Supporting Information

Regioselective Haloaromatization of 1,2-Bis(ethynyl)benzene via Platinum-catalyzed 6- π Electrocyclization of 1,2-Bis(1'-haloethenyl)-benzene Intermediates

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Spectral data of compounds 1, 2-(Cl-I), 3-(Cl-I), 5, 6, 7, 8-(Cl-I), 9-(Br-I), 10-(Br-I), 11, 12, 13, 14, 15-(Cl-I), 16-(Cl-I), 17-(Cl-I), 18-(Cl-I), 19 and 20-(Cl-I).----- S2-S12

Spectral data for 1,2-Diethynylbenzene (1) : IR (neat, cm^{-1}): 3286 (s), 3020(w), 2112 (w), 1622(w); ^1H NMR (400 MHz, CDCl_3): δ 3.24 (s, 2 H), 7.27~7.30 (m, 2 H), 7.49~7.52 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 81.2, 81.7, 125.0, 128.4, 132.5; HRMS calcd for C_{10}H_6 : 126.0470, found 126.0472.

Spectral data for 1,2-Bis-(1-chlorovinyl)benzene (2-Cl) : IR (neat, cm^{-1}): 3202 (m), 3003(m), 1906 (m), 1710(w); ^1H NMR (400 MHz, CDCl_3): δ 5.50 (dd, $J = 42.4$, 1.6 Hz, 4 H), 7.31~7.33 (m, 2 H), 7.39~7.41 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 122.0, 126.4, 127.6, 129.6, 136.5; HRMS calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2$: 198.0003, found 198.0001.

Spectral data for 1,2-Bis-(1-bromovinyl)benzene (2-Br) : IR (neat, cm^{-1}): 3210 (m), 3010(m), 1920 (m), 1690(w); ^1H NMR (400 MHz, CDCl_3): δ 5.90~5.93 (m, 4 H), 7.31~7.33 (m, 2 H), 7.39~7.41 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 122.0, 127.4, 128.6, 129.6, 138.5; HRMS calcd for $\text{C}_{10}\text{H}_8\text{Br}_2$: 285.8993, found 285.8995.

Spectral data for 1,2-Bis-(1-iodovinyl)benzene (2-I) : IR (neat, cm^{-1}): 3218 (m), 3016(m), 1924 (m), 1698(w); ^1H NMR (400 MHz, CDCl_3): δ 6.22 (dd, $J = 44$, 1.2Hz, 4 H), 7.23~7.25 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 102.4, 128.2, 129.5, 131.3, 140.8; HRMS calcd for $\text{C}_{10}\text{H}_8\text{I}_2$: 381.8715, found 381.8718.

Spectral data for 1-Chloronaphthalene (3-Cl) : IR (neat, cm^{-1}): 3048 (m), 1585(m), 1520 (m), 1505 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.37 (t, $J = 7.6$ Hz, 1 H), 7.48~7.60 (m, 3 H), 7.75 (d, $J = 8.2$ Hz, 1 H), 7.85 (d, $J = 8.2$ Hz, 1 H), 8.26(d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 124.4, 125.7, 126.1, 126.6, 127.0, 127.1, 128.2, 130.8, 131.9, 134.5; HRMS calcd for $\text{C}_{10}\text{H}_7\text{Cl}$: 162.0236, found 162.0235.

Spectral data for 1-Bromonaphthalene (3-Br): IR (neat, cm^{-1}): 3060 (m), 1580(m), 1510 (m), 1489 (s); ^1H NMR (500 MHz, CDCl_3): δ 7.30 (t, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 1 H), 7.58 (t, $J = 8.0$ Hz, 1 H), 7.76~7.83 (m, 3 H), 8.23 (d, $J = 8.0\text{Hz}$, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 122.8, 126.1, 126.6, 127.0, 127.3, 127.9, 128.2, 129.8, 131.9, 134.6; HRMS calcd for $\text{C}_{10}\text{H}_7\text{Br}$: 205.9731, found 205.9731.

