Supporting Information
for
“Intermolecular Amidation of Unactivated sp^2 and sp^3 C–H Bonds
via Palladium Catalyzed Cascade C-H Activation / Nitrene
Insertion”

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General Experimental Section:

Oximes were prepared by reacting the analogous aldehydes or ketones with $\text{MeONH}_2 \cdot \text{HCl}$ in H_2O or MeOH for 2 h, followed by a 20% NaOH work-up then extraction with diethyl ether.¹ 2-Phenylbenzamide was prepared by reacting 2-biphenylcarboxylic acid with thionyl chloride and ammonia.² $\text{PhI}=\text{NSO}_2\text{Ar}$ were synthesized according to a literature method.³ 2-Arylpyridines, 8-methylquinoline, $\text{PhI}(\text{OAc})_2$ and $\text{Pd}(\text{OAc})_2$ were commercially available and used as received. Control reactions (without the Pd catalyst) were run in parallel for each substrate and generally showed no product formation under our standard conditions. Flash column chromatography was performed on silica gel (Merck Kiesegel 60 F₂₅₄ 230-400 mesh); the R_f value for each product on the silica gel TLC is about 0.20-0.35 with an appropriate solvent system (see detail below). ^1H and ^{13}C -NMR spectra were recorded on a Bruker DPX-400 spectrometer. Chemical shifts (δ , ppm) were determined with TMS as internal reference, carbon multiplicities were determined by DEPT-135 experiments. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Science, Beijing.

General Experimental Procedures and Characterizations:

$\text{Pd}(\text{OAc})_2$ -catalyzed Amidation of 2-Arylpyridines:

A mixture of 2-arylpyridines (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (0.015 mmol, 5 mol%), $\text{K}_2\text{S}_2\text{O}_8$ (1.5 mmol, 5 equiv.), MgO (0.6 mmol, 2 equiv.) and amide (0.36 mmol, 1.2 equiv.) combined in 1,2-dichloroethane (2 mL) was sealed in a 10 mL vial with a Teflon lined cap. The vial was heated at 80°C until complete consumption of the substrate (based on TLC monitoring). After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel, and the filtrate was concentrated under vacuum to afford an oily substance. The oil was dissolved in CH_2Cl_2 (2 mL) and was purified by flash column chromatography.

Methyl *N*-(2-pyridylphenyl)carbamate.⁴ 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (77% yield). ^1H -NMR (500MHz, CDCl_3): δ_H 11.52 (br s, 1H), 8.66 (dd, $J=4.0, 0.6$ Hz, 1H), 8.31 (d, $J=6.8$ Hz, 1H), 7.82 (dt, $J=6.6, 1.5$ Hz, 1H), 7.72 (d, $J=6.7$ Hz, 1H), 7.63 (dd, $J=6.5, 1.1$ Hz, 1H), 7.40 (dt, $J=6.7, 1.1$ Hz, 1H), 7.26 (dt, $J=5.7, 0.7$ Hz, 1H), 7.12 (dt, $J=6.6, 0.9$ Hz, 1H), 3.76 (s, 3H). ^{13}C -NMR (125MHz, CDCl_3): δ_C 158.3(C=O), 154.5(C), 149.7(C), 147.6(CH), 137.6(CH), 130.1(CH), 128.9(CH), 128.2(C), 122.9(CH), 122.6(CH), 121.8(CH), 120.4(CH), 52.0(CH_3). MS (EI): 228(M^+ , 64), 197(100), 168(34). HRMS (EI): Found M^+ 228.0893, $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ requires 228.0899. Anal Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.54; H, 5.39; N, 12.33.

***N*-(2-pyridylphenyl)-2,2,2-trifluoroacetamide.** 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (92% yield). ^1H -NMR (400MHz, CDCl_3): δ_H 14.40 (br s, 1H), 8.63 (d, $J=4.9$ Hz, 1H), 8.60 (d, $J=8.3$ Hz, 1H), 7.91-7.87 (m, 2H), 7.82 (dd, $J=7.9, 1.3$ Hz, 1H), 7.47 (dt, $J=7.8, 1.3$ Hz, 1H), 7.34-7.27 (m, 2H). ^{19}F -NMR (376.5 MHz,

CDCl₃): δ_F -76.14 (s, 3F). ¹³C-NMR (125MHz, CDCl₃): δ_C 157.2 (C), 155.1 (q, $J=37.0$ Hz, C=O), 147.1(CH), 138.2(CH), 136.0(C), 130.9(CH), 128.3(CH), 125.3(CH), 125.2(C), 122.0(CH), 120.0(CH), 115.1(CH), 116.2(q, $J=288.6$ Hz, CF₃). MS (EI): 266(M⁺, 16), 197(100). HRMS (EI): Found M⁺ 266.0669, C₁₃H₉N₂OF₃ requires 266.0667. Anal Calcd for C₁₃H₉N₂OF₃: C, 58.65; H, 3.41; N, 10.52. Found: C, 59.10; H, 3.52; N, 10.61.

N-(5-methyl-2-pyridylphenyl)-2,2,2-trifluoroacetamide. 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (97% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 14.51 (br s, 1H), 8.59 (dd, $J=3.1, 0.6$ Hz, 1H), 8.43 (s, 1H), 7.86-7.83 (m, 2H), 7.70 (d, $J=8.1$ Hz, 1H), 7.28 (dd, $J=7.3, 1.9$ Hz, 1H), 7.09 (dd, $J=8.1, 1.0$ Hz, 1H), 2.43 (s, 3H). ¹⁹F-NMR (376.5 MHz, CDCl₃): δ_F -76.13 (s, 3F). ¹³C-NMR (125MHz, CDCl₃): δ_C 157.2 (C), 155.1 (q, $J=37.1$ Hz, C=O), 146.9(CH), 141.1(C), 138.0(CH), 136.0(C), 128.1(CH), 126.1(CH), 122.4(CH), 122.3(C), 122.0(CH), 118.5(q, $J=288.9$ Hz, CF₃), 21.5(CH₃). MS (EI): 280(M⁺, 16), 211(100), 153(30), 136(31), 106(29). HRMS (EI): Found M⁺ 280.0827, C₁₄H₁₁N₂OF₃ requires 280.0823. Anal Calcd for C₁₄H₁₁N₂OF₃: C, 60.00; H, 3.96; N, 10.00. Found: C, 59.83; H, 3.96; N, 9.57.

Pd(OAc)₂-catalyzed Amidation of *O*-methyl oximes:

A mixture of *O*-methyl oxime (0.3 mmol), Pd(OAc)₂ (0.015mmol, 5 mol%) in 1,2-dichloroethane (2 mL) was sealed with a Teflon lined cap in a 10 mL vial. The mixture was heated at 80°C for 1 h, and K₂S₂O₈ (0.75 mmol, 2.5 equiv) and amide (0.36 mmol, 1.2 equiv) were added. After heating the reaction mixture for 5 h, a second batch of K₂S₂O₈ (0.75 mmol, 2.5 equiv) was added, and the mixture was stirred for overnight at 80°C. After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel, and the filtrate was concentrated under vacuum. The resulting crude oil was dissolved in CH₂Cl₂ (2 mL) and was purified by flash chromatography.

