

Electronic Supplementary Information (ESI)

A facile one-pot method to synthesis of 2-alkylated indole and 2,2'-bis(indolyl)methane derivatives using ketones as electrophile and its anion sensing ability

Sinan Bayindir^{1,2} and Nurullah Saracoglu*¹

¹Department of Chemistry, Faculty of Sciences, Atatürk University, Erzurum, 25240, Turkey

²Department of Chemistry, Faculty of Sciences and Arts, Bingöl University, Bingöl, 12000, Turkey

Table of Contents

Experimental Section	S2-S10
General procedure for the synthesis of 2-alkylated indoles	S2
General procedure for the synthesis of 2,2'-bis(indolyl)methanes	S8
NMR spectra	S11-S32
Figure S1-S21. ¹ H NMR (400 MHz) and ¹³ C NMR (100 MHz) spectrums of indole derivatives	S11-S30
Figure S22. ¹ H NMR (400 MHz) spectra in CD ₃ CN of 3l in the presence of [Bu ₄ N]F	S31
Figure S22. ¹ H NMR (400 MHz) spectra in CD ₃ CN of 4c in the presence of [Bu ₄ N]HSO ₄	S32

General: All chemicals, reagents, and solvents were commercially available from Sigma-Aldrich or Merc and used as received. Melting points were determined on Buchi 539 capillary melting apparatus and uncorrected. Infrared spectra were recorded on a Mattson 1000 FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on 400 (100)-MHz Varian and Bruker spectrometer and are reported in terms of chemical shift (δ , ppm) with SiMe_4 as an internal standard. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quarted, p = pentet, m = multiplet, bs = broad singlet, bd = broad doublet) and coupling constant(s) in Hz, integration. Elemental analyses were carried out on a Leco CHNS-932 instrument. Column chromatography was carried out on silica gel 60 (230–400 mesh ASTM). The reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254). UV-vis spectra were recorded on a Shimadzu UV-3101PL UV-vis-NIR spectrometer.

Experimental Section

4,7-Dihydro-1H-indole (1): Compound **1** was prepared according to the literature method.¹⁶ Liquid ammonia (500 mL) was distilled under N_2 into a pre-dried, three-necked flask. Then, the solution of the indole (**12**) (25.00 g, 0.21 mol) in dry Et_2O (100 mL) was added, and the resulting solution was cooled to $-35\text{ }^\circ\text{C}$ and stirred as mechanical. The resulting solution was treated with lithium metal (6.00 g, 0.84 mol) added in small pieces for 5-10 min, which reacted very rapidly. The resulting deep blue solution was stirred at the same temperature for 1h and then the resulting mixture was permitted to room temperature. After the excess ammonia was evaporated, Et_2O (200 mL), NH_4Cl (5 g) and H_2O (300 mL) were carefully added to the reaction mixture. The layers were separated. The aqueous layer was extracted with Et_2O (2×200 mL), and the combined organic layers were washed with NaHCO_3 (2×100 mL), dried (MgSO_4), filtered, and concentrated. The ^1H NMR of the residue showed that the formation of 4,7-dihydro-1H-indole (**1**) and 4,5,6,7-tetrahydro-1H-indole in a 4:1 ratio. The crude product (23 g) was recrystallized with hexane to give the 4,7-dihydro-1H-indole (**1**) (white solid, m.p.: $38\text{--}39\text{ }^\circ\text{C}$, 19 g, 75%) as a colorless crystals. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (m, NH, 1H), 6.72 (t, $J = 2.5\text{ Hz}$, =CH, 1H), 6.07 (t, $J = 2.5\text{ Hz}$, =CH, 1H), 5.95 (bd, $J = 10.1\text{ Hz}$, =CH, 1H), 5.87 (bd, $J = 10.1\text{ Hz}$, =CH, 1H), 3.30 (bs, CH_2 , 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 128.0, 127.9, 125.98, 118.3, 115.9, 108.8, 27.1, 26.0.

General procedure (GP1) for the synthesis of 2-alkylated indoles: To a solution of 4,7-dihydro-1H-indole (**1**; 1.0 equiv) in MeCN (5 mL) was added ketone (**2a-p**; 1.0 equiv) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 mmol). The

reaction mixture was stirred magnetically in a flask at 80 °C. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethyl acetate (30 mL) and washed with water (2×50 mL). The organic phase was collected, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatograph and isolated compounds were given according to the elution sequence (EtOAc/Hexane) in general.

2-Cyclohexyl-1H-indole (3a)^{13d}: Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with cyclohexanone (**2a**; 165 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-cyclohexyl-1H-indole (**3a**; 325 mg (97%), yellow viscous liquid) was obtained. ¹H NMR (400 MHz, CDCl₃): δ 7.91 bs, NH, 1H), 7.53 (d, *J* = 7.7 Hz, =CH, 1H), 7.30 (d, *J* = 7.7 Hz, =CH, 1H), 7.13-7.04 (m, =CH, 2H), 6.23 (s, =CH, 1H), 2.75-2.69 (m, CH, 1H), 2.10-2.07 (m, CH₂, 2H), 1.87-1.74 (m, CH₂, 2H), 1.54-1.29 (m, CH₂, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 145.3, 135.7, 128.8, 121.1, 120.1, 119.8, 110.5, 97.7, 37.5, 29.9, 26.5, 26.3; IR (KBr, cm⁻¹): 3335, 2921, 2871, 1624, 1452, 1431, 1397, 1356, 1163, 1122, 908, 858, 811; Anal. Calcd. for C₁₄H₁₇N: C, 84.37; H, 8.60; N, 7.03; found: C, 84.32; H, 8.10; N, 7.27; TLC: R_f = 0.72 (EtOAc/hexane (5%), 254 nm).

2-Isopropyl-1H-indole (3b)^{13a,e,f}: Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with acetone (**2b**; 116 mg, 2.00 mmol) was performed at 80 °C for 1h in MeCN according to GP1. After purification, 2-isopropyl-1H-indole (**3b**; 256 mg (96%), yellow viscous liquid) was obtained. ¹H NMR (400 MHz, CDCl₃): δ 7.87 bs, NH, 1H), 7.53 (d, *J* = 7.7 Hz, =CH, 1H), 7.30 (d, *J* = 7.7 Hz, =CH, 1H), 7.13-7.04 (m, =CH, 2H), 6.24 (s, =CH, 1H), 3.10-3.03 (m, CH, 1H), 7.30 (d, *J* = 7.0 Hz, CH₃, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 145.9, 135.7, 128.6, 121.0, 119.9, 119.6, 110.3, 97.5, 27.7, 22.4; IR (KBr, cm⁻¹): 3356, 2925, 2852, 2341, 1672, 1631, 1627, 1607, 1397, 1206, 1165, 1083, 980, 909; Anal. Calcd. for C₁₁H₁₃N: C, 82.97; H, 8.23; N, 8.80, found: C, 82.92; H, 8.31; N, 8.86; TLC: R_f = 0.85 (EtOAc/hexane (5%), 254 nm).

2-(sec-Butyl)-1H-indole (3c): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with butan-2-one (**2c**; 121 mg, 1.68 mmol) was performed at 80°C for 1h in MeCN according to GP1. After purification, 2-(sec-butyl)-1H-indole (**3c**; 270 mg (93%), white viscous liquid) was obtained. ¹H NMR (400 MHz, CDCl₃): δ 7.81 (bs, NH, 1H), 7.53 (d, *J* = 7.5 Hz, =CH, 1H), 7.28 (d, *J* = 7.5 Hz, =CH, 1H), 7.13-7.04 (m, =CH, 2H), 6.23 (s, =CH, 1H), 2.83-2.77 (m, CH, 1H), 1.73-1.61 (m, CH₂, 2H), 1.32 (d, *J* = 7.2 Hz, CH₃, 3H), 0.91 (t, *J* = 7.2 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.7, 135.7, 128.7, 120.9, 119.9, 119.6, 110.4, 98.3, 34.9, 29.9, 20.1, 11.8; IR (KBr, cm⁻¹): 3348, 2928, 2340, 1627,

1605, 1453, 1432, 1323, 1292, 1253, 1206, 1164, 1085, 980, 870; **Anal. Calcd.** for C₁₂H₁₅N: C, 83.19; H, 8.73; N, 8.08, found: C, 83.14; H, 8.75; N, 8.15; **TLC:** R_f = 0.81 (EtOAc/hexane (5%), 254 nm).

2-Cyclopentyl-1H-indole (3d)^{13d}: Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with cyclopentanone (**2d**; 141 mg, 1.68 mmol) was performed at 80 °C for 4h in MeCN according to GP1. After purification, 2-cyclopentyl-1H-indole (**3d**, 295 mg (95%), pale yellow viscous liquid) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ 7.88 (bs, NH, 1H), 7.52 (d, *J* = 7.7 Hz, =CH, 1H), 7.30 (d, *J* = 7.7 Hz, =CH, 1H), 7.13-7.04 (m, =CH, 2H), 6.25 (s, =CH, 1H), 3.20-3.17 (m, CH, 1H), 2.13-2.11 (m, CH₂, 2H), 1.83-1.70 (m, CH₂, 6H); **¹³C NMR (100 MHz, CDCl₃):** δ 144.2, 136.1, 128.9, 121.2, 120.0, 119.8, 110.4, 98.2, 39.1, 33.1, 25.5; **IR (KBr, cm⁻¹):** 3018, 2920, 2844, 1608, 1581, 1430, 1447, 1230, 1198, 1116, 1023, 883; **Anal. Calcd.** for C₁₃H₁₅N: C, 84.28; H, 8.16; N, 7.56, found: C, 84.21; H, 8.13; N, 7.69; **TLC:** R_f = 0.73 (EtOAc/hexane (5%), 254 nm).

2-Cycloheptyl-1H-indole (3e): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with cycloheptanone (**2e**; 188 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-cycloheptyl-1H-indole (**3e**; 346 mg (97%), yellow viscous liquid) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ 7.82 (bs, NH, 1H), 7.52 (d, *J* = 7.7 Hz, =CH, 1H), 7.27 (d, *J* = 7.7 Hz, =CH, 1H), 7.12-7.03 (m, =CH, 2H), 6.22 (s, =CH, 1H), 2.94-2.86 (m, CH, 1H), 2.12-2.05 (m, CH₂, 2H), 1.82-1.52 (m, CH₂, 10H); **¹³C NMR (100 MHz, CDCl₃):** δ 146.4, 135.8, 128.8, 121.1, 120.1, 119.8, 110.5, 97.8, 39.7, 35.1, 28.5, 26.6; **IR (KBr, cm⁻¹):** 3318, 2921, 2861, 1647, 1556, 1397, 1356, 1206, 1323, 1163, 1122, 1084, 811; **Anal. Calcd.** for C₁₅H₁₉N: C, 84.46; H, 8.98; N, 6.57, found: C, 84.40; H, 8.92; N, 6.68; **TLC:** R_f = 0.75 (EtOAc/hexane (5%), 254 nm).

2-(2,3-Dihydro-1H-inden-2-yl)-1H-indole (3f): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with 1,3-dihydro-2H-inden-2-one (**2f**; 222 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-(2,3-dihydro-1H-inden-2-yl)-1H-indole (**3f**; 361 mg (92%), white solid, m.p. = 111-112 °C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ 7.83 (bs, NH, 1H), 7.53 (d, *J* = 7.7 Hz, =CH, 1H), 7.30-7.25 (m, =CH, 3H), 7.24-7.20 (m, =CH, 2H), 7.14-7.04 (m, =CH, 2H), 6.31 (s, =CH, 1H), 3.88-3.79 (m, CH, 1H), 3.41 (dd, *J* = 15.3, 7.9 Hz, CH₂, 2H), 3.15 (dd, *J* = 15.3, 7.9 Hz, CH₂, 2H); **¹³C NMR (100 MHz, CDCl₃):** δ 142.9, 142.3, 135.9, 128.4, 126.7, 124.5, 121.3, 120.0, 119.8, 110.4, 98.7, 39.6, 38.6; **IR (KBr, cm⁻¹):** 3318, 2919, 2848, 2605, 2525, 2445, 1680, 1550, 1445, 1249, 1199, 938, 883, 870; **Anal. Calcd.** for C₁₇H₁₅N: C, 87.52; H, 6.48; N, 6.00, found: C, 87.56; H, 6.46; N, 6.03; **TLC:** R_f = 0.45 (EtOAc/hexane (15%), 254 nm).

2-(2,3-Dihydro-1*H*-inden-1-yl)-1*H*-indole (3g): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1*H*-indole (**1**; 200 mg, 1.68 mmol) with 2,3-dihydro-1*H*-inden-1-one (**2g**; 222 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-(2,3-dihydro-1*H*-inden-1-yl)-1*H*-indole (**3g**; 372 mg (95%), pale green solid, m.p. = 76-77°C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ 7.80 (bs, NH, 1H), 7.55 (d, *J* = 7.5 Hz, =CH, 1H), 7.32 (d, *J* = 7.5 Hz, =CH, 1H), 7.27-7.22 (m, =CH, 2H), 7.18-7.06 (m, =CH, 4H), 6.36 (s, =CH, 1H), 4.59 (t, *J* = 8.1 Hz, CH, 1H), 3.08-2.98 (m, CH₂, 2H), 2.66-2.58 (m, CH₂, 1H), 2.25-2.17 (m, CH₂, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 144.6, 144.4, 141.9, 136.4, 128.8, 127.4, 126.9, 125.1, 124.9, 121.5, 120.2, 119.9, 110.7, 100.6, 45.0, 35.0, 31.9; **IR (KBr, cm⁻¹):** 3325, 3027, 2918, 2851, 2625, 1605, 1483, 1458, 1255, 1022, 938, 883, 870; **Anal. Calcd.** for C₁₇H₁₅N: C, 87.52; H, 6.48; N, 6.00, found: C, 87.47; H, 6.51; N, 5.97; **TLC:** R_f = 0.55 (EtOAc/hexane (15%), 254 nm).

2-(1-Phenylethyl)-1*H*-indole (3h)^{13c}: Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1*H*-indole (**1**; 200 mg, 1.68 mmol) with acetophenone (**2h**; 202 mg, 1.68 mmol) was performed at 80 °C for 4h in MeCN according to GP1. After purification, 2-(1-phenylethyl)-1*H*-indole (**3h**; 362 mg (97%), black solid, m.p. = 63-64 °C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ: δ 7.68 (bs, NH, 1H), 7.59 (d, *J* = 7.3 Hz, =CH, 1H), 7.36-7.32 (m, =CH, 2H), 7.28-7.21 (m, =CH, 4H), 7.14-7.07 (m, =CH, 2H), 6.44 (s, =CH, 1H), 4.28-4.26 (m, CH, 1H), 1.73 (d, *J* = 7.2 Hz, CH₃, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 144.8, 143.3, 136.4, 129.0, 128.7, 127.8, 127.0, 121.6, 120.3, 119.9, 110.7, 99.8, 39.4, 21.5; **IR (KBr, cm⁻¹):** 3225, 2978, 2109, 1609, 1526, 1462, 1467, 1301, 1218, 1122, 1081, 981, 870, 740; **Anal. Calcd.** For C₁₆H₁₅N: C, 86.84; H, 6.83; N, 6.33, found: C, 86.82; H, 6.86; N, 6.28; **TLC:** R_f = 0.65 (EtOAc/hexane (15%), 254 nm).

2-(1-(Naphthalen-2-yl)ethyl)-1*H*-indole (3i): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1*H*-indole (**1**; 200 mg, 1.68 mmol) with 1-(naphthalen-2-yl)ethan-1-one (**2h**; 286 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-(1-(naphthalen-2-yl)ethyl)-1*H*-indole (**3i**; 415 mg (91%), white solid, m.p. = 86-87 °C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ: δ 7.84-7.78 (m, =CH, 3H), 7.71 (s, =CH, 1H), 7.68 (bs, NH, 1H), 7.61 (d, *J* = 6.8 Hz, =CH, 1H), 7.50-7.44 (m, =CH, 2H), 7.34 (d, *J* = 6.8 Hz, =CH, 1H), 7.20-7.18 (m, =CH, 1H), 7.13-7.06 (m, =CH, 2H), 6.49 (s, =CH, 1H), 4.43-4.39 (m, CH, 1H), 1.81 (d, *J* = 7.3 Hz, CH₃, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 143.1, 142.2, 136.4, 133.8, 132.7, 128.8, 128.7, 127.9 (2C), 126.5, 126.3, 126.1, 126.0, 121.6, 120.3, 120.0, 110.7, 99.9, 39.5, 21.2; **IR (KBr, cm⁻¹):** 3375, 3033, 2924, 1615, 1564, 1453, 1381, 1331, 1249, 1177, 1159, 1107, 1053, 1023, 938, 870, 811, 740; **Anal. Calcd.** For C₂₀H₁₇N: C, 88.52; H, 6.31; N, 5.16, found: C, 88.44; H, 6.38; N, 5.12; **TLC:** R_f = 0.43 (EtOAc/hexane (15%), 254 nm).

