

Supporting Information

Chelation-assisted and steric-controlled selectivity in the Pd-catalyzed C–H/C–H oxidative coupling of indoles

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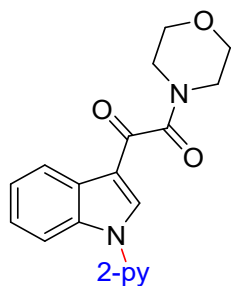
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1. General information

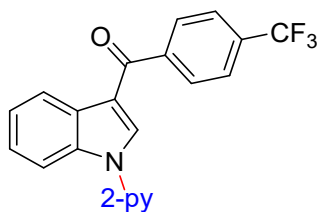
The catalytic reactions were performed in oven-dried reaction vessels with a Teflon screw cap under air. Solvents were dried over Na/benzophenone or CaH₂ and distilled before use. Liquid reagents were flushed with argon prior to use. The starting compounds **1a-9a**, **11a**, **13a**, **15a-18a**, and **20a-25a** were synthesized according to the previously described procedures.^{S1-S5} All other chemicals were obtained from commercial sources and were used without further purification. High-resolution mass spectrometry (HRMS) mass spectra were recorded on a Thermo Scientific Q-Exactive Accela 1250 pump. NMR: (¹H and ¹³C{¹H}) spectra were recorded at 400 or 500 MHz (¹H), 100 or 125 MHz {¹³C{¹H}}, DEPT (distortionless enhancement by polarization transfer)}, 377 MHz (¹⁹F), respectively in CDCl₃ and DMSO-*d*₆ solutions, if not otherwise specified; chemical shifts (δ) are given in ppm. The ¹H and ¹³C{¹H} NMR spectra are referenced to residual solvent signals (CDCl₃: δ H = 7.26 ppm, δ C = 77.2 ppm; DMSO-*d*₆: δ H = 2.50 ppm, δ C = 39.5 ppm). The splitting patterns of NMR are abbreviated as follows: s = singlet; br s = broad singlet; d = doublet; t = triplet; q = quartet; sept = septet; dd = doublet of doublets; ddd = doublet of doublet of doublets; td = triplet of doublets; m = multiplet.

2. Synthesis and characterization of starting compounds

Representative Procedure A. Synthesis of 1-Morpholino-2-(1-(pyridin-2-yl)-1H-indol-3-yl)ethane-1,2-dione (10a): In an oven-dried Schlenk flask, a solution of 1-(1H-indol-3-yl)-2-morpholinoethane-1,2-dione (0.50 g, 1.94 mmol) in DMF (10 mL) was slowly added to NaH (0.070 g, 2.91 mmol) in DMF (5.0 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was further cooled to 0 °C, and 2-fluoropyridine (0.283 g, 2.91 mmol) was added dropwise. The resultant reaction mixture was immersed in a preheated oil bath at 100 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, and was quenched with NH₄Cl (aq), diluted with EtOAc and washed with ice-cold water and brine. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in *vacuo*. The crude residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc: 1/1) to yield **10a** (0.58 g, 89%) as a pale yellow solid. M.pt: 124-126 °C.

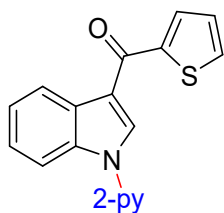


1-Morpholino-2-(1-(pyridin-2-yl)-1*H*-indol-3-yl)ethane-1,2-dione (10a): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.64-8.63 (m, 1H, Ar-H), 8.50 (s, 1H, Ar-H), 8.45-8.42 (m, 1H, Ar-H), 8.03 (dd, J = 6.2, 3.2 Hz, 1H, Ar-H), 7.94-7.90 (m, 1H, Ar-H), 7.61 (d, J = 8.1 Hz, 1H, Ar-H), 7.42-7.40 (m, 2H, Ar-H), 7.36 (dd, J = 7.4, 4.9 Hz, 1H, Ar-H), 3.82-3.76 (m, 4H, CH_2), 3.72-3.70 (m, 2H, CH_2), 3.60-3.58 (m, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ = 185.8 (CO), 165.8 (CO), 151.0 (C_q), 149.7 (CH), 139.1 (CH), 137.0 (CH), 136.2 (C_q), 127.3 (C_q), 125.3 (CH), 124.4 (CH), 122.7 (CH), 122.6 (CH), 116.4 (CH), 116.0 (C_q), 113.0 (CH), 67.2 (CH_2), 66.9 (CH_2), 46.8 (CH_2), 42.1 (CH_2). HRMS (ESI): m/z Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_3 + \text{H}^+$ [M + H] $^+$ 336.1343; Found 336.1334.

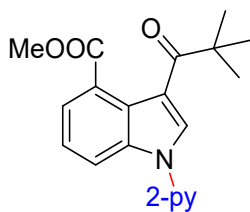


(1-(Pyridin-2-yl)-1*H*-indol-3-yl)(4-(trifluoromethyl)phenyl)methanone (12a): The representative procedure A was followed, using (1*H*-indol-3-yl)(4-(trifluoromethyl)phenyl)methanone (0.50 g, 1.73 mmol), NaH (0.062 g, 2.60 mmol), and 2-fluoropyridine (0.252 g, 2.60 mmol), and stirred at 100 °C in a preheated oil bath for 16 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) to yield **12a** (0.61 g, 96%) as a yellow solid. M.pt: 108-112 °C. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 8.62 (dd, J = 4.8, 1.1 Hz, 1H, Ar-H), 8.53-8.50 (m, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 8.04-8.01 (m, 1H, Ar-H), 7.99 (d, J = 8.1 Hz, 2H, Ar-H), 7.92 (td, J = 7.8, 1.8 Hz, 1H, Ar-H), 7.78 (d, J = 8.1 Hz, 2H, Ar-H), 7.61 (d, J = 8.1 Hz, 1H, Ar-H), 7.45-7.41 (m, 2H, Ar-H), 7.33 (dd, J = 7.4, 4.8 Hz, 1H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ = 190.2 (CO), 151.1 (C_q), 149.8 (CH), 143.7 (C_q), 139.1 (CH), 136.0 (C_q), 135.6 (CH), 133.1 (q, $^2J_{\text{C-F}}$ = 32.8 Hz, C_q), 129.2 (2C, CH), 128.3 (C_q), 125.7 (q, $^3J_{\text{C-F}}$ = 3.8 Hz, 2C, CH), 125.2 (CH), 124.1 (CH), 124.0 (q, $^1J_{\text{C-F}}$ = 272.4 Hz, CF_3), 123.1 (CH), 122.4 (CH), 118.1 (C_q), 116.3 (CH), 112.5 (CH). $^{19}\text{F-NMR}$ (377 MHz, CDCl_3): δ = -62.7 (s). HRMS (ESI): m/z Calcd for $\text{C}_{21}\text{H}_{13}\text{N}_2\text{OF}_3 + \text{H}^+$ [M +

$[H]^+$ 367.1053; Found 367.1040.



(1-(Pyridin-2-yl)-1H-indol-3-yl)(thiophen-2-yl)methanone (14a): The representative procedure A was followed, using (1H-indol-3-yl)(thiophen-2-yl)methanone (0.5 g, 2.20 mmol), NaH (0.079 g, 3.3 mmol), and 2-fluoropyridine (0.320 g, 3.30 mmol), and stirred at 100 °C in a preheated oil bath for 16 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) to yield **14a** (0.55 g, 82%) as a yellow liquid. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 8.87 (s, 1H, Ar-H), 8.66-8.64 (m, 1H, Ar-H), 8.63-8.59 (m, 1H, Ar-H), 8.04-8.01 (m, 1H, Ar-H), 7.93 (td, J = 7.8, 1.8 Hz, 1H, Ar-H), 7.66-7.64 (m, 2H, Ar-H), 7.41-7.37 (m, 3H, Ar-H), 7.33 (dd, J = 7.3, 5.1 Hz, 1H, Ar-H), 6.60 (dd, J = 3.5, 1.6 Hz, 1H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ = 176.9 (CO), 154.4 (C_q), 151.4 (C_q), 149.7 (CH), 145.4 (CH), 139.0 (CH), 135.5 (C_q), 134.5 (CH), 128.9 (C_q), 124.8 (CH), 123.8 (CH), 123.3 (CH), 122.1 (CH), 117.1 (CH), 117.0 (C_q), 116.3 (CH), 112.4 (CH), 112.3 (CH).

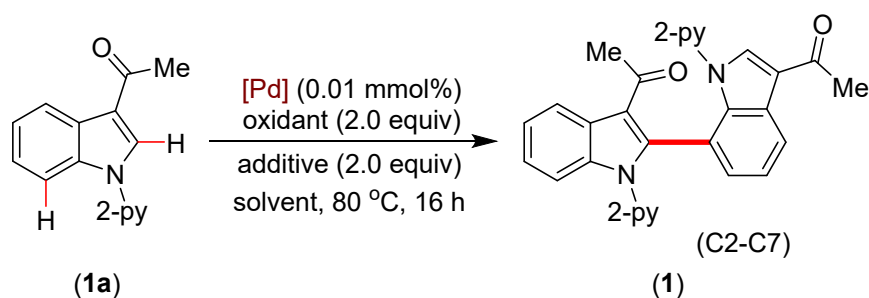


Methyl 3-pivaloyl-1-(pyridin-2-yl)-1H-indole-4-carboxylate (19a): The representative procedure A was followed, using methyl 3-pivaloyl-1H-indole-4-carboxylate (0.50 g, 1.93 mmol), NaH (0.070 g, 2.89 mmol), and 2-fluoropyridine (0.282 g, 2.90 mmol), and stirred at 100 °C in a preheated oil bath for 16 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) to yield **19a** (0.57 g, 88%) as a pale yellow solid. M.pt: 82-86 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.61 (dd, J = 4.8, 1.1 Hz, 1H, Ar-H), 8.21 (d, J = 8.4 Hz, 1H, Ar-H), 8.09 (s, 1H, Ar-H), 7.88 (td, J = 7.8, 1.8 Hz, 1H, Ar-H), 7.71-7.69 (m, 1H, Ar-H), 7.50 (d, J = 8.3 Hz, 1H, Ar-H), 7.36 (t, J = 7.9 Hz, 1H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 3.90 (s, 3H, CH_3), 1.40 (s, 9H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ = 205.6 (CO), 168.6 (CO), 151.4 (C_q), 149.6 (CH), 139.0 (CH), 135.6 (C_q), 128.5 (CH), 126.1 (C_q), 125.9 (C_q), 124.2 (CH), 123.6 (CH), 121.8 (CH), 119.0 (C_q), 116.1 (CH), 116.0 (CH), 52.2

(CH₃), 44.9 (C_q), 27.9 (3C, CH₃). HRMS (ESI): *m/z* Calcd for C₂₀H₂₀N₂O₃ + H⁺ [M + H]⁺ 337.1547; Found 337.1544.

3. Detailed optimization studies

Table S1. Optimization of reaction condition for C(2)–H/C(7)–H oxidative coupling ^a

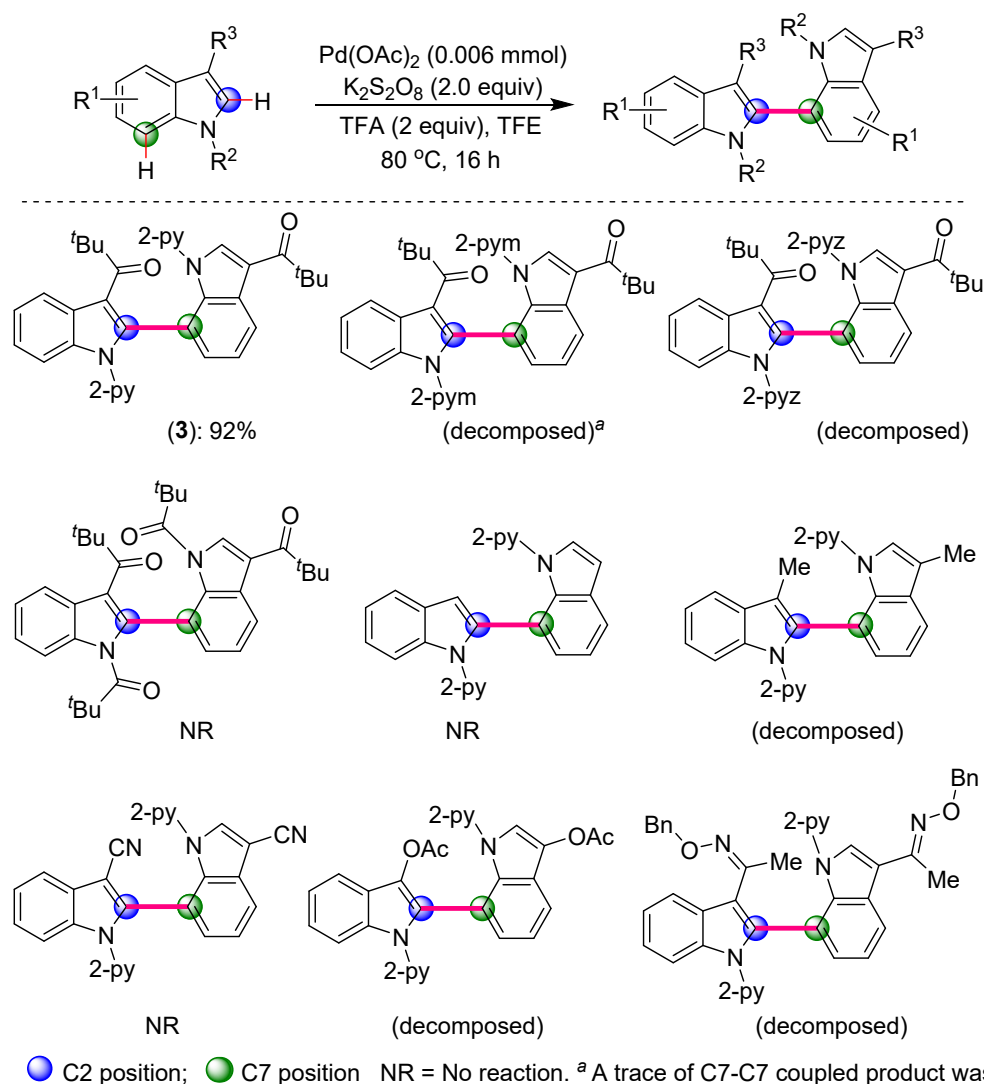


Entry	[Pd]	Oxidant	Additive	Solvent	Yield 1 (%) ^b
1	Pd(OAc) ₂	PhI(OAc) ₂	TFA	TFE	trace
2	Pd(OAc) ₂	AgTFA	TFA	TFE	trace
3	Pd(OAc) ₂	AgOAc	TFA	TFE	trace
4	Pd(OAc) ₂	Cu(OAc) ₂	TFA	TFE	trace
5	Pd(OAc) ₂	NFSI	TFA	TFE	trace
6	Pd(OAc) ₂	(NH ₄) ₂ S ₂ O ₈	TFA	TFE	NR
7	Pd(OAc) ₂	Na ₂ S ₂ O ₈	TFA	TFE	81
8	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	TFE	89
9	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	HFIP	68
10	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	AcOH	trace
11	Pd(OAc) ₂	K ₂ S ₂ O ₈	--	TFA	ND
12	Pd(OAc) ₂	K ₂ S ₂ O ₈	AcOH	TFE	trace
13	Pd(OAc) ₂	K ₂ S ₂ O ₈	H ₂ O	TFE	NR
14	Pd(OAc) ₂	K ₂ S ₂ O ₈	TfOH	TFE	NR
15	PdCl ₂	K ₂ S ₂ O ₈	TFA	TFE	41
16	Pd ₂ (dba) ₃	K ₂ S ₂ O ₈	TFA	TFE	NR
17 ^c	Pd(OAc)₂	K₂S₂O₈	TFA	TFE	88
18 ^{c,d}	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	TFE	76
19 ^{c,e}	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	TFE	65
20 ^{c,f}	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	TFE	79

21 ^{c,g}	Pd(OAc) ₂	K ₂ S ₂ O ₈	TFA	TFE	83
22 ^c	Pd(OAc) ₂	K ₂ S ₂ O ₈	--	TFE	NR
23 ^c	--	K ₂ S ₂ O ₈	TFA	TFE	NR
24 ^c	Pd(OAc) ₂	--	TFA	TFE	NR

^a Conditions: Substrate **1a** (0.048 g, 0.203 mmol), oxidant (0.40 mmol), [Pd] (0.01 mmol, 10 mol%), TFA (0.40 mmol), solvent (1.0 mL). ^b Isolated yield. ^c 6.0 mol% (0.006 mmol) of Pd(OAc)₂ used. ^d 1.5 equiv of K₂S₂O₈ was used. ^e 5.0 equiv of TFA was used. ^f Reaction performed at 70 °C. ^g Reaction performed at 100 °C. ND = Not Determined. NR = No Reaction. TFA = Trifluoroacetic acid. TFE = Trifluoroethanol.

4. Effect of C3 and N-substituents on C(2)-H/C(7)-H coupling



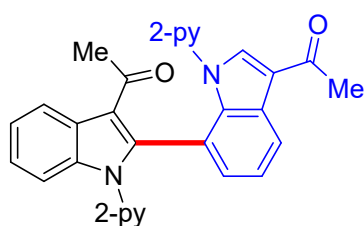
5. Procedure for the homocoupling of indoles

Representative Procedure B. Synthesis of 1,1'-(1,1'-Di(pyridin-2-yl)-1*H*, 1'*H*-[2,7'-biindole]-3,3'-diyl)bis(ethan-1-one) (1): To an oven-dried screw-cap tube equipped with magnetic stir bar were introduced 1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)ethan-1-one (**1a**; 0.048 g, 0.203 mmol), K₂S₂O₈ (0.109 g, 0.403 mmol), and Pd(OAc)₂ (0.0014 g, 0.0062 mmol, 6.0 mol%), followed by the addition of TFA (0.046 g, 0.403 mmol) and TFE (1.0 mL). The resultant reaction mixture in the tube was immersed in a preheated oil bath at 80 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, and all the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) to yield compound **1** (0.042 g, 88%) as a brown solid. M.pt: 167-170 °C.

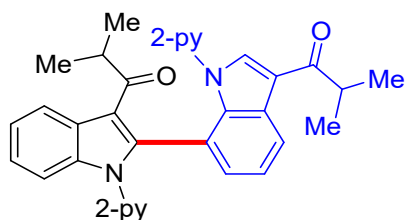
Procedure for Scale-up Synthesis of 3: To an oven-dried screw-cap tube equipped with a magnetic stir bar was introduced 2,2-dimethyl-1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**3a**; 0.557 g, 2.0 mmol), K₂S₂O₈ (1.08 g, 4.0 mmol), and Pd(OAc)₂ (0.014 g, 0.06 mmol, 6.0 mol%), followed by the addition of TFA (0.456 g, 4.0 mmol) and TFE (10 mL). The resultant reaction mixture in the tube was immersed in a preheated oil bath at 80 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, and all the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) to yield compound **3** (0.428 g, 77%) as a brown solid.

Procedure for Homocoupling of Indoles using Palladium Complex 27: To an oven-dried screw-cap tube equipped with a magnetic stir bar were introduced 2,2-dimethyl-1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**3a**; 0.056 g, 0.20 mmol), K₂S₂O₈ (0.108 g, 0.40 mmol), and **27** (0.006 g, 0.006 mmol, 6.0 mol%), followed by the addition of TFA (0.046 g, 0.40 mmol) and TFE (1.0 mL). The resultant reaction mixture was immersed in a preheated oil bath at 80 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, and all the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) to yield compound **3** (0.047 g, 85%) as a brown solid.

6. Characterization Data for C2–C7 Homocoupled Indoles

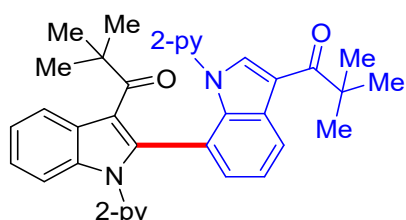


1,1'-(1,1'-Di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-diyl)bis(ethan-1-one) (1): $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 8.62 (dd, J = 8.1, 0.9 Hz, 1H, Ar-H), 8.56-8.54 (m, 1H, Ar-H), 8.20-8.18 (m, 1H, Ar-H), 8.12 (s, 1H, Ar-H), 7.90 (dd, J = 4.5, 1.3 Hz, 1H, Ar-H), 7.71 (td, J = 7.6, 1.9 Hz, 1H, Ar-H), 7.62-7.59 (m, 2H, Ar-H), 7.43-7.41 (m, 1H, Ar-H), 7.36-7.28 (m, 5H, Ar-H), 7.08 (d, J = 7.4 Hz, 1H, Ar-H), 6.84 (dd, J = 7.4, 4.9 Hz, 1H, Ar-H), 2.66 (s, 3H, CH_3), 1.83 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ = 194.4 (CO), 193.6 (CO), 151.1 (C_q), 150.5 (C_q), 149.3 (CH), 148.2 (CH), 141.3 (C_q), 138.3 (CH), 137.9 (CH), 136.6 (C_q), 136.2 (C_q), 136.1 (CH), 127.5 (C_q), 127.3 (CH), 126.6 (C_q), 124.3 (CH), 124.0 (CH), 123.2 (CH), 123.2 (CH), 123.0 (CH), 122.9 (CH), 122.5 (CH), 122.3 (CH), 119.4 (CH), 118.8 (C_q), 118.2 (C_q), 116.7 (C_q), 111.0 (CH), 29.6 (CH_3), 27.8 (CH_3). HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_2 + \text{H}^+$ $[\text{M} + \text{H}]^+$ 471.1816; Found 471.1805.

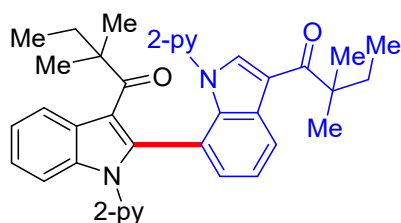


1,1'-(1,1'-Di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-diyl)bis(2-methylpropan-1-one) (2): The representative procedure **B** was followed, using substrate **2a** (0.053 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **2** (0.048 g, 91%) as a pale yellow solid. M.pt: 136-140 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.56 (d, J = 8.0 Hz, 1H, Ar-H), 8.50 (d, J = 4.5 Hz, 1H, Ar-H), 8.04 (s, 1H, Ar-H), 7.99-7.97 (m, 1H, Ar-H), 7.73 (d, J = 4.6 Hz, 1H, Ar-H), 7.59 (t, J = 7.6 Hz, 1H, Ar-H), 7.54 (d, J = 7.9 Hz, 1H, Ar-H), 7.43 (d, J = 7.9 Hz, 1H, Ar-H), 7.37-7.30 (m, 2H, Ar-H), 7.24-7.16 (m, 4H, Ar-H), 7.00 (d, J = 7.3 Hz, 1H, Ar-H), 6.77-6.74 (m, 1H, Ar-H), 3.38 (sept, J = 6.8 Hz, 1H, CH), 2.47 (sept, J = 6.8 Hz, 1H, CH), 1.37-1.27 (m, 6H, CH_3), 0.81 (d, J = 6.6 Hz, 3H, CH_3), 0.78 (d, J = 7.0 Hz, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ = 201.7 (CO), 201.0 (CO), 151.2 (C_q), 150.7 (C_q), 149.2 (CH), 147.8 (CH), 140.6 (C_q), 138.3 (CH), 137.9 (CH), 136.8 (C_q), 136.2 (C_q), 135.2 (CH), 128.0 (C_q), 127.4 (CH), 126.8 (C_q), 124.3 (CH),

123.8 (CH), 123.1 (CH), 123.0 (CH), 122.8 (CH), 122.6 (CH), 122.6 (CH), 121.9 (CH), 119.3 (CH), 117.3 (C_q), 116.9 (C_q), 116.8 (C_q), 111.2 (CH), 37.7 (CH), 37.5 (CH), 20.2 (CH₃), 20.0 (CH₃), 19.8 (CH₃), 17.8 (CH₃). HRMS (ESI): *m/z* Calcd for C₃₄H₃₀N₄O₂ + H⁺ [M + H]⁺ 527.2442; Found 527.2446. The structure of compound **2** is confirmed through a single crystal X-ray analysis (Figure S1).

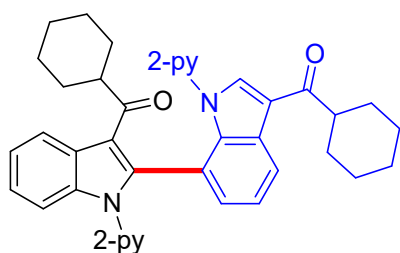


1,1'-(1,1'-Di(pyridin-2-yl)-1*H*,1'*H*-[2,7'-biindole]-3,3'-diyl)bis(2,2-dimethylpropan-1-one) (3**):** The representative procedure **B** was followed, using substrate **3a** (0.056 g, 0.201 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **3** (0.051 g, 92%) as a brown solid. M.pt: 154-158 °C. ¹H-NMR (500 MHz, CDCl₃): δ = 8.67 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.51 (d, *J* = 4.5 Hz, 1H, Ar-H), 8.18 (s, 1H, Ar-H), 8.05 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.71 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.59-7.55 (m, 2H, Ar-H), 7.47 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.34-7.15 (m, 7H, Ar-H), 6.88 (t, *J* = 6.1 Hz, 1H, Ar-H), 1.49 (s, 9H, CH₃), 1.08 (s, 9H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 210.1 (CO), 203.0 (CO), 150.5 (C_q), 150.2 (C_q), 148.8 (CH), 146.6 (CH), 138.2 (CH), 137.9 (CH), 136.1 (C_q), 135.4 (C_q), 134.7 (CH), 134.6 (C_q), 130.4 (C_q), 128.1 (CH), 126.6 (C_q), 124.6 (CH), 123.5 (CH), 122.9 (CH), 122.3 (CH), 122.1 (CH), 121.9 (CH), 121.2 (CH), 120.4 (CH), 119.5 (CH), 119.5 (C_q), 116.7 (C_q), 115.1 (C_q), 111.8 (CH), 44.8 (C_q), 44.7 (C_q), 28.9 (3C, CH₃), 27.4 (3C, CH₃). HRMS (ESI): *m/z* Calcd for C₃₆H₃₄N₄O₂ + H⁺ [M + H]⁺ 555.2755; Found 555.2759.

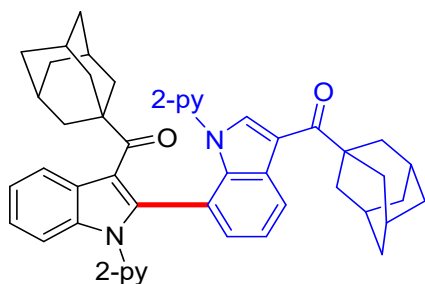


1,1'-(1,1'-Di(pyridin-2-yl)-1*H*, 1'*H*-[2,7'-biindole]-3,3'-diyl)bis(2,2-dimethylbutan-1-one) (4**):** The representative procedure **B** was followed, using substrate **4a** (0.059 g, 0.202 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **4** (0.055 g, 93%) as a yellow liquid. ¹H-NMR (500 MHz, CDCl₃): δ = 8.56 (d, *J* = 8.0 Hz, 1H,

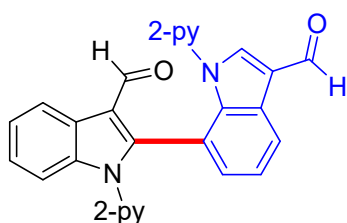
Ar-H), 8.47 (d, $J = 4.5$ Hz, 1H, Ar-H), 8.11 (s, 1H, Ar-H), 7.97 (d, $J = 4.6$ Hz, 1H, Ar-H), 7.68 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.56 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.46 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.38-7.11 (m, 7H, Ar-H), 7.06 (d, $J = 7.4$ Hz, 1H, Ar-H), 6.81 (t, $J = 6.0$ Hz, 1H, Ar-H), 1.87 (q, $J = 7.5$ Hz, 2H, CH₂), 1.42 (m, 8H, CH₂, CH₃), 0.93 (s, 3H, CH₃), 0.85 (t, $J = 7.4$ Hz, 3H, CH₃), 0.83 (s, 3H, CH₃), 0.56 (t, $J = 7.4$ Hz, 3H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): $\delta = 209.8$ (CO), 203.0 (CO), 150.5 (C_q), 150.1 (C_q), 148.8 (CH), 146.3 (CH), 138.4 (CH), 138.2 (CH), 136.2 (C_q), 135.0 (C_q), 134.8 (C_q), 134.1 (CH), 130.4 (C_q), 128.2 (CH), 126.7 (C_q), 124.5 (CH), 123.5 (CH), 123.0 (CH), 122.5 (CH), 122.1 (CH), 121.9 (CH), 121.6 (CH), 120.4 (CH), 119.7 (C_q), 119.6 (CH), 116.8 (C_q), 115.9 (C_q), 111.5 (CH), 48.6 (C_q), 48.4 (C_q), 34.9 (CH₂), 32.8 (CH₂), 26.3 (CH₃), 26.2 (CH₃), 24.6 (CH₃), 24.4 (CH₃), 9.4 (CH₃), 8.9 (CH₃). HRMS (ESI): m/z Calcd for C₃₈H₃₈N₄O₂ + H⁺ [M + H]⁺ 583.3068; Found 583.3054.



(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(cyclohexylmethanone) (5): The representative procedure **B** was followed, using substrate **5a** (0.061 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **5** (0.053 g, 87%) as a yellow liquid. ¹H-NMR (400 MHz, CDCl₃): $\delta = 8.58$ (d, $J = 8.0$ Hz, 1H, Ar-H), 8.51 (br s, 1H, Ar-H), 8.09 (s, 1H, Ar-H), 8.06-8.04 (m, 1H, Ar-H), 7.81 (br s, 1H, Ar-H), 7.68-7.59 (m, 2H, Ar-H), 7.51 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.35-7.18 (m, 6H, Ar-H), 6.99 (d, $J = 7.3$ Hz, 1H, Ar-H), 6.78-6.75 (m, 1H, Ar-H), 3.31-3.07 (m, 1H, CH), 2.11-1.85 (m, 4H, CH₂), 1.76-1.50 (m, 4H, CH₂), 1.45-1.21 (m, 8H, CH₂), 1.05-0.86 (m, 3H, CH₂, CH), 0.59-0.42 (m, 2H, CH₂). ¹³C{¹H}-NMR (100 MHz, CDCl₃): $\delta = 201.0$ (CO), 200.4 (CO), 151.0 (C_q), 150.6 (C_q), 149.3 (CH), 147.8 (CH), 140.4 (C_q), 138.5 (CH), 138.1 (CH), 136.7 (C_q), 136.3 (C_q), 135.2 (CH), 128.1 (C_q), 127.4 (CH), 127.0 (C_q), 124.4 (CH), 123.9 (CH), 123.2 (CH), 123.1 (CH), 122.9 (CH), 122.7 (2C, CH), 122.2 (CH), 119.5 (CH), 117.5 (C_q), 117.0 (C_q), 116.8 (C_q), 111.0 (CH), 48.3 (CH), 48.1 (CH), 30.8 (CH₂), 30.0 (CH₂), 30.0 (CH₂), 27.7 (CH₂), 26.1 (CH₂), 26.1 (2C, CH₂), 26.1 (CH₂), 25.8 (CH₂), 25.7 (CH₂). HRMS (ESI): m/z Calcd for C₄₀H₃₈N₄O₂ + H⁺ [M + H]⁺ 607.3068; Found 607.3054.

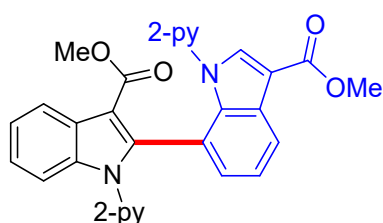


(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(((3r,5r,7r)-adamantan-1-yl)methanone) (6): The representative procedure **B** was followed, using substrate **6a** (0.071 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **6** (0.058 g, 82%) as a pale yellow solid. M.pt: 168-172 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.62 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar-H), 8.51-8.49 (m, 1H, Ar-H), 8.26 (s, 1H, Ar-H), 7.96-7.94 (m, 1H, Ar-H), 7.64 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.58 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.54 (td, *J* = 7.8, 1.9 Hz, 1H, Ar-H), 7.43-7.40 (m, 1H, Ar-H), 7.32-7.27 (m, 3H, Ar-H), 7.25-7.20 (m, 1H, Ar-H), 7.19-7.13 (m, 3H, Ar-H), 6.80 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H, Ar-H), 2.21-2.16 (m, 6H, CH₂, 3H, CH), 1.96-1.93 (m, 2H, CH₂), 1.91-1.80 (m, 6H, CH₂, 3H, CH), 1.79-1.73 (m, 2H, CH₂), 1.70-1.64 (m, 4H, CH₂), 1.57-1.49 (m, 4H, CH₂). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 209.9 (CO), 203.0 (CO), 150.8 (C_q), 150.8 (C_q), 148.8 (CH), 147.1 (CH), 138.0 (CH), 137.3 (CH), 136.0 (C_q), 134.7 (C_q), 134.5 (C_q), 134.5 (CH), 130.6 (C_q), 128.3 (CH), 126.9 (C_q), 124.4 (CH), 123.3 (CH), 122.7 (CH), 122.1 (CH), 121.9 (CH), 121.6 (CH), 121.1 (CH), 120.3 (CH), 119.3 (C_q), 119.2 (CH), 116.8 (C_q), 115.0 (C_q), 111.8 (CH), 47.5 (C_q), 47.2 (C_q), 40.6 (3C, CH₂), 38.5 (3C, CH₂), 37.0 (3C, CH₂), 36.6 (3C, CH₂), 28.6 (3C, CH), 28.2 (3C, CH). HRMS (ESI): *m/z* Calcd for C₄₈H₄₆N₄O₂ + H⁺ [M + H]⁺ 711.3694; Found 711.3691.

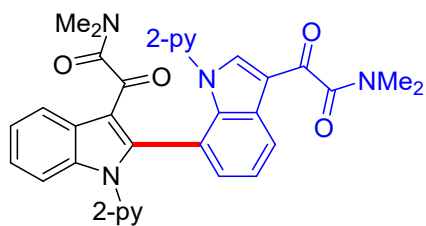


1,1'-Di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-dicarbaldehyde (7): The representative procedure **B** was followed, using substrate **7a** (0.045 g, 0.202 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **7** (0.036 g, 81%) as a pale yellow solid. M.pt: 176-180 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 10.16 (s, 1H, CHO), 9.50 (s, 1H, CHO), 8.57 (dd, *J* = 4.8, 1.3 Hz, 1H, Ar-H), 8.51 (dd, *J* = 7.9, 1.0 Hz, 1H, Ar-H), 8.11-8.08 (m, 1H, Ar-H), 8.06 (s, 1H, Ar-H), 7.79 (dd, *J* = 4.7, 1.0 Hz, 1H, Ar-H), 7.62 (td,

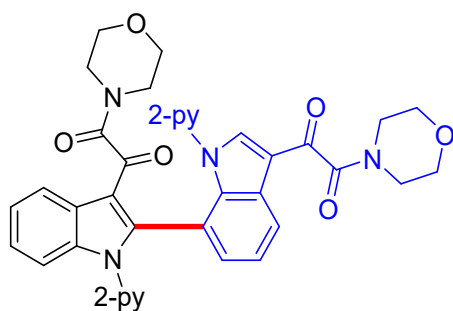
$J = 7.8, 1.9$ Hz, 1H, Ar-H), 7.53-7.41 (m, 4H, Ar-H), 7.33-7.25 (m, 4H, Ar-H), 7.14 (dd, $J = 7.4, 1.0$ Hz, 1H, Ar-H), 6.82-6.79 (m, 1H, Ar-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 186.3$ (CO), 185.3 (CO), 150.9 (C_q), 150.2 (C_q), 149.3 (CH), 148.1 (CH), 146.1 (C_q), 139.7 (CH), 138.6 (CH), 138.5 (CH), 137.0 (C_q), 136.1 (C_q), 129.0 (CH), 127.0 (C_q), 125.0 (C_q), 124.7 (CH), 124.1 (CH), 123.9 (CH), 123.5 (CH), 123.2 (CH), 123.0 (CH), 121.8 (CH), 121.7 (CH), 120.1 (C_q), 118.7 (CH), 117.3 (C_q), 114.3 (C_q), 111.7 (CH). HRMS (ESI): m/z Calcd for $\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2 + \text{H}^+$ $[\text{M} + \text{H}]^+$ 443.1503; Found 443.1486. The structure of compound **7** is confirmed through a single-crystal X-ray analysis (Figure S2).



Dimethyl 1,1'-di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-dicarboxylate (8): The representative procedure **B** was followed, using substrate **8a** (0.076 g, 0.301 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **8** (0.049 g, 65%) as a brown solid. M.pt: 180-184 °C. ^1H -NMR (400 MHz, CDCl_3): $\delta = 8.57$ (d, $J = 4.6$ Hz, 1H, Ar-H), 8.28 (d, $J = 8.0$ Hz, 1H, Ar-H), 8.10 (s, 1H, Ar-H), 7.91 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.66-7.61 (m, 2H, Ar-H), 7.57 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.50-7.45 (m, 2H, Ar-H), 7.38 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.24-7.19 (m, 3H, Ar-H), 7.14 (t, $J = 7.7$ Hz, 1H, Ar-H), 6.90 (d, $J = 7.3$ Hz, 1H, Ar-H), 6.75 (t, $J = 6.0$ Hz, 1H, Ar-H), 3.95 (s, 3H, CH_3), 3.51 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 165.4$ (CO), 164.7 (CO), 151.7 (C_q), 150.9 (C_q), 149.1 (CH), 147.4 (CH), 142.1 (C_q), 138.3 (CH), 138.0 (CH), 136.5 (C_q), 135.5 (C_q), 135.0 (CH), 127.6 (C_q), 127.0 (CH), 126.7 (C_q), 123.7 (CH), 122.9 (CH), 122.7 (CH), 122.7 (CH), 122.6 (CH), 122.4 (CH), 122.1 (CH), 121.5 (CH), 118.7 (CH), 117.1 (C_q), 111.5 (CH), 109.8 (C_q), 108.2 (C_q), 51.4 (CH_3), 50.8 (CH_3). HRMS (ESI): m/z Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_4 + \text{H}^+$ $[\text{M} + \text{H}]^+$ 503.1714; Found 503.1700.

