Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Palladium-catalyzed esterification of aryl halides using aryl formates without the use of external carbon monoxide

Tetsuaki Fujihara, Tomoya Hosoki, Yuko Katafuchi, Tomohiro Iwai, Jun Terao, and Yasushi Tsuji*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

* To whom correspondence should be addressed. E-mail: ytsuji@scl.kyoto-u.ac.jp

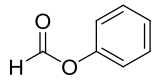
Contents

1. Instrumentation and chemicals

All manipulations were performed under an argon atmosphere using standard Schlenk-type glasswares on a dual-manifold Schlenk line. All solvents were dried and purified by usual procedures.[1] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. IR spectra were recorded on a SHIMADZU FTIR-8300 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). EI-MS were recorded on a Shimadzu GCMS-QP5050A with a direct inlet. Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. GC analysis was carried out using Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. × 25 m). Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 μm). TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$.

2. Preparation of substrates

Preparation of 2a[2]

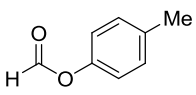


Acetic anhydride (150 mL) was added to a 500 mL-two-necked flask and the flask was cooled at 0 ºC. Then, formic acid (76 mL) was added at 0 ºC. After stirring at room temperature for 10 min, the mixture was heated at 60 ºC for 1 h. After cooling to room temperature, phenol (18.8 g, 200 mmol) and $NaHCO_3$ (33.8 g, 400 mmol) were added. The mixture was stirred at room temperature for 12 h. Then, CH_2Cl_2 and water was added to the mixture and the organic layer was extracted with CH_2Cl_2 (three times), washed with water (three times) and brine (one time), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using hexane-AcOEt (20:1) as an eluent. Colorless oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.38 (dd, J = 7.9, 8.7 Hz, 2H), 7.24 (dd, J = 7.1, 7.5 Hz, 1H),. 7.11 (d, J = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 149.7, 129.4, 126.1, 120.9.

Preparation of 2b-2e

Phenyl formate derivatives (**2b-2e**) were prepared by the same procedure as **2a** employing the corresponding phenol derivatives. All the resonances in ^{1}H NMR spectra were consistent with the reported values.[2,3]

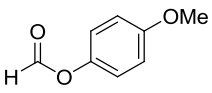
4-Methylphenyl formate (**2b**) [2]



Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.14 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ

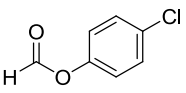
159.4, 147.5, 135.8, 129.9, 120.6, 20.6.

4-Methoxyphenyl formate (**2c**) [2]



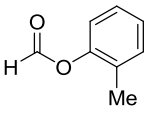
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.05 (dt, J = 9.1, 3.0 Hz, 2H), 6.70 (dt, J = 9.1, 3.0 Hz, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.7, 157.6, 140.3, 121.9, 114.6, 55.5.

4-Chlorophenyl formate (**2d**) [2]



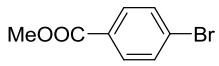
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.35 (d, J = 9.2 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.8, 148.1, 131.7, 129.6, 122.5.

2-Methylphenyl formate (**2e**) [3]



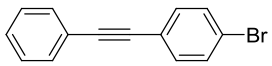
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.03-7.24 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 148.4, 131.2, 129.8, 127.0, 126.4, 121.3, 16.1.

Preparation of methyl 4-bromobenzoate (1g) [4]



4-Bromobenzoic acid (5.0 g, 0.025 mol), methanol (25 mL) and sulfuric acid were added to a 50 mL-recovery flask with a reflux condenser. The mixture was stirred at reflux for 12 h. Then, CH_2Cl_2 and water was added to the mixture and the organic layer was extracted with CH_2Cl_2 (three times), washed with water (three times) and brine (one time), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization with methanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, J = 8.2, 1.8 Hz, 2H), 7.58 (dt, J = 8.2, 1.8 Hz, 2H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.4, 131.7, 131.1, 129.0, 128.0, 52.3.

