Electronic Supplementary Information

Metal-free construction of contiguous quaternary stereocentres with polycyclic framework

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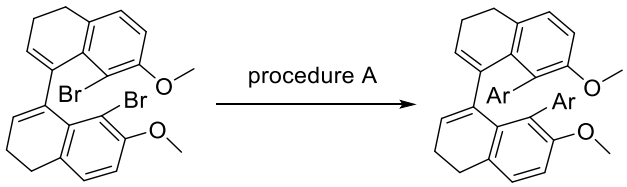
All reactions were carried out under argon using oven-dried glassware. Flash column chromatography was performed on 100-200 mesh silica gel. ^{1}H, and ^{13}C spectra were recorded on Bruker AVIII 300MHz, 400MHz or 500 MHz spectrometers at room temperature. High-resolution mass spectra (HRMS) were measured in the APCI mode. X-ray crystallographic data were collected by Rigaku Saturn 724 with graphite-monochromated Mo-Kα radiation. Commercial reagents were used without further purification. Anhydrous solvents were dried from 4 Å molecular sieves.

1. Synthesis and characterization of dienes 1a-l



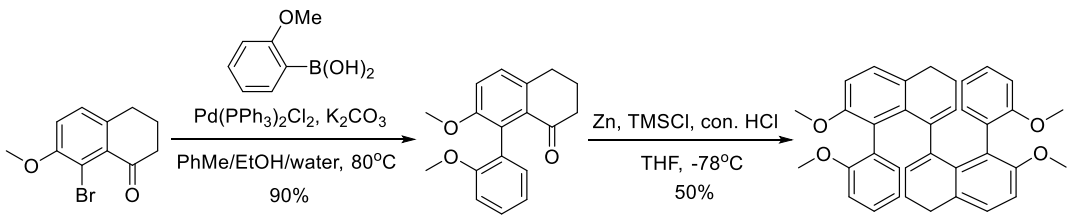
1.1 General procedure A[1] for 1a-1h, 1j

A mixture of the dibromide (4 mmol), boronic acid (10 mmol), and K_2CO_3 (40 mmol) dissolved in toluene (80 mL), EtOH (80 mL) and water (40 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_2Cl_2$ (around 10% mol). The resulting mixture was stirred for 12 hours at 80 °C under argon atmosphere, cooled to room temperature, and then added ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with water twice more (2×50 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was subjected to silica gel column chromatography to afford the pure product **1**.

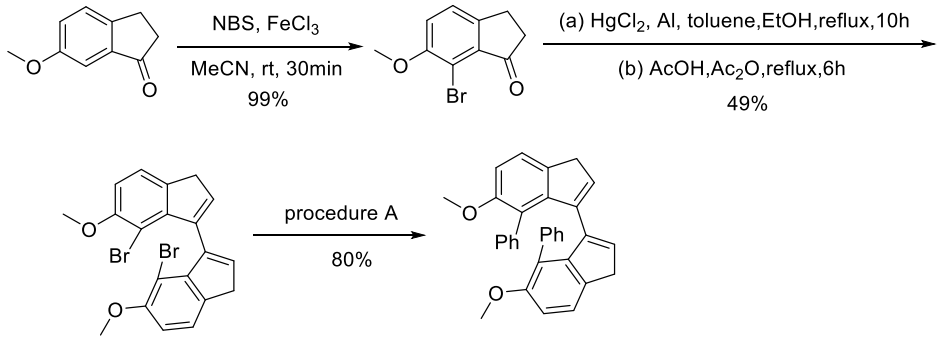
1.2 Synthesis of 1i

Similar to geneal procrdure A, a mixture of the 8-bromo-7-methoxy-1-tetralone (1.016 g, 4 mmol), 2-methoxy-phenylboronic acid (0.76 g, 5 mmol), and K_2CO_3 (5.52 g, 40 mmol) dissolved in toluene (80 mL), EtOH (80 mL) and water (40 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_2Cl_2$ (280 mg, around 10% mol). The resulting mixture was stirred for 12 hours at 80 °C under argon atmosphere, cooled to room temperature, and then added ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with water twice more (2×50 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was subjected to silica gel column chromatography to afford the 8-(o-methoxy)-phenyl-7-methoxy-1- tetralone (90%).

Similar to the synthesis of the dienes reported previously,[2] to a solution of 8-(o-methoxy)-phenyl-7-methoxy-1-tetralone (564 mg, 2 mmol) and Zn powder (250 mg, 4 mmol) in THF (10 mL) at −78 °C, trimethylsillylcholoride (0.5 mL, 5.8 mmol) and conc. HCl (1 mL, 11 mmol) was added over 10 min with vigorous stirring. After the temperature was warmed to room temperature, the mixture was stirred overnight. A yellow solution was obtained. After the solvents were evaporated under reduced pressure, CH_2Cl_2 (50 mL) and water (50 mL) were added. The separated organic phase was dried by anhydrous $MgSO_4$. After the solvent was removed by rotary evaporation, the crude product was subjected to silica gel column chromatography to get **1i.**



1.3 Synthesis of 1k



The reaction conditions are similar to the synthesis of the reported dienes.[2,3]

To a solution of indanone (6.48 g, 40 mmol) and NBS (*N*-bromosuccinimide, 7.48 g, 42 mmol) in MeCN (100 mL), $FeCl_3$ (648 mg, around 10% mol) was added. The resulting mixture was stirred for half an hour at room temperature, and then added CH_2Cl_2 (50 mL) and water (100 mL). The organic layer was washed with water twice more (2×50 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was subjected to a flash silica gel column chromatography to afford 7-bromo-6-methoxy-1-indanone (99%).

A mixture of activated aluminum flake (270 mg, 10 mmol), 7-bromo-6-methoxy-1-indanone (2.34 g, 10 mmol), toluene (7 mL), absolute ethanol (4 mL), $HgCl_2$ (25 mg, 0.092 mmol) was heated to reflux for 10 h. After the reaction mixture was cooled to room temperature, aqueous HCl (10%, 10 mL) and excess sulfur were added and vigorously

stirred for another 12 h. The mixture was filtrated, and the filtrate was extracted with ethyl acetate (3×150 mL). The combined organic layer was washed with water, dried over $MgSO_4$, and then concentrated under reduced pressure to give a residue. To the residue was added anhydride (2.1 mL) and acetic acid (1.5 mL), and the mixture was heated to reflux for 6 h. The remained anhydride and acetic acid were then removed under reduced pressure to give deep red sticky residue, which was dissolved in CH_2Cl_2 and washed by $NaHCO_3$ aqueous solution (3×20 mL). The combined organic layer was washed with water, dried over $MgSO_4$, and then concentrated under reduced pressure to give a residue, which was separated by chromatography to give diene 7,7'-dibromo-6,6'-dimethoxy-3H,3'H-1,1'-biindene.

Treatment of diene 7,7'-dibromo-6,6'-dimethoxy-3H,3'H-1,1'-biindene by general procedure A afforded the diene **1k**.

1.4 Synthesis of 1l

Similar to geneal procrdure A, a mixture of the dibromide (4 mmol), 4-methoxy-phenylboronic acid (0.76 g, 5 mmol), 4-chloro-phenylboronic acid (0.78 g, 5 mmol), and K_2CO_3 (5.52 g, 40 mmol) dissolved in toluene (80 mL), EtOH (80 mL) and water (40 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_2Cl_2$ (280 mg, around 10% mol). The resulting mixture was stirred for 12 hours at 80 °C under argon atmosphere, cooled to room temperature, and then added ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with water twice more (2×50 mL), dried over anhydrous

$MgSO_4$, and then concentrated in vacuo. The residue was subjected to silica gel column chromatography to afford the **1l** (45%).

1.5 Characterization of new compounds

Compound **1h**: Brown solid (62%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.25-6.86 (m, 4H), 6.74 (s, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.41-6.33 (m, 2H), 6.17-5.82 (m, 4H), 3.67 (s, 6H), 3.48 (s, 6H), 2.28-2.01 (m, 2H), 2.00–1.74 (m, 4H), 1.61-1.38 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.4, 155.1, 138.0, 134.2, 131.3, 129.7, 128.8, 126.7, 125.9, 116.6, 113.2, 109.4, 56.3, 55.32, 55.27, 54.9, 28.3, 22.8 ppm. HRMS (ACPI): *m/z* 531.2530 $[M+H]^+$; found: 531.2532.

Compound 8-(o-methoxy)-phenyl-7-methoxy-1-tetralone: Yellow powder (99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.07-6.97 (m, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.69 (s, 6H), 2.93 (t, *J* = 5.9 Hz, 2H), 2.53 (q, *J* = 6.0 Hz, 2H), 2.07-2.09 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 198.4, 156.5, 156.1, 136.8, 132.9, 130.0, 128.9, 128.1, 127.8, 127.0, 120.4, 116.2, 110.7, 56.5, 55.7, 40.2, 30.0, 23.3 ppm. HRMS (ACPI): *m/z* 283.1329 $[M+H]^+$; found: 283.1327.

Compound **1i**: Yellow powder (48%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.17 (t, *J* = 7.4 Hz, 2H), 6.89-6.77 (m, 2H), 6.74-6.36 (m, 7H), 6.24 (d, *J* = 7.5 Hz, 1H), 5.99-5.77 (m, 2H), 3.64-3.33 (m, 10H), 3.24 (s, 2H), 2.09-2.04 (m, 2H), 1.98-1.69 (m, 4H), 1.63-1.43 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 158.2, 155.2, 141.6, 134.3, 134.0, 132.7,

130.4, 129.3, 128.6, 126.2, 111.5, 109.2, 56.2, 55.3, 31.0, 28.4, 22.8 ppm. HRMS (ACPI): *m/z* 531.2530 $[M+H]^+$; found: 531.2520.

Compound **1j**: Yellow powder (72%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.20 (d, *J* = 5.0 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.83-6.74 (m, 2H), 6.63 (d, *J* = 8.2 Hz, 2H), 6.13 (s, 2H), 3.56 (s, 6H), 2.08-2.04 (m, 4H), 2.03-1.93 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.6, 141.1, 136.8, 135.6, 133.8, 132.1, 130.1, 129.9, 127.0, 125.6, 121.0, 109.2, 56.3, 28.6, 22.9 ppm. HRMS (ACPI): *m/z* 483.1447 $[M+H]^+$; found: 483.1435.

Compound 7,7'-dibromo-6,6'-dimethoxy-3H,3'H-1,1'-biindene: Yellow powder (49%). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.34 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.52 (s, 2H), 3.87 (s, 6H), 3.43 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.0, 142.1, 137.6, 136.2, 122.6, 108.6, 56.8, 37.5, 30.6, 29.9 ppm. HRMS (ACPI): *m/z* 446.9595 $[M+H]^+$; found: 446.9596.

Compound **1k**: Yellow powder (78%). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.13 (d, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 2H), 7.04 (d, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.97-6.90 (m, 2H), 6.75 (dt, *J* = 11.9, 7.9 Hz, 4H), 5.86 (s, 2H), 3.68 (s, 6H), 3.04 (d, *J* = 23.0 Hz, 2H), 2.64 (d, *J* = 23.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 141.0, 136.7, 135.3, 134.9, 130.9, 130.4, 126.09, 126.05, 126.0, 125.4, 122.3, 107.5, 56.4, 37.0 ppm. HRMS (ACPI): *m/z* 443.2006 $[M+H]^+$; found: 443.2003.

Compound **1l**: Yellow powder (45%). ^1H NMR ($CDCl_3$, 500 MHz): δ = 6.99 (dd, *J* = 7.2, 7.1 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.71 (dd, *J* = 17.6, 7.4 Hz, 2H), 6.65 (dd, *J* = 8.2,

3.7 Hz, 2H), 6.58 (dd, *J* = 22.6, 7.9 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 6.13–5.99 (m, 2H), 3.84 (s, 3H), 3.51 (d, *J* = 1.1 Hz, 6H), 2.20 (dd, *J* = 35.8, 13.3 Hz, 2H), 1.95 (dq, *J* = 11.5, 5.8 Hz, 4H), 1.53–1.36 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.3, 155.3, 154.8, 141.5, 141.2, 135.1, 134.3, 134.13, 134.06, 133.8, 133.06, 133.05, 132.6, 132.1, 131.0, 130.7, 129.1, 128.8, 127.6, 126.8, 126.4, 126.1, 125.9, 125.8, 111.5, 109.4, 109.2, 100.0, 56.2, 56.1, 55.3, 28.2, 28.0, 22.76, 22.75 ppm. HRMS (ACPI): *m/z* 535.2035 $[M+H]^+$; found: 535.2034.

2. Synthesis and characterization of products 2a-l

2.1 General procedure

In a solutin of diene (0.5 mmol) dissolved in DCM (5 mL), CF_3SOOH (0.05 mmol) was added. The reaction was stirred for 1 minute at room temperature, and then added water (5 mL). The organic layer was washed with water twice more (2×5 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was subjected to silica gel column chromatography to afford the pure product **2**.

2.2 Characterization of the new compounds

Compound **2a**: Yellow powder (99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.95 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 2H), 6.48 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 6H), 2.91-2.70 (m, 4H), 1.85-1.71 (m, 2H), 1.63-1.59 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 154.8, 143.4, 137.7, 131.7, 131.1, 129.1, 128.0, 127.5, 125.6, 125.3, 123.1, 110.9, 55.6, 46.9, 29.8, 28.8, 19.1

ppm. HRMS (ACPI): *m/z* 471.2319 $[M+H]^+$; found: 471.2311.

Compound **2b**: White powder (94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.83 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 10 Hz, 2H), 6.25 (s, 2H), 3.86 (s, 6H), 2.85 (dd, *J* = 15.8, 4.2 Hz, 2H), 2.81-2.70 (m, 2H), 1.75 (t, *J* = 12.2 Hz, 2H), 1.58 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.6, 143.6, 137.5, 135.0, 131.1, 129.0, 128.5, 128.2, 127.9, 125.9, 123.3, 110.8, 55.7, 46.9, 29.8, 28.9, 21.4, 19.0 ppm. HRMS (ACPI): *m/z* 499.26316 $[M+H]^+$; found: 499.2623.

Compound **2c**: Yellow powder (82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.06 (d, *J* = 8.6 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 8H), 6.92-6.85 (m, 14H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 7.5 Hz, 2H), 6.21 (s, 2H), 3.87 (s, 6H), 2.74-2.63 (m, 4H), 1.78-1.74 (m, 2H), 1.67-1.56 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.4, 147.3, 145.3, 136.6, 130.68, 129.0, 128.7, 128.5, 123.7, 122.2, 122.0, 121.0, 110.3, 55.3, 46.9, 29.8, 29.7, 28.7, 19.2, 14.1 ppm. HRMS (ACPI): *m/z* 805.3789 $[M+H]^+$; found: 805.3765.

Compound **2d**: Yellow powder (86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.98 (dd, *J* = 8.8, 6.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.65 (td, *J* = 8.6, 2.9 Hz, 2H), 6.18 (dd, *J* = 10.2, 2.8 Hz, 2H), 3.88 (s, 6H), 2.87-2.72 (m, 4H), 1.83-1.73 (m, 2H), 1.64-1.55 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 161.7, 159.7, 154.6, 146.3, 146.3, 136.4, 131.0, 123.0, 129.9, 129.3, 127.89, 127.86, 122.2, 114.6, 114.4, 112.2, 112.0, 111.2, 55.6, 47.0, 29.6, 28.6, 18.9 ppm. HRMS (ACPI): *m/z* 507.2130 $[M+H]^+$; found: 507.2122.

Compound **2e**: Yellow powder (81%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.02 (dd, *J* = 8.6, 2.1 Hz, 2H), 6.66 (s, 2H), 3.89 (s, 6H), 2.91-2.87 (m, 2H), 2.80-2.73 (m, 2H), 1.77 (t, *J* = 13.2 Hz, 2H), 1.64-1.58 (m, 4H), 1.52-1.48 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.0, 143.8, 136.6, 135.2, 131.1, 130.7, 128.3, 127.2, 127.0, 125.3, 123.80, 123.77, 123.1, 122.39, 122.36, 121.5, 111.3, 55.6, 47.0, 29.5, 28.4, 18.9 ppm. HRMS (ACPI): *m/z* 607.2072 $[M+H]^+$; found: 607.2051.

Compound **2f**: Yellow powder (85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.94 (dd, *J* = 8.5, 2.4 Hz, 2H), 6.41 (d, *J* = 2.3 Hz, 2H), 3.88 (s, 6H), 2.88-2.84 (m, 2H), 2.80-2.70 (m, 2H), 1.77-1.72 (m, 2H), 1.60-1.58 (m, 2H), 1.55-1.50 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.8, 145.4, 136.4, 131.3, 131.0, 130.3, 129.7, 129.6, 127.2, 125.7, 121.9, 111.2, 55.6, 47.0, 29.5, 28.5, 18.9 ppm. HRMS (ACPI): *m/z* 539.1539 $[M+H]^+$; found: 539.1530.

Compound **2g**: White powder (99%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 11.6 Hz, 2H), 6.07 (d, *J* = 2.8 Hz, 2H), 3.86 (s, 6H), 3.57 (s, 6H), 2.86-2.69 (m, 4H), 1.85-1.73 (m, 2H), 1.70-1.54 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 157.1, 154.4, 145.7, 136.7, 131.0, 129.3, 128.3, 125.0, 123.0, 114.9, 110.9, 109.1, 55.6, 54.9, 47.0, 29.8, 28.8, 19.0 ppm. HRMS (ACPI): *m/z* 531.2530 $[M+H]^+$; found: 531.2521.

