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Supporting Information

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A Bulky Biaryl Phosphine Ligand Allows for Palladium-Catalyzed Amidation of Five-Membered Heterocycles as Electrophiles**

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Supporting Information

General Procedures

All reactions were carried out under an argon atmosphere. Anhydrous 2-Methyl-2-Butanol was purchased from Aldrich Chemical Co. in Sure/Seal™ bottles and was used as received. $[(allyl)PdCl]_2$ and **L1** were purchased from Strem Chemicals Inc. and heterocycles, heteroaryl halides and amides were purchased from Aldrich Chemical Co., Alfa Aesar, TCI America or Combi-Blocks and were used without further purification. Anhydrous cesium carbonate was purchased from Alfa Aesar, and stored in a glovebox. Small portions were removed and stored in a desiccator for up to 2 weeks (All reactions were set-up in the air outside of the glovebox). **L2**,[1] **L3**[2] and **L4**[3] were prepared by literature procedure.

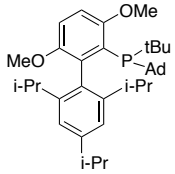
Reactions were monitored by GC and thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light. Flash silica gel chromatography was performed using Silicycle SiliaFlashP60 (230-400 mesh) silica gel. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR, and IR spectroscopy. Copies of the ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra can be found at the end of the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Varian 300 and Bruker 400 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), methylene chloride (5.32 ppm) or dimethylsulfoxide-*d6* (2.50 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.16 ppm), deuterated methylene chloride (53.84 ppm) or dimethylsulfoxide-*d6* (39.52 ppm) and all were obtained with 1H decoupling. All IR spectra were taken on a Perkin – Elmer 2000 FTIR. All GC analyses were performed on a Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column (10m, 0.1 mm I.D.). Melting points were obtained on a Mel-Temp II capillary melting point apparatus. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. The pure compounds are estimated to be ≥ 95% pure as determined by ^{1}H NMR and GC analysis.

Computational Methods

All calculations were carried out with Q-Chem suite of computational programs.[4] Ground state geometry optimizations were evaluated using B3LYP[5] density functional method. For C, H, O, N, P, and Br atoms, the 6-31G(d) basis set was used; while LANL2DZ effective core potentials of Hay and Wadt[6] with double-ζ basis sets were used for Pd atom. Frequency calculations were performed on all optimized structures to verify that they have no negative frequencies. The Gibbs free energies were calculated at 298.15 K and 1 atm.

Ligand Synthesis

tert-butyl-adamantyl(2',4',6'-triisopropyl-3,6-dimethoxybiphenyl-2-yl)phosphine (L5)

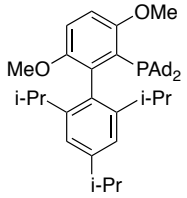


An oven-dried three-neck 250 mL round-bottom flask was charged with magnesium shavings (7.70 g, 0.32 mol) and 1-bromoadamantane (4.50 g, 0.02 mol). The necks were fitted with a reflux condenser, glass stopper, and rubber septum. The flask was then evacuated and backfilled with argon (this process was repeated a total of three times). To the reaction vessel was added Et_2O (26 mL) via syringe, and the mixture was heated to a gentle reflux for 15 h in an oil bath. Upon completion, the resulting Grignard reagent was taken up in a syringe, and added dropwise to a second oven-dried three-neck 250 mL round-bottom flask fitted with a reflux condenser, glass stopper and rubber septum and containing *t*$BuPCl_2$ (0.60 g, 3.77 mmol) and 6 mL Et_2O at -40 °C. The resulting mixture was stirred for 30 min at -40°C. The reaction mixture was allowed to slowly warm to room temperature where it was stirred for an additional 30 min. The reaction vessel was placed into a preheated oil bath and was warmed to a gentle reflux for 3 h. The mixture was cooled to room temperature, layered with anhydrous pentane (20 mL) and

filtered using a cannula filter. The volatiles were removed in vacuo, taking care to not expose the product to air, to afford crude tert-butyl-1-adamantylchlorophosphine.

An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 2-iodo-2',4',6'-triisopropyl-3,6-dimethoxybiphenyl[7] (1.10 g, 2.35 mmol). The flask was evacuated and backfilled with argon (this process was repeated a total of three times). Toluene (18 mL) was added via syringe and the reaction mixture was cooled to -78°C. *t*BuLi (1.7M in pentane, 2.8 mL, 4.7 mmol) was added in a dropwise fashion over a 10 min period via syringe. The resulting solution was stirred for 30 min at -78°C and CuCl (233 mg, 2.35 mmol) was added rapidly by removing the septum of the Schlenk tube under a positive pressure of argon. The septum was refitted and a solution of *tert*-butyl-1-adamantylchlorophosphine (in 8 mL toluene and 0.5 mL THF) was added via cannula in a dropwise fashion. The reaction mixture was then allowed to warm to rt. The Schlenk tube was sealed with a Teflon screw cap once the reaction mixture turned dark grey and was then heated to 140 °C for 24 h. The reaction mixture was cooled to rt, diluted with EtOAc, washed with 30% NH_4OH (three times), washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting solid was recrystallized from dichloromethane to give white crystals (0.50 g, 38%), mp 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.85 (q, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.55 (s, 3H), 2.94 (m, 1H), 2.49 (m, 2H), 1.84 (s, 10 H), 1.63 (s, 7H), 1.31 (d, *J* = 7.2 Hz, 6H), 1.21 (dd, *J* = 6.6, 2.4 Hz, 6H), 1.13 (d, *J* = 12.0 Hz, 8H), 0.92 (dd, *J* = 6.8, 2.8 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.7, 152.5, 152.4, 147.1, 146.7, 146.5, 140.6, 140.2, 133.0, 132.9, 126.7, 126.2, 120.0, 110.8, 108.0, 107.8, 54.3, 54.0, 41.8, 41.7, 38.4, 38.1, 37.2, 34.4, 34.1, 34.0, 32.3, 32.2, 31.2, 31.1, 29.4, 29.3, 29.2, 25.7, 25.6, 24.3, 24.1, 23.6, 23.6, 23.5 (observed complexity due to P–C splitting); ^{31}P NMR (161 MHz, $CDCl_3$) δ 37.2, 35.4; IR (film) ν_{max} 2903, 2362, 2337, 1653, 1606, 1580, 1457, 1421, 1382, 1359, 1301, 1252, 1172, 1127, 1088, 1046, 1020, 908, 873, 797, 735, 651 cm^{-1}.

di-adamantyl(2',4',6'-triisopropyl-3,6-dimethoxybiphenyl-2-yl)phosphine (L6)



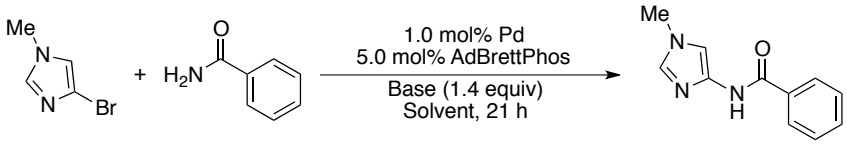
An oven-dried three-neck 250 mL round-bottom flask, charged with magnesium shavings (15.3 g, 0.63 mol) and 1-bromoadamantane (9.0 g, 0.04 mol). The necks were fitted with a reflux condenser, glass stopper, and rubber septum. The flask was evacuated and backfilled with argon (this process was repeated a total of three times). To the reaction vessel, Et_2O (55 mL) was added via syringe, and the mixture was heated to a gentle reflux for 15 h in an oil bath. Upon completion, the resulting Grignard reagent was taken up in a syringe, and added dropwise to a second oven-dried three-neck 250 mL round-bottom flask fitted with a reflux condenser, glass stopper and rubber septum, and containing PCl_3 (0.63 mL, 7.2 mmol) and 14 mL Et_2O at -40°C. The resulting mixture was stirred for 30 min at -40°C. The reaction mixture was allowed to slowly warm to room temperature where it was stirred for an additional 30 min. The reaction vessel was placed into a heated oil bath and was warmed to a gentle reflux for 3 h. The mixture was cooled to room temperature, layered with anhydrous pentane (30 mL) and filtered using a cannula filter. The volatiles were removed in vacuo, taking care to not expose the product to air, to afford crude crude di-1-adamantylchlorophosphine.

An oven-dried resealable Schlenk tube, which was equipped with a magnetic stir bar and charged with 2-iodo-2',4',6'-triisopropyl-3,6-dimethoxybiphenyl[7] (2.2 g, 4.7 mmol). The flask was evacuated and backfilled with argon (this process was repeated a total of three times). Toluene (30 mL) was added via syringe and the reaction mixture was cooled to -78°C. *t*BuLi (1.7M in pentane, 5.5 mL, 9.4 mmol) was added in a dropwise fashion over 10 min period via syringe. The resulting solution was stirred for 30 min at -78°C and CuCl (465 mg, 4.7 mmol) was added rapidly by removing the septum of the Schlenk tube under a positive pressure of argon. The septum was refitted and a solution of di-1-adamantylchlorophosphine in 15 mL toluene was added. The reaction mixture was then allowed to warm to rt. The Schlenk tube was sealed with a Teflon screw cap once the reaction mixture turned dark grey and was heated to 140°C for 24 h. The reaction mixture was cooled to rt, diluted with EtOAc, washed with

30% NH_4OH (three times), washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting solid was recrystallized from hot methanol to give white crystals (1.5 g, 50%), mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.85 (q, J = 8.0 Hz, 2H), 3.81 (s, 3H), 3.54 (s, 3H), 2.93 (m, 1H), 2.49 (m, 2H), 1.85 (m, 18 H), 1.63 (s, 12H), 1.31 (d, J = 4.0 Hz, 6H), 1.21 (d, J = 8.0 Hz, 6H), 0.91 (d, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 152.5, 152.4, 147.0, 146.6, 140.9, 140.6, 133.0, 132.9, 126.0, 125.6, 120.0, 110.7, 107.8, 60.6, 54.3, 54.0, 42.2, 42.1, 39.0, 38.7, 37.2, 34.0, 31.2, 29.4, 29.3, 25.7, 24.2, 23.7, 21.2, 14.4 (observed complexity due to P–C splitting); ^{31}P NMR (161 MHz, $CDCl_3$) δ 37.3; IR (film) ν_{max} 2903, 2361, 2338, 1576, 1457, 1417, 1341, 1247, 1084, 1038, 1015, 971, 910, 871, 797, 757, 733, 720, 668, 642, 479 cm^{-1}.

Optimization Table

Table S1. Optimization of reaction conditions for the amidation of 4-bromo-1-methylimidazole



Entry	Palladium	Base	Solvent	Conc. [M]	Temp. (°C)	Conv. [%]	GC Yield [%]
1[a]	$Pd(OAc)_2/H_2O$	Cs_2CO_3	Dioxane	0.5	130	40	32
2	$[Pd(\pi\text{-cinnamyl})Cl]_2$	Cs_2CO_3	Dioxane	0.5	130	40	36
3	$[(allyl)PdCl]_2$	Cs_2CO_3	Dioxane	0.5	130	80	62
4[b]	Pd_2dba_3	Cs_2CO_3	Dioxane	0.5	130	8	6
5	$[(allyl)PdCl]_2$	K_2CO_3	Dioxane	0.5	130	<5	<5
6	$[(allyl)PdCl]_2$	K_3PO_4	Dioxane	0.5	130	78	77
7	$[(allyl)PdCl]_2$	NaOtBu	Toluene	0.5	130	<5	<5
8	$[(allyl)PdCl]_2$	Cs_2CO_3	Toluene	0.5	130	77	13
9	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	130	82	80
10	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.25	130	37	36
11	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	1.0	130	81	68
12[c]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	130	90	85
13[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	130	100	90
14[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	130	100	90
15[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	120	100	90
16[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	110	100	88
17[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	100	100	92
18[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	90	100	90
19[d,e]	$[(allyl)PdCl]_2$	Cs_2CO_3	2-Methyl-2-butanol	0.5	80	98	90

[a] $Pd(OAc)_2$, ligand and H_2O were premixed in dioxane at 130 °C for 3 min. [b] Pd_2dba_3 and ligand were premixed in dioxane at 130 °C for 3 min. [c] 1.5 equiv of benzamide was used. [d] 2.0 equiv of benzamide and 2.0 equiv of base were used. [e] $[(allyl)PdCl]_2$ (0.75 mol%), AdBrettPhos (3.0 mol%).

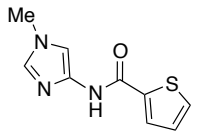
Substrate Synthesis

General Procedure A: Pd-Catalyzed Amidation of Heterocyclic Bromides

An oven-dried re-sealable screw cap test tube, equipped with a magnetic stir bar, was added $[(allyl)PdCl]_2$ (0.75 mol%), **L6** (3.0 mol %, Pd:L = 1:2), Cs_2CO_3 (650 mg, 2.0 mmol, 2.0 equiv), amide (2.0 mmol, 2.0 equiv) and the heteroaryl halide (if it is a solid) (1.0 mmol, 1.0 equiv). The vial was evacuated and backfilled with argon (this process was repeated a total of 3 times). Under argon, 2-methyl-2-butanol (2

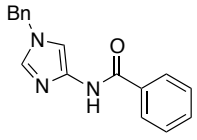
mL) was added followed by the aryl halide (if it is a liquid) (1.0 mmol, 1.0 equiv). The argon source was removed and the sealed test tube was placed into a pre-heated 90°C oil bath with vigorous stirring. After stirring for 21 h at 90°C, the vessel was cooled to room temperature, diluted with EtOAc, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, concentrated in vacuo and purified via flash chromatography.

