Supplementary Information

Fabrication and characterization of thin-film field-effect transistors with alkyl-phenyl[n]phenacenes (n = 4 – 6)

Yanting Zhang,[a] Ritsuko Eguchi,[a] Hideki Okamoto,[b] Kenta Goto,[c] Fumito Tani,[c] Minoru Yamaji,[d] Hidenori Goto,[a] Yoshihiro Kubozono[a*]

a) Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan

b) Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-7850, Japan

c) Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan

d) Division of Molecular Science, Graduate School of Science and Engineering, Gunma University, Ota 373-0057 Japan

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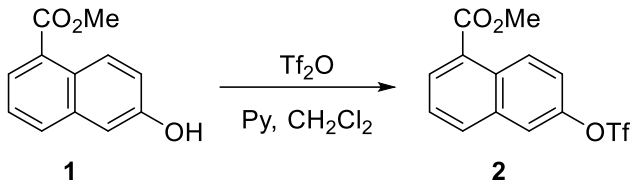
(6) Transfer and output characteristics of PhC10-CHR, PhC14-CHR, PhC10-FUL and PhC14-FUL thin-film FETs with ZrO_2 gate dielectric (Figures S6 and S7).

(1) Experimental details and physical data for samples synthesized in this study.

Methyl 6-trifluoromethanesulfonyloxy-1-naphthoate 2

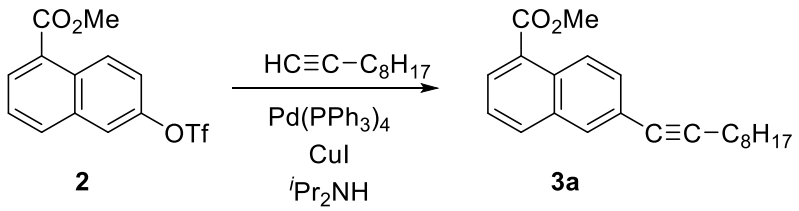


1 **2**

To a solution of methyl 6-hydroxy-1-naphthoate **1** (5.0 g, 24.7 mmol) in CH_2Cl_2 (250 ml) was dropwise added Tf_2O (10.5 g, 37.1 mmol) at −80 – −78°C. The solution was stirred at −80 – −75°C for 3 h. The reaction was quenched with saturated NH_4Cl (50 ml). The organic layer was washed successively with water, 1 M HCl, $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (toluene) to afford triflate **2** (8.07 g, 98%) as pale brown plates, mp 66–66.5ºC (Lit.[S1] 58–60°C). ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 9.10 (d, 1H, J = 9.5 Hz), 8.28 (dd, 1H, J = 7.3, 1.2 Hz), 8.05 (d, 1H, j = 8.3 Hz), 7.80 (d, 1H, J = 2.6 Hz), 7.62 (dd, 1H, J = 8.3, 7.3 Hz), 7.49 (dd, 1H, J = 9.5, 2.6 Hz), 4.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 167.4, 147.3, 134.2, 133.4, 131.6, 130.5, 129.30 127.31, 126.6, 122.1*, 121.3, 119.9*, 119.8, 117.8*, 115.7*, 52.6. Asterisked signals are assigned to CF_3 (J_{CF} = 320 Hz).

[S1] Y. Lv, M. Li, S. Cao, L. Tong, T. Peng, L. Wei, H. Xie, J. Ding, and W. Duan, *Med. Chem. Commun*., 2015, **6**, 1375.

Methyl 6-(1-decynyl)-1-naphthoate 3a



2 **3a**

A mixture of troflate **2** (1.34 g, 4.0 mmol), 1-decyne (660 mg, 4.8 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol), CuI (20 mg, 0.11 mmol) in ^{i}Pr$_2$NH (25 ml) was deaerated three evacuation-refilling with Ar cycles and refluxed for 22 h. The solvent was removed under reduced pressure. The residue was passed through a short silica-gel column (toluene). The crude material was

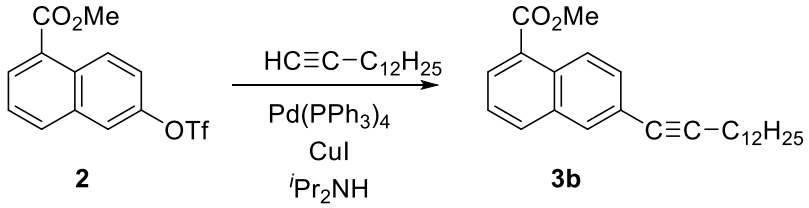
repeatedly separated by preparative liquid chromatography (silica-gel, hexane/AcOEt = 10/1) to afford compound **3a** (1.22 g, 94.5%) as pale brown waxy solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.34 (d, 1H, *J* = 8.8 Hz), 8.16 (dd, 1H, *J* = 7.3, 1.1 Hz), 7.95–7.92 (2H, two signals overlap), 7.58 (dd, 1H, *J* = 8.8, 1.7 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 4.00 (s, 3H), 2.46 (t, 2H, *J* = 7.0 Hz), 1.64 (quin, 2H, *J* = 7.2 Hz), 1.48 (quin, 2H, *J* = 7.2 Hz), 1.38–1.23 (m, 8H), 0.89 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (151 MHz, $CDCl_3$) δ_C 167.97, 133.67, 133.11, 131.52, 130.75, 130.64, 130.48, 127.05, 125.88, 125.18, 122.09, 91.88, 80.52, 52.36, 32.00, 29.36, 29.29, 29.12, 28.87, 22.82, 19.66, 14.28.

HRMS (FAB) *m*/*z* Calcd. for $C_{22}H_{26}O_2$: 322.1933. Found. 322.1933 (M^+).

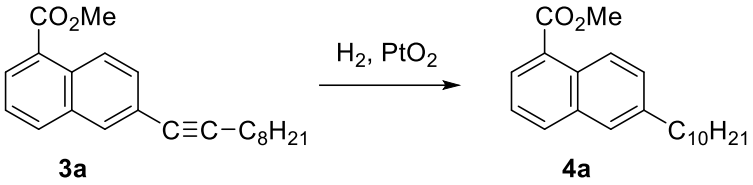
Methyl 6-(1-tetradecynyl)-1-naphthoate 3b



2 **3b**

A mixture of triflate **2** (2.00 g, 6.00 mmol), 1-tetradecyne (1.80 mL, 7.32 mmol), $Pd(PPh_3)_2Cl_2$ (440 mg, 0.692 mmol) and CuI (133 mg, 0.70 mmol), in diisopropylamine (30 mL) was refluxed under argon for 16 h. The mixture was concentrated and the residue was separated by activated alumina column chromatography using hexane : CH_2Cl_2 (10:1) as an eluent to give compound **3b** as a dark brown oil (1.31 g, 3.46 mmol **A**) along with a fraction containing the desired compound **3b**. The latter was further separated by alumina column chromatography using hexane as an eluent to give additional compound **3b** (499 mg, 1.32 mmol, **B**) as yellow oil. The total yield of compound **3b** (**A**+**B**) was 80% (1.81 g, 4.79 mmol). Yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.84 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 1.3 Hz, 1H), 7.94-7.93 (m, 2H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.48 (dd, *J* = 8.2, 9.0 Hz, 1H), 4.01 (s, 3H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.65 (quin, *J* = 7.2, Hz, 2H), 1.48 (quin, *J* = 7.0, Hz, 2H), 1.33-1.27 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 168.0, 133.7, 133.1, 131.5, 130.8 130.6, 130.5, 127.1, 125.9, 125.2, 122.1, 91.9, 80.6, 52.3, 32.1, 29.82, 29.80, 29.79, 29.7, 29.5, 29.3, 29.1, 28.9, 22.8, 19.7, 14.3. HRMS (FAB) Calcd. for $C_{26}H_{34}O_2$: 378.2559. Found: *m*/*z* 378.2554.

Methyl 6-decyl-1-naphthoate 4a



3a **4a**

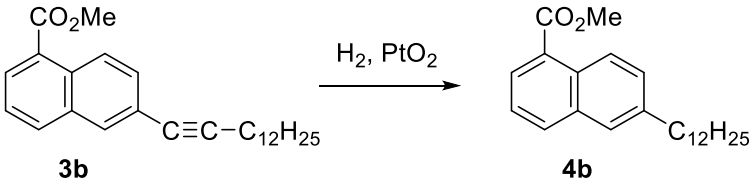
A mixture of compound **3a** (1.22 g, 3.78 mmol) and PtO_2 (42 mg, 0.19 mmol, 5 mol%) in AcOEt (30 ml) was vigorously stirred at r.t. under a H_2 atmosphere for 16 h. The mixture was filtered through a short silica-gel pad and the filtrate was concentrated under reduced pressure to afford compound **4a** (1.22 g, 99%) as an off-white waxy solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.23 (d, 1H, J = 8.8 hz), 8.12 (dd, 1H, J = 7.2 Hz, 1.2 Hz), 7.95 (d, 1H, J = 8.1 Hz), 7.65 (brd, 1H, J = 1.1 Hz), 7.47 (dd, 1H, J = 8.8, 1.8 Hz), 7.46 (dd, 1H, J = 8.1, 7.3 Hz), 4.00 (s, 3H), 2.78 (t, 2H, J = 7.5 Hz), 1.69 (quin, 2H, J = 7.5 Hz), 1.40–1.20 (m, 14H), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR (151 MHz, $CDCl_3$) δ_C 168.29, 140.99, 134.23, 133.06, 129.89, 129.54, 129.51, 127.03, 126.94, 125.75, 124.58, 52.25, 35.97, 32.039, 31.35, 29.76, 29.74, 29.67, 29.47, 29.46, 22.83, 14.28.

HRMS (FAB) *m/z* Calcd. for $C_{22}H_{30}O_2$: 326.2246. Found. 326.2236 (M^+)

Methyl 6-tetradecyl-1-naphthoate 4b

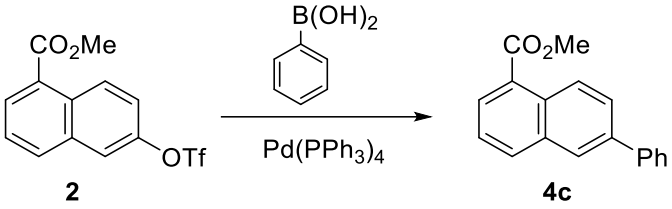


3b **4b**

A mixture of compound **3b** (1.07 g, 2.81 mmol), PtO_2 (60.5 mg, 0.266 mmol) was stirred under hydrogen atmosphere at r.t. for 24 h. The resulting mixture was chromatographed on silica gel using hexane : AcOEt (9:1) to remove the platinum catalyst to afford **4b** (942 mg, 2.46 mmol, 87.7%). Colorless crystals, m.p. 48.0-48.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.94 (d, J = 9.0 Hz, 1H), 8.16 (d, J = 1.2 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.65 (s.1H), 7.49 - 7.45 (m, 2H), 4.01 (s, 3H), 2.46 (t, J = 7.1 Hz, 2H), 1.65 (quin, J = 7.1, 2H), 1.48 (quin, J = 7.0, 2H) 1.46-1.27 (m, 20H), 0.88 (t, J = 7.0, Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 168.2, 141.0, 134.3,

133.0, 129.9, 129.5, 127.0, 126.9, 125.8, 124.5, 52.2, 36.0, 32.1, 31.3, 29.84, 29.82, 29.81*, 29.80, 29.74, 29.67, 29.51, 29.47, 22.8, 14.3. IR ν_{max} 3399 (C=O),3025 (C-H), 3007 (C-H), 2953 (C-H), 2912 (C-H), 2847 (C-H), 1731 (C=O), 1455, 1028 (C-O), 835 (C-H), 758 (C-H) cm^{-1}. Anal. Calcd. for C, 81.62; H, 10.01. Found C, 81.65; H, 9.93.

Methyl 6-phenyl-1-naphthoate 4b



2 **4c**

A mixture of methyl triflate **2** (1.00 g, 3.0 mmol), phenylboronic acid (549 mg, 4.5 mmol), $Pd(PPh_3)_4$ (173 mg, 0.15 mmol), and K_2CO_3 (1.24 g, 9.0 mmol) in a mixture of toluene (28 ml), EtOH (3 ml), and H_2O (3 ml) was degassed by three freeze-pump cycles. The resulting mixture was heated at 90°C for 4.5 h under Ar. The organic phase was filtered through a silica-gel pad and concentrated. The residue was chromatographed on silica-gel (toluene) to afford methyl compound **4c** (744 mg, 94%) as colorless solid.

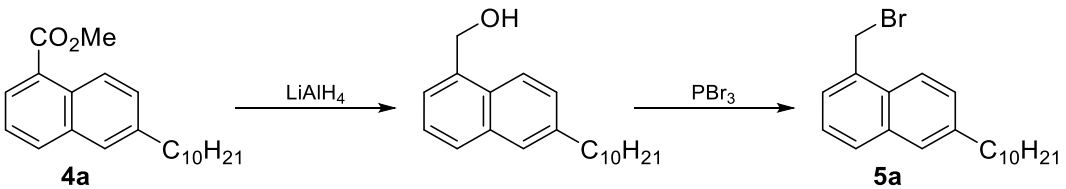
Mp, 77-78.5°C (lit.[S2] 61.3-62.9°C)

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.00 (d, 1H, J = 8.9 Hz), 8.20 (dd, 1H, J = 7.2, 1.2 Hz), 8.10-8.07 (m, 2H), 7.90 (dd, 1H, J = 8.8, 2.0 Hz), 7.76-7.70 (m, 2H), 7.55-7.49 (m, 3H), 7.41 (m, 1H), 4.03 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 168.13, 140.60, 138.89, 134.32, 133.80, 130.67, 130.37, 129.07, 127.77, 127.56, 127.53, 127.05, 126.56, 126.33, 125.10, 52.35.

[S2] P. Álvarez-Bercedo and R. Martin, *J. Am. Chem. Soc.* 2010, **132**, 17352.

1-(bromomethyl)-6-decylnaphthalene 5a



4a **5a**

To a mixture of $LiAlH_4$ (284 mg, 7.48 mmol) in THF (50 ml) was dropwise added a solution of compound **4a** (1.22 g, 3.74 mmol) in THF (10 ml). The reaction mixture was stirred at r.t. for 17.5 h. The reaction was quenched with water (5 ml) and the THF was removed under reduced pressure. The residue was shaken with a mixture of AcOEt (50 ml) and 10% HCl (20 ml). The organic phase was collected, washed with $NaHCO_3$ aq., dried (Na_2SO_4), and concentrated to afford (6-decylnaphthalen-1-yl)methanol (1.08 g, 96%) as an off-white solid.

Mp 48–50°C

^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.06 (d, 1H, J = 8.6 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.65 (brs, 1H), 7.45 (brd, 1H, J = 6.7 Hz), 7.43–7.39 (2H, d and dd signals overlap), 5.14 (s, 2H), 2.77 (t, 2H, J = 7.4 Hz), 1.70 (quin, 2H, J = 7.4 Hz), 1.40–1.20 (m, 14H), 0.88 (t, 3H, J = 6.9 Hz).

^{13}C NMR (151 MHz, $CDCl_3$) δ_C 140.70, 136.21, 134.17, 129.77, 128.32, 128.10, 127.24, 125.52, 124.71, 123.65, 63.97, 36.11, 32.05, 31.52, 29.77, 29.75, 29.69, 29.48 (2C), 22.83, 14.28.

HRMS (FAB) *m*/*z* Calcd. for $C_{21}H_{30}O$: 298.2297. Found. 298.2269 (M^+)

To a solution of (6-decylnaphthalen-1-yl)methanol (1.08 g, 3.62 mmol) in dioxane (20 ml) was added PBr_3 (1.95 g, 7.24 mmol). The mixture was stirred at r.t. for 15 h. The reaction was quenched with sat. $NaHCO_3$. Dioxane was removed under reduced pressure and the residue was extracted with a mixture of toluene (50 ml) and water (30 ml). The insoluble materials were filtered and washed with toluene. The extract and washings were combined and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford 1-(bromomethyl)-6-decylnaphthalene **5a** (1.04 g, 79%).

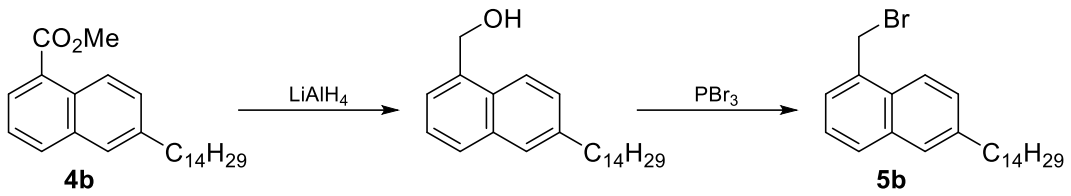
Mp 53–54°C

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.07 (d, 1H, J = 8.4 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.66 (brs, 1H), 7.45–7.46 (m, 2H), 7.37 (dd, J = 8.1, 7.0 Hz), 4.96 (s, 2H), 2.78 (t, 2H, J = 7.7 Hz), 1.71 (quin, 2H, J = 7.5 Hz), 1.41–1.20 (m, 14H), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 1510 MHz) δ_C 141.09, 134.38, 133.16, 129.60, 129.50, 128.34, 127.40, 127.06, 125.49, 123.69, 36.08, 32.09, 32.05, 31.46, 29.77, 29.74, 29.68, 29.50, 29.48, 22.84, 14.28.

HRMS (FAB) *m*/*z* Calcd. for $C_{21}H_{29}{}^{79}Br$: 360.1453. Found. 360.1424 (M^+).

1-(bromomethyl)-6-tetradecylnaphthalene 5b



A solution of compound **4b** (300 mg, 0.786 mmol) in dry THF (5 mL) was added dropwise to a suspension of $LiAlH_4$ (63.6 mg, 1.68 mmol) in dry THF (5 mL) at 0 °C. The resulting mixture was stirred at room temperature for 3 h. Then, water (0.5 mL) was dropwise added to quench the reaction and, subsequently, 10% aqueous NaOH (2 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated to afford (6-tetradecylnaphthalen-1-yl)methanol (269 mg, 0.759 mmol, 97%) as colorless needles.

Mp 63.0–64.0°C.

^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.06 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.46-7.40 (m, 3H), 5.14 (s, 2H), 2.78 (t, J = 7.5 Hz, 2H), 1.72-1.69 (m, 3H), 1.34-1.26 (m, 22H), 0.88 (t, J = 6.6, Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ_C 140.7, 136.2, 134.2, 129.8, 128.3 128.1, 127.3, 125.5, 124.7, 123.7, 64.0, 36.1, 32.1, 31.5, 29.9, 29.82*, 29.81, 29.75, 29.7, 29.51, 29.49, 22.8, 14.3.

Anal. Calcd. for C, 84.69; H, 10.80. Found C, 84.53; H, 10.49.

To a solution of (6-tetradecylnaphthalen-1-yl)methanol (925 mg, 2.61 mmol) in dioxane (20 ml) was added PBr_3 (1.41 g, 5.22 mmol). The mixture was stirred at r.t. for 15 h. The reaction was quenched with sat. $NaHCO_3$. Dioxane was removed under reduced pressure and the residue was extracted with a mixture of toluene (50 ml) and water (30 ml). The insoluble materials were filtered and washed with toluene. The extract and washings were combined and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford compound **5b** (654 g, 60%).

