

Supporting Information

Ruthenium(0)-Catalyzed Cross-Coupling of Aryl Methyl Ethers with Organoboranes by Selective C–O Cleavage

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List of Known Compounds and General Methods

All starting materials reported in the manuscript have been previously described in literature unless stated otherwise. Imines were prepared by standard methods.¹⁻⁵ Organoboranes were prepared by standard methods.^{6,7} All experiments involving ruthenium were performed using Schlenk or glovebox techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ¹H NMR and GC-MS analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ¹H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs), unless stated otherwise. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded in CDCl₃ on Bruker spectrometers at 400 (¹H NMR), 100 (¹³C NMR) and 376 MHz (¹⁹F NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl₃ peak (7.27 and 77.2 ppm, ¹H NMR and ¹³C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 280 °C, then hold at 280 °C for 30 min (splitless mode of injection, total run time of 53.00 min). High-resolution mass spectra (HRMS) were measured on a Thermo Fisher TSQ 8000 Evo Triple Quadrupole GC-MS/MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ¹H NMR, ¹³C NMR and HRMS data are reported for all new compounds.

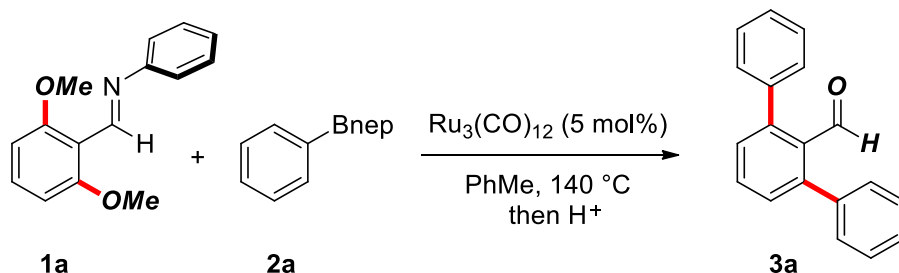
Experimental Procedures and Characterization Data

General Procedure. Ru(0)-Catalyzed C–OMe Arylation. An oven-dried vial equipped with a stir bar was charged with an imine substrate (typically, 0.2 mmol, 1.0 equiv), boronic ester (typically, 2.5 equiv), Ru₃(CO)₁₂ (typically, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (typically, 1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 140 °C, and stirred for an indicated time at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH₂Cl₂ (5 mL), filtered and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to obtain conversion, selectivity, and yield using an internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was subjected to the imine deprotection procedure using 1.0 *N* aqueous HCl in diethyl ether for 3 h at room temperature, and purified by chromatography on silica gel (EtOAc/hexanes) to afford analytically pure aldehyde products. Note that the imine product could typically be obtained directly by careful chromatography on silica gel or by recrystallization from methanol.^{1–5} Routinely, GC-MS analysis was used as a complementary method of analysis to confirm the product distribution.

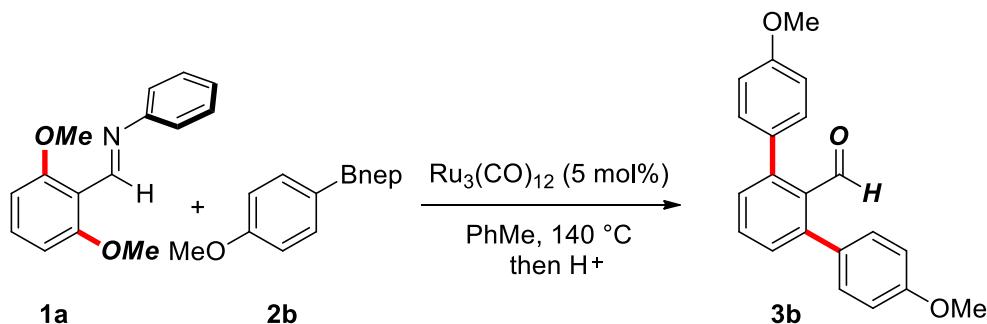
General Procedure. Imine Deprotection. To the solution of an imine substrate (typically, 0.2 mmol) in diethyl ether (typically, 10 mL), HCl (aq, 1.0 *N*, 10 mL) was added. The reaction mixture was stirred for 3 h at room temperature. After the indicated time, the reaction mixture was diluted with diethyl ether (10 mL), the aqueous layer was extracted with diethyl ether (3 x 20 mL), organic layers were combined, dried over Na₂SO₄, filtered and concentrated. Purification by chromatography using silica gel (EtOAc/hexanes) afforded the title product.

Ru(0)-Catalyzed C–OMe Arylation. 1.0 Mmol Scale. An oven-dried vial equipped with a stir bar was charged with *N*-((2-methoxynaphthalen-1-yl)methylene)aniline (261 mg, 1.0 mmol, 1.0 equiv), phenylboronic ester (475 mg, 2.5 mmol, 2.5 equiv), Ru₃(CO)₁₂ (32 mg, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 140 °C, and stirred at 140 °C for 10 h. After the indicated time, the reaction mixture was cooled down to room temperature, the reaction

mixture was analyzed by ^1H NMR (CDCl_3 , 400 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard. Acidic work-up and purification by chromatography (EtOAc/hexanes) afforded the title product (198 mg). Yellow solid. Yield 85%. Characterization data are included in the section below.

Ru(0)-Catalyzed C–O Arylation of Aryl Methyl Ethers**(1,1':3',1''-Terphenyl)-2'-carbaldehyde (3a)**

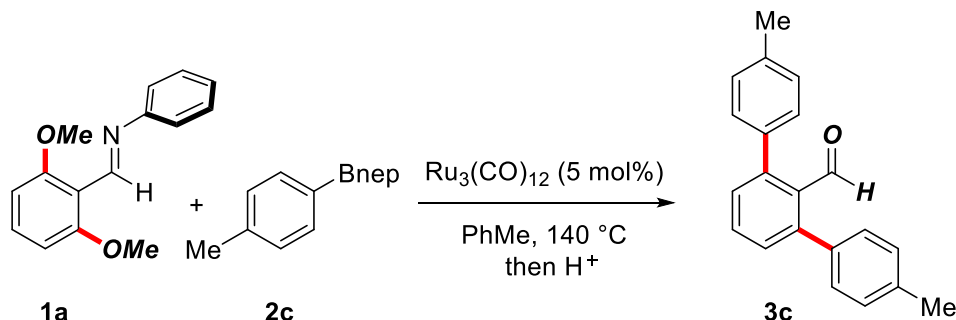
According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with Ph–Bnep (**2a**, 95.0 mg, 0.50 mmol), and $\text{Ru}_3(\text{CO})_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3a** in 73% yield (37.7 mg). White solid. **Mp** = 122–123 °C. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 9.96 (s, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.44 – 7.38 (m, 8H), 7.37 – 7.34 (m, 4H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ 193.7, 144.5, 139.8, 133.4, 131.6, 130.5, 129.7, 128.3, 127.8. **MS** = 258.1 (EI). **HRMS** calcd for $\text{C}_{19}\text{H}_{15}\text{O}$ ($\text{M}^+ + \text{H}$) 259.1117 found 259.1119.

4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (3b)

According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-MeO- C_4H_4 –Bnep (**2b**, 110.0 mg, 0.50 mmol), and $\text{Ru}_3(\text{CO})_{12}$ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3b** in 81% yield (51.5 mg). White solid. **Mp** = 121–122 °C. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 9.94 (s, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 4H), 6.98 (d, $J = 8.8$ Hz, 4H), 3.85 (s, 6H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)** δ 194.0, 159.5,

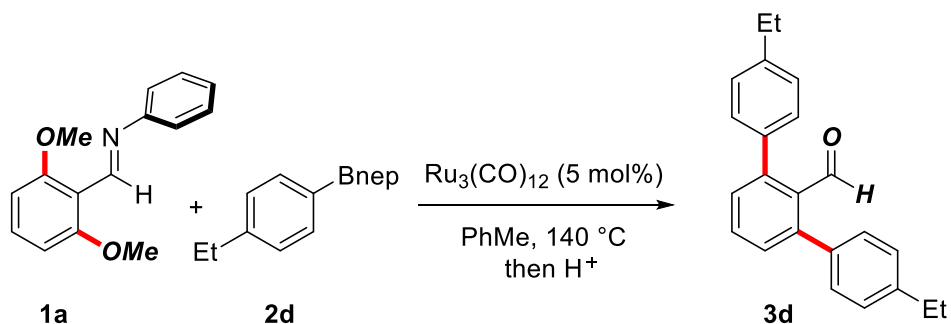
144.1, 133.5, 132.1, 131.5, 131.0, 130.2, 113.8, 55.5. **MS** = 318.1 (EI). **HRMS** calcd for C₂₁H₁₉O₃ (M⁺ + H) 319.1329 found 319.1327.

4,4''-Dimethyl-[1,1':3',1''-terphenyl]-2'-carbaldehyde (**3c**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-Me-C₄H₄-Bnep (**2c**, 102.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3c** in 66% yield (37.8 mg). White solid. **Mp** = 106–107 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.95 (s, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 (br, 8H), 2.41 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.9, 144.4, 137.5, 136.9, 133.5, 131.6, 130.3, 129.7, 129.0, 21.3. **MS** = 286.1 (EI). **HRMS** calcd for C₂₁H₁₉O (M⁺ + H) 287.1430 found 287.1431.

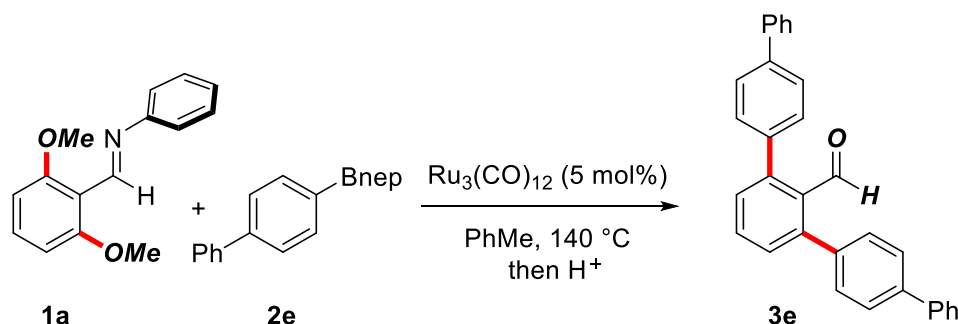
4,4''-Diethyl-[1,1':3',1''-terphenyl]-2'-carbaldehyde (**3d**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-Et-C₄H₄-Bnep (**2d**, 109.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3d** in 67% yield (42.1 mg). White solid. **Mp** = 60–61 °C. **¹H NMR**

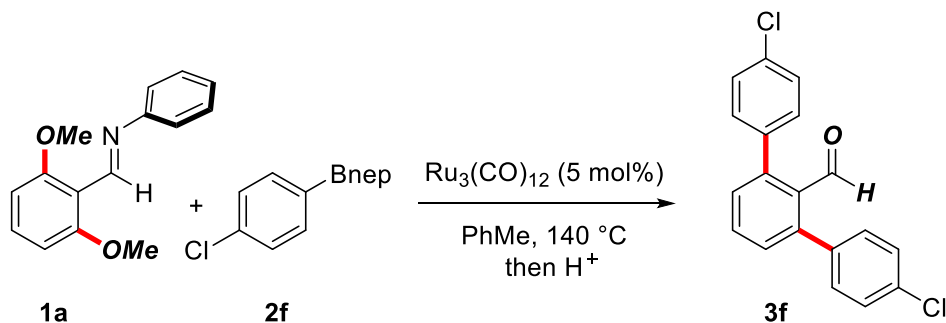
(400 MHz, CDCl₃) δ 9.96 (s, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.26 (br, 8H), 2.71 (q, J = 7.6 Hz, 4H), 1.29 (t, J = 7.6 Hz, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 194.0, 144.4, 143.8, 137.1, 133.5, 131.5, 130.4, 129.7, 127.8, 28.7, 15.5. **MS** = 314.2 (EI). **HRMS** calcd for C₂₃H₂₃O (M⁺ + H) 315.1743 found 315.1743.

[1,1':4',1'':3'',1''':4''',1''''-Quinquephenyl]-2''-carbaldehyde (3e)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-Ph-C₄H₄-Bnep (**2e**, 133.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3e** in 70% yield (57.5 mg). White solid. **Mp** = 230-231 °C. **¹H NMR (400 MHz, CDCl₃)** δ 10.06 (s, 1H), 7.68 – 7.61 (m, 9H), 7.48 – 7.43 (m, 10H), 7.36 (t, J = 7.6 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.8, 144.2, 140.7, 138.7, 133.4, 131.8, 130.6, 130.3, 129.0, 127.6, 127.3, 127.1. **MS** = 410.2 (EI). **HRMS** calcd for C₃₁H₂₃O (M⁺ + H) 411.1743 found 411.1745.

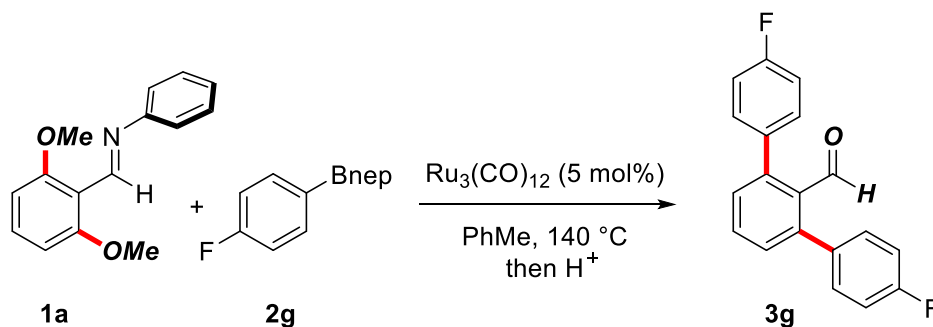
4,4''-Dichloro-[1,1':3',1''-terphenyl]-2''-carbaldehyde (3f)



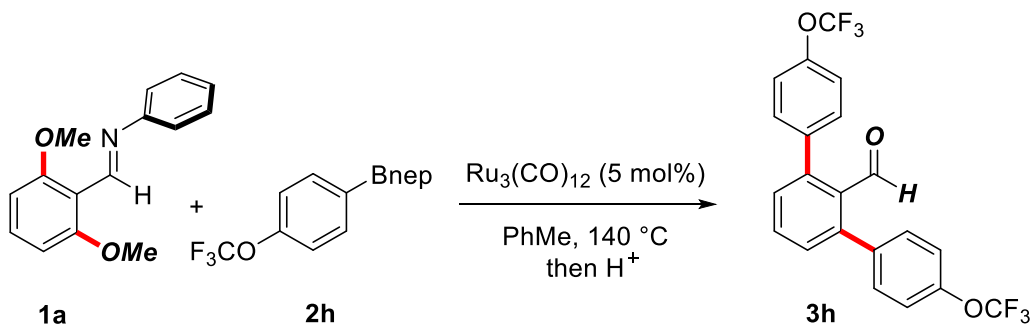
According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-Cl-C₆H₄-Bnep (**2f**, 112.3 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5

mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3f** in 58% yield (37.9 mg). White solid. **Mp** = 126-128 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.91 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.0, 143.4, 138.0, 134.2, 133.1, 132.0, 131.0, 130.8, 128.6. **MS** = 326.0 (EI). **HRMS** calcd for C₁₉H₁₃Cl₂O (M⁺ + H) 327.0338 found 327.0340.

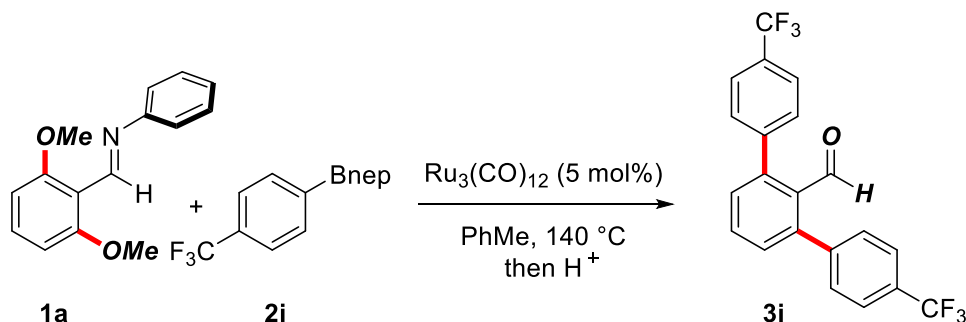
4,4''-Difluoro-[1,1':3',1''-terphenyl]-2'-carbaldehyde (**3g**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-F-C₆H₄-Bnep (**2g**, 104.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3g** in 67% yield (39.4 mg). White solid. **Mp** = 101-102 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.91 (s, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 (m, 4H), 7.11 (t, *J* = 8.4 Hz, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.3, 162.7 (d, *J* = 245.9 Hz), 143.5, 135.6 (d, *J* = 3.2 Hz), 133.3, 131.8, 131.3 (d, *J* = 7.1 Hz), 130.7, 115.3 (d, *J* = 21.4 Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -114.4 (s). **MS** = 294.1 (EI). **HRMS** calcd for C₁₉H₁₃F₂O (M⁺ + H) 295.0929 found 295.0928.

4,4''-Bis(trifluoromethoxy)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (3h)

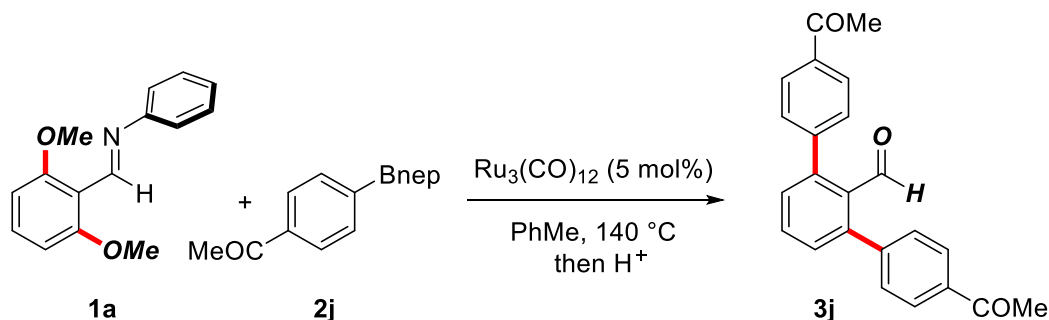
According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-CF₃O-C₆H₄-Bnep (**2h**, 104.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3h** in 77% yield (65.7 mg). White solid. **Mp** = 90-91 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.92 (s, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.38 (m, 6H), 7.28 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.9, 149.2, 143.2, 138.2, 133.1, 132.0, 131.1, 130.9, 120.8, 120.7 (q, *J* = 255.9 Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -57.7 (s). **MS** = 426.1 (EI). **HRMS** calcd for C₂₁H₁₃F₆O₃ (M⁺ + H) 427.0763 found 427.0763.

4,4''-Bis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (3i)

According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-CF₃-C₆H₄-Bnep (**2i**, 129.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3i** in 71% yield (56.0 mg). White solid. **Mp** = 102-103 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.91 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 4H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 7.6 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.5, 143.3 (d, *J* = 8.0 Hz), 133.0, 132.2, 131.1, 130.3 (q, *J* = 32.6 Hz), 130.0, 125.4 (q, *J* = 3.7 Hz), 124.3 (d, *J* = 270.4

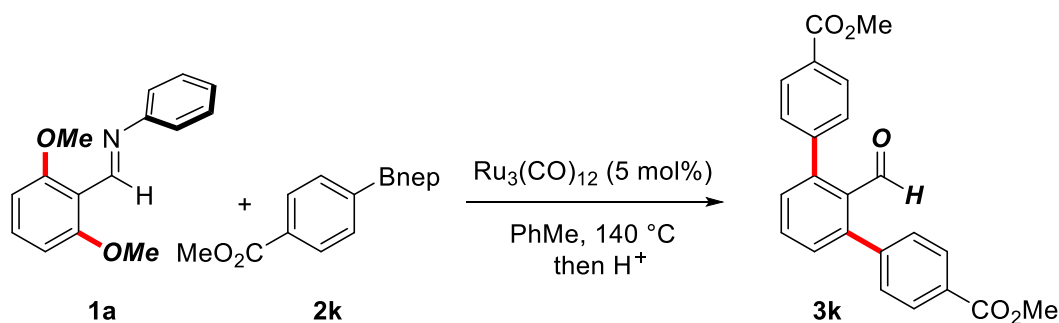
Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.5 (s). **MS** = 394.1 (EI). **HRMS** calcd for C₂₁H₁₂F₆ONa (M⁺ + Na) 417.0685 found 417.0686.

4,4''-Diacetyl-[1,1':3',1''-terphenyl]-2'-carbaldehyde (3j)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-MeCO-C₆H₄-Bnep (**2j**, 116.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3j** in 52% yield (35.6 mg). White solid. **Mp** = 155-156 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.93 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 4H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.44 (m, 6H), 2.65 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 197.7, 192.6, 144.5, 143.6, 136.5, 132.9, 132.1, 130.9, 129.9, 128.4, 26.8. **MS** = 342.1 (EI). **HRMS** calcd for C₂₃H₁₉O₃ (M⁺ + H) 343.1329 found 343.1327.

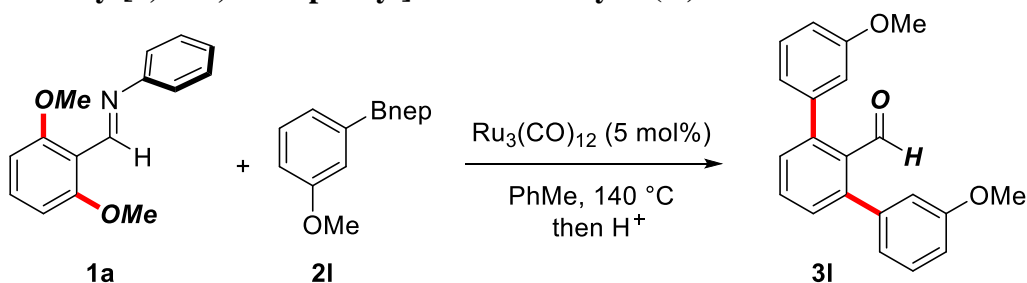
Dimethyl 2'-formyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (3k)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 4-MeO₂C-C₆H₄-Bnep (**2k**, 124.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3k** in 75% yield (56.2 mg). Yellow solid. **Mp** = 100-102 °C. **¹H NMR**

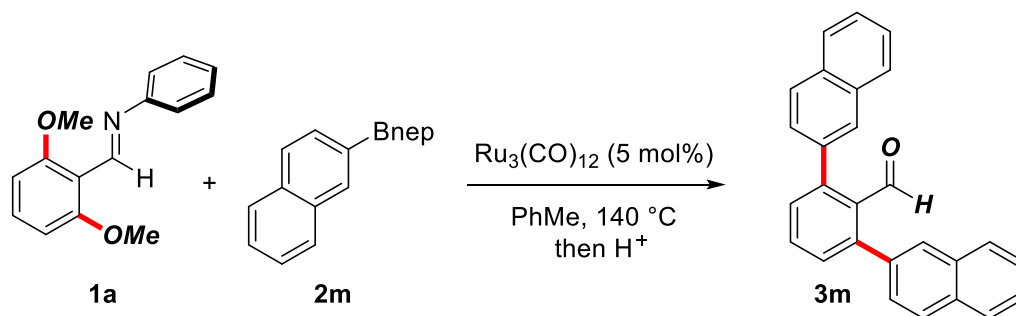
(400 MHz, CDCl₃) δ 9.92 (s, 1H), 8.12 (d, J = 8.4 Hz, 4H), 7.64 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 6H), 3.95 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.6, 166.9, 144.3, 143.7, 133.0, 132.0, 130.9, 129.7, 129.7, 52.3. **MS** = 374.1 (EI). **HRMS** calcd for C₂₃H₁₉O₅ (M⁺ + H) 375.1227 found 375.1228.

3,3'-Dimethoxy-[1,1':3',1''-terphenyl]-2'--carbaldehyde (**3l**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 3-MeO-C₆H₄-Bnep (**2l**, 110.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3l** in 55% yield (35.0 mg). White solid. **Mp** = 57-58 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.96 (s, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 8.0 Hz, 2H), 6.91 (m, 6H), 3.83 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.6, 159.5, 144.2, 141.2, 133.5, 131.5, 130.4, 129.3, 122.3, 115.4, 113.4, 55.4. **MS** = 318.1 (EI). **HRMS** calcd for C₂₁H₁₈ONa (M⁺ + Na) 341.1148 found 341.1146.

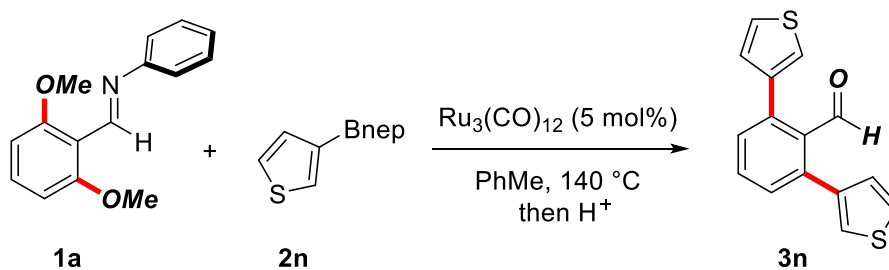
2,6-Di(naphthalen-2-yl)benzaldehyde (**3m**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with naphthalen-2-yl-Bnep (**2m**, 120.1 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3m** in 61% yield (39.4 mg). Yellow solid. **Mp** = 148-149 °C. **¹H NMR**

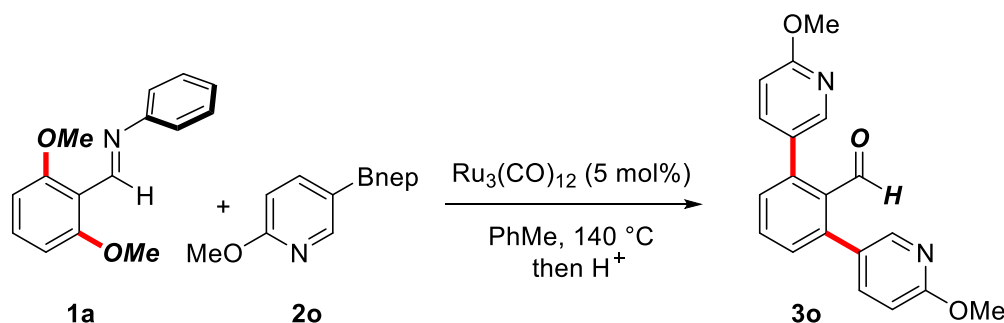
(400 MHz, CDCl₃) δ 10.02 (s, 1H), 7.87 (m, 8H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (m, 8H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.4, 144.6, 137.4, 133.5, 133.2, 132.8, 131.8, 130.9, 128.6, 128.2, 127.9, 127.8, 126.6, 126.4. **MS** = 358.1 (EI). **HRMS** calcd for C₂₇H₁₈ONa (M⁺ + Na) 381.1250 found 381.1246.

