Supporting Information for

Regio- and Stereoselective Cross-Coupling of *tert*-Propargyl Alcohols with Bis(trimethylsilyl)acetylene and Its Utilization in Constructing a Fluorescent Donor-Acceptor System

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General. ^1H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, for CDCl_3 solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m) on a Shimadzu QP-5050. Alcohols **1ap** and **1am** were commercially available. Other starting alcohols **1bp-1gp** were prepared by the Sonogashira coupling of the corresponding commercially available α,α -disubstituted propargyl alcohols with aryl iodides according to the published method.¹⁾ The chloro-complex $[(\text{cod})\text{RhCl}]_2$ was commercially available and the hydroxyl-complex $[(\text{cod})\text{Rh}(\text{OH})]_2$ was prepared according to the published method.²⁾ The fluorescence analyses of furans **6** in the solid state were carried out with the samples recrystallized from hexane-toluene or hexane-ethyl acetate and then powdered.³⁾

Rhodium-Catalyzed Reaction of 1,1,3-Triphenyl-2-propyn-1-ol (1ap) with Bis(trimethylsilyl)acetylene (2) (Entry 2 in Table 1): To a refluxing solution of $[(\text{cod})\text{Rh}(\text{OH})]_2$ (0.01 mmol, 4.3 mg), dppb (0.02 mmol, 8.5 mg), **2** (3.0 mmol, 510 mg), and 1-methylnaphthalene (ca. 50 mg) as internal standard in toluene (4.0 mL), a solution of **1ap** (0.50 mmol, 92.5 mg) in toluene (2.0 mL) was added over 2 h by using a syringe pump. The reaction mixture was refluxed for a further 2 h, and then the solvent was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane-ethyl acetate (99.8:0.2, v/v) to afford **4ap** as a colorless solid (93.8 mg, 98% yield).

Sequential Sonogashira Coupling/Cyclization of 2-Hydroxymethyl-(E)-enynes (4) (Transformation of 4dp to 6dp-NMe₂ in Scheme 4): A mixture of 2-hydroxymethyl-(E)-enyn **4dp** (0.50 mmol, 209 mg), 4-iodo-*N,N*-dimethylaniline (0.60 mmol, 209 mg), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.03 mmol, 23 mg), CuI (0.05 mmol, 10 mg),

DBU (3 mmol, 463 mg), and H₂O (0.10 mL) in toluene (4 mL) was stirred for 6 h at 100 °C, and then the solvent was evaporated. The residue was dissolved in DMSO (4 mL), and *t*-BuOK (1.0 mmol, 113 mg) was added to the mixture. The reaction was complete within 1 h, and then the solution was poured into water. The mixture was extracted with Et₂O and the organic phase was dried with Na₂SO₄. The solvent was evaporated and the residue was purified by thin-layer chromatography on silica gel using hexane-ethyl acetate as eluent to afford **6dp-NMe₂** as yellow microcrystals (177.7 mg, 77% yield). It is noted that ¹H NMR analysis of **6dp-NMe₂** suggested that it contained a minor amount of its (*Z*)-isomer (*ca.* 10%). However, it converted cleanly to the (*E*)-isomer in the CDCl₃ solution at room temperature. Similar behavior was observed in the case of **6ep-NMe₂** and **6fp-NMe₂**, while the other compounds had originally (*E*)-configuration.

4ap: Mp 100 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9H), 3.22 (s, 1H), 6.46 (s, 1H), 7.27-7.35 (m, 9H), 7.44 (d, 4H), 7.82 (d, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -0.49, 82.15, 103.32, 106.28, 127.48, 127.79, 128.05, 128.18, 128.64, 129.06, 135.50, 137.11, 144.56; MS *m/z* 382 (M⁺). Anal. Calcd for C₂₆H₂₆OSi: C, 81.63; H, 6.85. Found C, 81.59; H, 6.61.

4am: Mp 51-52 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 9H), 1.53 (s, 6H), 1.87 (s, 1H), 6.96 (s, 1H), 7.27-7.35 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -0.28, 29.52, 73.24, 103.16, 104.38, 128.02, 128.18, 128.88, 129.70, 131.87, 136.07; MS *m/z* 258 (M⁺). HRMS *m/z* (M⁺) calcd for C₁₆H₂₂OSi 258.1440. Found 258.1424.

