

Electronic Supplementary Information

Furanyl Bis(indolyl)methane as a Palladium Ion-Selective Chromogenic Agent

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Contents

1. General information.
2. Preparation of 5-chloromethyl-furan-2-yl bis(indolyl)methane (5)
3. Preparation and spectroscopic data of 5-aminomethyl furan-2-yl bis(indolyl)methanes (4) (Table 2).
 - 3-1. General procedure for synthesis of 4.
 - 3-2. Spectroscopic data of 4.
4. Optimization to synthesize 4a.
 - 4-1. Effect of solvent.
 - 4-2. Effect of acid catalyst.
 - 4-3. Effect of drying reagent.
5. Procedure of analysis of chromogenic properties (Figures 3, 4, and 5).
 - 5-1. Preparation of the stock solutions of BIM or metal ion.
 - 5-2. Effect of mixture ratio of BIM 4a and metal ion.
 - 5-3. Procedure for UV-Vis analysis (Figures 3 and 4).
 - 5-4. Time course study of UV-Vis absorption of the mixture of 4a and Pd²⁺ ion.
 - 5-5. Effect of concentration of Pd²⁺ salt solution.
6. Chromogenic property of 5-amine unit-substituted furan-2-yl BIM derivatives (4b-4e).

- 7. Preparation and spectroscopic data of bis(indolyl)methyl compounds (6) (Figure 4).**
- 8. UV-Vis absorbance property of 6a.**
- 9. UV-Vis absorbance property of 4b.**
- 10. References.**
- 11. ^1H NMR and ^{13}C NMR spectra of products.**

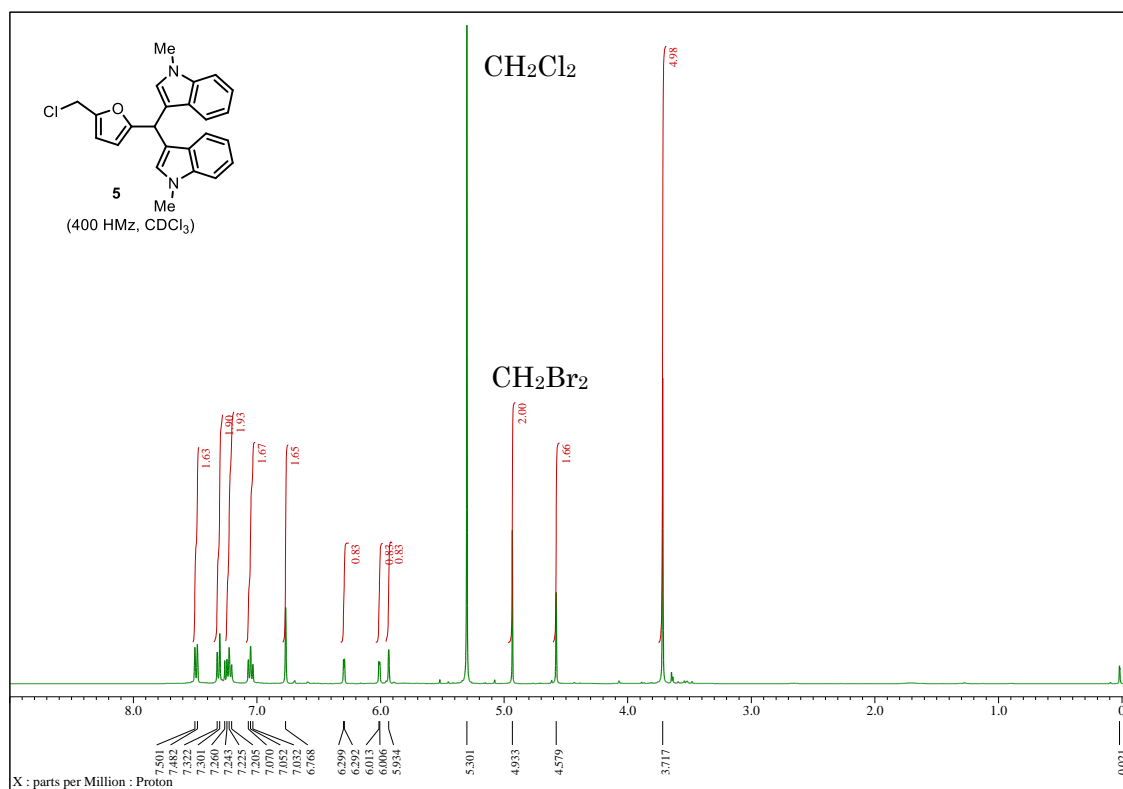
1. General information.

Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63—210 μm spherical, neutral). ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECS 300, ECS 400, ECZ 400 or ECA 500 spectrometer at room temperature in CDCl_3 as a solvent and internal standard (^1H NMR: $\delta = 7.26$ for CDCl_3 , ^{13}C NMR: $\delta = 77.0$ for CDCl_3) with tetramethylsilane as a further internal standard. IR spectra were recorded by a SHIMADZU IR Affinity-1S spectrophotometer as a thin film on NaCl. High resolution mass spectra were measured on JEOL JMS-3000 (MALDI). UV-Vis spectra were recorded by a SHIMADZU UV-1800 using quartz square cell (OPTIMMA INC. JAPAN; pathlength 10 mm, capacity 0.5 mL).

2. Preparation of 5-chloromethyl-furan-2-yl bis(indolyl)methane (5)

To the solution of 5-chloromethyl furfural (**1a**, 28.8 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added MS 4A (10 beads), *N*-methyl indole (**2b**, 50 μ L, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%) under Ar. The suspension was stirred at room temperature or under cooling conditions. After substrate **2a** was consumed by TLC monitoring, the mixture was warmed up to room temperature and extracted with CH₂Cl₂ (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The yield of 5-chloromethyl-furan-2-yl bis(indolyl)methane (**5**) was determined by ¹H NMR using dibromomethane (14.0 μ L, 0.20 mmol) as an internal standard (The purification of **5** with silica-gel chromatography was tried, but **5** was decomposed on the silica-gel.).

¹H NMR of the crude mixture of 5-chloromethyl-furan-2-yl bis(*N*-methyl-indolyl)methane (**5**) (Table 1, entry 4)



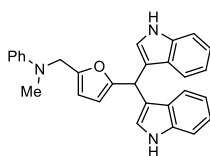
3. Preparation and spectroscopic data of 5-aminomethyl furan-2-yl bis(indolyl)methanes (**4**) (Table 2)

3-1. General procedure for synthesis of **4**

To the solution of 5-chloromethyl furfural (**1a**, 28.8 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added MS 4A (10 beads), indole derivative (**2**, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%). The suspension was stirred at -40 °C under Ar. After 18 h, amine derivative (**3**, 2.0 mmol, 10 equiv.) was added dropwise to the suspension and stirred at -40 °C for 12 h. The mixture was warmed up to room temperature and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to obtain bis(indolyl)methyl furanyl derivative **4**.

3-2. Spectroscopic data of **4**

5-(*N*-Methyl-*N*-phenyl-aminomethyl)-furan-2-yl bis(indolyl)methane (**4a**)



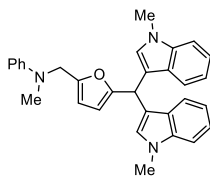
2a (46.9 mg, 0.40 mmol, 2 equiv.) and *N*-methylaniline (**3a**, 220 μ L, 2.0 mmol, 10 equiv.) were used as a substrate according to typical synthetic procedure (3-1) to afford **4a** (35% yield, 30.2 mg, 0.70 mmol) after silica-gel column chromatography (n-hexane / EtOAc = 5/1).

4a; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.91 (brs, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 7.7 Hz, 2H), 7.01 (t, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.76–6.72 (m, 3H), 6.03 (d, J = 2.9 Hz, 1H), 5.92 (d, J = 2.9 Hz, 1H), 5.87 (s, 1H), 4.42 (s, 2H), 2.93 (s, 3H). ¹³C NMR (125 MHz, CHCl₃): δ 156.2, 150.5, 149.3, 136.3, 129.0, 126.7, 123.1, 121.8, 119.6, 119.2, 117.0, 116.9, 113.3, 111.0, 107.9, 107.2, 50.0, 38.4, 34.0.

IR (NaCl) cm⁻¹: 3412, 1598, 1544, 1516, 1508, 1490, 1455, 1418, 1363, 1340, 1094, 1012, 909, 784, 744, 693.

HRMS (MALDI) m/z : 454.1892 (Calcd for C₂₉H₂₅N₃ONa [M+Na]⁺: 454.1890).

5-(*N*-Methyl-*N*-phenyl-aminomethyl)-furan-2-yl bis(*N*-methyl-indolyl)methane (**4b**)



2b (50 μ L, 0.4 mmol, 2 equiv.) and **3a** (220 μ L, 2.0 mmol, 10 equiv.) were used as a substrate according to typical synthetic procedure (3-1) to afford **4b** (80% yield, 73.4 mg, 0.16 mmol) after

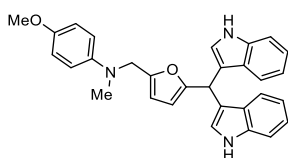
silica-gel column chromatography (n-hexane / EtOAc = 10/1).

4b; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.04 (m, 5H), 6.70 (s, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 5.91 (s, 1H), 5.88 (s, 1H), 5.85 (s, 1H), 3.84 (s, 2H), 3.68 (s, 6H), 2.83 (s, 3H). ¹³C NMR (125 MHz, CHCl₃): δ 155.9, 154.1, 147.8, 137.2, 129.5, 127.7, 127.3, 127.3, 121.3, 119.9, 118.6, 115.9, 112.5, 109.0, 107.0, 106.2, 33.9, 33.7, 32.6, 30.9.

IR (NaCl) cm⁻¹: 3410, 1927, 1614, 1521, 1472, 1423, 1370, 1328, 1264, 1181, 1153, 1062, 1012, 908, 784, 739.

HRMS (MALDI) *m/z*: 482.2212 (Calcd for C₃₁H₂₉N₃ONa [M+Na]⁺: 482.2203).

5-[*N*-Methyl-*N*-(4-methoxy)phenyl-aminomethyl]-furan-2-yl bis(*N*-methyl-indolyl)methane (**4c**)



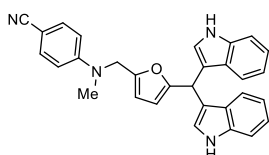
2a (46.9 mg, 0.40 mmol, 2 equiv.) and *N*-methyl-4-methoxyaniline (**3b**, 137 mg, 2.0 mmol, 10 equiv.), which was prepared according to the reference [1], were used as a substrate according to typical synthetic procedure (3-1) to afford **4c** (30% yield, 27.8 mg, 0.060 mmol) after silica-gel column chromatography (n-hexane / EtOAc = 3/1).

4c; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.87 (brs, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.82–6.77 (m, 4H), 6.66 (s, 2H), 6.02 (d, *J* = 2.9 Hz, 1H), 5.92 (d, *J* = 2.9 Hz, 1H), 5.86 (s, 1H), 4.32 (s, 2H), 3.78 (s, 3H), 2.83 (s, 3H). ¹³C NMR (125 MHz, CHCl₃): δ 155.9, 154.2, 147.8, 137.2, 129.5, 127.7, 127.3, 121.3, 119.9, 118.6, 115.9, 112.6, 112.5, 109.0, 107.0, 106.2, 33.9, 33.7, 32.6, 30.9.

IR (NaCl) cm⁻¹: 3413, 2833, 1512, 1455, 1421, 1339, 1244, 1181, 1095, 1036, 1014, 909, 819, 784, 742.

HRMS (MALDI) *m/z*: 484.1994 (Calcd for C₃₀H₂₇N₃O₂Na [M+Na]⁺: 484.1995).

5-[*N*-Methyl-*N*-(4-cyano)phenyl-aminomethyl]-furan-2-yl bis(*N*-methyl-indolyl)methane (**4d**)



2a (46.9 mg, 0.40 mmol, 2 equiv.) and *N*-methyl-4-cyanoaniline (**3c**, 132 mg, 2.0 mmol, 10 equiv.), which was prepared according to the reference [1], were used as a substrate according to typical synthetic procedure (3-1) to afford **4d** (17% yield, 16.6 mg, 0.034 mmol) after silica-gel column

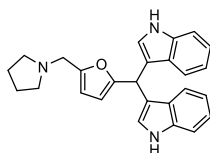
chromatography (n-hexane / EtOAc = 3/1).

