Supporting Information

Bis(N,N’-(2-indanoyl))-1,5-diazacyclooctane as Unique Metal Ligand: Self-Assembly of Palladium Nanoparticles And Catalytic Reactivity on C-C Bond Formation

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1. General information

All commercially available reagents were used without further purification. All anhydrous solvents were purchased from Wako Pure Chemical Industries Ltd., and palladium(II) acetate was purchased from Wako Pure Chemical Industries Ltd. 1,5-Diazacyclooctane 1 was prepared according to our report.¹

For Suzuki coupling, all aromatic bromides were purchased from Tokyo Chemical Industry Co., Ltd. and Sigma-Aldrich, and phenylboronic acid was purchased from Sigma-Aldrich. Potassium carbonate was purchased from Nacalai tesque. For general procedure of 4-Methoxybiphenyl 2 of entry 3 in table 2, 1-Pd NPs (3.6 mg) were prepared by repeating the general procedure of 1-Pd NPs.

For C-C bond-forming reaction via C(sp³)-H activation, 8-aminoquinoline and trimethylsilylacetylene were purchased from Tokyo Chemical Industry Co. 8-(N-acylamino)quinolone 4 and 6 were prepared according to the reported procedures.² (Bromoethynyl)triisopropylsilane was prepared according to the literature.³

Silica gel (Silica gel 60, 0.015–0.040 mm) for column chromatography was used. For preparative TLC, PLC glass plate Silica gel 60 F₂₅₄, 0.5 or 1 mm (Merck-Millipore) was used. HPLC grade hexane and 2-propanol from Wako Pure Chemical Industries Ltd. were used for HPLC analysis.

Normal phase HPLC analysis on enantiomeric excess of ethynylated products 5 and 7 was performed on a Shimadzu Prominence® system equipped with a CHIRALPAK (DAICEL CORPORATION) (AS-3, 4.6 x 250 mm), with isocratic elution of hexane and 2-propanol (iPrOH) (95:5). The mobile phase for HPLC were HPLC grade hexane (Buffer A) and HPLC grade 2-propanol (Buffer B). Simultaneous monitor of the eluent at 220 and 254 nm by UV detector was performed.
2. Synthesis of 1-Pd(II)

In a frame dried flask, 1,5-Diazacyclooctane 1 (104 mg, 0.27 mmol) and palladium(II) acetate (62 mg, 0.27 mmol) were dissolved in dry dichloromethane (2.5 ml) under nitrogen gas atmosphere and then stirred for 1.5 h at room temperature. To the reaction mixture was added diethyl ether to give precipitate. The obtained precipitate was filtered, washed with diethyl ether, and dried under low pressure to afford 1-Pd(II) (112 mg, 84%) as light yellow powder.

HRMS (ESI+) [M+H]+ calcd for C24H29N2O2Pd 483.1268, found 483.1277

3. Synthesis of 1-Pd NPs

In a frame dried flask, 1,5-Diazacyclooctane 1 (1.4 mg, 0.0062 mmol) and palladium(II) acetate (2.3 mg, 0.0060 mmol) were dissolved in dry dichloroethane (0.5 ml) under nitrogen gas atmosphere and heated at 80 °C for 12 h without stirring. After cooling to room temperature, the reaction mixture was transferred into eppendof tube and centrifuged for a second to give black precipitate. Supernatant solvent was removed, then hexane and tiny amount of dichloromethane were added, centrifuged again. After removal of supernatant solvent, the obtained black precipitate was dried in vacuo to afford 1-Pd NPs (1.6 mg, 55%) as black powder. Production of NPs was analyzed by TEM.

Note: In larger scale, the preparation yield of 1-Pd NPs was decreased. 1-Pd NPs were therefore prepared for each reaction under the conditions described above; e.g., 1,5-Diazacyclooctane 1 (6.0 mg, 0.015 mmol) and palladium(II) acetate (3.5 mg, 0.015 mmol) were dissolved in dry dichloroethane (1.3 ml) under nitrogen gas atmosphere. After heating at 80 °C for 12 h without stirring and subsequent isolation by centrifuge, 1-Pd NPs (2.3 mg, 30%) was obtained.