Preparation of 4-bromo-(2-phenylethynyl)benzene (1l) [5]



A flask was charged with $PdCl_2(PPh_3)_2$ (50 mg, 0.070 mmol), CuI (14 mg, 0.070 mmol), 4-bromoiodobenzene (4.0 g, 14 mmol), triethylamine (10 mL) and THF (20 mL). Phenylacetylene (1.5 mL, 14 mmol) was slowly added to the mixture, and the resulting mixture was stirred at room temperature for 24 h. After removal of all volatiles, the product was dissolved in CH_2Cl_2 (200 mL) and washed with 1N HCl aq. and water. The organic layer was dried over $MgSO_4$. After filtration, the solvent was removed and **1k** was obtained by silica gel column chromatography (eluent: Hexane/CH_2Cl_2 = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.34 -7.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0, 131.6, 131.6, 128.5, 128.4, 122.9 , 122.4, 122.2, 90.5, 88.3. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.

Preparation of $PdCl_2$(Xantphos) [6]

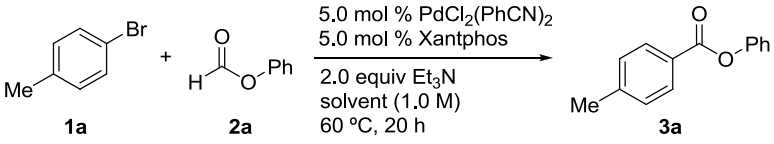
$PdCl_2(PhCN)_2$ (384 mg, 1.0 mmol) and xantphos (579 mg, 1.0 mmol) were added to a 50-mL flask. The flask was evacuated and backfilled with argon three times. Then, a degassed and anhydrous THF (35 mL) was added to the flask. The mixture was stirred for overnight at room temperature. Then, the solvent was removed and the residue was washed with hexane and dried *in vacuo*. Yellow solids were obtained.

3. Experimental procedures

3.1. Procedures of Table 1 and Table S1-S2.

To a 10-mL Schlenk flask with a reflux condenser were added a Pd precursor (9.5 mg, 0.025 mmol) and a ligand (0.025 mmol). The flask was evacuated and backfilled with argon three times. Then, a solvent (0.50 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. **2a** (85 μl, 0.75 mmol) and base (1.0 mmol) were added to the flask and the solution was stirred at room temperature for additional 10 min. Then, **1a** (62 μl, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 60 °C) for 20 h. After cooling to room temperature, the mixture was analyzed by GC analysis using tridecane as an internal standard.

Table S1 Effect of the solvent on the palladium-catalyzed esterifications of 4-bromotoluene employing phenyl formate [a]

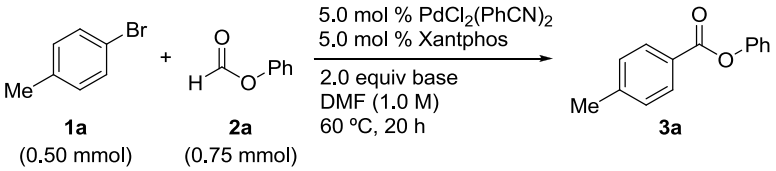


1a (0.50 mmol) **2a** (0.75 mmol) **3a**

Entry	Solvent	Yield (%)[b]
1	DMF	99
2	DMSO	99
3	DMA	81
4	Toluene	63
5	MeCN	58
6	1,4-Dioxane	52
7	Octane	29

[a] Reaction conditions: 4-bromotoluene (0.50 mmol), phenyl formate (0.75 mmol), $PdCl_2(PhCN)_2$ (0.025 mmol, 5.0 mol%), xantphos (0.025 mmol, 5.0 mol%), Et_3N (1.0 mmol) in solvent (0.50 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique.

Table S2 Effect of the base on the palladium-catalyzed esterifications of 4-bromotoluene employing phenyl formate [a]



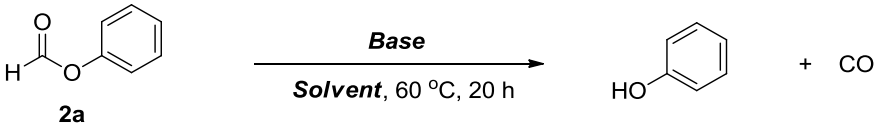
Entry	Base	Yield (%)[b]
1	Et_3N	99
2	none	0
3	$(i\text{-Pr})_2EtN$	82
4	DBU	70
5	Pyridine	0
6	K_2CO_3	57
7	KOH	0

[a] Reaction conditions: 4-bromotoluene (0.50 mmol), phenyl formate (0.75 mmol), $PdCl_2(PhCN)_2$ (0.025 mmol, 5.0 mol %), xantphos (0.025 mmol, 5.0 mol %), base (1.0 mmol) in DMF (0.50 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique.