4d; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.94 (brs, 2H), 7.44–7.35 (m, 6H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 1.7 Hz, 2H), 6.68 (d, *J* = 9.2 Hz, 2H), 6.07 (d, *J* = 3.8 Hz, 1H), 5.97 (d, *J* = 3.8 Hz, 1H), 5.86 (s, 1H), 4.43 (s, 2H), 2.98 (s, 3H). ¹³C NMR (125 MHz, CHCl₃): δ 156.9, 151.7, 149.1, 136.5, 133.3, 126.7, 122.9, 122.0, 120.6, 119.6, 119.3, 116.9, 112.2, 111.1, 108.3, 107.3, 98.0, 49.2, 38.3, 34.2.

IR (NaCl) cm⁻¹: 3408, 2212, 1680, 1607, 1544, 1455, 1423, 1387, 1340, 1177, 1098, 909, 819, 784, 744.

HRMS (MALDI) *m/z*: 455.1867 (Calcd for C₃₀H₂₃N₄O [M-H]⁺: 455.1866).

5-(*N*-Pyrrolidinylmethyl)-furan-2-yl bis(*N*-methyl-indolyl)methane (**4e**)



2a (46.9 mg, 0.40 mmol, 2 equiv.) and pyrrolidine (**3d**, 160 μL, 10 equiv.) were used as a substrate according to typical synthetic procedure (3-1) to afford **4e** (17% yield, 13.5 mg, 0.034 mmol) after silica-gel column chromatography (CHCl₃ / MeOH = 10/1).

4e; brown oil; ¹H NMR (500 MHz, CDCl₃): δ 8.30 (brs, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.59 (s, 2H), 6.12 (d, *J* = 2.9 Hz, 1H), 5.97 (d, *J* = 2.9 Hz, 1H), 5.84 (s, 1H), 3.64 (s, 2H), 2.57 (s, 4H), 1.71 (s, 4H). ¹³C NMR (125 MHz, CHCl₃): δ 156.9, 150.0, 136.4, 126.7, 123.4, 121.5, 119.4, 118.9, 116.7, 111.1, 109.4, 107.0, 53.2, 51.6, 34.0, 23.4.

IR (NaCl) cm⁻¹: 3412, 3057, 2963, 2925, 2895, 2810, 1618, 1455, 1419, 1340, 1244, 1215, 1125, 1095, 908, 785, 739.

HRMS (MALDI) *m/z*: 394.1918 (Calcd for C₂₆H₂₄N₃O [M-H]⁺: 394.1914).

4. Optimization to synthesize **4a**

4-1. Effect of solvent

To the solution of 5-chloromethyl furfural (**1a**, 28.8 mg, 0.20 mmol) in solvent (1 mL) were added MS 4A (10 beads), indole (**2a**, 46.9 mg, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%, 0.01 mmol) under Ar. The suspension was stirred at room temperature or under cooling condition. After substrate **2a** disappeared by TLC monitoring, *N*-methyl aniline (**3a**, 220 μL, 2.0 mmol, 10 equiv.) was added dropwise to the suspension and stirred at the same temperature for 12 h. The mixture was warmed up to room temperature and extracted with EtOAc (10 mL x 3). The organic layers were washed with

brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The yield of **4a** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane (21.0 μL, 0.20 mmol).

Table S1. Screening of solvent

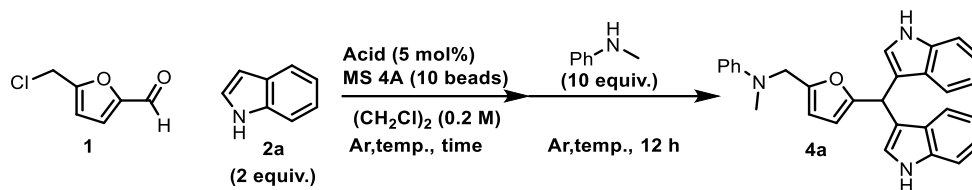
entry	solvent	condition	yield (%)
1	CH ₂ Cl ₂	-40 °C, 4 h	35
2	CH ₂ Cl ₂	-40 °C, 10 h	40
3	CH ₂ Cl ₂	-60 °C (4 h) to -40 °C (6 h)	41
4 ^{a)}	CH ₂ Cl ₂	-60 °C, 10 h	32
5	CHCl ₃	-60 °C, 10 h	19
6	(CH ₂ Cl) ₂	-40 °C, 6 h	48
7	PhCl	-40 °C, 6 h	26
8	(CH ₂ Cl) ₂	-40 °C, 6 h	37
9	MeCN	rt, 6 h	26
10	THF	rt, 6 h	26

^a0.1 M

4-2. Effect of acid catalyst

To the solution of **1a** (28.8 mg, 0.20 mmol) in (CH₂Cl)₂ (1 mL) were added MS 4A (10 beads), **2a** (46.9 mg, 0.4 mmol, 2 equiv.) and acid catalyst (5 mol%, 0.01 mmol) under Ar. The suspension was stirred at room temperature or under cooling condition. After substrate **2a** disappeared by TLC monitoring, *N*-methyl aniline (**3a**, 220 μL, 2.0 mmol, 10 equiv.) was added dropwise to the suspension and stirred at the same temperature for 12 h. The mixture was warmed up to room temperature and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The yield of **4a** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane (21.0 μL, 0.20 mmol).

Table S2. Screening of acid catalyst



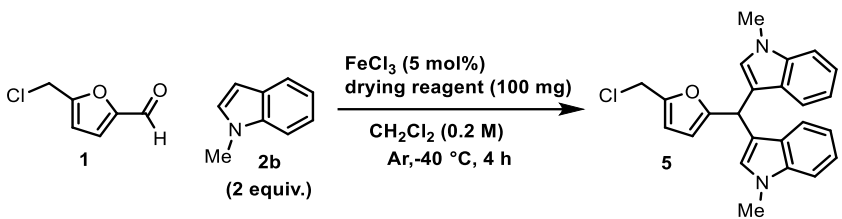
entry	acid	condition	yield (%)
1	FeCl ₃	-40 °C, 6 h	48
2 ^{a)}	TFA	-40 °C, 24 h	30
3	OP(OPh) ₂ OH	-40 °C, 12 h	51
4	InCl ₃	-40 °C, 12 h	18
5	IrCl ₃	-40 °C, 12 h	25
6	Zn(OTf) ₂	-40 °C, 4 h	23
7	Sn(OTf) ₂	-40 °C, 6 h	48
8	Y(OTf) ₂	-40 °C, 12 h	16
9	Yb(OTf) ₂	-40 °C, 12 h	55
10	CeCl ₃ ·7H ₂ O	-40 °C, 4 h	53
11	Sc(OTf) ₃	-40 °C, 12 h	37
12	MoOCl ₄	-40 °C, 18 h	51
13 ^{b)}	montmorillonite K10	-40 °C, 18 h	55
14	AMBERLITE IR 120B Na	-40 °C, 18 h	48

^a10 mol% was used. ^b10 mg was used.

4-3. Effect of drying reagent

To the solution of 5-chloromethyl furfural (**1a**, 28.8 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added drying reagent (100 mg), *N*-methyl indole (**2b**, 50 μL, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%) under Ar. The suspension was stirred at -40 °C. After 4 h, the mixture was warmed up to room temperature and extracted with CH₂Cl₂ (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The yield of 5-chloromethyl-furan-2-yl bis(indolyl)methane (**5**) was determined by ¹H NMR using dibromomethane (14.0 μL, 0.20 mmol) as an internal standard.

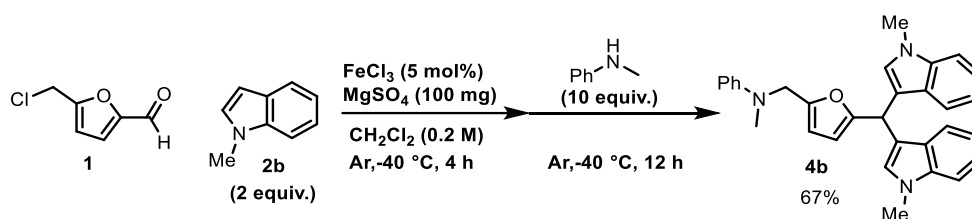
Table S3. Screening of drying reagent



entry	drying reagent	yield (%)	
		1	5
1 ^{a)}	MS 4A	1	83
2	Na ₂ SO ₄	7	80
3	MgSO ₄	0	86
4	activated alumina (neutral)	6	33

^a10 beads were used.

One-pot synthesis of 4b using MgSO₄ as drying reagent; To the solution of 5-chloromethyl furfural (**1a**, 28.8 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added MgSO₄ (100 mg), *N*-methyl indole (**2b**, 50 μL, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%). The suspension was stirred at -40 °C under Ar. After 18 h, *N*-methyl amine (**3a**, 2.0 mmol, 10 equiv.) was added dropwise to the suspension and stirred at -40 °C for 12 h. The mixture was warmed up to room temperature and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The yield of **4b** (67% yield) was determined by ¹H NMR using 1,1,2,2-tetrachloroethane (21 μL, 0.20 mmol) as an internal standard. Yield of **4b** was lower in comparison with the reaction using MS 4A. shown Table 2, entry 1.



5. Procedure of analysis of chromogenic properties (Figures 3, 4, and 5)

5-1. Preparation of the stock solutions of BIM or metal ion

The concentrations of stock solutions were referred to the reference [2].

Stock solutions (1.0 x10⁻⁴ M) of BIM (**4a–4e**, and **6a–6e**); BIM (0.010 mmol) was dissolved in MeCN/distilled water (7/3; 1 mL). This solution (100 μL) was further dissolved in MeCN/distilled water (7/3; 10 mL). **4a** (4.3 mg), **4b** (4.6 mg), **4c** (4.6 mg), **4d** (4.6 mg), **4e** (4.0 mg), **6a** (3.1 mg), **6b**

(3.4 mg), **6c** (3.2 mg), **6d** (3.2 mg), **6e** (2.5 mg) were used, respectively.

Stock solutions (4.0×10^{-4} M) **of metal ion**; Metal salts (0.040 mmol) were dissolved in MeCN/distilled water (7/3) (1 mL). The solution (100 μ L) was dissolved in MeCN/distilled water (7/3) (10 mL). PdCl₂ (7.1 mg), CuCl₂ (5.4 mg), FeCl₂ (5.1 mg), FeCl₃ (6.5mg), CrCl₂ (4.9 mg), CrCl₃ (6.3mg), NiCl₂ (5.2 mg), ZnCl₂ (5.5 mg), InCl₃ (8.8 mg), PtCl₂ (10.6mg), CeCl₃ (9.9 mg) were used, respectively.

5-2. Effect of mixture ratio of BIM 4a and metal ion

Stock solutions (1.0×10^{-4} M) **of Pd²⁺ ion**; PdCl₂ (1.8 mg, 0.010 mmol) was dissolved in MeCN/distilled water (7/3) (1 mL). The solution (100 μ L) was dissolved in MeCN/distilled water (7/3) (9 mL).

Stock solutions (4.0×10^{-3} M) **of Pd²⁺ ion**; PdCl₂ (7.1 mg, 0.040 mmol) was dissolved in MeCN/distilled water (7/3) (10 mL).

To the stock solution of BIM (0.25 mL) in a sample tube, each stock solution of Pd²⁺ ion (0.25 mL) was added. After 1 h, the color of the mixture was checked.

The color change in the mixture (**4a**/Pd²⁺ = 1/1) was subtle, and the color change in the mixture (**4a**/Pd²⁺ = 1/40) was comparable to the mixture (**4a**/Pd²⁺ = 1/4). Therefore, a mixing ratio of **4a**/Pd²⁺ = 1/4 was applied to further study.

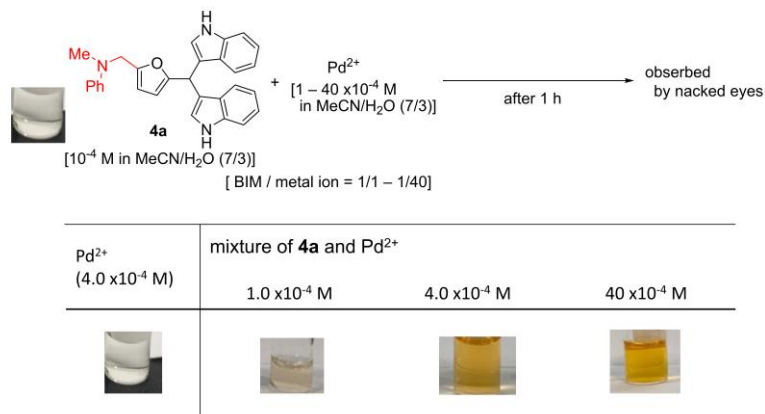


Figure S1. Screening of the mixing ratio of 4a and Pd²⁺

5-3. Procedure for UV-Vis analysis (Figures 3 and 4)

To the stock solution of BIM (0.25 mL) in a sample tube, the stock solution of metal ion (0.25 mL) was added, and the color of the mixture was checked. After 1 h, UV-Vis absorption of the mixture poured to the quartz square cell from the sample tube, was measured

5-4. Time course study of UV-Vis absorption of the mixture of 4a and Pd²⁺ ion

Background data of 4a (black dash line) or Pd²⁺ ion (gray dash line); The stock solution of **4a**

(0.5 mL) was poured to the quartz square cells, and UV-Vis absorption was measured from 190 to 700 nm. Independently, the stock solution of Pd²⁺ ion was poured to the quartz square cells, and UV-Vis absorption was measured.

