

Supporting Information

Enantioselective Synthesis of Calix[4]arenes with C–C Axial and Inherent Chirality via Palladium/Chiral Norbornene Cooperative Catalysis

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1. General information

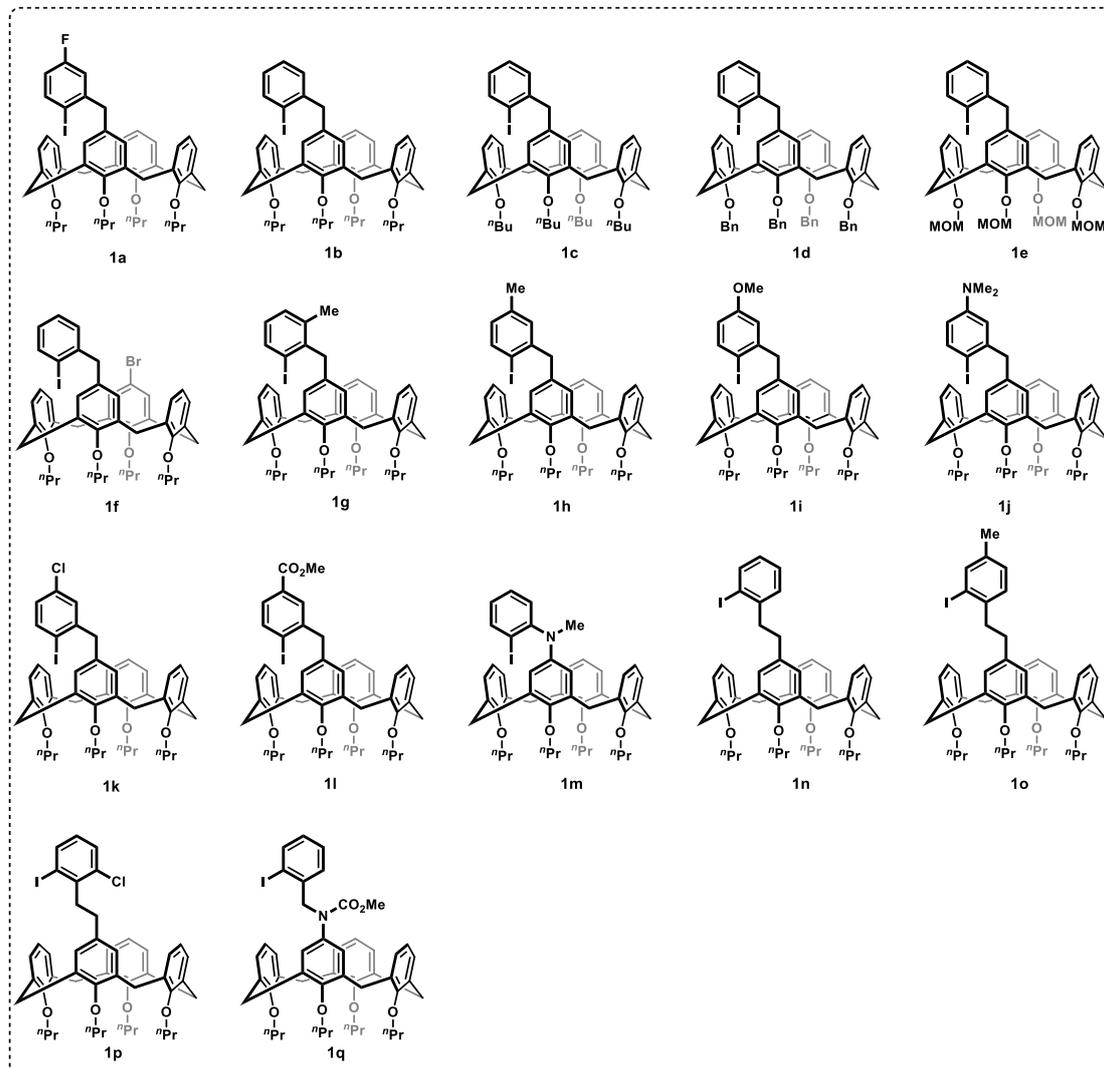
All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Anhydrous DMF, CH₃CN, THF, DCM and toluene were dried by JC Meyer Solvent Drying System. Anhydrous (over molecular sieve) DCE, DME, NMP and 1,4-dioxane were purchased from Energy Chemical and used as received. Most reagents were purchased from commercial sources (Energy Chemical, Macklin, Leyan, etc.) and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or ethanol solution of phosphomolybdic acid (PMA) and heat as a developing agent.

All NMR spectra were recorded on a Bruker spectrometer at 400 MHz or 600 MHz (¹H NMR), 100 MHz or 150 MHz (¹³C NMR), 376 MHz or 565 MHz (¹⁹F NMR), 162 MHz or 243 MHz (³¹P NMR). ¹H NMR and ¹³C NMR spectra were calibrated using residual undeuterated solvent as an internal reference (CDCl₃ @ 7.26 ppm ¹H NMR, 77.2 ppm ¹³C NMR). For ¹⁹F NMR, chemical shifts (δ) were reported in ppm (no decoupling). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, brs = broad singlet. Coupling constants are reported as a *J* value in Hertz (Hz). The number of protons (*n*) for a given resonance is indicated as *n*H and is based on spectral integration values. High resolution mass spectra (HRMS) were recorded on DIONEX

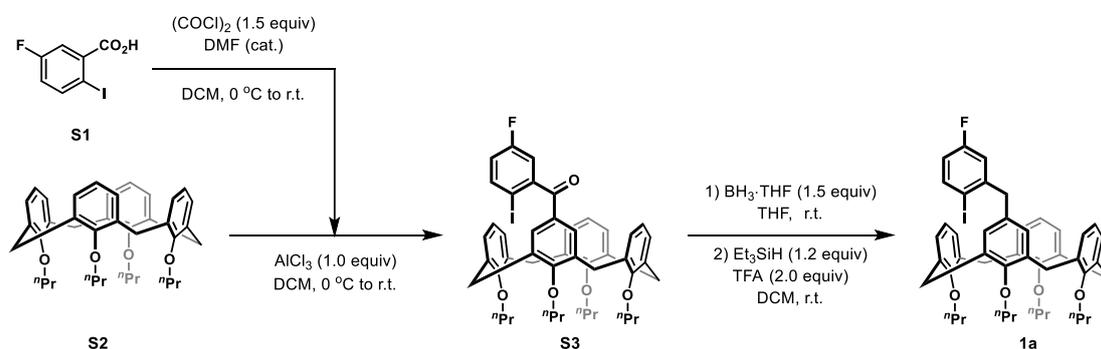
UltiMate 3000 & Bruker Compact TOF mass spectrometer. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. X-ray structure analyses were performed using a Bruker D8 Venture X-ray single crystal diffractometer. Enantiomeric excesses (*e.e.*) values were determined by chiral HPLC (Agilent 1260) using AD-H, OD-H, IA, IC, ID, IB, IB N-5 and IG columns with hexane and *t*PrOH as solvents. Melting point (M.P.) were measured with SGW® X-4 micro melting point apparatus. UV-vis spectra were conducted on Shimadzu UV-2700 spectrometer. Fluorescence intensity were measured on HORIBA-NanoLog®. CPL spectra were conducted on the JASCO CPL-300. CD spectra were conducted on the JASCO J-1500. Photoluminescence quantum yields were determined with FLS980 spectrometer.

2. Preparation of substrates

2.1 Preparation of aryl iodides



Preparation of **1a**, **1b**, **1g-1i** and **1k**.



S2 was synthesized by literature procedure.¹

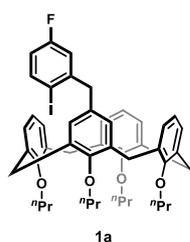
Taking the synthesis of **1a** as an example: to a solution of **S1** (1.33 g, 5.0 mmol, 1.0 equiv) and DMF (two drops) in CH₂Cl₂ (10 mL) was added oxalyl chloride (0.64 mL, 7.5 mmol, 1.5 equiv) dropwise at 0 °C. Then the reaction mixture was stirred at r.t. for

1 h until the bubbling stopped. After that, the reaction mixture was concentrated in vacuo to give the corresponding acetyl chloride, which was used in next step without further purification.

To a solution of above prepared acetyl chloride in DCM (20 mL) was added **S2** (2.96 g, 5.0 mmol, 1.0 equiv) and AlCl₃ (667 mg, 5 mmol, 1.0 equiv) at 0 °C. Then the reaction was warmed to r.t. and stirred overnight. The mixture was concentrated in vacuo, and the residue was directly purified by column chromatography on silica gel to give **S3** as a white foam (882 mg, 21% yield).

To the above **S3** (882 mg, 1.1 mmol, 1.0 equiv) was added BH₃ (1 M in THF, 1.5 equiv, 1.7 mL) at r.t., then the reaction mixture was stirred at r.t. for 6 hours. The mixture was poured into the ice water slowly. The aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding alcohol as a white foam (796 mg, 90% yield).

To a solution of above alcohol (796 mg, 0.9 mmol, 1.0 equiv) in DCM (20 mL) was added Et₃SiH (211 μL, 1.32 mmol, 1.2 equiv) at room temperature, then TFA (169 μL, 2.2 mmol, 2 equiv) was added dropwise. The resulting solution was quenched with aq. NaHCO₃ and the mixture was extracted with DCM. The combined organic phases were dried over anhydrous Na₂SO₄, concentrated in vacuo, and the residue was directly purified by column chromatography on silica gel to give the desired products **1a** as a white foam (699 mg, 94% yield).



Physical state: white foam;

Yield: 94%;

R_f = 0.4 (PE:EtOAc = 40:1);

Melting point: 116–118 °C;

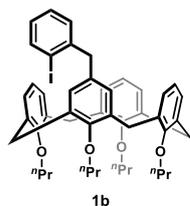
¹H NMR (400 MHz, CDCl₃): δ 7.75 (dd, *J* = 8.6, 5.7 Hz, 1H), 6.71 – 6.53 (m, 11H), 6.40 (s, 2H), 4.46 (dd, *J* = 13.2, 9.7 Hz, 4H), 3.85 (td, *J* = 7.4, 3.0 Hz, 8H), 3.69 (s, 2H), 3.14 (dd, *J* = 23.9, 13.3 Hz, 4H), 2.00 – 1.88 (m, 8H), 1.07 – 0.94 (m, 12H);

¹³C NMR (150 MHz, CDCl₃): δ 163.1 (d, *J* = 246.8 Hz), 156.7, 156.5, 155.5, 146.9 (d,

$J = 7.0$ Hz), 140.1 (d, $J = 7.6$ Hz), 135.3 (d, $J = 17.9$ Hz), 135.1 (d, $J = 22.1$ Hz), 131.6, 129.0, 128.2, 128.2, 122.0, 121.8, 117.2 (d, $J = 22.7$ Hz), 115.0 (d, $J = 21.9$ Hz), 93.9 (d, $J = 2.8$ Hz), 76.8, 76.7, 76.7, 46.2, 31.0, 31.0, 23.3, 23.3, 10.4, 10.4, 10.4;

^{19}F NMR (376 MHz, CDCl_3): δ -114.3;

HRMS (ESI-TOF) calculated for $\text{C}_{47}\text{H}_{56}\text{FIO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 844.3233, found 844.3230.



Physical state: white foam;

Yield: 22% (860 mg, **S2** to **1b**, 5.0 mmol scale);

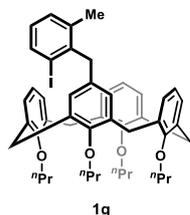
$R_f = 0.5$ (PE:EtOAc = 40:1);

Melting point: 71–73 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.92–6.81 (m, 2H), 6.71 (d, $J = 7.0$ Hz, 2H), 6.65 (dd, $J = 8.5, 6.1$ Hz, 1H), 6.61 – 6.49 (m, 6H), 6.46 (s, 2H), 4.51 – 4.39 (m, 4H), 3.85 (dt, $J = 12.9, 7.2$ Hz, 8H), 3.76 (s, 2H), 3.13 (dd, $J = 27.7, 13.3$ Hz, 4H), 1.94 (ddt, $J = 11.0, 7.5, 3.6$ Hz, 8H), 1.00 (td, $J = 7.5, 3.9$ Hz, 12H);

^{13}C NMR (150 MHz, CDCl_3): δ 156.9, 156.6, 155.4, 144.5, 139.4, 135.5, 135.3, 135.1, 132.5, 130.3, 129.2, 128.4, 128.3, 128.2, 128.2, 127.8, 122.1, 121.9, 101.6, 76.9, 46.3, 31.2, 31.1, 23.4, 23.4, 10.6, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $\text{C}_{47}\text{H}_{57}\text{IO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 826.3327, found 826.3326.



Physical state: white foam;

Yield: 22% (367 mg, **S2** to **1g**, 2.0 mmol scale);

$R_f = 0.5$ (PE:EtOAc = 40:1);

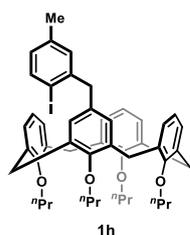
Melting point: 69–72 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.16 – 7.07 (m, 2H), 6.77 (d, $J = 7.0$ Hz, 2H), 6.74 –

6.65 (m, 2H), 6.64 – 6.54 (m, 6H), 6.52 (s, 2H), 4.57 – 4.42 (m, 4H), 3.98 – 3.79 (m, 10H), 3.17 (dd, $J = 28.3, 13.3$ Hz, 4H), 2.54 (s, 3H), 2.06 – 1.91 (m, 8H), 1.12 – 0.99 (m, 12H);

^{13}C NMR (100 MHz, CDCl_3): δ 156.9, 156.4, 155.3, 145.0, 142.2, 135.5, 135.2, 134.9, 134.9, 132.8, 129.2, 128.3, 128.2, 128.0, 127.6, 127.4, 127.4, 122.0, 121.8, 108.8, 76.8, 76.8, 76.7, 47.5, 31.1, 31.0, 30.1, 23.3, 23.3, 23.3, 10.5, 10.4, 10.4;

HRMS (ESI-TOF) calculated for $\text{C}_{48}\text{H}_{59}\text{IO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 840.3483, found 840.3482.



Physical state: white foam;

Yield: 24% (399 mg, **S2** to **1h**, 2.0 mmol scale);

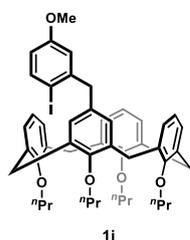
$R_f = 0.5$ (PE:EtOAc = 40:1);

Melting point: 66–70 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 7.9$ Hz, 1H), 6.81 (d, $J = 7.4$ Hz, 2H), 6.78 – 6.71 (m, 3H), 6.56 (s, 2H), 6.49 (s, 6H), 4.47 (t, $J = 12.5$ Hz, 4H), 3.92 (q, $J = 7.4, 6.9$ Hz, 4H), 3.84 – 3.77 (m, 6H), 3.15 (dd, $J = 24.9, 13.3$ Hz, 4H), 2.25 (s, 3H), 2.02 – 1.88 (m, 8H), 1.08 – 0.97 (m, 12H);

^{13}C NMR (100 MHz, CDCl_3): δ 157.2, 156.3, 155.7, 144.4, 139.2, 138.1, 135.9, 135.8, 134.7, 132.8, 131.3, 129.4, 128.8, 128.5, 128.1, 128.0, 122.1, 121.9, 97.4, 76.9, 76.8, 76.8, 46.0, 31.2, 31.1, 23.5, 23.4, 23.3, 21.1, 10.7, 10.4, 10.4;

HRMS (ESI-TOF) calculated for $\text{C}_{48}\text{H}_{59}\text{IO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 840.3483, found 840.3483.



Physical state: white foam;

Yield: 31% (240 mg, **S2** to **1i**, 2.0 mmol scale);

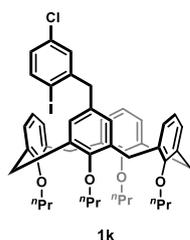
$R_f = 0.4$ (PE:EtOAc = 20:1);

Melting point: 115–118 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.4 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.80 – 6.75 (m, 1H), 6.60 (s, 2H), 6.59 – 6.49 (m, 8H), 4.51 (t, *J* = 12.0 Hz, 4H), 3.96 (q, *J* = 8.0 Hz, 4H), 3.85 (t, *J* = 7.3 Hz, 5H), 3.81 (s, 2H), 3.74 (s, 3H), 3.18 (dd, *J* = 24.4, 13.4 Hz, 4H), 2.05 – 1.93 (m, 8H), 1.08 (t, *J* = 7.4 Hz, 6H), 1.03 (td, *J* = 7.5, 2.0 Hz, 6H);

¹³C NMR (100 MHz, CDCl₃): δ 160.1, 157.2, 156.3, 155.7, 145.8, 139.7, 135.9, 135.80, 134.7, 134.7, 132.5, 129.4, 128.5, 128.1, 128.0, 122.0, 121.9, 116.2, 114.0, 89.9, 76.9, 76.7, 55.3, 46.4, 31.1, 31.1, 23.5, 23.4, 23.3, 10.6, 10.4, 10.4;

HRMS (ESI-TOF) calculated for C₄₈H₅₉IO₅N⁺, [M+NH₄]⁺ 856.3432, found 856.3430.



Physical state: white foam;

Yield: 25% (419 mg, **S2** to **1k**, 2.0 mmol scale);

R_f = 0.3 (PE:EtOAc = 40:1);

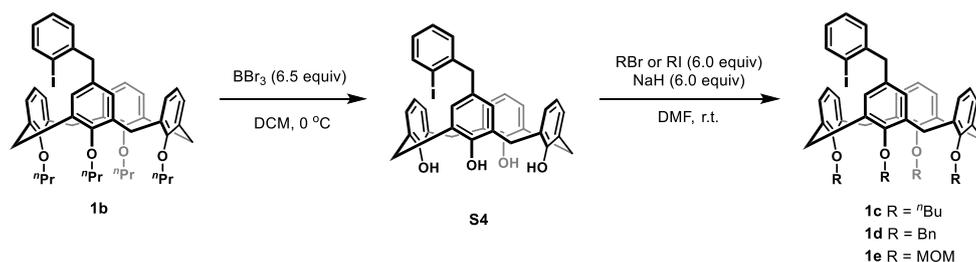
Melting point: 70–72 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.2 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.79 – 6.74 (m, 2H), 6.73 – 6.68 (m, 1H), 6.60 – 6.52 (m, 6H), 6.46 (s, 2H), 4.48 (dd, *J* = 13.3, 8.4 Hz, 4H), 3.90 (t, 4H), 3.84 (t, *J* = 7.4 Hz, 4H), 3.74 (s, 2H), 3.16 (dd, *J* = 22.9, 13.4 Hz, 4H), 2.02 – 1.89 (m, 8H), 1.06 – 0.98 (m, 12H);

¹³C NMR (100 MHz, CDCl₃): δ 157.0, 156.5, 155.8, 146.6, 140.3, 135.8, 135.6, 135.0, 134.8, 134.7, 131.7, 130.2, 129.2, 128.4, 128.2, 128.2, 128.0, 122.2, 121.9, 98.4, 76.9, 76.8, 76.8, 46.1, 31.2, 31.1, 23.5, 23.4, 23.4, 10.6, 10.5, 10.4;

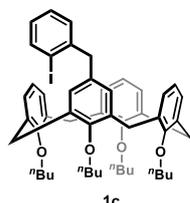
HRMS (ESI-TOF) calculated for C₄₇H₅₆ClIO₄N⁺, [M+NH₄]⁺ 860.2937, found 860.2938.

Preparation of 1c, 1d and 1e.



To a solution of **1b** (2.67 g, 3.3 mmol, 1.0 equiv) in DCM (33 mL) was added BBr₃ (2.0 M in DCM, 10.7 mL, 21.5 mmol, 6.5 equiv) dropwise at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was allowed to warm to 25 °C and stirred for another 4 h at this temperature. The reaction mixture was quenched with aq. NaHCO₃. The organic layer was washed with brine (50 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography to afford **S4** as a white solid (1.9 g, 90% yield).

To a solution of **S4** (256 mg, 0.4 mmol, 1.0 equiv) in DMF (4.0 mL) was added NaH (60% dispersion in oil, 0.16 g, 4.0 mmol, 10.0 equiv) at 0 °C. The mixture was stirred at room temperature for 1 h. Then, 1-iodobutane (0.46 mL, 4.0 mmol, 10.0 equiv) or benzyl bromide (0.48 mL, 4.0 mmol, 10.0 equiv) or bromo(methoxy)methane (0.33 mL, 4.0 mmol, 10.0 equiv) was added to mixture and stirred at room temperature for 14 h. The reaction mixture was poured into HCl (aq. 1.0 M, 20 mL) slowly and was diluted with EtOAc. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography to afford corresponding products.



Physical state: white foam;

Yield: 93% (321 mg, 0.4 mmol scale);

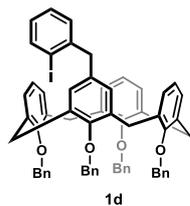
R_f = 0.5 (PE:EtOAc = 40:1);

Melting point: 114–117 °C;

¹H NMR (600 MHz, CDCl₃): δ 7.83 (d, J = 7.9 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.71 (d, J = 7.4 Hz, 2H), 6.68 – 6.63 (m, 1H), 6.62 – 6.50 (m, 6H), 6.46 (s, 2H), 4.45 (dd, J = 22.8, 13.2 Hz, 4H), 3.95 – 3.84 (m, 8H), 3.76 (s, 2H), 3.17 (d, J = 13.3 Hz, 2H), 3.10 (d, J = 13.3 Hz, 2H), 1.95 – 1.88 (m, 8H), 1.51 – 1.41 (m, 8H), 1.01 (t, J = 7.4 Hz, 12H);

¹³C NMR (150 MHz, CDCl₃): δ 156.9, 156.6, 155.4, 144.5, 139.4, 135.5, 135.3, 135.1, 132.5, 130.3, 129.2, 128.3, 128.3, 128.2, 128.2, 127.8, 122.1, 121.9, 101.6, 75.0, 75.0, 75.0, 46.3, 32.5, 32.5, 32.5, 31.1, 31.1, 19.6, 19.5, 14.3, 14.3;

HRMS (ESI-TOF) calculated for C₅₁H₆₅IO₄N⁺, [M+NH₄]⁺ 882.3953, found 882.3954.



Physical state: colorless oil;

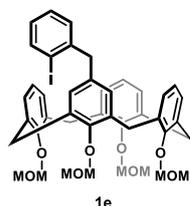
Yield: 99% (396 mg, 0.4 mmol scale);

$R_f = 0.4$ (PE:EtOAc = 40:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.86 (d, $J = 7.8$ Hz, 1H), 7.36 – 7.20 (m, 21H), 6.92 (t, $J = 7.4$ Hz, 1H), 6.86 (d, $J = 7.5$ Hz, 1H), 6.72 (s, 3H), 6.56 – 6.43 (m, 8H), 5.01 (d, $J = 10.7$ Hz, 4H), 4.96 – 4.89 (m, 4H), 4.25 (dd, $J = 22.1, 13.6$ Hz, 4H), 3.80 (s, 2H), 3.00 (d, $J = 13.6$ Hz, 2H), 2.92 (d, $J = 13.6$ Hz, 2H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 155.7, 155.4, 154.2, 144.5, 139.5, 138.0, 135.9, 135.9, 135.1, 132.9, 130.3, 129.9, 129.9, 129.6, 129.4, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 122.5, 122.2, 101.5, 76.7, 76.4, 76.3, 46.4, 31.6, 31.5;

HRMS (ESI-TOF) calculated for $\text{C}_{63}\text{H}_{57}\text{IO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 1018.3327, found 1018.3322.



Physical state: colorless oil;

Yield: 95% (310 mg, 0.4 mmol scale);

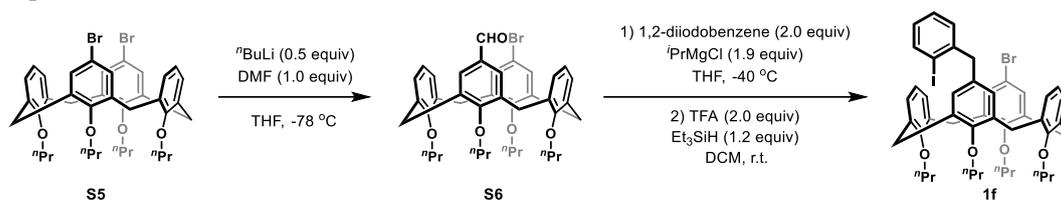
$R_f = 0.4$ (PE:EtOAc = 10:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.88 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.6$ Hz, 1H), 6.76 – 6.70 (m, 3H), 6.64 – 6.57 (m, 6H), 6.49 (s, 2H), 5.12 (d, $J = 10.4$ Hz, 4H), 5.09 (s, 4H), 4.47 (dd, $J = 27.1, 13.6$ Hz, 4H), 3.78 (s, 2H), 3.65 – 3.60 (m, 12H), 3.25 (d, $J = 13.6$ Hz, 2H), 3.18 (d, $J = 13.6$ Hz, 2H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 154.9, 154.5, 153.5, 144.2, 139.5, 135.2, 135.1, 134.8, 134.8, 133.7, 130.3, 129.5, 128.6, 128.6, 128.5, 128.3, 127.9, 123.1, 123.0, 101.5, 100.5, 100.5, 58.1, 58.1, 58.1, 46.2, 31.8, 31.7;

HRMS (ESI-TOF) calculated for $\text{C}_{43}\text{H}_{49}\text{IO}_8\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 834.2489, found 834.2481.

Preparation of **1f**.

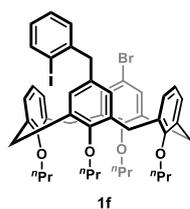


S5 was synthesized by literature procedure.¹

To a solution of **S5** (2.99 g, 4.0 mmol, 1.0 equiv) in THF (40 mL) was added $n\text{BuLi}$ (2.5 M, 0.8 mL, 2.0 mmol, 0.5 equiv) at $-78\text{ }^\circ\text{C}$ dropwise. After stirring at this temperature for 20 min, DMF (0.31 mL, 4.0 mmol, 1.0 equiv) was added. The reaction was stirred at $-78\text{ }^\circ\text{C}$ for 30 min and then quenched with aq. NH_4Cl . The aqueous layer was extracted with EtOAc. The combined organic layers dried over anhydrous Na_2SO_4 , concentrated in vacuo, and purified by flash column chromatograph to give the **S6** as white solid (1.66 g, 59% yield).

To a solution of 1,2-diiodobenzene (0.8 mL, 4.8 mmol, 2.0 equiv) in THF (20 mL) was added $i\text{PrMgCl}$ (2.0 M, 2.2 mL, 4.5 mmol, 1.9 equiv) dropwise at $-40\text{ }^\circ\text{C}$. After stirring at this temperature for 3 h, **S6** (1.66 g, 2.4 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. The reaction mixture was stirred at $25\text{ }^\circ\text{C}$ for 1 h, and quenched with aq. NH_4Cl . The aqueous layer was extracted with EtOAc. The combined extracts were dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding secondary alcohol as a white foam (1.76 g, 82% yield).

To a solution of above alcohol (1.76 mg, 2.0 mmol, 1.0 equiv) in DCM (20 mL) was added Et_3SiH (384 μL , 2.4 mmol, 1.2 equiv) dropwise at room temperature, then TFA (307 μL , 4.0 mmol, 2.0 equiv) was added dropwise. The resulting solution was quenched with aq. NaHCO_3 and the mixture was extracted with DCM. The combined organic phases were dried over anhydrous Na_2SO_4 , concentrated in vacuo, and the residue was directly purified by column chromatography on silica gel to give the desired products **1f** as a white foam.



Physical state: white foam;

Yield: 80% (1.69g, 2.0 mmol scale);

$R_f = 0.6$ (PE:EtOAc = 20:1);

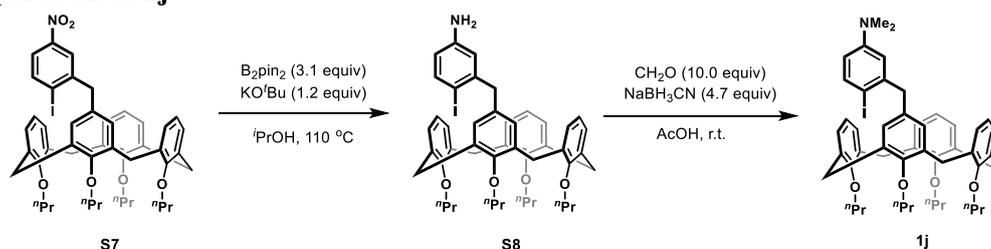
Melting point: 85–90 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.83 (d, $J = 7.8$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 6.92 – 6.85 (m, 2H), 6.82 (s, 2H), 6.65 – 6.55 (m, 6H), 6.47 (s, 2H), 4.43 (d, $J = 13.3$ Hz, 4H), 3.91 – 3.79 (m, 10H), 3.12 (dd, $J = 13.3, 2.4$ Hz, 4H), 1.99 – 1.88 (m, 8H), 1.03 – 0.96 (m, 12H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 156.5, 156.0, 155.3, 144.7, 139.5, 137.7, 135.3, 135.0, 134.3, 133.0, 130.9, 130.4, 129.1, 128.7, 128.2, 128.1, 127.7, 122.4, 114.6, 101.5, 77.0, 76.9, 76.9, 46.3, 31.1, 31.0, 23.4, 23.4, 23.3, 10.5, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $\text{C}_{47}\text{H}_{56}\text{BrIO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 904.2432, found 904.2428.

Preparation of **1j**.

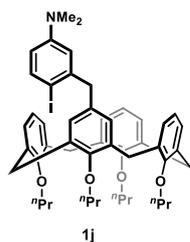


The synthetic method for **S7** is identical to that for **1a**.

Adapted from a literature procedure.² A dried glass reaction tube equipped with a magnetic stir bar was charged with **S7** (853 mg, 1.0 mmol, 1.0 equiv), B_2pin_2 (787 mg, 3.1 mmol, 3.1 equiv) and KO^tBu (135 mg, 1.2 mmol, 1.2 equiv), $i\text{PrOH}$ (4.0 mL, without any purification) was added and the mixture was then stirred in the preheated oil base at $110\text{ }^\circ\text{C}$ for 6 h. After cooling to room temperature, the crude production was diluted with ethyl acetate and then washed with saturated NaCl solution. The organic layers dried over anhydrous Na_2SO_4 , concentrated in vacuo, and purified by flash column chromatograph to give the **S8** as white foam (736 mg, 89% yield).

S8 (212 mg, 0.25 mmol, 1.0 equiv) was dissolved in acetic acid (2.5 mL). Paraformaldehyde (75 mg, 2.5 mmol, 10.0 equiv) was added to the solution, followed by the slow addition of sodium cyanoborohydride (63 mg, 1.2 mmol, 4.7 equiv). The reaction mixture was stirred at room temperature for 12 h. It was cooled and neutralized by adding 1 M NaOH solution until it was strongly basic. The suspension was extracted three times with chloroform, the combined organic layers were washed with brine and dried over sodium sulfate. After evaporating the solvent in vacuo, the residue was

purified by column chromatography on silica gel to give **1j**.



Physical state: white foam;

Yield: 88% (262 mg, 0.25 mmol scale);

$R_f = 0.7$ (PE:EtOAc = 20:1);

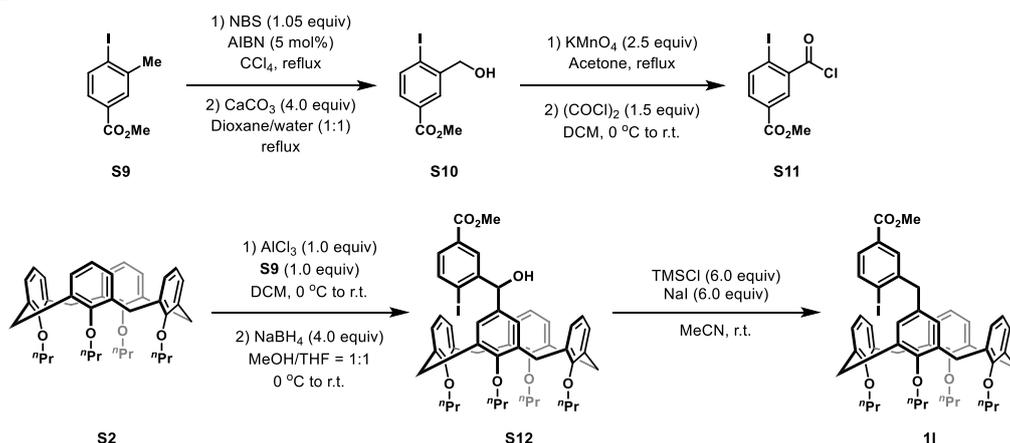
Melting point: 77–80 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.62 (d, $J = 8.5$ Hz, 1H), 6.89 (d, $J = 7.4$ Hz, 2H), 6.81 – 6.76 (m, 1H), 6.70 (s, 2H), 6.41 – 6.32 (m, 8H), 4.45 (t, $J = 12.9$ Hz, 4H), 3.99 – 3.90 (m, 4H), 3.82 (s, 2H), 3.76 (t, $J = 7.1$ Hz, 4H), 3.13 (dd, $J = 23.0, 13.4$ Hz, 4H), 2.85 (s, 6H), 2.03 – 1.85 (m, 8H), 1.05 (t, $J = 7.4$ Hz, 6H), 0.95 (t, $J = 7.5$ Hz, 6H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 157.5, 156.1, 155.9, 150.8, 144.9, 139.4, 136.3, 136.1, 134.4, 134.3, 133.0, 129.7, 128.7, 128.0, 127.8, 122.0, 121.9, 115.0, 112.8, 85.0, 77.0, 76.7, 76.7, 46.5, 40.6, 31.2, 31.1, 23.6, 23.3, 10.8, 10.3, 10.3;

HRMS (ESI-TOF) calculated for $\text{C}_{49}\text{H}_{62}\text{IO}_4\text{N}_2^+$, $[\text{M}+\text{NH}_4]^+$ 869.3749, found 869.3750.

Preparation of **1l**.



A solution of **S9** (5.52 g, 20.0 mmol, 1.0 equiv), NBS (3.74 g, 21.0 mmol, 1.05 equiv) and AIBN (164 mg, 1.0 mmol, 5 mol%) in dry CCl_4 (60 mL) was stirred at 85 °C for 3 h. Then, the reaction mixture was cooled to r.t. and filtered. After removal of solvent, EtOAc (40 mL) was added into the residue. Then the suspension was washed with 2 M $\text{Na}_2\text{S}_2\text{O}_3$, the aqueous layer was extracted with EtOAc. The combined organic layers

were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the methyl 3-(bromomethyl)-4-iodobenzoate (1.21 g, 17% yield) as a white solid.

CaCO₃ (1.36 g, 13.6 mmol, 4.0 equiv) was added into a solution of methyl 3-(bromomethyl)-4-iodobenzoate (1.21 g, 3.4 mmol, 1.0 equiv) in a mixed solvent of dioxane (20 mL) and H₂O (20 mL). The reaction mixture was heated to 100 °C and stirred for 5 h. After cooled to r.t., filtered, the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the product **S10** (874 mg, 88% yield).

A solution of **S10** (1.19g, 4.0 mmol, 1.0 equiv) and KMnO₄ (1.58 g, 10.0 mmol, 2.5 equiv) in acetone (20 mL) was stirred at 60 °C over night. Then, the reaction mixture was cooled to r.t. and 2 M HCl solution (20 mL) was added. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the 2-iodo-5-(methoxycarbonyl)benzoic acid (1.10 g, 88% yield).

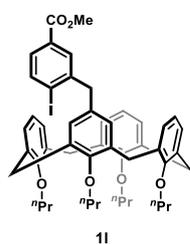
To a solution of 2-iodo-5-(methoxycarbonyl)benzoic acid (1.1 g, 3.6 mmol, 1.0 equiv) and DMF (two drops) in CH₂Cl₂ (10 mL) was added oxalyl chloride (0.46 mL, 5.4 mmol, 1.5 equiv) dropwise at 0 °C. Then the reaction mixture was stirred at r.t. for 1 h until the bubbling stopped. After that, the reaction mixture was concentrated in vacuo to give **S11**, which was used in next step without further purification.

To a solution of above prepared **S11** in DCM (15 mL) was added **S2** (2.96 g, 3.6 mmol, 1.0 equiv) and AlCl₃ (480 mg, 3.6 mmol, 1.0 equiv) at 0 °C. Then the reaction was warmed to r.t. and stirred over night. The mixture was concentrated in vacuo, and the residue was directly purified by column chromatography on silica gel to give the ketone as a white foam (0.73 g, 23% yield).

A round-bottom flask equipped with a stir bar was charged with the aforementioned ketone (0.73 g, 0.83 mmol, 1.0 equiv) and MeOH/DCM (2 mL/2 mL). The mixture was cooled to 0 °C in an ice bath, after which NaBH₄ (126 mg, 3.3 mmol, 4.0 equiv) was added as a solid. The reaction mixture was stirred at 0 °C for 30 minutes. The ice bath was then removed, and stirring was continued for an additional 3 h. The reaction was quenched by the addition of saturated aqueous NH₄Cl, and methanol was removed via rotary evaporation. The mixture was extracted with EtOAc. The combined organic

phases were washed with H₂O (35 mL) and brine (35 mL), dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to give **S12** (0.72 g, 99% yield).

TMSCl (631 μ L, 5.0 mmol, 6.0 equiv) was added to a stirred solution of NaI (750 mg, 5.0 mmol, 6.0 equiv) in anhydrous MeCN (4 mL) under argon, whereupon NaCl precipitated. A solution of **S12** (0.73 g, 0.83 mmol) in anhydrous DCM (2 mL) was added dropwise to the suspension, whereupon iodine colour developed immediately. After 10 min the reaction mixture was diluted with water then extracted with ether. The extract was washed with aqueous sodium thiosulfate solution and brine, dried and evaporated. The residue was purified by column chromatography on silica gel to give **11**.



Physical state: white foam;

Yield: 68% (489 mg, 0.83 mmol scale);

R_f = 0.5 (PE:EtOAc = 20:1);

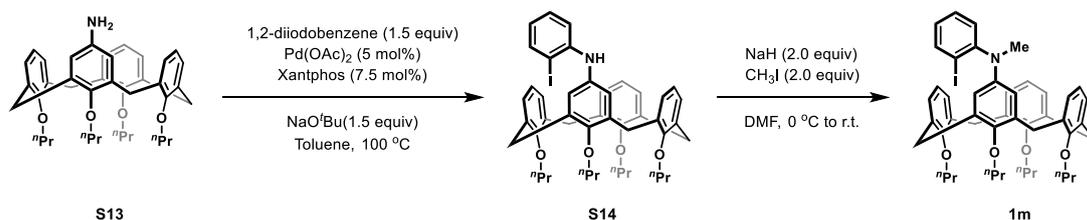
Melting point: 74–77 °C;

¹H NMR (600 MHz, CDCl₃): δ 7.93 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 1.7 Hz, 1H), 7.53 (dd, J = 8.2, 1.9 Hz, 1H), 6.76 – 6.68 (m, 3H), 6.57 – 6.49 (m, 6H), 6.44 (s, 2H), 4.44 (dd, J = 23.7, 13.3 Hz, 4H), 3.90 – 3.85 (m, 7H), 3.84 – 3.79 (m, 6H), 3.16 (d, J = 13.4 Hz, 2H), 3.09 (d, J = 13.4 Hz, 2H), 1.97 – 1.88 (m, 8H), 1.03 – 0.97 (m, 12H);

¹³C NMR (150 MHz, CDCl₃): δ 166.9, 157.1, 156.5, 155.7, 145.1, 139.8, 135.7, 135.6, 134.9, 132.0, 131.0, 130.4, 129.0, 128.5, 128.4, 128.3, 128.1, 122.1, 121.8, 107.7, 76.9, 76.8, 76.7, 52.4, 46.0, 31.2, 31.1, 23.5, 23.4, 10.6, 10.5, 10.4;

HRMS (ESI-TOF) calculated for C₄₉H₅₉IO₆N⁺, [M+NH₄]⁺ 884.3382, found 884.3389.

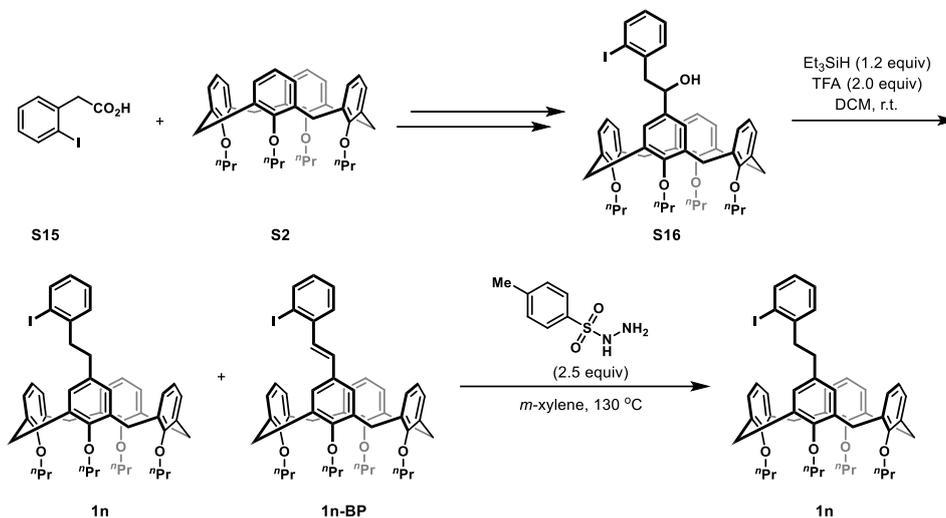
Preparation of **1m**.



76.8, 40.1, 31.3, 31.2, 23.4, 23.4, 23.4, 10.6, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $C_{47}H_{55}IO_4N^+$, $[M+H]^+$ 824.3170, found 824.3172.

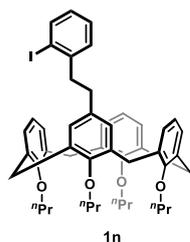
Preparation of **1n**, **1o** and **1p**.



2-(2-iodophenyl)acetic acid is commercially available, 2-(2-iodo-4-methylphenyl)acetic acid and 2-(2-chloro-6-iodophenyl)acetic acid⁴ were synthesized by literature procedure, the synthetic method of **S16** is the same as **S12**.

Taking the synthesis of **1n** as an example: to a solution of **S16** (335 mg, 0.4 mmol, 1.0 equiv) in DCM (5 mL) was added Et_3SiH (77 μ L, 0.48 mmol, 1.2 equiv) dropwise at room temperature, then TFA (62 μ L, 0.8 mmol, 2 equiv) was added dropwise. The resulting solution was quenched with aq. $NaHCO_3$ and the mixture was extracted with DCM. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a mixture of **1n** and **1n-BP** which were used for next step without purification.

At room temperature, under an "open" atmosphere, a round bottom flask equipped with a magnetic stirrer was charged with the mixture of **1n** and **1n-BP**, 4-methylbenzenesulfonylhydrazide (75 mg, 0.4 mmol, 2.5 equiv), *o*-xylene (0.5 mL). The reaction flask was fitted with a condenser. The reaction mixture was refluxed for 6 h. The mixture was cooled to room temperature, filtered through a pad of silica gel, eluted with a mixture of Hexane/EtOAc (1:1 v/v) and concentrated in vacuo. The residue was purified by column chromatography to afford **1n**.



Physical state: white foam;

Yield: 82% (270 mg, two steps);

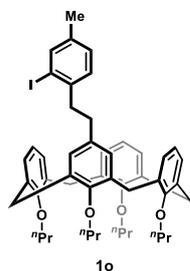
$R_f = 0.5$ (PE:EtOAc = 40:1);

Melting point: 61–64 °C;

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.82 (d, $J = 7.9$ Hz, 1H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.13 (d, $J = 7.5$ Hz, 1H), 6.88 (t, $J = 7.5$ Hz, 1H), 6.69 – 6.53 (m, 9H), 6.50 (s, 2H), 4.46 (t, $J = 14.1$ Hz, 4H), 3.91 – 3.81 (m, 8H), 3.15 (dd, $J = 20.4, 13.3$ Hz, 4H), 2.77 – 2.70 (m, 2H), 2.58 – 2.50 (m, 2H), 1.98 – 1.90 (m, 8H), 1.01 (t, $J = 7.2$ Hz, 12H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 156.8, 156.8, 155.1, 144.8, 139.6, 135.3, 135.3, 135.3, 135.0, 134.5, 129.7, 128.4, 128.4, 128.3, 128.3, 128.3, 127.8, 122.0, 100.8, 76.9, 76.9, 76.9, 43.3, 35.9, 31.2, 31.2, 23.4, 23.4, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $\text{C}_{48}\text{H}_{59}\text{IO}_4\text{N}^+$, $[\text{M}+\text{NH}_4]^+$ 840.3483, found 840.3482.



Physical state: white foam;

Yield: 74% (248 mg, two steps);

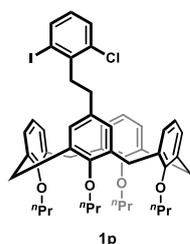
$R_f = 0.5$ (PE:EtOAc = 40:1);

Melting point: 67–70 °C;

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.68 (d, $J = 9.3$ Hz, 1H), 6.99 (s, 1H), 6.71 (s, 1H), 6.66 – 6.53 (m, 9H), 6.50 (s, 2H), 4.46 (t, $J = 12.9$ Hz, 4H), 3.90 – 3.81 (m, 8H), 3.16 (d, $J = 14.6$ Hz, 4H), 2.72 – 2.65 (m, 2H), 2.57 – 2.48 (m, 2H), 2.27 (s, 3H), 1.99 – 1.90 (m, 8H), 1.05 – 0.97 (m, 12H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 156.8, 156.7, 155.0, 144.6, 139.3, 138.3, 135.4, 135.3, 135.2, 134.9, 134.7, 130.6, 128.8, 128.4, 128.3, 128.3, 122.1, 96.7, 76.9, 76.9, 76.9, 43.2, 36.1, 31.2, 31.2, 23.4, 23.4, 21.1, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $C_{49}H_{61}IO_4N^+$, $[M+NH_4]^+$ 854.3640, found 854.3637.



Physical state: white foam;

Yield: 88% (301 mg, two steps);

$R_f = 0.5$ (PE:EtOAc = 40:1);

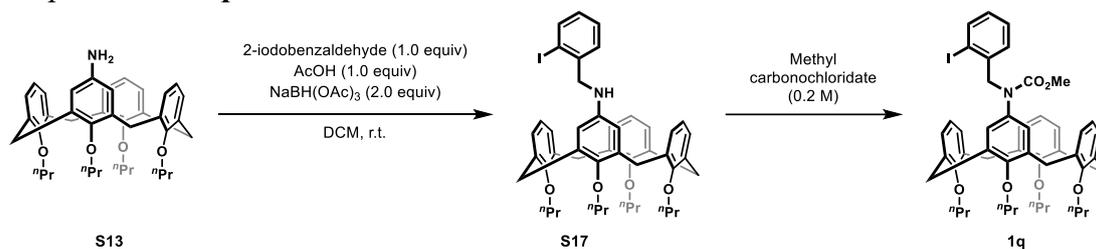
Melting point: 69–71 °C;

1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J = 7.9$ Hz, 1H), 7.33 (d, $J = 7.9$ Hz, 1H), 6.80 (t, $J = 7.9$ Hz, 1H), 6.72 – 6.68 (m, 3H), 6.65 – 6.57 (m, 4H), 6.57 – 6.44 (m, 4H), 4.46 (dd, $J = 13.2, 4.7$ Hz, 4H), 3.86 (dt, $J = 25.2, 7.4$ Hz, 8H), 3.15 (d, $J = 13.3$ Hz, 4H), 2.93 – 2.81 (m, 2H), 2.51 – 2.37 (m, 2H), 2.00 – 1.89 (m, 8H), 1.05 – 0.97 (m, 12H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.9, 156.6, 155.0, 142.3, 138.4, 135.6, 135.4, 135.0, 134.8, 134.5, 133.7, 129.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.2, 122.2, 122.0, 101.5, 76.9, 76.8, 42.1, 33.7, 31.7, 31.1, 23.5, 23.4, 10.6, 10.6, 10.5;

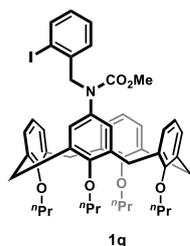
HRMS (ESI-TOF) calculated for $C_{48}H_{58}ClIO_4N^+$, $[M+NH_4]^+$ 874.3094, found 874.3092.

Preparation of **1q**.



2-iodobenzaldehyde (207 mg, 0.89 mmol, 1.0 equiv.), AcOH (52 μ L, 0.89 mmol, 1.0 equiv) were added sequentially to a solution of **S13** (534 mg, 0.89 mmol, 1.0 equiv) in DCM (5 mL) and the mixture was stirred at r.t. for 15 min. Then $NaBH(OAc)_3$ (377 mg, 2.7 mmol, 2.0 equiv) was added and stirring at r.t. was continued for further 12 h. The reaction mixture was quenched with 1 N NaOH solution and extracted with DCM. The combined organic layer extracts were washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure, and purified on silica gel chromatography to afford the corresponding products **S17** as white foam (667 mg, 91% yield).

A mixture of **S17** (667 mg, 0.81 mmol, 1.0 equiv) in methyl carbonochloridate (2.0 mL) was heated under reflux overnight. The mixture was poured into water and extracted with chloroform. The organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure after filtration. The crude material was purified by flash column chromatography to afford the corresponding products **1q**.



Physical state: white foam;

Yield: 99% (707 mg);

R_f = 0.2 (PE:EtOAc = 20:1);

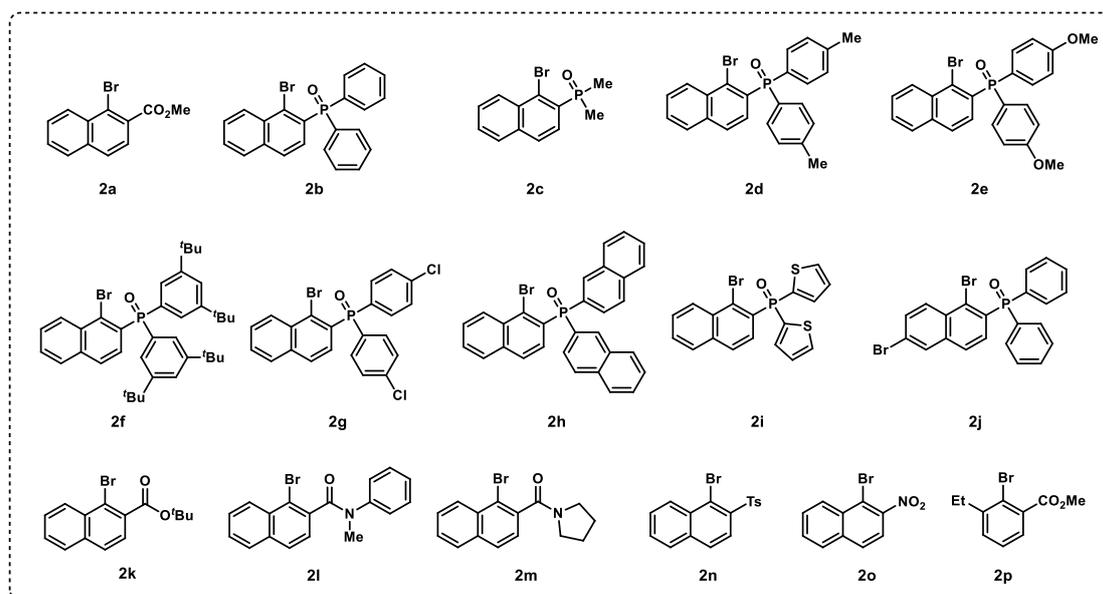
Melting point: 175–177 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 6.95 (t, *J* = 8.1 Hz, 1H), 6.71 – 6.25 (m, 11H), 4.59 (s, 2H), 4.41 (dd, *J* = 17.2, 13.3 Hz, 4H), 3.88 – 3.77 (m, 8H), 3.68 (s, 3H), 3.10 (dd, *J* = 35.2, 13.3 Hz, 4H), 1.97 – 1.86 (m, 8H), 1.02 – 0.96 (m, 12H);

¹³C NMR (100 MHz, CDCl₃, 60 °C): δ 156.9, 156.5, 156.5, 155.2, 140.4, 139.6, 135.8, 135.6, 135.4, 135.1, 134.6, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 125.8, 122.3, 122.0, 98.3, 77.0, 76.9, 76.9, 59.4, 53.0, 31.2, 31.2, 23.4, 23.4, 23.4, 10.5, 10.5, 10.4;

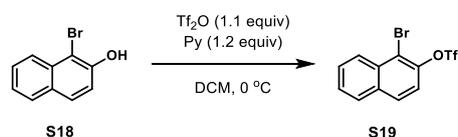
HRMS (ESI-TOF) calculated for C₄₉H₆₀IO₆N₂⁺, [M+NH₄]⁺ 899.3491, found 899.3495.

2.2 Preparation of aryl bromides

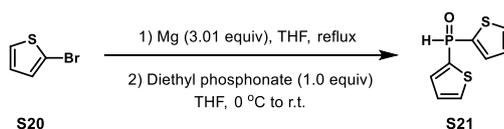


2a (CAS No.: 89555-39-5) and **2o** (CAS No.: 4185-55-1) were commercially available. **2b**, **2d**, **2e**, **2f**, **2g**, **2h** and **2p** were synthesized by literature procedure.⁵

Preparation of **2c** and **2i**.

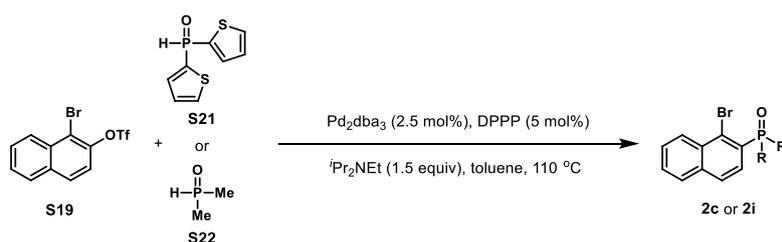


To a solution of **S18** (4.5 g, 20.0 mmol) in DCM under nitrogen at 0 °C was added dropwise pyridine (1.9 mL, 1.2 equiv) and triflic anhydride (3.7 mL, 1.1 equiv) over 10 min. After an additional 30 min at 0 °C, the cooling bath was removed and the mixture was stirred at room temperature overnight. The resulting mixture was then taken up in DCM and 2 N HCl (60 mL), and the aqueous layer was extracted with DCM. The combined organics were washed with saturated NaHCO₃ and brine, then dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **S19** as a liquid (6.70 g, 95% yield).

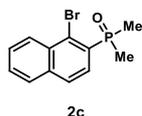


Diethylphosphite (1.29 mL, 10.0 mmol, 1.0 equiv) was added dropwise at 0 °C to a solution of thiophen-2-ylmagnesium bromide in THF which was prepared from **S20**

(2.9 mL, 30.0 mmol, 3.0 equiv) and magnesium (731 g, 30.1 mmol, 3.01 equiv). The mixture was stirred for 30 minutes at 0 °C, then stirred at ambient temperature for 16 h. After that it was cooled again to 0 °C, and NH₄Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with NaHCO₃ aqueous and brine, then it was dried over Na₂SO₄. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product **S21** (4.36 g, 68% yield).



A solution of **S19** (3.89 g, 11 mmol, 1.1 equiv), **S21** or **S22** (10 mmol, 1.0 equiv), *t*Pr₂NEt (2.5 mL, 15 mmol, 1.5 equiv), Pd₂(dba)₃ (230 mg, 0.25 mmol, 2.5 mol%), and DPPP (206 mg, 0.5 mmol, 5 mol%) in toluene (50 mL) under nitrogen was stirred at 120 °C for 40 h. After being cooled to room temperature, the mixture was filtered and concentrated and the residue was purified by flash column chromatography on silica gel chromatography to give **2c** or **2i**.



Physical state: white solid;

Yield: 67% (1.89 g);

R_f = 0.2 (DCM:MeOH = 20:1);

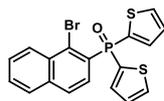
Melting point: 128–130 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.39 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 10.6, 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.69 – 7.59 (m, 2H), 2.04 (d, *J* = 13.5 Hz, 6H);

¹³C NMR (100 MHz, CDCl₃): δ 136.3 (d, *J* = 2.2 Hz), 133.2 (d, *J* = 96.0 Hz), 132.3 (d, *J* = 9.0 Hz), 129.4 (d, *J* = 6.8 Hz), 128.7, 128.6, 128.3, 128.2 (d, *J* = 9.9 Hz), 127.8, 125.7 (d, *J* = 6.0 Hz), 18.0 (d, *J* = 73.2 Hz);

³¹P NMR (162 MHz, CDCl₃) δ 36.9;

HRMS (ESI-TOF) calculated for C₁₂H₁₃BrOP⁺, [M+H]⁺ 284.9862, found 284.9860.



2i

Physical state: white solid;

Yield: 39% (1.63 g);

$R_f = 0.4$ (PE:EtOAc = 1:1);

Melting point: 146–150 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.47 – 8.39 (m, 1H), 7.91 – 7.85 (m, 2H), 7.78 (t, $J = 4.5$ Hz, 2H), 7.75 – 7.69 (m, 1H), 7.68 – 7.60 (m, 4H), 7.24 – 7.17 (m, 2H);

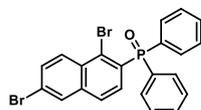
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 137.2 (d, $J = 10.8$ Hz), 136.1 (d, $J = 2.3$ Hz), 134.3 (d, $J = 5.7$ Hz), 133.8 (d, $J = 124.0$ Hz), 132.8 (d, $J = 9.6$ Hz), 131.7 (d, $J = 117.9$ Hz), 129.6 (d, $J = 4.8$ Hz), 129.5 (d, $J = 10.8$ Hz), 129.2, 128.5, 128.5, 128.4, 128.2, 127.8 (d, $J = 12.2$ Hz);

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): δ 15.3;

HRMS (ESI-TOF) calculated for $\text{C}_{18}\text{H}_{13}\text{BrOPS}_2^+$, $[\text{M}+\text{H}]^+$ 420.9303, found 420.9302.

Preparation of **2j**.

The synthesis method of **2j** is the same as **2b**.



2j

Physical state: white solid;

Yield: 33% (319 mg, 2 mmol scale);

$R_f = 0.5$ (PE: EtOAc = 1:1);

Melting point: 237–240 °C;

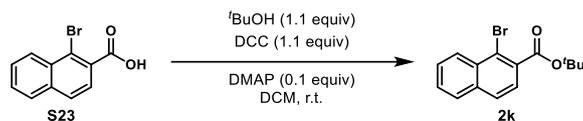
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.59 (s, 1H), 7.79 – 7.67 (m, 7H), 7.61 – 7.55 (m, 2H), 7.52 – 7.40 (m, 5H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 134.4 (d, $J = 2.2$ Hz), 134.1 (d, $J = 9.1$ Hz), 132.5, 132.4 (d, $J = 104.0$ Hz), 132.3, 132.3, 132.2, 132.2, 132 (d, $J = 108.1$ Hz), 130.6 (d, $J = 10.9$ Hz), 130.3 (d, $J = 42.9$ Hz), 128.9 (d, $J = 12.5$ Hz), 127.6 (d, $J = 11.5$ Hz), 123.1 (d, $J = 1.5$ Hz);

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): δ 31.4.

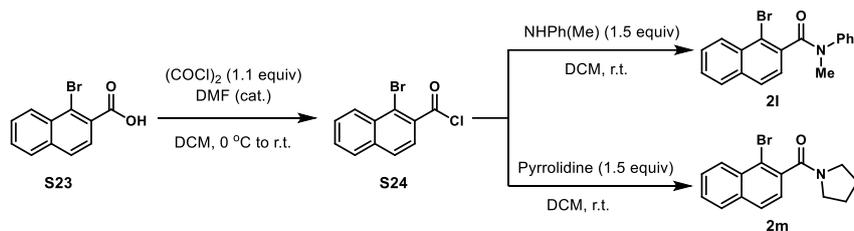
HRMS (ESI-TOF) calculated for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{OP}^+$, $[\text{M}+\text{H}]^+$ 486.9281, found 486.9281.

Preparation of **2k**.



Adapted from literature procedure.⁶ An oven-dried 100 mL round bottom flask was fitted with a stir bar and **S23** (2.51 g, 10 mmol, 1.0 equiv) was added. Then, anhydrous DCM (33 mL) and ^tBuOH (1.05 mL, 11 mmol, 1.1 equiv) were added sequentially via syringe. The rubber septum was momentarily removed to add DCC (2.27 g, 11 mmol, 1.1 equiv) and DMAP (0.12 g, 1 mmol, 0.1 equiv) sequentially. The reaction mixture was stirred at r.t. for 12 h. The reaction was filtered through a pad of celite and concentrated in vacuo. The crude residue was purified by flash silica gel chromatography to afford **2k** as light-yellow oil (1.85 g, 60% yield).

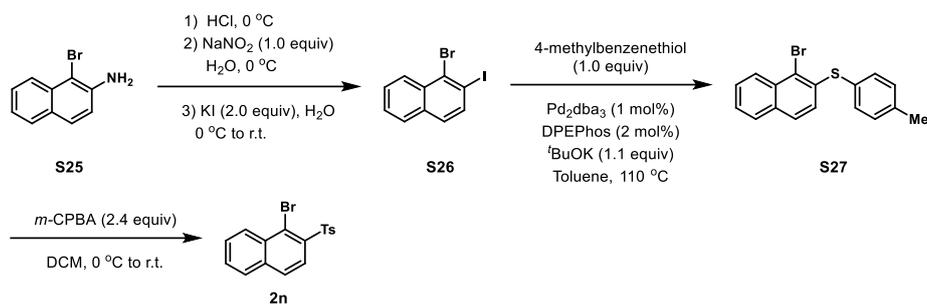
Preparation of **2l** and **2m**.



To a solution of **S23** (500.0 mg, 2.0 mmol, 1.0 equiv) and DMF (one drop) in DCM (2 mL) was added oxalyl chloride (279 mg, 2.2 mmol, 1.1 equiv) dropwise at 0 °C. Then the reaction mixture was stirred at r.t. for another 1 h until the bubbling stopped, concentrated in vacuo to give **S24** as a yellow liquid, which was used in next step without further purification.

To a solution of **S24** in DCM (2 mL) was added NHPH(Me) (325 μ L, 3.0 mmol, 1.5 equiv) or pyrrolidine (246 μ L, 3.0 mmol, 1.5 equiv) dropwise at 0 °C, then warmed to r.t. and stirred for 3 h. The mixture was concentrated in vacuo, the residue was directly purified by column chromatography on silica gel to give the desired product **2l** (570 mg, 84% yield) or **2m** (546 mg, 90% yield).

Preparation of **2n**.



To a solution of **S25** (884 mg, 4.0 mmol, 1.0 equiv) in 2 mL concentrated hydrochloric acid and 6 mL of H₂O cooled below 2 °C was added slowly a solution of NaNO₂ (276 mg, 4.0 mmol, 1.0 equiv) in 4 mL of H₂O. The mixture was stirred for 50 minutes at 0–5 °C, then an ice-cold solution of KI (1.33 g, 8.0 mmol, 2.0 equiv) in 5 mL of H₂O was added dropwise. The reaction mixture was warmed to 25 °C and stirred for 10 h. The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine and dried over MgSO₄. The solvents were evaporated and the residue was subjected to column chromatography on silica gel to afford **S26** as a white solid (1.0 g, 75% yield).

Under an argon atmosphere, a mixture of **S26** (1.0 g, 3.0 mmol, 1.0 equiv), 4-methylbenzenethiol (372 mg, 3.0 mmol, 1.0 equiv), Pd₂dba₃ (27.5 mg, 0.03 mmol, 1 mol%), DPEPhos (32.3 mg, 0.06 mmol, 2 mol%), and ^tBuOK (370.3 mg, 3.3 mmol, 1.1 equiv) in toluene (15 mL) was stirred at 110 °C for 2 h. After cooling, the crude mixture was filtered over a plug of celite, and the filtrate was washed with water. The organic layer was separated, dried over Mg₂SO₄. The solvents were evaporated and the residue was subjected to column chromatography on silica gel to afford **S27** as a white solid (840 mg, 85% yield).

m-CPBA (1.08 g, 6.2 mmol, 2.4 equiv) was added to a solution of **S27** (840 mg, 2.6 mmol, 1.0 equiv) in DCM (10 mL) and the reaction stirred at room temperature for 1.5 h. The reaction was quenched by dropwise addition of saturated Na₂S₂O₃ solution. Organics were extracted with dichloromethane, washed with 3 M sodium hydroxide solution and brine (20 mL), dried over MgSO₄ and solvents removed under reduced pressure. The crude product was purified by column chromatography to yield **2n**.



Physical state: white solid;

Yield: 92% (848 mg);

$R_f = 0.5$ (PE: EtOAc = 5:1);

Melting point: 161–163 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.43 (dd, $J = 9.0, 4.5$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 1H), 7.92 – 7.84 (m, 3H), 7.69 – 7.61 (m, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 2.40 (s, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 144.5, 138.5, 137.6, 136.2, 132.9, 129.6, 129.6, 128.8, 128.6, 128.6, 128.5, 125.8, 124.4, 21.8;

HRMS (ESI-TOF): calculated for $\text{C}_{17}\text{H}_{14}\text{BrO}_2\text{S}^+$, $[\text{M}+\text{H}]^+$ 360.9892, found 360.9894.

3. Optimization of reaction conditions

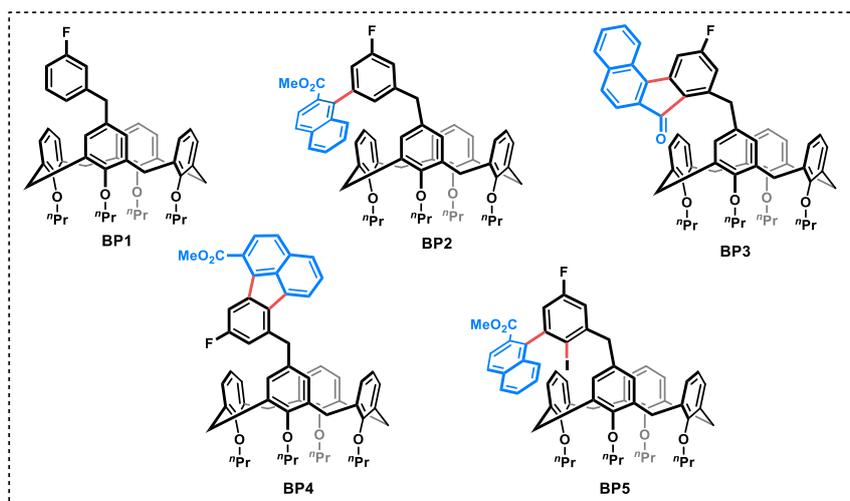
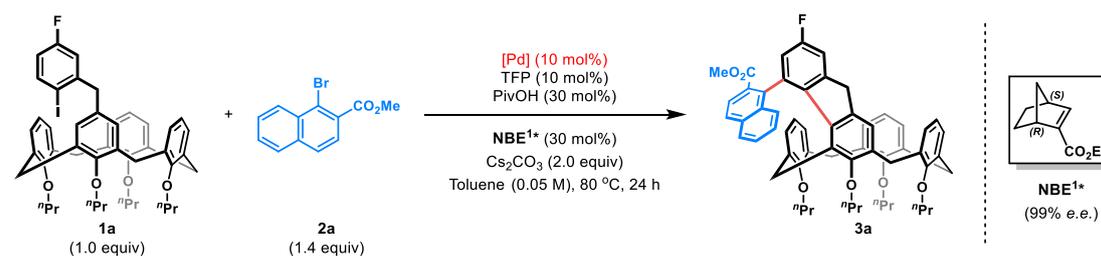


Figure S1. Discovered by-products. (All by-products were determined by HRMS and crude ^1H NMR.)

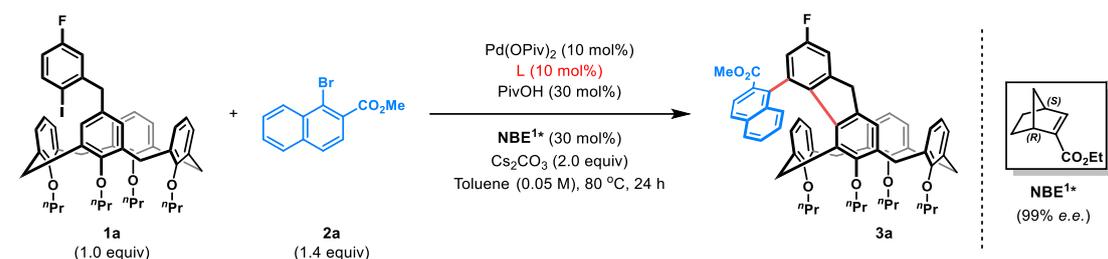
Table S1. Screening of palladium catalyst



Entry ^a	[Pd]	Yield (%) ^b	<i>e.e.</i> (%) ^c	<i>d.r.</i> ^d
1	Pd(acac) ₂	60	99	5:1
2	Pd(OPiv) ₂	75	99	6:1
3 ^e	Pd(OPiv) ₂	13	99	6:1
4	Pd(TFA) ₂	63	99	6:1
5	PdI ₂	49	99	6:1
6	Pd(MeCN) ₂ Cl ₂	47	99	6:1
7	PdCl ₂	21	99	6:1

^aAll reactions were performed on a 0.05 mmol scale. ^b ^{19}F NMR yield with 4,4'-difluoro-1,1'-biphenyl as an internal standard. ^c*e.e.* was determined by chiral HPLC analysis. ^d*d.r.* was determined by crude ^{19}F NMR analysis, EtOAc as solvent. ^e5 mol% Pd(OPiv)₂ and 5 mol% TFP were used.

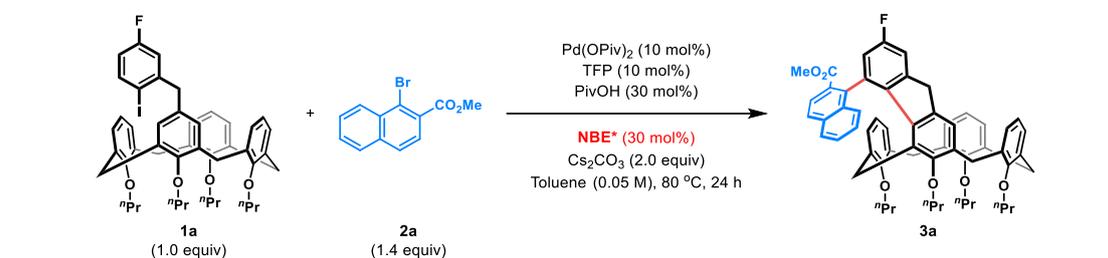
Table S2. Screening of ligand



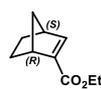
Entry ^a	L	Yield (%) ^b	<i>e.e.</i> (%) ^c	<i>d.r.</i> ^d
1	TFP	76	99	6:1
2	TFP ^e	40	99	6:1
3	PPh ₃	65	99	6:1
4	JohnPhos	16	98	6:1
5	XPhos	7	99	5:1
6	MePhos	67	99	5:1

^aAll reactions were performed on a 0.05 mmol scale. ^b¹⁹F NMR yield with 4,4'-difluoro-1,1'-biphenyl as an internal standard. ^c*e.e.* was determined by chiral HPLC analysis. ^d*d.r.* was determined by crude ¹⁹F NMR analysis, EtOAc as solvent. ^e20 mol% TFP was used.

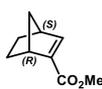
Table S3. Screening of NBE*



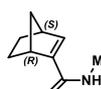
Entry ^a	NBE*	Yield (%) ^b	<i>e.e.</i> (%) ^c	<i>d.r.</i> ^d
1	NBE ^{1*}	76	99	6:1
2	NBE ^{2*}	61	99	6:1
3	NBE ^{3*}	5	-	-
4	NBE ^{4*}	7	-	-



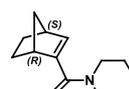
NBE^{1*} (99% *e.e.*)



NBE^{2*} (99% *e.e.*)



NBE^{3*} (97% *e.e.*)



NBE^{4*} (97% *e.e.*)

^aAll reactions were performed on a 0.05 mmol scale. ^b¹⁹F NMR yield with 4,4'-difluoro-1,1'-biphenyl as an internal standard. ^c*e.e.* was determined by chiral HPLC analysis. ^d*d.r.* was determined by crude ¹⁹F NMR analysis, EtOAc as solvent.

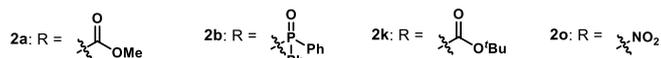
Table S4. Screening of reaction concentration

Entry ^a	Toluene (x M)	Yield (%) ^b	<i>e.e.</i> (%) ^c	<i>d.r.</i> ^d
1	0.2	43	98	6:1
2	0.1	73	99	6:1
3	0.05	78	99	6:1
4 ^e	0.05	6	-	-
5	0.025	62	99	6:1

^aAll reactions were performed on a 0.05 mmol scale. ^b¹⁹F NMR yield with 4,4'-difluoro-1,1'-biphenyl as an internal standard. ^c*e.e.* was determined by chiral HPLC analysis. ^d*d.r.* was determined by crude ¹⁹F NMR analysis, EtOAc as solvent. ^eMeCN as solvent.

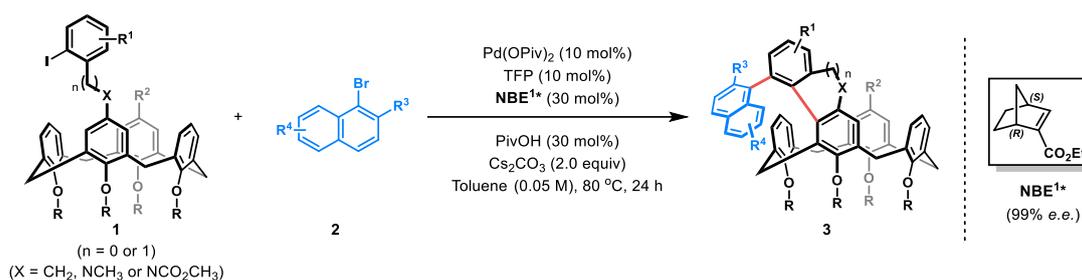
Table S5. Screening of electrophilic reagent 2

Entry ^a	2	Yield (%) ^b	<i>e.e.</i> (%) ^c	<i>d.r.</i> ^d
1	2a	76	99	6:1
2 ^e	2b	79	99	>19:1
3	2k	84	99	11:1
4	2o	4	-	-

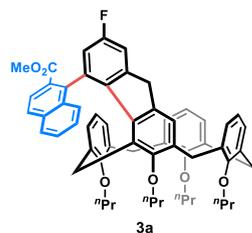


^aAll reactions were performed on a 0.05 mmol scale. ^b¹⁹F NMR yield with 4,4'-difluoro-1,1'-biphenyl as an internal standard. ^c*e.e.* was determined by chiral HPLC analysis. ^d*d.r.* was determined by crude ¹⁹F NMR analysis, EtOAc as solvent. ^e**2b** (1.6 equiv) was used.

4. General procedure for the asymmetric synthesis of 3



To a 10 mL of oven-dried vial equipped with a magnetic stir bar was charged with **1** (0.1 mmol, 1.0 equiv), Pd(OPiv)₂ (0.01 mmol, 10 mol%), TFP (0.01 mmol, 10 mol%), NBE^{1*} (0.03 mmol, 30 mol%), Cs₂CO₃ (0.2 mmol, 2.0 equiv), **2** (0.16 mmol, 1.6 equiv) and dry toluene (2 mL) under Ar. Then the reaction was stirred at 80 °C for 24 h. After cooling to r.t., the mixture was filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the desired product **3**.



Physical state: white foam;

Yield: 81% (71.7 mg), *d.r.* = 6:1 (determined by ¹⁹F NMR), the diastereoisomers were separable;

R_f = 0.4 (PE:EtOAc = 20:1);

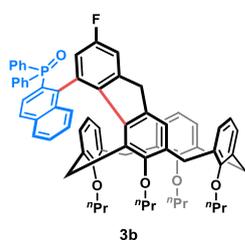
Melting point: 104–108 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 2% *i*PrOH in *n*hexane, 1 mL/min, λ = 320 nm), *t_R* (major) = 5.09 min;

[α]_D²⁵: 183.2 (c 0.2, CHCl₃);

¹H NMR (600 MHz, CDCl₃): δ 7.94 (dd, *J* = 12.1, 8.4 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 6.3 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.20 (t, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 6.5 Hz, 1H), 6.02 (d, *J* = 6.7 Hz, 1H), 5.94 (t, *J* = 7.6 Hz, 1H), 5.73 (d, *J* = 7.4 Hz, 1H), 5.51 (d, *J* = 7.4 Hz, 1H), 4.36 (t, *J* = 12.8 Hz, 2H), 4.25 (d, *J* = 13.5 Hz, 1H), 4.21 (d, *J* = 22.2 Hz, 1H), 4.06 (d, *J* = 22.2 Hz, 1H), 3.92 – 3.81 (m, 2H), 3.63 – 3.57 (m, 3H), 3.53 (s, 3H), 3.29 – 3.23 (m, 1H), 3.17 – 3.07

(m, 3H), 2.99 (d, $J = 13.6$ Hz, 1H), 2.96 – 2.90 (m, 1H), 2.74 (d, $J = 14.3$ Hz, 1H), 2.35 (d, $J = 14.2$ Hz, 1H), 1.87 – 1.76 (m, 4H), 1.63 – 1.57 (m, 2H), 1.42 – 1.33 (m, 2H), 1.06 (dt, $J = 11.3, 7.4$ Hz, 6H), 0.79 (t, $J = 7.5$ Hz, 3H), 0.63 (t, $J = 7.5$ Hz, 3H);
 ^{13}C NMR (150 MHz, CDCl_3): δ 169.3, 162.1, 160.5, 158.4 (d, $J = 1.8$ Hz), 154.9 (d, $J = 59.0$ Hz), 147.8 (d, $J = 8.6$ Hz), 143.0, 140.3, 138.7 (d, $J = 2.5$ Hz), 137.6, 137.4, 137.1 (d, $J = 1.5$ Hz), 135.5, 135.1 (d, $J = 8.2$ Hz), 134.7, 134.5, 133.5, 133.3, 132.9, 132.8, 131.0, 129.1, 128.7, 128.7, 128.2, 127.8, 127.5, 127.0, 126.9, 126.6, 126.4, 126.1, 124.7, 122.3, 122.1, 121.7, 116.6 (d, $J = 22.5$ Hz), 111.6 (d, $J = 21.6$ Hz), 76.9, 76.4, 76.3, 76.1, 52.2, 37.7, 31.2, 30.9, 30.8, 28.2, 23.7, 23.6, 23.0, 22.2, 11.0, 10.9, 9.9, 9.8;
 ^{19}F NMR (565 MHz, CDCl_3): δ -118.1;
HRMS (ESI-TOF) calculated for $\text{C}_{59}\text{H}_{59}\text{FO}_6\text{Na}^+$, $[\text{M}+\text{Na}]^+$ 905.4188, found 905.4185.



Physical state: white foam;

Yield: 75% (76.4 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.4$ (PE:EtOAc = 2:1);

Melting point: 165–170 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 12.29 min;

$[\alpha]_D^{25}$: 153.8 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 8.2$ Hz, 1H), 7.82 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.64 (dd, $J = 11.7, 7.3$ Hz, 2H), 7.54 (t, $J = 7.1$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 1H), 7.39 (dd, $J = 11.8, 8.6$ Hz, 1H), 7.33 – 7.26 (m, 4H), 7.25 – 7.18 (m, 4H), 7.15 – 7.07 (m, 3H), 6.97 (td, $J = 8.0, 2.8$ Hz, 2H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.69 (dd, $J = 9.8, 2.4$ Hz, 1H), 6.23 (dt, $J = 14.0, 6.7$ Hz, 2H), 6.01 (t, $J = 7.6$ Hz, 2H), 5.78 (d, $J = 7.3$ Hz, 1H), 5.67 (d, $J = 7.3$ Hz, 1H), 4.42 – 4.26 (m, 3H), 4.09 – 3.82 (m, 4H), 3.64 – 3.51 (m, 3H), 3.17 – 3.04 (m, 5H), 2.92 – 2.85 (m, 1H), 2.81 (d, $J = 14.5$ Hz, 1H), 2.44 (d, $J = 14.4$ Hz, 1H), 1.87 – 1.76 (m, 4H), 1.62 – 1.52 (m, 2H), 1.41 – 1.30 (m, 2H), 1.06 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 7.4$ Hz, 3H), 0.78 (t, $J = 7.5$ Hz, 3H), 0.61 (t, $J = 7.4$ Hz, 3H);

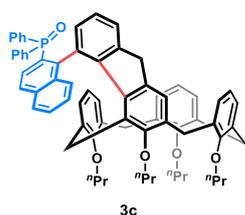
^{13}C NMR (150 MHz, CDCl_3): δ 161.3, 159.7, 158.4, 154.9, 154.6, 148.0, 147.9, 147.3, 147.3, 140.5, 139.0, 137.6, 137.5, 135.2, 134.5, 134.3, 134.2, 134.0, 133.8, 133.7, 133.6,

133.5, 133.2, 133.1, 132.8, 132.5, 131.8, 131.8, 131.7, 131.6, 131.5, 131.5, 130.7, 130.7, 129.7, 129.6, 129.4, 128.9, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.6, 127.3, 127.3, 127.0, 126.9, 126.6, 124.3, 122.5, 122.3, 121.5, 118.4, 118.2, 111.7, 111.6, 76.7, 76.3, 76.1, 75.7, 37.4, 31.1, 30.9, 30.6, 28.4, 27.2, 23.5, 23.5, 22.9, 22.1, 10.9, 10.8, 9.7, 9.7 (Due to C-P and C-F coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

¹⁹F NMR (376 MHz, CDCl₃): δ -118.4;

³¹P NMR (162 MHz, CDCl₃): δ 27.6;

HRMS (ESI-TOF) calculated for C₆₉H₆₇FO₅P⁺, [M+H]⁺ 1025.4705, found 1025.4707.



