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SUPPORTING INFORMATION

Metal-free intramolecular hydroarylation of alkynes

Chaofeng Zhang, Songkui Lv, Yanru Wang, Jingyi Zhang, Xiao-Na Wang,* and Junbiao Chang*

Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province, Key Laboratory of Advanced Drug Preparation Technologies, Ministry of Education, School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou, Henan 450001, P. R. China.

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Part I Experimental Part

General Information

Unless otherwise indicated, all reactions were performed in oven-dried glassware under a nitrogen atmosphere. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. ¹H NMR and ¹³C NMR spectra were obtained on Bruker's AscendTM 400 NMR spectrometer using CDCl₃ as solvent with TMS or residual solvent as standard unless otherwise noted. ¹³C NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as a standard. Infrared spectra were obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and KMnO₄ stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer.

1.1 Synthesis of C-Terthered Arene-Ynamides 1.

C-Terthered arene-ynamides **1a**,¹ **1k**,² **1n**,² **1o**,³ **1p**,⁴ **1r**,⁵ **1t**² and **1u**¹ were known compounds and synthesized according to corresponding literatures, the data were matched with reported values. *C*-Terthered arene-ynamides **1b–1j**, **1l**, **1m**, **1q**, **1s**, **1v** and **1w** was new compounds and synthesized according to Hsung's method.⁴

Synthesis of C-Terthered Arene-Ynamides 1b–1j, 1l, 1m, 1q, 1s, 1v and 1w.⁴



To an oven-dried round bottomed flask were added Z-phenylvinylacetylene (1.3 g, 10.0 mmol), acetone (25.0 mL, 0.4 *M*) and NBS (2.0 g, 11.0 mmol), then AgNO₃ (169.4 mg, 1.0 mmol) was added to the reaction mixture at rt. After the reaction mixture was stirred for 2.0 h, the acetone was removed under the reduced pressure. Then the reaction mixture was filtered through a pad of silica gel, washed with petroleum ether, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the Br-terminated enyne (2.1 g, 9.90 mmol, 99% yield). To an oven-dried round-bottomed flask was added amide (332.9 mg, 1.20 mmol), CuSO₄·5H₂O (37.5 mg, 0.15 mmol), 1,10-phenanthroline (54.2 mg, 0.3 mmol) , K₃PO₄ (636.9 mg,

3.0 mmol), toluene (15.0 mL, 0.1 *M*), and the Br-terminated enyne (310.7 mg, 1.5 mmol). Then the reaction mixture was stirred at 80 °C overnight. After the reaction was judged to be complete by TLC, the mixture was cooled to rt, filtered through a pad of silica gel, and purified by flash silica gel column chromatrography [isocratic eluent: 30:1 petroleum ether/EtOAc + 3% NEt₃] to afford terthered arene-ynamide **1b** (466.1 mg, 1.16 mmol, 77% yield).

1b: $R_f = 0.18$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 85–86 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.76 (m, 2H), 7.69-7.66 (m, 2H), 7.33-7.27 (m, 6H), 7.26-7.23 (m, 2H), 6.92-6.88 (m, 2H), 6.46 (d, 1H, J = 12.0 Hz), 5.70 (d, 1H, J = 11.9 Hz), 4.59 (s, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 136.6, 135.6, 134.7, 129.9, 129.4, 128.8, 128.6, 128.5, 128.4, 128.2, 114.5, 106.7, 89.6, 71.1, 55.85, 55.75, one carbon missing due to overlap; IR (neat) (cm⁻¹) 3069w, 2214w, 1594m, 1361s, 1267m, 1158s; HRMS (ESI): m/z calcd for C₂₄H₂₁NO₃SNa [M+Na]⁺ 426.1134, found 426.1136.

Cs_N^{Bn}

C-Terthered arene-ynamide **1c** (562.9 mg, 1.38 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (338.1 mg, 1.20 mmol) in 92% yield.

1c: $R_f = 0.45$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 54–55 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.66 (m, 4H), 7.39-7.36 (m, 2H), 7.31-7.26 (m, 8H), 6.51 (d, 1H, J = 11.9 Hz), 5.70 (d, 1H, J = 11.9 Hz), 4.62 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 136.5, 136.4, 136.3, 134.3, 129.6, 129.0, 128.9, 128.7, 128.5, 128.42, 128.37, 106.5, 88.6, 71.2, 56.1, one carbon missing due to overlap; IR (neat) (cm⁻¹) 3091w, 2215w, 1396w, 1166s, 1083m; HRMS (ESI): m/z calcd for C₂₃H₁₈ClNO₂SNa [M+Na]⁺ 430.0639, found 430.0632.

Ns N^{Bn}

C-Terthered arene-ynamide **1d** (470.8 mg, 1.13 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (350.8 mg, 1.20 mmol) in 75% yield.

1d: $R_f = 0.27$ [10:1 petroleum ether/EtOAc]; yellow solid; mp = 50–51 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.19-8.16 (m, 2H), 7.89-7.86 (m, 2H), 7.69-7.66 (m, 2H), 7.34-7.27 (m, 8H), 6.57 (d, 1H, J = 11.9 Hz), 5.71 (d, 1H, J = 11.9 Hz), 4.68 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 143.2, 137.3, 136.5, 134.0, 128.94, 128.86, 128.8, 128.6, 128.5, 124.3, 106.2, 87.6, 71.3, 56.5, two carbons

missing due to overlap; IR (neat) (cm⁻¹) 3101w, 2223w, 1808w, 1605w, 1346s, 1170s; HRMS (ESI): m/z calcd for $C_{23}H_{18}N_2O_4SNa [M+Na]^+ 441.0879$, found 441.0872.

C-Terthered arene-ynamide **1e** (191.5 mg, 0.62 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (222.3 mg, 1.20 mmol) in 41% yield.

1e: $R_f = 0.32$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 63–64 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.77 (m, 4H), 7.37 (t, 2H, J = 7.5 Hz), 7.31-7.28 (m, 3H), 6.53 (d, 1H, J = 11.9 Hz), 5.74 (d, 1H, J = 11.9 Hz), 3.15 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 136.7, 135.9, 133.5, 130.1, 128.5, 128.4, 128.3, 127.8, 106.7, 90.4, 69.2, 39.2, 21.8; IR (neat) (cm⁻¹) 2937w, 2219w, 1446w, 1361s, 1167s, 1028m; HRMS (ESI): m/z calcd for C₁₈H₁₇NO₂SNa [M+Na]⁺ 334.0872, found 334.0877.



C-Terthered arene-ynamide **1f** (318.1 mg, 0.90 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (272.8 mg, 1.20 mmol) in 60% yield.

1f: $R_f = 0.42$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 42–43 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.90-7.83 (m, 4H), 7.45 (d, 2H, J = 8.1 Hz), 7.40-7.29 (m, 3H), 6.60 (d, 1H, J = 12.0 Hz), 5.86 (d, 1H, J = 12.0 Hz), 3.47 (t, 2H, J = 7.1 Hz), 2.44 (s, 3H), 1.71-1.64 (m, 2H), 1.43-1.34 (m, 2H), 0.92 (t, 3H, J = 7.4 Hz); ¹³C NMR (100 MHz, CD₃COCD₃) δ 146.0, 137.6, 136.0, 135.7, 130.8, 129.2, 129.1, 129.0, 128.2, 107.3, 90.2, 71.2, 52.1, 30.7, 21.5, 20.0, 13.8; IR (neat) (cm⁻¹) 2955w, 2207m, 1493w, 1352s, 1168s; HRMS (ESI): m/z calcd for C₂₁H₂₃NO₂SNa [M+Na]⁺ 376.1342, found 376.1342.



C-Terthered arene-ynamide **1g** (308.8 mg, 0.92 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (253.5 mg, 1.20 mmol) in 61% yield.

1g: $R_f = 0.33$ [10:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ

7.81-7.77 (m, 4H), 7.35-7.26 (m, 5H), 6.51 (d, 1H, J = 12.0 Hz), 5.82-5.72 (m, 2H), 5.31-5.22 (m, 2H), 4.05 (dt, 2H, J = 6.3, 1.2 Hz), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 136.7, 135.7, 135.0, 131.1, 130.0, 128.5, 128.4, 128.3, 127.7, 120.2, 106.8, 89.1, 70.9, 54.5, 21.8; IR (neat) (cm⁻¹) 2922w, 2211m, 1493w, 1365s, 1167s; HRMS (ESI): m/z calcd for C₂₀H₁₉NO₂SNa [M+Na]⁺ 360.1029, found 360.1029.

Ts

C-Terthered arene-ynamide **1h** (140.1 mg, 0.38 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (296.8 mg, 1.20 mmol) in 25% yield.

1h: $R_f = 0.37$ [10:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.87-7.84 (m, 2H), 7.62-7.59 (m, 2H), 7.49-7.39 (m, 5H), 7.36-7.30 (m, 5H), 6.67 (d, 1H, J = 12.0 Hz), 5.88 (d, 1H, J = 12.0 Hz), 2.43 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 146.6, 139.5, 137.4, 137.0, 134.0, 130.7, 130.2, 129.5, 129.2, 129.1, 129.0, 128.7, 127.1, 107.0, 90.4, 70.7, 21.5; IR (neat) (cm⁻¹) 3024w, 2211m, 1488m, 1371s, 1172s; HRMS (ESI): m/z calcd for C₂₃H₁₉NO₂SNa [M+Na]⁺ 396.1029, found 396.1025.



C-Terthered arene-ynamide **1i** (369.0 mg, 1.19 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (222.3 mg, 1.20 mmol) in 79% yield.

1i: $R_f = 0.18$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 53–54 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, 2H, J = 7.2 Hz), 7.47-7.27 (m, 8H), 6.55 (d, 1H, J = 11.9 Hz), 5.77 (d, 1H, J = 11.9 Hz), 4.71 (s, 2H), 2.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 136.3, 134.7, 129.1, 128.92, 128.86, 128.5, 128.4, 128.3, 106.5, 88.4, 71.5, 55.9, 39.3; IR (neat) (cm⁻¹) 3019w, 2209m, 1493w, 1349s, 1162s; HRMS (ESI): m/z calcd for C₁₈H₁₇NO₂SNa [M+Na]⁺ 334.0872, found 334.0878.



C-Terthered arene-ynamide **1j** (73.6 mg, 0.35 mmol) was prepared from enyne **S1** (192.3 mg, 1.50 mmol) and the corresponding amide (104.5 mg, 1.20 mmol) in 23% yield.

1j: R_f = 0.55 [1:1 petroleum ether/EtOAc]; pale yellow solid; mp = 43–44 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.98-7.96 (m, 2H), 7.39-7.35 (m, 2H), 7.32-7.27 (m, 1H), 6.64 (d, 1H, *J* = 12.0 Hz), 5.86 (d, 1H, *J* = 12.0 Hz), 4.59-4.55 (m, 2H), 4.12-4.08 (m, 2H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 156.6, 137.5, 136.4, 129.2, 129.1, 129.0, 107.0, 88.3, 71.3, 64.5, 47.2; IR (neat) (cm⁻¹) 2988w, 2224m, 1757s, 1474m, 1391s, 1178m; HRMS (ESI): m/z calcd for C₁₃H₁₁NO₂Na [M+Na]⁺ 236.0682, found 236.0690.

C-Terthered arene-ynamide **11** (590.0 mg, 1.46 mmol) was prepared from 4-phenyl-1-butyne (0.21 mL, 1.50 mmol) and the corresponding amide (332.8 mg, 1.20 mmol) in 97% yield.

11: $R_f = 0.17$ [10:1 petroleum ether/EtOAc]; white solid; mp = 42–43 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.80-7.76 (m, 2H), 7.34-7.09 (m, 12H), 4.40 (s, 2H), 3.92 (s, 3H), 2.68 (t, 2H, J = 7.1 Hz), 2.47 (t, 2H, J = 7.1 Hz); ¹³C NMR (100 MHz, CD₃COCD₃) δ 173.3, 164.6, 142.3, 138.6, 132.2, 131.1, 129.3, 129.2, 129.1, 128.1, 128.0, 126.6, 115.1, 56.2, 50.0, 35.8, 35.2, 26.9; IR (neat) (cm⁻¹) 3032w, 2248w, 1596m, 1261s, 1160s, 1024m; HRMS (ESI): m/z calcd for C₂₄H₂₃NO₃SNa [M+Na]⁺ 428.1291, found 428.1284.

