Electronic Supplementary Information for:

Rational Molecular Designs for Drastic Acceleration of Color-Fading Speed of Photochromic Naphthopyrans

Katsutoshi Arai[†], Yoichi Kobayashi[†] and Jiro Abe*[,†,‡]

[†]*Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5–10–1 Fuchinobe, Chuo–ku, Sagamihara, Kanagawa 252–5258, Japan*

[‡]*CREST, Japan Science and Technology Agency (JST), K's Gobancho, 7 Gobancho, Chiyoda–ku, Tokyo 102–0076, Japan*

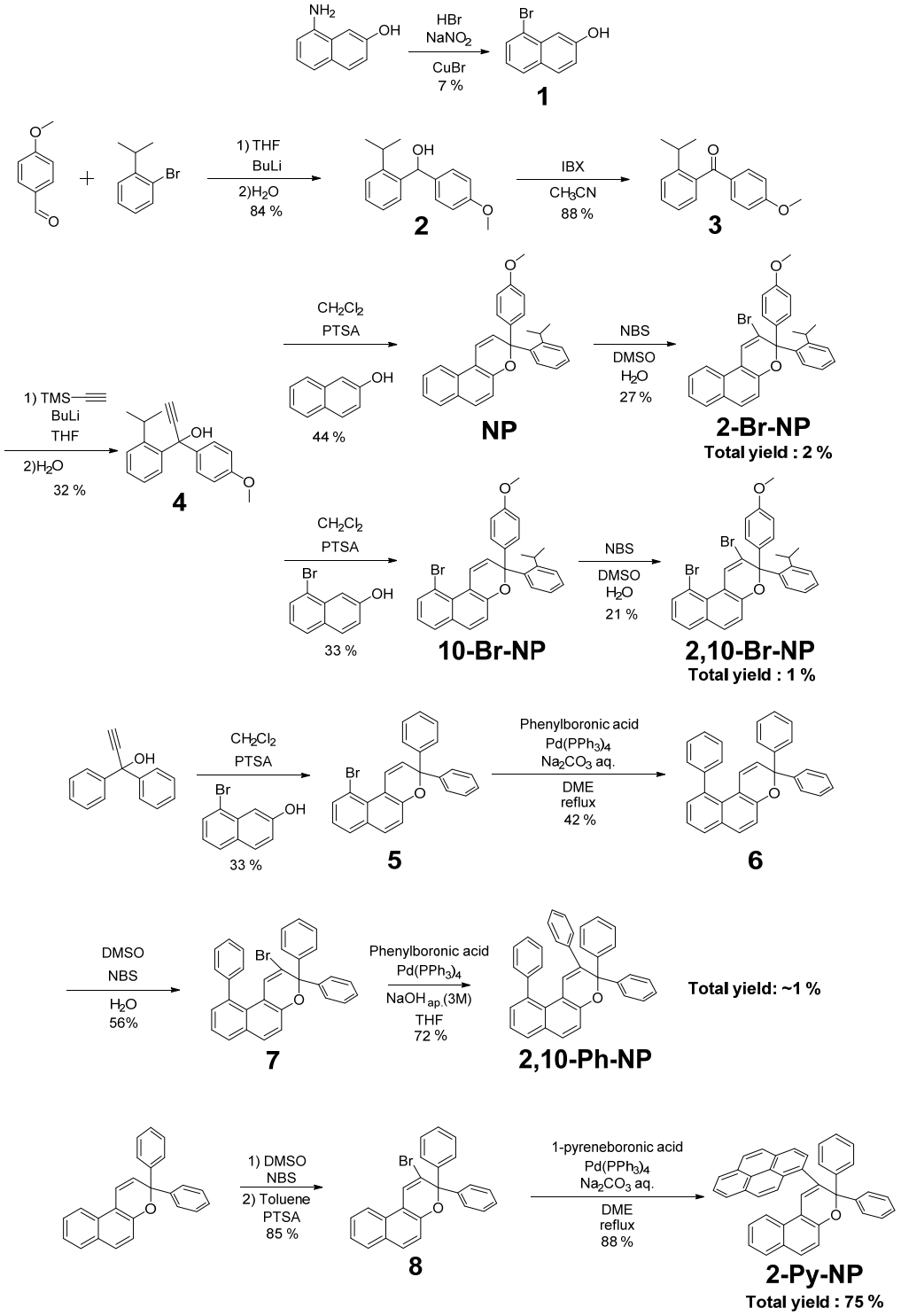
E–mail: *jiro_abe@chem.aoyama.ac.jp*

CONTENTS

1.	**Synthetic Procedures**	**S2**
2.	**^{1}H NMR Spectra**	**S9**
3.	**HR-ESI-TOF-MS-Spectra**	**S16**
4.	**HPLC Chromatogram**	**S23**
5.	**X–ray Crystallographic Analysis**	**S29**
6.	**UV–Vis Absorption Spectroscopy**	**S35**
7.	**Kinetics for the Thermal Back–Reaction**	**S37**
8.	**Fatigue Resistance**	**S38**
9.	**Transient Absorption Dynamics in Polymer Matrices**	**S40**
10.	**Experimental Detail for Laser Flash Photolysis Measurements**	**S42**
11.	**DFT Calculations**	**S42**
12.	**References**	**S76**

1. Synthetic Procedures

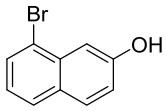
Scheme S1. Synthetic Procedures of naphthopyran derivatives.



All reactions were monitored by thin–layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F–254). Column chromatography was performed on silica gel (Silica Gel 60N

(spherical, neutral), 40−50 μm, Kanto Chemical Co., Inc.). ^{1}H–NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. DMSO–d_6 and $CDCl_3$ were used as deuterated solvents. MASS spectra (ESI–TOF–MS) were measured by using a Bruker micrOTOF II–AGA1. All reagents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Company, Inc, and ACROS Organics. These reagents were used without further purification. 2–Iodoxybenzoic acid (IBX) were prepared according to a literature procedure.[S1] Phase separator paper (Whatman 1PS) was purchased from GE. All glassware was washed with distilled water and dried before use.

8–bromonaphthalen–2–ol (1)

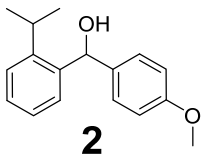


1

8–Aminonaphthalen–2–ol (6.04 g, 3.79 × 10^{-2} mol) was dissolved in 48% aqueous HBr (48 mL). After cooling to −10 °C, sodium nitrite (6.37 g, 3.79 × 10^{-2} mol) was added very slowly to the stirred solution with the temperature being kept within −10 and 0 °C. This diazonium salt solution was then poured into a flask containing CuBr (4.17 g, 2.91 × 10^{-2} mol) and 10 mL of 48% aqueous HBr. The solution was heated to reflux for 3 h and then extracted three times with dichloromethane. The organic layers were washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:1), to give **1** as a brown solid (432 mg, yield : 7%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.70 (m, 3 H), 7.55 (s, 1H), 7.21–7.13 (m, 2H), 5.10 (s, 1H). HRMS (ESI-TOF) calculated for $C_{10}H_7O$ $[M-H]^-$: 220.9597, found: 220.9611.

(2–isopropylphenyl)(4–methoxyphenyl)methanol (2)

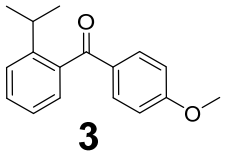


2

n–Butyllithium (1.6 M in hexane, 1.5 mL) was added dropwise to a stirred solution of 2–bromocumene (0.35 mL) at −78 °C in dry THF under N_2. On completion of the addition the reaction mixture was stirred for 30 min at −78 °C. The *p*–anisaldehyde (0.2 mL) was added at −78 °C to the reaction mixture. The mixture was allowed to warm to room temperature for 21 h with magnetic stirring. After the addition of NH_4Cl aq., the mixture was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:7), to give **2** as a white powder (353 mg, yield: 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J =7.5 Hz, 2H), 7.32–7.26 (m, 2H), 7.25–7.18 (m, 3H), 6.84 (d, J = 8.7 Hz 1H), 6.11 (d, J = 3.9 Hz, 1H), 3.78 (s, 3H), 3.23–3.01 (m, 1H), 2.08 (d, J = 3.9 Hz, 1H), 1.20 (d, J = 6.8 3H), 1.00 (d, J =6.8 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{17}H_{20}O_2$ $[M+Na]^+$: 279.1356, found: 279.1355.

(2–isopropylphenyl)(4–methoxyphenyl)methanone (3)

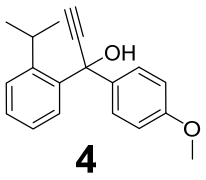


3

(2–Isopropylphenyl)(4–methoxyphenyl)methanol (1.029 g, 4.01 mmol) and IBX (3.279 g, 11.7 mmol) were refluxed in acetonitrile (36 mL) for 1.5 h. The reaction mixture was filtrated and evaporated. After the solvents were removed, the sample was purified by column chromatography (silica gel, hexane:ethyl acetate = 15:1), to give **3** as a yellow solid (895 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* =8.9 Hz, 2 H), 7.47–7.40 (m, 2H), 7.26– 7.17(m, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.00 (s, 1H), 3.09 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 6H). HRMS (ESI-TOF) calculated for $C_{17}H_{18}O_2$ [M+Na]$^+$: 277.1199, found: 277.1195.

1–(2–isopropylphenyl)–1–(4–methoxyphenyl) prop–2–yn–1–ol (4)

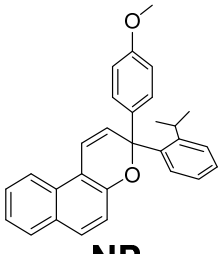


4

n–Butyllithium (1.6 M in hexanes) was added over 5 min with a syringe to a cold (0 °C), stirred solution of trimethylsilylacetylene (1.1 mL) in anhydrous THF (30 mL) under N_2. On completion of the addition (ca. 5 min), the cold solution was stirred for 30 min. A solution of (2–isopropylphenyl)(4–methoxyphenyl)methanone (895 mg, 3.52 mmol) in THF (30 mL) was then added to the reaction mixture. The cooling bath was removed and the mixture stirred for 2 days at room temperature. After the addition of NH_4Cl aq., the mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:8), to give **4** as a white powder (318 mg, yield : 32%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (d, *J* = 8.0 Hz, 1 H), 7.20–7.07 (m, 4H), 7.04–6.98 (m, 1H), 3.56 (s, 3H), 3.11–2.97 (m, 1H), 2.72 (s, 1H), 2.56 (s, 1H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.48 (d, *J* = 6.8 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{19}H_{20}O_2$ [M+Na]$^+$: 303.1356, found: 303.1357.

3–(2–isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f]chromene (NP)



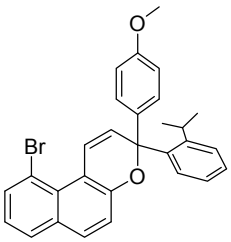
NP

A solution of the 2–naphthol (79 mg, 5.47 × 10^{-1} mmol) and 1–(2–isopropylphenyl)–1–(4–methoxyphenyl)pr– op–2–yn–1–ol (102 mg, 3.65 × 10^{-1} mmol) and PTSA (3 mg, 1.86 × 10^{-2} mmol) in dichloromethane (5 mL) were stirred for 5 h at room temperature. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 30:1) and recrystallized from dichloromethane/hexane to give **NP** as a yellow crystal (65 mg, yield : 44%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.91 (d, *J* = 8.4 Hz, 1 H), 7.64 (m, 2H), 7.60 (dd, *J* = 8.12 Hz, *J* = 1.0 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.27–7.16 (m, 4H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.10–7.01 (m,

2H), 5.79 (d, *J* = 9.8 Hz, 1H), 3.67 (s, 3H), 3.38–3.22 (m, 1H) , 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{29}H_{26}O_2$ $[M+H]^+$: 407.2006, found: 407.2008.

10–bromo–3–(2–isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f]chromene (10–Br–NP)

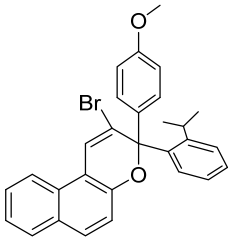


10-Br-NP

A solution of the 8–bromonaphthalene–2–ol (72 mg, 3.21×10^{-1} mmol) and 1–(2–isopropylphenyl)–1–(4–methoxyphenyl)prop–2–yn–1–ol (151 mg, 5.38×10^{-1} mmol) and PTSA (2 mg, 1.16×10^{-2} mmol) in dichloromethane (6 mL) were stirred for 8 h at room temperature. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 30:1) and recrystallized from dichloromethane/hexane to give **10–Br–NP** as a colorless crystal (88 mg, yield : 33%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.02 (d, *J* = 9.8 Hz, 1 H), 7.64 (d, *J* = 8.1 Hz, 1 H) , 7.58 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.44–7.36 (m, 1H), 7.29–7.14 (m, 6H), 7.08–6.97 (m, 2H), 6.78–6.73 (m, 1H), 3.68 (s, 3H), 3.39–3.25 (m, 1H) , 0.96 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{29}H_{25}BrO_2$ $[M+Na]^+$: 507.0930, found: 507.0918.

2–bromo–3–(2–isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f]chromene (2–Br–NP)

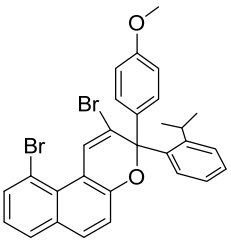


2-Br-NP

3–(2–Isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f]chromene (32 mg, 7.77×10^{-2} mmol) was dissolved in 15 mL of DMSO and magnetically stirred at room temperature. Water (100 μL) was added to the solution in a single portion followed by the dropwise addition of NBS (184 mg, 1.03 mmol) over a period of 25 min. The reaction mixture was stirred for further 5 min until only traces of the starting material remained detectable by TLC monitoring. Then the reaction mixture was added to water. The aqueous phase was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:6) and recrystallized from dichloromethane/hexane to give **2–Br–NP** as a colorless crystal (10 mg, yield : 27%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.86 (d, *J* = 8.4 Hz, 1 H), 7.82–7.67 (broad, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.46–7.39 (m, 1H), 7.36–7.31 (m, 1H), 7.30–7.19 (m, 2H) , 7.12–6.98 (m, 3H, broad), 6.97–6.91 (m, 1H), 6.89–6.56 (broad, 2H), 3.70 (s, 3H), 3.65–3.53 (m, 1H) , 1.17 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{29}H_{25}BrO_2$ $[M+Na]^+$: 507.0930, found: 507.0925.

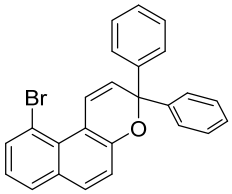
2,10–dibromo–3–(2–isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f]chromene (2,10–Br–NP)



2,10-Br-NP

10–Bromo–3–(2–isopropylphenyl)–3–(4–methoxyphenyl)–3H–benzo[f] chromene (32 mg, 6.65×10^{-2} mmol) was dissolved in 15 mL of DMSO and magnetically stirred at room temperature. Water (100 μL) was added to the solution in a single portion followed by the dropwise addition of NBS (58 mg, 3.26×10^{-1} mmol) over a period of 25 min. The reaction mixture was stirred for further 5 min until only traces of the starting material remained detectable by TLC monitoring. Then the reaction mixture was added to water and extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 30:1) and recrystallized from dichloromethane/hexane/methanol to give **2,10–Br–NP** as a colorless crystal (8 mg, yield : 21%).
^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.63 (s, 1H), 7.82 (dd, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.56–7.69 (m, 2H), 7.12–7.09 (m, 7H, broad), 7.08–6.60 (m, 3H, broad), 3.84 (s, 3H), 3.67–3.52 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H). HRMS (ESI-TOF) calculated for $C_{29}H_{24}Br_2O_2$ $[M+Na]^+$: 585.0035, found: 585.0021.

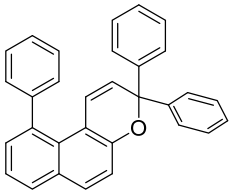
10–bromo–3,3–diphenyl–3H–benzo[f]chromene (5)



5

A solution of the 10–bromonaphthalene–2–ol (246 mg, 1.10 mmol), 1,1–diphenylprop–2–yn–1–ol (591 mg, 2.84 mmol) and PTSA (10 mg, 5.81×10^{-2} mmol) in dichloromethane (40 mL) were stirred for 11 h at room temperature. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 30:1), to give **5** as a red powder (393 mg, yield : 33%).
^{1}H NMR (400 MHz, DMSO–d_6): δ 8.16 (d, *J* = 9.9 Hz, 1H), 7.89–7.88 (m, 3H), 7.64–7.56 (m, 4H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.44–7.38 (m, 4H), 7.36–7.28 (m, 2H), 6.45 (d, *J* = 9.9 Hz, 1H). HRMS (ESI-TOF) calculated for $C_{25}H_{17}BrO$ $[M+Na]^+$: 435.0355, found: 435.0355.

3,3,10–triphenyl–3H–benzo[f]chromene (6)



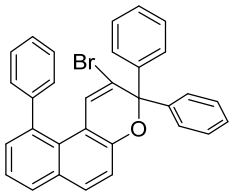
6

10–Bromo–3,3–diphenyl–3H–benzo[f]chromene (170 mg, 4.13×10^{-1} mmol) and 1–phenylboronic acid (90 mg, 7.41×10^{-1} mmol) were added to a suspension of Na_2CO_3 (293 mg, 27.7 mmol) in DME (6.5 mL) and H_2O (1.7 mL). The mixture was purged with N_2 gas. Tetrakis(triphenylphosphine) (16 mg, 1.40×10^{-2} mmol) was added to the resulting solution and the solution

was refluxed for 13 h. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 30:1) to give **6** as a white powder (72 mg, yield: 42%).

^{1}H NMR (400 MHz, DMSO–d_6): δ 7.89 (d, J = 8.8 Hz, 1 H), 7.83 (dd, J = 8.05 Hz, J = 1.0 Hz, 1H), 7.58–7.44 (m, 7H), 7.44–7.32 (m, 7H), 7.29–7.21 (m, 2H), 7.17–7.11 (m, 2H), 6.00 (d, J = 9.7 Hz, 1H), 5.82 (d, J = 9.7 Hz, 1H). HRMS (ESI-TOF) calculated for $C_{31}H_{22}O$ $[M+Na]^+$: 433.1563, found: 433.1573.

2–bromo–3,3,10–triphenyl–3H–benzo[f]chromene (7)

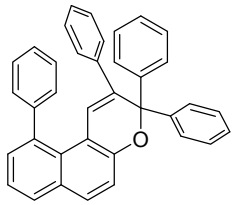


7

3,3,10–Triphenyl–3H–benzo[f]chromene (32 mg, 7.67×10^{-2} mmol) was dissolved in 5 mL of DMSO and magnetically stirred at room temperature. Water (0.6 mL) was added to the solution in a single portion followed by the dropwise addition of NBS (233 mg, 1.31 mmol) over a period of 15 min. The reaction mixture was stirred for further 5 min until only traces of starting material remained detectable by TLC monitoring. Then the reaction mixture was poured into water. The aqueous phase was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:10), to give **7** as a yellow powder (21 mg, yield : 56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.69 (m, 2H), 7.55–7.41 (m, 7H), 7.39–7.29 (m, 8H), 7.24–7.26 (m, 3H), 6.41 (s, 1H). HRMS (ESI-TOF) calculated for $C_{31}H_{21}BrO$ $[M+Na]^+$: 511.0668, found: 511.0657.

2,3,3,10–tetraphenyl–3H–benzo[f]chromene (2,10–Ph–NP)



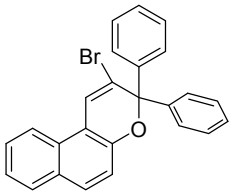
2,10-Ph-NP

2–Bromo–3,3,10–triphenyl–3H–benzo[f]chromene (95 mg, 1.95×10^{-1} mmol) and 1–phenylboronic acid (42 mg, 7.41×10^{-1} mmol) were dissolved in 1.8 mL of THF and 0.33 mL of aqueous 2.9 M NaOH and the mixture was purged with N_2 gas. Tetrakis(triphenylphosphine) (13 mg, 1.15×10^{-2} mmol) was added to the resulting solution and the solution was refluxed for 13 h. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:10) and recrystallized from dichloromethane/hexane/methanol to give **2,10–Ph–NP** as a colorless crystal (69 mg, yield: 72%).

^{1}H NMR (400 MHz, DMSO–d_6): δ 7.89 (d, J = 8.9 Hz, 1 H), 7.85 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.45–7.23 (m, 14H), 7.15 (d, 7.9 Hz, 2H), 7.03–6.90 (m, 3H), 6.54–6.47 (m, 2H), 6.25

(s, 1H). HRMS (ESI-TOF) calculated for $C_{37}H_{26}O$ $[M+Na]^+$: 509.1876, found: 509.1874.

2–bromo–3,3–diphenyl–3H–benzo[f]chromene (8)

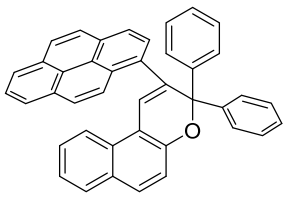


8

3,3–Diphenyl–3H–benzo[f]chromene (338 mg, 1.01×10^{-1} mmol) was dissolved in 20 mL DMSO and magnetically stirred at room temperature. Water (0.13 mL) was added to the solution in a single portion followed by the dropwise addition of NBS (459 mg, 2.58 mmol) over a period of 15 min. The reaction mixture was stirred for further 5 min until only traces of starting material remained detectable by TLC monitoring. Then the reaction mixture was poured into water and extracted with ethyl acetate. The solution was washed with water, and passed through the phase separator. After the solvent was removed, the crude mixture was dissolved in 10 mL of toluene. 4–Toluenesulfonic acid monohydrate (25 mg, 1.45×10^{-1} mmol) was added in a single portion and the resulting suspension was heated to reflux for 2.5 h until only traces of the starting material remained detectable by TLC monitoring. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:20), to give **8** as a white powder (354 mg, yield: 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.71 (d, J = 8.0 Hz 1H), 7.66 (d, J = 8.85 Hz, 1H), 7.55–7.45 (m, 5H), 7.37–7.29 (m, 7H), 7.15 (d, J = 8.8 Hz, 1H). HRMS (ESI-TOF) calculated for $C_{25}H_{17}BrO$ $[M+Na]^+$: 435.0355, found: 435.0347.