Physical state: white foam;

Yield: 81% (81.2 mg), > 19:1 *d.r.* (determined by ³¹P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 163–168 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 10.27 min;

[α]_D²⁵: 131.6 (c 0.2, CHCl₃);

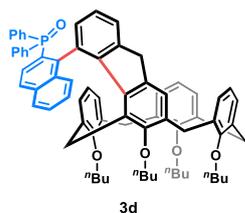
¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 11.4, 7.6 Hz, 2H), 7.57 – 7.39 (m, 4H), 7.34 – 7.27 (m, 3H), 7.26 – 7.15 (m, 5H), 7.12 (t, *J* = 6.3 Hz, 3H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 – 6.89 (m, 3H), 6.33 – 6.23 (m, 2H), 6.10 – 5.98 (m, 2H), 5.79 (d, *J* = 7.4 Hz, 1H), 5.66 (d, *J* = 7.4 Hz, 1H), 4.44 – 4.28 (m, 3H), 4.11 – 3.93 (m, 2H), 3.92 – 3.83 (m, 2H), 3.69 – 3.52 (m, 3H), 3.21 – 3.05 (m, 5H), 2.97 – 2.91 (m, 1H), 2.88 (d, *J* = 14.5 Hz, 1H), 2.47 (d, *J* = 14.5 Hz, 1H), 1.90 – 1.78 (m, 4H), 1.64 – 1.55 (m, 2H), 1.46 – 1.34 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 158.5, 158.4, 155.0, 154.7, 149.5, 149.4, 144.8, 142.8, 141.3, 137.7, 137.6, 137.6, 135.6, 135.2, 134.7, 134.4, 134.4, 134.3, 134.2, 133.7, 133.6, 133.2, 133.0, 132.6, 132.6, 132.5, 132.2, 132.0, 131.9, 131.8, 131.7, 131.3, 131.3, 130.5, 130.5, 130.0, 129.9, 129.3, 129.0, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.4, 127.1, 127.1, 127.0, 127.0, 126.8, 126.6, 125.5, 124.9, 124.4, 122.5, 122.4,

121.6, 76.8, 76.4, 76.2, 75.8, 37.4, 31.2, 31.0, 30.8, 28.7, 23.6, 23.6, 23.0, 22.3, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.7;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{67}\text{O}_5\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1029.4618, found 1029.4614.



Physical state: white foam;

Yield: 72% (76.1 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 151–155 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 20.65 min;

$[\alpha]_D^{25}$: 130.9 (c 0.2, CHCl_3);

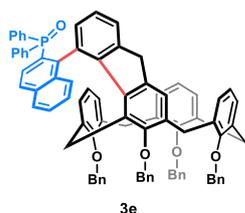
^1H NMR (600 MHz, CDCl_3): δ 7.89 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.59 (dd, J = 11.2, 7.9 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.31 – 7.26 (m, 2H), 7.24 – 7.14 (m, 6H), 7.12 – 7.08 (m, 2H), 7.04 (d, J = 7.4 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.90 (q, J = 7.2, 6.0 Hz, 3H), 6.27 – 6.20 (m, 2H), 6.02 (d, J = 7.1 Hz, 1H), 5.99 (t, J = 7.6 Hz, 1H), 5.76 (d, J = 7.4 Hz, 1H), 5.65 (d, J = 7.6 Hz, 1H), 4.38 – 4.26 (m, 3H), 4.02 (d, J = 21.9 Hz, 1H), 3.95 – 3.88 (m, 3H), 3.63 (t, J = 6.3 Hz, 3H), 3.19 (q, J = 6.5 Hz, 1H), 3.14 – 3.07 (m, 4H), 2.90 – 2.81 (m, 2H), 2.46 (d, J = 14.4 Hz, 1H), 1.81 – 1.74 (m, 4H), 1.60 – 1.50 (m, 4H), 1.47 – 1.36 (m, 4H), 1.20 – 1.13 (m, 2H), 1.06 – 0.99 (m, 5H), 0.96 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.5, 158.4, 155.1, 154.8, 149.6, 149.5, 144.9, 142.8, 141.3, 137.8, 137.6, 135.6, 135.0, 134.6, 134.4, 134.3, 134.3, 133.9, 133.6, 133.2, 133.0, 132.6, 132.6, 132.5, 132.2, 132.1, 131.9, 131.9, 131.9, 131.9, 131.6, 131.3, 130.6, 130.6, 130.0, 129.9, 129.1, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.4, 127.1, 127.1, 127.0, 126.8, 126.7, 125.4, 124.9, 124.5, 122.5, 122.4, 121.6, 74.7, 74.7, 74.6, 73.9, 37.4, 32.8, 32.7, 32.1, 31.4, 31.2, 31.0, 30.8, 28.6, 19.8, 19.8, 19.1,

19.0, 14.4, 14.3, 14.1 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 27.9;

HRMS (ESI-TOF) calculated for $\text{C}_{73}\text{H}_{75}\text{O}_5\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1085.5244, found 1085.5245.



Physical state: colorless and viscous liquid;

Yield: 52% (63.0 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 141–144 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IC column, 10% *i*PrOH in "hexane, 1 mL/min, λ = 254 nm), t_R (major) = 33.31 min;

$[\alpha]_D^{25}$: -46.7 (c 0.2, CHCl_3);

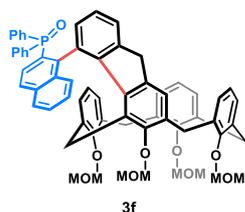
^1H NMR (600 MHz, CDCl_3): δ 7.66 – 7.57 (m, 3H), 7.50 – 7.39 (m, 6H), 7.32 (s, 8H), 7.28 – 7.17 (m, 8H), 7.14 (s, 1H), 7.10 (s, 1H), 7.04 – 6.84 (m, 14H), 6.80 – 6.74 (m, 2H), 6.28 – 6.22 (m, 1H), 6.15 – 6.07 (m, 2H), 5.98 (d, J = 6.1 Hz, 1H), 5.84 (d, J = 6.3 Hz, 1H), 5.76 (d, J = 6.2 Hz, 1H), 5.07 (d, J = 12.1 Hz, 1H), 4.98 – 4.92 (m, 2H), 4.59 (d, J = 11.2 Hz, 1H), 4.52 (d, J = 11.3 Hz, 1H), 4.27 (d, J = 13.5 Hz, 1H), 4.11 – 4.04 (m, 2H), 3.98 – 3.91 (m, 4H), 3.65 (d, J = 13.5 Hz, 1H), 3.32 (d, J = 14.5 Hz, 1H), 2.91 (dd, J = 28.2, 13.6 Hz, 2H), 2.68 (d, J = 9.5 Hz, 2H);

^{13}C NMR (150 MHz, CDCl_3): δ 156.6, 156.3, 154.7, 154.2, 149.5, 149.5, 144.9, 142.9, 142.0, 138.6, 138.1, 138.1, 138.0, 137.9, 137.7, 137.7, 136.5, 134.9, 134.8, 134.3, 134.2, 134.1, 133.2, 133.1, 132.9, 132.9, 132.9, 132.7, 132.3, 132.2, 132.1, 132.0, 132.0, 131.9, 131.5, 131.1, 130.8, 130.5, 130.3, 129.6, 129.5, 129.0, 129.0, 128.9, 128.8, 128.5, 128.4, 128.4, 128.4, 128.2, 128.0, 128.0, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.2, 127.1, 127.0, 125.4, 124.8, 124.4, 123.4, 122.8, 121.9, 77.1, 76.2, 75.7, 75.4, 37.5, 31.6, 31.1, 30.9, 28.5 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 27.9;

HRMS (ESI-TOF) calculated for $\text{C}_{85}\text{H}_{67}\text{O}_5\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1221.4618, found

1221.4614.



Physical state: white foam;

Yield: 64% (64.5 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.3 (PE:EtOAc = 1:1);

Melting point: 144–147 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% i PrOH in n hexane, 1 mL/min, λ = 254 nm), t_R (major) = 17.50 min;

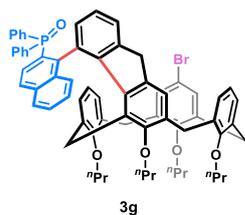
$[\alpha]_D^{25}$: 148.3 (c 0.2, CHCl_3);

^1H NMR (600 MHz, CDCl_3): δ 7.93 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 – 7.29 (m, 5H), 7.21 (q, J = 8.4 Hz, 2H), 7.18 – 7.08 (m, 4H), 7.02 – 6.92 (m, 4H), 6.89 (d, J = 7.4 Hz, 1H), 6.32 (t, J = 7.5 Hz, 1H), 6.22 (d, J = 7.4 Hz, 1H), 6.15 (t, J = 7.5 Hz, 1H), 6.08 (d, J = 7.3 Hz, 1H), 5.91 (d, J = 7.4 Hz, 1H), 5.85 (d, J = 7.3 Hz, 1H), 5.11 (dd, J = 33.6, 6.5 Hz, 2H), 4.97 – 4.84 (m, 3H), 4.50 – 4.35 (m, 3H), 4.28 (d, J = 5.0 Hz, 1H), 4.18 (d, J = 6.5 Hz, 1H), 4.12 (d, J = 21.9 Hz, 1H), 4.03 (d, J = 5.0 Hz, 1H), 3.97 (d, J = 22.0 Hz, 1H), 3.58 (s, 3H), 3.56 (s, 3H), 3.38 (s, 3H), 3.28 – 3.13 (m, 6H), 3.03 (d, J = 14.5 Hz, 1H), 2.29 (d, J = 14.5 Hz, 1H);

^{13}C NMR (150 MHz, CDCl_3): δ 156.9, 156.5, 153.0, 152.2, 149.7, 149.7, 144.9, 142.5, 141.5, 138.8, 137.4, 137.2, 135.3, 134.8, 134.7, 134.4, 134.4, 134.1, 134.0, 133.7, 132.9, 132.9, 132.9, 132.8, 132.8, 132.5, 132.4, 132.3, 131.9, 131.8, 131.5, 131.2, 130.9, 130.9, 129.8, 129.7, 129.3, 129.0, 128.6, 128.5, 128.4, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.4, 127.1, 127.0, 126.9, 125.5, 125.0, 124.9, 123.4, 123.2, 122.7, 100.5, 100.3, 100.0, 99.7, 58.0, 57.9, 57.7, 57.5, 37.5, 31.8, 31.6, 31.4, 28.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 27.8;

HRMS (ESI-TOF) calculated for $\text{C}_{65}\text{H}_{60}\text{O}_9\text{P}^+$, $[\text{M}+\text{H}]^+$ 1015.3969, found 1015.3966.



Physical state: white foam;

Yield: 74% (80.4 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 156–160 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 13.53 min;

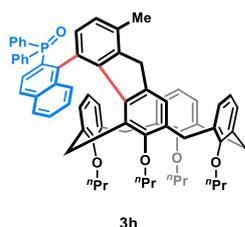
$[\alpha]_{25}^D$: 283.4 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.60 (dd, J = 11.4, 7.7 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.29 – 7.26 (m, 2H), 7.24 – 7.21 (m, 4H), 7.20 – 7.13 (m, 4H), 7.05 – 6.96 (m, 2H), 6.93 – 6.88 (m, 2H), 6.31 – 6.23 (m, 2H), 6.08 – 6.00 (m, 2H), 5.80 (d, J = 7.4 Hz, 1H), 5.67 (d, J = 7.5 Hz, 1H), 4.34 – 4.22 (m, 3H), 4.03 (d, J = 22.0 Hz, 1H), 3.94 – 3.81 (m, 3H), 3.60 – 3.48 (m, 3H), 3.12 – 3.01 (m, 5H), 2.90 – 2.81 (m, 2H), 2.42 (d, J = 14.4 Hz, 1H), 1.82 – 1.73 (m, 4H), 1.60 – 1.50 (m, 2H), 1.39 – 1.30 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.60 (t, J = 7.4 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 158.3, 157.7, 155.0, 154.7, 149.6, 149.5, 144.9, 142.8, 141.4, 139.8, 139.6, 137.7, 135.5, 135.1, 134.7, 134.5, 134.4, 134.4, 134.1, 133.7, 133.5, 133.1, 132.6, 132.6, 132.3, 132.2, 132.1, 131.9, 131.8, 131.7, 131.6, 131.4, 131.1, 130.6, 130.6, 130.0, 129.9, 129.3, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.7, 127.5, 127.4, 127.4, 127.1, 127.0, 126.9, 126.6, 125.5, 124.9, 124.5, 122.7, 122.6, 114.0, 76.9, 76.5, 76.2, 75.9, 37.4, 31.0, 30.9, 30.8, 28.7, 23.6, 23.5, 23.0, 22.3, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.9;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{67}\text{BrO}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1087.3904, found 1087.3906.



Physical state: white foam;

Yield: 55% (56.6 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 178–181 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 9.15 min;

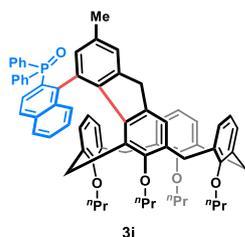
$[\alpha]_D^{25}$: 144.9 (c 0.2, CHCl_3);

^1H NMR (600 MHz, CDCl_3): δ 7.89 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.58 (dd, J = 11.4, 7.6 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.33 (d, J = 8.6 Hz, 1H), 7.27 – 7.13 (m, 8H), 7.10 (dd, J = 7.4, 2.6 Hz, 2H), 6.97 (td, J = 7.7, 2.5 Hz, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.81 (s, 1H), 6.29 – 6.18 (m, 2H), 6.06 – 5.95 (m, 2H), 5.76 (d, J = 7.4 Hz, 1H), 5.63 (d, J = 7.5 Hz, 1H), 4.36 (d, J = 13.2 Hz, 1H), 4.30 (t, J = 12.9 Hz, 2H), 3.97 (d, J = 21.8 Hz, 1H), 3.92 – 3.82 (m, 3H), 3.59 (t, J = 6.6 Hz, 2H), 3.55 (td, J = 10.9, 5.9 Hz, 1H), 3.22 – 3.03 (m, 5H), 2.96 – 2.89 (m, 1H), 2.80 (d, J = 14.5 Hz, 1H), 2.45 (d, J = 14.4 Hz, 1H), 2.09 (s, 3H), 1.85 – 1.76 (m, 4H), 1.63 – 1.52 (m, 2H), 1.42 – 1.31 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.61 (t, J = 7.5 Hz, 3H);

^{13}C NMR (151 MHz, CDCl_3): δ 158.5, 158.3, 155.0, 154.7, 149.5, 149.4, 145.3, 141.4, 140.2, 137.8, 137.6, 137.4, 135.3, 135.2, 135.1, 134.7, 134.6, 134.5, 134.5, 134.3, 134.0, 133.2, 133.2, 133.1, 132.7, 132.5, 132.2, 132.1, 132.0, 132.0, 131.8, 131.8, 131.7, 131.2, 131.2, 130.6, 130.6, 130.0, 129.9, 129.4, 129.0, 128.8, 128.4, 128.3, 128.1, 128.1, 128.0, 127.7, 127.6, 127.4, 127.2, 127.1, 127.0, 127.0, 126.9, 126.6, 125.6, 124.4, 122.6, 122.4, 121.6, 76.8, 76.4, 76.2, 75.8, 37.2, 31.2, 31.1, 30.8, 28.6, 23.7, 23.6, 23.1, 22.3, 21.0, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 27.6;

HRMS (ESI-TOF) calculated for $\text{C}_{70}\text{H}_{70}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1021.4955, found 1021.4957.



Physical state: white foam;

Yield: 70% (71.0 mg);

$R_f = 0.4$ (PE:EtOAc = 2:1), > 19:1 *d.r.* (determined by ^{31}P NMR);

Melting point: 161–163 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 10.89 min, t_R (minor) = 7.48 min;

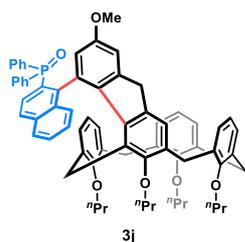
$[\alpha]_D^{25}$: 163.3 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.6$ Hz, 1H), 7.60 (dd, $J = 11.2, 7.9$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.37 (m, 2H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.26 – 7.15 (m, 8H), 7.11 (d, $J = 7.3$ Hz, 2H), 6.98 (t, $J = 6.6$ Hz, 2H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.82 (s, 1H), 6.25 (q, $J = 7.5$ Hz, 2H), 6.07 – 5.95 (m, 2H), 5.78 (d, $J = 7.5$ Hz, 1H), 5.65 (d, $J = 7.5$ Hz, 1H), 4.43 – 4.26 (m, 3H), 4.03 – 3.84 (m, 4H), 3.67 – 3.52 (m, 3H), 3.22 – 3.06 (m, 5H), 2.94 (q, $J = 6.7$ Hz, 1H), 2.82 (d, $J = 14.5$ Hz, 1H), 2.47 (d, $J = 14.4$ Hz, 1H), 2.10 (s, 3H), 1.88 – 1.76 (m, 4H), 1.64 – 1.53 (m, 2H), 1.45 – 1.34 (m, 2H), 1.07 (t, $J = 7.3$ Hz, 3H), 0.99 (t, $J = 7.3$ Hz, 3H), 0.79 (t, $J = 7.4$ Hz, 3H), 0.63 (t, $J = 7.4$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 158.3, 155.0, 154.7, 149.5, 149.4, 145.3, 141.4, 140.2, 137.8, 137.6, 137.4, 135.4, 135.2, 135.1, 134.9, 134.5, 134.4, 134.4, 134.3, 133.8, 133.2, 133.2, 133.1, 132.7, 132.5, 132.2, 132.1, 132.0, 132.0, 131.8, 131.8, 131.8, 131.7, 131.2, 131.2, 130.6, 130.6, 130.0, 129.9, 129.5, 129.0, 129.0, 128.8, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.8, 127.6, 127.4, 127.2, 127.1, 127.0, 127.0, 126.9, 126.6, 125.6, 124.4, 122.6, 122.4, 121.6, 76.8, 76.4, 76.2, 75.8, 37.2, 31.2, 31.1, 30.8, 28.6, 23.7, 23.6, 23.0, 22.3, 21.0, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.6;

HRMS (ESI-TOF) calculated for $\text{C}_{70}\text{H}_{70}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1021.4955, found 1021.4956.



Physical state: white foam;

Yield: 80% (82.5 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.3$ (PE:EtOAc = 2:1);

Melting point: 168–170 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 11.64 min;

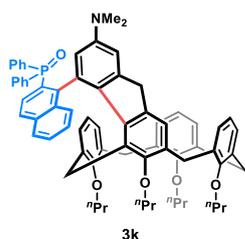
$[\alpha]_D^{25}$: 172.4 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 8.1$ Hz, 1H), 7.81 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.60 (dd, $J = 11.6, 7.3$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.46 – 7.34 (m, 3H), 7.26 – 7.14 (m, 7H), 7.12 – 7.08 (m, 2H), 6.99 – 6.87 (m, 4H), 6.74 (d, $J = 2.5$ Hz, 1H), 6.29 – 6.20 (m, 2H), 6.05 – 5.96 (m, 2H), 5.76 (d, $J = 7.3$ Hz, 1H), 5.62 (d, $J = 7.3$ Hz, 1H), 4.36 (d, $J = 13.2$ Hz, 1H), 4.30 (dd, $J = 13.5, 3.6$ Hz, 2H), 3.98 – 3.81 (m, 4H), 3.62 – 3.51 (m, 3H), 3.49 (s, 3H), 3.17 – 3.05 (m, 5H), 2.92 (dt, $J = 8.7, 6.4$ Hz, 1H), 2.75 (d, $J = 14.6$ Hz, 1H), 2.44 (d, $J = 14.5$ Hz, 1H), 1.86 – 1.75 (m, 4H), 1.62 – 1.52 (m, 2H), 1.42 – 1.31 (m, 2H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.77 (t, $J = 7.5$ Hz, 3H), 0.62 (t, $J = 7.5$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 158.5, 158.4, 157.4, 155.0, 154.8, 149.2, 149.2, 147.1, 141.2, 137.7, 137.6, 137.0, 136.1, 135.4, 134.7, 134.6, 134.5, 134.5, 134.4, 134.4, 133.7, 133.2, 133.1, 133.0, 132.9, 132.7, 132.6, 132.0, 131.9, 131.8, 131.7, 131.7, 131.6, 131.3, 131.3, 130.6, 130.5, 130.0, 129.9, 129.3, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.4, 127.3, 127.2, 127.0, 126.9, 126.7, 124.3, 122.5, 122.4, 121.6, 115.8, 112.1, 76.8, 76.4, 76.2, 75.8, 55.1, 37.3, 31.2, 31.1, 30.7, 28.7, 23.6, 23.6, 23.0, 22.3, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.8;

HRMS (ESI-TOF) calculated for $\text{C}_{70}\text{H}_{70}\text{O}_6\text{P}^+$, $[\text{M}+\text{H}]^+$ 1037.4905, found 1037.4907.



Physical state: yellow foam;

Yield: 78% (82.0 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.4$ (PE:EtOAc = 2:1);

Melting point: 165–169 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 5% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 230$ nm), t_R (major) = 46.41 min;

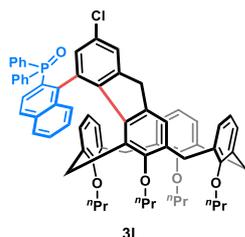
$[\alpha]_D^{25}$: 135.1 (c 0.2, CHCl_3);

^1H NMR (600 MHz, CDCl_3): δ 7.90 (d, $J = 8.2$ Hz, 1H), 7.80 (d, $J = 8.6$ Hz, 1H), 7.58 – 7.45 (m, 4H), 7.42 (d, $J = 8.5$ Hz, 1H), 7.34 (t, $J = 6.7$ Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.08 (m, 5H), 6.96 – 6.87 (m, 3H), 6.67 (d, $J = 29.7$ Hz, 2H), 6.27 (d, $J = 4.4$ Hz, 2H), 6.02 (t, $J = 6.0$ Hz, 1H), 5.98 (t, $J = 7.6$ Hz, 1H), 5.74 (d, $J = 7.4$ Hz, 1H), 5.59 (d, $J = 7.5$ Hz, 1H), 4.36 (d, $J = 13.2$ Hz, 1H), 4.29 (dd, $J = 13.5, 3.4$ Hz, 2H), 3.91 – 3.79 (m, 4H), 3.59 (t, $J = 6.5$ Hz, 2H), 3.57 – 3.49 (m, 1H), 3.18 – 3.05 (m, 5H), 2.99 – 2.92 (m, 1H), 2.80 (s, 6H), 2.67 (d, $J = 14.5$ Hz, 1H), 2.43 (d, $J = 14.6$ Hz, 1H), 1.83 – 1.76 (m, 4H), 1.64 – 1.55 (m, 2H), 1.41 – 1.33 (m, 2H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 7.3$ Hz, 3H), 0.77 (t, $J = 7.4$ Hz, 3H), 0.63 (t, $J = 7.4$ Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.5, 158.3, 155.0, 154.8, 147.0, 137.8, 137.6, 135.5, 134.9, 134.6, 134.5, 134.5, 134.4, 133.8, 133.3, 133.2, 132.7, 132.1, 132.0, 131.7, 131.7, 131.6, 131.5, 131.1, 130.2, 130.1, 130.0, 129.0, 128.8, 128.4, 128.4, 128.4, 128.3, 128.1, 127.9, 127.6, 127.5, 127.3, 127.2, 127.1, 127.1, 126.9, 126.7, 126.6, 124.1, 122.5, 122.4, 121.6, 76.8, 76.4, 76.1, 75.8, 40.4, 37.5, 31.2, 31.1, 30.7, 28.7, 23.6, 23.6, 23.0, 22.3, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 28.2;

HRMS (ESI-TOF) calculated for $\text{C}_{71}\text{H}_{73}\text{NO}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1050.5221, found 1050.5220.



Physical state: white foam;

Yield: 69% (72.0 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 190–192 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 5% *i*PrOH in *n*hexane, 1 mL/min, λ = 230 nm), t_R (major) = 17.84 min;

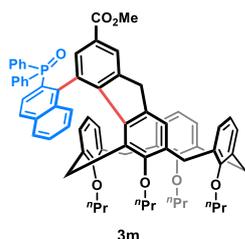
$[\alpha]_D^{25}$: 194.9 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 8.2 Hz, 1H), 7.82 (dd, J = 8.6, 1.9 Hz, 1H), 7.64 (dd, J = 11.7, 7.1 Hz, 2H), 7.53 (t, J = 6.9 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.41 – 7.26 (m, 6H), 7.25 – 7.16 (m, 4H), 7.11 (d, J = 7.3 Hz, 2H), 7.00 (td, J = 7.9, 2.9 Hz, 2H), 6.94 – 6.89 (m, 2H), 6.27 – 6.17 (m, 2H), 6.01 (t, J = 7.6 Hz, 2H), 5.79 (d, J = 7.1 Hz, 1H), 5.68 (d, J = 7.4 Hz, 1H), 4.41 – 4.26 (m, 3H), 4.09 – 3.84 (m, 4H), 3.64 – 3.52 (m, 3H), 3.17 – 3.07 (m, 5H), 2.93 – 2.85 (m, 1H), 2.82 (d, J = 14.4 Hz, 1H), 2.45 (d, J = 14.3 Hz, 1H), 1.87 – 1.77 (m, 4H), 1.62 – 1.51 (m, 2H), 1.42 – 1.31 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H), 0.78 (t, J = 7.5 Hz, 3H), 0.61 (t, J = 7.5 Hz, 3H);

^{13}C NMR (151 MHz, CDCl_3): δ 158.5, 158.5, 155.0, 154.7, 148.0, 147.9, 146.7, 141.5, 140.4, 137.7, 137.6, 137.4, 136.0, 134.5, 134.4, 134.4, 134.0, 133.8, 133.8, 133.7, 133.3, 132.8, 132.6, 132.0, 131.9, 131.8, 131.8, 131.5, 131.5, 131.2, 131.1, 130.9, 130.9, 129.8, 129.8, 129.7, 129.1, 129.0, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.5, 127.4, 127.1, 126.8, 124.8, 124.6, 122.6, 122.4, 121.7, 76.8, 76.4, 76.3, 75.9, 37.3, 31.2, 31.1, 30.8, 28.5, 23.7, 23.6, 23.0, 22.3, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.5;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{66}\text{ClO}_5\text{PK}^+$, $[\text{M}+\text{K}]^+$ 1079.3968, found 1079.3960.



Physical state: white foam;

Yield: 67% (71.8 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.5 (PE:EtOAc = 1:1);

Melting point: 175–178 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 15% *i*PrOH in *n*hexane, 1 mL/min, λ = 230 nm), t_R (major) = 9.23 min;

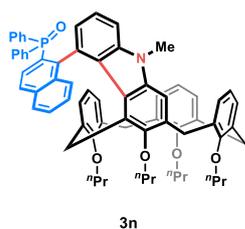
$[\alpha]_D^{25}$: 156.6 (c 0.2, CHCl_3);

^1H NMR (600 MHz, CDCl_3): δ 8.14 (s, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.63 (dd, J = 11.5, 7.8 Hz, 2H), 7.56 (s, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.26 – 7.18 (m, 3H), 7.13 – 7.07 (m, 4H), 6.95 (t, J = 8.5 Hz, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.24 (t, J = 7.5 Hz, 1H), 6.19 (d, J = 7.2 Hz, 1H), 6.05 – 5.99 (m, 2H), 5.79 (d, J = 7.4 Hz, 1H), 5.72 (d, J = 7.5 Hz, 1H), 4.35 (t, J = 14.0 Hz, 2H), 4.28 (d, J = 13.4 Hz, 1H), 4.16 (d, J = 22.2 Hz, 1H), 4.01 (d, J = 22.2 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.67 (s, 3H), 3.62 – 3.54 (m, 3H), 3.17 – 3.07 (m, 5H), 2.94 (d, J = 14.4 Hz, 1H), 2.87 – 2.81 (m, 1H), 2.46 (d, J = 14.3 Hz, 1H), 1.85 – 1.77 (m, 4H), 1.57 – 1.50 (m, 2H), 1.39 – 1.30 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), 0.60 (t, J = 7.4 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 167.1, 158.6, 158.5, 155.0, 154.7, 148.9, 148.8, 147.4, 145.2, 140.5, 138.9, 137.7, 137.6, 137.0, 134.6, 134.5, 134.4, 133.9, 133.3, 132.8, 132.7, 132.7, 132.6, 132.5, 132.1, 132.0, 132.0, 132.0, 131.9, 131.9, 131.3, 131.3, 131.0, 131.0, 129.8, 129.8, 129.0, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.5, 127.5, 127.3, 127.1, 127.1, 126.7, 126.5, 125.8, 124.7, 122.7, 122.5, 121.6, 76.8, 76.4, 76.3, 75.9, 51.8, 37.4, 31.2, 31.0, 30.9, 28.6, 27.5, 23.7, 23.6, 23.0, 22.2, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 28.0;

HRMS (ESI-TOF) calculated for $\text{C}_{71}\text{H}_{69}\text{O}_7\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1087.4673, found 1087.4678.



3n

Physical state: white foam;

Yield: 48% (49.0 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.3$ (PE:EtOAc = 2:1);

Melting point: 159–161 °C;

HPLC: 95% *e.e.* (Daicel chiralpak IC column, 20% i PrOH in n hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 24.58 min, t_R (minor) = 12.34 min;

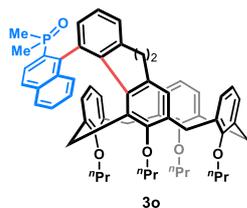
$[\alpha]_D^{25}$: 105.5 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 8.1$ Hz, 1H), 7.79 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.61 – 7.49 (m, 3H), 7.44 – 7.33 (m, 2H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.26 – 7.20 (m, 3H), 7.18 – 7.08 (m, 8H), 6.94 – 6.84 (m, 3H), 6.80 (d, $J = 7.0$ Hz, 1H), 6.23 (d, $J = 4.8$ Hz, 2H), 6.01 (t, $J = 4.7$ Hz, 1H), 5.94 (t, $J = 7.6$ Hz, 1H), 5.76 (d, $J = 7.2$ Hz, 1H), 5.59 (d, $J = 7.3$ Hz, 1H), 4.49 (d, $J = 13.4$ Hz, 1H), 4.36 (dd, $J = 27.8, 13.4$ Hz, 2H), 4.00 – 3.85 (m, 5H), 3.68 – 3.55 (m, 3H), 3.42 (td, $J = 11.0, 5.9$ Hz, 1H), 3.27 (d, $J = 13.5$ Hz, 1H), 3.18 (dt, $J = 8.7, 6.7$ Hz, 1H), 3.11 (dd, $J = 13.5, 2.7$ Hz, 2H), 2.94 (dt, $J = 8.8, 6.4$ Hz, 1H), 2.80 – 2.62 (m, 2H), 1.90 – 1.80 (m, 4H), 1.64 – 1.53 (m, 2H), 1.49 – 1.36 (m, 2H), 1.08 (t, $J = 7.4$ Hz, 3H), 1.00 (t, $J = 7.4$ Hz, 3H), 0.80 (t, $J = 7.5$ Hz, 3H), 0.63 (t, $J = 7.5$ Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.6, 155.1, 154.7, 152.5, 149.4, 149.4, 141.5, 137.9, 137.5, 137.5, 135.7, 135.1, 134.7, 134.5, 134.5, 134.4, 134.4, 134.0, 133.3, 133.1, 132.9, 132.8, 132.8, 132.4, 132.4, 132.4, 132.0, 131.9, 131.8, 131.3, 131.2, 130.5, 130.5, 129.9, 129.8, 129.4, 129.0, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.6, 127.4, 127.2, 127.2, 127.1, 127.0, 126.9, 126.6, 124.3, 123.6, 123.3, 122.6, 122.5, 122.4, 121.6, 108.5, 107.4, 76.8, 76.6, 76.4, 75.8, 31.8, 31.2, 31.1, 29.4, 28.5, 23.7, 23.6, 23.1, 22.1, 11.0, 11.0, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 28.1;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{68}\text{NO}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1022.4908, found 1022.4901.



Physical state: white foam;

Yield: 71% (63.2 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.4$ (DCM:MeOH = 40:1);

Melting point: 126–129 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 230$ nm), t_R (major) = 6.38 min;

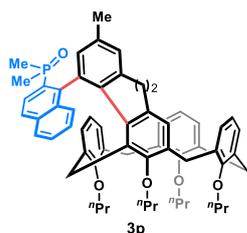
$[\alpha]_D^{25}$: 220.0 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 8.37 (t, $J = 9.5$ Hz, 1H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.75 (d, $J = 7.5$ Hz, 1H), 7.59 – 7.51 (m, 2H), 7.41 (t, $J = 6.0$ Hz, 1H), 7.33 (t, $J = 6.0$ Hz, 1H), 7.05 (dd, $J = 23.0, 5.7$ Hz, 2H), 7.01 – 6.93 (m, 2H), 6.91 – 6.84 (m, 2H), 6.21 – 6.15 (m, 1H), 6.13 (d, $J = 5.6$ Hz, 1H), 6.02 (d, $J = 6.0$ Hz, 1H), 5.98 – 5.91 (m, 1H), 5.79 (d, $J = 6.2$ Hz, 1H), 5.47 (d, $J = 6.3$ Hz, 1H), 4.32 (d, $J = 13.1$ Hz, 1H), 4.26 (d, $J = 13.4$ Hz, 1H), 4.11 (d, $J = 13.2$ Hz, 1H), 3.91 – 3.81 (m, 2H), 3.56 (d, $J = 27.5$ Hz, 3H), 3.43 (d, $J = 6.4$ Hz, 1H), 3.20 (t, $J = 12.0$ Hz, 1H), 3.10 – 2.95 (m, 5H), 2.90 (d, $J = 13.1$ Hz, 2H), 2.76 (d, $J = 13.5$ Hz, 1H), 2.70 (t, $J = 14.0$ Hz, 1H), 2.33 – 2.25 (m, 1H), 1.93 – 1.73 (m, 8H), 1.66 (d, $J = 12.3$ Hz, 3H), 1.48 (d, $J = 12.5$ Hz, 3H), 1.16 (t, $J = 5.4$ Hz, 3H), 1.01 (t, $J = 5.4$ Hz, 3H), 0.77 (t, $J = 5.5$ Hz, 3H), 0.69 (t, $J = 5.5$ Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.2, 157.7, 155.2, 155.0, 144.6, 144.6, 143.1, 137.7, 137.3, 136.9, 136.6, 136.6, 136.2, 135.4, 134.6, 134.6, 134.6, 133.7, 133.3, 133.3, 133.0, 132.6, 132.3, 130.4, 130.4, 129.0, 128.6, 128.6, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 127.3, 126.8, 126.8, 126.7, 126.2, 126.1, 122.1, 122.0, 121.7, 76.9, 76.8, 76.3, 75.9, 33.3, 31.9, 31.3, 30.9, 30.7, 30.0, 29.9, 23.9, 23.6, 22.9, 22.7, 21.6, 21.1, 18.4, 17.9, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 37.1;

HRMS (ESI-TOF) calculated for $\text{C}_{60}\text{H}_{66}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 897.4642, found 897.4641.



Physical state: white foam;

Yield: 54% (48.9 mg), *d.r.* = 14:1 (determined by ^{31}P NMR), the diastereoisomers were separable;

R_f = 0.4 (DCM:MeOH = 40:1);

Melting point: 128–130 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 3% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 51.08 min;

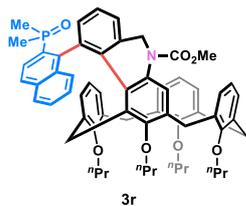
$[\alpha]_D^{25}$: 280.7 (c 0.2, CHCl_3);

^1H NMR (600 MHz, CDCl_3): δ 8.41 (t, J = 9.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.35 – 7.30 (m, 2H), 7.06 (dd, J = 21.5, 7.0 Hz, 2H), 7.00 – 6.91 (m, 3H), 6.87 (t, J = 6.9 Hz, 1H), 6.18 (t, J = 7.1 Hz, 1H), 6.14 (d, J = 6.0 Hz, 1H), 6.01 (d, J = 6.7 Hz, 1H), 5.94 (t, J = 7.3 Hz, 1H), 5.78 (d, J = 6.9 Hz, 1H), 5.45 (d, J = 7.0 Hz, 1H), 4.33 (d, J = 13.1 Hz, 1H), 4.27 (d, J = 13.4 Hz, 1H), 4.11 (d, J = 13.3 Hz, 1H), 3.89 – 3.81 (m, 2H), 3.63 – 3.57 (m, 1H), 3.54 (t, J = 6.0 Hz, 2H), 3.45 – 3.39 (m, 1H), 3.19 (t, J = 10.5 Hz, 1H), 3.10 – 2.93 (m, 6H), 2.89 (d, J = 13.9 Hz, 2H), 2.72 (d, J = 13.6 Hz, 2H), 2.45 (s, 3H), 2.28 (t, J = 12.0 Hz, 1H), 1.86 – 1.75 (m, 6H), 1.69 (d, J = 12.4 Hz, 3H), 1.43 (d, J = 12.6 Hz, 3H), 1.36 (s, 1H), 1.16 (t, J = 7.0 Hz, 3H), 1.12 (s, 1H), 1.02 (t, J = 7.0 Hz, 3H), 0.77 (t, J = 7.0 Hz, 3H), 0.68 (t, J = 7.0 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.2, 157.7, 155.2, 155.0, 144.7, 144.7, 143.1, 137.6, 137.3, 136.5, 136.5, 136.3, 136.0, 135.0, 134.6, 134.3, 134.1, 133.7, 133.3, 133.2, 133.1, 132.9, 132.7, 132.2, 130.3, 130.3, 129.3, 129.0, 128.6, 128.3, 128.2, 128.1, 127.7, 127.7, 127.7, 127.4, 127.4, 127.3, 126.8, 126.7, 126.1, 126.1, 122.1, 121.9, 121.6, 76.8, 76.8, 76.3, 75.9, 33.3, 31.9, 31.3, 30.9, 30.7, 30.0, 23.9, 23.6, 22.9, 22.6, 21.8, 21.4, 21.0, 18.2, 17.7, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (243 MHz, CDCl_3): δ 36.8;

HRMS (ESI-TOF) calculated for $\text{C}_{61}\text{H}_{68}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 911.4799, found 911.4798.



Physical state: white foam;

Yield: 66% (63 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

$R_f = 0.4$ (DCM:MeOH = 40:1);

Melting point: 129–133 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 9.28 min;

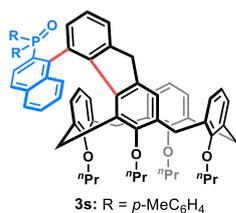
$[\alpha]_D^{25}$: 118.1 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 8.33 (t, $J = 9.9$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 7.5$ Hz, 1H), 7.62 (d, $J = 7.0$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.10 – 6.94 (m, 3H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.75 (d, $J = 8.6$ Hz, 1H), 6.17 (t, $J = 7.6$ Hz, 1H), 6.09 (d, $J = 7.1$ Hz, 1H), 6.02 (d, $J = 7.3$ Hz, 1H), 5.96 (t, $J = 7.6$ Hz, 1H), 5.81 (d, $J = 7.2$ Hz, 1H), 5.55 – 5.32 (m, 2H), 4.34 – 4.22 (m, 3H), 4.16 (d, $J = 13.3$ Hz, 1H), 3.90 – 3.78 (m, 5H), 3.59 – 3.50 (m, 3H), 3.43 (q, $J = 6.7$ Hz, 1H), 3.31 – 3.19 (m, 1H), 3.10 – 2.95 (m, 4H), 2.77 (d, $J = 13.7$ Hz, 1H), 2.42 – 2.31 (m, 1H), 1.87 – 1.71 (m, 7H), 1.65 (d, $J = 12.5$ Hz, 3H), 1.52 (d, $J = 12.7$ Hz, 3H), 1.42 – 1.35 (m, 1H), 1.15 (t, $J = 7.4$ Hz, 4H), 1.02 (t, $J = 7.4$ Hz, 3H), 0.91 – 0.82 (m, 1H), 0.78 (t, $J = 7.5$ Hz, 3H), 0.70 (t, $J = 7.4$ Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.2, 156.6, 155.1, 155.0, 154.4, 143.9, 143.8, 138.8, 137.6, 137.1, 136.9, 136.8, 136.7, 135.6, 134.6, 134.1, 133.4, 133.4, 132.6, 132.1, 131.6, 130.3, 130.2, 129.0, 128.7, 128.6, 128.2, 128.1, 127.9, 127.9, 127.7, 127.6, 127.4, 127.2, 127.1, 126.7, 126.6, 125.9, 125.3, 122.2, 122.1, 121.8, 76.9, 76.8, 76.4, 76.2, 53.3, 50.4, 31.3, 30.9, 30.6, 30.4, 29.9, 29.8, 23.9, 23.6, 22.9, 22.6, 21.4, 20.7, 18.7, 18.0, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 36.6;

HRMS (ESI-TOF) calculated for $\text{C}_{61}\text{H}_{67}\text{NO}_7\text{P}^+$, $[\text{M}+\text{H}]^+$ 956.4650, found 956.4654.



Physical state: white foam;

Yield: 67% (69.7 mg), > 19:1 *d.r.* (determined by ³¹P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 165–168 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 15.81 min;

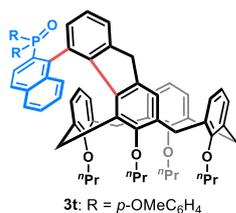
[α]_D²⁵: 135.4 (c 0.2, CHCl₃);

¹H NMR (600 MHz, CDCl₃): δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.41 (m, 5H), 7.34 – 7.28 (m, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.05 (m, 7H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.27 (dt, *J* = 14.1, 7.2 Hz, 2H), 6.05 (d, *J* = 7.0 Hz, 1H), 6.02 (t, *J* = 7.6 Hz, 1H), 5.79 (d, *J* = 7.4 Hz, 1H), 5.66 (d, *J* = 7.5 Hz, 1H), 4.43 – 4.28 (m, 3H), 4.06 (d, *J* = 21.8 Hz, 1H), 3.99 – 3.86 (m, 3H), 3.62 (t, *J* = 6.5 Hz, 2H), 3.60 – 3.52 (m, 1H), 3.17 – 3.04 (m, 5H), 2.92 – 2.80 (m, 2H), 2.42 (d, *J* = 14.4 Hz, 1H), 2.36 (s, 3H), 2.22 (s, 3H), 1.89 – 1.77 (m, 4H), 1.61 – 1.52 (m, 2H), 1.42 – 1.32 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.63 (t, *J* = 7.4 Hz, 3H);

¹³C NMR (150 MHz, CDCl₃): δ 158.5, 158.4, 155.0, 154.7, 149.4, 149.3, 144.8, 142.8, 141.6, 141.6, 141.4, 140.8, 140.8, 137.7, 137.6, 137.6, 135.5, 134.4, 134.4, 133.7, 133.2, 133.0, 132.7, 132.7, 132.5, 132.2, 132.1, 132.0, 132.0, 131.9, 131.9, 131.9, 131.7, 131.7, 131.3, 131.0, 130.1, 130.0, 129.5, 129.1, 129.0, 129.0, 128.8, 128.8, 128.5, 128.4, 128.0, 127.9, 127.4, 127.1, 127.1, 126.9, 126.8, 126.7, 126.5, 125.4, 124.7, 124.4, 122.5, 122.4, 121.6, 76.8, 76.4, 76.2, 75.8, 37.4, 31.2, 31.1, 30.8, 28.7, 23.6, 23.6, 23.0, 22.3, 21.7, 21.5, 11.0, 10.9, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

³¹P NMR (243 MHz, CDCl₃): δ 28.0;

HRMS (ESI-TOF) calculated for C₇₁H₇₁O₅PNa⁺, [M+Na]⁺ 1057.4931, found 1057.4936.



Physical state: white foam;

Yield: 72% (77.0 mg), > 19:1 *d.r.* (determined by ³¹P NMR);

R_f = 0.4 (PE:EtOAc = 1:1);

Melting point: 141–144 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% *i*PrOH in "hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 21.17 min;

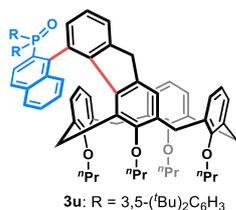
[α]_D²⁵: 149.7 (c 0.2, CHCl₃);

¹H NMR (600 MHz, CDCl₃): δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.45 (m, 5H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 6.0 Hz, 1H), 7.15 – 7.04 (m, 6H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.43 (d, *J* = 7.1 Hz, 2H), 6.26 (dt, *J* = 14.2, 7.0 Hz, 2H), 6.04 (d, *J* = 7.1 Hz, 1H), 6.01 (t, *J* = 7.6 Hz, 1H), 5.78 (d, *J* = 7.4 Hz, 1H), 5.63 (d, *J* = 7.5 Hz, 1H), 4.36 (dd, *J* = 29.3, 13.3 Hz, 2H), 4.31 (d, *J* = 13.5 Hz, 1H), 4.08 (d, *J* = 21.9 Hz, 1H), 3.95 (d, *J* = 21.9 Hz, 1H), 3.91 – 3.85 (m, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.56 (td, *J* = 10.9, 5.9 Hz, 1H), 3.14 – 3.05 (m, 5H), 2.89 – 2.82 (m, 2H), 2.42 (d, *J* = 14.5 Hz, 1H), 1.86 – 1.78 (m, 4H), 1.62 – 1.54 (m, 2H), 1.42 – 1.32 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H), 0.63 (t, *J* = 7.4 Hz, 3H);

¹³C NMR (150 MHz, CDCl₃): δ 161.9, 161.9, 161.3, 161.3, 158.5, 158.3, 155.0, 154.7, 149.2, 149.2, 144.8, 142.8, 141.4, 137.7, 137.6, 135.5, 134.4, 134.3, 134.3, 133.8, 133.7, 133.7, 133.6, 133.2, 133.0, 132.7, 132.6, 132.5, 132.2, 132.1, 131.7, 130.0, 129.9, 129.6, 129.0, 128.8, 128.0, 127.9, 127.4, 127.1, 127.1, 126.9, 126.8, 126.7, 126.5, 126.5, 125.8, 125.7, 125.4, 124.7, 124.4, 122.6, 122.4, 121.6, 113.9, 113.8, 113.4, 113.3, 76.8, 76.4, 76.2, 75.8, 55.4, 55.3, 37.4, 31.2, 31.1, 30.8, 28.7, 23.6, 23.6, 23.0, 22.2, 11.0, 10.9, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

³¹P NMR (243 MHz, CDCl₃): δ 27.6;

HRMS (ESI-TOF) calculated for C₇₁H₇₂O₇P⁺, [M+H]⁺ 1067.5010, found 1067.5014.



Physical state: white foam;

Yield: 85% (104.1 mg), > 19:1 *d.r.* (determined by ³¹P NMR);

R_f = 0.3 (PE:EtOAc = 10:1);

Melting point: 264–267 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak AD-H column, 0.5% *i*PrOH in *n*hexane, 0.5 mL/min, λ = 230 nm), *t_R* (major) = 7.34 min;

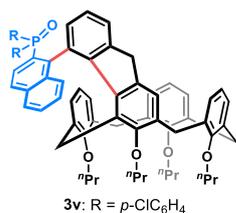
[α]_D²⁵: 172.5 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.43 (m, 5H), 7.39 (s, 1H), 7.30 – 7.19 (m, 5H), 7.18 – 7.12 (m, 1H), 7.10 – 7.04 (m, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 7.5 Hz, 1H), 6.20 (t, *J* = 7.6 Hz, 1H), 6.12 (d, *J* = 7.2 Hz, 1H), 6.03 (q, *J* = 6.6, 5.3 Hz, 3H), 5.61 (dd, *J* = 6.0, 2.8 Hz, 1H), 4.34 (dd, *J* = 17.6, 13.5 Hz, 2H), 4.26 – 4.13 (m, 2H), 3.95 – 3.80 (m, 3H), 3.63 – 3.53 (m, 3H), 3.12 – 2.94 (m, 5H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.13 (d, *J* = 14.0 Hz, 1H), 1.85 – 1.74 (m, 4H), 1.53 – 1.42 (m, 2H), 1.36 (dd, *J* = 15.3, 7.5 Hz, 2H), 1.28 (s, 18H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.00 (s, 18H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H), 0.58 (t, *J* = 7.4 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 158.6, 158.3, 155.0, 154.6, 150.8, 150.7, 150.6, 149.8, 149.8, 144.8, 143.4, 141.5, 137.7, 137.6, 137.5, 135.4, 135.0, 134.4, 134.4, 134.4, 134.2, 133.8, 133.1, 133.0, 132.8, 132.8, 132.8, 132.7, 132.6, 132.0, 130.8, 130.8, 129.8, 129.1, 129.0, 128.5, 127.9, 127.9, 127.6, 127.4, 127.0, 126.8, 126.7, 126.6, 126.5, 126.3, 125.9, 125.8, 125.0, 124.9, 124.4, 124.4, 122.9, 122.5, 121.4, 76.7, 76.4, 76.1, 75.9, 37.6, 35.1, 34.8, 31.6, 31.5, 31.5, 31.4, 31.3, 31.3, 30.9, 30.8, 28.7, 23.6, 23.6, 23.0, 22.1, 11.0, 10.8, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

³¹P NMR (162 MHz, CDCl₃): δ 28.4;

HRMS (ESI-TOF) calculated for C₈₅H₁₀₀O₅P⁺, [M+H]⁺ 1231.7303, found 1231.7304.



Physical state: white foam;

Yield: 63% (68.2 mg), > 19:1 *d.r.* (determined by ³¹P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: >300 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in "hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 10.42 min;

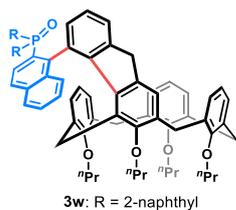
[α]_D²⁵: 144.9 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.33 – 7.28 (m, 2H), 7.25 – 7.08 (m, 8H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.33 – 6.25 (m, 2H), 6.05 (dd, *J* = 6.9, 2.1 Hz, 1H), 6.01 (t, *J* = 7.6 Hz, 1H), 5.81 (d, *J* = 7.2 Hz, 1H), 5.55 (d, *J* = 7.2 Hz, 1H), 4.43 – 4.26 (m, 3H), 4.07 (d, *J* = 22.1 Hz, 1H), 3.94 (d, *J* = 22.2 Hz, 1H), 3.91 – 3.81 (m, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.60 – 3.51 (m, 1H), 3.19 – 3.08 (m, 5H), 2.91 – 2.83 (m, 1H), 2.73 (d, *J* = 14.6 Hz, 1H), 2.48 (d, *J* = 14.5 Hz, 1H), 1.88 – 1.77 (m, 4H), 1.66 – 1.55 (m, 2H), 1.43 – 1.33 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H), 0.64 (t, *J* = 7.5 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 158.4, 158.3, 154.9, 154.7, 149.6, 149.5, 145.1, 142.7, 140.9, 138.0, 138.0, 137.6, 137.5, 137.4, 137.2, 137.1, 135.8, 134.4, 134.4, 134.1, 133.4, 133.3, 133.2, 133.1, 133.1, 133.0, 133.0, 132.9, 132.8, 132.7, 132.4, 132.1, 132.1, 132.0, 132.0, 131.7, 131.6, 129.4, 129.3, 128.9, 128.8, 128.6, 128.3, 128.3, 128.0, 127.9, 127.4, 127.3, 127.2, 127.0, 126.9, 126.3, 125.5, 125.0, 124.5, 122.5, 122.3, 121.6, 76.7, 76.3, 76.1, 75.7, 37.3, 31.1, 30.9, 30.7, 28.6, 23.5, 23.5, 22.9, 22.2, 10.9, 10.8, 9.7, 9.7 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

³¹P NMR (162 MHz, CDCl₃): δ 26.5;

HRMS (ESI-TOF) calculated for C₆₉H₆₅Cl₂O₅PNa⁺, [M+Na]⁺ 1097.3839, found 1097.3842.



Physical state: white foam;

Yield: 77% (84.9 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: 202–205 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 20% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 22.41 min, t_R (minor) = 12.98 min;

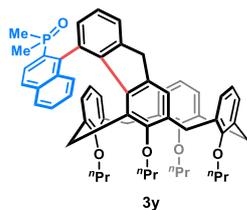
$[\alpha]_D^{25}$: 54.0 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 8.29 (d, J = 13.4 Hz, 1H), 8.00 – 7.91 (m, 2H), 7.87 – 7.79 (m, 2H), 7.73 – 7.65 (m, 3H), 7.58 – 7.45 (m, 6H), 7.41 (t, J = 7.4 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.26 – 7.13 (m, 5H), 7.09 (d, J = 7.1 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.36 – 6.27 (m, 2H), 6.16 – 6.07 (m, 2H), 5.89 (t, J = 6.2 Hz, 2H), 4.46 – 4.33 (m, 3H), 3.97 – 3.82 (m, 4H), 3.67 – 3.56 (m, 3H), 3.19 – 2.98 (m, 6H), 2.86 (dt, J = 8.8, 6.3 Hz, 1H), 2.50 (d, J = 14.4 Hz, 1H), 1.90 – 1.79 (m, 4H), 1.54 – 1.45 (m, 2H), 1.43 – 1.33 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H), 0.80 (t, J = 7.5 Hz, 3H), 0.64 (t, J = 7.5 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 158.6, 158.4, 155.1, 155.0, 149.7, 149.6, 144.7, 142.9, 141.3, 137.7, 137.6, 135.6, 134.7, 134.6, 134.6, 134.2, 134.1, 134.1, 133.7, 133.6, 133.5, 133.3, 133.0, 133.0, 132.7, 132.6, 132.6, 132.5, 132.4, 132.3, 132.2, 132.1, 132.0, 131.7, 131.6, 131.0, 130.1, 130.0, 129.5, 129.2, 129.1, 128.8, 128.5, 128.2, 128.0, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 127.1, 127.1, 127.0, 127.0, 126.9, 126.8, 126.7, 126.2, 125.2, 124.8, 124.5, 122.9, 122.5, 121.6, 76.8, 76.5, 76.2, 75.7, 37.3, 31.3, 31.2, 30.8, 28.9, 23.7, 23.5, 23.1, 22.3, 11.0, 10.8, 9.9, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.7;

HRMS (ESI-TOF) calculated for $\text{C}_{77}\text{H}_{71}\text{O}_5\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1129.4931, found 1129.4936.



Physical state: white foam;

Yield: 81% (71.2 mg), *d.r.* = 8.3:1 (determined by ^{31}P NMR), the diastereoisomers were separable;

R_f = 0.4 (DCM:MeOH = 40:1);

Melting point: 146–149 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak AD-H column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 320 nm), t_R (major) = 8.06 min;

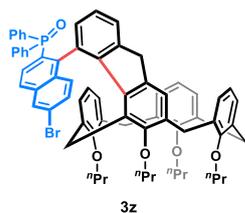
$[\alpha]_D^{25}$: 265.2 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 8.14 (dd, J = 11.0, 8.7 Hz, 1H), 8.00 (dd, J = 8.7, 1.4 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.72 (dd, J = 6.6, 2.0 Hz, 1H), 7.51 (ddd, J = 8.0, 6.7, 1.2 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.31 (s, 1H), 7.24 (s, 1H), 7.21 – 7.16 (m, 1H), 7.08 – 7.00 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 6.20 – 6.12 (m, 2H), 5.98 (dd, J = 7.0, 2.2 Hz, 1H), 5.83 (t, J = 7.6 Hz, 1H), 5.64 (d, J = 7.1 Hz, 1H), 5.22 (d, J = 6.9 Hz, 1H), 4.31 (dd, J = 13.3, 7.0 Hz, 2H), 4.25 – 4.17 (m, 2H), 4.05 (d, J = 22.3 Hz, 1H), 3.85 – 3.78 (m, 2H), 3.59 – 3.47 (m, 3H), 3.22 (dt, J = 8.7, 6.8 Hz, 1H), 3.17 – 3.03 (m, 3H), 2.99 – 2.89 (m, 2H), 2.47 – 2.31 (m, 2H), 1.83 – 1.72 (m, 4H), 1.67 – 1.56 (m, 2H), 1.42 (d, J = 13.1 Hz, 3H), 1.35 – 1.25 (m, 5H), 1.05 (dt, J = 14.6, 7.4 Hz, 6H), 0.75 (t, J = 7.5 Hz, 3H), 0.60 (t, J = 7.4 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 158.4, 155.1, 154.8, 146.5, 146.4, 145.8, 143.1, 140.5, 137.6, 137.5, 137.5, 136.3, 134.5, 134.5, 133.9, 133.7, 133.4, 133.2, 132.7, 132.6, 132.6, 132.5, 131.7, 131.6, 130.9, 130.0, 129.1, 128.7, 128.1, 128.0, 127.9, 127.8, 127.5, 126.9, 126.9, 126.7, 125.9, 125.8, 125.7, 124.8, 122.3, 122.2, 121.6, 76.8, 76.4, 76.3, 75.9, 37.6, 31.2, 30.9, 30.7, 28.2, 23.6, 23.0, 22.2, 20.3, 19.6, 19.1, 18.3, 11.0, 9.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 36.7;

HRMS (ESI-TOF) calculated for $\text{C}_{59}\text{H}_{64}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 883.4486, found 883.4485.



Physical state: white foam;

Yield: 60% (65.4 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.4 (PE:EtOAc = 2:1);

Melting point: >300 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 90% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 30.19 min;

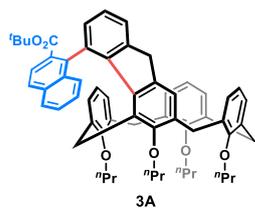
$[\alpha]_D^{25}$ -major: 243.1 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.78 (dd, J = 8.7, 2.5 Hz, 2H), 7.63 – 7.55 (m, 3H), 7.49 (dd, J = 11.9, 8.6 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.29 (s, 1H), 7.26 – 7.19 (m, 4H), 7.17 (t, J = 7.5 Hz, 1H), 7.13 – 7.08 (m, 3H), 7.02 (t, J = 7.5 Hz, 1H), 6.95 – 6.89 (m, 3H), 6.31 – 6.20 (m, 2H), 6.03 (dd, J = 6.9, 2.3 Hz, 1H), 6.00 (t, J = 7.6 Hz, 1H), 5.77 (d, J = 7.2 Hz, 1H), 5.60 (d, J = 7.1 Hz, 1H), 4.37 (dd, J = 13.3, 9.2 Hz, 2H), 4.29 (d, J = 13.5 Hz, 1H), 4.00 – 3.83 (m, 4H), 3.66 – 3.58 (m, 3H), 3.22 – 3.05 (m, 5H), 2.87 (dt, J = 8.8, 6.4 Hz, 1H), 2.80 (d, J = 14.4 Hz, 1H), 2.47 (d, J = 14.3 Hz, 1H), 1.88 – 1.76 (m, 6H), 1.60 – 1.51 (m, 2H), 1.50 – 1.39 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H), 0.79 (t, J = 7.5 Hz, 3H), 0.72 (t, J = 7.4 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.5, 158.4, 155.1, 154.8, 148.6, 148.6, 145.2, 142.7, 140.9, 137.7, 137.6, 135.9, 134.8, 134.2, 134.2, 134.1, 133.5, 133.2, 133.1, 133.1, 133.0, 133.0, 132.8, 132.8, 132.7, 131.9, 131.9, 131.8, 131.8, 131.8, 131.6, 131.5, 131.5, 131.5, 131.3, 130.7, 130.7, 130.6, 130.6, 130.4, 130.0, 129.6, 129.1, 129.0, 128.9, 128.4, 128.4, 127.9, 127.8, 127.4, 127.2, 126.9, 126.8, 126.8, 125.6, 125.3, 124.7, 122.6, 122.4, 121.6, 121.4, 76.9, 76.4, 76.3, 75.8, 37.4, 31.2, 31.1, 31.0, 28.9, 23.7, 23.6, 23.1, 22.4, 11.0, 11.0, 9.9, 9.9 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 27.8;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{67}\text{BrO}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1087.3904, found 1087.3904.



Physical state: white foam;

Yield: 68% (61.4 mg), *d.r.* = 11:1 (determined by ^1H NMR), the diastereoisomers were separable;

R_f = 0.5 (PE:EtOAc = 20:1);

Melting point: 119–121 °C;

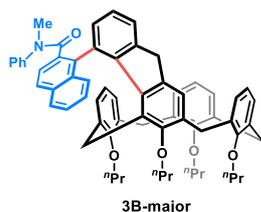
HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 1% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 6.71 min;

$[\alpha]_D^{25}$: 233.3 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.97 – 7.89 (m, 3H), 7.68 (d, J = 7.3 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.23 – 7.16 (m, 2H), 7.12 (d, J = 7.1 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.30 – 6.21 (m, 2H), 6.06 (t, J = 5.5 Hz, 1H), 5.90 (t, J = 7.6 Hz, 1H), 5.70 (d, J = 7.4 Hz, 1H), 5.45 (d, J = 7.4 Hz, 1H), 4.38 (t, J = 12.9 Hz, 2H), 4.32 – 4.19 (m, 2H), 4.09 (d, J = 22.1 Hz, 1H), 3.95 – 3.83 (m, 2H), 3.69 – 3.56 (m, 3H), 3.27 (q, J = 7.1 Hz, 1H), 3.14 (dd, J = 13.4, 5.6 Hz, 2H), 3.09 – 2.97 (m, 3H), 2.84 (d, J = 14.4 Hz, 1H), 2.32 (d, J = 14.3 Hz, 1H), 1.90 – 1.78 (m, 4H), 1.69 – 1.60 (m, 2H), 1.43 – 1.34 (m, 2H), 1.16 – 1.06 (m, 15H), 0.81 (t, J = 7.4 Hz, 3H), 0.65 (t, J = 7.4 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 168.7, 158.5, 158.4, 155.1, 154.7, 145.1, 143.4, 142.5, 141.2, 137.6, 137.5, 137.1, 135.6, 134.7, 134.5, 134.3, 133.9, 133.3, 133.0, 132.7, 131.3, 130.6, 130.2, 129.1, 128.7, 128.0, 127.7, 127.4, 127.3, 127.0, 126.7, 126.6, 126.5, 126.2, 125.8, 124.5, 124.1, 122.3, 121.9, 121.6, 81.6, 76.8, 76.4, 76.2, 76.0, 37.5, 31.2, 31.0, 30.8, 28.5, 27.7, 23.7, 23.6, 23.0, 22.2, 11.0, 10.9, 9.9, 9.8;

HRMS (ESI-TOF) calculated for $\text{C}_{62}\text{H}_{70}\text{NO}_6^+$, $[\text{M}+\text{NH}_4]^+$ 924.5198, found 924.5194.



Physical state: white foam;

Yield: 82% (77.1 mg);

R_f = 0.6 (PE:EtOAc = 2:1);

Melting point: 150–153 °C;

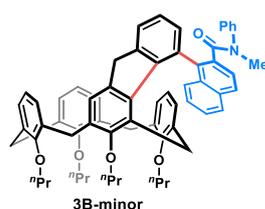
HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 17.59 min;

[α]_D²⁵: 193.2 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃, 60 °C): δ 7.92 (d, *J* = 7.4 Hz, 1H), 7.80 (s, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.66 – 7.34 (m, 5H), 7.34 – 7.28 (m, 3H), 7.26 – 7.12 (m, 4H), 7.10 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.24 – 6.15 (m, 2H), 6.04 (dd, *J* = 7.0, 2.1 Hz, 1H), 5.87 (t, *J* = 6.7 Hz, 1H), 5.67 (d, *J* = 7.3 Hz, 1H), 5.43 (s, 1H), 4.42 (d, *J* = 5.1 Hz, 1H), 4.39 (d, *J* = 5.3 Hz, 1H), 4.30 (d, *J* = 13.6 Hz, 1H), 4.22 (d, *J* = 22.0 Hz, 1H), 4.08 (d, *J* = 22.1 Hz, 1H), 3.98 – 3.86 (m, 2H), 3.68 – 3.59 (m, 3H), 3.43 – 2.91 (m, 9H), 2.73 (s, 1H), 2.36 (s, 1H), 1.91 – 1.80 (m, 4H), 1.72 (h, *J* = 7.3, 6.8 Hz, 2H), 1.49 (s, 2H), 1.13 (dt, *J* = 17.9, 7.4 Hz, 6H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.74 (t, *J* = 6.9 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃, 60 °C): δ 158.6, 158.5, 155.2, 154.8, 145.7, 144.1, 143.4, 141.3, 137.7, 137.5, 135.8, 134.7, 134.4, 133.6, 133.3, 132.9, 132.7, 131.9, 129.2, 129.2, 128.7, 128.1, 127.8, 127.6, 127.1, 126.8, 126.7, 126.6, 126.4, 126.0, 125.9, 124.9, 124.6, 122.4, 122.3, 121.6, 76.9, 76.4, 76.2, 76.0, 39.6, 37.7, 31.4, 31.1, 30.8, 28.7, 23.8, 23.7, 23.1, 22.6, 11.0, 11.0, 9.9, 9.9;

HRMS (ESI-TOF) calculated for C₆₅H₆₅NO₅Na⁺, [M+Na]⁺ 962.4755, found 962.4757;



Physical state: white foam;

Yield: 13% (12.8 mg);

R_f = 0.7 (PE:EtOAc = 2:1);

Melting point: 148–151 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IA column, 3% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 6.58 min;

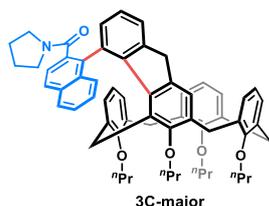
[α]_D²⁵: -151.1 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃, 60 °C): δ 7.94 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J*

= 8.2 Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 7.4$ Hz, 1H), 7.38 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.14 (s, 1H), 7.10 – 6.90 (m, 5H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.81 – 6.25 (m, 3H), 6.25 – 6.12 (m, 2H), 6.01 (dd, $J = 6.6, 2.2$ Hz, 1H), 5.77 (t, $J = 7.6$ Hz, 1H), 5.61 (d, $J = 7.4$ Hz, 1H), 5.25 (d, $J = 7.1$ Hz, 1H), 4.48 (d, $J = 13.3$ Hz, 1H), 4.42 (d, $J = 13.2$ Hz, 1H), 4.25 (d, $J = 13.6$ Hz, 1H), 4.16 (d, $J = 21.9$ Hz, 1H), 4.07 – 3.87 (m, 5H), 3.71 – 3.60 (m, 2H), 3.24 – 3.03 (m, 3H), 3.02 – 2.70 (m, 5H), 2.62 (d, $J = 11.7$ Hz, 1H), 2.48 – 2.35 (m, 1H), 2.10 – 1.91 (m, 2H), 1.90 – 1.78 (m, 4H), 1.60 – 1.50 (m, 2H), 1.10 (t, $J = 7.4$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 6.8$ Hz, 3H), 0.83 (t, $J = 7.5$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3 , 60 °C): δ 170.1, 158.7, 158.6, 155.3, 154.9, 146.0, 143.2, 141.0, 138.7, 137.7, 137.6, 136.8, 136.0, 134.7, 134.6, 134.5, 134.4, 133.3, 132.7, 132.4, 132.1, 131.8, 131.2, 129.1, 128.8, 128.3, 127.7, 127.4, 127.2, 127.0, 126.7, 126.6, 126.1, 125.8, 125.7, 125.3, 125.2, 124.4, 124.2, 122.3, 121.8, 121.5, 77.0, 76.4, 75.7, 37.7, 31.4, 31.2, 31.1, 28.1, 23.7, 23.6, 23.2, 23.1, 11.0, 11.0, 10.2, 10.0.

HRMS (ESI-TOF) calculated for $\text{C}_{65}\text{H}_{66}\text{NO}_5^+$, $[\text{M}+\text{H}]^+$ 940.4936, found 940.4935.



Physical state: white foam;

Yield: 76% (69.0 mg);

$R_f = 0.4$ (PE:EtOAc = 2:1);

Melting point: 146–148 °C;

HPLC: >99% *e.e.* (Daicel chiralpak IB N-5 column, 10% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 18.24 min;

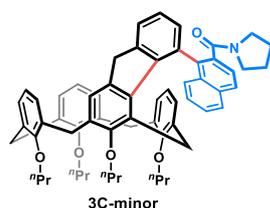
$[\alpha]_D^{25}$: 221.1 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.94 (dd, $J = 11.5, 8.4$ Hz, 2H), 7.64 (d, $J = 7.4$ Hz, 1H), 7.60 – 7.42 (m, 3H), 7.42 – 7.35 (m, 2H), 7.32 (s, 1H), 7.18 (t, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 7.3$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 1H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.19 (q, $J = 7.2$ Hz, 2H), 6.01 (dd, $J = 6.7, 2.3$ Hz, 1H), 5.82 (t, $J = 7.6$ Hz, 1H), 5.64 (d, $J = 7.4$ Hz, 1H), 5.17 (s, 1H), 4.36 (d, $J = 13.3$ Hz, 2H), 4.29 – 4.14 (m, 2H), 4.06 (d, $J = 22.2$ Hz, 1H), 3.93 – 3.79 (m, 2H), 3.65 – 3.48 (m, 4H), 3.38 – 3.27 (m, 1H), 3.21 (q, $J = 7.0$ Hz, 1H), 3.15 – 2.94 (m, 6H), 2.84 (s, 1H), 2.34 (d, $J = 11.0$ Hz, 2H), 1.88 – 1.76 (m, 4H),

1.76 – 1.57 (m, 4H), 1.57 – 1.38 (m, 4H), 1.14 (t, $J = 7.4$ Hz, 3H), 1.07 (t, $J = 7.4$ Hz, 3H), 0.79 (t, $J = 7.5$ Hz, 3H), 0.74 (t, $J = 7.4$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 170.0, 158.5, 158.4, 155.0, 154.7, 145.3, 142.7, 141.1, 137.5, 137.5, 137.4, 135.9, 134.8, 134.4, 134.0, 133.6, 133.3, 132.9, 132.8, 132.0, 131.3, 130.9, 129.0, 128.7, 128.4, 128.2, 127.6, 127.4, 126.9, 126.7, 126.5, 126.4, 126.1, 126.0, 125.4, 124.8, 124.6, 122.2, 121.9, 121.5, 76.8, 76.3, 76.2, 75.8, 48.3, 46.1, 37.6, 31.2, 30.9, 30.7, 28.8, 25.9, 24.0, 23.7, 23.6, 23.0, 22.6, 11.0, 11.0, 9.8, 9.8;

HRMS (ESI-TOF) calculated for $\text{C}_{62}\text{H}_{65}\text{NO}_5\text{Na}^+$, $[\text{M}+\text{Na}]^+$ 926.4759, found 926.4755.



Physical state: white foam;

Yield: 14% (12.6 mg);

$R_f = 0.5$ (PE:EtOAc = 2:1);

Melting point: 142–145 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IB N-5 column, 10% i -PrOH in n -hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 13.24 min;

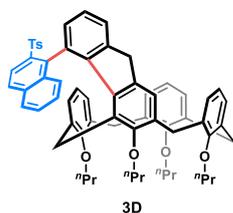
$[\alpha]_D^{25}$: -100.9 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.61 (dd, $J = 5.4, 2.9$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.36 – 7.30 (m, 3H), 7.28 (s, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 7.1$ Hz, 1H), 7.02 (d, $J = 7.3$ Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.20 – 6.12 (m, 2H), 5.99 (dd, $J = 6.7, 2.2$ Hz, 1H), 5.80 (t, $J = 7.6$ Hz, 1H), 5.64 (d, $J = 7.4$ Hz, 1H), 5.29 (d, $J = 7.4$ Hz, 1H), 4.40 (d, $J = 5.5$ Hz, 1H), 4.37 (d, $J = 5.4$ Hz, 1H), 4.21 (d, $J = 13.5$ Hz, 1H), 4.12 (d, $J = 22.0$ Hz, 1H), 3.99 (d, $J = 22.1$ Hz, 1H), 3.94 – 3.73 (m, 4H), 3.61 (t, $J = 6.7$ Hz, 2H), 3.15 – 2.84 (m, 9H), 2.78 (d, $J = 14.1$ Hz, 1H), 2.21 (q, $J = 6.6, 6.2$ Hz, 1H), 2.01 – 1.75 (m, 6H), 1.63 – 1.38 (m, 6H), 1.08 (t, $J = 7.4$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.81 (dt, $J = 15.0, 7.5$ Hz, 6H);

^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 158.4, 158.4, 155.1, 154.6, 146.2, 141.0, 137.6, 137.5, 135.7, 135.5, 134.2, 133.9, 133.7, 133.3, 133.1, 132.8, 132.3, 132.2, 131.8, 129.0, 128.8, 127.8, 127.8, 127.6, 127.4, 127.1, 126.5, 126.5, 126.1, 124.9, 124.9, 124.4, 123.9, 122.2, 121.7, 121.6, 76.5, 76.4, 75.6, 48.1, 48.0, 45.3, 37.6, 31.1, 31.0, 30.9, 27.6, 26.0,

24.3, 23.7, 23.5, 23.1, 23.0, 11.0, 11.0, 9.9, 9.9;

HRMS (ESI-TOF) calculated for $C_{62}H_{66}NO_5^+$, $[M+H]^+$ 904.4936, found 904.4931.



Physical state: white foam;

Yield: 24% (23.4 mg), > 19:1 *d.r.* (determined by 1H NMR);

R_f = 0.7 (PE:EtOAc = 5:1);

Melting point: 136–138 °C;

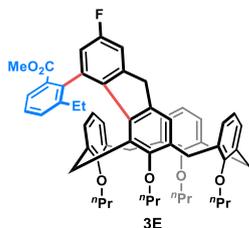
HPLC: > 99% *e.e.* (Daicel chiralpak IC column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 33.31 min;

$[\alpha]_D^{25}$: 63.7 (c 0.2, $CHCl_3$);

1H NMR (400 MHz, $CDCl_3$): δ 8.15 (t, J = 7.2 Hz, 2H), 8.01 – 7.87 (m, 3H), 7.62 – 7.50 (m, 2H), 7.50 – 7.40 (m, 2H), 7.24 (d, J = 28.3 Hz, 3H), 6.72 – 6.50 (m, 9H), 6.35 (d, J = 5.2 Hz, 2H), 4.55 – 4.35 (m, 4H), 3.97 – 3.79 (m, 9H), 3.67 (d, J = 15.7 Hz, 1H), 3.22 – 3.04 (m, 4H), 2.27 (s, 3H), 1.93 (dq, J = 13.9, 6.8 Hz, 8H), 1.01 (t, J = 7.2 Hz, 12H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 156.7, 156.6, 155.1, 142.4, 142.2, 142.0, 139.6, 137.9, 137.2, 136.0, 135.6, 135.5, 135.3, 135.3, 135.2, 135.1, 135.1, 135.1, 135.0, 134.4, 133.3, 132.3, 132.0, 130.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 127.2, 127.2, 125.6, 122.2, 122.0, 121.7, 121.0, 76.9, 76.9, 76.8, 39.8, 31.2, 31.1, 31.1, 23.4, 23.4, 23.4, 21.5, 10.5, 10.5;

HRMS (ESI-TOF) calculated for $C_{64}H_{68}NO_6S^+$, $[M+NH_4]^+$ 978.4762, found 978.4766.



Physical state: white foam;

Yield: 24% (20.3 mg, 0.1 mmol scale), *d.r.* = 6:1 (determined by ^{19}F NMR);

R_f = 0.4 (PE:EtOAc = 20:1);

Melting point: 170–172 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IE column, 2% *i*-PrOH in *n*-hexane, 1 mL/min, λ = 254 nm), t_R (major) = 6.39 min;

$[\alpha]_{25}^D$: 184.7 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, J = 7.6, 1.4 Hz, 1H), 7.47 (dd, J = 7.8, 1.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.31 (s, 1H), 7.26 – 7.22 (m, 1H), 7.12 (dd, J = 7.5, 1.7 Hz, 1H), 7.07 (dd, J = 7.5, 1.7 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.69 (dd, J = 9.7, 2.6 Hz, 1H), 6.25 – 6.15 (m, 2H), 6.05 (dd, J = 7.3, 2.1 Hz, 1H), 5.95 (t, J = 7.6 Hz, 1H), 5.74 (d, J = 7.3 Hz, 1H), 5.53 (d, J = 7.3 Hz, 1H), 4.43 (d, J = 5.2 Hz, 1H), 4.40 (d, J = 4.9 Hz, 1H), 4.33 (d, J = 13.5 Hz, 1H), 4.13 (d, J = 22.3 Hz, 1H), 4.03 – 3.90 (m, 4H), 3.76 (td, J = 10.9, 5.7 Hz, 1H), 3.64 (t, J = 6.7 Hz, 2H), 3.42 (s, 3H), 3.34 (dt, J = 9.1, 6.7 Hz, 1H), 3.20 – 3.10 (m, 3H), 3.08 – 2.99 (m, 3H), 2.29 – 2.17 (m, 2H), 1.96 – 1.78 (m, 6H), 1.67 (q, J = 7.0 Hz, 2H), 1.08 (dt, J = 10.4, 7.4 Hz, 6H), 0.90 – 0.77 (m, 9H);

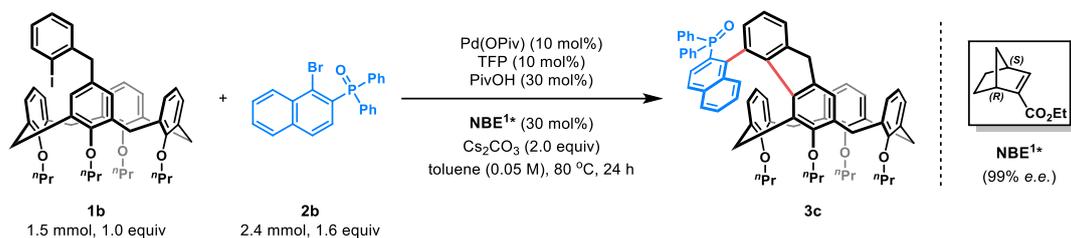
¹³C NMR (100 MHz, CDCl₃): δ 168.9, 161.1 (d, J = 246.0 Hz), 158.9, 158.5, 155.1, 154.8, 147.7 (d, J = 8.7 Hz), 143.3, 142.9, 140.7, 137.9 (d, J = 2.4 Hz), 137.6, 137.5, 137.2 (d, J = 1.7 Hz), 136.4 (d, J = 8.0 Hz), 135.6, 134.7, 133.5, 133.4, 132.9, 132.7, 132.0, 131.2, 129.1, 128.8, 127.8, 127.6, 127.0, 126.7, 126.4, 124.9, 122.3, 122.1, 121.7, 115.9 (d, J = 22.2 Hz), 110.9 (d, J = 21.5 Hz), 76.9, 76.8, 76.6, 76.1, 52.0, 37.7, 37.7, 31.3, 31.0, 30.9, 28.1, 26.0, 23.7, 23.7, 23.1, 22.8, 14.3, 11.0, 10.9, 10.1, 10.0;

¹⁹F NMR (376 MHz, CDCl₃): δ -118.4;

HRMS (ESI-TOF) calculated for C₅₇H₆₁FO₆Na⁺, [M+Na]⁺ 883.4344, found 883.4347.

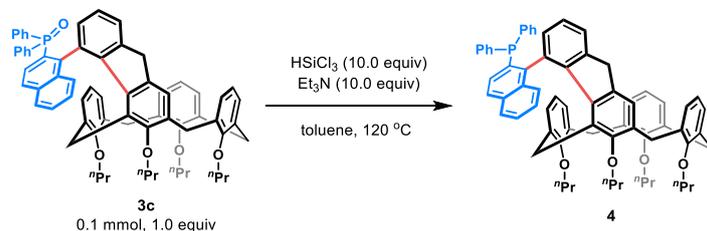
5. Scale-up reaction and derivatizations of **3c**

5.1 Scale-Up Reaction

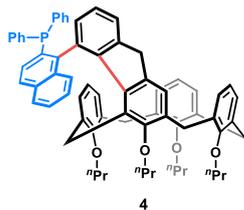


To a 50 mL of oven-dried flask equipped with a magnetic stir bar was charged with **1b** (1.21 g, 1.5 mmol, 1.0 equiv), Pd(OPiv)₂ (46.3 mg, 0.15 mmol, 10 mol%), TFP (34.8 mg, 0.15 mmol, 10 mol%), **NBE**^{1*} (74.7 mg, 0.45 mmol, 30 mol%), Cs₂CO₃ (977.4 mg, 3.0 mmol, 2.0 equiv), **2b** (974.4 mg, 2.4 mmol, 1.6 equiv) and dry toluene (30 mL) under Ar. Then the reaction was stirred at 80 °C for 24 h. After cooling to r.t., the mixture was filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the desired product **3c** (1.1 g, 76% yield, *e.e.* > 99%, *d.r.* >19:1). The **NBE**^{1*} was recovered in 88% yield (determined by GC analysis).

5.2 Synthesis of **4**



To a dried Schlenk flask charged with **3c** (100.6 mg, 0.1 mmol, 1.0 equiv) in dry toluene (1 mL) was added Et₃N (139 μL, 1.0 mmol, 10 equiv) and HSiCl₃ (101 μL, 1.0 mmol, 10 equiv) successively under argon at 0 °C. The resulting mixture was stirred at 105 °C for 3 h. After cooled to 0 °C, it was diluted by EtOAc (5 mL), quenched with small amounts of saturated Na₂CO₃ solution. The resulting suspension was filtered by a short celite column, and washed with EtOAc. The filtrate was dried over anhydrous Na₂SO₄, filtered, concentrated, and the residue was purified by flash chromatography on silica gel to afford the desired phosphine **4**.



4

Physical state: white foam;

Yield: 81% (80.6 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.6 (PE:EtOAc = 20:1);

Melting point: 133–136 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IB N-5 column, 1% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), t_R (major) = 7.53 min;

$[\alpha]_D^{25}$ -major: 170.0 (c 0.2, CHCl_3);

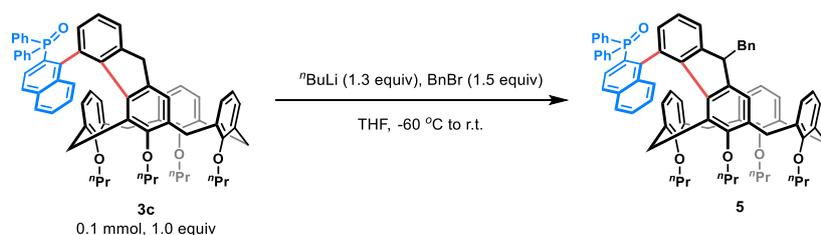
^1H NMR (600 MHz, CDCl_3): δ 7.91 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.45 – 7.39 (m, 3H), 7.37 (s, 1H), 7.35 – 7.30 (m, 2H), 7.20 (t, J = 7.7 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.03 (t, J = 7.1 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.74 – 6.63 (m, 4H), 6.28 (d, J = 4.7 Hz, 2H), 6.07 (t, J = 4.6 Hz, 1H), 6.03 (t, J = 7.6 Hz, 1H), 5.84 (d, J = 7.5 Hz, 1H), 5.61 (d, J = 7.5 Hz, 1H), 4.41 (t, J = 13.1 Hz, 2H), 4.33 – 4.24 (m, 2H), 4.12 (d, J = 22.1 Hz, 1H), 3.90 (t, J = 8.2 Hz, 2H), 3.66 (t, J = 6.6 Hz, 2H), 3.60 (td, J = 11.0, 5.3 Hz, 1H), 3.19 – 3.09 (m, 4H), 2.93 (q, J = 6.8 Hz, 1H), 2.80 (d, J = 14.6 Hz, 1H), 2.66 (q, J = 6.6 Hz, 1H), 2.49 (d, J = 14.5 Hz, 1H), 1.92 – 1.82 (m, 4H), 1.55 – 1.48 (m, 2H), 1.45 – 1.35 (m, 2H), 1.11 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.5 Hz, 3H), 0.68 (t, J = 7.4 Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 158.4, 158.4, 155.0, 154.8, 150.7, 150.5, 145.5, 142.5, 141.4, 139.4, 139.3, 137.8, 137.8, 137.7, 137.6, 137.5, 135.7, 134.8, 134.1, 134.0, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.3, 133.3, 133.2, 132.9, 132.7, 132.4, 132.3, 132.1, 132.1, 131.8, 131.7, 128.9, 128.7, 128.7, 128.6, 128.5, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 127.1, 126.9, 126.8, 126.5, 126.4, 125.1, 125.0, 124.5, 122.6, 122.4, 121.6, 76.8, 76.4, 76.3, 75.8, 37.7, 31.2, 31.0, 30.7, 28.3, 23.7, 23.5, 23.0, 22.3, 11.0, 10.8, 9.9, 9.9 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

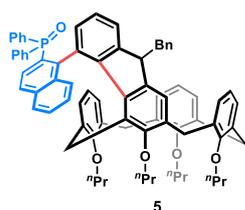
^{31}P NMR (162 MHz, CDCl_3): δ -14.5;

HRMS (ESI-TOF) calculated for $\text{C}_{69}\text{H}_{68}\text{O}_4\text{P}^+$, $[\text{M}+\text{H}]^+$ 991.4850, found 991.4853.