N-(1-methyl-1H-imidazol-4-yl)-2-thiophenecarboxamide



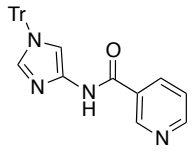
Following general procedure A, a mixture of 4-bromo-1-methylimidazole (161 mg, 1.0 mmol), 2-thiophenecarboxamide (254 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (100% EtOAc) to provide the title compound as white powder (145 mg, 70%), mp 166-167 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.74 (d, J = 2.8 Hz, 1H), 7.48 (d, J = 4.8, 0.8 Hz, 1H), 7.42 (s, 1H), 7.0 (m, 2H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 139.7, 138.3, 133.5, 130.4, 128.5, 127.5, 109.0, 33.9; IR (film) ν_{max} 3181, 3083, 1645, 1560, 1514, 1422, 1384, 1355, 1318, 1266, 1169, 1099, 1079, 1042, 999, 877, 856, 816, 762, 715, 624 cm^{-1}; Anal. Calcd. For $C_9H_9N_3OS$: C, 52.16; H, 4.38. Found: C, 52.02; H, 4.47.

N-(1-benzyl-1H-imidazol-4-yl)-benzamide



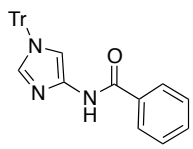
Following general procedure A, a mixture of 4-bromo-1-benzylimidazole (237 mg, 1.0 mmol), 2-pyridineactamide (272 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography ($MeOH/CH_2Cl_2$, 1:49) to provide the title compound as white powder (180 mg, 62%), mp 213-214 °C ^1H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 7.98-7.96 (m, 2H), 7.68 (d, J = 1.6 Hz, 1H), 7.53-7.31 (m, 9H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 138.4, 137.7, 134.0, 133.5, 131.3, 128.7, 128.3, 127.8, 127.7, 127.6, 107.3, 49.9; IR (film) ν_{max} 3171, 2987, 2361, 2339, 1650, 1562, 1514, 1464, 1418, 1347, 1272, 1121, 997, 760, 709, 668, 652, 598 cm^{-1}; Anal. Calcd. For $C_{17}H_{14}N_4O$: C, 73.63; H, 5,45. Found: C, 73.45; H, 5.41.

N-(1-trityl-1H-imidazol-4-yl)-nicotinamide



Following general procedure A, a mixture of 4-bromo-1-tritylimidazole (389 mg, 1.0 mmol), nicotinamide (244 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography ($MeOH/CH_2Cl_2$, 1:24) to provide the title compound as white powder (387 mg, 90%), mp 228-229 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 9.06 (s, 1H), 8.49 (d, J = 1.6Hz, 1H), 8.07 (d, J =8.0 Hz, 1H), 7.47 (s, 1H), 7.34-7.30 (m, 9H), 7.16-7.09 (m, 7H), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 152.0, 149.3, 142.0, 137.7, 135.2, 135.1, 130.8, 129.9, 128.3, 128.2, 122.9, 110.7, 75.9; IR (film) ν_{max} 3207, 3057, 1669, 1559, 1492, 1473, 1445, 1417, 1340, 1261, 1158, 1117, 1025, 1006, 896, 870, 824, 743, 701, 658, 639 cm^{-1}; Anal. Calcd. For $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15. Found: C, 78.02; H, 5.24.

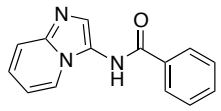
N-(1-trityl-1H-imidazol-4-yl)-benzamide



Following general procedure A, a mixture of 4-bromo-1-tritylimidazole (389 mg, 1.0 mmol), benzamide (242 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography ($MeOH/CH_2Cl_2$, 1:24) to provide the title compound as white powder (387 mg, 90%), mp 246-247°C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.51 (s, 1H), 7.34-7.28 (m, 10H), 7.19-7.14 (m, 8H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.2, 138.0,

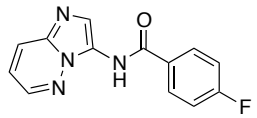
135.3, 135.0, 131.3, 129.9, 128.2, 128.1, 127.7, 110.3, 75.8; IR (film) ν_{max} 3199, 3060, 3031, 2362, 2338, 2247, 1663, 1559, 1494, 1476, 1446, 1340, 1259, 1226, 1186, 1158, 1114, 1087, 1028, 1007, 909, 871, 825, 801, 733, 701, 657, 491 cm^{-1}; Anal. Calcd. For $C_{29}H_{23}N_3O$: C, 81.09; H, 5.40. Found: C, 80.14; H, 5.38.

N-imidazo[1,2-a]pyridin-3-yl-benzamide (CAS: 860257-98-3)



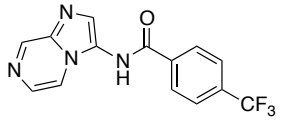
Following general procedure A, a mixture of 3-bromo-imidazo[1,2-a]pyridine (198 mg, 1.0 mmol), benzamide (242 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (100% EtOAc) to provide the title compound as pale yellow powder (200 mg, 84%), mp 170-171 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 6.8 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.26 (s, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 132.9, 132.4, 128.6, 128.1, 127.1, 124.5, 123.6, 120.3, 117.0, 112.1; IR (film) ν_{max} 3067, 2362, 2338, 1670, 1636, 1601, 1575, 1500, 1479, 1360, 1310, 1280, 1142, 1120, 1027, 1006, 909, 847, 803, 752, 733, 709, 669, 646, 608, 516, 425 cm^{-1}; Anal. Calcd. For $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67. Found: C, 70.65; H, 4.56.

4-fluoro-N-imidazo[1,2-b]pyridazin-3-yl-benzamide



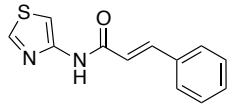
Following general procedure A, a mixture of 3-bromo-imidazo[1,2-b]pyridazine (198 mg, 1.0 mmol), 4-fluorobenzamide (167 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (100% EtOAc) to provide the title compound as pale yellow powder (225 mg, 88%), mp 175-176 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.34 (dd, *J* = 1.6, 1.6 Hz, 1H), 8.30 (s, 1H), 8.04-8.00 (m, 2H), 7.95 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.23-7.18 (m, 2H), 7.01 (dd, *J* = 4.4, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.0, 162.7, 142.8, 134.7, 130.0, 129.9, 129.3, 129.2, 126.1, 124.8, 123.5, 116.2, 116.0, 115.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -106.4; IR (film) ν_{max} 3245, 2362, 1675, 1604, 1564, 1540, 1522, 1504, 1397, 1350, 1295, 1274, 1236, 1160, 1121, 1069, 1015, 917, 850, 819, 788, 757, 730, 686, 648, 626, 602, 572, 511, 419 cm^{-1}; Anal. Calcd. For $C_{13}H_9FN_4O$: C, 60.94; H, 3.54. Found: C, 61.08; H, 3.50.

4-trifluoromethyl-N-imidazo[1,2-a]pyrazin-3-yl-benzamide



Following general procedure A, a mixture of 3-bromo-imidazo[1,2-b]pyrizine (198 mg, 1.0 mmol), 4-trifluorobenzamide (378 mg, 2.0 mmol), Cs_2CO_3 (650 mg, 2.0 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography ($MeOH/CH_2Cl_2$, 1:49) to provide the title compound as pale green powder (256 mg, 84%), mp 209-210 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 9.09 (s, 1H), 8.38 (d, *J* = 4.4 Hz, 1H), 8.28-8.26 (m, 2H), 7.99-7.90 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 143.2, 137.6, 136.8, 132.5, 132.2, 131.9, 131.6, 129.3, 129.1, 128.7, 128.0, 125.6, 125.5, 125.4, 125.3, 122.5, 121.7, 119.8, 117.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.3; IR (film) ν_{max} 3210, 2361, 2341, 1700, 1636, 1559, 1507, 1457, 1330, 1167, 1132, 1066, 857, 780, 668, 593, 433 cm^{-1}; Anal. Calcd. For $C_{14}H_9F_3N_4O$: C, 54.91; H, 2.96. Found: C, 54.99; H, 2.91.

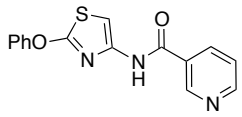
N-(thiazol-4-yl)-cinnamamide



Following general procedure A, a mixture of 4-bromothiazole (164 mg, 1.0 mmol), cinnamamide (177 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 2:3) to provide the title compound as pale yellow powder (216 mg, 94%), mp 129-130

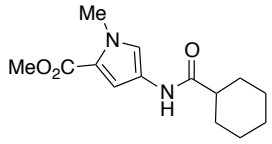
°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.66 (d, *J* = 2.0 Hz, 1H), 7.90 (d, 1H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.40-7.38 (m, 3H), 6.61 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 150.6, 148.8, 142.8, 134.6, 130.1, 129.0, 128.0, 120.0, 102.5; IR (film) ν_{max} 3269, 3151, 3054, 1677, 1631, 1579, 1555, 1525, 1449, 1404, 1339, 1297, 1281, 1205, 1189, 1131, 1071, 998, 972, 874, 852, 811, 761, 705, 667, 606, 562, 484 cm^{-1}; Anal. Calcd. For $C_{12}H_{10}N_2OS$: C, 62.59; H, 4.38. Found: C, 62.66; H, 4.44.

N-(2-phenoxy-thiazol-4-yl)-nicotinamide



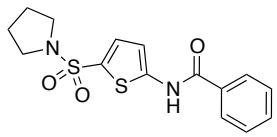
Following general procedure A, a mixture of 4-bromo-2-phenoxythiazole (256 mg, 1.0 mmol), nicotinamide (147 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 °C for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 2:3) to provide the title compound as pale orange powder (210 mg, 71%), mp 172-173 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.4 (s, 1H), 9.10 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.52-7.48 (m, 3H), 7.40-7.32 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.2, 163.7, 154.9, 152.2, 148.9, 142.0, 135.6, 130.3, 129.3, 126.4, 123.4, 120.5, 96.6; IR (film) ν_{max} 3163, 2360, 2342, 1663, 1594, 1528, 1504, 1486, 1242, 1194, 1162, 1119, 1028, 914, 743, 668 cm^{-1}; Anal. Calcd. For $C_{15}H_{11}N_3O_2S$: C, 60.59; H, 3.73. Found: C, 60.94; H, 3.84.

N-(2-methoxycarbonyl-pyrrol-4-yl)-cyclohexanecarboxamide



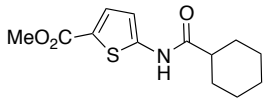
Following general procedure A, a mixture of 4-bromo-2-methoxycarbonylpyrrole (109 mg, 0.5 mmol), cyclohexanecarboxamide (76 mg, 0.6 mmol), Cs_2CO_3 (228 mg, 0.7 mmol), $[(allyl)PdCl]_2$ (1.4 mg, 0.75 mol%), **L6** (9.6 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 °C for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as pale yellow-green powder (121 mg, 91%), mp 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.38 (s, 1H), 6.66 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 2.20 (tt, *J* = 4.0, 12.0 Hz, 1H), 1.90-1.66 (m, 5H), 1.49 (q, *J* = 12, 2H), 1.29-1.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 161.6, 122.0, 121.3, 119.6, 108.1, 51.2, 45.7, 36.8, 29.8, 25.7; IR (film) ν_{max} 3283, 3118, 2931, 2855, 2362, 2338, 1711, 1653, 1577, 1450, 1407, 1374, 1354, 1250, 1209, 1148, 1128, 1100, 1063, 1005, 952, 914, 895, 822, 783, 756, 733, 668, 645, 630 cm^{-1}; Anal. Calcd. For $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63. Found: C, 63.09; H, 7.43.

N-(5-((pyrolidin-1-yl)sulfonyl)-thiophen-2-yl)-benzamide



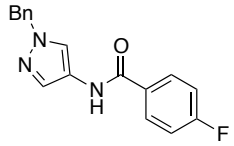
Following general procedure A, a mixture of 2-bromo-5-((pyrolidin-1-yl)sulfonyl)thiophene (221 mg, 1.0 mmol), benzamide (145 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 °C for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 1:1) to provide the title compound as pale orange powder (272 mg, 81%), mp 223-224 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.1 (s, 1H), 8.03 (d, *J* = 4.0 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 4.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.18 (t, *J* = 8.0 Hz, 4H), 1.69-1.66 (m, 4H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 164.2, 145.8, 132.6, 132.1, 130.7, 128.8, 127.9, 125.0, 112.3, 48.0, 24.8; IR (film) νmax 3309, 2090, 2976, 2361, 2340, 1700, 1663, 1602, 1554, 1507, 1485, 1441, 1385, 1332, 1292, 1198, 1150, 1091, 1062, 1012, 890, 800, 753, 704, 646, 599, 568 cm^{-1}; Anal. Calcd. For $C_{15}H_{16}N_2O_3S_2$: C, 53.55; H, 4.79. Found: C, 53.47; H, 4.64.

N-(5-methoxycarbonyl-thiophen-2-yl)-cyclohexanecarboxamide



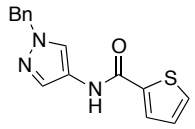
Following general procedure A, a mixture of 2-bromo-5-methoxycarbonylthiophene (221 mg, 1.0 mmol), cyclohexanecarboxamide (153 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (3.7 mg, 1.0 mol%), **L6** (25.6 mg, 4.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:1) to provide the title compound as pale orange powder (200 mg, 75%), mp 128-129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.59 (d, J = 4.0 Hz, 1H), 6.60 (d, J = 4.0 Hz, 1H), 3.84 (s, 3H), 2.34 (tt, J = 3.2, 11.6 Hz, 1H), 1.97-1.70 (m, 5H), 1.54 (q, J = 12, 24 Hz, 2H) 1.34-1.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 174.0, 164.0, 146.3, 146.2, 132.0, 123.4, 123.3, 112.1, 112.0, 52.0, 45.1, 29.5, 25.6, 25.5; IR (film) νmax 3280, 2932, 2855, 1706, 1684, 1560, 1507, 1452, 1386, 1344, 1297, 1259, 1188, 1171, 1099, 954, 894, 805, 750 cm^{-1}; Anal. Calcd. For $C_{13}H_{17}NO_3S$: C, 58.4; H, 6.41. Found: C, 58.53; H, 6.47.