Spectral data for 1-Iodonaphthalene (3-I): IR (neat, cm^{-1}): 3045 (m), 1558(m), 1499 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.17 (t, $J = 7.8$ Hz, 1 H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.57(t, $J = 7.8$ Hz, 1 H), 7.76(d, $J = 8.2$ Hz, 1 H), 7.82(d, $J = 8.2$ Hz, 1 H), 8.07~8.09 (m, 2 H); ^{13}C NMR(150 MHz, CDCl_3): δ 99.5, 126.6 ,126.8, 127.6, 128.5, 128.9, 132.0, 134.0, 134.2, 137.3: HRMS calcd for $\text{C}_{10}\text{H}_7\text{I}$: 253.9592, found 253.9592.

Spectral data for 5,6-Diethynylbenzo[1,3]dioxole (5) : IR (neat, cm^{-1}): 3245 (s), 3030 (m), 2112 (w) 1610 (s) ; ^1H NMR (600 MHz, CDCl_3): δ 3.24 (s, 2 H), 5.97(s, 2 H), 6.89(s, 2 H); ^{13}C NMR (150 MHz, CDCl_3): δ 79.9, 81.8, 101.9, 112.0, 119.4, 147.9; HRMS calcd for $\text{C}_{11}\text{H}_6\text{O}_2$: 170.0368, found 170.0366.

Spectral data for 1,2-Diethynyl-4,5-dimethoxybenzene (6) : IR (neat, cm^{-1}): 3230 (s), 2990 (m), 2110 (w) ; ^1H NMR (600 MHz, CDCl_3): δ 3.24 (s, 2 H), 3.83 (s, 6 H), 6.90 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 55.9, 79.7, 81.9, 114.5, 117.9, 149.2; HRMS calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$: 186.0681, found 186.0683.

Spectral data for 1,2-Diethynyl-4,5-difluoro-benzene (7) : IR (neat, cm^{-1}): 3258 (s), 3018 (m), 2110 (w) ; ^1H NMR (400 MHz, CDCl_3): δ 3.32 (s, 2 H), 7.28 (t, $J = 4.4\text{Hz}$, 2 H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 79.8, 81.9, 121.4 (dd, $J_{\text{CF}} = 12.2$; 7.6Hz), 122.2,

150.1 (dd, $J_{CF} = 253.4$; 15.2 Hz); HRMS calcd for $C_{10}H_4F_2$: 162.0281, found 162.0285.

Spectral data for 5-Chloro-naphtho[2,3-d][1,3]dioxole (8-Cl) : IR (neat, cm^{-1}):

3025 (m), 1620 (m), 1600 (s) ; 1H NMR (600 MHz, $CDCl_3$): δ 6.00 (s, 2 H), 7.09 (s, 1 H), 7.20 (t, $J = 8.0$ Hz, 1 H), 7.39 (d, $J = 8.0$ Hz, 1 H), 7.54 (d, $J = 8.0$ Hz, 1 H), 7.55 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 100.9, 101.0, 104.0, 124.3, 124.7, 126.0, 128.0, 130.8, 131.8, 148.1, 148.7; HRMS calcd for $C_{11}H_7ClO_2$: 206.0135, found 206.0134.

Spectral data for 5-Bromo-naphtho[2,3-d][1,3]dioxole (8-Br) : IR (neat, cm^{-1}):

3008 (m), 1600 (m), 1580 (s) ; 1H NMR (600 MHz, $CDCl_3$): δ 6.02 (s, 2 H), 7.06 (s, 1 H), 7.13 (t, $J = 8.0$ Hz, 1 H), 7.54 (s, 1H), 7.57~7.59 (m, 2 H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 101.4, 103.6, 104.0, 121.5, 124.6, 126.7, 128.3, 129.2, 131.7, 148.0, 148.9; HRMS calcd for $C_{11}H_7BrO_2$: 249.9629, found 249.9630.