2-(9H-Fluoren-9-yl)-1H-indole (3j): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with 9H-fluoren-9-one (**2j**; 302 mg, 1.68 mmol) was performed at 80 °C for 5h in MeCN according to GP1. After purification, 2-(9H-fluoren-9-yl)-1H-indole (**3j**; 382 mg (81%), white solid, m.p. = 125-126 °C (CH₂Cl₂/hexane)) was obtained. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.1 Hz, =CH, 2H), 7.62-7.60 (m, =CH, 1H), 7.44-7.42 (m, =CH, 4H), 7.40 (bs, NH, 1H), 7.30-7.25 (m, =CH, 2H), 7.10-7.06 (m, =CH, 3H), 6.72 (s, =CH, 1H), 5.34 (s, CH, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 145.3, 140.9, 137.2, 136.3, 128.5, 128.0, 127.6, 125.5, 121.6, 120.1, 120.0, 119.7, 110.6, 102.2, 48.0; IR (KBr, cm⁻¹): 3426, 2918, 2876, 2851, 2725, 2685, 1605, 1526, 1468, 1205, 870, 740; Anal. Calcd. For C₂₁H₁₅N: C, 89.65; H, 5.37; N, 4.98, found: C, 89.57; H, 5.31; N, 4.97; TLC: R_f = 0.42 (EtOAc/hexane (15%), 254 nm).

2-(1-(Furan-2-yl)ethyl)-1H-indole (3k): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with 1-(furan-2-yl)ethan-1-one (**2k**; 184 mg, 1.68 mmol) was performed at 80°C for 6h in MeCN according to GP1. After purification, 2-(1-(furan-2-yl)ethyl)-1H-indole (**3k**; 301 mg (85%), white solid, m.p. = 68-69 °C (CH₂Cl₂/hexane)) was obtained. ¹H NMR (400 MHz, CDCl₃): δ: δ 8.04 (bs, NH, 1H), 7.55 (d, *J* = 7.9 Hz, =CH, 1H), 7.37 (d, *J* = 1.4 Hz, =CH, 1H), 7.29 (d, *J* = 7.9 Hz, =CH, 1H), 7.14-7.05 (m, =CH, 2H), 6.35 (d, *J* = 1.4 Hz, =CH, 1H), 6.32 (t, *J* = 1.4 Hz, =CH, 1H), 6.11 (s, =CH, 1H), 4.37-4.32 (m, CH, 1H), 1.72 (d, *J* = 7.2 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.0, 141.7, 140.6, 136.0, 128.4, 121.5, 120.2, 119.7, 110.6, 110.2, 105.1, 99.1, 32.8, 18.6; IR (KBr, cm⁻¹): 3374, 3321, 2976, 2944, 2847, 1613, 1574, 1493, 1474, 1453, 1371, 1321, 1249, 1177, 1159, 1107, 1053, 1023, 938, 870; Anal. Calcd. For C₁₄H₁₃NO: C, 79.59; H, 6.20; N, 6.63, found: C, 79.49; H, 6.18; N, 6.58; TLC: R_f = 0.54 (EtOAc/hexane (15%), 254 nm).

2-(1-(Thiophen-2-yl)ethyl)-1H-indole (3l): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with 1-(thiophen-2-yl)ethan-1-one (**2l**; 212 mg, 1.68 mmol) was performed at 80°C for 5h in MeCN according to GP1. After purification, 2-(1-(thiophen-2-yl)ethyl)-1H-indole (**3l**; 355 mg (93%), pale red solid, m.p. = 65-66 °C (CH₂Cl₂/hexane)) was obtained. ¹H NMR (400 MHz, CDCl₃): δ: δ 7.82 (bs, NH, 1H), 7.57 (d, *J* = 7.7 Hz, =CH, 1H), 7.27-7.26 (m, =CH, 1H), 7.25 (d, *J* = 1.1 Hz, =CH, 1H), 7.15-7.06 (m, =CH, 2H), 6.98-6.96 (m, =CH, 1H), 6.91-6.90 (m, =CH, 1H), 6.41 (s, =CH, 1H), 4.59-4.54 (m, CH, 1H), 1.80 (d, *J* = 7.0 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 142.5, 136.2, 128.7, 127.0, 124.4, 124.3, 121.8, 120.5, 120.0, 110.8, 99.4, 34.8, 22.5; IR (KBr, cm⁻¹): 3082, 3028, 2972, 2839, 1605, 1479, 1452, 1384, 1332, 1309, 1256, 1232, 1184, 1023, 882, 824; Anal. Calcd. For C₁₄H₁₃NS:

C, 73.97; H, 5.76; N, 6.16; S, 14.11, found: C, 73.88; H, 5.72; N, 6.24; S, 14.13; **TLC:** R_f = 0.52 (EtOAc/hexane (15%), 254 nm).

2-(1-(Benzofuran-2-yl)ethyl)-1H-indole (3o): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with 1-(benzofuran-2-yl)ethan-1-one (**2o**; 268 mg, 1.68 mmol) was performed at 80°C for 6h in MeCN according to GP1. After purification, 2-(1-(benzofuran-2-yl)ethyl)-1H-indole (**3o**; 370 mg (84%), pale yellow solid, m.p. = 87-88 °C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ: δ 8.12 (bs, NH, 1H), 7.57 (d, J = 8.1 Hz, =CH, 1H), 7.51 (d, J = 8.1 Hz, =CH, 1H), 7.45 (d, J = 8.1 Hz, =CH, 1H), 7.30 (d, J = 8.1 Hz, =CH, 1H), 7.25-7.19 (m, =CH, 2H), 7.16-7.06 (m, =CH, 2H), 6.51 (s, =CH, 1H), 6.44 (s, =CH, 1H), 4.49-4.47 (m, CH, 1H), 1.83 (d, J = 6.8 Hz, CH₃, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 160.2, 155.1, 139.9, 136.3, 128.6 (2C), 124.1, 123.0, 121.9, 120.9, 120.5, 120.0, 111.3, 110.8, 102.5, 99.8, 33.6, 18.8; **IR (KBr, cm⁻¹):** 3374, 3325, 2934, 2846, 1615, 1576, 1494, 1464, 1453, 1177, 1159, 1107, 1053, 1023, 938, 870, 811, 740; **Anal. Calcd.** For C₁₈H₁₅NO: C, 82.73; H, 5.79; N, 5.36; O, 6.12, found: C, 82.63; H, 5.72; N, 5.34; **TLC:** R_f = 0.38 (EtOAc/hexane (15%), 254 nm).

2-(di(Pyridin-2-yl)methyl)-1H-indole (3p): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 200 mg, 1.68 mmol) with di(pyridin-2-yl)methanone (**2p**; 309 mg, 1.68 mmol) was performed at 80°C for 1h in MeCN according to GP1. After purification, 2-(di(pyridine-2-yl)methyl)-1H-indole (**3p**; 471 mg (98%), pale red solid, m.p. = 77-78 °C (CH₂Cl₂/hexane)) was obtained. **¹H NMR (400 MHz, CDCl₃):** δ: δ 9.88 (bs, NH, 1H), 8.59-8.57 (m, =CH, 2H), 7.68-7.64 (m, =CH, 2H), 7.56 (d, J = 7.7 Hz, =CH, 1H), 7.46 (d, J = 8.1 Hz, =CH, 1H), 7.38 (d, J = 8.1 Hz, =CH, 1H), 7.18-7.12 (m, =CH, 4H), 7.06 (t, J = 7.7 Hz, =CH, 1H), 6.47 (s, =CH, 1H), 5.91 (s, CH, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 160.8, 149.0, 137.8, 137.4, 136.6, 128.4, 124.1, 122.4, 121.8, 120.5, 119.9, 111.4, 102.1, 54.3; **IR (KBr, cm⁻¹):** 3405, 3052, 3025, 1947, 1709, 1648, 1621, 1599, 1558, 1462, 1437, 1390, 1372, 1326, 1153, 1134, 1084, 1069, 961, 870; **Anal. Calcd.** For C₁₉H₁₅N₃: C, 79.98; H, 5.30; N, 14.73, found: C, 79.86; H, 5.32; N, 14.64; **TLC:** R_f = 0.38 (EtOAc/hexane (15%), 254 nm).

N-Boc-2-acetylpyrrole (2n): Compound **2n** was prepared according to the literature method.^{12b} To a solution of 2-acetylpyrrole (**2m**; 500 mg, 4.6 mmol) and di-*tert*-butyl dicarbonate (1.1 g, 5.0 mmol) in freshly distilled THF (50 mL) was added slowly NaH (0.314 g, 2.8 mmol) in freshly distilled THF (50 mL). The mixture was stirred at rt for 1h. Then the reaction mixture was solved with EtOAc (3×30 mL) and the organic phase was washed with NH₄Cl (5%, 3×30 mL) and dried over Na₂SO₄. The crude product (958 mg) was purified on silica gel column (25 g) with EtOAc/hexane (13%) to yield *N*-Boc-2-acetylpyrrole (**2n**; 912

mg (95%), colorless viscous liquid). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.24-7.23 (m, =CH, 1H), 6.78 (dd, J = 3.6, 1.6 Hz, =CH, 1H), 6.08 (t, J = 3.6 Hz, =CH, 1H), 2.36 (s, CH_3 , 3H), 1.50 (s, CH_3 , 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 188.3, 148.9, 134.1, 127.8, 121.1, 109.9, 84.7, 27.8, 27.4, 27.4; IR (KBr, cm^{-1}): 3150, 2982, 2936, 2906, 1749, 1618, 1544, 1477, 1442, 1390, 1372, 1339, 1300, 1251, 1166, 1126, 1066, 1016, 894, 846; TLC: R_f = 0.53 (EtOAc/hexane (15%), 254 nm).

General procedure (GP2) for the synthesis of 2,2'-bis(indolyl)methanes: To a solution of 4,7-dihydro-1H-indole (**1**; 2.0 equiv) in MeCN (5 mL) was added ketone (**2a-p**; 1.0 equiv) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.1 mmol). The reaction mixture was stirred magnetically in a flask at 80 °C. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethyl acetate (30 mL) and washed with water (2×50 mL). The organic phase was collected, dried over Na_2SO_4 , filtered and concentrated. The crude product was dissolved in CH_2Cl_2 (15 mL) and *p*-benzoquinone (2.0 equiv.) was added. The mixture was stirred at the room temperature for overnight. After completion of the reaction, the solvent was evaporated and the crude product was dissolved with ethyl acetate (30 mL) and the organic phase was washed with NaOH (2N, 2×30 mL), brine (30 mL), and dried over Na_2SO_4 . The crude product was purified by silica gel column chromatograph and isolated compounds were given according to elution sequence (EtOAc/Hexane) in general.

2,2'-(Cyclohexane-1,1-diyl)bis(1H-indole) (4a): $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 300 mg, 2.52 mmol) with cyclohexanone (**2a**; 124 mg, 1.26 mmol) was performed at 80 °C for 2h in MeCN. *p*-Benzoquinone (272 mg, 2.52 mmol) was added to the reaction mixture (390 mg) according to GP2. After purification, 2,2'-(cyclohexane-1,1-diyl)bis(1H-indole) (**4a**; 292 mg (74%), red solid, m.p. = 101-102 °C (CH_2Cl_2 /hexane)) was obtained. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.74 (bs, NH, 2H), 7.59 (d, J = 7.9 Hz, =CH, 2H), 7.20 (d, J = 7.9 Hz, =CH, 2H), 7.13-7.07 (m, =CH, 4H), 6.55 (s, =CH, 2H), 2.34-2.31 (m, CH_2 , 4H), 1.72-1.67 (m, CH_2 , 4H), 1.57-1.55 (m, CH_2 , 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.1, 136.1, 128.5, 121.9, 120.4, 120.0, 111.0, 99.5, 41.0, 36.8, 26.2, 23.0; IR (KBr, cm^{-1}): 3039, 2968, 2928, 2109, 1509, 1464, 1451, 1305, 1228, 1163, 1122, 1084, 979, 908, 870, 811; Anal. Calcd. For $\text{C}_{22}\text{H}_{22}\text{N}_2$: C, 84.04; H, 7.05; N, 8.91, found: C, 84.06; H, 7.01; N, 8.87; TLC: R_f = 0.29 (EtOAc/hexane (15%), 254 nm).

The reaction of 4,7-dihydro-1H-indole (1, 2 equiv) with acetone (2b, 1 equiv): A $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 300 mg, 2.52 mmol) with acetone (**2b**; 73 mg, 1.26 mmol) was performed at 80 °C for 3h in MeCN. The reaction was monitored by TLC. The

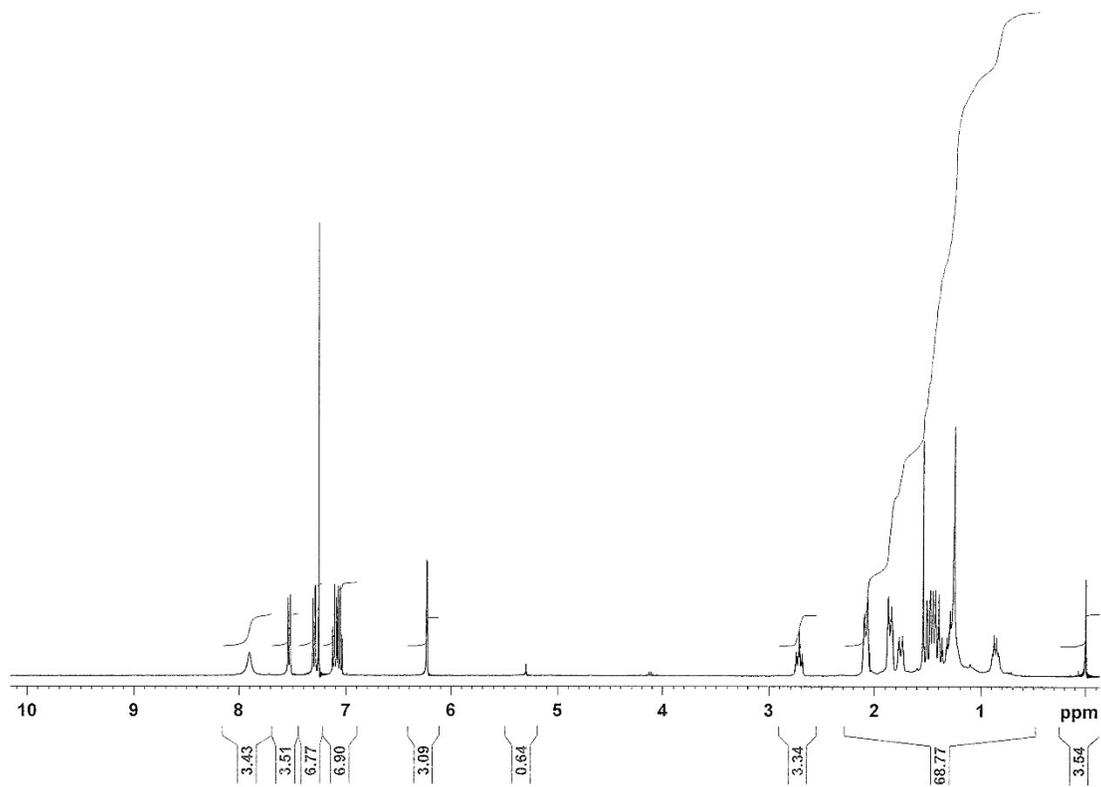
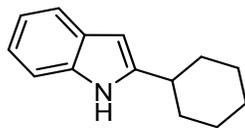
reaction mixture was diluted with ethyl acetate (30 mL) and washed with water (2×50 mL), and an organic phase was dried over Na₂SO₄. The crude product was purified by silica gel column chromatograph with EtOAc/Hexane (5%). After purification, 2-isopropyl-1*H*-indole (**3b**; 24 mg (12%) and 4,7-dihydro-1*H*-indole (**1**; 215 mg) were obtained. **B**) Bi(NO₃)₃·5H₂O (0.1 mmol)-catalyzed reaction of 4,7-dihydro-1*H*-indole (**1**; 300 mg, 2.52 mmol) with acetone (**2b**; 73 mg, 1.26 mmol) was performed at 80 °C for 3h in MeCN. *p*-Benzoquinone (272 mg, 2.52 mmol) was added to the reaction mixture (335 mg) according to GP2. After purification, 2,2'-(propane-2,2-diyl)bis(1*H*-indole) (**4b**; 231 mg (67%), red solid, m.p. = 111-112 °C (CH₂Cl₂/hexane)) and 2-isopropyl-2-(2-isopropyl-1*H*-indol-3-yl)indolin-3-one (**9**; 32 mg (8%), black solid, m.p. = 125-126 °C (CH₂Cl₂/hexane)) were obtained. **2,2'-(Propane-2,2-diyl)bis(1*H*-indole) (4b):** ¹H NMR (400 MHz, CDCl₃): δ 7.73 (bs, NH, 2H), 7.60 (d, *J* = 7.7 Hz, =CH, 2H), 7.19 (d, *J* = 7.9 Hz, =CH, 2H), 7.14-7.06 (m, =CH, 4H), 6.51 (s, =CH, 2H), 1.85 (s, CH₃, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 145.3, 136.4, 128.3, 122.1, 120.5, 120.1, 110.9, 98.8, 36.6, 28.8; IR (KBr, cm⁻¹): 3016, 3004, 2946, 2841, 1615, 1461, 1442, 1248, 1240, 740; Anal. Calcd. For C₁₉H₁₈N₂: C, 83.18; H, 6.61; N, 10.21 found: C, 83.21; H, 6.57; N, 10.13; TLC: R_f = 0.58 (EtOAc/hexane (15%), 254 nm). **2-Isopropyl-2-(2-isopropyl-1*H*-indol-3-yl)indolin-3-one (9):** ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, *J* = 8.1 Hz, =CH, 1H), 7.95 (bs, NH, 1H), 7.55 (d, *J* = 7.7 Hz, =CH, 1H), 7.46 (t, *J* = 7.7 Hz, =CH, 1H), 7.27-7.25 (m, =CH, 1H), 7.11-7.02 (m, =CH, 2H), 6.95 (d, *J* = 8.1 Hz, =CH, 1H), 6.77 (t, *J* = 7.7 Hz, =CH, 1H), 5.08 (s, NH, 1H), 3.97-3.93 (m, CH, 1H), 3.15-3.12 (m, CH, 1H), 1.32 (d, *J* = 7.0 Hz, CH₃, 3H), 1.22 (d, *J* = 7.0 Hz, CH₃, 3H), 0.95 (d, *J* = 7.0 Hz, CH₃, 3H), 0.88 (d, *J* = 7.0 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 203.4, 160.5, 142.5, 137.2, 135.5, 127.2, 125.2, 121.8, 121.7, 121.3, 119.6, 118.7, 111.6, 110.7, 107.7, 75.0, 34.7, 26.7, 23.7, 23.1, 18.2, 16.4; IR (KBr, cm⁻¹): 3028 (NH), 3005, 2940, 2448, 1716 (C=O), 1605, 1543, 1481, 1248, 1230, 1123, 870; Anal. Calcd. For C₂₂H₂₄N₂O: C, 79.48; H, 7.28; N, 8.43; found: C, 79.51; H, 7.28; N, 8.38; TLC: R_f = 0.45 (EtOAc/hexane (15%), 254 nm).

