%). Analytically pure material was obtained after flash chromatography (SiO_2, chloroform). Crystals suitable for X-ray analysis were obtained from a solution of **5** in ethyl acetate and CH_2Cl_2. m.p. 214 °C (capillary); R_f (cyclohexane/ethyl acetate 10:1 v/v) = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.71 (m, 2H, H_{Ar}), 7.56–7.52 (m, 1H, H_{Ar}), 7.49–7.44 (m, 2H, H_{Ar}), 7.41–7.37 (m, 1H, H_{Ar}), 7.31–7.26 (m, 2H, H_{Ar}), 7.20–7.15 (m, 2H, H_{Ar}), 7.78 (d, *J* = 7.6 Hz, 1H, H_{PC}), 6.65 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H, H_{PC}) 6.62–6.57 (m, 2H, H_{PC}), 6.37 (d, *J* = 1.4 Hz, 1H, H_{PC}), 6.33 (dd, *J* = 15.0 Hz, 1.6 Hz, 1H, H_{PC}), 4.26–4.20 (m, 1H, CH_2), 3.82–3.76 (m, 1H, CH_2), 3.16 (ddd, *J* = 13.2 Hz, 10.0 Hz, 3.2 Hz, 1H, CH_2), 3.00–2.84 (m, 4H, CH_2), 2.72 (ddd, *J* = 13.3 Hz, 10.4 Hz, 5.6 Hz, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4 (d, *J* = 6.8 Hz, C), 140.7 (C), 139.1 (C), 137.8 (d, *J* = 13.2 Hz, C), 136.3 (d, *J* = 11.6 Hz, CH), 135.9 (d, *J* = 3.4 Hz, CH), 135.7 (CH), 135.7 (d, *J* = 104.6 Hz, C), 134.9 (d, *J* = 12.7 Hz, CH), 134.4 (CH), 132.7 (d, *J* = 9.4 Hz, 2 x CH), 132.6 (d, *J* = 103.1 Hz, C), 131.5 (d, *J* = 9.2 Hz, 2 x CH), 131.3 (d, *J* = 2.6 Hz, CH), 131.0 (d, *J* = 3.1 Hz, CH), 131.0 (CH), 129.3 (d, *J* = 106.6 Hz, C), 128.0 (d, *J* = 6.6 Hz, 2 x CH), 127.9 (d, *J* = 6.6 Hz, 2 x CH), 126.8 (C), 35.7 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 33.2 (d, *J* = 3.4 Hz, CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = 41.13 ppm; FTIR (KBr): $\tilde{\nu}$= 3054 (m), 2926 (s), 2853 (w), 2053 (m), 1966 (w), 1901 (w), 1679 (vw), 1584 (m), 1477 (m), 1435 (s), 1392 (m), 1307 (w), 1181 (m), 1102 (s), 1068 (v), 1033 (m), 998 (w), 962 (w), 918 (m), 844 (m), 814 (w), 752 (s), 713 (s), 694 (s), 636 (s), 614 (m), 518 (s), 501 (s), 418 (m) cm^{-1}; MS (EI, 70 eV), m/z (%): 504.1 (2) $[M]^+$, 502.1 (2) $[M]^+$, 424.2 (38) $[C_{28}H_{25}PS]^+$, 423.2 (100) $[M–Br]^+$, 320.1 (50) $[C_{20}H_{17}PS]^+$, 58.1 (27), 43.0 (53); HR-EIMS calcd for $C_{28}H_{24}BrPS$: 502.0519; found 502.0518 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{24}BrPS$: C 66.80, H 4.81, S 6.37; found: C 66.80, H 4.64, S 6.39.

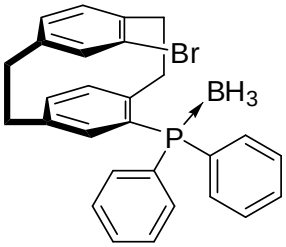
Rac-P-13-(4-bromo-[2.2]paracyclophanylene)-_P_,_P_-diphenyl phosphine (4)



To an oven-dried reaction vessel charged with *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenylphosphine sulifde (5) (1.20 g, 2.38 mmol, 1.0 equiv.) was added triethyl phosphite (4.2 mL, 4.07 g, 24.5 mmol, 10.0 equiv.). The reaction mixture was stirred for 4 h at 130 °C. Afterwards it was allowed to cool to room temperature. White crystals were obtained from the triethyl phosphite solution while standing over night. The supernatant was removed and the crystals were washed three times with *n*-hexane (3 x 8 mL) and dried under vacuum to give **4** as a white powder (930 mg, 1.97 mmol, 83%). Crystals suitable for X-ray analysis were obtained from a solution of **4** in toluene. m.p. 178 °C (capillary); R_f (cyclohexane/ethyl acetate 20:1 v/v) = 0.62; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 2H, H_{Ar}), 7.43–7.35 (m, 4H, H_{Ar}), 7.23–7.18 (m, 2H, H_{Ar}), 6.99–6.95 (m, 2H, H_{Ar}), 6.65–6.50 (m, 5H, H_{PC}), 6.02 (dd, *J* = 6.7 Hz, 1.5 Hz, 1H, H_{PC}), 4.05–3.97 (m, 1H, CH_2), 3.83–3.76 (m, 1H, CH_2), 3.07–2.93 (m, 4H, CH_2), 2.89–2.83 (m, 1H, CH_2), 2.81–2.74 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7 (d, *J* = 21.4 Hz, C), 141.1 (C), 139.5 (d, *J* = 11.7 Hz, C), 138.8 (C), 138.3 (C), 137.3 (d, *J* = 14.6 Hz, C), 136.9 (d, *J* = 13.9 Hz, C), 135.8 (CH), 135.3 (d, *J* = 19.6 Hz, 2 x CH), 134.7 (CH), 134.3 (d, *J* = 3.9 Hz, CH), 134.0 (d, *J* = 6.7 Hz, 2 x CH), 133.7 (d, *J* = 19.6 Hz, CH), 132.9 (d, *J* = 20.3 Hz, 2 x CH), 131.6 (CH), 128.7 (CH), 128.4 (d, *J* = 6.8 Hz, CH), 128.3 (d, *J* = 6.8 Hz, CH), 128.1 (CH), 128.0 (d, *J* = 6.4 Hz, CH), 126.7 (C), 35.7 (CH_2), 34.9 (CH_2), 34.5 (CH_2), 33.2(d, *J* = 21.0 Hz, CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = –9.75 ppm; FTIR (ATR): $\tilde{\nu}$ = 2919 (vw), 1580 (vw), 1475 (vw), 1431 (vw), 1388 (vw), 1186 (vw), 1181 (m), 1026 (vw), 835 (vw), 740 (w), 918 (m), 692 (s) cm^{-1}; MS (EI, 70 eV), m/z (%): 472.1 (18) $[M]^+$, 470.1 (17) $[M]^+$, 393.2 (25) $[C_{28}H_{26}P]^+$,

392.2 (100) $[C_{28}H_{25}P]^+$, 391.2 (84) $[M–Br]^+$, 288.2 (41) $[C_{20}H_{17}P]^+$, 92.1 (38) $[C_7H_8]^+$ HR-EIMS calcd for $C_{28}H_{24}BrP$: 470.0799; found 470.0799 $[M]^+$.

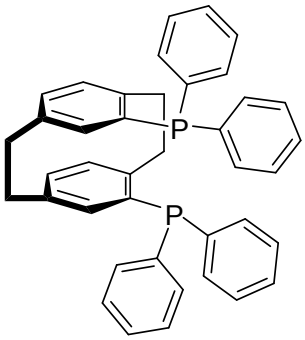
Rac-P-13-(4-bromo-[2.2]paracyclophanylene)-_P_,_P_-diphenylphosphine-borane (4·BH_3)



To a stirred solution of *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenylphosphine (4) (300 mg, 0.636 mmol, 1.0 equiv.) in THF (12 mL) was added a solution of borane in THF (2 M, 0.38 mL, 0.763 mmol, 1.2 equiv.) at room temperature. The reaction mixture was stirred for 4 h at room temperature. The volatiles were removed under reduced pressure and the residue was subjected to flash chromatography (cyclohexane/ethyl acetate 20:1 v/v) to give the title compound (296 mg, 0.61 mmol, 96%) as a white powder. m.p. 183 °C (capillary); R_f (cyclohexane/ethyl acetate 20:1 v/v) = 0.32; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.56–7.39 (m, 6H, H_{Ar}), 7.35–7.28 (m, 2H, H_{Ar}), 7.23–7.15 (m, 2H, H_{Ar}), 6.79–6.67 (m, 4H, H_{PC}), 6.59 (dd, J = 7.6 Hz, 4.5 Hz, 1H, H_{PC}), 6.33 (d, J = 1.6 Hz, 1H, H_{PC}), 3.98–3.88 (m, 1H, CH_2), 3.60–3.51 (m, 1H, CH_2), 3.25–3.15 (m, 1H, CH_2), 3.04–2.80 (m, 5H, CH_2), 2.50–1.00 (bm, 3H, BH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.0 (d, J = 9.3 Hz, C), 141.0 (C), 138.9 (C), 138.1 (d, J =9.6 Hz, C), 136.6 (d, J = 9.3 Hz, CH), 136.0 (CH), 135.7 (d, J = 2.8 Hz, CH), 135.4 (d, J = 5.9 Hz, CH), 134.4 (CH), 133.6 (d, J = 9.4 Hz, 2 x CH), 133.2 (d, J = 9.2 Hz, 2 x CH), 132.3 (d, J = 58.5 Hz, C), 131.7 (d, J = 57.8 Hz, C), 130.6–130.5 (m, 3 x CH), 128.3 (d, J = 9.3 Hz, 2 x CH), 128.2 (d, J = 9.1 Hz, 2 x CH), 127.1 (C), 125.0 (d, J = 53.9 Hz, C), 36.2 (CH_2), 34.9 (CH_2), 34.2 (CH_2), 32.5 (d, J = 3.0 Hz, CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = 18.0 (br.s, PPh_2BH_3) ppm; FTIR (ATR): $\tilde{\nu}$ = 2925 (vw), 2851 (vw), 2427 (vw), 2387 (w), 2341 (vw), 1434 (w), 1066 (v), 1031 (vw), 742 (w), 690 (m) 493 (w) cm^{-1}; MS

(EI, 70 eV), m/z (%): 484.1 (1) $[M]^+$, 472.1 (20) $[M\text{-}BH_3]^+$, 470.1 (19) $[M\text{-}BH_3]^+$, 392.2 (35) $[C_{28}H_{25}P]^+$, 391.2 (100) $[M–Br]^+$, 288.1 (62) $[C_{20}H_{17}P]^+$, 209.1 (24) $[C_{16}H_{17}]^+$, 178.1 (21) $[C_4H_{10}]^+$.

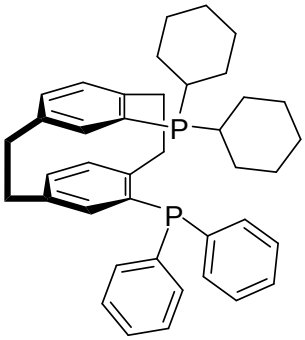
4,13-bis-(diphenylphosphino)-[2.2]paracyclophane (6), GemPhos



To a stirred solution of *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenyl-phosphine (4) (300 mg, 0.636 mmol, 1.0 equiv.) in THF (15 mL) was added *tert*-butyllithium (0.82 mL, 1.4 mmol, 2.2 equiv.,1.7 M in pentane) at – 78 °C. After stirring for 3 h at this temperature chlorodiphenylphosphine (376 mg, 1.91 mmol, 2.5 equiv.) was added at –78 °C. The reaction mixture was allowed to warm up to room temperature while stirring was continued overnight. The solvent was removed under reduced pressure and the residue was washed with degassed methanol (3 x 10 mL) to give **6** as a white powder (319 mg, 0.553 mmol, 87%). Crystals suitable for X-ray analysis were obtained from a solution of **6** in $CHCl_3$. m.p. 196.1 °C (capillary); R_f = 0.56 (cyclohexane/ethyl acetate, 20:1 v/v); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 4H, H_{Ar}), 7.35–7.28 (m, 6H, H_{Ar}), 7.25–7.20 (m, 10H, H_{Ar}), 6.63–6.58 (m, 4H, H_{PC}), 5.99–5.97 (m, 2H, H_{PC}), 3.67 (dd, *J* = 13.3 Hz, 4.6 Hz, 2H, CH_2), 2.95 (dd, *J* = 13.0 Hz, 4.6 Hz, 2H, CH_2), 2.82 (dd, *J* = 13.3 Hz, 4.6 Hz, 2H, CH_2), 2.68 (dd, *J* = 13.0 Hz, 4.6 Hz, 2H, CH_2) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.8 (t, *J* = 8.8 Hz, 2 x C), 139.8 (t, *J* = 4.7 Hz, 2 x C), 138.5 (2 x C), 138.3 (t, *J* = 7.6 Hz, 2 x C), 137.6 (t, *J* = 6.9 Hz, 2 x C), 135.9 (t, *J* = 11.4 Hz, 4 x CH), 134.0 (d, *J* = 13.1 Hz, 4 x CH), 133.2 (d, *J* = 5.3 Hz, 4 x CH), 133.1 (d, *J* = 10.4 Hz, 2 x CH), 128.8 (2 x CH), 128.2 (t, *J* = 3.7 Hz, 4 x CH), 128.2 (2 x CH), 128.0 (t, *J* = 3.6 Hz, 4 x CH), 35.1–34.9 (m, 4 x CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): *δ* = –7.78 ppm; FTIR (KBr): $\tilde{\nu}$ = 2927 (vw),

3363 (vw), 1573 (vw), 1477 (vw), 1433 (m), 1260 (w), 1183 (vw), 1088 (w), 1024 (w), 798 (vw), 740 (w), 693 (m), 504 (w) cm^{-1}; MS (EI, 70 eV), m/z (%): 576.2 (16) $[M]^+$, 393.2 (30) $[C_{28}H_{26}P]^+$, 392.2 (100) $[M+H-C_{12}H_{10}P]^+$, 288.1 (89) $[C_{20}H_{17}P]^+$, 287.1 (31) $[C_{20}H_{16}P]^+$, 209.1 (25) $[C_{16}H_{17}]^+$, 202.1 (73) $[C_{12}H_{11}OP]^+$, 201.1 (80) $[C_{12}H_{10}OP]^+$, 77.1 (36) $[C_6H_5]^+$ 43.0 (42) $[C_3H_7]^+$; HR-EIMS calcd for $C_{40}H_{34}P_2$: 576.2135, found 576.2139 $[M]^+$.

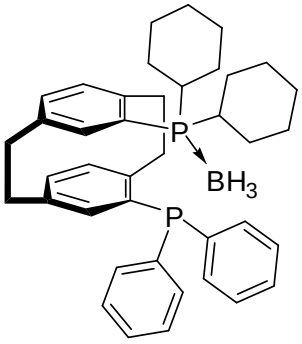
4-diphenylphosphino-13-dicyclohexylphosphino-[2.2]paracyclophane (1), CyGemPhos



To a stirred solution of *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenyl-phosphine (4) (500 mg, 1.06 mmol, 1.0 equiv.) in THF (40 mL) was added *tert*-butyllithium (1.5 mL, 2.33 mmol, 1.6 M in pentane, 2.2 equiv.) at –78 °C. After stirring for 3 h at this temperature, chlorodicyclohexylphosphine (0.328 mL, 345 mg, 1.48 mmol, 1.4 equiv.) was added at –78 °C. The reaction mixture was allowed to warm up to room temperature while stirring was continued overnight. Then degassed water (5 mL) was added and the mixture was stirred for 5 min under argon. After phase separation under argon, the aqueous layer was extracted with degassed THF (20 mL). The combined organics were filtrated under argon over sodium sulfate and silica. Then the volatiles were removed under reduced pressure and the residue was dissolved in degassed diethyl ether (1 mL). Then degassed methanol (12 mL) was added and argon was bubbled through the solution for 10 minutes to remove the diethyl ether. The white precipitate was isolated and washed with degassed methanol (2 x 10 mL) to give **1** as a white powder (447 mg, 0.76 mmol, 72%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48–7.35 (m, 5H, H_{Ar}), 7.27–7.14 (m, 5H, H_{Ar}), 6.63–

6.60 (m, 3H, H_{PC}), 6.56 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H, H_{PC}), 6.39 (br. s, 1H, H_{PC}), 6.01–5.98 (m, 1H, H_{PC}), 4.19–4.12 (m, 1H, CH_2), 3.24 (ddd, *J* = 13.4 Hz, 9.8 Hz, 3.0 Hz, 1H, CH_2), 3.10–2.90 (m, 4H, CH_2), 2.78–2.67 (m, 2H, CH_2), 2.12–1.63 (m, 8H, Cy), 1.48–1.27 (m, 8H, Cy), 1.20–1.07 (m, 3H, Cy), 0.98–0.78 (m, 3H, Cy) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.1 (dd, *J* = 12.6 Hz, 7.2 Hz, C), 143.9 (dd, *J* = 9.4 Hz, 5.2 Hz, C), 140.7 (dd, *J* = 8.0 Hz, 4.6 Hz, C), 138.8–138.7 (m, C), 138.3 (dd, *J* = 8.1 Hz, 5.5 Hz, C), 138.2 (C), 137.1 (C), 135.9–135.8 (m, C), 135.8 (d, *J* = 8.4 Hz, CH), 135.7 (d, *J* = 8.6 Hz, CH), 134.2 (CH), 134.1 (CH), 133.7 (CH), 133.0 (CH), 132.9 (d, *J* = 8.0 Hz, CH), 132.8 (d, *J* = 7.9 Hz, CH), 132.4 (CH), 131.3 (CH), 128.9 (CH), 128.2 (CH), 128.1 (CH), 128.1 (d, *J* = 2.3 Hz, CH), 128.0 (d, *J* = 3.0 Hz, CH), 127.9 (d, *J* = 2.9 Hz, CH), 36.1 (dd, *J* = 6.8 Hz, 4.8 Hz, CH_2), 35.5 (dd, *J* = 9.5 Hz, 2.6 Hz, CH), 35.2 (CH_2), 35.1 (CH_2), 34.6 (dd, *J* = 13.3 Hz, 8.5 Hz, CH_2), 32.6 (dd, *J* = 14.8 Hz, 10.5 Hz, CH_2), 30.8 (dd, *J* = 10.7 Hz, 6.0 Hz, CH_2), 30.4 (dd, *J* = 8.4 Hz, 3.6 Hz, CH), 28.7 (dd, *J* = 5.1 Hz, 3.0 Hz, CH_2), 27.8 (dd, *J* = 8.7 Hz, 5.0 Hz, CH_2), 27.5 (dd, *J* = 4.2 Hz, 2.7 Hz, CH_2), 27.2 (m, 3 x CH_2), 26.8 (CH_2), 26.3 (CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = -5.9 (s, PPh_2, PCy_2) ppm; FTIR (KBr): $\tilde{\nu}$ = 3042 (vw), 2918 (m), 2846 (w), 2283 (vw) 1575 (vw), 1433 (w), 1175 (w), 1084 (vw), 939 (vw), 845 (w), 751 (w), 720 (w), 690 (m), 508 (m) cm^{-1}; MS (EI, 70 eV), m/z (%): 588.2 (2) $[M]^+$, 506.2 (37) $[C_{34}H_{36}P_2]^+$, 505.2 (100) $[C_{34}H_{35}P_2]^+$, 392.1 (27) $[C_{28}H_{25}P]^+$, 391.1 (53) $[C_{28}H_{24}P]^+$, 288.1 (59) $[C_{20}H_{17}P]^+$, 287.1 (24) $[C_{20}H_{16}P]^+$, 209.1 (31) $[C_{16}H_{17}]^+$, 178.0 (22) $[C_4H_{10}]^+$, 89.0 $[C_7H_5]^+$; HR-EIMS calcd for $C_{40}H_{46}P_2$: 588.3074, found 588.3073 $[M]^+$.

4-diphenylphosphino-13-dicyclohexylphosphino-borane-[2.2]paracyclophane (1·BH_3)



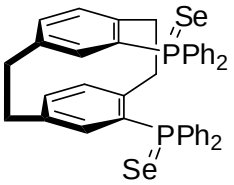
To a stirred solution of *rac-P*-13-(4-bromo-[2.2]paracyclophanylene)-*P*,*P*-diphenyl-phosphine (4) (500 mg, 1.06 mmol, 1.0 equiv.) in THF (40 mL) was added *tert*-butyllithium (1.5 mL, 2.33 mmol, 1.6 M in pentane, 2.2 equiv.) at –78 °C. After stirring for 3 h at this temperature, chlorodicyclohexylphosphine (0.585 mL, 617 mg, 2.65 mmol, 2.5 equiv.) was added at –78 °C. The reaction mixture was allowed to warm up to room temperature while stirring was continued overnight. Then a solution of borane in THF (2 M, 1.32 mL, 2.65 mmol, 2.5 equiv.) was added. The mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (cyclohexane/ethyl acetate 20:1 v/v) to give the title compound (481 mg, 0.79 mmol, 75%) as a white powder. R_f (cyclohexane/ethyl acetate 20:1 v/v) = 0.58; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.45–7.39 (m, 4H, H_{Ar}), 7.26–7.15 (m, 6H, H_{Ar}), 6.71–6.67 (m, 2H, H_{PC}), 6.65–6.60 (m, 2H, H_{PC}), 6.51 (dd, *J* = 9.9 Hz, 0.9 Hz, 1H, H_{PC}), 5.91 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H, H_{PC}), 4.12 (ddd, *J* = 13.7 Hz, 9.2 Hz, 4.7 Hz, 1H, CH_2), 3.18–3.05 (m, 2H, CH_2), 3.02–2.85 (m, 3H, CH_2), 2.85–2.74 (m, 1H, CH_2), 2.65 (ddd, *J* = 13.8 Hz, 9.7 Hz, 4.7 Hz, 1H, CH_2), 2.23–1.62 (m, 11H, Cy; BH_3), 1.49–0.97 (m, 11H, Cy; BH_3), 0.78–0.68 (m, 2H, Cy; BH_3) -0.05 – -0.14 (m, 1H, BH_3) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 146.5 (d, *J* = 8.9 Hz, C), 143.5 (d, *J* = 13.8 Hz, C), 139.9 (C), 139.8 (C), 138.7 (d, *J* = 16.2 Hz, C), 138.0 (C), 137.3 (d, *J* = 7.5 Hz, C), 135.7 (d, *J* = 9.4 Hz, CH), 135.6 (CH), 135.4 (CH), 134.9 (d, *J* = 2.9 Hz, CH), 133.8 (d, *J* = 1.3 Hz, CH), 133.5 (d, *J* = 5.7 Hz, CH),133.5 (CH), 133.3 (CH), 132.5 (d, *J* = 1.0 Hz, CH), 132.0 (CH), 128.9 (CH), 128.4 (CH), 128.2 (d, *J* = 8.2 Hz, 2 x CH), 128.1 (d, *J* = 7.9 Hz, 2 x CH), 122.4 (d, *J* = 43.9 Hz, C), 36.3 (d, *J* = 7.8 Hz, CH_2), 35.2–35.0 (m, 2 x CH_2), 34.8 (CH_2), 34.7 (d, *J* = 34.1 Hz, CH), 29.0 (d, *J* = 34.2 Hz, CH), 28.3 (d, *J* =8.9 Hz, CH_2), 27.1 (d, *J* = 10.9 Hz, CH_2), 26.9 (d, *J* = 12.3 Hz, CH_2), 26.9 (d, *J* = 11.4 Hz, CH_2), 26.6 (d, *J* = 9.2 Hz, CH_2), 26.4 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 25.6 (d, *J* = 4.7 Hz, CH_2), ppm; ^{31}P NMR (101 MHz, $CDCl_3$): *δ* = 24.9 (br.s, PCy_2BH_3), -5.1 (s, PPh_2) ppm; FTIR (KBr): $\tilde{\nu}$ = 2927 (vw), 2849 (vw), 2393 (vw), 2341 (vw) 1574 (vw), 1434 (vw), 912 (vw), 847 (vw), 751 (w), 721 (vw), 696 (vw), 503 (vw) cm^{-1}; MS (EI, 70 eV), m/z (%): 602.4 (4) $[M]^+$, 601.4 (6) $[M-H]^+$, 506.3 (37) $[C_{34}H_{36}P_2]^+$, 505.3

(100) $[C_{34}H_{35}P_2]^+$, 392.1 (27) $[C_{28}H_{25}P]^+$, 288.1 (59) $[C_{20}H_{17}P]^+$, 209.1 (21) $[C_{16}H_{17}]^+$; HR-EIMS calcd for $C_{40}H_{49}BP_2$: 602.3402, found 602.3401 $[M]^+$.

General procedure for synthesis of bisphosphine selenides

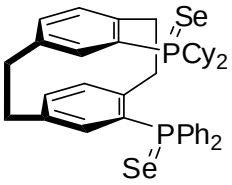
To a solution of the respective bisphosphine (0.03 mmol, 1.0 equiv.) in degassed $CHCl_3$ (2 mL) was added selenium powder (47 mg, 0.60 mmol, 20.0 equiv.). The reaction mixture was heated to reflux for 5 h. After cooling to room temperature the mixture was filtrated over Celite and the solvent was removed under reduced pressure to give the respective bisphosphine selenide as a white solid.

4,13-bis-(diphenylphosphino)-[2.2]paracyclophane-bisselenide



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4H, H_{Ar}), 7.41–7.28 (m, 12H, H_{Ar}), 7.25–7.21 (m, 4H, H_{Ar}), 6.87–6.85 (m, 2H, H_{PC}), 6.82 (d, *J* = 1.6 Hz, 1H, H_{PC}), 6.78–6.75 (m, 3H, H_{PC}), 3.63 (dd, *J* = 13.1 Hz, 4.7 Hz, 2H, CH_2), 3.06 (dd, *J* = 12.9 Hz, 4.8 Hz, 2H, CH_2), 2.88–2.83 (m, 2H, CH_2), 2.54 (dd, *J* = 13.2 Hz, 4.6 Hz, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2 (d, *J* = 7.2 Hz, 2 x C), 138.7 (d, *J* = 13.4 Hz, 2 x C), 135.9 (d, *J* = 15.4 Hz, 2 x CH), 135.8 (2 x CH), 135.5 (d, *J* = 74.1 Hz, 2 x C), 135.4 (d, *J* = 10.9 Hz, 2 x CH), 133.5 (d, *J* = 10.5 Hz, 4 x CH), 132.5 (d, *J* = 10.5 Hz, 4 x CH), 132.1 (d, *J* = 75.0 Hz, 2 x C), 131.0 (d, *J* = 2.9 Hz, 2 x CH), 130.4 (d, *J* = 2.9 Hz, 2 x CH), 128.5 (d, *J* = 80.9 Hz, 2 x C), 127.8 (d, *J* = 12.3 Hz, 4 x CH), 127.6 (d, *J* = 12.4 Hz, 4 x CH), 36.5 (d, *J* = 2.6 Hz, 2 x CH_2), 34.6 (2 x CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = 30.1 (s), 30.1 (d, *J* = 745.4 Hz) ppm.

4-diphenylphosphino-13-dicyclohexylphosphino-[2.2]paracyclophane-bisselenide

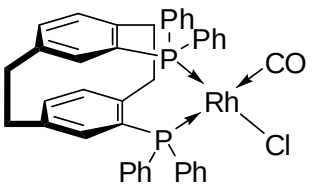


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.83 (m, 2H, H_{Ar}), 7.43–7.33 (m, 3H, H_{Ar}), 7.25–7.20 (m, 2H, H_{Ar}), 7.16–7.11 (m, 2H, H_{Ar}), 6.98–6.93 (m, 2H, H_{Ar}, H_{PC}), 6.85–6.83 (m, 1H, H_{PC}), 6.81–6.74 (m, 3H, H_{PC}), 6.68 (d, *J* = 12.1 Hz, 1H, H_{PC}), 4.57–4.52 (m, 1H, CH_2), 3.23–3.14 (m, 2H, CH_2), 3.11–3.00 (m, 2H, CH_2), 2.94–2.87 (m, 1H, CH_2), 2.74–2.67 (m, 1H, CH_2), 2.53–2.43 (m, 1H, CH_2), 2.43–2.34 (m, 1H, Cy), 2.26–2.21 (m, 1H, Cy), 2.10–2.07 (m, 2H, Cy), 1.93–1.25 (m, 14H, Cy), 1.19–0.96 (m, 3H, Cy), 0.87–0.78 (m, 1H, Cy) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0 (d, *J* = 6.3 Hz, C), 144.3 (d, *J* = 6.1 Hz, C), 138.4 (d, *J* = 14.0 Hz, C), 137.9 (d, *J* = 10.8 Hz, C), 137.5 (d, *J* = 77.9 Hz, C), 136.8 (d, *J* = 4.0 Hz, CH), 136.2 (d, *J* = 11.0 Hz, CH), 135.4 (d, *J* = 11.5 Hz, CH), 135.0 (d, *J* = 11.9 Hz, CH), 134.4 (d, *J* = 3.5 Hz, CH), 134.3 (d, *J* = 11.0 Hz, 2 x CH), 132.8 (d, *J* = 6.4 Hz, CH), 131.6 (d, *J* = 10.4 Hz, 2 x CH), 131.2 (d, *J* = 2.9 Hz, CH), 131.2 (d, *J* = 75.8 Hz, C), 130.2 (d, *J* = 2.9 Hz, CH), 129.2 (d, *J* = 80.6 Hz, C), 127.8 (d, *J* = 2.5 Hz, 2 x CH), 127.7 (d, *J* = 2.8 Hz, 2 x CH), 124.3 (d, *J* = 61.9 Hz, C), 41.3 (d, *J* = 42.6 Hz, CH), 37.5 (CH_2), 36.6 (d, *J* = 2.2 Hz, CH_2), 35.0 (CH_2), 34.7 (CH_2), 34.0 (d, *J* = 41.9 Hz, CH), 29.3 (CH_2), 26.7–25.8 (m, 9 x CH_2) ppm; ^{31}P NMR (101 MHz, $CDCl_3$): δ = 46.2 (s), 46.2 (d, *J* = 706.4 Hz, PCy_2Se), 32.0 (s), 32.0 (d, *J* = 744.2 Hz, PPh_2Se) ppm.

General procedure for synthesis of bisphosphine rhodium carbonyl complexes

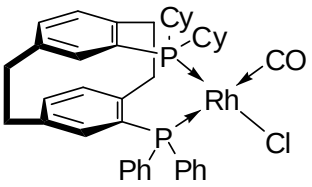
To a solution of $[Rh(CO)_2Cl]_2$ (11.66 mg, 0.03 mmol, 0.5 equiv.) in degassed CH_2Cl_2 (2 mL) was added the respective bisphosphine (0.06 mmol, 1.0 equiv.). The resulting orange solution was stirred for 1 h. Then the volatiles were removed under reduced pressure and an orange solid was obtained.

[(GemPhos)Rh(CO)Cl]



^{31}P NMR (101 MHz, $CDCl_3$): δ = 47.5 (dd, $_{P\text{-}Rh}J$ = 166.1 Hz, $_{P\text{-}P}J$ = 36.5 Hz), 30.9 (dd, $_{P\text{-}Rh}J$ = 123.7 Hz, $_{P\text{-}P}J$ = 36.5 Hz) ppm; FTIR (KBr): $\tilde{\nu}_{CO}$ = 2003.9 cm^{-1}.

[(CyGemPhos)Rh(CO)Cl]



Two diastereoisomers: Major: ^{31}P NMR (101 MHz, $CDCl_3$): δ = 47.2 (dd, $_{P\text{-}Rh}J$ = 176.1 Hz, $_{P\text{-}P}J$ = 32.4 Hz), 23.2 (dd, $_{P\text{-}Rh}J$ = 118.8 Hz, $_{P\text{-}P}J$ = 32.4 Hz) ppm. Minor: ^{31}P NMR (101 MHz, $CDCl_3$): δ = 46.4 (dd, $_{P\text{-}Rh}J$ = 155.6 Hz, $_{P\text{-}P}J$ = 32.7 Hz), 24.3 (dd, $_{P\text{-}Rh}J$ = 124.3 Hz, $_{P\text{-}P}J$ = 32.7 Hz) ppm; FTIR (KBr): $\tilde{\nu}_{CO}$ = 1987.9 cm^{-1}.

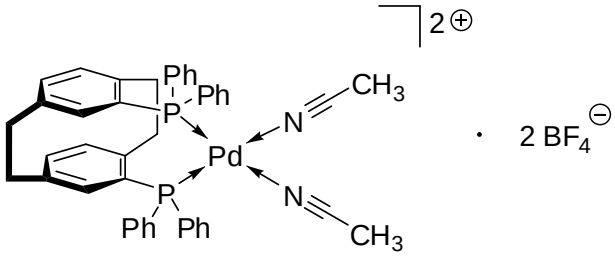
Si-Table 1: Electronic properties of phosphine ligands 3 and 9

entry	[PPRh(CO)Cl][a][b] ^{31}P /ppm ($^1J_{Rh-P}$, $^2J_{P-P}$)	IR /cm^{-1}[c]	Selenide[a] ^{31}P /ppm ($^1J_{P-Se}$)
1	major diastereoisomer: 47.2 (176.1 Hz, 32.4 Hz), 23.2 (118.8 Hz, 32.4 Hz); minor diastereoisomer: 46.4 (155.6 Hz, 32.7 Hz), 24.3 (124.3 Hz, 32.7 Hz)	1987.9	46.2 (706.4 Hz), 32.0 (744.2 Hz)
6	47.5 (166.1 Hz, 36.5 Hz), 30.9 (123.7 Hz, 36.5 Hz)	2003.9	30.1 (745.4 Hz)

General procedure for synthesis of palladium(II)-complexes

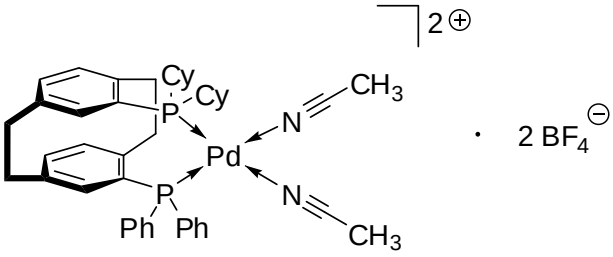
To a stirred solution of $Pd(NCPh)_2Cl_2$ (49.9 mg, 0.13 mmol, 1.0 equiv.) in degassed CH_3CN (3 mL) was added the respective bisphosphine (0.13 mmol, 1.0 equiv.) at room temperature. This solution was stirred for 30 minutes. Then $AgBF_4$ (56.5 mg, 0.29 mmol, 2.2 equiv.) was added and the reaction mixture was stirred for 1 h. The precipitate was separated by filtration. The volatiles were removed from the filtrate under reduced pressure and the residue was washed with dry diethyl ether (2 x 7 mL) to give the respective palladium species as a yellow solid (0.126 mmol, 97%). Crystals suitable for X-ray analysis were obtained by overlayering a saturated solution of the respective complex in CH_3CN with diethyl ether.

$[(GemPhos)(CH_3CN)_2Pd][BF_4]_2$



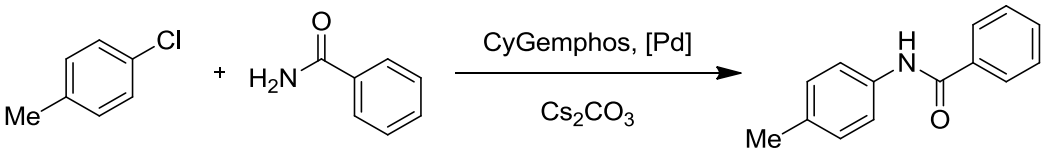
^{1}H NMR (400 MHz, CD_3CN): δ = 8.32–7.89 (m, 8H, H_{Ar}), 7.85–7.54 (m, 12H, H_{Ar}), 7.14–6.96 (m, 2H, H_{PC}), 6.66–6.47 (m, 2H, H_{PC}), 6.38–6.15 (m, 2H, H_{PC}), 3.10–2.79 (m, 4H, CH_2), 2.32–2.17 (m, 4H, CH_2), 2.06–1.82 (m, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, CD_3CN): δ = 146.8 (2 x C), 142.5 (2 x C), 139.1 (2 x CH), 138.6 (2 x CH), 138.0 (2 x CH), 137.6 (4 x CH), 135.5 (4 x CH), 134.8 (2 x CH), 133.9 (2 x CH), 130.6 (8 x CH), 34.8 (2 x CH_2), 33.7 (2 x CH_2), 1.7 (2 x CH_3) ppm; ^{31}P NMR (101 MHz, CD_3CN): δ = 42.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 2930 (vw), 2301 (vw), 1575 (vw), 1438 (vw), 1284 (vw), 1047 (w), 996 (w), 918 (vw), 753 (vw), 695 (vw), 536 (vw), 518 (vw), 486 (vw) cm^{-1}; MS (FAB, 70 eV), m/z (%): 682.0 (64) $[M–2 \times CH_3CN]^+$.

[(CyGemPhos)(CH$_3$CN)$_2$Pd][BF$_4$]$_2$



^{1}H NMR (400 MHz, CD_3CN): δ = 8.16–8.10 (m, 2H, H_{Ar}), 8.03–7.98 (m, 2H, H_{Ar}), 7.72–7.48 (m, 6H, H_{Ar}), 7.05 (d, *J* = 7.7 Hz, 1H, H_{PC}), 7.01 (d, *J* = 7.8 Hz, 1H, H_{PC}), 6.74 (dd, *J* = 7.8 Hz, 5.0 Hz, 1H, H_{PC}), 6.63 (dd, *J* = 7.7 Hz, 5.5 Hz, 1H, H_{PC}), 6.39 (d, *J* = 11.2 Hz, 1H, H_{PC}), 6.09 (d, *J* = 15.6 Hz, 1H, H_{PC}), 3.63–3.55 (m, 1H, CH_2), 3.24–3.18 (m, 2H, CH_2), 3.12–3.08 (m, 1H, CH_2), 2.96–2.88 (m, 1H, CH_2), 2.69–2.34 (m, 6H, CH_2, Cy), 2.13–2.01 (m, 2H, Cy), 1.97–1.92 (m, 9H, Cy, CH_3), 1.91–1.78 (m, 2H, Cy), 1.65–1.32 (m, 10H, Cy), 1.13–1.00 (m, 1H, Cy), 0.49–0.39 (m, 1H, Cy) ppm; ^{13}C NMR (100 MHz, CD_3CN): δ = 147.7 (d, *J* = 8.3 Hz, C), 144.6 (d, *J* = 7.8 Hz, C), 143.0 (d, *J* = 9.2 Hz, C), 141.3 (d, *J* = 11.9 Hz, C), 139.0–138.8 (m, 2 x CH), 138.2 (CH), 137.2–136.9 (m, 4 x CH), 136.6 (d, *J* = 11.3 Hz, 2 x CH), 135.1 (CH), 134.2 (CH), 133.7 (CH), 130.2 (d, *J* = 11.5 Hz, 2 x CH), 130.0 (d, *J* = 58.7 Hz, C), 129.4 (d, *J* = 11.7 Hz, 2 x CH), 127.6 (d, *J* = 59.2 Hz, C), 121.7 (dd, *J* = 57.1 Hz, 3.1 Hz, C), 112.5 (dd, *J* = 51.2 Hz, 3.6 Hz, C), 39.7 (d, *J* = 28.5 Hz, CH), 37.6 (CH_2), 36.3 (d, *J* = 28.2 Hz, CH), 34.1–33.8 (m, 4 x CH_2), 31.4 (CH_2), 30.5 (d, *J* = 6.2 Hz, CH_2), 29.4 (CH_2), 28.0 (d, *J* = 14.1 Hz, CH_2), 27.4 (d, *J* = 12.0 Hz, CH_2), 26.9–26.7 (m, 2 x CH_2), 26.1 (d, *J* = 15.7 Hz, 2 x CH_2) ppm; ^{31}P NMR (202 MHz, CD_3CN): δ = 53.65, 38.74 ppm. FTIR (KBr): $\tilde{\nu}$ = 2972 (vw), 2854 (vw), 2309 (vw), 1438 (vw), 1185 (vw), 1167 (vw), 1051 (m), 997 (w), 757 (vw), 701 (w), 601 (vw), 553 (1013 (w), 520 (w), 502 (w), 485 (vw), 461 (vw), 412 (vw) cm^{-1}.

Optimization for Buchwald-Hartwig coupling of chlorotoluene with benzamide



SI-Table 2: Optimization of reaction conditions

entry	[Pd] (mol%)	ligand (mol%)	solvent	temp. / °C	time / h	yield / %
			conventional heating			
1	$[Pd_2(dba)_3]$ (0.5)	2.0	1,4-dioxane	110	18	22
2	$Pd(OAc)_2$ (1.0)	2.0	1,4-dioxane	110	18	83
3	$Pd(OAc)_2$ (1.0) H_2O activated	3.0	1,4-dioxane	110	18	93
4	$Pd(OAc)_2$ (1.0) H_2O activated	3.0	toluene	110	18	28
5	$Pd(OAc)_2$ (1.0) H_2O activated	3.0	*t*-BuOH	110	18	33
			microwave irradiation			
6	$Pd(OAc)_2$ (1.0) H_2O activated	3.0	1,4-dioxane	125 MW	5	20
7	$Pd(OAc)_2$ (1.0) H_2O activated	3.0	1,4-dioxane	150 MW	5	53
8	$Pd(OAc)_2$ (2.0) H_2O activated	6.0	1,4-dioxane	150 MW	5	99

General procedure for Buchwald-Hartwig coupling of arylchlorides with amides

An oven-dried reaction vessel, was charged with $Pd(OAc)_2$ (1–4 mol%) and CyGemphos (1) (3–12 mol%). The vessel was fitted with a crimp cap (rubber septum) evacuated and backfilled with argon (repeated 3 times). Then 1,4-dioxane (2 mL) and degassed H_2O (4–16 mol%) were added via syringe and the solution was heated to 110 °C for 1.5 min.

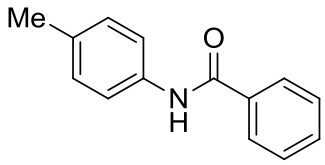
Reaction under conventional heating:

An oven-dried reaction vessel, which was equipped with a magnetic stir bar was charged with the aryl chloride (1.0 mmol), the amide (1.2–1.5mmol) and Cs_2CO_3 (1.4–2.0 mmol) (when the substrates were liquids at room temperature they were added after the evacuation process via syringe). The vessel was fitted with a crimp cap (rubber septum), evacuated and backfilled with argon (repeated 3 times), and then the preactivated catalyst solution was transferred from the first reaction vessel to the second via syringe. The reaction mixture was heated to the respective temperature for 24 h. Then it was cooled to room temperature, diluted with ethyl acetate, filtrated, concentrated in vacuo, and subjected to flash chromatography (SiO_2).

Reaction under microwave irradiation:

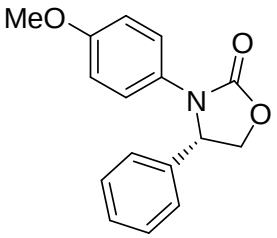
An oven-dried microwave reaction vessel, which was equipped with a magnetic stir bar was charged with the aryl chloride (1.0 mmol), the amide (1.2–1.5mmol) and Cs_2CO_3 (1.4–2.0 mmol) (when the substrates were liquids at room temperature they were added after the evacuation process via syringe). The vessel was fitted with a crimp cap (rubber septum), evacuated and backfilled with argon (repeated 3 times), and then the preactivated catalyst solution was transferred from the first reaction vessel to the second via syringe. The reaction mixture was heated to the respective temperature under microwave irradiation for 5 h. Then it was cooled to room temperature, diluted with ethyl acetate, filtrated, concentrated in vacuo, and subjected to flash chromatography (SiO_2).

_N_-(_p_-tolyl)-benzamide (9aa)[1]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol%), CyGemphos (1) (35.3 mg, 0.06 mmol, 6 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 4-chlorotoluene (7a) (118 µL, 126.6 mg, 1.0 mmol, 1.0 equiv.), benzamide (8a) (145.4 mg, 1.2 mmol, 1.2 equiv.) and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 110°C, 18 h, 99% yield. Microwave heating: 150 °C, 5 h, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (br. s, 1H, NH), 7.85 (d, J = 7.3 Hz, 2H, H_{Ar}), 7.53–7.51 (m, 3H, H_{Ar}), 7.47–7.43 (m, 2H, H_{Ar}), 7.16 (d, J = 8.2 Hz, 2H, H_{Ar}), 2.34 (s, 3H, Me) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7 (C), 135.4 (C), 135.0 (C), 134.2 (C), 131.6 (CH), 129.5 (2 x CH), 128.7 (2 x CH), 127.0 (2 x CH), 120.3 (2 x CH), 20.9 (CH_3) ppm.

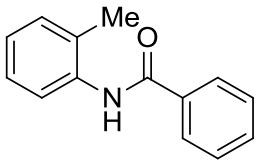
(_R_)-3-(4-methoxy-phenyl)-4-phenyl-oxazolidin-2-one (9bb)[2]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (2.8 µL, 0.16 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 4-chloroanisole (7b) (122 µL, 142.6 mg, 1.0 mmol, 1.0 equiv.), (_R_)-4-phenyl-oxazolidin-2-one (8b) (195.8 mg, 1.2 mmol, 1.2 equiv.) and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.)

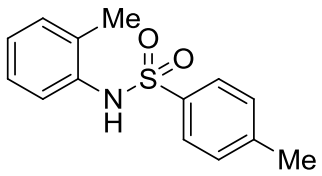
under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 2/1) to give the title compound as a yellow oil. Conventional heating: 125 °C, 24 h, 53% yield. Microwave heating: 125 °C, 5 h, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 5H, H_{Ar}), 7.24 (d, J = 9.1 Hz, 2H, H_{Ar}), 6.78 (d, J = 9.1 Hz, 2H, H_{Ar}), 5.32 (dd, J = 8.8 Hz, 6.4 Hz, 1H, CH), 4.77 (t, J = 8.8 Hz, 1H, CH_2), 4.21 (dd, J = 8.8 Hz, 6.4 Hz, 1H, CH_2), 3.72 (s, 3H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (C), 156.3 (C), 138.2 (C), 129.9 (C), 129.3 (2 x CH), 128.8 (CH), 126.5 (2 x CH), 123.3 (2 x CH), 114.2 (2 x CH), 69.7 (CH_2), 61.4 (CH), 55.3 (CH_3) ppm.

_N_-(_o_-tolyl)-benzamide (9ca)[3]



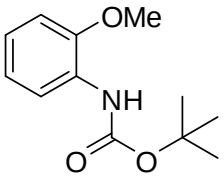
Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol%), CyGemphos (1) (35.3 mg, 0.06 mmol, 6 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chlorotoluene (7c) (117 µL, 117.0 mg, 1.0 mmol, 1.0 equiv.), benzamide (8a) (145.4 mg, 1.2 mmol, 1.2 equiv.), and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 125 °C, 24 h, 99% yield. Microwave heating: 125 °C, 5 h, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.87 (m, 3H, H_{Ar}), 7.76 (br. s, 1H, NH), 7.58–7.54 (m, 1H, H_{Ar}), 7.51–7.47 (m, 2H, H_{Ar}), 7.27–7.22 (m, 2H, H_{Ar}), 7.14–7.10 (m, 1H, H_{Ar}), 2.33 (s, 3H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6 (C), 135.7 (C), 135.0 (C), 131.8 (CH), 130.5 (CH), 129.4 (C), 128.8 (2 x CH), 127.0 (2 x CH), 126.8 (CH), 125.3 (CH), 123.2 (CH), 17.8 (CH_3) ppm.

_N_-(_o_-tolyl)-tosylamide (9cc)[4]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chlorotoluene (7c) (117 µL, 117.0 mg, 1.0 mmol, 1.0 equiv.), *p*-toluenesulfonamide (8c) (205.5 mg, 1.2 mmol, 1.2 equiv.), and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 150 °C, 24 h, 78% yield. Microwave heating: 150 °C, 5 h, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.32 (d, J = 7.8 Hz, 1H, H_{Ar}), 7.22 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.16–7.12 (m, 1H, H_{Ar}), 7.08–7.06 (m, 2H, H_{Ar}), 6.54 (br. s, 1H, NH), 2.39 (s, 3H, Me), 2.01 (s, 3H, Me) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8 (C), 136.7 (C), 134.5 (C), 131.3 (C), 130.7 (CH), 129.6 (2 x CH), 127.1 (2 x CH), 126.9 (CH), 126.1 (CH), 124.3 (CH), 21.5 (CH_3), 17.5 (CH_3) ppm.

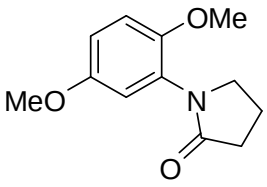
_N_-(_o_-methoxy-phenyl)-_O-tert_-butyl-carbamate (9ef)[5]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chloroanisole (7e) (127 µL, 142.6 mg, 1.0 mmol, 1.0 equiv.), *tert*-butyl carbamate (8f) (140.6 mg, 1.2 mmol, 1.2 equiv.), and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.) under the

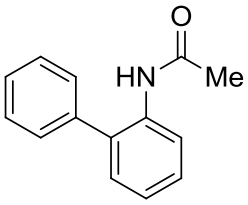
respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 20/1) to give the title compound as a colorless oil. Conventional heating: 125 °C, 24 h, 99% yield. Microwave heating: 125 °C, 5 h, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 5.2 Hz, 1H, H_{Ar}), 7.10 (br. s., 1H, NH), 6.99–6.83 (m, 3H, H_{Ar}), 3.86 (s, 3H, Me), 1.53 (s, 9H, *t*-Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7 (C), 147.4 (C), 128.1 (C), 122.2 (CH), 121.0 (CH), 118.0 (CH), 109.8 (CH), 80.2 (C), 55.5 (CH_3), 28.3 (3 x CH_3) ppm.

_N_-(2,5-dimethoxy-phenyl)-pyrrolidin-2-one (9fg)[6]



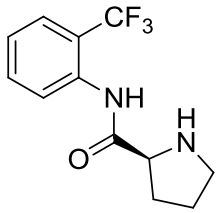
Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chloro-1,4-dimethoxybenzene (7f) (143 µL, 172.6 mg, 1.0 mmol, 1.0 equiv.), 2-pyrrolidinone (8g) (114 µL, 127.7 mg, 1.5 mmol, 1.5 equiv.), and Cs_2CO_3 (651.6 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 1/1) to give the title compound as a slight yellow oil. Conventional heating: 150 °C, 24 h, 99% yield. Microwave heating: 150 °C, 5 h, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (d, J = 8.9 Hz, 1H, H_{Ar}), 6.83–6.77 (m, 2H, H_{Ar}), 3.77 (s, 3H, Me), 3.75–3.72 (m, 2H, CH_2), 3.74 (s, 3H, Me), 2.53 (t, J = 8.1 Hz, 2H, CH_2), 2.19–2.12 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.0 (C), 153.5 (C), 148.9 (C), 127.8 (C), 114.2 (CH), 113.6 (CH), 113.1 (CH), 56.2 (CH_3), 55.7 (CH_3), 49.9 (CH_2), 31.1 (CH_2), 18.9 (CH_2) ppm.

_N_-biphenyl-2yl-acetamide (9gh)[7]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chlorobiphenyl (7g) (188.7 mg, 1.0 mmol, 1.0 equiv.), acetamide (8h) (88.6 mg, 1.5 mmol, 1.5 equiv.), and Cs_2CO_3 (651.6 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 1/1) to give the title compound as a slight yellow oil. Conventional heating: 150 °C, 24 h, 99% yield. Microwave heating: 150 °C, 5 h, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.2 Hz, 1H, H_{Ar}), 7.51–7.35 (m, 6H, H_{Ar}), 7.26–7.15 (m, 3H, H_{Ar}, NH), 2.02 (s, 3H, Me) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2 (C), 138.1 (C), 134.7 (C), 132.2 (CH), 130.0 (CH), 129.2 (2 x CH), 129.1 (2 x CH), 128.4 (CH), 127.9 (CH), 124.3 (CH), 121.6 (CH), 24.6 (CH_3) ppm.

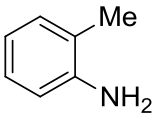
***(S)-N*-(2-trifluormethyl)-prolineamide (9de)**



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol%), CyGemphos (1) (35.3 mg, 0.06 mmol, 6 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chlorobenzotrifluoride (7d) (132 µL, 180.6 mg, 1.0 mmol, 1.0 equiv.), (*L*)-prolineamide (8e) (137.0 mg, 1.2 mmol, 1.2 equiv.) and Cs_2CO_3 (456.1 mg, 1.4 mmol, 1.4 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 2/1 to 1/1) to give the title

compound as a white solid. Conventional heating: 125 °C, 24 h, 94% yield. Microwave heating: 125 °C, 5 h, 92% yield; R_f (cyclohexane/ethyl acetate, 1:1 v/v) = 0.08; $[\alpha]^{20}_D$ = -241.33° (c = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.52 (br.s, 1H, NH), 8.41 (d, *J* = 8.3 Hz, 1H, H_{Ar}), 7.58 (d, *J* = 7.9 Hz, 1H, H_{Ar}), 7.55–7.51 (m, 1H, H_{Ar}), 7.18–7.14 (m, 1H, H_{Ar}), 3.90 (dd, *J* = 9.3 Hz, 4.7 Hz, 1H, CH), 3.12–2.98 (m, 2H, CH_2), 2.24–2.15 (m, 2H, CH_2, NH), 2.08–2.01 (m, 1H, CH_2), 1.78–1.72 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.0 (C), 135.7 (C), 132.8 (CH), 125.7 (q, *J* = 5.4 Hz, CH), 124.1 (q, *J* = 272.9 Hz, C), 123.5 (CH), 122.5 (CH), 119.2 (q, *J* = 29.9 Hz, C), 60.9 (CH), 47.1 (CH_2), 30.9 (CH_2), 26.1 (CH_2) ppm; FTIR (KBr): $\tilde{\nu}$ = 3241 (vw), 2934 (vw), 2871 (vw), 1671 (w), 1522 (m), 1457 (w), 1170 (w), 1112 (m), 763 (w), 652 (w) cm^{-1}; MS (EI, 70 eV), m/z (%): 259.1 (21) $[M]^+$, 258.1 (57) $[M]^+$, 187.1 (37) $[M–C_4H_9N]^+$, 168.0 (89) $[C_8H_4F_2NO]^+$, 141.0 (68) $[C_7H_5F_2N]^+$, 114.0 (28) $[C_5H_9N_2O]^+$, 70.1 (100) $[C_4H_8N]^+$ HR-EIMS calcd for $C_{12}H_{13}F_3N_2O$: 258.0980; found 258.0982 $[M]^+$.

