

Iron-catalysed Sonogashira reactions

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A catalytic system has been developed that used an iron/ligand combination for the Sonogashira cross coupling of terminal alkynes with aryl iodides, which affords products in good to excellent yields.

Keywords: iron-catalysis, terminal alkynes, aryl iodides, sonogashira reaction

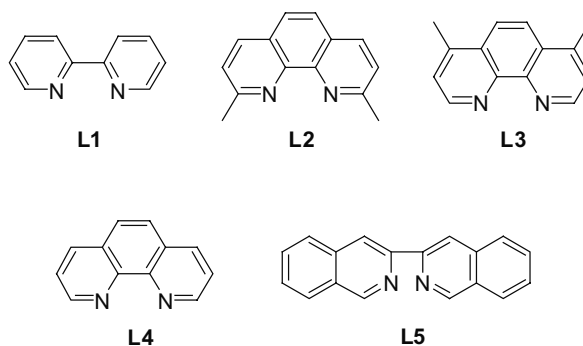
The Sonogashira reaction of aryl halides with terminal acetylenes, which provides a powerful tool for the formation of alkynes, has been widely applied to such diverse areas as natural product syntheses and material science.^{1,2} The existing protocols for these reactions involve the use of palladium, copper, nickel and ruthenium catalysts.^{3,4} Despite remarkable advances in both palladium and copper-catalysed reactions, the development of alternative catalysts involving more cost-efficient, nontoxic, and environmentally friendly metals to effect this reaction remains an issue of scientific interest and paramount industrial significance. In this respect, iron is an ideal metal that offers significant advantages in terms of its low cost, ready availability, and environmentally benign character.^{5,6}

Recently, the application of iron salts to C–C,^{7–19} C–N,^{20–21} C–O,²² C–S²³ bond formation has been developed. Iron salts as catalysts have attracted particular attention and are widely used in C–C cross-coupling reactions. Very recently, Bolm and co-workers were the first to successfully apply iron

salts to the Sonogashira reaction.¹⁹ Although their results were encouraging, a long reaction time was required. Thus, the development of a new procedure for the iron-catalysed Sonogashira reaction is still a desirable goal. Here, we report an iron-catalysed system for the Sonogashira cross-coupling reaction of aryl iodides with alkynes.

We initially studied the iron-catalysed Sonogashira reaction of phenylacetylene with 1-iodobenzene in toluene as a model reaction at 135°C in the presence of a series of ligands (Scheme 1) and 2 equiv of K₂CO₃. The results are summarised in Table 1.

The ligands used had dramatic effects on the yields of cross-coupling products in the Sonogashira reaction (Table 1, entries 1–5). **L1** is a highly effective ligand in this reaction (Table 1, entry 1), while **L3**, **L4** and **L5** were inferior. **L2** resulted in no coupled product (Table 1, entry 2). Then we turned our attention to screening bases and Cs₂CO₃ was shown to be the best. We also studied the effect of the iron sources. Fe(acac)₃ was the best, while the use of FeCl₃ resulted in only 13%



Scheme 1

Table 1 Selected results of iron sources, ligands, bases, and solvents screening^a

Entry	Iron source	Ligand	Base	t/h	Yield/% ^b
1	Fe(acac) ₃	L1	K ₂ CO ₃	42	85
2	Fe(acac) ₃	L2	K ₂ CO ₃	42	<5
3	Fe(acac) ₃	L3	K ₂ CO ₃	42	15
4	Fe(acac) ₃	L4	K ₂ CO ₃	42	10
5	Fe(acac) ₃	L5	K ₂ CO ₃	42	<5
6	Fe(acac) ₃	L1	Cs ₂ CO ₃	42	90
7	Fe(acac) ₃	L1	Na ₂ CO ₃	42	<5
8	Fe(acac) ₃	L1	K ₃ PO ₄	42	37
9	FeCl ₃	L1	Cs ₂ CO ₃	42	13
9	Fe(CH ₂ =CHCOO) ₃	L1	Cs ₂ CO ₃	42	86
10	Fe(acac) ₃	L1	Cs ₂ CO ₃	28	41

^aReaction conditions: **1** (0.5 mmol), **2** (1.5 equiv), iron source (0.1 equiv), ligand (0.20 equiv), base (2.0 equiv), toluene (2 mL), 135°C, under N₂.

