

Electronic Supplementary Information for:

## **Coordinative Alignment of Chiral Molecules to Control over the Chirality Transfer in Spontaneous Resolution and Asymmetric Catalysis**

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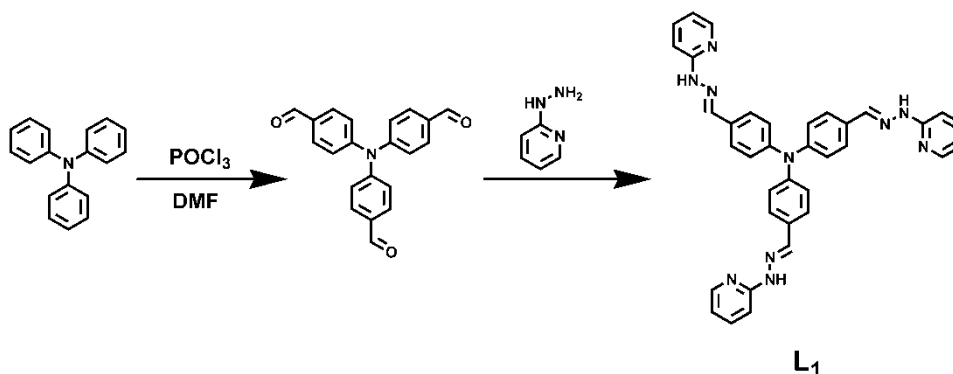
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### **Supplementary Methods**

#### **Synthesis of tris(4-formylphenyl)amine<sup>1</sup>**

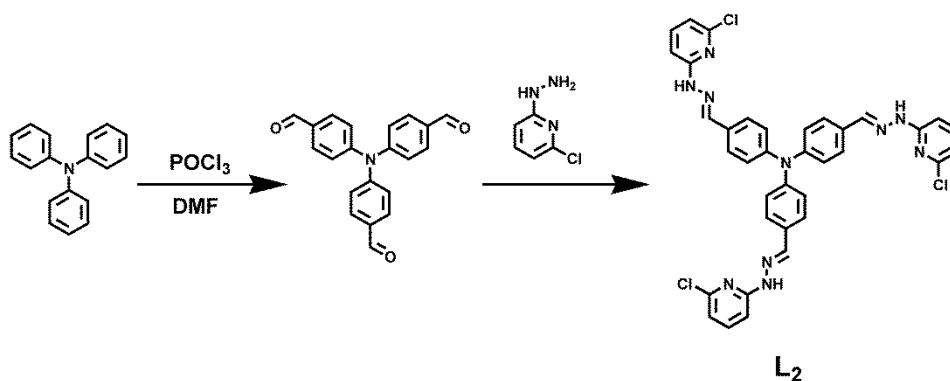
Phosphorus oxychloride (100 mL, 1.09 mol) was added dropwise at 0 °C under N<sub>2</sub> to DMF (75.0 mL, 0.97 mol) and the reaction mixture was stirred for 1 h. Triphenylamine (10.0 g, 40.8 mmol) was added in batches, and the resulting mixture was stirred at 95 °C for 8 h. After cooling to r.t., the mixture was poured into ice-water (500 mL), and basified with 1 M NaOH. After extraction with CH<sub>2</sub>Cl<sub>2</sub> (400 mL), the organic layer was washed with water (3 × 150 mL), dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of the solvent in vacuo, the residue was added on an ice-cooled mixture of POCl<sub>3</sub> (80.0 mL, 0.87 mol) and DMF (60.0 mL, 0.78 mol). The resulting mixture was stirred at 95 °C for 4 h, and after cooling to r.t., poured into ice-water (500 mL), and basified with 1 M NaOH. After extraction with CH<sub>2</sub>Cl<sub>2</sub> (400 mL), the organic layer was washed with water (3 × 150 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as an eluent to give a yellow solid (7.85 g, 58.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 9.95 (s, 3H), 7.85 (d,  $J$  = 8.6 Hz, 6H), 7.26 (d,  $J$  = 8.6 Hz, 6H).

### Synthesis of Tris(4-(2-pyridin-2-ylhydrazono)phenyl)amine (L<sub>1</sub>)



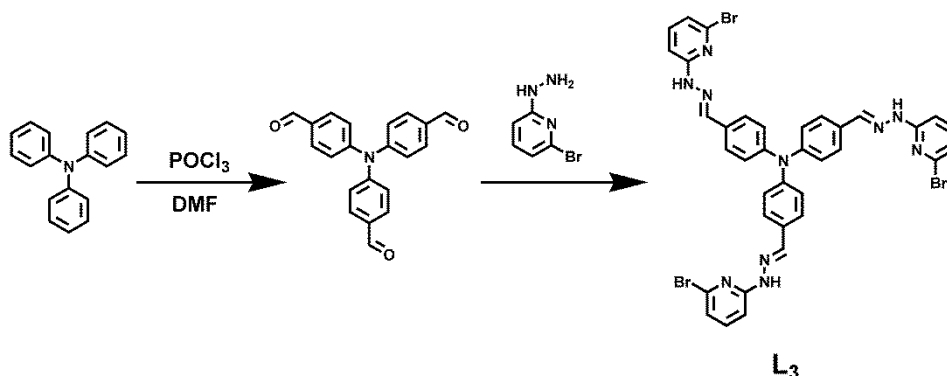
Five drops of acetic acid were added to a mixture of tris(4-formylphenyl)amine (0.33 g, 1 mmol) and 2-hydrazinopyridine (0.34 g, 3.1 mmol) in a dry CH<sub>3</sub>OH solution (25 mL). The mixture was refluxed over 4 h and a yellow precipitate (0.55 g) was isolated by filtration, washed with dry CH<sub>3</sub>OH and dried under vacuum. Yield: 91%. Anal. calcd. for C<sub>36</sub>H<sub>30</sub>N<sub>10</sub>: C, 71.74; H, 5.02; N, 23.24. Found: C, 71.78; H, 5.26; N, 22.91. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 10.82 (s, 3H), 8.10 (d, *J* = 3.9 Hz, 3H), 7.99 (s, 3H), 7.62 (t, *J* = 8.2 Hz, 9H), 7.20 (d, *J* = 8.5 Hz, 3H), 7.10 (dd, *J* = 16.9, 8.6 Hz, 6H), 6.78–6.70 (m, 3H). ESI-MS: *m/z* 603.1 (calcd. *m/z* 603.27 for [L+H]<sup>+</sup>).

### Synthesis of Tris(4-(6-chloro-2-pyridin-2-ylhydrazono)phenyl)amine (L<sub>2</sub>)



Five drops of acetic acid were added to a mixture of tris(4-formylphenyl)amine (0.33 g, 1 mmol) and 2-chloro-6-hydrazinopyridine (0.44 g, 3.1 mmol) in a dry CH<sub>3</sub>OH solution (25 mL). The mixture was refluxed for 6 h, and a yellow precipitate (0.62 g) was isolated by filtration, washed with dry CH<sub>3</sub>OH and dried under vacuum. Yield: 89%. Anal. calcd. for C<sub>36</sub>H<sub>27</sub>N<sub>10</sub>Cl<sub>3</sub>: C, 61.24; H, 3.85; N, 19.84. Found: C, 61.66; H, 3.46; N, 19.43. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 11.21 (s, 3H), 7.99 (s, 3H), 7.76–7.52 (m, 9H), 7.15 (d, *J* = 8.3 Hz, 3H), 7.06 (t, *J* = 11.4 Hz, 6H), 6.79 (d, *J* = 7.5 Hz, 3H). ESI-MS: *m/z* 705.1 (calcd. *m/z* 705.15 for [L-H]<sup>+</sup>).

### Synthesis of Tris(4-(6-bromo-2-pyridin-2-ylhydrazono)phenyl)amine (**L<sub>3</sub>**)



Five drops of acetic acid were added to a mixture of tris(4-formylphenyl)amine (0.33 g, 1 mmol) and 2-bromo-6-hydrazinopyridine (0.58 g, 3.1 mmol) in a dry CH<sub>3</sub>OH solution (25 mL). The mixture was refluxed for 6 h, and a yellow precipitate (0.78 g) was isolated by filtration, washed with dry CH<sub>3</sub>OH and dried under vacuum. Yield: 92%. Anal. calcd. for C<sub>36</sub>H<sub>27</sub>N<sub>10</sub>Br<sub>3</sub>: C, 51.51; H, 3.24; N, 16.69. Found: C, 51.88; H, 3.44; N, 16.63. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 11.23 (s, 3H), 7.98 (s, 3H), 7.63 (d, *J* = 8.6 Hz, 6H), 7.55 (t, *J* = 7.9 Hz, 3H), 7.17 (d, *J* = 8.2 Hz, 3H), 7.07 (d, *J* = 8.6 Hz, 6H), 6.92 (d, *J* = 7.4 Hz, 3H). ESI-MS: *m/z* 837.0 (calcd. *m/z* 836.99 for [L-H]).

**Synthesis of 1.** Two drops of acetic acid were added to the suspension of **L<sub>1</sub>** (15.2 mg, 0.025 mmol) in 4 mL CH<sub>3</sub>OH/CHCl<sub>3</sub> (*v:v* = 1:3); then, 8 mL CH<sub>3</sub>CN/CHCl<sub>3</sub> (*v:v* = 5:3) were layered carefully, over which AgClO<sub>4</sub> (7.8 mg, 0.0375 mmol) dissolved in CH<sub>3</sub>CN (6 mL) was layered. The container was covered and stored in the dark for slow diffusion of reactants at room temperature, which afforded yellow crystals within one week time. Yield: 46% (based on Ag). Elemental analysis (%) Calc. for C<sub>77</sub>H<sub>73</sub>N<sub>22</sub>Ag<sub>3</sub>Cl<sub>6</sub>O<sub>15</sub>: H, 3.53; C, 44.40.; N, 14.79. Found: H, 4.10; C, 44.62; N, 14.34. IR cm<sup>-1</sup> (KBr): 3476 (br), 3267 (w), 3032 (w), 1615 (s), 1598 (s), 1577 (m), 1538 (m), 1503 (s), 1483 (s), 1444 (m), 1423 (s), 1320 (s), 1286 (s), 1248 (s), 1177 (m), 1095 (s), 1004 (m), 927 (w), 827 (w), 768 (m), 738 (w), 667 (w), 622 (m), 555(w), 529 (w).

**Synthesis of 1-M.** Two drops of acetic acid were added to the suspension of **L<sub>1</sub>** (15.2 mg, 0.025 mmol) in 4 mL CH<sub>3</sub>OH/CHCl<sub>3</sub> (*v:v* = 1:3); then, the solution of (*S,E*)-methyl 2-(benzylideneamino)propanoate (**L-BPAM**)<sup>2</sup> (0.48 mg, 0.0025 mmol) in 8 mL CH<sub>3</sub>CN/CHCl<sub>3</sub> (*v:v* = 5:3) was layered carefully, over which AgClO<sub>4</sub> (7.8 mg, 0.0375 mmol) dissolved in CH<sub>3</sub>CN (6 mL) was layered. The container was covered and stored in the dark for slow diffusion of

reactants at room temperature, which afforded yellow crystals within one week time. Yield: 42% (based on Ag). Elemental analysis (%) Calc. for  $C_{77}H_{73}N_{22}Ag_3Cl_6O_{15}$ : H, 3.53; C, 44.40.; N, 14.79. Found: H, 3.72; C, 44.73; N, 14.74. IR  $cm^{-1}$  (KBr): 3443 (br), 3280 (w), 3032 (w), 1615 (s), 1599 (s), 1578 (m), 1538 (m), 1503 (s), 1483 (s), 1444 (w), 1423 (s), 1320 (s), 1286 (s), 1248 (s), 1177 (w), 1095 (s), 1004 (w), 926 (w), 827 (w), 768 (m), 738 (w), 667 (w), 622 (m), 555(w), 530 (w).

**Synthesis of 1-P.** An identical procedure with **1-M** was followed to prepare **1-P** except **L-BPAM** was replaced by (*R,E*)-methyl-2-(benzylideneamino)propanoate (**D-BPAM**).<sup>2</sup> Yellow crystals of **1-P** were collected in 44% yield (based on Ag). Elemental analysis (%) Calc. for  $C_{77}H_{73}N_{22}Ag_3Cl_6O_{15}$ : H, 3.53; C, 44.40.; N, 14.79. Found: H, 4.08; C, 45.10; N, 14.66. IR  $cm^{-1}$  (KBr): 3444 (br), 3276 (w), 1615 (s), 1600 (s), 1577 (m), 1538 (m), 1502 (s), 1483 (s), 1444 (m), 1423 (s), 1320 (s), 1286 (s), 1248 (s), 1177 (m), 1095 (s), 1004 (m), 926 (w), 827 (w), 768 (m), 738 (w), 667 (w), 622 (m), 556(w), 530 (w).

**Syntheses of 2, 2-M and 2-P.** **L<sub>2</sub>** (17.7 mg, 0.025 mmol) was dissolved in 4 mL  $CH_3OH/CHCl_3$  ( $v:v = 1:3$ ); then, 8 mL  $CH_3CN/CHCl_3$  ( $v:v = 5:3$ ) were layered carefully, over which  $AgClO_4$  (7.8 mg, 0.0375 mmol) dissolved in  $CH_3CN$  (6 mL) was layered. The container was covered and stored in the dark for slow diffusion of reactants at room temperature, which afforded yellow crystals within one week time. Yield: 38% (based on Ag). Elemental analysis (%) Calc. for  $C_{78}H_{62}N_{22}Ag_3Cl_{15}O_{12}$ : H, 2.65; C, 39.78.; N, 13.09. Found: H, 2.60; C, 39.82; N, 13.03. IR  $cm^{-1}$  (KBr): 3443 (br, m), 3262 (m), 2958 (s), 2868(m), 1601 (s), 1531 (m), 1503 (s), 1457 (s), 1401 (m), 1321 (s), 1280 (s), 1254 (s), 1174 (s), 1103 (s), 1073 (s), 996 (m), 959 (w), 925 (m), 885 (m), 826 (m), 762 (m), 731 (w), 663 (w), 617 (m), 553 (w), 522 (w). **2-M** and **2-P** were synthesized according to the same procedure except by adding **L-BPAM** (0.48 mg, 0.0025 mmol) and **D-BPAM** (0.48 mg, 0.0025 mmol) in the interlayer  $CH_3CN/CHCl_3$  solution, respectively.

**Syntheses of 3, 3-M and 3-P.** Two drops of acetic acid were added to the suspension of **L<sub>3</sub>** (20.9 mg, 0.025 mmol) in 3 mL  $CHCl_3$ ; then, 10 mL  $CH_3CN/CHCl_3$  ( $v:v = 1:1$ ) were layered carefully, over which  $AgClO_4$  (7.8 mg, 0.0375 mmol) dissolved in  $CH_3CN$  (3 mL) was layered. The container was covered and stored in the dark for slow diffusion of reactants at room temperature, which afforded yellow crystals within one week time. Yield: 32% (based on Ag). Elemental analysis (%) Calc. for  $C_{78}H_{62}N_{22}Ag_3Br_6Cl_9O_{12}$ : H, 2.38; C, 35.74.; N, 11.75. Found: H, 2.20; C,

35.62; N, 11.64. IR  $\text{cm}^{-1}$  (KBr): 3443 (br, m), 3262 (m), 2924 (w), 1612 (s), 1598 (s), 1580 (m), 1527 (m), 1500 (s), 1481 (s), 1457 (s), 1429 (m), 1398 (s), 1318 (s), 1279 (m), 1254 (s), 1171 (s), 1097 (s), 989 (m), 956 (m), 928 (m), 860 (w), 823 (m), 767 (m), 735 (w), 664 (w), 619 (m), 550 (w), 522 (w). **3-M** and **3-P** were synthesized according to the same procedure except by adding **L-BPAM** (0.48 mg, 0.0025 mmol) and **D-BPAM** (0.48 mg, 0.0025 mmol) in the interlayer  $\text{CH}_3\text{CN}/\text{CHCl}_3$  solution, respectively.

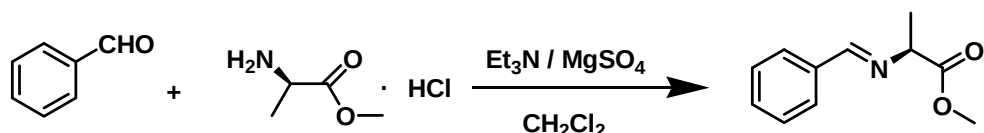
**Synthesis of L-BPAM@1-M.** Crystals of the compound were obtained soaking the crystals of **1-M** (0.01 mmol) in a  $\text{CHCl}_3$  (1 mL) solution containing **L-BPAM** (1 mmol) for 24 hours.

**Synthesis of D-BPAM@1-P.** Crystals of the compound were obtained soaking the crystals of **1-P** (0.01 mmol) in a  $\text{CHCl}_3$  (1 mL) solution containing **D-BPAM** (1 mmol) for 24 hours.

**Synthesis of D-BPAM@1-M.** Crystals of the compound were obtained soaking the crystals of **1-M** (0.01 mmol) in a  $\text{CHCl}_3$  (1 mL) solution containing **D-BPAM** (1 mmol) for 24 hours.

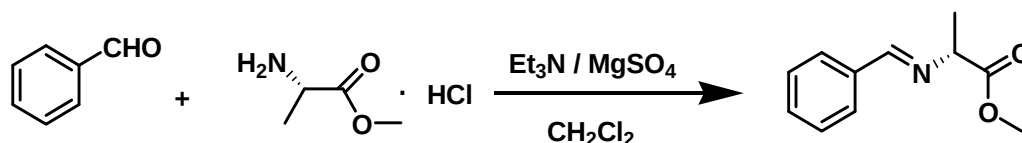
**Synthesis of L-BPAM@1-P.** Crystals of the compound were obtained soaking the crystals of **1-P** (0.01 mmol) in a  $\text{CHCl}_3$  (1 mL) solution containing **L-BPAM** (1 mmol) for 24 hours.

#### Synthesis of (S,E)-methyl 2-(benzylideneamino)propanoate (**L-BPAM**)<sup>2</sup>



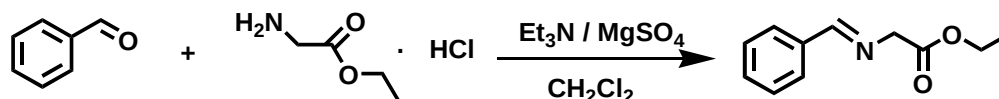
A suspension of *L*-alanine methyl ester hydrochloride (3.53 g, 25.3 mmol) and  $\text{MgSO}_4$  (3.2 g, 26.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was stirred at 0 °C, TEA (3.5 mL, 25.3 mmol) was added dropwise. And then benzaldehyde (2.1 mL, 21.1 mmol) was added dropwise over 10 min. The reaction was allowed to warm to ambient temperature and stirred for 24 h.  $\text{Et}_2\text{O}$  (50 mL) was then added and the solution was filtered. The filtrate was washed with water ( $\times 2$ ) and brine ( $\times 2$ ), dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo* to give the target compound as a light-yellow oil (3.59 g, 89 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.31 (s, 1H), 7.78 (dt,  $J = 3.7, 2.2$  Hz, 2H), 7.45–7.38 (m, 3H), 4.16 (q,  $J = 6.8$  Hz, 1H), 3.74 (s, 3H), 1.53 (d,  $J = 6.8$  Hz, 3H).

### Synthesis of (*R,E*)-methyl 2-(benzylideneamino)propanoate (*D*-BPAM)<sup>2</sup>



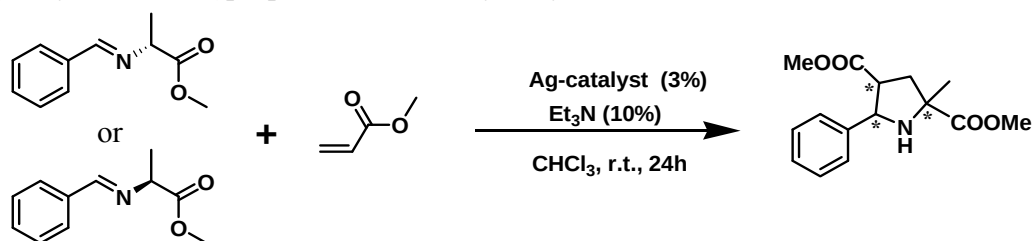
The same procedure as that for *L*-BPAM was used, except that *D*-alanine methyl ester hydrochloride was used instead of *L*-alanine methyl ester hydrochloride. Light-yellow oil (3.47 g, 86 %) was obtained in the end. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.31 (s, 1H), 7.85–7.72 (m, 2H), 7.45–7.37 (m, 3H), 4.15 (t, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H).

### Synthesis of N-(Phenylmethylene)-glycine ethyl ester (PGE)

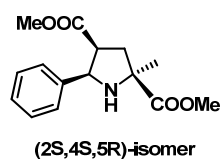


To a suspension of ethyl glycinate hydrochloride (2.065 g, 14.8 mmol) and MgSO<sub>4</sub> (2.17 g, 18.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (36 mL), TEA (2.10 mL, 14.8 mmol) was added dropwise. The mixture was stirred at 0 °C for one hour, and then benzaldehyde (1.06 mL, 10.0 mmol) was added dropwise over 10 min. The reaction was allowed to warm to ambient temperature and stirred for 12 h. The solution was filtered, and the filtrate was washed with water (10 mL  $\times$  2), the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL  $\times$  2). The combined organic layers were washed with brine ( $\times$  2), dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to give the target compound as a light-yellow oil (1.61 g, 84 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.28 (s, 1H), 7.88–7.68 (m, 2H), 7.49–7.26 (m, 3H), 4.39 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

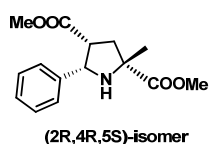
**General procedure for the 1,3-dipolar cycloaddition reaction between chiral methyl 2-(benzylideneamino)propanoate and methyl acrylate<sup>3</sup>**



A mixture of (*S,E*)-methyl 2-(benzylideneamino)propanoate (0.2 mmol) [or (*R,E*)-methyl 2-(benzylideneamino)propanoate (0.2 mmol)] and methyl acrylate (0.24 mmol) was added to a suspension of the Ag-catalyst (0.006 mmol) in chloroform (0.5 mL). To the resulting suspension Et<sub>3</sub>N (0.02 mmol, 2.77  $\mu$ L) was added and the mixture was stirred at room temperature for 24 h (in the absence of the light). The precipitate was filtered, washed with chloroform three times and then collected by centrifugation for catalyzing a new batch. The organic filtrate was directly evaporated and the residue was purified by preparative thin-layer chromatography (PTLC) with hexane-ethyl acetate (3:1) as the eluent to give the pure product as colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.32–7.20 (m, 5H), 4.66 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.35 (td, *J* = 7.5, 5.3 Hz, 1H), 3.20 (s, 3H), 3.15 (s, 1H), 2.72 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.05 (dd, *J* = 13.6, 7.5 Hz, 1H), 1.50 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  176.68, 173.15, 139.19, 128.30, 127.69, 126.81, 65.89, 65.09, 52.63, 51.27, 50.62, 40.44, 27.68. HPLC Chiral pak AS-H, *i*PrOH/hexane = 10:90, flow rate = 0.8 mL/min, 210 nm, *t<sub>R</sub>* = 13.9 min, (2*S*,4*S*,5*R*)-isomer; *t<sub>R</sub>* = 8.7 min, (2*R*,4*R*,5*S*)-isomer. ESI-HRMS (*m/z*) calcd. for C<sub>15</sub>H<sub>20</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 278.1392; found: 278.1393.



(2*S*,4*S*,5*R*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate: [ $\alpha$ ]<sub>D</sub><sup>20</sup> = 18.2 (*c* = 0.73, CHCl<sub>3</sub>, 91% ee). Absolute configuration determined in comparison to similar compound in Literature [ $\alpha$ ]<sub>D</sub> = 33.1 (*c* = 1.11, CH<sub>2</sub>Cl<sub>2</sub>).<sup>4</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR data were consistent with previously reported value.<sup>5</sup> ESI-HRMS (*m/z*) calcd. for C<sub>15</sub>H<sub>20</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 278.1392; found: 278.1394.



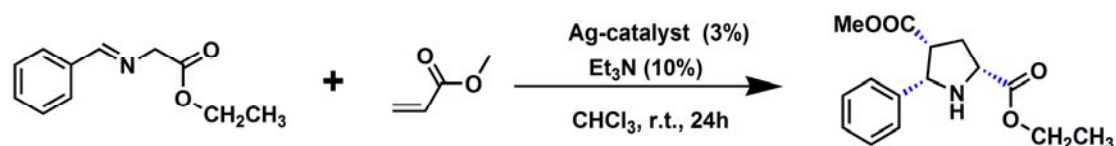
(2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate: [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -19.9 (*c* = 0.78, CHCl<sub>3</sub>, 92% ee). Absolute configuration determined in comparison to similar compound in Literature [ $\alpha$ ]<sub>D</sub> = 33.1 (*c* = 1.11, CH<sub>2</sub>Cl<sub>2</sub>).<sup>4</sup> <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-HRMS data please see above for details.

**Typical one-pot tandem procedure merging the homochiral Ag(I)-based MOFs formation and the abovementioned 1,3-dipolar cycloaddition.**

Onto a solution of **L**<sub>1</sub> (9.1 mg, 0.015 mmol) in 2 mL of CH<sub>3</sub>OH/CHCl<sub>3</sub> (*v:v* = 1:3), a solution of **L-BPAM** (95.5 mg, 0.5 mmol) or **D-BPAM** (95.5 mg, 0.5 mmol) in 3 mL of CH<sub>3</sub>CN/CHCl<sub>3</sub> (*v:v* = 1:1) was carefully layered, over which AgClO<sub>4</sub> (4.4 mg, 0.023 mmol) dissolved in acetonitrile (1 mL) was layered. The container was covered and stored in the dark for slow diffusion of reactants at room temperature. After complete crystallization, Et<sub>3</sub>N (0.05 mmol, 6.93 μL) and methyl acrylate (0.6 mmol) were added to the reaction system, which was then covered and stirred at room temperature for 24 h in the absence of light; the precipitate was filtered, and the complex was recovered. The organic filtrate was directly evaporated, and the residue was purified by preparative thin-layer chromatography (PTLC) with hexane-ethyl acetate (3:1) as the eluent to give the pure product as a colorless oil.

For the ‘ont-pot’ tandem asymmetric catalytic systems of **2** and **3**: a similar procedure as that of **1**, except **L**<sub>1</sub> (9.1 mg, 0.015 mmol) was replaced by **L**<sub>2</sub> (10.6 mg, 0.015 mmol) and **L**<sub>3</sub> (12.5 mg, 0.015 mmol), respectively.

**General procedure for the catalytic reaction between *N*-(phenylmethylene)-glycine ethyl ester (PGE) and methyl acrylate<sup>6</sup>**



A mixture of *N*-(phenylmethylene)-glycine ethyl ester (0.2 mmol) and methyl acrylate (0.24 mmol) was added to a suspension of the Ag-catalyst (0.006 mmol) in chloroform (0.5 mL). To the resulting suspension Et<sub>3</sub>N (0.02 mmol, 2.77 μL) was added and the mixture was stirred at room temperature for 24 h (in the absence of the light). The precipitate was filtered, washed with chloroform three times and then collected by centrifugation for catalyzing a new batch. The organic filtrate was directly evaporated and the residue was purified by preparative thin-layer chromatography (PTLC) with hexane-ethyl acetate (3:1) as the eluent to give the pure product as colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.31 (m, *J* = 7.0, 6.3 Hz, 5H), 4.55 (d, *J* = 7.8 Hz, 1H), 4.33–4.25 (m, 2H), 3.98 (s, 1H), 3.33 (d, *J* = 7.0 Hz, 1H), 3.22 (s, 3H), 2.53 (s, 1H), 2.45–2.38 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.45, 173.18, 139.24, 128.43, 127.86, 126.99, 66.09, 61.48, 60.27, 51.44, 49.99, 33.58, 14.45. HPLC Chiral pak AS-H, *i*PrOH/hexane = 15:85, flow rate = 0.8 mL/min, 210 nm, *t*<sub>R</sub> = 10.5 min; *t*<sub>R</sub> = 21.8 min.

## X-ray Crystallography

Summary of crystallographic data and details of data collection for **1-M**, **1-P**, **2-M**, **2-P** and **3-M** are given in Table S1, and **3-P**, **L-BPAM@1-M**, **D-BPAM@1-P**, **D-BPAM@1-M** and **L-BPAM@1-P** are listed in Table S2.

Single crystals with suitable dimensions were selected under an optical microscope and mounted onto a glass fiber for data collection. Intensity data for all crystals were collected at 220 K on a Bruker SMART APEX diffractometer equipped with a CCD area detector and a Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source. The data integration and reduction were processed using the SAINT software.<sup>7</sup> An empirical absorption correction was applied to the collected reflections with SADABS.<sup>8</sup> The structures were solved by direct methods using SHELXTL and were refined on  $F^2$  by the full-matrix least-squares method using the program SHELXL-97.<sup>9,10</sup> The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 1417887—1417898, 1417905—1417911, 1448704—1448709, 1448740—1448745, 1449160—1449171 and 1457367—1457369. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Refinements for 1-M, 1-P, 2-M, 2-P, 3-M and 3-P:** All non-hydrogen atoms were refined anisotropically till convergence is reached. Hydrogen atoms attached to the organic ligands, chloroform and acetonitrile molecules were located geometrically and refined in a riding model. The water hydrogen atoms were located from the difference Fourier maps, with distance restraints of O—H = 0.85±0.02 Å, and then refined with isotropic thermal parameters 1.5 times those of O atoms.

**Refinements for L-BPAM@1-M, D-BPAM@1-P, D-BPAM@1-M and L-BPAM@1-P:** All of the non-hydrogen atoms in the MOFs backbone were refined with anisotropically. Hydrogen atoms of organic ligands and the **BPAM** molecule were located geometrically and refined in a riding model, whereas those of solvent molecules were not treated during the structural refinements. The atoms in the **BPAM** molecule were refined disordered with the site occupancy factor (*s.o.f.*) of these atoms being fixed at 1/6. To help the stability of the refinement for the encapsulated **BPAM** molecule, bond distances between several atoms were fixed, the geometrical constraints of idealized regular polygons were used for its benzene rings, and thermal parameters on adjacent atoms in **BPAM** molecules were restrained to be similar.