2,2'-(Butane-2,2-diyl)bis(1*H*-indole) (4c): Bi(NO₃)₃·5H₂O (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1*H*-indole (**1**; 300 mg, 2.52 mmol) with butan-2-one (**2c**; 91 mg, 1.26 mmol) was performed at 80 °C for 1h in MeCN. *p*-Benzoquinone (272 mg, 2.52 mmol) was added to the reaction mixture (305 mg) according to GP2. After purification, 2,2'-(butane-2,2-diyl)bis(1*H*-indole) (**4d**; 259 mg (71%), red solid, m.p. = 78-79 °C (CH₂Cl₂/hexane)) was obtained. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (bs, NH, 2H), 7.60 (d, *J* = 7.3 Hz, =CH, 2H), 7.18 (d, *J* = 7.3 Hz, =CH, 2H), 7.14-7.08 (m, =CH, 4H), 6.51 (s, =CH, 2H), 2.25 (q, *J* = 7.4 Hz, CH₂, 2H), 1.76 (s, CH₃, 3H), 0.89 (t, *J* = 7.4 Hz, CH₃, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.1, 136.1, 128.1, 121.8, 120.2, 119.8, 110.7, 99.6, 40.4, 32.7, 25.0, 8.8; IR (KBr, cm⁻¹): 3024, 2830, 2147, 1601, 1584, 1439, 1455, 1348, 870, 740; Anal. Calcd. For C₂₀H₂₀N₂: C, 83.30; H, 6.99; N, 9.71 found: C, 83.31; H,

6.98; N, 9.68; **TLC:** $R_f = 0.35$ (EtOAc/hexane (15%), 254 nm).

2,2'-(Cyclopentane-1,1-diyl)bis(1H-indole) (4d): $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 300 mg, 2.52 mmol) with cyclopentanone (**2d**; 105 mg, 1.26 mmol) was performed at 80°C for 2h in MeCN. *p*-Benzoquinone (272 mg, 2.52 mmol) was added to the reaction mixture (356 mg) according to GP2. After purification, 2,2'-(cyclopentane-1,1-diyl)bis(1H-indole) (**4d**; 264 mg (70%)), red solid, m.p. = 98-99 °C ($\text{CH}_2\text{Cl}_2/\text{hexane}$) was obtained. **$^1\text{H NMR}$ (400 MHz, CDCl_3):** δ 7.74 (bs, NH, 2H), 7.59 (d, $J = 8.4$ Hz, =CH, 2H), 7.22-7.19 (m, =CH, 2H), 7.14-7.06 (m, =CH, 4H), 6.52 (s, =CH, 2H), 2.42-2.38 (m, CH_2 , 4H), 1.91-1.88 (m, CH_2 , 4H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3):** δ 143.9, 135.2, 128.3, 122.0, 120.4, 120.1, 110.9, 99.2, 46.0, 31.5, 24.9; **IR (KBr, cm^{-1}):** 3125, 3024, 2890, 2858, 1615, 1581, 1480, 1455, 1238, 1123, 870, 740; **Anal. Calcd.** For $\text{C}_{21}\text{H}_{20}\text{N}_2$: C, 83.96; H, 6.71; N, 9.33, found: C, 83.91; H, 6.68; N, 9.38; **TLC:** $R_f = 0.29$ (EtOAc/hexane (15%), 254 nm).

The reaction of 4,7-dihydro-1H-indole (1, 2 equiv) with 1-(furan-2-yl)ethan-1-one (2k, 1 equiv): $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (48.5 mg, 0.1 mmol)-catalyzed reaction of 4,7-dihydro-1H-indole (**1**; 300 mg, 2.52 mmol) with 1-(furan-2-yl)ethan-1-one (**2k**; 139 mg, 1.26 mmol) was performed at 80 °C for 1h in MeCN according to GP2. After purification, 4,7-dihydro-1H-indole (**1**; 80 mg), 2-(1-(furan-2-yl)ethyl)-4,7-dihydro-1H-indole (**17**; 19 mg (7%)), pale yellow viscous liquid, 2-(1-(furan-2-yl)ethyl)-1H-indole (**3k**; 226 mg (85%)) and indole (**12**; 13 mg (8%)) were obtained. **2-(1-(Furan-2-yl)ethyl)-4,7-dihydro-1H-indole (17):** **$^1\text{H NMR}$ (400 MHz, CDCl_3):** δ 7.64 (bs, NH, 1H), 7.34 (d, $J = 1.3$ Hz, =CH, 1H), 6.30 (d, $J = 1.3$ Hz, =CH, 2H), 6.07 (d, $J = 3.4$ Hz, =CH, 1H), 5.89-5.78 (m, =CH, 2H), 4.18-4.13 (m, CH, 1H), 3.24-3.17 (m, CH_2 , 4H), 1.60 (d, $J = 7.2$ Hz, CH_3 , 3H); **$^{13}\text{C NMR}$ (100 MHz, CDCl_3):** δ 158.1, 141.4, 132.4, 125.9, 123.2, 122.7, 113.7, 110.1, 104.4, 103.1, 32.3, 25.0, 24.0, 18.9; **IR (KBr, cm^{-1}):** 3475, 3351, 3215, 2975, 2943, 2857, 1617, 1578, 1498, 1252, 1237, 1145, 1117, , 938, 870; **Anal. Calcd.** For $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09; N, 6.57, found: C, 78.81; H, 7.08; N, 6.68; **TLC:** $R_f = 0.62$ (EtOAc/hexane (15%), 254 nm).



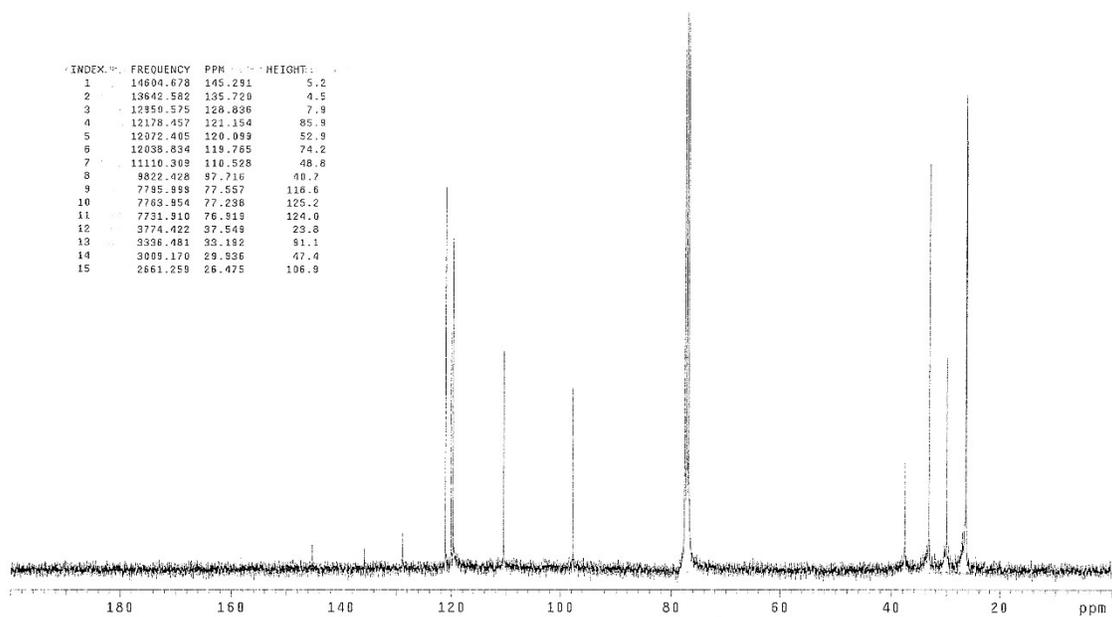
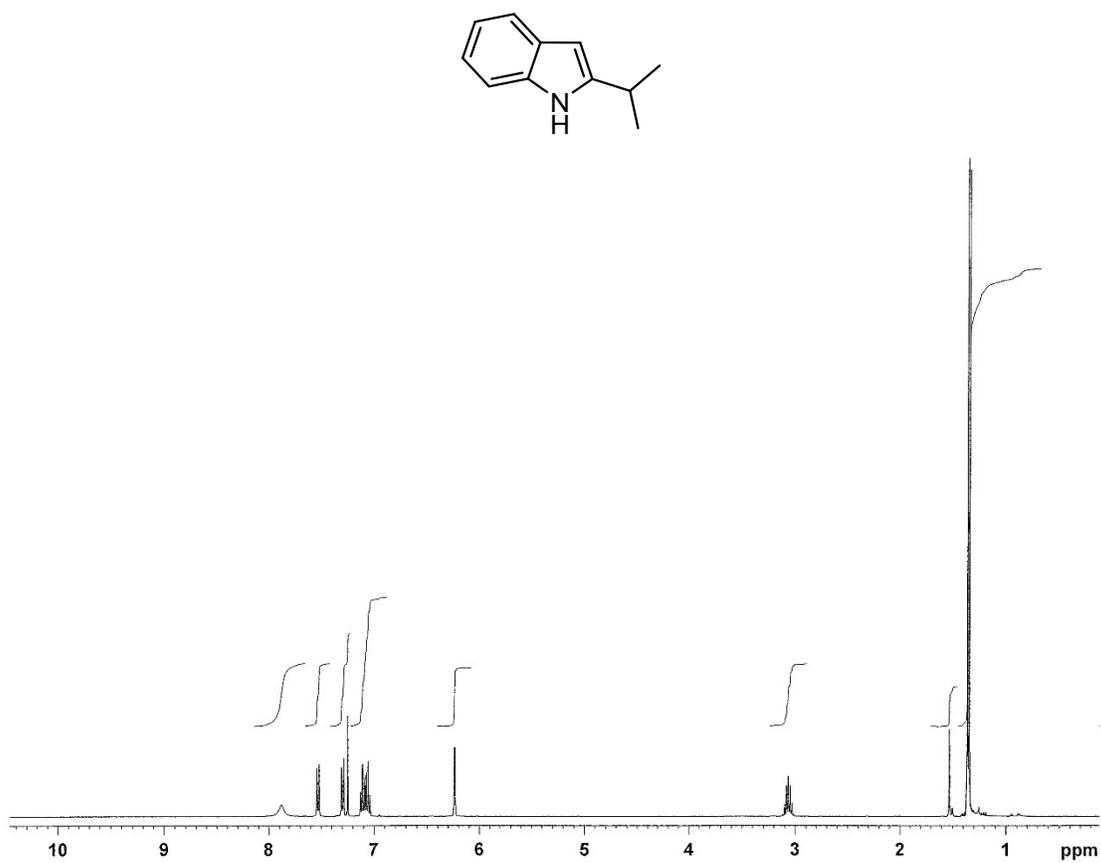


Figure S1. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-cyclohexyl-1H-indole (**3a**) (CDCl_3)



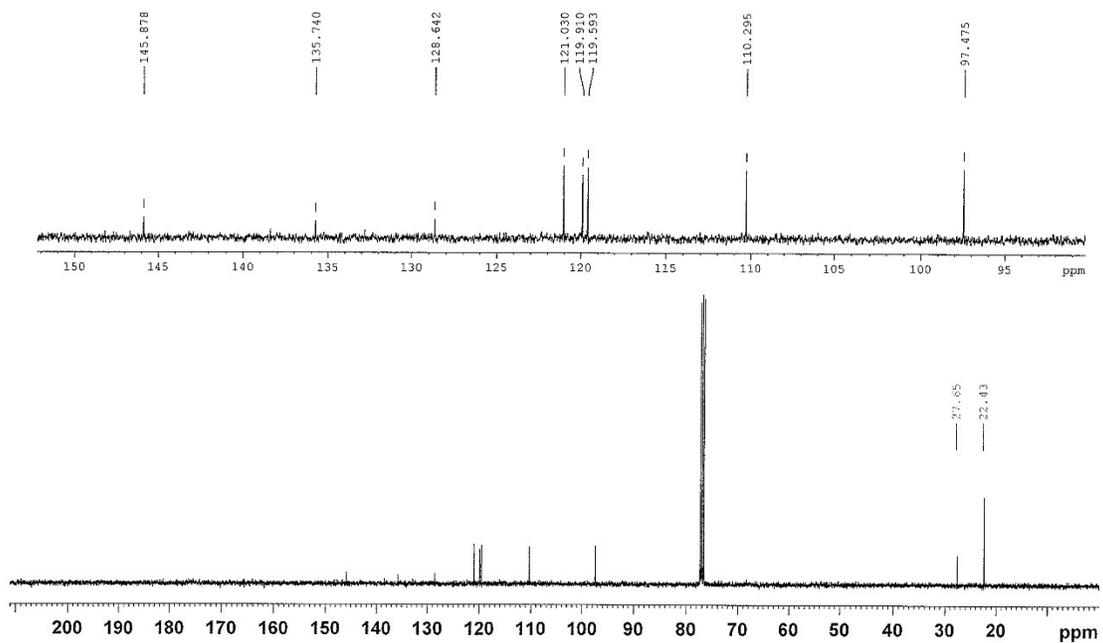
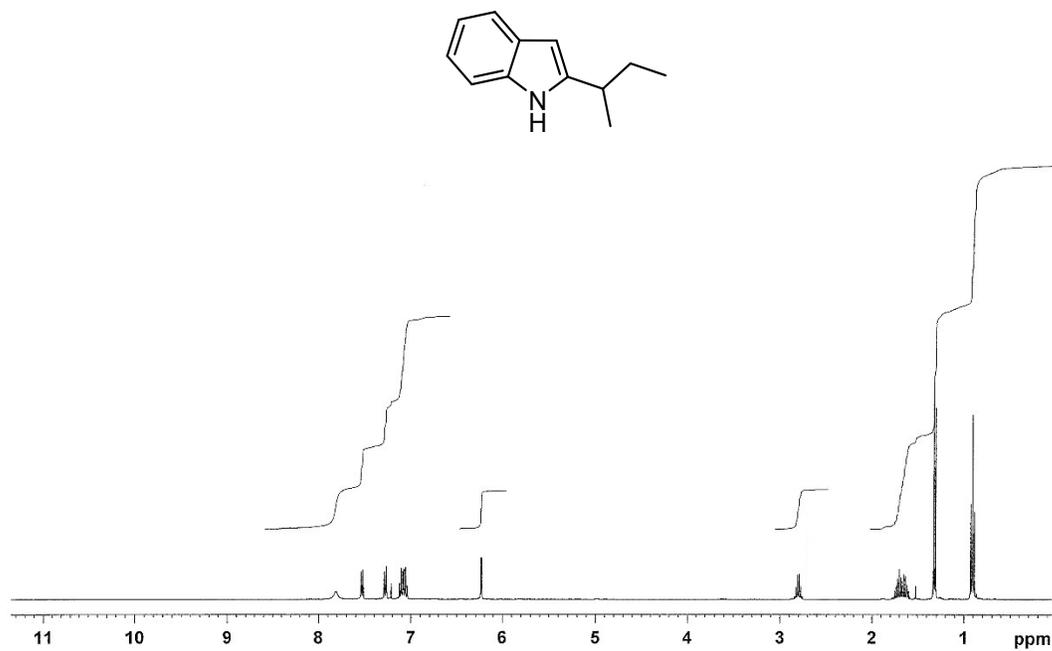