2,6-Di(thiophen-3-yl)benzaldehyde (3n)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 3-thienyl-Bnep (**2n**, 98.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3n** in 61% yield (32.9 mg). White solid. **Mp** = 81–82 °C. **¹H NMR (400 MHz, CDCl₃)** δ 10.05 (s, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 7.7 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.29 (d, J = 1.1 Hz, 2H), 7.15 (d, J = 4.8 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.9, 140.0, 138.7, 133.9, 131.8, 130.4, 129.5, 125.7, 124.6. **MS** = 270.0 (EI). **HRMS** calcd for C₁₅H₁₁OS₂ (M⁺ + H) 271.0246 found 271.0246.

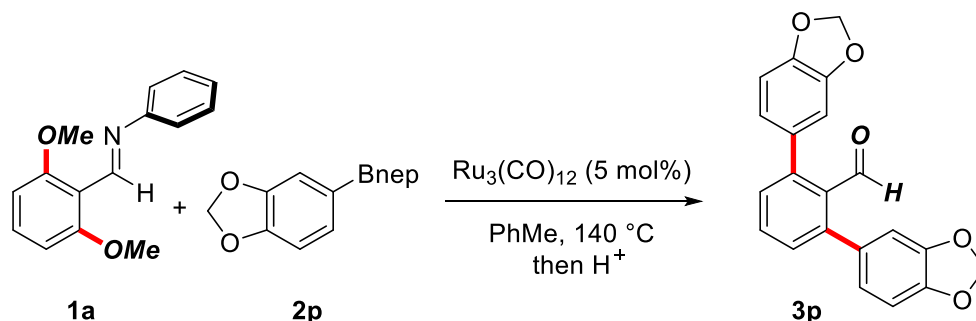
2,6-Bis-(6-methoxypyridin-3-yl)benzaldehyde (3o)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with 6-MeO-3-C₅H₃N-Bnep (**2o**, 110.6 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by

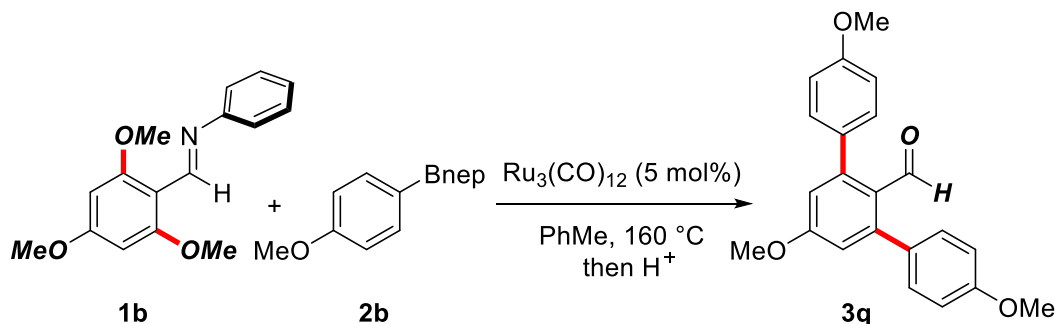
chromatography afforded **3o** in 73% yield (46.7 mg). White solid. **Mp** = 126-127 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.97 (s, 1H), 8.17 (s, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.02 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.8, 164.0, 147.0, 141.3, 140.2, 133.3, 132.4, 131.1, 128.3, 110.4, 53.8. **MS** = 320.1 (EI). **HRMS** calcd for C₁₉H₁₇N₂O₃ (M⁺ + H) 321.1234 found 321.1234.

2,6-Bis(benzo[*d*][1,3]dioxol-5-yl)benzaldehyde (**3p**)



According to the general procedure, *N*-(2,6-dimethoxybenzylidene)aniline (**1a**, 48.3 mg, 0.20 mmol) was reacted with benzo[*d*][1,3]dioxol-5-yl-Bnep (**2p**, 117.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3p** in 51% yield (35.3 mg). White solid. **Mp** = 150 - 151 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.95 (s, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 6.86 – 6.83 (m, 4H), 6.76 (dd, *J*₁ = 7.6, *J*₂ = 1.6 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.7, 147.7, 147.5, 144.0, 133.7, 133.6, 131.6, 130.4, 123.5, 110.3, 108.2, 101.4. **MS** = 346.1 (EI). **HRMS** calcd for C₂₁H₁₄O₅Na (M⁺ + Na) 369.0733 found 369.0732.

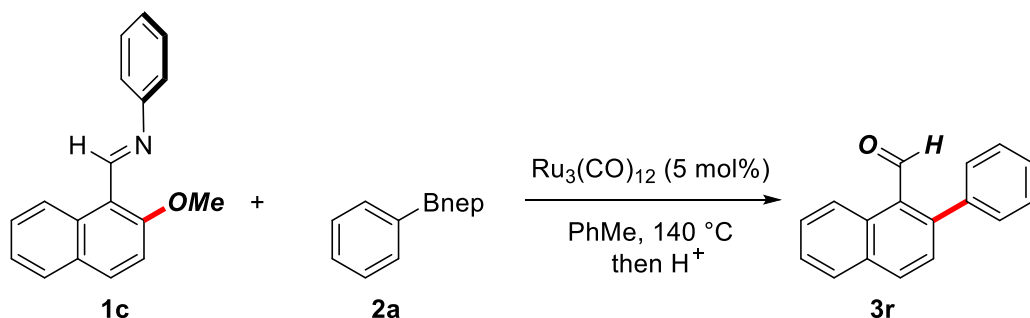
4,4',5'-Trimethoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (**3q**)



According to the general procedure, *N*-(2,4,6-trimethoxybenzylidene)aniline (**1b**, 54.3 mg, 0.20 mmol) was reacted with 4-MeO-C₆H₄-Bnep (**2b**, 110.0 mg, 0.50 mmol), and Ru₃(CO)₁₂ (6.4 mg,

5 mol%) in toluene (1.0 M) at 100 °C for 10 h. Acidic work-up and purification by chromatography afforded **3q** in 70% yield (48.8 mg). White solid. **Mp** = 132–133 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.82 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 6.82 (s, 2H), 3.89 (s, 3H), 3.85 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.2, 161.6, 159.5, 147.4, 132.4, 130.8, 126.4, 115.8, 113.7, 55.7, 55.5. **MS** = 348.1 (EI). **HRMS** calcd for C₂₂H₂₁O₄ (M⁺ + H) 349.1434 found 349.1433.

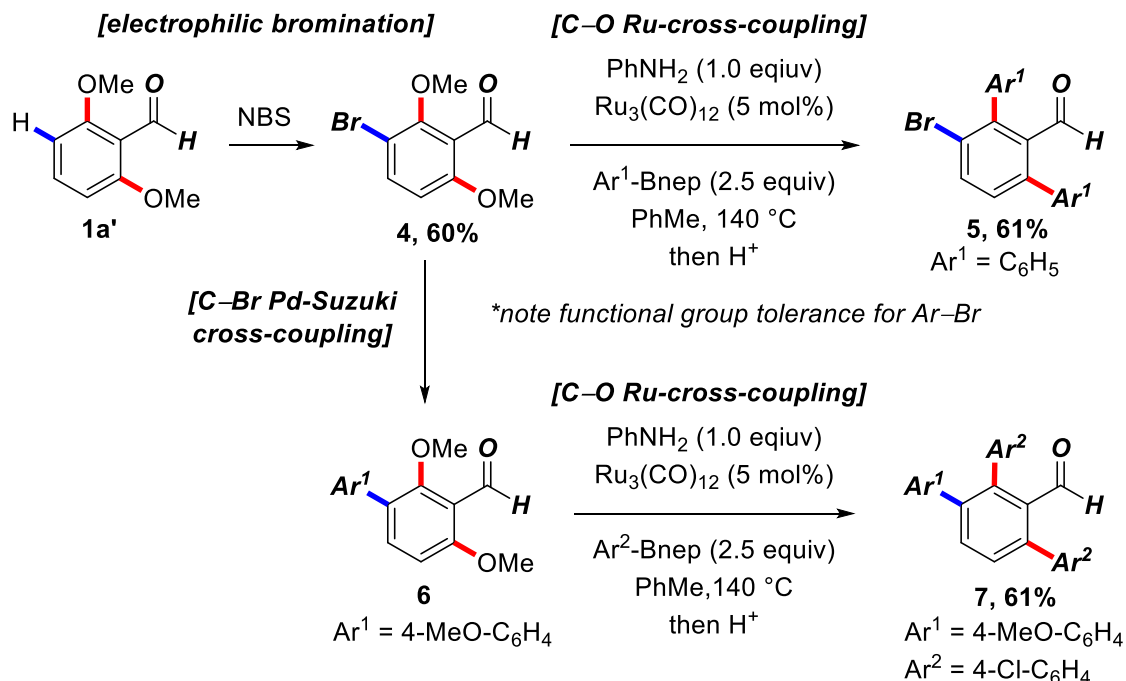
2-Phenyl-1-naphthaldehyde (**3r**)



According to the general procedure, *N*-((2-methoxynaphthalen-1-yl)methylene)aniline (**1c**, 261 mg, 1.0 mmol) was reacted with Ph-Bnep (**2a**, 475 mg, 2.50 mmol), and Ru₃(CO)₁₂ (32 mg, 5 mol%) in toluene (1.0 M) at 140 °C for 10 h. Acidic work-up and purification by chromatography afforded **3r** in 85% yield (198 mg). Yellow solid. **Mp** = 132–135 °C. **¹H NMR (400 MHz, CDCl₃)** δ 10.19 (s, 1H), 9.25 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.43 (m, 5H). **¹³C NMR (100 MHz, CDCl₃)** δ 194.8, 148.1, 138.9, 134.0, 133.1, 130.7, 130.5, 129.4, 129.0, 128.5, 128.5, 128.4, 126.9, 126.0. **MS** = 232.1 (EI). **HRMS** calcd for C₁₇H₁₃O (M⁺ + H) 233.0961 found 233.0961.

Ru(0)-Catalyzed C–O Arylation of Aryl Methyl Ethers: Synthetic Utility

Sequence 1. Sequential Bromination/ Suzuki Cross-Coupling/C–O Cross-Coupling.



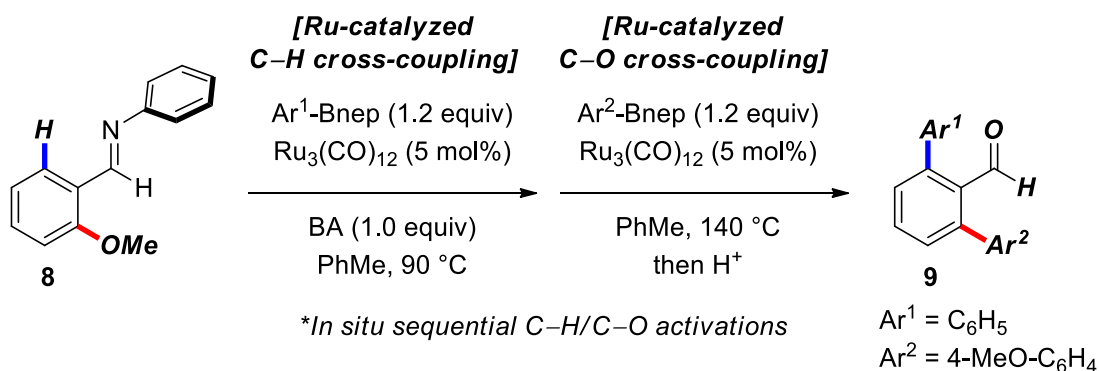
3-Bromo-2,6-dimethoxybenzaldehyde (4). To a solution of 2,6-dimethoxybenzaldehyde (10 mmol) in MeCN (1.0 M), NBS (12 mmol, 1.2 equiv) and NH₄OAc (5 mmol, 0.50 equiv) were added at 0 °C, the resulting reaction mixture was slowly warmed up to room temperature and stirred at room temperature for 6 hours. After the indicated time, the reaction mixture was quenched with water (10 mL), extracted with diethyl ether (3 x 20 mL), organic layers were combined, dried and concentrated. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product. Yield 60% (1.47 g). Yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 10.40 (s, 1H), 7.67 (d, *J* = 9.2 Hz, 1H), 6.63 (d, *J* = 9.2 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 188.5, 161.3, 159.0, 138.6, 120.6, 109.2, 108.9, 62.7, 56.3. **MS** = 244.0 (EI). **HRMS** calcd for C₉H₁₀BrO₃ (M⁺ + H) 244.9808 found 244.9809.

4'-Bromo-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5). According to the general procedure, an oven-dried vial equipped with a stir bar was charged with aldehyde **4** (0.2 mmol, 1.0 equiv), PhNH₂ (0.2 mmol, 1.0 equiv), Ph–Bnep (**2a**, 95.0 mg, 0.50 mmol), Ru₃(CO)₁₂ (6.4 mg, 5 mol%), MgSO₄ (1.0 equiv) and toluene (1.0 M), and the resulting reaction mixture was stirred at 140 °C for 10 h. After the indicated time, the reaction was cooled down to room temperature and

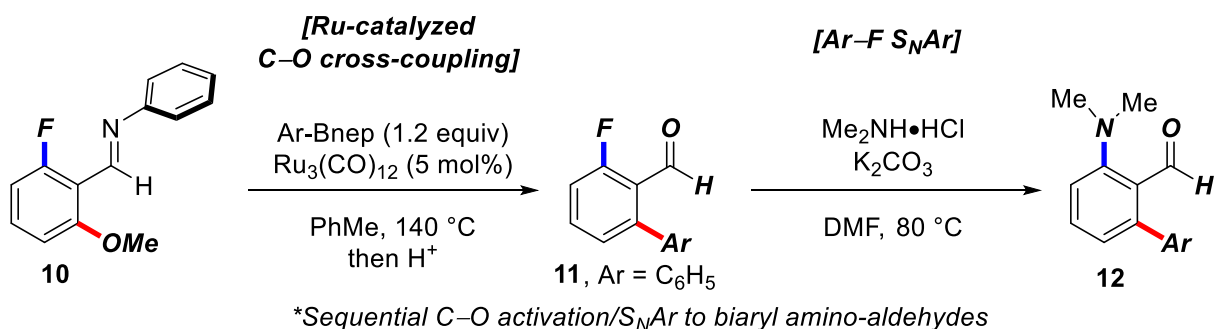
subjected to the standard imine deprotection procedure (diethyl ether, HCl, 1.0 N, aq, 3 h, room temperature). Purification by chromatography on silica gel afforded the title product. Yield 61% (41.1 mg). White solid. **Mp** = 118-119 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.72 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.40 (m, 6H), 7.32 – 7.28 (m, 2H), 7.26 – 7.23 (m, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 192.6, 143.7, 143.3, 138.7, 138.4, 135.9, 135.7, 131.8, 129.8, 129.6, 128.5, 128.3, 128.2, 128.1, 124.8. **MS** = 336.0 (EI). **HRMS** calcd for C₁₉H₁₄BrO (M⁺ + H) 337.0223 found 337.0222.

2,4,4'-Trimethoxy-[1,1'-biphenyl]-3-carbaldehyde (6). Under argon, to aldehyde **4** (neat, 1.0 mmol) were sequentially added 4-MeO-C₆H₄-B(OH)₂ (1.2 equiv, 1.2 mmol), Pd(OAc)₂ (0.01 mmol, 1 mol%), Na₂CO₃ (2.0 equiv, 2.0 mmol), and EtOH:water (0.10 M, 1:1 v/vol). The resulting mixture was stirred at 80 °C for 6 hours. After the indicated time, the reaction was cooled down to room temperature, extracted with diethyl ether (3 x 20 mL), washed with water (3 x 20 mL), organic layers were combined, dried and concentrated. The crude product **6** was directly used in the next step without further purification.

4''-Chloro-4'-(4-chlorophenyl)-4-methoxy-[1,1':2',1''-terphenyl]-3'-carbaldehyde (7). According to the general procedure, an oven-dried vial equipped with a stir bar was charged with aldehyde **6** (0.2 mmol, 1.0 equiv), PhNH₂ (0.2 mmol, 1.0 equiv), 4-Cl-C₆H₄-Bnep (0.50 mmol), Ru₃(CO)₁₂ (6.4 mg, 5 mol%), MgSO₄ (1.0 equiv) and toluene (1.0 M), and the resulting reaction mixture was stirred at 140 °C for 10 h. After the indicated time, the reaction was cooled down to room temperature and subjected to the standard imine deprotection procedure (diethyl ether, HCl, 1.0 N, aq, 3 h, room temperature). Purification by chromatography on silica gel afforded the title product. Yield 61% (52.9 mg). Yellow solid. **Mp** = 167-168 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.82 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.6, 158.8, 141.9, 141.4, 141.1, 138.2, 136.1, 134.5, 134.1, 133.8, 133.6, 132.4, 132.1, 131.0, 130.8, 128.6, 128.3, 113.7, 55.4. **MS** = 432.1 (EI). **HRMS** calcd for C₂₆H₁₉Cl₂O₂ (M⁺ + H) 433.0757 found 433.0756.

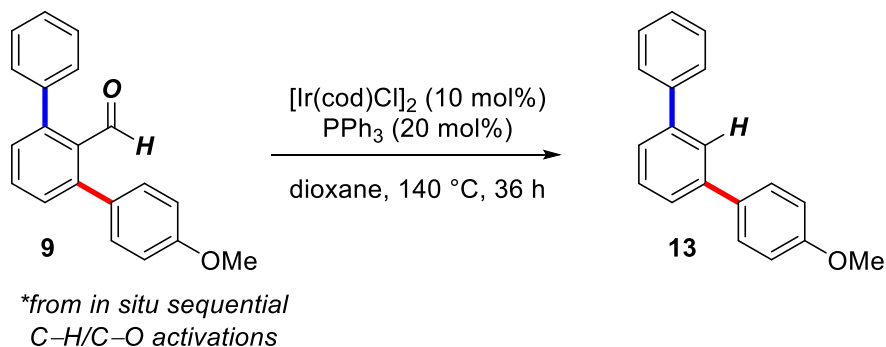
Sequence 2. Sequential Ru(0)-Catalyzed C–H/ C–O Cross-Coupling.

4-Methoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (9). An oven-dried vial equipped with a stir bar was charged with *N*-(2-methoxybenzylidene)aniline **8** (47.0 mg, 0.2 mmol), Ph–Bnep (38.0 mg, 0.2 mmol), (*E*)-4-phenylbut-3-en-2-one (BA, 35.1 mg, 0.24 mmol), Ru₃(CO)₁₂ (6.4 mg, 5 mol%) and toluene (1.0 M), and the resulting reaction mixture was stirred at 90 °C for 10 h. After the indicated time, the reaction mixture was cooled down to room temperature, 4-MeO-C₆H₄–Bnep (0.2 mmol) and Ru₃(CO)₁₂ (6.4 mg, 5 mol%) were sequentially added, and the resulting reaction mixture was stirred at 140 °C for 10 h. After the indicated time, the reaction was cooled down to room temperature and subjected to the standard imine deprotection procedure (diethyl ether, HCl, 1.0 N, aq, 3 h, room temperature). Purification by chromatography on silica gel afforded the title product. Yield 63% (36.3 mg). White solid. **Mp** = 101-102 °C. **¹H NMR (400 MHz, CDCl₃)** δ 9.95 (s, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.33 (m, 7H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 193.8, 159.6, 144.3, 144.2, 140.0, 133.5, 131.9, 131.6, 131.0, 130.6, 130.2, 129.7, 128.3, 127.7, 113.9, 55.5. **MS** = 288.1 (EI). **HRMS** calcd for C₂₀H₁₇O₂ (M⁺ + H) 289.1223 found 289.1223.

Sequence 3. Sequential Ru(0)-Catalyzed C–O Cross-Coupling/*S_NAr* Amination.

3-Fluoro-[1,1'-biphenyl]-2-carbaldehyde (11). According to the general procedure A, an oven-dried vial equipped with a stir bar was charged with *N*-(2-fluoro-6-methoxybenzylidene)aniline (0.20 mmol), Ph–Bnep (38.0 mg, 0.2 mmol), Ru₃(CO)₁₂ (6.4 mg, 5 mol%) and toluene (1.0 M), and the resulting reaction mixture was stirred at 140 °C for 10 h. After the indicated time, the reaction mixture was cooled down to room temperature, and subjected to the standard imine deprotection procedure (diethyl ether, HCl, 1.0 N, aq, 3 h, room temperature). Purification by chromatography on silica gel afforded the title product. Yield 70% (28.0 mg). Colorless oil. **¹H NMR (600 MHz, CDCl₃)** δ 9.95 (s, 1H), 7.60 – 7.55 (m, 1H), 7.48 – 7.43 (m, 3H), 7.36 – 7.32 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 9.0 Hz, 1H). **¹³C NMR (150 MHz, CDCl₃)** δ 189.5, 162.0 (d, *J* = 261.2 Hz), 147.0, 137.4 (d, *J* = 2.0 Hz), 134.5 (d, *J* = 10.0 Hz), 129.8, 128.5, 128.5, 126.7 (d, *J* = 3.3 Hz), 122.9 (d, *J* = 7.3 Hz), 115.9 (d, *J* = 21.4 Hz). **¹⁹F NMR (565 MHz, CDCl₃)** δ -116.0 (m, 1F). **MS** = 200.1 (EI). **HRMS** calcd for C₁₃H₉FONa (M⁺ + Na) 223.0530 found 223.0531.

3-(Dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde (12). To the above compound **11** (0.2 mmol), Me₂NH·HCl (10 mmol, 5 equiv), K₂CO₃ (15 mmol), and DMF (5 mL) were added. The mixture was heated at 80 °C for 12 hours. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel afforded the title product. Yield 91% (41.0 mg). Yellow solid. **¹H NMR (400 MHz, CDCl₃)** δ 9.80 (s, 1H), 7.45 – 7.34 (m, 6H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 2.99 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 190.2, 154.4, 149.2, 140.1, 133.4, 130.1, 128.3, 127.9, 123.9, 121.7, 116.1, 45.1. **MS** = 225.1 (EI). **HRMS** calcd for C₁₅H₁₆NO (M⁺ + H) 226.1226 found 226.1225.

Sequence 4. Traceless Ru(0)-Catalyzed C–H/C–O Cross-Coupling/Aldehyde Decarbonylation.

4-Methoxy-1,1':3',1''-terphenyl (13). An oven-dried vial equipped with a stir bar was charged with 4-methoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (10.0 mg, 0.035 mmol), [Ir(cod)Cl]₂ (2.4 mg, 0.0035 mmol), PPh₃ (1.9 mg, 0.007 mmol), and dioxane (0.2 M), and the resulting reaction mixture was stirred at 140 °C for 36 h. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel afforded the title product. Yield 63% (5.7 mg). White solid. **Mp** = 82-84 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.76 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.53 (m, 2H), 7.50 – 7.44 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 159.5, 142.0, 141.6, 141.5, 133.9, 129.3, 128.9, 128.4, 127.5, 127.4, 125.9, 125.9, 125.7, 114.5, 55.5. **MS** = 260.1 (EI). **HRMS** calcd for C₁₉H₁₆ONa (M⁺ + Na) 283.1099 found 283.1101.

