

Supporting Information

First synthetic entry to the trimer stage of 5,6-dihydroxyindole polymerization: *ortho*-alkynylaniline-based access to the missing 2,7':2',7"-triindole

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Materials and methods. All commercially available reagents were used as received. Anhydrous solvents were purchased from commercial sources and withdrawn from the container by syringe under a slight positive pressure of argon. All the solvents were of analytical grade quality. Compounds **8**, **10a** and **10b** were prepared according to reported procedures.¹

NMR spectra were recorded with 400 MHz instrument. ¹H and ¹³C NMR spectra were recorded in (CD₃)₂CO using TMS as the internal standard; *J* values are given in Hz. Assignments with identical superscripts may be interchanged. ¹H, ¹H COSY, ¹H, ¹³C HSQC, ¹H, ¹³C HMBC and ROESY experiments were run at 400.1 MHz using standard pulse programs. Mass spectra and high resolution mass spectra were registered in the electrospray ionization-positive ion (ESI+) mode. ESI analysis were performed with the cone and the fragmentator voltages set at 4 kV and 80 V, respectively; nitrogen was used as carrier gas at a flow of 8 mL/min and the nebulizer pressure was set at 50 psi. Analytical and preparative TLC analyses were performed on F₂₅₄ silica gel plates (0.25 and 0.5 mm, respectively). TLC plates were visualised using a UV lamp (λ = 254 nm) and a fluorescence lamp (λ = 366 nm). Liquid chromatography was performed on silica gel (60-230 mesh). LC-MS analyses were carried out on an instrument equipped with an ESI ion source; an octadecylsilane-coated column (4.6 × 150 mm, 3.5 μ) at 0.4 mL/min was used. The eluant system was 0.1% formic acid (eluant A) and methanol (eluant B), starting with 40% solvent B for 1 minute, and then from 40% to 50% solvent B gradient, for 4 minutes, from 50% to 60% solvent B gradient, for 35 minutes, and finally with 60% solvent B for 20 minutes. Mass spectra were registered in the electrospray ionization-positive ion (ESI+) mode with the cone and the fragmentator voltages set at 4 kV and 70 V, respectively. Ultrasound experiments were performed in a sonic bath at 320 W and at 45 °C.

Synthesis of 5,6-diacetoxy-7-iodoindole (11)

A solution of **10a** (900 mg, 2.5 mmol) in dry CH₂Cl₂ (63 mL) was treated with Cu(OAc)₂ (300 mg, 1.5 mmol) at 55 °C under an argon atmosphere. After 18 h the reaction mixture was brought to

room temperature and extracted with ethyl acetate and water. The organic layers were collected, dried over anhydrous sodium sulfate and evaporated under reduced pressure to afford pure **11** (720 mg, 80%). ^1H and ^{13}C NMR resonances were in good agreement with data reported in the literature.¹

Synthesis of 5,6-diacetoxy-7-(trimethylsilylethynyl)indole (**12a**)

A solution of (**11**) (700 mg, 1.9 mmol) in a mixture of triethylamine (16.3 mL), toluene (11.1 mL) and tetrahydrofuran (5.2 mL) was treated with PPh_3 (51.1 mg, 0.19 mmol), CuI (37 mg, 0.19 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (68.4 mg, 0.1 mmol) and trimethylsilylacetylene (278 μL , 1.9 mmol) at 60 °C under an argon atmosphere. After 30 min the reaction mixture was extracted with a 10% water solution of NH_4Cl and chloroform. The organic layers were collected, dried over anhydrous sodium sulfate, evaporated under reduced pressure and the residue fractionated on silica gel (petroleum ether/ethyl acetate, gradient from 90:10 to 85:15) to afford pure **12a** (450 mg, 70%, $R_f = 0.75$ eluant: chloroform/ethyl acetate 95:5 (v/v)).

12a: δ_{H} (400 MHz; $(\text{CD}_3)_2\text{CO}$) 0.28 (9H, s, $\text{Si}(\text{CH}_3)_3$), 2.28 (3H, s, CH_3), 2.33 (3H, s, CH_3), 6.55 (1H, t, J 2.6, 3-H), 7.40 (1H, t, J 2.6, 2-H), 7.45 (1H, s, 4-H), 10.53 (1H, br s, NH); δ_{C} (50 MHz, $(\text{CD}_3)_2\text{CO}$) 0.3 ($\text{Si}(\text{CH}_3)_3$), 20.1 (CH_3), 20.3 (CH_3), 96.6 ($\text{C}\equiv\text{C-Si}$), 102.3 ($\text{C}\equiv\text{C-Si}$), 103.3 (C-3), 103.9 (C-7), 115.7 (C-4), 126.8 (C-4a), 127.6 (C-2), 134.8 (C-7a), 137.5 (C-5), 140.1 (C-6), 168.2 (C=O), 169.1 (C=O); MS (ESI+) m/z 330 ($[\text{M}+\text{H}]^+$), 352 ($[\text{M}+\text{Na}]^+$), 368 ($[\text{M}+\text{K}]^+$); HRMS (ESI+) m/z $\text{C}_{17}\text{H}_{20}\text{NO}_4\text{Si}$ $[\text{M}+\text{H}]^+$ calcd 330.1161, found 330.1164.

Synthesis of 5,6-diacetoxy-7-ethynylindole (**12b**)

A solution of (**12a**) (500 mg, 1.5 mmol) in DMF (15 mL) was treated with KF (61.5 mg, 1.1 mmol) under vigorous stirring. After 30 min the reaction mixture was extracted with water and chloroform. The organic layers were collected, dried over anhydrous sodium sulfate and evaporated under

reduced pressure to afford pure **12b** (383 mg, 98% $R_f = 0.50$ eluant: chloroform/ethyl acetate 95:5 (v/v)).

12b: δ_H (400 MHz; $(CD_3)_2CO$) 2.27 (3H, s, CH₃), 2.32 (3H, s, CH₃), 4.13 (1H, s, C \equiv C-H), 6.56 (1H, t, J 2.6, 3-H), 7.44 (1H, t, J 2.6, 2-H), 7.47 (1H, s, 4-H), 10.63 (1H, br s, NH); δ_C (50 MHz, $(CD_3)_2CO$) 20.1 (CH₃), 20.3 (CH₃), 74.5 (C \equiv C-H), 87.6 (C \equiv C-H), 103.3 (C-3), 104.1 (C-7), 115.9 (C-4), 125.9 (C-4a), 127.7 (C-2), 134.8 (C-7a), 137.5 (C-5), 140.1 (C-6), 168.8 (C=O), 169.1 (C=O); MS (ESI+) m/z 258 ($[M+H]^+$), 280 ($[M+Na]^+$), 296 ($[M+K]^+$); HRMS (ESI+) m/z C₁₄H₁₂NO₄ $[M+H]^+$ calcd 258.0766, found 258.0762.

Synthesis of 3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (**13**)

A solution of **12b** (500 mg, 1.9 mmol) in a mixture of triethylamine (17 mL), toluene (7 mL) and tetrahydrofuran (10 mL) was treated with **8** (897 mg, 1.9 mmol), PPh₃ (51 mg, 0.19 mmol), CuI (37 mg, 0.19 mmol) and (PPh₃)₂PdCl₂ (68.3 mg, 0.1 mmol) at 60 °C under an argon atmosphere. After 20 min the reaction mixture was extracted with a 10% water solution of NH₄Cl and dichloromethane. The organic layers were collected, dried over anhydrous sodium sulfate, evaporated under reduced pressure and the residue fractionated on silica gel (petroleum ether/ethyl acetate, gradient from 70:30 to 65:35) to afford pure **13** (1 g, 90%, $R_f = 0.35$ eluant: chloroform/ethyl acetate 98:2 (v/v)).

13: δ_H (400 MHz; $(CD_3)_2CO$) 2.25 (3H, s, CH₃), 2.30 (3H, s, CH₃), 2.36 (3H, s, CH₃), 2.37 (3H, s, CH₃), 5.43 (2H, br s, NH₂), 6.59 (1H, t, J 2.9, 3''-H), 7.33 (1H, s, 5-H), 7.46 (1H, t, J 2.9, 2''-H), 7.49 (1H, s, 4''-H), 10.92 (1H, br s, NH); δ_C (100 MHz, $(CD_3)_2CO$) 20.3 (4 \times CH₃), 80.5 (C-2), 87.2 (C-2'), 93.4 (C-1'), 103.4 (C-3''), 103.6 (C-7''), 104.3 (C-6), 115.9 (C-4''), 125.8 (C-4a''), 127.1 (C-5), 127.6 (C-2''), 133.8 (C-1), 134.7 (C-7a''), 137.5 (C-5''), 140.0 (C-6''), 146.0 (C-4), 149.0 (C-3), 167.5 (C=O), 168.6 (C=O), 169.0 (C=O), 169.2 (C=O); MS (ESI+) m/z 613 ($[M+Na]^+$); HRMS (ESI+) m/z C₂₄H₁₉IN₂NaO₈ $[M+Na]^+$ calcd 613.0084, found 613.0087.

Synthesis of 5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

A solution of **13** (900 mg, 1.5 mmol) in dry ethanol (18 mL) was treated with AuCl₃ (60 mg, 0.15 mmol) under an argon atmosphere and kept in an ultrasound bath at 320 W and 45 °C. After 1h and 30 min the mixture was extracted with a 10% water solution of NH₄Cl and chloroform. The organic layers were collected, dried over anhydrous sodium sulfate and evaporated under reduced pressure to afford pure **14** (720 mg, 80%, R_f = 0.70 eluant: chloroform/ethyl acetate 7:3 (v/v)).