C-Terthered arene-ynamide **1m** (559.6 mg, 1.37 mmol) was prepared from 4-phenyl-1-butyne (0.21 mL, 1.50 mmol) and the corresponding amide (338.1 mg, 1.20 mmol) in 91% yield.

1m: $R_f = 0.39$ [10:1 petroleum ether/EtOAc]; white solid; mp = 38–39 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.82-7.78 (m, 2H), 7.63-7.60 (m, 2H), 7.32-7.14 (m, 10H), 4.46 (s, 2H), 2.70 (t, 2H, J = 7.1 Hz), 2.50 (t, 2H, J = 7.1 Hz); ¹³C NMR (100 MHz, CD₃COCD₃) δ 141.4, 140.3, 137.2, 135.9, 130.25, 130.16, 129.5, 129.34, 129.25, 129.1, 129.0, 126.9, 74.9, 70.9, 56.5, 35.5, 20.7; IR (neat) (cm⁻¹) 2934w, 2258w, 1477w, 1370m, 1171s; HRMS (ESI): m/z calcd for C₂₃H₂₀ClNO₂SNa [M+Na]⁺ 432.0795, found 432.0788.



C-Terthered arene-ynamide **1q** (249.5 mg, 0.74 mmol) was prepared from 4-phenyl-1-butyne (0.21 mL, 1.50 mmol) and the corresponding amide (253.5 mg, 1.20 mmol) in 49% yield.

1q: $R_f = 0.35$ [10:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.75-7.73 (m, 2H), 7.44 (d, 2H, J = 8.1 Hz), 7.29-7.18 (m, 5H), 5.71-5.62 (m, 1H), 5.21-5.12 (m, 2H), 3.88 (dt, 2H, J = 6.2, 1.2 Hz), 2.76 (t, 2H, J = 7.2 Hz), 2.55 (t, 2H, J = 7.2 Hz), 2.46 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 145.5, 141.5, 135.6, 132.3, 130.6, 129.4, 129.0, 128.5, 126.9, 119.7, 74.9, 70.1, 54.9, 35.8, 21.5, 20.9; IR (neat) (cm⁻¹) 2923w, 2252w, 1454w, 1362s, 1168s, 1090m; HRMS (ESI): m/z calcd for C₂₀H₂₁NO₂SNa [M+Na]⁺ 362.1185, found 362.1186.



C-Terthered arene-ynamide **1s** (404.3 mg, 1.29 mmol) was prepared from 4-phenyl-1-butyne (0.21 mL, 1.50 mmol) and the corresponding amide (222.3 mg, 1.20 mmol) in 86% yield.

1s: $R_f = 0.22$ [10:1 petroleum ether/EtOAc]; white solid; mp = 35–36 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.41-7.33 (m, 5H), 7.29-7.16 (m, 5H), 4.52 (s, 2H), 2.91 (s, 3H), 2.74 (t, 2H, J = 7.1 Hz), 2.53 (t, 2H, J = 7.1 Hz); ¹³C NMR (100 MHz, CD₃COCD₃) δ 141.5, 136.4, 129.5,129.4, 129.3, 129.03, 128.99, 126.9, 75.2, 70.5, 56.0, 38.0, 35.6, 20.9; IR (neat) (cm⁻¹) 2932w, 2256w, 1454m, 1332s, 1154s; HRMS (ESI): m/z calcd for C₁₈H₁₉NO₂SNa [M+Na]⁺ 336.1029, found 336.1028.



C-Terthered arene-ynamide **1v** (434.0 mg, 1.07 mmol) was prepared from phenyl propargyl ether (0.19 mL, 1.50 mmol) and the corresponding amide (332.8 mg, 1.20 mmol) in 71% yield.

1v: $R_f = 0.17$ [10:1 petroleum ether/EtOAc]; white solid; mp = 41–42 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.62 (m, 2H), 7.30-7.22 (m, 7H), 6.99 (tt, 1H, J = 7.3, 1.1 Hz), 6.89-6.86 (m, 2H), 6.82-6.78 (m, 2H), 4.74 (s, 2H), 4.43 (s, 2H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 157.6, 134.5, 129.9, 129.6, 129.1, 128.8, 128.7, 128.5, 121.3, 115.2, 114.4, 81.2, 67.4, 56.1, 55.8, 55.5; IR (neat) (cm⁻¹) 3034w, 2239w, 1593m, 1495s, 1362s, 1260s; HRMS (ESI): m/z calcd for C₂₃H₂₁NO₄SNa [M+Na]⁺ 430.1083, found 430.1065.

Ns _ Bn

1w

C-Terthered arene-ynamide **1w** (411.9 mg, 0.98 mmol) was prepared from phenyl propargyl ether (0.19 mL, 1.50 mmol) and the corresponding amide (350.8 mg, 1.20 mmol) in 65% yield.

1w: $R_f = 0.21$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 89–90 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 8.32-8.28 (m, 2H), 8.05-8.02 (m, 2H), 7.33-7.29 (m, 7H), 6.99 (tt, 1H, J = 7.3, 1.1 Hz), 6.93-6.91 (m, 2H), 4.87 (s, 2H), 4.64 (s, 2H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 158.3, 151.6, 143.3, 135.2, 130.3, 129.8, 129.6, 129.4, 129.3, 125.2, 121.9, 115.8, 80.6, 68.8, 56.6, 56.0; IR (neat) (cm⁻¹) 3098w, 2239w, 1598w, 1378m, 1348s, 1034m; HRMS (ESI): m/z calcd for C₂₂H₁₈N₂O₅SNa [M+Na]⁺ 445.0829, found 445.0828.

1.2 Hydroarylation of Terthered Arene-Ynamides (Table 1).

Terthered arene-ynamides 2j,⁶ 2t⁷ and 2t⁸ were known compounds, the data were matched with reported values. Terthered arene-ynamides 2a-2i, 2k-2s, 2u, 2v and 2w were new compounds.



To an oven-dried sealed tube was added terthered arene-ynamide **1a** (77.5 mg, 0.20 mmol), CH_2Cl_2 (0.5 mL, 0.40 *M*) and TfOH (8.9 μ L, 0.10 mmol). The reaction vessel was capped and stirred at rt for 10.0 minutes. After the reaction was judged to be complete by TLC, the mixture was quenched by Et₃N (13.9 μ L, 0.10 mmol) and purified by flash silica gel column chromatography [gradient eluent: 20:1~10:1 petroleum ether/EtOAc] to afford **2a** (76.0 mg, 0.20 mmol) in 98% yield.



2a: $R_f = 0.27$ [10:1 petroleum ether/EtOAc]; white solid; mp = 96–97 °C ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, 1H, J = 9.6 Hz), 7.76-7.73 (m, 2H), 7.62-7.60 (m, 2H), 7.42-7.34 (m, 2H), 7.28-7.23 (m, 3H), 7.13-7.09 (m, 5H), 6.85 (dd, 1H, J = 7.4, 1.1 Hz), 4.99 (d, 1H, J = 13.9 Hz), 4.66 (d, 1H, J = 13.9 Hz), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 136.2, 136.03, 135.96, 134.7, 132.9, 129.7, 129.4, 129.1, 128.3, 128.2, 128.0, 127.9, 127.2, 126.6, 126.4, 124.9, 124.3, 56.5, 21.8; IR (neat) (cm⁻¹) 2849w, 1596w, 1494w, 1344s, 1156s, 1088m; HRMS (ESI): m/z calcd for C₂₄H₂₁NO₂SNa [M+Na]⁺ 410.1185, found 410.1187.



Aminonaphthalene **2b** (79.1 mg, 0.20 mmol) was prepared from *C*-terthered arene-ynamide**1b** (80.7 mg, 0.20 mmol) in 98% yield after stirring at rt for 5.0 min.

2b: $R_f = 0.46$ [4:1 petroleum ether/EtOAc]; pale yellow solid; mp = 115–116 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.97-7.95 (m, 1H), 7.74-7.71 (m, 2H), 7.66-7.62 (m, 2H), 7.41-7.34 (m, 2H), 7.25-7.23 (m, 1H), 7.14-7.08 (m, 5H), 6.93-6.86 (m, 3H), 4.99 (d, 1H, J = 13.9 Hz), 4.65 (d, 1H, J = 13.9 Hz), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 136.1, 135.9, 134.6, 132.9, 130.7, 130.2, 129.3, 129.0, 128.3, 127.9, 127.8, 127.0, 126.5, 126.4, 124.9, 124.3, 114.1, 56.4, 55.7; IR (neat) (cm⁻¹) 2923w, 1578w, 1495m, 1337m, 1155s, 1025m; HRMS (ESI): m/z calcd for C₂₄H₂₁NO₃SNa [M+Na]⁺ 426.1134, found 426.1129.



Aminonaphthalene 2c (66.1 mg, 0.16 mmol) was prepared from *C*-terthered arene-ynamide 1c (81.6 mg, 0.20 mmol) in 81% yield after stirring at rt for 5.0 min.

2c: $R_f = 0.32$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 143–144 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, 1H, J = 8.2 Hz), 7.75 (d, 2H, J = 8.1 Hz), 7.64-7.60 (m, 2H), 7.43-7.34 (m, 4H), 7.28-7.24 (m, 1H), 7.12 (s, 5H), 6.85 (dd, 1H, J = 7.3, 0.9 Hz), 4.94 (d, 1H, J = 13.9 Hz), 4.73 (d, 1H, J = 13.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 137.7, 135.6, 135.5, 134.7, 132.6, 129.5, 129.4, 129.35, 129.30, 128.4, 128.11, 128.05, 127.4, 126.8, 126.5, 125.0, 123.9, 56.5; IR (neat) (cm⁻¹) 3063w, 1585w, 1394w, 1344s, 1164s, 1084m; HRMS (ESI): m/z calcd for C₂₃H₁₈ClNO₂SNa [M+Na]⁺ 430.0639, found 430.0635.



Aminonaphthalene **2d** (58.6 mg, 0.14 mmol) was prepared from *C*-terthered arene-ynamide **1d** (83.7 mg, 0.20 mmol) in 70% yield after stirring at rt for 5.0 min.

2d: $R_f = 0.19$ [10:1 petroleum ether/EtOAc]; yellow solid; mp = 148–149 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27-8.23 (m, 2H), 7.85-7.76 (m, 5H), 7.45-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.18-7.12 (m, 5H), 6.85 (dd, 1H, J = 7.4, 0.9 Hz), 4.92 (d, 1H, J = 14.0 Hz), 4.86 (d, 1H, J = 14.0 Hz); ¹³C NMR

(100 MHz, CDCl₃) δ 150.1, 145.2, 135.3, 134.9, 134.8, 132.2, 129.8, 129.4, 129.2, 128.6, 128.35, 128.33, 127.8, 127.0, 126.7, 125.1, 124.2, 123.5, 56.8; IR (neat) (cm⁻¹) 2921w, 1595w, 1524s, 1348s, 1029m; HRMS (ESI): m/z calcd for C₂₃H₁₈N₂O₄SNa [M+Na]⁺ 441.0879, found 441.0867.



Aminonaphthalene **2e** (59.8 mg, 0.19 mmol) was prepared from *C*-terthered arene-ynamide **1e** (62.3 mg, 0.20 mmol) in 96% yield after stirring at rt for 5.0 min.