Mechanistic Selectivity Studies – Imines

General Procedure. An oven-dried vial equipped with a stir bar was charged with two imine substrates (each 0.4 mmol, 2.0 equiv), Ph–Bnep (**2a**, 38.0 mg, 0.20 mmol, 1.0 equiv), Ru₃(CO)₁₂ (6.4 mg, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 M) was added at room temperature, the reaction mixture was placed in a preheated oil bath at 140 °C, and stirred for 10 h at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Mechanistic Selectivity Studies – Organoboranes

General Procedure. An oven-dried vial equipped with a stir bar was charged with an imine substrate (0.2 mmol, 1.0 equiv), two aryl boronic ester substrates (each 0.50 mmol, 2.5 equiv), Ru₃(CO)₁₂ (6.4 mg, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 M) was added at room temperature, the reaction mixture was placed in a preheated oil bath at 140 °C, and stirred for 10 h at 140 °C. After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ¹H NMR (CDCl₃, 400 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

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^1H , ^{13}C and ^{19}F NMR Spectra

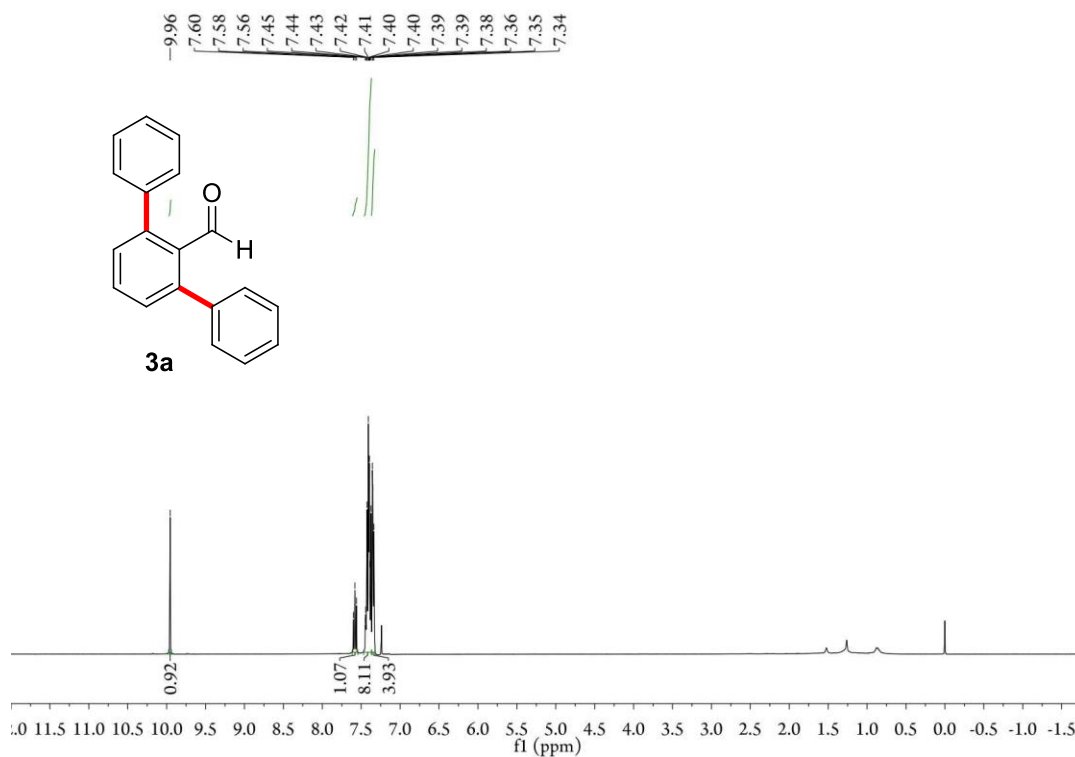


Figure S1. ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound **3a**

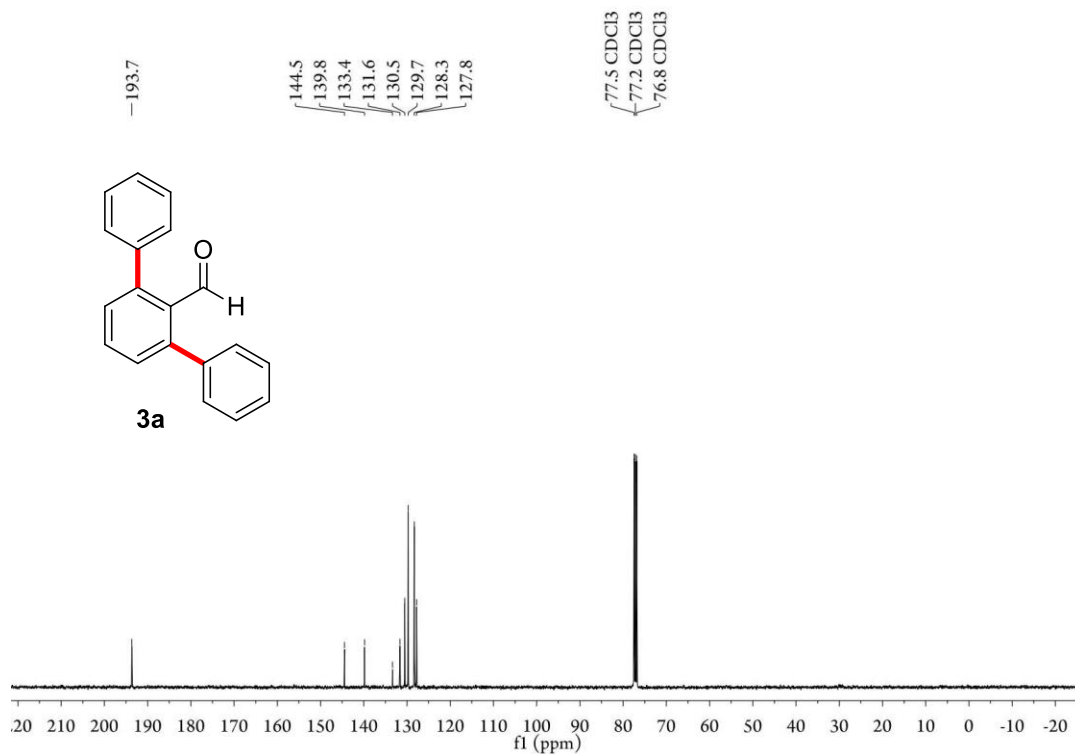


Figure S2. ^{13}C NMR (100 MHz, CDCl_3) Spectrum of Compound **3a**

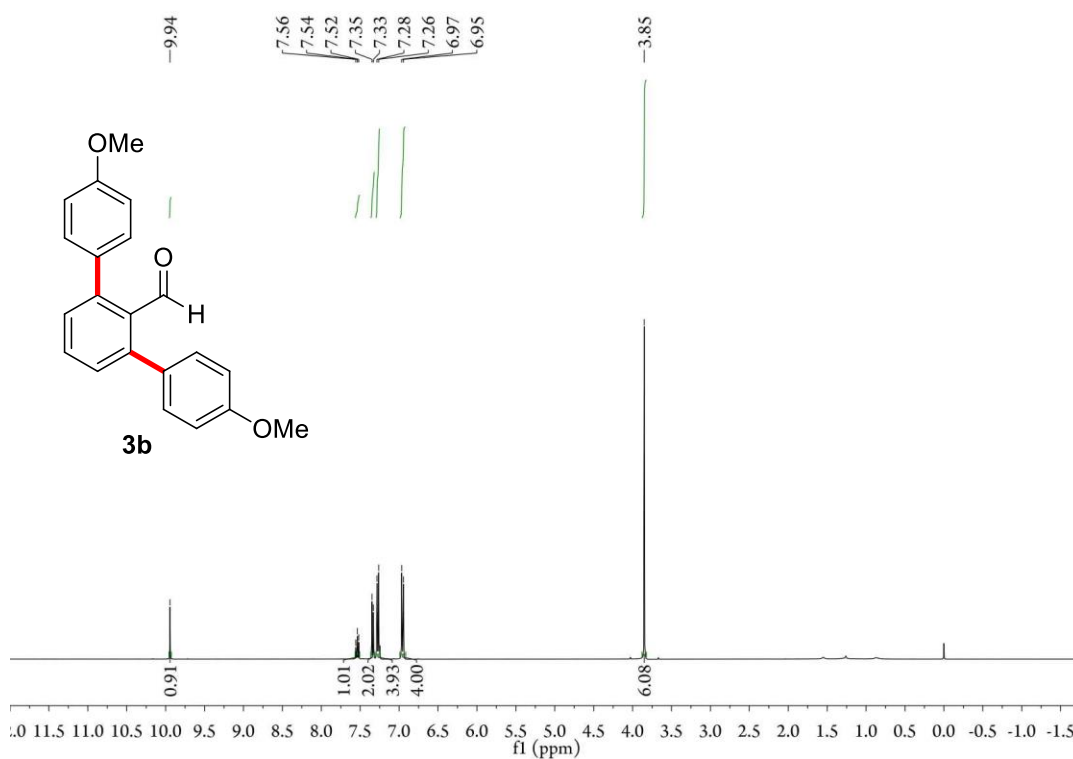


Figure S3. $^1\text{H NMR}$ (400 MHz, CDCl_3) Spectrum of Compound **3b**

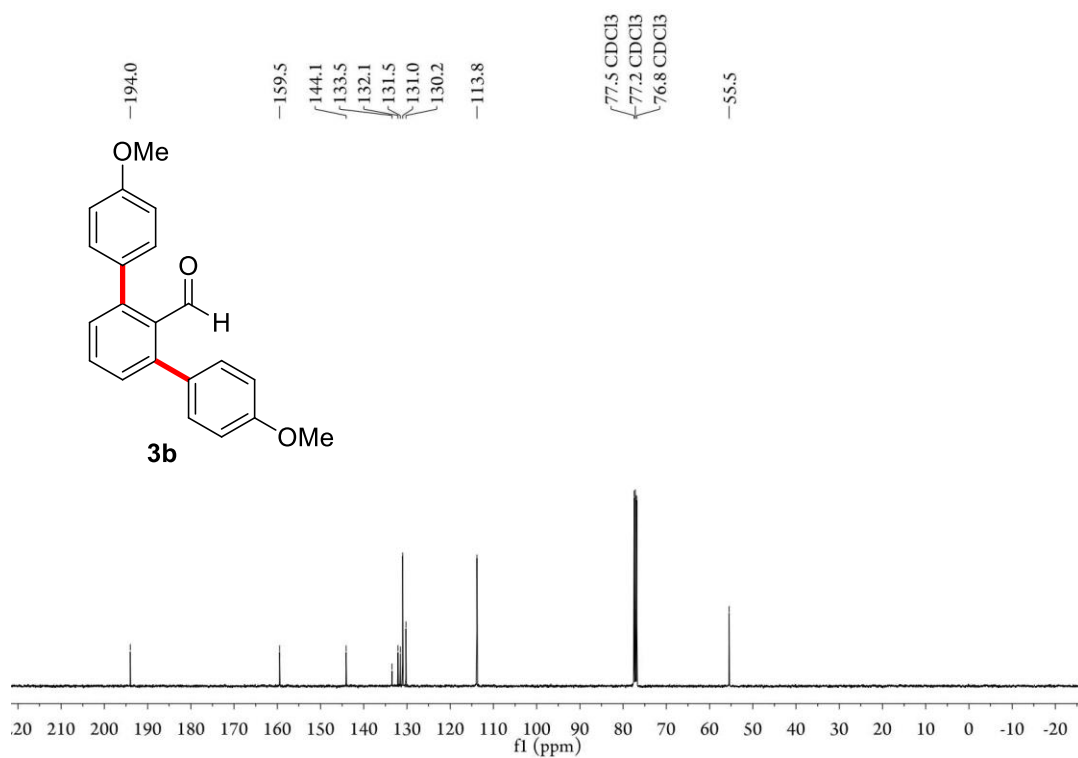
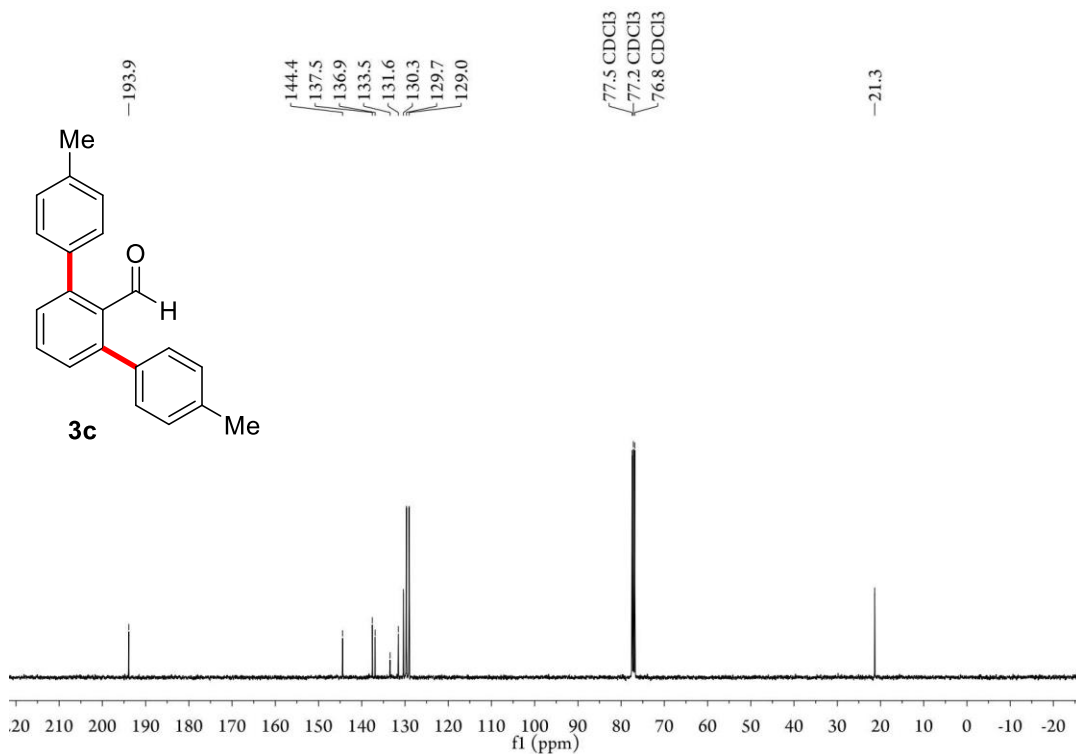
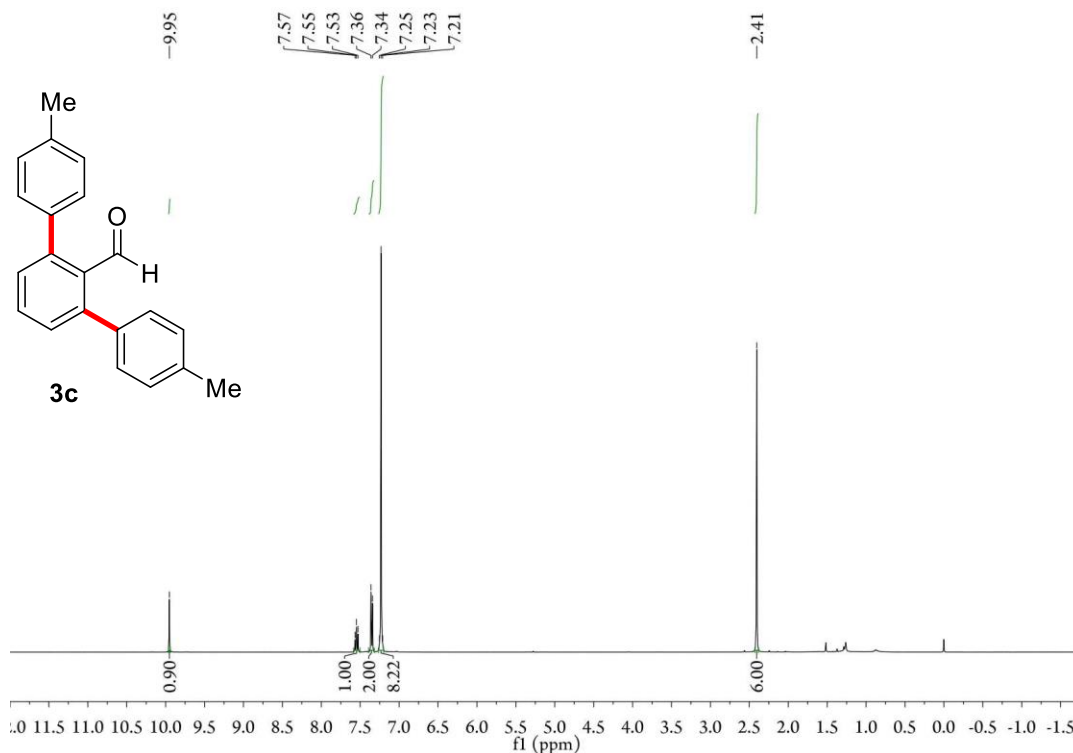
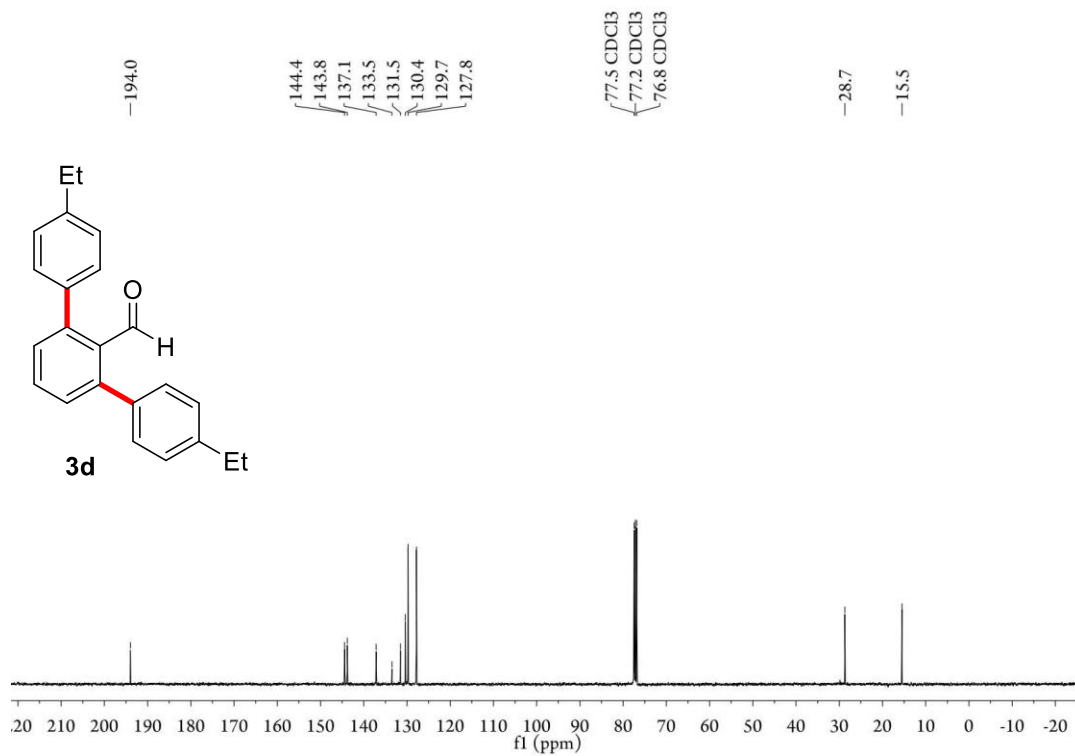
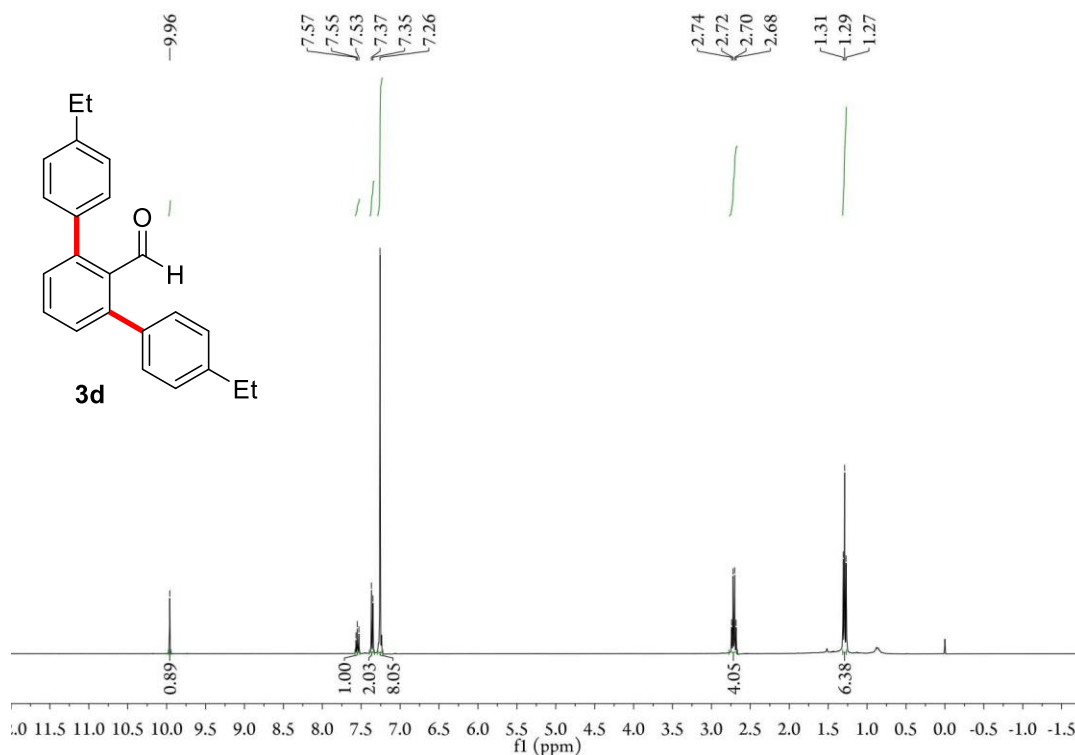


Figure S4. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) Spectrum of Compound **3b**





