Supporting Information
for

Nickel-Catalyzed Decarbonylation of N-Acylated N-Heteroarenes

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I. General Information.

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL, Tokyo, Japan) or VARIAN UNITY INOVA-600 spectrometer in CDCl$_3$ with tetramethylsilane as an internal reference standard. NMR data have been reported as follows: chemical shift ($\delta$) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant ($J$) in Hz, and integration. Infrared spectra (IR) were obtained on a JASCO FT/IR-4000 spectrometer, and the absorptions have been reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with an ionization voltage of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LP AccuTOF LC-plus in direct analysis real time (DART) method using PEG as the internal standard. Analytical gas chromatography (GC) was carried out on Shimadzu GC-2014, equipped with a flame ionization detector. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed over SiO$_2$ (Silycycle Silica Flash F60 (230-400 mesh)) and NH Silica (Silica Gel 60 (spherical) NH$_2$ (40–50 μm)). Some of the compounds were purified by LC-908 HPLC (GPC). Data collection for X-ray crystal analysis were performed on a Rigaku / XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Mo-Kα, $\lambda = 0.71075$ Å for 6a and Cu-Kα, $\lambda = 1.54184$ Å for 6f). The structure was solved with direct methods and refined with full-matrix least squares.

II. Materials.

Toluene (for Organic Synth.) was purchased from Wako Chemicals and used as received. Ni(cod)$_2$ was purchased from Strem Chemicals and used as received. PCy$_3$ (Sigma-Aldrich), dctype (Sigma-Aldrich), IPr·HCl (TCI), IMes·HCl (TCI), ICy·HCl (TCI) PPh$_3$ (TCI), and Ni(CO)$_2$(dctype) (Kanto Chemical) were purchased from commercial suppliers and used as received. IMes$_{\text{Me}}$·HCl$^1$ was prepared according to the literature procedures. 4-[(Benzylloxy)carbonyl]benzoic acid $^1$S1 [CAS: 18520-63-3]$^2$ was prepared according to the literature procedure. 4-(Morpholine-4-carbonyl)benzoic acid $^1$S4 [CAS: 160816-43-3]$^2$ was prepared according to the literature procedure. 2-(5-Methoxy-1H-indol-3-yl)-N,N-bis(phenylmethyl)ethanamine $^1$S6 [CAS: 300834-81-5]$^3$ was prepared according to the literature procedure. N-Acylated N-heteroarenes $^1$7a [CAS: 62573-86-8]$^4$ and $^1$7c [CAS: 28997-
were prepared according to the literature procedure. 1H-Benzimidazole-2-d S19 [CAS: 61233-51-0] was prepared according to the literature procedures.

III. Synthesis of Starting Materials.

**General Procedure I: Synthesis of amides from acid halides.** Aroyl chloride (20 mmol) was partially added to a solution of indole (20 mmol, 1 equiv), Et3N (1 equiv) and N,N-dimethyl-4-aminopyridine (0.4 mmol) in 20 mL of CH2Cl2 at 0 °C. After addition was complete, the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by the addition of H2O, and the resulting mixture was extracted with CH2Cl2. The combined extracts were washed with brine, dried (MgSO4), and concentrated to give a residue, which was purified by recrystallization or column chromatography to give the desired N-acylpyrrole derivative.

**General Procedure II: Synthesis of amides from carboxylic acids.** N,N-dimethylformamide (0.2 mL) was added to a solution of carboxylic acid (20 mmol) and oxalyl chloride (40 mmol, 2 equiv) in 200 mL of CH2Cl2 at 0 °C. After gas evolution ceased, the mixture was allowed to gradually warm to room temperature and was then stirred until the starting carboxylic acid disappeared by TLC. The solution was concentrated to give an aroyl chloride, which was used in the next step without further purification. The aroyl chloride was partially added to a solution of indole (20 mmol, 1 equiv), Et3N (1 equiv) and N,N-dimethyl-4-aminopyridine (0.4 mmol) in 20 mL of CH2Cl2 at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by the addition of H2O, and the resulting mixture was extracted with CH2Cl2. The combined extracts were washed with brine, dried (MgSO4), and concentrated to give a residue, which was purified by recrystallization or column chromatography to give the desired N-acylpyrrole derivative.

(1H-Indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1a) [CAS: 1018967-38-8].

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5 Ovian, J. M.; Kelly, C. B.; Pistritto, V. A.; Leadbeater, N. E. *Org. Lett.* 2017, 19, 1286.
6 Gröll, B.; Schnürch, M.; Mihovilovic, M. D. *J. Org. Chem.* 2012, 77, 4432.
7 Wang, L.; Neumann, H.; Spannenberg, A.; Beller, M. *Chem. Eur. J.* 2018, 24, 2164.
The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride (50 mmol scale). White solid (7.4g, 51%). Mp 132.9–133.1 °C. Rf 0.34 (SiO2, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl3, 399.78 MHz) $\delta$: 6.65 (d, $J = 3.7$ Hz, 1H), 7.19 (d, $J = 3.7$ Hz, 1H), 7.35 (dd, $J = 7.3$, 7.3 Hz, 1H), 7.40 (dd, $J = 7.3$, 8.0 Hz, 1H), 7.62 (d, $J = 7.3$ Hz, 1H), 7.87–7.80 (m, 4H), 8.41 (d, $J = 8.2$ Hz, 1H).

$^{13}$C NMR (CDCl3, 100.53 MHz) $\delta$: 109.5, 116.4, 121.1, 123.5 (q, $J_{CF} = 272.6$ Hz), 124.4, 125.3, 125.7 (q, $J_{CF} = 4.1$ Hz), 127.0, 129.4, 130.7, 133.5 (q, $J_{CF} = 33.2$ Hz), 135.9, 137.9, 167.3.

IR (ATR): 1679 s, 1542 w, 1452 w, 1407 w, 1328 m, 1205 m, 1170 s, 1128 s, 1068 m, 854 m, 769 w, 727 m.

MS, $m/z$ (relative intensity, %): 290 (10), 289 (M$^+$, 54), 173 (100), 145 (52).

HRMS Calcd for C$_{16}$H$_{11}$F$_3$NO ([M+H$^+$]): 290.0793. Found: 290.0792.

**Methyl 4-(1H-indole-1-carbonyl)benzoate (1b).**

The general procedure I was followed using methyl 4-(chloroformyl)benzoate.

White solid (4.3 g, 77%). Mp 167.5–167.8 °C. Rf 0.11 (SiO2, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl3, 399.78 MHz) $\delta$: 3.98 (s, 3H), 6.64 (d, $J = 3.7$ Hz, 1H), 7.21 (d, $J = 3.7$ Hz, 1H), 7.33 (dd, $J = 7.4$, 8.2 Hz, 1H), 7.40 (dd, $J = 7.4$, 8.2 Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 8.3$ Hz, 2H), 8.20 (d, $J = 8.3$ Hz, 2H), 8.40 (d, $J = 8.2$ Hz, 1H).

$^{13}$C NMR (CDCl3, 100.53 MHz) $\delta$: 52.6, 109.3, 116.4, 121.0, 124.2, 125.2, 127.1, 129.0, 129.8, 130.7, 132.9, 135.9, 138.5, 166.1, 167.8.

IR (ATR): 1720 m, 1679 s, 1448 m, 1378 w, 1347 s, 1278 s, 1209 m, 1109 m, 1018 w, 887 w, 769 s, 728 m.

MS, $m/z$ (relative intensity, %): 279 (M$^+$, 35), 164 (10), 163 (100), 135 (22), 103 (14).
HRMS Calcd for C$_{17}$H$_{14}$NO$_3$ ([M+H$^+$]): 280.0974. Found: 280.0978.

[1,1'-Biphenyl]-4-yl(1H-indol-1-yl)methanone (1c) [CAS 1018967-39-9].

The general procedure I was followed using 4-phenylbenzoyl chloride. Spectroscopic data were consistent with those reported in the literature.$^8$

(1H-Indol-1-yl)(phenyl)methanone (1d) [CAS 1496-76-0].

The general procedure I was followed using benzoyl chloride. Spectroscopic data were consistent with those reported in the literature.$^9$

(1H-Indol-1-yl)(p-tolyl)methanone (1e) [CAS 69888-36-4].

The general procedure I was followed using p-toluoyl chloride. Spectroscopic data were consistent with those reported in the literature.$^{10}$

(1H-Indol-1-yl)(4-methoxyphenyl)methanone (1f) [CAS 52498-87-0].

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$^8$ Abid, M.; De Paolis, O.; Török, B. *Synlett* **2008**, *3*, 410.

$^9$ Umehara, A.; Ueda, H.; Tokuyama, H. *J. Org. Chem.* **2016**, *81*, 11444.

$^{10}$ Aggarwal, R.; Benedetti, F.; Berti, F.; Buchini, S.; Colombatti, A.; Dinon, F.; Galasso, V.; Norbedo, S. *Chem. Eur. J.* **2003**, *9*, 3132.
The general procedure I was followed using 4-methoxybenzoyl chloride. Spectroscopic data were consistent with those reported in the literature.11

\[(1R,2S,5R)-2-\text{Isopropyl-5-methylcyclohexyl} \ 4-(1H-\text{indole-1-carbonyl})\text{benzoate (1g).}\]

\[\text{N,N-dimethylformamide} \ (50 \ \mu\text{L}) \ \text{was added to a solution of} \ 4-[(\text{benzyloxy})\text{carbonyl}]\text{benzoic acid (S1)} \ (10 \ \text{mmol}) \ \text{and oxaly chloride (25 mmol, 2.5 equiv) in} \ 30 \ \text{mL of CH}_2\text{Cl}_2 \ \text{at} \ 0 \ ^\circ\text{C}. \ \text{After gas evolution ceased, the mixture was allowed to be gradually warm to room temperature and was then stirred until the starting carboxylic acid was disappeared by TLC. The solution was concentrated to give an aroyl chloride, which was used in the next step without further purification. The aroyl chloride was partially added to a solution of (-)-\text{menthol} \ (10 \ \text{mmol, 1 equiv}), \ \text{Et}_3\text{N} \ (1 \ \text{equiv}) \ \text{and N,N-dimethyl-4-aminopyridine} \ (0.2 \ \text{mmol}) \ \text{in} \ 20 \ \text{mL of CH}_2\text{Cl}_2 \ \text{at} \ 0 ^\circ\text{C}. \ \text{After addition was completed, the reaction mixture was stirred at room temperature for 12 hours. The reaction was quenched by the addition of} \ \text{H}_2\text{O, and the resulting mixture was extracted with CH}_2\text{Cl}_2. \ \text{The combined extracts were washed with brine, dried (MgSO}_4), and concentrated to give a residue, which was purified by column chromatography to give S2 as a colorless oil.}\]

\text{Colorless oil (3.42 g, 87%). R}_f \ 0.43 \ (\text{SiO}_2, \ \text{hexane/EtOAc} = 9/1).}

\[\text{H NMR (CD}_2\text{Cl}_2, \ 399.78 \ \text{MHz}) \ \delta: \ 0.81 \ (d, J = 6.8 \ \text{Hz, 3H}), \ 0.93–0.96 \ (\text{m, 7H}), \ 1.09–1.21 \ (\text{m, 2H}), \]

11 Wu, X. F.; Oschatz, S.; Sharif, M.; Langer, P. \textit{Synthesis}, \textbf{2015} 47, 2641.
1.52–1.64 (m, 2H), 1.72–1.78 (m, 2H), 1.91–2.02 (m, 1H), 2.10–2.15 (m, 1H), 4.96 (td, \( J = 10.8, 4.4 \) Hz, 1H), 5.39 (s, 2H), 7.34–7.44 (m, 3H), 7.46–7.49 (m, 2H), 8.10–8.16 (m, 4H).

\(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 100.53 MHz) \( \delta \): 16.6, 20.9, 22.2, 23.9, 26.9, 31.8, 34.6, 41.2, 47.6, 67.6, 75.7, 128.6, 128.7, 128.9, 129.80, 129.85, 134.1, 135.2, 136.3, 165.4, 165.9.

IR (KBr, cm\(^{-1}\)): 3421 w, 3066 w, 3034 w, 2955 s, 2870 m, 1951 w, 1716 s, 1610 w, 1577 w, 1504 m, 1456 m, 1408 m, 1374 m, 1268 s, 1180 m, 1118 s, 1101 s, 1038 m, 1018 s, 982 m, 960 m, 915 m, 875 m, 846 m, 795 w, 731 s, 696 m.

HRMS Calcd for C\(_{25}\)H\(_{31}\)O\(_4\) ([M+H\(^+\)]): 395.2217. Found: 395.2222.

To a stirred solution of benzyl ester S\(_2\) (2.5 g, 6.3 mmol) in methanol (50 mL) was added 10% palladium on carbon (130 mg) slowly, in small portions. The mixture was then stirred vigorously under an atmosphere of hydrogen for 5 h, filtered through Celite® and the solvent was removed in vacuo to afford S\(_3\) (1.9 g, 100%) as a white solid.

Mp 46.3–48.5 °C. \( R_f \) 0.46 (SiO\(_2\), EtOAc/MeOH = 9/1).

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 399.78 MHz) \( \delta \): 0.80 (d, \( J = 6.8 \) Hz, 3H), 0.92–0.95 (m, 7H), 1.09–1.21 (m, 2H), 1.51–1.63 (m, 2H), 1.73–1.78 (m, 2H), 1.91–2.02 (m, 1H), 2.10–2.15 (m, 1H), 4.96 (td, \( J = 10.8, 4.4 \) Hz, 1H), 8.13–8.21 (m, 4H), 12.62 (s, 1H).

\(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 100.53 MHz) \( \delta \): 16.6, 20.9, 22.2, 23.9, 26.9, 31.8, 34.6, 41.2, 47.6, 75.9, 129.9, 130.4, 133.1, 136.0, 165.4, 171.8.

IR (KBr, cm\(^{-1}\)): 3417 w, 2956 s, 2928 s, 2871 s, 2667 m, 2545 m, 2285 w, 1952 w, 1822 w, 1716 s, 1695 s, 1614 w, 1577 m, 1507 m, 1455 m, 1423 s, 1388 m, 1371 m, 1272 s, 1180 m, 1129 s, 1104 s, 1038 m, 1019 s, 982 m, 959 s, 916 m, 879 m, 876 m, 846 m, 797 m, 768 m, 731 s, 693 s, 674 w.

HRMS Calcd for C\(_{18}\)H\(_{25}\)O\(_4\) ([M+H\(^+\)]): 305.1747. Found: 305.1741.

\( N,N\)-dimethylformamide (30 \( \mu \)L) was added to a solution of benzoic acid S\(_3\) (1.8 g, 6.0 mmol) and oxalyl chloride (12 mmol, 2.0 equiv) in 18 mL of CH\(_2\)Cl\(_2\) at 0 °C. After gas evolution ceased, the mixture was allowed to be gradually warm to room temperature and was then stirred until the starting carboxylic acid was disappeared by TLC. The solution was concentrated to give an aroyl chloride, which was used in the next step without further purification. The aroyl chloride was partially added to a solution of indole (6.0 mmol, 1 equiv), Et\(_3\)N (1 equiv) and \( N,N\)-dimethyl-4-aminopyridine (0.12 mmol) in 12 mL of CH\(_2\)Cl\(_2\) at 0 °C. After addition was completed, the reaction mixture was stirred at room temperature for 12 hour. The reaction was quenched by the addition of H\(_2\)O, and the resulting mixture was extracted with CH\(_2\)Cl\(_2\). The combined extracts were washed with brine, dried (MgSO\(_4\)),

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and concentrated to give a residue, which was purified by column chromatography on NH silica gel (hexane/CH₂Cl₂ = 1/1) to give 1g as a colorless oil.

Colorless oil (1.46 g, 60%). Rf 0.66 (NH silica, hexane/CH₂Cl₂ = 1/1).

¹H NMR (CD₂Cl₂, 399.78 MHz) δ: 0.82 (d, J = 6.8 Hz, 3H), 0.91–1.01 (m, 7H), 1.11–1.22 (m, 2H), 1.53–1.64 (m, 2H), 1.73–1.79 (m, 2H), 1.93–2.04 (m, 1H), 2.12–2.17 (m, 1H), 4.98 (td, J = 10.9, 5.6 Hz, 1H), 6.66 (dd, J = 3.7, 0.8 Hz, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.31–7.41 (m, 2H), 7.63 (dq, J = 7.7, 0.7 Hz, 1H), 7.79 (dt, J = 8.4, 1.6 Hz, 2H), 8.18–8.21 (m, 2H), 8.40 (dd, J = 8.2, 1.2 Hz, 1H).

¹³C NMR (CD₂Cl₂, 100.53 MHz) δ: 16.6, 20.9, 22.2, 23.9, 26.9, 31.8, 34.6, 41.2, 47.6, 75.8, 109.2, 116.6, 121.3, 124.4, 125.3, 127.7, 129.3, 130.0, 131.2, 134.1, 136.3, 138.6, 165.3, 168.2.

IR (KBr, cm⁻¹): 3416 w, 3363 w, 3150 m, 3120 m, 3053 m, 2955 s, 2870 s, 2722 w, 1942 w, 1713 s, 1692 s, 1606 m, 1585 m, 1572 m, 1536 s, 1504 s, 1451 s, 1405 s, 1381 s, 1343 s, 1275 s, 1244 s, 1206 s, 1186 s, 1152 s, 1117 s, 1108 s, 1065 s, 1038 m, 1018 s, 959 s, 917 s, 891 s, 864 s, 843 s, 750 s, 733 s, 715 s.

HRMS Calcd for C₂₆H₃₀NO₃ ([M+H⁺]): 404.2226. Found: 404.2220.

(1H-Indol-1-yl)(3-(trifluoromethyl)phenyl)methanone (1h) [CAS: 1792982-64-9].

The general procedure I was followed using 3-(trifluoromethyl)benzoyl chloride.

White solid (4.2 g, 73%). Mp 85.0–85.3 °C. Rf 0.23 (SiO₂, hexane/EtOAc = 10/1).

¹H NMR (CDCl₃, 399.78 MHz) δ: 6.66 (d, J = 3.7 Hz, 1H), 7.20 (d, J = 3.7 Hz, 1H), 7.34 (dd, J = 7.0, 8.0 Hz, 1H), 7.42 (dd, J = 7.0, 7.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.69 (dd, J = 7.8, 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 8.41 (d, J = 8.0 Hz, 1H).

¹³C NMR (CDCl₃, 100.53 MHz) δ: 109.5, 116.4, 121.1, 123.4 (q, Jₐₜ = 272.6 Hz), 124.3, 125.3, 126.0 (q, Jₐₜ = 4.2 Hz), 126.9, 128.4, 129.3, 130.7, 131.3 (q, Jₐₜ = 33.2 Hz), 132.3, 135.4, 135.9, 167.0.

IR (ATR): 2360 w, 1691 m, 1538 w, 1452 m, 1351 m, 1240 w, 1207 w, 1172 m, 1130 m, 1072 w, 902 w, 771 s, 703 m.

MS, m/z (relative intensity, %): 290 (12), 289 (M⁺, 67), 173 (100), 145 (50).

HRMS Calcd for C₁₆H₁₆F₃NO ([M+H⁺]): 290.0793. Found: 290.0808.
(3,5-Dimethoxyphenyl)(1H-indol-1-yl)methanone (1i).

The general procedure I was followed using 3,4-(dimethoxy)benzoyl chloride.
White solid (3.8 g, 68%). Mp 74.5–74.8 °C. R_f 0.31 (SiO2, hexane/EtOAc = 10/1).