4-fluoro-N-(1-benzyl-1H-pyrazol-4-yl)-benzamide



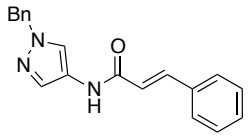
Following general procedure A, a mixture of 4-bromo-1-benzylpyrazole (237 mg, 1.0 mmol), 4-fluorobenzamide (167 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 1:1) to provide the title compound as white powder (257 mg, 87%), mp 162-163 °C ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.05 (s, 1H), 7.83 (dd, J = 8.8, 5.2 Hz, 2H), 7.53 (s, 1H), 7.33-7.20 (m, 5H), 7.09 (t, J = 8.8 Hz, 2H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.8, 136.3, 129.5, 129.0, 128.3, 127.9, 121.8, 121.5, 116.1, 115.8, 56.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -107.8; IR (film) ν_{max} 3270, 3067, 1645, 1602, 1506, 1385, 1278, 1234, 1159, 1020, 845, 705, 628, 594 cm^{-1}; Anal. Calcd. For $C_{17}H_{14}FN_3O$: C, 69.14; H, 4.78. Found: C, 69.36; H, 4.75.

N-(1-benzyl-1H-pyrazol-4-yl)- 2-thiophenecarboxamide



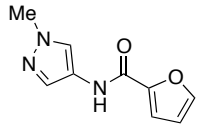
Following general procedure A, a mixture of 4-bromo-1-benzylpyrazole (237 mg, 1.0 mmol), 2-thiophenecarboxamide (153 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 90 ^oC for 21 h. The crude product was purified via flash chromatography (Et_2O/CH_2Cl_2, 1:3) to provide the title compound as off-white crystalline powder (230 mg, 81%), mp 145-146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.97 (s, 1H), 7.60 (d, J = 3.2 Hz, 1H), 7.47 (s, 1H), 7.45 (q, J = 0.8, 5.2 Hz, 1H), 7.26-7.23 (m, 3H), 7.16-7.14 (m, 2H), 6.99 (d, J = 4.8 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 138.7, 136.2, 130.8, 128.9, 128.6, 128.2, 128.0, 127.9, 121.9, 121.4, 56.5; IR (film) ν_{max} 3279, 3089, 1633, 1586, 1560, 1496, 1423, 1393, 1423, 1393, 1351, 1285, 1159, 1096, 1075, 1016, 993, 858, 788, 730, 700, 651, 628 cm^{-1}; Anal. Calcd. For $C_{15}H_{13}N_3OS$: C, 63.58; H, 4.62. Found: C, 63.51; H, 4.55.

N-(1-benzyl-1H-pyrazol-4-yl)-cinnamamide



Following general procedure A, a mixture of 4-bromo-1-benzylpyrazole (237 mg, 1.0 mmol), cinnamamide (177 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 120 ^oC for 21 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 1:1) to provide the title compound as pale yellow powder (260 mg, 86%), mp 141-142 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.09 (s, 1H), 7.69 (d, J =15.6 Hz, 1H), 7.53 (s, 1H), 7.34-7.15 (m, 10H), 6.61 (d, J = 15.6 Hz, 1H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 141.7, 136.1, 134.6, 130.8, 129.9, 128.9, 128.8, 128.1, 127.9, 127.7, 121.9, 121.7, 120.2, 56.4; IR (film) ν_{max} 3267, 3085, 1657, 1623, 1588, 1496, 1394, 1342, 1211, 1150, 1023, 992, 836, 762, 728, 700, 629, 562, 491 cm^{-1}; Anal. Calcd. For $C_{19}H_{17}N_3O$: C, 75.23; H, 5.65. Found: C, 75.36; H, 5.71.

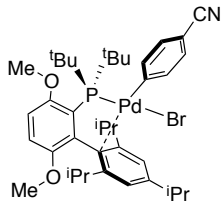
N-(1-methyl-1H-pyrazol-4-yl)- 2-furancarboxamide



Following general procedure A, a mixture of 4-bromo-1-methylpyrazole (161 mg, 1.0 mmol), cinnamamide (134 mg, 1.2 mmol), Cs_2CO_3 (456 mg, 1.4 mmol), $[(allyl)PdCl]_2$ (2.8 mg, 0.75 mol%), **L6** (19.2 mg, 3.0 mol%) in 2-methyl-2-butanol (2.0 mL) was heated to 120 °C for 21 h. The crude product was purified via flash chromatography (CH_2Cl_2/Et_2O, 1:4) to provide the title compound as pale yellow powder (170 mg, 89%), mp 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.98 (s, 1H), 7.49 (s, 1H), 7.45 (s, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 6.51 (dd, *J* = 1.6, 3.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 147.6, 144.3, 130.4, 122.4, 120.5, 115.0, 112.6, 39.4; IR (film) ν_{max} 3269, 3124, 2937, 1654, 1594, 1539, 1476, 1444, 1406, 1348, 1288, 1228, 1183, 1159, 1122, 1075, 1011, 984, 938, 884, 867, 836, 761, 653, 608 cm^{-1}; Anal. Calcd. For $C_9H_9N_3O_2$: C, 56.54; H, 4.74. Found: C, 55.72; H, 4.81.

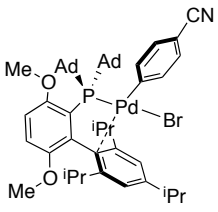
Synthesis of Complexes 2a and 2b

Complex 2a



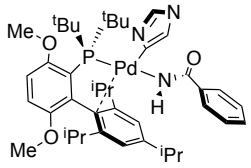
In a nitrogen-filled glovebox, to an oven-dried 20 mL vial was added *t*BuBrettPhos (**L3)** (137 mg, 0.28 mmol, 1.1 equiv.) and 4-bromobenzonitrile (140 mg, 0.77 mmol, 3 equiv.). With rapid stirring, cyclohexane was added dropwise until all reagents had completely dissolved (10 mL total). $(COD)Pd(CH_2TMS)_2$ (100 mg, 0.26 mmol, 1 equiv.) was added rapidly in one portion and the mixture was vigorously stirred at room temperature for 12 h, during which period a precipitate formed. The mixture was filtrered through a sintered glass frit, washed with pentane (3 X 3 mL), and dried under reduced pressure to afford **2a** as a yellow solid (130 mg, 66 %). To obtain X-ray quality crystals, a small sample (10 mg) was dissolved in a minimal quantity of CH_2Cl_2, layered with pentane, and placed in a -20 °C freezer. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30 (d, *J* = 7.2 Hz, 2H), 7.05-7.00 (m, 4H), 6.96-6.87 (m, 2H), 3.79 (s, 3H), 3.32 (s, 3H), 3.06-3.01 (m, 1H), 2.62-2.55 (m, 2H), 1.57 (d, *J* = 6.4 Hz, 6H), 1.40-1.34 (m, 25H), 0.82 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 158.4, 155.0, 154.0, 153.9, 151.8, 151.7, 147.1, 147.0, 140.9, 137.8, 137.6, 127.2, 127.1, 127.0, 124.9, 119.9, 115.5, 115.4, 113.6, 110.7, 110.6, 105.1, 54.4, 53.9, 53.8, 41.3, 41.2, 34.5, 32.4, 32.3, 31.4, 30.1, 30.0, 26.9, 25.5, 24.5, 24.2 (observed complexity is due to C–P splitting); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 82.7, 72.4.[8]

Complex 2b



In a nitrogen-filled glovebox, to an oven-dried 20 mL vial was added AdBrettPhos (**L6)** (91 mg, 0.14 mmol, 1.1 equiv.) and 4-bromobenzonitrile (70 mg, 0.39 mmol, 3 equiv.). With rapid stirring, cyclohexane was added dropwise until all reagents had completely dissolved (10 mL total). $(COD)Pd(CH_2TMS)_2$ (50 mg, 0.13 mmol, 1 equiv.) was added rapidly in one portion and the mixture was vigorously stirred at room temperature for 12 h, during which period a precipitate formed. The mixture was filtrered through a sintered glass frit, washed with pentane (3 X 3 mL), and dried under reduced pressure to afford **2b** as a yellow solid (52 mg, 46 %). To obtain X-ray quality crystals, a small sample (10 mg) was dissolved in a minimal quantity of CH_2Cl_2, layered with pentane, and placed in a -20 °C freezer. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.04-7.02 (m, 4H), 6.97-6.86 (m, 2H), 3.84 (s, 3H), 3.32 (s, 3H), 3.02 (m, 1H), 2.57 (m, 2H), 2.23-1.93 (m, 20H), 1.69-1.59 (m, 20H), 1.43 (s, 2H), 1.35 (d, *J* = 4.0 Hz, 6H), 0.82 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 158.3, 155.6, 154.3, 154.3, 152.2, 152.8, 147.4, 147.3, 141.4, 138.9, 138.7, 127.5, 126.3, 126.1, 125.3, 120.3, 116.3, 116.2, 113.7, 110.9, 110.8, 105.3, 54.7, 47.7, 47.6, 41.7, 36.6, 34.8, 31.6, 29.9, 29.8, 27.3, 26.2, 24.8, 24.7 (observed complexity is due to C–P splitting); ^{31}P NMR (121 MHz, THF-*d8*) δ 67.91.

Cartesian Coordinates for all Calculated Complexes:



Complex A

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H	6.553181	-1.751554	-1.651055
H	6.894155	-0.489640	-0.444549
C	4.975635	1.625899	-0.518865
H	6.027057	1.679704	-0.754016
C	4.303409	2.786952	-0.141280
H	4.850418	3.714803	-0.075638
C	2.939357	2.736804	0.110657
C	2.207579	1.518437	0.041102
C	0.710432	1.696475	0.243343
C	-0.069279	2.155411	-0.864761
C	0.447161	2.129609	-2.304824
H	1.356786	1.531036	-2.321968
C	-0.563541	1.488081	-3.283020
H	-1.434548	2.131333	-3.427782
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H	1.558440	4.011457	-2.119312
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C	-2.865759	5.168678	1.176065
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C	2.858292	5.164114	0.497735
H	3.302152	5.432673	-0.463700
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H	3.624903	5.177288	1.276068
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C	2.228252	-3.898952	1.077388
C	4.382982	-2.595609	1.116647
C	2.449040	-1.863104	2.526330
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H	4.862773	-1.629440	1.258990
H	4.740957	-3.023550	0.185226
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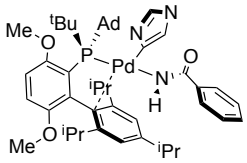

Complex B

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H	0.608725	4.366017	3.895736
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H	2.236957	6.259644	0.290122
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C	2.316489	-2.477501	2.672658
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H	1.246152	-2.661561	2.585833
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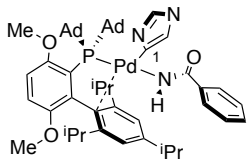

Complex C

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H	3.684132	2.362219	1.476188
C	3.496624	2.400901	-0.658178
C	4.979691	2.599811	-0.944526
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H	5.221427	4.392465	0.284573
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H	2.952902	2.411576	-2.729359
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C	0.636887	1.345689	-3.811293
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H	-2.826643	-0.036869	-4.655208
H	-5.641741	-2.612305	-1.437395
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H	-2.163057	-2.347236	-3.990962
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H	-1.412449	-0.092329	5.172488
C	-3.214469	-1.170831	4.612992
C	-0.864244	-2.047756	4.396660
H	-4.721223	-2.390557	3.631271
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C	0.549903	-2.193417	-1.189627
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C	0.804918	-3.439506	-0.663613
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H	3.227252	-0.672427	-1.196556
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C	4.606246	-2.092250	0.412420
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C	5.163996	-2.354850	-0.847818
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C	7.208986	-3.136818	0.183266
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H	8.215480	-3.538212	0.094876
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H	0.452231	-4.015442	-3.829820

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2.550
2.533
2.517
2.500
2.479
2.462
2.445
2.429
1.845
1.634
1.518
1.300
1.220
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1.203
1.198
1.143
1.113
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0.926
0.916
0.909
OMe
tBu
P
Ad
i-Pr
i-Pr
MeO
i-Pr
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2.03
3.09
3.10
1.00
2.05
9.93
6.81
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6.31
8
7
6
5
4
3
2
1
0
f1 (ppm)

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29.24
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31.21
32.18
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34.42
37.20
38.11
38.40
41.67
41.80
53.97
54.29
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77.16
77.48
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107.97
110.75
120.01
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140.22
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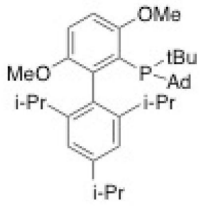
tBu
P
Ad
i-Pr
i-Pr
MeO
i-Pr
f1 (ppm)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i-Pr
MeO
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f1 (ppm)

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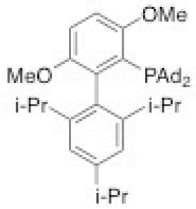
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f1 (ppm)
S
O
NH
N
N
H3C

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139.65
159.45
f1 (ppm)
S
O
NH
N
N
H3C

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7.507
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8.99
f1 (ppm)