5.3 Synthesis of 5



To a dried Schlenk flask, $n\text{BuLi}$ (52 μL , 2.5 M in hexane, 0.13 mmol, 1.3 equiv) was added at $-60\text{ }^\circ\text{C}$ to a solution of **3c** (100.6 mg, 0.1 mmol, 1.0 equiv) in dry THF (1 mL). The solution immediately turned brownish and was stirred for 1.0 h at r.t.. After cooling to $-60\text{ }^\circ\text{C}$ again, the reaction mixture was quenched with BnBr (18 μL , 0.15 mmol, 1.5 equiv), stirred for 10 min at $-60\text{ }^\circ\text{C}$, then for an additional 2 h at r.t.. Water was added to the reaction mixture which was then extracted with EtOAc . The combined organic phases were dried over MgSO_4 . After filtration, the crude product was purified by column chromatography on silica gel to give the desired product **5**.



Physical state: white foam;

Yield: 53% (57.7 mg), > 19:1 *d.r.* (determined by ^{31}P NMR);

R_f = 0.5 (PE:EtOAc = 2:1);

Melting point: 127–130 $^\circ\text{C}$;

HPLC: > 99% *e.e.* (Daicel chiralpak IC column, 20% $i\text{PrOH}$ in $n\text{hexane}$, 1 mL/min, λ = 254 nm), t_R (major) = 16.52 min;

$[\alpha]_D^{25}$ -major: -121.1 (c 0.2, CHCl_3);

^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, J = 8.1 Hz, 1H), 7.83 (dd, J = 8.7, 1.7 Hz, 1H), 7.64 – 7.47 (m, 4H), 7.43 – 7.27 (m, 9H), 7.24 – 7.09 (m, 8H), 7.01 (t, J = 7.5 Hz, 1H), 6.98 – 6.90 (m, 3H), 6.75 (s, 1H), 6.29 (t, J = 7.6 Hz, 1H), 6.13 (d, J = 7.0 Hz, 1H), 6.07 – 5.99 (m, 2H), 5.76 (d, J = 7.3 Hz, 1H), 5.43 (d, J = 7.3 Hz, 1H), 4.35 (d, J = 13.2 Hz, 1H), 4.29 (d, J = 13.5 Hz, 1H), 4.22 (d, J = 13.3 Hz, 1H), 4.16 (t, J = 7.2 Hz, 1H), 3.91 – 3.79 (m, 2H), 3.59 – 3.45 (m, 3H), 3.24 (dd, J = 13.6, 7.2 Hz, 1H), 3.19 – 3.06 (m, 4H), 2.98 – 2.88 (m, 3H), 2.80 (d, J = 14.5 Hz, 1H), 2.40 (d, J = 14.5 Hz, 1H), 1.82 – 1.74 (m, 4H), 1.63 – 1.56 (m, 2H), 1.35 – 1.30 (m, 2H), 1.01 (dt, J = 15.6, 7.4 Hz,

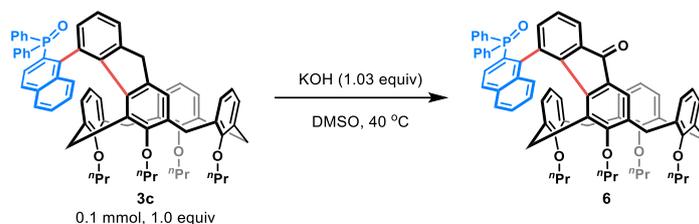
6H), 0.77 (t, $J = 7.5$ Hz, 3H), 0.61 (t, $J = 7.5$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 158.6, 158.5, 155.0, 154.8, 149.1, 149.1, 148.4, 141.9, 141.0, 140.3, 140.3, 137.7, 137.6, 135.4, 135.2, 134.6, 134.6, 134.3, 134.2, 133.6, 133.4, 133.3, 133.0, 132.6, 132.4, 132.3, 132.0, 132.0, 131.9, 131.9, 131.8, 131.4, 131.4, 130.7, 130.7, 130.1, 130.0, 129.9, 129.2, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.4, 127.3, 127.2, 127.2, 126.8, 126.7, 126.5, 125.7, 124.7, 124.6, 122.5, 122.3, 121.6, 76.8, 76.4, 76.2, 75.9, 48.7, 42.0, 31.2, 31.1, 30.8, 29.9, 28.9, 23.6, 23.0, 22.4, 11.0, 10.9, 9.9, 9.8. (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

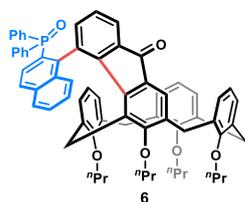
^{31}P NMR (162 MHz, CDCl_3): δ 27.8;

HRMS (ESI-TOF) calculated for $\text{C}_{76}\text{H}_{74}\text{O}_5\text{P}^+$, $[\text{M}+\text{H}]^+$ 1097.5268, found 1097.5269.

5.4 Synthesis of 6



A glass vial was charged with **3c** (100.6 mg, 0.1 mmol, 1.0 equiv), KOH (6.2 mg, 0.11 mmol, 1.1 equiv), DMSO (1 mL) and a stir bar. The resulting mixture was stirred at 40 °C for 5 h under air. Water was added to the reaction mixture which was then extracted with EtOAc. The combined organic phases were dried over MgSO_4 . After filtration, the crude product was purified by column chromatography on silica gel to give the desired product **6**.



Physical state: yellow solid;

Yield: 92% (94.3 mg), > 19:1 *d.r.* (determined by ^{31}P NMR analysis);

$R_f = 0.3$ (PE:EtOAc = 2:1);

Melting point: >300 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak IG column, 30% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 16.97 min;

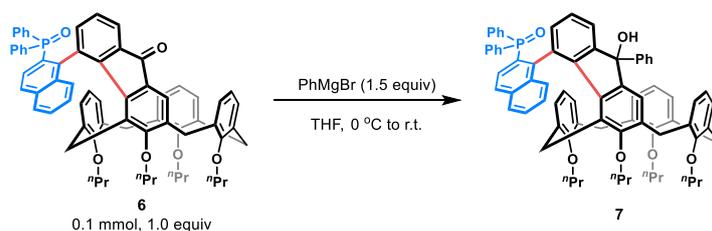
$[\alpha]_D^{25}$ -major: 260.5 (c 0.2, CHCl₃);

¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.61 – 7.55 (m, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.30 (m, 4H), 7.25 – 7.15 (m, 3H), 7.14 – 7.08 (m, 3H), 7.02 – 6.90 (m, 4H), 6.28 (t, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 6.4 Hz, 1H), 6.12 (t, *J* = 7.6 Hz, 1H), 6.05 (d, *J* = 6.5 Hz, 1H), 5.95 (d, *J* = 7.3 Hz, 1H), 5.85 (d, *J* = 7.3 Hz, 1H), 4.35 (d, *J* = 13.3 Hz, 1H), 4.26 (dd, *J* = 13.5, 9.4 Hz, 2H), 3.92 – 3.75 (m, 2H), 3.73 – 3.63 (m, 1H), 3.59 (td, *J* = 6.6, 2.4 Hz, 2H), 3.19 – 3.06 (m, 5H), 2.78 (dt, *J* = 8.7, 6.5 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 1.87 – 1.74 (m, 4H), 1.59 – 1.48 (m, 2H), 1.43 – 1.30 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H), 0.63 (t, *J* = 7.4 Hz, 3H);
¹³C NMR (150 MHz, CDCl₃): δ 193.7, 166.0, 158.3, 154.9, 154.7, 147.3, 147.2, 145.3, 144.8, 138.7, 137.5, 137.0, 136.1, 135.3, 134.4, 134.4, 134.2, 133.7, 133.5, 133.3, 133.2, 133.2, 132.9, 132.5, 131.9, 131.9, 131.8, 131.8, 131.7, 131.7, 131.2, 131.2, 129.7, 129.6, 129.3, 129.2, 129.0, 128.9, 128.6, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.3, 127.3, 127.2, 127.0, 127.0, 125.1, 123.8, 122.9, 122.6, 121.8, 76.9, 76.4, 76.4, 75.9, 31.1, 31.0, 30.5, 28.2, 23.6, 23.5, 23.0, 22.6, 10.9, 10.8, 9.8 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

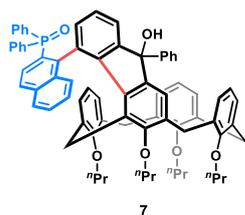
³¹P NMR (162 MHz, CDCl₃): δ 27.8;

HRMS (ESI-TOF) calculated for C₆₉H₆₅O₆PNa⁺, [M+Na]⁺ 1043.4411, found 1043.4412.

5.5 Synthesis of 7



To a solution of **6** (102.0 mg, 0.1 mmol, 1.0 equiv) in THF (1 mL) was added PhMgBr (150 μL, 1 M in THF, 0.15 mmol, 1.5 equiv) at 0 °C. Then the reaction was stirred at room temperature for 4 hours. After completion of the reaction (monitored by TLC), water was added to the reaction mixture which was then extracted with EtOAc. The combined organic phases were dried over MgSO₄. After filtration, the crude product was purified by column chromatography on silica gel to give the desired product **7**.



Physical state: white solid;

Yield: 84% (92.0 mg), > 19:1 *d.r.* (determined by ^{31}P NMR analysis);

$R_f = 0.3$ (PE:EtOAc = 2:1);

Melting point: 166–169 °C;

HPLC: > 99% *e.e.* (Daicel chiralpak ID column, 5% *i*PrOH in *n*hexane, 1 mL/min, $\lambda = 254$ nm), t_R (major) = 16.62 min;

$[\alpha]_D^{25}$ -major: 61.0 (c 0.2, CHCl_3);

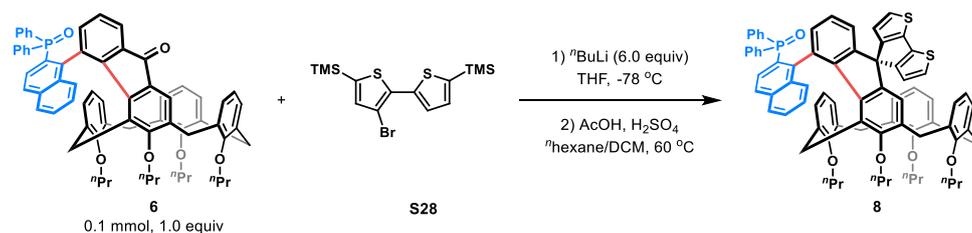
^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.70 – 7.48 (m, 7H), 7.43 – 7.26 (m, 9H), 7.17 – 7.05 (m, 5H), 7.04 – 6.97 (m, 2H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.88 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 7.4$ Hz, 1H), 6.36 – 6.21 (m, 2H), 6.10 (t, $J = 7.6$ Hz, 1H), 6.07 – 6.01 (m, 1H), 5.96 (d, $J = 7.3$ Hz, 1H), 5.85 (d, $J = 7.3$ Hz, 1H), 4.36 (dd, $J = 20.4, 13.4$ Hz, 2H), 4.24 (d, $J = 13.5$ Hz, 1H), 3.89 (t, $J = 8.0$ Hz, 2H), 3.65 – 3.52 (m, 3H), 3.29 (td, $J = 11.1, 5.4$ Hz, 1H), 3.13 (dd, $J = 13.0, 6.4$ Hz, 3H), 3.02 (d, $J = 13.6$ Hz, 1H), 2.91 – 2.81 (m, 2H), 2.51 (d, $J = 14.3$ Hz, 1H), 1.91 – 1.73 (m, 4H), 1.64 – 1.51 (m, 2H), 1.51 – 1.22 (m, 3H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 7.3$ Hz, 3H), 0.81 (t, $J = 7.4$ Hz, 3H), 0.65 (t, $J = 7.4$ Hz, 3H);

^{13}C NMR (150 MHz, CDCl_3): δ 160.0, 158.5, 155.0, 154.7, 152.2, 149.4, 149.4, 145.5, 145.5, 145.3, 141.0, 139.0, 137.7, 137.6, 137.1, 134.6, 134.5, 134.1, 134.1, 133.9, 133.8, 133.5, 133.1, 133.0, 132.7, 132.5, 132.5, 132.2, 132.2, 132.1, 132.1, 131.9, 131.9, 131.7, 131.7, 131.1, 129.7, 129.7, 128.9, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 127.6, 127.4, 127.3, 127.2, 127.1, 127.1, 127.0, 126.9, 126.8, 126.2, 125.4, 125.0, 122.7, 122.5, 121.6, 81.8, 76.7, 76.4, 76.1, 75.8, 31.1, 31.1, 30.9, 28.3, 23.6, 23.5, 23.0, 22.2, 11.0, 10.9, 9.8, 9.7 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets);

^{31}P NMR (162 MHz, CDCl_3): δ 28.7;

HRMS (ESI-TOF) calculated for $\text{C}_{75}\text{H}_{71}\text{O}_6\text{PNa}^+$, $[\text{M}+\text{Na}]^+$ 1121.4880, found 1121.4890.

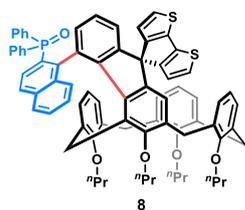
5.6 Synthesis of 8



S28 was synthesized by literature procedure.⁷

To a dried Schlenk flask charged with compound **S28** (234 mg, 0.6 mmol, 6.0 equiv), and evacuated and refilled with argon three times. After addition of THF (0.5 mL), n BuLi in hexanes (240 μ L, 2.5 M, 0.6 mmol, 6.0 equiv) was added slowly at -78 °C. The mixture was stirred at room temperature for 1 hour. Then, **6** (102.0 mg, 0.1 mmol, 1.0 equiv) was added into mixture at -78 °C, and the resulting solution was stirred at room temperature overnight. The mixture was washed with water and extracted with EtOAc three times. The combined organic layer was washed with brine and dried over MgSO₄. After filtration, the crude product was purified by column chromatography on silica gel to give the desired alcohol products (121.4 mg, 90% yield, *d.r.* > 19:1, white solid).

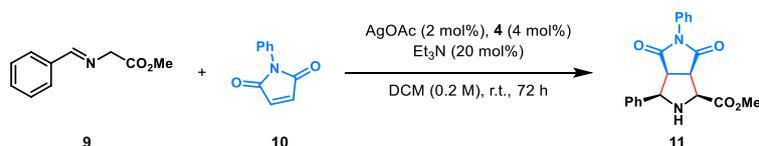
A dried Schlenk flask was charged with above alcohol (121.4 mg, 0.09 mmol). After addition of *n*-hexane/DCM (0.6 mL/0.4 mL), CH₃COOH (2 mL) was added slowly at 60 °C, and the resulting mixture was stirred for 10 minutes. Then, H₂SO₄ (50 μ L) was added into flask dropwise. The mixture was stirred at 60 °C for 20 minutes and poured into NaHCO₃ solution. Then the mixture was extracted with EtOAc three times. The combined organic layer was washed with brine and dried over MgSO₄. After filtration, the crude product was purified by column chromatography on silica gel to give the desired product **8** (60.0 mg, 57% yield).



Physical state: white solid; **Yield:** 51% (two steps), > 19:1 *d.r.* (determined by ³¹P NMR analysis); **R_f** = 0.6 (PE:EtOAc = 2:1); **Melting point:** 165–168 °C; **HPLC:** > 99% *e.e.* (Daicel chiralpak IA column, 10% *i*PrOH in *n*hexane, 1 mL/min, λ = 254 nm), *t_R* (major) = 11.18 min; **[α]_D²⁵-major:** 35.0 (c 0.2, CHCl₃); **¹H NMR** (400 MHz, CDCl₃):

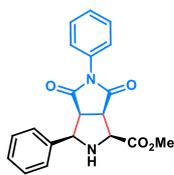
δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.87 (d, $J = 8.6$ Hz, 1H), 7.64 (dd, $J = 11.4, 7.6$ Hz, 2H), 7.59 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.35 – 7.26 (m, 4H), 7.25 – 7.18 (m, 4H), 7.16 (d, $J = 4.9$ Hz, 1H), 7.14 – 7.08 (m, 2H), 7.01 (td, $J = 7.7, 2.7$ Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.72 (dd, $J = 8.4, 6.3$ Hz, 2H), 6.57 – 6.50 (m, 2H), 6.17 (t, $J = 7.6$ Hz, 1H), 6.11 (t, $J = 7.6$ Hz, 1H), 5.98 (d, $J = 7.3$ Hz, 1H), 5.85 (d, $J = 7.3$ Hz, 1H), 5.81 (d, $J = 7.5$ Hz, 1H), 5.76 (d, $J = 7.4$ Hz, 1H), 4.33 (dd, $J = 13.4, 8.0$ Hz, 2H), 4.17 (d, $J = 13.5$ Hz, 1H), 3.92 – 3.79 (m, 2H), 3.59 – 3.45 (m, 3H), 3.25 – 3.16 (m, 1H), 3.15 – 3.05 (m, 3H), 3.03 – 2.95 (m, 1H), 2.88 (dd, $J = 28.8, 14.1$ Hz, 2H), 2.51 (d, $J = 14.4$ Hz, 1H), 1.83 – 1.70 (m, 4H), 1.67 – 1.57 (m, 2H), 1.43 – 1.27 (m, 2H), 1.01 (t, $J = 7.3$ Hz, 6H), 0.78 (t, $J = 7.5$ Hz, 3H), 0.63 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 159.2, 158.5, 156.6, 156.5, 155.0, 154.9, 148.8, 148.7, 146.0, 142.9, 141.2, 138.6, 138.4, 137.8, 137.7, 137.6, 136.7, 134.8, 134.7, 134.5, 134.5, 134.1, 134.0, 133.8, 133.2, 133.1, 132.9, 132.7, 132.6, 132.6, 132.1, 132.0, 131.9, 131.5, 131.0, 130.1, 130.1, 129.0, 128.8, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.9, 127.4, 127.3, 127.3, 126.9, 126.9, 126.8, 126.6, 125.9, 125.6, 123.6, 123.1, 122.7, 122.4, 122.0, 121.6, 121.5, 76.7, 76.4, 76.1, 75.9, 61.7, 31.2, 31.1, 30.6, 28.6, 23.6, 23.6, 23.0, 22.2, 11.0, 10.9, 9.9, 9.7 (Due to C-P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets); ^{31}P NMR (162 MHz, CDCl_3): δ 28.3; HRMS (ESI-TOF) calculated for $\text{C}_{77}\text{H}_{70}\text{O}_5\text{PS}_2^+$, $[\text{M}+\text{H}]^+$ 1169.4397, found 1169.4394.

5.7 The application of chiral phosphine **4** in Ag-catalyzed asymmetric [3+2] cycloaddition.



9 was synthesized by literature procedure.⁸

Under argon atmosphere, the solution of ligand **4** (4.0 mg, 0.004 mmol, 4.0 mol%) and AgOAc (0.3 mg, 0.002 mmol, 2.0 mol%) was stirred at room temperature for about 1 h. Then Et₃N (2.8 μL , 0.02 mmol, 20 mol%), **9** (17.7 mg, 0.1 mmol, 1.0 equiv) and **10** (20.8 mg, 0.12 mmol, 1.2 equiv) was added. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The residue was purified by flash column chromatography on silica gel to afford the product as a colorless oil (22.2 mg, 63% yield, > 19:1 *d.r.*).



11

Physical state: colorless liquid;

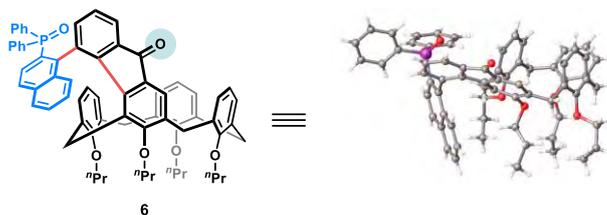
Yield: 63%;

R_f = 0.5 (PE:EtOAc = 1:1);

HPLC: 93% *e.e.* (Daicel chiralpak IA column, 50% *i*PrOH in *n*hexane, 1 mL/min, λ = 210 nm), t_R (major) = 10.23 min, t_R (minor) = 16.53 min;

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.45 (d, J = 7.3 Hz, 2H), 7.41 – 7.28 (m, 6H), 7.14 (d, J = 7.6 Hz, 2H), 4.58 (d, J = 8.8 Hz, 1H), 4.11 (d, J = 6.6 Hz, 1H), 3.87 (s, 3H), 3.70 (t, J = 7.2 Hz, 1H), 3.53 (t, J = 8.3 Hz, 1H), 2.37 (s, 1H).

6. X-ray crystallographic data



Identification code (CCDC)	2403829
Empirical formula	C70 H66 Cl3 O6 P
Formula weight	1140.54
Temperature	298.6(6) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 11.6469(4) Å α = 90°. b = 20.7272(6) Å β = 111.001(3)°. c = 13.9592(4) Å γ = 90°.
Volume	3146.01(18) Å ³
Z	2
Density (calculated)	1.204 Mg/m ³
Absorption coefficient	1.956 mm ⁻¹
F(000)	1200
Crystal size	0.05 x 0.04 x 0.03 mm ³
Theta range for data collection	3.391 to 67.483°.
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -16 ≤ l ≤ 16
Reflections collected	35174
Independent reflections	11298 [R(int) = 0.0415]
Completeness to theta = 67.483°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.55188
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11298 / 148 / 701
Goodness-of-fit on F ²	1.098
Final R indices [I > 2σ(I)]	R1 = 0.0867, wR2 = 0.2450
R indices (all data)	R1 = 0.0955, wR2 = 0.2604

Absolute structure parameter	0.036(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.933 and -0.727 e.Å ⁻³

7. Photophysical and chiroptical properties study

6.1 Copies of UV-vis spectra of 3c, 3y, 3p and 8

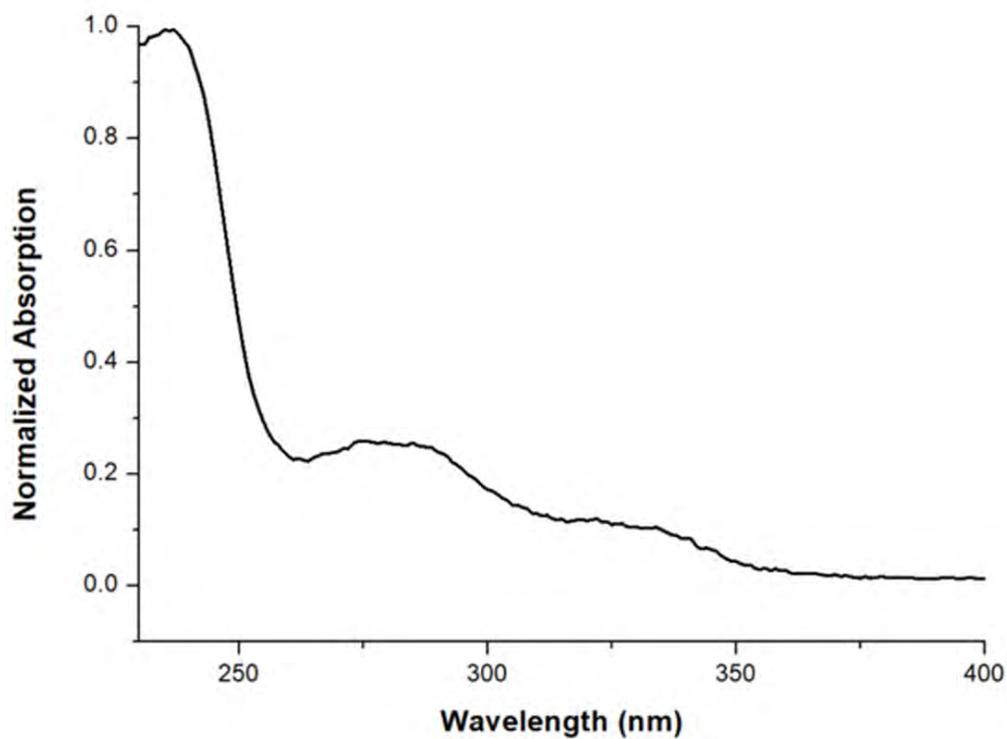


Figure S2. UV-vis spectra of **3c** in DCM at 25 °C (ca. 5×10^{-5} M)

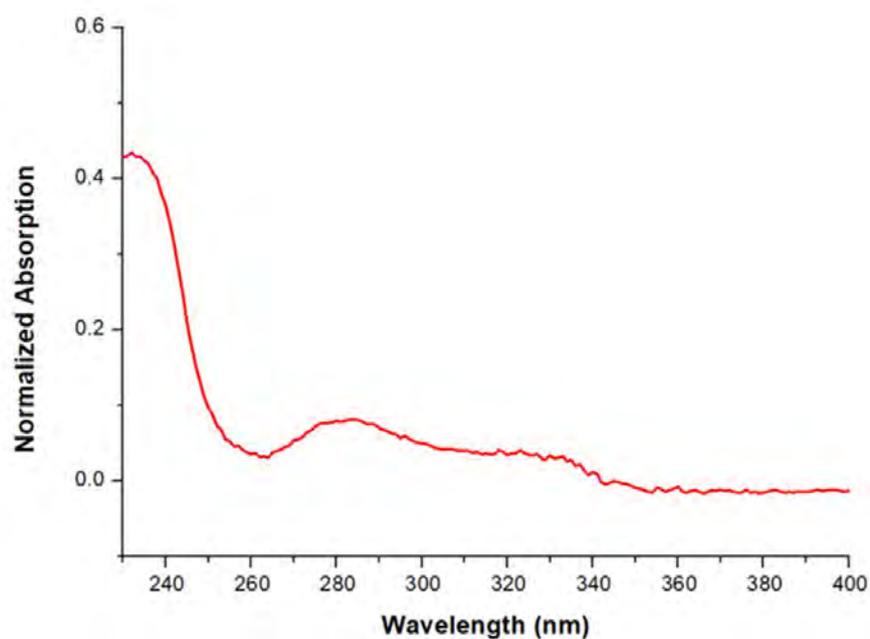


Figure S3. UV-vis spectra of **3y** in DCM at 25 °C (ca. 5×10^{-5} M)

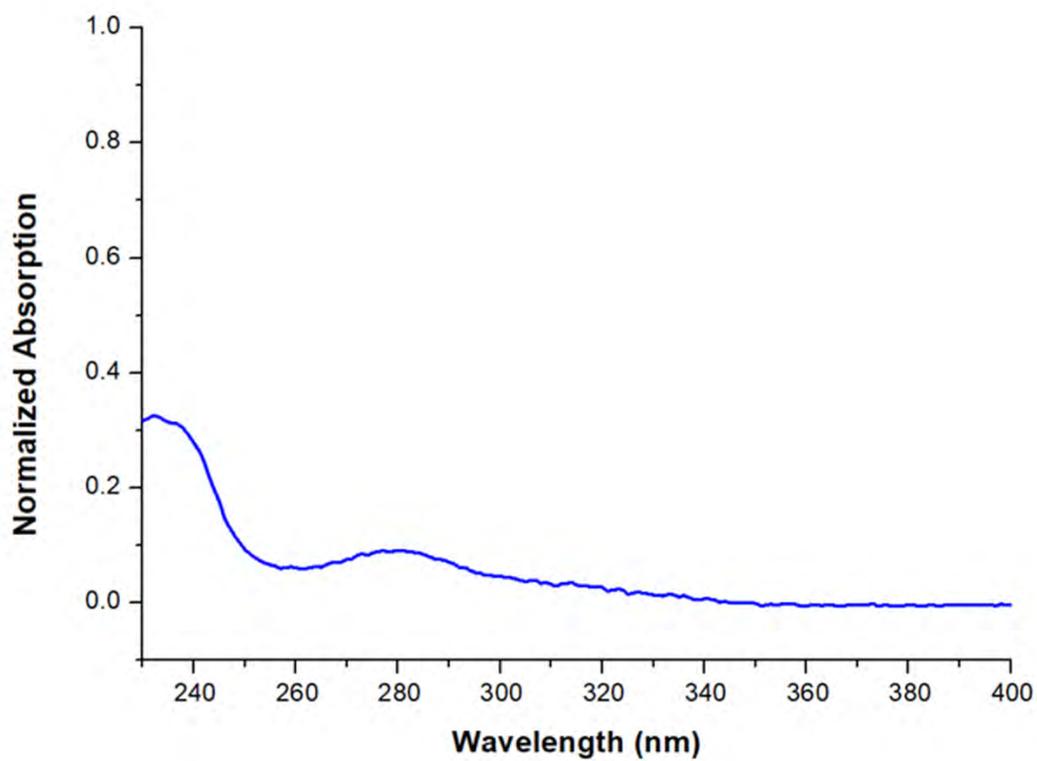


Figure S4. UV-vis spectra of **3p** in DCM at 25 °C (ca. 5×10^{-5} M)

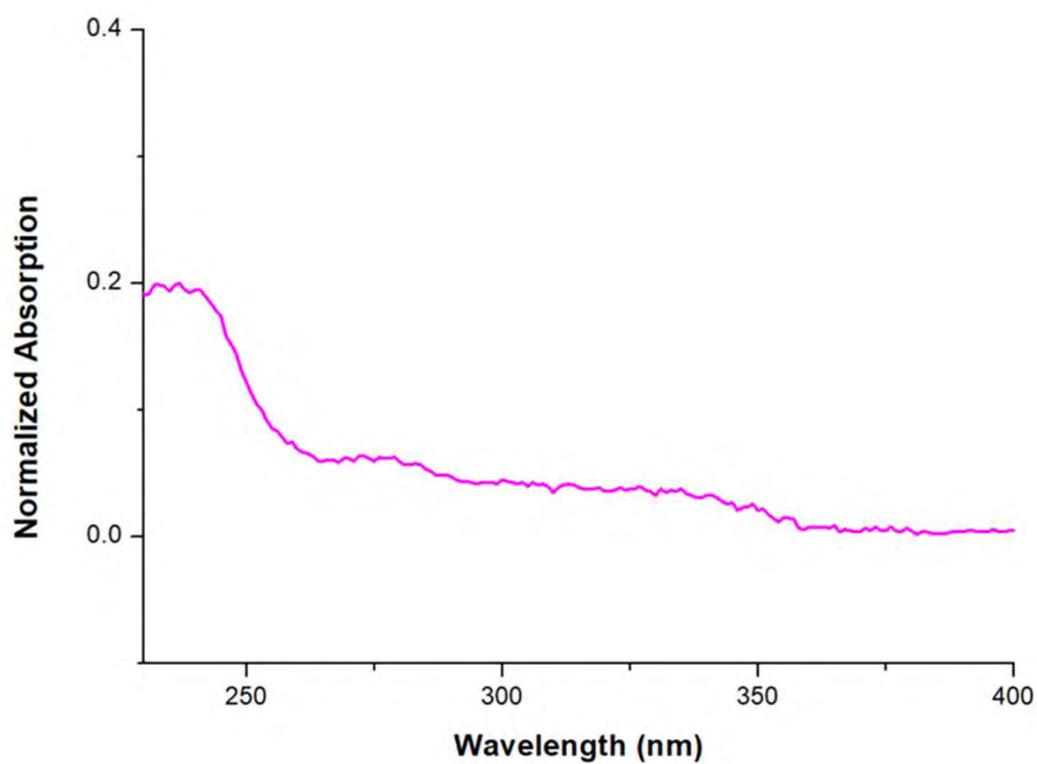


Figure S5. UV-vis spectra of **8** in DCM at 25 °C (ca. 5×10^{-5} M)

6.2 Copies of fluorescence spectra of 3c, 3y, 3p and 8

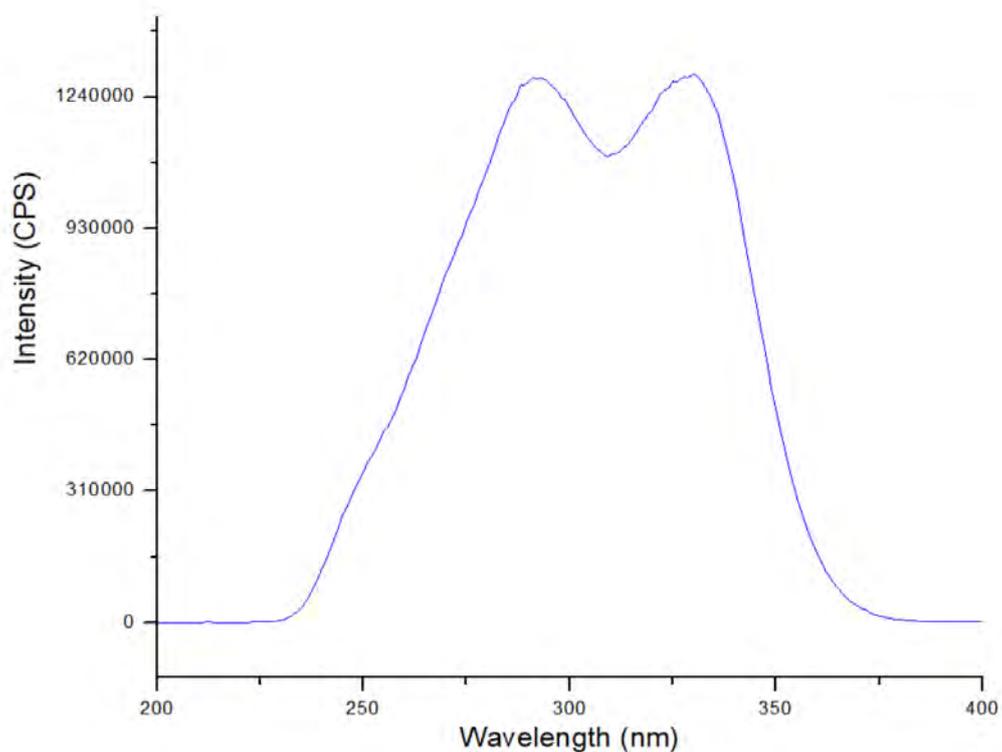


Figure S6. excitation spectrum of 3c in DCM at 25 °C (ca. 5×10^{-5} M)

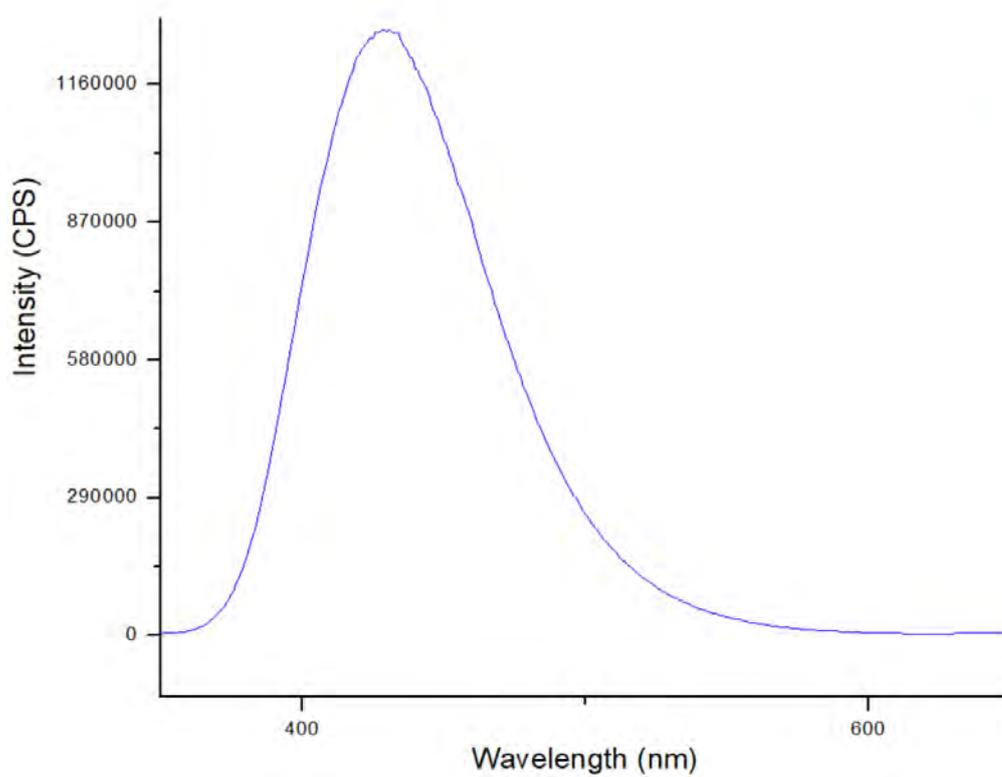


Figure S7. emission spectrum of 3c in DCM at 25 °C (ca. 5×10^{-5} M)

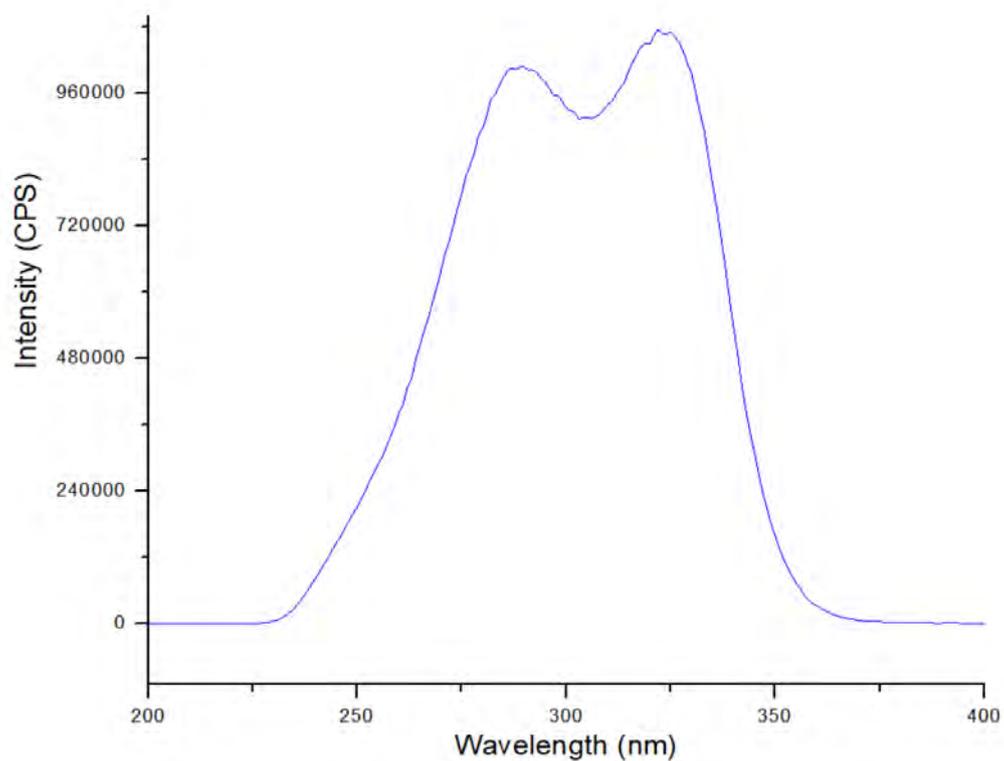


Figure S8. excitation spectrum of **3y** in DCM at 25 °C (ca. 5×10^{-5} M)

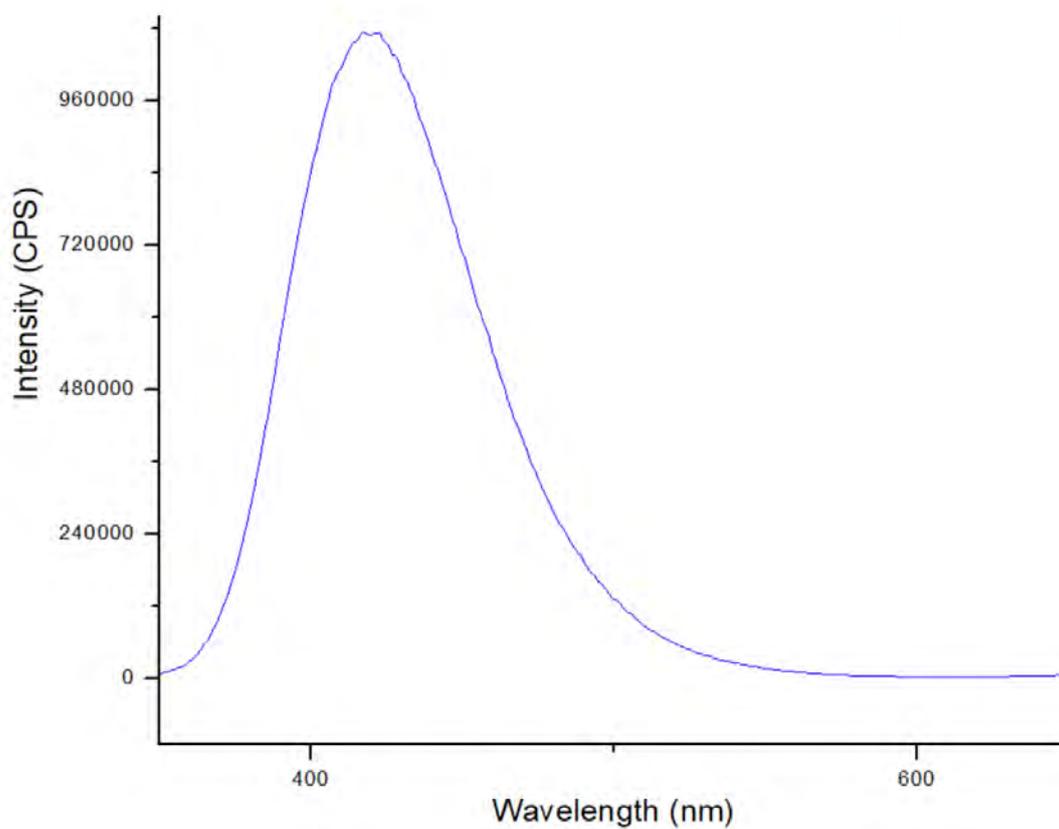


Figure S9. emission spectrum of **3y** in DCM at 25 °C (ca. 5×10^{-5} M)

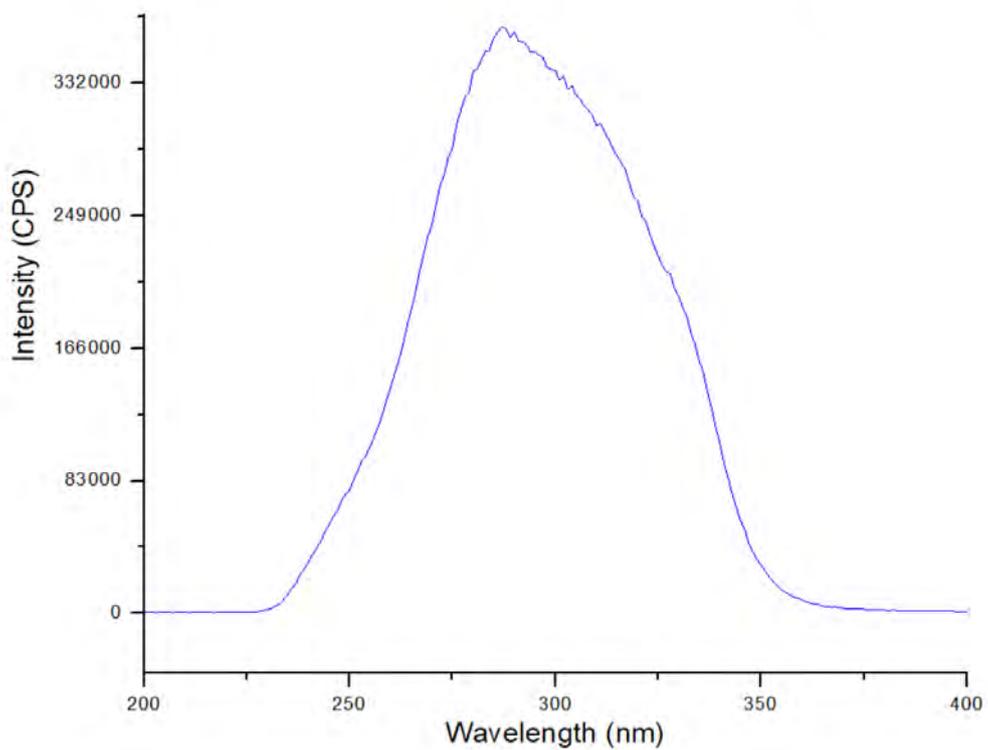


Figure S10. excitation spectrum of **3p** in DCM at 25 °C (ca. 5×10^{-5} M)

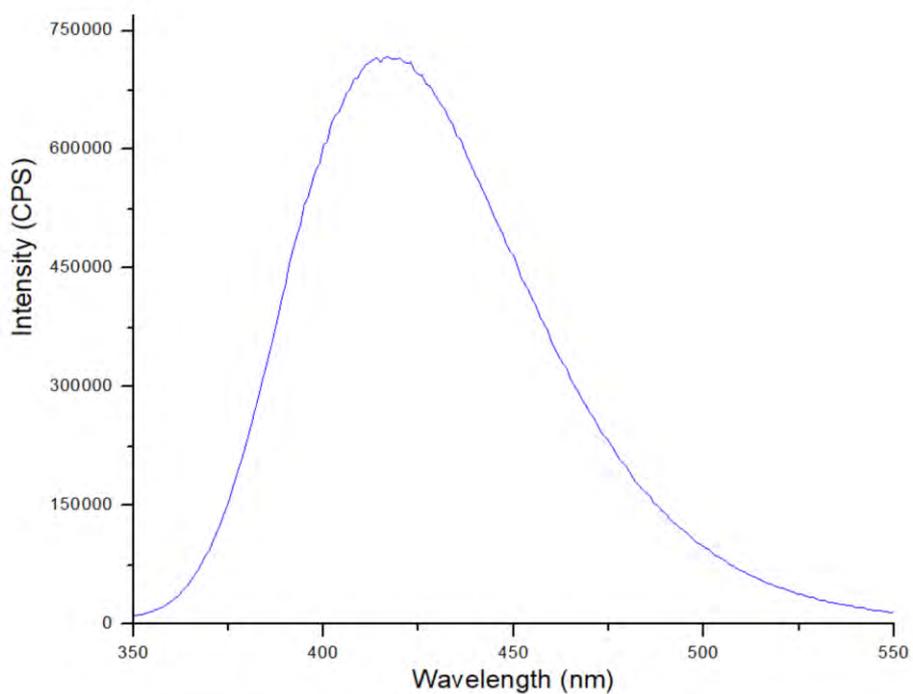


Figure S11. emission spectrum of **3p** in DCM at 25 °C (ca. 5×10^{-5} M)

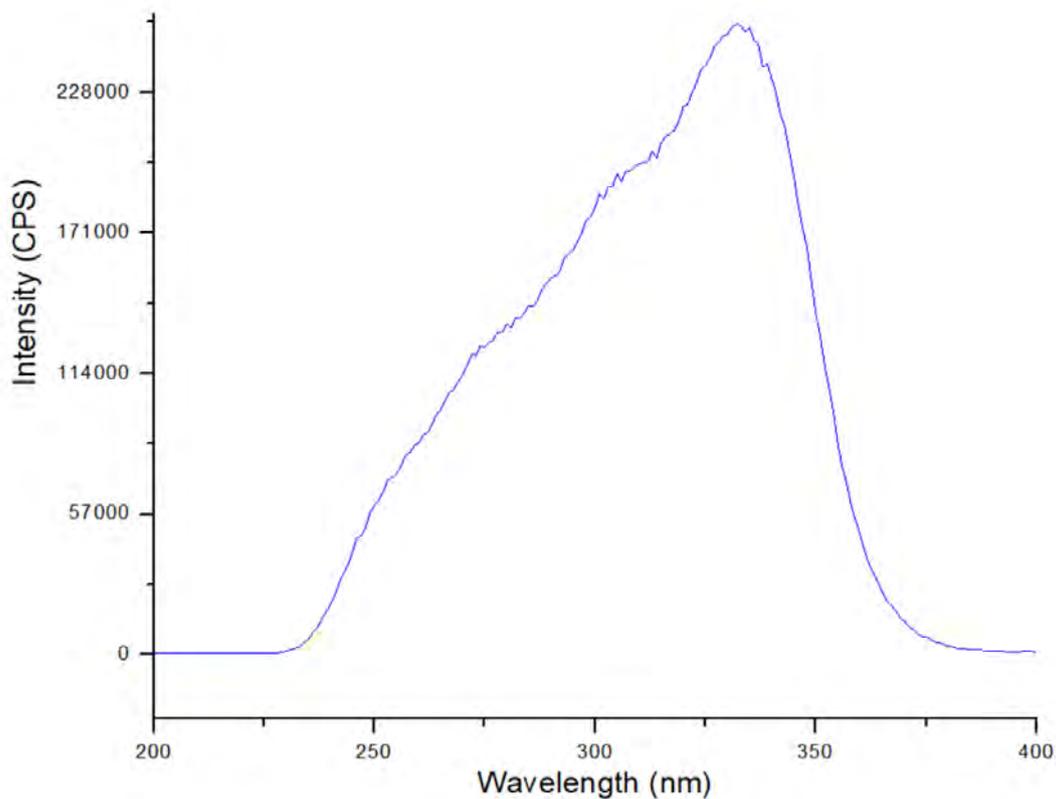


Figure S12. excitation spectrum of **8** in DCM at 25 °C (ca. 5×10^{-5} M)

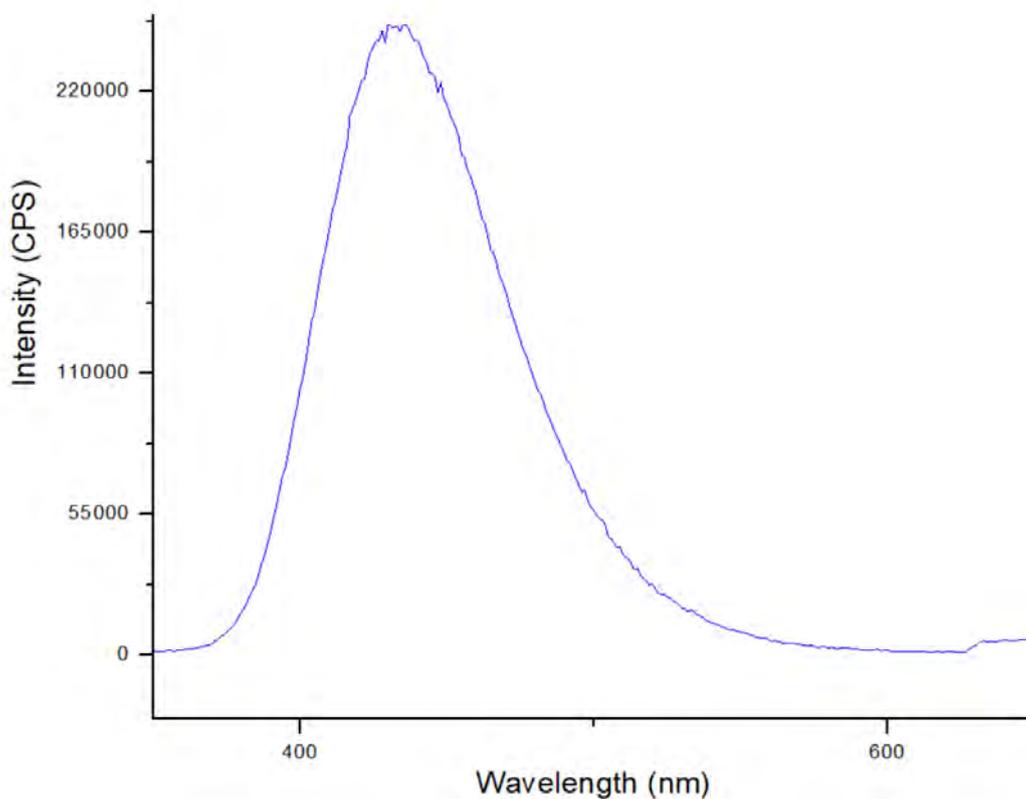


Figure S13. emission spectrum of **8** in DCM at 25 °C (ca. 5×10^{-5} M)

6.3 Quantum yield measurements

Compound	QY
3c	0.241
3y	0.359
3p	0.134
8	0.146

6.4 Copies of CD spectra of 3c, 3y, 3p and 8

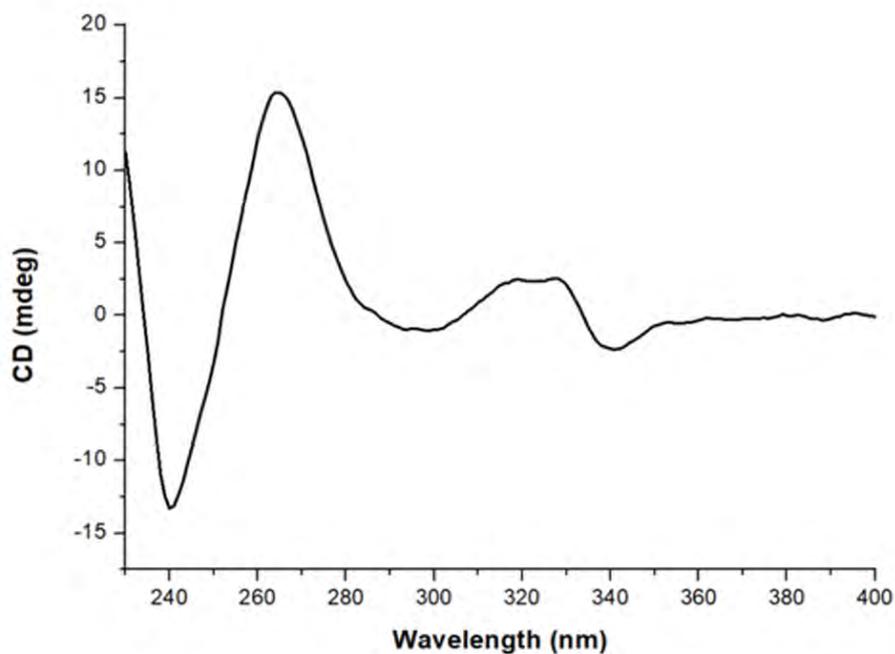


Figure S14. CD of 3c in DCM at 25 °C (ca. 5×10^{-5} M)

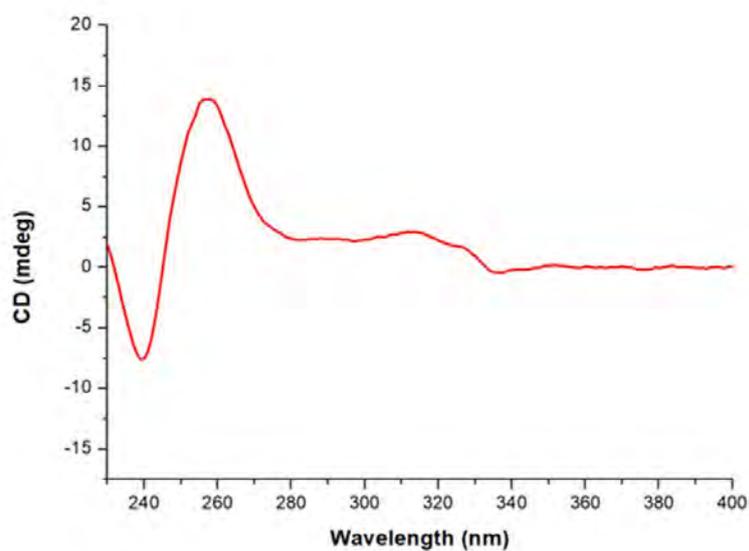


Figure S15. CD of 3y in DCM at 25 °C (ca. 5×10^{-5} M)

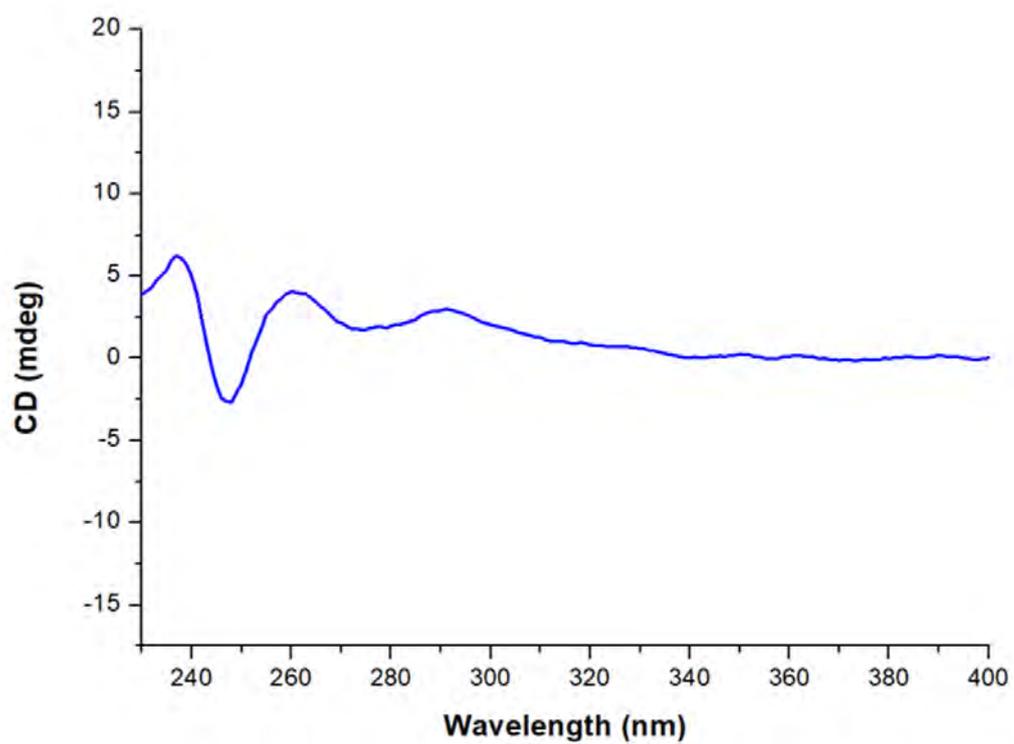


Figure S16. CD of **3p** in DCM at 25 °C (ca. 5×10^{-5} M)

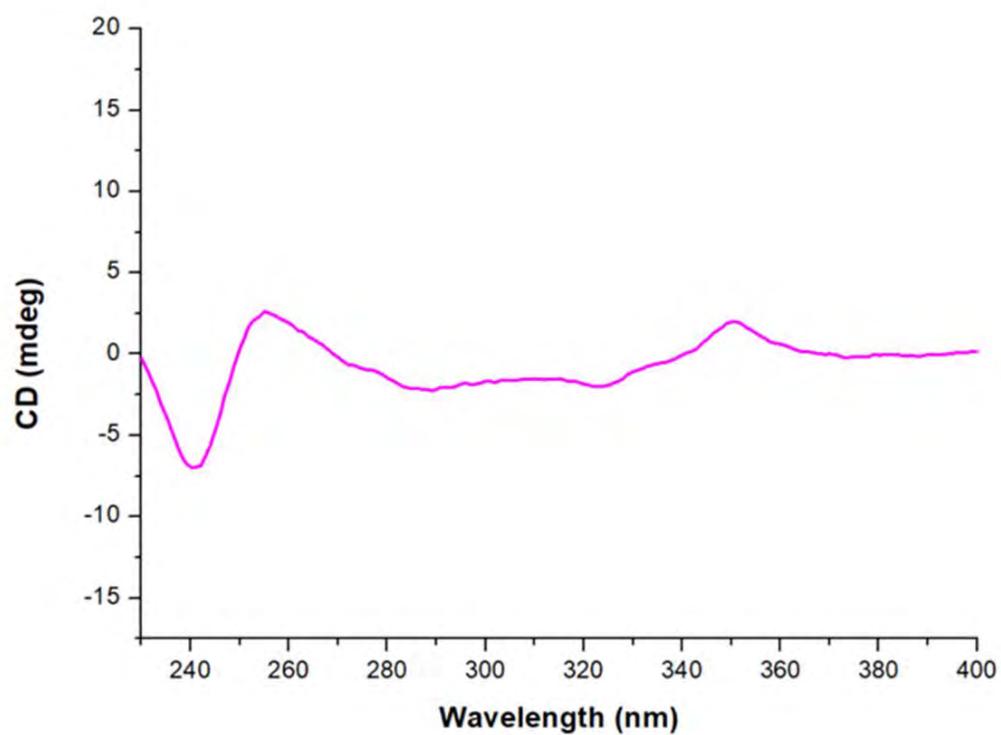


Figure S17. CD of **8** in DCM at 25 °C (ca. 5×10^{-5} M)

6.5 Copies of CPL spectra of 3c, 3y, 3p and 8

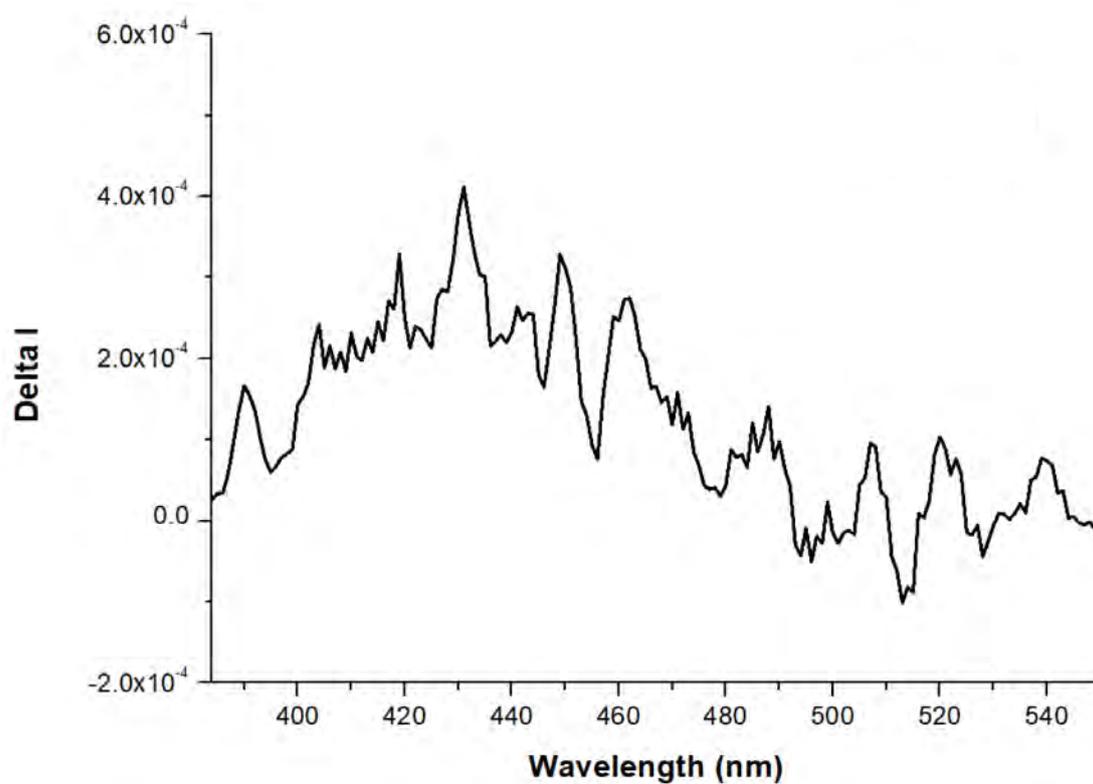


Figure S18. CPL of **3c** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 328$ nm

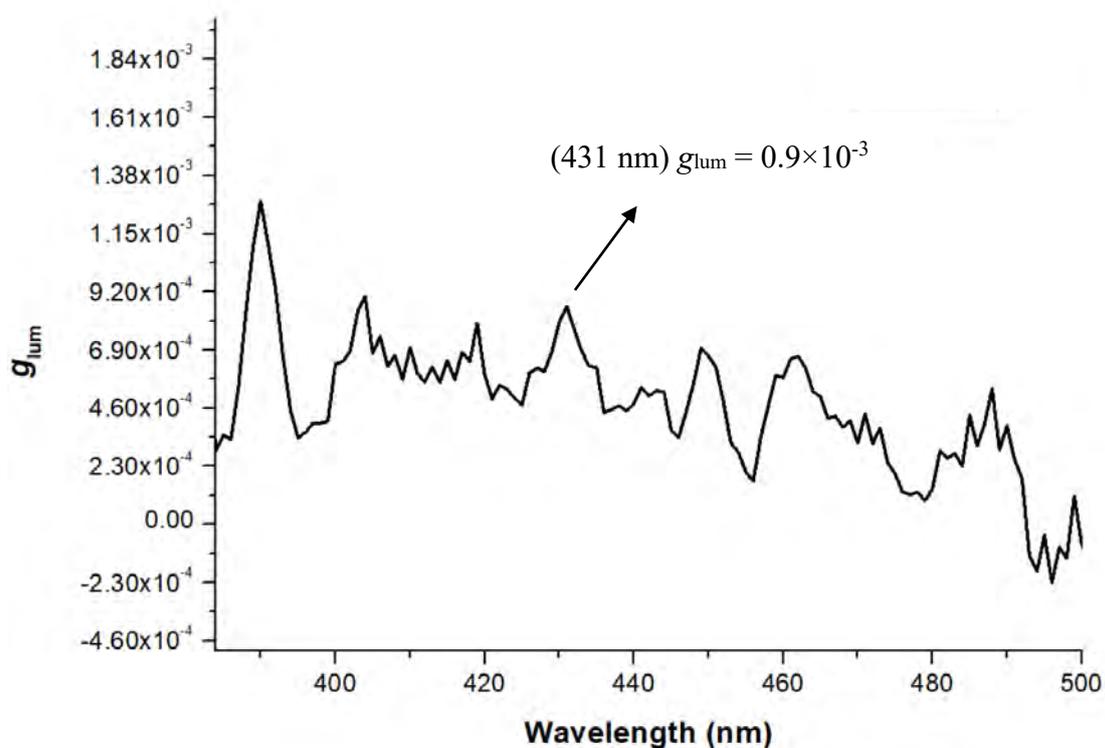


Figure S19. CPL (g_{lum}) of **3c** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 328$ nm

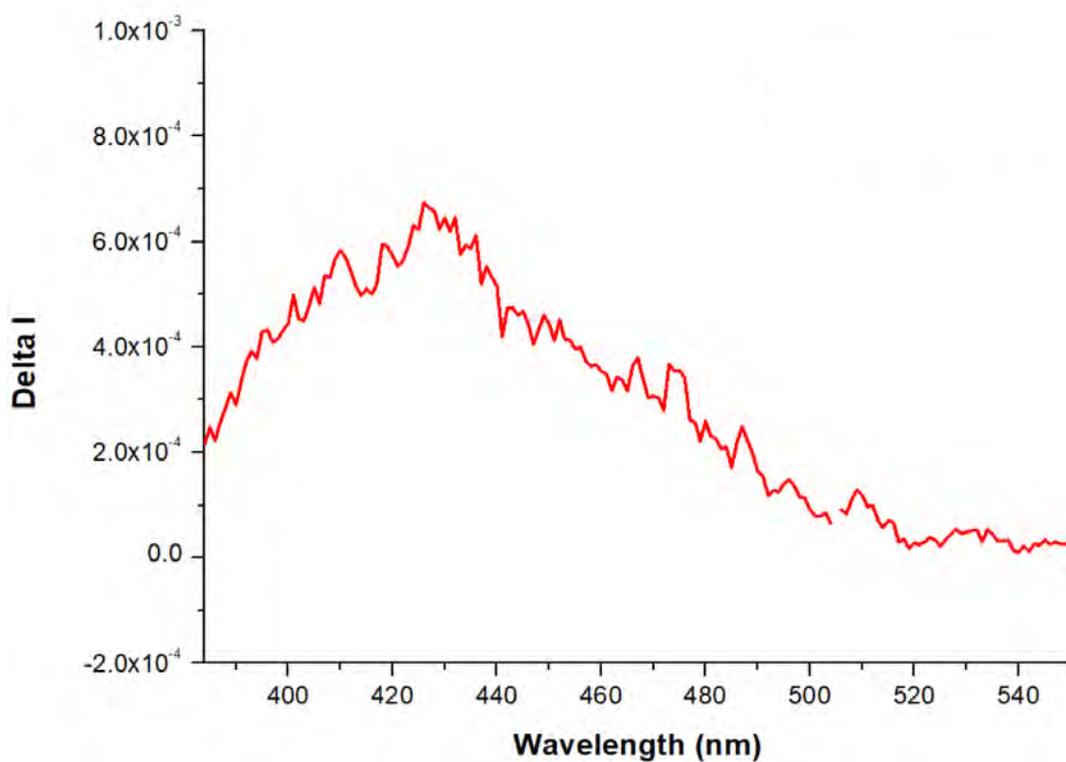


Figure S20. CPL of **3y** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 325$ nm

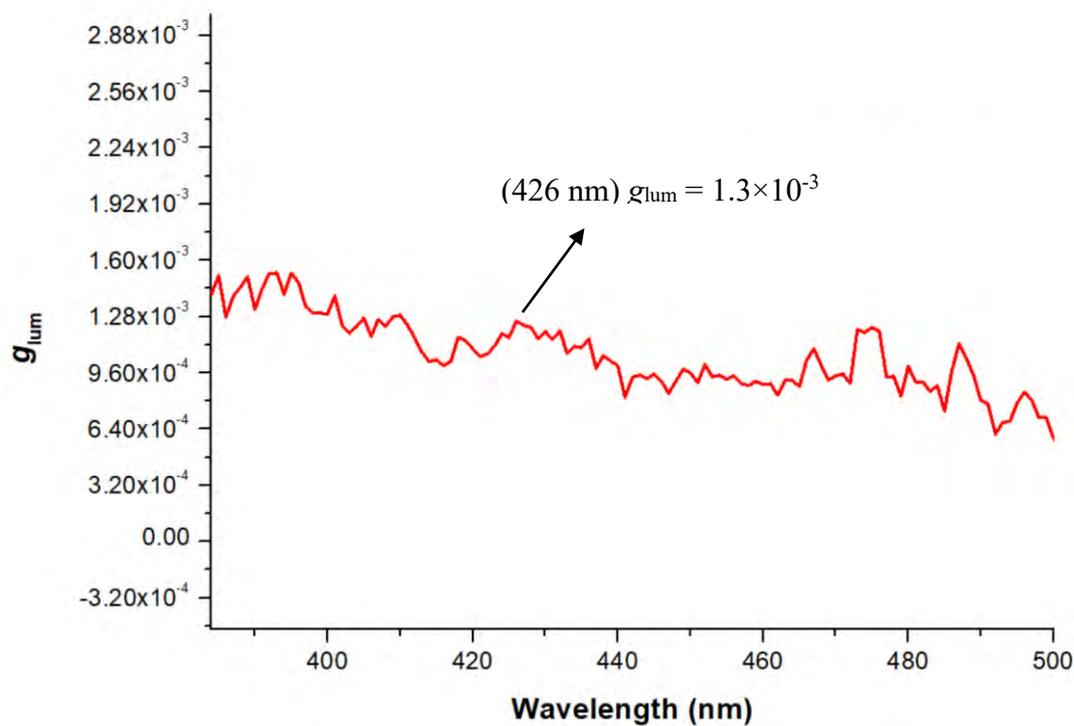


Figure S21. CPL (g_{lum}) of **3y** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 325$ nm

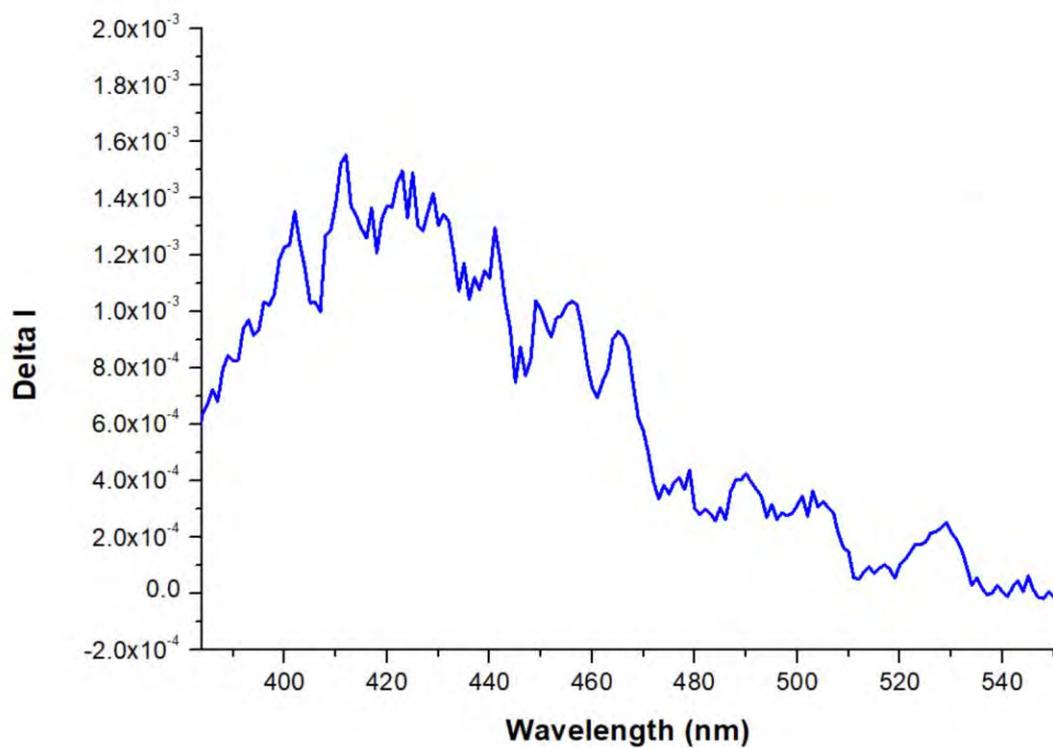


Figure S22. CPL of **3p** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 288$ nm

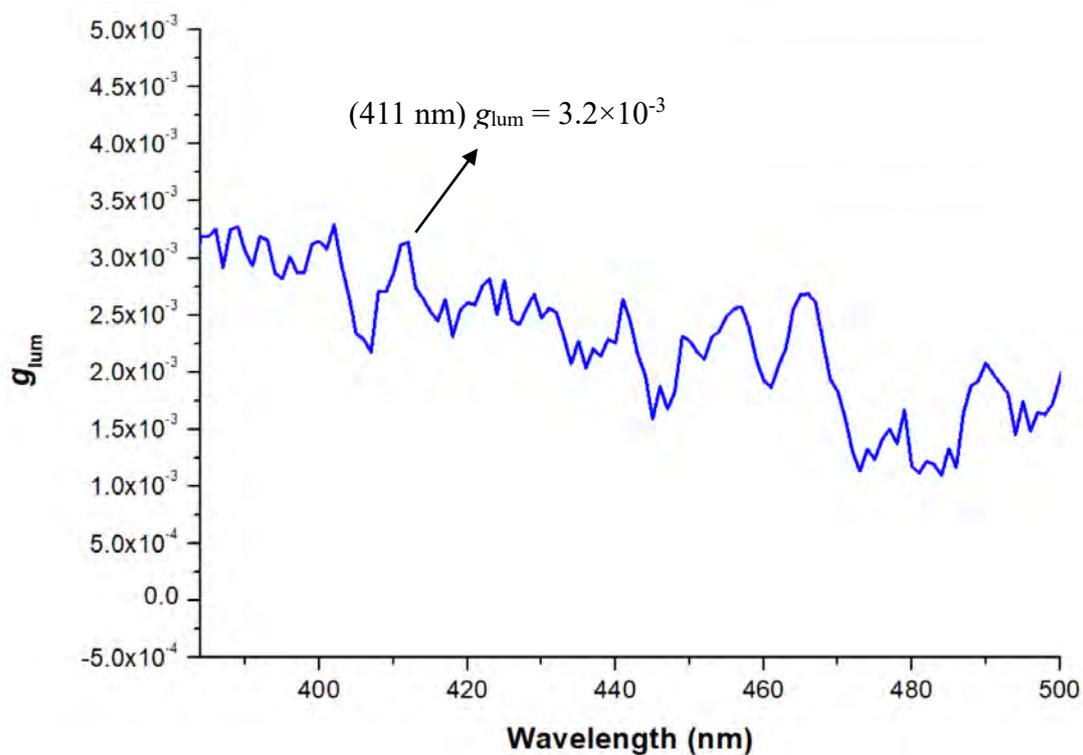


Figure S23. CPL (g_{lum}) of **3p** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 288$ nm

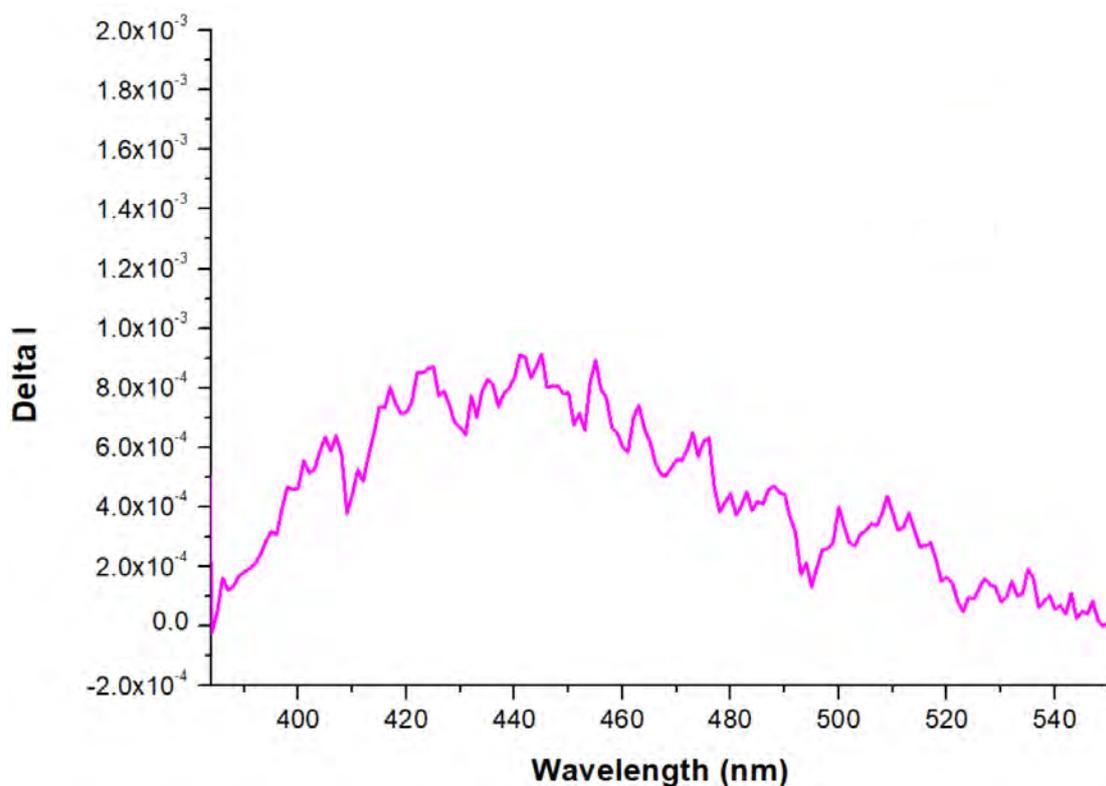


Figure S24. CPL of **8** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 333$ nm

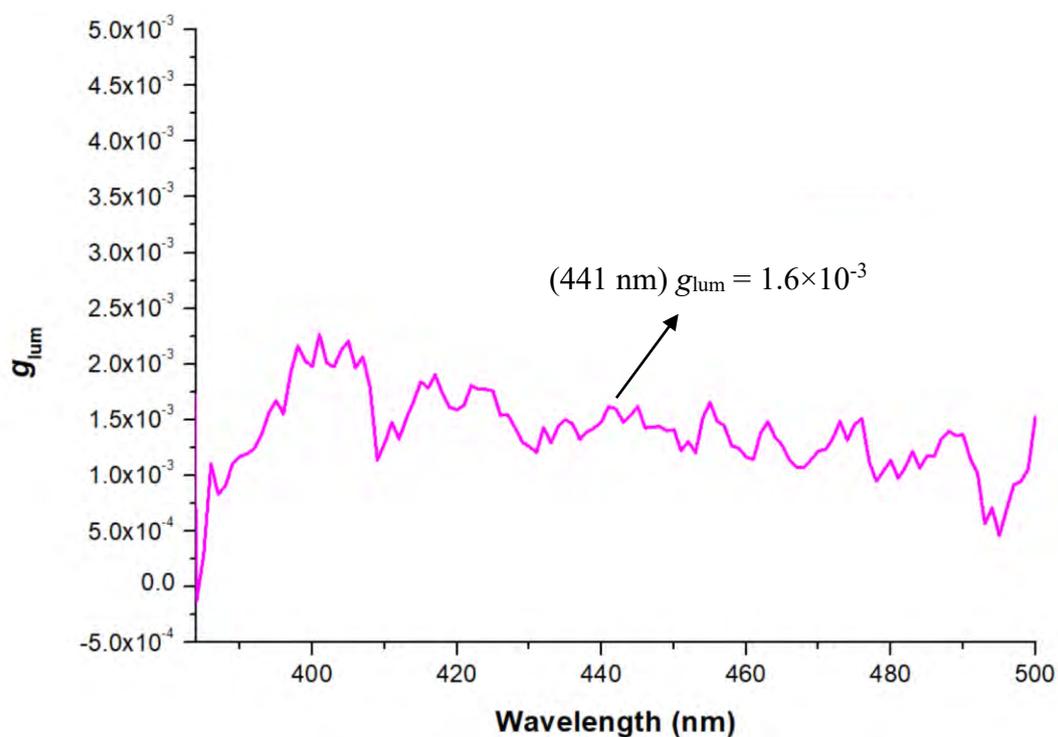
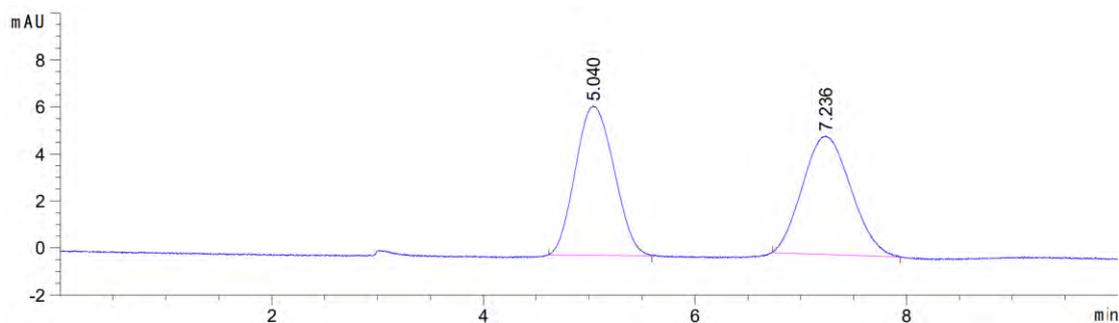
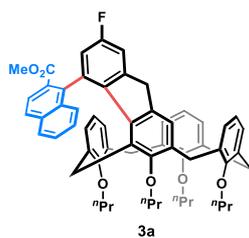