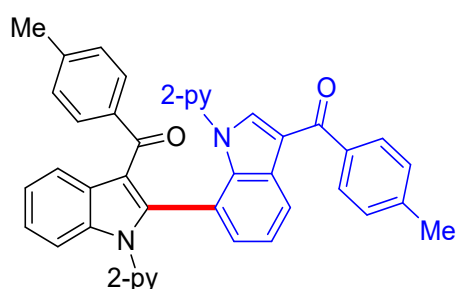


2,2'-(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(N,N-dimethyl-2-oxoacetamide) (9): The representative procedure **B** was followed, using substrate **9a** (0.059 g, 0.201 mmol) at 120 °C for 24 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 1/2) yielded **9** (0.045 g, 77%) as a brown liquid. ¹H-NMR (400 MHz, CDCl₃): δ = 8.56-8.54 (m, 1H, Ar-H), 8.52 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar-H), 8.19 (s, 1H, Ar-H), 8.13-8.10 (m, 1H, Ar-H), 7.78 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.61-7.54 (m, 4H, Ar-H), 7.43-7.41 (m, 1H, Ar-H), 7.30-7.27 (m, 2H, Ar-H), 7.26-7.21 (m, 1H, Ar-H), 7.19-7.22 (m, 1H, Ar-H), 7.06 (dd, *J* = 7.4, 1.1 Hz, 1H, Ar-H), 6.75 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H, Ar-H), 3.15 (s, 3H, CH₃), 3.10 (s, 3H, CH₃), 2.63 (s, 3H, CH₃), 2.24 (s, 3H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 187.5 (CO), 186.3 (CO), 167.1 (CO), 167.1 (CO), 150.9 (C_q), 150.1 (C_q), 149.1 (CH), 146.9 (CH), 143.8 (C_q), 140.3 (CH), 138.6 (CH), 138.6 (CH), 136.9 (C_q), 136.2 (C_q), 127.7 (C_q), 127.5 (CH), 126.4 (C_q), 124.8 (CH), 124.4 (CH), 124.0 (CH), 123.5 (CH), 122.8 (CH), 122.4 (CH), 122.3 (CH), 121.7 (CH), 120.6 (CH), 114.8 (C_q), 114.8 (C_q), 114.2 (C_q), 111.8 (CH), 37.9 (CH₃), 36.8 (CH₃), 34.8 (CH₃), 33.2 (CH₃). HRMS (ESI): *m/z* Calcd for C₃₄H₂₈N₆O₄ + H⁺ [M + H]⁺ 585.2245; Found 585.2241.

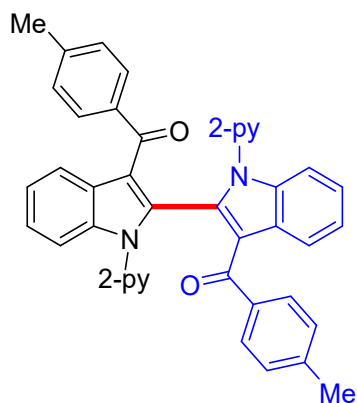


2,2'-(1,1'-Di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-diyl)bis(1-morpholinoethane-1,2-dione) (10): The representative procedure **B** was followed, using substrate **10a** (0.067 g, 0.20 mmol) at 120 °C for 24 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 1/3) yielded **10** (0.041 g, 61%) as a pale yellow solid. M.pt: > 200 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.57 (d, *J* = 4.9 Hz, 1H, Ar-H), 8.51 (dd, *J* = 8.0, 0.9 Hz, 1H, Ar-H), 8.19 (s, 1H, Ar-H), 8.06-8.03 (m, 1H, Ar-H), 7.72 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.59-7.53 (m, 4H, Ar-H), 7.42-7.39 (m, 1H, Ar-H), 7.31-7.24 (m, 4H, Ar-H), 7.08 (d, *J* = 6.8 Hz, 1H, Ar-

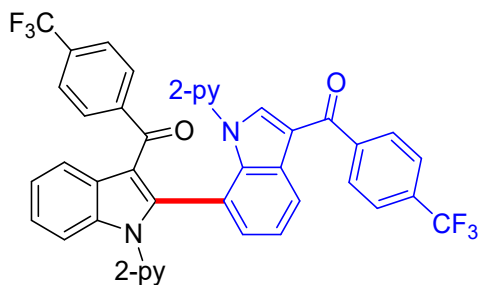
H), 6.77 (dd, $J = 6.9, 5.1$ Hz, 1H, Ar-H), 3.80-3.72 (m, 6H, CH₂), 3.70-3.59 (m, 2H, CH₂), 3.50-3.43 (m, 2H, CH₂), 3.36-3.27 (m, 2H, CH₂), 3.25-3.14 (m, 2H, CH₂), 3.05-2.99 (m, 1H, CH₂), 2.65-2.61 (m, 1H, CH₂). ¹³C{¹H}-NMR (100 MHz, CDCl₃): $\delta = 186.7$ (CO), 185.4 (CO), 165.7 (CO), 165.5 (CO), 150.9 (C_q), 150.0 (C_q), 149.2 (CH), 147.1 (CH), 143.7 (C_q), 140.2 (CH), 138.6 (2C, CH), 136.9 (C_q), 136.4 (C_q), 128.0 (CH), 127.5 (C_q), 126.1 (C_q), 124.9 (CH), 124.4 (CH), 124.1 (CH), 123.6 (CH), 123.0 (CH), 122.7 (CH), 122.3 (CH), 121.5 (CH), 120.5 (CH), 114.9 (C_q), 114.8 (C_q), 114.2 (C_q), 111.8 (CH), 67.1 (CH₂), 66.9 (CH₂), 66.3 (CH₂), 66.1 (CH₂), 46.8 (CH₂), 45.8 (CH₂), 42.2 (CH₂), 40.6 (CH₂). HRMS (ESI): m/z Calcd for C₃₈H₃₂N₆O₆ + H⁺ [M + H]⁺ 669.2456; Found 669.2451.



(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(*p*-tolylmethanone) (11): The representative procedure **B** was followed, using substrate **11a** (0.063 g, 0.202 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded C2-C7 coupled product **11** (0.044 g, 70%) and C2-C2 coupled product **11'** (0.011 g, 18%). ¹H-NMR (500 MHz, CDCl₃): $\delta = 8.59$ (d, $J = 4.5$ Hz, 1H, Ar-H), 8.23 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.79-7.77 (m, 3H, Ar-H), 7.73-7.68 (m, 3H, Ar-H), 7.63 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.53 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.39 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.33 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.27-7.23 (m, 2H, Ar-H), 7.20-7.16 (m, 3H, Ar-H), 7.10 (t, $J = 7.6$ Hz, 1H, Ar-H), 6.94 (d, $J = 7.4$ Hz, 1H, Ar-H), 6.75 (t, $J = 6.1$ Hz, 1H, Ar-H), 6.71 (d, $J = 7.6$ Hz, 2H, Ar-H), 2.46 (s, 3H, CH₃), 2.13 (s, 3H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): $\delta = 192.3$ (CO), 190.9 (CO), 151.0 (C_q), 150.9 (C_q), 149.2 (CH), 147.3 (CH), 142.3 (C_q), 141.9 (C_q), 141.4 (C_q), 138.4 (CH), 138.0 (CH), 137.8 (C_q), 137.1 (CH), 136.7 (C_q), 136.5 (2C, C_q), 135.8 (C_q), 129.3 (2C, CH), 129.1 (2C, CH), 129.0 (C_q), 128.3 (CH), 128.1 (2C, CH), 127.6 (2C, CH), 124.0 (CH), 123.3 (CH), 123.0 (CH), 122.8 (2C, CH), 122.6 (CH), 122.0 (CH), 121.8 (CH), 118.1 (CH), 117.7 (C_q), 117.1 (C_q), 116.9 (C_q), 111.3 (CH), 21.8 (CH₃), 21.5 (CH₃). HRMS (ESI): m/z Calcd for C₄₂H₃₀N₄O₂ + H⁺ [M + H]⁺ 623.2442; Found 623.2444.

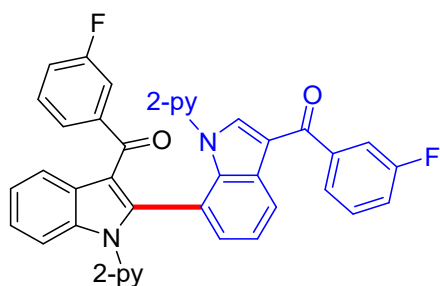


(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,2'-biindole]-3,3'-diyl)bis(*p*-tolylmethanone) (11'): Yield **11'** (0.011 g, 18%) as a yellow solid. M.pt: > 200 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.34 (d, *J* = 4.6 Hz, 2H, Ar-H), 7.56-7.48 (m, 10H, Ar-H), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.19 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.14-7.07 (m, 4H, Ar-H), 6.97 (d, *J* = 7.9 Hz, 4H, Ar-H), 2.25 (s, 6H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 191.7 (2C, CO), 150.4 (2C, C_q), 148.9 (2C, CH), 142.8 (2C, C_q), 138.3 (2C, CH), 136.7 (2C, C_q), 136.4 (2C, C_q), 133.1 (2C, C_q), 130.0 (4C, CH), 128.5 (4C, CH), 127.1 (2C, C_q), 124.2 (2C, CH), 122.6 (2C, CH), 122.4 (2C, CH), 121.6 (2C, CH), 121.5 (2C, CH), 120.2 (2C, C_q), 112.0 (2C, CH), 21.7 (2C, CH₃). HRMS (ESI): *m/z* Calcd for C₄₂H₃₀N₄O₂ + H⁺ [M + H]⁺ 623.2442; Found 623.2432.



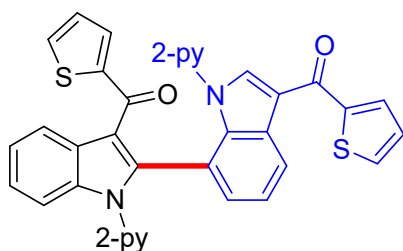
(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis((4-(trifluoromethyl)phenyl)methanone) (12): The representative procedure **B** was followed, using substrate **12a** (0.073 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **12** (0.042 g, 57%) as a brown solid. M.pt: >200 °C. ¹H-NMR (500 MHz, CDCl₃): δ = 8.58-8.54 (m, 1H, Ar-H), 8.21 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.93-7.91 (m, 3H, Ar-H), 7.87 (dd, *J* = 4.8, 1.1 Hz, 1H, Ar-H), 7.80 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.77-7.75 (m, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.48 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.34-7.25 (m, 6H, Ar-H), 7.13-7.09 (m, 3H, Ar-H), 6.92-6.90 (m, 1H, Ar-H), 6.80 (dd, *J* = 6.9, 5.2 Hz, 1H, Ar-H). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 191.2 (CO), 189.4 (CO), 150.6 (C_q), 150.6 (C_q), 149.6 (CH), 147.9 (CH), 143.5 (C_q), 142.3 (C_q), 142.1 (C_q),

138.7 (CH), 138.0 (CH), 137.4 (CH), 137.3 (C_q), 136.9 (C_q), 135.8 (C_q), 133.3 (q, ²J_{C-F} = 32.8 Hz, C_q), 131.8 (q, ²J_{C-F} = 32.8 Hz, C_q), 129.0 (CH), 128.9 (2C, CH), 128.5 (C_q), 128.2 (CH), 127.8 (2C, CH), 127.2 (C_q), 125.8 (q, ³J_{C-F} = 3.2 Hz, 2C, CH), 124.5 (CH), 124.0 (q, ¹J_{C-F} = 273.1 Hz, CF₃), 124.0 (CH), 123.7 (q, ¹J_{C-F} = 273.1 Hz, CF₃), 123.5 (q, ³J_{C-F} = 3.2 Hz, 2C, CH), 123.5 (CH), 123.1 (CH), 122.7 (CH), 122.5 (CH), 122.0 (CH), 118.3 (CH), 117.4 (C_q), 116.7 (C_q), 111.1 (CH). ¹⁹F-NMR (377 MHz, CDCl₃): δ = -62.9 (s), -63.3 (s). HRMS (ESI): *m/z* Calcd for C₄₂H₂₄N₄O₂F₆ + H⁺ [M + H]⁺ 731.1876; Found 731.1856.



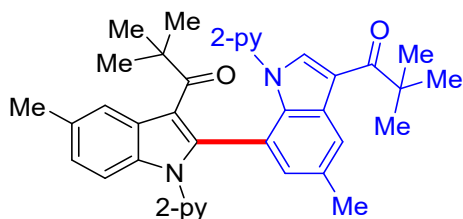
(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis((3-fluorophenyl)methanone)

(13): The representative procedure **B** was followed, using substrate **13a** (0.063 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **13** (0.041 g, 65%) as a yellow solid. M.pt: 188-192 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.58 (dd, *J* = 4.8, 0.9 Hz, 1H, Ar-H), 8.21 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar-H), 7.86 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.80-7.74 (m, 3H, Ar-H), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H, Ar-H), 7.65 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.57-7.54 (m, 2H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.38 (td, *J* = 7.8, 1.8 Hz, 1H, Ar-H), 7.32-7.26 (m, 3H, Ar-H), 7.22 (vt, *J* = 7.5 Hz, 1H, Ar-H), 7.11 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.00-6.97 (m, 1H, Ar-H), 6.93 (d, *J* = 7.5, 2H, Ar-H), 6.84-6.71 (m, 3H, Ar-H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 191.0 (d, ⁴J_{C-F} = 2.3 Hz, CO), 189.6 (d, ⁴J_{C-F} = 2.3 Hz, CO), 162.8 (d, ¹J_{C-F} = 257.9 Hz, C_q), 161.8 (d, ¹J_{C-F} = 246.4 Hz, C_q), 150.8 (C_q), 149.5 (CH), 147.6 (CH), 142.5 (C_q), 142.4 (d, ³J_{C-F} = 6.1 Hz, C_q), 142.1 (C_q), 141.3 (d, ³J_{C-F} = 6.1 Hz, C_q), 138.5 (CH), 138.1 (CH), 137.4 (CH), 136.8 (C_q), 135.8 (C_q), 130.4 (d, ³J_{C-F} = 7.6 Hz, CH), 128.7 (C_q), 128.4 (d, ³J_{C-F} = 7.6 Hz, CH), 128.2 (CH), 127.3 (C_q), 124.6 (d, ⁴J_{C-F} = 2.3 Hz, CH), 124.3 (CH), 123.8 (CH), 123.6 (d, ⁴J_{C-F} = 2.3 Hz, CH), 123.3 (CH), 123.3 (CH), 123.0 (CH), 122.7 (CH), 122.3 (CH), 121.8 (CH), 118.8 (d, ²J_{C-F} = 21.4 Hz, CH), 118.1 (CH), 117.6 (d, ²J_{C-F} = 21.3 Hz, CH), 117.4 (C_q), 116.9 (C_q), 116.5 (C_q), 115.8 (d, ²J_{C-F} = 22.1 Hz, CH), 114.5 (d, ²J_{C-F} = 22.1 Hz, CH), 111.2 (CH). ¹⁹F-NMR (377 MHz, CDCl₃): δ = -111.9 (s), -113.6 (s). HRMS (ESI): *m/z* Calcd for C₄₀H₂₄N₄O₂F₂ + H⁺ [M + H]⁺ 631.1940; Found 631.1926.



(1,1'-Di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(thiophen-2-ylmethanone) (14):

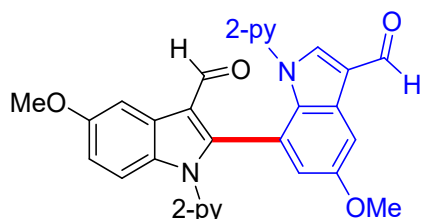
The representative procedure **B** was followed, using substrate **14a** (0.061 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **14** (0.032 g, 53%) as a brown solid. M.pt: >200 °C. ¹H-NMR (500 MHz, CDCl₃): δ = 8.59-8.57 (m, 1H, Ar-H), 8.54 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar-H), 8.51 (s, 1H, Ar-H), 7.75-7.73 (m, 2H, Ar-H), 7.62 (dd, *J* = 1.7, 0.8 Hz, 1H, Ar-H), 7.59-7.52 (m, 4H, Ar-H), 7.47 (td, *J* = 7.8, 1.9 Hz, 1H, Ar-H), 7.35 (dd, *J* = 3.5, 0.8 Hz, 1H, Ar-H), 7.25-7.17 (m, 4H, Ar-H), 7.14 (dd, *J* = 1.6, 0.6 Hz, 1H, Ar-H), 7.07 (dd, *J* = 7.4, 1.1 Hz, 1H, Ar-H), 6.80 (ddd, *J* = 7.4, 4.8, 0.9 Hz, 1H, Ar-H), 6.66 (dd, *J* = 3.6, 0.7 Hz, 1H, Ar-H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H, Ar-H), 6.12 (dd, *J* = 3.6, 1.7 Hz, 1H, Ar-H). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 178.5 (CO), 176.7 (CO), 154.3 (C_q), 152.8 (C_q), 151.1 (C_q), 150.8 (C_q), 149.1 (CH), 147.2 (CH), 145.5 (CH), 145.4 (CH), 141.1 (C_q), 138.3 (CH), 138.2 (CH), 137.3 (CH), 136.7 (C_q), 135.3 (C_q), 129.3 (C_q), 128.4 (CH), 127.2 (C_q), 124.0 (CH), 123.9 (CH), 123.0 (CH), 122.9 (CH), 122.7 (CH), 122.3 (CH), 122.2 (CH), 121.2 (CH), 118.8 (CH), 117.7 (CH), 117.1 (CH), 116.7 (C_q), 116.4 (C_q), 116.2 (C_q), 112.3 (CH), 111.7 (CH), 111.5 (CH).



1,1'-(5,5'-Dimethyl-1,1'-di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(2,2-dimethylpropan-1-one) (15):

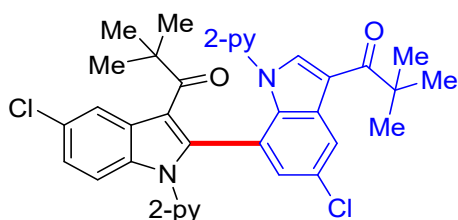
The representative procedure **B** was followed, using substrate **15a** (0.059 g, 0.202 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **15** (0.055 g, 93%) as a pale yellow liquid. ¹H-NMR (500 MHz, CDCl₃): δ = 8.41 (br s, 2H, Ar-H), 8.08 (s, 1H, Ar-H), 7.94 (d, *J* = 4.8 Hz, 1H, Ar-H), 7.50-7.42 (m, 3H, Ar-H), 7.21 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 7.10-7.05 (m, 2H, Ar-H), 6.99 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.93 (s, 1H, Ar-H), 6.80 (t, *J* = 6.0 Hz, 1H, Ar-H), 2.42 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 1.41 (s, 9H, CH₃), 1.02 (s, 9H, CH₃). ¹³C{¹H}-NMR

(125 MHz, CDCl₃): δ = 210.6 (CO), 203.2 (CO), 150.9 (C_q), 150.6 (C_q), 148.7 (CH), 147.2 (CH), 137.7 (CH), 137.3 (CH), 135.5 (C_q), 134.8 (CH), 134.4 (C_q), 132.7 (C_q), 132.5 (C_q), 131.1 (C_q), 130.8 (C_q), 129.5 (CH), 127.0 (C_q), 124.9 (CH), 124.3 (CH), 121.8 (2C, CH), 120.7 (CH), 119.9 (CH), 119.3 (C_q), 118.7 (CH), 116.7 (C_q), 114.6 (C_q), 111.7 (CH), 44.8 (C_q), 44.6 (C_q), 29.0 (3C, CH₃), 27.4 (3C, CH₃), 21.8 (CH₃), 21.4 (CH₃). HRMS (ESI): m/z Calcd for C₃₈H₃₈N₄O₂ + H⁺ [M + H]⁺ 583.3068; Found 583.3068.



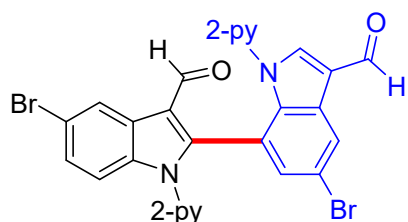
5,5'-Dimethoxy-1,1'-di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-dicarbaldehyde (16):

The representative procedure **B** was followed, using substrate **16a** (0.051 g, 0.202 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **16** (0.031 g, 61%) as a brown solid. M.pt: 188-192 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 10.09 (s, 1H, CHO), 9.49 (s, 1H, CHO), 8.53 (dd, J = 4.8, 1.1 Hz, 1H, Ar-H), 8.00 (s, 1H, Ar-H), 7.98 (d, J = 2.5 Hz, 1H, Ar-H), 7.82-7.79 (m, 1H, Ar-H), 7.63-7.58 (m, 2H, Ar-H), 7.46-7.40 (m, 3H, Ar-H), 7.33 (d, J = 8.0 Hz, 1H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 6.89 (dd, J = 9.0, 2.6 Hz, 1H, Ar-H), 6.83 (dd, J = 7.3, 4.9 Hz, 1H, Ar-H), 6.78 (d, J = 2.5 Hz, 1H, Ar-H), 3.86 (s, 3H, CH₃), 3.83 (s, 3H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 186.4 (CO), 185.4 (CO), 157.1 (C_q), 156.3 (C_q), 150.7 (C_q), 150.1 (C_q), 149.2 (CH), 148.0 (CH), 145.5 (C_q), 140.0 (CH), 138.5 (CH), 138.5 (CH), 131.8 (C_q), 130.9 (C_q), 128.0 (C_q), 125.8 (C_q), 123.1 (CH), 122.8 (CH), 121.3 (CH), 119.8 (C_q), 118.6 (CH), 118.2 (CH), 117.1 (C_q), 115.2 (C_q), 115.0 (CH), 112.9 (CH), 105.7 (CH), 102.6 (CH), 56.0 (CH₃), 55.9 (CH₃). HRMS (ESI): m/z Calcd for C₃₀H₂₂N₄O₄ + H⁺ [M + H]⁺ 503.1714; Found 503.1710.

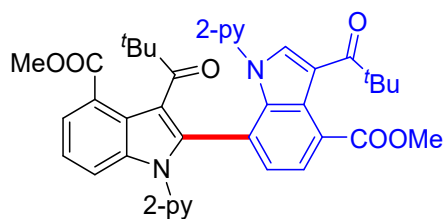


1,1'-(5,5'-Dichloro-1,1'-di(pyridin-2-yl)-1H,1'H-[2,7'-biindole]-3,3'-diyl)bis(2,2-dimethylpropan-1-one) (17): The representative procedure **B** was followed, using substrate **17a** (0.063 g, 0.201 mmol). Purification by column chromatography on silica gel (petroleum

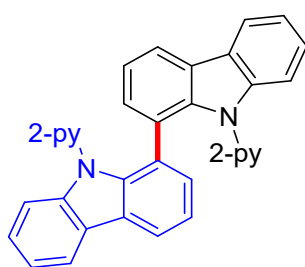
ether/EtOAc: 3/1) yielded **17** (0.052 g, 83%) as a colorless solid. M.pt: >200 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.62 (d, *J* = 2.1 Hz, 1H, Ar-H), 8.47 (dd, *J* = 4.8, 1.2 Hz, 1H, Ar-H), 8.08 (s, 1H, Ar-H), 7.81 (dd, *J* = 4.8, 1.1 Hz, 1H, Ar-H), 7.53 (td, *J* = 7.8, 1.9 Hz, 1H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 7.34-7.30 (m, 2H, Ar-H), 7.24 (s, 1H, Ar-H), 7.17 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H, Ar-H), 7.13 (dd, *J* = 8.9, 2.0 Hz, 1H, Ar-H), 7.02 (d, *J* = 2.1 Hz, 1H, Ar-H), 6.84-6.80 (m, 1H, Ar-H), 1.39 (s, 9H, CH₃), 0.96 (s, 9H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 209.0 (CO), 202.6 (CO), 150.5 (C_q), 150.2 (C_q), 149.1 (CH), 147.2 (CH), 138.3 (CH), 137.7 (CH), 135.6 (CH), 135.4 (C_q), 134.5 (C_q), 133.1 (C_q), 131.4 (C_q), 128.5 (C_q), 127.6 (CH), 127.5 (C_q), 127.3 (C_q), 124.3 (CH), 124.0 (CH), 122.7 (CH), 122.3 (CH), 121.0 (CH), 119.8 (CH), 119.0 (C_q), 118.9 (CH), 117.7 (C_q), 114.5 (C_q), 113.2 (CH), 44.9 (C_q), 44.7 (C_q), 28.8 (3C, CH₃), 27.3 (3C, CH₃). HRMS (ESI): *m/z* Calcd for C₃₆H₃₂N₄O₂Cl₂ [M]⁺ 623.1975; Found 623.1965. The structure of compound **17** is confirmed through a single crystal X-ray analysis (Figure S3).



5,5'-Bibromo-1,1'-di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-3,3'-dicarbaldehyde (18): The representative procedure **B** was followed, using substrate **18a** (0.060 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 2/1) yielded **18** (0.047 g, 78%) as a yellow solid. M.pt: 128-132 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 10.12 (s, 1H, CHO), 9.46 (s, 1H, CHO), 8.68 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.58 (dd, *J* = 4.9, 1.3 Hz, 1H, Ar-H), 8.25 (s, 1H, Ar-H), 8.04 (s, 1H, Ar-H), 7.78 (dd, *J* = 4.8, 1.2 Hz, 1H, Ar-H), 7.68 (td, *J* = 7.8, 1.9 Hz, 1H, Ar-H), 7.51 (td, *J* = 7.8, 1.9 Hz, 1H, Ar-H), 7.48 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.39-7.37 (m, 3H, Ar-H), 7.34-7.31 (m, 1H, Ar-H), 7.25 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.91-6.88 (m, 1H, Ar-H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 185.5 (CO), 184.9 (CO), 150.5 (C_q), 149.6 (CH), 149.5 (C_q), 148.2 (CH), 144.7 (C_q), 140.2 (CH), 138.9 (CH), 138.8 (CH), 135.7 (C_q), 134.8 (C_q), 131.2 (CH), 128.4 (C_q), 128.0 (CH), 127.0 (CH), 126.4 (C_q), 124.2 (CH), 123.7 (CH), 123.4 (CH), 121.6 (CH), 119.4 (C_q), 118.7 (CH), 117.5 (C_q), 116.7 (C_q), 116.7 (C_q), 115.5 (C_q), 113.4 (CH). HRMS (ESI): *m/z* Calcd for C₂₈H₁₆N₄O₂Br₂ [M]⁺ 600.9692; Found 600.9675.



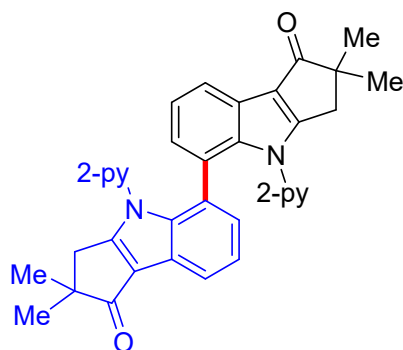
Dimethyl 3,3'-dipivaloyl-1,1'-di(pyridin-2-yl)-1H, 1'H-[2,7'-biindole]-4,4'-dicarboxylate (19): The representative procedure **B** was followed, using substrate **19a** (0.067 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **19** (0.049 g, 73%) as a yellow solid. M.pt: 168-172 °C. ¹H-NMR (500 MHz, CDCl₃): δ = 8.62 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.81 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.79-7.76 (m, 2H, Ar-H), 7.74 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.57 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.53 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.39 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.32 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.27-7.23 (m, 2H, Ar-H), 6.94 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.56 (dd, *J* = 7.2, 5.0 Hz, 1H, Ar-H), 3.89 (s, 3H, CH₃), 3.80 (s, 3H, CH₃), 1.43 (s, 9H, CH₃), 0.72 (s, 9H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 208.0 (CO), 204.5 (CO), 168.7 (CO), 167.6 (CO), 152.1 (C_q), 150.8 (C_q), 148.9 (CH), 145.8 (CH), 138.8 (CH), 137.8 (CH), 137.0 (C_q), 136.6 (C_q), 135.6 (C_q), 132.7 (CH), 127.6 (CH), 127.2 (C_q), 126.3 (C_q), 125.0 (C_q), 124.7 (CH), 122.8 (CH), 122.6 (CH), 122.4 (CH), 122.3 (CH), 122.1 (C_q), 121.8 (C_q), 121.5 (CH), 120.8 (CH), 118.8 (C_q), 117.6 (C_q), 116.7 (CH), 52.3 (CH₃), 51.9 (CH₃), 46.6 (C_q), 44.8 (C_q), 28.3 (3C, CH₃), 27.2 (3C, CH₃). HRMS (ESI): *m/z* Calcd for C₄₀H₃₈N₄O₆ + H⁺ [M + H]⁺ 671.2864; Found 671.2840.



9,9'-Di(pyridin-2-yl)-9H, 9'H-1,1'-bicarbazole (20): The representative procedure **B** was followed, using substrate **20a** (0.049 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **20** (0.041 g, 84%) as a white solid. M.pt: >200 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.94 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.67 (d, *J* = 4.4 Hz, 2H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.30-7.23 (m, 4H, Ar-H), 7.18 (t, *J* = 7.5 Hz, 4H, Ar-H), 7.07 (br s, 2H, Ar-H), 6.99 (t, *J* = 6.9 Hz, 2H, Ar-H), 6.74-6.72 (m, 2H, Ar-H). HRMS (ESI): *m/z* Calcd for C₃₄H₂₂N₄ + H⁺ [M + H]⁺ 487.1917;

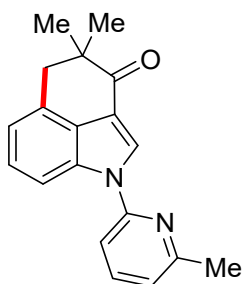
Found 487.1911.

Note: Compound 20 is partially soluble in most of the deuterated solvents; therefore, a good $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound could not be obtained. However, the molecular structure of the compound 20 is confirmed by single crystal X-ray analysis (Figure S4).

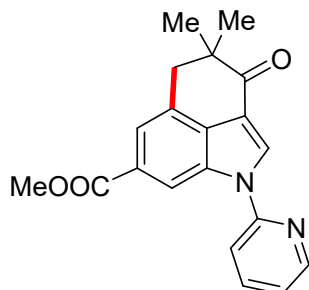


2,2,2',2'-Tetramethyl-4,4'-di(pyridin-2-yl)-3,3',4,4'-tetrahydro-[5,5'-

bi(cyclopenta[*b*]indole)]-1,1' (2*H*, 2'*H*)-dione (21): The representative procedure **B** was followed, using substrate **21a** (0.055 g, 0.20 mmol) at 120 °C for 24 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 2/1) yielded **21** (0.024 g, 44%) as a brown solid. M.pt: >200 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.89 (d, J = 3.9 Hz, 2H, Ar-H), 7.67 (dd, J = 7.8, 1.3 Hz, 2H, Ar-H), 7.35-7.3 (m, 2H, Ar-H), 7.27 (t, J = 7.6 Hz, 2H, Ar-H), 7.10-7.07 (m, 2H, Ar-H), 6.82-6.79 (m, 4H, Ar-H), 3.12 (d, J = 17.9 Hz, 2H, CH_2), 2.51 (d, J = 17.9 Hz, 2H, CH_2), 1.39 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ = 201.2 (2C, CO), 165.5 (2C, C_q), 148.4 (2C, C_q), 147.1 (2C, CH), 138.9 (2C, C_q), 135.8 (2C, CH), 126.0 (2C, CH), 124.7 (2C, C_q), 123.3 (2C, CH), 122.7 (2C, C_q), 122.3 (2C, CH), 120.6 (2C, CH), 118.6 (2C, CH), 118.6 (2C, C_q), 51.3 (2C, C_q), 38.2 (2C, CH_2), 26.3 (2C, CH_3), 25.6 (2C, CH_3). HRMS (ESI): m/z Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_4\text{O}_2 + \text{H}^+$ [$\text{M} + \text{H}$] $^+$ 551.2442; Found 551.2440. The structure of compound **21** is confirmed through a single crystal X-ray analysis (Figure S5).



4,4-Dimethyl-1-(6-methylpyridin-2-yl)-4,5-dihydrobenzo[cd]indol-3(1H)-one (22): The representative procedure **B** was followed, using substrate **22a** (0.059 g, 0.202 mmol) at 120 °C for 24 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) yielded **22** (0.041 g, 70%) as a yellow solid. M.pt: 132-136 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 7.99-7.97 (m, 1H, Ar-H), 7.82-7.76 (m, 2H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.32-7.28 (m, 2H, Ar-H), 7.19 (d, *J* = 7.6 Hz, 1H, Ar-H), 3.17 (s, 2H, CH₂), 2.63 (s, 3H, CH₃), 1.34 (s, 6H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 201.7 (CO), 164.5 (C_q), 159.3 (C_q), 149.8 (C_q), 141.9 (C_q), 139.1 (CH), 124.2 (CH), 123.3 (CH), 122.7 (C_q), 121.8 (CH), 121.3 (CH), 120.0 (C_q), 114.3 (CH), 112.6 (CH), 51.4 (C_q), 39.7 (CH₂), 25.9 (2C, CH₃), 24.5 (CH₃). HRMS (ESI): *m/z* Calcd for C₁₉H₁₈N₂O + H⁺ [M + H]⁺ 291.1492; Found 291.1491.



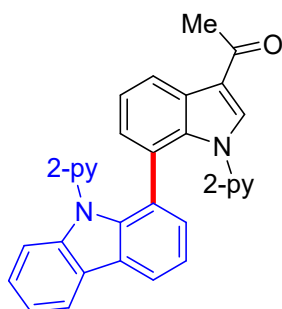
Methyl 4,4-dimethyl-3-oxo-1-(pyridin-2-yl)-1,3,4,5-tetrahydrobenzo[cd]indole-7-carboxylate (23): The representative procedure **B** was followed, using substrate **23a** (0.067 g, 0.20 mmol) at 120 °C for 24 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) yielded **23** (0.038 g, 57%) as a brown solid. M.pt: 144-148 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.68-8.66 (m, 1H, Ar-H), 8.47 (t, *J* = 1.0 Hz, 1H, Ar-H), 8.02 (d, *J* = 1.0 Hz, 2H, Ar-H), 8.01-7.97 (m, 1H, Ar-H), 7.61 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.40 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H, Ar-H), 3.94 (s, 3H, CH₃), 3.22 (s, 2H, CH₂), 1.36 (s, 6H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 201.5 (CO), 167.6 (CO), 166.6 (C_q), 150.2 (C_q), 150.0 (CH), 141.5 (C_q), 139.3 (CH), 126.4 (C_q), 126.1 (C_q), 124.7 (CH), 122.8 (CH), 121.0 (CH), 120.1 (C_q), 117.8 (CH), 114.4 (CH), 52.4 (CH₃), 51.6 (C_q), 39.8 (CH₂), 25.8 (2C,

CH₃). HRMS (ESI): *m/z* Calcd for C₂₀H₁₈N₂O₃ + H⁺ [M + H]⁺ 335.1390; Found 335.1386.

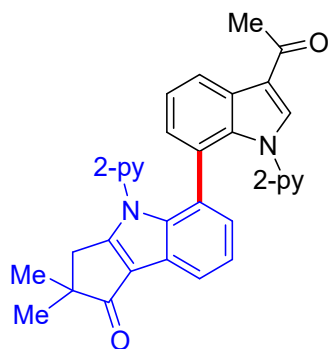
7. Procedure for the Heterocoupling of Indoles (*Representative Procedure C*)

Synthesis of 1-(1-(Pyridin-2-yl)-7-(9-(pyridin-2-yl)-9*H*-carbazol-1-yl)-1*H*-indol-3-yl)ethan-1-one (24): To an oven-dried screw-cap tube equipped with magnetic stir bar were introduced 1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)ethan-1-one (**1a**; 0.048 g, 0.203 mmol), 9-(pyridin-2-yl)-9*H*-carbazole (**20a**; 0.049 g, 0.20 mmol), K₂S₂O₈ (0.217 g, 0.803 mmol), and Pd(OAc)₂ (0.0027 g, 0.012 mmol), followed by the addition of TFE (2 mL) and TFA (0.091 g, 0.80 mmol). The resultant reaction mixture was immersed in a preheated oil bath at 80 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, and all the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) to yield compounds **24** (0.022 g, 23%), **1** (0.026 g, 28%), and **20** (0.030 g, 31%).

8. Characterization Data for C2–C7 Heterocoupled Indoles



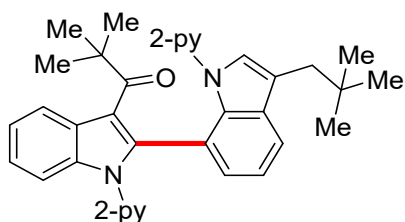
1-(1-(Pyridin-2-yl)-7-(9-(pyridin-2-yl)-9*H*-carbazol-1-yl)-1*H*-indol-3-yl)ethan-1-one (24): ¹H-NMR (500 MHz, CDCl₃): δ = 8.55 (dd, *J* = 4.8, 1.3 Hz, 1H, Ar-H), 8.17-8.15 (m, 3H, Ar-H), 7.73-7.70 (m, 2H, Ar-H), 7.55-7.50 (m, 3H, Ar-H), 7.45-7.41 (m, 1H, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.24-7.22 (m, 2H, Ar-H), 7.21-7.19 (m, 1H, Ar-H), 7.17-7.15 (m, 1H, Ar-H), 7.13-7.11 (m, 1H, Ar-H), 6.72-6.68 (m, 1H, Ar-H), 1.79 (s, 3H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 194.6 (CO), 150.9 (C_q), 150.7 (C_q), 149.1 (CH), 148.6 (CH), 141.9 (C_q), 141.3 (C_q), 139.9 (C_q), 138.3 (CH), 138.1 (CH), 136.6 (C_q), 129.2 (CH), 126.9 (CH), 125.0 (C_q), 123.9 (CH), 123.4 (C_q), 123.2 (CH), 123.0 (CH), 122.8 (CH), 122.5 (CH), 122.3 (CH), 121.6 (2C, CH), 121.2 (CH), 120.5 (CH), 120.2 (CH), 118.0 (C_q), 115.9 (2C, C_q), 111.2 (CH), 110.2 (CH), 29.7 (CH₃). HRMS (ESI): *m/z* Calcd for C₃₂H₂₂N₄O + H⁺ [M + H]⁺ 479.1866; Found 479.1870.



5-(3-Acetyl-1-(pyridin-2-yl)-1*H*-indol-7-yl)-2,2-dimethyl-4-(pyridin-2-yl)-3,4-

dihydrocyclopenta[*b*]indol-1(2*H*)-one (25): The representative procedure C was followed, using 1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)ethan-1-one (**1a**; 0.048 g, 0.202 mmol) and 2,2-dimethyl-4-(pyridin-2-yl)-3,4-dihydrocyclopenta[*b*]indol-1(2*H*)-one (**21a**; 0.055 g, 0.20 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) to yield compounds **25** (0.028 g, 27%), **1** (0.020 g, 21%), and **21** (0.005 g, 5%). ¹H-NMR (500 MHz, CDCl₃): δ = 8.16 (d, *J* = 7.9 Hz, 1H, Ar-H), 8.02 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.92 (d, *J* = 4.3 Hz, 1H, Ar-H), 7.89 (s, 1H, Ar-H), 7.69 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.38 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.31 (td, *J* = 7.5, 2.7 Hz, 2H, Ar-H), 7.04 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.00-6.96 (m, 1H, Ar-H), 6.82 (dd, *J* = 7.4, 5.0 Hz, 1H, Ar-H), 6.74 (dd, *J* = 7.4, 5.0 Hz, 1H, Ar-H), 6.63 (br s, 1H, Ar-H), 6.54 (d, *J* = 7.9 Hz, 1H, Ar-H), 3.14 (d, *J* = 17.9 Hz, 1H, CH₂), 2.49 (d, *J* = 17.9 Hz, 1H, CH₂), 2.49 (s, 3H, CH₃), 1.37 (s, 3H, CH₃), 1.17 (s, 3H, CH₃). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ = 201.3 (CO), 193.4 (CO), 165.8 (C_q), 149.4 (C_q), 148.1 (C_q), 147.2 (2C, CH), 139.1 (C_q), 136.1 (CH), 135.6 (CH), 135.6 (CH), 132.9 (C_q), 127.4 (C_q), 125.9 (CH), 125.7 (CH), 125.1 (C_q), 123.9 (C_q), 123.6 (CH), 123.5 (CH), 122.8 (C_q), 122.5 (CH), 122.2 (CH), 121.8 (CH), 120.6 (CH), 118.6 (C_q), 118.5 (C_q), 118.0 (CH), 118.0 (CH), 51.3 (C_q), 38.2 (CH₂), 27.7 (CH₃), 26.3 (CH₃), 25.5 (CH₃). HRMS (ESI): *m/z* Calcd for (compound **25**) C₃₃H₂₆N₄O₂ + H⁺ [M + H]⁺ 511.2129; Found 511.2115. The structure of compound **25** is confirmed through a single crystal X-ray analysis (Figure S6).