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127.79
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128.72
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133.95
137.68
138.39
163.39
f1 (ppm)

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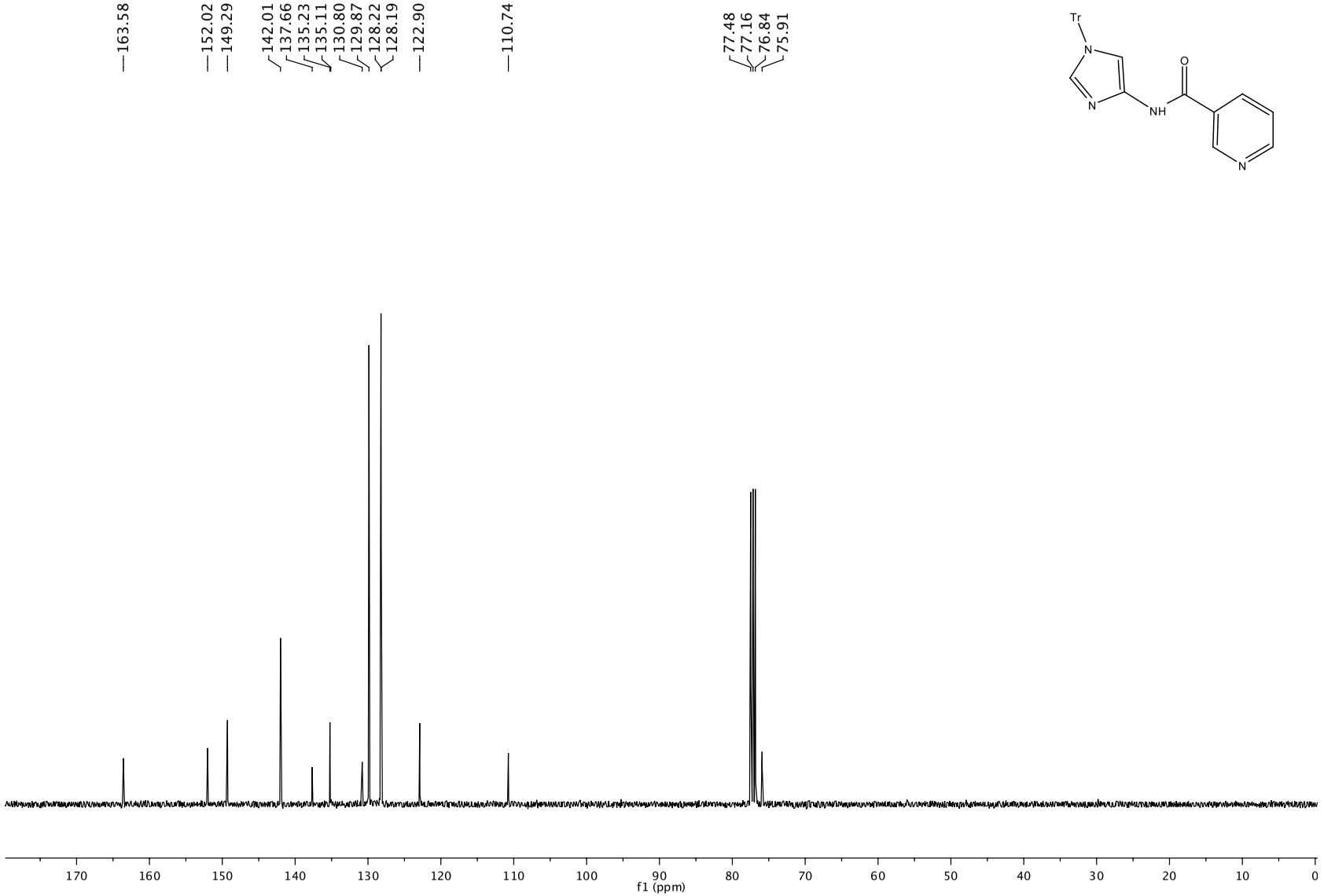
N
NH
O
N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77.16
76.84
75.91
Tr
N
N
NH
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11.42
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7.51
7.34
7.33
7.32
7.30
7.28
7.26
7.19
7.17
7.16
7.16
7.15
7.14
6.87
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10.70
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f1 (ppm)

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135.27
135.03
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127.70
110.31
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77.16
76.84
75.76
f1 (ppm)
O
NH
N
N
Tr

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1.99
1.03
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1.00
f1 (ppm)

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77.16
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124.54
127.13
128.11
128.57
132.36
132.89
143.11
f1 (ppm)

F
O
NH
N
N
N
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7
6
5
4
3
2
1
f1 (ppm)

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N
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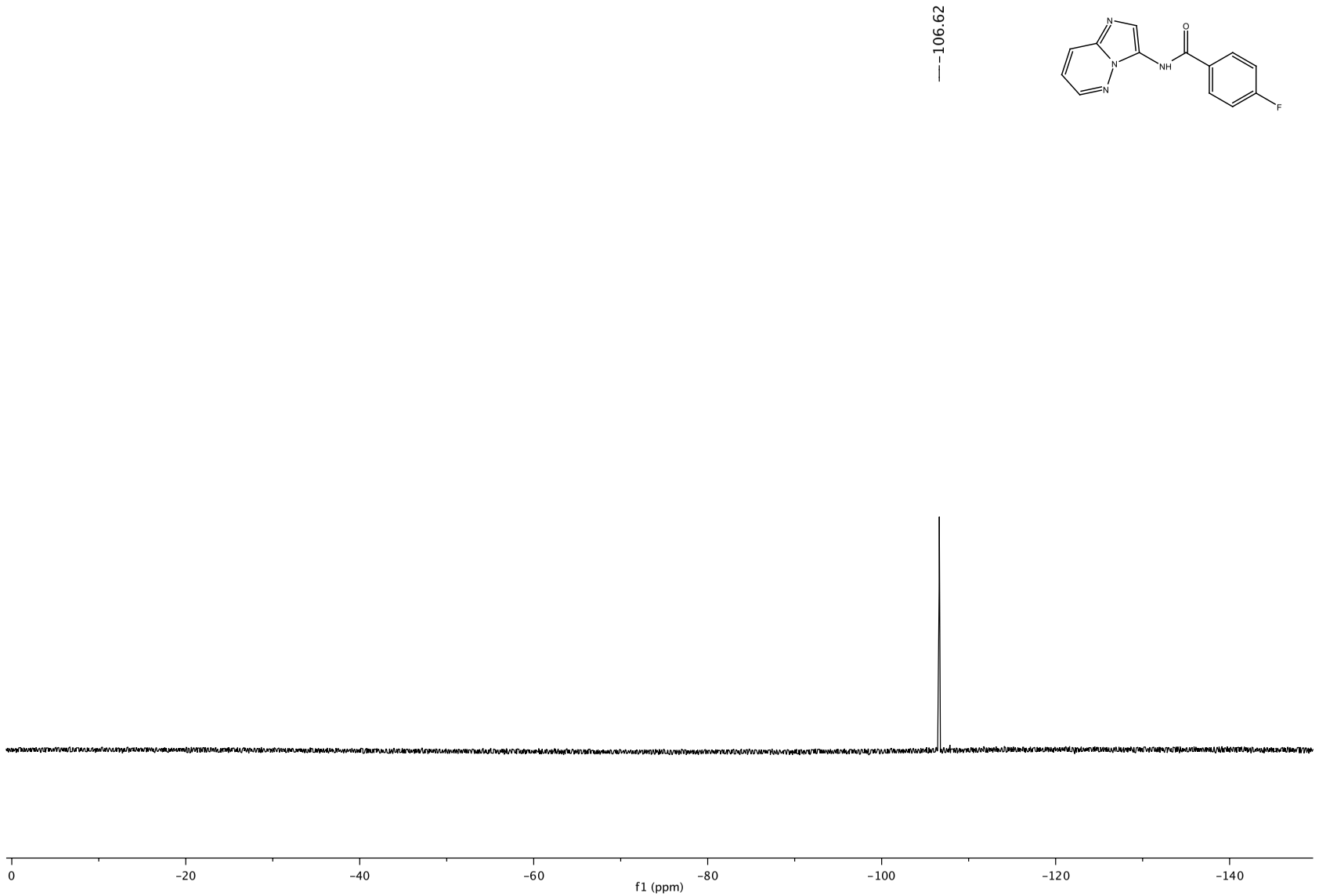
f1 (ppm)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−120
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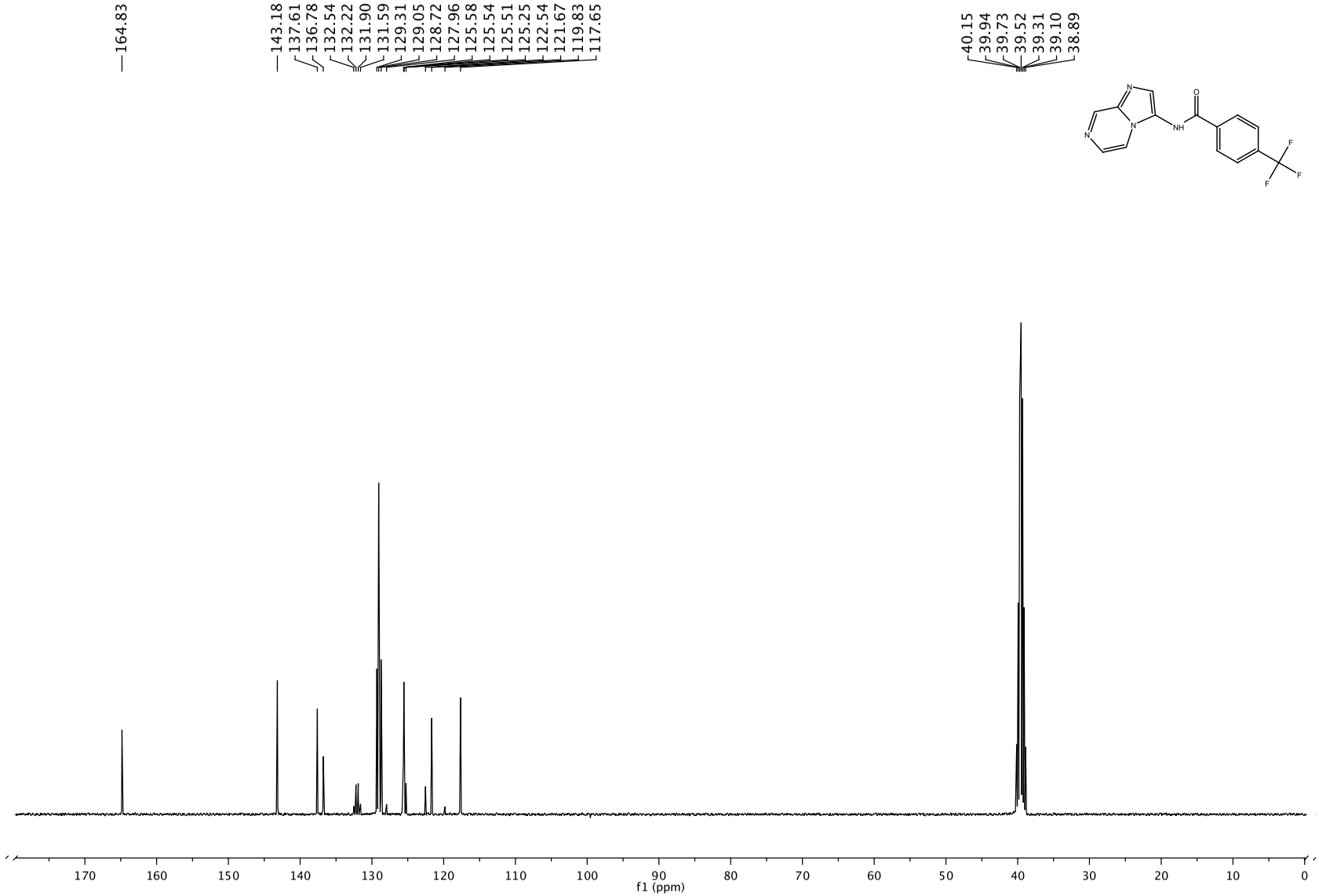
f1 (ppm)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39.73
39.52
39.31
39.10
38.89
N
O
NH
F
F
F
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120
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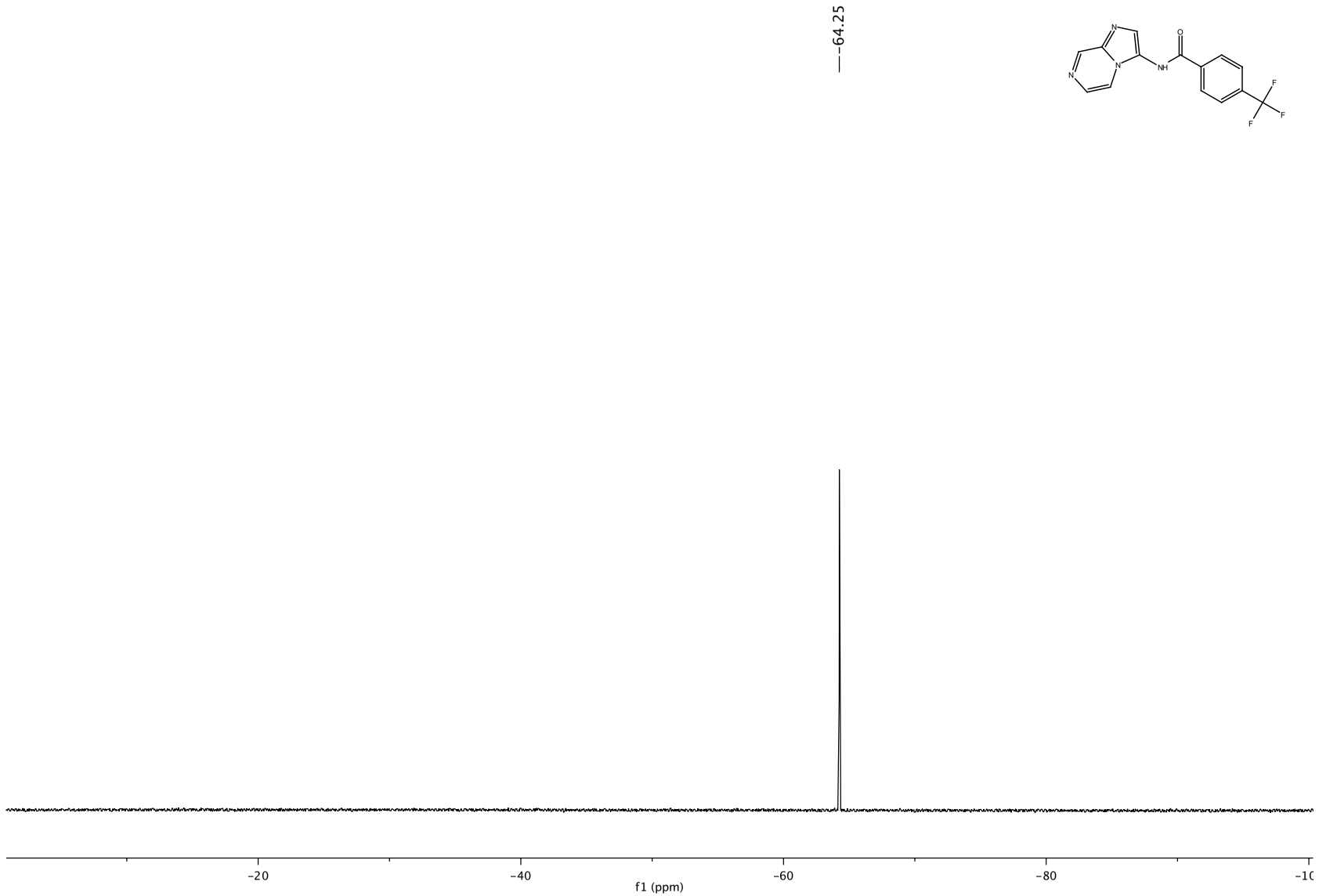
50
40
30
20
10
0
f1 (ppm)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7.522
7.399
7.398
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7.383
7.260
6.626
6.587
0.98
1.00
0.97
1.04
2.11
3.14
1.04
f1 (ppm)
O
NH
N
S