## Supplementary Tables

**Table S1.** Crystal data and refinement parameters for complexes **1-M**, **1-P**, **2-M**, **2-P** and **3-M**.

| Compound                                                          | <b>1-M</b>                                                                                      | <b>1-P</b>                                                                                      | <b>2-M</b>                                                                                       | <b>2-P</b>                                                                                       | <b>3-M</b>                                                                                                      |
|-------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| Empirical formula                                                 | C <sub>77</sub> H <sub>73</sub> Ag <sub>3</sub> Cl <sub>6</sub> N <sub>22</sub> O <sub>15</sub> | C <sub>77</sub> H <sub>73</sub> Ag <sub>3</sub> Cl <sub>6</sub> N <sub>22</sub> O <sub>15</sub> | C <sub>78</sub> H <sub>62</sub> Ag <sub>3</sub> Cl <sub>15</sub> N <sub>22</sub> O <sub>12</sub> | C <sub>78</sub> H <sub>62</sub> Ag <sub>3</sub> Cl <sub>15</sub> N <sub>22</sub> O <sub>12</sub> | C <sub>78</sub> H <sub>62</sub> Ag <sub>3</sub> Br <sub>6</sub> Cl <sub>9</sub> N <sub>22</sub> O <sub>12</sub> |
| Formula weight                                                    | 2082.88                                                                                         | 2082.88                                                                                         | 2354.86                                                                                          | 2354.86                                                                                          | 2621.62                                                                                                         |
| Crystal system                                                    | Cubic                                                                                           | Cubic                                                                                           | Cubic                                                                                            | Cubic                                                                                            | Cubic                                                                                                           |
| Space group                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                        | <i>I</i> 2 <sub>1</sub> 3                                                                        | <i>I</i> 2 <sub>1</sub> 3                                                                                       |
| <i>a</i> /Å                                                       | 21.3062(3)                                                                                      | 21.3212(3)                                                                                      | 21.3930(4)                                                                                       | 21.3239(4)                                                                                       | 21.2844(3)                                                                                                      |
| <i>b</i> /Å                                                       | 21.3062(3)                                                                                      | 21.3212(3)                                                                                      | 21.3930(4)                                                                                       | 21.3239(4)                                                                                       | 21.2844(3)                                                                                                      |
| <i>c</i> /Å                                                       | 21.3062(3)                                                                                      | 21.3212(3)                                                                                      | 21.3930(4)                                                                                       | 21.3239(4)                                                                                       | 21.2844(3)                                                                                                      |
| $\alpha$ /°                                                       | 90                                                                                              | 90                                                                                              | 90                                                                                               | 90                                                                                               | 90                                                                                                              |
| $\beta$ /°                                                        | 90                                                                                              | 90                                                                                              | 90                                                                                               | 90                                                                                               | 90                                                                                                              |
| $\gamma$ /°                                                       | 90                                                                                              | 90                                                                                              | 90                                                                                               | 90                                                                                               | 90                                                                                                              |
| <i>V</i> /Å <sup>3</sup>                                          | 9672.0(2)                                                                                       | 9692.5(2)                                                                                       | 9790.7(3)                                                                                        | 9696.2(3)                                                                                        | 9642.4(2)                                                                                                       |
| <i>Z</i>                                                          | 4                                                                                               | 4                                                                                               | 4                                                                                                | 4                                                                                                | 4                                                                                                               |
| <i>D<sub>c</sub></i> /(g·cm <sup>-3</sup> )                       | 1.430                                                                                           | 1.427                                                                                           | 1.598                                                                                            | 1.613                                                                                            | 1.806                                                                                                           |
| <i>T</i> (K)                                                      | 220(2)                                                                                          | 220(2)                                                                                          | 220(2)                                                                                           | 220(2)                                                                                           | 220(2)                                                                                                          |
| <i>F</i> (000)                                                    | 4208                                                                                            | 4208                                                                                            | 4704                                                                                             | 4704                                                                                             | 5136                                                                                                            |
| Absorption coefficient/mm <sup>-1</sup>                           | 0.835                                                                                           | 0.834                                                                                           | 1.071                                                                                            | 1.081                                                                                            | 3.407                                                                                                           |
| Reflections collected/unique                                      | 35408 / 3675                                                                                    | 36053 / 3685                                                                                    | 33168 / 3743                                                                                     | 27746 / 3670                                                                                     | 38059 / 3673                                                                                                    |
| <i>R</i> (int)                                                    | 0.0483                                                                                          | 0.0443                                                                                          | 0.0435                                                                                           | 0.0620                                                                                           | 0.0710                                                                                                          |
| Data/restraints/parameters                                        | 3675 / 6 / 200                                                                                  | 3685 / 6 / 200                                                                                  | 3743 / 0 / 198                                                                                   | 3670 / 0 / 198                                                                                   | 3673 / 0 / 198                                                                                                  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                          | 1.029                                                                                           | 1.025                                                                                           | 1.039                                                                                            | 1.015                                                                                            | 1.017                                                                                                           |
| <i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]   | 0.0566                                                                                          | 0.0546                                                                                          | 0.0366                                                                                           | 0.0546                                                                                           | 0.0427                                                                                                          |
| w <i>R</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )] | 0.1492                                                                                          | 0.1466                                                                                          | 0.1046                                                                                           | 0.1180                                                                                           | 0.1100                                                                                                          |
| <i>R</i> <sub>1</sub> <sup>a</sup> (all data)                     | 0.0731                                                                                          | 0.0703                                                                                          | 0.0429                                                                                           | 0.0903                                                                                           | 0.0612                                                                                                          |
| w <i>R</i> <sub>2</sub> <sup>b</sup> (all data)                   | 0.1627                                                                                          | 0.1606                                                                                          | 0.1091                                                                                           | 0.1336                                                                                           | 0.1199                                                                                                          |
| Flack parameter                                                   | -0.01(5)                                                                                        | -0.04(5)                                                                                        | 0.04(3)                                                                                          | 0.02(5)                                                                                          | 0.034(15)                                                                                                       |
| CCDC number                                                       | 1417887                                                                                         | 1417893                                                                                         | 1448704                                                                                          | 1448740                                                                                          | 1449166                                                                                                         |

<sup>[a]</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

<sup>[b]</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

**Table S2.** Crystal data and refinement parameters for complexes **3-P**, **L-BPAM@1-M**, **D-BPAM@1-P**, **D-BPAM@1-M** and **L-BPAM@1-P**.

| Compound                                                          | <b>3-P</b>                                                                                                      | <b>L-BPAM@1-M</b>                                                                               | <b>D-BPAM@1-P</b>                                                                               | <b>D-BPAM@1-M</b>                                                                               | <b>L-BPAM@1-P</b>                                                                               |
|-------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Empirical formula                                                 | C <sub>78</sub> H <sub>62</sub> Ag <sub>3</sub> Br <sub>6</sub> Cl <sub>9</sub> N <sub>22</sub> O <sub>12</sub> | C <sub>83</sub> H <sub>75</sub> Ag <sub>3</sub> Cl <sub>3</sub> N <sub>21</sub> O <sub>15</sub> | C <sub>83</sub> H <sub>75</sub> Ag <sub>3</sub> Cl <sub>3</sub> N <sub>21</sub> O <sub>15</sub> | C <sub>83</sub> H <sub>75</sub> Ag <sub>3</sub> Cl <sub>3</sub> N <sub>21</sub> O <sub>15</sub> | C <sub>83</sub> H <sub>75</sub> Ag <sub>3</sub> Cl <sub>3</sub> N <sub>21</sub> O <sub>15</sub> |
| Formula weight                                                    | 2621.62                                                                                                         | 2036.60                                                                                         | 2036.60                                                                                         | 2036.60                                                                                         | 2036.60                                                                                         |
| Crystal system                                                    | Cubic                                                                                                           | Cubic                                                                                           | Cubic                                                                                           | Cubic                                                                                           | Cubic                                                                                           |
| Space group                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       | <i>I</i> 2 <sub>1</sub> 3                                                                       |
| <i>a</i> /Å                                                       | 21.3221(3)                                                                                                      | 21.5932(13)                                                                                     | 21.5496(3)                                                                                      | 21.6586(5)                                                                                      | 21.6426(5)                                                                                      |
| <i>b</i> /Å                                                       | 21.3221(3)                                                                                                      | 21.5932(13)                                                                                     | 21.5496(3)                                                                                      | 21.6586(5)                                                                                      | 21.6426(5)                                                                                      |
| <i>c</i> /Å                                                       | 21.3221(3)                                                                                                      | 21.5932(13)                                                                                     | 21.5496(3)                                                                                      | 21.6586(5)                                                                                      | 21.6426(5)                                                                                      |
| $\alpha$ /°                                                       | 90                                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              |
| $\beta$ /°                                                        | 90                                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              |
| $\gamma$ /°                                                       | 90                                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              | 90                                                                                              |
| <i>V</i> /Å <sup>3</sup>                                          | 9693.7(2)                                                                                                       | 10068.2(10)                                                                                     | 10007.3(2)                                                                                      | 10159.9(4)                                                                                      | 10137.4(4)                                                                                      |
| <i>Z</i>                                                          | 4                                                                                                               | 4                                                                                               | 4                                                                                               | 4                                                                                               | 4                                                                                               |
| <i>D<sub>c</sub></i> /(g·cm <sup>-3</sup> )                       | 1.796                                                                                                           | 1.344                                                                                           | 1.352                                                                                           | 1.331                                                                                           | 1.334                                                                                           |
| <i>T</i> (K)                                                      | 220(2)                                                                                                          | 220(2)                                                                                          | 220(2)                                                                                          | 220(2)                                                                                          | 220(2)                                                                                          |
| <i>F</i> (000)                                                    | 5136                                                                                                            | 4128                                                                                            | 4128                                                                                            | 4128                                                                                            | 4128                                                                                            |
| Absorption coefficient/mm <sup>-1</sup>                           | 3.389                                                                                                           | 0.724                                                                                           | 0.728                                                                                           | 0.717                                                                                           | 0.719                                                                                           |
| Reflections collected/unique                                      | 37153 / 3668                                                                                                    | 27952 / 2952                                                                                    | 29235 / 2941                                                                                    | 25307 / 2982                                                                                    | 29312 / 2986                                                                                    |
| <i>R</i> (int)                                                    | 0.0512                                                                                                          | 0.0582                                                                                          | 0.0541                                                                                          | 0.0989                                                                                          | 0.0907                                                                                          |
| Data/restraints/parameters                                        | 3668 / 0 / 198                                                                                                  | 2952 / 58 / 223                                                                                 | 2941 / 62 / 223                                                                                 | 2982 / 62 / 223                                                                                 | 2986 / 62 / 223                                                                                 |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                          | 1.073                                                                                                           | 1.058                                                                                           | 1.075                                                                                           | 1.048                                                                                           | 1.068                                                                                           |
| <i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]   | 0.0373                                                                                                          | 0.0665                                                                                          | 0.0722                                                                                          | 0.0785                                                                                          | 0.0774                                                                                          |
| w <i>R</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )] | 0.1085                                                                                                          | 0.1696                                                                                          | 0.1917                                                                                          | 0.1987                                                                                          | 0.1976                                                                                          |
| <i>R</i> <sub>1</sub> <sup>a</sup> (all data)                     | 0.0466                                                                                                          | 0.1041                                                                                          | 0.0952                                                                                          | 0.1182                                                                                          | 0.1099                                                                                          |
| w <i>R</i> <sub>2</sub> <sup>b</sup> (all data)                   | 0.1155                                                                                                          | 0.1870                                                                                          | 0.2093                                                                                          | 0.2215                                                                                          | 0.2193                                                                                          |
| Flack parameter                                                   | 0.048(13)                                                                                                       | 0.01(7)                                                                                         | 0.07(7)                                                                                         | 0.07(8)                                                                                         | 0.03(8)                                                                                         |
| CCDC number                                                       | 1449160                                                                                                         | 1417911                                                                                         | 1457367                                                                                         | 1457368                                                                                         | 1457369                                                                                         |

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

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**Table S3.** A summary of structure determinations of six randomly selected crystals for **1** grown in the absence of chiral templates: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)    | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.3203(3) | 9691.3(2)             | 0.0566 | 0.1635 | -0.05(5)        | $P$                         | 1417905  |
| 2  | $I2_13$     | 21.3457(3) | 9725.9(2)             | 0.0583 | 0.1658 | 0.01(5)         | $M$                         | 1417906  |
| 3  | $I2_13$     | 21.3361(4) | 9712.8(3)             | 0.0600 | 0.1775 | -0.03(5)        | $P$                         | 1417907  |
| 4  | $I2_13$     | 21.2948(3) | 9656.5(2)             | 0.0598 | 0.1714 | -0.05(6)        | $M$                         | 1417908  |
| 5  | $I2_13$     | 21.3220(3) | 9693.6(2)             | 0.0619 | 0.1717 | -0.01(5)        | $M$                         | 1417909  |
| 6  | $I2_13$     | 21.3474(4) | 9728.3(3)             | 0.0646 | 0.1967 | 0.02(6)         | $P$                         | 1417910  |

**Table S4.** A summary of structure determinations of six randomly selected crystals for **1-M** grown in the presence of **L-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)     | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|-------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.3062(3)  | 9672.0(2)             | 0.0566 | 0.1627 | -0.01(5)        | $M$                         | 1417887  |
| 2  | $I2_13$     | 21.2987(3)  | 9661.8(2)             | 0.0589 | 0.1661 | 0.00(5)         | $M$                         | 1417888  |
| 3  | $I2_13$     | 21.3054(3)  | 9671.0(2)             | 0.0616 | 0.1726 | 0.00(6)         | $M$                         | 1417889  |
| 4  | $I2_13$     | 21.3483(4)  | 9729.5(3)             | 0.0659 | 0.1840 | 0.03(6)         | $M$                         | 1417890  |
| 5  | $I2_13$     | 21.3000(5)  | 9663.6(4)             | 0.0667 | 0.1757 | 0.01(6)         | $M$                         | 1417891  |
| 6  | $I2_13$     | 21.4745(11) | 9903.1(9)             | 0.0695 | 0.2019 | 0.01(6)         | $M$                         | 1417892  |

**Table S5.** A summary of structure determinations of six randomly selected crystals for **1-P** grown in the presence of **D-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)    | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.3212(3) | 9692.5(2)             | 0.0546 | 0.1606 | -0.04(5)        | $P$                         | 1417893  |
| 2  | $I2_13$     | 21.3496(3) | 9731.3(2)             | 0.0594 | 0.1724 | -0.07(5)        | $P$                         | 1417894  |
| 3  | $I2_13$     | 21.2904(3) | 9650.5(2)             | 0.0601 | 0.1703 | -0.05(5)        | $P$                         | 1417895  |
| 4  | $I2_13$     | 21.3038(3) | 9668.8(2)             | 0.0602 | 0.1705 | -0.06(5)        | $P$                         | 1417896  |
| 5  | $I2_13$     | 21.3228(3) | 9694.7(2)             | 0.0618 | 0.1756 | -0.04(6)        | $P$                         | 1417897  |
| 6  | $I2_13$     | 21.3193(3) | 9689.9(2)             | 0.0621 | 0.1737 | -0.01(6)        | $P$                         | 1417898  |

**Table S6.** A summary of structure determinations of six randomly selected crystals for **2-M** grown in the presence of **L-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)     | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|-------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.3930(4)  | 9790.7(3)             | 0.0366 | 0.1091 | 0.04(3)         | $M$                         | 1448704  |
| 2  | $I2_13$     | 21.3180(3)  | 9688.1(2)             | 0.0466 | 0.1217 | -0.01(4)        | $M$                         | 1448705  |
| 3  | $I2_13$     | 21.3281(11) | 9701.9(9)             | 0.0501 | 0.1162 | 0.00(4)         | $M$                         | 1448706  |
| 4  | $I2_13$     | 21.3446(3)  | 9724.4(2)             | 0.0500 | 0.1260 | -0.04(4)        | $M$                         | 1448707  |
| 5  | $I2_13$     | 21.3528(3)  | 9735.6(2)             | 0.0552 | 0.1319 | -0.01(4)        | $M$                         | 1448708  |
| 6  | $I2_13$     | 21.3847(5)  | 9779.3(4)             | 0.0568 | 0.1351 | -0.03(5)        | $M$                         | 1448709  |

**Table S7.** A summary of structure determinations of six randomly selected crystals for **2-P** grown in the presence of **D-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)    | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.3239(4) | 9696.2(3)             | 0.0546 | 0.1336 | 0.02(5)         | $P$                         | 1448740  |
| 2  | $I2_13$     | 21.3432(3) | 9722.5(2)             | 0.0666 | 0.1653 | -0.02(6)        | $P$                         | 1448741  |
| 3  | $I2_13$     | 21.2788(5) | 9634.8(4)             | 0.0555 | 0.1307 | 0.00(5)         | $P$                         | 1448742  |
| 4  | $I2_13$     | 21.3154(4) | 9684.6(3)             | 0.0597 | 0.1425 | -0.01(5)        | $P$                         | 1448743  |
| 5  | $I2_13$     | 21.3288(4) | 9702.8(3)             | 0.0542 | 0.1308 | -0.04(5)        | $P$                         | 1448744  |
| 6  | $I2_13$     | 21.3018(4) | 9666.0(3)             | 0.0573 | 0.1496 | 0.01(5)         | $P$                         | 1448745  |

**Table S8.** A summary of structure determinations of six randomly selected crystals for **3-M** grown in the presence of **L-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group | $a$ (Å)    | $V$ (Å <sup>3</sup> ) | $R_1$  | $wR_2$ | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|-------------|------------|-----------------------|--------|--------|-----------------|-----------------------------|----------|
| 1  | $I2_13$     | 21.2844(3) | 9642.4(2)             | 0.0427 | 0.1199 | 0.034(15)       | $M$                         | 1449166  |
| 2  | $I2_13$     | 21.160(16) | 9474.3(2)             | 0.1185 | 0.2948 | 0.07(5)         | $M$                         | 1449167  |
| 3  | $I2_13$     | 21.287(2)  | 9645.9(2)             | 0.1032 | 0.2570 | 0.06(4)         | $M$                         | 1449168  |
| 4  | $I2_13$     | 21.3238(3) | 9696.0(2)             | 0.0344 | 0.1074 | 0.05(12)        | $M$                         | 1449169  |
| 5  | $I2_13$     | 21.154(2)  | 9466.9(2)             | 0.1079 | 0.2839 | 0.07(4)         | $M$                         | 1449170  |
| 6  | $I2_13$     | 21.2804(4) | 9636.9(3)             | 0.0461 | 0.1202 | 0.022(15)       | $M$                         | 1449171  |

**Table S9.** A summary of structure determinations of six randomly selected crystals for **3-P** grown in the presence of **D-BPAM**: Cell parameters, R factors, Flack absolute structure parameters for each refinement are given.

| SN | Space group               | <i>a</i> (Å) | <i>V</i> (Å <sup>3</sup> ) | <i>R</i> <sub>1</sub> | <i>wR</i> <sub>2</sub> | Flack parameter | Configuration of silver (I) | CCDC No. |
|----|---------------------------|--------------|----------------------------|-----------------------|------------------------|-----------------|-----------------------------|----------|
| 1  | <i>I</i> 2 <sub>1</sub> 3 | 21.3221(3)   | 9693.7(2)                  | 0.0373                | 0.1155                 | 0.048(13)       | <i>P</i>                    | 1449160  |
| 2  | <i>I</i> 2 <sub>1</sub> 3 | 21.3186(11)  | 9688.9(9)                  | 0.0372                | 0.1147                 | 0.061(13)       | <i>P</i>                    | 1449161  |
| 3  | <i>I</i> 2 <sub>1</sub> 3 | 21.3189(3)   | 9689.3(2)                  | 0.0366                | 0.1150                 | 0.058(13)       | <i>P</i>                    | 1449162  |
| 4  | <i>I</i> 2 <sub>1</sub> 3 | 21.2287(5)   | 9566.9(4)                  | 0.0787                | 0.2828                 | 0.110(4)        | <i>P</i>                    | 1449163  |
| 5  | <i>I</i> 2 <sub>1</sub> 3 | 21.3154(3)   | 9684.6(2)                  | 0.0355                | 0.1109                 | 0.029(13)       | <i>P</i>                    | 1449164  |
| 6  | <i>I</i> 2 <sub>1</sub> 3 | 21.3139(3)   | 9682.5(2)                  | 0.0432                | 0.1294                 | 0.010(16)       | <i>P</i>                    | 1449165  |

**Table S10.** Catalytic results of five parallel cycloaddition reactions between **PGE** and methyl acrylate catalyzed by **1** randomly collected from five isolated crystallization batches.

| Entry | Conversion | <i>ee</i> |
|-------|------------|-----------|
| a     | 84%        | -26%      |
| b     | 85%        | 38%       |
| c     | 80%        | 27%       |
| d     | 87%        | -11%      |
| e     | 81%        | -45%      |

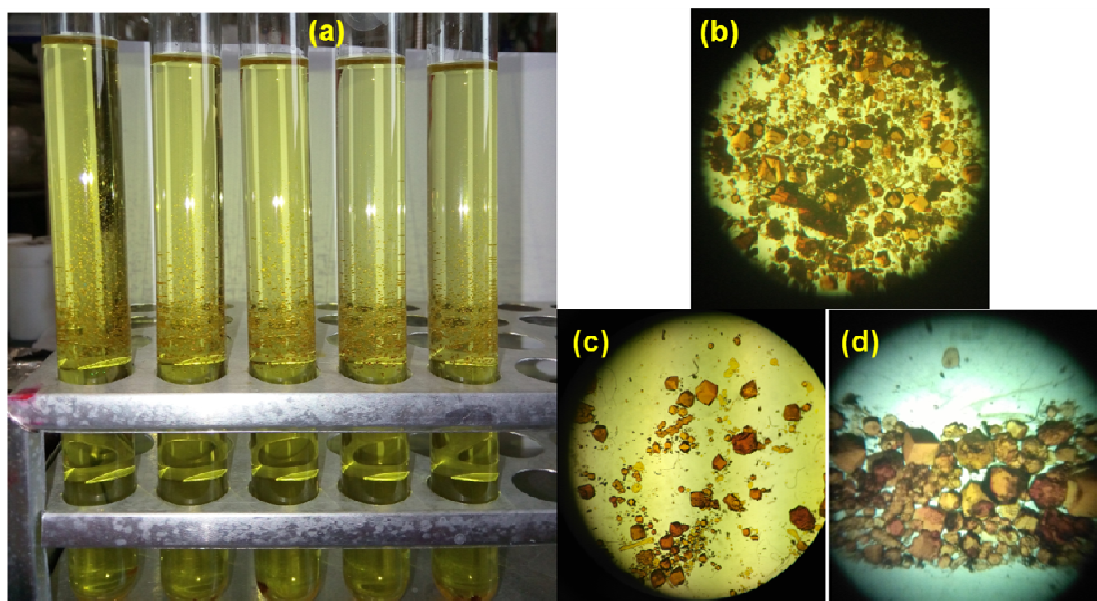
**Table S11.** The catalytic results of the tandem systems of **2+L-BPAM** and **3+L-BPAM**.

| <b>2+L-BPAM</b> |            |           | <b>3+L-BPAM</b> |            |           |
|-----------------|------------|-----------|-----------------|------------|-----------|
| Entry           | Conversion | <i>ee</i> | Entry           | Conversion | <i>ee</i> |
| a               | 89%        | 51%       | f               | 90%        | 60%       |
| b               | 92%        | 53%       | g               | 89%        | 56%       |
| c               | 87%        | 47%       | h               | 91%        | 54%       |
| d               | 91%        | 52%       | i               | 90%        | 67%       |
| e               | 92%        | 60%       | j               | 86%        | 59%       |

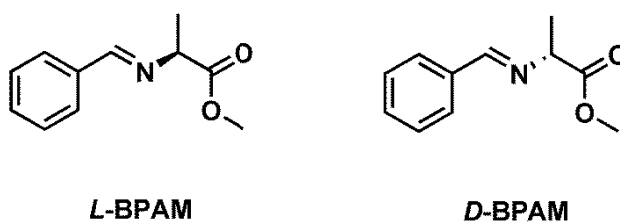
**Table S12.** The catalytic results of the tandem systems of **2+D-BPAM** and **3+D-BPAM**.

| <b>2+D-BPAM</b> |            |           | <b>3+D-BPAM</b> |            |           |
|-----------------|------------|-----------|-----------------|------------|-----------|
| Entry           | Conversion | <i>ee</i> | Entry           | Conversion | <i>ee</i> |
| a               | 90%        | -57%      | f               | 87%        | -58%      |
| b               | 88%        | -54%      | g               | 91%        | -64%      |
| c               | 89%        | -49%      | h               | 89%        | -60%      |
| d               | 86%        | -52%      | i               | 88%        | -55%      |
| e               | 91%        | -58%      | j               | 92%        | -59%      |

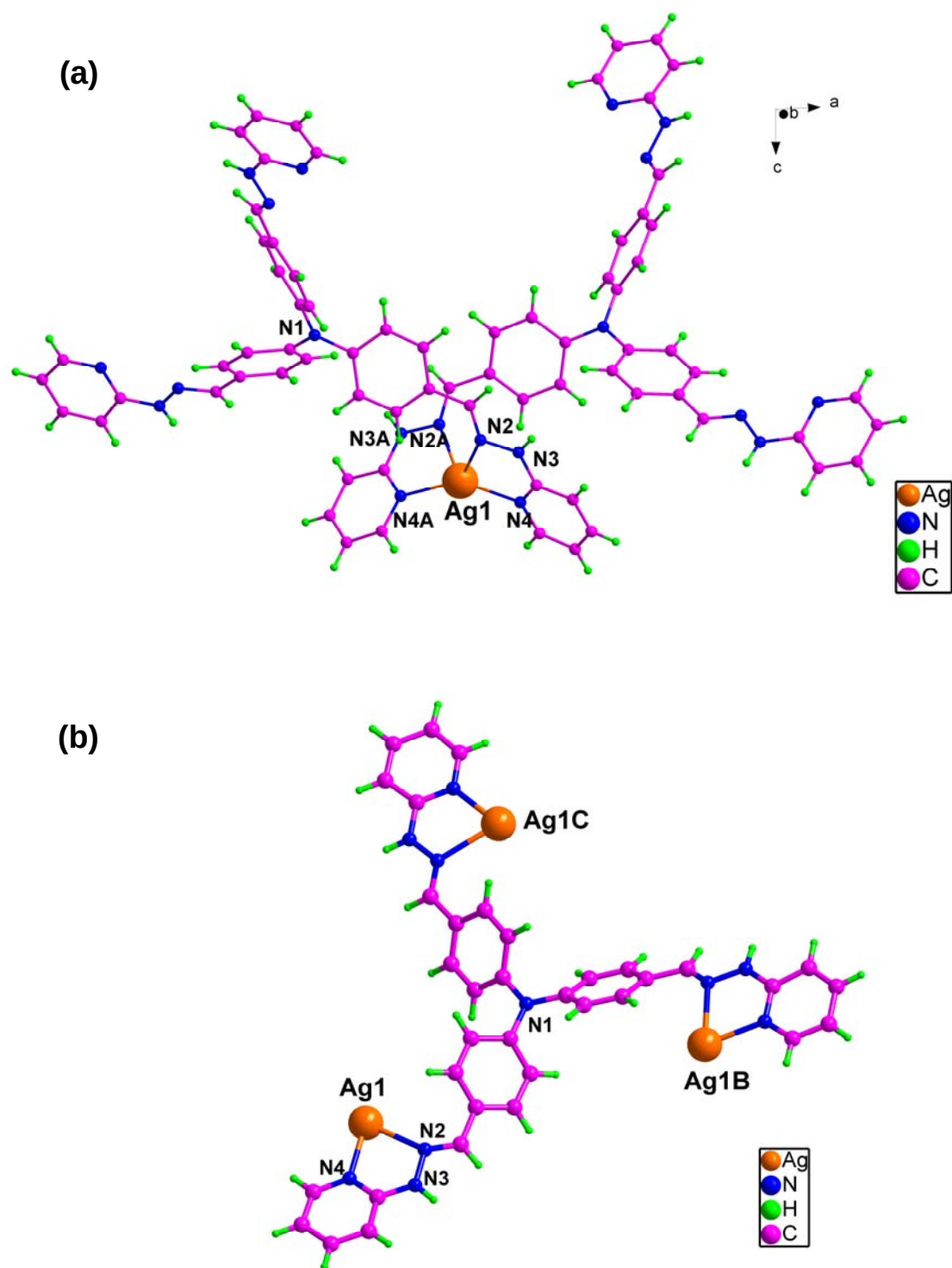
## Supplementary Figures



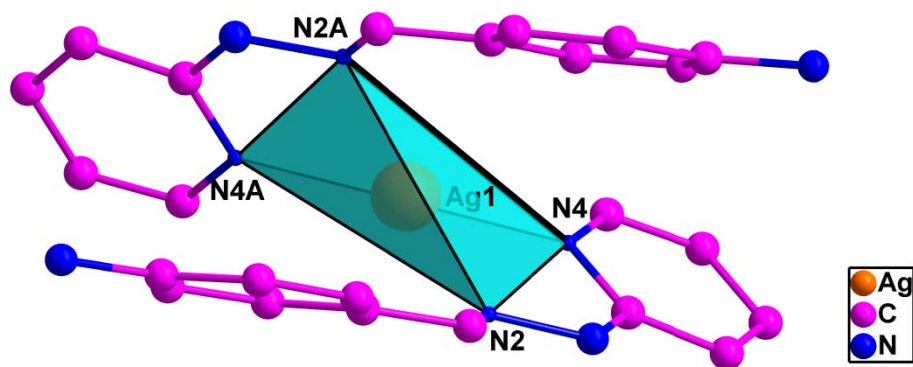
**Figure S1.** (a) The crystallization of Ag(I)-based MOFs *via* solution-layering diffusion. Optical microscope images of single crystals for **1** (b), **2** (c) and **3** (d).



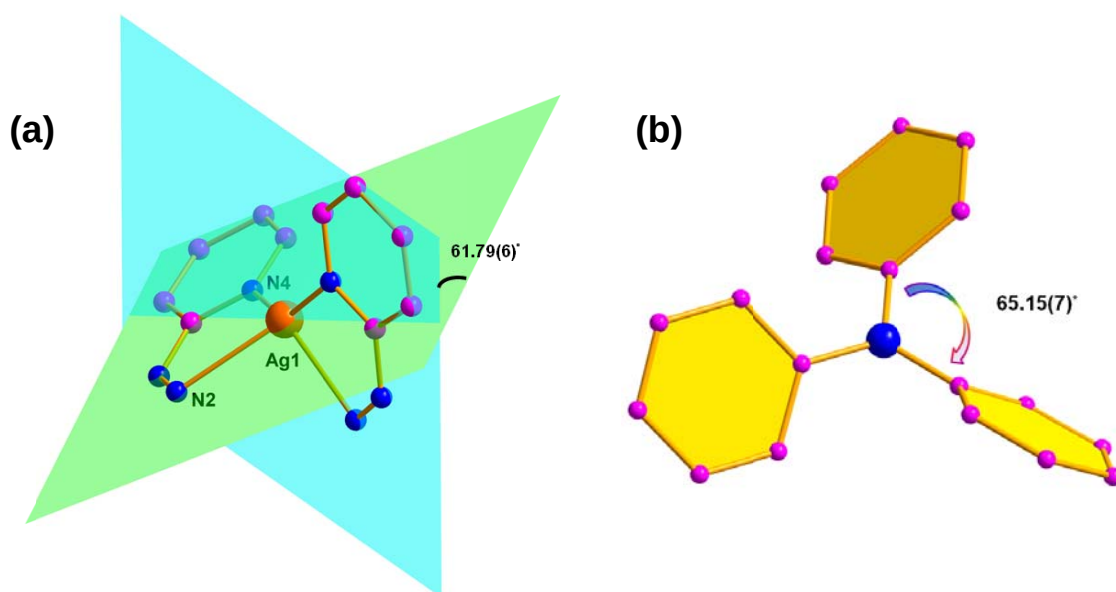
**Figure S2.** Structural formula of (*S,E*)-methyl-2-(benzylideneamino)propanoate (**L-BPAM**) and (*R,E*)-methyl-2-(benzylideneamino)propanoate (**D-BPAM**).