Spectral data for 5-Iodo-naphtho[2,3-d][1,3]dioxole (8-I) : IR (neat, cm^{-1}): 3060

(m), 1624 (m), 1590 (s) ; 1H NMR (600 MHz, $CDCl_3$): δ 6.05 (s, 2 H), 7.01 (t, $J = 8.0$ Hz, 1 H), 7.02 (s, 1 H), 7.47 (s, 1 H), 7.61 (d, $J = 8.0$ Hz, 1 H), 7.89 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 97.9, 101.4, 104.1, 108.8, 125.3, 127.9, 131.0, 131.8, 135.9, 148.0, 149.2; HRMS calcd for $C_{11}H_7IO_2$: 297.9491, found 297.9494.

Spectral data for 1-Bromo-6,7-dimethoxynaphthalene (9-Br) : IR (neat, cm^{-1}):

3078 (m), 1612 (m), 1500 (s) ; 1H NMR (600 MHz, $CDCl_3$): δ 3.99 (s, 3 H), 4.03 (s, 3 H), 7.09 (s, 1 H), 7.15 (t, $J = 8.0$ Hz, 1 H), 7.47 (s, 1H), 7.59~7.62 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.9, 105.8, 106.5, 121.0, 124.5, 126.1, 127.8, 128.0, 130.2, 149.9, 150.5; HRMS calcd for $C_{12}H_{11}BrO_2$: 265.9942, found 265.9943.

Spectral data for 1-Iodo-6,7-dimethoxynaphthalene(9-I) : IR (neat, cm^{-1}): 3046 (m), 1620 (m), 1510 (s) ; ^1H NMR (600 MHz, CDCl_3): δ 3.98 (s, 3 H), 4.03 (s, 3 H), 6.99 (t, $J = 8.0\text{Hz}$, 1 H), 7.04 (s, 1 H), 7.36 (s, 1 H), 7.63 (d, $J = 8.0\text{ Hz}$, 1 H) ,7.89 (d, $J = 8.0\text{ Hz}$, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 55.9, 56.0, 97.5, 106.5, 111.0, 125.1, 127.2, 129.3, 130.2, 135.4, 149.8, 150.7; HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{IO}_2$: 313.9804, found 313.9804.

Spectral data for 1-Bromo-6,7-difluoronaphthalene(10-Br) : IR (neat, cm^{-1}): 3048 (m), 1600 (m), 1506 (s) ; ^1H NMR (600 MHz, CDCl_3): δ 7.30 (t, $J = 8.0\text{Hz}$, 1 H), 7.55~7.58 (m, 1 H), 7.71 (d, $J = 8.0\text{ Hz}$, 1 H), 7.75 (d, $J = 8.0\text{ Hz}$, 1 H), 7.98~8.02 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 113.9(d, $J_{\text{CF}} = 16.8\text{Hz}$), 114.1(d, $J_{\text{CF}} = 16.8\text{Hz}$), 121.6, 126.7, 127.1, 129.3, 130.1, 131.2, 149.8 (dd, $J = 58, 15.6\text{Hz}$), 151.5 (dd, $J = 58, 15.6\text{ Hz}$); HRMS calcd for $\text{C}_{10}\text{H}_5\text{BrF}_2$: 241.9543, found 241.9545.