^bIsolated yield.

yield (Table 1, entry 9). Moreover, the solvents played an important role in the reaction. Acetonitrile, 1,2-dichloroethane, or dioxane had a detrimental effect on the outcome of the reaction.

It should be noted that the reaction time and temperature were key parameters in the process. When the coupling reaction between **1** and **2** was allowed to proceed for short time, the target acetylene **3** was obtained only in 41% yield (Table 1, entry 11). In addition, no product was obtained when the reaction temperature was lower than 135 °C. Hence, it was concluded that the best conditions involved 10 mol% Fe(acac)₃, 20 mol% **L1**, and 2 equivalents of Cs₂CO₃ in toluene at 135 °C for 42 h.

Next, we explored the scope of this new method. By using the conditions optimised in the model reaction, we were able to apply this new method to a broad range of substrates, including terminal alkynes and aryl iodides substituted by both electron-withdrawing and electron-donating groups (Table 2). In general, electron-rich aryl iodides provided products in higher yield than electron-deficient aryl iodides. 2-Thiophenyl iodide led to the corresponding arylated alkynes in good yields (Table 2, entries 5, 10, 15, 19 and 24). In regard to the alkynes, electron-deficient aryl alkynes proved less reactive. Fortunately, both 1-chloro-4-ethynylbenzene **1c** and 1-bromo-4-ethynylbenzene **1d** were suitable substrates. It is noteworthy that alkyne homocoupling

products were not detected in any reaction.

In summary, we have developed an iron-catalysed system for the Sonogashira reaction, which affords products in good to excellent yields. Our system needs less time than the Bolm's procedure.

Experimental

Melting points were determined with an X4 micro hot-stage apparatus. IR spectra were determined as KBr pellets on a Bruker model EQUINOX55 spectrophotometer. ¹H NMR and ¹³C NMR spectra were determined in a CDCl₃ solution with a Bruker Avance300 (300 MHz) spectrometer using tetramethylsilane as the internal standard. All chemical shifts (δ) were expressed in parts per million, and coupling constants (*J*) were given in Hertz. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

General procedure for the Sonogashira cross coupling of terminal alkynes with aryl iodides

A sealable tube was charged with alkyne (0.5 mmol), aryl iodide (0.75 mmol), Fe(acac)₃ (17.6 mg, 10 mol%), **L1** (15.6 mg, 20 mol%), Cs₂CO₃ (325.8 mg, 1.0 mmol) and toluene (2 mL) under nitrogen. After the mixture was heated to 135 °C for 42 h, it was cooled to room temperature and then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the product. The physical and spectra data of all compounds are as follows.

Table 2 Fe(acac)₃-catalysed Sonogashira coupling of terminal alkynes with aryl iodides^a

$\text{Ar}^1\text{—}\text{C}\equiv\text{CH} \quad \text{1} + \quad \text{Ar}^2\text{—I} \quad \text{2} \xrightarrow[\text{Cs}_2\text{CO}_3, \text{toluene}, 135^\circ\text{C}]{\text{Fe(acac)}_3 / \text{L1}} \text{Ar}^1\text{—}\text{C}\equiv\text{C—Ar}^2 \quad \text{3}$							
Entry	1	2	Yield/% ^b	Entry	1	2	Yield/% ^b
1			90	12	1c	2c	89
2	1a		96	13	1c	2e	90
3	1a		94	14		2a	84
4	1a		86	15	1d	2b	88
5	1a		87	16	1d	2c	86
6		2a	89	17	1d	2d	81
7	1b	2b	90	18		2a	86
8	1b	2c	93	19	1e	2b	93
9	1b	2e	89	20	1e	2c	90
10		2a	85	21	1e	2d	80
11	1c	2b	90	22	1e	2e	87

^aReaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), Fe(acac)₃ (17.6 mg, 10 mol%), **L1** (15.6 mg, 20 mol%), Cs₂CO₃ (325.8 mg, 1.0 mmol), toluene (2 mL), 135 °C, 42 h, under N₂.