^1^H NMR (CDCl₃, 399.78 MHz) δ: 3.83 (s, 6H), 6.61 (d, J = 3.8 Hz, 1H), 6.67 (t, J = 2.3 Hz, 1H), 6.85 (d, J = 2.3 Hz, 2H), 7.35–7.30 (m, 2H), 7.40 (dd, 7.3, 8.1 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 8.41 (d, J = 8.1 Hz, 1H).

^1^C NMR (CDCl₃, 100.53 MHz) δ: 55.6, 103.9, 106.9, 108.6, 116.4, 120.9, 124.0, 124.9, 127.6, 130.8, 135.9, 136.3, 160.7, 168.4.

IR (ATR): 2939 w, 1687 m, 1595 m, 1527 w, 1450 m, 1331 s, 1201 m, 1157 m, 1124 m, 1065 m, 931 w, 847 w, 754 m, 688 w.
MS, m/z (relative intensity, %): 281 (M^+, 26), 166 (11), 165 (100), 137 (27), 122 (19), 107 (11), 77 (10).

HRMS Calcd for C_{17}H_{16}NO_{3} ([M+H^+]): 282.1130. Found: 282.1135.

(1H-Indol-1-yl)(3-methoxy-4-(trifluoromethyl)phenyl)methanone (1j).

The general procedure II was followed using 3-methoxy-4-(trifluoromethyl)benzoic acid (5 mmol scale).
Pale yellow solid (0.4 g, 26%). Mp 106.8–107.0 °C. R_f 0.2 (SiO2, hexane/EtOAc = 10/1).

^1^H NMR (CDCl₃, 399.78 MHz) δ: 3.97 (s, 3H), 6.66 (d, J = 3.7 Hz, 1H), 7.23 (d, J = 3.7 Hz, 1H), 7.37–7.31 (m, 3H), 7.34 (dd, J = 7.3, 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 8.42 (d, J = 7.6 Hz, 1H).

^1^C NMR (CDCl₃, 100.53 MHz) δ: 56.2, 109.4, 112.3, 116.4, 120.2, 120.3 (q, J_{CF} = 273.6 Hz), 121.0,
121.6 (q, $J_{CF} = 31.1$ Hz), 124.4, 125.3, 127.0, 127.4 (q, $J_{CF} = 5.2$ Hz), 130.8, 135.8, 139.4, 157.7, 167.3.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) $\delta$: –62.8 (s, 3F).

IR (ATR): 1690 m, 1617 w, 1581 w, 1536 w, 1508 w, 1452 m, 1412 m, 1380 w, 1315 s, 1275 w, 1232 m, 1206 m, 1176 m, 1127 m, 1073 w, 1042 m, 913 w, 879 w, 808 m, 769 m, 752 m.

MS, $m/z$ (relative intensity, %): 319 (M$^+$, 43), 203 (100), 175 (21), 127 (21).

HRMS Calcd for C$_{17}$H$_{13}$F$_3$NO$_2$ ([M+H$^+$]): 320.0898. Found: 320.0916.

**1-(4-(1H-Indole-1-carbonyl)phenyl)(morpholino)methanone (1k).**

![](image)

The general procedure II was followed using 4-(morpholine-4-carbonyl)benzoic acid S4 (15 mmol scale).

White solid (1.6 g, 22%). Mp 176.5–176.8 °C. R$_f$ 0.08 (SiO$_2$, hexane/EtOAc = 1/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 3.46–3.82 (m, 8H), 6.64 (d, $J = 3.8$ Hz, 1H), 7.24 (d, $J = 3.8$ Hz, 1H), 7.33 (dd, $J = 7.2$, 7.6 Hz, 1H), 7.40 (dd, $J = 7.2$, 8.3 Hz, 1H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 2H), 8.41 (d, $J = 8.3$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 150.92 MHz) $\delta$: 42.5 (br), 48.1 (br), 66.8, 109.1, 116.3, 120.9, 124.2, 125.1, 127.1, 127.3, 129.3, 130.7, 135.9, 138.6, 167.7, 169.0.

IR (ATR): 2925 w, 1687 m, 1633 m, 1508 w, 1454 s, 1340 s, 1265 w, 1211 m, 1160 w, 1118 m, 1068 w, 1018 w, 889 w, 843 w, 746 m.

MS, $m/z$ (relative intensity, %): 334 (M$^+$, 31), 219 (15), 218 (100), 105 (13), 104 (30), 103 (10), 76 (19).

HRMS Calcd for C$_{20}$H$_{19}$N$_2$O$_3$ ([M+H$^+$]): 335.1396. Found: 335.1395.

**1-(4-(1H-Indole-1-carbonyl)phenyl)ethanone (1l).**

The general procedure II was followed using 4-acetylbenzoyl chloride (10 mmol scale).
Pale yellow solid (0.2 g, 5%). Mp 160.0–160.3 °C. R$_f$ 0.2 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 2.69 (s, 3H), 6.66 (d, $J = 3.7$ Hz, 1H), 7.20 (d, $J = 3.7$ Hz, 1H), 7.33 (dd, $J = 7.0$, 7.3 Hz, 1H), 7.41 (dd, $J = 7.0$, 8.2 Hz, 1H), 7.61 (d, $J = 7.3$ Hz, 1H), 7.82 (d, $J = 7.8$ Hz, 2H), 8.10 (d, $J = 8.3$ Hz, 2H), 8.40 (d, $J = 8.3$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 26.9, 109.3, 116.4, 121.0, 124.3, 125.2, 127.0, 128.4, 129.2, 130.7, 135.8, 138.5, 139.2, 167.7, 197.2.

IR (ATR): 1690 m, 1617 w, 1581 w, 1536 w, 1508 w, 1452 m, 1412 m, 1380 w, 1343 s, 1315 s, 1275 w, 1232 m, 1206 m, 1176 m, 1127 m, 1073 w, 1042 m, 913 w, 879 w, 808 m, 769 m, 752 m.

MS, $m/z$ (relative intensity, %): 263 (M$^+$, 36), 148 (13), 147 (100), 119 (20), 91 (25), 76 (13), 43 (25).

HRMS Calcd for C$_{17}$H$_{14}$NO$_2$ ([M+H$^+$]): 264.1025. Found: 264.1027.

4-(1H-Indole-1-carbonyl)benzonitrile (1m).

The general procedure I was followed using 4-cyanobenzoyl chloride.

White solid (2.7 g, 54%). Mp 117.1–117.4 °C. R$_f$ 0.11 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 6.66 (d, $J = 3.7$ Hz, 1H), 7.14 (d, $J = 3.7$ Hz, 1H), 7.35 (dd, $J = 7.3$, 7.7 Hz, 1H), 7.40 (dd, $J = 7.7$, 8.3 Hz, 1H), 7.62 (d, $J = 7.3$ Hz, 1H), 7.84 (m, 4H), 8.38 (d, $J = 8.3$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 109.8, 115.4, 116.4, 117.7, 121.1, 124.5, 125.4, 126.6, 129.5, 130.7, 132.4, 135.8, 166.7.

IR (ATR): 2360 w, 2233 w, 1689 m, 1536 w, 1450 w, 1378 w, 1342 m, 1211 w, 1066 w, 1018 w, 889 w, 848 w, 769 s.

MS, $m/z$ (relative intensity, %): 246 (M$^+$, 35), 130 (100), 102 (46).

HRMS Calcd for C$_{16}$H$_{11}$N$_2$O ([M+H$^+$]): 247.0871. Found: 247.0884.

(3,5-Difluorophenyl)(1H-indol-1-yl)methanone (1n).
The general procedure I was followed using 3,5-difluorobenzoyl chloride.

Pale yellow solid (0.20 g, 4%). Mp 55.3–55.5 °C. R_f 0.31 (SiO_2, hexane/EtOAc = 10/1).

^1^H NMR (CDCl_3, 399.78 MHz) δ: 6.67 (d, J = 3.7 Hz, 1H), 7.06 (tt, J = 2.3, 8.7 Hz, 1H), 7.23 (d, J = 3.7 Hz, 1H), 7.30–7.25 (m, 2H), 7.34 (dd, J = 7.3, 7.8 Hz, 1H), 7.40 (dd, J = 7.8, 8.2 Hz, 1H), 7.61 (d, J = 7.3 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H).

^1^3^C NMR (CDCl_3, 100.53 MHz) δ: 107.4 (t, J = 25.9 Hz), 109.7, 112.3 (dd, J = 18.7 Hz), 116.4, 121.1, 124.5, 125.3, 126.7, 130.7 (t, J = 9.3 Hz), 135.8, 137.4, 162.7 (dd, J = 251.9 Hz), 165.9.

^1^9^F NMR (CDCl_3, 376.17 MHz) δ: –106.9 (s, 2F).

IR (ATR): 1691 m, 1595 m, 1537 w, 1452 m, 1381 m, 1350 s, 1205 m, 1124 m, 992 w, 878 w, 791 m, 754 m.

MS, m/z (relative intensity, %): 257 (M^+ , 44), 141 (100), 113 (50), 63 (10).

HRMS Calcd for C_{15}H_{10}F_{2}NO ([M+H^+]): 258.0730. Found: 258.0740.

(1H-Indol-1-y1)(naphthalen-2-y1)methanone (1o) [CAS: 74117-26-3].

The general procedure I was followed using 2-naphthoyl chloride (27 mmol scale).

Pale pink solid (1.5 g, 20%). Mp 167.5–167.8 °C. R_f 0.11 (SiO_2, hexane/EtOAc = 10/1).

^1^H NMR (CDCl_3, 399.78 MHz) δ: 6.64 (d, J = 3.6 Hz, 1H), 7.43–7.32 (m, 3H), 7.67–7.59 (m, 3H), 7.82 (d, J = 8.7 Hz, 1H), 8.01–7.94 (m, 3H), 8.25 (s, 1H), 8.44 (d, J = 8.2 Hz, 1H).

^1^3^C NMR (CDCl_3, 100.53 MHz) δ: 108.6, 116.4, 120.9, 123.9, 124.9, 125.3, 127.1, 127.7, 127.9, 128.2, 128.5, 129.0, 130.2, 130.7, 131.7, 132.2, 134.7, 136.0, 168.7.

IR (ATR): 3054 w, 1727 w, 1677 m, 1536 w, 1446 m, 1336 m, 1199 m, 1116 w, 1068 w, 1012 w, 960 w, 912 w, 800 w, 771 s.

MS, m/z (relative intensity, %): 271 (M^+ , 33), 156 (12), 155 (100), 127 (70).
HRMS Calcd for C₁₉H₁₄NO ([M+H⁺]): 272.1075. Found: 272.1074.

(1H-Indol-1-yl)(4’-(trifluoromethyl)-[1,1’-biphenyl]-4-yl)methanone (1p).

The general procedure I was followed using 4-bromobenzoyl chloride to give (4-bromophenyl)(1H-indol-1-yl)methanone S₅, which was purified by recrystallization with hexane/EtOAc (100m L/20 mL) (white solid, 3.2 g, 53%).

Mp 120.9–121.5 °C. Rᵢ 0.36 (SiO₂, hexane/EtOAc = 9/1).

¹H NMR (CD₂Cl₂, 399.78 MHz) δ: 6.66 (dd, J = 3.6, 0.4 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 7.30–7.40 (m, 2H), 7.60–7.65 (m, 3H), 7.70 (dt, J = 8.4, 2.0 Hz, 2H), 8.36 (dd, J = 8.0, 0.8 Hz, 1H).

¹³C NMR (CD₂Cl₂, 100.53 MHz) δ: 109.1, 116.5, 121.3, 124.4, 125.3, 126.9, 127.7, 131.1, 132.3, 132.7, 133.8, 136.4, 167.9.

¹⁹F NMR (CD₂Cl₂, 376.17 MHz) δ: –62.4 (s, 3F).

IR (KBr): 3348 w, 3173 w, 3116 w, 3079 m, 3051 w, 3034 w, 1945 w, 1925 w, 1800 w, 1742 w, 1678 s, 1604 m, 1587 s, 1540 m, 1504 w, 1482 m, 1471 m, 1451 s, 1395 s, 1381 s, 1351 s, 1292 m, 1277 m, 1246 m, 1205 s, 1186 s, 1149 s, 1126 m, 1113 m, 1090 m, 1073 m, 1065 m, 1010 s, 971 w, 957 w, 944 m, 889 s, 872 s, 841 s, 769 s, 746 s, 732 s, 689 m.

HRMS Calcd for C₁₅H₁₁NOBr ([M+H⁺]): 300.0019. Found: 300.0011.

A dry three-necked flask was charged with (4-bromophenyl)(1H-indol-1-yl)methanone S₅ (1.5 g, 5 mmol), 4-(trifluoromethyl)phenylboronic acid (1.07 g, 5.6 mmol), 2M K₂CO₃ aq. (15 mL), Pd(PPh₃)₄ (18.8 mg, 0.015 mmol), and THF (50 mL) under a nitrogen atmosphere, and the resulting mixture was heated at reflux for 12 h. The mixture was then cooled to room temperature and treated with deionized water, and the resulting mixture was extracted with EtOAc. The combined extracts were then washed with brine, dried (MgSO₄) and concentrated to give a residue, which was purified by column chromatography (hexane/EtOAc = 10/1) to give 1p as a white solid.

White solid (1.3 g, 37%). Mp 192.2–292.3 °C. Rᵢ 0.26 (SiO₂, hexane/EtOAc = 10/1).

¹H NMR (CDCl₃, 399.78 MHz) δ: 6.66 (d, J = 3.6 Hz, 1H), 7.32–7.36 (m, 2H), 7.42 (dd, J = 7.4, 8.1 Hz, 1H), 7.63 (d, J = 7.5 Hz, 1 H), 7.71–7.75 (m, 6H), 7.86 (d, J = 8.5 Hz, 2H), 8.44 (d, J = 8.2 Hz,
1H).  

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 108.8, 116.4, 120.9, 124.1 (q, $J_{CF} = 272.1$ Hz), 124.1, 125.0, 126.0 (q, $J_{CF} = 3.7$ Hz), 127.4, 127.5, 127.6, 130.0, 130.3 (q, $J_{CF} = 32.9$ Hz), 130.8, 134.1, 136.0, 143.2, 143.3, 168.2.

IR (ATR): 3005 w, 2360 w, 1710 s, 1423 w, 1360 m, 1228 m, 1092 w, 899 w.

MS, $m/z$ (relative intensity, %): 365 (M+, 23), 249 (100), 250 (16), 201 (21), 152 (29).

HRMS Calcd for C$_{22}$H$_{15}$F$_3$NO ([M+H$^+$]): 366.1106. Found: 366.1121.

$(E)$-1-(1H-indol-1-yl)-3-phenylprop-2-en-1-one (1q) [CAS 201486-55-7].

![1q](image)

The general procedure I was followed using ciannamoyl chloride. Spectroscopic data were consistent with those reported in the literature.$^{12}$

$(1H$-Indol-1-yl)(quinolin-6-yl)methanone (1r).

![1r](image)

The general procedure II was followed using quinoline-6-carboxylic acid (30 mmol scale). White solid (1.1 g, 13%). Mp 129.0–129.5 °C. R$_f$ 0.1 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 6.66 (d, $J = 3.7$ Hz, 1H), 7.36–7.31 (m, 2H), 7.41 (dd, $J = 7.4$, 7.8 Hz, 1H), 7.53 (dd, $J = 4.1$, 8.3 Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 8.29–8.25 (m, 3H), 8.41 (d, $J = 8.2$ Hz, 1H), 9.06 (d, $J = 4.1$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 109.1, 116.4, 121.1, 122.3, 124.1, 125.1, 126.0, 130.0, 130.2, 130.7, 132.5, 136.0, 137.0, 149.2, 152.5, 168.0.

IR (ATR): 1690 m, 1617 w, 1581 w, 1536 w, 1508 w, 1452 m, 1412 m, 1380 w, 1343 s, 1315 s, 1275

$^{12}$ Yang, Y.; Duan, X.-H.; Deng, J.-Y.; Jin, B.; Jia, H.-M.; Liu, B.-L. Bioorg. Med. Chem. Lett. 2011, 21, 5594.
w, 1232 m, 1206 m, 1176 m, 1127 m, 1042 m, 913 w, 879 w, 808 m, 769 m, 752 m. 
MS, m/z (relative intensity, %): 272 (M⁺, 37), 157 (11), 156 (100), 101 (18).
HRMS Calcd for C₁₈H₁₃N₂O ([M+H⁺]): 273.1028. Found: 273.1034.

Methyl 1-(4-(trifluoromethyl)benzoyl)-1H-indole-5-carboxylate (1s).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.
White solid (5.4 g, 78%). Mp 142.9–143.2 ºC. R₂ 0.14 (SiO₂, hexane/EtOAc = 10/1).
¹H NMR (CDCl₃, 399.78 MHz) δ: 3.96 (s, 3H), 6.72 (d, J = 3.7 Hz, 1H), 7.27 (d, J = 3.7 Hz, 1H), 7.87–7.81 (m, 4H), 8.10 (d, J = 8.7 Hz, 1H), 8.35 (s, 1H), 8.44 (d, J = 8.7 Hz, 1H).
¹³C NMR (CDCl₃, 100.53 MHz) δ: 52.2, 109.6, 116.1, 123.2, 123.4 (q, J_CF = 272.6 Hz), 125.8 (q, J_CF = 3.1 Hz), 126.2, 126.5, 128.1, 129.5, 130.5, 133.8 (q, J_CF = 33.2 Hz), 137.3, 138.5, 167.2, 167.3.
¹⁹F NMR (CDCl₃, 376.17 MHz) δ: –63.0 (s, 3F).
IR (ATR): 3127 w, 1697 m, 1609 w, 1580 w, 1536 w, 1469 w, 1440 m, 1407 w, 1376 m, 1348 w, 1320 s, 1284 w, 1235 m, 1176 s, 1106 s, 1063 m, 1016 w, 989 w, 908 w, 887 m, 852 m, 759 m, 727 w, 701 w, 670 w.
MS, m/z (relative intensity, %): 347 (M⁺, 35), 173 (100), 145 (39).
HRMS Calcd for C₁₈H₁₃F₃NO₃ ([M+H⁺]): 348.0848. Found: 348.0848.

(5-Methyl-1H-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1t).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride (18 mmol).
White solid (3.7 g, 67%). Mp 157.0–159.9 ºC. R₂ 0.34 (SiO₂, hexane/EtOAc = 10/1).
¹H NMR (CDCl₃, 399.78 MHz) δ: 2.48 (s, 3H), 6.58 (d, J = 3.5 Hz, 1H), 7.14 (d, J = 3.5 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.40 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 8.28 (d, J = 8.4
$^1$H NMR (CDCl$_3$, 100.53 MHz) $\delta$: 21.4, 109.3, 116.1, 121.0, 123.5 (q, $J_{CF} = 272.6$ Hz), 125.6 (q, $J_{CF} = 3.1$ Hz), 126.6, 127.0, 129.3, 131.0, 133.4 (q, $J_{CF} = 32.1$ Hz), 134.0, 138.0, 138.0, 167.1.

$^13$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 21.4, 109.3, 116.1, 121.0, 123.5 (q, $J_{CF} = 272.6$ Hz), 125.6 (q, $J_{CF} = 3.1$ Hz), 126.6, 127.0, 129.3, 131.0, 133.4 (q, $J_{CF} = 32.1$ Hz), 134.0, 138.0, 138.0, 167.1.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) $\delta$: –62.9 (s, 3F).

IR (ATR): 1675 w, 1467 w, 1407 w, 1375 w, 1323 m, 1215 w, 1191 w, 1163 m, 1128 m, 1110 w, 1073 w, 1017 w, 908 m, 888 w, 854 w, 814 w, 756 s, 687 w, 669 w.