4. Control experiment: Image of the reaction mixture after heating in absence of ligand 1

In a frame dried flask, 1,5-Diazacyclooctane 1 (0.4 mg, 0.002 mmol) and palladium(II) acetate (2.3 mg, 0.0060 mmol) were dissolved in dry dichloroethane (0.2 ml) under nitrogen gas atmosphere and heated at 80 °C overnight.
5. Procedure for 1-Pd NPs-catalyzed Suzuki coupling

General procedure: 4-Methoxybiphenyl 2

(Table 2, entry 3): 1-Pd NPs (3.6 mg, 0.0075 mmol) was added to a frame dried flask and filled with N₂ gas. To the flask were added phenylboronic acid (83 mg, 0.68 mmol), potassium carbonate (106 mg, 0.76 mmol), and 4-bromoanisole (47 μl, 0.37 mmol), and dry toluene (1.0 ml), then the reaction mixture was heated at 100 °C. After stirring for 5 h, the reaction mixture was cooled to room temperature, filtered, extracted with hexane, washed with brine. The combined organic layer was dried over Na₂SO₄, evaporated. The crude material was purified by silica gel column chromatography (hexane to hexane:EtOAc 100:1) to give 2 (62 mg, 90%) as white solid.¹H NMR (300 MHz, CDCl₃): δ 7.56-7.50 (m, 4H), 7.41 (d, J = 7.5, 7.2 Hz, 2H), 7.32-7.27 (m, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. These NMR spectra were in accordance with the reported data.

(Table 2, entry 4): According to the general procedure, 1-Pd NPs (0.3 mg, 0.0006 mmol), phenylboronic acid (26 mg, 0.21 mmol), potassium carbonate (32 mg, 0.23 mmol), and 4-bromoanisole (15 μl, 0.12 mmol), and dry toluene (0.34 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 5 h. Purification by preparative TLC (hexane:EtOAc 15:1) provided 2 (19 mg, 89%) as white solid.

(Table 2, entry 5): According to the general procedure, 1-Pd NPs (0.85 mg, 0.0017 mmol), phenylboronic acid (778 mg, 6.3 mmol), potassium carbonate (961 mg, 6.9 mmol), and 4-bromoanisole (445 μl, 3.5 mmol), and dry toluene (9.2 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 21 h. Purification by silica gel column (hexane to hexane:EtOAc 100:1) provided 2 (416 mg, 64%) as white solid.

4-Acetyl biphenyl 3a (Table 3, entry 1)

According to the general procedure, 1-Pd NPs (0.85 mg, 0.0017 mmol), phenylboronic acid (78 mg, 0.64 mmol), potassium carbonate (98 mg, 0.70 mmol), and 4-bromoacetophenone (71 mg, 0.35 mmol), and dry toluene (0.94 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 4 h. Purification by preparative TLC (hexane:EtOAc 4:1) provided 3a (71 mg, 99%) as white solid.¹H NMR (300 MHz, CDCl₃): δ 8.03 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.51-7.37 (m, 3H), 6.97 (dt, J = 8.7, 1.8 Hz, 2H), 2.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 197.7, 145.7, 139.8, 135.8, 128.91, 128.88, 128.20, 127.23, 127.18, 26.6. δ These NMR spectra were in accordance with the reported data.
3-Phenylphenol 3b (Table 3, entry 2)

According to the general procedure, 1-Pd NPs (1.0 mg, 0.0022 mmol), phenylboronic acid (98 mg, 0.80 mmol), potassium carbonate (123 mg, 0.89 mmol), and 3-bromophenol (77 mg, 0.44 mmol), and dry toluene (1.2 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 4 h. Purification by silica gel column chromatography (hexane:EtOAc 20:1 to toluene:EtOAc 30:1) provided 3b (56 mg, 75%) as light orange solid.

1H NMR (300 MHz, CDCl₃): δ 7.68-7.55 (m, 2H), 7.45-7.40 (m, 2H), 7.37-7.25 (m, 2H), 7.18-7.15 (m, 1H), 7.07-7.05 (m, 1H), 4.86 (s, 1H); 13C NMR (75 MHz, CDCl₃): δ 155.7, 142.9, 140.6, 129.9, 128.7, 127.47, 127.08, 119.8, 114.17, 114.07. These NMR spectra were in accordance with the reported data.

2-Phenylphenol 3c (Table 3, entry 3)

According to the general procedure, 1-Pd NPs (0.85 mg, 0.0017 mmol), phenylboronic acid (76 mg, 0.62 mmol), potassium carbonate (97 mg, 0.70 mmol), and 2-bromophenol (41 μl, 0.35 mmol), and dry toluene (0.94 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 4 h. Purification by preparative TLC (hexane:EtOAc 5:1) provided 3c (45 mg, 75%) as white solid.