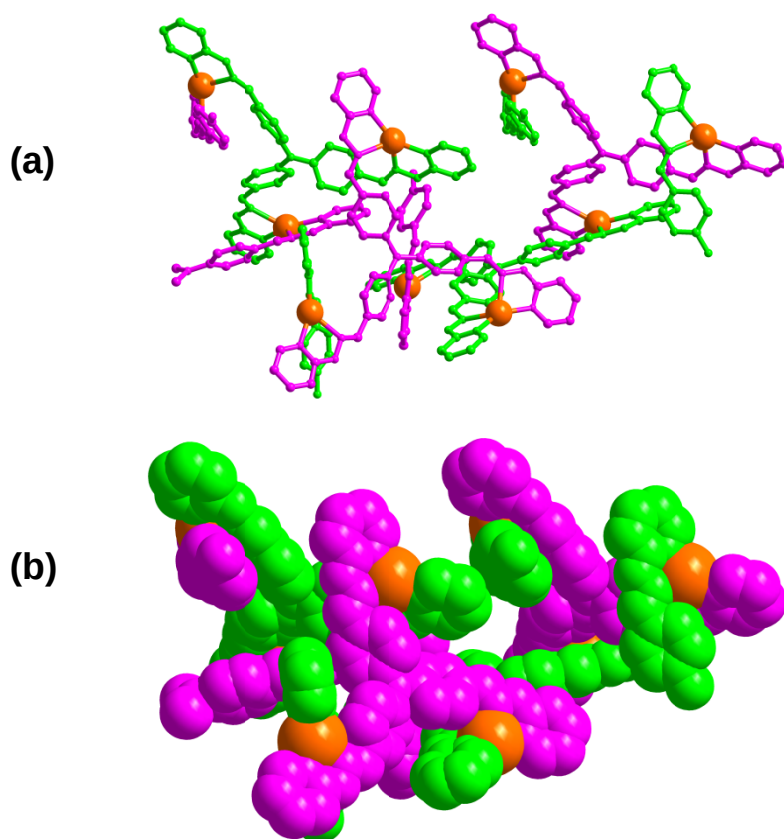
**Figure S3.** Coordination environments of the silver(I) ion (a) and  $L_1$  ligand (b) in **1**. Symmetry code: A,  $-x, -y+1/2, z$ ; B:  $x+1/2, y-1/2, z-1/2$ ; C,  $-x, y+1/2, -z+1/2$ .



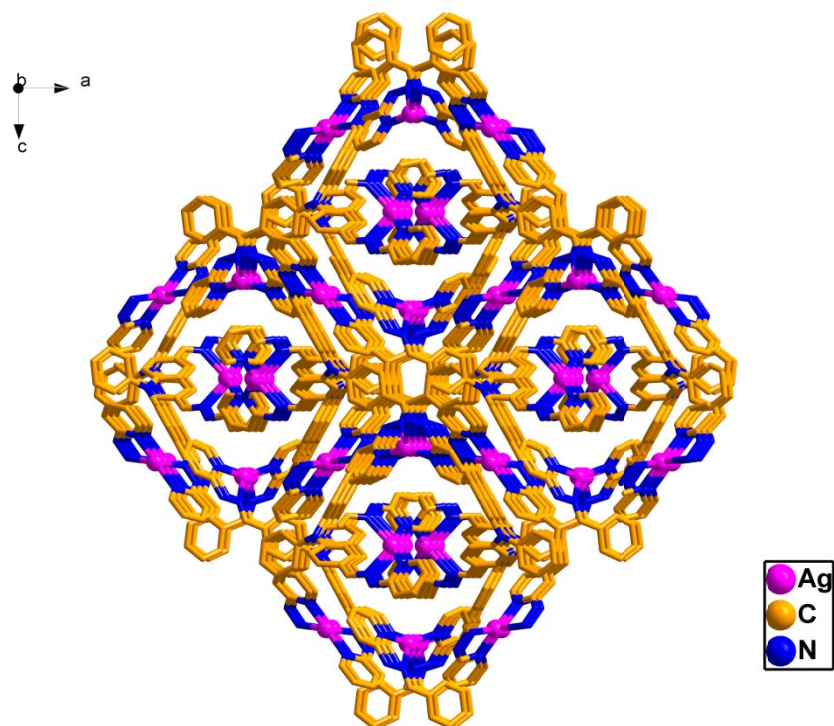
**Figure S4.** The distorted tetrahedral coordination geometry of Ag(I) ion with selected labelling scheme in **1** (Symmetry code: A  $-x+5/2, y, -z$ ). In the tetrahedron, the crystallographically independent Ag(1) ion is coordinated by two nitrogen atoms from one  $L_1$  ligand [Ag(1)-N(4) 2.197(4) Å, Ag(1)-N(2) 2.429(3) Å] and two equivalent nitrogen atoms from another  $L_1$  ligand. Selected bond angle: N(4A)-Ag(1)-N(4) 147.25(19)°, N(4A)-Ag(1)-N(2) 132.96(14)°, N(4)-Ag(1)-N(2) 72.17(13)°, N(2)-Ag(1)-N(2A) 96.53(16)°.



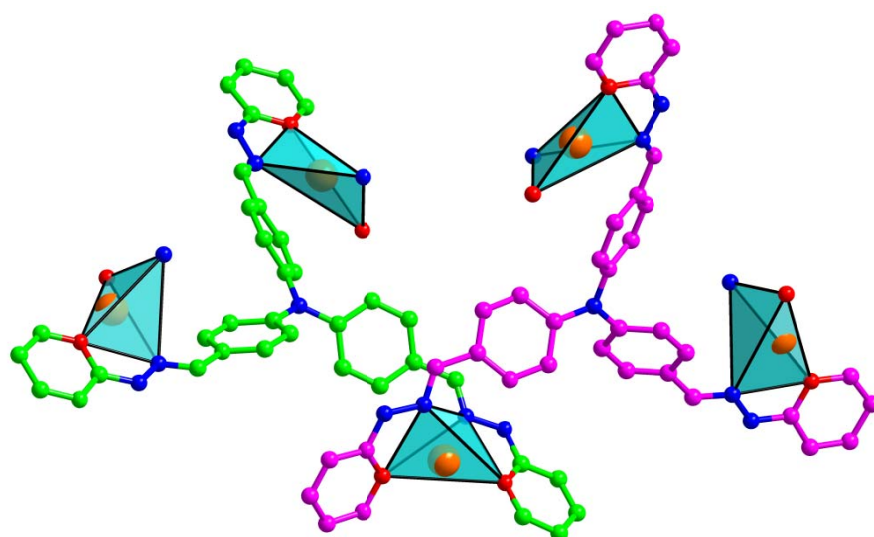
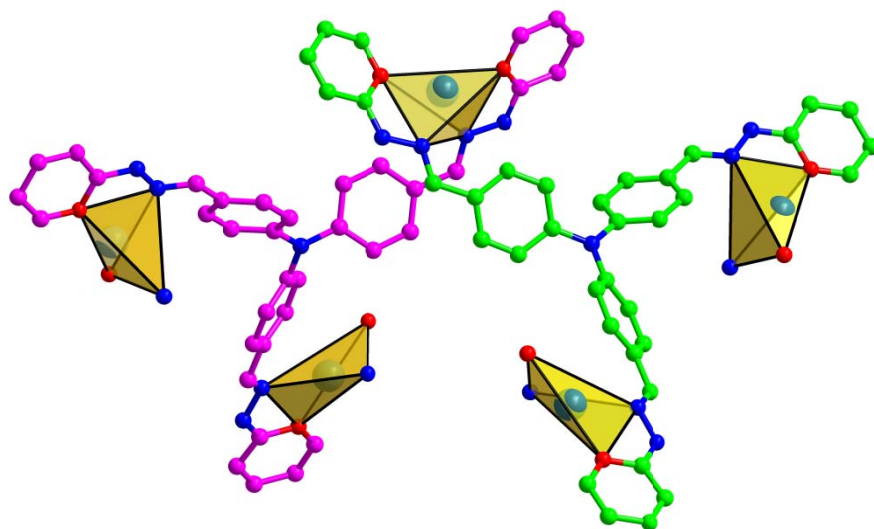
**Figure S5.** (a) The dihedral angle [61.79(6)°] between the bidentate chelating planes in **1**. (b) The dihedral angle [65.15(7)°] between the two phenyl rings of triphenylamine moiety in **1**.



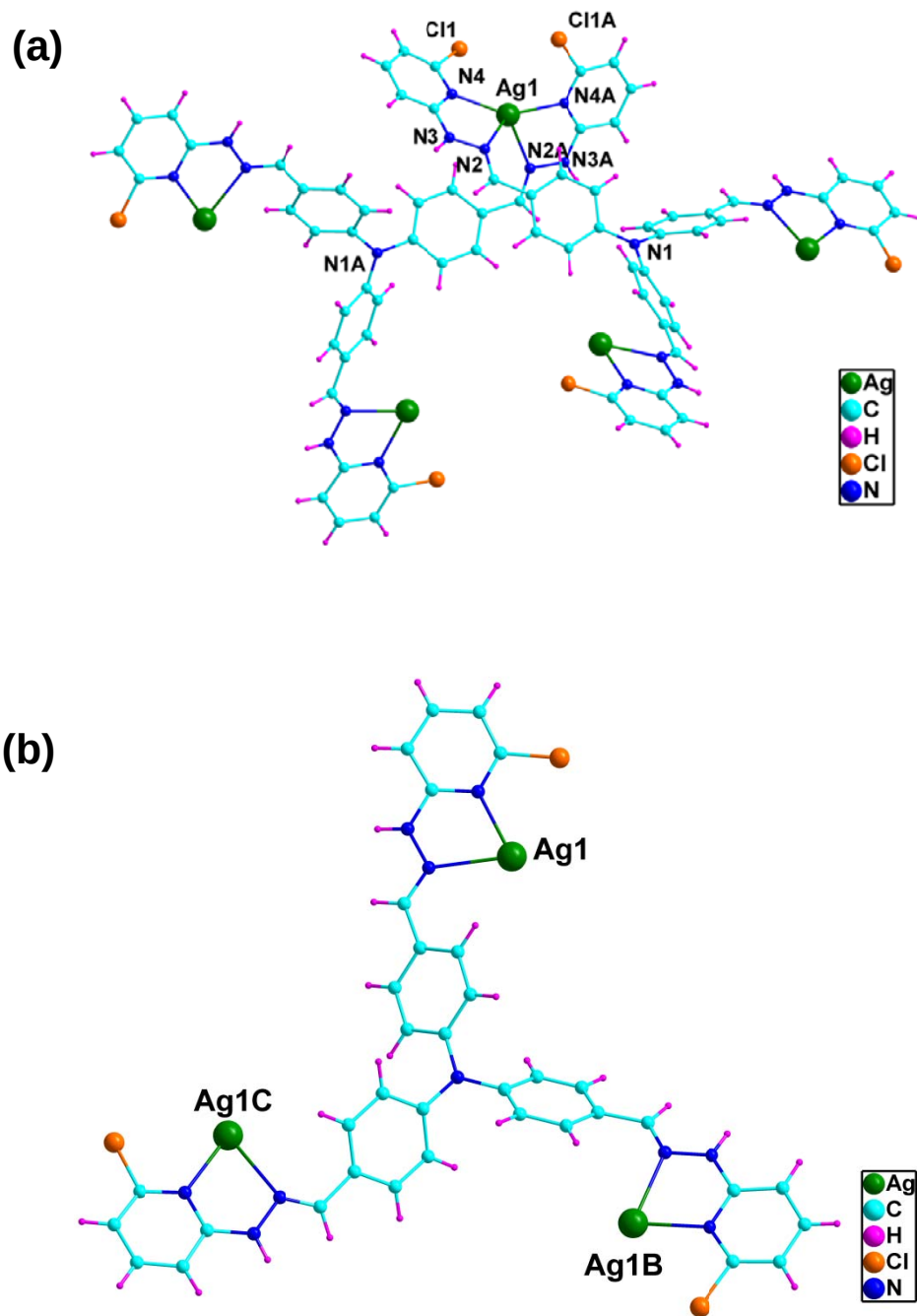
**Figure S6.** Helical moieties in **1** shown in Ball-Stick mode (a) and Spacefill mode (b), respectively.



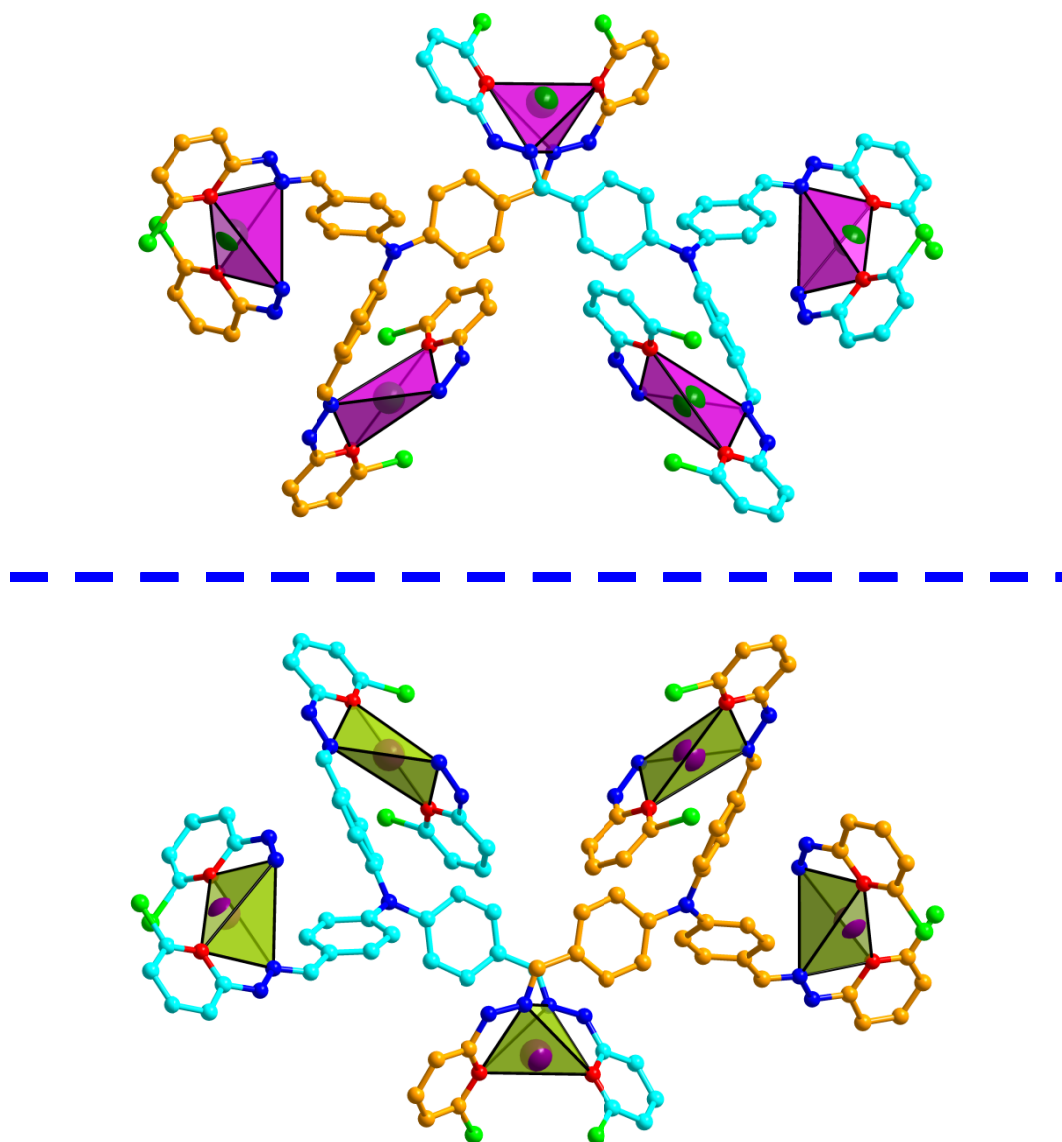
**Figure S7.** 3D framework of **1**. All H atoms, counter ions and solvent molecules are omitted for clarity.



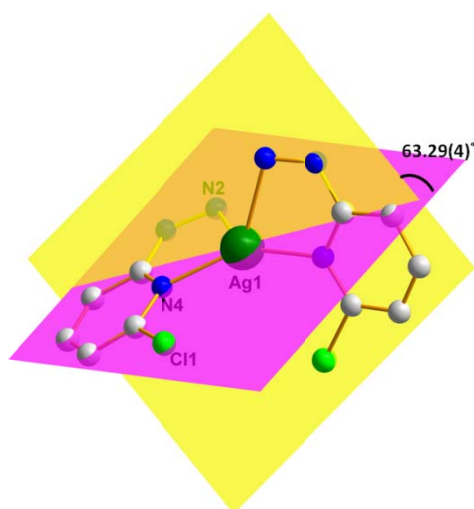
**Figure S8.** The mirror relationship chart of **1-M** (up) and **1-P** (down), showing the distorted tetrahedral silver(I) centers, red balls represent the pyridine N atoms.



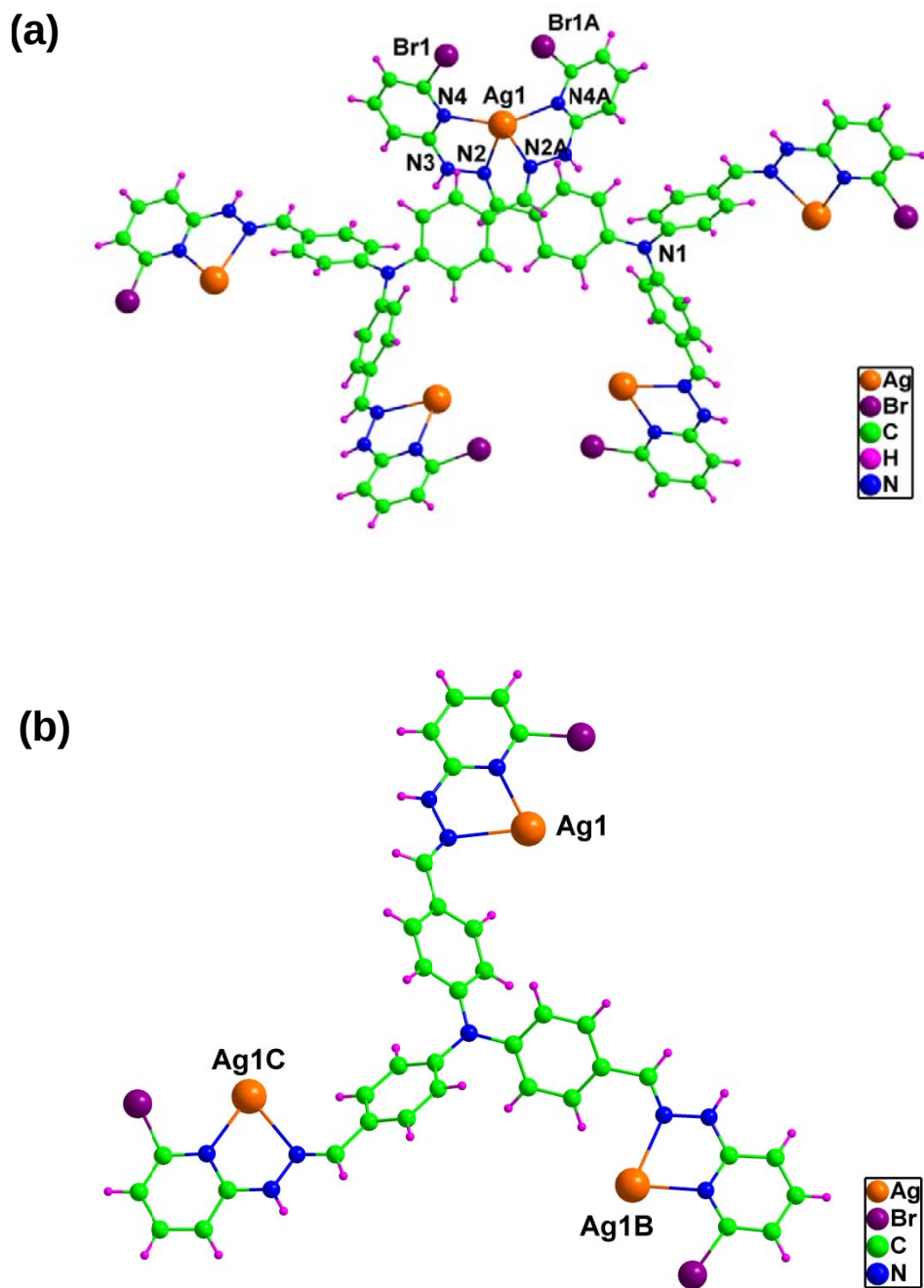
**Figure S9.** Coordination environments of silver(I) (a) and  $L_2$  ligand (b) in **2**. Selected bond lengths and angles: Ag(1)-N(4) 2.227(3) Å, Ag(1)-N(2) 2.434(3) Å; N(4A)-Ag(1)-N(4) 148.07(15)°, N(4A)-Ag(1)-N(2) 132.92(10)°, N(4)-Ag(1)-N(2) 71.93(9)°, N(2)-Ag(1)-N(2A) 95.26(11)°. Symmetry code: A,  $x+1/2, y-1/2, z-1/2$ ; B:  $x+1/2, -y+3/2, -z+2$ ; C,  $x+1/2, y+1/2, z-1/2$ .



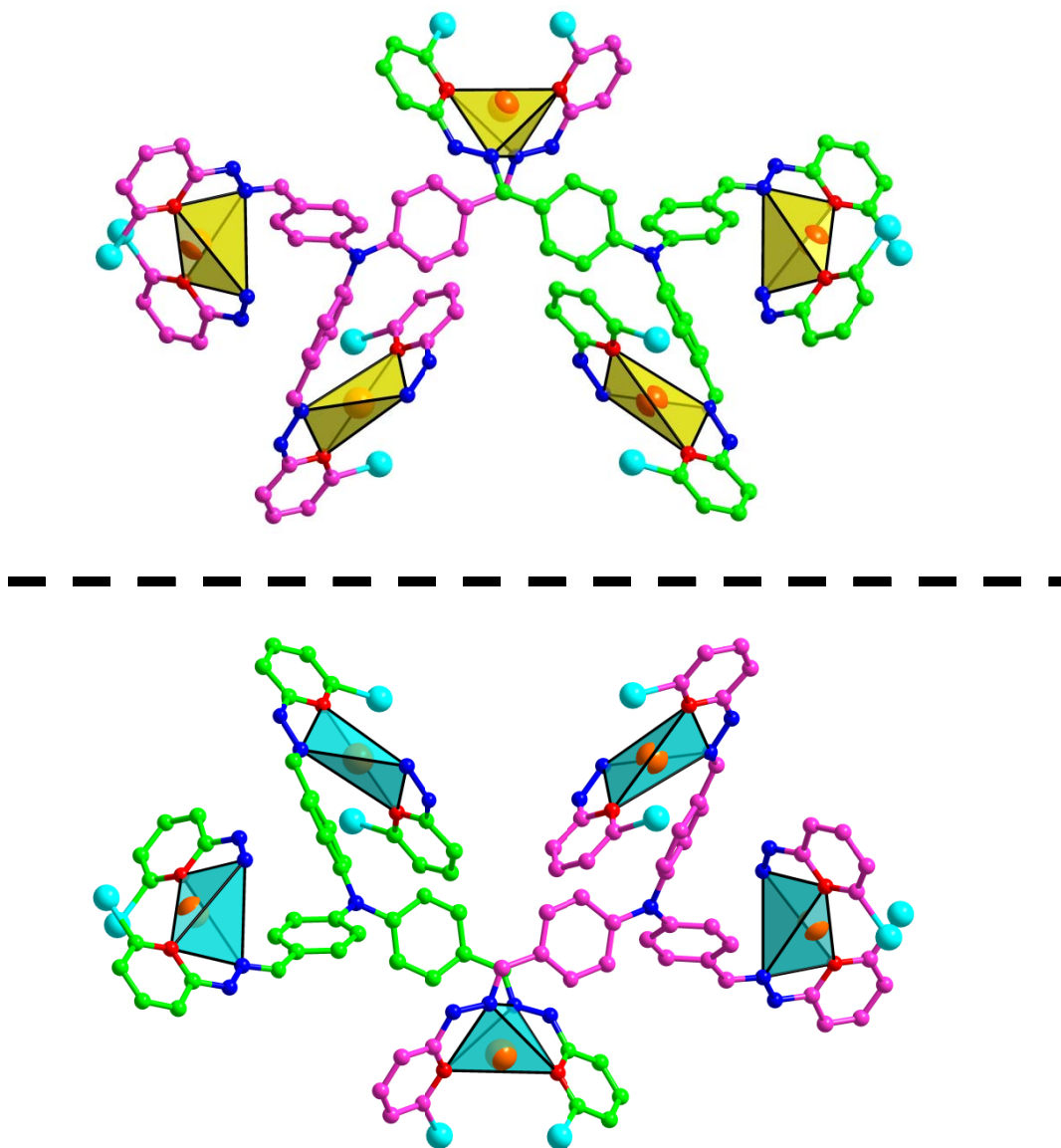
**Figure S10.** The mirror image structures of **2-M** (up) and **2-P** (down), showing the distorted tetrahedral silver(I) centers. Red balls: pyridine N atoms; bright green balls: chloro atoms.



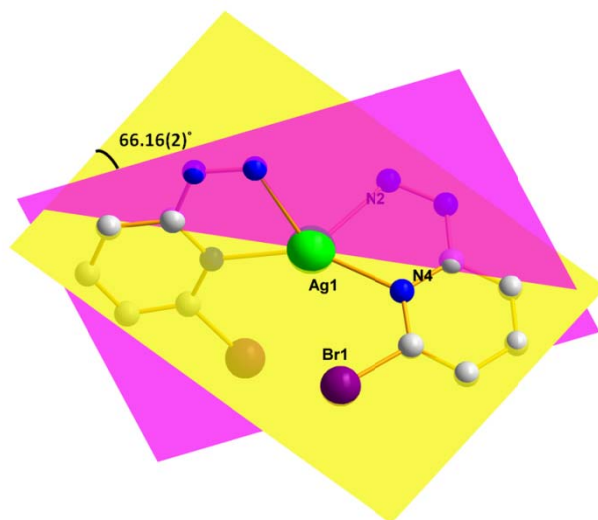
**Figure S11.** The dihedral angle [ $63.29(4)^\circ$ ] between the bidentate chelating planes in **2**.



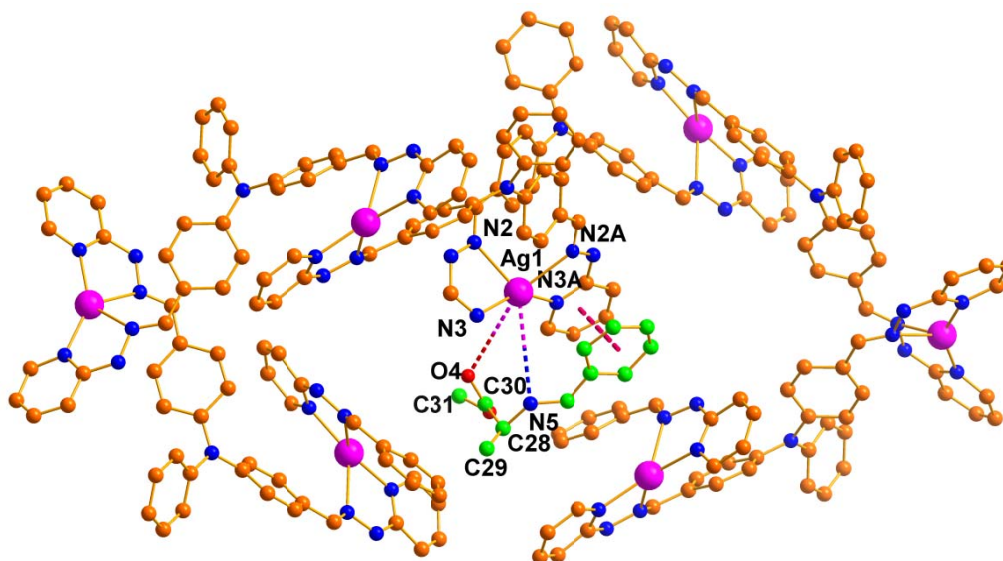
**Figure S12.** Coordination environments of silver(I) (a) and  $L_3$  ligand (b) in **3**. Selected bond lengths and angles: Ag(1)-N(4) 2.238(3) Å, Ag(1)-N(2) 2.439(3) Å; N(4A)-Ag(1)-N(4) 150.8(2)°, N(4A)-Ag(1)-N(2) 131.15(12)°, N(4)-Ag(1)-N(2) 71.71(12)°, N(2)-Ag(1)-N(2A) 93.89(16)°. Symmetry code: A,  $-x+1/2, y, -z+1$ ; B:  $x+1/2, y+1/2, z-1/2$ ; C,  $-x, -y+1/2, z$ .



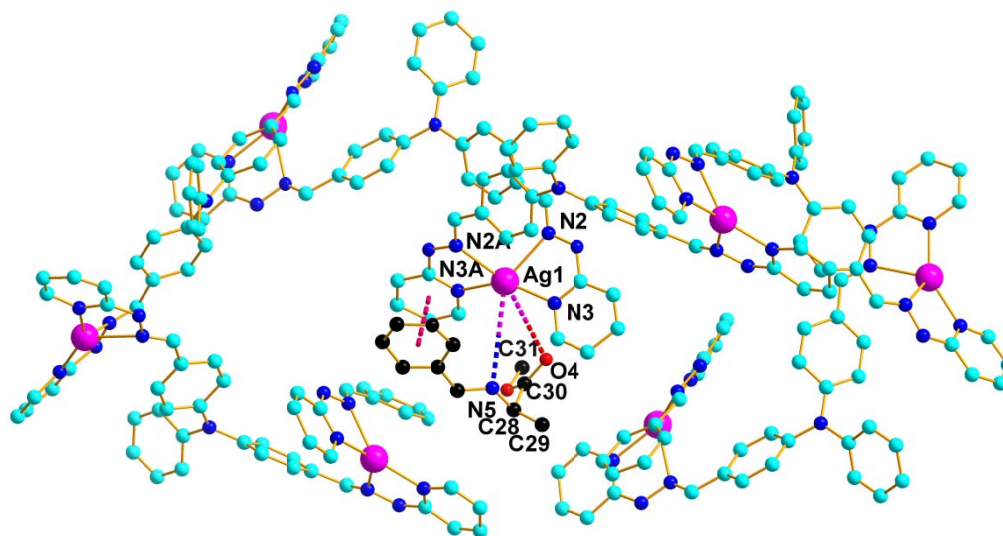
**Figure S13.** The mirror image structures of **3-M** (up) and **3-P** (down), showing the distorted tetrahedral silver(I) centers. Red balls: pyridine N atoms; turquoise balls: bromo atoms.



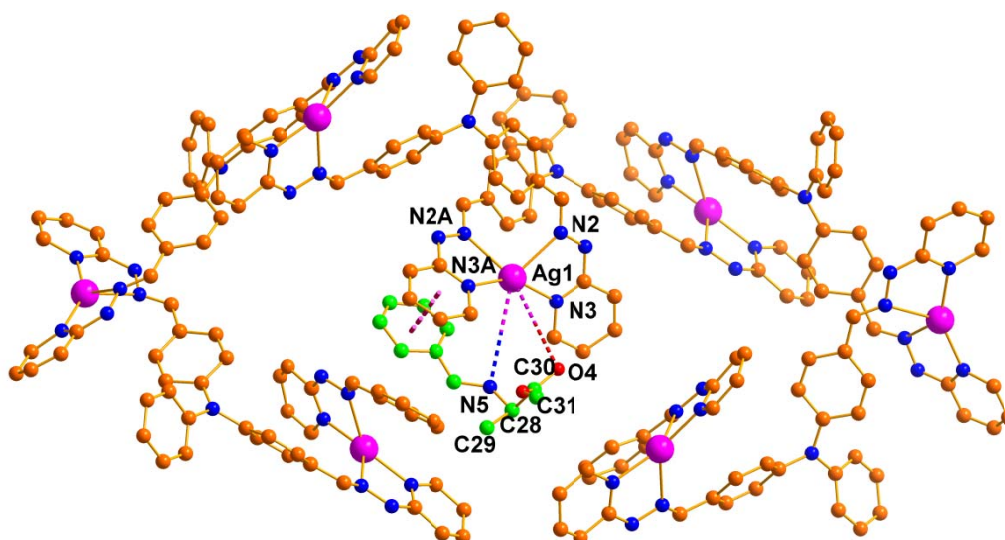
**Figure S14.** The dihedral angle [ $66.16(2)^\circ$ ] between the bidentate chelating planes in **3**.