Mixing of 4a and Pd²⁺ ion; To the stock solution of **4a** (0.25 mL) in the quartz square cells, the stock solution of Pd²⁺ ion (0.25 mL) was added. UV-Vis absorption of the mixture was measured [2 min. (black), 5 min. (gray), 10 min. (purple), 15 min. (blue), 30 min. (green), 45 min. (orange), 60 min. (red) after mixed].

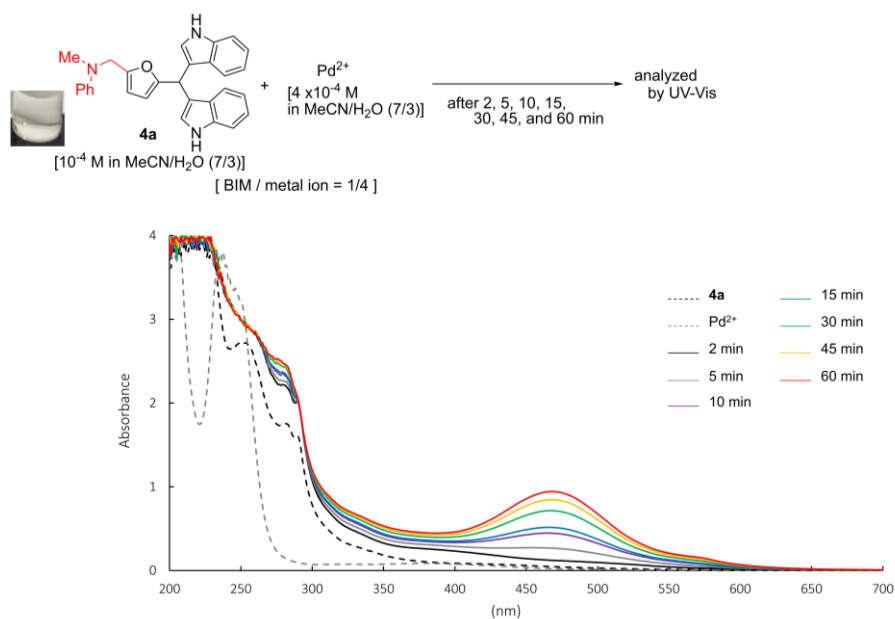


Figure S2. Time course study of UV-Vis absorption of the mixture of 4a and Pd²⁺

5-5. Effect of concentration of Pd²⁺ salt solution

Stock solutions (4.0 x 10⁻⁵ M) of Pd²⁺ ion; The stock solution (4.0 x 10⁻⁴ M, 1 mL) was dissolved in MeCN/distilled water (7/3) (9 mL).

Mixing of 4a and Pd²⁺ ion; To the stock solution of 4a (0.25 mL) in the quartz square cells, the stock solution of Pd²⁺ ion (0.25 mL) was added. After 1 h, UV-Vis absorption of the mixture was measured. [The concentration of PdCl₂ solution (MeCN/distilled water (7/3)) ; 4 x 10⁻⁴ M (red), 1 x 10⁻⁴ M (blue), 4 x 10⁻⁵ M (gray)]

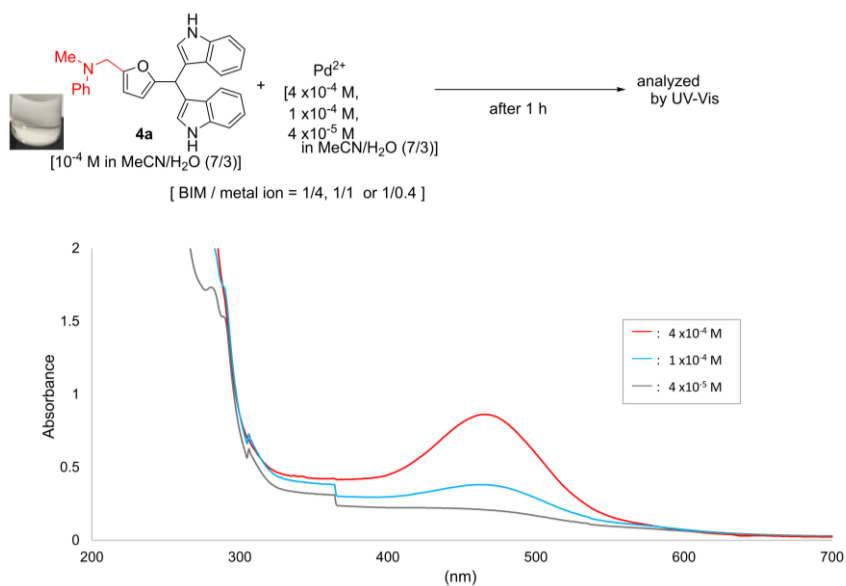


Figure S3. Effect of concentration of PdCl₂ solution

6. Chromogenic property of 5-amine unit-substituted furan-2-yl BIM derivatives (4a-e)

To the stock solution of **4** (0.25 mL) in a sample tube, the stock solution of Pd²⁺ ion (0.25 mL) was added. After 1 h, the color of the mixture was checked.

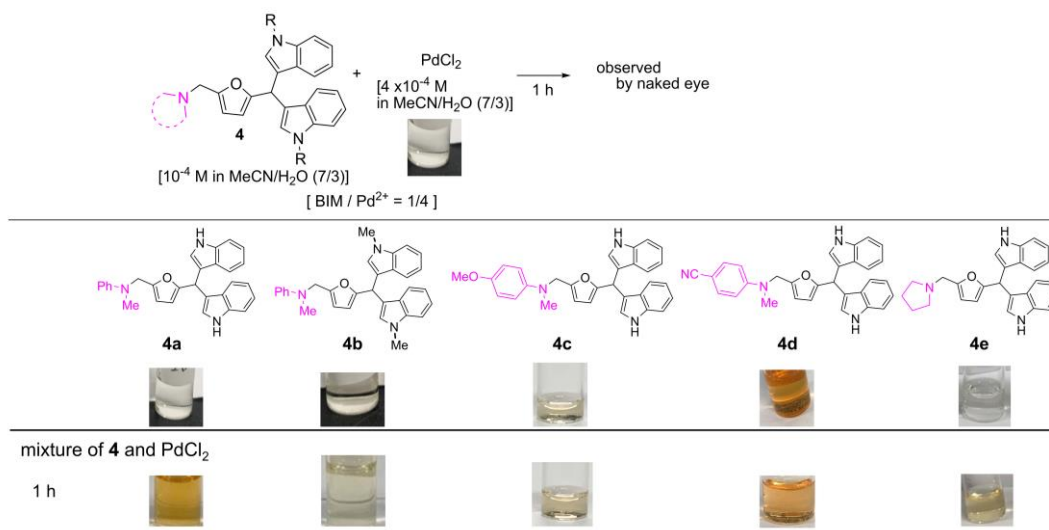
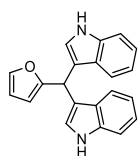


Figure S4. Chromogenic property of the mixture of **4** and Pd²⁺

7. Preparation and spectroscopic data of bis(indolyl)methyl compounds (6)

Furan-2-yl bis(indolyl)methane (**6a**)

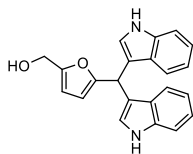


Furan-2-yl bis(indolyl)methane (**6a**) was prepared according to the reference [3]. The suspension of furfural (50 mg, 0.50 mmol) and **2a** (117 mg, 1.0 mmol, 2.0 equiv.) in CH₂Cl₂ (2 mL) was added amberlyst-15 (50 mg), and stirred at room temperature under Ar atmosphere. After 6 h, the suspension was filtrated and the filtrate was concentrated. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to obtain **6a** (72% yield, 119 mg, 0.38 mmol).

6a; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.97 (s, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.37–7.36 (m, 3H), 7.19–7.16 (m, 2H), 7.06–7.03 (m, 2H), 6.88 (d, *J* = 1.7 Hz, 2H), 6.30 (dd, *J* = 2.7, 1.5 Hz, 1H), 6.06 (d, *J* = 2.7 Hz, 1H), 5.95 (s, 1H). ¹³C NMR (125 MHz, CHCl₃): δ 157.0, 141.2, 136.4, 126.7, 123.0, 121.9, 119.6, 119.3, 117.0, 111.1, 110.1, 106.6, 34.0.

¹H and ¹³C NMR spectra of **6a** was identical to that of the reference [4].

5-Hydroxymethyl-furan-2-yl bis(indolyl)methane (**6b**)

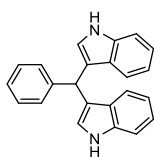


To the solution of 5-hydroxymethyl furfural (25.2 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added **2a** (46.9 mg, 0.4 mmol, 2 equiv.) and FeCl₃ (1.6 mg, 5 mol%). The solution was stirred at 0 °C under Ar. After 2 h, the mixture was warmed up to room temperature and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. To the residue were added MeOH (1 mL) and NaBH₄ (1.9 mg, 0.05 mmol) to reduce the unreacted 5-hydroxymethyl furfural since 5-hydroxymethyl furfural and **6b** could not be separated by silica-gel chromatography, and the solution was stirred at 0 °C under Ar atmosphere. After 30 min, the mixture was quenched with water, and extracted with EtOAc (10 mL x3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 2/1) to obtain **6b** (44% yield, 30.2 mg, 0.057 mmol).

6b; wine-red oil; ¹H NMR (500 MHz, CDCl₃): δ 7.83 (brs, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.67 (s, 2H), 6.14 (s, 1H), 5.97 (s, 1H), 5.87 (s, 1H), 4.40 (s, 2H). ¹³C NMR (125 MHz, CHCl₃): δ 157.2, 152.5, 136.4, 126.6, 123.3, 121.8, 119.5, 119.2, 116.6, 111.2, 108.6, 107.3, 57.4, 34.1

¹H and ¹³C NMR spectrum of **6b** was identical to that of the reference [5].

Phenyl bis(indolyl)methane (**6c**)

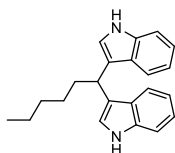


Phenyl bis(indolyl)methane (**6c**) was prepared according to the reference [3]. The suspension of furfural (50 mg, 0.50 mmol) and **2a** (117 mg, 1.0 mmol, 2.0 equiv.) in CH₂Cl₂ (2 mL) was added amberlyst-15 (50 mg), and stirred at room temperature under Ar atmosphere. After 6 h, the suspension was filtrated and the filtrate was concentrated. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to obtain **6c** (64% yield, 102 mg, 0.32 mmol).

6c; brown oil; ¹H NMR (500 MHz, CDCl₃): δ 7.89 (brs, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37–7.35 (m, 4H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.65 (s, 2H), 5.89 (s, 1H). ¹³C NMR (125 MHz, CHCl₃): δ 143.9, 136.6, 128.7, 128.2, 127.0, 126.1, 123.6, 121.9, 119.9, 119.7, 119.2, 111.0, 40.1.

^1H and ^{13}C NMR spectrum of **6c** was identical to that of the reference [4].

1,1-Bis(indolyl)hexane (**6d**)

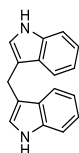


To the solution of hexanal (20.0 mg, 0.20 mmol) in $(\text{CH}_2\text{Cl})_2$ (1 mL) were added indole (46.9 mg, 0.4 mmol, 2 equiv.) and FeCl_3 (1.6 mg, 5 mol%). The solution was stirred at rt under Ar. After 6 h, the mixture was extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to obtain **6d** (73% yield, 46.2 mg, 0.146 mmol).

6d; wine-red oil; ^1H NMR (500 MHz, CDCl_3): δ 7.69–7.67 (m, 4H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.23–7.20 (m, 2H), 7.14–7.10 (m, 2H), 6.91 (d, $J = 2.3$ Hz, 2H), 4.53 (t, $J = 7.3$ Hz, 1H), 2.27 (q, $J = 7.3$ Hz, 2H), 1.52–1.30 (m, 6H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, CHCl_3): δ 136.4, 127.1, 121.6, 121.4, 120.4, 119.6, 118.9, 111.0, 35.8, 33.9, 32.0, 28.0, 22.6, 14.1.

^1H and ^{13}C NMR spectrum of **6d** was identical to that of the reference [6].