Spectral data for 6,7-Difluoro-1-iodonaphthalene(10-I) : IR (neat, cm^{-1}): 3030 (m), 1612 (m), 1498 (s) ; ^1H NMR (600 MHz, CDCl_3): δ 7.18 (t, $J = 8.0\text{ Hz}$, 1 H), 7.56~7.62 (m, 1 H), 7.77 (d, $J = 8.0\text{Hz}$, 1 H), 7.95~7.97 (m, 1 H), 8.07 (d, $J = 8.0\text{Hz}$, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 97.5, 114.2 (d, $J_{\text{CF}} = 16.6\text{Hz}$), 118.6 (J_{CF} , $J = 16.6\text{ Hz}$), 127.1, 128.1, 130.4, 131.8, 139.9 (dd, $J_{\text{CF}} = 91.2, 5.6\text{ Hz}$), 151.5 (dd, $J_{\text{CF}} = 91.2, 15.6\text{ Hz}$); HRMS calcd for $\text{C}_{10}\text{H}_5\text{F}_2\text{I}$: 289.9404, found 289.9404.

Spectral data for 1,2-Diethynyl-4-methylbenzene(11) : IR (neat, cm^{-1}): 3300 (s), 3020(w), 2100 (w), 1622(w); ^1H NMR (600 MHz, CDCl_3): δ 2.31 (s, 3 H), 3.29 (s, 1 H), 3.30 (s, 1 H), 7.07 (d, $J = 8.0\text{ Hz}$, 1 H), 7.29 (s, 1 H), 7.37 (d, $J = 8.0\text{ Hz}$, 1 H) ; ^{13}C NMR (150 MHz, CDCl_3): δ 21.0, 80.3, 80.7, 81.8, 81.9, 121.9, 124.6, 129.4,

132.3, 133.0, 138.6; HRMS calcd for $C_{11}H_8$: 140.0626, found 140.0625.

Spectral data for 1,2-diethynyl-4-methoxybenzene (12) : IR (neat, cm^{-1}): 3296 (s), 3015(w), 2080 (w), 1622(w); 1H NMR (600 MHz, $CDCl_3$): δ 3.21 (s, 1 H), 3.29 (s, 1 H), 3.71 (s, 3 H), 6.77 (d, $J=8.8Hz$, 1 H), 6.94 (s, 1 H), 7.35 (d, $J=8.8Hz$, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.2, 79.6, 80.9, 81.6, 81.7, 113.8, 115.2, 117.1, 126.1, 159.2; HRMS calcd for $C_{11}H_8O$: 156.0575, found 156.0577

Spectral data for 2,3-Diethynyl-benzofuran(13) : IR (neat, cm^{-1}): 3286 (s), 3010(w), 2108 (w), 1600 (w); 1H NMR (600 MHz, $CDCl_3$): δ 3.51(s, 1 H), 3.75(s, 1 H), 7.30(t, $J=7.8Hz$, 1 H), 7.38(t, $J=7.8Hz$, 1 H), 7.43(d, $J=7.8Hz$), 7.63(d, $J=7.8Hz$, 1 H); ^{13}C NMR(150 MHz, $CDCl_3$): δ 73.1, 83.3, 85.4, 87.2, 111.3, 111.5, 120.6, 123.9, 126.8, 127.3, 141.1, 153.9; HRMS calcd for $C_{12}H_6O$: 166.0419, found 166.0418.

Spectral data for 2,3-Diethynyl-benzo[b]thiophene(14) : IR (neat, cm^{-1}): 3312 (s), 3020(m), 2106 (w), 1600 (w); 1H NMR (600 MHz, $CDCl_3$): δ 3.56(s, 1 H), 3.72(s, 1 H), 7.41~7.44(m, 2 H), 7.72~7.73(m, 1 H), 7.87~7.89(m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.0, 76.3, 84.0, 87.2, 122.1, 122.8, 123.4, 124.7, 125.3, 126.6, 138.3, 153.1; HRMS calcd for $C_{12}H_6S$: 182.0190, found 182.0193.