Compound **2h**: Yellow powder (65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (s, 2H),

7.15 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.38-6.30 (m, 4H), 3.88 (s, 6H), 3.67 (s, 6H), 2.87-2.69 (m, 4H), 1.79-1.72 (m, 2H), 1.63-1.54 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 154.9, 138.1, 136.1, 132.5, 131.1, 129.3, 128.2, 122.9, 114.0, 110.9, 110.8, 55.7, 55.0, 46.5, 29.8, 29.0, 19.0 ppm. HRMS (ACPI): *m/z* 531.2530 $[M+H]^+$; found: 531.2528.

Compound **2i**: Yellow powder (60%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.17 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.79 (t, *J* = 7.7 Hz, 2H), 6.56 (d, *J* = 8.2 Hz, 2H), 6.35 (d, *J* = 7.5 Hz, 2H), 3.86 (s, 6H), 3.70 (s, 6H), 2.91-2.64 (m, 4H), 1.77-1.70 (m, 2H), 1.64-1.35 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.0, 154.6, 145.6, 138.2, 130.5, 128.8, 126.5, 121.6, 121.5, 121.0, 110.5, 110.3, 56.2, 55.6, 48.8, 29.2, 28.0, 19.3 ppm. HRMS (ACPI): *m/z* 531.2530 $[M+H]^+$; found: 531.2532.

Compound **2j**: Yellow powder (76%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.07 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 5.2 Hz, 2H), 6.01 (d, *J* = 5.2 Hz, 2H), 3.95 (s, 6H), 2.85-2.77 (m, 4H), 2.09 (td, *J* = 12.9, 3.1 Hz, 2H), 1.78-1.70 (m, 2H), 1.68-1.55 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 152.2, 144.3, 135.4, 130.7, 129.8, 128.1, 127.3, 122.6, 119.8, 109.7, 55.5, 46.4, 29.9, 29.3, 19.7 ppm. HRMS (ACPI): *m/z* 483.1447 $[M+H]^+$; found: 483.1438.

Compound **2k**: Yellow powder (65%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.30 (d, *J* = 8.9 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.09-7.02 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.86-6.80 (m, 2H), 6.47 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 6H), 2.98-2.87(m, 2H), 2.80-2.76 (m, 2H),

2.56-2.44 (m, 2H), 1.68 (dd, *J* = 12.8, 7.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.7, 145.3, 141.9, 136.7, 131.7, 128.0, 126.8, 126.2, 124.7, 123. 8, 120.4, 111.5, 55.8, 54.5, 35.5, 29.3 ppm. HRMS (ACPI): *m/z* 443.2006 $[M+H]^+$; found: 443.2003.

Compound **2l**: White powder (82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.99 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 10.3 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.55 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.46 (d, *J* = 2.3 Hz, 1H), 6.07 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.61 (s, 3H), 2.93–2.82 (m, 2H), 2.82–2.70 (m, 2H), 1.77-1.79 (m, 2H), 1.71–1.48 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 157.2, 154.7, 154.4, 145.9, 145.2, 138.3, 137.1, 136.0, 131.2, 131.1, 130.9, 130.4, 129.5, 129.4, 128.5, 127.1, 125.5, 124.9, 122.8, 122.1, 115.2, 111.1, 111.0, 109.1, 55.60, 55.59, 55.0, 47.01, 46.98, 29.67, 29.65, 28.7, 22.7, 19.0, 18.9 ppm. HRMS (ACPI): *m/z* 535.2035 $[M+H]^+$; found: 535.2031.

3. References

1. W.-B. Lin, M. Li, L. Fang, Y. Shen and C.-F. Chen, *Chem. Asian J.*, 2017, **12**, 86.
2. Y. Shen, H.-Y. Lu and C.-F. Chen, *Angew. Chem., Int. Ed.*, 2014, **53**, 4648.
3. Y. Y. Li, H.-Y. Lu, M. Li, X.-J. Li and C.-F. Chen, *J. Org. Chem.*, 2014, **79**, 2139.

4. Copies of ^{1}H and ^{13}C NMR Spectra of new compounds

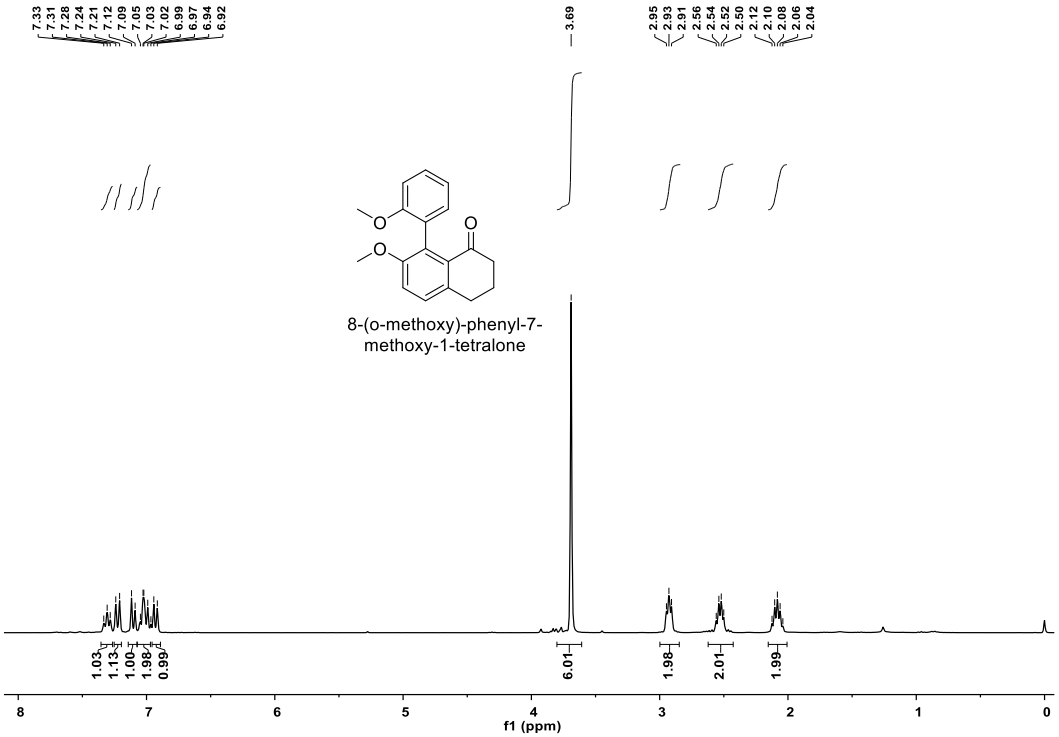


Fig. S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 8-(o-methoxy)-phenyl-7-methoxy-1-tetralone.

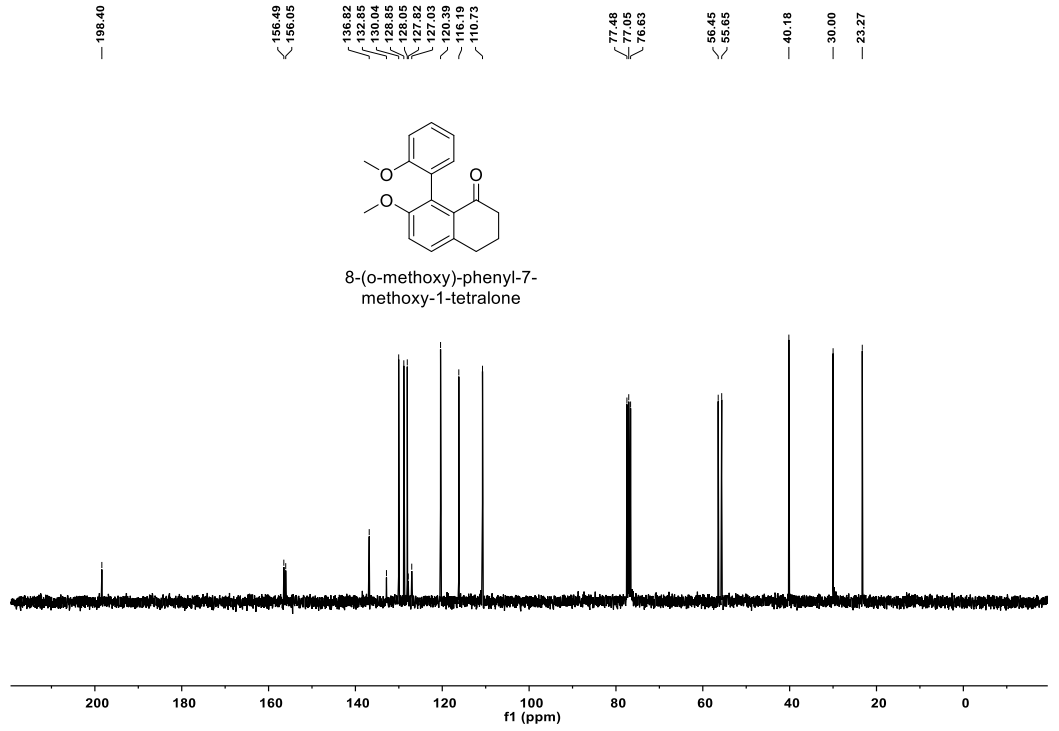


Fig. S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of 8-(o-methoxy)-phenyl-7-methoxy-1-tetralone.

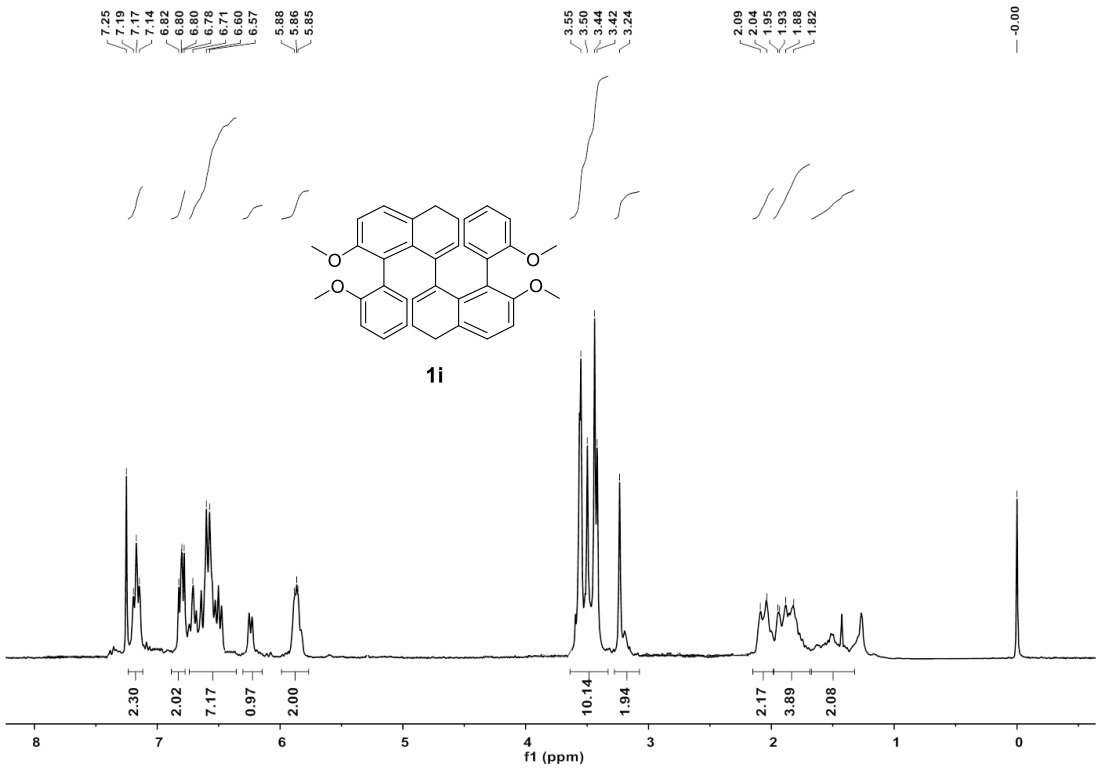


Fig. S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1i**.

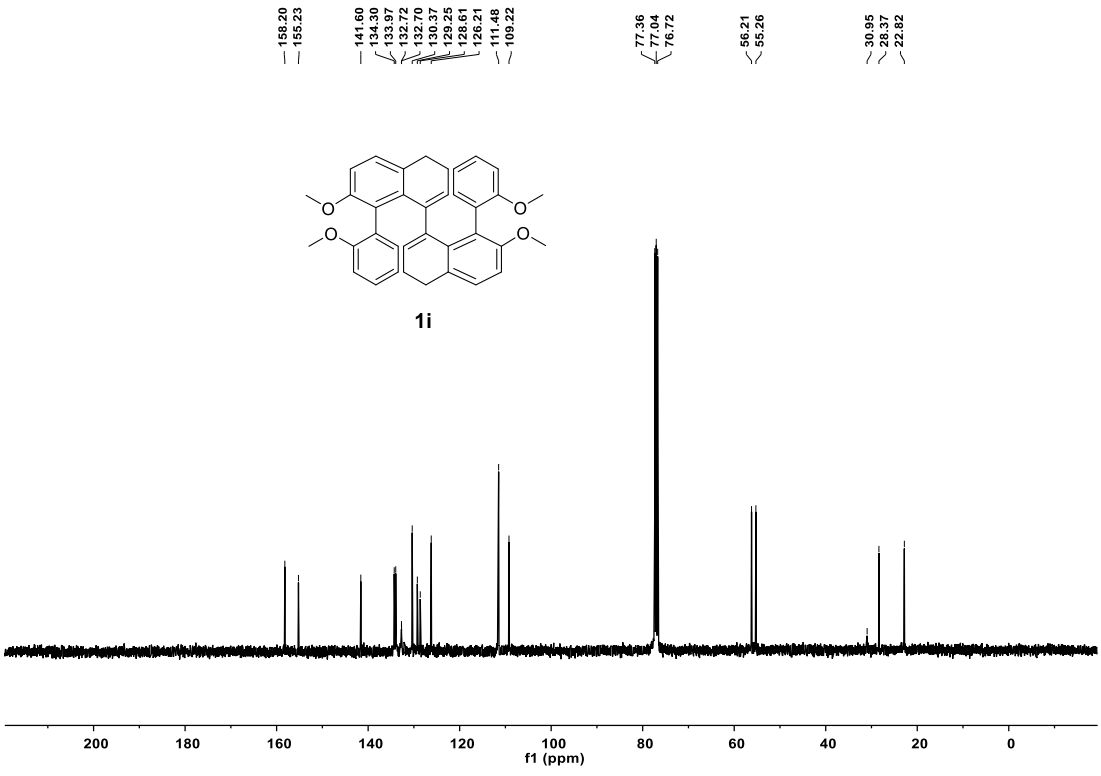


Fig. S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **1i**.

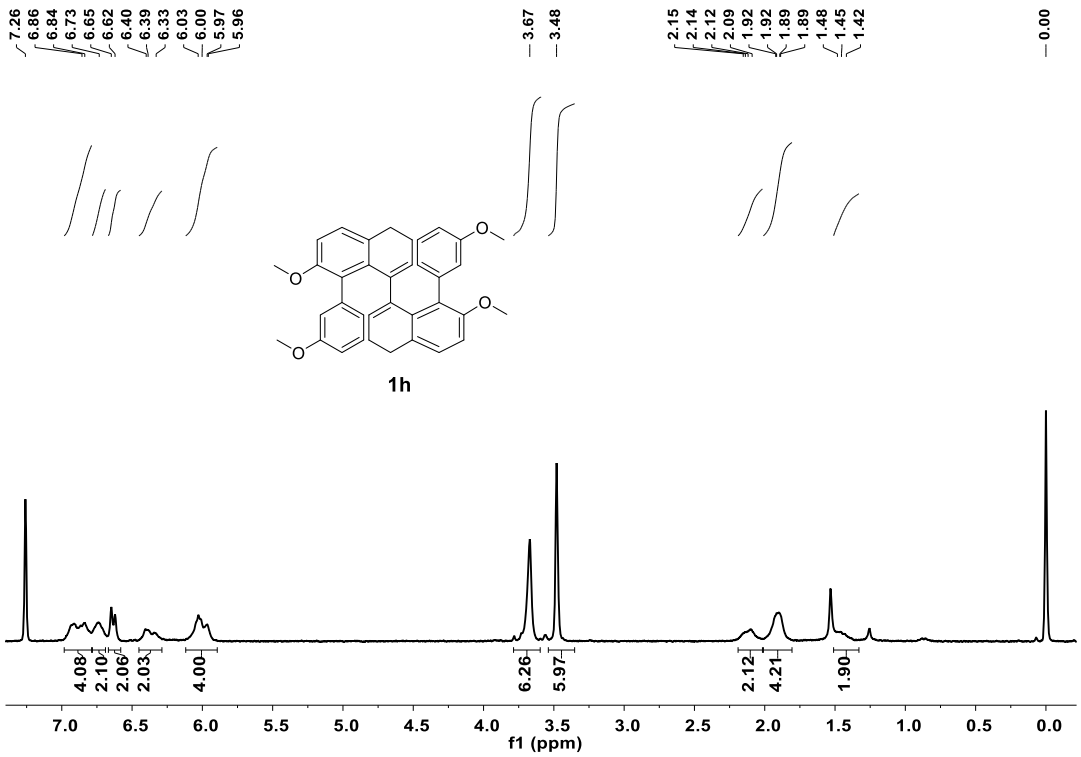


Fig. S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1h**.