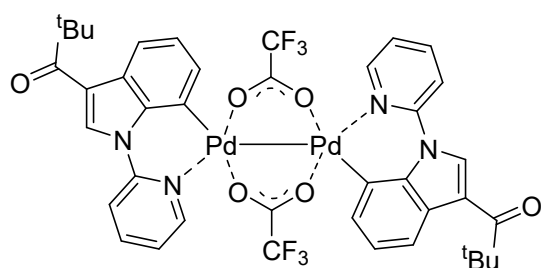
9. Procedure for Synthetic Utility



Synthesis of Compound 26: To a solution of 1,1'-(1,1'-di(pyridin-2-yl)-1*H*, 1'*H*-[2,7'-

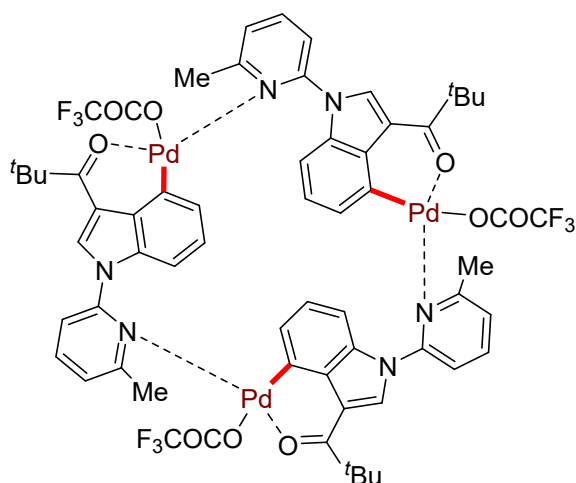
biindole]-3,3'-diyl)bis(2,2-dimethylpropan-1-one) (**3**; 0.05 g, 0.09 mmol) in trifluoroacetic acid (0.5 mL) was added Et₃SiH (0.144 mL, 0.9 mmol) under argon at room temperature. The reaction mixture was stirred at 50 °C for 12 h. At ambient temperature, the resultant mixture was quenched with aqueous sodium bicarbonate and saturated brine solution. The crude product was extracted with EtOAc (10 mL x 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 3/1) to yield **26** (0.035 g, 72%) as white solid. M.pt: 145-149 °C. ¹H-NMR (400 MHz, CDCl₃): δ = 8.50 (dd, *J* = 4.9, 1.1 Hz, 1H, Ar-H), 7.66 (d, *J* = 4.5 Hz, 1H, Ar-H), 7.62-7.59 (m, 2H, Ar-H), 7.46-7.42 (m, 1H, Ar-H), 7.37-7.32 (m, 4H, Ar-H), 7.21 (s, 1H, Ar-H), 7.18-7.14 (m, 1H, Ar-H), 7.13-7.07 (m, 3H, Ar-H), 7.00-6.98 (m, 1H, Ar-H), 6.69-6.65 (m, 1H, Ar-H), 2.59-2.72 (m, 2H, CH₂), 0.96 (s, 9H, CH₃), 0.87 (s, 9H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 210.3 (CO), 151.5 (C_q), 151.3 (C_q), 148.6 (CH), 146.5 (CH), 137.7 (CH), 137.3 (CH), 136.1 (C_q), 135.8 (C_q), 134.5 (C_q), 132.8 (C_q), 128.4 (CH), 127.4 (C_q), 126.8 (CH), 123.1 (CH), 121.9 (CH), 121.6 (CH), 121.4 (CH), 120.7 (CH), 120.3 (CH), 120.2 (CH), 119.9 (CH), 118.7 (C_q), 117.6 (C_q), 117.4 (CH), 116.3 (C_q), 111.7 (CH), 45.0 (C_q), 38.9 (CH₂), 32.3 (C_q), 29.9 (3C, CH₃), 27.3 (3C, CH₃). HRMS (ESI): *m/z* Calcd for C₃₆H₃₆N₄O + H⁺ [M + H]⁺ 541.2962; Found 541.2957. The structure of compound **26** is confirmed through a single crystal X-ray analysis (Figure S7).

10. Procedure for Synthesis of Complexes **27** and **28**



Synthesis of Palladium Complex **27:** To a Schlenk tube (10 mL) was added 2,2-dimethyl-1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**3a**; 0.030 g, 0.108 mmol), Pd(OAc)₂ (0.024 g, 0.107 mmol) and TFA (1 mL). The reaction mixture was stirred at room temperature for 24 h. Then, the reaction mixture was filtered, and the volatiles were evaporated under reduced pressure and washed with hexane to give the desired palladacycle product **27**, yielded (0.050 g, 94%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 8.98 (s, 2H, Ar-H), 8.80 (br s, 2H, Ar-H), 8.47 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.20-8.17 (m, 2H, Ar-

H), 7.91 (d, $J = 7.1$ Hz, 2H, Ar-H), 7.34 (t, $J = 6.5$ Hz, 2H, Ar-H), 7.05 (br s, 4H, Ar-H), 1.41 (s, 18H, CH₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃): $\delta = 202.1$ (2C, CO), 150.1 (2C, CH), 144.9 (2C, C_q), 141.0 (2C, CH), 131.0 (2C, C_q), 128.9 (2C, CH), 128.4 (2C, C_q), 125.5 (2C, C_q), 123.2 (2C, CH), 120.1 (2C, CH), 118.9 (2C, CH), 118.8 (2C, CH), 118.5 (2C, C_q), 114.9 (2C, CH), 44.0 (2C, C_q), 28.0 (6C, CH₃). ¹⁹F-NMR (377 MHz, CDCl₃): $\delta = -73.8$ (s). The structure of compound **27** is confirmed through a single crystal X-ray analysis (Figure S8).



Synthesis of Palladium Complex 28: To a pressure tube (10 mL) was added 2,2-dimethyl-1-(1-(6-methylpyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**23a**; 0.029 g, 0.10 mmol), Pd(OAc)₂ (0.023 g, 0.10 mmol) and TFA (1 mL). The reaction mixture was stirred at room temperature for 24 h. Then, the reaction mixture was filtered, and the volatiles were evaporated under reduced pressure and washed with hexane to give the desired palladacycle product **28**, yielded (0.045 g, 88%) as a grey solid. ¹H-NMR (500 MHz, DMSO-*d*₆): $\delta = 8.00$ -7.77 (m, 4H, Ar-H), 7.41 (br s, 1H, Ar-H), 7.18 (br s, 2H, Ar-H), 2.59 (br s, 3H, CH₃), 1.49 (br s, 9H, CH₃). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): $\delta = 200.5$ (CO), 158.1 (C_q), 149.3 (C_q), 139.9 (CH), 137.6 (CH), 132.3 (C_q), 127.5 (C_q), 123.7 (CH), 123.0 (CH), 117.1 (C_q), 115.6 (CH), 115.2 (C_q), 114.9 (CH), 111.3 (CH), 43.2 (C_q), 29.3 (3C, CH₃), 23.8 (CH₃). ¹⁹F-NMR (377 MHz, CDCl₃): $\delta = -73.2$ (s). The structure of compound **28** is confirmed through a single crystal X-ray analysis (Figure S9).

11. Procedure for *H/D* Scrambling Experiment

To an oven-dried screw-cap tube equipped with magnetic stir bar were introduced 2,2-dimethyl-1-(1-(pyridin-2-yl)-1*H*-indol-3-yl)propan-1-one (**3a**; 0.056 g, 0.20 mmol), K₂S₂O₈ (0.108 g, 0.40 mmol), and Pd(OAc)₂ (0.0014 g, 0.006 mmol, 6.0 mol%), followed by the addition of TFA (0.046 g, 0.4 mmol) and TFE (1.0 mL). To the resulting mixture, D₂O (0.040

g, 2.0 mmol) was added and stirred at 80 °C in a preheated oil bath for 1 h. The reaction mixture was allowed to cool to room temperature, and all the volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc: 5/1) to recover the starting compound. The ¹H NMR analysis of the recovered compound does not show incorporation of deuterium at the C(2)–H or C(7)–H position.

12. X-ray Structural Analysis

Crystal of compounds **2**, **7**, **17**, **20**, **21**, **25**, **26**, **27** and **28** were grown by slow evaporation of DCE/n-hexane. X-ray intensity data measurements of compounds **2**, **7**, **17**, **20**, **21**, **25**, **26**, **27** and **28** were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (MoK_α= 0.71073 Å) at low temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three matrix sets of 36 frames (each matrix run consists of 12 frames). Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10-20 sec depending on the diffraction power of the crystals keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).^{S6} All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)^{S7} structure solution program, using direct methods. The model was refined with a version of ShelXL-2018/3 (Sheldrick, 2015)^{S8} using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP* III^{S9} view of the compounds was drawn with 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii. The crystal data for all the compounds is summarized in Table S2 and S3. CCDC: 2365832 (compound **2**), CCDC: 2365829 (compound **7**), CCDC: 2365830 (compound **17**), CCDC: 2365825 (compound **20**), CCDC: 2365833 (compound **21**), CCDC: 2365831 (compound **25**), CCDC: 2365828 (compound **26**), CCDC: 2365827 (compound **27**) (CIF), and CCDC: 2365826 (compound **28**).

Table S2. Crystal data of compounds 2, 7, 17, 20 and 21.

Crystal Data	2	7	17	20	21
Formula	C ₃₄ H ₃₀ N ₄ O ₂	C ₂₈ H ₁₈ N ₄ O ₂	C ₃₆ H ₃₂ Cl ₂ N ₄ O ₂ , 0.5(CH ₃ CH ₂ CO OCH ₃)	C ₃₄ H ₂₂ N ₄	C ₃₆ H ₃₂ N ₄ O ₃ , 0.5(C ₇ H ₈)
Molecular weight	526.62	442.46	667.61	486.55	614.72
Crystal Size, mm	0.12 × 0.06 × 0.03	0.14 × 0.11 × 0.07	0.33 × 0.18 × 0.11	0.09 × 0.08 × 0.06	0.144 × 0.05 × 0.03
Temp. (K)	105(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal Syst.	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space Group	<i>C2/c</i>	<i>Pna2₁</i>	<i>P-1</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> (Å)	17.7407(14)	17.8407(10)	9.1994(3)	12.5223(8)	25.5909(11)
<i>b</i> (Å)	11.1622(10)	8.7838(5)	13.5661(5)	12.3066(7)	14.0921(6)
<i>c</i> (Å)	27.225(2)	13.7388(8)	14.2548(5)	15.2608(10)	20.2630(9)
α (°)	90	90	93.7000(10)	90	90
β (°)	90.328(3)	90	100.6210(10)	90.707(2)	120.7910(10)
γ (°)	90	90	107.1050(10)	90	90
<i>V</i> /Å ³	5391.2(8)	2153.0(2)	1657.77(10)	2351.6(3)	6277.4(5)
<i>Z</i>	8	4	2	4	8
<i>D</i> _{calc} /g cm ⁻³	1.298	1.365	1.337	1.374	1.301
μ /mm ⁻¹	0.082	0.089	0.240	0.082	0.083
<i>F</i> (000)	2224	920	700	1016	2600
<i>Ab. Correct.</i>	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.6675/0.7457	0.6271/0.7462	0.6384/0.7467	0.5783/0.7462	0.6748/0.7457
2 θ _{max}	56.66	62.68	68	62	56.6
Total reflns.	70627	43471	52079	69074	97240
Unique reflns.	6648	6034	11451	7479	7781
Obs. reflns.	3945	5640	9434	5271	5767
<i>h, k, l</i> (min, max)	(-22, 23), (-14, 14), (-36, 33)	(-20, 26), (-12, 12), (-20, 20)	(-12, 14), (-21, 17), (-22, 22)	(-23, 23), (-12, 12), (-26, 26)	(-34, 34), (-18, 17), (-27, 27)
<i>R</i> _{int} / <i>R</i> _{sig}	0.1418/0.0780	0.0484/0.0323	0.0455/0.0388	0.1027/0.0612	0.0866/0.0391
No. of para./restraints	366/24	307/1	403/0	343	398
<i>RI</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0633	0.0402	0.0469	0.0598	0.0445
<i>wR2</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.1423	0.0980	0.1072	0.1332	0.0973
<i>RI</i> [all data]	0.1354	0.0450	0.0609	0.0955	0.0693
<i>wR2</i> [all data]	0.1858	0.1018	0.1162	0.1519	0.1097
goodness-of-fit	1.052	1.036	1.032	1.051	1.030
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (eÅ ⁻³)	+0.402, -0.439	+0.310, -0.213	+0.679, -0.539	+0.432, -0.307	+0.279, -0.244
CCDC No.	2365832	2365829	2365830	2365825	2365833

Table S3. Crystal data of compounds 25, 26, 27 and 28.

Crystal Data	25	26	27	28
Formula	C ₃₃ H ₂₈ N ₄ O ₃	C ₃₆ H ₃₆ N ₄ O	C ₄₀ H ₃₄ F ₆ N ₄ O ₆ Pd ₂ , 3(ClCH ₂ CH ₂ Cl)	C ₆₃ H ₅₇ F ₉ N ₆ O ₉ Pd ₃ , 1.50 (CH ₃ SOCH ₃)
Molecular weight	528.59	540.69	1308.36	1649.53
Crystal Size, mm	0.10 × 0.09 × 0.08	0.13 × 0.10 × 0.09	0.11 × 0.09 × 0.06	0.11 × 0.09 × 0.07
Temp. (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal Syst.	monoclinic	monoclinic	triclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.2208(6)	10.4599(4)	11.1926(3)	15.9963(7)
<i>b</i> (Å)	16.2811(8)	24.1253(8)	14.3110(4)	21.8997(12)
<i>c</i> (Å)	13.3170(7)	11.7099(4)	15.3221(4)	20.1858(11)
<i>α</i> (°)	90	90	74.2790(10)	90
<i>β</i> (°)	115.094(2)	96.3960(10)	75.9160(10)	90.029(2)
<i>γ</i> (°)	90	90	69.7240(10)	90
<i>V</i> /Å ³	2595.9(2)	2936.58(18)	2185.49(10)	7071.4(6)
<i>Z</i>	4	4	2	4
<i>D</i> _{calc} /g cm ⁻³	1.353	1.223	1.988	1.549
<i>μ</i> /mm ⁻¹	0.088	0.075	1.279	0.082
<i>F</i> (000)	1112	1152	1310	3324
<i>Ab. Correct.</i>	multi-scan	multi-scan	multi-scan	multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.6236/0.7457	0.6591/0.7465	0.6158/0.7457	0.5656/0.7458
2 <i>θ</i> _{max}	56.66	66.12	56.60	52
Total reflns.	65679	102626	61959	174764
Unique reflns.	6403	10655	10805	13864
Obs. reflns.	5431	8580	9883	11404
<i>h, k, l</i> (min, max)	(-17, 17), (-21, 21), (-17, 17)	(-16, 15), (-28, 36), (-17, 17)	(-14, 11), (-19, 19), (-20, 20)	(-18, 19), (-27, 27), (-24, 24)
<i>R</i> _{int} / <i>R</i> _{sig}	0.0528/0.0259	0.0622/0.0414	0.0405/0.0259	0.1091/0.0431
No. of para./restraints	370/0	376/0	602/122	978/180
<i>RI</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0482	0.0587	0.0316	0.0576
<i>wR2</i> [<i>I</i> > 2σ(<i>I</i>)]	0.1144	0.1309	0.0769	0.1422
<i>RI</i> [all data]	0.0588	0.0795	0.0352	0.0724
<i>wR2</i> [all data]	0.1224	0.1416	0.0793	0.1549
goodness-of-fit	1.037	1.073	1.027	1.021
Δρ _{max} , Δρ _{min} (eÅ ⁻³)	+0.450, -0.265	+0.445, -0.294	+2.144, -1.000	+3.924, -1.701
CCDC No.	2365831	2365828	2365827	2365826

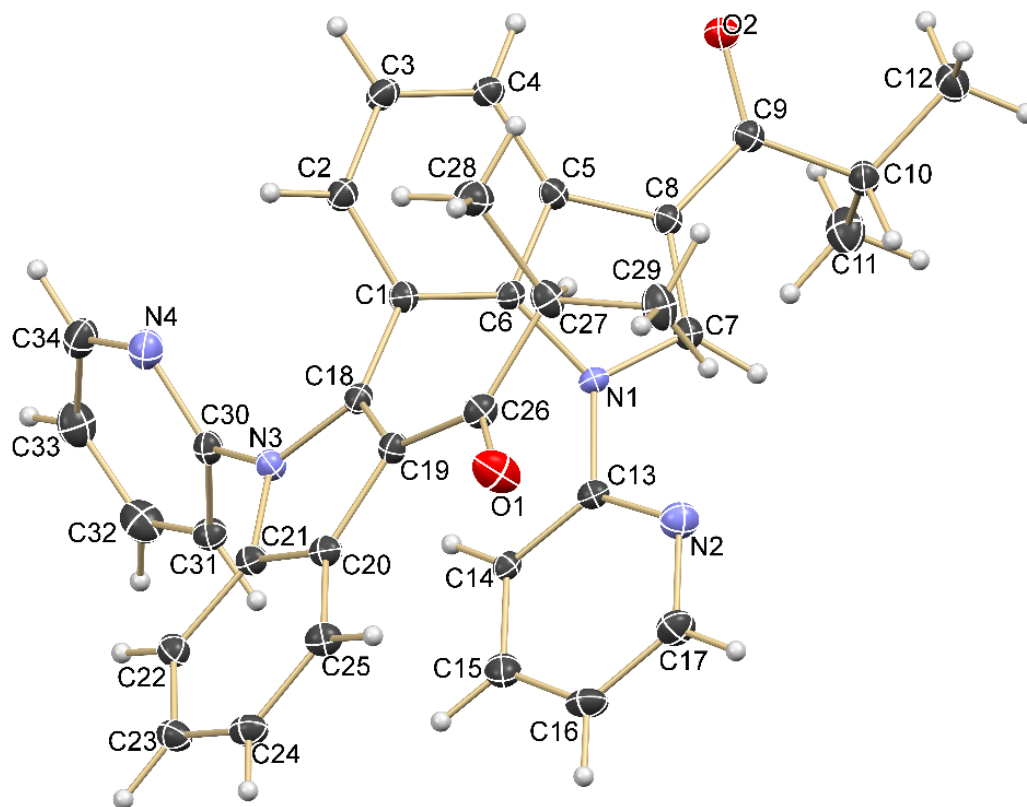


Fig S1 ORTEP of compound 2 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

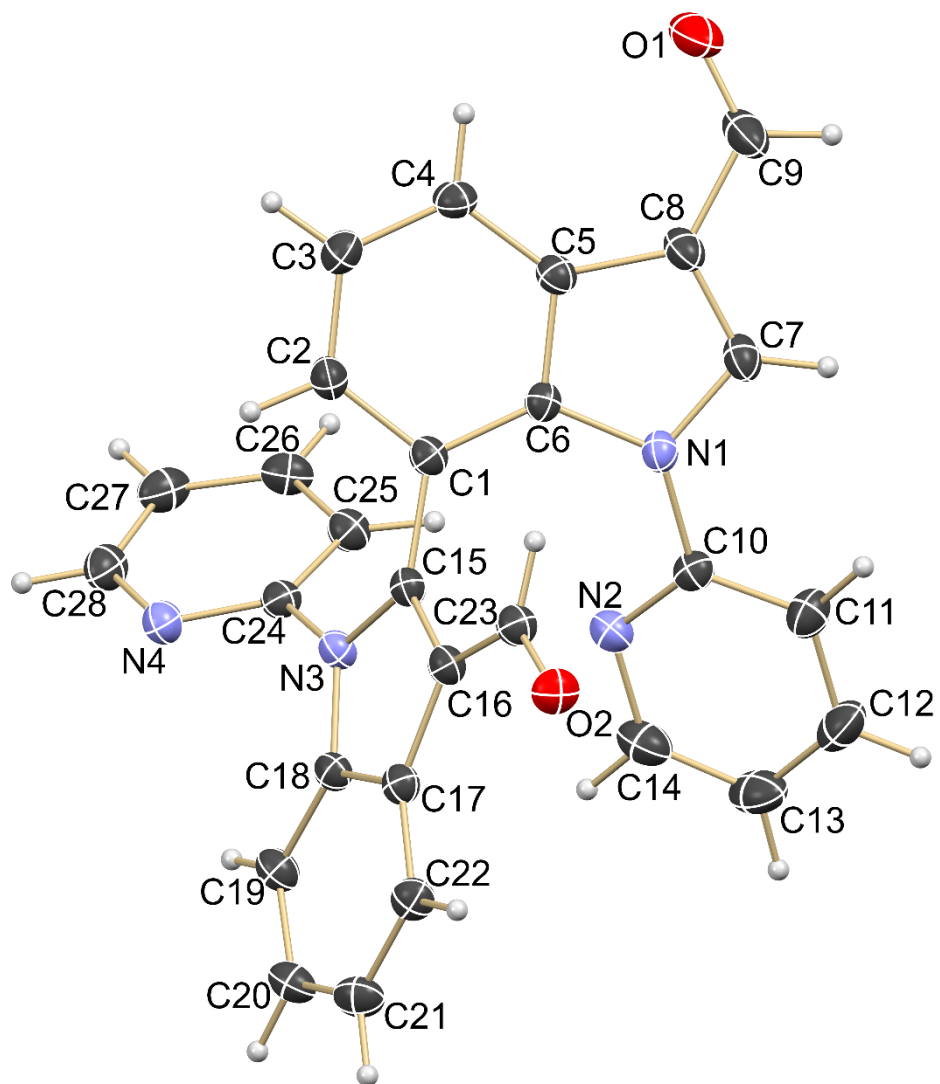


Fig S2 ORTEP of compound 7 showing the atom-numbering scheme for both conformers present in the asymmetric unit. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

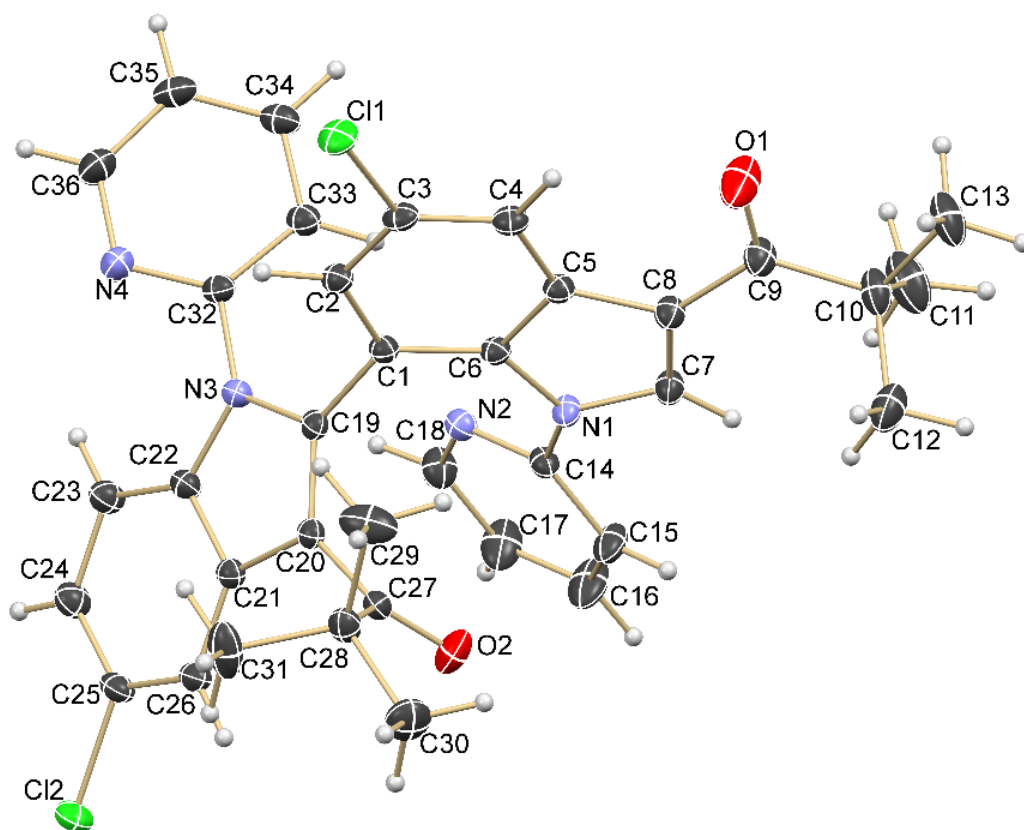


Fig S3 ORTEP of compound 17 showing the atom-numbering scheme for both conformers present in the asymmetric unit. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

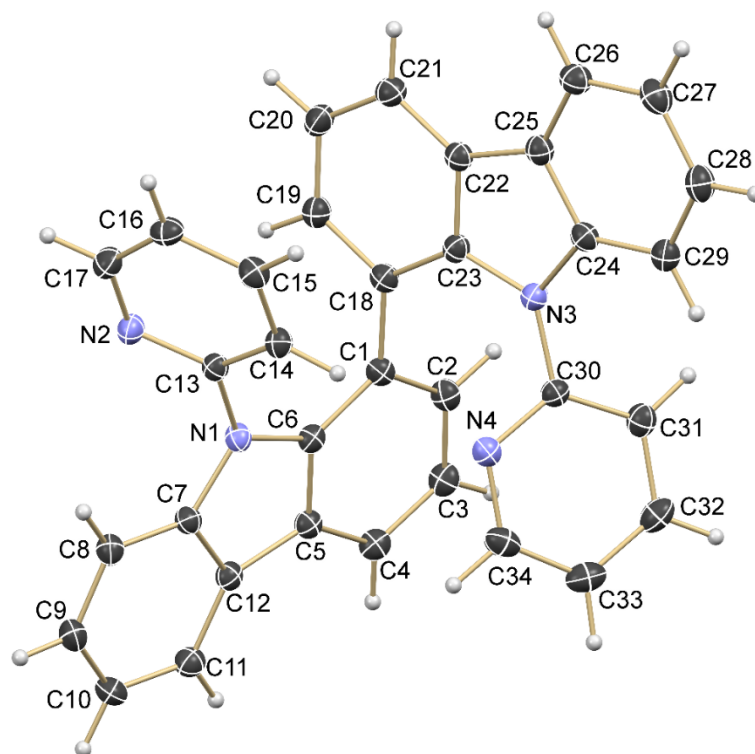


Fig S4 ORTEP of compound 20 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

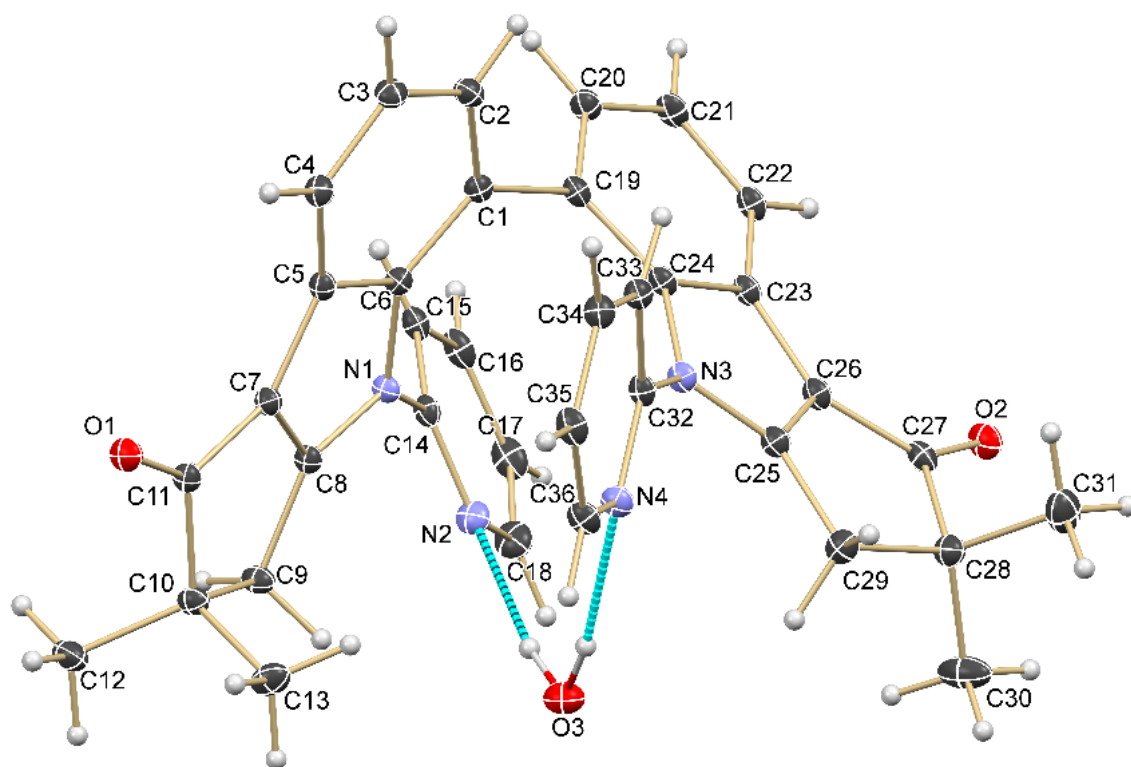


Fig S5 ORTEP of compound 21 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

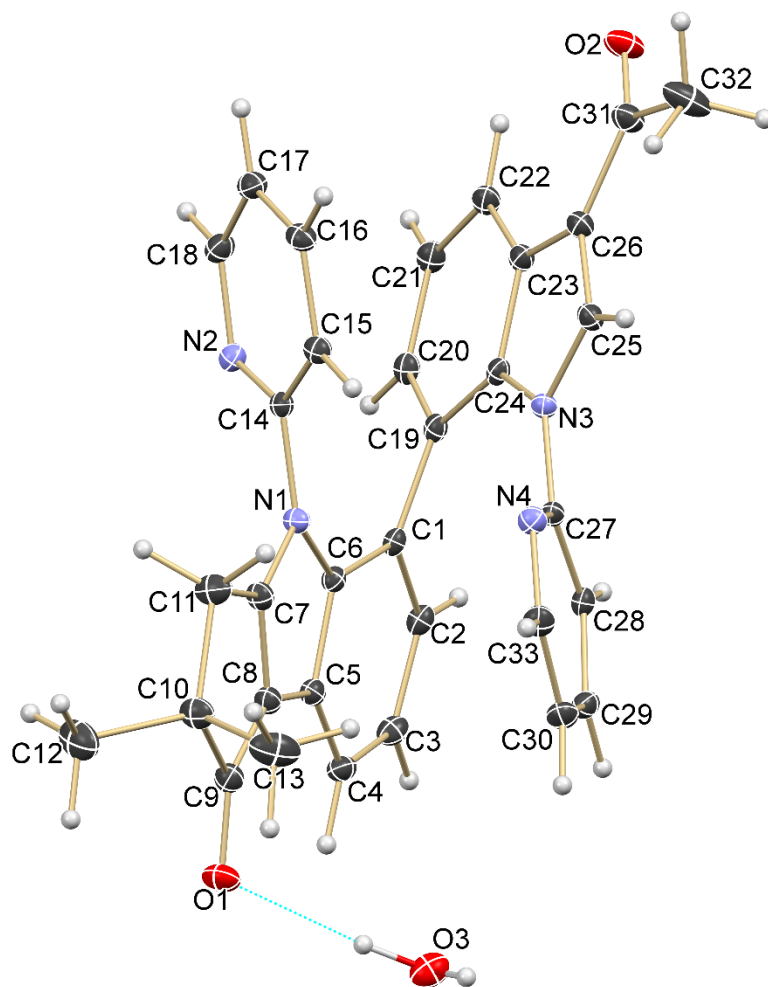


Fig S6 ORTEP of compound 25 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

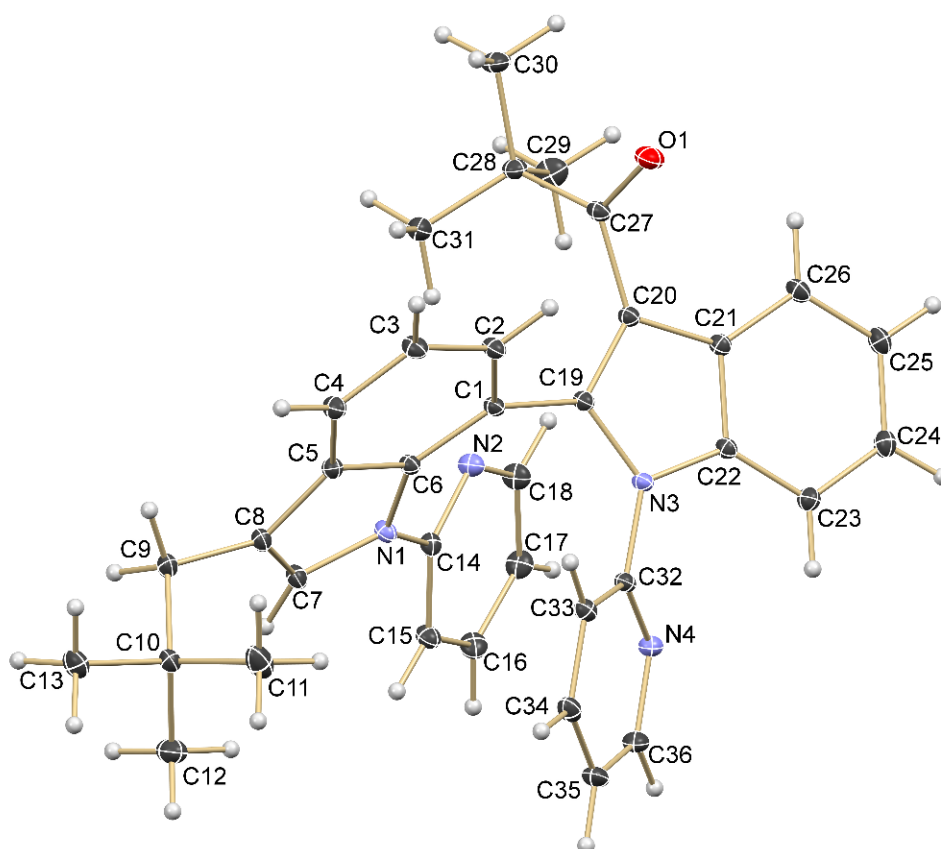


Fig S7 ORTEP of compound 26 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii.

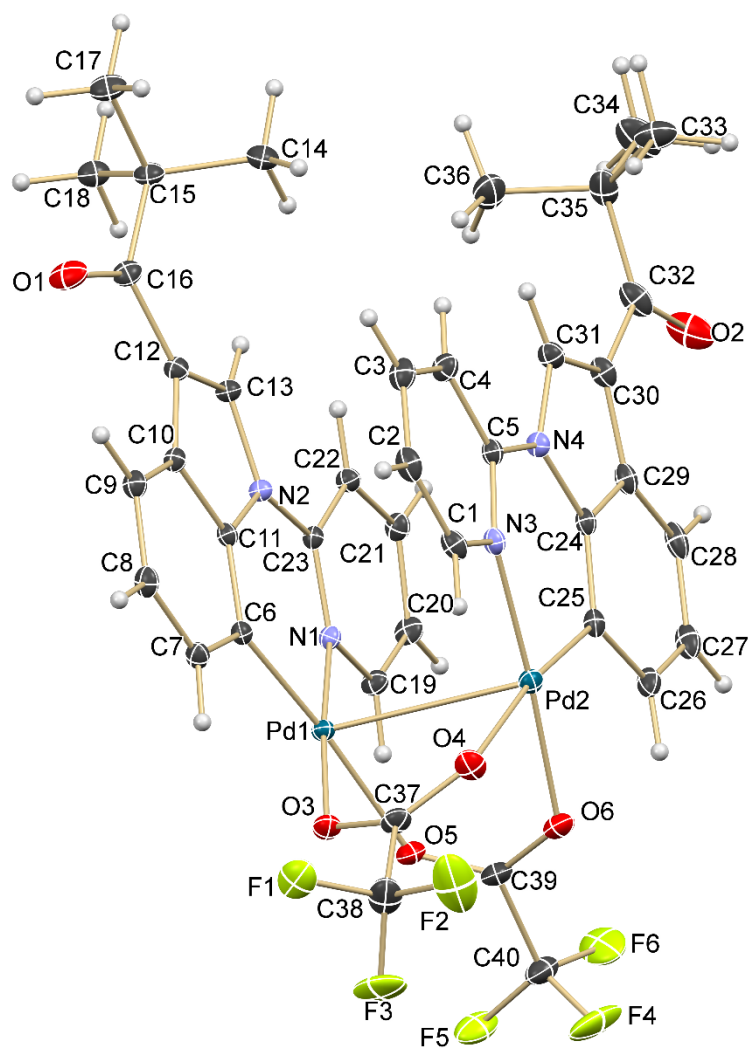


Fig S8 ORTEP of compound 27 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres with arbitrary radii. The thermal disorder shown by F-atoms of the triflate moieties is omitted for clarity.