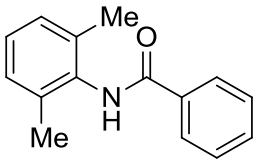
2-methyl-anilin (9cd)[7]



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol%), CyGemphos (1) (35.3 mg, 0.06 mmol, 6 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-chlorotoluene (7c) (117 µL, 117.0 mg, 1.0 mmol, 1.0 equiv.) and a 1 M solution of LiHMDS in THF (8d) (2 mL, 2 mmol, 2.0 equiv.) under the respective conditions. After cooling to room temperature the reaction mixture was diluted with ethyl acetate (10 mL) and aqueous HCl (2 M, 2 mL) was added under stirring. Then aqueous NaOH (2 M, 3 mL) was added and after phase separation the aqueous layer was extracted with ethyl acetate (2 x 5 mL). The combined organics were dried over $MgSO_4$, filtrated, and the solvent was removed under rotary evaporation. The product was dedected by GCMS.

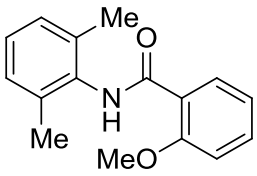
For pure isolation the volatile 2-methyl-anilin (9cf) was converted to the respective tosylamide (9ce): The residue was dissolved in CH_2Cl_2 (4 mL) and p-toluenesulfonyl chloride (477 mg, 2.5 mmol, 2.5 equiv.) and triethylamine (1 mL) were added. The reaction mixture was stirred over night at room temperature. Then SiO_2 was added, the solvent was removed under reduced pressure, and the residue was subjected to flash chromatography (cyclohexane/ethyl acetate 3/1) to give *N*-(*o*-tolyl)-tosylamide (9cc) as a white solid. Conventional heating: 125 °C, 24 h, 47% yield. Microwave heating: 125 °C, 5 h, 43% yield. The NMR-spectra were identical to **9cc** synthesized by direct coupling.

***N*-(2,6-dimethylphenyl)-benzamide (9ha)**



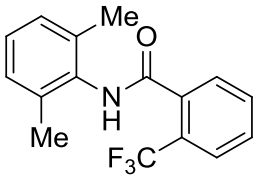
Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (4.5 mg, 0.04 mmol, 2 mol%), CyGemphos (1) (35.3 mg, 0.06 mmol, 6 mol%), and water (1.4 µL, 0.08 mmol, 8 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-Chloro-1,3-dimethylbenzene (7h) (133 µL, 140.6 mg, 1.0 mmol, 1.0 equiv.), Benzamide (8a) (181.7 mg, 1.5 mmol, 1.5 equiv.) and Cs_2CO_3 (650 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 150 °C, 24 h, 94% yield. Microwave heating: 150 °C, 5 h, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.87 (m, 2H, H_{Ar}), 7.79 (br.s, 1H, NH), 7.56–7.52 (m, 1H, H_{Ar}), 7.45–7.41 (m, 2H, H_{Ar}), 7.16–7.08 (m, 3H, H_{Ar}), 2.22 (s, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C), 135.6 (2 x C), 134.3 (C), 134.0 (C), 131.6 (CH), 128.6 (2 x CH), 128.1 (2 x CH), 127.2 (3 x CH), 18.3 (2 x CH_3) ppm.

_N_-(2,6-dimethylphenyl)-2-methoxybenzamide (9hj)



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (2.8 µL, 0.16 mmol, 16 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-Chloro-1,3-dimethylbenzene (7h) (133 µL, 140.6 mg, 1.0 mmol, 1.0 equiv.), 2-Methoxybenzamide (8j) (226.8 mg, 1.5 mmol, 1.5 equiv.) and Cs_2CO_3 (650 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 150 °C, 24 h, 87% yield. Microwave heating: 150 °C, 5 h, 89% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.17 (br.s, 1H, NH), 8.30 (dd, J = 7.8 Hz, 1.9 Hz, 1H, H_{Ar}), 7.55–7.49 (m, 1H, H_{Ar}), 7.17–7.12 (m, 4H, H_{Ar}), 7.07 (d, J = 8.3 Hz, 1H, H_{Ar}), 4.04 (s, 3H, CH_3), 2.31 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.4 (C), 157.4 (C), 135.3 (2 x C), 134.7 C), 133.0 (CH), 132.6 (CH), 128.0 (2 x CH), 126.9 (CH), 121.8 (C), 121.5 (CH), 56.0 (CH_3), 18.6 (CH_3) ppm.

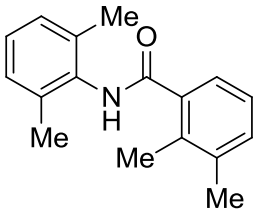
_N_-(2,6-dimethylphenyl)-2-trifluormethylbenzamide (9hi)



Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (2.8 µL, 0.16 mmol, 16 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-Chloro-1,3-dimethylbenzene (7h) (133 µL, 140.6 mg, 1.0 mmol, 1.0 equiv.), 2-trifluormethylbenzamide (8i) (283.7 mg, 1.5 mmol, 1.5 equiv.) and Cs_2CO_3 (650 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was

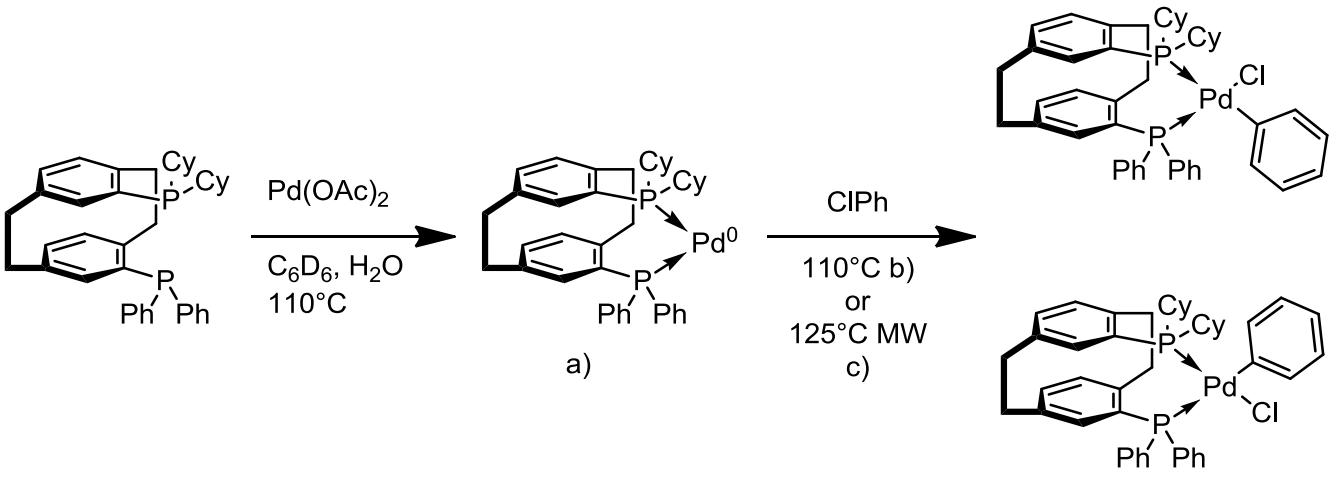
purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 150 °C, 24 h, 72% yield. Microwave heating: 150 °C, 5 h, 71% yield; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.79–7.56 (m, 4H, H_{Ar}), 7.19–7.09 (m, 4H, H_{Ar}, NH), 2.33 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1 (C), 135.9 (C), 135.7 (2 x C), 133.1 (C), 132.1 (CH), 130.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (2 x CH), 127.2–125.7 (m, 2 x C), 18.4 (CH_3) ppm.

***N*-(2,6-dimethylphenyl)-2,3-dimethylbenzamide (9hk)**



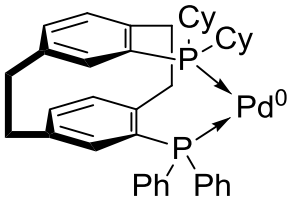
Following the general procedure a preactivated mixture of $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 4 mol%), CyGemphos (1) (70.6 mg, 0.12 mmol, 12 mol%), and water (2.8 µL, 0.16 mmol, 16 mol%) in 1,4-dioxane (2 mL) were allowed to react with 2-Chloro-1,3-dimethylbenzene (7h) (133 µL, 140.6 mg, 1.0 mmol, 1.0 equiv.), 2,3-dimethylbenzamide (8k) (223.8 mg, 1.5 mmol, 1.5 equiv.) and Cs_2CO_3 (650 mg, 2.0 mmol, 2.0 equiv.) under the respective conditions. The crude material was purified by flash chromatography (cyclohexane/ethyl acetate 3/1) to give the title compound as a white solid. Conventional heating: 150 °C, 24 h, 81% yield. Microwave heating: 150 °C, 5 h, 81% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.33 (m, 1H, H_{Ar}), 7.26–7.24 (m, 1H, H_{Ar}), 7.19 (br.s, 1H, NH), 7.18–7.09 (m, 4H, H_{Ar}), 7.18–7.14 (m, 1H, H_{Ar}), 2.38 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1 (C), 138.0 (C), 137.1 (C), 135.5 (CH), 134.5 (C), 133.7 (C), 131.3 (CH), 128.2 (2 x CH), 127.3 (CH), 125.4 (CH), 124.2 (CH), 20.2 (CH_3), 18.5 (CH_3), 16.2 (CH_3), ppm.

^{31}P-NMR investigation of the palladium complexes (A, B)



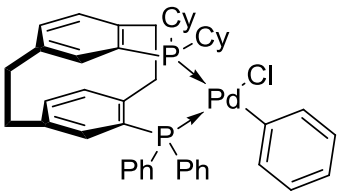
An oven-dried reaction vessel, was charged with $Pd(OAc)_2$ (2.25 mg, 0.01 mmol, 1.0 equiv.) and CyGemphos (4) (17.7 mg, 0.03 mmol, 3.0 equiv.). The vessel was fitted with a crimp cap (rubber septum) evacuated and backfilled with argon (repeated 3 times). Then the respective solvent (toluene d_8 or C_6D_6, 1 mL) and degassed H_2O (1 µL, 0.72 mg, 0.04 mmol, 4.0 equiv.) were added via syringe and the solution was heated to 110 °C for 1.5 min. After cooling to room temperature, the red solution of the complex **A** was investigated by ^{31}P-NMR. Then the catalyst solution was transferred to a respective reaction vessel (vial or microwave reaction vessel) via canula and chlorobenzene (102 µL, 112.6 mg, 1.0 mmol, 100 equiv.) was added. The reaction mixture was heated for 2–4 hours under the respective conditions (see main document). After cooling to room temperature the catalyst solution was investigated by ^{31}P-NMR.

[(CyGemphos)Pd(0)] (A)



^{31}P NMR (101 MHz, C_6D_6): δ = 33.4 (d, J = 12.4 Hz), 26.3 (d, J = 12.4 Hz) ppm.

[(CyGemphos)Pd(C_6H_5)Cl] (B)



Two diastereoisomers; major: ^{31}P NMR (101 MHz, C_6D_6): δ = 26.9 (d, J = 28.9 Hz), 16.0 (d, J = 28.9 Hz) ppm; minor: ^{31}P NMR (101 MHz, C_6D_6): δ = 18.9 (d, J = 28.4 Hz), 15.2 (d, J = 28.4 Hz) ppm.

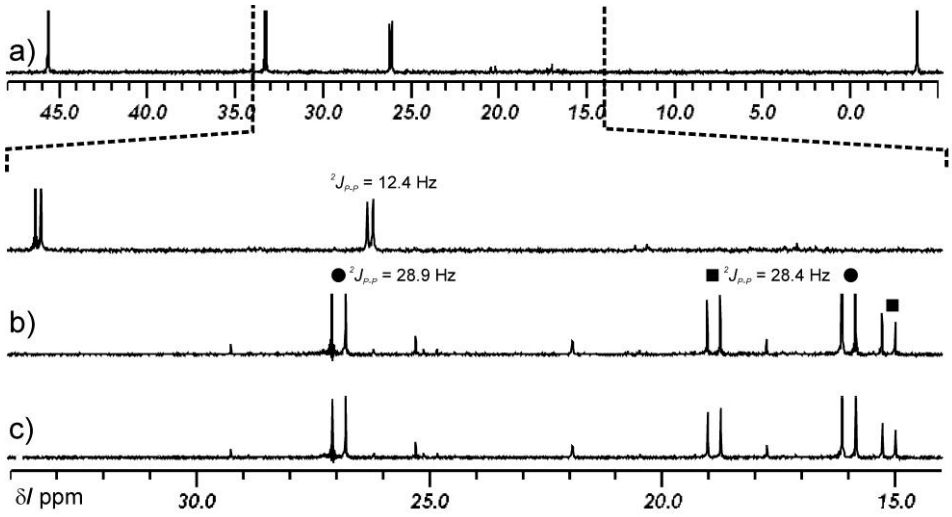
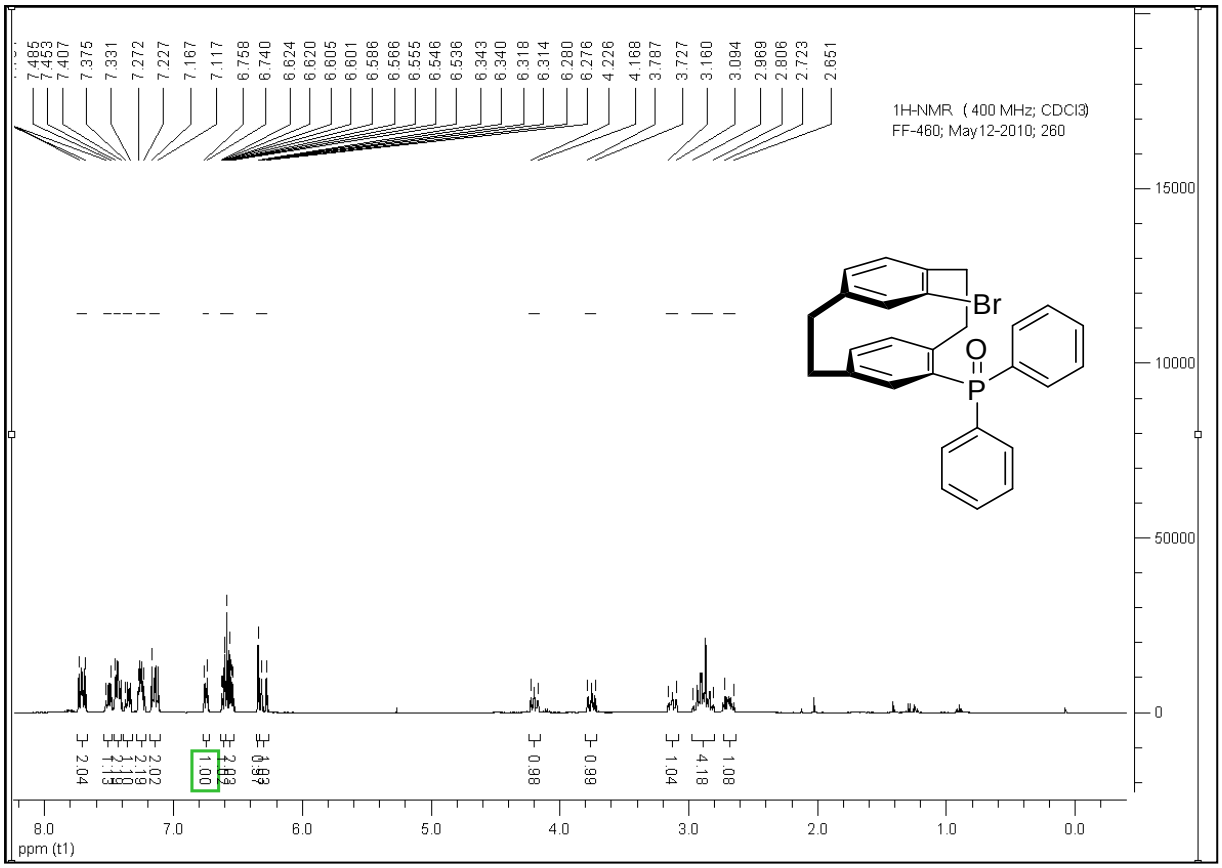
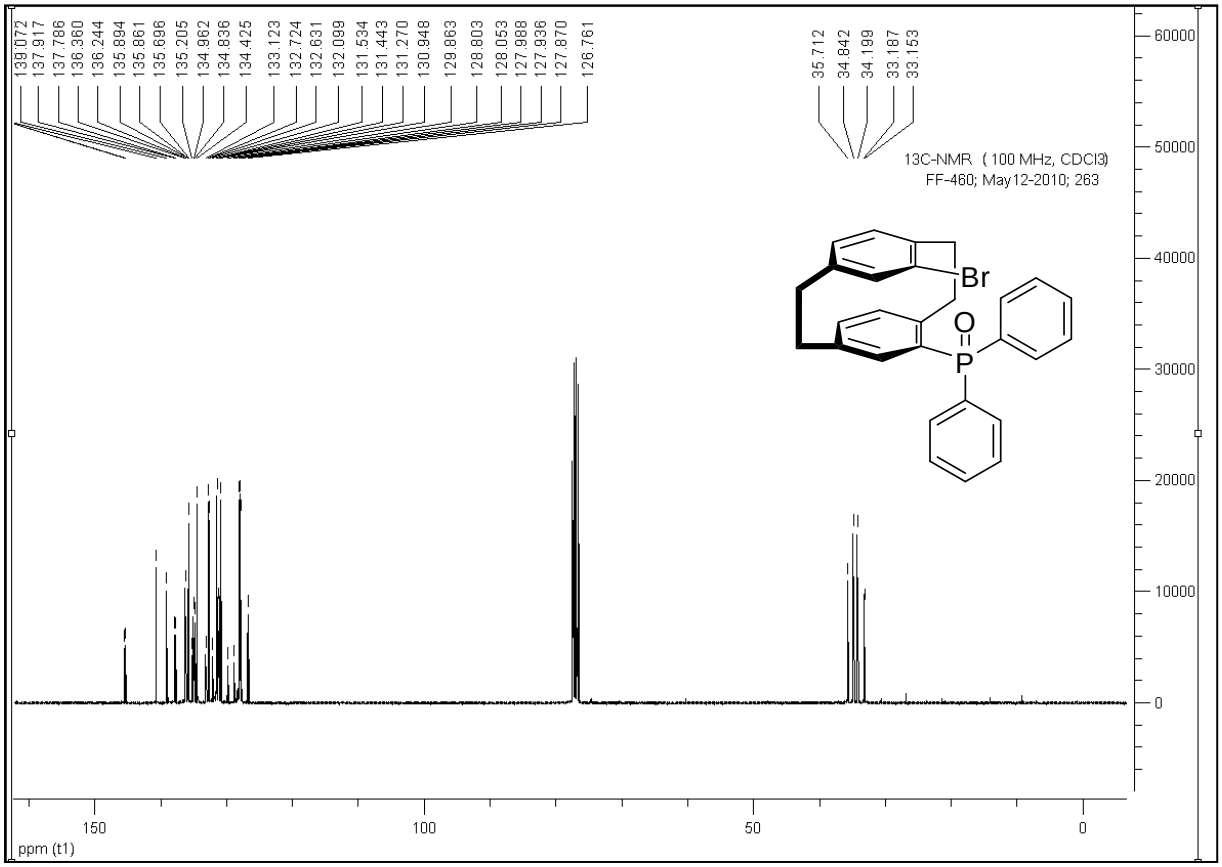
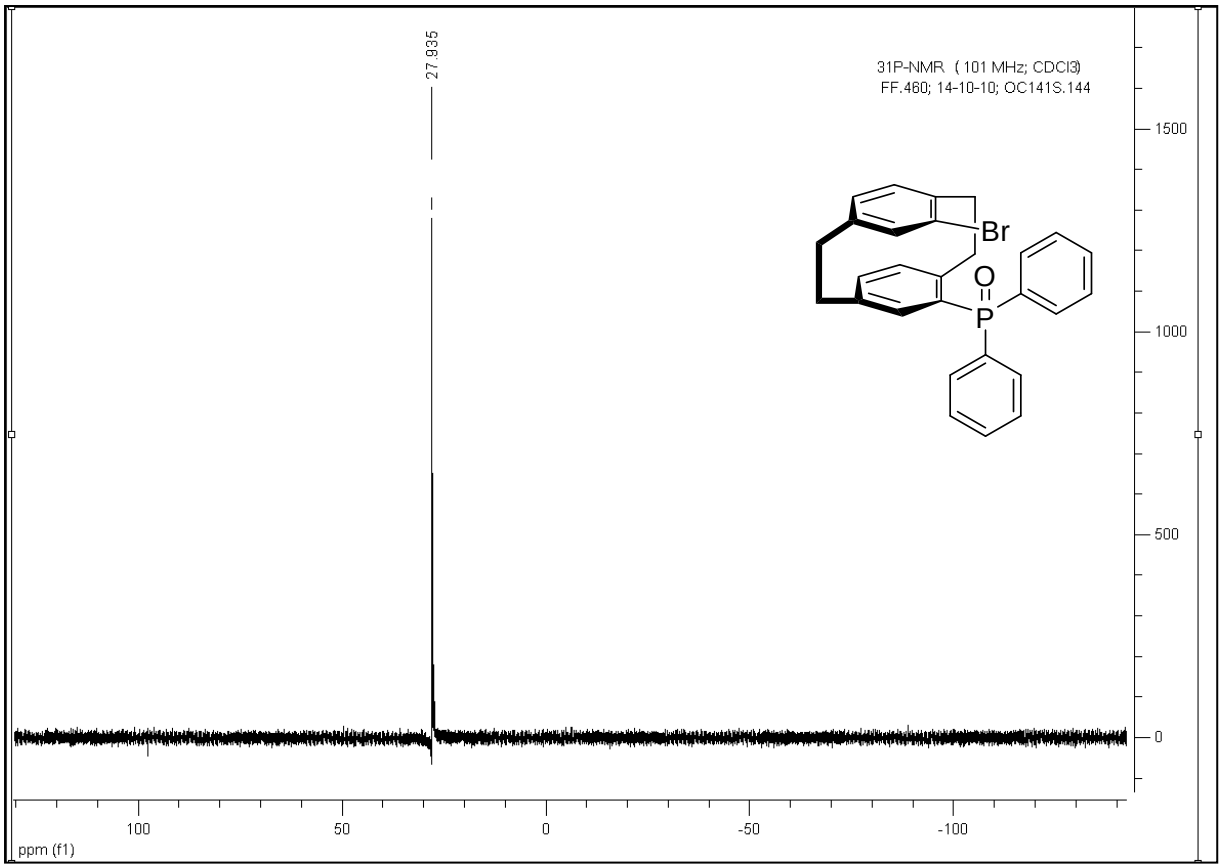
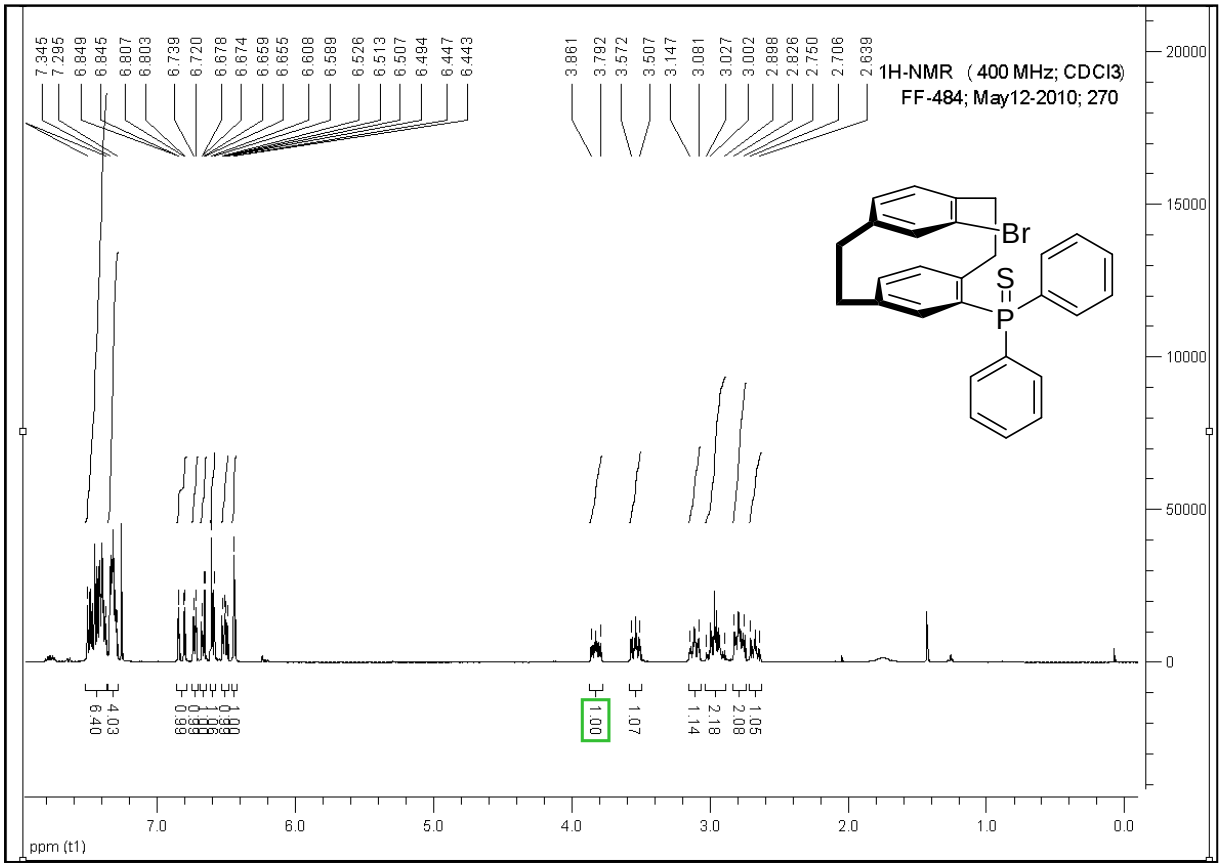


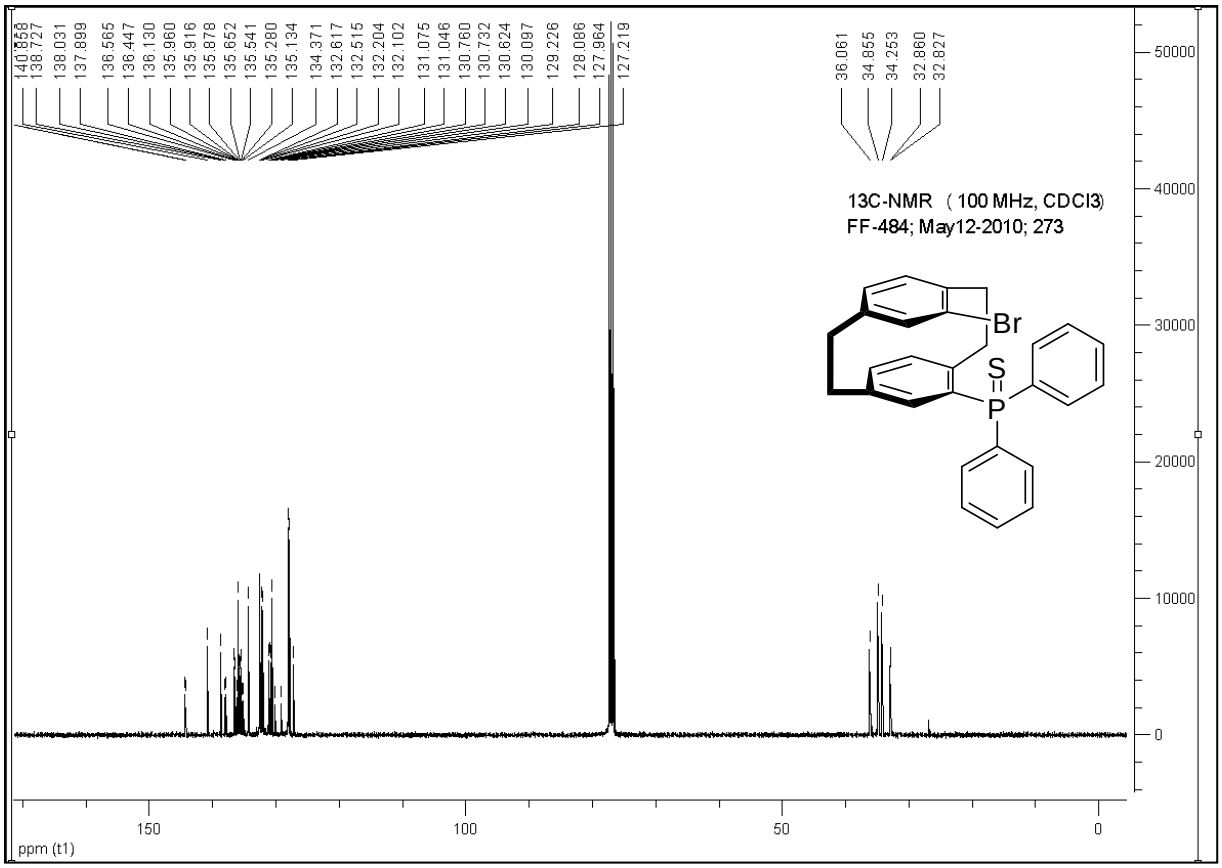
Figure ^{31}P{^{1}H} NMR spectra in d_6-benzene at room temperature; a) ^{31}P{^{1}H} NMR spectrum from the reaction of $Pd(OAc)_2$ with 3 equiv. **4** and 1 equiv. water (below: spectra region from 34 ppm to 14 ppm); b) ^{31}P{^{1}H} NMR spectrum after addition of chlorobenzene and heating to 125 °C for four hours; c) ^{31}P{^{1}H} NMR spectrum after heating to 125 °C in the microwave reactor for two hours (● or ■ correspond to the diastereomers *cis*-**B** and *trans*-**B** (not assigned); resonances of phosphine oxide and free phosphine are present but not depicted for clarity).


7.485
7.453
7.407
7.375
7.331
7.272
7.227
7.167
7.117
6.758
6.740
6.624
6.620
6.605
6.601
6.586
6.566
6.555
6.546
6.536
6.343
6.340
6.318
6.314
6.280
6.276
4.226
4.168
3.787
3.727
3.160
3.094
2.969
2.806
2.723
2.651
1H-NMR (400 MHz; CDCl3)
FF-460; May12-2010; 260
Br
O
P
15000
10000
50000
0
2.04
2.13
1.19
2.19
2.02
1.00
2.83
1.03
0.98
0.99
1.04
4.18
1.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


138.072
137.917
137.786
136.360
136.244
135.894
135.861
135.696
135.205
134.962
134.836
134.425
133.123
132.724
132.631
132.099
131.534
131.443
131.270
130.948
129.863
128.803
128.053
127.988
127.936
127.870
126.761
35.712
34.842
34.199
33.187
33.153
13C-NMR (100 MHz, CDCl3)
FF-460; May12-2010; 263
Br
O
P
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)


27.935
31P-NMR (101 MHz; CDCl3)
FF-460; 14-10-10; OC141S.144
Br
O
P
1500
1000
500
0
100
50
0
-50
-100
ppm (f1)


7.345
7.295
6.849
6.845
6.807
6.803
6.739
6.720
6.678
6.674
6.659
6.655
6.608
6.589
6.526
6.513
6.507
6.484
6.447
6.443
3.861
3.792
3.572
3.507
3.147
3.081
3.027
3.002
2.898
2.826
2.750
2.706
2.639
1H-NMR (400 MHz; CDCl3)
FF-484; May12-2010; 270
Br
S
P
20000
15000
10000
50000
0
6.40
4.03
1.00
1.07
1.14
2.18
2.08
1.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


140.558
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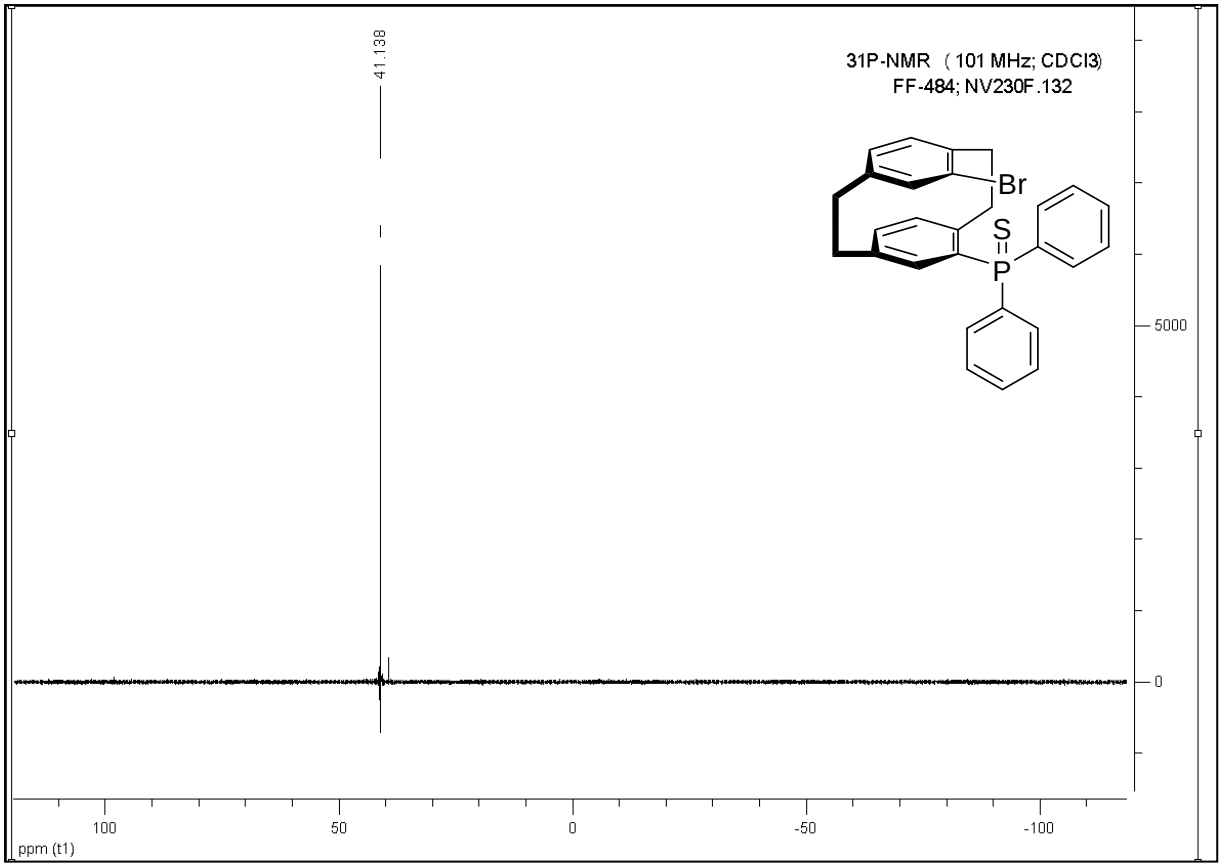
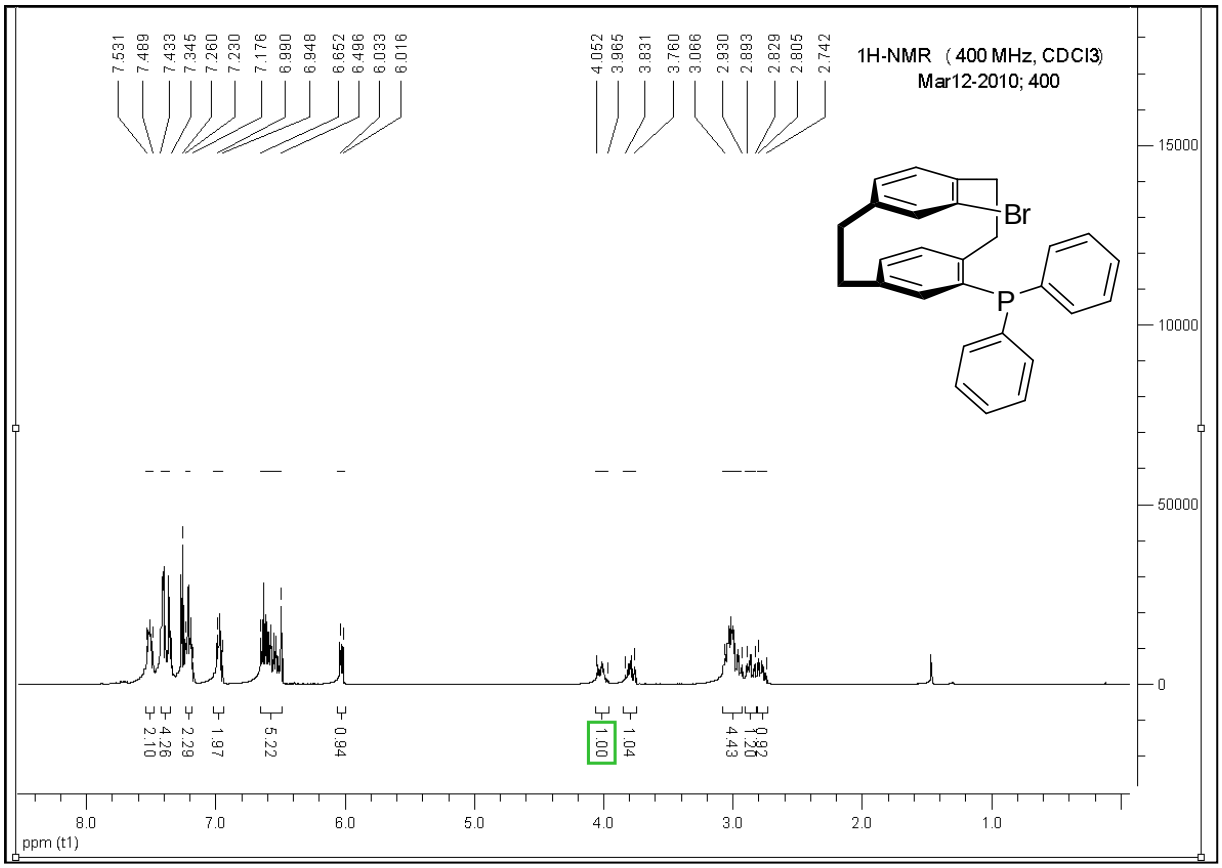
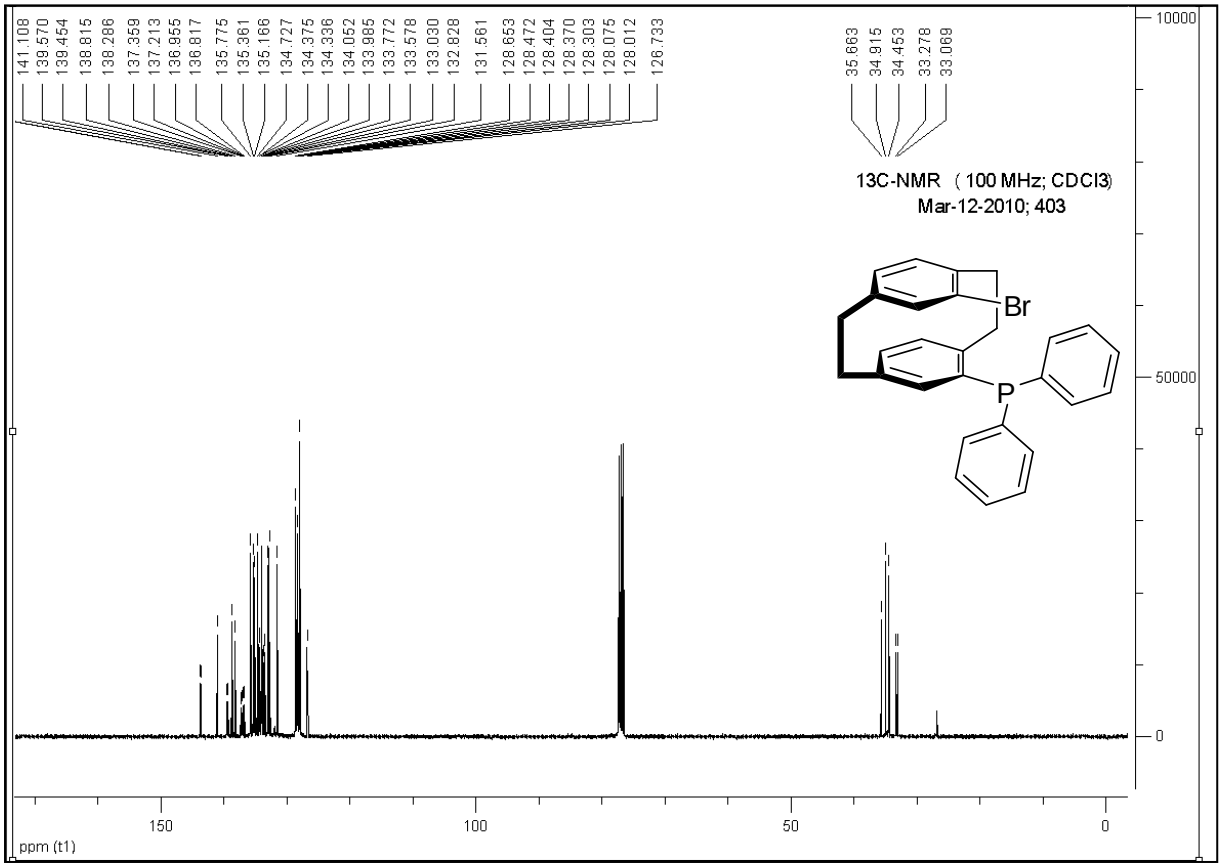
138.031
137.899
136.565
136.447
136.130
135.960
135.916
135.878
135.652
135.541
135.280
135.134
134.371
132.617
132.515
132.204
132.102
131.075
131.046
130.760
130.732
130.624
130.097
129.226
128.086
127.964
127.219
36.061
34.855
34.253
32.860
32.827
13C-NMR (100 MHz, CDCl3)
FF-484; May12-2010; 273
Br
S
P
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)


41.138
31P-NMR (101 MHz; CDCl3)
FF-484; NV230F.132
Br
S
P
5000
0
100
50
0
-50
-100
ppm (t1)


7.531
7.489
7.433
7.345
7.260
7.230
7.176
6.990
6.948
6.652
6.496
6.033
6.016
4.052
3.965
3.831
3.760
3.066
2.930
2.893
2.829
2.805
2.742
1H-NMR (400 MHz, CDCl3)
Mar12-2010; 400
Br
P
15000
10000
50000
0
2.10
4.26
2.29
1.97
5.22
0.84
1.00
1.04
4.43
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


141.108
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139.454
138.815
138.286
137.359
137.213
136.955
136.817
135.775
135.361
135.166
134.727
134.375
134.336
134.052
133.985
133.772
133.578
133.030
132.828
131.561
128.853
128.472
128.404
128.370
128.303
128.075
128.012
126.733
35.663
34.915
34.453
33.278
33.069
13C-NMR (100 MHz; CDCl3)
Mar-12-2010; 403
Br
P
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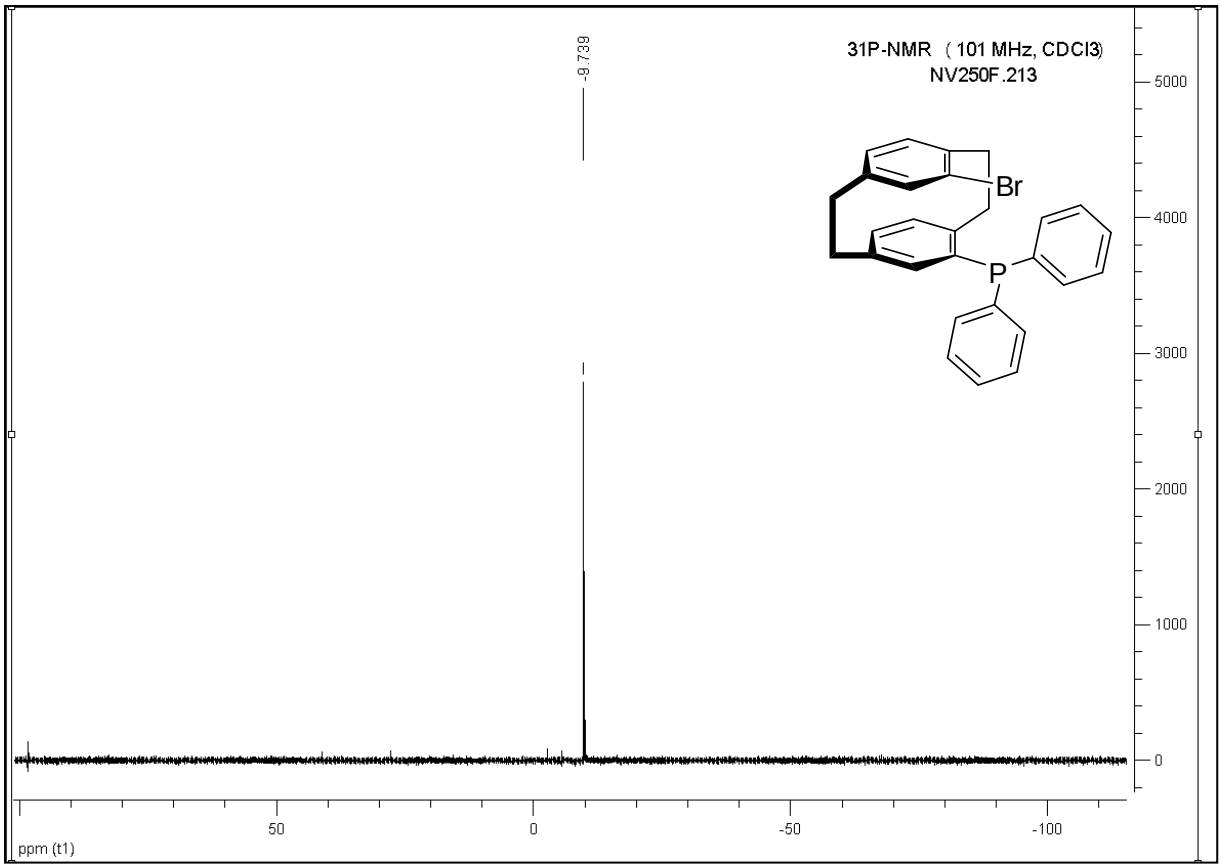
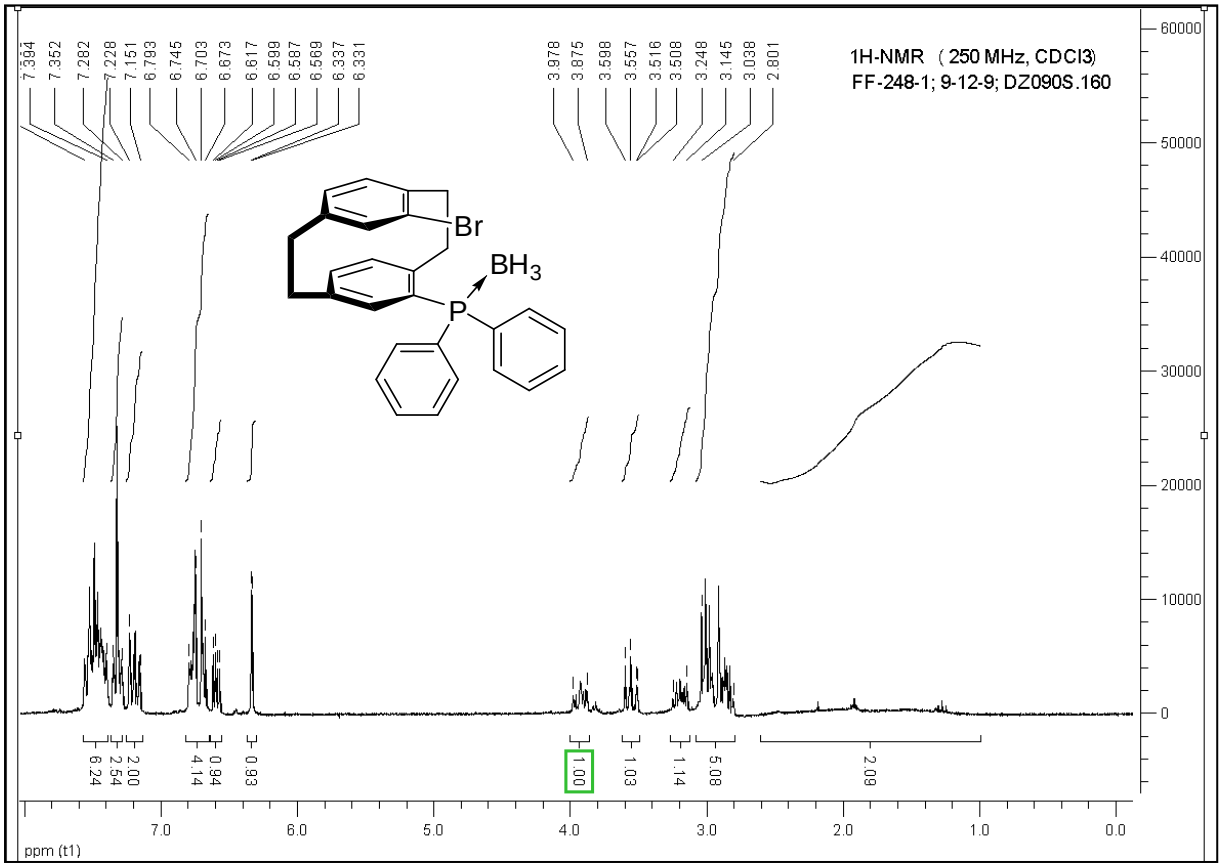
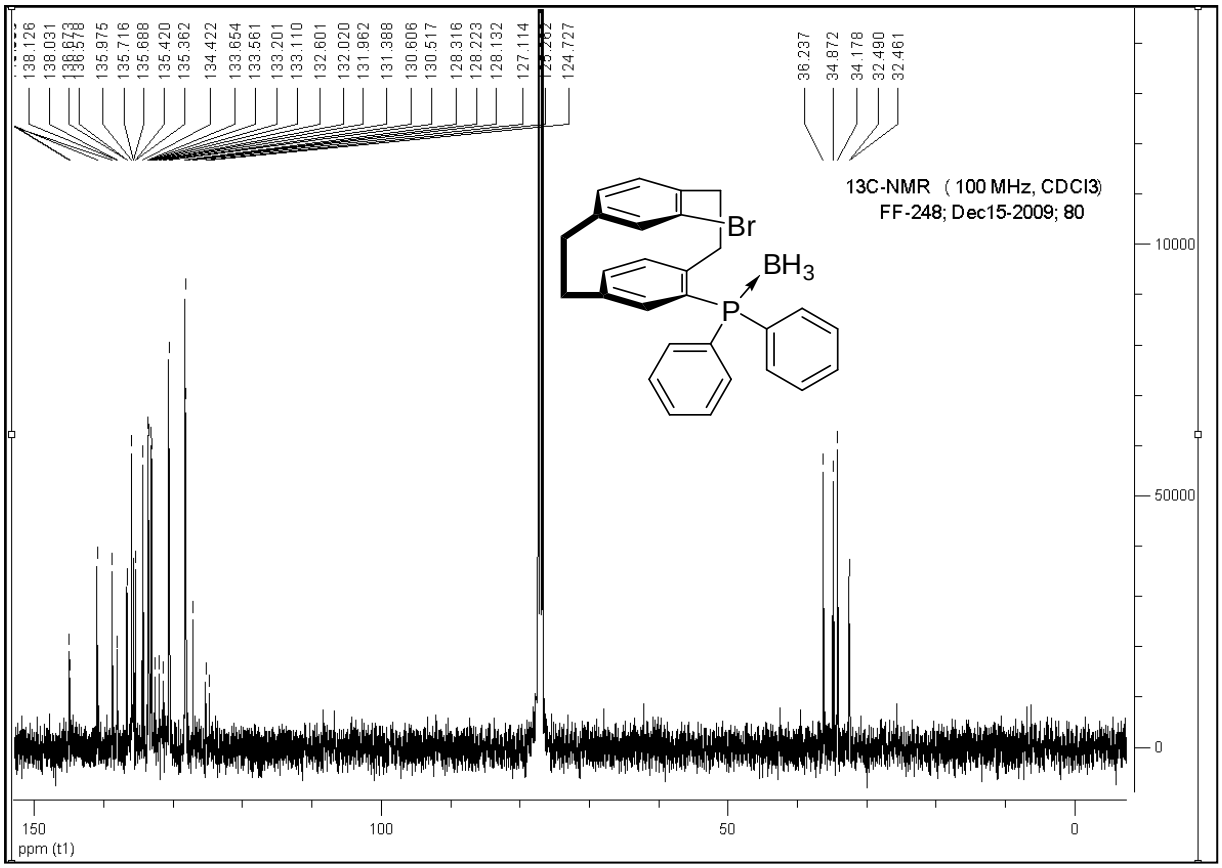
50000
0
150
100
50
0
ppm (t1)