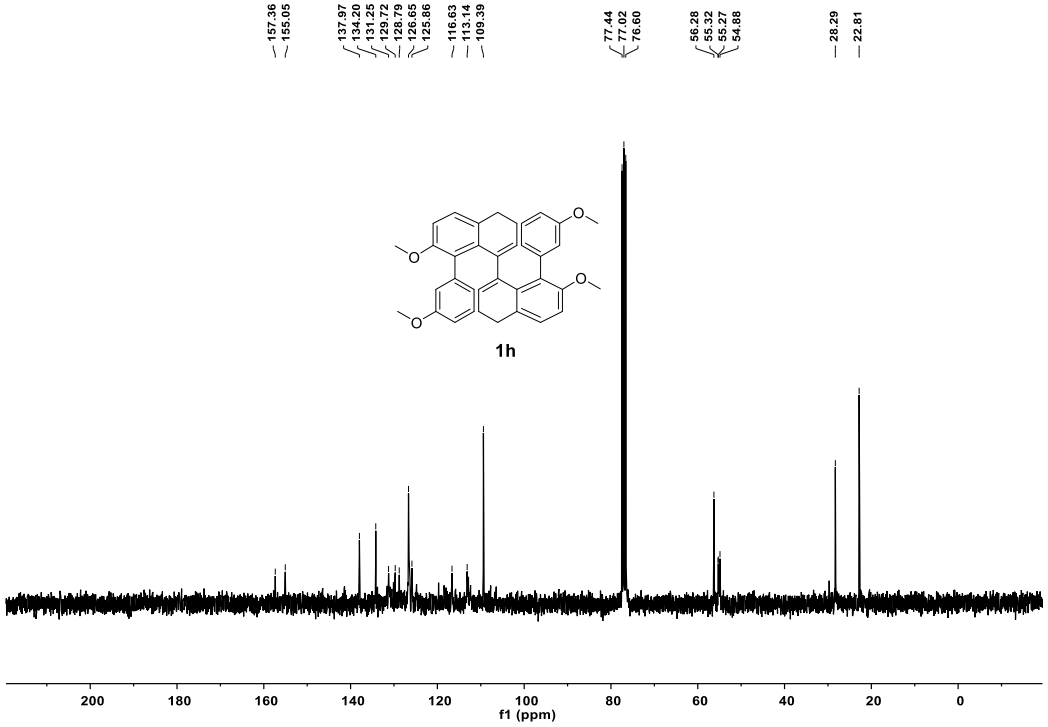


Fig. S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **1h**.

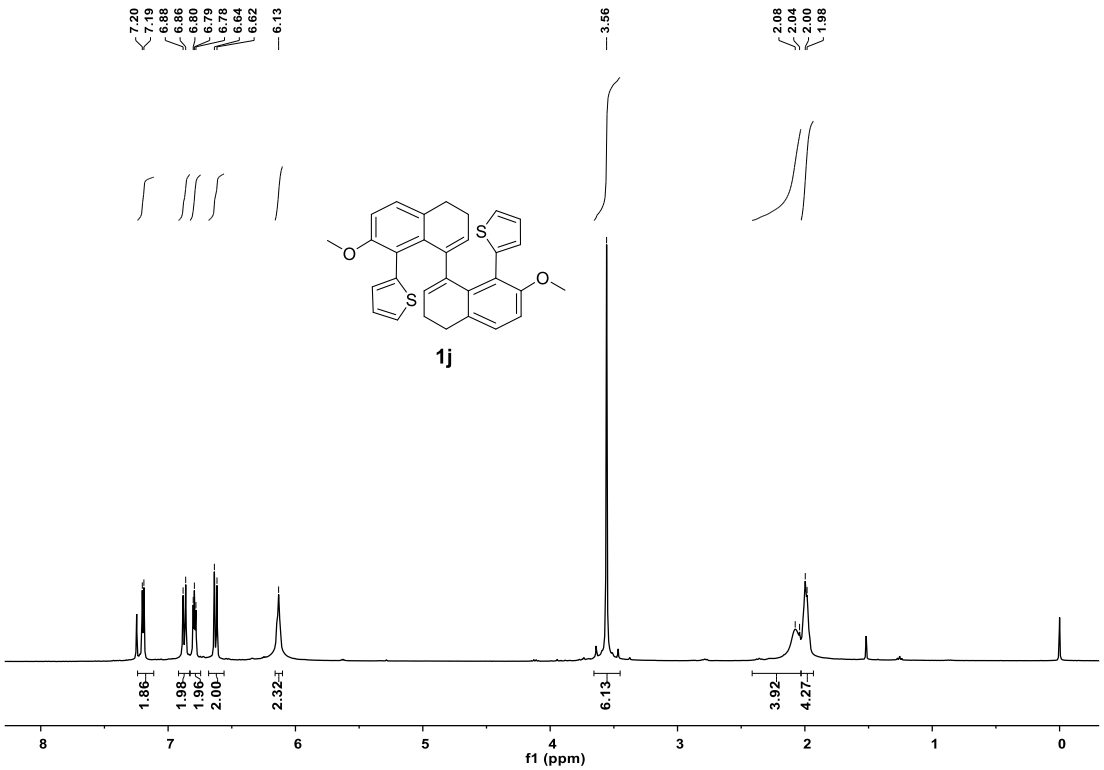


Fig. S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1j**.

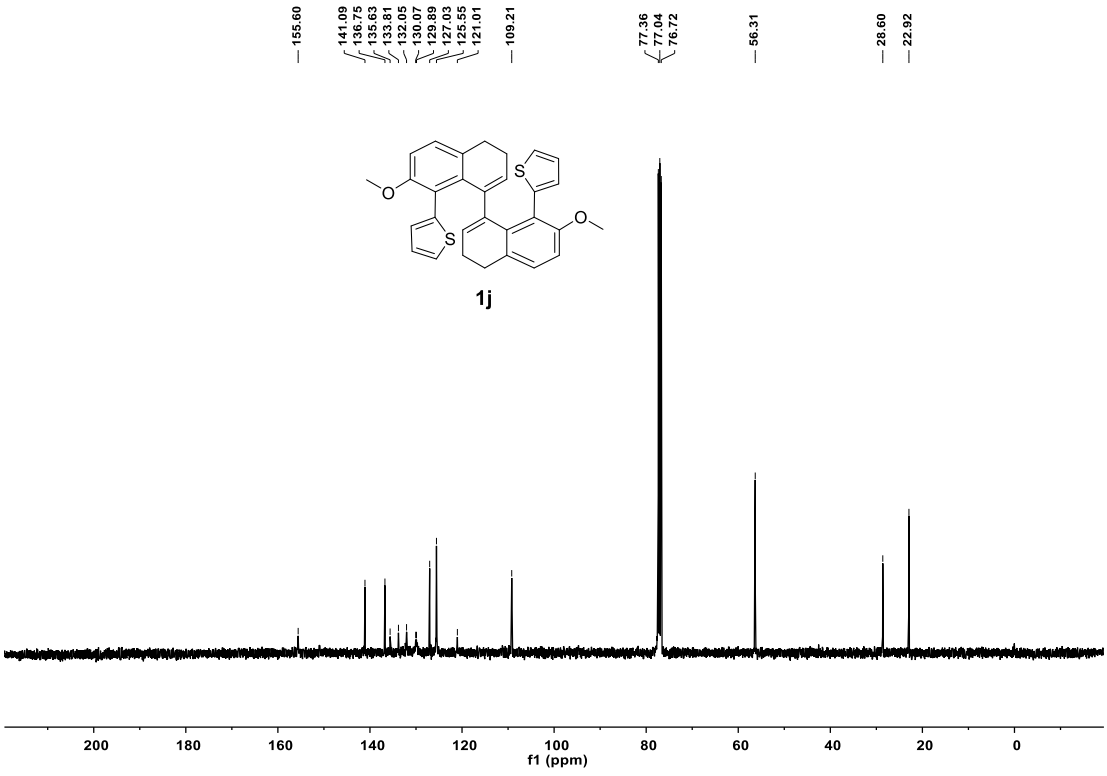


Fig. S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1j**.

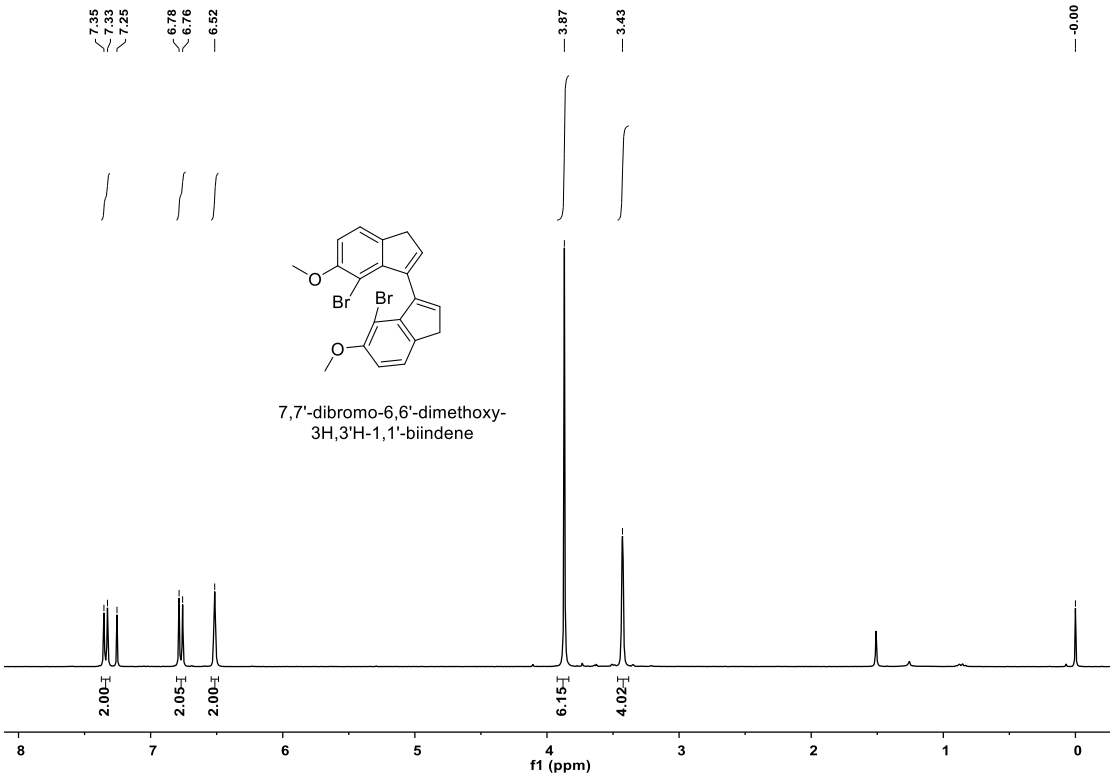


Fig. S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 7,7'-dibromo-6,6'-dimethoxy-3H,3'H-1,1'-biindene.

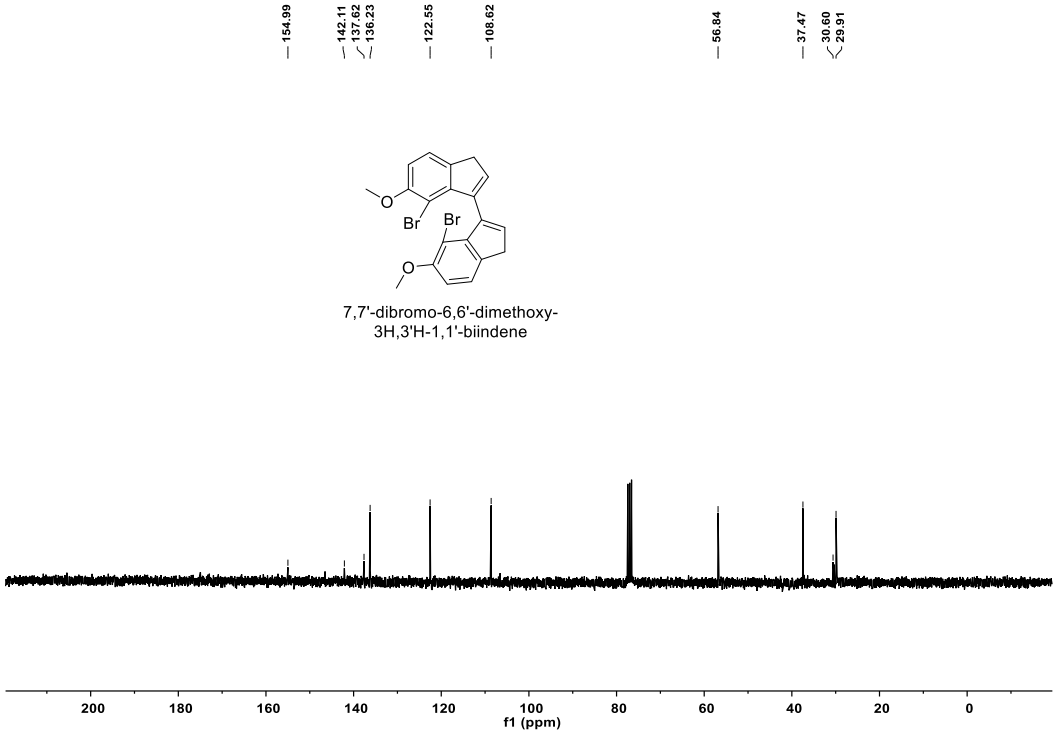


Fig. S10. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of 7,7'-dibromo-6,6'-dimethoxy-3H,3'H-1,1'-biindene.

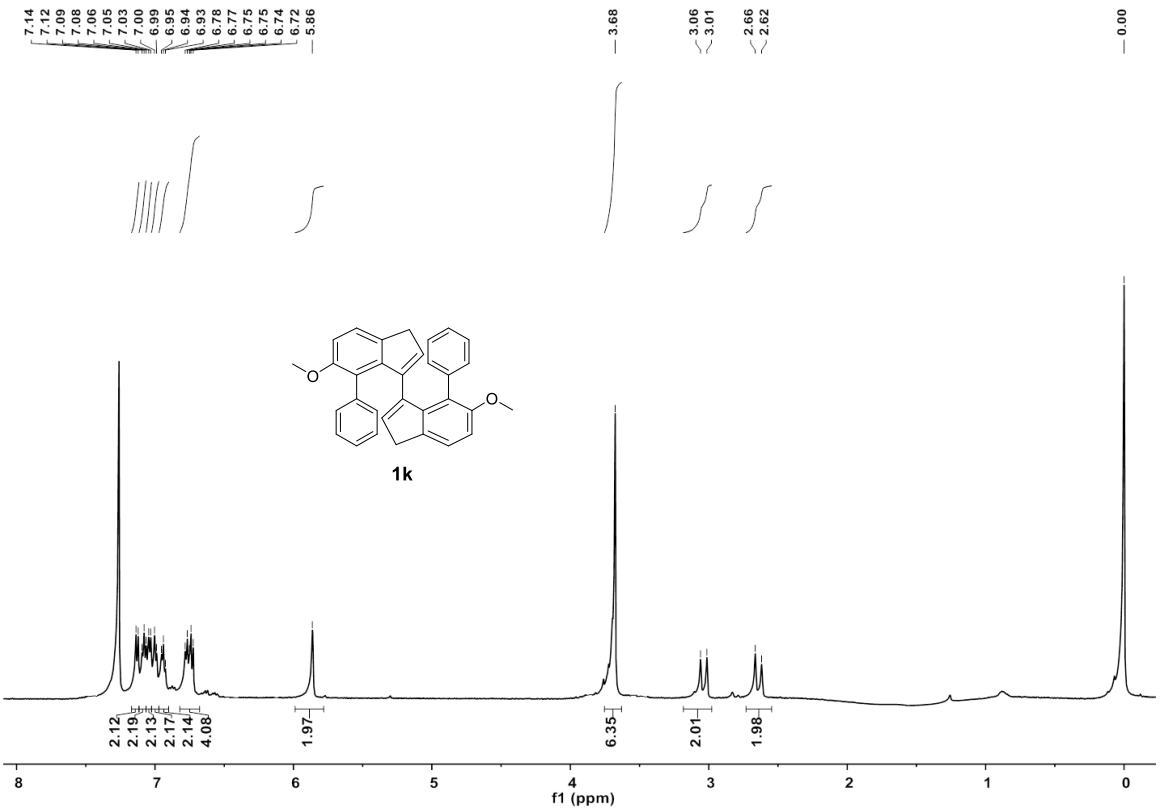


Fig. S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1k**.

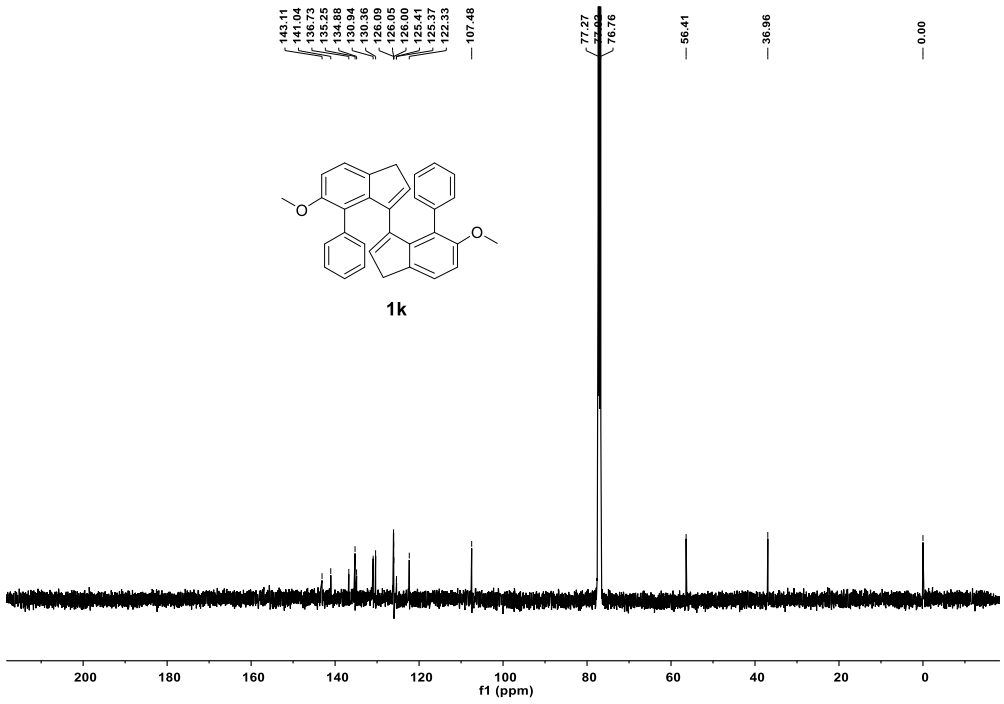


Fig. S12. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1k**.