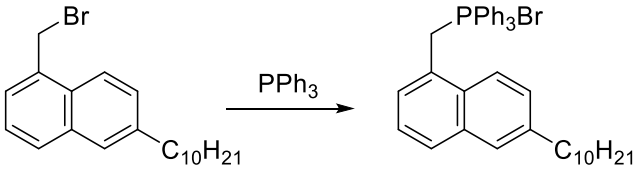
Mp 69–71 °C

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.07 (d, 1H, J = 8.4 Hz), 7.78 (d, 1H, J = 8.2 Hz), 7.65 (brs, 1H), 7.50–7.46 (m, 2H), 7.37 (dd, J = 8.1, 7.1 Hz), 4.96 (s, 2H), 2.78 (t, 2H, J = 7.2 Hz), 1.71 (quin, 2H, J = 7.5 Hz), 1.43–1.22 (m, 22H), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 1510 MHz) δ_C 141.09, 134.39, 133.16, 129.60, 129.50, 128.34, 127.40, 127.06, 125.50, 123.69, 36.08, 32.07, 31.46, 29.84, 29.82 (4C), 29.81, 29.74, 29.68, 29.51, 29.50, 22.85, 14.29,

HRMS (FAB) *m*/*z* Calcd. for $C_{25}H_{37}{}^{79}Br$: 416.2079. Found. 416.2078 (M^+)**.**

((6-Decylnaphthalen-1-yl)methyl)triphenylphosphonium bromide 6a



5a **6a**

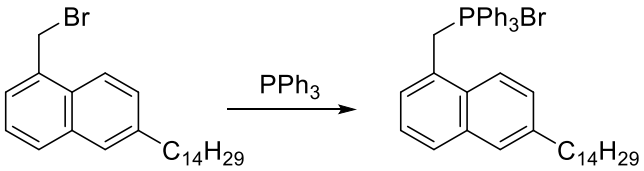
A solution of compound **5a** (900 mg, 2.49 mmol) and PPh_3 (784 mg, 2.99 mmol) in toluene (20 ml) was refluxed for 14 h. The solvent was removed under reduced pressure and the residue was washed with Et_2O mixture to afford phosphonium salt **6a** as white powder (1.50 g, 96%). This compound was used without further purification in the next Wittig reaction.

Mp 158–159°C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.68–7.60 (m, 10H), 7.52–7.47 (m, 6H), 7.43 (brs, 1H), 7.41–7.37 (m, 1H), 7.24 (d, 1H, J = 8.7 Hz), 7.14 (t, 1H, J = 7.5 Hz), 6.83 (dd, 1H, J = 8.7, 1.3 Hz), 5.70 (d, 2H, J_{CP} = 14.0 Hz), 2.58 (t, 2H, J = 7.3 Hz), 1.57 (quin, 2H, J = 7.3 Hz), 1.35–1.20 (m, 14H), 0.86 (t, 3H, J = 6.8 Hz).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 140.37, 134.93/134.91 (J_{CP} = 2.9 Hz), 134.40/134.3, (J_{CP} = 9.8 Hz), 133.75/133.73 (J_{CP} = 2.9 Hz), 130.87/130.84 (J_{CP} = 4.0 Hz), 130.15/130.06 (J_{CP} = 12.4 Hz), 129.71/129.66 (J_{CP} = 6.6 Hz), 128.84/128.81 (J_{CP} = 4.3 Hz), 127.91, 126.99, 125.41/125.38 (J_{CP} = 4.0 Hz), 123.05, 122.87/122.81 (J_{CP} = 9.2 Hz), 118.06/117.49 (J_{CP} = 85.0 Hz), 35.68, 31.98, 31.24, 29.74, 29.73, 29.61, 29.42, 29.26, 27.87/27.56 (J_{CP} = 47.3 Hz), 22.77, 14.22.

Triphenyl((6-Tetradecylnaphthalen-1-yl)methyl)phosphonium bromide 6b



5b **6b**

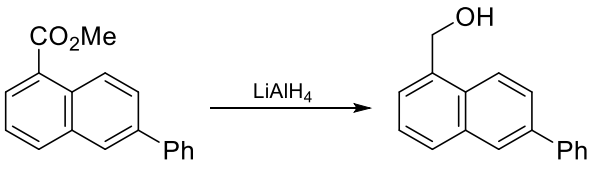
A solution of compound **5b** (600 mg, 1.44 mmol) and PPh_3 (452 mg, 1.72 mmol) in toluene (20 ml) was refluxed for 14 h. The solvent was removed under reduced pressure and the residue was washed with Et_2O mixture to afford phosphonium salt **6b** as white powder (905 mg, 92%). This compound was used without further purification in the next Wittig reaction.

Mp >300°C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.70–7.62 (m, 10H), 7.53–7.48 (m, 6H), 7.45 (brs, 1H), 7.44–7.40 (m, 1H), 7.25 (d, 1H, overlapped with $CHCl_3$ signal), 7.18 (t, 1H, J = 7.6 Hz), 6.84 (dd, 1H, J = 8.7, 1.3 Hz), 5.77 (d, 2H, J_{CP} = 13.7 Hz), 2.60 (t, 2H, J = 7.4 Hz), 1.56 (quin, 2H, J = 7.3 Hz), 1.35–1.20 (m, 22H), 0.87 (t, 3H, J = 6.8 Hz).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 140.38, 134.93/134.91 (JCP = 2.9 Hz),134.47/134.40 (JCP = 9.8 Hz), 133.80/133.78 (JCP = 2.6 Hz), 130.93/130.91 (JCP = 4.3 Hz), 130.16/130.08 (JCP = 12.4 Hz), 129.81/129.76 (JCP = 7.2 Hz), 128.86/128.83 (JCP = 4.3 Hz), 127.94, 127.04, 125.46/125.43 (JCP = 4.0 Hz), 123.08, 122.92/122.86 (JCP = 9.2 Hz), 118.18/117.62 (JCP = 85.0 Hz), 35.72, 32.03, 31.28, 29.82, 29.81, 29.79, 29.77, 29.66, 29.48, 29.31, 27.93/27.61 (JCP = 47.3 Hz), 22.81, 14.25.

(6-Phenylnaphthalen-1-yl)methanol 7



4c **7**

To an ice-cooled suspension of $LiAlH_4$ (307 mmol) in THF (20 ml) was added a solution of compound **4c** (1.41 g, 5.39 mmol) in THF (15 ml). The resulting mixture was stirred at r.t. for 19.3 h. The reaction was quenched with EtOH and the solvent was removed under reduced pressure. The residue was extracted with a mixture of AcOEt (50 ml) and 10% HCl (30 ml).

The organic phase was collected and the aqueous phase was extracted with AcOEt (2 × 30 ml). The combined organic phases were washed with $NaHCO_3$ aq. and dried (Na_2SO_4). The solvent was removed and washed with toluene to afford desired product **7** (**A** 859 mg). The washings were concentrated and residual material was separated with silica-gel column (toluene) to afford additional product **7** (**B** 217 mg). The total yield (**A** + **B**) of compound **7** was 1.07 g (85%).

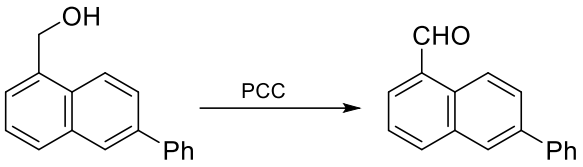
Mp: 130–131°C (colorless crystals).

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.22 (d, 1H, *J* = 8.6 Hz), 8.08 (d, 1H, *J* = 2.0 Hz), 7.88 (d, 1H, *J* = 8.1 Hz), 7.83 (dd, 1H, *J* = 8.6, 2.0 Hz), 7.76-7.71 (m, 2H), 7.55-7.46 (m, 4H), 7.42-7.37 (m, 1H), 5.19 (s, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 140.98, 138.69, 136.33, 134.25, 130.55, 129.05, 129.04, 127.61, 127.53, 126.62, 126.16, 126.02, 125.56, 124.43, 63.90.

HRMS (FAB) Calcd. for $C_{17}H_{14}O$, 234.1045. Found, *m*/*z* 234.1067 (M^+).

6-Phenyl-1-naphthaldehyde 8



7 **8**

To a solution of compound **7** (344 mg, 1.46 mmol) in CH_2Cl_2 (10 ml) was added pyridinium chlororchromate (PCC, 629 mg, 2.92 mmol). The dark brown mixture was stirred at r.t. for 1 h. The reaction mixture was filtered through a short silica-gel column using CH_2Cl_2. The solvent was removed to afford aldehyde **8** (320 mg, 92 %).

Mp: 91–92.5°C (colorless plates).

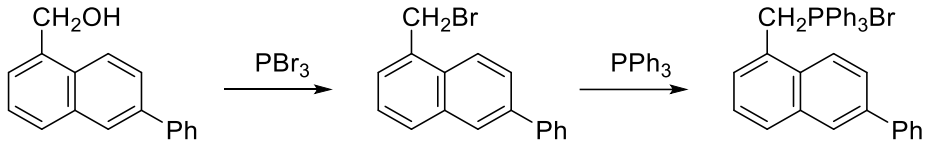
^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 10.41 (s, 1H), 9.33 (d, 1H, *J* = 8.8 Hz), 8.15 (d, 1H, *J* = 8.2 Hz), 8.11 (d, 1H,*J* = 1.9 Hz), 7.99 (dd, 1H, *J* = 7.0, 1.1 Hz), 7.97 (dd, 1H, *J* = 8.8, 1.9 Hz), 7.75–7.72 (m, 2H), 7.66 (dd, 1H, *J* = 8.1, 7.1 Hz), 7.53–7.49 (m, 2H), 7.44–7.40 (m, 1H), .

^{13}C NMR ($CDCl_3$, 151 MHz): δ_H 193.70, 140.42, 139.68, 136.74, 135.63, 134.22, 131.45, 129.73, 129.11, 128.80, 127.91, 127.53, 126.23, 125.60, 125.45.

The NMR spectral data were identical with those previously reported.[S3]

[S3] Y. Mao, J. Jiang, D. Yuan, X. Chen, Y. Wang, L. Hu, Y. Zhang, Overcoming peri- and ortho-selectivity in C–H methylation of 1-naphthaldehydes by a tunable transient ligand strategy, *Chem. Sci*., 2022, **13**, 2900–2908.

Triphenyl((6-phenylnaphthalen-1-yl)methyl)phosphonium bromide 8



7 **8**

To an ice-cooled solution of 1-hyrdoxymethyl-6-phenylnaphthalene (980 mg, 4.18 mmol) in CH_2Cl_2 (20 ml) was dropwise added a solution of PBr_3 (2.72 g, 10 mmol) in CH_2Cl_2 (5 ml). The resulting mixture was stirred at 0°C for 10 min. Then, the reaction was allowed to warm to r.t. and stirred at r.t. for 2 h. The reaction was quenched with water and the organic phase was collected, washed with water, $NaHCO_3$ aq., and dried (Na_2SO_4). The solvent was removed and the residue was passed through a short silica-gel column (toluene) to afford 1-bromomethyl-6-phenylnaphthalene (1.16 g, 93%).

Colorless crystals, mp, 143-145°C**.**

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.24 (d, 1H, *J* = 8.8 Hz), 8.09 (d, 1H, *J* = 1.9 Hz), 7.92-7.88 (m, 2H, d and dd signals overlap), 7.76-7.72 (m, 2H), 7.55 (dd, 1H, *J* = 7.0, 1.0 Hz), 7.52-7.49 (m, 2H), 7.44 (dd, 1H, *J* = 8.2, 7.0). 7.42-7.38 (m, 1H), 5.00 (s, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 140.82, 139.11, 134.50, 133.37, 130.36, 130.23, 129.09, 127.90, 127.74, 127.58, 126.81, 126.46, 126.03, 124.47, 31.84.

HRMS (FAB) Calcd. for $C_{17}H_{13}{}^{79}Br$, 296.0201. Found, *m*/*z* 296.0177 (M^+).

A solution of 1-bromomethyl-6-phenylnaphthalene (1.00 g, 3.36 mmol) and PPh_3 (1.06 g, 4.04 mmol) in toluene (40 ml) was refluxed for 14.5 h. The precipitate formed was collected and washed with toluene to afford phosphonium salt **9** as colorless crystals (1.79 g, 95%).

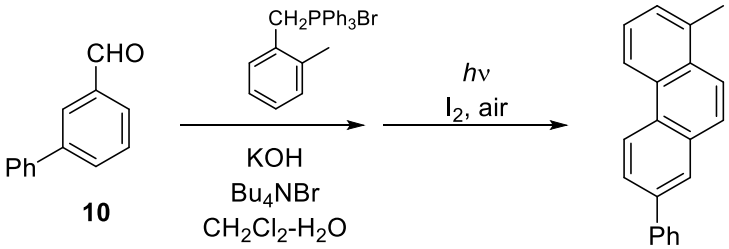
Mp, 271-273°C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.82 (d, 1H, J = 1.7 Hz), 7.70-7.61 (m, 10H), 7.56-7.52 (m, 2H), 7.51-7.46 8m, 6H), 7.46-7.40 (m, 4H), 7.36–7.32 (m, 1H), 7.22 (dd, 1H, J = 8.6, 1.7 Hz), 7.16 (ddd, 1H, J = 8.0, 7.2, 0.8 Hz).

^{13}C NMR ($CDCl_3$, 151 MHz) δ_C 140.25, 137.99, 134.94*, 134.92* ($J_{C\text{-}P}$ = 2.8 Hz), 134.50*, 134.44*($J_{C\text{-}P}$ = 9.8 Hz), 133.75*, 133.73* ($J_{C\text{-}P}$ = 2.8 Hz), 131.57*, 131.54* ($J_{C\text{-}P}$ = 4.3 Hz), 130.68*, 130.64* ($J_{C\text{-}P}$ = 6.6 Hz), 130.16*, 130.08* ($J_{C\text{-}P}$ = 12.4 Hz), 129.49*, 129.46* ($J_{C\text{-}P}$ = 4.3 Hz), 128.99, 127.68, 127.22, 126.09, 125.86*, 125.84* ($J_{C\text{-}P}$ = 4.3 Hz), 125.73, 124.12, 123.20*, 123.14* ($J_{C\text{-}P}$ = 9.2 Hz), 118.06*, 117.49* ($J_{C\text{-}P}$ = 85.3 Hz), 27.89, 27.58 ($J_{C\text{-}P}$ = 47.3 Hz). (The asterisked signals show coupling with ^{31}P.)

HRMS (FAB) Calcd. for $C_{35}H_{28}P^+$, 479.1929. Found, m/z 479.1932 (M^+)

1-Methyl-7-phenylphenanthrene 12



Method 1: To a solution of (*o*-tolylmethyl)triphenylphosphonium bromide (984 mg, 2.2 mmol), 3-phentylbenzaldehyde **10** (364 mg, 2.0 mmol) and Bu_4NBr (64 mg, 0.20 mmol) in CH_2Cl_2 (10 ml) was added a solution of KOH (1.2 g, 21 mmol) in water (1.2 ml). The mixture was stirred at r.t. for 15 h. The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica-gel (hexane). The obtained oil (438 mg) was dissolved in cyclohexane (500 ml) and small pieces of I_2 was added. The solution was irradiated with black-light lamps (16 × 16 W) with air-bubbling for 22 h. The solvent was removed and the residue was dissolved in CH_2Cl_2 and the solution was washed with aqueous sodium thiosulfate (10%) and dried (Na_2SO_4). CH_2Cl_2 was removed and the residue was recrystallized from EtOH to afford 1-methyl-7-phenylphenanthrene **12** (156 mg, 29 % for two steps) as colorless plates.

Mp 224–225°C.

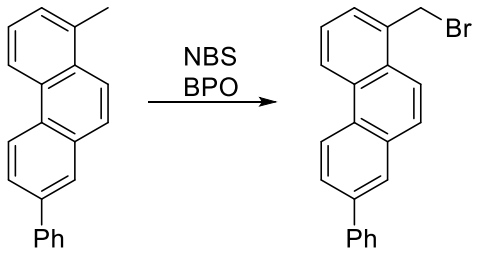
^{1}H NMR: ($CDCl_3$, 600 MHz) δ_H 8.77 (d, 1H, *J* = 8.5 Hz), 8.01 (d, 1H, *J* = 8.3 Hz), 8.12 (d, 1H, *J* = 1.9 Hz), 8.00 (d, 1H, *J* =9.0 Hz), 7.92 (dd, 1H, *J* = 8.5, 1.9 Hz), 7.85 (d, 1H, *J* = 9.0 Hz), 7.79 (m, 2H), 7.57 (dd, 1H, *J* = 8.2, 7.1 Hz), 7.15 (n, 2H), 7.66 (d, 1H, *J*= 7.1 Hz), 7.41 (m, 1H), 2.78 (s, 3H).

^{13}C NMR: ($CDCl_3$, 151 MHz) δ_C 140.95, 139.19, 135.09, 132.12, 130.97, 130.33, 129.92, 129.04, 127.97, 127.57, 127.51, 127.02, 126.61, 126.43, 125.96, 123.71, 123.47, 121.05, 20.11.

Anal: Calcd. for $C_{21}H_{16}$, C, 93.99; H, 6.01. Found C, 93.75; H, 5.83.

Method 2: To a solution of phosphonium salt **10** (1.18 g, 2.31 mmol) and *o*-tolualdehyde (263 mg, 2.19 mmol) and dicyclohexano-18-crown-6 (86 mg, 0.23 mmol) in CH_2Cl_2 (20 ml) was added a mixture of KOH (2.6 g) in water (2.6 ml). The mixture was stirred at rt for 14 h. The resulting mixture was washed with water and the organic phase was collected and dried (Na_2SO_4). The solvent was removed and the residue was chromatographed (silica gel, hexane). The obtained colorless oil was dissolved in cyclohexane (500 ml) and small pieces of I_2 were added. The resulting solution was irradiated with black-light lamps (16 × 16 W) with air-bubbling for 22 h. The resulting solution was washed with $Na_2S_2O_4$ aq, dried (Na_2SO_4) The solvent was removed and the residue was recrystallized from EtOH to afford 1-methyl-6-phenylphenanthrene **12** (156 mg, 29 % for two steps) as colorless plates. The NMR spectral data for the obtained product were the same as those observed for the product produced by the Method 1.

1-Bromomethyl-7-phenylnaphthalene 13



12 **13**

A mixture of compound **12** (250 mg, 0.93 mmol), NBS (164 mg, 0.93 mmol), and BPO (75wt% 30 mg, 0.09 mmol) in CCl_4 (20 ml) was refluxed for 16 h. The solvent was removed and the residue was chromatographed on silica gel (toluene). The crude product, (12 : 13 = 1 : 4), was

recrystallized from a CH_2Cl_2-hexane mixture to afford the desired product **13** as pale brown plates (169 mg, 52 %).