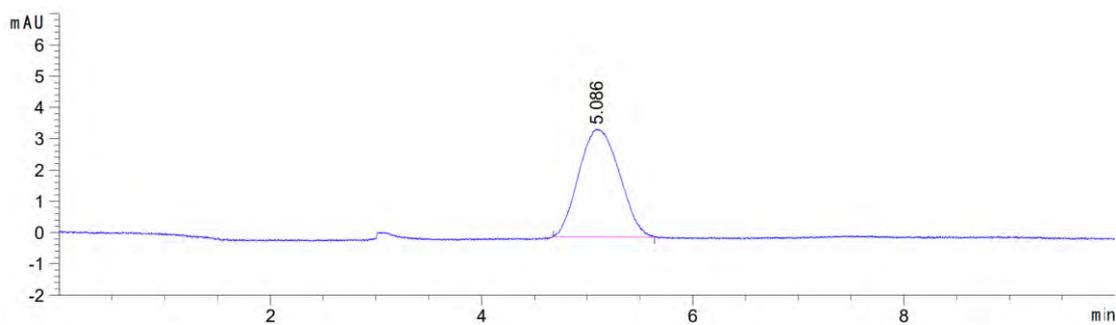
Figure S25. CPL (g_{lum}) of **8** in DCM at 25 °C (ca. 5×10^{-5} M), $\lambda_{\text{ex}} = 333$ nm

8. HPLC traces of the products



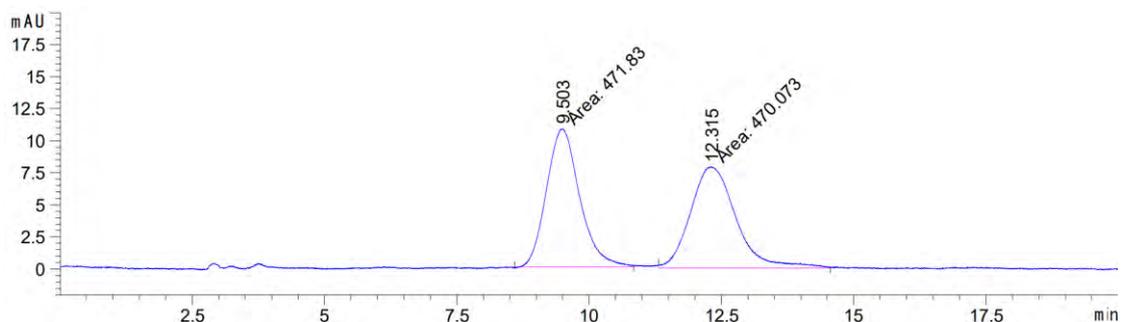
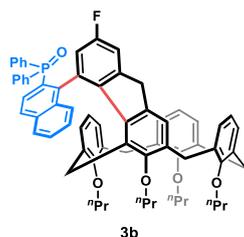
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.040	BB	0.2978	160.55247	6.35484	50.0090
2	7.236	BB	0.3748	160.49478	5.04330	49.9910



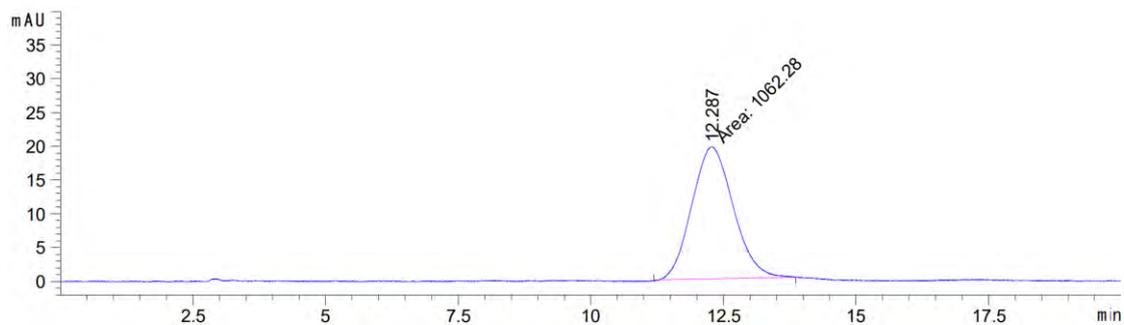
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.086	BB	0.3153	92.12873	3.44748	100.0000



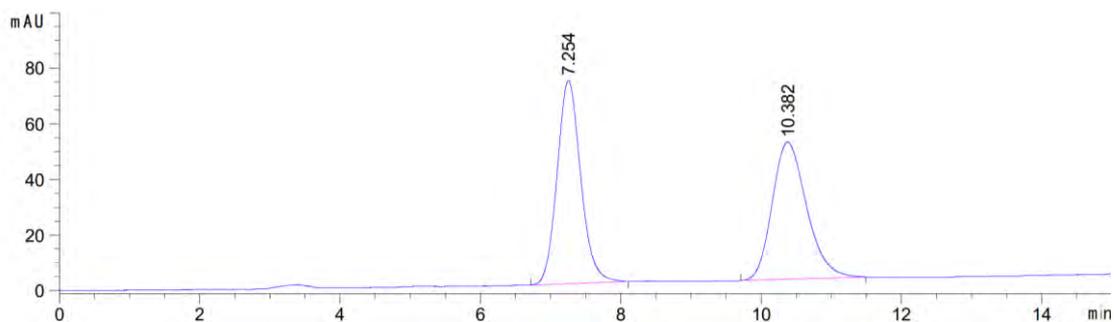
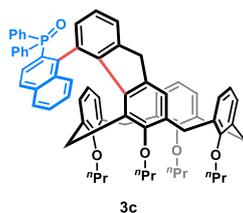
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.503	MM	0.7287	471.83044	10.79200	50.0933
2	12.315	MM	0.9912	470.07260	7.90373	49.9067



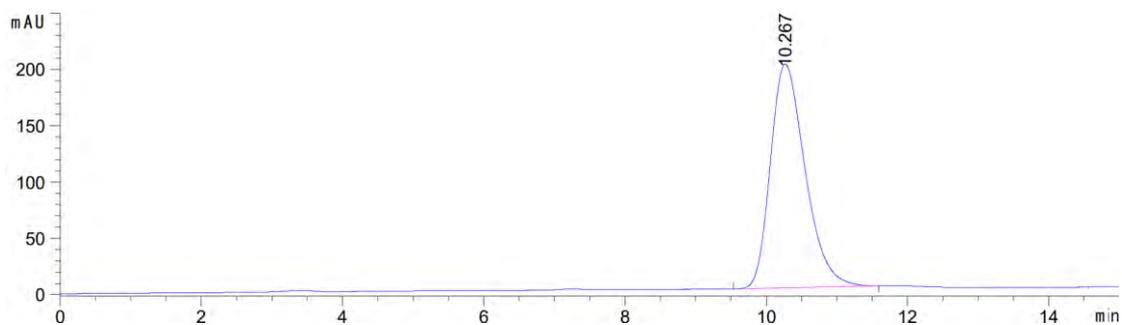
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.287	MM	0.9052	1062.28027	19.55950	100.0000



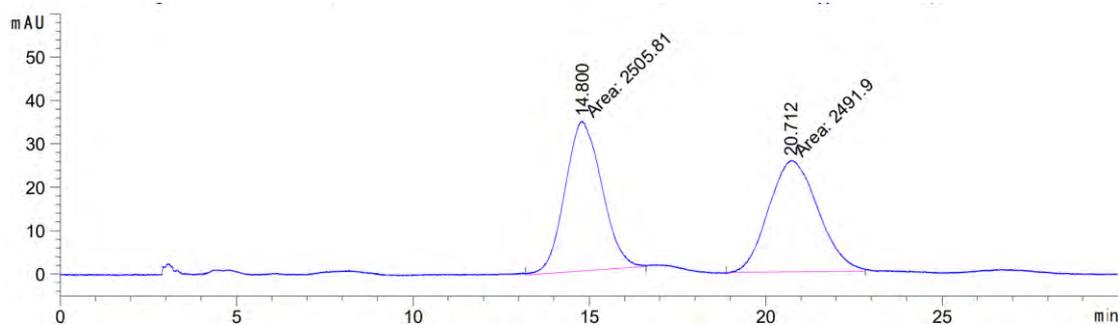
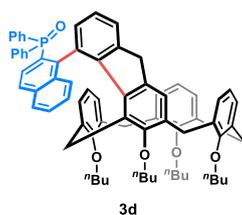
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.254	BB	0.3382	1708.03259	73.07301	50.4022
2	10.382	BB	0.4060	1680.76990	49.26880	49.5978



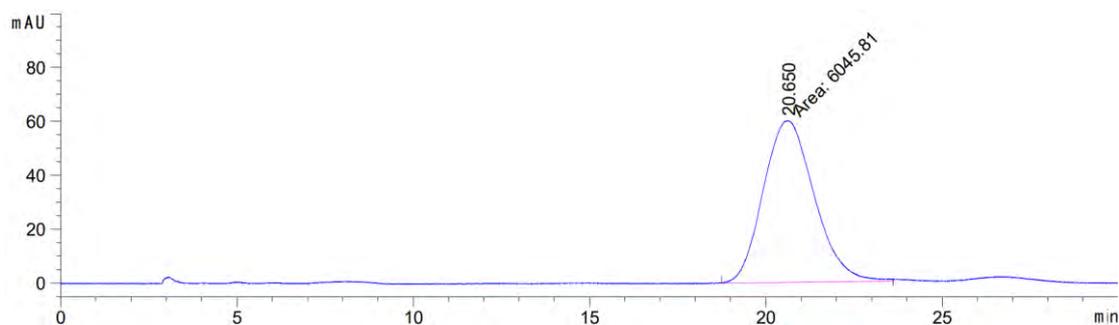
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.267	BB	0.4892	6801.75879	198.77654	100.0000



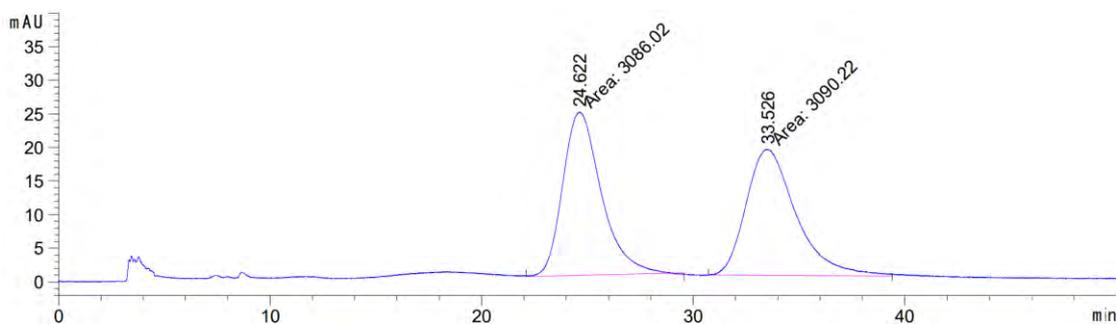
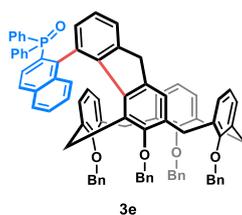
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.800	MM	1.2095	2505.81274	34.52979	50.1392
2	20.712	MM	1.6170	2491.89868	25.68499	49.8608



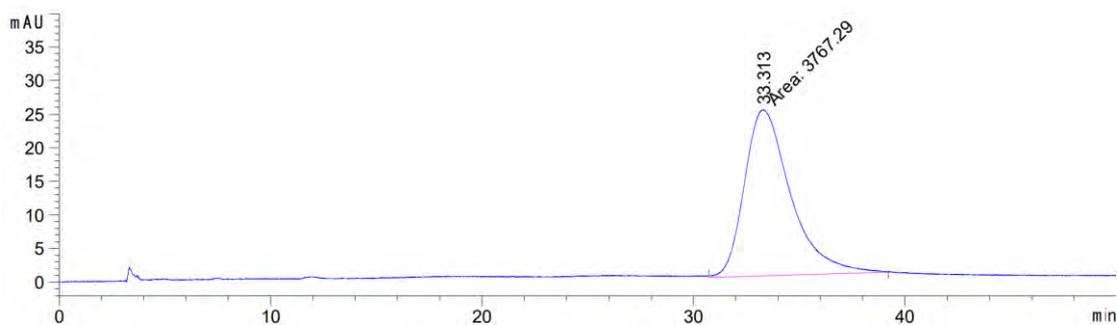
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.650	MM	1.6762	6045.81494	60.11486	100.0000



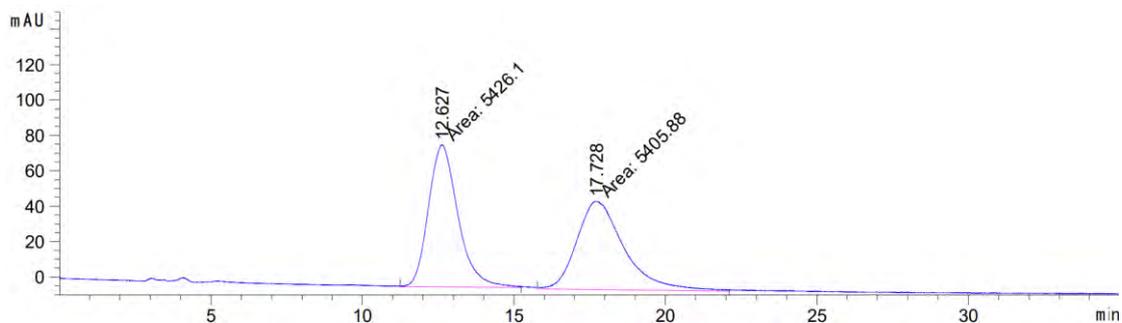
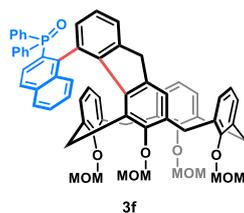
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.622	MM	2.1164	3086.02441	24.30194	49.9660
2	33.526	MM	2.7376	3090.22437	18.81336	50.0340



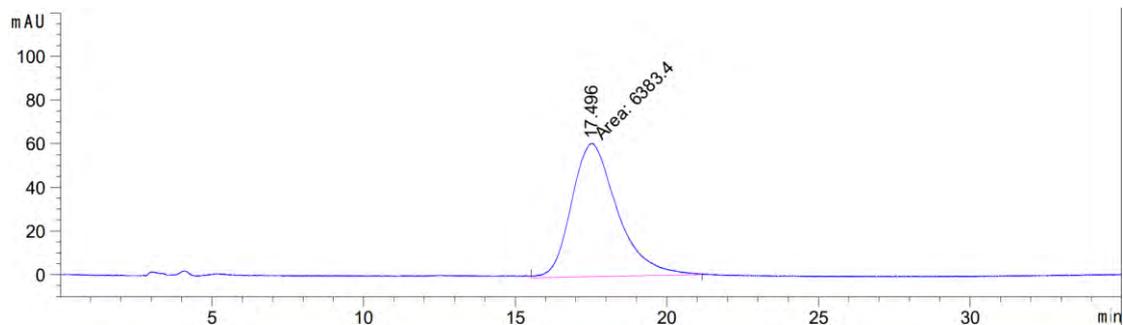
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.313	MM	2.5372	3767.28760	24.74732	100.0000



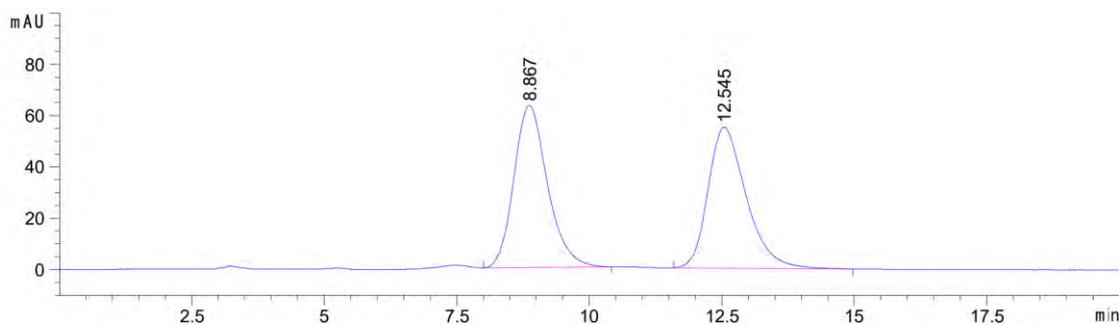
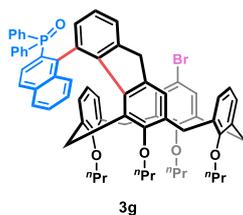
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.627	MM	1.1274	5426.10107	80.21354	50.0934
2	17.728	MM	1.8069	5405.87646	49.86302	49.9066



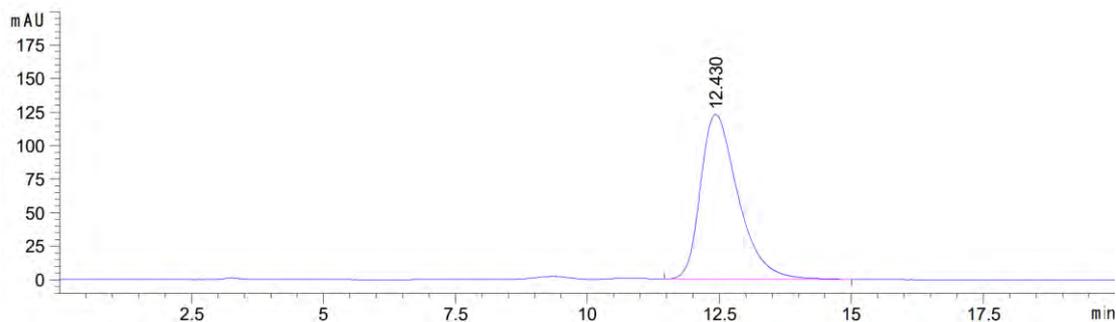
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.496	MM	1.7433	6383.40381	61.02914	100.0000



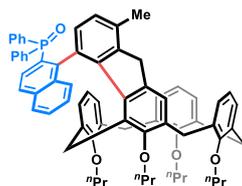
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.867	BB	0.6622	2781.15454	63.09950	50.2863
2	12.545	BB	0.7404	2749.48999	54.88477	49.7137

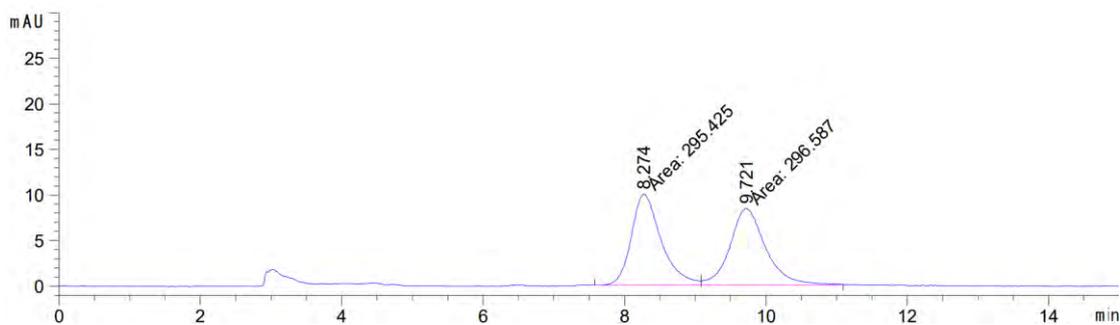


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.430	BB	0.7452	6079.27002	122.87100	100.0000

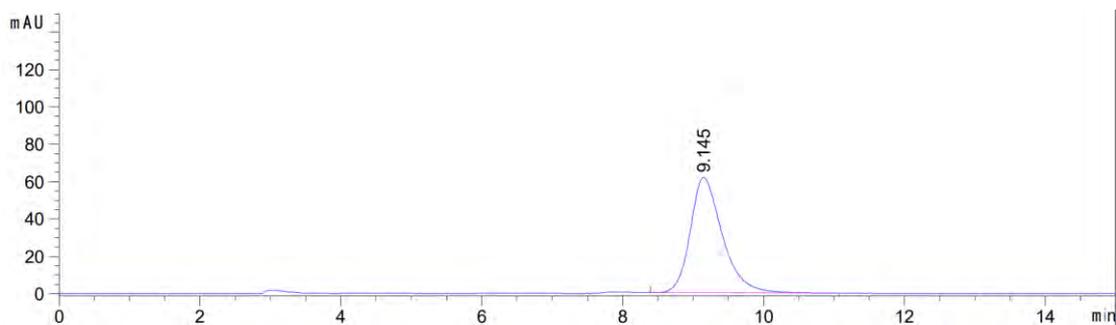


3h



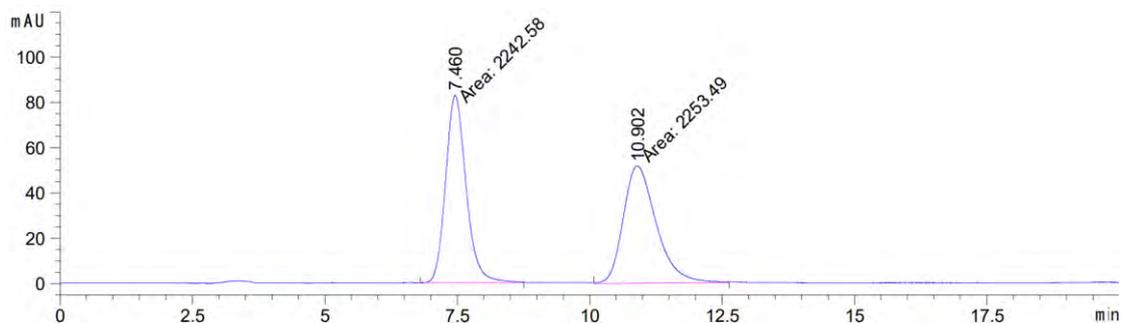
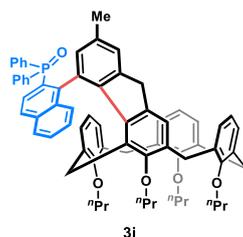
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.274	MF	0.4922	295.42453	10.00446	49.9018
2	9.721	FM	0.5874	296.58731	8.41556	50.0982



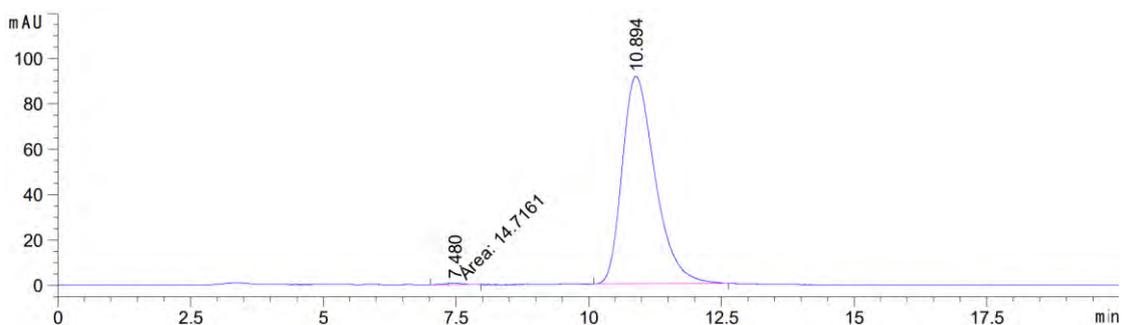
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.145	BB	0.4750	1967.15063	61.86145	100.0000



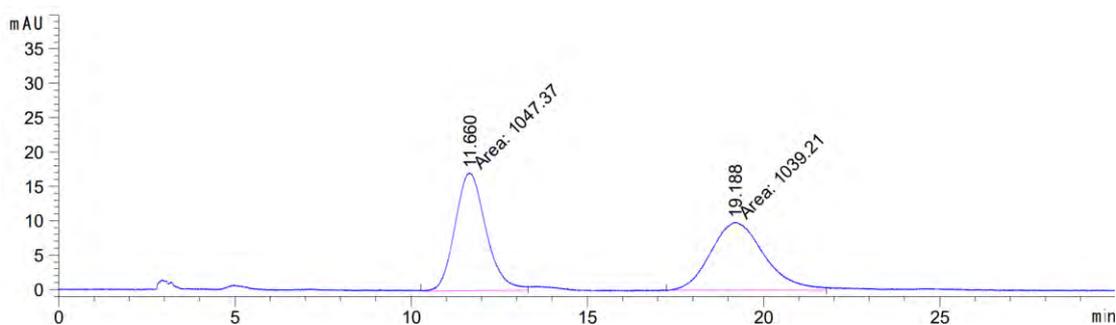
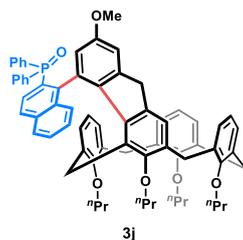
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.460	MM	0.4510	2242.58252	82.88280	49.8787
2	10.902	MM	0.7236	2253.48755	51.90775	50.1213



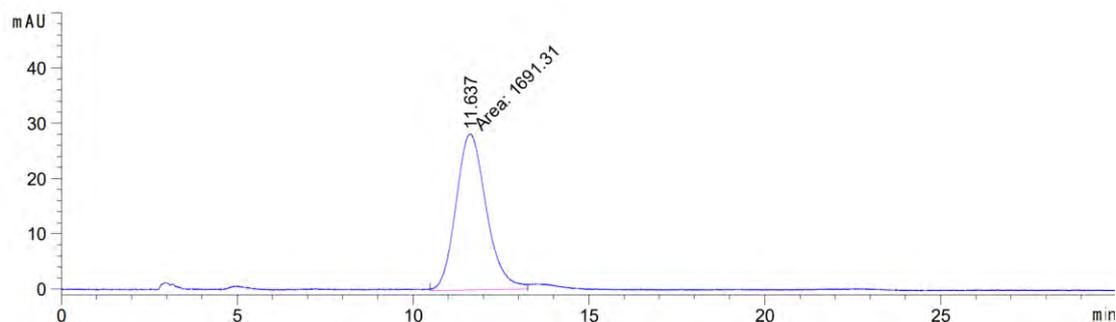
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.480	MM	0.3798	14.71610	6.45865e-1	0.3716
2	10.894	BB	0.5177	3945.32886	91.66096	99.6284



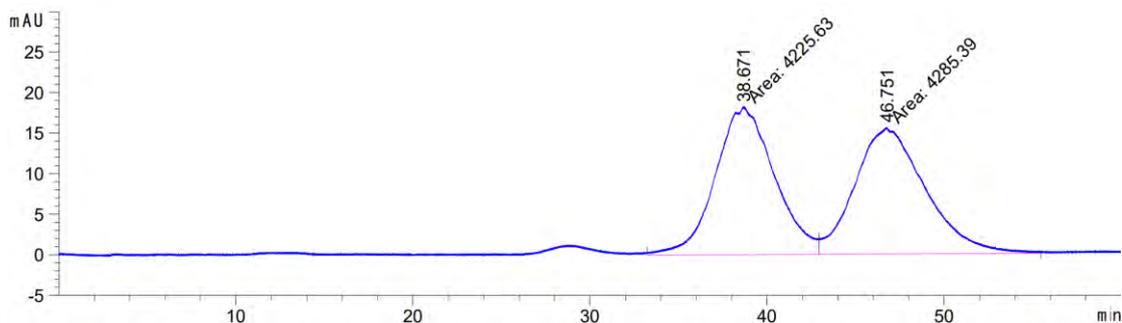
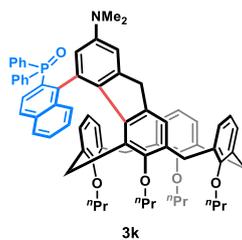
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.660	MM	1.0179	1047.36609	17.14886	50.1956
2	19.188	MM	1.7494	1039.20520	9.90051	49.8044



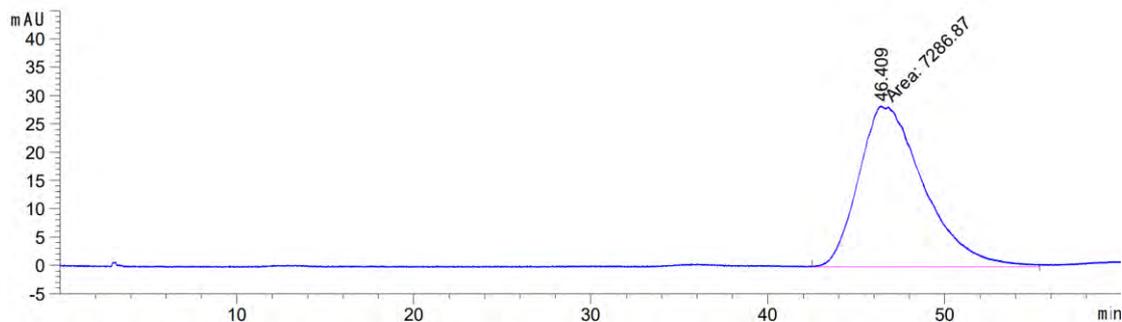
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.637	MM	0.9989	1691.31323	28.21836	100.0000



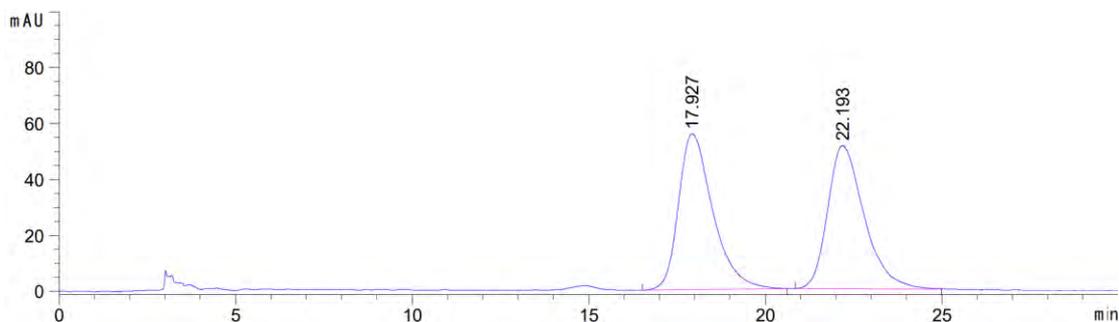
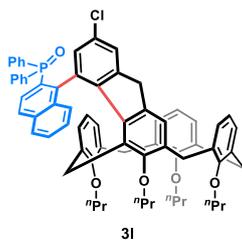
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.671	MF	3.8476	4225.62744	18.30439	49.6489
2	46.751	FM	4.5607	4285.38965	15.66055	50.3511



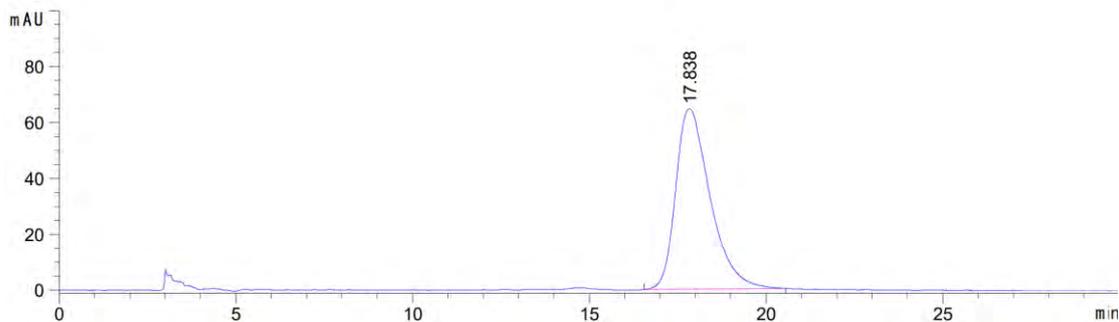
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.409	MM	4.2602	7286.87256	28.50746	100.0000



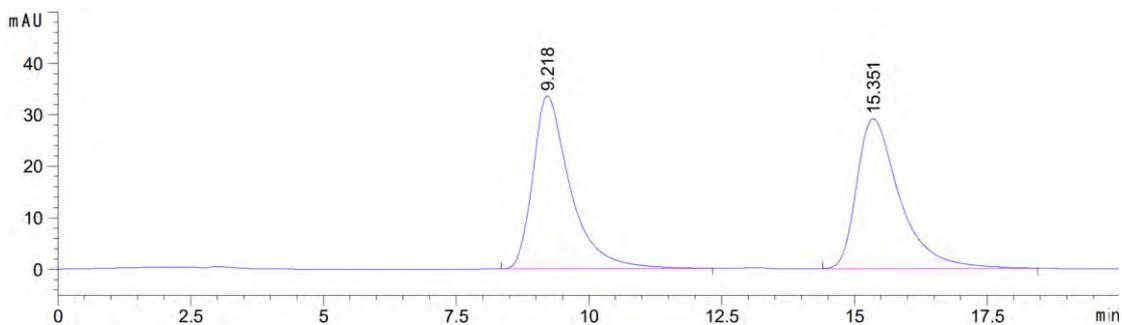
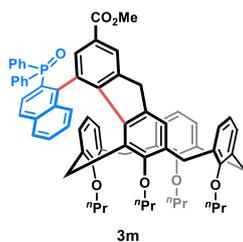
Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.927	BB	0.9707	3765.89453	55.70587	50.6784
2	22.193	BB	1.0019	3665.07520	51.03208	49.3216



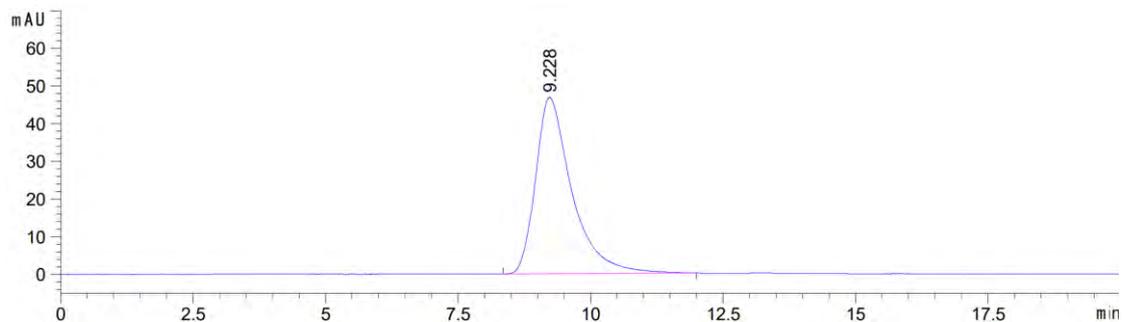
Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.838	BB	0.9719	4375.71729	64.46263	100.0000



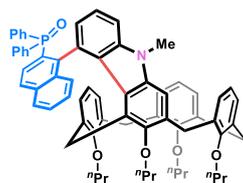
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.218	BB	0.6907	1646.87915	33.54715	50.1318
2	15.351	BB	0.7917	1638.21667	29.06158	49.8682

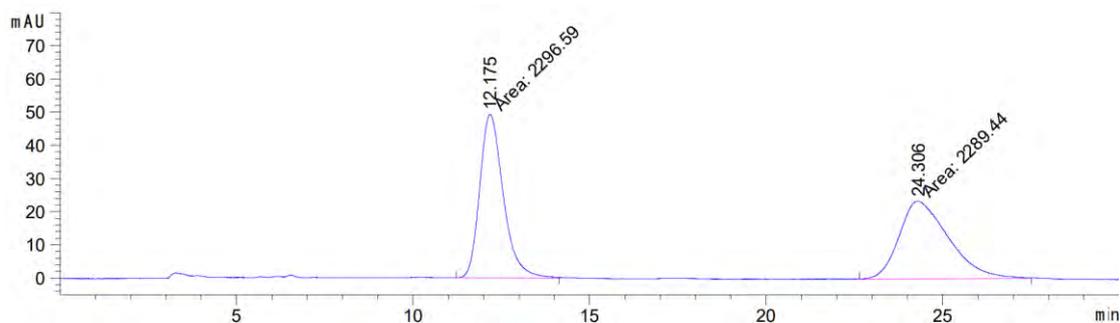


Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.228	BB	0.6799	2232.22192	46.84579	100.0000

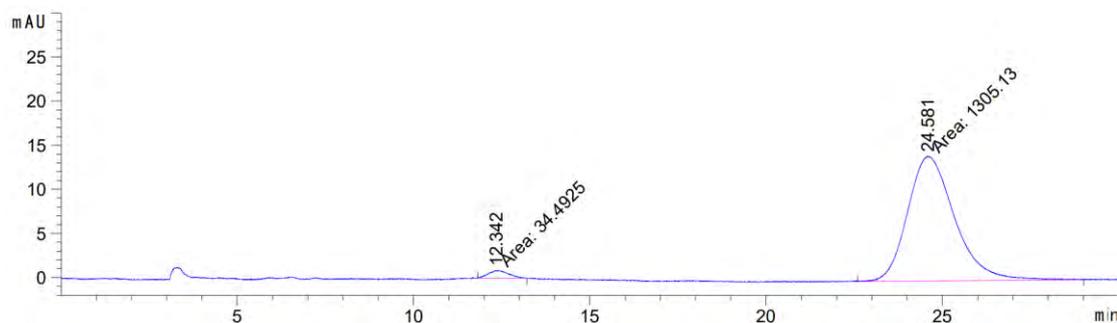


3n



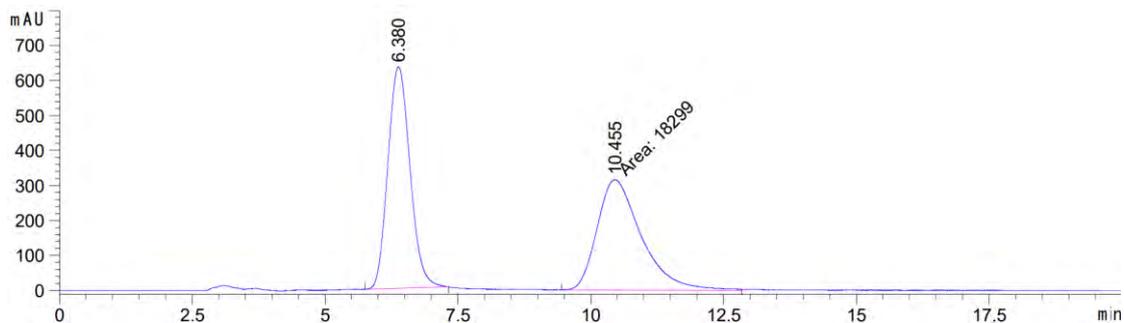
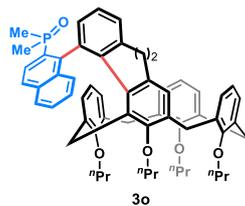
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.175	MM	0.7763	2296.59204	49.30544	50.0779
2	24.306	MM	1.6246	2289.44458	23.48789	49.9221



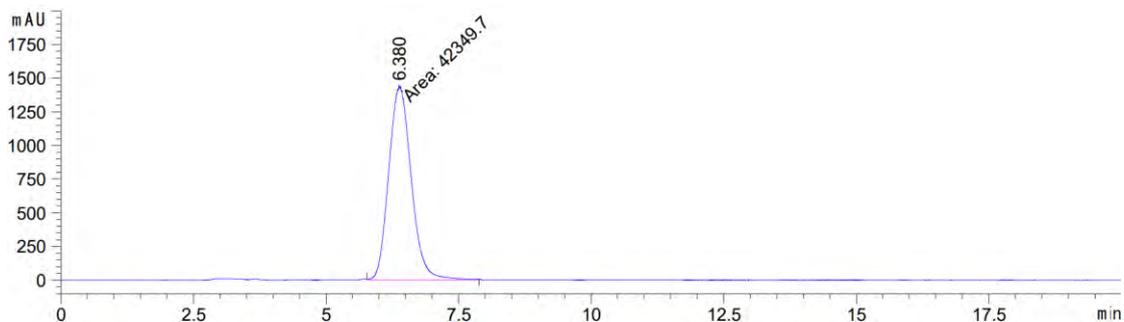
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.342	MM	0.6512	34.49245	8.82768e-1	2.5748
2	24.581	MM	1.5402	1305.13428	14.12305	97.4252



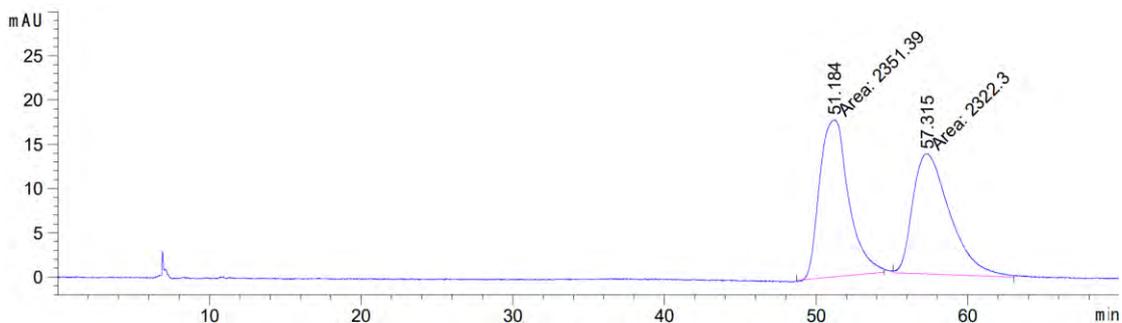
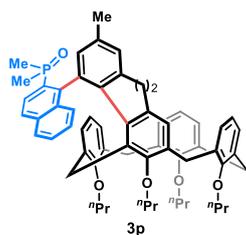
Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.380	VV R	0.3405	1.83098e4	631.92780	50.0148
2	10.455	MM	0.9675	1.82990e4	315.23038	49.9852



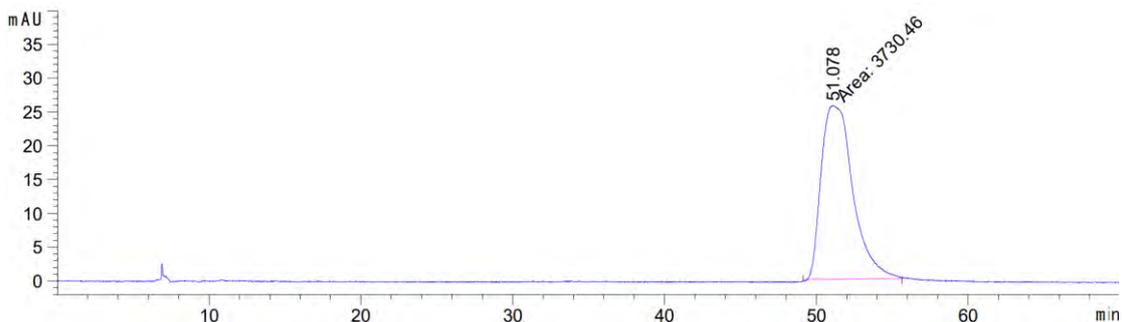
Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.380	MM	0.4893	4.23497e4	1442.57593	100.0000



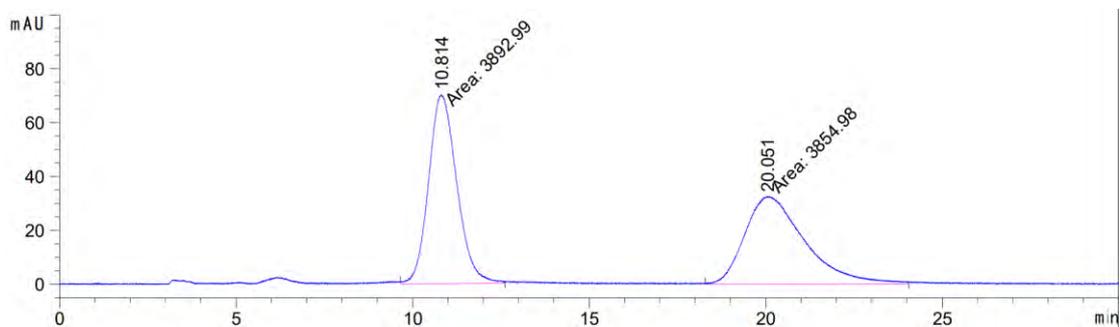
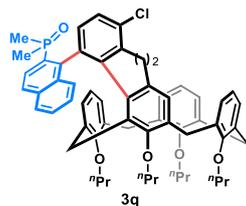
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.184	MM	2.2129	2351.39233	17.70999	50.3113
2	57.315	MM	2.8416	2322.29736	13.62091	49.6887



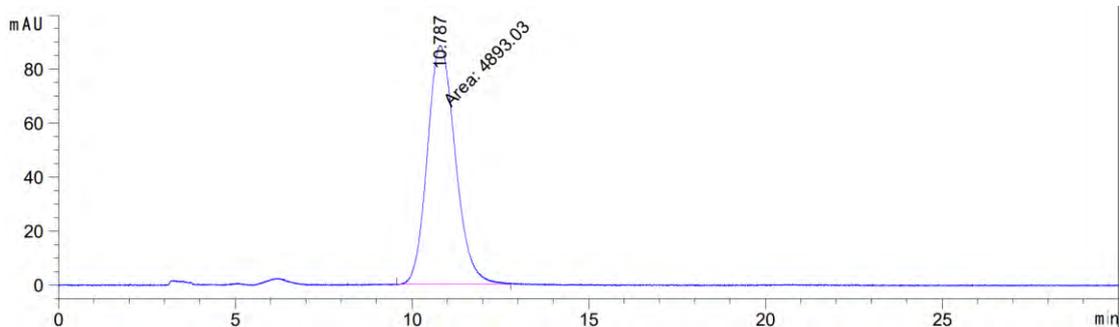
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.078	MM	2.4193	3730.45801	25.69934	100.0000



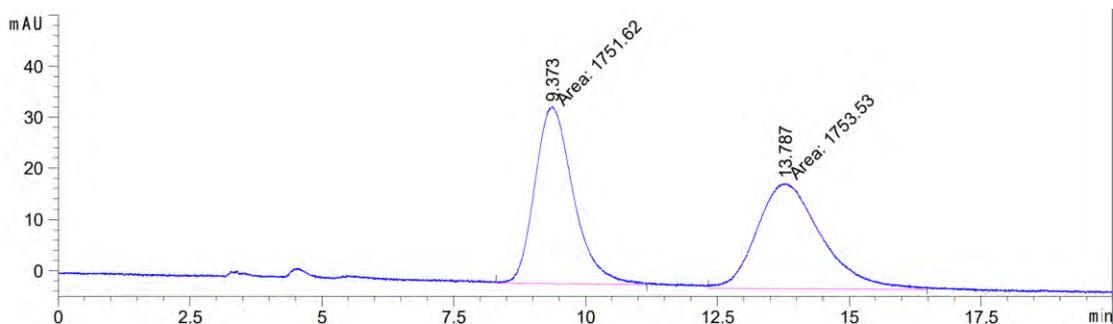
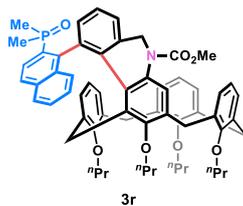
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.814	MM	0.9240	3892.99365	70.21750	50.2453
2	20.051	MM	1.9687	3854.97900	32.63496	49.7547



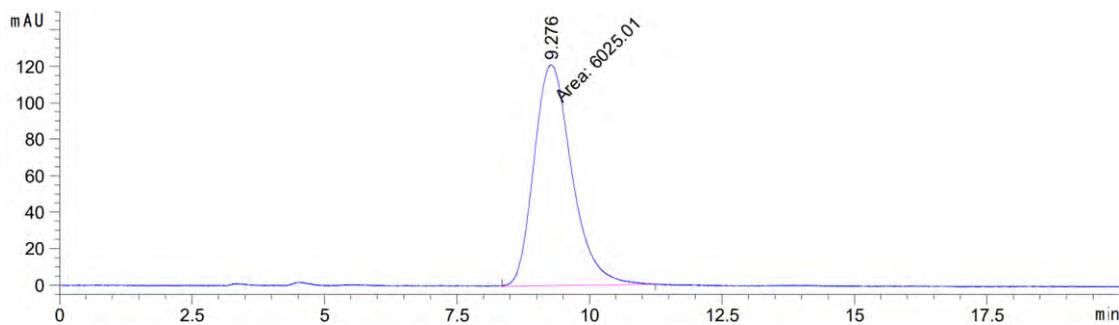
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.787	MM	0.9199	4893.02686	88.64822	100.0000



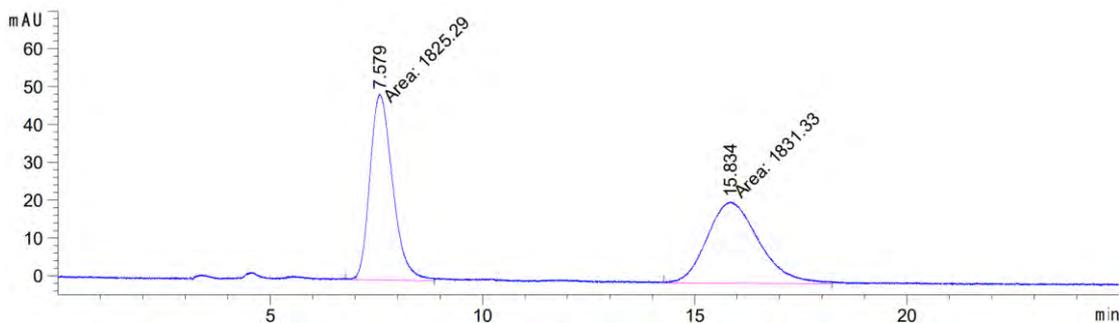
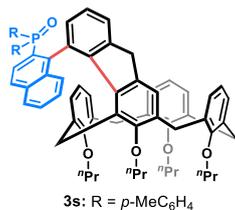
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.373	MM	0.8434	1751.62427	34.61596	49.9728
2	13.787	MM	1.4178	1753.52869	20.61275	50.0272



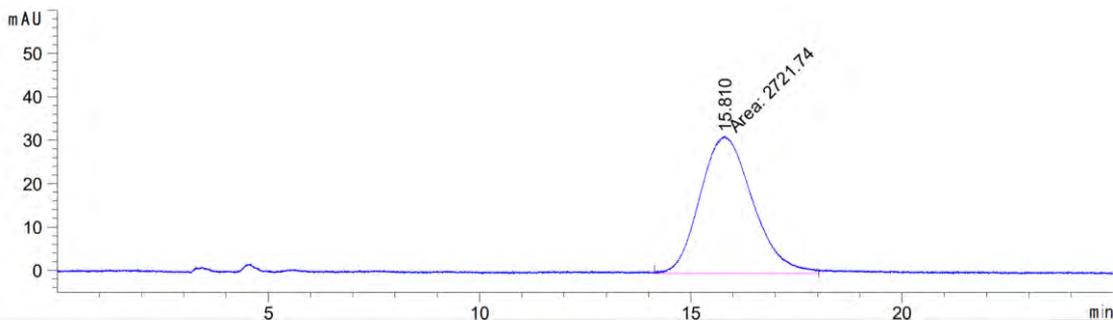
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.276	MM	0.8274	6025.00635	121.37015	100.0000



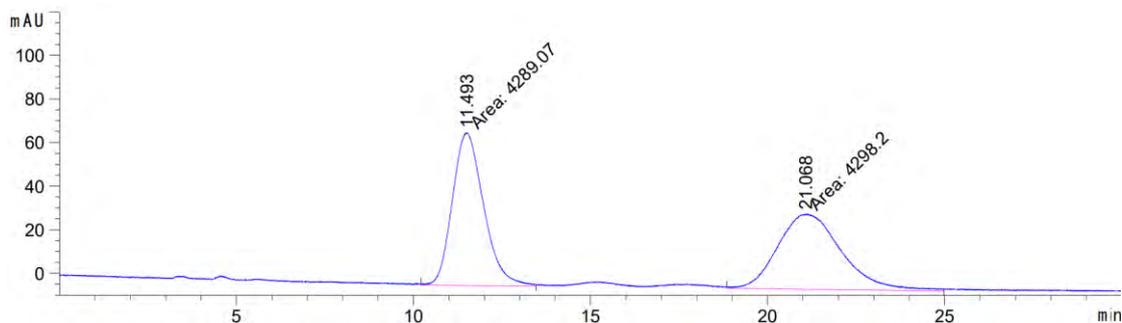
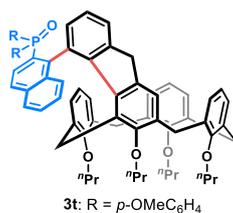
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.579	MM	0.6192	1825.28992	49.13086	49.9175
2	15.834	MM	1.4110	1831.32556	21.63222	50.0825



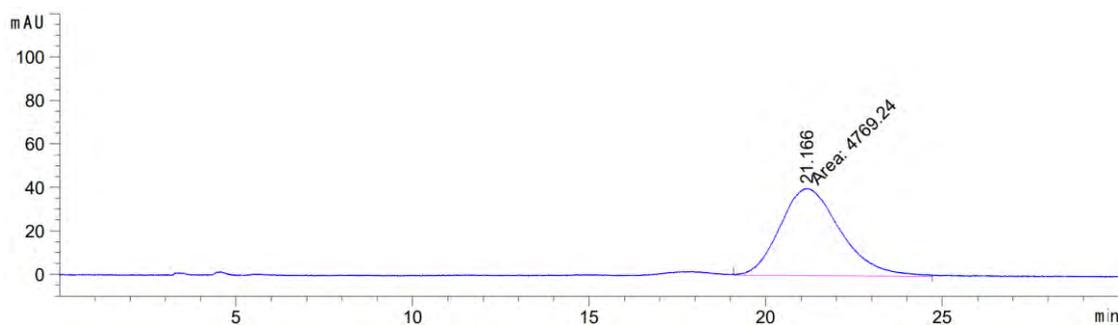
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.810	MM	1.4359	2721.73828	31.59082	100.0000



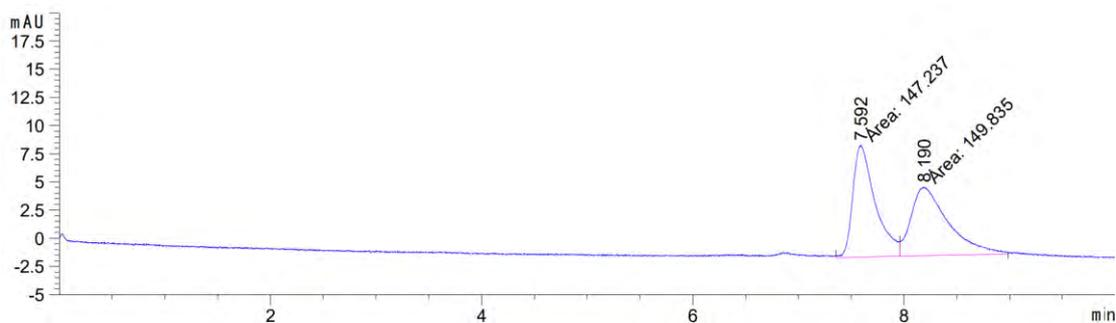
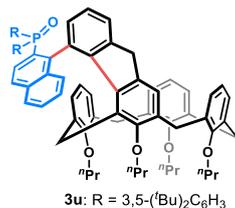
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.493	MM	1.0207	4289.06982	70.03417	49.9469
2	21.068	MM	2.0732	4298.19531	34.55340	50.0531



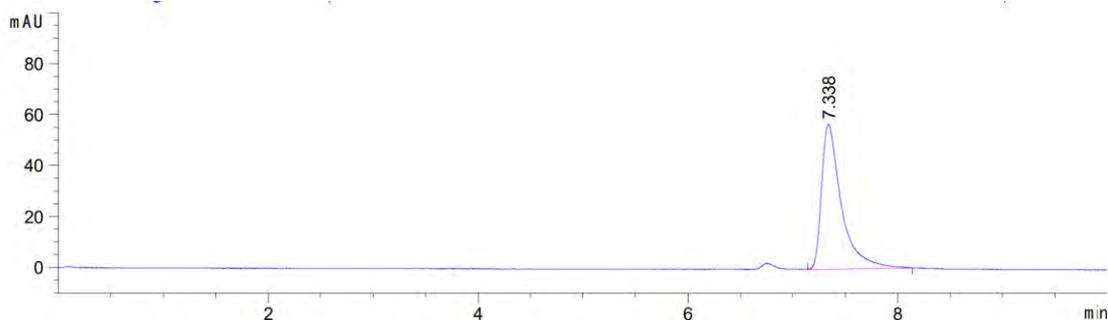
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.166	MM	1.9806	4769.24072	40.13384	100.0000



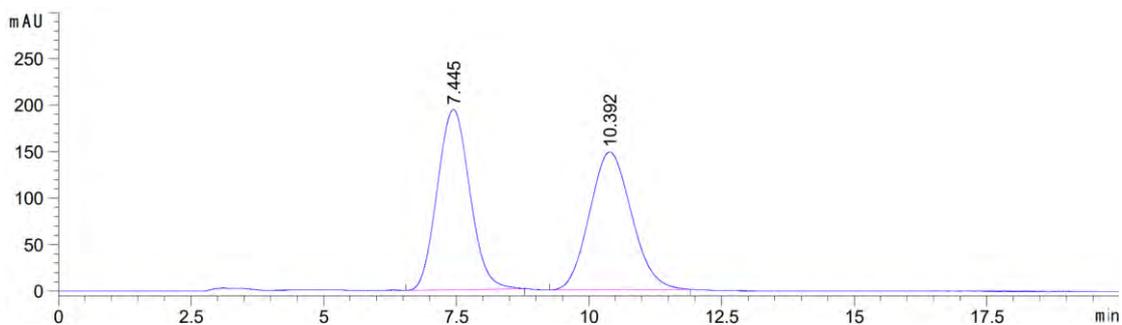
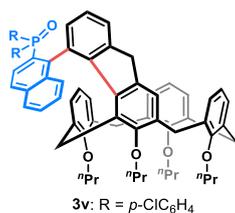
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.592	MF	0.2474	147.23668	9.91932	49.5626
2	8.190	FM	0.4099	149.83525	6.09167	50.4374



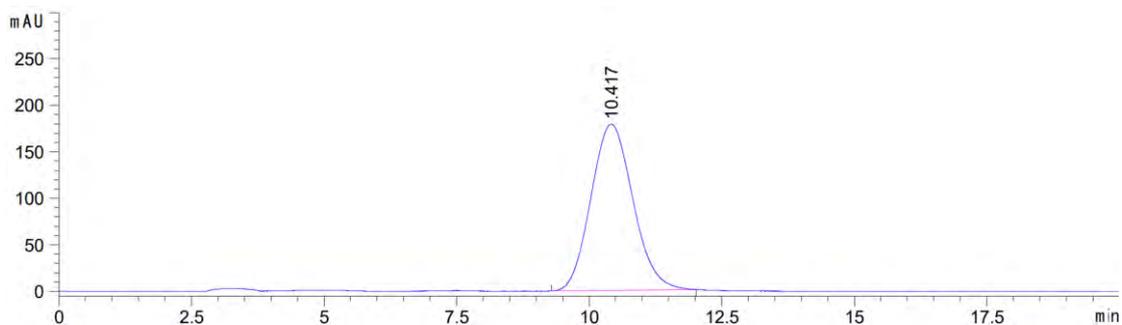
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.338	BV R	0.1792	743.45325	56.78891	100.0000



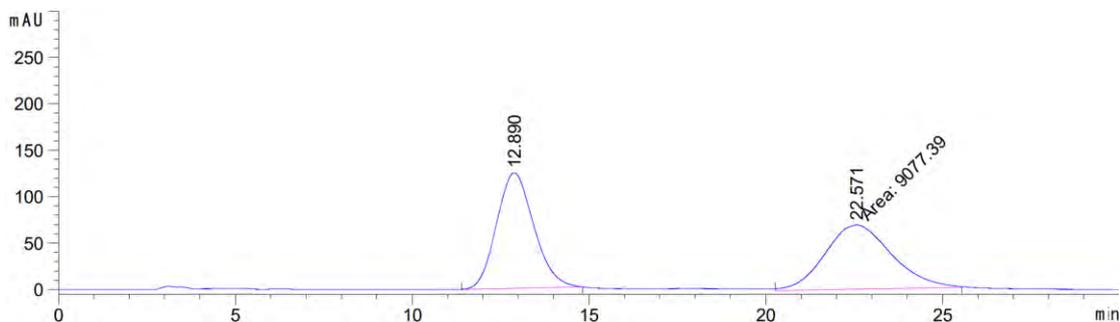
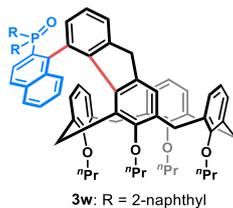
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.445	VV R	0.4996	8274.30957	194.01436	50.3303
2	10.392	VV R	0.6442	8165.69531	148.35240	49.6697



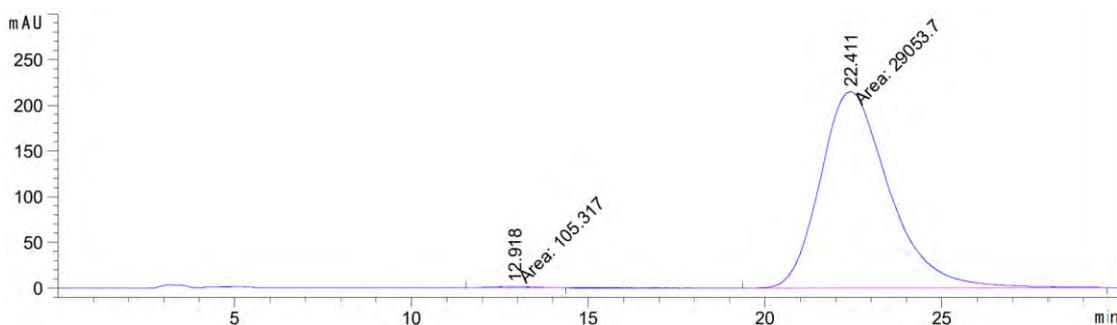
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.417	BV R	0.6444	9836.58496	178.78038	100.0000



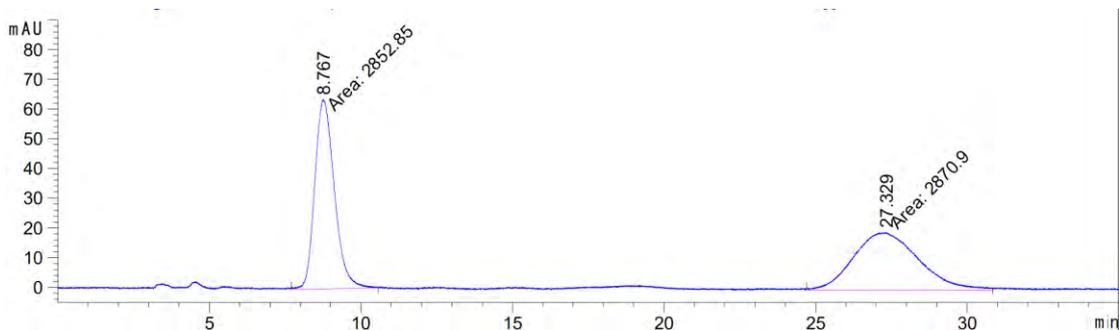
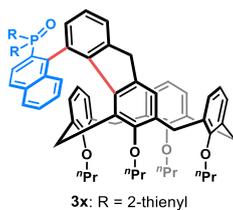
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.890	VV R	0.8557	9116.03223	124.57632	50.1062
2	22.571	MM	2.1832	9077.38574	69.29701	49.8938



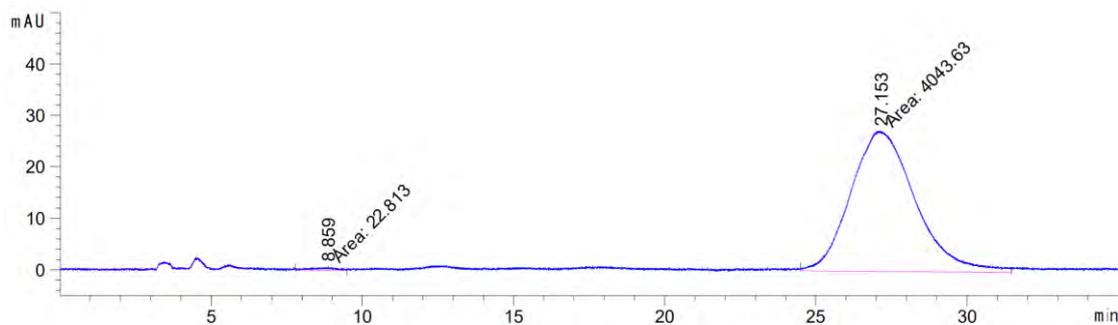
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.918	MM	1.2413	105.31722	1.41406	0.3612
2	22.411	MM	2.2547	2.90537e4	214.76195	99.6388



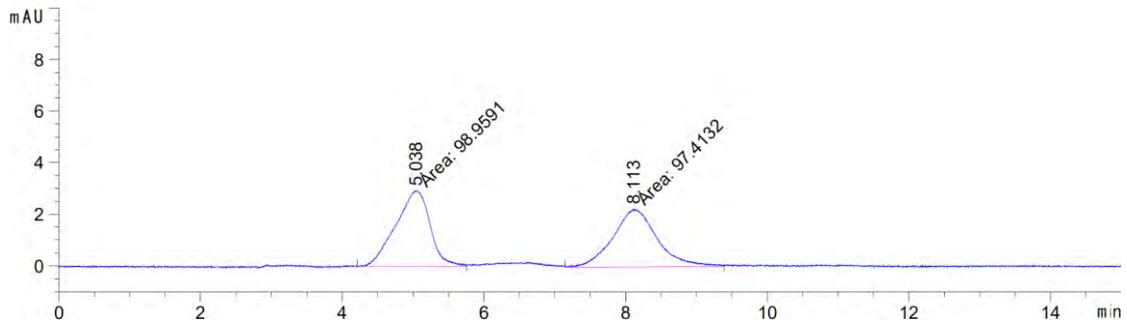
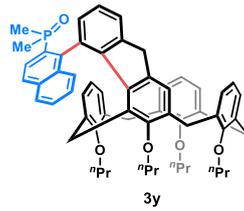
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.767	MM	0.7474	2852.85400	63.61478	49.8424
2	27.329	MM	2.4775	2870.89648	19.31312	50.1576



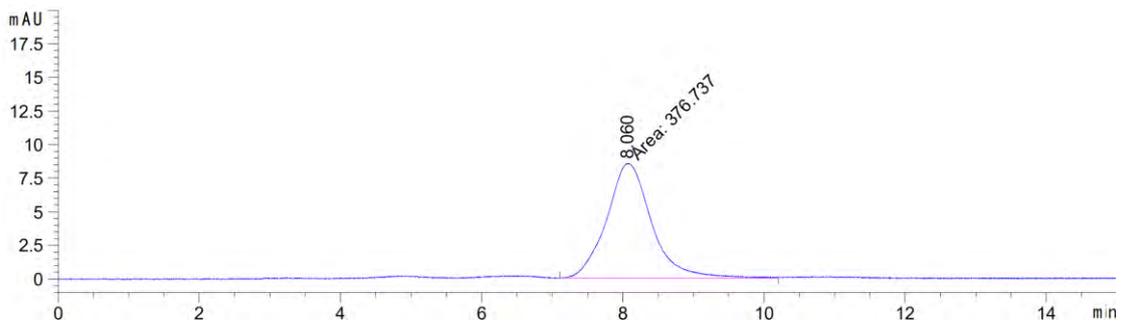
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.859	MM	0.5852	22.81298	6.49773e-1	0.5610
2	27.153	MM	2.4626	4043.62524	27.36655	99.4390



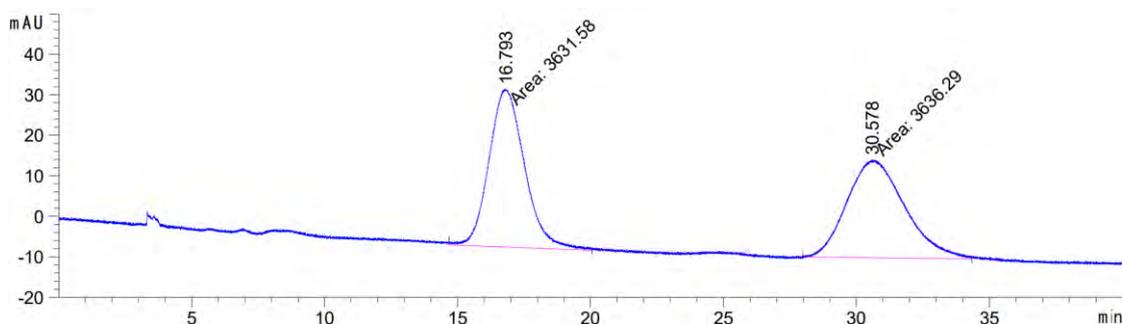
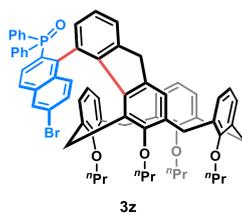
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.038	MM	0.5618	98.95909	2.93564	50.3936
2	8.113	MM	0.7229	97.41316	2.24577	49.6064



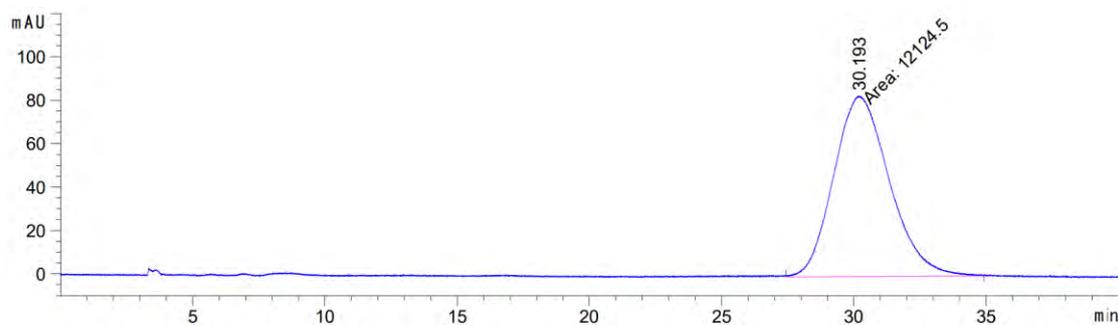
Signal 1: DAD1 E, Sig=320,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.060	MM	0.7367	376.73697	8.52363	100.0000



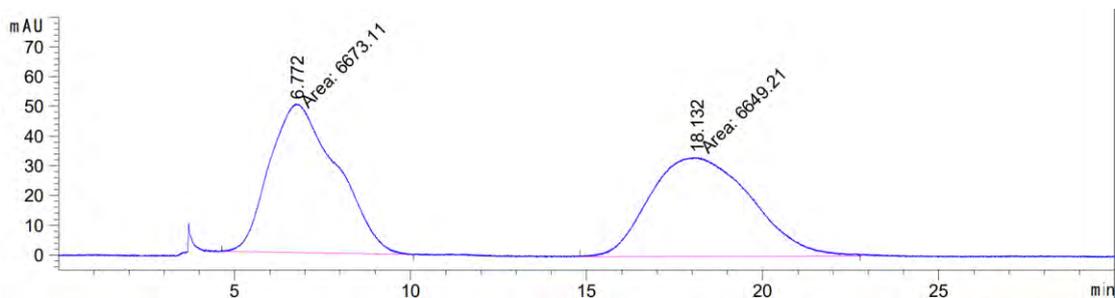
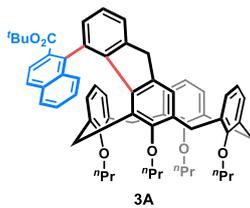
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.793	MM	1.5499	3631.57520	39.05183	49.9675
2	30.578	MM	2.4973	3636.29224	24.26818	50.0325



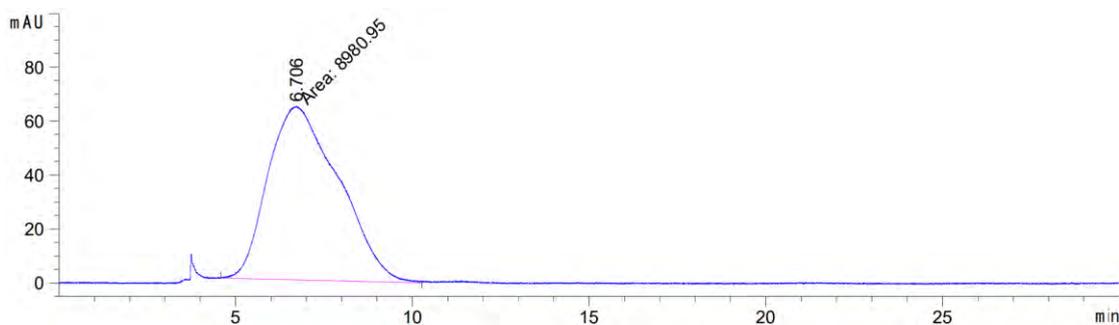
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.193	MM	2.4274	1.21245e4	83.24802	100.0000



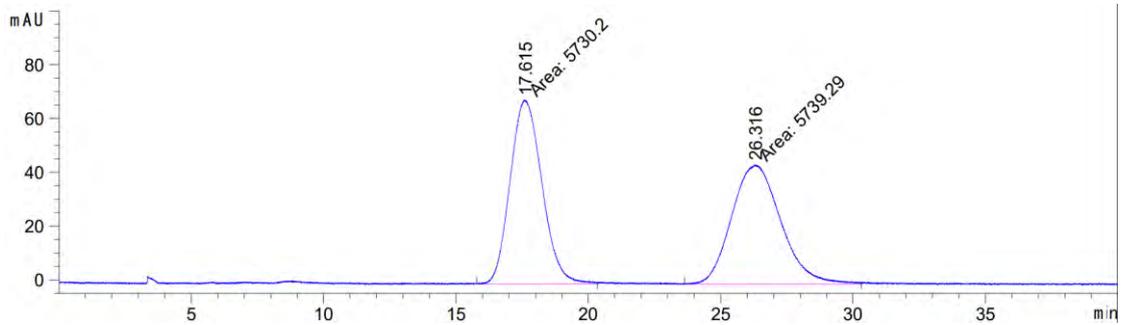
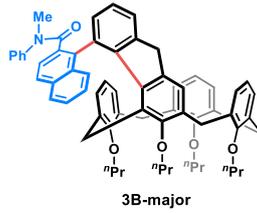
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.772	MM	2.2210	6673.10791	50.07680	50.0897
2	18.132	MM	3.3348	6649.20557	33.23099	49.9103



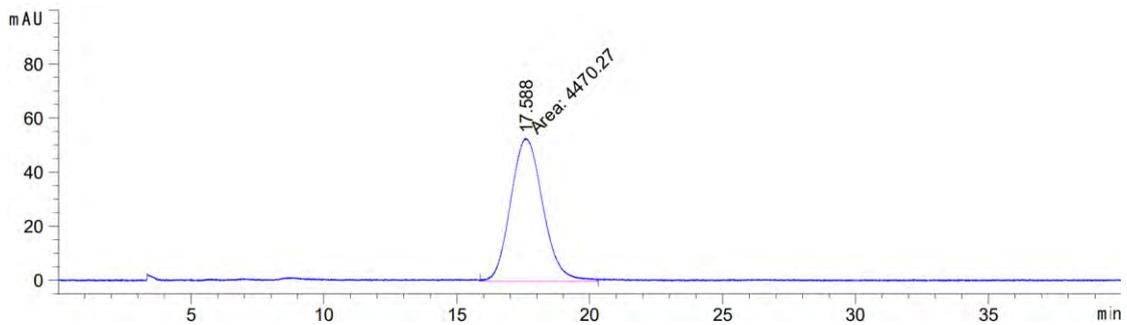
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.706	MM	2.3260	8980.94824	64.35223	100.0000



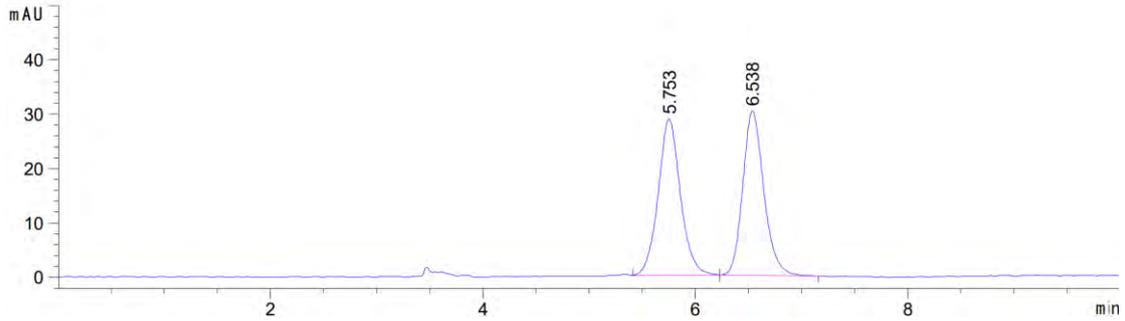
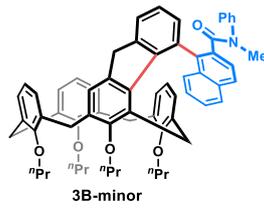
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.615	MM	1.3936	5730.20459	68.52858	49.9604
2	26.316	MM	2.1484	5739.29004	44.52426	50.0396



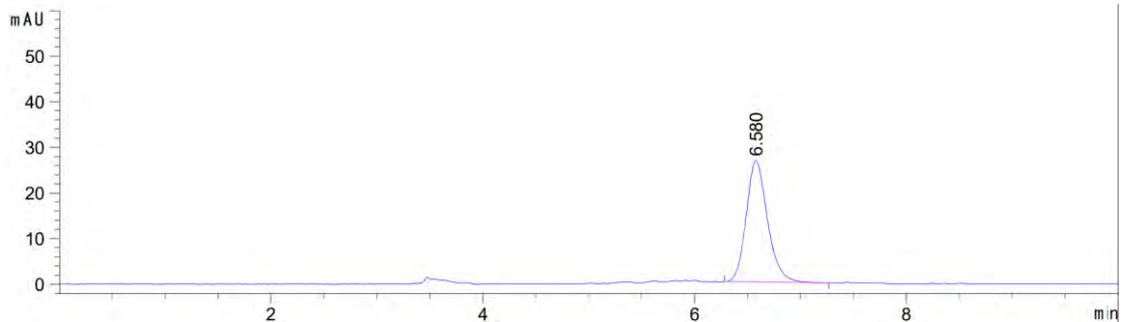
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.588	MM	1.4059	4470.27393	52.99489	100.0000



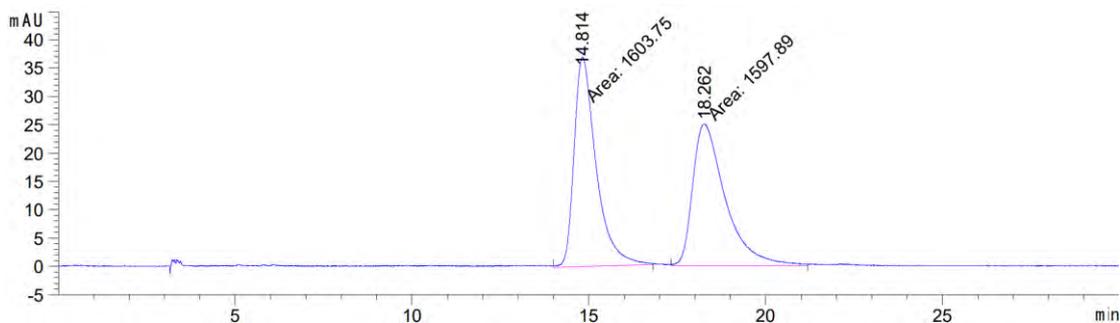
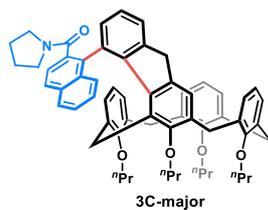
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.753	BB	0.2215	416.94666	28.69240	49.9521
2	6.538	BB	0.2112	417.74579	30.24008	50.0479



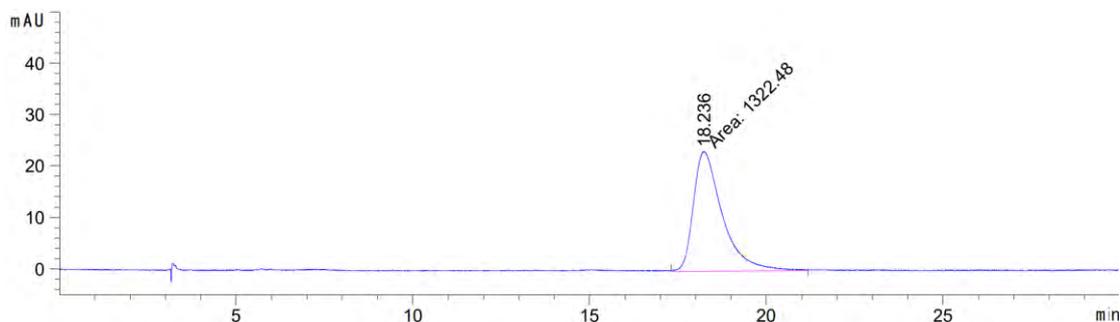
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.580	BB	0.2098	373.90060	26.62971	100.0000