3,3–diphenyl–2–(pyren–1–yl)–3H–benzo[f]chromene (2–Py–NP)

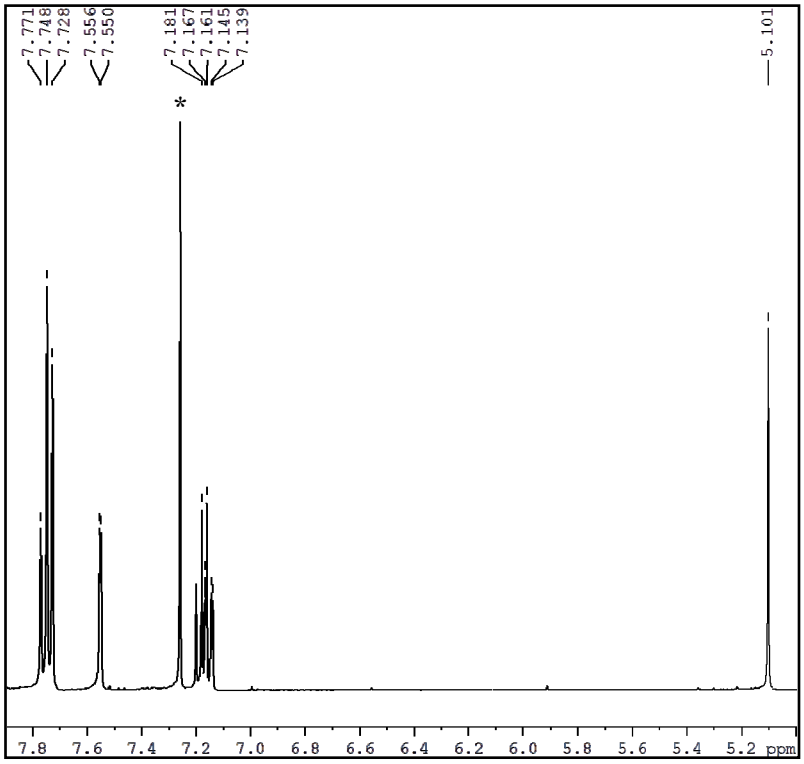


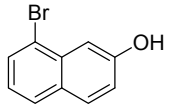
2-Py-NP

2–Bromo–3,3–diphenyl–3H–benzo[f]chromene (73 mg, 1.76×10^{-1} mmol) and 1–pyreneboronic Acid (71 mg, 2.89×10^{-1} mmol) were dissolved in 2.6 mL of THF and 0.33 mL of aqueous 3.0 M NaOH and the mixture was purged with N_2 gas. Tetrakis(triphenylphosphine) (8.6 mg, 7.44×10^{-3} mmol) was added to the resulting solution and refluxed for 15 h. The mixture was extracted with ethyl acetate. The solution was washed with water, and passed through phase separator paper. After the solvent was removed, the crude mixture was purified by silica gel column chromatography (ethyl acetate:hexane = 1:5) and recrystallized from methanol/ ethyl acetate to give **2–Py–NP** as a yellow crystal (83 mg, yield: 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 9.3 Hz, 1H), 8.18–8.07 (m, 2H), 8.05–7.80 (m, 9H, broad), 7.76 (d, J = 8.0 Hz 1H), 7.69 (d, J = 8.9 Hz, 1H), 7.64 (s, 1H), 7.48–7.28 (m, 7H, broad), 7.22 (d, J = 8.8 Hz, 1H), 6.95–6.97 (m, 3H, broad). HRMS (ESI-TOF) calculated for $C_{41}H_{26}O$ $[M+Na]^+$: 557.1876, found: 557.1868.

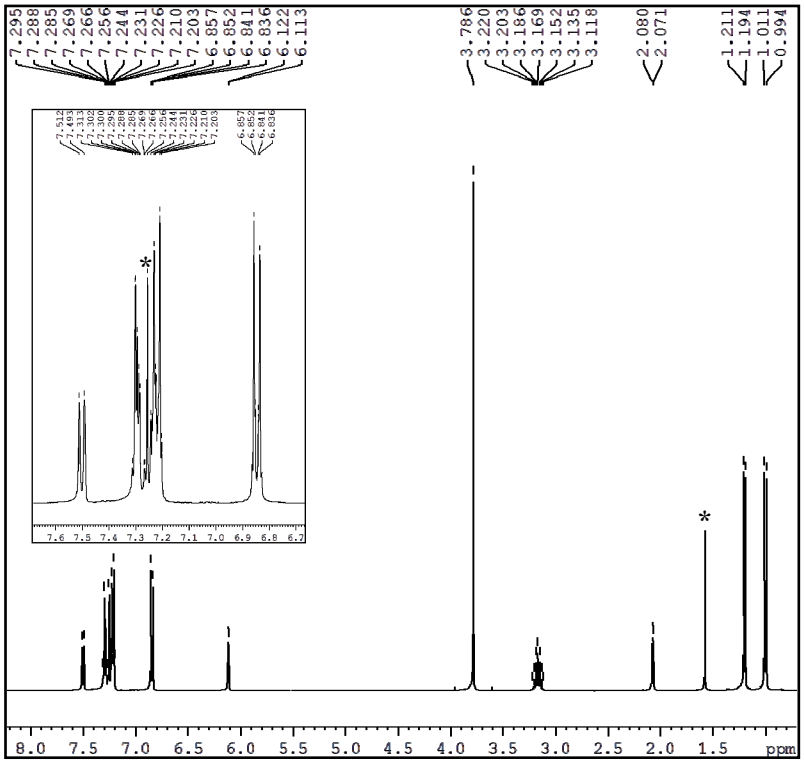
2. ^{1}H NMR Spectra

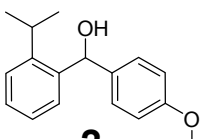




1

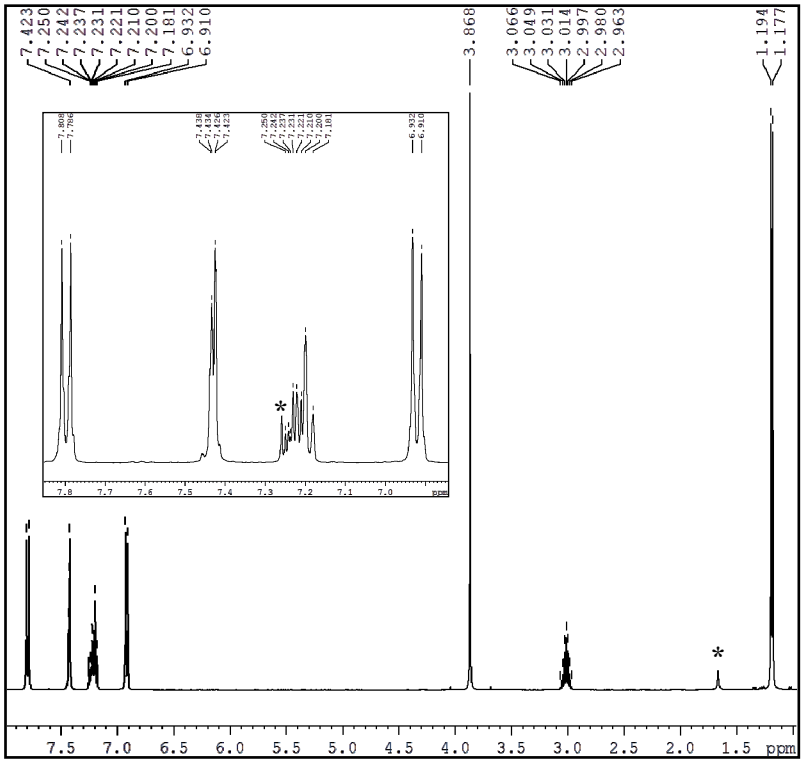
Fig. S1 ^{1}H NMR spectrum (400 MHz) of **1** in $CDCl_3$ (* solvent peaks).

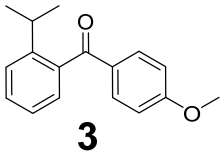




2

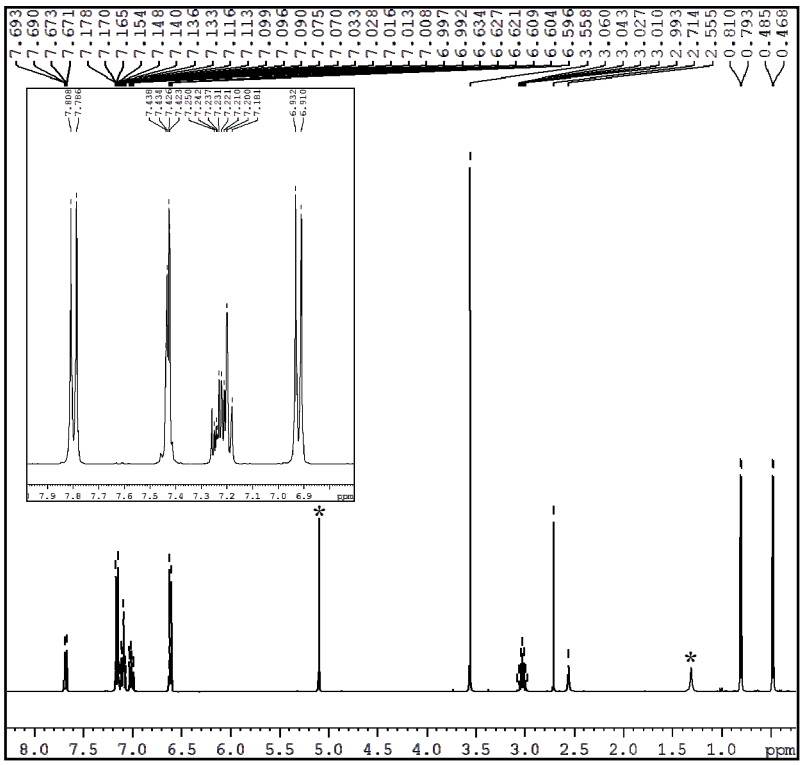
Fig. S2 ^{1}H NMR spectrum (400 MHz) of **2** in $CDCl_3$ (* solvent peaks).

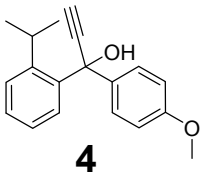




3

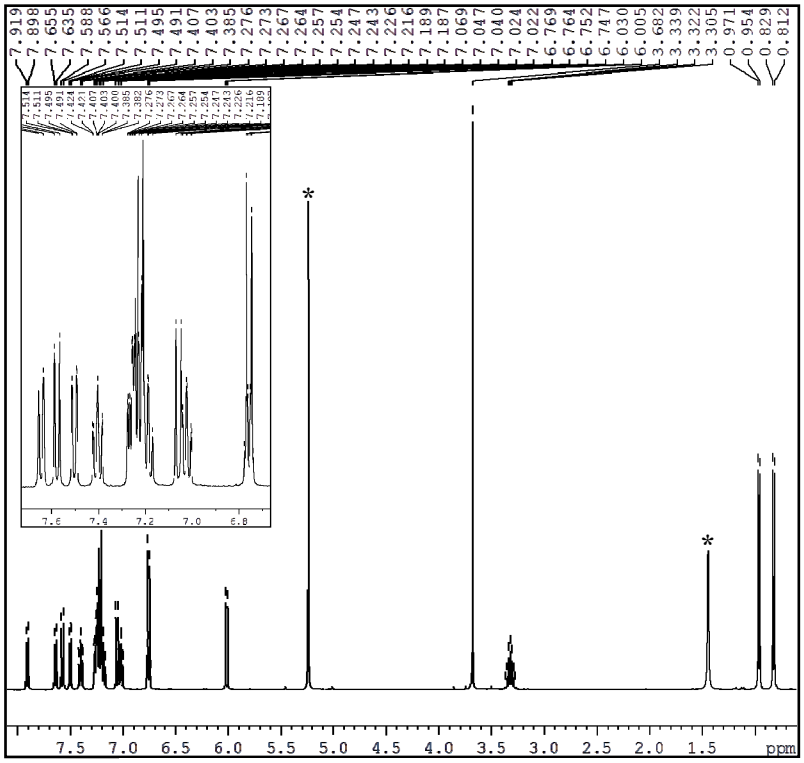
Fig. S3 ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$ (* solvent peaks).

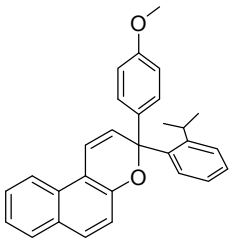




4

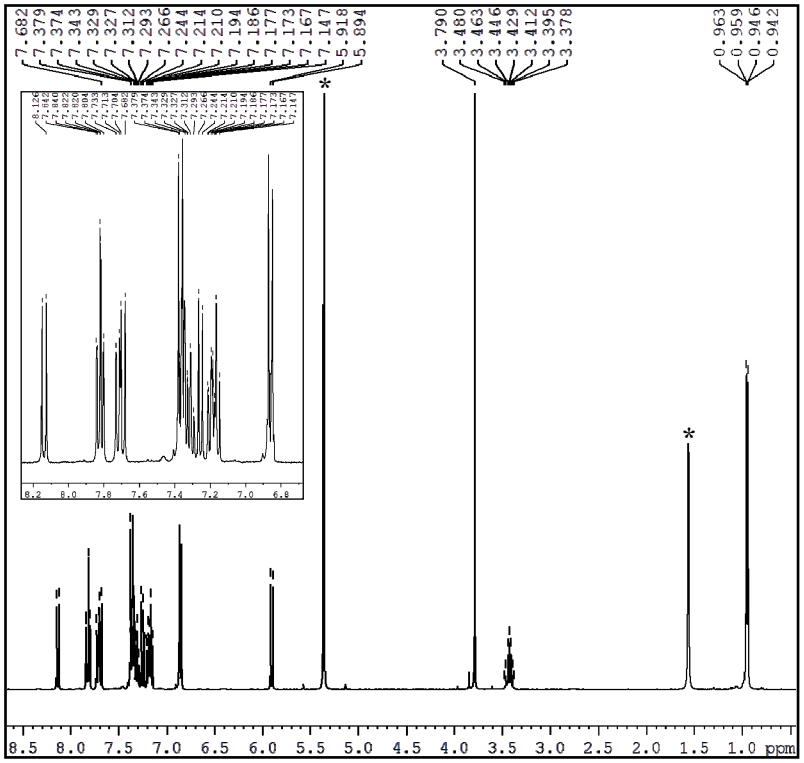
Fig. S4 ^{1}H NMR spectrum (400 MHz) of **4** in CD_2Cl_2 (* solvent peaks).

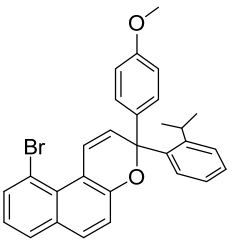




NP

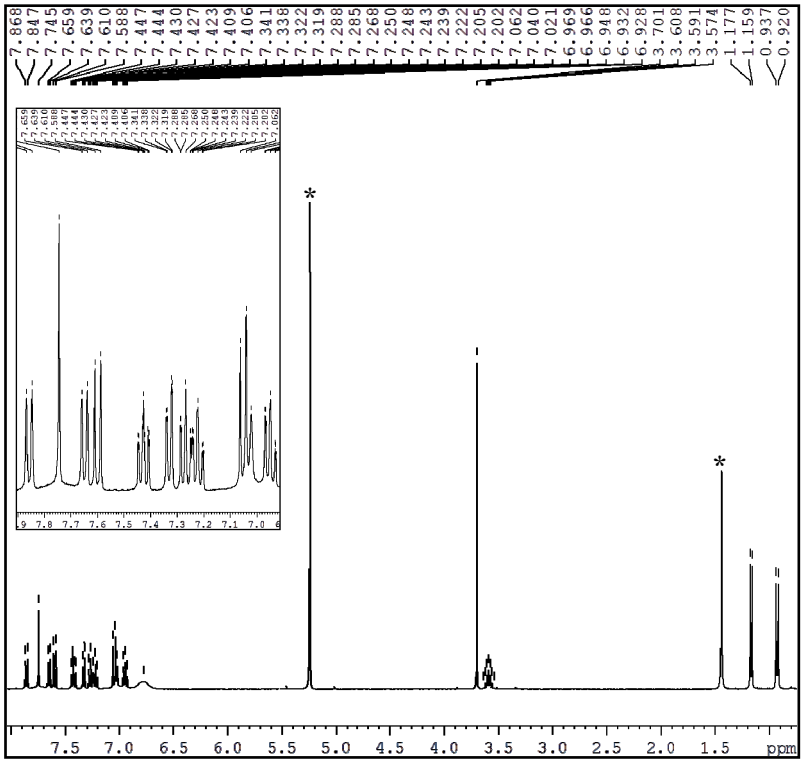
Fig. S5 ^{1}H NMR spectrum (400 MHz) of **NP** in CD_2Cl_2 (* solvent peaks).

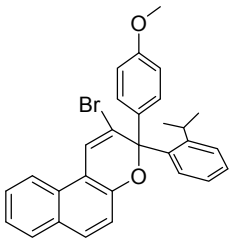




10-Br-NP

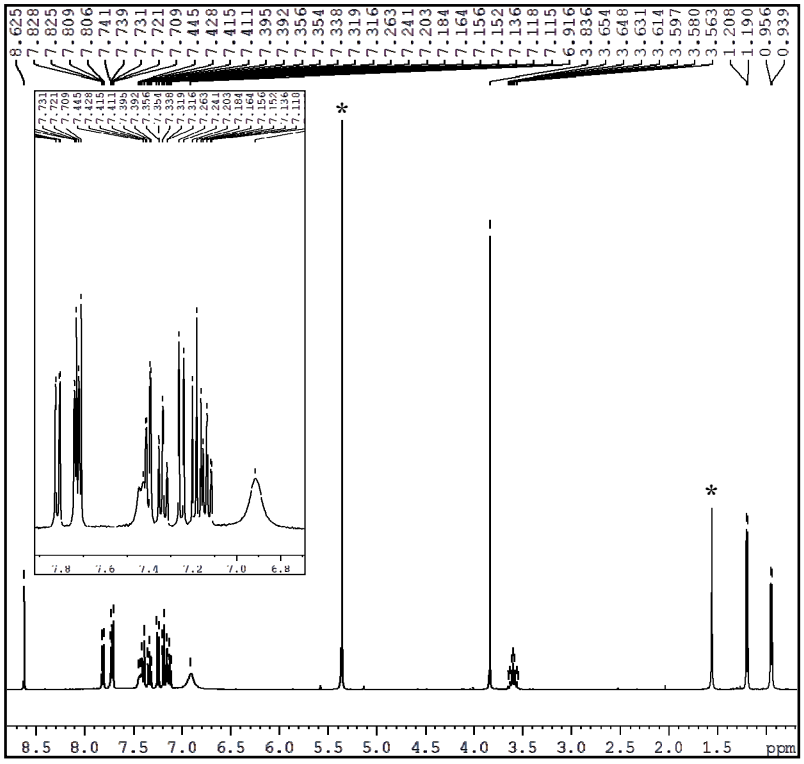
Fig. S6 ^{1}H NMR spectrum (400 MHz) of **10**–**Br**–**NP** in CD_2Cl_2 (* solvent peaks).

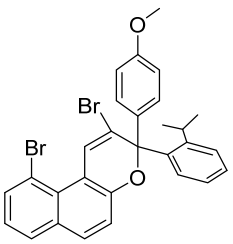




2-Br-NP

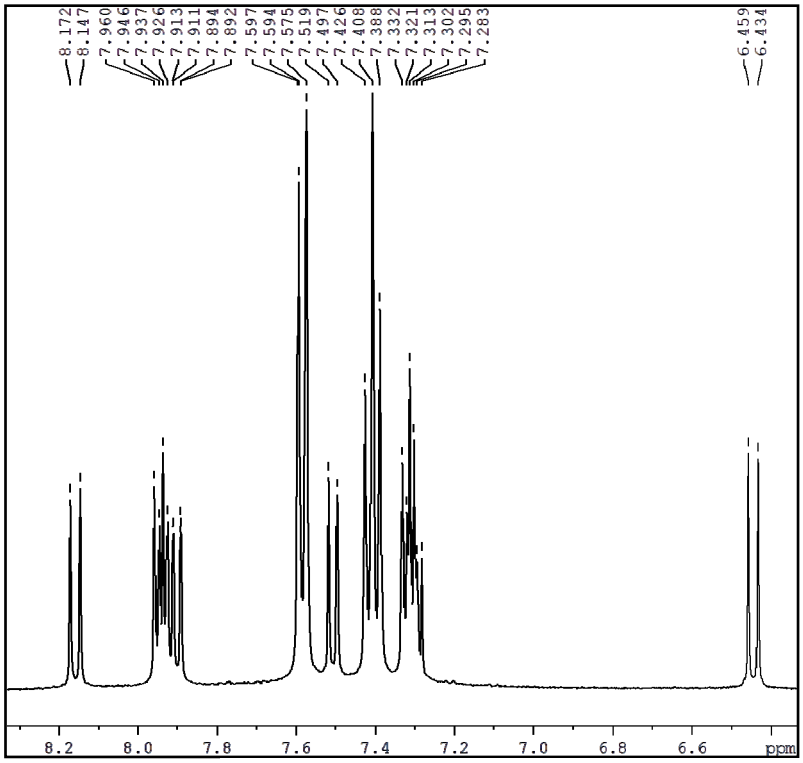
Fig. S7 ^{1}H NMR spectrum (400 MHz) of **2**–**Br**–**NP** in CD_2Cl_2 (* solvent peaks).

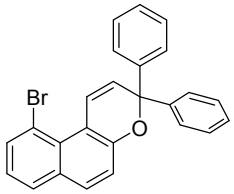




2,10-Br-NP

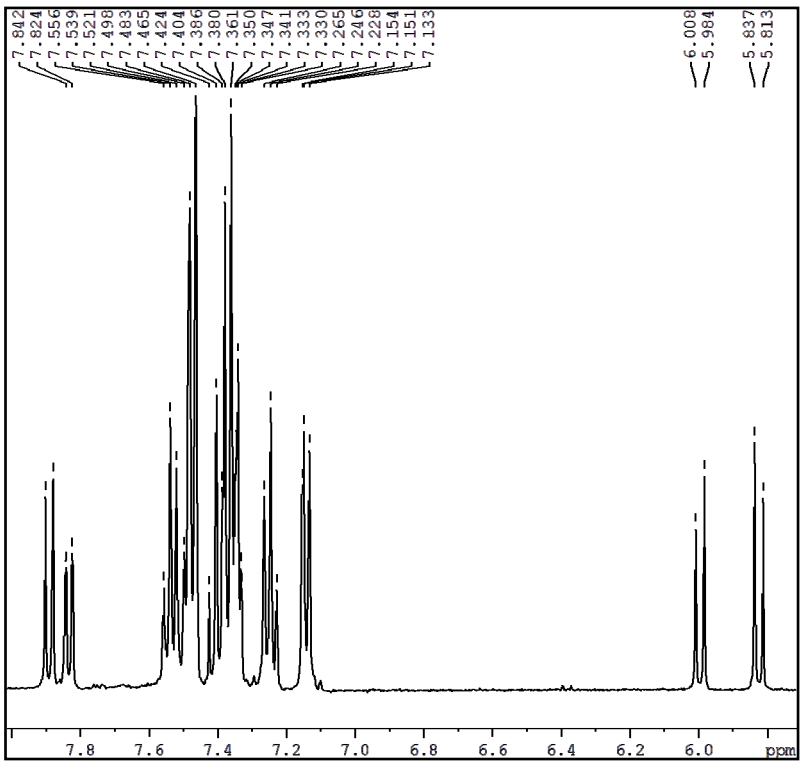
Fig. S8 ^{1}H NMR spectrum (400 MHz) of **2,10**–**Br**–**NP** in CD_2Cl_2 (* solvent peaks).