MS, m/z (relative intensity, %): 303 (M$^+$, 49), 173 (100), 145 (45).

HRMS Calcd for C$_{17}$H$_{13}$F$_3$NO ([M+H$^+$]): 304.0949. Found: 304.0945.

(5-Methoxy-1H-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1u).

![Chemical structure of 1u](image)

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

Pale yellow solid (4.9 g, 77%). Mp 139.5–140.0 °C. R$_f$ 0.2 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 3.88 (s, 3H), 6.58 (d, $J = 3.6$ Hz, 1H), 7.01 (dd, $J = 2.8$, 8.7 Hz, 1H), 7.07 (d, $J = 2.8$ Hz, 1H), 7.14 (d, $J = 3.6$ Hz, 1H), 7.85–7.79 (m, 4H), 8.33 (d, $J = 8.7$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 55.6, 103.7, 109.4, 113.6, 117.3, 123.5 (q, $J_{CF} = 272.6$ Hz), 125.6 (q, $J_{CF} = 4.1$ Hz), 127.6, 129.3, 130.5, 131.8, 133.2 (q, $J_{CF} = 33.2$ Hz), 137.9, 156.9, 166.9.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) $\delta$: –62.9 (s, 3F).

IR (ATR): 2965 w, 1676 m, 1613 m, 1588 w, 1540 w, 1476 m, 1440 m, 1406 m, 1380 m, 1321 m, 1275 m, 1200 m, 1187 m, 1164 s, 1131 s, 1110 m, 1074 m, 1027 m, 941 w, 911 w, 888 m, 853 m, 821 m, 796 w, 755 m, 726 m, 688 w.

MS, m/z (relative intensity, %): 320 (13), 319 (M$^+$, 67), 173 (100), 145 (40).

HRMS Calcd for C$_{17}$H$_{13}$F$_3$NO$_2$ ([M+H$^+$]): 320.0898. Found: 320.0886.

(5-(Benzyloxy)-1H-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1v).

![Chemical structure of 1v](image)
The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (5.5 g, 69%). Mp 177.0–177.3 °C. R_f 0.2 (SiO2, hexane/EtOAc = 10/1).

^1^H NMR (CDCl3, 399.78 MHz) δ: 5.15 (s, 2H), 6.57 (d, J = 3.7 Hz, 1H), 7.10 (d, J = 9.2 Hz, 1H), 7.15–7.14 (m, 2H), 7.34 (d, J = 7.6 Hz, 1H), 7.41 (dd, J = 7.0, 7.6 Hz, 2H), 7.48 (d, J = 7.0 Hz, 2H), 7.85–7.79 (m, 4H), 8.34 (d, J = 9.2 Hz, 1H).

^13^C NMR (CDCl3, 100.53 MHz) δ: 70.5, 105.1, 109.4, 114.4, 117.3, 123.5 (q, J_CF = 272.6 Hz), 125.6 (q, J_CF = 3.1 Hz), 127.5, 127.6, 127.9, 128.6, 129.3, 130.7, 131.7, 133.3 (q, J_CF = 33.2 Hz), 137.0, 137.9, 156.1, 166.9.

^19^F NMR (CDCl3, 376.17 MHz) δ: –62.9 (s, 3F).

IR (ATR): 1673 s, 1586 w, 1538 w, 1454 w, 1406 w, 1383 m, 1334 w, 1272 w, 1193 m, 1156 m, 1138 m, 1114 s, 1078 m, 1017 w, 909 w, 889 w, 855 w, 815 w, 751 s, 727 m, 704 m.

MS, m/z (relative intensity, %): 395 (M^+, 27), 173 (37), 145 (18), 91 (100).

HRMS Calcd for C_{23}H_{17}F_{3}NO_{2} ([M+H^+]): 396.1211. Found: 396.1210.

(3-(2-(Dibenzylamino)ethyl)-5-methoxy-1H-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1w).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride and 2-(5-methoxy-1H-indol-3-yl)-N,N-bis(phenylmethyl)ethanamine S6.

White solid (2.4 g, 44%). Mp 122.5–123.4 °C. R_f 0.23 (SiO2, hexane/EtOAc = 9/1).

^1^H NMR (CD_{2}Cl_{2}, 399.78 MHz) δ: 2.72–2.78 (m, 2H), 2.81–2.86 (m, 2H), 3.62 (s, 4H), 3.75 (s, 3H), 6.77 (d, J = 2.4 Hz, 1H), 6.90 (s, 1H), 6.94 (dd, J = 8.8, 2.4 Hz, 1H), 7.16–7.25 (m, 6H), 7.28–7.31 (m, 4H), 7.79 (s, 4H), 8.27 (d, J = 8.8 Hz, 1H).

^13^C NMR (CD_{2}Cl_{2}, 100.53 MHz) δ: 23.2, 53.0, 55.9, 58.6, 102.1, 113.7, 117.6, 121.7, 124.1 (q, J_CF =
272.4 Hz), 125.0, 125.9 (qt, $J_{CF} = 3.6$ Hz), 127.1, 128.4, 128.9, 129.6, 131.0, 132.6, 133.1 (q, $J_{CF} = 32.6$ Hz), 138.8, 140.1, 157.2, 166.8.

$^{19}$F NMR (CD$_2$Cl$_2$, 376.17 MHz) $\delta$: –63.2 (s, 3F).

IR (KBr, cm$^{-1}$): 3069 m, 3031 m, 2963 m, 2838 m, 2807 m, 1934 w, 1859 w, 1804 w, 1747 w, 1734 w, 1681 s, 1620 m, 1601 s, 1576 m, 1514 m, 1496 m, 1477 s, 1451 s, 1439 s, 1389 s, 1325 s, 1265 s, 1227 s, 1209 s, 1173 s, 1117 s, 1065 s, 1029 s, 980 s, 930 s, 901 s, 849 s, 819 s, 778 s, 770 s, 747 s, 728 s, 698 s, 660 m.

HRMS Calcd for C$_{33}$H$_{30}$F$_3$N$_2$O$_2$ ([M+H$^+$]): 543.2259. Found: 543.2254.

(1H-Pyrrol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1x) [CAS 633313-82-3].

![Chemical Structure](image1.png)

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride. Spectroscopic data were consistent with those reported in the literature.$^{13}$

(9H-Carbazol-9-yl)(4-(trifluoromethyl)phenyl)methanone (1y).

![Chemical Structure](image2.png)

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (5.42 g, 77%). Mp 143.5–143.7 °C. R$_f$ 0.31 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 7.33–7.40 (m, 4H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.80–7.86 (m, 4H), 8.02 (d, $J = 7.8$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 115.7, 120.0, 123.5 (q, $J_{CF} = 272.6$ Hz), 123.9, 126.0 (q, $J_{CF} = 3.1$ Hz), 126.2, 127.0, 129.3, 133.8 (q, $J_{CF} = 32.2$ Hz), 138.8, 139.0, 168.1.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) $\delta$: –62.8 (s, 3F).

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$^{13}$ Meng, G.; Szostak, R.; Szostak, M. Org. Lett. 2017, 19, 3596.
IR (ATR): 1678 m, 1585 w, 1513 w, 1478 w, 1443 m, 1408 w, 1360 w, 1302 s, 1214 w, 1169 m, 1128 s, 1075 m, 1064 m, 1018 w, 948 w, 873 w, 840 w, 753 s, 722 m, 700 w, 672 w.

MS, m/z (relative intensity, %): 339 (M⁺, 44), 173 (100), 145 (41).

HRMS Calcd for C₂₀H₁₃F₃NO ([M+H⁺]): 340.0944. Found: 340.0945

(1H-Pyrrolo[2,3-b]pyridin-1-yl)(4-(trifluoromethyl)phenyl)methanone (1z).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (3.1 g, 53%). Mp 91.7–92.0 °C. Rᵣ 0.2 (SiO₂, hexane/EtOAc = 10/1).

¹H NMR (CDCl₃, 399.78 MHz) δ: 6.68 (d, J = 4.1 Hz, 1H), 7.19 (dd, J = 4.6, 7.8 Hz, 1H), 7.74–7.77 (m, 3H), 7.89–7.93 (m, 3H), 8.23 (d, J = 4.6 Hz, 1H).

¹³C NMR (CDCl₃, 100.53 MHz) δ: 106.6, 119.3, 123.3, 125.0 (q, JCF = 272.6 Hz), 127.0, 127.7 (q, JCF = 3.1 Hz), 129.4, 130.3, 133.8 (q, JCF = 32.2 Hz), 137.4, 144.4, 148.0, 166.5.

¹⁹F NMR (CDCl₃, 376.17 MHz) δ: –62.9 (s, 3F).

IR (ATR): 1687 s, 1583 w, 1531 w, 1409 s, 1330 w, 1268 m, 1160 m, 1112 s, 1068 m, 1018 w, 925 w, 852 w, 804 w, 771 m, 725 w, 692 w.

MS, m/z (relative intensity, %): 290 (M⁺, 33), 289 (50), 263 (13), 262 (80), 173 (100).

HRMS Calcd for C₁₅H₁₀F₃N₂O ([M+H⁺]): 291.0748. Found: 291.0745.

(10H-Phenoxazin-10-yl)(4-(trifluoromethyl)phenyl)methanone (1aa).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

Pale yellow solid (5.5 g, 77%). Mp 131.1–131.6 °C. Rᵣ 0.2 (SiO₂, hexane/EtOAc = 10/1).

¹H NMR (CDCl₃, 399.78 MHz) δ: 6.94–6.99 (m, 2H), 7.15–7.17 (m, 4H), 7.32 (d, J = 8.2 Hz, 2H), 7.55 (m, 4H).
$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 116.8, 123.45, 123.53 (q, $J_{CF}$ = 272.6 Hz), 124.6, 125.1 (q, $J_{CF}$ = 3.1 Hz), 126.9, 129.2, 129.5, 132.2 (q, $J_{CF}$ = 33.2 Hz), 138.5, 150.3, 166.7.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) δ: −62.8 (s, 3F).

IR (ATR): 1668 m, 1579 w, 1481 m, 1409 w, 1321 s, 1272 m, 1170 w, 1128 m, 1087 w, 1066 w, 1020 w, 883 w, 842 w, 765 m, 669 w.

MS, $m/z$ (relative intensity, %): 355 (M$^+$, 22), 182 (100), 173 (28), 145 (11).

HRMS Calcd for C$_{20}$H$_{13}$F$_3$NO$_2$ ([M+H$^+$]): 356.0898. Found: 356.0894.

$N,N$-Diphenyl-4-(trifluoromethyl)benzamide (S7) [CAS 77826-14-3].

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (3.7 g, 54%). Mp 142.0–142.4 °C. R$_f$ 0.1 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) δ: 7.15–7.23 (m, 6H), 7.29–7.33 (m, 4H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 123.6 (q, $J_{CF}$ = 272.6 Hz), 124.9 (q, $J_{CF}$ = 4.2 Hz), 126.8, 127.4, 129.26, 129.34, 131.7 (q, $J_{CF}$ = 32.1 Hz), 139.6, 143.2, 169.1.

IR (ATR): 2356 w, 1660 m, 1592 w, 1488 w, 1407 w, 1319 s, 1218 w, 1168 m, 1124 m, 1066 w, 1020 w, 840 w, 769 s, 696 m.

MS, $m/z$ (relative intensity, %): 341 (M$^+$, 29), 248 (39), 173 (100), 167 (10), 145 (41).

HRMS Calcd for C$_{20}$H$_{15}$F$_3$NO ([M+H$^+$]): 342.1100. Found: 342.1101.

$4$-(Trifluoromethyl)-$N,N$-bis(4-(trifluoromethyl)phenyl)benzamide (1ab).

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (685 mg, 18%). Mp 112.4–112.8 °C. R$_f$ 0.14 (SiO$_2$, hexane/CHCl$_3$ = 1/1).
1H NMR (CD2Cl2, 399.78 MHz) δ: 7.27 (d, J = 8.4 Hz, 4H), 7.54–7.62 (m, 8H).
13C NMR (CD2Cl2, 100.53 MHz) δ: 124.0(q, JCF = 272.6 Hz), 124.2(q, JCF = 272.2 Hz), 125.7(qt, JCF = 3.6 Hz), 126.9(qt, JCF = 3.8 Hz), 128.1, 129.0(q, JCF = 32.8 Hz), 129.9, 132.6(q, JCF = 32.6 Hz), 139.0, 146.4, 169.3.
19F NMR (CD2Cl2, 376.17 MHz) δ: –61.4 (s, 6F), –60.8 (s, 3F).
IR (KBr, cm\(^{-1}\)):
3314 w, 3082 w, 2931 w, 2640 w, 1919 w, 1805 w, 1752 w, 1666 s, 1613 s, 1583 m, 1516 s, 1409 s, 1325 s, 1170 s, 1127 s, 1068 s, 1019 s, 963 m, 876 m, 845 s, 770 s, 741 w, 722 w, 703 m, 656 m.
HRMS Calcd for C22H13F9NO ([M+H\(^+\)]): 478.0848. Found: 478.0853.

3-(9H-Carbazol-9-yl)benzoic acid (4) [CAS: 19287-67-3].

A mixture of carbazole (4.68 g, 28.0 mmol), ethyl 3-iodobenzoate 3 (5.52 g, 20.0 mmol), CuI (762 mg, 4.0 mmol), Cs2CO3 (13.0 g, 40 mmol) in DMF (40 mL) was vigorously stirred at 120 °C under nitrogen atmosphere for 24 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (160 mL) and washed with H2O (2×120 mL). The aqueous phase was extracted with EtOAc (2×120 mL), and the combined organic phases were dried over Na2SO4. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 9/1) to give S8\(^{14}\) (3.00 g, 48%) as a white solid.

White solid (3.00 mg, 48%). Mp 91.1–92.0 °C. R\(_f\) 0.37 (SiO2, hexane/EtOAc = 9/1).
1H NMR (CDCl3, 399.78 MHz) δ: 1.41 (t, J = 7.1 Hz, 3H), 4.43 (q, J = 7.0 Hz, 2H), 7.30–7.34 (m, 2H), 7.39–7.46 (m, 4H), 7.70 (t, J = 7.8 Hz, 1H), 7.78 (dt, J = 7.9, 1.7 Hz, 1H), 8.17 (dd, J = 7.8, 0.9 Hz, 3H), 8.28 (t, J = 1.8 Hz, 1H).
13C NMR (CDCl3, 100.53 MHz) δ: 14.3, 61.4, 109.6, 120.2, 120.4, 123.5, 126.1, 128.2, 128.5, 130.0, 131.5, 132.6, 138.0, 140.7, 165.8.
IR (KBr, cm\(^{-1}\)):
3042 w, 2991 w, 1732 s, 1596 m, 1498 m, 1480 m, 1451 s, 1365 s, 1336 m, 1314 m, 1292 s, 1260 s, 1227 s, 1179 m, 1120 m, 1099 m, 1080 s, 1023 s, 1003 w, 920 m, 879 w, 750 s, 721 s, 690 s.
MS, m/z (relative intensity, %): 316(23), 315 (M\(^+\), 100), 288(15), 287 (70), 242(23), 241 (42), 240(11),

\(^{14}\) Swapna, K.; Murthy, S. N.; Nageswar, Y. V. D. *Eur. J. Org. Chem.* **2010**, 2010, 6678.
Ethyl 3-(9H-carbazol-9-yl)benzoate **S8** (2.71 g, 8.6 mmol) in mixed solution of MeOH (25 mL), THF (25 mL), 1 M NaOH aq. (17.2 mL, 17.2 mmol) was stirred at 50 °C for 8 h. After cooling the mixture to ambient temperature, 1M HCl aq (17.2 mL, 17.2 mmol) was added to the reaction solution, and the precipitated solid was collected by filtration and dried to give **4**.

White solid (2.36 g, 96%). Mp 233.4–234.3 °C. Rf 0.71 (SiO2, methanol/EtOAc = 1/1).

$^1$H NMR (CD3OD, 399.78 MHz) δ: 4.85 (s, 1H), 7.25–7.28 (m, 2H), 7.34–7.42 (m, 4H), 7.73–7.81 (m, 2H), 8.13–8.16 (m, 3H), 8.18 (t, $J = 1.8$ Hz, 1H).

$^{13}$C NMR (CD3OD, 100.53 MHz) δ: 110.5, 121.3, 121.4, 124.9, 127.3, 129.0, 129.7, 131.4, 132.5, 134.2, 139.4, 142.0, 168.9.

IR (KBr, cm$^{-1}$): 3042 m, 2827 m, 2679 m, 2575 m, 1683 s, 1586 s, 1492 s, 1463 s, 1450 s, 1362 s, 1307 s, 1229 s, 1166 m, 1149 m, 1199 m, 1084 w, 1002 m, 979 m, 939 m, 927 m, 815 w, 746 s, 722 s, 691 s, 669 m.

HRMS Calcd for C19H13NO2 ([M+] ): 287.0946. Found: 287.0946.

(3-(9H-Carbazol-9-yl)phenyl)(1H-indol-1-yl)methanone (**S9**).

DMF (30 µL) was added to a solution of (3 mmol) and oxalyl chloride (6 mmol, 2 equiv) in 30 mL of CH2Cl2 at 0 °C. After gas evolution ceased, the mixture was allowed to be gradually warm to room temperature and was then stirred until the starting carboxylic acid was disappeared by TLC. The solution was concentrated to give an aroyl chloride, which was used in the next step without further purification. The aroyl chloride was partially added to a solution of indole (3 mmol, 1 equiv), Et3N (1 equiv) and N,N-dimethyl-4-aminopyridine (0.06 mmol) in 40 mL of CH2Cl2 at 0 °C. After addition was completed, the reaction mixture was stirred at room temperature for 12 hour. The reaction was quenched by the addition of H2O, and the resulting mixture was extracted with CH2Cl2. The combined extracts were washed with brine, dried (MgSO4), and concentrated to give a residue, which was purified by column chromatography and GPC to give a white solid.

S22
White solid (712 mg, 60%). Mp 74.2–76.1 °C. R\textsubscript{f} 0.69 (NH silica, hexane/CH\textsubscript{2}Cl\textsubscript{2} = 1/1).

\textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 399.78 MHz) \(\delta: 6.69\) (d, \(J = 3.7\) Hz, 1H), 7.31–7.36 (m, 3H), 7.39–7.51 (m, 6H), 7.64 (d, \(J = 7.8\) Hz, 1H), 7.79–7.89 (m, 3H), 7.98 (t, \(J = 1.6\) Hz, 1H), 8.17 (d, \(J = 7.8\) Hz, 2H), 8.43 (d, \(J = 8.2\) Hz, 1H).

\textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}, 100.53 MHz) \(\delta: 119.2, 120.1, 126.8, 130.8, 130.9, 131.5, 133.9, 134.5, 135.4, 136.7, 137.8, 138.0, 138.4, 140.7, 140.9, 141.3, 146.5, 147.0, 148.5, 150.9, 177.9.\)

IR (KBr, cm\textsuperscript{-1}): 3055 w, 1687 s, 1597 m, 1584 m, 1535 m, 1495 s, 1477 m, 1451 s, 1378 s, 1362 s, 1337 s, 1230 s, 1206 s, 1150 m, 1123 w, 1067 w, 1016 w, 926 w, 889 m, 872 w, 809 w, 750 s, 699 m.

MS, \(m/z\) (relative intensity, %): 387 (19), 386 (M\textsuperscript{+}, 57), 271 (13), 270 (57), 243 (17), 242 (100), 241 (71), 240 (11), 207 (22), 193 (15), 121 (15), 116 (11), 73 (20), 44 (11).