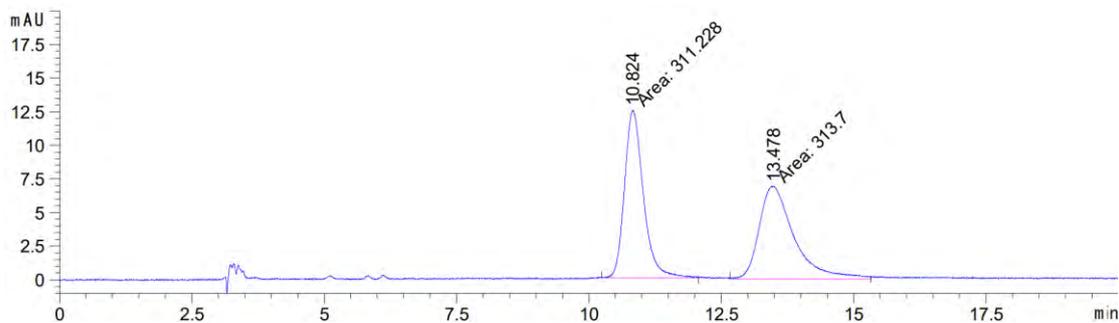
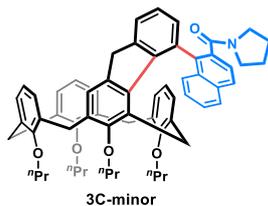
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.814	MM	0.7235	1603.74670	36.94180	50.0915
2	18.262	MM	1.0653	1597.88879	24.99791	49.9085



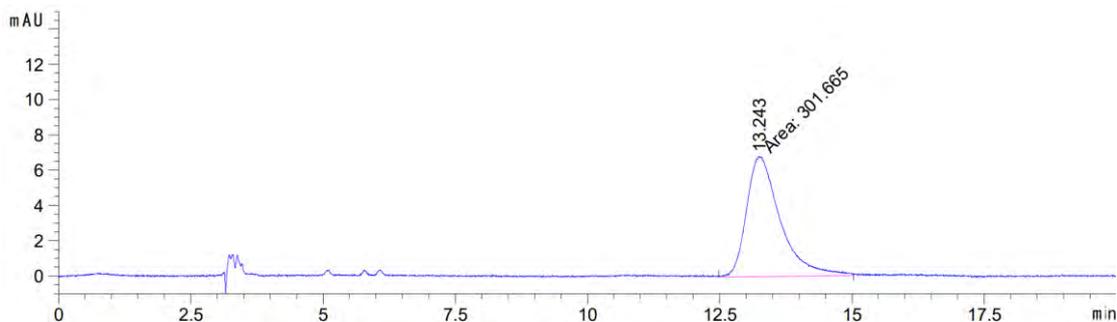
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.236	MM	0.9477	1322.47571	23.25857	100.0000



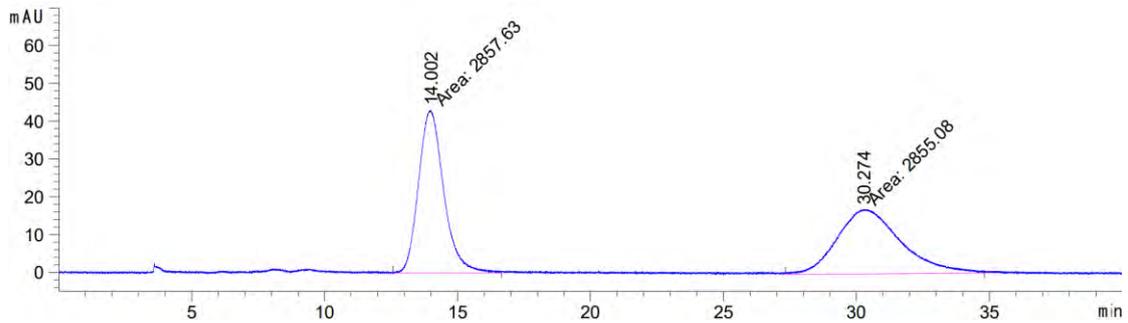
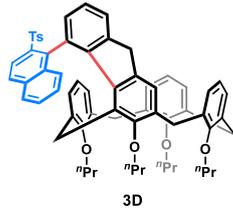
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.824	MM	0.4156	311.22769	12.47969	49.8022
2	13.478	MM	0.7578	313.69992	6.89952	50.1978



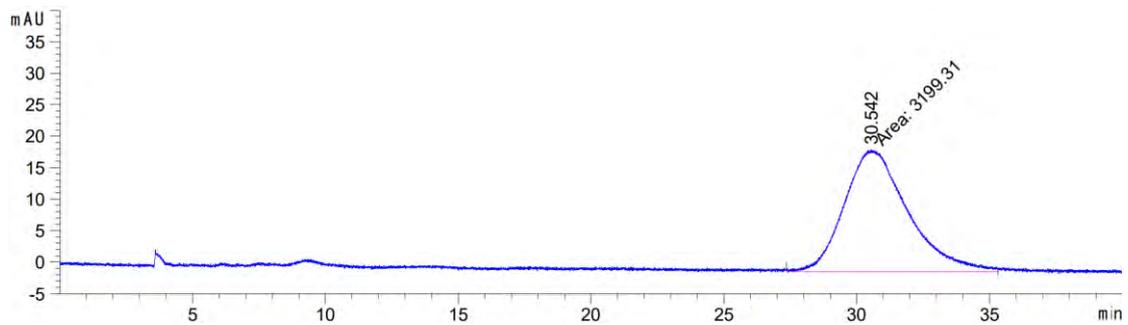
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.243	MM	0.7396	301.66486	6.79793	100.0000



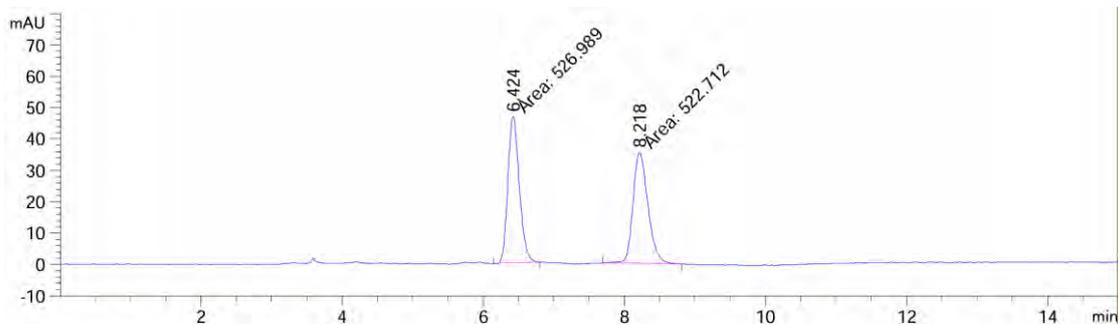
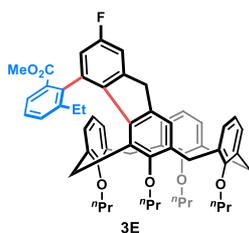
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.002	MM	1.1019	2857.62720	43.22298	50.0223
2	30.274	MM	2.7685	2855.07568	17.18773	49.9777



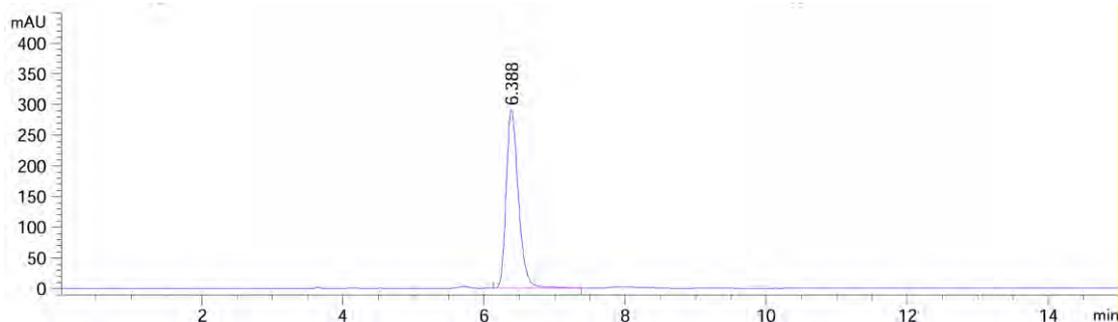
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.542	MM	2.7502	3199.31274	19.38856	100.0000



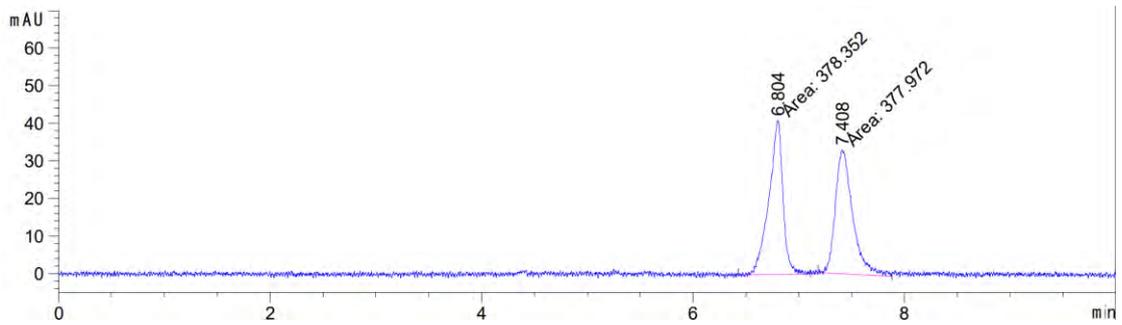
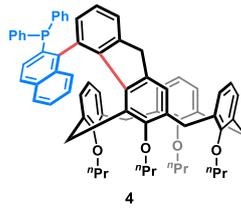
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.424	MM	0.1884	526.98914	46.62738	50.2037
2	8.218	MM	0.2456	522.71198	35.47049	49.7963



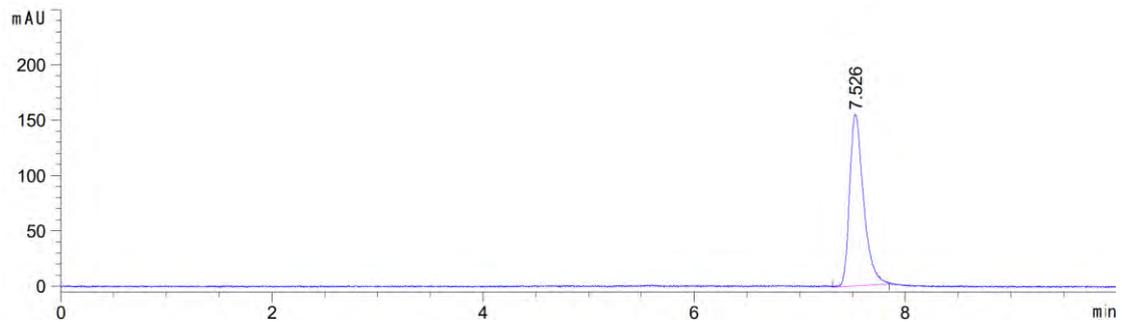
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.388	BB	0.1855	3521.07861	290.32388	100.0000



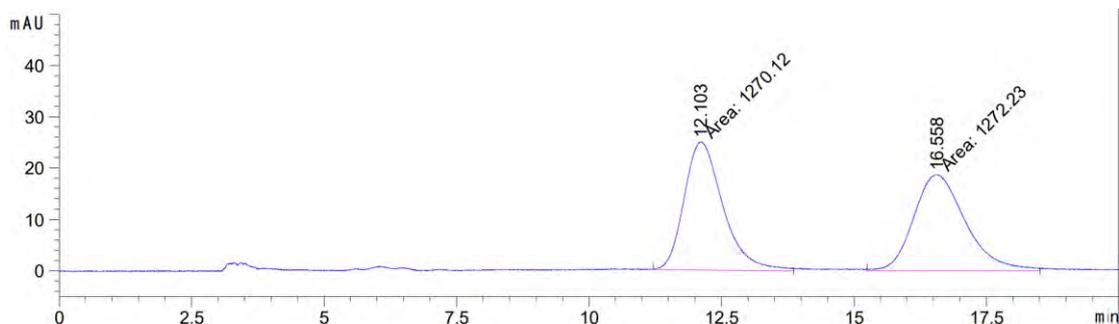
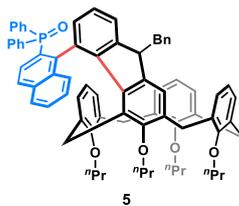
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.804	MM	0.1542	378.35150	40.90284	50.0251
2	7.408	MM	0.1910	377.97229	32.97613	49.9749



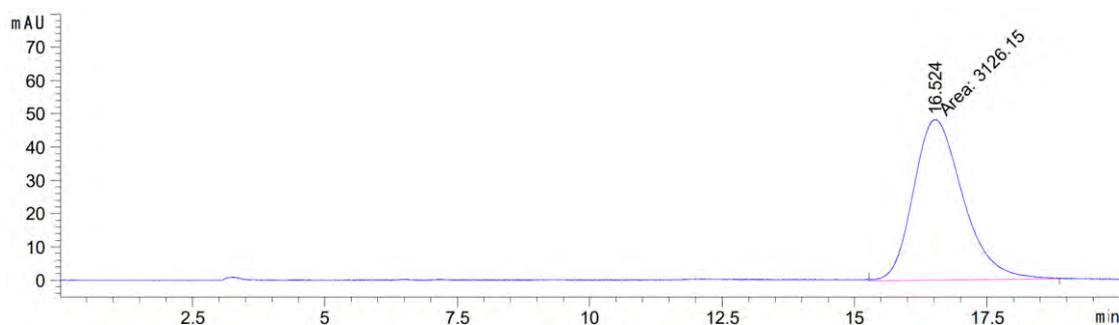
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.526	VV R	0.1123	1426.45117	154.44365	100.0000



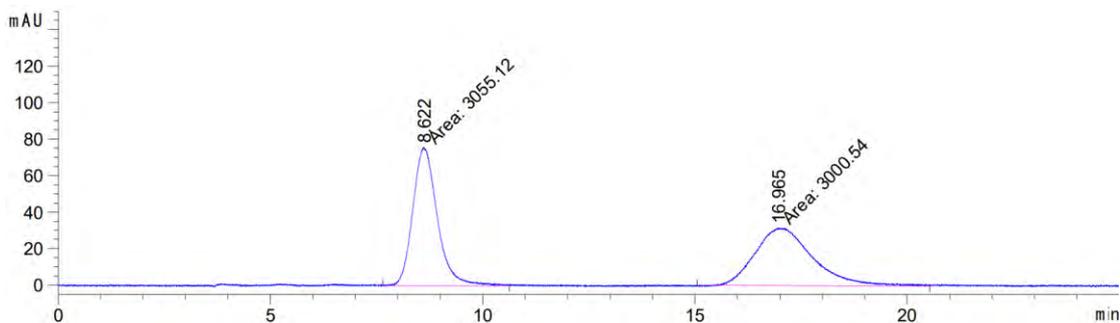
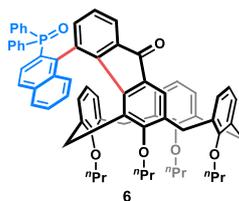
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.103	MM	0.8489	1270.12341	24.93573	49.9585
2	16.558	MM	1.1330	1272.23486	18.71520	50.0415



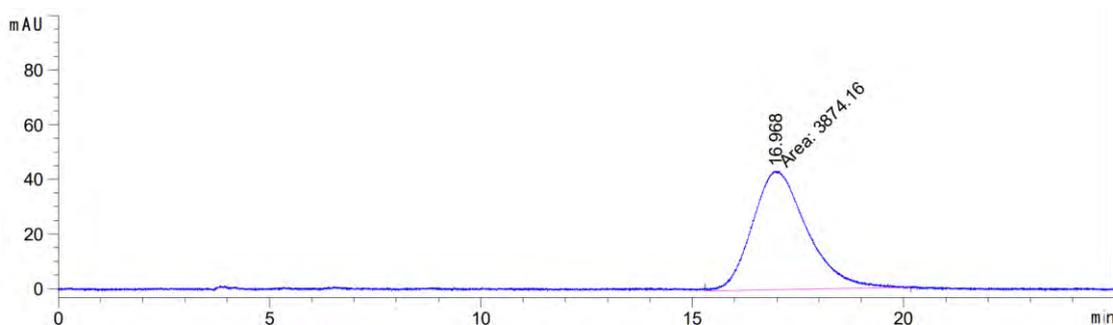
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.524	MM	1.0801	3126.15356	48.23949	100.0000



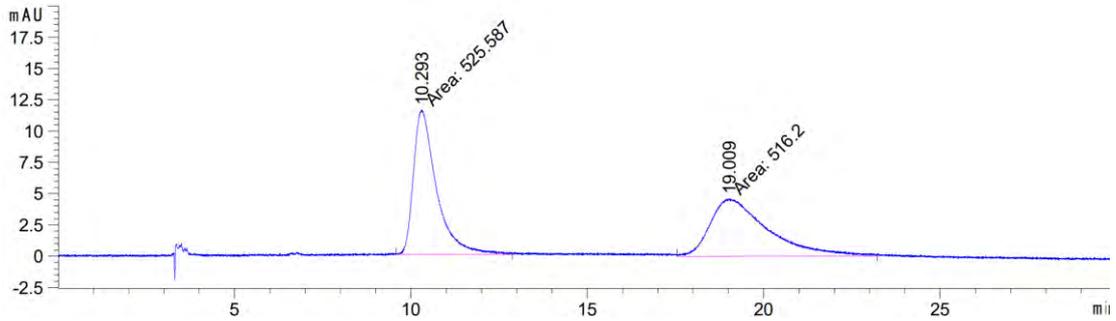
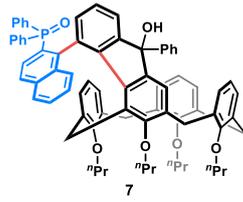
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.622	MM	0.6717	3055.11963	75.80602	50.4506
2	16.965	MM	1.5772	3000.54395	31.70709	49.5494



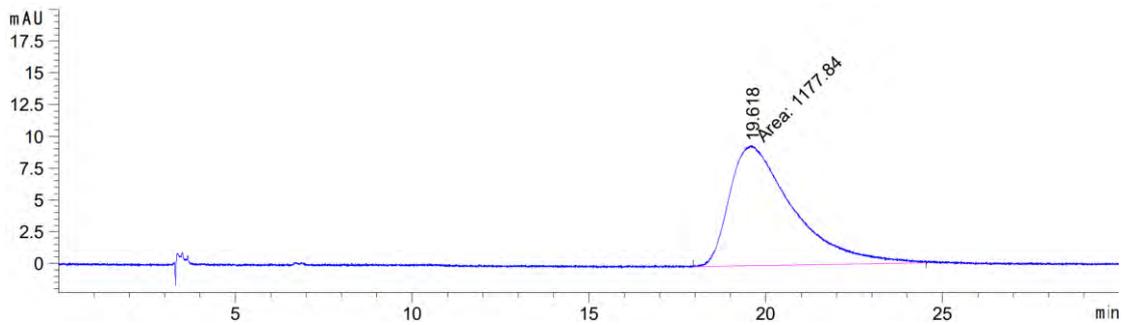
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.968	MM	1.4882	3874.15967	43.38755	100.0000



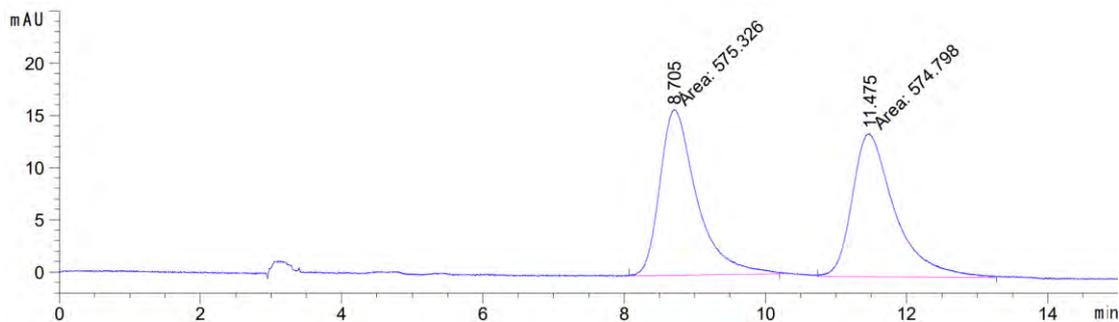
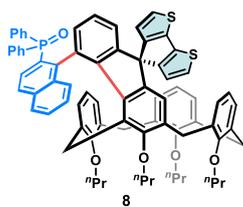
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.293	MM	0.7596	525.58740	11.53275	50.4506
2	19.009	MM	1.8762	516.19977	4.58550	49.5494



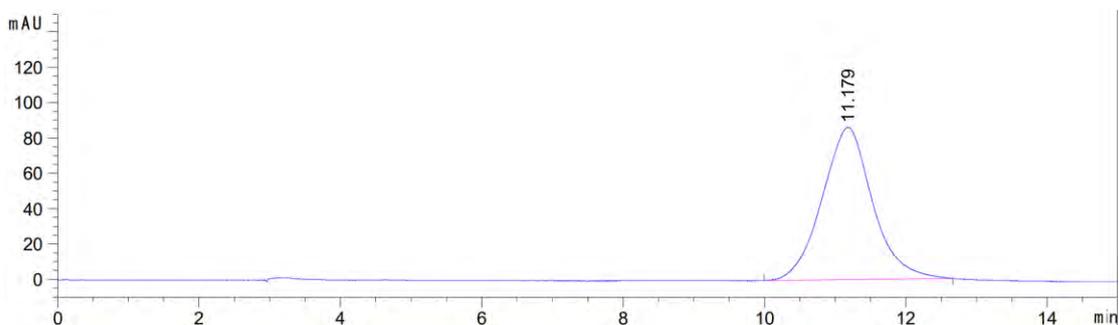
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.618	MM	2.0722	1177.83618	9.47347	100.0000



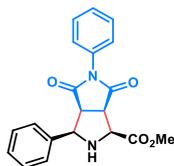
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.705	MM	0.6059	575.32648	15.82673	50.0230
2	11.475	MM	0.6980	574.79816	13.72394	49.9770

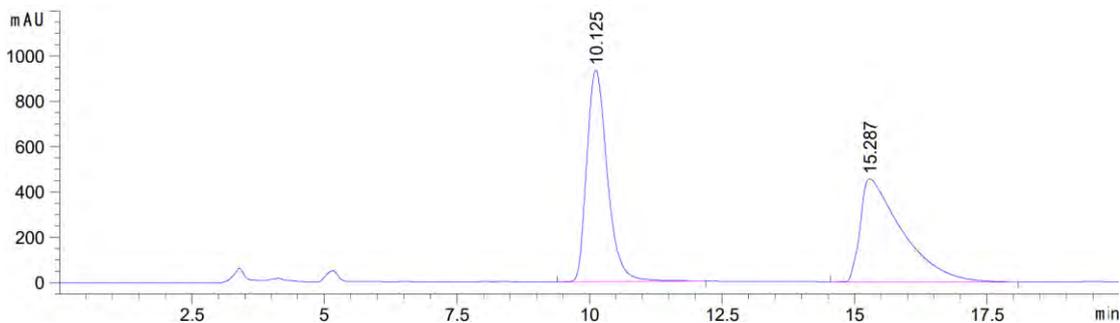


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.179	VB	0.5815	4269.68799	86.10563	100.0000

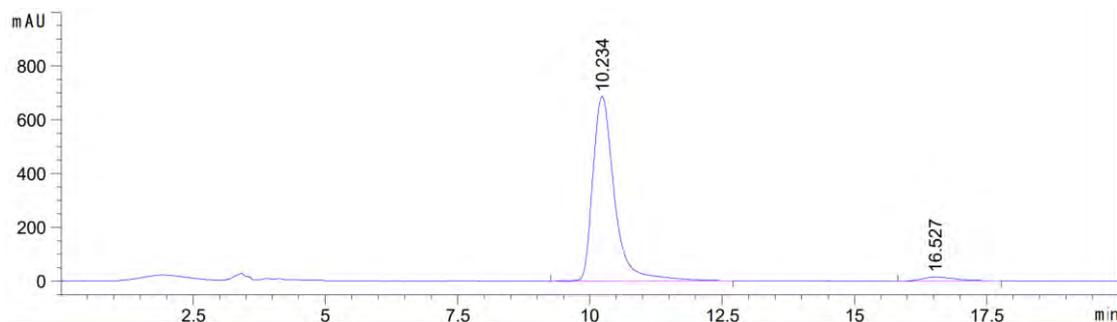


11



Signal 1: DAD1 C, Sig=210,4 Ref=360,100

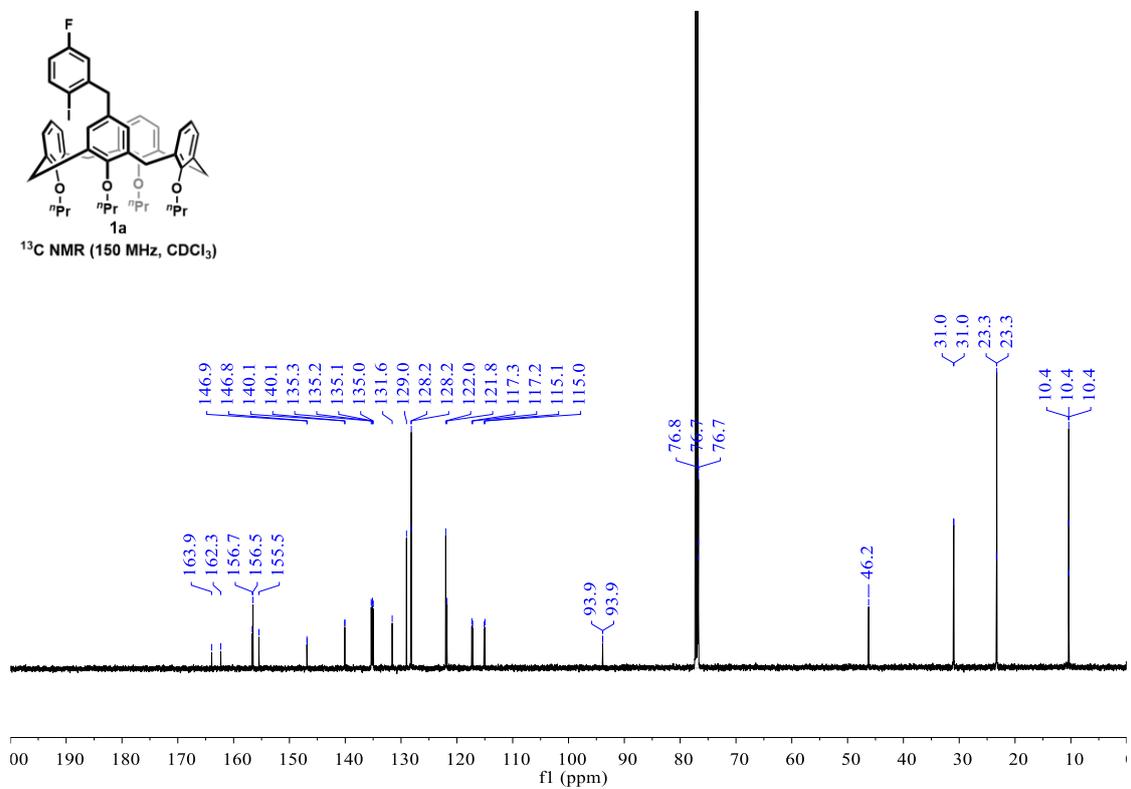
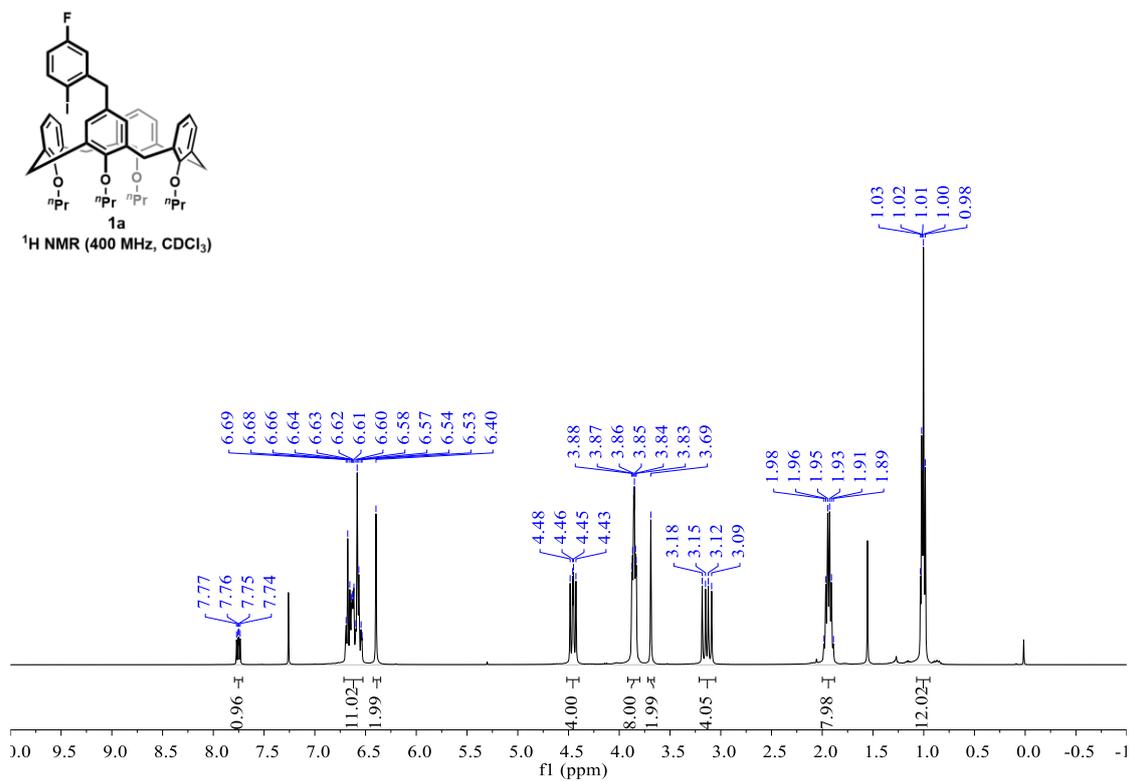
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.125	BB	0.4179	2.53319e4	935.69214	50.2792
2	15.287	BB	0.7034	2.50506e4	455.62064	49.7208

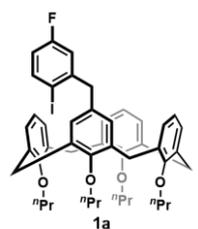


Signal 1: DAD1 C, Sig=210,4 Ref=360,100

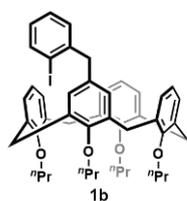
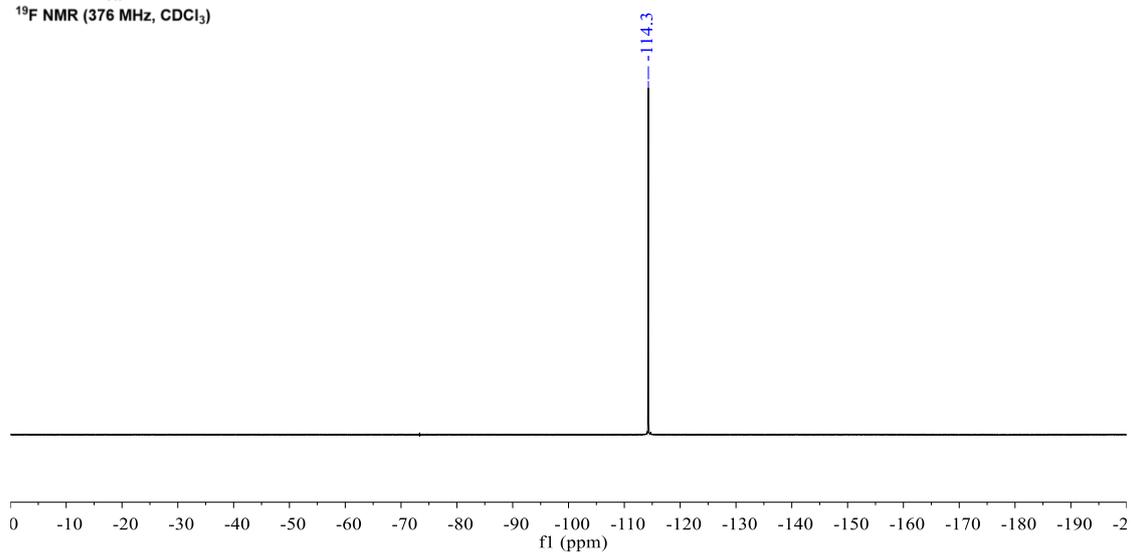
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.234	BB	0.4346	1.95681e4	686.48676	96.6995
2	16.527	BV R	0.5284	667.89294	14.93970	3.3005

9. NMR spectra

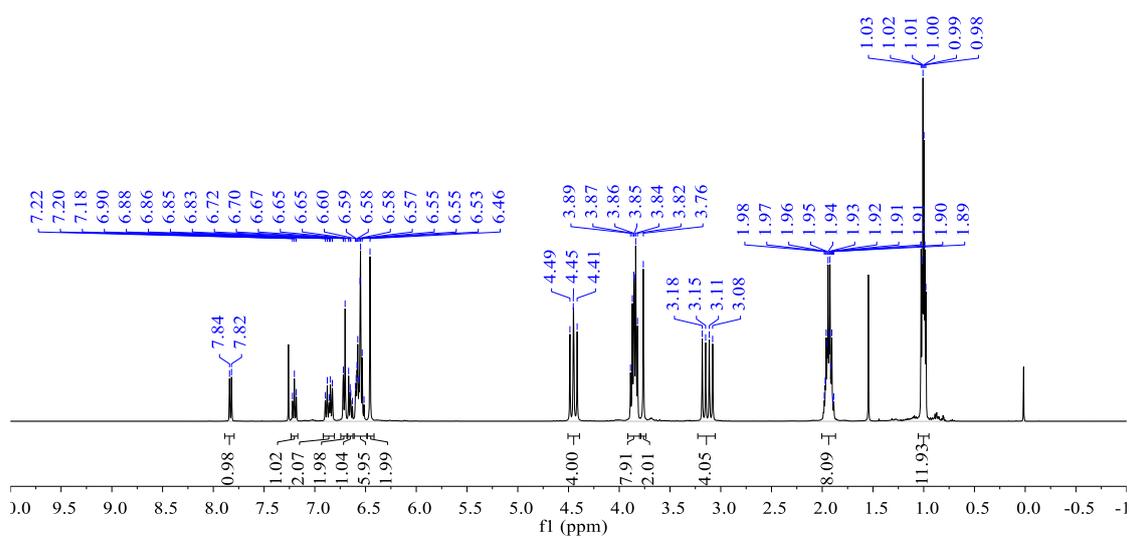


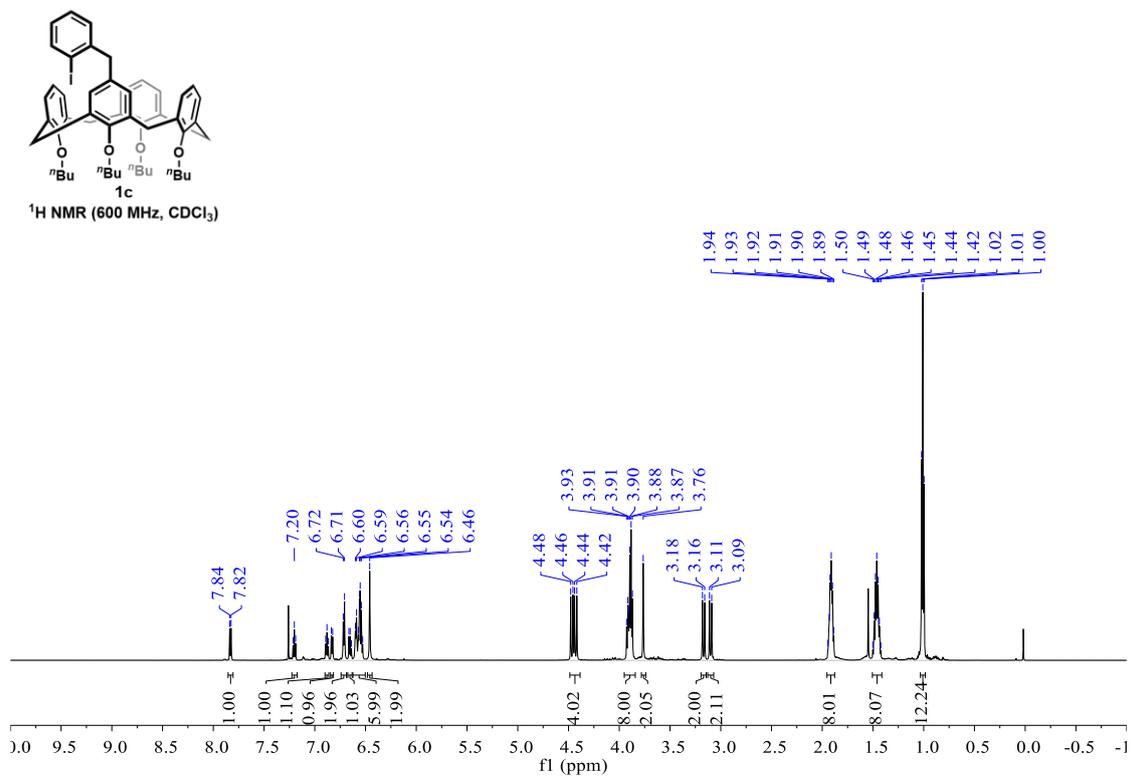
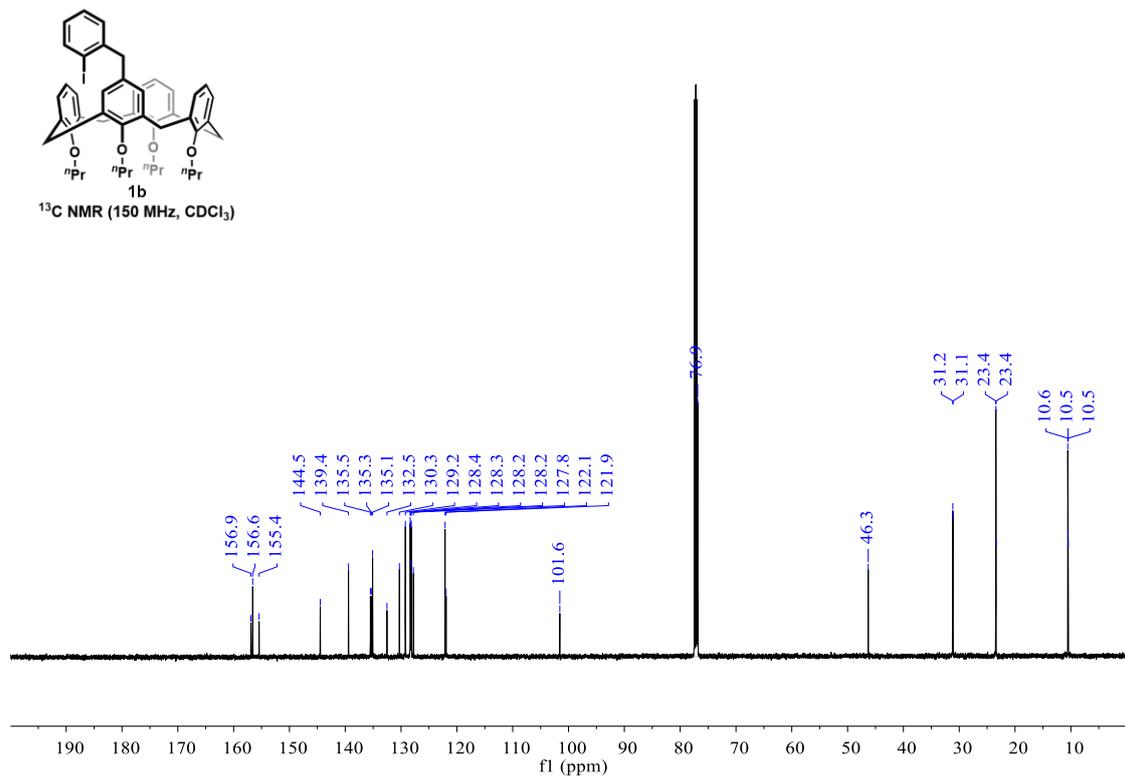


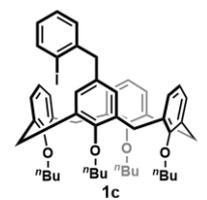
¹⁹F NMR (376 MHz, CDCl₃)



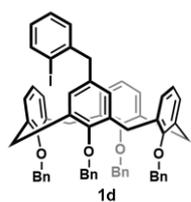
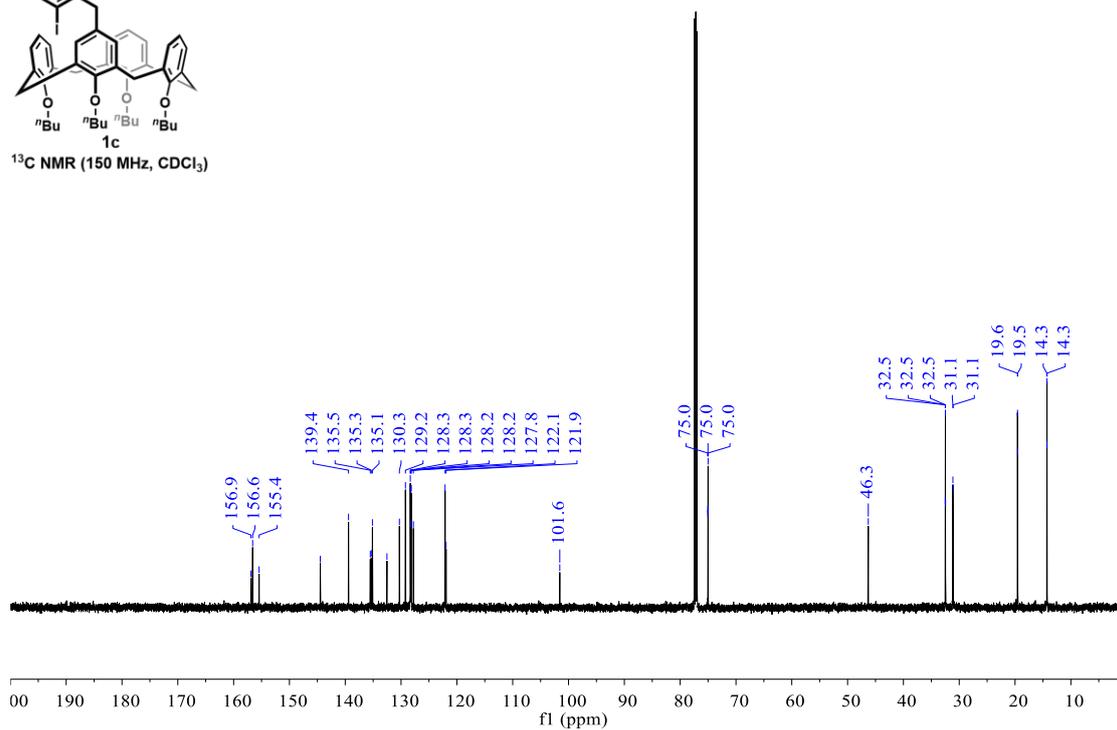
¹H NMR (400 MHz, CDCl₃)



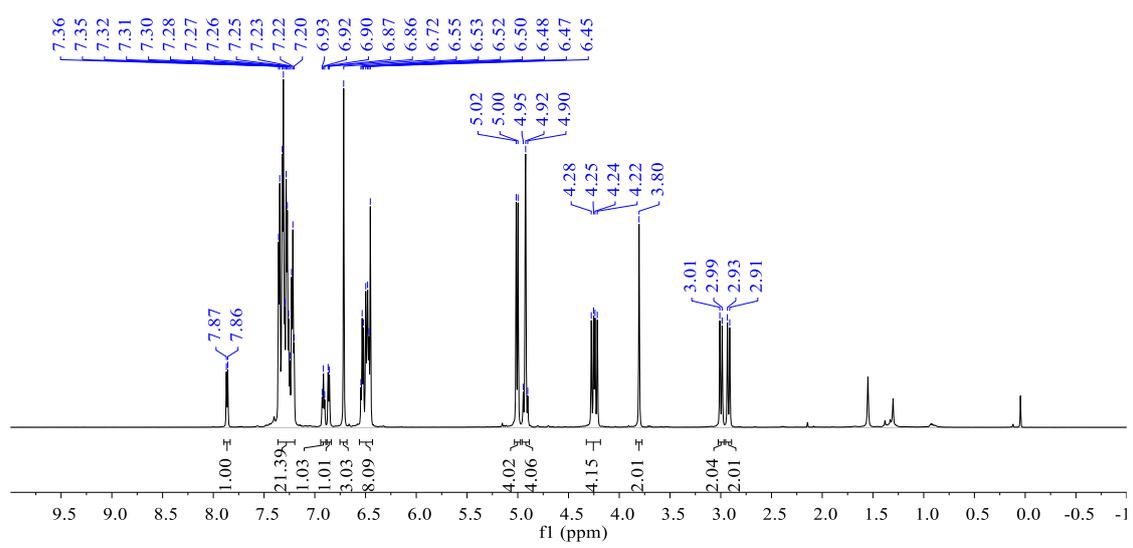


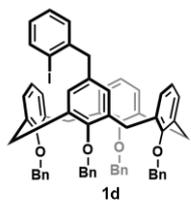


^{13}C NMR (150 MHz, CDCl_3)

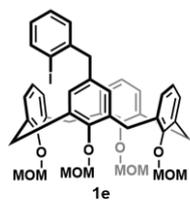
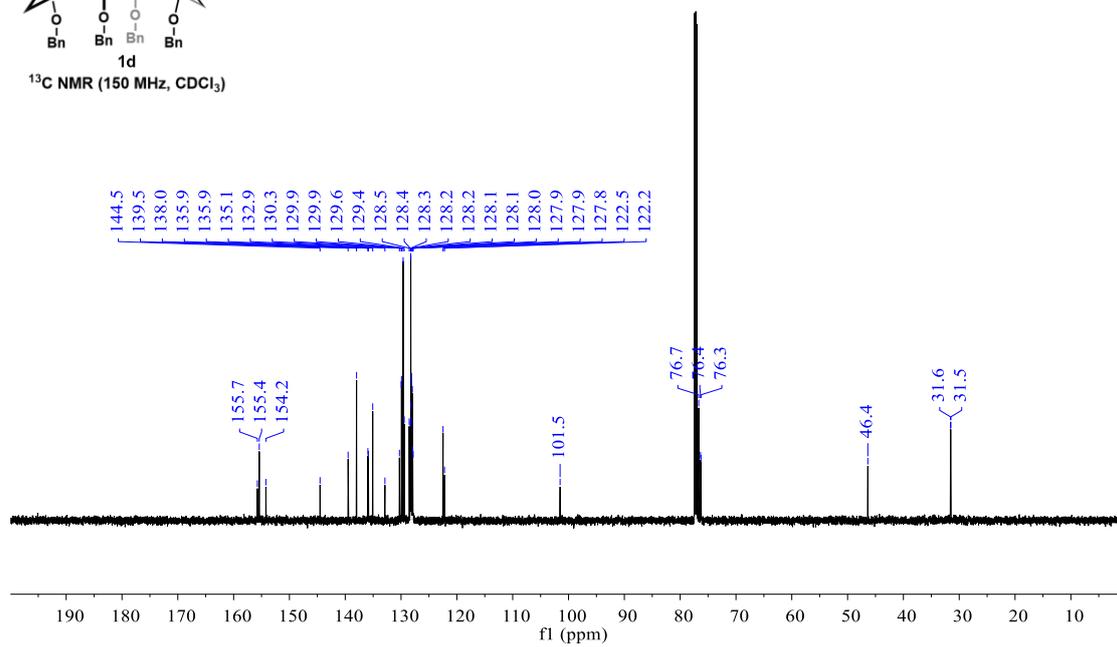


^1H NMR (600 MHz, CDCl_3)

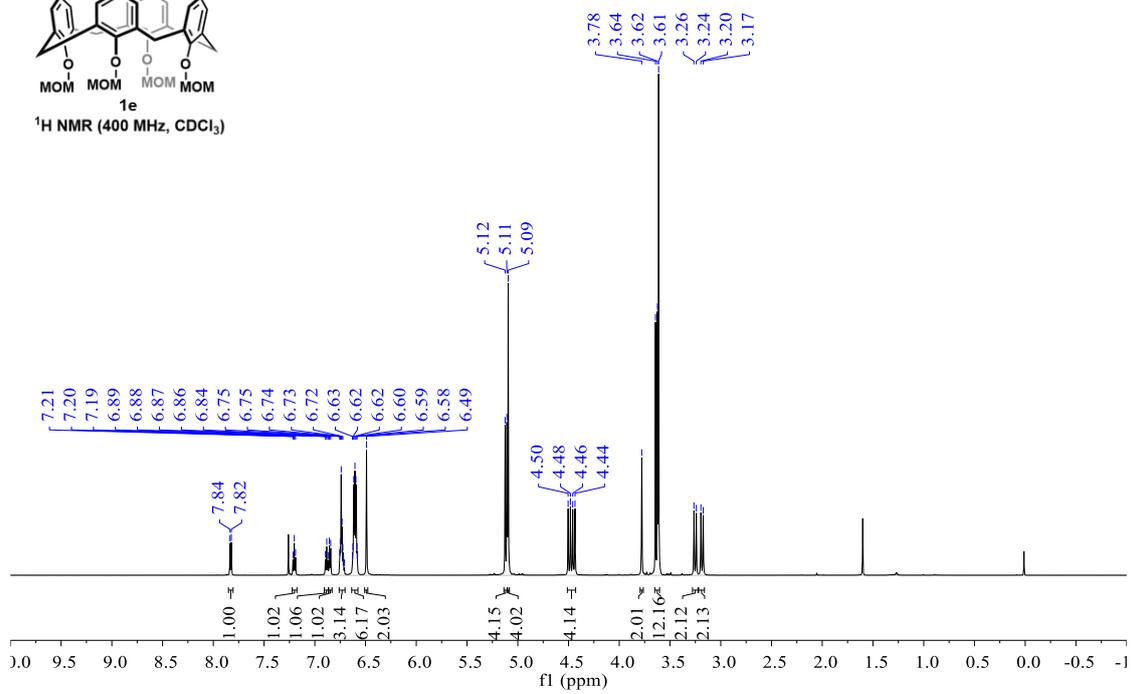


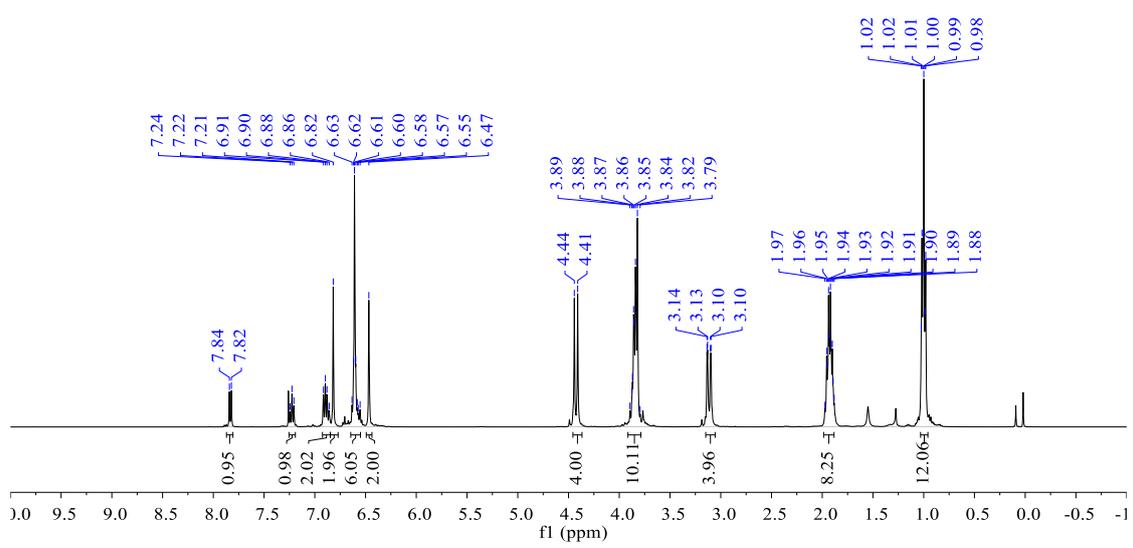
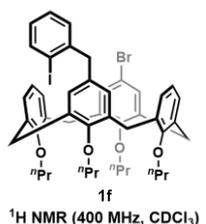
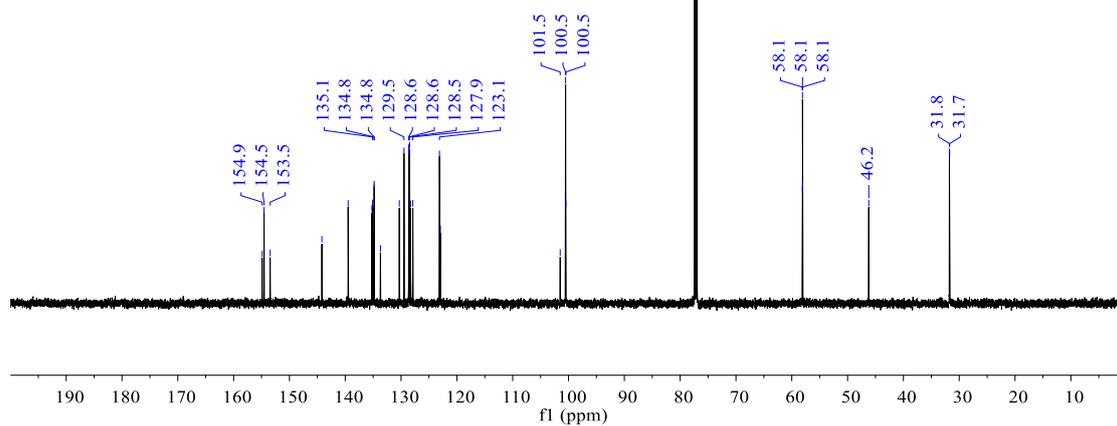
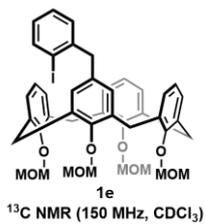


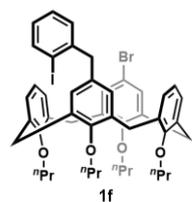
¹³C NMR (150 MHz, CDCl₃)



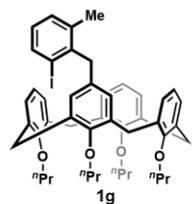
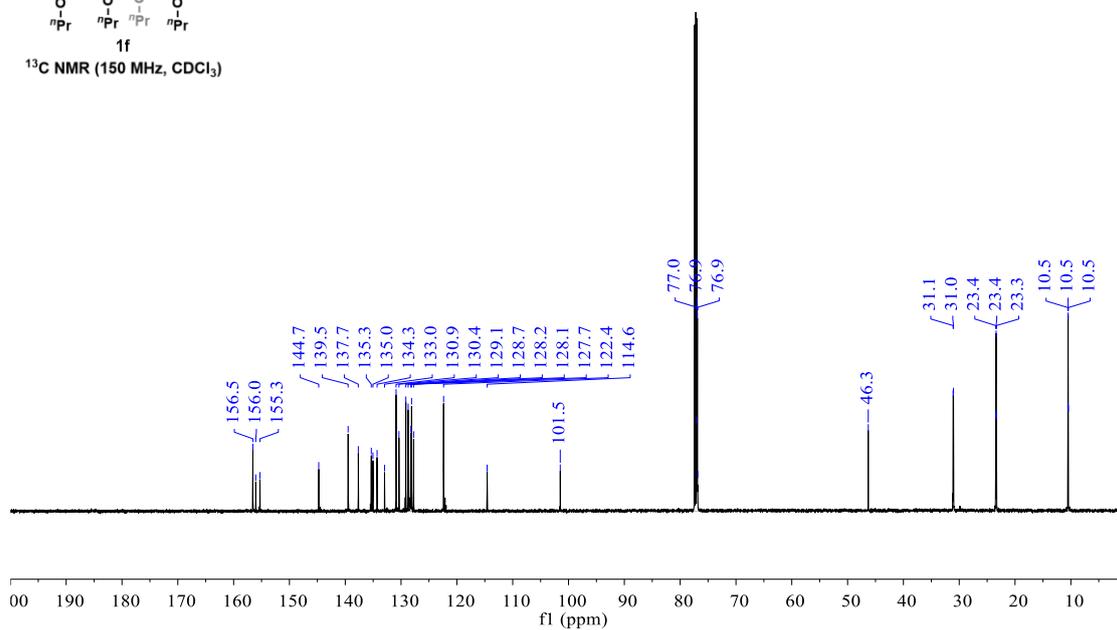
¹H NMR (400 MHz, CDCl₃)



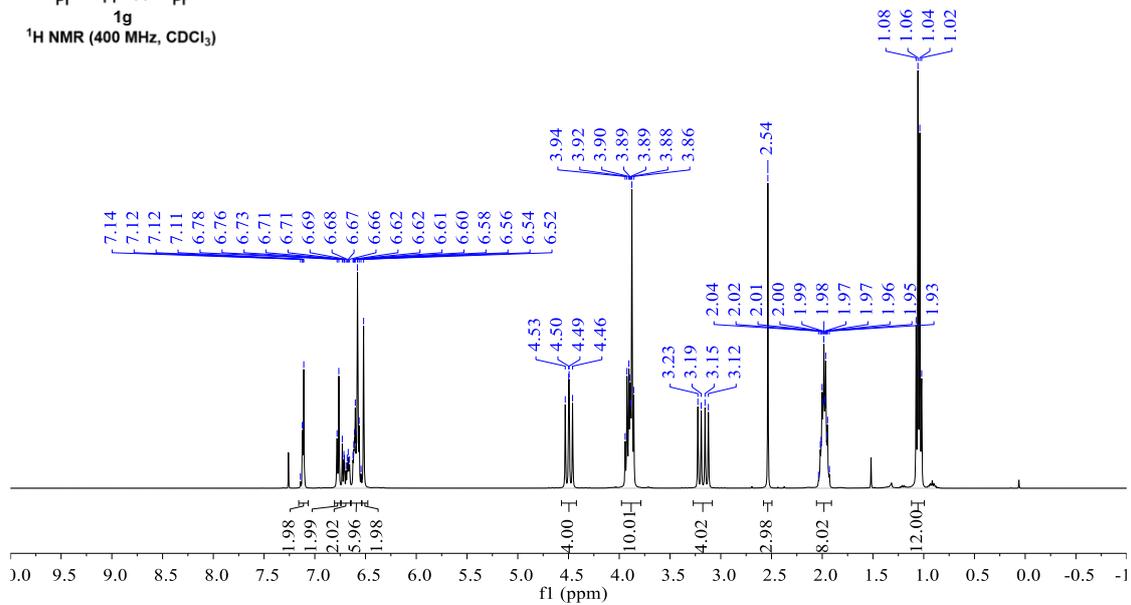


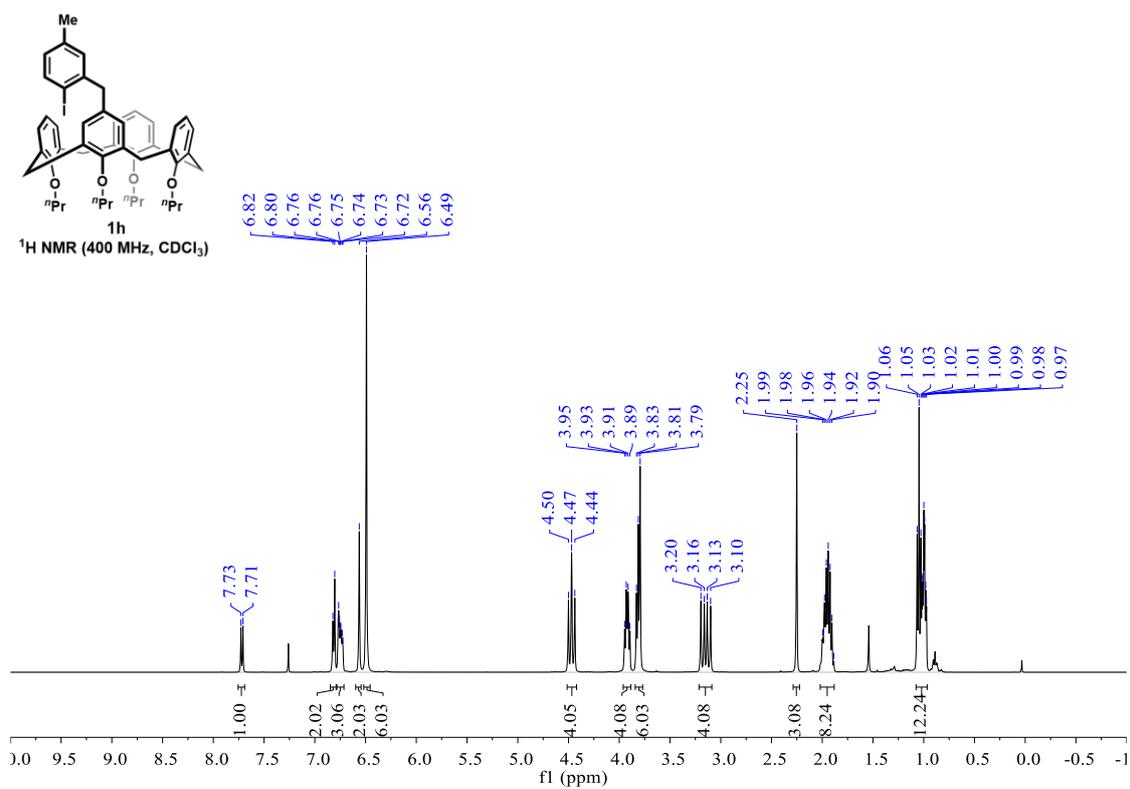
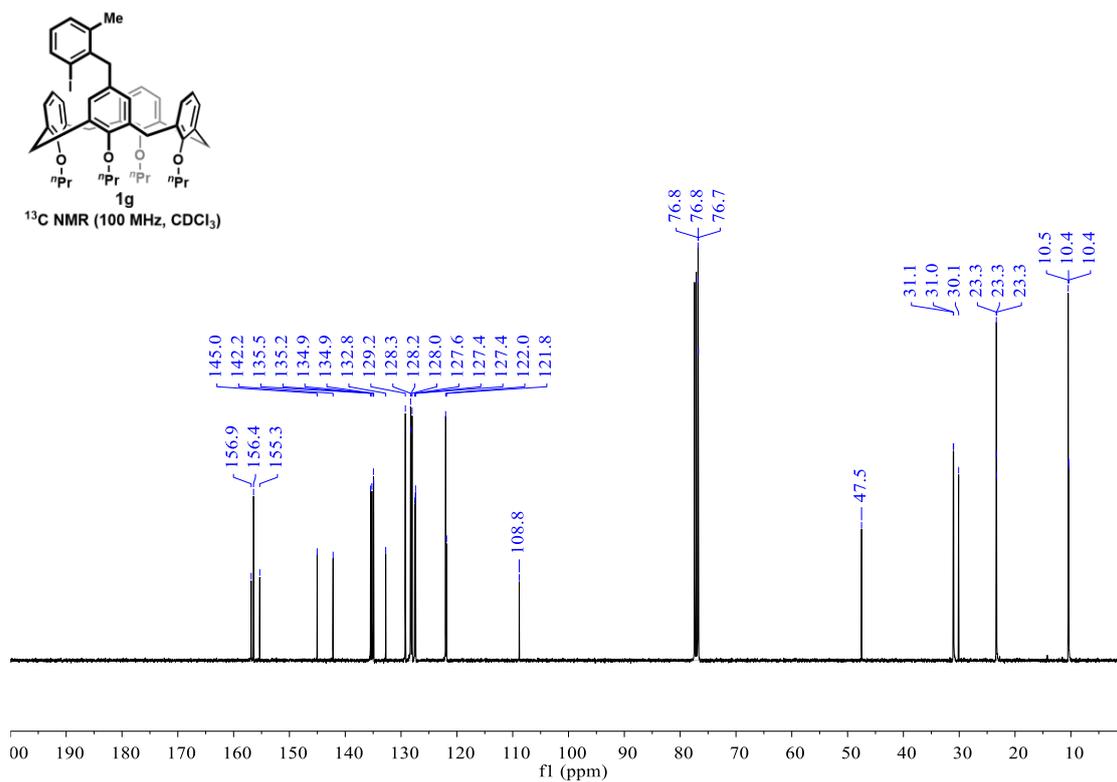


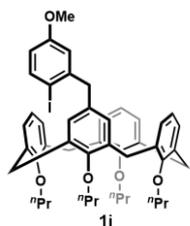
^{13}C NMR (150 MHz, CDCl_3)



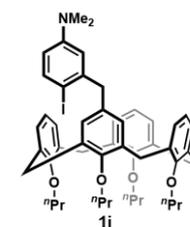
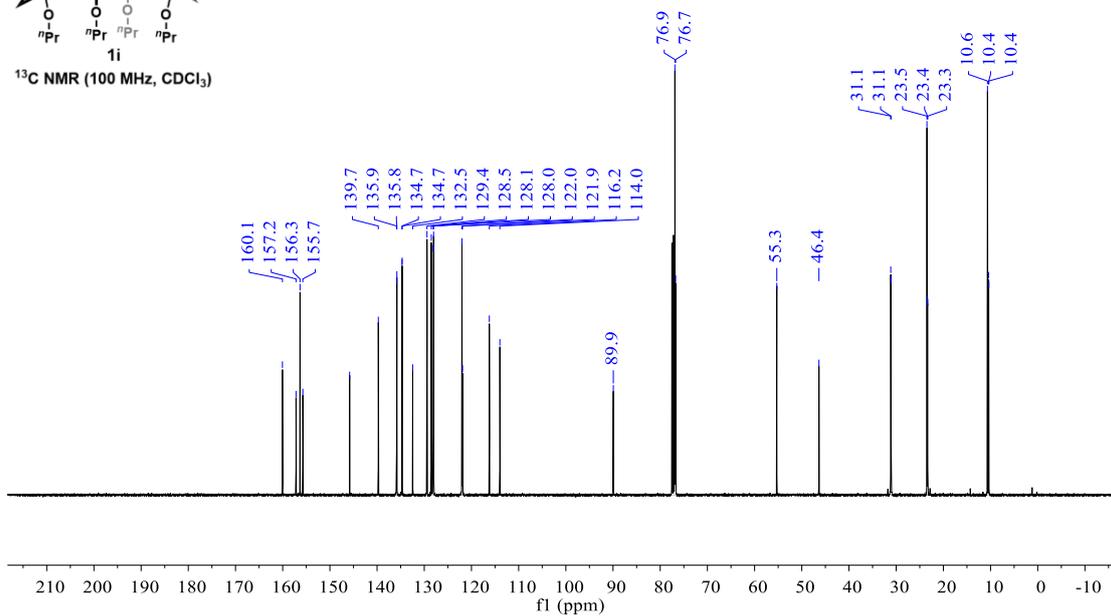
^1H NMR (400 MHz, CDCl_3)



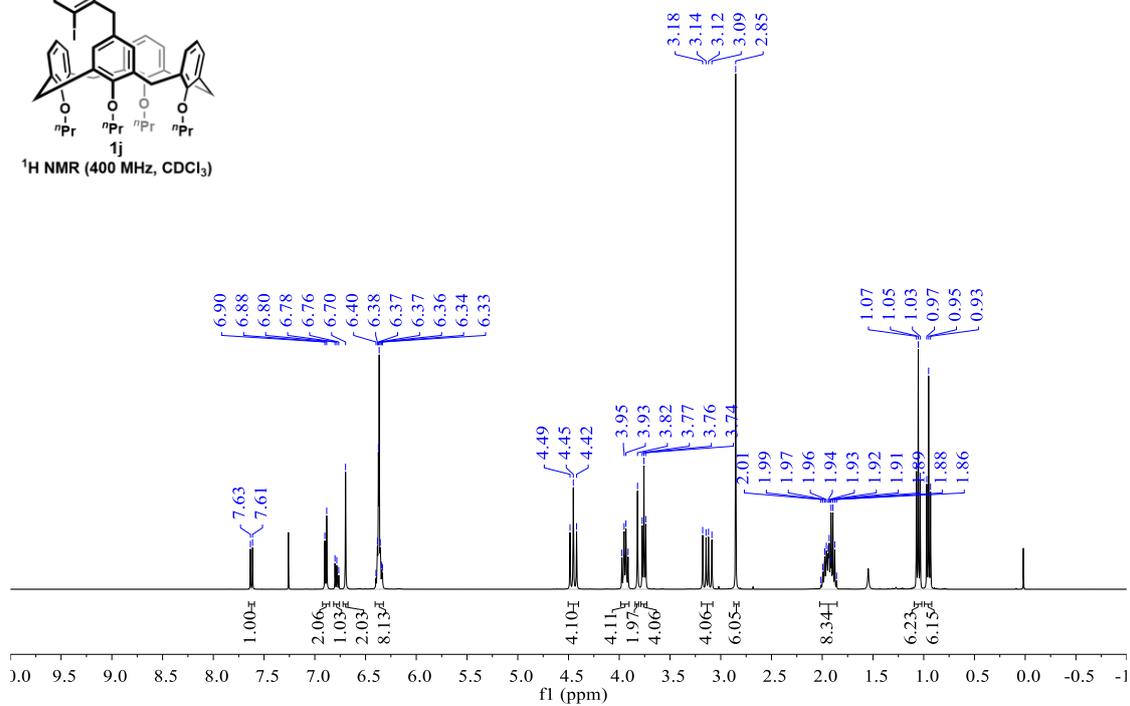


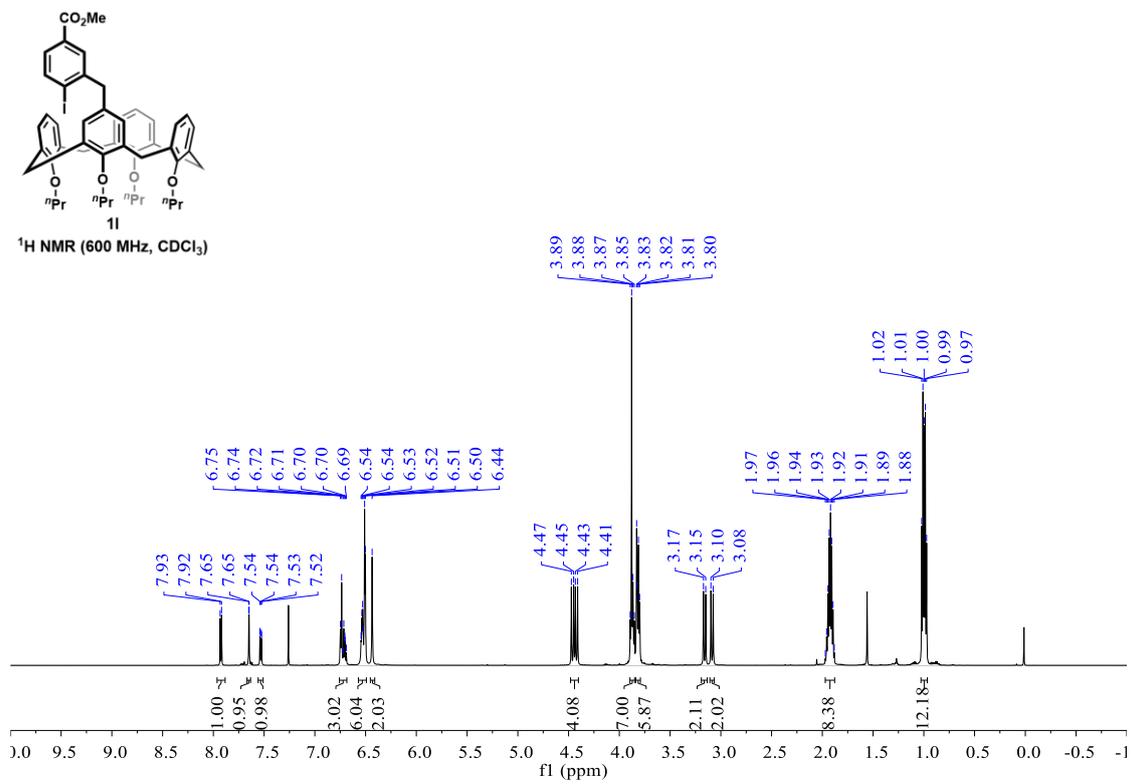
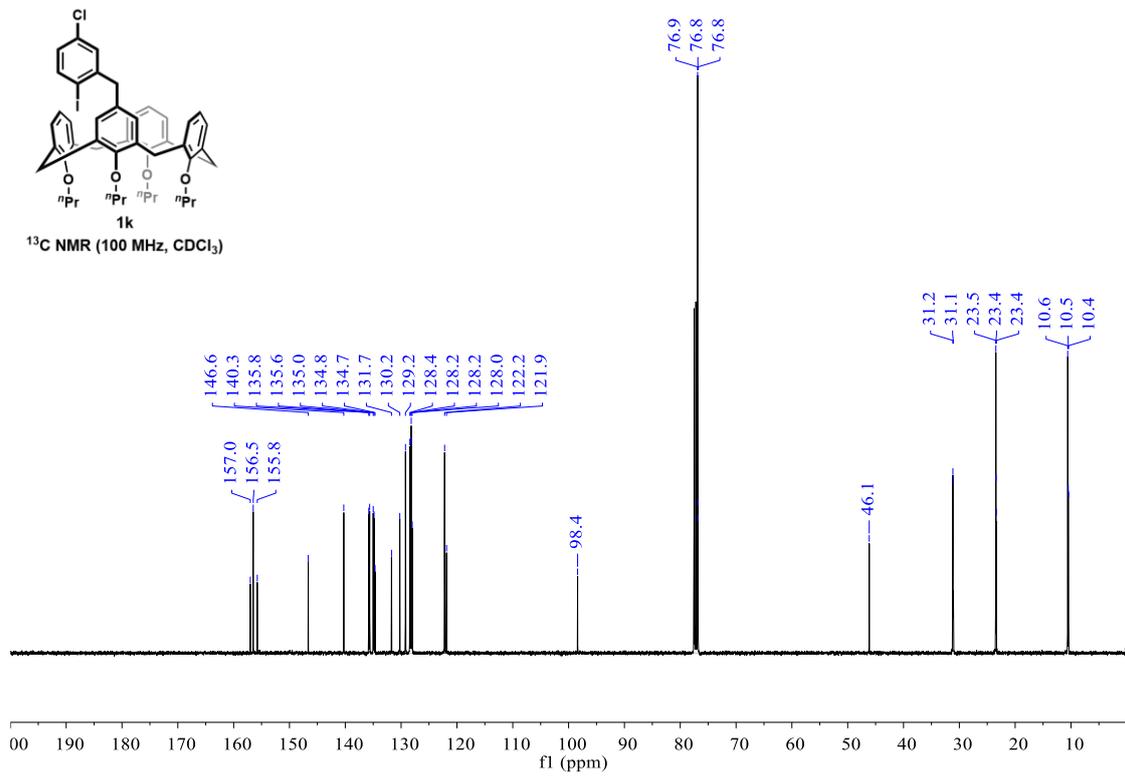


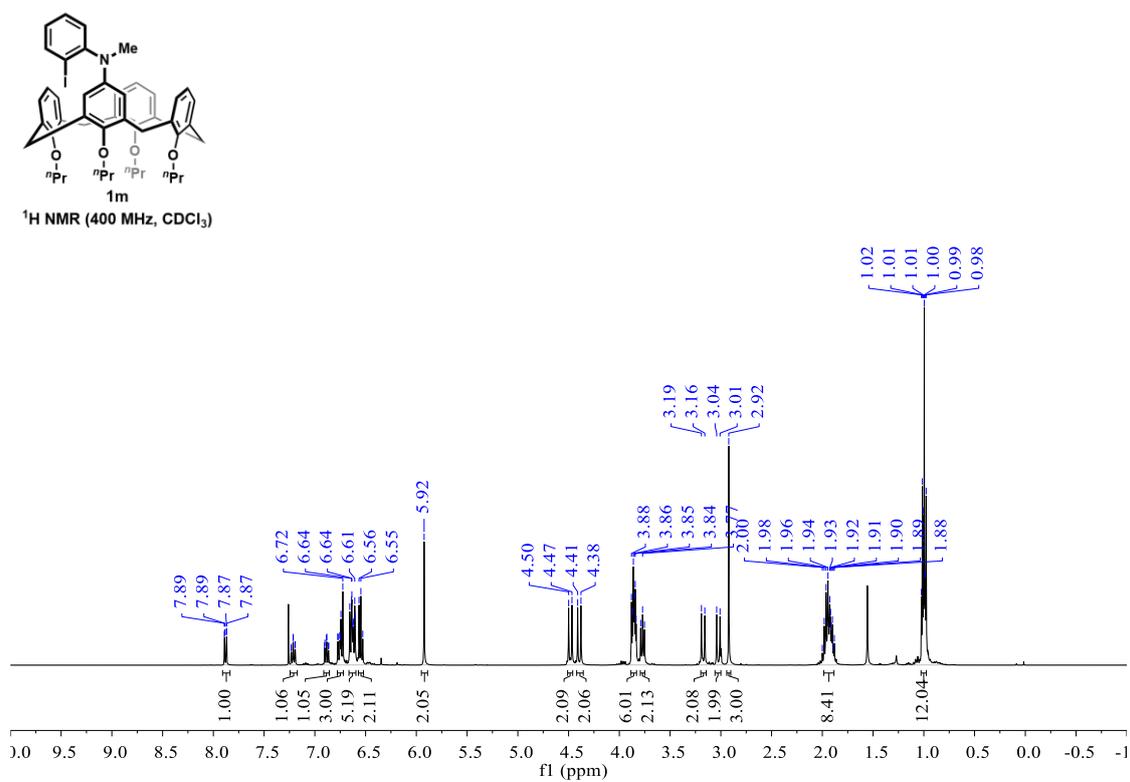
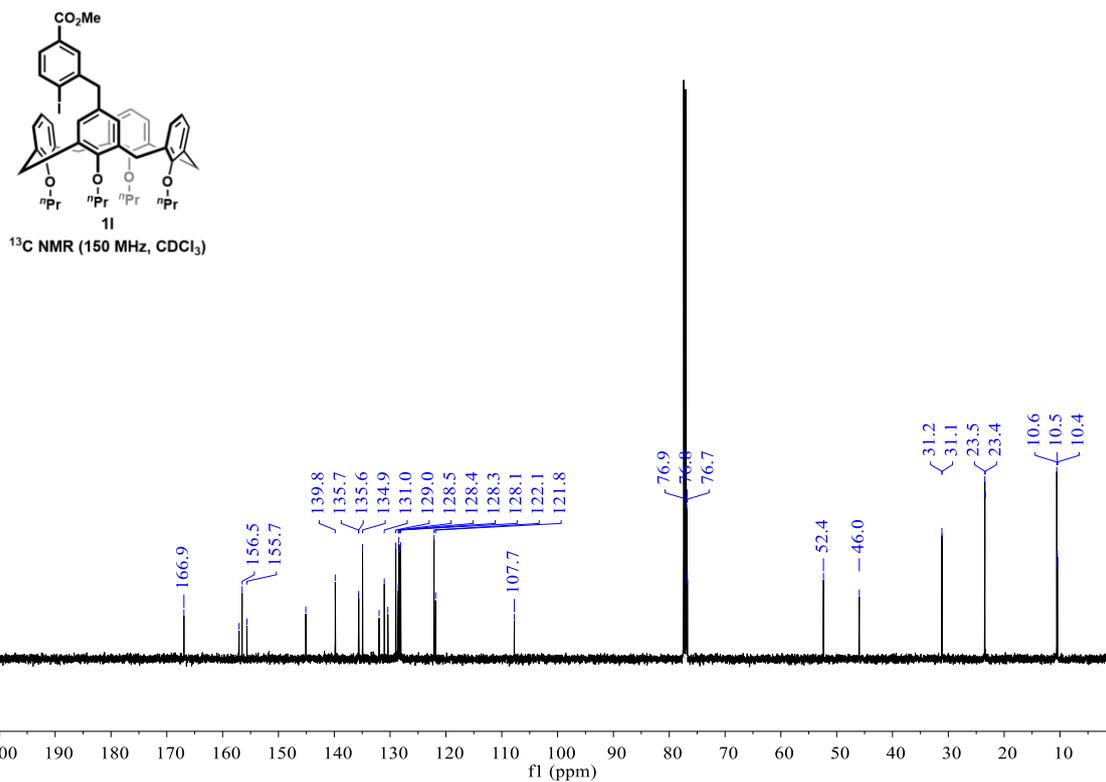
^{13}C NMR (100 MHz, CDCl_3)