31P-NMR (101 MHz, CDCl3)
NV250F.213
-8.739
Br
P
5000
4000
3000
2000
1000
0
50
0
-50
-100
ppm (t1)


1H-NMR (250 MHz, CDCl3)
FF-248-1; 9-12-9; DZ090S.160
7.394
7.352
7.282
7.228
7.151
6.793
6.745
6.703
6.673
6.617
6.599
6.587
6.569
6.337
6.331
3.978
3.875
3.598
3.557
3.516
3.508
3.248
3.145
3.038
2.801
Br
BH3
P
6.24
2.54
2.00
4.14
0.94
0.93
1.00
1.03
1.14
5.08
2.09
60000
50000
40000
30000
20000
10000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


138.126
138.031
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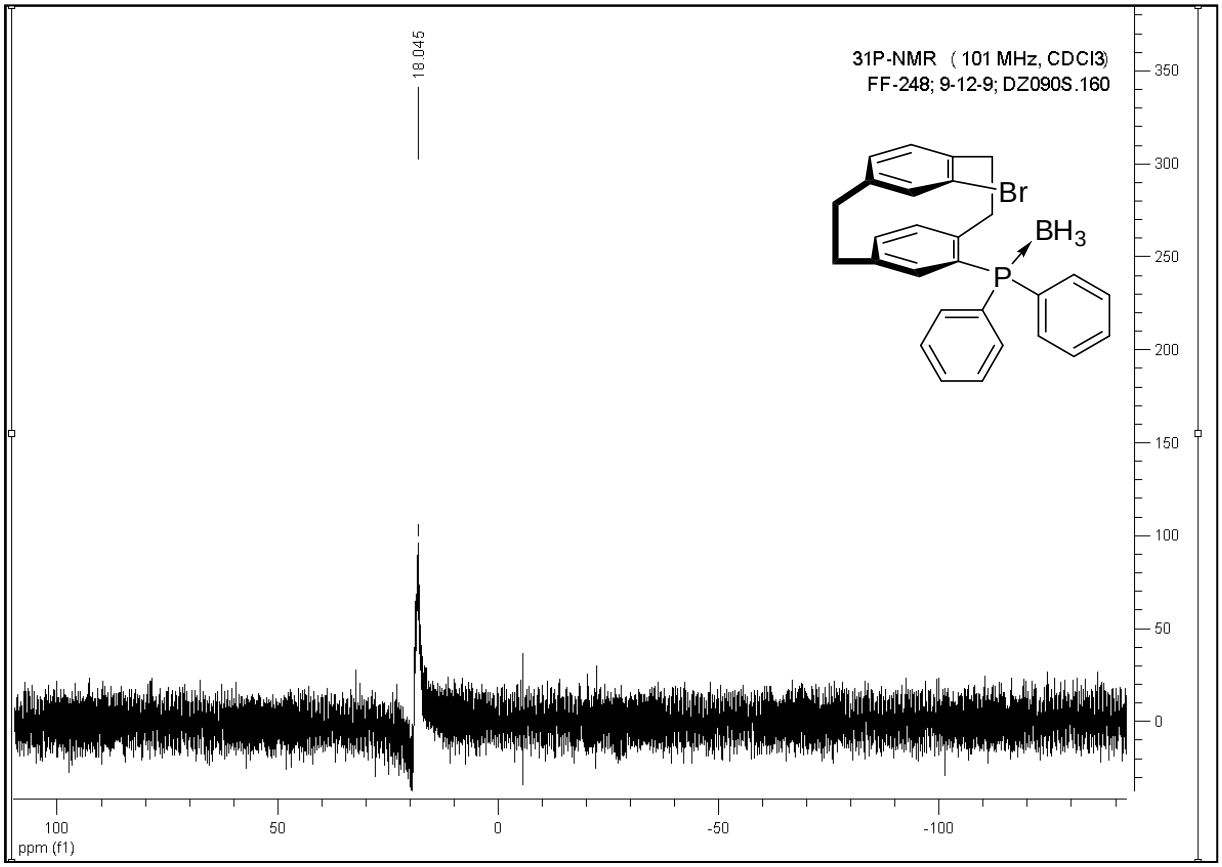
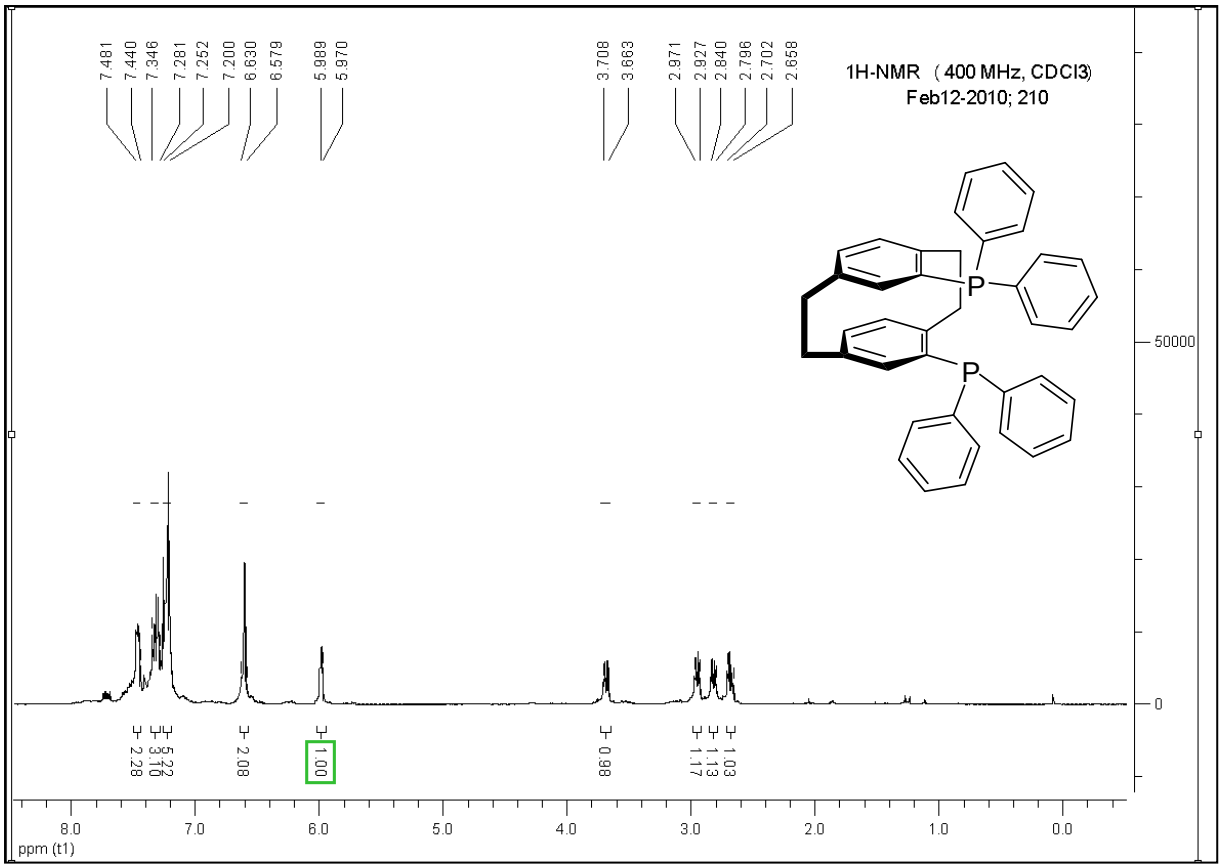
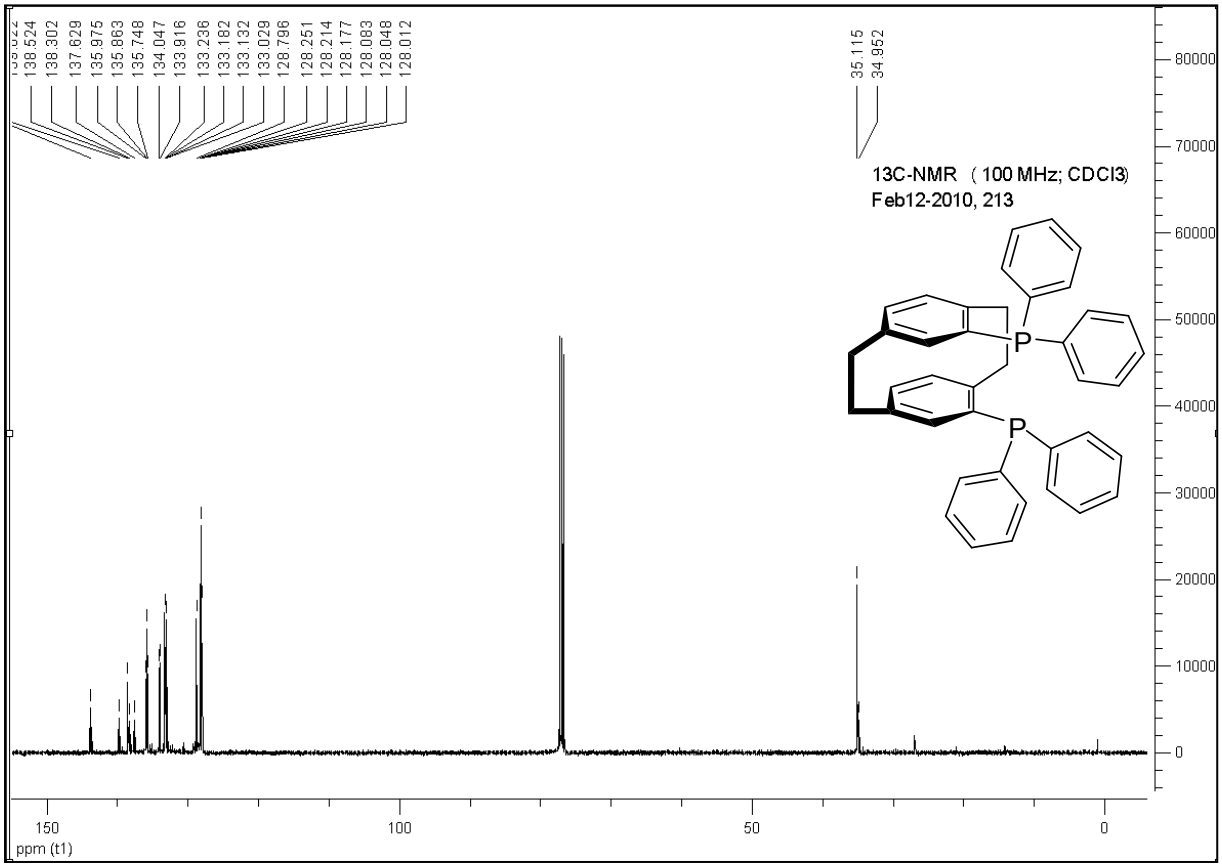
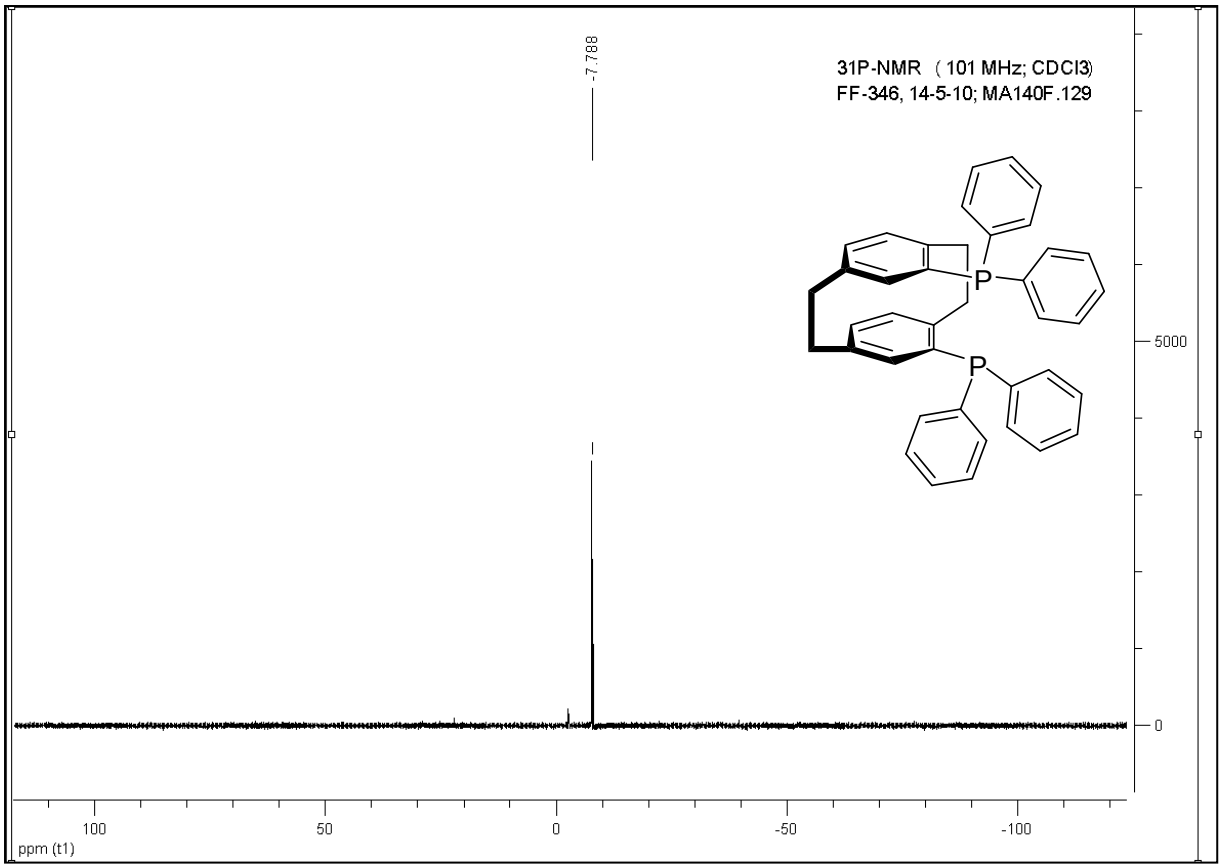
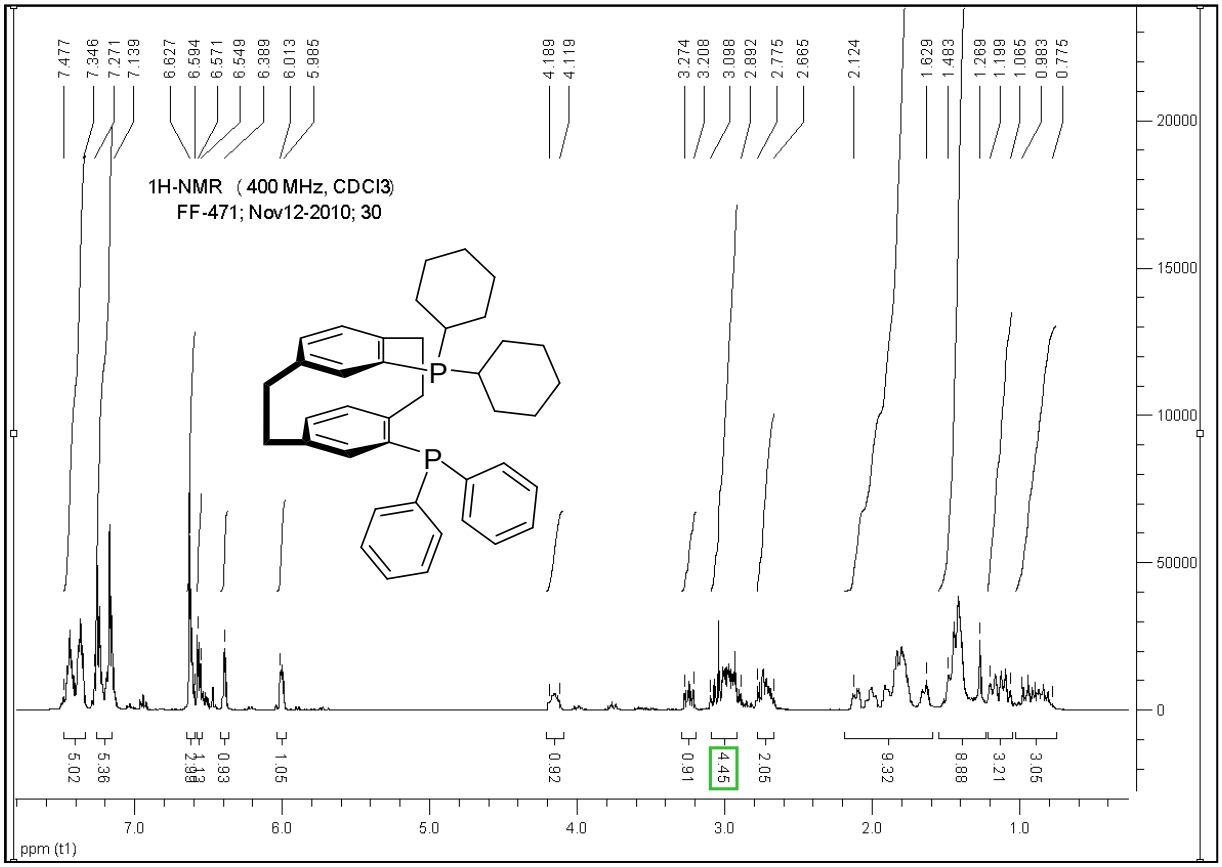
135.716
135.688
135.420
135.362
134.422
133.654
133.561
133.201
133.110
132.601
132.020
131.962
131.388
130.606
130.517
128.316
128.223
128.132
127.114
124.727
36.237
34.872
34.178
32.490
32.461
13C-NMR (100 MHz, CDCl3)
FF-248; Dec15-2009; 80
Br
BH3
P
10000
50000
0
150
100
50
0
ppm (t1)

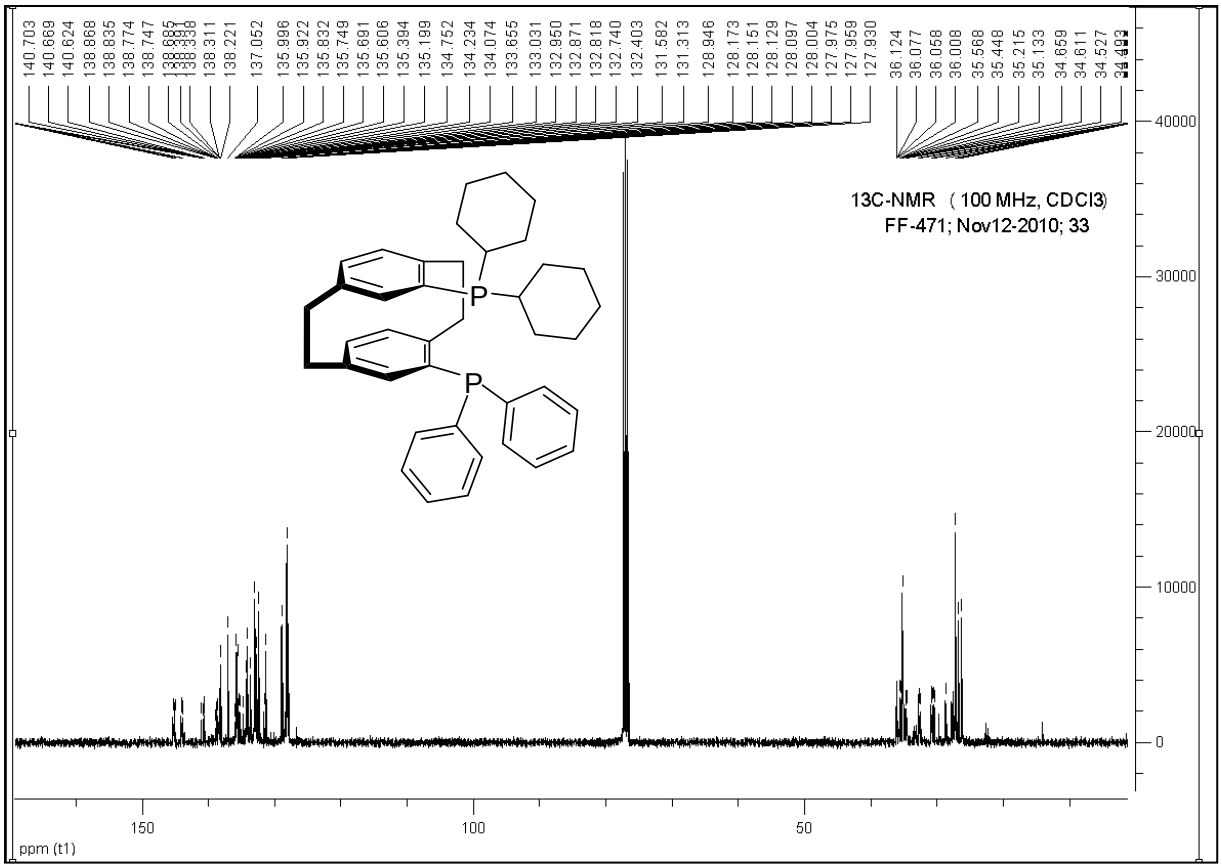

18.045
31P-NMR (101 MHz, CDCl3)
FF-248; 9-12-9; DZ090S.160
Br
BH3
P
350
300
250
200
150
100
50
0
100
50
0
-50
-100
ppm (f1)

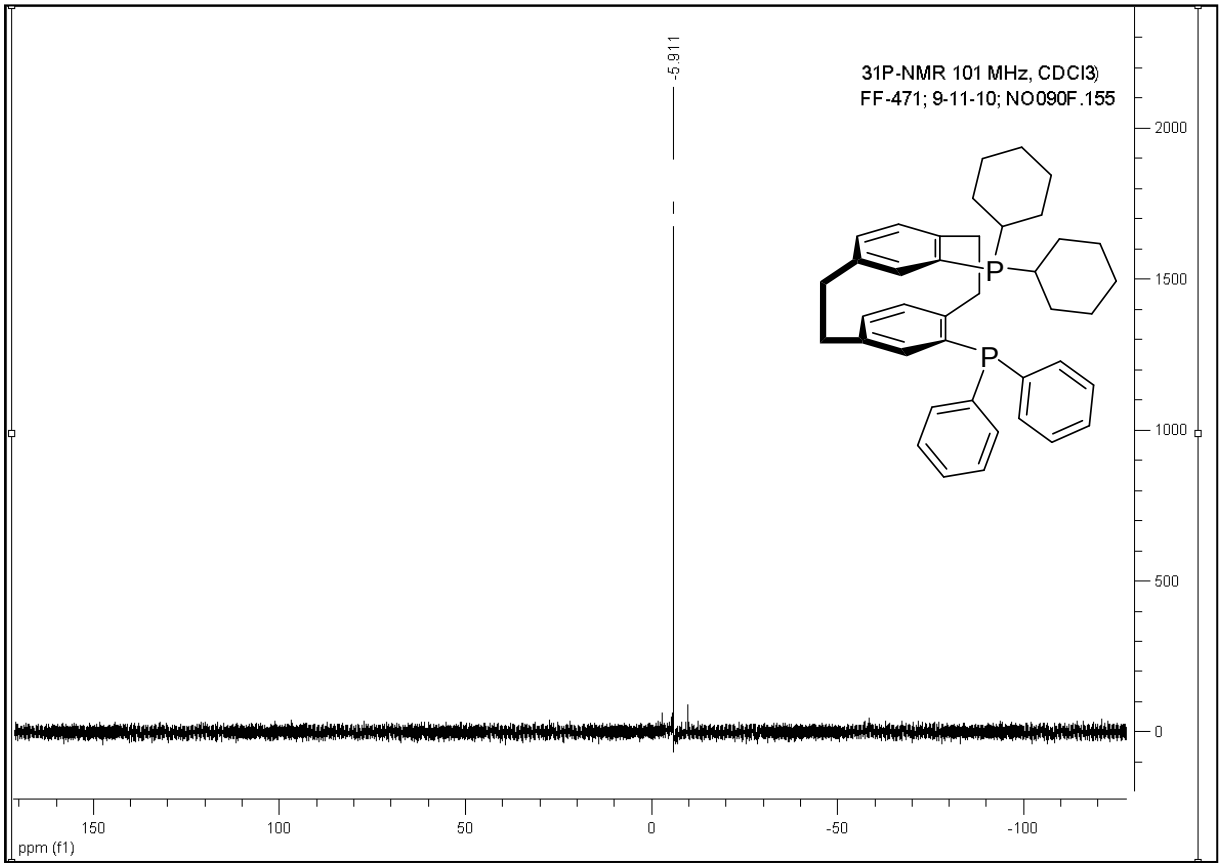

7.481
7.440
7.346
7.281
7.252
7.200
6.630
6.579
5.989
5.970
3.708
3.663
2.971
2.927
2.840
2.796
2.702
2.658
1H-NMR （400 MHz, CDCl3)
Feb12-2010; 210
P
P
50000
0
2.28
3.10
5.22
2.08
1.00
0.88
1.17
1.13
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

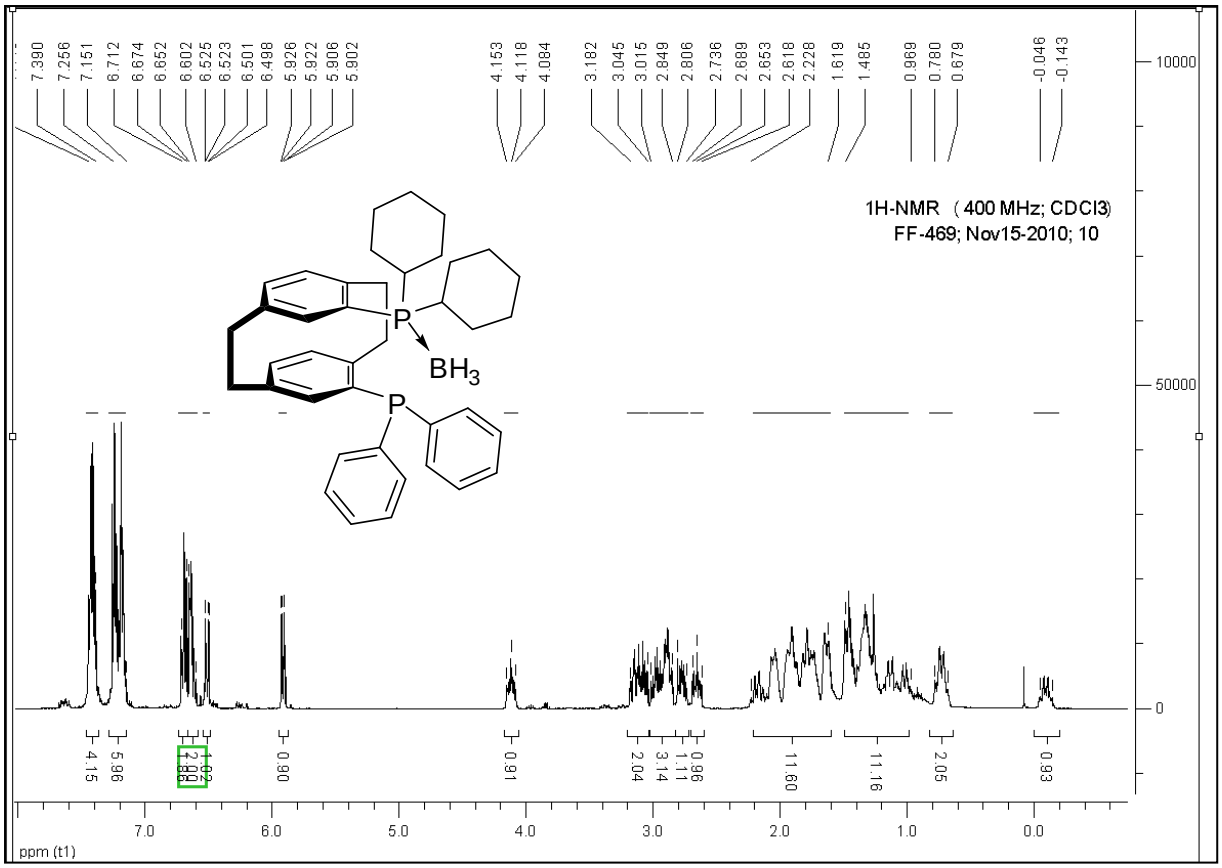

138.524
138.302
137.629
135.975
135.863
135.748
134.047
133.916
133.236
133.182
133.132
133.029
128.796
128.251
128.214
128.177
128.083
128.048
128.012
35.115
34.952
13C-NMR （100 MHz; CDCl3)
Feb12-2010, 213
P
P
80000
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

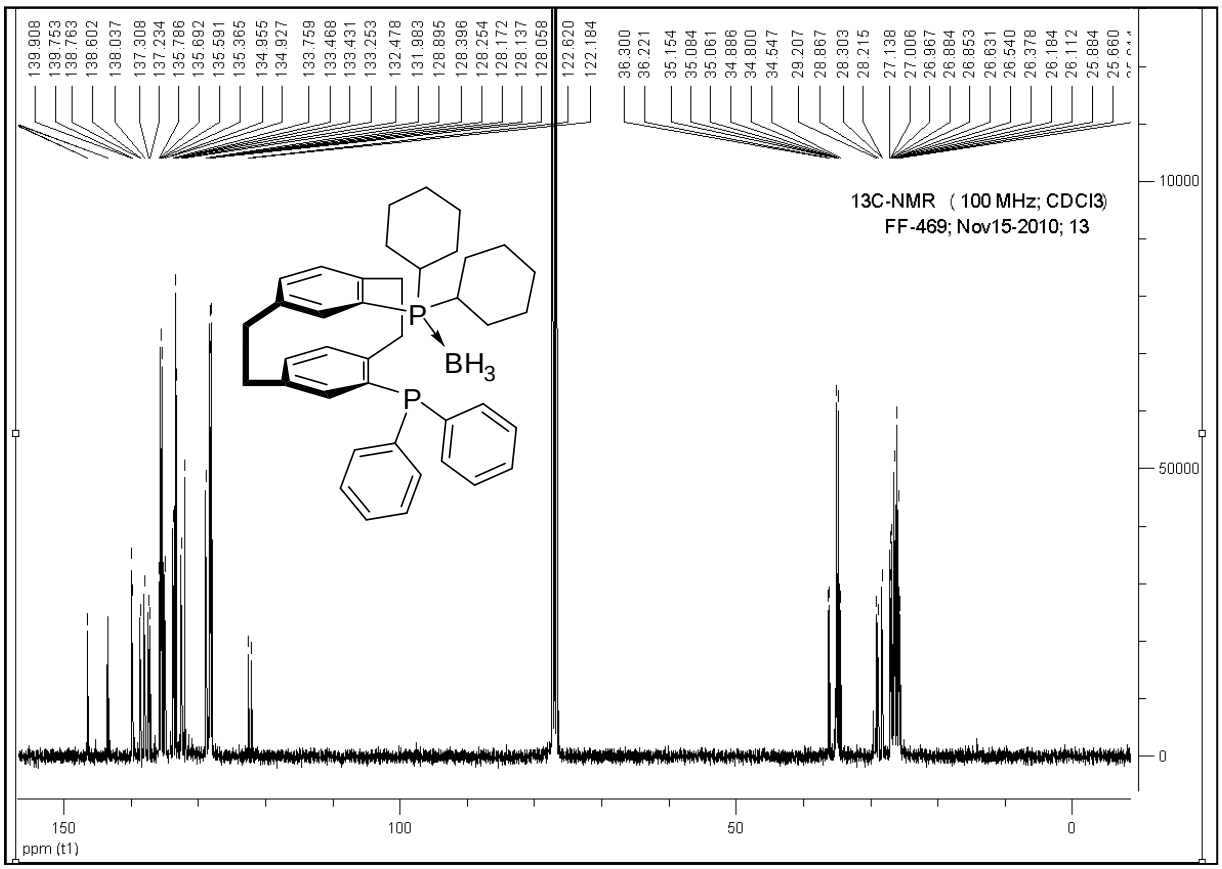

31P-NMR (101 MHz; CDCl3)
FF-346, 14-5-10; MA140F.129
-7.788
P
P
5000
0
100
50
0
-50
-100
ppm (t1)

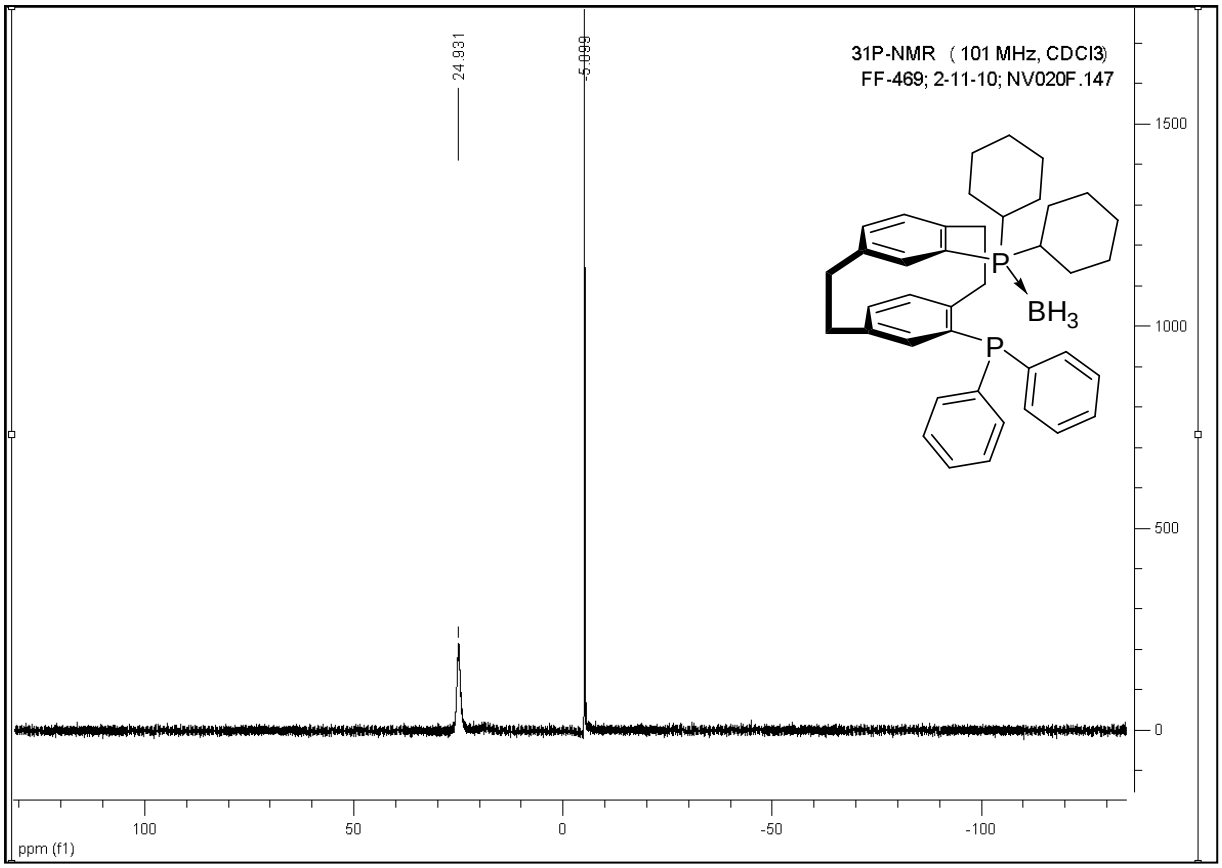

7.477
7.346
7.271
7.139
6.627
6.594
6.571
6.549
6.389
6.013
5.985
4.189
4.119
3.274
3.208
3.088
2.892
2.775
2.665
2.124
1.629
1.483
1.289
1.199
1.065
0.983
0.775
1H-NMR (400 MHz, CDCl3)
FF-471; Nov12-2010; 30
P
P
20000
15000
10000
50000
0
5.02
5.36
1.88
0.88
1.05
0.92
0.81
4.45
2.05
8.32
8.88
3.21
3.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

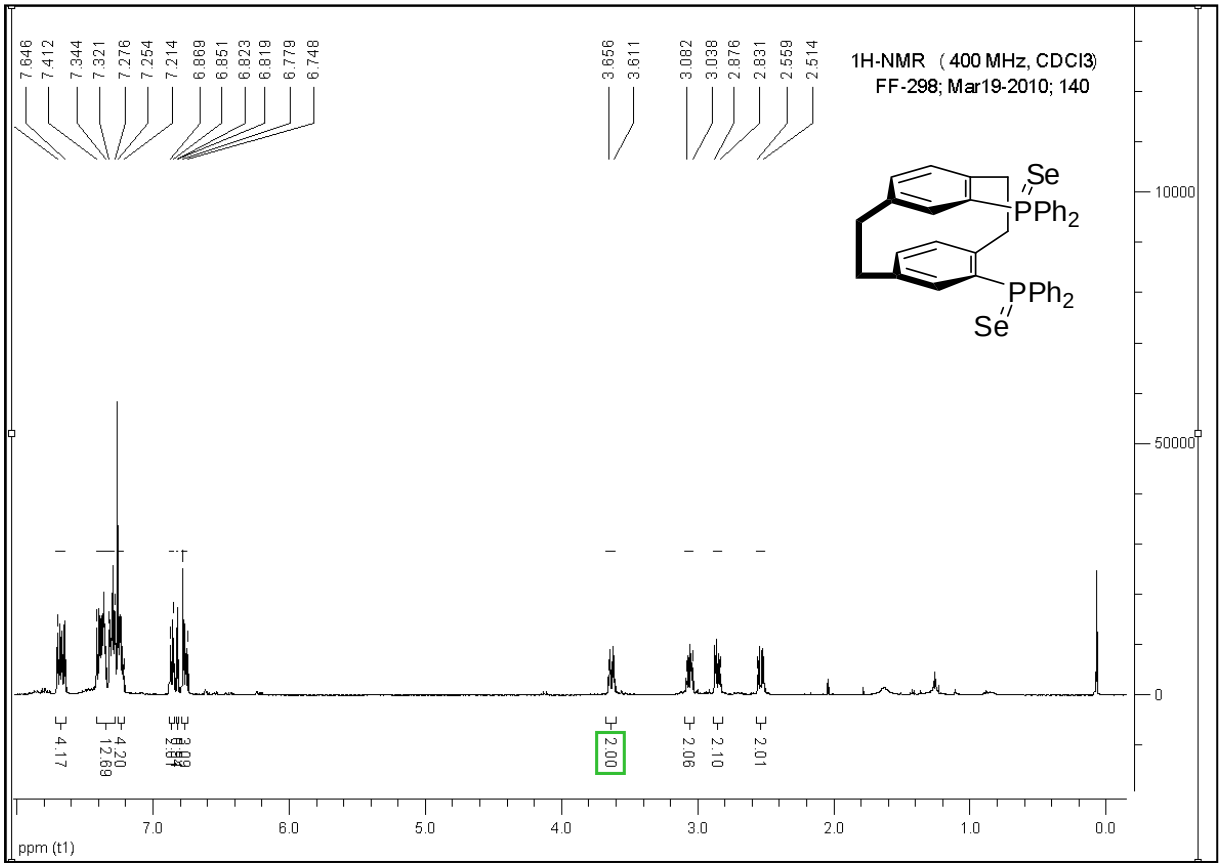

140.703
140.669
140.624
138.868
138.835
138.774
138.747
138.311
138.221
137.052
135.996
135.922
135.832
135.749
135.691
135.606
135.394
135.199
134.752
134.234
134.074
133.655
133.031
132.950
132.871
132.818
132.740
132.403
131.582
131.313
128.946
128.173
128.151
128.129
128.097
128.004
127.975
127.959
127.930
36.124
36.077
36.058
36.008
35.568
35.448
35.215
35.133
34.659
34.611
34.527
13C-NMR (100 MHz, CDCl3)
FF-471; Nov12-2010; 33
P
P
40000
30000
20000
10000
0
150
100
50
ppm (t1)

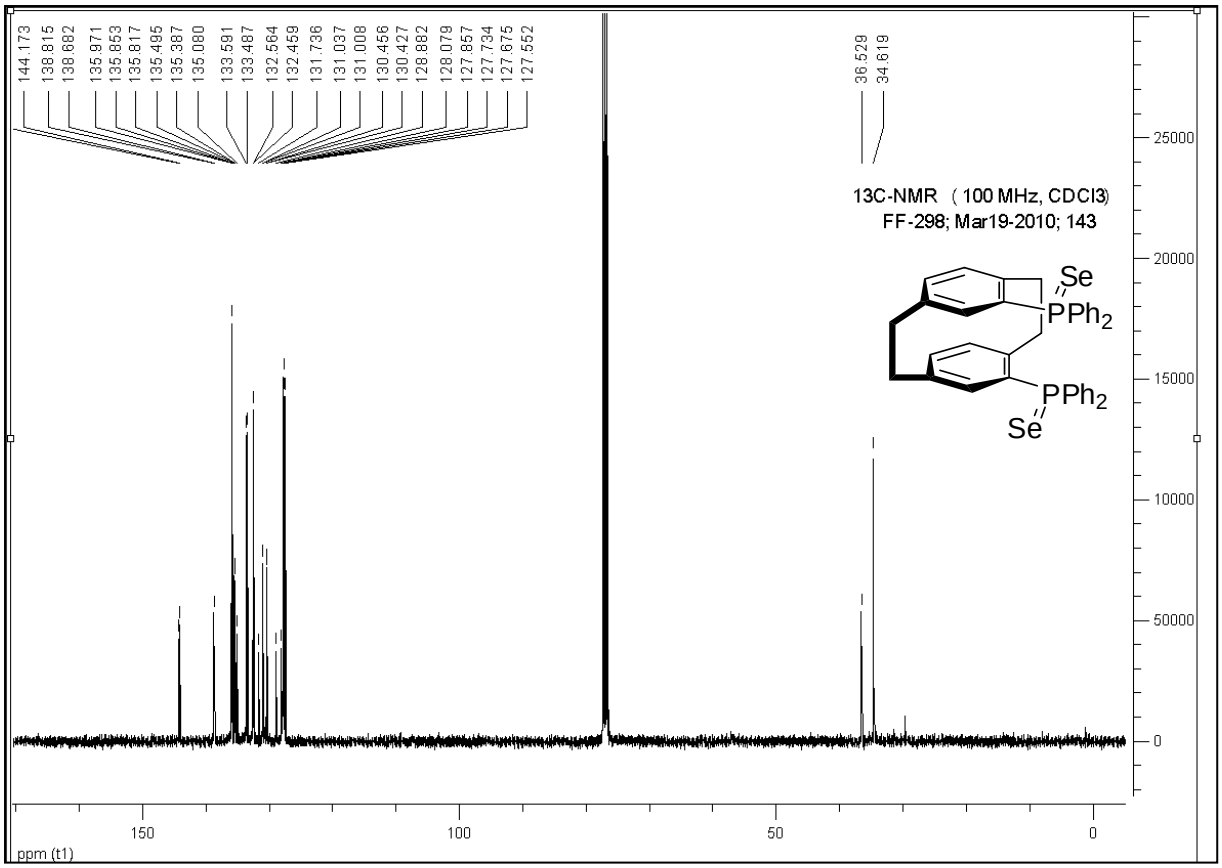

-5.911
31P-NMR 101 MHz, CDCl3)
FF-471; 9-11-10; NO090F.155
P
P
2000
1500
1000
500
0
150
100
50
0
-50
-100
ppm (f1)

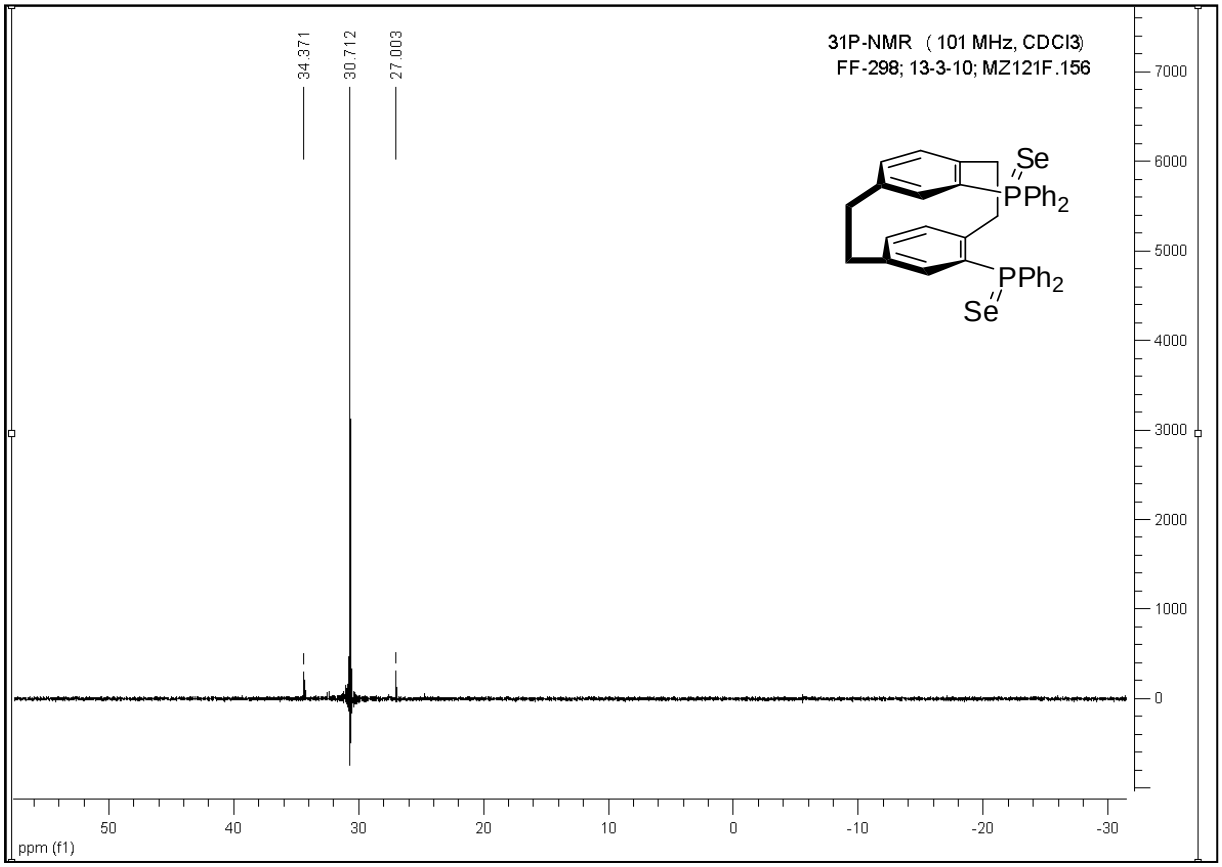

7.390
7.256
7.151
6.712
6.674
6.652
6.602
6.525
6.523
6.501
6.498
5.926
5.922
5.906
5.902
4.153
4.118
4.084
3.182
3.045
3.015
2.849
2.806
2.736
2.689
2.653
2.618
2.228
1.619
1.485
0.969
0.780
0.679
-0.046
-0.143
1H-NMR (400 MHz; CDCl3)
FF-469; Nov15-2010; 10
P
BH3
P
4.15
5.98
1.00
2.05
0.90
0.81
2.04
3.14
1.11
0.96
11.60
11.16
2.05
0.83
10000
50000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

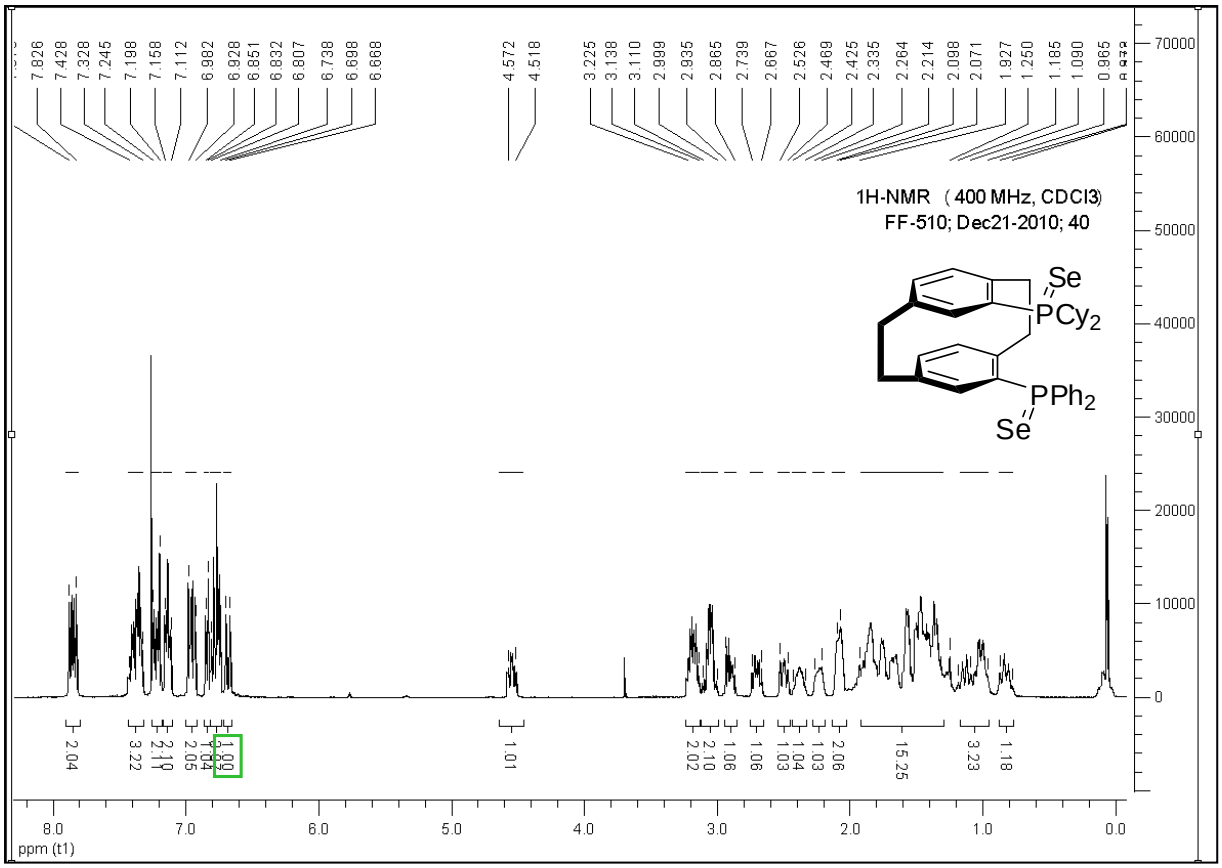

139.908
139.753
138.763
138.602
138.037
137.308
137.234
135.786
135.692
135.591
135.365
134.955
134.927
133.759
133.468
133.431
133.253
132.478
131.983
128.895
128.396
128.254
128.172
128.137
128.058
122.620
122.184
36.300
36.221
35.154
35.084
35.061
34.886
34.800
34.547
29.207
28.867
28.303
28.215
27.138
27.006
26.967
26.884
26.853
26.631
26.540
26.378
26.184
26.112
25.884
25.660
13C-NMR (100 MHz; CDCl3)
FF-469; Nov15-2010; 13
P
BH3
P
10000
50000
0
150
100
50
0
ppm (t1)

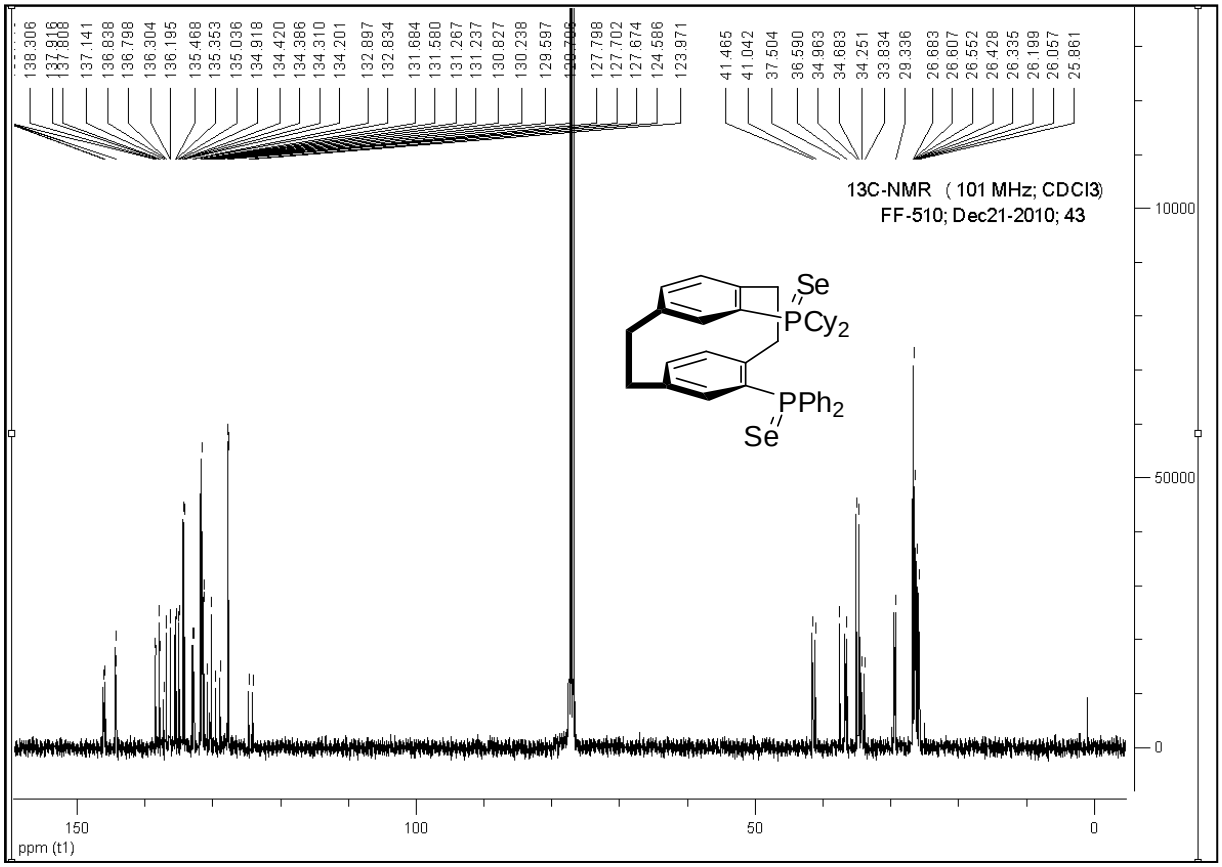

31P-NMR (101 MHz, CDCl3)
FF-469; 2-11-10; NV020F.147
24.931
-5.099
P
BH3
P
1500
1000
500
0
100
50
0
-50
-100
ppm (f1)