^bIsolated yield.

Diphenylacetylene (3aa): M.p. 54–55°C. IR (KBr, cm^{-1}): 2214 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.75–7.52 (m, 4H), 7.36–7.33 (m, 6H). ^{13}C NMR (75 MHz): δ 131.6, 128.4, 128.3, 123.3, 89.4. MS (ESI) m/z 179 ($\text{M} + \text{H}^+$). Anal. Calcd for C_{10}H_8 : C, 94.34; H, 5.66. Found: C, 94.16; H, 5.84%.

4-(phenylethynyl)toluene (3ab): M.p. 71–72°C. IR (KBr, cm^{-1}): 2216 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.55–7.52 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.36–7.32 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz): δ 138.4, 131.5, 131.4, 129.1, 128.3, 128.0, 123.5, 120.2, 89.5, 88.7, 21.5. MS (ESI) m/z 193 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{12}$: C, 93.71; H, 6.29. Found: C, 93.52; H, 6.48%.

4-(phenylethynyl)anisole (3ac): M.p. 58–60°C. IR (KBr, cm^{-1}): 2220 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.55–7.48 (m, 4H), 7.37–7.33 (m, 3H), 6.90 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz): δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3. MS (ESI) m/z 209 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}$: C, 86.51; H, 5.81. Found: C, 86.74; H, 5.69%.

1-bromo-4-(2-phenylethynyl)benzene (3ad): M.p. 83–84°C. IR (KBr, cm^{-1}): 2212 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.54–7.47 (m, 4H), 7.41–7.34 (m, 5H). ^{13}C NMR (75 MHz): δ 132.9, 131.6, 128.5, 128.3, 122.9, 122.4, 122.2, 90.5, 88.3. MS (ESI) m/z 256 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_9\text{Br}$: C, 65.40; H, 3.53. Found: C, 65.26; H, 3.71%.

2-(2-phenylethynyl)thiophene (3ae): M.p. 49–50°C. IR (KBr, cm^{-1}): 2205 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.54 (d, $J = 8.0$ Hz, 2H), 7.39–7.30 (m, 5H), 7.04–7.01 (m, 1H). ^{13}C NMR (75 MHz): δ 131.9, 131.4, 128.4, 128.3, 127.2, 127.1, 123.3, 122.9, 93.0, 82.6. MS (ESI) m/z 185 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{12}\text{H}_8\text{S}$: C, 78.22; H, 4.38. Found: C, 78.08; H, 4.46%.

4-(phenylethynyl)toluene (3ba): M.p. 71–72°C. IR (KBr, cm^{-1}): 2214 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.52 (d, $J = 7.9$ Hz, 2H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.34–7.30 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz): δ 138.4, 131.5, 131.4, 129.1, 128.3, 128.0, 123.5, 120.1, 89.5, 88.7. MS (ESI) m/z 193 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{12}$: C, 93.71; H, 6.29. Found: C, 93.53; H, 6.47%.

1, 2-di-4-tolylethyne (3bb): M.p. 132–134°C. IR (KBr, cm^{-1}): 2208 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.41 (d, $J = 8.1$ Hz, 4H), 7.14 (d, $J = 8.1$ Hz, 4H), 2.35 (s, 6H). ^{13}C NMR (75 MHz): δ 138.1, 131.4, 129.1, 120.4, 88.8. MS (ESI) m/z 207 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84. Found: C, 93.35; H, 6.65%.

1-(2-(4-methoxyphenyl)ethynyl)-4-methylbenzene (3bc): M.p. 125–126°C. IR (KBr, cm^{-1}): 2226 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.47–7.39 (m, 4H), 7.14 (d, $J = 7.9$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz): δ 159.5, 137.9, 132.9, 131.3, 129.0, 120.5, 115.6, 113.9, 88.6, 88.2, 55.3, 29.7. MS (ESI) m/z 223 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.45; H, 6.35. Found: C, 86.31; H, 6.50%.