Spectral data for 1-Chloro-6-methyl-naphthalene and 1-Chloro-7-methylnaphthalene (15-Cl(A/B)) : IR (neat, cm^{-1}): 3048 (m), 1595(m), 1530 (m), 1500 (m); 1H NMR(600 MHz, $CDCl_3$): species **A**: δ 2.49 (s, 3 H), 7.35 (t, $J=8.0Hz$, 1 H), 7.41 (d, $J=8.0Hz$, 1H), 7.48 (d, $J=8.0Hz$, 1 H), 7.60 (s, 1 H), 7.65 (d, $J=8.0 Hz$, 1 H), 8.15 (d, $J=8.0Hz$, 1 H); species **B**: selected peaks: δ 2.56(s, 3 H), 7.30 (t, $J=8.0 Hz$, 1 H), 7.36 (d, $J=8.0 Hz$, 1 H), 7.52 (d, $J=8.0 Hz$, 1 H), 7.70(d, $J=8.0Hz$, 1 H), 7.74(d, $J=8.0Hz$, 1 H), 8.03 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): species A: δ 21.5, 124.2,

125.2, 125.7, 126.4, 127.1, 129.0, 129.2, 131.7, 134.7, 136.4; species B: δ 21.9, 123.3, 124.7, 126.1, 126.8, 128.0, 128.9, 130.8, 131.2, 132.8, 136.9; HRMS calcd for $C_{11}H_9Cl$: 172.0393, found 172.0395.

<p>15Cl(A)</p>	irradiation	enhancement
	H^1 δ 7.61	H^7 (δ 2.49, 1.45%)
		H^6 (δ 8.15, 1.05%)
	H^6 δ 8.15	H^1 (δ 7.61, 0.88%)
		H^5 (δ 7.33, 1.22%)

Spectral data for 1-Bromo-6-methylnaphthalene and 1-Bromo-7-methylnaphthalene

(15-Br(A/B)): IR (neat, cm^{-1}): 3058 (m), 1580(m), 1510 (m), 1495 (m); 1H NMR (600 MHz, $CDCl_3$): species **A**: δ 2.53 (s, 3 H), 7.27(t, J = 8.0 Hz, 1 H), 7.41 (d, J = 8.0Hz, 1 H), 7.58 (s, 1 H), 7.69~7.73 (m, 2 H), 8.12 (d, J = 8.0Hz, 1 H); species **B**: selected peaks: δ 2.56 (s, 3 H), 7.23 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.74 (t, J = 8.0 Hz, 1 H), 8.02 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): species **A**: δ 21.4, 122.6, 126.1, 126.8, 127.1, 127.2, 128.9, 129.5, 130.2, 134.7, 136.4; species **B**: δ 21.9, 119.8, 122.1, 125.2, 125.9, 127.6, 128.1, 129.8, 132.1, 132.8, 137.3; HRMS calcd for $C_{11}H_9Br$ 219.9888, found 219.9887.

Spectral data for 1-Iodo-6-methylnaphthalene and 1-Iodo-7-methylnaphthalene

(15-I(A/B)): IR (neat, cm^{-1}): 3050 (m), 1559(m), 1500 (s); 1H NMR (600 MHz, $CDCl_3$): species **A**: δ 7.12 (t, J = 8.0 Hz, 1 H), 7.53 (s, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.73 (d, J = 8.0 Hz, 1 H), 7.96~8.01 (m, 2H); species **B**: δ 7.11 (t, J = 8.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.39 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H); 7.86 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): species **A**: δ 21.3, 99.2, 126.8, 127.3, 128.2,

129.8, 131.8, 132.3, 134.1, 136.4, 136.5; species **B**: δ 21.8, 98.8, 125.9, 128.4, 128.6, 128.9, 131.0, 132.6, 134.3, 137.3, 137.6; HRMS calcd for $C_{11}H_9I$ 267.9749, found 267.9750.