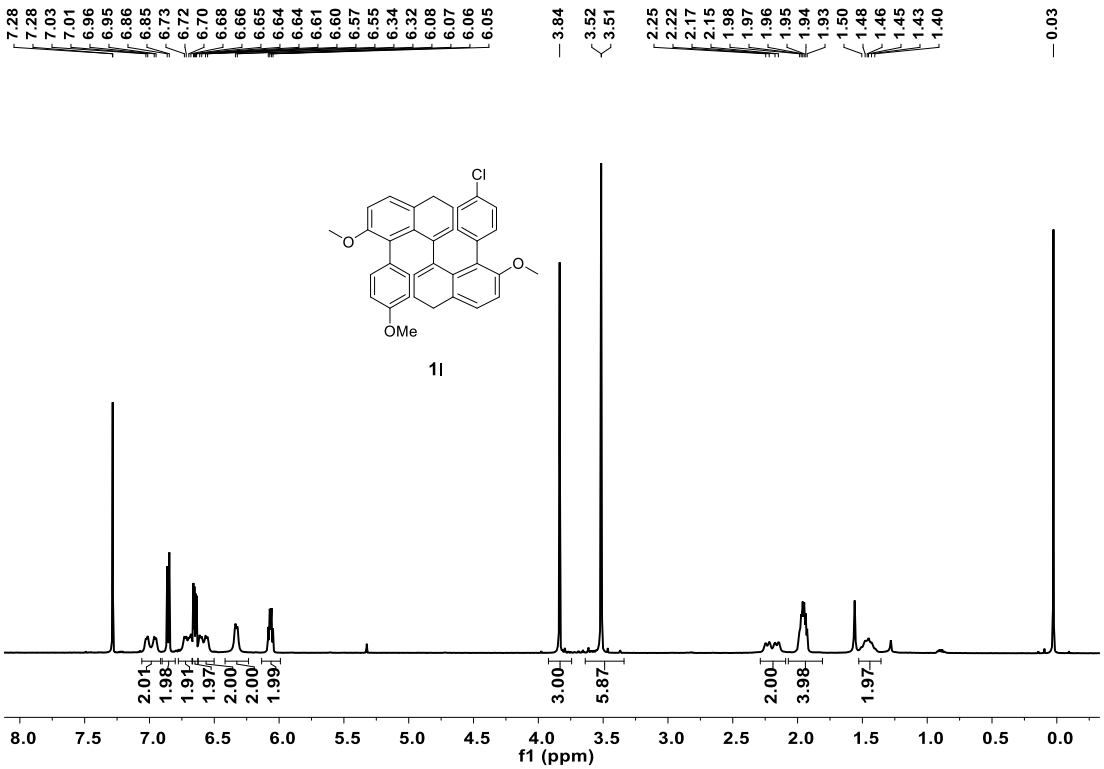


Fig. S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1l**.

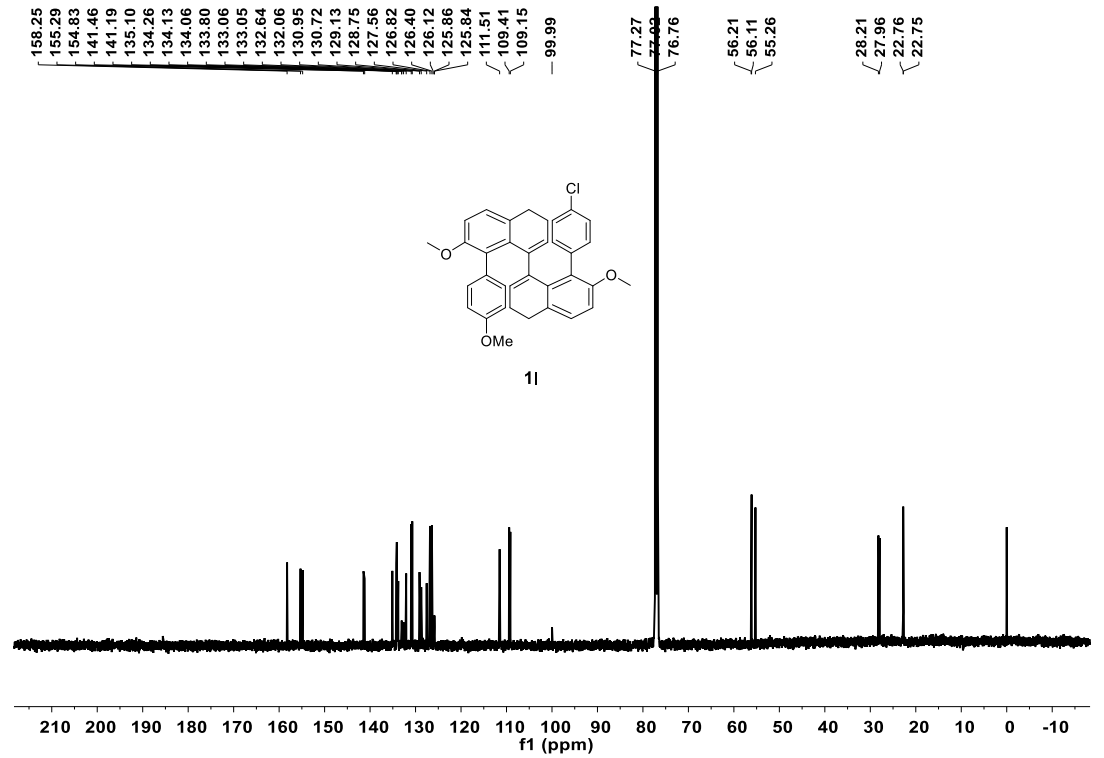


Fig. S14. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **1l**.

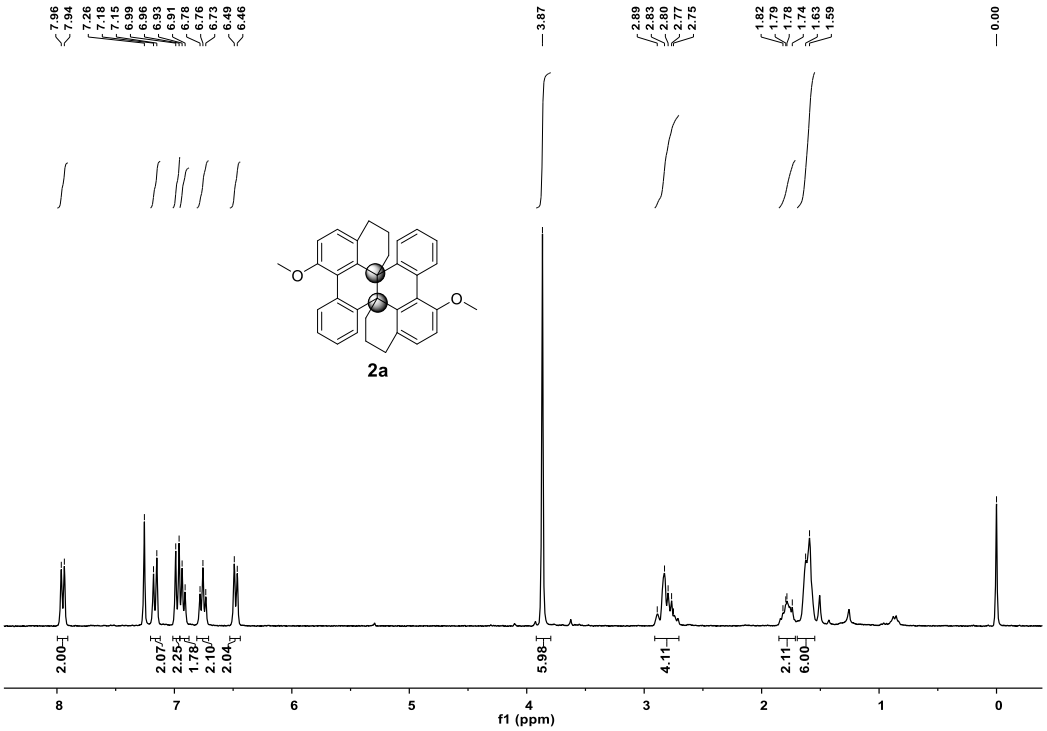


Fig. S15. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2a**.

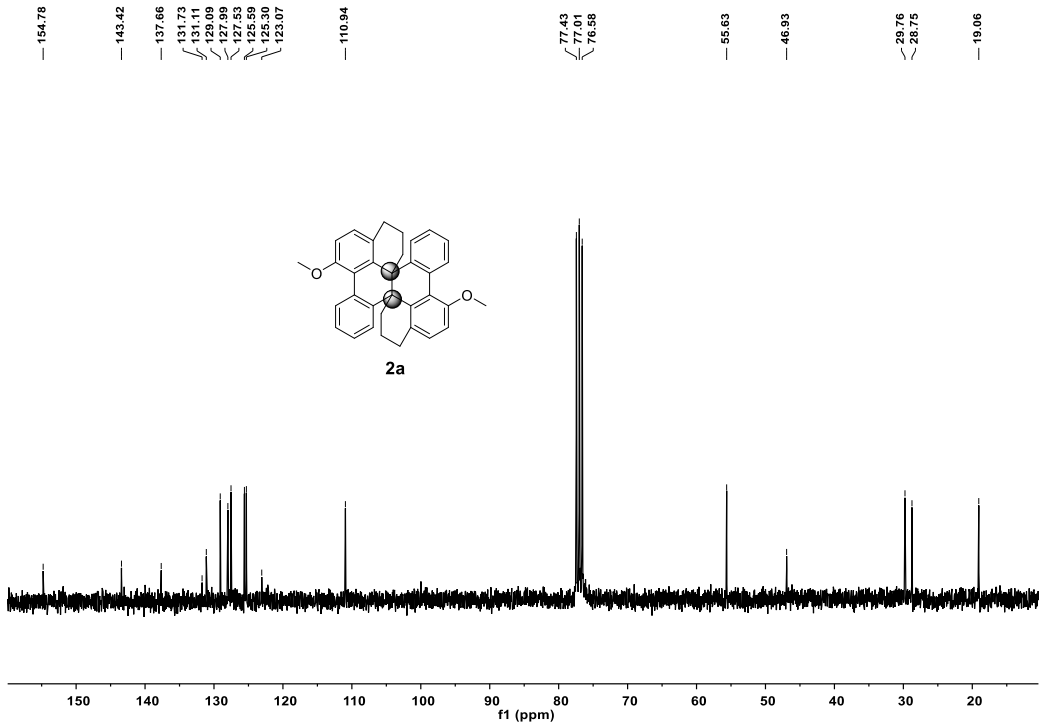


Fig. S16. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2a**.

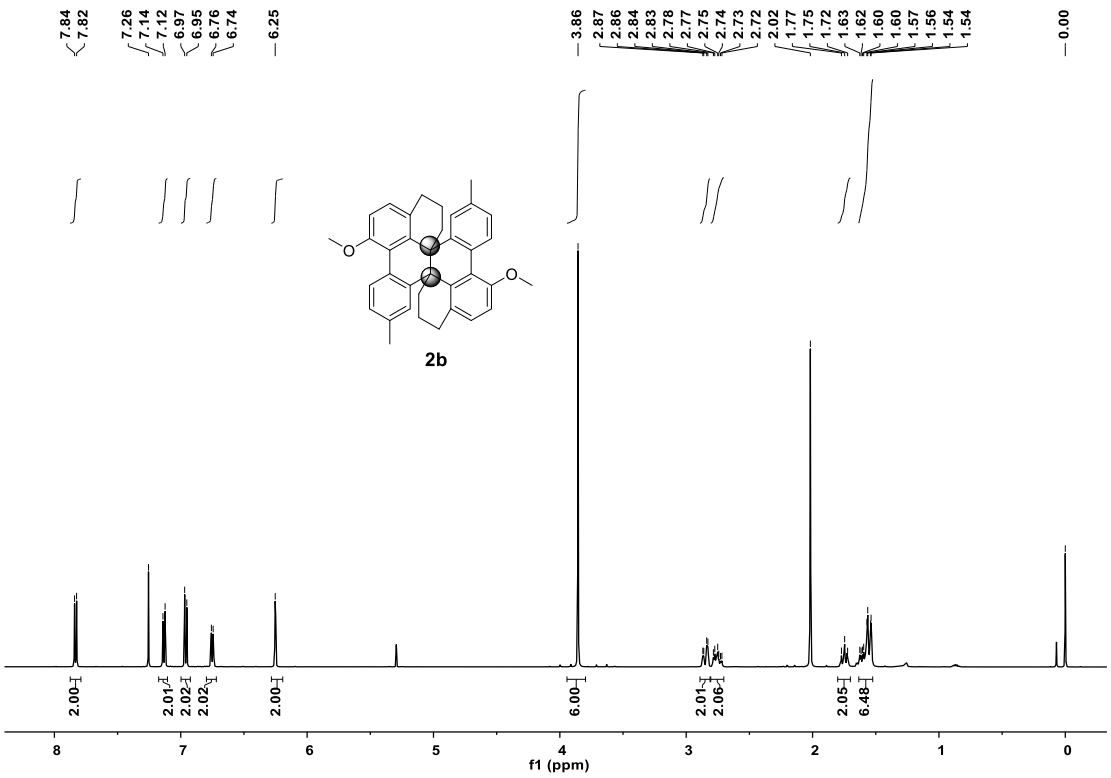


Fig. S17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2b**.

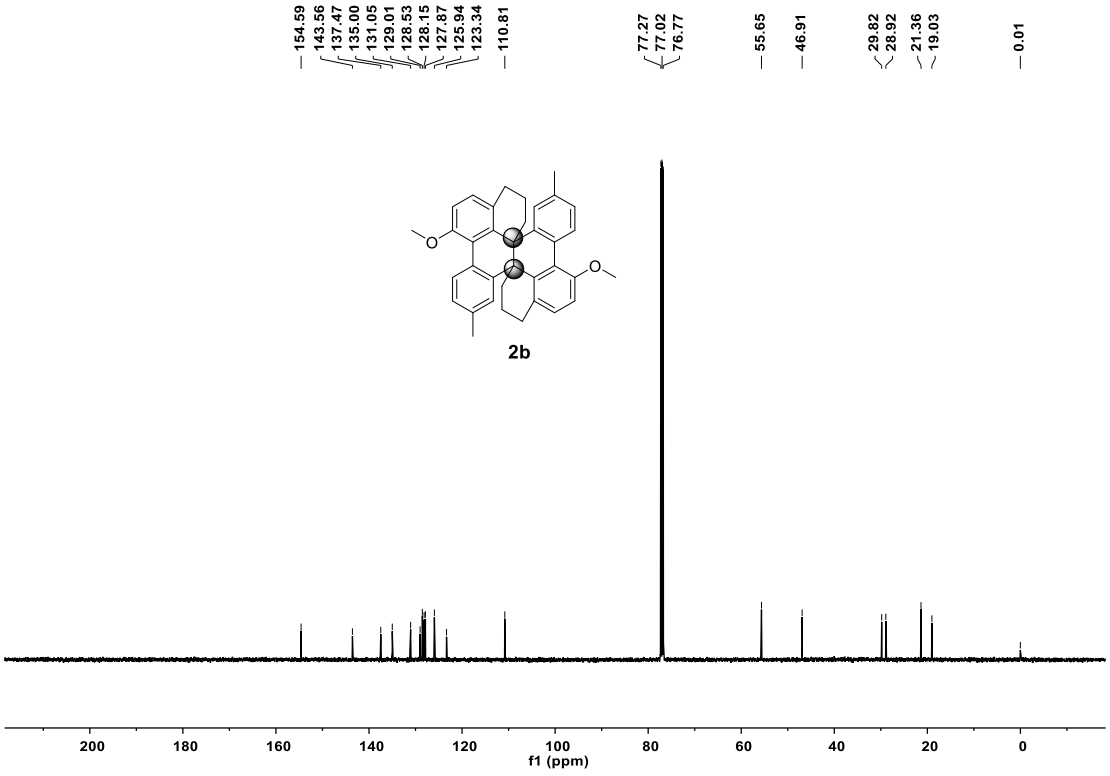


Fig. S18. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2b**.