2e: $R_f = 0.23$ [10:1 petroleum ether/EtOAc]; white solid; mp = 118–119 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.29-8.26 (m, 1H), 7.85-7.79 (m, 2H), 7.64-7.61 (m, 2H), 7.57-7.49 (m, 2H), 7.33-7.29 (m, 3H), 6.85 (dd, 1H, J = 7.4, 0.9 Hz), 3.29 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 138.6, 134.81, 134.77, 132.4, 129.7, 128.9, 128.3, 128.1, 127.0, 126.7, 125.1, 124.9, 124.2, 39.9, 21.7; IR (neat) (cm⁻¹) 2923w, 1596w, 1342s, 1327w, 1176m, 1003m; HRMS (ESI): m/z calcd for C₁₈H₁₇NO₂SNa [M+Na]⁺ 334.0872, found 334.0876.



Aminonaphthalene **2f** (63.6 mg, 0.18 mmol) was prepared from *C*-terthered arene-ynamide **1f** (70.7 mg, 0.20 mmol) in 90% yield after stirring at rt for 5.0 min.

2f: $R_f = 0.33$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 45–46 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.24-8.22 (m, 1H), 7.84-7.80 (m, 2H), 7.59-7.57 (m, 2H), 7.54-7.47 (m, 2H), 7.34-7.30 (m, 1H), 7.25-7.24 (m, 2H), 6.86 (dd, 1H, J = 7.4, 0.8 Hz), 3.91-3.84 (m, 1H), 3.43-3.37 (m, 1H), 2.42 (s, 3H), 1.53-1.44 (m, 1H), 1.33-1.21 (m, 3H), 0.79 (t, 3H, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 136.6, 135.7, 134.7, 133.6, 129.6, 129.0, 128.1, 128.0, 126.8, 126.6, 125.9, 125.1, 124.5, 52.5, 30.7, 21.7, 20.1, 13.8; IR (neat) (cm⁻¹) 2871w, 1595w, 1394w, 1343s, 1163s, 1089m; HRMS (ESI): m/z calcd for C₂₁H₂₃NO₂SNa [M+Na]⁺ 376.1342, found 376.1344.



Aminonaphthalene 2g (64.1 mg, 0.19 mmol) was prepared from *C*-terthered arene-ynamide 1g (67.5 mg, 0.20 mmol) in 95% yield after stirring at rt for 5.0 min.

2g: $R_f = 0.30$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 80–81 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.20-8.17 (m, 1H), 7.84-7.79 (m, 2H), 7.63-7.60 (m, 2H), 7.54-7.47 (m, 2H), 7.33-7.26 (m, 3H), 6.88 (dd, 1H, J = 7.4, 1.2 Hz), 5.82-5.72 (m, 1H), 4.95-4.90 (m, 2H), 4.42 (tdd, 1H, J = 14.3, 6.1, 1.4 Hz), 4.14 (tdd, 1H, J = 14.3, 7.2, 1.1 Hz), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 136.0, 134.8, 133.3, 132.7, 129.7, 129.1, 128.14, 128.13, 126.9, 126.62, 126.59, 125.0, 124.3, 119.4, 55.3, 21.7, one carbon missing due to overlap; IR (neat) (cm⁻¹) 2920w, 1595w, 1394w, 1342s, 1156s, 1088m; HRMS (ESI): m/z calcd for C₂₀H₁₉NO₂SNa [M+Na]⁺ 360.1029, found 360.1030.



Aminonaphthalene **2h** (69.5 mg, 0.19 mmol) was prepared from *C*-terthered arene-ynamide **1h** (74.7 mg, 0.20 mmol) in 93% yield after stirring at rt for 10.0 min.

2h: $R_f = 0.27$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 55–56 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.36-8.33 (m, 1H), 7.83 (dd, 2H, J = 7.9, 4.3 Hz), 7.63-7.60 (m, 2H), 7.55-7.45 (m, 4H), 7.40 (t, 1H, J = 7.8 Hz), 7.33-7.23 (m, 5H), 7.19-7.14 (m, 1H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 141.6, 137.4, 137.3, 135.0, 132.6, 129.7, 129.4, 129.2, 128.3, 128.2, 127.5, 127.3, 127.0, 126.9, 126.7, 125.2, 124.0, 21.7; IR (neat) (cm⁻¹) 2922w, 1594w, 1348s, 1167m, 1157s; HRMS (ESI): m/z calcd for C₂₃H₁₉NO₂SNa [M+Na]⁺ 396.1029, found 396.1025.



Aminonaphthalene **2i** (59.2 mg, 0.19 mmol) was prepared from *C*-terthered arene-ynamide **1i** (62.3 mg, 0.20 mmol) in 95% yield after stirring at rt for 5.0 min.

2i: $R_f = 0.24$ [4:1 petroleum ether/EtOAc]; white solid; mp = 88–89 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.08-8.06 (m, 1H), 7.85-7.81 (m, 2H), 7.55-7.47 (m, 2H), 7.40-7.36 (m, 1H), 7.25-7.19 (m, 6H), 5.11 (d, 1H, J = 14.4 Hz), 4.69 (d, 1H, J = 14.4 Hz), 2.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.3, 135.7, 135.0, 132.1, 129.51, 129.48, 128.6, 128.5, 128.2, 128.1, 127.2, 126.7, 125.3, 123.6, 56.0, 39.8; IR (neat) (cm⁻¹) 2928w, 1595w, 1456w, 1331s, 1147s, 1040m; HRMS (ESI): m/z calcd for C₁₈H₁₇NO₂SNa [M+Na]⁺ 334.0872, found 334.0874.



Aminonaphthalene **2j** (33.7 mg, 0.16 mmol) was prepared from *C*-terthered arene-ynamide **1j** (42.6 mg, 0.20 mmol) in 79% yield after stirring at rt for 10.0 min.

2j: $R_f = 0.30$ [1:1 petroleum ether/EtOAc]; white solid; mp = 118–119 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.84 (m, 3H), 7.58-7.46 (m, 4H), 4.62 (t, 2H, J = 7.8 Hz), 4.07 (t, 2H, J = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 134.7, 134.1, 130.0, 128.9, 128.8, 127.1, 126.7, 125.8, 124.7, 122.5, 62.7, 49.2; IR (neat) (cm⁻¹) 2988w, 1699w, 1488m, 1415s, 1081m; HRMS (ESI): m/z calcd for C₁₃H₁₁NO₂Na [M+Na]⁺ 236.0682, found 236.0692. Spectral data are in agreement with literature values.⁶



Amino-substituted dihydronaphthalene **2k** (70.9 mg, 0.18 mmol) was prepared from *C*-terthered arene-ynamide **1k** (77.9 mg, 0.20 mmol) in 91% yield after stirring at rt for 0.5 h.

2k: $R_f = 0.30$ [10:1 petroleum ether/EtOAc]; white solid; mp = 61–62 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, 2H, J = 7.9 Hz), 7.27-7.19 (m, 7H), 7.11-7.01 (m, 4H), 5.60 (t, 1H, J = 4.7 Hz), 4.59 (s, 2H), 2.63 (s, 2H), 2.40 (s, 3H), 2.20 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 136.7, 136.5, 136.21, 136.18, 132.3, 130.0, 129.5, 129.3, 128.3, 127.9, 127.8, 127.6, 127.4, 126.3, 123.6, 53.9, 27.3, 23.0, 21.6; IR (neat) (cm⁻¹) 2940w, 1634w, 1452w, 1336s, 1161m, 1061m; HRMS (ESI): m/z calcd for C₂₄H₂₃NO₂SNa [M+Na]⁺ 412.1342, found 412.1341.



Amino-substituted dihydronaphthalene **2l** (73.0 mg, 0.18 mmol) was prepared from *C*-terthered arene-ynamide **1l** (81.1 mg, 0.20 mmol) in 90% yield after stirring at rt for 0.5 h.

21: $R_f = 0.16$ [10:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.75 (m, 2H), 7.24-7.01 (m, 9H), 6.95-6.92 (m, 2H), 5.62 (t, 1H, J = 4.7 Hz), 4.58 (s, 2H), 3.84 (s, 3H), 2.64 (s, 2H), 2.21 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 136.5, 136.3, 136.2, 132.4, 131.3, 130.0, 129.9, 129.3, 128.3, 127.8, 127.6, 127.4, 126.4, 123.6, 114.0, 55.7, 53.9, 27.3, 23.0; IR (neat) (cm⁻¹) 2936w, 1734w, 1595m, 1342s, 1153s; HRMS (ESI): m/z calcd for C₂₄H₂₃NO₃SNa [M+Na]⁺ 428.1291, found 428.1284.



Amino-substituted dihydronaphthalene **2m** (68.9 mg, 0.17 mmol) was prepared from *C*-terthered arene-ynamide **1m** (82.0 mg, 0.20 mmol) in 84% yield after stirring at rt for 0.5 h.

2m: (68.9 mg, 84%); $R_f = 0.43$ [10:1 petroleum ether/EtOAc]; white solid; mp = 107–108 °C;¹H NMR (400 MHz, CDCl₃) δ 7.76-7.73 (m, 2H), 7.45-7.43 (m, 2H), 7.24-7.19 (m, 5H), 7.13-7.02 (m, 4H), 5.61 (t, 1H, J = 4.7 Hz), 4.63 (s, 1H), 4.58 (s, 1H), 2.66 (s, 2H), 2.23 (s, 2H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 139.3, 138.5, 137.2, 137.1, 136.9, 133.6, 130.5, 130.3, 130.1, 130.0, 129.0, 128.5, 128.2, 127.9, 126.7, 124.4, 55.0, 27.6, 23.4; IR (neat) (cm⁻¹) 3032w, 1583w, 1474w, 1339m, 1161m, 1090w; HRMS (ESI): m/z calcd for C₂₃H₂₀ClNO₂SNa [M+Na]⁺ 432.0795, found 432.0796.



Amino-substituted dihydronaphthalene 2n (69.0 mg, 0.16 mmol) was prepared from *C*-terthered arene-ynamide 1n (84.1 mg, 0.20 mmol) in 82% yield after stirring at rt for 0.25 h.

2n: $R_f = 0.23$ [10:1 petroleum ether/EtOAc]; yellow solid; mp = 126–127 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.29-8.27 (m, 2H), 7.97-7.94 (m, 2H), 7.26-7.21 (m, 5H), 7.14-7.03 (m, 3H), 6.97 (d, 1H, J = 7.5 Hz), 5.61 (t, 1H, J = 4.7 Hz), 4.78 (s, 1H), 4.54 (s, 1H), 2.69 (s, 2H), 2.26 (s, 2H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 151.1, 145.2, 137.1, 137.0, 136.7, 133.3, 130.9, 130.21, 130.16, 129.1, 128.7, 128.4, 128.0, 126.8, 125.1, 124.3, 55.2, 27.6, 23.5; IR (neat) (cm⁻¹) 2932w, 1526s, 1455w, 1350s, 1169s, 1091m; HRMS (ESI): m/z calcd for C₂₃H₂₀N₂O₄SNa [M+Na]⁺ 443.1036, found 443.1035.



Amino-substituted dihydronaphthalene **20** (53.9 mg, 0.17 mmol) was prepared from *C*-terthered arene-ynamide **10** (62.7 mg, 0.20 mmol) in 86% yield after stirring at rt for 0.25 h.

20: $R_f = 0.23$ [10:1 petroleum ether/EtOAc]; white solid; mp = 89–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.72 (m, 2H), 7.43-7.41 (m, 1H), 7.31 (d, 2H, J = 8.0 Hz), 7.22-7.10 (m, 3H), 5.57 (t, 1H, J = 4.7 Hz), 3.07 (s, 3H), 2.77 (t, 2H, J = 8.0 Hz), 2.44 (s, 3H), 2.32-2.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 139.4, 136.3, 135.2, 132.6, 129.5, 128.1, 128.0, 127.6, 126.74, 126.68, 123.5, 38.6, 27.4, 23.0, 21.7; IR (neat) (cm⁻¹) 2938w, 1453w, 1339s, 1154s, 1008s; HRMS (ESI): m/z calcd for C₁₈H₁₉NO₂SNa [M+Na]⁺ 336.1029, found 336.1029.



Amino-substituted dihydronaphthalene **2p** (62.6 mg, 0.18 mmol) was prepared from *C*-terthered arene-ynamide **1p** (71.1 mg, 0.20 mmol) in 88% yield after stirring at rt for 0.25 h.