3.2. General procedures of Table 2 and Table S3

To a 10-mL Schlenk flask with a reflux condenser was evacuated and backfilled with argon three times. Then, a solvent (0.50 ml), **2a** (1.0 mmol) and base (1.0 mmol) were added to the flask. The reaction mixture was heated (bath temp. 60 °C) for 4 h. After cooling to room temperature, HCl aq. (1.0 M, 1 mL) and ether (5 mL) was added the mixture. Then the mixture was stirred for 15 min. The organic layer was analysed by GC analysis using tridecane as an internal standard.

Table S3 Effect of the base on the conversion of **2a** [a]



Entry	Base	Solvent	Yield (%)[b]
1	Et_3N	DMF	99
2	$(i\text{-Pr})_2EtN$	DMF	51 (99% at 120 °C)
3	DBU	DMF	99
4	DMAP	DMF	99
5	Pyridine	DMF	6
6	K_2CO_3	DMF	99
7	Et_3N	DMSO	99
8	Et_3N	CH_2Cl_2	99
9	Et_3N	THF	41
10	Et_3N	toluene	48

[a] Reaction conditions: **2a** (1.0 mmol) in DMF (0.5 mL) at 60 °C for 20 h. [b] Yield based on the GC internal standard technique.

3.3. General procedures of Table 3

To a 10-mL Schlenk flask with a reflux condenser were added $PdCl_2(PhCN)_2$ (9.5 mg, 0.025 mmol) and a xantphos (14 mg, 0.025 mmol). The flask was evacuated and backfilled with argon three times. Then, a degassed DMF (0.50 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. Formates (**2**, 0.75 mmol) and Et_3N (139 μl, 1.0 mmol) were added to the flask and the solution was stirred at room temperature for additional 10 min. Then, aryl bromides (**1**, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 60 °C) for 20 h. After

cooling to room temperature, the mixture was filtered and evaporated. The product (**3**) was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

3.4. Procedures of Scheme 2a and 2b

To a 10-mL Schlenk flask with a reflux condenser were added $PdCl_2(PhCN)_2$ (9.5 mg, 0.025 mmol) and a xantphos (14 mg, 0.025 mmol). The flask was evacuated and backfilled with argon three times. Then, a degassed DMF (0.50 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. **2a** (0.75 mmol) and Et_3N (139 μl, 1.0 mmol) were added to the flask and the solution was stirred at room temperature for additional 10 min. Then, substrate (**1o**, **4** or **5**, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 60 °C) for 20 h. After cooling to room temperature, the mixture was filtered and evaporated. The product (**3s** or **3t**) was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

3.5. Procedures of Scheme 2c and 2d

To a 10-mL Schlenk flask with a reflux condenser were added $PdCl_2(PhCN)_2$ (9.5 mg, 0.025 mmol) and a xantphos (14 mg, 0.025 mmol in Scheme 2c) or $P(OPh)_3$ (16 mg, 0.050 mmol in Scheme 2d). The flask was evacuated and backfilled with argon three times. Then, a degassed DMF (0.50 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. **2a** (0.75 mmol) and $(i\text{-Pr})_2EtN$ (174 μl, 1.0 mmol) were added to the flask and the solution was stirred at room temperature for additional 10 min. Then, substrate (**6** or **7**, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 120 °C) for 20 h. After cooling to room temperature, the mixture was filtered and evaporated. The product (**3f** or **3u**) was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

3.6. Procedures of Scheme 3

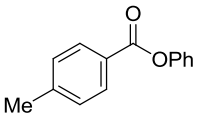
Procedure A (the reactions with **1a** or **1e**): To a 5-mL Schlenk flask with a reflux condenser were added $PdCl_2$(Xantphos) (18.9 mg, 0.025 mmol). The flask was evacuated and backfilled with argon three times. Then, degassed DMF (0.10 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. **2a** (0.50 mmol) and Et_3N (139 μl, 1.0 mmol) were added to the flask and the solution was stirred at room temperature for additional 10 min. Then, substrate (**1a** or **1e**, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 60 °C) for 20 h. After cooling to room temperature, the mixture was filtered and evaporated. The product was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