14: δ_H (400 MHz; (CD₃)₂CO) 2.20 (3H, s, CH₃), 2.31 (2 × 3H, s, CH₃), 2.40 (3H, s, CH₃), 6.59 (1H, t, *J* 2.5, 3'-H), 6.87 (1H, d, *J* 1.7, 3-H), 7.43 (1H, t, *J* 2.5, 2'-H), 7.48 (1H, s, 4-H), 7.50 (1H, s, 4'-H), 10.37 (1H, br s, NH), 10.67 (1H, br s, NH'); δ_C (100 MHz, (CD₃)₂CO) 20.0 (CH₃), 20.3 (2 × CH₃), 20.4 (CH₃), 73.4 (C-7), 102.6 (C-3'), 104.8 (C-3), 111.1 (C-7'), 114.6 (C-4, C-4'), 126.0 (C-4a, C-4a'), 127.5 (C-2'), 127.8 (C-2), 133.0 (C-7a, C-7a'), 137.4 (C-O), 137.5 (C-O), 137.6 (C-O), 140.4 (C-O), 168.2 (C=O), 169.0 (2 × C=O), 169.1 (C=O); MS (ESI+) *m/z* 591 ([M+H]⁺), 613 ([M+Na]⁺); HRMS (ESI+) *m/z* C₂₄H₂₀IN₂O₈ [M+H]⁺ calcd 591.0264, found 591.0261.

Synthesis of 4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

A solution of **14** (200 mg, 0.34 mmol) in triethylamine (3 mL) and tetrahydrofuran (3 mL) was treated with **10b** (130.4 mg, 0.56 mmol), PPh₃ (8.9 mg, 0.034 mmol), CuI (6.4 mg, 0.034 mmol) and (PPh₃)₂PdCl₂ (12 mg, 0.017 mmol) at 60 °C under an argon atmosphere. After 1h the reaction mixture was extracted with a 10% water solution of NH₄Cl and chloroform. The organic layers were collected, dried over anhydrous sodium sulfate, evaporated under reduced pressure and the residue fractionated on silica gel (eluant chloroform/ethyl acetate 1:1 (v/v)) to afford pure **15** (118 mg, 50%, R_f = 0.50 eluant: chloroform/ethyl acetate 6:4 (v/v)).

15: δ_H (400 MHz; (CD₃)₂CO) 2.17 (3H, s, CH₃), 2.21 (3H, s, CH₃), 2.23 (3H, s, CH₃), 2.30 (3H, s, CH₃), 2.33 (3H, s, CH₃), 2.40 (3H, s, CH₃), 5.33 (2H, br s, NH₂), 6.58 (1H, t, *J* 2.3, 3''''-H), 6.66 (1H, s, 6-H), 6.73 (1H, d, *J* 1.7, 3''-H), 7.19 (1H, s, 3-H), 7.43 (1H, t, *J* 2.3 Hz, 2''''-H), 7.48 (1H, s,

4'''-H), 7.51 (1H, s, 4''-H), 10.80 (1H, br s, NH'''), 11.05 (1H, br s, NH''); δ_{C} (100 MHz, (CD₃)₂CO) 20.1 (CH₃), 20.2 (2 × CH₃), 20.3 (2 × CH₃), 20.6 (CH₃), 86.3 (C-2'), 94.4 (C-1'), 102.4 (C-7''), 102.7 (C-3'''), 104.3 (C-3''), 104.5 (C-2), 109.1 (C-6), 111.5 (C-7'''), 114.7 (C-4'''), 115.2 (C-4''), 126.2 (C-4a''), 126.4 (C-4a'''), 126.8 (C-3), 127.6 (C-2'''), 133.1 (C-7a'', C-7a'''), 133.4 (C-1), 135.4 (C-2''), 136.6 (C-5'''), 137.7 (C-5'', C-6'''), 140.1 (C-6''), 144.9 (C-4), 148.7 (C-5), 168.2 (C=O), 168.7 (C=O), 168.9 (C=O), 169.1 (C=O), 169.3 (2 × C=O); MS (ESI+) *m/z* 696 ([M+H]⁺), 718 ([M+Na]⁺), 734 ([M+K]⁺); HRMS (ESI+) *m/z* C₃₆H₃₀N₃O₁₂ [M+H]⁺ calcd 696.1829, found 696.1831.

Synthesis of 5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-triindole (6-Ac)

A solution of **15** (200 mg, 0.29 mmol) in dry ethanol (4 mL) was treated with AuCl₃ (66.7 mg, 0.17 mmol) under an argon atmosphere and kept in an ultrasound bath at 320 W and 45 °C. After 30 min the mixture was extracted with a 10% water solution of NH₄Cl and chloroform. The organic layers were collected, dried over anhydrous sodium sulfate and evaporated under reduced pressure to afford pure **6-Ac** (160 mg, 80%, R_f = 0.54 eluant: chloroform/ethyl acetate 1:1 (v/v)).

6-Ac:³ δ_{H} (400 MHz; (CD₃)₂CO) 2.17 (3H, s, CH₃), 2.22 (3H, s, CH₃), 2.26 (3H × 3, s, CH₃), 2.33 (3H, s, CH₃), 6.56 (1H, t, *J* 2.8, 3''-H), 6.76 (1H, s, 3'-H), 6.87 (1H, s, 3-H), 7.32 (1H, s, 7-H), 7.39 (1H, s, 4-H), 7.41 (1H, t, *J* 2.8, 2''-H), 7.45 (1H, s, 4''-H), 7.51 (1H, s, 4'-H), 10.66 (1H × 2, br s, NH, NH''), 10.80 (1H, br s, NH'); δ_{C} (100 MHz; (CD₃)₂CO plus 1% of NH₄Cl (10% in H₂O)) 2.15 (3H, s, CH₃), 2.21 (3H, s, CH₃), 2.27 (3H × 3, s, CH₃), 2.33 (3H, s, CH₃), 6.56 (1H, t, *J* 2.8, 3''-H), 6.76 (1H, s, 3'-H), 6.85 (1H, s, 3-H), 7.32 (1H, s, 7-H), 7.38 (1H, s, 4-H), 7.40 (1H, t, *J* 2.8, 2''-H), 7.43 (1H, s, 4''-H), 7.50 (1H, s, 4'-H), 10.64 (1H, br s, NH''), 10.71 (1H, br s, NH), 10.74 (1H, br s, NH'); δ_{C} (100 MHz, (CD₃)₂CO) 20.3 (6 × CH₃), 102.7 (C-3''), 103.7 (C-3), 104.2 (C-3'), 106.2 (C-7), 111.7 (C-7''), 112.1 (C-7'), 114.1 (C-4), 114.4 (C-4'), 114.6 (C-4''), 126.1 (C-4a''), 126.5 (C-4a), 127.0 (C-4a'), 127.3 (C-2''), 129.5 (C-7a''), 132.8 (C-2), 133.1 (C-7a'), 133.5 (C-2'), 134.7 (C-7a), 136.5^a (C-5'), 136.6^a (C-5''), 137.4^b (C-6'), 137.6^b (C-6''), 138.1 (C-6'), 139.3 (C-5), 169.0 (2 ×

C=O), 169.2 (2 × C=O), 169.3 (2 × C=O); MS (ESI+) m/z 696 ([M+H]⁺), 718 ([M+Na]⁺); HRMS (ESI+) m/z C₃₆H₃₀N₃O₁₂ [M+H]⁺ calcd 696.1829, found 696.1826.

Intramolecular cyclization of **15 to **6-Ac**⁴**

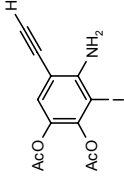
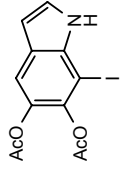
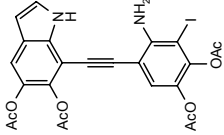
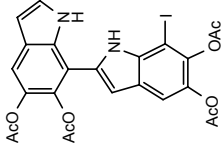
A solution of **15** (150 mg, 0.22 mmol) in ethanol (1.8 mL) was treated with NaAuCl₄·2H₂O (3.3 mg, 8.4 μmol) under an argon atmosphere. After 5 h the mixture was extracted with a 10% water solution of NH₄Cl and ethyl acetate. The organic layers were collected, dried over anhydrous sodium sulfate and evaporated under reduced pressure to afford pure **6-Ac** (125 mg, 83%, R_f = 0.54 eluant: chloroform/ethyl acetate 1:1 (v/v)).

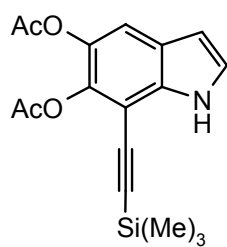
LC-MS analysis of the oxidation mixture of **1**

The oxidative polymerization of **1** under biomimetic conditions has been carried out as previously reported.² In brief, a solution of **1** in 0.05 M phosphate buffer, pH 7.4, was treated with horseradish peroxidase (36 U/mL) and hydrogen peroxide (1.1 molar equivalents). After 25 s reaction time, the oxidation mixture was halted by the addition of a solution of sodium dithionite in water and worked up. After acetylation with acetic anhydride and pyridine overnight at r.t., the mixture was subjected to LC-MS analysis.