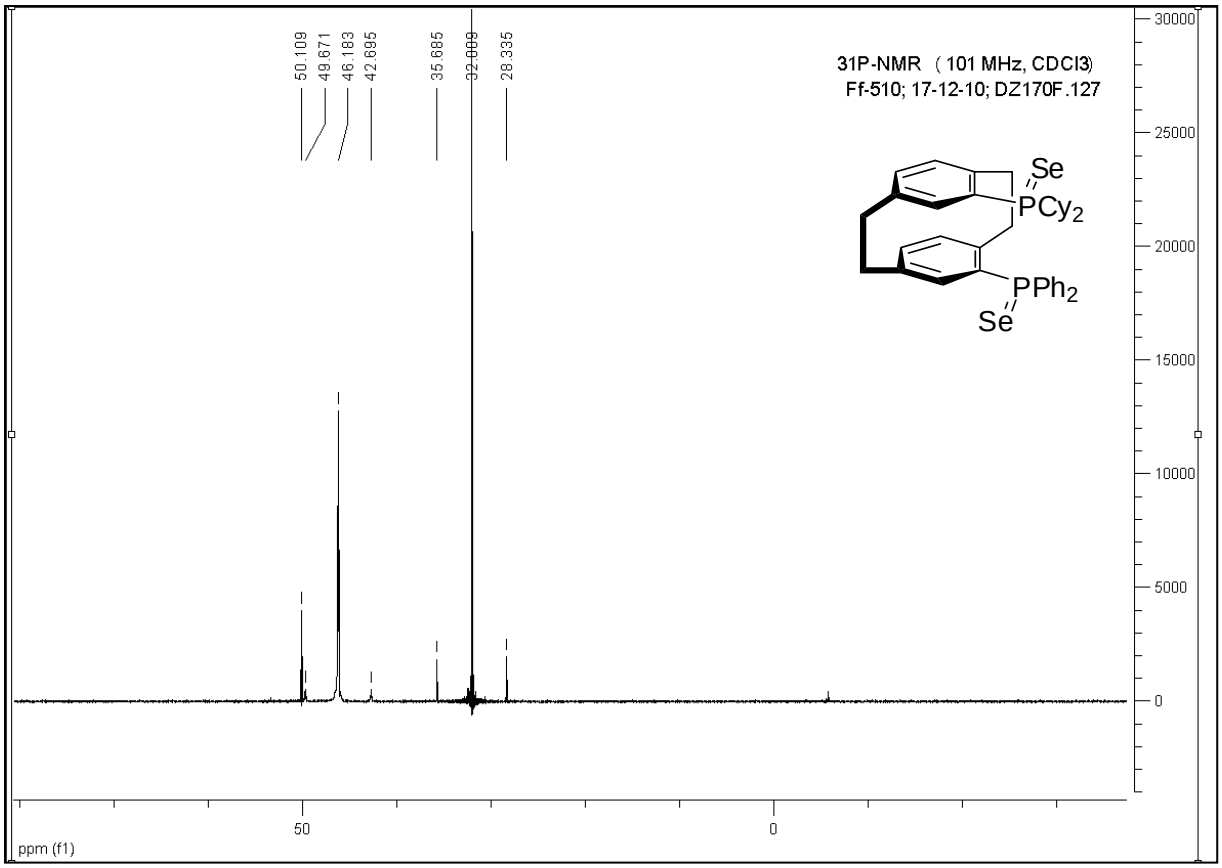

1H-NMR (400 MHz, CDCl3)
FF-298; Mar19-2010; 140
7.646
7.412
7.344
7.321
7.276
7.254
7.214
6.869
6.851
6.823
6.819
6.779
6.748
3.656
3.611
3.082
3.038
2.876
2.831
2.559
2.514
Se
PPh2
PPh2
Se
4.17
12.68
5.94
2.00
2.06
2.10
2.01
10000
50000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

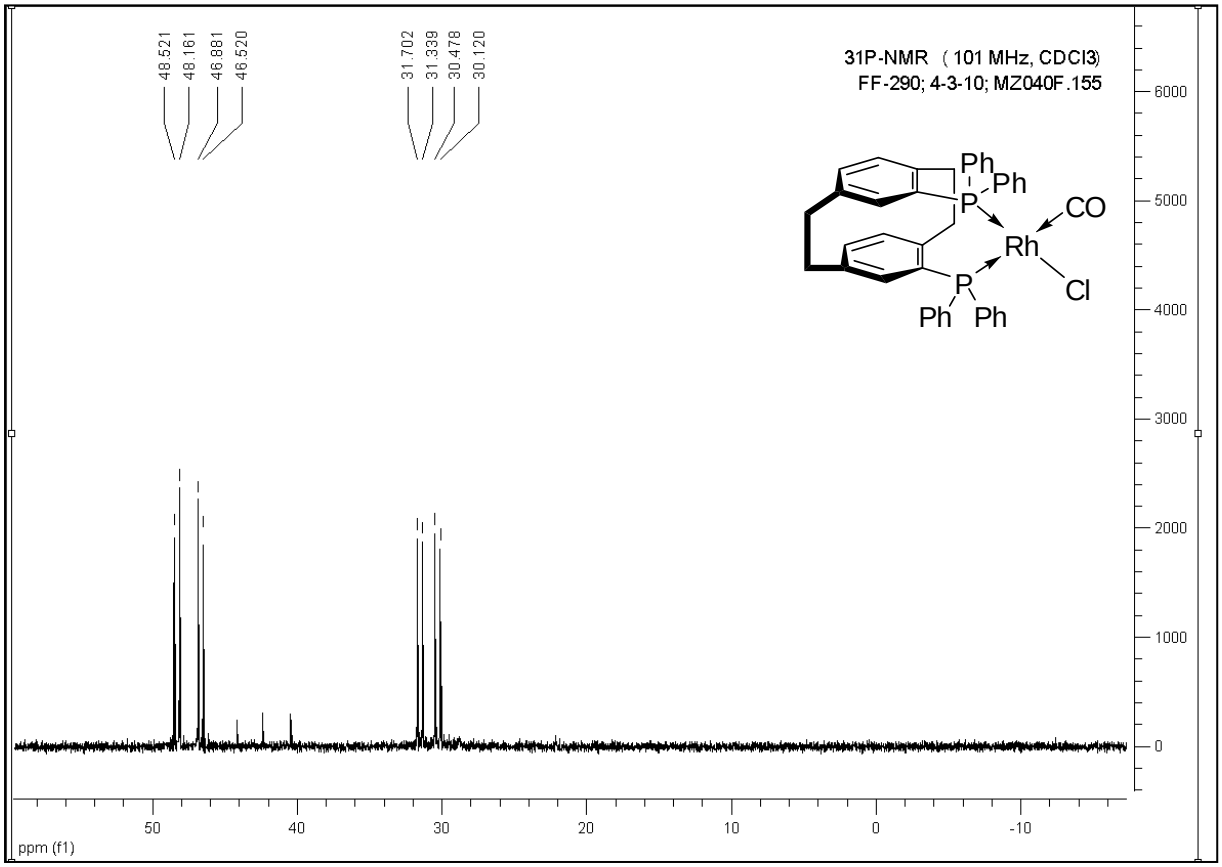

144.173
138.815
138.682
135.971
135.853
135.817
135.495
135.387
135.080
133.591
133.487
132.564
132.459
131.736
131.037
131.008
130.456
130.427
128.882
128.079
127.857
127.734
127.675
127.552
36.529
34.619
13C-NMR (100 MHz, CDCl3)
FF-298; Mar19-2010; 143
Se
PPh2
PPh2
Se
25000
20000
15000
10000
50000
0
150
100
50
0
ppm (t1)

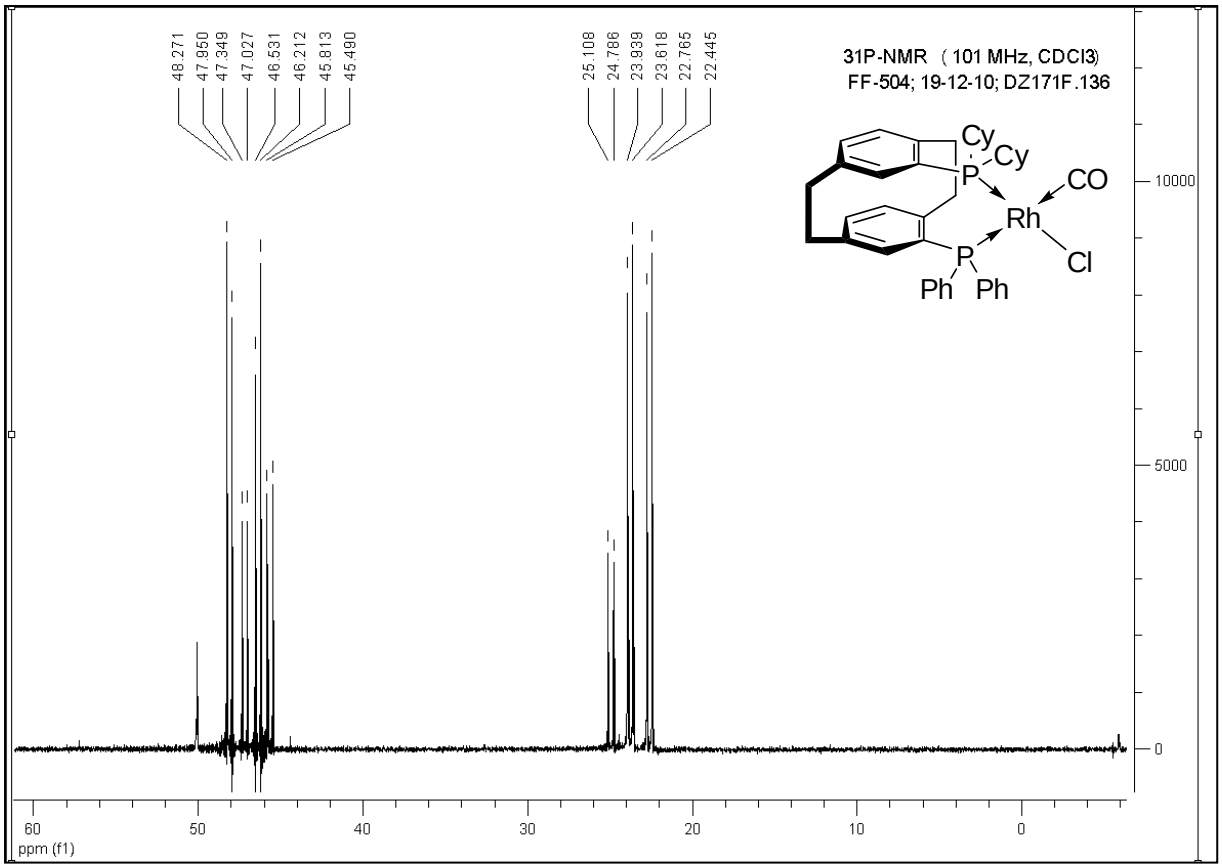

34.371
30.712
27.003
31P-NMR (101 MHz, CDCl3)
FF-298; 13-3-10; MZ121F.156
Se
PPh2
PPh2
Se
7000
6000
5000
4000
3000
2000
1000
0
50
40
30
20
10
0
-10
-20
-30
ppm (f1)

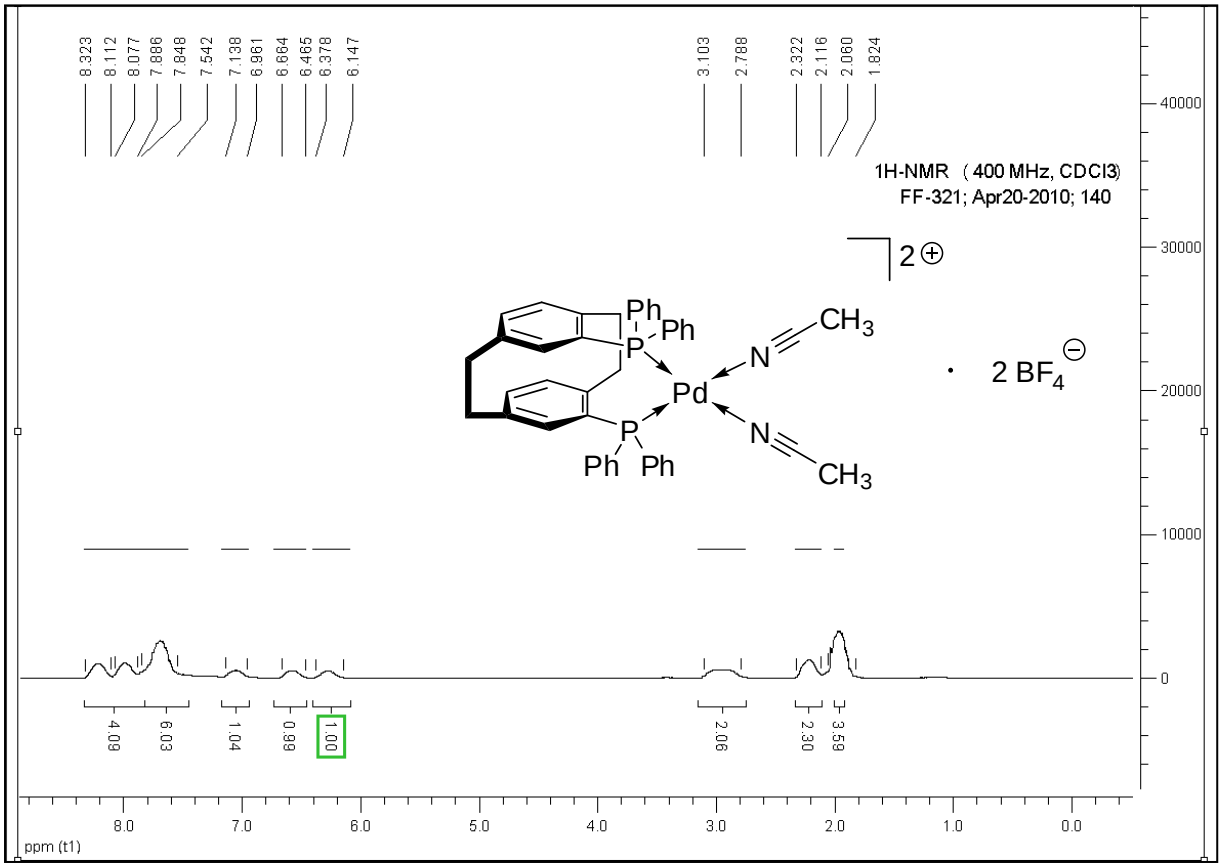

1H-NMR （400 MHz, CDCl3)
FF-510; Dec21-2010; 40
Se
PCy2
PPh2
Se
ppm (t1)

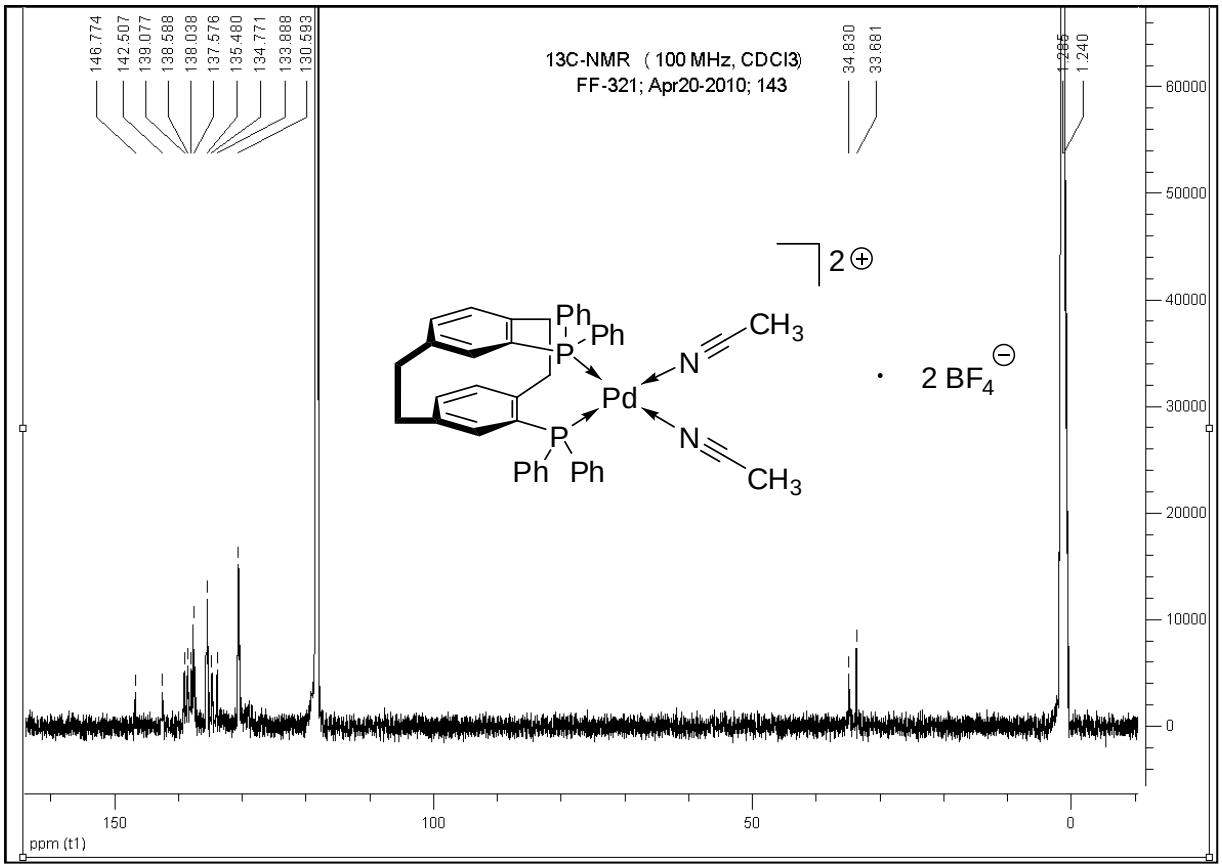

13C-NMR （101 MHz; CDCl3)
FF-510; Dec21-2010; 43
Se
PCy2
PPh2
Se
ppm (t1)

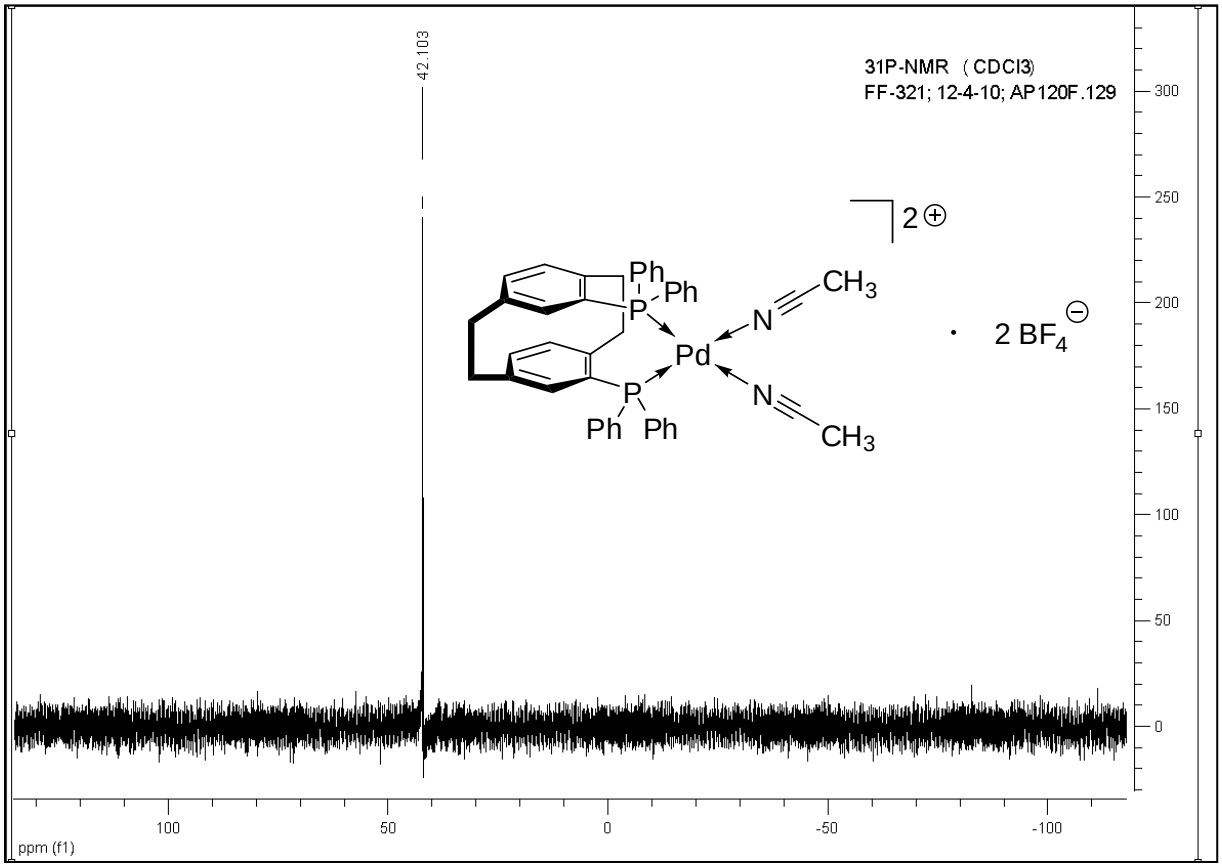

50.109
49.671
46.183
42.695
35.685
32.009
28.335
31P-NMR (101 MHz, CDCl3)
Ff-510; 17-12-10; DZ170F.127
Se
PCy2
PPh2
Se
30000
25000
20000
15000
10000
5000
0
50
0
ppm (f1)

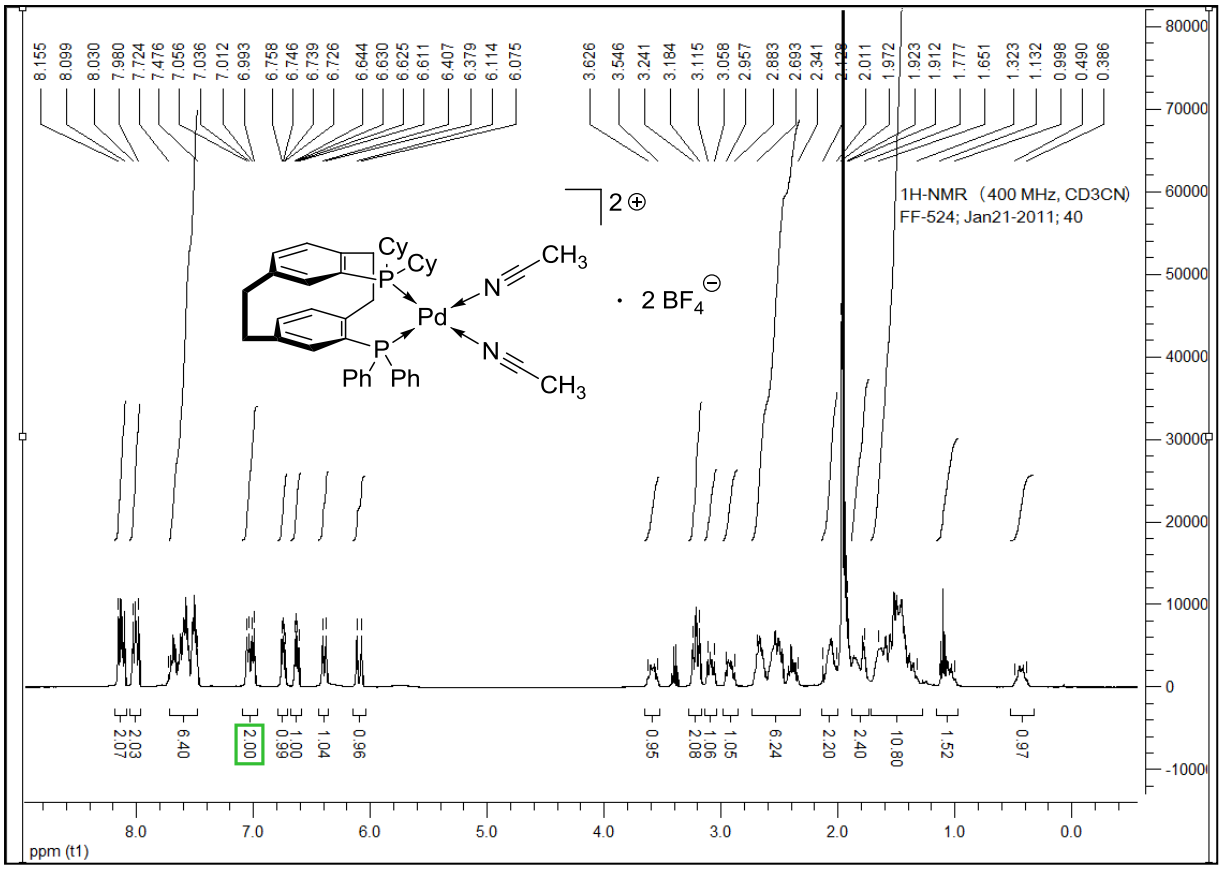

48.521
48.161
46.881
46.520
31.702
31.339
30.478
30.120
31P-NMR (101 MHz, CDCl3)
FF-290; 4-3-10; MZ040F.155
Ph
Ph
P
CO
Rh
P
Cl
Ph
Ph
6000
5000
4000
3000
2000
1000
0
50
40
30
20
10
0
-10
ppm (f1)

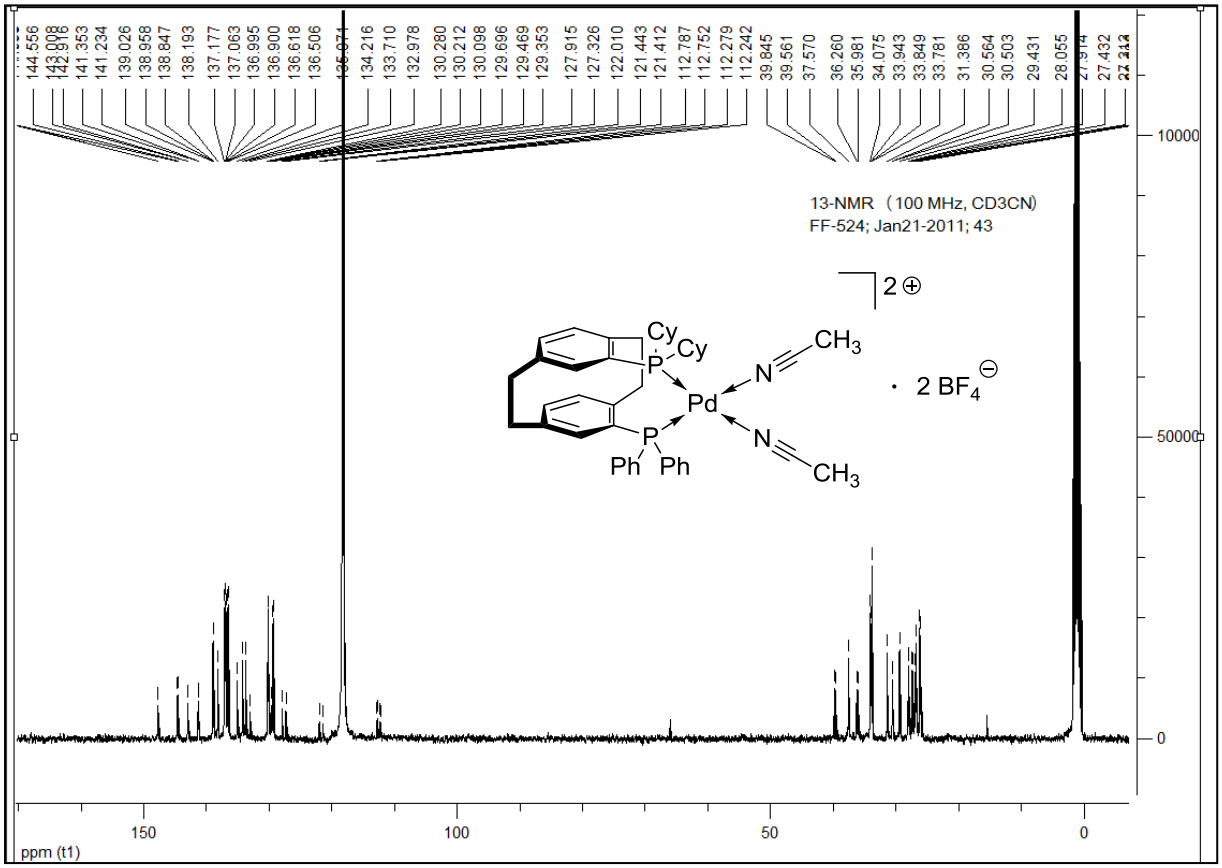

48.271
47.950
47.348
47.027
46.531
46.212
45.813
45.490
25.108
24.786
23.939
23.618
22.765
22.445
31P-NMR (101 MHz, CDCl3)
FF-504; 19-12-10; DZ171F.136
Cy
Cy
P
CO
Rh
P
Cl
Ph
Ph
10000
5000
0
60
50
40
30
20
10
0
ppm (f1)

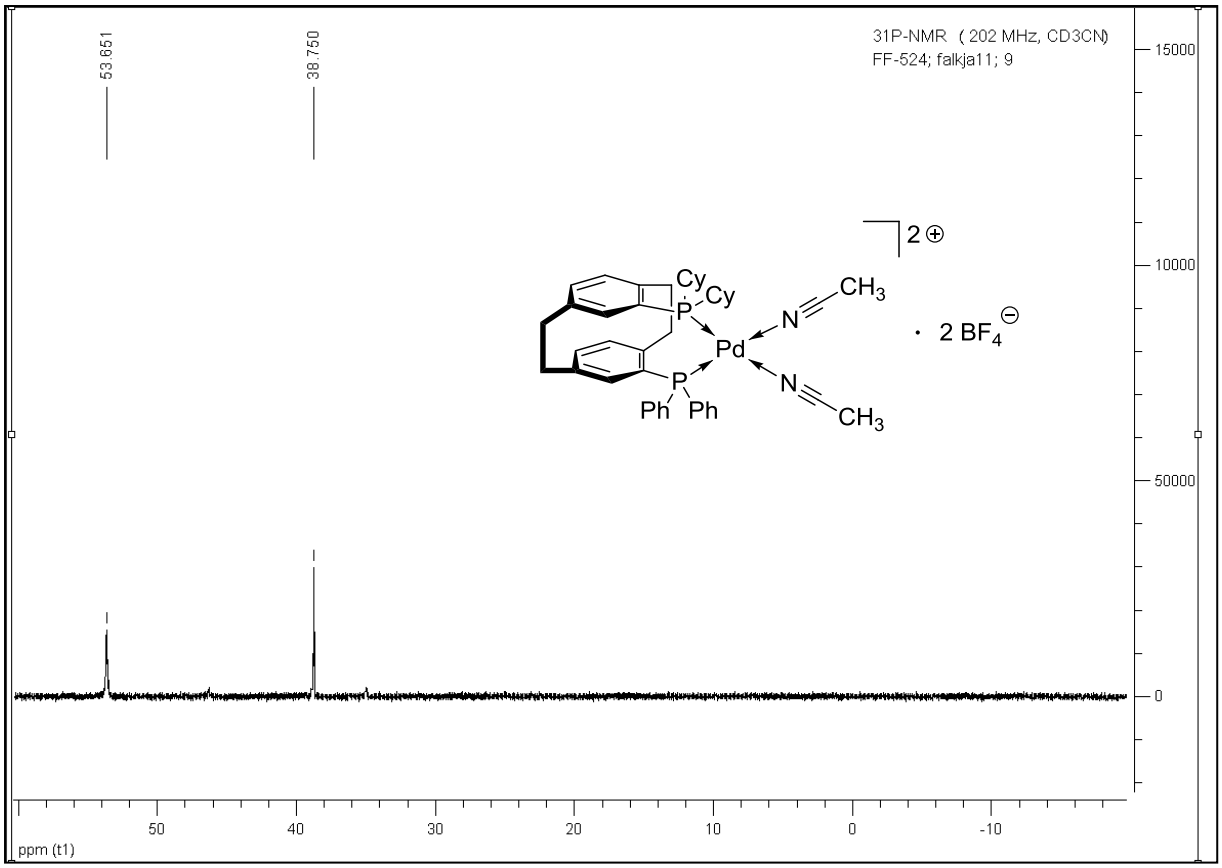

8.323
8.112
8.077
7.886
7.848
7.542
7.138
6.961
6.664
6.465
6.378
6.147
3.103
2.788
2.322
2.116
2.060
1.824
1H-NMR (400 MHz, CDCl3)
FF-321; Apr20-2010; 140
2⊕
Ph
Ph
P
CH3
N
Pd
· 2 BF4⊖
P
N
Ph
Ph
CH3
4.08
6.03
1.04
0.98
1.00
2.08
2.30
3.58
40000
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

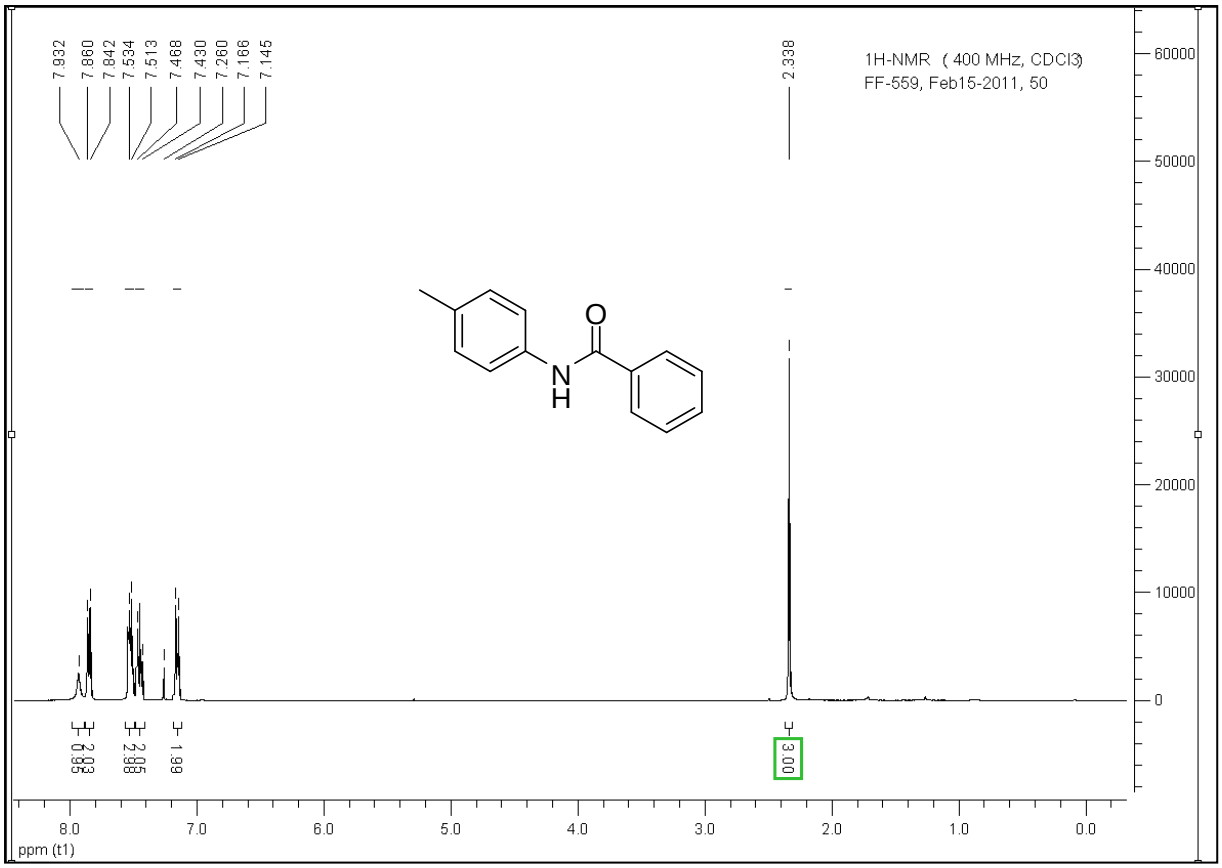

13C-NMR (100 MHz, CDCl3)
FF-321; Apr20-2010; 143
146.774
142.507
139.077
138.588
138.038
137.576
135.480
134.771
133.888
130.593
34.830
33.681
1.285
1.240
2⊕
Ph
Ph
P
CH3
N
Pd
P
N
Ph
Ph
CH3
· 2 BF4⊖
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

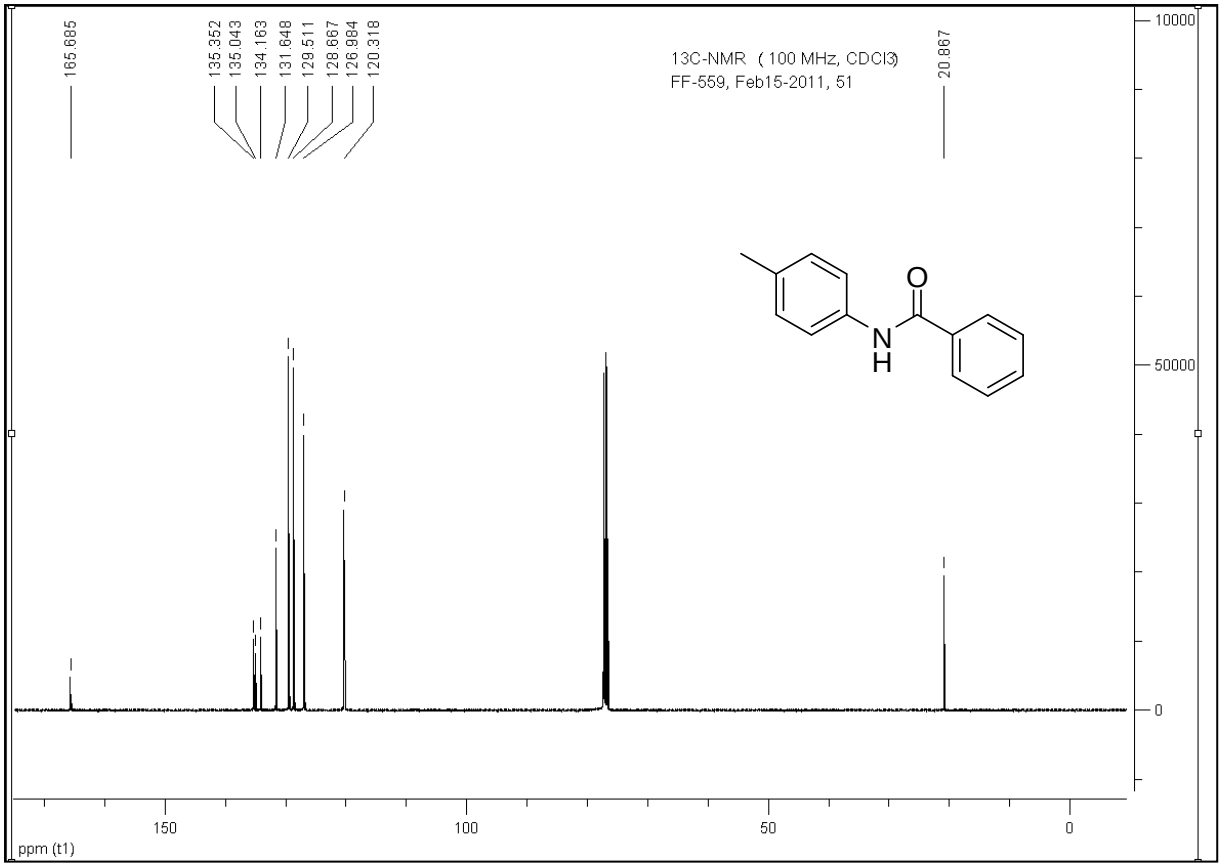

31P-NMR (CDCl3)
FF-321; 12-4-10; AP120F.129
42.103
2⊕
Ph
Ph
P
CH3
N
Pd
P
N
Ph
Ph
CH3
· 2 BF4⊖
300
250
200
150
100
50
0
100
50
0
-50
-100
ppm (f1)

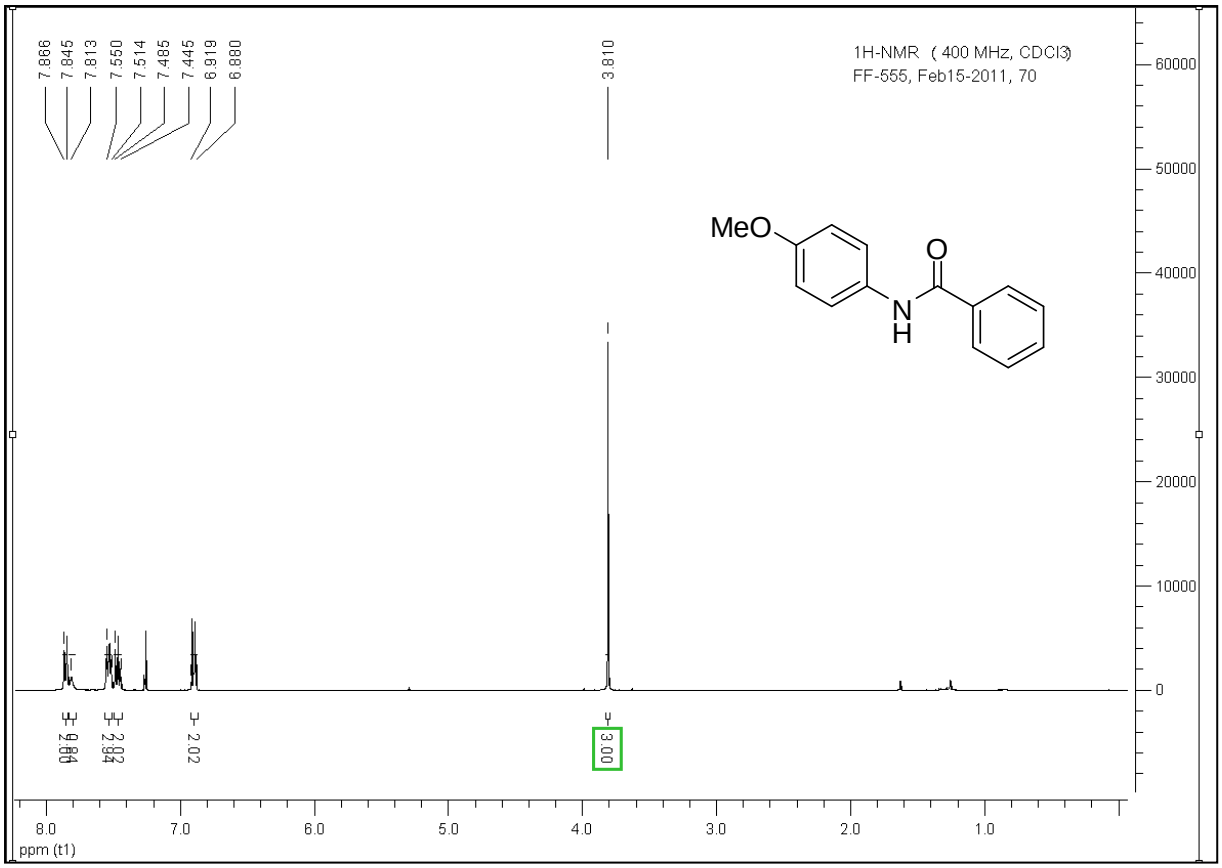

1H-NMR (400 MHz, CD3CN)
FF-524; Jan21-2011; 40
2⊕
· 2 BF4⊖
Cy
Cy
P
Pd
N
CH3
Ph
Ph
ppm (t1)

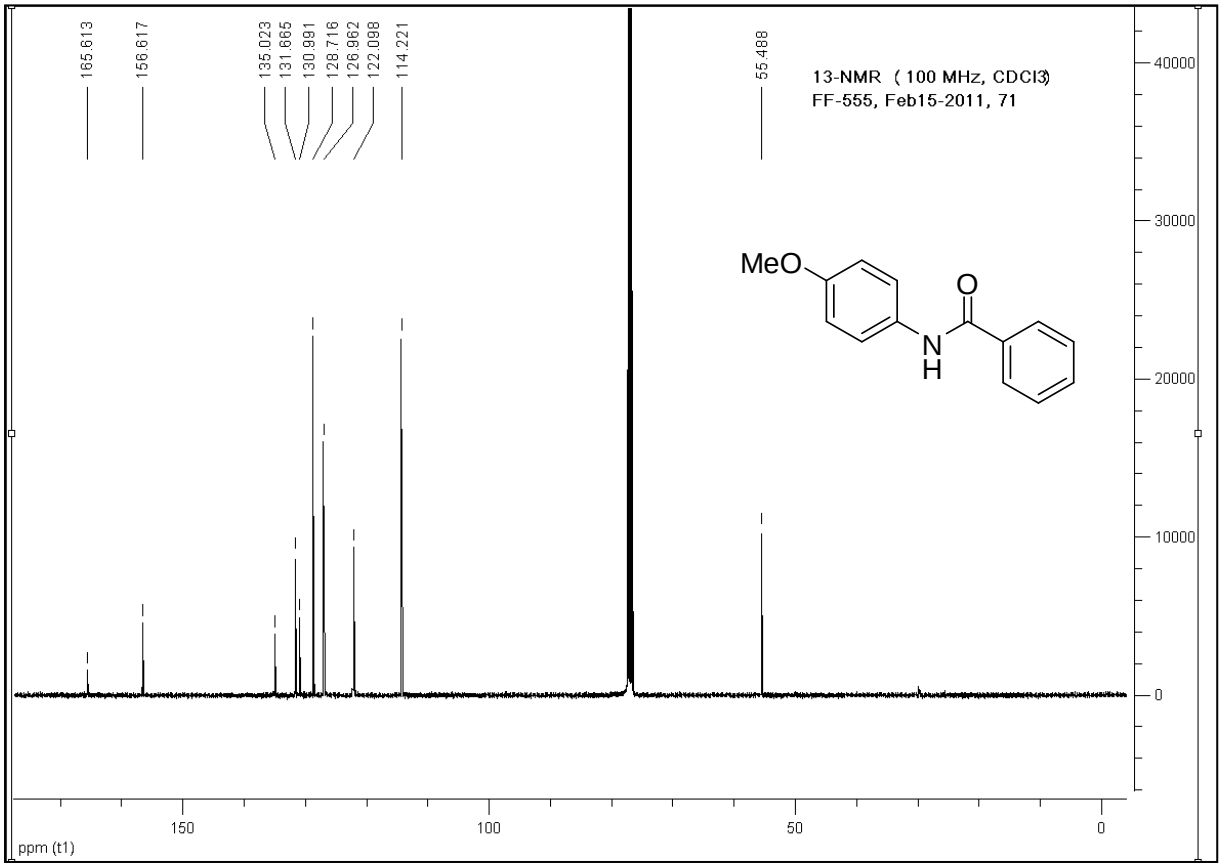

13-NMR (100 MHz, CD3CN)
FF-524; Jan21-2011; 43
2⊕
· 2 BF4⊖
Cy
Cy
P
Pd
N
CH3
Ph
Ph
ppm (t1)

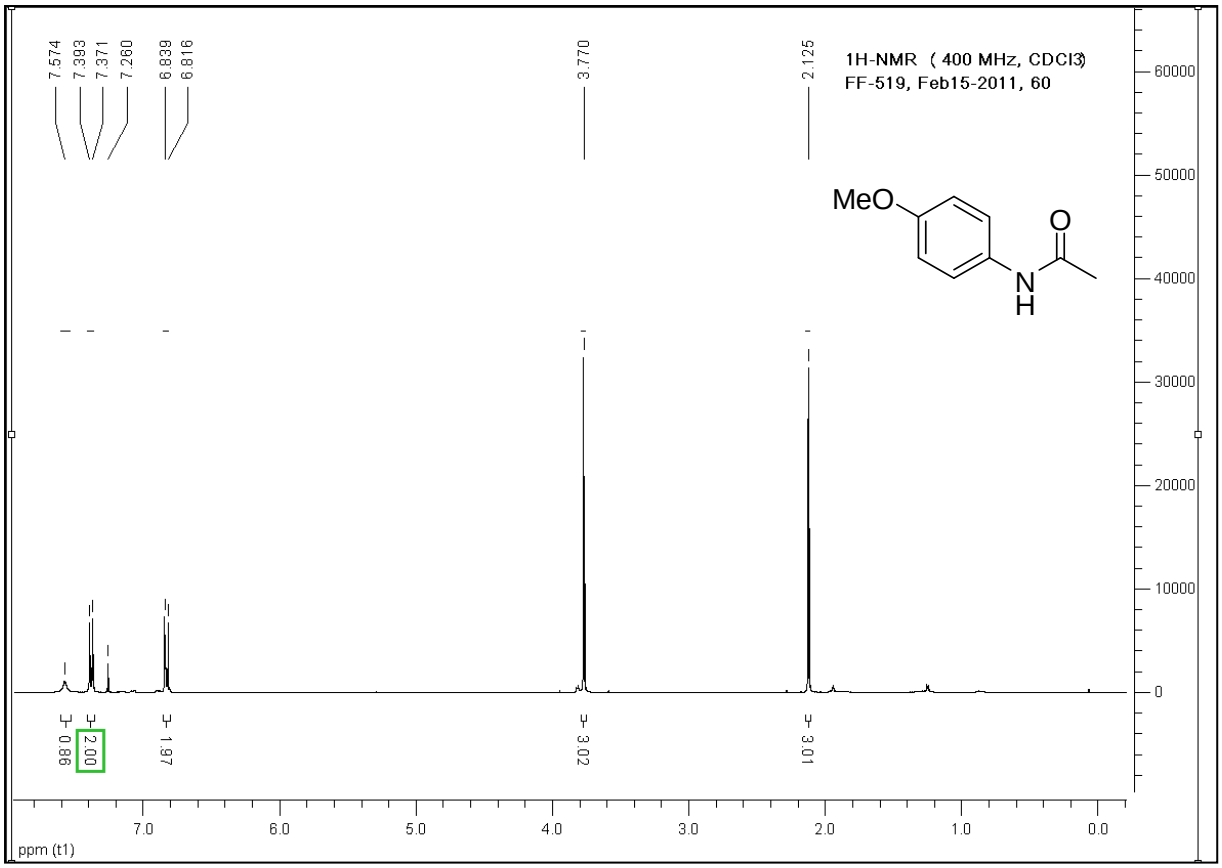

31P-NMR (202 MHz, CD3CN)
FF-524; falkja11; 9
53.651
38.750
15000
10000
50000
0
50
40
30
20
10
0
-10
ppm (t1)
2⊕
Cy
Cy
P
Pd
N
CH3
P
Ph
Ph
N
CH3
· 2 BF4⊖

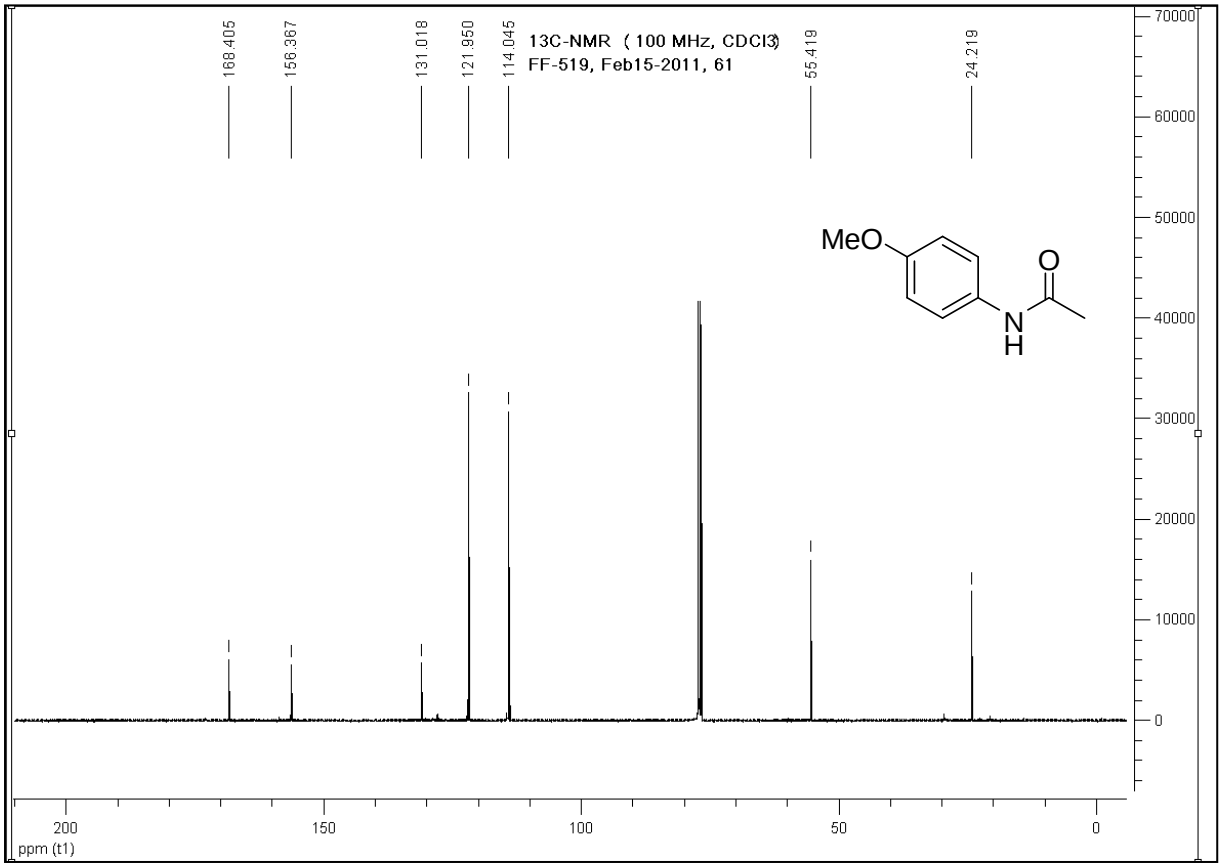

7.932
7.880
7.842
7.534
7.513
7.468
7.430
7.260
7.166
7.145
2.338
1H-NMR (400 MHz, CDCl3)
FF-559, Feb15-2011, 50
O
N
H
2.03
2.05
1.99
3.00
60000
50000
40000
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