Methyl N-(2-benzaldehyde *O*-methyl oxime)carbamate (1a-A1). 70% *n*-Hexane/ 30% diethyl ether as eluant. The product was obtained as a yellow oil (92% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 10.13 (br s, 1H), 8.38 (d, $J=8.4$ Hz, 1H), 8.14 (s, 1H), 7.36 (t, $J=4.1$ Hz, 1H), 7.18 (dd, $J=7.7, 1.6$ Hz, 1H), 7.04 (dt, $J=7.5, 1.1$ Hz, 1H), 4.20 (s, 3H), 3.80 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 154.4(C=O), 151.3(CH), 138.2(C), 132.0(CH), 130.7(CH), 122.1(CH), 118.5(CH), 117.7(C), 62.5(CH₃), 52.2(CH₃). MS (EI): 208(M⁺, 92), 177(30), 145(100). HRMS (EI): Found M⁺ 208.0844, C₁₀H₁₂N₂O₃ requires 208.0848. Anal Calcd for C₁₀H₁₂N₂O₃: C, 57.68; H, 5.81; N, 13.45. Found: C, 57.67; H, 5.81; N, 12.52.

Methyl N-(2-acetophenone *O*-methyl oxime) carbamate (1b-A1). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (93% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 10.47 (br s, 1H), 8.29 (d, $J=8.3$ Hz, 1H), 7.42 (dd, $J=8.0, 1.5$ Hz, 1H), 7.33 (dt, $J=7.4, 1.4$ Hz, 1H), 7.05 (dt, $J=7.7, 1.3$ Hz, 1H), 4.04 (s, 3H), 3.77 (s, 3H), 2.28 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 156.4(C=O), 154.5(C), 137.1(C), 129.7(CH), 128.3(CH), 122.4(CH), 122.2(C), 119.7(CH), 62.3(CH₃), 52.1(CH₃), 13.7(CH₃). MS (EI): 222(M⁺,

100), 191(65), 176(40), 159(28), 131(25). HRMS (EI): Found M^+ 222.1001, $C_{11}H_{14}N_2O_3$ requires 222.0901. Anal Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.61. Found: C, 59.62; H, 6.09; N, 12.98.

***N*-(2-acetophenone *O*-methyl oxime)-2,2,2-trifluoroacetamide (1b-A2).** 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (95% yield). 1H -NMR (600MHz, $CDCl_3$): δ_H 12.46 (br s, 1H), 8.58 (d, $J=8.3$ Hz, 1H), 7.55 (dd, $J=8.0, 1.2$ Hz, 1H), 7.41 (dt, $J=7.9, 1.2$ Hz, 1H), 7.24 (dt, $J=7.7, 0.9$ Hz, 1H), 4.03 (s, 3H), 2.33 (s, 3H). ^{19}F -NMR (376.5 MHz, $CDCl_3$): δ_F -76.03 (s, 3F). ^{13}C -NMR (150MHz, $CDCl_3$): δ_C 156.7(C=N), 155.1(q, $J=37.1$ Hz, C=O), 134.9(C), 130.2(CH), 129.9(CH), 125.1(CH), 123.1(C), 121.3(CH), 116.1(q, $J=288.8$ Hz, CF_3), 62.3(CH_3), 13.2(CH_3). MS (EI): 260(M^+ , 100), 229(27), 214(50), 202(13). HRMS (EI): Found M^+ 260.0772, $C_{11}H_{11}N_2O_3F_3$ requires 260.0773.

***tert*-Butyl *N*-(2-acetophenone *O*-methyl oxime)carbamate (1b-A3).** 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a orange oil (90% yield). 1H -NMR (300MHz, $CDCl_3$): δ_H 10.31 (br s, 1H), 8.26 (d, $J=8.4$ Hz, 1H), 7.40 (d, $J=8.0$ Hz, 1H), 7.31 (t, $J=7.3$ Hz, 1H), 7.04 (t, $J=7.7$ Hz, 1H), 4.02 (s, 3H), 2.22 (s, 3H), 1.52 (s, 9H). ^{13}C -NMR (125MHz, $CDCl_3$): δ_C 156.7(C=O), 153.6(C), 138.5(C), 130.2(C), 130.0(CH), 128.7(CH), 122.1(CH), 120.0(CH), 62.6(CH_3), 28.7(tBu), 14.1(CH_3). MS (EI): 264(M^+ , 42), 208(75), 164(59), 133(100). HRMS (EI): Found M^+ 264.1474, $C_{14}H_{20}N_2O_3$ requires 264.1474. Anal Calcd for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.91; H, 8.12; N, 9.13.

***N*-(2-acetophenone *O*-methyl oxime)methanesulfonamide (1b-A4).** 75% *n*-Hexane/ 25% ethyl acetate as eluant. The product was obtained as a yellow solid (77% yield). 1H -NMR (500MHz, $CDCl_3$): δ_H 10.77 (br s, 1H), 7.69 (d, $J=7.3$ Hz, 1H), 7.51 (dd, $J=8.0, 1.4$ Hz, 1H), 7.36 (t, $J=7.9$ Hz, 1H), 7.16 (t, $J=7.8$ Hz, 1H), 4.05 (s, 3H), 3.00 (s, 3H), 2.31 (s, 3H). ^{13}C -NMR (125MHz, $CDCl_3$): δ_C 156.8(C=N), 136.9(C), 130.5(CH), 129.7(C), 124.0(CH), 120.0(CH), 62.3(CH_3), 39.9(CH_3), 21.2(CH_3). MS (EI): 242(M^+ , 63), 211(4). HRMS (EI): Found M^+ 242.0725, $C_{10}H_{14}SN_2O_3$ requires 242.0728. Anal Calcd for $C_{10}H_{14}SN_2O_3$: C, 49.57; H, 5.82; N, 11.56. Found: C, 50.10; H, 5.86; N, 10.24.

4-Chloro-*N*-(2-acetophenone *O*-methyl oxime)benzenesulfonamide (1b-A5). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a yellow solid (89% yield). 1H -NMR (500MHz, $CDCl_3$): δ_H 10.85 (br s, 1H), 7.91 (dd, $J=22.8, 86$ Hz, 1H), 7.63 (d, $J=8.5$ Hz, 2H), 7.55 (d, $J=7.4$ Hz, 1H), 7.37 (d, $J=8.5$ Hz, 2H), 7.35 (t, $J=6.7$ Hz, 1H), 7.12 (t, $J=7.5$ Hz, 1H), 4.05 (s, 3H), 1.19 (s, 3H). ^{13}C -NMR (125MHz, $CDCl_3$): δ_C 156.0(C=N), 139.2(C), 137.9(C), 135.4(C), 129.8(CH), 127.3(C), 129.6(CH), 129.5(CH), 129.3(CH), 124.5(CH), 122.0(CH), 62.7(CH_3), 13.1(CH_3). MS (EI): 338(M^+ , 3), 254(4), 206(26), 175(79), 111(100). HRMS (EI): Found M^+ 338.0489, $C_{15}H_{15}ClSN_2O_3$ requires 338.0492.

***N*-(2-acetophenone *O*-methyl oxime)-3-phenyl-2-propenamide (1b-A6).** 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (63% conversion and 68% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 11.38 (br s, 1H), 8.71 (d, *J*=8.0Hz, 1H), 7.73 (d, *J*=15.7Hz, 1H), 7.55-7.53 (m, 2H), 7.49 (dd, *J*=8.0, 1.4Hz, 1H), 7.39 (m, 4H), 7.15 (t, *J*=1.25Hz, 1H), 6.52 (d, *J*=15.7Hz, 1H), 4.12 (s, 3H), 2.34 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 164.3(C=O), 157.2(C=N), 141.3(CH), 137.2(C), 134.8(C), 129.9 (CH), 129.8(CH), 128.9(CH), 128.4(CH), 127.8(CH), 123.2(CH), 122.5(CH), 122.4(CH), 121.3(C), 62.4(CH₃), 13.8(CH₃). MS (EI): 294(M⁺, 17), 191(65), 263(31), 248(42), 164(19), 131(100), 103(40). HRMS (EI): Found M⁺ 294.1361, C₁₈H₁₈N₂O₂ requires 294.1368. Anal Calcd for C₁₈H₁₈N₂O₂: C, 73.45; H, 6.16; N, 9.52. Found: C, 72.89; H, 6.25; N, 9.49.