Procedure B (the reactions with **1d** or **1f**, and the reaction of **1o** with **2c**): To a 5-mL Schlenk flask with a reflux condenser were added $Pd(dba)_2$ (14.4 mg, 0.025 mmol) and xantphos (14 mg, 0.025 mmol). The flask was evacuated and backfilled with argon three times. Then, degassed DMF (0.20 ml) was added to the flask and the resultant solution was stirred at room temperature for 15 min. Formate (**2a** or **2c**, 0.50 mmol) and Et_3N (139 μl, 1.0 mmol) were added to the flask and the solution was

stirred at room temperature for additional 10 min. Then, substrate (**1d**, **1f**, or **1o**, 0.50 mmol) was added to the flask. The reaction mixture was heated (bath temp. 60 °C, in the case of the reaction of **1o** with **2c** at 70 °C) for 20 h. After cooling to room temperature, the mixture was filtered and evaporated. The product was isolated by silica gel chromatography using hexane-AcOEt as an eluent.

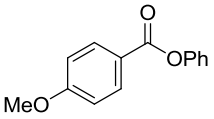
4. Characterization of the products

Phenyl 4-methylbenzoate (**3a**)[7]



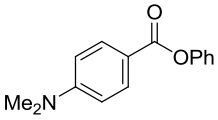
White solid, 99.7 mg (94%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.2 Hz, 2H), 7.42 (td, J = 8.2, 2.3 Hz, 2H), 7.19-7.31 (m, 5H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.2, 150.9, 144.4, 130.2, 129.4, 129.3, 126.8, 125.7, 121.7. 21.7.

Phenyl 4-methoxybenzoate (**3b**)[7]



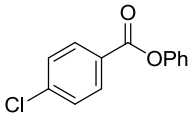
White solid, 103.9 mg (91%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dt, J = 9.2, 2.5 Hz, 2H), 7.42 (tt, J = 8.0, 2.3 Hz, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 2H), 7.00 (dt, J = 8.7, 2.5 Hz, 2H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.9, 163.9, 151.0, 132.3, 129.4, 125.7, 121.8, 121.8, 113.8, 55.5.

Phenyl 4-(*N*,*N*-dimethylamino)benzoate (**3c**)[8]



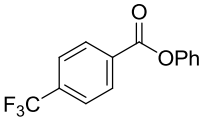
White solid, 100.1 mg (83%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 9.2 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.24 (d, J = 6.0 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 9.2 Hz, 2H), 3.07 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.5, 153.7, 151.3, 131.9, 129.3, 125.3, 121.9, 115.9, 110.7, 40.0.

Phenyl 4-chlorobenzoate (**3d**)[7]



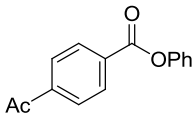
White solid, 111.4 mg (96%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.7 Hz, 2H), 7.49 (t, J = 8.7 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.3, 150.7, 140.1, 131.5, 129.5, 128.9, 128.0, 126.0, 121.6.

Phenyl 4-trifluoromethylbenzoate (**3e**)[9]



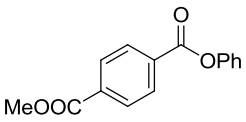
White solid, 118.5 mg (89%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.45 (dd, J = 7.8, 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.0, 150.6, 135.0 (q, $^2J_{C-F}$ = 32.6 Hz), 132.8, 130.6, 129.6, 162.2, 125.6 (q, $^3J_{C-F}$ = 3.8 Hz), 123.6 (q, $^1J_{C-F}$ = 274.0 Hz), 121.5.

Phenyl 4-acethylbenzoate (**3f**)



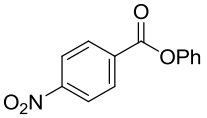
White Solid, 111.0 mg (92%): m.p. 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 87 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H) 7.30 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.8 Hz, 2H), 2.68 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ197.5, 164.3, 150.7, 140.7, 133.3, 130.4, 129.6, 128.3, 126.1, 121.6, 26.9. IR (KBr): 2368.4, 2345.3, 1733.9, 1678.0, 1286.4, 1215.0, 1089.7, 761.8 cm^{-1}. EI-MS: *m/z* 242 (1.2%, $[M+2]^+$), 241 (16.2, $[M+1]^+$), 240 (100, $[M]^+$). Anal. Calcd. for C15H12O3: C, 74.99; H, 5.03. Found: C, 74.94; H, 4.87.