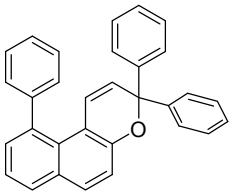




5

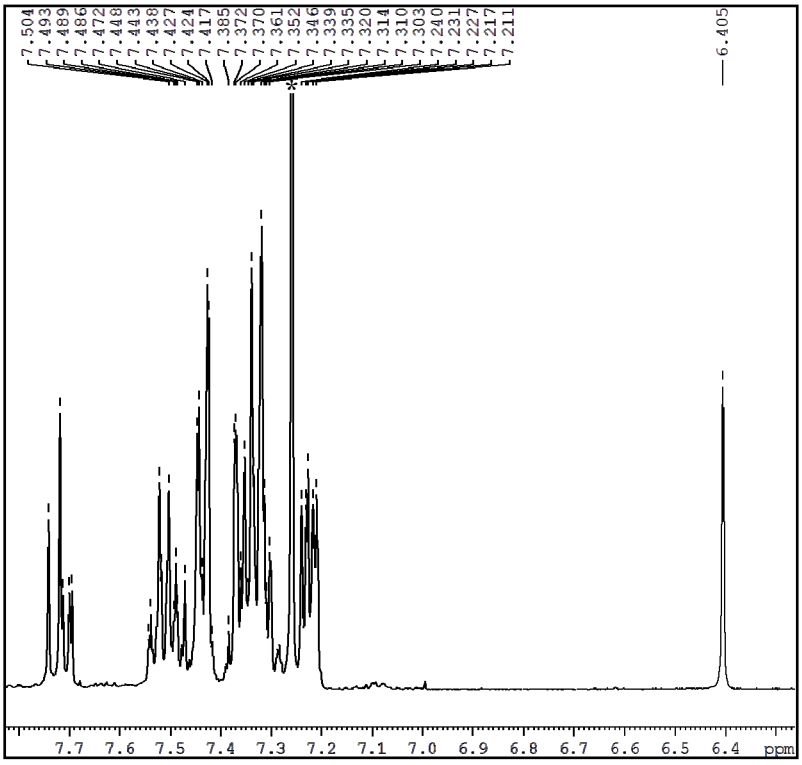
Fig. S9 ^{1}H NMR spectrum (400 MHz) of **5** in DMSO-d_6.

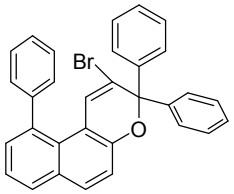




6

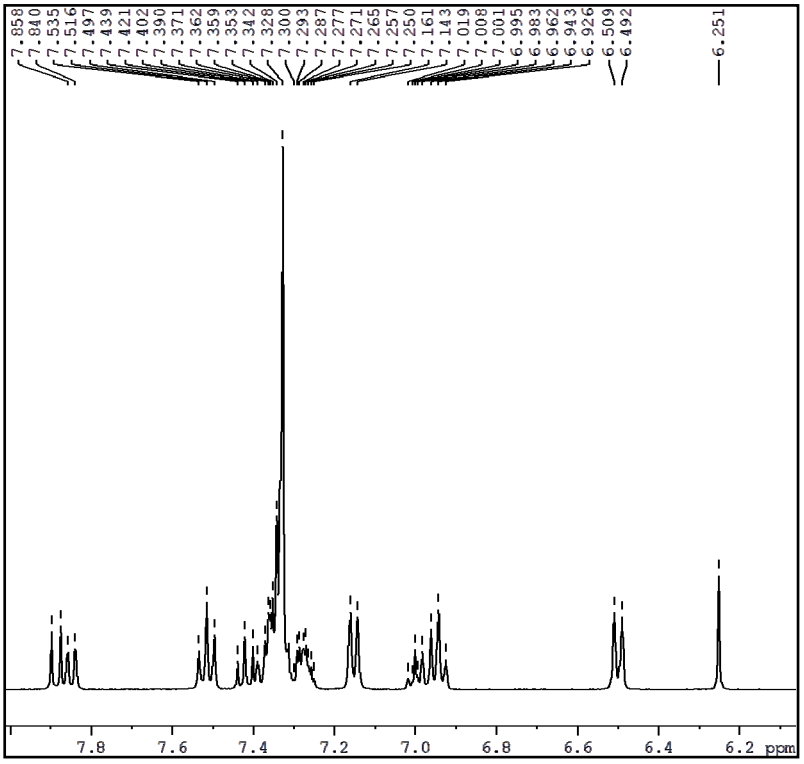
Fig. S10 ^{1}H NMR spectrum (400 MHz) of **6** in DMSO-d_6.

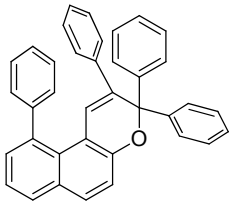




7

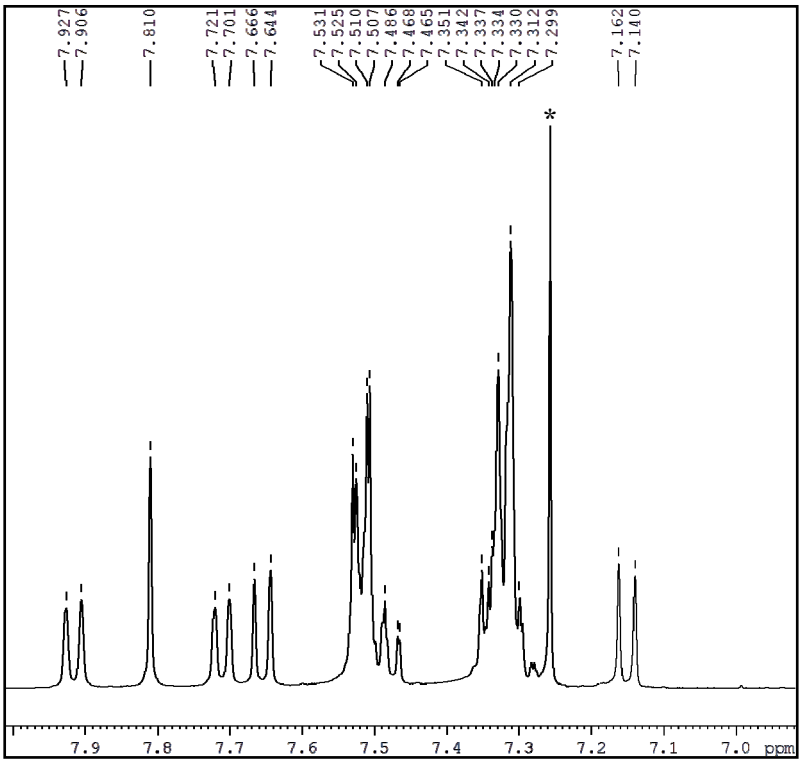
Fig. S11 ^{1}H NMR spectrum (400 MHz) of **7** in $CDCl_3$ (* solvent peaks).

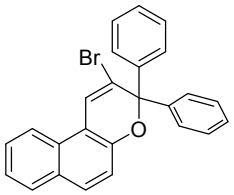




2,10-Ph-NP

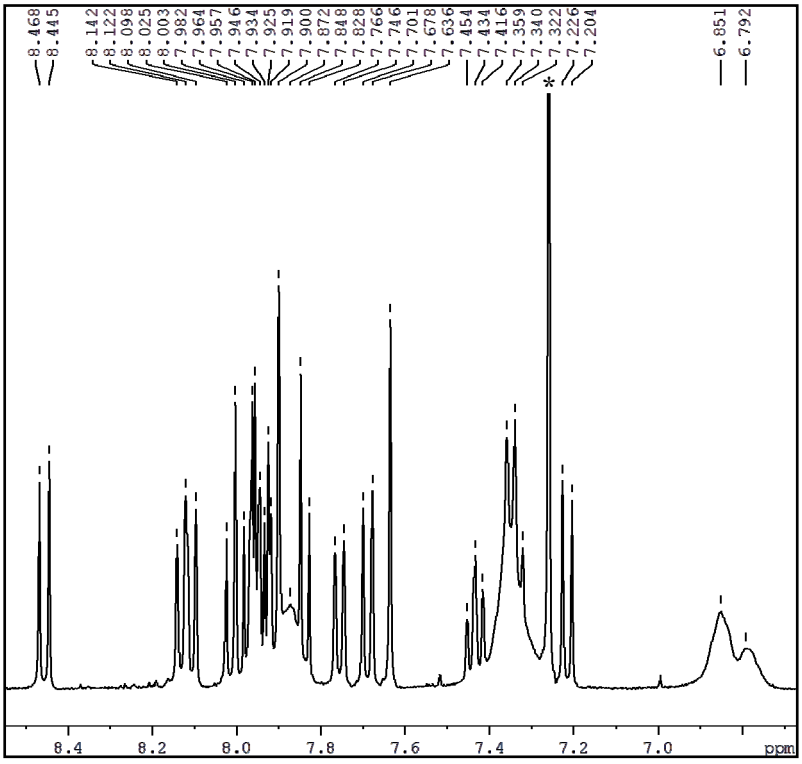
Fig. S12 ^{1}H NMR spectrum (400 MHz) of **2,10**–**Ph**–**NP** in DMSO-d_6.

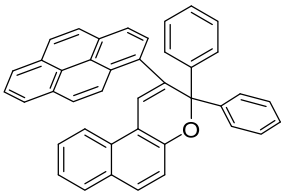




8

Fig. S13 ^{1}H NMR spectrum (400 MHz) of **8** in $CDCl_3$ (* solvent peaks).

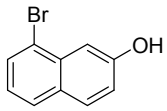




2-Py-NP

Fig. S14 ^{1}H NMR spectrum (400 MHz) of **2**–**Py**–**NP** in $CDCl_3$ (* solvent peaks).

3. HR-ESI-TOF-MS



1

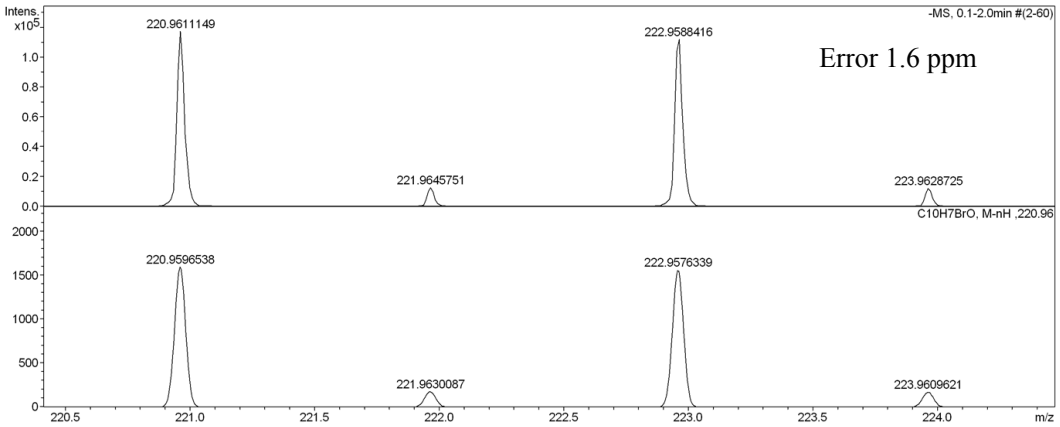
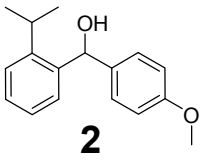


Fig. S15 HR-ESI-TOF-MS of **1**.



2

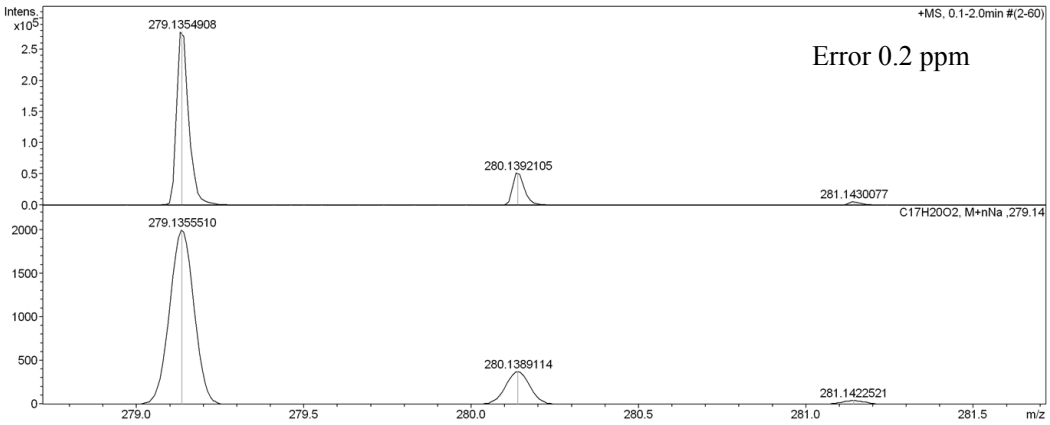
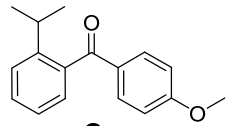


Fig. S16 HR-ESI-TOF-MS of **2**.



3

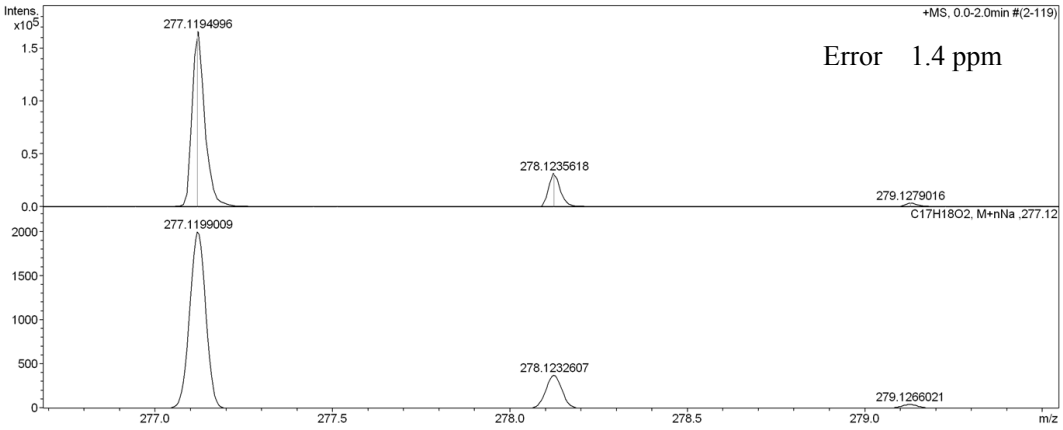
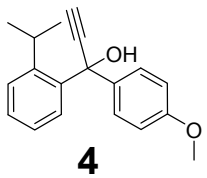


Fig. S17 HR-ESI-TOF-MS of **3**.



4

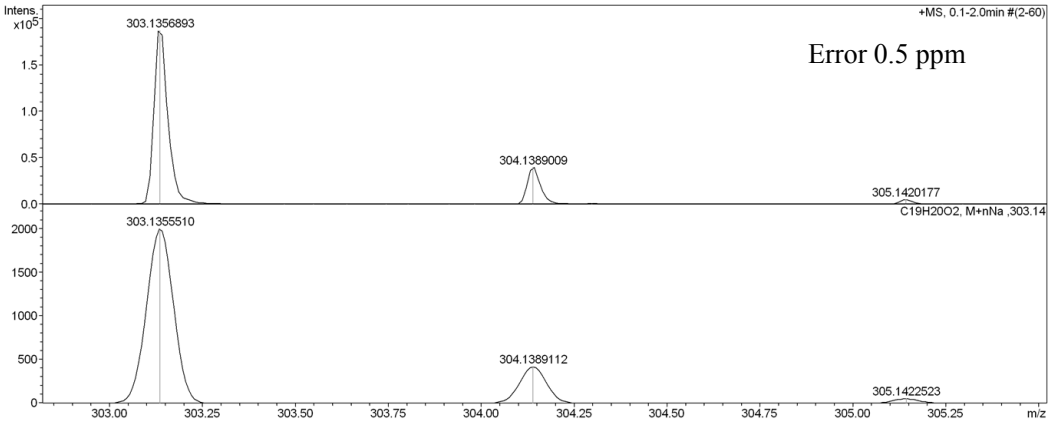
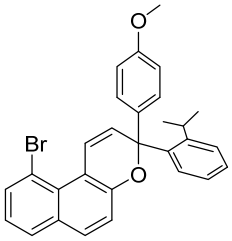


Fig. S18 HR-ESI-TOF-MS of **4**.



10-Br-NP

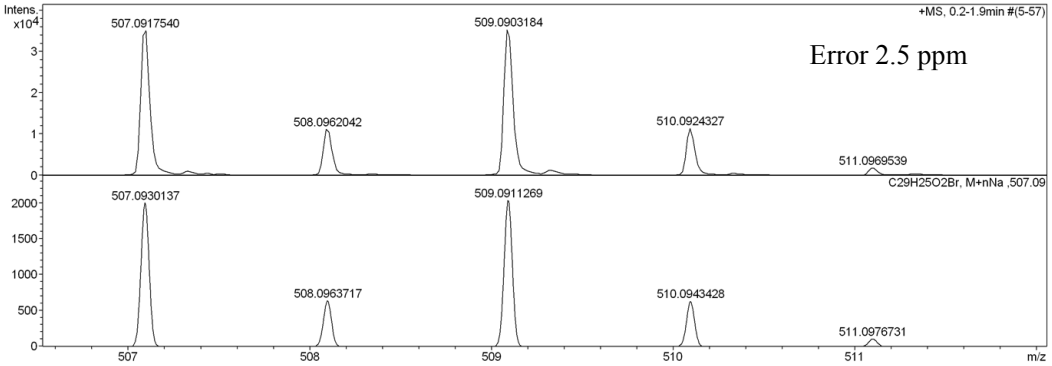
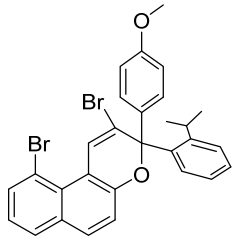


Fig. S19 HR-ESI-TOF-MS of **10**–**Br**–**NP**.



2,10-Br-NP

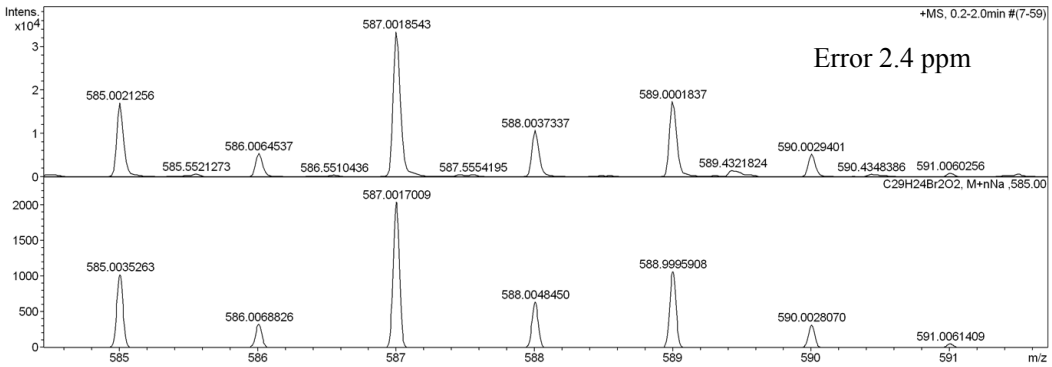
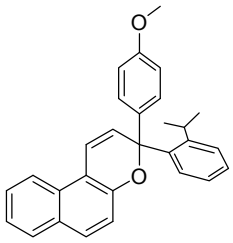


Fig. S20 HR-ESI-TOF-MS of **2,10**–**Br**–**NP**.



NP

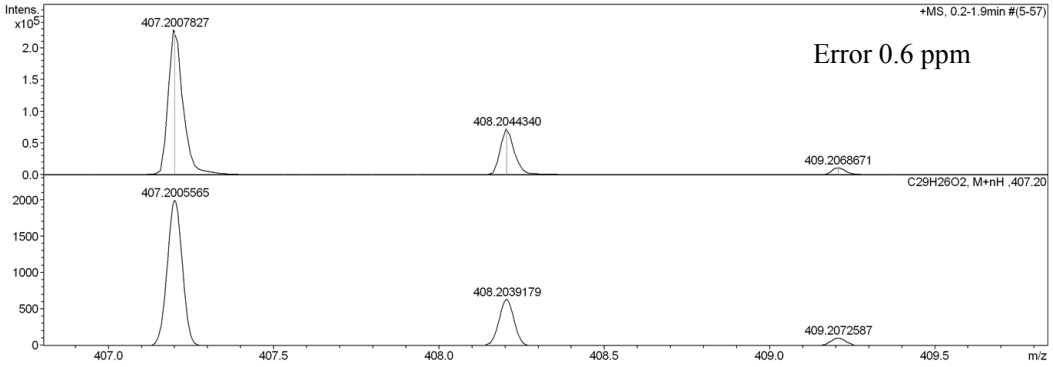
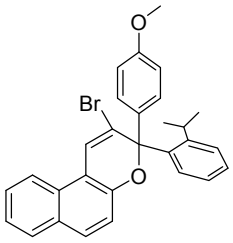


Fig. S21 HR-ESI-TOF-MS of **NP**.