References

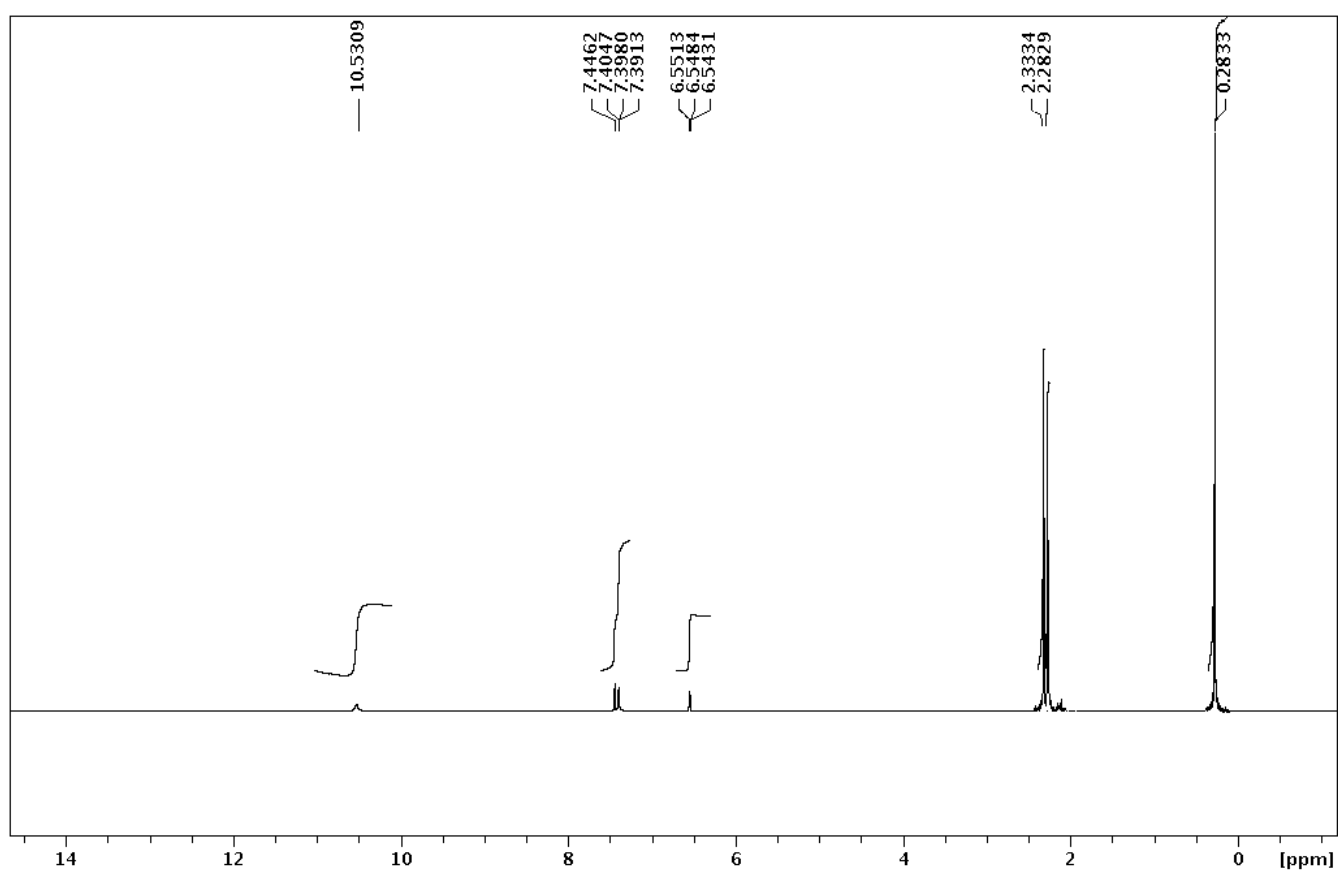
- 1 L. Capelli, P. Manini, A. Pezzella, A. Napolitano and M. d'Ischia, *J. Org. Chem.*, 2009, **74**, 7191-7194.
- 2 A. Pezzella, L. Panzella, O. Crescenzi, A. Napolitano, S. Navaratman, R. Edge, E. J. Land, V. Barone and M. d'Ischia, *J. Am. Chem. Soc.*, 2006, **128**, 15490-11221.
- 3 Structural assignment was secured by comparing 1D and 2D NMR spectra registered in $(\text{CD}_3)_2\text{CO}$ with or without the addition of 5 μL of a 10% solution of NH_4Cl in H_2O .
- 4 A. Arcadi, G. Bianchi and F. Marinelli, *Synthesis*, 2004, 610-618.

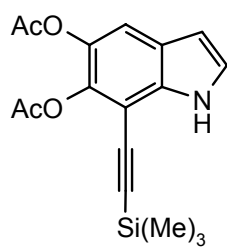
Substrate	Product	Reaction conditions	T (°C)	Time (h)	Yield (%)
		FeCl ₃ /PdCl ₂ /dry CH ₂ Cl ₂	55	4	-
		CuI/DMF	110	5	30
		CuI/TEA/toluene	130	1.5	50
		AuCl ₃ /dry ethanol/(ultrasound bath)	25	1.5	30
		NaAuCl ₄ ·2H ₂ O/ethanol	rt	4	70
		Cu(OAc) ₂ /CH ₂ Cl ₂	55	18	80
		Cu(OAc) ₂ /CH ₂ Cl ₂	55	24	-
		CuI/TEA/toluene	130	4	-
		CuI (2 eq)/DMF	110	4	20
		CuI (5 eq)/DMF	110	3	5
		Cu(OAc) ₂ /dry methanol/(ultrasound bath)	70	5	10
		LiCl/toluene	110	2	30
		AlCl ₃ /toluene	110	3.5	50
		AuCl ₃ /dry ethanol/(ultrasound bath)	45	1.5	80
		NaAuCl ₄ ·2H ₂ O /ethanol	rt	5	82
					



5,6-diacetoxy-7-(trimethylsilylethynyl)indole (12a)

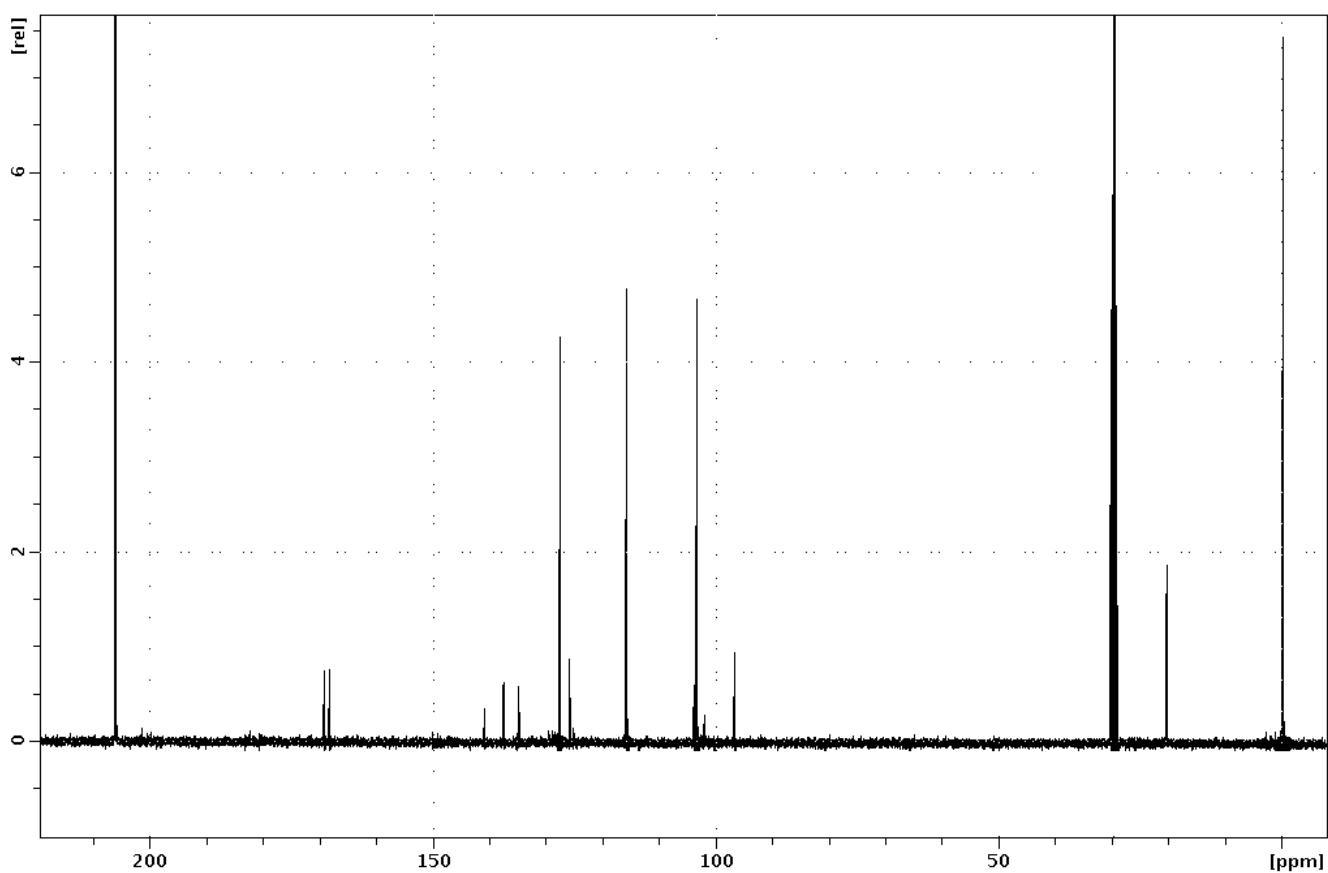
¹H NMR (400 MHz; (CD₃)₂CO)

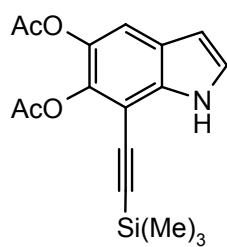




5,6-diacetoxy-7-(trimethylsilylethynyl)indole (12a)