HRMS Calcd for C\textsubscript{27}H\textsubscript{18}N\textsubscript{2}O ([M+]): 386.1419. Found: 386.1425.

(1\textit{H}-Benzo[\textit{d}][imidazol-1-yl])(4-(trifluoromethyl)phenyl)methanone (7b) [CAS: 1907216-47-0].

The general procedure I was followed using 4-(trifluoromethyl)benzoyl chloride.

White solid (4.4 g, 75%). Mp 161.1–161.4 °C. R\textsubscript{f} 0.49 (SiO\textsubscript{2}, hexane/EtOAc = 1/1).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 399.78 MHz) \(\delta: 7.43–7.49\) (m, 2H), 7.83–7.88 (m, 3H), 7.93 (d, \(J = 8.1\) Hz, 2H), 8.14 (s, 1H), 8.18–8.20 (m, 1H).

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100.53 MHz) \(\delta: 165.8, 144.0, 142.5, 136.1, 134.6\) (q, \(J\textsubscript{CF} = 33.2\) Hz), 131.8, 129.8, 126.1 (q, \(J\textsubscript{CF} = 4.2\) Hz), 126.1, 125.7, 123.2 (q, \(J\textsubscript{CF} = 272.6\) Hz), 120.7, 115.5.

IR (ATR): 3101 w, 2360 w, 1697 m, 1606 w, 1514 w, 1452 w, 1410 w, 1369 w, 1327 m, 1198 m, 1167 m, 1130 m, 1066 w, 906 w, 852 w, 756 w.

MS, \(m/z\) (relative intensity, %): 290 (M\textsuperscript{+}, 46), 174 (14), 173 (100), 145 (89), 95 (16), 90 (10).

HRMS Calcd for C\textsubscript{15}H\textsubscript{10}F\textsubscript{3}N\textsubscript{2}O ([M+H\textsuperscript{+}]): 291.0740. Found: 291.0747.

(1\textit{H}-Benzo[\textit{d}][imidazol-1-yl])(4-methoxyphenyl)methanone (7d) [CAS: 13361-55-2].
The general procedure I was followed using 4-methoxybenzoyl chloride. Spectroscopic data were consistent with those reported in the literature.\(^{15}\)

(1H-Benzol[d]imidazol-1-yl)(3,5-bis(trifluoromethyl)phenyl)methanone (7e) [CAS: 1899226-42-6].

The general procedure I was followed using 3,5-bis(trifluoromethyl)benzoyl chloride (6 mmol scale). White solid (1.2 g, 55%). Mp 84.7–84.1 °C. Rf 0.66 (SiO\(_2\), hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \(\delta\): 8.27 (s, 2H), 8.21 (s, 1H), 8.21–8.16 (m, 1H), 8.10 (s, 1H), 7.87–7.85 (m, 1H), 7.52–7.46 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\), 100.53 MHz) \(\delta\): 164.1, 144.1, 141.8, 134.9, 133.0 (q, \(J_{CF} = 34.2\) Hz), 131.7, 129.4 (q, \(J_{CF} = 3.1\) Hz), 126.5 (qt, \(J_{CF} = 3.1\) Hz), 126.0, 122.5 (q, \(J_{CF} = 273.1\) Hz), 120.9, 118.4, 115.4.

IR (ATR): 2360 w, 1707 m, 1512 w, 1452 w, 1396 w, 1356 m, 1284 s, 1180 s, 1142 s, 910 w, 771 s, 708 w.

MS, \(m/z\) (relative intensity, %): 358 (M\(^+\), 33), 242 (10), 241 (100), 213 (48), 163 (10).

HRMS calcd for C\(_{16}\)H\(_9\)F\(_6\)N\(_2\)O ([M+H\(^+\)]): 359.0614. Found: 359.0628.

(1H-Benzol[d]imidazol-1-yl)(3,5-dimethylphenyl)methanone (7f).

\(^{15}\) Ding, W.; Mai, S.; Song, Q. Beilstein. J. Org. Chem. 2015, 11, 2158.
The general procedure I was followed using 3,5-dimethylbenzoyl chloride.
White solid (1.7 g, 35%). Mp 197.4–197.8 °C. Rf 0.54 (SiO₂, hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl₃, 399.78 MHz) \(\delta\): 8.23 (s, 1H), 8.22–8.20 (m, 1H), 7.85–7.83 (m, 1H), 7.48–7.40 (m, 4H), 7.31 (s, 1H), 2.42 (s, 6H).

\(^{13}\)C NMR (CDCl₃, 100.53 MHz) \(\delta\): 167.5, 144.1, 143.3, 138.9, 134.8, 132.8, 132.1, 127.2, 125.7, 125.2, 120.5, 115.5, 21.2.
IR (ATR): 2349 w, 1720 w, 1650 w, 1518 m, 1364 m, 1281 m, 1241 m, 1217 m, 1176 m, 1145 m, 1024 w, 912 w, 771 s, 709 m, 663 w.
MS, \(m/z\) (relative intensity, %): 250 (M⁺, 18), 133 (100), 105 (34), 103 (10), 79 (17), 77 (17).
HRMS calcd for C₁₆H₁₅N₂O ([M+H⁺]): 251.1179. Found: 251.1186.

\((1H\text{-}\text{Benzo}[d]\text{imidazol-1-yl})(3,5\text{-dimethoxyphenyl})\text{methanone (7g)}\) [CAS: 333347-97-0].

\begin{center}
\includegraphics[width=0.2\textwidth]{7g.png}
\end{center}

The general procedure I was followed using 3,5-dimethoxybenzoyl chloride.
White solid (4.1 g, 73%). Mp 109.2–109.5 °C. Rf 0.36 (SiO₂, hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl₃, 399.78 MHz) \(\delta\): 8.27 (s, 1H), 8.23–8.20 (m, 1H), 7.85–7.83 (m, 1H), 7.49–7.42 (m, 2H), 6.89 (d, \(J = 2.3\) Hz, 2H), 6.73 (d, \(J = 2.3\) Hz, 1H), 2.29 (s, 6H).

\(^{13}\)C NMR (CDCl₃, 100.53 MHz) \(\delta\): 166.9, 161.1, 144.1, 143.1, 134.6, 132.1, 125.8, 125.3, 120.6, 115.5, 107.2, 105.1, 55.7.
IR (ATR): 2360 m, 1705 m, 1599 m, 1510 m, 1452 m, 1360 m, 1284 s, 1146 m, 1063 m, 771 s.
MS, \(m/z\) (relative intensity, %): 282 (M⁺, 24), 165 (100), 137 (29), 122 (22), 107 (13), 77 (12).
HRMS calcd for C₁₆H₁₅N₂O₃ ([M+H⁺]): 283.1077. Found: 283.1099.

\((1H\text{-}\text{Benzo}[d]\text{imidazol-1-yl})(3,5\text{-difluorophenyl})\text{methanone (7h)}\) [CAS: 1789402-95-4].

\begin{center}
\includegraphics[width=0.2\textwidth]{7h.png}
\end{center}

S25
The general procedure I was followed using 3,5-difluorobenzoyl chloride.

White solid (3.4 g, 66%). Mp 125.0–125.3 °C. R$_f$ 0.54 (SiO$_2$, hexane/EtOAc = 1/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) δ: 8.20–8.16 (m, 2H), 7.86–7.83 (m, 1H), 7.50–7.44 (m, 2H), 7.37-7.31 (m, 2H), 7.16 (tt, $J = 2.3, 8.5$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 164.4 (t, $J_{CF} = 3.0$ Hz), 163.0 (dd, $J_{CF} = 12.0, 253.5$ Hz), 144.1, 142.2, 135.6 (t, $J_{CF} = 8.8$ Hz), 131.8, 126.2, 125.7, 120.8, 115.4, 112.72 (dd, $J_{CF} = 8.3, 19.4$ Hz), 108.7 (t, $J_{CF} = 24.9$ Hz).

IR (ATR): 3094 m, 1692 m, 1598 m, 1513 m, 1477 m, 1452 m, 1378 s, 1324 m, 1287 m, 1221 m, 1193 m, 1133 m, 1000 m, 978 m, 912 w, 869 m, 799 s, 772 s, 754 s, 678 w.

MS, m/z (relative intensity, %): 259 (10), 258 (M$^+$, 60), 142 (18), 141 (100), 113 (86), 90 (11), 63 (35).

HRMS calcd for C$_{14}$H$_9$F$_2$N$_2$O ([M+H$^+$]): 259.0677. Found: 259.0703.

**3,5-bis(trifluoromethyl)phenyl)(1$H$-imidazol-1-yl)methanone (7i).**

![3,5-bis(trifluoromethyl)phenyl)(1$H$-imidazol-1-yl)methanone (7i)](image)

The general procedure I was followed using 3,5-bis(trifluoromethyl)benzoyl chloride.

White solid (4.6 g, 75%). Mp 125.0–125.3 °C. R$_f$ 0.66 (SiO$_2$, EtOAc).

$^1$H NMR (CDCl$_3$, 399.78 MHz) δ: 8.30 (s, 2H), 8.20 (s, 1H), 8.06 (s, 1H), 7.51 (t, $J = 1.5$ Hz, 1H), 7.24 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 163.4, 137.7, 134.0, 133.1 (q, $J_{CF} = 34.5$ Hz), 132.1, 129.6 (q, $J_{CF}$ = 3.6 Hz), 126.9 (qt, $J_{CF} = 3.7$ Hz), 122.4 (q, $J_{CF} = 273.2$ Hz), 117.7.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) δ: –62.9 (s, 6F).

IR (ATR): 1720 m, 1621 w, 1472 w, 1397 m, 1365 m, 1281 s, 1242 m, 1175 m, 1137 s, 1024 m, 947 w, 911 m, 774 s, 710 m, 681 m.

MS, m/z (relative intensity, %): 308 (M$^+$, 13), 242 (13), 241 (100), 213 (76), 163 (21), 144 (11), 143 (10).

HRMS calcd for C$_{12}$H$_7$F$_6$N$_2$O ([M+H$^+$]): 309.0457. Found: 309.0469.

**IV. Optimization Studies.**
1,2-Migratory decarbonylation of N-acyl imidazoles.

![Chemical structure](image)

**V. Typical Procedures.**

**Condition A: Procedure for the Ni/dcype-catalyzed decarbonylation of N-acylpyrrole derivatives.** Ni(cod)$_2$ (13.8 mg, 0.050 mmol), dcype (21.1 mg, 0.050 mmol), N-acylpyrrole derivatives and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was then closed. The contents of the vial were then stirred at 180 °C for 18 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel before being analyzed by GC. The filtrate was then concentrated *in vacuo* to give a residue, which was purified by flash column chromatography over silica gel.

| entry | ligand | GC yields (%)$^a$ |
|-------|--------|------------------|
|       |        | 9b   | 7b   |
| 1     | PPh$_3$ | 0    | 0    |
| 2     | PCy$_3$ | 0    | 58   |
| 3     | dcype   | 77   | 0    |
| 4     | dcypb   | 11   | 36   |
| 5     | dcypf   | 0    | 57   |
| 7     | dppe    | 0    | 68   |
| 8$^b$ | ICy     | 0    | 35   |
| 9$^b$ | IMes    | 0    | 35   |
| 10$^b$| IMes$_{Me}$ | 0    | 34   |
| 11$^b$| IPr     | 0    | 78   |

$^a$Determined by GC using undecane as an internal standard.

$^b$Carbene was generated in situ from the corresponding imidazolium salt and NaO'Bu (25 mol%) was used to generate carbene.
Condition B: Procedure for the Ni/PCy3-mediated decarbonylation of N-acylpyrrole derivatives.
Ni(cod)₂ (68.8 mg, 0.25 mmol), PCy₃ (70.1 mg, 0.25 mmol), N-acylpyrrole derivatives and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was then closed. The contents of the vial were then stirred at 80 °C for 18 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel before being analyzed by GC. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography over silica gel.

VI. Spectroscopic Data of Products.
1-(4-(Trifluoromethyl)phenyl)-1H-indole (2a) [CAS: 174621-55-7].

\[ \text{F}_3\text{C} \quad \text{2a} \]

White solid (54.9 mg, 84%). Rf 0.57 (SiO₂, hexane/EtOAc = 20/1).
\[ ^1\text{H} \text{NMR (CDCl₃, 399.78 MHz) } \delta: 6.76 (d, J = 3.2 \text{ Hz, 1H}), 7.23 (dd, J = 6.9, 7.8 \text{ Hz, 1H}), 7.29 (dd, J = 6.8, 8.2 \text{ Hz, 1H}), 7.37 (d, J = 3.2 \text{ Hz, 1H}), 7.61-7.66 (m, 3H), 7.72 (d, J = 7.8 \text{ Hz, 1H}), 7.80 (d, J = 8.7 \text{ Hz, 2H}). \]
\[ ^{13}\text{C} \text{NMR (CDCl₃, 100.53 MHz)} \delta: 104.9, 110.3, 121.0, 121.4, 122.9, 123.9, 124.0 (q, J_{CF} = 272.6 \text{ Hz}), 126.9 (q, J_{CF} = 4.1 \text{ Hz}), 127.4, 128.2 (q, J_{CF} = 28.0 \text{ Hz}), 129.7, 135.5, 142.8. \]
HRMS Calcd for C₁₅H₁₁F₃N ([M+H⁺]): 262.0838. Found: 262.0839.

Methyl 4-(1H-indol-1-yl)benzoate (2b) [CAS: 212382-74-6].

\[ \text{MeO₂C} \quad \text{2b} \]

Methyl 4-(1H-indol-1-yl)benzoate (2b) [CAS: 212382-74-6].
The typical procedure (Condition A) was followed using 1b as the substrate.

Colorless oil (53.4 mg, 85%). R_f 0.23 (SiO2, hexane/EtOAc = 20/1).

^{1}H NMR (CDCl3, 399.78 MHz) δ: 3.97 (s, 3H), 6.73 (d, J = 3.6 Hz, 1H), 7.21 (dd, J = 7.3, 7.8 Hz, 1H), 7.27 (dd, J = 7.3, 8.2 Hz, 1H), 7.38 (d, J = 3.6 Hz, 1H), 7.60 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 8.7 Hz, 2H).

^{13}C NMR (CDCl3, 100.53 MHz) δ: 52.2, 104.9, 110.5, 120.9, 121.4, 122.9, 123.2, 127.4, 127.6, 129.8, 131.2, 135.4, 143.7, 166.4.

HRMS Calcd for C_{16}H_{14}NO_{2} ([M+H]^+): 252.1019. Found: 252.1017.

1-(1,1'-Biphenyl)-4-yl-1H-indole (2c) [CAS: 174621-51-3].

The typical procedure (Conditions A and B) was followed using 1c as the substrate.

White solid (30% GC yield for Condition A, 53.2 mg, 79% for Condition B).

R_f 0.57 (SiO2, hexane/EtOAc = 20/1).

^{1}H NMR (CDCl3, 399.78 MHz) δ: 6.75 (d, J = 3.2 Hz, 1H), 7.22 (dd, J = 6.8, 7.3 Hz, 1H), 7.29 (dd, J = 7.3, 8.2 Hz, 1H), 7.39–7.44 (m, 2H), 7.49–7.54 (m, 2H), 7.59–7.62 (m, 2H), 7.66–7.70 (m, 3H), 7.34–7.78 (m, 3H).

^{13}C NMR (CDCl3, 100.53 MHz) δ: 103.7, 110.6, 120.4, 121.2, 122.4, 124.5, 127.0, 127.5, 127.8, 128.2, 128.9, 129.4, 135.8, 139.0, 139.3, 140.2.

HRMS Calcd for C_{20}H_{16}N ([M+H]^+): 270.1277. Found: 270.1274.

1-Phenyl-1H-indole (2d) [CAS: 16096-33-6].

The typical procedure (Conditions A and B) was followed using 1d as the substrate.

White solid (23% GC yield for Condition A, 34.3 mg, 71% for Condition B).
Rf 0.49 (SiO2, hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl3, 399.78 MHz) \(\delta\): 6.70 (d, \(J = 3.2\) Hz, 1H), 7.19 (dd, \(J = 6.9, 7.3\) Hz, 1H), 7.24 (dd, \(J = 7.3, 8.2\) Hz, 1H), 7.39–7.35 (m, 2H), 7.52–7.54 (m, 4H), 7.59 (d, \(J = 6.8\) Hz, 1H), 7.71 (d, \(J = 8.2\) Hz, 1H).

\(^{13}\)C NMR (CDCl3, 100.53 MHz) \(\delta\): 103.5, 110.5, 120.3, 121.1, 122.3, 124.4, 126.4, 127.9, 129.3, 129.6, 135.8, 139.8.

HRMS Calcd for C_{14}H_{12}N ([M+H]+): 194.0964. Found: 194.0974.

1-(p-Tolyl)-1H-indole (2e) [CAS: 167283-32-1].

The typical procedure (Conditions A and B) was followed using 1e as the substrate.

Colorless oil (18% GC yield for Condition A, 32.6 mg, 63% for Condition B).

Rf 0.49 (SiO2, hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl3, 399.78 MHz) \(\delta\): 2.45 (s, 3H), 6.67 (d, \(J = 3.2\) Hz, 1H), 7.17 (dd, \(J = 6.9, 7.8\) Hz, 1H), 7.21 (dd, \(J = 6.9, 8.3\) Hz, 1H), 7.33–7.31 (m, 3H), 7.40 (d, \(J = 8.3\) Hz, 2H), 7.54 (d, \(J = 8.3\) Hz, 1H), 7.70 (d, \(J = 7.8\) Hz, 1H).

\(^{13}\)C NMR (CDCl3, 100.53 MHz) \(\delta\): 21.0, 103.2, 110.5, 120.1, 121.0, 122.2, 124.3, 128.0, 129.1, 130.1, 136.0, 136.3, 137.3.

HRMS Calcd for C_{15}H_{14}N ([M+H]+): 208.1121. Found: 208.1122.

1-(4-Methoxyphenyl)-1H-indole (2f) [CAS: 93597-01-4].

The typical procedure (Conditions A and B) was followed using 1f as the substrate.

The yield under condition A was determined to be 8% by GC. The yield under condition B was determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard (14%). Isolated
yield under condition B was 12% (6.7 mg). The yield was increased to 33% GC yield when Ni(cod)$_2$ (100 mol%) and 3,4-bis(dicyclohexylphosphino)thiophene (100 mol%) were used as the catalyst at 180 °C.

$R_f$ 0.47 (SiO$_2$, hexane/EtOAc = 9/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 3.90 (s, 3H), 6.70 (dd, $J = 3.2$, 0.7 Hz, 1H), 7.04–7.08 (m, 2H), 7.18–7.27 (m, 2H), 7.32 (d, $J = 3.2$ Hz, 1H), 7.42–7.46 (m, 2H), 7.50 (dd, $J = 8.1$, 0.9 Hz, 1H), 7.72–7.74 (m, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 55.5, 102.8, 110.3, 114.7, 120.0, 121.0, 122.1, 125.9, 128.2, 128.9, 132.8, 136.2, 158.2.

HRMS Calcd for C$_{15}$H$_{14}$NO ([M+H$^+$]): 224.1070. Found: 224.1077.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(1H-indol-1-yl)benzoate (2g).

The typical procedure (Condition A) was followed using 1g as the substrate.

Colorless oil (89.2 mg, 95%). $R_f$ 0.71 (NH silica, hexane/CH$_2$Cl$_2$ – 1/1).