2-Br-NP

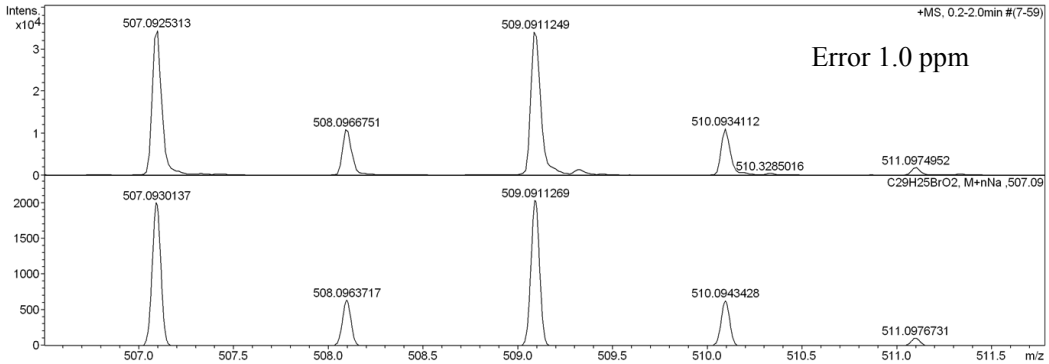
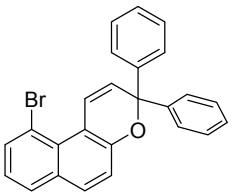


Fig. S22 HR-ESI-TOF-MS of **2**–**Br**–**NP**.



5

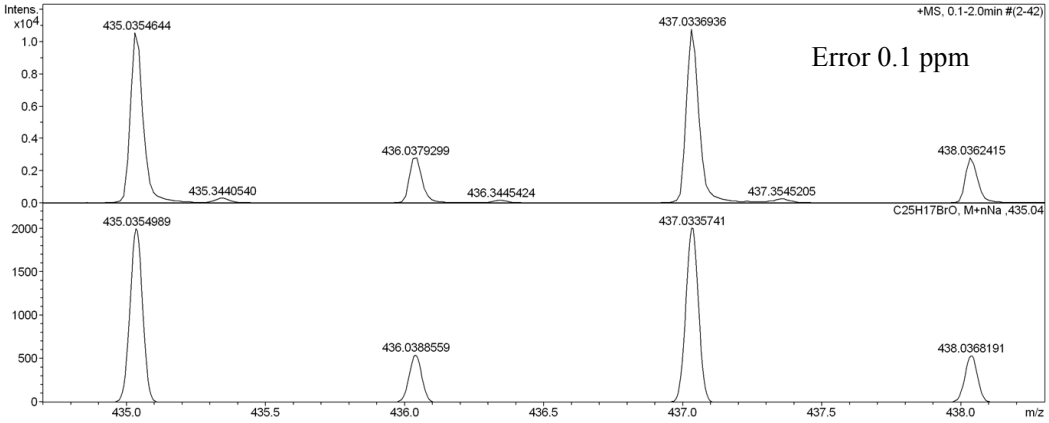
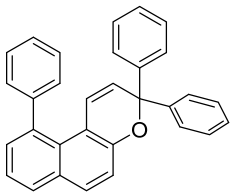


Fig. S23 HR-ESI-TOF-MS of **5**.



6

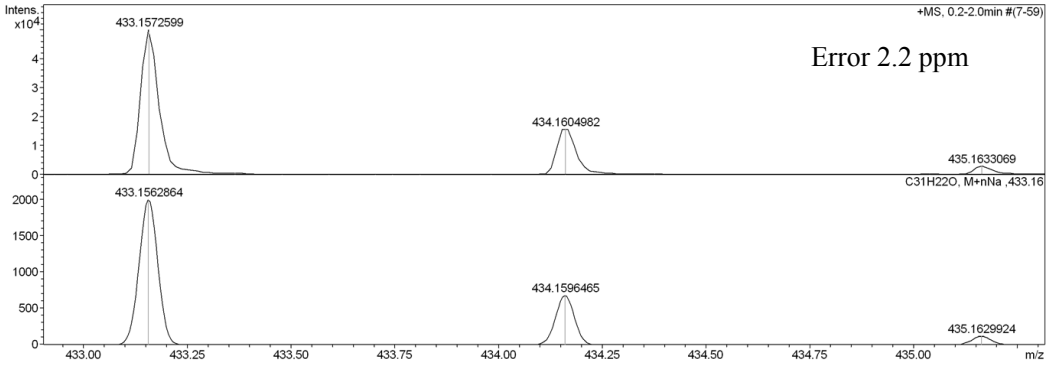


Fig. S24 HR-ESI-TOF-MS of **6**.

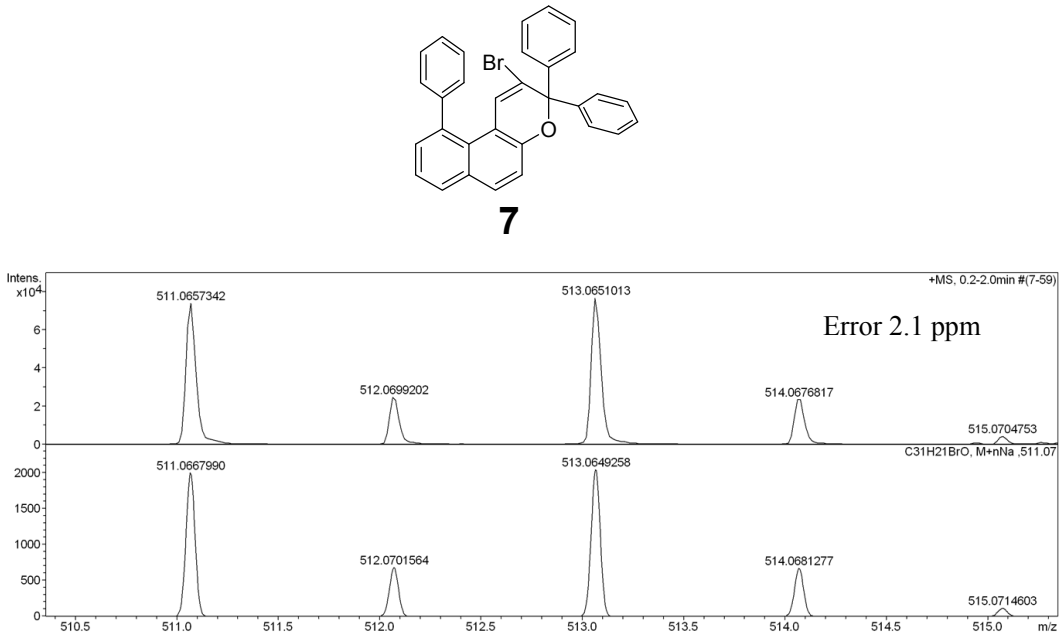


Fig. S25 HR-ESI-TOF-MS of **7**.

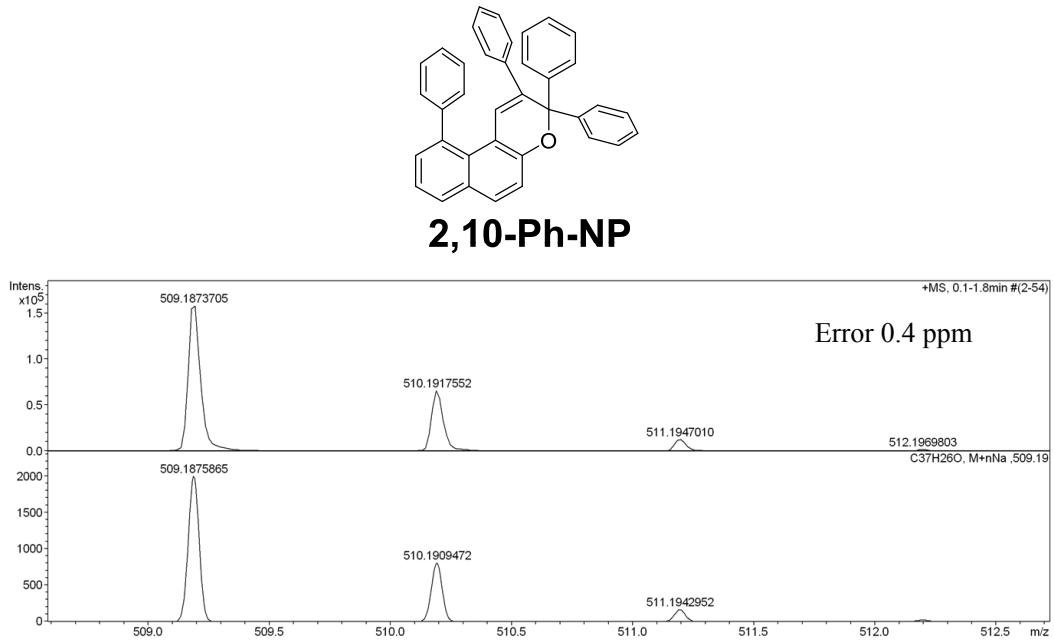
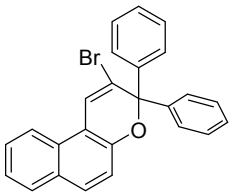


Fig. S26 HR-ESI-TOF-MS of **2,10–Ph–NP**.



8

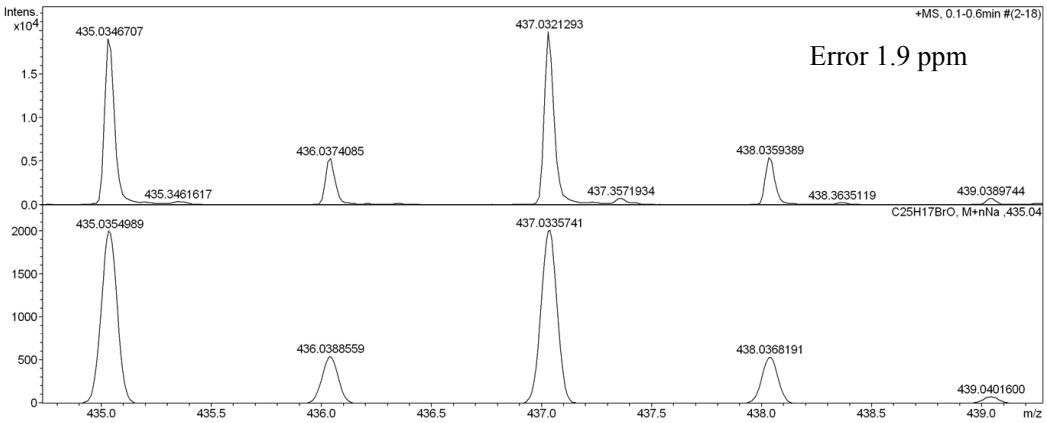
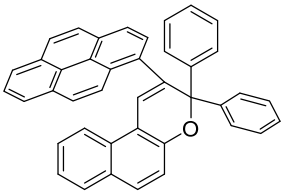


Fig. S27 HR-ESI-TOF-MS of **8**.



2-Py-NP

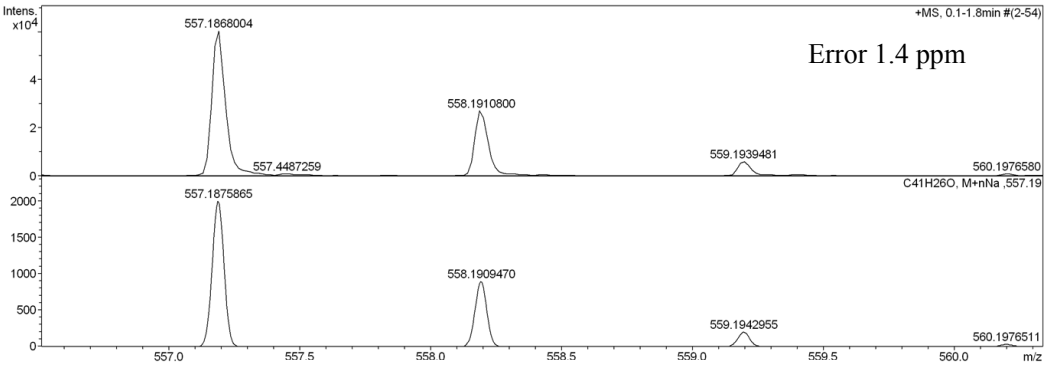
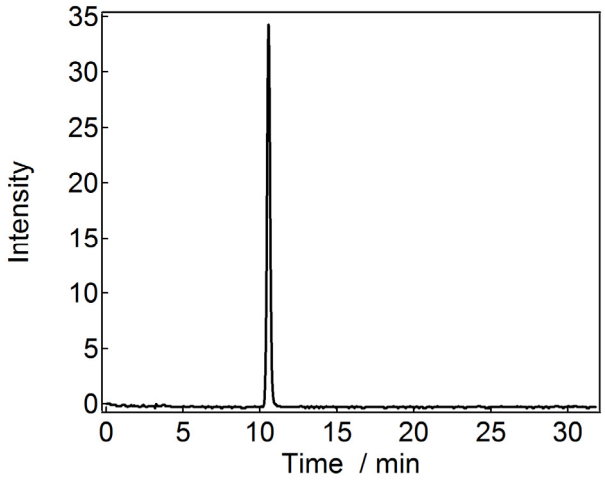
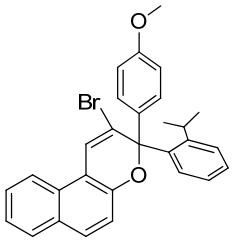


Fig. S28 HR-ESI-TOF-MS of **2**–**Py**–**NP**.

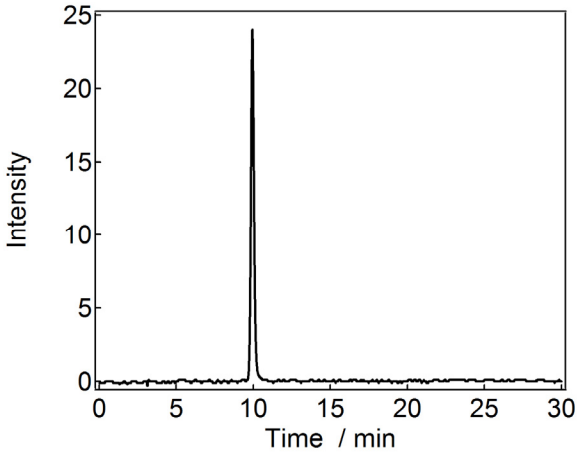
4. HPLC Chromatograms

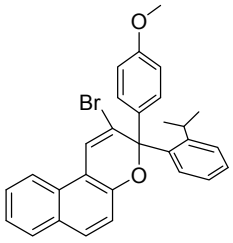




2-Br-NP

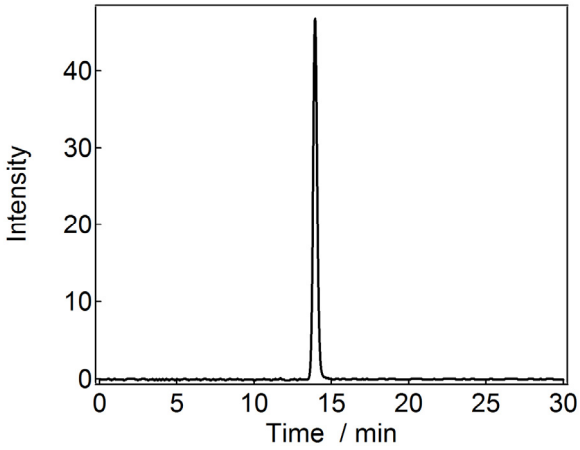
Fig. S29. HPLC chromatogram of **2–Br–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH:H_2O = 95:5 with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.

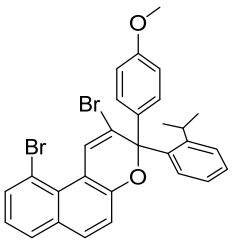




2-Br-NP

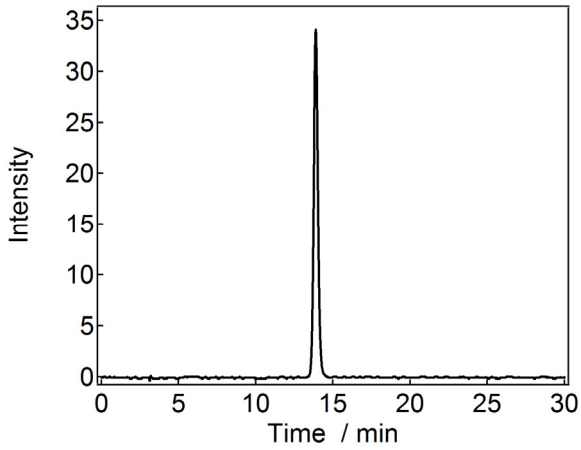
Fig. S30. HPLC chromatogram of **2–Br–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH:H_2O = 95:5 with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.

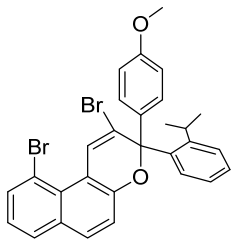




2,10-Br-NP

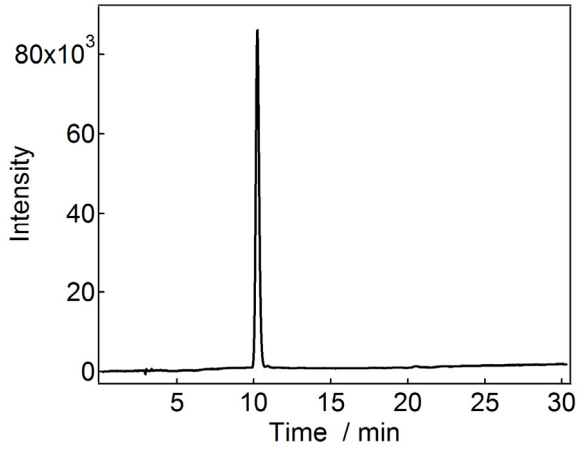
Fig. S31. HPLC chromatogram of **2,10–Br–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH:H_2O = 95:5 with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.





2,10-Br-NP

Fig. S32. HPLC chromatogram of **2,10–Br–NP**; 99% purity. HPLC analysis was performedusing a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH:H_2O = 95:5 with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.



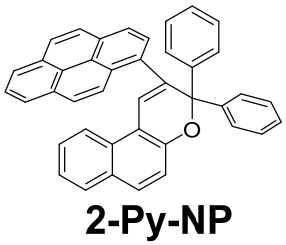
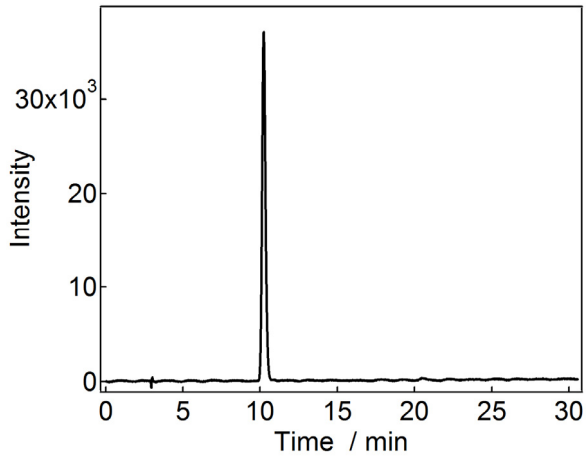


Fig. S33. HPLC chromatogram of **2–Py–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.



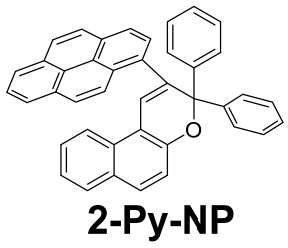
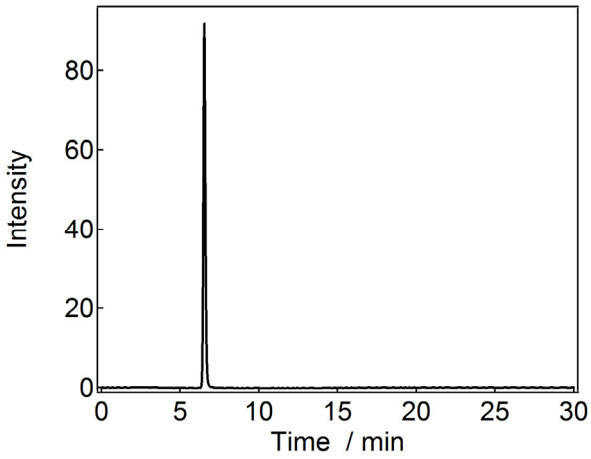
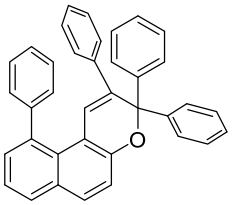


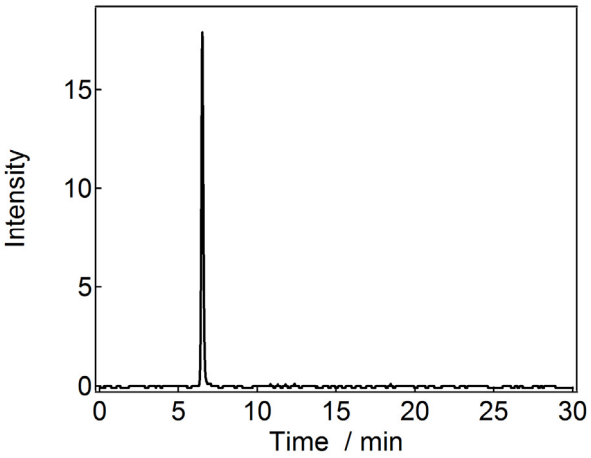
Fig. S34. HPLC chromatogram of **2–Py–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.

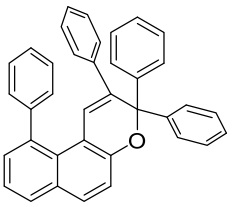




2,10-Ph-NP

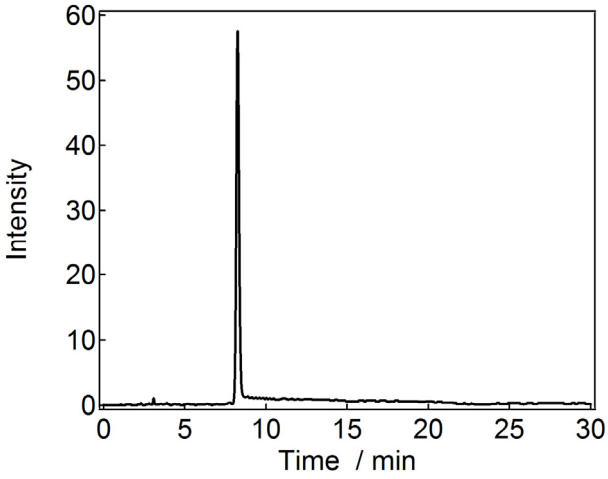
Fig. S35. HPLC chromatogram of **2,10–Ph–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.