4bp: Mp 94-95 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.13 (s, 9H), 2.98 (s, 6H), 3.29 (s, 1H), 6.28 (s, 1H), 6.62 (d, *J* = 9.1 Hz, 2H), 7.26-7.41 (m, 6H), 7.43 (d, *J* = 8.2 Hz, 4H),

7.76 (d, $J = 9.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.32, 40.26, 82.18, 104.51, 105.27, 111.38, 122.81, 123.71, 127.24, 127.66, 128.27, 130.44, 137.50, 145.06, 150.61; MS m/z 425 (M^+). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{NOSi}$: C, 79.01; H, 7.34; N, 3.29. Found C, 79.02; H, 7.45; N, 3.25.

4cp: Mp 114-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.12 (s, 9H), 3.23 (s, 1H), 3.82 (s, 3H), 6.38 (s, 1H), 6.83 (d, $J = 8.7$ Hz, 2H), 7.28-7.35 (m, 6H), 7.43 (d, $J = 8.7$ Hz, 4H), 7.80 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.42, 55.30, 82.13, 103.77, 105.81, 113.42, 125.58, 127.39, 127.74, 128.19, 128.31, 130.58, 136.67, 144.75, 159.88; MS m/z 412 (M^+). Anal. Calcd for $\text{C}_{27}\text{H}_{28}\text{O}_2\text{Si}$: C, 78.60; H, 6.84. Found C, 78.78; H, 6.67.

4dp: Mp 107-108 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.11 (s, 9H), 3.16 (s, 1H), 6.45 (s, 1H), 7.28-7.42 (m, 8H), 7.43 (d, $J = 8.2$ Hz, 4H), 7.77 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.52, 82.12, 103.05, 107.04, 127.56, 127.84, 128.11, 128.21, 128.66, 130.26, 134.00, 134.16, 135.52, 144.41; MS m/z 416 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{ClOSi}$: C, 74.88; H, 6.04. Found C, 74.69; H, 5.85.

4ep: Mp 115-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.11 (s, 9H), 3.14 (s, 1H), 6.57 (s, 1H), 7.31-7.37 (m, 6H), 7.44 (d, $J = 8.2$ Hz, 4H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.93 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.57, 82.17, 102.76, 107.56, 124.04 (d, $J = 272$ Hz), 124.93 (q, $J = 4$ Hz), 127.68, 127.89, 128.10, 129.15, 130.08 (d, $J = 33$ Hz), 130.63, 135.09, 138.99, 144.25; MS m/z 450 (M^+). Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{OSi}$: C, 71.97; H, 5.59. Found C, 71.62; H, 5.47.

4fp: Mp 146-147 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.11 (s, 9H), 3.09 (s, 1H), 6.61 (s, 1H), 7.31-7.37 (m, 6H), 7.43 (d, $J = 8.0$ Hz, 4H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.92 (d, $J =$

8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.63, 82.14, 102.52, 108.39, 111.43, 118.80, 127.73, 127.90, 128.02, 129.35, 131.75 (overlapped), 134.45, 139.99, 144.04; MS m/z 425 (M^+). Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{NOSi}$: C, 79.56; H, 6.18; N, 3.44. Found C, 79.53; H, 6.21; N, 3.43.

6bp-CN: Mp 212-215 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.97 (s, 6H), 5.90 (s, 1H), 6.72 (d, J = 8.5 Hz, 2H), 6.88 (s, 1H), 7.29 (m, 8H), 7.43 (d, J = 8.2 Hz, 4H), 7.63 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.47, 95.81, 102.58, 111.68, 112.40, 118.83, 121.34, 125.76, 126.15, 127.57, 127.87, 128.06, 128.99, 132.17, 134.58, 142.71, 143.29, 149.32, 158.28; HRMS m/z (M^+) calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}$ 454.2045. Found 454.2037.