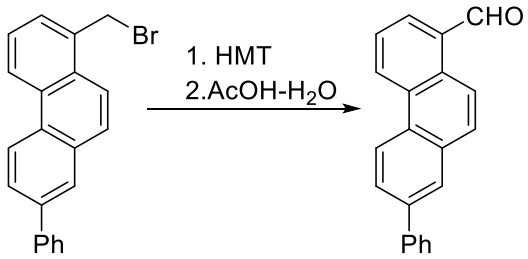
Mp 201–203°C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.75 (d, 1H, *J* = 8.5 Hz), 8.74 (d, 1H, *J* = 8.1 Hz), 8.07 (d, 1H, *J* = 1.8 Hz), 8.13 (d, 1H, *J* = 9.1 Hz), 7.96 (d, 1H, *J* = 9.1 Hz), 7.94 (dd, 1H, *J* = 8.5, 1.9 Hz), 7.80–7.77 (m, 2H), 7.66 (dd, 1H, *J* = 7.0, 0.9 Hz), 7.61 (t, 1H *J* = 7.8 Hz), 7.54–7.50 (m, 2H), 7.44–7.39 (m, 1H), 5.03 (s, 2H).

^{13}C NMR ($CDCl_3$, 1510 MHz) δ_C 140.72. 139.70, 134.07, 132.21, 131.11, 130.02, 129.70, 129.09, 128.54, 128.12, 127.72, 127.52, 126.71, 126.40, 126.32, 124.29, 123.63, 122.60, 32.18.

Anal: Calcd. for $C_{21}H_{15}Br$, C, 72.64; H, 4.35. Found C, 72.52; H, 4.72.

7-Phenylphenanthrene-1-carbaldehyde 14



13 **14**

A solution of compound **13** (321 mg, 0.924 mmol) and hexamethylenetetramine (HMT) (259 mg, 1.85 mmol) in $CHCl_3$ (20 ml) was refluxed for 2.5 h. Another portion of HMT (130 mg, 0.93 mol) was added and the resulting mixture was further refluxed for 2 h. $CHCl_3$ was removed under reduced pressure and the residue was dissolved in AcOH (15 ml) and water (5 ml). The brown solution was refluxed for 12. The obtained mixture was diluted with sat. NaCl aq. (50 ml) and extracted with $CHCl_3$ (2 × 30 ml). The extracts were combined, washed with sat. NaH CO3 aq. then water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica-gel ($CHCl_3$) to afford phenanthrene carboaldehyde (169 mg, 65%) as colorless fine needles.

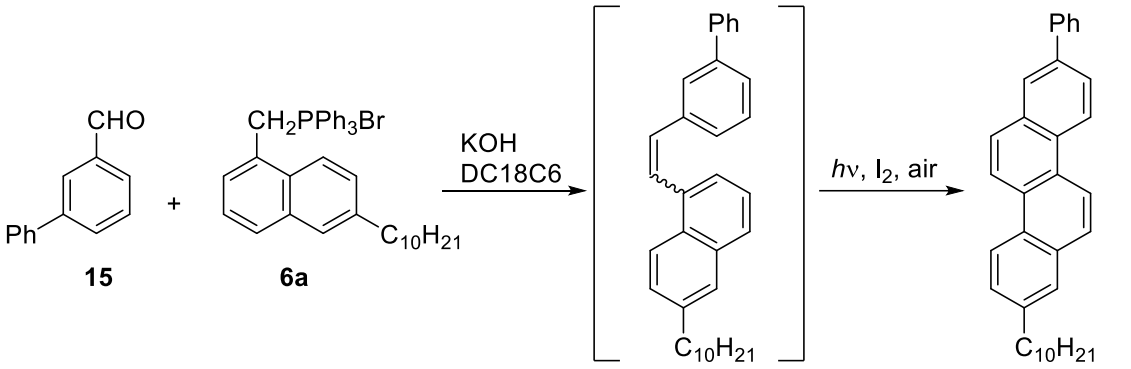
Mp: 202–204°C

^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 10.53 (s, 1H), 9.19 (d, 1H, *J* = 9.1), 9.00 (d, 1H, *J* = 8.3 Hz), 8.76 (d, 1H, *J* = 8.5 Hz), 8.15 (d, 1H, *J* = 1.9 Hz), 8.11 (dd, 1H, *J* = 7.1, 1.0 Hz), 8.02 (d, 1H, *J*

= 9.1 Hz), 7.97 (dd, 1H, *J* = 8.5, 1.9 Hz), 7.83 (dd, 1H, *J* = 8.2, 7.2 Hz), 7.80–7.77 (m, 2H), 7.55–7.51 (m, 2H), 7.45–7.41 (m, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_C 193.75, 140.54, 140.12, 135.35, 132.29, 131.83, 130.92, 130.60, 130.53, 129.22, 129.13, 128.99, 127.85, 127.54, 126.71, 126.61, 125.98, 123.60, 122.81.

3-Decyl-9-phenylchrysene (PhC10-CHR)



To a mixture of aldehyde **15** (100 mg, 0.55 mmol)), phosphonium salt **6a** (311 mg, 0.50 mmol), and dicyclohexano-18-crown-6 (DC18C6, 20 mg, 0.055 mmol) in CH_2Cl_2 (10 ml) was added a solution of KOH (0.68 g, 12 mmol) in water (0.7 ml). The mixture was stirred at r.t. for 17 h. Water (20 ml) was added to the resulting mixture. The organic phase was collected, dried (Na_2SO_4), filtered through a short silica-gel column, and concentrated. The residual diarylethene **17a** (224 mg) was used for the Mallory photoreaction without purification. The crude diarylethene **17a** was dissolved in cyclohexane (200 ml) and small portions of I_2 was added. The solution was irradiated with black-light lamps (6 × 15 W) for 4 h. The precipitate formed was collected and washed with toluene and EtOH to afford **PhC10-CHR** as off-white fine plates (74.3 mg, **A**). The filtrate was irradiated for 14 h. The second crop of **PhC10-CHR** was collected and washed with toluene and EtOH (14.8 mg, **B**). The total yield (**A** + **B**) of **PhC10-CHR** was 89.1 mg (40% for two steps).

Mp >300°C (colorless plates).

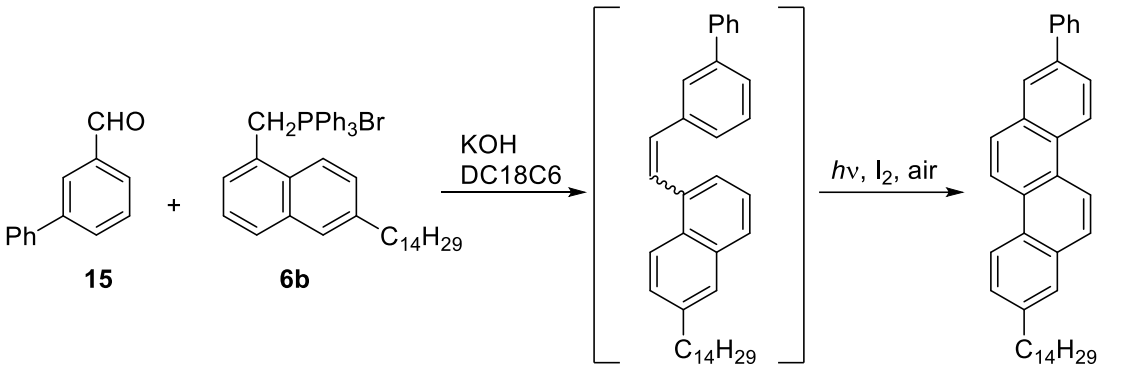
^{1}H NMR ($CDCl_3$, 600 MHz, 50°C) δ_H 8.83 (d, 1H, *J* = 8.6 Hz), 8.75–8.67 (m, 3H), 8.19 (brs, 1H), 8.04 (d, 1H,*J* = 8.8 Hz), 8.00–7.94 (m, 2H), 7.85–7.75 (m, 3H), 7.56 (d, 1H, *J* = 8.6 Hz),

7.54–7.49 (m, 2H), 7.44–7.38 (m, 1H), 2.87 (t, 2H, J = 7.7 Hz), 1.79 (quin, 2H, J = 7.3 Hz), 1.47–1.23 (m, 14H), 0.89 (t, 3H, J = 6.7 Hz).

^{13}C NMR ($CDCl_3$, 151 MHz, 50°C) δ_H 141.43, 141.16, 139.09, 132.70, 132.63, 130.09, 129.09, 128.59, 128.22, 127.91, 127.60, 127.55, 127.49, 126.65, 126.17, 123.89, 123.26, 121.90, 121.38, 36.14, 32.09, 31.57, 29.81, 29.79, 29.73, 29.59, 29.49, 22.83, 14.19.

Anal: Calcd. for $C_{34}H_{36}$, C, 91.84; H, 8.16. Found, C, 91.79; H, 8.25.

3-Tetradecyl-9-phenylchrysene (PhC14-CHR)



To a mixture of aldehyde **15** (100 mg, 0.55 mmol)), phosphonium salt **6b** (340 mg, 0.50 mmol), and dicyclohexano-18-crown-6 (20 mg, 0.055 mmol) in CH_2Cl_2 (10 ml) was added a solution of KOH (0.68 g, 12 mmol) in water (0.7 ml). The mixture was stirred at r.t. for 17.5 h. Water (20 ml) was added to the resulting mixture. The organic phase was collected, dried (Na_2SO_4), filtered through a short silica-gel column, and concentrated. The residual diarylethene **17b** (248 mg) was used for the Mallory photoreaction without purification. The crude diarylethene **17b** was dissolved in cyclohexane (200 ml) and small portions of I_2 was added. The solution was irradiated with black-light lamps (6 × 15 W) for 5 h. The precipitate formed was collected and washed with toluene and EtOH to afford **PhC14-CHR** as off-white fine plates (109 mg, 43% for two steps).

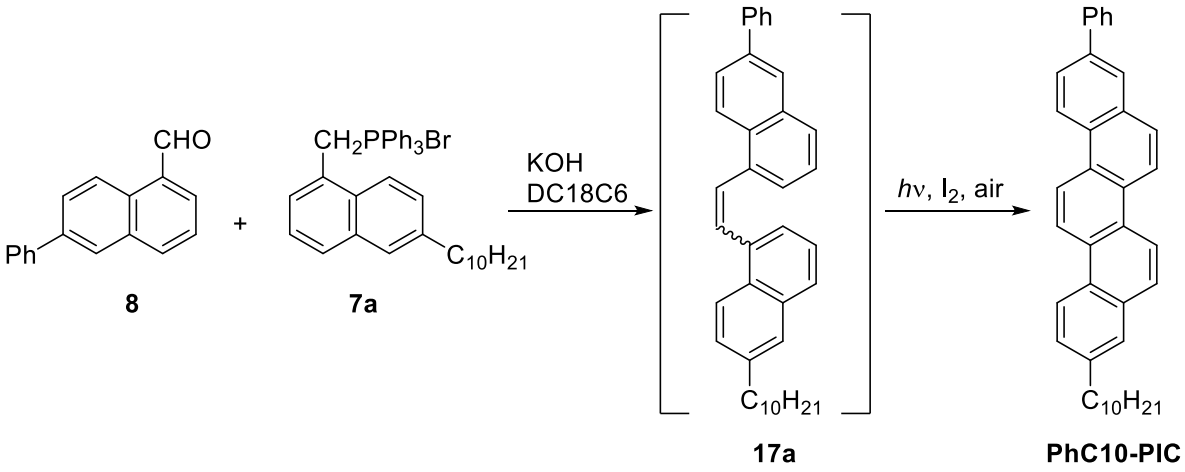
Mp: >300°C.

^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 600 MHz, 85°C) δ_H 8.85 (d, 1H, J = 8.7 Hz), 8.76–8.69 (m, 3H), 8.22 (brs, 1H), 8.08 (d, 1H,J = 8.9 Hz), 8.02–7.98 (m, 2H), 7.85–7.80 (m, 3H), 7.61 (d, 1H, J = 8.6 Hz), 7.57–7.53 (m, 2H), 7.46–7.42 (m, 1H), 2.90 (t, 2H, J = 7.5 Hz), 1.84 (quin, 2H, J = 7.3 Hz), 1.53–1.27 (m, 22H), 0.89 (t, 3H, J = 6.7 Hz).

^{13}C NMR (1,1,2,2-tetrachloroethane-d_2, 151 MHz, 80°C) δ_C 141.43, 140.78, 138.88, 132.51, 132.44, 129.88, 128.98, 128.87, 128.40, 128.17, 127.70, 127.56, 127.52, 127.43, 127.40, 127.39, 126.46, 126.02, 123.76, 123.14, 121.80, 121.23, 35.93, 31.91, 31.26, 29.66, 29.64, 29.60, 29.53, 29.45, 29.30, 22.65, 14.07.

Anal: Calcd. for $C_{38}H_{44}$, C, 91.14; H, 8.86. Found, C, 91.13; H, 8.99.

3-Decyl-10-phenylpicene (PhC10-PIC)



To a solution of phosphonium salt **7a** (250 mg, 0.40 mmol) and aldehyde **8** (102 mg, 0.44 mmol) and dicyclohecano-18-crown-6 (15 mg, 0.04 mmol) in CH_2Cl_2 (10 ml) was added a solution of KOH (500 mg, 8.9 mmol) in water (0.5 ml). The mixture was vigorously stirred at r.t. for 17.5 h. CH_2Cl_2 (10 ml) and water (10 ml) were added to the resulting mixture. The organic phase was collected, washed with water, dried (Na_2SO_4). The solution was filtered through a short silica-gel column and concentrated. The residue was dissolved in toluene (200 ml) and a small portion of I_2 was added. The solution was irradiated with black-light lamps (6 × 16 W) for 4 h. The precipitate formed was collected and successively washed with toluene and MeOH to afford **PhC10-PIC** as off-white fine plates (172 mg, 87 % for two steps).

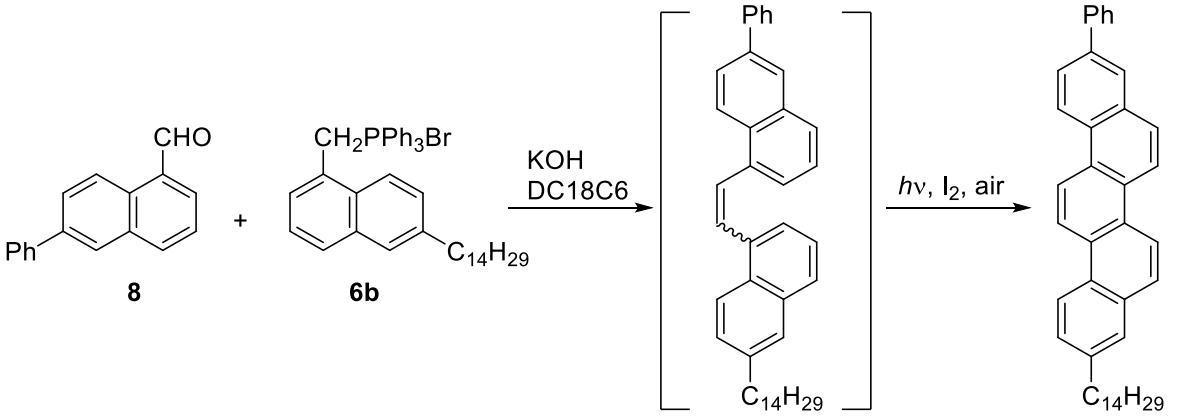
Mp >300°C.

^{1}H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d_2, 100°C): δ_H 8.99–8.94 (m, 2H), .8.93 (d, 1H, J = 8.9 Hz), 8.82 (d, 1H, J = 9.1 Hz), 8.80–8.76 (two doublets overlap, 2H), 8.25 (s, 1H), 8.11 (d, 1H, J = 9.1 Hz), 8.05–8.01 (two doublets overlap, 2H), 7.87–7.82 (m, 3H), 7.64 (d, 1H, J = 8.4 Hz), 7.56 (t, 2H, J = 7.3 Hz), 7.45 (t, 1H, J = 7.0 Hz), 2.93 (t, 2H, J = 7.5 Hz), 1.86 (quin, 2H, J = 7.4 Hz), 1.56–1.19 (m, 14H), 0.95 (t, 3H), J = 6.0 Hz). ^{13}C NMR (151 MHz, 1,1,2,2-

tetrachloroethane-d_2, 100°C): δ_C 141.66, 140.83, 139.31, 132.35, 132.32, 129.84, 128.94, 128.85, 128.83, 128.46, 128.37, 128.18, 127.67, 127.54, 127.40, 127.36, 126.44, 126.15, 123.74, 123.11, 122.19, 121.87, 121.63, 121.56, 35.93, 31.85, 31.18, 29.56 (2C), 29.49, 29.41, 29.23, 22.58, 13.94.

Anal Calcd. for $C_{38}H_{38}$, C, 92.26; H, 7.74. Found C, 92.14; H, 7.73.

3-Tetradecyl-10-phenylpicene (PhC10-PIC)



To a solution of phosphonium salt **6b** (272 mg, 0.40 mmol) and aldehyde **8** (102 mg, 0.44 mmol) and dicyclohecano-18-crown-6 (15 mg, 0.04 mmol) in CH_2Cl_2 (10 ml) was added a solution of KOH (500 mg, 8.9 mmol) in water (0.5 ml). The mixture was vigorously stirred at r.t. for 17.5 h. CH_2Cl_2 (10 ml) and water (10 ml) were added to the resulting mixture. The organic phase was collected, washed with water, dried (Na_2SO_4). The solution was filtered through a short silica-gel column and concentrated. The residue was dissolved in toluene (200 ml) and a small portion of I_2 was added. The solution was irradiated with black-light lamps (6 × 16 W) for 4 h. The precipitate formed was collected and successively washed with toluene and MeOH to afford **PhC14-PIC** as off-white fine plates (183 mg, 83 % for two steps).

Mp >300°C.

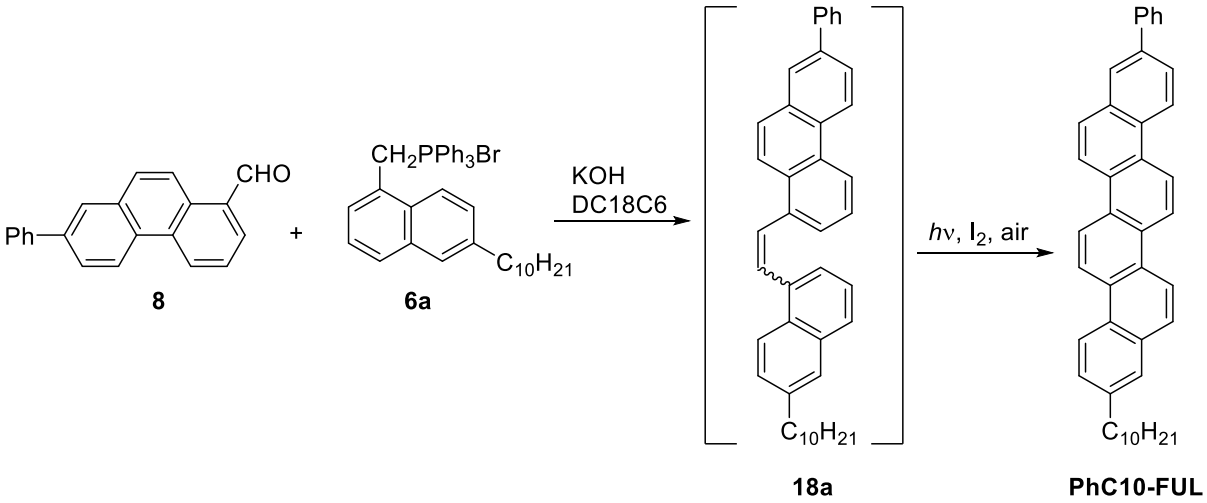
^{1}H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d_2, 100°C): δ_H 8.98–8.94 (m, 2H), .8.93 (d, 1H, J = 8.7 Hz), 8.82 (d, 1H, J = 8.9 Hz), 8.80–8.76 (two doublets overlap, 2H), 8.25 (s, 1H), 8.11 (d, 1H, J =8.9 Hz), 8.05–8.01 (two doublets overlap, 2H), 7.87–7.82 (m, 3H), 7.64 (d, 1H, J =

8.2 Hz), 7.56 (t, 2H, *J* = 7.4 Hz), 7.45 (t, 1H, *J* = 7.0 Hz), 2.93 (t, 2H, *J* = 7.5 Hz), 1.86 (quin, 2H, *J* = 7.2 Hz), 1.56–1.27 (m, 22H), 0.95 (t, 3H), *J* = 6.0 Hz).