Figure S2. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-isopropyl-1*H*-indole (**3b**) (CDCl_3)



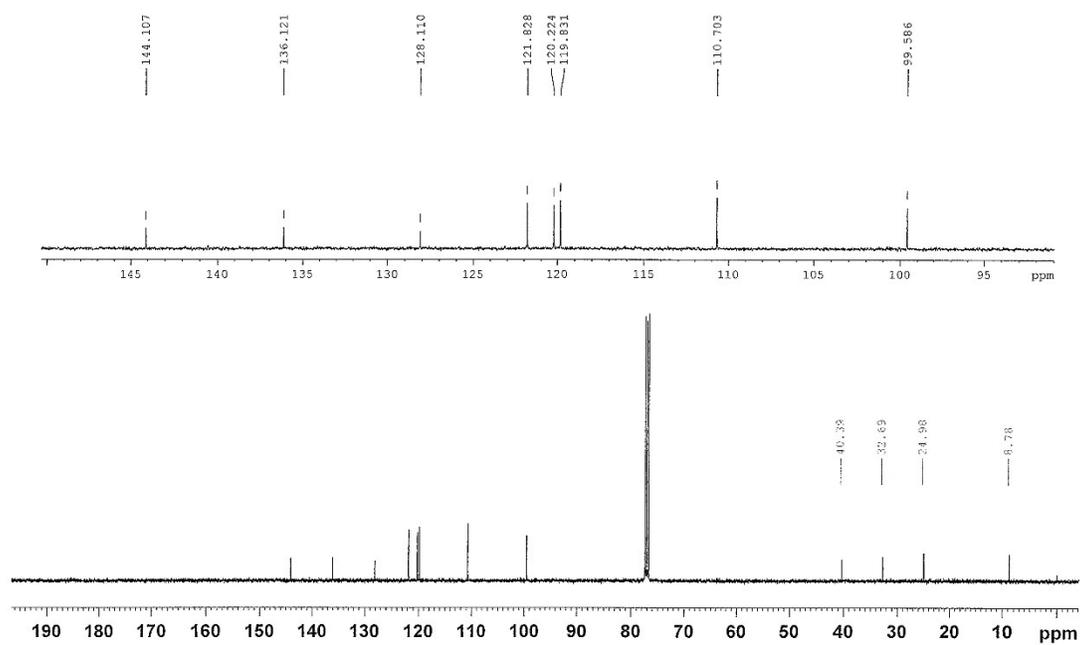
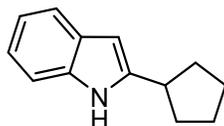


Figure S3. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2-(sec-butyl)-1H-indole (**3c**) (CDCl₃)



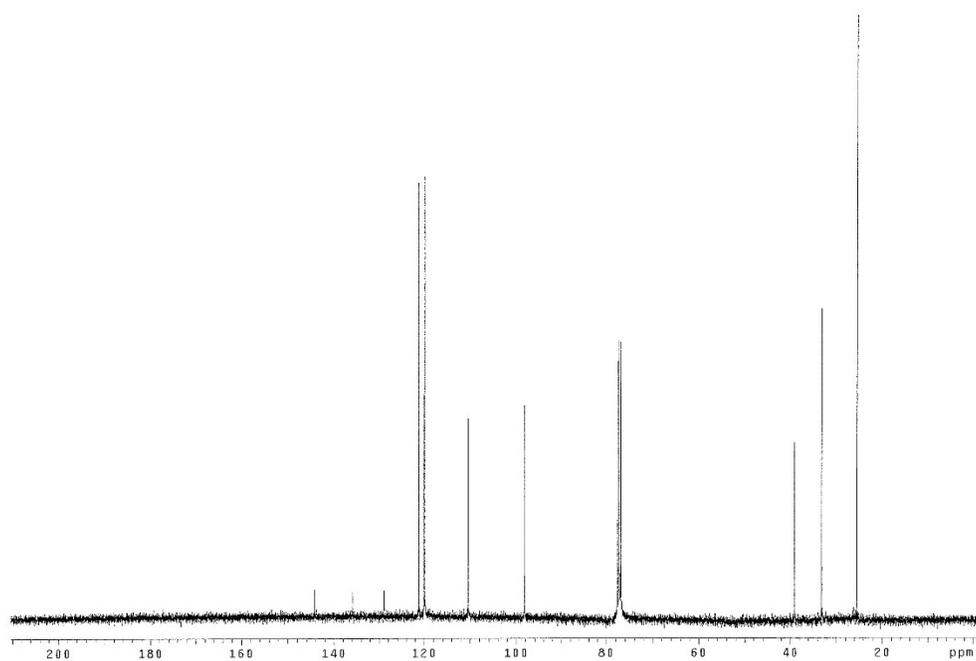
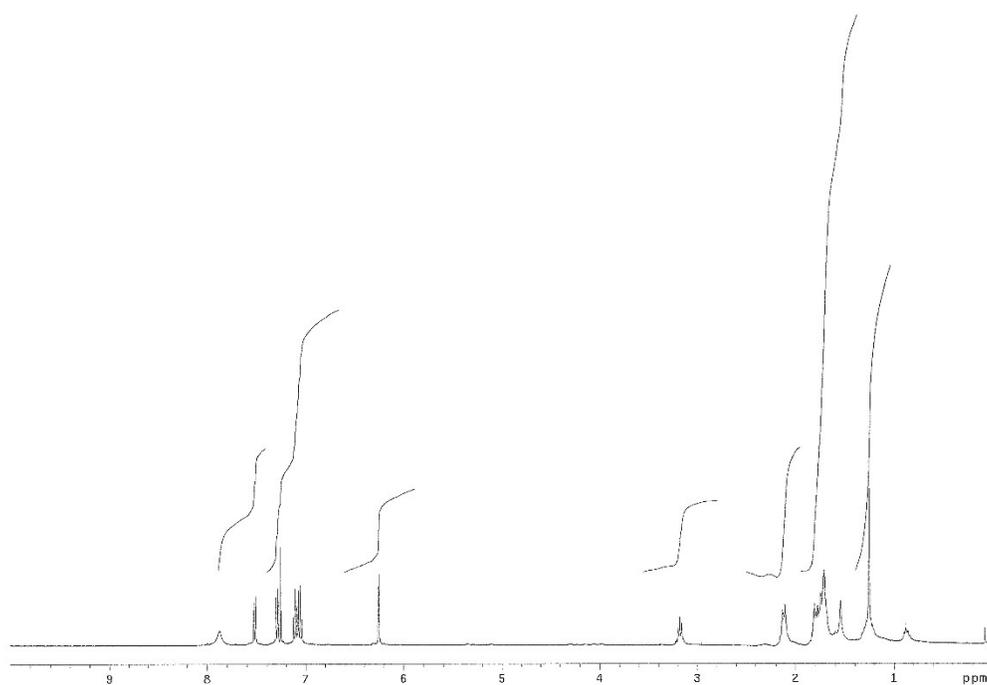
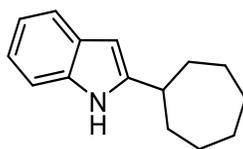


Figure S4. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-cyclopentyl-1*H*-indole (**3d**) (CDCl_3)



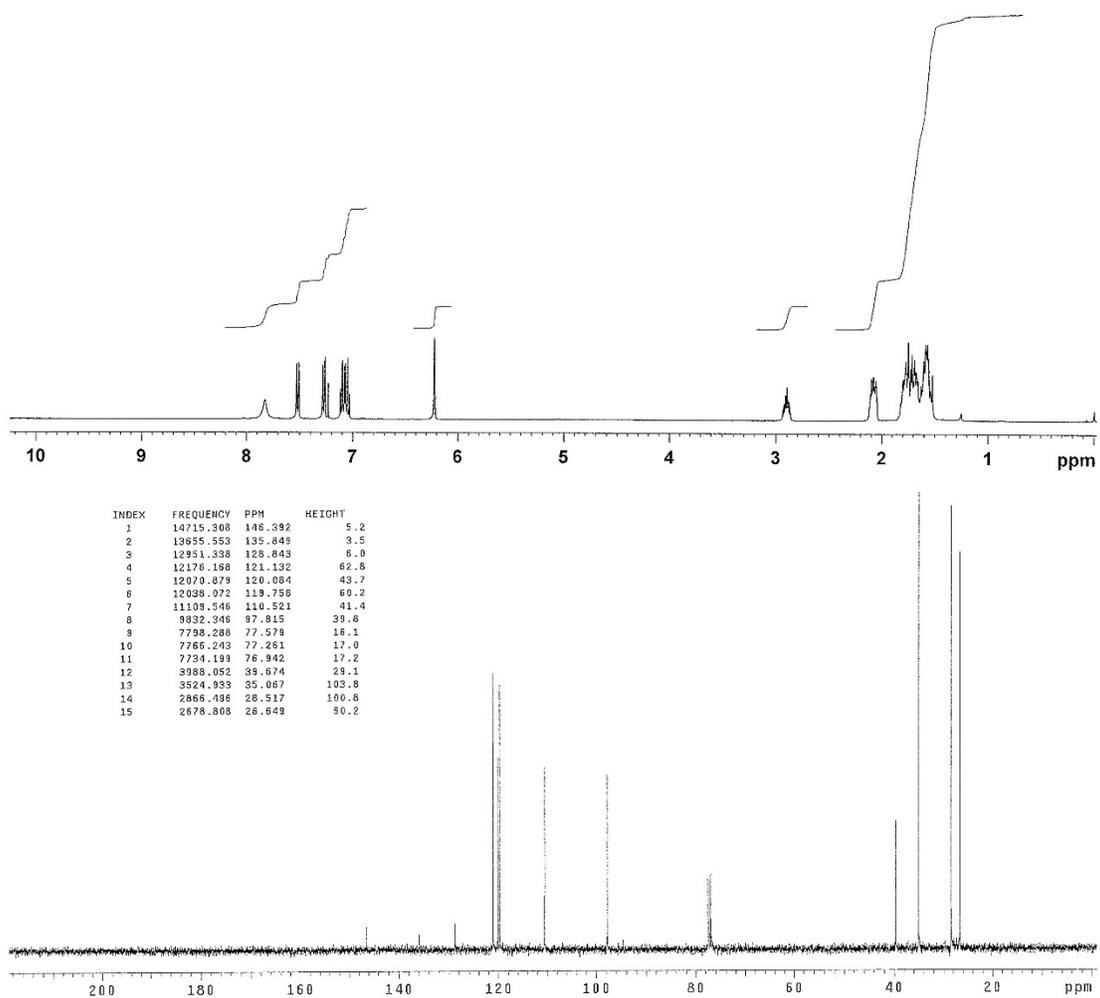
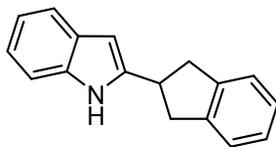


Figure S5. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-cycloheptyl-1*H*-indole (**3e**) (CDCl_3)



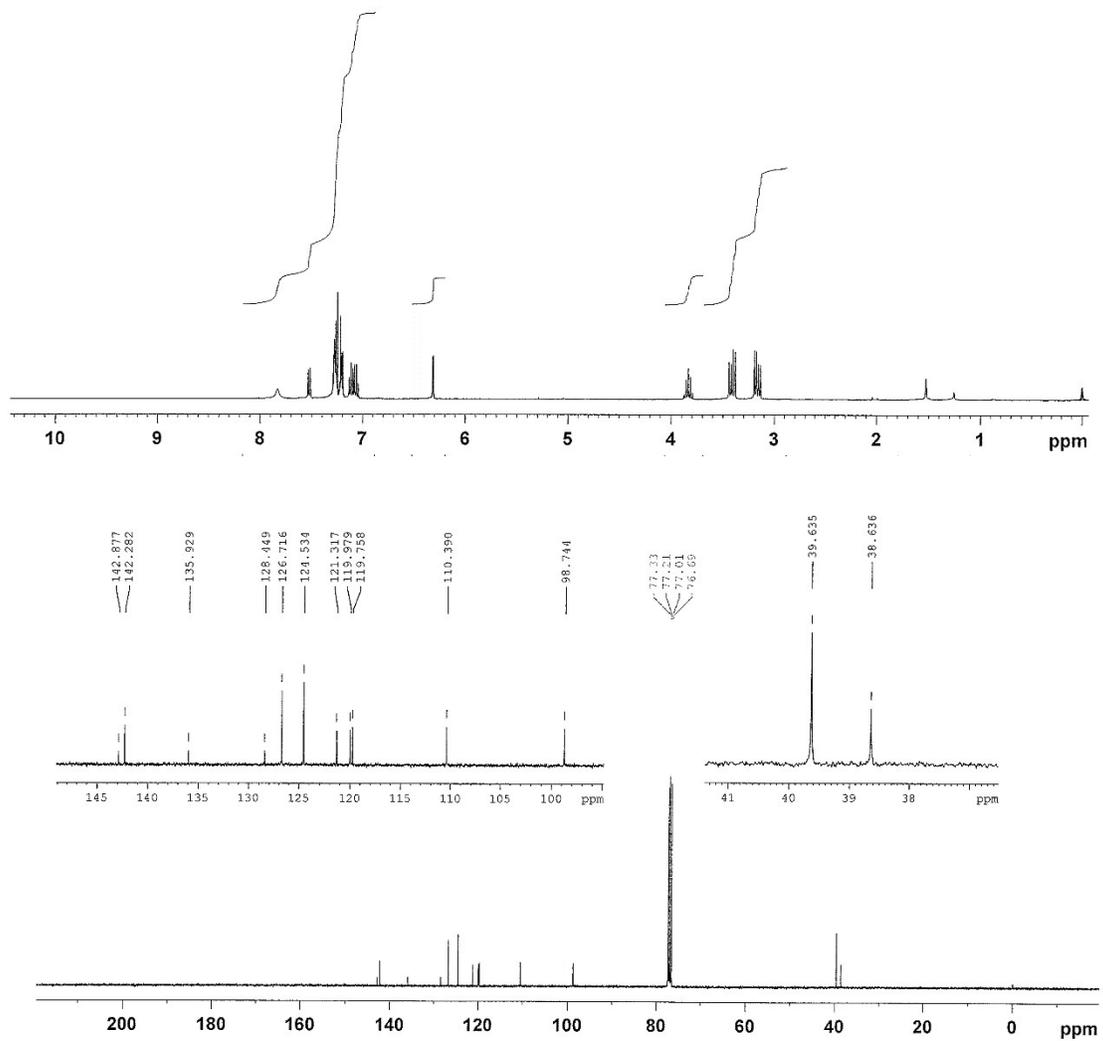
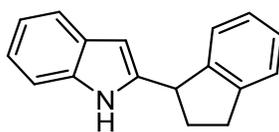