2p: $R_f = 0.62$ [10:1 petroleum ether/EtOAc]; white solid; mp = 57–58 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.71 (m, 2H), 7.33-7.27 (m, 3H), 7.17-7.09 (m, 3H), 5.63 (t, 1H, J = 4.7 Hz), 3.51 (s, 1H), 3.28 (s, 1H), 2.78 (q, 2H, J = 8.9 Hz), 2.42 (s, 3H), 2.36-2.29 (m, 2H), 1.52-1.44 (m, 2H), 1.32-1.23 (m, 2H), 0.84 (t, 3H, J = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 137.0, 136.34, 136.29, 133.2, 129.5, 128.5, 128.0, 127.8, 127.5, 126.6, 123.8, 50.5, 30.6, 27.5, 23.2, 21.7, 20.1, 13.9; IR (neat) (cm⁻¹) 2953w, 1462w, 1339s, 1154s, 1088m, 1034m; HRMS (ESI): m/z calcd for C₂₁H₂₅NO₂SNa [M+Na]⁺ 378.1498, found 378.1499.



Amino-substituted dihydronaphthalene 2q (58.4 mg, 0.17 mmol) was prepared from *C*-terthered arene-ynamide 1q (67.9 mg, 0.20 mmol) in 86% yield after stirring at rt for 20.0 min.

2q: $R_f = 0.30$ [10:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.72 (m, 2H), 7.33-7.28 (m, 3H), 7.18-7.08 (m, 3H), 5.81-5.71 (m, 1H), 5.62 (t, 1H, J = 4.7 Hz), 5.07-5.03 (m, 2H), 4.04 (d, 2H, J = 6.1 Hz), 2.77 (t, 2H, J = 8.6 Hz), 2.43 (s, 3H), 2.31 (q, 2H, J =7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 136.5, 136.42, 136.40, 133.0, 129.6, 129.3, 128.0, 127.9, 127.5, 126.6, 123.6, 119.1, 53.3, 27.4, 23.1, 21.7, one carbon missing due to overlap; IR (neat) (cm⁻¹) 2831w, 1598w, 1451w, 1343s, 1161s, 1036m; HRMS (ESI): m/z calcd for C₂₀H₂₁NO₂SNa [M+Na]⁺ 362.1185, found 362.1181.



Amino-substituted dihydronaphthalene 2r (64.6 mg, 0.17 mmol) was prepared from *C*-terthered arene-ynamide 1r (75.1 mg, 0.20 mmol) in 86% yield after stirring at rt for 0.5 h.

2r: $R_f = 0.27$ [10:1 petroleum ether/EtOAc]; pale yellow solid; mp = 150–151 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.61 (m, 2H), 7.56 (d, 1H, J = 7.5 Hz), 7.47-7.45 (m, 2H), 7.29-7.25 (m, 2H), 7.24-7.04 (m, 6H), 5.98 (t, 1H, J = 4.7 Hz), 2.75 (t, 2H, J = 8.1 Hz), 2.42-2.36 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 140.5, 138.4, 137.7, 136.7, 132.7, 129.6, 129.2, 129.0, 128.01, 127.98,

127.6, 127.1, 127.0, 126.7, 123.8, 27.2, 23.3, 21.7; IR (neat) (cm⁻¹) 2927w, 1484w, 1349s, 1165s, 1092s; HRMS (ESI): m/z calcd for C₂₃H₂₁NO₂SNa [M+Na]⁺ 398.1185, found 398.1181.



Amino-substituted dihydronaphthalene **2s** (57.0 mg, 0.18 mmol) was prepared from *C*-terthered arene-ynamide **1s** (62.7 mg, 0.20 mmol) in 91% yield after stirring at rt for 0.25 h.

2s: $R_f = 0.32$ [4:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.27 (m, 5H), 7.24-7.11 (m, 4H), 5.92 (t, 1H, J = 4.7 Hz), 4.94 (s, 1H), 4.36 (s, 1H), 2.92 (s, 3H), 2.74 (t, 2H, J = 8.0 Hz), 2.34 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 136.5, 136.2, 131.8, 130.2, 129.4, 128.6, 128.11, 128.09, 127.9, 126.8, 123.1, 53.4, 40.5, 27.3, 23.1; IR (neat) (cm⁻¹) 2934w, 1495w, 1332s, 1147s, 1057m; HRMS (ESI): m/z calcd for C₁₈H₁₉NO₂SNa [M+Na]⁺ 336.1029, found 336.1028.



Amino-substituted dihydronaphthalene 2t (36.6 mg, 0.17 mmol) and 3,4-dihydronaphthalen-1(2*H*)-one 2t' (3.2 mg, 0.02 mmol) were prepared from *C*-terthered arene-ynamide 1t (43.1 mg, 0.20 mmol) in 85% yield and 11% yield, respectively, after stirring at rt for 0.5 h.

2t: $R_f = 0.36$ [1:1 petroleum ether/EtOAc]; pale yellow oil; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.21-7.18 (m, 4H), 6.13 (t, 1H, J = 4.7 Hz), 4.50 (t, 2H, J = 7.8 Hz), 3.91 (t, 2H, J = 7.8 Hz), 2.81-2.76 (m, 2H), 2.40-2.35 (m, 2H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 157.2, 137.3, 135.8, 131.8, 128.5, 128.4, 127.2, 125.1, 123.2, 62.8, 48.0, 27.9, 23.1; IR (neat) (cm⁻¹) 2933w, 1744s, 1484w, 1409m, 1034m; HRMS (ESI): m/z calcd for C₁₃H₁₃NO₂Na [M+Na]⁺ 238.0838, found 238.0834. Spectral data are in agreement with literature values.⁷

2t': $R_f = 0.42$ [10:1 petroleum ether/EtOAc]; white solid; mp = 58–59 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, 1H, J = 7.8, 0.9 Hz), 7.47 (td, 1H, J = 7.5, 1.4 Hz), 7.33-7.25 (m, 2H), 2.98 (t, 2H, J = 6.2 Hz), 2.67 (t, 2H, J = 6.5 Hz), 2.18-2.12 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 144.7, 133.6, 132.8, 129.0, 127.4, 126.8, 39.4, 29.9, 23.5; IR (neat) (cm⁻¹) 3066w, 2867w, 1600s, 1323s, 1115m; HRMS (ESI): m/z calcd for C₁₀H₁₁O [M+H]⁺ 147.0804, found 147.0806. Spectral data are in agreement with literature values.⁸



Amino-2*H*-chromene **2u** (63.4 mg, 0.16 mmol) was prepared from *C*-terthered arene-ynamide **1u** (78.3 mg, 0.20 mmol) in 81% yield after stirring at rt for 0.5 h.

2u: $R_f = 0.22$ [10:1 petroleum ether/EtOAc]; white solid; mp = 74–75 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.82-7.80 (m, 2H), 7.45 (d, 2H, J = 8.0 Hz), 7.33-7.19 (m, 5H), 7.10-7.04 (m, 2H), 6.76 (dt, 1H, J = 7.6, 0.9 Hz), 6.67 (dd, 1H, J = 8.1, 1.1 Hz), 5.51 (t, 1H, J = 3.9 Hz), 4.69 (d, 2H, J = 3.7 Hz), 4.61 (s, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 155.9, 144.7, 137.0, 136.7, 134.9, 130.5, 130.3, 129.9, 129.1, 128.8, 128.5, 125.2, 123.6, 122.9, 121.6, 116.3, 65.9, 54.8, 21.4; IR (neat) (cm⁻¹) 2921w, 1602w, 1452w, 1348m, 1159m, 1091m; HRMS (ESI): m/z calcd for C₂₃H₂₁NO₃SNa [M+Na]⁺ 414.1134, found 414.1136.



Amino-2*H*-chromene 2v (65.2 mg, 0.16 mmol) was prepared from *C*-terthered arene-ynamide 1v (81.5 mg, 0.20 mmol) in 80% yield after stirring at rt for 0.5 h.

2v: $R_f = 0.31$ [4:1 petroleum ether/EtOAc]; colourless oil; ¹H NMR (400 MHz, CD₃COCD₃) δ 7.88-7.85 (m, 2H), 7.34-7.32 (m, 2H), 7.28-7.21 (m, 3H), 7.16-7.13 (m, 3H), 7.06 (dt, 1H, J = 7.8, 1.5 Hz), 6.78 (dt, 1H, J = 7.6, 0.9 Hz), 6.67 (dd, 1H, J = 8.0, 1.2 Hz), 5.53 (t, 1H, J = 3.9 Hz), 4.69 (d, 2H, J = 3.4 Hz), 4.60 (s, 2H), 3.93 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃) δ 164.2, 155.9, 137.1, 135.0, 131.0, 130.2, 129.9, 129.0, 128.5, 125.3, 123.4, 123.0, 121.6, 116.2, 115.0, 65.8, 56.1, 54.7, one carbon missing due to overlap; IR (neat) (cm⁻¹) 2925w, 1594m, 1496m, 1259s, 1153s, 1067m; HRMS (ESI): m/z calcd for C₂₃H₂₁NO₄SNa [M+Na]⁺ 430.1083, found 430.1076.



Amino-2*H*-chromene **2w** (73.5 mg, 0.17 mmol) was prepared from *C*-terthered arene-ynamide **1w** (84.5 mg, 0.20 mmol) in 87% yield after stirring at rt for 10.0 min.

2w: $R_f = 0.16$ [10:1 petroleum ether/EtOAc]; yellow solid; mp = 133–134 °C; ¹H NMR (400 MHz, CD₃COCD₃) δ 8.50-8.46 (m, 2H), 8.22-8.19 (m, 2H), 7.36-7.24 (m, 6H), 7.09-7.04 (m, 1H), 6.78 (dt, 1H, *J* = 7.6, 0.9 Hz), 6.69 (dd, 1H, *J* = 8.1, 1.2 Hz), 5.61 (t, 1H, *J* = 3.9 Hz), 4.73 (s, 4H); ¹³C NMR

(100 MHz, CD₃COCD₃) δ 155.9, 151.3, 144.8, 136.5, 134.4, 130.6, 130.2, 130.0, 129.2, 128.8, 125.2, 125.0, 124.5, 122.4, 121.7, 116.4, 65.8, 55.2; IR (neat) (cm⁻¹) 3100w, 1529s, 1347s, 1162s, 1013m; HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_5SNa [M+Na]^+$ 445.0829, found 445.0820.

Ph catalyst (0.5 equiv) CH_2Cl_2 , temp 4a 5a 6a								
	Entry ^a	Catalyst	CH_2Cl_2 (mL)	Temp (°C)	Time (h)	Yield (%) ^b 4a and 5a	Yield (%) ^b 6a	
	1	TfOH	0.5	rt	0.5	88 (1:1)	5	
	2	Tf_2O	0.5	60	3.5	90 (1:1)	0	
	3	Tf_2O	1.0	60	3.5	99 (1:1)	0	
	4	TfOH	1.0	rt	0.5	91 (1:1)	6	

1.3 Condition Optimization of the Hydroarylation (Table 2).

Ρh

^aUnless otherwise noted, reactions were carried out using **3a** (0.20 mmol) with catalyst (0.10 mmol) in CH₂Cl₂ under N₂. ^bIsolated yields. The ratio of **4a** to **5a** in parenthesis was determined by ¹H NMR spectroscopy of the unpurified reaction mixture.

To an oven-dried sealed tube was added methylene-tethered arylalkyne 3a (41.3 mg, 0.20 mmol), CH₂Cl₂ and catalyst (0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at the specified temperature. After the reaction was judged to be complete by TLC, the reaction mixture was filtered through a pad of silica gel and concentrated in vacuo. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford an unseparable mixture of 4a and 5a.

1.4 Hydroarylation of Methylene-Tethered Arylalkynes (Table 3).

tetrahydronaphthalenes 5a,¹⁸ (5b, 5d, 5g, 5h, 5j)¹⁹, 5f,²⁰ 5k,²¹ 5m,²² dihydronaphalenes $6b^{23}$ and $6d^{24}$ were known compounds, the data were matched with reported values. Tetrahydronaphthalenes 5c, 5e, 5i, 5l, 5n, 5o, dihydronaphalenes 6c and 6e were new compounds.