Phenyl methyl terephthalate (**3g**) [10]



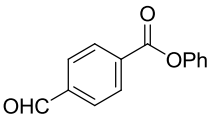
White solid, 112.8 mg (88%): ^{1}H NMR (400 MHz, $CDCl_3$): δ8.27 (d, J = 8.7 Hz, 2H), 8.17 (d, J = 8.7 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.21-7.24 (m, 2H), 3.97 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ166.1, 164.3, 150.7, 134.4, 133.3, 130.1, 129.7, 129.5, 126.1, 121.5, 52.5.

Phenyl 4-nitrobenzoate (**3h**) [10]



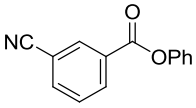
Pale yellow solid, 87.6 mg (72%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35-8.40 (m, 4H), 7.46 (tt, J = 7.8, 2.3 Hz, 2H), 7.32 (tt, J = 7.3, 1.1 Hz, 1H), 7.23-7.25(m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ163.3, 150.9, 150.5, 135.0, 131.3, 129.7, 126.4, 123.7, 121.4. Note: This compound was rather unstable under the air and moisture, and turned to dark brown solid in a few days.

Phenyl 4-formylbenzoate (**3i**)



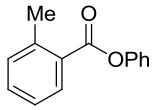
White Solid, 99.5 mg (88%): m.p. 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.37 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 7.46 (tt, J = 8.0, 2.1 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.23-7.25 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ191.5, 164.2, 150.7, 139.6, 134.5, 130.8, 129.6, 129.6, 126.2, 121.5. IR (KBr): 2842.9, 2364.6, 2345.3, 1733.9, 1708.8, 1284.5, 1163.0, 1083.9, 756.0 cm^{-1}. EI-MS: *m/z* 226 (1.1%, $[M+2]^+$), 225 (15, $[M+1]^+$), 224 (100, $[M]^+$). EI-HRMS: Calcd. for $C_{15}H_{18}ClNO$ ($[M]^+$), 236.0630. Found, 236.0628.

Phenyl 3-cyanobenzoate (**3j**) [9]



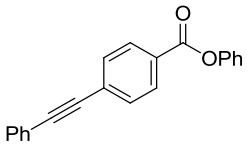
Pale Yellow solid, 93.8 mg (84%): ^{1}H NMR (400 MHz, $CDCl_3$): δ8.50 (s, 1H), 8.43 (dt, J = 7.8, 1.4 Hz, 1H), 7.91 (dt, J = 7.8, 1.4 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ163.2, 150.4, 136.5, 134.1, 133.7, 130.9, 129.6, 129.6, 126.3, 121.4, 117.7, 113.2.

Phenyl 2-methylbenzoate (**3k**) [7]



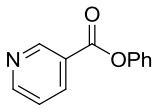
Colorless oil, 94.4 mg (89%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.8 Hz, 2H), 7.39-7.47 (m, 3H), 7.19-7.32 (m, 5H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.7, 150.8, 141.2, 132.7, 131.9, 131.1, 129.4, 128.5, 125.9, 125.7, 121.8, 21.9.

Phenyl 4-(2-phenylethynyl)benzoate (**3l**)



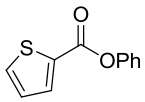
White solid, 129.8 mg (87%): m.p. 153-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.55-7.57 (m, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.35-7.37 (m, 3H), 7.27 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.6, 150.8, 131.7, 131.6, 130.0, 129.5, 128.8, 128.8, 128.7, 128.4, 125.9, 122.5, 121.6, 92.8, 88.5. IR (KBr): 2362.6, 1730.0, 1265.2, 1190.0, 1174.6, 1076.2, 756.0 cm^{-1}. EI-MS: *m/z* 300 (2.5%, $[M+2]^+$), 299 (23, $[M+1]^+$), 298 (100, $[M]^+$). Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.67; H, 4.72.

Phenyl nicotinate (**3m**) [9]



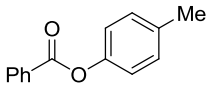
White solid, 90.6 mg (91%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (d, J = 1.8 Hz, 1H), 8.86 (dd, 4.8, 1.6 Hz, 1H), 8.46 (dt, 8.2, 2.1 Hz, 1H). 7.32-7.49 (m, 3H), 7.31 (t, 7.5 Hz, 1H), 7.25-7.22 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.9, 154.0, 151.4, 150.5, 137.6, 129.6, 126.2, 125.6, 123.4, 121.5.