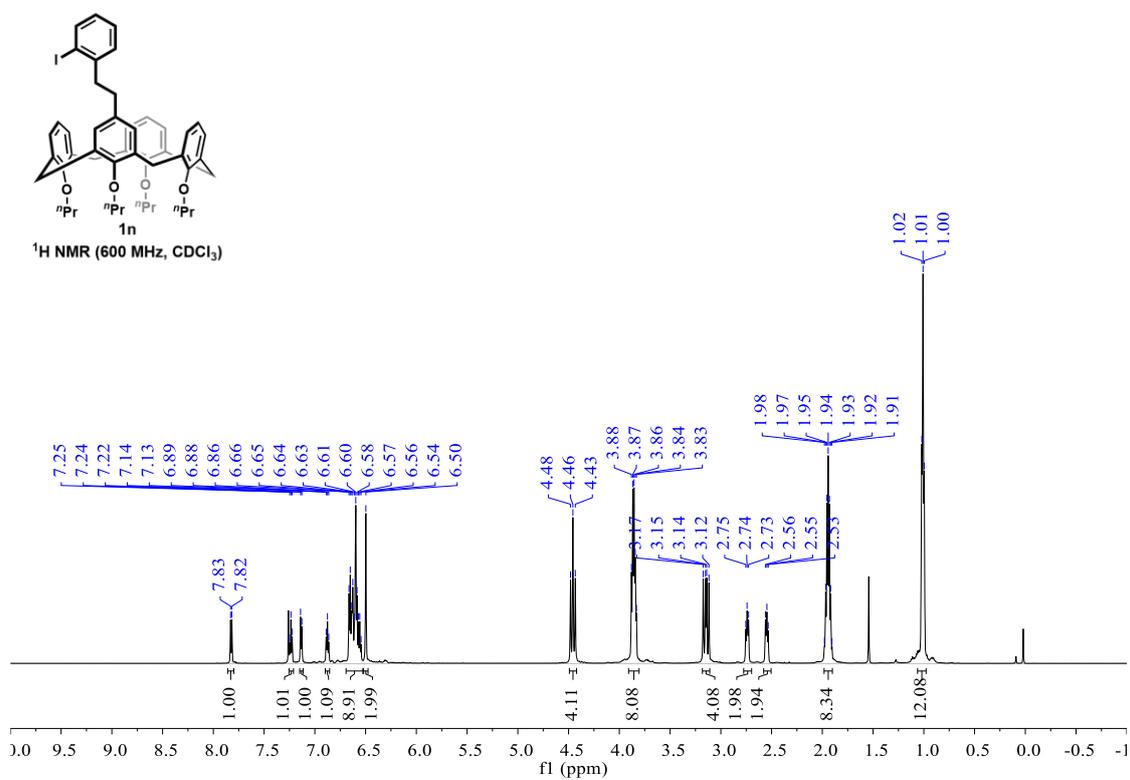
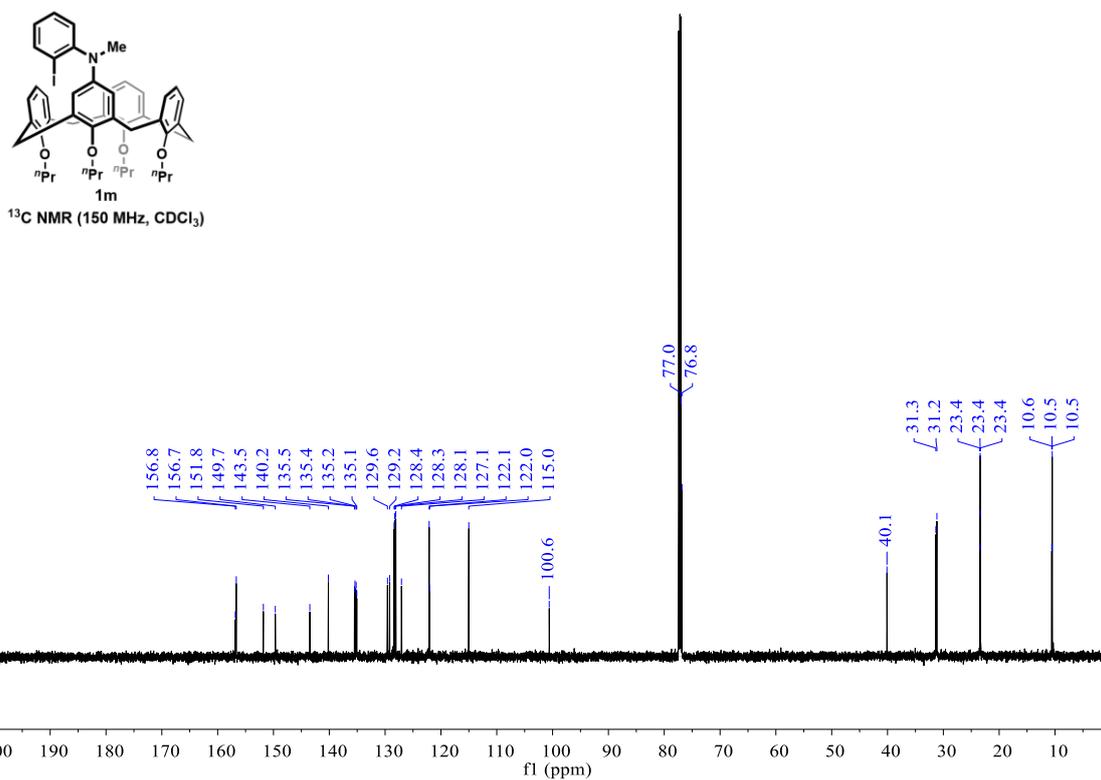


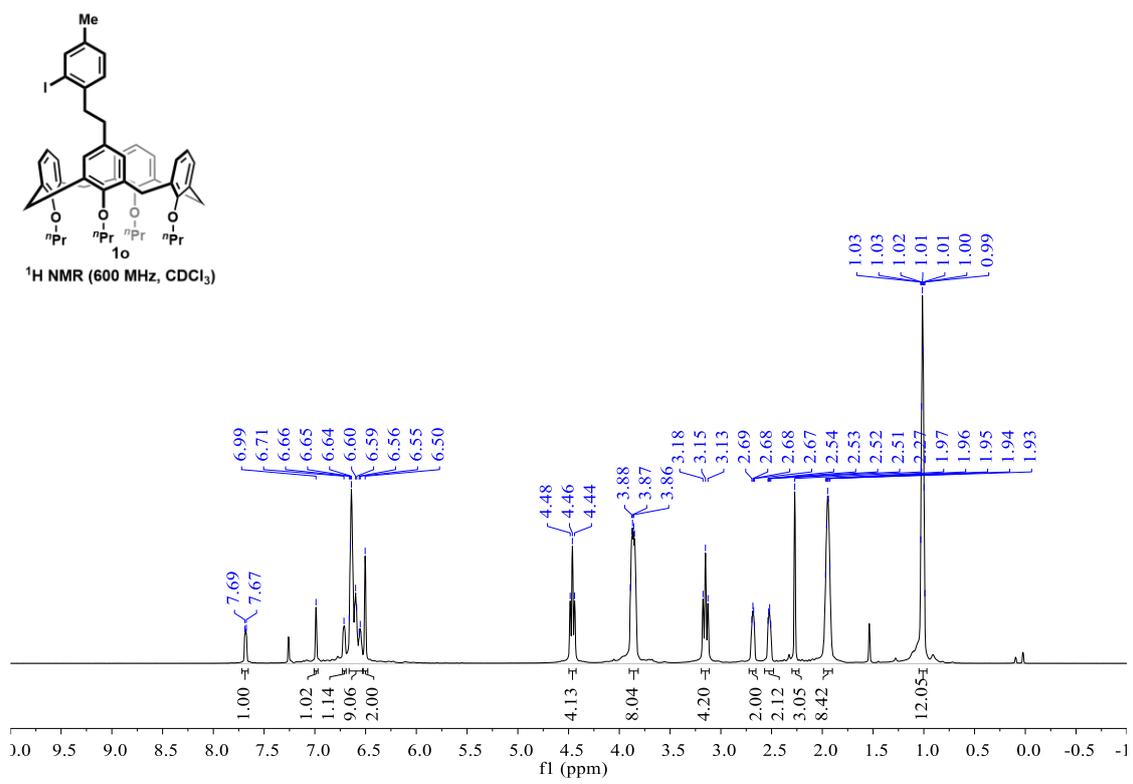
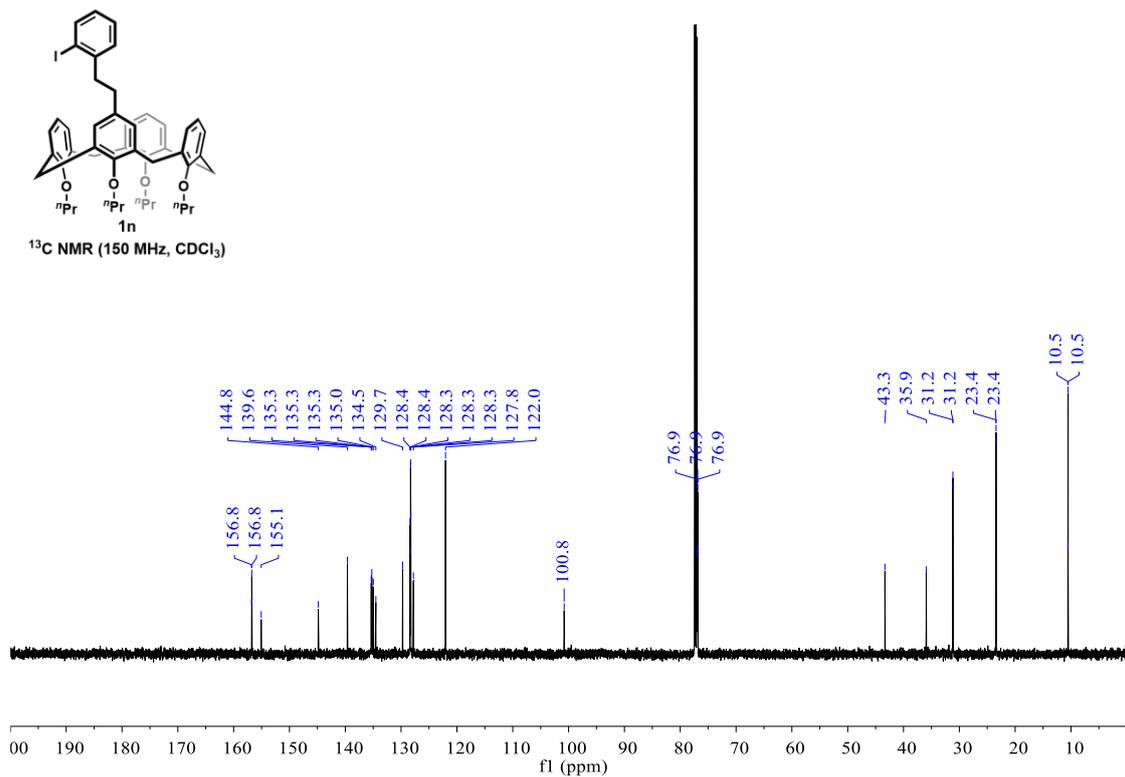
^1H NMR (400 MHz, CDCl_3)

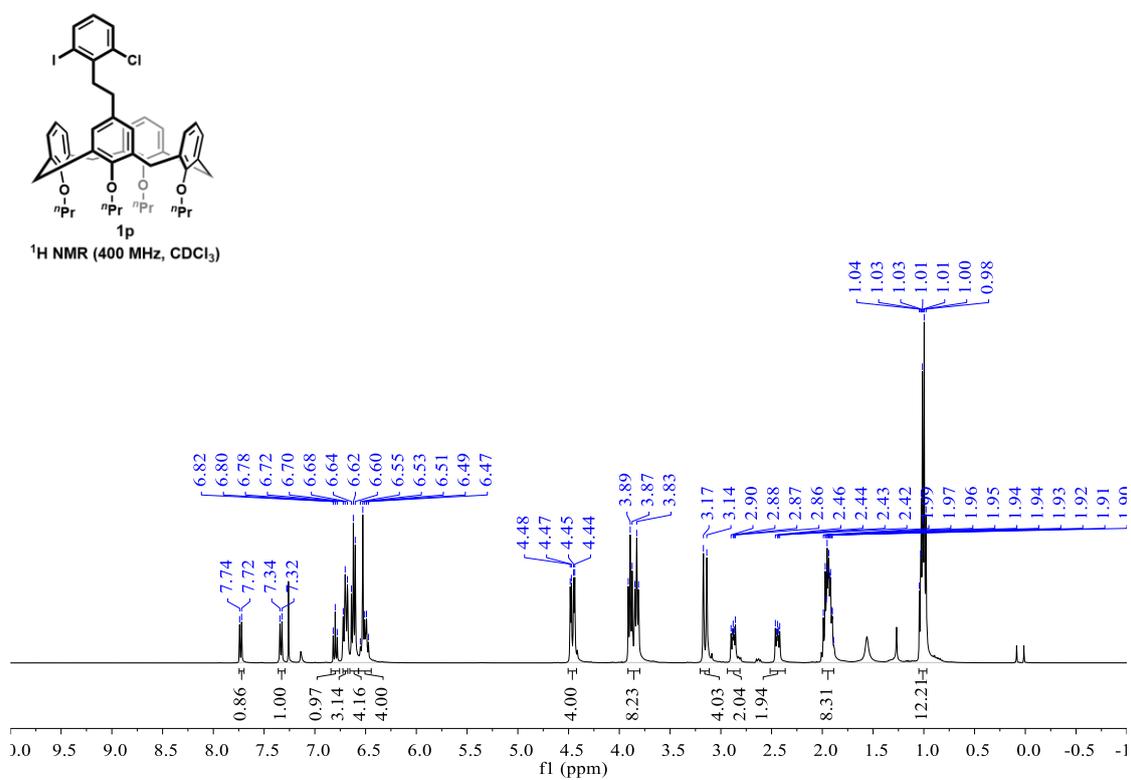
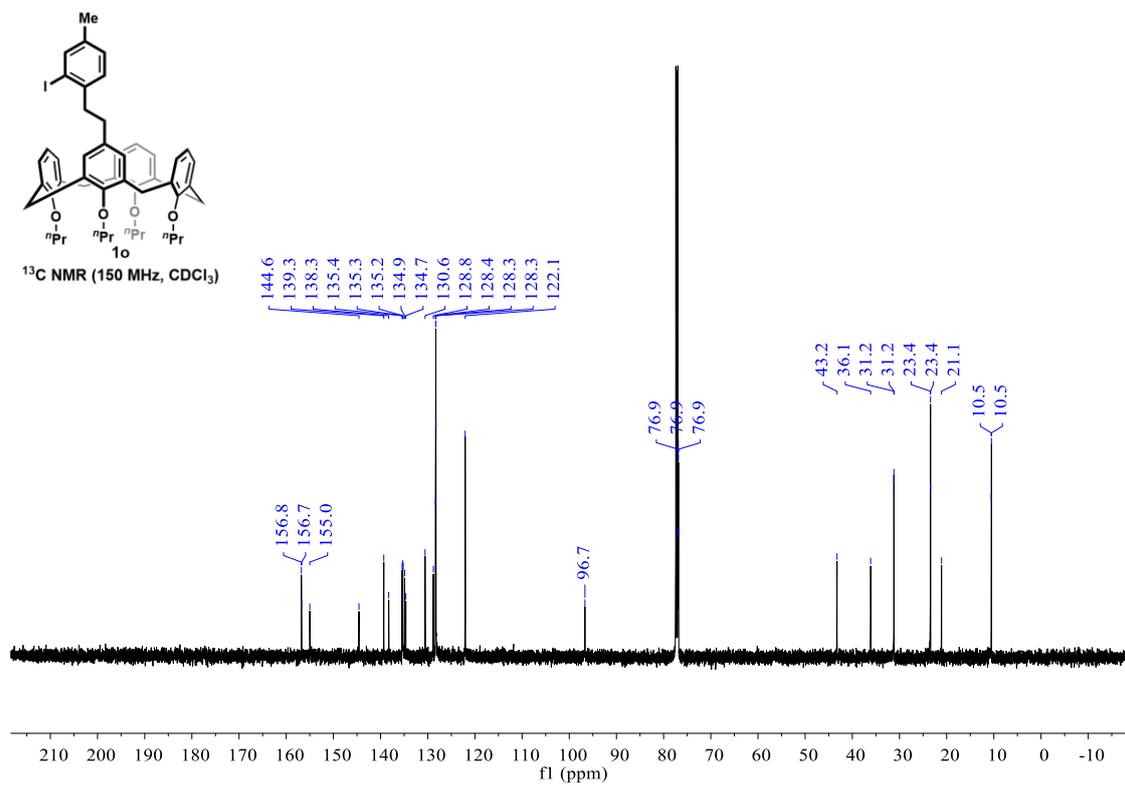


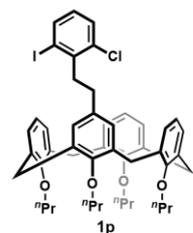




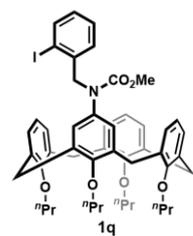
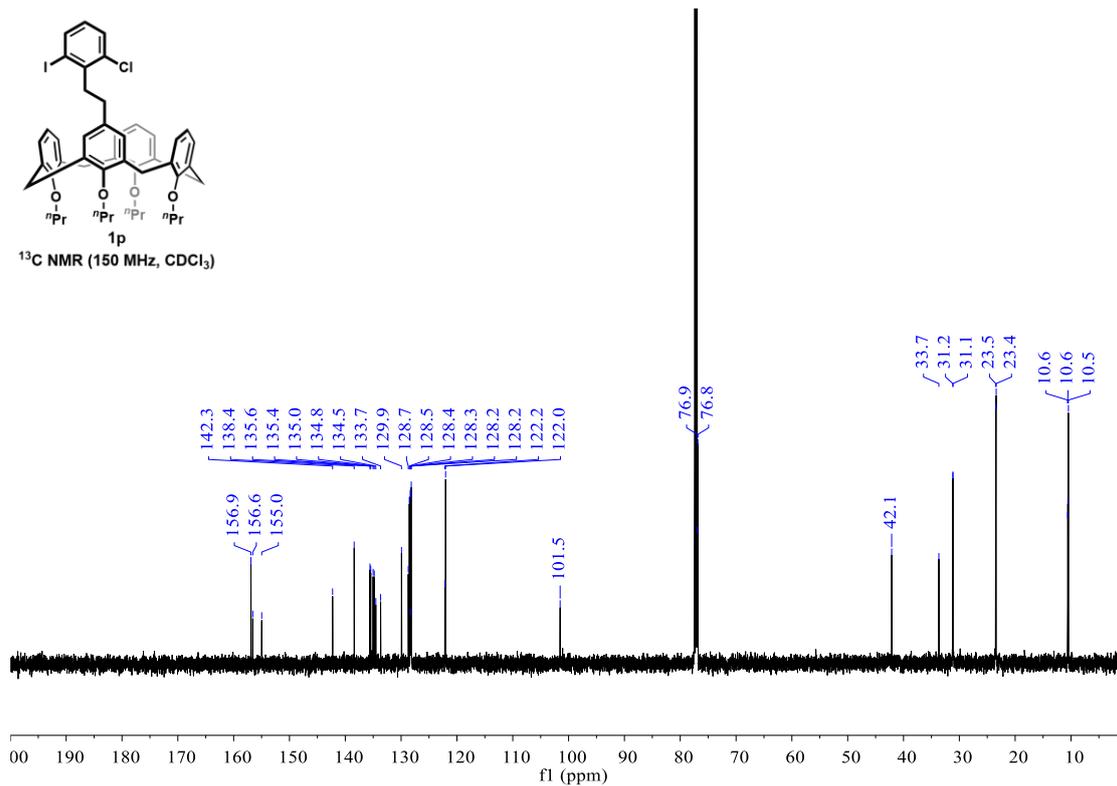




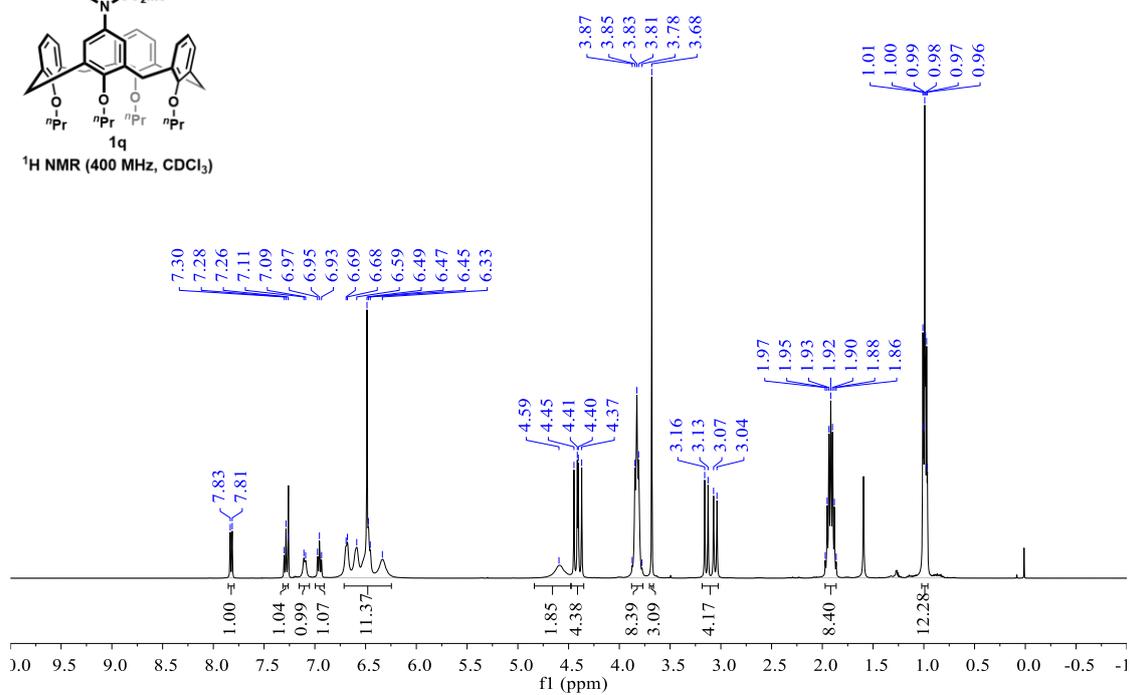


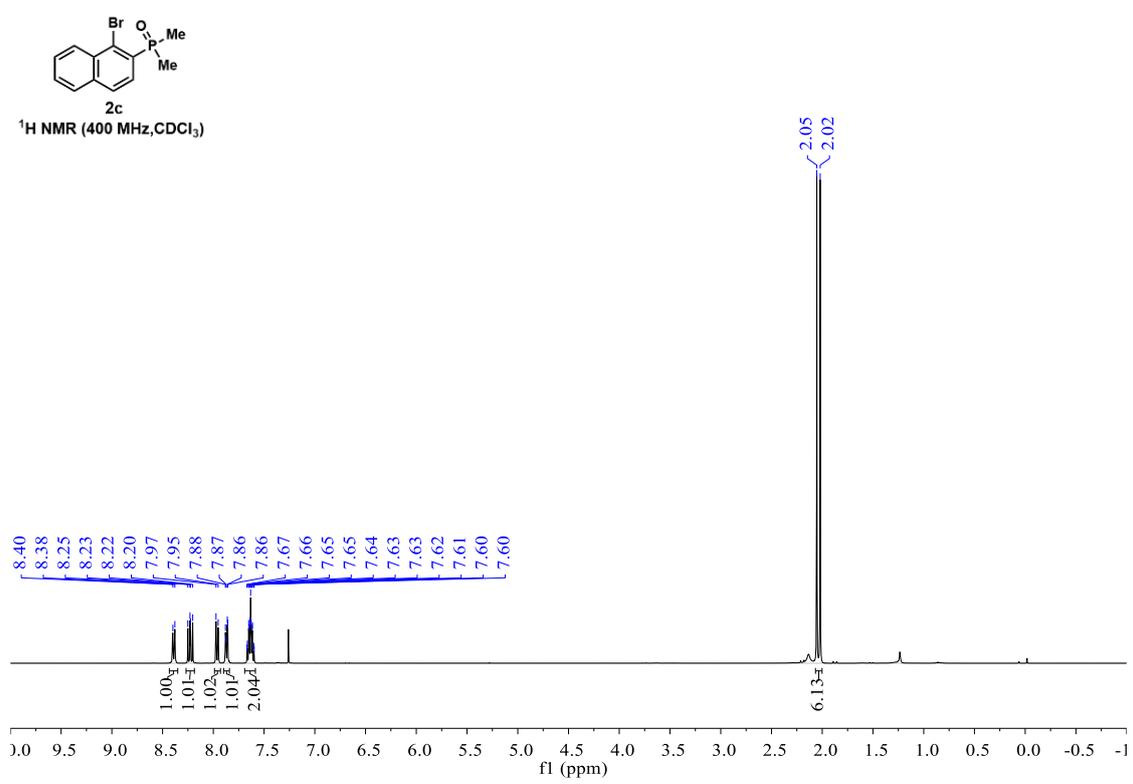
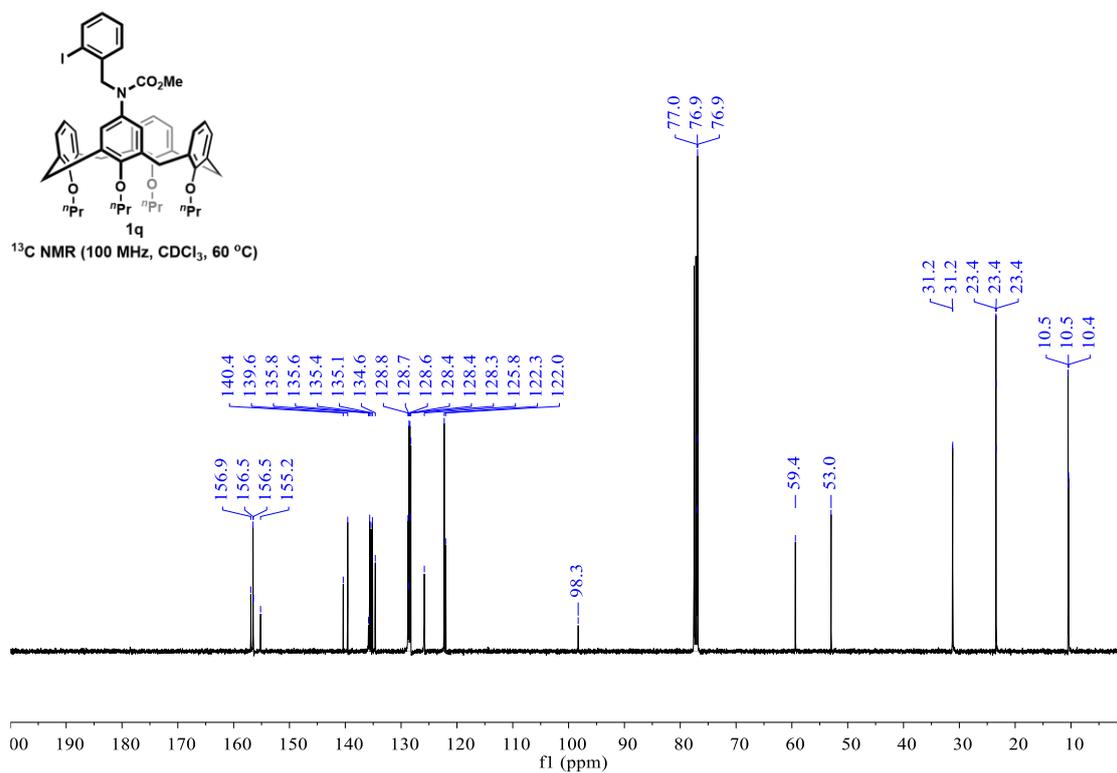


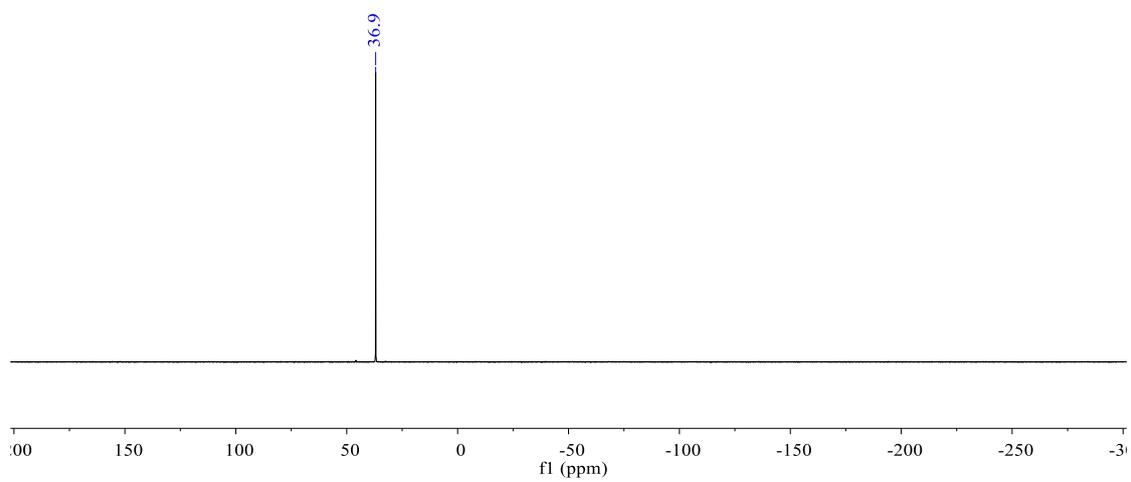
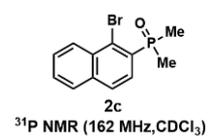
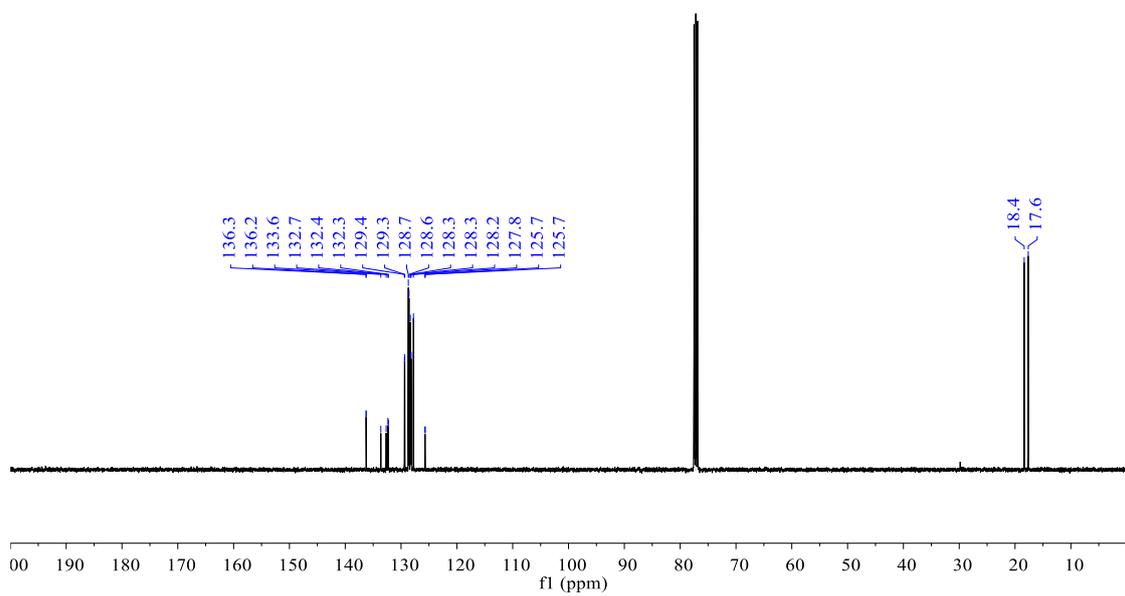
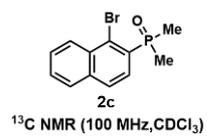
^{13}C NMR (150 MHz, CDCl_3)

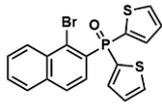


^1H NMR (400 MHz, CDCl_3)



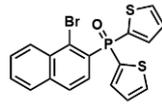
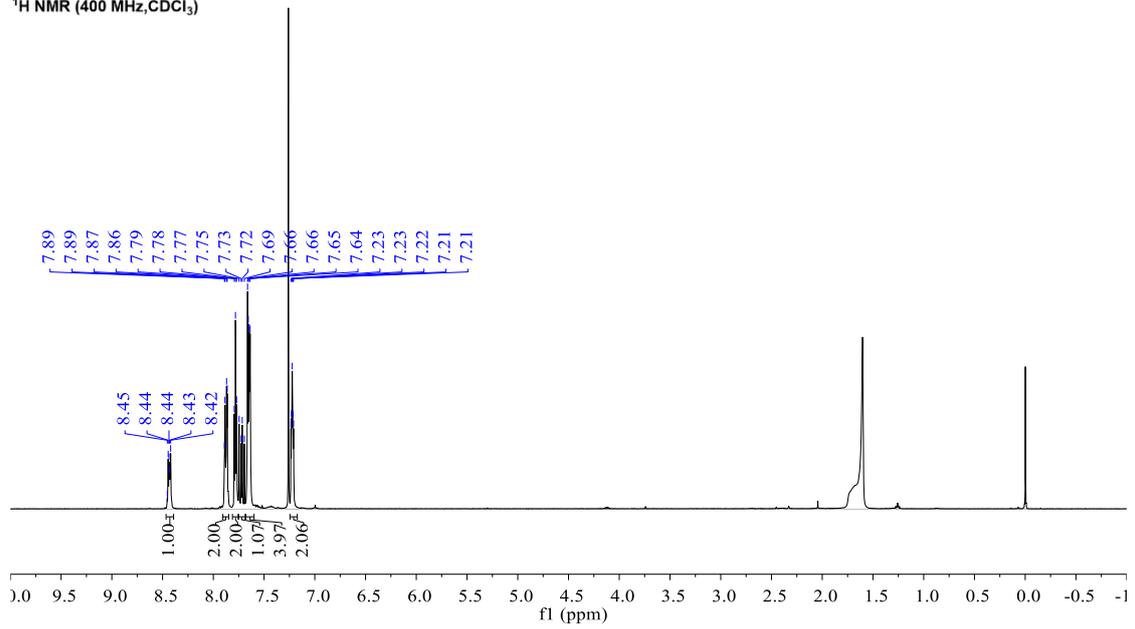






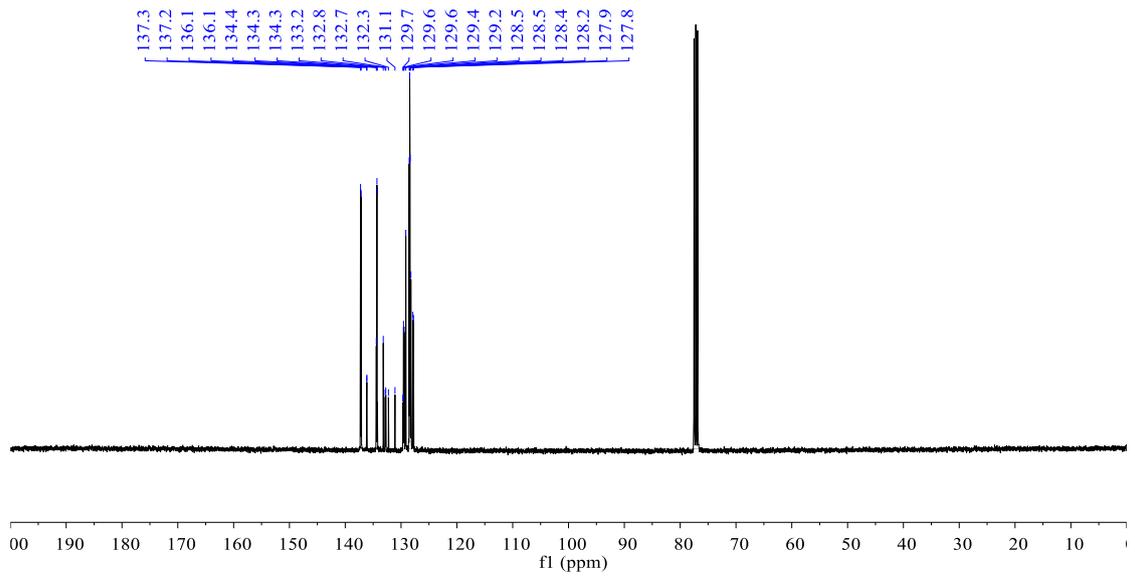
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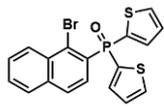
¹H NMR (400 MHz, CDCl₃)



2i

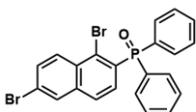
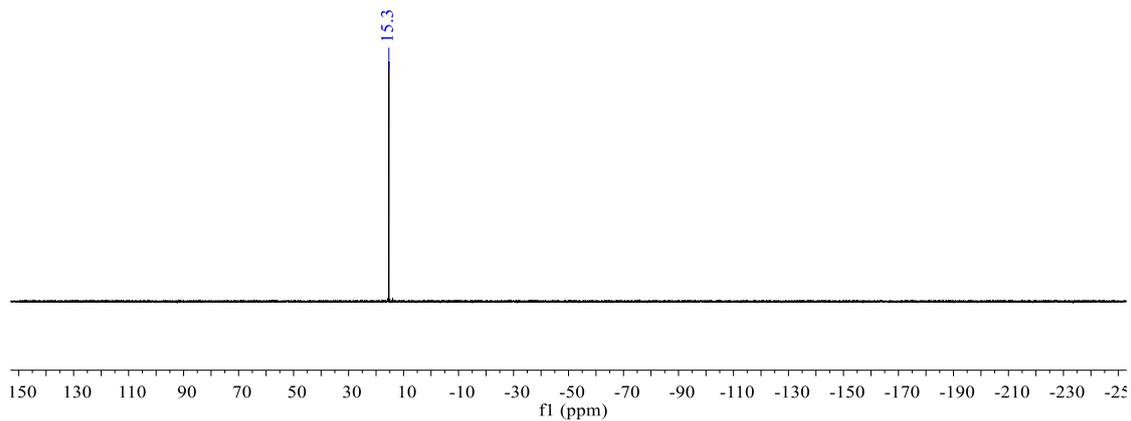
¹³C NMR (100 MHz, CDCl₃)





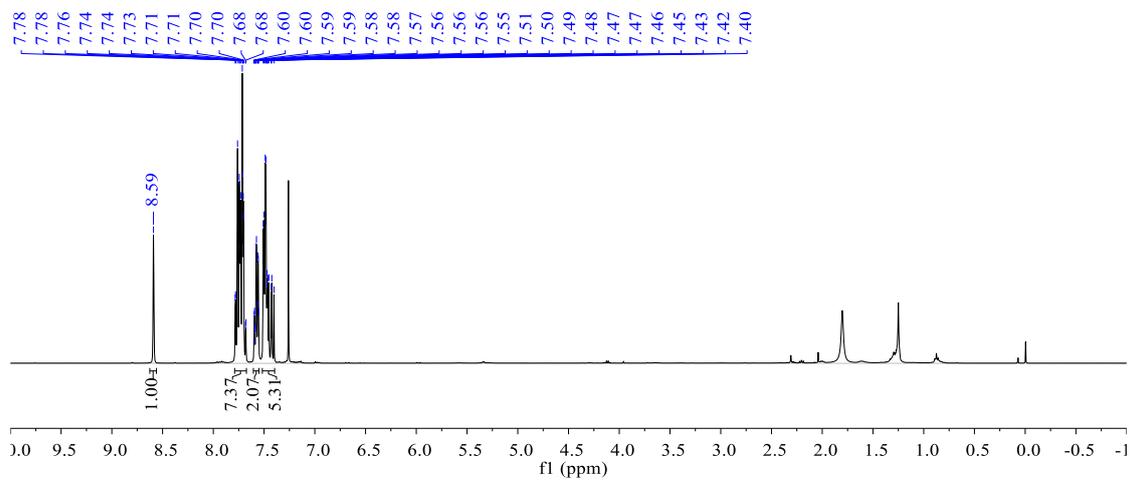
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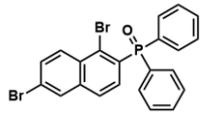
³¹P NMR (162 MHz, CDCl₃)



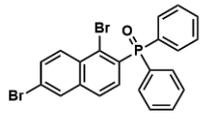
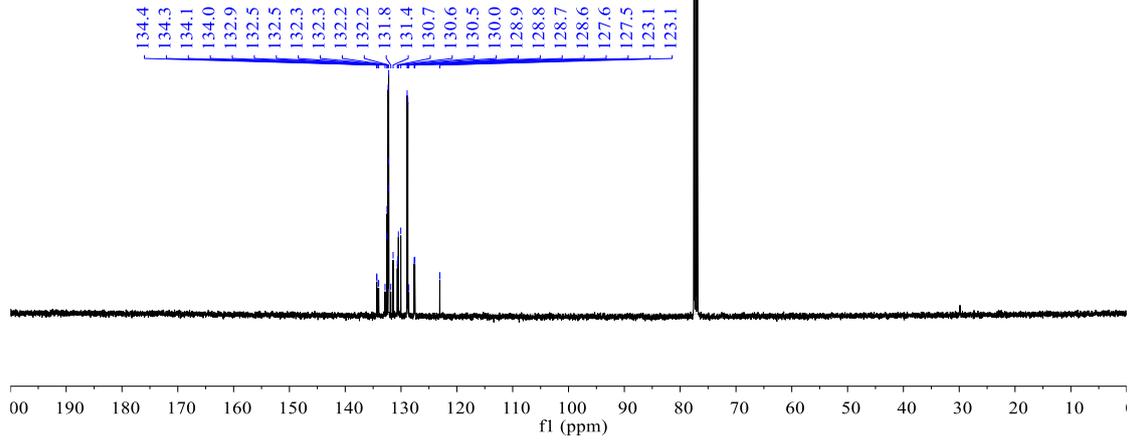
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¹H NMR (400 MHz, CDCl₃)

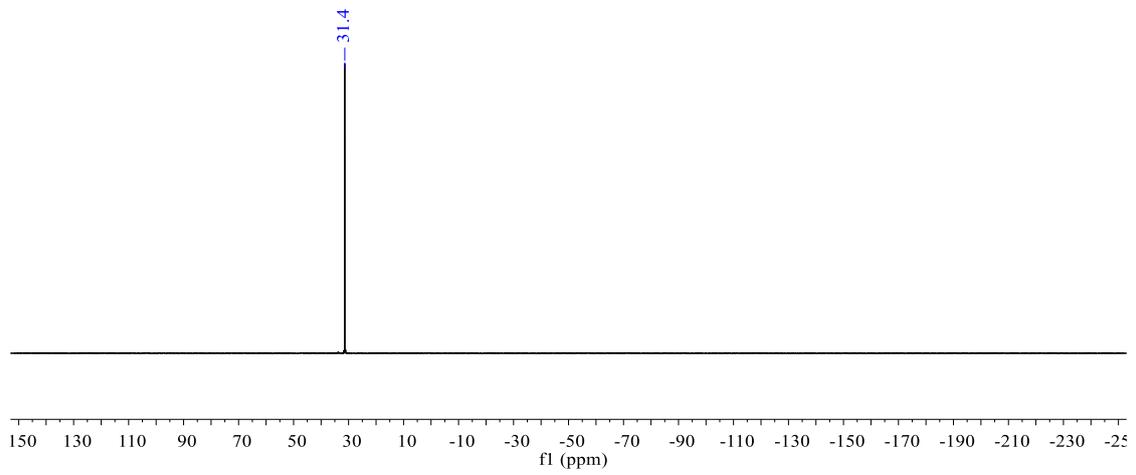


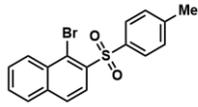


¹³C NMR (100 MHz, CDCl₃)

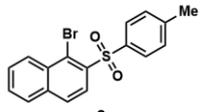
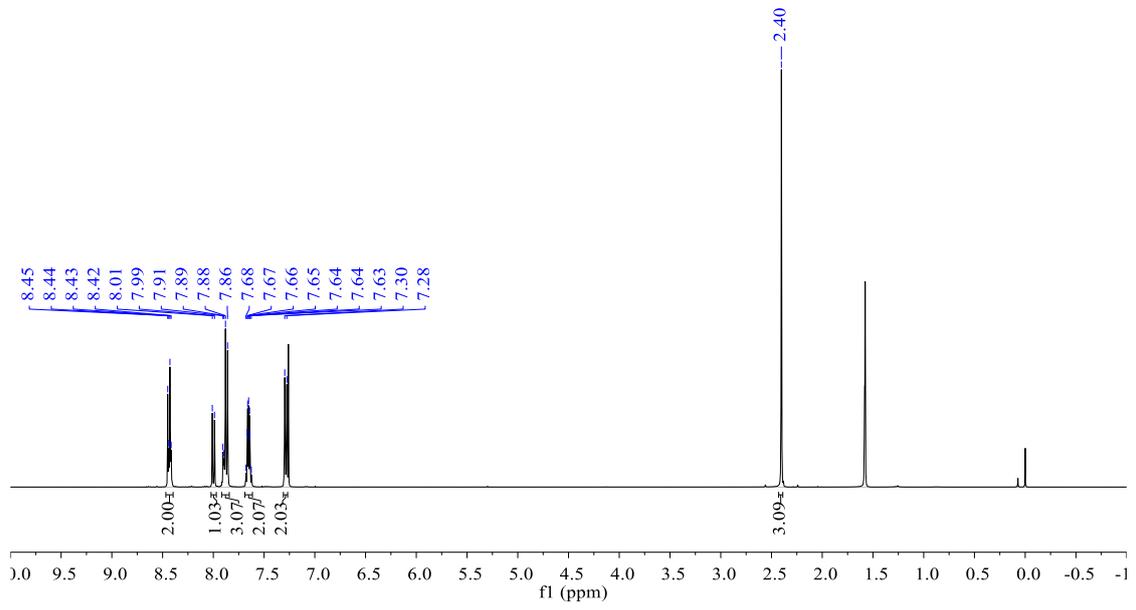


³¹P NMR (162 MHz, CDCl₃)

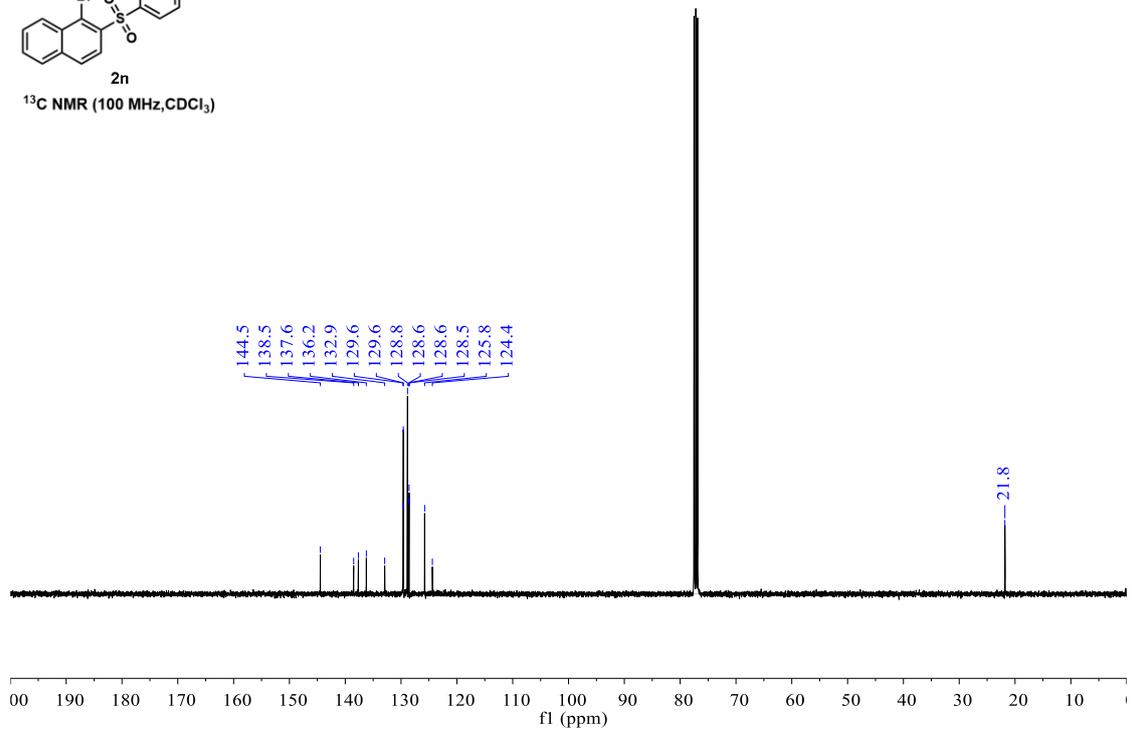


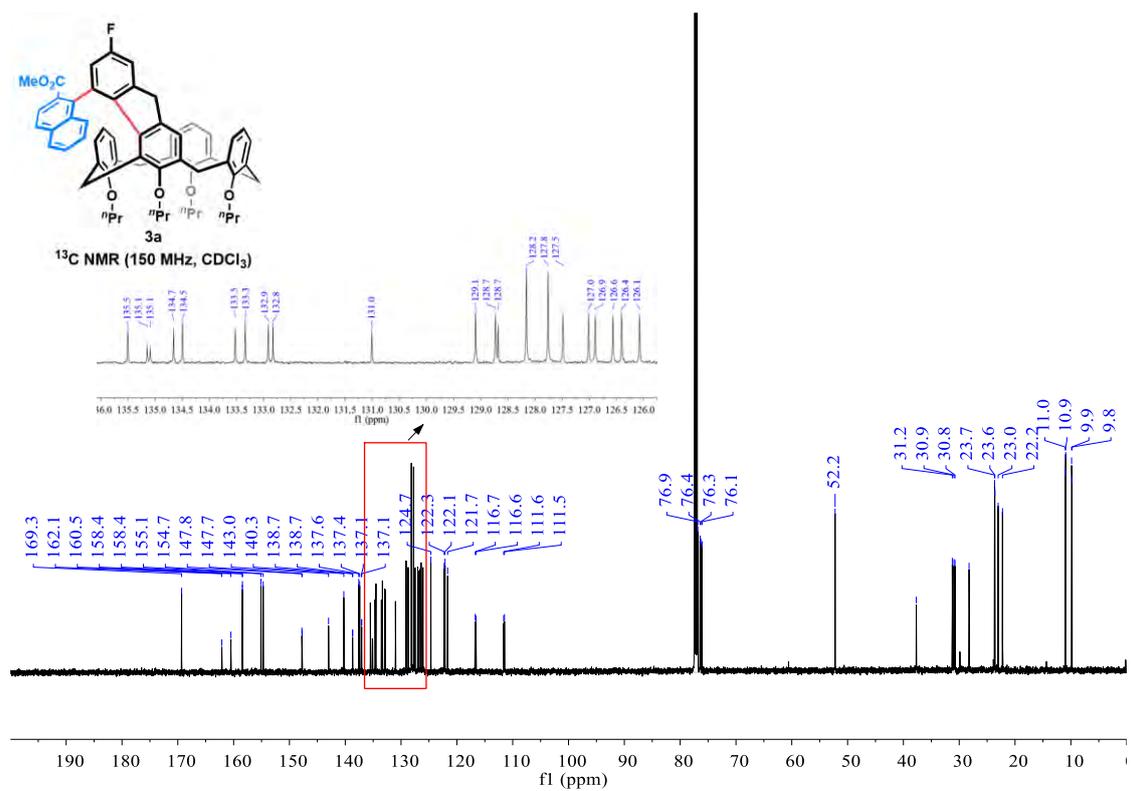
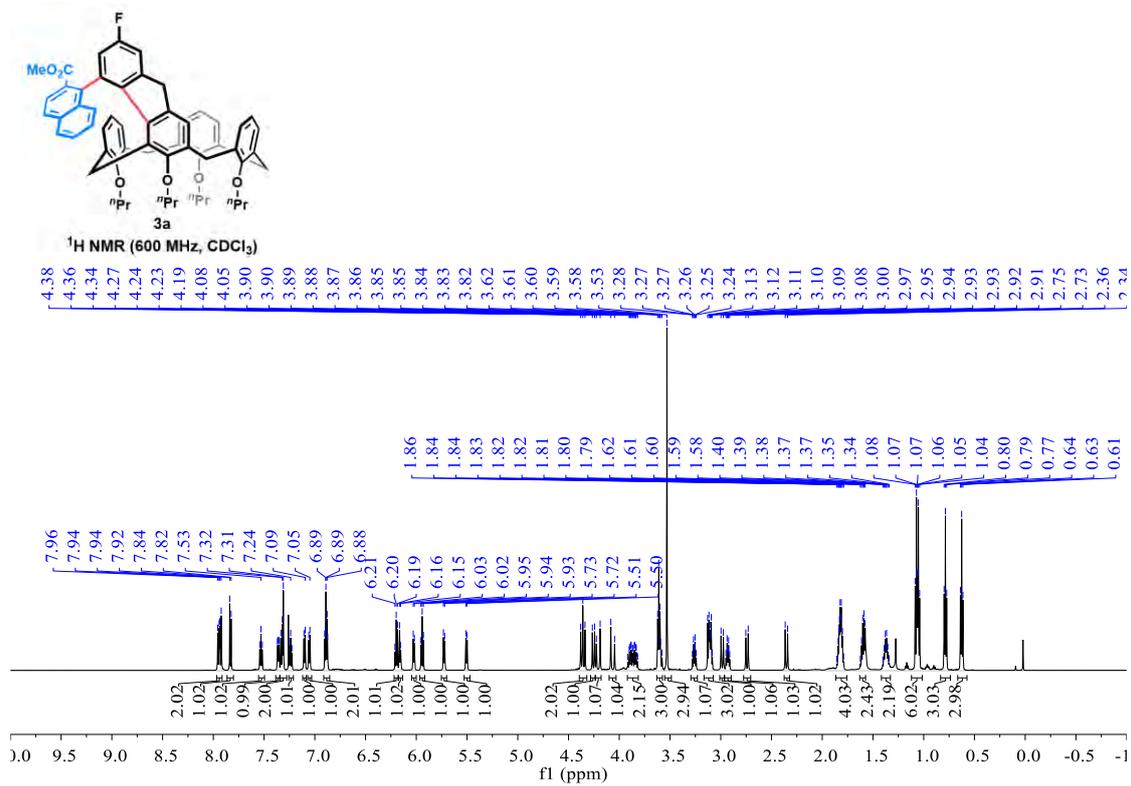


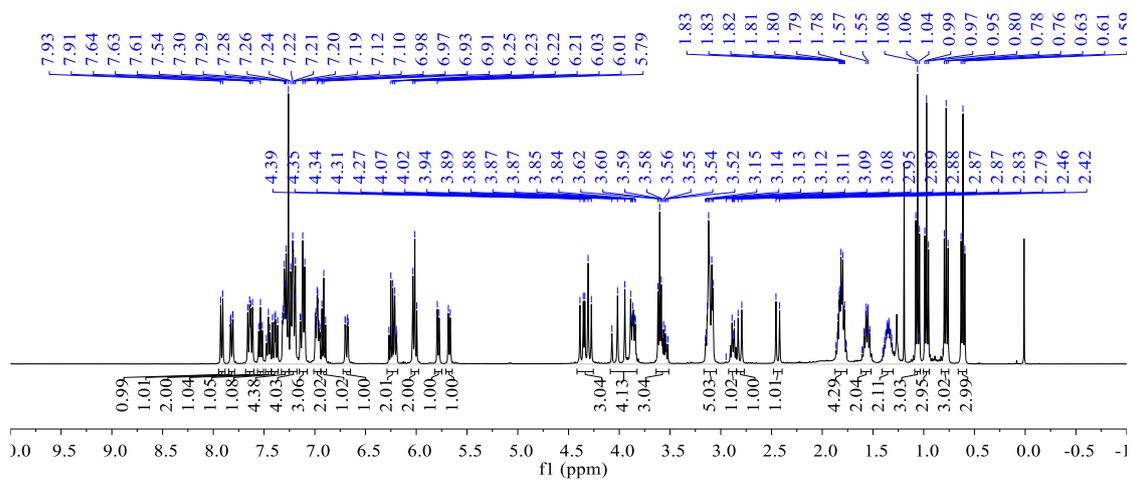
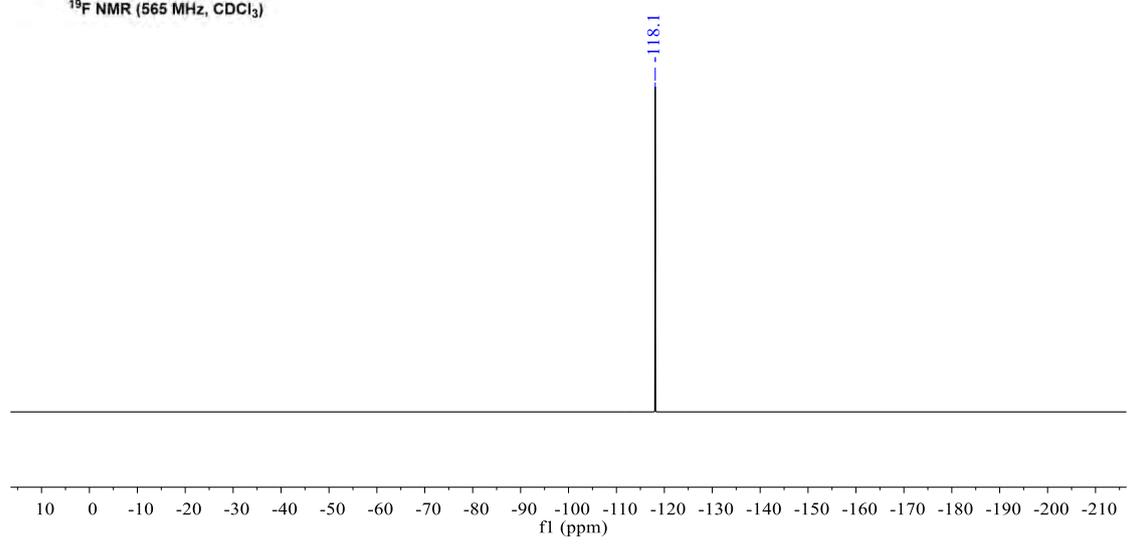
2n
¹H NMR (400 MHz, CDCl₃)

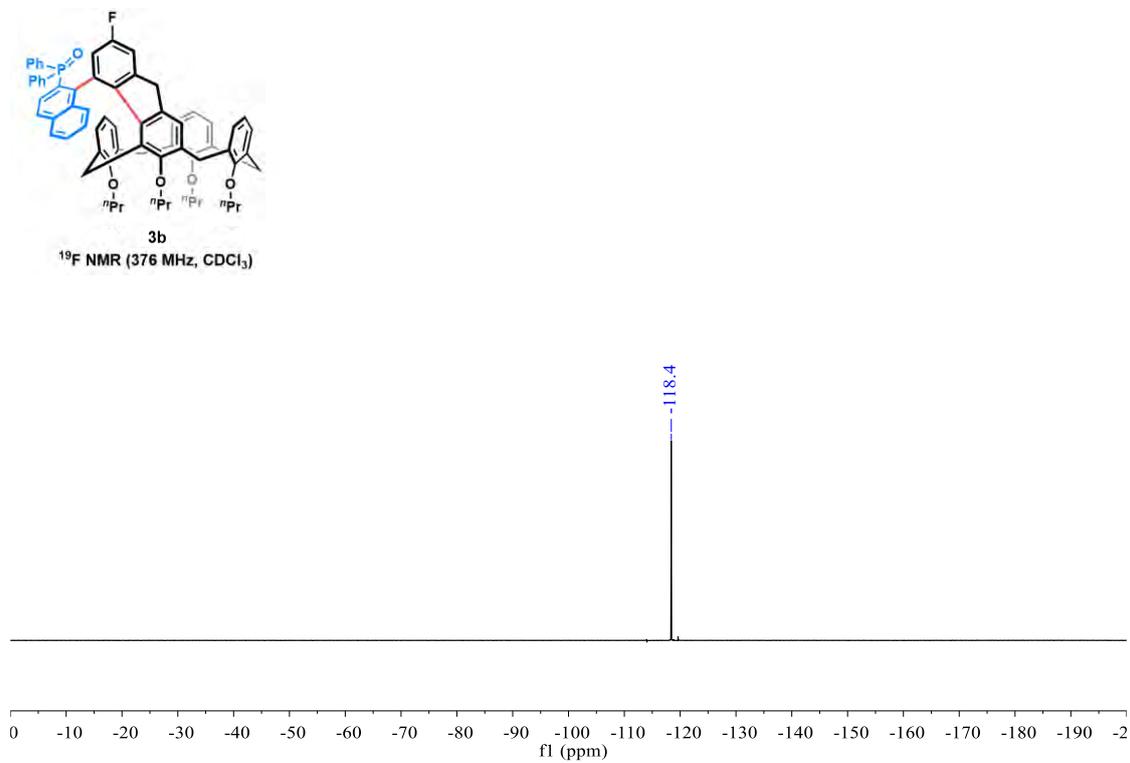
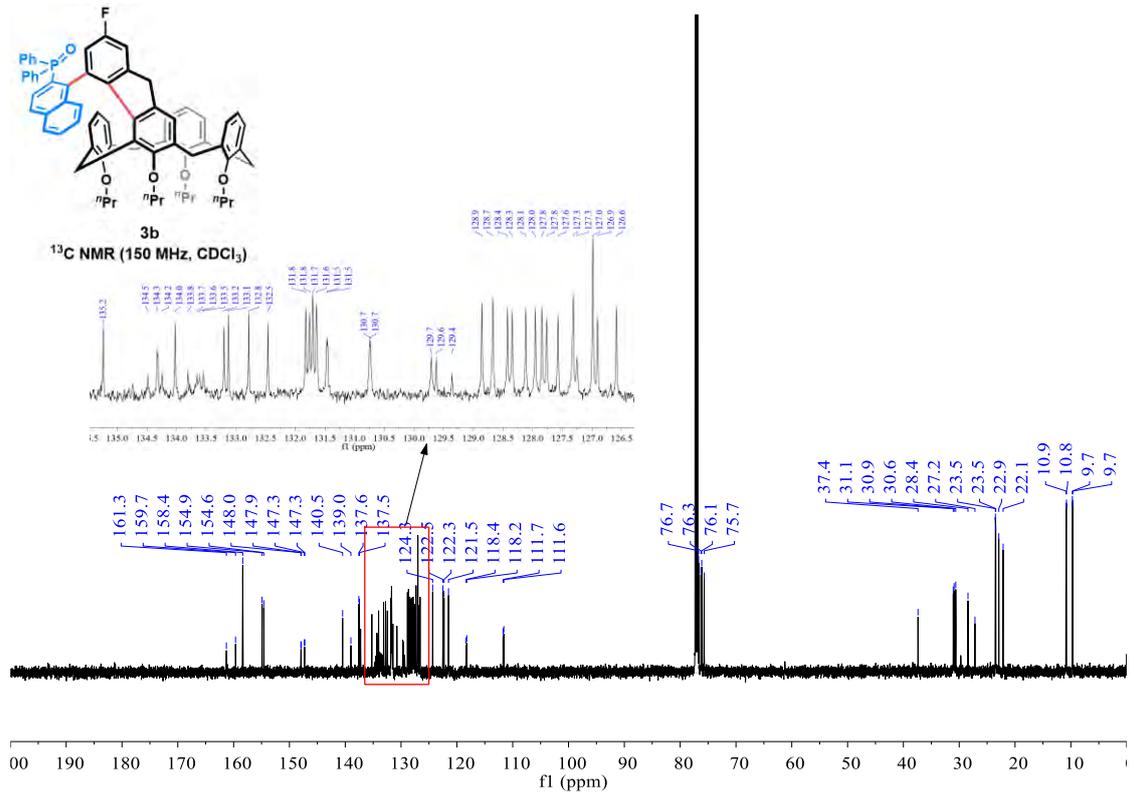


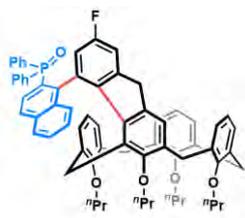
2n
¹³C NMR (100 MHz, CDCl₃)



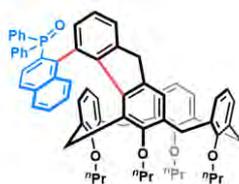
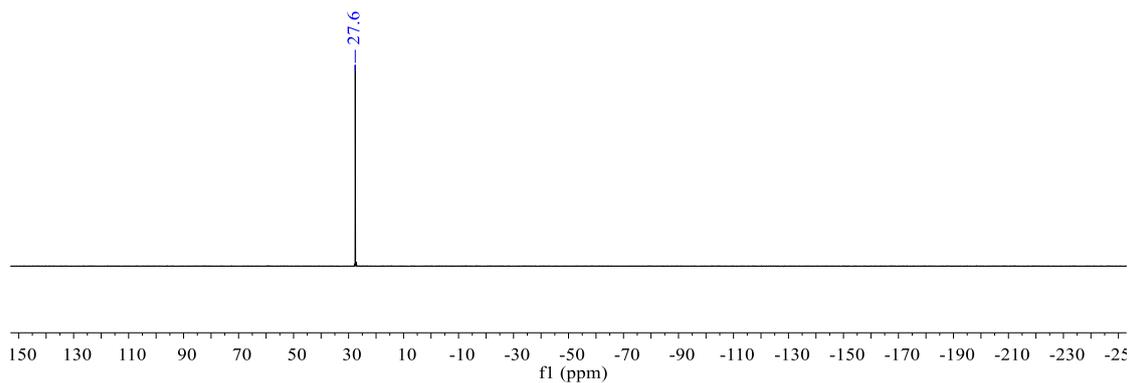




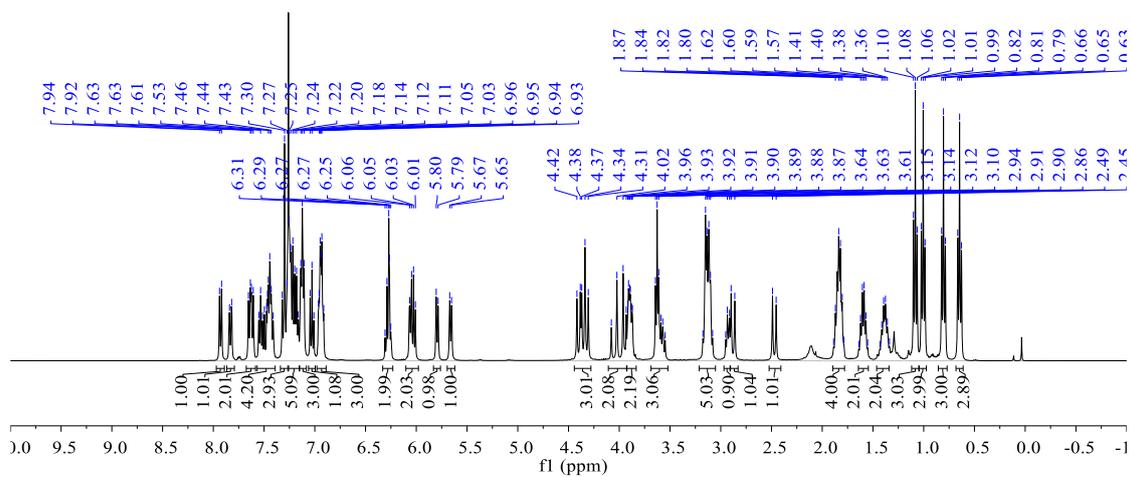


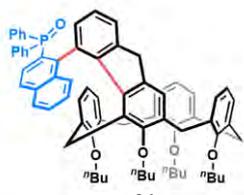


3b
 ^{31}P NMR (162 MHz, CDCl_3)

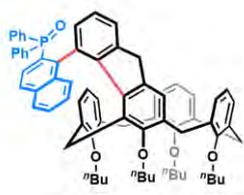
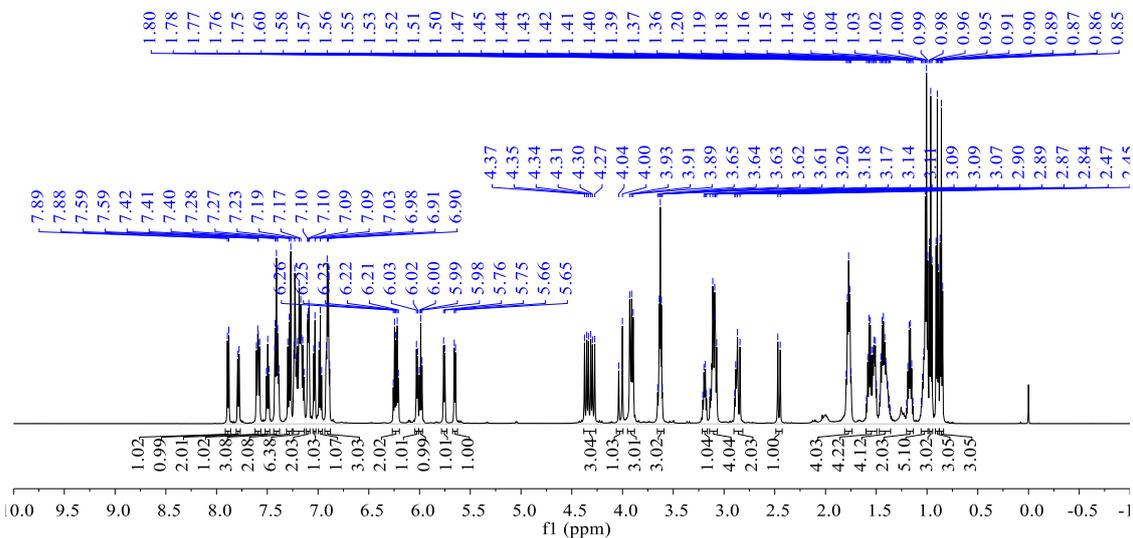


3c
 ^1H NMR (400 MHz, CDCl_3)

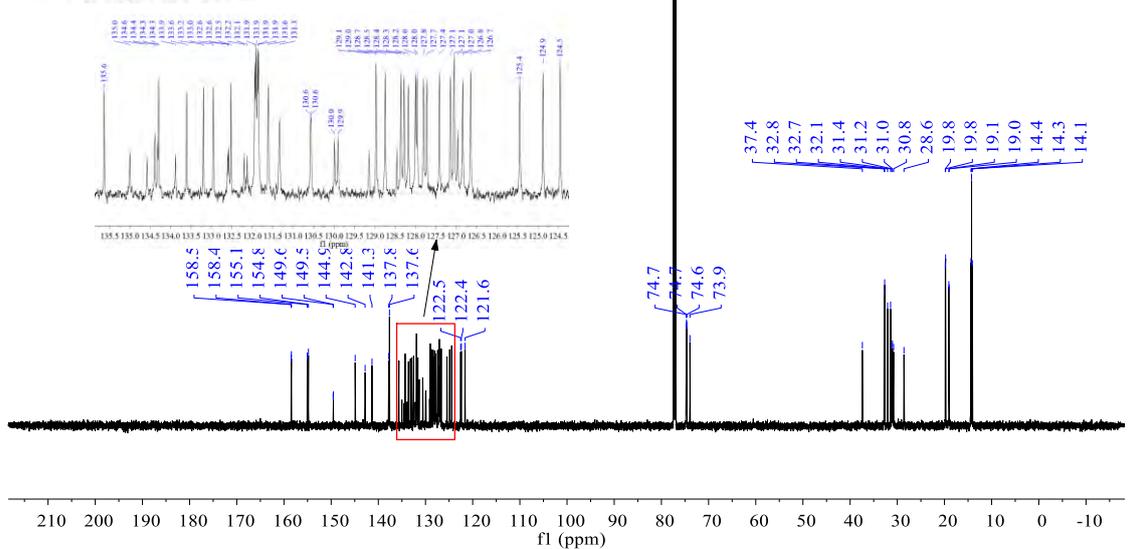


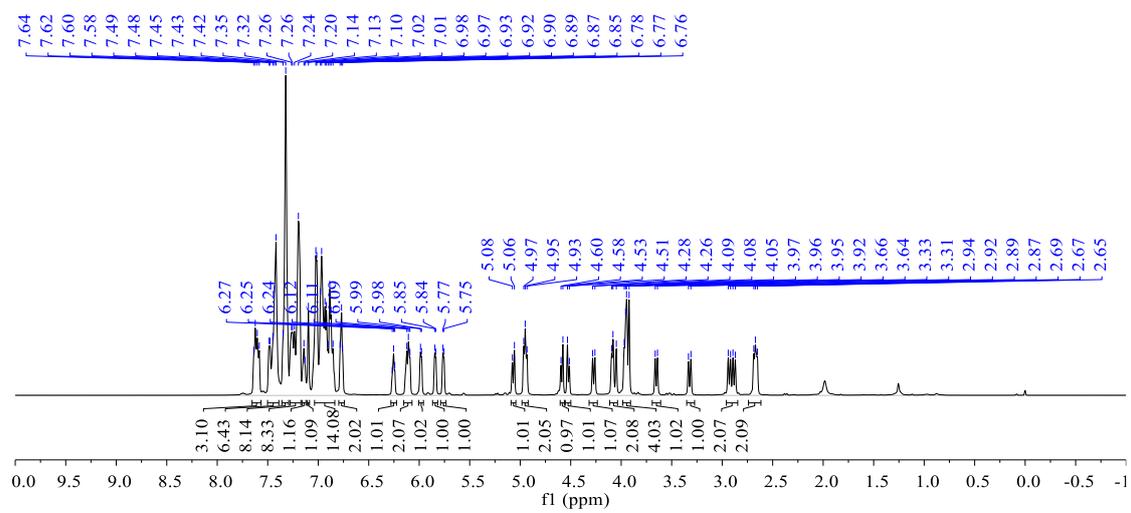
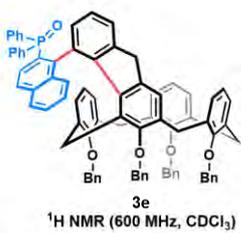
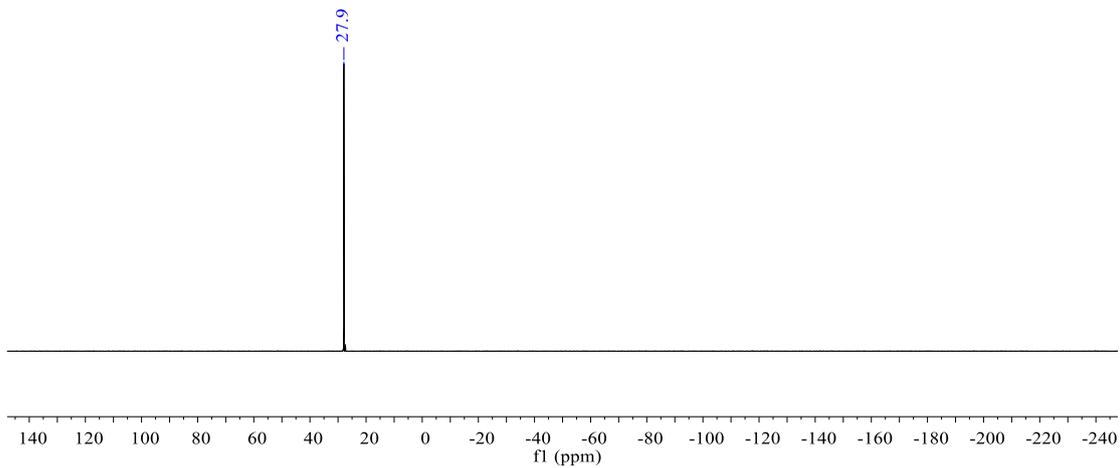
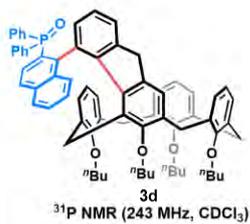


3d
¹H NMR (600 MHz, CDCl₃)



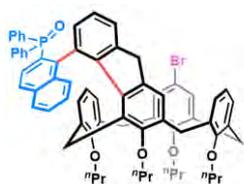
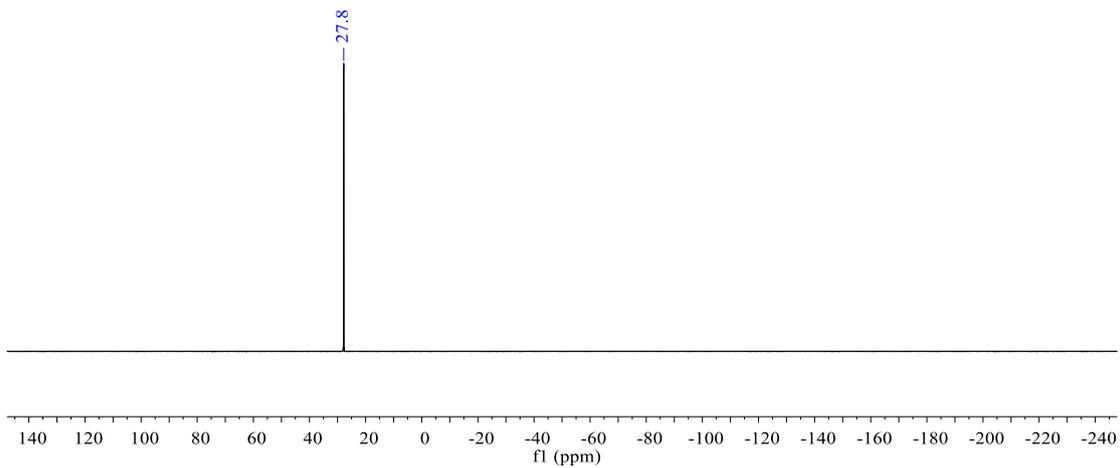
3d
¹³C NMR (150 MHz, CDCl₃)



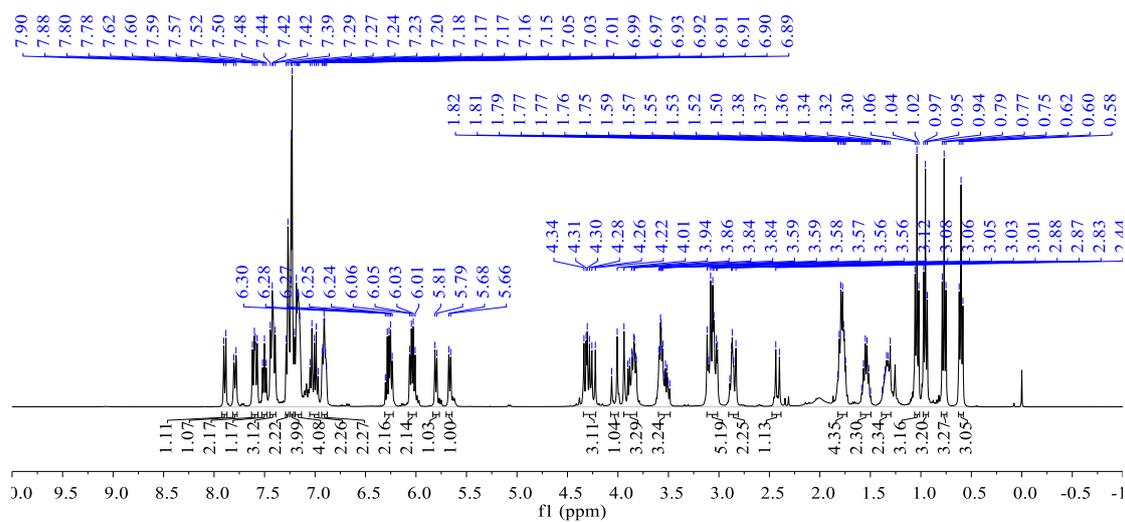


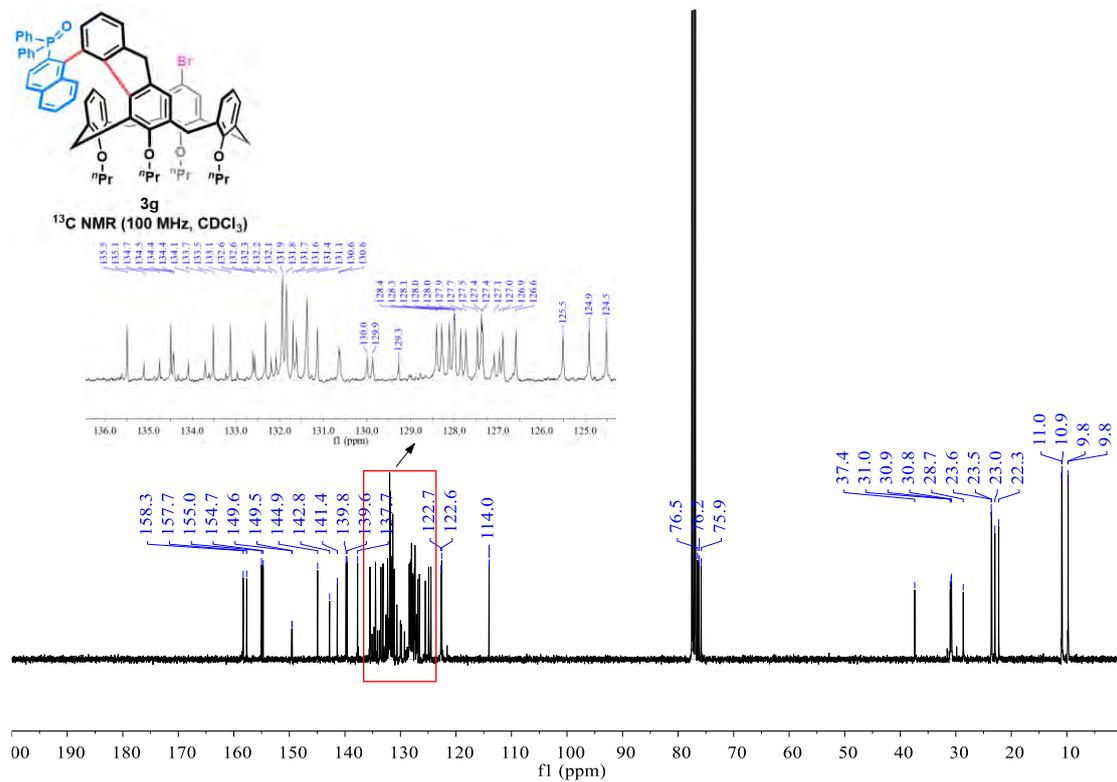


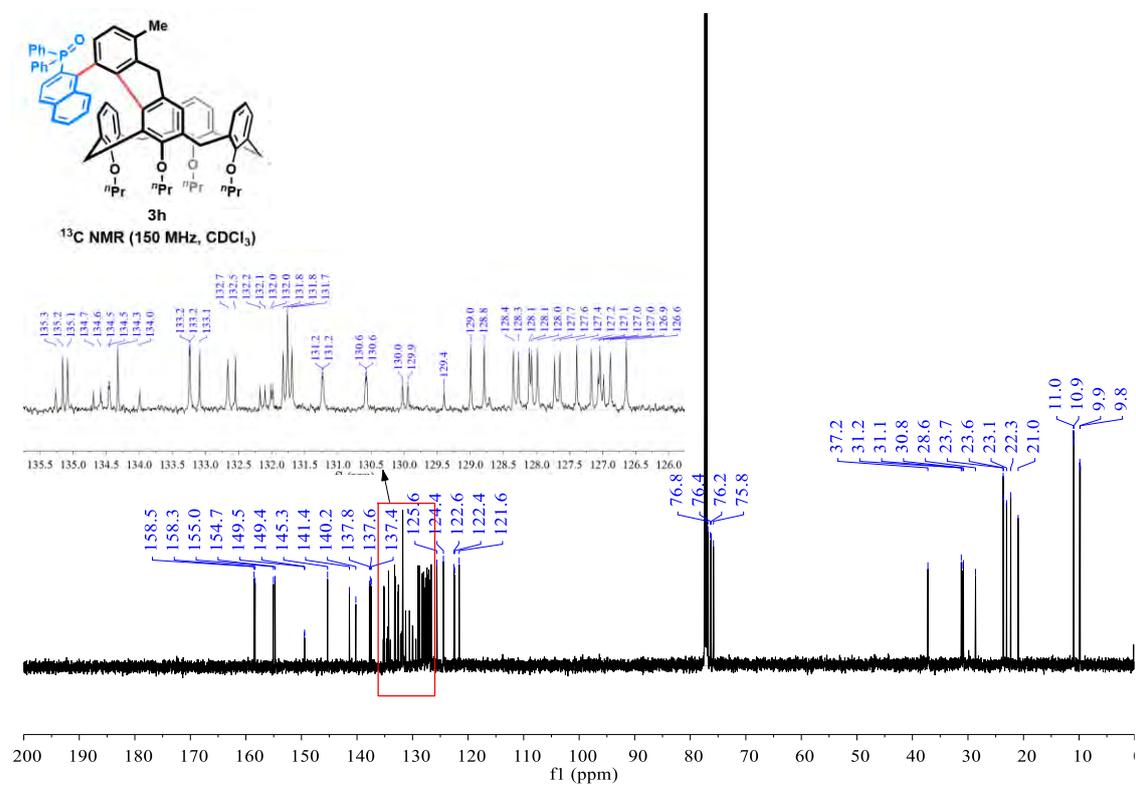
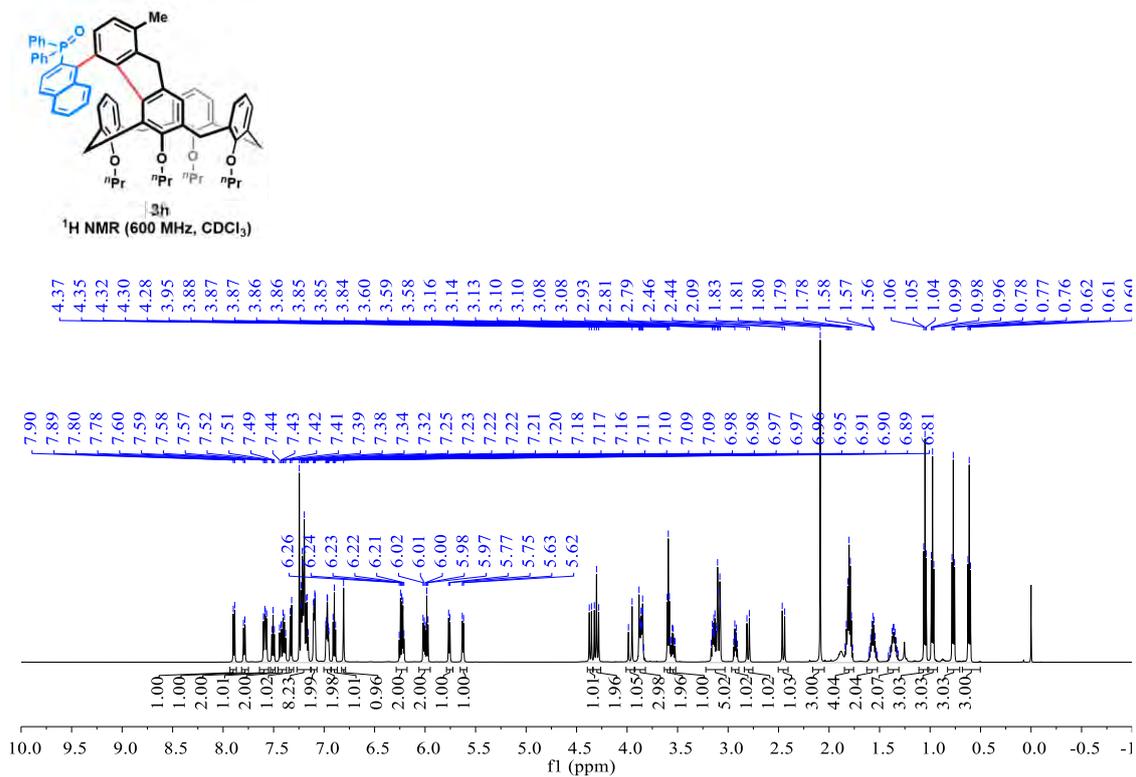
3f
³¹P NMR (243 MHz, CDCl₃)