^{13}C NMR (151 MHz, 1,1,2,2-tetrachloroethane-d_2, 100°C): δ_C 141.67, 140.84, 139.32, 132.37, 132.33, 129.85, 128.95, 128.86, 128.83, 128.47, 128.37, 128.19, 127.68, 127.55, 127.41, 127.37, 126.44, 126.15, 123.74, 123.12, 122.19, 121.87, 121.64, 121.57, 35.92, 31.86, 31.17, 29.61 (4C), 29.58, 29.55, 29.482, 29.40, 29.24, 22.57, 13.94.

Anal Calcd. for $C_{42}H_{46}$, C, 91.58; H, 8.42. Found C, 91.48; H, 8.41%.

3-Decyl-11-phenyl-fulminene PhC10-FUL



8 **6a** **18a** **PhC10-FUL**

To a mixture of phosphonium salt **6a** (189 mg, 0.30 mmol), aldehyde **14** (90 mg, 0.32 mmol), and dicyclohexano-18-crown-6 (11 mg, 0.03 mmol) in CH_2Cl_2 (5 ml) was added an aqueous solution of KOH (0.5 g in 0.5 ml). The mixture was stirred for 22 h. The precipitate was collected, washed with water then EtOH, and dried. The obtained solid (diarylethene **18a**) was dissolved in toluene (200 ml) and small pieces of I_2 were added. The resulting solution was irradiated with black-light lamps (6 × 16 W) for 2 h. The precipitated product was collected by suction filtration and washed with toluene. The crude product was recrystallized from *o*-dichlorobenzene to afford **PhC10-FUL** (108 mg, 65 %) as off-white plates.

MP >300°C.

^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 100°C) δ_H 9.05 (d, 1H, *J* = 9.2 Hz), 9.03 (d, 1H, *J* = 9.4 Hz) 9.01 (d, 1H, *J* = 9.2 Hz), 8.98 (d, 1H, *J* = 8.9 Hz), 8.96 (d, 1H, *J* = 8.4 Hz), 8.91 (d, 2H, *J* = 8.9 Hz), 8.86 (d, 1H, *J* = 8.8 Hz), 8.81 (d, 1H, *J* = 8.3 Hz), 8.26 (s, 1H), 8.16 (d, *J* = 8.9 Hz), 8.08–8.04 (m, 2H), 7.88–7.83 (m, 3H), 7.65 (d, 1H, *J* =8.4 Hz), 7.57 (t, 2H, *J* = 7.3 Hz), 7.46

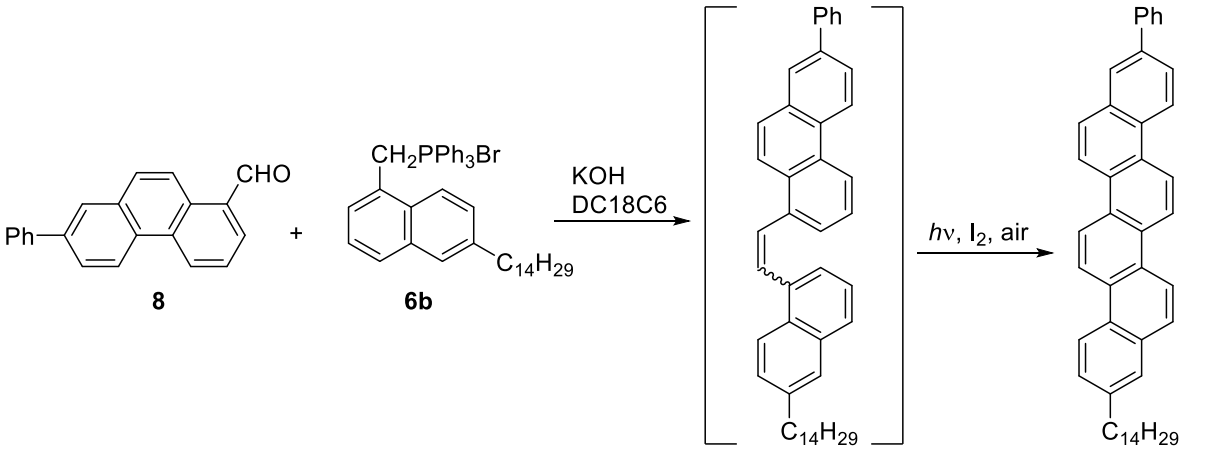
(t, 1H, J = 7.3 Hz), 2.95 (t, 2H, J = 7.5 Hz), 1.88 (quin, 2H, J = 7.5 Hz), 1.57–1.30 (m, 14 H, overlapped with H_2O), 0.96 (t, 3H, J = 6.5 Hz).

^{13}C NMR Not obtained due to low solubility.

Anal Calcd for $C_{46}H_{48}$; C, 92.60; H, 7.40. Found; C, 92.35; H, 7.24.

3-Tetradecyl-11-phenyl-fulminene PhC14-FUL

To a mixture of phosphonium salt **6b** (115 mg, 0.21 mmol), aldehyde **14** (50 mg, 0.17 mmol), and dicyclohexano-18-crown-6 (7.5 mg, 0.02 mmol) in CH_2Cl_2 (5 ml) was added an aqueous solution of KOH (0.3 g in 0.3 ml). The mixture was stirred for 22 h. The precipitate was collected, washed with water then EtOH, and dried. The obtained solid was dissolved in toluene (100 ml) and small pieces of I_2 were added. The resulting solution was irradiated with black-light lamps (6 × 16 W) for 2h. The precipitated product was collected by suction filtration and washed with toluene. The crude product was recrystallized from *o*-dichlorobenzene to afford **PhC14-FUL** (61 mg, 61 %) as off-white plates.



MP >300°C.

^{1}H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d_2, 100°C) δ_H 9.05 (d, 1H, J = 9.4 Hz), 9.03 (d, 1H, J = 9.4 Hz) 9.01 (d, 1H, J = 9.2 Hz), 8.99 (d, 1H, J = 9.2 Hz), 8.95 (d, 1H, J = 8.7 Hz), 8.91 (d, 2H, J = 9.1 Hz), 8.86 (d, 1H, J = 9.1 Hz), 8.80 (d, 1H, J = 8.6 Hz), 8.27 (d, 1H, J = 1.0 Hz), 8.16 (d, J = 8.9 Hz), 8.08–8.04 (m, 2H), 7.88–7.83 (m, 2H), 7.65 (dd, 1H, J =8.6, 1.1 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.3 Hz), 2.94 (t, 2H, J = 7.5 Hz), 1.86 (quin, 2H, J = 7.5 Hz), 1.56–1.28 (m, 22 H, overlapped with H_2O), 0.94 (t, 3H, J = 7.0 Hz).

^{13}C NMR Not obtained due to low solubility.

Anal Calcd for $C_{46}H_{48}$; C, 91.95; H, 8.05. Found; C, 91.55; H, 8.04.

(2) NMR spectra (Figure S1-1 – S1-24) of compounds synthesized in this study.

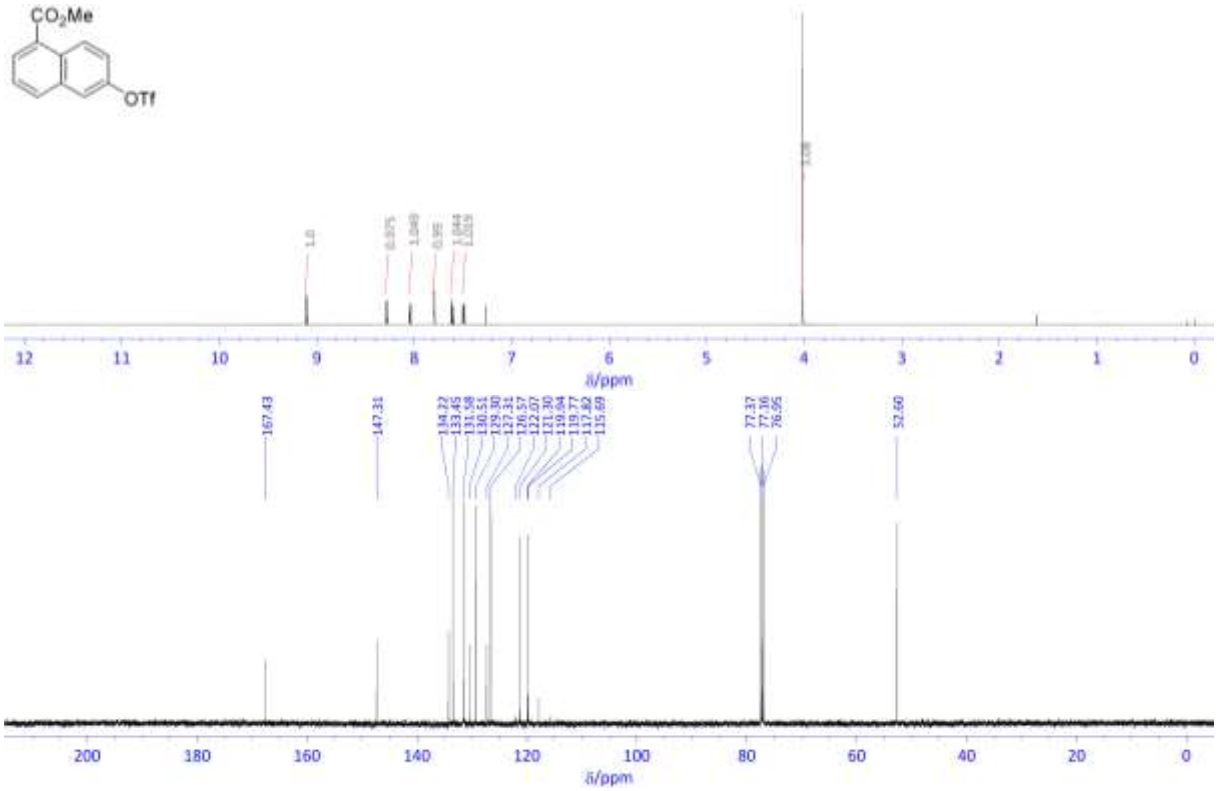


Figure S1-1. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of triflate **2** ($CDCl_3$).

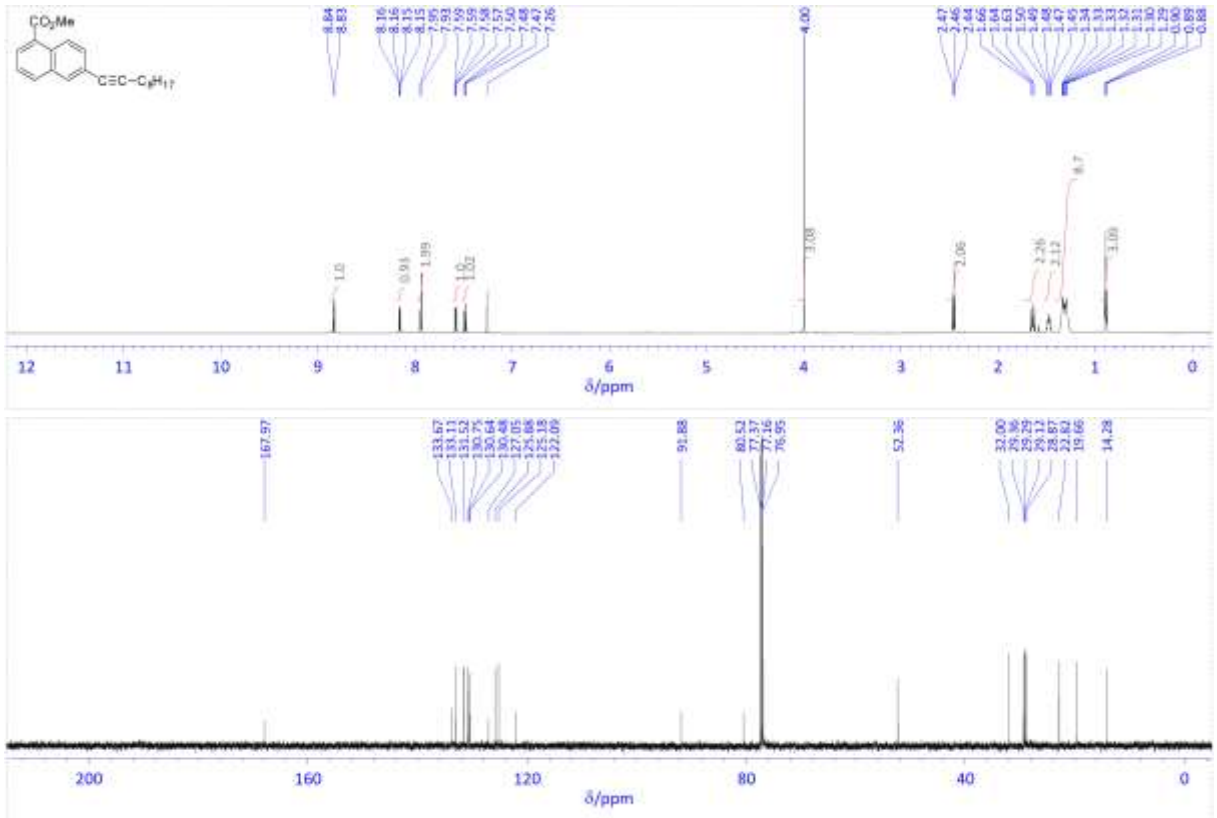


Figure S1-2. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3a** ($CDCl_3$).

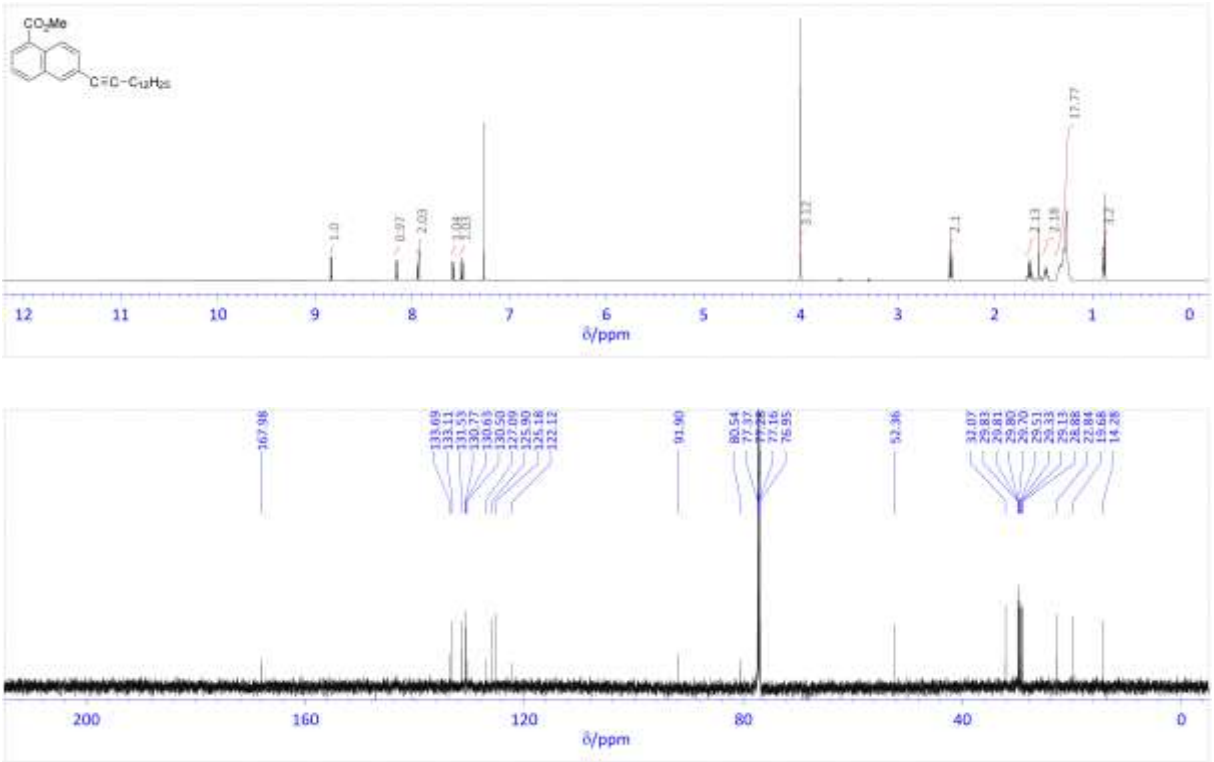


Figure S1-3. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **3b** ($CDCl_3$).

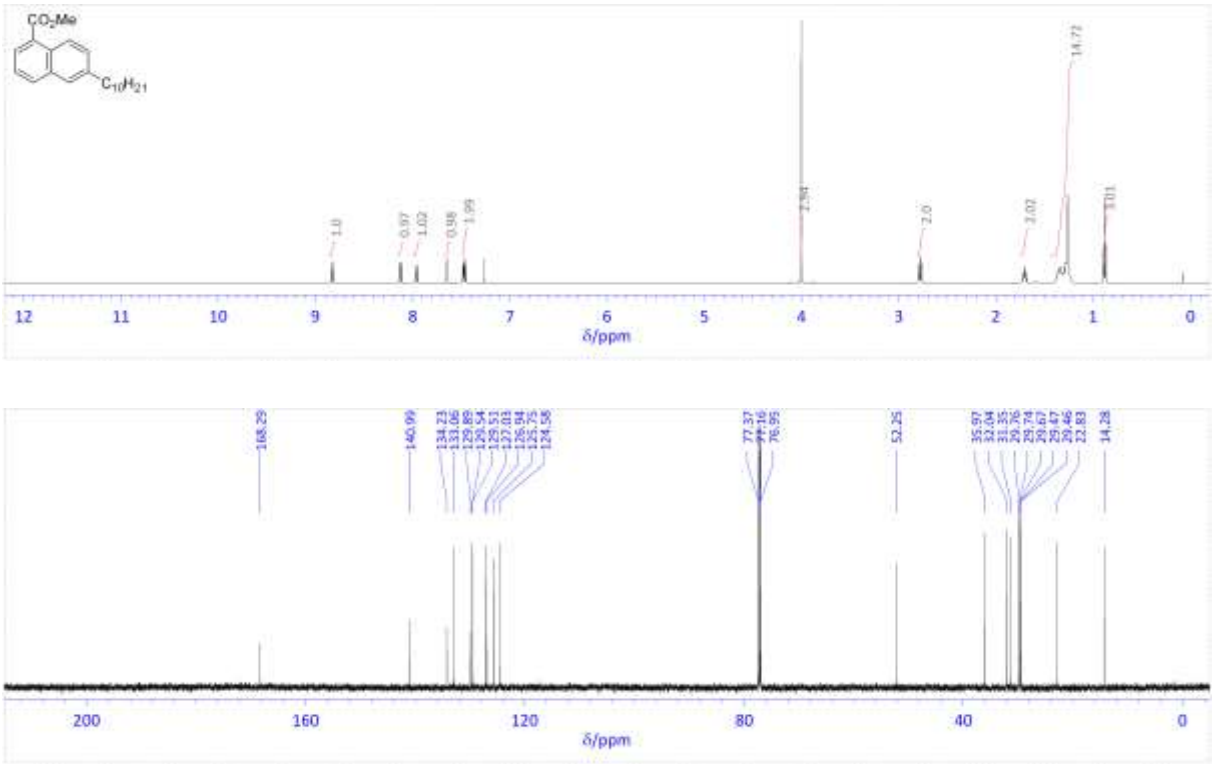


Figure S1-4. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4a** ($CDCl_3$).