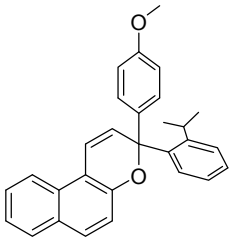




2,10-Ph-NP

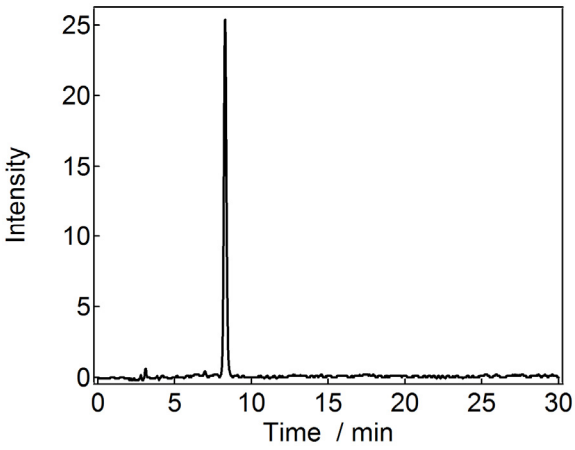
Fig. S36. HPLC chromatogram of **2,10–Ph–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.

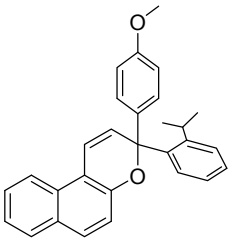




NP

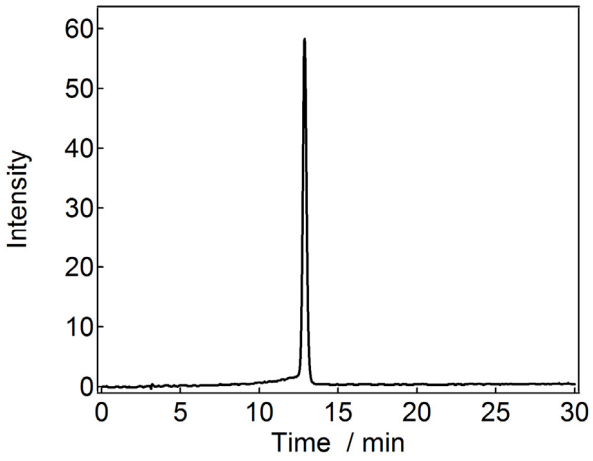
Fig. S37. HPLC chromatogram of **NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.

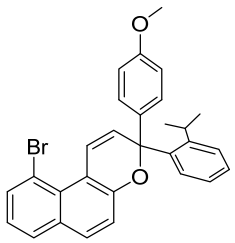




NP

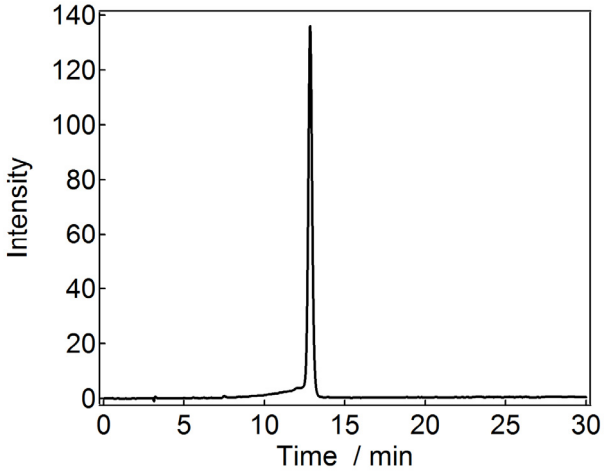
Fig. S38. HPLC chromatogram of **NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm×4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.

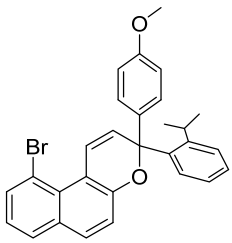




10-Br-NP

Fig. S39. HPLC chromatogram of **10–Br–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 254 nm.





10-Br-NP

Fig. S40. HPLC chromatogram of **10–Br–NP**; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm × 4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was MeOH with a flow rate of 1.0 mL/min, detection wavelength; 355 nm.

5. X–ray Crystallographic Analysis

The diffraction data of the single crystals were collected on the Bruker APEX II CCD area detector (Mo Kα, λ = 0.71073 nm). The data refinement was carried out by the Bruker APEXII software package with SHELXT program.[S2,S3] All non-hydrogen atoms were anisotropically refined.

Table S1. X–ray crystallographic data of **NP** (CCDC 1031286).

Identification code	**NP**	
Empirical formula	$C_{29}H_{26}O_2$	
Formula weight	406.50	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.4797(6) Å	α = 90°
	b = 16.5725(12) Å	β = 103.4540(9) °
	c = 15.9445(11) Å	γ = 90°
Volume	2179.2(3) $Å^3$	
Z	4	
Density(calculated)	1.239 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	864	
Theta range for data collection	1.80 to 26.30°	
Index ranges	–10<=h<=6, –20<=k<=20, –19<=l<=19	
Reflections collected	11304	
Independent reflections	4419 [R(int) = 0.0155]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4419 / 0 / 283	
Goodness–of–fit on F^2	1.024	
Final R indices [I>sigma (I)]	R1 = 0.0366, wR2 = 0.0887	
R indices (all data)	R1 = 0.0430, wR2 = 0.0937	
Largest diff. peak and hole	0.275 and –0.211 e $Å^{-3}$	

Table S2. X–ray crystallographic data of **10–Br–NP** (CCDC 1031285).

Identification code	**10–Br–NP**	
Empirical formula	$C_{29}H_{25}BrO_2$	
Formula weight	485.40	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 8.4457(4) Å	α = 90°
	b = 15.2032(7) Å	β = 92.8463(6) °
	c = 17.4327(8) Å	γ = 90°
Volume	2235.63 $Å^3$	
Z	4	
Density(calculated)	1.442 Mg/m^3	
Absorption coefficient	0.0863 mm^{-1}	
F(000)	1000	
Theta range for data collection	1.78 to 26.38°	
Index ranges	–10<=h<=8, –18<=k<=19, –20<=l<=21	
Reflections collected	11698	
Independent reflections	4568 [R(int) = 0.0139]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4568 / 0 / 292	
Goodness–of–fit on F^2	1.063	
Final R indices [I>sigma (I)]	R1 = 0.0234, wR2 = 0.0608	
R indices (all data)	R1 = 0.0256, wR2 = 0.0619	
Largest diff. peak and hole	0.390 and –0.519 e $Å^{-3}$	

Table S3. X–ray crystallographic data of **2–Br–NP** (CCDC 1031283).

Identification code	**2–Br–NP**	
Empirical formula	$C_{29}H_{25}Br_2O_2$	
Formula weight	485.40	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.4379(3) Å	α = 90°
	b = 16.1157(6) Å	β = 101.440(5)°
	c = 16.8070(6) Å	γ = 90°
Volume	2240.06(14) $Å^3$	
Z	4	
Density(calculated)	1.439 Mg/m^3	
Absorption coefficient	1.860 mm^{-1}	
F(000)	1000	
Theta range for data collection	1.77 to 26.04°	
Index ranges	–10<=h<=9, –19<=k<=19, –20<=l<=17	
Reflections collected	11385	
Independent reflections	4403 [R(int) = 0.0134]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4403 / 0 / 292	
Goodness–of–fit on F^2	1.047	
Final R indices [I>sigma (I)]	R1 = 0.0227, wR2 = 0.0589	
R indices (all data)	R1 = 0.0258, wR2 = 0.0601	
Largest diff. peak and hole	0.366 and –0.316 $eÅ^{-3}$	

Table S4. X–ray crystallographic data of **2,10–Br–NP** (CCDC 1031281).

Identification code	**2,10–Br–NP**	
Empirical formula	$C_{29}H_{24}Br_2O_2$	
Formula weight	564.30	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P –1	
Unit cell dimensions	a = 8.9872(17) Å	α = 79.651(2)°
	b = 9.0894(17) Å	β = 77.966(2)°
	c = 15.463(3) Å	γ = 77.931(2)°
Volume	1195.8(4) $Å^3$	
Z	2	
Density(calculated)	1.567 Mg/m^3	
Absorption coefficient	3.414 mm^{-1}	
F(000)	568	
Theta range for data collection	1.36 to 26.34°	
Index ranges	–11<=h<=9, –11<=k<=11, –19<=l<=15	
Reflections collected	6211	
Independent reflections	4637 [R(int) = 0.0159]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4637 / 0 / 301	
Goodness–of–fit on F^2	1.088	
Final R indices [I>sigma (I)]	R1 = 0.0440, wR2 = 0.1332	
R indices (all data)	R1 = 0.0477, wR2 = 0.1351	
Largest diff. peak and hole	1.876 and –0.515 e $Å^{-3}$	

Table S5. X–ray crystallographic data of **2,10–Ph–NP** (CCDC 1031282).

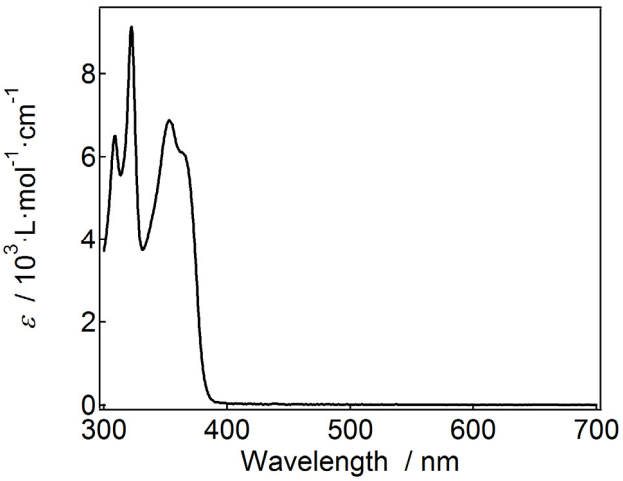
Identification code	**2,10–Ph–NP**	
Empirical formula	$C_{37}H_{26}O$	
Formula weight	486.58	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P –1	
Unit cell dimensions	a = 9.9865(6) Å	α = 86.2498(7)°
	b = 10.5600(7) Å	β = 84.3378(7)°
	c = 13.7281(8) Å	γ = 64.1270(5)°
Volume	1295.86(14) $Å^3$	
Z	2	
Density(calculated)	1.247 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	512	
Theta range for data collection	1.49 to 25.32°	
Index ranges	–12<=h<=8, –12<=k<=12, –16<=l<=15	
Reflections collected	6396	
Independent reflections	4641 [R(int) = 0.0094]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4641 / 0 / 343	
Goodness–of–fit on F^2	1.001	
Final R indices [I>sigma (I)]	R1 = 0.0343, wR2 = 0.0807	
R indices (all data)	R1 = 0.0399, wR2 = 0.0845	
Largest diff. peak and hole	0.232 and –0.205 e $Å^{-3}$	

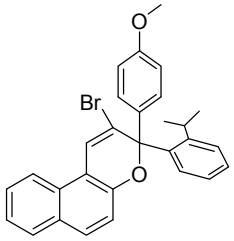
Table S6. X–ray crystallographic data of **2–Py–NP** (CCDC 1031284).

Identification code	**2–Py–NP**	
Empirical formula	$C_{41}H_{26}O$	
Formula weight	534.62	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 41.059(2) Å	α = 90°
	b = 10.4431(6) Å	β = 98.5570(10)°
	c = 13.0847(8) Å	γ = 90°
Volume	5548.0(6) $Å^3$	
Z	8	
Density(calculated)	1.280 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	2240	
Theta range for data collection	2.01 to 24.71°	
Index ranges	–42<=h<=48, –12<=k<=9, –15<=l<=14	
Reflections collected	12608	
Independent reflections	4734 [R(int) = 0.0153]	
Absorption correction	Empirical	
Refinement method	Full–matrix least–squares on F^2	
Data / restrains / parameters	4734 / 0 / 379	
Goodness–of–fit on F^2	0.954	
Final R indices [I>sigma (I)]	R1 = 0.0323, wR2 = 0.1084	
R indices (all data)	R1 = 0.0387, wR2 = 0.1173	
Largest diff. peak and hole	0.194 and –0.183 e $Å^{-3}$	

6. UV–Vis Absorption Spectroscopy

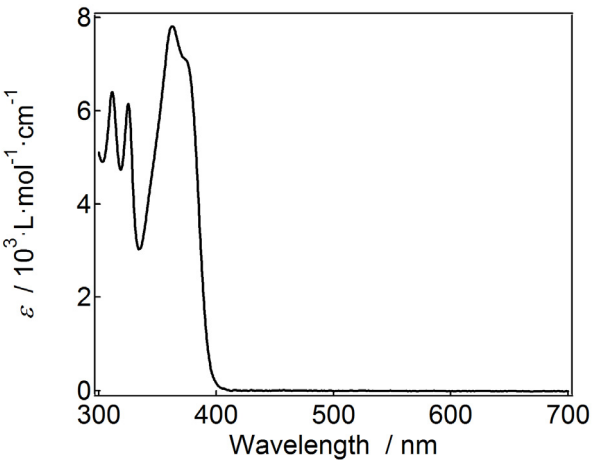
The steady state UV–vis absorption spectra were recorded with a Shimadzu UV3150 spectrometer.

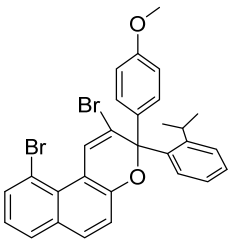




2-Br-NP

Fig. S41. UV–vis absorption spectrum of **2–Br–NP** in benzene at 298 K.





2,10-Br-NP

Fig. S42. UV–vis absorption spectrum of **2,10–Br–NP** in benzene at 298 K.

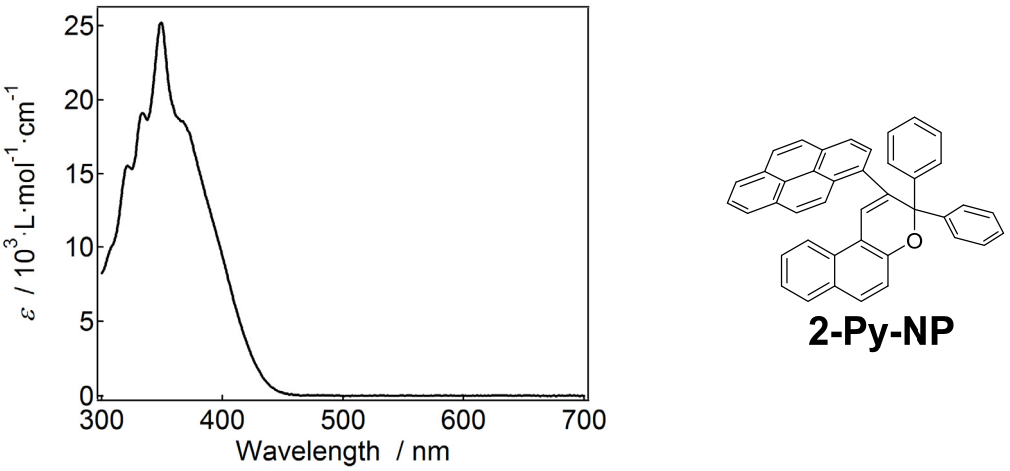


Fig. S43. UV–vis absorption spectrum of **2–Py–NP** in benzene at 298 K.

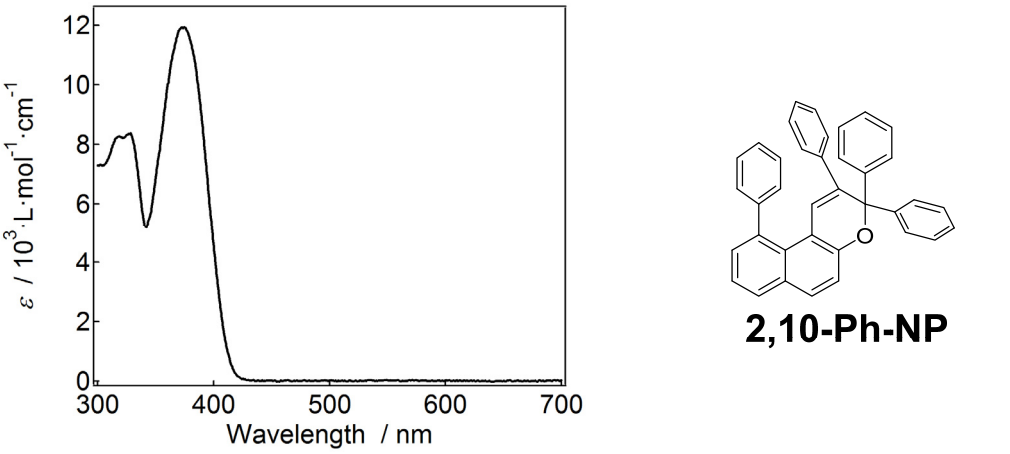
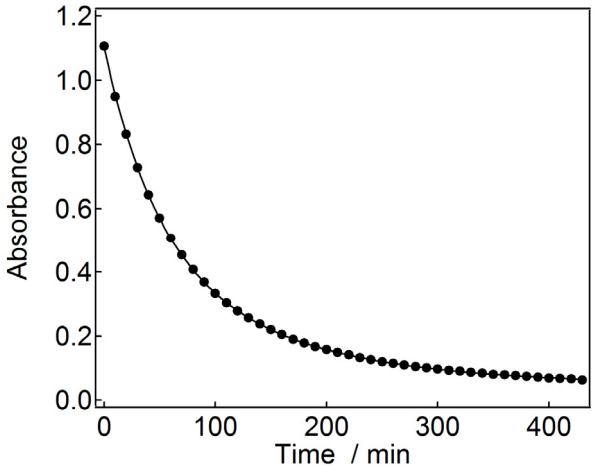
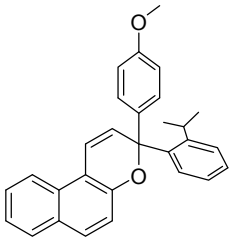


Fig. S44. UV–vis absorption spectrum of **2,10–Ph–NP** in benzene at 298 K.

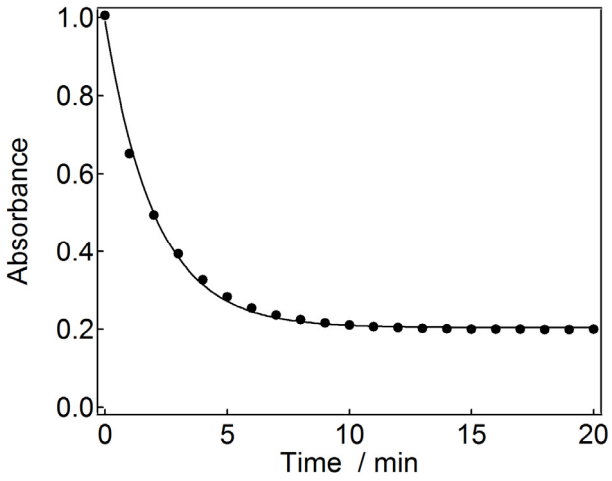
7. Kinetics for the Thermal Back Reaction

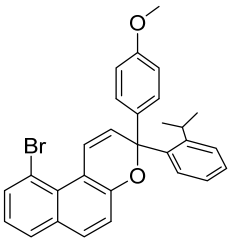




NP

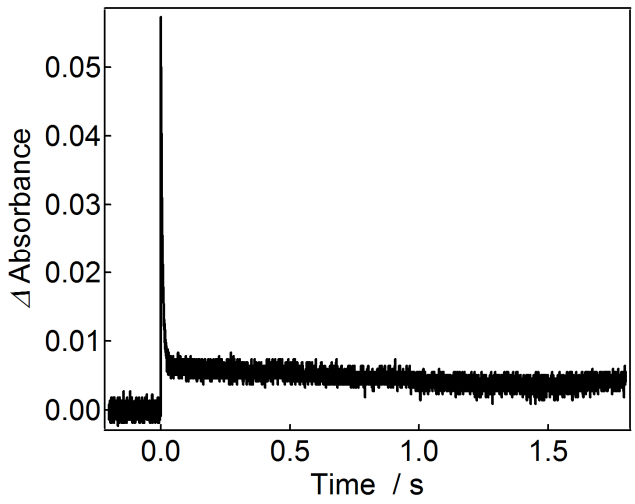
Fig. S45. Decay profiles of the transient absorbance of the solution of **NP** (4.9×10^{-5} M) observed at 460 nm in benzene at room temperature after irradiation of CW UV light (excitation wavelength, 365 nm; power, 2.6 W/cm^2). The solid line indicates the fitted curve by a double exponential decay function.





10-Br-NP

Fig. S46. Decay profiles of the transient absorbance of the solution of **10–Br–NP** (5.7×10^{-5} M) observed at 450 nm in benzene at room temperature after irradiation of CW UV light (excitation wavelength, 365 nm; power, 2.6 W/cm^2). The solid line indicates the fitted curve by a double exponential decay function.



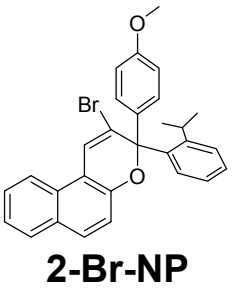
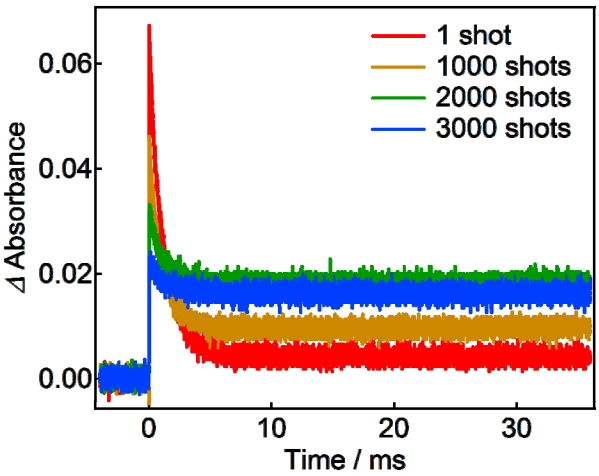


Fig. S47. Transient absorption dynamics of **2–Br–NP** in benzene (1.0×10^{-4} M) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 4 mJ/pulse). The decays were monitored at 400 nm and performed at room temperature.

8. Fatigue Resistance

The fatigue resistances of **2,10–Br–NP**, **2,10–Ph–NP** and **2–Py–NP** were measured using a Q-switch Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (ca. 5 mJ per 5 ns pulse) as the excitation beam.