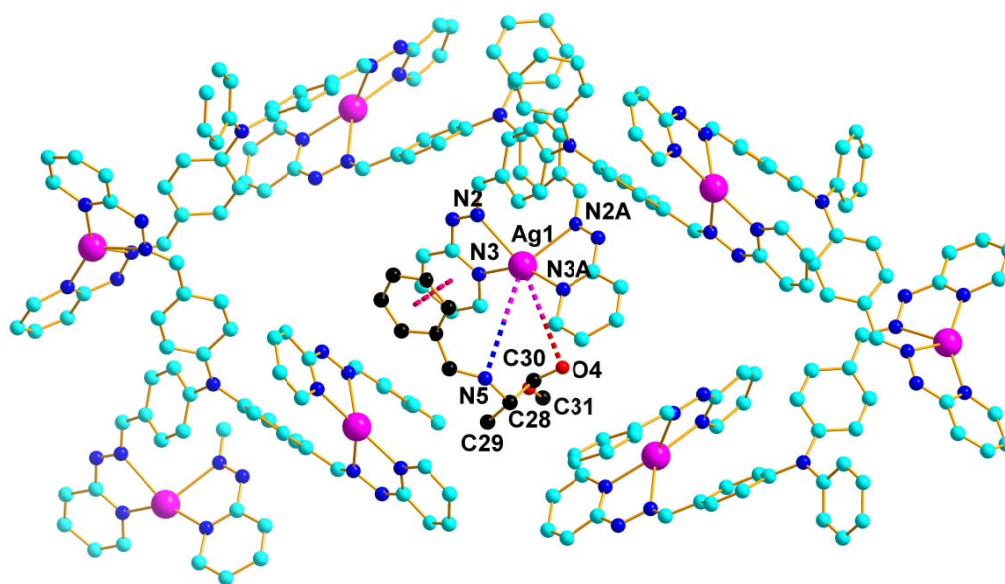
**Figure S15.** Ball-and-stick representation of the crystal structure of **1-M** impregnated **L-BPAM** molecule with selected labeling scheme, displaying potential interactions between the framework and the substrate molecules adsorbed. Selected bond distances (Å) and angle (°): Ag(1)–N(2) 2.464(3), Ag(1)–N(3) 2.198(4), C(30)–O(4) 1.346(9); N(3A)–Ag(1)–N(3) 146.6(2), N(3A)–Ag(1)–N(2A) 71.96(14), N(3)–Ag(1)–N(2A) 134.85(15), N(2A)–Ag(1)–N(2) 93.04(15). Potential intermolecular interactions: Ag(1)–N(5) 4.108(4) Å, Ag(1)–O(4) 3.835(3) Å;  $\pi$ - $\pi$  stacking interaction between **L-BPAM** and **1-M**: Cg...Cg = 3.40 Å. (Symmetry code: A  $3/2-x, y, l-z$ ).



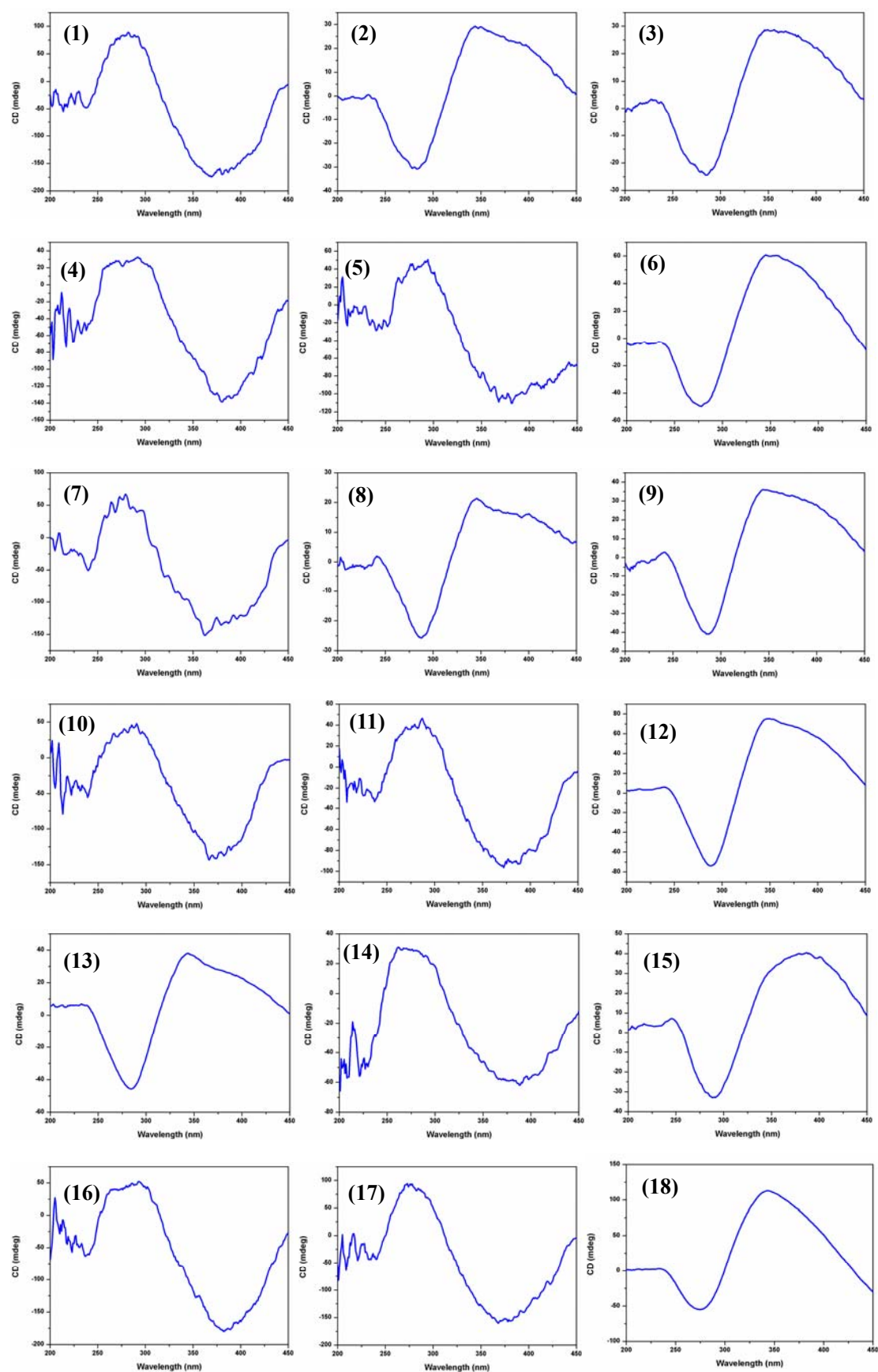
**Figure S16.** Ball-and-stick representation of the crystal structure of **1-P** impregnated **D-BPAM** molecule with selected labeling scheme, displaying potential interactions between the framework and the substrate molecules adsorbed. Selected bond distances (Å) and angle (°): Ag(1)–N(2) 2.457(4), Ag(1)–N(3) 2.211(4), C(30)–O(4) 1.350(9); N(3A)–Ag(1)–N(3) 147.0(2), N(3A)–Ag(1)–N(2A) 71.68(14), N(3)–Ag(1)–N(2A) 134.65(15), N(2A)–Ag(1)–N(2) 93.66(17). Potential intermolecular interactions: Ag(1)–N(5) 4.143(4) Å, Ag(1)–O(4) 3.892(3) Å;  $\pi$ - $\pi$  stacking interaction between **D-BPAM** and **1-P**: Cg...Cg = 3.437 Å. (Symmetry code: A  $1/2-x, y, l-z$ ).

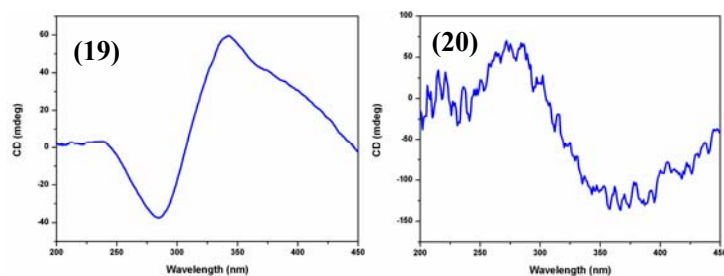


**Figure S17.** Ball-and-stick representation of the crystal structure of **1-M** impregnated **D-BPAM** molecule with selected labeling scheme, displaying potential interactions between the framework and the substrate molecules adsorbed. Selected bond distances (Å) and angle (°): Ag(1)–N(2) 2.473(4), Ag(1)–N(3) 2.206(5), C(30)–O(4) 1.346(9); N(3A)–Ag(1)–N(3) 148.4(2), N(3A)–Ag(1)–N(2A) 71.38(16), N(3)–Ag(1)–N(2A) 134.07(16), N(2A)–Ag(1)–N(2) 92.79(19). Potential intermolecular interactions: Ag(1)–N(5) 4.146(4) Å, Ag(1)–O(4) 3.984(3) Å;  $\pi$ - $\pi$  stacking interaction between **D-BPAM** and **1-M**: Cg...Cg = 3.441 Å. (Symmetry code: A  $3/2-x, y, l-z$ ).

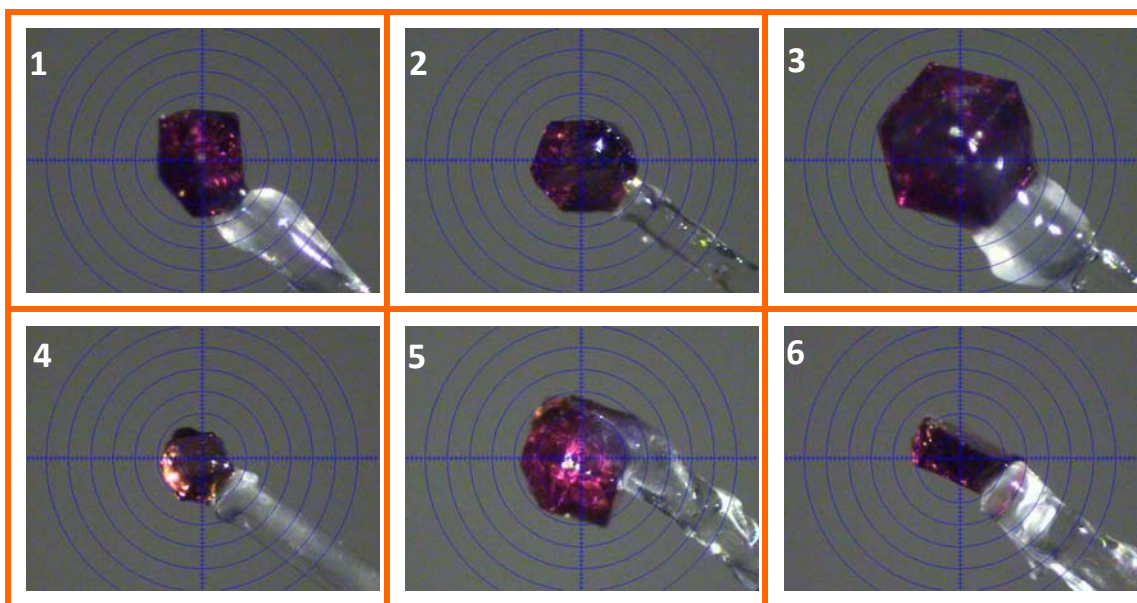


**Figure S18.** Ball-and-stick representation of the crystal structure of **1-P** impregnated **L-BPAM** molecule with selected labeling scheme, displaying potential interactions between the framework and the substrate molecules adsorbed. Selected bond distances (Å) and angle (°): Ag(1)–N(2) 2.483(4), Ag(1)–N(3) 2.209(5), C(30)–O(4) 1.349(9); N(3A)–Ag(1)–N(3) 148.6(2), N(3A)–Ag(1)–N(2A) 70.98(16), N(3)–Ag(1)–N(2A) 134.20(16), N(2A)–Ag(1)–N(2) 93.34(18). Potential intermolecular interactions: Ag(1)–N(5) 4.350(4) Å, Ag(1)–O(4) 4.040(2) Å;  $\pi$ - $\pi$  stacking interaction between **L-BPAM** and **1-P**: Cg...Cg = 3.493 Å. (Symmetry code: A  $1/2-x, y, l-z$ ).

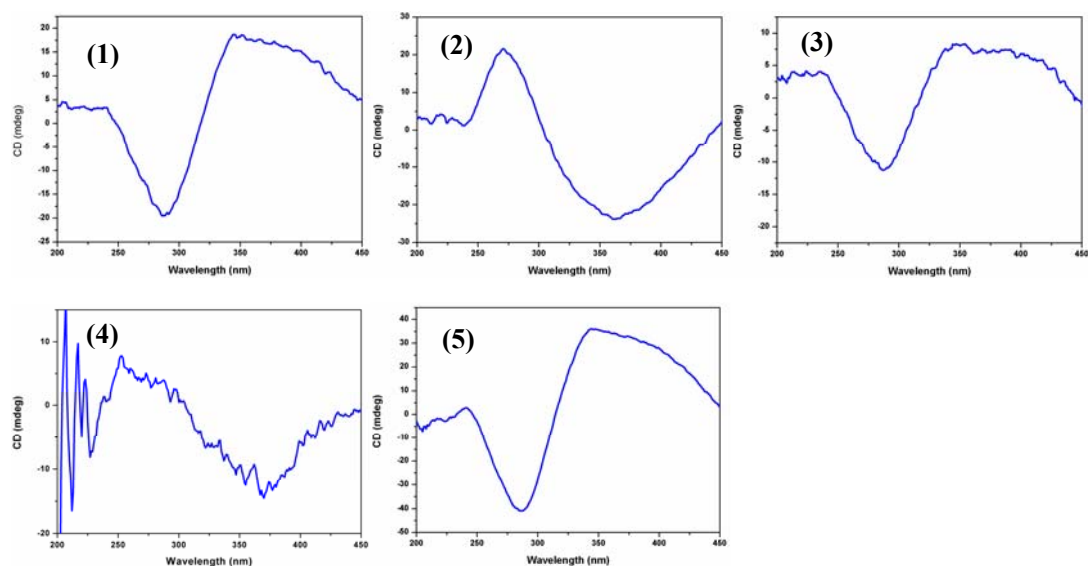




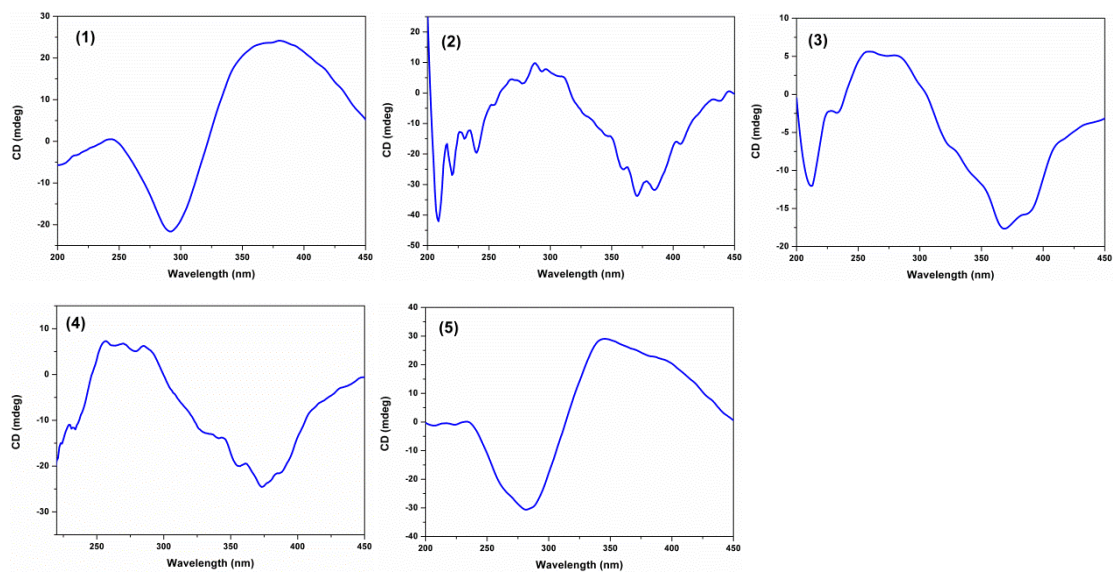
**Figure S19.** Solid state CD spectra for 20 bulk samples of **1** from twenty independent crystallization batches.



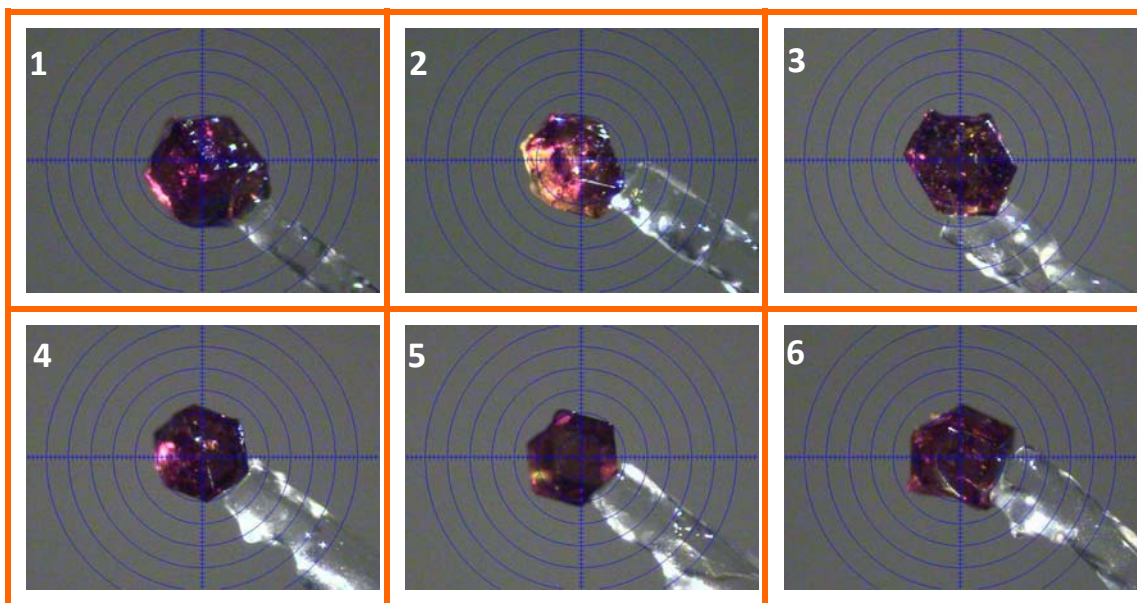
**Figure S20.** Photographs of six randomly selected crystals for **1** grown in the absence of chiral templates and used for X-ray data collection.



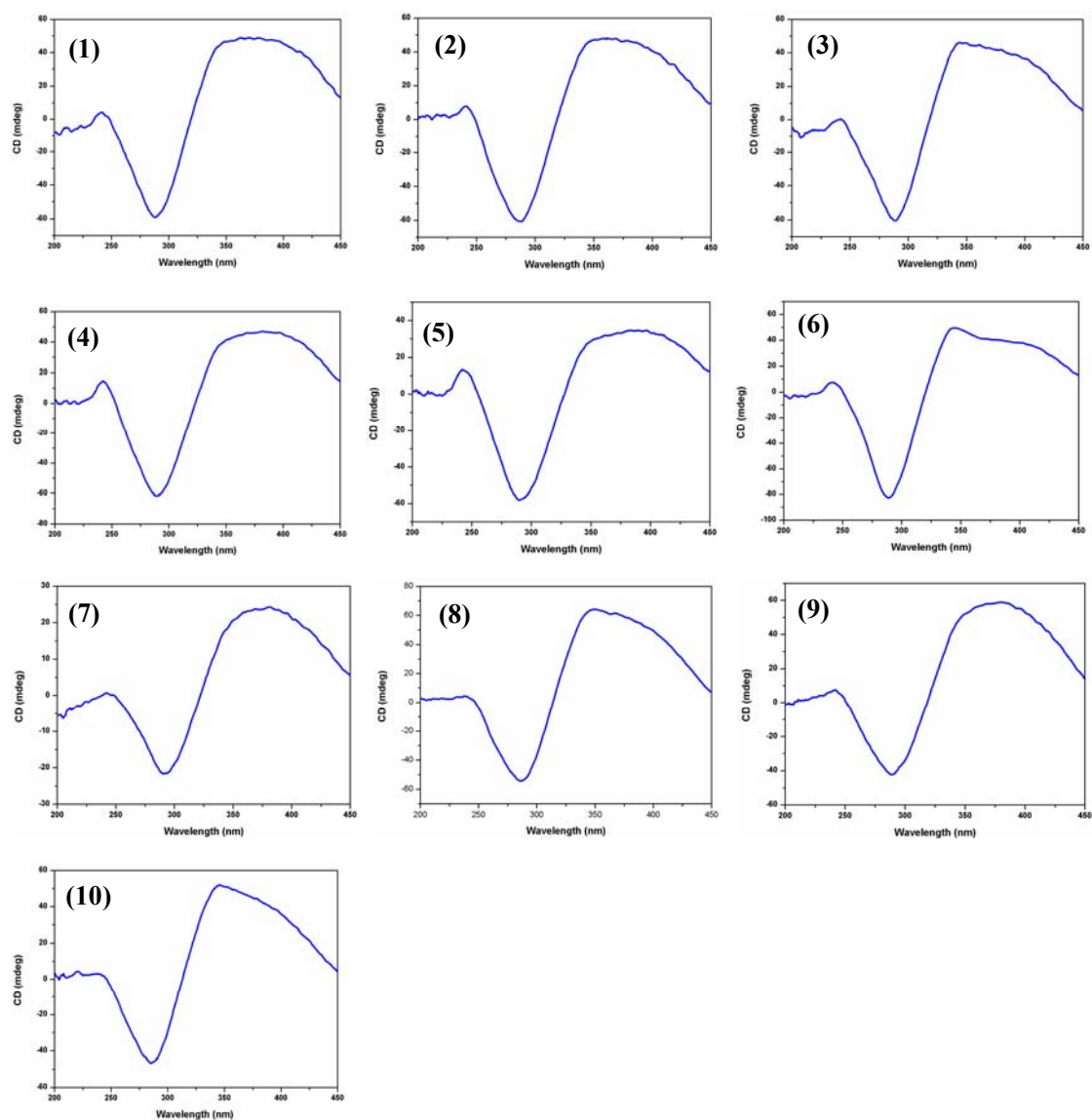
**Figure S21.** Solid state CD spectra of compound **1** used to catalyze the cycloaddition reactions between *L*-BPAM and methyl acrylate (the crystalline solids of **1** was randomly collected from five isolated crystallization batches).



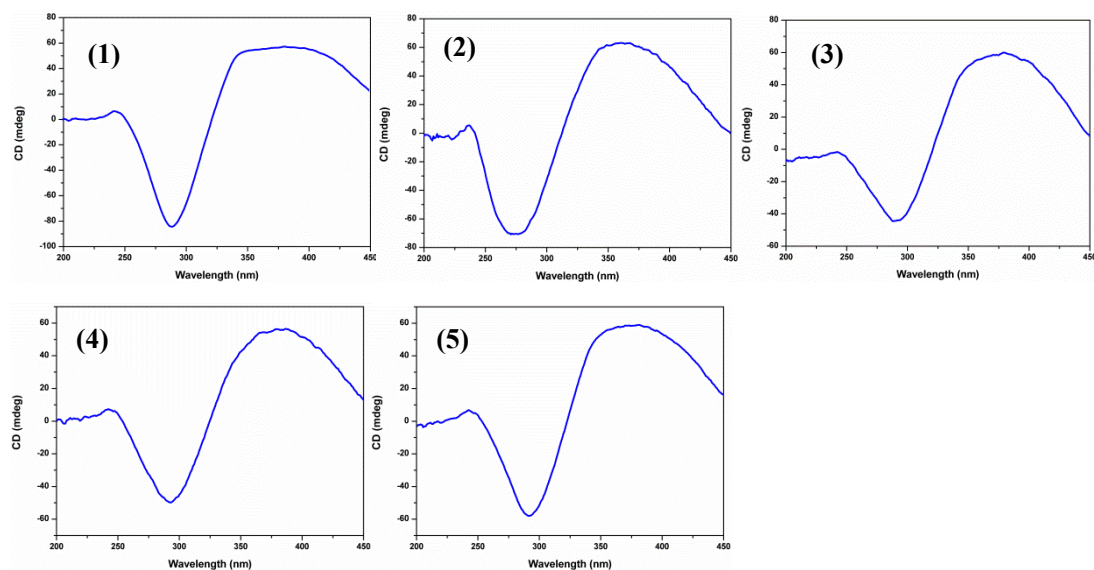
**Figure S22.** Solid state CD spectra of compound **1** used to catalyze the cycloaddition reactions between **D-BPAM** and methyl acrylate (the crystalline solids of **1** was randomly collected from five isolated crystallization batches).



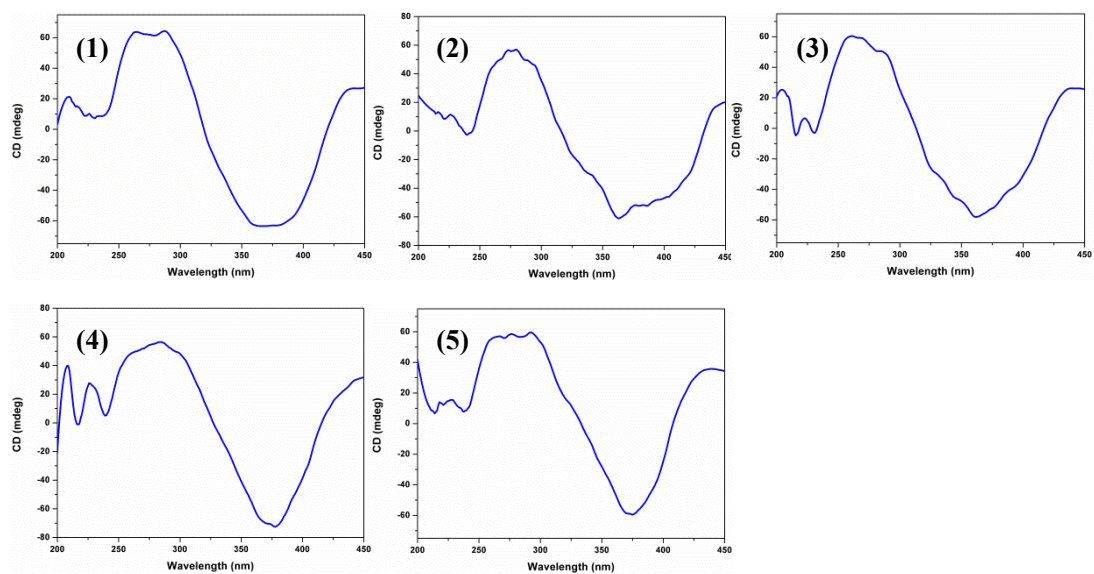
**Figure S23.** Photographs of six randomly selected crystals for **1-M** grown in the presence of **L-BPAM** and used for X-ray data collection.



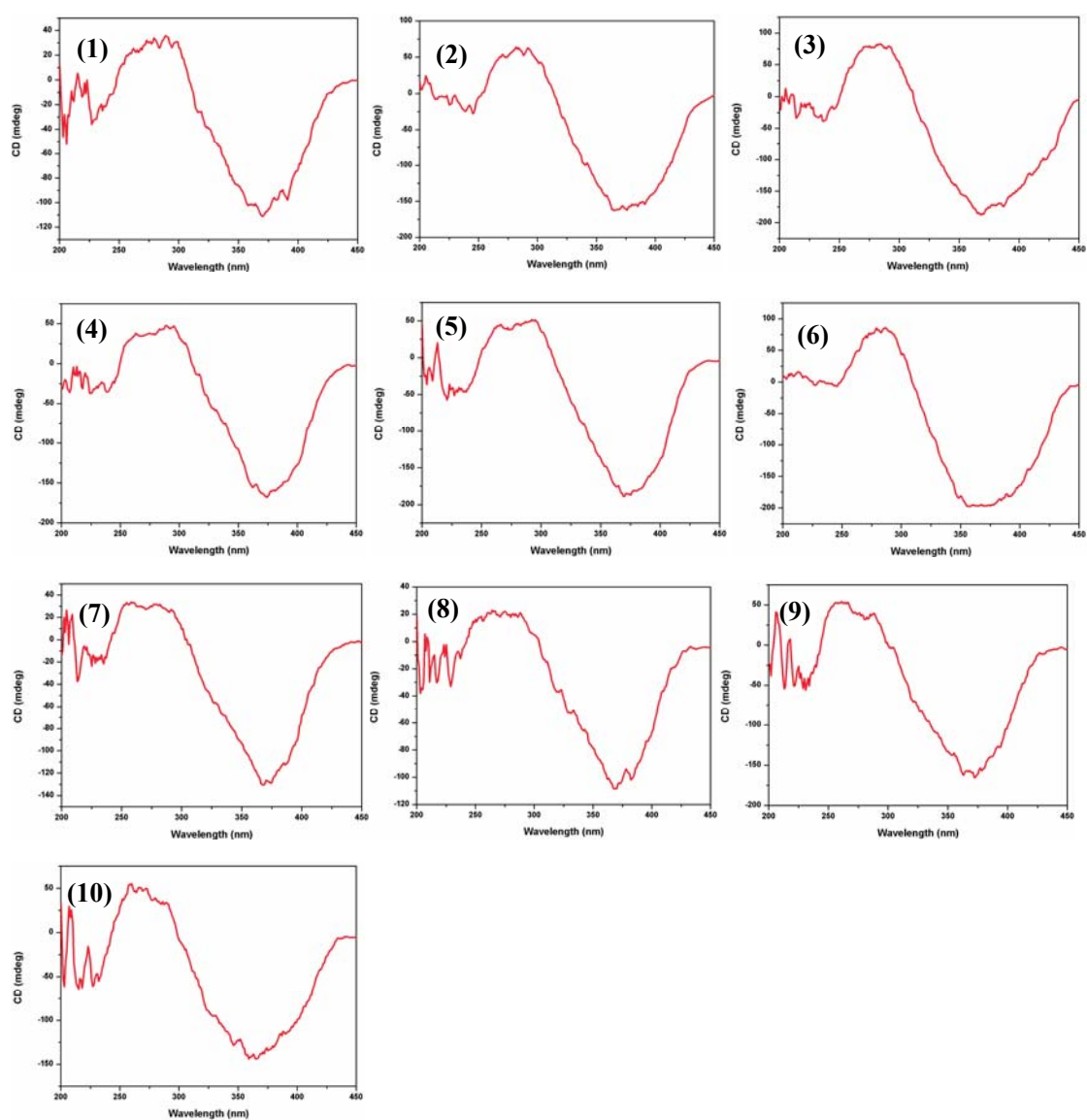
**Figure S24.** Solid state CD spectra for 10 bulk samples of **1-M** from ten independent crystallization batches (induced by **L-BPAM**).



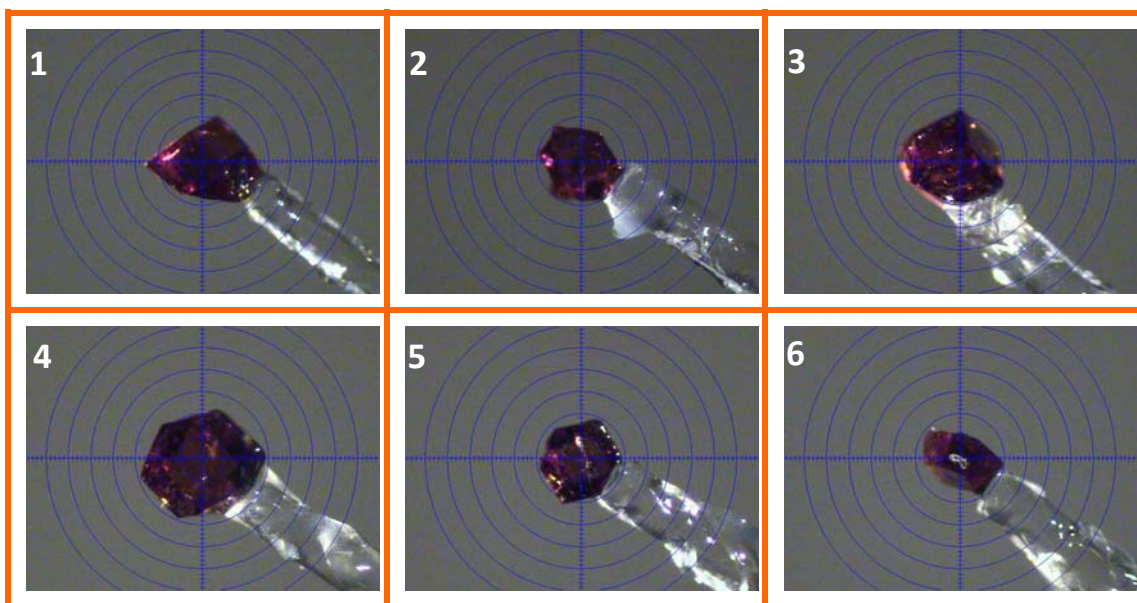
**Figure S25.** Solid state CD spectra of **1-M** used to catalyze the cycloaddition reactions between chiral **BPAM** and methyl acrylate (the crystalline solids of **1-M** was collected from five isolated crystallization batches).