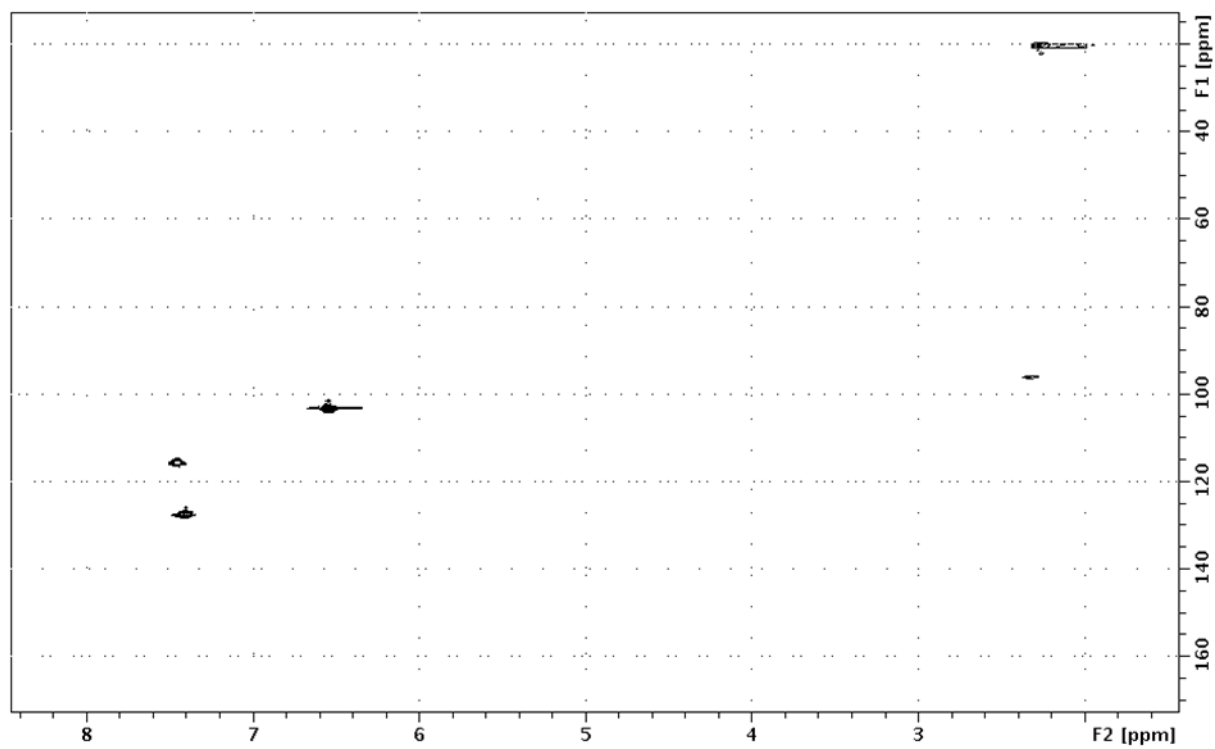
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

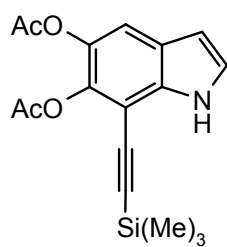




5,6-diacetoxy-7-(trimethylsilylethynyl)indole (12a)

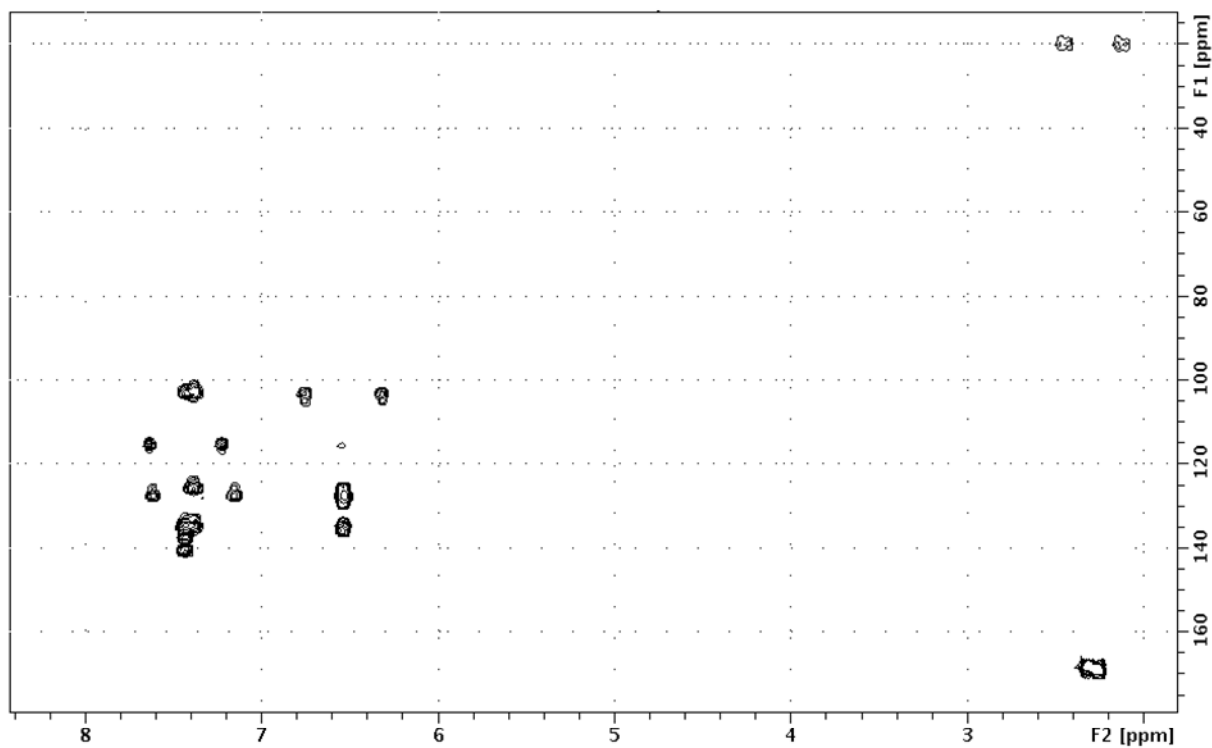
$^1\text{H}, ^{13}\text{C}$ HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

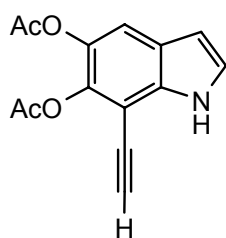




5,6-diacetoxy-7-(trimethylsilylethynyl)indole (12a)

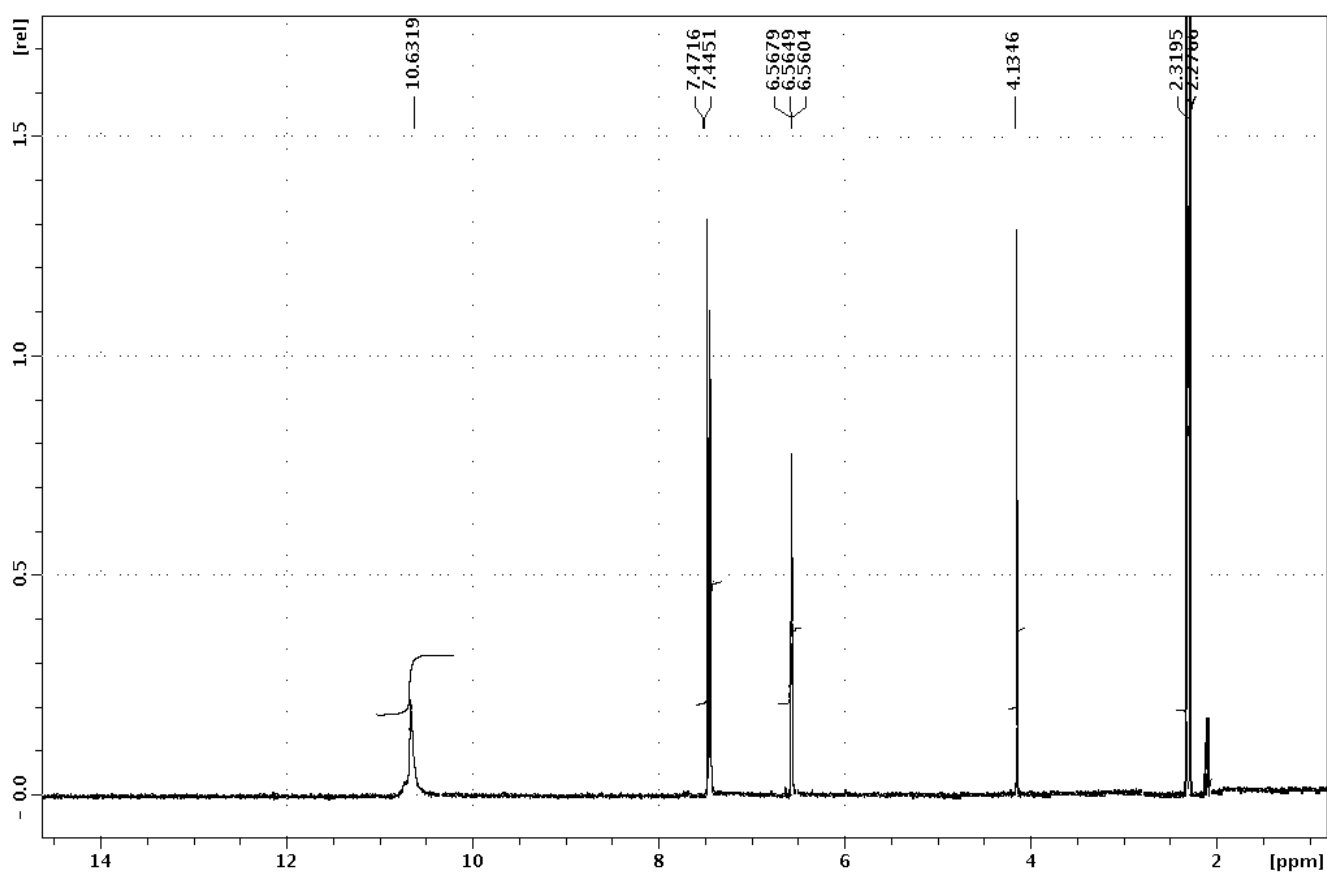
$^1\text{H}, ^{13}\text{C}$ HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