2-(2-p-tolylethynyl)thiophene (3be): M.p. 68–70°C. IR (KBr, cm^{-1}): 2202 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.40 (d, $J = 8.1$ Hz, 2H), 7.26–7.24 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 6.99–6.97 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz): δ 138.6, 131.6, 131.3, 129.1, 127.0, 126.9, 123.6, 119.8, 93.2, 81.9, 21.5. MS (ESI) m/z 199 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{S}$: C, 78.75; H, 5.08. Found: C, 78.58; H, 5.21%.

1-chloro-4-(2-phenylethynyl)benzene (3ca): M.p. 81–82°C. IR (KBr, cm^{-1}): 2208 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.52–7.43 (m, 4H), 7.36–7.31 (m, 5H). ^{13}C NMR (75 MHz): δ 134.2, 132.8, 131.6, 128.6, 128.4, 128.3, 122.9, 121.8, 90.3, 88.2. MS (ESI) m/z 214 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_9\text{Cl}$: C, 79.06; H, 4.27. Found: C, 79.20; H, 4.12%.

1-(2-(4-chlorophenyl)ethynyl)-4-methylbenzene (3cb): M.p. 149–150°C. IR (KBr, cm^{-1}): 2215 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.44–7.39 (m, 4H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz): δ 138.6, 134.0, 132.7, 131.4, 129.1, 128.6, 121.9, 119.8, 90.5, 87.6, 21.5. MS (ESI) m/z 228 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{Cl}$: C, 79.47; H, 4.89. Found: C, 79.67; H, 4.75%.

1-chloro-4-(2-(4-methoxyphenyl)ethynyl)benzene (3cc): M.p. 120–121°C. IR (KBr, cm^{-1}): 2220 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.50–7.41 (m, 4H), 7.30 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz): δ 159.7, 133.8, 133.0, 132.6, 128.6, 122.1, 114.9, 114.0, 90.3, 86.9, 55.3. MS (ESI) m/z 244 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{ClO}$: C, 74.23; H, 4.57. Found: C, 74.38; H, 4.43%.

2-(2-(4-chlorophenyl)ethynyl)thiophene (3ce): M.p. 92–94°C. IR (KBr, cm^{-1}): 2199 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.44–7.42 (m, 2H), 7.32–7.27 (m, 4H), 7.02–6.99 (m, 1H). ^{13}C NMR (75 MHz): δ 134.4, 132.6, 132.1, 128.7, 127.5, 127.1, 121.4, 91.8, 83.6. MS (ESI) m/z 220 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{12}\text{H}_7\text{ClS}$: C, 65.90; H, 3.23. Found: C, 65.76; H, 3.35%.

1-bromo-4-(2-phenylethynyl)benzene (3da): M.p. 82–84°C. IR (KBr, cm^{-1}): 2208 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.52–7.46 (m, 4H), 7.38–7.32 (m, 5H). ^{13}C NMR (75 MHz): δ 133.0, 131.6, 128.5, 128.4, 122.9, 122.5, 122.2, 90.5, 88.3. MS (ESI) m/z 258 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_9\text{Br}$: C, 65.40; H, 3.53. Found: C, 65.24; H, 3.67%.

1-(2-(4-bromophenyl)ethynyl)-4-methylbenzene (3db): M.p. 156–158°C. IR (KBr, cm^{-1}): 2216 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.47–7.35 (m, 6H), 7.15 (d, $J = 8.2$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz): δ 138.6, 132.9, 131.5, 131.4, 129.1, 122.4, 122.2, 119.8, 90.7, 87.7, 21.5. MS (ESI) m/z 272 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{Br}$: C, 66.44; H, 4.09. Found: C, 66.31; H, 4.23%.

1-bromo-4-(2-(4-methoxyphenyl)ethynyl)benzene (3dc): M.p. 234–236°C. IR (KBr, cm^{-1}): 2210 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.49–7.44 (m, 4H), 7.35 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz): δ 159.8, 133.0, 132.8, 131.5, 122.6, 122.0, 114.9, 114.0, 90.5, 87.0, 55.3. MS (ESI) m/z 288 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{BrO}$: C, 62.74; H, 3.86. Found: C, 62.90; H, 3.72%.