Methyl *N*-(5-iodo-2-acetophenone *O*-methyl oxime)carbamate (1c-A1). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (87% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 10.60 (br s, 1H), 8.73 (d, *J*=1.6Hz, 1H), 7.39 (dd, *J*=8.4, 1.8Hz, 1H), 7.11 (d, *J*=8.4Hz, 1H), 4.04 (s, 3H), 3.77 (s, 3H), 2.25 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 156.0(C=O), 154.2(C=N), 138.1(C), 135.8(C), 131.2(CH), 129.6(C), 128.2(CH), 121.4(CH), 62.5(CH₃), 52.3(CH₃), 13.5(CH₃). MS (EI): 348(M⁺, 2), 278(6), 196(15), 147(100), 121(24), 106(14). HRMS (EI): Found M⁺ 347.9962, C₁₁H₁₃IN₂O₃ requires 347.9971. Anal Calcd for C₁₁H₁₃IN₂O₃: C, 37.95; H, 3.76; N, 8.05. Found: C, 37.85; H, 3.77; N, 7.35.

Methyl *N*-(5-methyl-2-benzaldehyde *O*-methyl oxime)carbamate (1d-A1). 75% *n*-Hexane/ 25% diethyl ether as eluant. The product was obtained as a yellow oil (95% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 10.13 (br s, 1H), 8.38 (d, *J*=8.4Hz, 1H), 8.14 (s, 1H), 7.36 (t, *J*=4.1Hz, 1H), 7.18 (dd, *J*=7.7, 1.6Hz, 1H), 7.04 (dt, *J*=7.5, 1.1Hz, 1H), 4.20 (s, 3H), 3.80 (s, 3H). ¹³C-NMR (75MHz, CDCl₃): δ_C 154.8(C=O), 151.6(CH), 141.8(C), 138.4(C), 132.3(CH), 123.4(CH), 119.4(CH), 115.7(C), 62.7(CH₃), 52.6(CH₃), 22.2(CH₃). MS (EI): 222(M⁺, 65), 191(23), 159(100), 131(15). HRMS (EI): Found M⁺ 222.1002, C₁₁H₁₄N₂O₃ requires 222.1004. Anal Calcd for C₁₁H₁₄N₂O₃: C, 59.45; H, 6.35; N, 12.61. Found: C, 59.43; H, 6.42; N, 11.88.

***N*-(5-methoxy-2-benzaldehyde *O*-methyl oxime)-2,2,2-trifluoroacetamide (1e-A2).** 85% *n*-Hexane/ 15% ethyl acetate as eluant. The product was obtained as a white solid (96% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 12.07 (br s, 1H), 8.27 (d, *J*=2.6Hz, 1H), 8.10 (s, 1H), 7.18 (d, *J*=8.6Hz, 1H), 6.768 (dd, *J*=8.6, 2.6Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H). ¹⁹F-NMR (376.5 MHz, CDCl₃): δ_F -75.88 (s, 3F). ¹³C-NMR (125MHz, CDCl₃): δ_C 161.5(CH), 155.5(q, *J*=37.5Hz, C=O), 150.4(CH), 137.1(C), 133.2(CH), 115.9(q, *J*=289.0Hz, CF₃), 112.3(C), 111.5(CH), 111.4(C), 105.9(CH), 62.4(CH₃), 55.6(CH₃). MS (EI): 276(M⁺, 100), 230(70), 207(57), 176(48), 148(41), 136, (25), 106(21). HRMS (EI): Found M⁺

276.0720, C₁₁H₁₁N₂O₃F₃ requires 276.0722. Anal Calcd for C₁₁H₁₁N₂O₃F₃: C, 47.83; H, 4.01; N, 10.14. Found: C, 49.34; H, 4.34; N, 9.71.

Methyl N-(3-chloro-2-benzaldehyde O-methyl oxime)carbamate (1f-A1). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (88% yield). ¹H-NMR (400MHz, CDCl₃): δ_H 10.46 (br s, 1H), 8.76 (s, 1H), 8.33 (d, *J*=8.5Hz, 1H), 7.26 (t, *J*=7.7Hz, 1H), 7.08 (dd, *J*=8.0, 1.0Hz, 1H), 4.05 (s, 3H), 3.79 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 154.3(C=O), 148.3(CH), 139.9(C), 135.4(C), 131.1(CH), 123.5(CH), 117.3(CH), 115.2(C), 62.7(CH₃), 52.4(CH₃). MS (EI): 242(M⁺, 56), 211(24), 196(23), 179(100). HRMS (EI): Found M⁺ 242.0456, C₁₀H₁₁ClN₂O₃ requires 242.0428. Anal Calcd for C₁₀H₁₁ClN₂O₃: C, 49.50; H, 4.57; Cl, 14.61; N, 11.54. Found: C, 49.62; H, 4.63; Cl, 14.68; N, 11.50.

Methyl N-(4-bromo-2-benzaldehyde O-methyl oxime) carbamate (1g-A1). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (72% yield). ¹H-NMR (300MHz, CDCl₃): δ_H 10.10 (br s, 1H), 8.31 (d, *J*=8.9Hz, 1H), 8.05 (s, 1H), 7.45 (dd, *J*=9.0, 2.3Hz, 1H), 7.31 (d, *J*=2.3Hz, 1H), 4.03 (s, 3H), 3.79 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 154.2(C=O), 150.0(CH), 137.2(C), 134.1(CH), 133.3(CH), 120.2(CH), 119.5(C), 114.2(C), 62.7(CH₃), 52.4(CH₃). MS (EI): 286(M⁺, 75), 257(25), 225(100), 153(28), 136(21). HRMS (EI): Found M⁺ 285.9951, C₁₀H₁₁BrN₂O₃ requires 285.9953. Anal Calcd for C₁₀H₁₁BrN₂O₃: C, 41.83; H, 3.86; N, 9.76. Found: C, 41.85; H, 3.57; N, 9.41.

N-(4,5-dimethoxy-2-benzaldehyde O-methyl oxime)-2,2,2-trifluoroacetamide (1h-A2). 70% *n*-Hexane/ 30% diethyl ether as eluant. The product was obtained as a white solid (66% conversion and 94% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 11.88 (br s, 1H), 8.46(s, 1H), 8.25 (s, 1H), 6.53 (s, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 3.76 (s, 3H). ¹⁹F-NMR (376.5 MHz, CDCl₃): δ_F -75.97 (s, 3F). ¹³C-NMR (125MHz, CDCl₃): δ_C 155.3(q, *J*=37.1Hz, C=O), 150.3(CH), 145.9(C), 130.2(C), 125.1(C), 115.9(q, *J*=288.9Hz, CF₃), 113.9(CH), 111.7(C), 104.5(CH), 62.4(CH₃), 56.2(CH₃), 56.0(CH₃). MS (EI): 306(M⁺, 11), 211(100), 180(87), 164(29). HRMS (EI): Found M⁺ 306.0821, C₁₂H₁₃N₂O₄F₃ requires 306.0827. Anal Calcd for C₁₂H₁₃N₂O₄F₃: C, 47.06; H, 4.28; N, 9.15. Found: C, 46.93; H, 4.57; N, 9.15.