1H NMR (400 MHz, CDCl₃): δ 7.49-7.45 (m, 4H), 7.41-7.37 (m, 1H), 7.26-7.23 (m, 2H), 7.01-6.97 (m, 2H), 5.18 (s, 1H); 13C NMR (75 MHz, CDCl₃): δ 152.3, 137.0, 130.2, 129.25, 129.12, 129.06, 128.0, 115.8. These NMR spectra were in accordance with the reported data.

4-Aminobiphenyl 3d (Table 3, entry 4)

According to the general procedure, 1-Pd NPs (0.7 mg, 0.0014 mmol), phenylboronic acid (63 mg, 0.51 mmol), potassium carbonate (80 mg, 0.58 mmol), and 4-bromoaniline (49 mg, 0.29 mmol), and dry toluene (0.76 ml) were added to N₂ gas-filled flask, the reaction mixture was heated at 100 °C for 13 h. Purification by silica gel column chromatography (hexane:EtOAc 4:1) provided 3d (46 mg, 93%) as light brown solid.

1H NMR (300 MHz, CDCl₃): δ 7.54-7.51 (m, 2H), 7.42-7.38 (m, 4H), 7.36-7.22 (m, 1H), 6.74 (d, J = 8.4 Hz, 2H), 3.70 (brs, 2H); 13C NMR (75 MHz, CDCl₃): δ 145.7, 141.1, 131.5, 128.6, 127.9, 126.3, 126.2, 115.3. These NMR spectra were in accordance with the reported data.

2-Phenylthiophene 3e (Table 3, entry 5)

According to the general procedure, 1-Pd NPs (0.6 mg, 0.0012 mmol), phenylboronic acid (55 mg, 0.45 mmol), potassium carbonate (68 mg, 0.49 mmol), and 2-bromothiophene (24 μl, 0.25 mmol), and dry toluene (0.66 ml) were added to
N$_2$ gas-filled flask, the reaction mixture was heated at 100 °C for 6 h. Purification by silica gel column chromatography (hexane:EtOAc 50:1) provided 3e (27 mg, 68%) as white solid.$^1$H NMR (400 MHz, CDCl$_3$): δ 7.62-7.59 (m, 2H), 7.37 (td, $J = 7.2$, 2.0 Hz, 2H), 7.31-7.25 (m, 3H), 7.08-7.06 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.4, 134.4, 1128.8, 127.9, 127.4, 125.9, 124.8, 123.0. These NMR spectra were in accordance with the reported data.$^7$

3-Methyl-2-phenylpyridine 3f (Table 3, entry 6)

According to the general procedure, 1-Pd NPs (0.6 mg, 0.0012 mmol), phenylboronic acid (53 mg, 0.43 mmol), potassium carbonate (67 mg, 0.48 mmol), and 2-bromo-3-methylpyridine (28 μl, 0.25 mmol), and dry toluene (0.66 ml) were added to N$_2$ gas-filled flask, the reaction mixture was heated at 100 °C for 24 h. Purification by preparative TLC (hexane:EtOAc 3:1) provided 3f (28 mg, 67%) as colorless oil.$^1$H NMR (400 MHz, CDCl$_3$): δ 8.53 (dd, $J = 4.8$, 0.8 Hz, 1H), 7.57 (dd, $J = 7.6$, 0.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.47-7.42 (m, 2H), 7.41-7.36 (m, 1H), 7.17 (dd, $J = 7.6$, 4.8 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.6, 146.9, 140.6, 138.4, 130.7, 128.9, 128.1, 127.8, 122.0, 20.0. These NMR spectra were in accordance with the reported data.$^8$

6-phenyl-2-pyridinemethanol 3g (Table 3, entry 7)

According to the general procedure, 1-Pd NPs (0.3 mg, 0.0006 mmol), phenylboronic acid (28 mg, 0.23 mmol), potassium carbonate (34 mg, 0.25 mmol), and 2-bromo-6-(hydroxymethyl)pyridine (24 mg, 0.12 mmol), and dry toluene (0.33 ml) were added to N$_2$ gas-filled flask, the reaction mixture was heated at 100 °C for 6 h. Purification by preparative TLC (hexane:EtOAc 15:1) provided 3g (18 mg, 78%) as colorless oil.$^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, $J = 6.8$ Hz, 2H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.48-7.43 (m, 3H), 7.47-7.42 (m, 2H), 7.16 (d, $J = 7.2$ Hz, 1H), 4.82 (s, 2H), 4.14 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.4, 156.0, 138.4, 130.7, 128.9, 128.1, 127.8, 122.0, 119.2, 118.7, 63.9. These NMR spectra were in accordance with the reported data.$^9$