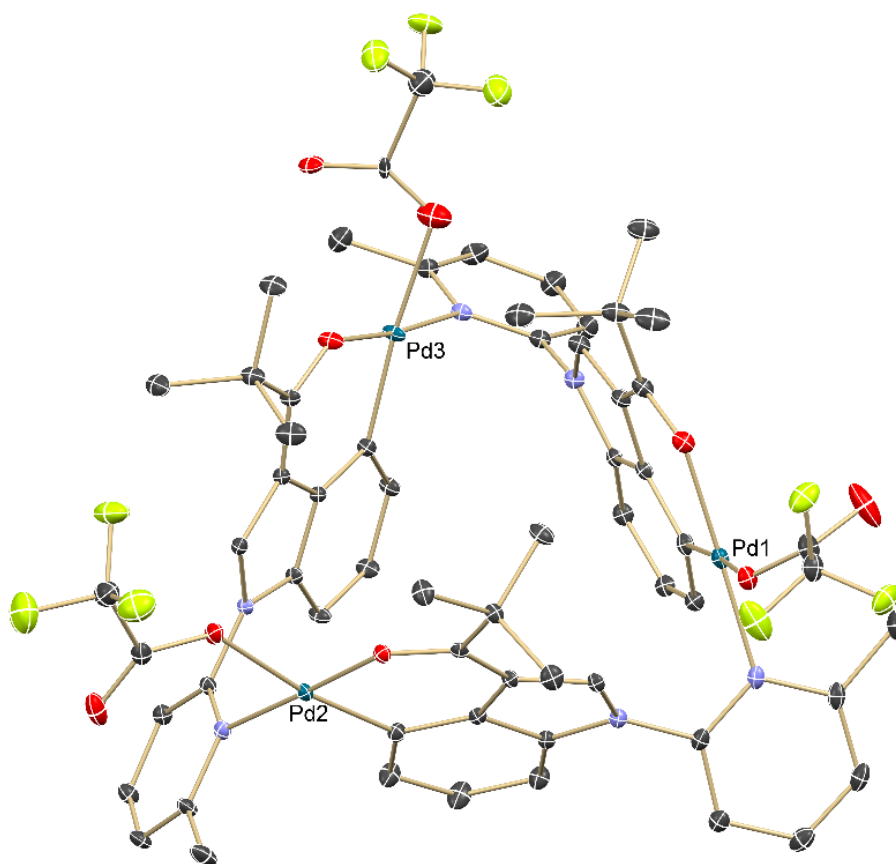
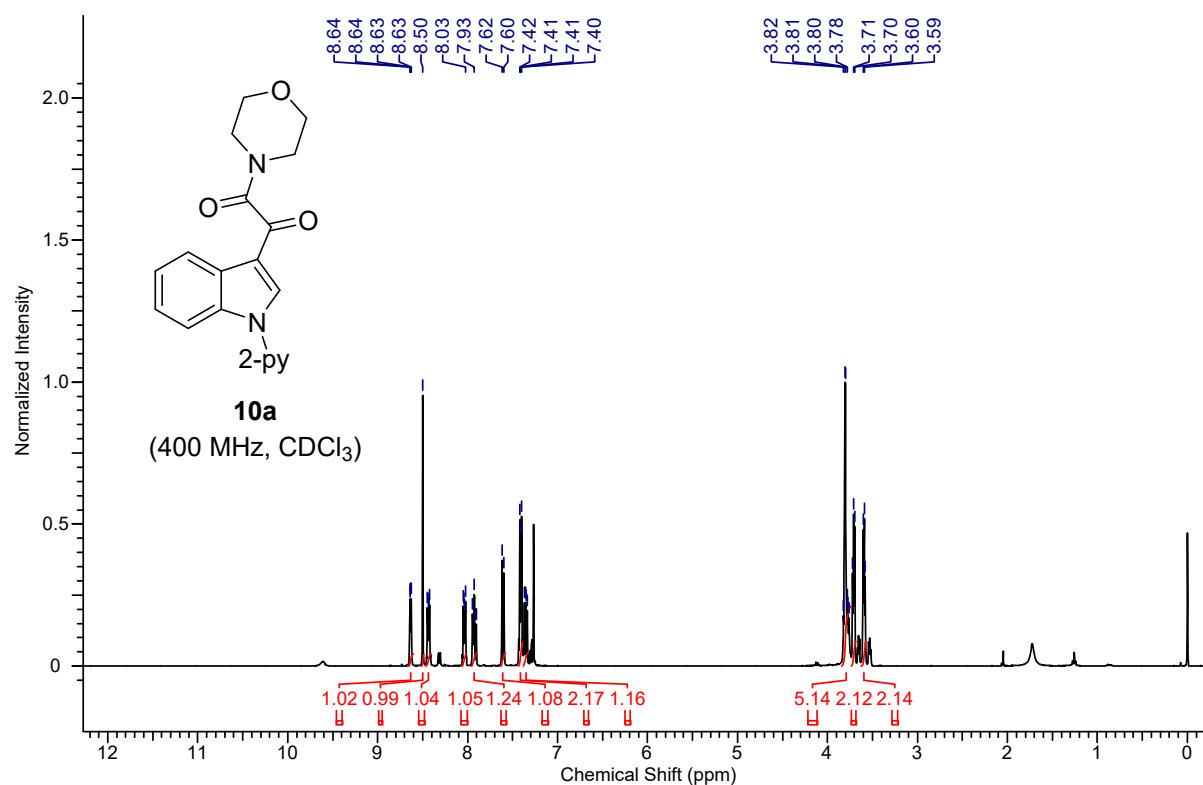


Fig S9 ORTEP of compound 28 showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres with arbitrary radii. The thermal disorder shown by F-atoms of one of the CF₃ moieties are omitted for clarity.

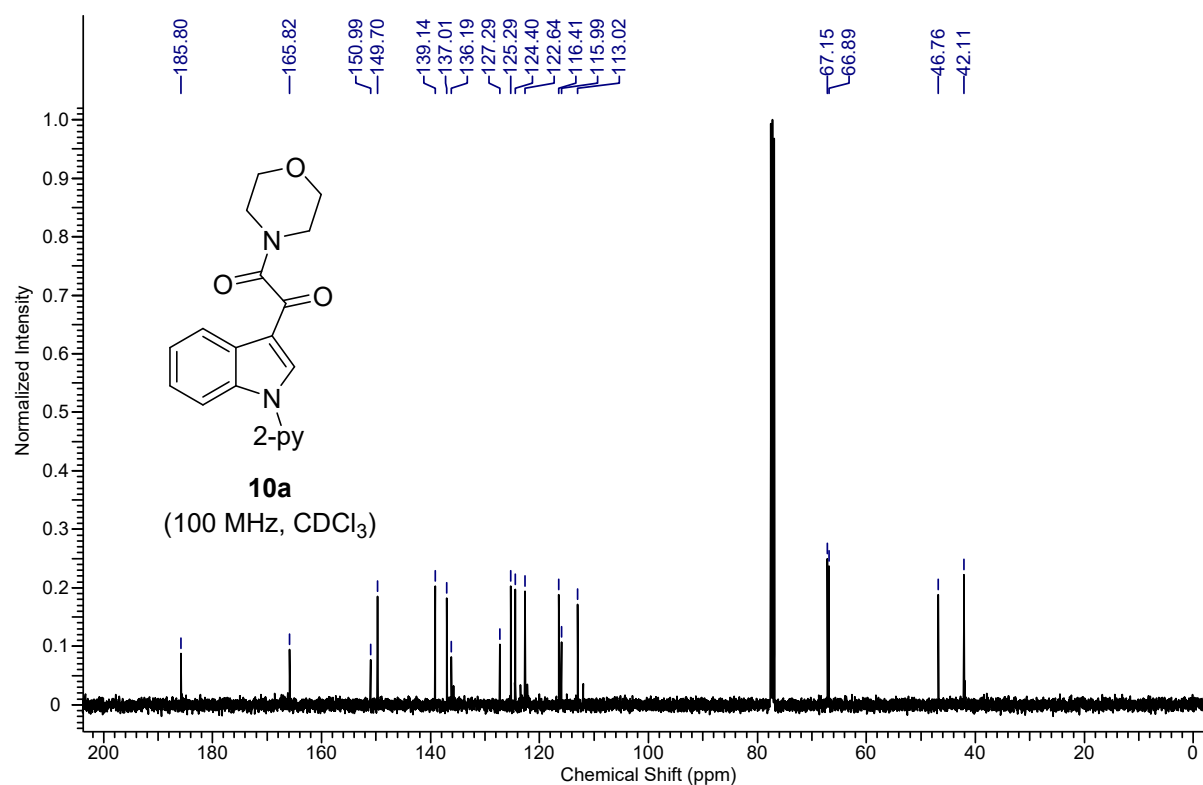
13. References

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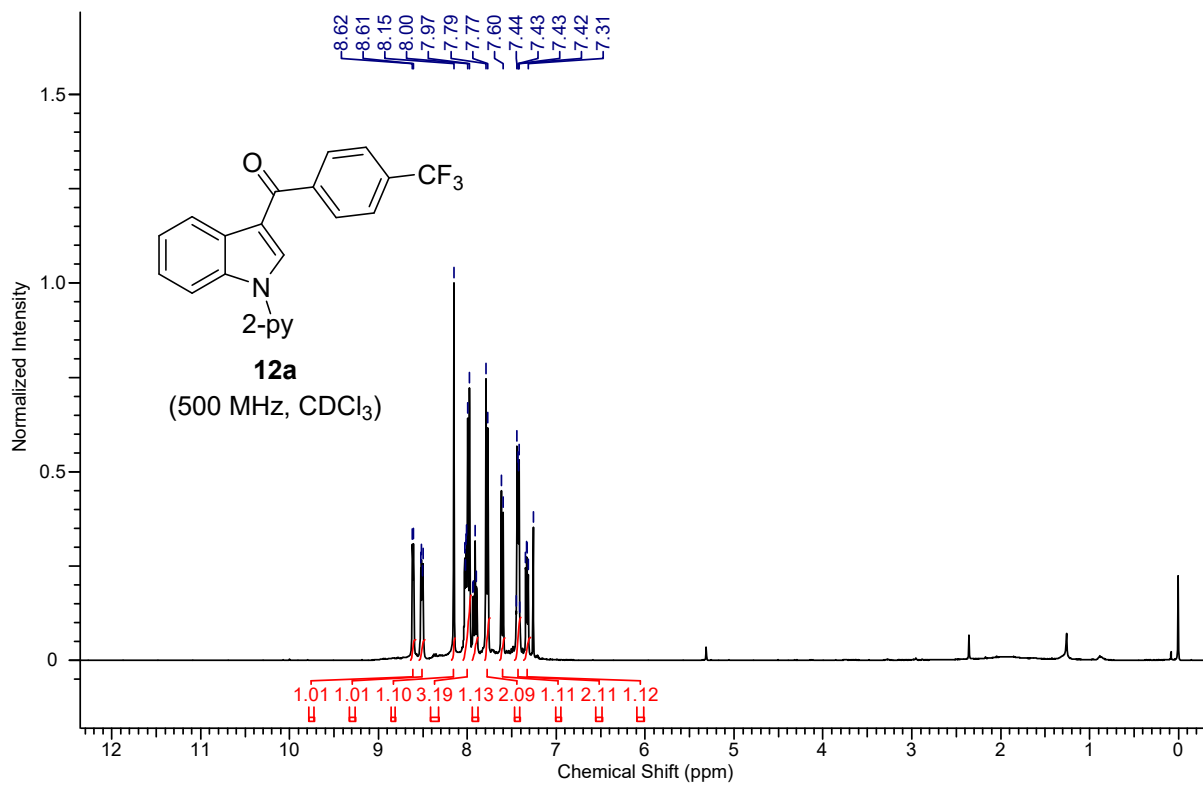
14. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of Starting Compounds



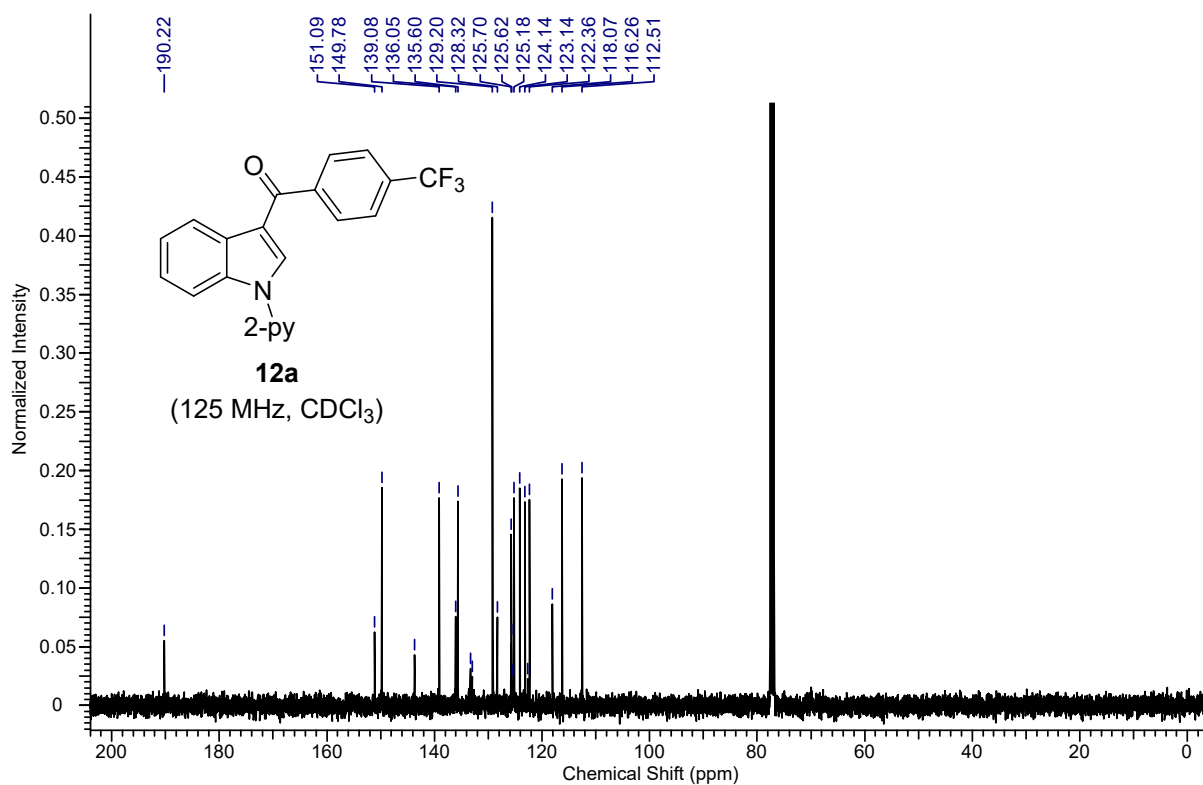
^1H -NMR spectrum of compound **10a**



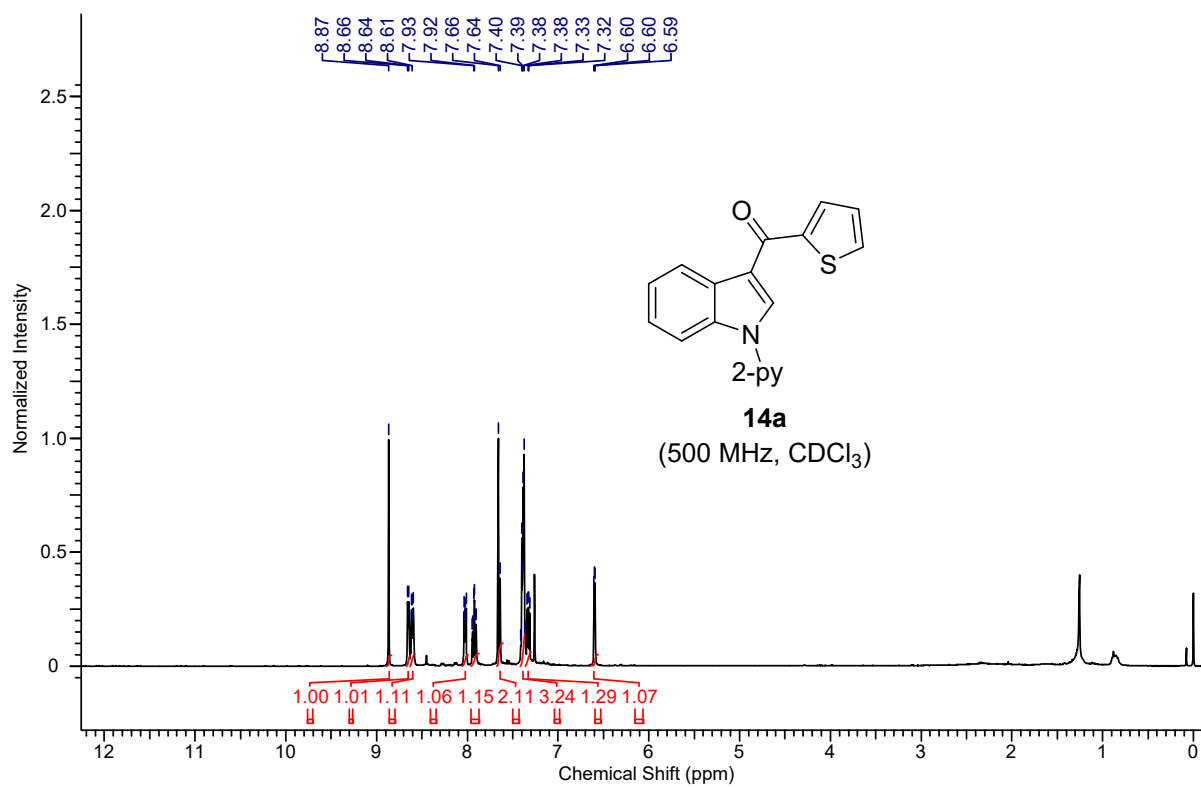
^{13}C -NMR spectrum of compound **10a**



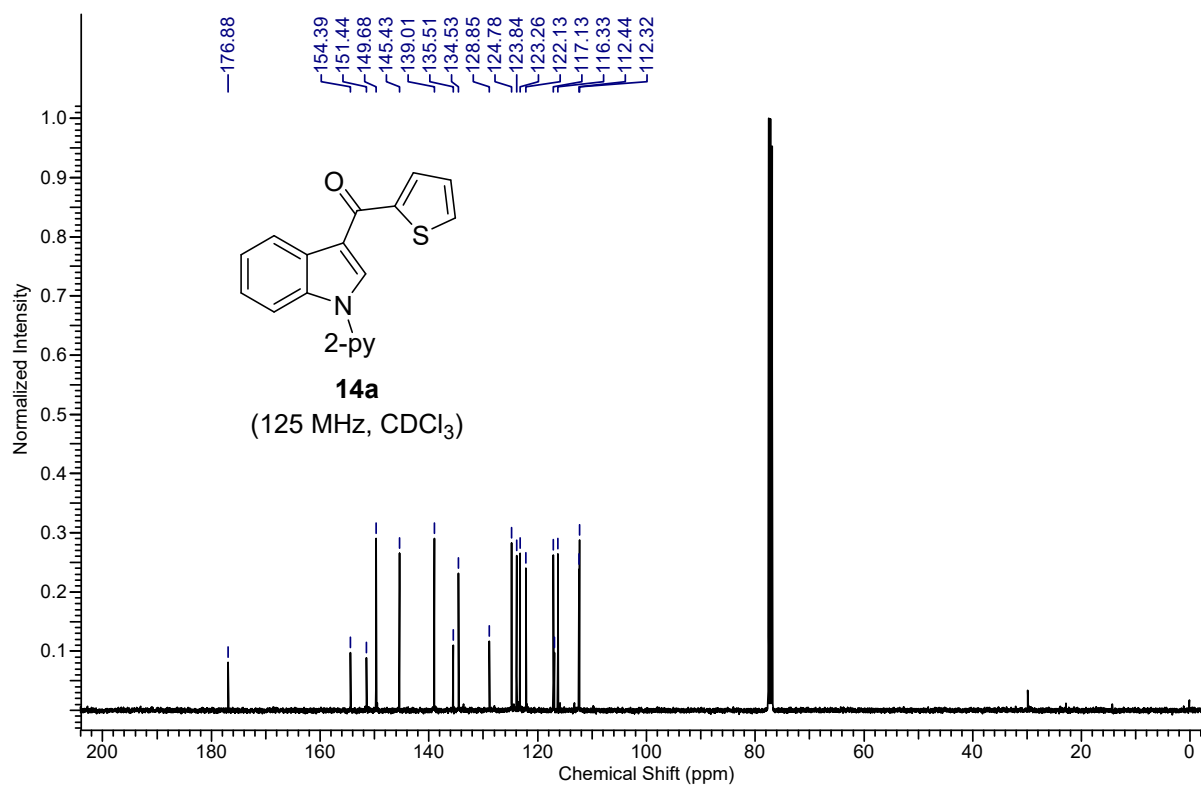
¹H-NMR spectrum of compound **12a**



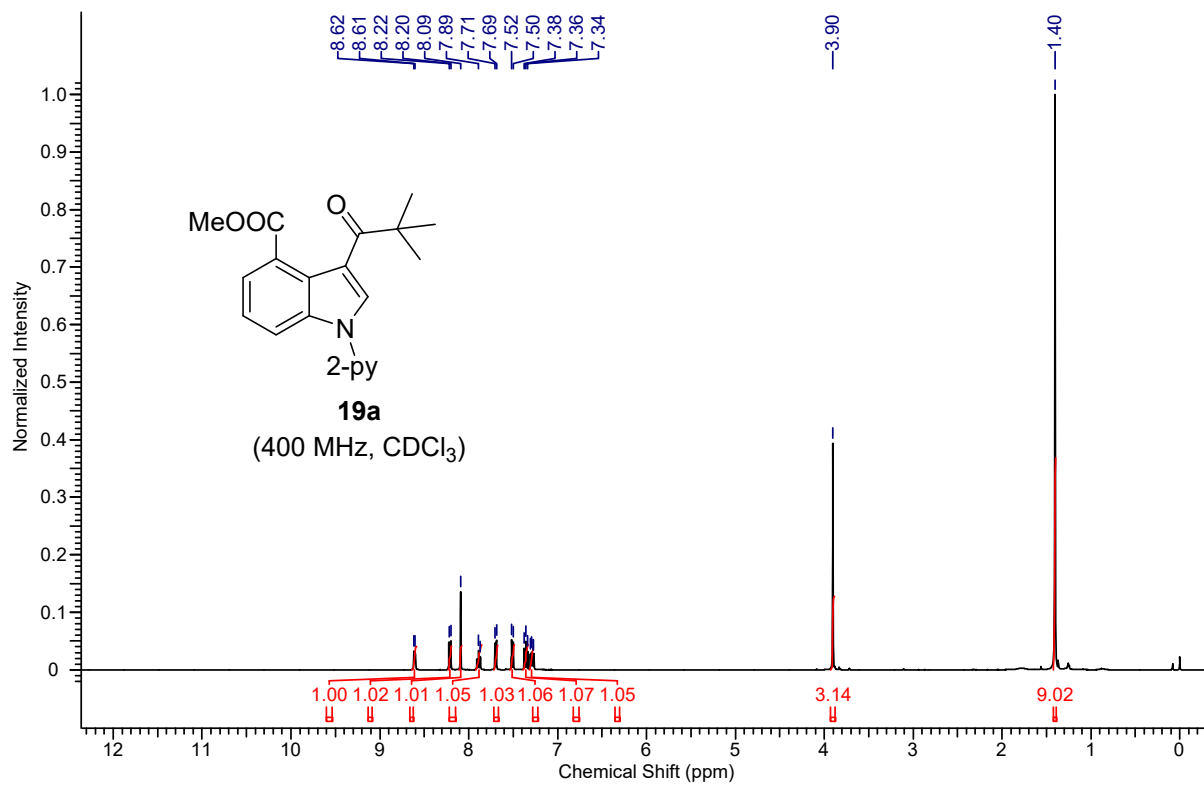
¹³C-NMR spectrum of compound **12a**



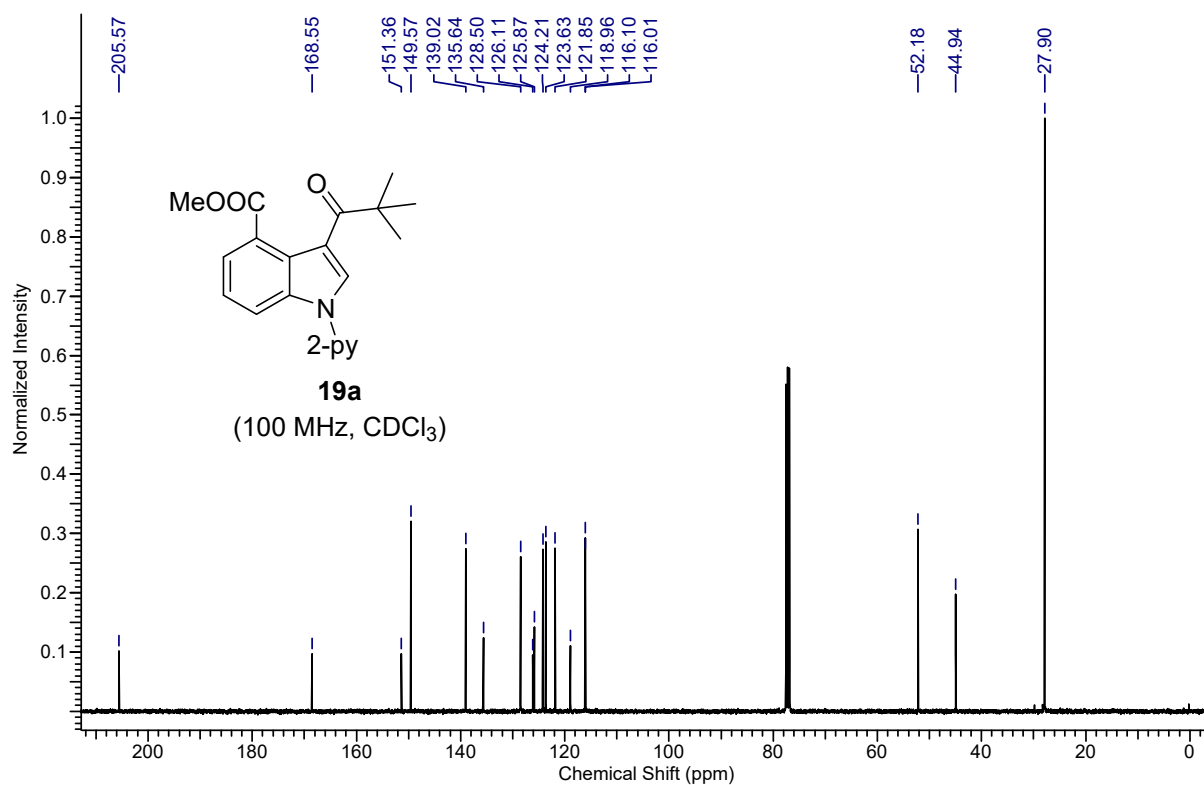
¹H-NMR spectrum of compound **14a**



¹³C-NMR spectrum of compound **14a**

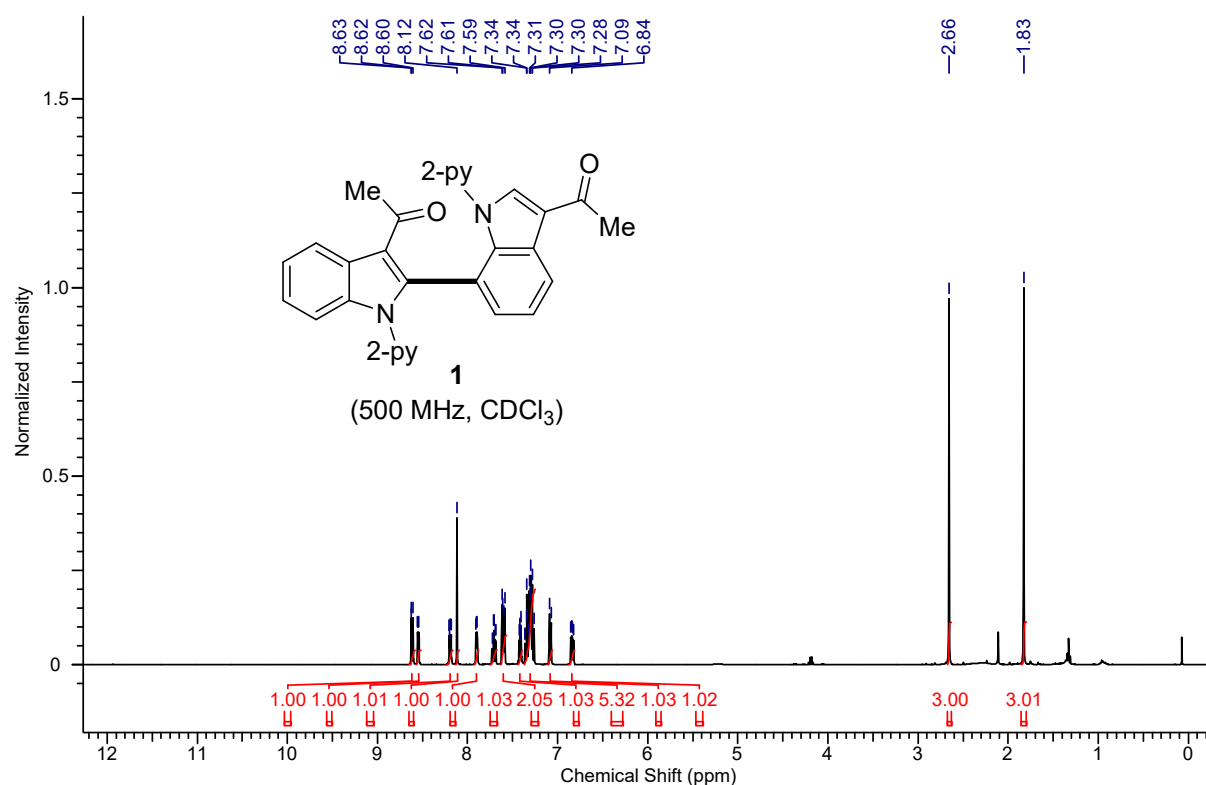


¹H-NMR spectrum of compound **19a**

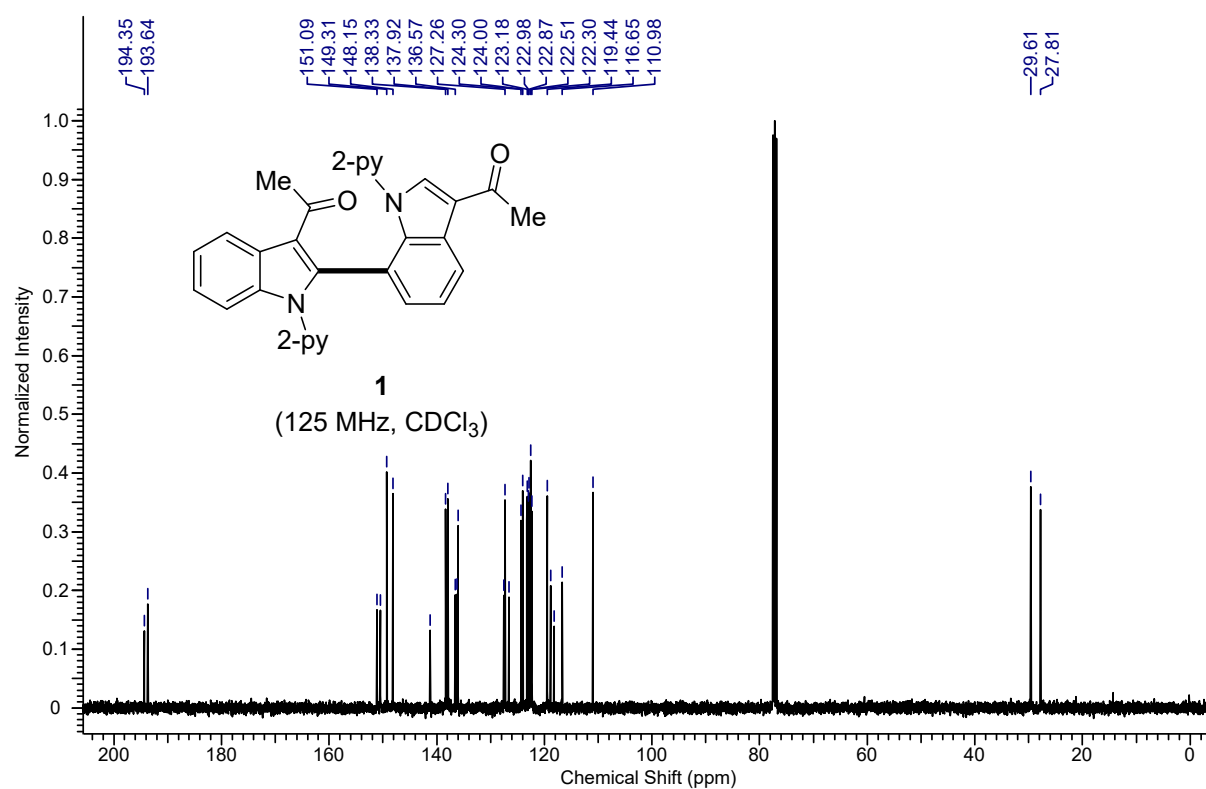


¹³C-NMR spectrum of compound **19a**

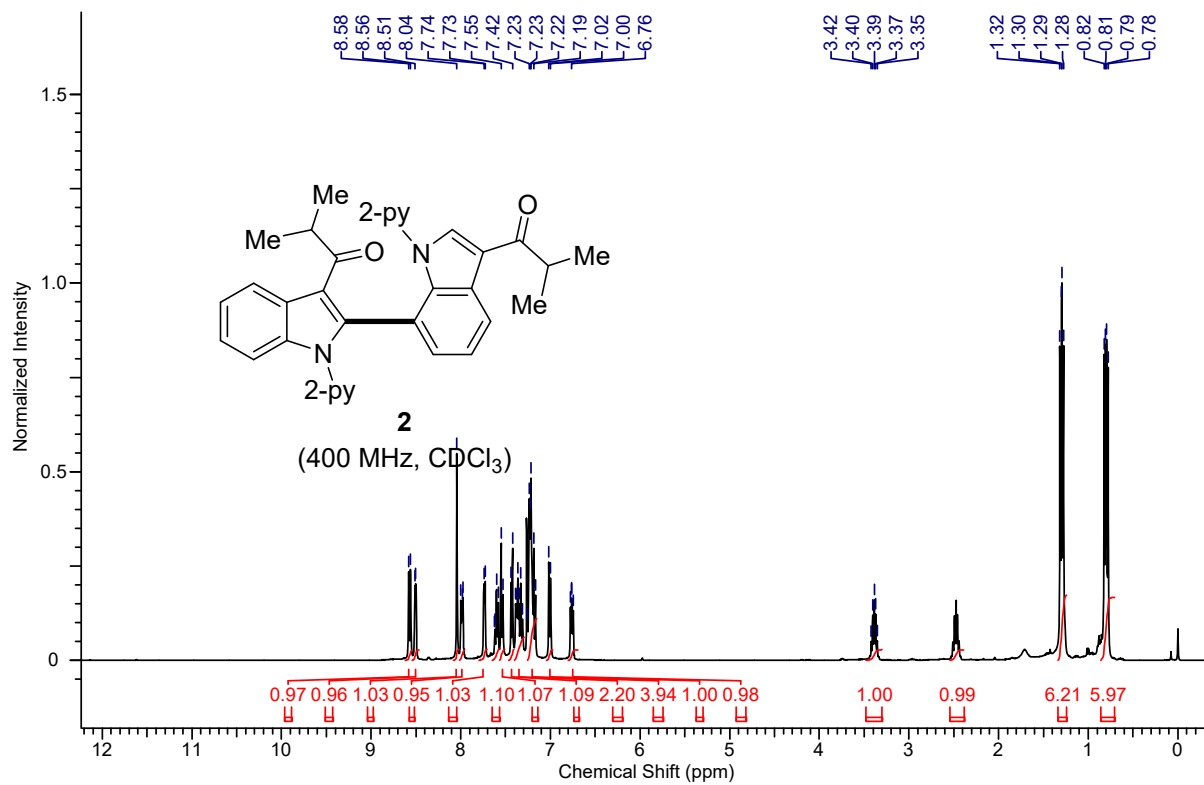
15. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of Coupled Products