Methyl N-(2-tetralone O-methyl oxime)carbamate (1i-A1). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a white solid (74% yield). ¹H-NMR (600MHz, CDCl₃): δ_H 11.14 (br s, 1H), 8.20 (d, *J*=8.4Hz, 1H), 7.22 (t, *J*=7.9Hz, 1H), 6.82(d, *J*=7.4Hz, 1H), 4.03 (s, 3H), 3.77 (s, 3H), 2.79 (t, *J*=6.7Hz, 3H), 2.73 (t, *J*=6.1Hz, 3H), 1.79 (q, *J*=6.4Hz, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 157.6(C=O), 154.6(C=N), 141.4(C), 138.3(C), 129.5(CH), 122.6(CH), 117.4(CH), 116.7(C), 62.4(CH₃), 52.1(CH₃), 31.1(CH₂), 25.4(CH₂), 20.9(CH₂). MS (EI): 248(M⁺, 100), 202(92), 186(13), 153(44), 136(42), 106(32), 89(56). HRMS (EI): Found M⁺ 248.1157, C₁₃H₁₆N₂O₃ requires

248.1161. Anal Calcd for $C_{13}H_{16}N_2O_3$: C, 62.89; H, 6.50; N, 11.28. Found: C, 62.14; H, 6.29; N, 10.53.

4-Chloro-*N*-(2-methylcyclohexanone *O*-methyl oxime) benzenesulfonamide (2a-A5). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a yellow oil

(88% yield, two isomers were obtained in a ratio of 3 : 1). *Major isomer*: 1H -NMR (300MHz, $CDCl_3$): δ_H 7.87 (d, $J=8.6$ Hz, 2H), 7.54 (d, $J=8.6$ Hz, 2H), 5.13 (br s, 1H), 4.43 (dd, $J=10.0$, 4.8Hz, 1H), 4.03 (t, $J=9.6$ Hz, 1H), 3.73 (s, 3H), 3.03-2.98 (m, 1H), 2.53-2.47 (m, 1H), 2.11 – 2.07 (m, 1H), 1.78-1.71 (m, 2H), 1.46-1.38(m, 2H), 1.29-1.21 (m, 2H). *Minor isomer*: 1H -NMR (300MHz, $CDCl_3$): δ_H 7.86 (d, $J=8.5$ Hz, 2H), 7.55 (d, $J=8.5$ Hz, 2H), 5.32 (br s, 1H), 4.64 (dd, $J=7.5$, 3.8Hz, 1H), 4.24 (t, $J=6.2$ Hz, 1H), 3.79 (s, 3H), 3.12 (m, 1H), 2.17 (m, 1H), 2.11 – 2.08 (m, 1H), 1.84-1.76 (m, 2H), 1.47-1.378(m, 2H), 1.25 (m, 2H). ^{13}C -NMR (75MHz, $CDCl_3$): δ_C 158.3(C=N), 140.7(C), 135.1(C), 129.9(CH), 129.8(CH), 71.7(CH₂), 61.7(CH₃), 41.8(CH), 30.7(CH₂), 26.0(CH₂), 24.9(CH₂), 24.7(CH₂). MS (EI): 330 (M^+ , 22), 175(54), 156(66), 139(66), 111(100). HRMS (EI): Found M^+ 330.0805, $C_{14}H_{19}SClN_2O_3$ requires 330.0809. Anal Calcd for $C_{14}H_{19}SClN_2O_3$: C, 50.83; H, 5.79; Cl, 10.72; N, 8.47. Found: C, 50.49; H, 5.92; Cl, 11.01; N, 7.88.

***N*-(2,2-dimethylcyclohexanone *O*-methyl oxime)-2,2,2-trifluoroacetamide (2b-A2).** 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a yellow oil (89% yield). 1H -NMR

(500MHz, $CDCl_3$): δ_H 6.57 (br s, 1H), 4.41 (dd, $J=16.6$, 10.9Hz, 2H), 3.77 (s, 3H), 2.94-2.90 (m, 1H), 2.08-2.06 (m, 1H), 1.66-1.57 (m, 5H), 1.43 (m, 1H), 1.21 (s, 3H). ^{19}F -NMR (376.5 MHz, $CDCl_3$): δ_F -75.08 (s, 3F). ^{13}C -NMR (125MHz, $CDCl_3$): δ_C 160.2(C=N), 157.4(q, $J=41.9$ Hz, C=O), 114.7(q, $J=41.9$ Hz, C=O), 114.7(q, $J=224$ Hz, CF₃), 73.3(CH₂), 61.4(CH₃), 40.5(CH), 35.5(CH₂), 25.4(CH₂), 21.4(CH), 21.1(CH₂), 20.0(CH₂). MS (EI): 266(M^+ , 18), 154(100), 140(61), 136(34), 120(17). HRMS (EI): Found M^+ 266.1244, $C_{11}H_{17}N_2O_2F_3$ requires 266.1242.

4-Chloro-*N*-(DL-camphor *O*-methyl oxime)benzenesulfonamide (2c-A5). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a yellow oil (93% yield).

1H -NMR (500MHz, $CDCl_3$): δ_H 7.90 (d, $J=8.3$ Hz, 2H), 7.54 (d, $J=8.3$ Hz, 2H), 5.22 (br s, 1H), 4.25 (dd, $J=30.2$, 7.8Hz, 2H), 3.73 (s, 3H), 2.48-2.43 (m, 1H), 2.05-1.84 (m, 4H), 1.40-1.39 (m, 1H), 1.25 (m, 1H), 1.02 (s, 3H), 0.84 (s, 3H). ^{13}C -NMR (125MHz, $CDCl_3$): δ_C 165.5(C=N), 140.7(C), 134.9(C), 129.9(CH), 129.8(CH), 69.0(CH₂), 61.8(CH), 54.2(C), 49.0(C), 45.0(CH), 33.6(CH₂), 28.3(CH₂), 27.1(CH₂), 20.3(CH₃), 20.2(CH₃). MS (EI): 370(M^+ , 1), 290(8), 179(100), 147(35), 136(46), 107(36). HRMS (EI): Found M^+ 370.1120, $C_{17}H_{23}SClN_2O_3$ requires 370.1118. Anal Calcd for $C_{17}H_{23}SClN_2O_3$: C, 55.05; H, 6.25; Cl, 9.56; N, 7.55. Found: C, 55.11; H, 6.22; Cl, 9.55; N, 7.49.

4-Chloro-*N*-(3-heptanone *O*-methyl oxime)benzene sulfonamide (2d-A5). 80% *n*-Hexane/ 20% diethyl ether as eluant. The product was obtained as a yellow oil (68% conversion and 76% yield, two isomers were obtained in a ratio of 1.3 : 1). *Major isomer*: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ_{H} 7.87 (d, $J=8.6\text{Hz}$, 2H), 7.55 (d, $J=8.6\text{Hz}$, 2H), 5.13 (br s, 1H), 4.29 (t, $J=7.1\text{Hz}$, 1H), 3.79 (s, 3H), 2.55 (t, $J=7.1\text{Hz}$, 2H), 2.23 (t, $J=8.1\text{Hz}$, 2H), 1.44 – 1.26 (m, 6H), 0.90 (t, $J=7.1\text{Hz}$, 3H). *Minor isomer*: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ_{H} 7.87 (d, $J=8.6\text{Hz}$, 2H), 7.56 (d, $J=8.6\text{Hz}$, 2H), 5.19 (br s, 1H), 4.28 (t, $J=7.1\text{Hz}$, 2H), 3.74 (s, 3H), 2.54 (t, $J=7.1\text{Hz}$, 2H), 2.30 (t, $J=7.8\text{Hz}$, 2H), 1.44 – 1.26 (m, 6H), 0.89 (t, $J=7.1\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ_{C} 162.9(C=N), 140.9(C), 134.7(C), 128.3(CH), 129.8(CH), 70.7(CH_2), 61.4(CH_3), 33.9(CH_2), 27.8(CH_2), 23.4(CH_2), 21.5(CH_2), 11.6(CH_3). MS (EI): 332(M^+ , 7), 291(40), 175(89), 141(23), 112(77), 111(100). HRMS (EI): Found M^+ 332.0962, $\text{C}_{14}\text{H}_{21}\text{SClN}_2\text{O}_3$ requires 332.0961.