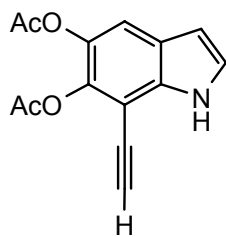




5,6-diacetoxy-7-ethynylindole (12b)

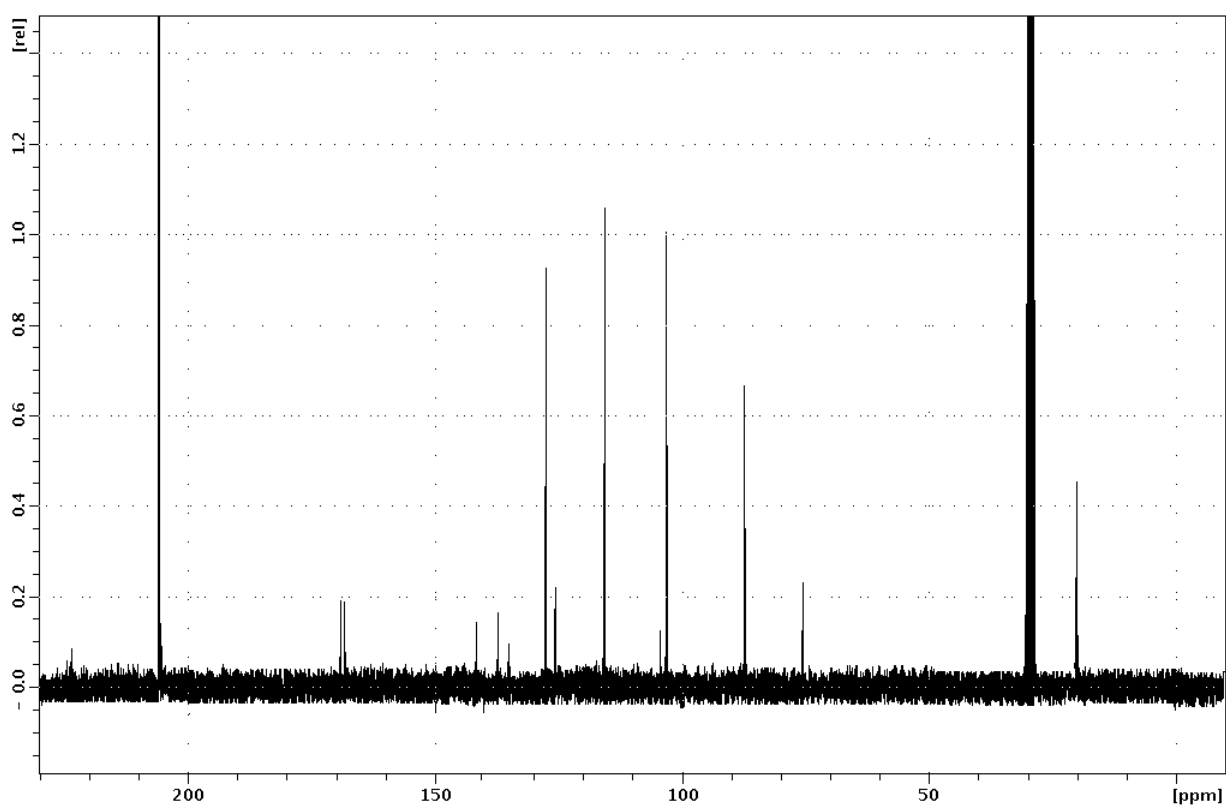
^1H NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

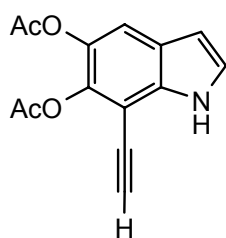




5,6-diacetoxy-7-ethynylindole (12b)

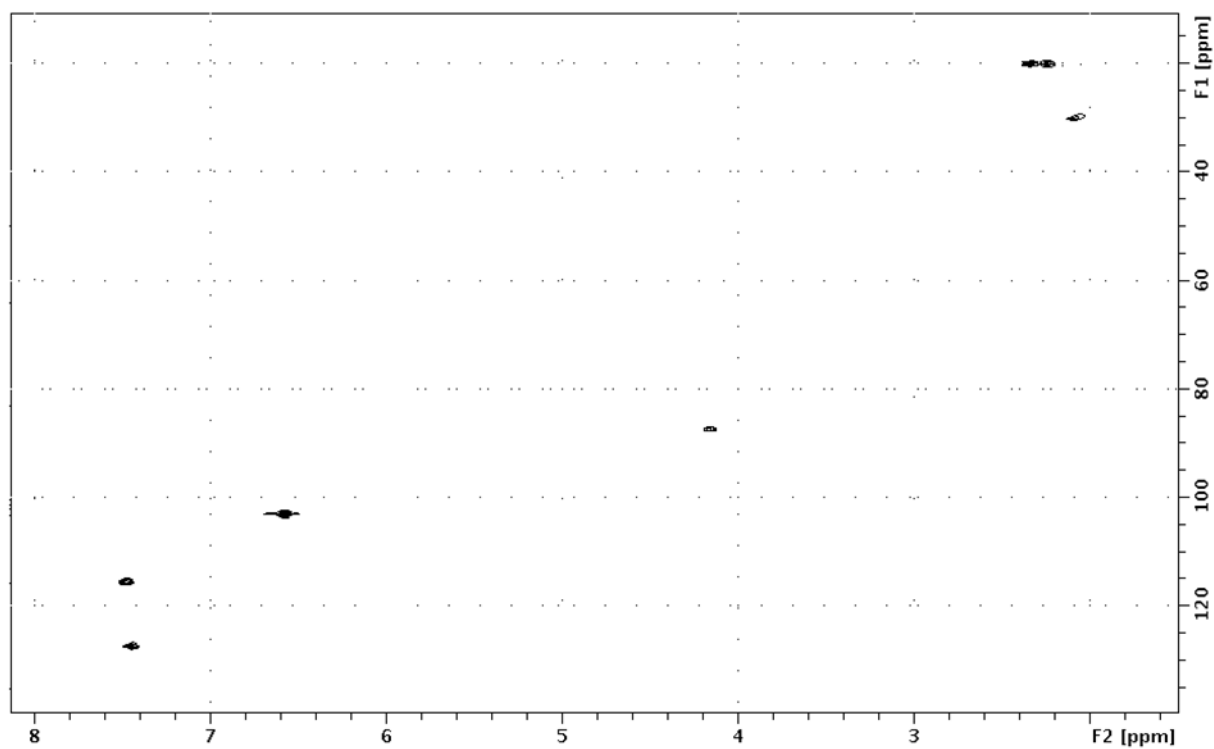
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

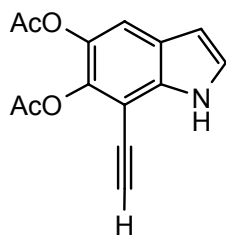




5,6-diacetoxy-7-ethynylindole (12b)

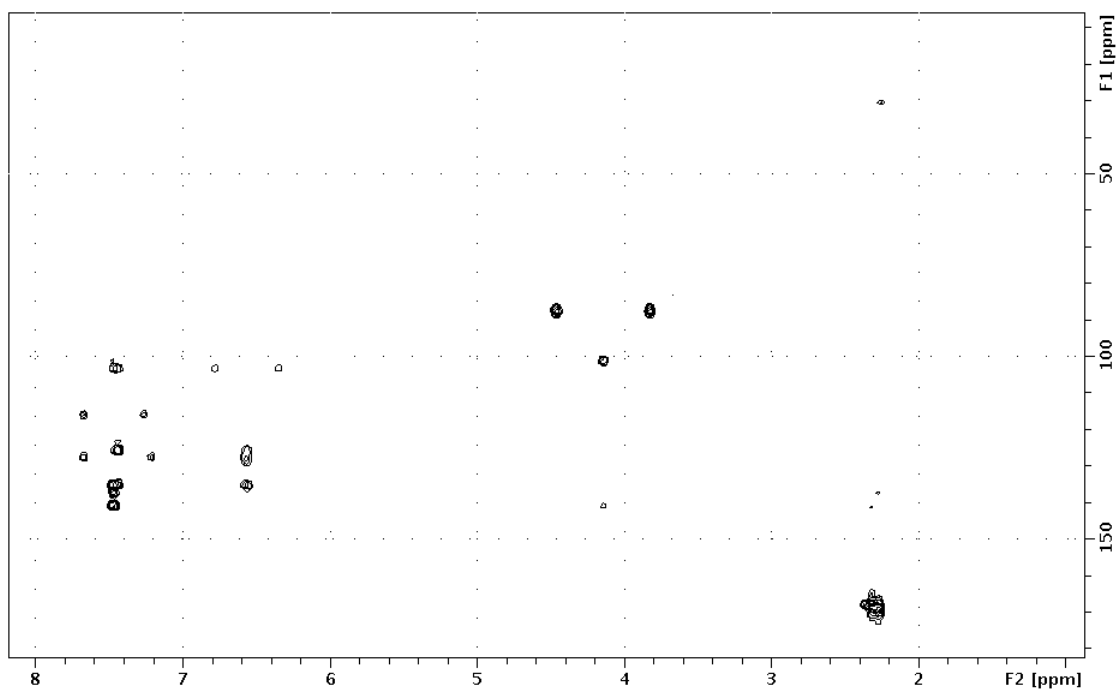
^1H , ^{13}C HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