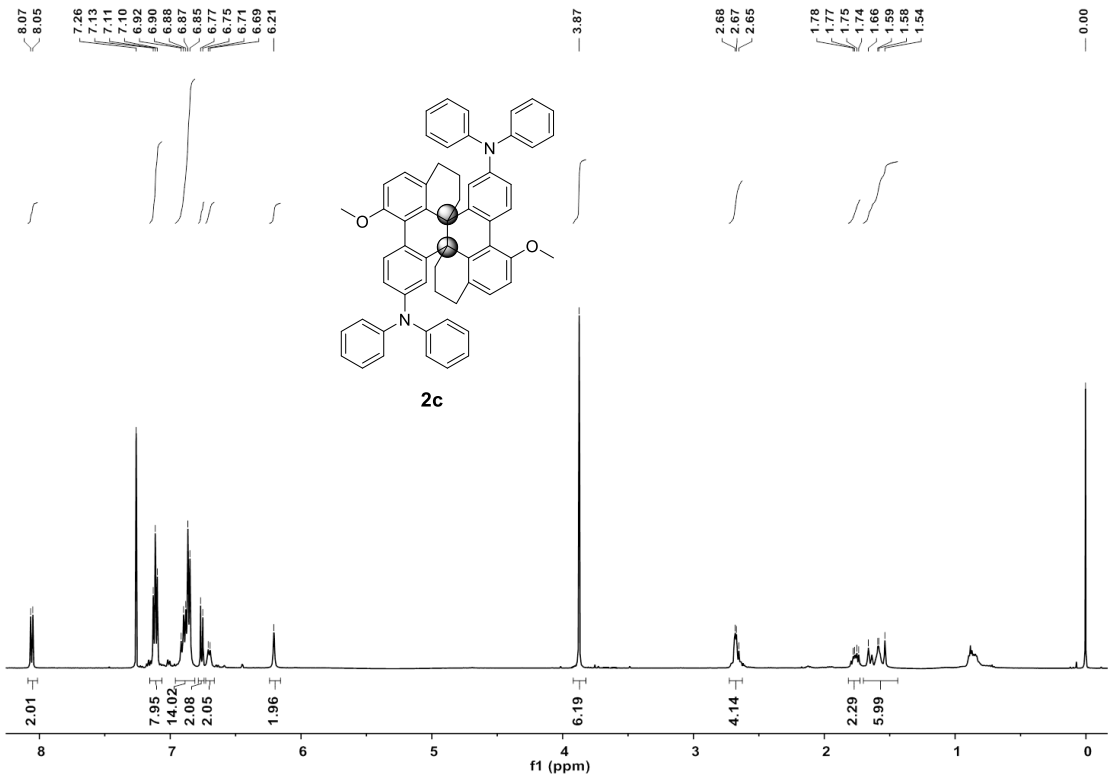


Fig. S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2c**.

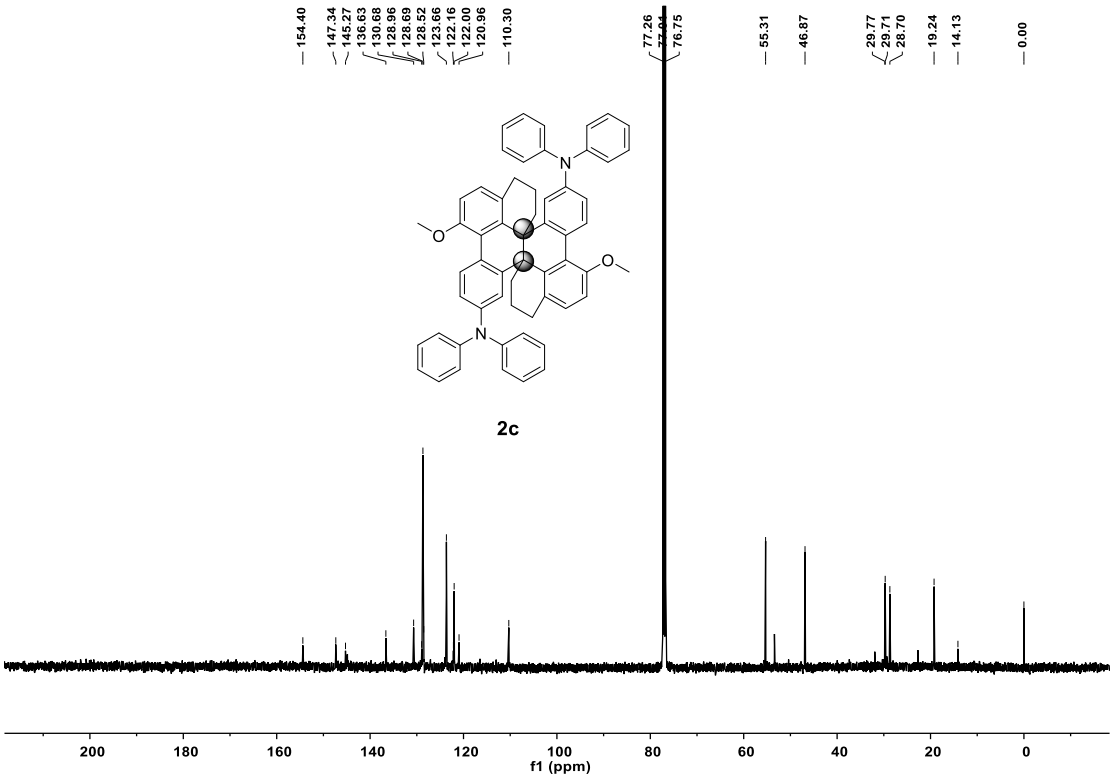


Fig. S20. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2c**.

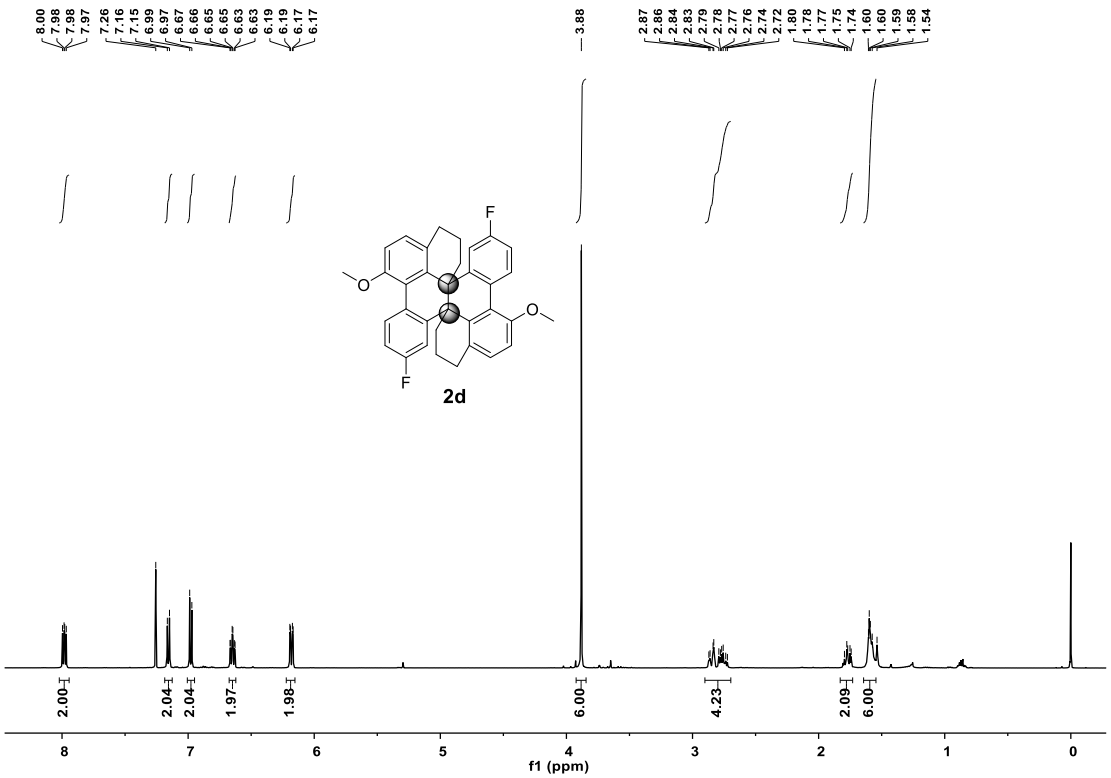


Fig. S21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2d**.

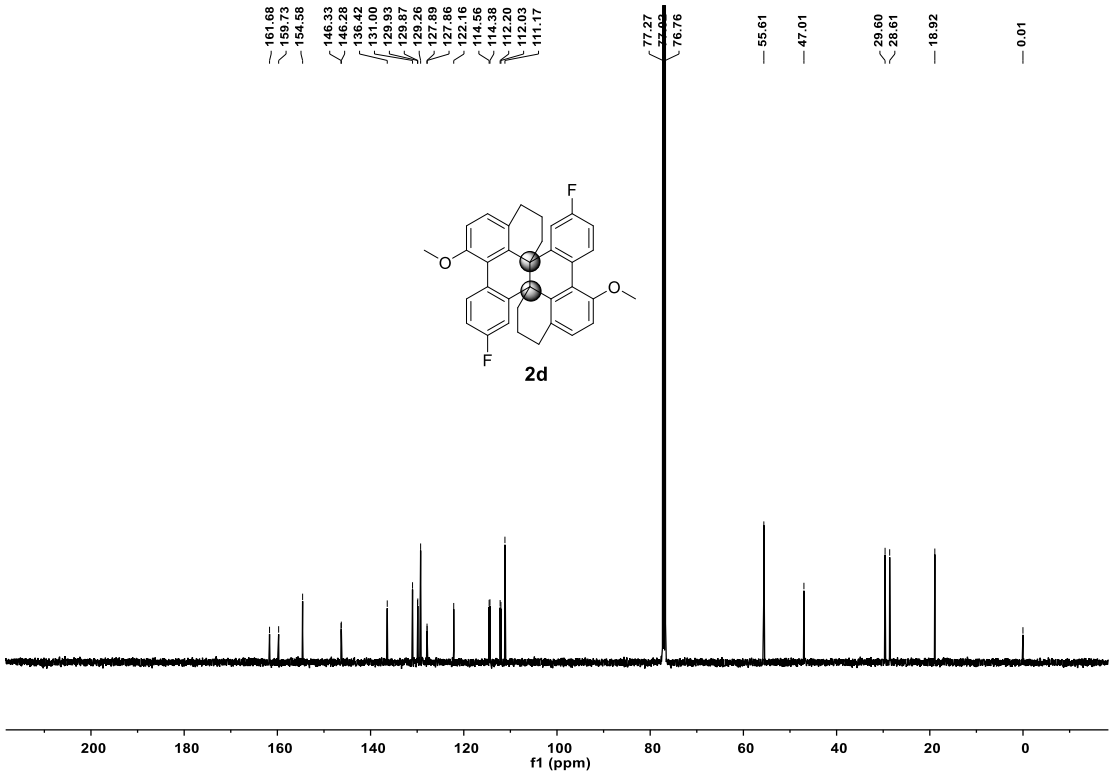


Fig. S22. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2d**.

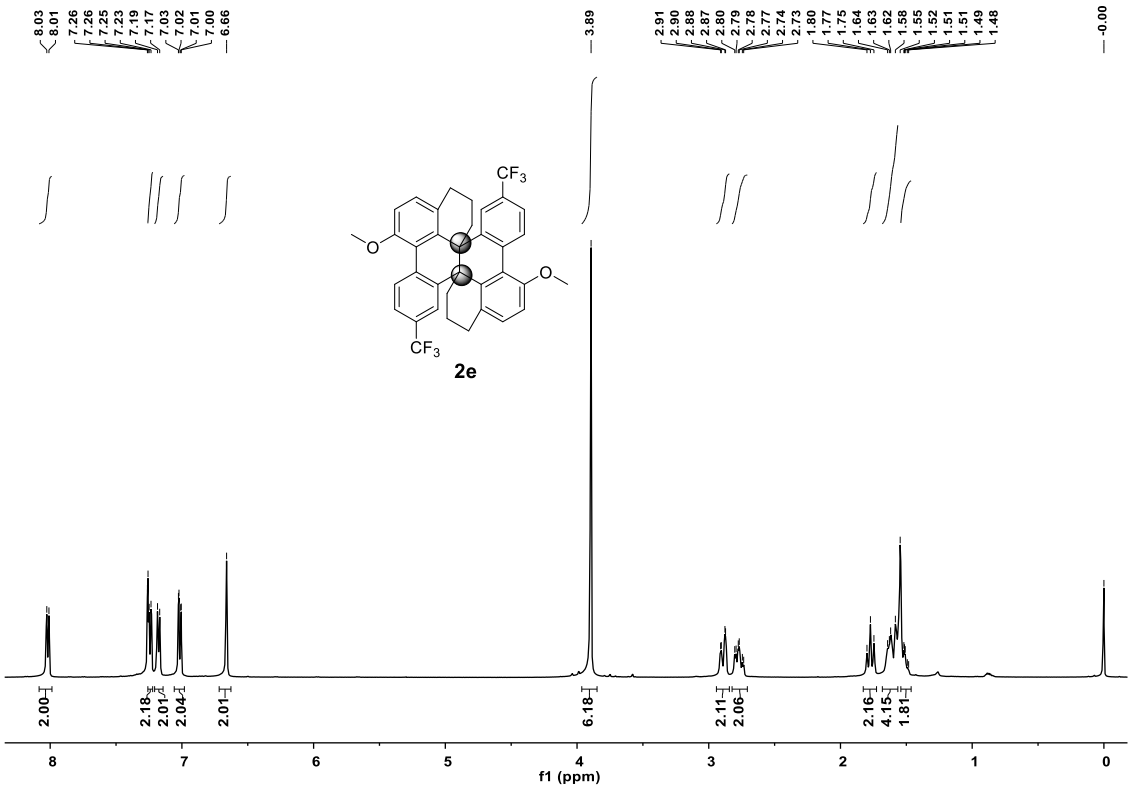


Fig. S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2e**.

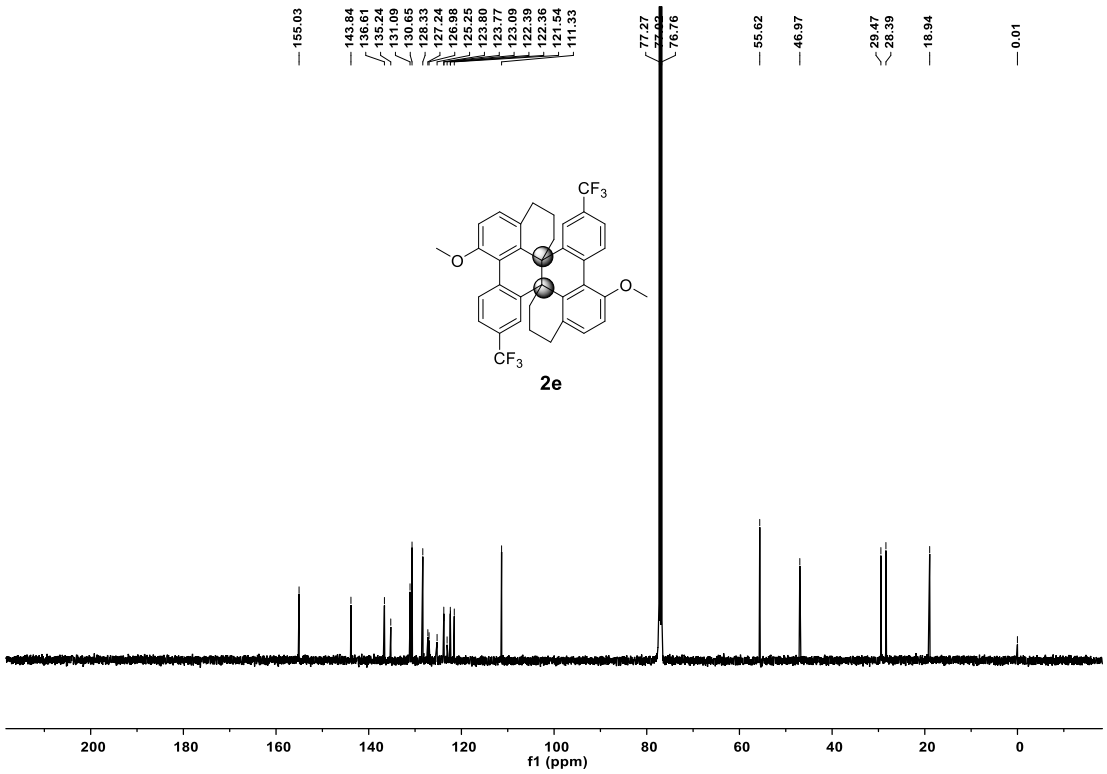


Fig. S24. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2e**

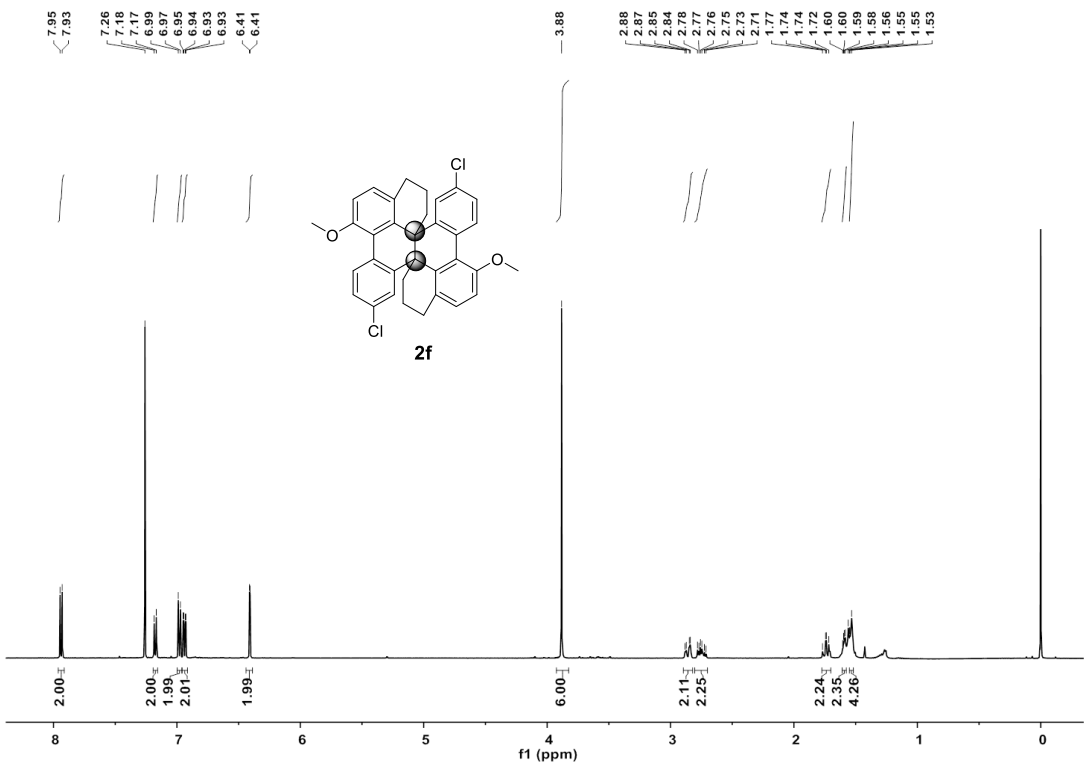


Fig. S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2f**.