8-Chloromethylquinoline (2e-Cl).⁵ 80% *n*-Hexane/ 20% ethyl acetate. The product was obtained as a yellow solid (85% yield). $^1\text{H-NMR}$ (400MHz, CDCl_3): δ_{H} 9.00 (dd, $J=4.2$, 1.7Hz, 1H), 8.19 (dd, $J=8.3$, 1.7Hz, 1H), 7.87 (d, $J=7.0\text{Hz}$, 1H), 7.82 (dd, $J=8.3$, 1.0Hz, 1H), 7.56 (t, $J=7.3\text{Hz}$, 1H), 7.46 (dd, $J=8.3$, 4.2Hz, 1H), 5.36 (s, 2H). $^{13}\text{C-NMR}$ (125MHz, CDCl_3): δ_{C} 149.5(CH), 147.0(C), 136.0(CH), 135.2(C), 129.7(CH), 127.8(C), 126.9(CH), 125.8(CH), 120.1(CH), 46.1(CH_2). MS (EI): 177(M^+ , 65), 142(100), 115(11). HRMS (EI): Found M^+ 177.0341, $\text{C}_{10}\text{H}_8\text{NCl}$ requires 177.0345.

***N,N*-di-(4-chlorobenzenesulfonyl)-8-quinolinemethanamide (2e-A5).** A mixture of **2e** (0.3 mmol, 1 equiv) and $\text{Pd}(\text{OAc})_2$ (0.015 mmol, 5 mol%) in dry CH_2Cl_2 (2 mL) was stirred under a nitrogen atmosphere for 1 h; $[\text{Ru}(\text{TTP})(\text{CO})]$ (0.003 mmol, 1 mol%) and $\text{PhI}=\text{NSO}_2(p\text{-Cl-C}_6\text{H}_4)$ (0.9 mmol, 3 equiv) were added in one portion and the resulting mixture was stirred at room temperature for 10 h. Afterwards, the reaction mixture was filtered through a plug of silica gel then the filtrate was concentrated under vacuum. The resulting crude oil was dissolved in CH_2Cl_2 (2 mL) and was purified by flash chromatography (80% *n*-Hexane/ 20% ethyl acetate). The product was obtained as a white solid (79% yield). $^1\text{H-NMR}$ (500MHz, CDCl_3): δ_{H} 8.91 (dd, $J=4.16$, 1.7Hz, 1H), 8.14 (d, $J=1.7\text{Hz}$, 1H), 7.81 (d, $J=9.4\text{Hz}$, 4H), 7.71 (d, $J=7.9\text{Hz}$, 1H), 7.52 (d, $J=8.7\text{Hz}$, 1H), 7.44 (dd, $J=8.3$, 4.2Hz, 1H), 7.40 (d, $J=11.2\text{Hz}$, 4H), 7.32 (t, $J=7.8\text{Hz}$, 1H), 5.81 (s, 2H). $^{13}\text{C-NMR}$ (125MHz, CDCl_3): δ_{C} 149.7 (CH), 145.7(C), 140.6(C), 138.1(C), 136.2(CH), 132.5(C), 129.8(CH), 129.1(CH), 128.4(CH), 128.0(C), 127.7(CH), 125.9(CH), 121.4(CH), 49.1(CH_2). MS (EI): 506(M^+ , 2), 331(100), 155(35). HRMS (EI): Found M^+ 505.9921, $\text{C}_{22}\text{H}_{16}\text{N}_2\text{S}_2\text{Cl}_2\text{O}_4$ requires 505.9928. Anal Calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{S}_2\text{Cl}_2\text{O}_4$: C, 52.08; H, 3.18; Cl, 13.97; N, 5.52. Found: C, 52.12; H, 3.66; Cl, 14.07; N, 5.10.

Experimental for Probing the Nitrene Intermediate

Rearrangement of Benzamide to Methyl *N*-(2-methoxyphenyl)carbamate

Benzamide (0.36 mmol, 1.2 equiv.) was treated with 2-phenylpyridine (0.3 mmol), Pd(OAc)₂ (0.015 mmol, 5 mol%), K₂S₂O₈ (1.5 mmol, 5 equiv.) and methanol (0.9 mmol, 3 equiv.) in 1,2-dichloroethane (2 mL). The mixture was sealed in a 10 mL vial with a Teflon-lined cap and was heated at 80°C for 16 h. After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel, and the filtrate was concentrated under vacuum to give an oily substance. The oily substance was dissolved in CH₂Cl₂ and was purified by column chromatography using silica gel, and methyl *N*-(2-methoxyphenyl)carbamate was isolated in 55% yield.

Methyl *N*-(2-methoxyphenyl)carbamate.⁶ 70% *n*-Hexane/ 30% ethyl acetate as eluant. The product was obtained as a yellow oil (55% yield). ¹H-NMR (300MHz, CDCl₃): δ_H 8.22 (dd, *J*=7.8, 1.8Hz, 1H), 7.71 (br s, 1H), 7.09 (t, *J*=7.5Hz, 1H), 7.00 (d, *J*=8.3Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H). ¹³C-NMR (125MHz, CDCl₃): δ_C 154.8(C=O), 153.9(C), 125.1(CH), 123.8(C), 121.4(CH), 121.0(CH), 114.3(CH), 56.0(CH₃), 47.8(CH₃). MS (EI): 181(M⁺, 19), 164(100), 150(26), 135(28), 105(19), 77(17). HRMS (EI): Found M⁺ 181.0740, C₉H₁₁NO₃ requires 181.0739

To account for the carbamate formation, nitrene may have been formed by oxidation of the benzamide. The nitrene intermediate then underwent Curtius rearrangement to ketene. Nucleophilic attack of the ketene by methanol gave methyl *N*-phenylcarbamate, subsequent C-H activation / *ortho*-methoxylation should afford the product (Scheme S1).

Scheme S1

Intramolecular Nitrene Insertion Into Aromatic C-H bond

2-Phenylbenzamide (0.36 mmol, 1.2 equiv.) was treated with 2-phenylpyridine (0.3 mmol), Pd(OAc)₂ (0.015 mmol, 5 mol%), K₂S₂O₈ (1.5 mmol, 5 equiv.) in 1,2-dichloroethane (2 mL). The mixture was sealed in a 10 mL vial with a Teflon lined cap and was heated at 80°C for 16 h. After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel, and the filtrate was concentrated under vacuum. The resulting crude oil was dissolved in CH₂Cl₂ and was purified by flash chromatography to obtain 6(5*H*)-Phenanthridinone in 60% yield without any amidation product of 2-phenylpyridine being formed.