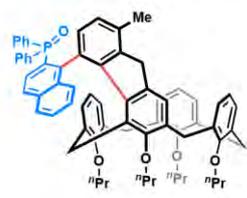


3g
¹H NMR (400 MHz, CDCl₃)



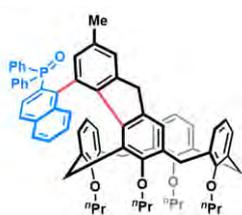
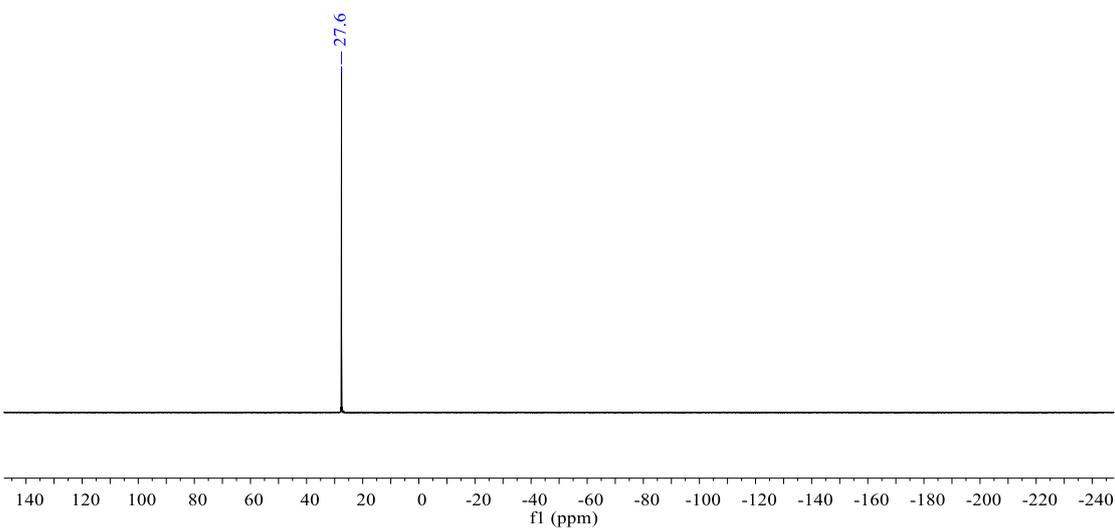






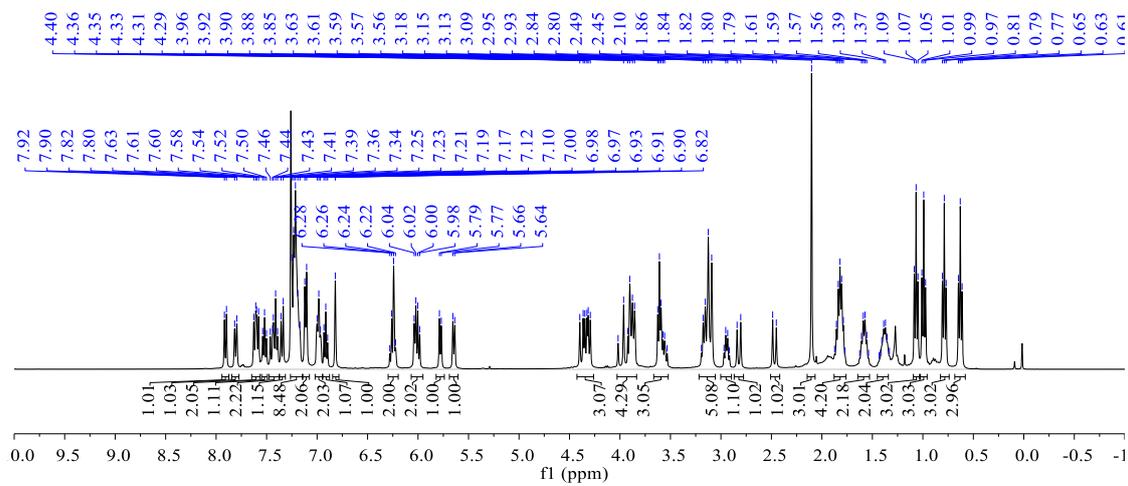
3h

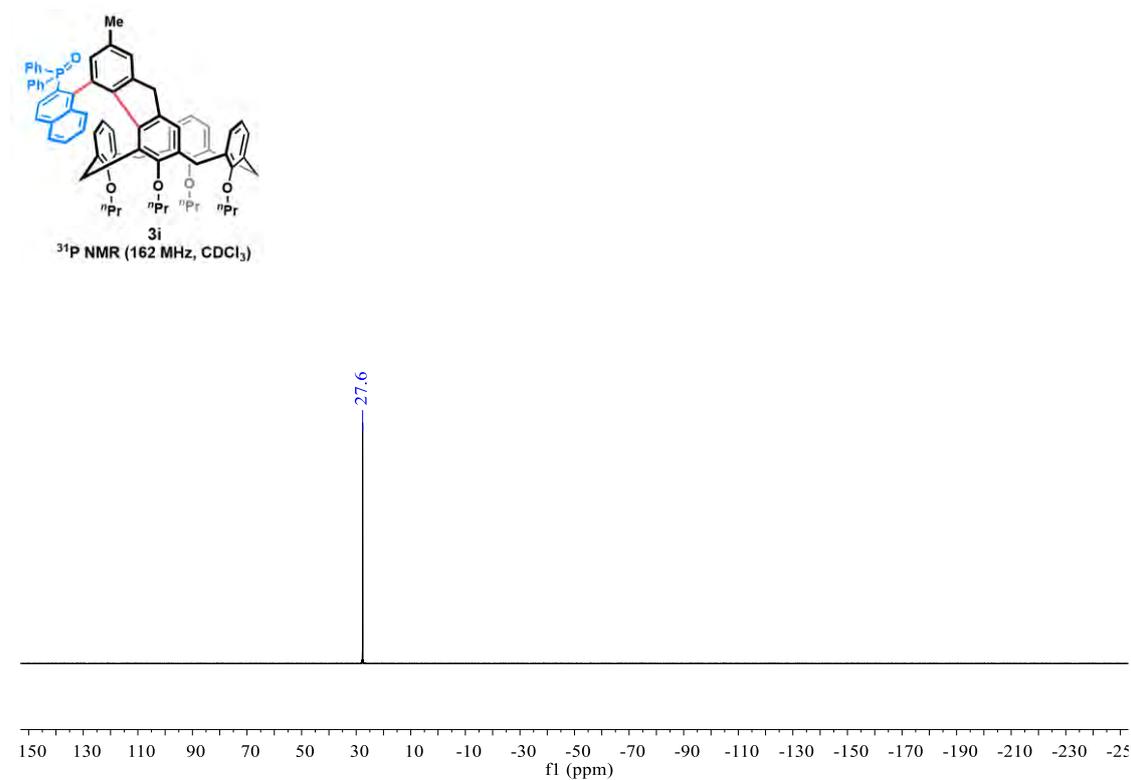
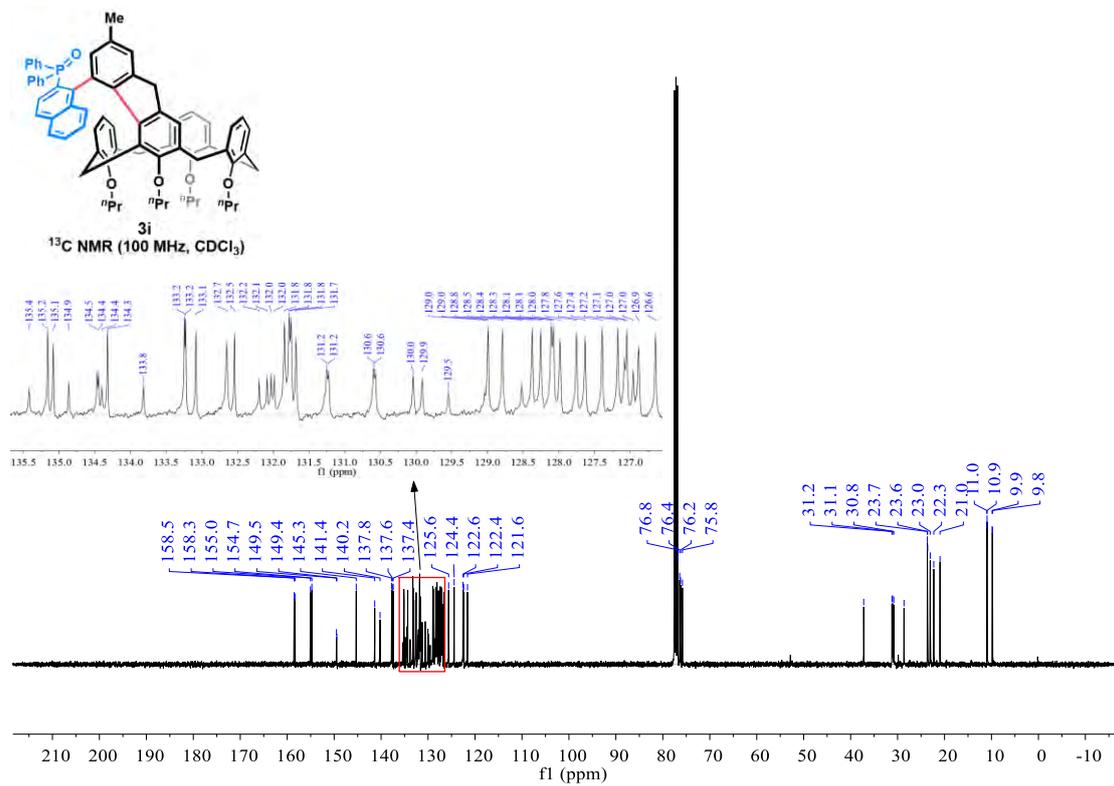
³¹P NMR (243 MHz, CDCl₃)

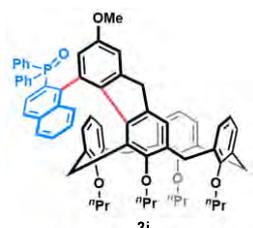


3i

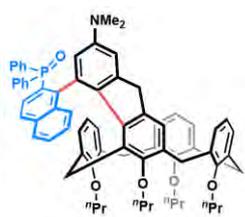
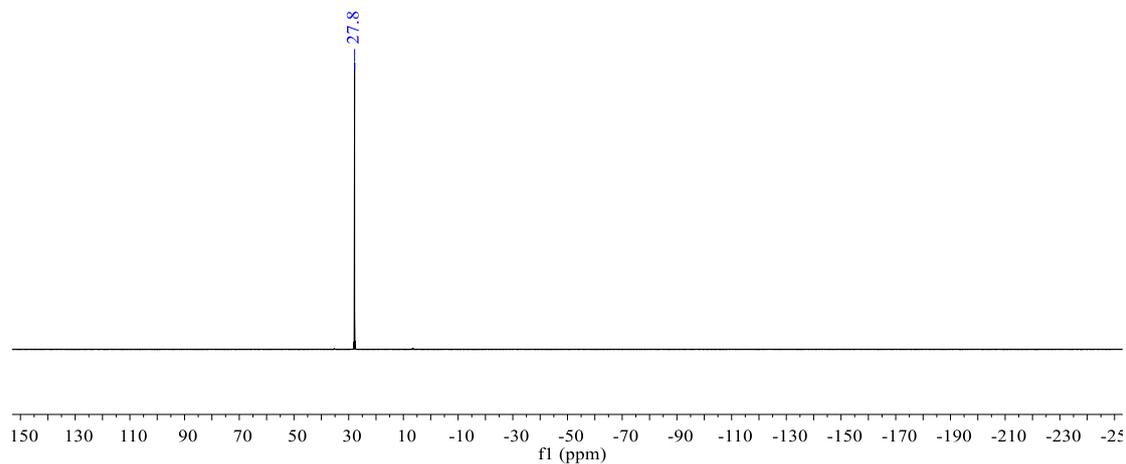
¹H NMR (400 MHz, CDCl₃)



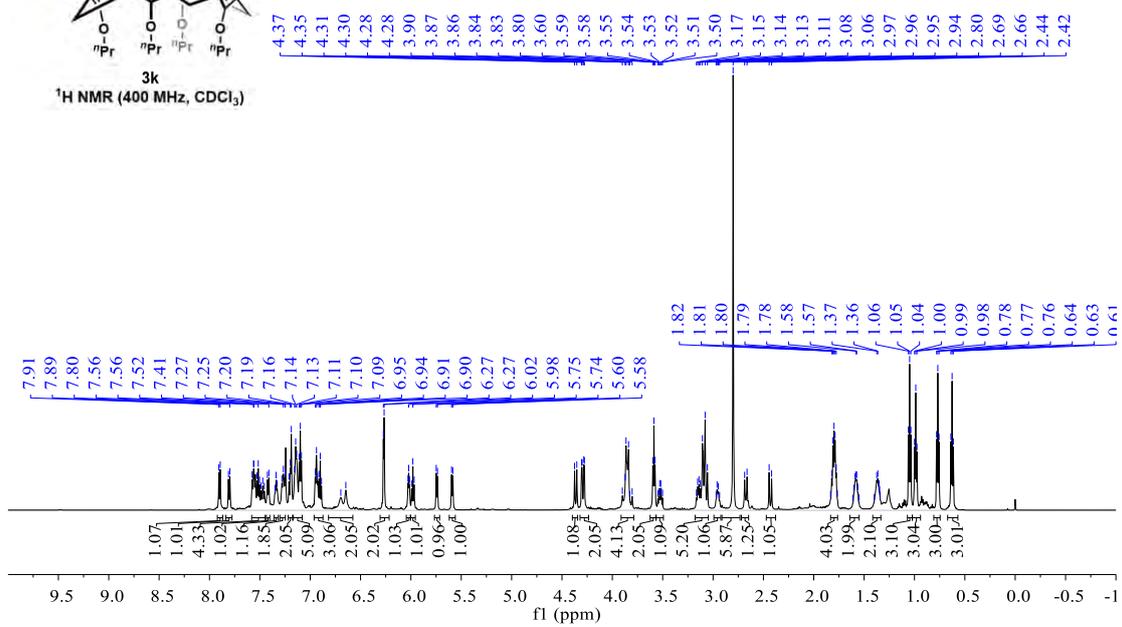


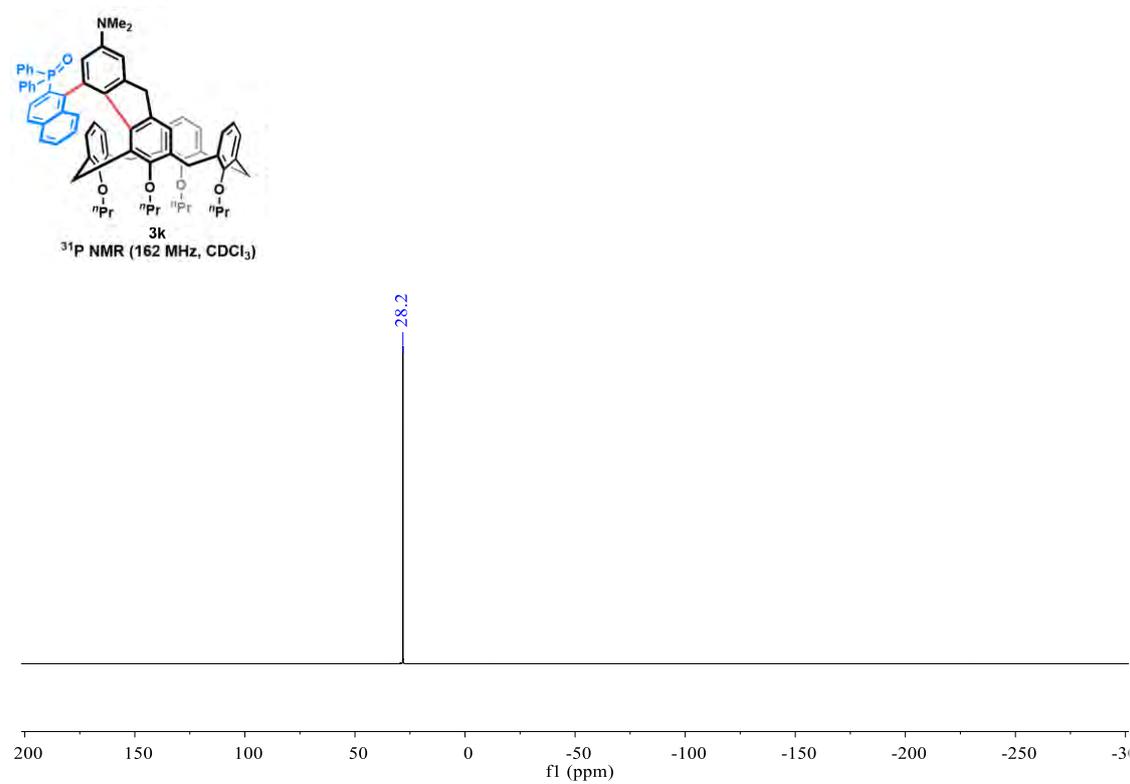
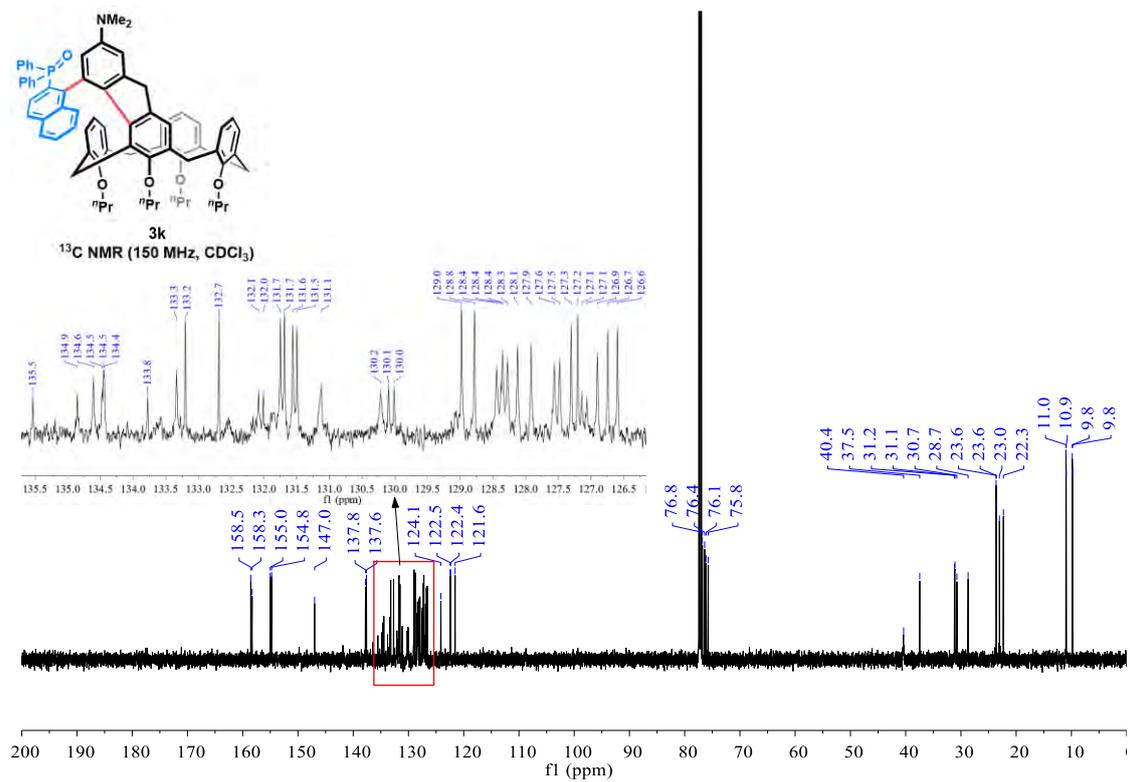


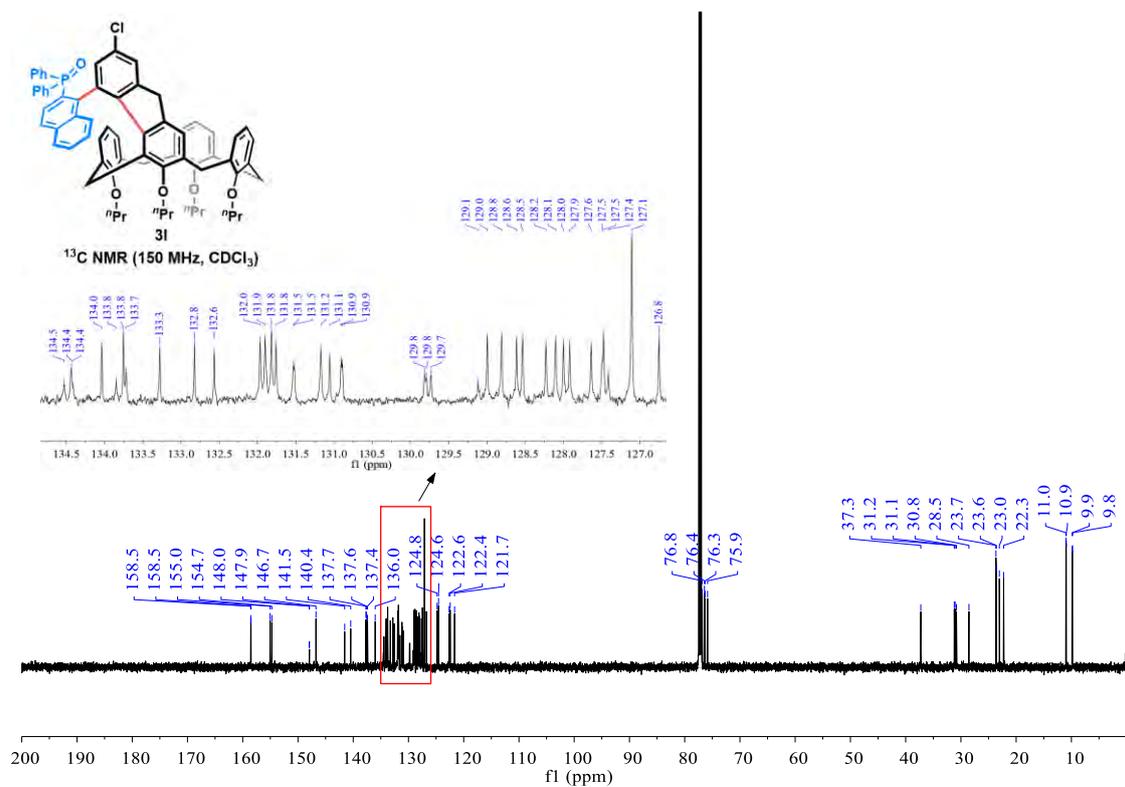
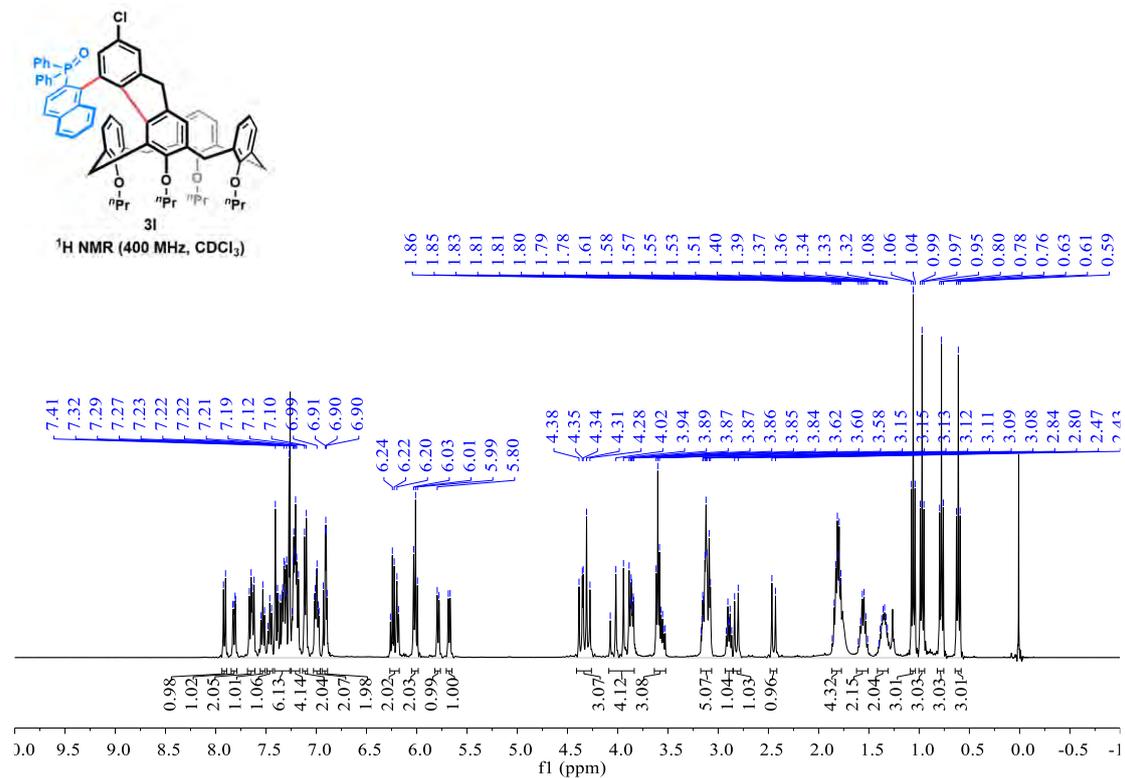
^{31}P NMR (162 MHz, CDCl_3)

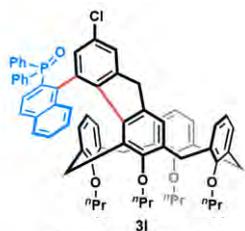


^1H NMR (400 MHz, CDCl_3)

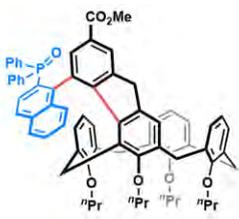
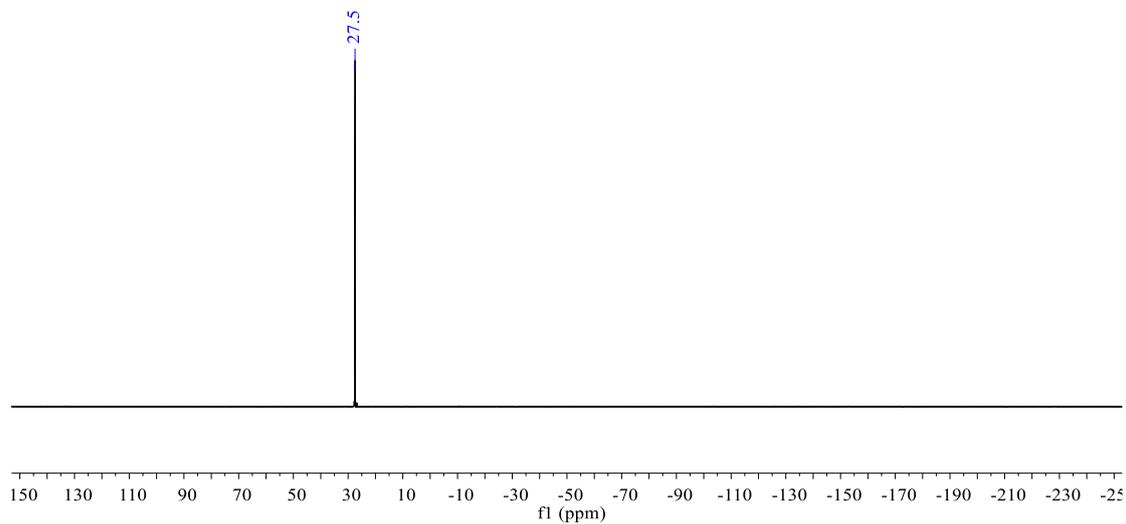




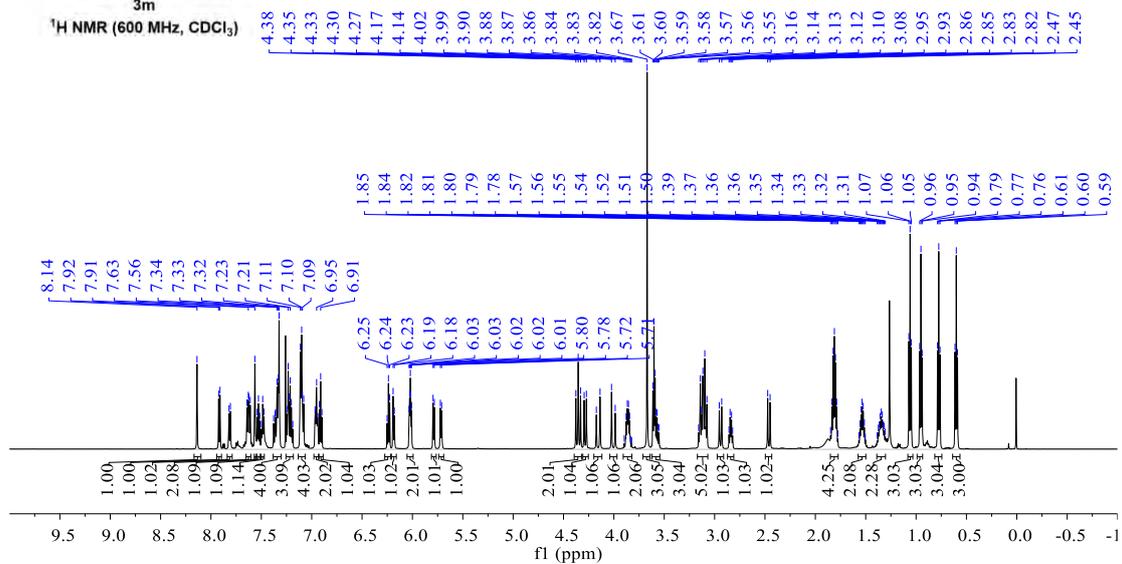


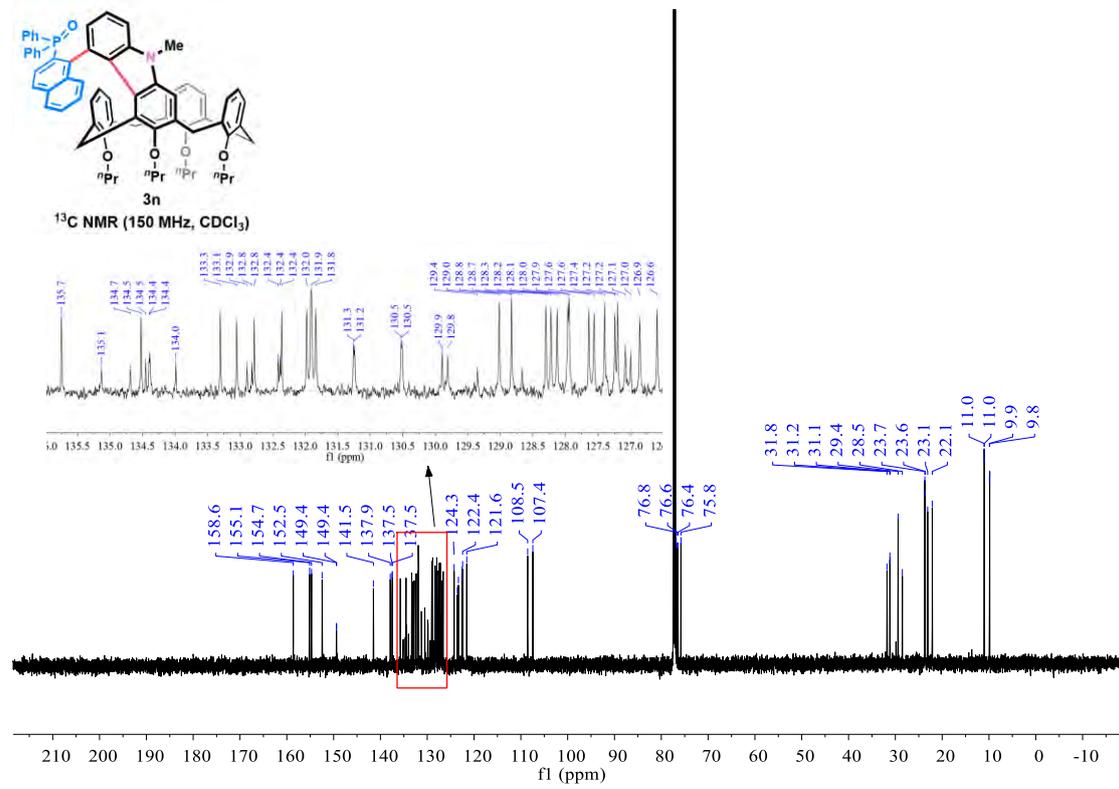
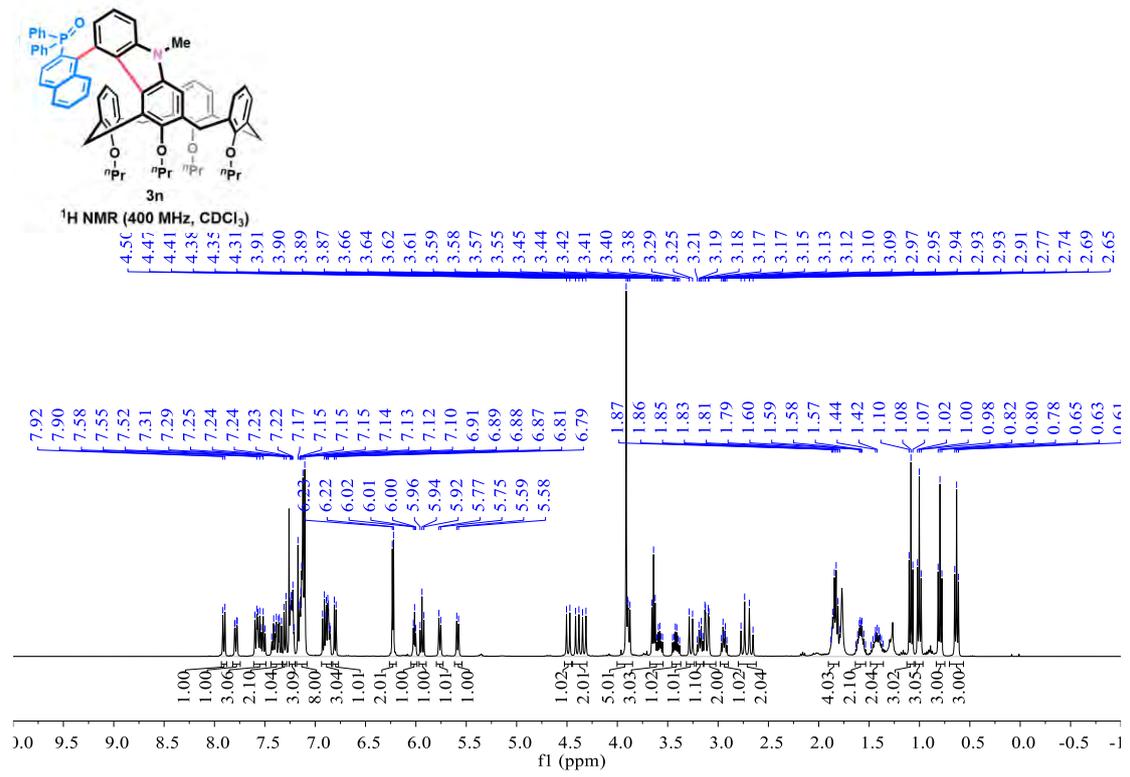


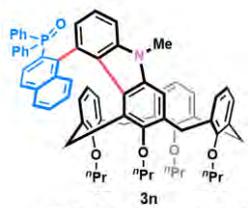
3l
³¹P NMR (162 MHz, CDCl₃)



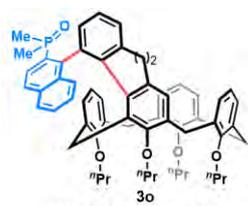
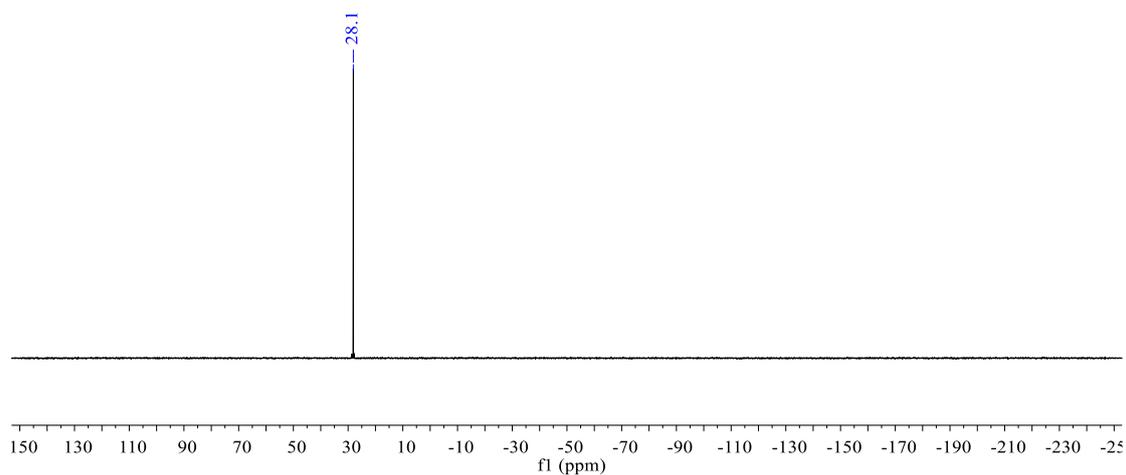
3m
¹H NMR (600 MHz, CDCl₃)



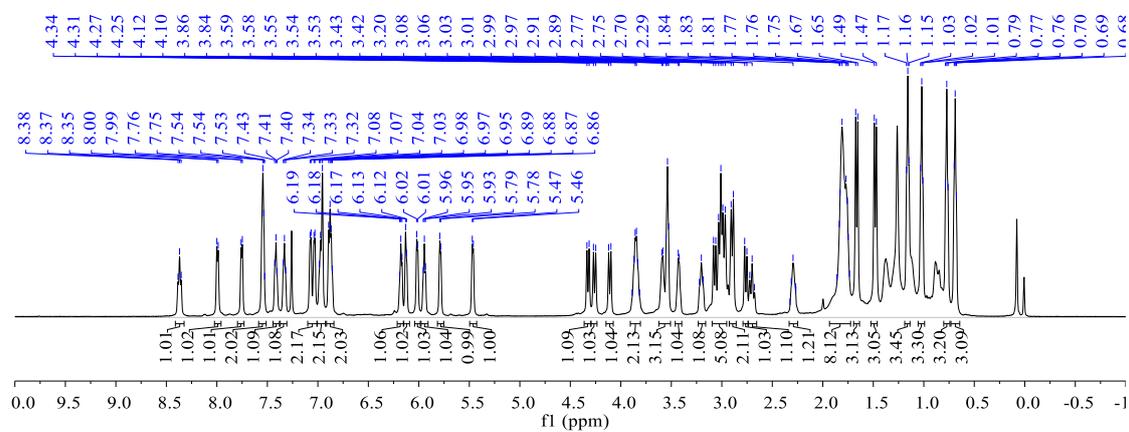


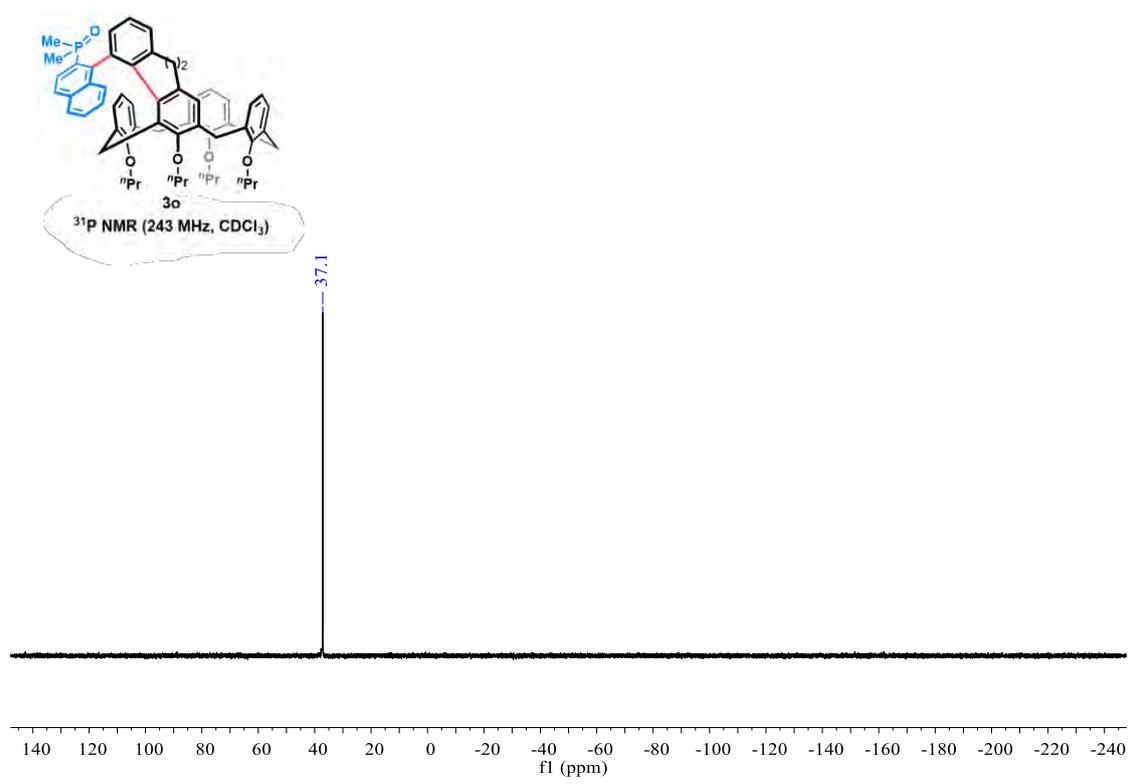
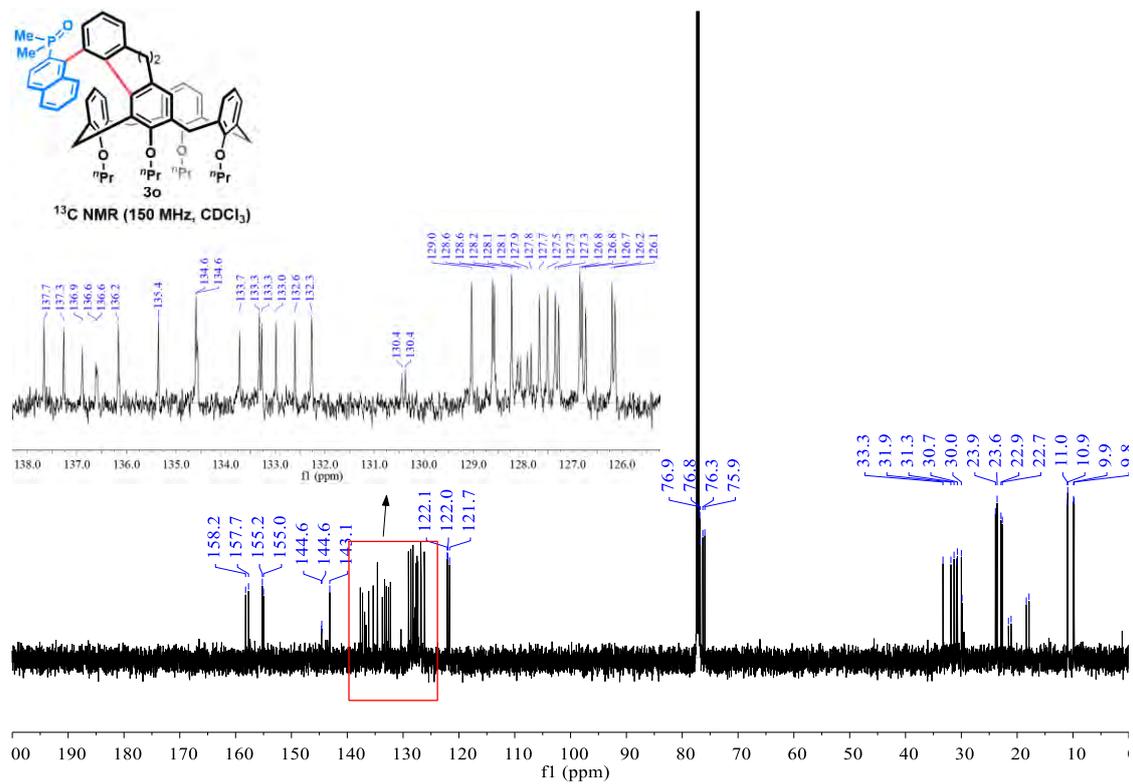


3n
³¹P NMR (162 MHz, CDCl₃)



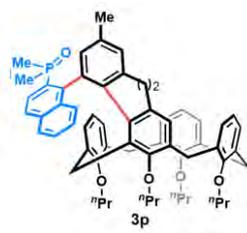
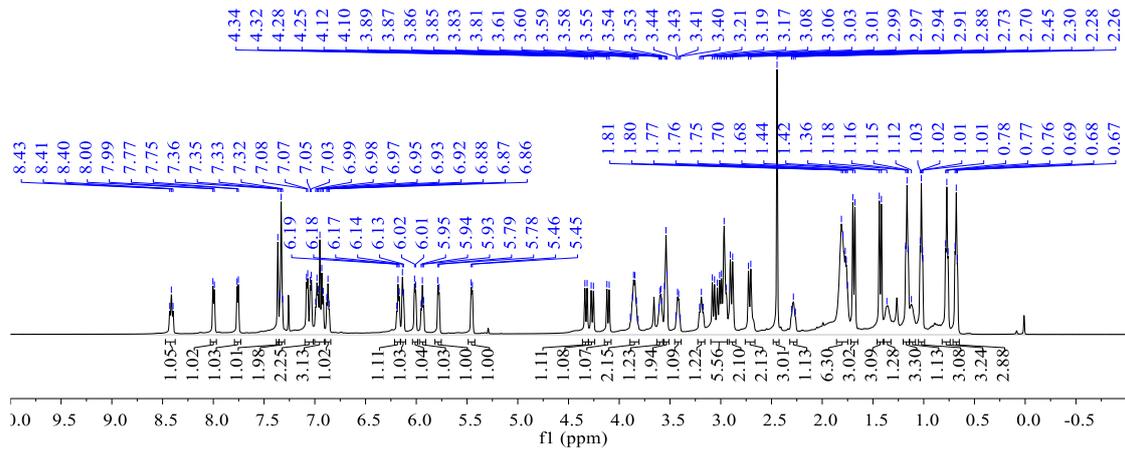
3o
¹H NMR (600 MHz, CDCl₃)



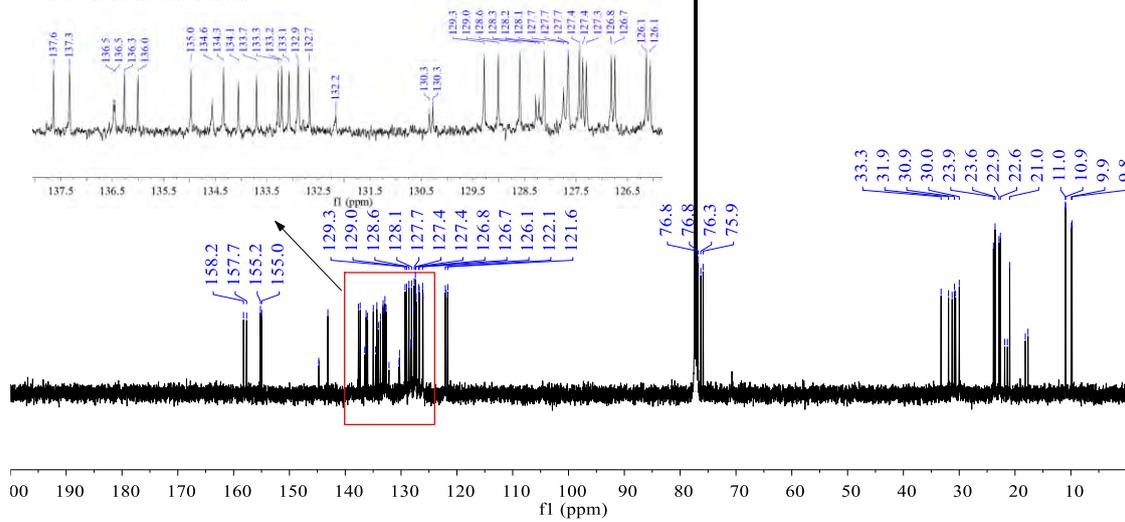


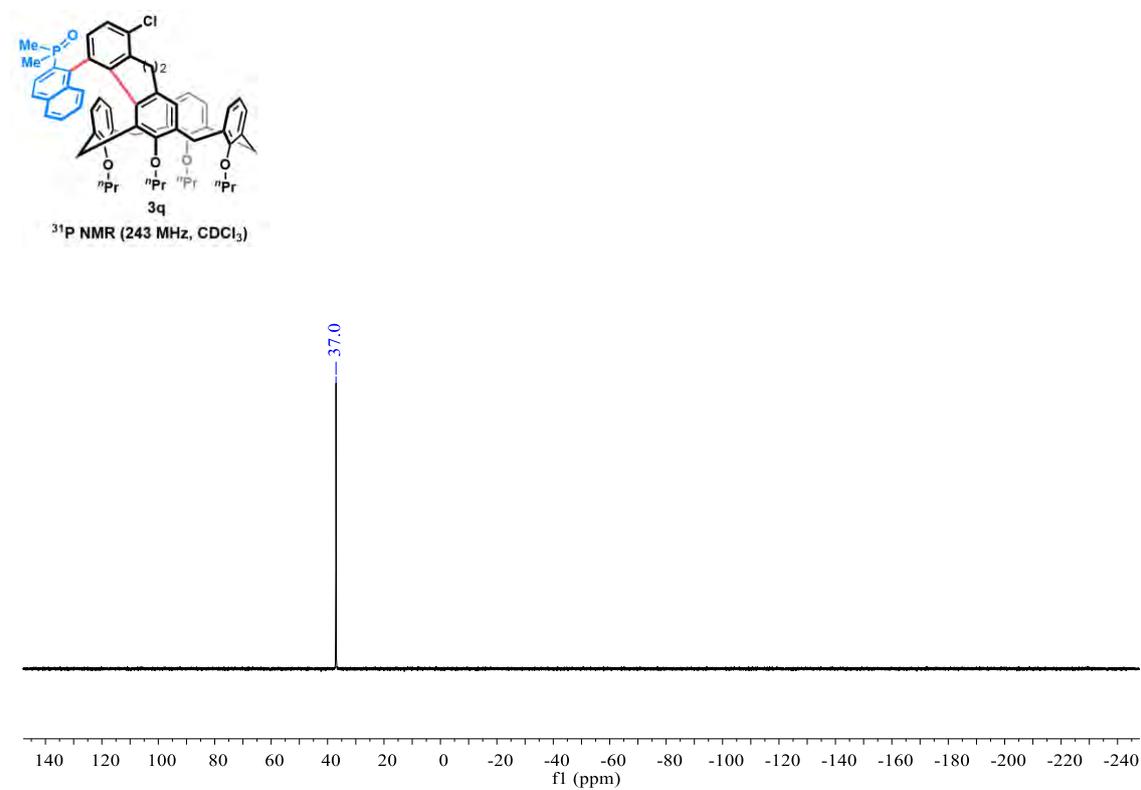
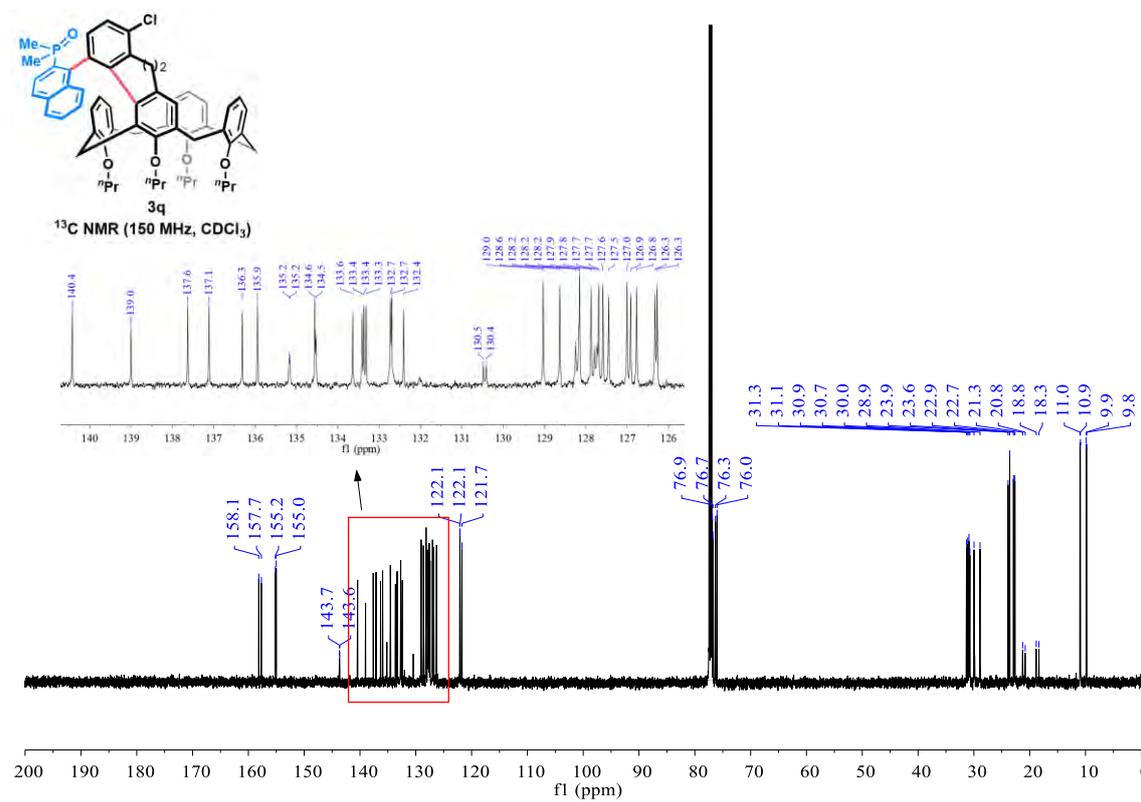


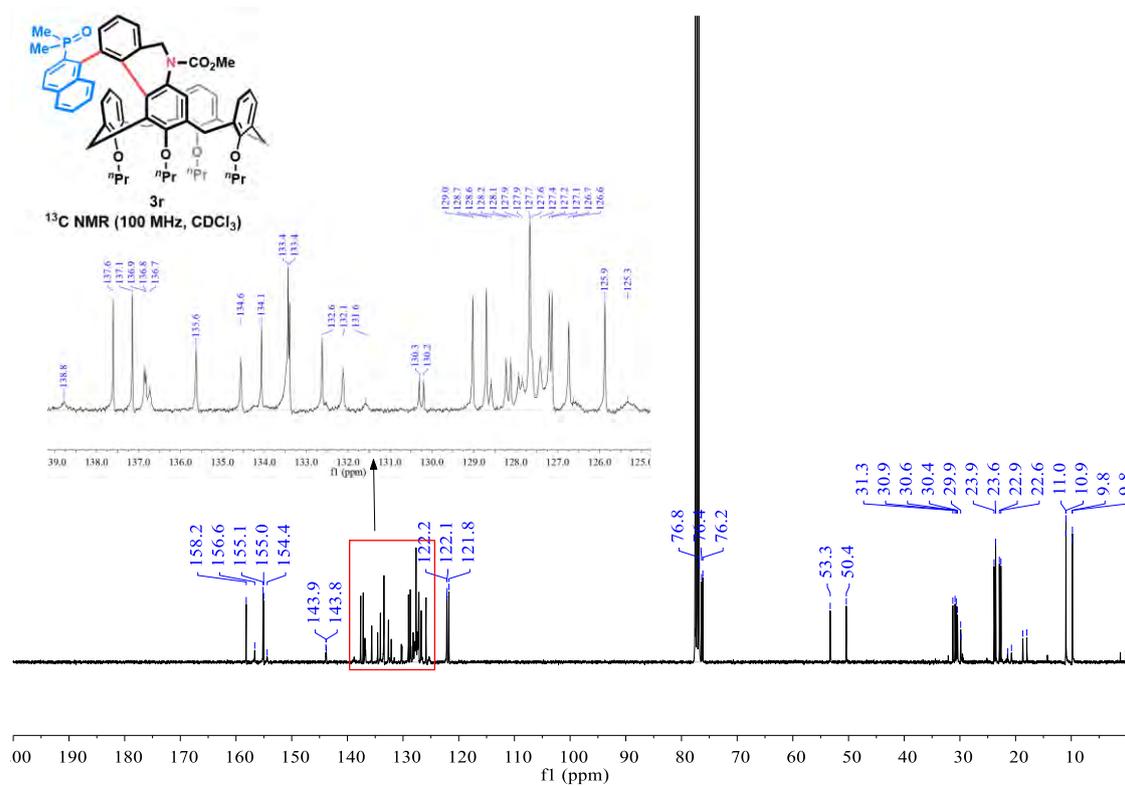
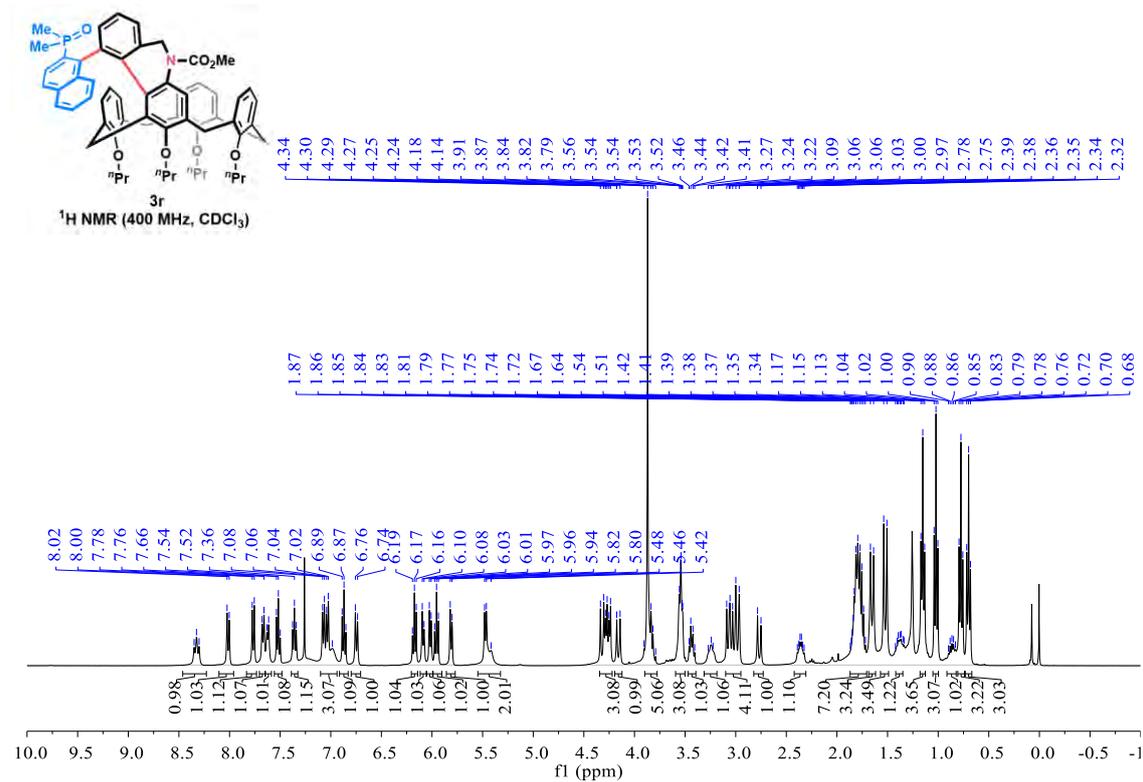
¹H NMR (600 MHz, CDCl₃)

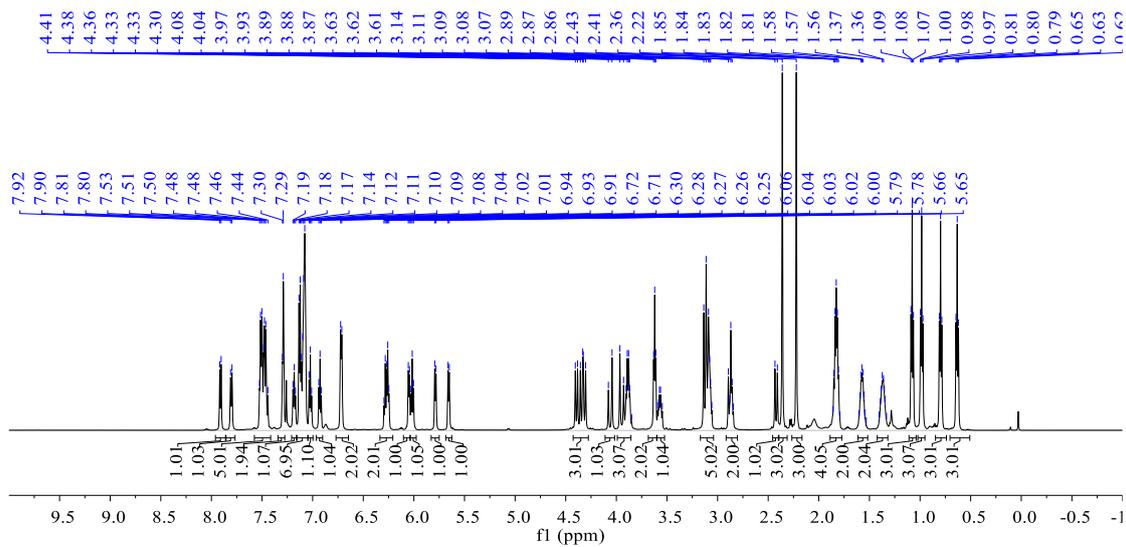
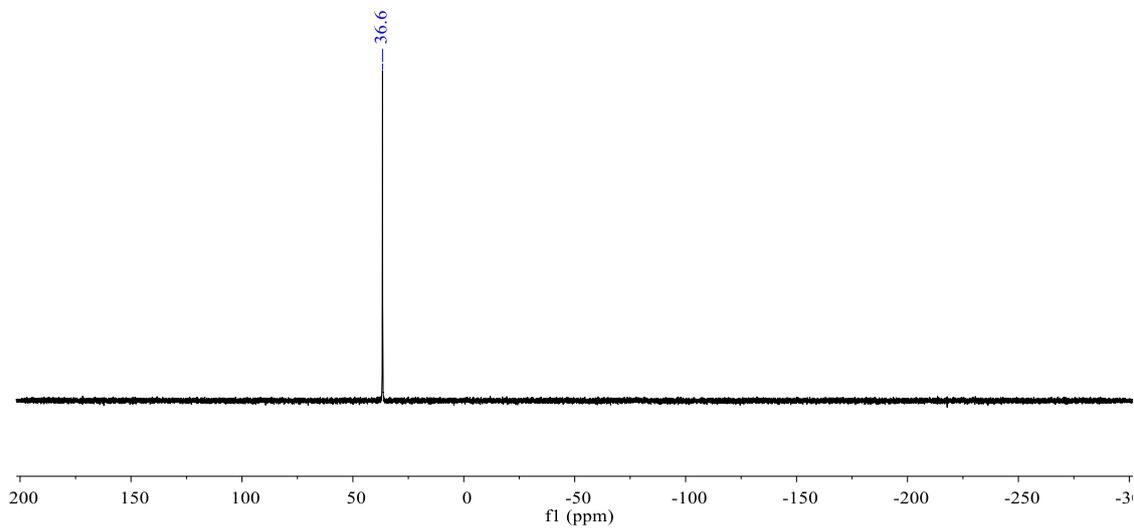
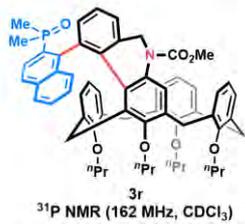


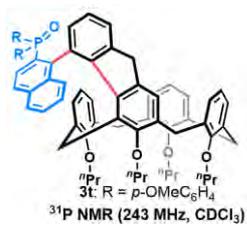
¹³C NMR (150 MHz, CDCl₃)



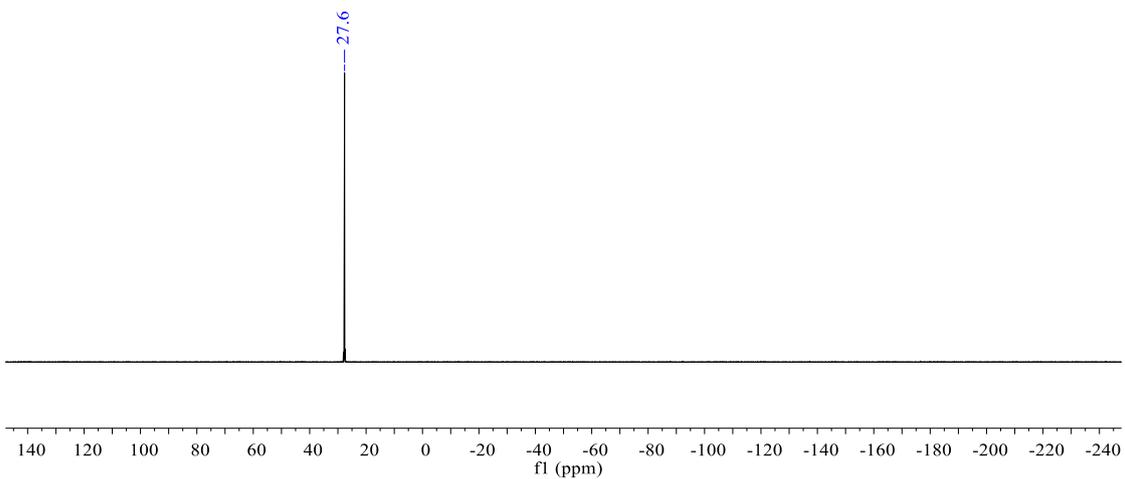




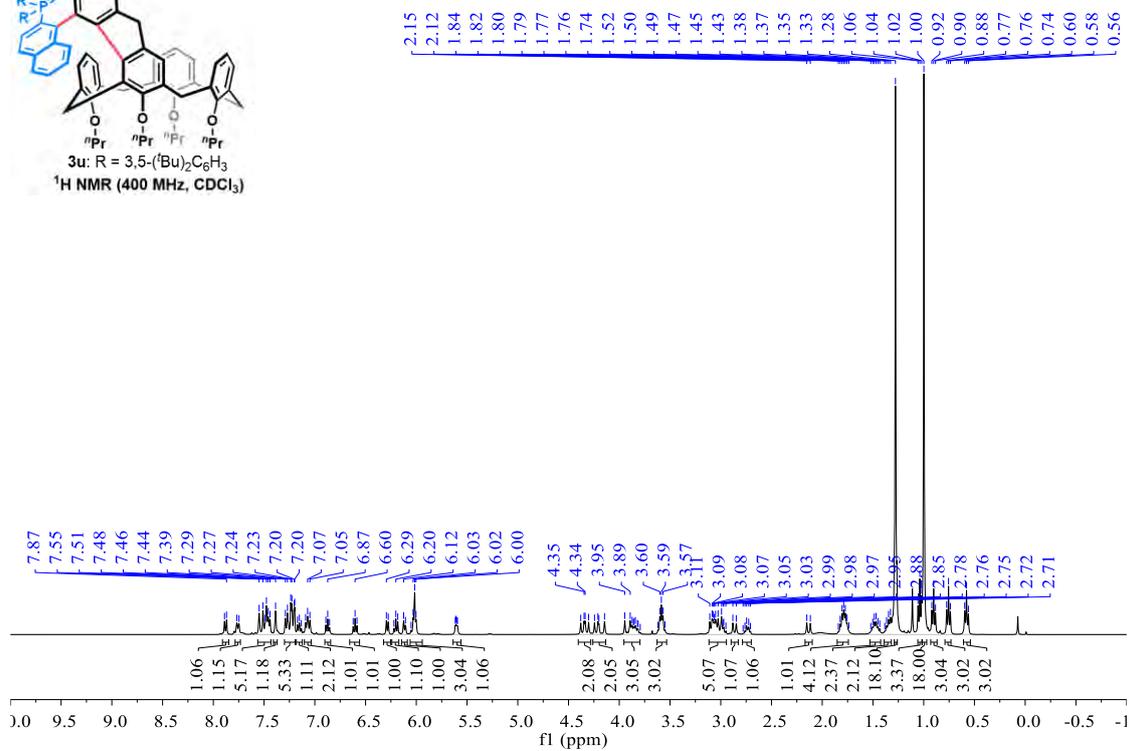


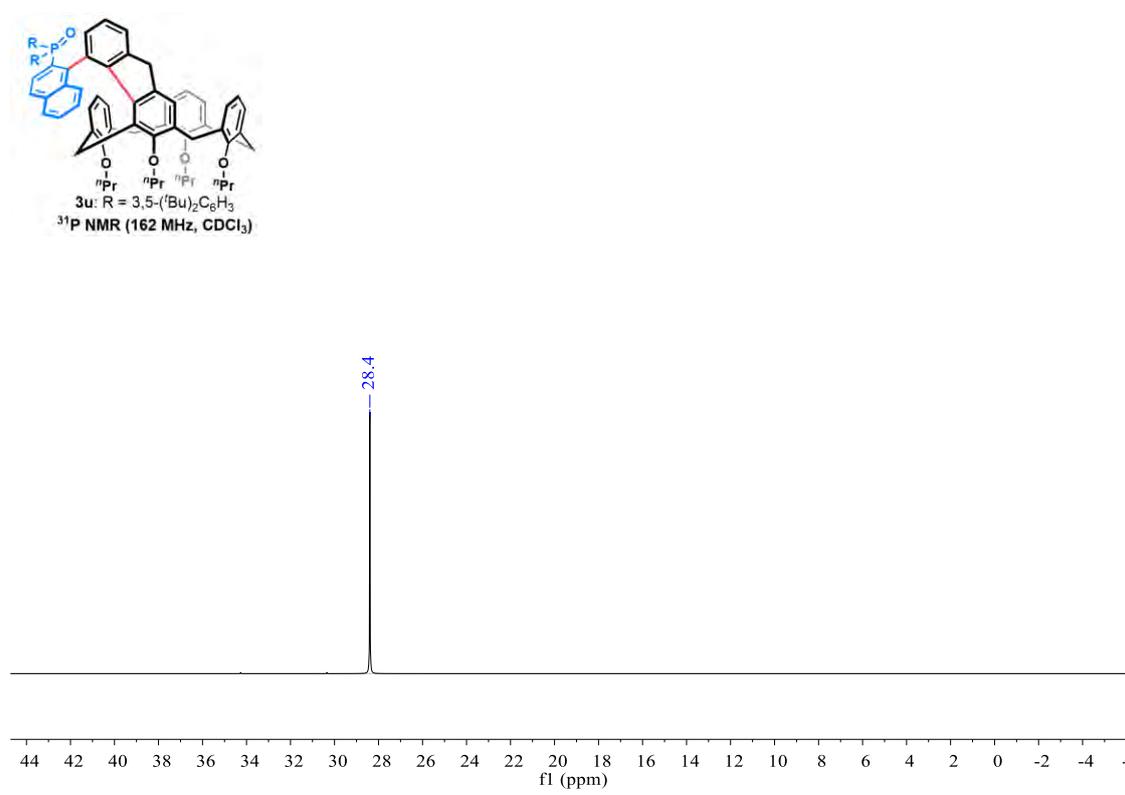
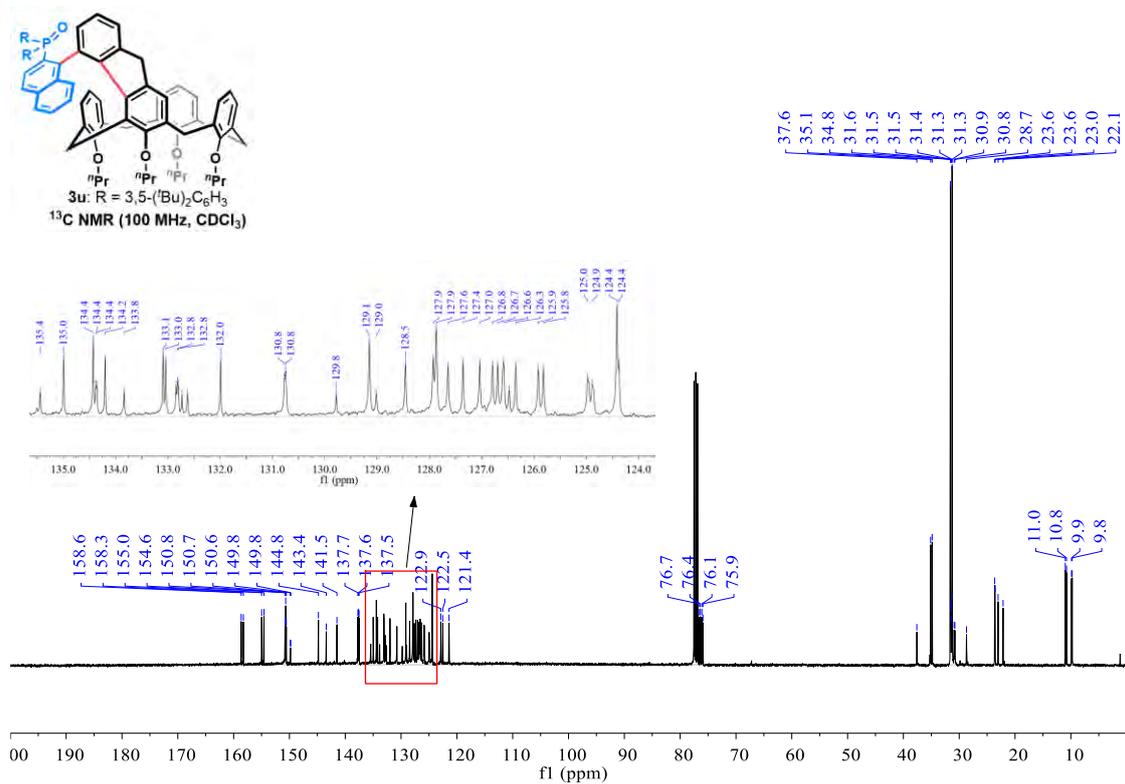


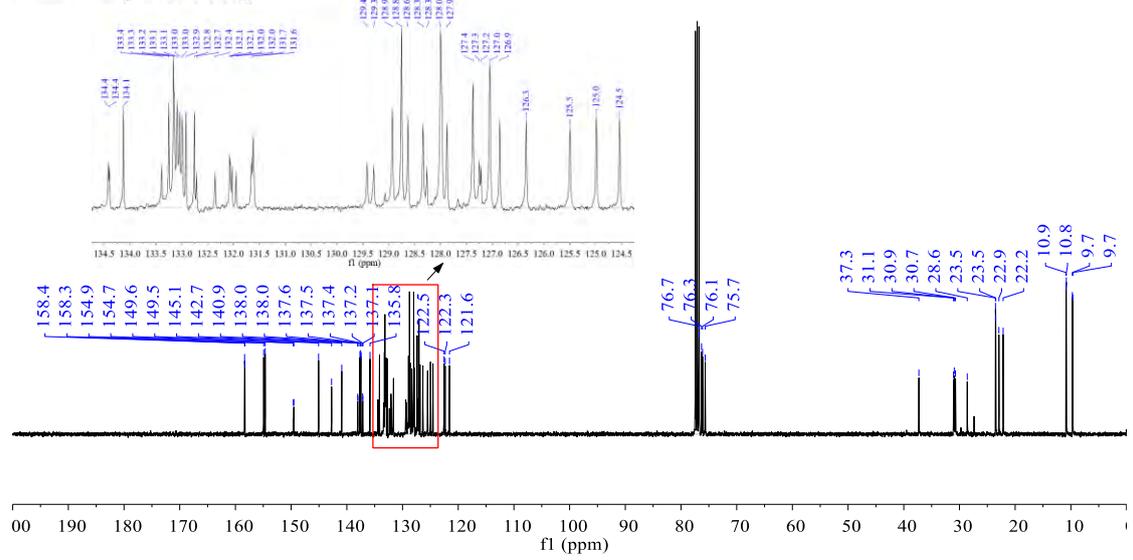
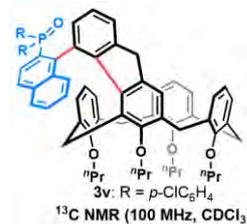
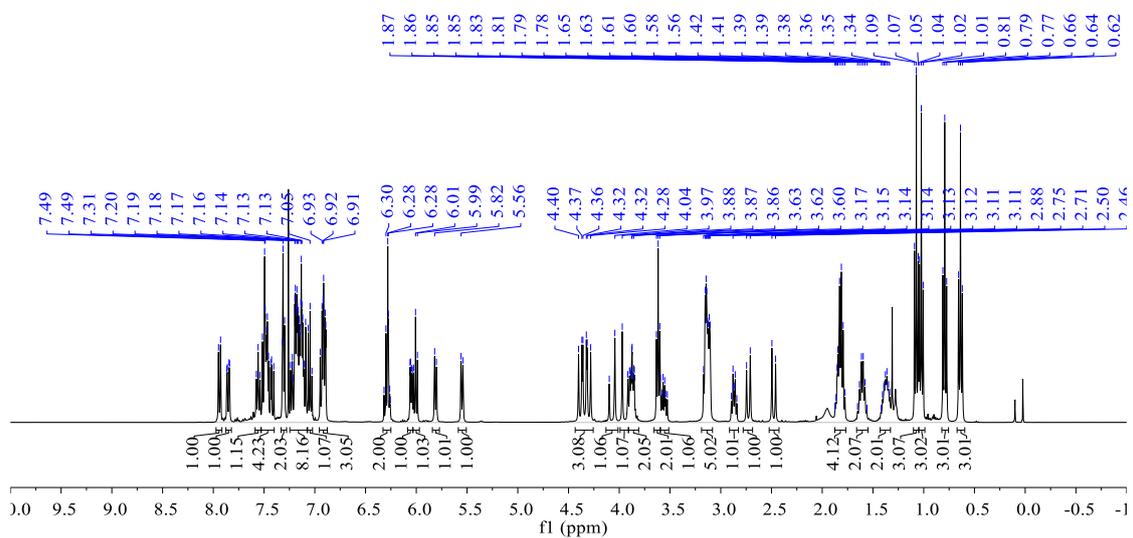
³¹P NMR (243 MHz, CDCl₃)