Diindolylmethane (**6e**)



Diindolylmethane (**6e**) was prepared according to the reference [7]. To the solution of indole-2-nal (29.0 mg, 0.20 mmol) in $(\text{CH}_2\text{Cl})_2$ (2 mL) were added indole (70.4 mg, 0.60 mmol, 3 equiv.), AcOH (29 μL , 2.5 mmol, 5 equiv.) and NaBH_4 (11.5 mg, 0.30 mmol, 1.5 equiv.). The mixture was heated to reflux under Ar. After 6 h, the mixture was cooled to room temperature, quenched with saturated sodium bicarbonate (4 mL), and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (10 mL), dried over with anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to obtain **6e** (60% yield, 29.5 mg, 0.12 mmol).

6e; brown oil; ^1H NMR (500 MHz, CDCl_3): δ 7.90 (brs, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 8.0$ Hz, 2H), 6.95 (s, 2H), 4.25 (s, 2H). ^{13}C NMR (125 MHz, CHCl_3): δ 136.5, 127.6, 122.2, 121.9, 119.2, 119.2, 115.7, 111.0, 21.2.

^1H and ^{13}C NMR spectrum of **6e** was identical to that of the reference [7].

8. UV-Vis absorbance property of 6a

To the stock solution of **6a** (0.25 mL) in a sample tube, the stock solution of the metal ion (0.25 mL) was added. After 1 h, UV-Vis absorption of the mixture poured to the quartz square cell from the sample tube was measured.

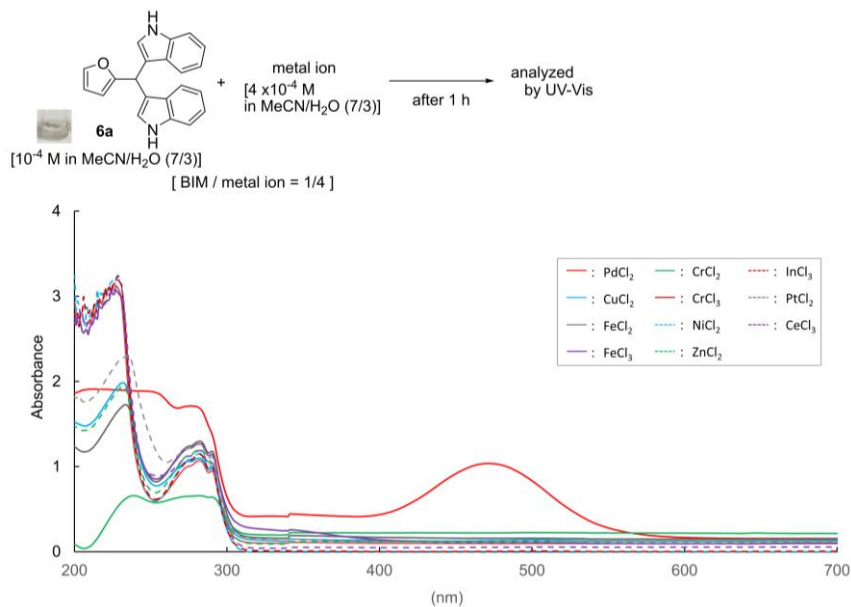


Figure S5. Chromogenic property of the mixture of **6a** and metal ions

9. UV-Vis absorbance property of 4b

To the stock solution of **4b** (0.25 mL) in a sample tube, the stock solution of the metal ion (0.25 mL) was added. After 1 h, UV-Vis absorption of the mixture poured to the quartz square cell from the sample tube was measured.

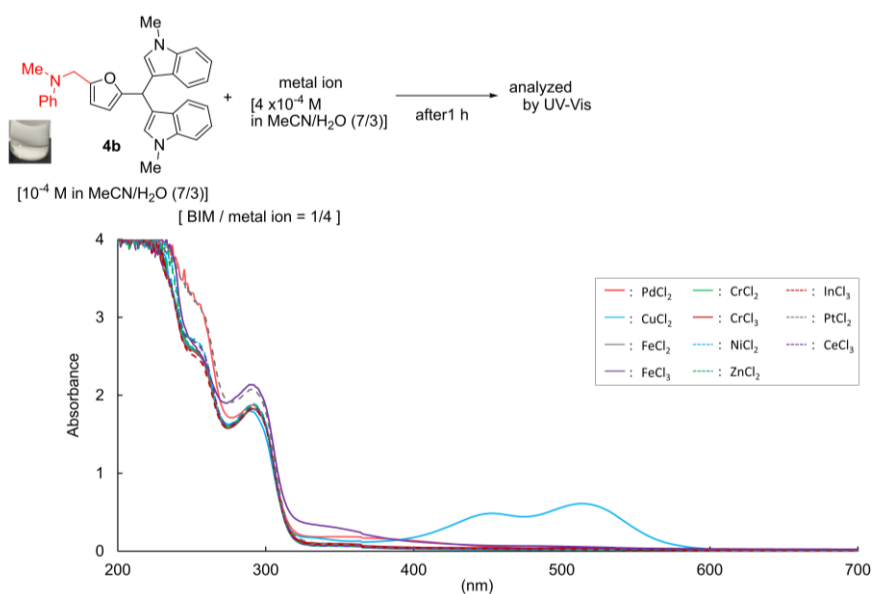


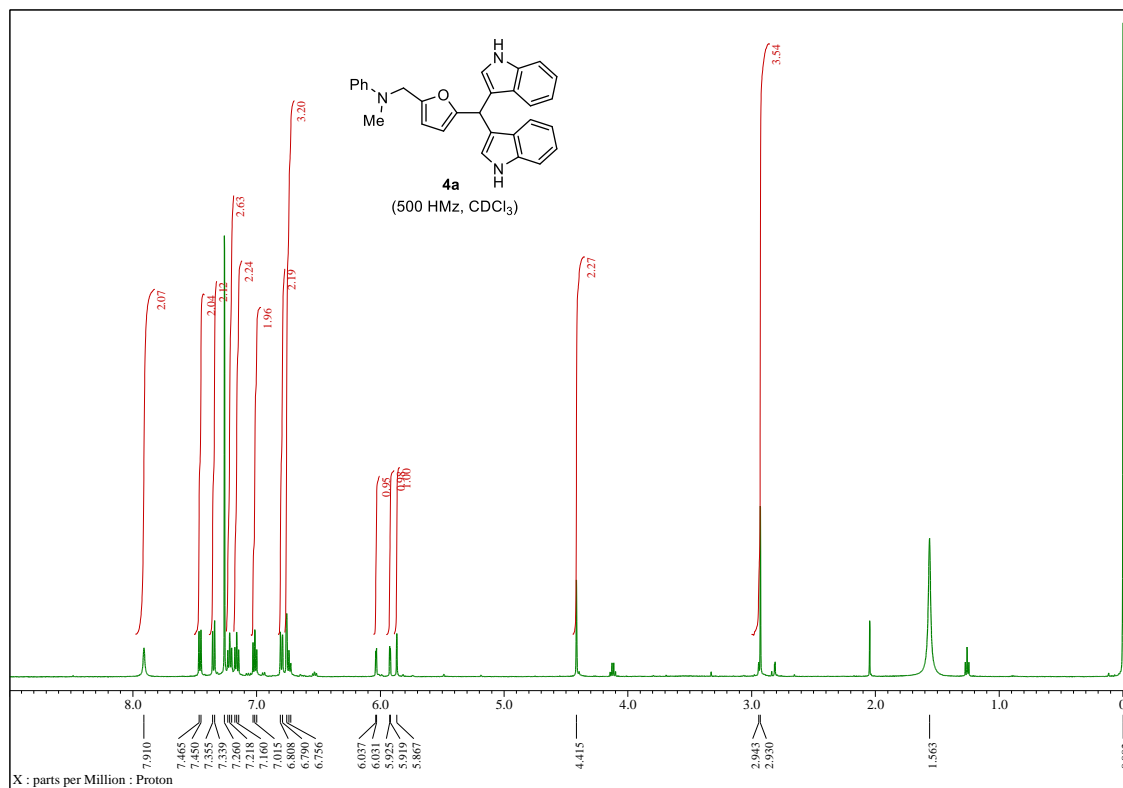
Figure S6. Chromogenic property of the mixture of **4b** and metal ions

10. References

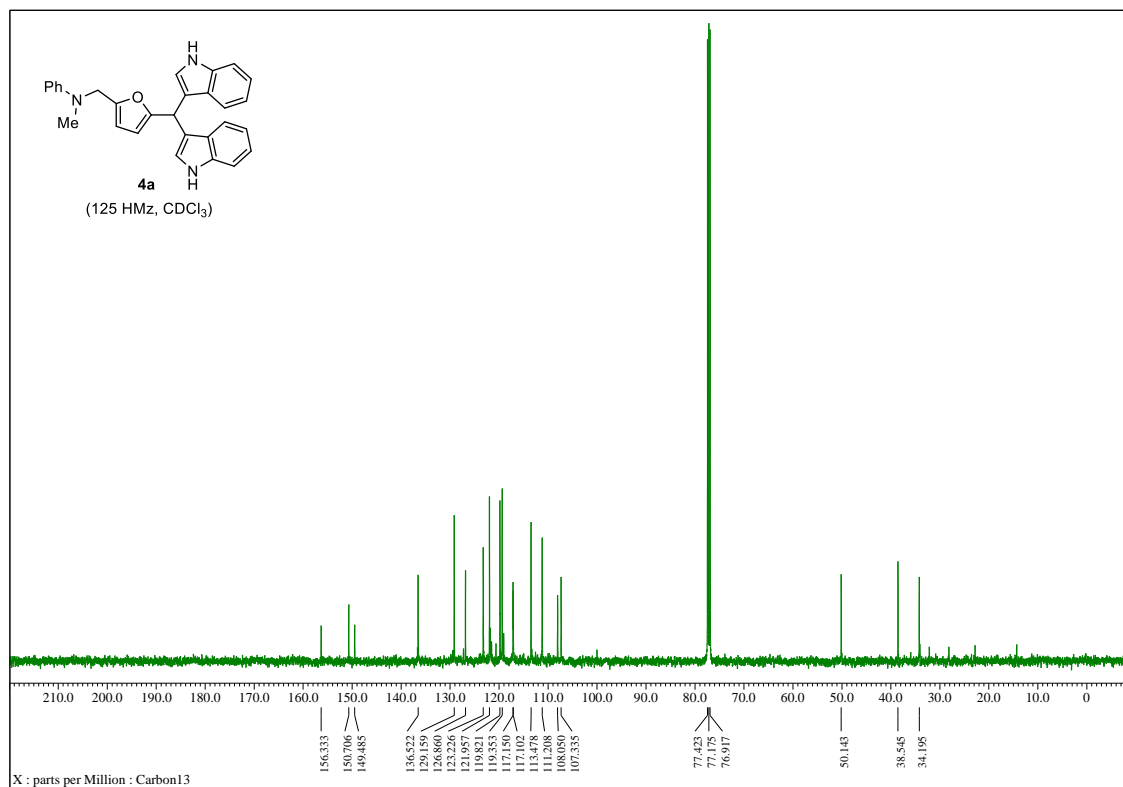
- [1] Y. Zhang, H. Zhang, K. Gao, *Org. Lett.* 2021, **23**, 8282-8286.
- [2] R. M. F. Batista, S. P. G. Costa, R. M. P. Silva, N. E. M. Lima and M. M. M. Raposo, *Dyes Pigm.*, 2014, **102**, 293-300.
- [3] C. Ramesh, J. Banerjee, R. Pal, B. Das, *Adv. Synth. Catal.* 2003, **345**, 557-559.
- [4] Z. M. Salem, J. Saway, J. J. Badillo, *Org. Lett.* 2019, **21**, 8528-8532.
- [5] H. B. Phan, C. M. Luong, L. P. Nguyen, B. T. Bui, H. T. Nguyen, B. V. Mai, T. V.-T. Mai, L. K. Huynh and P. H. Tran, *ACS Sustainable Chem. Eng.*, 2022, **10**, 8673-8684.
- [6] S. Rinkam, W. Senapak, S. Watchasit, R. Saeeng, U. Sirion, *Synlett*, 2022, **33**, 1383-1390.
- [7] H. Zhou, Z. Huang, H. Huang, C. Song, J. Chang, *Tetrahedron*, 2021, **94**, 132338.

11. ¹H NMR and ¹³C NMR spectra of products.