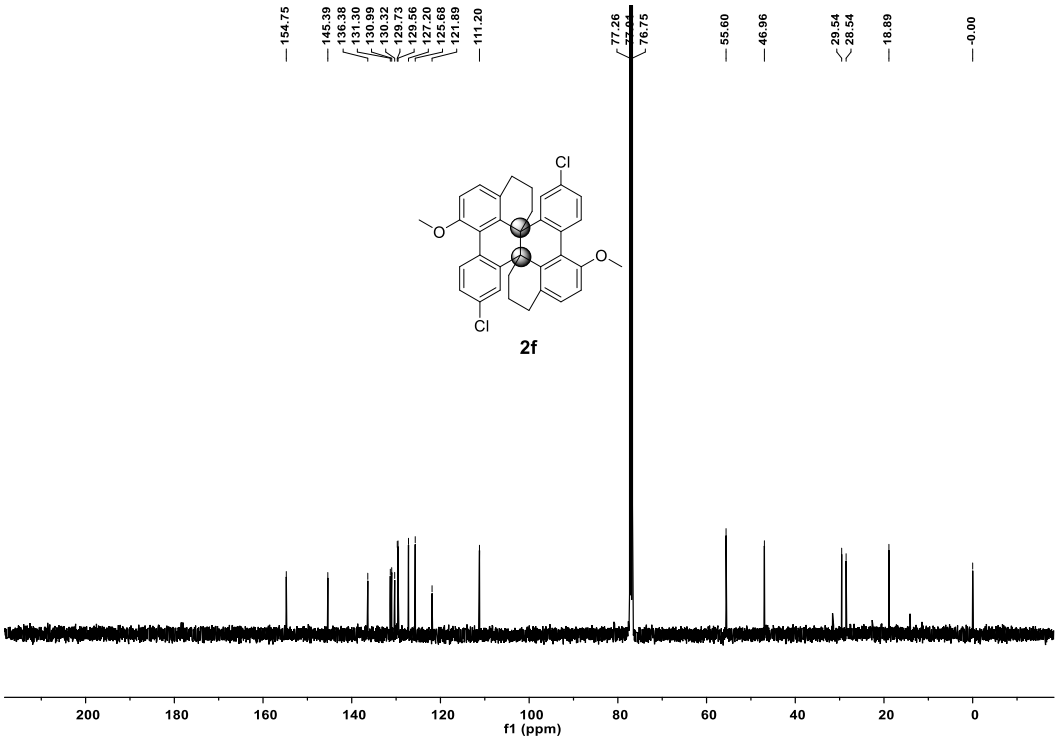


Fig. S26. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2f**.

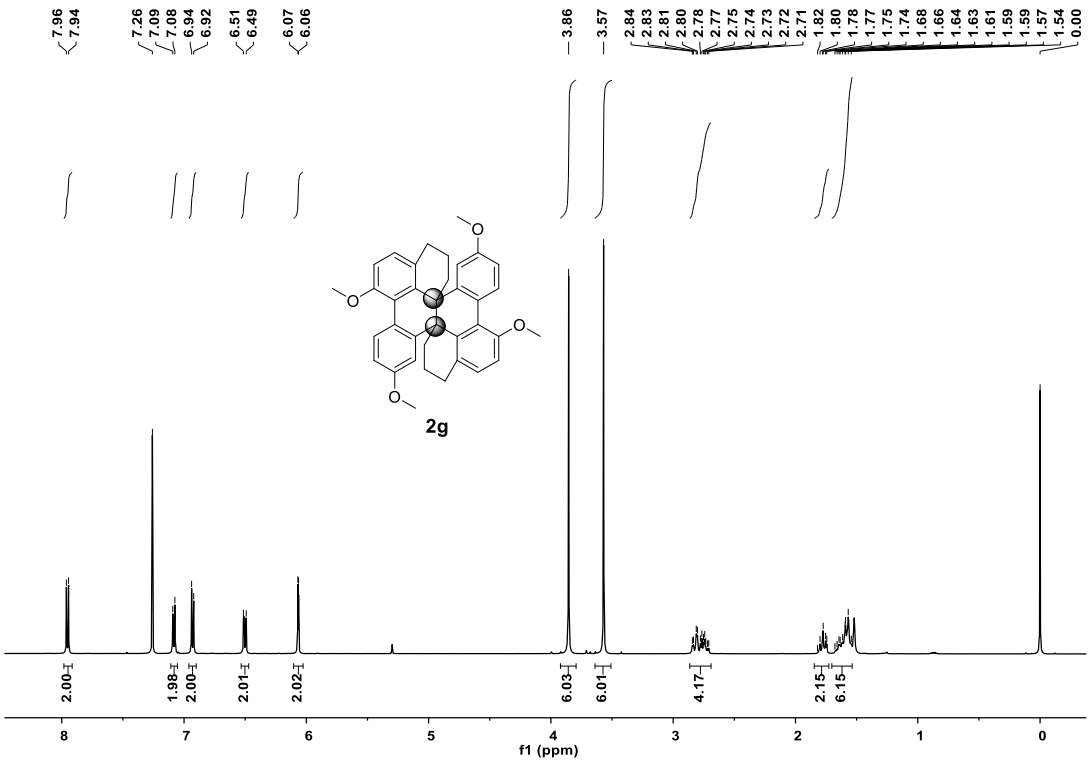


Fig. S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2g**.

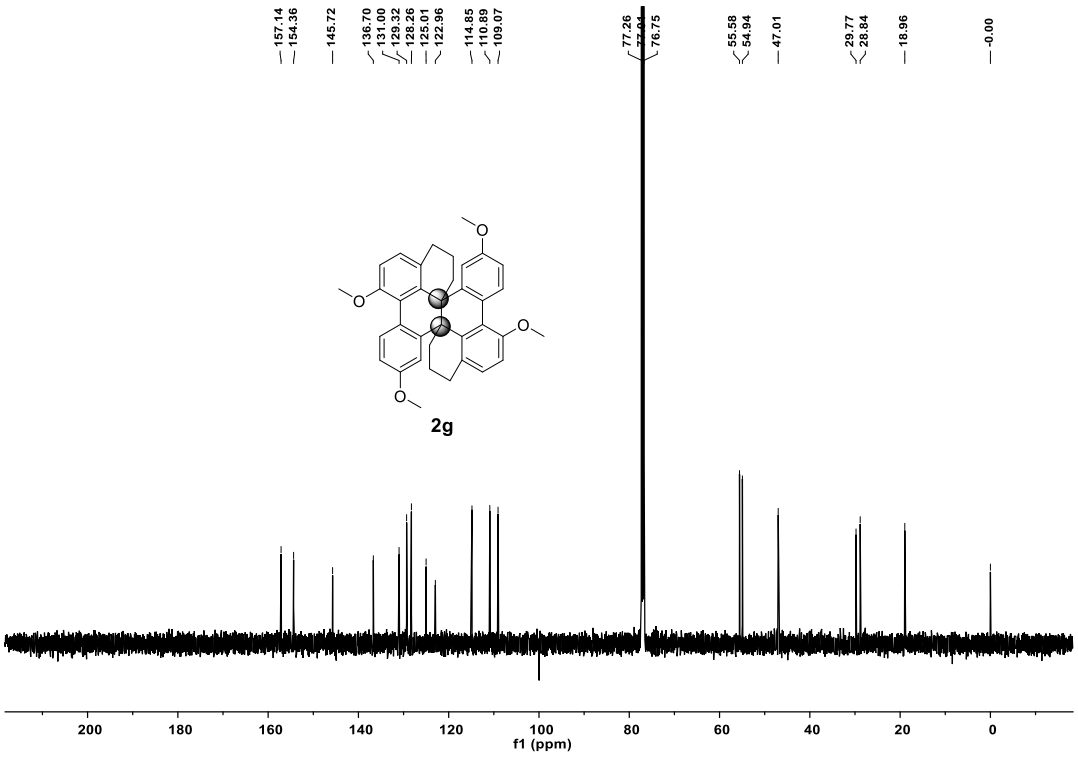


Fig. S28. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2g**.

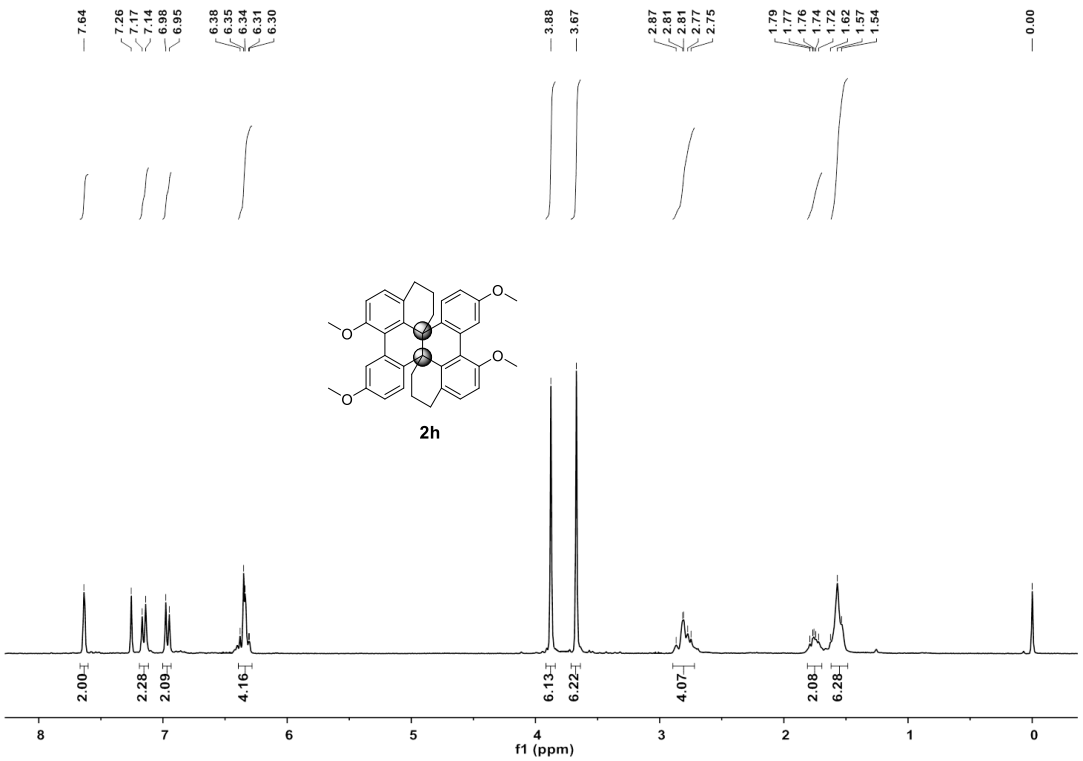


Fig. S29. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2h**.

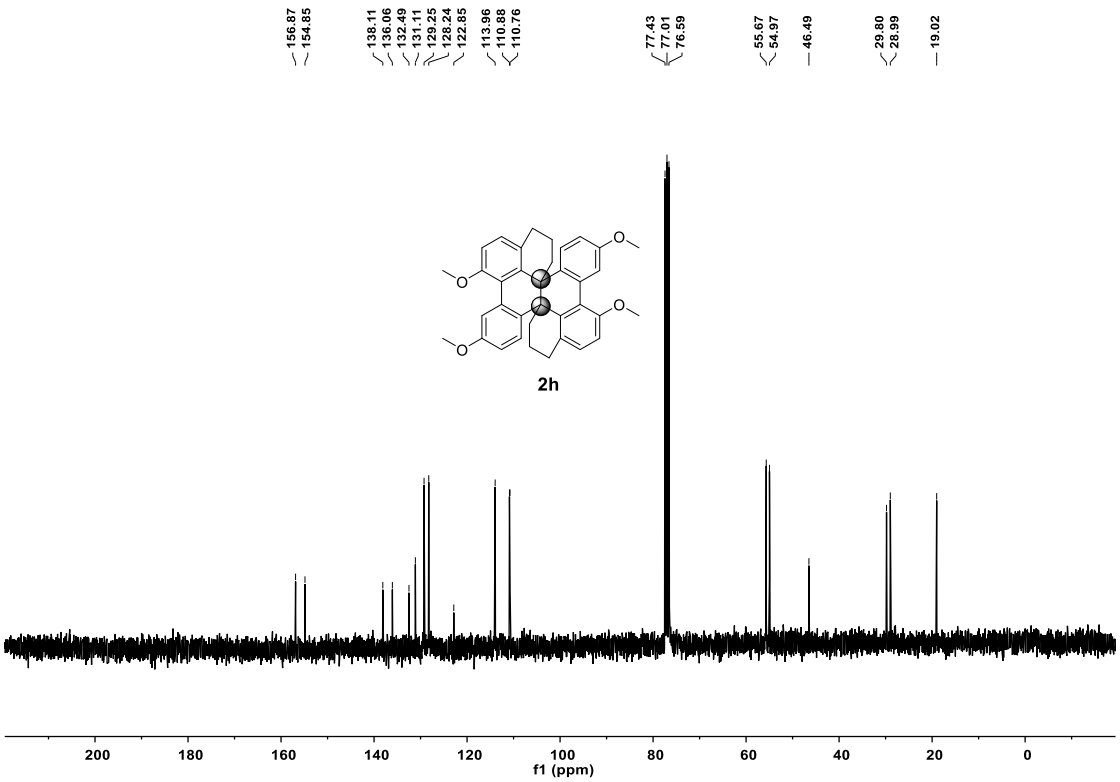


Fig. S30. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2h**.

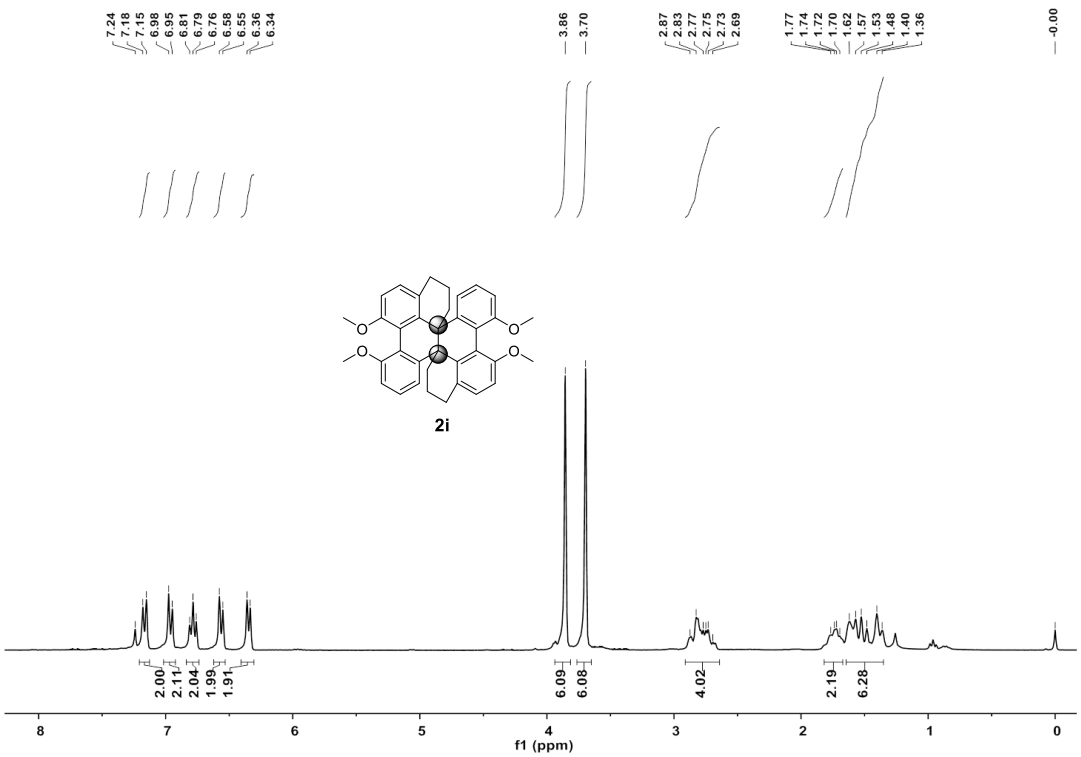


Fig. S31. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2i**

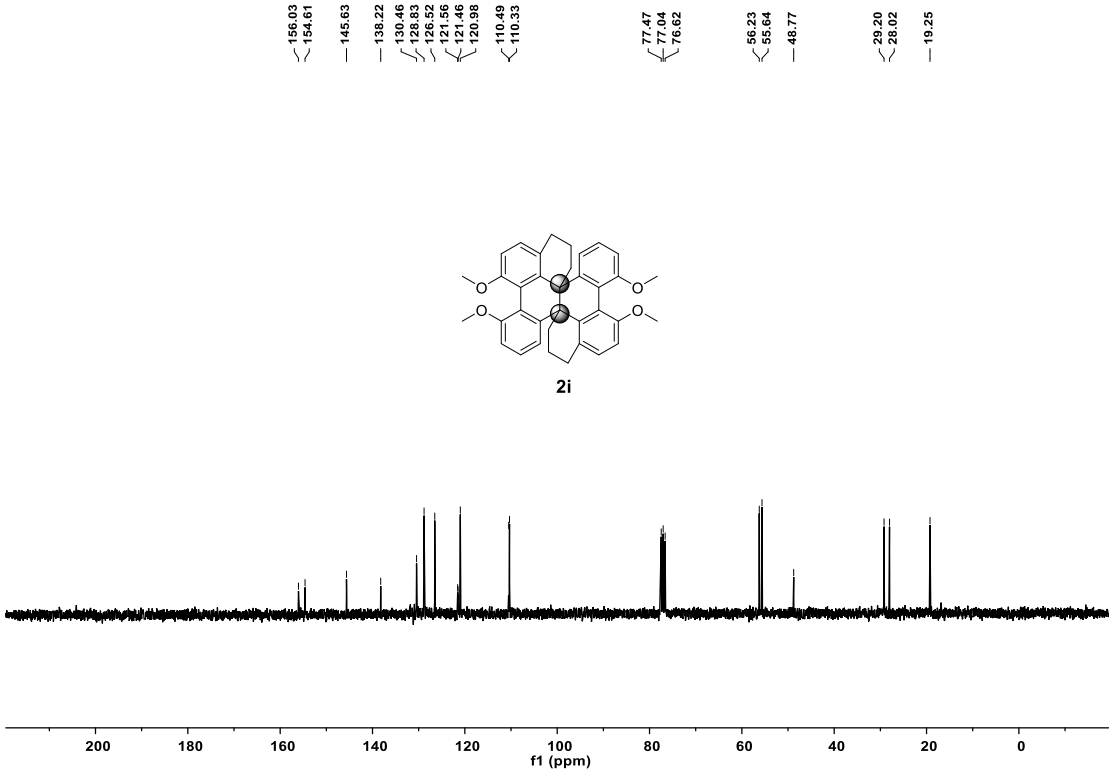


Fig. S32. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2i**.