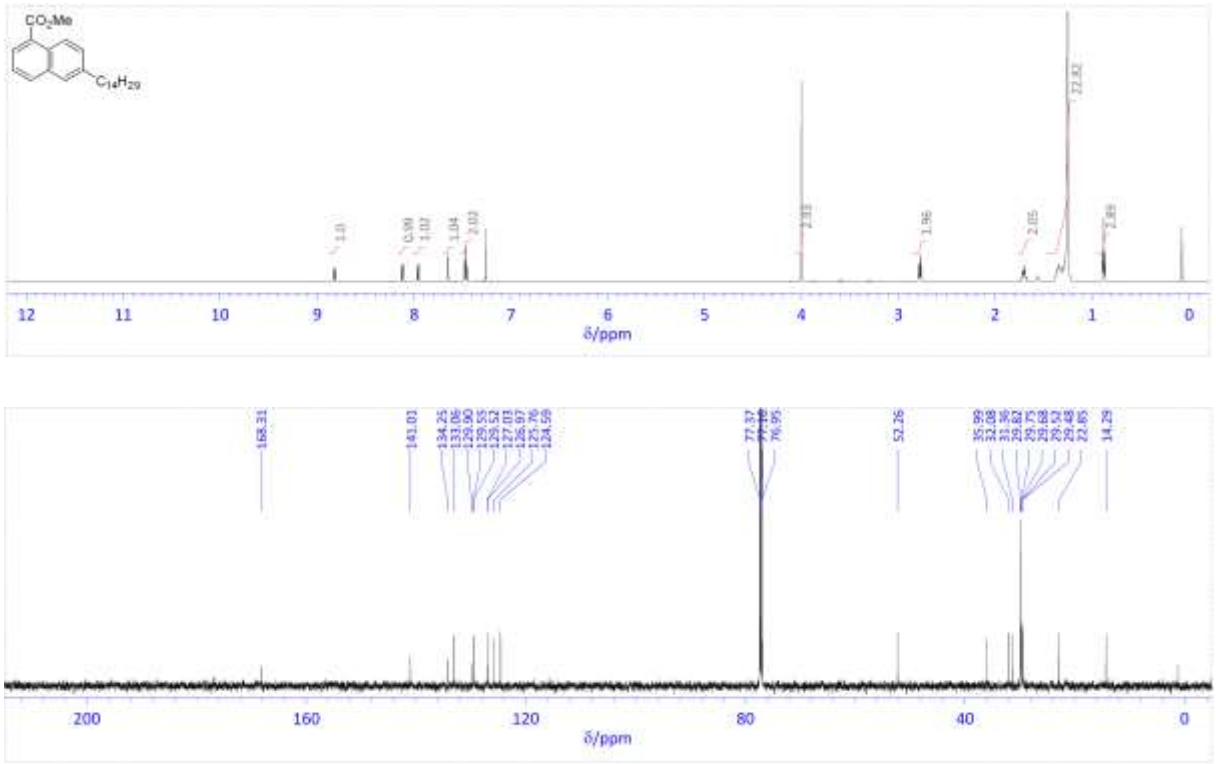


Figure S1-5. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **4b** ($CDCl_3$).

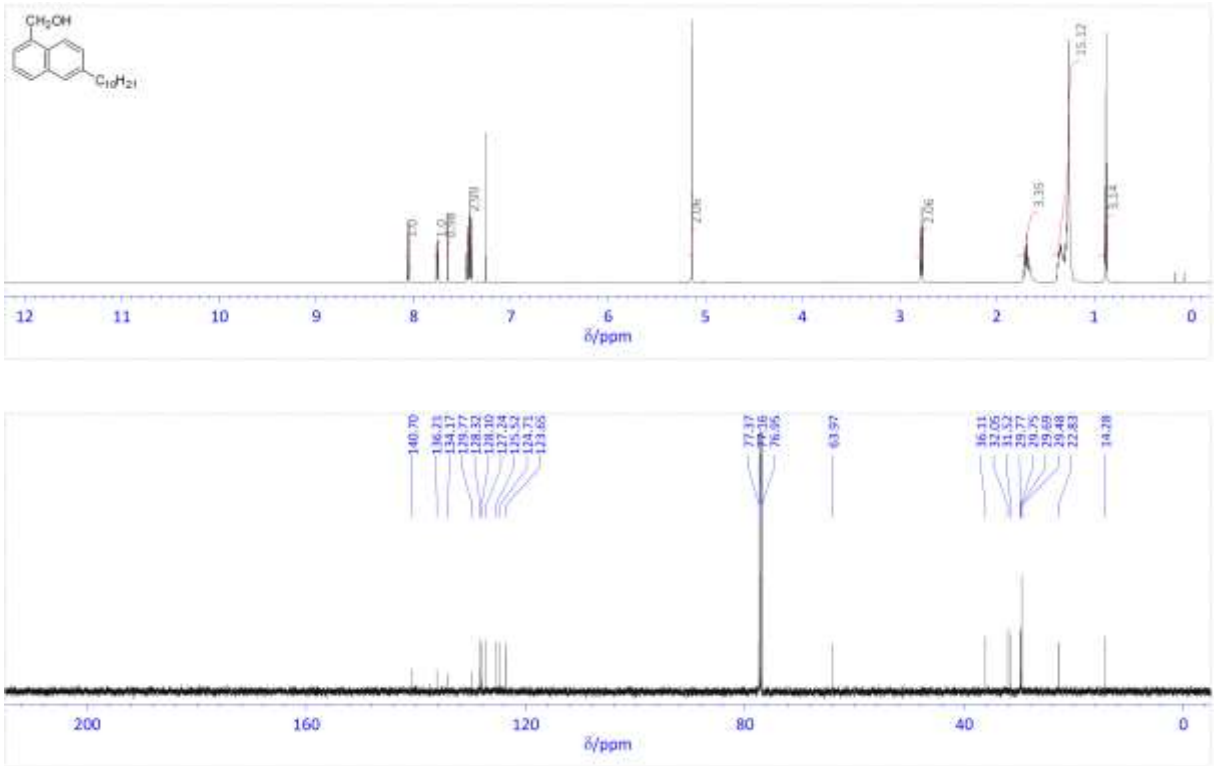


Figure S1-6. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound (6-decylnaphthalen-1-yl)methanol ($CDCl_3$).

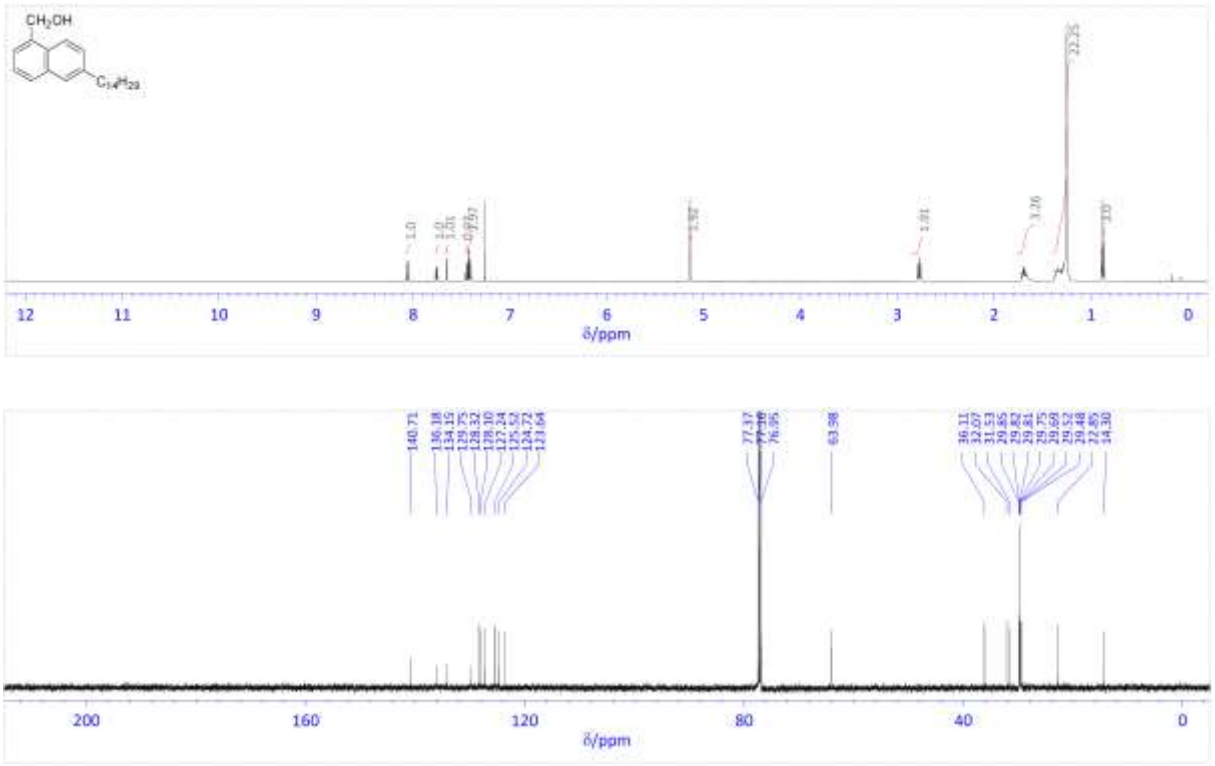


Figure S1-7. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound (6-tetradecylnaphthalen-1-yl)methanol ($CDCl_3$).

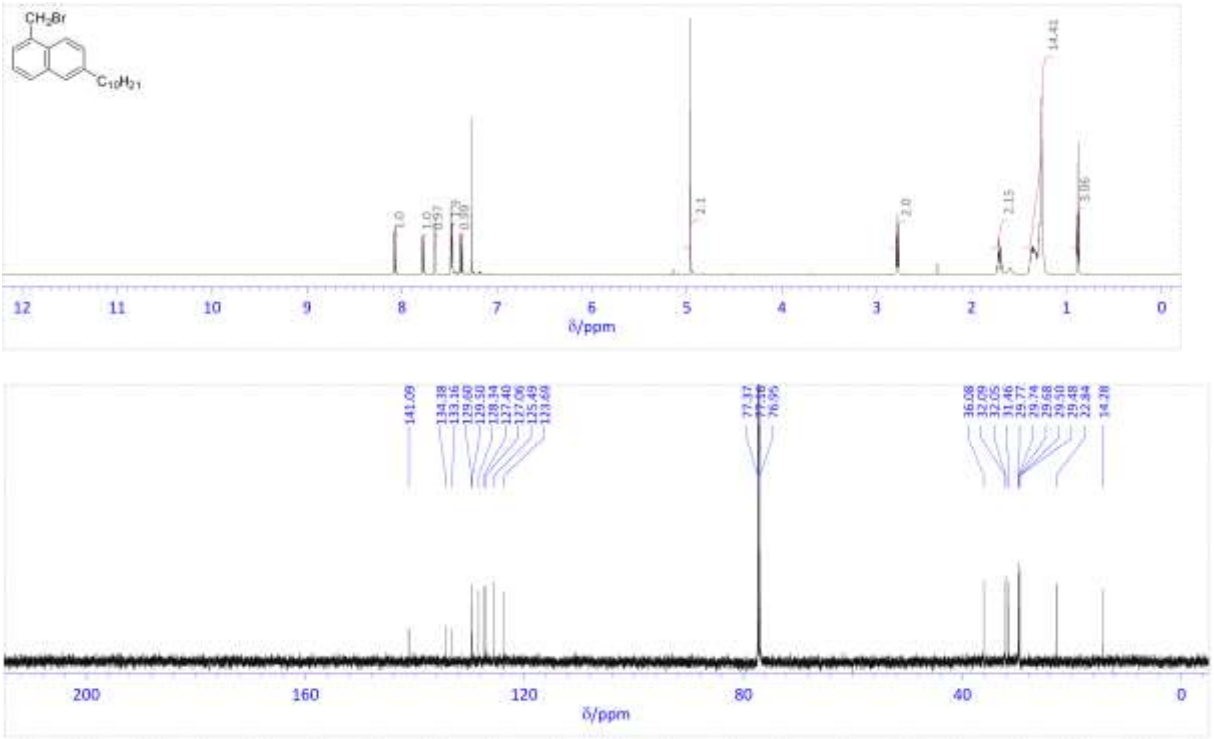


Figure S1-8. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound 1-bromomethyl-6-decylnaphthalene **5a** ($CDCl_3$).

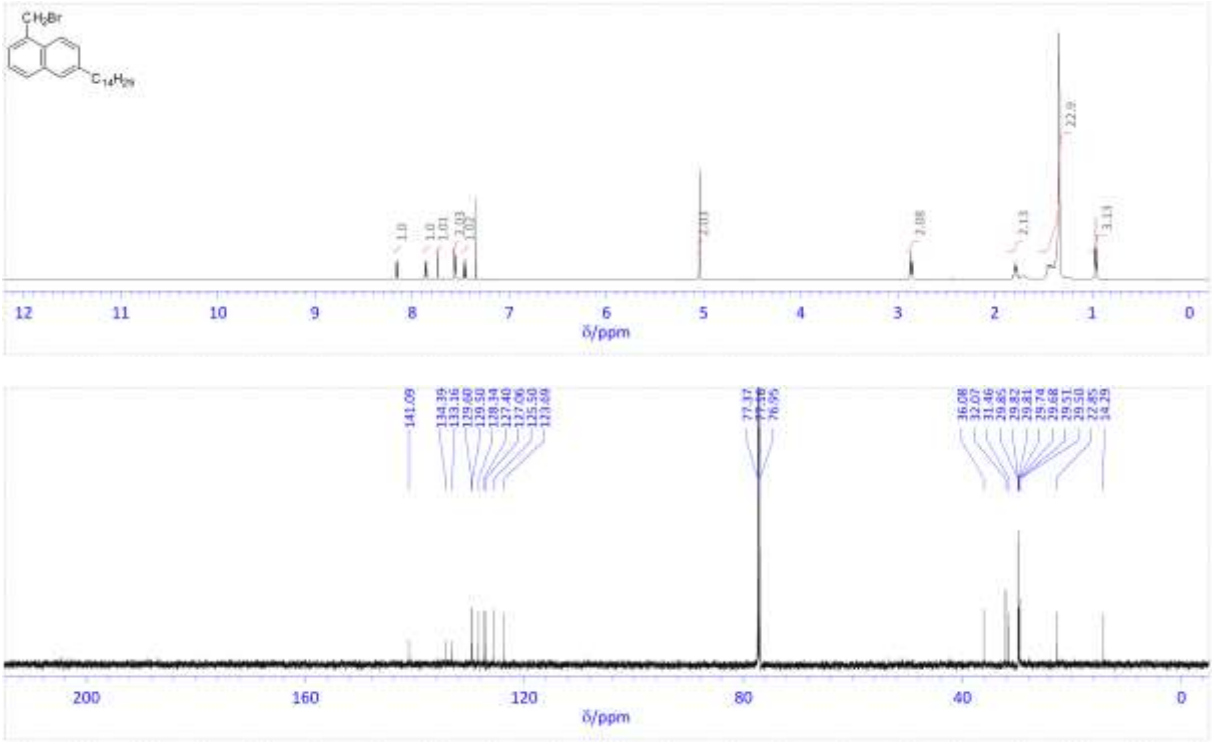


Figure S1-9. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound 1-bromomethyl-6-tetradecylnaphthalene **5b** ($CDCl_3$).

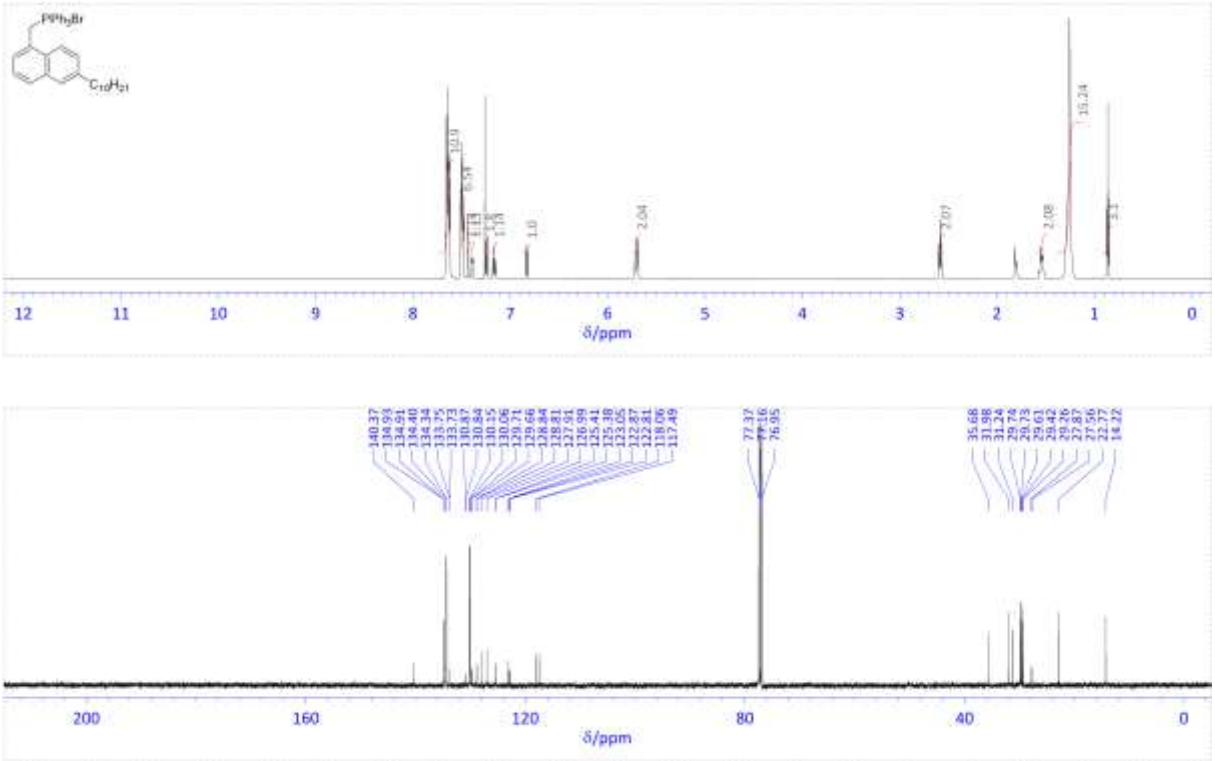


Figure S1-10. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound phophonium salt **6a** ($CDCl_3$).