Phenyl thiophene-2-carboxylate (**3n**) [9]



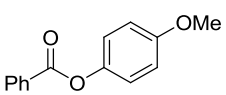
Colorless oil, 94.0 mg (92%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 3.7, 1.4 Hz, 1H), 7.63 (dd, J = 5.0, 1.4 Hz, 1H), 7.38-7.43 (m, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.19-7.25 (m, 2H), 7.15 (dd, J = 5.0, 3.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 150.5, 134.6, 133.4, 132.8, 129.4, 128.0, 125.9, 121.6.

4-Methylphenyl benzoate (**3o**) [11]



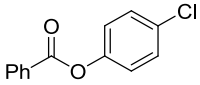
White solid, 81.7 mg (77%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 7.4 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.3, 148.6, 135.4, 133.4, 130.1, 129.9, 129.6, 128.5, 121.3, 20.8.

4-Methoxyphenyl benzoate (**3p**) [11]



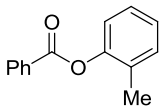
White solid, 105.0 mg (92%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 7.3 Hz, 2H), 7.61 (t, J = 9.1 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.13 (d, J = 9.1 Hz, 2H), 6.93 (d, J = 9.1 Hz, 2H), 3.81 (s. 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5, 157.3, 144.4, 133.5, 130.1, 129.6, 128.5, 122.4, 114.5, 55.6.

4-Chlorophenyl benzoate (**3q**) [11]



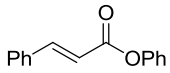
White solid, 112.8 mg (97%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 9.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.8, 149.4, 133.7, 131.2, 130.1, 129.5, 129.1, 128.6, 123.1.

2-Methylphenyl benzoate (**3r**) [7]



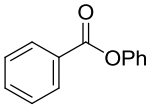
Colorless Oil, 94.4 mg (89%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dt, J = 6.8 Hz, 1.2 Hz, 1H), 7.62 (dt, J = 7.6 Hz, 1.6 Hz, 1H), 7.53–7.48 (m, 1H), 7.28–7.22 (m, 1H), 7.20–7.13 (m, 1H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.8, 149.5, 133.6, 131.2, 130.3, 130.2, 129.5, 128.6, 127.0, 126.1, 122.0, 16.2.

Phenyl cinnamate (**3s**) [7]



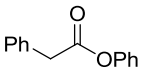
Pale Yellow solid, 74.0 mg (66%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 16.0 Hz, 1H), 7.57-7.60 (m, 2H), 7.38-7.44 (m, 5H), 7.23-7.27 (m, 1H), 7.16-7.19 (m, 2H), 6.63 (d, J = 16.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.4, 150.8, 146.5, 134.1, 130.7, 129.4, 129.0, 128.3, 125.8, 121.6, 117.3.

Phenyl benzoate (**3t**) [8]



White solid, 87.1 mg (88%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, J = 8.2, 1.4 Hz, 2H), 7.61 (tt, J = 7.6, 1.4 Hz, 1H), 7.49 (dd, J = 8.0, 7.6 Hz, 2H), 7.41 (dd, J = 8.4, 7.5 Hz, 2H), 7.26 (tt, J = 7.5, 1.4 Hz, 1H), 7.20-7.22 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.1, 150.9, 133.5, 130.0, 129.5, 129.4, 128.5, 125.8, 121.6.

Phenyl 2-phenylethanoate(**3u**) [12]



Colorless Oil, 74.0 mg (78%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.29 (m, 7H), 7.19 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 3.84 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.9, 150.7, 133.4, 129.3, 129.3, 128.7, 127.3, 125.8, 121.4, 41.4.