Figure S6. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-(2,3-dihydro-1H-inden-2-yl)-1H-indole (**3f**) (CDCl_3)



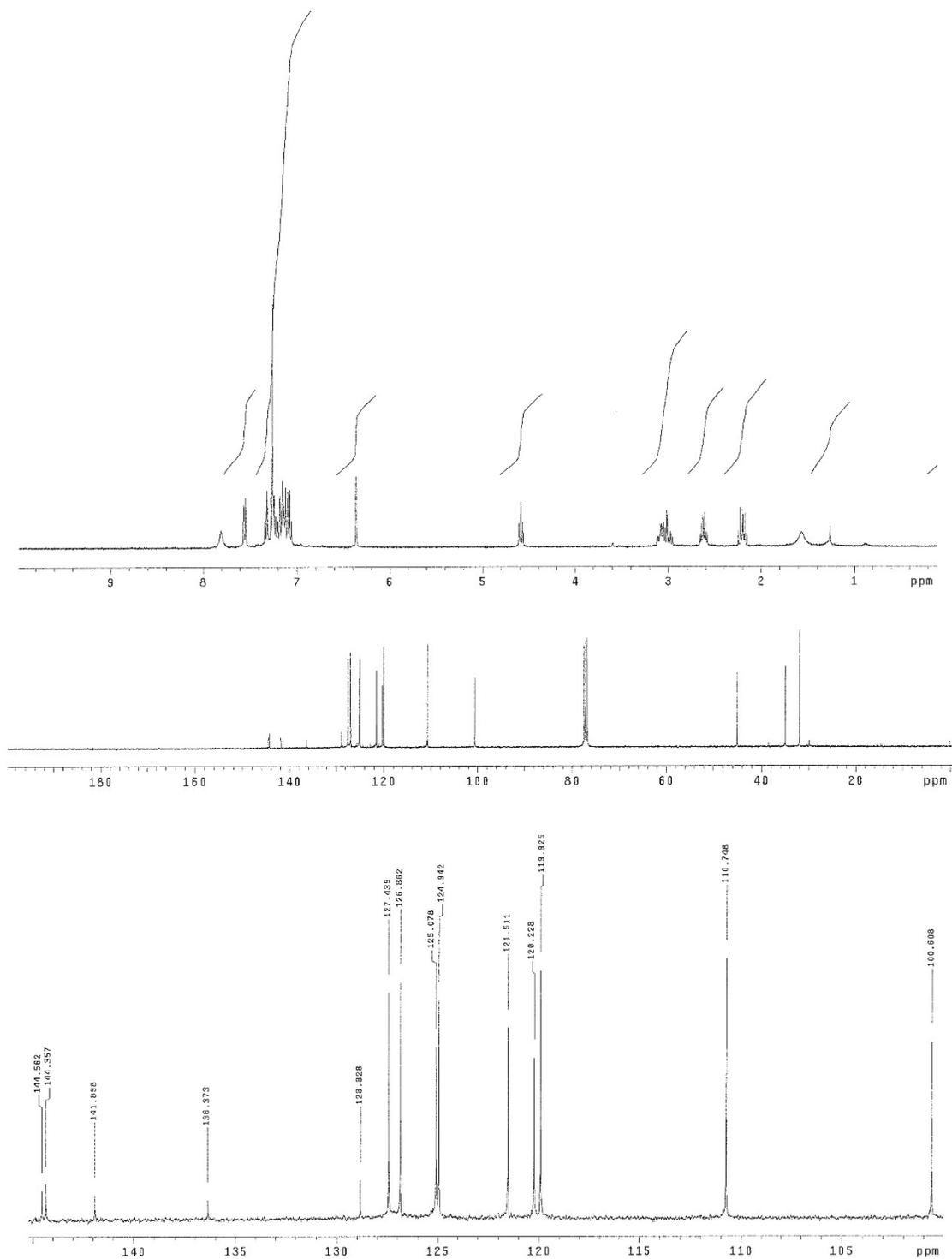


Figure S7. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2-(2,3-dihydro-1H-inden-1-yl)-1H-indole (**3g**) (CDCl₃)

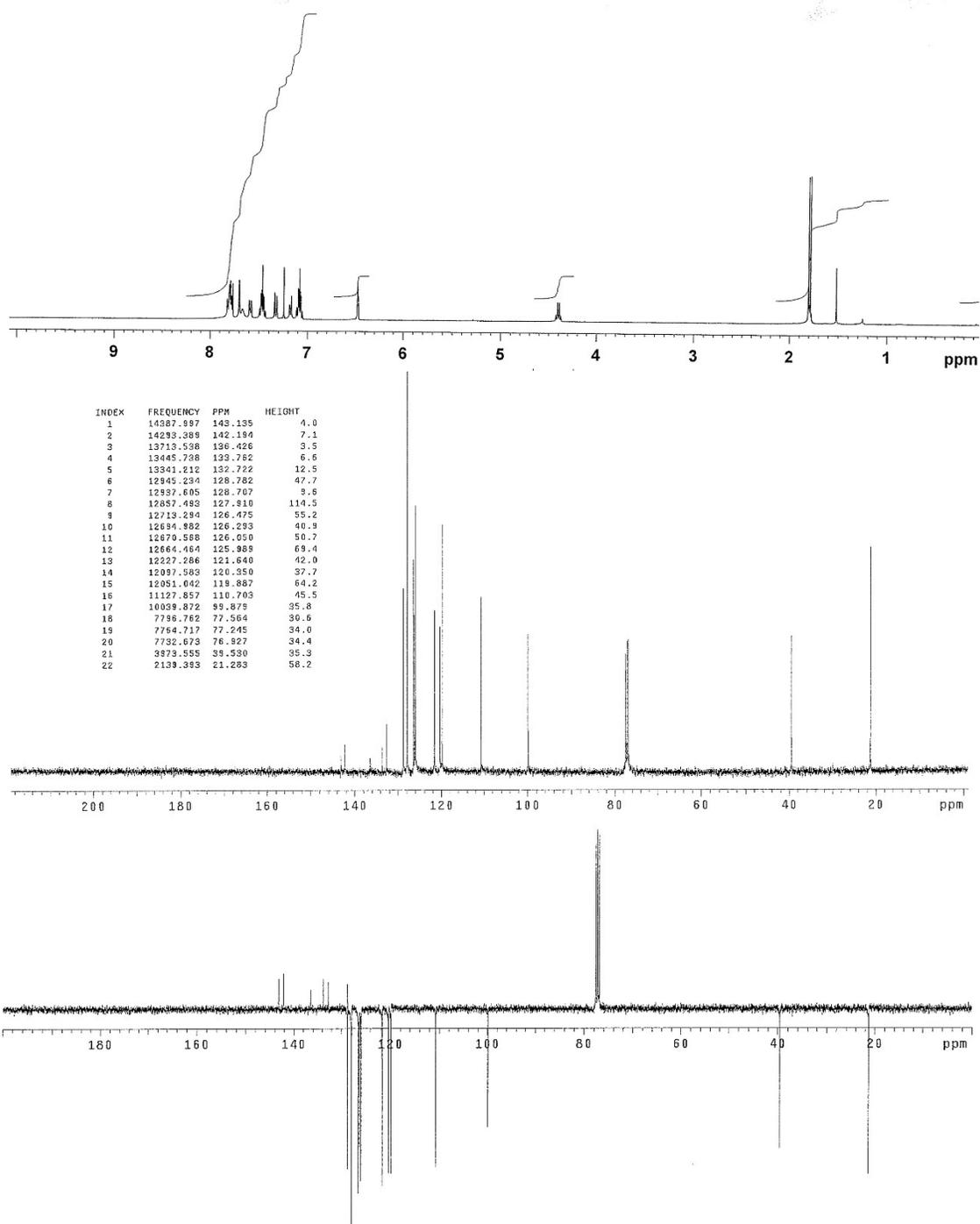
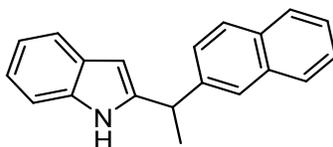


Figure S9. ^1H NMR (400 MHz) and APT ^{13}C NMR (100 MHz) spectrums of 2-(1-(XXXyridineXXXne-2-yl)ethyl)-1*H*-indole (**3i**) (CDCl_3)

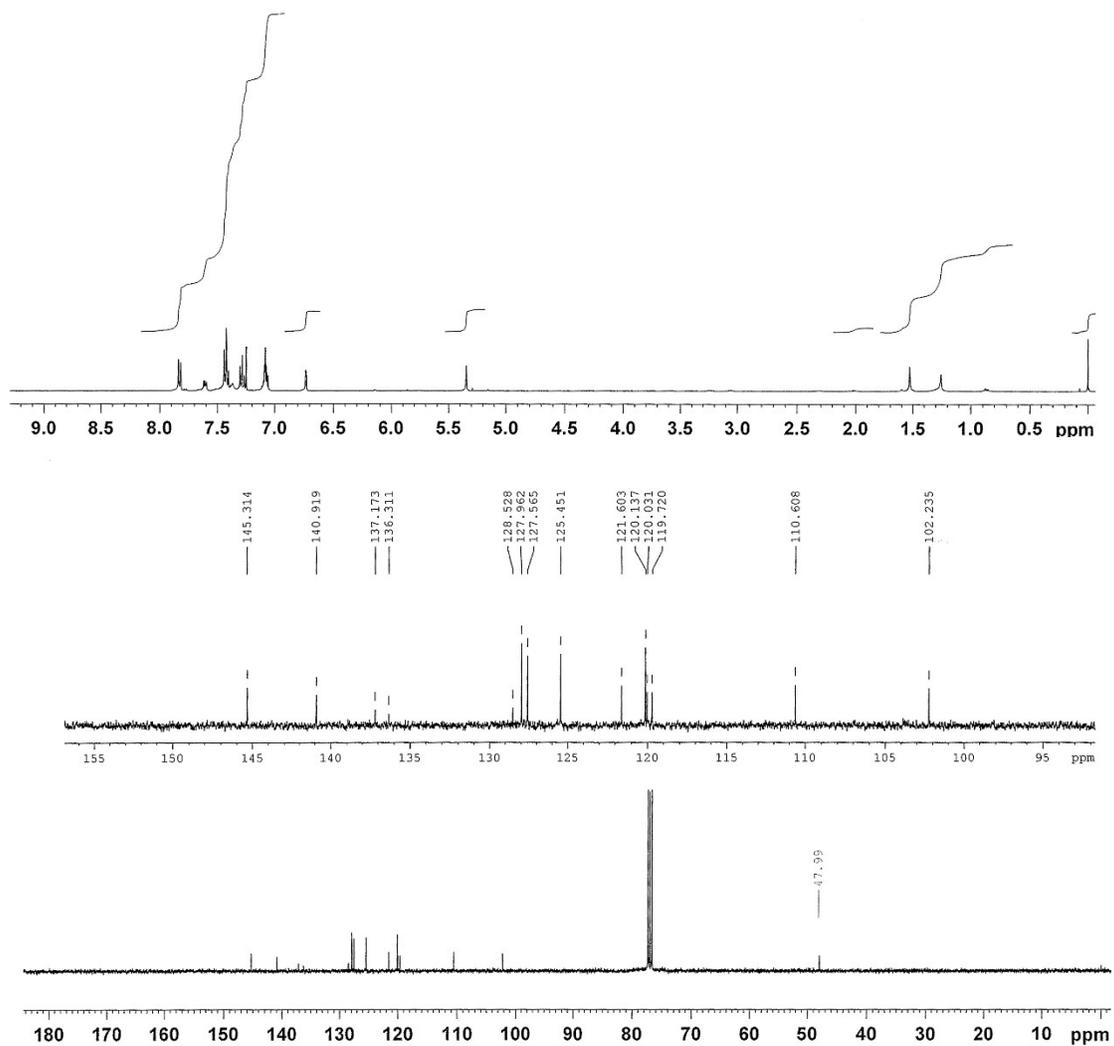
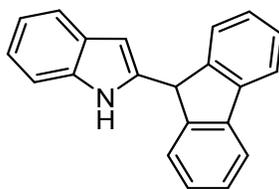


Figure S10. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2-(9H-fluoren-9-yl)-1H-indole (**3j**) (CDCl₃)

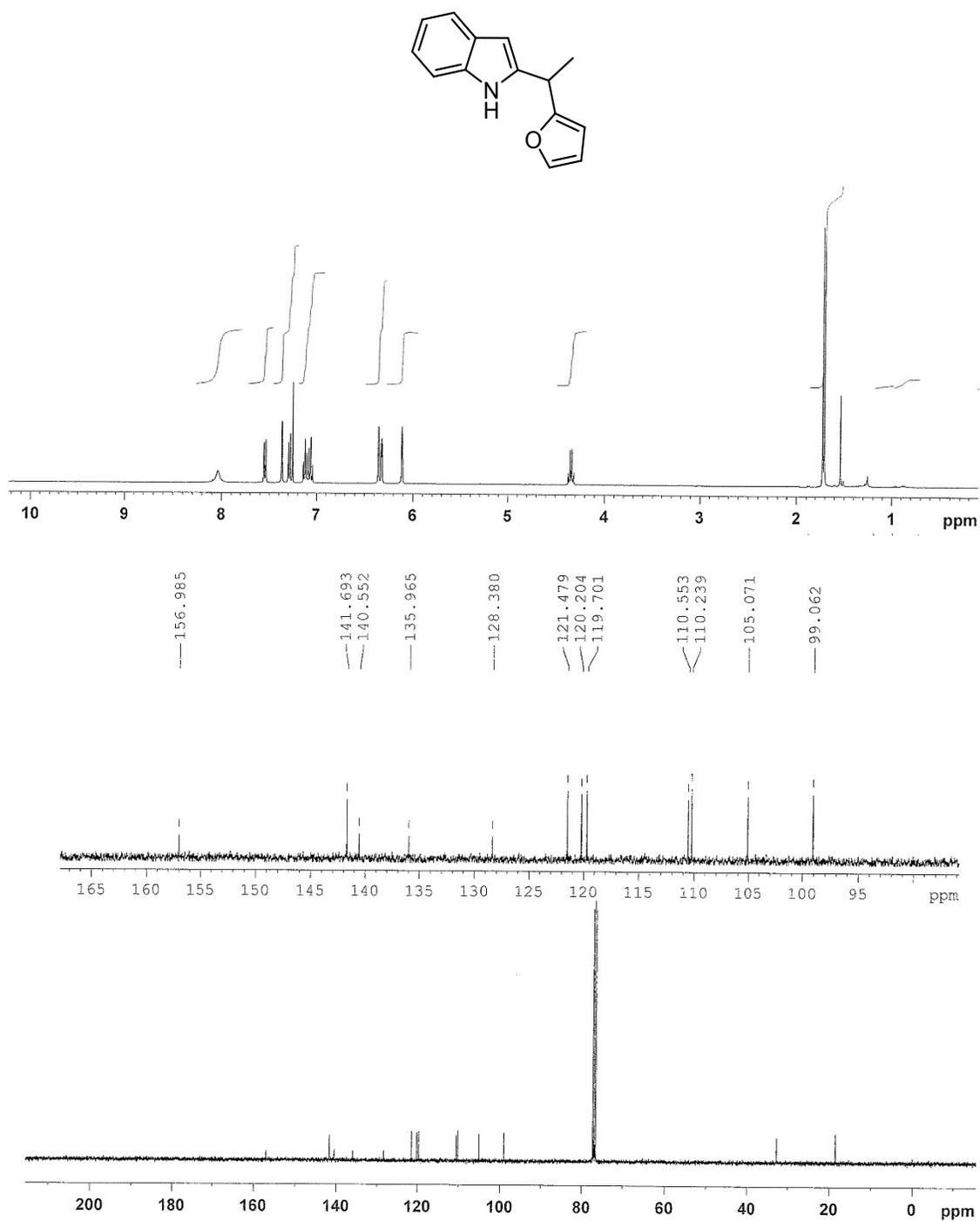


Figure S11. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2-(1-(furan-2-yl)ethyl)-1H-indole (**3k**) (CDCl₃)