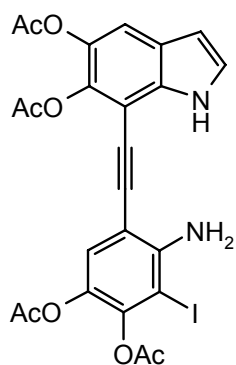




5,6-diacetoxy-7-ethynylindole (12b)

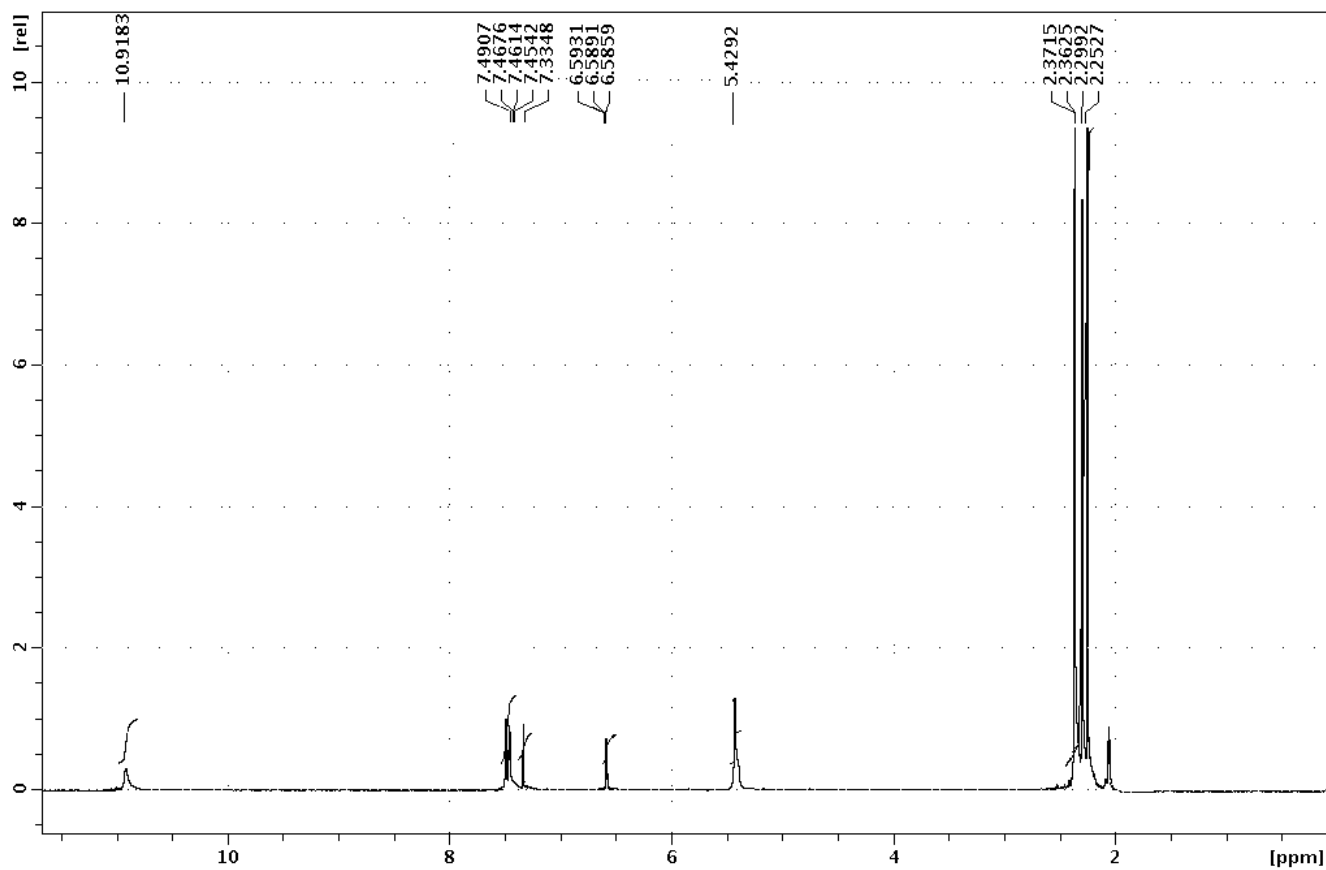
^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

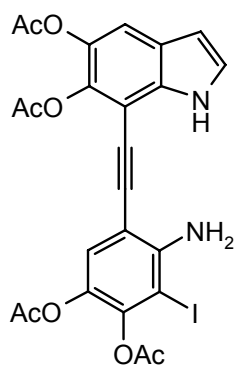




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

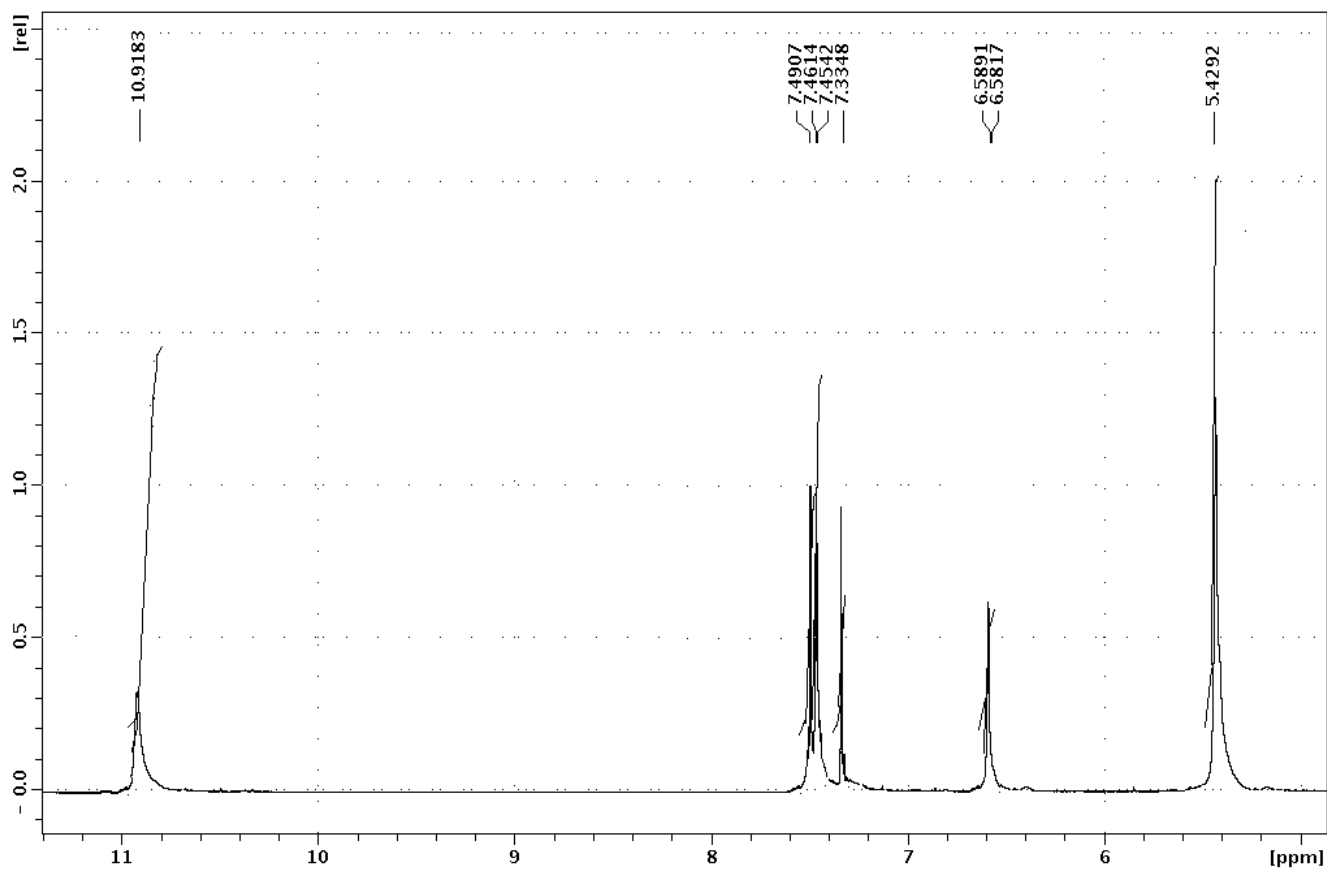
¹H NMR (400 MHz; (CD₃)₂CO)