5. NMR Chart

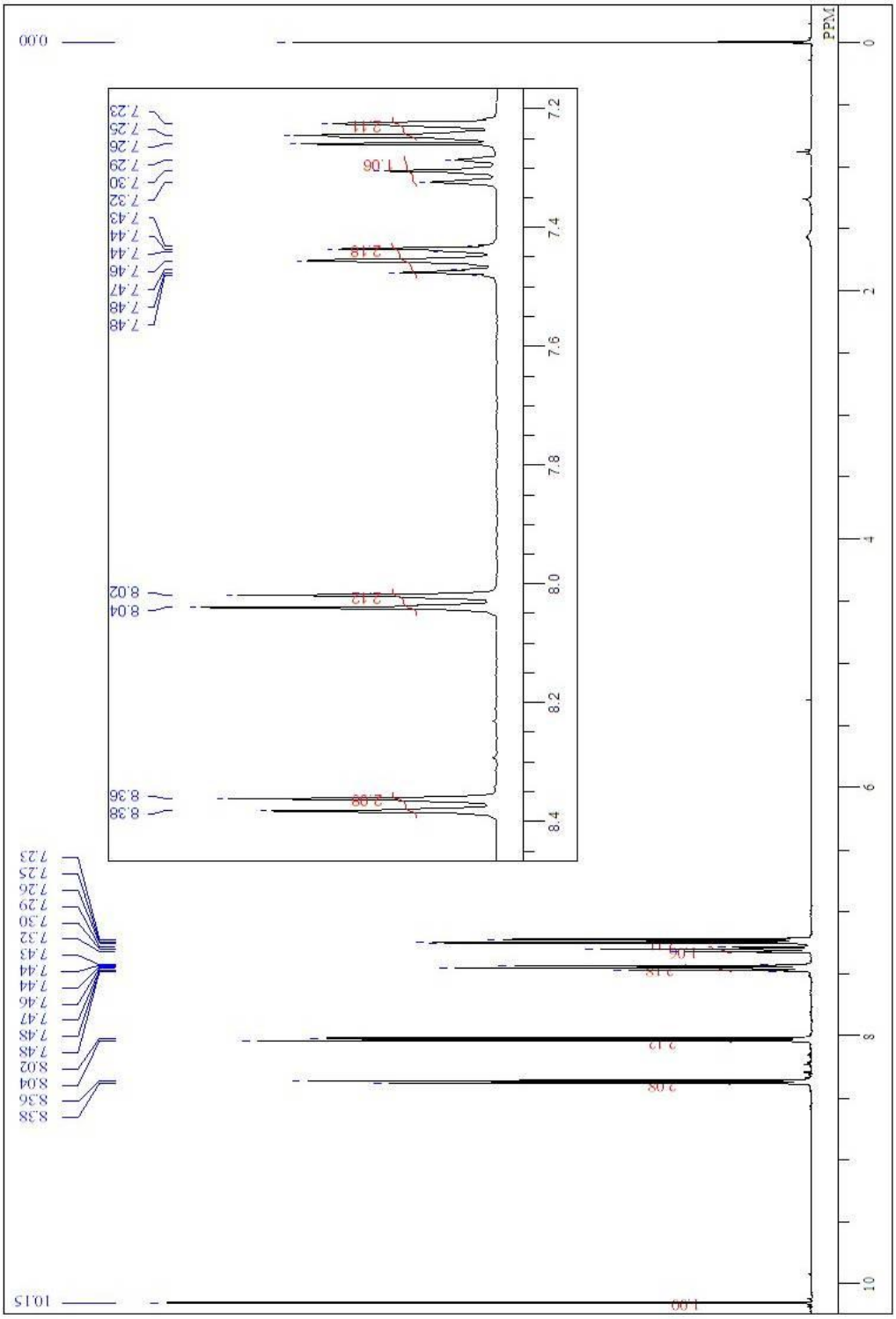


Figure S1. ^{1}H NMR spectrum of **3l**.

