

Copper-Catalyzed Trifluoromethylation of Organic Zinc Reagents with Electrophilic Trifluoromethylating Reagent

Chang-Sheng Wang,[†] Haoyang Wang,[§] Cheng Yao,^{†,*}

[†] College of Science, Nanjing Tech University, 30 Puzhu South Road, Nanjing 211816, China

e-mail: yaochengnjut@126.com, yaocheng@njtech.edu.cn

[§] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road,
Shanghai 200032, China

Supporting Information

Contents:

General Information.....	S2
General Procedure for Copper-Catalyzed Trifluoromethylation of Zinc Reagents.....	S3
Mechanistic Experiments Section.....	S14
Copies of the ¹ H, ¹⁹ F and ¹³ C NMR Spectra of Compounds 4a-m , 1b-e	S20
X-Ray Diffraction data of Single Crystal of bimetallic copper(II) species 8	S43

General information. All solvents were purified by standard method. ^1H NMR, ^{19}F NMR spectra and ^{13}C NMR were recorded on 400 MHz, 376 MHz and 101 MHz spectrometer, respectively. ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to CFCl_3 as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

Materials. All reagents were received from commercial sources. Pure CuI was freshly prepared under the condition of the reference (Dieter, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 4679). Solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using.

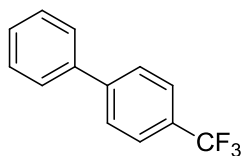
General Procedure for the Preparation of Zinc Reagent.

Anhydrous LiCl (381 mg, 9.0 mmol) was placed in an argon-flushed flask and dried 30 min at 150 °C under vacuum (1 mbar). Zinc powder (13.5 mmol, 883 mg, 1.5 equiv, 150 mesh, Chemetall, 99.9 % or 325 mesh, Strem, 99.9 %); in the case of active sensitive substrates 1.4 equiv) was added under Ar and heterogeneous mixture of Zn and LiCl was dried again for 30 min at 150 °C under vacuum (1 mbar). The reaction flask was cooled to room temperature and then evacuated and refilled with argon three times. THF (10 mL) was added and Zn was activated by BrCH₂CH₂Br (5.0 mol %) and Me₃SiCl (1.0 mol %). The aryl iodide or aryl bromide (9 mmol) was added neat at the room temperature. The reaction mixture was stirred at 50 °C. The completion of the insertion reaction was checked by GC analysis of reaction aliquots quenched with a solution of NH₄Cl in water (the conversion was more than 96%). An aliquot of organozinc reagent (1.0 mL) was titrated using iodine. The titrated organozinc reagent solution in THF (9.0 mL) were carefully separated from the remaining zinc powder using a syringe and transferred to another dry and argon-flushed flask.

Reference: Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 6040.

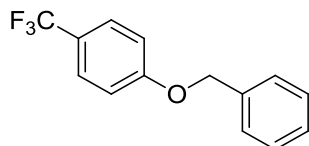
General procedure for Copper-Catalyzed Trifluoromethylation of Organic Zinc Reagents with Electrophilic Trifluoromethylating Reagent

Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.5 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under argon, after that organozinc reagents in THF (0.5 mmol, 0.3 M, 1.65 mL) was then added dropwise. The reaction was stirred at room temperature and monitored by ¹⁹F NMR spectroscopy until the disappearance of Togni's reagent II (typically 20 minute). 25 mL of Distilled water and 10 mL of Et₂O was added and the organic phase was separated. The aqueous phase was extracted with Et₂O (3 x 10 mL) and the combined organic extracts were dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel with pentane and further purified by preparation TLC.



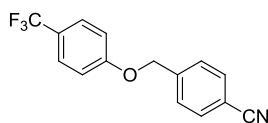
4-(Trifluoromethyl)-1,1'-biphenyl (4a). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 64% yield (71 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 1.2$ Hz, 4 H), 7.60 (d, $J = 8.1$ Hz, 2 H), 7.48 (t, $J = 7.4$ Hz, 2 H), 7.41 (t, $J = 7.3$ Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.7, 139.7, 129.0, 128.2, 127.4, 127.3, 125.7, 125.7, 121.6 (q, $J = 271.7$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.42 (s, 3 F) ppm. MS (EI) m/z (%): 222 (100).

Reference: Chu, L.-L.; Qing, F.-L. *Org. Lett.* **2010**, *12*, 5060.

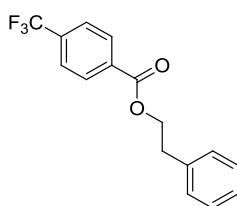


1-(Benzyloxy)-4-(trifluoromethyl)benzene (4b). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 54% yield (68 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.5$ Hz, 2 H), 7.41 (t, $J = 7.9$ Hz, 4 H), 7.35 (t, $J = 6.9$ Hz, 1 H), 7.03 (d, $J = 8.5$ Hz, 2 H), 5.11 (s, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.1, 136.2, 128.7, 128.3, 127.5, 127.0 (d, $J = 3.7$ Hz), 124.4 (q, $J = 271.1$ Hz), 122.7 (d, $J = 32.8$ Hz), 114.8, 70.1; ^{19}F NMR (376 MHz, CDCl_3) δ -61.56 (s, 3 F) ppm. MS (EI) m/z (%): 252.1, 91.1(100).

Reference: Gamido, E. M.; Gamido, J.; Calheiros, R.; Marques, M.; Borges, F. J. *Phys.Chem. A* **2009**, *113*, 9934.



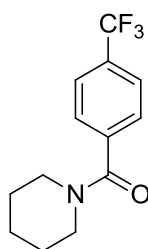
4-((4-(Trifluoromethyl)phenoxy)methyl)benzonitrile (4c). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 32% yield (44 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.2$ Hz, 2 H), 7.55 (d, $J = 8.0$ Hz, 2 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 6.96 (d, $J = 6.3$ Hz, 2 H), 5.13 (s, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.2, 142.7, 132.4, 129.7, 128.6 (q, $J = 282.4$ Hz), 127.6, 121.5, 118.9, 114.8, 111.7, 68.6; ^{19}F NMR (376 MHz, CDCl_3) δ -61.67 (s, 3 F) ppm. MS (EI) m/z (%) 277.1, 116.1(100). HRMS (EI) Calcd for: $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}$: 277.0714; Found: 277.0719. IR (thin film): ν_{max} 3059, 2228, 1611, 1600, 1586, 1497, 1485, 1450, 1377, 1311, 1244, 1078, 1054, 823, 752, 687, 549 cm^{-1} . Mp: 58-60 $^{\circ}\text{C}$



Phenethyl 4-(trifluoromethyl)benzoate (4d). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a colorless liquid in 65%

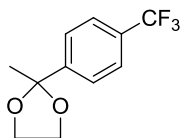
yield (95 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.1$ Hz, 2 H), 7.69 (d, $J = 8.1$ Hz, 2 H), 7.32 (d, $J = 7.1$ Hz, 2 H), 7.27 (m, 3 H), 4.57 (t, $J = 7.0$ Hz, 2 H), 3.09 (t, $J = 6.9$ Hz, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 137.7, 132.4 (d, $J = 246.9$ Hz, 0H), 130.1, 129.1, 128.6, 126.9, 125.6, 125.5, 123.8 (q, $J = 272.8$ Hz), 66.1, 35.3; ^{19}F NMR (376 MHz, CDCl_3) δ -63.18 (s, 3 F) ppm. MS (EI) m/z (%) 293.1(M^+-1), 104.1(100). HRMS (EI) Calcd for: $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_2$ (M^+-1): 293.0789; Found: 293.0790. IR (thin film): ν_{max} 3066, 2960, 1724, 1497, 1513, 1412, 1326, 1311, 1275, 1169, 1128, 1066, 1018, 775, 749, 700 cm^{-1} .

Reference: Zhang, C.; Feng, P.; Jiao, N. *J. Am. Chem. Soc.* **2013**, *135*, 15257.



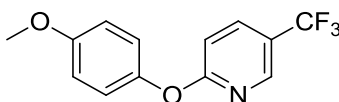
Piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (4e). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane. The compound was further purified by prep-HPLC with a C18 column (Kineten, 4.6×100 mm, 2.6 μm) using a water-acetonitrile mixed solvent as the eluent ($\text{CH}_3\text{CN} : \text{H}_2\text{O} = 50 : 50$, flow = 1.8 mL/min, 250/220 nm) to give the titled compound as a white solid in 60% yield (77 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 8.0$ Hz, 2 H), 7.51 (d, $J = 7.9$ Hz, 2 H), 3.73 (s, 2 H), 3.30 (s, 2 H), 1.70 (s, 4 H), 1.53 (s, 2 H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 140.0, 131.4 (q, $J = 32.7$ Hz), 127.1, 125.5 (q, $J = 3.7$ Hz), 123.8 (q, $J = 272.3$ Hz), 48.7, 43.2, 26.5, 25.5, 24.5; ^{19}F NMR (376 MHz, CDCl_3) δ -62.90 (s, 3 F) ppm. MS (EI) m/z (%) 255.9 (100).

Reference: Wang, X.; Wang, J.-B. *J. Am. Chem. Soc.* **2013**, *135*, 10330.



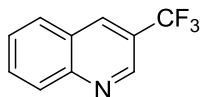
2-Methyl-2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane (4f). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 67% yield (78 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.3$ Hz, 2 H), 7.22 (d, $J = 8.4$ Hz, 2 H), 4.02 (t, $J = 6.8$ Hz, 2 H), 3.74 (t, $J = 6.9$ Hz, 2 H), 1.61 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 137.4, 127.5, 126.7 (q, $J = 258.1$ Hz), 108.6, 93.8, 64.6, 27.7, 27.6; ^{19}F NMR (376 MHz, CDCl_3) δ -62.54 (s, 3 F) ppm. MS (EI) m/z (%) 232.1 (100).

Reference: Kondolff, I.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2006**, 3, 765.



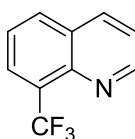
2-(4-Methoxyphenoxy)-5-(trifluoromethyl)pyridine(4g). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a light yellow liquid in 68% yield (91 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, $J = 1.4$ Hz, 1 H), 7.87 (dd, $J = 8.7, 2.3$ Hz, 1 H), 7.09 – 7.04 (m, 2 H), 6.99 – 6.92 (m, 3 H), 3.82 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.2, 157.0, 146.4, 145.4 (dd, $J = 8.4, 4.1$ Hz), 136.6 (d, $J = 3.0$ Hz), 126.4 (q, $J = 271.3$ Hz), 122.4, 121.2 (q, $J = 33.2$ Hz), 114.8, 111.0, 55.5; ^{19}F NMR (376 MHz, CDCl_3) δ -61.68 (s, 3 F) ppm. MS (EI) m/z (%) 269.1

(100). HRMS (EI) Calcd for: C₁₃H₁₀F₃NO₂: 269.0664; Found: 269.0661. IR (thin film): ν_{\max} 3070, 2935, 2838, 1616, 1508, 1487, 1442, 1397, 1327, 1286, 1244, 1196, 1127, 1078, 1036, 835, 819 cm⁻¹.



3-(Trifluoromethyl)quinoline (4h). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ¹⁹F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a colorless liquid in 60% yield (59 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.09 (s, 1 H), 8.44 (s, 1 H), 8.18 (d, *J* = 8.5 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.85 (t, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 7.5 Hz, 1 H); ¹⁹F NMR (376 MHz, CDCl₃) δ -61.83 (s, 3 F); ¹³C NMR (101 MHz, CDCl₃) δ 149.3, 146.0 (d, *J* = 3.0 Hz), 133.9 (q, *J* = 2.2 Hz), 131.7, 130.0, 128.6, 128.0, 126.2, 123.6 (q, *J* = 272.3 Hz), 123.6 (q, *J* = 33.0 Hz) ppm. MS (EI) *m/z* (%): 197.1(100).

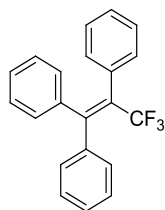
Reference: Jiang, X.-L.; Qing, F.-L. *J. Org. Chem.* **2012**, *77*, 1251



8-(Trifluoromethyl)quinoline (4i). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ¹⁹F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a light yellow liquid in 53% yield (52 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.07 (dd, *J* = 4.1, 1.6 Hz, 1 H), 8.21 (dd,

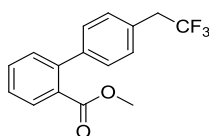
$J = 8.3, 1.6$ Hz, 1 H), 8.07 (d, $J = 7.2$ Hz, 1 H), 8.00 (d, $J = 8.2$ Hz, 1 H), 7.58 (t, $J = 7.8$ Hz, 1 H), 7.50 (dd, $J = 8.3, 4.2$ Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 144.7, 136.2, 132.4, 128.6, 128.0 (q, $J = 5.7$ Hz), 127.8 (q, $J = 29.2$ Hz), 125.2, 124.1 (q, $J = 273.4$ Hz), 121.9; ^{19}F NMR (376 MHz, CDCl_3) δ -60.26 (s, 3 F) ppm. MS (EI) $m/z(\%)$: 197.1(100).

Reference: Dai, J.-J.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 8436.



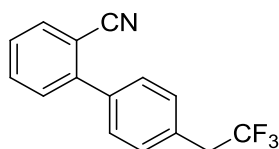
(3,3,3-Trifluoroprop-1-ene-1,1,2-triyl)tribenzene (4j). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). Yields were determined by ^{19}F NMR analysis of the crude product using *p*-Fluorotoluene as an internal standard in 57% yield. ^{19}F NMR (376 MHz, CDCl_3) δ -55.62 (s, 3 F) ppm. MS (EI) m/z (%) 324.2 (100). HRMS (EI) Calcd for: $\text{C}_{21}\text{H}_{15}\text{F}_3$ (M^+): 324.1126; Found: 324.1131.

Reference: Liu, X.; Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 879.

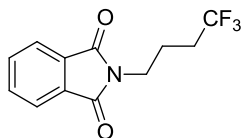


Methyl 4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carboxylate(4k). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The

product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 56% yield (82 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.8$ Hz, 1 H), 7.54 (t, $J = 7.5$ Hz, 1 H), 7.42 (t, $J = 7.6$ Hz, 1 H), 7.37 (d, $J = 7.7$ Hz, 1 H), 7.31 (dd, $J = 8.1$ Hz, 4 H), 3.63 (s, 3 H), 3.41 (q, $J = 10.8$ Hz, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 141.9, 141.2, 131.4, 130.9, 130.7, 129.9, 129.8, 129.0, 128.6, 127.4, 125.8 (q, $J = 276.6$ Hz), 51.9, 40.0 (q, $J = 29.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -65.88 (t, $J = 10.8$ Hz, 3 F) ppm. MS (EI) m/z (%) 294.1, 263.1 (100). HRMS (EI) Calcd for: $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_2$: 294.0868; Found: 294.0870. IR (thin film): ν_{max} 3063, 2958, 2928, 1720, 1596, 1436, 1260, 1132, 809, 762, 725, 708, 664, 652 cm^{-1} . Mp: 70-72 $^\circ\text{C}$.



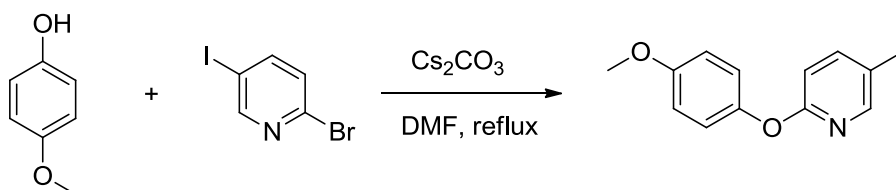
4'-(2,2,2-Trifluoroethyl)-[1,1'-biphenyl]-2-carbonitrile (41). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a light yellow liquid in 48% yield (62 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.8$ Hz, 1 H), 7.65 (t, $J = 7.6$ Hz, 1 H), 7.56 (d, $J = 8.0$ Hz, 2 H), 7.51 (d, $J = 7.7$ Hz, 1 H), δ 7.46 (d, $J = 7.7$ Hz, 1H), 7.43 (d, $J = 7.7$ Hz, 2H), 3.44 (q, $J = 10.7$ Hz, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.7, 138.0, 133.8, 132.9, 130.8, 130.7, 130.5, 130.0, 127.8, 125.7 (q, $J = 276.9$ Hz), 118.6, 111.2, 39.9 (q, $J = 29.8$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -65.70 (t, $J = 10.8$ Hz, 3 F) ppm. MS (EI) m/z (%) 261.1(100). HRMS (EI) Calcd for: $\text{C}_{15}\text{H}_{10}\text{F}_3\text{N}$: 261.0765; Found: 261.0766. IR (thin film): ν_{max} 3065, 2919, 2224, 1479, 1445, 1361, 1260, 1138, 1077, 911, 813, 764, 657 cm^{-1} .



2-(4,4,4-Trifluorobutyl)isoindoline-1,3-dione (4m). Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II (typically 20 min as monitored by ^{19}F NMR spectroscopy). The product was purified by flash chromatography on silica gel with pentane and isolated as a white solid in 49% yield (63 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (dd, $J = 5.4, 3.1$ Hz, 2 H), 7.71 (dd, $J = 5.4, 3.0$ Hz, 2 H), 3.73 (t, $J = 7.0$ Hz, 2 H), 2.21 – 2.07 (m, 2 H), 2.00 – 1.86 (m, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.2, 134.1, 131.9, 126.7 (q, $J = 276.2$ Hz), 123.4, 36.7, 31.5 (q, $J = 29.4$ Hz), 21.5 (q, $J = 2.9$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -66.43 (t, $J = 10.6$ Hz, 3F).

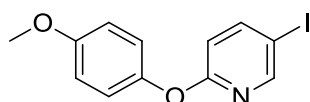
Reference: Mizuta, S.; Verhoog, S.; Engle, K. M.; Khotavivattana, T.; O'Duill, M.; Wheelhouse, K.; Rassias, G.; Médebielle, M.; Gouverneur, V. *J. Am. Chem. Soc.* **2013**, *135*, 2505.

General Procedure for Preparation of Aryl Iodides



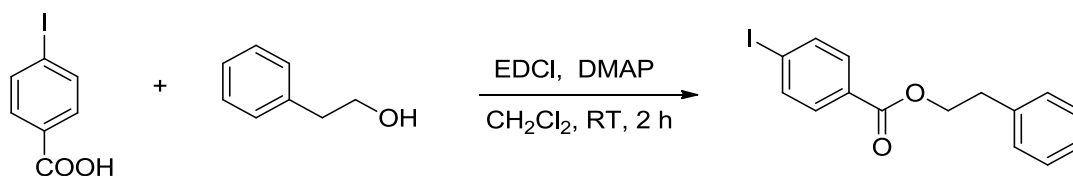
The procedure described for 5-iodo-2-(4-methoxyphenoxy) pyridine was applied with 4-methoxyphenol (0.44 g, 3.5 mmol) 2-bromo-5-iodopyridine (1.0 g, 3.5 mmol),

Cs₂CO₃ (2.6 g, 8.0 mmol), and DMF (20 mL) to give title compound as a white solid.

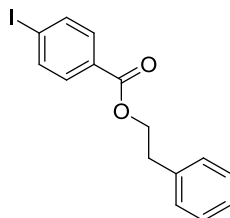


5-Iodo-2-(4-methoxyphenoxy)pyridine (1b). White solid. ¹H NMR (300 MHz, CDCl₃) δ 7.48 (t, *J* = 7.8 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.17 (d, *J* = 9.0 Hz, 2 H), 6.92 (d, *J* = 9.1 Hz, 2 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 3.82 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 163.9, 157.0, 153.7, 147.3, 147.1, 122.5 (d, *J* = 5.0 Hz), 115.0, 113.5, 83.9, 55.8 ppm. MS (EI) *m/z* (%) 327.0 (100).

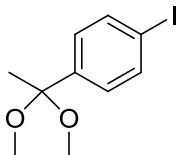
Reference: Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 6040.



The procedure described for phenethyl 4-iodobenzoate was applied with 4-iodobenzoic acid (2.0 g, 8.1 mmol), 2-phenylethanol (1.1 g, 8.8 mmol), DMAP (0.11 g, 0.88 mmol), and EDCI (1.5 g, 8.1 mmol) to give title compound as a white solid.



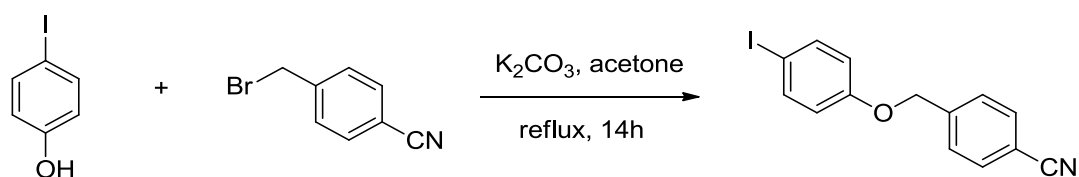
Phenethyl 4-iodobenzoate (1c). White solid. ¹H NMR (300 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.37 – 7.26 (m, 5 H), 4.52 (t, *J* = 7.0 Hz, 2 H), 3.07 (t, *J* = 7.0 Hz, 2 H); ¹³C NMR (101 MHz, CDCl₃) δ 166.0, 137.7, 131.0, 129.7, 129.0, 128.6, 126.7, 100.8, 65.7, 35.2 ppm. MS (EI) *m/z* (%) 352.0, 104 (100).