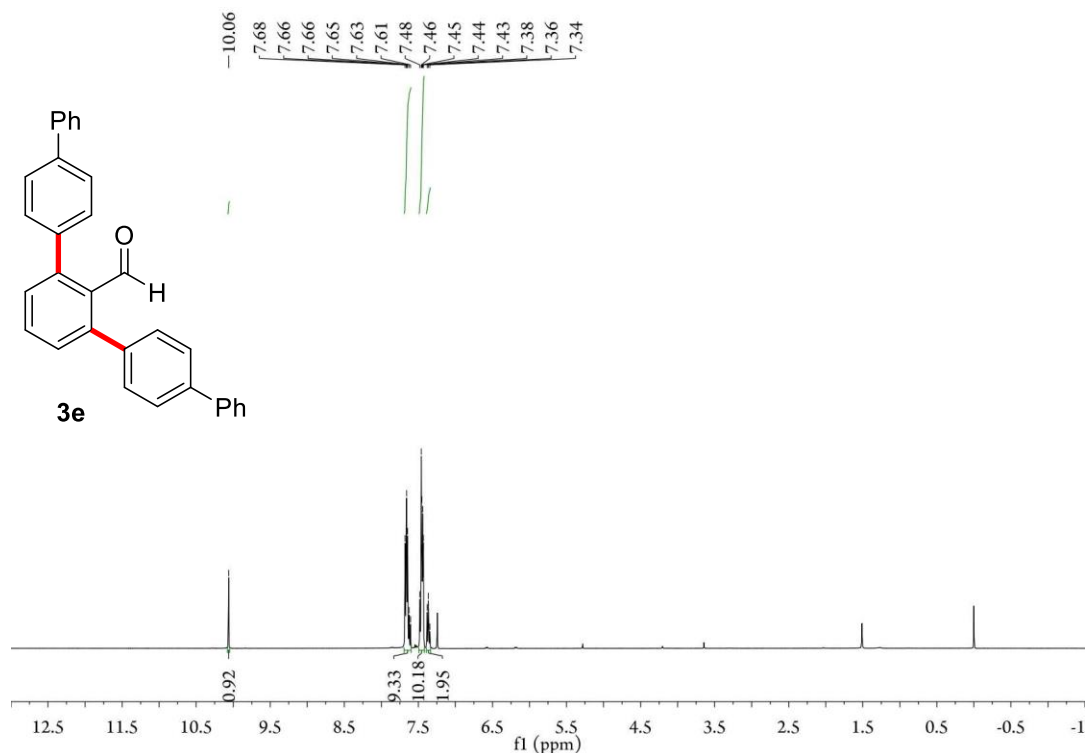


Figure S9. ^1H NMR (400 MHz, CDCl_3) Spectrum of Compound **3e**

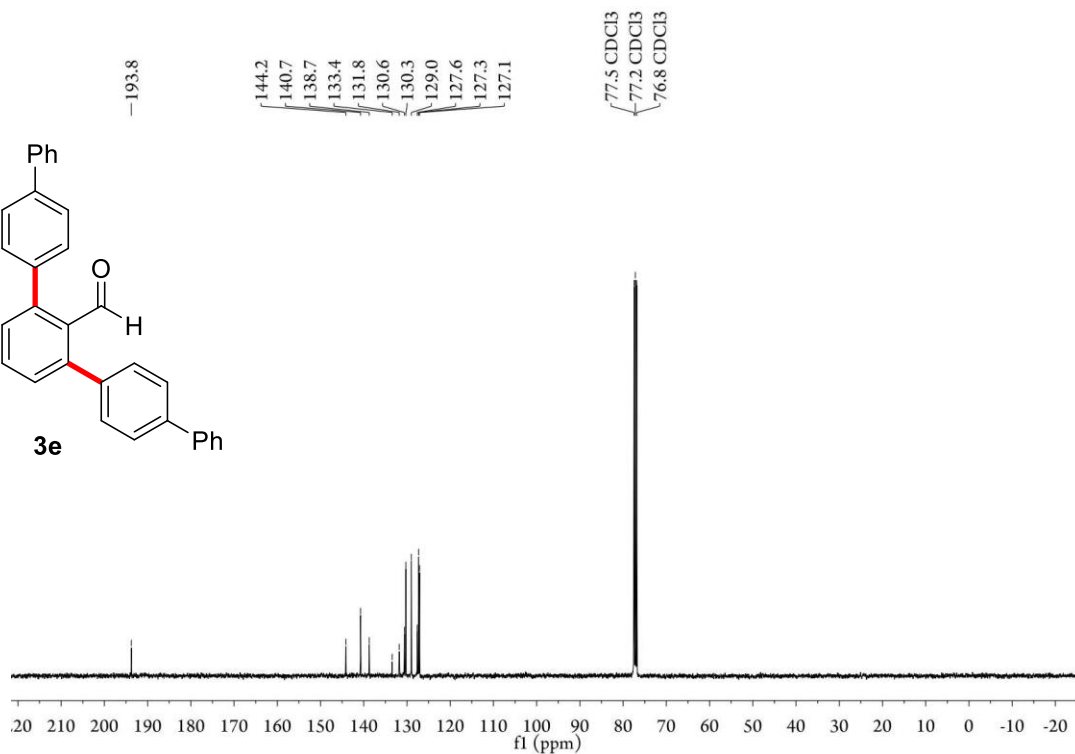


Figure S10. ^{13}C NMR (100 MHz, CDCl_3) Spectrum of Compound **3e**

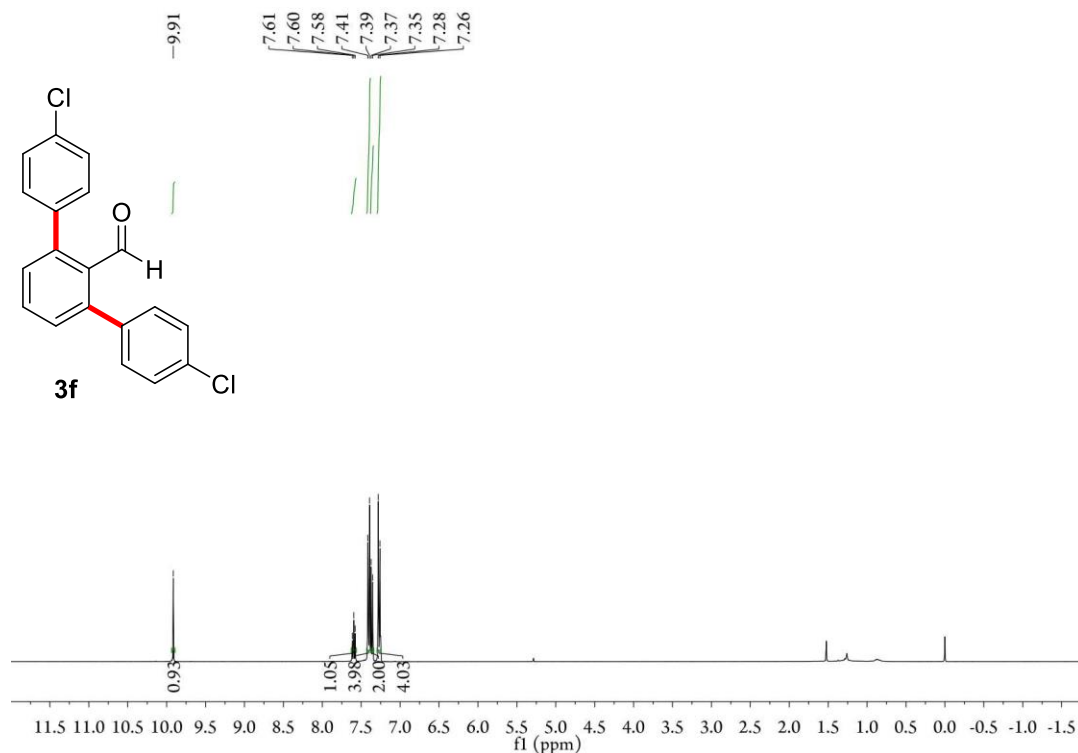


Figure S11. $^1\text{H NMR}$ (400 MHz, CDCl_3) Spectrum of Compound **3f**

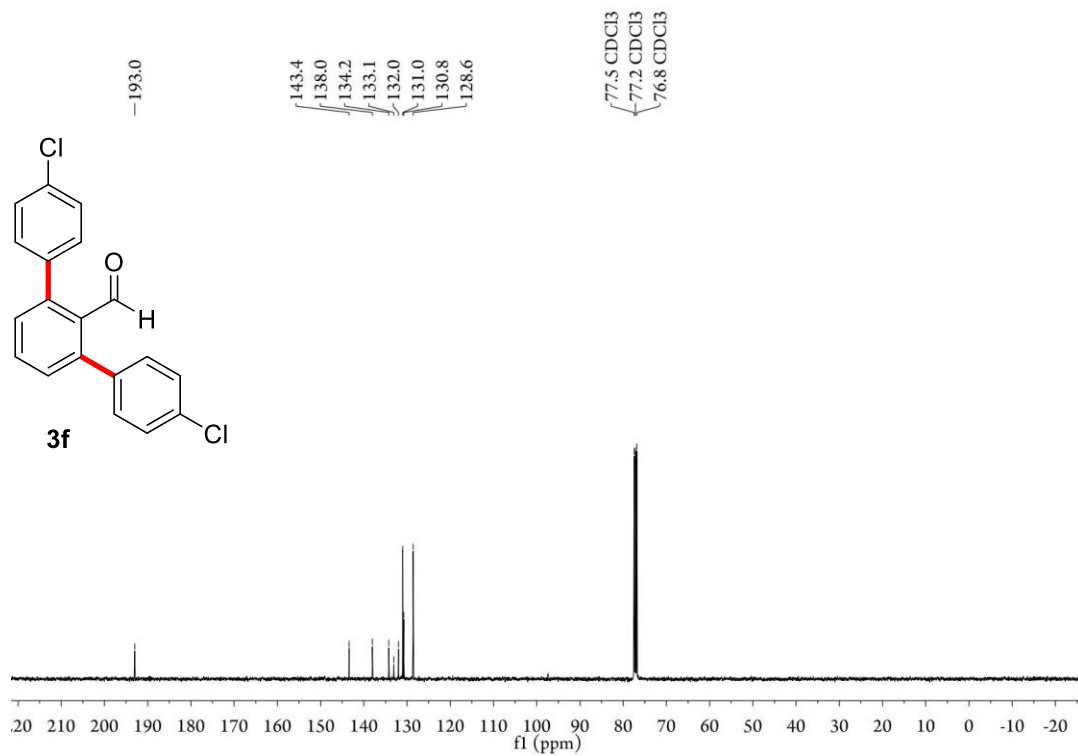


Figure S12. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) Spectrum of Compound **3f**