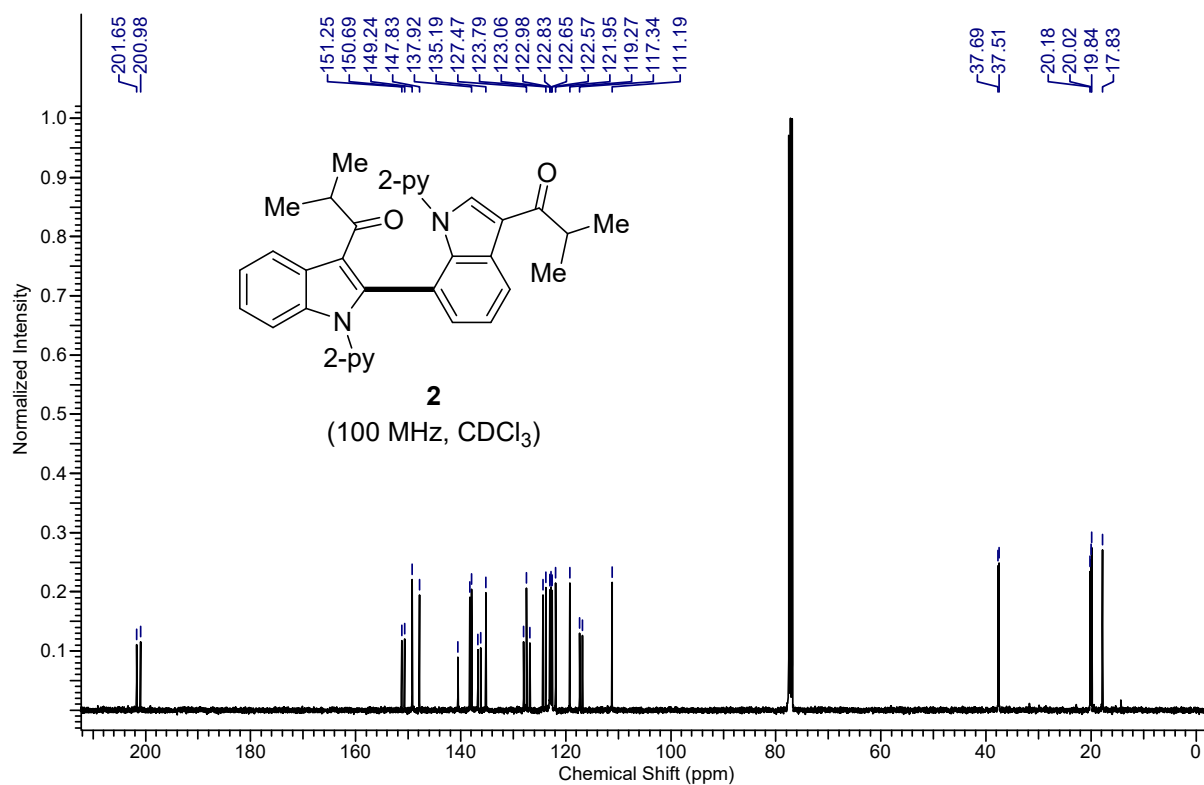
^1H -NMR spectrum of compound **1**



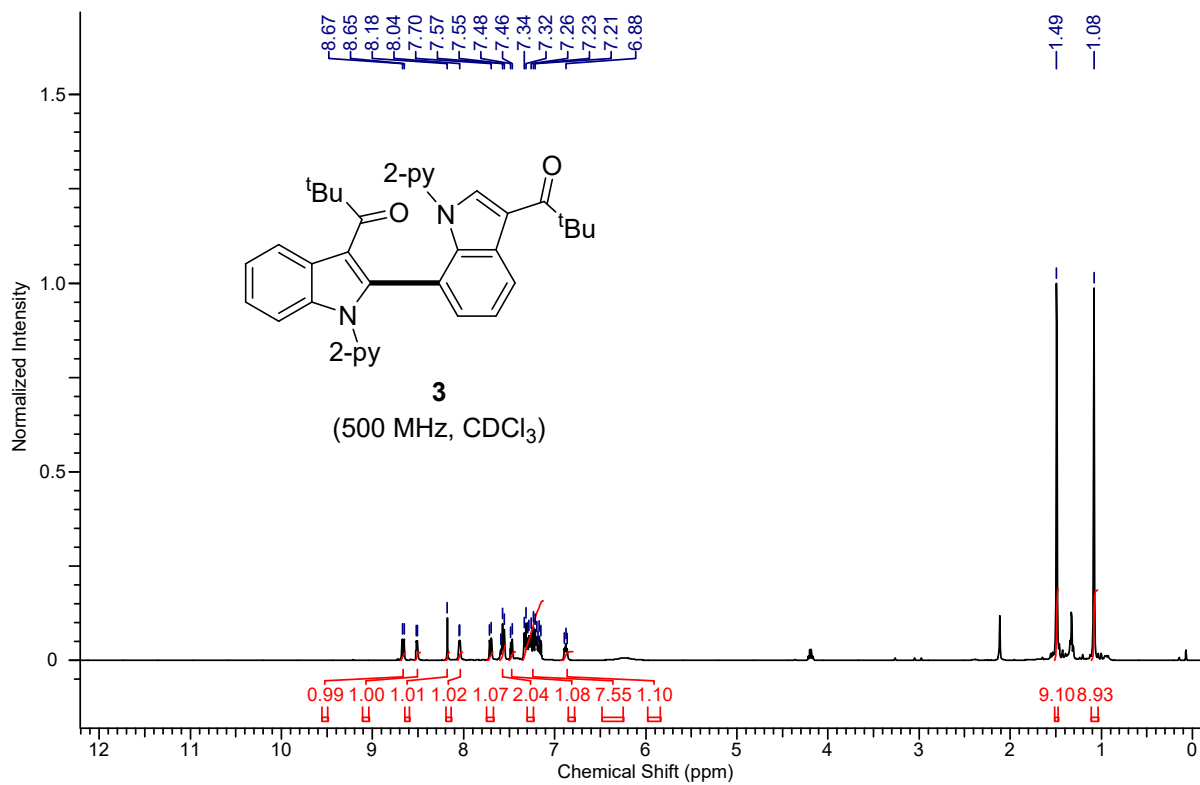
^{13}C -NMR spectrum of compound **1**



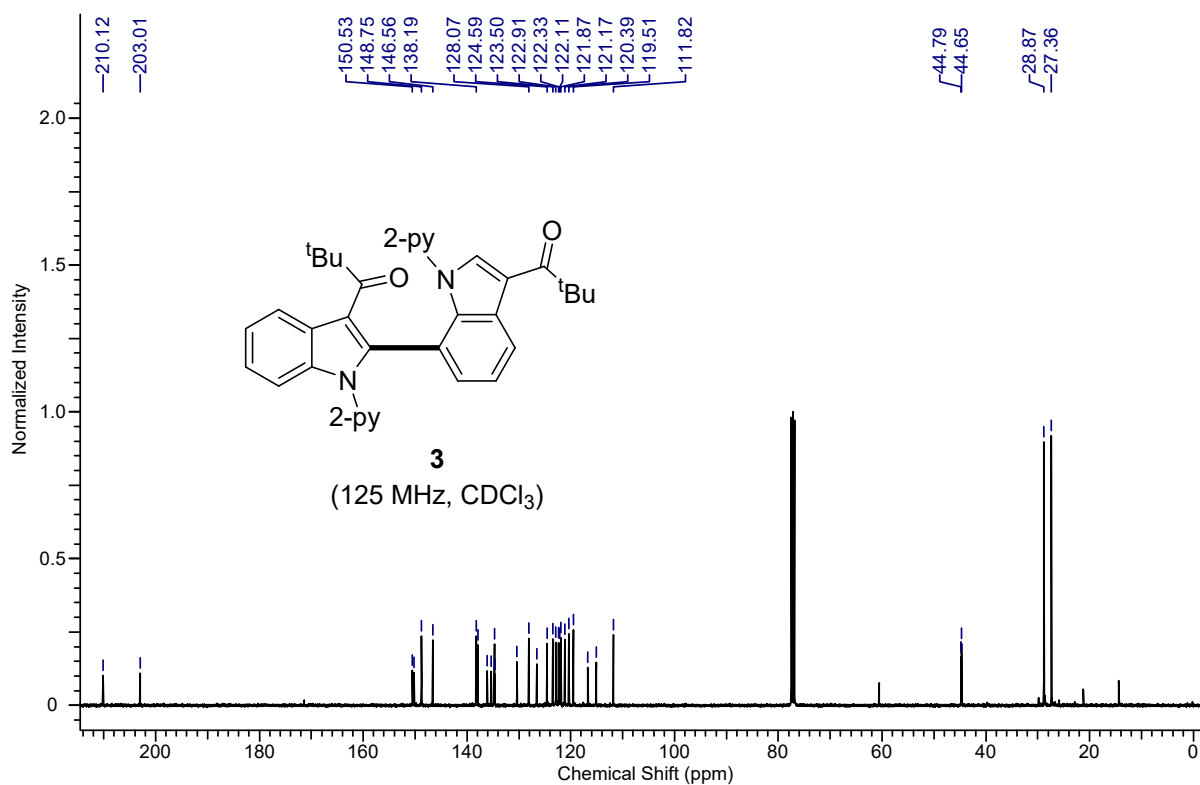
¹H-NMR spectrum of compound **2**



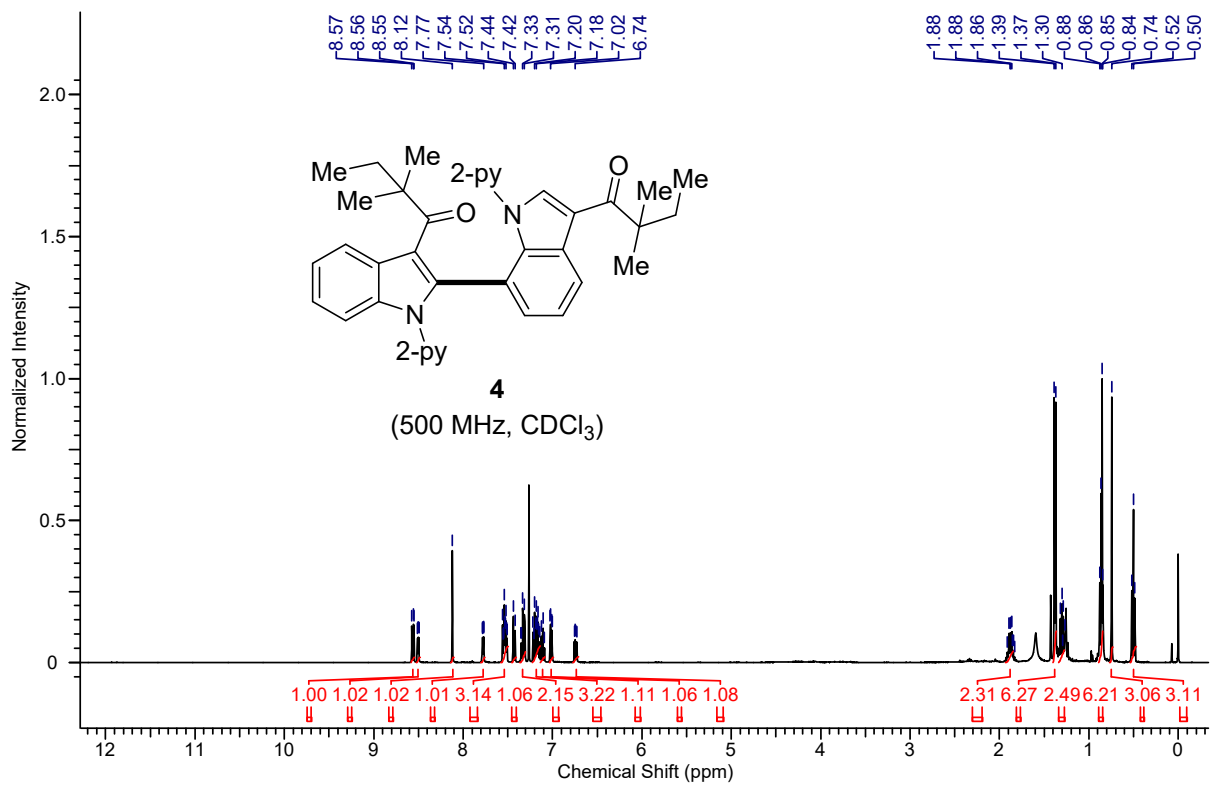
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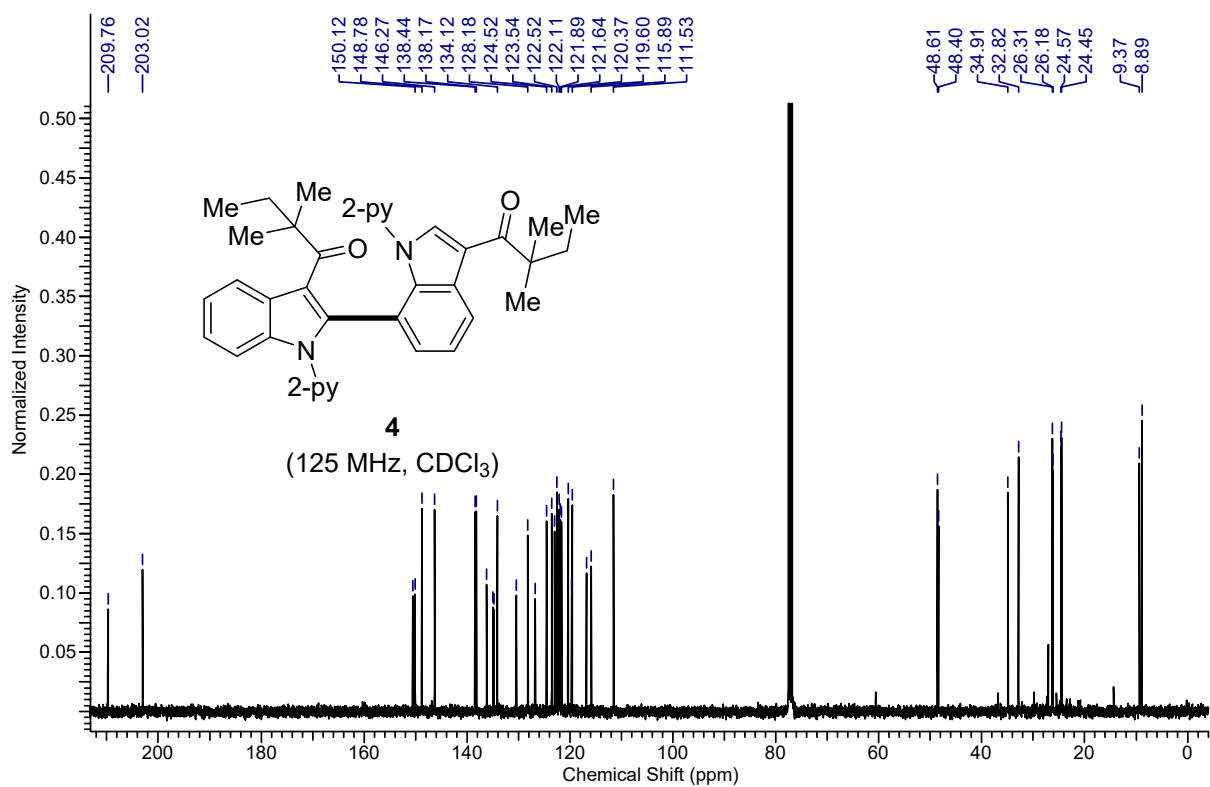
¹H-NMR spectrum of compound **3**