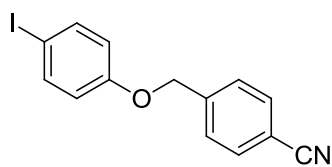
2-(4-Iodophenyl)-2-methyl-1,3-dioxolane (1d). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 4.02 (t, *J* = 6.9 Hz, 2 H), 3.74 (t, *J* = 6.9 Hz, 2 H), 1.61 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 137.5,

127.6, 108.7, 93.8, 64.7, 27.7 ppm. MS (EI) m/z (%) 290.0, 275.0 (100).

Reference: Jefferson, N,-W.; Wayland, M,-A. US 2011/0190489.A1.



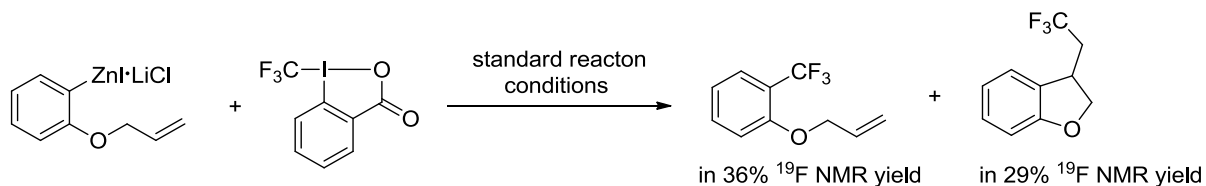
To a flask, 4-iodophenol (4.22 g, 19.2 mmol), K_2CO_3 (13.32 g, 96.4 mmol), and 4-(bromomethyl)benzonitrile (3.20 g, 16.0 mmol) were dissolved in 120 mL of acetone and the mixture was stirred under reflux for 14 h. After filtered, the mixture was concentrated *in vacuo*. The residue was dissolved in 30 mL of Et_2O , washed with H_2O (10 mL x 3), and brine. The organic layer was dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to yield the title compound as a white solid.



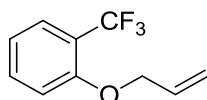
4-((4-Iodophenoxy)methyl)benzonitrile (1e). White solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, $J = 8.2$ Hz, 2 H), 7.57 (d, $J = 8.9$ Hz, 2 H), 7.52 (d, $J = 8.1$ Hz, 2 H), 6.72 (d, $J = 8.8$ Hz, 2 H), 5.09 (s, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 142.2, 138.6, 132.6, 127.7, 118.2, 117.4, 112.0, 83.9, 69.1 ppm. MS (EI) m/z (%) 335.0, 116.1 (100).

Mechanistic Experiments

a) Radical-clock experiment.

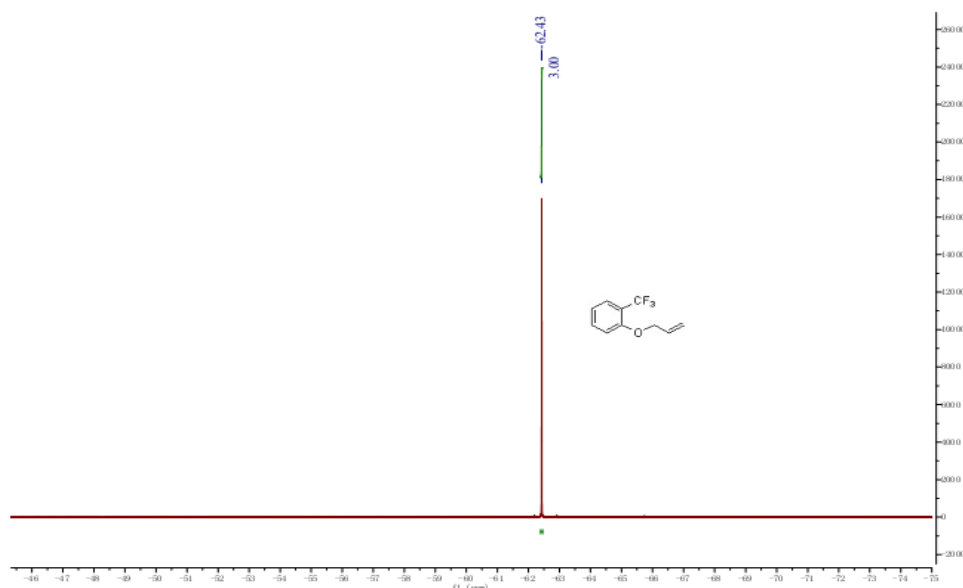


Freshly prepared CuI (28 mg, 0.15 mmol), Togni's reagent II (474 mg, 1.50 mmol) and anhydrous DMF (5.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. Organozinc reagents (0.5 mmol) was then added dropwise. The reaction was stirred at room temperature until the disappearance of Togni's reagent II. The product was purified by flash chromatography on silica gel with pentane.

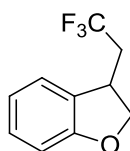
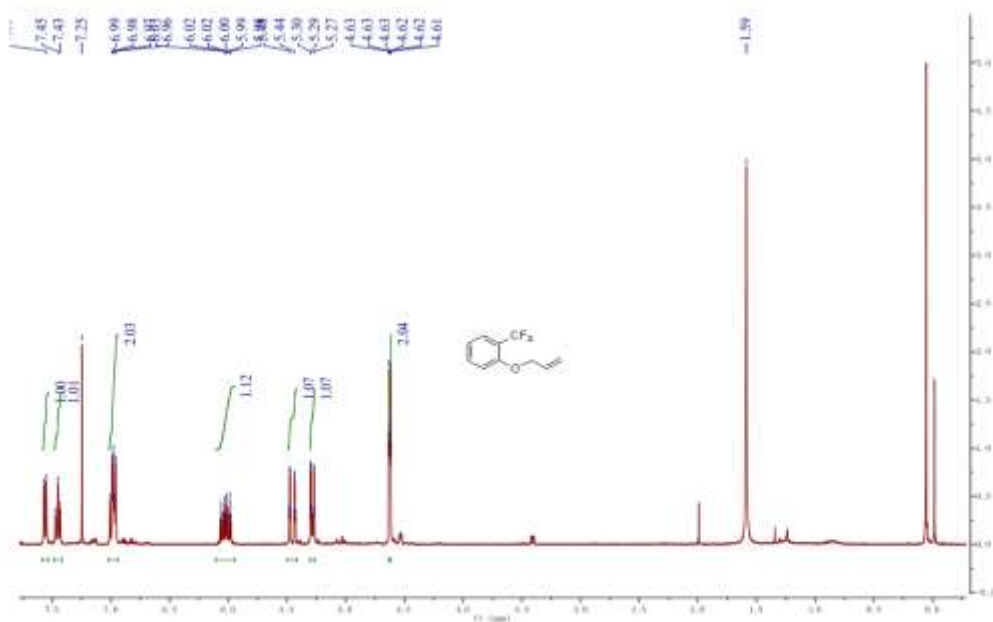


1-(Allyloxy)-2-(trifluoromethyl)benzene. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.7 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.02 – 6.94 (m, 2 H), 6.08 – 5.97 (m, 1 H), 5.46 (m, 1 H), 5.31 – 5.26 (m, 1 H), 4.62 (dt, *J* = 4.7, 1.6 Hz, 2 H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.43 (s, 3 F). MS (EI) *m/z* (%) 201.9 (100). HRMS (EI) Calcd for: C₁₀H₉F₃O: 202.0605; Found: 202.0602.

¹⁹F NMR Spectrum of 1-(allyloxy)-2-(trifluoromethyl)benzene

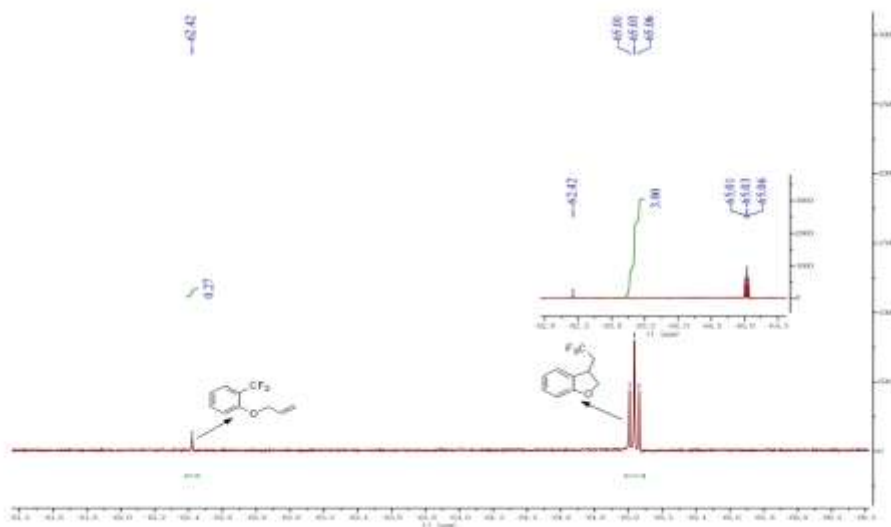


¹H NMR Spectrum of 1-(allyloxy)-2-(trifluoromethyl)benzene

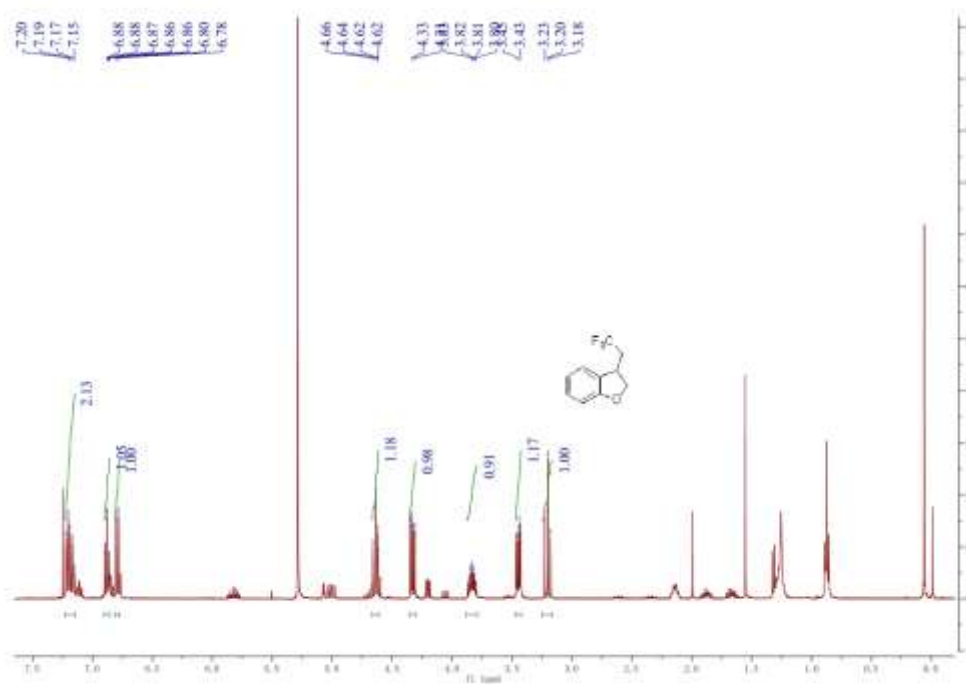


3-(2,2,2-Trifluoroethyl)-2,3-dihydrobenzofuran. ¹H NMR (400 MHz, CDCl₃) δ 7.19 (m, *J* = 14.4, 2 H), 6.90 – 6.85 (m, 1 H), 6.79 (m, 1 H), 4.63 (m, 1 H), 4.33 (dd, *J* = 9.4, 5.5 Hz, 1 H), 3.83 (tt, *J* = 9.4, 4.9 Hz, 1 H), 3.45 (dd, *J* = 9.9, 4.4 Hz, 1 H), 3.20 (t, *J* = 9.8 Hz, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ -65.03 (t, *J* = 10.9 Hz, 3 F). MS (EI) *m/z*(%) 201.9 (100). HRMS (EI) Calcd for: C₁₀H₉F₃O: 202.0605; Found: 202.0606.

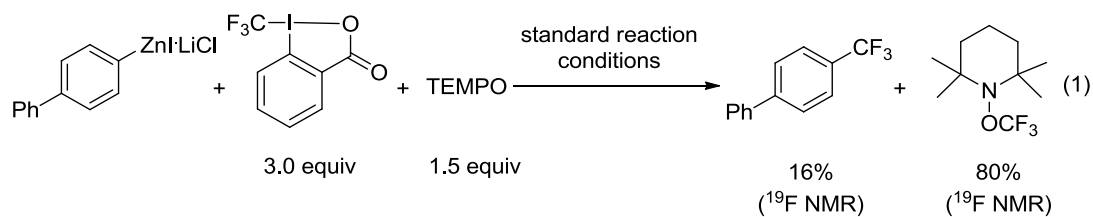
¹⁹F NMR Spectrum of 3-(2,2,2-trifluoroethyl)-2,3-dihydrobenzofuran.



¹H NMR Spectrum of 3-(2,2,2-trifluoroethyl)-2,3-dihydrobenzofuran.



b) Radical Trap experiment.



Freshly prepared CuI (6 mg, 0.03 mmol), Togni's reagent II (95 mg, 0.30 mmol) and anhydrous DMF (1.0 mL) were placed into an oven-dried Schlenk tube that is

equipped with a stirring bar under Ar. Organozinc reagents (0.1 mmol) and 1.5 equivalents of TEMPO were then added. The reaction was stirred at room temperature until the disappearance of Togni's reagent II. The reaction was monitored by ^{19}F NMR spectroscopy.

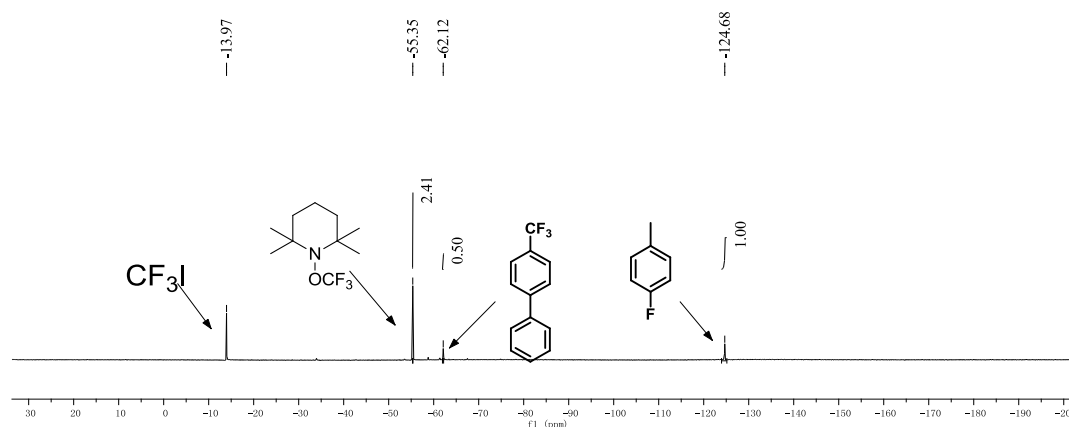
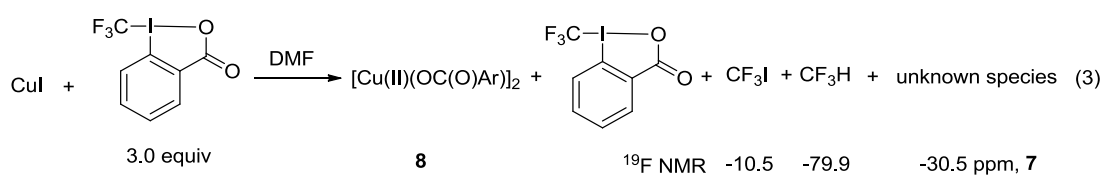


Figure S1. The reaction was monitored by ^{19}F NMR spectroscopy using *p*-Fluorotoluene as an internal standard (it showed the formation of CF_3I (resonated at $\delta = -13.97$ ppm in ^{19}F NMR), trifluoromethylated TEMPO (resonated at $\delta = -55.35$ ppm in ^{19}F NMR), trifluoromethylated biphenyl (resonated at $\delta = -62.12$ ppm in ^{19}F NMR).

c) Stoichiometric reaction monitored by ^{19}F NMR spectroscopy.

Freshly prepared CuI (19 mg, 0.1 mmol), Togni's reagent II (95 mg, 0.3 mmol) and anhydrous DMF (1.0 mL) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. A clear blue solution was formed within 1.0 min at room temperature upon. The reaction was monitored by ^{19}F NMR spectroscopy. Addition of 10 mL of diethyl ether precipitated a blue solid which was characterized to be bimetallic copper(II) species **8**, as determined by X-ray diffraction of its single crystals. After the diethyl ether was removed under vacuum, the DMF solution of the reaction mixture was treated with 1.0 equivalent of 4-biphenyl zinc reagent. After 20 min, the peak at -30.5 ppm disappeared and a new peak at -62.4 ppm which corresponds to the trifluoromethylated biphenyl formed in 47% yield, as determined by ^{19}F NMR spectroscopy (Fig. S3).



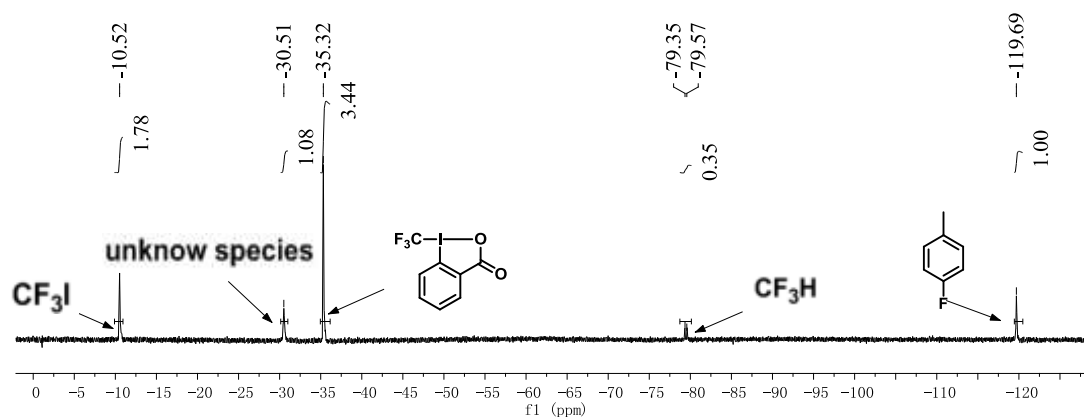


Figure S2. The reaction was monitored by ^{19}F NMR spectroscopy using *p*-Fluorotoluene as an internal standard (it showed the formation of CF_3I (resonated at $\delta = -10.5$ ppm in ^{19}F NMR), CF_3H (resonated at $\delta = -79.5$ ppm in ^{19}F NMR), unreacted reagent **2** and an unknown species **7** (resonated at $\delta = -30.5$ ppm in ^{19}F NMR).

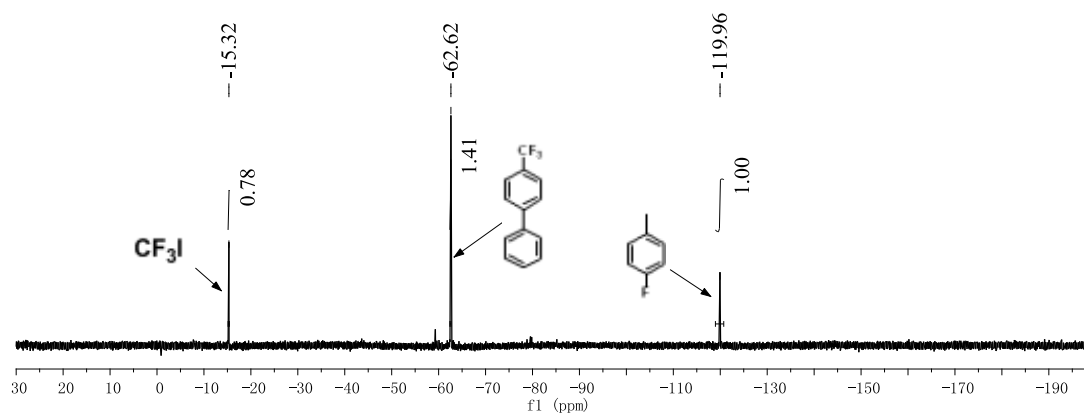


Figure S3. ^{19}F NMR spectroscopy for reaction of the DMF solution of above solution after removing the copper(II) salts with aryl zinc reagent **2** after 20 min at room temperature, using *p*-Fluorotoluene as an internal standard.

d) Evidence supports that the chemical shift of ^{19}F NMR spectroscopy of CF_3I in a mixed THF/DMF solvent shifted to -15.32 ppm.

To gain evidence that the peak at -15.32 ppm corresponds to the signal of CF_3I , we added a small amount of authentic CF_3I to the reaction mixture and the mixture was monitored by ^{19}F NMR spectroscopy. It was found that the peak at -15.32 ppm increased sharply and no new peak was discovered.