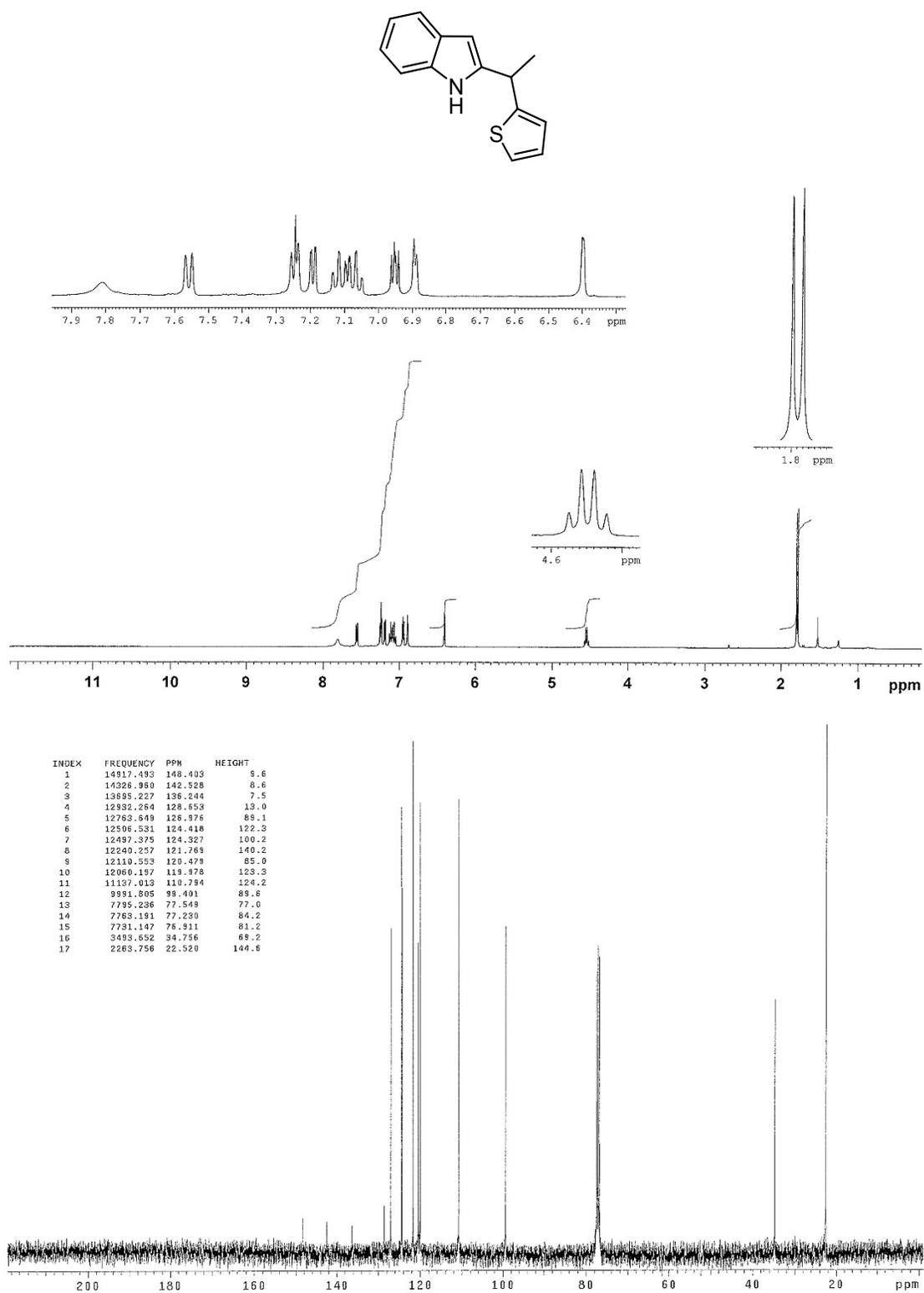


Figure S12. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-(1-(thiophen-2-yl)ethyl)-1*H*-indole (**3I**) (CDCl_3)

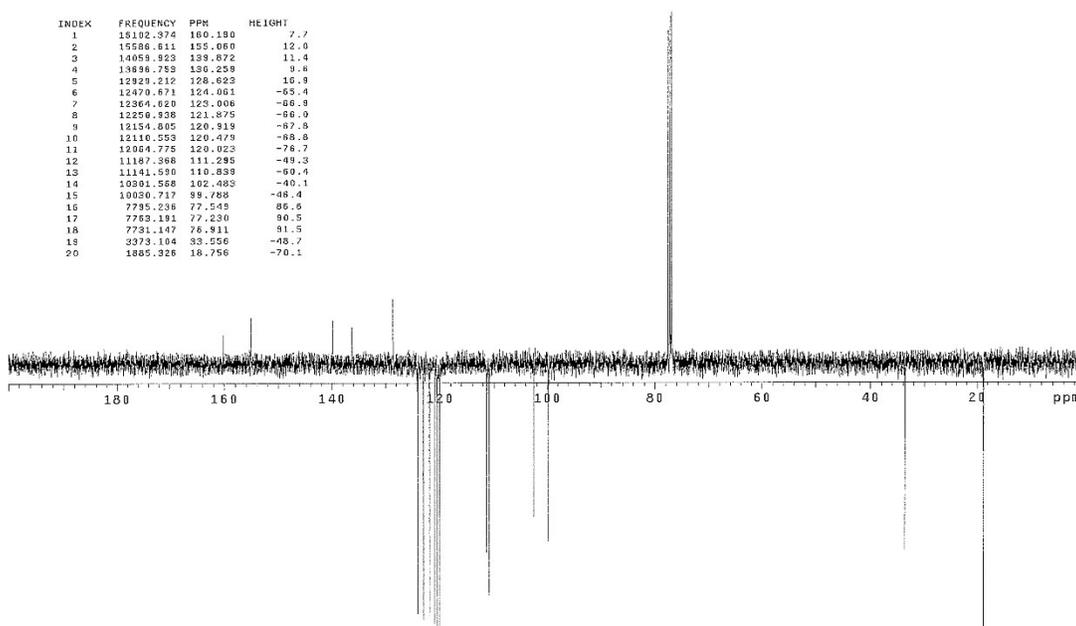
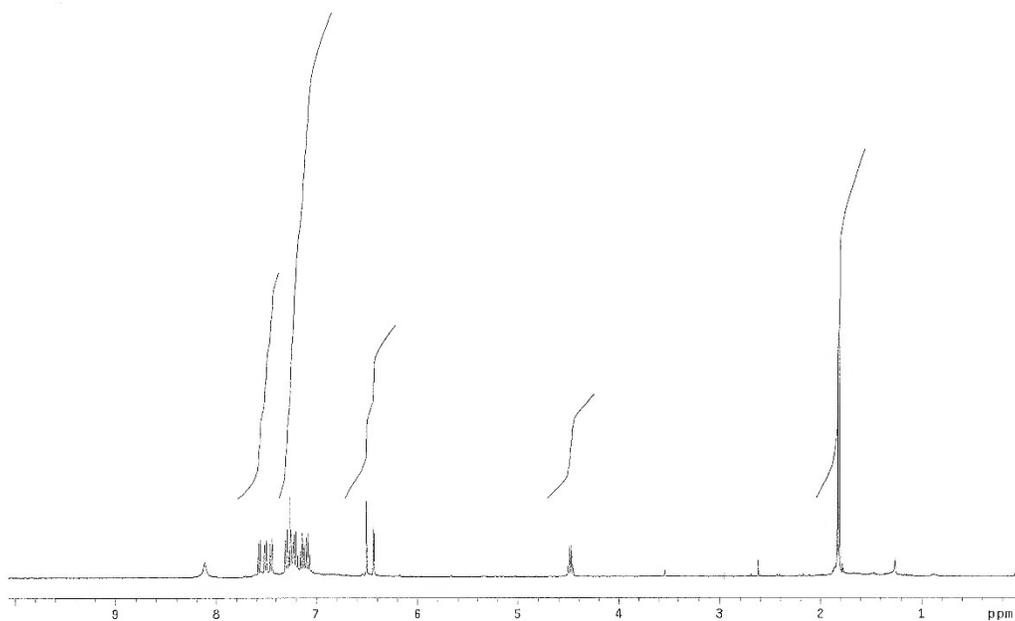
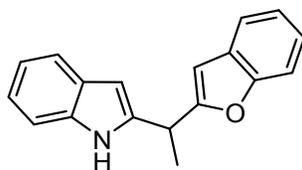


Figure S13. ^1H NMR (400 MHz) and APT ^{13}C NMR (100 MHz) spectrums of 2-(1-(benzofuran-2-yl)ethyl)-1H-indole (**3o**) (CDCl_3)

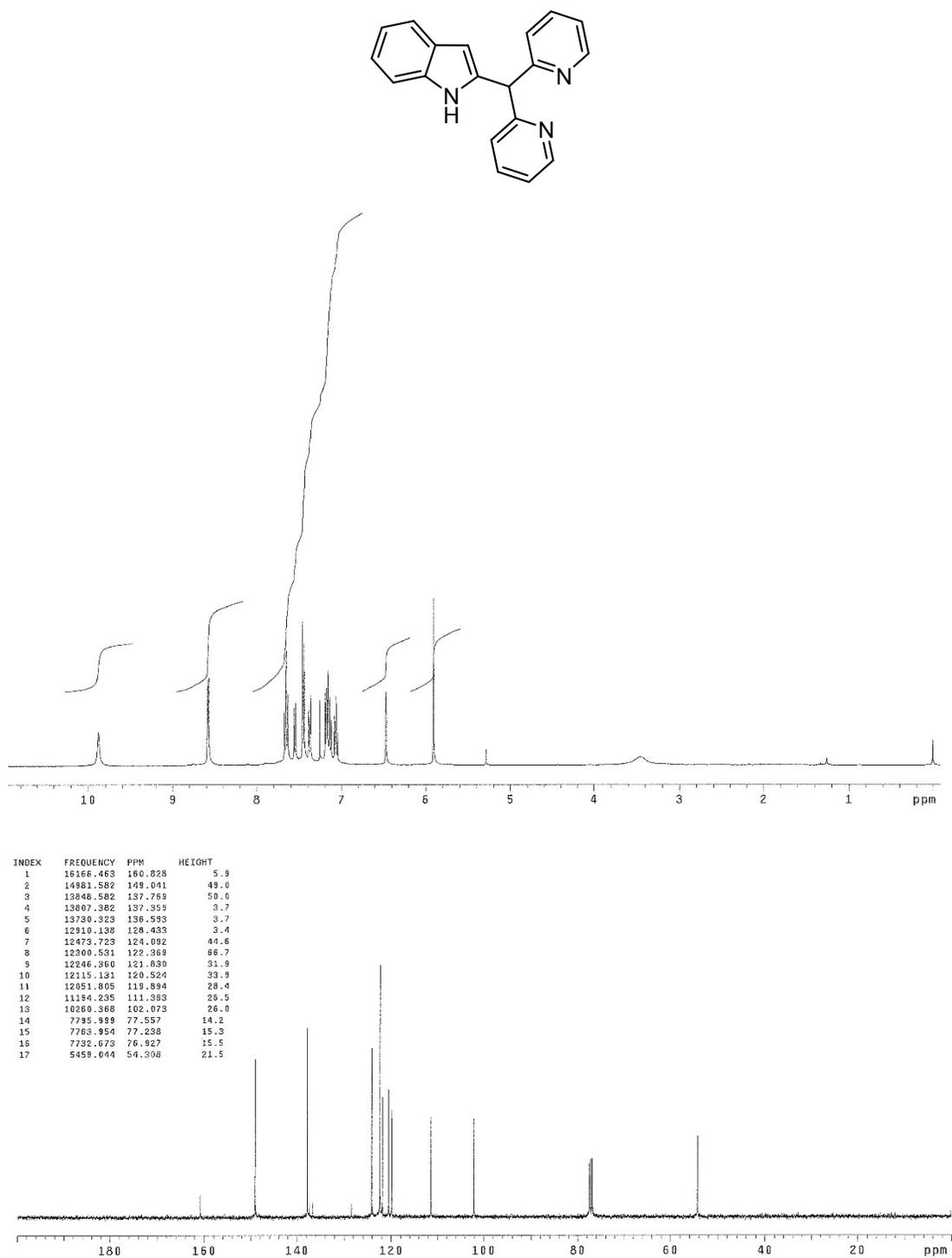
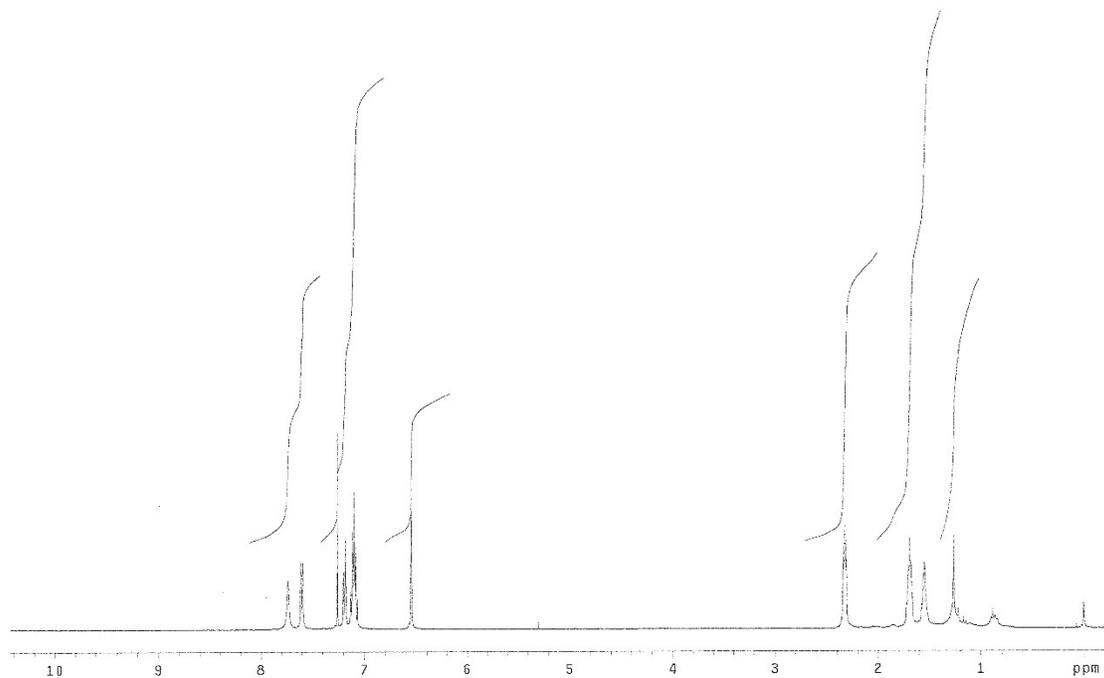
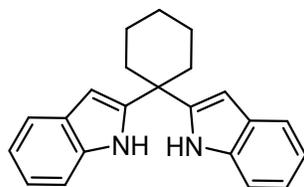


Figure S14. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2-(di(XXX)ridine-2-yl)methyl-1*H*-indole (**3p**) (CDCl_3)



INDEX	FREQUENCY	PPM	HEIGHT
1	14487.045	144.130	4.0
2	13683.013	136.122	8.4
3	12921.582	126.547	20.8
4	12257.042	121.936	82.0
5	12100.654	120.580	73.7
6	12065.538	120.031	86.3
7	11157.613	110.399	76.4
8	9998.672	99.469	31.5
9	7796.762	77.564	40.8
10	7785.317	77.450	7.4
11	7764.717	77.245	43.7
12	7752.873	76.927	46.0
13	4119.281	40.980	12.5
14	3899.652	36.805	93.4
15	2629.976	26.164	48.0
16	2309.534	22.976	98.4

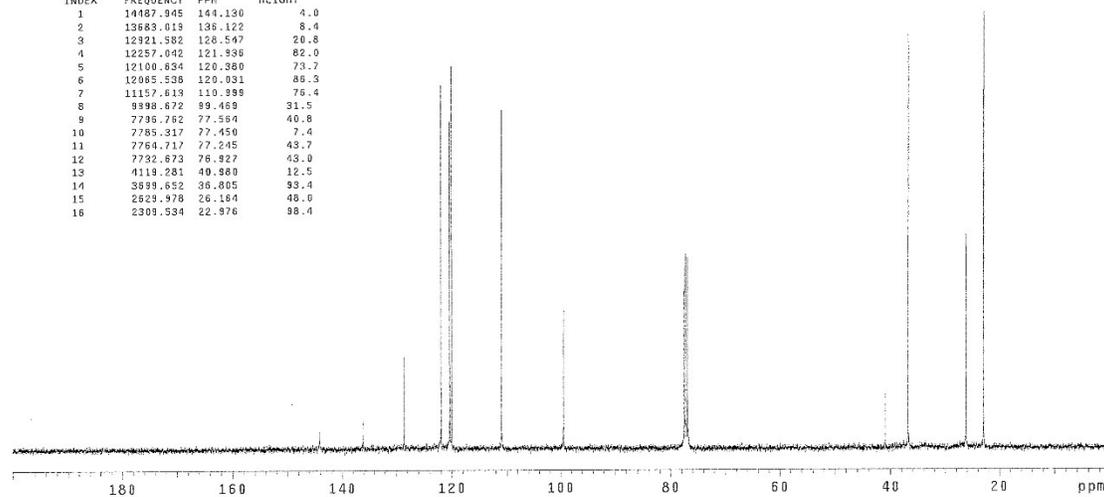


Figure S15. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of 2,2'-(cyclohexane-1,1-diyl)bis(1H-indole) (**4a**) (CDCl_3)