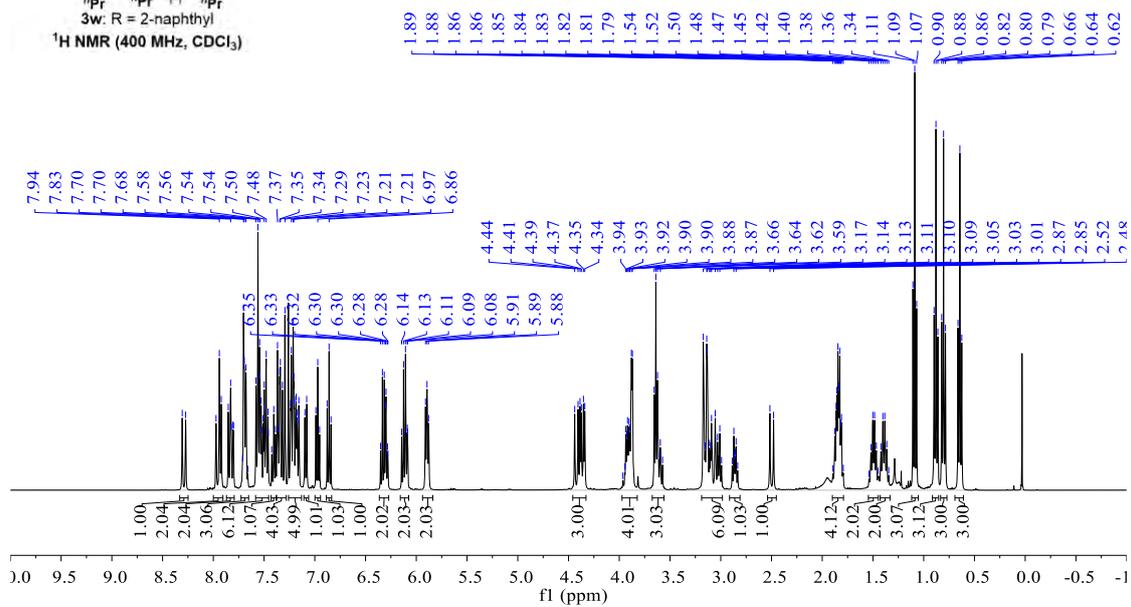
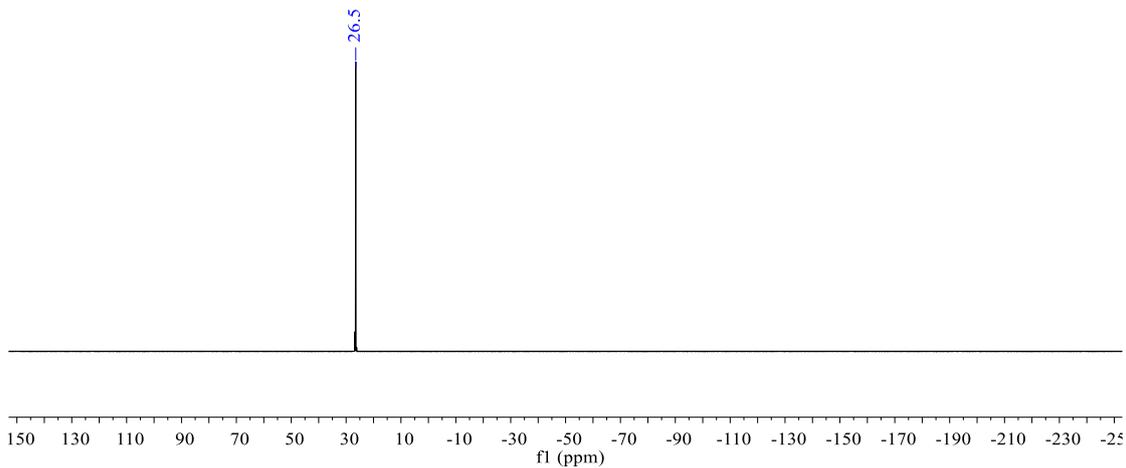


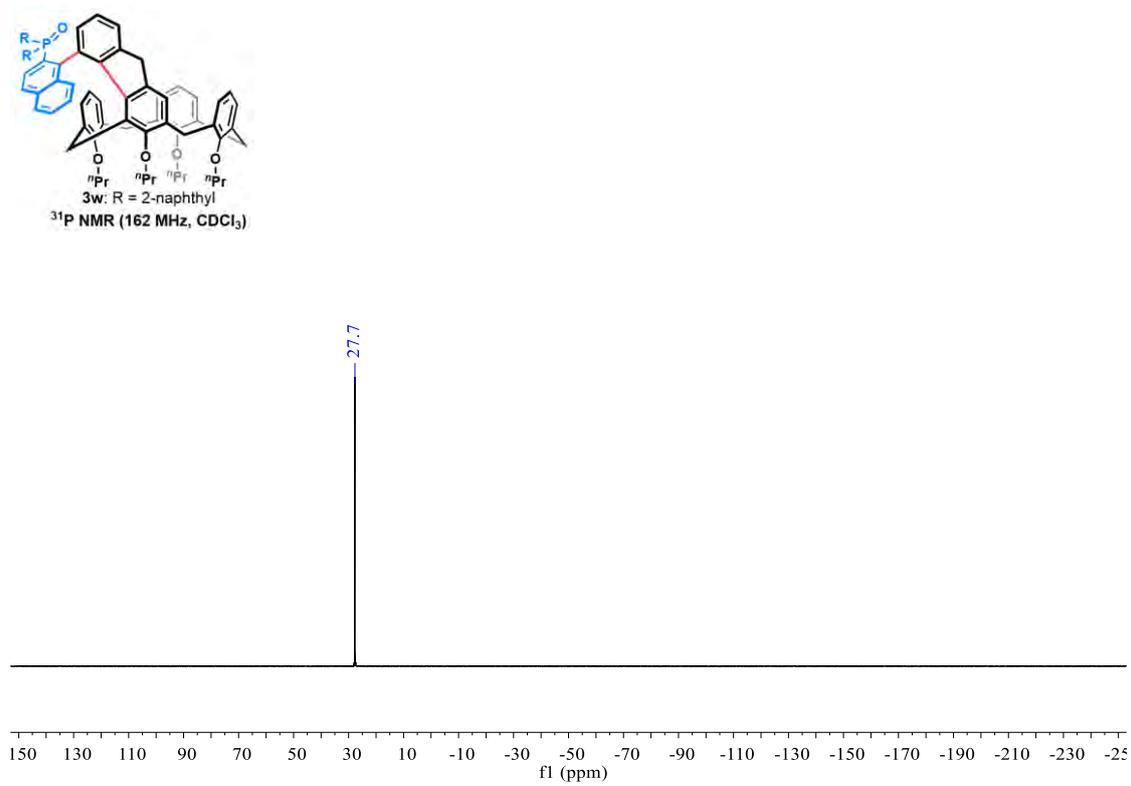
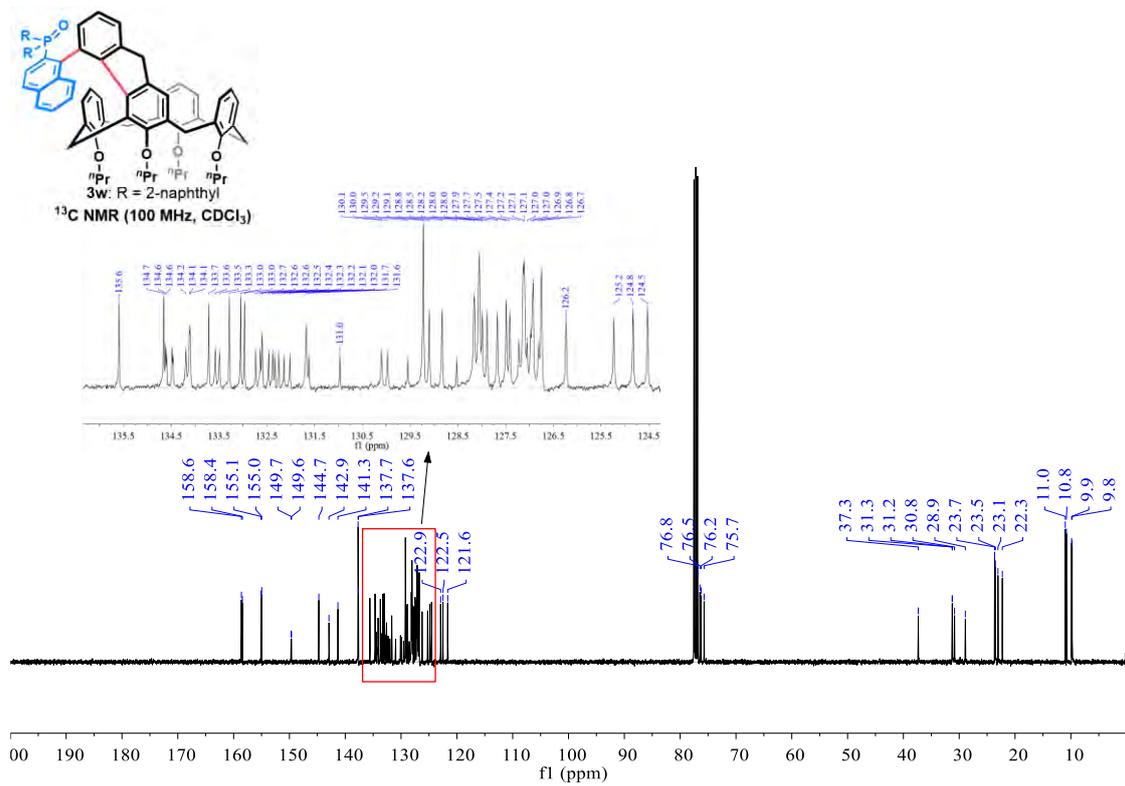
¹H NMR (400 MHz, CDCl₃)

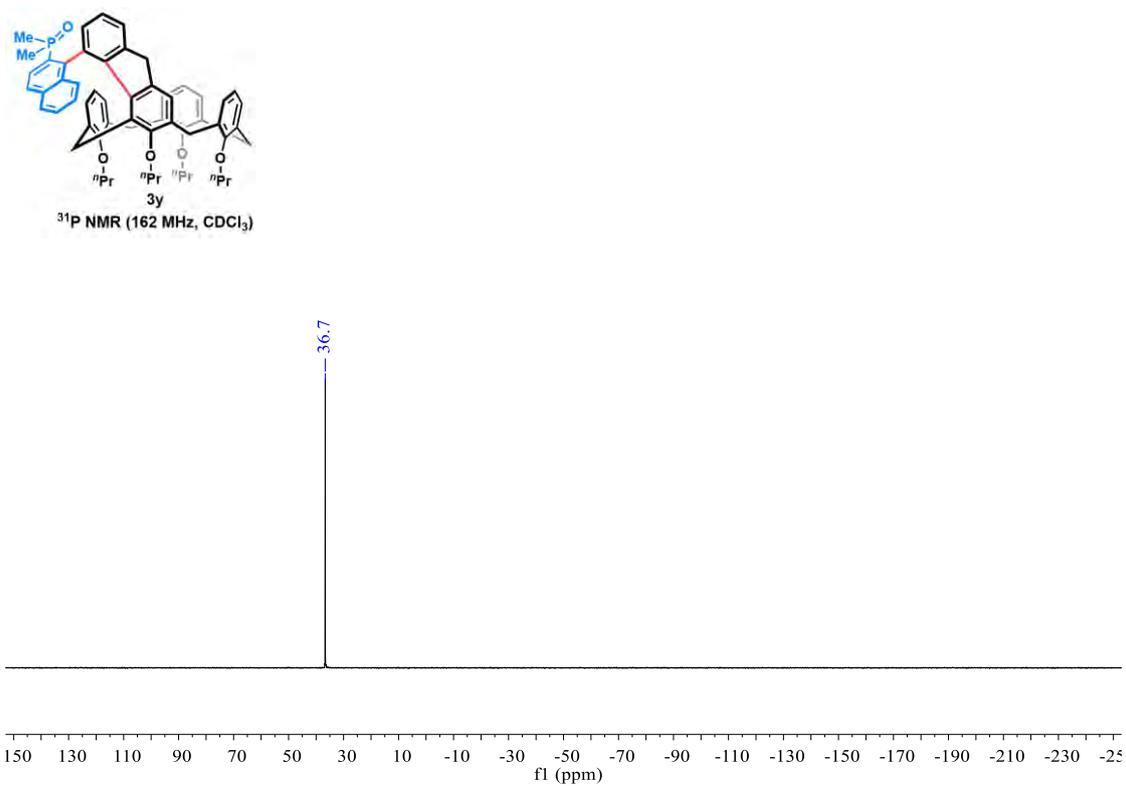
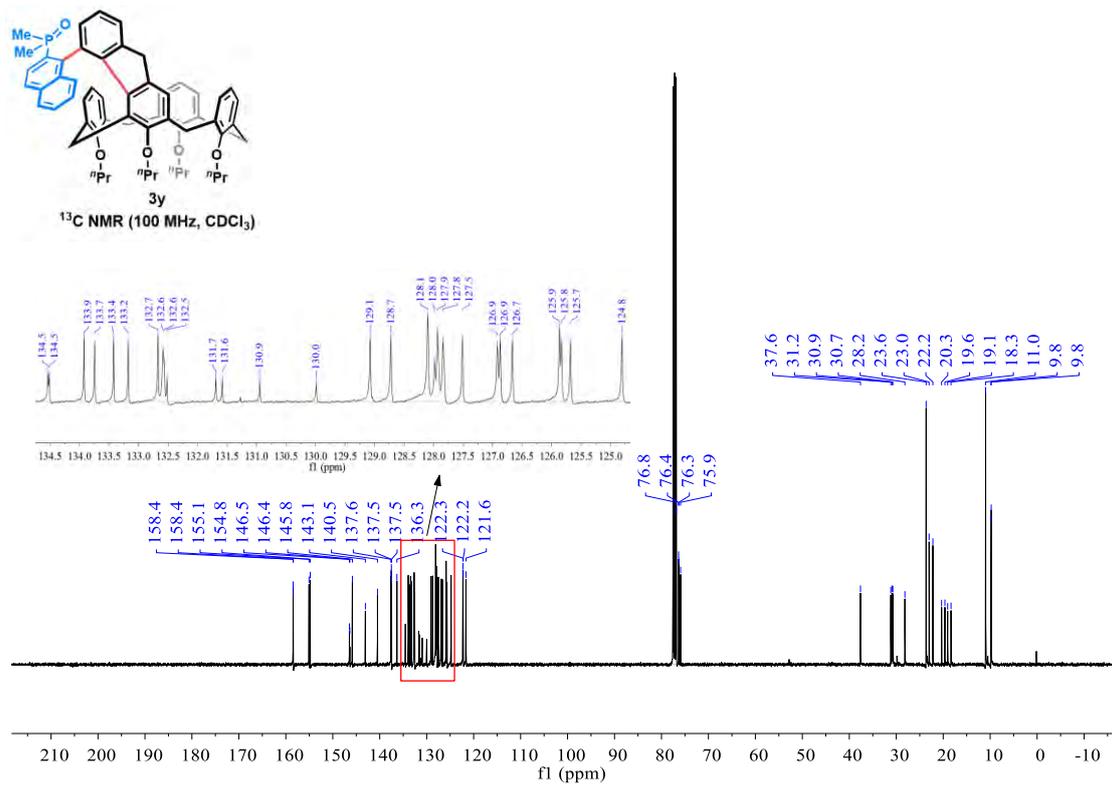


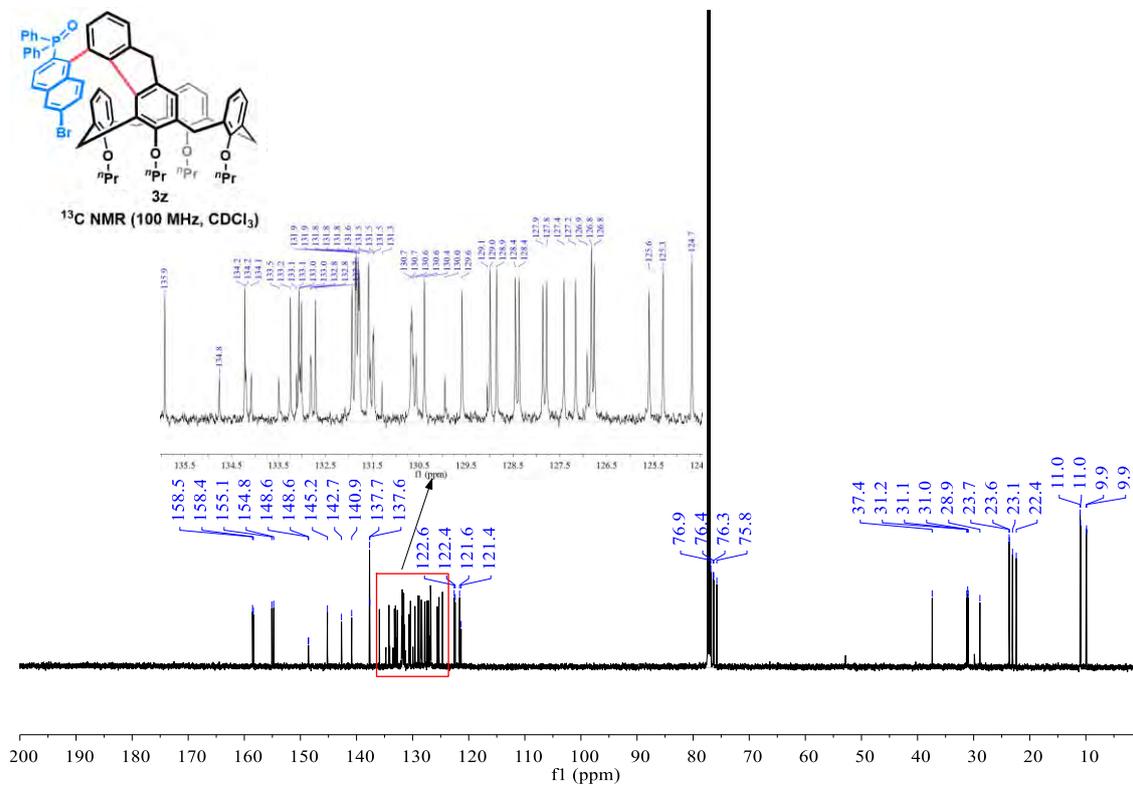
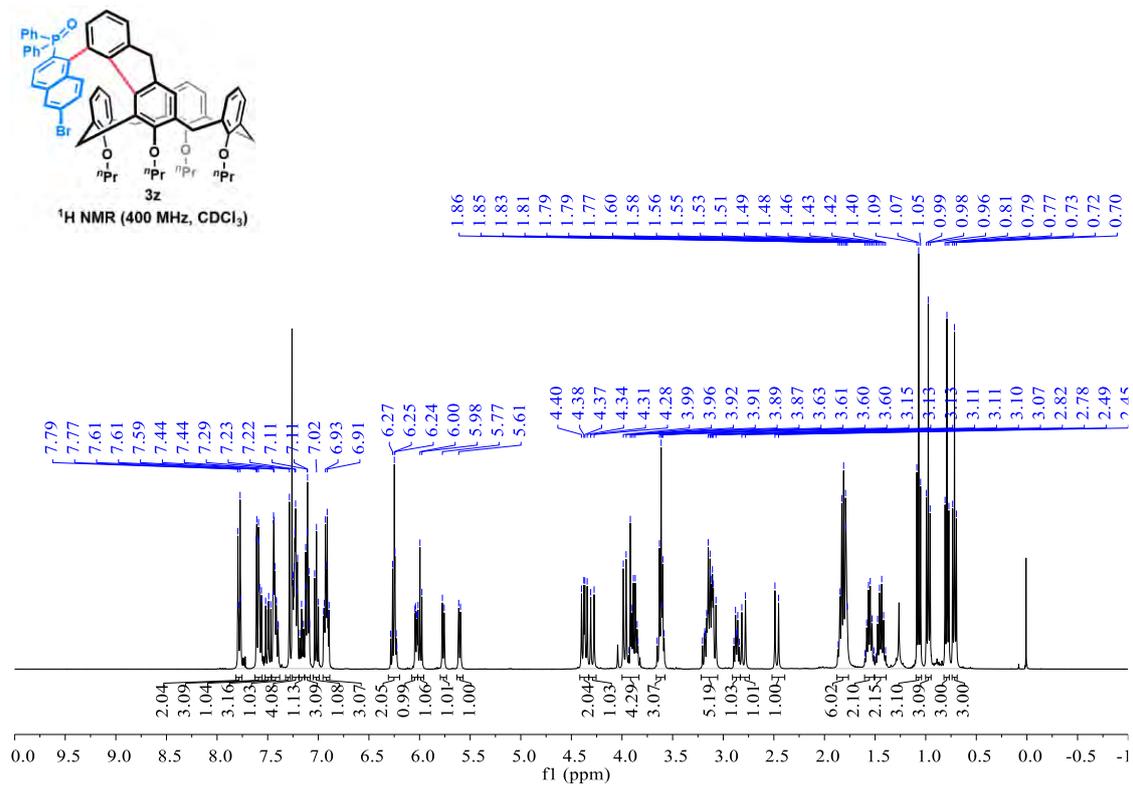


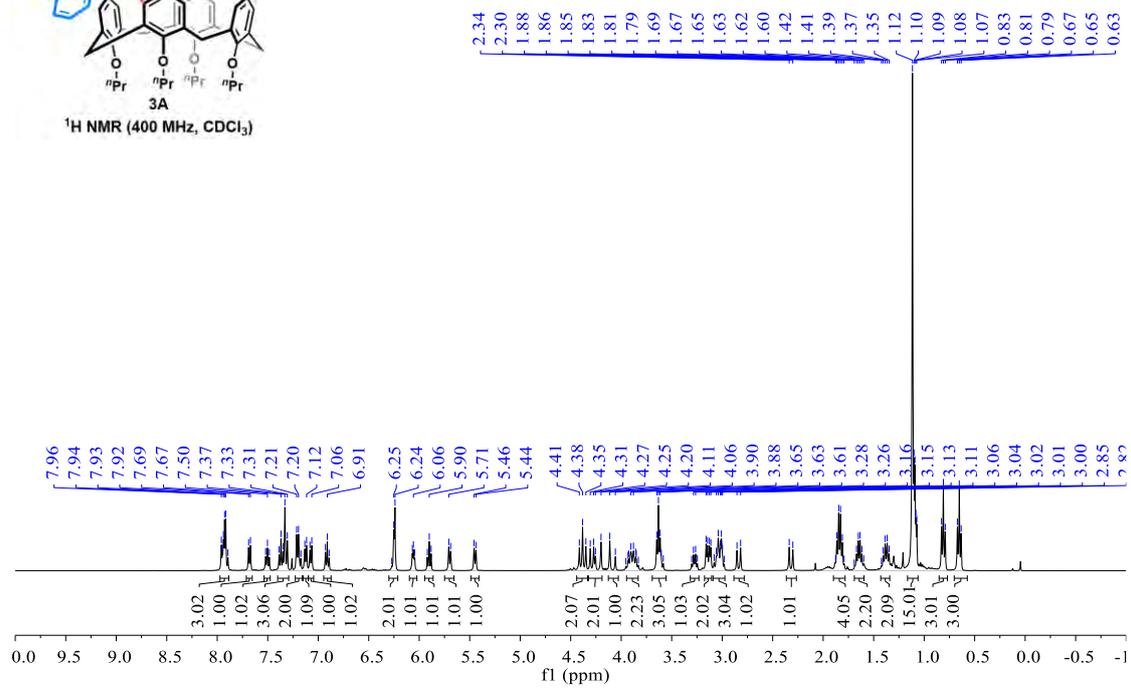
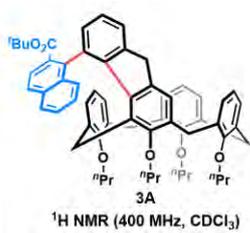
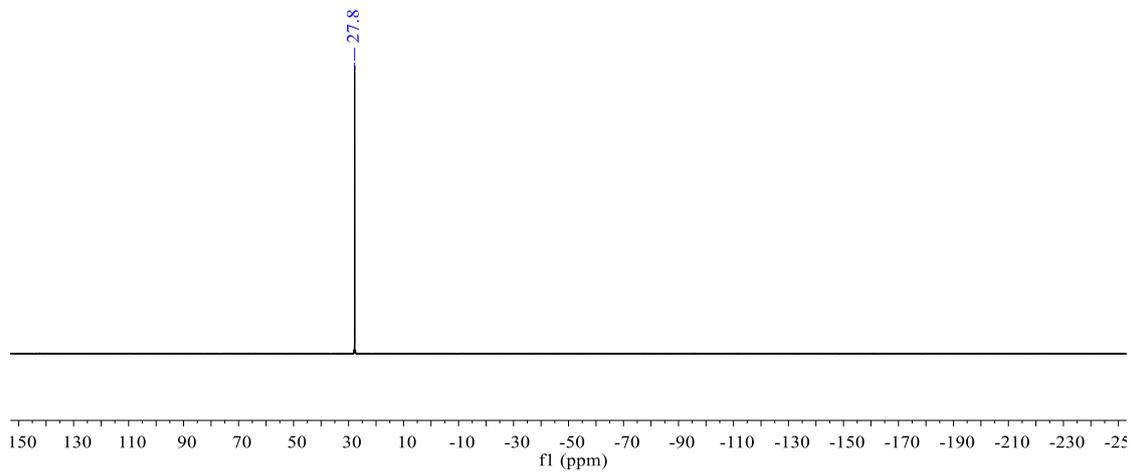


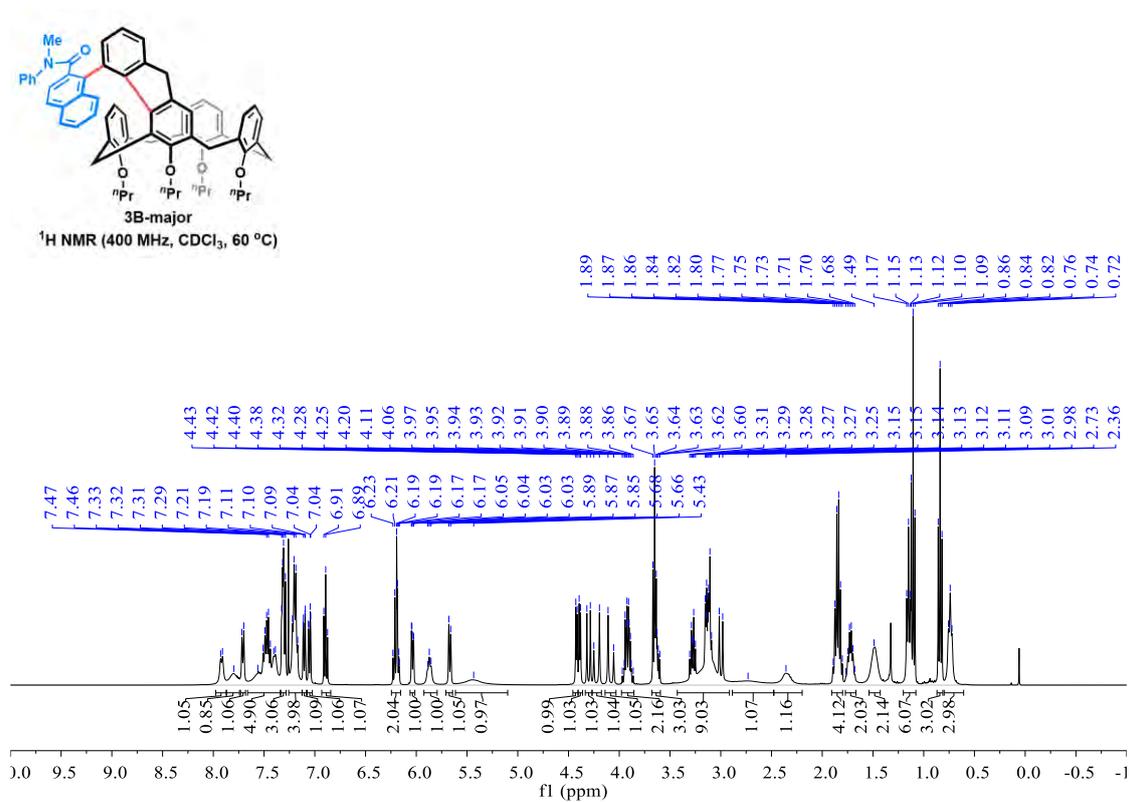
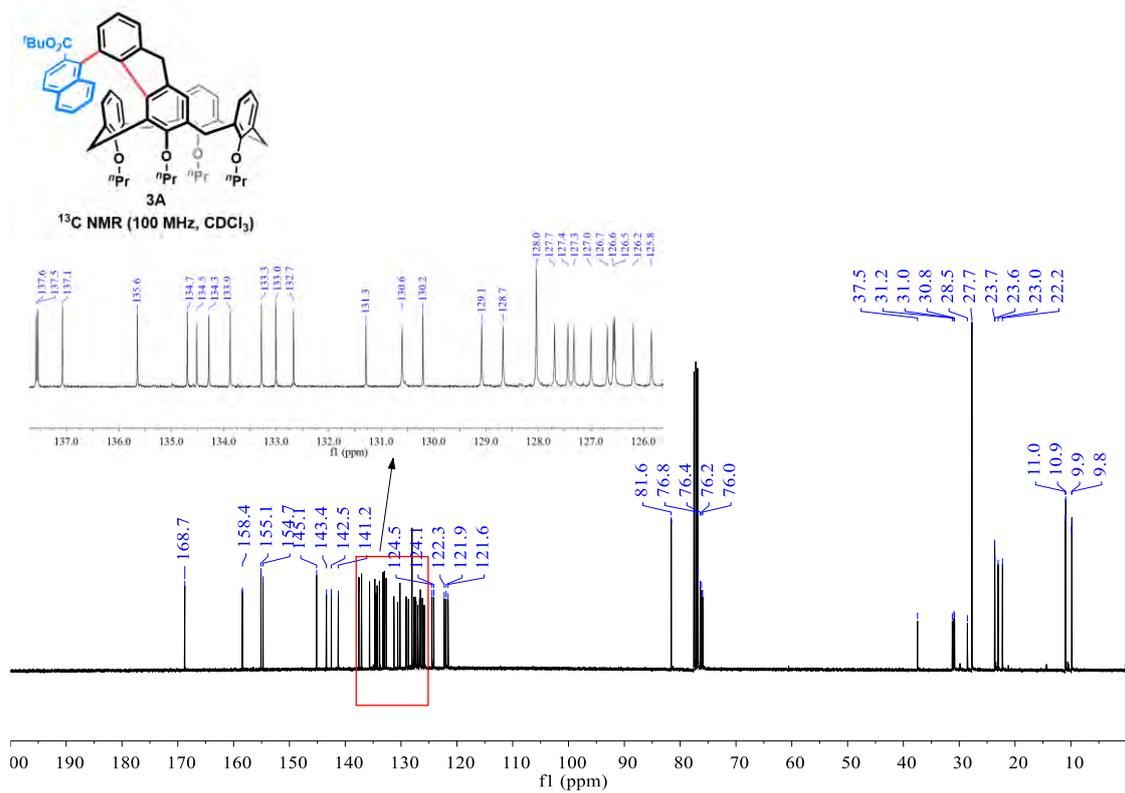


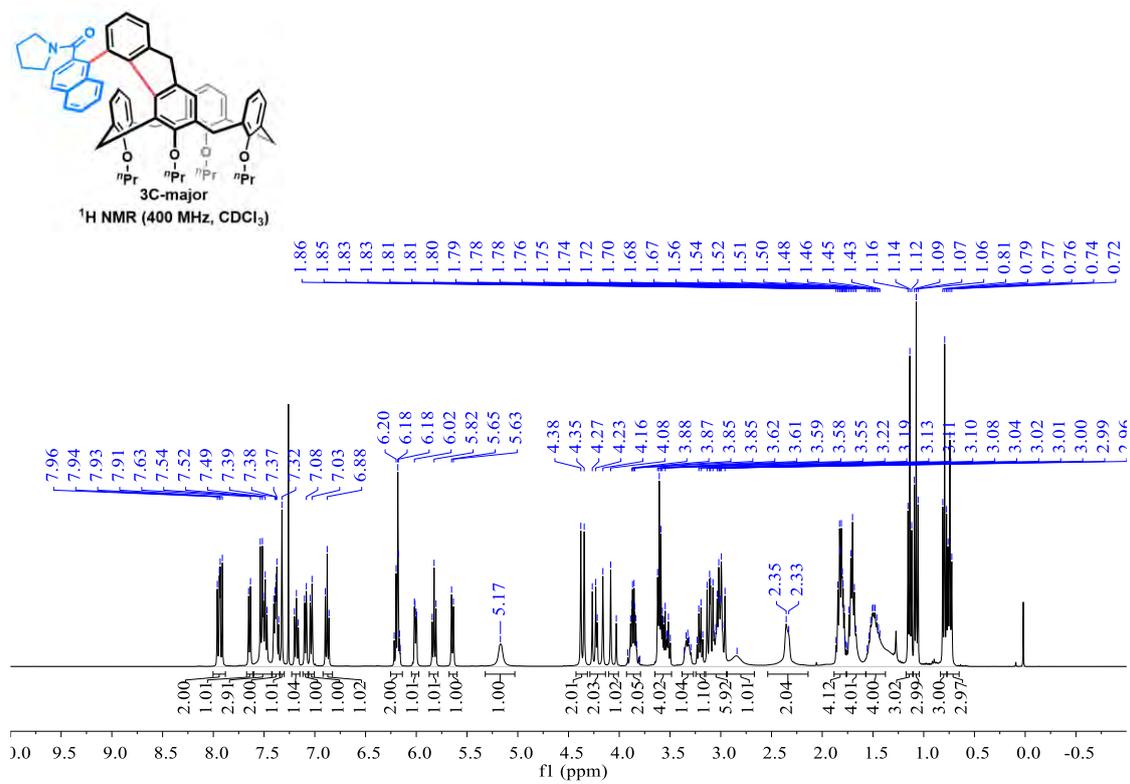
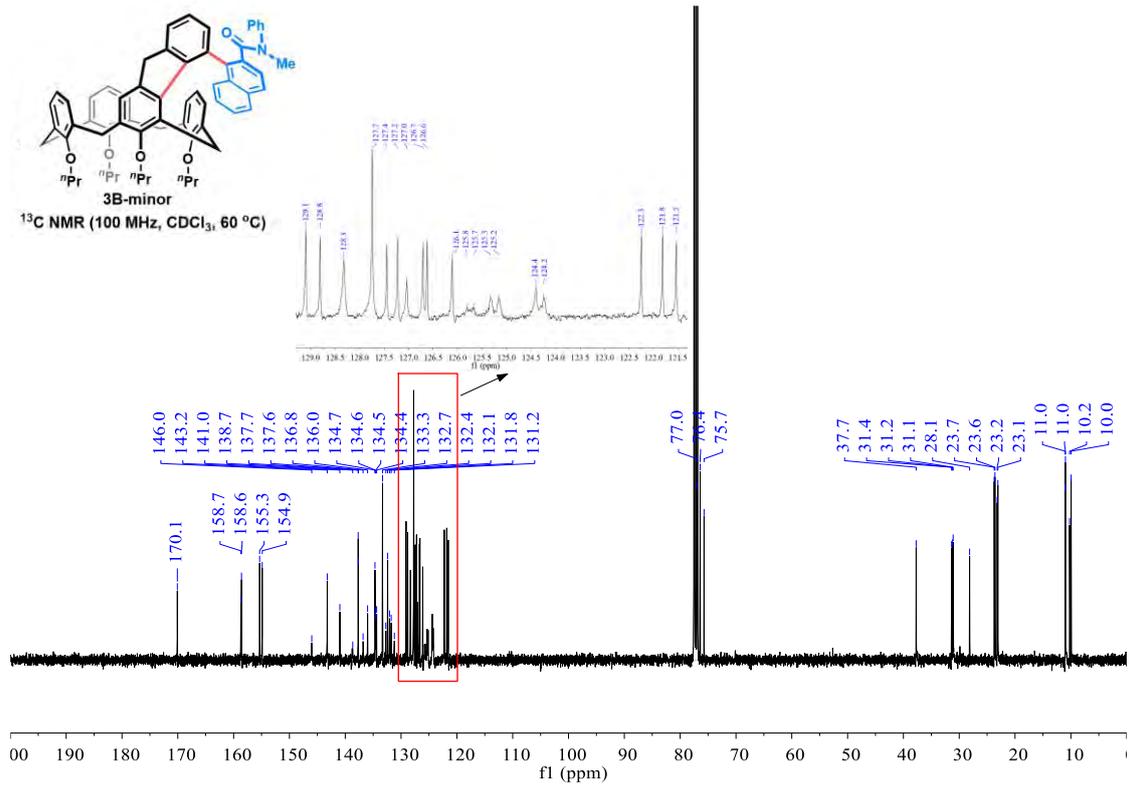


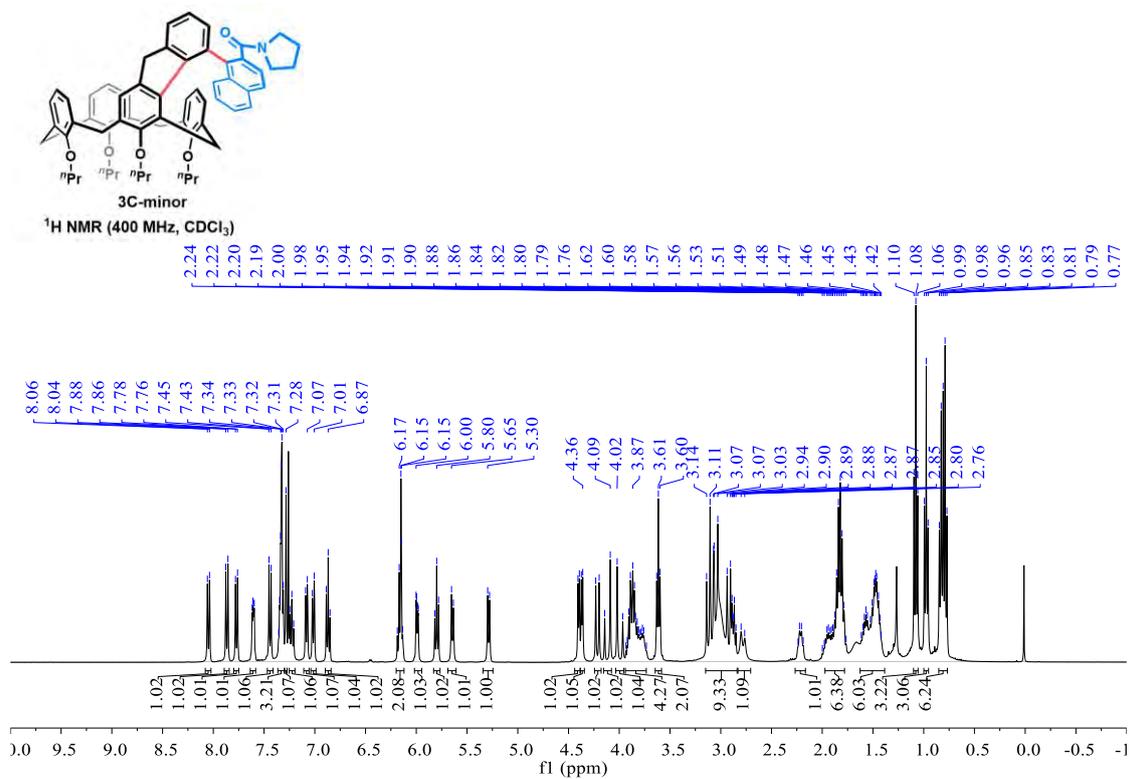
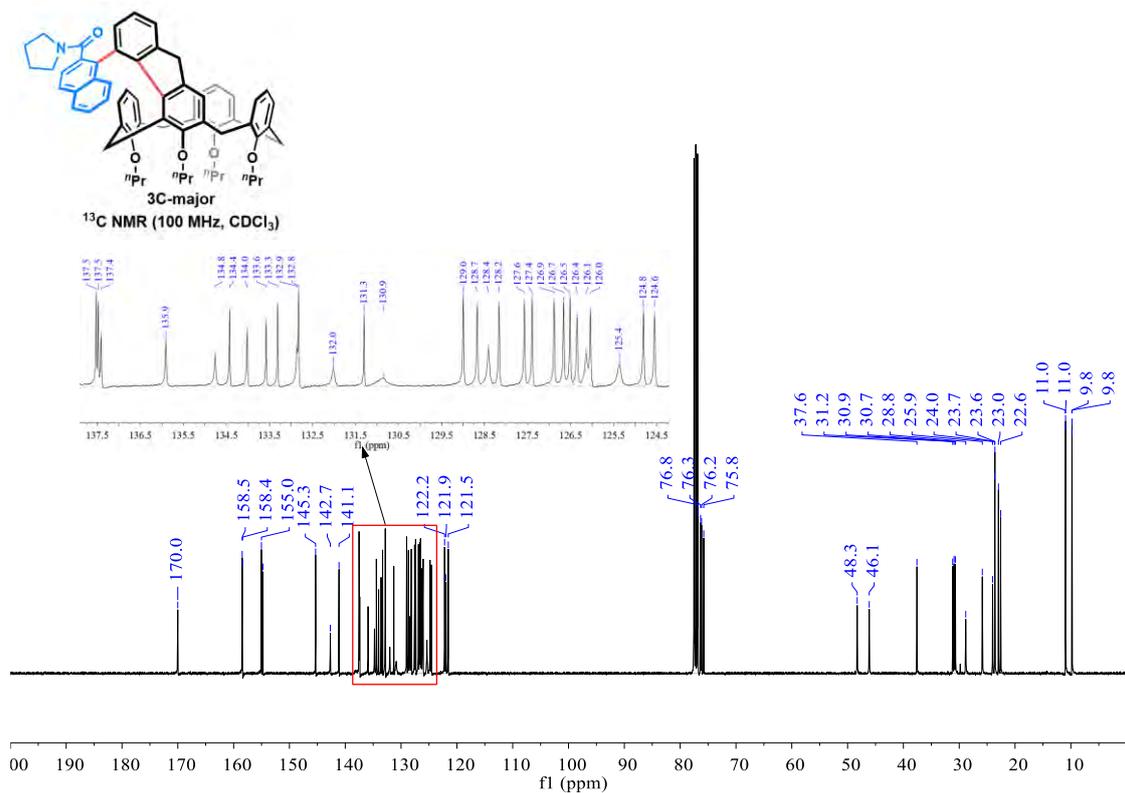


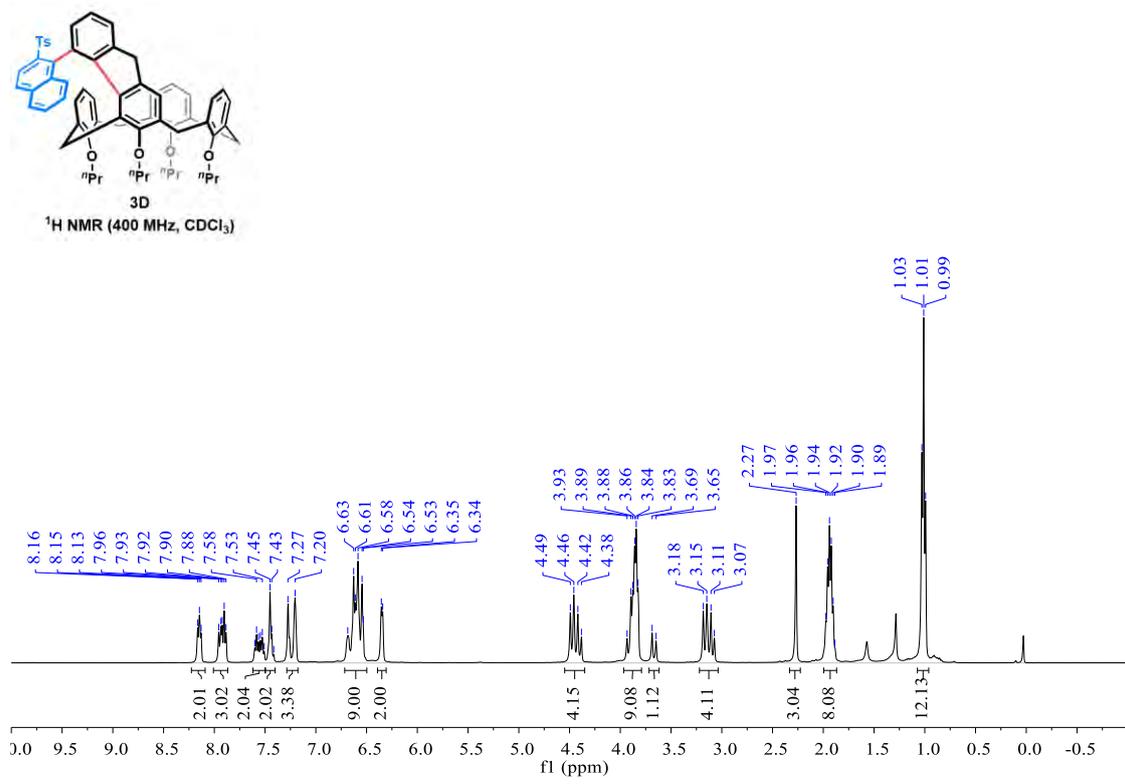
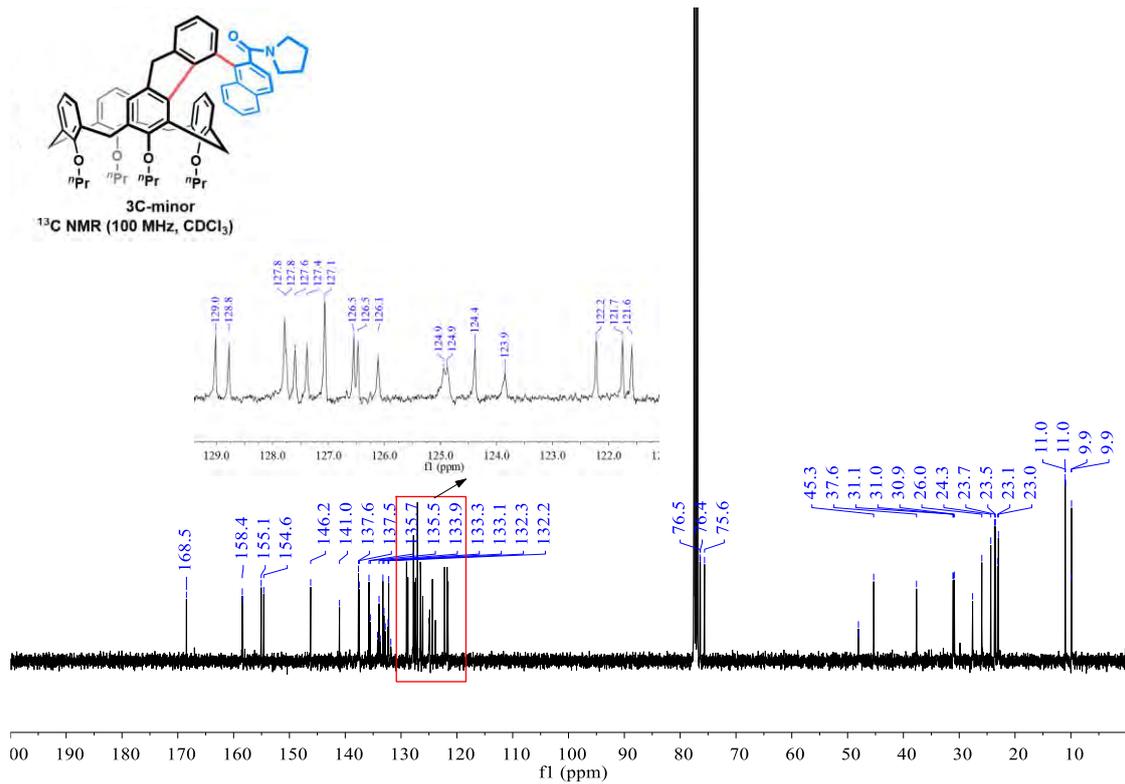


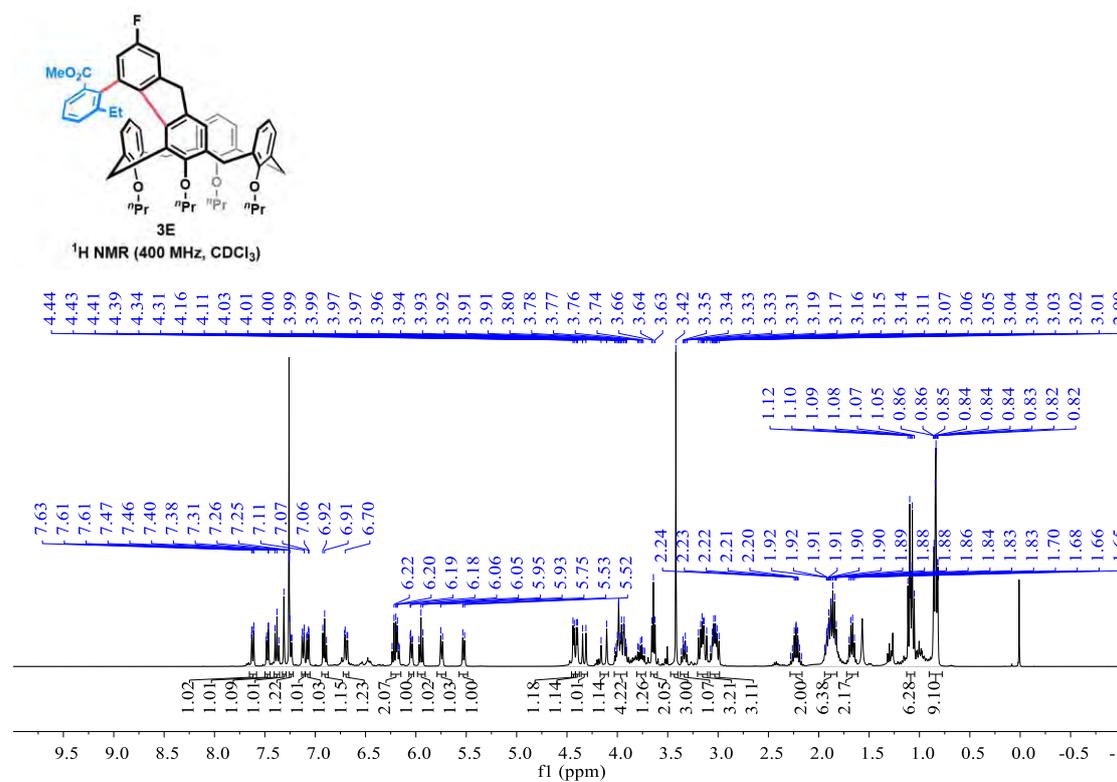
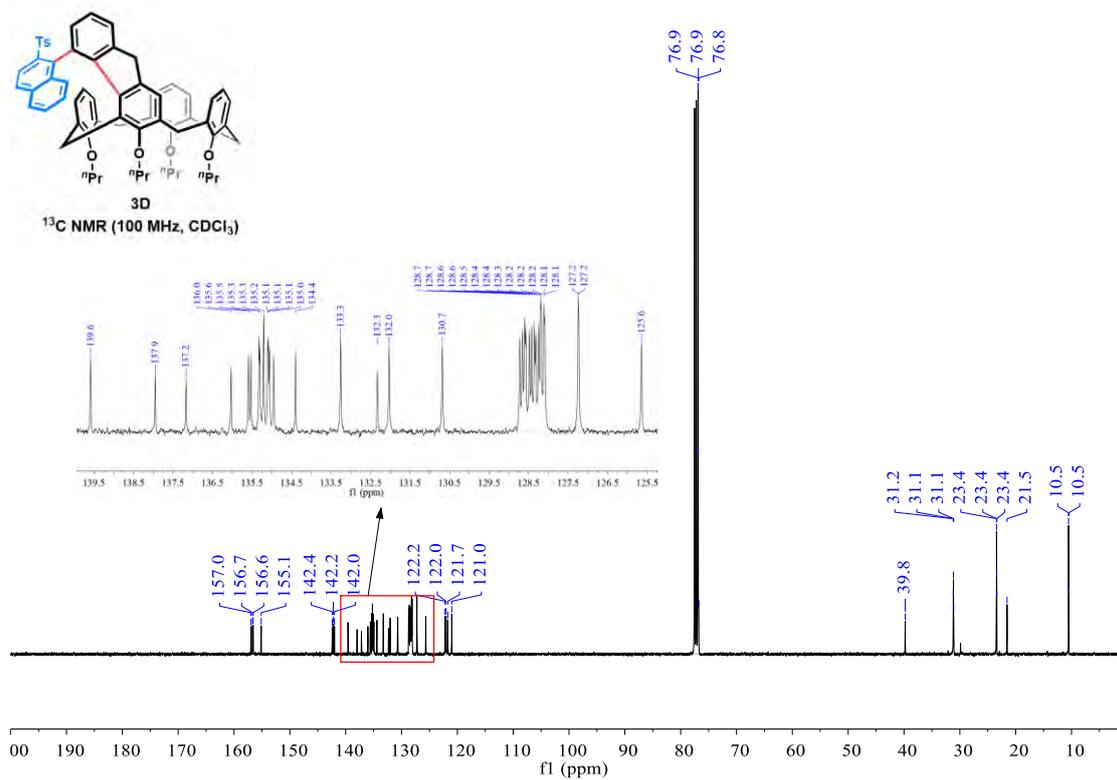


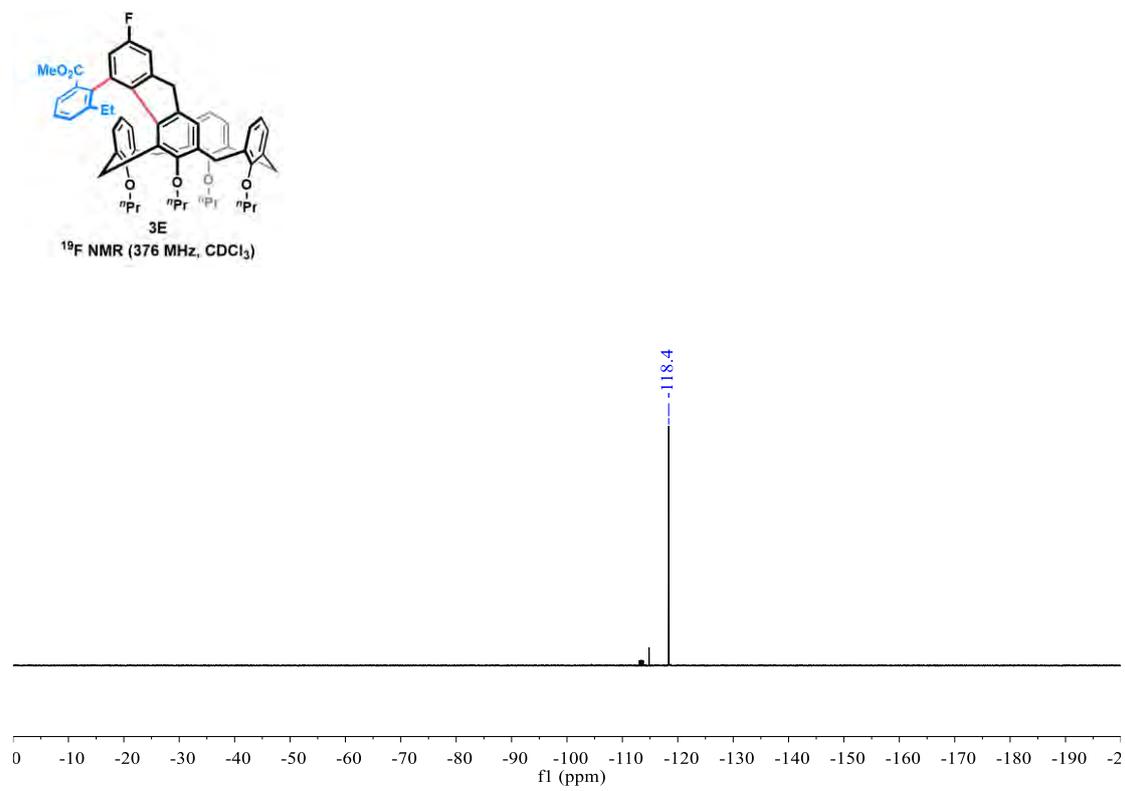
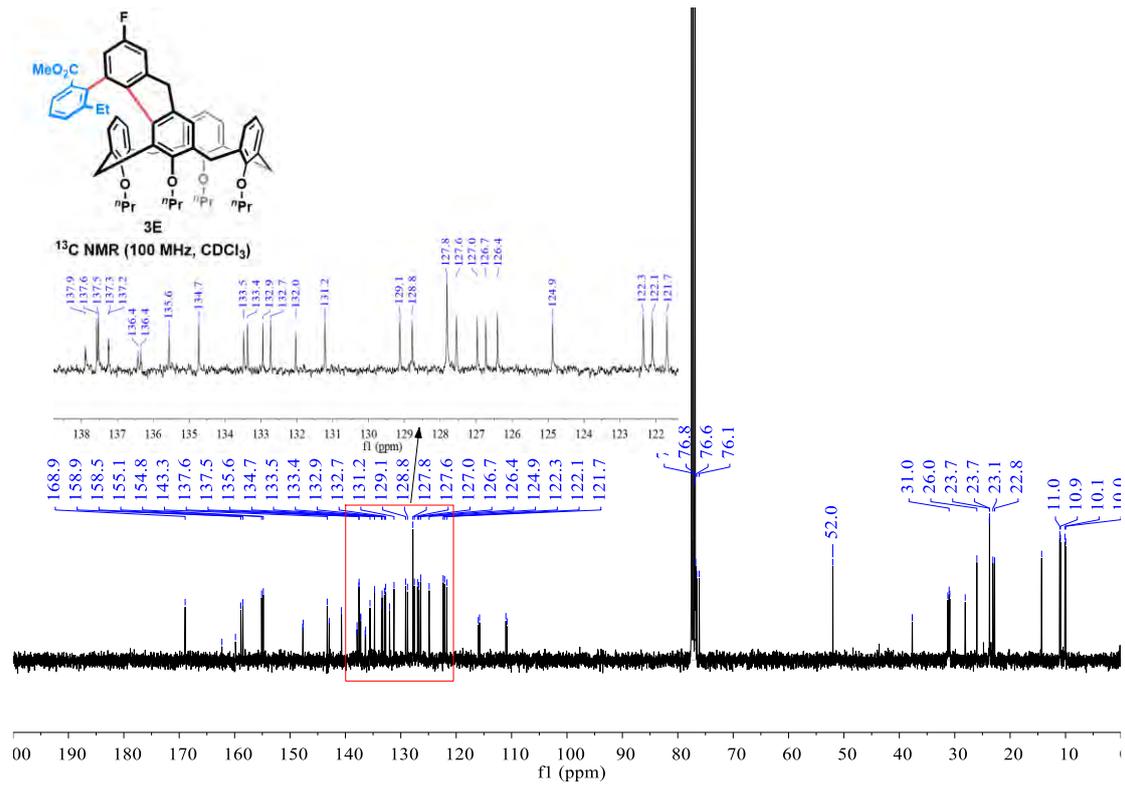


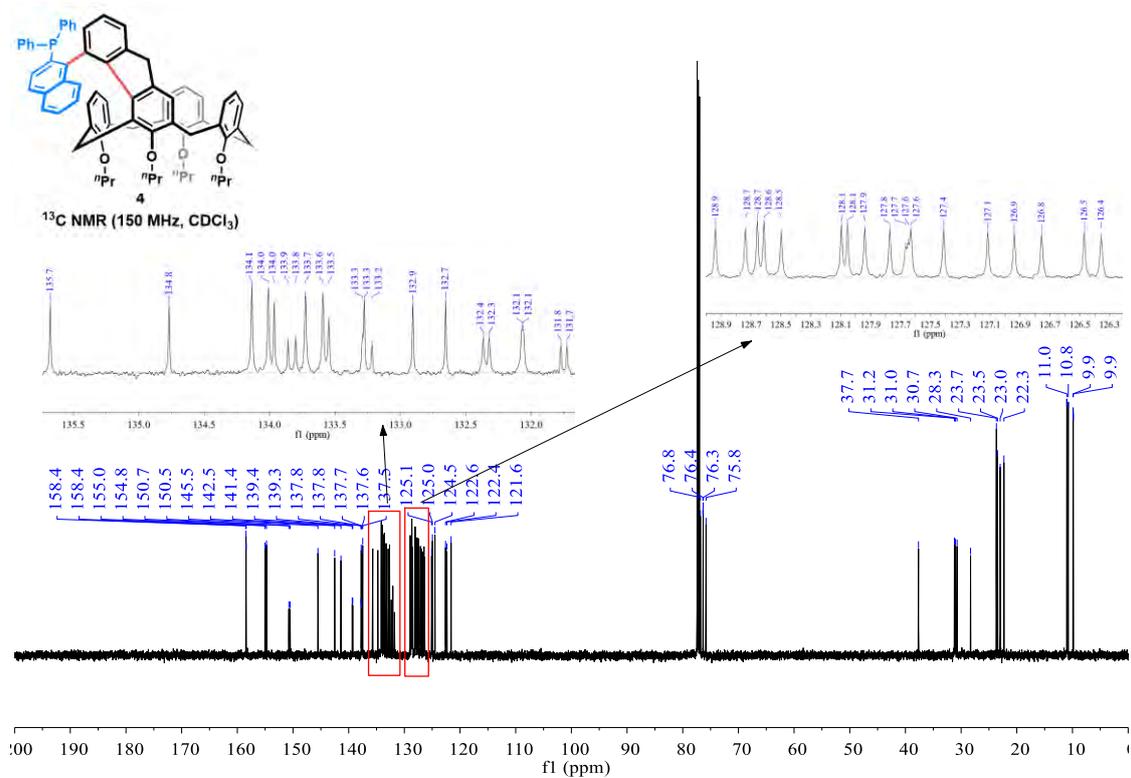
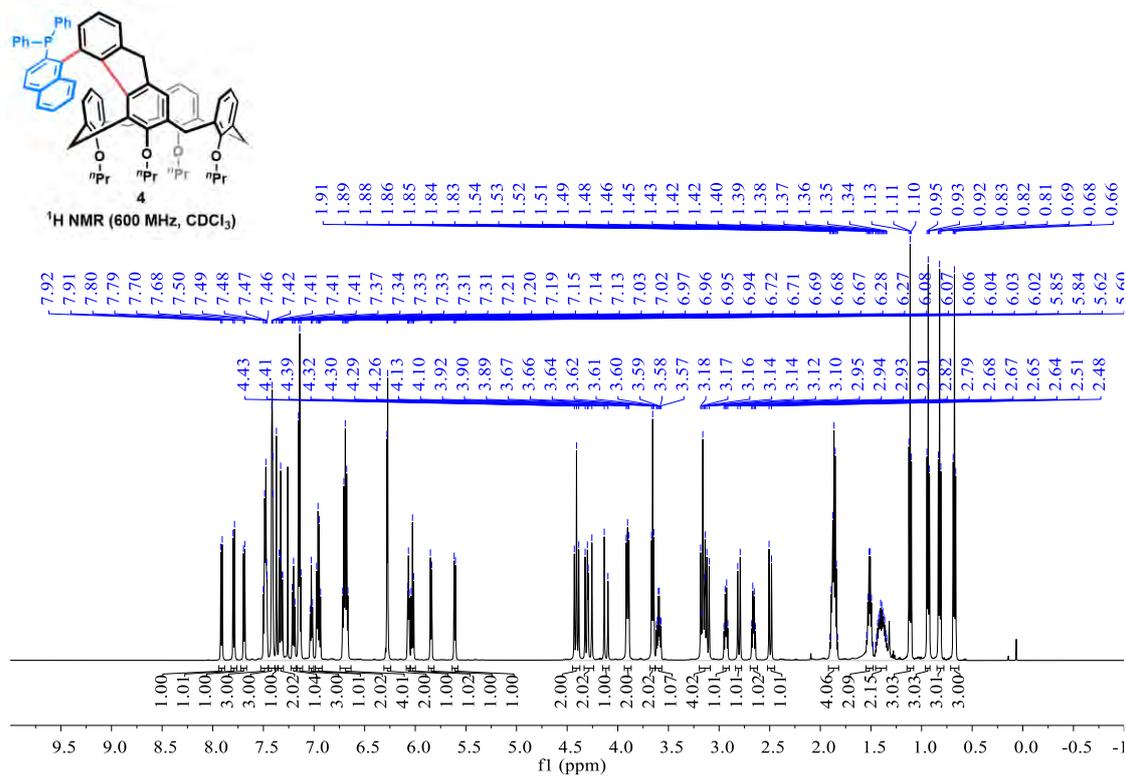


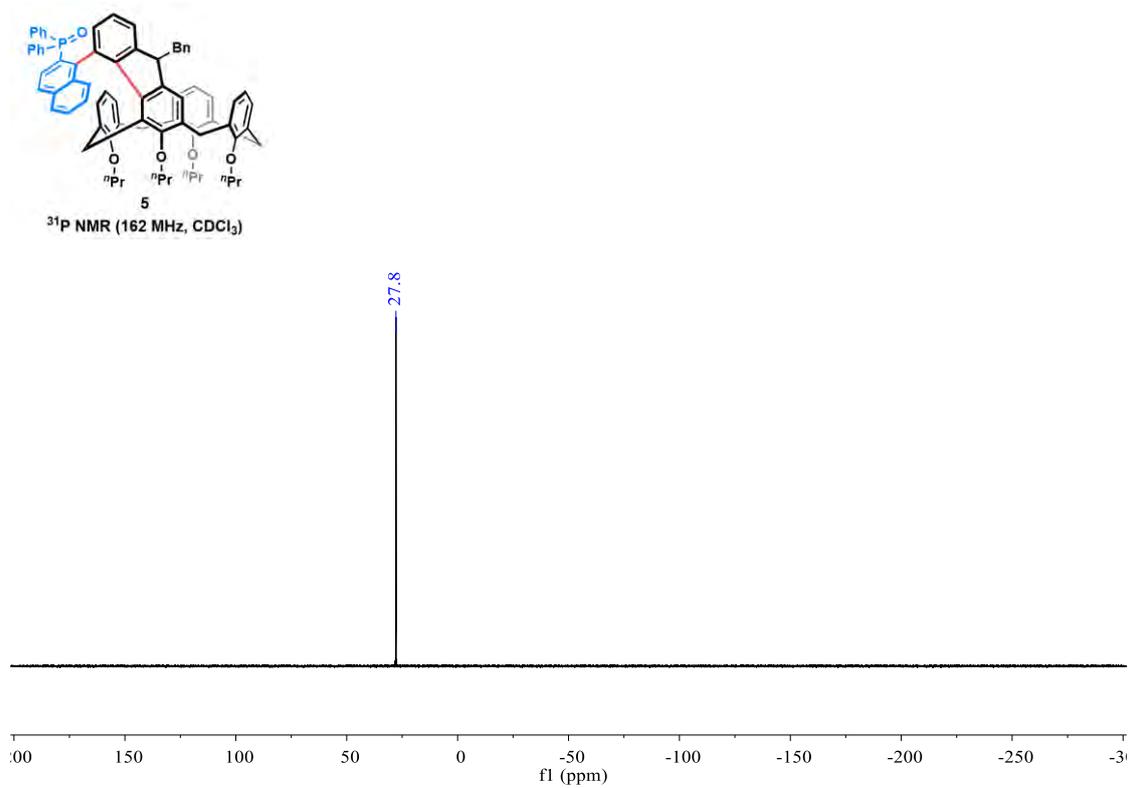
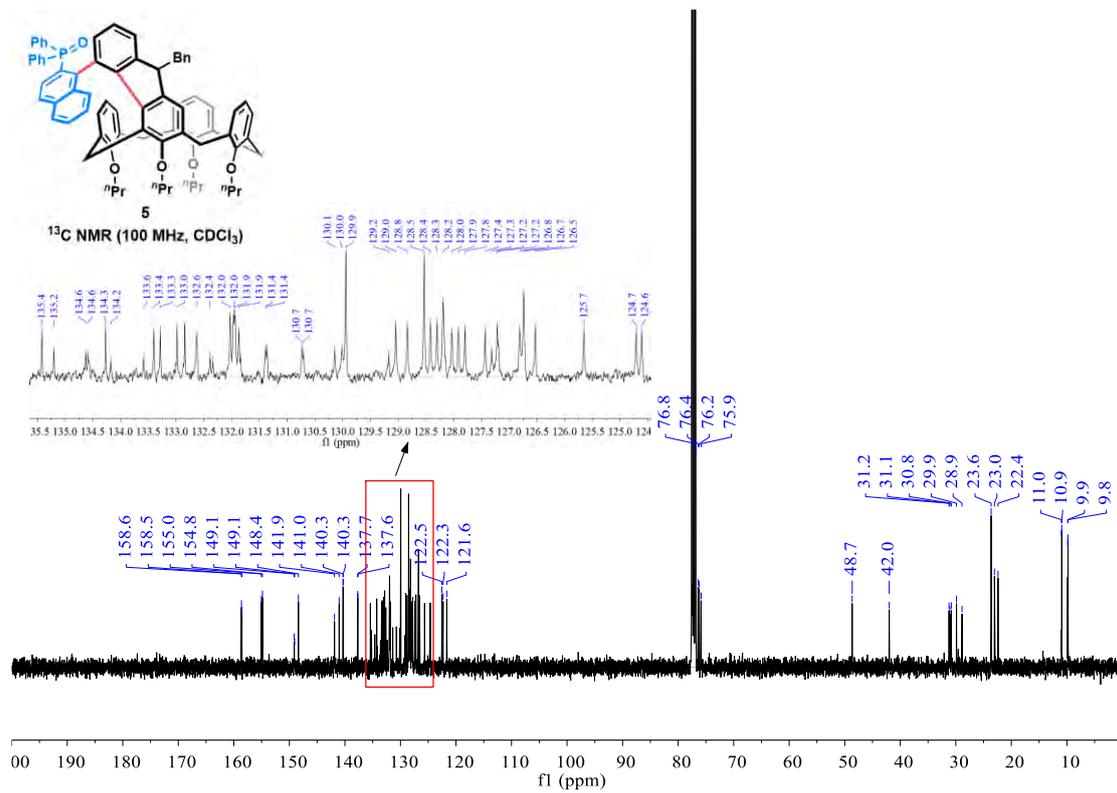


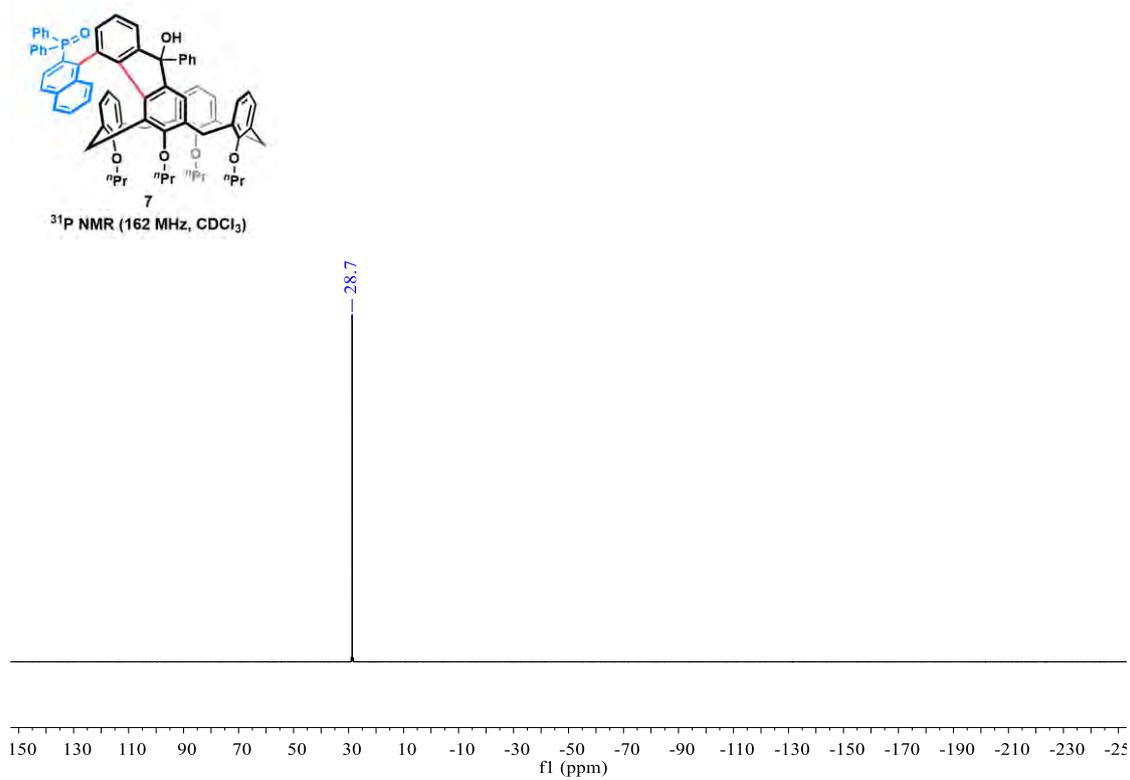
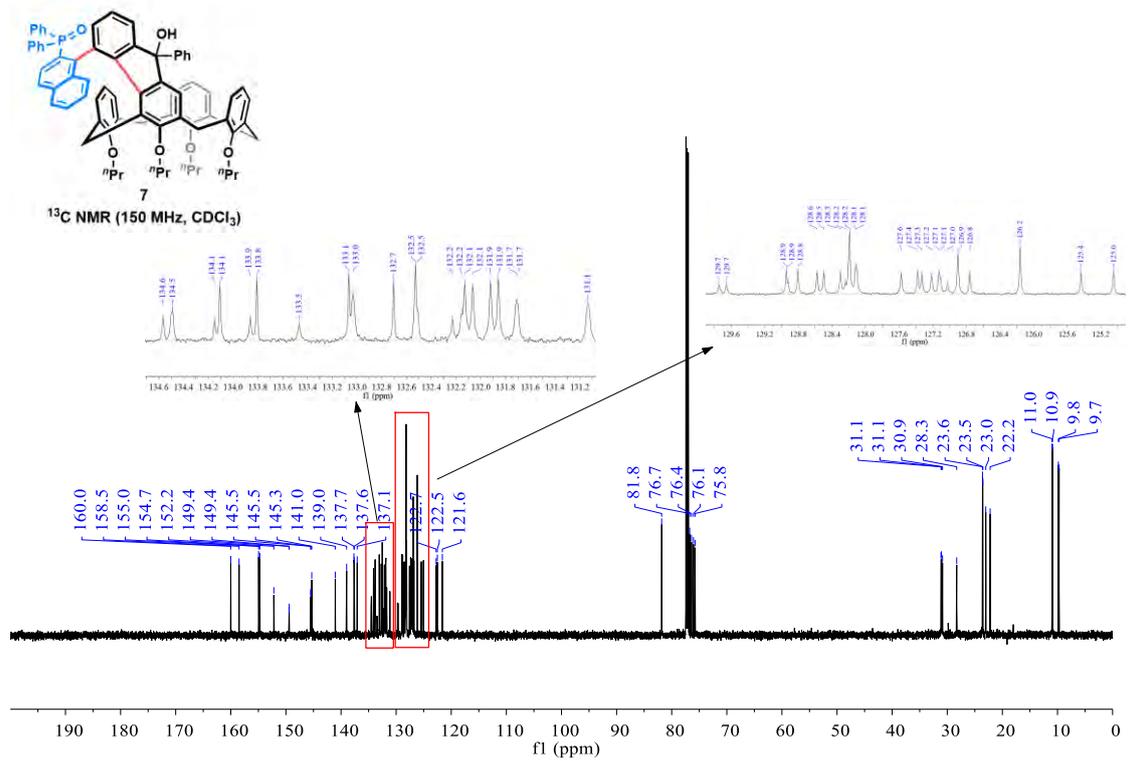


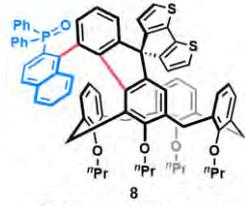




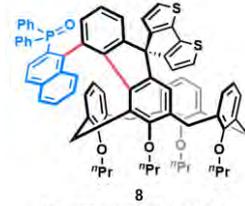
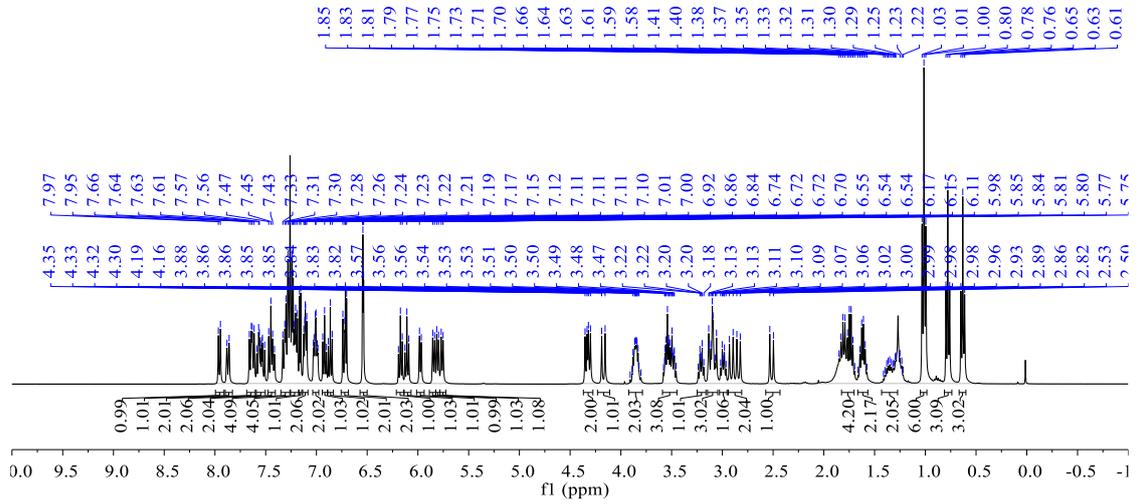




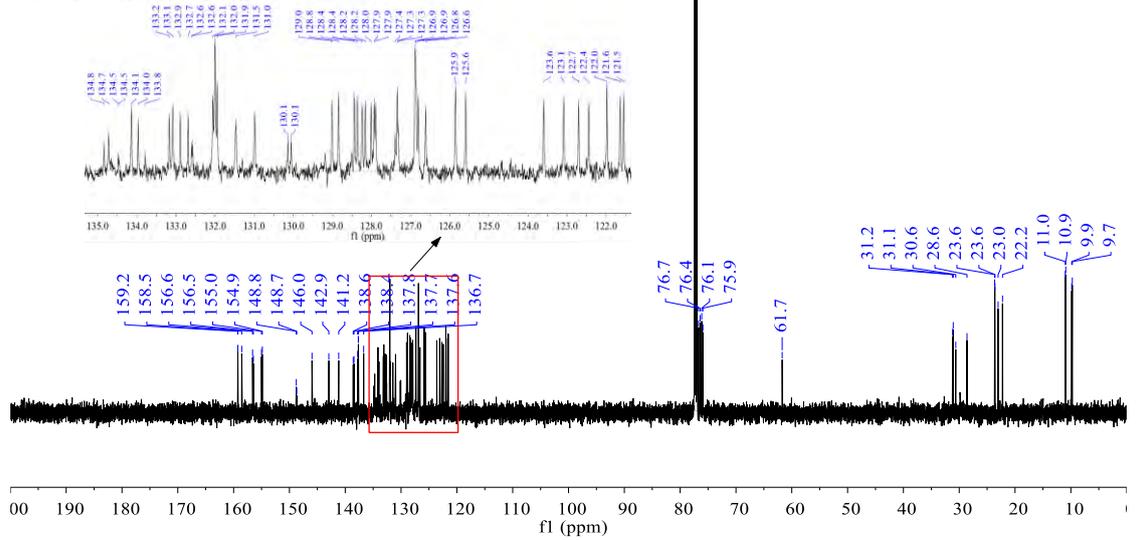


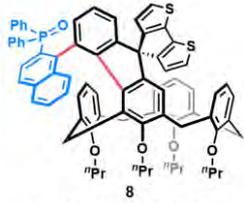


¹H NMR (400 MHz, CDCl₃)

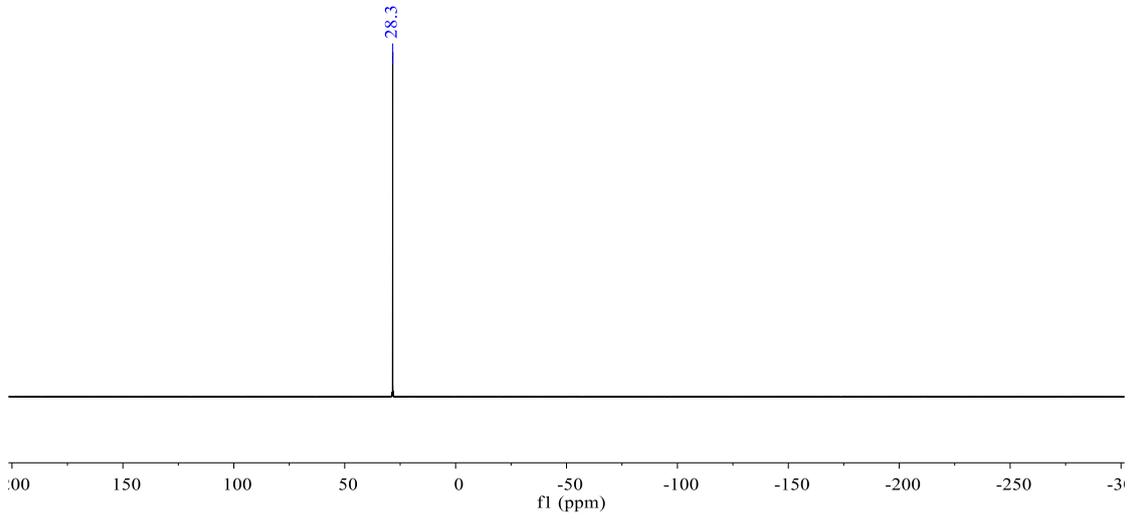


¹³C NMR (100 MHz, CDCl₃)

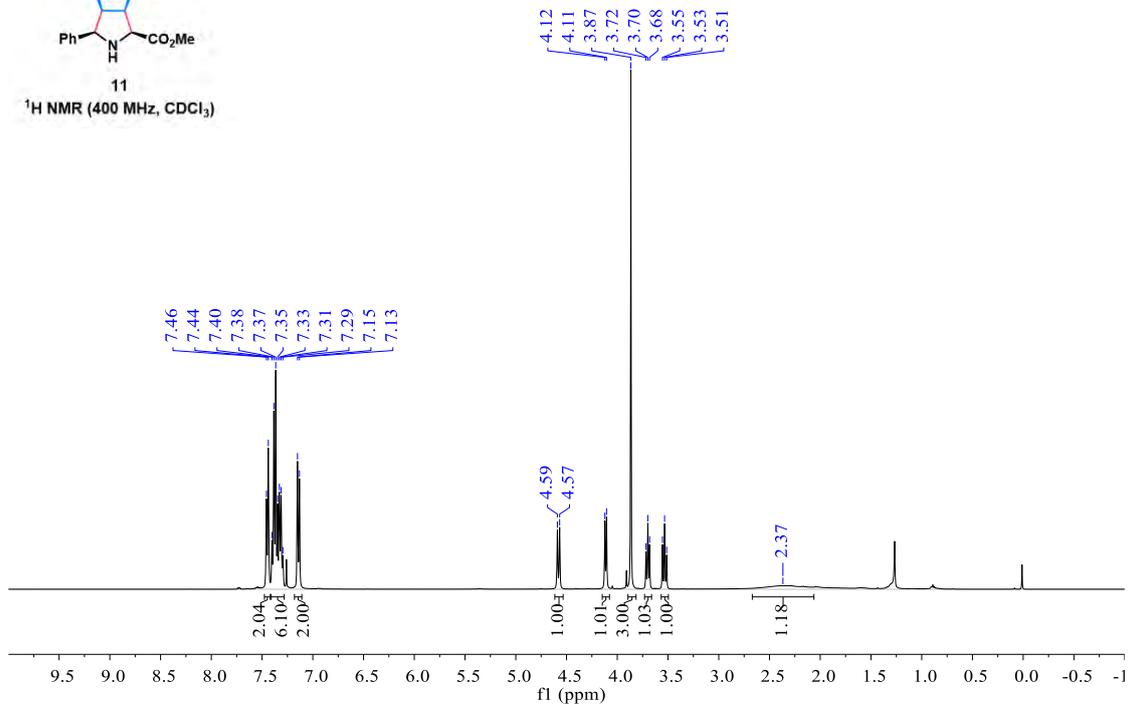




^{31}P NMR (162 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)



10. References

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