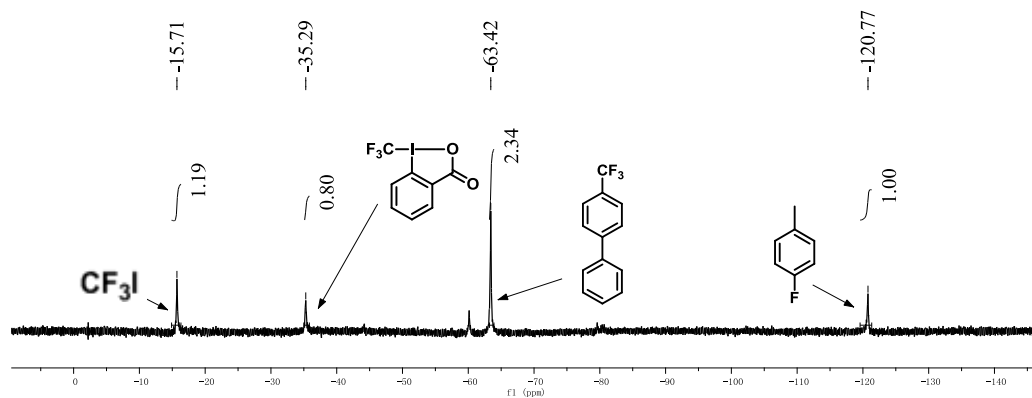


Figure S4. ^{19}F NMR analysis of the crude product using *p*-Fluorotoluene as an internal standard.

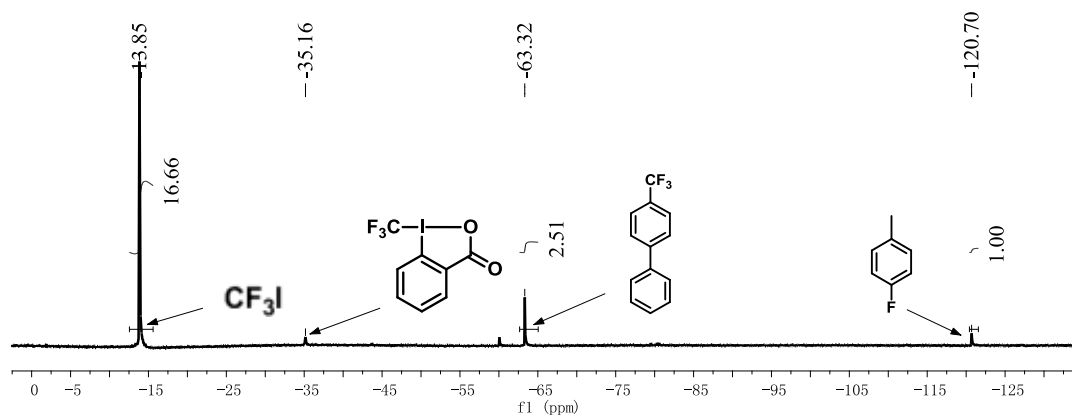
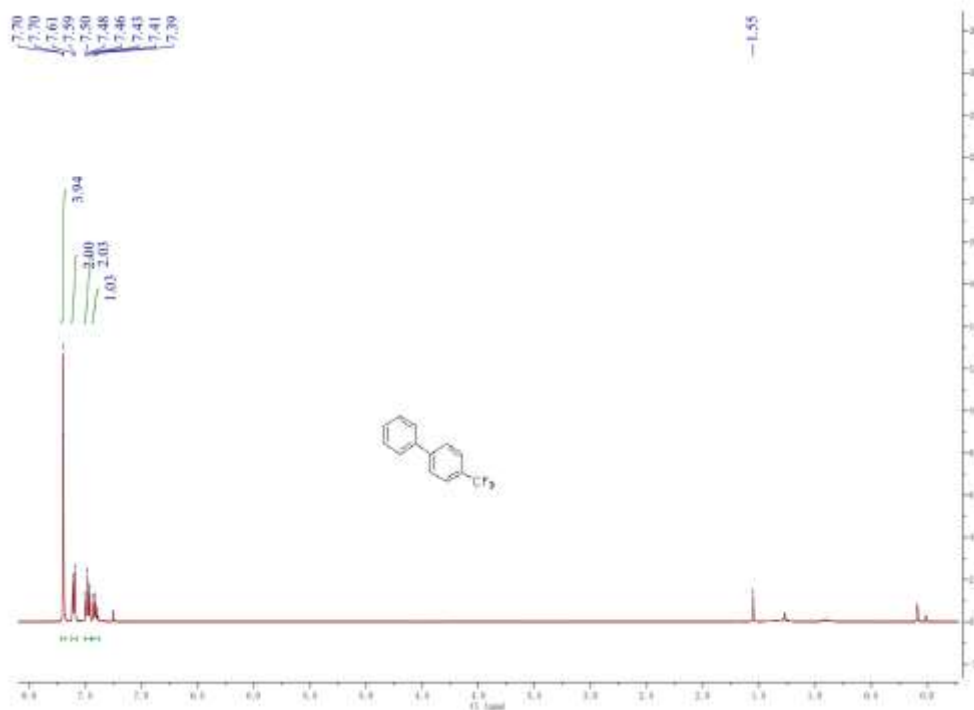
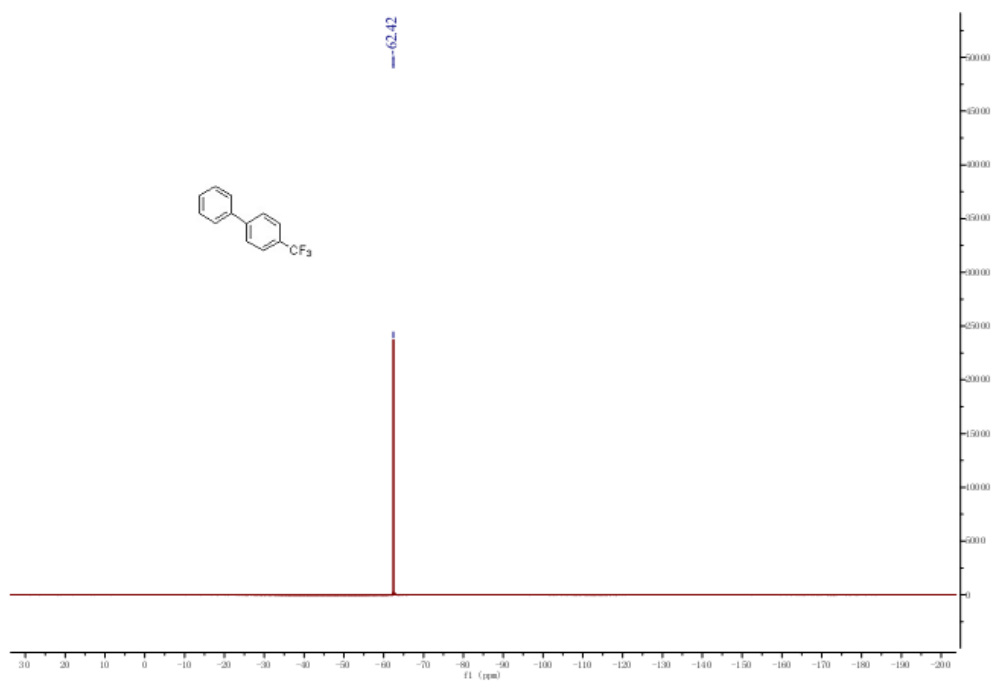


Figure S5. ^{19}F NMR spectroscopy after the addition of a small amount of CF_3I .

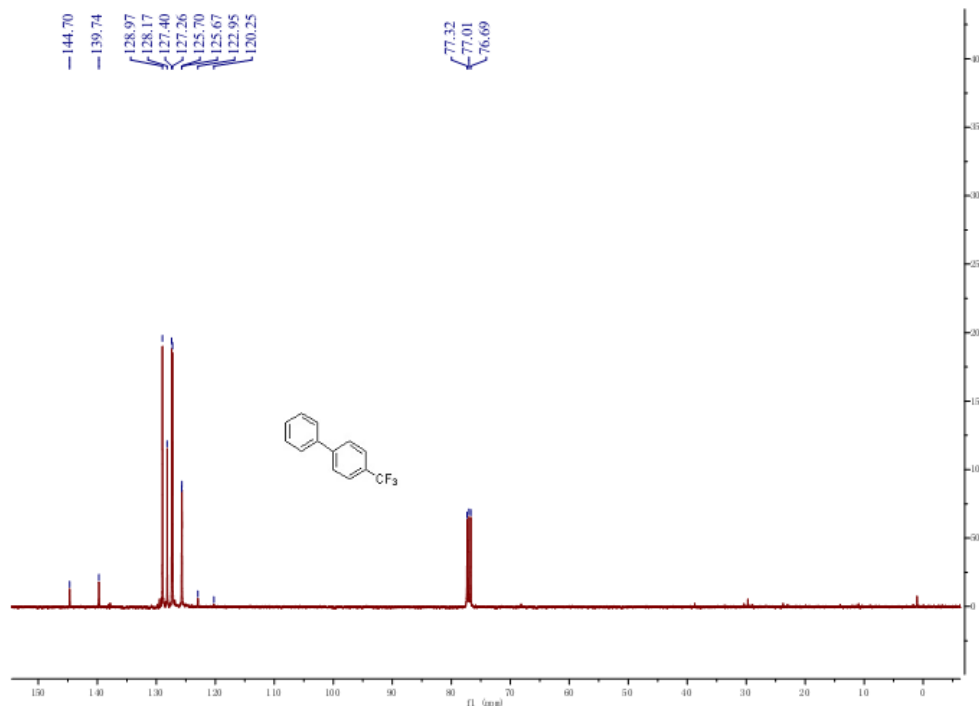
¹H NMR Spectrum of 4-(trifluoromethyl)-1,1'-biphenyl (4a)



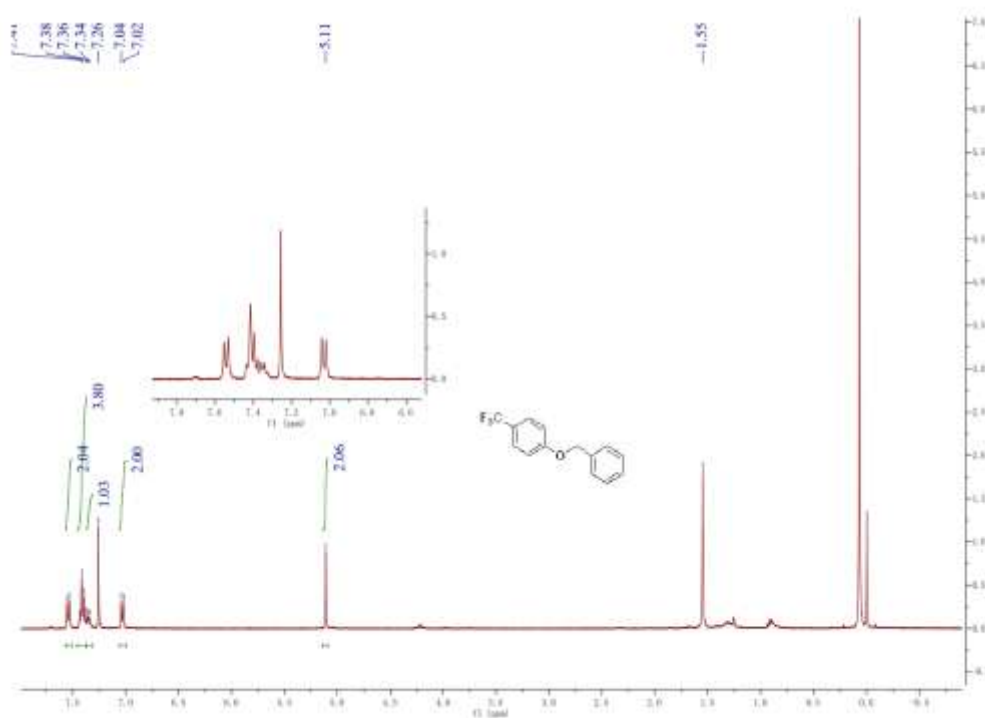
¹⁹F NMR Spectrum of 4-(trifluoromethyl)-1,1'-biphenyl (4a)



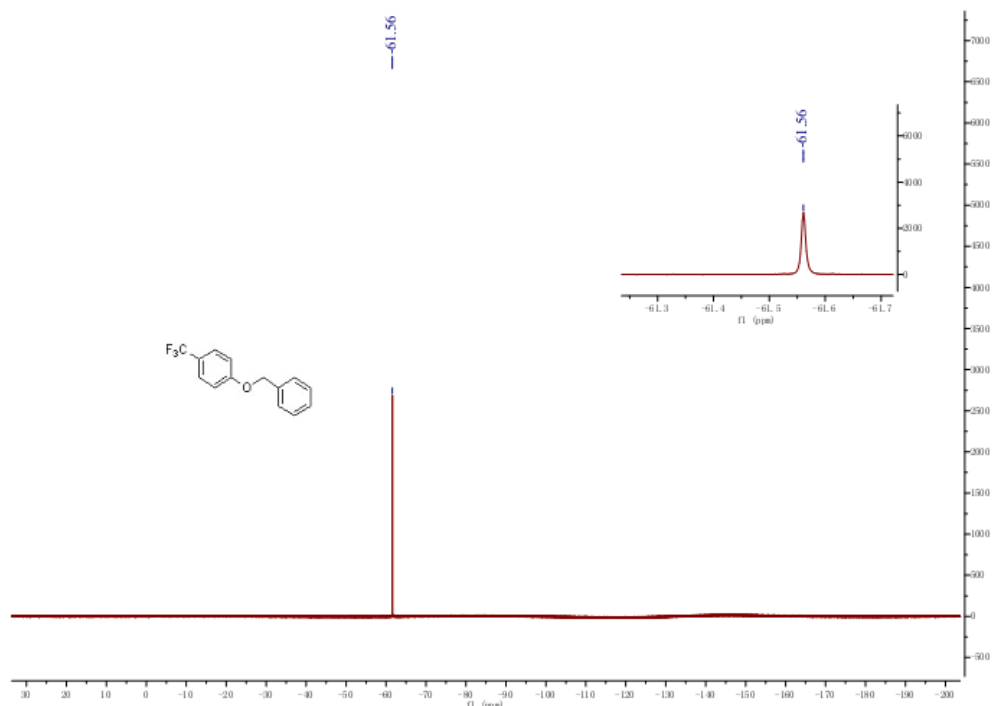
¹³C NMR Spectrum of 4-(trifluoromethyl)-1,1'-biphenyl (4a)



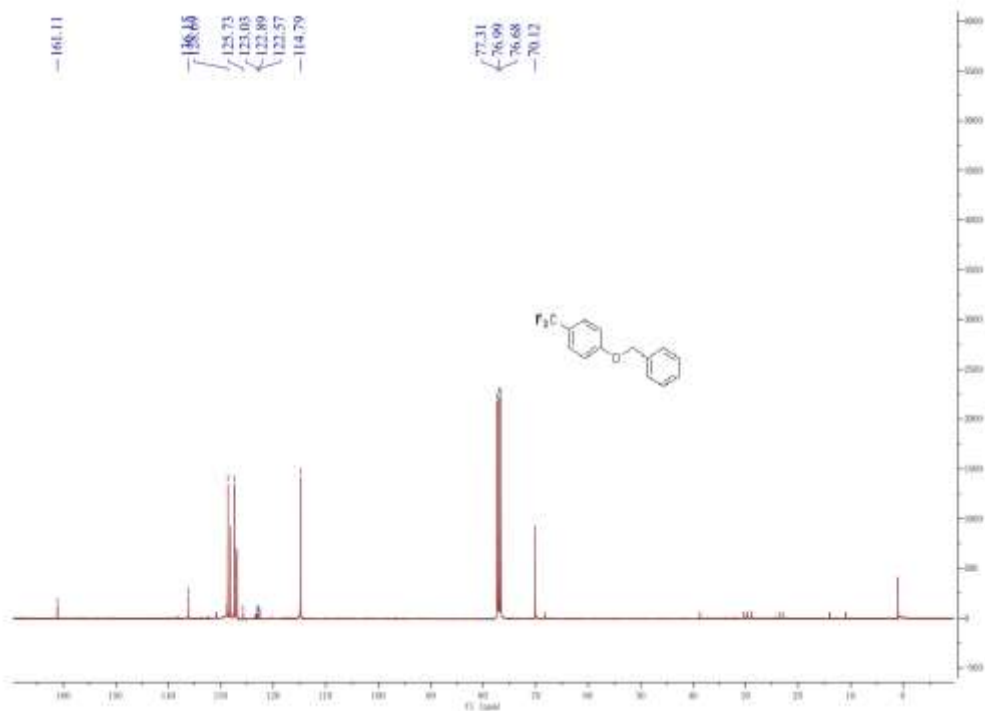
¹H NMR Spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene (4b)



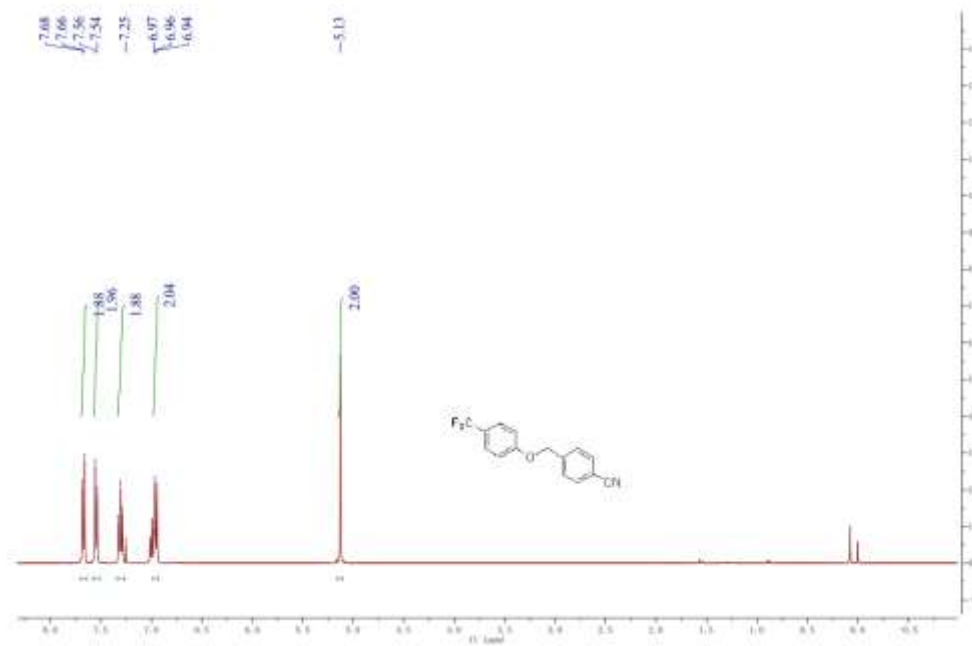
¹⁹F NMR Spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene (4b)



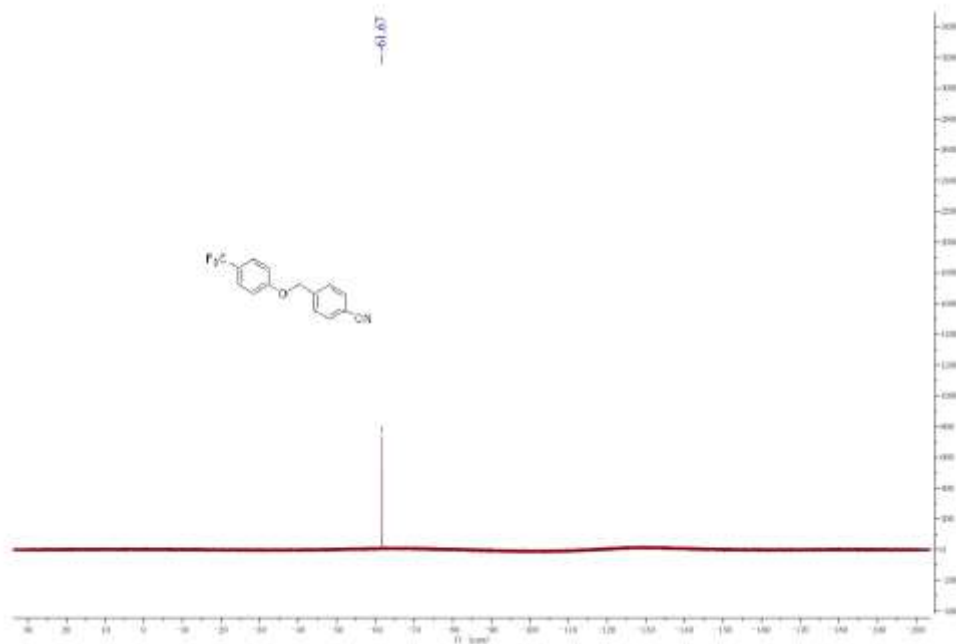
¹³C NMR Spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene (4b)