163.83
150.60
148.77
142.78
134.59
130.11
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127.96
120.04
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77.16
76.84
f1 (ppm)

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f1 (ppm)

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f1 (ppm)

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6.66
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2.20
2.19
2.18
2.17
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1.77
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1.53
1.50
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1.29
1.26
1.23
1.21
1.18
0.97
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3.03
1.01
5.23
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3.17
f1 (ppm)

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45.68
36.76
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25.73
f1 (ppm)

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7.57
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3.20
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4.20
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1.502
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1.08
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2.17
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f1 (ppm)

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146.19
131.97
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123.32
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77.16
76.84
52.00
45.14
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25.57
25.49
f1 (ppm)

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2.02
2.02
f1 (ppm)

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115.84
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77.16
76.84
56.62
f1 (ppm)

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O
NH
N
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-50
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-70
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-90
-100
-110
-120
-130
-140
f1 (ppm)

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1.01
1.00
0.99
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2.01
1.01
2.04
f1 (ppm)

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128.23
127.96
127.86
121.89
121.36
77.48
77.16
76.84
56.51
f1 (ppm)

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77.16
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56.35
f1 (ppm)

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6.506
6.502
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0.99
1.00
1.00
1.01
3.12
f1 (ppm)

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O
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N
N
H3C
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147.61
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f1 (ppm)

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6.938
6.932
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3.323
3.064
3.047
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0.809
6.17
26.74
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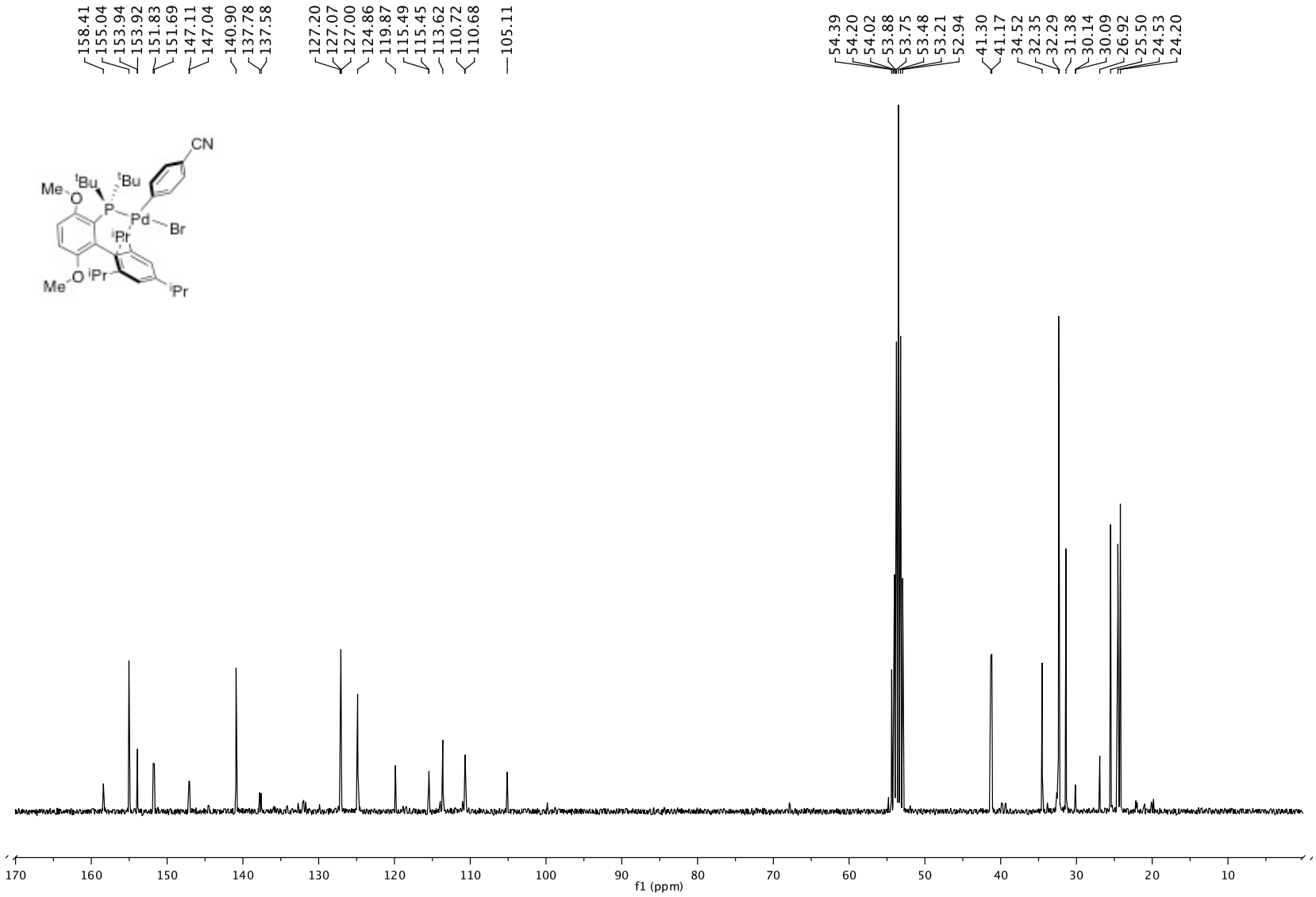
1.00
3.12
3.36
2.04
4.25
2.19
f1 (ppm)
CN
Br
Pd
P
tBu
tBu
iPr
iPr
O
Me
O
Me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127.00
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115.49
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110.68
105.11
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54.20
54.02
53.88
53.75
53.48
53.21
52.94
41.30
41.17
34.52
32.35
32.29
31.38
30.14
30.09
26.92
25.50
24.53
24.20
CN
Me
O
tBu
tBu
P
Pd
Br
iPr
Me
O
iPr
iPr
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140
130
120
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80
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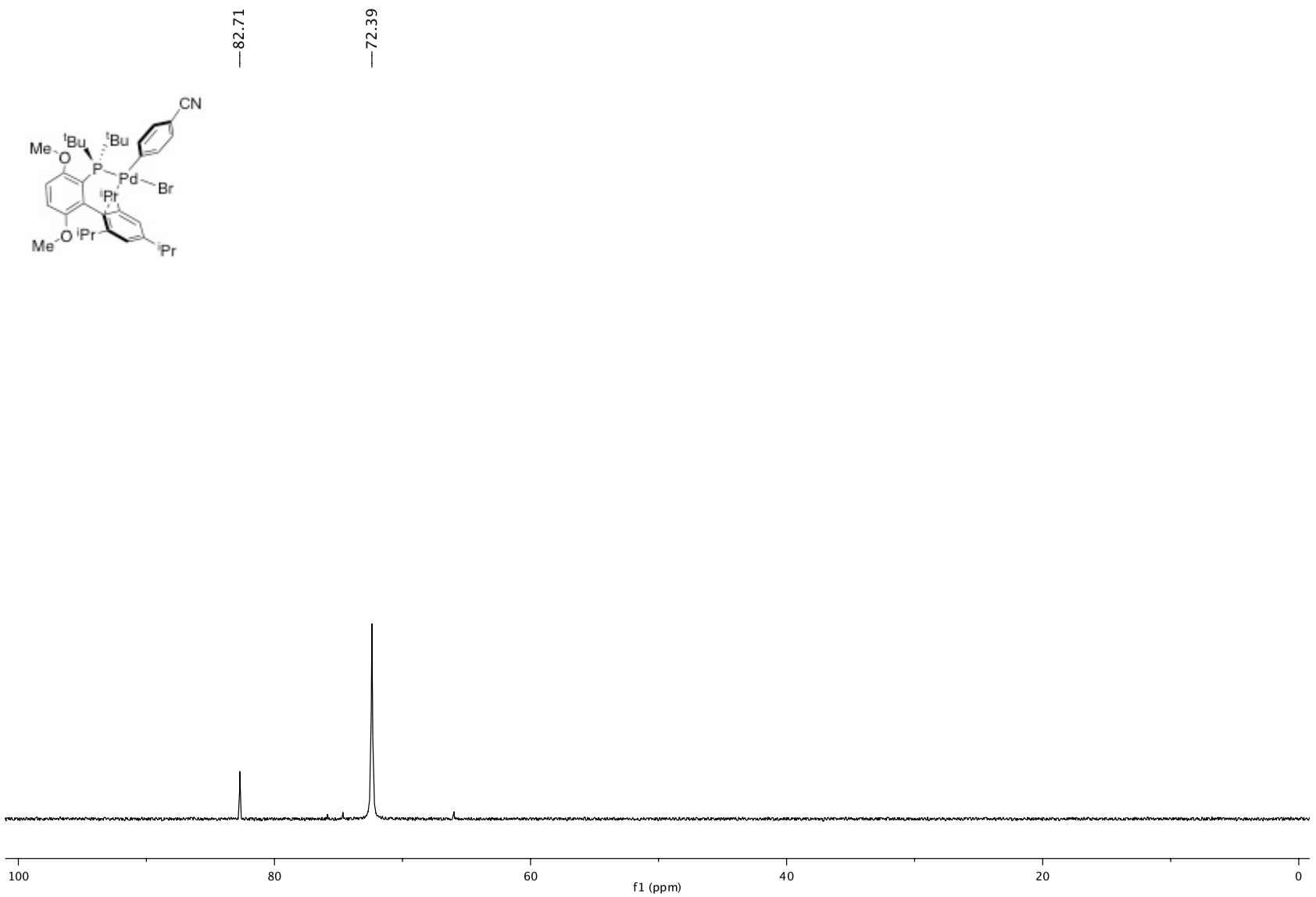
60
50
40
30
20
10
f1 (ppm)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P
Pd
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O
iPr
iPr
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80
60
40
20
0
f1 (ppm)