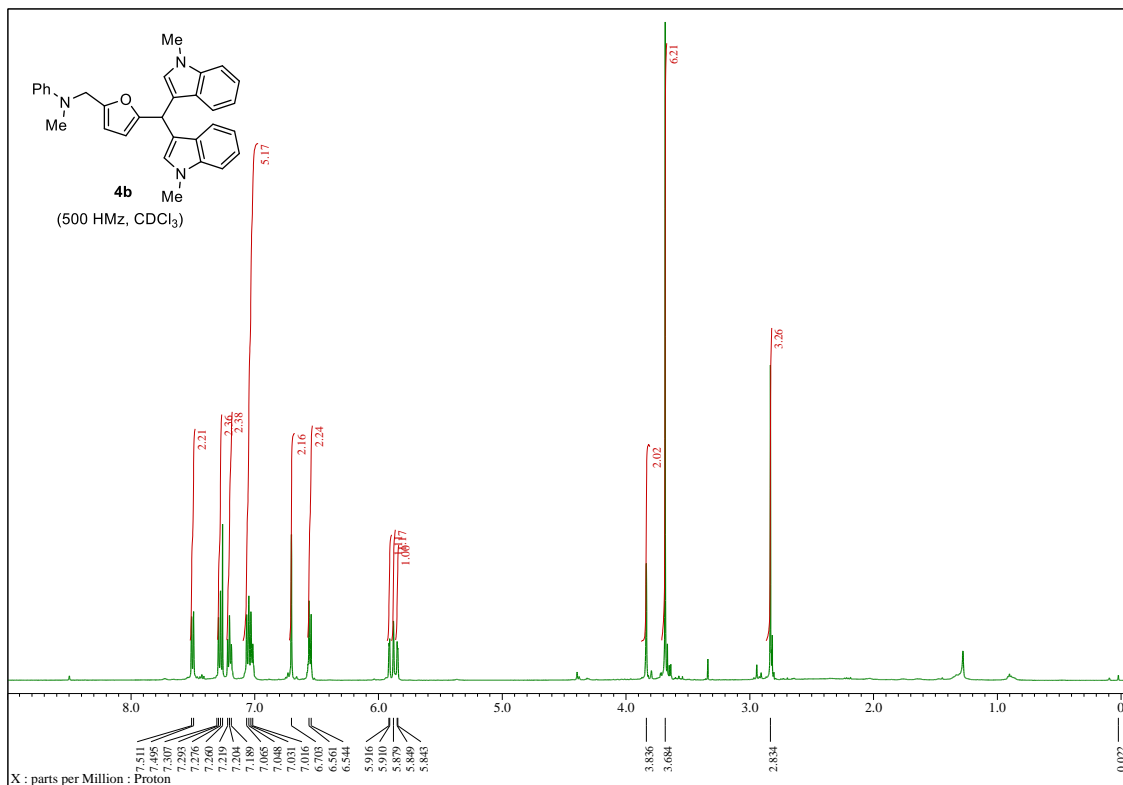
¹H NMR of 5-(*N*-methyl-*N*-phenyl-aminomethyl)-furan-2-yl bis(indolyl)methane (4a)



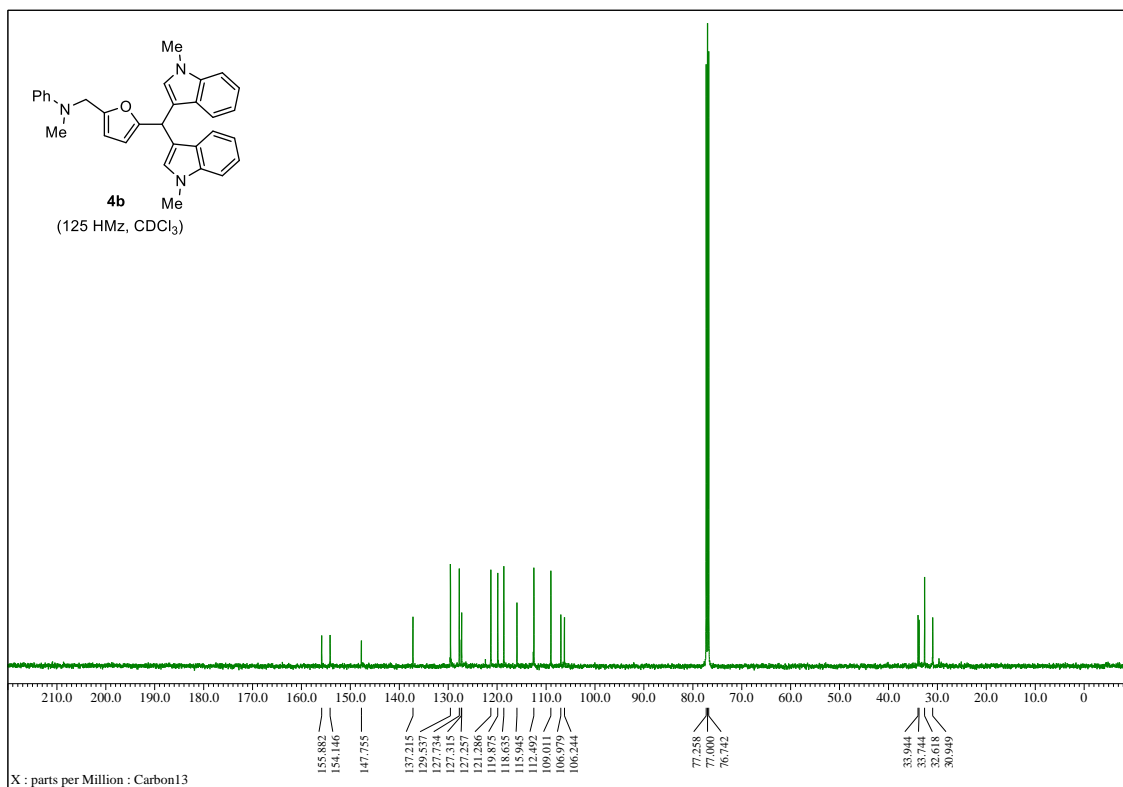
¹³C NMR of 5-(*N*-methyl-*N*-phenyl-aminomethyl)-furan-2-yl bis(indolyl)methane (4a)



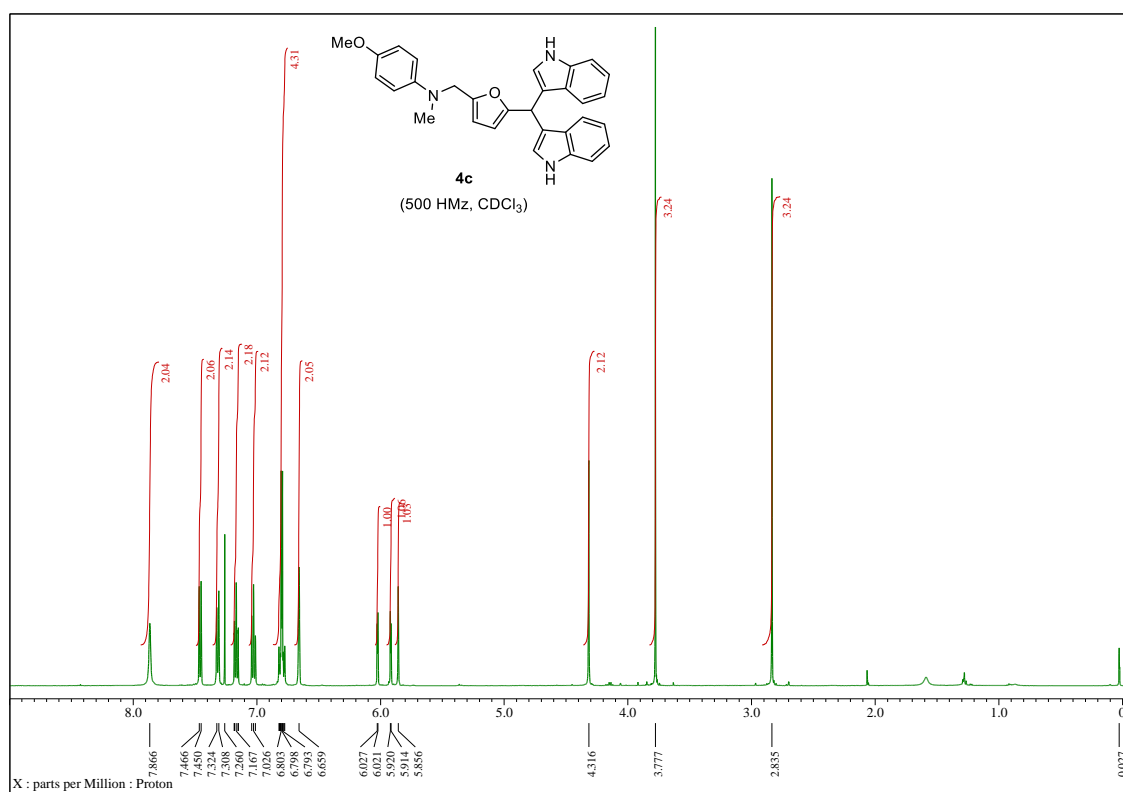
¹H NMR of 5-(*N*-methyl-*N*-phenyl-aminomethyl)-furan-2-yl bis(*N*-methyl-indolyl)methane (4b)



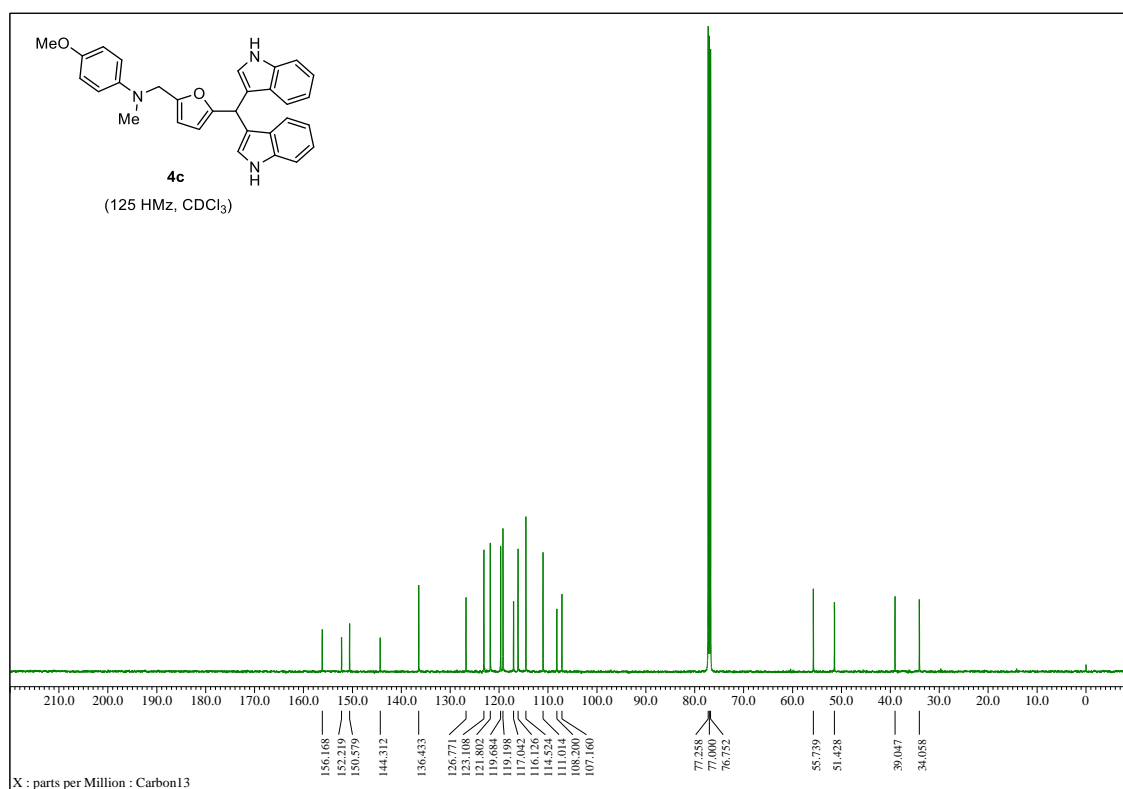
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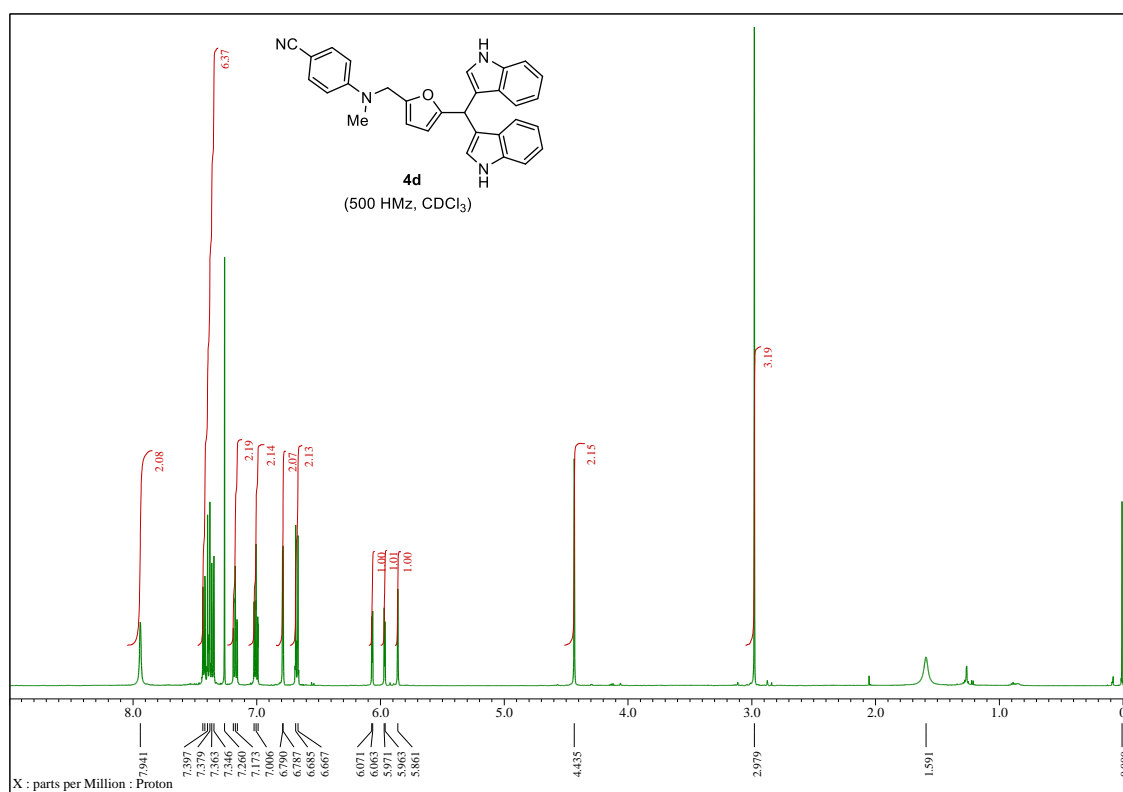
¹H NMR of 5-[N-methyl-N-(4-methoxy)phenyl-aminomethyl]-furan-2-yl bis(N-methyl-indolyl)methane (4c)