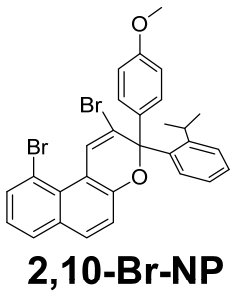
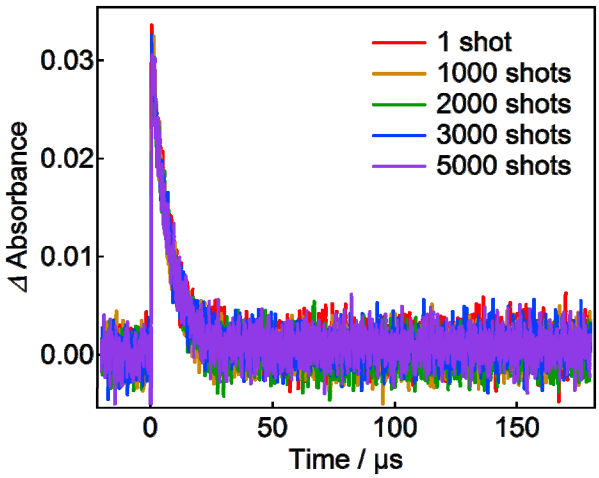
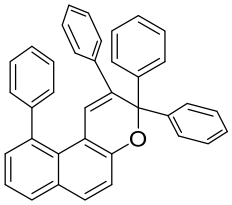


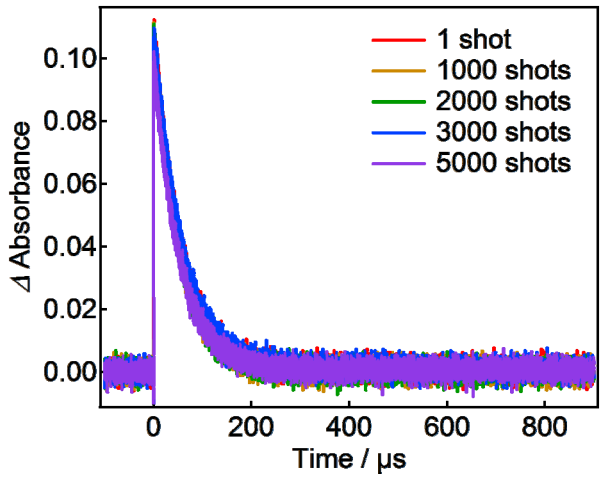
Fig. S48. Transient absorption dynamics of **2,10–Br–NP** in benzene (4.3×10^{-5} M) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 5 mJ/pulse). The decays were monitored at 400 nm and performed at room temperature.

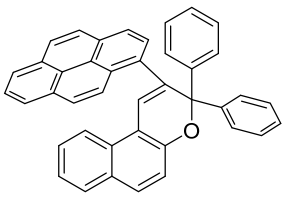




2,10-Ph-NP

Fig. S49. Transient absorption dynamics of **2,10–Ph–NP** in benzene (3.9×10^{-5} M) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 5 mJ/pulse). The decays were monitored at 450 nm and performed at room temperature.



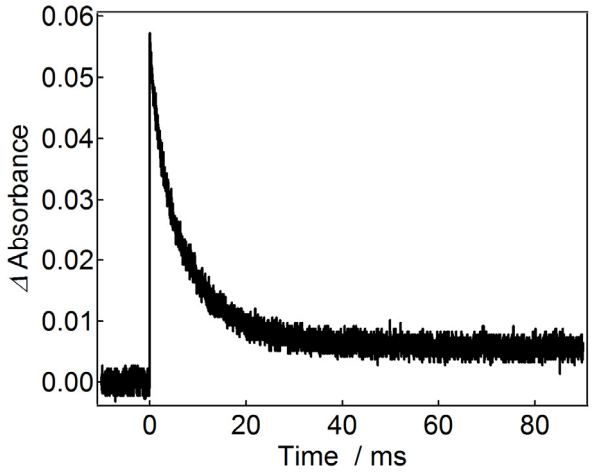


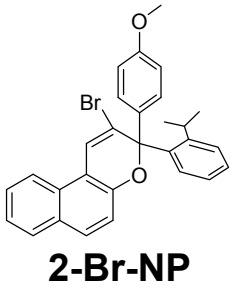
2-Py-NP

Fig. S50. Transient absorption dynamics of **2–Py–NP** in benzene (4.6×10^{-5} M) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 5 mJ/pulse). The decays were monitored at 450 nm and performed at room temperature.

9. Transient Absorption Dynamics in Polymer Matrices

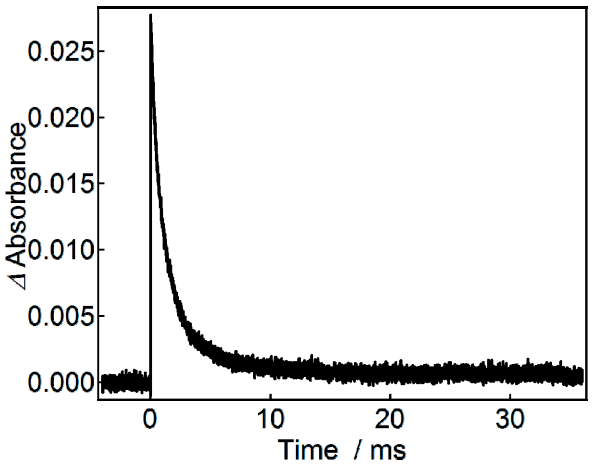
Transient absorption dynamics of **2–Br–NP, 2,10–Br–NP**, **2,10–Ph–NP** and **2–Py–NP** in polymer matrix were measured using a Q-switch Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (ca. 4 mJ per 5 ns pulse) as the excitation beam. Polymethylmethacrylate (PMMA) and polybutylacrylate (PBA) block copolymer was used as a host polymer (M_n: 7.51×10^4 g/mol, M_w/M_n: 1.09, glass transition temperature (T_g): −42 and 127 ℃, and PMMA: PBA = 5 : 9).

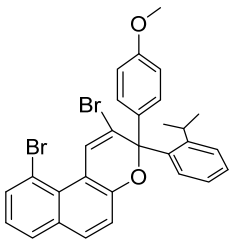




2-Br-NP

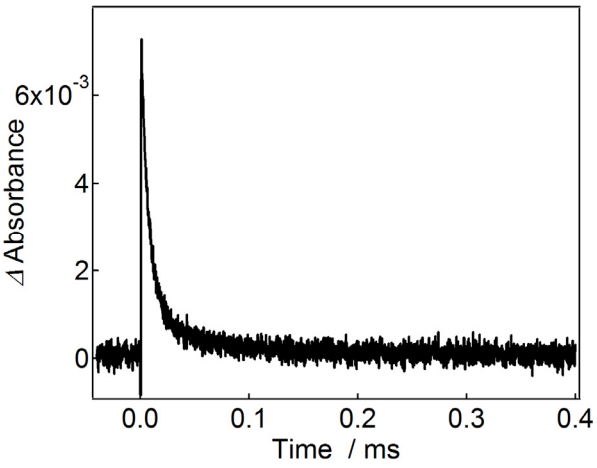
Fig. S51. Transient absorption dynamics of **2–Br–NP** in polymer matrix (19 wt. %, film thickness: 216 μm) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 4 mJ/pulse). The decays were monitored at 400 nm and performed at room temperature.

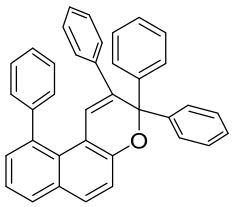




2,10-Br-NP

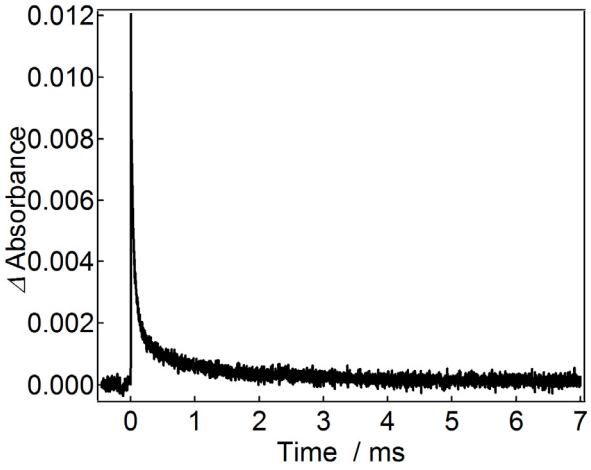
Fig. S52. Transient absorption dynamics of **2,10–Br–NP** in polymer matrix (26 wt. %, film thickness: 177 μm) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 4 mJ/pulse). The decays were monitored at 400 nm and performed at room temperature.

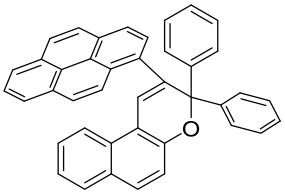




2,10-Ph-NP

Fig. S53. Transient absorption dynamics of **2,10–Ph–NP** in polymer matrix (11 wt. %, film thickness: 173 μm) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 4 mJ/pulse). The decays were monitored at 450 nm and performed at room temperature.





2-Py-NP

Fig. S54. Transient absorption dynamics of **2–Py–NP** in polymer matrix (14 wt. %, film thickness: 180 μm) excited at 355 nm after repetitive exposures of ns laser pulses (excitation wavelength, 355 nm; pulse duration, 5 ns; power 4 mJ/pulse). The decays were monitored at 450 nm and performed at room temperature.

10. Experimental Detail for Laser Flash Photolysis Measurements

The laser flash photolysis experiments were carried out with a TSP–1000 time resolved spectrophotometer (Unisoku). A 10 Hz Q–switched Nd:YAG (Continuum Minilite II) laser with the third harmonic at 355 nm (ca. 7 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from a halogen lamp (OSRAM HLX64623) was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the decay profile of the colored species and with multi–channel spectrophotometer (Unisoku MSP–1000–V1) for the transient absorption spectroscopy.

11. DFT Calculations

All calculations were carried out using the Gaussian 09 program (Revision D.01)[S4]. The molecular structures were fully optimized at the CAM-B3LYP/6-31G(d) level of theory, and analytical second derivatives of the energy were calculated using vibrational analysis to confirm each stationary point to be a minimum, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. Calculations have been carried out in the gas phase.

NP: *transoid-trans* (TT)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.	
Zero-point correction=	0.477108 (Hartree/Particle)
Thermal correction to Energy=	0.504106
Thermal correction to Enthalpy=	0.505050
Thermal correction to Gibbs Free Energy=	0.416704
Sum of electronic and zero-point Energies=	− 1269.979274
Sum of electronic and thermal Energies=	− 1269.952276
Sum of electronic and thermal Enthalpies=	− 1269.951332
Sum of electronic and thermal Free Energies=	− 1270.039677

NP: *transoid-cis* (TC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.	
Zero-point correction=	0.477092 (Hartree/Particle)
Thermal correction to Energy=	0.504122
Thermal correction to Enthalpy=	0.505066

Thermal correction to Gibbs Free Energy=	0.417151
Sum of electronic and zero-point Energies=	− 1269.983856
Sum of electronic and thermal Energies=	− 1269.956826
Sum of electronic and thermal Enthalpies=	− 1269.955882
Sum of electronic and thermal Free Energies=	− 1270.043797

NP: *cisoid-cis* (CC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.476818 (Hartree/Particle)
Thermal correction to Energy=	0.503521
Thermal correction to Enthalpy=	0.504465
Thermal correction to Gibbs Free Energy=	0.419013
Sum of electronic and zero-point Energies=	− 1269.968995
Sum of electronic and thermal Energies=	− 1269.942292
Sum of electronic and thermal Enthalpies=	− 1269.941347
Sum of electronic and thermal Free Energies=	− 1270.026799

NP: *closed form* (CF)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.478677 (Hartree/Particle)
Thermal correction to Energy=	0.504356
Thermal correction to Enthalpy=	0.505300
Thermal correction to Gibbs Free Energy=	0.422778
Sum of electronic and zero-point Energies=	− 1269.996062
Sum of electronic and thermal Energies=	− 1269.970382
Sum of electronic and thermal Enthalpies=	− 1269.969438
Sum of electronic and thermal Free Energies=	− 1270.051961

10-Br-NP: *transoid-trans* (TT)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.466872 (Hartree/Particle)
Thermal correction to Energy=	0.495271
Thermal correction to Enthalpy=	0.496215
Thermal correction to Gibbs Free Energy=	0.405483
Sum of electronic and zero-point Energies=	− 3841.189814
Sum of electronic and thermal Energies=	− 3841.161415

Sum of electronic and thermal Enthalpies= − 3841.160471

Sum of electronic and thermal Free Energies= − 3841.251203

10-Br-NP: *transoid-cis* (TC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.466852 (Hartree/Particle)

Thermal correction to Energy= 0.495288

Thermal correction to Enthalpy= 0.496232

Thermal correction to Gibbs Free Energy= 0.404576

Sum of electronic and zero-point Energies= − 3841.190439

Sum of electronic and thermal Energies= − 3841.162003

Sum of electronic and thermal Enthalpies= − 3841.161059

Sum of electronic and thermal Free Energies= − 3841.252715

10-Br-NP: *cisoid-cis* (CC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.466641 (Hartree/Particle)

Thermal correction to Energy= 0.494791

Thermal correction to Enthalpy= 0.495735

Thermal correction to Gibbs Free Energy= 0.406314

Sum of electronic and zero-point Energies= − 3841.177444

Sum of electronic and thermal Energies= − 3841.149294

Sum of electronic and thermal Enthalpies= − 3841.148349

Sum of electronic and thermal Free Energies= − 3841.237770

10-Br-NP: *closed form* (CF)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.468624 (Hartree/Particle)

Thermal correction to Energy= 0.495768

Thermal correction to Enthalpy= 0.496712

Thermal correction to Gibbs Free Energy= 0.409847

Sum of electronic and zero-point Energies= − 3841.202251

Sum of electronic and thermal Energies= − 3841.175107

Sum of electronic and thermal Enthalpies= − 3841.174163

Sum of electronic and thermal Free Energies= − 3841.261028

2-Br-NP: *transoid-trans* (TT)

Temperature	298.150 Kelvin.	Pressure	1.00000 Atm.
Zero-point correction=			0.466349 (Hartree/Particle)
Thermal correction to Energy=			0.494802
Thermal correction to Enthalpy=			0.495746
Thermal correction to Gibbs Free Energy=			0.404752
Sum of electronic and zero-point Energies=			− 3841.185972
Sum of electronic and thermal Energies=			− 3841.157519
Sum of electronic and thermal Enthalpies=			− 3841.156574
Sum of electronic and thermal Free Energies=			− 3841.247569

2-Br-NP: *transoid-cis* (TC)

Temperature	298.150 Kelvin.	Pressure	1.00000 Atm.
Zero-point correction=			0.466002 (Hartree/Particle)
Thermal correction to Energy=			0.494659
Thermal correction to Enthalpy=			0.495603
Thermal correction to Gibbs Free Energy=			0.403579
Sum of electronic and zero-point Energies=			− 3841.185282
Sum of electronic and thermal Energies=			− 3841.156626
Sum of electronic and thermal Enthalpies=			− 3841.155681
Sum of electronic and thermal Free Energies=			− 3841.247705

2-Br-NP: *cisoid-cis* (CC)

Temperature	298.150 Kelvin.	Pressure	1.00000 Atm.
Zero-point correction=			0.466108 (Hartree/Particle)
Thermal correction to Energy=			0.494643
Thermal correction to Enthalpy=			0.495587
Thermal correction to Gibbs Free Energy=			0.404818
Sum of electronic and zero-point Energies=			− 3841.182806
Sum of electronic and thermal Energies=			− 3841.154271
Sum of electronic and thermal Enthalpies=			− 3841.153327
Sum of electronic and thermal Free Energies=			− 3841.244096

2-Br-NP: *closed form* (CF)

Temperature	298.150 Kelvin.	Pressure	1.00000 Atm.
Zero-point correction=			0.468698 (Hartree/Particle)

Thermal correction to Energy=	0.495853
Thermal correction to Enthalpy=	0.496798
Thermal correction to Gibbs Free Energy=	0.410763
Sum of electronic and zero-point Energies=	− 3841.210306
Sum of electronic and thermal Energies=	− 3841.183151
Sum of electronic and thermal Enthalpies=	− 3841.182207
Sum of electronic and thermal Free Energies=	− 3841.268241

2,10-Br-NP: *transoid-trans* (TT)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.456266 (Hartree/Particle)
Thermal correction to Energy=	0.486100
Thermal correction to Enthalpy=	0.487044
Thermal correction to Gibbs Free Energy=	0.393445
Sum of electronic and zero-point Energies=	− 6412.396954
Sum of electronic and thermal Energies=	− 6412.367120
Sum of electronic and thermal Enthalpies=	− 6412.366176
Sum of electronic and thermal Free Energies=	− 6412.459775

2,10-Br-NP: *transoid-cis* (TC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.455871 (Hartree/Particle)
Thermal correction to Energy=	0.485936
Thermal correction to Enthalpy=	0.486881
Thermal correction to Gibbs Free Energy=	0.391656
Sum of electronic and zero-point Energies=	− 6412.392536
Sum of electronic and thermal Energies=	− 6412.362471
Sum of electronic and thermal Enthalpies=	− 6412.361526
Sum of electronic and thermal Free Energies=	− 6412.456751

2,10-Br-NP: *cisoid-cis* (CC)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.456026 (Hartree/Particle)
Thermal correction to Energy=	0.485915
Thermal correction to Enthalpy=	0.486859
Thermal correction to Gibbs Free Energy=	0.392491

Sum of electronic and zero-point Energies=	− 6412.389130
Sum of electronic and thermal Energies=	− 6412.359241
Sum of electronic and thermal Enthalpies=	− 6412.358297
Sum of electronic and thermal Free Energies=	− 6412.452665

2,10-Br-NP: *closed form* (CF)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction=	0.458545 (Hartree/Particle)
Thermal correction to Energy=	0.487230
Thermal correction to Enthalpy=	0.488174
Thermal correction to Gibbs Free Energy=	0.397421
Sum of electronic and zero-point Energies=	− 6412.416364
Sum of electronic and thermal Energies=	− 6412.387679
Sum of electronic and thermal Enthalpies=	− 6412.386735
Sum of electronic and thermal Free Energies=	− 6412.477488

Table S7. The molecular structures of the isomers of NP, 10-Br-NP, 2-Br-NP, and 2,10-Br-NP optimized at the DFT CAM-B3LYP/6-31G(d) level of theory, and the calculated relative energies (kJ mol^{-1}) with the CF isomers of each naphthopyran derivatives. The relative energies were calculated by using the total energy corrected for zero-point vibrational energy (sum of electronic and zero-point energies).

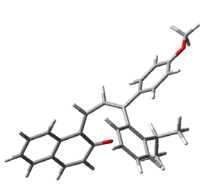
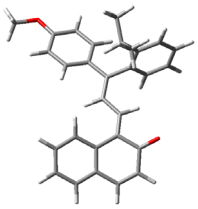
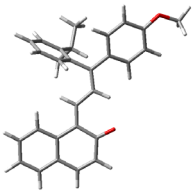
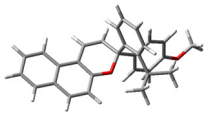
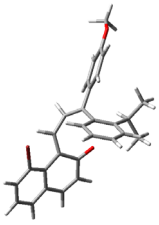
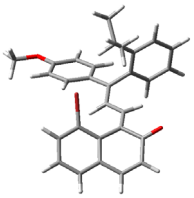
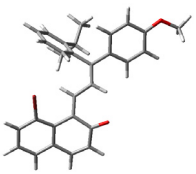
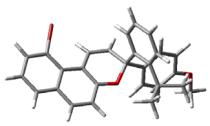
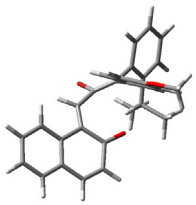
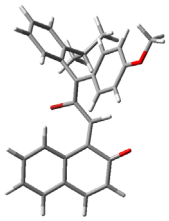
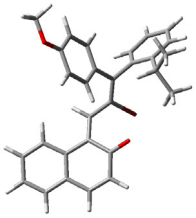
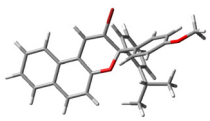
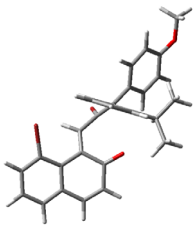
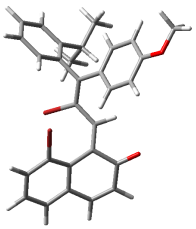
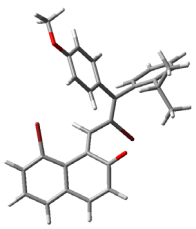
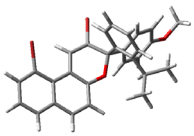
	cisoid-cis (CC)	*transoid-trans* (TT)	*transoid-cis* (TC)	*closed form* (CF)
NP				
Relative Energy (kJ mol^{-1})	71.06	44.08	32.05	0.0
10-Br-NP				
Relative Energy (kJ mol^{-1})	65.13	32.65	31.01	0.0
2-Br-NP				
Relative Energy (kJ mol^{-1})	72.20	63.89	65.70	0.0
2,10-Br-NP				
Relative Energy (kJ mol^{-1})	71.50	50.96	62.56	0.0

Table S8. Standard orientation of the optimized geometry for the TT isomer of NP.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.597288	3.562445	0.684170
2	6	-5.362053	2.573611	0.086946
3	6	-4.836611	1.301228	-0.147699
4	6	-3.493402	1.015130	0.184817
5	6	-2.759287	2.009407	0.843042
6	6	-3.297462	3.265981	1.082542
7	6	-5.692881	0.244458	-0.665552
8	6	-2.955768	-0.320953	-0.114406
9	6	-3.922861	-1.430717	-0.397093
10	6	-5.291453	-1.030931	-0.753930
11	6	-0.479609	0.167065	-0.343667
12	6	-1.651075	-0.669236	-0.272553
13	1	-6.710992	0.518015	-0.932927
14	1	-5.017877	4.546363	0.864846
15	1	-6.393555	2.773925	-0.189949
16	1	-2.701515	4.014091	1.596255
17	1	-5.950810	-1.827687	-1.080659
18	1	-0.625731	1.239784	-0.386073
19	1	-1.497060	-1.732553	-0.434806
20	8	-3.591185	-2.608751	-0.407745
21	6	0.789884	-0.301396	-0.423046
22	6	1.087524	-1.765134	-0.506673
23	6	1.651121	-2.473553	0.566743
24	6	0.823080	-2.425049	-1.710969
25	6	1.933019	-3.829188	0.387371
26	6	1.113163	-3.772501	-1.869794
27	1	0.384052	-1.863268	-2.529992
28	6	1.673871	-4.477389	-0.812197
29	1	2.362113	-4.393174	1.210569
30	1	0.898704	-4.267395	-2.811587
31	1	1.904567	-5.532995	-0.918168
32	6	1.943681	0.624076	-0.475439
33	6	3.142123	0.242289	-1.101017