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7.387
7.043
7.019
6.966
6.946
6.882
6.860
5.320
3.835
3.321
3.051
3.036
3.019
3.003
2.987
2.571
2.555
2.231
2.152
1.930
1.713
1.672
1.604
1.588
1.429
1.352
1.335
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0.811
6.29
3.32
3.01
1.00
2.18
13.84
7.21
14.04
6.43
2.16
6.81
1.94
4.16
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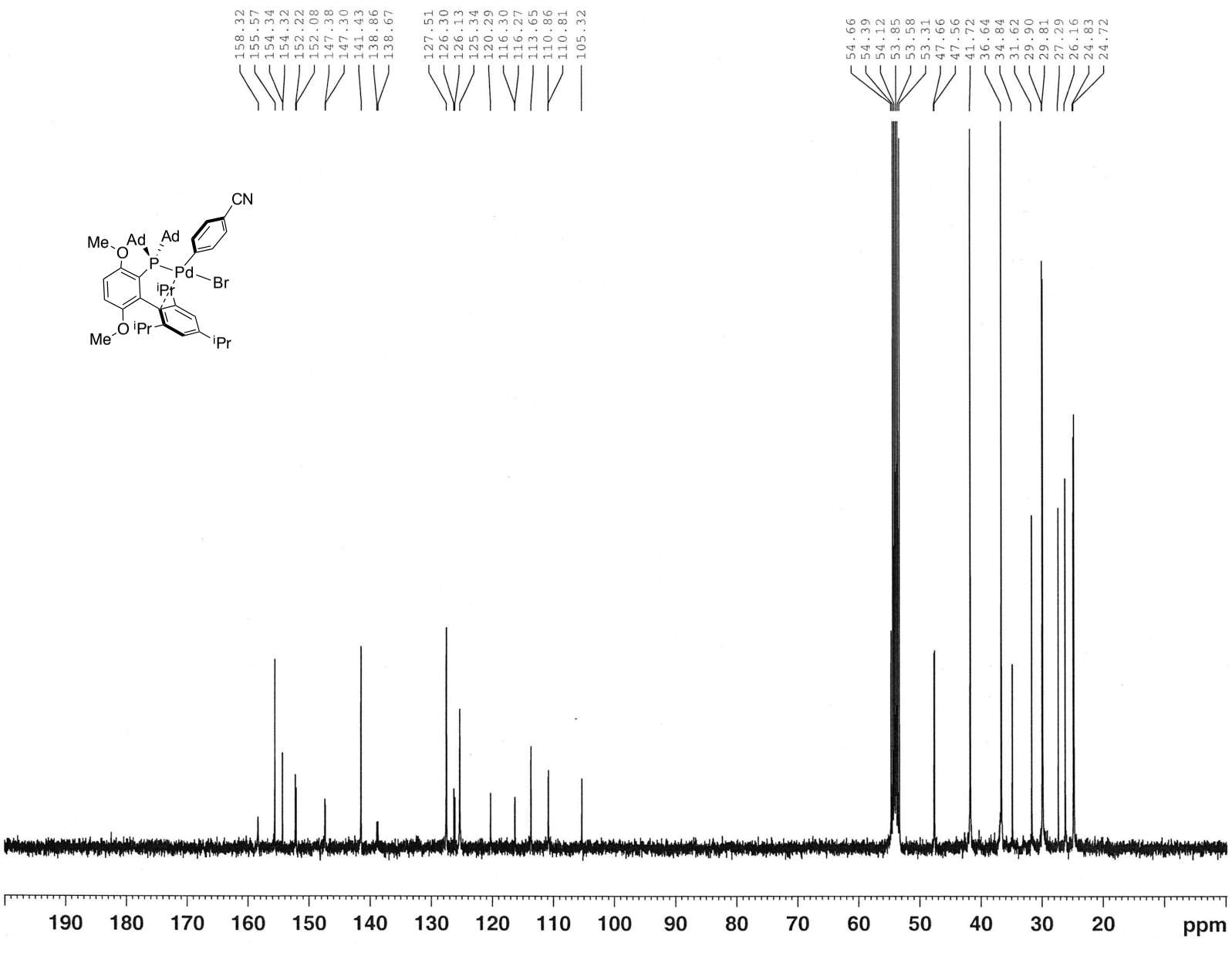
f1 (ppm)
CN
Br
Pd
P
Ad
Ad
iPr
iPr
iPr
O
O
Me
Me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54.39
54.12
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53.58
53.31
47.66
47.56
41.72
36.64
34.84
31.62
29.90
29.81
27.29
26.16
24.83
24.72
CN
Me
O
Ad
Ad
P
Pd
Br
iPr
iPr
Me
O
iPr
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180
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160
150
140
130
120
110
100
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60
50
40
30
20
ppm

67.91
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O
f1 (ppm)

X-ray crystallographic data for complex 2a

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 'Br'  'Br'  -0.2901   2.4595
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 'x, y, z'
 '-x, -y, -z'

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_cell_angle_beta                 93.507(5)
_cell_angle_gamma                    101.724(5)
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_cell_formula_units_Z           2
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_cell_measurement_reflns_used   9236
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_exptl_crystal_size_max         0.30
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_exptl_crystal_density_diffrn   1.404
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_exptl_crystal_F_000            800
_exptl_absorpt_coefficient_mu   1.676
_exptl_absorpt_correction_type  multi-scan
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_exptl_absorpt_process_details  'SADABS (Sheldrick, 2009)'

_exptl_special_details
;
 Bruker X8 Kappa DUO four-circle diffractometer, Bruker APEX2 CCD.
 The instrument was purchased with the help of funding from the
 National Science Foundation (NSF) under Grant Number
 CHE-0946721.
;

_diffrn_ambient_temperature     100(2)
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_diffrn_measurement_device_type 'Bruker Smart APEX2 CCD'
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_computing_data_reduction         'SAINT 7.46A (Bruker-AXS, 2010)'
_computing_structure_solution     'SHELXS-97 (Sheldrick, 2008)'
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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_refine_ls_extinction_method      none
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P1 P 0.36846(5) 0.00263(5) 0.17848(2) 0.01364(8) Uani 1 1 d . . .
C1 C 0.4579(2) -0.13416(19) 0.13578(9) 0.0189(3) Uani 1 1 d . . .
C2 C 0.3596(2) -0.2057(2) 0.07844(9) 0.0239(4) Uani 1 1 d . . .
H2A H 0.4156 -0.2717 0.0595 0.036 Uiso 1 1 calc R . .
H2B H 0.3447 -0.1363 0.0496 0.036 Uiso 1 1 calc R . .
H2C H 0.2556 -0.2549 0.0897 0.036 Uiso 1 1 calc R . .
C3 C 0.4898(3) -0.2456(2) 0.17822(9) 0.0249(4) Uani 1 1 d . . .
H3A H 0.3894 -0.2926 0.1933 0.037 Uiso 1 1 calc R . .
H3B H 0.5631 -0.2023 0.2128 0.037 Uiso 1 1 calc R . .
H3C H 0.5372 -0.3129 0.1557 0.037 Uiso 1 1 calc R . .
C4 C 0.6193(2) -0.0611(2) 0.11524(10) 0.0266(4) Uani 1 1 d . . .
H4A H 0.6892 -0.0201 0.1510 0.040 Uiso 1 1 calc R . .
H4B H 0.6036 0.0116 0.0883 0.040 Uiso 1 1 calc R . .
H4C H 0.6681 -0.1284 0.0933 0.040 Uiso 1 1 calc R . .
C5 C 0.2136(2) 0.0627(2) 0.12669(9) 0.0187(3) Uani 1 1 d . . .
C6 C 0.2875(2) 0.1128(2) 0.06744(9) 0.0226(4) Uani 1 1 d . . .
H6A H 0.2397 0.1881 0.0529 0.034 Uiso 1 1 calc R . .
H6B H 0.2673 0.0360 0.0363 0.034 Uiso 1 1 calc R . .
H6C H 0.4025 0.1460 0.0756 0.034 Uiso 1 1 calc R . .
C7 C 0.0567(2) -0.0409(2) 0.10872(10) 0.0268(4) Uani 1 1 d . . .
H7A H -0.0138 0.0035 0.0835 0.040 Uiso 1 1 calc R . .
H7B H 0.0050 -0.0712 0.1456 0.040 Uiso 1 1 calc R . .
H7C H 0.0789 -0.1211 0.0856 0.040 Uiso 1 1 calc R . .
C8 C 0.1690(2) 0.1832(2) 0.16340(9) 0.0218(4) Uani 1 1 d . . .
H8A H 0.2660 0.2460 0.1810 0.033 Uiso 1 1 calc R . .
H8B H 0.1033 0.1472 0.1962 0.033 Uiso 1 1 calc R . .
H8C H 0.1091 0.2335 0.1364 0.033 Uiso 1 1 calc R . .
C11 C 0.2625(2) -0.08054(18) 0.24159(8) 0.0149(3) Uani 1 1 d . . .
C12 C 0.1479(2) -0.20582(19) 0.23257(9) 0.0172(3) Uani 1 1 d . . .
O1 O 0.12546(17) -0.26479(15) 0.17500(7) 0.0239(3) Uani 1 1 d . . .
C17 C 0.0091(3) -0.3893(2) 0.16273(11) 0.0337(5) Uani 1 1 d . . .
H17A H 0.0349 -0.4603 0.1888 0.051 Uiso 1 1 calc R . .
H17B H 0.0083 -0.4210 0.1198 0.051 Uiso 1 1 calc R . .
H17C H -0.0960 -0.3722 0.1711 0.051 Uiso 1 1 calc R . .
C13 C 0.0682(2) -0.26485(19) 0.28070(9) 0.0199(4) Uani 1 1 d . . .
H13 H -0.0099 -0.3480 0.2738 0.024 Uiso 1 1 calc R . .
C14 C 0.1030(2) -0.2020(2) 0.33899(9) 0.0195(3) Uani 1 1 d . . .
H14 H 0.0477 -0.2416 0.3720 0.023 Uiso 1 1 calc R . .
C15 C 0.2178(2) -0.08186(19) 0.34921(8) 0.0172(3) Uani 1 1 d . . .
O2 O 0.26337(17) -0.01844(15) 0.40619(6) 0.0222(3) Uani 1 1 d . . .
C18 C 0.1603(3) -0.0568(2) 0.45332(10) 0.0295(4) Uani 1 1 d . . .
H18A H 0.0526 -0.0466 0.4402 0.044 Uiso 1 1 calc R . .
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H18B H 0.1987 0.0031 0.4902 0.044 Uiso 1 1 calc R . .
H18C H 0.1585 -0.1532 0.4621 0.044 Uiso 1 1 calc R . .
C16 C 0.29963(19) -0.01952(18) 0.30082(8) 0.0142(3) Uani 1 1 d . . .
C21 C 0.4318(2) 0.10265(18) 0.32102(8) 0.0143(3) Uani 1 1 d . . .
C22 C 0.5808(2) 0.07290(18) 0.34167(8) 0.0150(3) Uani 1 1 d . . .
C27 C 0.6297(2) -0.0601(2) 0.32197(9) 0.0199(4) Uani 1 1 d . . .
H27 H 0.5474 -0.1102 0.2902 0.024 Uiso 1 1 calc R . .
C28 C 0.6355(3) -0.1549(2) 0.37419(12) 0.0358(5) Uani 1 1 d . . .
H28A H 0.7203 -0.1113 0.4049 0.054 Uiso 1 1 calc R . .
H28B H 0.6568 -0.2432 0.3585 0.054 Uiso 1 1 calc R . .
H28C H 0.5332 -0.1712 0.3927 0.054 Uiso 1 1 calc R . .
C29 C 0.7889(2) -0.0306(2) 0.29271(10) 0.0273(4) Uani 1 1 d . . .
H29A H 0.7832 0.0316 0.2597 0.041 Uiso 1 1 calc R . .
H29B H 0.8120 -0.1175 0.2762 0.041 Uiso 1 1 calc R . .
H29C H 0.8735 0.0130 0.3235 0.041 Uiso 1 1 calc R . .
C23 C 0.6812(2) 0.16414(19) 0.38407(8) 0.0168(3) Uani 1 1 d . . .
H23 H 0.7803 0.1434 0.3974 0.020 Uiso 1 1 calc R . .
C24 C 0.6418(2) 0.28381(19) 0.40754(8) 0.0165(3) Uani 1 1 d . . .
C30 C 0.7501(2) 0.3748(2) 0.45673(9) 0.0196(3) Uani 1 1 d . . .
H30 H 0.8481 0.3360 0.4627 0.024 Uiso 1 1 calc R . .
C31 C 0.6708(3) 0.3688(2) 0.51730(9) 0.0274(4) Uani 1 1 d . . .
H31A H 0.7477 0.4166 0.5500 0.041 Uiso 1 1 calc R . .
H31B H 0.6344 0.2721 0.5266 0.041 Uiso 1 1 calc R . .
H31C H 0.5795 0.4140 0.5141 0.041 Uiso 1 1 calc R . .
C32 C 0.8021(3) 0.5239(2) 0.43937(11) 0.0321(5) Uani 1 1 d . . .
H32A H 0.8507 0.5249 0.4002 0.048 Uiso 1 1 calc R . .
H32B H 0.8797 0.5756 0.4709 0.048 Uiso 1 1 calc R . .
H32C H 0.7092 0.5670 0.4358 0.048 Uiso 1 1 calc R . .
C25 C 0.4985(2) 0.31551(19) 0.38563(9) 0.0179(3) Uani 1 1 d . . .
H25 H 0.4723 0.3996 0.4000 0.021 Uiso 1 1 calc R . .
C26 C 0.3932(2) 0.22851(18) 0.34368(8) 0.0155(3) Uani 1 1 d . . .
C33 C 0.2371(2) 0.2687(2) 0.32444(9) 0.0192(3) Uani 1 1 d . . .
H33 H 0.1795 0.1983 0.2924 0.023 Uiso 1 1 calc R . .
C34 C 0.1298(2) 0.2701(2) 0.37726(10) 0.0249(4) Uani 1 1 d . . .
H34A H 0.1848 0.3367 0.4099 0.037 Uiso 1 1 calc R . .
H34B H 0.1049 0.1777 0.3929 0.037 Uiso 1 1 calc R . .
H34C H 0.0310 0.2969 0.3628 0.037 Uiso 1 1 calc R . .
C35 C 0.2656(3) 0.4098(2) 0.29665(10) 0.0256(4) Uani 1 1 d . . .
H35A H 0.3075 0.4825 0.3287 0.038 Uiso 1 1 calc R . .
H35B H 0.1650 0.4255 0.2780 0.038 Uiso 1 1 calc R . .
H35C H 0.3425 0.4117 0.2655 0.038 Uiso 1 1 calc R . .
C41 C 0.6164(2) 0.28332(18) 0.15258(8) 0.0159(3) Uani 1 1 d . . .
C42 C 0.5391(2) 0.38341(19) 0.13014(9) 0.0186(3) Uani 1 1 d . . .
H42 H 0.4490 0.4021 0.1492 0.022 Uiso 1 1 calc R . .
C43 C 0.5916(2) 0.45619(19) 0.08045(9) 0.0180(3) Uani 1 1 d . . .
H43 H 0.5369 0.5234 0.0654 0.022 Uiso 1 1 calc R . .
C44 C 0.7250(2) 0.43065(19) 0.05253(8) 0.0166(3) Uani 1 1 d . . .
C47 C 0.7812(2) 0.5079(2) 0.00190(9) 0.0196(3) Uani 1 1 d . . .
N1 N 0.8241(2) 0.5696(2) -0.03877(9) 0.0271(4) Uani 1 1 d . . .
C45 C 0.8063(2) 0.33289(19) 0.07555(9) 0.0182(3) Uani 1 1 d . . .
H45 H 0.8974 0.3151 0.0569 0.022 Uiso 1 1 calc R . .