3-Phenylquinoline 3h (Table 3, entry 8)

According to the general procedure, 1-Pd NPs (0.2 mg, 0.0004 mmol), phenylboronic acid (4.7 mg, 0.038 mmol), potassium carbonate (5.5 mg, 0.039 mmol), and 3-bromoquinoline (2.8 μl, 0.021 mmol), and dry toluene (0.15 ml) were added to N$_2$ gas-filled flask, the reaction mixture was heated at 100 °C for 15 h. Purification by preparative TLC (hexane:EtOAc 5:2) provided 3h (2.6 mg, 62%) as white solid.$^1$H NMR (300 MHz, CDCl$_3$): δ 9.19 (d, $J = 2.1$ Hz, 1H), 8.31 (d, $J = 2.4$ Hz, 1H), 8.15 (d, $J =
8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.76-7.70 (m, 3H), 7.61-7.51 (m, 3H), 7.47-7.42 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.9, 147.3, 137.9, 133.2, 129.4, 129.21, 129.16, 128.1, 128.00, 127.99, 127.4, 127.0. These NMR spectra were in accordance with the reported data.$^{10}$

2,6-Diphenylpyridine 3i (Table 3, entry 9)

According to the general procedure, 1-Pd NPs (0.5 mg, 0.001 mmol), phenylboronic acid (45 mg, 0.37 mmol), potassium carbonate (59 mg, 0.43 mmol), and 2-bromothiophene (24 mg, 0.10 mmol), and dry toluene (0.27 ml) were added to N$_2$ gas-filled flask, the reaction mixture was heated at 100 °C for 8 h. Purification by preparative TLC (hexane:EtOAc 10:1) provided 3i (18 mg, 74%) as white solid.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.15 (dt, J = 7.6, 5.2 Hz, 4H), 7.82, 7.80 (d, d, J = 7.2, 7.2 Hz, 1H), 7.69 (d, J = 7.2 Hz, 2H), 7.51-7.48 (m, 4H), 7.45-7.40 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.8, 139.5, 137.5, 128.9, 128.7, 127.0, 118.6. These NMR spectra were in accordance with the reported data.$^{11}$
6. Reusability of 1-Pd NPs for Suzuki coupling

Synthesis of 4-Acetylbiphenyl 3a

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Run</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
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<tr>
<td>Yield (%)</td>
<td>94</td>
<td>35(^a)</td>
<td>47(^a)</td>
<td>19(^a)</td>
</tr>
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</table>

\(^a\) NMR yield. DMF was used as standard material to measure the amount of 3a.

Run 1st: 1-Pd NPs (0.6 mg, 0.0012 mmol) was added to a frame dried flask and filled with N\(_2\) gas. To the flask were added phenylboronic acid (54 mg, 0.44 mmol), potassium carbonate (67 mg, 0.48 mmol), and 4-acetylbromobenzene (49 mg, 0.24 mmol), and dry toluene (0.66 ml), then the reaction mixture was heated at 100 °C. After stirring for 4 h, the reaction mixture was cooled to room temperature and transferred to eppendolf tube, centrifuged. After removing the solution, the precipitated 1-Pd NPs were washed with toluene and water, centrifuged. This procedure for wash was repeated 3 times. The recovered 1-Pd NPs were reused in next run. The solution was extracted with EtOAc, washed with brine. The combined organic layer was dried over Na\(_2\)SO\(_4\), evaporated. The crude material was purified by preparative TLC (hexane:EtOAc 4:1) provided 3a (45 mg, 94%) as white solid.

Run 2nd: 1-Pd NPs (0.6 mg, 0.0012 mmol) was added to a frame dried flask and filled with N\(_2\) gas. To the flask were added phenylboronic acid (54 mg, 0.44 mmol), potassium carbonate (67 mg, 0.48 mmol), and 4-acetylbromobenzene (49 mg, 0.24 mmol), and dry toluene (0.66 ml), then the reaction mixture was heated at 100 °C. After stirring for 4 h, the reaction mixture was cooled to room temperature and transferred to eppendolf tube, centrifuged. After removing the solution, the precipitated 1-Pd NPs were washed with toluene and water, centrifuged. This procedure for wash was repeated 3 times. Then, the recovered 1-Pd NPs were reused in next run. The solution was extracted with EtOAc, washed with brine. The combined organic layer was dried over Na\(_2\)SO\(_4\), evaporated. The yield of 3a (35%) was estimated by \(^1\)H NMR of the crude material using DMF as standard material. Purification by preparative TLC (hexane:EtOAc 4:1) did not give the pure 3a.