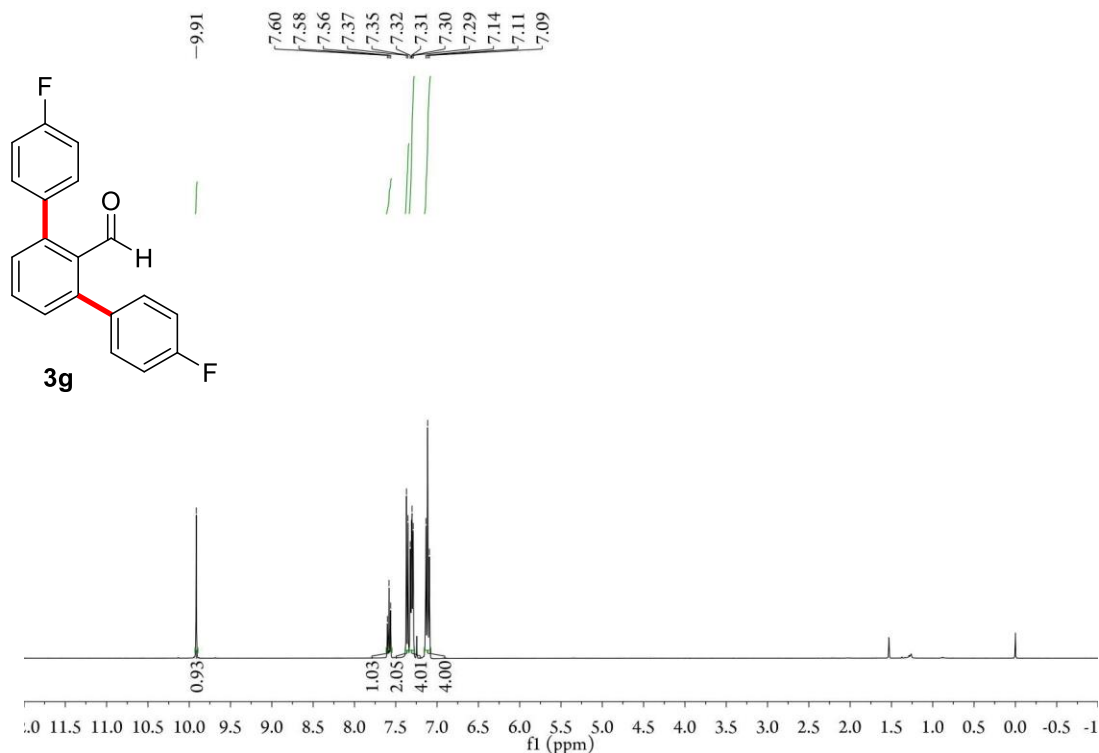


Figure S13. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3g**

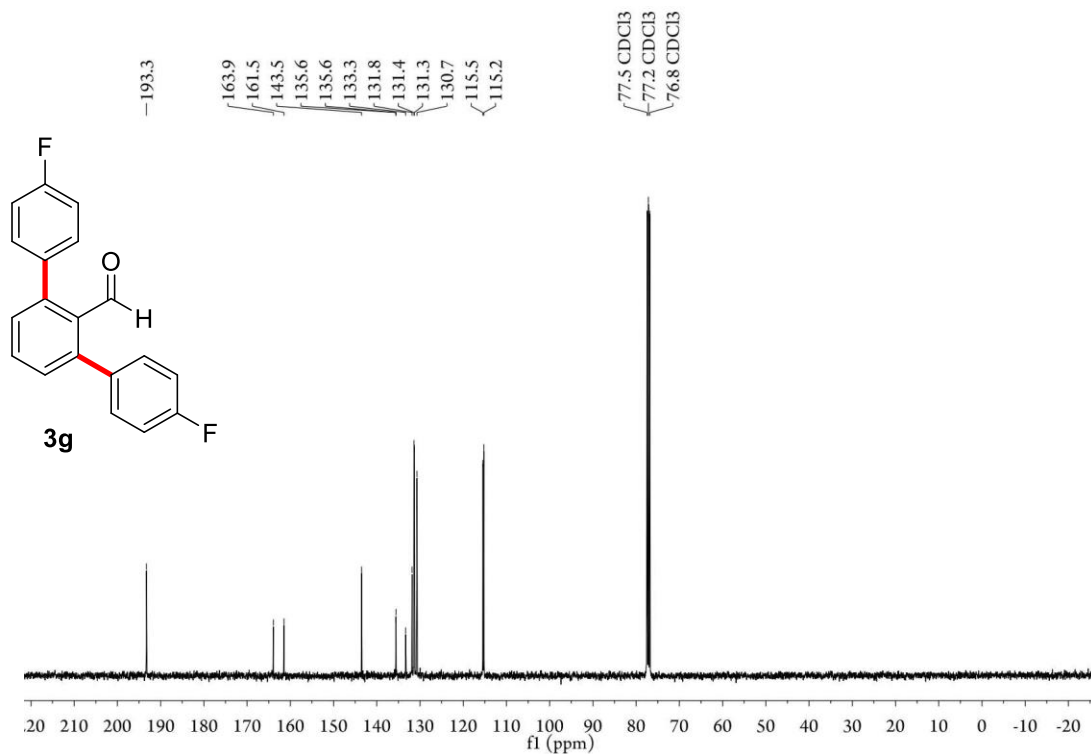


Figure S14. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3g**

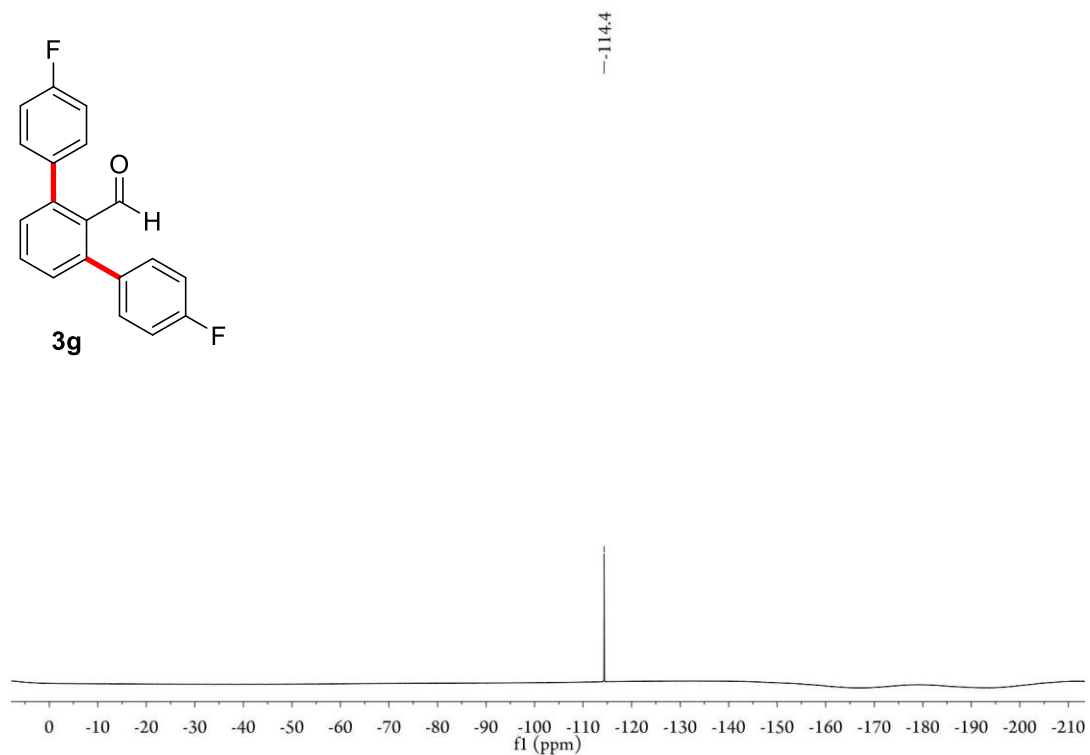


Figure S15. ^{19}F NMR (376 MHz, CDCl_3) Spectrum of Compound **3g**

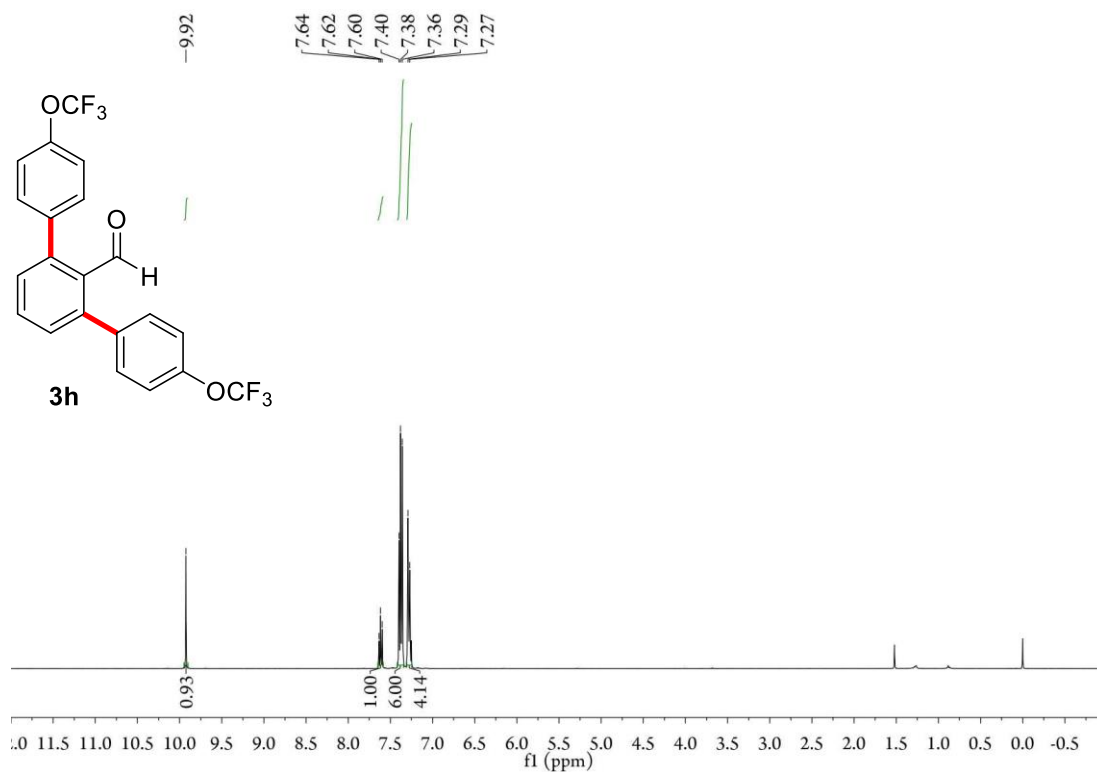


Figure S16. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3h**

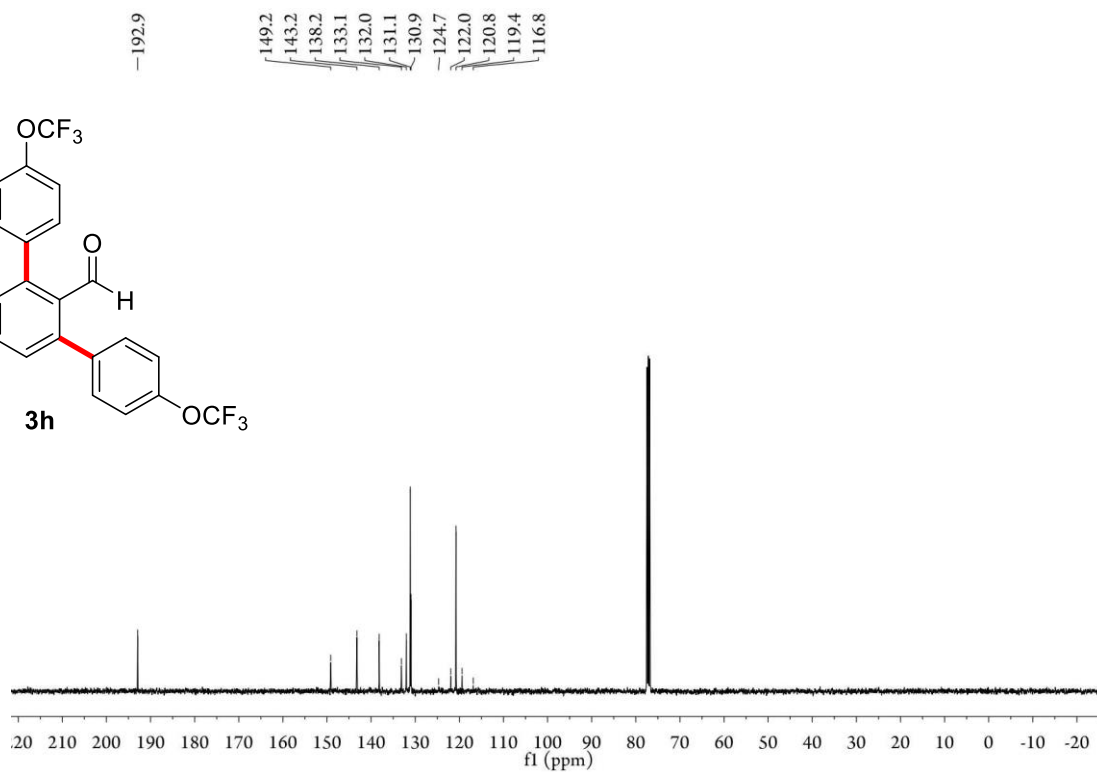


Figure S17. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3h**

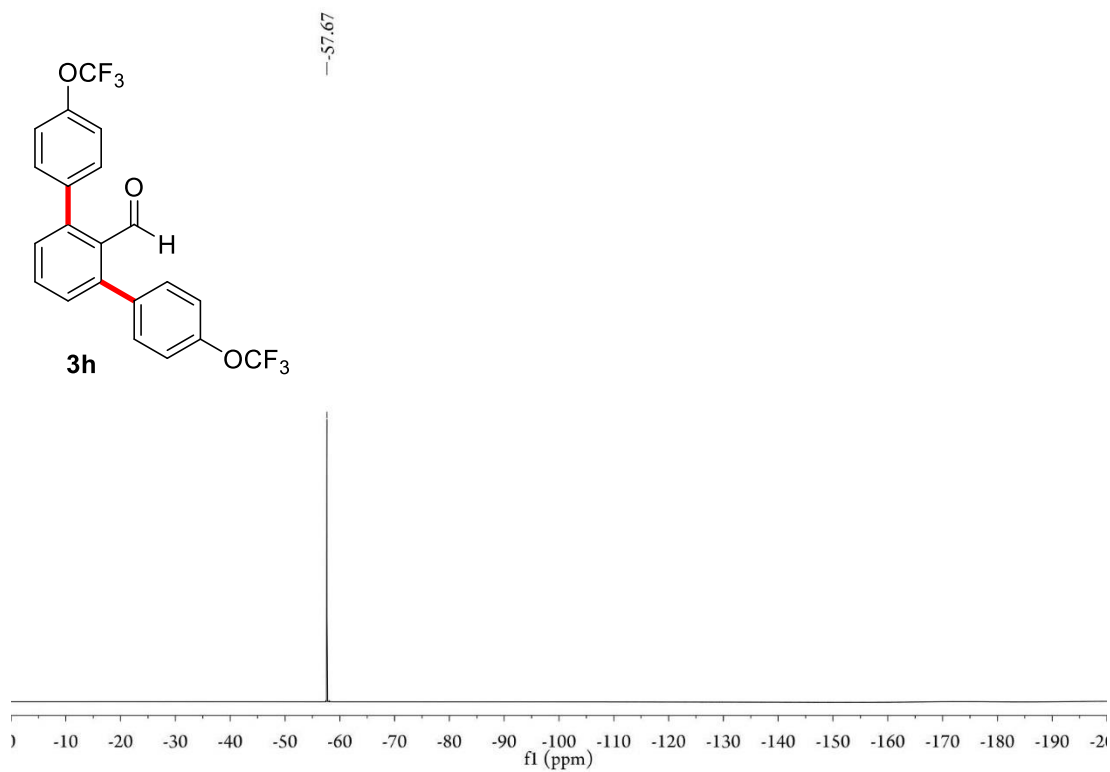


Figure S18. ^{19}F NMR (376 MHz, CDCl_3) Spectrum of Compound **3h**

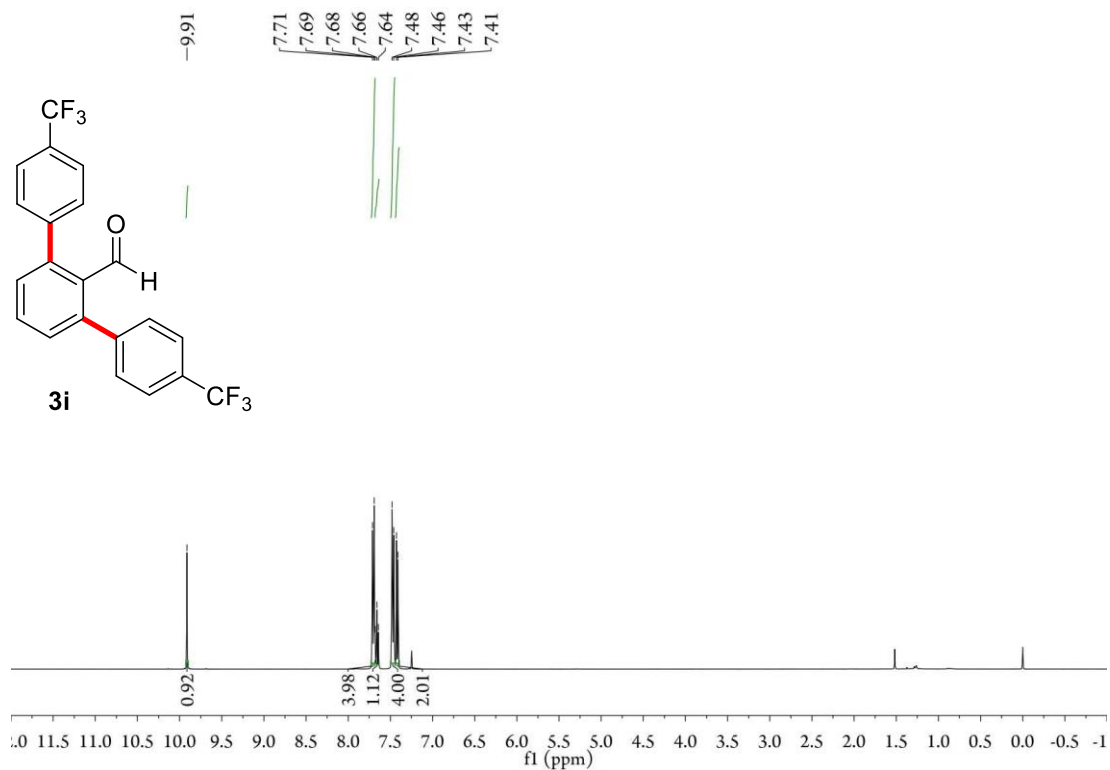


Figure S19. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3i**

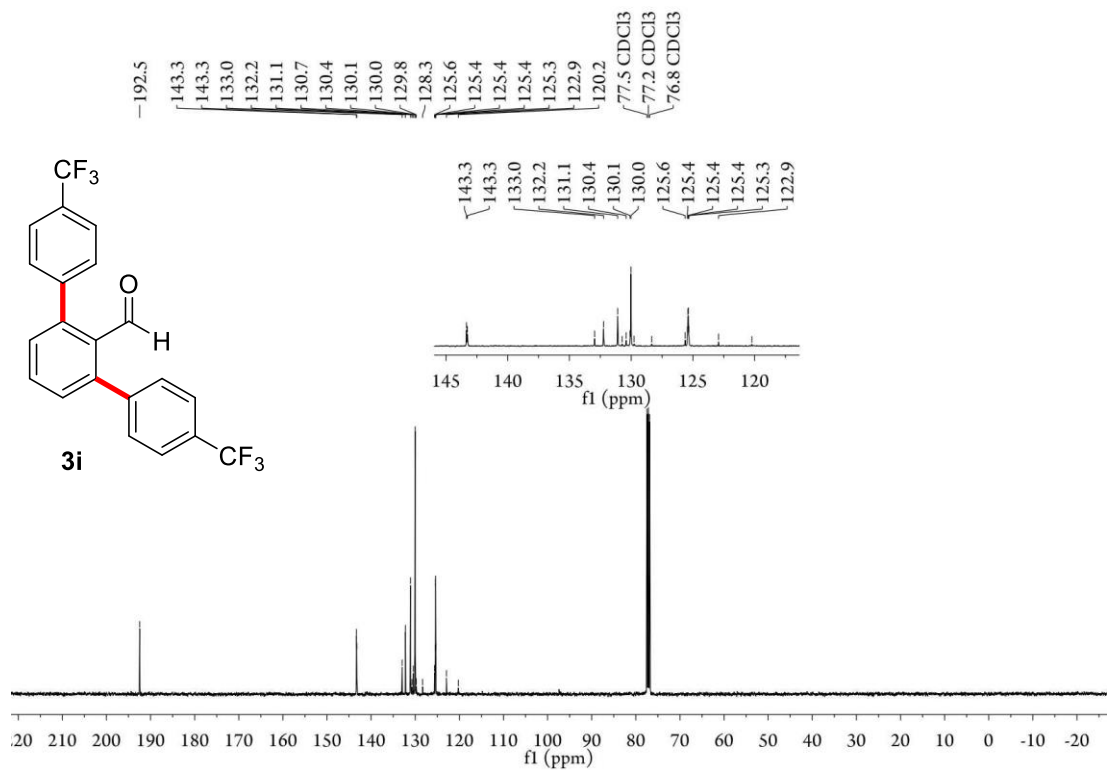


Figure S20. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3i**

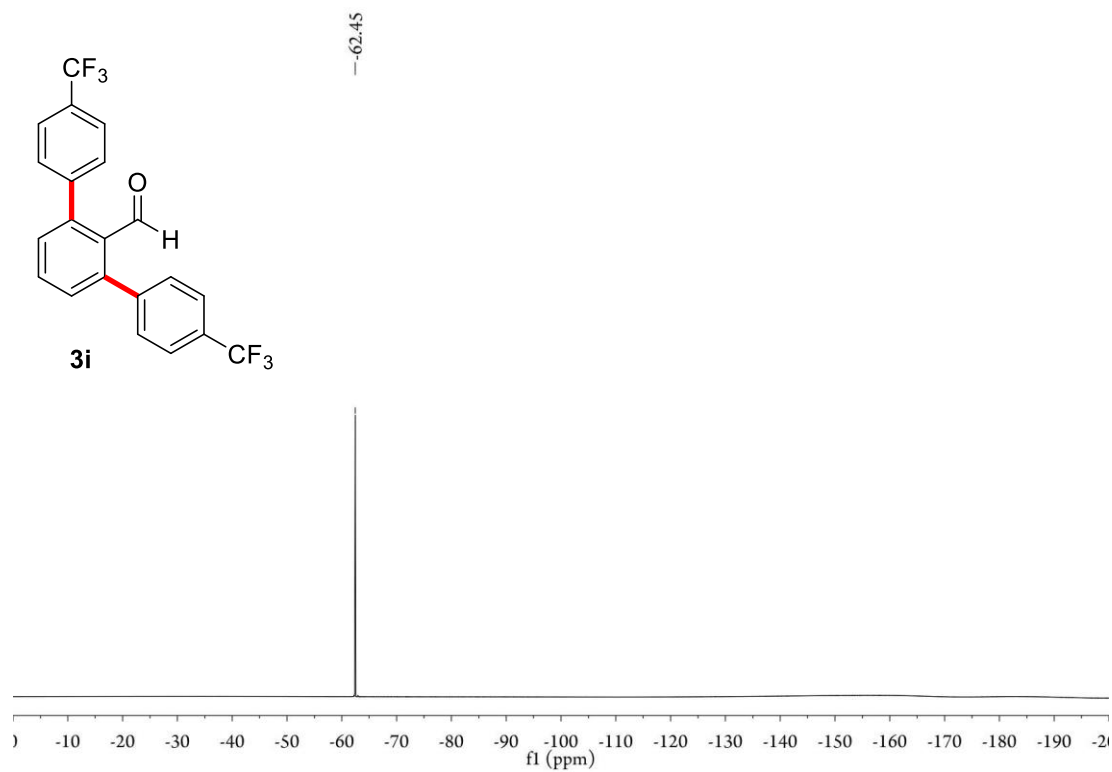


Figure S21. ^{19}F NMR (376 MHz, CDCl_3) Spectrum of Compound **3i**

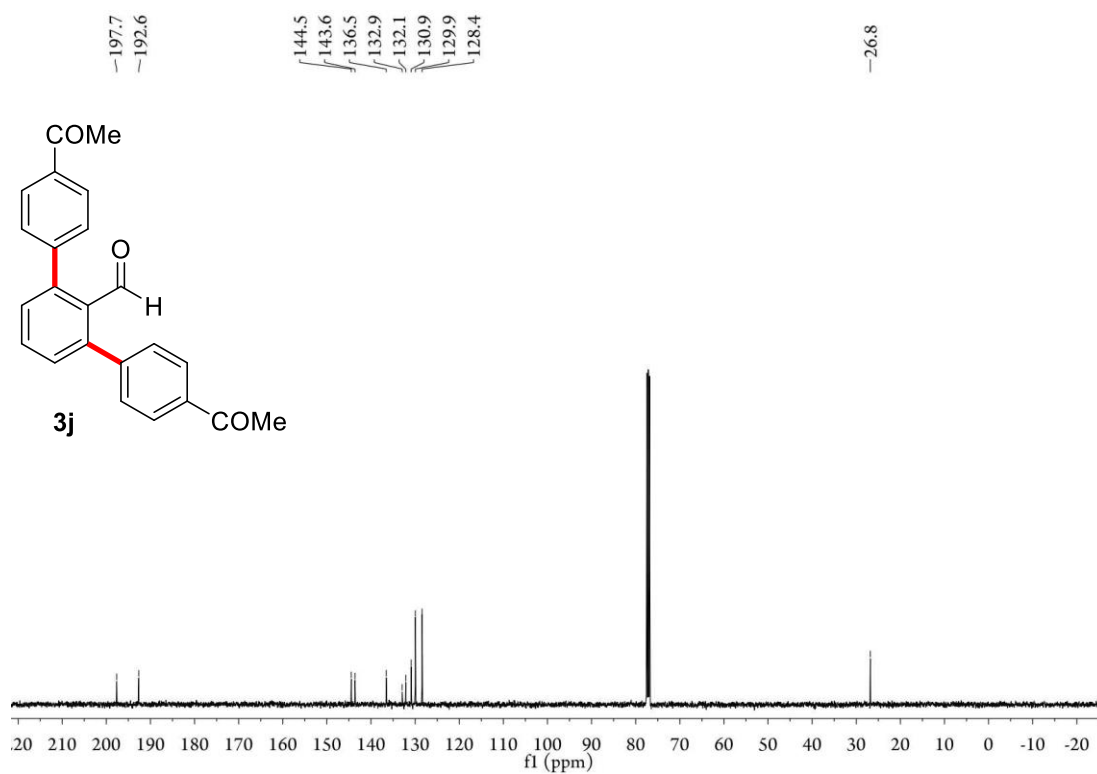
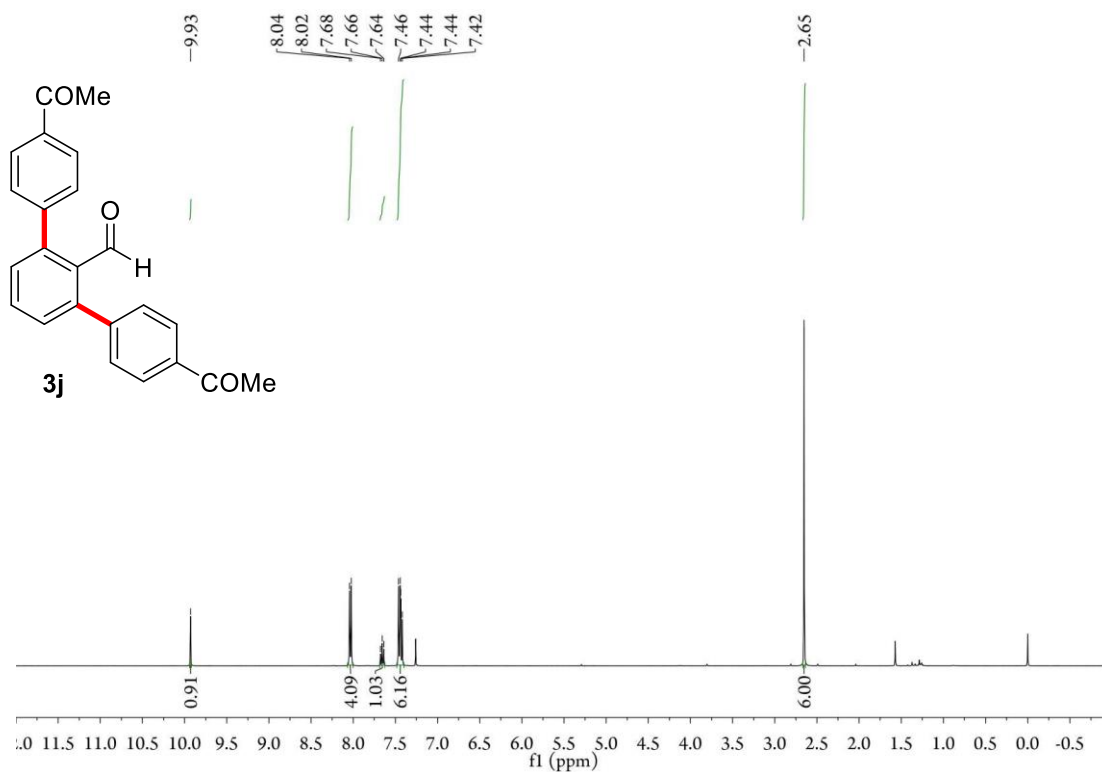


Figure S23. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3j**

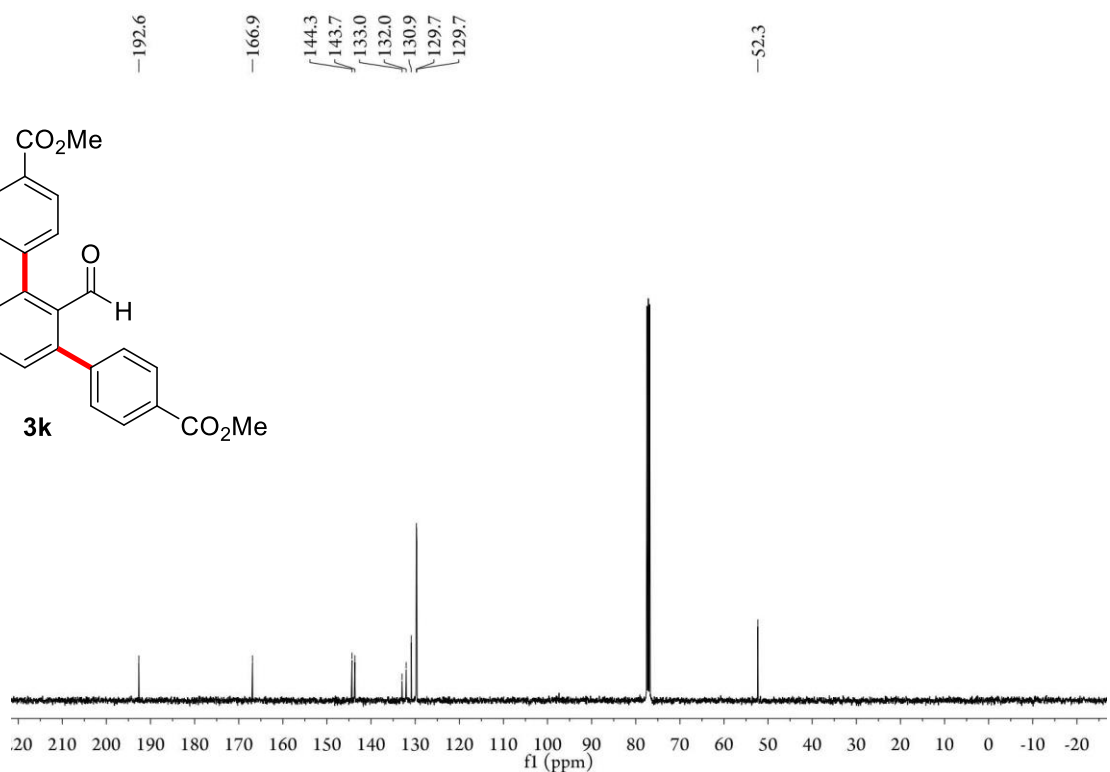
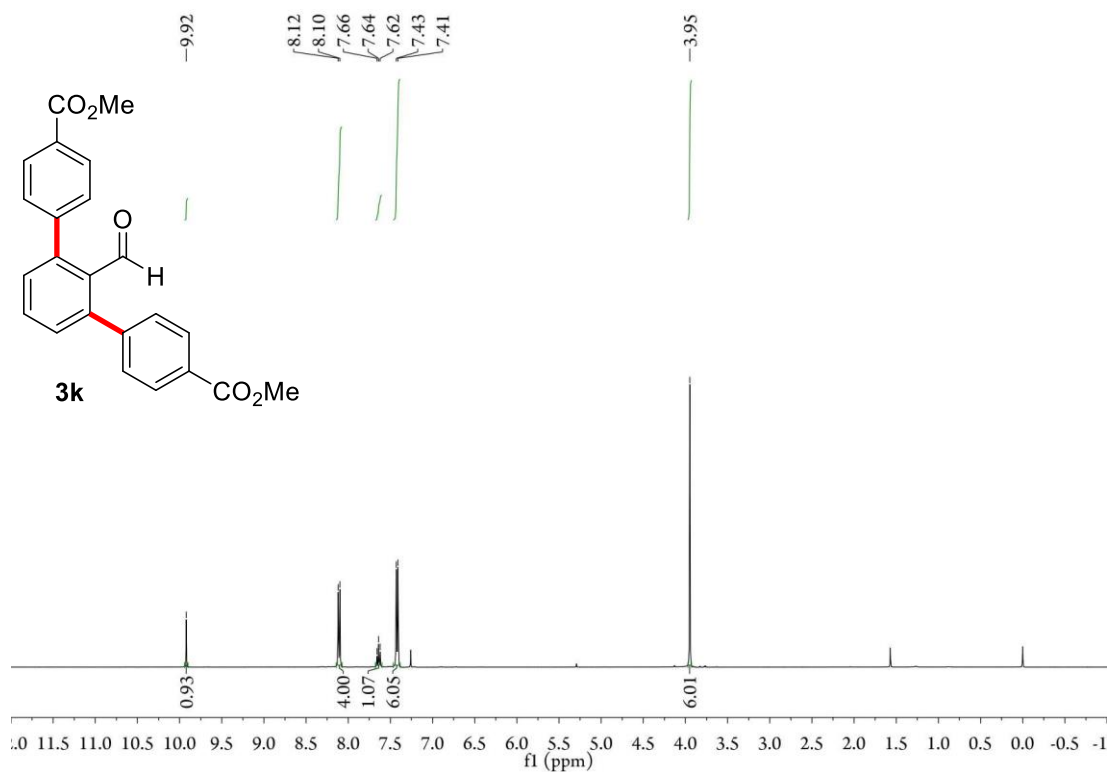