34	6	1.894465	1.901977	0.088120
35	6	4.218595	1.103679	-1.182788
36	1	3.219749	-0.745313	-1.542041
37	6	2.970062	2.778316	0.018807
38	1	1.004706	2.220044	0.621486
39	6	4.141651	2.382229	-0.625015
40	1	5.138252	0.810300	-1.677057
41	1	2.888476	3.754999	0.479519
42	8	5.250417	3.152481	-0.750118
43	6	1.928851	-1.816376	1.909347
44	1	1.632504	-0.766193	1.836120
45	6	1.085544	-2.448940	3.023379
46	1	1.346605	-3.501701	3.174146
47	1	1.250579	-1.927028	3.971864
48	1	0.018400	-2.400982	2.787427
49	6	3.421268	-1.846107	2.258344
50	1	4.016781	-1.349838	1.486476
51	1	3.602187	-1.334620	3.209530
52	1	3.788145	-2.873111	2.359460
53	1	-1.767295	1.783995	1.213339
54	6	5.225167	4.454292	-0.204754
55	1	4.441508	5.067760	-0.665001
56	1	5.074409	4.432395	0.881158
57	1	6.199315	4.892087	-0.423264

Table S9. Standard orientation of the optimized geometry for the TC isomer of NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	6.486775	0.657934	-0.000690
2	6	6.318295	-0.680541	0.302442
3	6	5.057171	-1.281807	0.235257
4	6	3.923089	-0.525018	-0.129503
5	6	4.123881	0.822996	-0.459437
6	6	5.378534	1.406334	-0.391730
7	6	4.916130	-2.699003	0.515005
8	6	2.592541	-1.170917	-0.165923

9	6	2.517166	-2.652262	-0.009267
10	6	3.747357	-3.342962	0.394308
11	6	0.092558	-0.842344	-0.314326
12	6	1.463057	-0.411994	-0.262862
13	1	5.812593	-3.240729	0.807863
14	1	7.469721	1.114595	0.052466
15	1	7.171594	-1.287791	0.592290
16	1	5.494248	2.453220	-0.654900
17	1	3.648101	-4.408032	0.573298
18	1	-0.083365	-1.907551	-0.280859
19	1	1.594961	0.664273	-0.271635
20	8	1.485816	-3.301539	-0.168537
21	6	-0.953369	0.018592	-0.407093
22	6	-0.743882	1.486689	-0.606386
23	6	-1.026549	2.426592	0.399231
24	6	-0.265885	1.923793	-1.846729
25	6	-0.819673	3.778720	0.117039
26	6	-0.071009	3.272668	-2.108650
27	1	-0.053332	1.184377	-2.612950
28	6	-0.352069	4.205754	-1.118151
29	1	-1.025858	4.516400	0.887238
30	1	0.295979	3.590915	-3.079425
31	1	-0.205062	5.265229	-1.304904
32	6	-2.347057	-0.471326	-0.375414
33	6	-3.387932	0.273937	-0.953988
34	6	-2.685454	-1.689569	0.223193
35	6	-4.690868	-0.184647	-0.951696
36	1	-3.163793	1.223295	-1.427825
37	6	-3.990787	-2.161683	0.236438
38	1	-1.917135	-2.279948	0.710459
39	6	-5.004197	-1.409232	-0.357184
40	1	-5.490525	0.387259	-1.409566
41	1	-4.205913	-3.107389	0.718106
42	8	-6.309299	-1.773358	-0.400392
43	6	-1.507766	2.010910	1.780743
44	1	-1.605391	0.922117	1.788641

45	6	-0.482525	2.381786	2.859743
46	1	-0.345781	3.466303	2.926706
47	1	-0.814604	2.027316	3.840988
48	1	0.493444	1.934074	2.649271
49	6	-2.887098	2.596847	2.103115
50	1	-3.629427	2.289224	1.361025
51	1	-3.227293	2.254269	3.085838
52	1	-2.863004	3.691652	2.124036
53	1	3.293358	1.431536	-0.798147
54	6	-6.678732	-3.007879	0.177012
55	1	-7.753553	-3.103693	0.021913
56	1	-6.166764	-3.847428	-0.307831
57	1	-6.465562	-3.028522	1.252360

Table S10. Standard orientation of the optimized geometry for the CC isomer of NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	6.580903	-1.570570	0.616980
2	6	6.232683	-0.862553	-0.520074
3	6	4.894233	-0.585048	-0.812769
4	6	3.871538	-1.042783	0.043454
5	6	4.248263	-1.723068	1.207507
6	6	5.579031	-1.992734	1.487478
7	6	4.548918	0.204987	-1.982035
8	6	2.458087	-0.773994	-0.295624
9	6	2.162498	0.185033	-1.394504
10	6	3.289088	0.571230	-2.254702
11	6	0.020729	-1.492249	0.144153
12	6	1.469618	-1.529322	0.250826
13	1	5.364087	0.522705	-2.627969
14	1	7.623294	-1.778171	0.835861
15	1	7.002277	-0.505366	-1.198964
16	1	5.837308	-2.524438	2.398016
17	1	3.036243	1.190585	-3.108490
18	1	-0.418209	-2.480538	0.014661
19	1	1.809308	-2.391537	0.824710

20	8	1.033966	0.593638	-1.639565
21	6	-0.848111	-0.479919	0.366037
22	6	-0.436009	0.852998	0.890510
23	6	-0.820555	2.075772	0.302641
24	6	0.311811	0.867574	2.073930
25	6	-0.432164	3.256837	0.937170
26	6	0.688191	2.054037	2.685210
27	1	0.583916	-0.080195	2.527143
28	6	0.310273	3.259374	2.110220
29	1	-0.717285	4.206742	0.495149
30	1	1.263477	2.034324	3.605630
31	1	0.589647	4.201423	2.572706
32	6	-2.301122	-0.770163	0.275055
33	6	-3.194304	-0.281094	1.239507
34	6	-2.819583	-1.573340	-0.740635
35	6	-4.538279	-0.599707	1.198640
36	1	-2.819397	0.348220	2.040114
37	6	-4.171699	-1.893458	-0.802553
38	1	-2.154706	-1.937709	-1.517542
39	6	-5.038463	-1.408859	0.175115
40	1	-5.228323	-0.233468	1.951037
41	1	-4.534682	-2.507957	-1.617206
42	8	-6.372349	-1.659151	0.215985
43	6	-1.622336	2.168173	-0.988497
44	1	-1.713823	1.160748	-1.399718
45	6	-3.034080	2.712364	-0.730247
46	1	-2.994647	3.731030	-0.328315
47	1	-3.604019	2.747483	-1.664885
48	1	-3.586175	2.091101	-0.020846
49	6	-0.913823	3.019836	-2.049811
50	1	0.076397	2.617272	-2.265690
51	1	-1.498727	3.018566	-2.976206
52	1	-0.812343	4.062956	-1.731209
53	1	3.492329	-2.025832	1.923690
54	6	-6.929617	-2.467882	-0.796889
55	1	-7.994327	-2.541284	-0.573887

56	1	-6.798543	-2.018600	-1.788658
57	1	-6.490336	-3.472783	-0.797057

Table S11. Standard orientation of the optimized geometry for the CF isomer of NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	8	-0.297821	-0.337331	0.810104
2	8	5.525467	-2.578227	0.390251
3	6	-3.776295	-0.975402	-0.230719
4	6	-0.246674	-1.093003	-1.477793
5	1	0.380600	-1.481398	-2.272774
6	6	-2.349632	-0.904640	-0.289725
7	6	1.817479	-0.777045	-0.189062
8	6	-4.442034	-0.566580	0.958306
9	6	3.260502	-2.368395	0.923266
10	1	3.422138	-3.150532	1.657220
11	6	0.963621	2.273282	0.014878
12	6	-5.854645	-0.638194	1.025865
13	1	-6.345626	-0.321456	1.942119
14	6	-3.673646	-0.098671	2.055812
15	1	-4.189111	0.202914	2.963111
16	6	-2.312903	-0.016870	1.981034
17	1	-1.712751	0.338013	2.811350
18	6	-5.933766	-1.494507	-1.218067
19	1	-6.517686	-1.848741	-2.062136
20	6	0.453913	1.277950	-0.844939
21	6	-1.656504	-0.405131	0.794136
22	6	4.343770	-1.951947	0.146152
23	6	0.419839	-0.208690	-0.441025
24	6	-4.567728	-1.435731	-1.313566
25	1	-4.087450	-1.733761	-2.238876
26	6	2.900154	-0.375039	-0.961353
27	1	2.772720	0.409541	-1.700354
28	6	2.014951	-1.793888	0.749474
29	1	1.179537	-2.125128	1.354727
30	6	-1.542909	-1.395269	-1.399317

31	1	-1.992735	-2.049685	-2.138288
32	6	-0.026606	1.649612	-2.101117
33	1	-0.432948	0.887600	-2.755507
34	6	0.961631	3.594751	-0.435887
35	1	1.344904	4.371496	0.219212
36	6	-6.590055	-1.093425	-0.035179
37	1	-7.672409	-1.143775	0.027432
38	6	0.486902	3.951428	-1.690563
39	1	0.504498	4.991313	-2.002921
40	6	1.503402	2.002051	1.415064
41	1	1.457626	0.931963	1.606905
42	6	4.159273	-0.951882	-0.804337
43	1	4.979254	-0.608663	-1.423111
44	6	0.633542	2.685225	2.478052
45	1	0.662532	3.776028	2.383679
46	1	0.987724	2.429864	3.482595
47	1	-0.410815	2.372101	2.391793
48	6	-0.010670	2.969566	-2.532449
49	1	-0.392878	3.223055	-3.516399
50	6	2.970377	2.427649	1.551119
51	1	3.600813	1.906128	0.825369
52	1	3.340976	2.189474	2.553733
53	1	3.097971	3.504537	1.398895
54	6	6.649992	-2.192377	-0.368098
55	1	6.495822	-2.373018	-1.438998
56	1	7.478468	-2.807894	-0.016327
57	1	6.895972	-1.134466	-0.215055

Table S12. Standard orientation of the optimized geometry for the TT isomer of 10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	4.192844	-3.328414	-0.043435
2	6	4.854532	-2.385798	-0.814527
3	6	4.372785	-1.082076	-0.911274
4	6	3.165821	-0.702336	-0.272568
5	6	2.593583	-1.646216	0.592477

6	6	3.079193	-2.945292	0.689830
7	6	5.172600	-0.065276	-1.584728
8	6	2.663556	0.657558	-0.517303
9	6	3.647894	1.721823	-0.883074
10	6	4.881882	1.241202	-1.527732
11	6	0.221076	0.148471	-0.790581
12	6	1.365515	1.017497	-0.684939
13	1	6.080630	-0.404084	-2.077511
14	1	4.565974	-4.344470	0.028781
15	1	5.771145	-2.648799	-1.334164
16	1	2.593183	-3.641473	1.362984
17	1	5.528825	2.000612	-1.953402
18	1	0.414789	-0.909744	-0.929895
19	1	1.199799	2.080711	-0.837071
20	8	3.410041	2.914652	-0.772937
21	6	-1.063259	0.565285	-0.748179
22	6	-1.406518	2.014359	-0.607728
23	6	-1.693505	2.572148	0.648169
24	6	-1.441807	2.815544	-1.751800
25	6	-2.007312	3.931021	0.709002
26	6	-1.762457	4.163803	-1.670479
27	1	-1.208539	2.368400	-2.713832
28	6	-2.046730	4.722643	-0.430893
29	1	-2.220345	4.382783	1.673475
30	1	-1.783394	4.773184	-2.568453
31	1	-2.293653	5.776768	-0.349320
32	6	-2.177817	-0.405206	-0.802832
33	6	-3.421556	-0.048879	-1.347392
34	6	-2.034478	-1.704398	-0.307027
35	6	-4.454274	-0.961568	-1.432721
36	1	-3.571398	0.958929	-1.719390
37	6	-3.068516	-2.629840	-0.379009
38	1	-1.114004	-1.982696	0.195844
39	6	-4.284444	-2.263300	-0.953931
40	1	-5.411391	-0.691586	-1.865450
41	1	-2.920019	-3.621507	0.030199

42	8	-5.357080	-3.084760	-1.077506
43	6	-1.629138	1.744041	1.922271
44	1	-1.477848	0.699977	1.634516
45	6	-0.424871	2.146909	2.783131
46	1	-0.488156	3.196372	3.089896
47	1	-0.381208	1.534485	3.690480
48	1	0.513756	2.009139	2.239150
49	6	-2.934898	1.813361	2.721071
50	1	-3.788190	1.502679	2.110795
51	1	-2.882347	1.154488	3.593945
52	1	-3.133386	2.826437	3.086302
53	35	1.215923	-1.187438	1.825775
54	6	-5.240607	-4.410075	-0.606697
55	1	-4.444871	-4.954147	-1.129455
56	1	-5.046553	-4.438325	0.472234
57	1	-6.198338	-4.888884	-0.811852

Table S13. Standard orientation of the optimized geometry for the TC isomer of 10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-6.065485	0.273313	0.797864
2	6	-5.598972	1.528170	1.143847
3	6	-4.310461	1.931138	0.793849
4	6	-3.421717	1.061031	0.111704
5	6	-3.961119	-0.173682	-0.290257
6	6	-5.247622	-0.567183	0.056374
7	6	-3.901674	3.298029	1.075600
8	6	-2.040637	1.528434	-0.131614
9	6	-1.784754	2.996782	-0.118233
10	6	-2.751643	3.814531	0.625951
11	6	0.405413	0.963481	-0.317881
12	6	-0.989835	0.657552	-0.147387
13	1	-4.606901	3.919067	1.622405
14	1	-7.066962	-0.042945	1.069337
15	1	-6.237803	2.223575	1.680191
16	1	-5.608022	-1.533247	-0.276179

17	1	-2.480599	4.854386	0.772848
18	1	0.662493	1.998207	-0.494752
19	1	-1.208663	-0.385492	0.042059
20	8	-0.793676	3.521310	-0.615234
21	6	1.383556	0.023809	-0.279045
22	6	1.071134	-1.437614	-0.214692
23	6	1.338749	-2.210146	0.928569
24	6	0.523938	-2.046360	-1.348787
25	6	1.047237	-3.574882	0.886740
26	6	0.246777	-3.406103	-1.371733
27	1	0.318133	-1.434126	-2.221234
28	6	0.513040	-4.174477	-0.245768
29	1	1.239772	-4.183541	1.765605
30	1	-0.174142	-3.860479	-2.263303
31	1	0.300738	-5.239306	-0.245666
32	6	2.807945	0.409241	-0.369594
33	6	3.770542	-0.494030	-0.849830
34	6	3.251986	1.680118	0.009543
35	6	5.100021	-0.137295	-0.963840
36	1	3.462385	-1.488380	-1.153660
37	6	4.585426	2.052065	-0.095944
38	1	2.545699	2.395433	0.416885
39	6	5.519582	1.141451	-0.589366
40	1	5.839361	-0.832371	-1.346497
41	1	4.883803	3.044936	0.216892
42	8	6.843073	1.397709	-0.733341
43	6	1.893165	-1.596887	2.204967
44	1	2.052272	-0.530569	2.023451
45	6	0.889515	-1.716591	3.358773
46	1	0.696990	-2.763956	3.614343
47	1	1.275749	-1.220966	4.255527
48	1	-0.068119	-1.254705	3.100275
49	6	3.248540	-2.202483	2.587092
50	1	3.979078	-2.072373	1.783542
51	1	3.643202	-1.718696	3.486619
52	1	3.163972	-3.274074	2.797275

53	35	-3.040941	-1.394136	-1.432601
54	6	7.317658	2.680706	-0.383870
55	1	6.840201	3.463227	-0.985305
56	1	7.154865	2.893945	0.679335
57	1	8.388416	2.672357	-0.588571

Table S14. Standard orientation of the optimized geometry for the CC isomer of 10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	6.245090	-0.506082	-0.850219
2	6	5.658876	0.455721	-1.651954
3	6	4.277654	0.649945	-1.638409
4	6	3.427255	-0.151273	-0.835957
5	6	4.067781	-1.068109	0.015145
6	6	5.444209	-1.253786	0.001536
7	6	3.711326	1.740053	-2.417141
8	6	1.968032	0.061029	-0.933797
9	6	1.472119	1.341995	-1.502705
10	6	2.421303	2.087568	-2.340420
11	6	-0.350823	-1.035958	-0.794238
12	6	1.098756	-0.973016	-0.779035
13	1	4.398921	2.310911	-3.036164
14	1	7.318987	-0.658839	-0.859180
15	1	6.270145	1.083635	-2.293285
16	1	5.883948	-1.978586	0.675983
17	1	2.013969	2.939355	-2.874205
18	1	-0.732891	-1.885091	-1.358379
19	1	1.548619	-1.958455	-0.693463
20	8	0.315155	1.725261	-1.392562
21	6	-1.258362	-0.349245	-0.061096
22	6	-0.890961	0.605227	1.023613
23	6	-1.441204	1.898601	1.140119
24	6	-0.004058	0.147336	2.004959
25	6	-1.080972	2.665431	2.249380
26	6	0.344576	0.930962	3.094555
27	1	0.419755	-0.845459	1.905575

28	6	-0.204447	2.199366	3.219816
29	1	-1.494537	3.664217	2.352516
30	1	1.035645	0.547906	3.838990
31	1	0.049067	2.828309	4.068158
32	6	-2.689394	-0.718172	-0.203089
33	6	-3.512173	-0.857176	0.924191
34	6	-3.249608	-0.985326	-1.452246
35	6	-4.826985	-1.265087	0.804906
36	1	-3.103160	-0.654850	1.908651
37	6	-4.574807	-1.384120	-1.590211
38	1	-2.642330	-0.853944	-2.342381
39	6	-5.369752	-1.530841	-0.455029
40	1	-5.461324	-1.387261	1.676147
41	1	-4.974035	-1.566511	-2.580325
42	8	-6.671204	-1.917227	-0.469485
43	6	-2.380959	2.506327	0.107486
44	1	-2.452895	1.812693	-0.732641
45	6	-3.789293	2.711107	0.681489
46	1	-3.773245	3.415506	1.520586
47	1	-4.455054	3.123972	-0.083966
48	1	-4.223193	1.773206	1.036788
49	6	-1.839511	3.828457	-0.452219
50	1	-0.852118	3.683676	-0.892238
51	1	-2.513595	4.206412	-1.228919
52	1	-1.772585	4.598774	0.323675
53	35	3.150451	-2.089925	1.345737
54	6	-7.269247	-2.198574	-1.715907
55	1	-7.274263	-1.317208	-2.368515
56	1	-6.760548	-3.023146	-2.229838
57	1	-8.297193	-2.490274	-1.499131

Table S15. Standard orientation of the optimized geometry for the CF isomer of 10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	35	-3.979509	-1.370220	-1.776430
2	8	6.275760	-2.282739	-0.095666

3	8	0.536438	-0.003180	1.153304
4	6	-1.140705	-1.437606	-0.443323
5	1	-1.729259	-2.255654	-0.831958
6	6	5.006000	-1.800291	-0.039625
7	6	-4.209919	-0.788070	0.028359
8	6	-3.120341	-0.403753	0.864423
9	6	-3.485652	0.210821	2.103766
10	6	0.886027	1.139750	-0.969513
11	6	-1.722727	-0.554591	0.566677
12	6	-4.840203	0.319776	2.491920
13	1	-5.065482	0.780542	3.449177
14	6	0.144577	1.194372	-2.150850
15	1	-0.372439	0.304735	-2.489983
16	6	0.036776	2.362176	-2.894531
17	1	-0.549065	2.369846	-3.808354
18	6	4.146409	-1.955350	1.044689
19	1	4.457916	-2.491201	1.932961
20	6	2.421087	-0.710681	-0.120884
21	6	0.134985	-1.300939	-0.805395
22	1	0.607689	-1.992865	-1.493321
23	6	3.292512	-0.568960	-1.204382
24	1	2.970623	-0.024411	-2.086255
25	6	-2.475355	0.733194	2.954087
26	1	-2.777538	1.194928	3.889198
27	6	2.862255	-1.418848	0.990011
28	1	2.196582	-1.546628	1.835380
29	6	-5.517931	-0.673644	0.427019
30	1	-6.304304	-0.978802	-0.252926
31	6	-0.795743	0.056859	1.394918
32	6	0.674199	3.510128	-2.451368
33	1	0.600732	4.435968	-3.014109
34	6	1.706589	3.339022	1.777980
35	1	1.686642	4.368348	1.404404
36	1	2.266569	3.339269	2.719475
37	1	0.675221	3.043644	1.991727
38	6	1.407442	3.469594	-1.273545

39	1	1.898687	4.375446	-0.930934
40	6	4.567479	-1.105388	-1.168525
41	1	5.248487	-0.995081	-2.005437
42	6	-5.843313	-0.135219	1.683110
43	1	-6.883342	-0.055755	1.980887
44	6	-1.162016	0.686778	2.602396
45	1	-0.379556	1.099901	3.228773
46	6	1.535795	2.305691	-0.513167
47	6	3.810451	2.786739	0.490218
48	1	4.291250	2.079482	-0.191415
49	1	4.384400	2.801321	1.422862
50	1	3.878124	3.785035	0.045393
51	6	0.984638	-0.198023	-0.212534
52	6	6.766645	-2.990118	1.021224
53	1	6.780809	-2.363289	1.921202
54	1	7.787103	-3.281502	0.770813
55	1	6.173123	-3.890544	1.221366
56	6	2.357294	2.383774	0.769093
57	1	2.378741	1.399161	1.231533

Table S16. Standard orientation of the optimized geometry for the TT isomer of 2-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-5.255753	-0.532148	-2.195638
2	6	-5.675361	0.129372	-1.052450
3	6	-4.750198	0.629475	-0.134594
4	6	-3.368326	0.431901	-0.343386
5	6	-2.964247	-0.198909	-1.523947
6	6	-3.893645	-0.679487	-2.435687
7	6	-5.209195	1.413940	1.002865
8	6	-2.415036	0.962297	0.645199
9	6	-2.915003	1.954056	1.662965
10	6	-4.369644	2.055831	1.826275
11	6	-0.282336	-0.399935	0.200268
12	6	-1.105790	0.655955	0.783481
13	1	-6.284317	1.506379	1.137983