Spectral data for 1-Chloro-6-methoxy-naphthalene (16-Cl) : IR (neat, cm^{-1}): 3058 (m), 1580(m), 1585 (m), 1510 (s); 1H NMR (600 MHz, $CDCl_3$): δ 3.88 (s, 3 H), 7.09 (s, 1 H), 7.20 (d, $J = 9.2Hz$, 1 H), 7.60 (d, $J = 8.0Hz$, 1 H), 8.12 (d, $J = 9.2Hz$, 1 H), 8.12 (d, $J = 9.2Hz$, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.3, 106.0, 108.3, 119.7, 123.8, 125.9, 126.0, 126.3, 131.7, 135.8, 158.1; HRMS calcd for $C_{11}H_9ClO$ 192.0342, found 192.0342.

Spectral data for 1-Bromo-6-methoxy-naphthalene(16-Br) : IR (neat, cm^{-1}): 3065 (m), 1588(m), 1510 (m), 1500 (s); 1H NMR (600 MHz, $CDCl_3$): δ 3.88 (s, 3 H), 7.07 (s, 1 H), 7.18~7.23 (m, 2 H), 7.56 (d, $J = 8.0 Hz$, 1 H), 7.64 (d, $J = 8.0 Hz$, 1 H), 8.09 (d, $J = 9.2 Hz$, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.4, 106.0, 119.9, 122.6, 126.7, 126.8, 127.4, 128.7, 135.8, 158.1; HRMS calcd for $C_{11}H_9BrO$: 235.9837, found 235.9834.

irradiation	enhancement
$H^4 \delta 7.12$	$H^3 (\delta 7.69, 1.05\%)$
	$H^7 (\delta 3.93, 1.76\%)$
$H^3 \delta 7.69$	$H^4 (\delta 7.12, 1.07\%)$
	$H^2 (\delta 7.24, 0.80\%)$

Spectral data for 1-Iodo-6-methoxy-naphthalene (16-I): IR (neat, cm^{-1}): 3045 (m),

1568(m), 1510 (m); ^1H NMR (600 MHz, CDCl_3): δ 3.92 (s, 3 H), 7.05 (s, 1 H), 7.10 (t, $J = 8.0\text{Hz}$, 1 H), 7.19 (d, $J = 9.2\text{Hz}$, 1 H), 7.70(d, $J = 8.0\text{ Hz}$, 1 H), 7.90 (d, $J = 8.0\text{Hz}$, 1 H), 7.97 (d, $J = 9.2\text{Hz}$, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 55.4, 99.1, 106.1, 120.2, 127.3, 127.9, 129.8, 133.7, 135.0, 158.1; HRMS calcd for $\text{C}_{11}\text{H}_9\text{IO}$ 283.9698, found 283.9699.

Spectral data for 1-Chloro-dibenzofuran (17-Cl): IR (neat, cm^{-1}): 3056 (m), 1588(m), 1520 (m); ^1H NMR (600 MHz, CDCl_3): δ 7.30 (d, $J = 7.2\text{ Hz}$, 1 H), 7.34~7.39 (m, 2 H), 7.45~7.50 (m, 2 H), 7.56 (d, $J = 8.0\text{ Hz}$, 1 H), 8.35 (d, $J = 8.0\text{ Hz}$, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 110.3, 111.4, 122.4, 122.9, 123.0, 123.1, 123.4, 127.7, 128.3, 156.0, 156.6; HRMS calcd for $\text{C}_{12}\text{H}_7\text{ClO}$ 202.0185, found 202.0187.

Spectral data for 1-Bromo-dibenzofuran (17-Br): IR (neat, cm^{-1}): 3062 (m), 1580(m), 1510 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.29 (t, $J = 8.0\text{Hz}$, 1H), 7.39 (t, $J = 8.0\text{Hz}$, 1H), 7.47~7.52 (m, 3 H), 7.56 (d, $J = 8.0\text{ Hz}$, 1 H), 8.48 (d, $J = 8.0\text{ Hz}$, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 110.5, 111.4, 115.9, 122.6, 122.7, 123.7, 124.0, 126.5, 127.6, 127.8, 156.1, 156.5; HRMS calcd for $\text{C}_{12}\text{H}_7\text{BrO}$ 245.9680, found 245.9680.