C46 C 0.7532(2) 0.26246(19) 0.12545(9) 0.0175(3) Uani 1 1 d . . .
H46 H 0.8107 0.1985 0.1417 0.021 Uiso 1 1 calc R . .

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C2 0.0244(9) 0.0225(9) 0.0233(9) -0.0046(7) 0.0004(7) 0.0031(8)
C3 0.0294(10) 0.0212(9) 0.0253(10) -0.0024(7) 0.0009(8) 0.0093(8)
C4 0.0195(9) 0.0233(10) 0.0358(11) -0.0069(8) 0.0090(8) 0.0016(8)
C5 0.0130(7) 0.0200(8) 0.0221(9) 0.0026(7) -0.0022(6) 0.0021(6)
C6 0.0237(9) 0.0231(9) 0.0204(9) 0.0030(7) -0.0001(7) 0.0038(7)
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C8 0.0153(8) 0.0264(10) 0.0249(9) 0.0030(7) 0.0007(7) 0.0068(7)
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C12 0.0117(7) 0.0159(8) 0.0226(8) 0.0012(6) -0.0007(6) -0.0005(6)
O1 0.0217(7) 0.0192(7) 0.0245(7) -0.0034(5) 0.0006(5) -0.0090(5)
C17 0.0312(11) 0.0274(11) 0.0320(11) -0.0053(9) 0.0010(9) -0.0166(9)
C13 0.0143(8) 0.0147(8) 0.0290(10) 0.0037(7) 0.0028(7) -0.0016(6)
C14 0.0152(8) 0.0186(8) 0.0244(9) 0.0054(7) 0.0051(7) 0.0005(7)
C15 0.0136(7) 0.0170(8) 0.0207(8) 0.0025(6) 0.0016(6) 0.0019(6)
O2 0.0220(7) 0.0239(7) 0.0189(6) 0.0011(5) 0.0053(5) -0.0004(5)
C18 0.0322(11) 0.0333(11) 0.0222(10) 0.0044(8) 0.0094(8) 0.0023(9)
C16 0.0096(7) 0.0129(7) 0.0201(8) 0.0020(6) 0.0014(6) 0.0019(6)
C21 0.0109(7) 0.0145(7) 0.0163(7) 0.0013(6) 0.0008(6) -0.0002(6)
C22 0.0115(7) 0.0148(8) 0.0184(8) 0.0019(6) 0.0021(6) 0.0018(6)
C27 0.0153(8) 0.0193(9) 0.0255(9) -0.0027(7) -0.0023(7) 0.0064(7)
C28 0.0451(14) 0.0239(11) 0.0418(13) 0.0084(9) 0.0040(11) 0.0137(10)
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C23 0.0118(7) 0.0185(8) 0.0195(8) 0.0018(6) 0.0008(6) 0.0015(6)
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C31 0.0273(10) 0.0320(11) 0.0218(9) -0.0046(8) -0.0003(8) 0.0058(9)
C32 0.0355(12) 0.0216(10) 0.0320(11) 0.0007(8) -0.0091(9) -0.0070(9)
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C44 0.0133(7) 0.0162(8) 0.0185(8) 0.0011(6) 0.0006(6) -0.0011(6)

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C47 0.0143(8) 0.0193(8) 0.0243(9) 0.0016(7) 0.0012(7) 0.0013(7)
N1 0.0202(8) 0.0300(9) 0.0328(9) 0.0117(7) 0.0076(7) 0.0055(7)
C45 0.0126(7) 0.0178(8) 0.0238(9) 0.0018(7) 0.0032(6) 0.0013(6)
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 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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C1 C2 H2C 109.5 . . ?
H2A C2 H2C 109.5 . . ?

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X-ray crystallographic data for Complex 2b

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'-x, -y, -z'

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Bruker X8 Kappa DUO four-circle diffractometer, Bruker APEX2 CCD.
The instrument was purchased with the help of funding from the
National Science Foundation (NSF) under Grant Number
CHE-0946721.
;