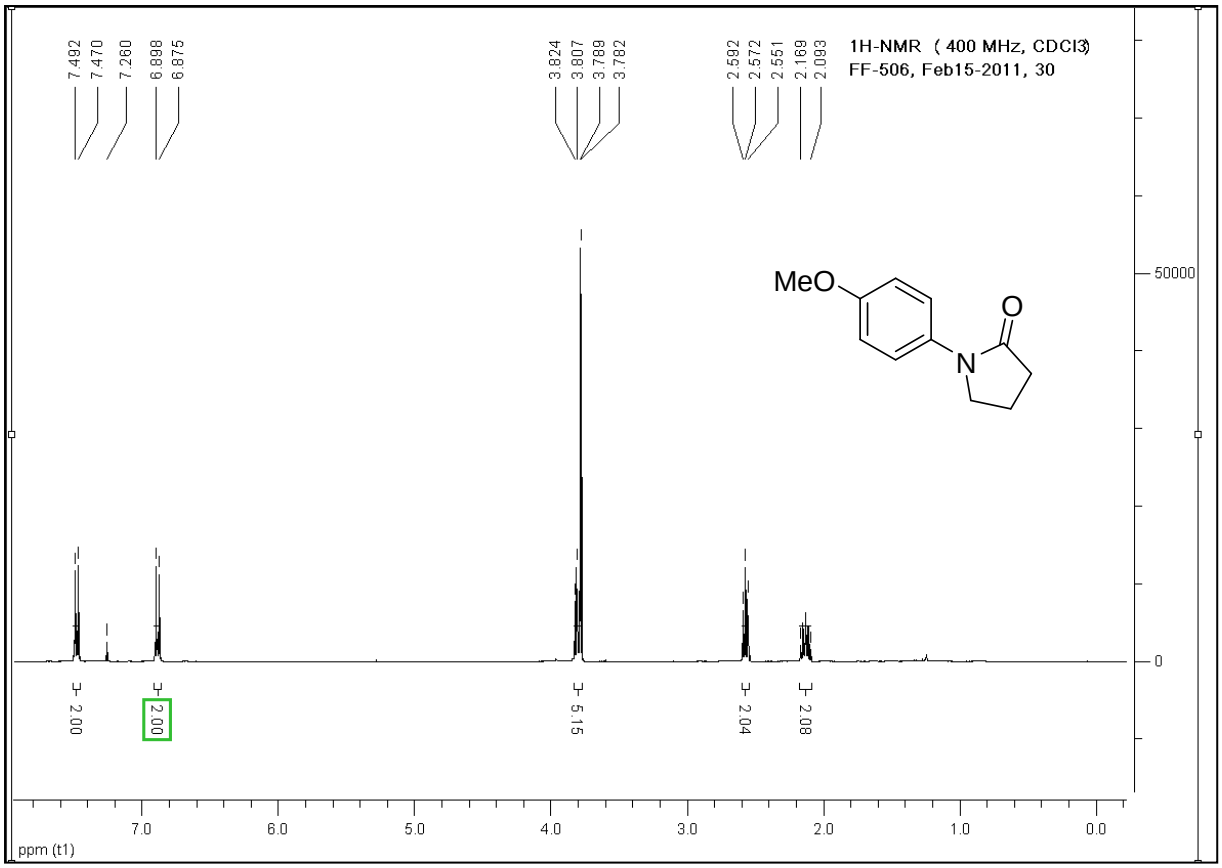

165.685
135.352
135.043
134.163
131.648
129.511
128.867
126.884
120.318
20.867
13C-NMR (100 MHz, CDCl3)
FF-559, Feb15-2011, 51
O
N
H
10000
50000
0
150
100
50
0
ppm (t1)

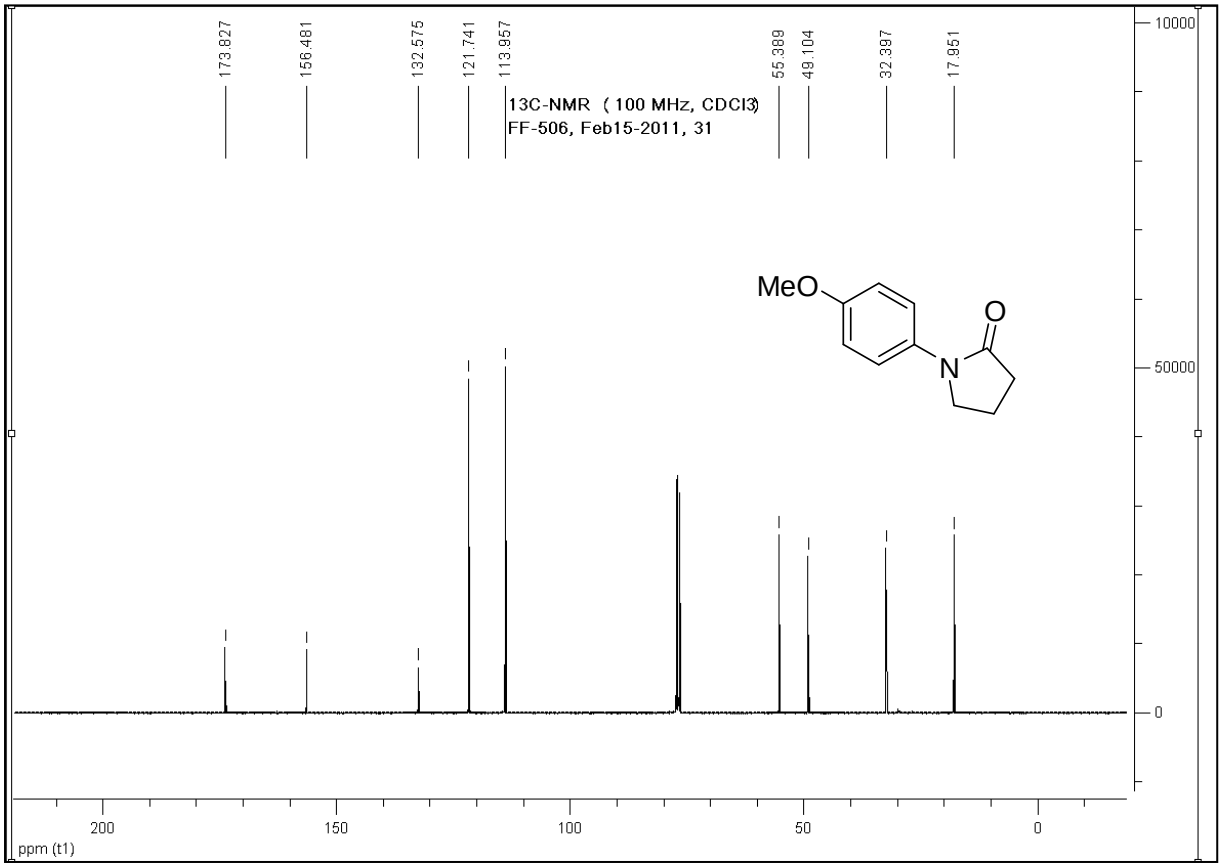

7.886
7.845
7.813
7.550
7.514
7.485
7.445
6.919
6.880
3.810
1H-NMR (400 MHz, CDCl3)
FF-555, Feb15-2011, 70
MeO
O
N
H
2.00
2.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
60000
50000
40000
30000
20000
10000
0

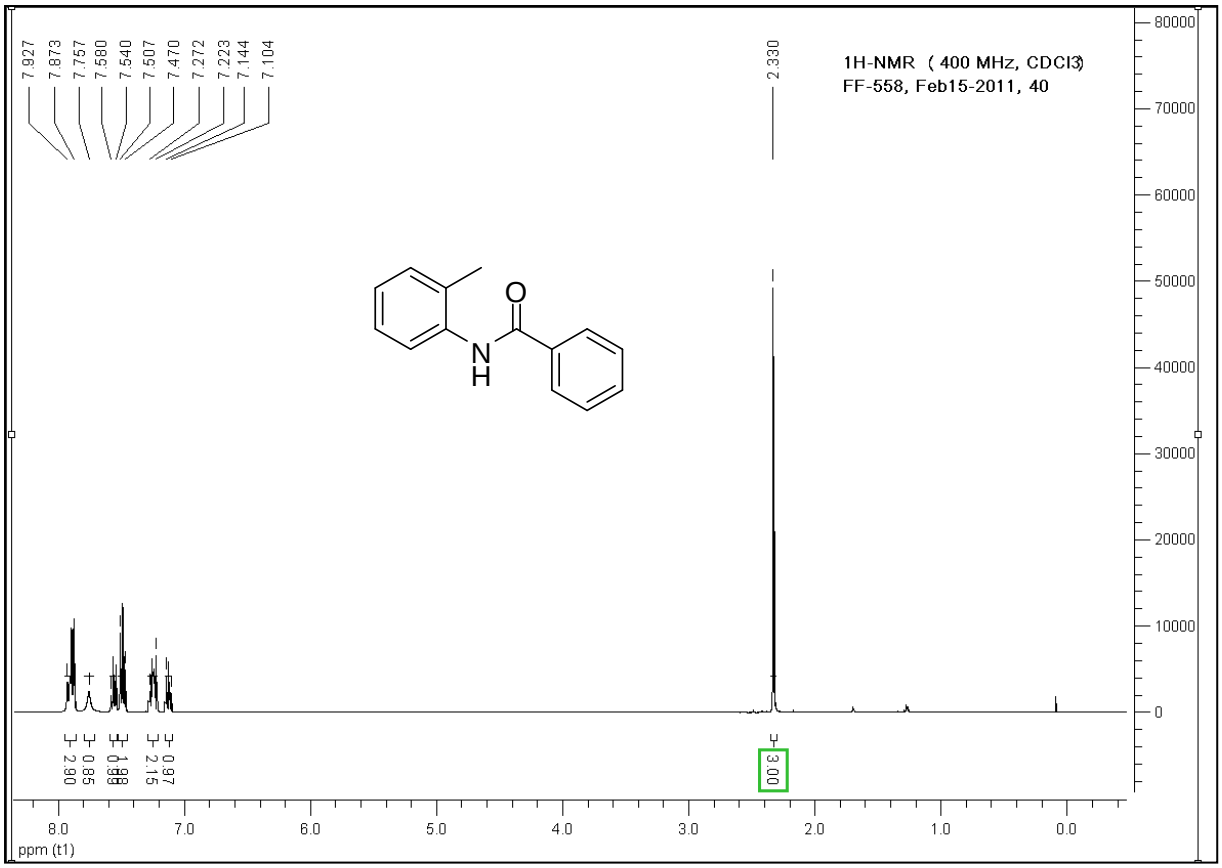

165.613
158.617
135.023
131.665
130.991
128.716
126.962
122.098
114.221
55.488
13-NMR (100 MHz, CDCl3)
FF-555, Feb15-2011, 71
MeO
O
N
H
150
100
50
0
ppm (t1)
40000
30000
20000
10000
0

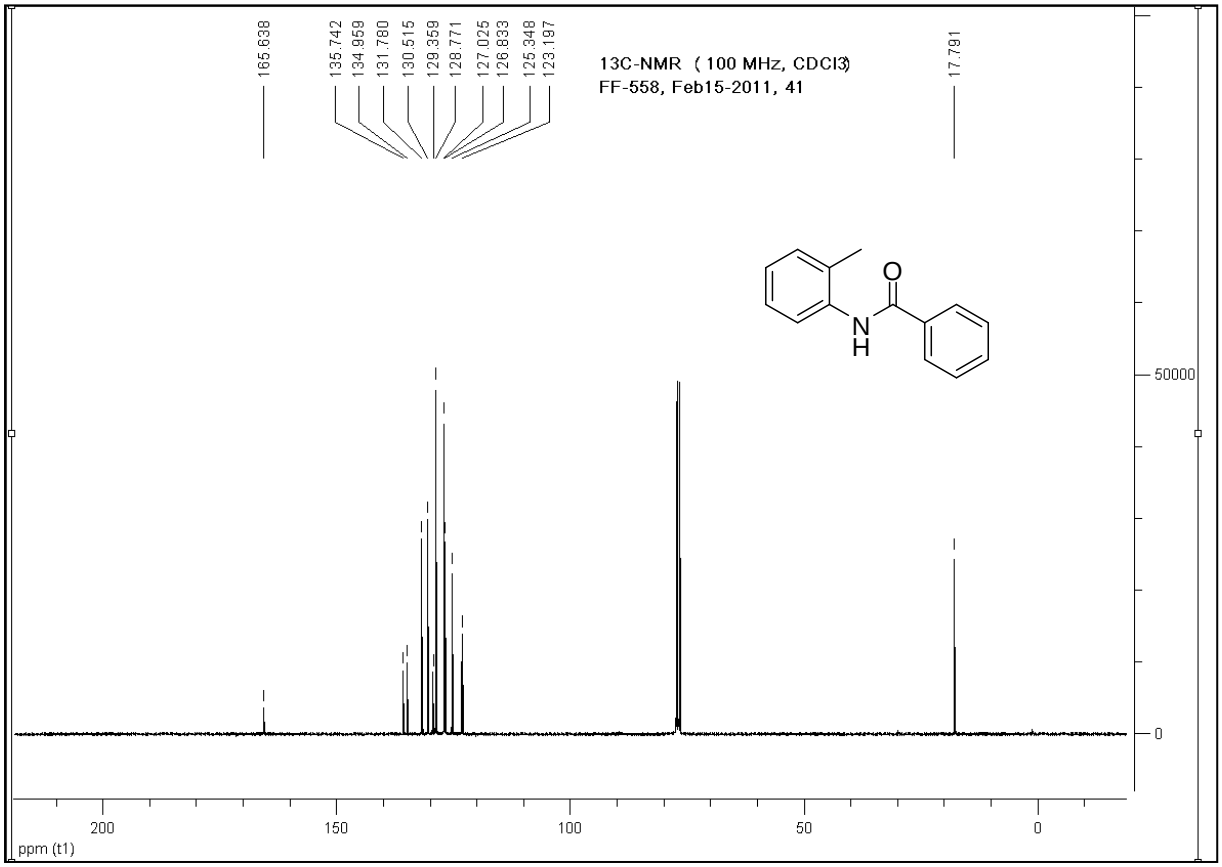

7.574
7.393
7.371
7.260
6.839
6.816
3.770
2.125
1H-NMR (400 MHz, CDCl3)
FF-519, Feb15-2011, 60
MeO
O
N
H
0.86
2.00
1.97
3.02
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
60000
50000
40000
30000
20000
10000
0

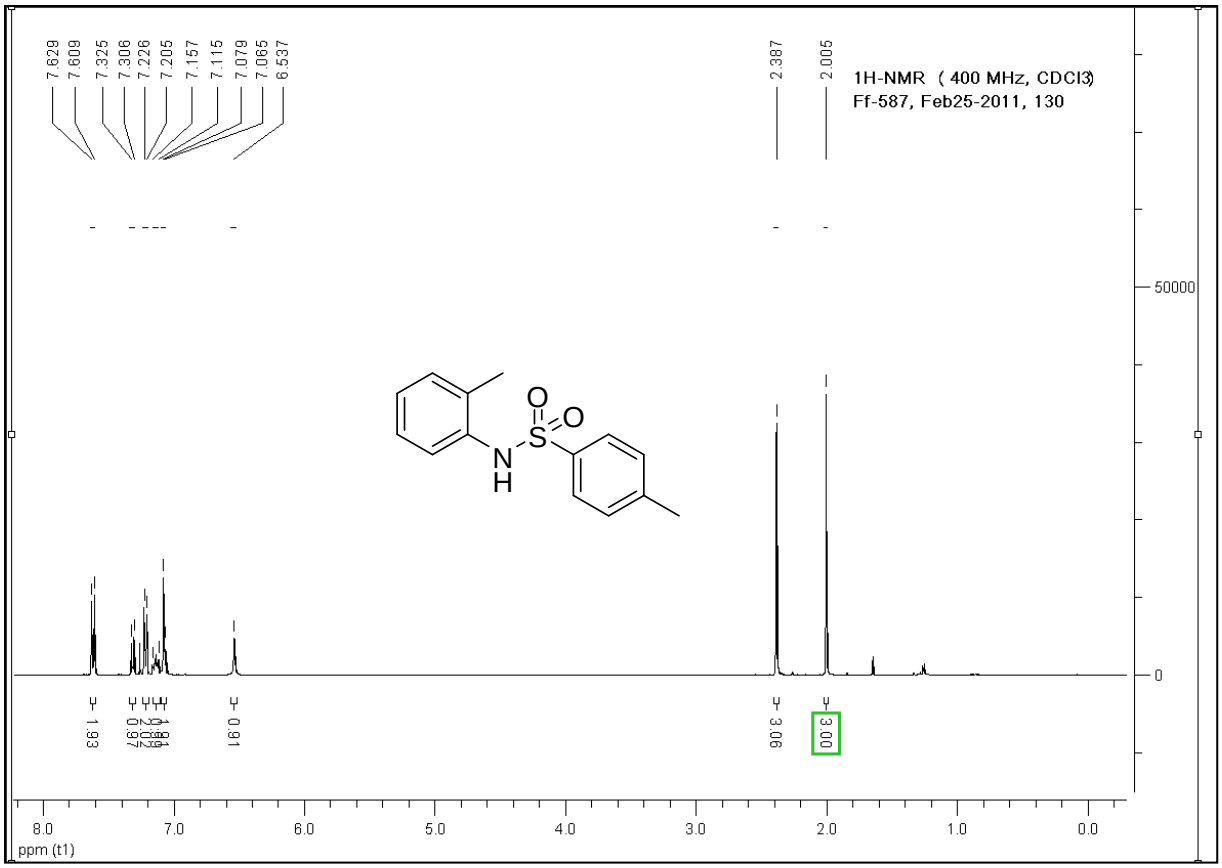

168.405
156.367
131.018
121.950
114.045
55.419
24.219
13C-NMR (100 MHz, CDCl3)
FF-519, Feb15-2011, 61
MeO
O
N
H
200
150
100
50
0
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0

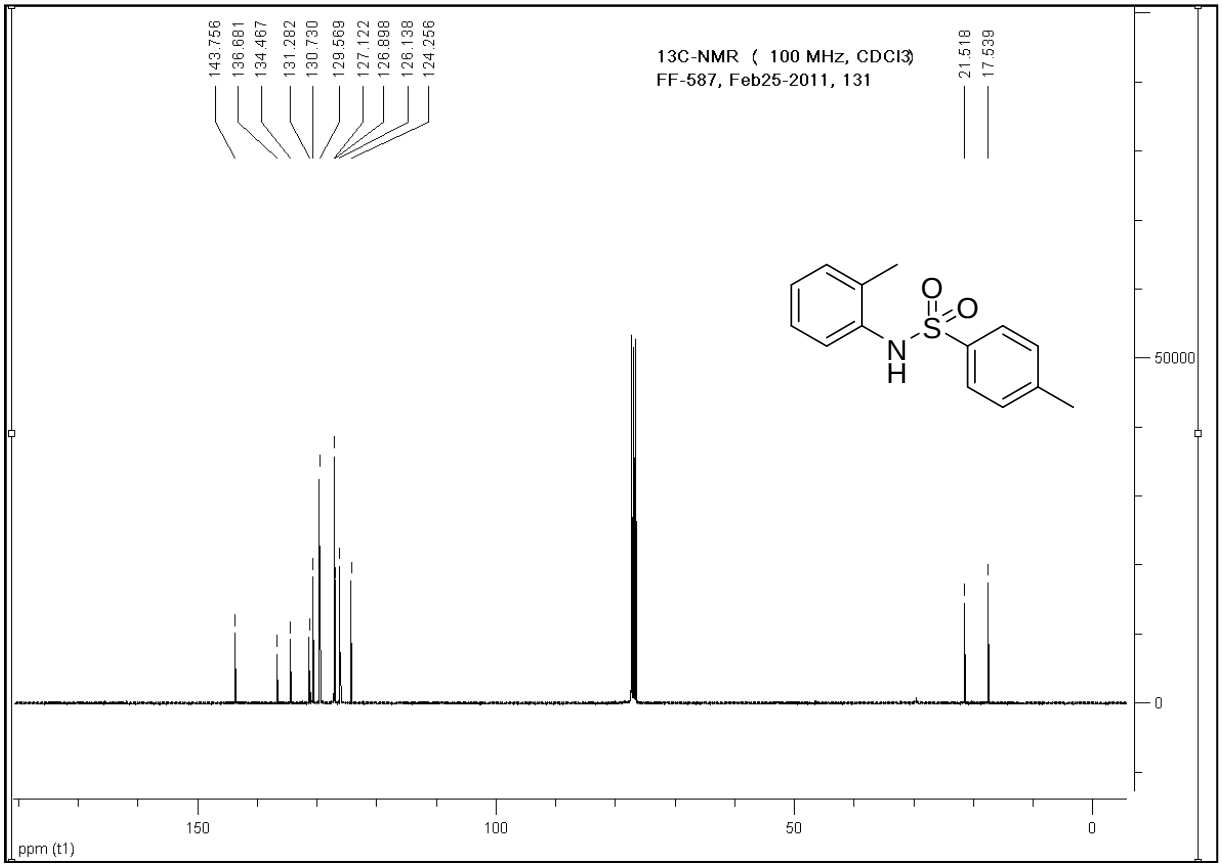

7.482
7.470
7.260
6.888
6.875
3.824
3.807
3.789
3.782
2.592
2.572
2.551
2.169
2.093
1H-NMR (400 MHz, CDCl3)
FF-506, Feb15-2011, 30
MeO
O
N
50000
0
2.00
2.00
5.15
2.04
2.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

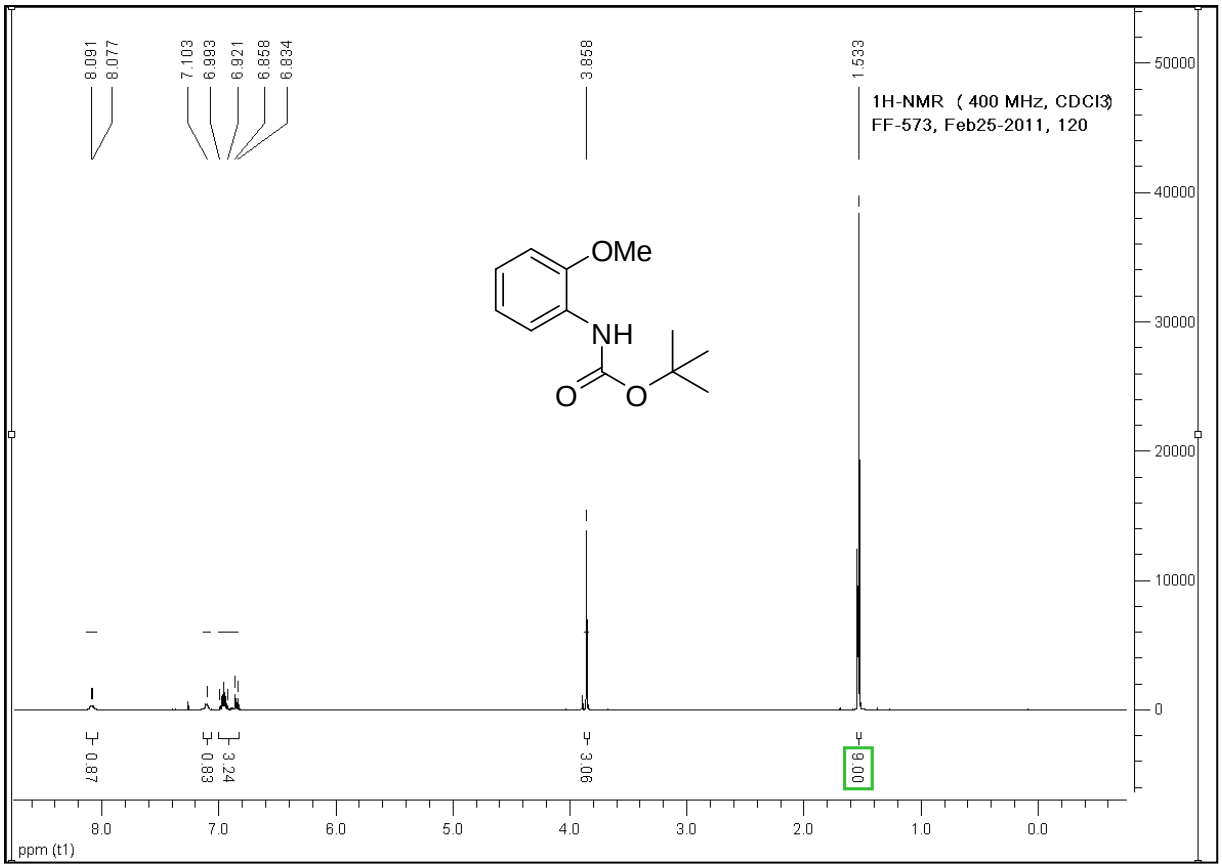

173.827
156.481
132.575
121.741
113.957
55.389
49.104
32.397
17.951
13C-NMR (100 MHz, CDCl3)
FF-506, Feb15-2011, 31
MeO
O
N
10000
50000
0
200
150
100
50
0
ppm (t1)

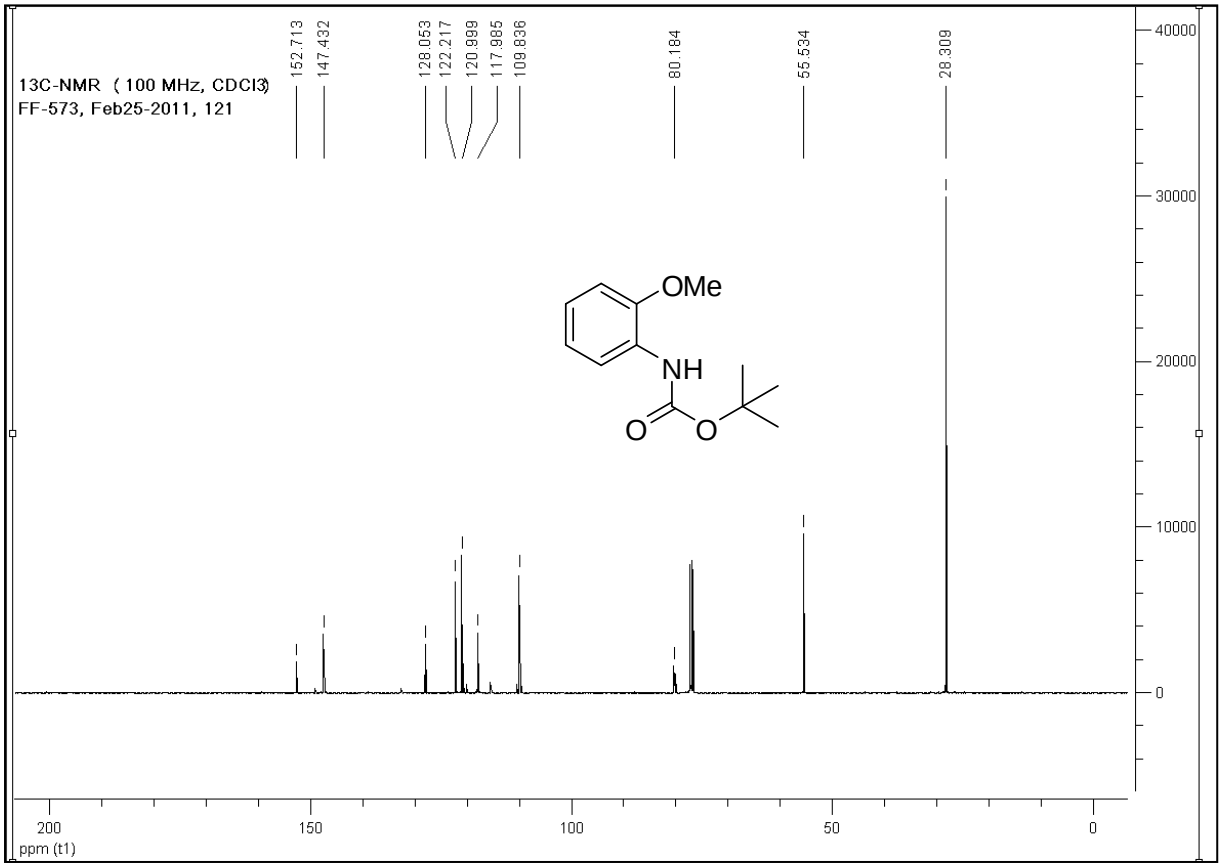

7.927
7.873
7.757
7.580
7.540
7.507
7.470
7.272
7.223
7.144
7.104
2.330
1H-NMR (400 MHz, CDCl3)
FF-558, Feb15-2011, 40
O
N
H
2.90
0.86
0.88
0.88
2.15
0.97
3.00
80000
70000
60000
50000
40000
30000
20000
10000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

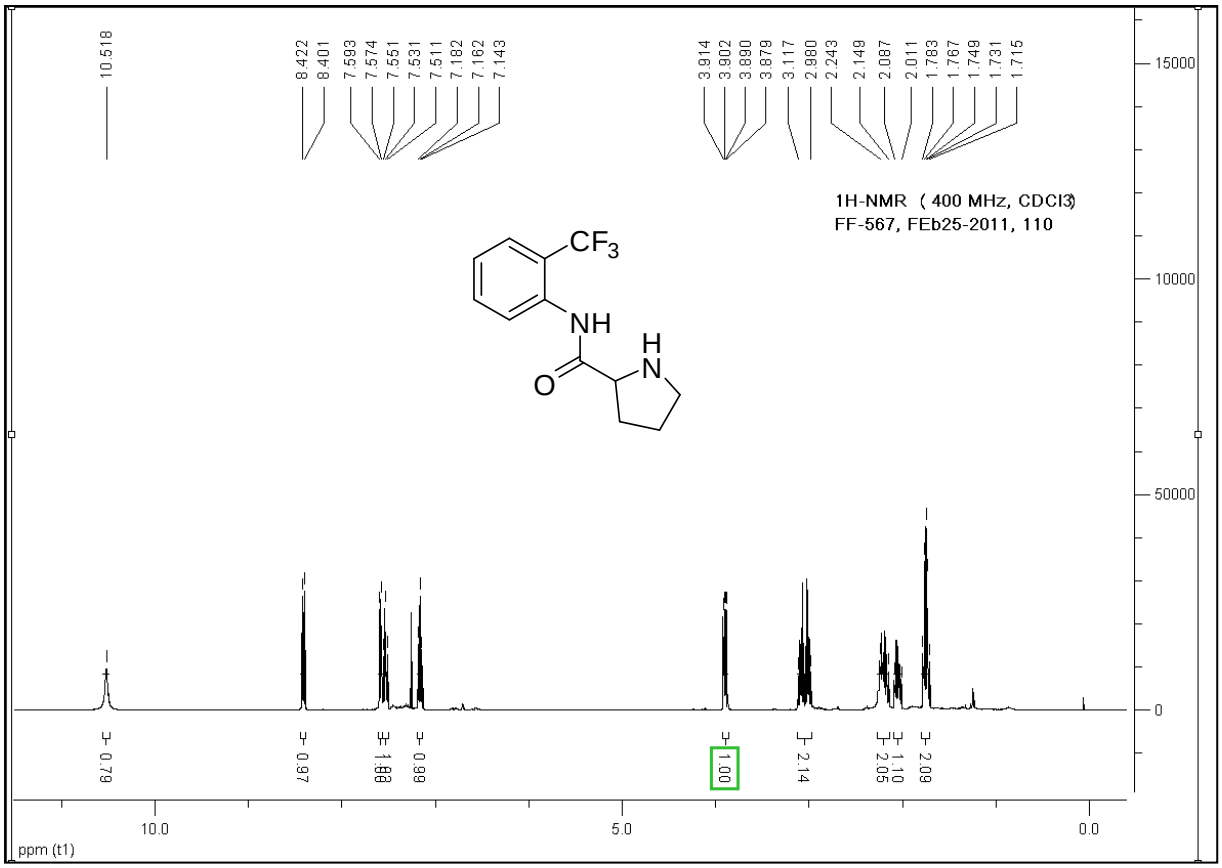

165.638
135.742
134.959
131.780
130.515
129.359
128.771
127.025
126.833
125.348
123.197
17.791
13C-NMR (100 MHz, CDCl3)
FF-558, Feb15-2011, 41
O
N
H
50000
0
200
150
100
50
0
ppm (t1)

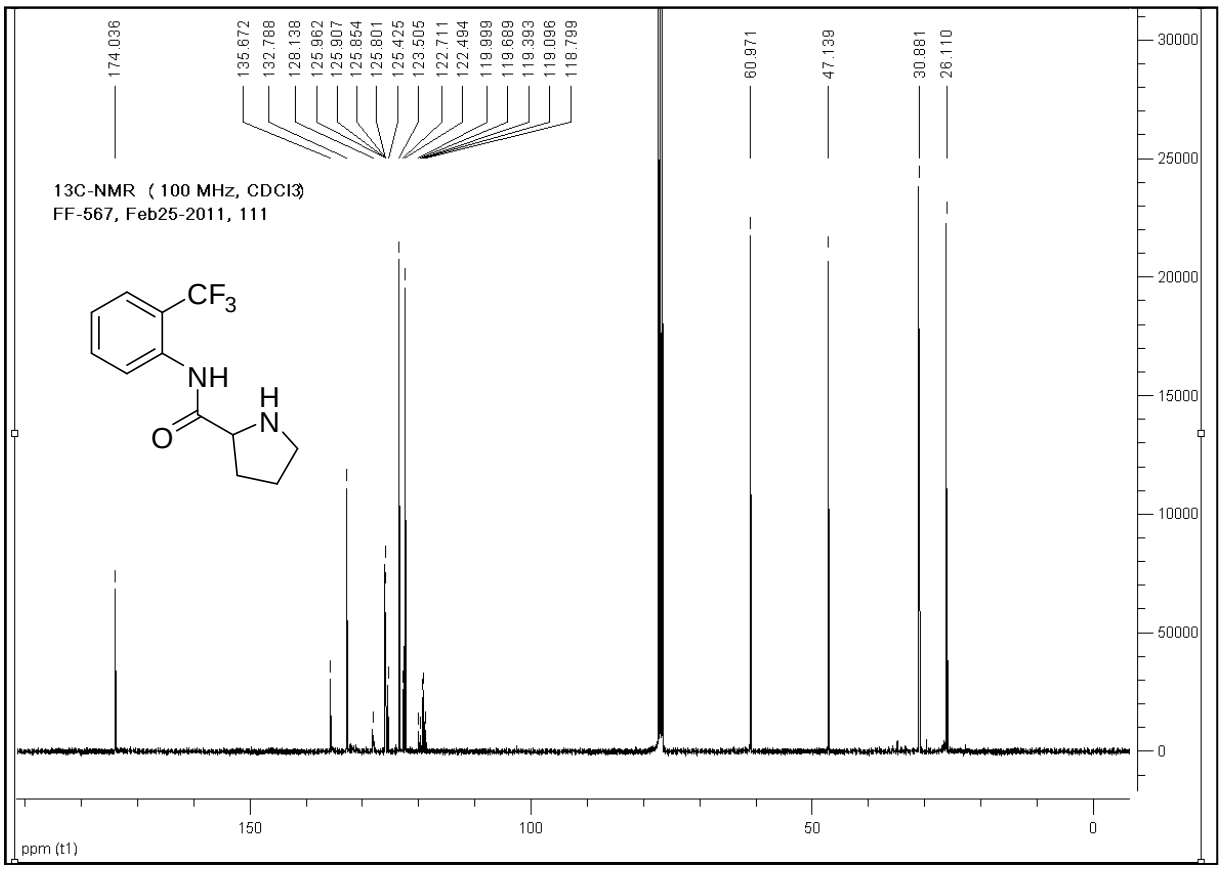

7.629
7.609
7.325
7.306
7.226
7.205
7.157
7.115
7.079
7.065
6.537
2.387
2.005
1H-NMR (400 MHz, CDCl3)
Ff-587, Feb25-2011, 130
50000
0
1.93
0.97
0.91
3.06
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

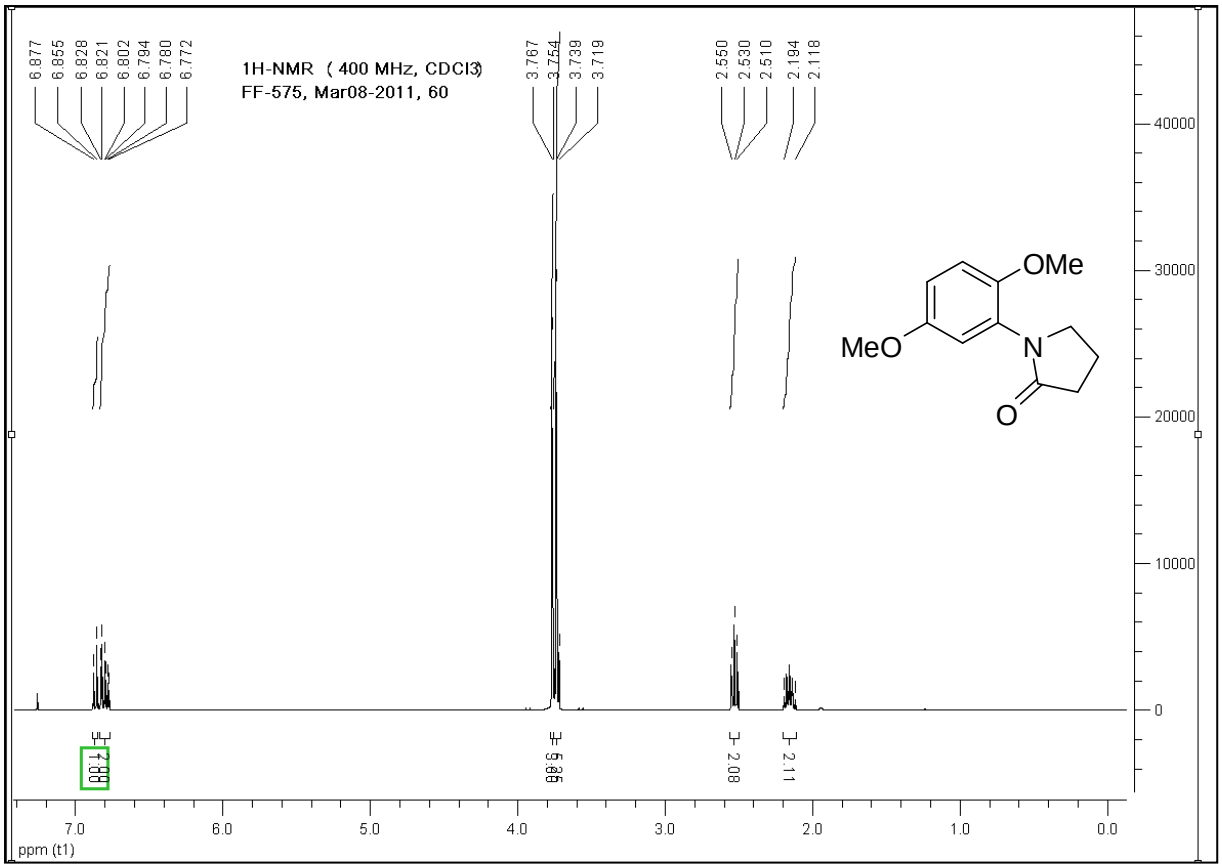

143.756
136.681
134.467
131.282
130.730
129.569
127.122
126.898
126.138
124.256
21.518
17.539
13C-NMR (100 MHz, CDCl3)
FF-587, Feb25-2011, 131
50000
0
150
100
50
0
ppm (t1)

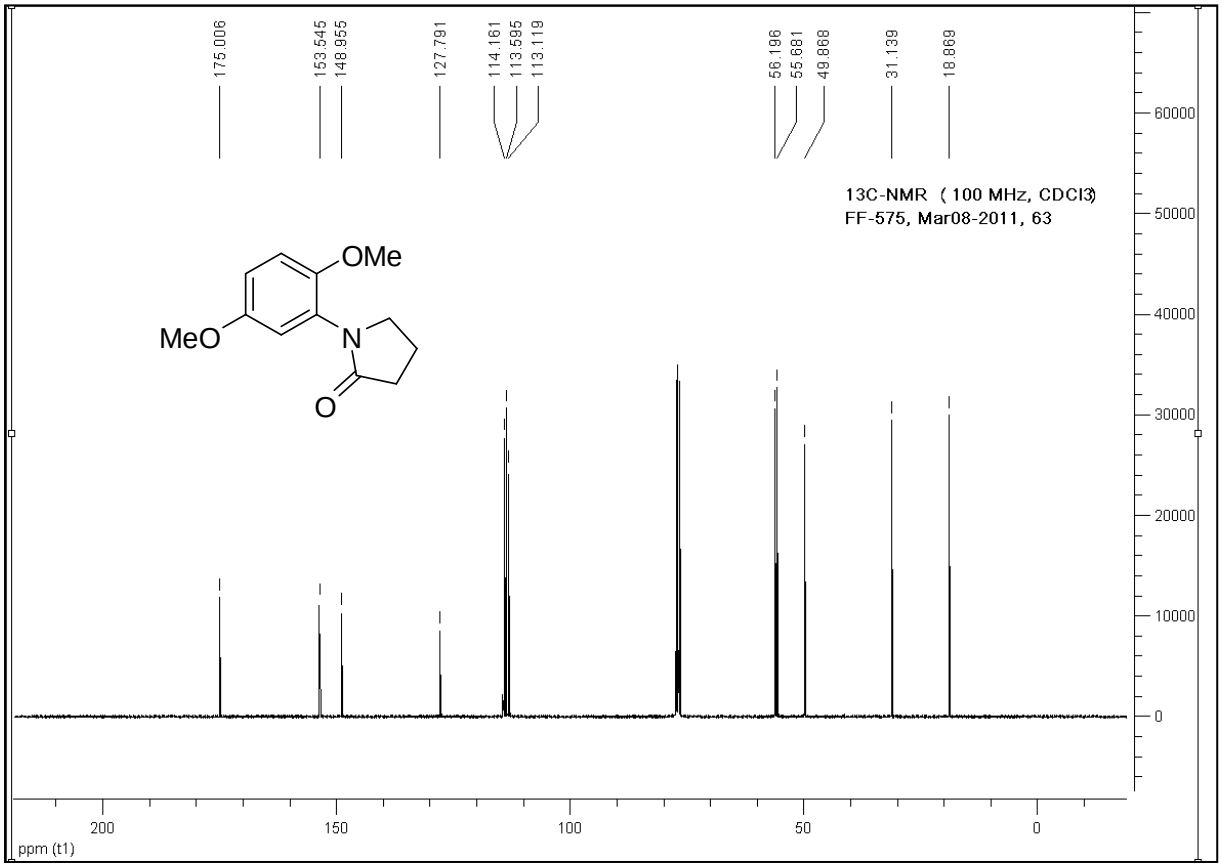

8.091
8.077
7.103
6.993
6.921
6.858
6.834
3.858
1.533
1H-NMR (400 MHz, CDCl3)
FF-573, Feb25-2011, 120
OMe
NH
O
O
0.87
0.88
2.24
3.06
9.00
ppm (t1)

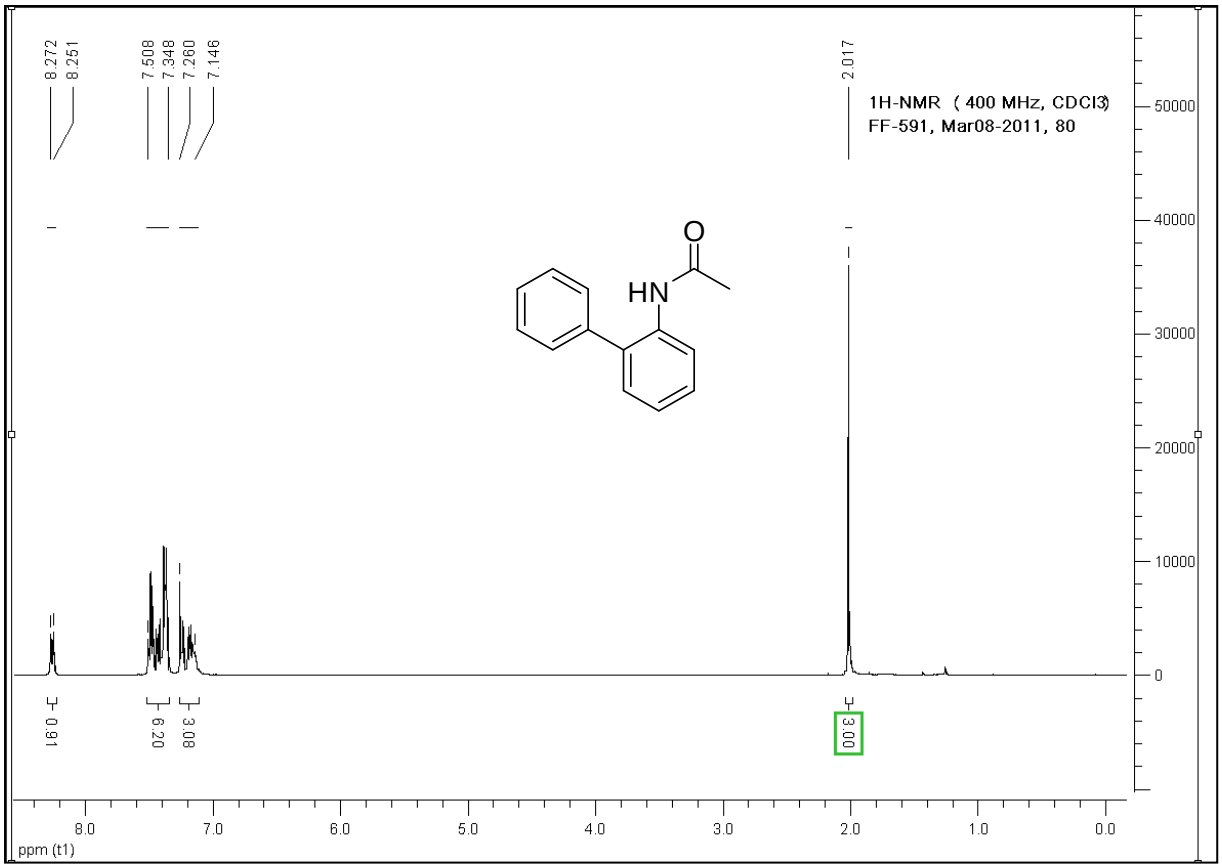

152.713
147.432
128.053
122.217
120.998
117.985
108.836
80.184
55.534
28.309
13C-NMR (100 MHz, CDCl3)
FF-573, Feb25-2011, 121
OMe
NH
O
O
ppm (t1)

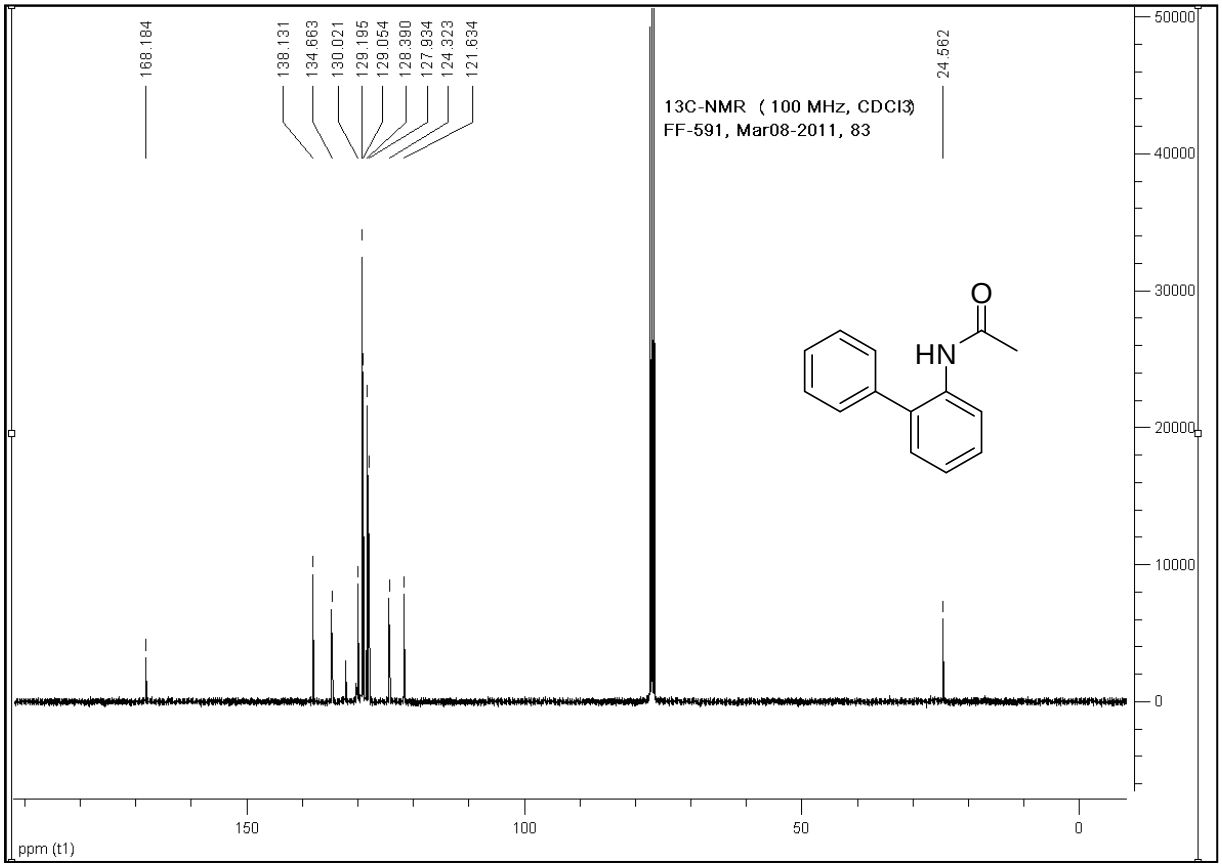

10.518
8.422
8.401
7.593
7.574
7.551
7.531
7.511
7.182
7.162
7.143
3.914
3.902
3.890
3.879
3.117
2.980
2.243
2.149
2.087
2.011
1.783
1.767
1.749
1.731
1.715
1H-NMR (400 MHz, CDCl3)
FF-567, FEb25-2011, 110
CF3
NH
H
N
O
0.79
0.97
1.88
0.98
1.00
2.14
2.05
1.10
2.09
15000
10000
50000
0
10.0
5.0
0.0
ppm (t1)