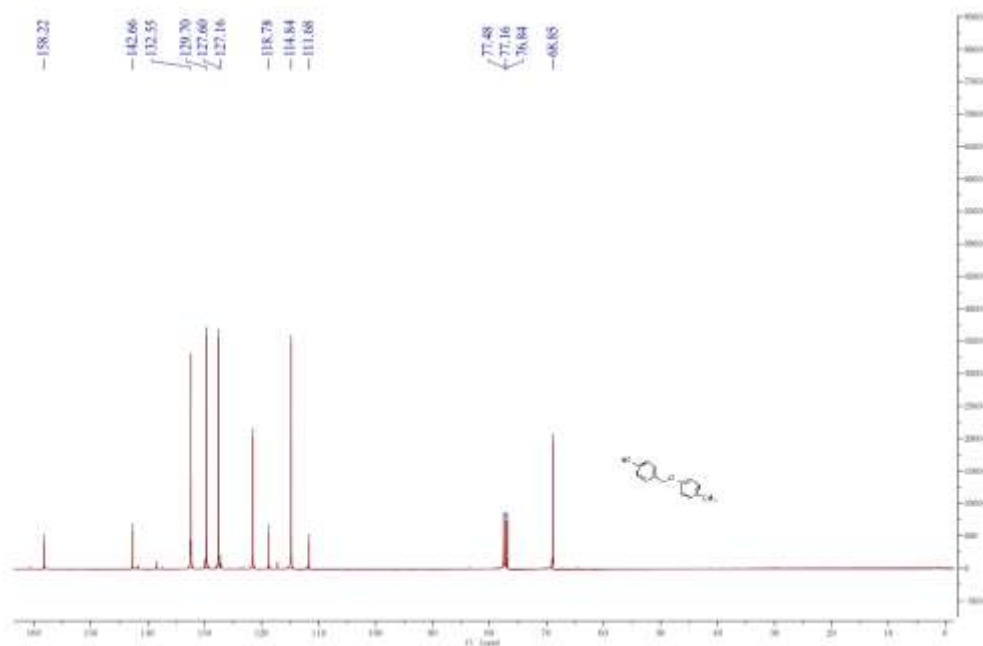
¹H NMR Spectrum of 4-((4-(trifluoromethyl)phenoxy)methyl)benzonitrile(4c)



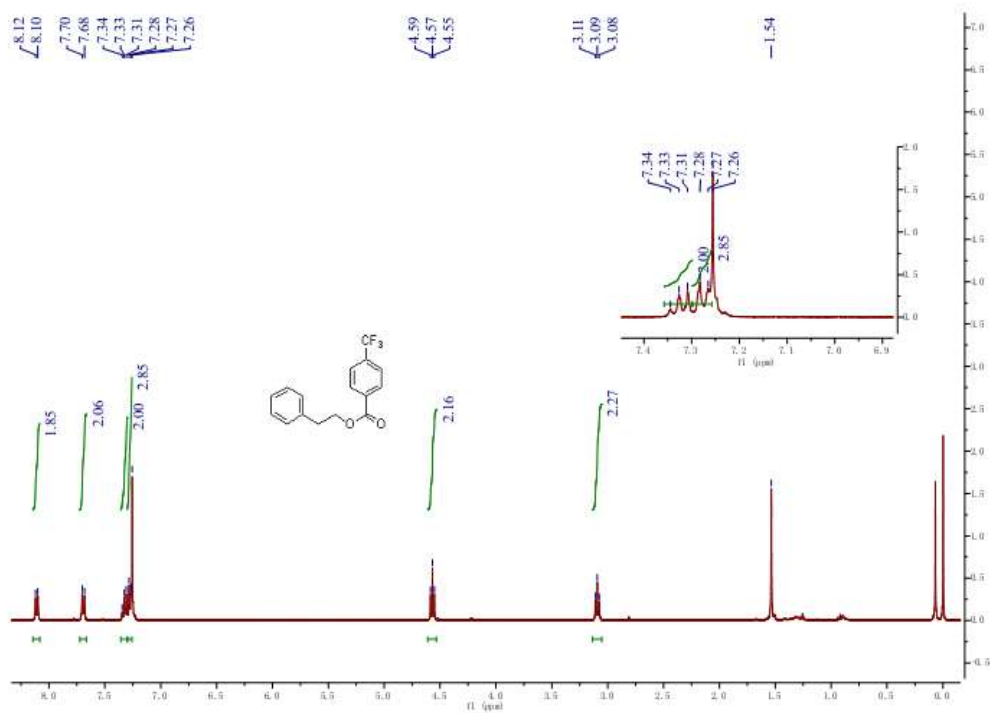
¹⁹F NMR Spectrum of 4-((4-(trifluoromethyl)phenoxy)methyl)benzonitrile(4c)



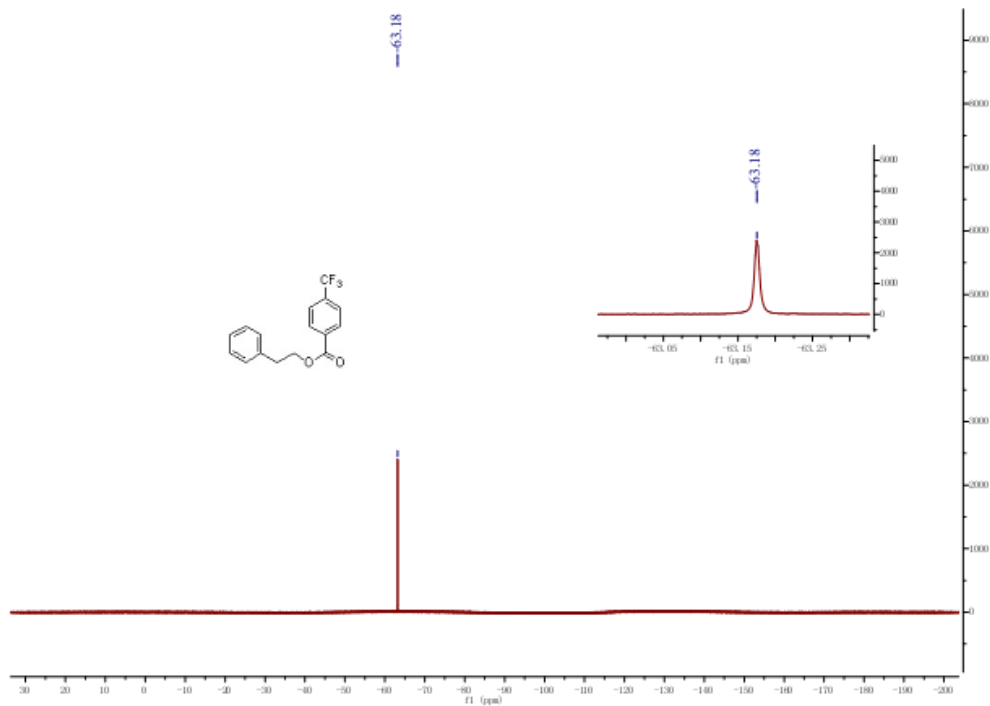
^{13}C NMR Spectrum of 4-((4-(trifluoromethyl)phenoxy)methyl)benzotrile(4c)



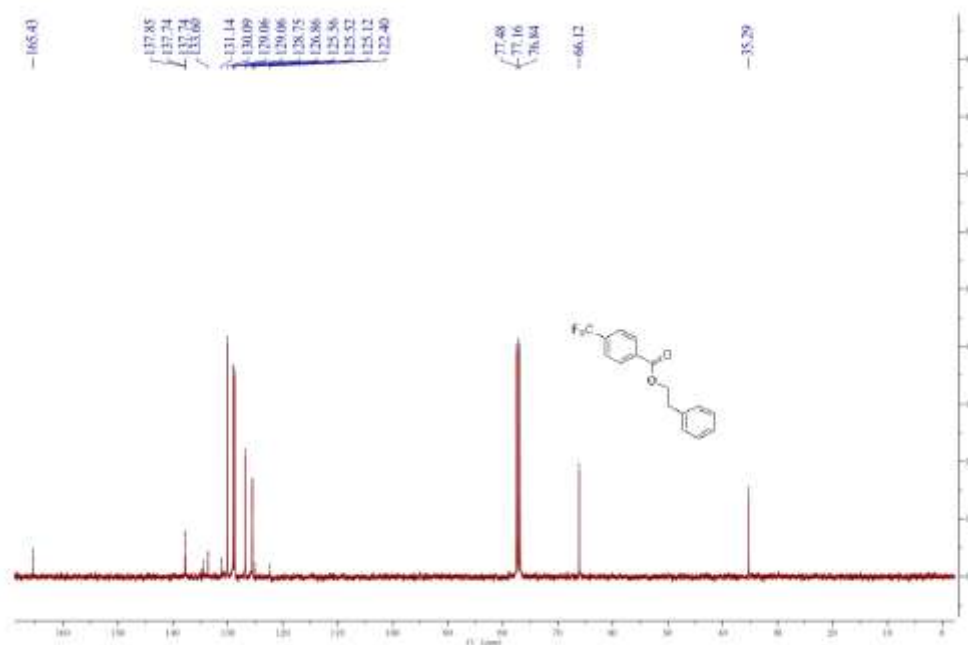
^1H NMR Spectrum of phenethyl 4-(trifluoromethyl)benzoate (4d)



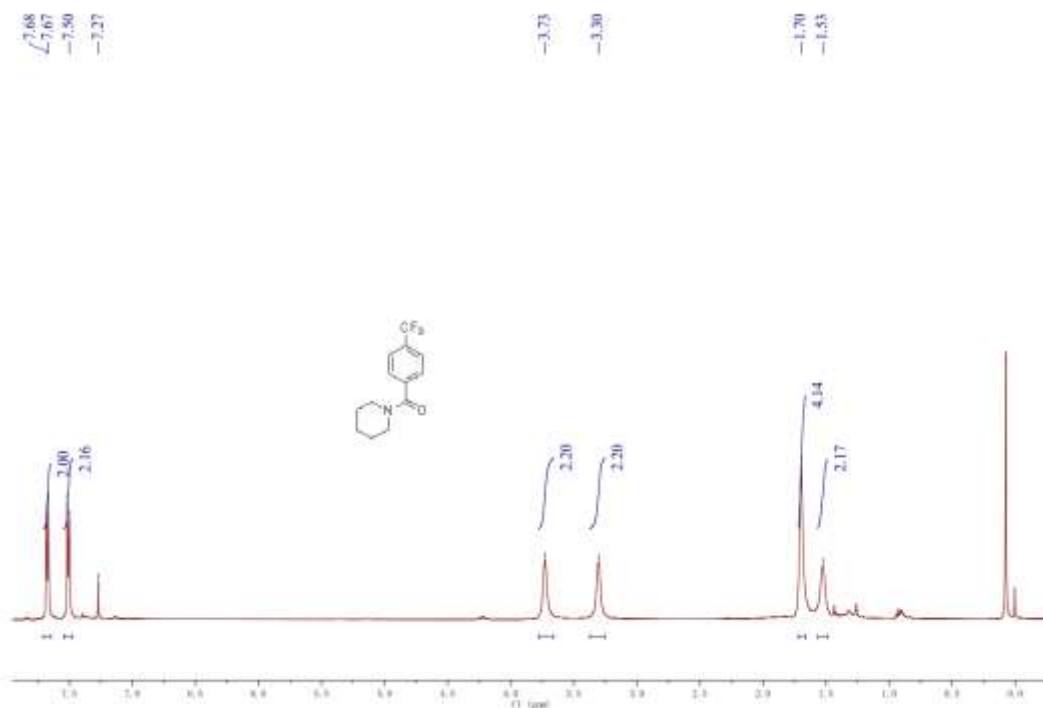
¹⁹F NMR Spectrum of phenethyl 4-(trifluoromethyl)benzoate (4d)



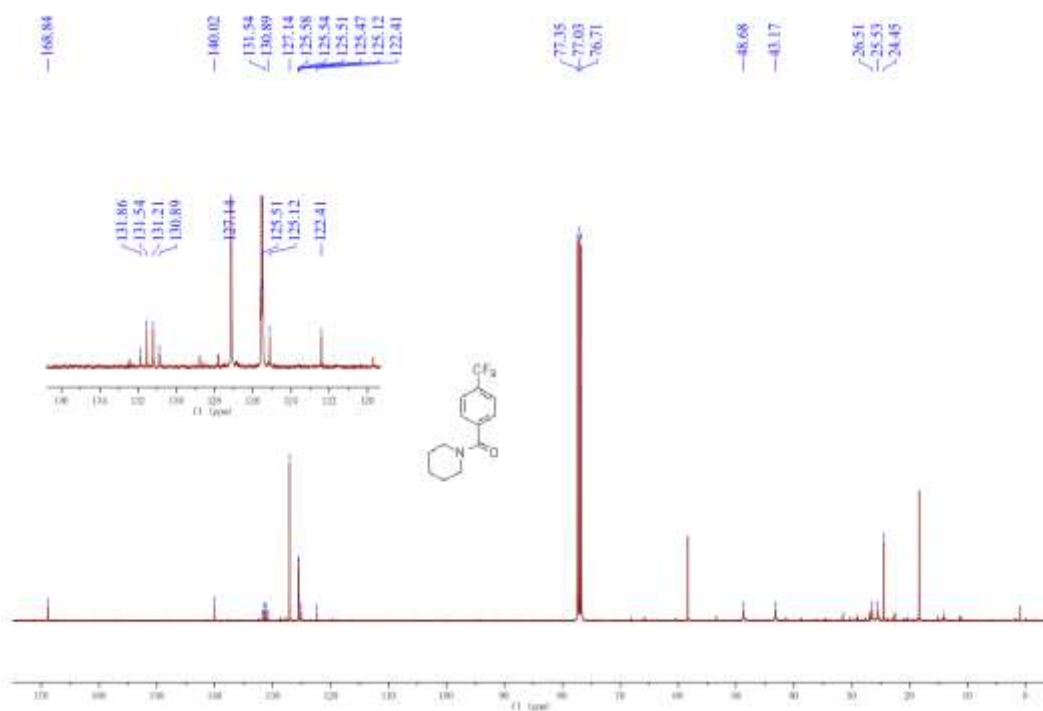
¹³C NMR Spectrum of phenethyl 4-(trifluoromethyl)benzoate (4d)



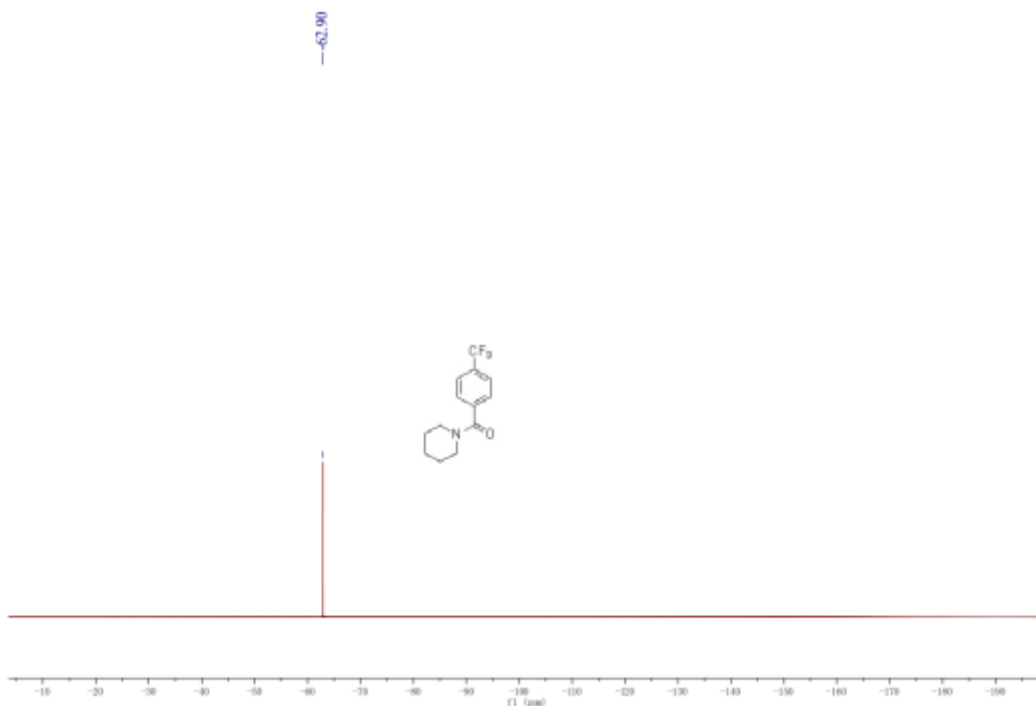
¹H NMR Spectrum of piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (4e)



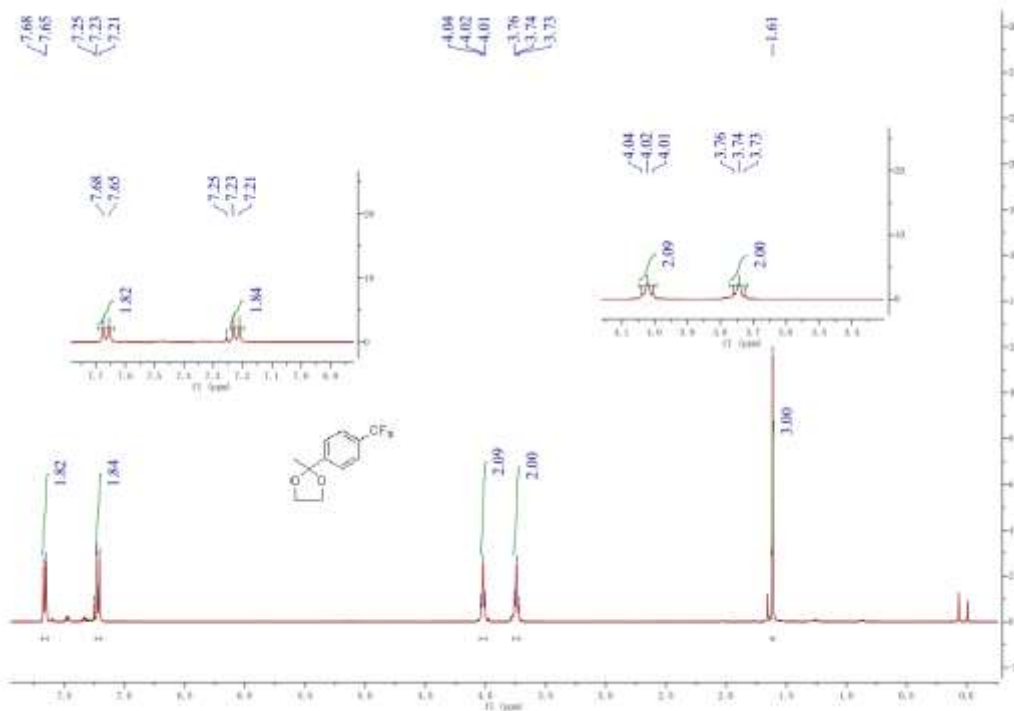
¹³C NMR Spectrum of piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (4e)



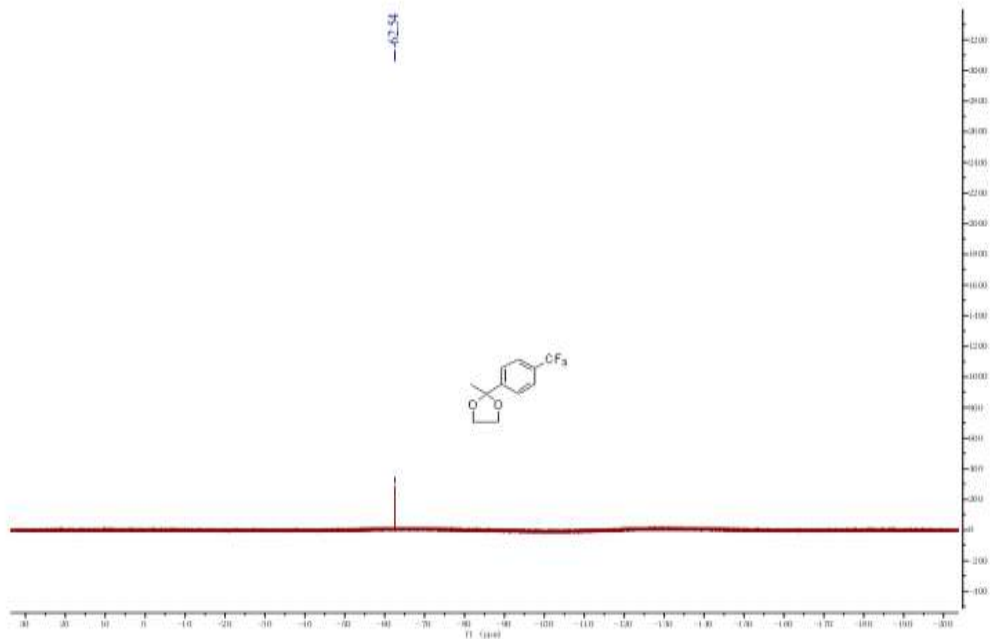
¹⁹F NMR Spectrum of piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (4e)