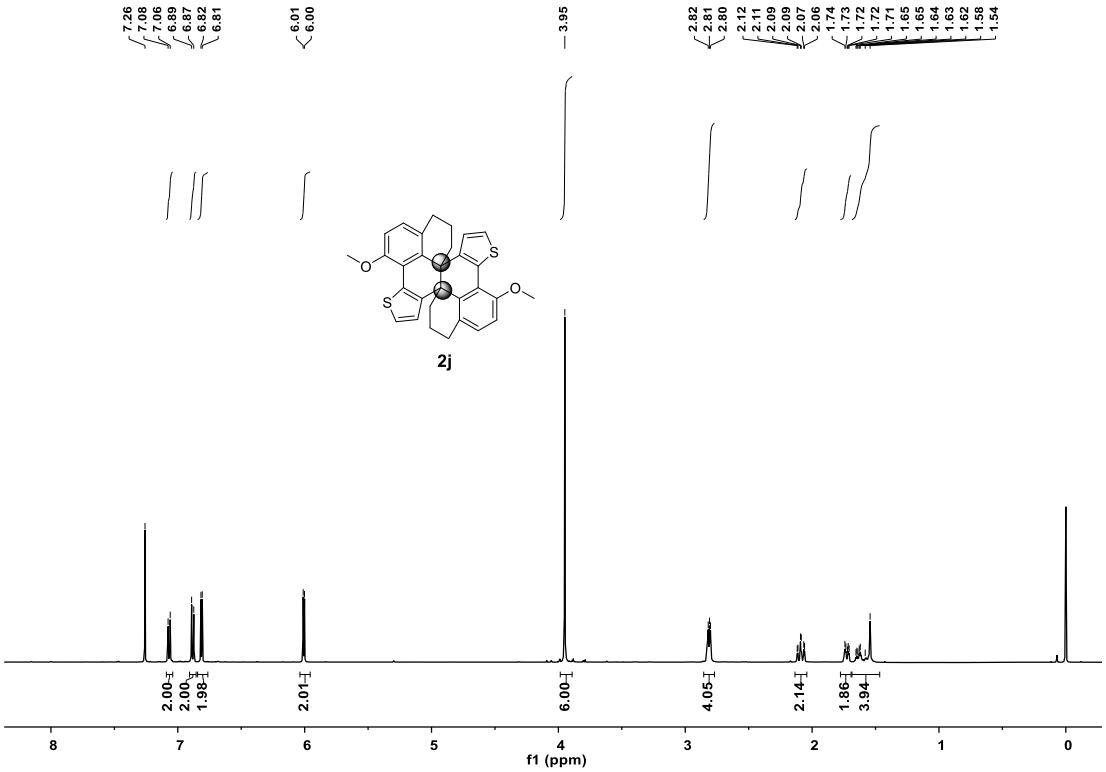


Fig. S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2j**.

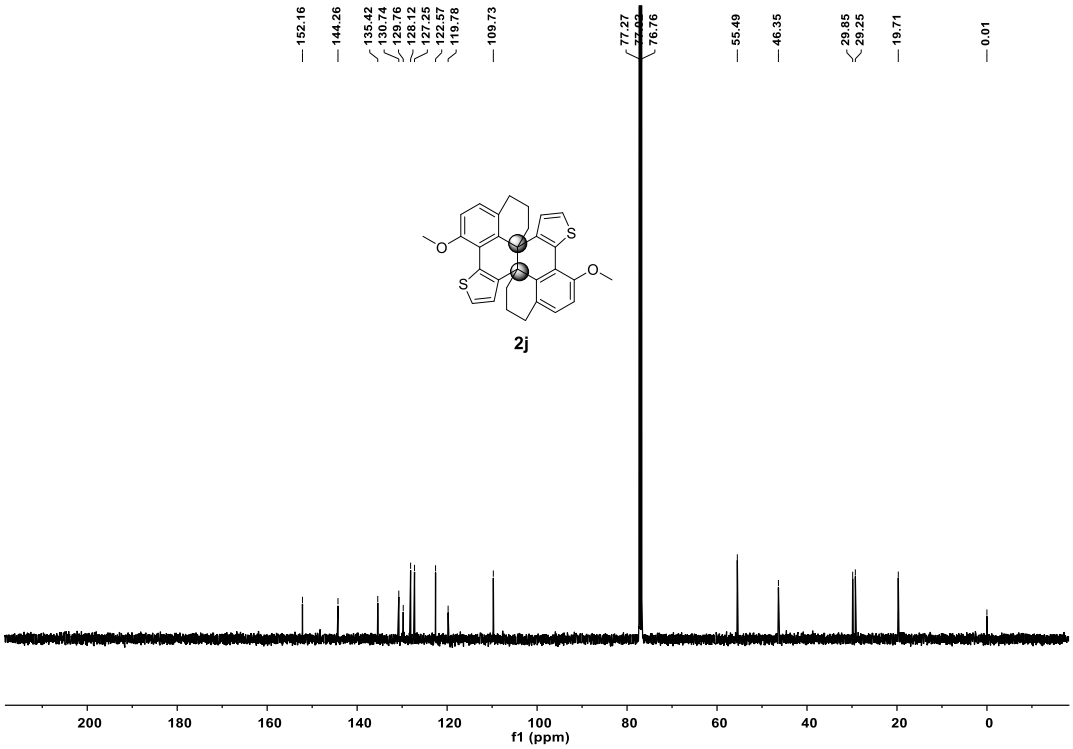


Fig. S34. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2j**.

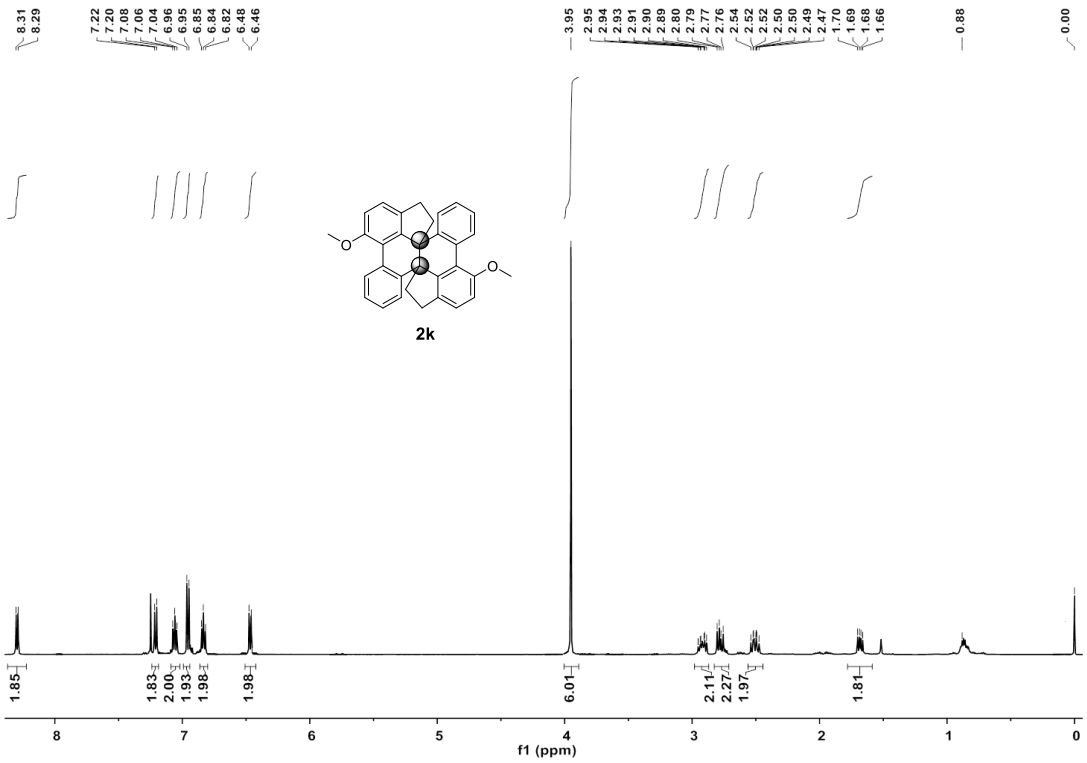


Fig. S35. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2k**.

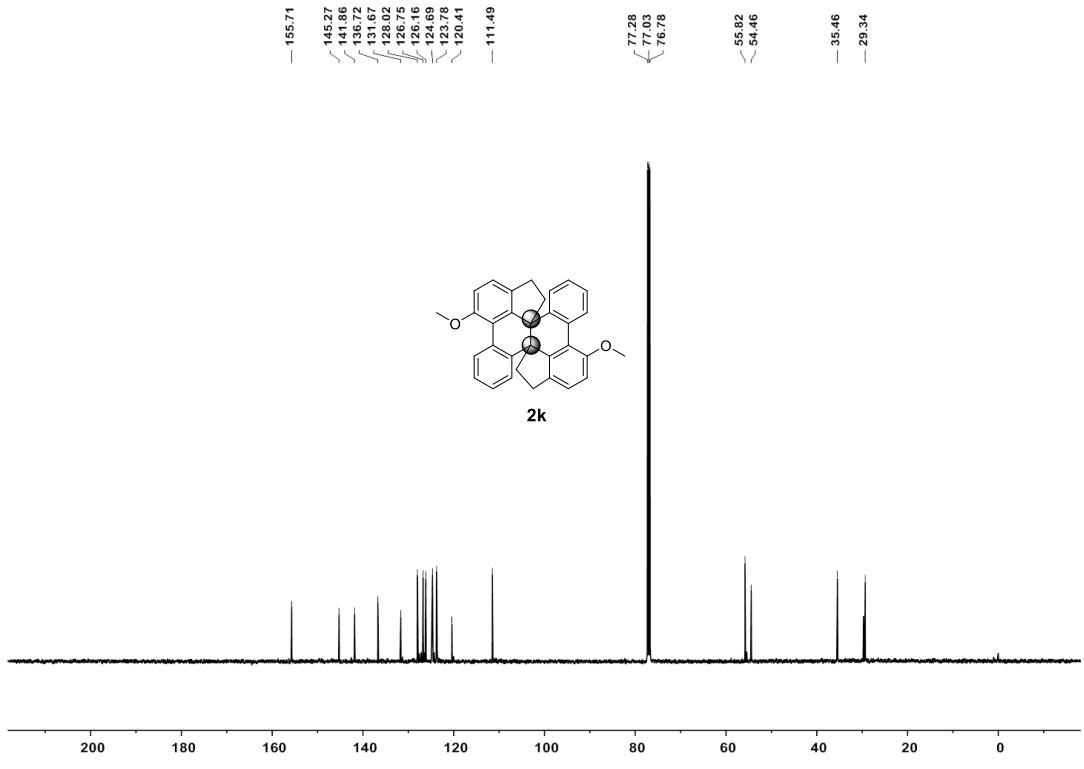


Fig. S36. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2k**.

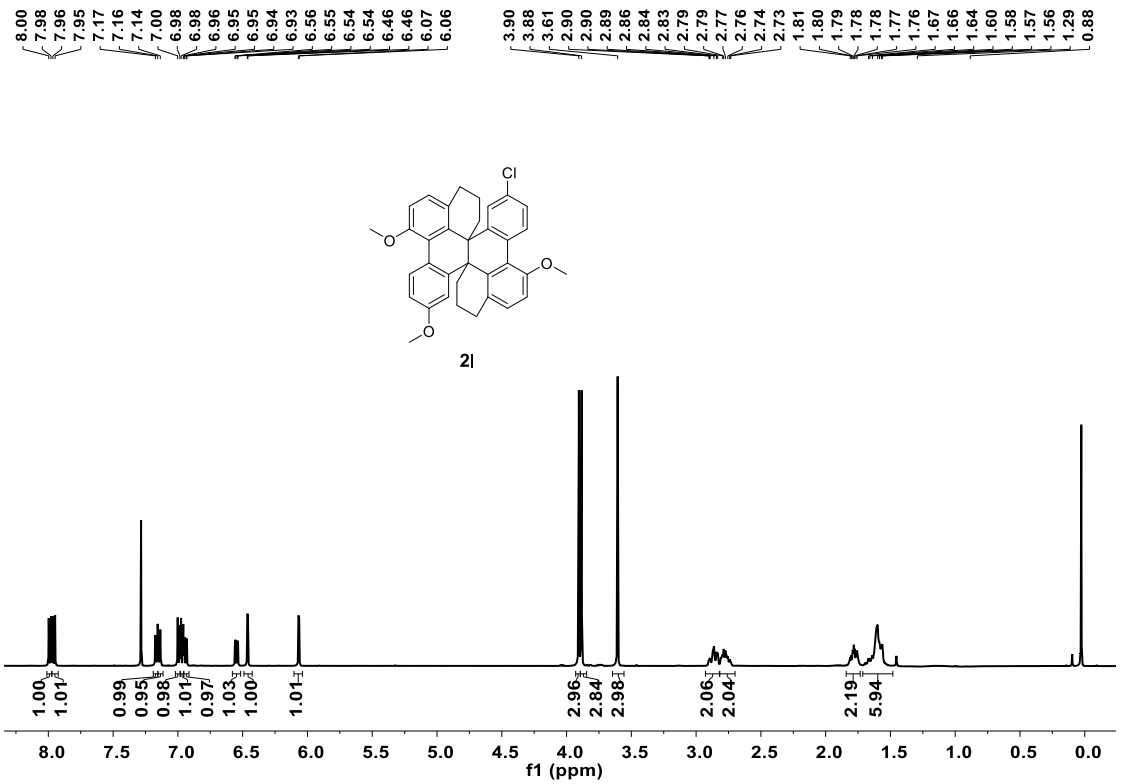


Fig. S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2l**.

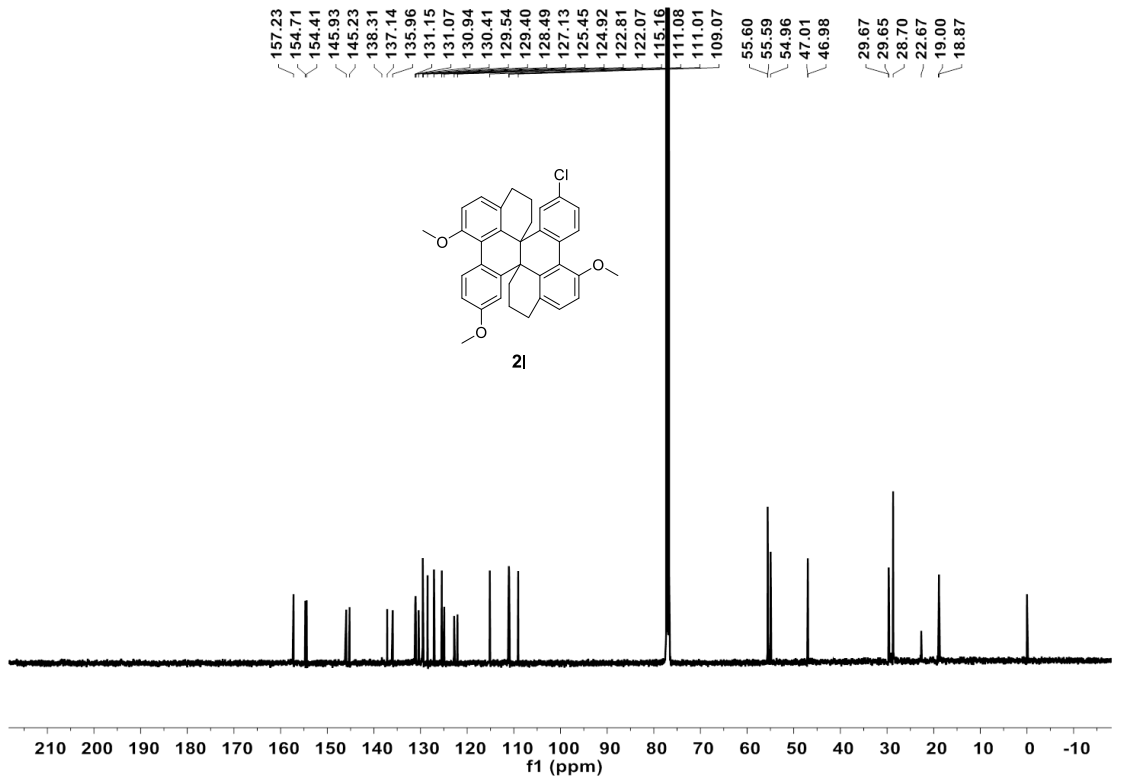


Fig. S38. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **2l**.