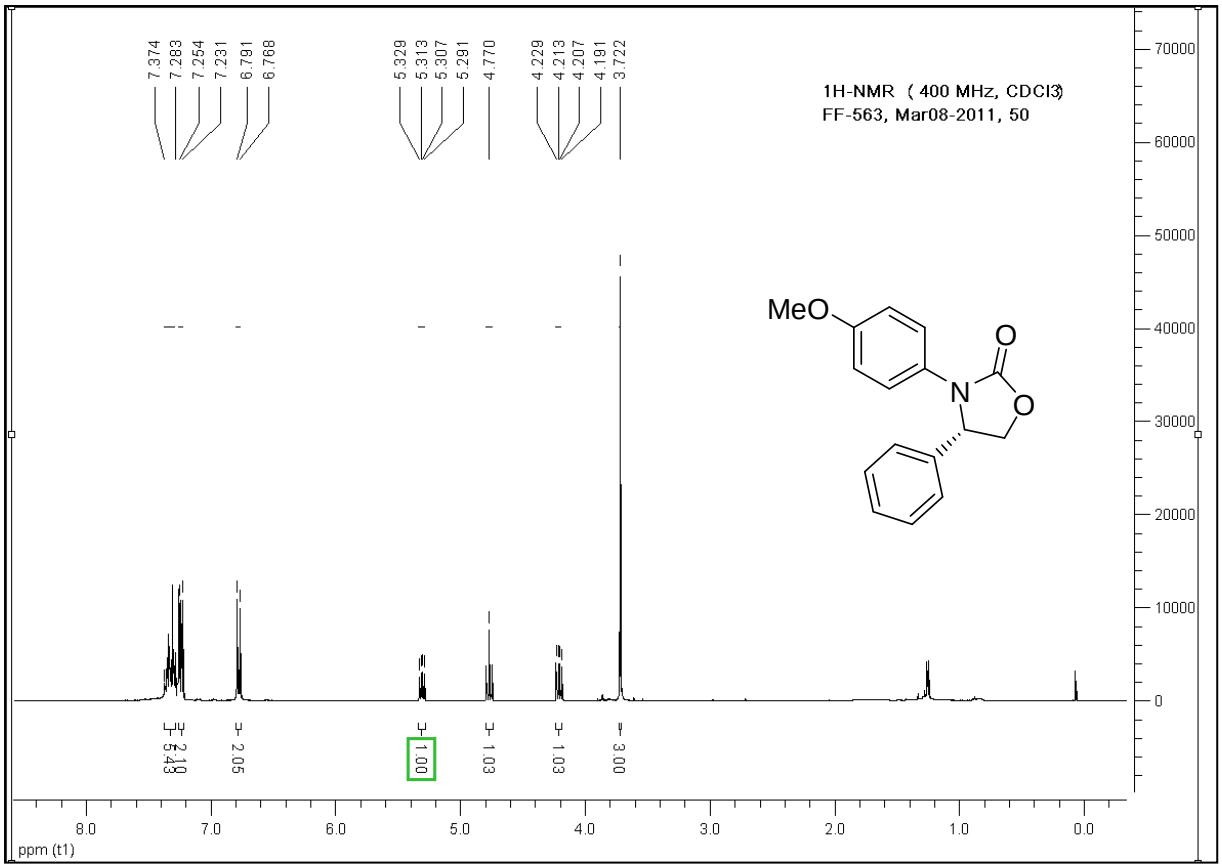

174.036
135.672
132.788
128.138
125.962
125.907
125.854
125.801
125.425
123.505
122.711
122.494
119.999
119.889
119.393
119.096
118.799
60.971
47.139
30.881
26.110
13C-NMR (100 MHz, CDCl3)
FF-567, Feb25-2011, 111
CF3
NH
H
N
O
30000
25000
20000
15000
10000
50000
0
150
100
50
0
ppm (t1)

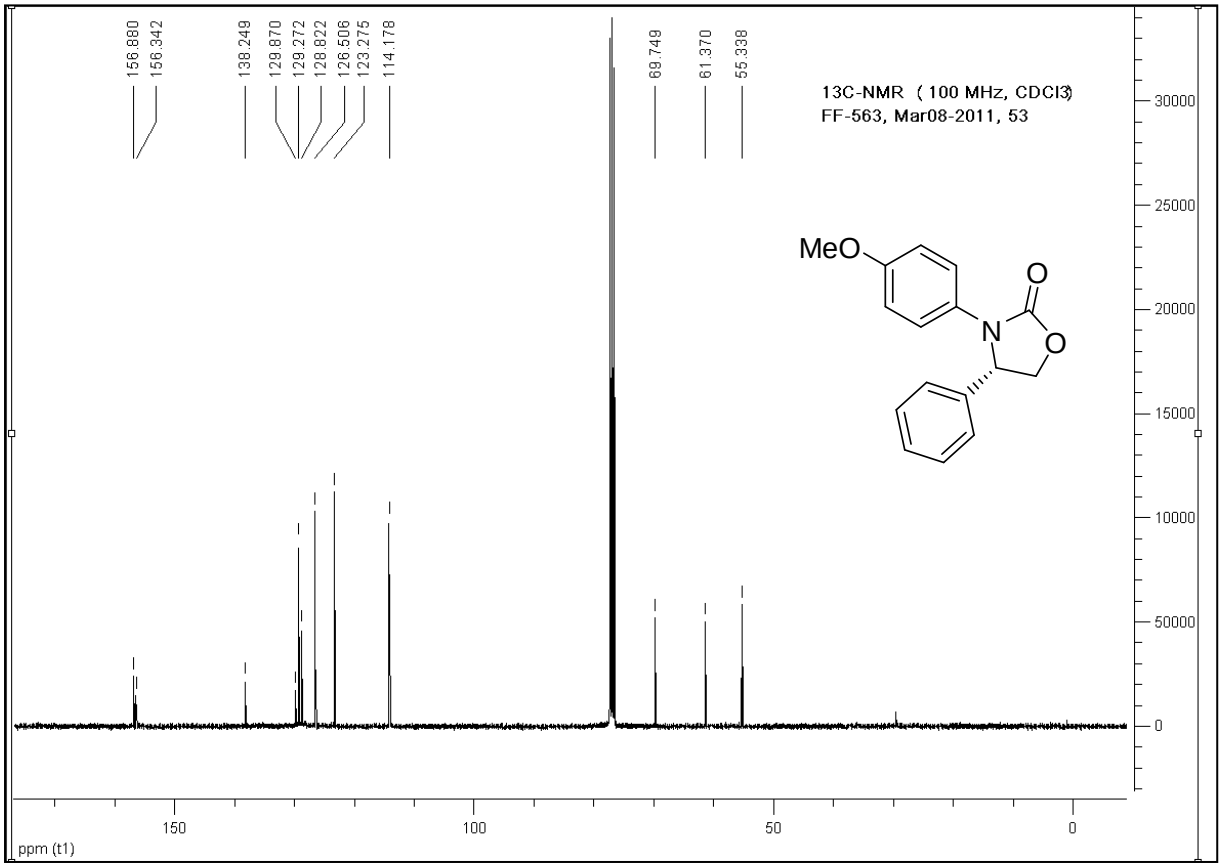

1H-NMR (400 MHz, CDCl3)
FF-575, Mar08-2011, 60
6.877
6.855
6.828
6.821
6.802
6.794
6.780
6.772
3.767
3.754
3.739
3.719
2.550
2.530
2.510
2.194
2.118
OMe
MeO
N
O
1.00
3.86
2.08
2.11
ppm (t1)

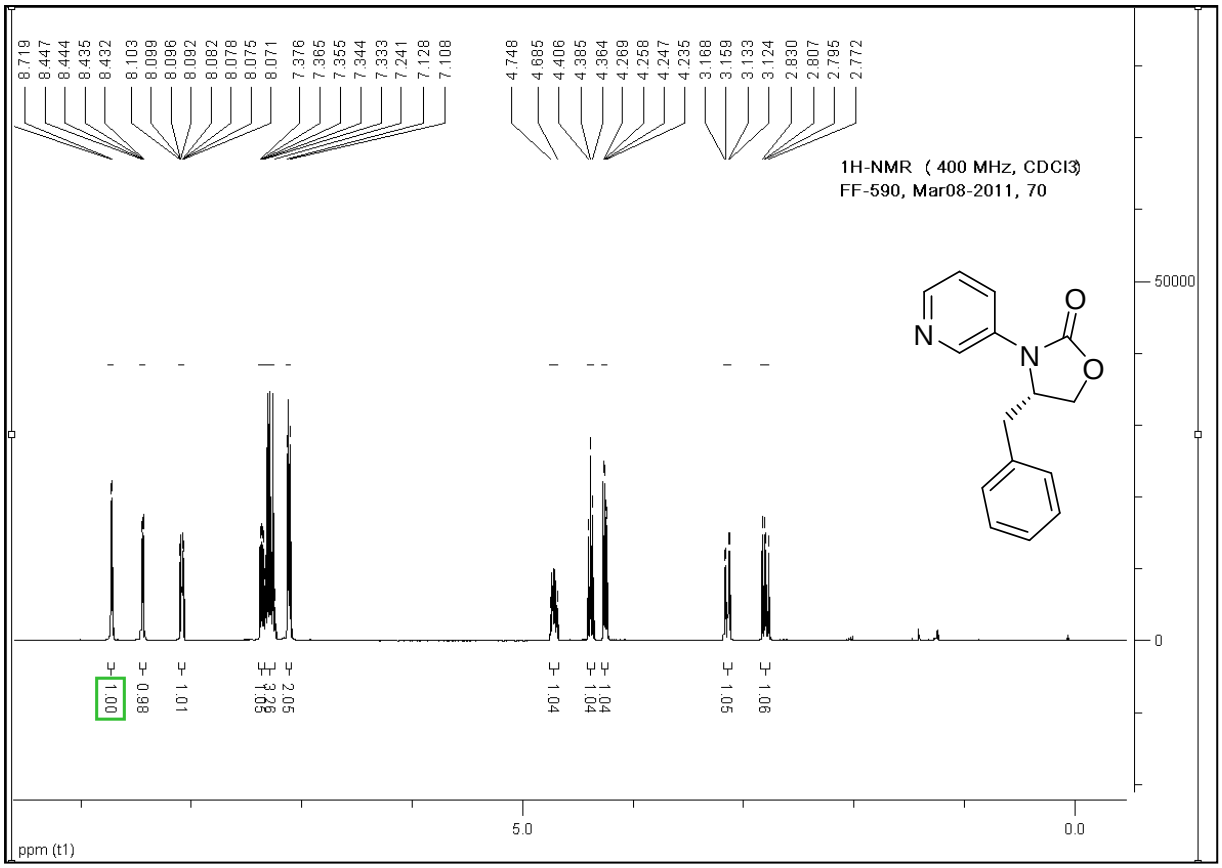

175.006
153.545
148.955
127.791
114.161
113.595
113.119
56.196
55.681
49.868
31.139
18.869
13C-NMR (100 MHz, CDCl3)
FF-575, Mar08-2011, 63
OMe
MeO
N
O
ppm (t1)

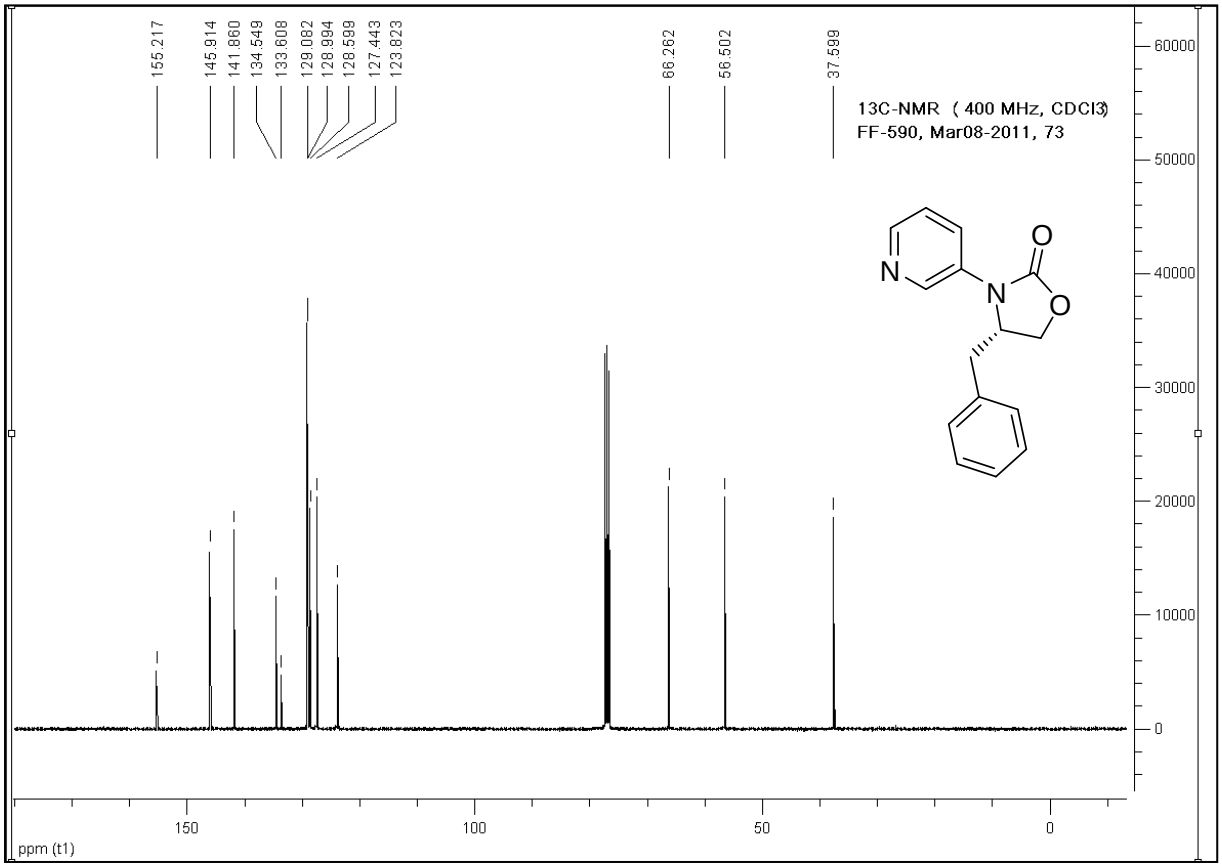

8.272
8.251
7.508
7.348
7.260
7.146
2.017
1H-NMR (400 MHz, CDCl3)
FF-591, Mar08-2011, 80
O
HN
0.91
6.20
3.08
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
50000
40000
30000
20000
10000
0

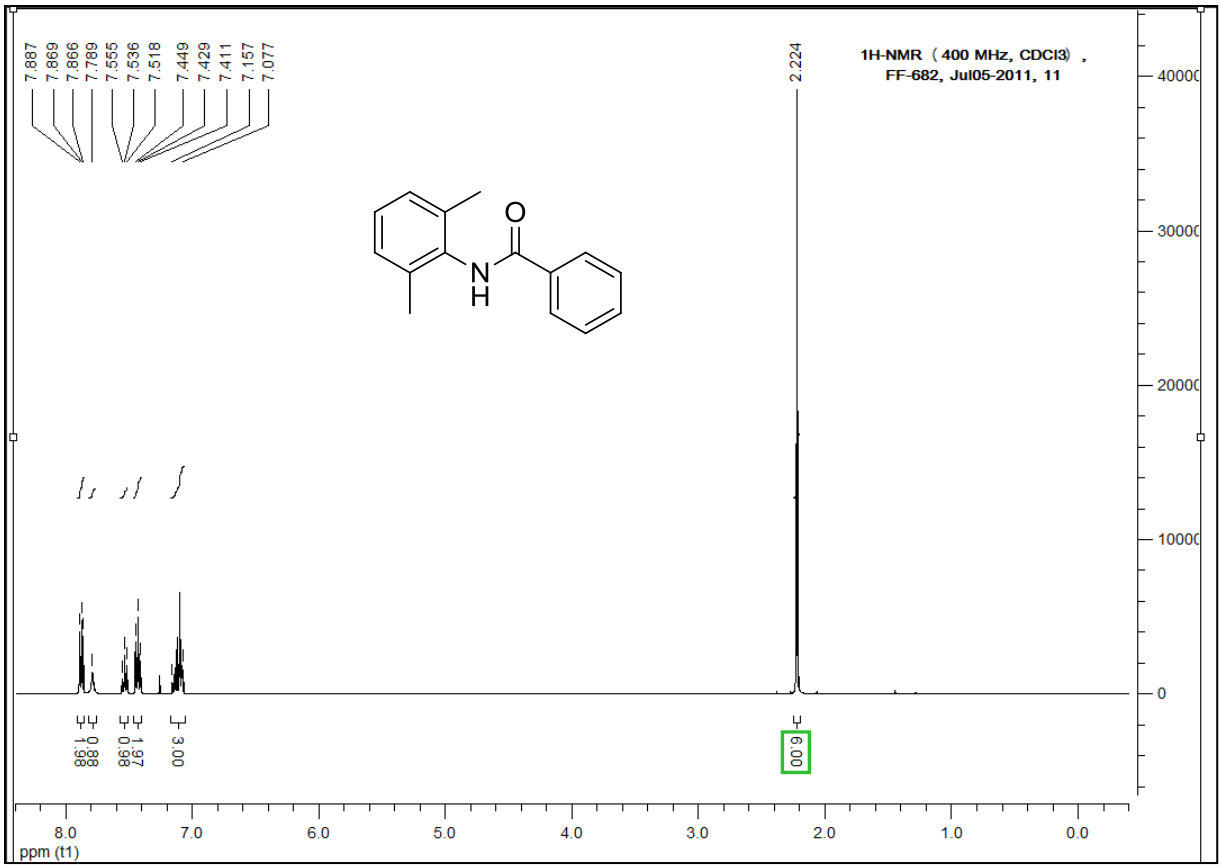

168.184
138.131
134.663
130.021
129.195
129.054
128.390
127.934
124.323
121.634
24.562
13C-NMR (100 MHz, CDCl3)
FF-591, Mar08-2011, 83
O
HN
150
100
50
0
ppm (t1)
50000
40000
30000
20000
10000
0

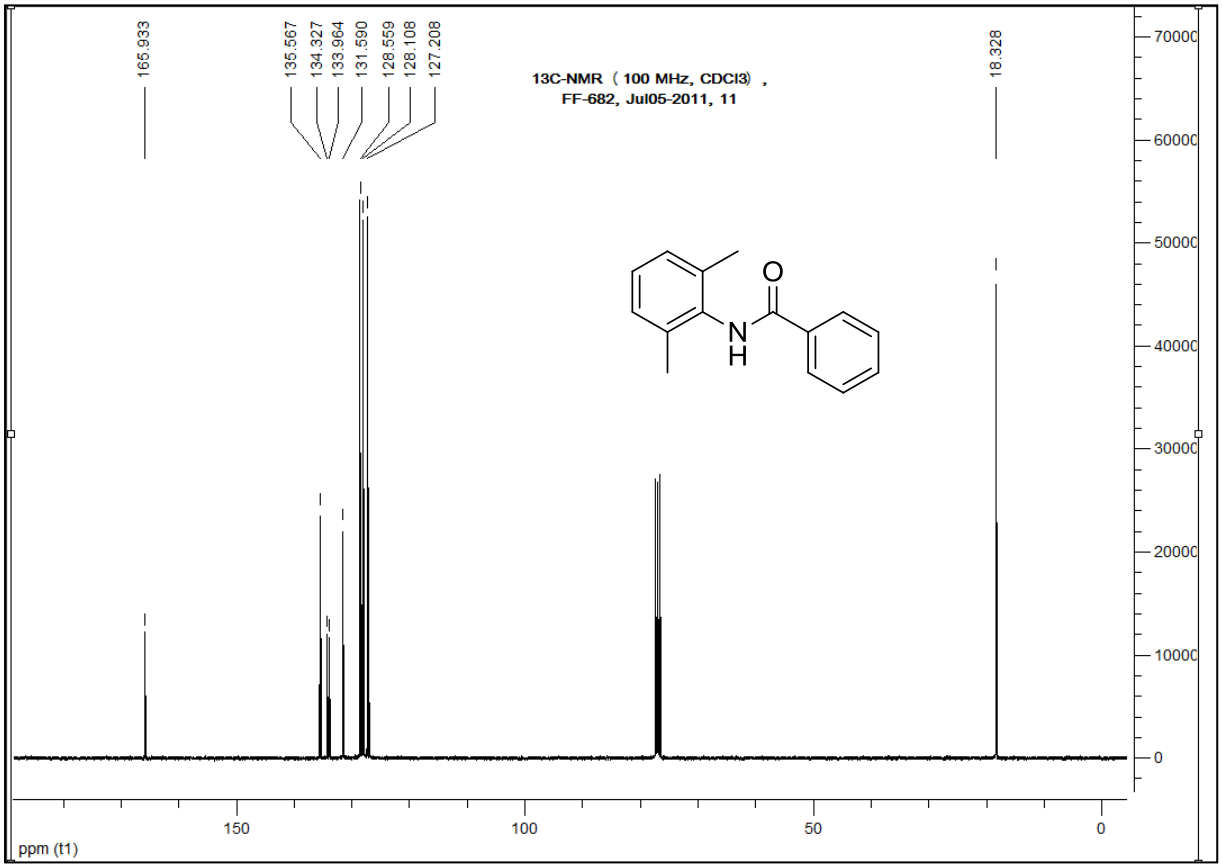

7.374
7.283
7.254
7.231
6.791
6.768
5.329
5.313
5.307
5.291
4.770
4.229
4.213
4.207
4.191
3.722
1H-NMR (400 MHz, CDCl3)
FF-563, Mar08-2011, 50
MeO
O
N
O
2.10
2.05
1.00
1.03
1.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
70000
60000
50000
40000
30000
20000
10000
0

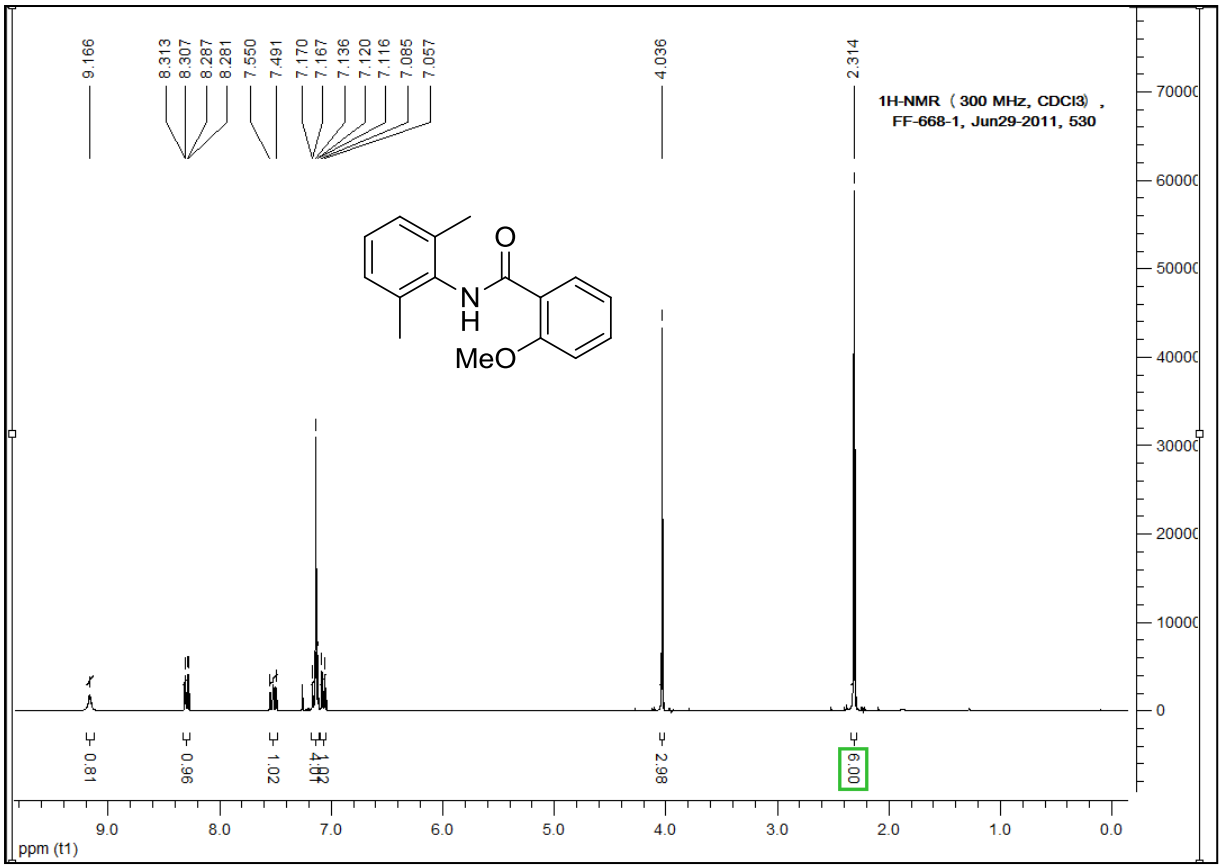

156.880
156.342
138.249
129.870
129.272
128.822
126.506
123.275
114.178
69.749
61.370
55.338
13C-NMR (100 MHz, CDCl3)
FF-563, Mar08-2011, 53
MeO
O
N
O
150
100
50
0
ppm (t1)
30000
25000
20000
15000
10000
50000
0

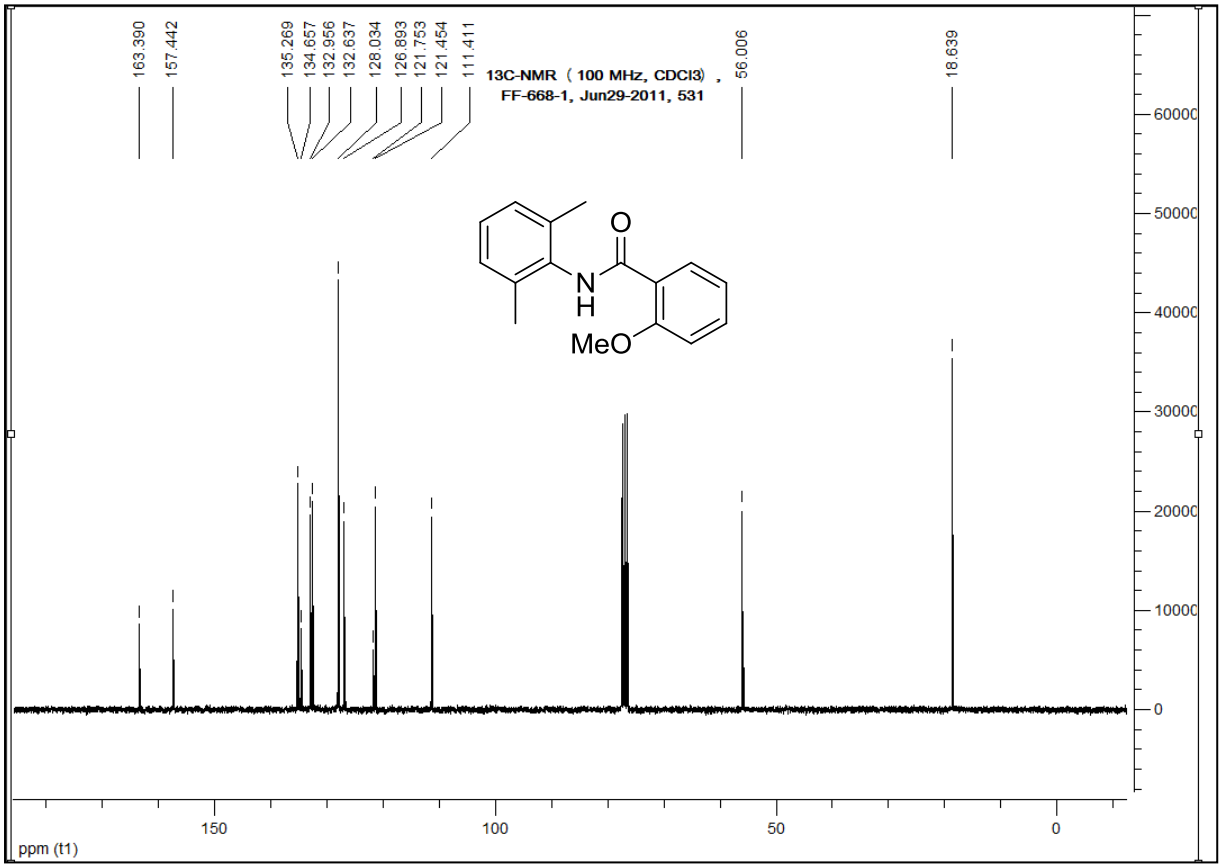

8.719
8.447
8.444
8.435
8.432
8.103
8.099
8.096
8.092
8.082
8.078
8.075
8.071
7.376
7.365
7.355
7.344
7.333
7.241
7.128
7.108
4.748
4.685
4.406
4.385
4.364
4.269
4.258
4.247
4.235
3.168
3.159
3.133
3.124
2.830
2.807
2.795
2.772
1H-NMR (400 MHz, CDCl3)
FF-590, Mar08-2011, 70
1.00
0.98
1.01
3.28
3.05
2.05
1.04
1.04
1.04
1.05
1.06
50000
0
5.0
0.0
ppm (t1)

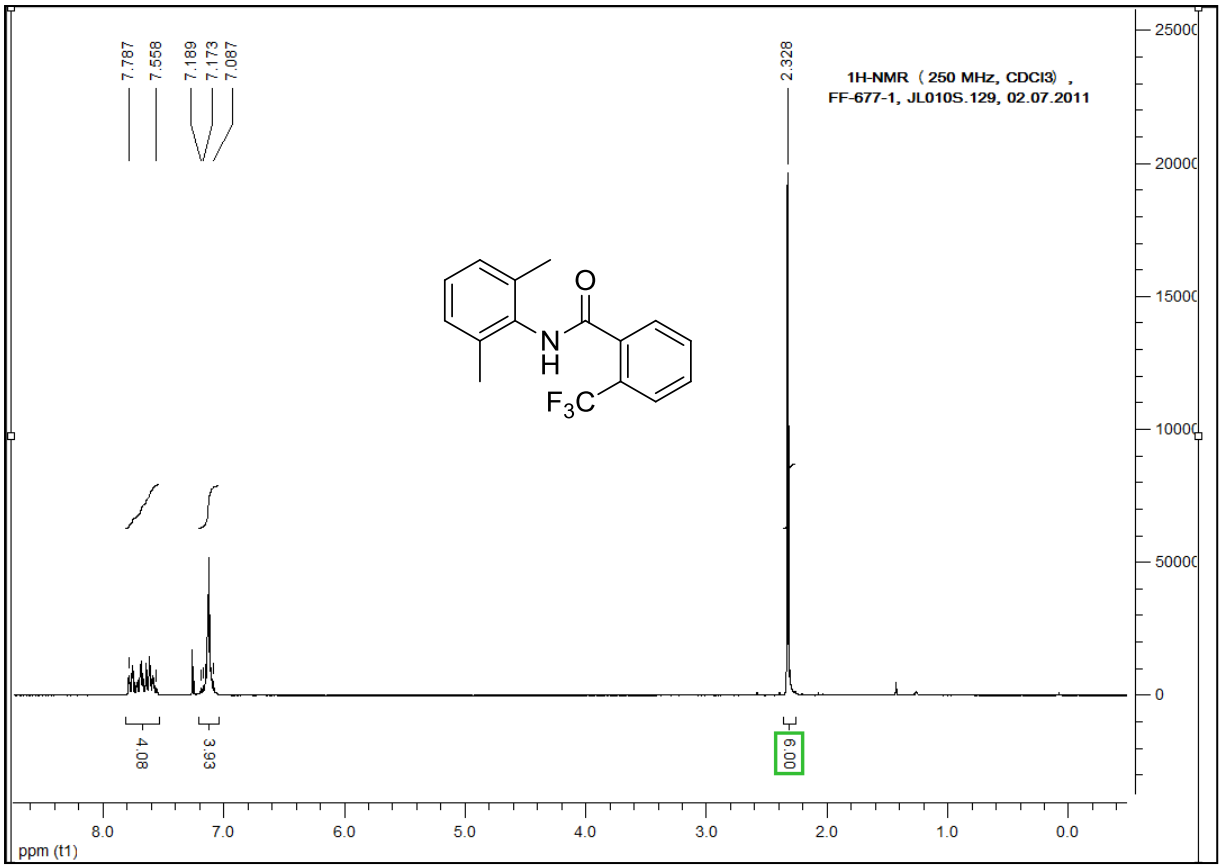

155.217
145.914
141.860
134.549
133.608
129.082
128.994
128.599
127.443
123.823
66.262
56.502
37.599
13C-NMR (400 MHz, CDCl3)
FF-590, Mar08-2011, 73
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

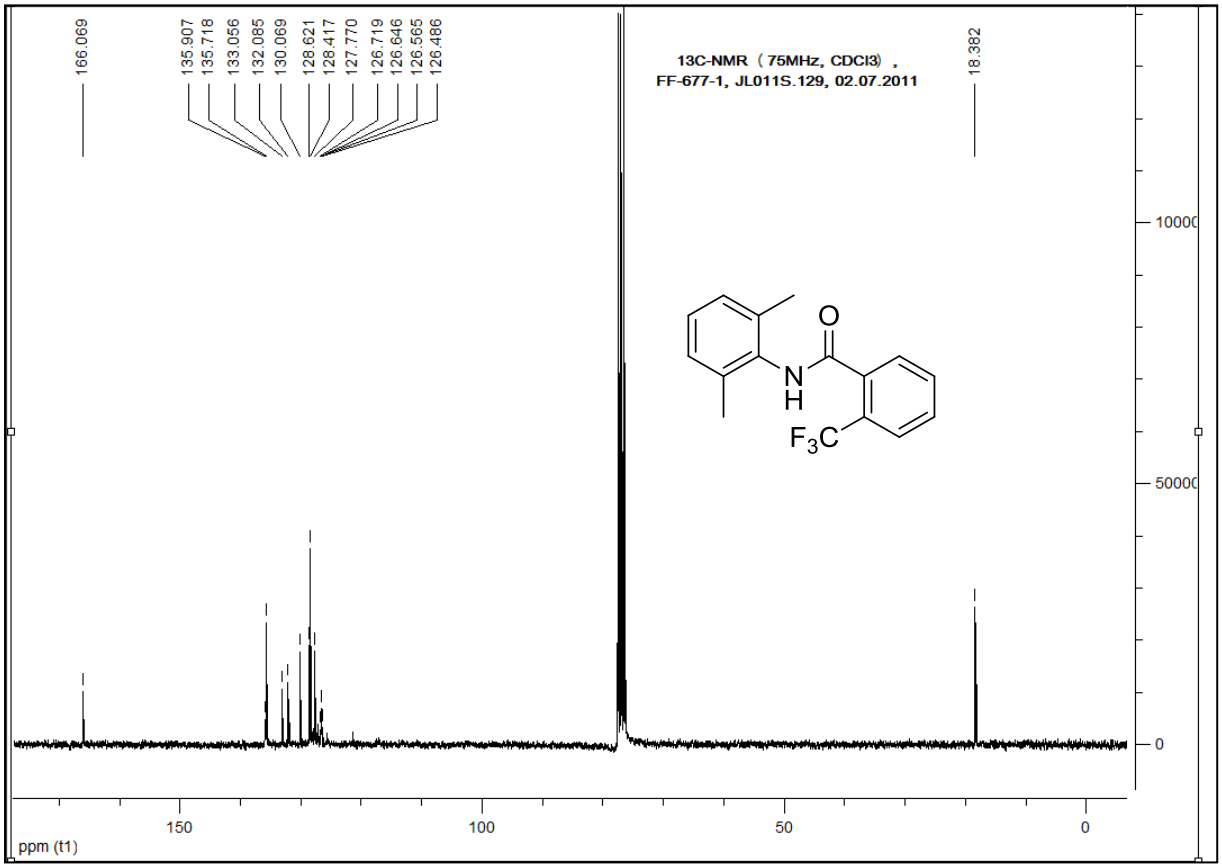

7.887
7.869
7.866
7.789
7.555
7.536
7.518
7.449
7.429
7.411
7.157
7.077
2.224
1H-NMR（400 MHz, CDCl3），
FF-682, Jul05-2011, 11
O
N
H
0.88
1.98
1.97
0.98
3.00
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

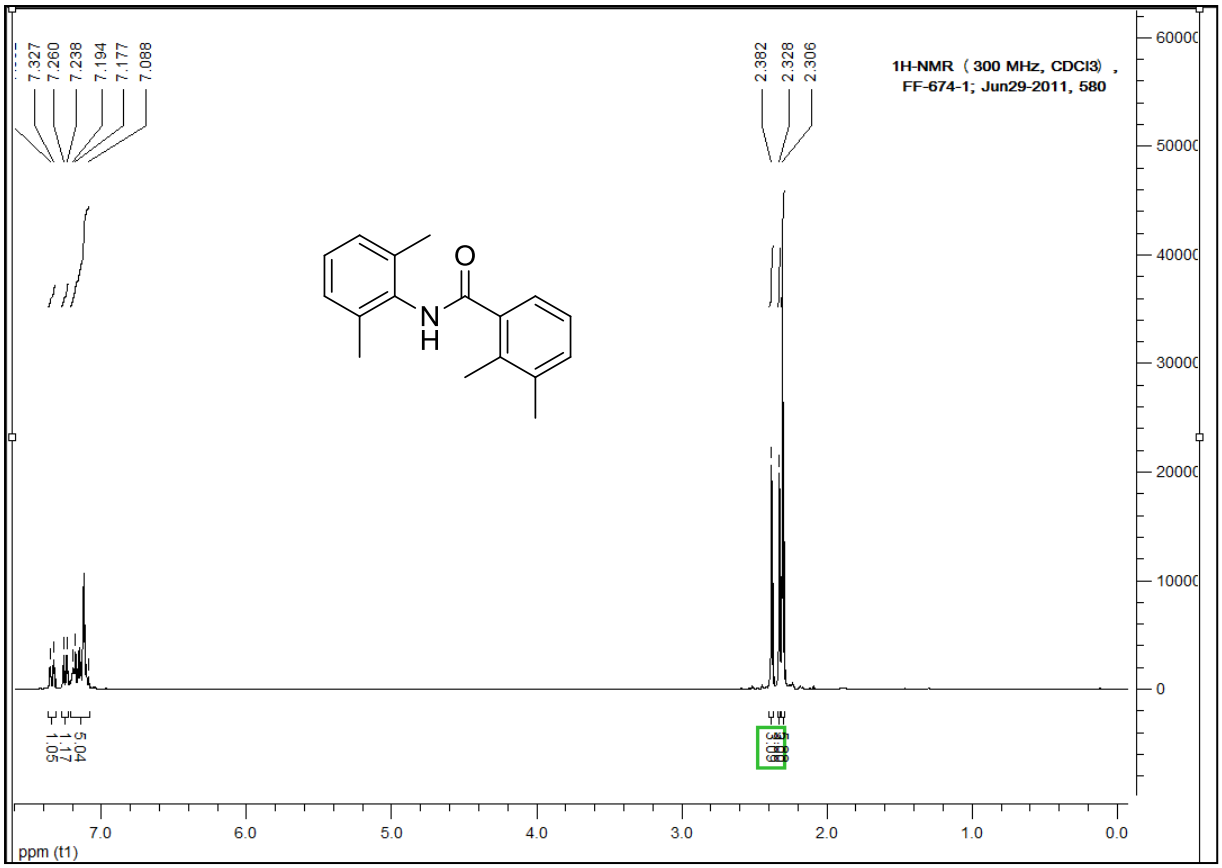

165.933
135.567
134.327
133.964
131.590
128.559
128.108
127.208
18.328
13C-NMR（100 MHz, CDCl3），
FF-682, Jul05-2011, 11
O
N
H
150
100
50
0
ppm (t1)

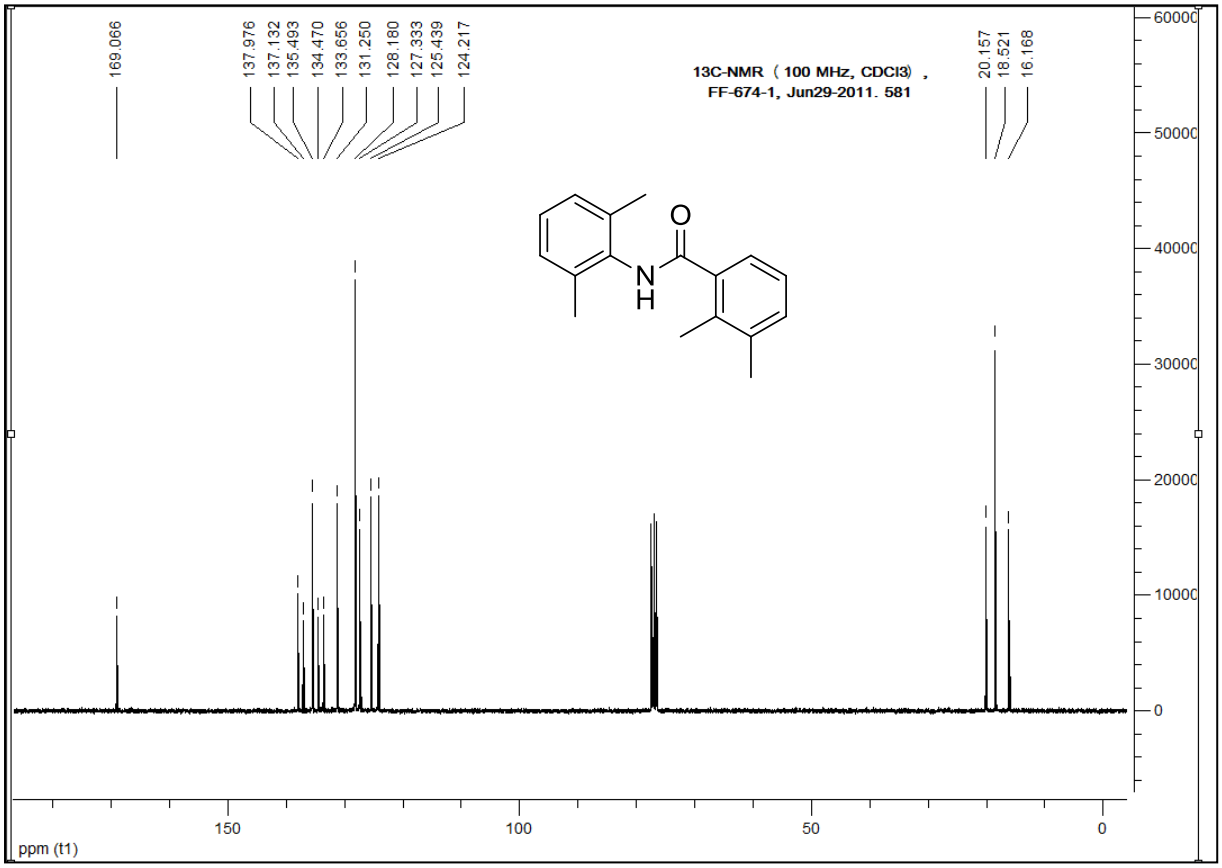

9.166
8.313
8.307
8.287
8.281
7.550
7.491
7.170
7.167
7.136
7.120
7.116
7.085
7.057
4.036
2.314
1H-NMR （300 MHz, CDCl3），
FF-668-1, Jun29-2011, 530
O
N
H
MeO
0.81
0.96
1.02
4.12
2.98
6.00
ppm (t1)


163.390
157.442
135.269
134.657
132.956
132.637
128.034
126.893
121.753
121.454
111.411
56.006
18.639
13C-NMR （100 MHz, CDCl3），
FF-668-1, Jun29-2011, 531
O
N
H
MeO
ppm (t1)


7.787
7.558
7.189
7.173
7.087
2.328
1H-NMR（250 MHz, CDCl3），
FF-677-1, JL010S.129, 02.07.2011
O
N
H
F3C
4.08
3.93
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


166.069
135.907
135.718
133.056
132.085
130.069
128.621
128.417
127.770
126.719
126.646
126.565
126.486
18.382
13C-NMR（75MHz, CDCl3），
FF-677-1, JL011S.129, 02.07.2011
O
N
H
F3C
150
100
50
0
ppm (t1)


7.327
7.260
7.238
7.194
7.177
7.088
2.382
2.328
2.306
1H-NMR （300 MHz, CDCl3），
FF-674-1; Jun29-2011, 580
O
N
H
5.04
1.17
1.05
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
ppm (t1)


169.066
137.976
137.132
135.493
134.470
133.656
131.250
128.180
127.333
125.439
124.217
20.157
18.521
16.168
13C-NMR （100 MHz, CDCl3），
FF-674-1, Jun29-2011. 581
O
N
H
150
100
50
0
ppm (t1)

Supplementary crystal structure data

Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

CCDC 816638 - 816643 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

X-ray crystal structure analysis of **3 (816643)**: formula $C_{28}H_{24}BrOP$, M = 487.35, colourless crystal 0.25 x 0.10 x 0.05 mm, a = 8.7032(2), b = 10.9880(2), c = 11.9218(3)Å, α = 82.583(1), β = 76.308(1), γ = 78.288(2)°, V = 1080.69(4) Å^3, ρ_{calc} = 1.498 g cm^{-3}, μ = 3.427 mm^{-1}, empirical absorption correction ($0.481 \leq T \leq 0.847$), Z = 2, triclinic, space group *P*1bar (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 12873 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3751 independent (R_{int} = 0.049) and 3402 observed reflections [$I \geq 2\ \sigma(I)$], 280 refined parameters, R = 0.049, wR^2 = 0.136, max. (min.) residual electron

density 0.68 (-0.95) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**
Empirical formula	C_{28} H_{24} Br O P
Formula weight	487.35
Temperature	223(2) K
Wavelength	1.54178 Å
Crystal system, space group	triclinic, P-1 (No.2)
Unit cell dimensions	a = 8.7032(2) Å α = 82.583(1)°. b = 10.9880(2) Å β = 76.308(1)°. c = 11.9218(3) Å γ = 78.288(2)°.
Volume	1080.69(4) $Å^3$
Z, Calculated density	2, 1.498 Mg/m^3
Absorption coefficient	3.427 mm^{-1}
F(000)	500
Crystal size	0.25 x 0.10 x 0.05 mm
Theta range for data collection	4.12 to 68.09°.
Limiting indices	-10<=h<=10, -12<=k<=13, -13<=l<=14
Reflections collected / unique	12873 / 3751 [R(int) = 0.049]
Completeness to theta = 68.09	94.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8473 and 0.4812
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3751 / 0 / 280
Goodness-of-fit on F^2	1.067
Final R indices [I>2σ(I)]	R1 = 0.0487, wR^2 = 0.1307
R indices (all data)	R1 = 0.0529, wR^2 = 0.1359
Largest diff. peak and hole	0.676 and -0.945 $eÅ^{-3}$

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

	x	y	z	U(eq)
Br(1)	3670(1)	7444(1)	5169(1)	49(1)
P(1)	2756(1)	7680(1)	8634(1)	26(1)
O(1)	4175(3)	6900(2)	7970(2)	34(1)
C(11)	-2258(4)	7324(3)	8357(3)	38(1)
C(12)	-1170(4)	6296(3)	8610(3)	38(1)
C(13)	444(4)	6341(3)	8466(2)	32(1)
C(14)	847(4)	7533(3)	8375(2)	28(1)
C(15)	-262(4)	8560(3)	8118(2)	30(1)
C(16)	-1754(4)	8447(3)	7963(3)	33(1)
C(17)	-2633(4)	9408(3)	7208(3)	42(1)
C(18)	-2633(5)	8914(4)	6031(3)	45(1)
C(21)	1535(4)	7110(3)	5603(3)	35(1)
C(22)	317(4)	8055(3)	5411(3)	37(1)
C(23)	-1264(4)	7868(3)	5711(3)	38(1)
C(24)	-1500(5)	6648(4)	5945(3)	44(1)
C(25)	-256(5)	5722(3)	6153(3)	45(1)
C(26)	1255(5)	5958(3)	6130(3)	39(1)
C(27)	2336(5)	5125(4)	6843(3)	51(1)
C(28)	1645(4)	5179(3)	8184(3)	40(1)
C(31)	2552(4)	7298(3)	10174(3)	29(1)
C(32)	3799(4)	6494(3)	10546(3)	34(1)
C(33)	3705(5)	6186(3)	11725(3)	44(1)
C(34)	2412(5)	6700(4)	12507(3)	44(1)
C(35)	1152(5)	7497(4)	12143(3)	44(1)
C(36)	1216(4)	7784(3)	10982(3)	38(1)
C(41)	2910(3)	9307(3)	8390(3)	28(1)
C(42)	3131(4)	9960(3)	9242(3)	36(1)
C(43)	3447(5)	11159(3)	8971(3)	42(1)
C(44)	3513(4)	11717(3)	7876(3)	40(1)
C(45)	3268(4)	11084(3)	7025(3)	39(1)
C(46)	2985(4)	9887(3)	7279(3)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Br(1)-C(21)	1.905(3)
P(1)-O(1)	1.473(2)
P(1)-C(41)	1.800(3)
P(1)-C(14)	1.802(3)
P(1)-C(31)	1.804(3)
C(11)-C(12)	1.370(5)
C(11)-C(16)	1.381(5)
C(12)-C(13)	1.385(5)
C(13)-C(14)	1.408(4)
C(13)-C(28)	1.496(5)
C(14)-C(15)	1.381(4)
C(15)-C(16)	1.385(4)
C(16)-C(17)	1.504(5)
C(17)-C(18)	1.568(5)
C(18)-C(23)	1.492(5)
C(21)-C(22)	1.364(5)
C(21)-C(26)	1.380(5)
C(22)-C(23)	1.388(5)
C(23)-C(24)	1.380(5)
C(24)-C(25)	1.373(6)
C(25)-C(26)	1.385(6)
C(26)-C(27)	1.508(5)
C(27)-C(28)	1.574(5)
C(31)-C(32)	1.376(4)
C(31)-C(36)	1.385(5)
C(32)-C(33)	1.389(5)
C(33)-C(34)	1.355(6)
C(34)-C(35)	1.377(6)
C(35)-C(36)	1.369(5)
C(41)-C(46)	1.386(4)
C(41)-C(42)	1.387(4)
C(42)-C(43)	1.383(5)
C(43)-C(44)	1.362(5)
C(44)-C(45)	1.380(5)
C(45)-C(46)	1.370(5)
O(1)-P(1)-C(41)	111.50(13)
O(1)-P(1)-C(14)	115.65(13)
C(41)-P(1)-C(14)	107.74(14)
O(1)-P(1)-C(31)	111.56(13)
C(41)-P(1)-C(31)	105.65(14)
C(14)-P(1)-C(31)	104.01(13)
C(12)-C(11)-C(16)	119.8(3)
C(11)-C(12)-C(13)	121.8(3)
C(12)-C(13)-C(14)	116.6(3)
C(12)-C(13)-C(28)	118.3(3)
C(14)-C(13)-C(28)	123.9(3)
C(15)-C(14)-C(13)	118.5(3)
C(15)-C(14)-P(1)	122.0(2)
C(13)-C(14)-P(1)	119.4(2)
C(14)-C(15)-C(16)	121.9(3)
C(11)-C(16)-C(15)	117.0(3)
C(11)-C(16)-C(17)	121.2(3)
C(15)-C(16)-C(17)	120.8(3)
C(16)-C(17)-C(18)	112.4(3)
C(23)-C(18)-C(17)	111.8(3)
C(22)-C(21)-C(26)	122.1(3)
C(22)-C(21)-Br(1)	117.8(3)
C(26)-C(21)-Br(1)	120.1(3)
C(21)-C(22)-C(23)	120.4(3)
C(24)-C(23)-C(22)	116.7(3)
C(24)-C(23)-C(18)	120.2(3)
C(22)-C(23)-C(18)	121.7(3)
C(25)-C(24)-C(23)	119.7(3)

C(24)-C(25)-C(26)	122.5(3)
C(21)-C(26)-C(25)	114.5(3)
C(21)-C(26)-C(27)	123.4(3)
C(25)-C(26)-C(27)	120.9(3)
C(26)-C(27)-C(28)	112.7(3)
C(13)-C(28)-C(27)	112.4(3)
C(32)-C(31)-C(36)	119.3(3)
C(32)-C(31)-P(1)	117.7(2)
C(36)-C(31)-P(1)	123.0(2)
C(31)-C(32)-C(33)	119.7(3)
C(34)-C(33)-C(32)	120.3(3)
C(33)-C(34)-C(35)	120.4(3)
C(36)-C(35)-C(34)	119.8(3)
C(35)-C(36)-C(31)	120.4(3)
C(46)-C(41)-C(42)	118.8(3)
C(46)-C(41)-P(1)	118.7(2)
C(42)-C(41)-P(1)	122.1(2)
C(43)-C(42)-C(41)	119.9(3)
C(44)-C(43)-C(42)	120.6(3)
C(43)-C(44)-C(45)	120.0(3)
C(46)-C(45)-C(44)	119.9(3)
C(45)-C(46)-C(41)	120.9(3)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3**.
The anisotropic displacement factor exponent takes the form:
$-2\ \pi^2\ [\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U11	U22	U33	U23	U13	U12
Br(1)	43(1)	63(1)	40(1)	-10(1)	-4(1)	-12(1)
P(1)	26(1)	30(1)	24(1)	-2(1)	-8(1)	-6(1)
O(1)	29(1)	39(1)	34(1)	-8(1)	-6(1)	-3(1)
C(11)	27(2)	62(2)	28(2)	-9(1)	-3(1)	-16(1)
C(12)	43(2)	50(2)	26(2)	2(1)	-7(1)	-24(2)
C(13)	38(2)	38(2)	23(1)	3(1)	-10(1)	-14(1)
C(14)	29(2)	36(2)	21(1)	-5(1)	-7(1)	-9(1)
C(15)	29(2)	35(2)	26(1)	-8(1)	-5(1)	-6(1)
C(16)	26(2)	47(2)	28(2)	-12(1)	-6(1)	-3(1)
C(17)	32(2)	48(2)	47(2)	-10(2)	-14(1)	1(1)
C(18)	45(2)	54(2)	40(2)	1(2)	-20(2)	-3(2)
C(21)	42(2)	41(2)	22(1)	-6(1)	-4(1)	-8(1)
C(22)	48(2)	39(2)	23(1)	0(1)	-8(1)	-10(1)
C(23)	47(2)	48(2)	22(1)	-2(1)	-13(1)	-8(2)
C(24)	52(2)	54(2)	33(2)	-10(2)	-13(2)	-19(2)
C(25)	67(2)	37(2)	35(2)	-9(1)	-9(2)	-16(2)
C(26)	53(2)	33(2)	30(2)	-9(1)	-7(1)	-2(1)
C(27)	59(2)	39(2)	47(2)	-2(2)	-11(2)	5(2)
C(28)	50(2)	31(2)	43(2)	2(1)	-19(2)	-9(1)
C(31)	33(2)	30(2)	29(2)	0(1)	-12(1)	-9(1)
C(32)	32(2)	36(2)	35(2)	1(1)	-11(1)	-7(1)
C(33)	46(2)	48(2)	42(2)	9(2)	-23(2)	-14(2)
C(34)	59(2)	54(2)	28(2)	4(1)	-17(2)	-27(2)
C(35)	48(2)	50(2)	31(2)	-6(1)	-2(2)	-12(2)
C(36)	37(2)	42(2)	31(2)	1(1)	-6(1)	-5(1)
C(41)	25(1)	31(2)	29(1)	-1(1)	-7(1)	-6(1)
C(42)	42(2)	38(2)	28(2)	-3(1)	-7(1)	-11(1)
C(43)	50(2)	41(2)	37(2)	-12(1)	-5(2)	-13(2)
C(44)	45(2)	27(2)	49(2)	0(1)	-11(2)	-6(1)
C(45)	38(2)	42(2)	38(2)	6(1)	-12(1)	-9(1)
C(46)	37(2)	40(2)	29(2)	0(1)	-12(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3.**

	x	y	z	U(eq)
H(11)	-3345	7266	8450	45
H(12)	-1529	5540	8888	45
H(15)	3	9359	8045	36
H(17A)	-2126	10149	7047	51
H(17B)	-3746	9657	7625	51
H(18A)	-3647	8626	6095	54
H(18B)	-2561	9597	5416	54
H(22)	549	8837	5074	44
H(24)	-2508	6453	5962	53
H(25)	-437	4896	6317	54
H(27A)	3393	5375	6643	61
H(27B)	2483	4263	6648	61
H(28A)	1134	4451	8486	48
H(28B)	2533	5137	8571	48
H(32)	4710	6154	10006	41
H(33)	4542	5620	11981	52
H(34)	2375	6511	13304	53
H(35)	252	7843	12688	53
H(36)	346	8315	10733	45
H(42)	3068	9588	10003	43
H(43)	3617	11594	9547	50
H(44)	3724	12534	7701	48
H(45)	3297	11473	6272	47
H(46)	2840	9453	6693	41

X-ray crystal structure analysis of **5 (816642)**: formula $C_{28}H_{24}BrPS$, M = 503.41, colourless crystal 0.40 x 0.15 x 0.15 mm, a = 7.9519(1), b = 17.2205(3), c = 16.6525(4)Å, β = 93.739(1)°, V = 2275.47(7) Å^3, ρ_{calc} = 1.469 g cm^{-3}, μ = 1.983 mm^{-1}, empirical absorption correction (0.504 ≤ T ≤ 0.755), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 13470 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 5306 independent (R_{int} = 0.042) and 4090 observed reflections [$I \geq 2\ \sigma(I)$], 280 refined parameters, R = 0.052, wR^2 = 0.118, max. (min.) residual electron density 0.67 (-0.59) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Table 1. Crystal data and structure refinement for **5**.