$^1$H NMR (CD$_2$Cl$_2$, 399.78 MHz) $\delta$: 0.83 (d, $J = 6.8$ Hz, 3H), 0.91–1.02 (m, 7H), 1.09–1.27 (m, 2H), 1.53–1.65 (m, 2H), 1.74–1.79 (m, 2H), 1.95–2.05 (m, 1H), 2.12–2.17 (m, 1H), 4.96 (td, $J = 10.8$, 4.0 Hz, 1H), 6.73 (dd, $J = 3.3$, 0.8 Hz, 1H), 7.17–7.27 (m, 2H), 7.42 (d, $J = 3.2$ Hz, 1H), 7.60–7.69 (m, 4H), 8.20 (dt, $J = 8.8$, 2.0 Hz, 2H).

$^{13}$C NMR (CD$_2$Cl$_2$, 100.53 MHz) $\delta$: 16.6, 20.9, 22.2, 23.9, 26.9, 31.8, 34.6, 41.3, 47.6, 75.3, 104.9, 110.9, 121.2, 121.6, 123.1, 123.5, 127.9, 128.8, 130.1, 131.4, 135.8, 143.8, 165.5.

IR (KBr, cm$^{-1}$): 3400 w, 3053 m, 2954 s, 2925 s, 2868 s, 1928 w, 1712 s, 1604 s, 1519 s, 1455 s, 1335 s, 1311 s, 1274 s, 1236 s, 1211 s, 1175 s, 1117 s, 1099 s, 1038 m, 1014 s, 983 s, 954 s, 917 m, 883 m, 862 s, 775 s, 759 s, 741 s, 715 s, 700 s.

HRMS Calcd for C$_{25}$H$_{30}$NO$_2$ ([M+H$^+$]): 376.2271. Found: 376.2271.

1-(3-(Trifluoromethyl)phenyl)-1H-indole (2h) [CAS: 167283-36-5].
The typical procedure (Condition A) was followed using 1h as the substrate. Colorless oil (47.0 mg, 72%). Rf 0.4 (SiO2, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl3, 399.78 MHz) $\delta$: 6.74 (d, $J = 3.2$ Hz, 1H), 7.22 (dd, $J = 6.9, 7.8$ Hz, 1H), 7.28 (dd, $J = 6.9, 7.4$ Hz, 1H), 7.36 (d, $J = 3.2$ Hz, 1H), 7.56 (d, $J = 3.2$ Hz, 1H), 7.69–7.62 (m, 2H), 7.74–7.71 (m, 2H), 7.79 (s, 1H).

$^{13}$C NMR (CDCl3, 100.53 MHz) $\delta$: 104.6, 110.1, 120.9, 121.0 (q, $J_{CF} = 3.8$ Hz), 121.4, 122.9, 123.0 (q, $J_{CF} = 3.8$ Hz), 123.7 (q, $J_{CF} = 273.1$ Hz), 127.3, 127.5, 129.5, 130.3, 132.4 (q, $J_{CF} = 32.6$ Hz), 135.6, 140.3.

IR (ATR): 3058 w, 1698 w, 1598 w, 1496 w, 1461 m, 1319 m, 1272 w, 1213 w, 1170 m, 1128 s, 1070 w, 975 w, 894 w, 800 w, 742 m, 703 m.

MS, m/z (relative intensity, %): 262.2 (17), 261.1 (M+, 100), 165.1 (9), 90 (9), 89 (9).

HRMS Calcd for C15H11F3N ([M+H+]): 262.0838. Found: 262.0840.

1-(3,5-Dimethoxyphenyl)-1H-indole (2i).

The typical procedure (Conditions A and B) was followed using 1i as the substrate. White solid (30.9 mg, 49% for Condition A, 43.8 mg, 69% for Condition B). Rf 0.17 (SiO2, hexane/EtOAc = 20/1).

$^1$H NMR (CDCl3, 399.78 MHz) $\delta$: 3.86 (s, 6H), 6.48 (t, $J = 2.2$ Hz, 1H), 6.68 (m, 3H), 7.18 (dd, 7.1, 7.7 Hz, 1H), 7.24 (dd, 7.1, 8.2 Hz, 1H), 7.35 (d, $J = 3.4$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1 H), 7.69 (d, $J = 7.7$ Hz, 1H).

$^{13}$C NMR (CDCl3, 100.53 MHz) $\delta$: 55.5, 98.4, 102.7, 103.5, 110.8, 120.4, 121.1, 122.4, 127.9, 129.3, 135.7, 141.4, 161.4.

IR (ATR): 2937 w, 2360 w, 1716 w, 1601 s, 1516 m, 1459 m, 1321 m, 1275 m, 1211 s, 1157 m, 1128
m, 1061 w, 931 w, 839 w, 742 m, 690 w.

MS, m/z (relative intensity, %): 254 (18), 253 (M+, 100), 224 (11), 167 (16).

HRMS Calcd for C_{16}H_{16}NO_{2} ([M+H^{+}]): 254.1176. Found: 254.1166.

1-(3-Methoxy-4-(trifluoromethyl)phenyl)-1H-indole (2j).

![Chemical Structure of 1-(3-Methoxy-4-(trifluoromethyl)phenyl)-1H-indole (2j)](image)

The typical procedure (Conditions A and B) was followed using 1j as the substrate. White solid (64.8 mg, 89% for Condition A, 61.7 mg, 85% for Condition B). Mp 80.3–80.5 °C. R_{f} 0.29 (SiO_{2}, hexane/EtOAc = 10/1).

^{1}H NMR (CDCl_{3}, 399.78 MHz) δ: 4.00 (s, 3H), 6.78 (d, J = 3.7 Hz, 1H), 7.18–7.20 (m, 2H), 7.26 (dd, J = 6.9, 7.8 Hz, 1H), 7.32 (dd, J = 6.9, 8.3 Hz, 1H), 7.40 (d, J = 3.7 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.74–7.77 (m, 2H).

^{13}C NMR (CDCl_{3}, 100.53 MHz) δ: 56.1, 104.7, 107.6, 110.4, 115.0, 116.4 (q, J_{CF} = 31.1 Hz), 120.9, 121.4, 122.9, 123.4 (q, J_{CF} = 272.6 Hz), 127.4, 128.4 (q, J_{CF} = 5.2 Hz), 129.7, 135.4, 144.2, 158.5.

^{19}F NMR (CDCl_{3}, 376.17 MHz) δ: –62.0 (s, 3F).

IR (ATR): 3016 w, 2937 w, 1612 m, 1517 m, 1459 m, 1423 w, 1313 s, 1261 m, 1122 s, 1072 w, 1043 m, 954 w, 850 w, 825 w, 746 s, 661 w.

MS, m/z (relative intensity, %): 292 (19), 291 (M+, 100), 248 (22).

HRMS Calcd for C_{16}H_{13}F_{3}NO ([M+H^{+}]): 292.0944. Found: 292.0966.

(4-(1H-Indol-1-yl)phenyl)(morpholino)methanone (2k).

![Chemical Structure of (4-(1H-Indol-1-yl)phenyl)(morpholino)methanone (2k)](image)

The typical procedure (Condition A) was followed using 1k as the substrate. White solid (68.9 mg, 90%). Mp 123.6–124.1 °C. R_{f} 0.23 (SiO_{2}, hexane/EtOAc = 1/1).

^{1}H NMR (CDCl_{3}, 399.78 MHz) δ: 3.75 (m, 8H), 6.72 (d, J = 3.3 Hz, 1H), 7.20 (dd, J = 7.1, 7.6 Hz,
1H), 7.25 (dd, J = 7.1, 8.3 Hz, 1H), 7.34 (d, J = 3.3 Hz, 1H), 7.61–7.58 (m, 5H), 7.70 (d, J = 8.3 Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 42.7 (br), 48.2 (br), 66.9, 104.4, 110.4, 120.7, 121.3, 122.7, 123.9, 127.5, 128.8, 129.5, 132.9, 135.5, 141.1, 169.6.

IR (ATR): 2966 w, 2918 w, 2856 w, 2360 w, 1712 m, 1629 s, 1517 m, 1454 s, 1429 s, 1338 m, 1277 m, 1068 w, 1016 m, 891 w, 842 m, 744 m.

MS, m/z (relative intensity, %): 307 (12), 306 (M+, 56), 221 (17), 220 (100), 192 (37), 191 (38), 110 (14), 96 (19).

HRMS Calcd for C$_{19}$H$_{19}$N$_2$O$_2$ ([M+H$^+$]): 307.1441. Found: 307.1442.

1-(4-(1H-Indol-1-yl)phenyl)ethanone (2l) [CAS: 25700-07-6].

The typical procedure (Conditions A and B) was followed using 1l as the substrate.

Colorless oil (33.1 mg, 56% for Condition A, 45.0 mg, 61% for Condition B). $R_f$ 0.14 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) δ: 2.67 (s, 3H), 6.75 (d, J = 3.2 Hz, 1H), 7.22 (dd, J = 6.5, 7.6 Hz, 1H), 7.28 (dd, J = 6.5, 8.2 Hz, 1H), 7.39 (d, J = 3.2 Hz, 1H), 7.63 (d, J = 6.9 Hz, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 6.9 Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 26.6, 105.0, 110.5, 121.0, 121.4, 122.9, 123.3, 127.3, 129.8, 130.0, 134.5, 135.3, 143.8, 196.8.

HRMS Calcd for C$_{16}$H$_{14}$NO ([M+H$^+$]): 236.1070. Found: 236.1066.

4-(1H-Indol-1-yl)benzonitrile (2m) [CAS: 25699-92-7].

The typical procedure (Condition A) was followed using 1m as the substrate and 1,3-
bis(dicyclohexylphosphino)propane as the ligand. Colorless oil (38.2 mg, 69%). \( R_f \) 0.28 (SiO\(_2\), hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \( \delta \): 6.76 (d, \( J = 3.2 \) Hz, 1H), 7.22 (dd, \( J = 7.3, 7.8 \) Hz, 1H), 7.28 (dd, \( J = 7.3, 8.7 \) Hz, 1H), 7.34 (d, \( J = 3.2 \) Hz, 1H), 7.61–7.66 (m, 3H), 7.70 (d, \( J = 8.7 \) Hz, 1H), 7.79–7.83 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\), 100.53 MHz) \( \delta \): 105.7, 109.2, 110.3, 118.4, 121.4, 121.6, 123.2, 123.8, 127.0, 129.9, 133.8, 135.2, 143.6.

HRMS Calcd for C\(_{15}\)H\(_{11}\)N\(_2\) ([M+H\(^+\)]): 219.0917. Found: 219.0931.

**1-(3,5-Difluorophenyl)-1\textsuperscript{H}-indole (2n).**

The typical procedure (Condition A) was followed using 1n as the substrate. Colorless oil (43.8 mg, 76%). \( R_f \) 0.6 (SiO\(_2\), hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \( \delta \): 6.73 (d, \( J = 3.2 \) Hz, 1H), 6.82 (tt, \( J = 2.3, 8.7 \) Hz, 1H), 7.12–7.07 (m, 2H), 7.24 (dd, \( J = 7.4, 7.8 \) Hz, 1H), 7.28–7.32 (m, 2H), 7.64 (\( J = 8.2 \) Hz, 1H), 7.70 (\( J = 7.8 \) Hz, 1H).

\(^{13}\)C NMR (CDCl\(_3\), 100.53 MHz) \( \delta \): 101.6 (t, \( J = 24.9 \) Hz), 105.0, 107.0 (dd, \( J = 19.7 \) Hz), 110.3, 121.1, 121.4, 123.0, 127.3, 129.6, 135.2, 141.9 (t, \( J = 12.4 \) Hz), 163.5 (dd, \( J = 249.8 \) Hz).

\(^{19}\)F NMR (CDCl\(_3\), 376.17 MHz) \( \delta \): –107.6 (s, 2F).

IR (ATR): 3091 w, 2360 m, 1614 s, 1521 m, 1481 s, 1357 w, 1305 w, 1270 m, 1203 m, 989 w, 848 w, 767 m, 742 m, 680 w.

MS, \textit{m/z} (relative intensity, %): 230 (16), 229 (M\(^+\), 100), 202 (22), 90 (18), 89 (16).

HRMS Calcd for C\(_{14}\)H\(_{10}\)F\(_2\)N ([M+H\(^+\)]): 230.0776. Found: 230.0788.

**1-(Naphthalen-2-yl)-1\textsuperscript{H}-indole (2o) [CAS: 348111-49-9].**
The typical procedure (Conditions A and B) was followed using 1o as the substrate.

Colorless oil (35.9 mg, 59% for Condition A, 45.0 mg, 90% for Condition B). Rf 0.40 (SiO2, hexane/EtOAc = 20/1).

1H NMR (CDCl3, 399.78 MHz) δ: 6.77 (d, J = 3.2 Hz, 1H), 7.21–7.30 (m, 2H), 7.47–7.49 (m, 1H), 7.60–7.53 (m, 2H), 7.67–7.71 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.90–7.96 (m, 3H), 8.01 (d, J = 8.7 Hz, 1H)

13C NMR (CDCl3, 100.53 MHz) δ: 103.8, 110.5, 120.5, 121.2, 121.9, 122.4, 123.2, 126.0, 126.9, 127.7, 127.8, 128.1, 129.4, 129.6, 131.8, 133.8, 136.0, 137.3.

HRMS Calcd for C18H14N ([M+H+]): 244.1121. Found: 244.1135.

1-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)-1H-indole (2p).

The typical procedure (Conditions A and B) was followed using 1p as the substrate.

White solid (60.1 mg, 71% for Condition A, 72.7 mg, 86% for Condition B). Mp 133.3–133.8 °C. Rf 0.23 (SiO2, hexane/EtOAc = 20/1).

1H NMR (CDCl3, 399.78 MHz) δ: 6.74 (d, J = 3.3 Hz, 1H), 7.21 (dd, J = 6.9, 7.2 Hz, 1H), 7.27 (dd, J = 7.1, 8.2 Hz, 1H), 7.40 (d, J = 3.3 Hz, 1H), 7.66–7.62 (m, 3H), 7.79–7.72 (m, 7H).

13C NMR (CDCl3, 100.53 MHz) δ: 104.1, 110.5, 120.6, 121.3, 122.6, 124.2 (q, JCF = 272.2 Hz), 124.6, 125.9 (q, JCF = 2.9 Hz), 127.3, 127.7, 128.4, 129.5, 129.6 (q, JCF = 32.6 Hz), 135.7, 137.7, 139.8, 143.7.

19F NMR (CDCl3, 376.17 MHz) δ: –62.3 (s, 3F).

IR (ATR): 2942 w, 2865 w, 1713 m, 1616 w, 1526w, 1473 m, 1379 w, 1324 s, 1263 m, 1217 w, 1163 m, 1124 m, 1069 m, 1016 w, 958 w, 883 w, 848 w, 830 w, 770 w, 743 w, 718 w, 696 w, 677 w.

MS, m/z (relative intensity, %): 338 (23), 337 (M+), 100, 89 (13).

HRMS Calcd for C21H15F3N ([M+H+]): 338.1151. Found: 338.1149.

S36
(E)-1-Styryl-1H-indole (2q) [CAS: 405150-29-0].

The typical procedure (Condition A and B) was followed using 1q as the substrate. Under condition A, no 2q was formed and 77% of 1q was remained unreacted.

White solid (49.9 mg, 91% for Condition B). White solid (49.9 mg, 91%). \( R_f \) 0.34 (SiO\(_2\), hexane/EtOAc = 20/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \( \delta \): 6.74–6.70 (m, 2H), 7.22 (t, \( J = 7.4 \) Hz, 1H), 7.35–7.27 (m, 2H), 7.41 (dd, \( J = 7.4, 7.8 \) Hz, 2H), 7.48 (d, \( J = 7.8 \) Hz, 2H), 7.55 (d, \( J = 3.2 \) Hz, 1H), 7.59 (d, \( J = 8.2 \) Hz, 1H), 7.73–7.67 (m, 2H).

\(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 100.53 MHz) \( \delta \): 105.6, 109.9, 114.1, 121.2, 121.5, 123.1, 123.8, 124.0, 125.9, 127.2, 129.1, 129.5, 136.0, 136.5.

HRMS Calcd for C\(_{16}\)H\(_{14}\)N ([M+H\(^+\)]): 220.1121. Found: 220.1128.

6-(1H-Indol-1-yl)quinoline (2r).

The typical procedure (Condition A) was followed using 1r as the substrate.

Colorless oil (56.8 mg, 69%). \( R_f \) 0.43 (SiO\(_2\), hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \( \delta \): 6.76 (d, \( J = 3.2 \) Hz, 1H), 7.22 (dd, \( J = 6.6, 7.6 \) Hz, 1H), 7.27 (dd, \( J = 6.6, 8.2 \) Hz, 1H), 7.44–7.49 (m, 2H), 7.66 (d, \( J = 8.2 \) Hz, 1H), 7.73 (d, \( J = 7.6 \) Hz, 1H), 7.90–7.94 (m, 2H), 8.20 (d, \( J = 6.9 \) Hz, 1H), 8.27 (d, \( J = 8.7 \) Hz, 1H), 8.96 (d, \( J = 4.1 \) Hz, 1H).

\(^{13}\)C NMR (CDCl\(_3\), 100.53 MHz) \( \delta \): 104.4, 110.3, 120.7, 121.2, 121.3, 121.9, 122.7, 126.6, 127.9, 128.7, 129.5, 131.1, 135.8, 137.8, 146.48, 146.49, 150.4.

IR (ATR): 3052 w, 2360 w, 1612 m, 1506 s, 1457 s, 1423 w, 1423 w, 1311 s, 1261 w, 1216 m, 1126 s, 1043 m, 883 w, 838 m, 765 s, 742 s.
MS, \textit{m/z} (relative intensity, %): 245 (19), 244 (M\(^{+}\), 100), 243 (31), 242 (11), 216 (13), 1221 (16), 108 (11).
HRMS Calcd for C\(_{17}\)H\(_{13}\)N\(_2\) ([M+H\(^{+}\)]): 245.1073. Found: 245.1095.

**Methyl 1-(4-(trifluoromethyl)phenyl)-1\textit{H}-indole-5-carboxylate (2s) [CAS: 1373525-79-1].**

The typical procedure (Condition A) was followed using 1s as the substrate.
White solid (60.6 mg, 76%). Mp 141.8–142.1 °C. \(R_f\) 0.18 (SiO\(_2\), hexane/EtOAc = 20/1).

\(^1\text{H} \text{NMR (CDCl}_3\), 399.78 MHz} \delta: 3.95 (s, 3H), 6.81 (d, \(J = 3.2\) Hz, 1H), 7.41 (d, \(J = 3.2\) Hz, 1H), 7.57 (d, \(J = 8.8\) Hz, 1H), 7.63 (d, \(J = 8.3\) Hz, 2H), 7.81 (d, \(J = 8.4\) Hz, 2H), 7.95 (d, \(J = 8.8\) Hz, 1H), 8.45 (s, 1H).

\(^{13}\text{C} \text{NMR (CDCl}_3\), 100.53 MHz} \delta: 52.0, 105.96, 105.97, 110.0, 123.0, 123.8 (q, \(J_{CF} = 272.2\) Hz), 124.2, 127.0 (q, \(J_{CF} = 3.8\) Hz), 128.8 (q, \(J_{CF} = 15.3\) Hz), 128.9, 129.2, 137.91, 137.92, 142.2, 167.7.

IR (ATR): 2951 w, 1712 m, 1610 m, 1526 w, 1475 w, 1436 w, 1377 w, 1359 w, 1324 s, 1272 m, 1228 m, 1198 m, 1164 m, 1123 mm, 1087 w, 1068 m, 1016 w, 987 w, 954 w, 909 w, 848 w, 754 m, 676 w.