6cp-CN: Mp 114-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 5.94 (s, 1H), 6.83 (s, 1H), 6.90 (d, J = 8.2 Hz, 2H), 7.32-7.39 (m, 8H), 7.43 (d, J = 7.7 Hz, 4H), 7.64 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.34, 95.86, 101.95, 112.08, 114.05, 118.73, 120.46, 125.95, 127.52, 127.99, 128.13, 129.17, 130.49, 132.21, 134.36, 143.01, 144.79, 158.43, 159.19; MS m/z 441 (M^+). Anal. Calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_2$: C, 84.33; H, 5.25; N, 3.17. Found C, 83.92; H, 5.18; N, 3.13.

6dp-NMe₂: Mp 188 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.00 (s, 6H), 5.67 (s, 1H), 6.50 (s, 1H), 6.68 (d, J = 8.9 Hz, 2H), 7.24-7.36 (m, 10H), 7.45 (d, J = 8.5 Hz, 4H), 7.67 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.21, 94.82, 95.45, 111.56, 113.94, 117.61, 127.32, 127.63, 127.72, 127.99, 128.45, 128.73, 130.66, 137.29, 143.35, 149.05, 151.33, 164.06; MS m/z 463 (M^+). Anal. Calcd for $\text{C}_{31}\text{H}_{26}\text{ClNO}$: C, 80.24; H, 5.65; N, 3.02. Found C, 80.08; H, 5.94; N, 2.87.

6dp-OMe: Mp 168 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.83 (s, 3H), 5.74 (s, 1H), 6.55 (s,

1H), 6.91 (d, $J = 9.1$ Hz, 2H), 7.27-7.38 (m, 10H), 7.44 (d, $J = 8.1$ Hz, 4H), 7.73 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.98, 96.27, 97.17, 114.56, 116.15, 123.32, 128.14, 128.20, 128.47, 128.68, 129.14, 129.48, 131.76, 137.29, 143.35, 149.05, 151.33, 164.06; MS m/z 450 (M^+). Anal. Calcd for $\text{C}_{30}\text{H}_{23}\text{ClO}_2$: C, 79.90; H, 5.14. Found C, 79.63; H, 5.10.

6ep-NMe₂: Mp 198 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.00 (s, 6H), 5.73 (s, 1H), 6.55 (s, 1H), 6.68 (d, $J = 9.2$ Hz, 2H), 7.29-7.37 (m, 6H), 7.44-7.47 (m, 6H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.16, 94.75, 95.72, 111.53, 113.52, 117.31, 124.18 (d, $J = 271$ Hz), 125.27 (br q, $J = 3$ Hz), 126.76 (d, $J = 32$ Hz), 127.46, 127.49, 127.64, 127.83, 128.05, 142.37, 143.11, 150.99, 151.49, 165.09; MS m/z 497 (M^+). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{F}_3\text{NO}$: C, 77.25; H, 5.27; N, 2.82. Found C, 76.92; H, 5.36; N, 2.79.

6fp-NMe₂: Mp 188 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.03 (s, 6H), 5.68 (s, 1H), 6.55 (s, 1H), 6.69 (d, $J = 8.9$ Hz, 2H), 7.32-7.37 (m, 6H), 7.41-7.45 (m, 6H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.15, 94.71, 96.10, 107.50, 111.48, 113.00, 116.94, 119.61, 127.60, 127.62, 127.69, 127.93, 128.09, 132.14, 142.80, 143.50, 151.66, 152.38, 166.13; MS m/z 454 (M^+). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}$: C, 84.55; H, 5.77; N, 6.16. Found C, 84.29; H, 5.51; N, 6.14.

Figure S1. NOE Enhancements in ^1H NMR of Compounds **3bp** and **3am**. Conditions: irradiation time 3s, acquisition time 2.76 s, delay 1s.

Figure S2. Fluorescence spectra for the powders of **6** and Alq₃ upon excitation at 380 nm.³⁾

Figure S3. Normalized fluorescence spectra of **6bp-CN** and **6cp-CN** in solution upon excitation at the absorption maximum.

Table S1. Optical Properties of Compounds **6**.