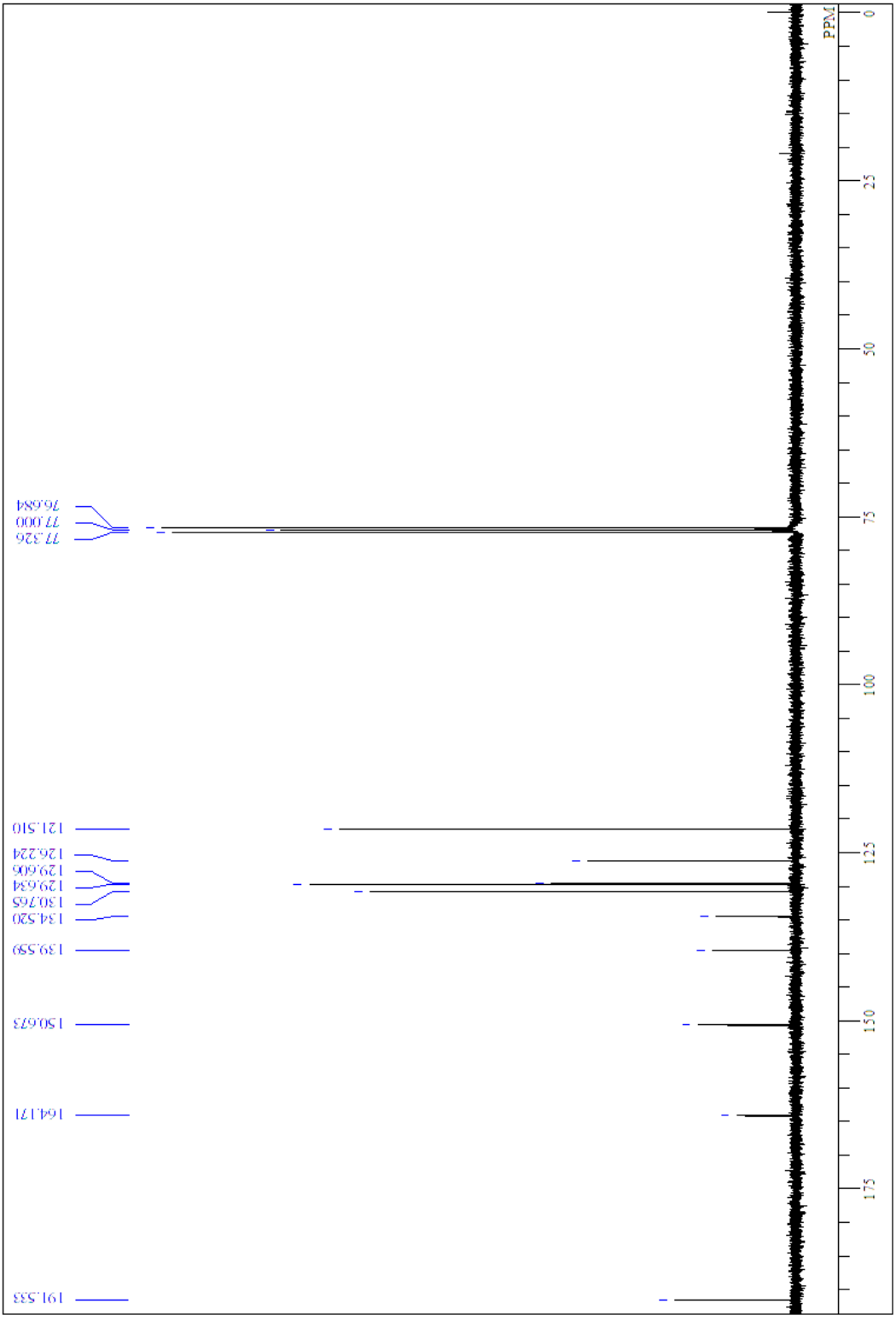


Figure S2. ^{13}C NMR spectrum of **3l**.

6. Reference

1. W. L. F. Armargo, C. L. L. Chai, *Purification of Laboratory Chemicals, 5th Ed.*; Burrerworth-Heinemann: Oxford. U. K., **2003**.
2. Y. Katafuchi, T. Fujihara, T. Iwai, J. Terao and Y. Tsuji, *Adv. Synth. Catal.*, 2011, **353**, 475.
3. M. Ochiai, A. Yoshimura, K. Miyamoto, S. Hayashi and W. Nakanishi, *J. Am. Chem. Soc.*, 2010, **132**, 9236.
4. P. A. Melissaris and H. M. Litt, *J. Org. Chem.*, 1992, **57**, 6998.
5. X. Zheng, E. M. Mulcahy, D. Horinek, F. Galeotti, F. T. Magnera, and J. Michl.. *J. Am. Chem. Soc.*, 2004, **126**, 4540.
6. M. Kranenburg, C. J. P. Kamer and P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.*, 1998, 155.
7. F. Luo, C. Pan, P. Qian and J. Cheng, *Synthesis*, 2010, 2005.
8. H. Nuyvonen, K. Neuvonen and P. Pasanen, *J. Org. Chem.*, 2004, **69**, 3794.
9. A. D. Watson, X. Fan and L. S. Buchward, *J. Org. Chem.*, 2008, **73**, 7096.
10. C. Qin, H. Wu, J. Chen, M. Liu, J. Cheng, W. Su and J. Ding, *Org. Lett.*, 2008, **10**, 1537.
11. L. Zhang, G. Zhang, M. Zhang and J. Cheng, *J. Org. Chem.*, 2010, **75**, 7472.
12. H. N. Roy and A. H. Mamun, *Synth. Commun.*, 2006, **36**, 2975.