**Figure S26.** Solid state CD spectra of **1-P** used to catalyze the cycloaddition reactions between chiral **BPAM** and methyl acrylate (the crystalline solids of **1-P** was collected from five isolated crystallization batches).

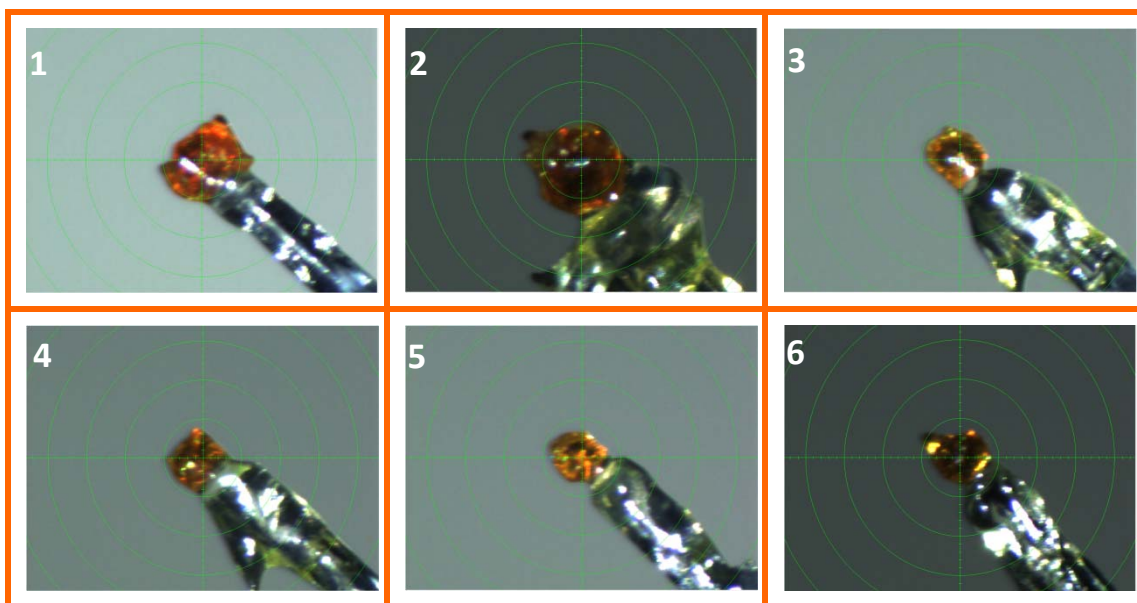


**Figure S27.** Solid state CD spectra for 10 bulk samples of **1-P** from ten independent crystallization batches (induced by **D-BPAM**).

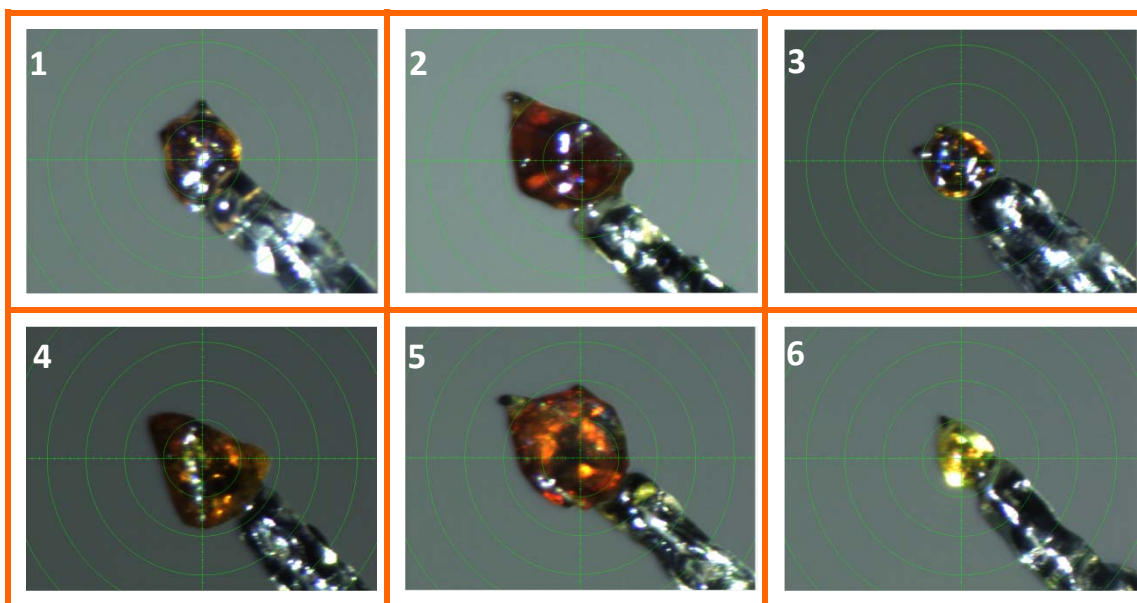


**Figure S28.** Photographs of six randomly selected crystals for **1-P** grown in the presence of **D-BPAM** and used for X-ray data collection.

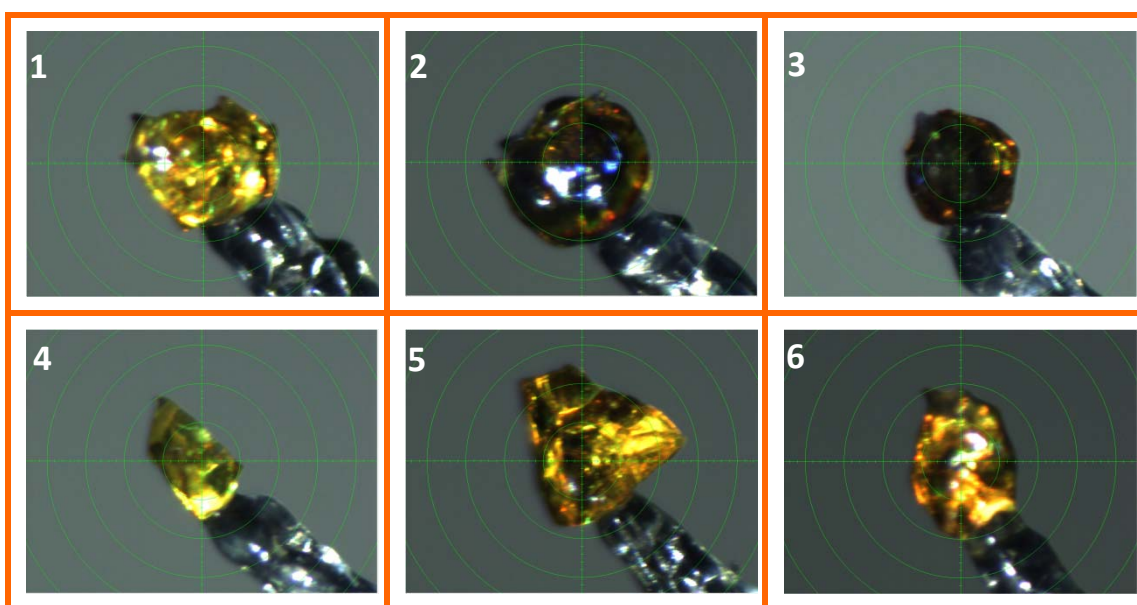
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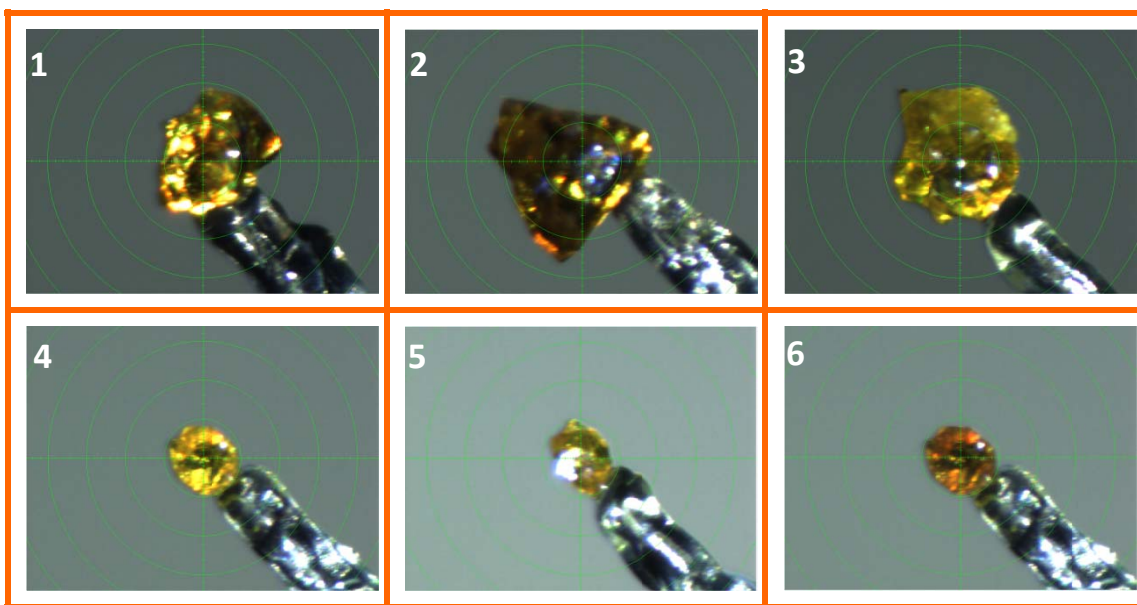
**Figure S29.** Photographs of six randomly selected crystals for **2-M** grown in the presence of **L-BPAM** and used for X-ray data collection.



**Figure S30.** Photographs of six randomly selected crystals for **2-P** grown in the presence of **D-BPAM** and used for X-ray data collection.

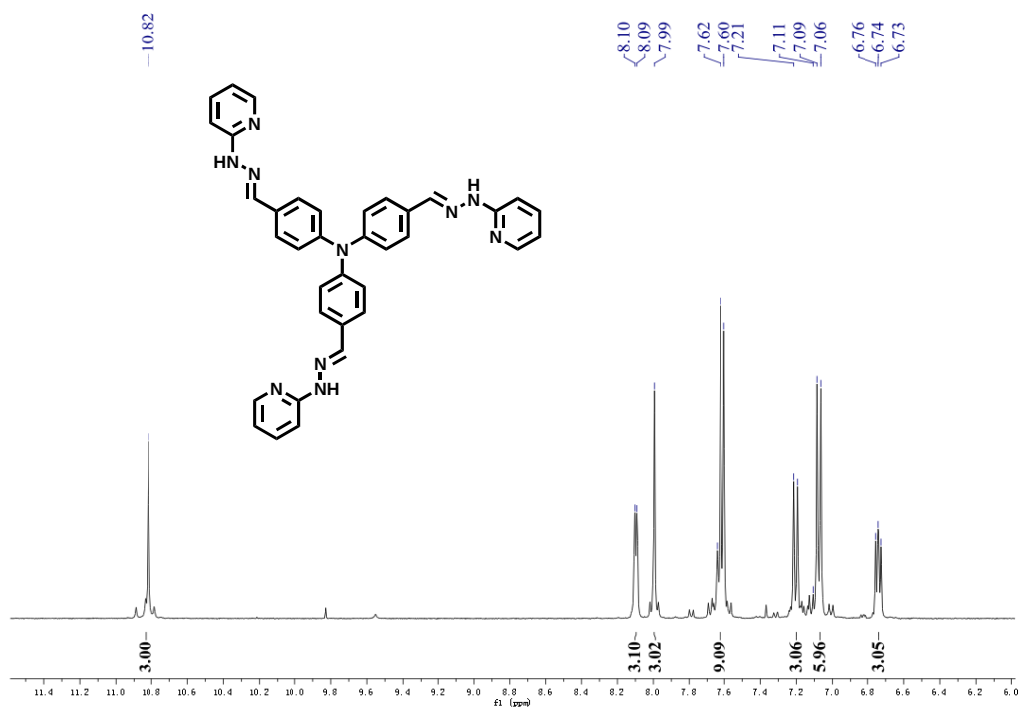


**Figure S31.** Photographs of six randomly selected crystals for **3-M** grown in the presence of **L-BPAM** and used for X-ray data collection.

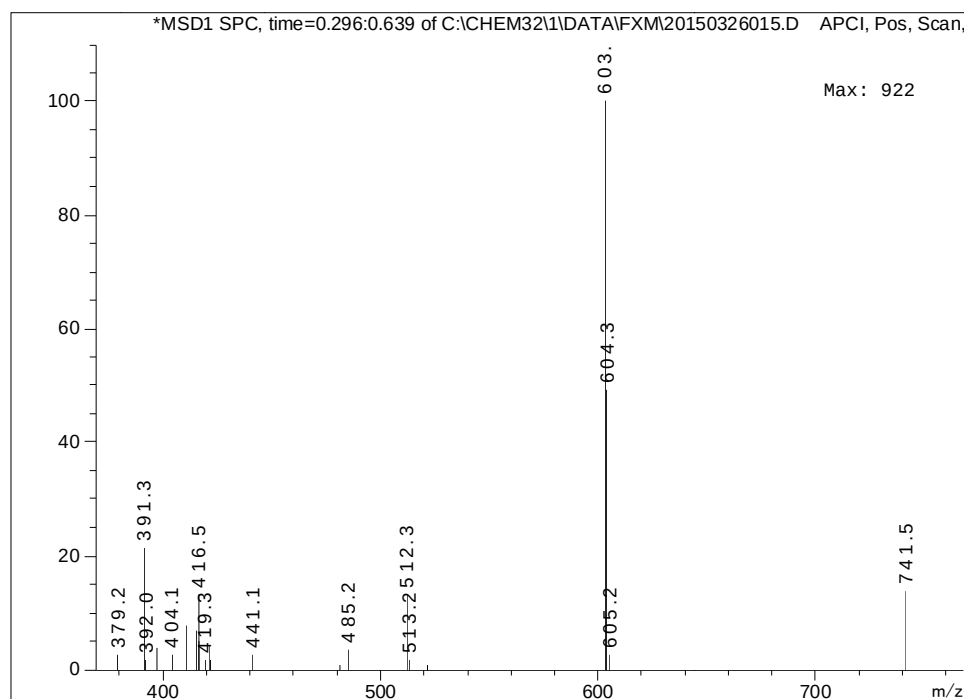


**Figure S32.** Photographs of six randomly selected crystals for **3-P** grown in the presence of **D-BPAM** and used for X-ray data collection.

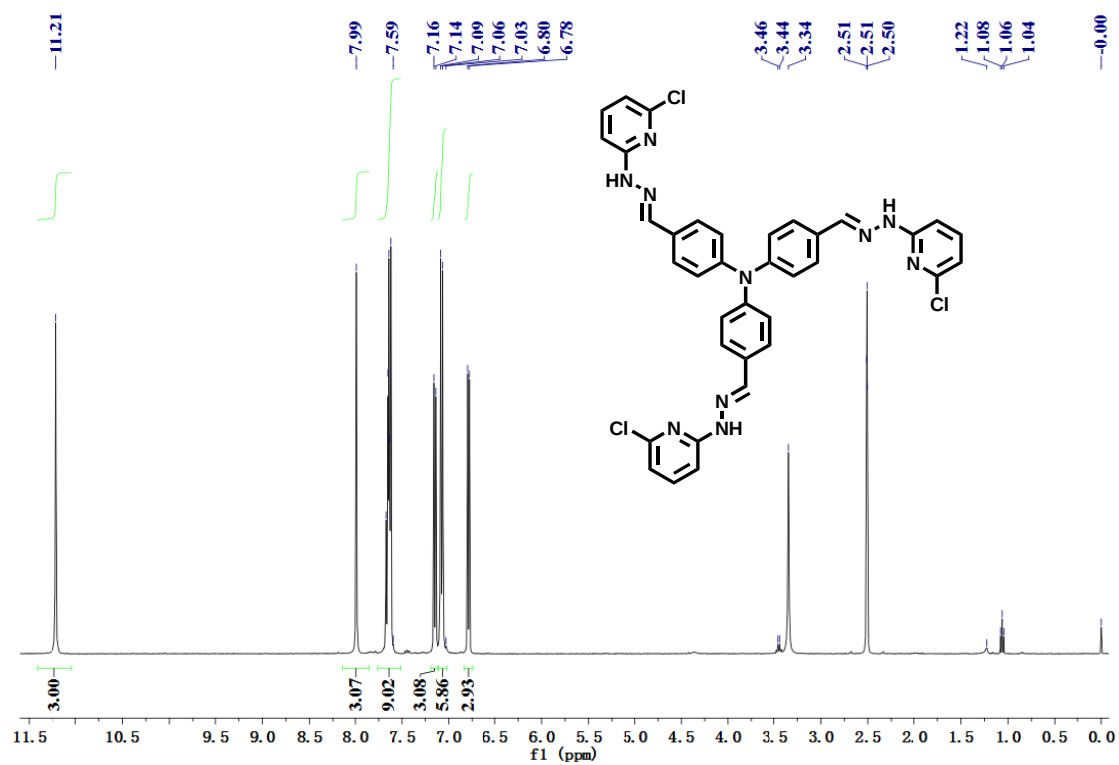
### NMR and ESI-MS spectrum



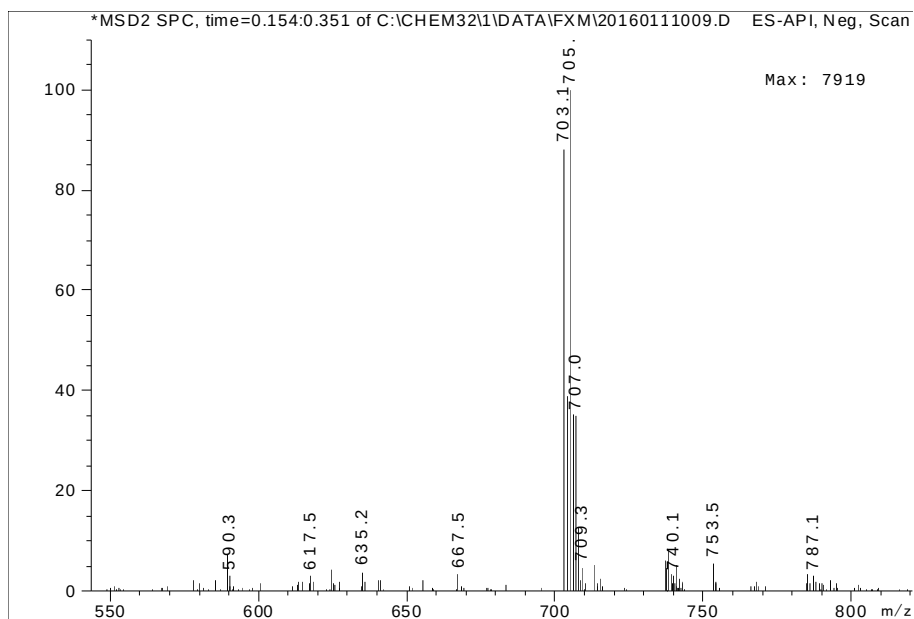
**Figure S33.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) spectrum of tris(4-(2-pyridin-2-ylhydrazono)phenyl)amine



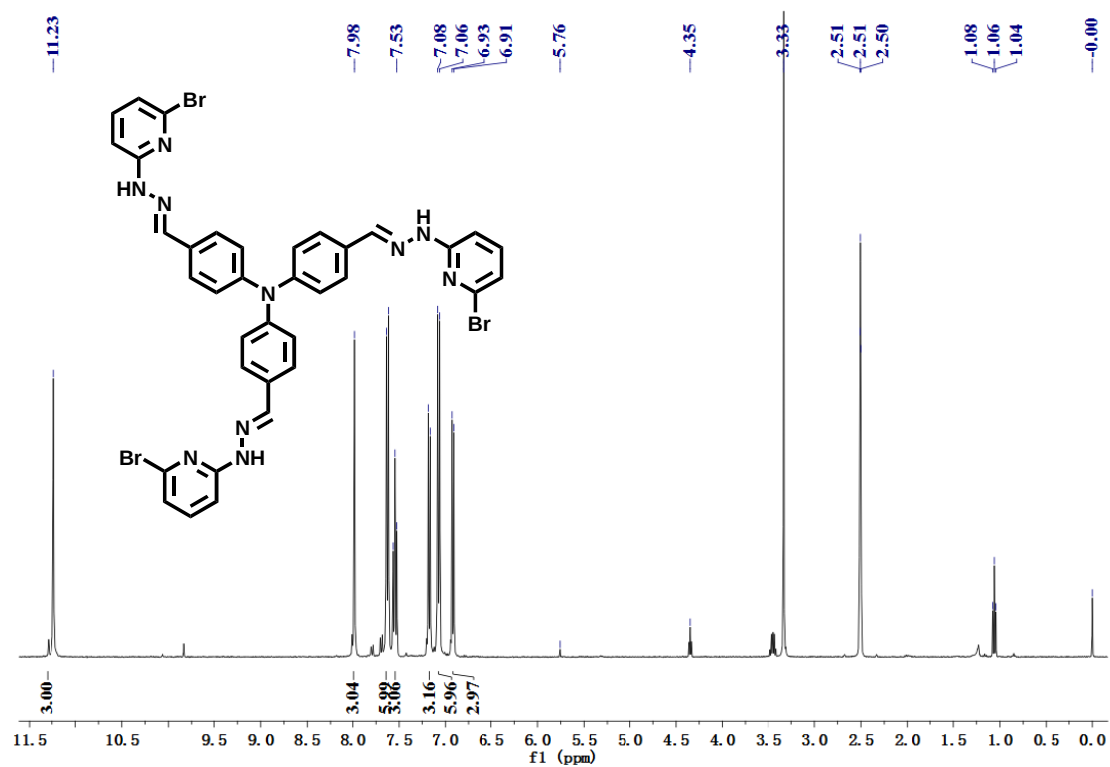
**Figure S34.** ESI-MS of tris(4-(2-pyridin-2-ylhydrazono)phenyl)amine



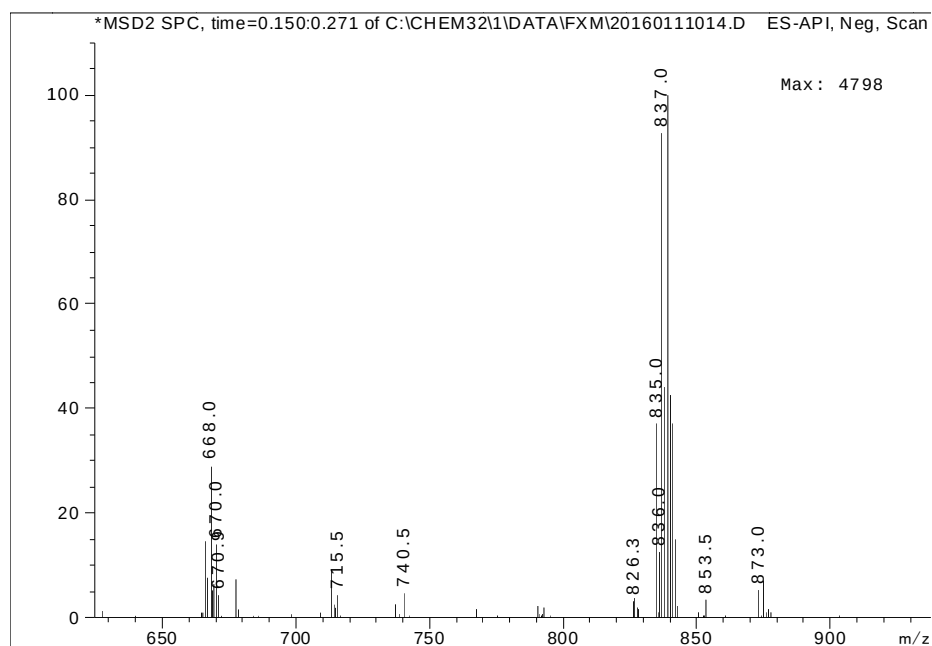
**Figure S35.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) of tris(4-(6-chloro-2-pyridin-2-ylhydrazono)phenyl)amine



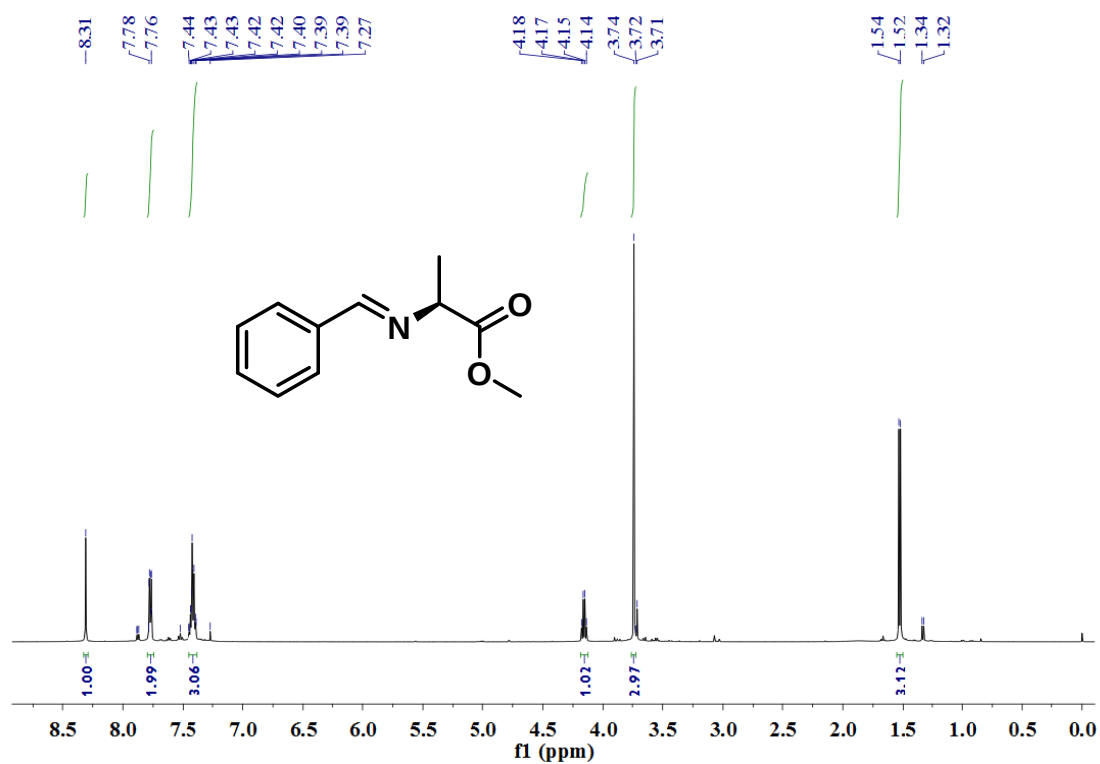
**Figure S36.** ESI-MS of tris(4-(6-chloro-2-pyridin-2-ylhydrazono)phenyl)amine



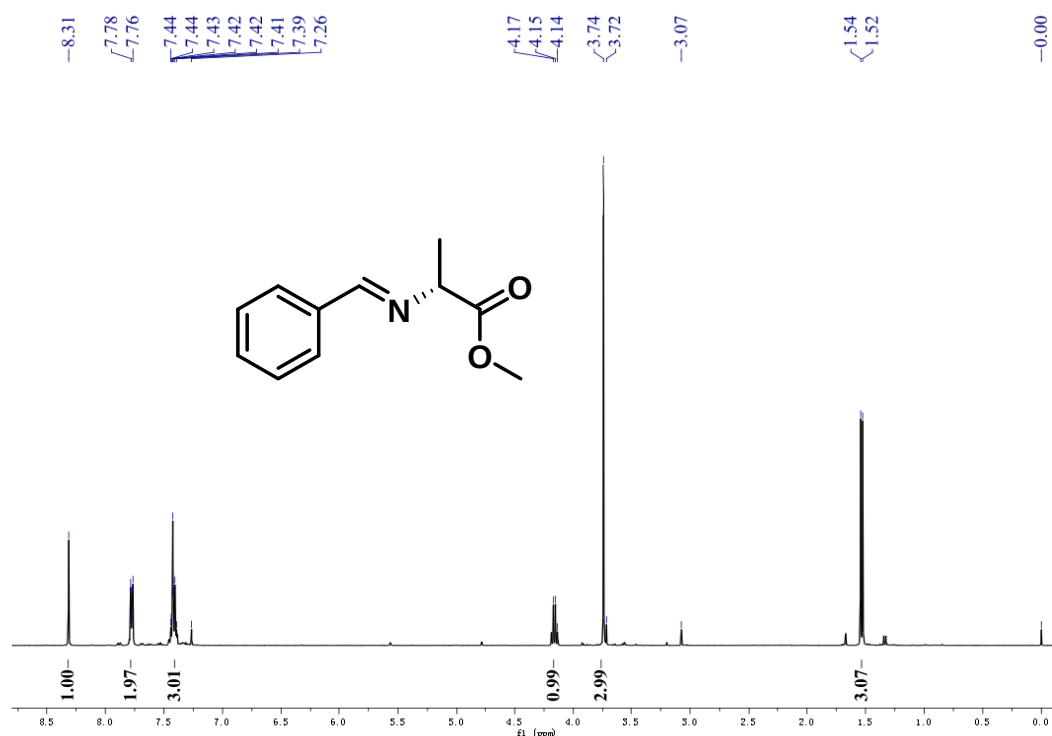
**Figure S37.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ) of tris(4-(6-bromo-2-pyridin-2-ylhydrazono)phenyl)amine