Run 3rd: 1-Pd NPs (0.3 mg, 0.00062 mmol) was added to a frame dried flask and filled with N\(_2\) gas. To the flask were added phenylboronic acid (28 mg, 0.23 mmol), potassium carbonate (34 mg, 0.24 mmol), and 4-acetylbromobenzene (25 mg, 0.13 mmol), and dry toluene (0.33 ml), then the reaction mixture was heated at 100 °C. After stirring for 4 h, the reaction mixture was cooled to room
temperature and transferred to eppendolf tube, centrifuged. After removing the solution, the precipitated 1-Pd NPs were washed with toluene and water, centrifuged. This procedure for wash was repeated 3 times. Then, the recovered 1-Pd NPs were reused in next run. The solution was extracted with EtOAc, washed with brine. The combined organic layer was dried over Na$_2$SO$_4$, evaporated. The yield of 3a (47%) was estimated by $^1$H NMR of the crude material using DMF as standard material.

Run 4th: 1-Pd NPs (0.3 mg, 0.00062 mmol) was added to a frame dried flask and filled with N$_2$ gas. To the flask were added phenylboronic acid (27 mg, 0.23 mmol), potassium carbonate (34 mg, 0.24 mmol), and 4-acetylbromobenzene (25 mg, 0.13 mmol), and dry toluene (0.33 ml), then the reaction mixture was heated at 100 °C. After stirring for 4 h, the reaction mixture was cooled to room temperature and transferred to eppendolf tube, centrifuged. After removing the solution, the precipitated 1-Pd NPs were washed with toluene and water, centrifuged. This procedure for wash was repeated 3 times. Then, the recovered 1-Pd NPs were reused in next run. The solution was extracted with EtOAc, washed with brine. The combined organic layer was dried over Na$_2$SO$_4$, evaporated. The yield of 3a (19%) was estimated by $^1$H NMR of the crude material using DMF as standard material.

**7. Procedure for 1-Pd NPs-catalyzed ethynylation via C(sp$^3$)-H activation**

General procedure: 8-((3-(triisopropylethynyl)-n-hexanoyl)amino)quinoline 5 (Scheme 1a)  

(Ethynylation reaction at 100 °C): 1-Pd NPs (0.4 mg, 0.0008 mmol) was added to a frame dried flask and filled with N$_2$ gas. To the flask were added 8-(N-(n-hexanoyl)amino)quinoline 4 (19 mg, 0.080 mmol), (bromoethynyl)triisopropylsilane (30 μl, 0.12 mmol), and silver(I) acetate (28 mg, 0.17 mmol), and dry toluene (0.22 ml), then the reaction mixture was heated at 100 °C. After stirring for 22 h, the reaction mixture was cooled to room temperature, filtered, extracted with EtOAc, washed with brine. The combined organic layer was dried over Na$_2$SO$_4$, evaporated. The crude material was purified by preparative TLC (hexane:EtOAc 5:1) to give 5 (21 mg, 61%) as colorless oil with racemic form. $^1$H NMR (400 MHz, CDCl$_3$): δ 9.87 (brs, 1H), 8.80-8.78 (m, 2H), 8.15 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.49-7.43 (m, 1H), 3.13 (brs, 1H), 2.75, 2.68 (q, q, $J = 7.6$, 7.2 Hz, 2H), 1.64-1.51 (m, 4H), 0.97-0.87 (m, 24H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 169.5, 148.0, 138.3, 136.2, 134.4, 127.8, 127.3, 121.49, 121.45, 116.5, 110.4, 82.0, 44.4, 36.9, 29.8, 20.4, 18.4, 13.8, 11.1. These NMR spectra were in accordance with the reported data.  

(Ethynylation reaction at 60 °C): According to the procedure for 5, 1-Pd NPs (0.3 mg, 0.0006 mmol), 8-((3-methyl-n-pentanoyl)amino)quinoline 6 (15 mg, 0.064 mmol), (bromoethynyl)triisopropylsilane
(23 μl, 0.096 mmol), and silver(I) acetate (22 mg, 0.13 mmol) in dry toluene (0.18 ml) were heated at 60 °C for 36 h. Purification by preparative TLC (hexane:EtOAc 5:1) gave 5 (3.8 mg, 14%) as colorless oil with 2% ee. Flow rate: 0.6 mL/min; detection: 254 nm. Retention time: t<sub>R</sub> = 7.6 min (minor), 8.3 min (major).