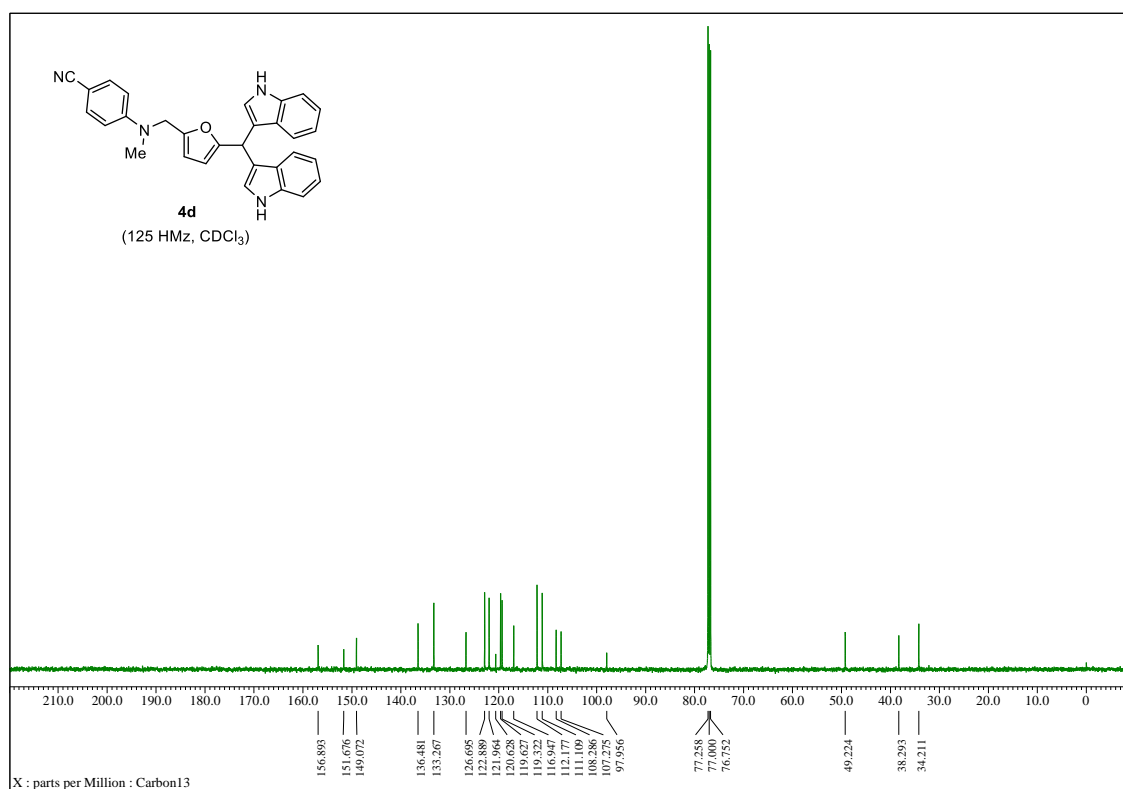
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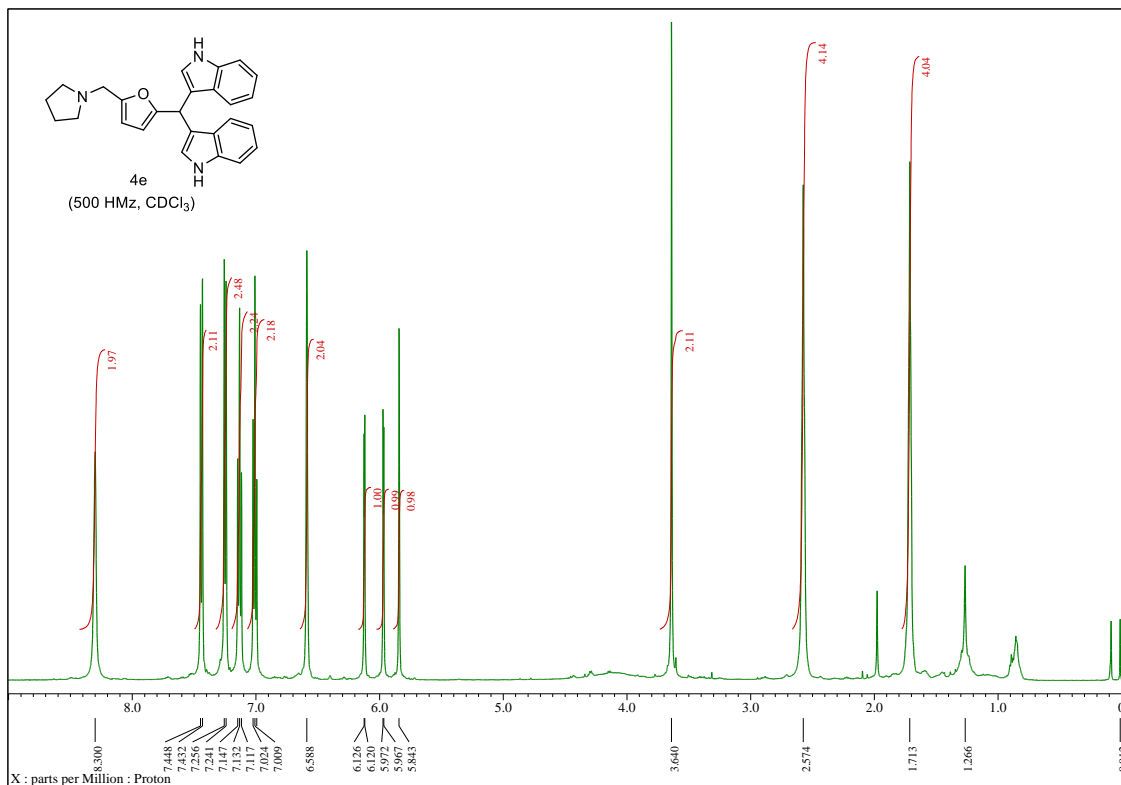
¹H NMR of 5-[N-methyl-N-(4-cyano)phenyl-aminomethyl]-furan-2-yl bis(N-methyl-indolyl)methane (4d)



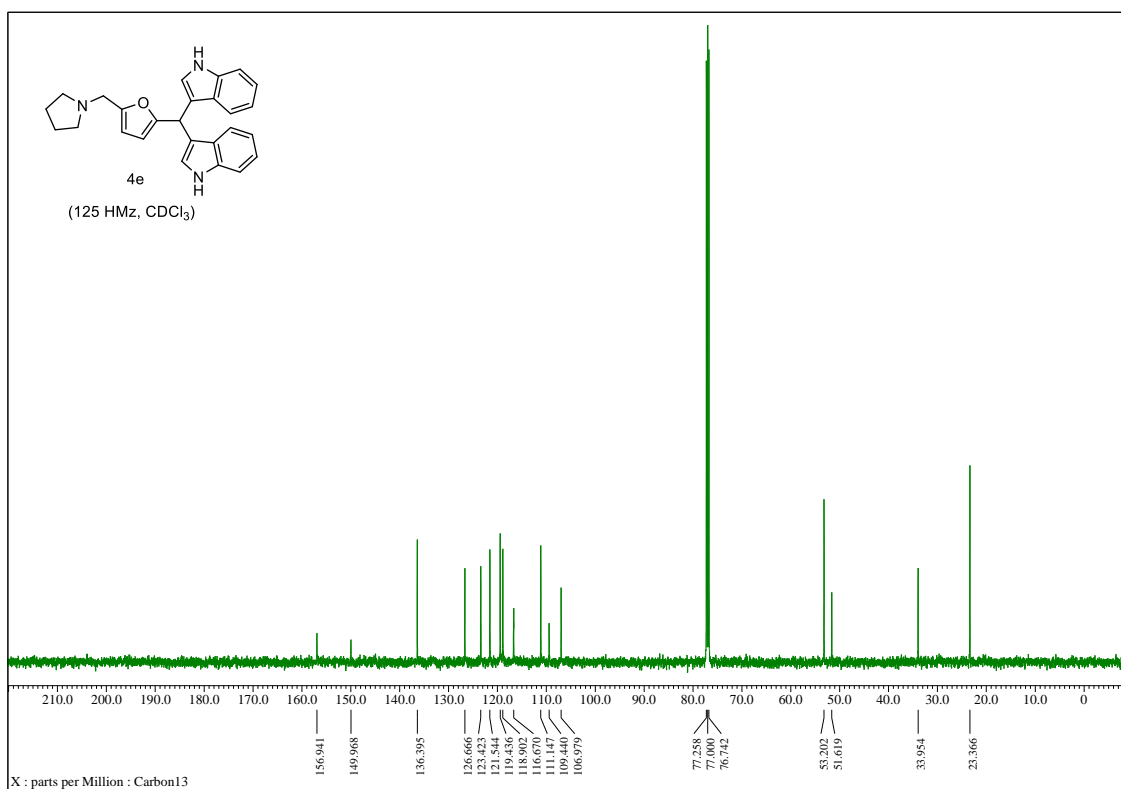
¹³C NMR of 5-[N-methyl-N-(4-cyano)phenyl-aminomethyl]-furan-2-yl bis(N-methyl-indolyl)methane (4d)



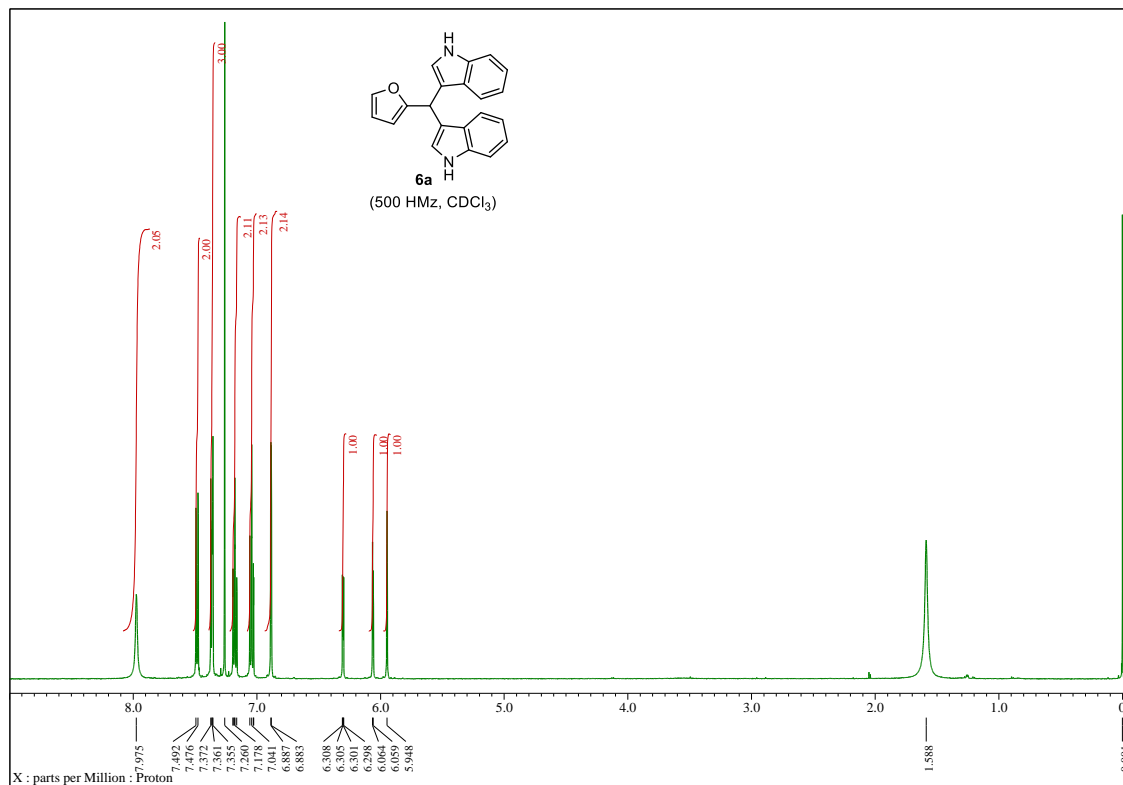
¹H NMR of 5-(*N*-pyrrolidinylmethyl)-furan-2-yl bis(*N*-methyl-indolyl)methane (4e)