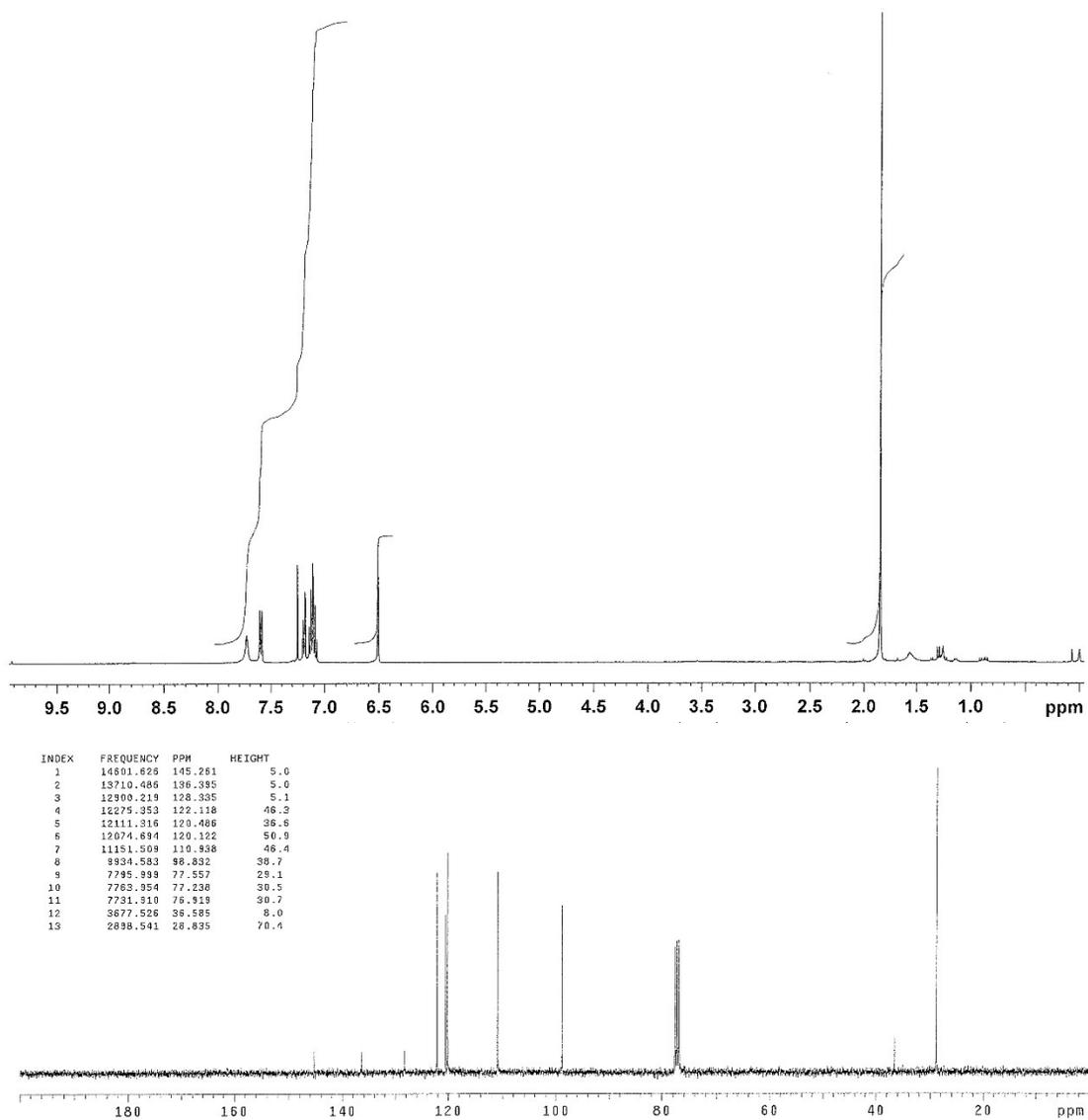
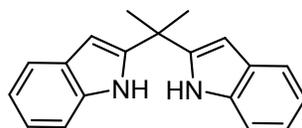
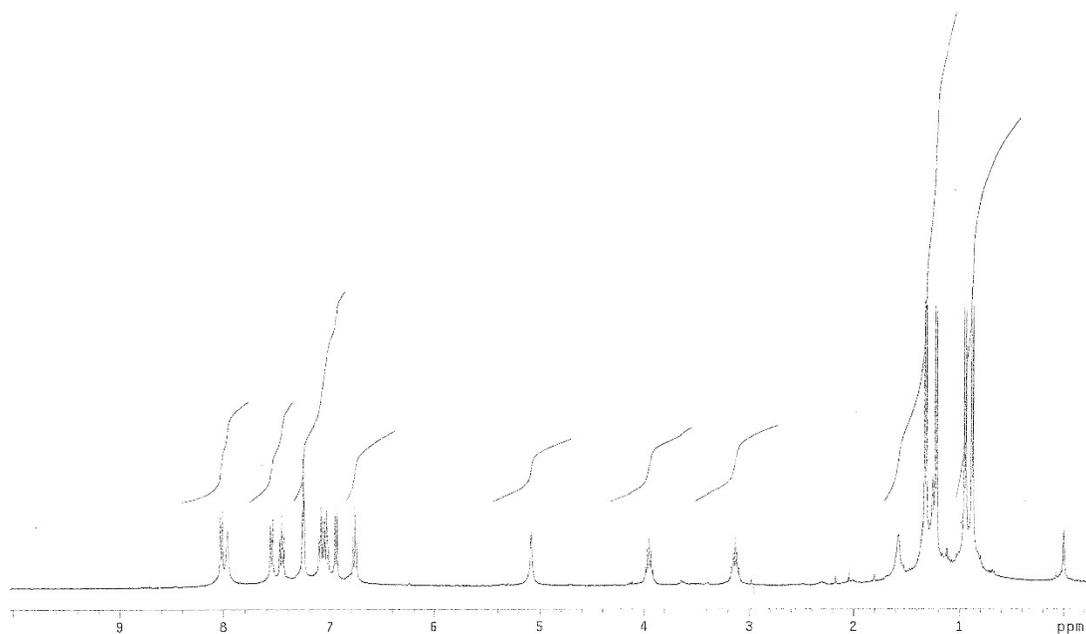
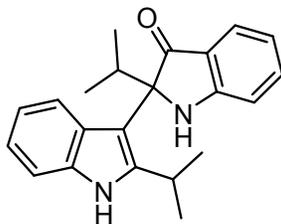


Figure S16. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrums of 2,2'-(propane-2,2-diyl)bis(1H-indole) (**4b**) (CDCl_3)



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20448.210	203.424	2.6	16	7795.236	77.545	79.8
2	16132.130	160.487	5.5	17	7783.191	77.230	89.1
3	14320.856	142.467	4.4	18	7731.147	76.311	85.9
4	13786.701	137.253	-29.5	19	7535.065	74.951	6.8
5	13616.601	135.452	5.4	20	3488.311	34.703	-25.2
6	12786.538	127.204	4.0	21	2587.200	25.733	-26.4
7	12585.116	125.200	-34.3	22	2382.015	23.637	-29.6
8	12247.886	121.845	3.1	23	2320.978	23.090	-31.4
9	12231.101	121.678	-27.8	24	1830.393	18.209	-29.3
10	12197.531	121.344	-32.0	25	1647.282	16.388	-26.6
11	12026.627	119.644	-34.7				
12	11935.835	118.741	-30.3				
13	11216.361	111.583	-29.5				
14	11124.805	110.672	-34.3				
15	10829.538	107.735	3.2				

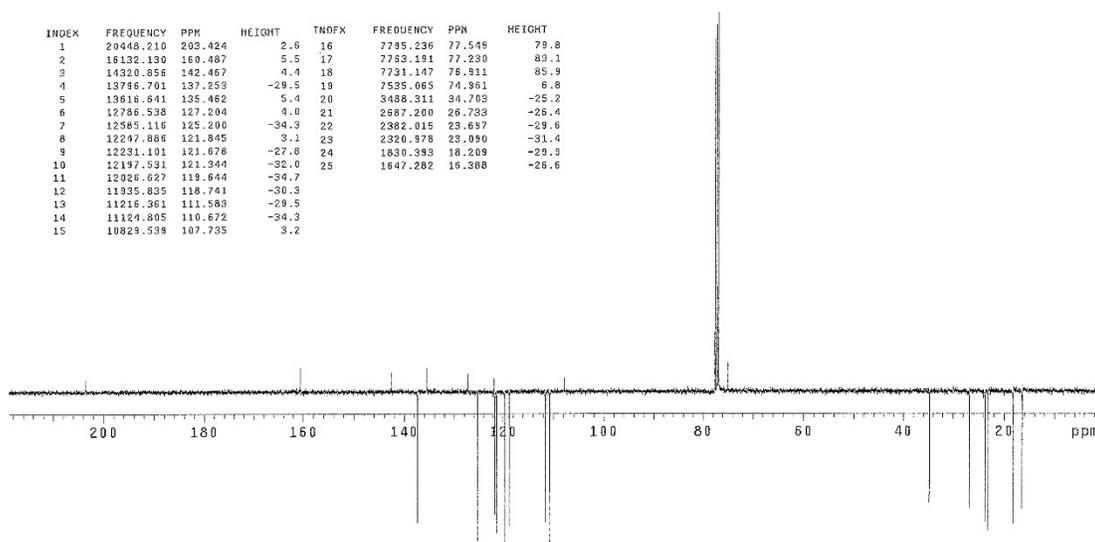


Figure S17. ^1H NMR (400 MHz) and APT ^{13}C NMR (100 MHz) spectrums of 2-isopropyl-2-(2-isopropyl-1H-indol-3-yl)indolin-3-one (9) (CDCl_3)

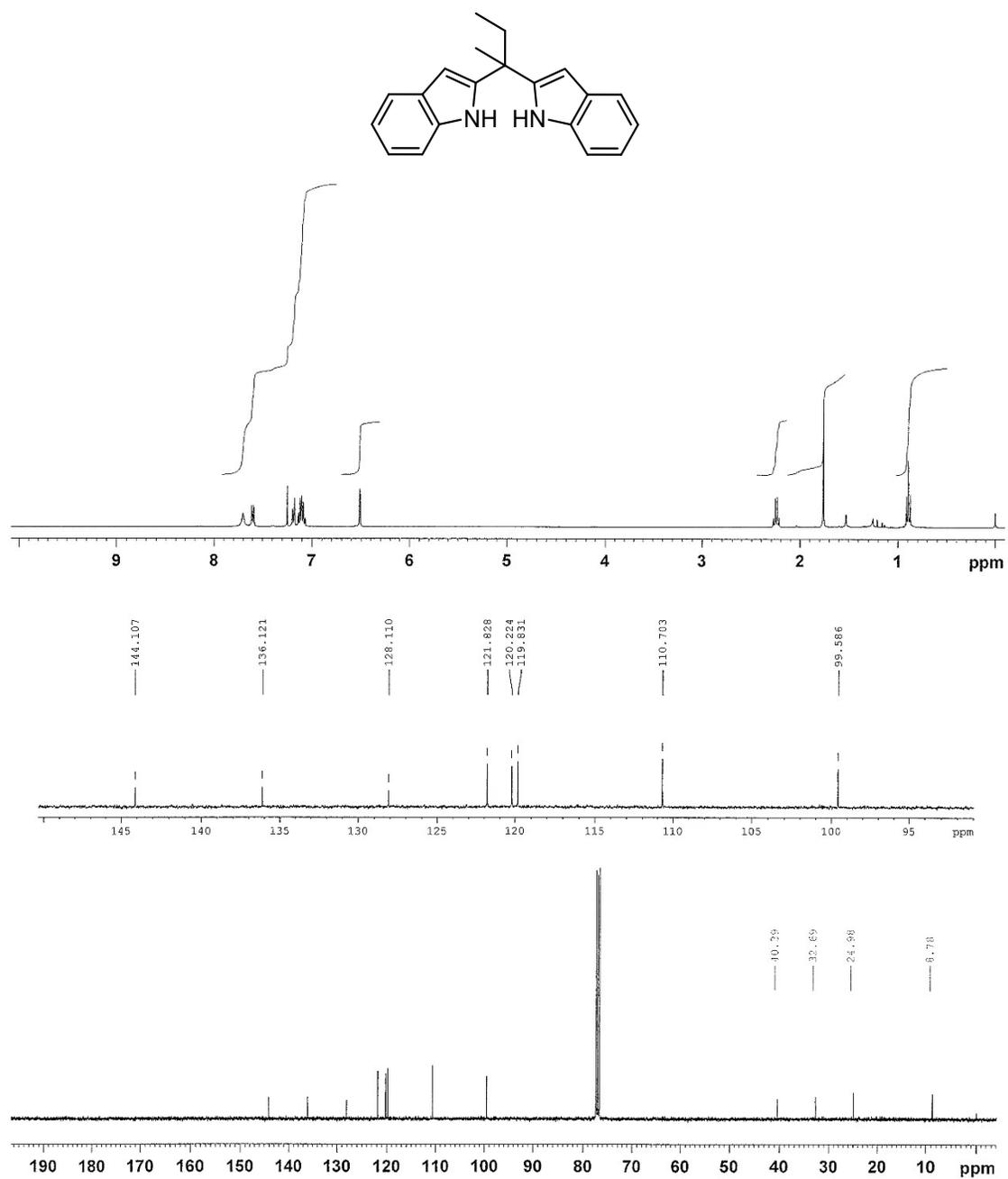


Figure S18. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2,2'-(butane-2,2-diyl)bis(1H-indole) (4c) (CDCl₃)

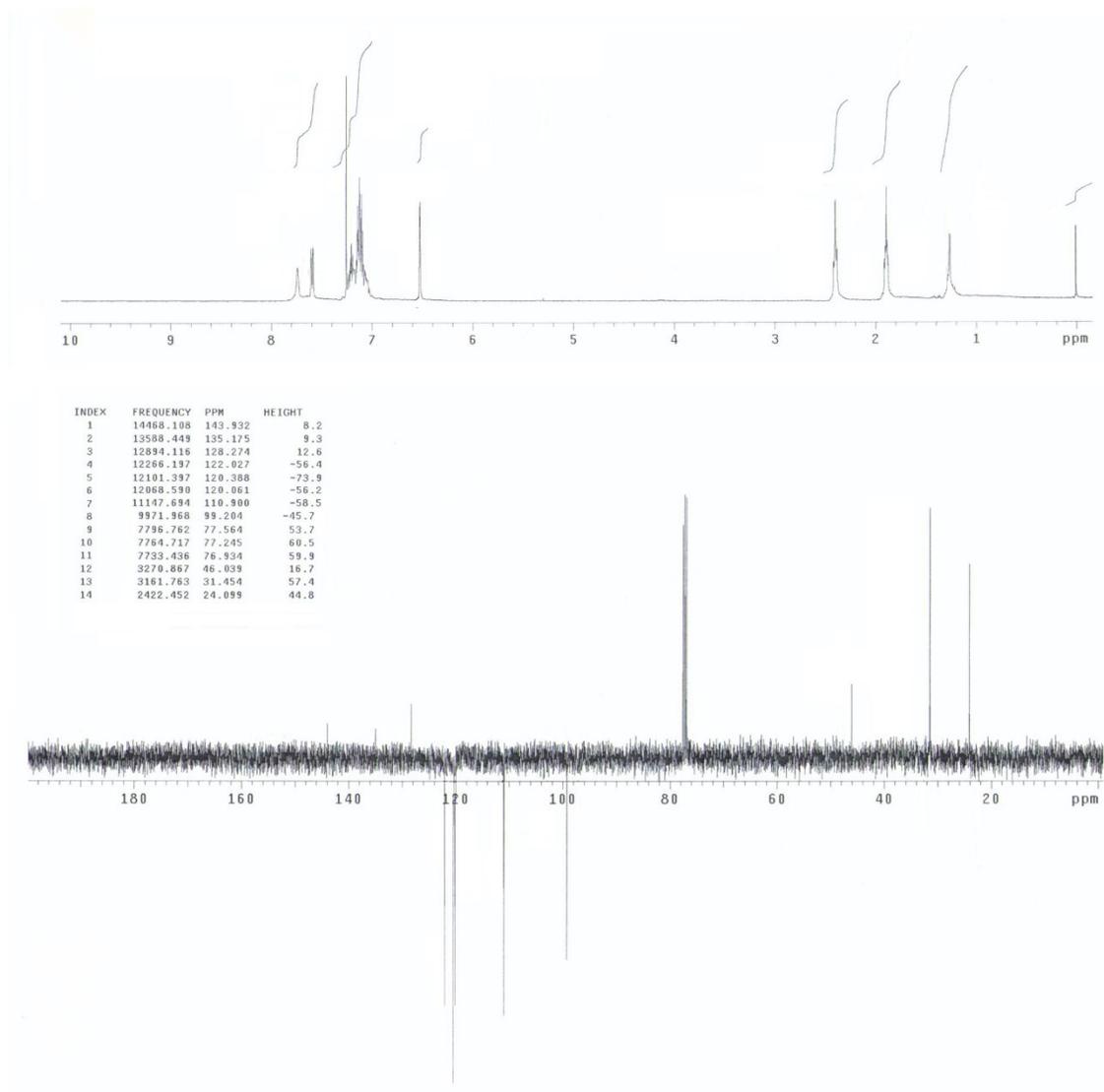
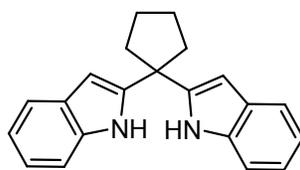