6bp-CN : $R^1 = \text{NMe}_2$, $R^2 = \text{CN}$

6cp-CN : $R^1 = \text{OMe}$, $R^2 = \text{CN}$

6dp-OMe : $R^1 = \text{Cl}$, $R^2 = \text{OMe}$

6dp-NMe₂ : $R^1 = \text{Cl}$, $R^2 = \text{NMe}_2$

6ep-NMe₂ : $R^1 = \text{CF}_3$, $R^2 = \text{NMe}_2$

6fp-NMe₂ : $R^1 = \text{CN}$, $R^2 = \text{NMe}_2$

	$\lambda_{\text{abs}}^{\text{a)}}$ (nm)	$\log \epsilon$	$\lambda_{\text{ems}}^{\text{b)}}$ (nm)	Φ_{F}	$\lambda_{\text{ems}}^{\text{e)}}$ (nm)	rel. int. ^{f)}
6bp-CN	442	4.25	541	0.76 ^{c)}	589	0.1
6cp-CN	399	4.45	490, 515	0.53 ^{c)}	534	1.6
6dp-OMe	372	4.49	440	< 0.01 ^{d)}	492, 524sh	0.4
6dp-NMe₂	403	4.72	485, 507	< 0.01 ^{d)}	535	< 0.1
6ep-NMe₂	392	4.72	470sh, 500	< 0.01 ^{d)}	525, 560sh	0.3
6fp-NMe₂	422	4.36	505, 540sh	< 0.01 ^{d)}	575	0.2

a) Absorption maximum in dioxane. b) Emission maximum in dioxane excited at $\lambda_{365\text{nm}}$. c) Determined by comparison of coumarin 153 solution in ethanol ($\Phi_{\text{F}} = 0.38$) excited at $\lambda_{421\text{nm}}$.⁴⁾ d) Determined by comparison of quinine solution in 0.1 M sulfuric acid ($\Phi_{\text{F}} = 0.546$) excited at $\lambda_{365\text{nm}}$. e) Emission maximum in powder excited at 380 nm. f) Relative emission intensity to Alq₃ (1.0).

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[¹H and ¹³C NMR Spectra of 4ap]

[¹H and ¹³C NMR Spectra of 4am]

[¹H and ¹³C NMR Spectra of 4bp]

[¹H and ¹³C NMR Spectra of 4cp]

[¹H and ¹³C NMR Spectra of 4dp]

[¹H and ¹³C NMR Spectra of 4ep]

[¹H and ¹³C NMR Spectra of 4fp]

[¹H and ¹³C NMR Spectra of 6bp-CN]

[¹H and ¹³C NMR Spectra of 6cp-CN]

No.	ppm	Hz	Height
1	159.19	15846.9	11.90
2	158.43	15770.7	11.03
3	144.79	14413.2	11.33
4	143.01	14236.3	18.40
5	134.36	13374.4	10.42
6	132.21	13160.6	38.38
7	130.49	12989.3	12.60
8	129.17	12858.3	49.66
9	128.13	12755.0	100
10	127.99	12741.1	40.94
11	127.52	12694.4	91.41
12	125.95	12537.9	39.54
13	120.46	11991.5	22.06
14	118.73	11818.6	7.90
15	114.05	11353.3	48.47
16	112.08	11157.5	9.78
17	101.95	10148.1	20.77
18	95.86	9542.7	7.99
19	55.34	5508.6	23.85

[¹H and ¹³C NMR Spectra of 6dp-NMe₂]

[¹H and ¹³C NMR Spectra of 6dp-OMe]

No.	ppm	Hz	Height
1	163.60	16285.3	12.00
2	161.53	16079.7	12.12
3	149.20	14851.6	11.73
4	145.76	14310.1	19.73
5	137.55	13692.4	11.89
6	131.76	13116.4	9.83
7	129.48	12889.5	51.60
8	129.14	12855.1	53.33
9	128.68	12809.2	97.21
10	128.47	12788.7	42.51
11	128.20	12761.7	100
12	128.14	12755.9	48.55
13	123.32	12275.8	11.92
14	116.15	11562.3	23.53
15	114.56	11404.2	45.94
16	97.17	9673.0	23.87
17	96.27	9582.9	7.24
18	55.98	5572.6	27.35

[¹H and ¹³C NMR Spectra of 6ep-NMe₂]

[^1H and ^{13}C NMR Spectra of 6fp-NM₂]