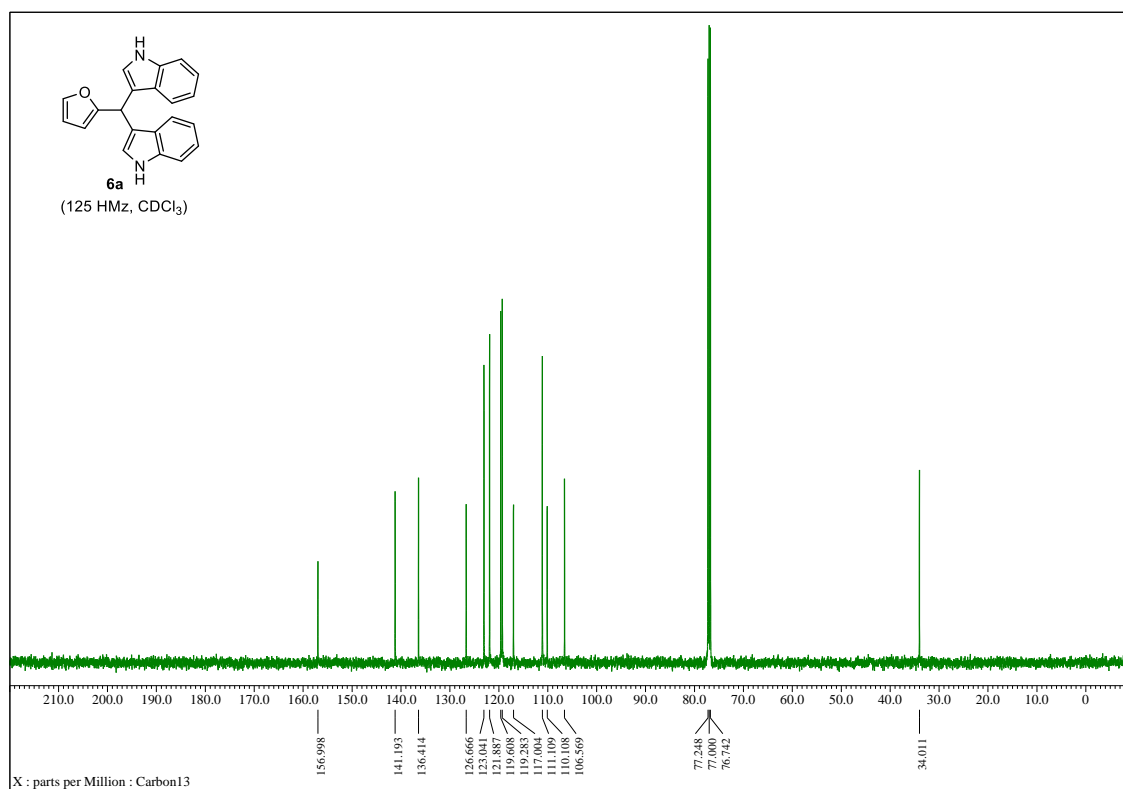
¹³C NMR of 5-(*N*-pyrrolidinylmethyl)-furan-2-yl bis(*N*-methyl-indolyl)methane (4e)



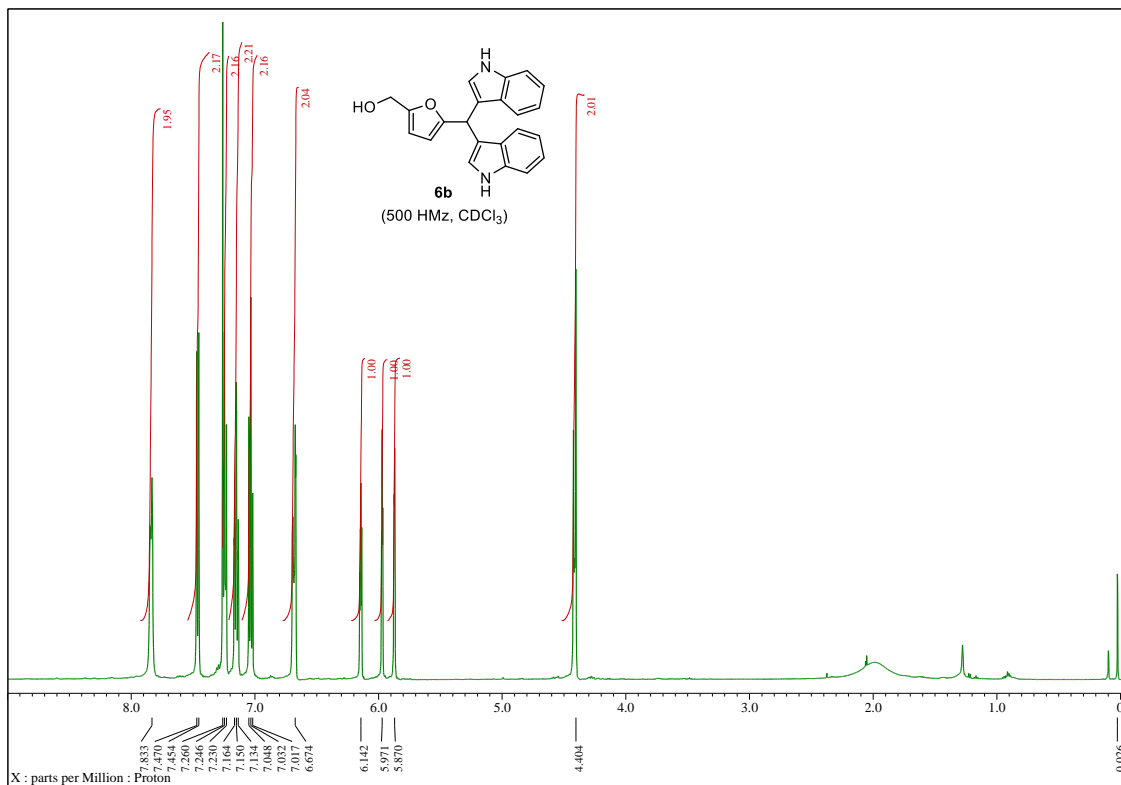
¹H NMR of furan-2-yl bis(indolyl)methane (6a)



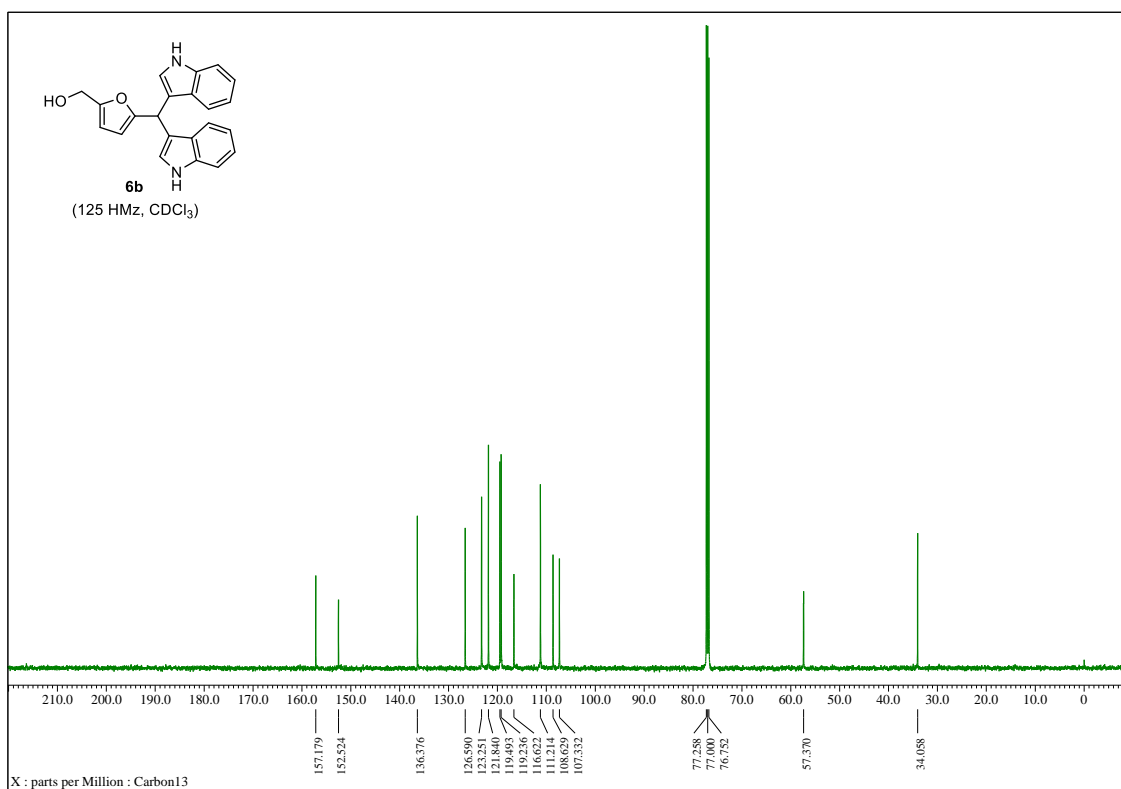
¹³C NMR of furan-2-yl bis(indolyl)methane (6a)



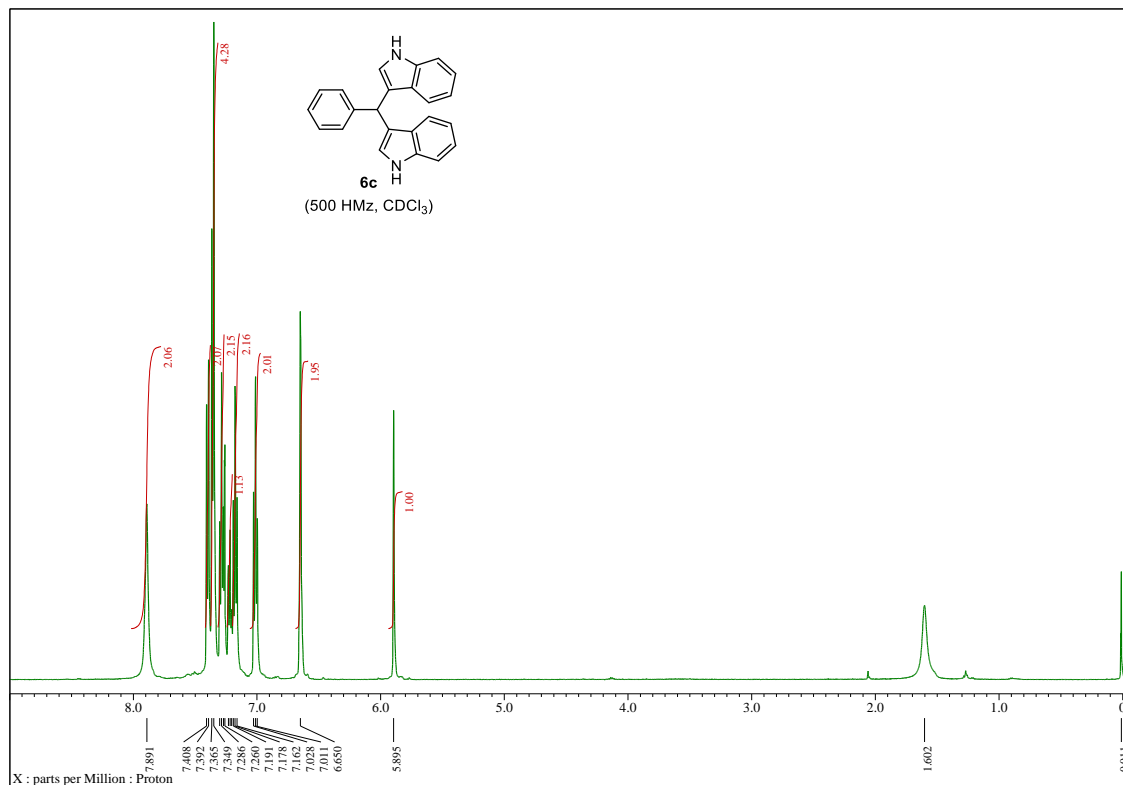
¹H NMR of 5-hydroxymethyl-furan-2-yl bis(indolyl)methane (6b)