Figure S19. ^1H NMR (400 MHz) and APT ^{13}C NMR (100 MHz) spectrums of 2,2'-(cyclopentane-1,1-diyl)bis(1*H*-indole) (**4d**) (CDCl_3)

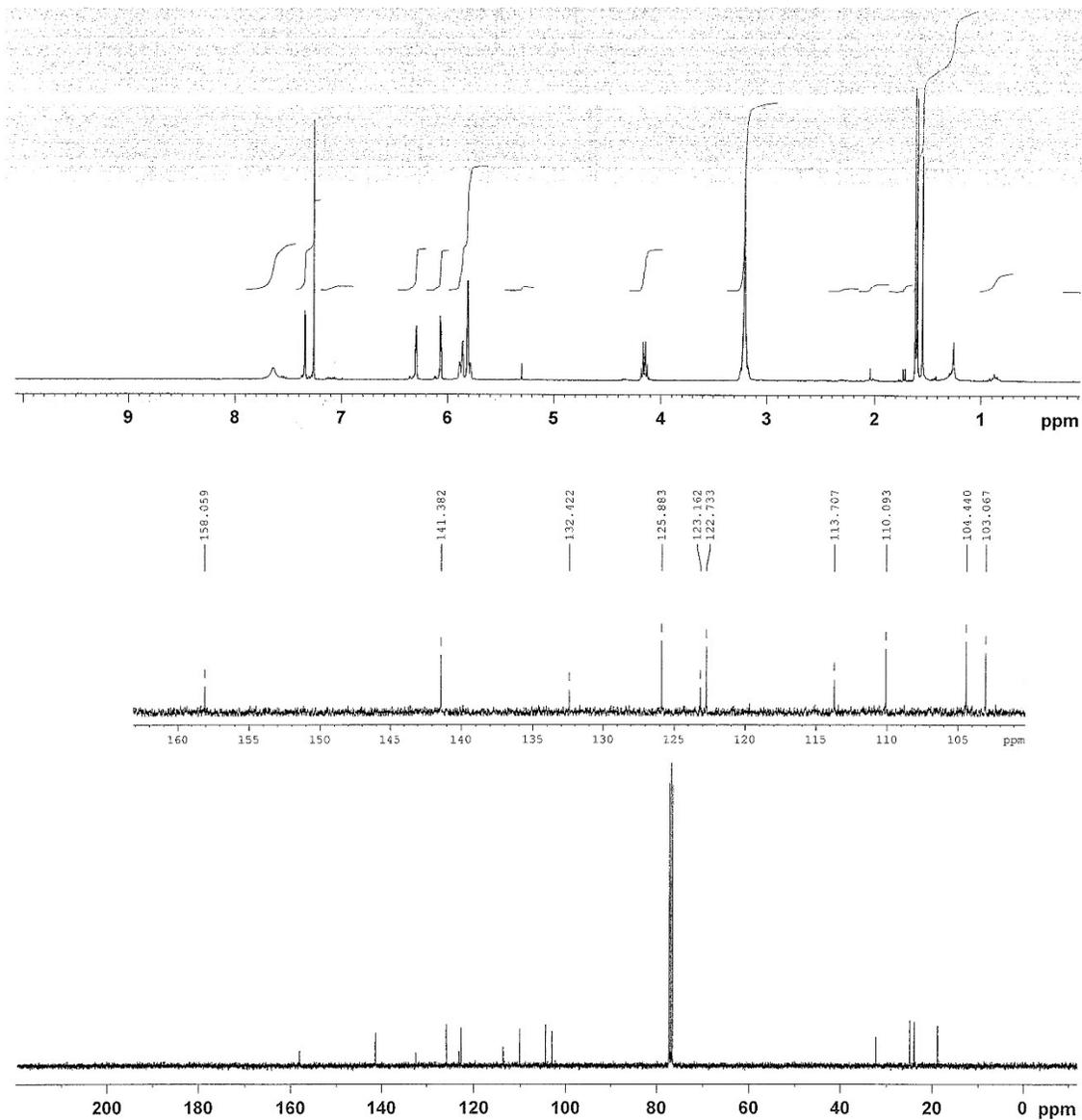
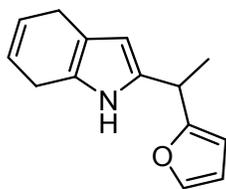


Figure S20. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectrums of 2-(1-(furan-2-yl)ethyl)-4,7-dihydro-1H-indole (**17**) (CDCl₃)

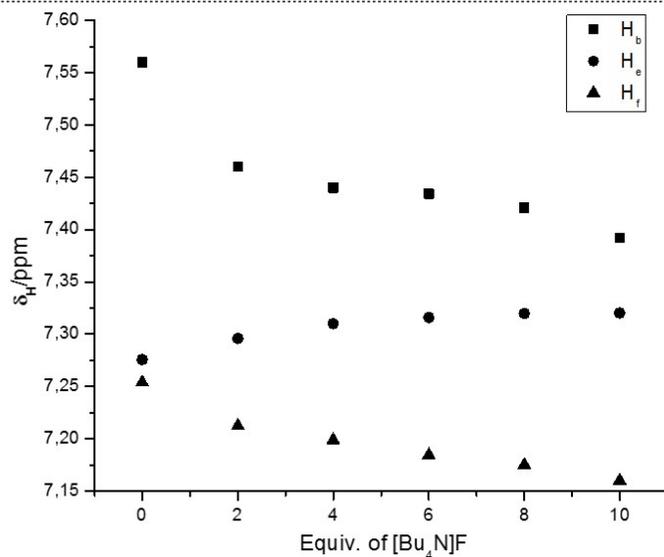
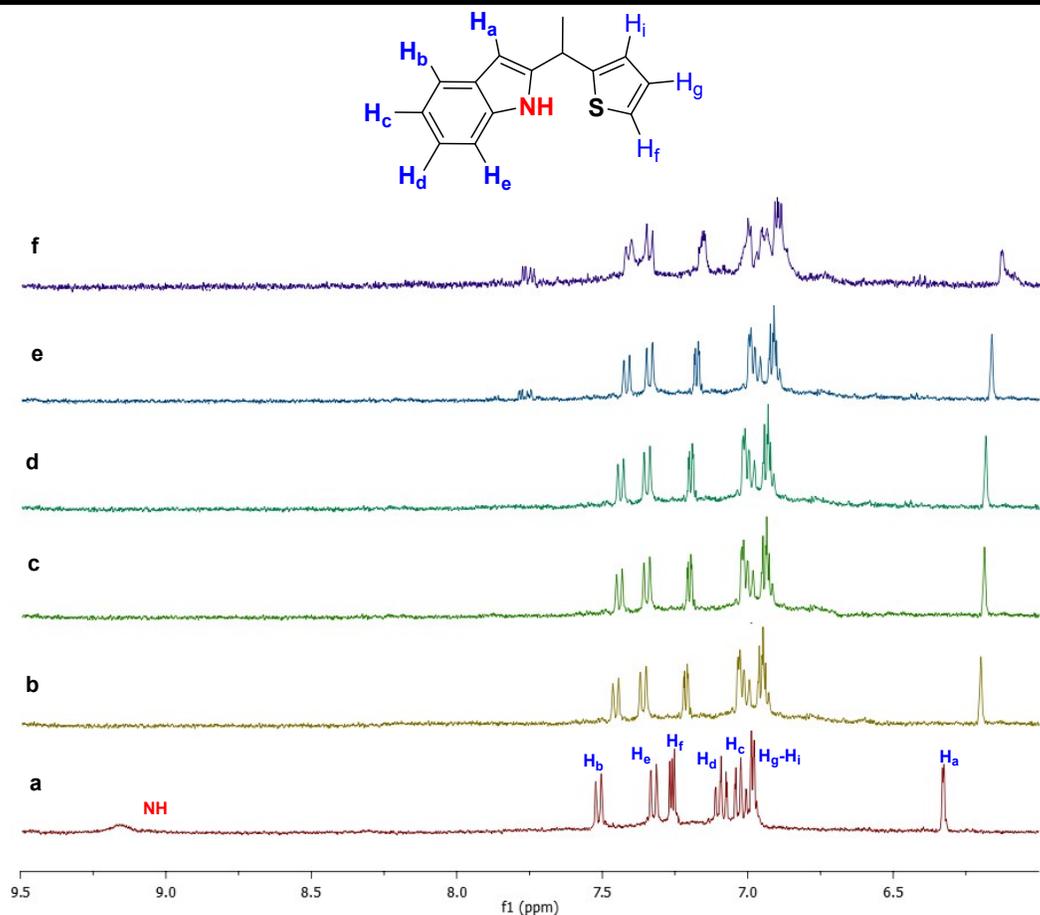


Figure S21. ^1H NMR (400 MHz) spectra in CD_3CN of the sensor **3I** (1×10^{-2} M) with presence of $[\text{Bu}_4\text{N}]\text{F}$; (a) 0 equiv. of $[\text{Bu}_4\text{N}]\text{F}$, (b) 2 equiv. of $[\text{Bu}_4\text{N}]\text{F}$, (c) 4 equiv. of $[\text{Bu}_4\text{N}]\text{F}$, (d) 6 equiv. of $[\text{Bu}_4\text{N}]\text{F}$, (e) 8 equiv. of $[\text{Bu}_4\text{N}]\text{F}$ and (f) 10 equiv. of $[\text{Bu}_4\text{N}]\text{F}$

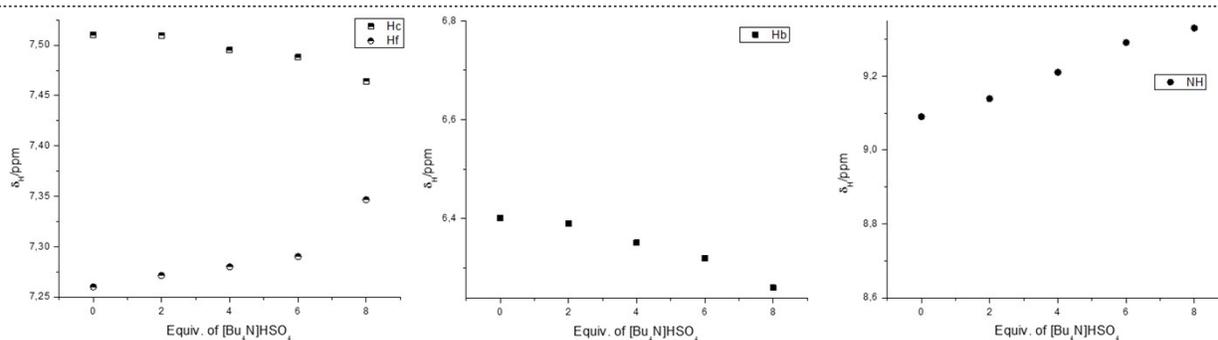
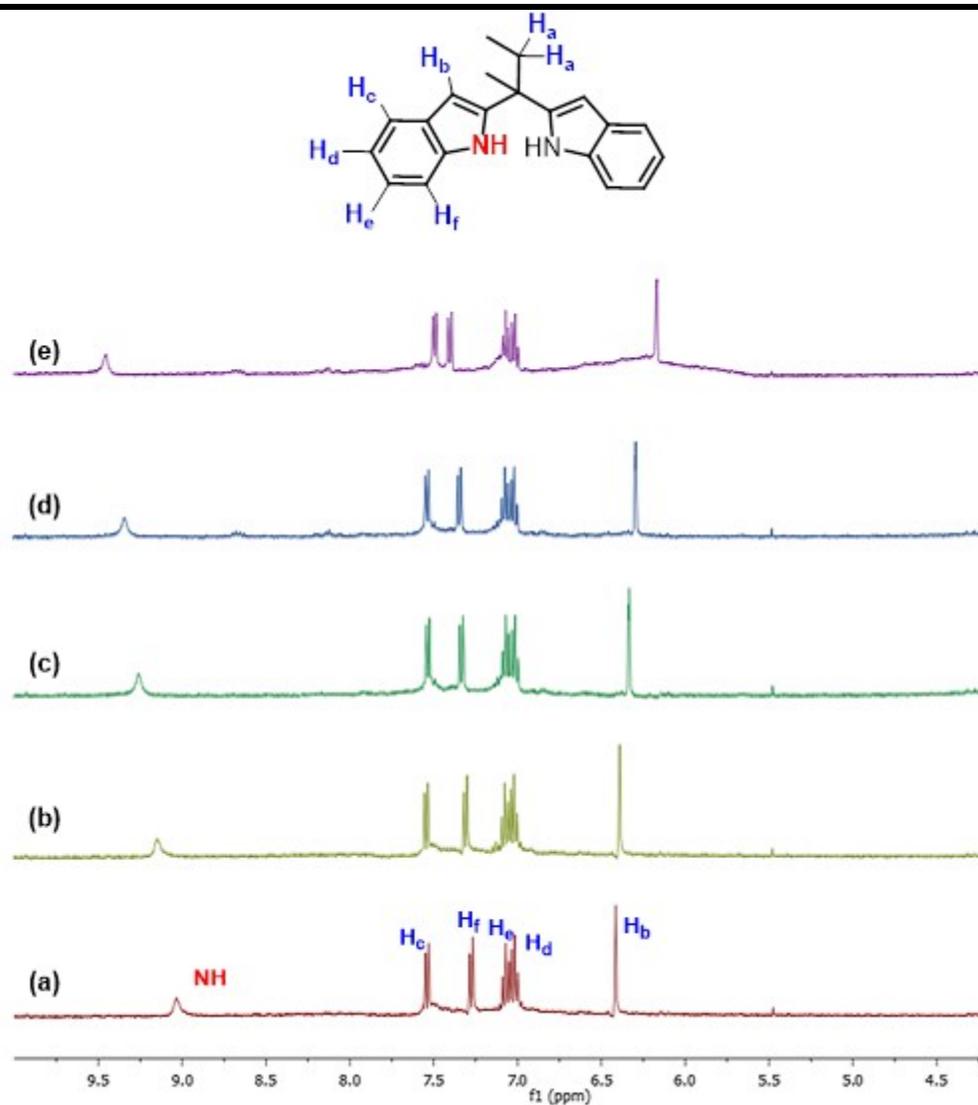


Figure S22. ¹H NMR (400 MHz) spectra in CD₃CN of the sensor **4c** (1×10^{-2} M) with presence of [Bu₄N]HSO₄; (a) 0 equiv. of [Bu₄N]HSO₄, (b) 2 equiv. of [Bu₄N]HSO₄, (c) 4 equiv. of [Bu₄N]HSO₄, (d) 6 equiv. of [Bu₄N]HSO₄ and (e) 8 equiv. of [Bu₄N]HSO₄