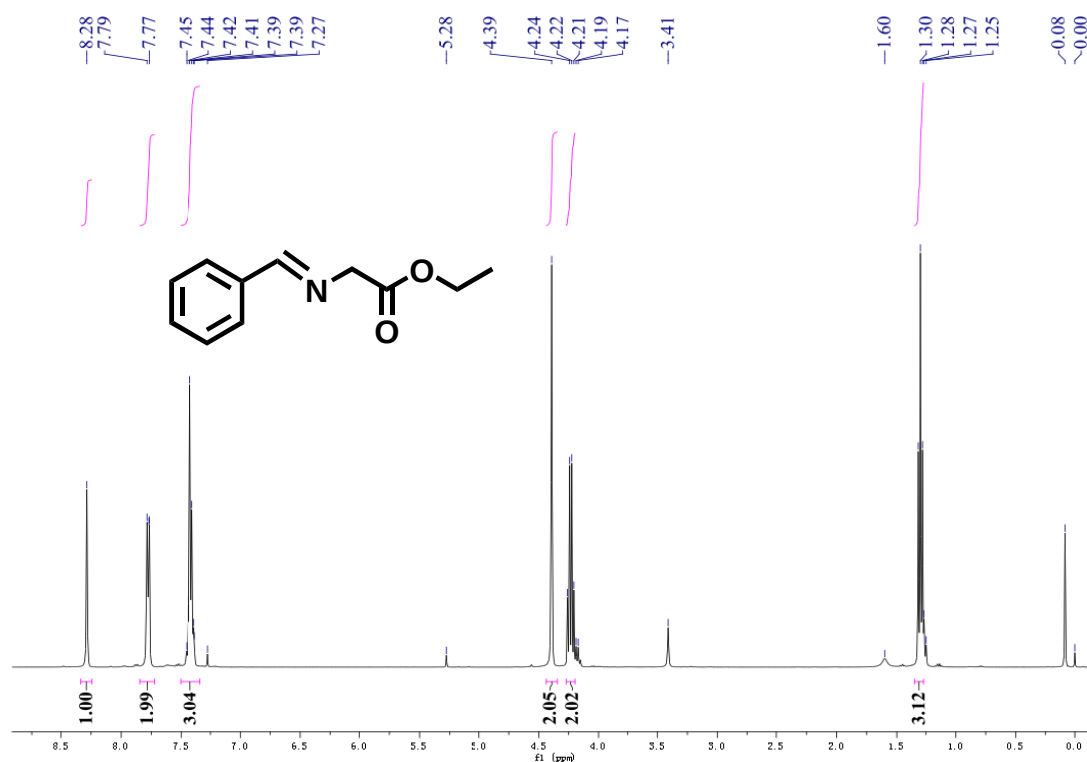
**Figure S38.** ESI-MS of tris(4-(6-bromo-2-pyridin-2-ylhydrazono)phenyl)amine



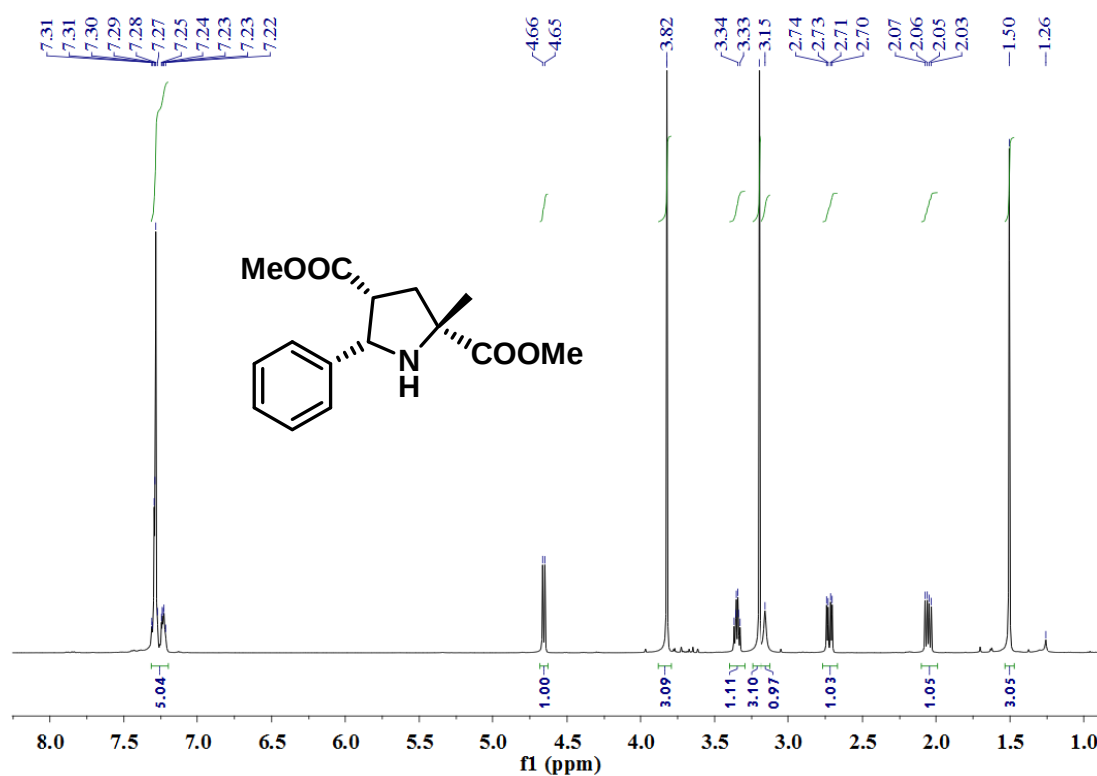
**Figure S39.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of (*S,E*)-methyl 2-(benzylideneamino)propanoate



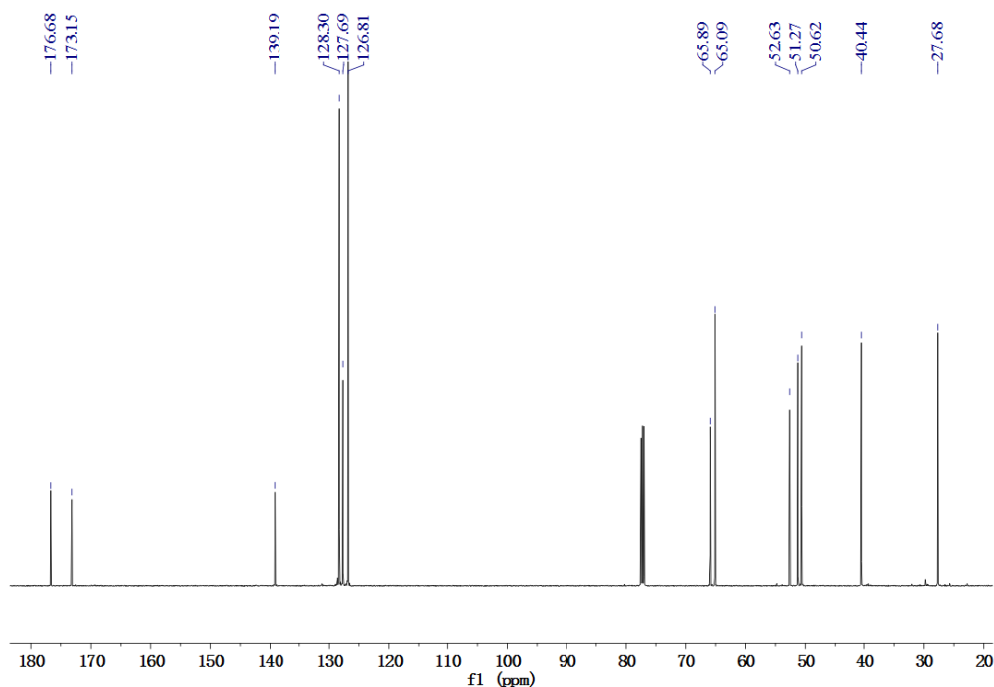
**Figure S40.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of (R,E)-methyl 2-(benzylideneamino)propanoate



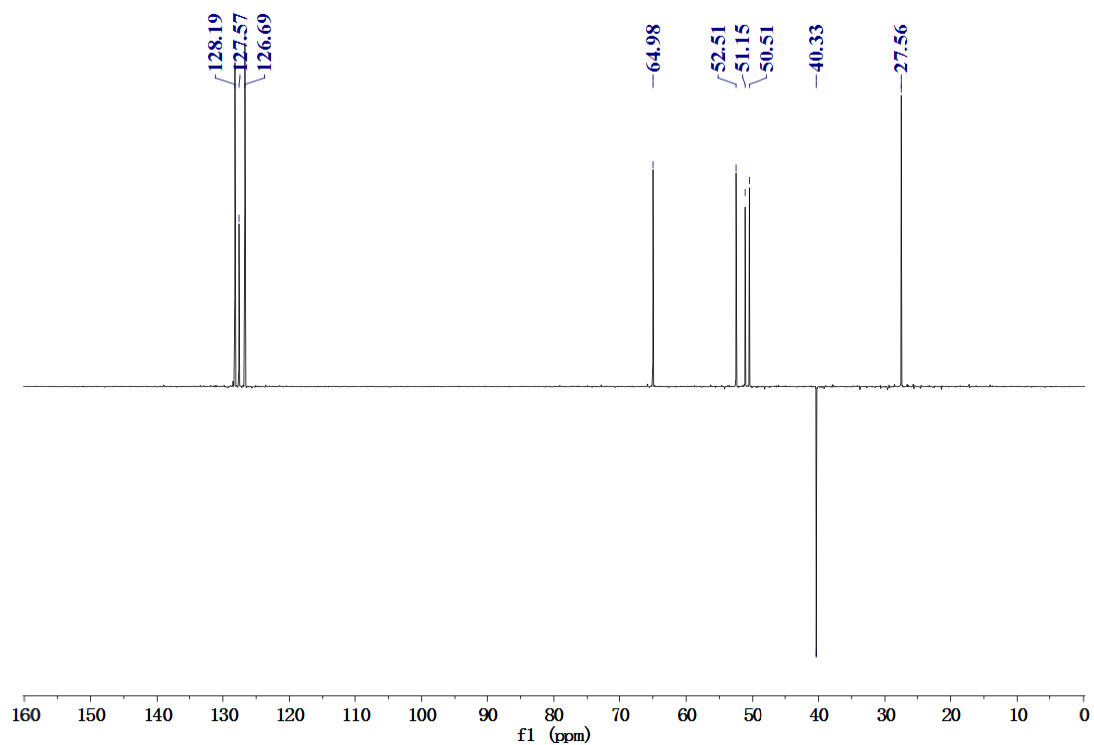
**Figure S41.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of N-(Phenylmethylene)-glycine ethyl ester



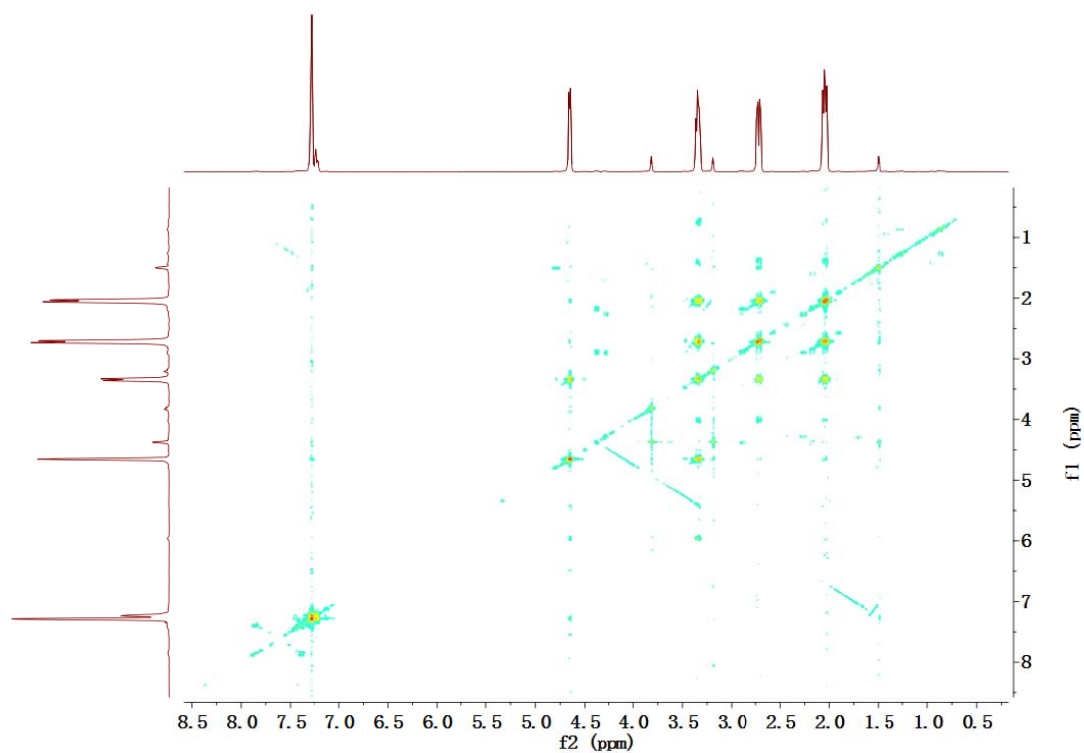
**Figure S42.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of (2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate



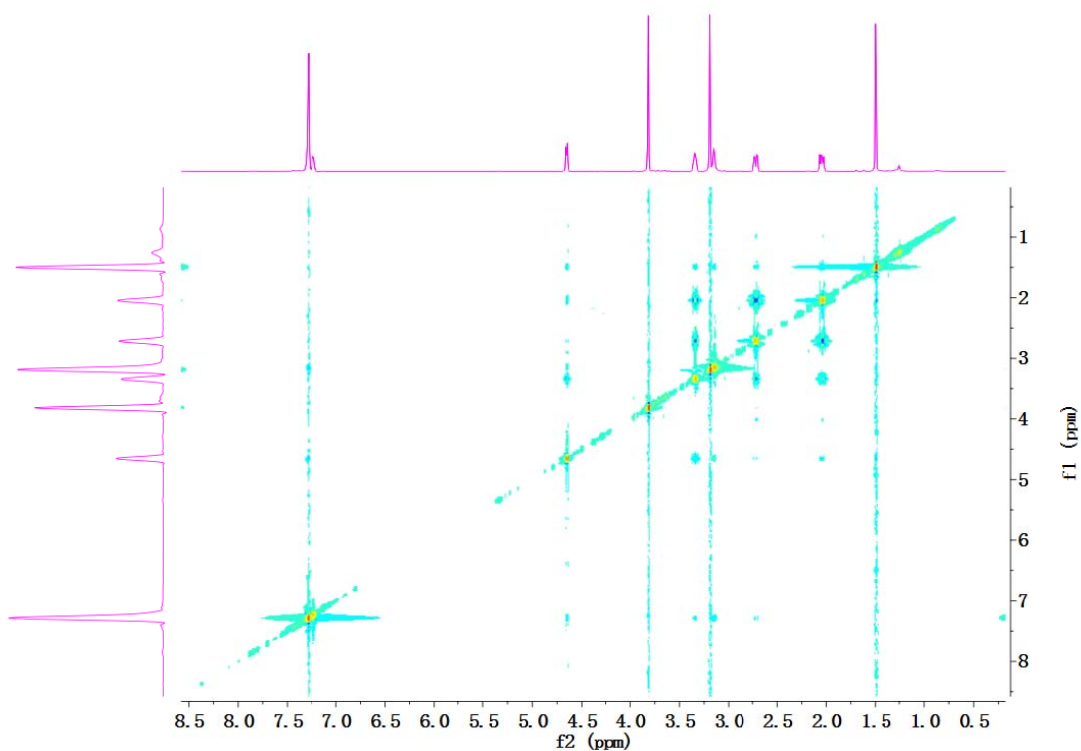
**Figure S43.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of (2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate



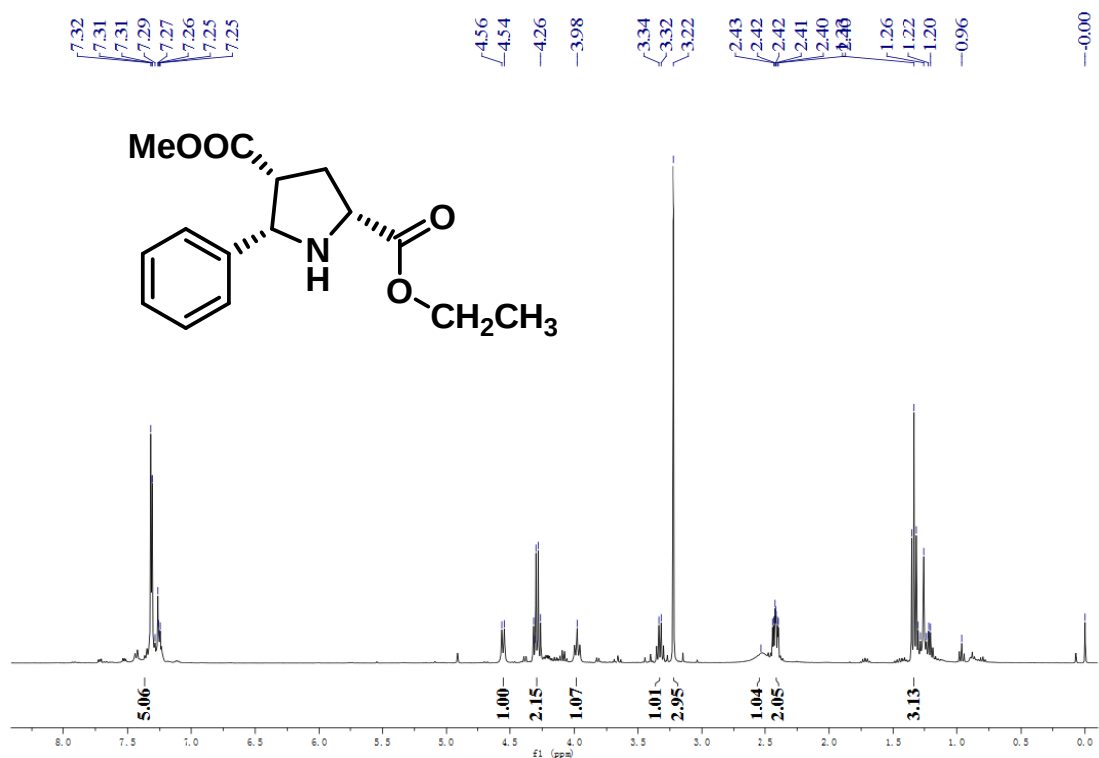
**Figure S44.** DEPT-135 spectrum of (2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate



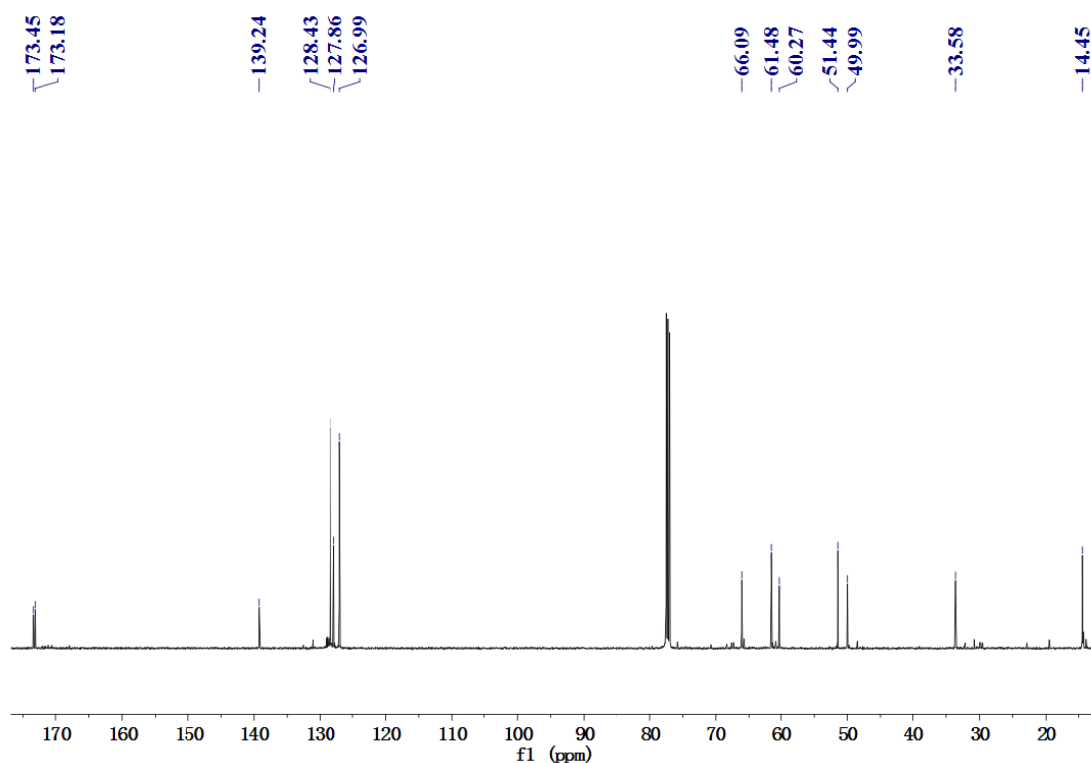
**Figure S45.** 2D-COSY spectrum of (2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate



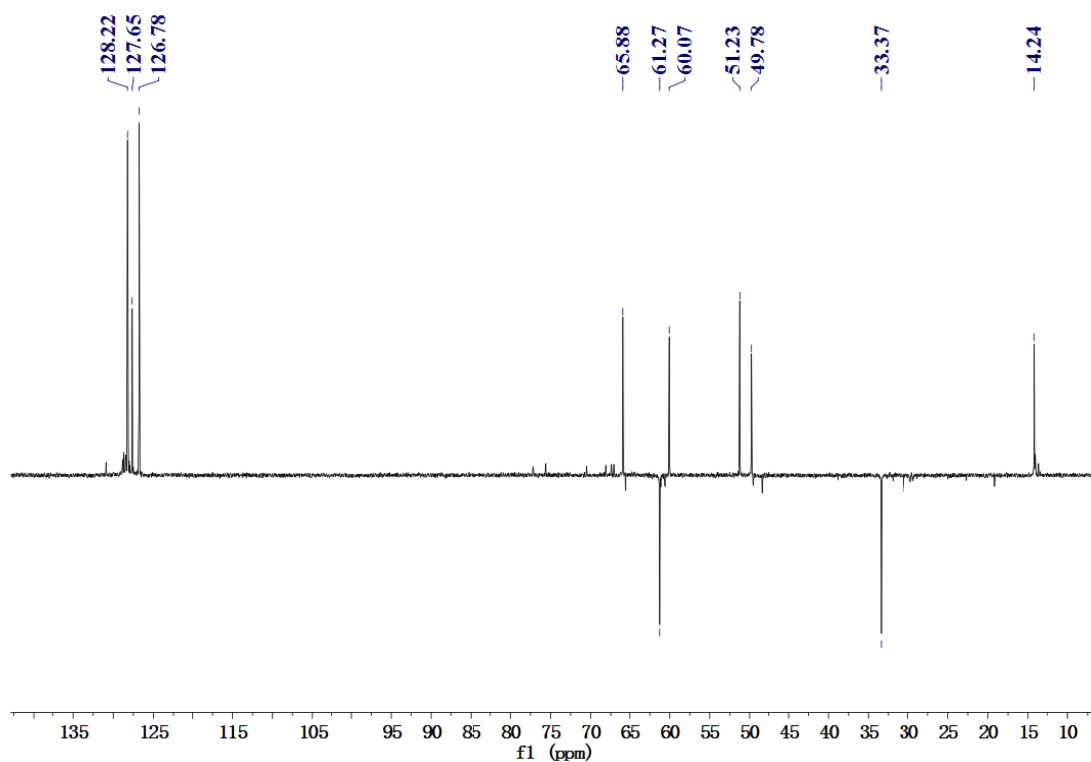
**Figure S46.** 2D-NOESY spectrum of (2*R*,4*R*,5*S*)-Dimethyl-2-methyl-5-phenylpyrrolidine-2,4-dicarboxylate



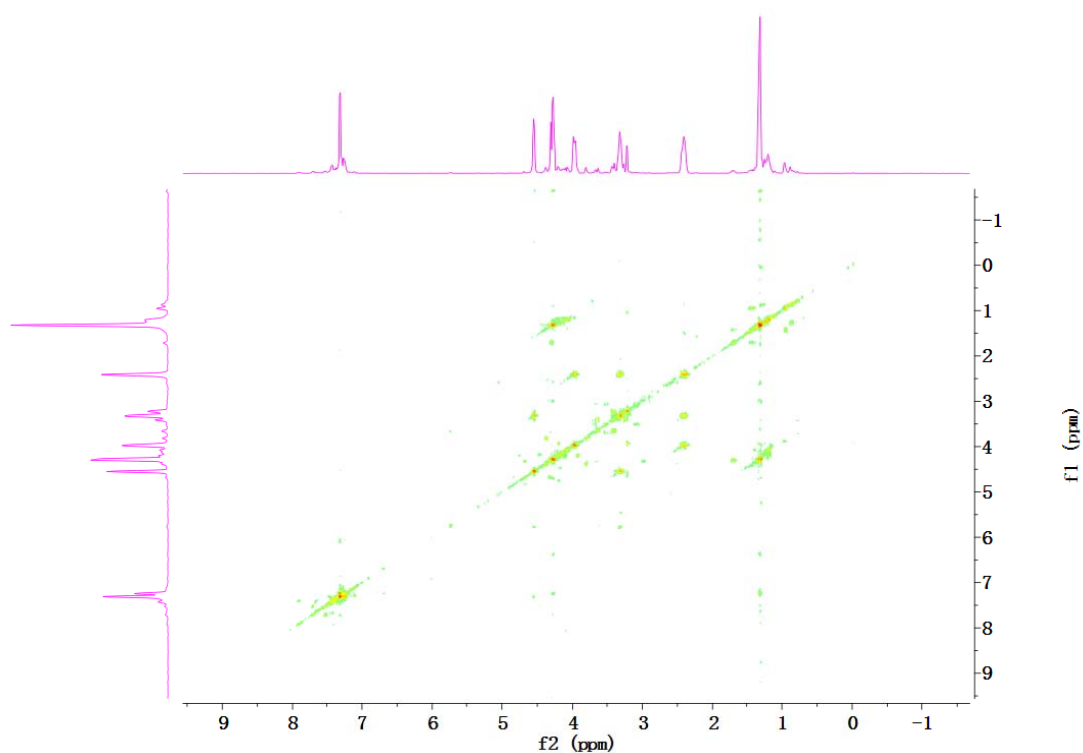
**Figure S47.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of (2*R*,4*R*,5*S*)-4-methylester-2-ethyl-5-phenylpyrrolidine-2,4-dicarboxylate



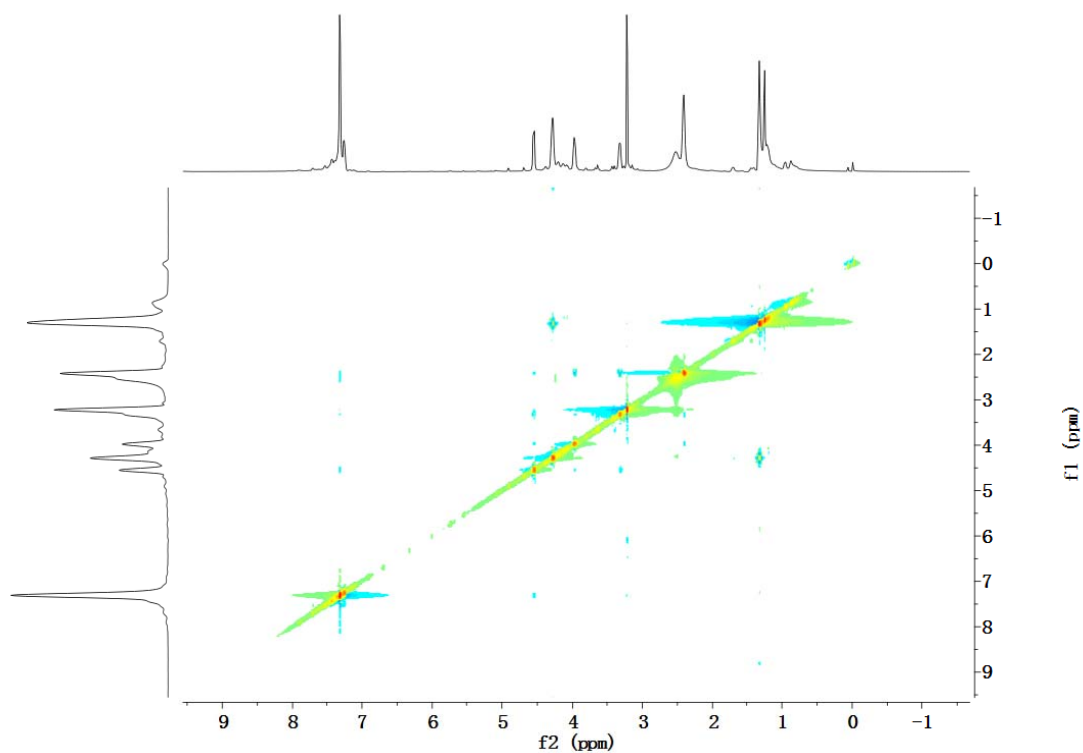
**Figure S48.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of (2*R*,4*R*,5*S*)-4-methylester-2-ethyl-5-phenylpyrrolidine-2,4-dicarboxylate



**Figure S49.** DEPT-135 spectrum of (2*R*,4*R*,5*S*)-4-methylester-2-ethyl-5-phenylpyrrolidine-2,4-dicarboxylate



**Figure S50.** 2D-COSY spectrum of (2*R*,4*R*,5*S*)-4-methylester-2-ethyl-5-phenylpyrrolidine-2,4-dicarboxylate

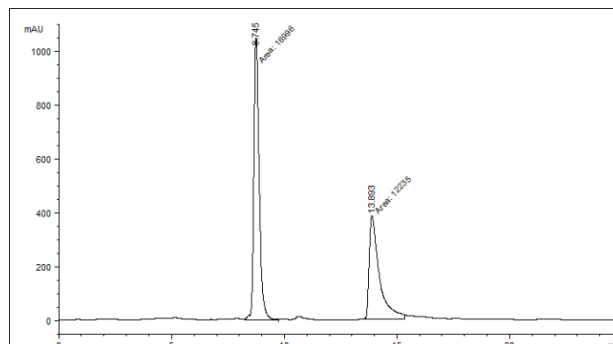


**Figure S51.** 2D-NOESY spectrum of (2*R*,4*R*,5*S*)-4-methylester-2-ethyl-5-phenylpyrrolidine-2,4-dicarboxylate

## HPLC chromatograms

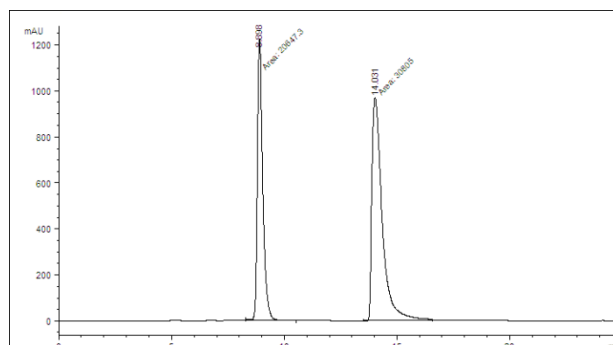
**Figure S52.** HPLC traces of the products from five parallel cycloaddition reactions between **L-BPAM** and methyl acrylate (catalyzed by **1** from five isolated crystallization batches).