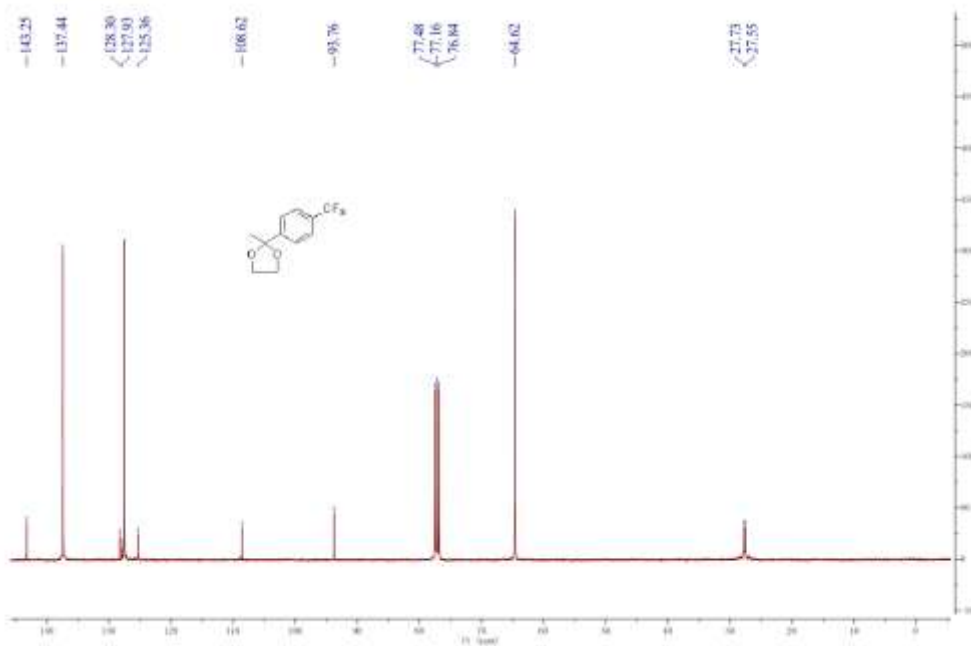
¹H NMR Spectrum of 2-methyl-2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane(4f)



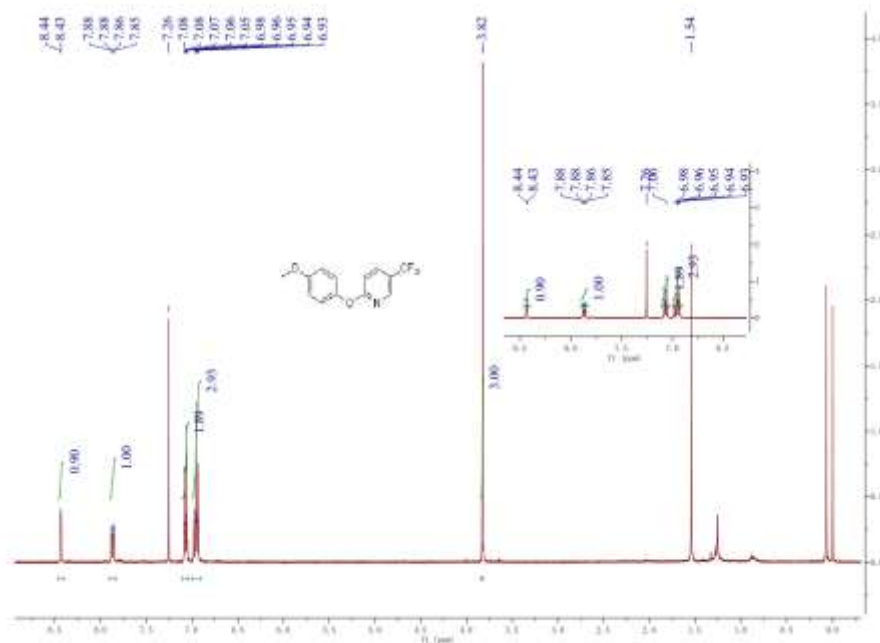
¹⁹F NMR Spectrum of 2-methyl-2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane(4f)



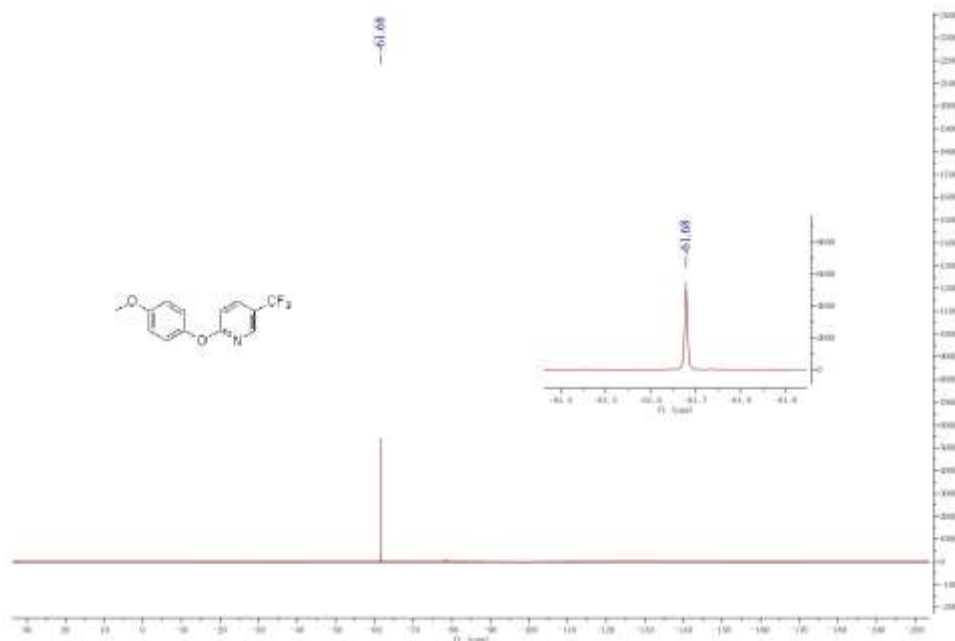
¹³C NMR Spectrum of 2-methyl-2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane(4f)



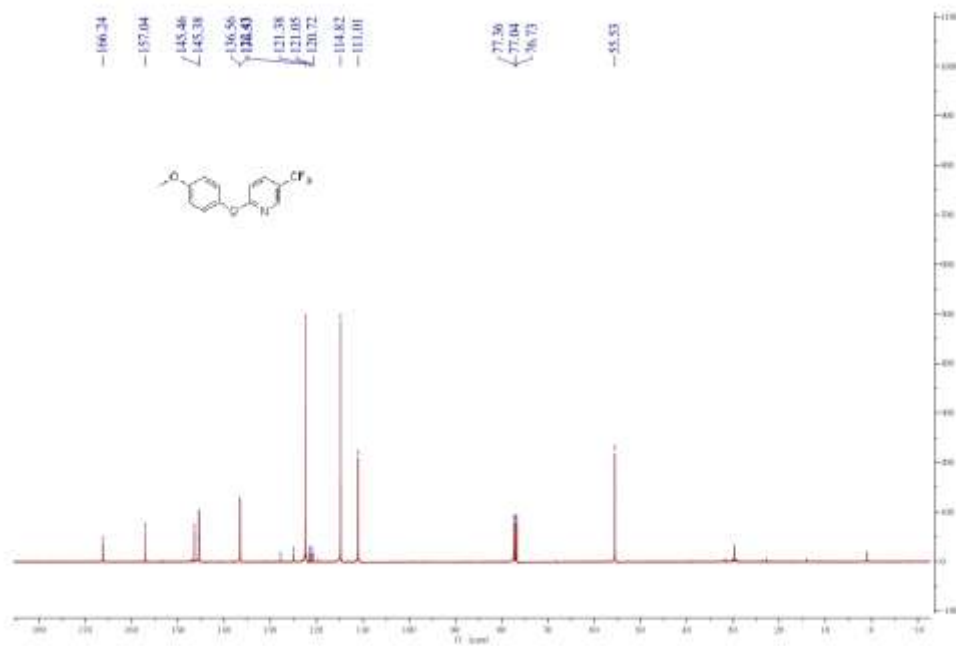
¹H NMR Spectrum of phenethyl2-(4-methoxyphenoxy)-5-(trifluoromethyl)pyridine(4g)



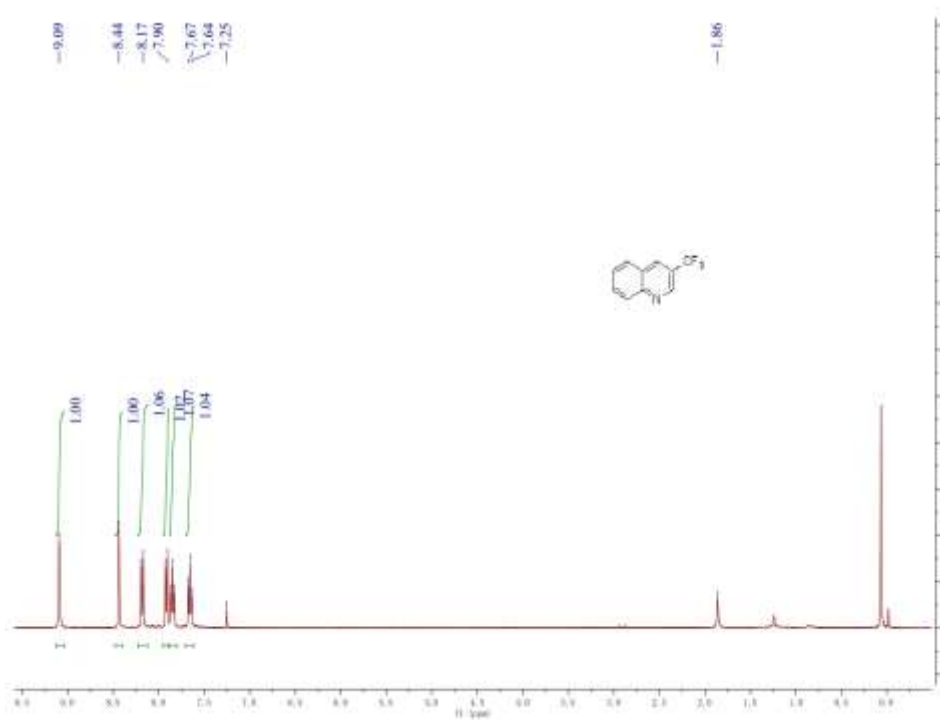
¹⁹F NMR Spectrum of phenethyl2-(4-methoxyphenoxy)-5-(trifluoromethyl)pyridine (4g)



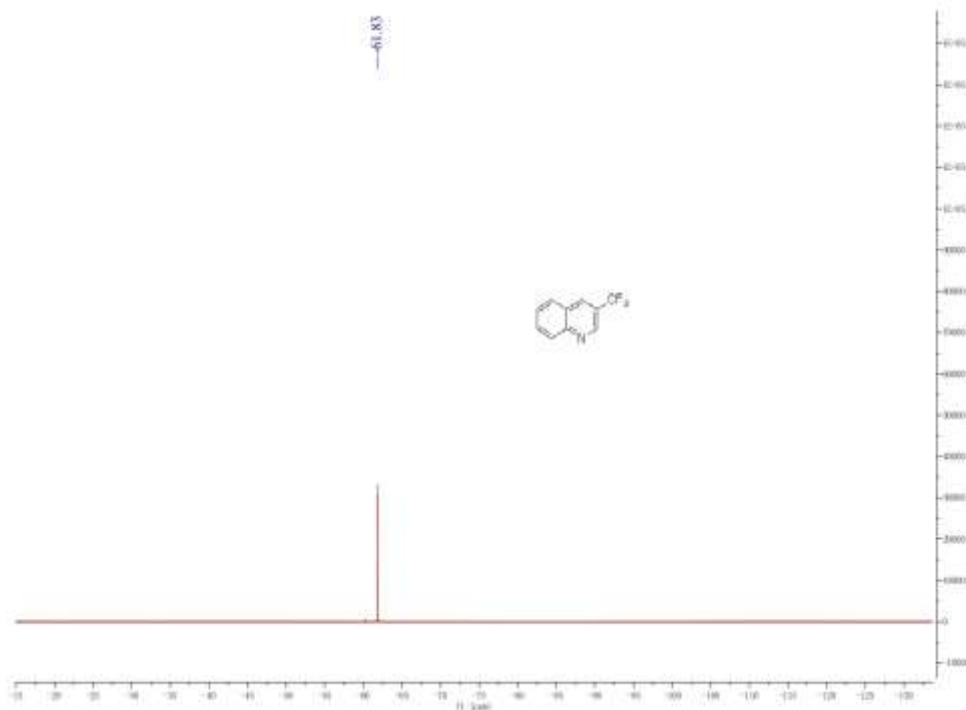
¹³C NMR Spectrum of phenethyl2-(4-methoxyphenoxy)-5-(trifluoromethyl)pyridine(4g)



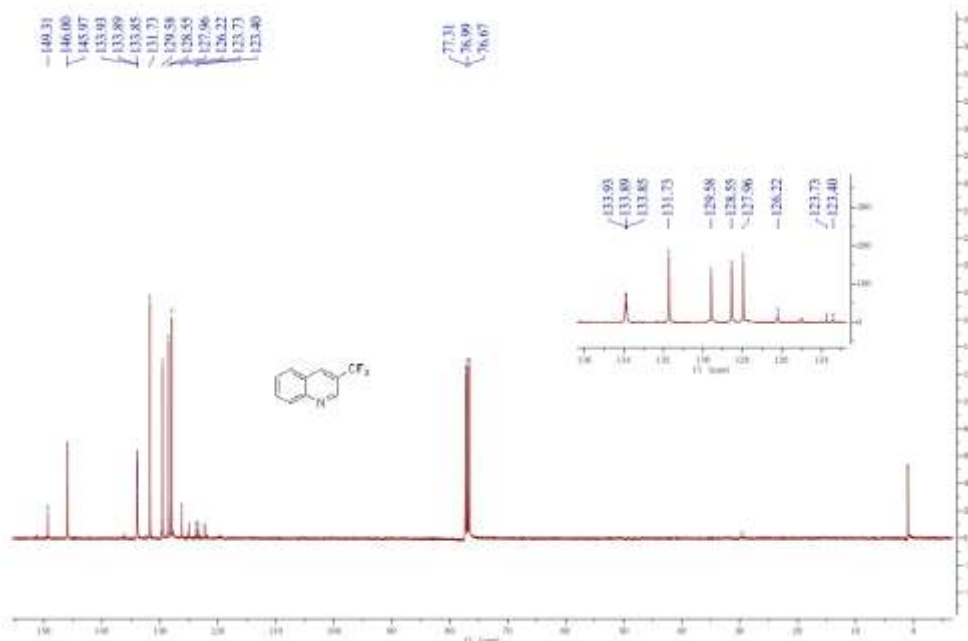
¹H NMR Spectrum of 3-(trifluoromethyl)quinoline (4h)



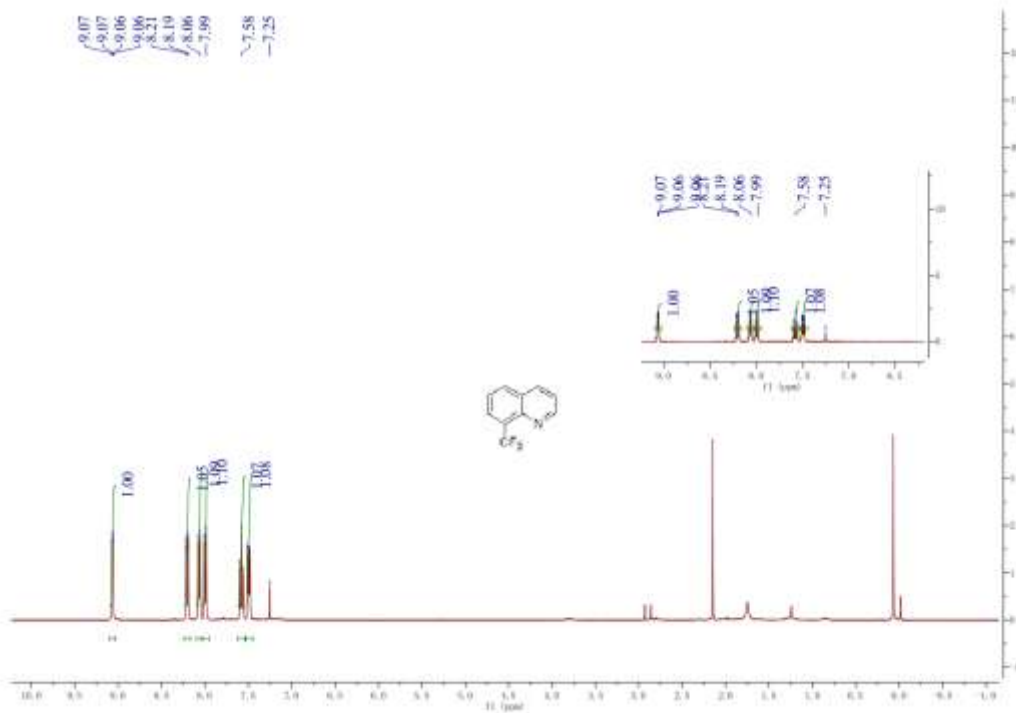
¹⁹F NMR Spectrum of 3-(trifluoromethyl)quinoline (4h)



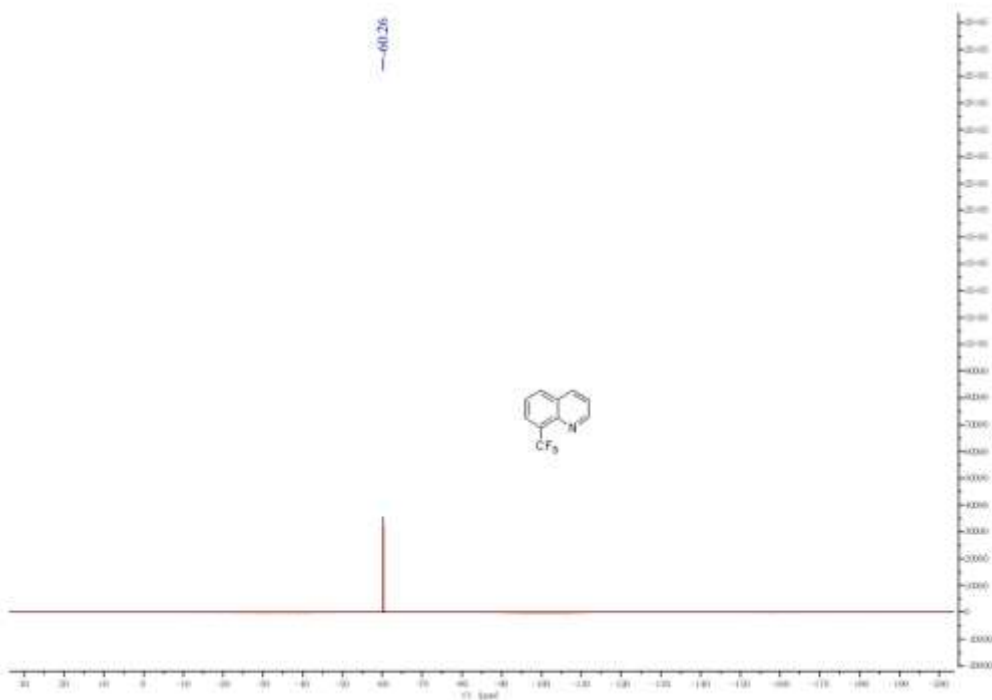
¹³C NMR Spectrum of 3-(trifluoromethyl)quinoline (4h)



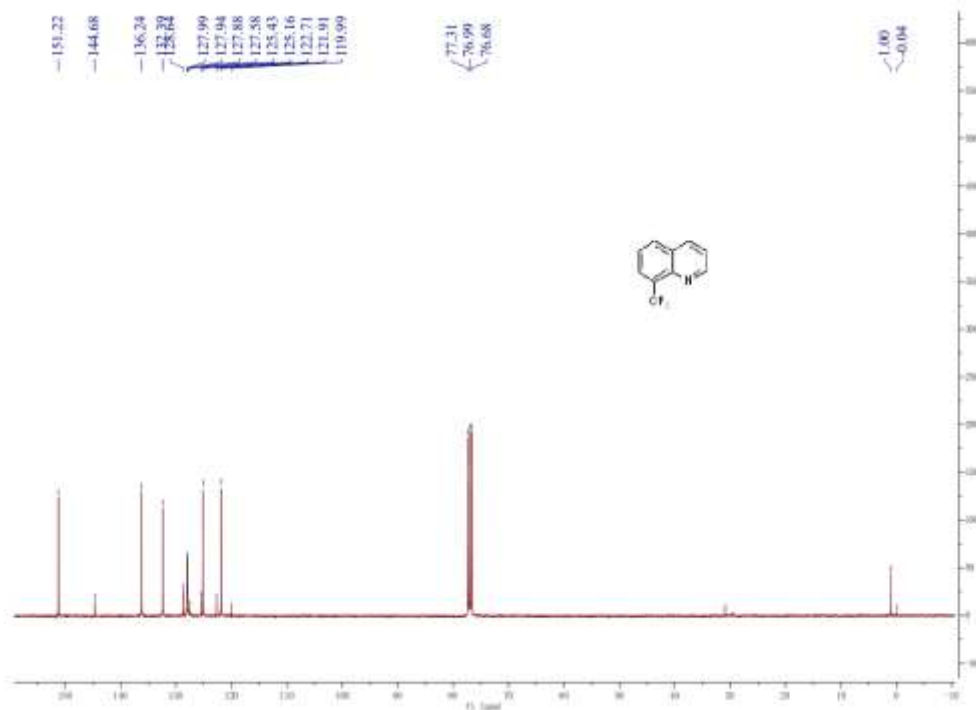
¹H NMR Spectrum of 8-(trifluoromethyl)quinoline (4i)