6(5H)-Phenanthridinone.⁷ 80% *n*-Hexane/ 20% ethyl acetate as eluant. The product was obtained as a white solid (60% yield). ¹H NMR (300MHz, CDCl₃): δ_H 9.46 (br s, 1H), 7.75–7.08 (m, 8H). ¹³C NMR (125MHz, CDCl₃): δ_C 169.5(C=O), 138.2(C), 132.3(C), 132.1(C), 130.2(CH), 129.8(C), 128.9(CH), 128.7(CH), 128.5(CH), 128.2(CH), 127.4(CH), 124.5(CH), 120.1(CH). MS (EI): 195(M⁺, 14), 122(70), 106(100). HRMS (EI): Found M⁺ 195.0682, C₁₃H₉NO requires 195.0684.

This result is rationalized by nitrene formation from oxidation of 2-phenylbenzamide, followed by intramolecular nitrene C-H bond insertion (Scheme S2).

Nitrene Transfer to Cyclopalladated Complex 3

Di- μ -acetatobis[phenylpyridine-2C,N]dipalladium(II) (3).⁸ Under nitrogen, 2-phenylpyridine and Pd(OAc)₂ were combined in 10 mL MeOH and stirred at room temperature for 20 h. The resulting yellow complex was filtered and washed with diethyl ether to obtain the product. The product was obtained as a yellow solid (83% yield). ¹H-NMR (400MHz, CDCl₃): δ_H 7.88 (d, *J*=5.4Hz, 2H), 7.37 (t, *J*=6.0Hz, 2H), 7.09 (d, *J*=8.0Hz, 2H), 7.08-6.81 (m, 6H), 6.46 (t, *J*=5.8Hz, 2H), 2.27 (s, 6H). MS (FAB): 640(M⁺), 581[(M-OAc)⁺].

Cyclopalladated complex **3** (0.1 mmol) and PhI=NSO₂(*p*-Cl-C₆H₄) (1 mmol, 10 equiv.) or PhI=NSO₂(*p*-Cl-C₆H₄) (0.3 mmol, 3 equiv.) and [Ru(TTP)(CO)] (0.001 mmol, 1 mol%) were combined in dichloromethane (5 mL) under N₂. After stirring at room temperature for 16 h, the reaction mixture was filtered through a plug of silica ge and the filtrate was concentrated under vacuum. The “**3** + [NSO₂(*p*-Cl-C₆H₄)]” adduct was precipitated upon addition of methanol as a yellow powder (Scheme S3).

Acidolysis of “3 + [NSO₂(*p*-Cl-C₆H₄)]” Complex

The adduct was dissolved in 1,2-dichloroethane and treated with concentrated HCl. The combined mixture was stirred at 80°C for 5 h. After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel and the filtrate was concentrated under vacuum. The resulting crude oil was dissolved in CH₂Cl₂ and was purified by flash chromatography to obtain 4-chloro-*N*-(2-pyridylphenyl) benzenesulfonamide in 85% yield (based on the amount of complex **3** employed).

4-Chloro-*N*-(2-pyridylphenyl)benzenesulfonamide. 70% *n*-Hexane/ 30% ethyl acetate as eluant. The product was obtained as a white solid (85% yield). ¹H-NMR (500MHz, CDCl₃): δ_H 12.10 (br s, 1H), 8.60 (dd, *J*=4.9, 0.9Hz, 1H), 7.71-7.69(m, 2H), 7.53 (d, *J*=1.5Hz, 1H), 7.40-7.38(m, 4H), 7.35 (d, *J*=8.7Hz, 1H), 7.21 (d, *J*=1.1Hz, 1H), 7.11(d, *J*=8.7Hz, 2H). ¹³C-NMR (125MHz, CDCl₃): δ_C 156.9(C), 147.4(C), 138.7(C), 137.6(CH), 136.3(C), 130.3(CH), 128.7(CH), 128.6(CH), 128.4(CH), 128.1(CH), 128.0(C), 125.3(CH), 124.2(CH), 122.4(CH), 122.2(CH). MS (EI): 344(M⁺, 34), 169(100), 149(37), 136(29), 106(27). HRMS (EI): Found M⁺ 344.0386, C₁₇H₁₃SClN₂O₂ requires 344.0386.

Figure S1. Positive-ion electrospray mass spectrum of “**3** + [NSO₂(*p*-Cl-C₆H₄)]” complex in dichloromethane.

Screening Studies For The Intermolecular Amidation Reaction:

Table S1. Screening for effective catalysts

entry	catalysts	%conversion	%yield (a + b) ^a	selectivity (a : b) ^b
1	Pd(OAc) ₂	55	89	1 : 2
2	Pd(PPh ₃) ₄	22	65	b only
3	Pd(dba) ₂ ·CHCl ₃	16	70	b only
4	Pd(OCOCF ₃) ₂	100	- ^c	-
5	Ru ₃ (CO) ₁₂	< 10	not determined	1 : 1
6	PdCl ₂ (PhCN) ₂	0	0	-
7	Pd(bipy)(OAc) ₂	0	0	-
8	Rh(PPh ₃) ₃ Cl	0	0	-
9	[Rh(TTP)Me]	0	0	-
10	[Ru(TTP)CO]	0	0	-

^aIsolated yields based on conversion. ^bDetermined by ¹H-NMR of the crude reaction mixture. ^cOnly decomposition products were observed.

Table S2. Solvent effect

entry	solvent	conversion (%)	total yield (%)	selectivity (a : b)
1	Toluene	55	89	1 : 2
2	Benzene	51	84	1 : 2.3
3	1,2-Dichloroethane	72	88	1 : 5.5
4	Dichloromethane	70	85	1 : 7
5	Acetic acid	88	90	>1 : 99
6	Acetonitrile	67	92	>1 : 99
7	Trifluoroacetic acid	0	0	-

Table S3. Effect of PhI(OAc)₂ and H₂NCO₂CH₃ loading

entry	PhI(OAc) ₂ (equiv.)	solvent	H ₂ NCO ₂ CH ₃ (equiv.)	conversion (%)	total yield (%)	selectivity (a : b)
1	2	-	as solvent	54	93	1.7 : 1
2	2.5	Toluene	20	30	86	1 : 1.4
3	1.2	Toluene	5	22	88	1 : 2.4
4	2.5	Toluene	10	52	82	1 : 2
5	1.2	DCE	5	53	90	1 : 5.7

Table S4. Effect of inorganic bases

entry	solvent	additive (equiv.)	conversion (%)	total yield (%)	selectivity (a : b)
1	Toluene	Al ₂ O ₃ (2.5)	59	89	1 : 2.2
2	Toluene	MgO (2.5)	70	77	1 : 2.1
3	Toluene	K ₂ CO ₃ (2.5)	13	91	1 : 2
4	Toluene	NaOH (2.5)	0	0	-

Table S5. Effect of oxidants

entry	substrate	oxidant (equiv.)	amide (equiv.)	additive (equiv.)	T°C	Time (h)	Conversion (%)	Yield (%) ^a
1	2	K ₂ S ₂ O ₈ (5)	A2 (1.2)	2 MgO	80	7	>99	97
2	1	K ₂ S ₂ O ₈ (5)	A2 (1.2)	2 MgO	80	7	>99	92
3	1	K ₂ S ₂ O ₈ (5)	A1 (1.2)	2 MgO	80	12	>99	77
4	1	K ₂ S ₂ O ₈ (5)	A1 (1.2)	-	80	16	>99	63
5	1	K ₂ S ₂ O ₈ (2)	A1 (5)	-	100	20	>99	51
6	1	PhINTs	-	-	100	20	12	41
7	1	HTIB (2)	A1 (5)	-	100	20	55	30
8	1	IBX (2)	A1 (5)	-	100	20	57	11
9	1	PhI=O (2)	A2 (5)	-	100	20	0	0
10	1	Oxone	A1 (5)	-	100	24	0	0
11	1	TBHP	A1 (5)	-	100	24	0	0
12	1	O ₂ (1 atm)	A1 (5)	-	100	24	0	0
13	1	O ₂ (1 atm)	A1 (5)	CuCl ₂ (5 mol%)	100	24	0	0
14	1	K ₃ Fe(CN) ₆	A1 (5)	-	100	24	0	0
15	1	KIO ₄	A1 (5)	-	100	24	0	0
16	1	K ₂ Cr ₂ O ₇	A1 (5)	-	100	24	0	0

^aIsolated yield.