Spectral data for 4-Iodo-dibenzofuran (17-I): IR (neat, cm^{-1}): 3048 (m), 1558(m), 1500 (s); ^1H NMR(600 MHz, CDCl_3): δ 7.09 (t, $J = 7.6\text{Hz}$, 1 H), 7.35 (t, $J = 7.6\text{Hz}$, 1 H), 7.47 (t, $J = 7.6\text{Hz}$, 1 H), 7.64 (d, $J = 7.6\text{Hz}$, 1 H), 7.79 (d, $J = 7.6\text{Hz}$, 1 H), 7.88~7.92 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 112.0, 120.5, 121.1, 123.1, 124.3, 124.5, 124.6, 127.7, 135.9, 155.6, 156.4; HRMS calcd for $\text{C}_{12}\text{H}_7\text{IO}$ 293.9542, found 293.9545.

Spectral data for 1-Chlorodibenzothiophene (18-Cl): IR (neat, cm^{-1}): 3048 (m), 1568(m), 1500 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.34 (t, $J = 7.8\text{Hz}$, 1 H), 7.44 (dd, $J = 7.8$, 0.9 Hz, 1 H), 7.48~7.50 (m, 2 H), 7.75 (dd, $J = 7.8$, 0.9 Hz, 1 H), 7.84~7.85 (m, 1 H), 8.97~8.99 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 121.2, 122.4, 124.3, 125.8, 126.3, 126.5, 126.9, 130.3, 131.7, 134.7, 139.6, 141.4; HRMS calcd for $\text{C}_{12}\text{H}_7\text{ClS}$: 217.9957, found 217.9958.

irradiation	enhancement
$\text{H}^7 \delta$ 8.98	$\text{H}^6 (\delta$ 7.49, 0.77%)
$\text{H}^1 \delta$ 7.75	$\text{H}^2 (\delta$ 7.35, 1.11%)

Spectral data for 1-Bromodibenzothiophene (18-Br) : IR (neat, cm^{-1}): 3054 (m), 1568(m), 1500 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.26 (t, $J = 7.8\text{Hz}$, 1 H), 7.49~7.51 (m, 2 H), 7.65 (dd, $J = 7.8$, 0.8Hz, 1 H), 7.79 (dd, $J = 7.8$, 0.8 Hz, 1H), 7.83~7.85 (m, 1 H), 9.17~9.18 (m, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 118.2, 121.8, 122.4, 123.9, 125.5, 126.7, 127.0, 130.0, 132.7, 135.1, 139.8, 141.6; HRMS calcd for $\text{C}_{12}\text{H}_7\text{BrS}$: 261.9452, found 261.9254.

irradiation	enhancement
$\text{H}^7 \delta$ 9.17	$\text{H}^6 (\delta$ 7.50, 0.88%)
$\text{H}^1 \delta$ 7.79	$\text{H}^2 (\delta$ 7.25, 1.13%)

Spectral data for 4-Iodo-dibenzothiophene (18-I) : IR (neat, cm^{-1}): 3048 (m),

1568(m), 1500 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.18 (t, $J = 7.8$ Hz, 1 H), 7.45~7.48 (m, 2 H), 7.79 (dd, $J = 7.8$ Hz, 1 Hz, 1 H), 7.85~7.87 (m, 1 H), 8.06~8.07 (m, 1 H), 8.13 (dd, $J = 7.8$, 1.0 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 88.1, 121.0, 122.3, 122.7, 124.6, 125.6, 127.1, 135.6, 135.7, 136.5, 138.5, 146.0; HRMS calcd for $\text{C}_{12}\text{H}_7\text{IS}$ 309.9313, found 309.9315.