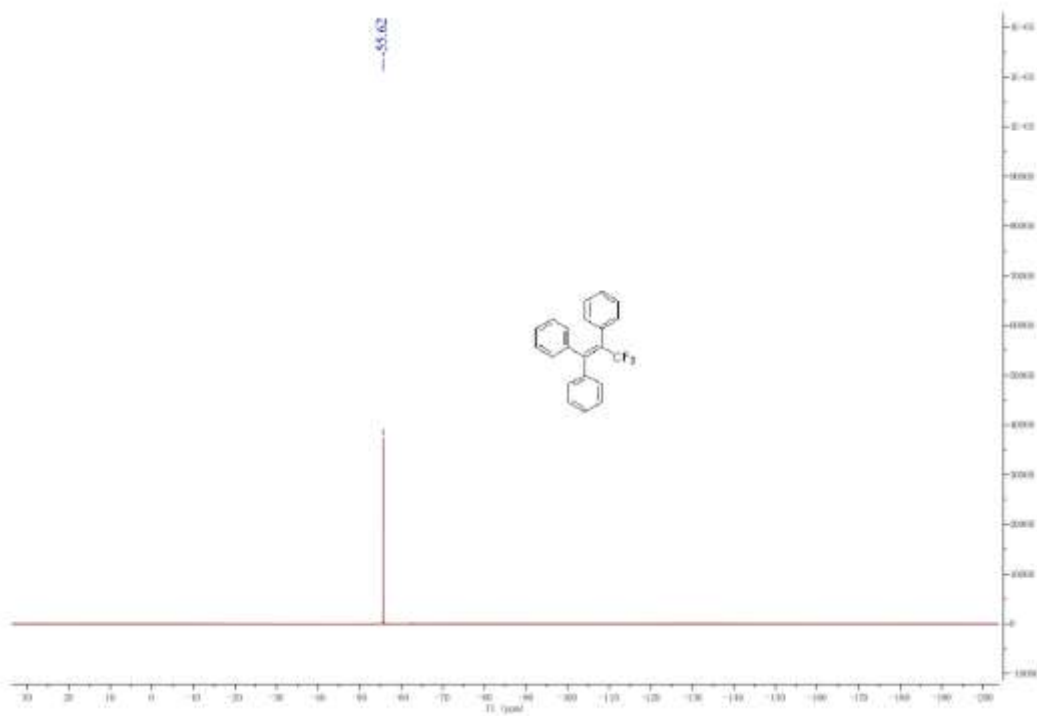
¹⁹F NMR Spectrum of 8-(trifluoromethyl)quinoline (4i)



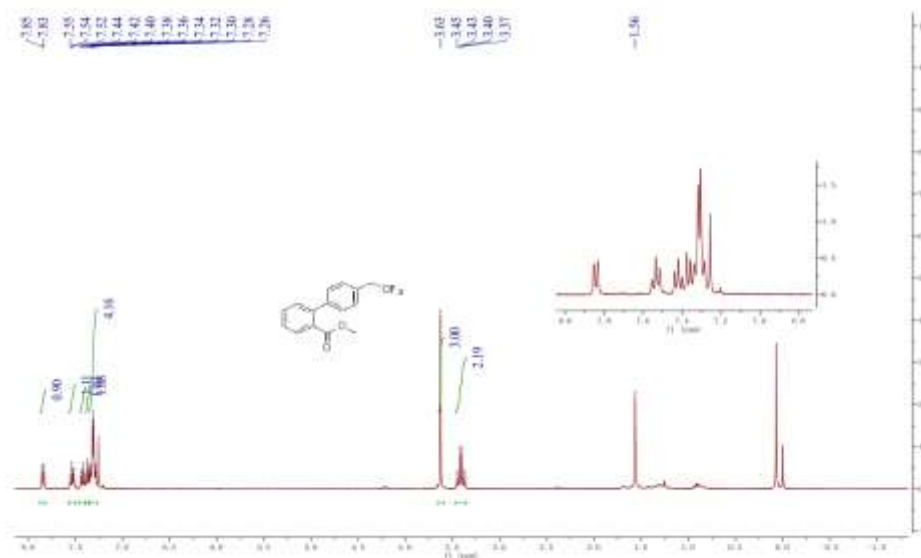
¹³C NMR Spectrum of 8-(trifluoromethyl)quinoline (4i)



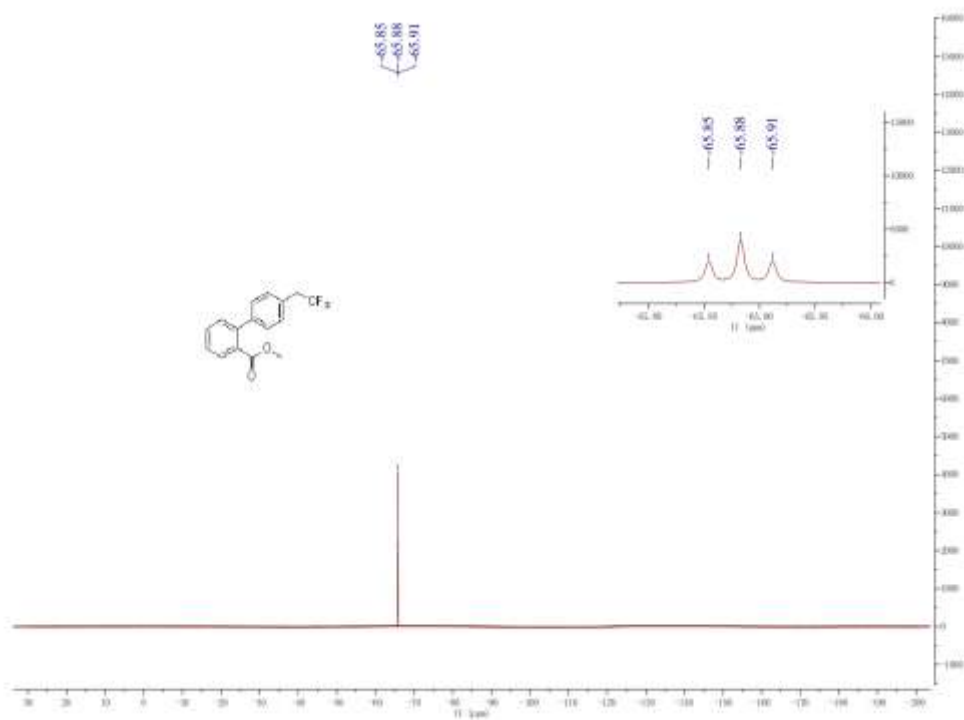
¹⁹F NMR Spectrum of (3,3,3-Trifluoroprop-1-ene-1,1,2-triyl)tribenzene (4j)



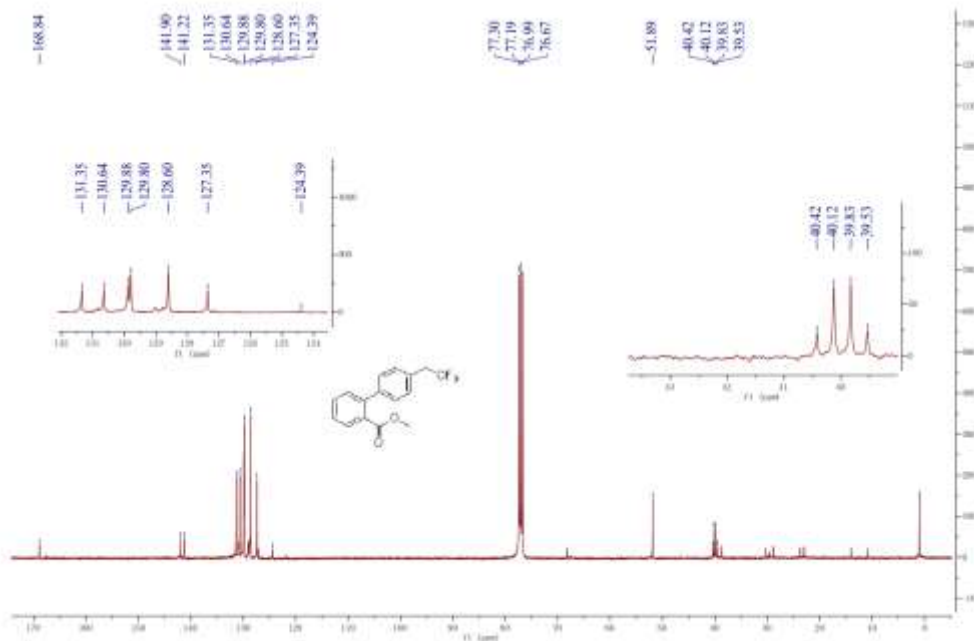
¹H NMR Spectrum of methyl4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carboxylate (4k)



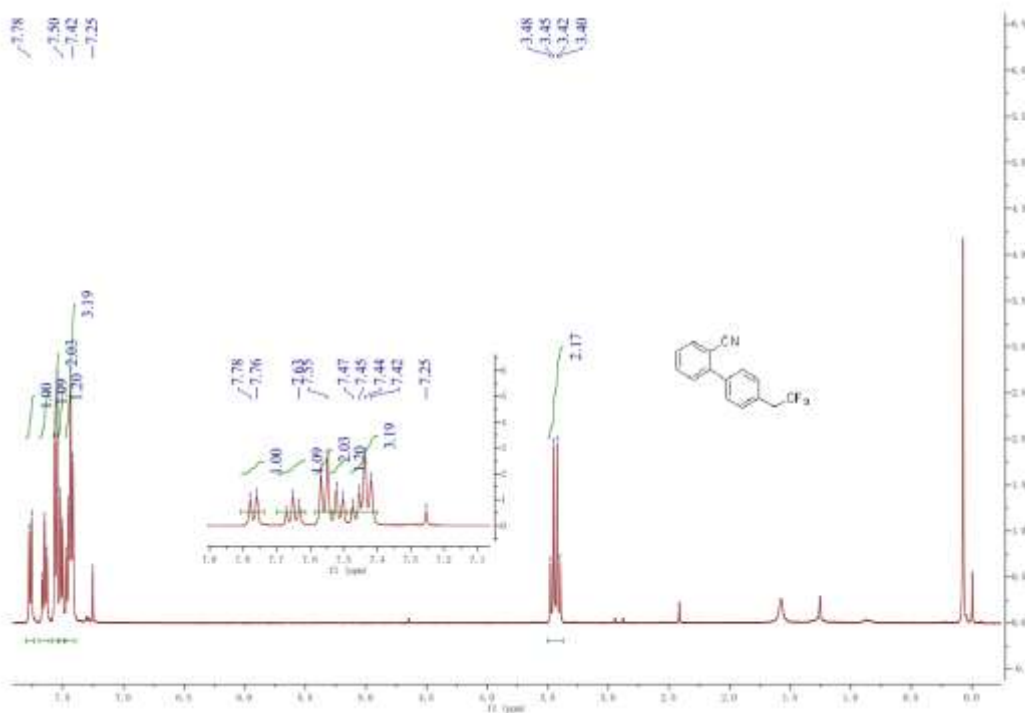
¹⁹F NMR Spectrum of methyl4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carboxylate (4k)



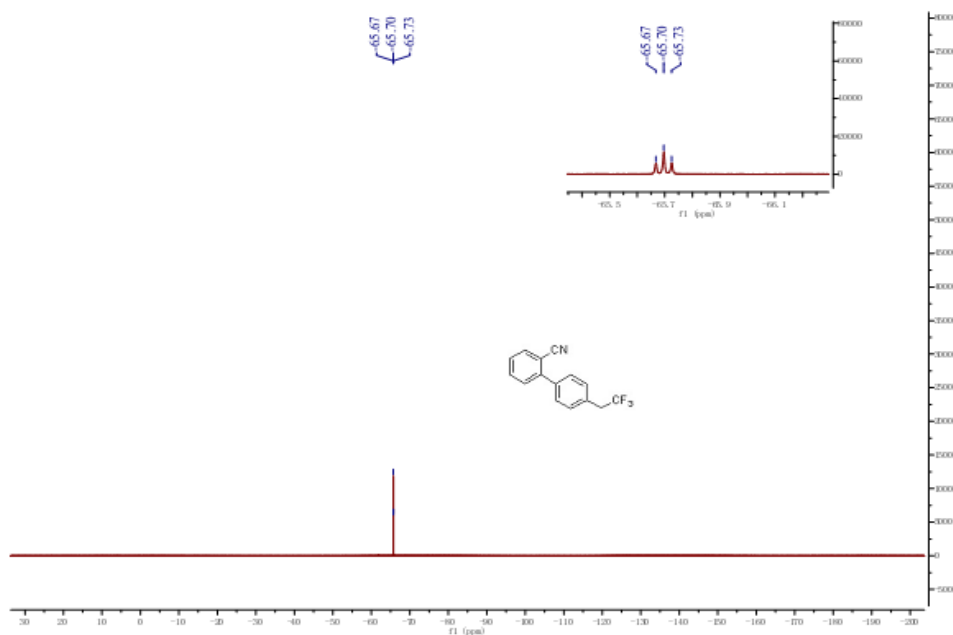
¹³C NMR Spectrum of methyl 4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carboxylate (4k)



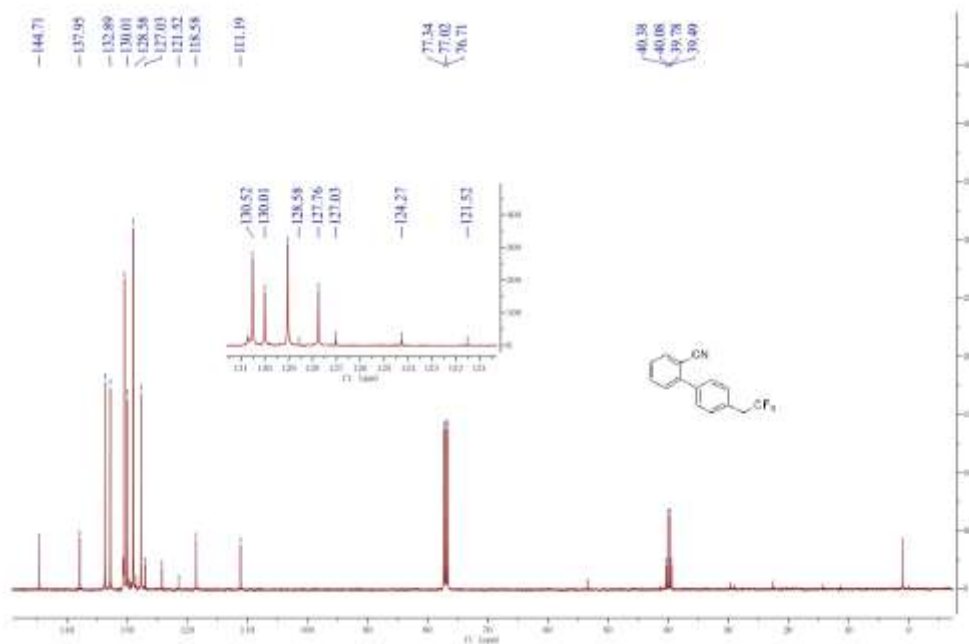
¹H NMR Spectrum of 4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carbonitrile (4l)



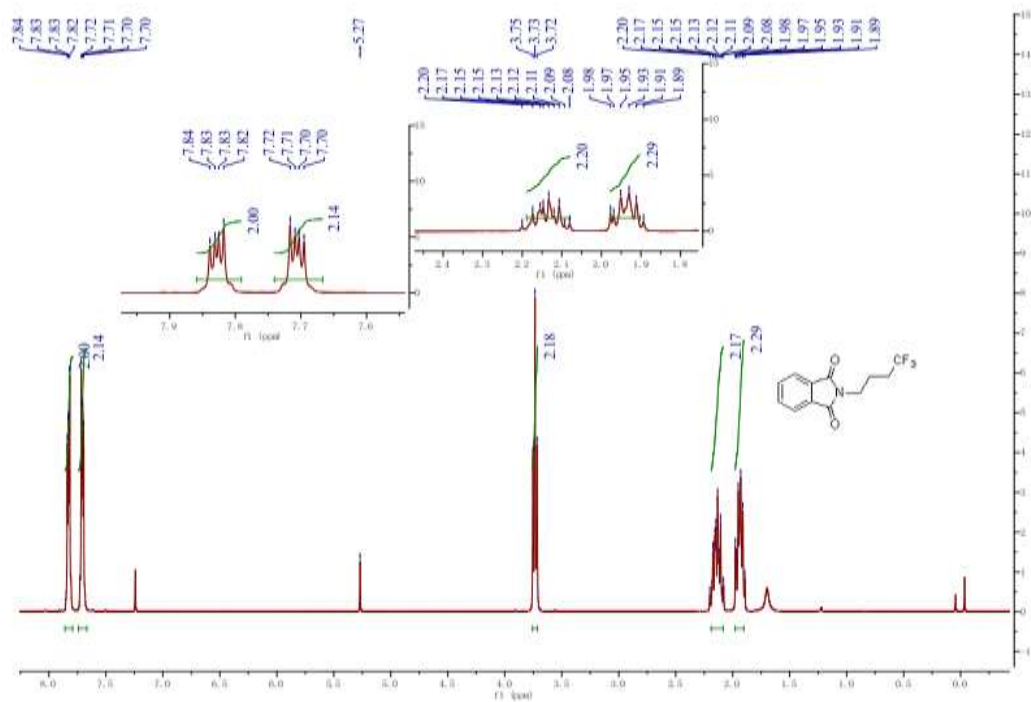
¹⁹F NMR Spectrum of 4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carbonitrile (41)



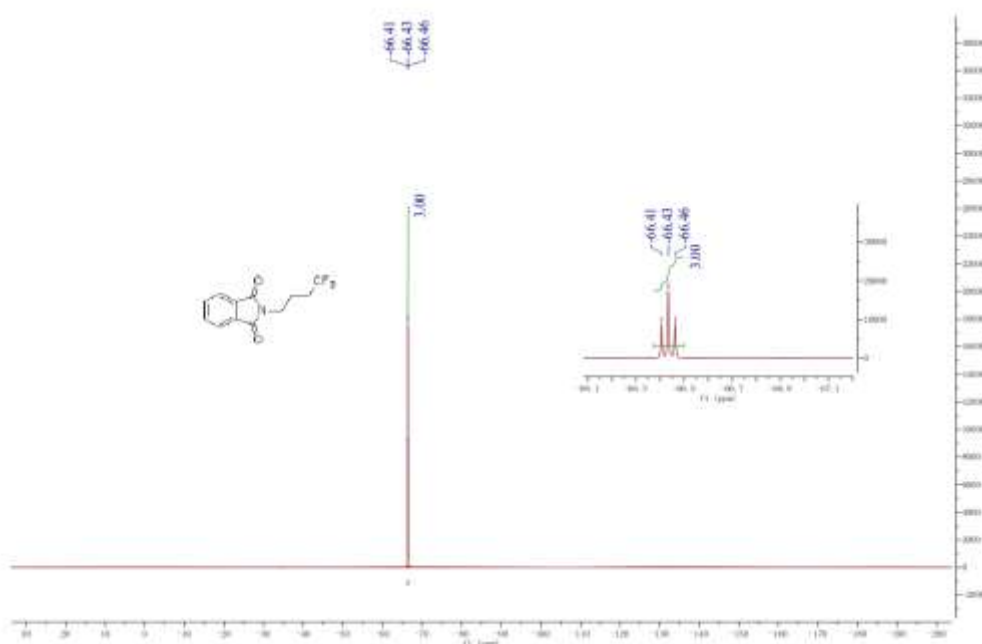
¹³C NMR Spectrum of 4'-(2,2,2-trifluoroethyl)-[1,1'-biphenyl]-2-carbonitrile (41)