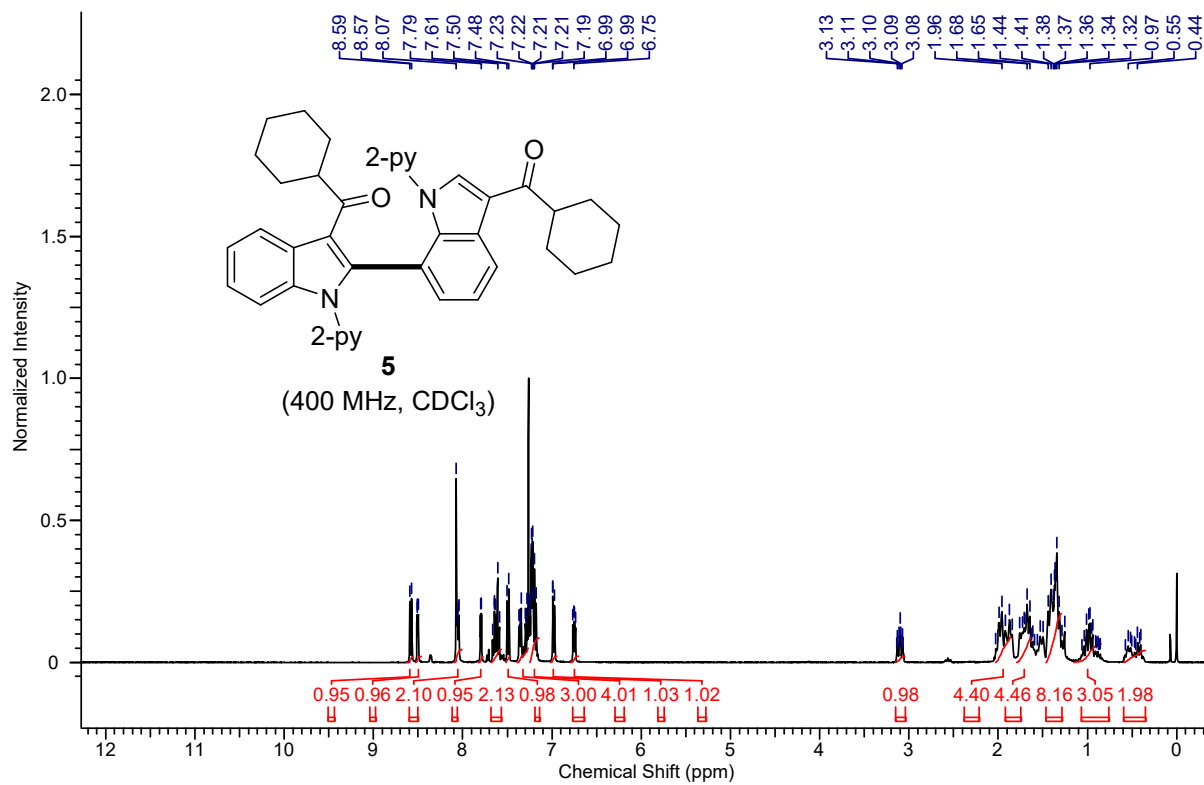
¹³C-NMR spectrum of compound **3**



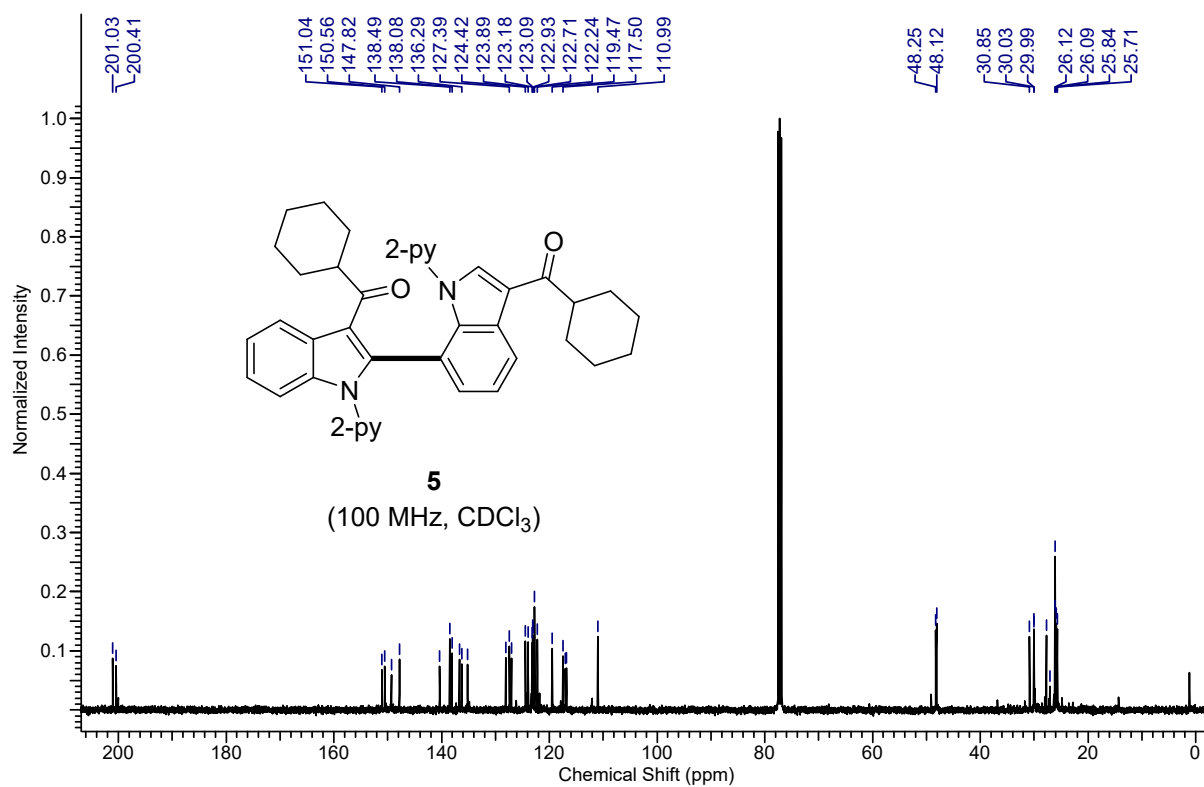
¹H-NMR spectrum of compound 4



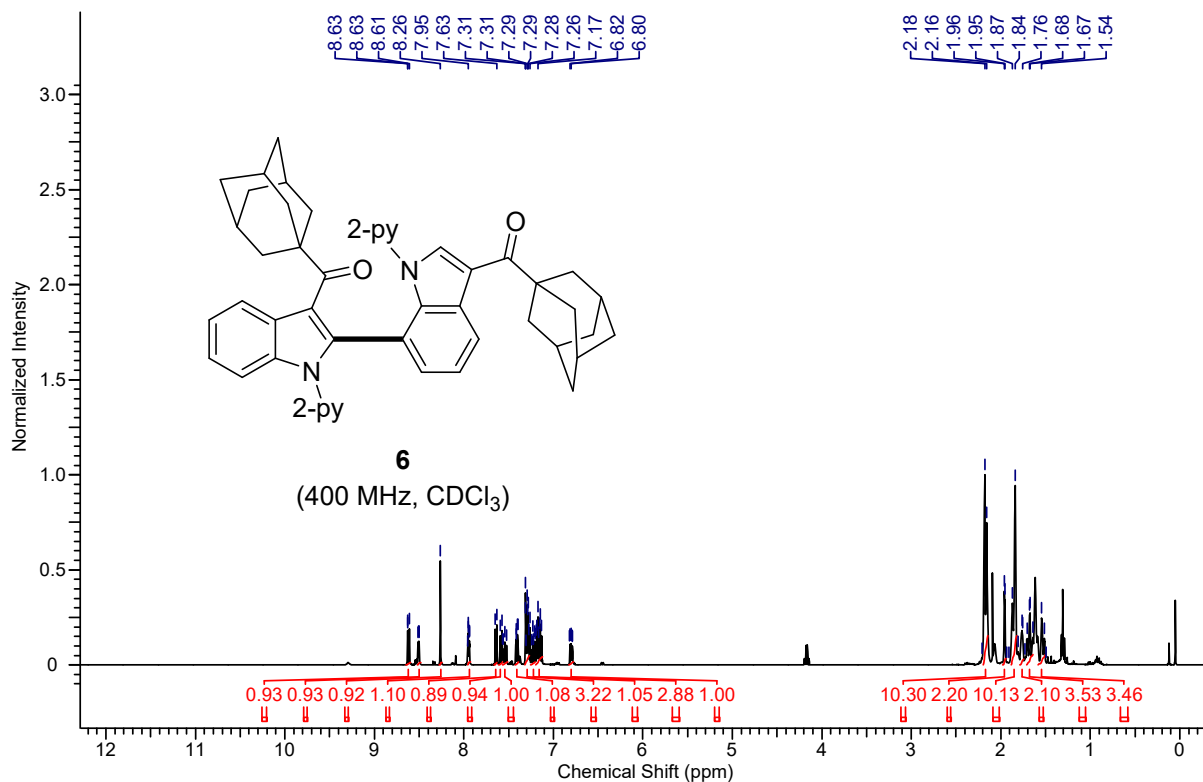
¹³C-NMR spectrum of compound 4



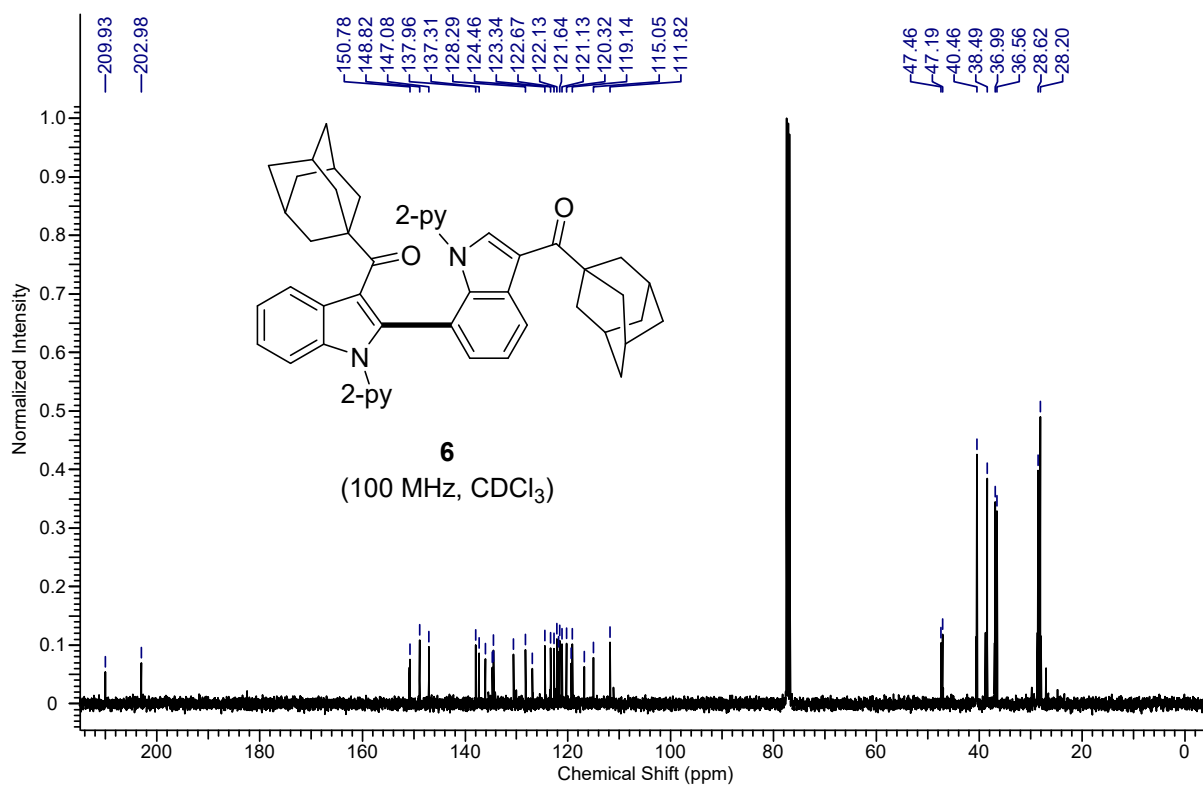
¹H-NMR spectrum of compound **5**



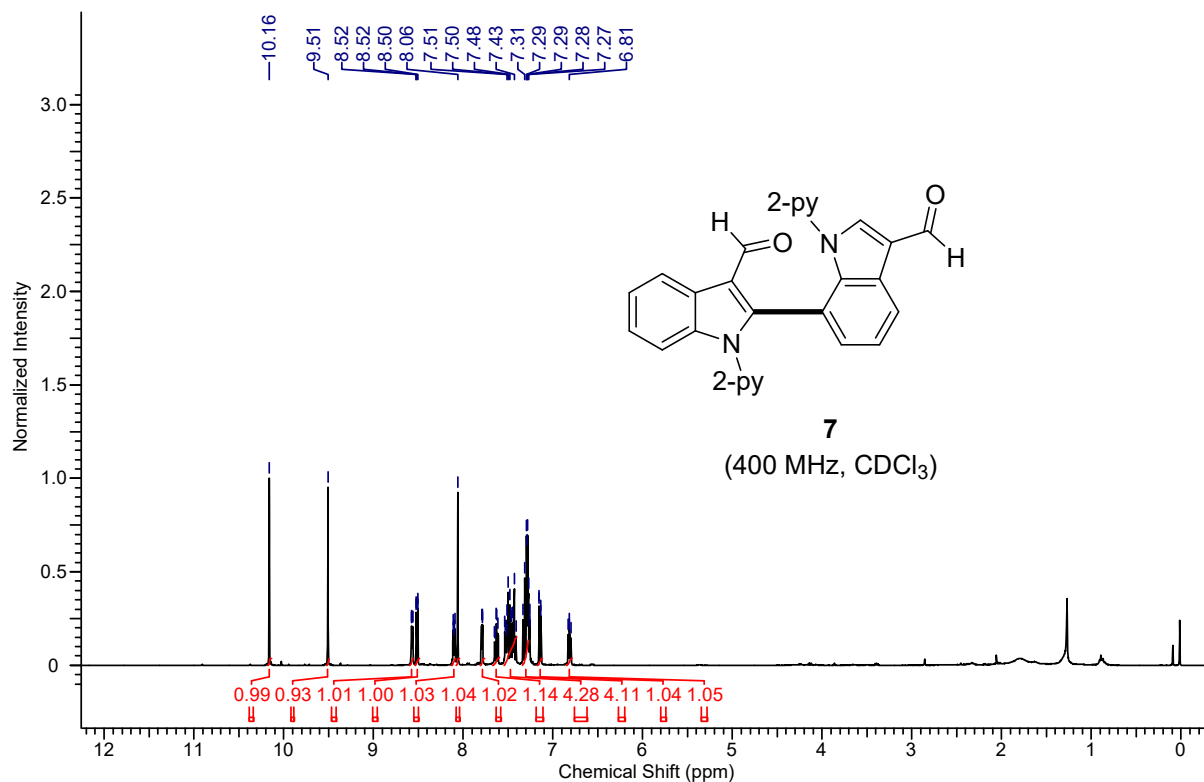
¹³C-NMR spectrum of compound **5**



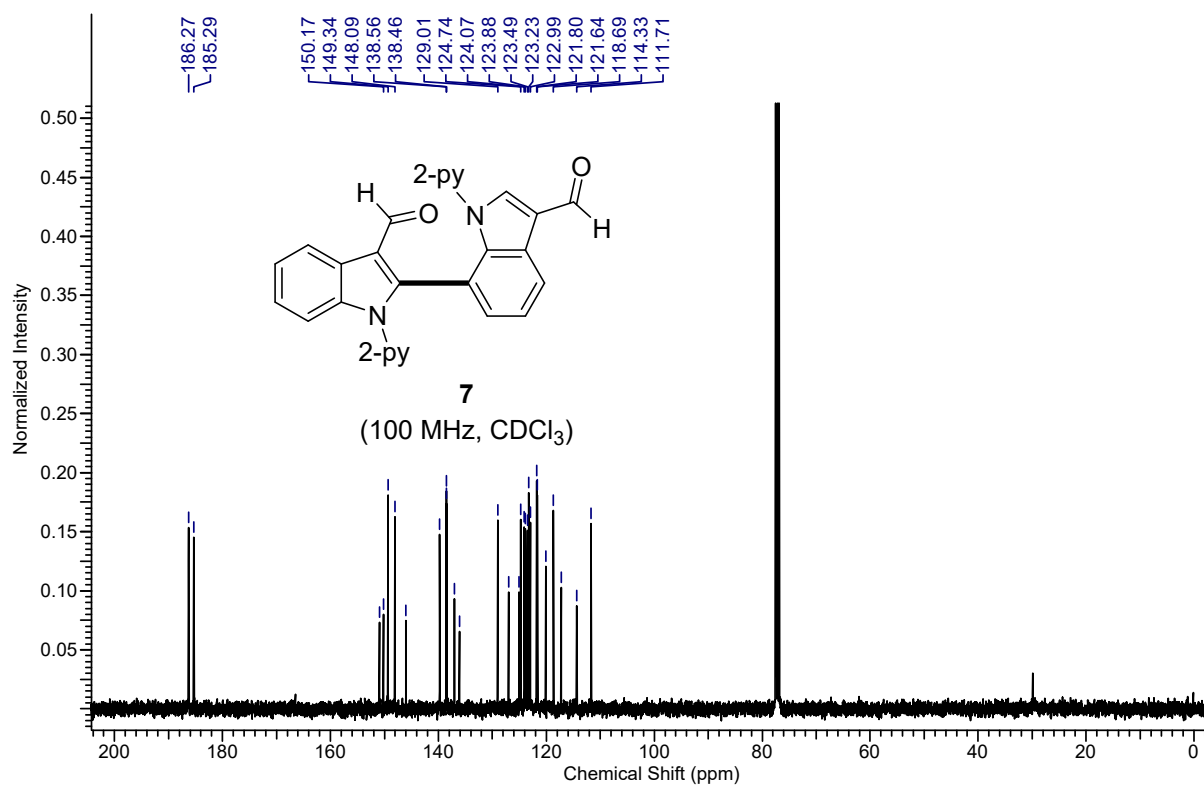
¹H-NMR spectrum of compound **6**



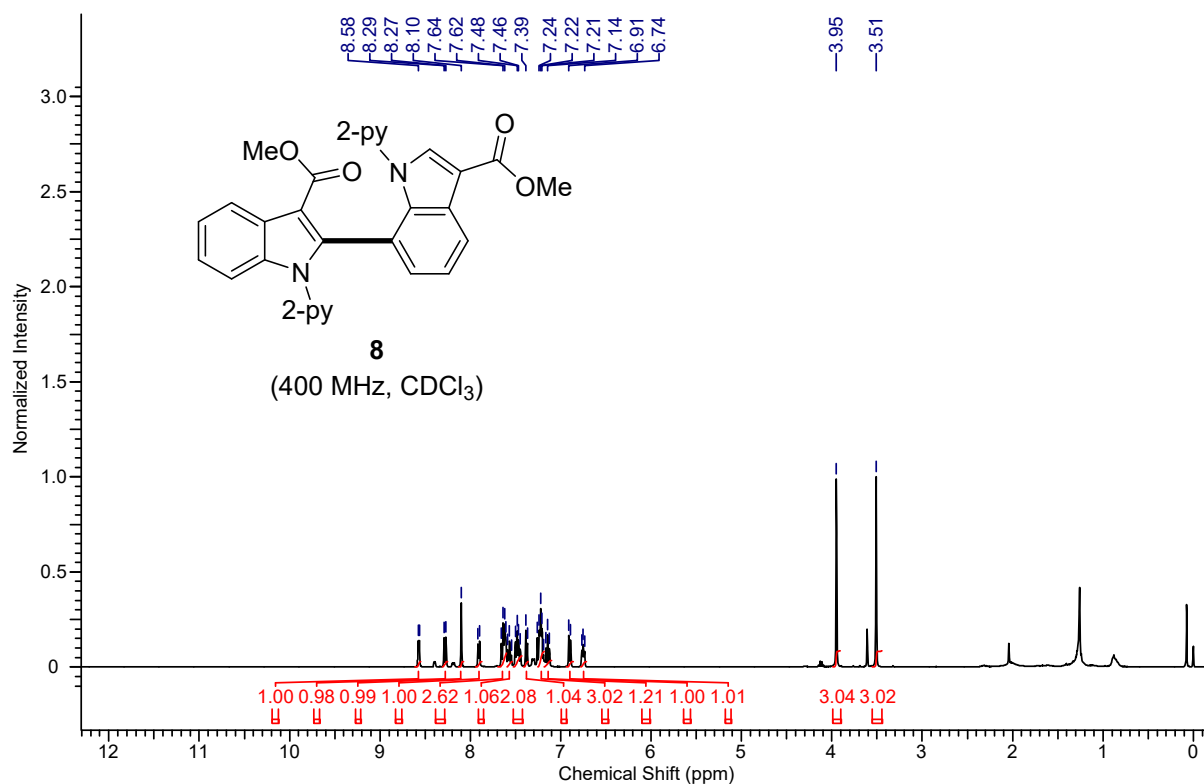
¹³C-NMR spectrum of compound **6**



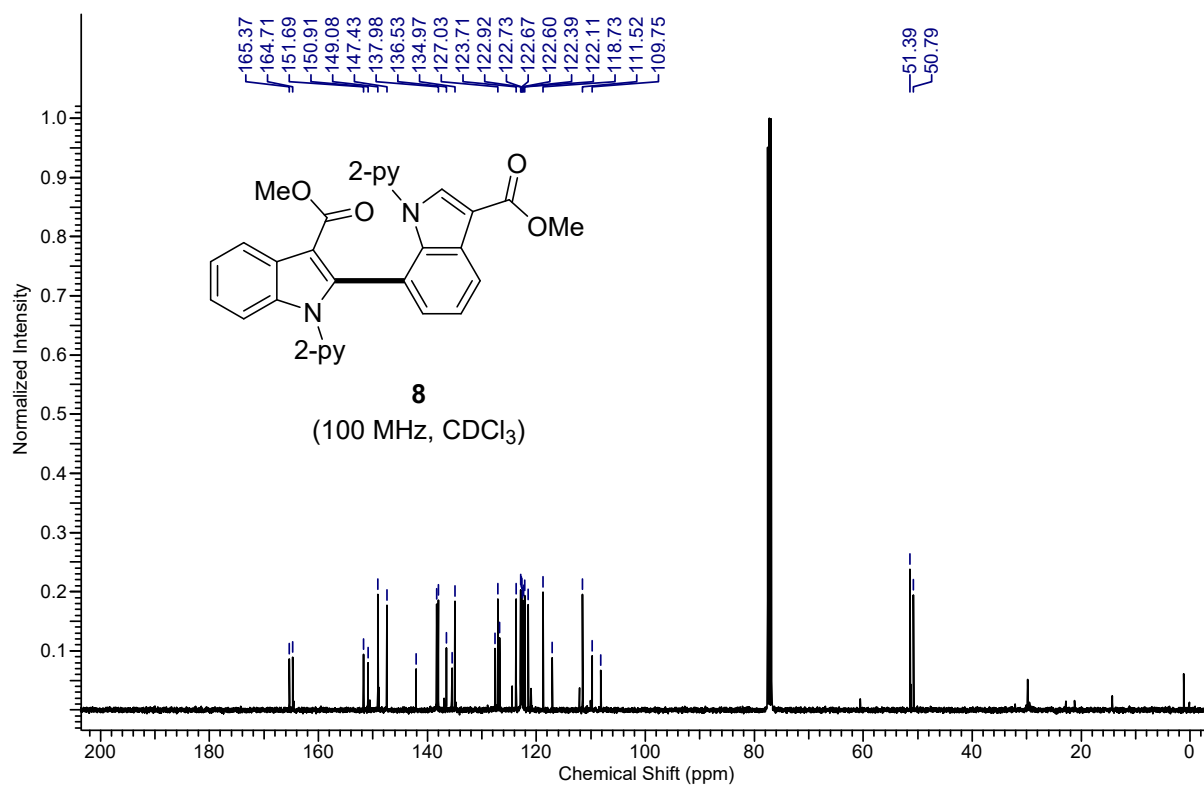
¹H-NMR spectrum of compound **7**



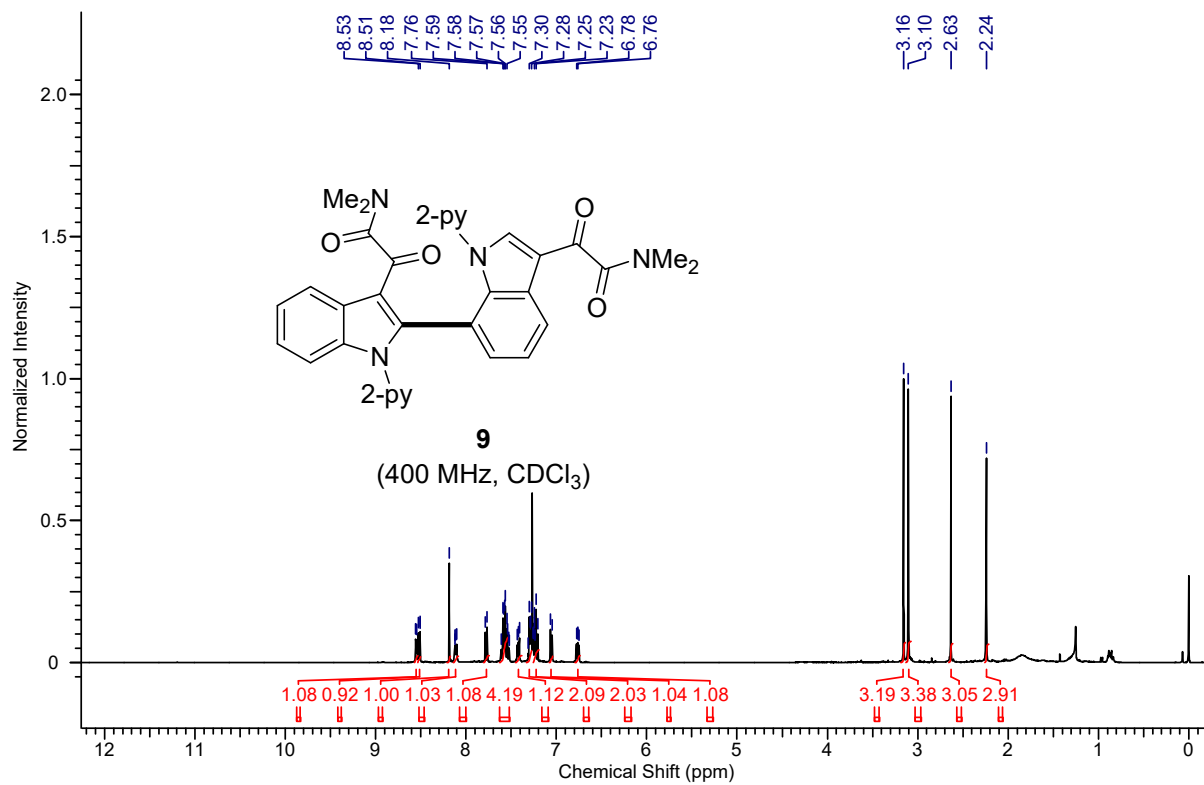
¹³C-NMR spectrum of compound **7**



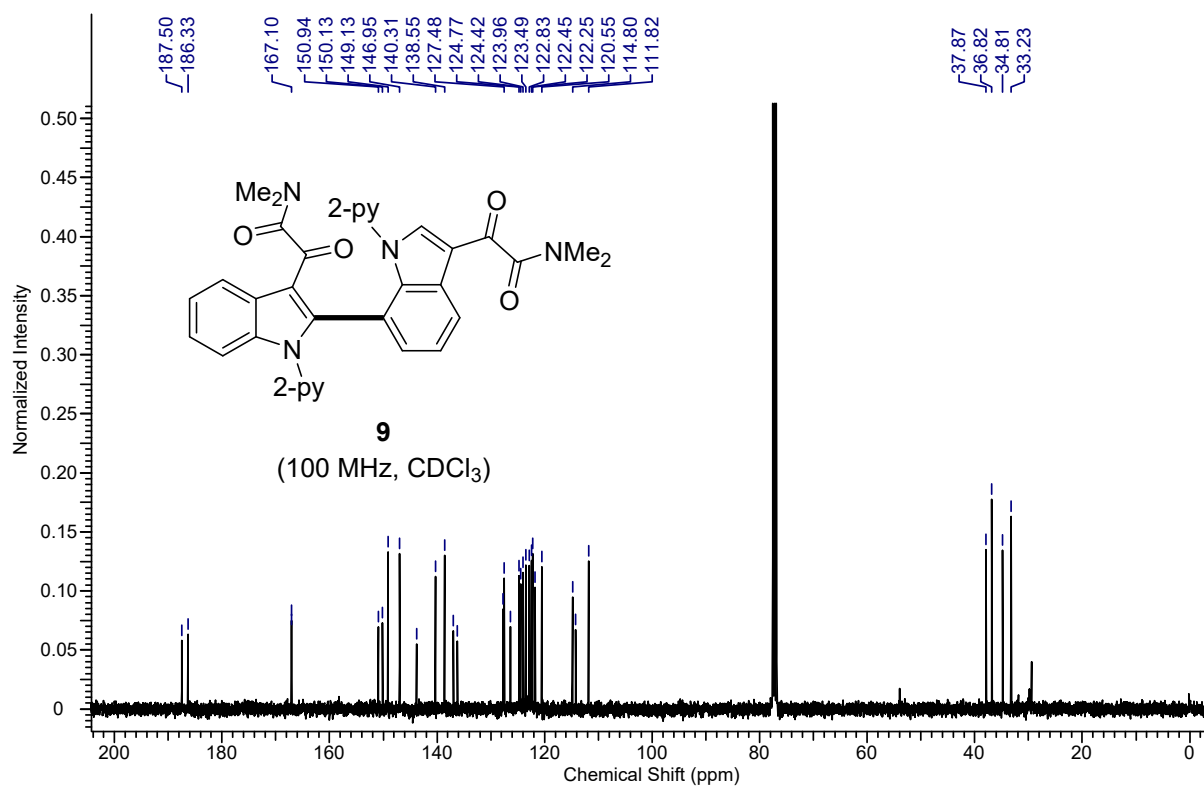
¹H-NMR spectrum of compound **8**



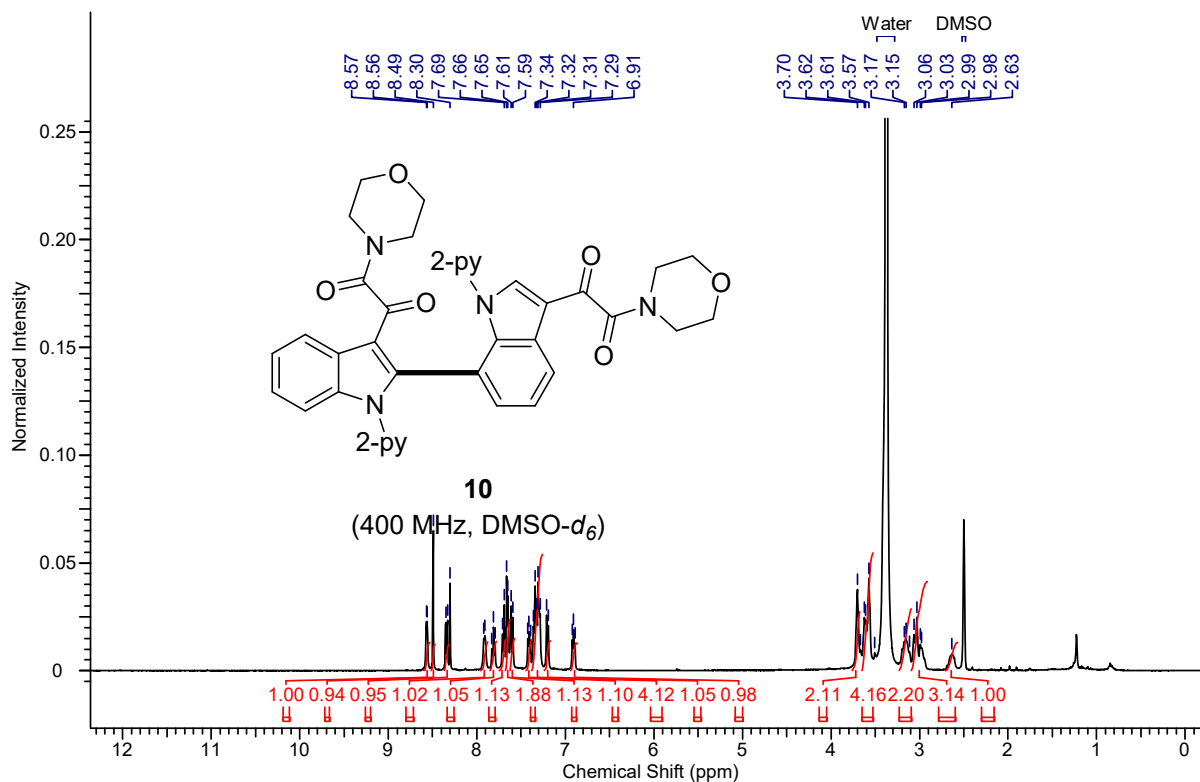
¹³C-NMR spectrum of compound **8**



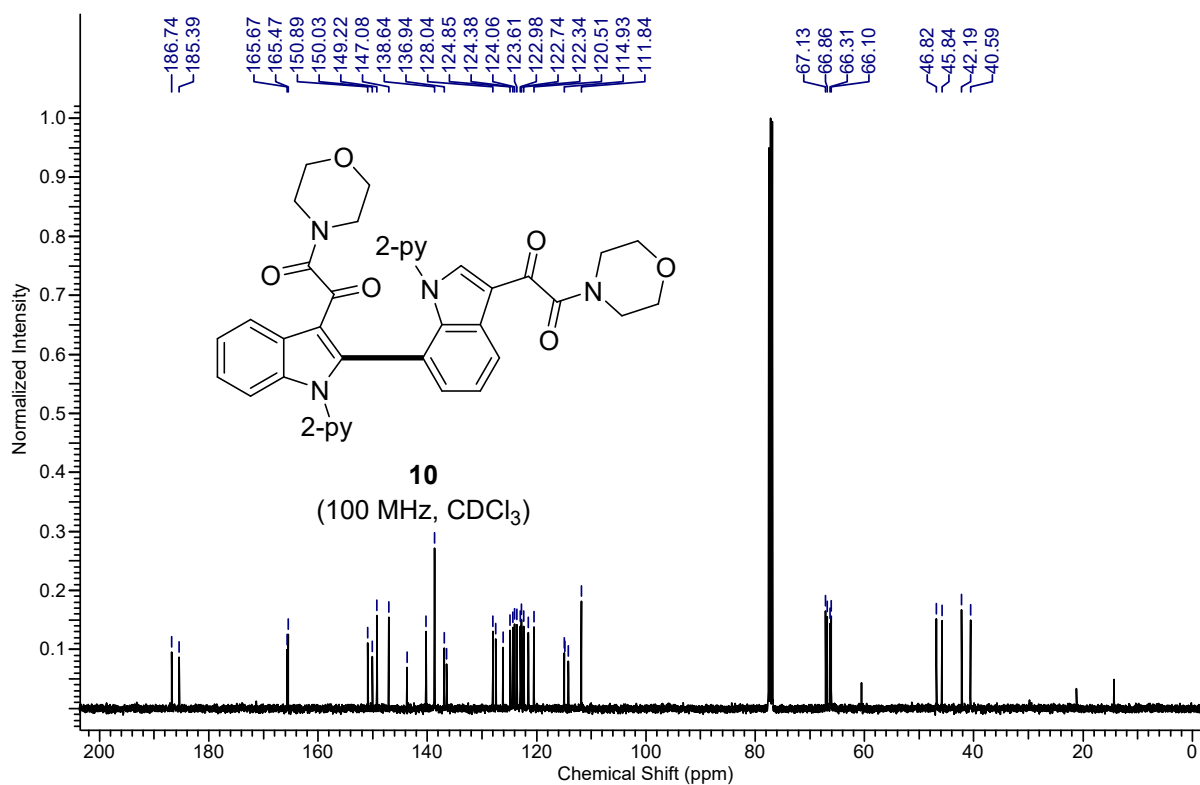
¹H-NMR spectrum of compound **9**



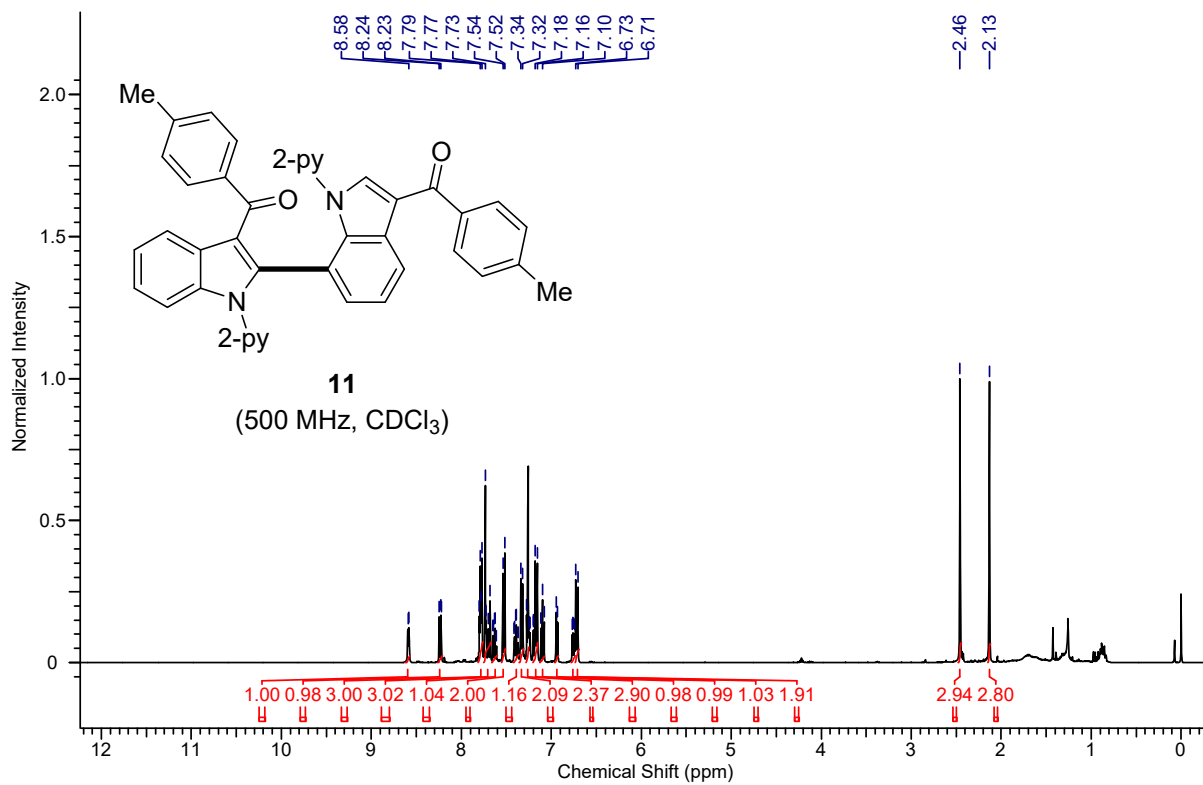
¹³C-NMR spectrum of compound **9**



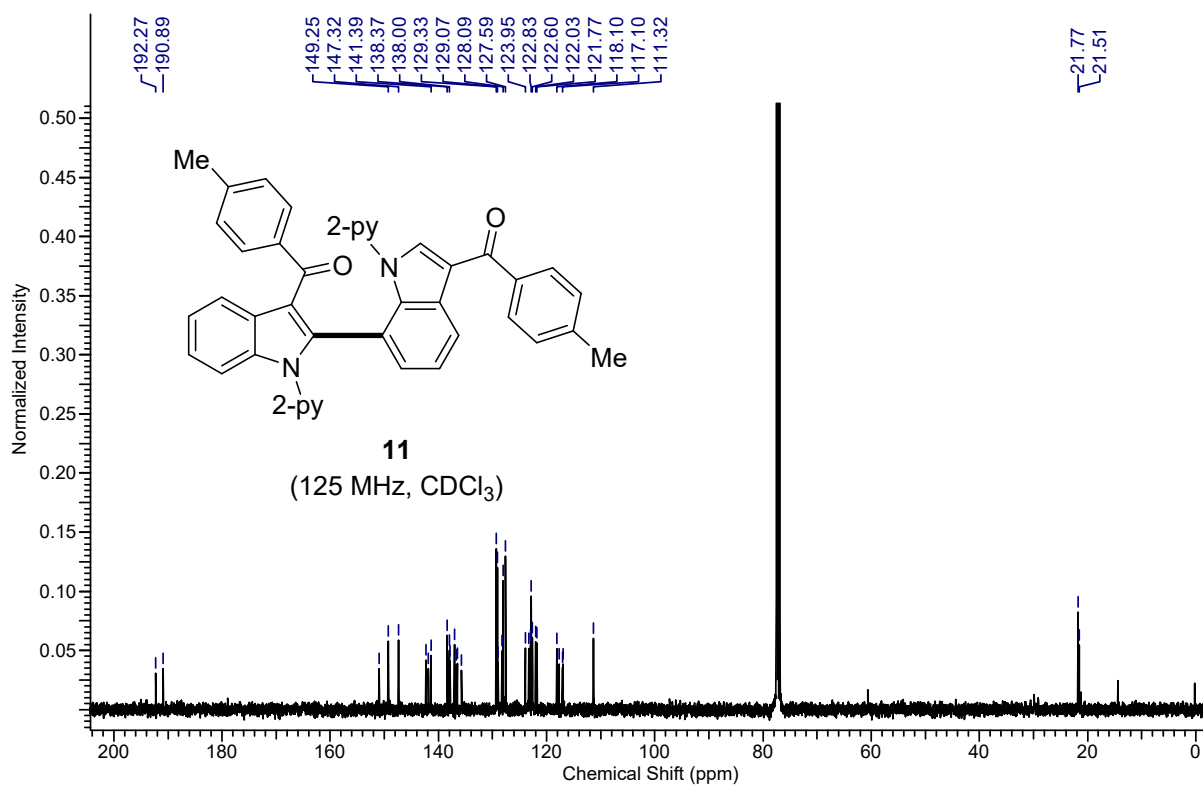
¹H-NMR spectrum of compound 10



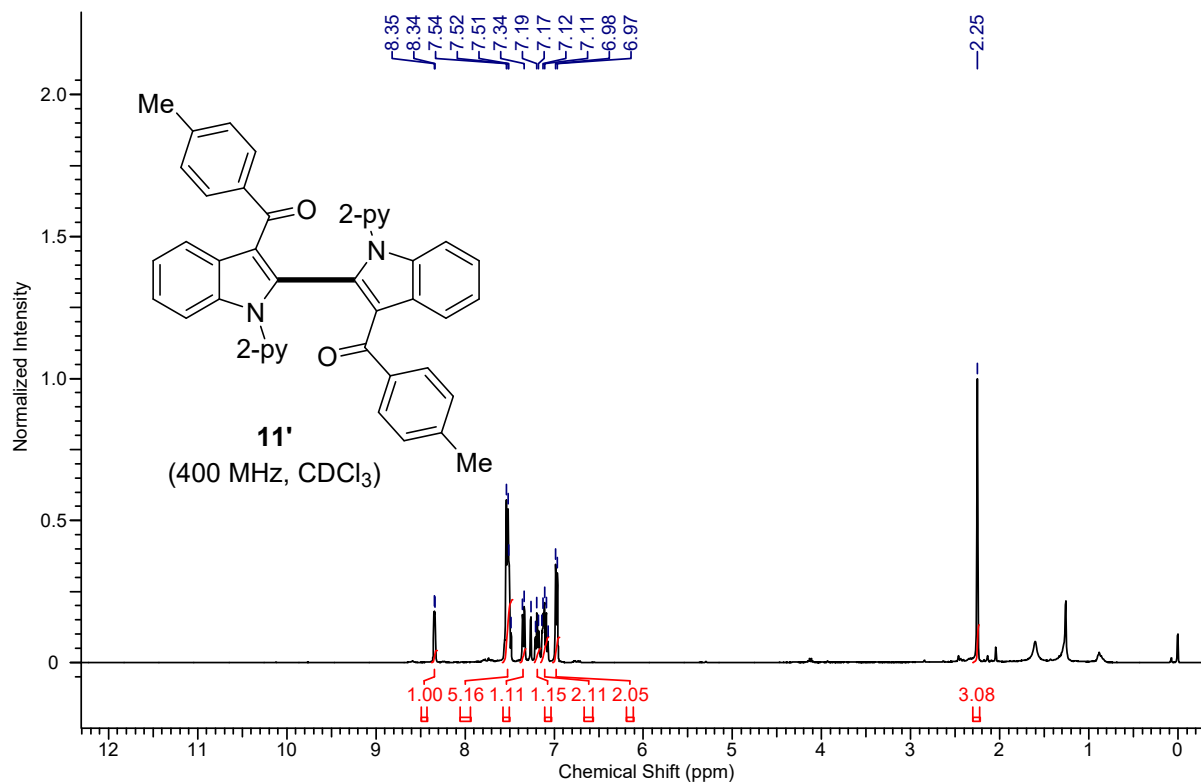
¹³C-NMR spectrum of compound 10



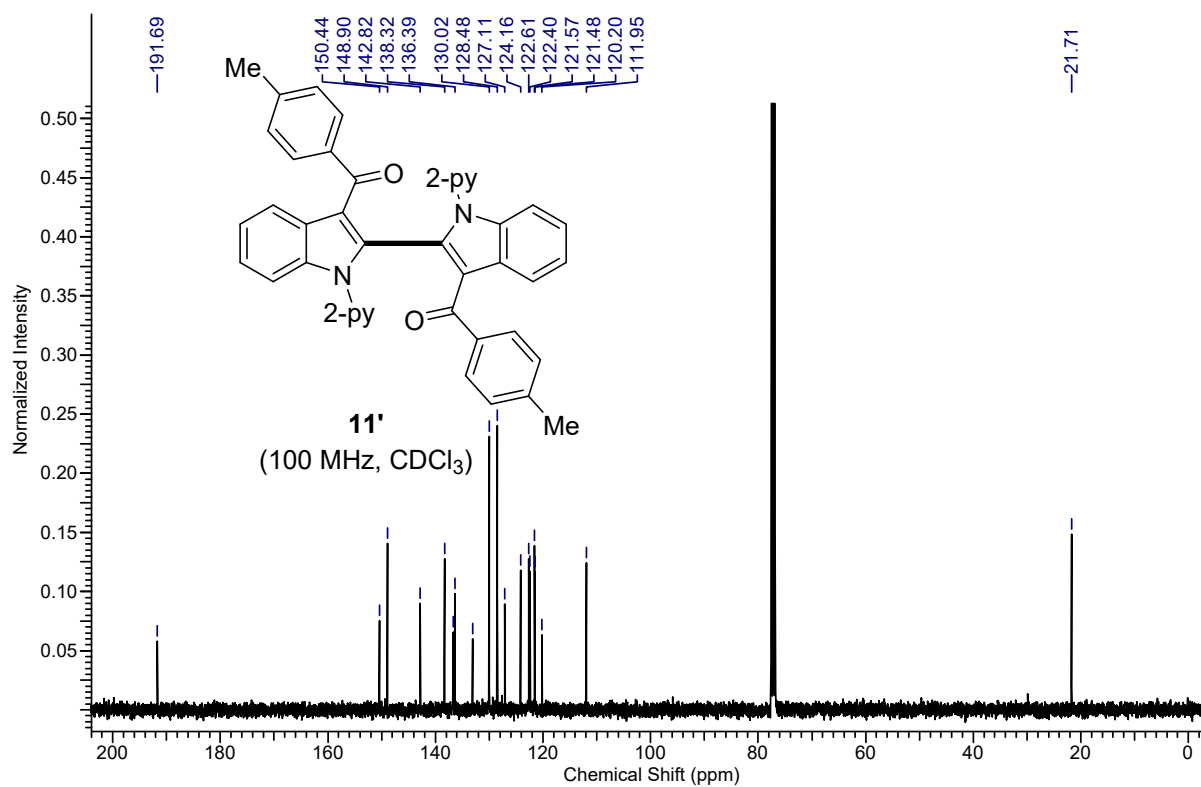
¹H-NMR spectrum of compound **11**



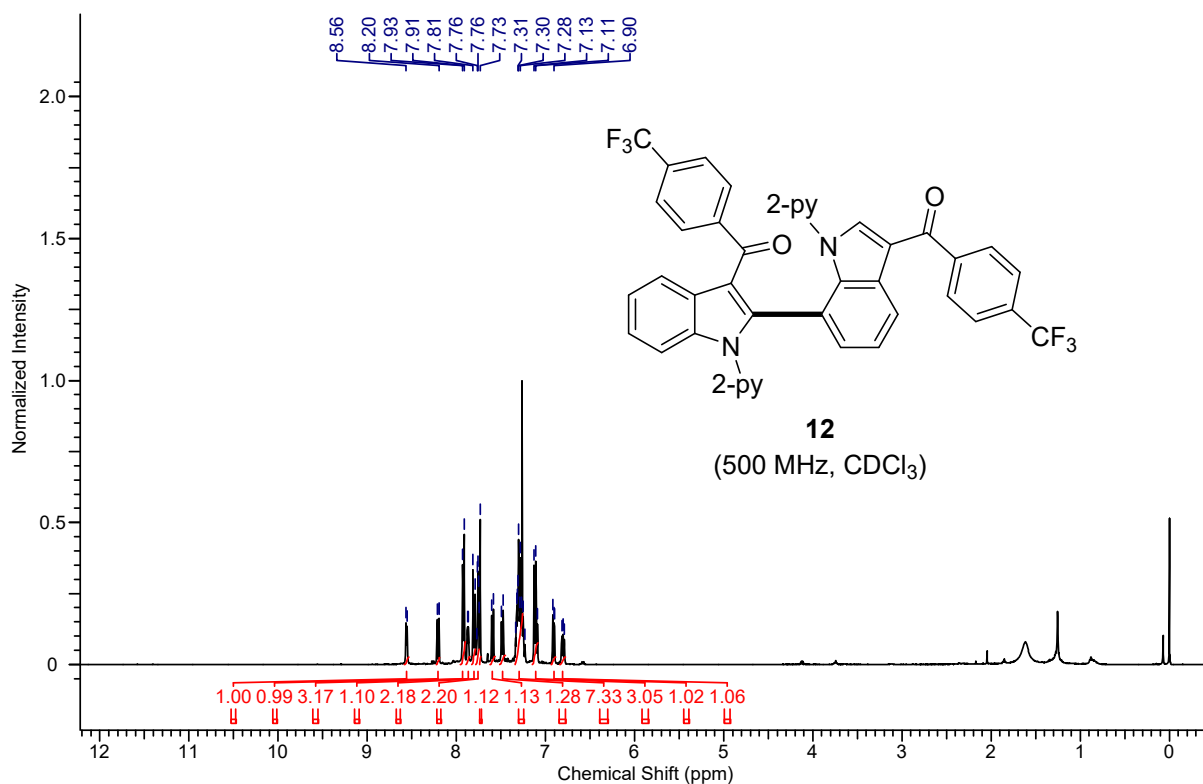
¹³C-NMR spectrum of compound **11**



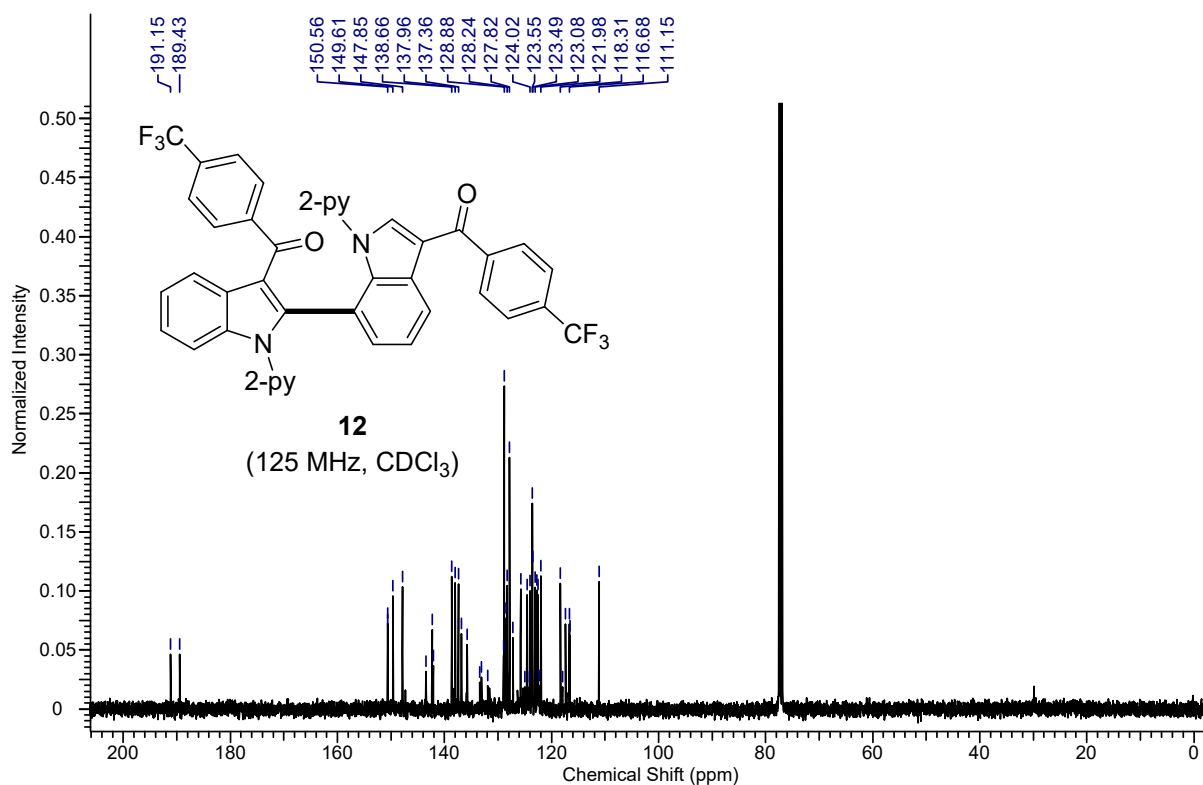
¹H-NMR spectrum of compound 11'



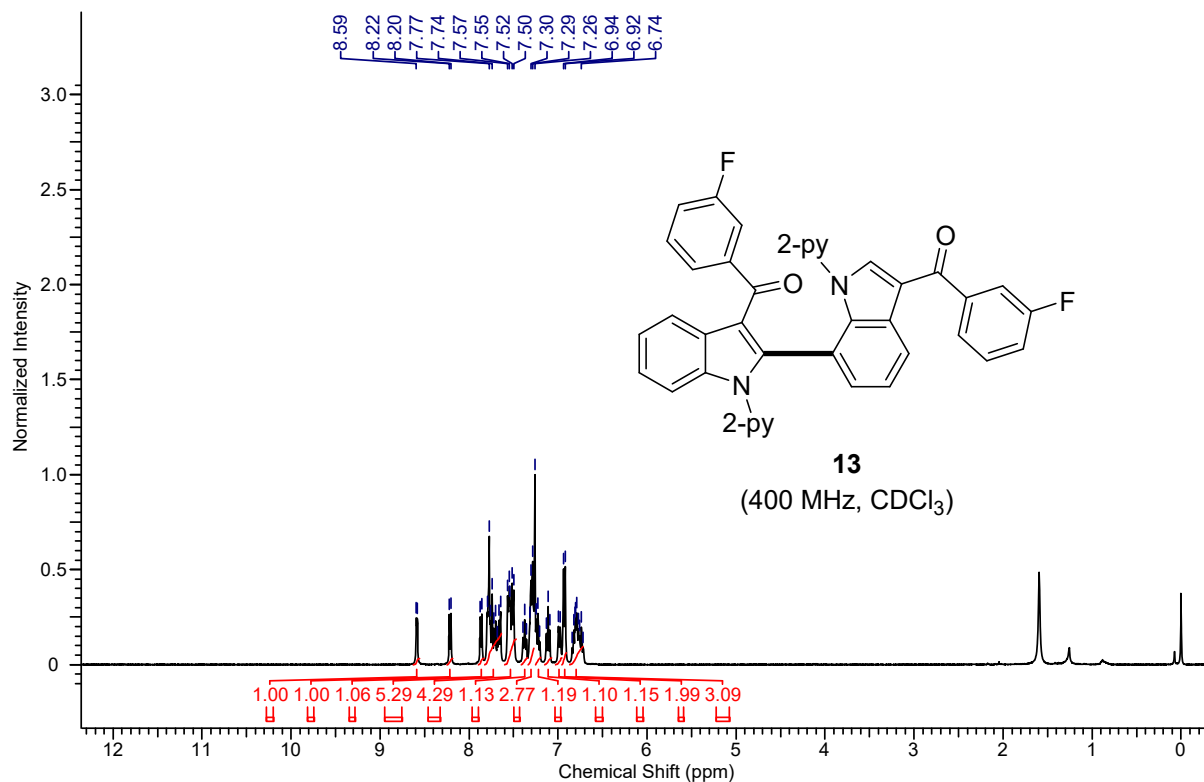
¹³C-NMR spectrum of compound 11'