Table S6. Effect of different amides.

entry	amide	product	conversion (%)	yield (%) ^a
1	Methyl carbamate (A1)	1b-A1	100	93
2	Trifluoroacetamide (A2)	1b-A2	100	95
3	<i>tert</i> -Butyl carbamate (A3)	1b-A3	100	90
4	Methansulfonamide (A4)	1b-A4	100	77
5	<i>p</i> -Chlorosulphonamide (A5)	1b-A5	100	89
6	Cinnamide (A6)	1b-A6	63	68
7	Benzamide (A7)	1b-A7	14	< 10
8	Acetamide (A8)	-	0	0
9	Pyrrolidinone (A9)	-	0	0
10	Succinimide (A10)	-	0	0
11	<i>N</i> -Methylformamide (A11)	-	0	0
12	<i>n</i> -Hexylamine (A12)	-	0	0
13	<i>N,N</i> -Diethylamine (A13)	-	0	0
14	Aniline (A14)	-	0	0

^aIsolated yield.**References:**

Reference no.	Compound	Reference
1		Donaruma, L. G. <i>J. Org. Chem.</i> 1957 , 22, 1024.
2		Kwasaki, S.; Nakamura, A.; Toyota, K.; Yoshifuji, M. <i>Bull. Chem. Soc. Jpn.</i> 2005 , 78, 1110.
3	PhI=NAr	Yamada, Y.; Yamamoto, T.; Okawara, M. <i>Chem. Lett.</i> 1975 , 361.
4		Crich, D.; Petel, M. <i>Heterocycles</i> 2004 , 64, 499.
5		Newkome, G. R.; Kiefer, G. E.; Xia, Y.-J.; Gupta, V. K. <i>Synthesis</i> 1984 , 676.
6		Oh, L. M.; Spoors, P. G.; Goodman, R. M. <i>Tetrahedron Lett.</i> 2004 , 45, 4769.
7		6(5 <i>H</i>)-Phenanthridinone is commercially available (CAS: 1015-89-0). For recently related synthesis of this class of compounds, see: a) S.-M. Lu, H. Alper, <i>J. Am. Chem. Soc.</i> 2005 , 127, 14776. b) S. Goswami, A. K. Adak, R. Mukherjee, S. Jana, S. Day, J. F. Gallagher, <i>Tetrahedron</i> , 2005 , 61, 4298.
8		Kalyani, D. K.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. <i>J. Am. Chem. Soc.</i> 2005 , 127, 7330.

Figure S2. ^1H -NMR (400MHz) of *N*-(2-pyridylphenyl)-2,2,2-trifluoroacetamide

Figure S3. ^{13}C -NMR (125MHz) of *N*-(2-pyridylphenyl)-2,2,2-trifluoroacetamide

Figure S4. ^1H -NMR (500MHz) of *N*-(2-acetophenone *O*-methyl oxime)-2,2,2-trifluoroacetamide (**1b-A2**)

Figure S5. ^{13}C -NMR (125MHz) of *N*-(2-acetophenone *O*-methyl oxime)-2,2,2-trifluoroacetamide (**1b-A2**)

Figure S6. ^1H -NMR (300MHz) of 4-chloro-*N*-(2-acetophenone *O*-methyl oxime) benzenesulfonamide (**1b-A5**)

Figure S7. ^{13}C -NMR (125MHz) of 4-chloro-*N*-(2-acetophenone *O*-methyl oxime) benzenesulfonamide (**1b-A5**)

Figure S8. ^1H -NMR (500MHz) of *N*-(2-acetophenone *O*-methyl oxime)-3-phenyl-2-propenamide (**1b-A6**)

Figure S9. ^{13}C -NMR (125MHz) of *N*-(2-acetophenone *O*-methyl oxime)-3-phenyl-2-propenamide (**1b-A6**)

Figure S10. ^1H -NMR (500MHz) of methyl *N*-(4-bromo-2-benzaldehyde *O*-methyl oxime) carbamate (**1g-A1**)

Figure S11. ^{13}C -NMR (125MHz) of methyl *N*-(4-bromo-2-benzaldehyde *O*-methyl oxime)carbamate (**1g-A1**)

Figure S12. ^1H -NMR (500MHz) of methyl *N*-(2-tetralone *O*-methyl oxime)carbamate (**1j-A1**)

Figure S13. ^{13}C -NMR (125MHz) of methyl *N*-(2-tetralone *O*-methyl oxime)carbamate (**1j-A1**)

Figure S14. ^1H -NMR (500MHz) of *N*-(2,2-dimethylcyclohexanone *O*-methyl oxime)-2,2,2-trifluoroacetamide (**2b-A2**)

Figure S15. ^{13}C -NMR (125MHz) of *N*-(2,2-dimethylcyclohexanone *O*-methyl oxime)-2,2,2-trifluoroacetamide (**2b-A2**)

Figure S16. ^1H -NMR (300MHz) of 4-chloro-*N*-(3-heptanone *O*-methyl oxime) benzenesulfonamide (**2d-A5**)

Figure S17. ^{13}C -NMR (100MHz) of 4-chloro-*N*-(3-heptanone *O*-methyl oxime) benzenesulfonamide (**2d-A5**)

Figure S18. ^1H -NMR (500MHz) of *N,N*-di-(4chlorobenzenesulfonyl)-8-quinoline methanamide (**2e-A5**)

Figure S19. ^{13}C -NMR (125MHz) of *N,N*-di-(4chlorobenzenesulfonyl)-8-quinoline methanamide (**2e-A5**)

Figure S20. ^1H -NMR (500MHz) of 4-chloro-*N*-(2-pyridylphenyl)benzenesulfonamide (**6**)

Figure S21. ^{13}C -NMR (125MHz) of 4-chloro-*N*-(2-pyridylphenyl)benzenesulfonamide (**6**)

Figure S22. The ORTEP drawing of *N*-(5-methyl-2-pyridylphenyl)-2,2,2-trifluoroacetamide with the atom-numbering scheme. Thermal ellipsoids are drawn on a 30% probability level

Table S7. Crystal data and structure refinement for *N*-(5-methyl-2-pyridylphenyl)-2,2,2-trifluoroacetamide.