1,2-bis(4-bromophenyl)ethyne (3dd): M.p. 182–184°C. IR (KBr, cm^{-1}): 2204 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 7.48 (d, $J = 8.3$ Hz, 4H), 7.36 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (75 MHz): δ 132.9, 131.6, 122.7, 121.8, 89.4. MS (ESI) m/z 334 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{14}\text{H}_8\text{Br}_2$: C, 50.04; H, 2.40. Found: C, 50.20; H, 2.26%.

2-(2-phenylethynyl)naphthalene (3ea): M.p. 113–115°C. IR (KBr, cm^{-1}): 2218 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 8.05 (s, 1H), 7.83–7.78 (m, 3H), 7.59–7.56 (m, 3H), 7.49–7.46 (m, 2H), 7.36–7.34 (m, 3H). ^{13}C NMR (75 MHz): δ 133.0, 132.8, 131.7, 131.6, 131.4, 128.4, 128.38, 128.30, 127.9, 127.7, 126.6, 126.5, 123.3, 120.6, 89.8, 89.7. MS (ESI) m/z 229 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{18}\text{H}_{12}$: C, 94.70; H, 5.30. Found: C, 94.52; H, 5.48%.

2-(2-4-tolylethynyl)naphthalene (3eb): M.p. 150–152°C. IR (KBr, cm^{-1}): 2220 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 8.03 (s, 1H), 7.81–7.77 (m, 3H), 7.58–7.55 (m, 1H), 7.50–7.45 (m, 4H), 7.16 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz): δ 138.4, 133.0, 132.7, 131.5, 131.3, 129.1, 128.4, 127.9, 127.7, 126.6, 126.5, 120.8, 120.2, 89.9, 89.2, 21.5. MS (ESI) m/z 243 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{19}\text{H}_{14}$: C, 94.18; H, 5.82. Found: C, 94.34; H, 5.66%.

2-(2-(4-methoxyphenyl)ethynyl)naphthalene (3ec): M.p. 122–124°C. IR (KBr, cm^{-1}): 2214 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 8.02 (s, 1H), 7.81–7.77 (m, 3H), 7.57–7.45 (m, 5H), 6.88 (d, $J = 8.7$ Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz): δ 159.7, 133.1, 133.0, 132.6, 131.1, 128.4, 127.9, 127.74, 127.71, 126.5, 120.9, 115.4, 114.04, 114.01, 89.8, 88.5, 55.3. MS (ESI) m/z 259 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{O}$: C, 88.34; H, 5.46. Found: C, 88.12; H, 5.62%.

2-(2-(4-bromophenyl)ethynyl)naphthalene (3ed): M.p. 146–147°C. IR (KBr, cm^{-1}): 2210 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 8.0 (s, 1H), 7.82–7.80 (m, 3H), 7.57–7.41 (m, 7H). ^{13}C NMR (75 MHz): δ 133.0, 132.9, 132.8, 131.6, 131.5, 128.2, 128.0, 127.8, 126.8, 126.6, 122.5, 120.2, 90.9, 88.6. MS (ESI) m/z 308 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{Br}$: C, 70.38; H, 3.61. Found: C, 70.20; H, 3.75%.

2-(2-(naphthalen-2-yl)ethynyl)thiophene (3ee): M.p. 126–128°C. IR (KBr, cm^{-1}): 2192 ($\text{C}\equiv\text{C}$). ^1H NMR (CDCl_3 , 300 MHz): δ 8.06 (s, 1H), 7.81–7.78 (m, 3H), 7.56–7.47 (m, 3H), 7.31 (d, $J = 8.7$ Hz, 2H), 7.09–7.01 (m, 1H). ^{13}C NMR (75 MHz): δ 132.9, 132.8, 131.9, 131.3, 128.1, 128.0, 127.8, 127.7, 127.1, 126.7, 126.6, 123.3, 120.2, 93.4, 82.9. MS (ESI) m/z 305 ($\text{M} + \text{H}^+$). Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{S}$: C, 82.01; H, 4.30. Found: C, 81.78; H, 4.43%.

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