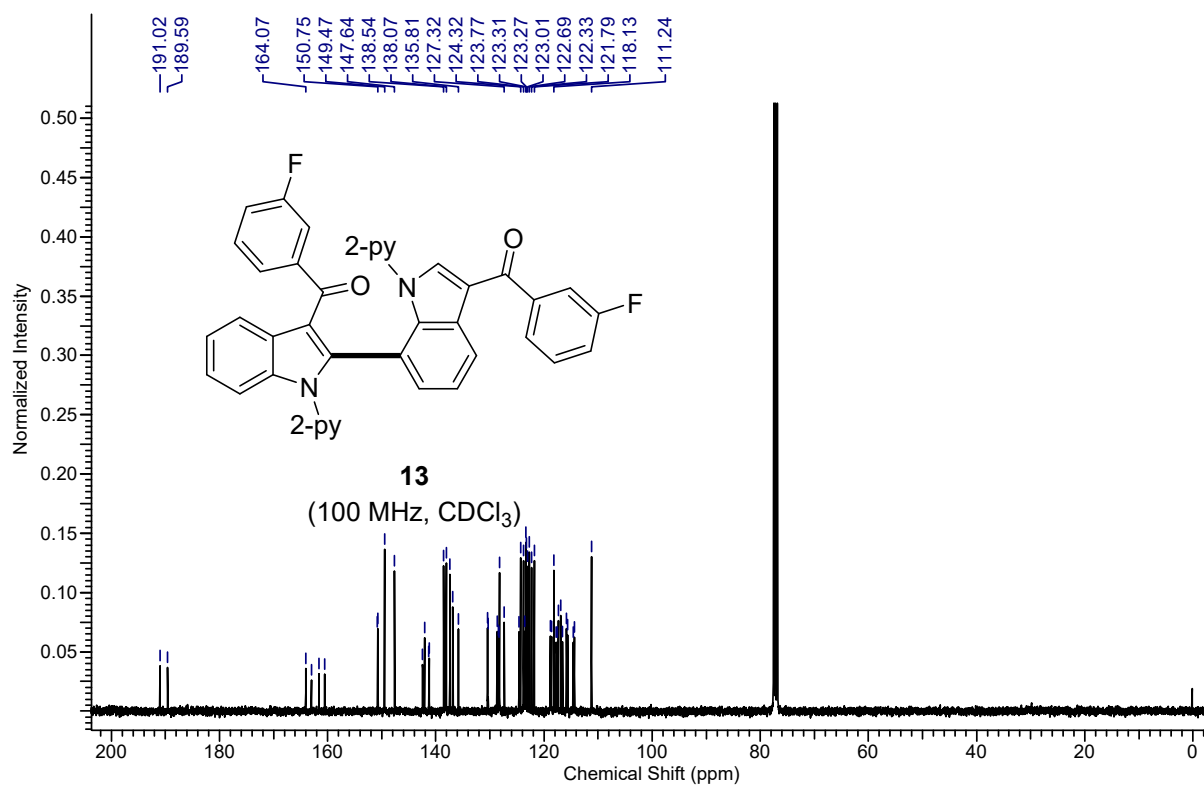
¹H-NMR spectrum of compound **12**



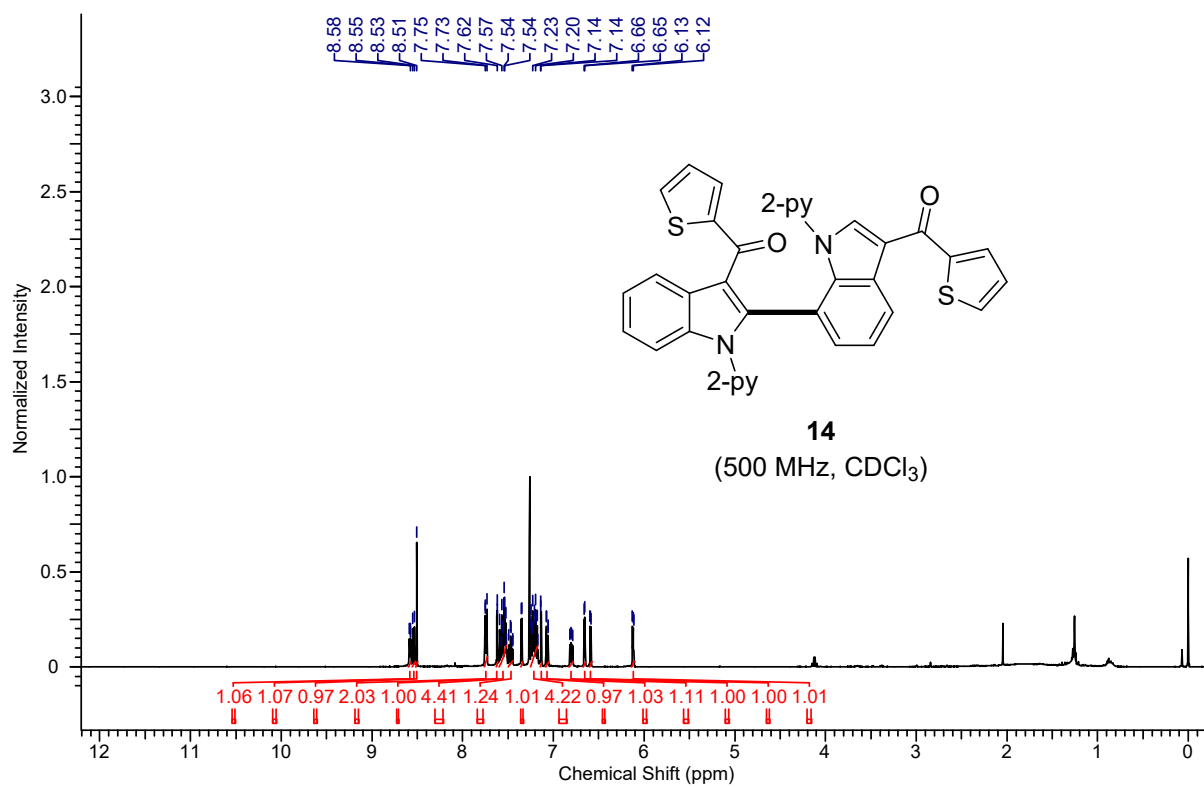
¹³C-NMR spectrum of compound **12**



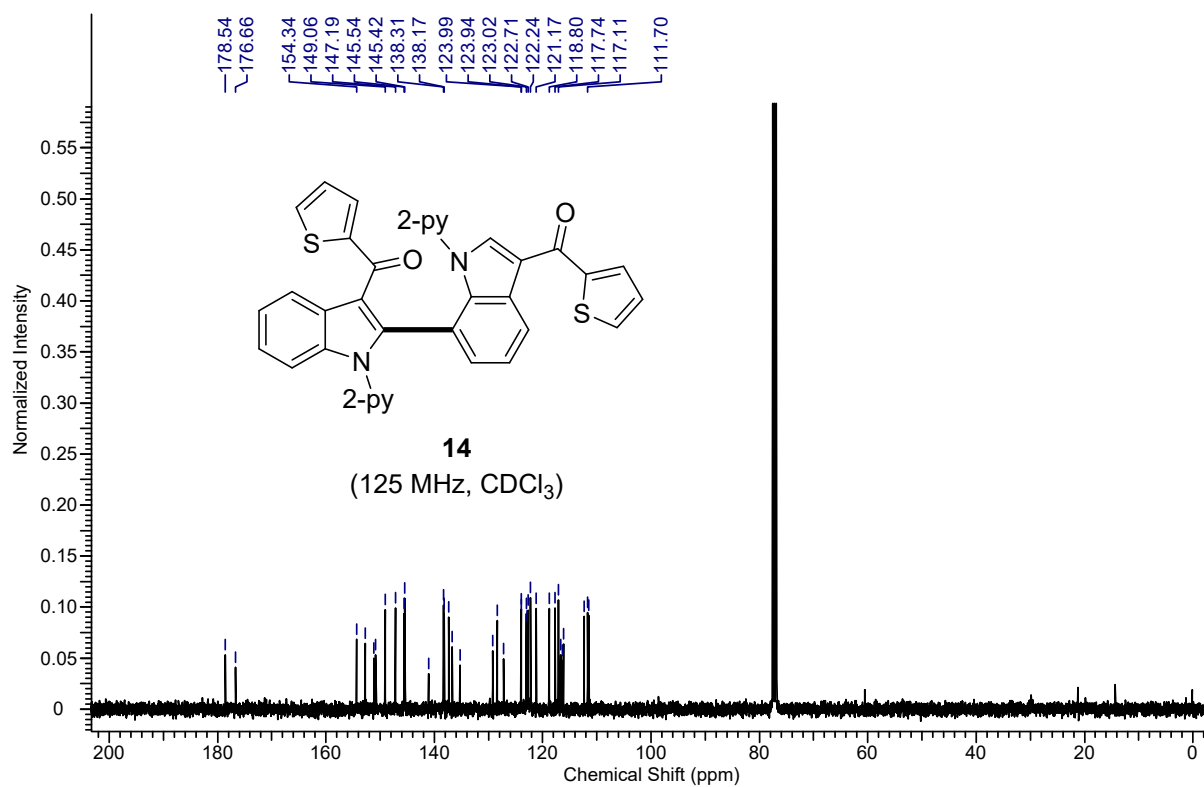
¹H-NMR spectrum of compound **13**



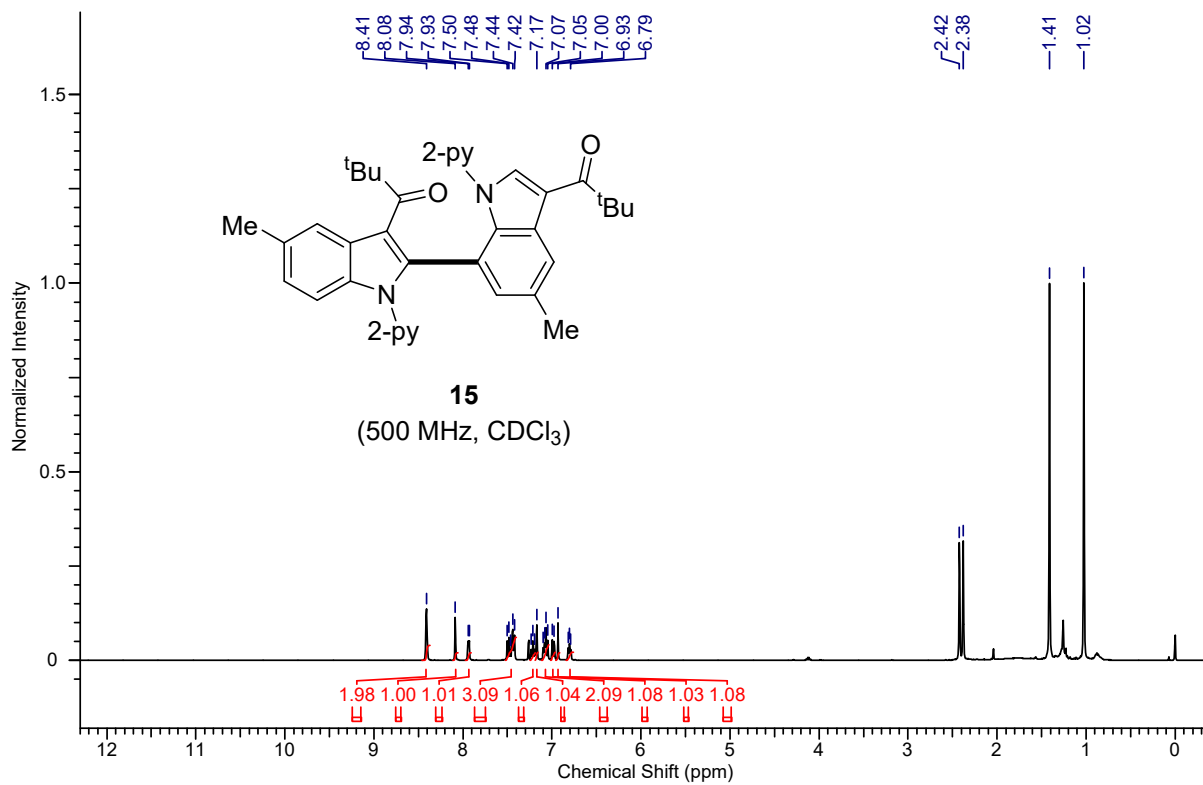
¹³C-NMR spectrum of compound **13**



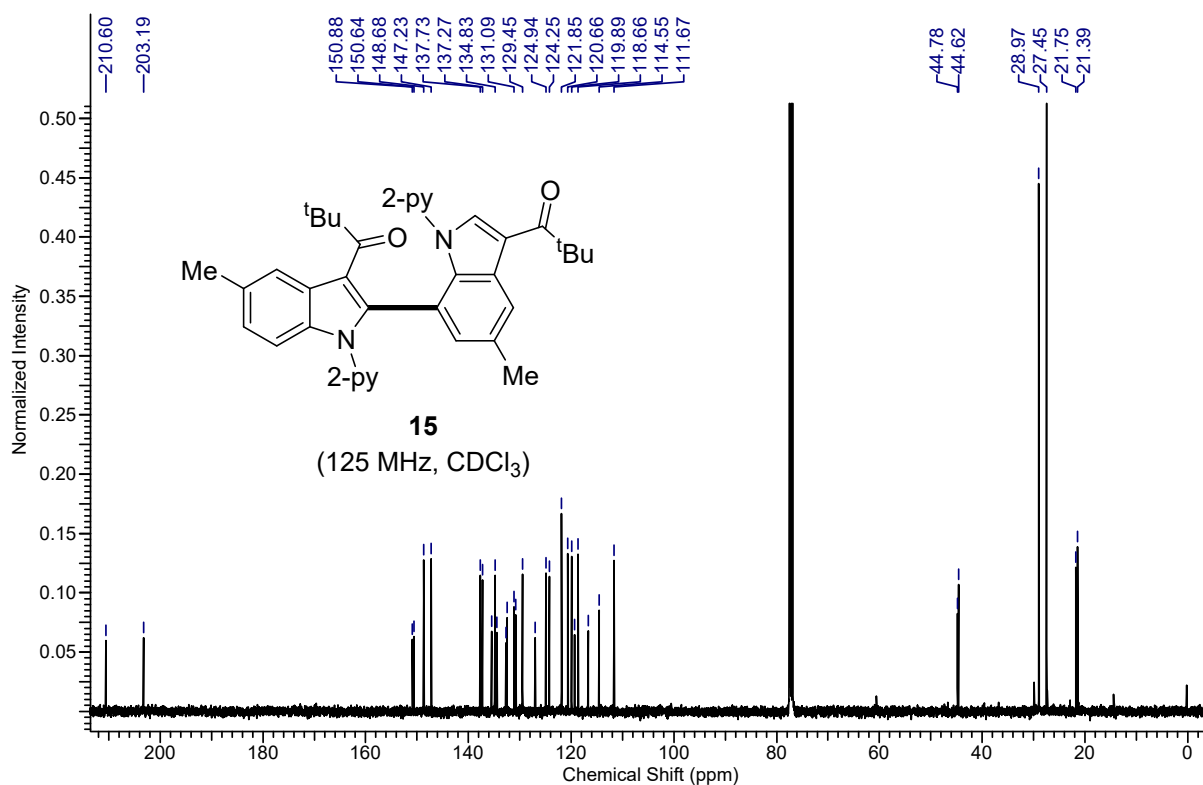
¹H-NMR spectrum of compound **14**



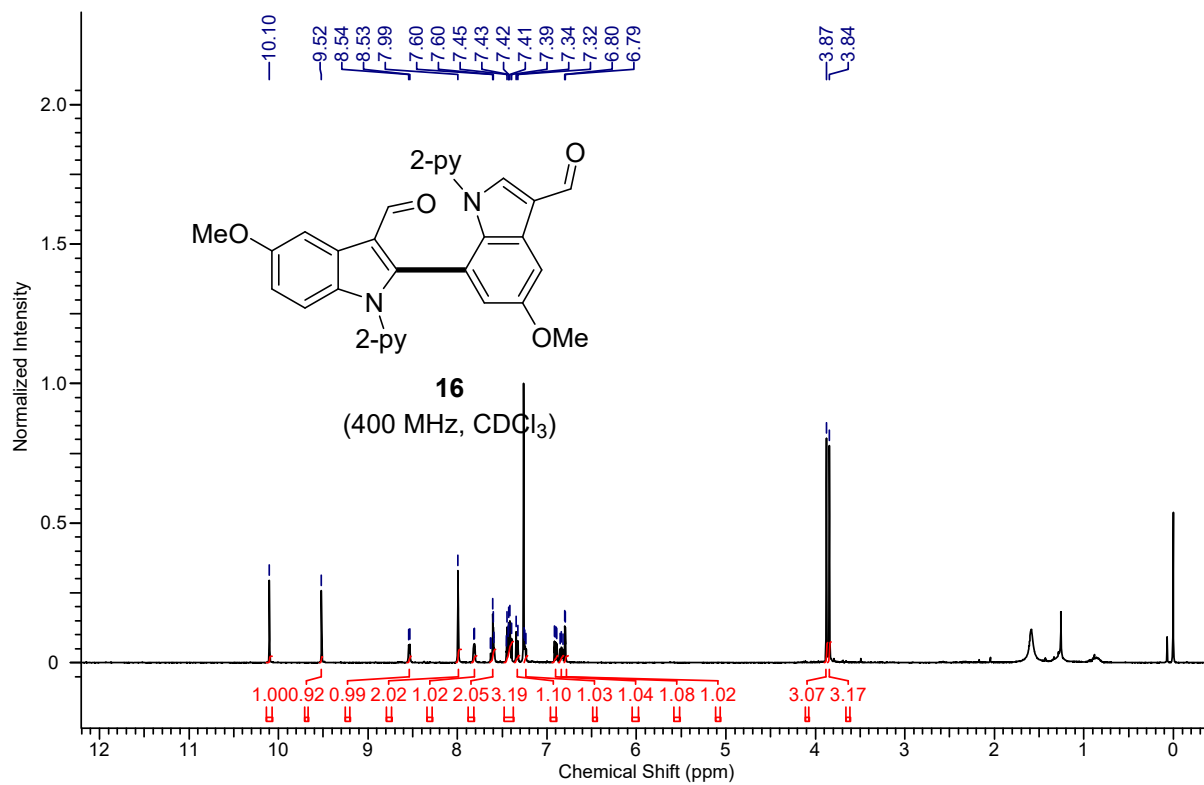
¹³C-NMR spectrum of compound **14**



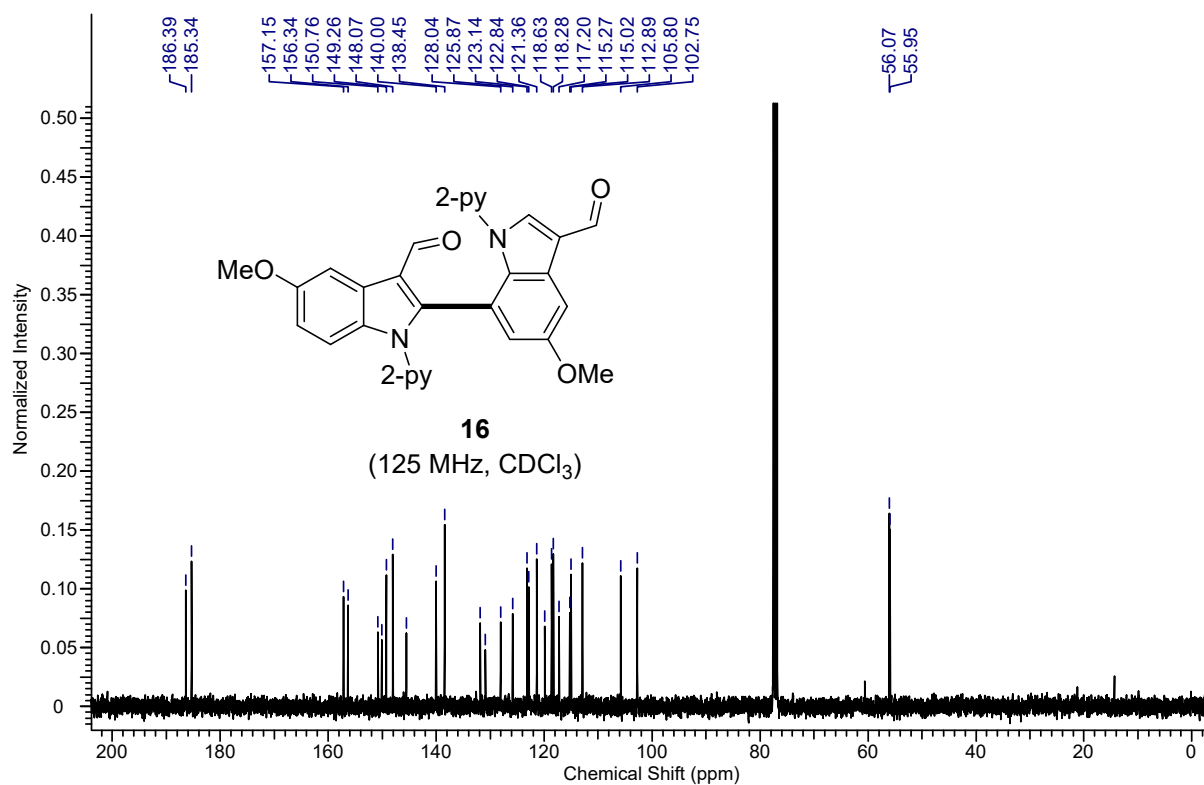
¹H-NMR spectrum of compound **15**



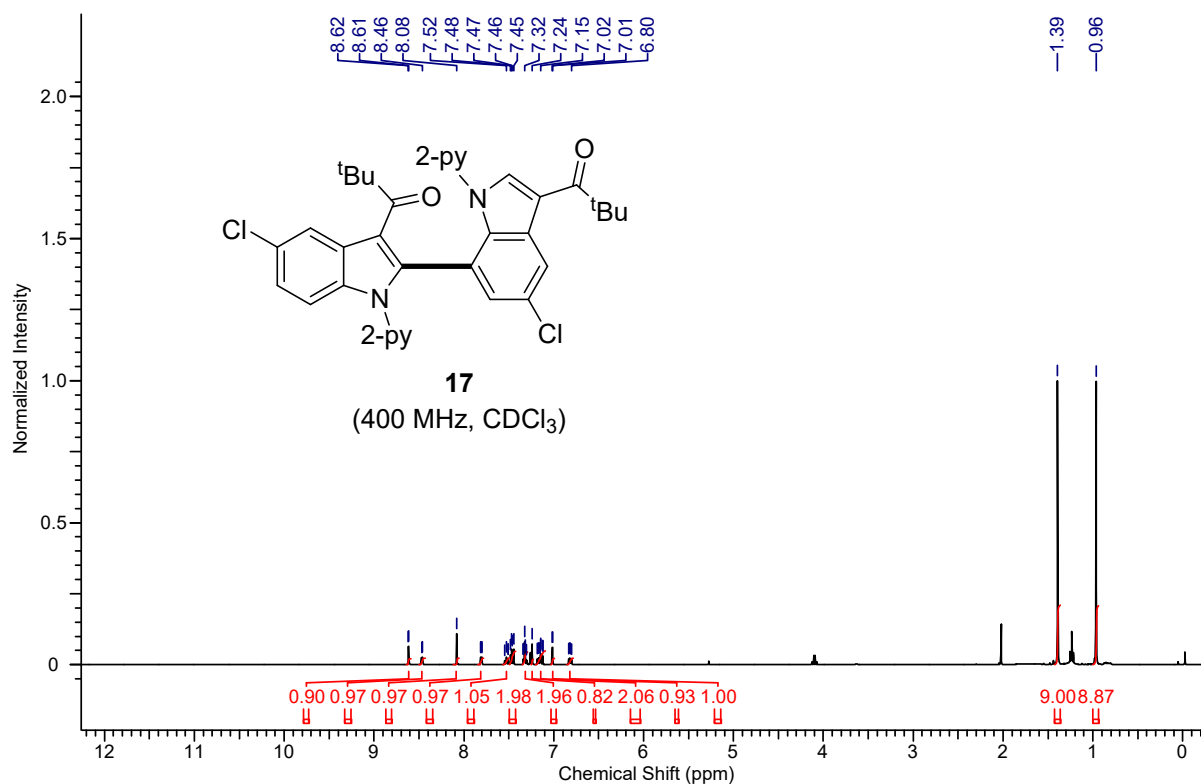
¹³C-NMR spectrum of compound **15**



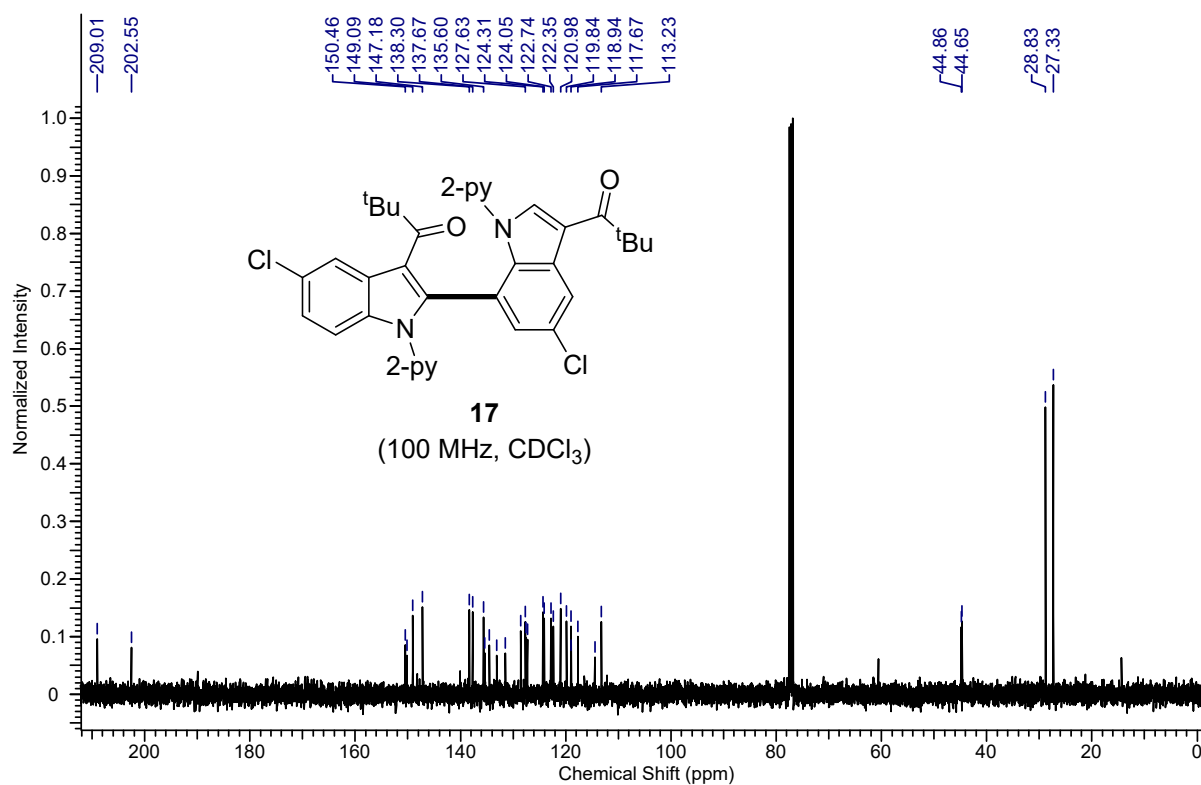
¹H-NMR spectrum of compound **16**



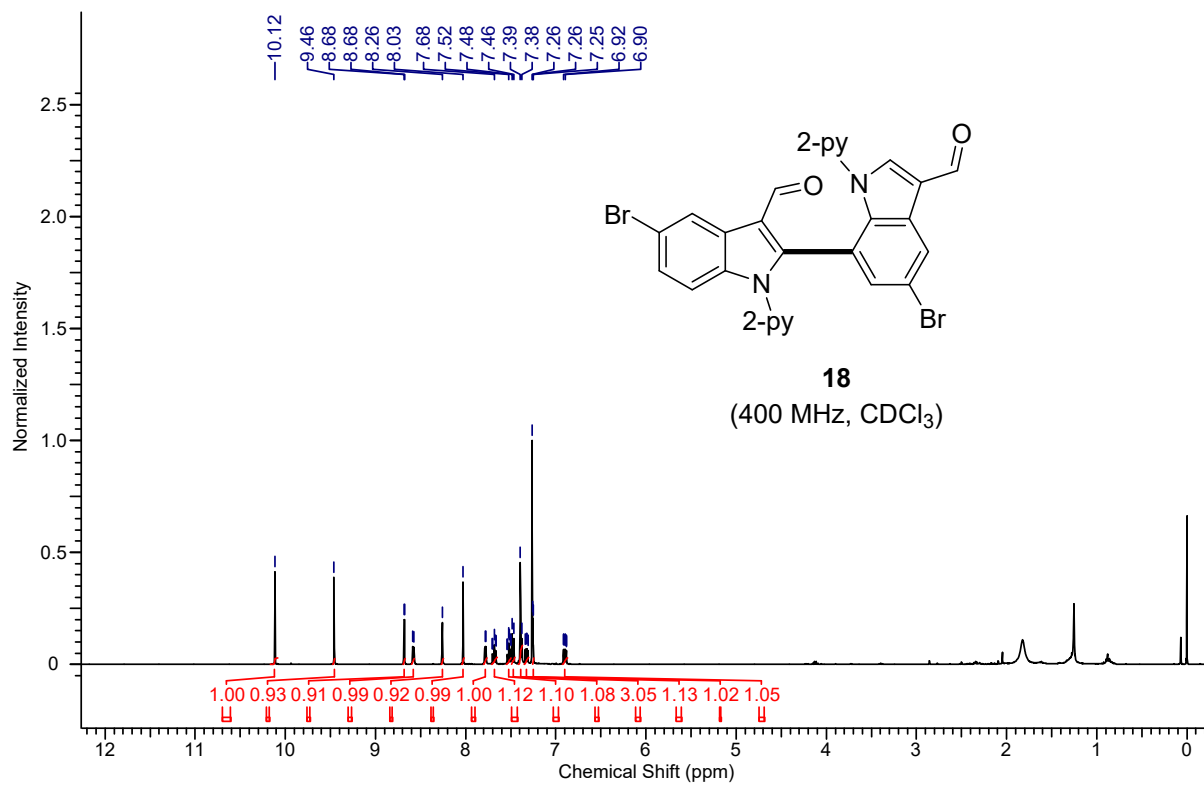
¹³C-NMR spectrum of compound **16**



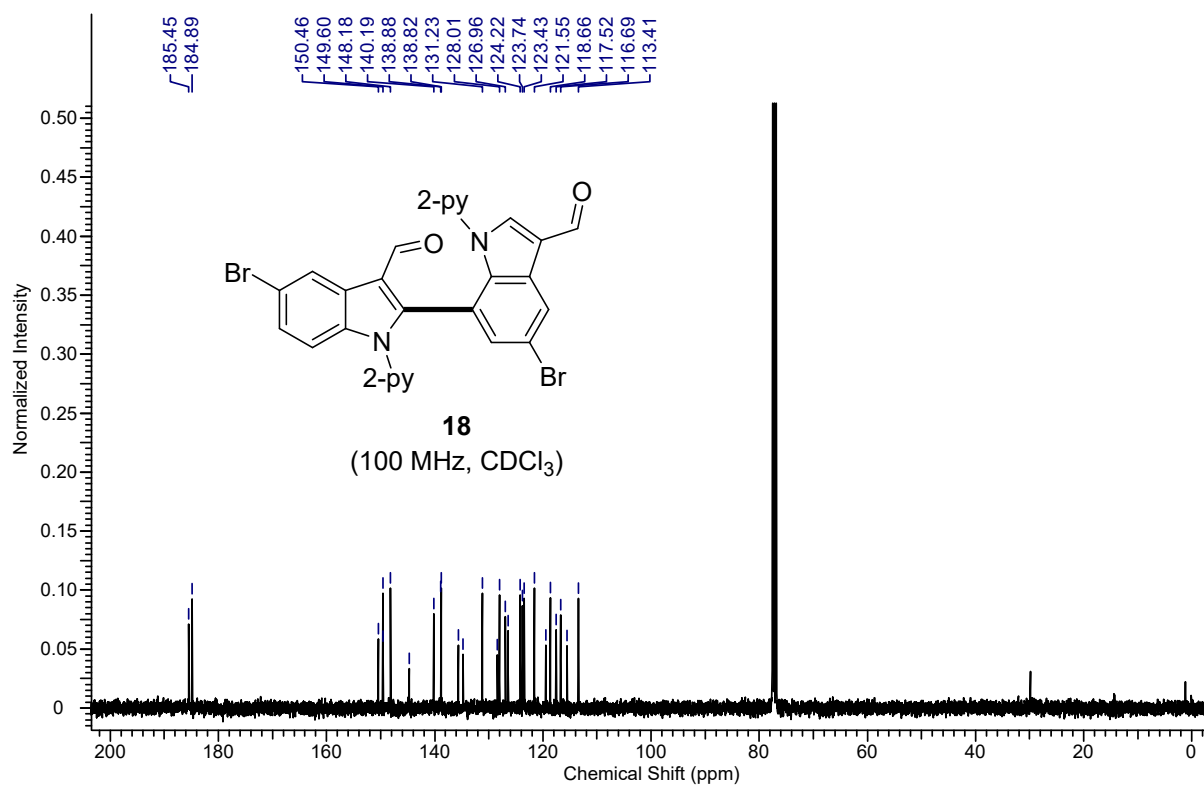
¹H-NMR spectrum of compound **17**



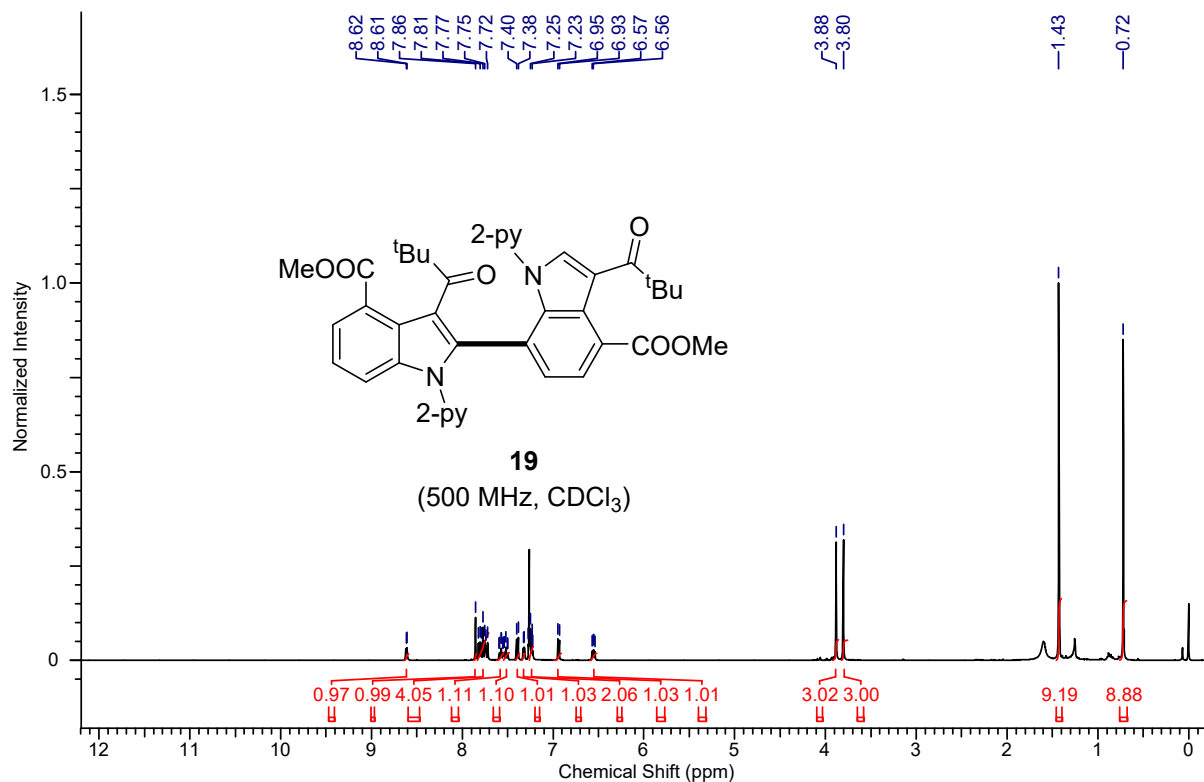
¹³C-NMR spectrum of compound **17**



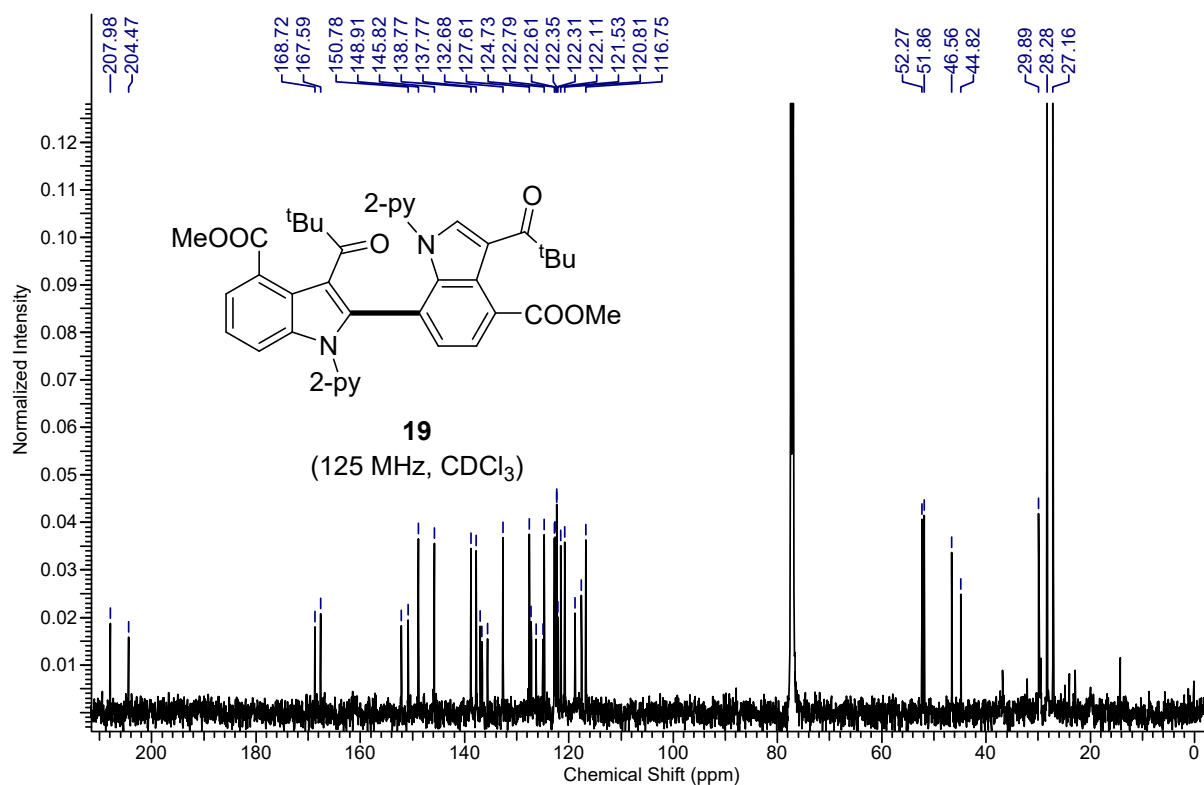
¹H-NMR spectrum of compound **18**



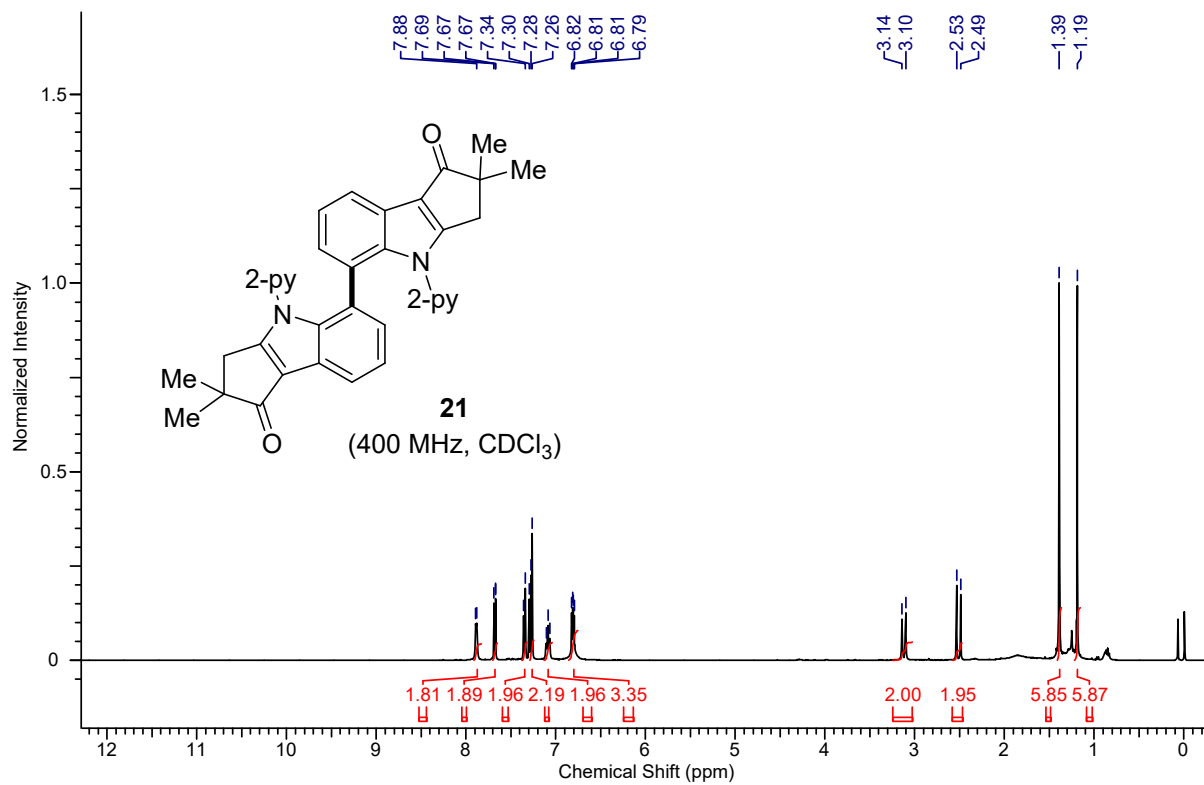
¹³C-NMR spectrum of compound **18**



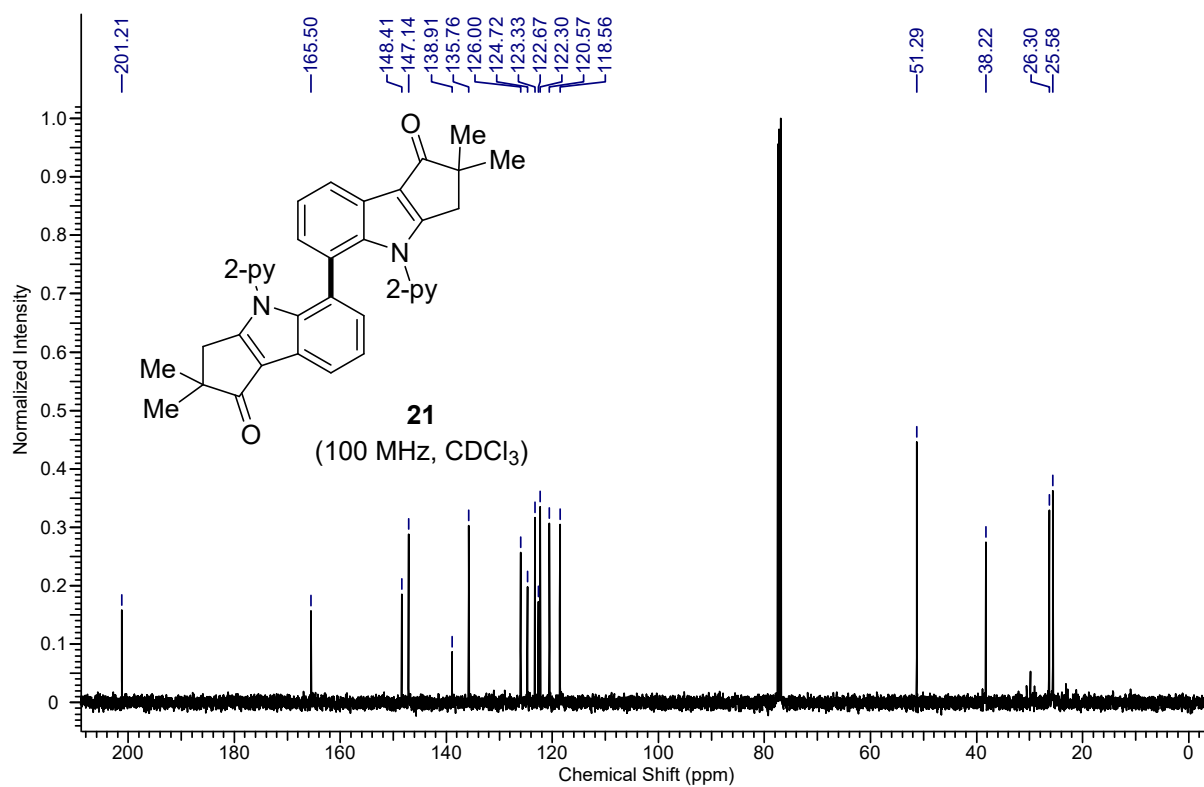
¹H-NMR spectrum of compound **19**