MS, \textit{m/z} (relative intensity, %): 320 (17), 319 (M\(^{+}\), 89), 289 (18), 288 (100), 260 (28), 240 (13), 191 (30), 144 (16).
HRMS Calcd for C\(_{17}\)H\(_{13}\)F\(_3\)NO\(_2\) ([M+H\(^{+}\)]): 320.0893. Found: 320.0881.

**5-Methyl-1-(4-(trifluoromethyl)phenyl)-1\textit{H}-indole (2t).**

The typical procedure (Condition A) was followed using 1t as the substrate.
White solid (49.5 mg, 72%). Mp 60.5–60.9 °C. \(R_f\) 0.45 (SiO\(_2\), hexane/EtOAc = 20/1).

\(^1\text{H} \text{NMR (CDCl}_3\), 399.78 MHz} \delta: 2.48 (s, 3H), 6.66 (d, \(J = 3.2\) Hz, 1H), 7.10 (d, \(J = 8.6\) Hz, 1H), 7.32
(d, J = 3.2 Hz, 1H), 7.49–7.52 (m, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 21.3, 104.5, 110.0, 121.1, 123.6, 124.0, 124.5, 126.8, 127.4, 127.9, 130.0, 130.3, 133.8, 142.9.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) δ: -62.1 (s, 3F).

IR (ATR): 2941 w, 2865 w, 2156 w, 1712 w, 1616 w, 1473 m, 1451 w, 1378 w, 1323 s, 1260 m, 1218 w, 1162 m, 1122 m, 1066 m, 1015 w, 958 w, 913 w, 882 w, 846 w, 800 w, 770 w, 751 w, 717 w, 696 w, 677 w.

MS, m/z (relative intensity, %): 276 (17), 275 (M$^+$, 100), 274 (65), 77 (12).

HRMS Calcd for C$_{16}$H$_{13}$F$_3$N ([M+H$^+$]): 276.0995. Found: 276.0987.

**5-Methoxy-1-(4-(trifluoromethyl)phenyl)-1$H$-indole (2u).**

![Structure of 2u](image)

The typical procedure (Condition A) was followed using 1u as the substrate.

White solid (53.1 mg, 73%). Mp 84.8–85.1 °C. $R_f$ 0.38 (SiO$_2$, hexane/EtOAc = 20/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) δ: 3.89 (s, 3H), 6.66 (d, J = 3.2 Hz, 1H), 6.92 (d, J = 2.3, 9.2 Hz, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.33 (d, J = 3.2 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 55.8, 103.0, 104.6, 111.2, 112.9, 123.5, 124.0 (q, $J_{CF} = 271.8$ Hz), 126.9 (q, $J_{CF} = 3.7$ Hz), 127.7 (q, $J_{CF} = 32.7$ Hz), 127.8, 130.3, 130.5, 142.8, 154.9.

$^{19}$F NMR (CDCl$_3$, 376.17 MHz) δ: -62.1 (s, 3F).

IR (ATR): 2941 w, 1712 w, 1616 w, 1476 m, 1449 w, 1378 w, 1323 s, 1262 m, 1217 w, 1159 m, 1120 m, 1066 m, 1033 w, 1016 w, 957 w, 846 w, 803 w, 771 w, 754 w, 717 w.

MS, m/z (relative intensity, %): 292 (18), 291 (M$^+$, 100), 277 (12), 276 (70), 248 (42).

HRMS Calcd for C$_{16}$H$_{13}$F$_3$NO ([M+H$^+$]): 292.0944. Found: 292.0937.

**5-(Benzylxoy)-1-(4-(trifluoromethyl)phenyl)-1$H$-indole (2v) [CAS: 161460-21-5].**
The typical procedure (Condition A) was followed using 1v as the substrate.

White solid (69.8 mg, 76%). Mp 104.3–104.8 °C. Rf 0.34 (SiO₂, hexane/EtOAc = 10/1).

\(^{1}\)H NMR (CDCl₃, 399.78 MHz) δ: 5.15 (s, 2H), 6.65 (d, J = 3.2 Hz, 1H), 7.00 (dd, J = 2.8, 8.7 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 7.32–7.34 (m, 2H), 7.39–7.42 (m, 2H), 7.52–7.65 (m, 3H), 7.61 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H).

\(^{13}\)C NMR (CDCl₃, 100.53 MHz) δ: 70.7, 104.5, 104.6, 111.2, 113.6, 123.5, 123.9 (q, Jₐℓₜ = 272.6 Hz), 126.9 (q, Jₐℓₜ = 3.1 Hz), 127.5, 127.8, 127.9 (q, Jₐℓₜ = 32.1 Hz), 128.5, 128.6, 130.3, 130.7, 137.4, 142.8, 154.0.

IR (ATR): 3033 w, 2863 w, 1708 w, 1616 m, 1572 w, 1524 m, 1472 m, 1450 m, 1379 w, 1322 s, 1258 m, 1217 w, 1159 s, 1115 s, 1065 m, 1015 m, 957 w, 911 w, 845 m, 802 w, 737 m, 717 m, 697 m.

MS, m/z (relative intensity, %): 367 (M⁺, 39), 277 (18), 276 (100), 248 (27), 91 (65).

HRMS Calcd for C₂₂H₁₇F₃NO ([M+H⁺]): 368.1257. Found: 368.1251.

\(N,N\)-Dibenzyl-2-(5-methoxy-1-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)ethan-1-amine (2w).

The typical procedure (Condition A) was followed using 1w as the substrate.

Colorless oil (88.1 mg, 69%). Rf 0.29 (SiO₂, hexane/EtOAc = 9/1).

\(^{1}\)H NMR (CD₂Cl₂, 399.78 MHz) δ: 2.84 (t, J = 7.2 Hz, 2H), 3.00 (t, J = 7.2 Hz, 2H), 3.71 (s, 4H), 3.74 (s, 3H), 6.83–6.86 (m, 2H), 7.11 (s, 1H), 7.20–7.24 (m, 2H), 7.28–7.31 (m, 4H), 7.41 (d, J = 7.2 Hz, 4H), 7.49 (dd, J = 8.2, 1.6 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H).

\(^{13}\)C NMR (CDCl₃, 100.53 MHz) δ: 23.0, 53.4, 55.8, 58.4, 101.0, 111.2, 112.8, 116.6, 123.0, 124.0 (q, Jₐℓₜ = 271.7 Hz), 125.2, 126.8, 126.8 (qt, Jₐℓₜ = 2.6 Hz), 127.1, 127.4, 128.2, 128.7, 130.3 (q, Jₐℓₜ = 34.5 Hz).
(Hz), 139.8, 142.9, 154.5.

$^{19}$F NMR (CD$_2$Cl$_2$, 376.17 MHz) $\delta$: -62.3 (s, 3F).

IR (KBr, cm$^{-1}$): 3061 m, 3028 m, 2930 m, 2832 m, 2798 m, 2714 w, 1616 s, 1524 s, 1480 s, 1452 s,
1390 m, 1325 s, 1255 s, 1213 m, 1166 s, 1122 s, 1067 s, 1030 m, 1014 m, 973 s, 952 s, 846 m, 790 m,
744 m, 699 m.

HRMS Calcd for C$_{32}$H$_{30}$F$_3$N$_2$O ([M+H$^+$]): 515.2305. Found: 515.2310.

1-(4-(Trifluoromethyl)phenyl)-1$H$-pyrrole (2x) [CAS: 92636-38-9].

The typical procedure (Condition A) was followed using 1x as the substrate.

White solid (40.1 mg, 76%). $R_f$ 0.40 (SiO$_2$, hexane/EtOAc = 20/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 6.39 (d, $J = 3.7$ Hz, 2H), 7.13 (d, $J = 3.7$ Hz, 2H), 7.49 (d, $J = 8.8, 2H$), 7.68 (d, $J = 8.8$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 111.5, 119.1, 112.0, 124.0 (q, $J_{CF} = 271.6$ Hz), 126.9 (q, $J_{CF} = 3.1$
Hz), 127.4 (q, $J_{CF} = 33.2$ Hz), 143.2.

HRMS Calcd for C$_{11}$H$_9$F$_3$N ([M+H$^+$]): 212.0682. Found: 212.0688.

9-(4-(Trifluoromethyl)phenyl)-9$H$-carbazole (2y) [CAS: 204066-03-5].

The typical procedure (Condition A) was followed using 1y as the substrate.

White solid (69.3 mg, 89%). $R_f$ 0.43 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 7.31–7.34 (m, 2H), 7.41–7.45 (m, 4H), 7.73 (d, $J = 8.2$ Hz, 2H),
7.88 (d, $J = 8.2$ Hz, 2H), 8.15 (d, $J = 8.9$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 109.5, 120.45, 120.56, 123.7, 123.9 (q, $J_{CF} = 272.6$ Hz), 126.2,
127.0, 127.1 (q, $J_{CF} = 3.2$ Hz), 129.1 (q, $J_{CF} = 33.2$ Hz), 140.3, 141.0.

HRMS Calcd for C$_{19}$H$_{13}$F$_3$N ([M+H$^+$]): 312.0995. Found: 312.0991.

1-(4-(Trifluoromethyl)phenyl)-1$_H$-pyrrolo[2,3-b]pyridine (2z) [CAS: 1797430-69-3].

The typical procedure (Condition A) was followed using 1z as the substrate and 1,3-bis(dicyclohexylphosphino)propane as the ligand.

White solid (49.8 mg, 70%). $R_f$ 0.34 (SiO$_2$, hexane/EtOAc = 10/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 6.69 (d, $J = 3.7$ Hz, 1H), 7.18 (dd, $J = 4.8$, 7.8 Hz, 1H), 7.55 (d, $J = 3.7$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.97–8.00 (m, 3H), 8.39 (d, $J = 4.8$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 102.9, 117.3, 121.9, 123.3, 124.0 (q, $J_{CF} = 271.6$ Hz), 126.6 (q, $J_{CF} = 3.2$ Hz), 127.0, 127.8 (q, $J_{CF} = 33.2$ Hz), 129.4, 141.4, 143.8, 137.4.

HRMS Calcd for C$_{14}$H$_{10}$F$_3$N$_2$ ([M+H$^+$]): 263.0791. Found: 263.0796.

10-(4-(Trifluoromethyl)phenyl)-10$_H$-phenoxazine (2aa) [CAS: 58736-86-0].

The typical procedure (Condition A) was followed using 1aa as the substrate.

White solid (49.1 mg, 60%). $R_f$ 0.54 (SiO$_2$, hexane/EtOAc = 20/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 5.90 (d, $J = 7.8$ Hz, 2H), 6.61 (dd, $J = 7.3$, 7.8 Hz, 2H), 6.67–6.74 (m, 4H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 113.2, 115.7, 121.9, 123.3, 123.8 (q, $J_{CF} = 272.6$ Hz), 128.2 (q, $J_{CF} = 4.1$ Hz), 130.6 (q, $J_{CF} = 32.1$ Hz), 131.5, 133.7, 142.5, 143.9.

HRMS Calcd for C$_{19}$H$_{13}$F$_3$NO ([M+H$^+$]): 328.0944. Found: 328.0944.
**N,N-Diphenyl-4-(trifluoromethyl)aniline (S10) [CAS: 36809-32-2].**

![Chemical structure of S10]

The typical procedure (Conditions A or B) was followed using S7 as the substrate. White solid (7.0 mg, 9% for Condition A, 7.6 mg, 10% for Condition B).

\[ \text{H NMR (CDCl}_3, 399.78 \text{ MHz} \] \( \delta \): 7.05 (d, \( J = 8.3 \text{ Hz} \), 2H), 7.14–7.10 (m, 6H), 7.32–7.28 (m, 4H), 7.41 (d, \( J = 8.7 \text{ Hz} \), 2H).

\[ \text{13C NMR (CDCl}_3, 100.53 \text{ MHz} \] \( \delta \): 121.0, 122.7 (q, \( J_{CF} = 33.2 \text{ Hz} \)), 124.2, 123.3 (q, \( J_{CF} = 300.0 \text{ Hz} \)), 125.4, 126.2 (q, \( J_{CF} = 4.1 \text{ Hz} \)), 129.5, 146.8, 150.8.

HRMS Calcd for C_{19}H_{15}F_{3}N ([M+H\text{]}) 314.1151. Found: 314.1149.

**Tris(4-(trifluoromethyl)phenyl)amine (2ab) [CAS: 135761-41-0].**

![Chemical structure of 2ab]

The modified condition A as specified below was used for substrate 1ab, which gave the product 2ab as a white solid. Isolated yield was 60% (55.0 mg) when Ni(cod)\textsubscript{2} (20 mol%) and dcype (20 mol%) were used as the catalyst for 48 h at 180 °C. Isolated yield was 60% (55.0 mg) when Ni(cod)\textsubscript{2} (100 mol%) and dcype (100 mol%) were used as the catalyst for 18 h at 180 °C.

White solid. \( R_f 0.26 (\text{SiO}_2, \text{hexane/EtOAc} = 9/1) \).

\[ \text{1H NMR (CDCl}_3, 399.78 \text{ MHz} \] \( \delta \): 7.55 (d, \( J = 8.4 \text{ Hz} \), 6H), 7.18 (d, \( J = 8.4 \text{ Hz} \), 6H).

\[ \text{13C NMR (CDCl}_3, 100.53 \text{ MHz} \] \( \delta \): 149.4, 126.9(qt, \( J_{CF} = 3.8 \text{ Hz} \)), 125.9(q, \( J_{CF} = 32.8 \text{ Hz} \)), 124.1, 124.0(q, \( J_{CF} = 271.7 \text{ Hz} \)).

MS, \text{m/z (relative intensity, %)}: 359 (M\textsuperscript{+}, 20), 358 (100), 357 (M\textsuperscript{+}, 53), 344 (12), 343 (66), 118 (12), 116 (11), 91 (31), 77 (12), 65 (17).

HRMS Calcd for C_{21}H_{15}F_{9}N ([M+H\text{]}) 450.0899. Found: 450.0899.
9-(3-(1H-Indol-1-yl)phenyl)-9H-carbazole (5) [CAS: 1688701-25-8].

The typical procedure (Condition A) was followed using S9 as the substrate.
White solid (56.0 mg, 63%). Mp 164.4–166.7 °C. Rf 0.29 (NH silica, hexane/CH2Cl2 = 9/1).

1H NMR (CD2Cl2, 399.78 MHz) δ: 6.72 (d, J = 4.1 Hz, 1H), 7.16 (td, J = 7.6, 0.9 Hz, 1H), 7.24 (td, J = 7.7, 1.0 Hz, 1H), 7.29–7.33 (m, 2H), 7.43–7.47 (m, 3H), 7.52 (s, 1H), 7.54 (s, 1H), 7.60 (dq, J = 7.8, 1.1 Hz, 1H), 7.66–7.69 (m, 3H), 7.76 (t, J = 2.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 8.17 (d, J = 7.8 Hz, 2H).

13C NMR (CD2Cl2, 100.53 MHz) δ: 104.5, 110.1, 110.8, 120.6, 120.7, 121.0, 121.5, 122.7, 122.9, 123.3, 123.8, 125.1, 126.5, 128.2, 129.9, 131.4, 136.0, 139.3, 141.0, 141.7.

IR (KBr, cm⁻¹): 3054 w, 1601 s, 1576 w, 1516 m, 1497 m, 1451 s, 1333 s, 1318 m, 1229 s, 1213 m, 1174 w, 1166 w, 1153 w, 1134 w, 1120 w, 1016 w, 933 w, 902 w, 849 w, 799 w, 748 s, 727 s, 700 m.

MS, m/z (relative intensity, %): 359 (29), 358 (M⁺, 100), 357 (12), 241 (14), 179 (19).
HRMS Calcd for C26H18N2 ([M⁺]): 358.1465. Found: 358.1466.

2-Phenyl-1H-benzo[d]imidazole (8a) [CAS: 716-79-0].

The typical procedure (Condition A) was followed using 7a as the substrate.
White solid (35.0 mg, 72%). Rf 0.40 (SiO2, hexane/EtOAc = 1/1).

1H NMR (DMSO-d6, 399.78 MHz) δ: 7.18–7.21 (m, 2H), 7.48–7.57 (m, 4H), 7.66 (d, J = 7.0 Hz, 1H), 8.16–8.19 (m, 2H), 12.90 (s, 1H).

13C NMR (DMSO-d6, 100.53 MHz) δ: 111.3, 118.9, 121.7, 122.5, 126.4, 129.0, 129.9, 130.2, 135.0, 143.8, 151.2.

HRMS Calcd for C13H11N2 ([M+H⁺]): 195.0917. Found: 195.0922.
2-(4-(Trifluoromethyl)phenyl)-1H-benzo[d]imidazole (8b) [CAS: 400073-79-2].

The typical procedure (Condition A) was followed using 7b as the substrate. The ratio of \( p \)- and \( m \)-derivatives were determined by \( ^1 \)H-NMR based on the literature data.\(^{16}\)

White solid [50.5 mg, 77\% (\( p:m = 52:1 \))]. \( R_f \) 0.51 (SiO\(_2\); hexane/EtOAc = 1/1).

\( p \)-Isomer:

\(^1\)H NMR (DMSO-\( d_6 \), 399.78 MHz) \( \delta \): 7.14–7.31 (m, 2H), 7.57 (d, \( J = 6.9 \) Hz, 1H), 7.70 (d, \( J = 6.8 \) Hz, 1H), 7.92 (d, \( J = 8.2 \) Hz, 2H), 8.31 (d, \( J = 8.2 \) Hz, 2H), 13.16 (s, 1H).

\(^{13}\)C NMR (DMSO-\( d_6 \), 100.53 MHz) \( \delta \): 122.6, 124.2 (q, \( J_{CF} = 272.2 \) Hz), 126.0 (q, \( J_{CF} = 3.8 \) Hz), 127.1, 129.6 (q, \( J_{CF} = 31.9 \) Hz), 133.9, 134.0, 134.0, 149.6.

HRMS Calcd for C\(_{14}\)H\(_{10}\)F\(_3\)N\(_2\) ([M+H\(^+\)]): 263.0791. Found: 263.0815.

\( m \)-Isomer: This compound was identified based the following spectroscopic data.\(^{15}\)

\(^1\)H NMR (DMSO-\( d_6 \), 399.78 MHz) \( \delta \): 8.52 (s, 1H). Other peaks were overlapped with those of \( p \)-isomers.

MS, \( m/\ell \) (relative intensity, %): 263 (21), 262 (M\(^+\), 100), 64 (18), 223 (18), 63 (16), 242 (13), 131 (13), 241 (12), 90 (12).

2-(\( p \)-Tolyl)-1H-benzo[d]imidazole (8c) [CAS: 120-03-6].

The typical procedure (Condition A) was followed using 7c as the substrate. The ratio of \( p \)- and \( m \)-derivatives were determined by \( ^1 \)H-NMR.\(^{15}\)

White solid [25.5 mg, 49\% (\( p:m = 9:1 \))]. \( R_f \) 0.46 (SiO\(_2\); hexane/EtOAc = 1/1).

\( p \)-Isomer:

\(^{16}\) Marri, M. R.; Peraka, S.; Macharla, A. K.; Mameda, N.; Kodumari, S.; Nama, N. Tetrahedron Lett. 2014, 55, 6520.
$^{1}$H NMR (DMSO-$d_6$, 399.78 MHz) $\delta$: 2.37 (s, 3H), 7.22–7.16 (m, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 7.0$ Hz, 1H), 7.65 (d, $J = 7.0$ Hz, 1H), 8.08 (d, $J = 8.2$ Hz, 2H), 12.85 (s, 1H).

$^{13}$C NMR (DMSO-$d_6$, 100.53 MHz) $\delta$: 21.0, 111.2, 118.7, 121.6, 122.3, 126.4, 127.5, 129.5, 135.0, 139.6, 143.8, 151.4.