Empirical formula	C ₁₄ H ₁₁ F ₃ N ₂ O
Formula weight	280.25
Temperature	301(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	a = 10.356(2) Å = 90°. b = 17.055(3) Å = 95.65(3)°. c = 7.401(2) Å = 90°.
Volume	1300.8(5) Å ³
Z	4
Density (calculated)	1.431 Mg/m ³
Absorption coefficient	0.121 mm ⁻¹
F(000)	576
Crystal size	0.40 x 0.30 x 0.25 mm ³
Theta range for data collection	1.98 to 25.45°.
Index ranges	-11 ≤ h ≤ 10, -17 ≤ k ≤ 18, -7 ≤ l ≤ 7
Reflections collected	5855
Independent reflections	1710 [R(int) = 0.0337]
Completeness to theta = 25.45°	71.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1710 / 0 / 186
Goodness-of-fit on F ²	1.042
Final R indices [I > 2sigma(I)]	R1 = 0.0589, wR2 = 0.1734
R indices (all data)	R1 = 0.0857, wR2 = 0.1868
Largest diff. peak and hole	0.368 and -0.243 e.Å ⁻³

Table S8. Bond lengths and bond angles for *N*-(5-methyl-2-pyridyl phenyl)-2,2,2-trifluoro-acetamide.

Bond lengths		Bond angles	
F(1)-C(2)	1.324(5)	C(1)-N(1)-C(3)	128.4(3)
F(2)-C(2)	1.281(4)	C(13)-N(2)-C(9)	118.9(3)
F(3)-C(2)	1.297(5)	O(1)-C(1)-N(1)	129.5(3)
O(1)-C(1)	1.204(4)	O(1)-C(1)-C(2)	117.2(3)
N(1)-C(1)	1.337(4)	N(1)-C(1)-C(2)	113.3(3)
N(1)-C(3)	1.416(4)	F(2)-C(2)-F(3)	106.7(3)
N(2)-C(13)	1.333(4)	F(2)-C(2)-F(1)	104.5(4)
N(2)-C(9)	1.343(4)	F(3)-C(2)-F(1)	104.1(4)
C(1)-C(2)	1.508(5)	F(2)-C(2)-C(1)	113.4(4)
C(3)-C(4)	1.382(4)	F(3)-C(2)-C(1)	112.3(4)
C(3)-C(8)	1.414(4)	F(1)-C(2)-C(1)	115.0(3)
C(4)-C(5)	1.389(4)	C(4)-C(3)-C(8)	121.0(3)
C(5)-C(6)	1.390(5)	C(4)-C(3)-N(1)	121.6(3)
C(5)-C(14)	1.496(4)	C(8)-C(3)-N(1)	117.4(3)
C(6)-C(7)	1.362(5)	C(3)-C(4)-C(5)	121.8(3)
C(7)-C(8)	1.406(4)	C(4)-C(5)-C(6)	117.5(3)
C(8)-C(9)	1.480(4)	C(4)-C(5)-C(14)	120.8(3)
C(9)-C(10)	1.388(4)	C(6)-C(5)-C(14)	121.7(3)
C(10)-C(11)	1.369(5)	C(7)-C(6)-C(5)	121.2(3)
C(11)-C(12)	1.356(5)	C(6)-C(7)-C(8)	122.8(3)
C(12)-C(13)	1.364(5)	C(7)-C(8)-C(3)	115.6(3)
		C(7)-C(8)-C(9)	118.9(3)
		C(3)-C(8)-C(9)	125.4(3)
		N(2)-C(9)-C(10)	119.7(3)
		N(2)-C(9)-C(8)	117.9(3)
		C(10)-C(9)-C(8)	122.4(3)
		C(11)-C(10)-C(9)	119.7(4)
		C(12)-C(11)-C(10)	120.5(4)
		C(11)-C(12)-C(13)	117.3(4)
		N(2)-C(13)-C(12)	123.9(4)

Figure S23. The ORTEP drawing of di- μ -acetatobis[phenylpyridine-2*C,N*] dipalladium(II) (complex **3**) with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn on a 30% probability level

Table S9. Crystal data of di- μ -acetatobis[phenylpyridine-2*C,N*]dipalladium(II) (complex **3**)

Empirical formula	C ₂₆ H ₂₂ N ₂ O ₄ Pd ₂
Formula weight	639.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	a = 9.918(2) Å = 90°. b = 13.261(3) Å = 95.05(3)°. c = 17.723(4) Å = 90°.
Volume	2321.9(8) Å ³
Z	4
Density (calculated)	1.829 Mg/m ³
Absorption coefficient	1.585 mm ⁻¹
F(000)	1264
Crystal size	0.3 x 0.2 x 0.1 mm ³
Theta range for data collection	1.92 to 25.44°.
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	15243
Independent reflections	4167 [R(int) = 0.0417]
Completeness to theta = 25.44°	97.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4167 / 0 / 307
Goodness-of-fit on F ²	0.833
Final R indices [I > 2σ(I)]	R1 = 0.0265, wR2 = 0.0562
R indices (all data)	R1 = 0.0471, wR2 = 0.0589
Largest diff. peak and hole	0.411 and -0.453 e.Å ⁻³

Table S10. Selected bond lengths and bond angles for di- μ -acetatobis [phenylpyridine-2*C,N*]dipalladium(II) (complex **3**)

Bond lengths		Bond angles	
Pd(1)-C(5)	1.969(3)	C(5)-Pd(1)-N(1)	81.39(13)
Pd(1)-N(1)	2.002(3)	C(5)-Pd(1)-O(1)	94.44(12)
Pd(1)-O(1)	2.056(2)	N(1)-Pd(1)-O(1)	175.40(10)
Pd(1)-O(3)	2.156(2)	C(5)-Pd(1)-O(3)	175.65(12)
Pd(1)-Pd(2)	2.8801(7)	N(1)-Pd(1)-O(3)	95.25(11)
O(1)-C(1)	1.266(4)	O(1)-Pd(1)-O(3)	88.83(10)
O(2)-C(1)	1.241(4)	C(5)-Pd(1)-Pd(2)	96.22(9)
O(3)-C(3)	1.244(4)	N(1)-Pd(1)-Pd(2)	90.66(8)
O(4)-C(3)	1.241(4)	O(1)-Pd(1)-Pd(2)	87.87(7)
N(1)-C(15)	1.327(4)	O(3)-Pd(1)-Pd(2)	81.01(7)
N(1)-C(11)	1.358(4)	C(1)-O(1)-Pd(1)	119.1(2)
C(1)-C(2)	1.500(5)	C(3)-O(3)-Pd(1)	122.9(2)
C(3)-C(4)	1.515(5)	C(15)-N(1)-C(11)	119.2(3)
C(5)-C(6)	1.385(4)	C(15)-N(1)-Pd(1)	125.1(3)
C(5)-C(10)	1.402(4)	C(11)-N(1)-Pd(1)	115.5(2)
C(6)-C(7)	1.365(5)	C(26)-N(2)-C(22)	119.3(3)
C(7)-C(8)	1.384(5)	O(2)-C(1)-O(1)	125.3(3)
C(8)-C(9)	1.363(5)	O(2)-C(1)-C(2)	118.2(4)
C(9)-C(10)	1.385(5)	O(1)-C(1)-C(2)	116.5(3)
C(10)-C(11)	1.460(5)	O(4)-C(3)-O(3)	127.4(3)
C(11)-C(12)	1.383(5)	O(4)-C(3)-C(4)	115.8(4)
C(12)-C(13)	1.377(5)	O(3)-C(3)-C(4)	116.9(3)
C(13)-C(14)	1.346(5)	C(6)-C(5)-C(10)	118.8(3)
C(14)-C(15)	1.385(5)	C(6)-C(5)-Pd(1)	126.8(3)
		C(10)-C(5)-Pd(1)	114.3(2)
		N(1)-C(11)-C(12)	120.3(3)
		N(1)-C(11)-C(10)	113.6(3)
		N(1)-C(15)-C(14)	122.3(4)