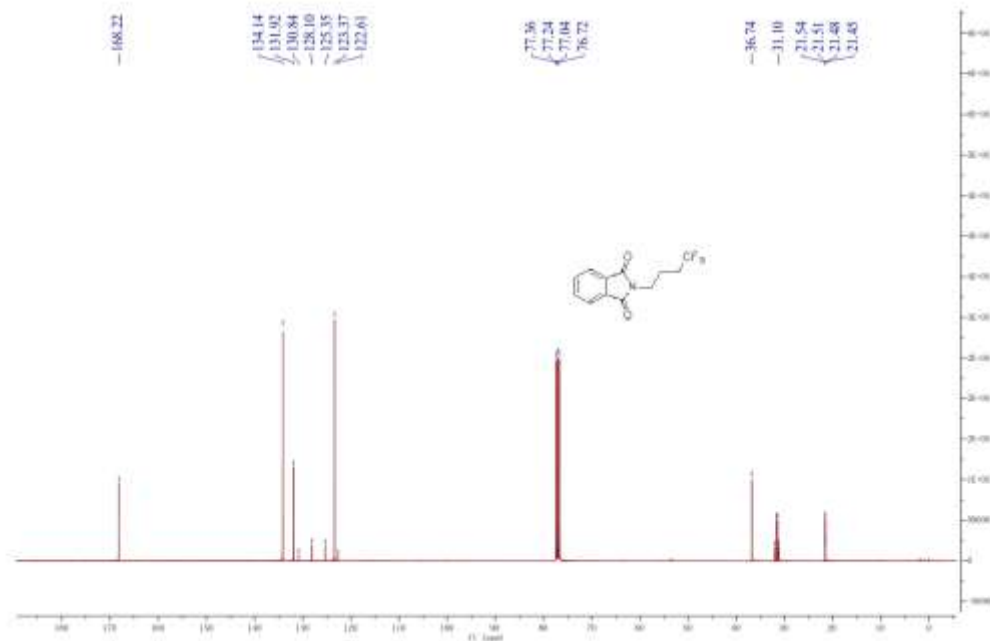
¹H NMR Spectrum of 2-(4,4,4-trifluorobutyl)isoindoline-1,3-dione (4m)



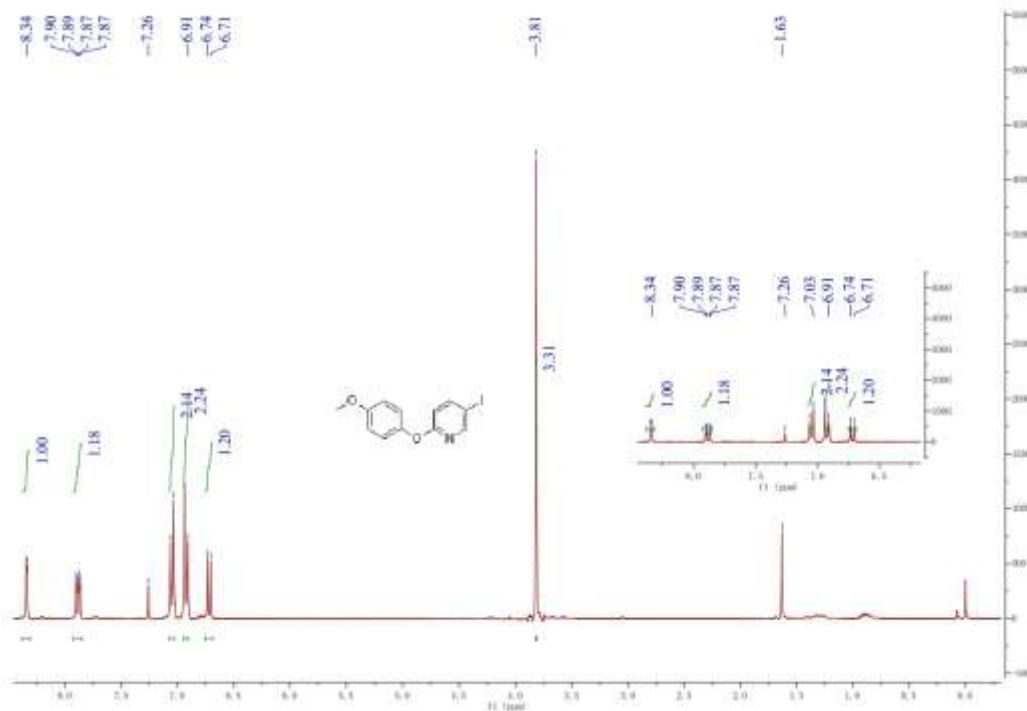
¹⁹F NMR Spectrum of 2-(4,4,4-trifluorobutyl)isoindoline-1,3-dione (4m)



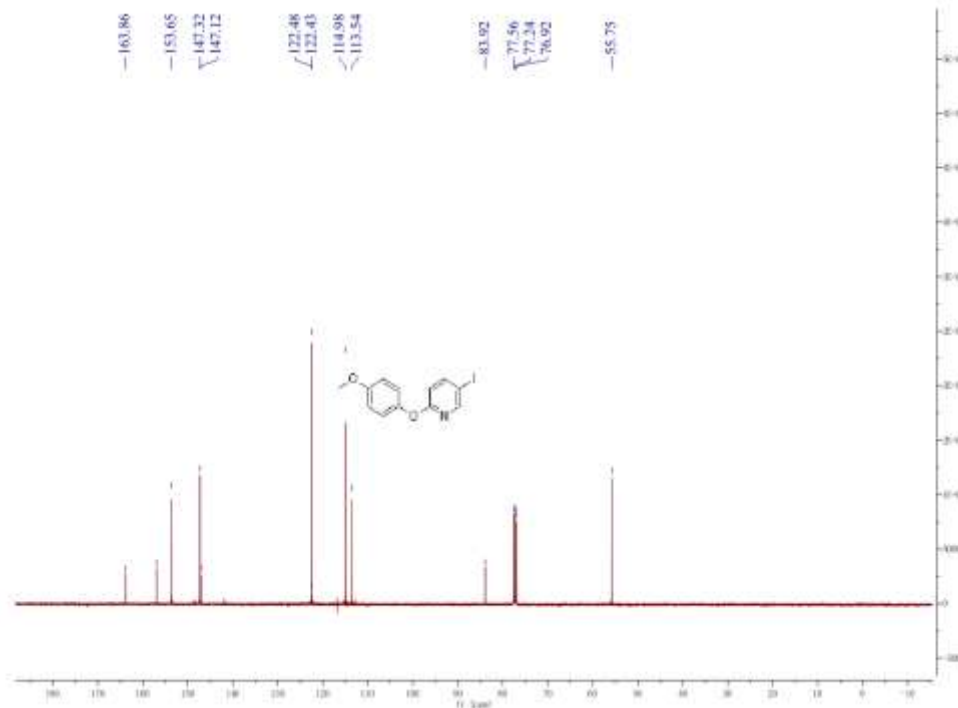
¹³C NMR Spectrum of 2-(4,4,4-trifluorobutyl)isoindoline-1,3-dione (4m)



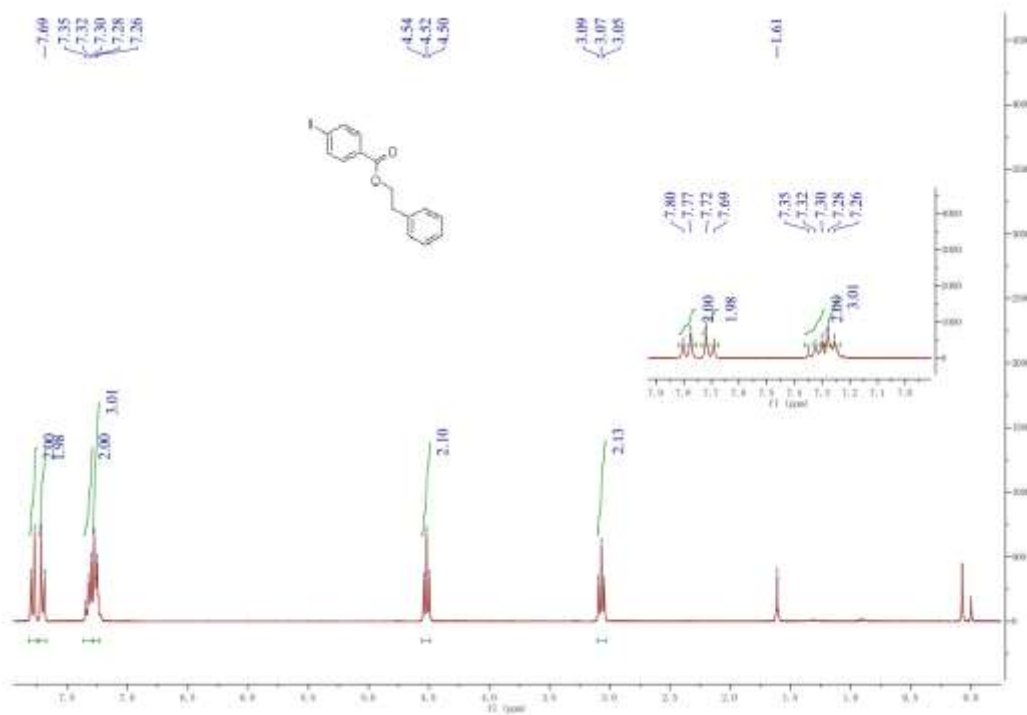
¹H NMR Spectrum of 5-iodo-2-(4-methoxyphenoxy) pyridine (1b)



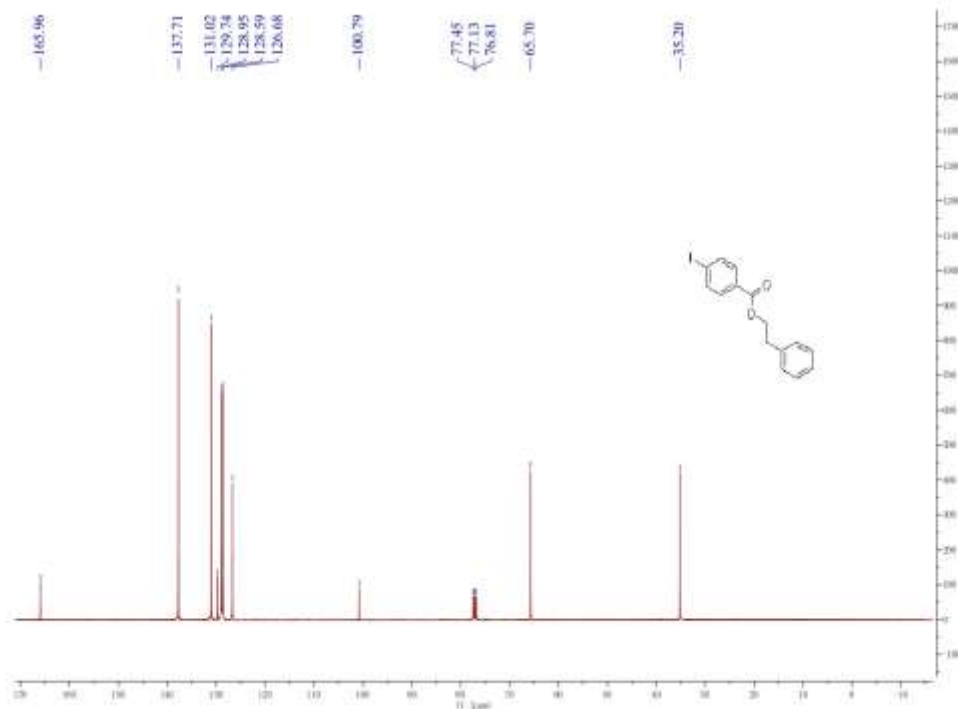
¹³C NMR Spectrum of 5-iodo-2-(4-methoxyphenoxy)pyridine (1b)



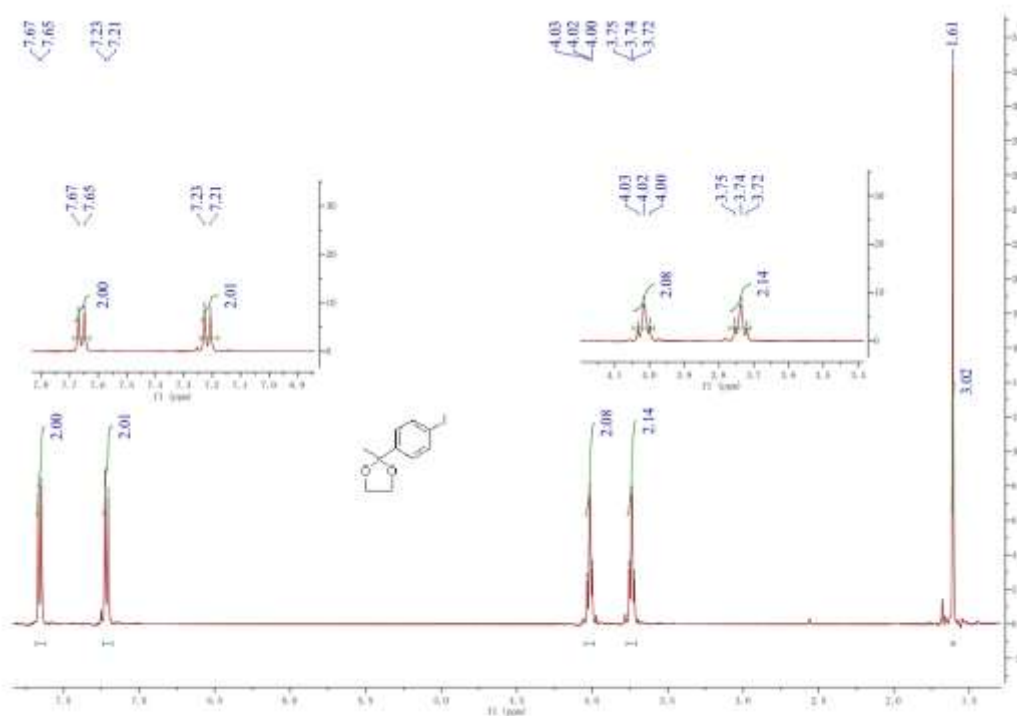
¹H NMR Spectrum of phenethyl 4-iodobenzoate (1c)



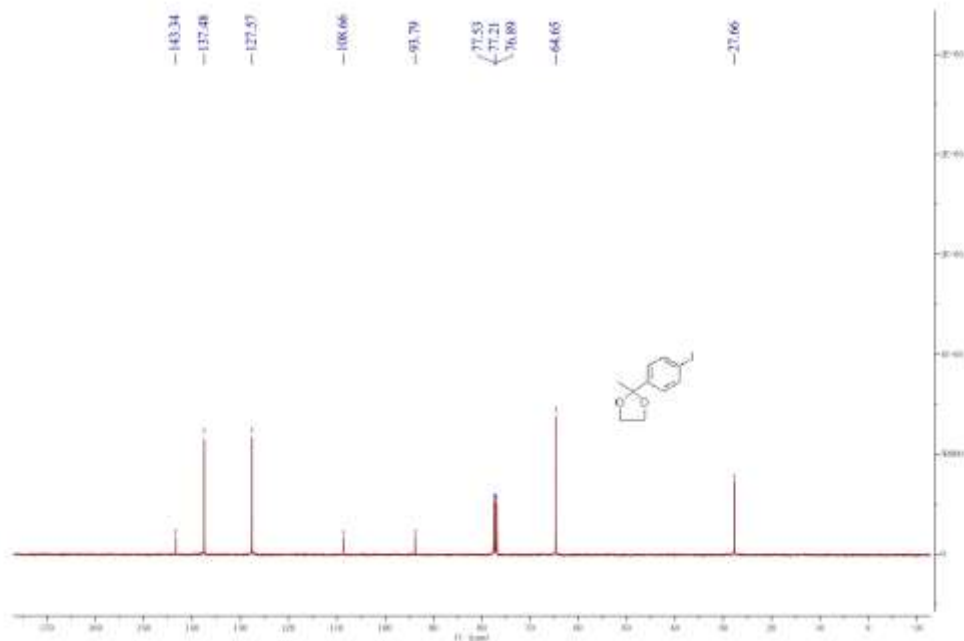
^{13}C NMR Spectrum of phenethyl 4-iodobenzoate (1c)



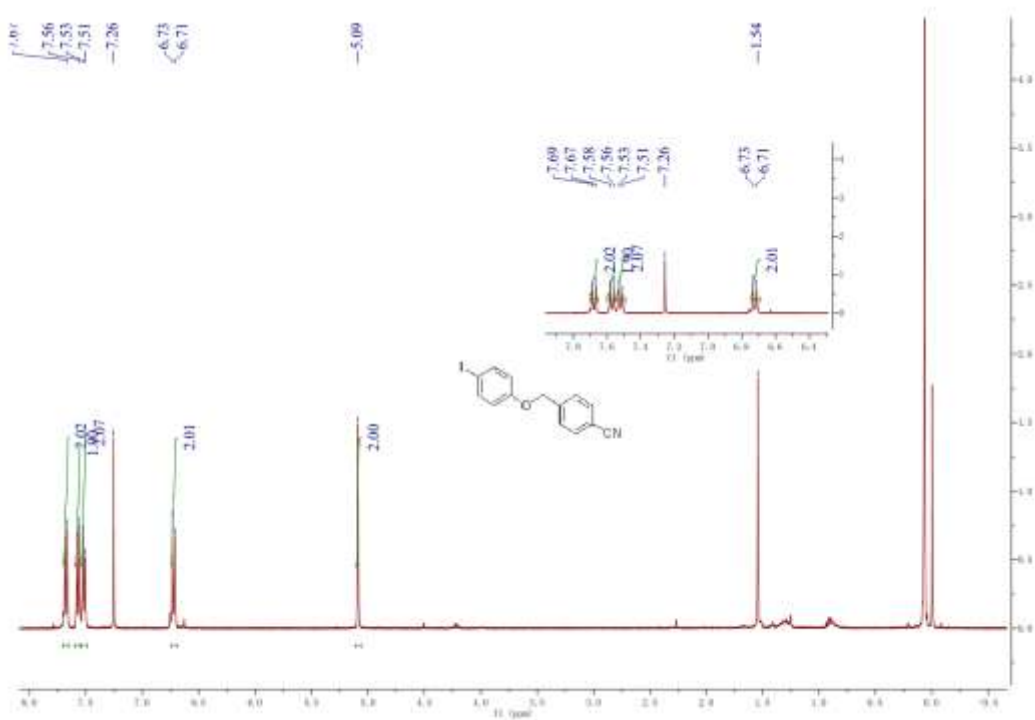
^1H NMR Spectrum of phenethyl 2-(4-iodophenyl)-2-methyl-1,3-dioxolane (1d)



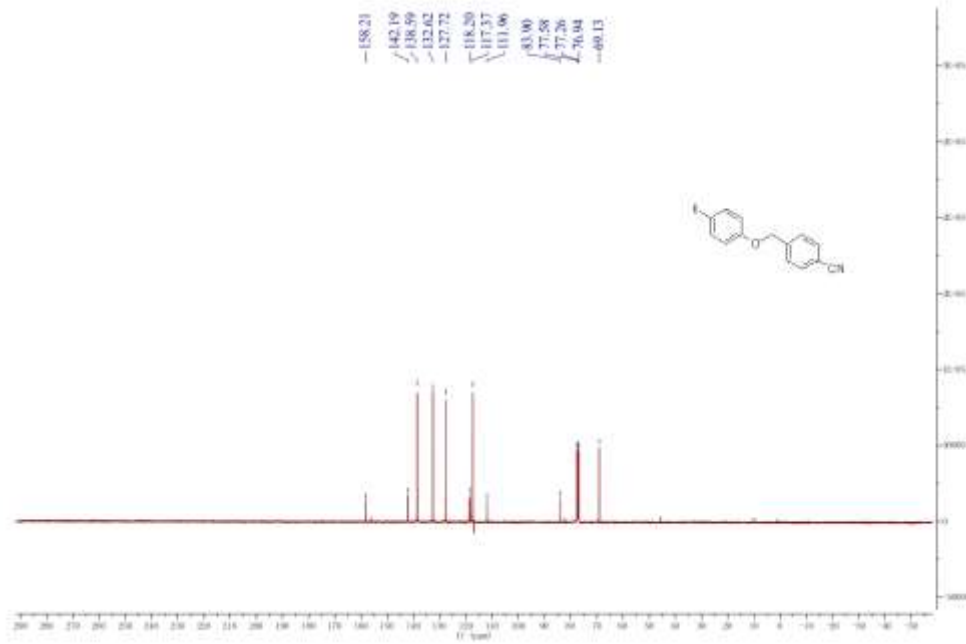
¹³C NMR Spectrum of phenethyl 2-(4-iodophenyl)-2-methyl-1,3-dioxolane (1d)



¹H NMR Spectrum of phenethyl 4-((4-iodophenoxy)methyl)benzotrile (1e)



¹³C NMR Spectrum of phenethyl 4-((4-iodophenoxy)methyl)benzonitrile (1e)



Single crystals of bimetallic copper(II) species **8**

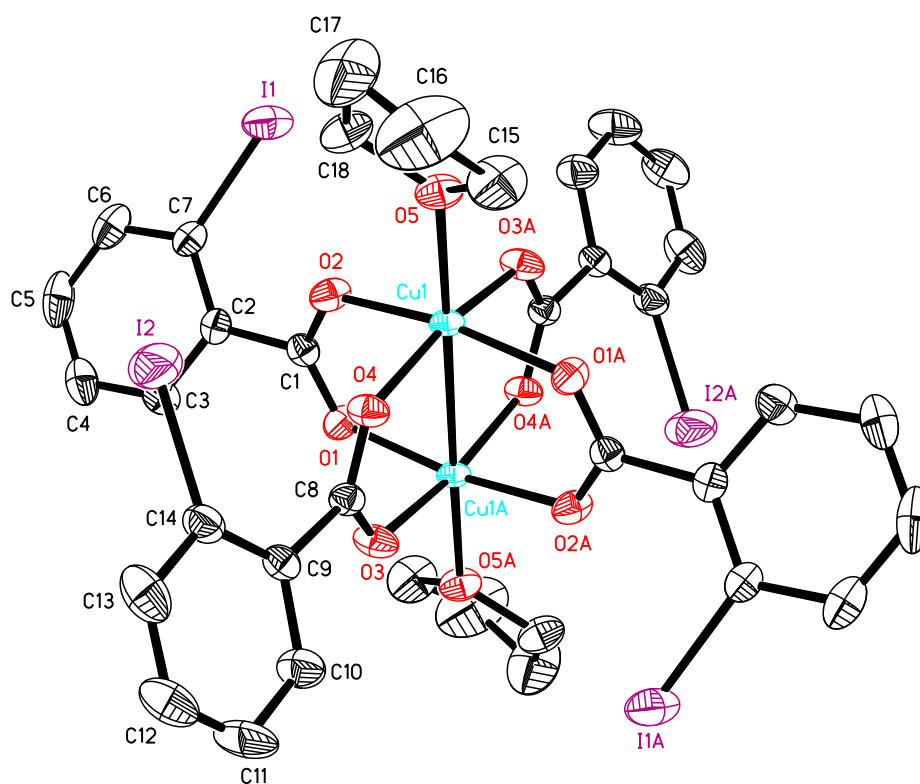


Table 1. Crystal data and structure refinement for cd214505.