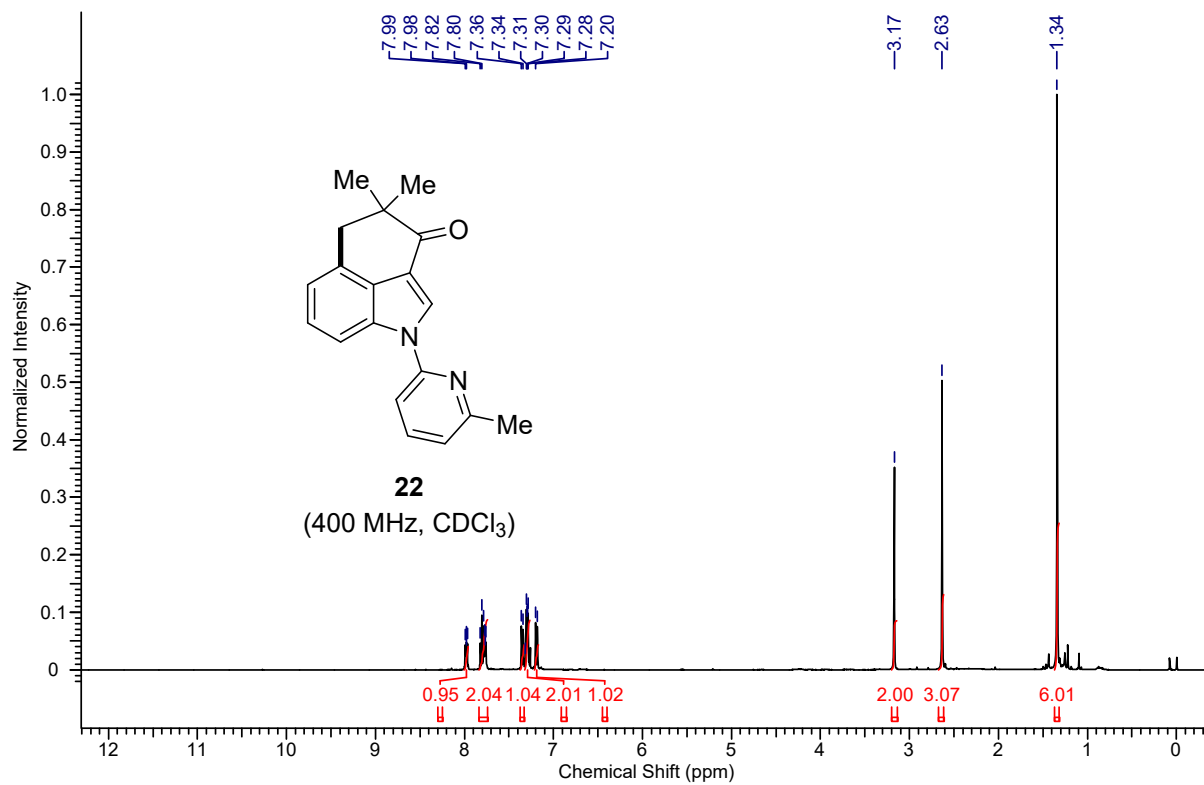
¹³C-NMR spectrum of compound **19**



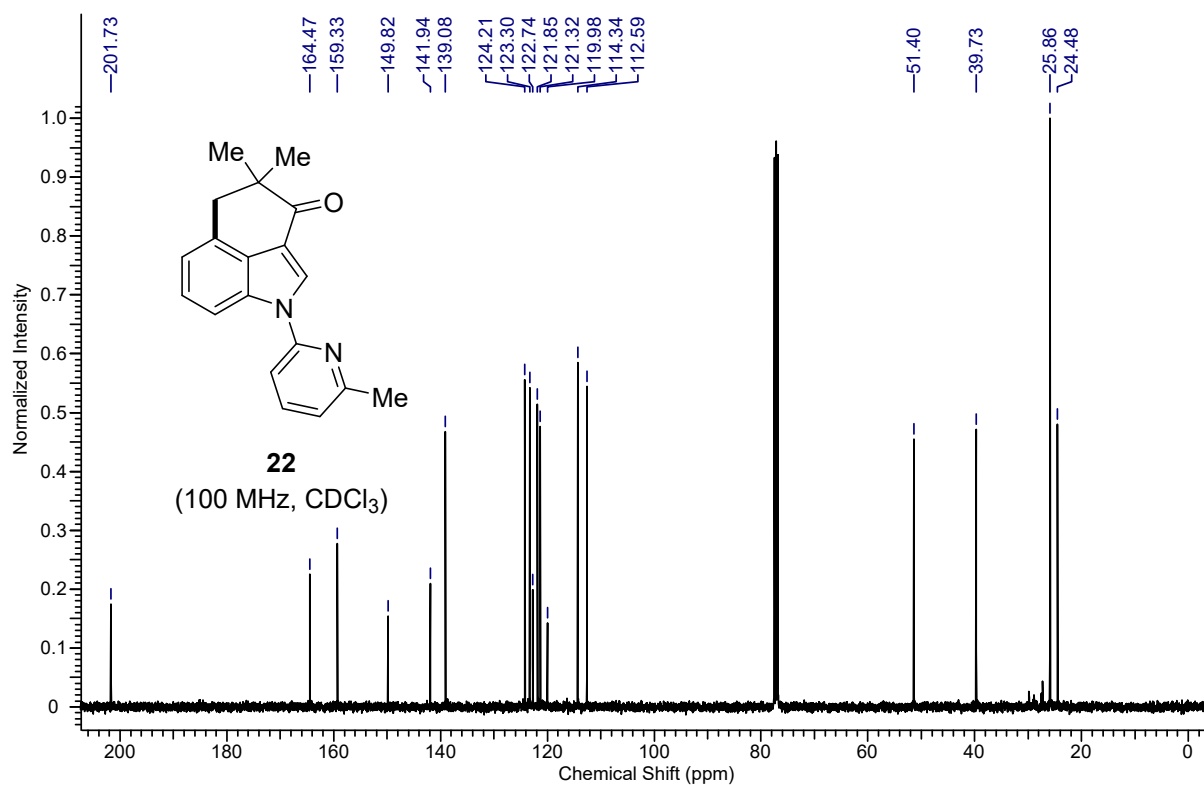
¹H-NMR spectrum of compound **21**



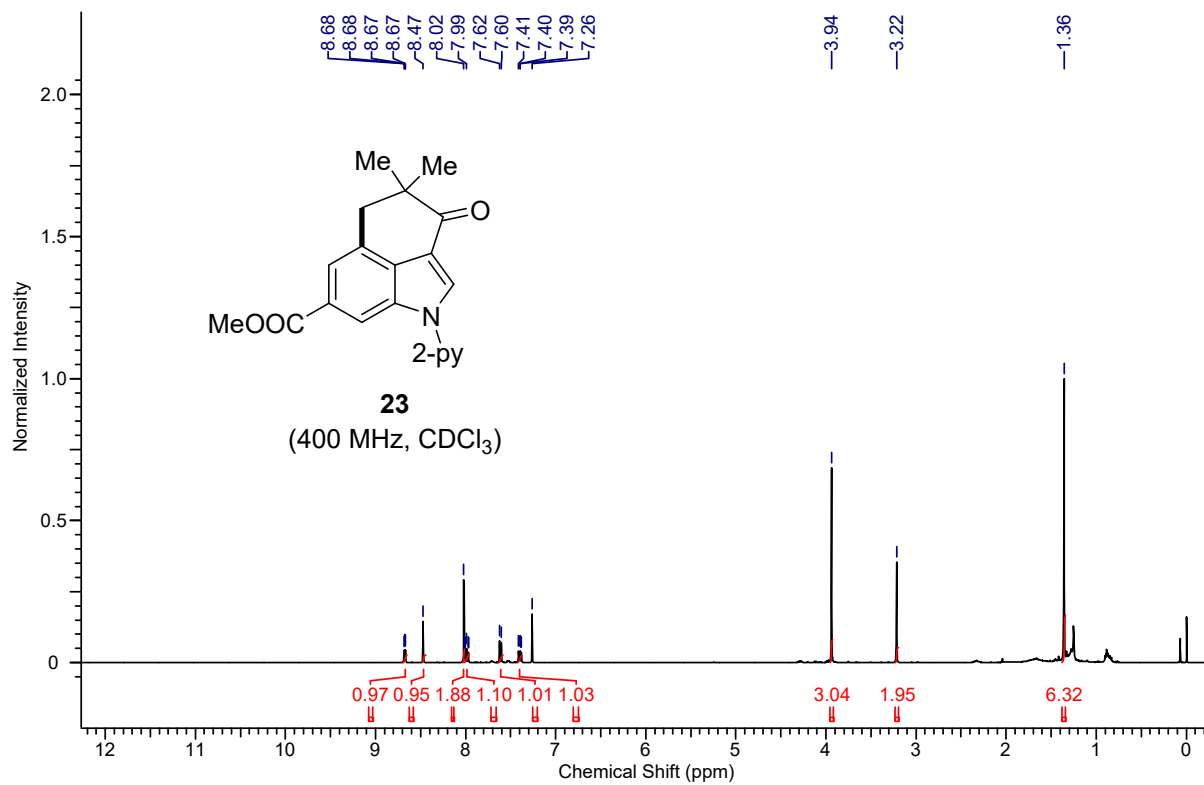
¹³C-NMR spectrum of compound **21**



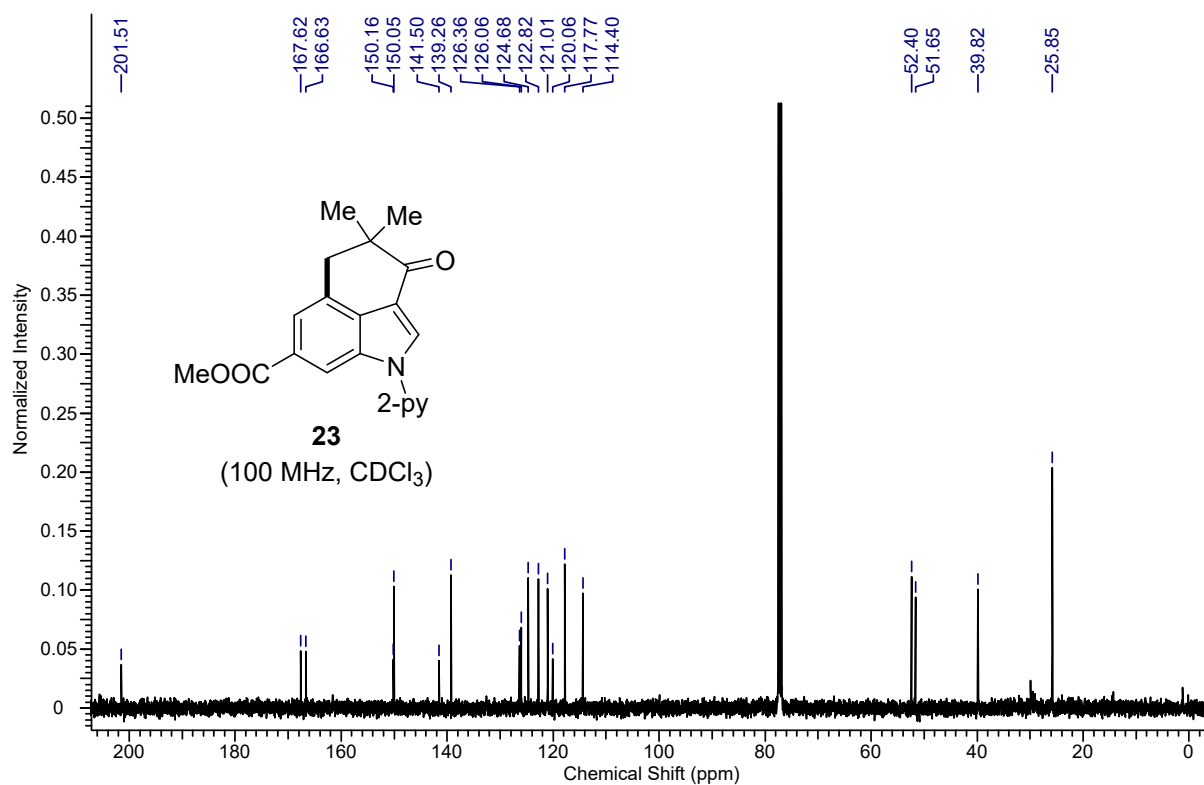
¹H-NMR spectrum of compound **22**



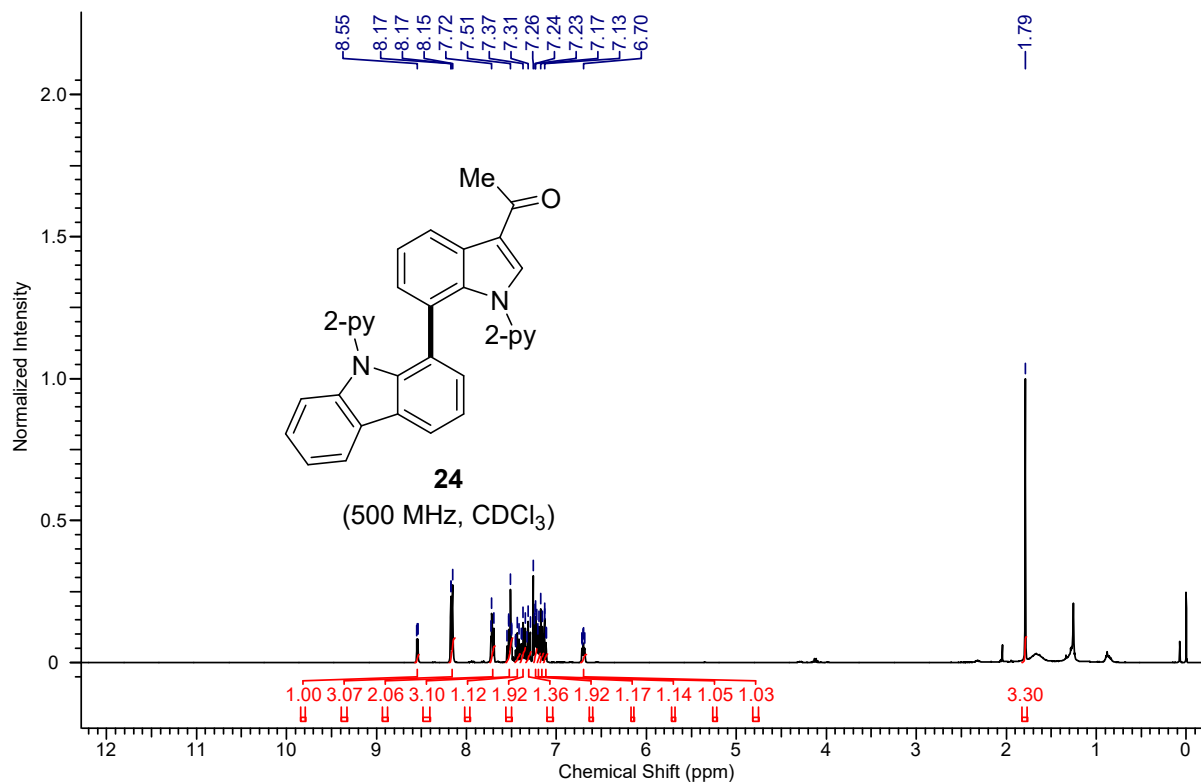
¹³C-NMR spectrum of compound **22**



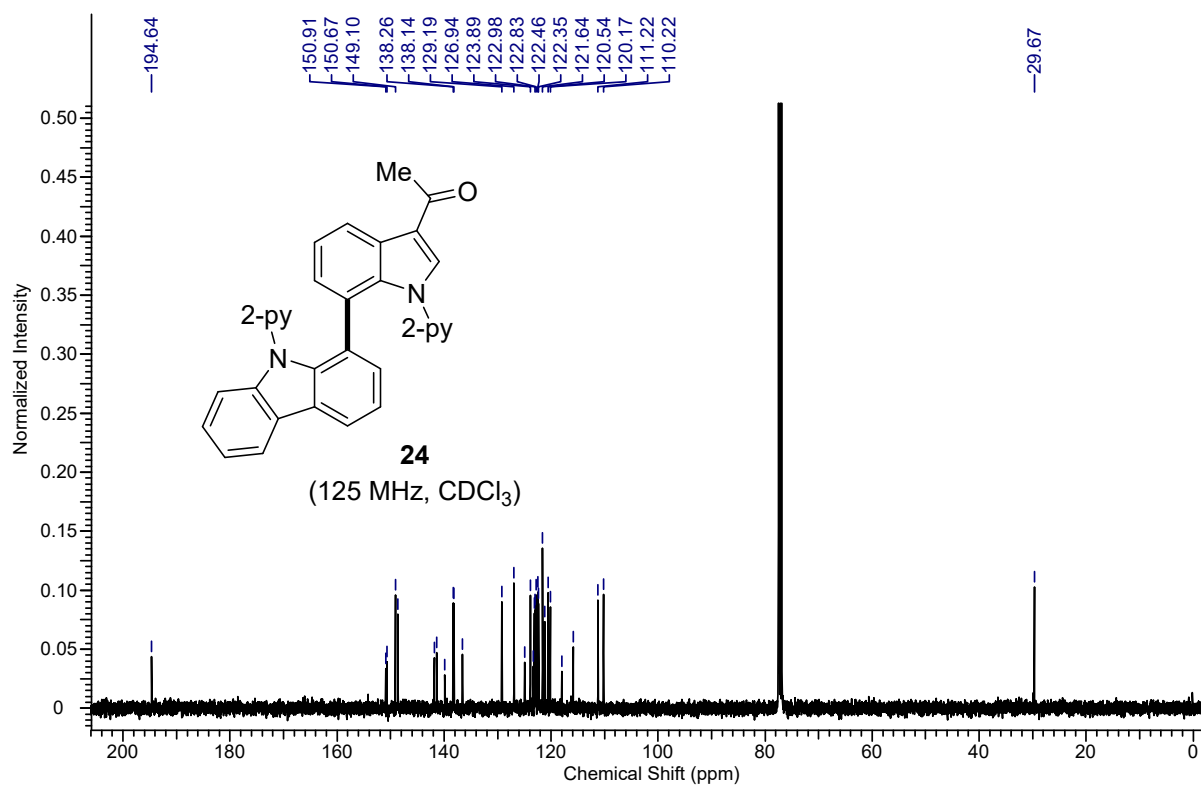
¹H-NMR spectrum of compound **23**



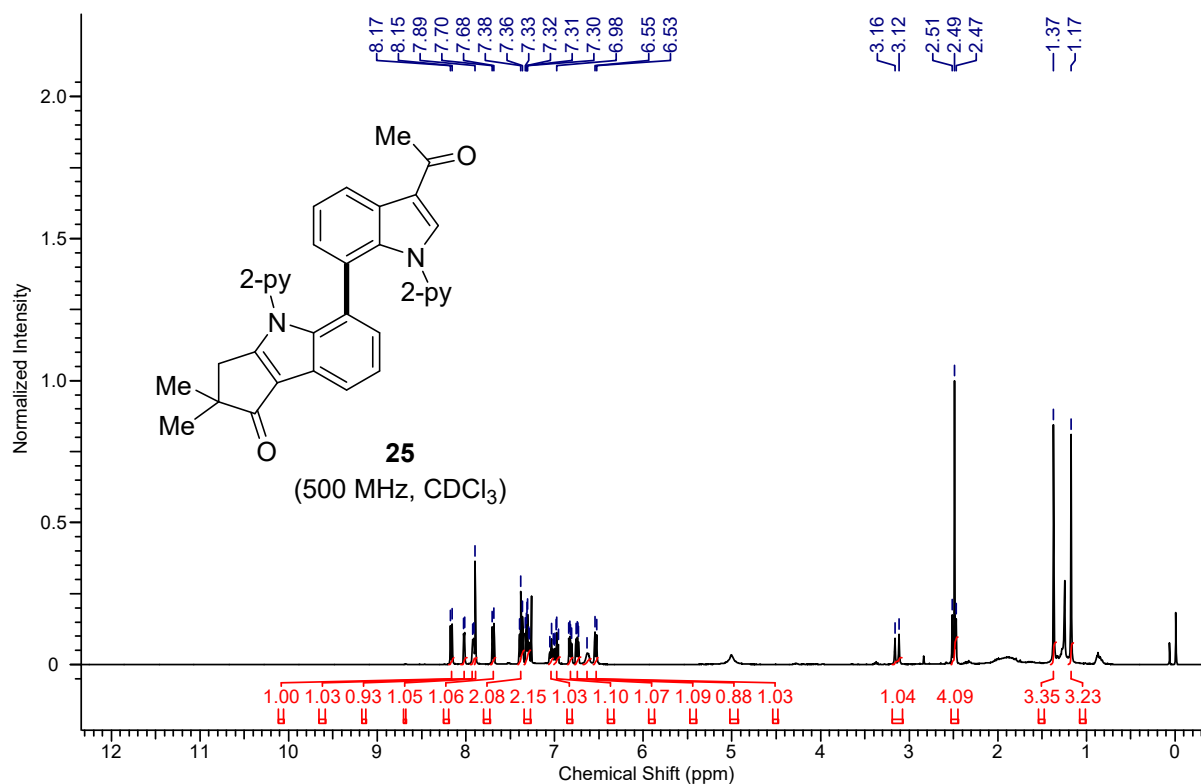
¹³C-NMR spectrum of compound **23**



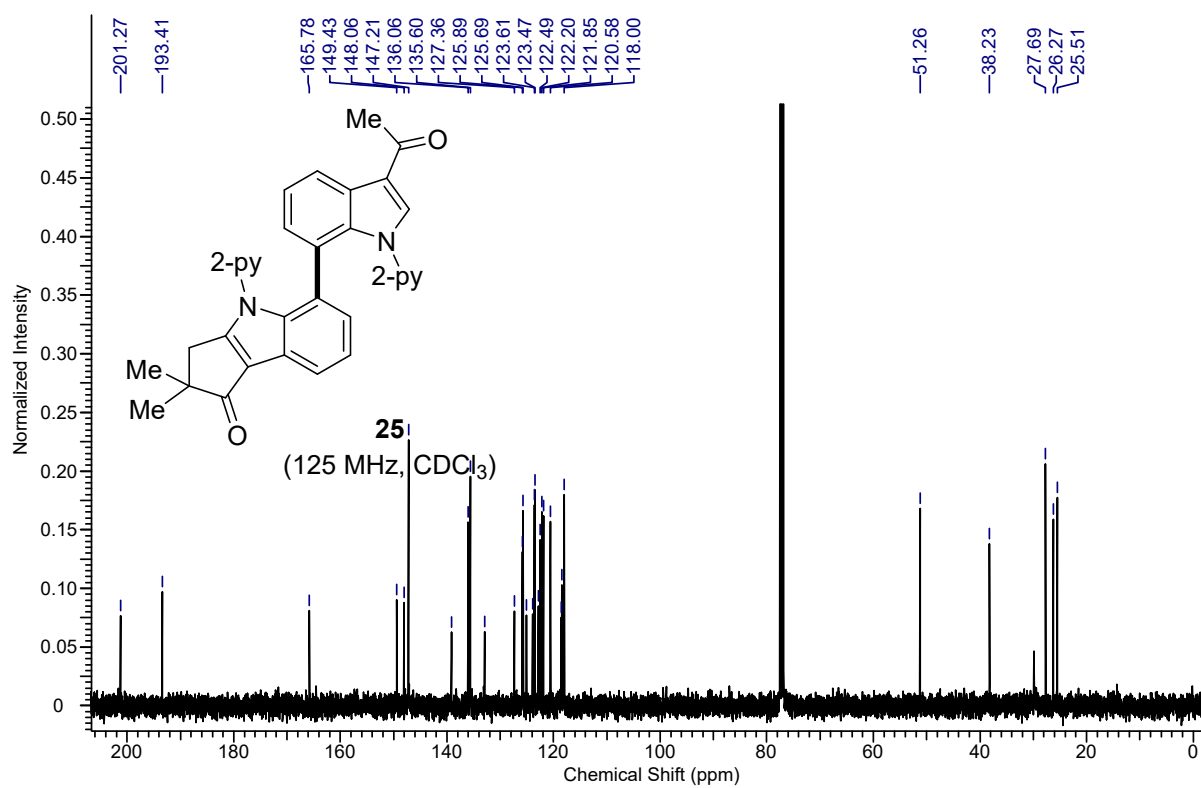
¹H-NMR spectrum of compound **24**



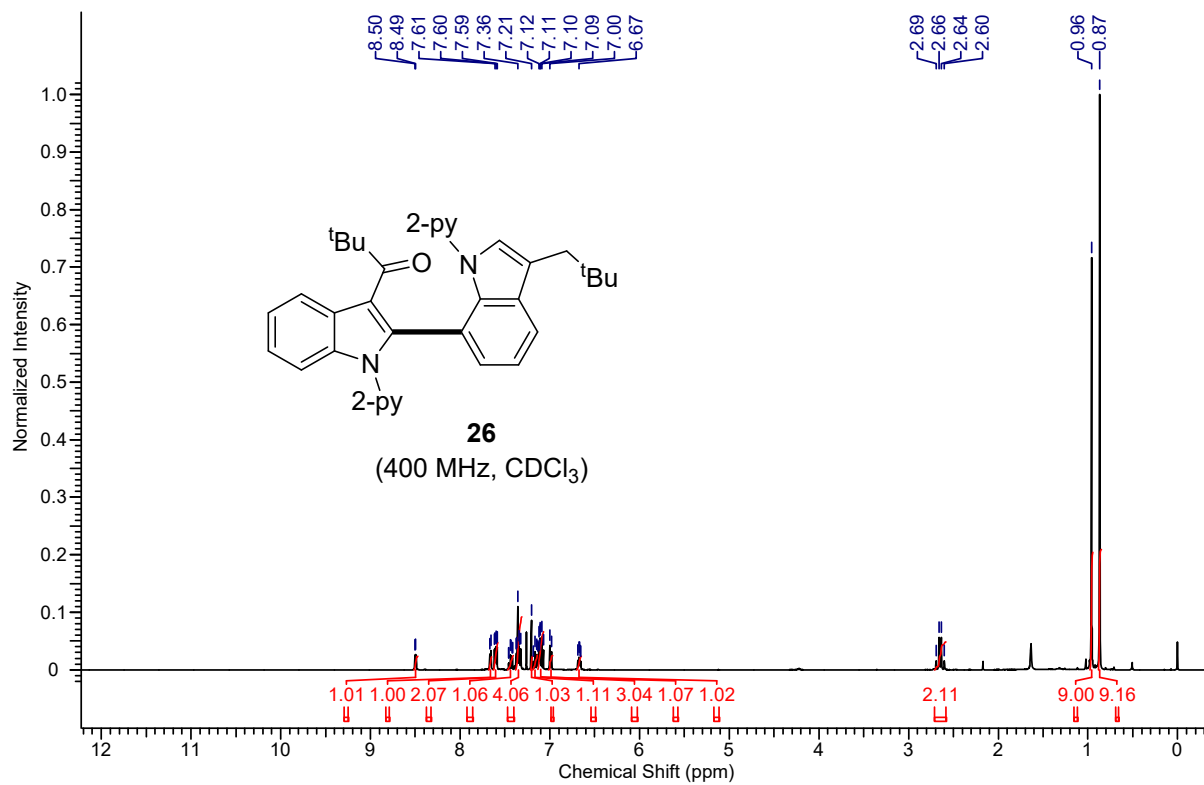
¹³C-NMR spectrum of compound **24**



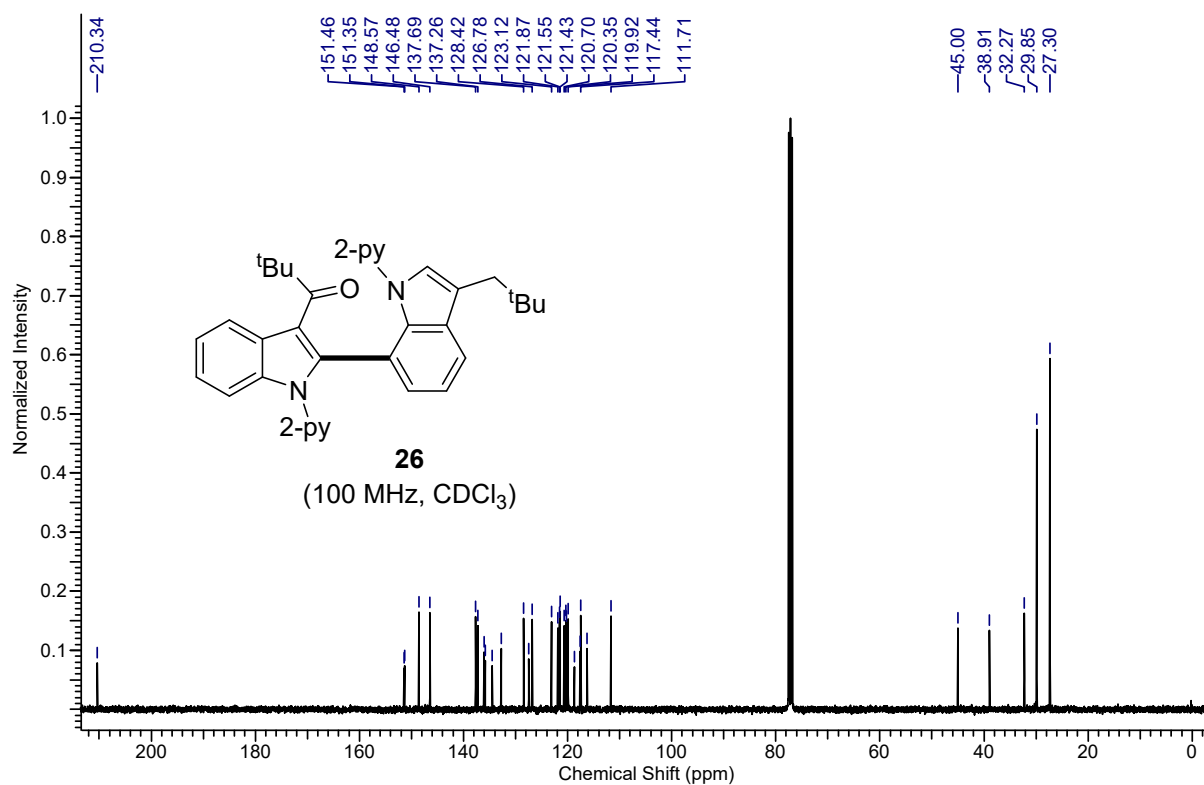
¹H-NMR spectrum of compound **25**



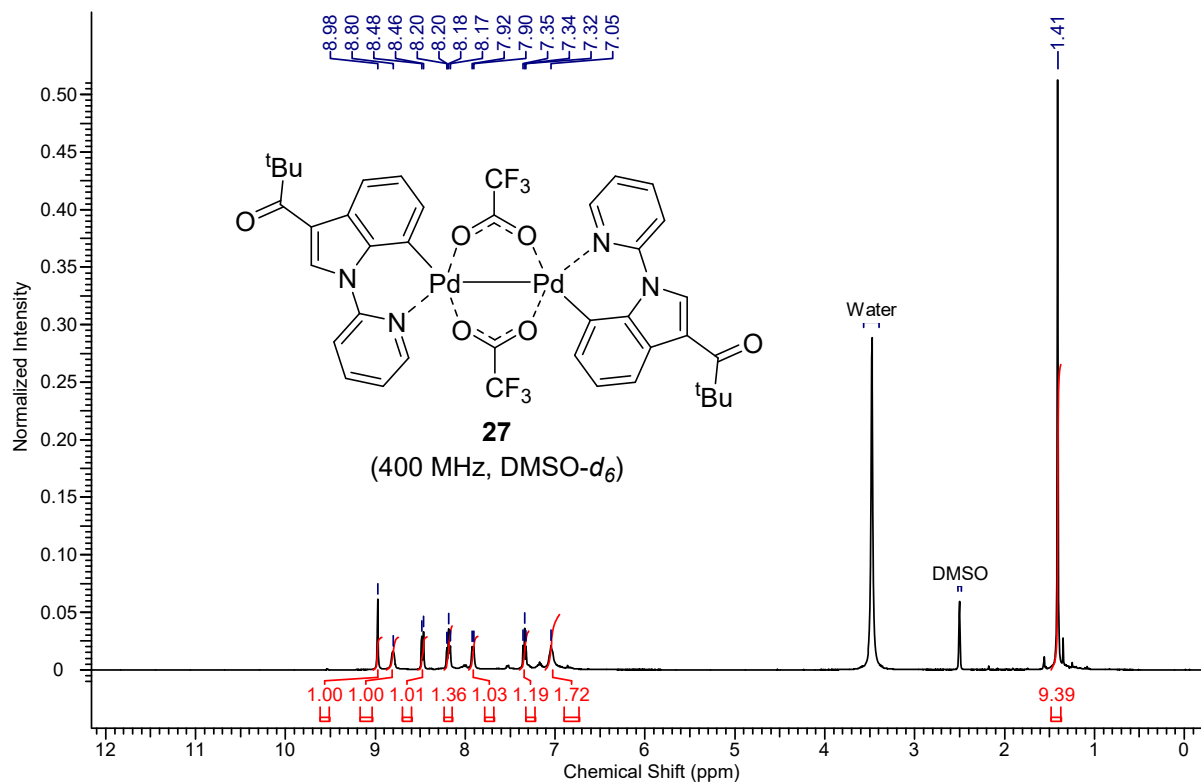
¹³C-NMR spectrum of compound **25**



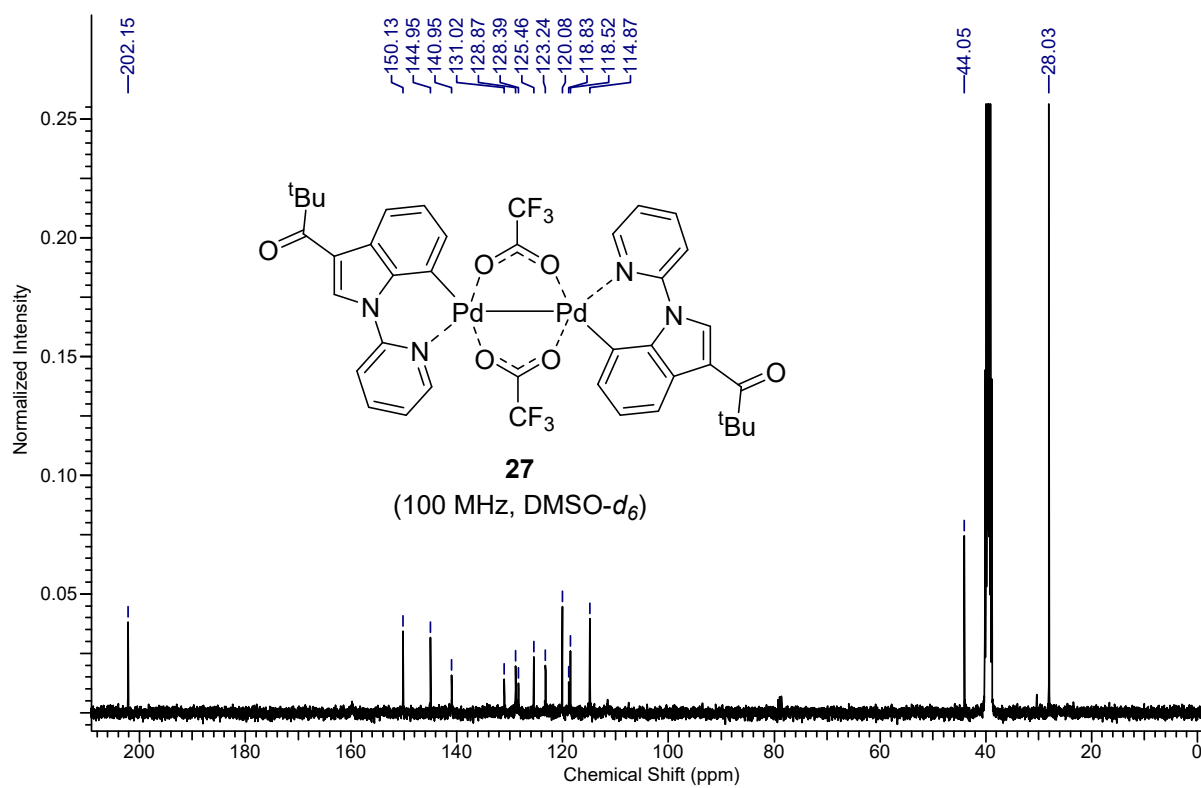
¹H-NMR spectrum of compound **26**



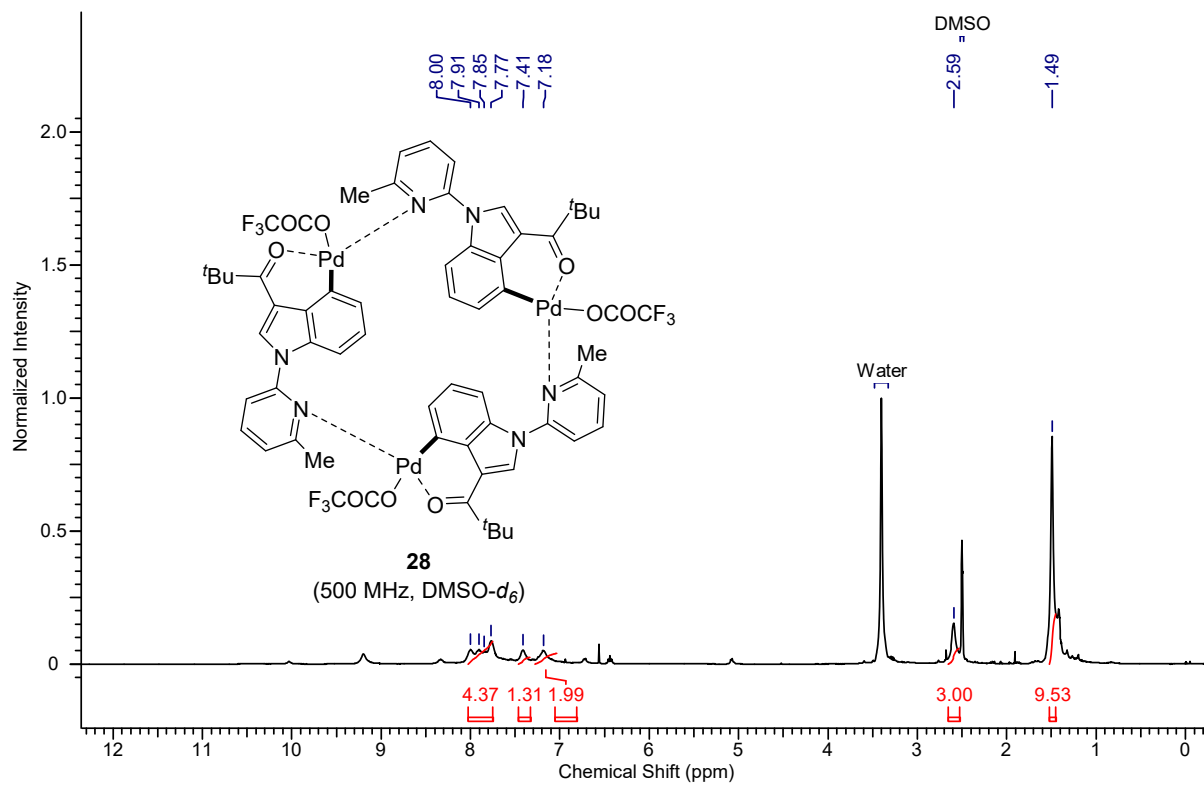
¹³C-NMR spectrum of compound **26**



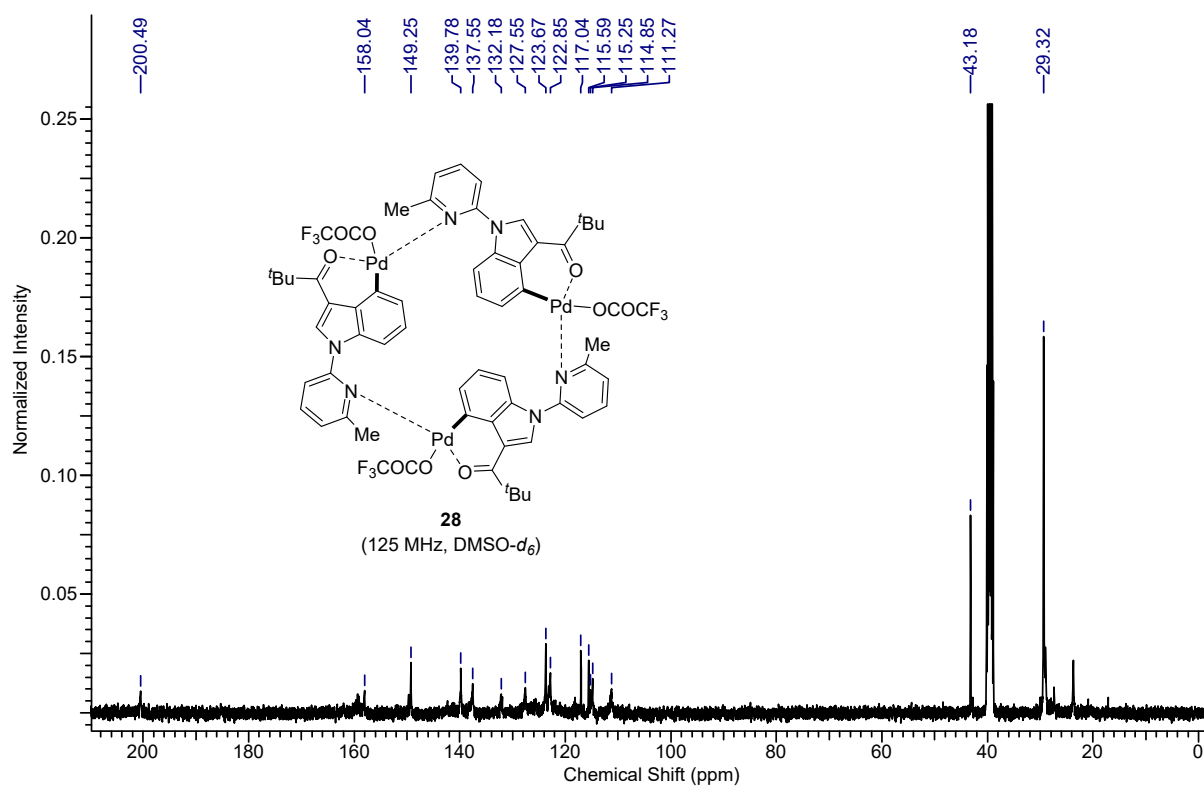
¹H-NMR spectrum of compound **27**



¹³C-NMR spectrum of compound **27**



¹H-NMR spectrum of compound **28**



¹³C-NMR spectrum of compound **28**