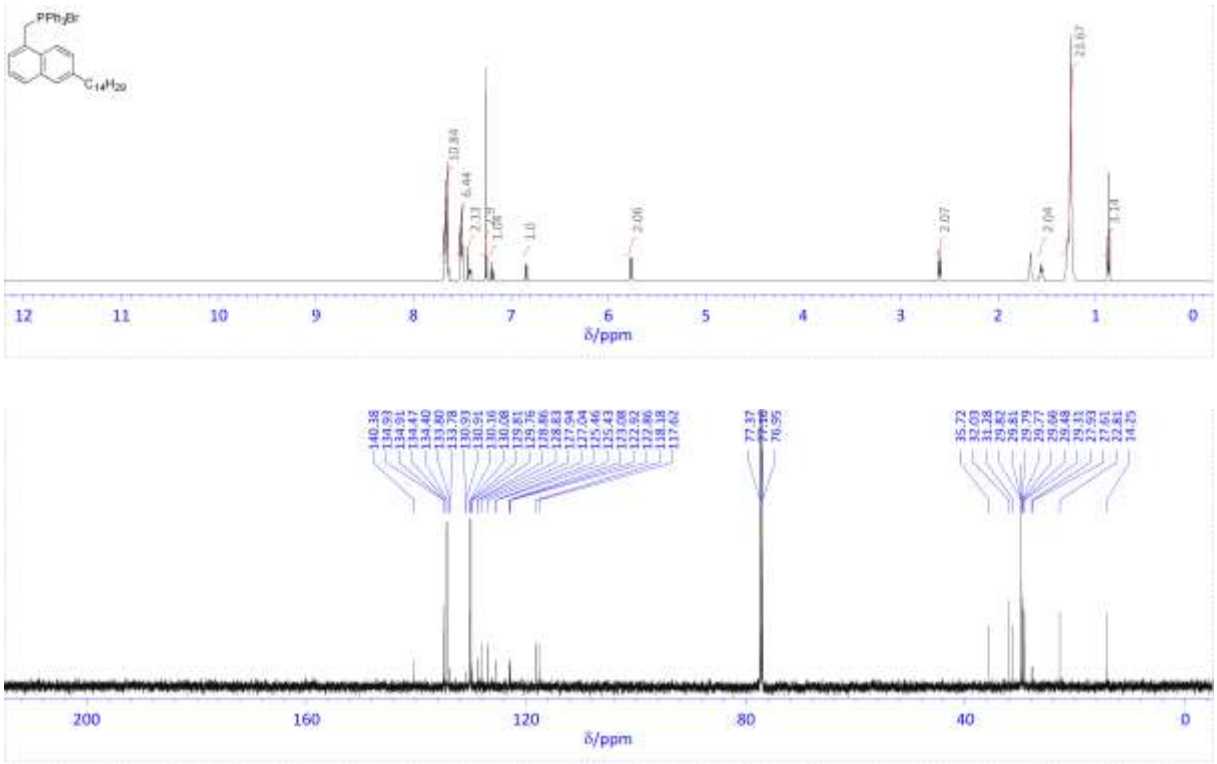


Figure S1-11. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound phophonium salt **6b** ($CDCl_3$).

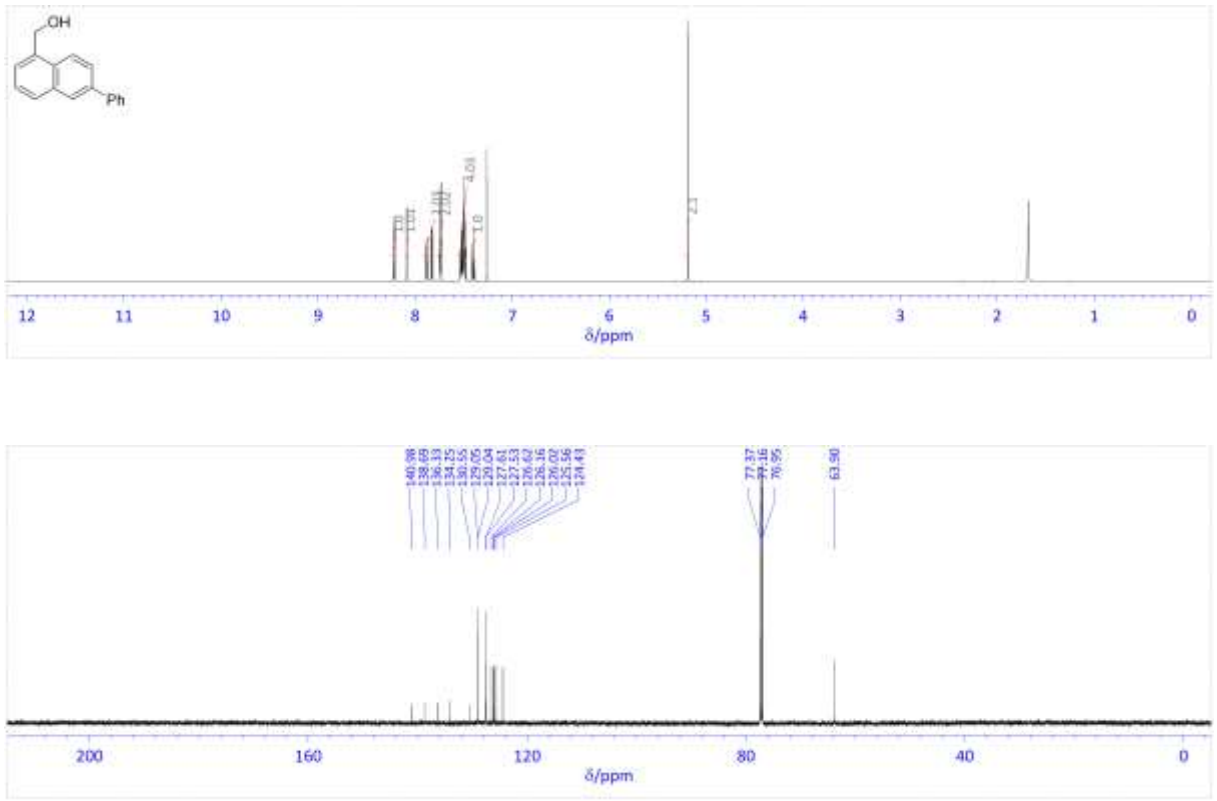


Figure S1-12. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **7** ($CDCl_3$).

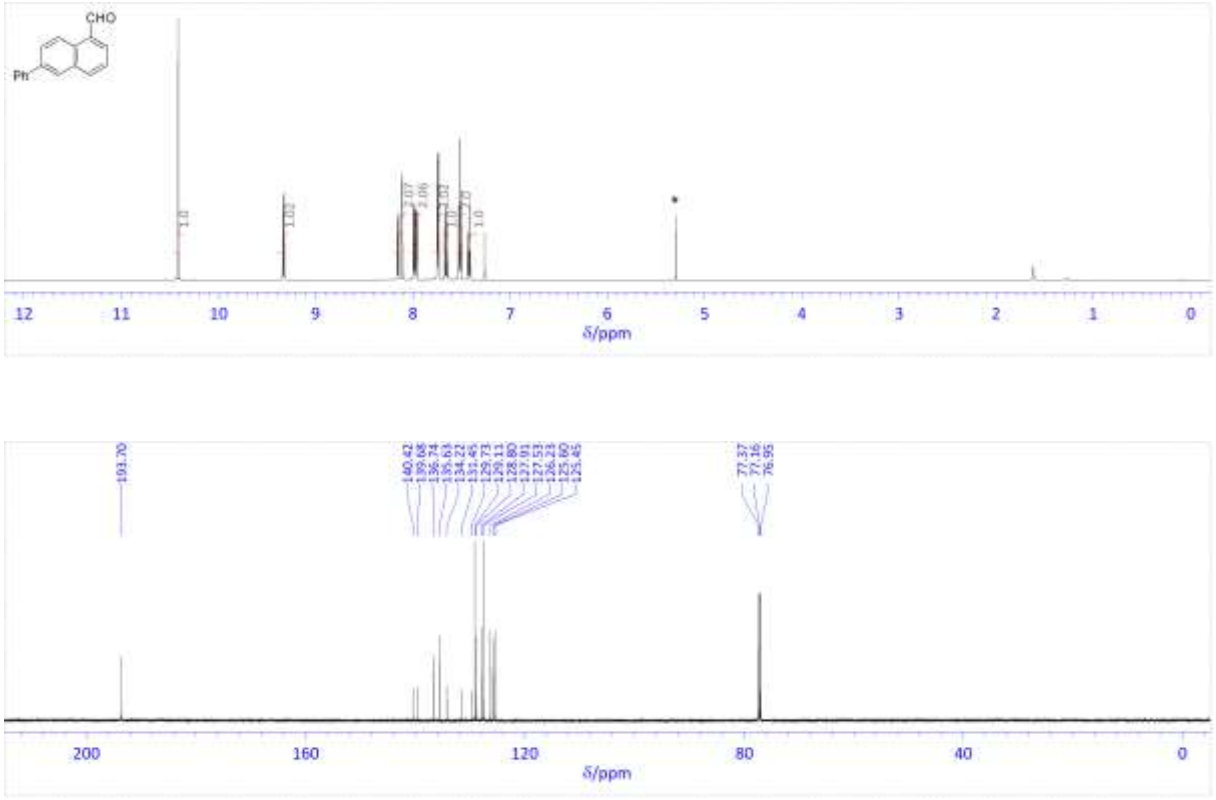


Figure S1-13. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of compound **8** ($CDCl_3$).

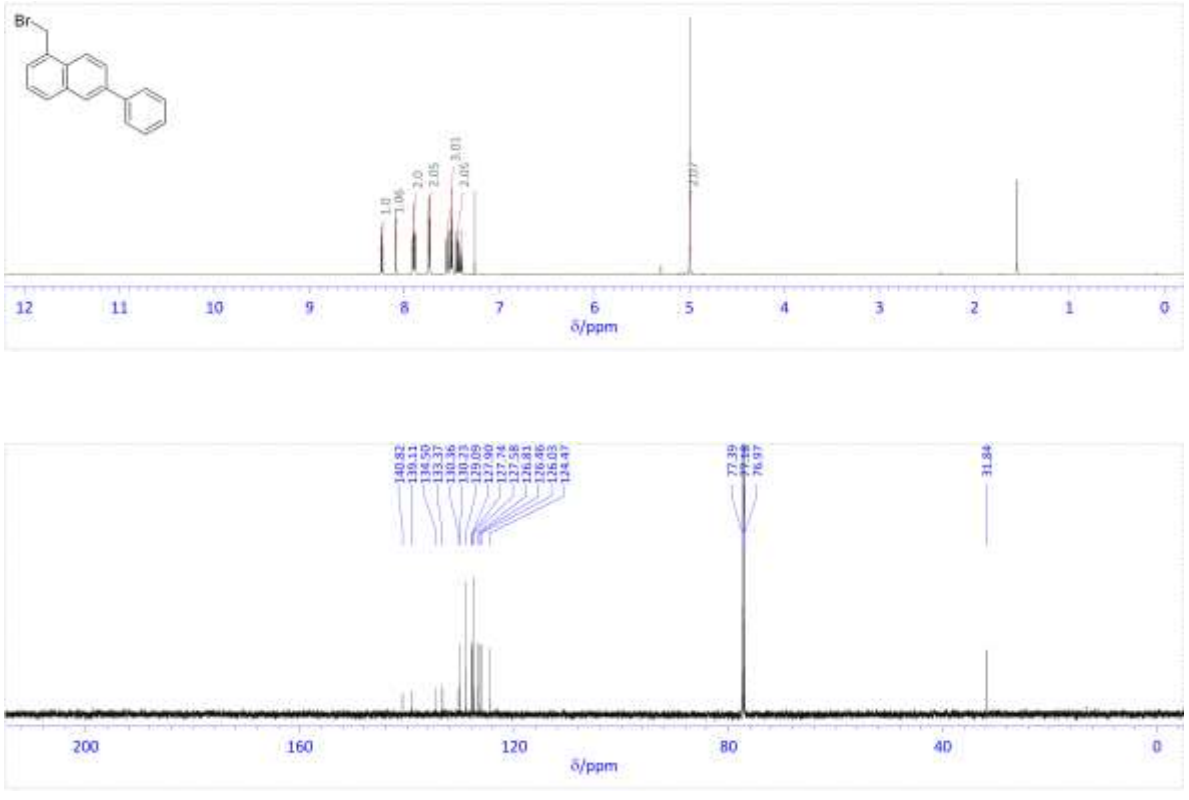


Figure S1-14. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of 1-bromomethyl-6-phenylnaphthalene ($CDCl_3$).

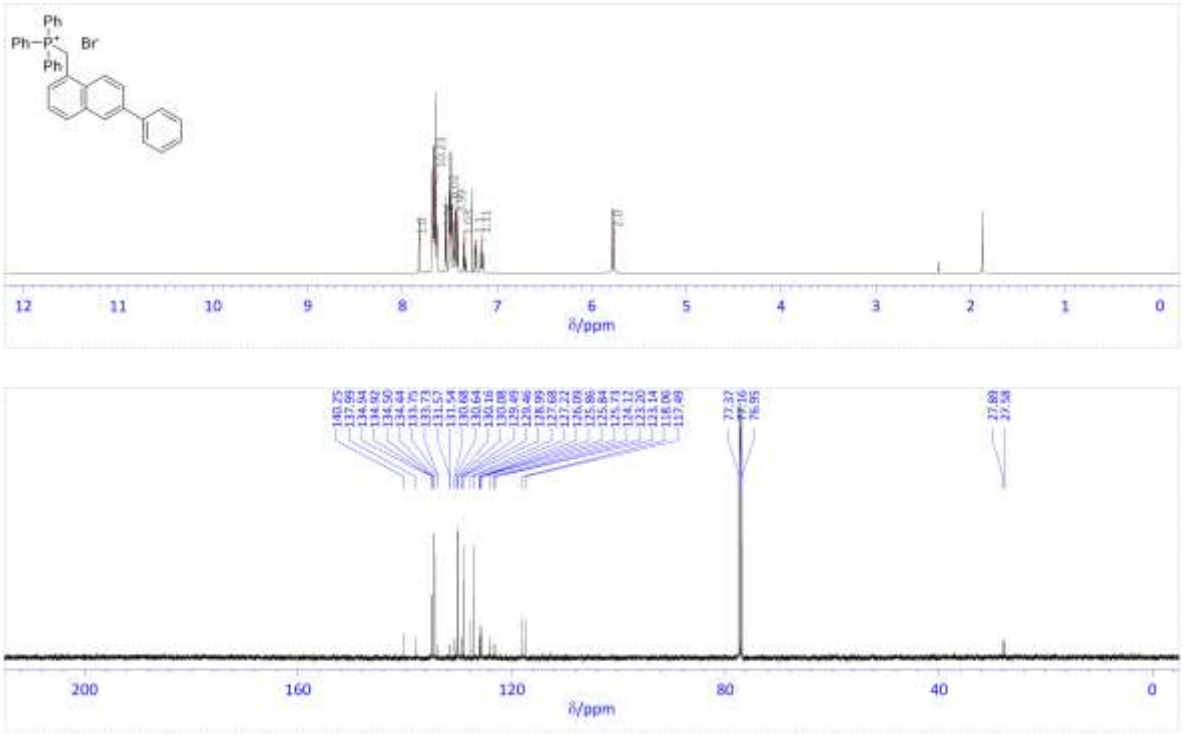


Figure S1-15. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of phosphonium salt **9** ($CDCl_3$).

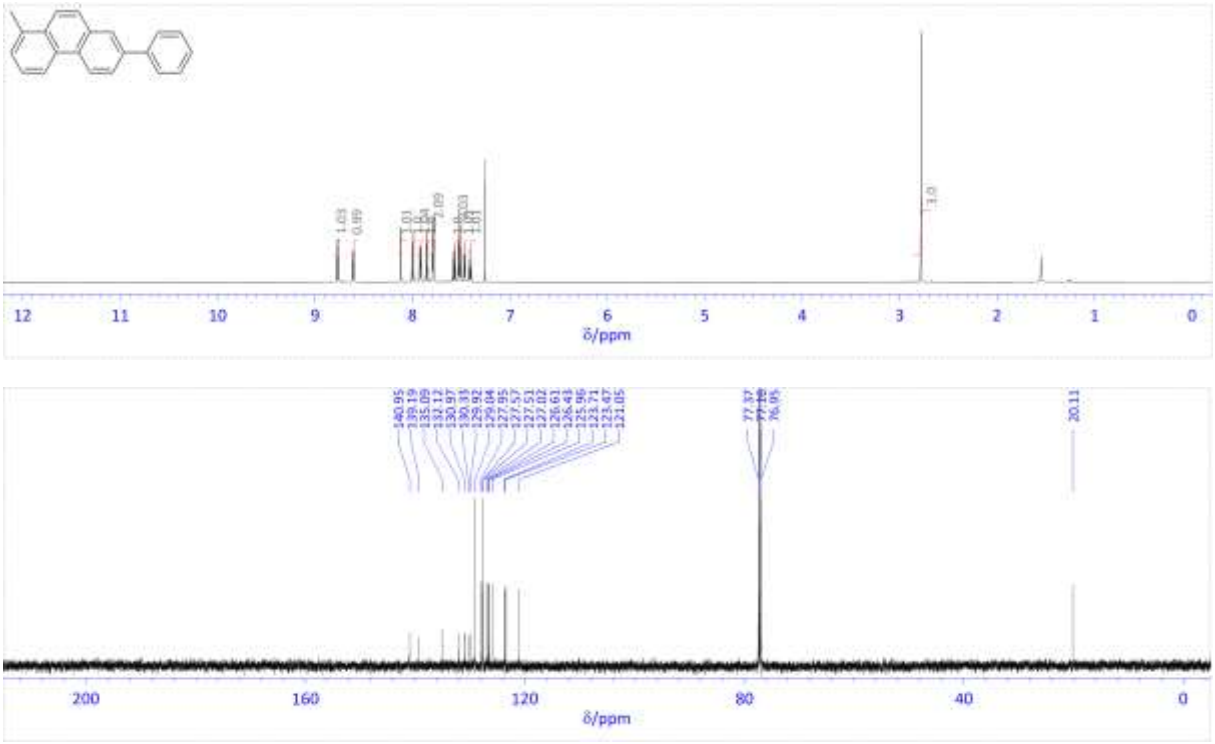


Figure S1-16. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of 1-methyl-7-phenylphenanthrene **12** ($CDCl_3$).