(a)



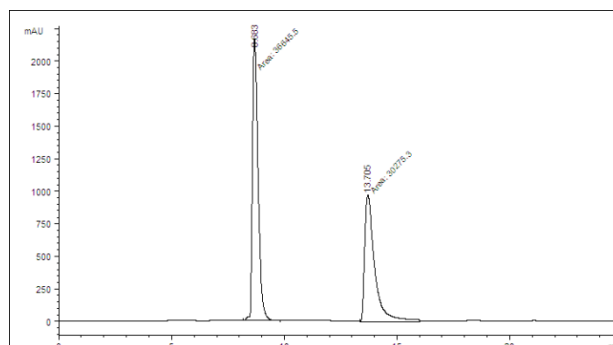
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.745         | 16996.000     | 1050.444     | 58.144   |
| 2      | 13.893        | 12234.980     | 385.574      | 41.856   |
| Total  | —             | 29230.980     | 1436.018     | 100.000  |

(b)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.898         | 20647.330     | 1222.807     | 40.129   |
| 2      | 14.031        | 30804.968     | 970.169      | 59.871   |
| Total  | —             | 51452.298     | 2192.976     | 100.000  |

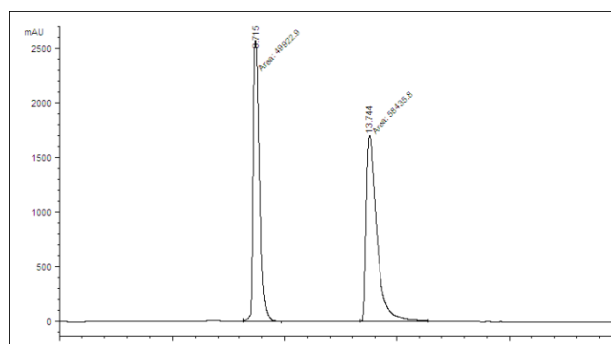
(c)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.683         | 36645.523     | 2160.269     | 54.759   |

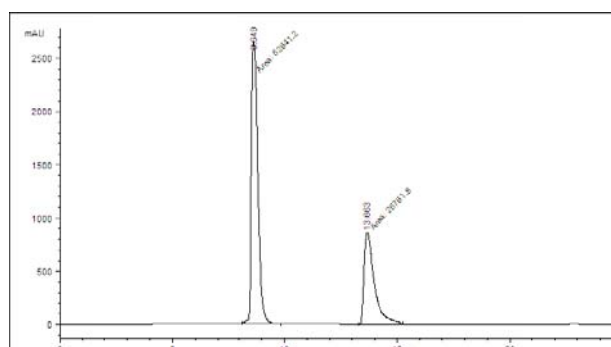
|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 2     | 13.705 | 30275.289 | 973.463  | 45.241  |
| Total | —      | 66920.812 | 3133.732 | 100.000 |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.715         | 49922.902     | 2573.321     | 46.072   |
| 2      | 13.744        | 58435.765     | 1700.359     | 53.928   |
| Total  | —             | 108358.667    | 4273.68      | 100.000  |

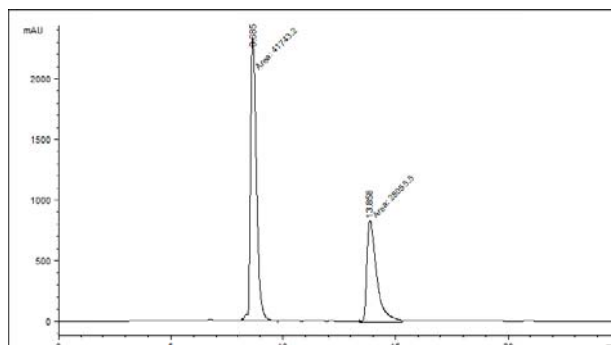
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.649         | 52641.152     | 2650.247     | 66.296   |
| 2      | 13.663        | 26761.754     | 868.767      | 33.704   |
| Total  | —             | 79402.906     | 3519.014     | 100.000  |

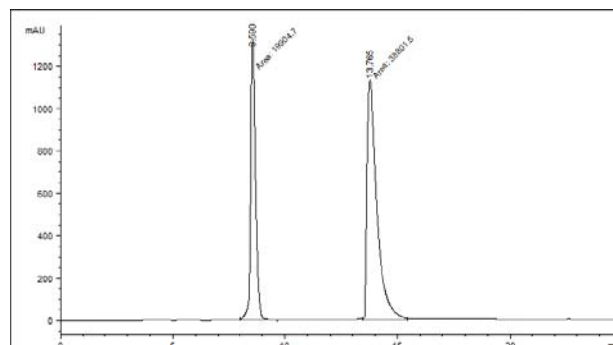
**Figure S53.** HPLC traces of the products from five parallel cycloaddition reactions between *D*-BPAM and methyl acrylate (catalyzed by **1** from five isolated crystallization batches).

(a)



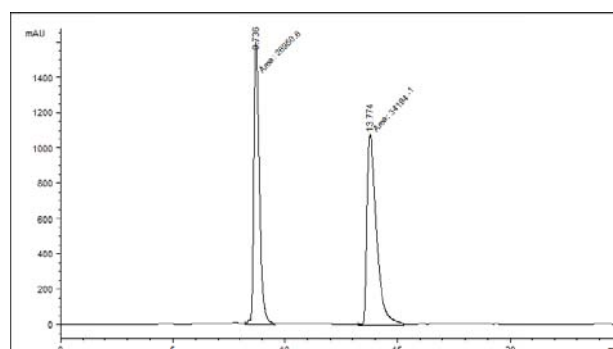
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.685         | 41743.230     | 2328.582     | 59.805   |
| 2      | 13.858        | 28055.518     | 865.444      | 40.195   |
| Total  | —             | 69798.748     | 3194.026     | 100.000  |

(b)



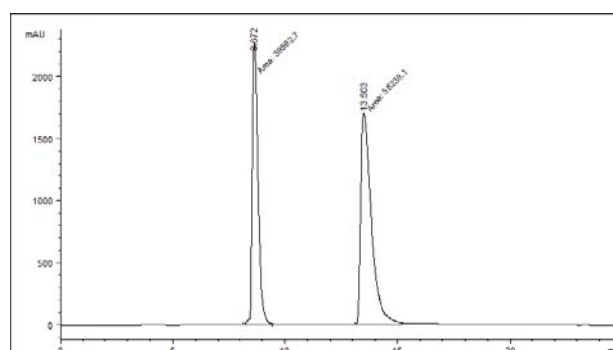
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.590         | 19904.742     | 1321.453     | 33.906   |
| 2      | 13.765        | 38801.531     | 1163.686     | 66.094   |
| Total  | —             | 58706.273     | 2485.139     | 100.000  |

(c)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.736         | 26950.605     | 1599.896     | 44.077   |
| 2      | 13.774        | 34194.109     | 1101.019     | 55.923   |
| Total  | —             | 61144.715     | 2700.916     | 100.000  |

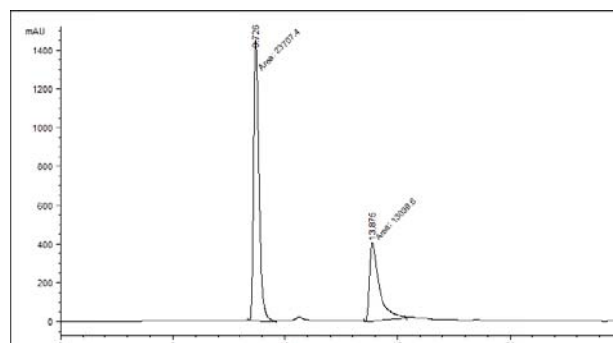
(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 1     | 8.672  | 39592.723 | 2266.334 | 40.471  |
| 2     | 13.503 | 58238.105 | 1717.554 | 59.529  |
| Total | —      | 97830.828 | 3983.888 | 100.000 |

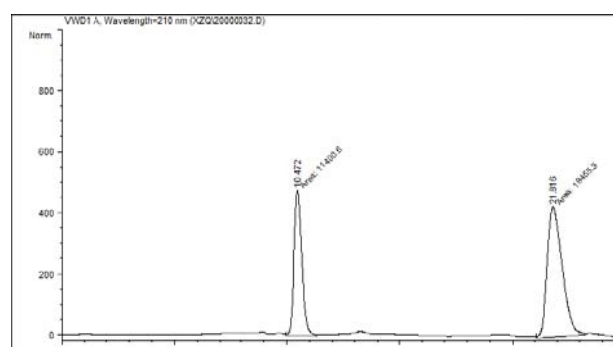
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.726         | 23707.395     | 1448.698     | 64.515   |
| 2      | 13.875        | 13039.558     | 408.471      | 35.485   |
| Total  | —             | 36746.953     | 1857.169     | 100.000  |

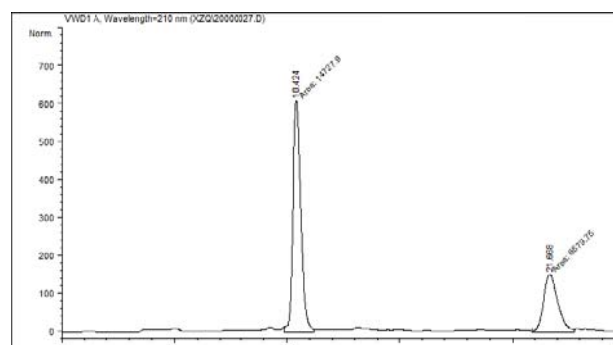
**Figure S54.** HPLC chromatograms of the products in five parallel reactions between **PGE** and methyl acrylate (catalyzed by **1** from five isolated crystallization batches).

(a)



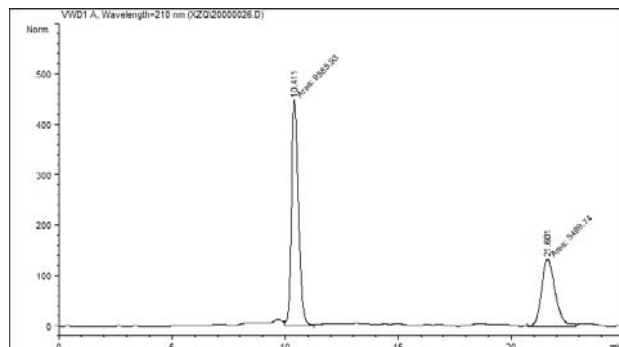
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 10.472        | 11400.623     | 476.316      | 36.948   |
| 2      | 21.816        | 19455.295     | 425.783      | 63.052   |
| Total  | —             | 30855.918     | 902.099      | 100.000  |

(b)



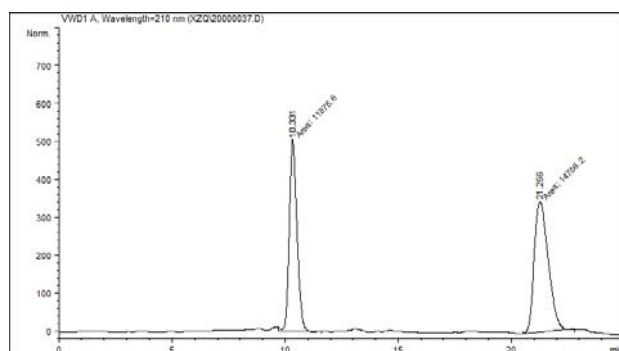
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU ] | Area [%] |
|--------|---------------|---------------|---------------|----------|
| 1      | 10.424        | 14727.923     | 611.393       | 69.120   |
| 2      | 21.668        | 6579.746      | 151.073       | 30.880   |
| Total  | —             | 21307.669     | 762.466       | 100.000  |

(c)



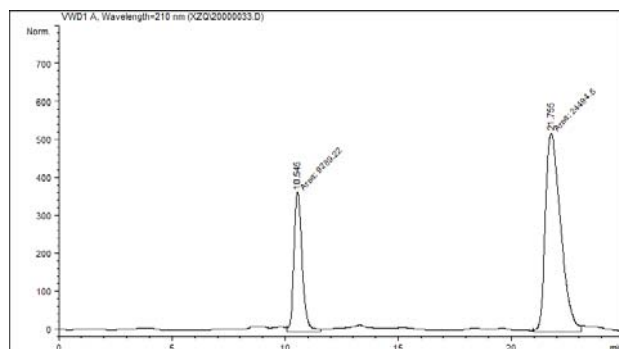
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU ] | Area [%] |
|--------|---------------|---------------|---------------|----------|
| 1      | 10.411        | 9585.929      | 448.796       | 63.543   |
| 2      | 21.601        | 5499.740      | 132.353       | 36.457   |
| Total  | —             | 15085.669     | 581.149       | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU ] | Area [%] |
|--------|---------------|---------------|---------------|----------|
| 1      | 10.331        | 11875.571     | 502.935       | 44.592   |
| 2      | 21.266        | 14756.199     | 342.689       | 55.408   |
| Total  | —             | 26631.770     | 845.624       | 100.000  |

(e)

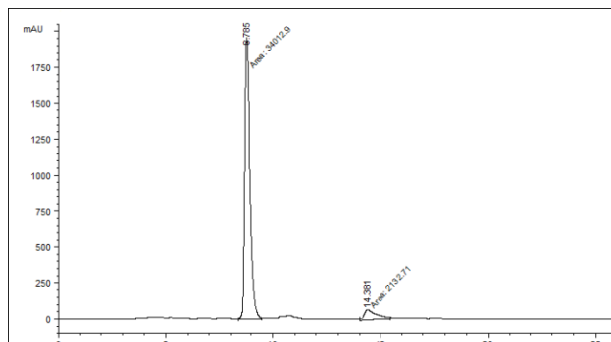


| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU ] | Area [%] |
|--------|---------------|---------------|---------------|----------|
|--------|---------------|---------------|---------------|----------|

|       |        |           |         |         |
|-------|--------|-----------|---------|---------|
| 1     | 10.545 | 9289.221  | 367.765 | 27.496  |
| 2     | 21.755 | 24494.549 | 522.577 | 72.504  |
| Total | —      | 33783.770 | 890.342 | 100.000 |

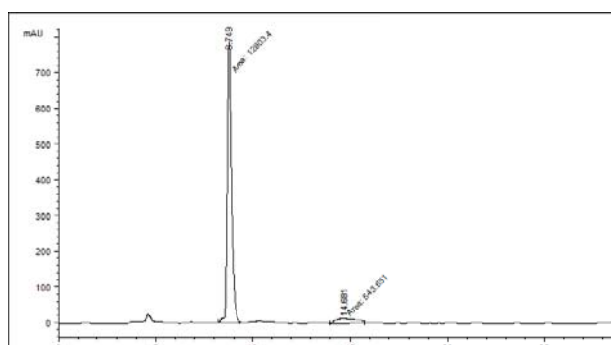
**Figure S55.** HPLC traces of the products from five parallel cycloaddition reactions between **L-BPAM** and methyl acrylate (catalyzed by **1-M** from five isolated crystallization batches).

(a)



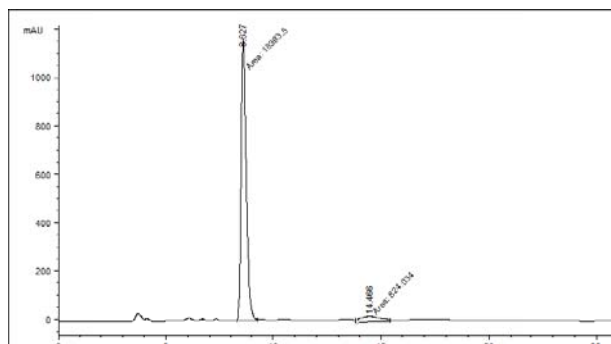
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.785         | 34012.852     | 1964.106     | 94.099   |
| 2      | 14.381        | 2132.711      | 64.497       | 5.901    |
| Total  | —             | 36145.563     | 2028.603     | 100.000  |

(b)



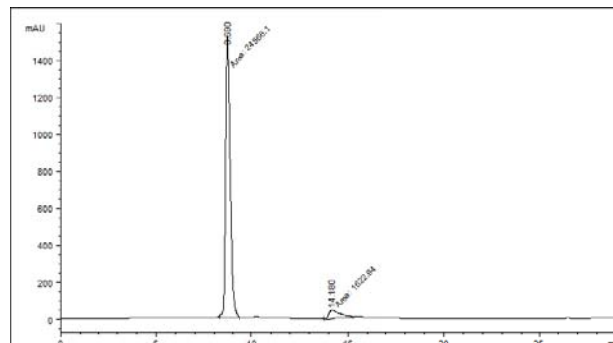
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.749         | 12603.403     | 788.802      | 95.865   |
| 2      | 14.681        | 543.651       | 16.364       | 4.135    |
| Total  | —             | 13147.054     | 805.166      | 100.000  |

(c)



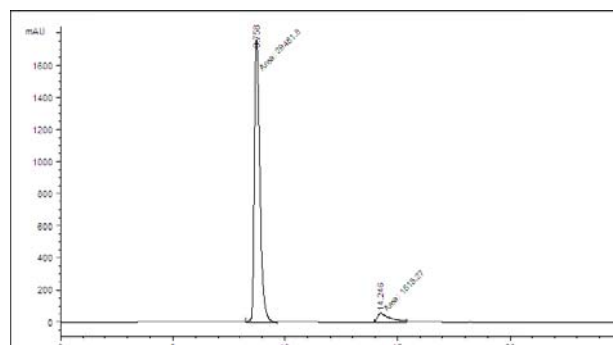
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.627         | 18393.465     | 1163.297     | 95.712   |
| 2      | 14.466        | 824.034       | 15.554       | 4.288    |
| Total  | —             | 19217.499     | 1178.851     | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.690         | 24566.127     | 1519.472     | 93.803   |
| 2      | 14.180        | 1622.936      | 46.543       | 6.197    |
| Total  | —             | 26189.063     | 1566.015     | 100.000  |

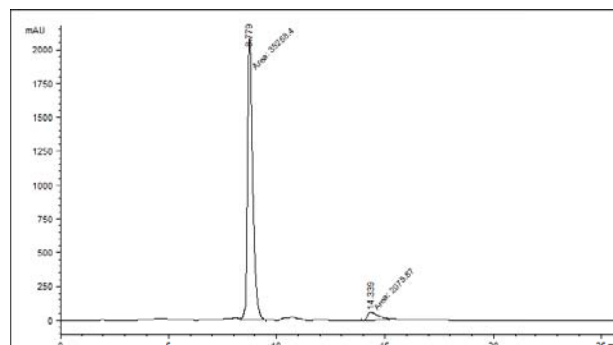
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.758         | 29481.789     | 1756.231     | 95.112   |
| 2      | 14.246        | 1515.268      | 54.252       | 4.888    |
| Total  | —             | 30997.057     | 1810.484     | 100.000  |

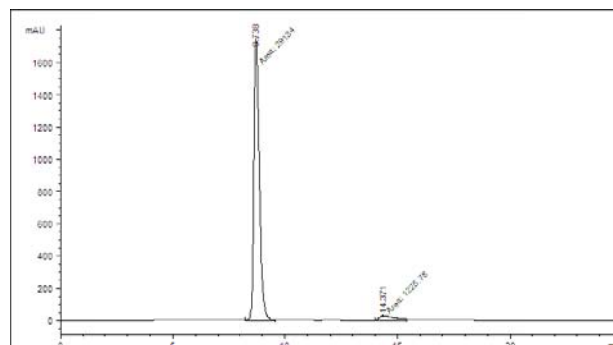
**Figure S56.** HPLC traces of the products from five parallel cycloaddition reactions between **D-BPAM** and methyl acrylate (catalyzed by **1-M** from five isolated crystallization batches).

(a)



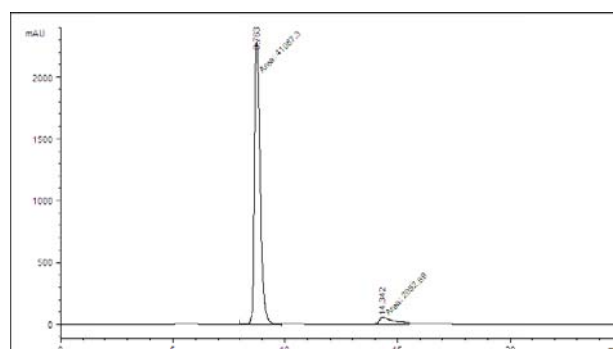
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.779         | 35258.367     | 2078.778     | 94.439   |
| 2      | 14.339        | 2075.872      | 60.877       | 5.561    |
| Total  | —             | 37334.239     | 2139.655     | 100.000  |

(b)



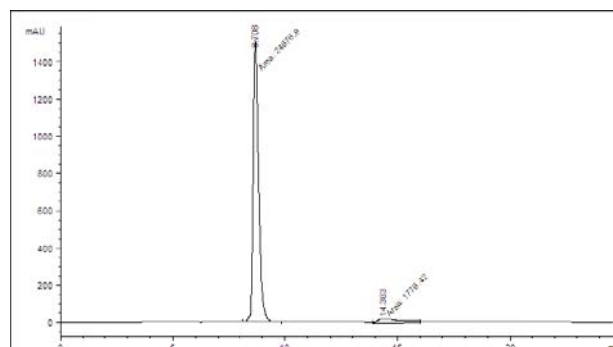
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.738         | 29134.004     | 1748.341     | 95.963   |
| 2      | 14.371        | 1225.775      | 26.240       | 4.037    |
| Total  | —             | 30359.779     | 1774.581     | 100.000  |

(c)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.763         | 41087.320     | 2290.699     | 95.242   |
| 2      | 14.342        | 2052.690      | 55.571       | 4.758    |
| Total  | —             | 43140.010     | 2346.27      | 100.000  |

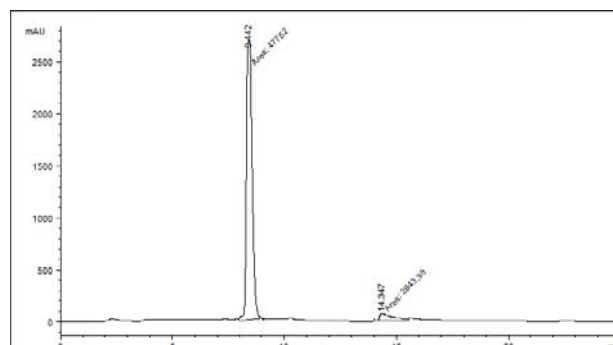
(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 1     | 8.708  | 24676.853 | 1513.741 | 93.285  |
| 2     | 14.383 | 1776.415  | 26.744   | 6.715   |
| Total | —      | 26453.268 | 1540.485 | 100.000 |

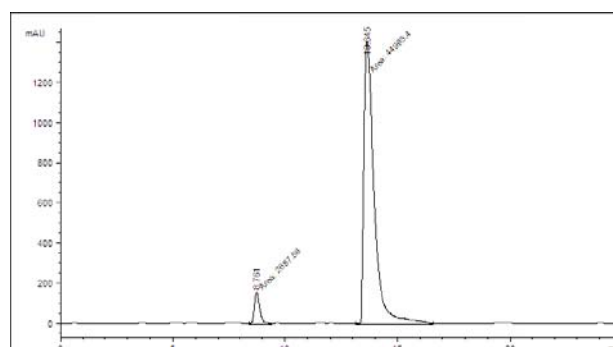
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.442         | 47752.015     | 2692.983     | 94.755   |
| 2      | 14.347        | 2643.376      | 69.244       | 5.245    |
| Total  | —             | 50395.391     | 2762.227     | 100.000  |

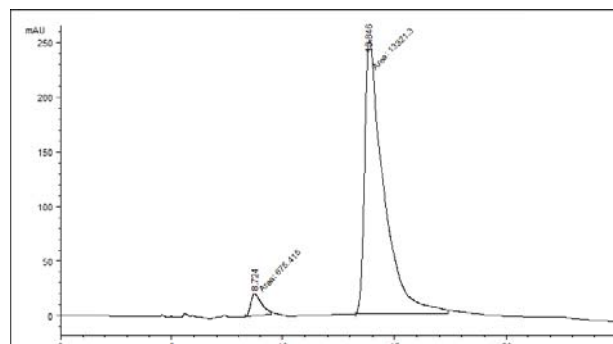
**Figure S57.** HPLC traces of the products from five parallel cycloaddition reactions between *L*-BPAM and methyl acrylate (catalyzed by **1-P** from five isolated crystallization batches).

(a)



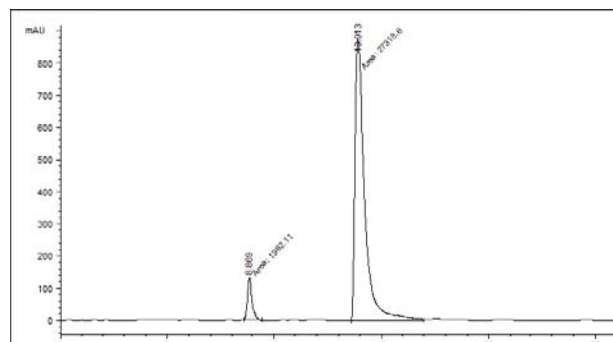
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.761         | 2687.558      | 159.155      | 5.636    |
| 2      | 13.645        | 44995.410     | 1408.927     | 94.364   |
| Total  | —             | 47682.968     | 1568.082     | 100.000  |

(b)



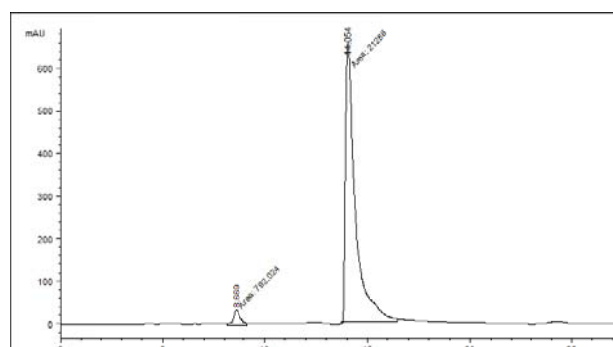
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.724         | 675.415       | 20.078       | 4.826    |
| 2      | 13.846        | 13321.303     | 252.114      | 95.174   |
| Total  | —             | 13996.718     | 272.192      | 100.000  |

(c)



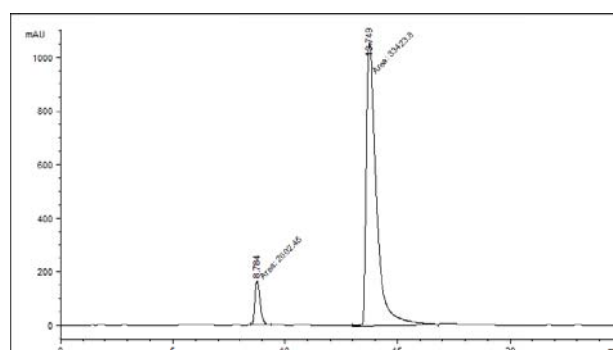
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.869         | 1962.114      | 141.163      | 6.701    |
| 2      | 13.913        | 27318.576     | 878.058      | 93.299   |
| Total  | —             | 29280.69      | 1019.221     | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.669         | 792.024       | 26.658       | 3.587    |
| 2      | 14.054        | 21286.003     | 661.888      | 96.413   |
| Total  | —             | 22078.027     | 688.546      | 100.000  |

(e)

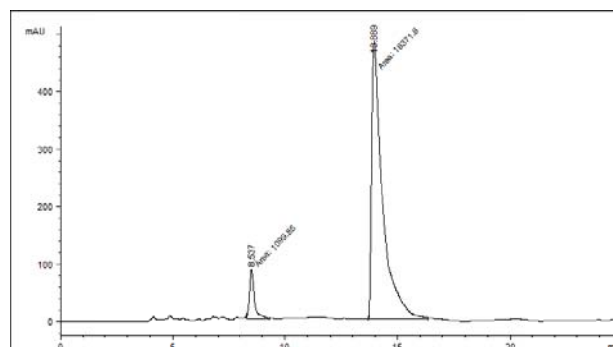


| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 1     | 8.784  | 2002.455  | 148.024  | 5.652   |
| 2     | 13.749 | 33423.836 | 1058.411 | 94.348  |
| Total | —      | 35426.291 | 1206.436 | 100.000 |

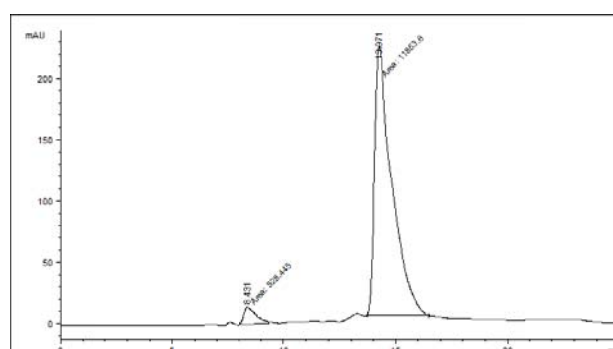
**Figure S58.** HPLC traces of the products from five parallel cycloaddition reactions between **D-BPAM** and methyl acrylate (catalyzed by **1-P** from five isolated crystallization batches).

(a)



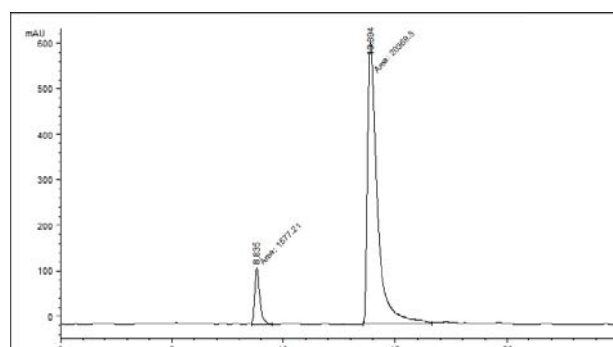
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.537         | 1099.849      | 91.711       | 6.295    |
| 2      | 13.889        | 16371.593     | 484.245      | 93.705   |
| Total  | —             | 17471.442     | 575.956      | 100.000  |

(b)



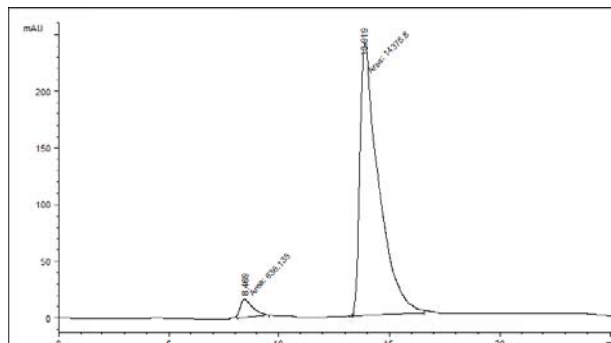
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.431         | 528.445       | 17.138       | 4.268    |
| 2      | 13.971        | 11853.604     | 228.809      | 95.732   |
| Total  | —             | 12382.049     | 245.947      | 100.000  |

(c)



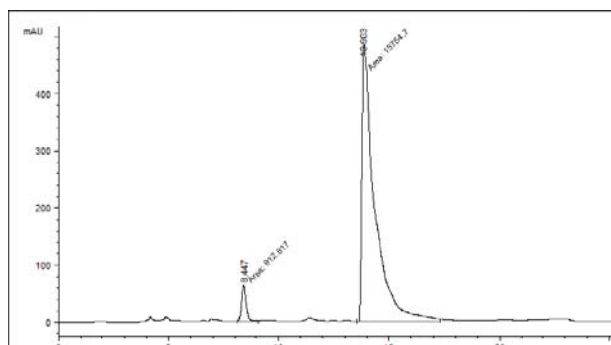
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.835         | 1577.208      | 130.618      | 7.187    |
| 2      | 13.894        | 20369.451     | 627.660      | 92.813   |
| Total  | —             | 21946.659     | 758.278      | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.469         | 636.135       | 18.573       | 4.238    |
| 2      | 13.919        | 14375.812     | 247.200      | 95.762   |
| Total  | —             | 15011.948     | 265.773      | 100.000  |

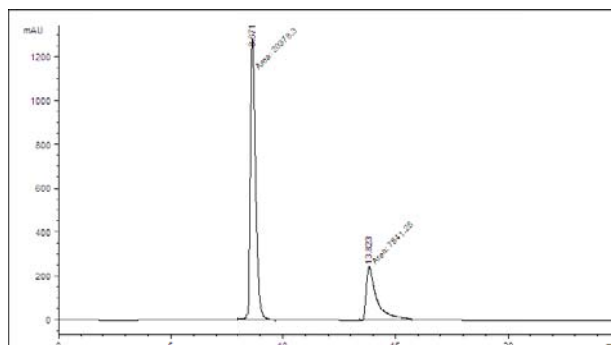
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.447         | 912.617       | 61.512       | 5.475    |
| 2      | 13.903        | 15754.732     | 490.313      | 94.525   |
| Total  | —             | 16667.349     | 551.825      | 100.000  |

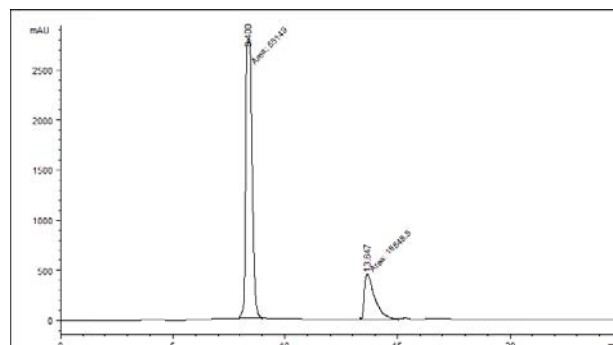
**Figure S59.** HPLC traces of the products from five parallel tandem catalytic systems of **1+L-BPAM** (entry 7, Table 1).