<p style="text-align: center;">18I</p>	irradiation	enhancement
	H^3 δ 8.13	H^4 (δ 8.06, 0.85%)
		H^2 (δ 7.18, 0.90%)

Spectral data for 1,2-Diethynylcyclohexene (19) : IR (neat, cm^{-1}): 3288 (m), 2110 (w), 1654 (w), 1483 (s); ^1H NMR (600 MHz, CDCl_3): δ 1.60 (m, 4 H), 2.22 (m, 4 H), 3.22 (s, 2 H); ^{13}C NMR (150 MHz, CDCl_3): δ 21.5, 29.8, 80.9, 83.8, 126.7; HRMS calcd for $\text{C}_{10}\text{H}_{10}$ 130.1864, found 130.1866.

Spectral data for 5-Chloro-1,2,3,4-tetrahydronaphthalene(20-Cl(B)) : IR (neat, cm^{-1}): 3042 (m), 1580 (m), 1500 (m), 1483 (s); ^1H NMR (600 MHz, CDCl_3): δ 1.72~1.83 (m, 4 H), 2.66~2.75 (m, 4 H), 6.94~7.01 (m, 2 H), 7.15 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 22.6, 22.9, 27.1, 29.6, 126.0, 126.2, 127.5, 134.5, 134.8, 139.5; HRMS calcd for $\text{C}_{10}\text{H}_{11}\text{Cl}$ 166.0549, found 166.0550.

Spectral data for 5-Bromo-1,2,3,4-tetrahydronaphthalene(20-Br(B)) : IR (neat, cm^{-1}): 3052 (m), 1585 (m), 1521 (m), 1478 (s); ^1H NMR (600 MHz, CDCl_3): δ 1.72~1.75 (m, 2 H), 1.79~1.81 (m, 2 H), 2.70~2.75 (m, 4 H), 6.92 (t, $J = 7.8$ Hz, 1 H), 6.99 (d, $J = 7.8$ Hz, 1 H), 7.34 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3): δ 22.3, 22.7, 22.9, 30.0, 125.8, 126.5, 128.2, 132.0, 136.4, 139.8; HRMS calcd for

C₁₀H₁₁Br: 210.0044, found 210.0045.

Spectral data for 5,8-Diiodo-1,2,3,4-tetrahydronaphthalene(20-I(C)) : IR (neat, cm⁻¹): 3042 (m), 1586 (m), 1511 (m), 1489 (s); ¹H NMR (400 MHz, CDCl₃): δ 1.55~1.75 (m, 4 H), 2.61~2.63 (m, 4 H), 7.35 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 23.8, 37.1, 103.4, 137.8, 141.5; HRMS calcd for C₁₀H₁₀I: HRMS calcd for C₁₀H₁₀I₂: 383.8872, found 383.8872.

Spectral data for 3-Dibenzothiophen-4-yl-propan-1-ol (ref 13): IR (neat, cm⁻¹): 3044 (m), 1550 (w), 1511 (m); ¹H NMR (400 MHz, CDCl₃): δ 2.02-2.09 (m, 2H), 2.98 (t, *J* = 7.8 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.42-7.46 (m, 2 H), 7.83-7.86 (m, 2 H), 8.00 (d, *J* = 7.6 Hz, 1 H), 8.11-8.13 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 31.1, 31.8, 62.0, 119.3, 121.6, 122.7, 124.3, 124.7, 126.0, 135.6, 136.0, 136.1, 138.9, 139.0; HRMS calcd for C₁₅H₁₄OS: HRMS calcd for C₁₅H₁₄OS: 242.0765, found 242.0766.

¹H-NOE map for 3-Dibenzothiophen-4-yl-propan-1-ol (ref 13):

irradiation	enhancement
H ⁸ δ 2.98	H ⁹ (δ 2.06, 0.84%) H ¹ (δ 7.28, 0.72%)
H ³ δ 7.99	H ⁴ (δ 8.12, 1.85%) H ² (δ 7.39, 1.20%)