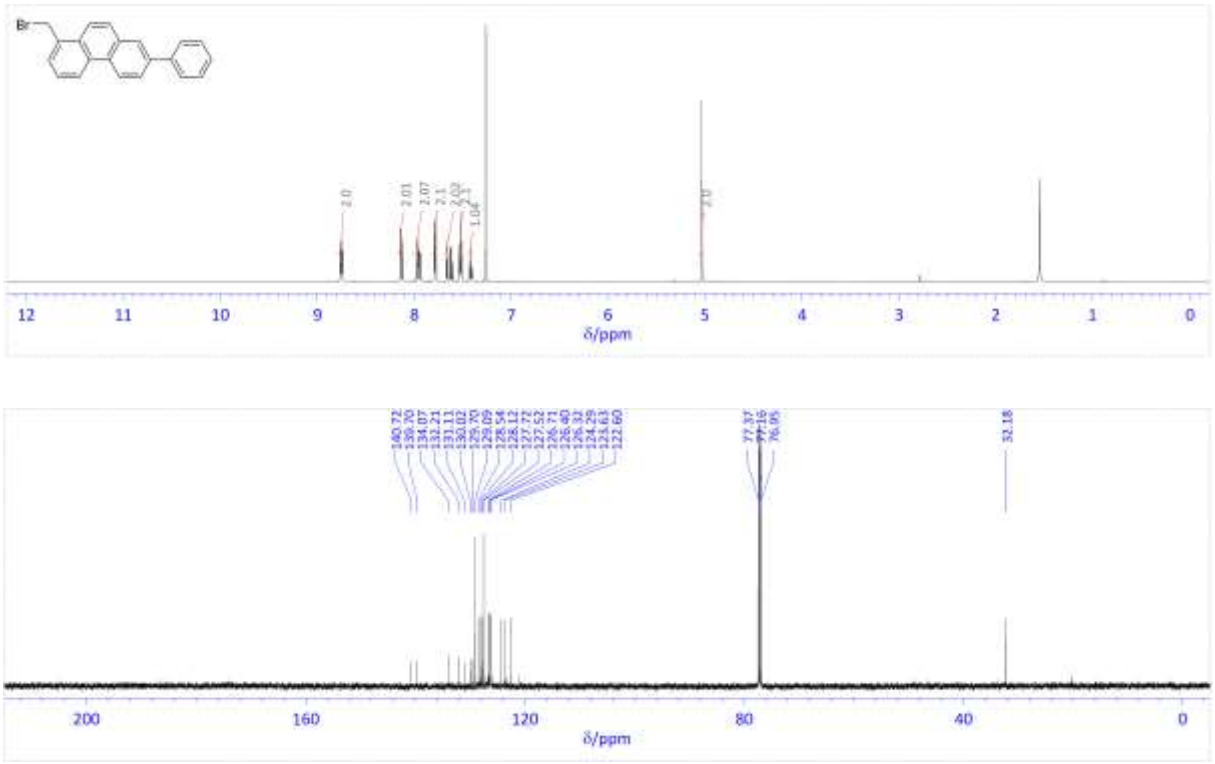


Figure S1-17. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of 1-bromomethyl-7-phenylphenanthrene **13** ($CDCl_3$).

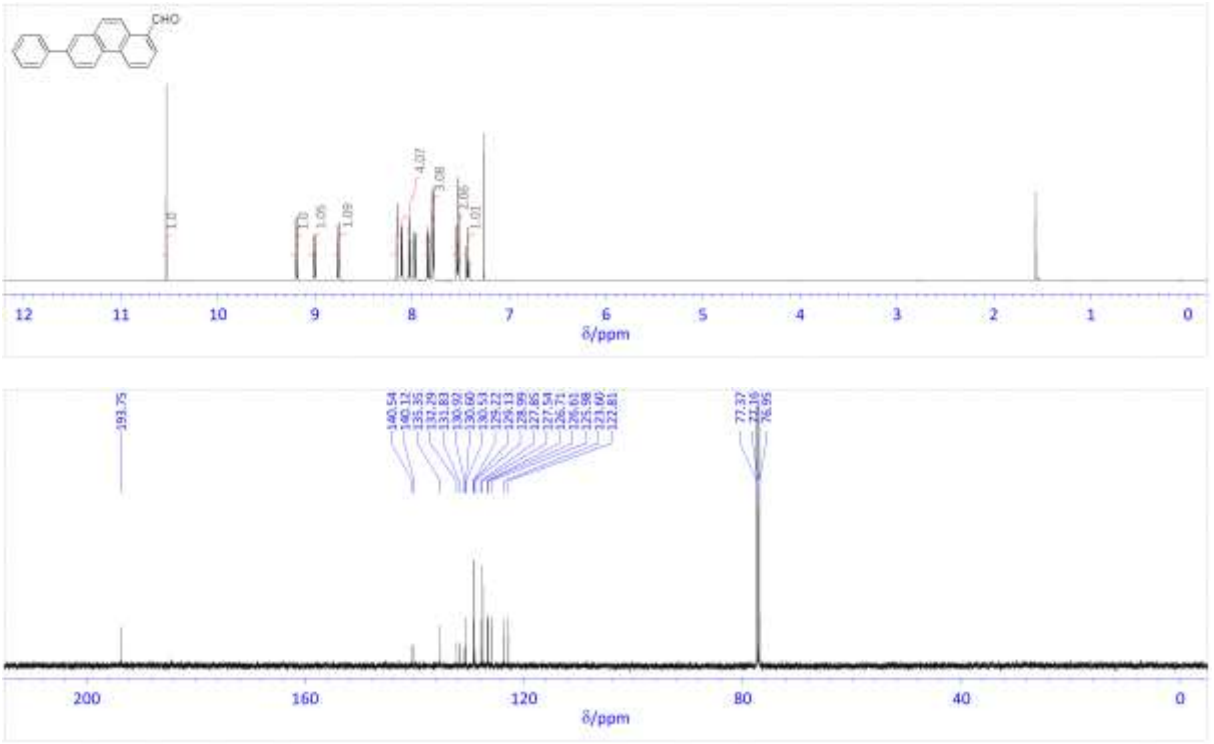


Figure S1-18. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of 7-phenylphenanthrene-1-carbaldehyde **14** ($CDCl_3$).

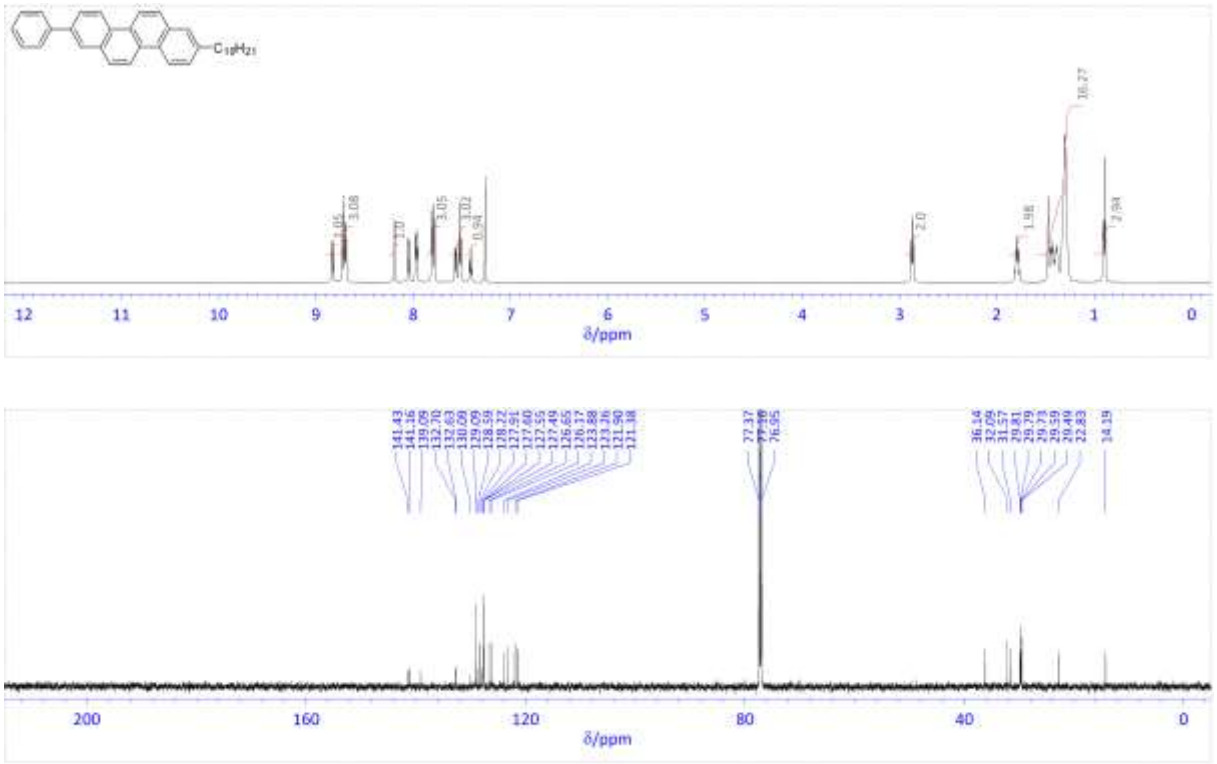


Figure S1-19. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of **PhC10-CHR** ($CDCl_3$ at 50°C).

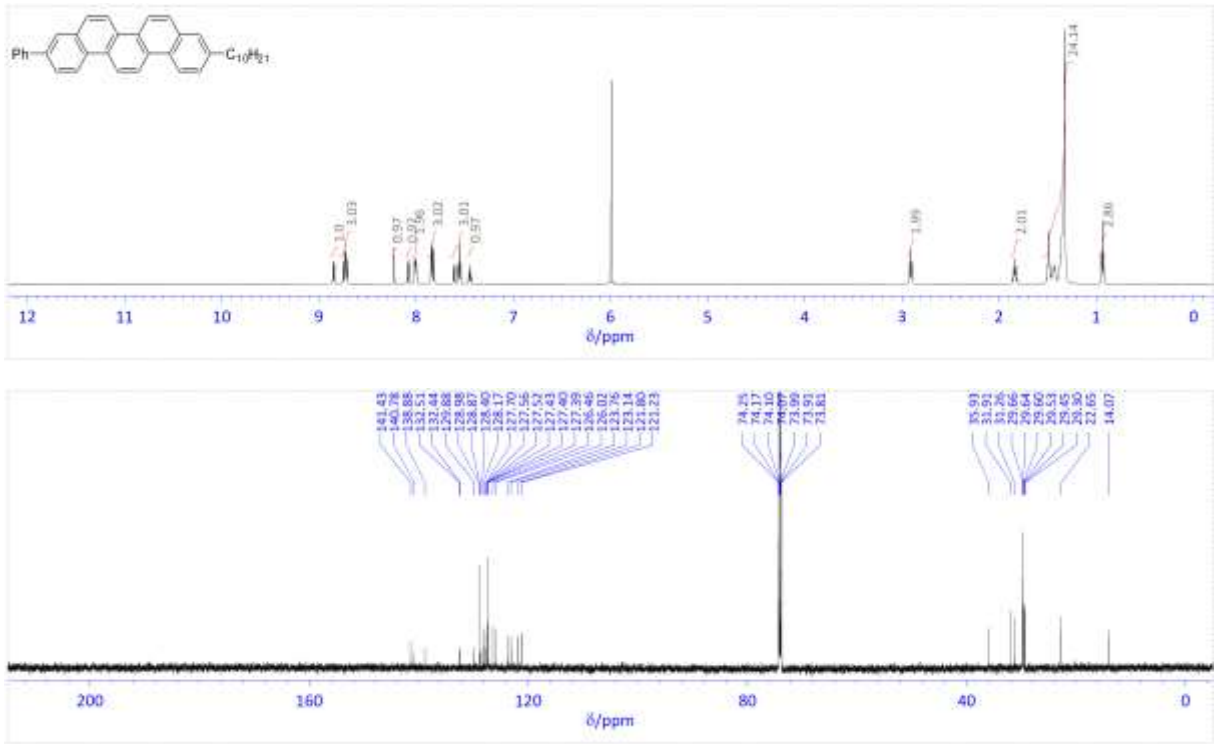


Figure S1-20. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of **PhC14-CHR** (1,1,2,2-tetrachloroethane-d_2 at 85°C).

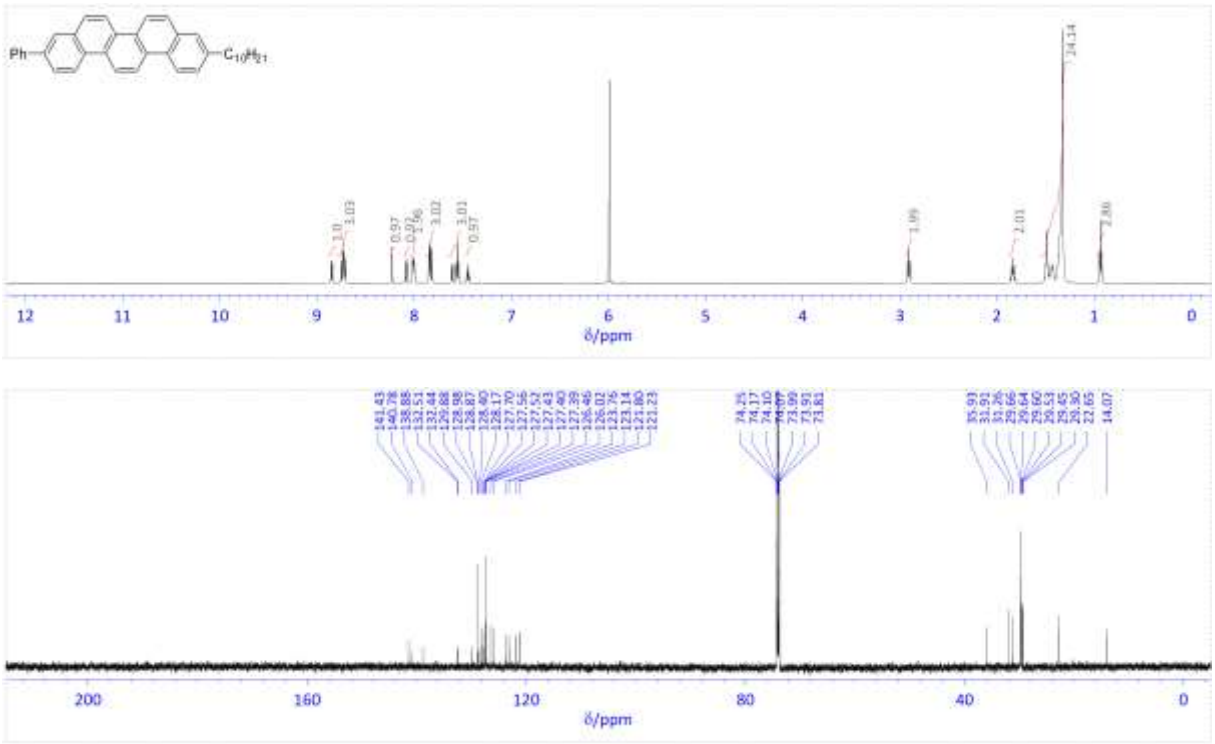


Figure S1-21. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of **PhC10-CHR** (1,1,2,2-tetrachloroethane-d_2, at 100°C).

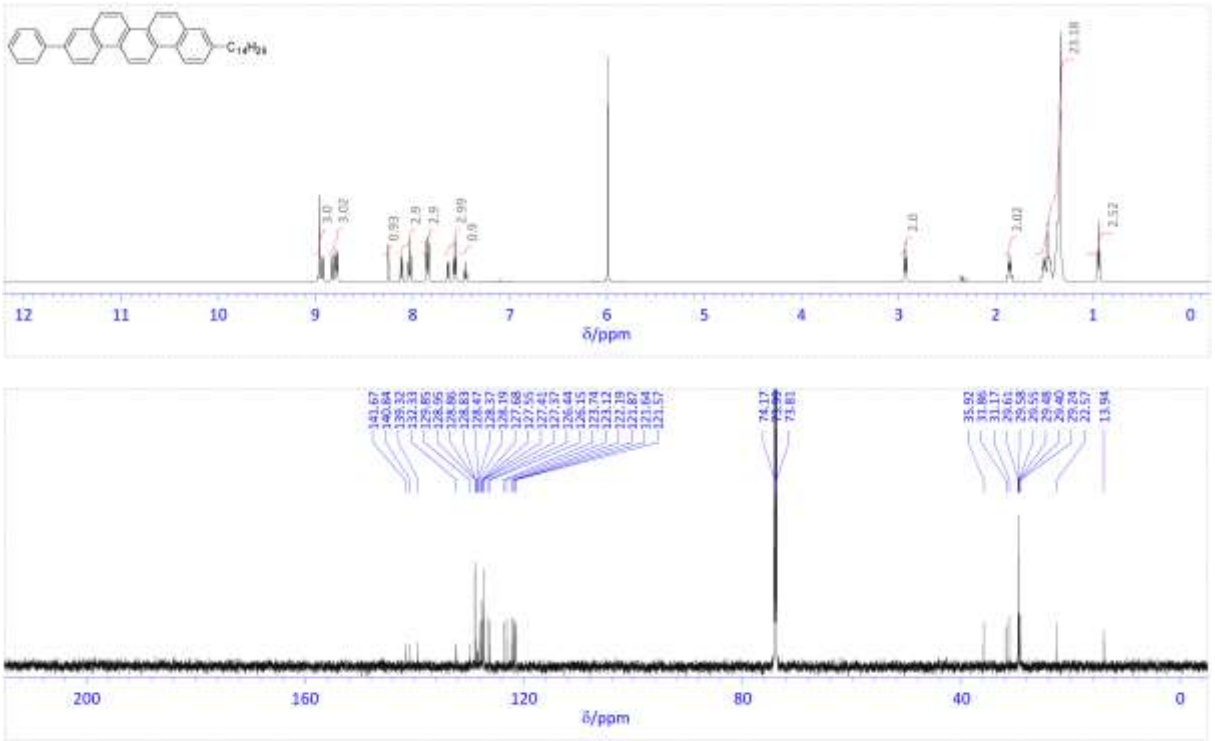


Figure S1-22. ^{1}H (600 MHz) and ^{13}C NMR (151 MHz) spectra of **PhC14-PIC** (1,1,2,2-tetrachloroethane-d_2, at 100°C).

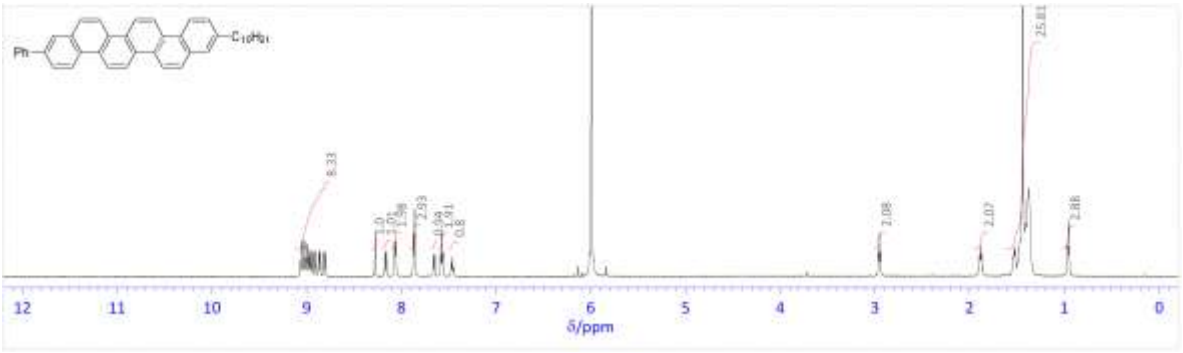


Figure S1-23. ^{1}H (600 MHz) spectrum of **PhC10-FUL** (1,1,2,2-tetrachloroethane-d_2, at 100°C).