14	1	-5.983425	-0.914052	-2.904447
15	1	-6.735026	0.281615	-0.866849
16	1	-3.549426	-1.168075	-3.341679
17	1	-4.715747	2.685708	2.638260
18	1	-0.582288	1.280905	1.506927
19	8	-2.156088	2.606022	2.365920
20	6	0.997740	-0.261017	-0.205222
21	6	1.626176	1.076407	-0.319983
22	6	0.907961	2.224218	-0.693826
23	6	2.995782	1.226856	-0.079239
24	6	1.519559	3.459788	-0.779952
25	6	3.622264	2.463053	-0.153172
26	1	3.589536	0.355668	0.173324
27	6	2.880878	3.592702	-0.500132
28	1	0.962457	4.342333	-1.073816
29	1	4.682715	2.532482	0.054774
30	6	1.845855	-1.423139	-0.618276
31	6	2.125090	-1.547291	-1.982606
32	6	2.402576	-2.335481	0.294692
33	6	2.923771	-2.571920	-2.464589
34	1	1.700092	-0.822429	-2.670613
35	6	3.220080	-3.349615	-0.212018
36	6	3.477985	-3.478364	-1.568762
37	1	3.117464	-2.657576	-3.529170
38	1	3.666925	-4.059031	0.478200
39	1	-1.909861	-0.307697	-1.742697
40	8	3.390188	4.843365	-0.608802
41	1	4.113656	-4.283368	-1.924989
42	6	2.181700	-2.240281	1.797876
43	1	1.422203	-1.475531	1.977919
44	6	3.462615	-1.801644	2.520761
45	1	3.814441	-0.828869	2.164618
46	1	3.284358	-1.719268	3.597971
47	1	4.270133	-2.526151	2.369942
48	6	1.654885	-3.552753	2.389763
49	1	0.740101	-3.867820	1.883439

50	1	2.390319	-4.359685	2.306467
51	1	1.429450	-3.422628	3.453151
52	1	-0.142638	2.143904	-0.946228
53	35	-1.055132	-2.149901	0.253554
54	6	4.762862	5.033349	-0.337575
55	1	5.011244	4.751963	0.692523
56	1	5.392290	4.461421	-1.029696
57	1	4.952676	6.097940	-0.475174

Table S17. Standard orientation of the optimized geometry for the TC isomer of 2-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-6.292261	1.193122	-0.801548
2	6	-6.168566	0.080741	0.012376
3	6	-4.913036	-0.457242	0.309072
4	6	-3.748846	0.121421	-0.237867
5	6	-3.894567	1.253045	-1.046894
6	6	-5.144809	1.783470	-1.324870
7	6	-4.807618	-1.603505	1.200591
8	6	-2.438424	-0.498460	0.059668
9	6	-2.367207	-1.509006	1.159641
10	6	-3.631419	-2.102047	1.605112
11	6	0.010111	-0.792742	-0.584006
12	6	-1.319642	-0.171868	-0.620790
13	1	-5.737841	-2.032748	1.565158
14	1	-7.271790	1.604662	-1.022017
15	1	-7.052489	-0.385606	0.438572
16	1	-5.223606	2.666125	-1.951665
17	1	-3.554821	-2.924607	2.307450
18	1	-1.384358	0.628617	-1.353666
19	8	-1.303646	-1.816090	1.679775
20	6	1.168982	-0.118797	-0.494585
21	6	1.169681	1.335209	-0.194999
22	6	0.304928	1.891987	0.760459
23	6	2.058548	2.193883	-0.845254
24	6	0.305337	3.249225	1.022670

25	6	2.064600	3.560894	-0.596792
26	1	2.758719	1.786658	-1.566941
27	6	1.179865	4.096420	0.339200
28	1	-0.354059	3.678782	1.768868
29	1	2.762427	4.193453	-1.131382
30	6	2.495253	-0.769893	-0.718483
31	6	2.895002	-1.008834	-2.034994
32	6	3.344640	-1.107358	0.347289
33	6	4.137091	-1.559501	-2.316494
34	1	2.213284	-0.760023	-2.843073
35	6	4.585639	-1.669518	0.043079
36	6	4.986819	-1.888927	-1.268321
37	1	4.435346	-1.734119	-3.345578
38	1	5.254650	-1.947510	0.851245
39	1	-3.020276	1.746027	-1.456627
40	8	1.104022	5.412149	0.662053
41	1	5.961141	-2.324267	-1.469435
42	6	2.888353	-0.958773	1.789108
43	1	2.086396	-0.215082	1.807863
44	6	3.988240	-0.460974	2.729797
45	1	4.437996	0.468103	2.366019
46	1	3.571195	-0.270443	3.723663
47	1	4.788172	-1.198618	2.852777
48	6	2.289136	-2.283344	2.284819
49	1	1.488174	-2.621293	1.623643
50	1	3.057736	-3.064139	2.319295
51	1	1.874141	-2.167640	3.291269
52	1	-0.349298	1.238378	1.326716
53	35	0.041235	-2.670376	-0.915139
54	6	1.985731	6.309519	0.022232
55	1	1.759665	7.295805	0.428104
56	1	3.033326	6.063534	0.232999
57	1	1.830566	6.321755	-1.063306

Table S18. Standard orientation of the optimized geometry for the CC isomer of 2-Br-NP.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-6.192702	-1.365623	-0.671082
2	6	-5.722125	-1.277537	0.627892
3	6	-4.366171	-1.061674	0.887586
4	6	-3.450670	-0.950402	-0.178560
5	6	-3.951785	-1.006279	-1.483523
6	6	-5.299878	-1.218973	-1.729312
7	6	-3.896171	-0.917023	2.255278
8	6	-2.011991	-0.765006	0.110838
9	6	-1.610655	-0.410745	1.506679
10	6	-2.625665	-0.610169	2.549638
11	6	0.363212	-0.985648	-0.796844
12	6	-1.090700	-1.078475	-0.833658
13	1	-4.629423	-1.035103	3.049532
14	1	-7.248207	-1.530535	-0.861287
15	1	-6.408312	-1.368626	1.465352
16	1	-5.657409	-1.258754	-2.753406
17	1	-2.284067	-0.460389	3.567935
18	1	-1.459231	-1.567067	-1.733052
19	8	-0.487347	-0.029979	1.809954
20	6	1.156819	0.079578	-0.589761
21	6	0.585484	1.445275	-0.512708
22	6	-0.381483	1.890694	-1.423190
23	6	1.043533	2.351612	0.443786
24	6	-0.890966	3.173805	-1.359309
25	6	0.535905	3.641218	0.527640
26	1	1.806404	2.038437	1.147651
27	6	-0.441647	4.057153	-0.375644
28	1	-1.631555	3.523588	-2.070102
29	1	0.908445	4.308209	1.295026
30	6	2.646093	-0.008089	-0.524417
31	6	3.357868	0.646428	-1.536142
32	6	3.341167	-0.652417	0.515451
33	6	4.742552	0.649466	-1.558841

34	1	2.802920	1.155509	-2.318339
35	6	4.738485	-0.614959	0.482634
36	6	5.437418	0.014542	-0.536205
37	1	5.274072	1.149656	-2.362303
38	1	5.294205	-1.094288	1.282846
39	1	-3.284659	-0.857168	-2.325244
40	8	-1.000803	5.294029	-0.389567
41	1	6.523342	0.013924	-0.528432
42	6	2.647115	-1.332974	1.686585
43	1	1.580178	-1.381312	1.469840
44	6	2.801178	-0.506856	2.970020
45	1	2.355085	0.485232	2.858087
46	1	2.293796	-1.003664	3.803327
47	1	3.855241	-0.381282	3.241810
48	6	3.145131	-2.767194	1.899790
49	1	3.038027	-3.357154	0.986403
50	1	4.196391	-2.796097	2.205415
51	1	2.561890	-3.252728	2.689009
52	1	-0.723238	1.224070	-2.207987
53	35	1.141865	-2.686372	-1.238002
54	6	-0.574934	6.229021	0.577996
55	1	-1.145337	7.139074	0.390301
56	1	-0.780618	5.877078	1.595940
57	1	0.495475	6.447507	0.482952

Table S19. Standard orientation of the optimized geometry for the CF isomer of 2-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	35	0.753237	-2.626943	1.429017
2	8	-0.388963	0.405646	-1.104678
3	8	5.547584	-1.243726	-1.924670
4	6	-0.303221	-1.357701	0.505351
5	6	-1.747058	0.336439	-1.112905
6	6	-0.115843	0.684472	2.433428
7	1	-0.391698	-0.340276	2.645465
8	6	0.304960	1.031985	1.148068

9	6	-1.601215	-1.593377	0.316029
10	1	-2.034561	-2.523821	0.661773
11	6	-3.781321	1.187423	-2.051499
12	1	-4.311247	1.881145	-2.697702
13	6	0.176924	2.930970	3.207733
14	1	0.128421	3.678576	3.993740
15	6	3.236626	-1.082685	-2.218991
16	1	3.399624	-1.440053	-3.229927
17	6	0.684460	2.365979	0.888477
18	6	-2.422414	-0.631280	-0.400497
19	6	0.351849	-0.053185	0.053128
20	6	1.767571	-0.315715	-0.457749
21	6	-0.180283	1.616050	3.460214
22	1	-0.512630	1.309621	4.447008
23	6	1.967709	-0.786513	-1.758289
24	1	1.116076	-0.908791	-2.416923
25	6	4.343315	-0.928195	-1.381010
26	6	2.873676	-0.173571	0.369823
27	1	2.742607	0.174752	1.388459
28	6	-6.663387	-0.721130	-0.666018
29	1	-7.746211	-0.746755	-0.733975
30	6	-5.989077	-1.635611	0.170275
31	1	-6.559434	-2.358897	0.744899
32	6	-2.419696	1.239162	-1.962213
33	1	-1.833839	1.954140	-2.528287
34	6	-4.532484	0.242091	-1.305179
35	6	1.176662	2.879767	-0.460985
36	1	1.192337	2.052515	-1.167329
37	6	-4.622020	-1.615925	0.268444
38	1	-4.127475	-2.318063	0.930428
39	6	4.157776	-0.473755	-0.078198
40	1	4.995576	-0.349385	0.596686
41	6	-5.945515	0.196917	-1.384303
42	1	-6.450977	0.910113	-2.029709
43	6	0.602336	3.286294	1.936009
44	1	0.882707	4.318156	1.747359

45	6	-3.849819	-0.682072	-0.466656
46	6	6.696743	-1.108586	-1.117966
47	1	6.840585	-0.071215	-0.792166
48	1	7.540306	-1.409888	-1.739652
49	1	6.648289	-1.758068	-0.235547
50	6	0.223869	3.940507	-1.027719
51	1	-0.799521	3.560688	-1.091242
52	1	0.542939	4.241265	-2.031459
53	1	0.204970	4.840600	-0.404176
54	6	2.606154	3.428332	-0.369529
55	1	2.670987	4.285251	0.309337
56	1	2.945374	3.761682	-1.356016
57	1	3.300883	2.661821	-0.015507

Table S20. Standard orientation of the optimized geometry for the TT isomer of 2,10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-5.450146	-0.584562	-0.998804
2	6	-5.551639	-0.017647	0.261688
3	6	-4.453041	0.604657	0.849780
4	6	-3.192711	0.621970	0.203656
5	6	-3.157825	0.136946	-1.109593
6	6	-4.257235	-0.477179	-1.697311
7	6	-4.633857	1.340653	2.095951
8	6	-2.060398	1.212297	0.935907
9	6	-2.366073	2.248686	1.982056
10	6	-3.696621	2.153130	2.599945
11	6	-0.079693	-0.328025	0.393808
12	6	-0.759684	0.839527	0.930854
13	1	-5.610781	1.271103	2.567847
14	1	-6.304442	-1.071777	-1.456634
15	1	-6.497175	-0.032470	0.795444
16	1	-4.172731	-0.853315	-2.709752
17	1	-3.867490	2.772445	3.473569
18	1	-0.112938	1.496153	1.510390
19	8	-1.535383	3.049425	2.380272

20	6	1.208253	-0.350686	-0.010460
21	6	1.986633	0.897614	-0.171409
22	6	1.399629	2.081715	-0.649156
23	6	3.357668	0.921072	0.101861
24	6	2.138857	3.239633	-0.794735
25	6	4.109511	2.079709	-0.030543
26	1	3.852348	0.013117	0.427214
27	6	3.497357	3.252823	-0.474366
28	1	1.685557	4.150808	-1.168747
29	1	5.165929	2.055750	0.206283
30	6	1.872609	-1.628061	-0.418103
31	6	1.772567	-1.993329	-1.762317
32	6	2.572517	-2.442302	0.484613
33	6	2.361935	-3.156626	-2.230826
34	1	1.199513	-1.358859	-2.431912
35	6	3.159230	-3.610533	-0.009437
36	6	3.062924	-3.968424	-1.346301
37	1	2.271642	-3.429692	-3.277507
38	1	3.700752	-4.259465	0.672399
39	8	4.135958	4.435499	-0.644968
40	1	3.531083	-4.883576	-1.696109
41	6	2.665269	-2.112048	1.967489
42	1	2.311487	-1.084768	2.102579
43	6	4.100680	-2.175899	2.501450
44	1	4.778374	-1.535310	1.928118
45	1	4.129369	-1.848777	3.545672
46	1	4.500486	-3.194493	2.467658
47	6	1.741677	-3.023382	2.787368
48	1	0.710583	-2.943579	2.436582
49	1	2.050187	-4.071125	2.701302
50	1	1.770935	-2.749501	3.847368
51	1	0.359947	2.077460	-0.954306
52	35	-1.648521	0.370922	-2.239164
53	35	-1.067004	-1.960118	0.399708
54	6	5.513037	4.504006	-0.341027
55	1	6.098932	3.827074	-0.974155

56	1	5.814636	5.532612	-0.539522
57	1	5.704010	4.268240	0.712540

Table S21. Standard orientation of the optimized geometry for the TC isomer of 2,10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-6.140521	-0.390440	-0.481816
2	6	-5.668385	-1.596080	0.007271
3	6	-4.315547	-1.766570	0.296684
4	6	-3.379401	-0.728287	0.060114
5	6	-3.904347	0.498854	-0.368469
6	6	-5.256330	0.664859	-0.646395
7	6	-3.883108	-3.014204	0.919138
8	6	-1.951392	-1.058514	0.281108
9	6	-1.639268	-2.143912	1.263407
10	6	-2.650745	-3.195595	1.409290
11	6	0.462893	-0.966454	-0.502663
12	6	-0.942723	-0.534447	-0.444773
13	1	-4.640363	-3.784647	1.040165
14	1	-7.193202	-0.257172	-0.707069
15	1	-6.351715	-2.420629	0.186727
16	1	-5.608792	1.633957	-0.978653
17	1	-2.357977	-4.087981	1.951090
18	1	-1.168102	0.268817	-1.137774
19	8	-0.587637	-2.163812	1.881702
20	6	1.524880	-0.146003	-0.456855
21	6	1.355946	1.288411	-0.112579
22	6	0.487870	1.703406	0.907939
23	6	2.085509	2.270382	-0.786433
24	6	0.330258	3.042478	1.213104
25	6	1.932405	3.619757	-0.494548
26	1	2.785310	1.975673	-1.561268
27	6	1.046113	4.012282	0.508927
28	1	-0.336929	3.363282	2.005538
29	1	2.508494	4.350612	-1.048480
30	6	2.910433	-0.611845	-0.767968

31	6	3.266176	-0.765709	-2.109491
32	6	3.852041	-0.860178	0.243296
33	6	4.551868	-1.143766	-2.469251
34	1	2.515771	-0.588198	-2.874393
35	6	5.136808	-1.249138	-0.139604
36	6	5.491941	-1.384242	-1.475419
37	1	4.814562	-1.253781	-3.516795
38	1	5.878269	-1.456472	0.625413
39	8	0.823586	5.299030	0.878298
40	1	6.501960	-1.684471	-1.738098
41	6	3.459529	-0.805066	1.710544
42	1	2.566979	-0.178072	1.792013
43	6	4.532735	-0.181570	2.606298
44	1	4.829857	0.808659	2.247314
45	1	4.150466	-0.072937	3.626145
46	1	5.431525	-0.804409	2.664109
47	6	3.072650	-2.208486	2.199951
48	1	2.289604	-2.638079	1.571313
49	1	3.939727	-2.878648	2.173044
50	1	2.701139	-2.170626	3.229002
51	1	-0.047472	0.957293	1.484460
52	35	-2.849985	2.077539	-0.512924
53	35	0.732397	-2.819413	-0.881370
54	6	1.541622	6.317684	0.216139
55	1	1.218689	7.256550	0.666585
56	1	2.623251	6.203126	0.355396
57	1	1.317474	6.336365	-0.857193

Table S22. Standard orientation of the optimized geometry for the CC isomer of 2,10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	6.357409	-0.440707	-0.346548
2	6	5.770831	-0.171073	-1.569646
3	6	4.386949	-0.042994	-1.682634
4	6	3.537057	-0.219509	-0.562665
5	6	4.173013	-0.430215	0.670881

6	6	5.553353	-0.549788	0.778376
7	6	3.818901	0.339458	-2.967521
8	6	2.075502	-0.152036	-0.788164
9	6	1.577226	0.543653	-2.010086
10	6	2.524624	0.638982	-3.127503
11	6	-0.235808	-1.034975	-0.168500
12	6	1.218196	-0.914750	-0.071100
13	1	4.510619	0.431139	-3.801016
14	1	7.433742	-0.540372	-0.256223
15	1	6.383820	-0.041992	-2.456529
16	1	5.991747	-0.716480	1.754843
17	1	2.117064	0.988836	-4.069588
18	1	1.647844	-1.625489	0.627521
19	8	0.426200	0.934816	-2.134264
20	6	-1.188547	-0.133302	0.128295
21	6	-0.796787	1.194177	0.695550
22	6	-1.223680	2.423423	0.153506
23	6	-0.027110	1.187784	1.863817
24	6	-0.854564	3.592152	0.821016
25	6	0.336697	2.363371	2.503462
26	1	0.285662	0.235725	2.277357
27	6	-0.086115	3.575627	1.977831
28	1	-1.174086	4.548305	0.418143
29	1	0.941697	2.326882	3.403936
30	1	0.180517	4.509508	2.463791
31	6	-2.641353	-0.436289	0.077381
32	6	-3.255650	-0.964837	-1.066302
33	6	-3.442389	-0.162697	1.183696
34	6	-4.613393	-1.213463	-1.093550
35	1	-2.655608	-1.168004	-1.946254
36	6	-4.808594	-0.427696	1.178706
37	1	-2.991219	0.263471	2.074148
38	6	-5.400016	-0.954059	0.032571
39	1	-5.095930	-1.610375	-1.979903
40	1	-5.394047	-0.214392	2.064365
41	8	-6.721001	-1.240156	-0.090926

42	6	-2.058108	2.532156	-1.114644
43	1	-2.085760	1.547333	-1.583089
44	6	-3.498358	2.955119	-0.794856
45	1	-3.521230	3.948778	-0.333147
46	1	-4.094074	3.001153	-1.712726
47	1	-3.983164	2.254105	-0.110645
48	6	-1.436534	3.488722	-2.139330
49	1	-0.421340	3.178765	-2.391956
50	1	-2.033203	3.484924	-3.057790
51	1	-1.410424	4.520641	-1.773269
52	35	3.245111	-0.491616	2.338121
53	35	-0.675772	-2.870252	-0.542002
54	6	-7.563041	-0.989701	1.013282
55	1	-7.266815	-1.581349	1.887831
56	1	-7.567210	0.073217	1.283174
57	1	-8.565343	-1.285432	0.702416

Table S23. Standard orientation of the optimized geometry for the CF isomer of 2,10-Br-NP.

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	35	-0.867656	-2.820800	0.357997
2	35	4.004146	-1.859413	0.884701
3	8	-0.348121	0.933213	-1.138495
4	6	1.873545	0.108693	-0.809112
5	8	-6.179971	-1.123532	-1.782563
6	6	-0.103965	0.763589	3.594340
7	1	0.362212	0.224177	4.412665
8	6	4.329426	-0.441073	-0.350986
9	6	3.286943	0.348212	-0.919582
10	6	3.716647	1.500013	-1.651349
11	6	-0.056404	-1.180196	-0.115982
12	6	1.240684	-1.146941	-0.418903
13	1	1.808721	-2.063552	-0.438744
14	6	-0.591828	2.048034	3.776566
15	1	-0.513847	2.537496	4.742722
16	6	-0.209361	0.167033	2.345741

17	1	0.173298	-0.836897	2.213303
18	6	2.754052	2.411827	-2.160487
19	1	3.107081	3.277012	-2.713261
20	6	-3.326522	-0.417321	0.435129
21	1	-3.091276	-0.355277	1.491908
22	6	-1.187320	2.706842	2.710531
23	1	-1.570199	3.711370	2.864106
24	6	-4.627769	-0.735392	0.054158
25	1	-5.374750	-0.908023	0.818957
26	6	-0.798935	0.824638	1.264040
27	6	6.048233	0.922162	-1.361975
28	1	7.102549	1.113762	-1.530102
29	6	-4.946042	-0.827217	-1.298021
30	6	-3.952374	-0.605300	-2.254246
31	1	-4.217339	-0.684532	-3.302954
32	6	5.656767	-0.174112	-0.575942
33	1	6.406270	-0.806319	-0.114891
34	6	-0.892228	0.092812	-0.088612
35	6	-2.002816	2.942557	0.359027
36	1	-2.036935	2.352776	-0.554908
37	6	-2.333409	-0.185787	-0.507499
38	6	5.089835	1.754832	-1.867404
39	1	5.365735	2.633943	-2.442081
40	6	-2.663940	-0.296727	-1.860860
41	1	-1.900523	-0.128110	-2.611016
42	6	1.423070	2.230168	-1.944698
43	1	0.676062	2.925458	-2.309697
44	6	-3.450823	3.278858	0.736791
45	1	-4.034007	2.369946	0.908252
46	1	-3.930724	3.840701	-0.071523
47	1	-3.503548	3.891857	1.642591
48	6	0.994300	1.082399	-1.247779
49	6	-1.211879	4.219281	0.045340
50	1	-1.184900	4.898120	0.904304
51	1	-1.675218	4.759259	-0.787491
52	1	-0.178057	3.989096	-0.227319

53	6	-7.216303	-1.367553	-0.857179
54	1	-6.988793	-2.226850	-0.214863
55	1	-8.105305	-1.587004	-1.449093
56	1	-7.409283	-0.490362	-0.227700
57	6	-1.314861	2.124329	1.447428

12. References

S1. M. Frigerio, M. Santagostino, S. Squtore, *J. Org. Chem*. 1999, **64**, 4537–4538.

S2. Sheldrick GM. *SHELXS-97* and *SHELXL-97*; University of Gottingen, Germany, 1997.

S3. Sheldrick GM. *SADABS*; University of Gottingen, Germany, 1996.

S4. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.