To an oven-dried sealed tube was added methylene-tethered arylalkyne **3a** (41.3 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, 0.20 *M*), and Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford an unseparable mixture of **4a** and **5a** (41.2 mg, 0.20 mmol) in 99% yield.



4a and **5a**: $R_f = 0.63$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.88 (m, 2H), 7.85 (d, 1H, J = 8.2 Hz), 7.52-7.39 (m, 9H), 7.28-7.24 (m, 2H), 7.20-7.18 (m, 1H), 7.12-7.08 (m, 4H), 7.03-6.99 (m, 1H), 6.83 (d, 1H, J = 8.0 Hz), 4.10 (t, 1H, J = 6.7 Hz), 2.95-2.80 (m, 2H), 2.17-2.12 (m, 1H), 1.93-1.82 (m, 2H), 1.77-1.72 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 140.9, 140.4, 139.5, 137.7, 133.9, 131.8, 130.3, 130.2, 129.1, 129.0, 128.42, 128.39, 127.8, 127.4, 127.1, 126.2, 126.10, 126.06, 125.9, 125.8, 125.5, 45.8, 33.4, 30.0, 21.1, two carbons missing due to overlap, overlapped signals at 130.2 and 128.38 ppm. Spectral data are in agreement with literature values.^{9,18}



To a solution of **3b** (44.1 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4b** and **5b** (44.5 mg, 0.20 mmol) in 99% yield.

4b and **5b**: $R_f = 0.48$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.82 (m, 3H), 7.52-7.38 (m, 6H), 7.30-7.28 (m, 2H), 7.11-6.97 (m, 7H), 6.84 (d, 1H, J = 7.5 Hz), 4.07 (t, 1H, J = 6.8 Hz), 2.94-2.78 (m, 2H), 2.45 (s, 3H), 2.31 (s, 3H), 2.17-2.10 (m, 1H), 1.93-1.69 (m, 3H); ¹³C

NMR (100 MHz, CDCl₃) δ 144.7, 140.4, 139.8, 138.0, 137.7, 137.1, 135.6, 134.0, 131.9, 130.3, 130.1, 129.14, 129.10, 128.9, 128.4, 127.6, 127.0, 126.3, 126.1, 126.0, 125.9, 125.8, 125.6, 45.4, 33.5, 30.0, 21.4, 21.19, 21.17, one carbon missing due to overlap, overlapped signal at 129.10 ppm. Spectral data are in agreement with literature values.^{9,19}



To a solution of **3c** (56.5 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4c** and **5c** (51.5 mg, 0.18 mmol) in 92% yield.

4c and **5c**: $R_f = 0.27$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, 1H, J = 8.4 Hz), 7.91-7.84 (m, 2H), 7.72-7.66 (m, 4H), 7.58-7.27 (m, 16H), 7.16-7.01 (m, 5H), 6.89 (d, 1H, J = 7.7 Hz), 4.15 (t, 1H, J = 6.7 Hz), 2.94-2.78 (m, 2H), 2.17-2.10 (m, 1H), 1.93-1.69 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 141.2, 141.0, 140.3, 140.0, 139.9, 139.4, 139.0, 137.8, 134.0, 131.8, 130.7, 130.4, 129.4, 129.2, 129.0, 128.9, 128.5, 127.9, 127.6, 127.3, 127.2, 127.1, 126.3, 126.2, 126.1, 126.0, 125.9, 125.6, 45.4, 33.4, 30.0, 21.1, three carbons missing due to overlap, overlapped signals at 129.0, 127.3 and 127.2 ppm; IR (neat) (cm⁻¹) 3054w, 3024w, 2935w, 1590m, 1578m, 1505m, 1485s, 1393s, 1175m, 1005s; HRMS of **4c** (ESI): m/z calcd for C₂₂H₁₆Na [M+Na]⁺ 303.1144, found 303.1152; HRMS of **5c** (ESI): m/z calcd for C₂₂H₁₉ [M-H]⁻ 283.1492, found 283.1485.



To a solution of **3d** (47.3 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered

through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [gradient eluent: 30:1 petroleum ether/EtOAc] to afford the desired mixture of **4d** and **5d** (38.8 mg, 0.17 mmol) in 82% yield.

4d and 5d: $R_f = 0.51$ [20:1 petroleum ether/EtOAc]; pale yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.81 (m, 3H), 7.52-7.39 (m, 6H), 7.13-6.98 (m, 7H), 6.85-6.79 (m, 3H), 4.05 (t, 1H, J = 6.7 Hz), 3.87 (s, 3H), 3.77 (s, 3H), 2.94-2.78 (m, 2H), 2.16-2.09 (m, 1H), 1.92-1.68 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 157.9, 140.0, 139.9, 139.8, 137.7, 134.0, 133.3, 132.0, 131.3, 130.3, 129.9, 129.1, 128.4, 127.5, 127.1, 126.2, 126.1, 126.0, 125.9, 125.8, 125.6, 113.9, 113.7, 55.5, 55.4, 44.9, 33.5, 29.9, 21.1. Spectral data are in agreement with literature values.^{10,19}



To a solution of 3e (57.2 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of 4e and 5e (57.2 mg, 0.20 mmol) in 99% yield.

4e and 5e: $R_f = 0.47$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.82 (m, 3H), 7.62-7.58 (m, 2H), 7.52-7.34 (m, 8H), 7.13-7.11 (m, 2H), 7.04-6.99 (m, 1H), 6.96-6.94 (m, 2H), 6.79 (d, 1H, J = 7.7 Hz), 4.06 (t, 1H, J = 6.4 Hz), 2.93-2.78 (m, 2H), 2.17-2.09 (m, 1H), 1.89-1.68 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 139.8, 139.1, 138.8, 137.7. 133.9, 131.9, 131.6, 131.49, 131.45, 130.7, 130.2, 129.2, 128.5, 128.2, 127.0, 126.4, 126.3, 126.1, 125.9, 125.8, 125.5, 121.6, 119.9, 45.2, 33.3, 29.8, 21.0; IR (neat) (cm⁻¹) 2924w, 2878w, 1591m, 1507m, 1343s, 1111s; HRMS (ESI) of 4e: m/z calcd for C₁₆H₁₂Br [M+H]⁺ 283.0117, found 283.0115; HRMS (ESI) of 5e: m/z calcd for C₁₆H₁₆Br [M+H]⁺ 287.0430, found 287.0427.



To a solution of **3f** (44.9 mg, 0.2 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4f** and **5f** (44.8 mg, 0.20 mmol) in 99% yield.

4f and 5f: $R_f = 0.53$ [petroleum ether]; white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.82 (m, 3H), 7.52-7.36 (m, 8H), 7.24-7.20 (m, 2H), 7.12-7.09 (m, 2H), 7.04-6.98 (m, 3H), 6.79 (d, 1H, J = 7.8 Hz), 4.08 (t, 1H, J = 6.6 Hz), 2.93-2.78 (m, 2H), 2.17-2.08 (m, 1H), 1.89-1.67 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 139.3, 139.1, 138.9, 137.7, 133.9, 133.5, 131.8, 131.6, 131.5, 130.3, 130.2, 129.2, 128.6, 128.53, 128.51, 128.2, 127.1, 126.4, 126.3, 126.1, 125.9, 125.8, 125.5, 45.2, 33.4, 29.8, 21.0. Spectral data are in agreement with literature values.^{12,20}



To a solution of **3g** (44.9 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4g** and **5g** (44.8 mg, 0.20mmol) in 99% yield.

4g and **5g**: $R_f = 0.50$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.82 (m, 3H), 7.52-7.37 (m, 6H), 7.18-7.10 (m, 4H), 7.04-7.01 (m, 3H), 6.96-6.92 (m, 2H), 6.80 (d, 1H, J = 7.7 Hz), 4.08 (t, 1H, J = 6.7 Hz), 2.93-2.78 (m, 2H), 2.16-2.09 (m, 1H), 1.90-1.68 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.4 (d, J = 244.6 Hz), 161.4 (d, J = 243.8 Hz), 143.3 (d, J = 3.2 Hz), 139.3, 137.7, 136.8 (d, J = 3.5 Hz), 134.0, 131.8, 131.7 (d, J = 7.9 Hz), 130.3 (d, J = 7.7 Hz), 130.2, 129.2,

128.5,128.0, 127.2, 126.3, 126.2, 126.0, 125.93, 125.88, 125.5, 115.4 (d, J = 21.2 Hz), 115.2, 115.0, 45.0, 33.5, 29.9, 21.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.5, -117.6. Spectral data are in agreement with literature values.^{9,19}



To a solution of **3h** (54.9 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 30. h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4h** and **5h** (51.1 mg, 0.19 mmol) in 93% yield.

4h and **5h**: $R_f = 0.28$ [petroleum ether]; white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.87 (m, 2H), 7.80 (d, 1H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 7.9 Hz), 7.54-7.38 (m, 6H), 7.20-7.11 (m, 4H), 7.05-7.01 (m, 1H), 6.77 (d, 1H, J = 7.6 Hz), 4.17 (t, 1H, J = 6.7 Hz), 2.95-2.80 (m, 2H), 2.20-2.12 (m, 1H), 1.90-1.69 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.8 (q, J = 1.2 Hz), 144.6 (q, J = 1.2 Hz), 138.9, 138.5, 137.8. 134.0, 131.4, 130.6, 130.2, 129.6 (q, J = 32.3 Hz), 129.4, 129.3, 128.61, 128.57, 128.4 (q, J = 32.0 Hz), 127.2, 126.6, 126.5, 126.2, 126.0, 125.7, 125.5, 125.42 (q, J = 3.7 Hz), 125.36 (q, J = 3.9 Hz), 124.54 (q, J = 270.1 Hz), 124.52 (q, J = 270.3 Hz), 45.6, 33.3, 29.8, 20.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.2, -62.3. Spectral data are in agreement with literature values.^{13,19}



To a solution of **3i** (50.3 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column

chromatography [isocratic eluent: 30:1 petroleum ether/EtOAc] to afford the desired mixture of **4i** and **5i** (45.0 mg, 0.18 mmol) in 90% yield.

4i and **5i**: $R_f = 0.50$ [20:1 petroleum ether/EtOAc]; pale yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.36-8.33 (m, 2H), 8.14-8.12 (m, 2H), 7.95-7.92 (m, 2H), 7.78 (d, 1H, J = 8.4 Hz), 7.68-7.64 (m, 2H), 7.57-7.41 (m, 4H), 7.25-7.23 (m, 2H), 7.17-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.75 (d, 1H, J = 7.6 Hz), 4.24 (t, 1H, J = 6.0 Hz), 2.97-2.82 (m, 2H), 2.24-2.17 (m, 1H), 1.90-1.72 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.5, 147.8, 147.3, 146.5, 137.9, 137.7, 133.9, 131.0, 130.1, 129.7, 129.5, 129.1, 128.7, 127.3, 126.9, 126.7, 126.4, 126.1, 125.5, 125.3, 123.74, 123.72, 45.7, 33.2, 29.7, 20.8, two carbons missing due to overlap, overlapped signals at 131.0 and 129.7 ppm; IR (neat) (cm⁻¹) 3072w, 3056w, 2920w, 2856w, 1597s, 1514s, 1488s, 1347s, 1106w, 1014w; HRMS of **4i** (ESI): m/z calcd for C₁₆H₁₂NO₂ [M+H]⁺ 250.0863; found 250.0863; HRMS of **5i**: m/z calcd for C₁₆H₁₆NO₂ [M+H]⁺ 254.1176, found 254.1168.



To a solution of **3j** (44.1 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4j** and **5j** (44.1 mg, 0.20 mmol) in 99% yield.