HRMS Calcd for C$_{14}$H$_{13}$N$_2$ ([M+H$^+$]): 209.1073. Found: 209.1100.

$m$-Isomer: This compound was identified based the following spectroscopic data.$^{15}$

$^{1}$H NMR (DMSO-$d_6$, 399.78 MHz) $\delta$: 7.97 (d, $J = 7.6$ Hz, 1H). Other peaks were overlapped with those of $p$-isomers.

MS, $m/z$ (relative intensity, %): 209 (19), 208 (M$^+$, 100), 207 (42), 104 (14), 103 (16), 91 (11), 63 (11).

$^{2}$-(4-Methoxyphenyl)-$^{1}$H-benzo[d]imidazole (8d) [CAS: 2620-81-7].

The modified condition A as specified below was used for substrate 7d, which gave the product 8d as a white solid. Isolated yield was 70% (39.2 mg) when Ni(cod)$_2$ (40 mol%) and dcype (40 mol%) were used as the catalyst for 24 h at 180 °C. The ratio of $p$- and $m$- derivatives were determined by $^{1}$H-NMR.$^{17}$ White solid [39.2 mg, 70% ($p$:m = 94:6)]. R$_f$ 0.26 (NH silica, hexane/EtOAc = 1/1).

$p$-Isomer:

$^{1}$H NMR (DMSO-$d_6$, 399.78 MHz) $\delta$: 3.83 (s, 3H), 7.10 (d, $J = 8.8$ Hz, 2H), 7.14–7.19 (m, 2H), 7.48 (d, $J = 7.0$ Hz, 1H), 7.61 (d, $J = 7.0$ Hz, 1H), 8.11 (d, $J = 8.8$ Hz, 2H), 12.75 (s, 1H).

$^{13}$C NMR (DMSO-$d_6$, 100.53 MHz) $\delta$: 55.4, 111.1, 114.4, 118.5, 121.5, 122.1, 122.7, 128.0, 135.0, 143.9, 151.4, 160.6.

HRMS Calcd for C$_{14}$H$_{13}$N$_2$O ([M+H$^+$]): 225.1022. Found: 225.1021.

$m$-Isomer: This compound was identified based the following spectroscopic data.$^{16}$

$^{1}$H NMR (DMSO-$d_6$, 399.78 MHz) $\delta$: 12.9 (s, 1H). Other peaks were overlapped with those of $p$-isomers.

MS, $m/z$ (relative intensity, %): 225 (15), 224 (M$^+$, 100), 223 (66), 195 (16), 194 (36), 193 (26), 112 (14), 90 (13), 77 (14), 64 (12), 63 (15).

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$^{17}$ Das, K.; Mondal, A.; Srimani, D. *J. Org. Chem.* 2018, 83, 9553.
2-(3,5-Bis(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (8e) [CAS: 1280585-62-7].

The typical procedure (Condition A) was followed using 7e as the substrate.

White solid (64.4 mg, 78%). Mp 201.5–201.7 °C. Rf 0.66 (SiO2, hexane/EtOAc = 1/1).

1H NMR (DMSO-d6, 399.78 MHz) δ: 13.34 (s, 1H), 8.79 (s, 2H), 8.20 (s, 1H), 7.77–7.55 (m, 2H), 7.27–7.25 (m, 2H).

13C NMR (Acetone-d6, 100.53 MHz) δ: 149.2, 133.9, 132.7 (q, JCF = 33.5 Hz), 127.5 (q, JCF = 2.9 Hz), 124.3 (q, JCF = 272.2 Hz), 124.0, 123.6 (qt, JCF = 2.9 Hz), 116.4 (br).

IR (ATR): 3064 w, 1737 w, 1351 m, 1280 s, 1184 m, 1137 s, 902 w, 848 w, 746 w, 701 w.

MS, m/z (relative intensity, %): 331 (12), 330 (M+, 100), 311 (12), 310 (17), 291 (26), 165 (15), 90 (19), 64 (24), 63 (19).

HRMS calcd for C15H9F6N2 ([M+H+]): 331.0664. Found: 331.0703.

2-(3,5-Dimethylphenyl)-1H-benzo[d]imidazole (8f) [CAS: 1011735-85-5].

The typical procedure (Condition A) was followed using 7f as the substrate.

Isolated yield was 70% (38.8 mg) when Ni(cod)2 (40 mol%) and dcype (40 mol%) were used as the catalyst for 24 h at 180 °C.

White solid (38.8 mg, 70%). Rf 0.47 (SiO2, hexane/EtOAc = 1/1).

1H NMR (DMSO-d6, 399.78 MHz) δ: 12.83 (s, 1H), 7.81 (s, 2H), 7.64 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 7.0 Hz, 1H), 7.22–7.16 (m, 2H), 7.13 (s, 1H), 2.37 (s, 6H).

13C NMR (DMSO-d6, 100.53 MHz) δ: 151.4, 143.8, 138.0, 134.9, 131.3, 130.0, 124.2, 122.4, 121.6, 118.8, 111.3, 21.0.

HRMS calcd for C15H15N2 ([M+H+]): 223.1230. Found: 223.1246.
2-(3,5-Dimethoxyphenyl)-1H-benzo[d]imidazole (8g) [CAS: 393134-67-3].

![Structure of 8g]

The typical procedure (Condition A) was followed using 7g as the substrate. Isolated yield was 60% (38.2 mg) when Ni(cod)\(_2\) (40 mol\%) and dcype (40 mol\%) were used as the catalyst for 24 h at 180 °C. Pale yellow solid (38.2 mg, 60%). \(R_f\) 0.29 (SiO\(_2\), hexane/EtOAc = 1/1).

\(^1\)H NMR (DMSO-\(d_6\), 399.78 MHz) \(\delta\): 12.90 (s, 1H), 7.67 (d, \(J = 7.4\) Hz, 1H), 7.53 (d, \(J = 7.4\) Hz, 1H), 7.38 (d, \(J = 2.3\) Hz, 2H), 7.25–7.17 (m, 2H), 6.62 (t, \(J = 2.3\) Hz, 1H), 3.85 (s, 6H).

\(^{13}\)C NMR (DMSO-\(d_6\), 100.53 MHz) \(\delta\): 160.8, 151.0, 143.6, 134.9, 131.9, 122.7, 121.7, 118.9, 111.3, 104.2, 102.1, 55.5.

HRMS calcd for C\(_{15}\)H\(_{15}\)N\(_2\)O\(_2\) ([M+H\(^+\)]): 255.1128. Found: 255.1146.

2-(3,5-Difluorophenyl)-1H-benzo[d]imidazole (8h) [CAS: 1094668-21-9].

![Structure of 8h]

The typical procedure (Condition A) was followed using 7h as the substrate. White solid (29.4 mg, 51\%). \(R_f\) 0.57 (SiO\(_2\), hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \(\delta\): 10.36 (s, 1H), 7.84–7.82 (m, 1H), 7.61–7.48 (m, 3H), 7.34–7.29 (m, 2H), 6.89 (tt, \(J = 2.3\), 8.7 Hz, 1H).

\(^{13}\)C NMR (DMSO-\(d_6\), 100.53 MHz) \(\delta\): 162.8 (dd, \(J_{CF} = 13.5\), 245.3 Hz), 148.9 (t, \(J_{CF} = 2.8\) Hz), 143.4, 135.0, 133.6 (t, \(J_{CF} = 10.5\) Hz), 123.1, 122.5, 119.2, 111.8, 109.5 (dd, \(J_{CF} = 7.7\), 20.1 Hz), 105.1 (t, \(J_{CF} = 25.9\) Hz).

HRMS calcd for C\(_{13}\)H\(_8\)F\(_2\)N\(_2\) ([M+H\(^+\)]): 231.0728. Found: 231.0744.

2-(3,5-Bis(trifluoromethyl)phenyl)-1H-imidazole (8i) [CAS: 1097069-74-3].

![Structure of 8i]
The typical procedure (Condition A) was followed using 7i as the substrate. $^{13}$C NMR spectrum of 8i was recorded with $^{19}$F decoupling.

White solid (32.9 g, 47%). Mp 162.2–163.0 °C. $R_f$ 0.43 (SiO$_2$, hexane/EtOAc = 1/1).

$^1$H NMR (DMSO-$d_6$, 399.78 MHz) $\delta$: 13.03 (s, 1H), 8.57 (s, 2H), 8.04 (s, 1H), 7.35–7.21 (m, 2H).

$^{13}$C NMR (DMSO-$d_6$, 100.53 MHz) $\delta$: 142.8, 133.0, 130.9, 129.9, 124.9, 123.3, 120.90, 119.5.

$^{19}$F NMR (DMSO-$d_6$, 376.17 MHz) $\delta$: –61.5 (s, 6F).

IR (ATR): 1718 m, 1481 w, 1417 m, 1347 m, 1282 s, 1180 m, 1135 s, 900 m.

MS, $m/z$ (relative intensity, %): 281 (12), 280 (M$^+$, 100), 261 (17), 260 (28), 253 (18), 191 (10), 41 (23), 140 (20).

HRMS calcd for C$_{11}$H$_7$F$_6$N$_2$ ([M+H$^+$]): 281.0508. Found: 281.0508.

**VII. Mechanistic Studies.**

**VII-1. Crossover experiments using indole amides (Scheme 4a).**

Ni(cod)$_2$ (13.8 mg, 0.050 mmol), dcype (21.1 mg, 0.050 mmol), 1a (36.2 mg, 0.125 mmol), 1ac (41.2 mg, 0.125 mmol) and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was closed. The contents of the vial were then stirred at 180 °C for 18 h. The reaction
was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel before being analyzed by GC. As a result of GC analysis of the crude mixture, crossover products were not observed. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography over silica gel to give 2a (30.4 mg, 0.116 mmol) and 2ac (36.5 mg, 0.121 mmol) as white solids.

**Methyl 4-(9H-carbazole-9-carbonyl)benzoate (1ac).**

The general procedure I was followed using methyl 4-(chloroformyl)benzoate.

White solid (3.4 g, 52%). Mp 139.7–139.9 °C. R
\(_f\) 0.14 (SiO\(_2\), hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \(\delta\): 3.99 (s, 3H), 7.39–7.30 (m, 4H), 7.48 (d, \(J = 8.0\) Hz, 2H), 7.78 (d, \(J = 8.2\) Hz, 2H), 8.01 (d, \(J = 8.2\) Hz, 2H), 8.20 (d, \(J = 8.2\) Hz, 2H).

\(^13\)C NMR (CDCl\(_3\), 100.53 MHz) \(\delta\): 52.6, 115.8, 119.9, 123.8, 126.2, 126.9, 128.8, 130.1, 133.3, 138.8, 139.7, 166.1, 168.6.

IR (ATR): 2360 w, 1725 s, 1677 m, 1482 w, 1444 m, 1328 m, 1278 s, 1218 m, 1074 w, 1020 w, 948 w, 852 w, 821 w, 757 s, 723 m, 678 w.

MS, \(m/z\) (relative intensity, %): 329 (M\(^+\), 36), 164 (10), 163 (100), 103 (12).

HRMS calcd for C\(_{21}\)H\(_{16}\)NO\(_3\) ([M+H\(^+\)]): 330.1130. Found: 330.1134.

**Methyl 4-(9H-carbazol-9-yl)benzoate (2ac) [CAS: 57103-16-9].**

The typical procedure (Condition A) was followed using 1ac as the substrate.

White solid (70.8 mg, 94%). R
\(_f\) 0.23 (SiO\(_2\), hexane/EtOAc = 10/1).

\(^1\)H NMR (CDCl\(_3\), 399.78 MHz) \(\delta\): 4.00 (s, 3H), 7.32 (dd, \(J = 6.9, 7.8\) Hz, 2H), 7.43 (dd, \(J = 6.9, 8.2\) Hz, 2H).
Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 8.16 (d, J = 7.8 Hz, 2H), 8.29 (d, J = 8.2 Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) δ: 52.3, 109.7, 120.4, 120.5, 123.8, 126.2, 126.4, 128.6, 131.3, 140.2, 142.0, 166.4.

HRMS calcd for C$_{20}$H$_{15}$NO$_2$ ([M+H$^+$]): 302.1176. Found: 302.1172.

VII-2. Stoichiometric reactions (Scheme 4b).

NMR Studies.

Ni(cod)$_2$ (22.0 mg, 0.08 mmol), dcype (33.8 mg, 0.08 mmol), 1a (23.1 mg, 0.08 mmol) and toluene-$d_8$ (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 1 h and transferred to a NMR tube equipped with a screw cap. The cap was closed, and then it was taken out of the glovebox. The contents were then heated at 40 °C for 1 h. The contents were cooled to room temperature, the reaction was monitored by $^{31}$P NMR spectroscopy at room temperature. The same procedure was performed at 60, 80, 100 and 120 °C (Figure S1).

During the course of the reaction, two new downfield peaks (b: δ = 63.0 and 59.9 ppm, $J_{PP}$ = 56.6 Hz) appeared at 40 °C alongside the signal of the Ni(cod)(dcype) (a: δ = 60.3 ppm, s)$^{18}$ on $^{31}$P NMR. The signal of the Ni(dcype)(CO)$_2$ (d: δ = 64.0 ppm)$^{19}$ started to appear at 60 °C. Another two new downfield peaks (6a) (c: δ = 60.7 and 57.9 ppm, $J_{PP}$ = 13.1 Hz) appeared at 80 °C.

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$^{18}$ Muto, K.; Yamaguchi, J.; Lei, A.; Itami, K. J. Am. Chem. Soc. 2013, 135, 16384.

$^{19}$ Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. J. Am. Chem. Soc. 2012, 134, 13573.
Ni(cod)$_2$ (22.0 mg, 0.08 mmol), dcype (33.8 mg, 0.08 mmol), If (20.1 mg, 0.08 mmol) and toluene-$d_8$ (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 1 h and transferred to a NMR tube equipped with a screwed cap. The cap was closed, and then it was taken out of the glovebox. The contents were then heated at 100 °C for 1 h. The contents were cooled to room temperature, the reaction was monitored by $^{31}$P NMR spectroscopy at room temperature. (Figure S2).

At 100 °C, resonances derived from the following three species were observed: $\delta = 60.3$ ppm (s, a, [Ni(cod)(dcype)], $\delta = 60.2$ ppm and 57.1 ppm (d, $J = 13.2$ Hz, c', 6f), $\delta = 64.0$ ppm [s, d, Ni(dcype)(CO)$_2$].
Complex 6a.

Ni(cod)$_2$ (66.0 mg, 0.24 mmol), dcype (101 mg, 0.24 mmol), 1a (69.3 mg, 0.24 mmol) and toluene (3 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 1 h to give a homogeneous yellow solution, which was transferred to another vial without a stirrer bar. The cap was closed. The contents of the vial were then heated at 100 °C for 12 h without stirring. The reaction was cooled to room temperature, and the precipitated orange crystal was collected by filtration and dried in a glovebox filled with nitrogen.
Orange crystal (79.5 mg, 45%). Decomposition temperature 185.0 °C.

$^1$H NMR (CD$_2$Cl$_2$, 399.78 MHz) δ: 0.18–0.25 (m, 48H), 6.38 (d, $J = 2.3$ Hz, 1H), 6.71 (td, $J = 7.3$, 0.9 Hz, 1H), 6.87 (td, $J = 7.4$, 1.1 Hz, 1H) 7.05 (d, $J = 7.8$ Hz, 2H), 7.20 (d, $J = 2.7$ Hz, 1H), 7.35 (d, $J = 7.8$ Hz, 1H), 7.74 (t, $J = 6.2$ Hz, 2H), 7.79 (d, $J = 8.2$ Hz, 1H).

$^{19}$F NMR (CD$_2$Cl$_2$, 376.17 MHz) δ: –61.9 (s, 3F).

$^{31}$P NMR (CD$_2$Cl$_2$, 161.83 MHz) δ: 61.8 (d, $J_{PP} = 17.5$ Hz, 1P), 59.6 (d, $J_{PP} = 17.5$ Hz, 1P).

IR (KBr, cm$^{-1}$): 3047 w, 3005 w, 2926 s, 2851 s, 2666 m, 1580 s, 1445 s, 1415 m, 1319 s, 1293 s, 1265 m, 1212 m, 1182 m, 1159 s, 1110 s, 1068 s, 1008 s, 914 m, 888 m, 851 s, 819 s, 795 m, 742 s, 712 m, 674 m.

HRMS Calcd for C$_{41}$H$_{58}$F$_3$NNiP$_2$ ([M$^+$]): 741.3345. Found: 741.3353.

The structure of 6a was unambiguously determined by X-ray crystallography.

Figure S3 ORTEP drawing of 6a with thermal ellipsoids set at the 50% probability level. All hydrogen atoms are omitted for the sake of clarity.$^a$

$^a$ Crystal data for 6a, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.8932(6)$ Å, $b = 36.2820(11)$ Å, $c = 13.0079(5)$ Å, $\beta = 103.787(4)^\circ$, $V = 7743.1(5)$ Å$^3$, $T = 123$ K, $Z = 4$, $R_1$ (w$R_2$) = 0.0825 (0.2308) for 899 parameters and 19566 unique reflections. GOF = 1.050. CCDC 1901697.

Reactive elimination from 6a.

Complex 6a (28.8 mg, 0.04 mmol) and toluene (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room
temperature for 3 min and the cap was closed, and then it was taken out of the glovebox. The contents of the vial were then heated at 120 °C (or 180 °C) for 18 h. The contents were cooled to room temperature, the product yield was determined by GC using undecane as an internal standard: 23% at 120 °C and 41% at 180 °C.

To investigate the possibility that CO accelerates the reductive elimination process, we examined the reductive elimination of 6a in the presence of Ni(CO)₂(dcype), which is a potential CO source under the catalytic conditions used in this study. Complex 6a (28.8 mg, 0.04 mmol) and Ni(dcype)(CO)₂ (20.8 mg, 0.04 mmol) toluene (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was closed, and then it was taken out of the glovebox. The contents of the vial were then stirred at 180 °C for 18 h. The contents were cooled to room temperature, the product yield was determined by GC using undecane as an internal standard. The yield of 2a increased from 41% to 51%, indicating that CO can, in fact, promote the reductive elimination process under catalytic conditions.

Complex 6f.

Ni(cod)₂ (26.4 mg, 96 µmol), dcype (40.6 mg, 96 µmol), 1f (24.1 mg, 96 µmol) and toluene (1.2 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 1 h to give a homogeneous yellow solution, which was transferred to an NMR tube equipped with a screw cap. The cap was closed. The contents were then heated at 80 °C for 12 h. The contents were cooled to room temperature, and the precipitated
orange crystal was collected by filtration and dried in a glovebox filled with nitrogen. Orange crystal (35.2 mg, 52%). Decomposition temperature 180.0 °C.

$^1$H NMR (CD$_2$Cl$_2$, 399.78 MHz) δ: 2.30–3.60 (m, 48H), 5.16 (s, 3H), 7.92 (d, $J = 2.4$ Hz, 1H), 8.08 (d, $J = 7.3$ Hz, 2H), 8.25 (t, $J = 7.3$ Hz, 1H), 8.42 (t, $J = 7.3$ Hz, 1H), 8.81 (d, $J = 7.3$ Hz, 1H), 8.90 (d, $J = 7.9$ Hz, 1H), 8.97 (t, $J = 5.8$ Hz, 2H), 9.38 (d, $J = 7.9$ Hz, 1H).

$^{31}$P NMR (CD$_2$Cl$_2$, 161.83 MHz) δ: 62.6 (d, $J_{PP} = 13.0$ Hz, 1P), 60.3 (d, $J_{PP} = 13.0$ Hz, 1P).