Figure S25. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3k**

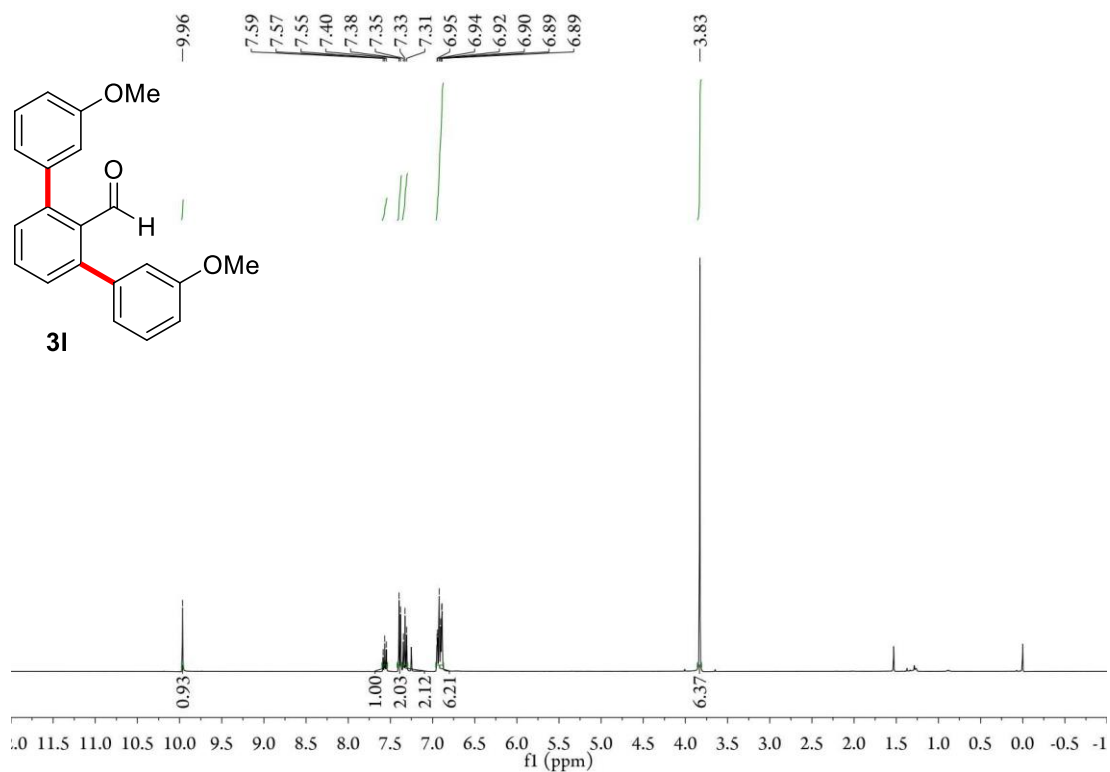


Figure S26. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3I**

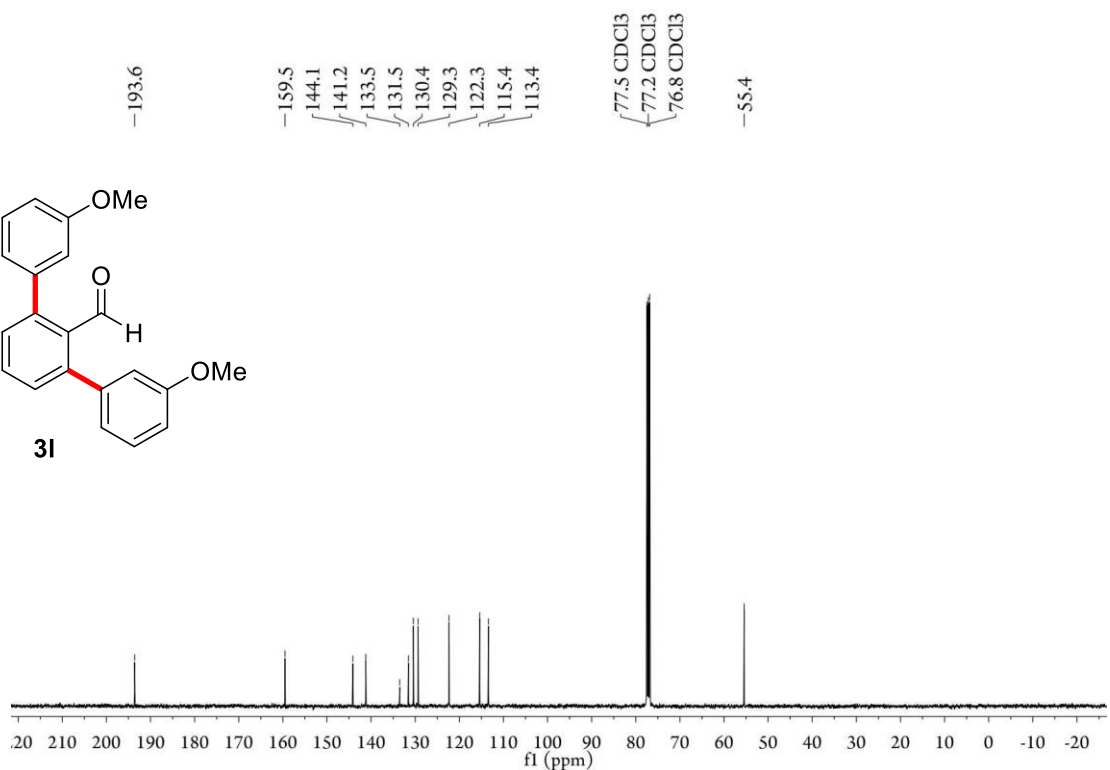


Figure S27. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3I**

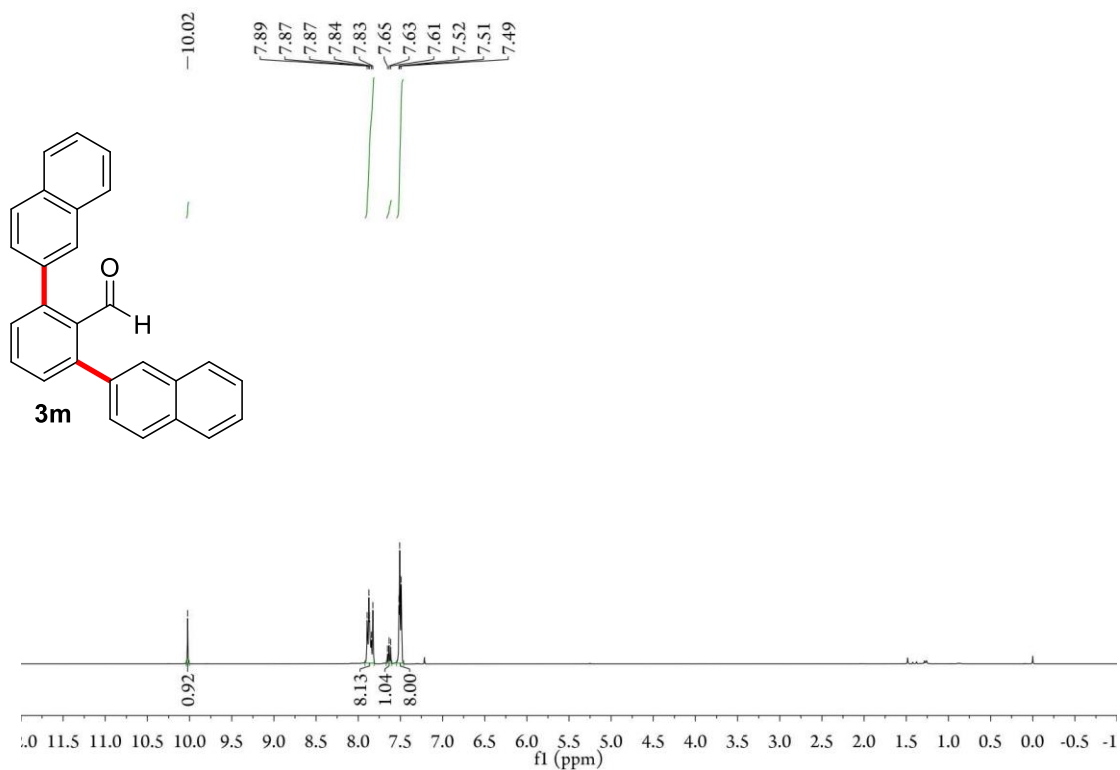


Figure S28. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3m**

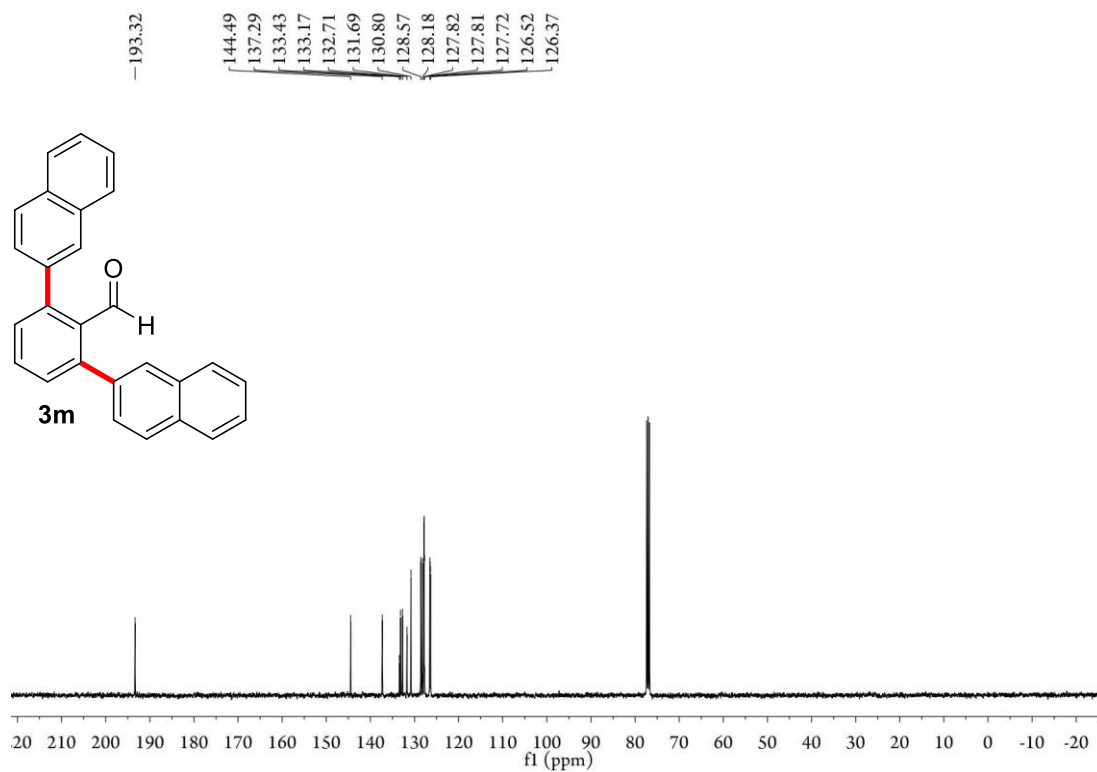


Figure S29. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3m**

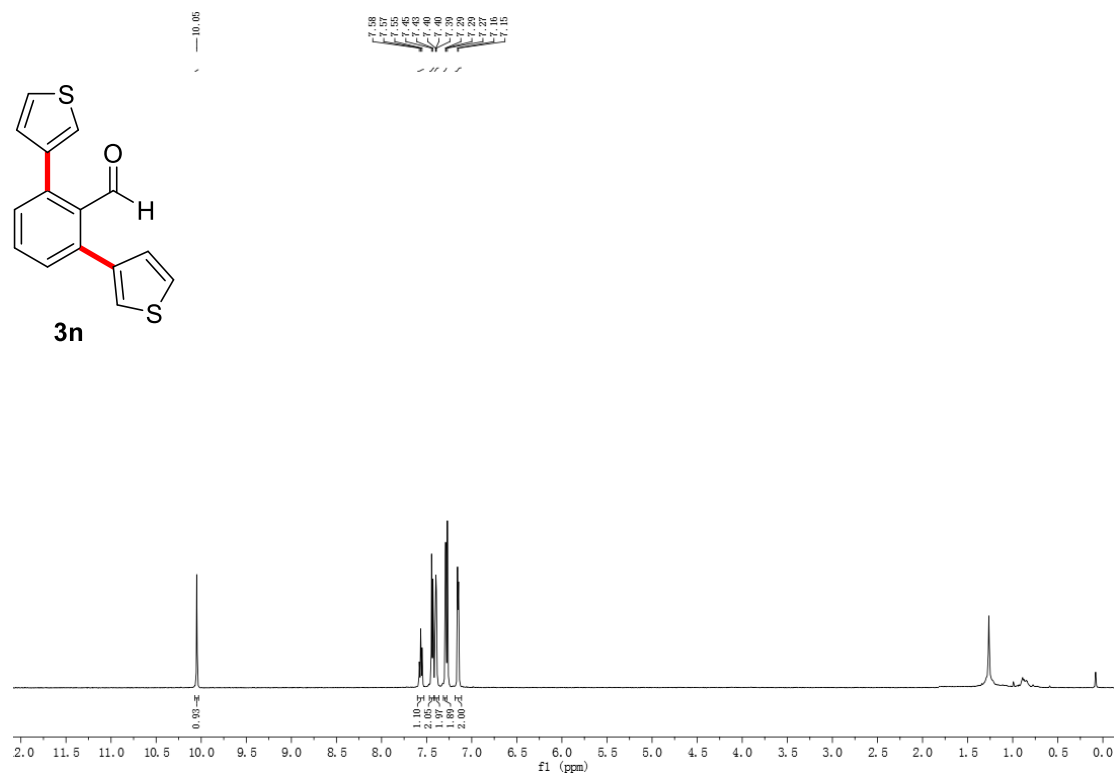


Figure S30. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3n**

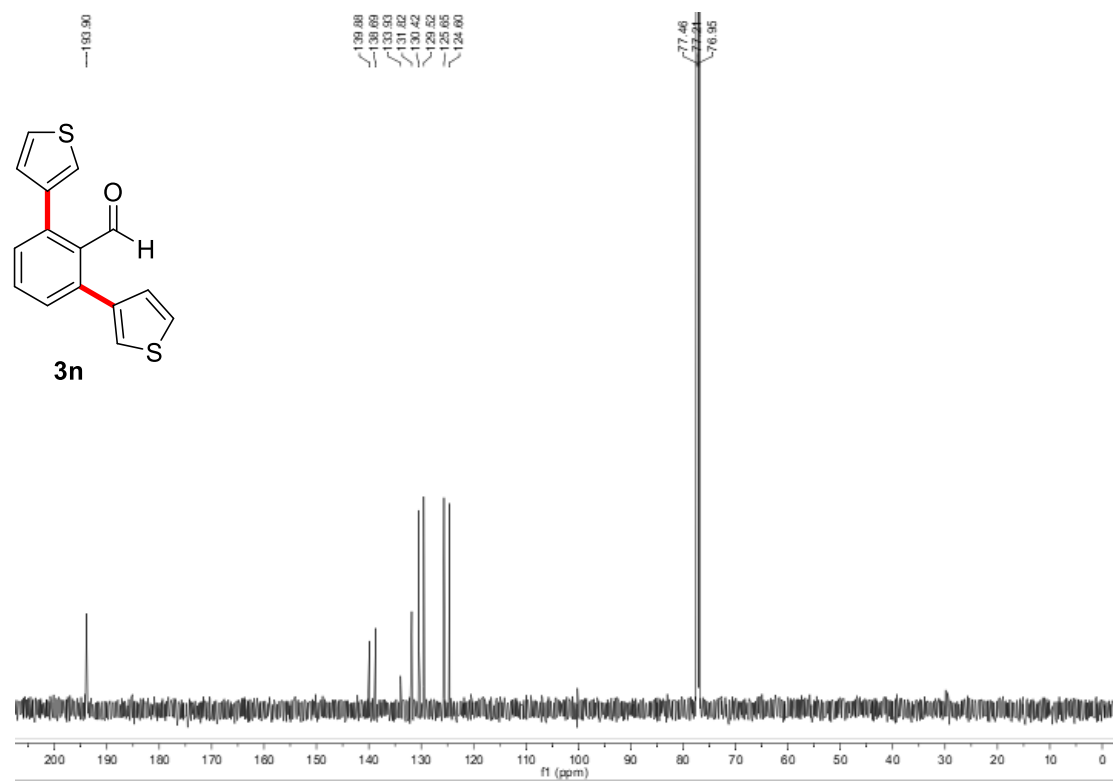
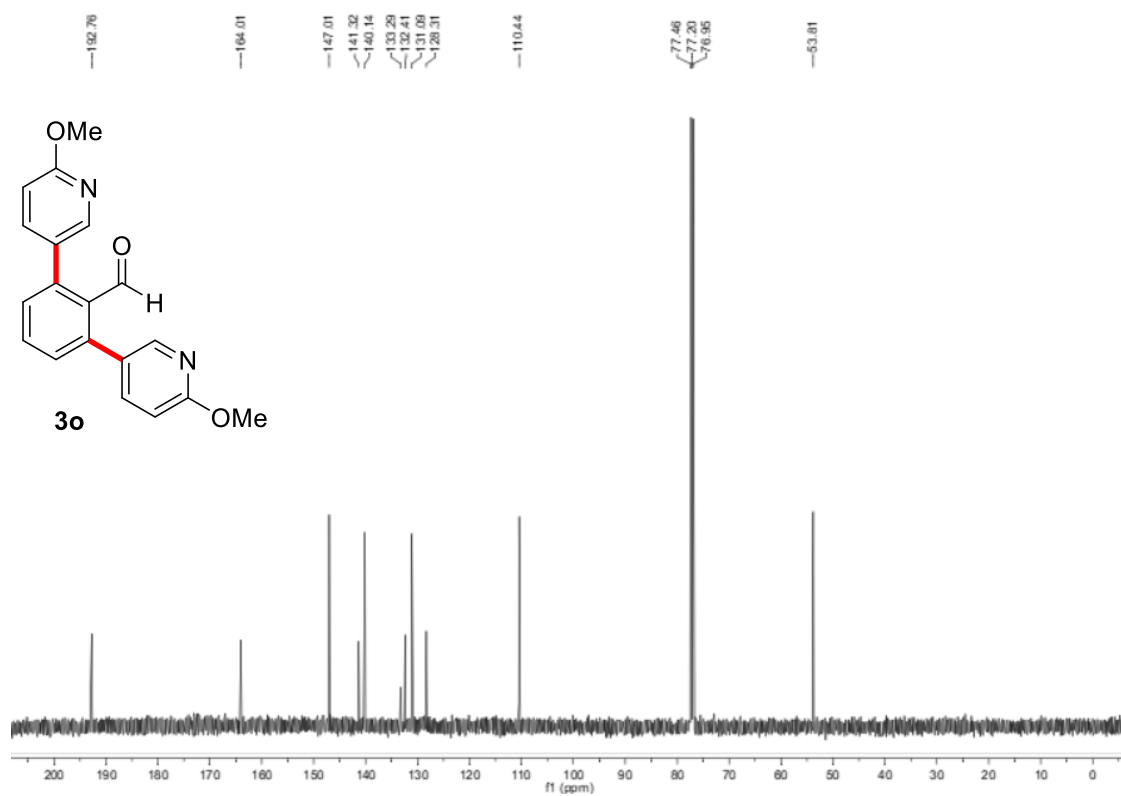
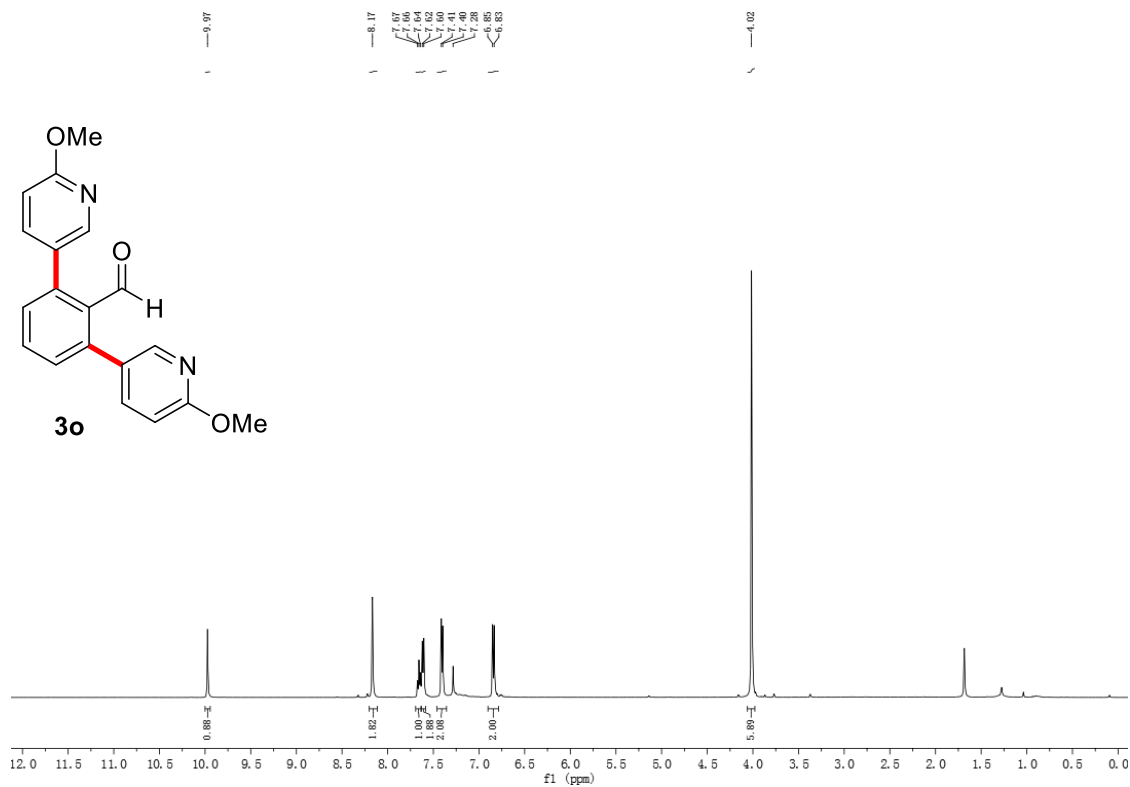


Figure S31. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3n**



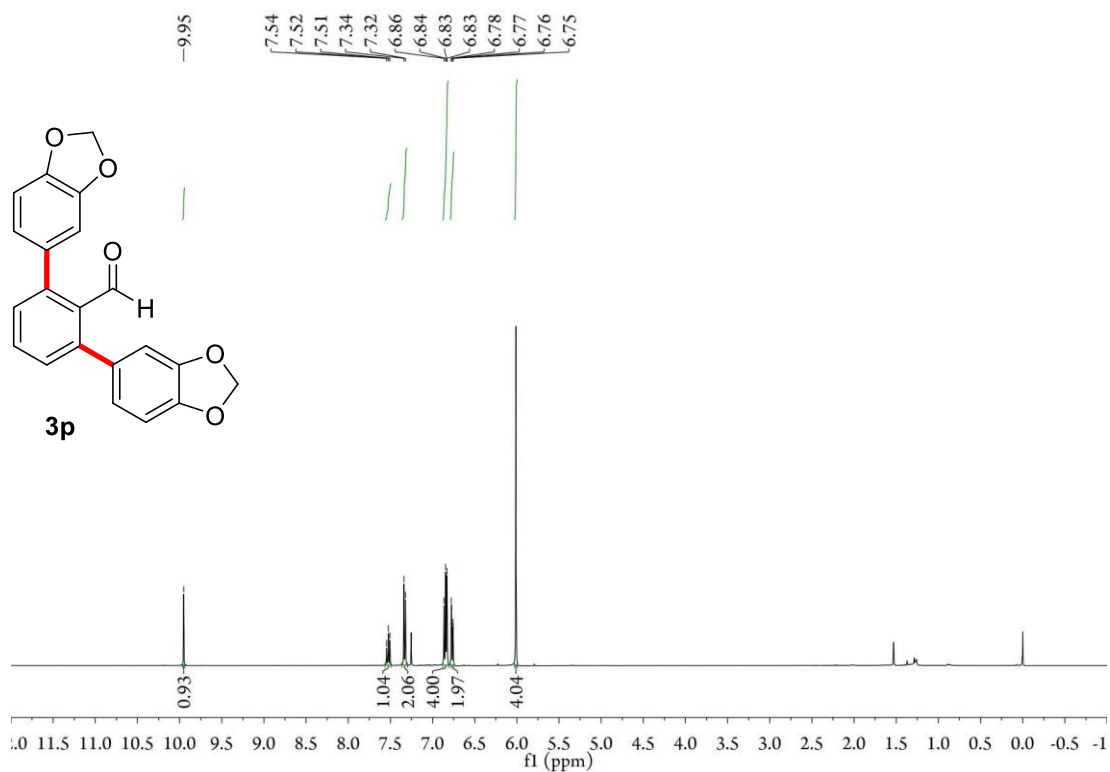


Figure S34. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3p**

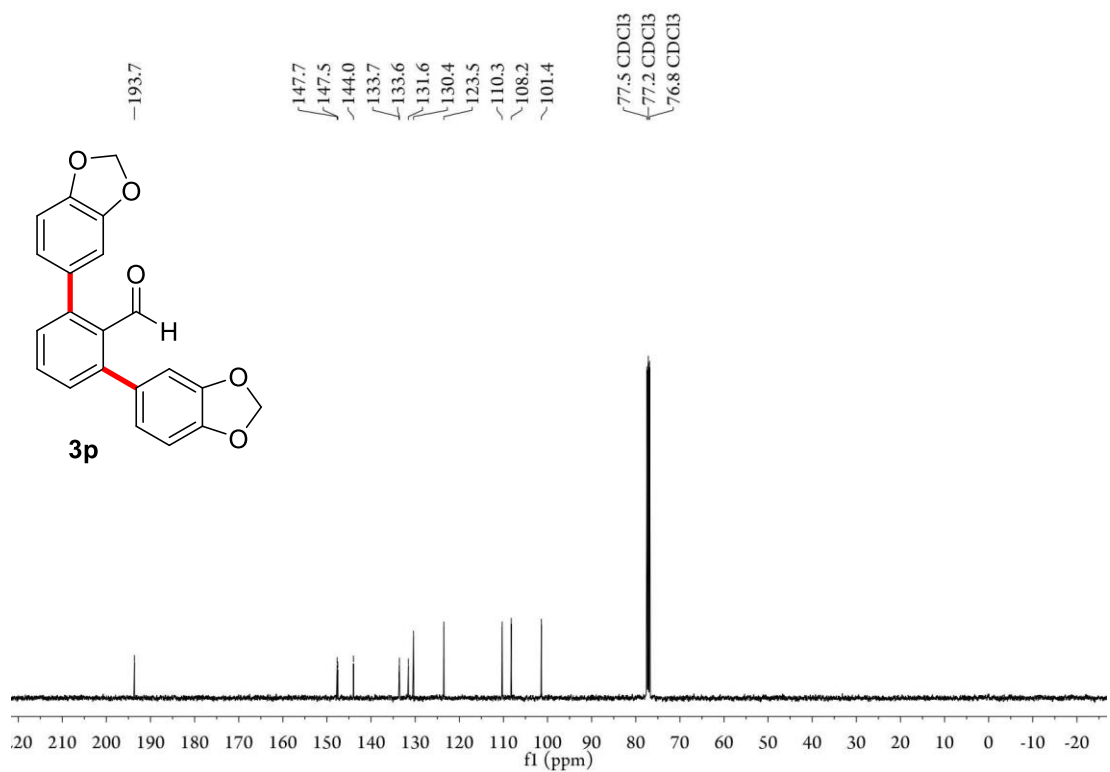
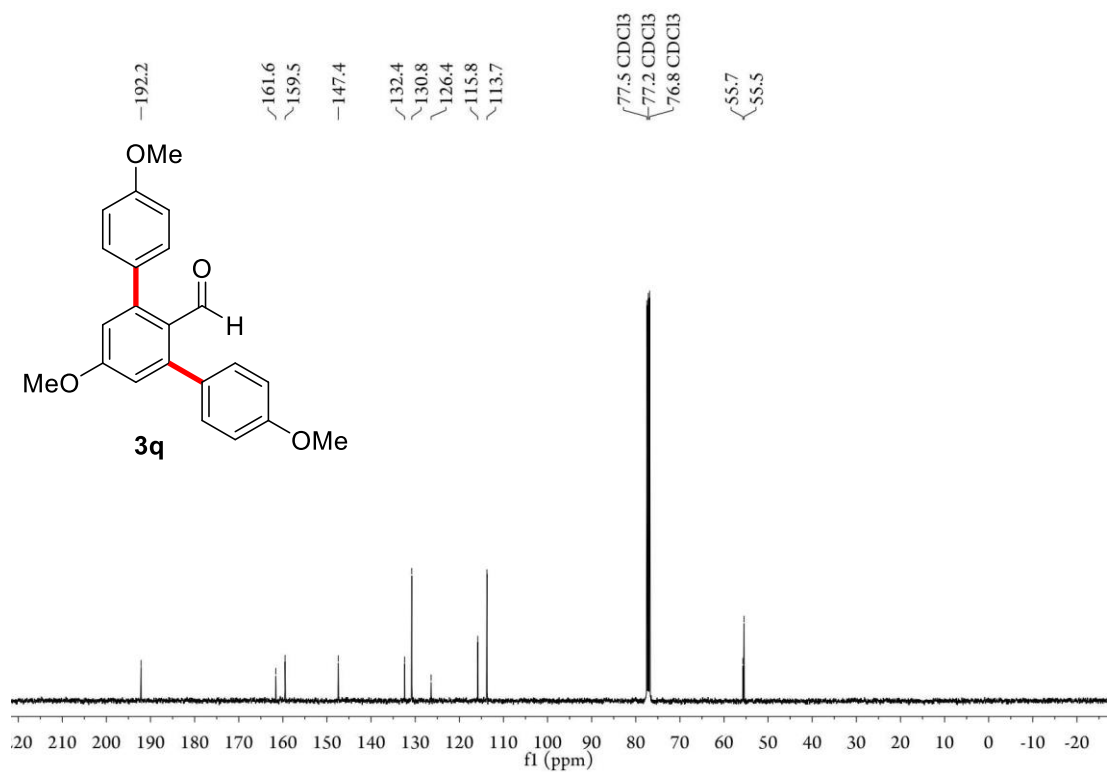
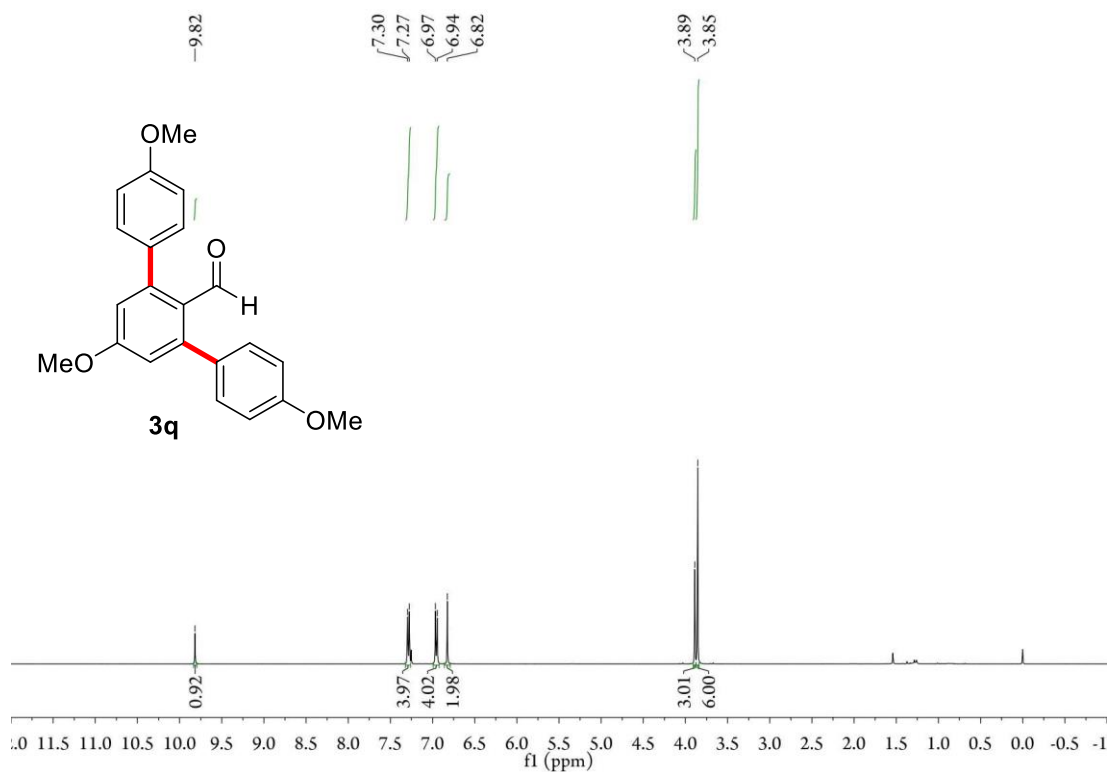