Identification code	**5**
Empirical formula	C_{28} H_{24} Br P S
Formula weight	503.41
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$ (No.14)
Unit cell dimensions	a = 7.9519(1) Å b = 17.2205(3) Å β = 93.739(1)°. c = 16.6525(4) Å
Volume	2275.47(7) Å^3
Z, Calculated density	4, 1.469 Mg/m^3
Absorption coefficient	1.983 mm^{-1}
F(000)	1032
Crystal size	0.40 x 0.15 x 0.15 mm
Theta range for data collection	4.32 to 27.88°.
Limiting indices	-10<=h<=10, -22<=k<=20, -21<=l<=21
Reflections collected / unique	13470 / 5306 [R(int) = 0.042]
Completeness to theta = 27.88	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7552 and 0.5043
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5306 / 0 / 280
Goodness-of-fit on F^2	1.050
Final R indices [I>2σ(I)]	R1 = 0.0523, wR^2 = 0.1022

R indices (all data)	R1 = 0.0755, wR^2 = 0.1178
Largest diff. peak and hole	0.669 and -0.591 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **5**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	2424(1)	5254(1)	8912(1)	61(1)
P(1)	-1579(1)	5250(1)	7110(1)	31(1)
S(1)	536(1)	4777(1)	6823(1)	48(1)
C(11)	-2438(4)	7467(2)	8489(2)	42(1)
C(12)	-1348(5)	7463(2)	7868(2)	44(1)
C(13)	-718(4)	6781(2)	7574(2)	38(1)
C(14)	-1551(4)	6088(2)	7775(2)	31(1)
C(15)	-2579(4)	6098(2)	8422(2)	33(1)
C(16)	-2875(4)	6782(2)	8844(2)	36(1)
C(17)	-3361(5)	6768(2)	9711(2)	49(1)
C(18)	-1883(5)	7051(3)	10315(2)	61(1)
C(21)	1595(4)	6259(2)	9150(2)	43(1)
C(22)	476(4)	6306(2)	9752(2)	43(1)
C(23)	-208(5)	7025(2)	9942(2)	51(1)
C(24)	539(6)	7676(3)	9636(3)	64(1)
C(25)	1615(5)	7609(3)	9015(3)	67(1)
C(26)	2020(4)	6894(3)	8696(3)	55(1)
C(27)	2492(5)	6810(3)	7831(3)	70(1)
C(28)	963(5)	6813(2)	7199(2)	53(1)
C(31)	-2904(4)	4542(2)	7572(2)	31(1)
C(32)	-2180(4)	4060(2)	8172(2)	40(1)
C(33)	-3142(5)	3514(2)	8541(2)	44(1)
C(34)	-4829(5)	3435(2)	8309(2)	42(1)
C(35)	-5561(4)	3910(2)	7722(2)	42(1)
C(36)	-4615(4)	4469(2)	7361(2)	36(1)
C(41)	-2815(4)	5622(2)	6236(2)	33(1)
C(42)	-2410(4)	5408(2)	5468(2)	39(1)
C(43)	-3375(5)	5673(2)	4795(2)	44(1)
C(44)	-4746(5)	6143(2)	4890(2)	46(1)
C(45)	-5162(4)	6364(2)	5649(2)	42(1)
C(46)	-4191(4)	6111(2)	6320(2)	37(1)

Table 3. Bond lengths [Å] and angles [°] for **5.**

Br(1)-C(21)	1.903(4)
P(1)-C(31)	1.816(3)
P(1)-C(14)	1.818(3)
P(1)-C(41)	1.819(3)
P(1)-S(1)	1.9559(11)
C(11)-C(16)	1.375(5)
C(11)-C(12)	1.392(5)
C(11)-H(11)	0.9400
C(12)-C(13)	1.378(5)
C(12)-H(12)	0.9400
C(13)-C(14)	1.415(4)
C(13)-C(28)	1.513(5)
C(14)-C(15)	1.395(4)
C(15)-C(16)	1.399(4)
C(15)-H(15)	0.9400
C(16)-C(17)	1.519(5)
C(17)-C(18)	1.574(6)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(18)-C(23)	1.507(6)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(21)-C(26)	1.384(5)
C(21)-C(22)	1.385(5)
C(22)-C(23)	1.397(5)
C(22)-H(22)	0.9400
C(23)-C(24)	1.382(6)
C(24)-C(25)	1.389(7)
C(24)-H(24)	0.9400
C(25)-C(26)	1.388(6)
C(25)-H(25)	0.9400
C(26)-C(27)	1.518(6)
C(27)-C(28)	1.555(6)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(31)-C(36)	1.388(4)
C(31)-C(32)	1.394(4)
C(32)-C(33)	1.382(5)
C(32)-H(32)	0.9400
C(33)-C(34)	1.378(5)
C(33)-H(33)	0.9400
C(34)-C(35)	1.376(5)
C(34)-H(34)	0.9400
C(35)-C(36)	1.383(5)
C(35)-H(35)	0.9400
C(36)-H(36)	0.9400
C(41)-C(42)	1.389(4)
C(41)-C(46)	1.395(4)
C(42)-C(43)	1.393(5)
C(42)-H(42)	0.9400
C(43)-C(44)	1.375(5)
C(43)-H(43)	0.9400
C(44)-C(45)	1.381(5)
C(44)-H(44)	0.9400
C(45)-C(46)	1.387(5)
C(45)-H(45)	0.9400
C(46)-H(46)	0.9400
C(31)-P(1)-C(14)	105.07(14)
C(31)-P(1)-C(41)	106.11(14)
C(14)-P(1)-C(41)	101.11(14)
C(31)-P(1)-S(1)	110.79(11)

C(14)-P(1)-S(1)	120.17(11)
C(41)-P(1)-S(1)	112.32(11)
C(16)-C(11)-C(12)	120.1(3)
C(16)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(13)-C(12)-C(11)	121.8(3)
C(13)-C(12)-H(12)	119.1
C(11)-C(12)-H(12)	119.1
C(12)-C(13)-C(14)	116.6(3)
C(12)-C(13)-C(28)	117.9(3)
C(14)-C(13)-C(28)	124.5(3)
C(15)-C(14)-C(13)	118.6(3)
C(15)-C(14)-P(1)	119.7(2)
C(13)-C(14)-P(1)	120.9(2)
C(14)-C(15)-C(16)	121.7(3)
C(14)-C(15)-H(15)	119.2
C(16)-C(15)-H(15)	119.2
C(11)-C(16)-C(15)	116.8(3)
C(11)-C(16)-C(17)	120.6(3)
C(15)-C(16)-C(17)	121.7(3)
C(16)-C(17)-C(18)	112.2(3)
C(16)-C(17)-H(17A)	109.2
C(18)-C(17)-H(17A)	109.2
C(16)-C(17)-H(17B)	109.2
C(18)-C(17)-H(17B)	109.2
H(17A)-C(17)-H(17B)	107.9
C(23)-C(18)-C(17)	111.7(3)
C(23)-C(18)-H(18A)	109.3
C(17)-C(18)-H(18A)	109.3
C(23)-C(18)-H(18B)	109.3
C(17)-C(18)-H(18B)	109.3
H(18A)-C(18)-H(18B)	107.9
C(26)-C(21)-C(22)	122.8(4)
C(26)-C(21)-Br(1)	120.2(3)
C(22)-C(21)-Br(1)	116.9(3)
C(21)-C(22)-C(23)	119.6(4)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	116.9(4)
C(24)-C(23)-C(18)	122.8(4)
C(22)-C(23)-C(18)	119.1(4)
C(23)-C(24)-C(25)	120.5(4)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(26)-C(25)-C(24)	121.9(4)
C(26)-C(25)-H(25)	119.0
C(24)-C(25)-H(25)	119.0
C(21)-C(26)-C(25)	114.8(4)
C(21)-C(26)-C(27)	121.9(4)
C(25)-C(26)-C(27)	121.7(4)
C(26)-C(27)-C(28)	114.3(3)
C(26)-C(27)-H(27A)	108.7
C(28)-C(27)-H(27A)	108.7
C(26)-C(27)-H(27B)	108.7
C(28)-C(27)-H(27B)	108.7
H(27A)-C(27)-H(27B)	107.6
C(13)-C(28)-C(27)	113.2(3)
C(13)-C(28)-H(28A)	108.9
C(27)-C(28)-H(28A)	108.9
C(13)-C(28)-H(28B)	108.9
C(27)-C(28)-H(28B)	108.9
H(28A)-C(28)-H(28B)	107.8
C(36)-C(31)-C(32)	118.7(3)
C(36)-C(31)-P(1)	122.7(2)
C(32)-C(31)-P(1)	118.7(2)
C(33)-C(32)-C(31)	120.6(3)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7

C(34)-C(33)-C(32)	120.0(3)
C(34)-C(33)-H(33)	120.0
C(32)-C(33)-H(33)	120.0
C(35)-C(34)-C(33)	120.0(3)
C(35)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0
C(34)-C(35)-C(36)	120.4(3)
C(34)-C(35)-H(35)	119.8
C(36)-C(35)-H(35)	119.8
C(35)-C(36)-C(31)	120.3(3)
C(35)-C(36)-H(36)	119.8
C(31)-C(36)-H(36)	119.8
C(42)-C(41)-C(46)	119.0(3)
C(42)-C(41)-P(1)	119.9(2)
C(46)-C(41)-P(1)	121.2(2)
C(41)-C(42)-C(43)	120.3(3)
C(41)-C(42)-H(42)	119.9
C(43)-C(42)-H(42)	119.9
C(44)-C(43)-C(42)	120.0(3)
C(44)-C(43)-H(43)	120.0
C(42)-C(43)-H(43)	120.0
C(43)-C(44)-C(45)	120.5(3)
C(43)-C(44)-H(44)	119.8
C(45)-C(44)-H(44)	119.8
C(44)-C(45)-C(46)	119.8(3)
C(44)-C(45)-H(45)	120.1
C(46)-C(45)-H(45)	120.1
C(45)-C(46)-C(41)	120.5(3)
C(45)-C(46)-H(46)	119.8
C(41)-C(46)-H(46)	119.8

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **5**.
The anisotropic displacement factor exponent takes the form:
$-2\ \pi^2\ [\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U11	U22	U33	U23	U13	U12
Br(1)	58(1)	59(1)	64(1)	-8(1)	3(1)	16(1)
P(1)	30(1)	34(1)	30(1)	-3(1)	1(1)	4(1)
S(1)	37(1)	55(1)	53(1)	-5(1)	7(1)	14(1)
C(11)	46(2)	36(2)	44(2)	-5(2)	-6(2)	11(2)
C(12)	55(2)	35(2)	42(2)	3(2)	-3(2)	2(2)
C(13)	42(2)	39(2)	34(2)	-1(1)	2(1)	-3(1)
C(14)	30(2)	33(2)	31(2)	-3(1)	-2(1)	0(1)
C(15)	29(2)	38(2)	32(2)	-4(1)	-2(1)	0(1)
C(16)	33(2)	41(2)	34(2)	-7(1)	-1(1)	6(1)
C(17)	54(2)	53(2)	41(2)	-9(2)	10(2)	9(2)
C(18)	68(3)	76(3)	37(2)	-15(2)	-2(2)	26(2)
C(21)	35(2)	47(2)	46(2)	-2(2)	-10(1)	6(2)
C(22)	45(2)	48(2)	33(2)	2(2)	-9(1)	6(2)
C(23)	56(2)	55(2)	38(2)	-11(2)	-17(2)	14(2)
C(24)	57(2)	50(2)	79(3)	-19(2)	-32(2)	7(2)
C(25)	46(2)	50(2)	101(4)	11(3)	-18(2)	-9(2)
C(26)	29(2)	66(3)	68(3)	13(2)	-7(2)	-5(2)
C(27)	43(2)	92(4)	77(3)	34(3)	14(2)	4(2)
C(28)	54(2)	50(2)	57(2)	-5(2)	19(2)	-13(2)
C(31)	36(2)	28(2)	29(2)	-4(1)	-1(1)	4(1)
C(32)	37(2)	40(2)	41(2)	3(2)	-8(1)	1(1)
C(33)	55(2)	39(2)	36(2)	7(2)	-3(2)	3(2)
C(34)	50(2)	35(2)	41(2)	-1(1)	10(2)	0(2)
C(35)	35(2)	38(2)	51(2)	-1(2)	-4(2)	-2(1)
C(36)	38(2)	32(2)	37(2)	3(1)	-6(1)	1(1)
C(41)	37(2)	32(2)	29(2)	-1(1)	3(1)	-1(1)
C(42)	38(2)	44(2)	35(2)	-5(2)	7(1)	-5(1)
C(43)	51(2)	52(2)	29(2)	1(2)	2(1)	-7(2)
C(44)	50(2)	48(2)	37(2)	9(2)	-9(2)	-10(2)
C(45)	42(2)	39(2)	44(2)	7(2)	-3(1)	1(1)
C(46)	40(2)	39(2)	34(2)	-1(1)	3(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **5**.

	x	y	z	U(eq)
H(11)	-2877	7940	8666	51
H(12)	-1032	7938	7643	53
H(15)	-3086	5634	8579	40
H(17A)	-3678	6237	9852	59
H(17B)	-4345	7102	9763	59
H(18A)	-2110	7584	10485	73
H(18B)	-1834	6720	10795	73
H(22)	180	5857	10031	51
H(24)	318	8169	9849	76
H(25)	2083	8061	8805	80
H(27A)	3115	6324	7780	84
H(27B)	3249	7237	7709	84
H(28A)	1007	7283	6871	64
H(28B)	1053	6365	6841	64
H(32)	-1026	4107	8326	48
H(33)	-2646	3197	8951	52
H(34)	-5479	3056	8553	50
H(35)	-6712	3855	7564	50
H(36)	-5132	4801	6971	43
H(42)	-1480	5082	5401	47
H(43)	-3090	5531	4276	53
H(44)	-5404	6315	4435	55
H(45)	-6100	6686	5711	50
H(46)	-4462	6270	6836	45

X-ray crystal structure analysis of **4 (816641)**: formula $C_{28}H_{24}BrP$, M = 471.35, colourless crystal 0.35 x 0.30 x 0.17 mm, a = 8.7264(2), b = 11.1117(3), c = 13.1982(3)Å, α = 81.623(1), β = 73.365(1), γ = 78.493(1)°, V = 1105.57(5) Å^3, ρ_{calc} = 1.416 g cm^{-3}, μ = 1.944 mm^{-1}, empirical absorption correction ($0.549 \leq T \leq 0.733$), Z = 2, triclinic, space group *P*1bar (No. 2), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 10091 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 Å^{-1}, 5012 independent (R_{int} = 0.047) and 4481 observed reflections [$I \geq 2\ \sigma(I)$], 271 refined parameters, R = 0.046, wR^2 = 0.125, max. (min.) residual electron density 0.84 (-0.63) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Table 1. Crystal data and structure refinement for **4**.

Identification code	**4**
Empirical formula	C28 H24 Br P
Formula weight	471.35
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1 (No.2)
Unit cell dimensions	a = 8.7264(2) Å a = 81.623(1)°
	b = 11.1117(3) Å b = 73.365(1)°
	c = 12.1982(3) Å g = 78.493(1)°
Volume	1105.57(5) Å3
Z, Calculated density	2, 1.416 Mg/m3
Absorption coefficient	1.944 mm-1
F(000)	484
Crystal size	0.35 x 0.30 x 0.17 mm
Theta range for data collection	4.08 to 27.86°
Limiting indices	-11<=h<=11, -14<=k<=12, -15<=l<=15
Reflections collected / unique	10091 / 5012 [R(int) = 0.047]
Completeness to theta = 27.86	95.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7334 and 0.5494
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5012 / 0 / 271
Goodness-of-fit on F2	1.063
Final R indices [I>2s(I)]	R1 = 0.0464, wR2 = 0.1169
R indices (all data)	R1 = 0.0537, wR2 = 0.1252
Largest diff. peak and hole	0.836 and -0.634 e.Å-3

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2 x 103) for **4**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)
Br(1)	-4423(1)	8321(1)	19311(1)	49(1)
P(1)	-3118(1)	7662(1)	16150(1)	30(1)
C(11)	-1165(3)	7769(2)	16397(2)	28(1)
C(12)	-39(3)	6716(2)	16565(2)	30(1)
C(13)	1439(3)	6810(3)	16738(2)	34(1)
C(14)	1930(3)	7954(3)	16456(2)	38(1)
C(15)	829(4)	9005(3)	16300(2)	37(1)
C(16)	-792(3)	8941(2)	16419(2)	31(1)
C(17)	2319(3)	5778(3)	17398(3)	43(1)
C(18)	1528(4)	5745(3)	18727(3)	55(1)
C(21)	-2154(3)	8210(3)	19112(2)	35(1)
C(22)	-1234(4)	7059(3)	19247(2)	38(1)
C(23)	430(4)	6943(3)	19086(2)	43(1)

C(24)	1037(4)	8023(4)	19039(3)	52(1)
C(25)	108(4)	9164(3)	18853(2)	49(1)
C(26)	-1463(4)	9270(3)	18749(2)	40(1)
C(27)	-2166(4)	10359(3)	18048(3)	45(1)
C(28)	-2068(4)	10048(2)	16796(2)	41(1)
C(31)	-2549(3)	7758(2)	14572(2)	32(1)
C(32)	-1072(3)	7166(3)	13913(2)	39(1)
C(33)	-746(4)	7252(3)	12732(3)	45(1)
C(34)	-1865(4)	7950(3)	12181(3)	49(1)
C(35)	-3299(4)	8554(3)	12816(3)	51(1)
C(36)	-3651(4)	8458(3)	14007(2)	41(1)
C(41)	-3270(3)	6018(3)	16535(2)	33(1)
C(42)	-3531(4)	5570(3)	17698(3)	42(1)
C(43)	-3820(4)	4386(3)	18074(3)	49(1)
C(44)	-3879(4)	3613(3)	17296(3)	53(1)
C(45)	-3628(4)	4031(3)	16155(3)	54(1)
C(46)	-3314(4)	5225(3)	15772(3)	44(1)

Table 3. Bond lengths [Å] and angles [°] for **4.**

Br(1)-C(21)	1.905(3)
P(1)-C(31)	1.837(3)
P(1)-C(41)	1.839(3)
P(1)-C(11)	1.843(2)
C(11)-C(12)	1.400(3)
C(11)-C(16)	1.410(3)
C(12)-C(13)	1.391(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.387(4)
C(13)-C(17)	1.511(4)
C(14)-C(15)	1.384(4)
C(14)-H(14)	0.9400
C(15)-C(16)	1.396(4)
C(15)-H(15)	0.9400
C(16)-C(28)	1.513(4)
C(17)-C(18)	1.568(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(18)-C(23)	1.518(5)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(21)-C(22)	1.383(4)
C(21)-C(26)	1.388(4)
C(22)-C(23)	1.390(4)
C(22)-H(22)	0.9400
C(23)-C(24)	1.393(5)
C(24)-C(25)	1.388(5)
C(24)-H(24)	0.9400
C(25)-C(26)	1.393(5)
C(25)-H(25)	0.9400
C(26)-C(27)	1.508(4)
C(27)-C(28)	1.589(4)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(31)-C(36)	1.389(4)
C(31)-C(32)	1.401(4)
C(32)-C(33)	1.379(4)
C(32)-H(32)	0.9400
C(33)-C(34)	1.389(5)
C(33)-H(33)	0.9400
C(34)-C(35)	1.370(5)
C(34)-H(34)	0.9400
C(35)-C(36)	1.389(4)
C(35)-H(35)	0.9400

C(36)-H(36) 0.9400
C(41)-C(46) 1.385(4)
C(41)-C(42) 1.402(4)
C(42)-C(43) 1.376(4)
C(42)-H(42) 0.9400
C(43)-C(44) 1.388(5)
C(43)-H(43) 0.9400
C(44)-C(45) 1.371(5)
C(44)-H(44) 0.9400
C(45)-C(46) 1.394(5)
C(45)-H(45) 0.9400
C(46)-H(46) 0.9400
C(31)-P(1)-C(41) 101.82(12)
C(31)-P(1)-C(11) 100.16(11)
C(41)-P(1)-C(11) 103.29(11)
C(12)-C(11)-C(16) 119.0(2)
C(12)-C(11)-P(1) 121.79(19)
C(16)-C(11)-P(1) 119.17(19)
4
C(13)-C(12)-C(11) 121.3(2)
C(13)-C(12)-H(12) 119.4
C(11)-C(12)-H(12) 119.4
C(14)-C(13)-C(12) 117.2(2)
C(14)-C(13)-C(17) 120.9(3)
C(12)-C(13)-C(17) 121.0(3)
C(15)-C(14)-C(13) 120.4(2)
C(15)-C(14)-H(14) 119.8
C(13)-C(14)-H(14) 119.8
C(14)-C(15)-C(16) 121.1(2)
C(14)-C(15)-H(15) 119.5
C(16)-C(15)-H(15) 119.5
C(15)-C(16)-C(11) 116.9(2)
C(15)-C(16)-C(28) 118.6(2)
C(11)-C(16)-C(28) 123.2(2)
C(13)-C(17)-C(18) 112.1(2)
C(13)-C(17)-H(17A) 109.2
C(18)-C(17)-H(17A) 109.2
C(13)-C(17)-H(17B) 109.2
C(18)-C(17)-H(17B) 109.2
H(17A)-C(17)-H(17B) 107.9
C(23)-C(18)-C(17) 112.9(3)
C(23)-C(18)-H(18A) 109.0
C(17)-C(18)-H(18A) 109.0
C(23)-C(18)-H(18B) 109.0
C(17)-C(18)-H(18B) 109.0
H(18A)-C(18)-H(18B) 107.8
C(22)-C(21)-C(26) 122.2(3)
C(22)-C(21)-Br(1) 118.6(2)
C(26)-C(21)-Br(1) 118.9(2)
C(21)-C(22)-C(23) 120.1(3)
C(21)-C(22)-H(22) 120.0
C(23)-C(22)-H(22) 120.0
C(22)-C(23)-C(24) 116.8(3)
C(22)-C(23)-C(18) 119.8(3)
C(24)-C(23)-C(18) 122.1(3)
C(25)-C(24)-C(23) 120.2(3)
C(25)-C(24)-H(24) 119.9
C(23)-C(24)-H(24) 119.9
C(24)-C(25)-C(26) 121.7(3)
C(24)-C(25)-H(25) 119.2
C(26)-C(25)-H(25) 119.2
C(21)-C(26)-C(25) 115.0(3)
C(21)-C(26)-C(27) 123.0(3)
C(25)-C(26)-C(27) 120.6(3)
C(26)-C(27)-C(28) 112.6(2)
C(26)-C(27)-H(27A) 109.1
C(28)-C(27)-H(27A) 109.1
C(26)-C(27)-H(27B) 109.1

C(28)-C(27)-H(27B) 109.1
H(27A)-C(27)-H(27B) 107.8
C(16)-C(28)-C(27) 112.6(2)
C(16)-C(28)-H(28A) 109.1
C(27)-C(28)-H(28A) 109.1
C(16)-C(28)-H(28B) 109.1
C(27)-C(28)-H(28B) 109.1
H(28A)-C(28)-H(28B) 107.8
C(36)-C(31)-C(32) 118.5(2)
C(36)-C(31)-P(1) 117.8(2)
C(32)-C(31)-P(1) 123.7(2)
C(33)-C(32)-C(31) 120.5(3)
C(33)-C(32)-H(32) 119.8
C(31)-C(32)-H(32) 119.8
C(32)-C(33)-C(34) 120.3(3)
C(32)-C(33)-H(33) 119.9
C(34)-C(33)-H(33) 119.9
C(35)-C(34)-C(33) 119.7(3)
C(35)-C(34)-H(34) 120.2
5
C(33)-C(34)-H(34) 120.2
C(34)-C(35)-C(36) 120.5(3)
C(34)-C(35)-H(35) 119.7
C(36)-C(35)-H(35) 119.7
C(35)-C(36)-C(31) 120.5(3)
C(35)-C(36)-H(36) 119.7
C(31)-C(36)-H(36) 119.7
C(46)-C(41)-C(42) 117.5(3)
C(46)-C(41)-P(1) 124.2(2)
C(42)-C(41)-P(1) 117.9(2)
C(43)-C(42)-C(41) 121.6(3)
C(43)-C(42)-H(42) 119.2
C(41)-C(42)-H(42) 119.2
C(42)-C(43)-C(44) 119.8(3)
C(42)-C(43)-H(43) 120.1
C(44)-C(43)-H(43) 120.1
C(45)-C(44)-C(43) 119.6(3)
C(45)-C(44)-H(44) 120.2
C(43)-C(44)-H(44) 120.2
C(44)-C(45)-C(46) 120.5(3)
C(44)-C(45)-H(45) 119.7
C(46)-C(45)-H(45) 119.7
C(41)-C(46)-C(45) 120.9(3)
C(41)-C(46)-H(46) 119.5
C(45)-C(46)-H(46) 119.5

Table 4. Anisotropic displacement parameters (Å2 x 103) for **4**.
The anisotropic displacement factor exponent takes the form:
-2 p2 [h2 a*2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12
Br(1)	43(1)	53(1)	45(1)	-9(1)	0(1)	-6(1)
P(1)	28(1)	36(1)	26(1)	-4(1)	-6(1)	-4(1)
C(11)	28(1)	34(1)	21(1)	-4(1)	-4(1)	-6(1)
C(12)	30(1)	32(1)	27(1)	-5(1)	-4(1)	-5(1)
C(13)	28(1)	43(1)	29(1)	-6(1)	-4(1)	-4(1)
C(14)	33(1)	53(2)	30(1)	-1(1)	-5(1)	-16(1)
C(15)	45(2)	42(1)	26(1)	3(1)	-7(1)	-19(1)
C(16)	40(1)	30(1)	20(1)	1(1)	-7(1)	-7(1)
C(17)	31(1)	48(2)	47(2)	0(1)	-12(1)	-1(1)
C(18)	49(2)	60(2)	46(2)	10(2)	-14(1)	1(2)
C(21)	44(1)	40(1)	20(1)	-4(1)	-4(1)	-9(1)
C(22)	48(2)	43(1)	23(1)	3(1)	-8(1)	-11(1)
C(23)	50(2)	54(2)	24(1)	5(1)	-12(1)	-9(1)
C(24)	53(2)	77(2)	32(1)	-1(1)	-17(1)	-22(2)

C(25)	67(2)	59(2)	29(1)	-7(1)	-9(1)	-29(2)
C(26)	56(2)	39(1)	24(1)	-9(1)	-3(1)	-13(1)
C(27)	61(2)	31(1)	38(2)	-7(1)	-4(1)	-7(1)
C(28)	54(2)	29(1)	37(1)	0(1)	-14(1)	1(1)
C(31)	32(1)	37(1)	28(1)	-2(1)	-8(1)	-9(1)
C(32)	39(1)	45(2)	32(1)	-6(1)	-8(1)	-5(1)
C(33)	49(2)	51(2)	32(1)	-9(1)	0(1)	-14(1)
C(34)	62(2)	63(2)	28(1)	0(1)	-11(1)	-29(2)
C(35)	55(2)	65(2)	38(2)	7(1)	-23(1)	-16(2)
C(36)	36(1)	51(2)	36(1)	-1(1)	-14(1)	-6(1)
C(41)	25(1)	40(1)	35(1)	-4(1)	-7(1)	-7(1)
C(42)	45(2)	46(2)	40(2)	1(1)	-16(1)	-15(1)
C(43)	49(2)	50(2)	49(2)	11(1)	-20(1)	-13(1)
C(44)	45(2)	32(1)	76(2)	0(1)	-12(2)	-4(1)
C(45)	55(2)	44(2)	62(2)	-20(2)	-2(2)	-12(1)
C(46)	48(2)	45(2)	37(2)	-10(1)	-2(1)	-14(1)

Table 5. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2 x 103) for **4.**

x	y	z	U(eq)
H(12)	-287	5932	16560	36
H(14)	3018	8016	16370	46
H(15)	1179	9774	16112	45
H(17A)	3453	5886	17235	52
H(17B)	2308	4988	17135	52
H(18A)	896	5070	18968	65
H(18B)	2390	5571	19124	65
H(22)	-1733	6353	19447	46
H(24)	2079	7979	19134	62
H(25)	551	9883	18795	59
H(27A)	-1578	11042	17982	54
H(27B)	-3303	10630	18450	54
H(28A)	-3128	9887	16785	49
H(28B)	-1823	10765	16248	49
H(32)	-298	6707	14278	47
H(33)	239	6837	12298	54
H(34)	-1640	8007	11375	59
H(35)	-4050	9036	12443	61
H(36)	-4644	8870	14434	49
H(42)	-3508	6090	18233	50
H(43)	-3978	4102	18857	59
H(44)	-4090	2807	17550	63
H(45)	-3668	3509	15626	65
H(46)	-3130	5495	14986	53

X-ray crystal structure analysis of **6 (816640)**: formula $C_{40}H_{34}P_2$, M = 576.61, colourless crystal 0.40 x 0.15 x 0.05 mm, a = 8.9076(2), b = 10.8103(2), c = 16.3061(4)Å, α = 92.514(1), β = 93.546(1), γ = 101.289(1)˚, V = 1534.33(6) Å^3, ρ_{calc} = 1.248 g cm^{-3}, μ = 0.170 mm^{-1}, empirical absorption correction ($0.935 \leq T \leq 0.992$), Z = 2, triclinic, space group P1bar (No. 2), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 14101 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 7124 independent (R_{int} = 0.042) and 5989 observed reflections [$I \geq 2\ \sigma(I)$], 379 refined parameters, R = 0.077, wR^2 = 0.204, max. (min.) residual electron density 1.88 (-0.27) e Å^{-3} close to the phosphorus atoms, hydrogen atoms calculated and refined as riding atoms.

Table 1. Crystal data and structure refinement for **6**.

Identification code	**6**
Empirical formula	$C_{40}\ H_{34}\ P_2$
Formula weight	576.61
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1 (No.2)
Unit cell dimensions	a = 8.9076(2) Å α = 92.514(1)° b = 10.8103(2) Å β = 93.546(1)° c = 16.3061(4) Å γ = 101.289(1)°
Volume	1534.33(6) Å^3
Z, Calculated density	2, 1.248 Mg/m^3
Absorption coefficient	0.170 mm^{-1}
F(000)	608
Crystal size	0.40 x 0.15 x 0.05 mm
Theta range for data collection	4.09 to 27.89°
Limiting indices	-11<=h<=11, -14<=k<=14, -19<=l<=21
Reflections collected / unique	14101 / 7124 [R(int) = 0.042]
Completeness to theta = 27.89	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9916 and 0.9353

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7124 / 0 / 379
Goodness-of-fit on F^2	1.029
Final R indices [I>2σ(I)]	R1 = 0.0773, wR^2 = 0.1905
R indices (all data)	R1 = 0.0905, wR^2 = 0.2044
Largest diff. peak and hole	1.879 and -0.274 e.Å^{-3}

2

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **6**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
P(1)	2571(1)	6548(1)	3222(1)	35(1)
P(2)	2456(1)	7286(1)	797(1)	37(1)
C(1)	3770(4)	4835(3)	1318(2)	50(1)
C(2)	4141(4)	4529(3)	2236(2)	41(1)
C(3)	5148(3)	5623(3)	2738(2)	34(1)
C(4)	4607(3)	6665(3)	3064(2)	30(1)
C(5)	5607(3)	7841(3)	3146(2)	30(1)
C(6)	7146(3)	7991(3)	2960(2)	31(1)
C(7)	7731(3)	6891(3)	2879(2)	37(1)
C(8)	6734(4)	5723(3)	2766(2)	38(1)
C(9)	8003(3)	9239(3)	2687(2)	38(1)
C(10)	8338(3)	9160(3)	1751(2)	41(1)
C(11)	7189(3)	8149(3)	1265(2)	36(1)
C(12)	5647(3)	8249(3)	1140(2)	34(1)
C(13)	4471(3)	7184(3)	1017(2)	32(1)
C(14)	4845(4)	5973(3)	1041(2)	37(1)
C(15)	6375(4)	5909(3)	949(2)	45(1)
C(16)	7529(4)	6976(3)	1057(2)	44(1)
C(21)	2096(3)	5171(3)	3844(2)	37(1)
C(22)	3118(4)	4667(4)	4328(3)	60(1)
C(23)	2598(5)	3661(4)	4808(3)	70(1)
C(24)	1068(5)	3146(4)	4804(3)	63(1)
C(25)	43(5)	3637(4)	4326(3)	62(1)
C(26)	544(4)	4642(3)	3846(2)	49(1)
C(31)	2624(3)	7833(3)	4004(2)	36(1)
C(32)	3478(4)	7956(3)	4759(2)	47(1)
C(33)	3439(5)	8961(4)	5317(2)	56(1)
C(34)	2553(5)	9832(4)	5133(3)	57(1)
C(35)	1711(4)	9723(4)	4398(3)	55(1)
C(36)	1741(4)	8728(3)	3832(2)	43(1)
C(41)	2355(3)	7260(3)	-327(2)	38(1)
C(42)	1021(4)	6572(3)	-751(2)	49(1)
C(43)	847(5)	6546(4)	-1601(3)	60(1)
C(44)	1977(5)	7196(4)	-2038(2)	56(1)
C(45)	3332(5)	7875(3)	-1632(2)	49(1)
C(46)	3513(4)	7891(3)	-782(2)	44(1)
C(51)	2427(3)	8946(3)	1064(2)	34(1)
C(52)	2766(4)	9387(3)	1878(2)	42(1)
C(53)	2602(4)	10589(3)	2139(2)	49(1)
C(54)	2086(4)	11374(3)	1586(2)	46(1)
C(55)	1772(4)	10956(3)	778(2)	50(1)

C(56)	1943(4)	9758(3)	514(2)	44(1)

Table 3. Bond lengths [Å] and angles [°] for **6.**

P(1)-C(4)	1.828(3)
P(1)-C(21)	1.834(3)
P(1)-C(31)	1.835(3)
P(2)-C(41)	1.829(3)
P(2)-C(51)	1.833(3)
P(2)-C(13)	1.834(3)
C(1)-C(14)	1.508(5)
C(1)-C(2)	1.576(5)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(2)-C(3)	1.511(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(3)-C(8)	1.393(4)
C(3)-C(4)	1.405(4)
C(4)-C(5)	1.398(4)
C(5)-C(6)	1.402(4)
C(5)-H(5)	0.9400
C(6)-C(7)	1.393(4)
C(6)-C(9)	1.513(4)
C(7)-C(8)	1.392(4)
C(7)-H(7)	0.9400
C(8)-H(8)	0.9400
C(9)-C(10)	1.576(4)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-C(11)	1.502(4)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(16)	1.393(4)
C(11)-C(12)	1.402(4)
C(12)-C(13)	1.394(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.414(4)
C(14)-C(15)	1.395(5)
C(15)-C(16)	1.384(5)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(21)-C(22)	1.374(5)
C(21)-C(26)	1.390(4)
C(22)-C(23)	1.391(5)
C(22)-H(22)	0.9400
C(23)-C(24)	1.367(6)
C(23)-H(23)	0.9400
C(24)-C(25)	1.364(7)
C(24)-H(24)	0.9400
C(25)-C(26)	1.385(5)
C(25)-H(25)	0.9400
C(26)-H(26)	0.9400
C(31)-C(36)	1.388(4)
C(31)-C(32)	1.394(5)
C(32)-C(33)	1.393(5)
C(32)-H(32)	0.9400
C(33)-C(34)	1.373(6)
C(33)-H(33)	0.9400
C(34)-C(35)	1.362(6)
C(34)-H(34)	0.9400
C(35)-C(36)	1.392(5)
C(35)-H(35)	0.9400

C(36)-H(36)	0.9400
C(41)-C(46)	1.394(5)
C(41)-C(42)	1.397(4)
C(42)-C(43)	1.383(6)
C(42)-H(42)	0.9400
C(43)-C(44)	1.368(6)

C(43)-H(43)	0.9400
C(44)-C(45)	1.394(6)
C(44)-H(44)	0.9400
C(45)-C(46)	1.384(5)
C(45)-H(45)	0.9400
C(46)-H(46)	0.9400
C(51)-C(52)	1.385(5)
C(51)-C(56)	1.390(4)
C(52)-C(53)	1.387(5)
C(52)-H(52)	0.9400
C(53)-C(54)	1.383(5)
C(53)-H(53)	0.9400
C(54)-C(55)	1.368(5)
C(54)-H(54)	0.9400
C(55)-C(56)	1.386(5)
C(55)-H(55)	0.9400
C(56)-H(56)	0.9400

C(4)-P(1)-C(21)	104.18(13)
C(4)-P(1)-C(31)	101.98(13)
C(21)-P(1)-C(31)	100.58(14)
C(41)-P(2)-C(51)	101.50(14)
C(41)-P(2)-C(13)	100.51(13)
C(51)-P(2)-C(13)	103.66(13)
C(14)-C(1)-C(2)	113.6(3)
C(14)-C(1)-H(1A)	108.8
C(2)-C(1)-H(1A)	108.8
C(14)-C(1)-H(1B)	108.8
C(2)-C(1)-H(1B)	108.8
H(1A)-C(1)-H(1B)	107.7
C(3)-C(2)-C(1)	113.5(3)
C(3)-C(2)-H(2A)	108.9
C(1)-C(2)-H(2A)	108.9
C(3)-C(2)-H(2B)	108.9
C(1)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	107.7
C(8)-C(3)-C(4)	116.9(3)
C(8)-C(3)-C(2)	118.6(3)
C(4)-C(3)-C(2)	123.6(3)
C(5)-C(4)-C(3)	118.4(3)
C(5)-C(4)-P(1)	120.1(2)
C(3)-C(4)-P(1)	120.8(2)
C(4)-C(5)-C(6)	122.0(3)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(7)-C(6)-C(5)	116.4(3)
C(7)-C(6)-C(9)	121.5(3)
C(5)-C(6)-C(9)	120.8(3)
C(8)-C(7)-C(6)	119.9(3)
C(8)-C(7)-H(7)	120.1
C(6)-C(7)-H(7)	120.1
C(3)-C(8)-C(7)	121.4(3)
C(3)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(6)-C(9)-C(10)	112.0(2)
C(6)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9A)	109.2
C(6)-C(9)-H(9B)	109.2

C(10)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	112.0(2)
C(11)-C(10)-H(10A)	109.2
C(9)-C(10)-H(10A)	109.2
C(11)-C(10)-H(10B)	109.2
C(9)-C(10)-H(10B)	109.2
H(10A)-C(10)-H(10B)	107.9
C(16)-C(11)-C(12)	116.3(3)
C(16)-C(11)-C(10)	121.4(3)

C(12)-C(11)-C(10)	121.2(3)
C(13)-C(12)-C(11)	121.7(3)
C(13)-C(12)-H(12)	119.1
C(11)-C(12)-H(12)	119.1
C(12)-C(13)-C(14)	119.0(3)
C(12)-C(13)-P(2)	122.6(2)
C(14)-C(13)-P(2)	118.4(2)
C(15)-C(14)-C(13)	116.6(3)
C(15)-C(14)-C(1)	119.1(3)
C(13)-C(14)-C(1)	123.1(3)
C(16)-C(15)-C(14)	121.3(3)
C(16)-C(15)-H(15)	119.3
C(14)-C(15)-H(15)	119.3
C(15)-C(16)-C(11)	120.5(3)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7
C(22)-C(21)-C(26)	118.2(3)
C(22)-C(21)-P(1)	126.1(2)
C(26)-C(21)-P(1)	115.6(3)
C(21)-C(22)-C(23)	120.4(4)
C(21)-C(22)-H(22)	119.8
C(23)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	120.9(4)
C(24)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
C(25)-C(24)-C(23)	119.3(4)
C(25)-C(24)-H(24)	120.4
C(23)-C(24)-H(24)	120.4
C(24)-C(25)-C(26)	120.5(4)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(25)-C(26)-C(21)	120.7(4)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
C(36)-C(31)-C(32)	118.2(3)
C(36)-C(31)-P(1)	117.6(2)
C(32)-C(31)-P(1)	124.1(2)
C(33)-C(32)-C(31)	120.1(3)
C(33)-C(32)-H(32)	119.9
C(31)-C(32)-H(32)	119.9
C(34)-C(33)-C(32)	120.5(4)
C(34)-C(33)-H(33)	119.7
C(32)-C(33)-H(33)	119.7
C(35)-C(34)-C(33)	120.0(3)
C(35)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0
C(34)-C(35)-C(36)	120.2(4)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(31)-C(36)-C(35)	120.9(3)
C(31)-C(36)-H(36)	119.5
C(35)-C(36)-H(36)	119.6
C(46)-C(41)-C(42)	118.4(3)
C(46)-C(41)-P(2)	124.2(2)

C(42)-C(41)-P(2)	117.4(3)
C(43)-C(42)-C(41)	120.5(4)
C(43)-C(42)-H(42)	119.8
C(41)-C(42)-H(42)	119.8
C(44)-C(43)-C(42)	120.5(4)
C(44)-C(43)-H(43)	119.8
C(42)-C(43)-H(43)	119.8
C(43)-C(44)-C(45)	120.4(4)
C(43)-C(44)-H(44)	119.8
C(45)-C(44)-H(44)	119.8
C(46)-C(45)-C(44)	119.2(4)
C(46)-C(45)-H(45)	120.4
C(44)-C(45)-H(45)	120.4
C(45)-C(46)-C(41)	121.1(3)

C(45)-C(46)-H(46)	119.5
C(41)-C(46)-H(46)	119.5
C(52)-C(51)-C(56)	117.6(3)
C(52)-C(51)-P(2)	118.3(2)
C(56)-C(51)-P(2)	123.8(2)
C(51)-C(52)-C(53)	121.3(3)
C(51)-C(52)-H(52)	119.3
C(53)-C(52)-H(52)	119.3
C(54)-C(53)-C(52)	120.2(3)
C(54)-C(53)-H(53)	119.9
C(52)-C(53)-H(53)	119.9
C(55)-C(54)-C(53)	119.0(3)
C(55)-C(54)-H(54)	120.5
C(53)-C(54)-H(54)	120.5
C(54)-C(55)-C(56)	120.9(3)
C(54)-C(55)-H(55)	119.5
C(56)-C(55)-H(55)	119.5
C(55)-C(56)-C(51)	120.9(3)
C(55)-C(56)-H(56)	119.6
C(51)-C(56)-H(56)	119.6

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6**.
The anisotropic displacement factor exponent takes the form:
$-2\ \pi^2\ [\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U11	U22	U33	U23	U13	U12
P(1)	30(1)	30(1)	43(1)	0(1)	5(1)	4(1)
P(2)	31(1)	34(1)	46(1)	0(1)	5(1)	5(1)
C(1)	56(2)	30(2)	57(2)	-3(1)	-15(2)	5(1)
C(2)	45(2)	28(1)	50(2)	-5(1)	10(1)	4(1)
C(3)	39(2)	27(1)	35(1)	1(1)	6(1)	6(1)
C(4)	31(1)	28(1)	30(1)	1(1)	4(1)	5(1)
C(5)	30(1)	29(1)	30(1)	-1(1)	3(1)	7(1)
C(6)	31(1)	33(1)	29(1)	0(1)	-1(1)	5(1)
C(7)	30(1)	42(2)	40(2)	3(1)	2(1)	11(1)
C(8)	41(2)	32(1)	45(2)	5(1)	7(1)	15(1)
C(9)	30(1)	34(1)	48(2)	3(1)	4(1)	1(1)
C(10)	29(1)	46(2)	48(2)	10(1)	11(1)	5(1)
C(11)	33(1)	42(2)	34(1)	7(1)	8(1)	10(1)
C(12)	34(1)	34(1)	37(2)	8(1)	7(1)	11(1)
C(13)	35(1)	34(1)	30(1)	3(1)	4(1)	10(1)

C(14)	47(2)	33(1)	31(1)	-4(1)	-3(1)	11(1)
C(15)	56(2)	45(2)	40(2)	-8(1)	-1(1)	25(2)
C(16)	43(2)	57(2)	38(2)	3(1)	10(1)	23(2)
C(21)	37(2)	31(1)	41(2)	1(1)	10(1)	2(1)
C(22)	44(2)	58(2)	80(3)	32(2)	11(2)	7(2)
C(23)	65(3)	65(3)	87(3)	39(2)	19(2)	15(2)
C(24)	80(3)	41(2)	67(3)	11(2)	32(2)	0(2)
C(25)	52(2)	56(2)	70(3)	3(2)	22(2)	-17(2)
C(26)	38(2)	51(2)	53(2)	0(2)	7(1)	-2(1)
C(31)	31(1)	35(1)	42(2)	-1(1)	10(1)	3(1)
C(32)	44(2)	51(2)	44(2)	0(1)	6(1)	9(2)
C(33)	54(2)	64(2)	43(2)	-11(2)	6(2)	-1(2)
C(34)	55(2)	54(2)	59(2)	-20(2)	15(2)	2(2)
C(35)	51(2)	46(2)	70(2)	-9(2)	13(2)	15(2)
C(36)	37(2)	39(2)	53(2)	-5(1)	8(1)	8(1)
C(41)	33(1)	36(2)	45(2)	-6(1)	-1(1)	11(1)
C(42)	38(2)	50(2)	58(2)	-9(2)	-1(2)	11(1)
C(43)	50(2)	70(3)	61(2)	-21(2)	-12(2)	21(2)
C(44)	68(2)	59(2)	45(2)	-12(2)	-8(2)	33(2)
C(45)	61(2)	46(2)	45(2)	-1(1)	8(2)	19(2)
C(46)	44(2)	41(2)	46(2)	-5(1)	0(1)	9(1)
C(51)	27(1)	35(1)	40(2)	5(1)	6(1)	8(1)
C(52)	41(2)	44(2)	45(2)	3(1)	1(1)	15(1)
C(53)	47(2)	46(2)	51(2)	-8(2)	-1(2)	9(2)
C(54)	42(2)	30(2)	63(2)	-2(1)	10(2)	4(1)
C(55)	56(2)	42(2)	60(2)	16(2)	13(2)	21(2)
C(56)	52(2)	46(2)	39(2)	7(1)	8(1)	19(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **6**.

	x	y	z	U(eq)
H(1A)	3823	4099	956	59
H(1B)	2718	4979	1259	59
H(2A)	3175	4287	2499	50
H(2B)	4653	3805	2236	50
H(5)	5237	8552	3332	36
H(7)	8798	6938	2901	44
H(8)	7139	4987	2708	46
H(9A)	8977	9490	3022	46
H(9B)	7395	9889	2780	46
H(10A)	8314	9978	1519	49
H(10B)	9369	8986	1704	49
H(12)	5399	9055	1138	41
H(15)	6627	5124	811	54
H(16)	8551	6909	989	53
H(22)	4175	5006	4334	72
H(23)	3308	3330	5140	84
H(24)	726	2462	5127	76
H(25)	-1011	3291	4323	75
H(26)	-175	4970	3519	58
H(32)	4080	7360	4892	56
H(33)	4025	9044	5823	67
H(34)	2527	10504	5515	69
H(35)	1108	10322	4273	66
H(36)	1154	8660	3327	52
H(42)	236	6122	-457	59
H(43)	-55	6078	-1880	72
H(44)	1840	7186	-2614	67

H(45)	4113	8315	-1932	59
H(46)	4432	8335	-507	52
H(52)	3114	8862	2260	51
H(53)	2842	10870	2694	58
H(54)	1954	12183	1763	55
H(55)	1435	11489	397	60
H(56)	1728	9492	-45	53

X-ray crystal structure analysis of **(816638)**: formula $C_{44}H_{52}B_2F_8N_2P_2Pd$, M = 950.84, yellow crystal 0.23 x 0.20 x 0.15 mm, a = 11.5738(2), b = 11.8493(2), c = 17.8777(3)Å, α = 71.202(1), β = 73.601(1), γ = 74.227(1)°, V = 2181.98(6) Å^3, ρ_{calc} = 1.447 g cm^{-3}, μ = 0.567 mm^{-1}, empirical absorption correction ($0.881 \leq T \leq 0.920$), Z = 2, triclinic, space group P1bar (No. 2), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 21445 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 10073 independent (R_{int} = 0.055) and 9059 observed reflections [$I \geq 2\ \sigma(I)$], 534 refined parameters, R = 0.050, wR^2 = 0.124, max. (min.) residual electron density 0.68 (-0.86) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

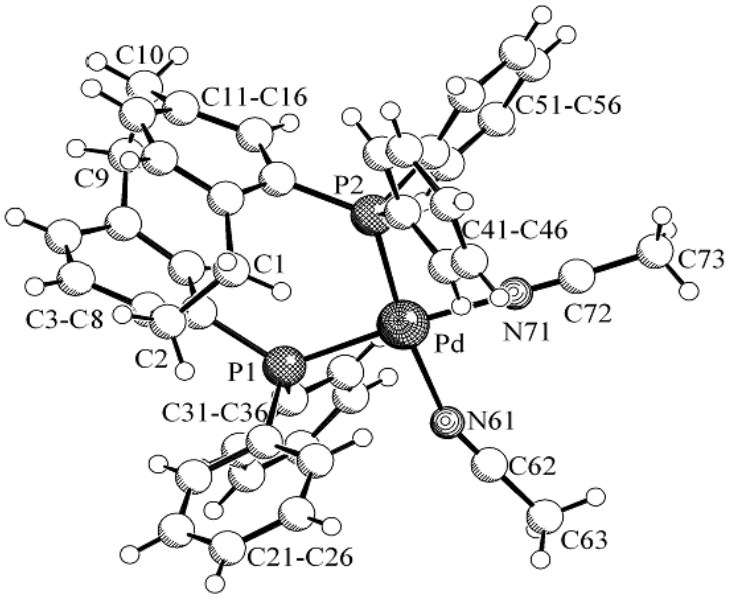


Table 1. Crystal data and structure refinement for **816638**.