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_refine_special_details
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Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
goodness of fit S are based on F^2^, conventional R-factors R are based
on F, with F set to zero for negative F^2^. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement.  R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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Br1 Br 0.43403(3) 1.01319(3) 0.76327(2) 0.02903(8) Uani 1 1 d . . .
Pd1 Pd 0.596894(18) 0.933647(18) 0.731975(15) 0.01950(6) Uani 1 1 d . . .
P1 P 0.74565(6) 0.85353(6) 0.67714(5) 0.01856(14) Uani 1 1 d . . .
C1 C 0.7525(2) 0.8174(2) 0.5433(2) 0.0215(5) Uani 1 1 d . . .
C2 C 0.8084(3) 0.7289(3) 0.4897(2) 0.0265(6) Uani 1 1 d . . .
H2A H 0.7591 0.6585 0.4913 0.032 Uiso 1 1 calc R . .
H2B H 0.8918 0.7495 0.5225 0.032 Uiso 1 1 calc R . .
C3 C 0.8256(3) 0.9256(2) 0.5346(2) 0.0238(6) Uani 1 1 d . . .
H3A H 0.7882 0.9820 0.5662 0.029 Uiso 1 1 calc R . .
H3B H 0.9102 0.9521 0.5678 0.029 Uiso 1 1 calc R . .
C4 C 0.6220(3) 0.7805(3) 0.4897(2) 0.0282(6) Uani 1 1 d . . .
H4A H 0.5720 0.7118 0.4939 0.034 Uiso 1 1 calc R . .
H4B H 0.5844 0.8369 0.5211 0.034 Uiso 1 1 calc R . .
C5 C 0.8129(3) 0.7148(3) 0.3844(2) 0.0281(6) Uani 1 1 d . . .
H5A H 0.8514 0.6585 0.3522 0.034 Uiso 1 1 calc R . .
C6 C 0.8882(3) 0.8238(3) 0.3814(2) 0.0265(6) Uani 1 1 d . . .
H6A H 0.9718 0.8486 0.4157 0.032 Uiso 1 1 calc R . .
H6B H 0.8935 0.8145 0.3141 0.032 Uiso 1 1 calc R . .
C7 C 0.8274(3) 0.9082(3) 0.4287(2) 0.0272(6) Uani 1 1 d . . .
H7A H 0.8753 0.9789 0.4254 0.033 Uiso 1 1 calc R . .
C8 C 0.6969(3) 0.8709(3) 0.3782(2) 0.0340(7) Uani 1 1 d . . .
H8A H 0.6976 0.8611 0.3104 0.041 Uiso 1 1 calc R . .
H8B H 0.6591 0.9270 0.4097 0.041 Uiso 1 1 calc R . .
C9 C 0.6228(3) 0.7622(3) 0.3832(2) 0.0325(7) Uani 1 1 d . . .
H9A H 0.5375 0.7371 0.3501 0.039 Uiso 1 1 calc R . .
C10 C 0.6834(3) 0.6772(3) 0.3330(2) 0.0345(7) Uani 1 1 d . . .
```

H10A H 0.6358 0.6059 0.3337 0.041 Uiso 1 1 calc R . .
H10B H 0.6852 0.6679 0.2654 0.041 Uiso 1 1 calc R . .
C11 C 0.7374(3) 0.7326(2) 0.7077(2) 0.0234(6) Uani 1 1 d . . .
C12 C 0.7186(3) 0.7651(2) 0.8130(2) 0.0251(6) Uani 1 1 d . . .
H12A H 0.6497 0.7934 0.8230 0.030 Uiso 1 1 calc R . .
H12B H 0.7925 0.8242 0.8545 0.030 Uiso 1 1 calc R . .
C13 C 0.8464(3) 0.6905(3) 0.6964(3) 0.0317(7) Uani 1 1 d . . .
H13A H 0.9204 0.7498 0.7377 0.038 Uiso 1 1 calc R . .
H13B H 0.8613 0.6686 0.6291 0.038 Uiso 1 1 calc R . .
C14 C 0.6228(3) 0.6370(3) 0.6433(2) 0.0306(7) Uani 1 1 d . . .
H14A H 0.5511 0.6616 0.6501 0.037 Uiso 1 1 calc R . .
H14B H 0.6349 0.6141 0.5753 0.037 Uiso 1 1 calc R . .
C15 C 0.6921(3) 0.6668(3) 0.8417(2) 0.0299(7) Uani 1 1 d . . .
H15A H 0.6788 0.6898 0.9101 0.036 Uiso 1 1 calc R . .
C16 C 0.8012(3) 0.6268(3) 0.8290(3) 0.0364(8) Uani 1 1 d . . .
H16A H 0.8749 0.6861 0.8708 0.044 Uiso 1 1 calc R . .
H16B H 0.7863 0.5643 0.8479 0.044 Uiso 1 1 calc R . .
C17 C 0.8212(4) 0.5916(3) 0.7244(3) 0.0384(8) Uani 1 1 d . . .
H17A H 0.8924 0.5651 0.7162 0.046 Uiso 1 1 calc R . .
C18 C 0.7088(4) 0.5014(3) 0.6609(3) 0.0475(10) Uani 1 1 d . . .
H18A H 0.6932 0.4374 0.6778 0.057 Uiso 1 1 calc R . .
H18B H 0.7220 0.4785 0.5932 0.057 Uiso 1 1 calc R . .
C19 C 0.5998(4) 0.5394(3) 0.6727(2) 0.0383(8) Uani 1 1 d . . .
H19A H 0.5260 0.4783 0.6308 0.046 Uiso 1 1 calc R . .
C20 C 0.5791(3) 0.5750(3) 0.7772(2) 0.0337(7) Uani 1 1 d . . .
H20A H 0.5081 0.6005 0.7850 0.040 Uiso 1 1 calc R . .
H20B H 0.5617 0.5121 0.7958 0.040 Uiso 1 1 calc R . .
C21 C 0.8901(2) 0.9661(2) 0.74296(19) 0.0169(5) Uani 1 1 d . . .
C22 C 1.0055(2) 0.9541(2) 0.73021(19) 0.0193(5) Uani 1 1 d . . .
O1 O 1.00527(18) 0.86120(17) 0.65683(15) 0.0254(4) Uani 1 1 d . . .
C27 C 1.1154(3) 0.8365(3) 0.6464(2) 0.0296(7) Uani 1 1 d . . .
H27A H 1.1008 0.7674 0.5910 0.044 Uiso 1 1 calc R . .
H27B H 1.1434 0.8300 0.7044 0.044 Uiso 1 1 calc R . .
H27C H 1.1777 0.8952 0.6368 0.044 Uiso 1 1 calc R . .
C23 C 1.1117(2) 1.0359(2) 0.7850(2) 0.0221(6) Uani 1 1 d . . .
H23A H 1.1877 1.0241 0.7791 0.026 Uiso 1 1 calc R . .
C24 C 1.1062(3) 1.1349(2) 0.8484(2) 0.0231(6) Uani 1 1 d . . .
H24A H 1.1784 1.1910 0.8870 0.028 Uiso 1 1 calc R . .
C25 C 0.9962(3) 1.1523(2) 0.8556(2) 0.0214(5) Uani 1 1 d . . .
O2 O 0.98580(19) 1.25158(17) 0.91278(15) 0.0276(5) Uani 1 1 d . . .
C28 C 1.0924(3) 1.3449(3) 0.9362(3) 0.0349(7) Uani 1 1 d . . .
H28A H 1.0752 1.4106 0.9766 0.052 Uiso 1 1 calc R . .
H28B H 1.1174 1.3515 0.8772 0.052 Uiso 1 1 calc R . .
H28C H 1.1581 1.3367 0.9709 0.052 Uiso 1 1 calc R . .
C26 C 0.8854(2) 1.0679(2) 0.80579(18) 0.0174(5) Uani 1 1 d . . .
C31 C 0.7739(2) 1.0997(2) 0.82879(19) 0.0184(5) Uani 1 1 d . . .
C32 C 0.7453(2) 1.1696(2) 0.7897(2) 0.0197(5) Uani 1 1 d . . .
C37 C 0.7943(3) 1.1817(3) 0.7012(2) 0.0250(6) Uani 1 1 d . . .
H37A H 0.8449 1.1334 0.6789 0.030 Uiso 1 1 calc R . .
C38 C 0.8750(3) 1.2985(3) 0.7229(3) 0.0352(8) Uani 1 1 d . . .
H38A H 0.9415 1.3217 0.7749 0.053 Uiso 1 1 calc R . .

H38B H 0.8266 1.3471 0.7424 0.053 Uiso 1 1 calc R . .
H38C H 0.9089 1.3019 0.6655 0.053 Uiso 1 1 calc R . .
C39 C 0.6893(3) 1.1436(3) 0.6197(2) 0.0340(8) Uani 1 1 d . . .
H39A H 0.6387 1.0683 0.6060 0.051 Uiso 1 1 calc R . .
H39B H 0.7226 1.1471 0.5621 0.051 Uiso 1 1 calc R . .
H39C H 0.6397 1.1912 0.6391 0.051 Uiso 1 1 calc R . .
C33 C 0.6776(3) 1.2337(2) 0.8367(2) 0.0222(6) Uani 1 1 d . . .
H33A H 0.6583 1.2789 0.8095 0.027 Uiso 1 1 calc R . .
C34 C 0.6364(2) 1.2349(2) 0.9221(2) 0.0209(5) Uani 1 1 d . . .
C40 C 0.5674(3) 1.3095(2) 0.9754(2) 0.0254(6) Uani 1 1 d . . .
H40A H 0.5285 1.2820 1.0230 0.030 Uiso 1 1 calc R . .
C41 C 0.6565(3) 1.4249(3) 1.0316(3) 0.0430(9) Uani 1 1 d . . .
H41A H 0.7201 1.4224 1.0729 0.065 Uiso 1 1 calc R . .
H41B H 0.6128 1.4710 1.0711 0.065 Uiso 1 1 calc R . .
H41C H 0.6938 1.4555 0.9868 0.065 Uiso 1 1 calc R . .
C42 C 0.4664(3) 1.3098(3) 0.9105(3) 0.0399(8) Uani 1 1 d . . .
H42A H 0.4102 1.2350 0.8758 0.060 Uiso 1 1 calc R . .
H42B H 0.5020 1.3391 0.8644 0.060 Uiso 1 1 calc R . .
H42C H 0.4220 1.3556 0.9494 0.060 Uiso 1 1 calc R . .
C35 C 0.6656(3) 1.1673(2) 0.9602(2) 0.0211(5) Uani 1 1 d . . .
H35A H 0.6380 1.1666 1.0182 0.025 Uiso 1 1 calc R . .
C36 C 0.7329(2) 1.1013(2) 0.91691(19) 0.0187(5) Uani 1 1 d . . .
C43 C 0.7718(3) 1.0408(2) 0.9696(2) 0.0216(5) Uani 1 1 d . . .
H43A H 0.8089 0.9897 0.9248 0.026 Uiso 1 1 calc R . .
C44 C 0.8685(3) 1.1196(3) 1.0575(2) 0.0349(7) Uani 1 1 d . . .
H44A H 0.9375 1.1628 1.0376 0.052 Uiso 1 1 calc R . .
H44B H 0.8965 1.0779 1.0870 0.052 Uiso 1 1 calc R . .
H44C H 0.8332 1.1686 1.1039 0.052 Uiso 1 1 calc R . .
C45 C 0.6632(3) 0.9723(3) 0.9996(2) 0.0286(6) Uani 1 1 d . . .
H45A H 0.6020 0.9220 0.9430 0.043 Uiso 1 1 calc R . .
H45B H 0.6272 1.0208 1.0458 0.043 Uiso 1 1 calc R . .
H45C H 0.6909 0.9304 1.0291 0.043 Uiso 1 1 calc R . .
C51 C 0.4485(2) 0.7978(3) 0.6834(2) 0.0234(6) Uani 1 1 d . . .
C52 C 0.3752(3) 0.7570(2) 0.5951(2) 0.0235(6) Uani 1 1 d . . .
H52A H 0.3998 0.7896 0.5510 0.028 Uiso 1 1 calc R . .
C53 C 0.2670(3) 0.6698(2) 0.5701(2) 0.0250(6) Uani 1 1 d . . .
H53A H 0.2186 0.6433 0.5095 0.030 Uiso 1 1 calc R . .
C54 C 0.2293(3) 0.6213(3) 0.6340(2) 0.0271(6) Uani 1 1 d . . .
C57 C 0.1165(3) 0.5306(3) 0.6076(3) 0.0339(7) Uani 1 1 d . . .
N1 N 0.0281(3) 0.4577(3) 0.5866(3) 0.0440(8) Uani 1 1 d . . .
C55 C 0.2984(3) 0.6634(3) 0.7241(3) 0.0321(7) Uani 1 1 d . . .
H55A H 0.2722 0.6322 0.7688 0.038 Uiso 1 1 calc R . .
C56 C 0.4061(3) 0.7514(3) 0.7483(2) 0.0301(7) Uani 1 1 d . . .
H56A H 0.4520 0.7807 0.8104 0.036 Uiso 1 1 calc R . .

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P1 0.0137(3) 0.0218(4) 0.0222(3) 0.0098(3) 0.0071(2) 0.0073(3)
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C2 0.0263(15) 0.0297(16) 0.0254(14) 0.0131(13) 0.0102(11) 0.0090(12)
C3 0.0206(13) 0.0303(16) 0.0259(14) 0.0157(12) 0.0076(11) 0.0099(12)
C4 0.0176(13) 0.0385(18) 0.0268(15) 0.0126(13) 0.0074(11) 0.0077(12)
C5 0.0282(15) 0.0367(18) 0.0248(14) 0.0151(13) 0.0124(12) 0.0141(13)
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C7 0.0246(14) 0.0389(18) 0.0295(15) 0.0235(14) 0.0110(12) 0.0133(13)
C8 0.0260(15) 0.057(2) 0.0291(16) 0.0230(16) 0.0081(12) 0.0207(16)
C9 0.0221(14) 0.052(2) 0.0237(14) 0.0158(15) 0.0064(12) 0.0112(14)
C10 0.0270(16) 0.044(2) 0.0272(15) 0.0122(14) 0.0084(12) 0.0072(14)
C11 0.0231(14) 0.0209(14) 0.0280(14) 0.0116(12) 0.0121(11) 0.0070(11)
C12 0.0258(14) 0.0259(15) 0.0268(14) 0.0126(12) 0.0082(11) 0.0102(12)
C13 0.0358(17) 0.0379(18) 0.0411(18) 0.0269(15) 0.0232(14) 0.0236(15)
C14 0.0350(17) 0.0278(16) 0.0242(14) 0.0111(13) 0.0097(12) 0.0028(13)
C15 0.0340(17) 0.0283(16) 0.0314(16) 0.0153(13) 0.0111(13) 0.0111(13)
C16 0.0401(19) 0.0369(19) 0.047(2) 0.0270(17) 0.0161(16) 0.0188(16)
C17 0.047(2) 0.042(2) 0.050(2) 0.0328(18) 0.0269(17) 0.0276(17)
C18 0.081(3) 0.0272(18) 0.044(2) 0.0180(16) 0.029(2) 0.0240(19)
C19 0.049(2) 0.0248(17) 0.0316(17) 0.0114(14) 0.0092(15) -0.0003(15)
C20 0.045(2) 0.0275(16) 0.0290(16) 0.0163(14) 0.0120(14) 0.0057(14)
C21 0.0136(11) 0.0219(13) 0.0206(12) 0.0138(11) 0.0055(9) 0.0065(10)
C22 0.0175(12) 0.0249(14) 0.0221(13) 0.0138(11) 0.0057(10) 0.0102(11)
O1 0.0164(9) 0.0280(11) 0.0339(11) 0.0103(9) 0.0088(8) 0.0126(8)
C27 0.0196(14) 0.0363(18) 0.0401(17) 0.0158(14) 0.0110(12) 0.0181(13)
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C24 0.0172(12) 0.0272(15) 0.0227(13) 0.0104(12) 0.0028(10) 0.0040(11)
C25 0.0237(13) 0.0221(14) 0.0214(13) 0.0106(11) 0.0069(10) 0.0090(11)
O2 0.0259(11) 0.0198(10) 0.0311(11) 0.0065(9) 0.0060(9) 0.0040(9)
C28 0.0336(17) 0.0258(16) 0.0369(18) 0.0102(14) 0.0059(14) 0.0016(14)
C26 0.0173(12) 0.0231(13) 0.0178(12) 0.0129(11) 0.0066(9) 0.0089(10)
C31 0.0202(12) 0.0199(13) 0.0189(12) 0.0101(10) 0.0063(10) 0.0085(10)
C32 0.0180(12) 0.0229(14) 0.0247(13) 0.0147(11) 0.0084(10) 0.0088(11)
C37 0.0307(15) 0.0332(16) 0.0272(14) 0.0208(13) 0.0169(12) 0.0209(13)
C38 0.0400(19) 0.0377(19) 0.0459(19) 0.0308(16) 0.0240(16) 0.0184(15)
C39 0.0402(18) 0.054(2) 0.0288(16) 0.0265(16) 0.0148(14) 0.0314(17)
C33 0.0223(13) 0.0255(14) 0.0292(14) 0.0180(12) 0.0119(11) 0.0128(11)
C34 0.0189(12) 0.0223(14) 0.0244(13) 0.0109(11) 0.0087(10) 0.0087(11)
C40 0.0281(15) 0.0240(15) 0.0313(15) 0.0137(12) 0.0156(12) 0.0146(12)
C41 0.040(2) 0.0296(18) 0.051(2) 0.0045(16) 0.0094(17) 0.0154(16)
C42 0.0361(19) 0.049(2) 0.046(2) 0.0179(17) 0.0138(16) 0.0303(17)
C35 0.0218(13) 0.0231(14) 0.0212(13) 0.0116(11) 0.0093(10) 0.0074(11)
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C43 0.0264(14) 0.0254(14) 0.0210(13) 0.0151(11) 0.0101(11) 0.0117(12)
C44 0.0399(18) 0.0391(19) 0.0267(16) 0.0189(15) -0.0027(13) 0.0079(15)
C45 0.0352(17) 0.0320(17) 0.0305(15) 0.0220(14) 0.0178(13) 0.0145(14)
C51 0.0138(12) 0.0308(16) 0.0287(14) 0.0147(12) 0.0086(10) 0.0080(11)

C52 0.0182(13) 0.0303(15) 0.0274(14) 0.0155(12) 0.0089(11) 0.0102(12)
C53 0.0176(13) 0.0269(15) 0.0324(15) 0.0112(13) 0.0056(11) 0.0112(11)
C54 0.0177(13) 0.0269(15) 0.0421(17) 0.0181(14) 0.0088(12) 0.0092(12)
C57 0.0256(15) 0.0295(17) 0.055(2) 0.0238(16) 0.0104(15) 0.0124(13)
N1 0.0301(15) 0.0389(18) 0.070(2) 0.0325(17) 0.0075(15) 0.0070(13)
C55 0.0214(14) 0.0429(19) 0.0460(19) 0.0313(16) 0.0137(13) 0.0122(14)
C56 0.0219(14) 0.0431(19) 0.0324(16) 0.0220(15) 0.0075(12) 0.0116(13)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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Pd1 C51 2.015(3) . ?
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Pd1 C31 2.496(3) . ?
P1 C21 1.860(3) . ?
P1 C11 1.897(3) . ?
P1 C1 1.918(3) . ?
C1 C2 1.544(4) . ?
C1 C4 1.550(4) . ?
C1 C3 1.555(4) . ?
C2 C5 1.546(4) . ?
C2 H2A 0.9900 . ?
C2 H2B 0.9900 . ?
C3 C7 1.541(4) . ?
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C3 H3B 0.9900 . ?
C4 C9 1.547(4) . ?
C4 H4A 0.9900 . ?
C4 H4B 0.9900 . ?
C5 C10 1.526(4) . ?
C5 C6 1.533(4) . ?
C5 H5A 1.0000 . ?
C6 C7 1.521(4) . ?
C6 H6A 0.9900 . ?
C6 H6B 0.9900 . ?
C7 C8 1.531(4) . ?
C7 H7A 1.0000 . ?

C8 C9 1.539(5) . ?
C8 H8A 0.9900 . ?
C8 H8B 0.9900 . ?
C9 C10 1.534(5) . ?
C9 H9A 1.0000 . ?
C10 H10A 0.9900 . ?
C10 H10B 0.9900 . ?
C11 C12 1.535(4) . ?
C11 C13 1.544(4) . ?
C11 C14 1.554(4) . ?
C12 C15 1.546(4) . ?
C12 H12A 0.9900 . ?
C12 H12B 0.9900 . ?
C13 C17 1.548(4) . ?
C13 H13A 0.9900 . ?
C13 H13B 0.9900 . ?
C14 C19 1.546(5) . ?
C14 H14A 0.9900 . ?
C14 H14B 0.9900 . ?
C15 C20 1.524(5) . ?
C15 C16 1.528(5) . ?
C15 H15A 1.0000 . ?
C16 C17 1.528(5) . ?
C16 H16A 0.9900 . ?
C16 H16B 0.9900 . ?
C17 C18 1.509(6) . ?
C17 H17A 1.0000 . ?
C18 C19 1.511(6) . ?
C18 H18A 0.9900 . ?
C18 H18B 0.9900 . ?
C19 C20 1.530(5) . ?
C19 H19A 1.0000 . ?
C20 H20A 0.9900 . ?
C20 H20B 0.9900 . ?
C21 C26 1.406(4) . ?
C21 C22 1.416(4) . ?
C22 O1 1.360(3) . ?
C22 C23 1.386(4) . ?
O1 C27 1.426(3) . ?
C27 H27A 0.9800 . ?
C27 H27B 0.9800 . ?
C27 H27C 0.9800 . ?
C23 C24 1.383(4) . ?
C23 H23A 0.9500 . ?
C24 C25 1.376(4) . ?
C24 H24A 0.9500 . ?
C25 O2 1.381(3) . ?
C25 C26 1.415(4) . ?
O2 C28 1.425(4) . ?
C28 H28A 0.9800 . ?
C28 H28B 0.9800 . ?

C28 H28C 0.9800 . ?
C26 C31 1.506(4) . ?
C31 C36 1.430(4) . ?
C31 C32 1.434(4) . ?
C32 C33 1.385(4) . ?
C32 C37 1.524(4) . ?
C37 C38 1.525(5) . ?
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