4j and **5j**: $R_f = 0.27$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.82 (m, 3H), 7.51-7.22 (m, 8H), 7.17-7.08 (m, 3H), 7.03-6.99 (m, 2H), 6.93-6.83 (m, 3H), 4.06 (t, 1H, J = 6.8 Hz), 2.95-2.79 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.19-2.10 (m, 1H), 1.94-1.67 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 140.8, 140.5, 139.7, 138.0, 137.9, 137.6, 133.9, 131.8, 130.9, 130.4, 129.7, 129.1, 128.4, 128.28, 128.26, 128.1, 127.7, 127.3, 127.0, 126.9, 126.3, 126.15, 126.11, 126.0, 125.9, 125.8, 125.5, 45.8, 33.5, 30.0, 21.70, 21.65, 21.3. Spectral data are in agreement with literature values.^{14,19}



To a solution of **3k** (42.4 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4k** and **5k** (8.9 mg, 0.04 mmol) in 21% yield.

4k and **5k**: $R_f = 0.32$ [petroleum ether]; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.19 (m, 2H), 7.92-7.82 (m, 2H), 7.85 (d, 2H, J = 8.2 Hz), 7.57 (dd, 2H, J = 7.1 Hz, 1.3 Hz), 7.53-7.47 (m, 6H), 7.43 (dd, 2H, J = 5.1 Hz, 1.3 Hz), 7.26 (d, 1H, J = 1.2 Hz), 7.25 (d, 1H, J = 1.2 Hz), 7.19 (d, 1H, J = 3.5 Hz), 7.18 (d, 1H, J = 3.5 Hz), 7.16-7.14 (m, 1H), 7.08-7.03 (m, 2H), 7.13-7.09 (m, 2H), 6.91 (dd, 1H, J = 5.1 Hz, 3.4 Hz), 6.69 (dt, 1H, J = 3.4 Hz, 1.0 Hz), 4.40 (t, 1H, J = 6.1 Hz), 2.92-2.78 (m, 2H), 2.23-2.16 (m, 1H), 2.05-1.96 (m, 1H), 1.96-1.87 (m, 1H), 1.82-1.73 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 141.9, 138.9, 137.1, 134.0, 132.6, 132.0, 130.2, 129.3, 128.6, 128.5, 128.4, 127.6, 127.4, 126.6, 126.53, 126.51, 126.2, 125.9, 125.80, 125.79, 125.4, 125.3, 123.7, 40.6, 33.5, 29.6, 20.6. Spectral data are in agreement with literature values.^{15,21}



To a solution of **31** (44.1 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **41** and **51** (43.2 mg, 0.20 mmol) in 98% yield.

41 and 51: $R_f = 0.44$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, 2H, J =

8.3 Hz), 7.66 (s, 1H), 7.49-7.40 (m, 6H), 7.38-7.25 (m, 4H), 7.20-7.18 (m, 1H), 7.08 (d, 2H, J = 7.2 Hz), 7.02 (d, 1H, J = 7.7 Hz), 6.93 (d, 1H, J = 7.6 Hz), 6.66 (s, 1H), 4.07 (t, 1H, J = 6.7 Hz), 2.90-2.74 (m, 2H), 2.42 (s, 3H), 2.21-2.09 (m, 1H), 2.17 (s, 3H), 1.87-1.80 (m, 2H), 1.75-1.66 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 141.1, 139.7, 139.2, 135.9, 135.2, 134.7, 132.2, 131.9, 130.8, 130.2, 129.03, 129.01, 128.4, 128.34, 128.29, 128.2, 127.5, 127.3, 127.2, 127.0, 126.0, 125.0, 124.6, 45.7, 33.5, 29.6, 22.1, 21.15, 21.07; IR (neat) (cm⁻¹) 3050w, 3027w, 2925w, 2857w, 1602w, 1492s, 1447s, 1367s, 1028w; HRMS of **4I** (ESI): m/z calcd for C₁₇H₁₅ [M+H]⁺ 219.1168, found 219.1177; HRMS of **5I** (ESI): m/z calcd for C₁₇H₁₉ [M+H]⁺ 223.1482, found 223.1473.



To a solution of **3m** (47.3 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 12 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4m** and **5m** (44.4 mg, 0.19 mmol) in 94% yield.

4m and **5m**: $R_f = 0.33$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.75 (m, 2H), 7.51-7.46 (m, 4H), 7.42-7.36 (m, 3H), 7.28-7.26 (m, 3H), 7.20-7.14 (m, 2H), 7.09 (d, 2H, J = 7.1 Hz), 7.04 (d, 1H, J = 8.4 Hz), 6.70 (dd, 1H, J = 8.4 Hz, 2.7Hz), 6.38 (d, 1H, J = 2.6 Hz), 4.07 (t, 1H, J = 6.6 Hz), 3.73 (s, 3H), 3.62 (s, 3H), 2.87-2.72 (m, 2H), 2.15-2.09 (m, 1H), 1.89-1.80 (m, 2H), 1.75-1.65 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 157.6, 147.4, 141.1, 140.5, 139.2, 132.8, 130.02, 129.96, 129.9, 129.5, 129.0, 128.5, 128.4, 127.7, 127.5, 127.3, 126.1, 123.3, 118.4, 115.0, 112.4, 104.6, 55.32, 55.28, 46.0, 33.4, 29.1, 21.2, one carbon missing due to overlap, overlapped signal at 129.96 ppm. Spectral data are in agreement with literature values.^{16,22}



To a solution of **3n** (48.1 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 µL,

0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 17.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **4n** and **5n** (43.3 mg, 0.18 mmol) in 90% yield.

4n and **5n**: $R_f = 0.53$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, 1H, J = 2.1 Hz), 7.83 (d, 1H, J = 2.7 Hz), 7.80 (d, 1H, J = 1.9 Hz), 7.52-7.40 (m, 8H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 7.07-7.02 (m, 4H), 6.82 (s, 1H), 4.04 (t, 1H, J = 6.8 Hz), 2.89-2.73 (m, 2H), 2.15-2.08 (m, 1H), 1.91-1.79 (m, 2H), 1.76-1.66 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 141.4, 140.2, 139.8, 136.1, 132.5, 132.19, 132.16, 131.3, 130.4, 130.1, 130.0, 129.9, 128.9, 128.63, 128.56, 128.1, 127.7, 127.6, 126.9, 126.4, 126.3, 125.8, 125.0, 45.7, 33.1, 29.4, 20.9; IR (neat) (cm⁻¹) 3058w, 3020w, 2936w, 2852w, 1589s, 1492s, 1484s, 1447s, 1122s, 1082w; HRMS of **4n** (ESI): m/z calcd for C₁₆H₁₁NaCl [M+Na]⁺ 261.0441, found 261.0448; HRMS of **5n** (ESI): m/z calcd for C₁₆H₁₆Cl [M+H]⁺ 243.0935, found 243.0939.



To a solution of **30** (57.0 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel and concentrated *in vacuo*. After the ratio of the crude product was confirmed by ¹H NMR spectroscopy, the mixture was purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired mixture of **40** and **50** (52.5 mg, 0.18 mmol) in 92% yield.

40 and **50**: $R_f = 0.52$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, 1H, J = 8.6 Hz), 7.85 (d, 1H, J = 8.5 Hz), 7.78 (d, 1H, J = 7.4 Hz), 7.62 (dd, 1H, J = 8.5, 7.1 Hz), 7.50-7.39 (m, 7H), 7.28-7.17 (m, 4H), 7.05 (d, 2H, J = 7.1 Hz), 6.89 (t, 1H, J = 7.7 Hz), 6.80 (d, 1H, J = 7.7 Hz), 4.11 (t, 1H, J = 6.5 Hz), 2.84 (t, 2H, J = 6.5 Hz), 2.13-2.05 (m, 1H), 1.93-1.87 (m, 2H), 1.79-1.70 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.0, 142.2, 140.9, 140.5, 137.2, 133.2, 132.4, 130.4, 130.2, 130.1, 129.7, 128.9, 128.48, 128.45, 128.0, 127.6, 127.0, 126.91, 126.89, 126.33,

126.29, 125.9, 123.4, 46.1, 32.6, 30.8, 20.7, one carbon missing due to overlap, overlapped signal at 126.29 ppm; IR (neat) (cm⁻¹) 3055w, 3025w, 2930w, 2856w, 1591w, 1555s, 1490s, 1450s, 1391s, 1119w, 1029w; HRMS of **4o** (ESI): m/z calcd for $C_{16}H_{12}Br [M+H]^+$ 283.0117, found 283.0126; HRMS of **5o** (ESI): m/z calcd for $C_{16}H_{16}Br [M+H]^+$ 287.0430, found 287.0436.



To an oven-dried sealed tube was added **3p** (57.2 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*) and Tf_2O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 7.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo* and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **6b** (57.1 mg, 0.20 mmol) in 99% yield.



6b: $R_f = 0.50$ [petroleum ether]; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, 1H, J = 8.0, 1.1 Hz), 7.33 (td, 1H, J = 7.4, 1.2 Hz), 7.27 (dd, 1H, J = 7.5, 1.9 Hz), 7.21-7.17 (m, 2H), 7.13 (td, 1H, J = 7.3, 1.3 Hz), 7.05 (td, 1H, J = 7.5, 1.4 Hz), 6.61 (d, 1H, J = 7.5 Hz), 5.97 (t, 1H, J = 4.5 Hz), 2.99-2.81 (m, 2H), 2.52-2.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 139.6, 135.8, 134.6, 132.9, 131.8, 129.0, 128.9, 127.7, 127.5, 127.2, 126.5, 124.9, 124.2, 28.1, 23.6. Spectral data are in agreement with literature values.²³



To a solution of **3q** (46.9 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 4.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered

through a pad of silica gel, concentrated *in vacuo* and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired product **6c** (46.0 mg, 0.19 mmol) in 98% yield.

6c: $R_f = 0.45$ [petroleum ether]; colorless oil; ¹H NMR(400MHz,CDCl₃) δ 7.18-7.01 (m, 6H), 6.64 (d, 1H, J = 7.5 Hz), 5.93-5.90 (m, 1H), 2.91-2.84 (m, 2H), 2.42-2.38 (m, 2H), 2.36 (s, 3H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 137.6, 136.9, 136.5, 136.0, 135.5, 130.8, 130.1, 127.8, 127.6, 126.9, 126.6, 126.5, 125.0, 28.4, 23.6, 21.3, 20.0; IR (neat) (cm⁻¹) 2932w, 2926w, 2829w, 2358s, 1748m, 1483m, 1448m, 1376s, 1253s, 1151s, 1099s; HRMS (ESI): m/z calcd for C₁₈H₁₉ [M+H]⁺ 235.1481, found 235.1477.



To a solution of $3\mathbf{r}$ (51.3 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo* and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford the desired product **6d** (51.1 mg, 0.20 mmol) in 99% yield.

6d: $R_f = 0.42$ [petroleum ether]; white solid; mp = 116–117 °C; ¹H NMR(400MHz,CDCl₃) δ 7.83 (t, 2H, J = 8.5 Hz), 7.73 (d, 1H, J = 8.5 Hz), 7.50-7.37 (m, 3H), 7.33-7.29 (m, 1H), 7.20 (d, 1H, J = 7.3 Hz), 7.09 (td, 1H, J = 7.4, 1.1 Hz), 6.91 (t, 1H, J = 7.5 Hz), 6.52 (d, 1H, J = 7.6 Hz), 6.11 (t, 1H, J = 4.5 Hz), 3.08-2.89 (m, 2H), 2.53-2.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.5, 136.0, 135.7, 132.5, 129.5, 128.3, 127.8, 127.6, 127.3, 127.1, 126.58, 126.55, 125.90, 125.85, 125.8, 125.7, 28.4, 23.8. Spectral data are in agreement with literature values.²⁴



To a solution of **3s** (46.2 mg, 0.20 mmol) in CH₂Cl₂ (1.0 mL, 0.20 *M*) was added Tf₂O (16.8 μ L, 0.10 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 24 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered

through a pad of silica gel, concentrated *in vacuo* and purified by flash silica gel column chromatography [isocratic eluent: 30:1 petroleum ether/EtOAc] to afford the desired product **6e** (40.2 mg, 0.17 mmol) in 87% yield.