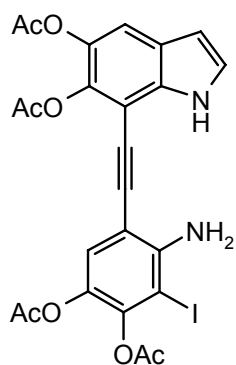




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

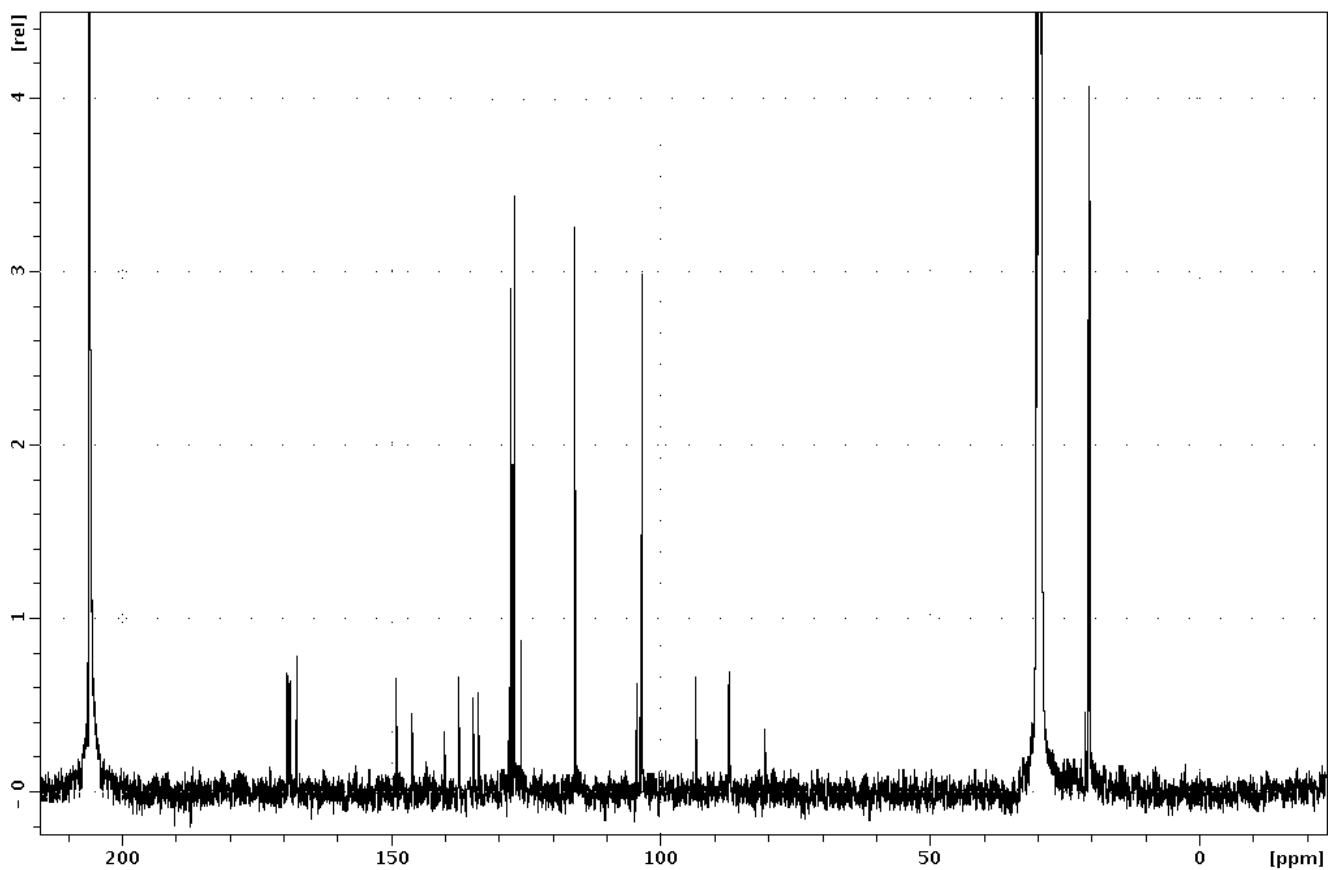
^1H NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

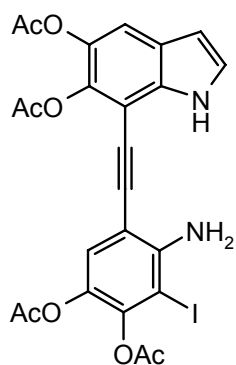




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

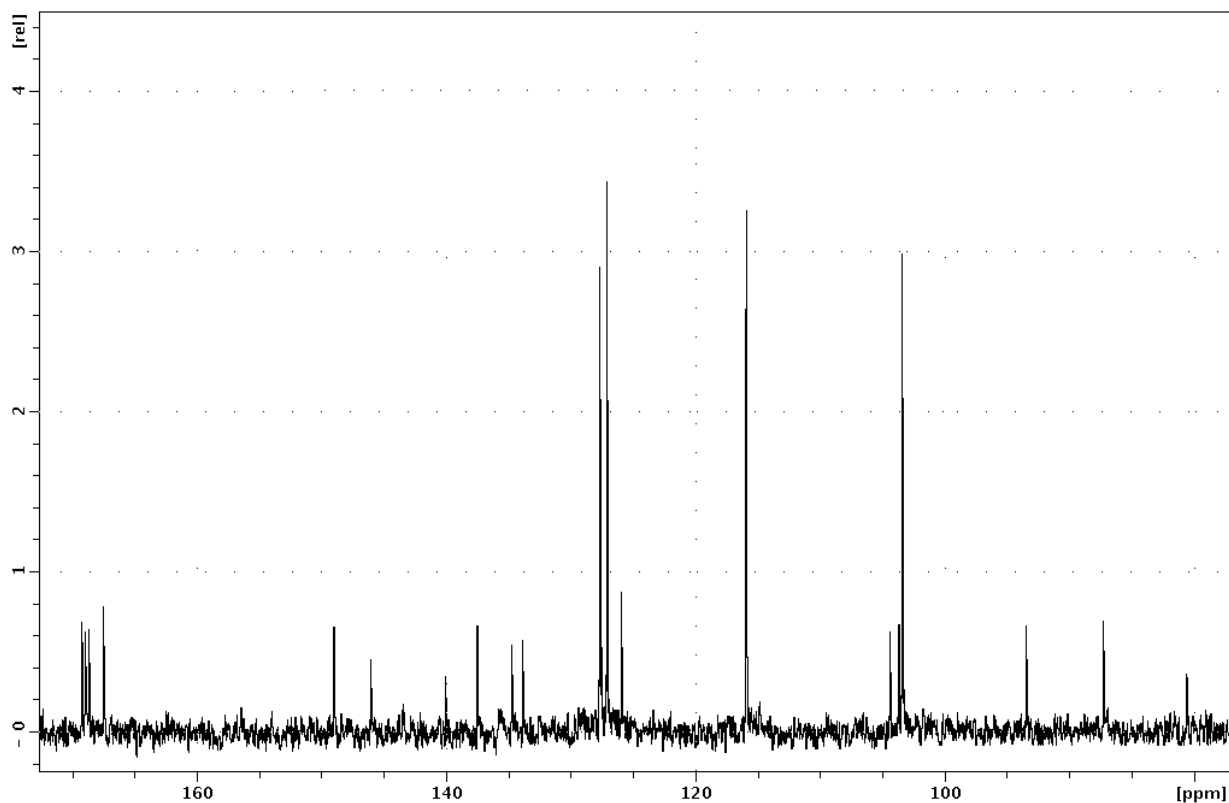
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

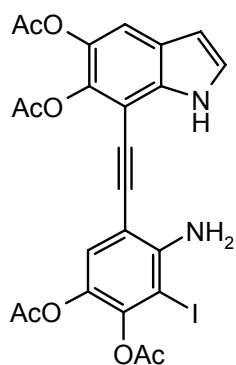




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

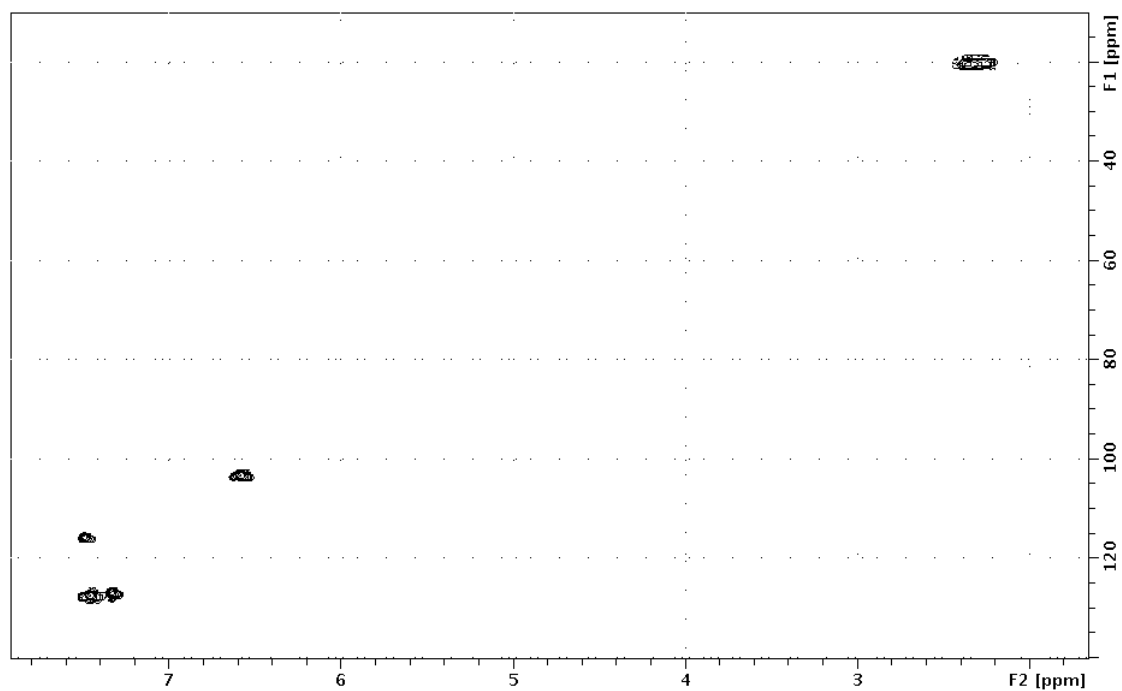
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