(a)



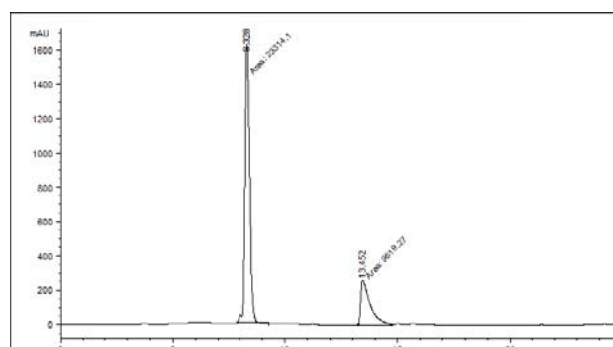
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.671         | 20378.318     | 1284.030     | 72.213   |
| 2      | 13.823        | 7841.246      | 243.656      | 27.787   |
| Total  | —             | 28219.564     | 1527.686     | 100.000  |

(b)



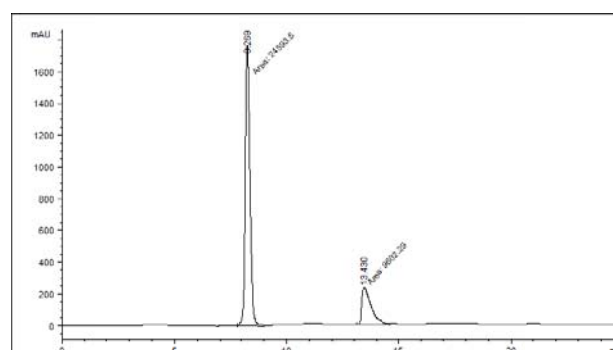
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.400         | 55148.988     | 2779.704     | 74.528   |
| 2      | 13.647        | 18848.533     | 500.258      | 25.472   |
| Total  | —             | 73997.521     | 3279.962     | 100.000  |

(c)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.328         | 23314.055     | 1630.087     | 70.792   |
| 2      | 13.452        | 9619.270      | 280.619      | 29.208   |
| Total  | —             | 32933.324     | 1910.706     | 100.000  |

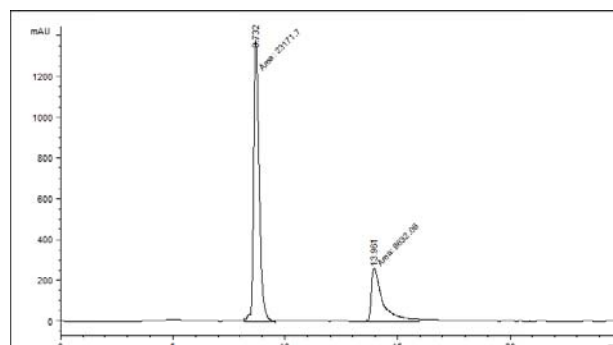
(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 1     | 8.269  | 24593.459 | 1761.181 | 71.920  |
| 2     | 13.430 | 9602.290  | 269.030  | 28.080  |
| Total | —      | 34195.749 | 2030.211 | 100.000 |

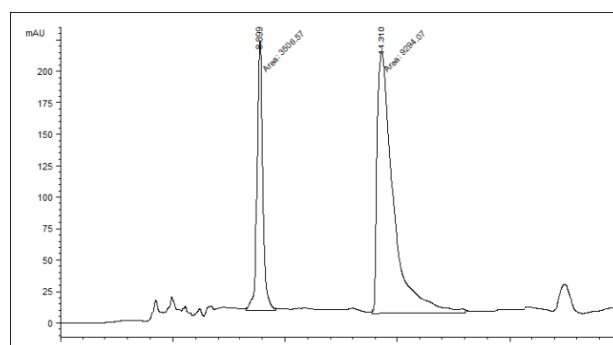
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.732         | 23171.740     | 1384.061     | 70.637   |
| 2      | 13.961        | 9632.063      | 263.862      | 29.363   |
| Total  | —             | 32803.803     | 1647.923     | 100.000  |

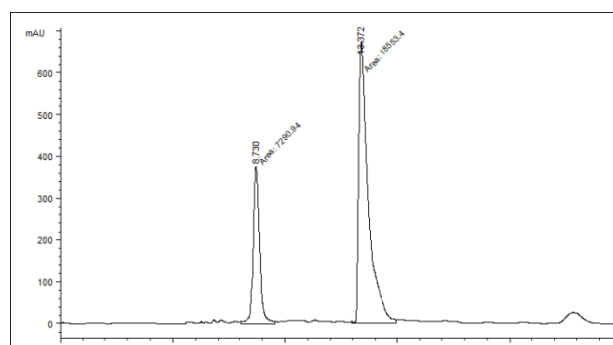
**Figure S60.** HPLC traces of the products from five parallel tandem catalytic systems of **1+D-BPAM** (entry 8, Table 1).

(a)



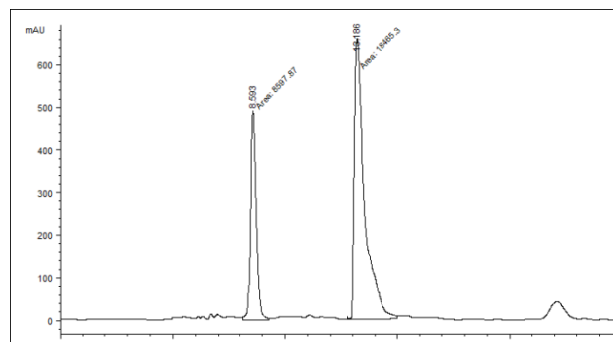
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.899         | 3506.568      | 210.240      | 27.394   |
| 2      | 14.310        | 9294.073      | 210.059      | 72.606   |
| Total  | —             | 12800.642     | 420.298      | 100.000  |

(b)



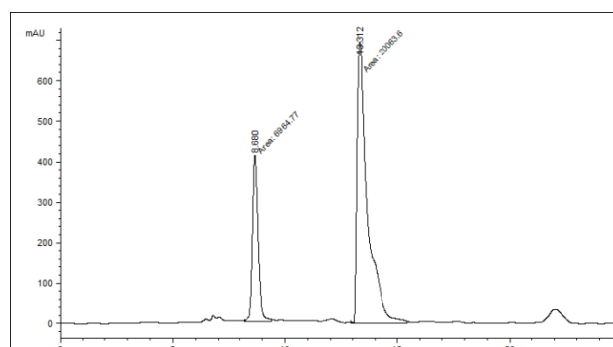
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.730         | 7290.941      | 379.183      | 28.211   |
| 2      | 13.372        | 18553.389     | 674.415      | 71.789   |
| Total  | —             | 25844.330     | 1053.598     | 100.000  |

(c)



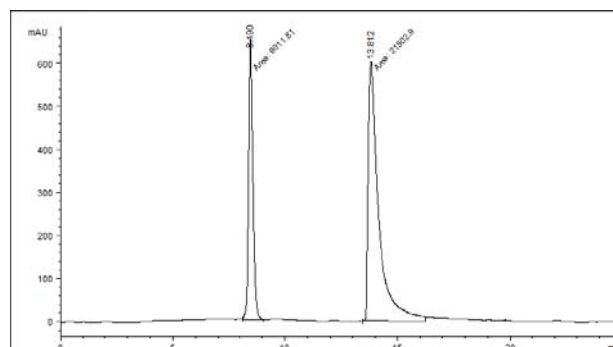
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.593         | 8597.870      | 491.639      | 31.770   |
| 2      | 13.186        | 18465.318     | 659.148      | 68.230   |
| Total  | —             | 27063.188     | 1150.787     | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.680         | 6964.773      | 410.698      | 25.768   |
| 2      | 13.312        | 20063.639     | 697.459      | 74.232   |
| Total  | —             | 27028.412     | 1108.157     | 100.000  |

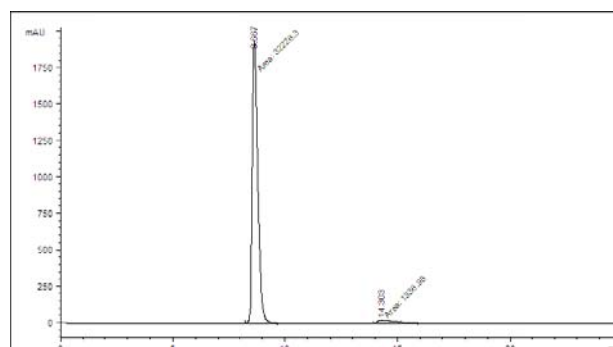
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

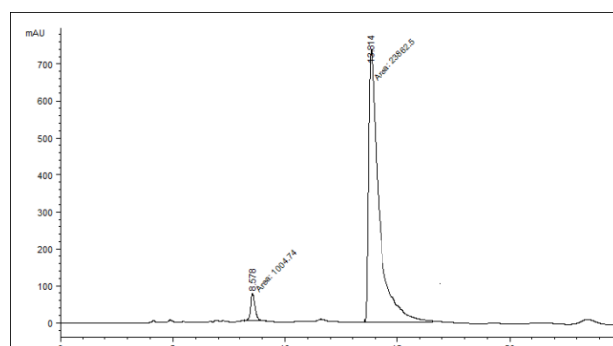
|       |        |           |          |         |
|-------|--------|-----------|----------|---------|
| 1     | 8.490  | 9011.808  | 649.603  | 29.533  |
| 2     | 13.812 | 21502.949 | 605.420  | 70.467  |
| Total | —      | 30514.757 | 1255.023 | 100.000 |

**Figure S61.** HPLC trace of the product from the cycloaddition reaction between **D-BPAM** and methyl acrylate (catalyzed by **2-M**).



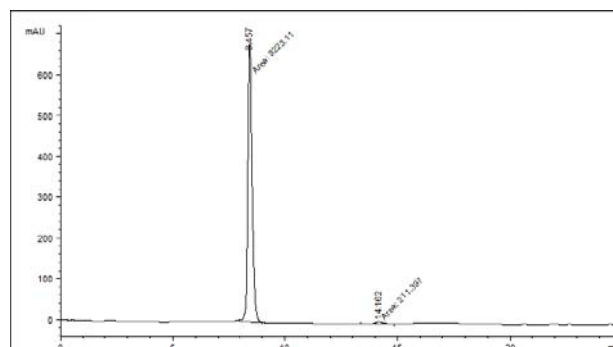
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.667         | 32226.299     | 1934.385     | 96.016   |
| 2      | 14.303        | 1336.953      | 23.927       | 3.984    |
| Total  | —             | 33563.252     | 1958.312     | 100.000  |

**Figure S62.** HPLC trace of the product from the cycloaddition reaction between **D-BPAM** and methyl acrylate (catalyzed by **2-P**).



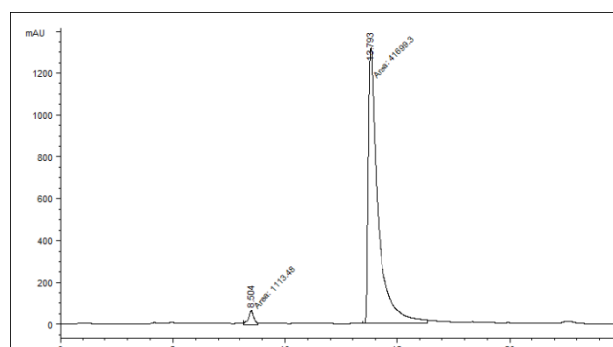
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.578         | 1004.736      | 72.762       | 4.040    |
| 2      | 13.814        | 23862.504     | 760.413      | 95.960   |
| Total  | —             | 24867.240     | 833.176      | 100.000  |

**Figure S63.** HPLC trace of the product from the cycloaddition reaction between **D-BPAM** and methyl acrylate (catalyzed by **3-M**).



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.457         | 9223.109      | 685.570      | 97.759   |
| 2      | 14.162        | 211.397       | 6.492        | 2.241    |
| Total  | —             | 9434.507      | 692.062      | 100.000  |

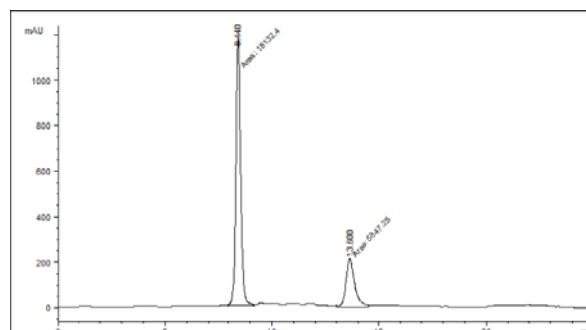
**Figure S64.** HPLC trace of the product from the cycloaddition reaction between **D-BPAM** and methyl acrylate (catalyzed by **3-P**).



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.504         | 1113.476      | 69.102       | 2.601    |
| 2      | 13.793        | 41699.266     | 1347.262     | 97.399   |
| Total  | —             | 42812.742     | 1416.363     | 100.000  |

**Figure S65.** HPLC traces of the products from five parallel tandem catalytic systems of **2+L-BPAM** (entries a-e in Table S11).

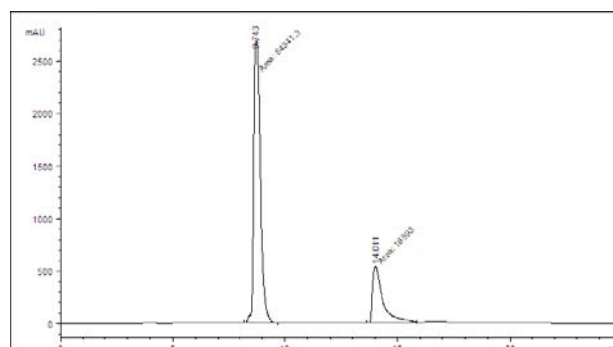
(a)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.440         | 18132.391     | 1174.235     | 75.616   |
| 2      | 13.600        | 5847.249      | 212.049      | 24.384   |

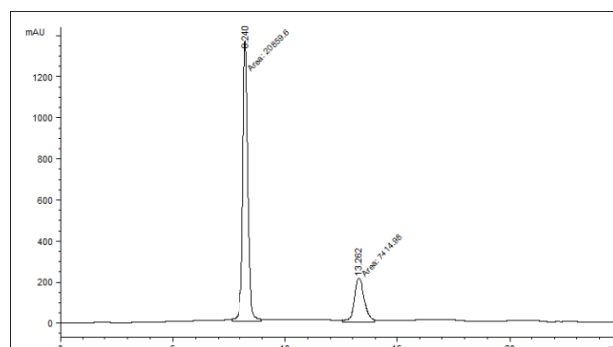
|       |   |           |          |         |
|-------|---|-----------|----------|---------|
| Total | — | 23979.640 | 1386.284 | 100.000 |
|-------|---|-----------|----------|---------|

(b)



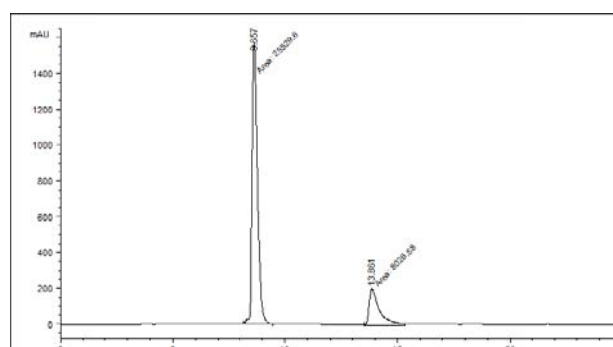
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.743         | 54341.324     | 2685.315     | 76.607   |
| 2      | 14.011        | 16592.988     | 534.350      | 23.393   |
| Total  | —             | 70934.312     | 3219.665     | 100.000  |

(c)



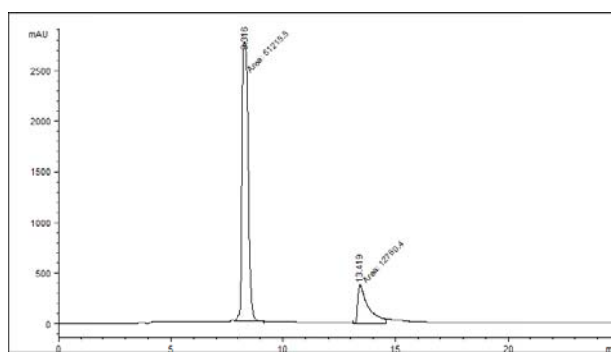
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.240         | 20859.619     | 1373.198     | 73.775   |
| 2      | 13.262        | 7414.980      | 222.580      | 26.225   |
| Total  | —             | 28274.599     | 1595.778     | 100.000  |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.657         | 25529.590     | 1571.436     | 76.080   |
| 2      | 13.861        | 8026.575      | 215.820      | 23.920   |
| Total  | —             | 33556.165     | 1787.256     | 100.000  |

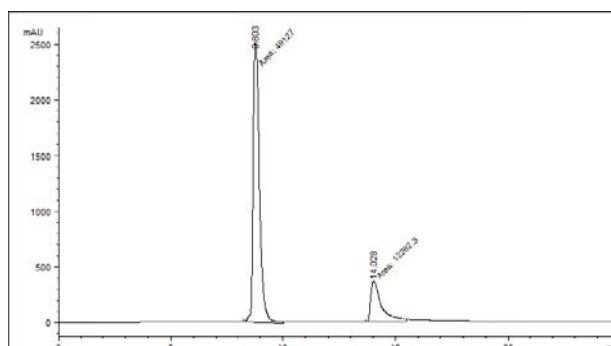
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.316         | 51215.535     | 2755.052     | 80.054   |
| 2      | 13.419        | 12760.384     | 382.854      | 19.946   |
| Total  | —             | 63975.919     | 3137.906     | 100.000  |

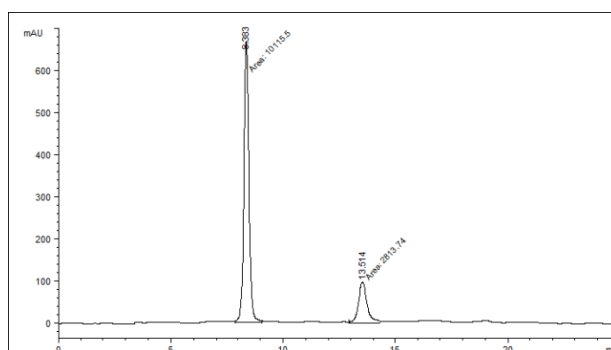
**Figure S66.** HPLC traces of the products from five parallel tandem catalytic systems of **3+L-BPAM** (entries f-j in Table S11).

(f)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.803         | 49126.965     | 2529.323     | 80.025   |
| 2      | 14.028        | 12262.342     | 363.609      | 19.975   |
| Total  | —             | 61389.307     | 2892.932     | 100.000  |

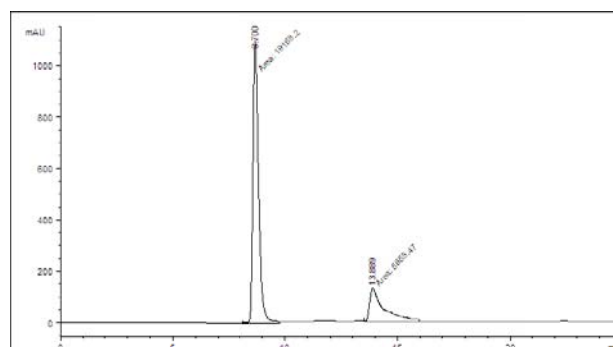
(g)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.383         | 10115.515     | 669.809      | 78.237   |

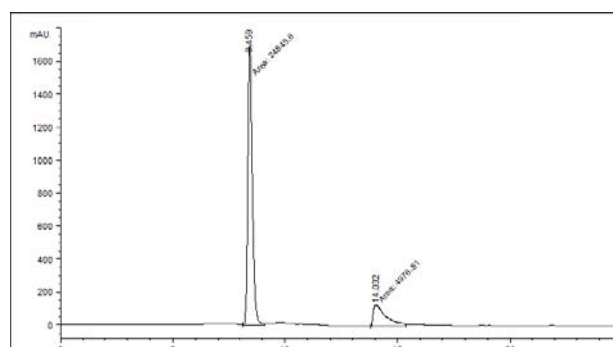
|       |        |           |         |         |
|-------|--------|-----------|---------|---------|
| 2     | 13.514 | 2813.735  | 97.878  | 21.763  |
| Total | —      | 12929.250 | 767.687 | 100.000 |

(h)



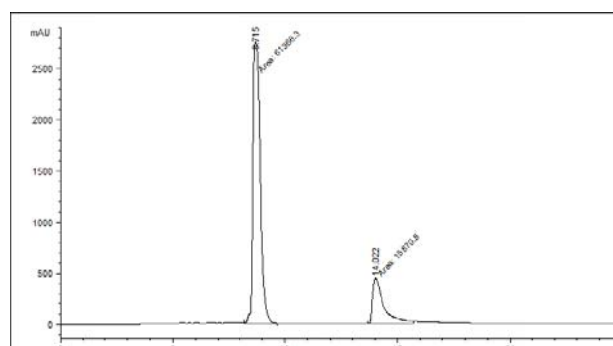
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.700         | 19168.175     | 1100.271     | 77.217   |
| 2      | 13.889        | 5655.466      | 130.599      | 22.783   |
| Total  | —             | 24823.641     | 1230.870     | 100.000  |

(i)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.459         | 24845.627     | 1708.910     | 83.312   |
| 2      | 14.032        | 4976.813      | 130.507      | 16.688   |
| Total  | —             | 29822.439     | 1839.417     | 100.000  |

(j)

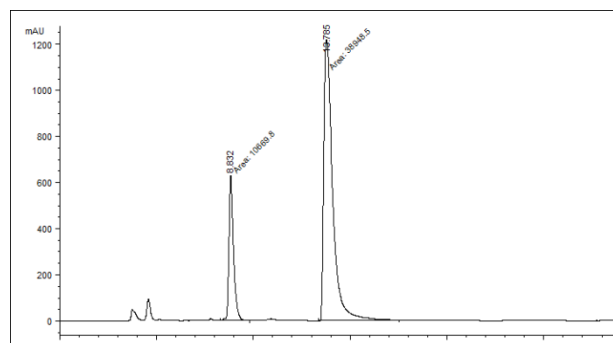


| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.715         | 61366.270     | 2756.679     | 79.452   |
| 2      | 14.022        | 15870.824     | 445.675      | 20.548   |

|       |   |           |          |         |
|-------|---|-----------|----------|---------|
| Total | — | 77237.094 | 3202.355 | 100.000 |
|-------|---|-----------|----------|---------|

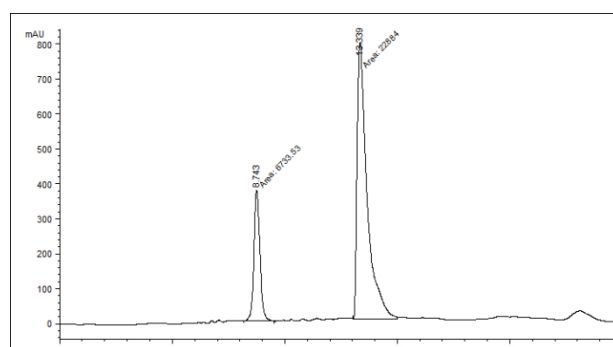
**Figure S67.** HPLC traces of the products from five parallel tandem catalytic systems of **2+D-BPAM** (entries a-e in Table S12).

(a)



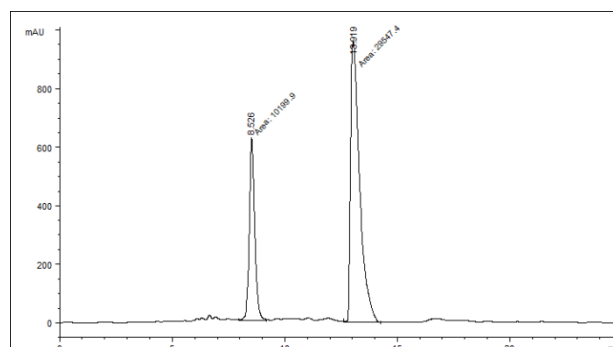
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.832         | 10669.752     | 629.071      | 21.504   |
| 2      | 13.785        | 38948.531     | 1220.065     | 78.496   |
| Total  | —             | 49618.283     | 1849.136     | 100.000  |

(b)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.743         | 6733.534      | 375.276      | 22.735   |
| 2      | 13.339        | 22883.965     | 793.149      | 77.265   |
| Total  | —             | 29617.499     | 1168.425     | 100.000  |

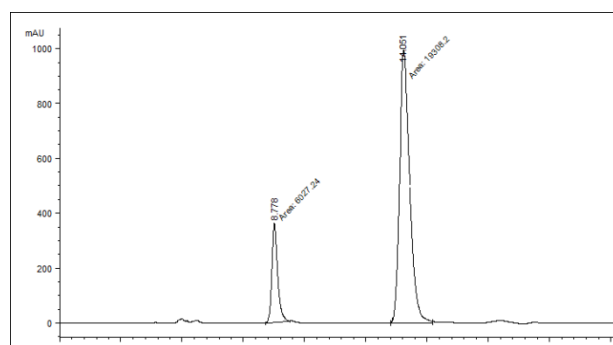
(c)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.820         | 10669.752     | 629.071      | 21.504   |
| 2      | 13.719        | 38948.531     | 1220.065     | 78.496   |
| Total  | —             | 49618.283     | 1849.136     | 100.000  |

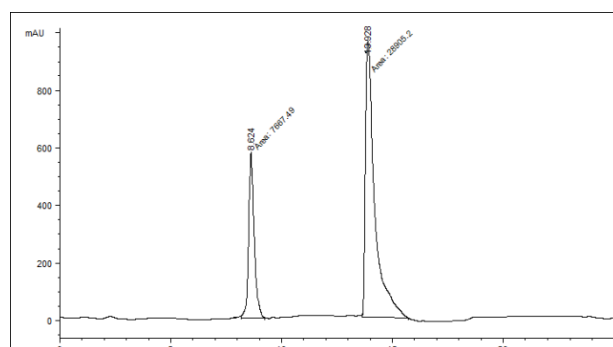
|       |        |           |         |         |
|-------|--------|-----------|---------|---------|
| 1     | 8.526  | 10199.854 | 620.344 | 25.662  |
| 2     | 13.919 | 29547.391 | 955.376 | 74.338  |
| Total | —      | 39747.245 | 1575.72 | 100.000 |

(d)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.778         | 6027.241      | 360.991      | 23.789   |
| 2      | 14.051        | 19308.236     | 999.753      | 76.211   |
| Total  | —             | 25335.477     | 1360.744     | 100.000  |

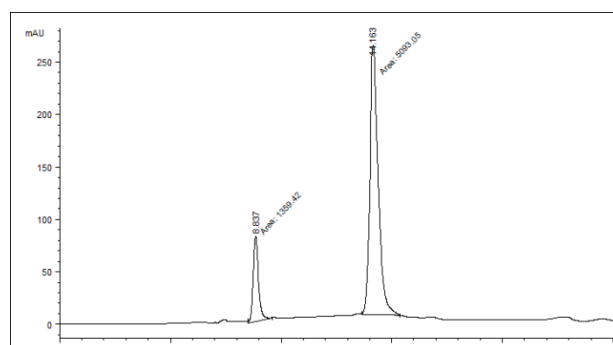
(e)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.624         | 7667.491      | 587.227      | 20.965   |
| 2      | 13.928        | 28905.211     | 958.994      | 79.035   |
| Total  | —             | 36572.702     | 1546.221     | 100.000  |

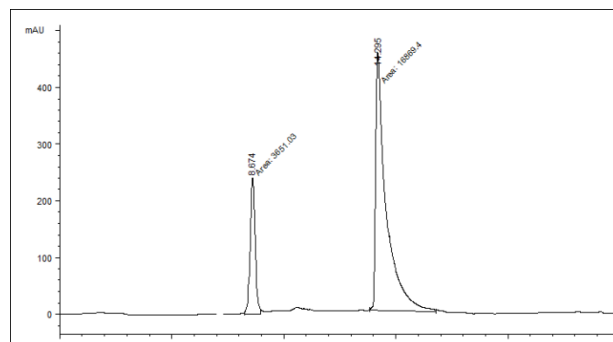
**Figure S68.** HPLC traces of the products from five parallel tandem catalytic systems of **3+D-BPAM** (entries f-j in Table S12).

(f)



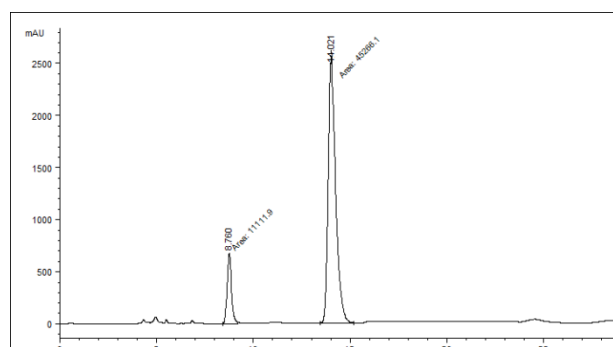
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.837         | 1359.422      | 81.592       | 21.068   |
| 2      | 14.163        | 5093.047      | 195.991      | 79.035   |
| Total  | —             | 6452.469      | 277.583      | 100.000  |

(g)



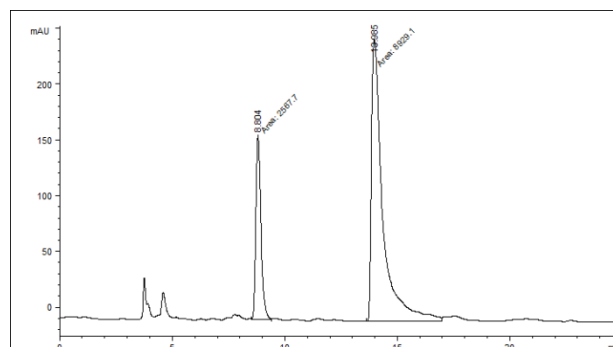
| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.674         | 3651.026      | 241.806      | 17.792   |
| 2      | 14.295        | 16869.402     | 457.655      | 82.208   |
| Total  | —             | 20520.428     | 699.461      | 100.000  |

(h)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.760         | 11111.895     | 686.331      | 19.709   |
| 2      | 14.021        | 45266.111     | 2614.807     | 80.291   |
| Total  | —             | 56378.006     | 3301.138     | 100.000  |

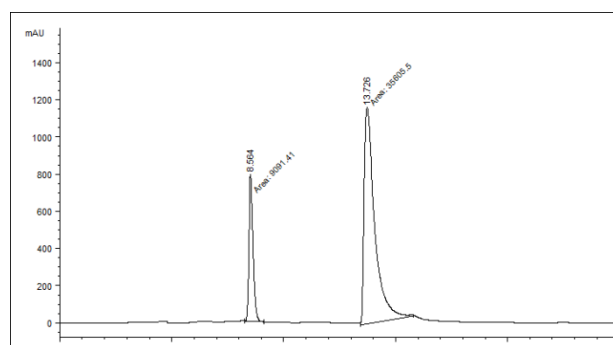
(i)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
|--------|---------------|---------------|--------------|----------|

|       |        |           |         |         |
|-------|--------|-----------|---------|---------|
| 1     | 8.804  | 2567.699  | 164.892 | 22.334  |
| 2     | 13.985 | 8929.095  | 252.481 | 77.666  |
| Total | —      | 11496.794 | 417.373 | 100.000 |

(j)



| Peak # | RetTime [min] | Area [mAU *s] | Height [mAU] | Area [%] |
|--------|---------------|---------------|--------------|----------|
| 1      | 8.564         | 9091.414      | 974.751      | 20.341   |
| 2      | 13.726        | 35605.508     | 1150.716     | 79.659   |
| Total  | —             | 44696.922     | 2125.467     | 100.000  |

## Supplementary References

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