Figure S35. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3p**



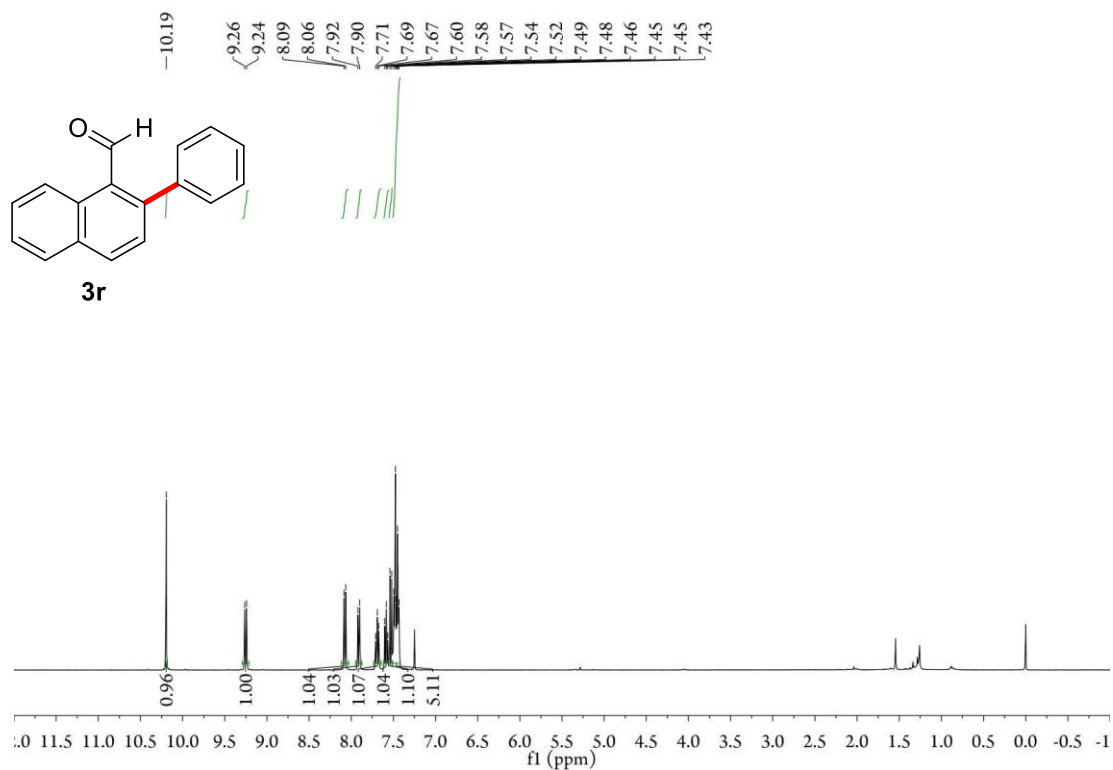


Figure S38. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **3r**

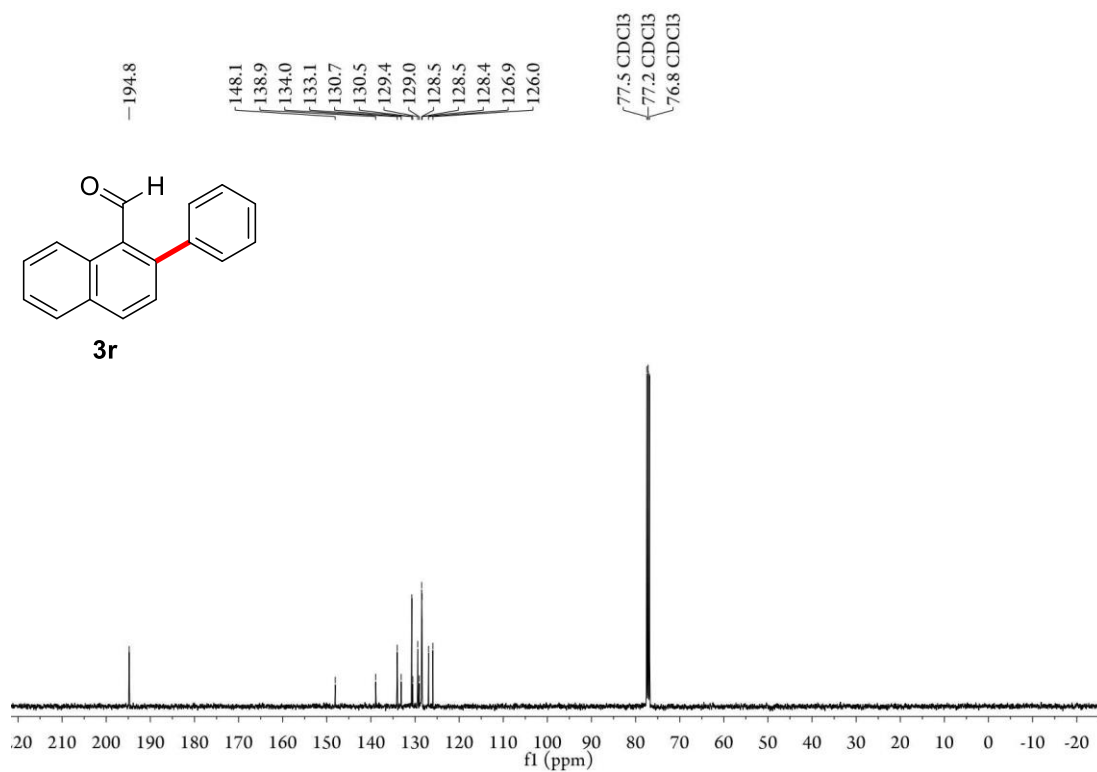
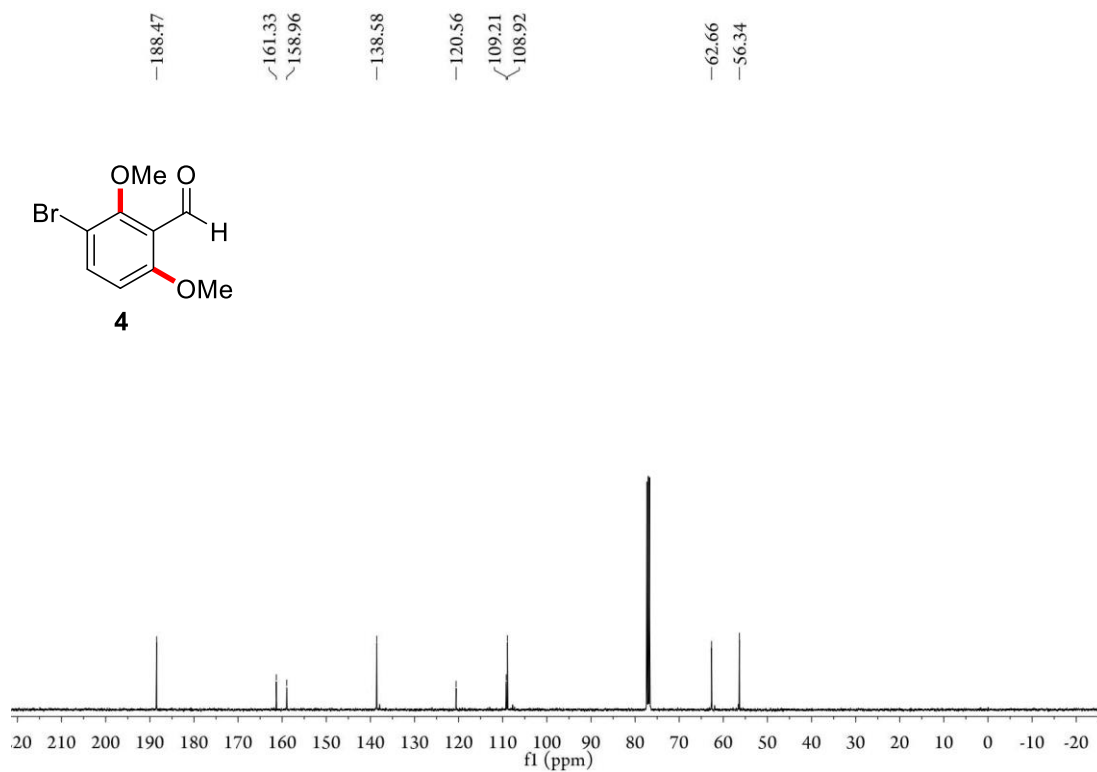
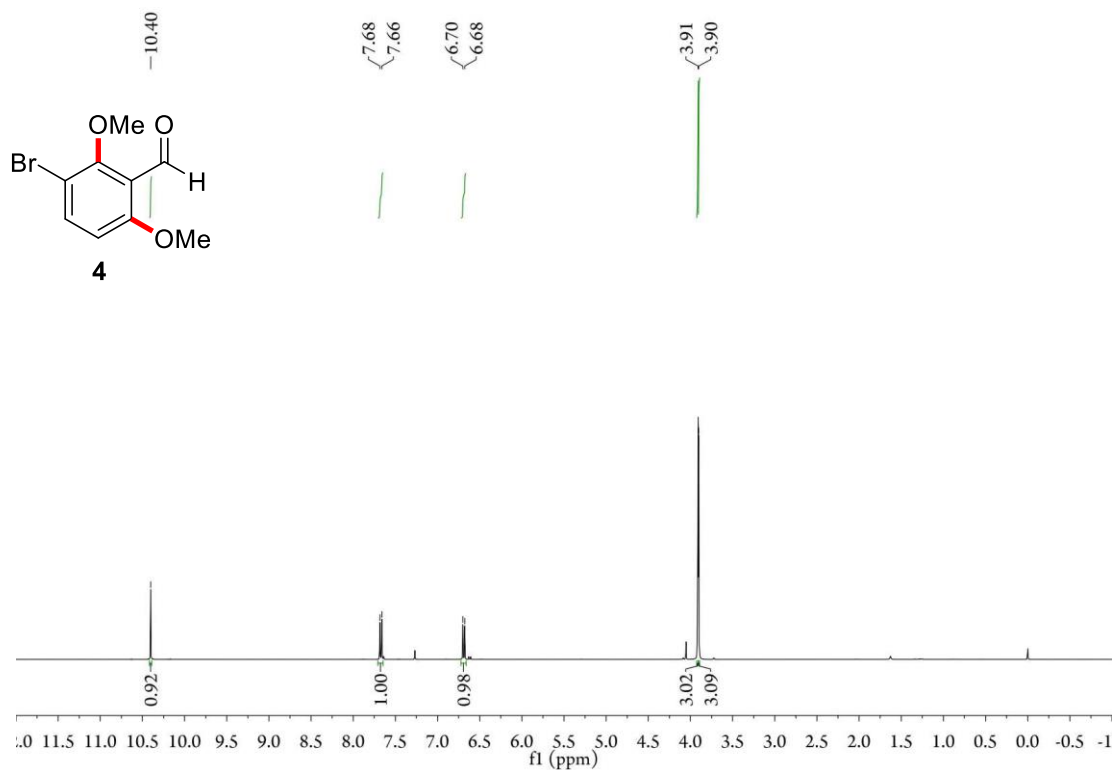


Figure S39. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **3r**



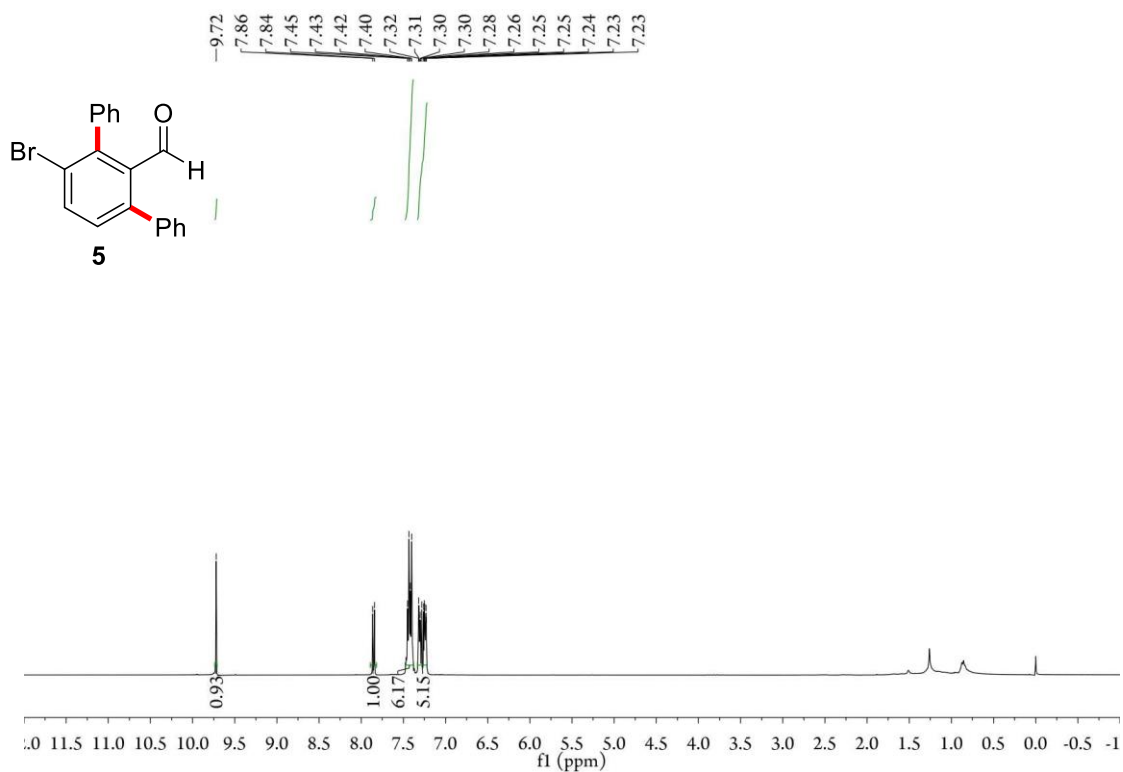


Figure S42. $^1\text{H NMR}$ (400 MHz, CDCl_3) Spectrum of Compound **5**

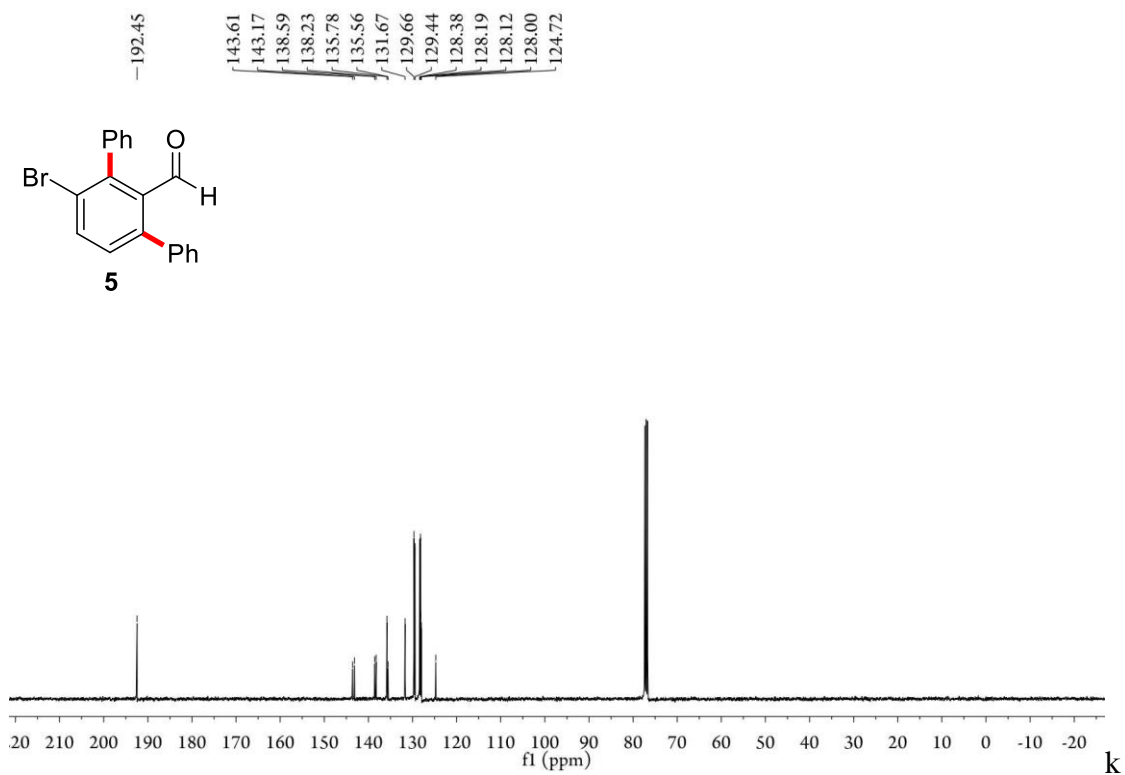


Figure S43. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) Spectrum of Compound **5**