6e: $R_f = 0.28$ [20:1 petroleum ether/EtOAc]; white solid; mp = 161–162 °C; ¹H NMR (400MHz, CDCl₃) δ 7.67 (d, 2H, J = 8.4 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.22-7.10 (m, 3H), 6.89 (d, 1H, J = 7.5 Hz), 6.15 (t, 1H, J = 4.8 Hz), 2.86 (t, 2H, J = 7.9 Hz), 2.46-2.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 139.0, 136.9, 134.2, 132.3, 129.9, 129.5, 128.0, 127.7, 126.6, 125.2, 119.2, 111.0, 28.2, 23.7; IR (neat) (cm⁻¹) 3402w, 3023w, 2947w, 2877w, 2823w, 2224m, 1604m, 1500m, 1448m, 1402m, 1273s, 1179s, 1108s, 1020s; HRMS (ESI): m/z calcd for C₁₇H₁₄N [M+H]⁺ 232.1121, found 232.1119.

1.5 Applications toward 1-Aryl Naphthalene Syntheses (Table 4).

Naphthalenes (4a, 4b, 4g),⁹ (4c, 4d),¹⁰ (4e, 4i),¹¹ 4f,¹² 4h,¹³ 4j,¹⁴ 4k,¹⁵ (4l, 4m, 4n),¹⁶ 4o¹⁷ 4p²⁵ 4q,²⁶ 4r,²⁷ and 4s²⁸ were known compounds,

the data were matched with reported values.

A. Ar Ar DDQ (1.0 equiv)
4 5
$$CH_2Cl_2, 60^{\circ}C$$

To an oven-dried sealed tube was added the mixture of **4a** and **5a** (41.2 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4a** (40.4 mg, 0.20 mmol) in 98% yield.



4a: $R_f = 0.63$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dt, 2H, J = 8.2, 1.6 Hz), 7.84 (m, 1H), 7.52-7.39 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 140.4, 133.9, 131.8, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 125.9, 125.5, two carbons missing due to overlap, overlapped signals at 130.2 and 128.4 ppm; Spectral data are in agreement with literature values.⁹



To an oven-dried sealed tube was added the mixture of **4b** and **5b** (44.0 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4b** (42.7 mg, 0.20 mmol) in 98% yield.

4b: $R_f = 0.48$ [petroleum ether]; white solid; mp = 50–51 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.82 (m, 3H), 7.52-7.37 (m, 6H), 7.29 (d, 2H, J = 7.8 Hz), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4, 138.0, 137.1, 134.0, 131.9, 130.1, 129.1, 128.4, 127.6, 127.1, 126.3, 126.1, 125.9, 125.6, 21.4. Spectral data are in agreement with literature values.⁹



To an oven-dried sealed tube was added the mixture of 4c and 5c (56.4 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford 4c (52.1 mg, 0.19 mmol) in 93% yield.

4c: $R_f = 0.30$ [petroleum ether]; white solid; mp = 143–144 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, 1H, J = 8.4 Hz), 7.91 (d, 1H, J = 7.5 Hz), 7.86 (d, 1H, J = 8.1 Hz), 7.72-7.67 (m, 4H), 7.58-7.42 (m, 8H), 7.39-7.35 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.3, 140.0, 139.9, 134.0, 131.8, 130.7, 129.0, 128.5, 127.9, 127.5, 127.3, 127.2, 127.1, 126.3, 126.2, 125.9, 125.5. Spectral data are in agreement with literature values.¹⁰



To an oven-dried sealed tube was added the mixture of **4d** and **5d** (47.3 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: 30:1 petroleum ether/EtOAc] to afford **4c** (42.8 mg, 0.18 mmol) in 88% yield.

4d: $R_f = 0.51$ [20:1 petroleum ether/EtOAc]; white solid; mp = 123–124 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.87 (m, 2H), 7.82 (d, 1H, J = 8.2 Hz), 7.51-7.38 (m, 6H), 7.02 (dt, 2H, J = 8.7, 2.5 Hz), 3.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 140.1, 134.0, 133.3, 132.0, 131.3, 128.4, 127.5, 127.1, 126.2, 126.1, 125.9, 125.6, 113.9, 55.5. Spectral data are in agreement with literature values.¹⁰



To an oven-dried sealed tube was added the mixture of **4e** and **5e** (56.6 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4e** (54.4 mg, 0.19 mmol) in 96% yield.

4e: $R_f = 0.47$ [petroleum ether]; white solid; mp = 73–74 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.82 (m, 3H), 7.60 (dt, 2H, J = 8.4, 2.1 Hz), 7.52-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.38-7.33 (m 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 139.1, 133.9, 131.9, 131.6, 131.5, 128.5, 128.2, 127.0, 126.4, 126.1, 125.8, 125.5, 121.6. Spectral data are in agreement with literature values.¹¹



To an oven-dried sealed tube was added the mixture of **4f** and **5f** (44.0 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4f** (41.0 mg, 0.19 mmol) in 93% yield.

4f: $R_f = 0.53$ [petroleum ether]; white solid; mp = 31–32 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.82 (m, 3H), 7.52-7.37 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 139.1, 133.9, 133.5, 131.6, 131.5, 128.6, 128.5, 128.2, 127.1, 126.4, 126.1, 125.8, 125.5. Spectral data are in agreement with literature values.¹²



To an oven-dried sealed tube was added the mixture of 4g and 5g (44.5 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford 4g (42.7 mg, 0.19 mmol) in 96% yield.

4g: $R_f = 0.50$ [petroleum ether]; white solid; mp = 69–70 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, 1H, J = 8.2 Hz), 7.85 (t, 2H, J = 8.3 Hz), 7.53-7.38 (m, 6H), 7.18 (t, 2H, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 162.4 (d, J = 244.5 Hz), 139.3, 136.8 (d, J = 3.4 Hz), 134.0, 131.8, 131.7 (d, J = 7.8 Hz), 128.5, 128.0, 127.2, 126.3, 126.0, 125.9, 125.5, 115.4 (d, J = 21.2 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -115.5. Spectral data are in agreement with literature values.⁹



To an oven-dried sealed tube was added the mixture of **4h** and **5h** (54.9 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4h** (49.0 mg, 0.18 mmol) in 90% yield.

4h: $R_f = 0.62$ [petroleum ether]; white solid; mp = 43–44 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.87 (m, 2H), 7.80 (d, 1H, J = 8.6 Hz), 7.74 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 7.9 Hz), 7.54-7.48 (m, 2H), 7.46-7.44 (m, 1H), 7.39 (dd, 1H, J = 7.0, 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 144.6 (q, J = 1.2 Hz), 138.9, 133.9, 131.4, 130.6, 129.6 (q, J = 32.1 Hz), 128.61, 128.56, 127.2, 126.6, 126.2, 125.7, 125.5, 125.4 (q, J = 3.8 Hz), 124.5 (q, J = 272.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3. Spectral data are in agreement with literature values.¹³



To an oven-dried sealed tube was added the mixture of **4i** and **5i** (49.9 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: 30:1 petroleum ether/EtOAc] to afford **4i** (46.0 mg, 0.18 mmol) in 92% yield.

4i: $R_f = 0.50$ [20:1 petroleum ether/EtOAc]; yellow solid; mp = 115–116 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, 2H, J = 8.8 Hz), 7.94 (dd, 2H, J = 7.9 Hz, 3.1 Hz), 7.79 (d, 1H, J = 8.4 Hz), 7.68 (d, 2H, J = 8.8 Hz), 7.58-7.52 (m, 2H), 7.50-7.46 (m, 1H), 7.43 (dd, 1H, J = 7.0, 1.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 147.3, 137.9, 133.9, 131.10, 131.07, 129.1, 128.8, 127.3, 126.9, 126.4, 125.5, 125.3, 123.8. Spectral data are in agreement with literature values.¹¹



To an oven-dried sealed tube was added the mixture of 4j and 5j (44.1 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 4.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford 4j (44.1 mg, 0.20 mmol) in 99% yield.

4j: $R_f = 0.41$ [petroleum ether]; white solid; mp = 62–63 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.87 (m, 2H), 7.83 (d, 1H, J = 8.2 Hz), 7.52-7.35 (m, 5H), 7.31-7.28 (m, 2H), 7.24-7.22 (m, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 140.6, 138.0, 134.0, 131.8, 131.0, 128.4, 128.3, 128.1, 127.7, 127.3, 127.0, 126.3, 126.1, 125.9, 125.5, 21.7. Spectral data are in agreement with literature values.¹⁴



To an oven-dried sealed tube was added **4k** and **5k** (42.3 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 19.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4k** (38.0 mg, 0.18 mmol) in 90% yield.

4k: $R_f = 0.32$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.23-8.20 (m, 1H), 7.91-7.87 (m, 1H), 7.85 (d, 1H, J = 8.2 Hz), 7.57 (dd, 1H, J = 7.1 Hz, 1.3 Hz), 7.52-7.46 (m, 3H), 7.42 (dd, 1H, J = 5.1Hz, 1.2 Hz), 7.24 (dd, 1H, J = 3.4 Hz, 1.2 Hz), 7.18 (dd, 1H, J = 5.1 Hz, 3.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 141.9, 134.0, 132.6, 132.0, 128.6, 128.5, 128.4, 127.6, 127.4, 126.6, 126.2, 125.9, 125.8, 125.4. Spectral data are in agreement with literature values.¹⁵



To an oven-dried sealed tube was added **41** and **51** (43.9 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **41** (42.1 mg, 0.19 mmol) in 96% yield.

41: $R_f = 0.44$ [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, 2H, J = 8.4 Hz), 7.66 (s, 1H), 7.49-7.40 (m, 6H), 7.37 (dd, 1H, J = 7.1 Hz, 1.3 Hz), 7.32 (dd, 1H, J = 8.3 Hz, 1.7 Hz), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 139.7, 135.9, 132.2, 131.9, 130.2, 128.4, 128.3, 128.2, 127.6, 127.3, 127.2, 125.0, 124.7, 22.2. Spectral data are in agreement with literature values.¹⁶



To an oven-dried sealed tube was added **4m** and **5m** (47.1 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4m** (47.0 mg, 0.20 mmol) in 99% yield.

4m: Rf = 0.33 [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.75 (m, 2H), 7.52-7.45 (m, 4H), 7.42-7.34 (m, 3H), 7.22 (d, 1H, J = 2.6 Hz), 7.15 (dd, 1H, J = 8.9 Hz, 2.6 Hz), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 141.2, 139.2, 132.8, 130.03, 129.97, 129.5, 128.5, 127.7, 127.5, 127.3, 123.3, 118.4, 104.6, 55.3. Spectral data are in agreement with literature values.¹⁶



To an oven-dried sealed tube was added 4n and 5n (47.9 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford 4n (47.2 mg, 0.20 mmol) in 99% yield.

4n: Rf = 0.53 [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, 1H, J = 2.1 Hz), 7.82 (dd, 2H, J = 8.6 Hz, 2.9 Hz), 7.53-7.41 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 139.8, 132.5, 132.20, 132.17, 130.1, 130.0, 128.6, 128.1, 127.7, 127.6, 126.9, 125.8, 125.1. Spectral data are in agreement with literature values.¹⁶



To an oven-dried sealed tube was added **40** and **50** (57.2 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **40** (54.9 mg, 0.19 mmol) in 96% yield.

40: Rf = 0.52 [petroleum ether]; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, 1H, J = 8.6 Hz), 7.85 (d, 1H, J = 8.5 Hz), 7.78 (d, 1H, J = 8.2 Hz), 7.62 (dd, 1H, J = 8.6Hz, 7.0 Hz), 7.50-7.41 (m, 6H), 7.23 (dd, 1H, J = 8.5Hz, 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 140.5, 133.2, 132.4, 130.2, 130.1, 128.5, 128.0, 127.6, 127.0, 126.9, 126.4, 126.3, 123.4. Spectral data are in agreement with literature values.¹⁷



To an oven-dried sealed tube was added **6b** (57.1 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 3.0 h. After the reaction was judged to be complete by TLC, the
reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4p** (55.7 mg, 0.20 mmol) in 99% yield.