Identification code	cd214505	
Empirical formula	C ₃₆ H ₃₂ Cu ₂ I ₄ O ₁₀	
Formula weight	1259.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6433(12) Å	α = 104.470(3) °
	b = 11.2513(15) Å	β = 91.909(3) °
	c = 21.811(3) Å	γ = 93.409(3) °
Volume	2047.7(5) Å ³	
Z	2	
Density (calculated)	2.042 Mg/m ³	
Absorption coefficient	4.106 mm ⁻¹	
F(000)	1196	
Crystal size	0.211 x 0.134 x 0.112 mm ³	

Theta range for data collection	0.965 to 26.000 °
Index ranges	-10<=h<=10, -9<=k<=13, -26<=l<=26
Reflections collected	12508
Independent reflections	8017 [R(int) = 0.0295]
Completeness to theta = 25.242 °	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.3852
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8017 / 12 / 487
Goodness-of-fit on F ²	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1552
R indices (all data)	R1 = 0.0693, wR2 = 0.1691
Extinction coefficient	n/a
Largest diff. peak and hole	1.083 and -1.463 e.Å ⁻³

Table 2. Bond lengths [Å] and angles [°] for cd214505.

Cu(1)-O(2)	1.951(4)
Cu(1)-O(1)#1	1.951(4)
Cu(1)-O(3)#1	1.952(4)
Cu(1)-O(4)	1.968(4)
Cu(1)-O(5)	2.172(4)
Cu(1)-Cu(1)#1	2.6171(12)
Cu(2)-O(9)#2	1.958(4)
Cu(2)-O(8)	1.961(4)
Cu(2)-O(7)#2	1.965(4)
Cu(2)-O(6)	1.966(4)
Cu(2)-O(10)	2.138(4)
Cu(2)-Cu(2)#2	2.6129(12)
I(1)-C(7)	2.077(7)
I(3)-C(25)	2.075(6)
I(2)-C(14)	2.070(7)
I(4)-C(32)	2.123(7)
I(2')-C(14)	2.139(8)
I(4')-C(32)	2.130(7)
O(1)-C(1)	1.242(7)
O(1)-Cu(1)#1	1.951(4)
O(2)-C(1)	1.262(7)
O(3)-C(8)	1.262(7)

O(3)-Cu(1)#1	1.952(4)
O(4)-C(8)	1.247(7)
O(5)-C(18)	1.435(9)
O(5)-C(15)	1.440(9)
O(6)-C(19)	1.236(7)
O(7)-C(19)	1.240(7)
O(7)-Cu(2)#2	1.965(4)
O(8)-C(26)	1.247(7)
O(9)-C(26)	1.243(7)
O(9)-Cu(2)#2	1.958(4)
O(10)-C(36)	1.405(10)
O(10)-C(33)	1.427(9)
C(1)-C(2)	1.514(8)
C(2)-C(3)	1.367(9)
C(2)-C(7)	1.397(9)
C(3)-C(4)	1.382(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.341(13)
C(4)-H(4)	0.9300
C(5)-C(6)	1.393(13)
C(5)-H(5)	0.9300
C(6)-C(7)	1.394(10)
C(6)-H(6)	0.9300
C(8)-C(9)	1.501(8)
C(9)-C(14)	1.377(9)
C(9)-C(10)	1.384(9)
C(10)-C(11)	1.374(10)
C(10)-H(10)	0.9300
C(11)-C(12)	1.352(13)
C(11)-H(11)	0.9300
C(12)-C(13)	1.345(13)
C(12)-H(12)	0.9300
C(13)-C(14)	1.401(10)
C(13)-H(13)	0.9300
C(15)-C(16)	1.495(16)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.457(18)

C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18)	1.478(12)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.513(7)
C(20)-C(25)	1.383(8)
C(20)-C(21)	1.402(9)
C(21)-C(22)	1.374(10)
C(21)-H(21)	0.9300
C(22)-C(23)	1.366(12)
C(22)-H(22)	0.9300
C(23)-C(24)	1.360(12)
C(23)-H(23)	0.9300
C(24)-C(25)	1.403(10)
C(24)-H(24)	0.9300
C(26)-C(27)	1.512(8)
C(27)-C(28)	1.364(9)
C(27)-C(32)	1.380(9)
C(28)-C(29)	1.366(10)
C(28)-H(28)	0.9300
C(29)-C(30)	1.392(11)
C(29)-H(29)	0.9300
C(30)-C(31)	1.350(11)
C(30)-H(30)	0.9300
C(31)-C(32)	1.388(10)
C(31)-H(31)	0.9300
C(33)-C(34)	1.470(11)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-C(35)	1.478(13)
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(36)	1.467(14)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700

C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
O(2)-Cu(1)-O(1)#1	168.89(17)
O(2)-Cu(1)-O(3)#1	90.4(2)
O(1)#1-Cu(1)-O(3)#1	89.2(2)
O(2)-Cu(1)-O(4)	89.41(19)
O(1)#1-Cu(1)-O(4)	88.86(19)
O(3)#1-Cu(1)-O(4)	168.72(17)
O(2)-Cu(1)-O(5)	96.34(18)
O(1)#1-Cu(1)-O(5)	94.72(18)
O(3)#1-Cu(1)-O(5)	97.46(17)
O(4)-Cu(1)-O(5)	93.77(17)
O(2)-Cu(1)-Cu(1)#1	85.14(12)
O(1)#1-Cu(1)-Cu(1)#1	83.76(12)
O(3)#1-Cu(1)-Cu(1)#1	85.88(12)
O(4)-Cu(1)-Cu(1)#1	82.87(12)
O(5)-Cu(1)-Cu(1)#1	176.32(12)
O(9)#2-Cu(2)-O(8)	168.14(17)
O(9)#2-Cu(2)-O(7)#2	88.2(2)
O(8)-Cu(2)-O(7)#2	89.31(19)
O(9)#2-Cu(2)-O(6)	90.5(2)
O(8)-Cu(2)-O(6)	89.58(19)
O(7)#2-Cu(2)-O(6)	168.47(16)
O(9)#2-Cu(2)-O(10)	95.93(19)
O(8)-Cu(2)-O(10)	95.85(19)
O(7)#2-Cu(2)-O(10)	95.46(17)
O(6)-Cu(2)-O(10)	96.07(18)
O(9)#2-Cu(2)-Cu(2)#2	83.64(12)
O(8)-Cu(2)-Cu(2)#2	84.55(12)
O(7)#2-Cu(2)-Cu(2)#2	83.78(11)
O(6)-Cu(2)-Cu(2)#2	84.69(11)
O(10)-Cu(2)-Cu(2)#2	179.14(13)
C(1)-O(1)-Cu(1)#1	123.1(4)
C(1)-O(2)-Cu(1)	121.0(4)
C(8)-O(3)-Cu(1)#1	121.2(4)
C(8)-O(4)-Cu(1)	124.3(4)
C(18)-O(5)-C(15)	108.3(6)

C(18)-O(5)-Cu(1)	122.1(4)
C(15)-O(5)-Cu(1)	121.8(5)
C(19)-O(6)-Cu(2)	121.5(4)
C(19)-O(7)-Cu(2)#2	122.6(4)
C(26)-O(8)-Cu(2)	122.7(4)
C(26)-O(9)-Cu(2)#2	124.0(4)
C(36)-O(10)-C(33)	107.6(6)
C(36)-O(10)-Cu(2)	126.6(5)
C(33)-O(10)-Cu(2)	124.3(4)
O(1)-C(1)-O(2)	126.9(6)
O(1)-C(1)-C(2)	115.4(5)
O(2)-C(1)-C(2)	117.6(5)
C(3)-C(2)-C(7)	118.8(6)
C(3)-C(2)-C(1)	116.9(6)
C(7)-C(2)-C(1)	124.3(5)
C(2)-C(3)-C(4)	121.3(7)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	120.1(7)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	121.0(7)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(7)	119.0(8)
C(5)-C(6)-H(6)	120.5
C(7)-C(6)-H(6)	120.5
C(6)-C(7)-C(2)	119.8(6)
C(6)-C(7)-I(1)	115.9(5)
C(2)-C(7)-I(1)	124.1(5)
O(4)-C(8)-O(3)	125.7(5)
O(4)-C(8)-C(9)	117.9(5)
O(3)-C(8)-C(9)	116.3(5)
C(14)-C(9)-C(10)	117.7(6)
C(14)-C(9)-C(8)	124.7(5)
C(10)-C(9)-C(8)	117.5(6)
C(11)-C(10)-C(9)	121.2(8)
C(11)-C(10)-H(10)	119.4

C(9)-C(10)-H(10)	119.4
C(12)-C(11)-C(10)	120.3(8)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(13)-C(12)-C(11)	120.0(7)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.7(8)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-H(13)	119.7
C(9)-C(14)-C(13)	119.9(7)
C(9)-C(14)-I(2)	126.5(4)
C(13)-C(14)-I(2)	113.3(6)
C(9)-C(14)-I(2')	120.3(5)
C(13)-C(14)-I(2')	118.4(6)
O(5)-C(15)-C(16)	105.8(9)
O(5)-C(15)-H(15A)	110.6
C(16)-C(15)-H(15A)	110.6
O(5)-C(15)-H(15B)	110.6
C(16)-C(15)-H(15B)	110.6
H(15A)-C(15)-H(15B)	108.7
C(17)-C(16)-C(15)	104.8(10)
C(17)-C(16)-H(16A)	110.8
C(15)-C(16)-H(16A)	110.8
C(17)-C(16)-H(16B)	110.8
C(15)-C(16)-H(16B)	110.8
H(16A)-C(16)-H(16B)	108.9
C(16)-C(17)-C(18)	104.5(9)
C(16)-C(17)-H(17A)	110.9
C(18)-C(17)-H(17A)	110.9
C(16)-C(17)-H(17B)	110.9
C(18)-C(17)-H(17B)	110.9
H(17A)-C(17)-H(17B)	108.9
O(5)-C(18)-C(17)	107.6(7)
O(5)-C(18)-H(18A)	110.2
C(17)-C(18)-H(18A)	110.2
O(5)-C(18)-H(18B)	110.2
C(17)-C(18)-H(18B)	110.2

H(18A)-C(18)-H(18B)	108.5
O(6)-C(19)-O(7)	127.2(5)
O(6)-C(19)-C(20)	117.6(5)
O(7)-C(19)-C(20)	115.1(5)
C(25)-C(20)-C(21)	118.7(5)
C(25)-C(20)-C(19)	124.3(5)
C(21)-C(20)-C(19)	116.9(5)
C(22)-C(21)-C(20)	120.4(6)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(23)-C(22)-C(21)	119.8(7)
C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(24)-C(23)-C(22)	121.5(7)
C(24)-C(23)-H(23)	119.2
C(22)-C(23)-H(23)	119.2
C(23)-C(24)-C(25)	119.4(7)
C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3
C(20)-C(25)-C(24)	120.1(6)
C(20)-C(25)-I(3)	121.6(5)
C(24)-C(25)-I(3)	118.3(5)
O(9)-C(26)-O(8)	125.1(5)
O(9)-C(26)-C(27)	116.7(5)
O(8)-C(26)-C(27)	118.2(5)
C(28)-C(27)-C(32)	117.4(6)
C(28)-C(27)-C(26)	116.9(5)
C(32)-C(27)-C(26)	125.7(5)
C(27)-C(28)-C(29)	123.2(7)
C(27)-C(28)-H(28)	118.4
C(29)-C(28)-H(28)	118.4
C(28)-C(29)-C(30)	118.8(7)
C(28)-C(29)-H(29)	120.6
C(30)-C(29)-H(29)	120.6
C(31)-C(30)-C(29)	118.7(6)
C(31)-C(30)-H(30)	120.7
C(29)-C(30)-H(30)	120.7
C(30)-C(31)-C(32)	121.7(7)

C(30)-C(31)-H(31)	119.1
C(32)-C(31)-H(31)	119.1
C(27)-C(32)-C(31)	119.8(7)
C(27)-C(32)-I(4)	124.9(5)
C(31)-C(32)-I(4)	114.3(6)
C(27)-C(32)-I(4')	123.1(5)
C(31)-C(32)-I(4')	113.4(6)
O(10)-C(33)-C(34)	107.2(7)
O(10)-C(33)-H(33A)	110.3
C(34)-C(33)-H(33A)	110.3
O(10)-C(33)-H(33B)	110.3
C(34)-C(33)-H(33B)	110.3
H(33A)-C(33)-H(33B)	108.5
C(33)-C(34)-C(35)	106.2(7)
C(33)-C(34)-H(34A)	110.5
C(35)-C(34)-H(34A)	110.5
C(33)-C(34)-H(34B)	110.5
C(35)-C(34)-H(34B)	110.5
H(34A)-C(34)-H(34B)	108.7
C(36)-C(35)-C(34)	102.8(8)
C(36)-C(35)-H(35A)	111.2
C(34)-C(35)-H(35A)	111.2
C(36)-C(35)-H(35B)	111.2
C(34)-C(35)-H(35B)	111.2
H(35A)-C(35)-H(35B)	109.1
O(10)-C(36)-C(35)	107.3(8)
O(10)-C(36)-H(36A)	110.3
C(35)-C(36)-H(36A)	110.3
O(10)-C(36)-H(36B)	110.3
C(35)-C(36)-H(36B)	110.3
H(36A)-C(36)-H(36B)	108.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 -x,-y+1,-z+1

Table 3. Torsion angles [°] for cd214505.

Cu(1)#1-O(1)-C(1)-O(2)	1.6(8)
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Cu(1)#1-O(1)-C(1)-C(2)	-176.0(3)
Cu(1)-O(2)-C(1)-O(1)	-1.0(8)
Cu(1)-O(2)-C(1)-C(2)	176.5(4)
O(1)-C(1)-C(2)-C(3)	36.1(7)
O(2)-C(1)-C(2)-C(3)	-141.7(6)
O(1)-C(1)-C(2)-C(7)	-145.5(6)
O(2)-C(1)-C(2)-C(7)	36.7(8)
C(7)-C(2)-C(3)-C(4)	-1.6(10)
C(1)-C(2)-C(3)-C(4)	176.9(6)
C(2)-C(3)-C(4)-C(5)	2.9(11)
C(3)-C(4)-C(5)-C(6)	-0.8(12)
C(4)-C(5)-C(6)-C(7)	-2.5(12)
C(5)-C(6)-C(7)-C(2)	3.7(10)
C(5)-C(6)-C(7)-I(1)	179.0(6)
C(3)-C(2)-C(7)-C(6)	-1.7(9)
C(1)-C(2)-C(7)-C(6)	179.9(6)
C(3)-C(2)-C(7)-I(1)	-176.6(5)
C(1)-C(2)-C(7)-I(1)	5.0(8)
Cu(1)-O(4)-C(8)-O(3)	3.0(9)
Cu(1)-O(4)-C(8)-C(9)	-179.7(4)
Cu(1)#1-O(3)-C(8)-O(4)	-1.8(9)
Cu(1)#1-O(3)-C(8)-C(9)	-179.2(4)
O(4)-C(8)-C(9)-C(14)	29.9(9)
O(3)-C(8)-C(9)-C(14)	-152.5(6)
O(4)-C(8)-C(9)-C(10)	-145.9(6)
O(3)-C(8)-C(9)-C(10)	31.8(8)
C(14)-C(9)-C(10)-C(11)	-0.3(11)
C(8)-C(9)-C(10)-C(11)	175.7(8)
C(9)-C(10)-C(11)-C(12)	-2.4(15)
C(10)-C(11)-C(12)-C(13)	4.1(16)
C(11)-C(12)-C(13)-C(14)	-3.1(15)
C(10)-C(9)-C(14)-C(13)	1.4(10)
C(8)-C(9)-C(14)-C(13)	-174.4(6)
C(10)-C(9)-C(14)-I(2)	175.8(5)
C(8)-C(9)-C(14)-I(2)	0.1(10)
C(10)-C(9)-C(14)-I(2')	-165.2(5)
C(8)-C(9)-C(14)-I(2')	19.0(9)
C(12)-C(13)-C(14)-C(9)	0.3(12)

C(12)-C(13)-C(14)-I(2)	-174.8(7)
C(12)-C(13)-C(14)-I(2')	167.2(7)
C(18)-O(5)-C(15)-C(16)	13.4(11)
Cu(1)-O(5)-C(15)-C(16)	-136.2(8)
O(5)-C(15)-C(16)-C(17)	-27.2(14)
C(15)-C(16)-C(17)-C(18)	30.0(15)
C(15)-O(5)-C(18)-C(17)	5.3(10)
Cu(1)-O(5)-C(18)-C(17)	154.9(7)
C(16)-C(17)-C(18)-O(5)	-22.4(14)
Cu(2)-O(6)-C(19)-O(7)	5.0(8)
Cu(2)-O(6)-C(19)-C(20)	-176.6(4)
Cu(2)#2-O(7)-C(19)-O(6)	-5.1(8)
Cu(2)#2-O(7)-C(19)-C(20)	176.4(4)
O(6)-C(19)-C(20)-C(25)	55.9(8)
O(7)-C(19)-C(20)-C(25)	-125.5(6)
O(6)-C(19)-C(20)-C(21)	-125.8(6)
O(7)-C(19)-C(20)-C(21)	52.9(7)
C(25)-C(20)-C(21)-C(22)	-1.3(10)
C(19)-C(20)-C(21)-C(22)	-179.7(7)
C(20)-C(21)-C(22)-C(23)	1.9(13)
C(21)-C(22)-C(23)-C(24)	-2.0(15)
C(22)-C(23)-C(24)-C(25)	1.5(14)
C(21)-C(20)-C(25)-C(24)	0.8(10)
C(19)-C(20)-C(25)-C(24)	179.1(6)
C(21)-C(20)-C(25)-I(3)	-176.2(5)
C(19)-C(20)-C(25)-I(3)	2.1(8)
C(23)-C(24)-C(25)-C(20)	-0.9(12)
C(23)-C(24)-C(25)-I(3)	176.2(7)
Cu(2)#2-O(9)-C(26)-O(8)	-0.3(9)
Cu(2)#2-O(9)-C(26)-C(27)	178.8(4)
Cu(2)-O(8)-C(26)-O(9)	-1.4(8)
Cu(2)-O(8)-C(26)-C(27)	179.5(4)
O(9)-C(26)-C(27)-C(28)	1.6(8)
O(8)-C(26)-C(27)-C(28)	-179.2(6)
O(9)-C(26)-C(27)-C(32)	-178.5(7)
O(8)-C(26)-C(27)-C(32)	0.7(10)
C(32)-C(27)-C(28)-C(29)	3.7(11)
C(26)-C(27)-C(28)-C(29)	-176.4(7)

C(27)-C(28)-C(29)-C(30)	-2.3(12)
C(28)-C(29)-C(30)-C(31)	2.4(14)
C(29)-C(30)-C(31)-C(32)	-4.2(15)
C(28)-C(27)-C(32)-C(31)	-5.2(12)
C(26)-C(27)-C(32)-C(31)	174.9(8)
C(28)-C(27)-C(32)-I(4)	163.2(6)
C(26)-C(27)-C(32)-I(4)	-16.7(11)
C(28)-C(27)-C(32)-I(4')	-162.2(6)
C(26)-C(27)-C(32)-I(4')	17.9(11)
C(30)-C(31)-C(32)-C(27)	5.7(15)
C(30)-C(31)-C(32)-I(4)	-163.9(8)
C(30)-C(31)-C(32)-I(4')	164.7(8)
C(36)-O(10)-C(33)-C(34)	10.2(13)
Cu(2)-O(10)-C(33)-C(34)	-156.7(7)
O(10)-C(33)-C(34)-C(35)	8.9(12)
C(33)-C(34)-C(35)-C(36)	-23.5(13)
C(33)-O(10)-C(36)-C(35)	-25.8(14)
Cu(2)-O(10)-C(36)-C(35)	140.7(7)
C(34)-C(35)-C(36)-O(10)	30.4(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 -x,-y+1,-z+1