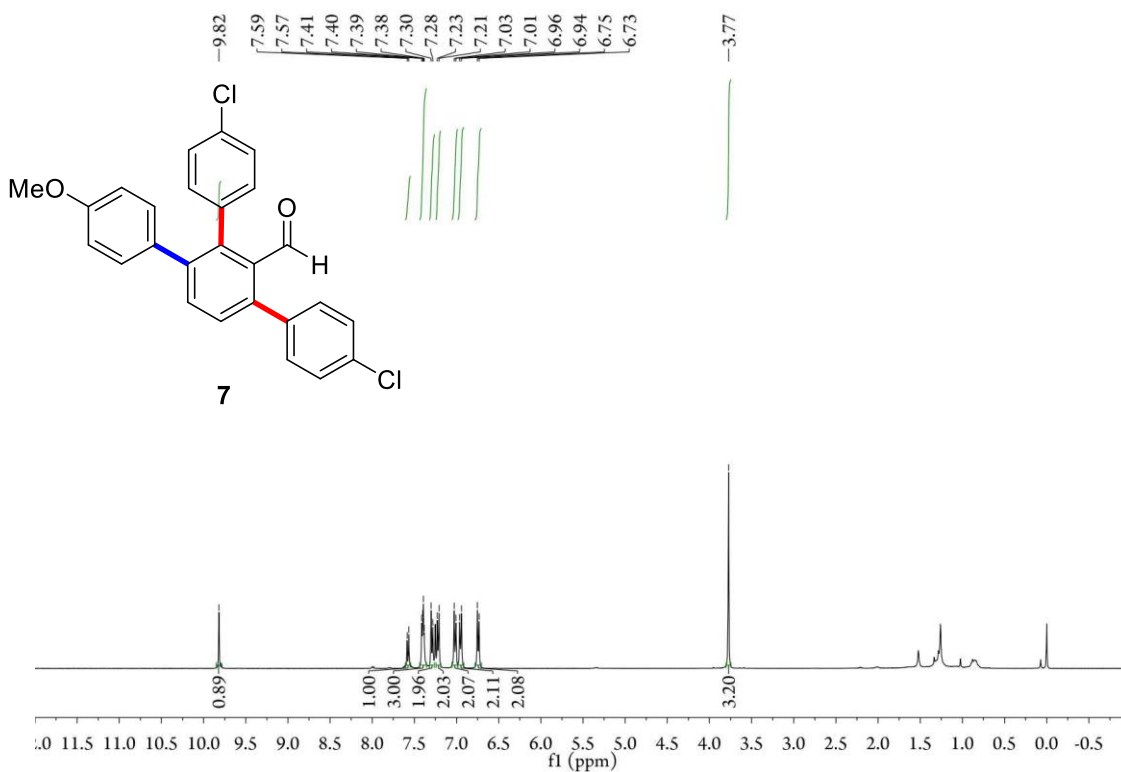


Figure S44. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound 7

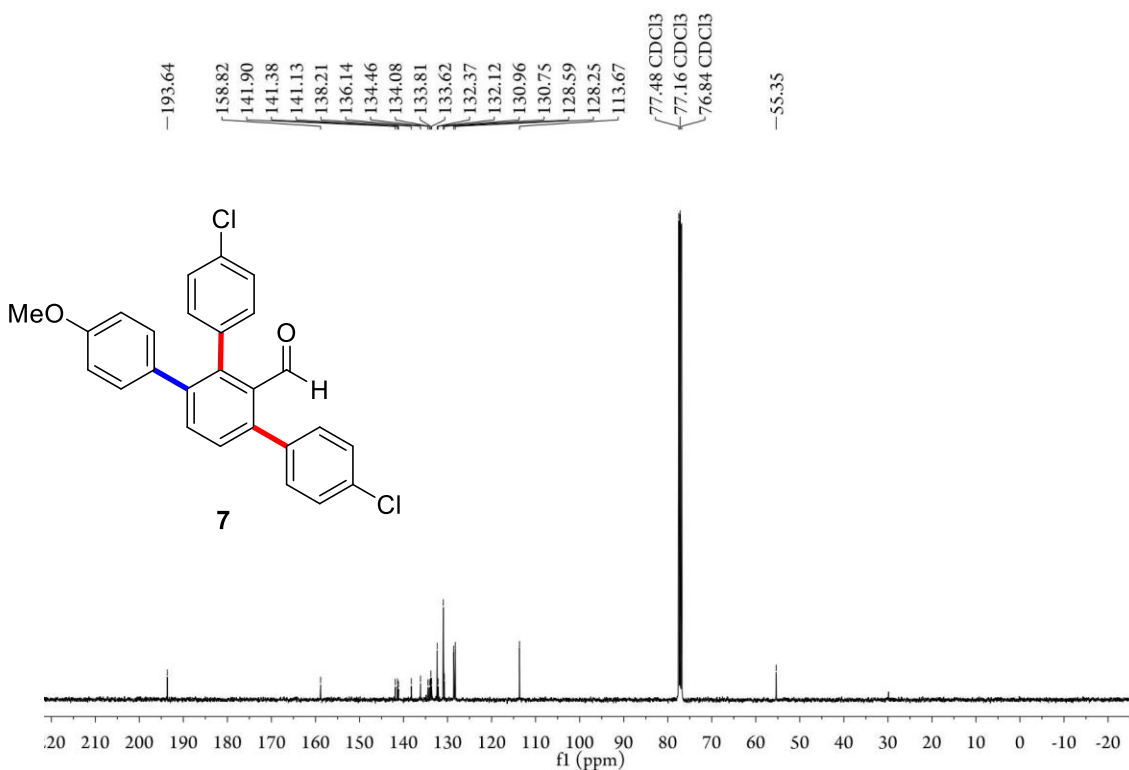


Figure S45. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound 7

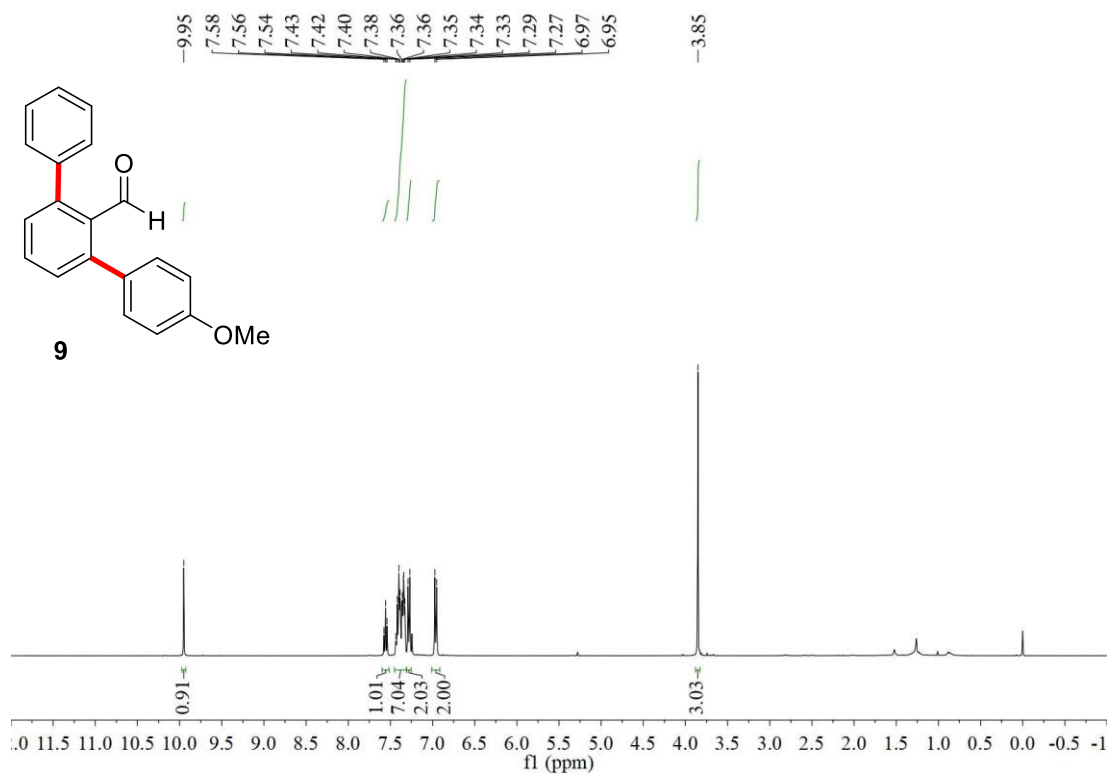


Figure S46. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **9**

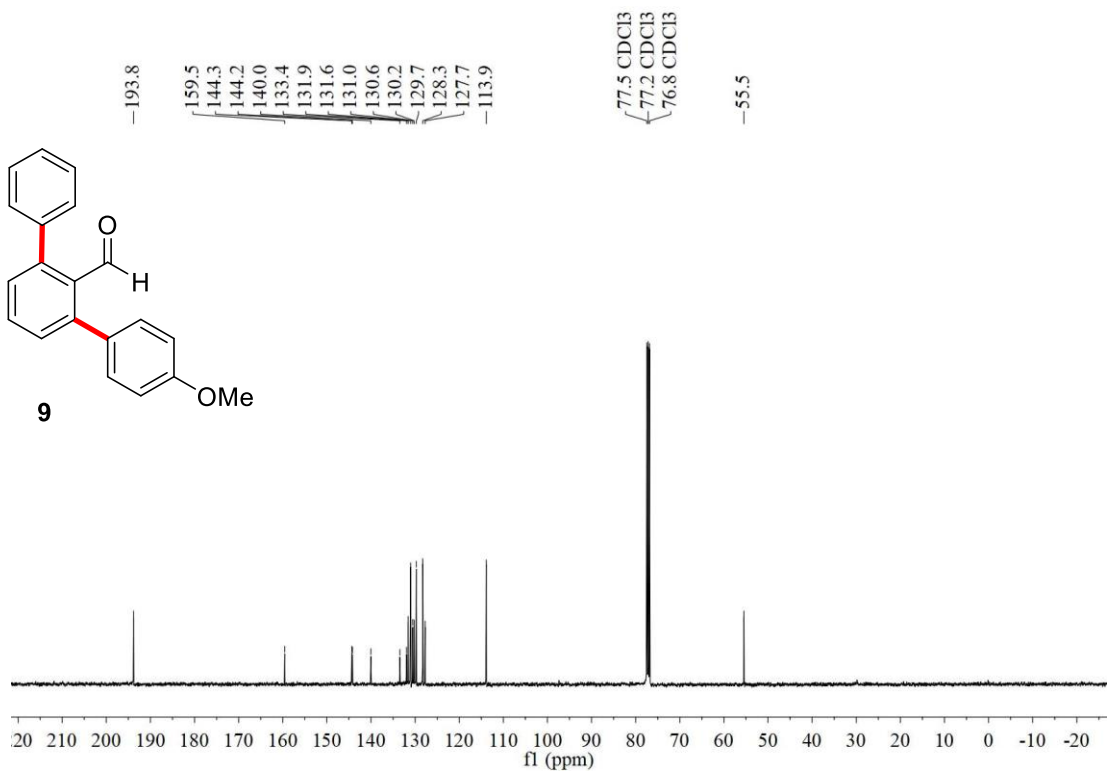


Figure S47. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **9**

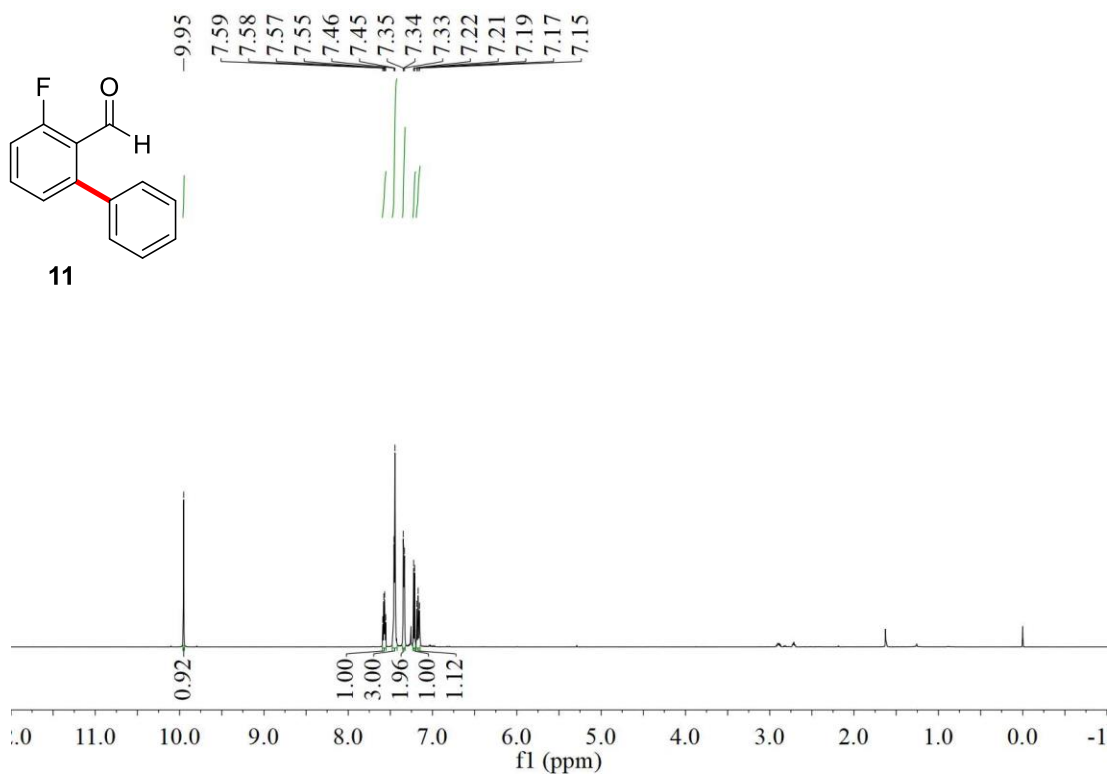


Figure S48. ¹H NMR (600 MHz, CDCl₃) Spectrum of Compound **11**

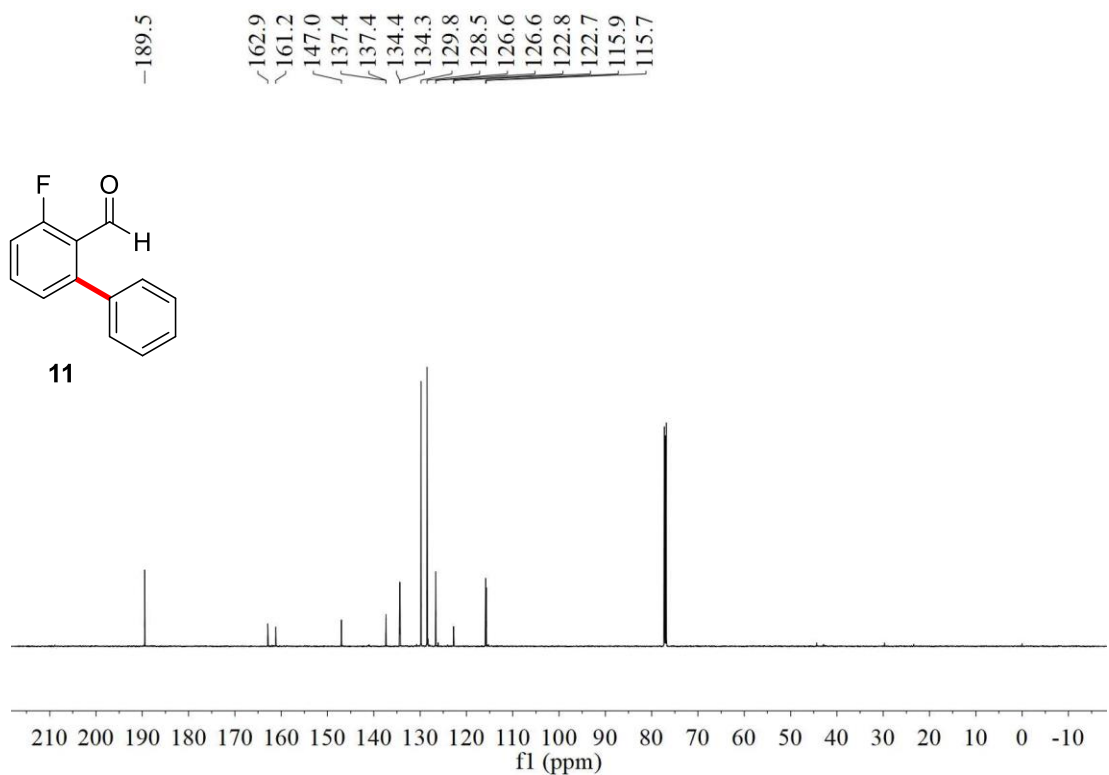


Figure S49. ¹³C NMR (150 MHz, CDCl₃) Spectrum of Compound **11**

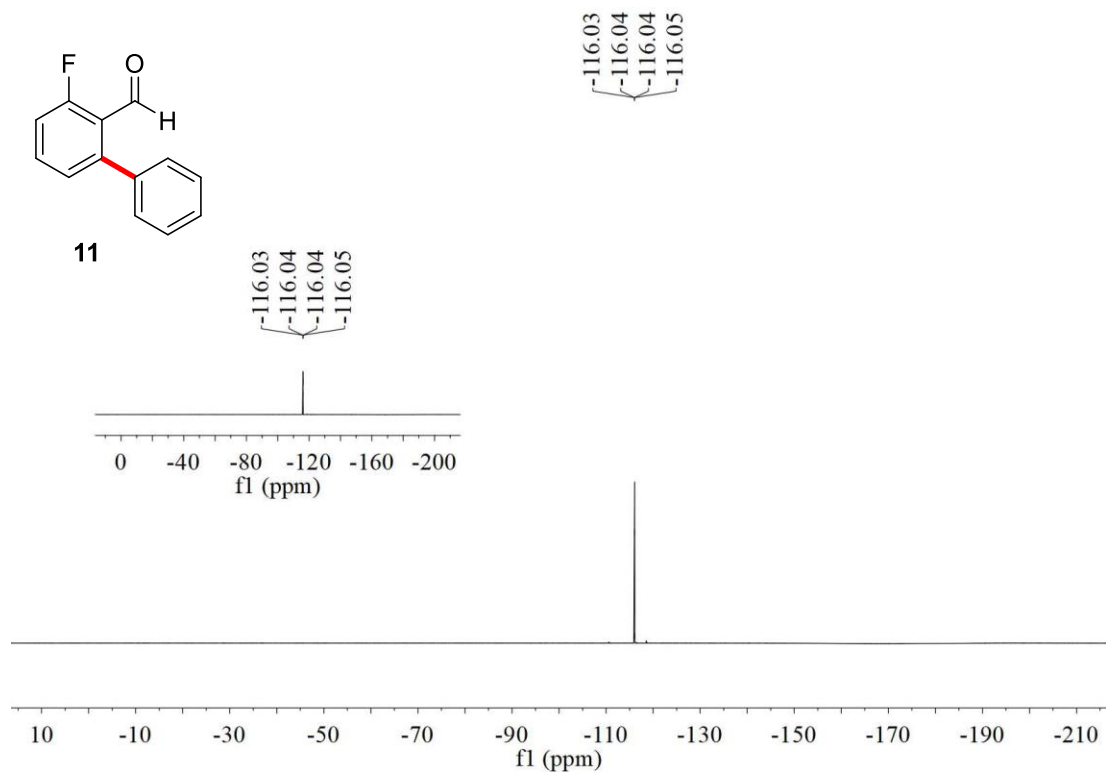


Figure S50. ^{19}F NMR (565 MHz, CDCl_3) Spectrum of Compound **11**

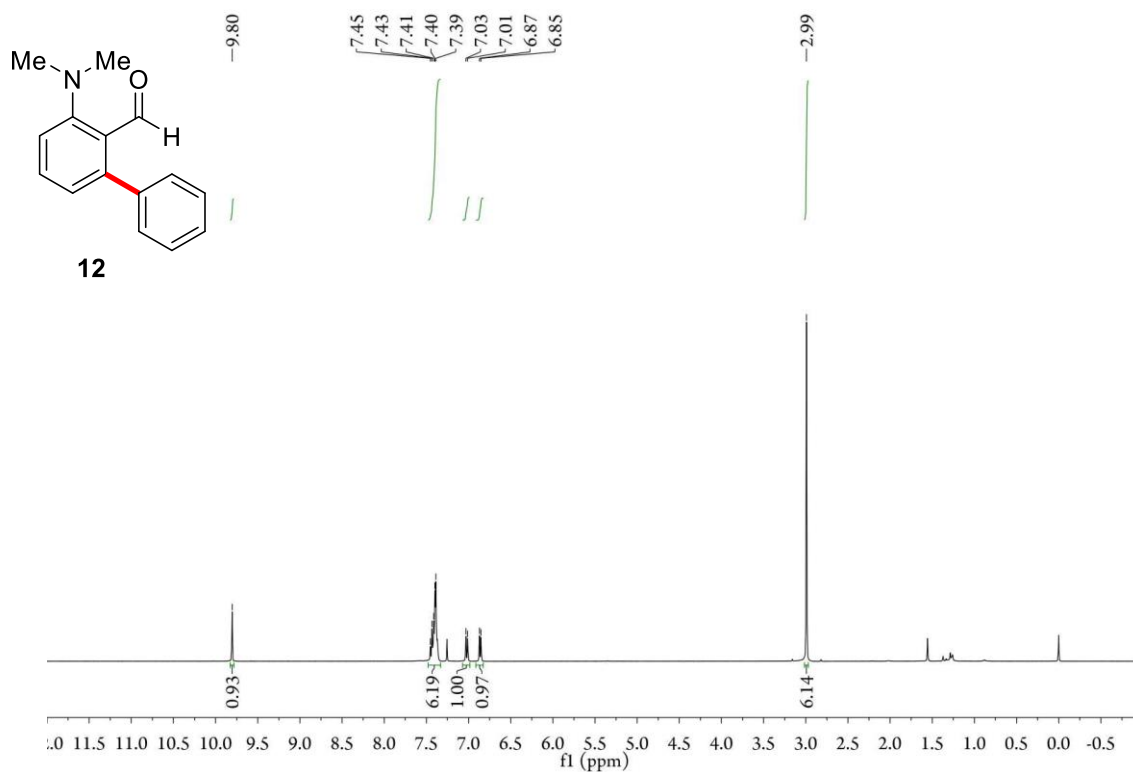


Figure S51. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **12**

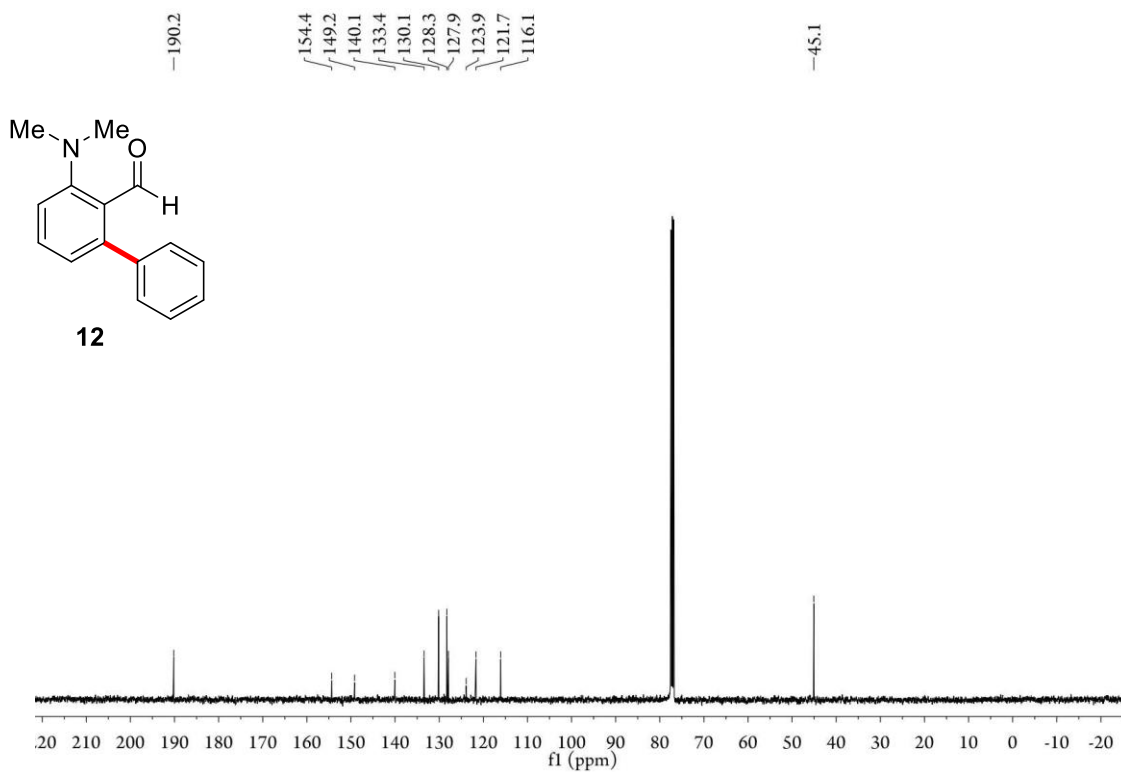


Figure S52. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **12**

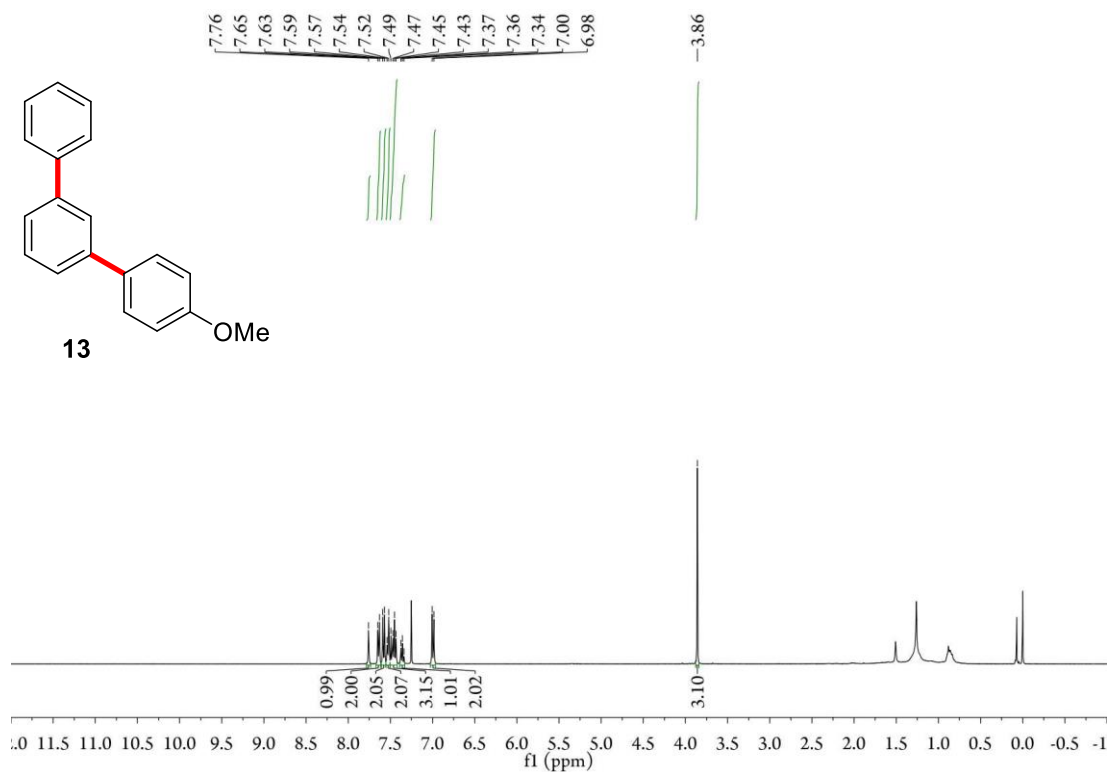


Figure S53. ¹H NMR (400 MHz, CDCl₃) Spectrum of Compound **13**

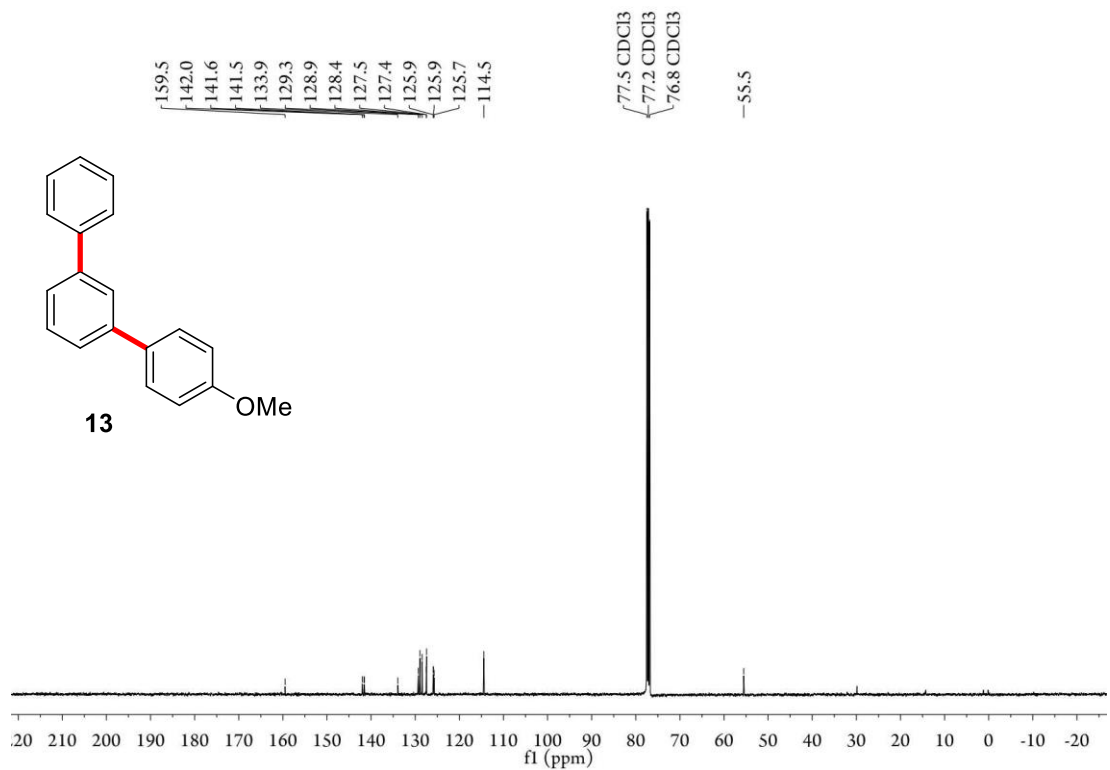


Figure S54. ¹³C NMR (100 MHz, CDCl₃) Spectrum of Compound **13**

Computational Details

All calculations were carried out with the Gaussian 09 programs.^{s1} The geometries of all the species were fully optimized by using density functional theory (DFT)^{s2} and the B3LYP method^{s3} with the 6-31G(d) basis set for all atoms except for Ru. The Lanl2dz^{s4} basis set was used for Ru (BSI). Vibrational frequency calculations carried out at the B3LYP/6-31G (d, p) level of theory were used to characterize all of the stationary points as either minima (the number of imaginary frequencies (NIMAG=0) or transition states (NIMAG=1)). The relative energies were corrected for the vibrational zero-point energies (ZPE, not scaled). The convergence criteria were used as default and the vibrational analysis was also carried out at standard conditions (1 atm., 298.15 K). The solvent effect was taken into account by single-point calculations with integral equation formalism polarizable continuum model (IEFPCM) in DCM at the M06^{s6}/6-311++G (d, p) (for Ru, SDD, (BSII) was used). The radii and nonelectrostatic terms were taken from Truhlar and co-workers' universal solvation model (SMD).^{s7} Unless stated otherwise, all the relative free energies discussed in the main text are calculated in solution (ΔG_{sol}), which were obtained by M06/SMD/6-311++G (d, p) //B3LYP/6-31G (d) (Lanl2dz).

(s1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R.

Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, D.01, Gaussian, Inc., Wallingford CT, **2013**.

(s2) Parr, R. G.; Yang, W. *Density-functional Theory of Atoms and Molecules*; Oxford University Press: New York, **1989**.

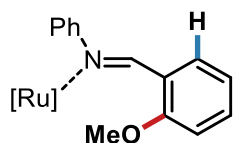
(s3) (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) C. Lee, W. Yang, R. G. Parr *Phys. Rev. B* **1988**, *37*, 785–789.

(s4) (a) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, **1985**, *82*, 284-298; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **1985**, *82*, 299-310.

(s5) W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking *Chem. Phys. Lett.*, **1993**, *208*, 111-114.

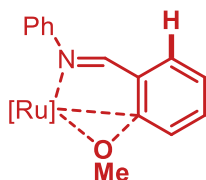
(s6) (a) Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory. Comput.* **2006**, *2*, 364-382; (b) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A.* **2006**, *110*, 13126-13130.

(s7) (a) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. Lett.* **2008**, *112*, 1095-1099; (b) D. Jacquemin, E. A. Perpète, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D. Truhlar, *J. Chem. Theory Comput.* **2010**, *6*, 2071-2085.

The Cartesian coordinates of the stationary points**INT1**

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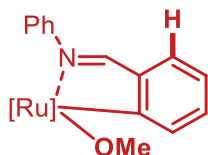
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TS^{C-OMe}

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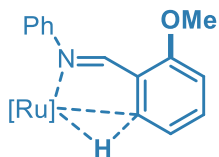
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 H, 0, 0.208220583, -2.0344290361, -3.2559631412

INT^{C-OMe}



Ru, 0, 0.279346276, -1.0339187306, 0.102930283
 C, 0, 1.5928564335, -2.3988502584, -0.1126465474
 O, 0, 2.4164412217, -3.1914654494, -0.2421060431
 C, 0, 0.2150361473, -1.2634094232, 2.0264046418
 O, 0, 0.2033575252, -1.3702522875, 3.1731358063
 C, 0, -1.264615163, -2.2621629321, -0.4219611555
 O, 0, -2.0998502479, -2.9247076353, -0.8330035477
 C, 0, -2.9718570958, 1.544561334, -0.9838975022
 C, 0, -2.3785559502, 0.8331137928, 0.0683775294
 C, 0, -3.1851530289, 0.1578513294, 0.9947933412
 C, 0, -4.5725341028, 0.221140546, 0.8842885899

C, 0, -5.1659579095, 0.9405095802, -0.1566564896
 C, 0, -4.3618471019, 1.5964093806, -1.0898901518
 C, 0, 3.3667587844, 2.7945403791, 0.3247242698
 C, 0, 3.930582818, 1.5186787574, 0.4213821753
 C, 0, 3.1280187543, 0.3707375772, 0.4028011129
 C, 0, 1.7373083802, 0.4583816902, 0.2863039555
 C, 0, 1.1838898178, 1.7637353422, 0.2009336823
 C, 0, 1.9861688058, 2.9178296284, 0.2161476996
 C, 0, -0.2528150919, 1.8497099294, 0.1251499496
 H, 0, -0.7462605525, 2.8210976964, 0.0367994142
 N, 0, -0.9654972054, 0.7696172669, 0.1964277199
 H, 0, -2.3407680348, 2.0161639427, -1.7301067617
 H, 0, -2.7184379639, -0.3929689684, 1.8053122548
 H, 0, -5.1916449691, -0.2935730421, 1.613081637
 H, 0, -6.2473939073, 0.9797562171, -0.2447197623
 H, 0, -4.8149415565, 2.1406845206, -1.9132845888
 H, 0, 3.6145495614, -0.5979891961, 0.4769520214
 H, 0, 5.0090226113, 1.4143336326, 0.5111100885
 H, 0, 3.9987155909, 3.6771473677, 0.3383872668
 H, 0, 1.5251897147, 3.900247358, 0.1432086406
 O, 0, 0.2125636546, -0.5601346354, -1.9158345387
 C, 0, 1.2768639249, -0.8387510871, -2.7742530123
 H, 0, 2.2366882012, -0.400406975, -2.4456766936
 H, 0, 1.4505563959, -1.9216231976, -2.9308017325
 H, 0, 1.050244212, -0.4116729807, -3.7646345526

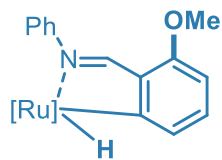
TS^{C-H}

Ru, 0, -0.4006658941, -1.2620896835, -0.0738159147
 C, 0, 0.4528042682, -2.9533595229, -0.2892182433

O, 0, 1.0095267139, -3.953497602, -0.4329511721
C, 0, -0.714519437, -1.5293600078, 1.8526039426
O, 0, -0.8695783734, -1.6863826303, 2.9840733788
C, 0, -2.0693703186, -1.8979298018, -0.9430398022
O, 0, -3.0161612205, -2.246844391, -1.4957499646
C, 0, -2.8413818201, 2.2671569977, -0.8971399271
C, 0, -2.4398951448, 1.2482171336, -0.0196085613
C, 0, -3.3836849159, 0.6708922849, 0.8408277542
C, 0, -4.7020083385, 1.1226120925, 0.8354576306
C, 0, -5.0987259236, 2.1429479661, -0.032059842
C, 0, -4.1636491207, 2.7105529608, -0.8985979317
C, 0, 3.6198587574, 1.6551217785, -0.0354933869
C, 0, 3.8182180999, 0.270454486, -0.1931706985
C, 0, 2.7620533039, -0.6208051807, -0.297535818
C, 0, 1.4269539435, -0.1618401484, -0.2193895126
C, 0, 1.223287216, 1.2441640841, -0.0608739007
C, 0, 2.3214497208, 2.1447894229, 0.024450726
C, 0, -0.1270098886, 1.6828623876, 0.0102322341
H, 0, -0.3676772683, 2.7417363143, 0.0823523677
N, 0, -1.0896590471, 0.7927198834, -0.0108954775
H, 0, -2.1226478707, 2.684796741, -1.5953813695
H, 0, -3.0748203924, -0.115880667, 1.5195978691
H, 0, -5.4215980014, 0.6741103273, 1.5140760036
H, 0, -6.1288058034, 2.48604924, -0.0378552449
H, 0, -4.4637293265, 3.4934595426, -1.589087767
H, 0, 0.5923076117, -0.6660166514, -1.3266260751
H, 0, 2.9674754989, -1.6771147533, -0.4374940178
H, 0, 4.8379513951, -0.1043690933, -0.2340077764
H, 0, 4.4745915998, 2.3161845959, 0.0305010918
O, 0, 1.9949245124, 3.4597979663, 0.169680692
C, 0, 3.0467745185, 4.4104615864, 0.270411913

H, 0, 2.563741262, 5.382038139, 0.3825013133
 H, 0, 3.6795930695, 4.2164206032, 1.144966492
 H, 0, 3.6698454942, 4.4161973396, -0.6322572051

INT^{C-H}



Ru, 0, -0.2311414093, -1.3564019796, -0.2795750437
 C, 0, 0.3985128093, -3.0780354728, -0.7798989153
 O, 0, 0.8267425381, -4.0901904756, -1.1261796765
 C, 0, -0.2631876609, -1.6860831791, 1.7022285558
 O, 0, -0.2271695986, -1.8795942177, 2.833526823
 C, 0, -2.114800956, -1.7781921597, -0.7471423091
 O, 0, -3.1808597783, -2.0054917657, -1.1087500648
 C, 0, -2.0484287233, 2.5624132298, -0.9156970402
 C, 0, -1.8267451101, 1.4758747239, -0.0564566884
 C, 0, -2.8550856876, 1.0496083876, 0.7953020992
 C, 0, -4.07791926, 1.7175272881, 0.8027413044
 C, 0, -4.2949300295, 2.8055574998, -0.0463490413
 C, 0, -3.2773212267, 3.2222134201, -0.9057658814
 C, 0, 4.2151529877, 0.8221326598, -0.0110892635
 C, 0, 4.1769638253, -0.5728038725, -0.1188782455
 C, 0, 2.9736417103, -1.276770523, -0.1931541041
 C, 0, 1.7461622831, -0.6031920273, -0.1641141829
 C, 0, 1.7854392963, 0.8128021316, -0.0499252714
 C, 0, 3.0115688169, 1.5241419926, 0.0255804936
 C, 0, 0.523986853, 1.4906789113, -0.0055281345
 H, 0, 0.4788725731, 2.5759047055, 0.0797032427
 N, 0, -0.5773477791, 0.7957214829, -0.0480942773
 H, 0, -1.2681231194, 2.8641620757, -1.6074648729
 H, 0, -2.681673846, 0.2082796353, 1.4579553965

H, 0, -4.8640754884, 1.385444189, 1.4744171001
H, 0, -5.2524166283, 3.3174466365, -0.0443517571
H, 0, -3.4413876372, 4.0564649632, -1.5816649289
H, 0, -0.0368111874, -0.9985009517, -1.8669543239
H, 0, 3.0096645863, -2.3584899533, -0.2784936565
H, 0, 5.1178594807, -1.1175334475, -0.145486432
H, 0, 5.1674626208, 1.3346255177, 0.0440066907
O, 0, 2.9140379828, 2.8805782574, 0.1321220477
C, 0, 4.1113718498, 3.6416061621, 0.2154051341
H, 0, 3.7998222817, 4.6841147696, 0.2940173722
H, 0, 4.6983431782, 3.3707960551, 1.1015340587
H, 0, 4.7308880827, 3.5145247008, -0.6807171373