4p: $R_f = 0.47$ [petroleum ether]; yellow solid; mp = 71–72 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, 2H, J = 8.0, 1.3 Hz), 7.72 (dd, 1H, J = 8.0, 1.2 Hz), 7.54-7.45 (m, 3H), 7.41-7.33 (m, 4H), 7.30-7.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.5, 139.2, 133.6, 132.9, 132.1, 131.7, 129.3, 128.4, 128.35, 127.3, 127.1, 126.3, 126.1, 126.0, 125.3, 124.5. Spectral data are in agreement with literature values.²⁵



To an oven-dried sealed tube was added **6c** (46.9 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4q** (41.3 mg, 0.18 mmol) in 88% yield.

4q: $R_f = 0.49$ [petroleum ether]; colorless oil; ¹H NMR (400MHz, CDCl₃) δ 7.88 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 8.3 Hz), 7.52-7.43 (m, 3H), 7.37-7.31 (m, 2H), 7.15-7.09 (m, 3H), 2.42 (s, 3H), 1.99 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 137.5, 137.3, 136.8, 133.7, 132.3, 130.8, 130.5, 128.4, 127.5, 127.0, 126.44, 126.35, 126.1, 125.8, 125.6, 21.4, 20.2. Spectral data are in agreement with literature values.²⁶



To an oven-dried sealed tube was added 6d (51.1 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, alkyne concn

= 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: petroleum ether] to afford **4r** (51.0 mg, 0.20 mmol) in 99% yield

4r: $R_f = 0.49$ [petroleum ether]; yellow solid; mp = 138–139 °C; ¹H NMR (400MHz, CDCl₃) δ 7.97-7.93 (m, 4H), 7.61-7.57 (m, 2H), 7.50-7.45 (m, 4H), 7.39 (d, 2H, J = 8.4 Hz), 7.31-7.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 133.7, 133.0, 128.3, 128.1, 128.0, 126.7, 126.1, 126.0, 125.6. Spectral data are in agreement with literature values.²⁷



To an oven-dried sealed tube was added **6e** (46.3 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, alkyne *concn* = 0.20 *M*), and DDQ (45.4 mg, 0.20 mmol) in the glove box at rt. Then the reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, filtered through a pad of silica gel, concentrated *in vacuo*, and purified by flash silica gel column chromatography [isocratic eluent: 30:1 petroleum ether/EtOAc] to afford **4s** (42.2 mg, 0.18 mmol) in 92% yield.

4s: $R_f = 0.35$ [20:1 petroleum ether/EtOAc]; white solid; mp = 65–66 °C; ¹H NMR (400MHz, CDCl₃) δ 7.94-7.90 (m, 2H), 7.79-7.76 (m, 3H), 7.61-7.58 (m, 2H), 7.56-7.50 (m, 2H), 7.48-7.44 (m, 1H), 7.39 (dd, 1H, J = 7.1, 1.2 Hz),; ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 138.3, 133.9, 132.3, 131.1, 131.0, 128.9, 128.7, 127.2, 126.8, 126.3, 125.5, 125.3, 119.1, 111.3. Spectral data are in agreement with literature values.²⁸

1.6 Synthesis of 4,4'-Disubstituted-1,1'-Binaphthyls (Table 5).

4,4'-Disubstituted-1,1'-binaphthyl $7a^{29}$ was known compound, the data were matched with reported values. 4,4'-Disubstituted-1,1'-binaphthyl **7b-7h** were new compounds.



To an oven-dried sealed tube was added **3a** (41.3 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 3.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 15:1 petroleum ether/CH₂Cl₂] to afford **7a** (40.8 mg, 0.10 mmol) in 99% yield.



7a: $R_f = 0.59$ [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 178–179 °C; ¹H NMR (400MHz, CDCl₃) δ 8.01 (d, 2H, *J*= 8.2 Hz), 7.61-7.50 (m, 14H), 7.47-7.38 (m, 4H), 7.32-7.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.3, 138.3, 133.4, 131.9, 130.4, 128.5, 127.7, 127.5, 127.2, 126.7, 126.5, 126.1, 126.0. Spectral data are in agreement with literature values.²⁹



To an oven-dried sealed tube was added **3b** (44.1 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, 0.20 M), and

Tf₂O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 10:1 petroleum ether/CH₂Cl₂] to afford **7b** (30.3 mg, 0.07 mmol) in 70% yield.

7b: $R_f = 0.58$ [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 115–116 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, 2H, J = 8.5 Hz), 7.57-7.50 (m, 10H), 7.43-7.40 (m, 2H), 7.35 (d, 4H, J = 8.0 Hz), 7.33-7.30 (m, 2H), 2.49 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 138.12, 138.08, 137.2, 133.4, 132.0, 130.3, 129.2, 127.7, 127.2, 126.6, 126.5, 125.97, 125.94, 21.5; IR (neat) (cm⁻¹) 2919w, 1513m, 1502m, 1423m, 1379s, 1182s, 1157s, 1022s; HRMS (ESI): m/z calcd for C₃₄H₂₇ [M+H]⁺ 435.2107, found 435.2127.



To an oven-dried sealed tube was added 3c (56.5 mg, 0.20 mmol), CH₂Cl₂ (1.0 mL, 0.20 *M*), and Tf₂O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 5.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 15:1 petroleum ether/CH₂Cl₂] to afford 7c (40.2 mg, 0.07 mmol) in 72% yield.

7c: $R_f = 0.42$ [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 285–286 °C; ¹H NMR (400MHz, CDCl₃) δ 8.11 (d, 2H, J = 8.4 Hz,), 7.81-7.70 (m 12H), 7.62-7.59 (m, 6H), 7.53-7.34 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.4, 140.0, 139.9, 138.4, 133.4, 131.9, 130.9, 129.1, 127.7, 127.6, 127.4, 127.3, 126.7, 126.5, 126.2, 126.1, one carbon missing due to overlap, overlapped signal at 127.4 ppm; IR (neat) (cm⁻¹) 3029w, 2955w, 2919w, 2849w, 1486m, 1399m, 1079m, 1005m, 966s; HRMS (ESI): m/z calcd for C₄₄H₃₀Na [M+Na]⁺ 581.2240, found 581.2235.



To an oven-dried sealed tube was added **3j** (44.1 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 2.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 15:1 petroleum ether/CH₂Cl₂] to afford **7d** (33.1 mg, 0.08 mmol) in 76% yield.

7d: $R_f = 0.57$ [20:1 petroleum ether/EtOAc]; pale yellow solid; mp = 178–179 °C; ¹H NMR (400MHz, CDCl₃) δ 8.03 (d, 2H, J = 8.4 Hz), 7.58-7.53 (m, 6H), 7.46-7.41 (m, 8H), 7.33-7.28 (m, 4H), 2.49 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.4, 138.2, 138.1, 133.4, 131.9, 131.1, 128.4, 128.2, 127.6, 127.5, 127.2, 126.58, 126.57, 126.0, 125.96, 21.8; IR (neat) (cm⁻¹) 2921w, 2851w, 1601m, 1508m, 1490m, 1508m, 1442m, 1379s, 1072s, 1028s; HRMS (ESI): m/z calcd for C₃₄H₂₇ [M+H]⁺ 435.2107; found 435.2127.



To an oven-dried sealed tube was added **3e** (57.0 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 3.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina

column chromatography [isocratic eluent: 30:1 petroleum ether/CH₂Cl₂] to afford 7e (55.8 mg, 0.10 mmol) in 99% yield.

7e: $R_f = 0.28$ [petroleum ether]; white solid; mp = 173–174 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, 2H, J = 8.4 Hz), 7.67 (d, 4H, J = 8.4 Hz), 7.55-7.42 (m, 12H), 7.34-7.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 139.1, 138.5, 133.3, 132.0, 131.7, 131.6, 127.6, 127.2, 126.6, 126.4, 126.2, 126.1, 121.8; IR (neat) (cm⁻¹) 2922w, 2851w, 1508m, 1486m, 1423m, 1378s, 1070s, 1010s; HRMS (ESI): m/z calcd for C₃₂H₂₀Br₂K [M+K]⁺ 600.9563, found 600.9563.



To an oven-dried sealed tube was added **3f** (48.1 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 3.5 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 30:1 petroleum ether/ EtOAc] to afford **7f** (47.1 mg, 0.10 mmol) in 99% yield.

7f: $R_f = 0.52$ [20:1 petroleum ether/EtOAc]; white solid; mp = 215–216 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, 2H, J = 8.4 Hz), 7.56-7.51 (m, 14H), 7.45 (t, 2H, J = 7.4 Hz), 7.35-7.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 139.1, 138.5, 133.6, 133.3, 131.71, 131.66, 128.8, 127.6, 127.2, 126.7, 126.3, 126.21, 126.17; IR (neat) (cm⁻¹) 1594m, 1577m, 1508m, 1488m, 1424m, 1379s, 1247s, 1094s, 1014s; HRMS (ESI): m/z calcd for C₃₂H₂₀Cl₂K [M+K]⁺ 513.0574, found 513.0582.



To an oven-dried sealed tube was added **3g** (44.8 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 30:1 petroleum ether/CH₂Cl₂] to afford **7g** (41.8 mg, 0.10 mmol) in 94% yield.

7g: $R_f = 0.52$ [20:1 petroleum ether/EtOAc]; white solid; mp = 215–216 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, 2H, J = 8.4 Hz), 7.59-7.52 (m, 10H), 7.47-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.26-7.22 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 162.5 (d, J = 244.8 Hz), 139.2, 138.3, 136.86 (d, J = 3.3 Hz), 133.3, 131.90, 131.88 (d, J = 7.9 Hz), 127.6, 127.2, 126.8, 126.3, 126.1, 115.4 (d, J = 21.2 Hz), one carbon missing due to overlap, overlapped signal at 126.3 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.3; IR (neat) (cm⁻¹) 1604m, 1511m, 1501m, 1455m, 1426m, 1379s, 1229s, 1157s, 1096s, 1015s; HRMS (ESI): m/z calcd for C₃₂H₂₁F₂ [M+H]⁺ 443.1606, found 443.1614.



To an oven-dried sealed tube was added **3h** (54.9 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL, 0.20 *M*), and Tf_2O (33.6 μ L, 0.20 mmol) in the glove box at rt. The reaction vessel was capped and stirred at 60 °C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was cooled to rt, DDQ (90.8 mg, 0.40 mmol) was added. Then the reaction mixture was stirred at 60 °C for 5.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by alumina column chromatography [isocratic eluent: 15:1 petroleum ether/CH₂Cl₂] to afford **7h** (47.7 mg, 0.09 mmol) in 88% yield.

7h: $R_f = 0.57$ [petroleum ether]; pale yellow solid; mp = 198–199 °C; ¹H NMR (400MHz, CDCl₃) δ 7.93 (d, 2H, J = 8.5 Hz), 7.82 (d, 4H, J = 8.0 Hz), 7.73 (d, 4H, J = 7.80 Hz), 7.60-7.53 (m, 6H), 7.47-7.44 (m, 2H), 7.37-7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 138.9, 138.8, 133.3, 131.5, 130.7, 129.8 (q, J = 32.5 Hz), 127.6, 127.3, 126.8, 126.6, 126.4, 126.0, 125.5 (q, J = 3.7 Hz), 124.5 (q, J = 272.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3; IR (neat) (cm⁻¹) 3025w, 2922m, 2851m, 1616m, 1570m, 1405m, 1324s, 1129s, 1157s, 1064s, 1019s; HRMS (ESI): m/z calcd for C₃₄H₁₉F₆ [M-H]⁻ 541.1396, found 541.1395.

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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm) S63









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





f1 (ppm)





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f1 (ppm) S89















S96




















































































TitleZCF-IV-25SolventCDCl3Spectrometer Frequency100.62Nucleus13C





Title ZCF-IV-25 Solvent CDC13 Spectrometer Frequency 376.46 Nucleus 19F













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S216




S218





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