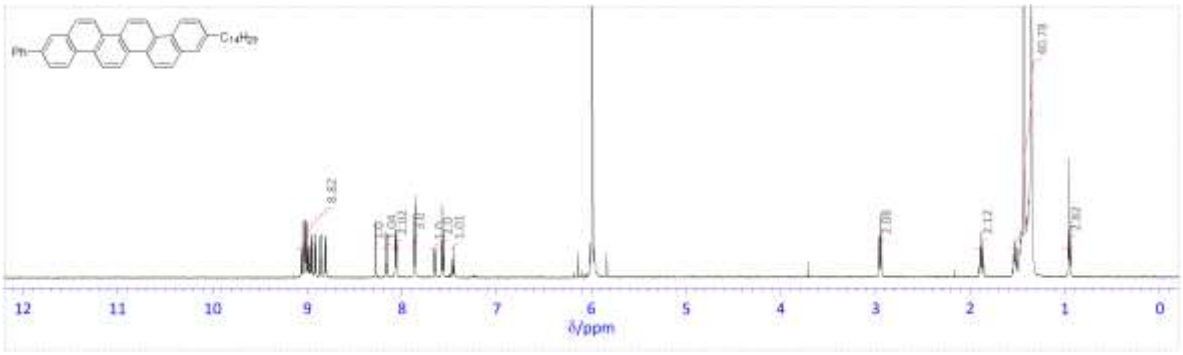


Figure S1-24. ^{1}H (600 MHz) spectrum of **PhC10-FUL** (1,1,2,2-tetrachloroethane-d_2, at 100°C).

(3) UV-Vis absorption and fluorescence spectra of PhCn'-[n]phenacenes in solution (in o-dichlorobenzene) and solid phases（Figure S2）.

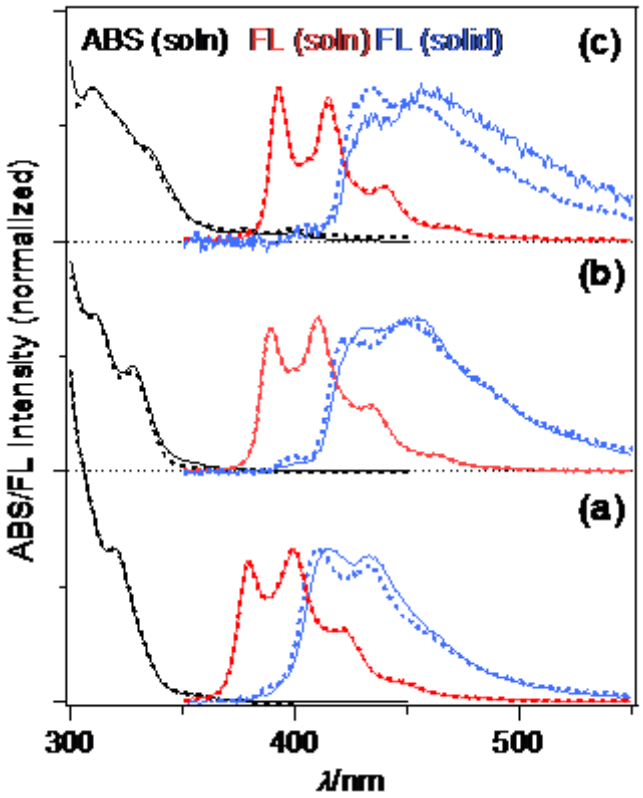


Figure S2. Absorption (in solution, black), fluorescence (in solution, red), and fluorescence (in solid, blue) spectra of (a) PhCn'-CHR, (b) PhCn'-PIC, and (c) PhCn'-FUL. Full lines are for n' = 10 and dotted lines are for n' = 14. The absorption and fluorescence spectra in solution were measured in *o*-

(4) AFM images of thin films of PhC10-CHR, PhC14-CHR, PhC10-PIC, PhC14-PIC, PhC10-FUL and PhC14-FUL.

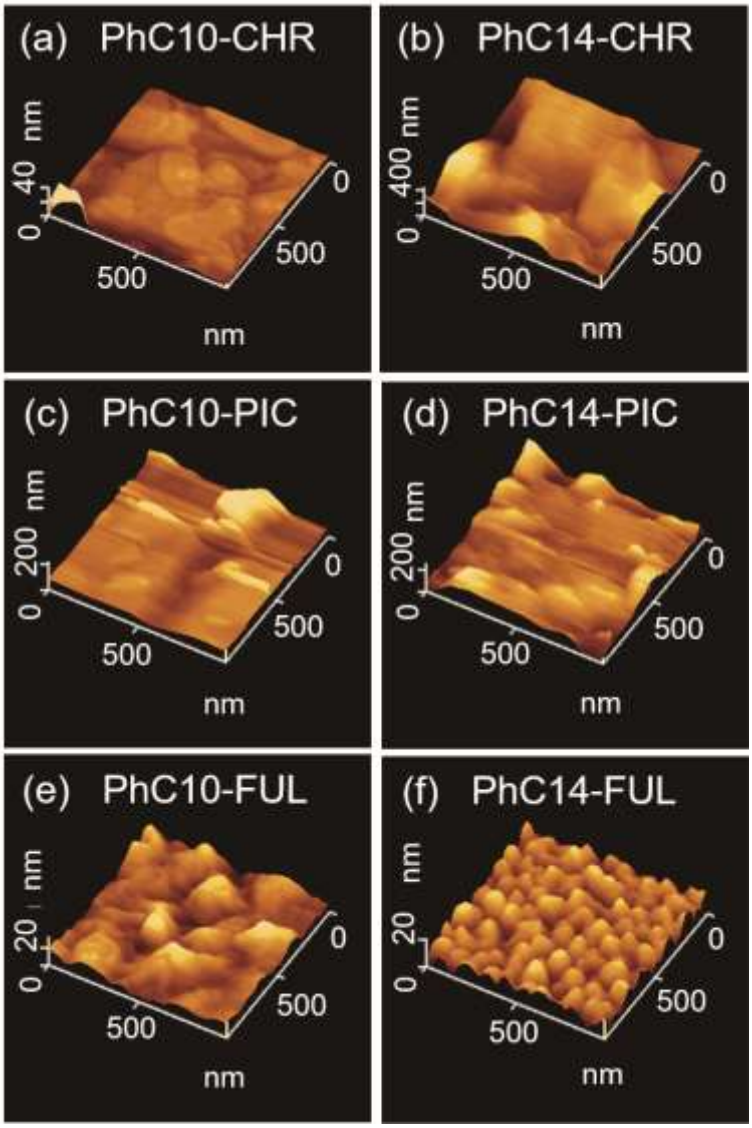


Figure S3. AFM images of thin films of (a) PhC10-CHR, (b) PhC14-CHR, (c) PhC10-PIC, (d) PhC14-PIC, (e) PhC10-FUL and (f) PhC14-FUL.

(5) Transfer and output characteristics of PhC10-CHR, PhC14-CHR, PhC10-FUL and PhC14-FUL thin-film FETs with SiO_2 gate dielectric (Figures S4 and S5).

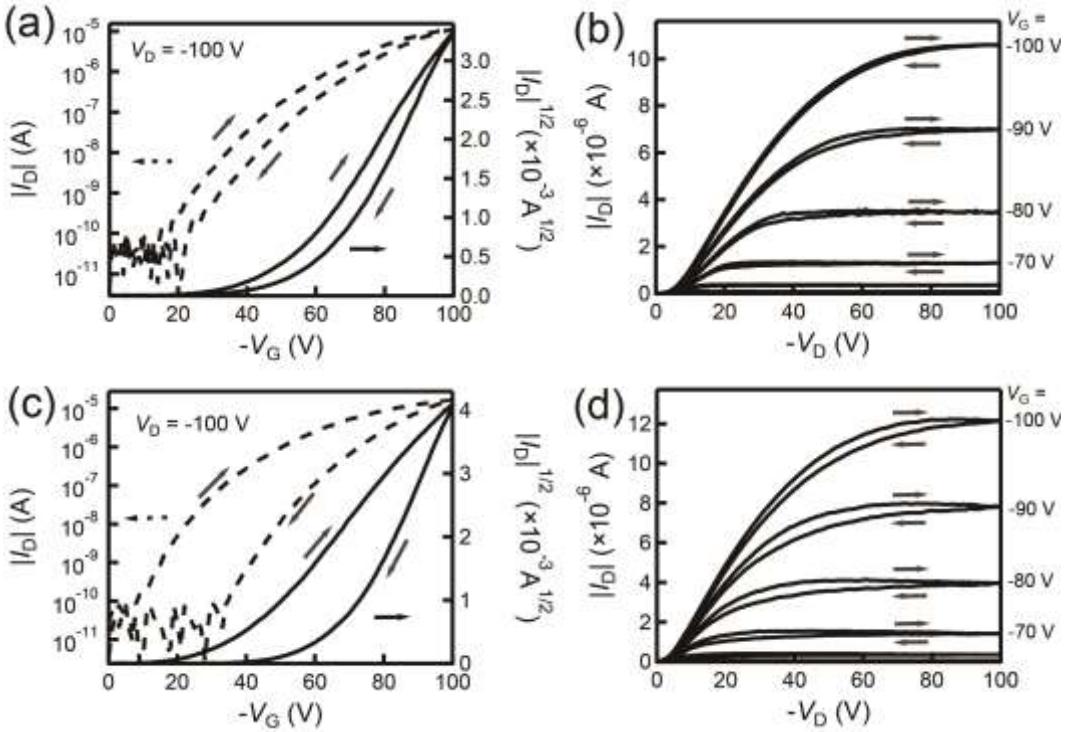


Figure S4. (a) Transfer and (b) output characteristics of FET with thin film of PhC10-CHR. (c)Transfer and (d) output characteristics of FET with thin film of PhC14-CHR. The thin films are formed on SiO_2/Si substrate. The FETs of PhC10-CHR and PhC14-CHR refer to the devices which are marked with an asterisk (*) in Table 4.

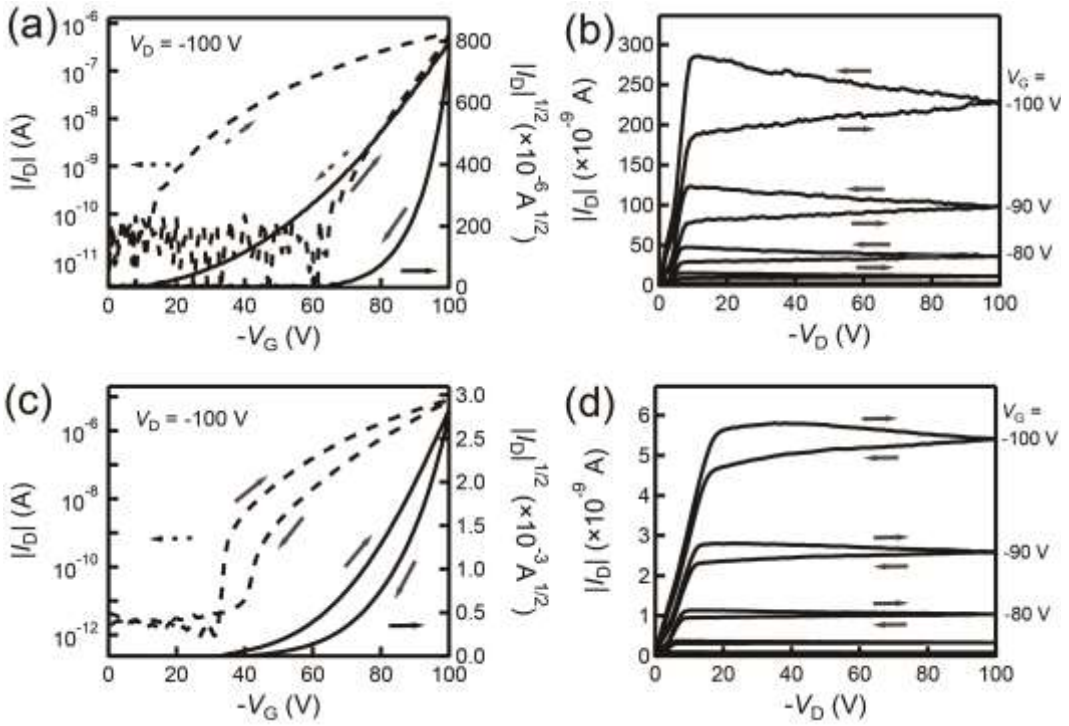


Figure S5. (a) Transfer and (b) output characteristics of FET with thin film of PhC10-FUL. (c)Transfer and (d) output characteristics of FET with thin film of PhC14-FUL. The thin films are formed on SiO_2/Si substrate. The FETs of PhC10-FUL and PhC14-FUL refer to the devices which are marked with an asterisk (*) in Table 5.

(6) Transfer and output characteristics of PhC10-CHR, PhC14-CHR, PhC10-FUL and PhC14-FUL thin-film FETs with ZrO_2 gate dielectric (Figures S6 and S7).

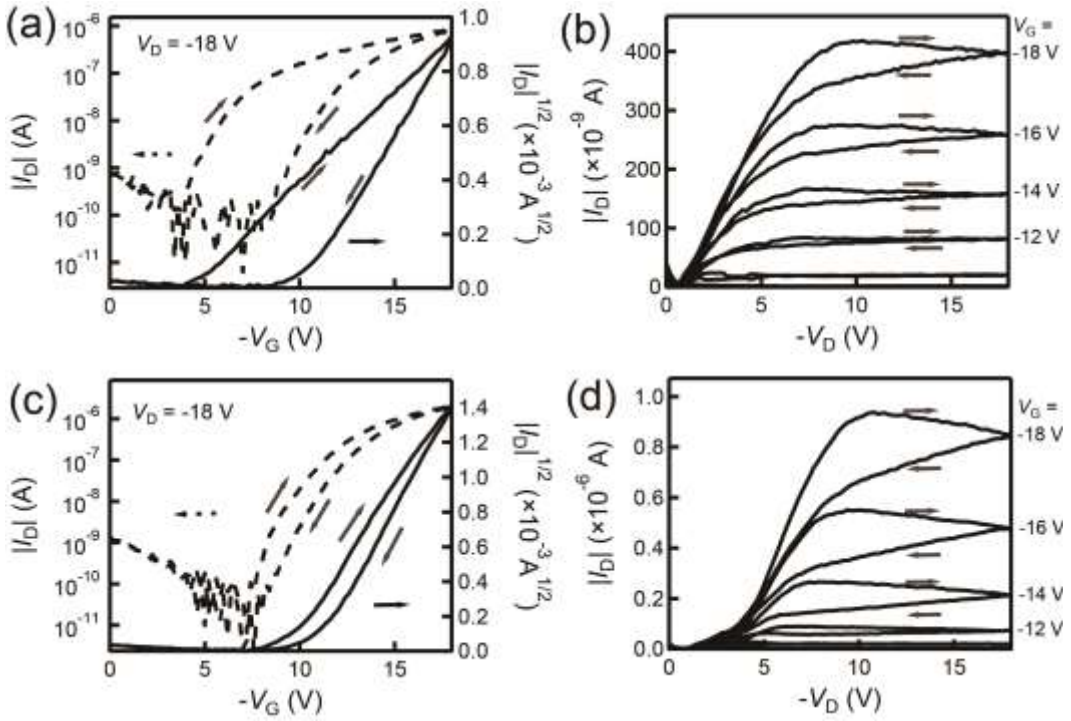


Figure S6. (a) Transfer and (b) output characteristics of FET with thin film of PhC10-CHR. (c)Transfer and (d) output characteristics of FET with thin film of PhC14-CHR. The thin films are formed on ZrO_2/Si substrate. The FETs of PhC10-CHR and PhC14-CHR refer to the devices which are marked with an asterisk (*) in Table 7.

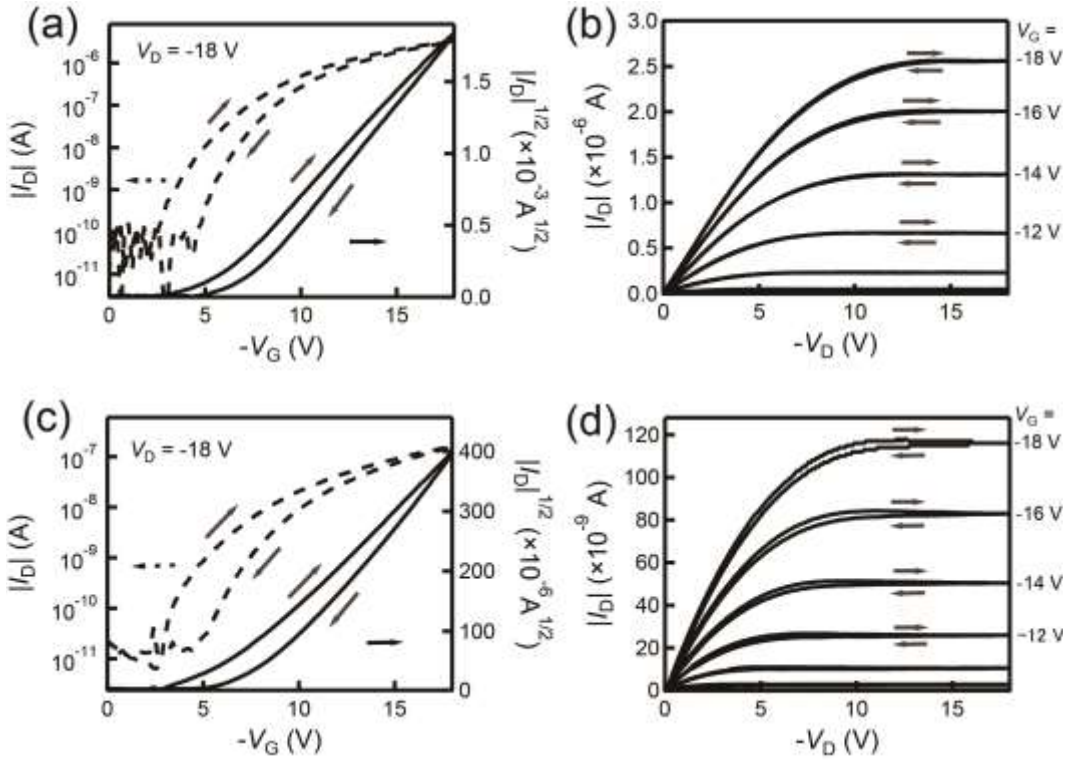


Figure S7. (a) Transfer and (b) output characteristics of FET with thin film of PhC10-FUL. (c)Transfer and (d) output characteristics of FET with thin film of PhC14-FUL. The thin films are formed on ZrO_2/Si substrate. The FETs of PhC10-FUL and PhC14-FUL refer to the devices which are marked with an asterisk (*) in Table 8.