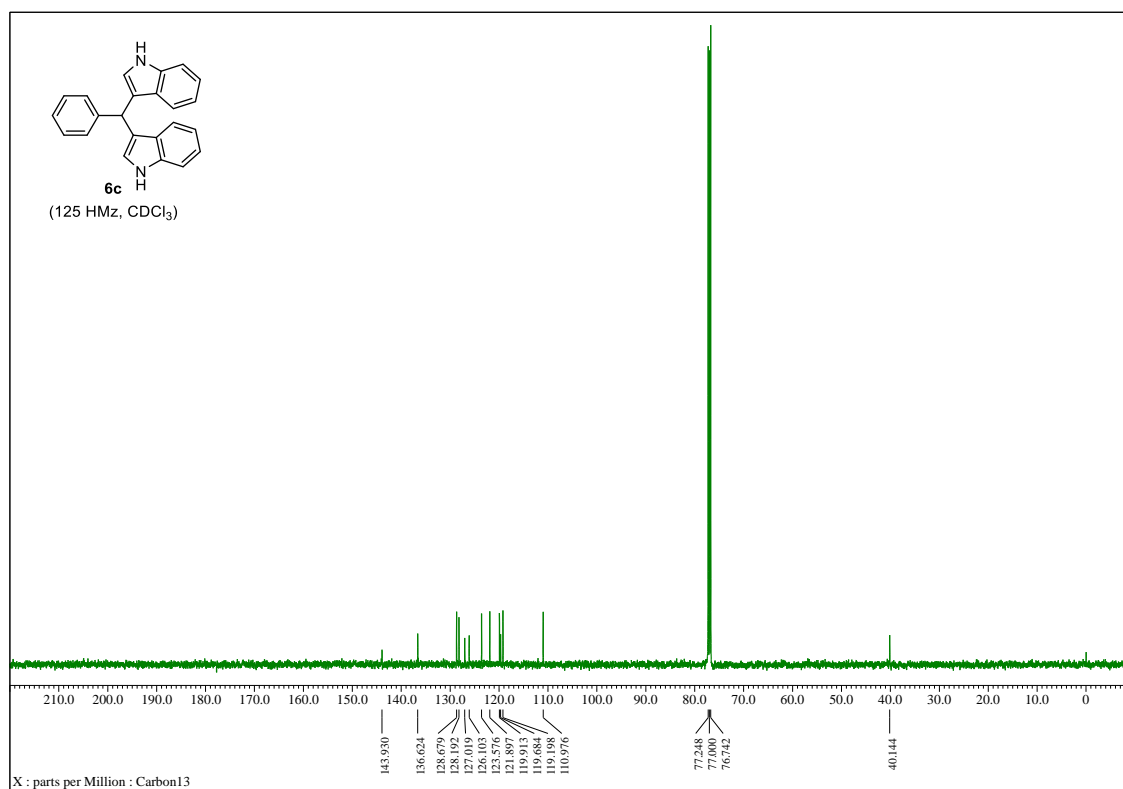
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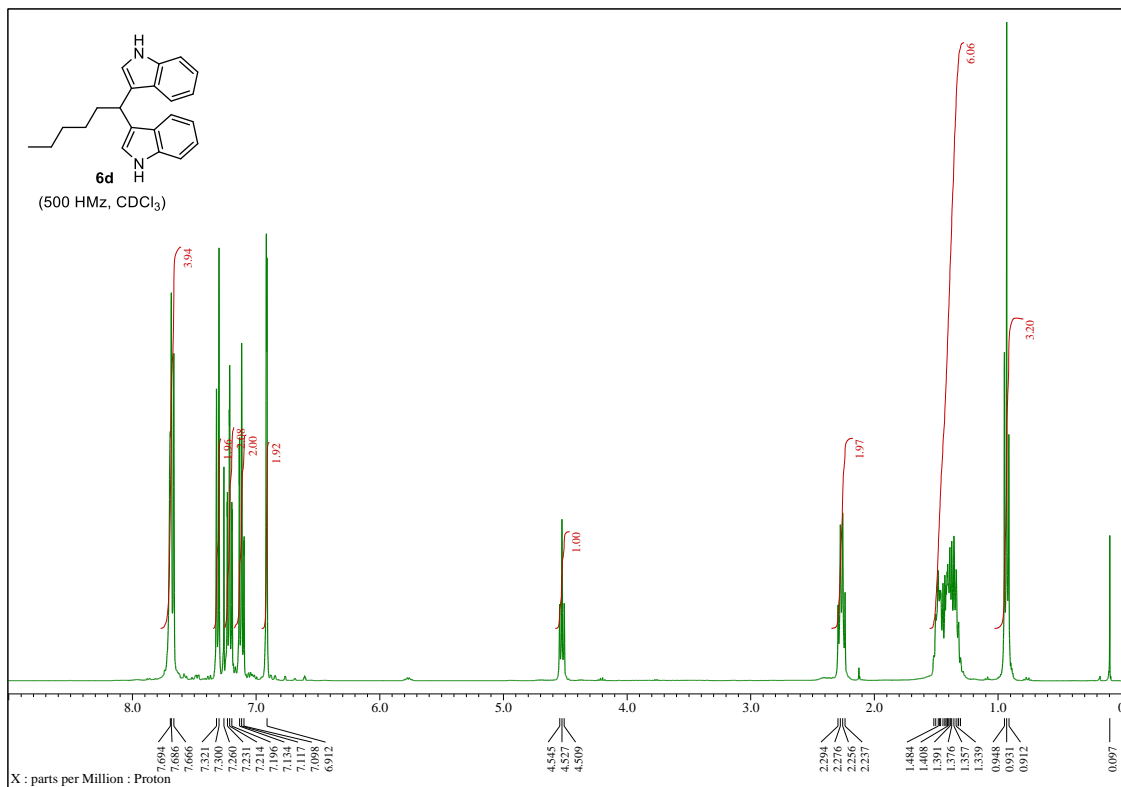
¹H NMR of phenyl bis(indolyl)methane (6c)



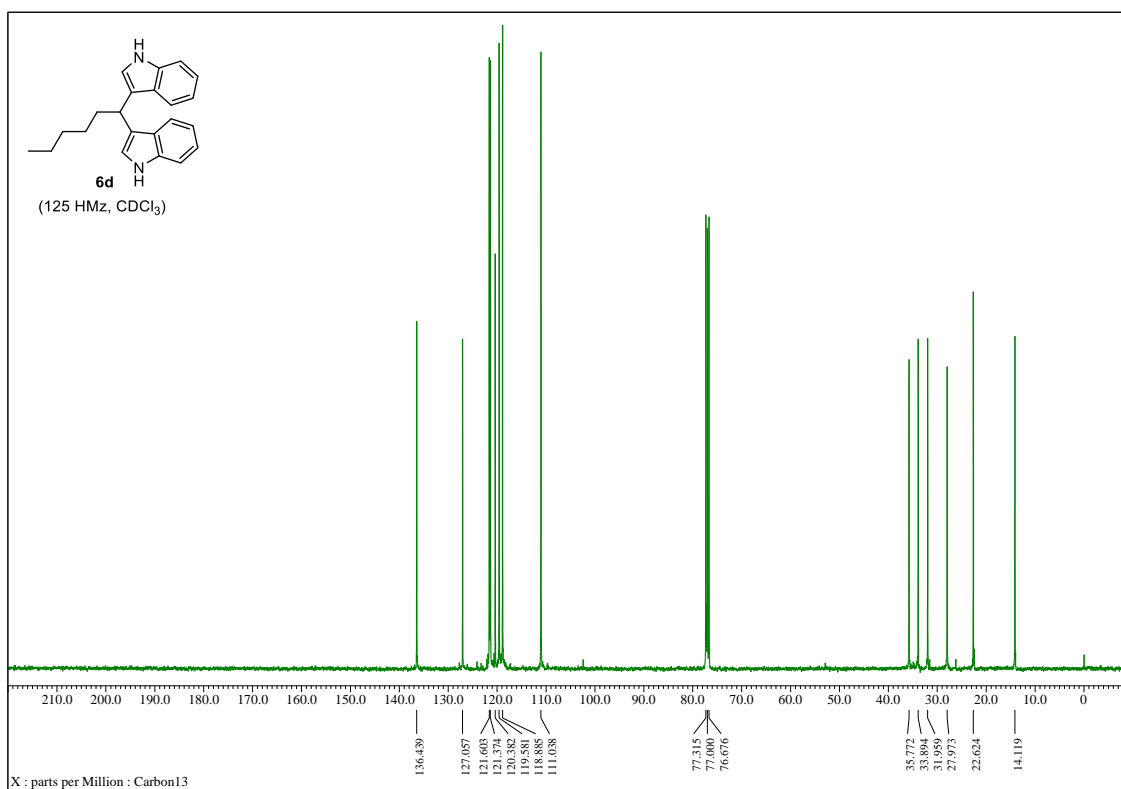
¹³C NMR of phenyl bis(indolyl)methane (6c)



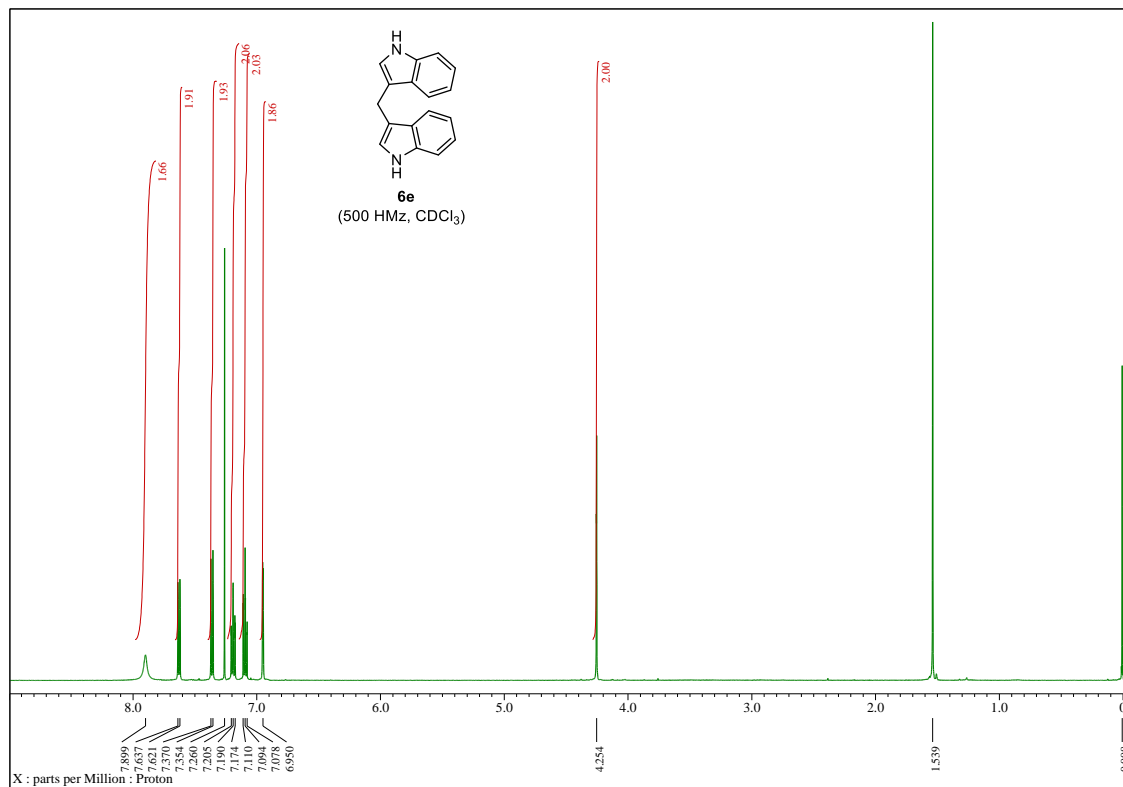
¹H NMR of 1,1-bis(indolyl)hexane (6d)



¹³C NMR of 1,1-bis(indolyl)hexane (6d)



¹H NMR of diindolylmethane (6e)



¹³C NMR of diindolylmethane (6e)