IR (KBr, cm$^{-1}$): 3033 m, 2998 m, 2926 s, 2847 s, 2359 w, 1598 m, 1574 m, 1478 s, 1446 s, 1415 m, 1342 m, 1292 s, 1258 s, 1229 s, 1214 s, 1170 s, 1159 s, 1119 w, 1081 w, 1051 m, 1026 m, 914 w, 889 m, 852 s, 816 s, 741 s, 664 m.

HRMS Calcd for C$_{41}$H$_{61}$NNiOP$_2$ ([M$^+$]): 703.3576. Found: 703.3577.

The structure of $6f$ was unambiguously determined by X-ray crystallography.

![Figure S4 ORTEP drawing of $6f$ with thermal ellipsoids set at the 50% probability level. All hydrogen atoms are omitted for the sake of clarity.](image)

$^a$Crystal data for $6f$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.2163(3)$ Å, $b = 19.2858(3)$ Å, $c = 17.1259(3)$ Å, $\beta = 111.810(2)$ °, $V = 4052.71(14)$ Å$^3$, $T = 123$ K, $Z = 4$, $R_1$ (wR$_2$) = 0.1119 (0.2828) for 415 parameters and 8146 unique reflections. GOF = 1.107. CCDC 1901702. The SQUEEZE subroutine of PLATON$^{20}$ was used because the refinement for the structure of solvent molecule was unsuccessful due to a significant disorder of chlorobenzene used as a solvent.

**Reductive elimination from $6f$.**

$^{20}$ Spek, A. L. *Acta. Crystallogr. Sect. D* 2009, 65, 148.
Complex 6f (0.04 mmol) and toluene (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was closed, and then it was taken out of the glovebox. The contents of the vial were then stirred at 180 °C for 18 h. The contents were cooled to room temperature, the product yield was determined by GC using undecane as an internal standard: 0% at 120 °C and 44% at 180 °C. Therefore, the reductive elimination from 6f requires higher temperature to occur than required for 6a.

VII-3. Effect of CO ligand.

Ni(CO)2(dcypt) (0.050 mmol), 1a (0.25 mmol) and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was closed. The contents of the vial were then stirred at 120 (or 180 °C) for 18 h. The contents were cooled to room temperature, the product yield was determined by GC using undecane as an internal standard: 1% at 120 °C and 73% at 180 °C.

VII-4. Crossover experiments using N-acylated benzimidazoles.
Ni(cod)$_2$ (13.8 mg, 0.050 mmol), dctype (21.1 mg, 0.050 mmol), S11 (44.8 mg, 0.125 mmol), S12 (31.3 mg, 0.125 mmol) and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was closed. The contents of the vial were then stirred at 180 °C for 18 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated in vacuo to give a residue, which was purified by flash column chromatography (hexane:EtOAc = 5:1→1:1) over silica gel to give two fractions. The first fraction contained S13 and S15 \( [R_f = 0.46 (\text{hexane}:\text{EtOAc} = 5:1), 30.8 \text{mg}] \). The second fraction contained S14 and 8a \( [R_f = 0.09 (\text{hexane}:\text{EtOAc} = 5:1), 3.8 \text{mg}] \). The yields for the four compounds were determined by $^1$H-NMR using 1,1,2,2-tetrachloroethane as an internal standard by comparison with the spectroscopic data of the independently synthesized authentic compounds. The NMR yields of S13, S14, S15 and 8a were 34%, 7%, 37% and 7%, respectively.

(1H-Benzod[d]imidazol-1-yl)(3,5-bis(trifluoromethyl)phenyl)methanone (S11) [CAS: 1899226-42-6].

The general procedure I was followed using 3,5-bis(trifluoromethyl)benzoyl chloride (6 mmol scale). White solid (1.2 g, 55%). Mp 84.7–84.1 °C. $R_f$ 0.66 (SiO$_2$, hexane/EtOAc = 1/1).

$^1$H NMR (CDCl$_3$, 399.78 MHz) $\delta$: 7.46–7.52 (m, 2H), 7.85–7.87 (m, 1H), 8.10 (s, 1H), 8.16–8.21 (m,
1H), 8.21 (s, 1H), 8.27 (s, 2H).

$^{13}$C NMR (CDCl$_3$, 100.53 MHz) $\delta$: 115.4, 118.4, 120.9, 122.5 (q, $J_{CF} = 273.1$ Hz), 126.0, 126.5 (qt, $J_{CF} = 3.1$ Hz), 129.4 (q, $J_{CF} = 3.1$ Hz), 131.7, 133.0 (q, $J_{CF} = 34.2$ Hz), 134.9, 141.8, 144.1, 164.1.

IR (ATR): 2360 w, 1707 m, 1512 w, 1452 w, 1396 w, 1356 m, 1284 s, 1180 s, 1142 s, 910 w, 771 s, 708 w.

MS, $m/z$ (relative intensity, %): 358 (M$^+$, 33), 242 (10), 241 (100), 213 (48), 163 (10).

HRMS Calcd for C$_{16}$H$_9$F$_6$N$_2$O ([M+H$^+$]): 359.0614. Found: 359.0628.

2-(3,5-Bis(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (S13) [CAS: 1280585-62-7].

The typical procedure (Condition A) was followed using S11 as the substrate.

White solid (64.4 mg, 78%). Mp 201.5–201.7 °C. $R_f$ 0.66 (SiO$_2$, hexane/EtOAc = 1/1).

$^1$H NMR (DMSO- d$_6$, 399.78 MHz) $\delta$: 7.25–7.27 (m, 2H), 7.53–7.77 (m, 2H), 8.20 (s, 1H), 8.79 (s, 2H), 13.34 (s, 1H).

$^{13}$C NMR (Acetone-d$_6$, 100.53 MHz) $\delta$: 116.4 (br), 123.6 (qt, $J_{CF} = 2.9$ Hz), 124.0, 124.3 (q, $J_{CF} = 272.2$ Hz), 127.5 (q, $J_{CF} = 2.9$ Hz), 132.7 (q, $J_{CF} = 33.5$ Hz), 133.9, 149.2.

IR (ATR): 3064 w, 1737 w, 1351 m, 1280 s, 1184 m, 1137 s, 902 w, 848 w, 746 w, 701 w.

MS, $m/z$ (relative intensity, %): 331 (12), 330 (M$^+$, 100), 311 (12), 310 (17), 291 (26), 165 (15), 90 (19), 64 (24), 63 (19).

HRMS Calcd for C$_{15}$H$_9$F$_6$N$_2$ ([M+H$^+$]): 331.0664. Found: 331.0703.

(5,6-Dimethyl-1H-benzo[d]imidazol-1-yl)(phenyl)methanone (S12) [CAS 16109-46-9].

The general procedure I was followed using benzoyl chloride. Spectroscopic data were consistent with
those reported in the literature.21

5,6-Dimethyl-2-phenyl-1H-benzo[d]imidazole (S14) [CAS: 14313-45-2].

![Chemical structure of S14](image)

The typical procedure (Condition A) was followed using S12 as the substrate.

White solid (31.7 mg, 57%). R_f 0.40 (SiO2, hexane/EtOAc = 1/1).

1H NMR (DMSO-d6, 399.78 MHz) δ: 2.31 (s, 3H), 2.33 (s, 3H), 7.29 (s, 1H), 7.43–7.48 (m, 2H), 7.50–7.55 (m, 2H), 8.12–8.15 (m, 2H), 12.64 (s, 1H).

13C NMR (DMSO-d6, 100.53 MHz) δ: 20.0, 20.1, 111.3, 118.9, 126.2, 128.9, 129.5, 129.9, 130.5, 131.2, 133.5, 142.5, 150.3.

HRMS Calcd for C15H15N2 ([M+H+]): 223.1230. Found: 223.1240.

(3,5-Bis(trifluoromethyl)phenyl)(5,6-dimethyl-1H-benzo[d]imidazol-1-yl)methanone (S16).

![Chemical structure of S16](image)

The general procedure I was followed using 3,5-bis(trifluoromethyl)benzoyl chloride.

White solid (3.1 g, 40%). Mp 91.3–92.1 °C. R_f 0.71 (SiO2, hexane/EtOAc = 1/1).

1H NMR (CDCl3, 399.78 MHz) δ: 2.41 (s, 3H), 2.42 (s, 3H), 7.60 (s, 1H), 7.95 (s, 1H), 7.98 (s, 1H), 8.19 (s, 1H), 8.25 (s, 2H).

13C NMR (CDCl3, 100.53 MHz) δ: 20.4, 20.6, 115.6, 120.9, 122.5 (q, J_CF = 273.1 Hz), 126.4 (qt, J_CF = 2.8 Hz), 129.4 (q, J_CF = 2.8 Hz), 130.1, 132.9 (q, J_CF = 69.1 Hz), 135.2, 135.2, 135.9, 141.1 142.5, 164.0.

19F NMR (CDCl3, 376.17 MHz) δ: −62.8 (s, 6F).

21 Yu, L.; Wang, M.; Wang, L. *Tetrahedron* **2014**, *70*, 5391.
IR (KBr, cm⁻¹): 3055 m, 2954 w, 1752 m, 1709 s, 1624 m, 1515 s, 1471 s, 1397 s, 1356 s, 1301 s, 1280 s, 1190 s, 1174 s, 1133 s, 1111 s, 1025 m, 943 m, 908 s, 876 m, 850 m, 813 m, 760 m, 712 m, 681 s, 652 m.

MS, m/z (relative intensity, %): 386 (M⁺, 37), 241 (100), 213 (42).

HRMS Calcd for C₁₈H₁₂F₆N₂O ([M+H⁺]): 387.0932. Found: 387.0930.

2-[3,5-Bis(trifluoromethyl)phenyl]-5,6-dimethyl-1H-benzimidazole (S15).

![Chemical Structure](image)

The typical procedure (Condition A) was followed using S16 as the substrate.

White solid (58.4 mg, 65%). Mp 280.3–281.9 °C. Rf 0.26 (SiO₂, hexane/EtOAc = 9/1).

¹H NMR (acetone-d₆, 399.78 MHz) δ: 2.35 (s, 6H), 7.41 (s, 2H), 8.08 (s, 1H), 8.74 (s, 2H), 12.09 (s, 1H).

¹³C NMR (acetone-d₆, 100.53 MHz) δ: 20.4, 112.5 (br), 120.7 (br), 123.1 (qt, JCF = 3.7 Hz), 124.3 (q, JCF = 272.2 Hz), 127.2 (q, JCF = 2.8 Hz), 132.7 (br), 132.7 (q, JCF = 33.5 Hz), 134.2, 148.3.

¹⁹F NMR (acetone-d₆, 376.17 MHz) δ: –63.4 (s, 6F).

IR (KBr, cm⁻¹): 2924 m, 1818 w, 1718 w, 1623 m, 1588 m, 1537 w, 1476 m, 1449 s, 1432 m, 1402 s, 1376 s, 1341 s, 1283 s, 1233 m, 1171 s, 1135 s, 1024 m, 984 s, 901 s, 854 s, 722 m, 696 s, 683 s.

MS, m/z (relative intensity, %): 359 (M⁺, 20), 358 (100), 357 (M⁺, 53), 344 (12), 343 (66), 118 (12), 116 (11), 91 (31), 77 (12), 65 (17).

HRMS Calcd for C₁₇H₁₂F₆N₂ ([M+H⁺]): 359.0983. Found: 359.0989.

VII-5. A control experiment using N-phenylbenzimidazole and 2-benzoylbenzimidazole.
The typical procedure (Condition A) was followed using \(N\)-phenylbenzimidazole (S17) or 2-benzoylbenzimidazole (S18) as the substrate. 2-Phenylbenzimidazole (8a) was not obtained under these conditions, suggesting that S17 and S18 are not involved as an intermediate of this 1,2-migratory decarbonylation.

**VII-6. Labeling studies.**

*(1H-Benzimidazol-1-yl-2-d)(phenyl)methanone (7a-D)*

The general procedure I was followed using benzoyl chloride and 1H-benzimidazole-2-d S19.

White solid (3.1 g, 70%). Mp 89.7–90.1 °C. R

\(f\) 0.37 (SiO2, hexane/EtOAc = 1/1).

\(^1\)H NMR (CDCl3, 399.78 MHz) \(\delta\): 7.41–7.47 (m, 2H), 7.56–7.61 (m, 2H), 7.67–7.71 (m, 1H), 7.79–7.85 (m, 3H), 8.18–8.21 (m, 1H).

\(^2\)H NMR (CHCl3, 61.37 MHz, internal standard CDCl3) \(\delta\): 8.25.

\(^13\)C NMR (CDCl3, 100.53 MHz) \(\delta\): 115.4, 120.5, 125.2, 125.7, 129.0, 129.5, 132.1, 132.8, 133.2, 142.8 (t, \(J_{CD} = 31.7\) Hz), 144.0, 167.0.

IR (KBr, cm

\(^{-1}\)): 3117 w, 3058 w, 2328 w, 1908 w, 1800 w, 1772 w, 1699 s, 1601 m, 1488 m, 1467 s, 1447 s, 1353 s, 1293 m, 1259 s, 1238 m, 1179 s, 1146 m, 1095 m, 1077 m, 1031 m, 1002 m, 979 m, 940 m, 889 s, 856 m, 788 m, 753 s, 736 s, 720 s, 699 s.

MS, \(m/z\) (relative intensity, %): 223 (M

\(^{+}\), 16), 105 (100), 77 (58), 51 (15).

HRMS Calcd for C14H11DN2O ([M+H

\(^{+}\]): 224.0929. Found: 224.0934.
A typical procedure for kinetic studies.

Ni(cod)$_2$ (13.8 mg, 0.050 mmol), dcype (21.1 mg, 0.050 mmol), N-acylpyrrole derivatives (0.25 mmol) and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 3 min and the cap was then closed. The contents of the vial were then stirred at 180 °C. At the indicated times, the vial was rapidly cooled with running water. The crude mixture was filtered through a pad of silica gel before being analyzed by GC (Table S1, Figure S5). The progress of the reaction was monitored by GC. Dodecane was added as an internal standard. The $k_H/k_D$ value was determined to be 1.16.

**Table S1** Time dependence of ln$[[7a]/[7a]_0]$ and ln$[[7a-D]/[7a-D]_0]$.  

| time / s | 0 | 1800 | 3600 | 7200 | 10800 | 14400 |
|----------|---|-------|------|------|-------|-------|
| ln$[[7a]/[7a]_0]$ | 0 | -0.403 | -0.631 | -1.033 | -1.191 | -1.484 |
| ln$[[7a-D]/[7a-D]_0]$ | 0 | -0.228 | -0.412 | -0.799 | -1.065 | -1.163 |

$^a$ Average of two runs were used for ln$[7a]$ and ln$[7a-D]$. 

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**(Diagram)**

- **7a**
- Ni(cod)$_2$ (20 mol%)
- dcype (20 mol%)
- toluene, 180 °C, 0.5–4 h
- **8a**

- **7a-D**
- Ni(cod)$_2$ (20 mol%)
- dcype (20 mol%)
- toluene, 180 °C, 0.5–4 h
- **8a**

$k_H/k_D = 1.16$
Figure S5  Time dependence of ln[7a]/[7a]₀. Reactions were performed using 7a and 7a-D. Average of two runs were plotted for both 7a and (red circle) and 7a-D (blue triangle). The linear regression fit to the data is also shown.

VII-7. NMR monitoring of the stoichiometric reaction of Ni(cod)₂, PCy₃ and 1a.

Ni(cod)₂ (22.0 mg, 0.08 mmol), PCy₃ (22.4 mg, 0.08 mmol), 1a (23.1 mg, 0.08 mmol) and toluene-d₈ (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen. The resulting mixture was stirred at room temperature for 1 h and transferred to a NMR tube equipped with a screw cap. The cap was closed, and then it was taken out of the glovebox. The contents were then heated at 40 °C for 1 h. The contents were cooled to room temperature, the reaction was monitored by ³¹P NMR spectroscopy at room temperature. The same procedure was performed at 60 and 80 °C.
$^{31}$P NMR analysis of the solution revealed that new resonances appeared after 1 h stirring at rt (a: δ = 37.9 ppm, d, $J = 35$ Hz; δ = 33.1 ppm, d, $J = 35$ Hz) (see the chart below). As the temperature increased, these resonances decreased and additional new resonances (b: δ = 42.5 ppm, s; c: δ = 38.2 ppm, s; d: δ = 34.9 ppm, s) appeared in addition to the resonance assignable to [Ni(PCy$_3$)$_2$(CO)$_2$] (δ = 41.0 ppm, s). Unfortunately, however, we were unable to isolate these complexes at this stage. (Figure S6).

Ref. Ni(CO)(PCy$_3$)$_2$ δ 37.5,$^{22}$ Ni(CO)$_2$(PCy$_3$)$_2$ δ 41.0,$^{23}$ Ni(PCy$_3$)$_2$ δ 46.0,$^2$ Ni(CO)$_3$(PCy$_3$)$_3$ δ 45.0,$^{24}$ PCy$_3$-oxide δ 48.0.$^{25}$

VII-8. NMR monitoring of the catalytic reaction of Ni(cod)$_2$, dcype and 1a.

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Ni(cod)$_2$ (13.8 mg, 0.05 mmol), dcype (21.1 mg, 0.05 mmol), 1a (72.6 mg, 0.25 mmol) and toluene-
$	ext{d}_8$ (1.0 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled
with nitrogen. The resulting mixture was stirred at room temperature for 1 h and transferred to a NMR
tube equipped with a screwed cap. The cap was closed, and then it was taken out of the glovebox. The
contents were then heated at 180 °C for 1 h. The contents were cooled to room temperature, the
reaction was monitored by $^{31}$P NMR spectroscopy at room temperature. (Figure S7). The product
yield was determined to be 70% by GC using undecane as an internal standard. The results showed
that complex 6a is NOT a resting state of this catalytic reaction, but Ni(CO)$_2$(dcype) is.
X: parts per Million: Carbon13

167.971
152.534
149.193
136.984
135.984
132.498
130.725
130.189
129.982
128.889
127.384
127.363
125.105
124.146
122.279
120.980
116.381
109.060
77.320
77.000
76.691
X : parts per Million : Proton

8.200
8.193
8.179
8.176
8.138
7.936
7.916
7.877
7.856
7.852
7.848
7.842
7.836
7.829
7.822
7.476
7.471
7.461
7.452
7.447

F₃C

7b

3.07
2.05
2.00
$\text{F}_3\text{C}-\text{N}\text{H}$

2h
X: parts per Million: ppm13

- 149.372
- 128.051
- 128.051
- 126.964
- 126.930
- 126.892
- 126.856
- 126.394
- 126.067
- 125.741
- 125.414
- 125.350
- 124.129
- 122.647
- 77.000
$X_\text{ parts per Million : arn13}$

$^{13}C$ Spectra:

- $163.352$
- $137.678$
- $133.999$
- $133.451$
- $133.106$
- $132.763$
- $132.019$
- $129.657$
- $129.632$
- $129.596$
- $129.586$
- $129.550$
- $126.976$
- $126.940$
- $126.903$
- $123.777$
- $121.058$
- $117.725$

$^{77}Cl$ Spectra:

- $77.317$
- $77.205$
- $77.000$
- $76.682$
X: parts per Million: Proton

- 12.828
- 7.808
- 7.644
- 7.626
- 7.516
- 7.498
- 7.218
- 7.205
- 7.191
- 7.183
- 7.169
- 7.156
- 7.125

- 2.509
- 2.505
- 2.500
- 2.495
- 2.491
- 2.407
- 2.370
- 2.333
X: parts per Million: cemt

8.253

7.260

7a-D