Identification code	**816638**
Empirical formula	$C_{44}\ H_{52}\ B_2\ F_8\ N_2\ P_2\ Pd$
Formula weight	950.84
Temperature	223(2) K
Wavelength	0.71073 Å

Crystal system, space group	triclinic, P-1 (No.2)
Unit cell dimensions	a = 11.5738(2) Å α = 71.202(1)° b = 11.8493(2) Å β = 73.601(1)° c = 17.8777(3) Å γ = 74.227(1)°
Volume	2181.98(6) $Å^3$
Z, Calculated density	2, 1.447 Mg/m^3
Absorption coefficient	0.567 mm^{-1}
F(000)	976
Crystal size	0.23 x 0.20 x 0.15 mm
Theta range for data collection	4.19 to 27.85°
Limiting indices	-15<=h<=15, -15<=k<=14, -23<=l<=23
Reflections collected / unique	21445 / 10073 [R(int) = 0.055]
Completeness to theta = 27.85	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9198 and 0.8807
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10073 / 0 / 534
Goodness-of-fit on F^2	1.035
Final R indices [I>2σ(I)]	R1 = 0.0502, wR^2 = 0.1179
R indices (all data)	R1 = 0.0567, wR^2 = 0.1242
Largest diff. peak and hole	0.684 and -0.857 $e.Å^{-3}$

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **816638.**
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pd	6938(1)	6214(1)	7422(1)	24(1)
P(1)	6322(1)	7984(1)	7807(1)	25(1)
P(2)	5100(1)	6075(1)	7269(1)	22(1)
C(1)	4288(3)	6080(3)	9192(2)	30(1)
C(2)	4378(3)	7113(3)	9533(2)	30(1)
C(3)	4095(3)	8359(3)	8954(2)	29(1)
C(4)	4729(3)	8693(3)	8143(2)	25(1)
C(5)	4084(3)	9526(3)	7572(2)	30(1)
C(6)	2858(3)	10076(3)	7789(2)	37(1)
C(7)	2375(3)	9977(3)	8609(2)	40(1)
C(8)	2980(3)	9126(3)	9179(2)	35(1)
C(9)	2035(4)	10522(4)	7189(3)	48(1)
C(10)	1194(4)	9598(4)	7320(3)	46(1)

C(11)	1756(3)	8322(3)	7746(2)	35(1)
C(12)	2843(3)	7693(3)	7366(2)	31(1)
C(13)	3654(3)	6803(3)	7808(2)	24(1)
C(14)	3346(3)	6535(3)	8663(2)	28(1)
C(15)	2134(3)	6956(3)	9019(2)	35(1)
C(16)	1359(3)	7843(3)	8570(2)	39(1)
C(21)	7080(3)	7821(3)	8617(2)	32(1)
C(22)	7279(4)	8851(4)	8737(3)	45(1)
C(23)	7879(4)	8730(5)	9347(3)	59(1)
C(24)	8264(4)	7599(6)	9832(3)	60(1)
C(25)	8061(4)	6584(5)	9719(3)	56(1)
C(26)	7472(3)	6679(4)	9119(2)	41(1)
C(31)	6977(3)	9121(3)	6942(2)	32(1)
C(32)	7905(4)	8749(4)	6333(2)	42(1)
C(33)	8445(4)	9602(4)	5684(3)	57(1)
C(34)	8071(5)	10818(4)	5647(3)	62(1)
C(35)	7162(4)	11206(4)	6248(3)	54(1)
C(36)	6610(4)	10364(3)	6898(2)	41(1)
C(41)	5082(3)	4438(3)	7557(2)	25(1)
C(42)	5431(3)	3701(3)	8366(2)	32(1)
C(43)	5548(4)	2350(3)	8470(2)	38(1)
C(44)	4373(4)	2079(3)	8409(2)	42(1)
C(45)	3964(4)	2853(3)	7633(2)	39(1)
C(46)	3869(3)	4206(3)	7515(2)	33(1)
C(51)	5052(3)	6646(3)	6181(2)	28(1)
C(52)	5463(4)	7883(3)	5820(2)	36(1)
C(53)	5358(5)	8419(4)	4932(2)	50(1)
C(54)	6066(5)	7519(4)	4436(2)	48(1)
C(55)	5655(4)	6314(3)	4803(2)	41(1)
C(56)	5817(4)	5767(3)	5678(2)	37(1)
N(61)	7803(3)	4733(3)	6941(2)	35(1)
C(62)	8553(4)	4036(3)	6695(2)	40(1)
C(63)	9523(5)	3129(5)	6376(3)	69(2)
N(71)	8696(3)	6120(3)	7549(2)	37(1)
C(72)	9626(3)	5797(4)	7699(2)	41(1)
C(73)	10815(4)	5377(5)	7917(3)	62(1)
B(1)	1420(7)	6147(6)	5693(4)	66(2)
F(11)	289(4)	6808(5)	5648(3)	129(2)
F(12)	1942(7)	6655(5)	6063(3)	168(3)
F(13)	2098(3)	6210(3)	4925(2)	83(1)
F(14)	1377(4)	4982(3)	6146(3)	109(1)
B(2)	-849(5)	12561(5)	8753(3)	50(1)
F(21)	53(3)	12882(3)	8102(2)	93(1)
F(22)	-1457(5)	11899(5)	8556(4)	141(2)
F(23)	-1709(3)	13555(3)	8911(2)	93(1)
F(24)	-403(3)	11852(4)	9411(2)	96(1)

Table 3. Bond lengths [Å] and angles [°] for **816638**.

Pd-N(71)	2.079(3)
Pd-N(61)	2.086(3)
Pd-P(2)	2.2757(8)
Pd-P(1)	2.2848(8)
P(1)-C(4)	1.823(3)
P(1)-C(31)	1.826(3)
P(1)-C(21)	1.830(3)
P(2)-C(13)	1.820(3)
P(2)-C(41)	1.843(3)
P(2)-C(51)	1.854(3)
C(1)-C(14)	1.519(5)
C(1)-C(2)	1.571(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800

C(2)-C(3)	1.517(5)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(3)-C(8)	1.399(5)
C(3)-C(4)	1.410(4)
C(4)-C(5)	1.398(4)
C(5)-C(6)	1.393(5)
C(5)-H(5)	0.9400
C(6)-C(7)	1.393(5)
C(6)-C(9)	1.508(6)
C(7)-C(8)	1.379(5)
C(7)-H(7)	0.9400
C(8)-H(8)	0.9400
C(9)-C(10)	1.576(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-C(11)	1.514(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(16)	1.388(5)
C(11)-C(12)	1.391(5)
C(12)-C(13)	1.400(4)
C(12)-H(12)	0.9400
C(13)-C(14)	1.417(4)
C(14)-C(15)	1.394(5)
C(15)-C(16)	1.380(5)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(21)-C(22)	1.391(5)
C(21)-C(26)	1.399(5)
C(22)-C(23)	1.402(6)
C(22)-H(22)	0.9400
C(23)-C(24)	1.375(8)
C(23)-H(23)	0.9400
C(24)-C(25)	1.371(7)
C(24)-H(24)	0.9400
C(25)-C(26)	1.386(5)
C(25)-H(25)	0.9400
C(26)-H(26)	0.9400
C(31)-C(32)	1.387(5)
C(31)-C(36)	1.400(5)
C(32)-C(33)	1.392(5)
C(32)-H(32)	0.9400
C(33)-C(34)	1.372(7)
C(33)-H(33)	0.9400
C(34)-C(35)	1.374(7)
C(34)-H(34)	0.9400
C(35)-C(36)	1.391(5)
C(35)-H(35)	0.9400
C(36)-H(36)	0.9400
C(41)-C(46)	1.528(4)

C(41)-C(42)	1.530(4)
C(41)-H(41)	0.9900
C(42)-C(43)	1.523(4)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(43)-C(44)	1.519(5)
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(44)-C(45)	1.518(5)
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(45)-C(46)	1.525(5)
C(45)-H(45A)	0.9800

C(45)-H(45B)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(51)-C(56)	1.527(4)
C(51)-C(52)	1.545(5)
C(51)-H(51)	0.9900
C(52)-C(53)	1.536(5)
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(53)-C(54)	1.523(6)
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(54)-C(55)	1.512(5)
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(55)-C(56)	1.533(5)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
N(61)-C(62)	1.121(5)
C(62)-C(63)	1.455(5)
C(63)-H(63A)	0.9700
C(63)-H(63B)	0.9700
C(63)-H(63C)	0.9700
N(71)-C(72)	1.119(5)
C(72)-C(73)	1.449(5)
C(73)-H(73A)	0.9700
C(73)-H(73B)	0.9700
C(73)-H(73C)	0.9700
B(1)-F(11)	1.340(8)
B(1)-F(12)	1.358(8)
B(1)-F(14)	1.363(7)
B(1)-F(13)	1.365(7)
B(2)-F(24)	1.352(6)
B(2)-F(21)	1.354(6)
B(2)-F(22)	1.361(7)
B(2)-F(23)	1.369(6)

N(71)-Pd-N(61)	83.25(11)
N(71)-Pd-P(2)	172.84(8)
N(61)-Pd-P(2)	89.94(8)
N(71)-Pd-P(1)	88.41(9)
N(61)-Pd-P(1)	168.92(9)
P(2)-Pd-P(1)	98.62(3)
C(4)-P(1)-C(31)	106.03(15)
C(4)-P(1)-C(21)	105.00(15)
C(31)-P(1)-C(21)	105.68(16)
C(4)-P(1)-Pd	125.00(10)
C(31)-P(1)-Pd	105.32(11)
C(21)-P(1)-Pd	108.41(12)
C(13)-P(2)-C(41)	106.87(14)
C(13)-P(2)-C(51)	106.26(14)
C(41)-P(2)-C(51)	106.25(14)
C(13)-P(2)-Pd	121.34(10)

C(41)-P(2)-Pd	106.37(10)
C(51)-P(2)-Pd	108.86(11)
C(14)-C(1)-C(2)	111.1(3)
C(14)-C(1)-H(1A)	109.4
C(2)-C(1)-H(1A)	109.4
C(14)-C(1)-H(1B)	109.4
C(2)-C(1)-H(1B)	109.4
H(1A)-C(1)-H(1B)	108.0
C(3)-C(2)-C(1)	111.4(3)

C(3)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	108.0
C(8)-C(3)-C(4)	116.8(3)
C(8)-C(3)-C(2)	117.4(3)
C(4)-C(3)-C(2)	124.2(3)
C(5)-C(4)-C(3)	118.6(3)
C(5)-C(4)-P(1)	119.3(2)
C(3)-C(4)-P(1)	121.9(2)
C(6)-C(5)-C(4)	122.0(3)
C(6)-C(5)-H(5)	119.0
C(4)-C(5)-H(5)	119.0
C(5)-C(6)-C(7)	116.8(3)
C(5)-C(6)-C(9)	120.7(4)
C(7)-C(6)-C(9)	121.2(3)
C(8)-C(7)-C(6)	120.2(3)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(3)	121.5(3)
C(7)-C(8)-H(8)	119.3
C(3)-C(8)-H(8)	119.3
C(6)-C(9)-C(10)	112.0(3)
C(6)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9A)	109.2
C(6)-C(9)-H(9B)	109.2
C(10)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	111.1(3)
C(11)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10A)	109.4
C(11)-C(10)-H(10B)	109.4
C(9)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0
C(16)-C(11)-C(12)	117.0(3)
C(16)-C(11)-C(10)	121.0(3)
C(12)-C(11)-C(10)	120.7(3)
C(11)-C(12)-C(13)	121.7(3)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(12)-C(13)-C(14)	118.8(3)
C(12)-C(13)-P(2)	119.3(2)
C(14)-C(13)-P(2)	121.9(2)
C(15)-C(14)-C(13)	117.1(3)
C(15)-C(14)-C(1)	117.5(3)
C(13)-C(14)-C(1)	123.9(3)
C(16)-C(15)-C(14)	121.1(3)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	120.9(3)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5
C(22)-C(21)-C(26)	119.1(3)
C(22)-C(21)-P(1)	119.6(3)
C(26)-C(21)-P(1)	121.3(3)
C(21)-C(22)-C(23)	119.8(4)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1

C(24)-C(23)-C(22)	120.4(4)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(25)-C(24)-C(23)	119.9(4)
C(25)-C(24)-H(24)	120.0

C(23)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	120.8(5)
C(24)-C(25)-H(25)	119.6
C(26)-C(25)-H(25)	119.6
C(25)-C(26)-C(21)	120.0(4)
C(25)-C(26)-H(26)	120.0
C(21)-C(26)-H(26)	120.0
C(32)-C(31)-C(36)	118.9(3)
C(32)-C(31)-P(1)	119.6(3)
C(36)-C(31)-P(1)	121.4(3)
C(31)-C(32)-C(33)	120.3(4)
C(31)-C(32)-H(32)	119.8
C(33)-C(32)-H(32)	119.8
C(34)-C(33)-C(32)	120.1(4)
C(34)-C(33)-H(33)	119.9
C(32)-C(33)-H(33)	119.9
C(33)-C(34)-C(35)	120.5(4)
C(33)-C(34)-H(34)	119.8
C(35)-C(34)-H(34)	119.8
C(34)-C(35)-C(36)	120.0(4)
C(34)-C(35)-H(35)	120.0
C(36)-C(35)-H(35)	120.0
C(35)-C(36)-C(31)	120.1(4)
C(35)-C(36)-H(36)	119.9
C(31)-C(36)-H(36)	119.9
C(46)-C(41)-C(42)	110.5(3)
C(46)-C(41)-P(2)	112.2(2)
C(42)-C(41)-P(2)	115.7(2)
C(46)-C(41)-H(41)	105.9
C(42)-C(41)-H(41)	105.9
P(2)-C(41)-H(41)	105.9
C(43)-C(42)-C(41)	109.9(3)
C(43)-C(42)-H(42A)	109.7
C(41)-C(42)-H(42A)	109.7
C(43)-C(42)-H(42B)	109.7
C(41)-C(42)-H(42B)	109.7
H(42A)-C(42)-H(42B)	108.2
C(44)-C(43)-C(42)	111.6(3)
C(44)-C(43)-H(43A)	109.3
C(42)-C(43)-H(43A)	109.3
C(44)-C(43)-H(43B)	109.3
C(42)-C(43)-H(43B)	109.3
H(43A)-C(43)-H(43B)	108.0
C(45)-C(44)-C(43)	112.0(3)
C(45)-C(44)-H(44A)	109.2
C(43)-C(44)-H(44A)	109.2
C(45)-C(44)-H(44B)	109.2
C(43)-C(44)-H(44B)	109.2
H(44A)-C(44)-H(44B)	107.9
C(44)-C(45)-C(46)	112.1(3)
C(44)-C(45)-H(45A)	109.2
C(46)-C(45)-H(45A)	109.2
C(44)-C(45)-H(45B)	109.2
C(46)-C(45)-H(45B)	109.2
H(45A)-C(45)-H(45B)	107.9
C(45)-C(46)-C(41)	110.3(3)
C(45)-C(46)-H(46A)	109.6
C(41)-C(46)-H(46A)	109.6
C(45)-C(46)-H(46B)	109.6
C(41)-C(46)-H(46B)	109.6
H(46A)-C(46)-H(46B)	108.1
C(56)-C(51)-C(52)	109.8(3)
C(56)-C(51)-P(2)	114.2(2)

C(52)-C(51)-P(2)	109.9(2)

C(56)-C(51)-H(51)	107.6
C(52)-C(51)-H(51)	107.6
P(2)-C(51)-H(51)	107.6
C(53)-C(52)-C(51)	111.1(3)
C(53)-C(52)-H(52A)	109.4
C(51)-C(52)-H(52A)	109.4
C(53)-C(52)-H(52B)	109.4
C(51)-C(52)-H(52B)	109.4
H(52A)-C(52)-H(52B)	108.0
C(54)-C(53)-C(52)	111.0(3)
C(54)-C(53)-H(53A)	109.4
C(52)-C(53)-H(53A)	109.4
C(54)-C(53)-H(53B)	109.4
C(52)-C(53)-H(53B)	109.4
H(53A)-C(53)-H(53B)	108.0
C(55)-C(54)-C(53)	111.0(3)
C(55)-C(54)-H(54A)	109.4
C(53)-C(54)-H(54A)	109.4
C(55)-C(54)-H(54B)	109.4
C(53)-C(54)-H(54B)	109.4
H(54A)-C(54)-H(54B)	108.0
C(54)-C(55)-C(56)	111.3(3)
C(54)-C(55)-H(55A)	109.4
C(56)-C(55)-H(55A)	109.4
C(54)-C(55)-H(55B)	109.4
C(56)-C(55)-H(55B)	109.4
H(55A)-C(55)-H(55B)	108.0
C(51)-C(56)-C(55)	109.2(3)
C(51)-C(56)-H(56A)	109.8
C(55)-C(56)-H(56A)	109.8
C(51)-C(56)-H(56B)	109.8
C(55)-C(56)-H(56B)	109.8
H(56A)-C(56)-H(56B)	108.3
C(62)-N(61)-Pd	160.1(3)
N(61)-C(62)-C(63)	179.8(5)
C(62)-C(63)-H(63A)	109.5
C(62)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5
C(62)-C(63)-H(63C)	109.5
H(63A)-C(63)-H(63C)	109.5
H(63B)-C(63)-H(63C)	109.5
C(72)-N(71)-Pd	164.0(3)
N(71)-C(72)-C(73)	178.4(5)
C(72)-C(73)-H(73A)	109.5
C(72)-C(73)-H(73B)	109.5
H(73A)-C(73)-H(73B)	109.5
C(72)-C(73)-H(73C)	109.5
H(73A)-C(73)-H(73C)	109.5
H(73B)-C(73)-H(73C)	109.5
F(11)-B(1)-F(12)	108.1(6)
F(11)-B(1)-F(14)	111.2(6)
F(12)-B(1)-F(14)	107.8(5)
F(11)-B(1)-F(13)	108.4(5)
F(12)-B(1)-F(13)	108.5(6)
F(14)-B(1)-F(13)	112.8(5)
F(24)-B(2)-F(21)	112.4(4)
F(24)-B(2)-F(22)	107.5(5)
F(21)-B(2)-F(22)	107.1(5)
F(24)-B(2)-F(23)	112.2(4)
F(21)-B(2)-F(23)	111.7(4)
F(22)-B(2)-F(23)	105.5(5)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **816638.** The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Pd	22(1)	22(1)	29(1)	-10(1)	-5(1)	-2(1)
P(1)	25(1)	22(1)	27(1)	-9(1)	-3(1)	-5(1)
P(2)	25(1)	21(1)	21(1)	-7(1)	-5(1)	-3(1)
C(1)	40(2)	27(2)	21(1)	-6(1)	-4(1)	-7(1)
C(2)	35(2)	34(2)	22(1)	-10(1)	-3(1)	-11(1)
C(3)	31(2)	31(2)	28(2)	-13(1)	-3(1)	-9(1)
C(4)	26(1)	20(1)	30(2)	-9(1)	-4(1)	-5(1)
C(5)	30(2)	23(1)	35(2)	-7(1)	-4(1)	-5(1)
C(6)	34(2)	23(2)	49(2)	-7(1)	-6(2)	-3(1)
C(7)	32(2)	30(2)	56(2)	-21(2)	-1(2)	-2(1)
C(8)	34(2)	33(2)	39(2)	-20(1)	3(1)	-9(1)
C(9)	42(2)	32(2)	59(2)	-1(2)	-14(2)	5(2)
C(10)	36(2)	42(2)	57(2)	-15(2)	-16(2)	4(2)
C(11)	27(2)	35(2)	46(2)	-15(2)	-12(1)	-1(1)
C(12)	32(2)	32(2)	30(2)	-10(1)	-10(1)	-5(1)
C(13)	25(1)	24(1)	27(1)	-10(1)	-5(1)	-6(1)
C(14)	33(2)	25(2)	27(2)	-9(1)	-4(1)	-10(1)
C(15)	36(2)	37(2)	34(2)	-13(1)	3(1)	-15(1)
C(16)	24(2)	43(2)	48(2)	-20(2)	1(1)	-7(1)
C(21)	28(2)	38(2)	35(2)	-16(1)	-3(1)	-9(1)
C(22)	45(2)	55(2)	48(2)	-30(2)	-9(2)	-13(2)
C(23)	52(3)	85(4)	61(3)	-45(3)	-3(2)	-26(2)
C(24)	43(2)	110(4)	41(2)	-31(3)	-7(2)	-27(3)
C(25)	43(2)	82(3)	39(2)	-10(2)	-15(2)	-11(2)
C(26)	36(2)	49(2)	39(2)	-10(2)	-9(2)	-11(2)
C(31)	29(2)	24(2)	39(2)	-6(1)	-3(1)	-8(1)
C(32)	38(2)	33(2)	47(2)	-11(2)	5(2)	-7(2)
C(33)	52(3)	47(2)	53(3)	-10(2)	16(2)	-15(2)
C(34)	57(3)	48(3)	62(3)	2(2)	9(2)	-25(2)
C(35)	53(2)	32(2)	65(3)	-5(2)	2(2)	-15(2)
C(36)	39(2)	30(2)	47(2)	-11(2)	3(2)	-9(2)
C(41)	27(2)	22(1)	28(1)	-7(1)	-7(1)	-4(1)
C(42)	45(2)	24(2)	31(2)	-6(1)	-16(1)	-6(1)
C(43)	55(2)	24(2)	36(2)	-5(1)	-14(2)	-6(2)
C(44)	56(2)	31(2)	40(2)	-10(2)	-1(2)	-21(2)
C(45)	42(2)	32(2)	50(2)	-15(2)	-10(2)	-13(2)
C(46)	32(2)	32(2)	40(2)	-13(1)	-10(1)	-9(1)
C(51)	37(2)	26(2)	21(1)	-8(1)	-7(1)	-6(1)
C(52)	55(2)	28(2)	26(2)	-9(1)	-7(2)	-10(2)
C(53)	80(3)	34(2)	31(2)	-4(2)	-12(2)	-13(2)
C(54)	76(3)	42(2)	26(2)	-10(2)	-7(2)	-16(2)
C(55)	65(3)	36(2)	26(2)	-12(1)	-10(2)	-11(2)
C(56)	52(2)	31(2)	28(2)	-11(1)	-7(2)	-5(2)
N(61)	29(1)	34(2)	44(2)	-20(1)	-8(1)	1(1)
C(62)	39(2)	38(2)	46(2)	-20(2)	-14(2)	3(2)
C(63)	61(3)	70(3)	82(3)	-54(3)	-28(3)	30(3)
N(71)	28(2)	36(2)	50(2)	-18(1)	-10(1)	-2(1)
C(72)	34(2)	40(2)	52(2)	-18(2)	-10(2)	-7(2)
C(73)	39(2)	71(3)	84(3)	-26(3)	-28(2)	-6(2)
B(1)	85(4)	50(3)	56(3)	-7(3)	-10(3)	-16(3)
F(11)	98(3)	132(4)	93(3)	-23(3)	13(2)	37(3)
F(12)	297(8)	165(5)	97(3)	10(3)	-83(4)	-147(5)
F(13)	86(2)	67(2)	69(2)	-16(2)	4(2)	1(2)
F(14)	133(3)	59(2)	105(3)	0(2)	9(3)	-32(2)
B(2)	46(3)	55(3)	41(2)	-10(2)	-3(2)	-8(2)
F(21)	94(3)	84(2)	74(2)	-21(2)	31(2)	-24(2)
F(22)	143(4)	138(4)	190(5)	-51(4)	-64(4)	-64(4)
F(23)	97(3)	81(2)	63(2)	-13(2)	4(2)	14(2)

F(24)	82(2)	123(3)	60(2)	-20(2)	-25(2)	22(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **816638.**

	x	y	z	U(eq)
H(1A)	5093	5792	8875	36
H(1B)	4055	5392	9644	36
H(2A)	3797	7088	10054	36
H(2B)	5208	6972	9624	36
H(5)	4490	9720	7025	36
H(7)	1635	10492	8775	48
H(8)	2636	9059	9731	42
H(9A)	2542	10644	6639	58
H(9B)	1514	11308	7242	58
H(10A)	382	9855	7644	55
H(10B)	1084	9604	6795	55
H(12)	3039	7870	6798	37
H(15)	1839	6631	9575	42
H(16)	551	8127	8826	46
H(22)	7012	9627	8409	54
H(23)	8018	9425	9425	71
H(24)	8665	7522	10240	72
H(25)	8325	5813	10053	67
H(26)	7335	5976	9050	49
H(32)	8170	7916	6359	51
H(33)	9068	9345	5271	68
H(34)	8439	11391	5207	74
H(35)	6912	12040	6219	64
H(36)	5991	10630	7310	49
H(41)	5717	4102	7139	30
H(42A)	6214	3853	8382	39
H(42B)	4800	3956	8809	39
H(43A)	6229	2085	8053	46
H(43B)	5737	1889	8999	46
H(44A)	4507	1218	8430	50
H(44B)	3720	2232	8873	50
H(45A)	3162	2713	7645	47
H(45B)	4552	2603	7172	47
H(46A)	3207	4485	7937	39
H(46B)	3669	4666	6989	39
H(51)	4187	6786	6140	33
H(52A)	4950	8452	6135	44
H(52B)	6317	7775	5858	44
H(53A)	4491	8623	4900	59
H(53B)	5683	9169	4706	59
H(54A)	5934	7855	3882	57
H(54B)	6947	7392	4412	57
H(55A)	6136	5746	4480	49
H(55B)	4788	6432	4790	49
H(56A)	5549	4986	5902	45
H(56B)	6686	5624	5693	45
H(63A)	10308	3194	6436	103
H(63B)	9544	3266	5808	103
H(63C)	9364	2323	6672	103
H(73A)	10709	5267	8492	92
H(73B)	11326	5973	7617	92
H(73C)	11207	4608	7787	92

X-ray crystal structure analysis of **(816639)**: formula $C_{44}H_{40}B_2F_8N_2P_2Pd$ * ½ CH_3CN, M = 959.27, yellow crystal 0.30 x 0.15 x 0.15 mm, a = 12.1729(1), b = 16.7826(2), c = 21.2782(3)Å, β = 100.027(1)°, V = 4289.59(9) Å^3, ρ_{calc} = 1.488 g cm^{-3}, μ = 0.579 mm^{-1}, empirical absorption correction (0.845 ≤ T ≤ 0.918), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 27747 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 9924 independent (R_{int} = 0.048) and 8360 observed reflections [$I \geq 2\ \sigma(I)$], 654 refined parameters, R = 0.049, wR^2 = 0.124, max. (min.) residual electron density 0.59 (-0.67) e Å^{-3}, BF_4-anions refined with split positions, hydrogen atoms calculated and refined as riding atoms.

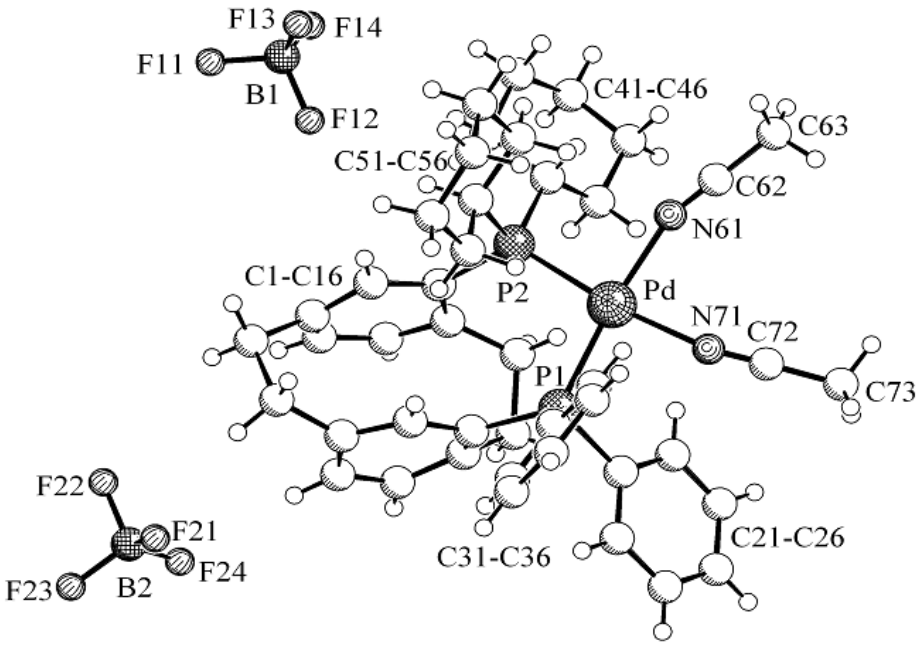

Table 1. Crystal data and structure refinement for **816639**.

Identification code	**816639**
Empirical formula	$C_{45}\ H_{41.50}\ B_2\ F_8\ N_{2.50}\ P_2\ Pd$
Formula weight	959.27
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$ (No.14)
Unit cell dimensions	a = 12.1729(1) Å b = 16.7826(2) Å β = 100.027(1)° c = 21.2782(3) Å
Volume	4280.59(9) Å^3
Z, Calculated density	4, 1.488 Mg/m^3

Absorption coefficient	0.579 mm^{-1}
F(000)	1948
Crystal size	0.30 x 0.15 x 0.15 mm
Theta range for data collection	4.13 to 27.90°
Limiting indices	-15<=h<=15, -22<=k<=20, -28<=l<=27
Reflections collected / unique	27747 / 9924 [R(int) = 0.048]
Completeness to theta = 27.90	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9182 and 0.8454
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9924 / 537 / 654
Goodness-of-fit on F^2	1.084
Final R indices [I>2σ(I)]	R1 = 0.0493, wR^2 = 0.1137
R indices (all data)	R1 = 0.0615, wR^2 = 0.1243
Largest diff. peak and hole	0.589 and -0.667 e.$Å^{-3}$

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **816639**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pd	5346(1)	7694(1)	8112(1)	32(1)
P(1)	6477(1)	7098(1)	7505(1)	29(1)
P(2)	4529(1)	8621(1)	7405(1)	30(1)
C(1)	4162(3)	7450(2)	6201(2)	45(1)
C(2)	5042(3)	6866(2)	6010(2)	42(1)
C(3)	6203(3)	7212(2)	6150(2)	37(1)
C(4)	6749(3)	7484(2)	6749(2)	31(1)
C(5)	7505(3)	8115(2)	6779(2)	36(1)
C(6)	7768(3)	8462(2)	6230(2)	43(1)
C(7)	7464(3)	8047(3)	5668(2)	48(1)
C(8)	6695(3)	7436(2)	5628(2)	45(1)
C(9)	8149(3)	9326(3)	6237(2)	57(1)
C(10)	7158(4)	9907(3)	5974(2)	53(1)
C(11)	6039(3)	9535(2)	6001(2)	43(1)
C(12)	5693(3)	9403(2)	6583(2)	37(1)
C(13)	4928(3)	8801(2)	6638(2)	32(1)
C(14)	4512(3)	8311(2)	6116(2)	38(1)
C(15)	4668(3)	8578(3)	5519(2)	46(1)
C(16)	5424(3)	9172(3)	5465(2)	50(1)
C(21)	6009(3)	6079(2)	7343(2)	33(1)
C(22)	6558(3)	5578(2)	6967(2)	39(1)
C(23)	6148(3)	4825(2)	6803(2)	45(1)

C(24)	5181(4)	4566(2)	6993(2)	52(1)
C(25)	4635(3)	5054(2)	7360(2)	52(1)
C(26)	5045(3)	5807(2)	7536(2)	41(1)
C(31)	7852(3)	7083(2)	8011(2)	31(1)
C(32)	8664(3)	6534(2)	7916(2)	42(1)
C(33)	9686(3)	6523(2)	8319(2)	47(1)
C(34)	9925(3)	7067(3)	8807(2)	49(1)
C(35)	9138(3)	7621(3)	8898(2)	50(1)
C(36)	8097(3)	7625(2)	8505(2)	41(1)
C(41)	3043(3)	8405(2)	7226(2)	39(1)
C(42)	2569(3)	7835(2)	7571(2)	50(1)
C(43)	1430(4)	7697(3)	7425(3)	67(1)
C(44)	774(4)	8110(4)	6947(3)	73(2)
C(45)	1238(3)	8675(3)	6603(2)	61(1)
C(46)	2374(3)	8828(3)	6740(2)	47(1)
C(51)	4686(3)	9562(2)	7831(2)	34(1)
C(52)	5661(3)	9715(2)	8263(2)	42(1)
C(53)	5757(4)	10403(2)	8632(2)	53(1)
C(54)	4880(5)	10928(3)	8577(2)	68(1)
C(55)	3924(5)	10784(3)	8154(3)	71(1)
C(56)	3821(4)	10112(2)	7773(2)	55(1)
N(61)	5906(3)	6882(2)	8839(1)	43(1)
C(62)	6060(3)	6589(2)	9323(2)	44(1)
C(63)	6256(5)	6240(3)	9953(2)	68(1)
N(71)	4458(3)	8210(2)	8754(1)	43(1)
C(72)	4065(4)	8515(3)	9131(2)	55(1)
C(73)	3560(5)	8938(5)	9605(3)	107(2)
B(1A)	2185(11)	6162(7)	4955(5)	56(3)
F(11A)	2820(12)	5856(8)	5484(5)	91(4)
F(12A)	1101(9)	5953(10)	4929(7)	128(5)
F(13A)	2546(7)	5871(6)	4429(3)	85(3)
F(14A)	2276(12)	6972(4)	4948(4)	100(3)
B(1B)	2024(13)	6163(8)	5058(8)	61(6)
F(11B)	2711(14)	5915(10)	5589(8)	73(4)
F(12B)	1143(11)	5657(8)	4917(7)	74(3)
F(13B)	2577(14)	6178(14)	4557(10)	160(7)

F(14B)	1615(17)	6894(7)	5149(9)	129(6)
B(2A)	13134(11)	5900(7)	9019(5)	54(4)
F(21A)	12268(10)	5551(8)	9238(7)	109(4)
F(22A)	12879(10)	6063(8)	8385(4)	105(4)
F(23A)	13438(11)	6586(6)	9344(5)	105(4)
F(24A)	14008(6)	5389(5)	9108(6)	105(3)
B(2B)	12955(11)	5981(8)	9029(6)	56(5)
F(21B)	11990(8)	5582(8)	9044(7)	90(4)
F(22B)	13246(12)	5883(9)	8449(6)	109(5)
F(23B)	12787(11)	6765(5)	9138(5)	92(3)
F(24B)	13774(8)	5711(8)	9495(7)	126(5)
N(81)	5875(8)	5899(6)	4577(5)	89(3)
C(82)	5450(14)	5404(10)	4793(8)	76(4)
C(83)	4818(17)	4796(11)	5066(9)	82(5)

Table 3. Bond lengths [Å] and angles [°] for **816639.**

Pd-N(71)	2.074(3)
Pd-N(61)	2.085(3)
Pd-P(2)	2.2709(8)
Pd-P(1)	2.2777(8)
P(1)-C(4)	1.816(3)
P(1)-C(21)	1.816(3)

P(1)-C(31)	1.826(3)
P(2)-C(13)	1.807(3)
P(2)-C(51)	1.813(3)
P(2)-C(41)	1.818(3)
C(1)-C(14)	1.525(5)
C(1)-C(2)	1.557(5)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(2)-C(3)	1.509(5)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(3)-C(8)	1.401(5)
C(3)-C(4)	1.408(5)
C(4)-C(5)	1.397(5)
C(5)-C(6)	1.393(5)
C(5)-H(5)	0.9400
C(6)-C(7)	1.379(6)
C(6)-C(9)	1.521(6)
C(7)-C(8)	1.382(6)
C(7)-H(7)	0.9400
C(8)-H(8)	0.9400
C(9)-C(10)	1.575(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-C(11)	1.509(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(16)	1.391(6)
C(11)-C(12)	1.393(5)
C(12)-C(13)	1.391(5)
C(12)-H(12)	0.9400
C(13)-C(14)	1.404(5)
C(14)-C(15)	1.393(5)
C(15)-C(16)	1.374(6)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(21)-C(26)	1.387(5)
C(21)-C(22)	1.406(4)
C(22)-C(23)	1.380(5)
C(22)-H(22)	0.9400
C(23)-C(24)	1.380(6)
C(23)-H(23)	0.9400
C(24)-C(25)	1.380(6)
C(24)-H(24)	0.9400
C(25)-C(26)	1.387(5)
C(25)-H(25)	0.9400
C(26)-H(26)	0.9400
C(31)-C(36)	1.383(5)
C(31)-C(32)	1.392(5)
C(32)-C(33)	1.383(5)
C(32)-H(32)	0.9400
C(33)-C(34)	1.374(6)
C(33)-H(33)	0.9400
C(34)-C(35)	1.374(6)
C(34)-H(34)	0.9400
C(35)-C(36)	1.391(5)
C(35)-H(35)	0.9400
C(36)-H(36)	0.9400
C(41)-C(42)	1.391(5)

C(41)-C(46)	1.395(5)
C(42)-C(43)	1.387(6)
C(42)-H(42)	0.9400
C(43)-C(44)	1.368(8)
C(43)-H(43)	0.9400

C(44)-C(45)	1.377(8)
C(44)-H(44)	0.9400
C(45)-C(46)	1.386(5)
C(45)-H(45)	0.9400
C(46)-H(46)	0.9400
C(51)-C(56)	1.391(5)
C(51)-C(52)	1.393(5)
C(52)-C(53)	1.389(5)
C(52)-H(52)	0.9400
C(53)-C(54)	1.374(7)
C(53)-H(53)	0.9400
C(54)-C(55)	1.364(7)
C(54)-H(54)	0.9400
C(55)-C(56)	1.381(6)
C(55)-H(55)	0.9400
C(56)-H(56)	0.9400
N(61)-C(62)	1.128(4)
C(62)-C(63)	1.444(5)
C(63)-H(63A)	0.9700
C(63)-H(63B)	0.9700
C(63)-H(63C)	0.9700
N(71)-C(72)	1.125(5)
C(72)-C(73)	1.455(6)
C(73)-H(73A)	0.9700
C(73)-H(73B)	0.9700
C(73)-H(73C)	0.9700
B(1A)-F(11A)	1.351(10)
B(1A)-F(12A)	1.358(11)
B(1A)-F(13A)	1.364(11)
B(1A)-F(14A)	1.364(10)
B(1B)-F(11B)	1.349(12)
B(1B)-F(14B)	1.350(12)
B(1B)-F(13B)	1.358(12)
B(1B)-F(12B)	1.360(11)
B(2A)-F(24A)	1.354(12)
B(2A)-F(21A)	1.358(11)
B(2A)-F(22A)	1.359(11)
B(2A)-F(23A)	1.361(10)
B(2B)-F(22B)	1.351(11)
B(2B)-F(24B)	1.356(12)
B(2B)-F(23B)	1.358(12)
B(2B)-F(21B)	1.359(11)
N(81)-C(82)	1.120(14)
C(82)-C(83)	1.458(14)
C(83)-H(83A)	0.9700
C(83)-H(83B)	0.9700
C(83)-H(83C)	0.9700

N(71)-Pd-N(61)	85.73(12)
N(71)-Pd-P(2)	86.12(9)
N(61)-Pd-P(2)	171.41(8)
N(71)-Pd-P(1)	173.47(9)
N(61)-Pd-P(1)	88.95(8)
P(2)-Pd-P(1)	99.36(3)
C(4)-P(1)-C(21)	105.49(15)
C(4)-P(1)-C(31)	103.69(14)
C(21)-P(1)-C(31)	108.88(15)
C(4)-P(1)-Pd	124.59(10)
C(21)-P(1)-Pd	108.73(11)
C(31)-P(1)-Pd	104.70(10)
C(13)-P(2)-C(51)	106.50(15)
C(13)-P(2)-C(41)	105.01(16)
C(51)-P(2)-C(41)	107.07(15)

C(13)-P(2)-Pd	123.88(10)

C(51)-P(2)-Pd	105.58(11)
C(41)-P(2)-Pd	107.86(13)
C(14)-C(1)-C(2)	110.2(3)
C(14)-C(1)-H(1A)	109.6
C(2)-C(1)-H(1A)	109.6
C(14)-C(1)-H(1B)	109.6
C(2)-C(1)-H(1B)	109.6
H(1A)-C(1)-H(1B)	108.1
C(3)-C(2)-C(1)	111.7(3)
C(3)-C(2)-H(2A)	109.3
C(1)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.3
C(1)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	107.9
C(8)-C(3)-C(4)	115.6(3)
C(8)-C(3)-C(2)	117.5(3)
C(4)-C(3)-C(2)	125.6(3)
C(5)-C(4)-C(3)	119.3(3)
C(5)-C(4)-P(1)	116.8(2)
C(3)-C(4)-P(1)	123.8(3)
C(6)-C(5)-C(4)	121.7(3)
C(6)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	116.8(4)
C(7)-C(6)-C(9)	121.7(3)
C(5)-C(6)-C(9)	120.4(4)
C(6)-C(7)-C(8)	120.4(3)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-C(3)	121.9(3)
C(7)-C(8)-H(8)	119.0
C(3)-C(8)-H(8)	119.0
C(6)-C(9)-C(10)	111.9(3)
C(6)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9A)	109.2
C(6)-C(9)-H(9B)	109.2
C(10)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	111.8(3)
C(11)-C(10)-H(10A)	109.3
C(9)-C(10)-H(10A)	109.3
C(11)-C(10)-H(10B)	109.3
C(9)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	107.9
C(16)-C(11)-C(12)	117.1(4)
C(16)-C(11)-C(10)	120.7(3)
C(12)-C(11)-C(10)	121.0(4)
C(13)-C(12)-C(11)	120.1(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.9(3)
C(12)-C(13)-P(2)	119.1(3)
C(14)-C(13)-P(2)	119.9(3)
C(15)-C(14)-C(13)	116.4(3)
C(15)-C(14)-C(1)	119.9(3)
C(13)-C(14)-C(1)	122.1(3)
C(16)-C(15)-C(14)	120.6(3)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(15)-C(16)-C(11)	121.4(3)
C(15)-C(16)-H(16)	119.3
C(11)-C(16)-H(16)	119.3
C(26)-C(21)-C(22)	118.8(3)
C(26)-C(21)-P(1)	120.5(3)
C(22)-C(21)-P(1)	120.5(2)
C(23)-C(22)-C(21)	120.4(3)
C(23)-C(22)-H(22)	119.8

C(21)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	120.2(4)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(25)-C(24)-C(23)	119.9(4)
C(25)-C(24)-H(24)	120.0
C(23)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	120.5(4)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(25)-C(26)-C(21)	120.2(3)
C(25)-C(26)-H(26)	119.9
C(21)-C(26)-H(26)	119.9
C(36)-C(31)-C(32)	118.7(3)
C(36)-C(31)-P(1)	119.6(3)
C(32)-C(31)-P(1)	121.7(3)
C(33)-C(32)-C(31)	120.3(3)
C(33)-C(32)-H(32)	119.9
C(31)-C(32)-H(32)	119.9
C(34)-C(33)-C(32)	120.6(3)
C(34)-C(33)-H(33)	119.7
C(32)-C(33)-H(33)	119.7
C(35)-C(34)-C(33)	119.7(4)
C(35)-C(34)-H(34)	120.2
C(33)-C(34)-H(34)	120.2
C(34)-C(35)-C(36)	120.1(4)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(31)-C(36)-C(35)	120.6(3)
C(31)-C(36)-H(36)	119.7
C(35)-C(36)-H(36)	119.7
C(42)-C(41)-C(46)	119.9(3)
C(42)-C(41)-P(2)	121.1(3)
C(46)-C(41)-P(2)	119.0(3)
C(43)-C(42)-C(41)	119.1(4)
C(43)-C(42)-H(42)	120.4
C(41)-C(42)-H(42)	120.4
C(44)-C(43)-C(42)	120.9(5)
C(44)-C(43)-H(43)	119.5
C(42)-C(43)-H(43)	119.5
C(43)-C(44)-C(45)	120.2(4)
C(43)-C(44)-H(44)	119.9
C(45)-C(44)-H(44)	119.9
C(44)-C(45)-C(46)	120.2(5)
C(44)-C(45)-H(45)	119.9
C(46)-C(45)-H(45)	119.9
C(45)-C(46)-C(41)	119.6(4)
C(45)-C(46)-H(46)	120.2
C(41)-C(46)-H(46)	120.2
C(56)-C(51)-C(52)	118.7(3)
C(56)-C(51)-P(2)	121.4(3)
C(52)-C(51)-P(2)	119.7(3)
C(53)-C(52)-C(51)	120.3(4)
C(53)-C(52)-H(52)	119.8
C(51)-C(52)-H(52)	119.8
C(54)-C(53)-C(52)	119.8(4)
C(54)-C(53)-H(53)	120.1
C(52)-C(53)-H(53)	120.1
C(55)-C(54)-C(53)	120.3(4)
C(55)-C(54)-H(54)	119.9
C(53)-C(54)-H(54)	119.9
C(54)-C(55)-C(56)	120.8(4)
C(54)-C(55)-H(55)	119.6
C(56)-C(55)-H(55)	119.6
C(55)-C(56)-C(51)	120.0(4)

C(55)-C(56)-H(56)	120.0
C(51)-C(56)-H(56)	120.0
C(62)-N(61)-Pd	160.6(3)

N(61)-C(62)-C(63)	178.1(4)
C(62)-C(63)-H(63A)	109.5
C(62)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5
C(62)-C(63)-H(63C)	109.5
H(63A)-C(63)-H(63C)	109.5
H(63B)-C(63)-H(63C)	109.5
C(72)-N(71)-Pd	173.8(4)
N(71)-C(72)-C(73)	177.8(6)
C(72)-C(73)-H(73A)	109.5
C(72)-C(73)-H(73B)	109.5
H(73A)-C(73)-H(73B)	109.5
C(72)-C(73)-H(73C)	109.5
H(73A)-C(73)-H(73C)	109.5
H(73B)-C(73)-H(73C)	109.5
F(11A)-B(1A)-F(12A)	110.3(10)
F(11A)-B(1A)-F(13A)	109.2(9)
F(12A)-B(1A)-F(13A)	108.9(9)
F(11A)-B(1A)-F(14A)	110.6(9)
F(12A)-B(1A)-F(14A)	109.8(9)
F(13A)-B(1A)-F(14A)	108.0(9)
F(11B)-B(1B)-F(14B)	110.5(11)
F(11B)-B(1B)-F(13B)	110.1(11)
F(14B)-B(1B)-F(13B)	110.0(11)
F(11B)-B(1B)-F(12B)	110.0(11)
F(14B)-B(1B)-F(12B)	107.6(11)
F(13B)-B(1B)-F(12B)	108.6(11)
F(24A)-B(2A)-F(21A)	108.5(9)
F(24A)-B(2A)-F(22A)	107.7(9)
F(21A)-B(2A)-F(22A)	111.8(10)
F(24A)-B(2A)-F(23A)	109.1(9)
F(21A)-B(2A)-F(23A)	110.4(10)
F(22A)-B(2A)-F(23A)	109.3(9)
F(22B)-B(2B)-F(24B)	110.5(11)
F(22B)-B(2B)-F(23B)	110.3(10)
F(24B)-B(2B)-F(23B)	108.2(10)
F(22B)-B(2B)-F(21B)	109.1(10)
F(24B)-B(2B)-F(21B)	110.3(10)
F(23B)-B(2B)-F(21B)	108.5(10)
N(81)-C(82)-C(83)	175.5(14)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **816639**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Pd	37(1)	31(1)	31(1)	1(1)	13(1)	4(1)
P(1)	30(1)	26(1)	31(1)	0(1)	9(1)	2(1)
P(2)	29(1)	29(1)	34(1)	0(1)	10(1)	2(1)
C(1)	38(2)	47(2)	49(2)	-13(2)	9(2)	-6(2)
C(2)	47(2)	39(2)	39(2)	-8(2)	4(2)	1(2)
C(3)	41(2)	37(2)	34(2)	-2(1)	7(1)	8(1)

C(4)	29(2)	33(2)	30(2)	2(1)	8(1)	5(1)
C(5)	27(2)	43(2)	37(2)	7(1)	5(1)	2(1)
C(6)	31(2)	53(2)	46(2)	16(2)	11(1)	2(2)
C(7)	47(2)	62(2)	38(2)	13(2)	20(2)	15(2)
C(8)	54(2)	48(2)	34(2)	-2(2)	13(2)	13(2)
C(9)	49(2)	67(3)	57(2)	21(2)	10(2)	-18(2)
C(10)	61(2)	45(2)	60(2)	6(2)	30(2)	-4(2)
C(11)	51(2)	36(2)	46(2)	10(2)	18(2)	10(2)
C(12)	42(2)	28(2)	42(2)	1(1)	12(1)	4(1)
C(13)	30(2)	31(2)	37(2)	2(1)	9(1)	7(1)
C(14)	28(2)	45(2)	40(2)	-5(2)	5(1)	7(1)
C(15)	43(2)	58(2)	34(2)	-4(2)	2(1)	14(2)
C(16)	65(2)	54(2)	34(2)	14(2)	17(2)	24(2)
C(21)	34(2)	27(2)	36(2)	1(1)	5(1)	1(1)
C(22)	40(2)	34(2)	43(2)	-4(1)	11(1)	1(1)
C(23)	55(2)	30(2)	50(2)	-6(2)	7(2)	4(2)
C(24)	63(3)	33(2)	61(2)	-3(2)	12(2)	-11(2)
C(25)	52(2)	45(2)	61(2)	3(2)	15(2)	-16(2)
C(26)	41(2)	38(2)	45(2)	2(2)	14(2)	0(2)
C(31)	32(2)	32(2)	31(2)	3(1)	8(1)	-1(1)
C(32)	35(2)	42(2)	49(2)	-6(2)	9(1)	4(2)
C(33)	34(2)	45(2)	61(2)	6(2)	8(2)	8(2)
C(34)	40(2)	59(2)	46(2)	10(2)	1(2)	-5(2)
C(35)	50(2)	55(2)	43(2)	-10(2)	-1(2)	1(2)
C(36)	43(2)	41(2)	39(2)	-7(2)	5(1)	5(2)
C(41)	30(2)	42(2)	47(2)	-10(2)	14(1)	3(1)
C(42)	43(2)	49(2)	62(2)	-8(2)	19(2)	-9(2)
C(43)	46(2)	70(3)	94(4)	-21(3)	34(2)	-23(2)
C(44)	34(2)	96(4)	89(4)	-38(3)	15(2)	-8(2)
C(45)	34(2)	92(4)	57(2)	-25(2)	7(2)	12(2)
C(46)	35(2)	60(2)	47(2)	-11(2)	9(2)	8(2)
C(51)	40(2)	28(2)	36(2)	1(1)	13(1)	2(1)
C(52)	45(2)	39(2)	44(2)	-5(2)	12(2)	-2(2)
C(53)	72(3)	45(2)	42(2)	-10(2)	15(2)	-15(2)
C(54)	102(4)	43(2)	61(3)	-18(2)	21(3)	-2(2)
C(55)	82(3)	46(2)	88(4)	-15(2)	18(3)	23(2)
C(56)	55(2)	41(2)	67(3)	-7(2)	7(2)	11(2)
N(61)	50(2)	44(2)	38(2)	4(1)	14(1)	4(1)
C(62)	53(2)	40(2)	40(2)	2(2)	13(2)	3(2)
C(63)	93(4)	69(3)	43(2)	18(2)	13(2)	10(3)
N(71)	53(2)	41(2)	41(2)	3(1)	23(1)	3(1)
C(72)	54(2)	66(3)	48(2)	-5(2)	22(2)	-1(2)
C(73)	87(4)	156(7)	90(4)	-53(4)	51(3)	6(4)
B(1A)	51(6)	75(7)	45(5)	14(4)	12(5)	4(5)
F(11A)	93(6)	92(6)	78(6)	-5(5)	-15(5)	15(5)
F(12A)	81(5)	168(9)	132(7)	21(7)	7(5)	-24(6)
F(13A)	100(5)	97(5)	60(3)	-15(3)	22(3)	-14(3)
F(14A)	152(8)	66(4)	73(4)	7(3)	-3(4)	18(4)
B(1B)	48(8)	72(9)	61(9)	2(6)	1(6)	-20(6)
F(11B)	74(7)	83(7)	58(5)	13(5)	-2(5)	-15(5)
F(12B)	68(6)	74(6)	79(6)	-6(4)	4(4)	-29(4)
F(13B)	183(10)	164(11)	149(10)	47(8)	76(8)	-14(8)
F(14B)	147(9)	90(7)	137(8)	-6(6)	-10(7)	31(6)

B(2A)	57(6)	57(7)	51(7)	-5(5)	20(5)	-7(5)
F(21A)	97(7)	128(7)	115(7)	1(5)	57(6)	-45(5)
F(22A)	116(7)	124(7)	70(5)	13(4)	5(4)	12(5)
F(23A)	118(7)	99(6)	112(6)	-45(5)	54(5)	-38(5)
F(24A)	84(4)	84(5)	142(7)	5(5)	6(4)	7(4)
B(2B)	52(7)	63(8)	53(8)	2(6)	15(5)	1(6)
F(21B)	60(4)	102(6)	108(7)	-9(5)	18(4)	-13(4)
F(22B)	111(7)	145(8)	89(7)	-26(6)	69(6)	-11(6)
F(23B)	113(7)	70(5)	99(6)	7(4)	36(5)	-2(4)
F(24B)	94(6)	144(8)	127(8)	38(6)	-17(5)	20(5)
N(81)	80(5)	83(6)	97(6)	-25(5)	-4(5)	20(5)

C(82)	83(8)	69(7)	74(8)	-18(6)	8(6)	11(6)
C(83)	91(9)	82(10)	74(8)	-20(7)	15(6)	9(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **816639.**

	x	y	z	U(eq)
H(1A)	3434	7351	5935	53
H(1B)	4092	7360	6647	53
H(2A)	5026	6366	6245	50
H(2B)	4848	6747	5553	50
H(5)	7844	8310	7180	43
H(7)	7782	8180	5310	57
H(8)	6496	7162	5239	54
H(9A)	8733	9378	5975	69
H(9B)	8470	9479	6675	69
H(10A)	7237	10398	6226	64
H(10B)	7196	10047	5531	64
H(12)	5976	9720	6938	44
H(15)	4253	8351	5148	55
H(16)	5527	9337	5057	60
H(22)	7206	5756	6827	46
H(23)	6530	4488	6562	54
H(24)	4894	4058	6872	63
H(25)	3980	4874	7492	62
H(26)	4668	6135	7787	49
H(32)	8517	6168	7577	50
H(33)	10222	6141	8259	56
H(34)	10624	7060	9076	59
H(35)	9302	7999	9227	60
H(36)	7557	7998	8576	49
H(42)	3015	7546	7899	60
H(43)	1104	7315	7658	81
H(44)	4	8008	6852	87
H(45)	784	8958	6275	74
H(46)	2691	9215	6507	56
H(52)	6256	9351	8306	50
H(53)	6421	10508	8918	63
H(54)	4940	11389	8831	81
H(55)	3327	11146	8121	86
H(56)	3165	10027	7475	66
H(63A)	7046	6263	10128	103
H(63B)	6012	5689	9927	103
H(63C)	5842	6534	10228	103
H(73A)	4077	9337	9812	160
H(73B)	3387	8564	9921	160
H(73C)	2880	9196	9398	160
H(83A)	4591	5003	5450	123
H(83B)	5281	4328	5172	123
H(83C)	4162	4654	4759	123

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