8-((3-(triisopropylethynyl)-4-methyl-<i>n</i>-pentanoyl)amino)quinoline 7 (Scheme 1b)

According to the procedure for 5, 1-Pd NPs (0.3 mg, 0.0006 mmol), 8-((3-methyl-<i>n</i>-pentanoyl)amino)quinoline 6 (15 mg, 0.064 mmol), (bromoethynyl)triisopropylsilane (23 μl, 0.096 mmol), and silver(I) acetate (21 mg, 0.12 mmol) in dry toluene (0.17 ml) were heated at 100 °C for 24 h. Purification by preparative TLC (hexane:EtOAc 5:1) gave 7 (3.7 mg, 14%) as colorless oil with racemic form. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.88 (brs, 1H), 8.81-8.79 (m, 2H), 8.16 (dd, <i>J</i> = 8.4, 1.6 Hz, 1H), 7.55-7.44 (m, 3H), 3.13-3.08 (m, 1H), 2.72-2.69 (m, 2H), 1.88-1.86 (m, 1H), 1.10-1.07 (m, 6H), 0.94-0.90 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.9, 148.0, 138.3, 136.3, 134.4, 127.8, 127.4, 121.50, 121.45, 116.5, 108.3, 42.3, 36.8, 31.1, 21.3, 18.5, 17.8, 11.1. These NMR spectra were in accordance with the reported data. <sup>12</sup>
8. NMR spectra

4-Methoxybiphenyl 2

$^1$H NMR (300 MHz, CDCl$_3$)

(Table 2, entry 3, 4, 5)
4-Methoxybiphenyl 2

$^{13}$C NMR (100 MHz, CDCl$_3$)

(Table 2, entry 3, 4, 5)
4-Acetyl biphenyl 3a

$^1$H NMR (300 MHz, CDCl$_3$)
4-Acetylbiphenyl 3a

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Phenylphenol 3b

$^1$H NMR (300 MHz, CDCl$_3$)
3-Phenylphenol 3b

$^{13}$C NMR (75 MHz, CDCl$_3$)
2-Phenylphenol 3c

$^1$H NMR (400 MHz, CDCl$_3$)
2-Phenylphenol 3c
$^{13}$C NMR (75 MHz, CDCl$_3$)
4-Aminobiphenyl 3d

$^1$H NMR (300 MHz, CDCl$_3$)
4-Aminobiphenyl 3d

$^{13}$C NMR (75 MHz, CDCl$_3$)
2-Phenylthiophene 3e

$^1$H NMR (400 MHz, CDCl$_3$)
2-Phenylthiophene 3e

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Methyl-2-phenylpyridine 3f

$^1$H NMR (400 MHz, CDCl$_3$)
3-Methyl-2-phenylpyridine 3f

$^{13}$C NMR (100 MHz, CDCl$_3$)
6-phenyl-2-pyridinemethanol 3g
\(^1\)H NMR (400 MHz, CDCl\(_3\))
6-phenyl-2-pyridinemethanol 3g

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-Phenylquinoline 3h

$^1$H NMR (300 MHz, CDCl$_3$)
3-Phenylquinoline 3h

$^{13}$C NMR (75 MHz, CDCl$_3$)
2,6-Diphenylpyridine 3i

$^1$H NMR (400 MHz, CDCl$_3$)
2,6-Diphenylpyridine 3i

$^{13}$C NMR (100 MHz, CDCl$_3$)
8-((3-(triisopropylethenyl)-n-hexanoyl)amino)quinoline 5

$^1$H NMR (400 MHz, CDCl$_3$)
8-((3-(triisopropylethynyl)-n-hexanoyl)amino)quinoline 5

$^{13}$C NMR (100 MHz, CDCl$_3$)
8-((3-(triisopropylethynyl)-4-methyl-n-pentanoyl)amino)quinoline 7

$^1$H NMR (400 MHz, CDCl$_3$)
8-((3-(triisopropylethynyl)-4-methyl-\textit{n}-pentanoyl)amino)quinoline 7

$^{13}$C NMR (100 MHz, CDCl$_3$)
9. References