5. X-Ray crystallographic data

Table 1. Crystal data and structure refinement for **2a**.

Identification code	mx5290_sq	
Empirical formula	C34 H30 O2	
Formula weight	470.58	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.3791(14) Å	a= 90 °.
	b = 19.941(3) Å	b= 93.294(2) °.
	c = 16.727(3) Å	g = 90 °.
Volume	2790.4(8) $Å^3$	
Z	4	
Density (calculated)	1.120 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	1000	
Crystal size	0.213 x 0.134 x 0.072 mm^3	
Theta range for data collection	1.591 to 27.474 °.	
Index ranges	-10<=h<=10, -24<=k<=25, -21<=l<=14	
Reflections collected	20272	
Independent reflections	6369 [R(int) = 0.0688]	
Completeness to theta = 26.000 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85941	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6369 / 0 / 327	
Goodness-of-fit on F^2	1.153	
Final R indices [I>2sigma(I)]	R1 = 0.0848, wR2 = 0.1609	
R indices (all data)	R1 = 0.1027, wR2 = 0.1697	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.233 and -0.236 $e.Å^{-3}$	

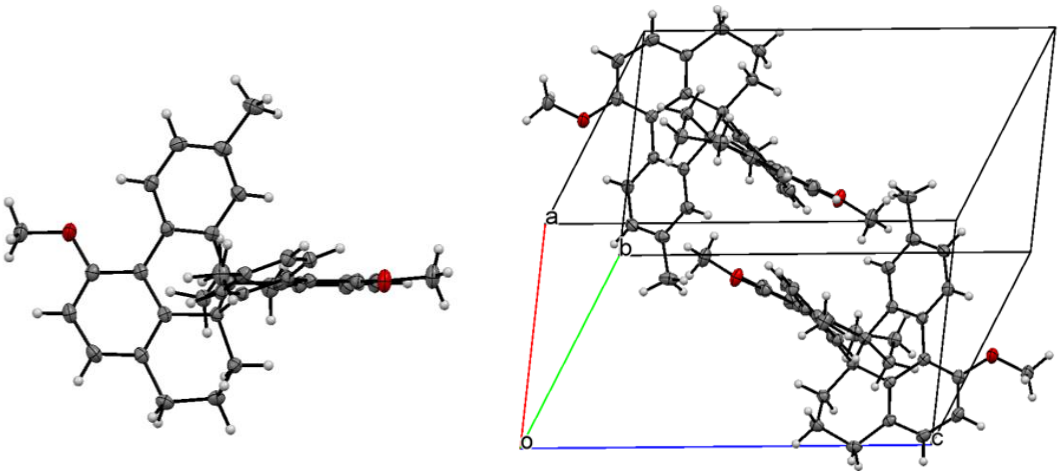


Fig. S39 X-ray structure and crystal packing of **2b** (CCDC 1893900).

Table 2. Crystal data and structure refinement for **2b**.

Identification code	mx7334	
Empirical formula	C36 H34 O2	
Formula weight	498.63	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6540(3) Å	a= 73.127(3) °.
	b = 9.8517(3) Å	b= 81.424(2) °.
	c = 14.1628(4) Å	g = 79.786(2) °.
Volume	1261.75(7) $Å^3$	
Z	2	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	532	
Crystal size	0.472 x 0.194 x 0.143 mm^3	
Theta range for data collection	2.155 to 27.484 °.	
Index ranges	-12<=h<=12, -12<=k<=12, -18<=l<=18	
Reflections collected	15089	
Independent reflections	5772 [R(int) = 0.0339]	
Completeness to theta = 25.242 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	1.00000 and 0.94344
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5772 / 0 / 347
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1172
R indices (all data)	R1 = 0.0526, wR2 = 0.1241
Extinction coefficient	n/a
Largest diff. peak and hole	0.322 and -0.207 e.Å^{-3}

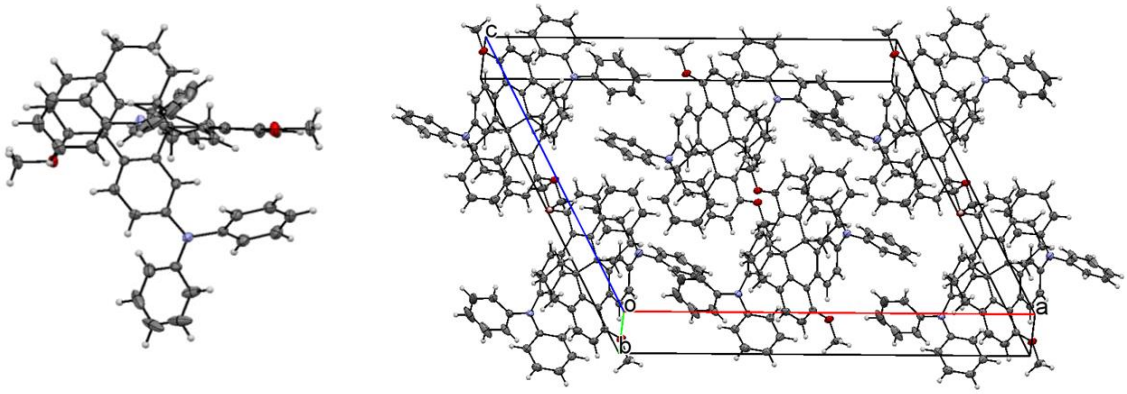


Fig. S40 X-ray structure and crystal packing of **2c** (CCDC 1893901).

Table 3. Crystal data and structure refinement for **2c**.

Identification code	mx7344	
Empirical formula	C58 H48 N2 O2	
Formula weight	804.98	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 24.780(7) Å	a= 90 °.
	b = 9.939(2) Å	b= 115.965(3) °.
	c = 19.014(5) Å	g = 90 °.
Volume	4210.1(19) Å^3	
Z	4	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	

F(000)	1704
Crystal size	0.544 x 0.217 x 0.217 mm^3
Theta range for data collection	1.828 to 27.469 °.
Index ranges	-32<=h<=32, -12<=k<=11, -24<=l<=23
Reflections collected	19466
Independent reflections	4801 [R(int) = 0.0428]
Completeness to theta = 25.242 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84321
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4801 / 0 / 281
Goodness-of-fit on F^2	1.131
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1328
R indices (all data)	R1 = 0.0639, wR2 = 0.1358
Extinction coefficient	n/a
Largest diff. peak and hole	0.745 and -0.243 $e.Å^{-3}$

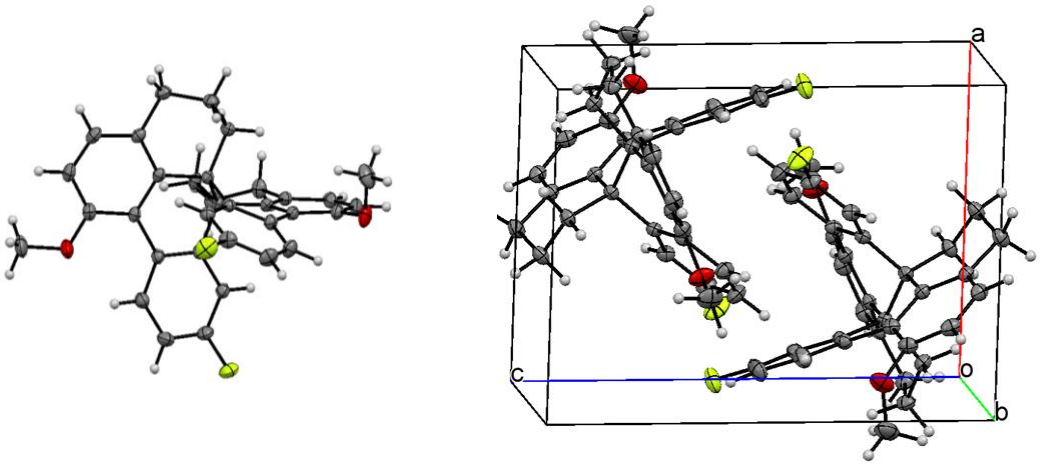


Fig. S41 X-ray structure and crystal packing of **2d** (CCDC 1893899).

Table 4. Crystal data and structure refinement for **2d**.

Identification code	mx7327
Empirical formula	C34 H28 F2 O2
Formula weight	506.56
Temperature	173.15 K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.993(2) Å	a= 77.48(3) °.
	b = 10.659(2) Å	b= 84.57(3) °.
	c = 12.618(3) Å	g = 70.54(3) °.
Volume	1236.7(5) $Å^3$	
Z	2	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	532	
Crystal size	0.52 x 0.37 x 0.3 mm^3	
Theta range for data collection	1.654 to 27.481 °.	
Index ranges	-12<=h<=12, -13<=k<=13, -16<=l<=16	
Reflections collected	16694	
Independent reflections	5601 [R(int) = 0.0278]	
Completeness to theta = 25.242 °	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5601 / 0 / 345	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1108	
R indices (all data)	R1 = 0.0440, wR2 = 0.1121	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.320 and -0.194 $e.Å^{-3}$	

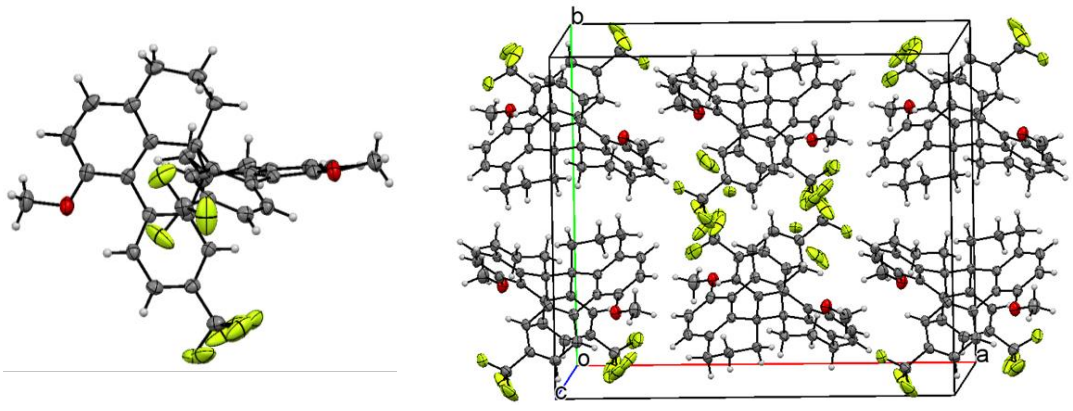


Fig. S42 X-ray structure and crystal packing of **2e** (CCDC 1893897).

Table 5. Crystal data and structure refinement for **2e**.

Identification code	mx7328	
Empirical formula	C36 H28 F6 O2	
Formula weight	606.58	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 19.2726(9) Å	a= 90 °.
	b = 16.7645(9) Å	b= 94.329(3) °.
	c = 8.6005(3) Å	g = 90 °.
Volume	2770.9(2) $Å^3$	
Z	4	
Density (calculated)	1.454 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	1256	
Crystal size	0.52 x 0.38 x 0.13 mm^3	
Theta range for data collection	1.612 to 25.999 °.	
Index ranges	-23<=h<=23, -20<=k<=20, -10<=l<=10	
Reflections collected	8403	
Independent reflections	2733 [R(int) = 0.0234]	
Completeness to theta = 25.242 °	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2733 / 72 / 229	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1107	
R indices (all data)	R1 = 0.0535, wR2 = 0.1158	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.290 and -0.215 e.$Å^{-3}$	

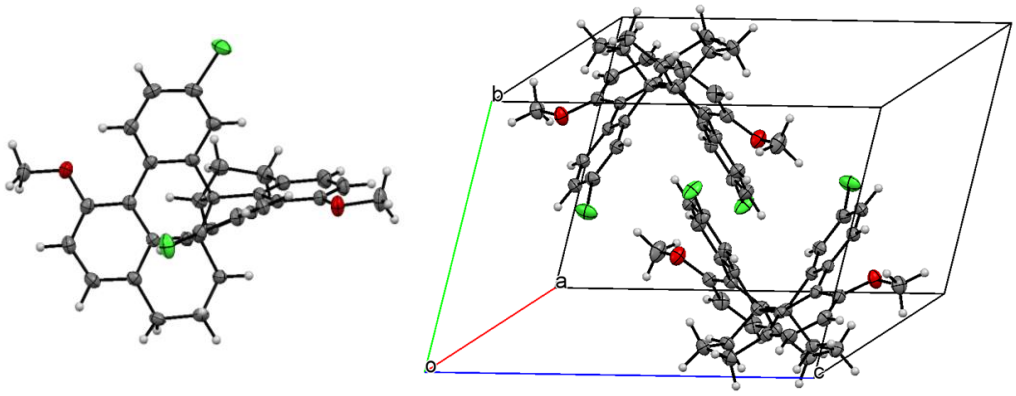


Fig. S43 X-ray structure and crystal packing of **2f** (CCDC 1893898).

Table 6. Crystal data and structure refinement for **2f**.

Identification code	mx7348	
Empirical formula	C34 H28 Cl2 O2	
Formula weight	539.46	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.615(2) Å	a= 73.061(8) °.
	b = 9.899(2) Å	b= 81.149(10) °.
	c = 14.184(3) Å	g = 79.776(9) °.
Volume	1263.3(5) $Å^3$	
Z	2	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	0.290 mm^{-1}	
F(000)	564	
Crystal size	0.443 x 0.18 x 0.17 mm^3	
Theta range for data collection	1.510 to 27.489 °.	
Index ranges	-12<=h<=12, -12<=k<=12, -18<=l<=18	
Reflections collected	16079	
Independent reflections	5769 [R(int) = 0.0312]	
Completeness to theta = 25.242 °	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82118	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5769 / 0 / 345
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1338
R indices (all data)	R1 = 0.0539, wR2 = 0.1357
Extinction coefficient	n/a
Largest diff. peak and hole	0.686 and -0.593 e.$Å^{-3}$

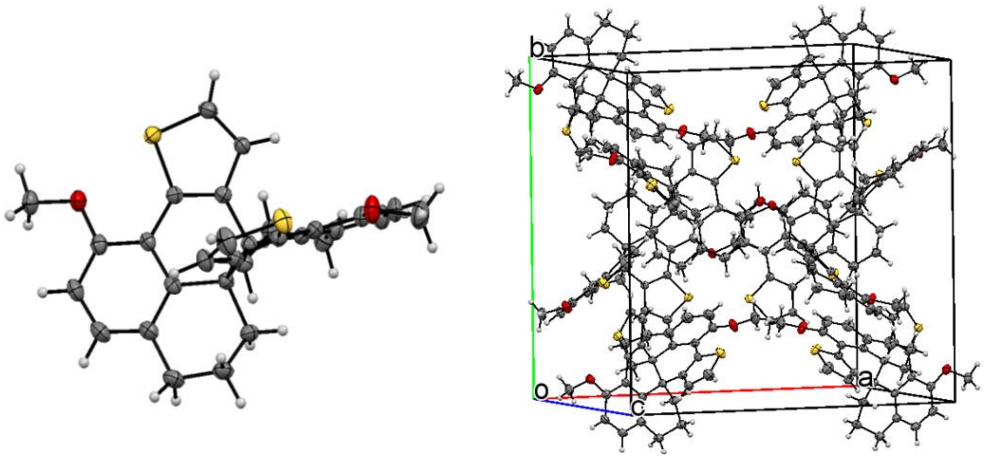


Fig. S44 X-ray structure and crystal packing of **2j** (CCDC 1893902).

Table 7. Crystal data and structure refinement for **2j**.

Identification code	a_sq	
Empirical formula	C33 H26 O2 S2	
Formula weight	518.66	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 19.288(4) Å	a= 90 °.
	b = 18.960(4) Å	b= 90 °.
	c = 14.565(3) Å	g = 90 °.
Volume	5326.3(19) $Å^3$	
Z	8	
Density (calculated)	1.294 Mg/m^3	

Absorption coefficient	0.229 mm^{-1}
F(000)	2176
Crystal size	0.469 x 0.423 x 0.411 mm^3
Theta range for data collection	2.055 to 27.473 °.
Index ranges	-25<=h<=25, -24<=k<=24, -18<=l<=18
Reflections collected	39721
Independent reflections	6078 [R(int) = 0.0520]
Completeness to theta = 25.242 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.86541
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6078 / 0 / 309
Goodness-of-fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1134
R indices (all data)	R1 = 0.0518, wR2 = 0.1137
Extinction coefficient	n/a
Largest diff. peak and hole	0.253 and -0.264 e.$Å^{-3}$