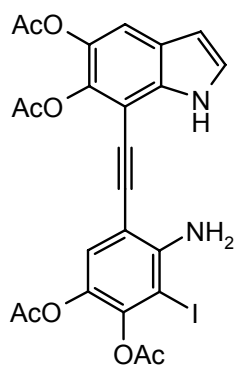




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

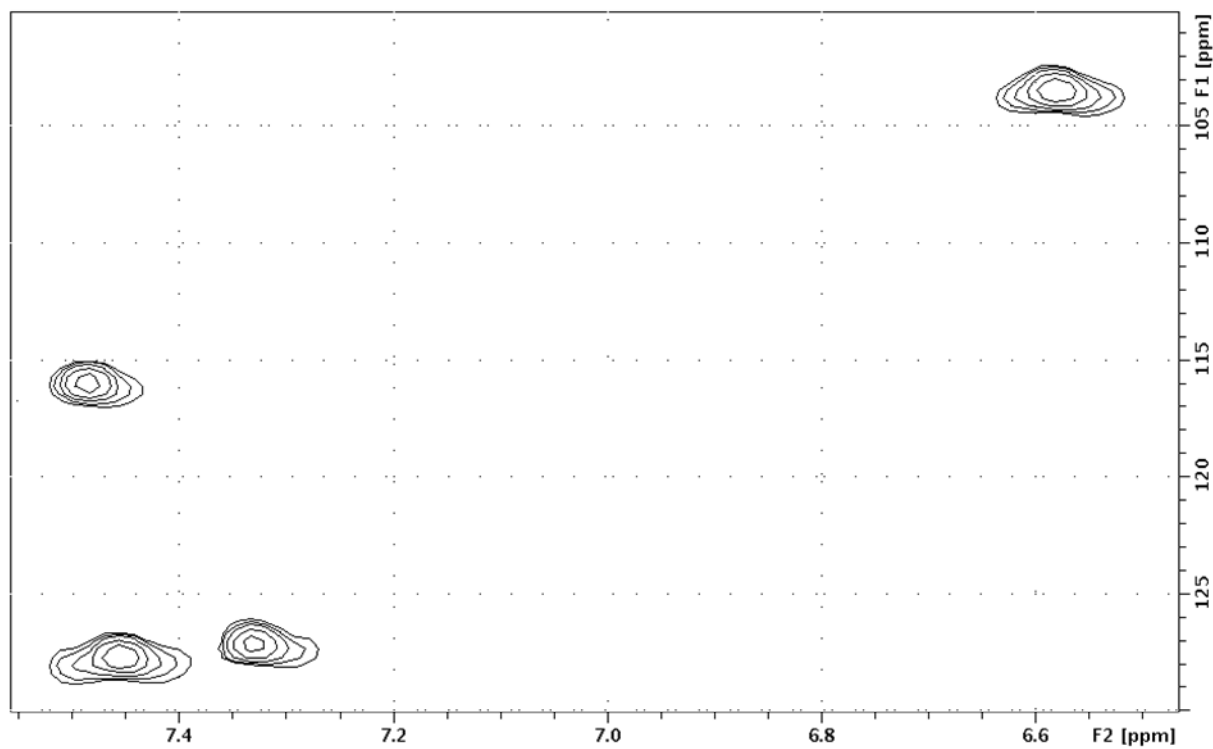
^1H , ^{13}C HSQC(400 MHz; $(\text{CD}_3)_2\text{CO}$)

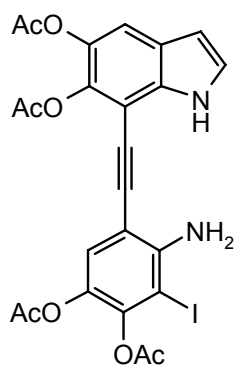




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

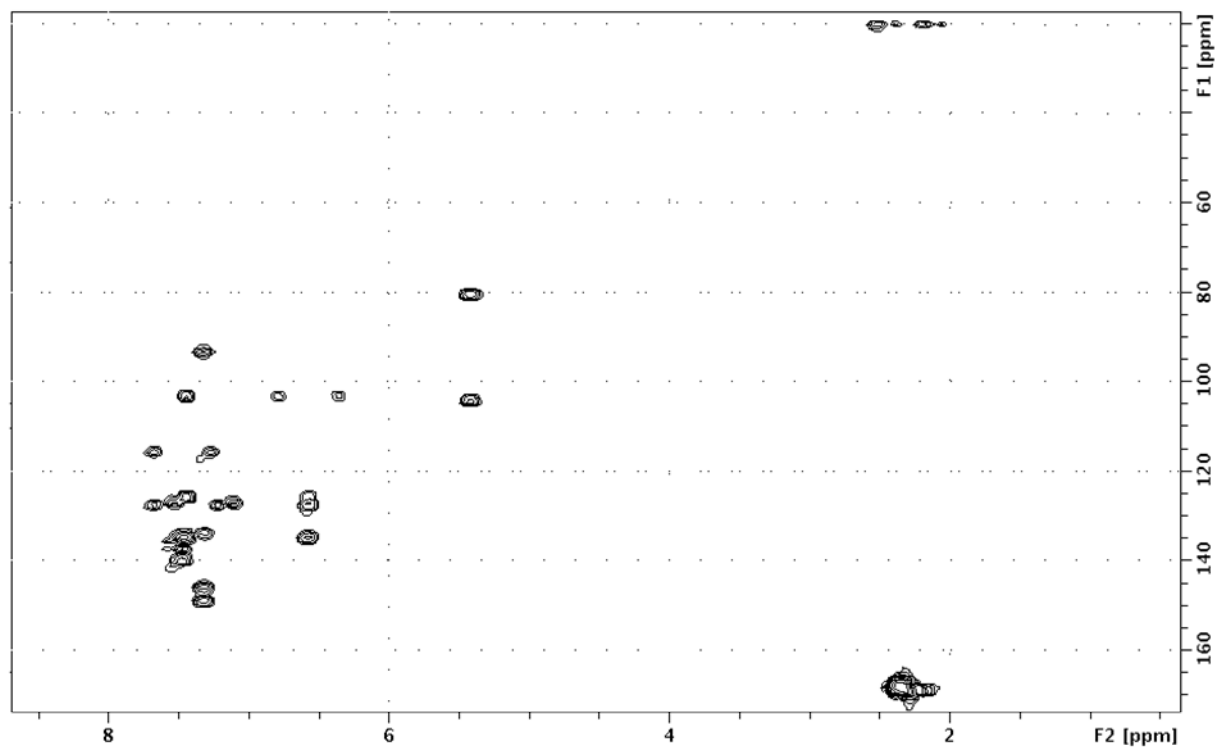
^1H , ^{13}C HSQC(400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

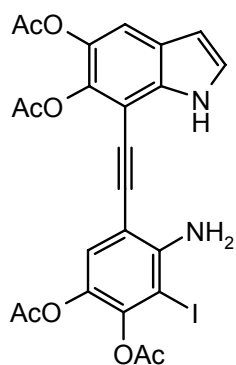




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

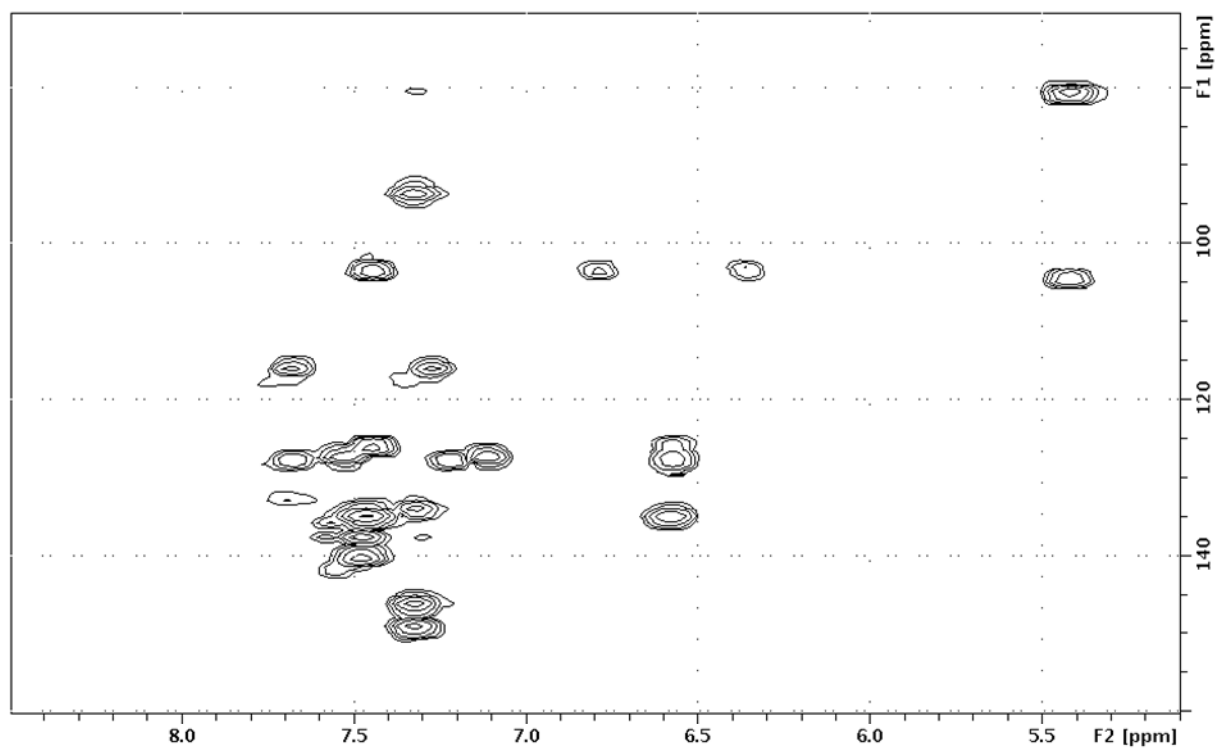
^1H , ^{13}C HMBC(400 MHz; $(\text{CD}_3)_2\text{CO}$)

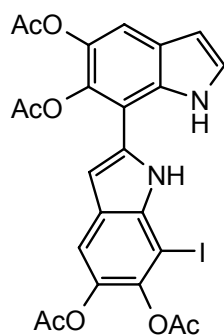




3,4-diacetoxy-6-[2'-(5'',6''-diacetoxy-indol-7''-yl)-1'-ethynyl]-2-iodoaniline (13)

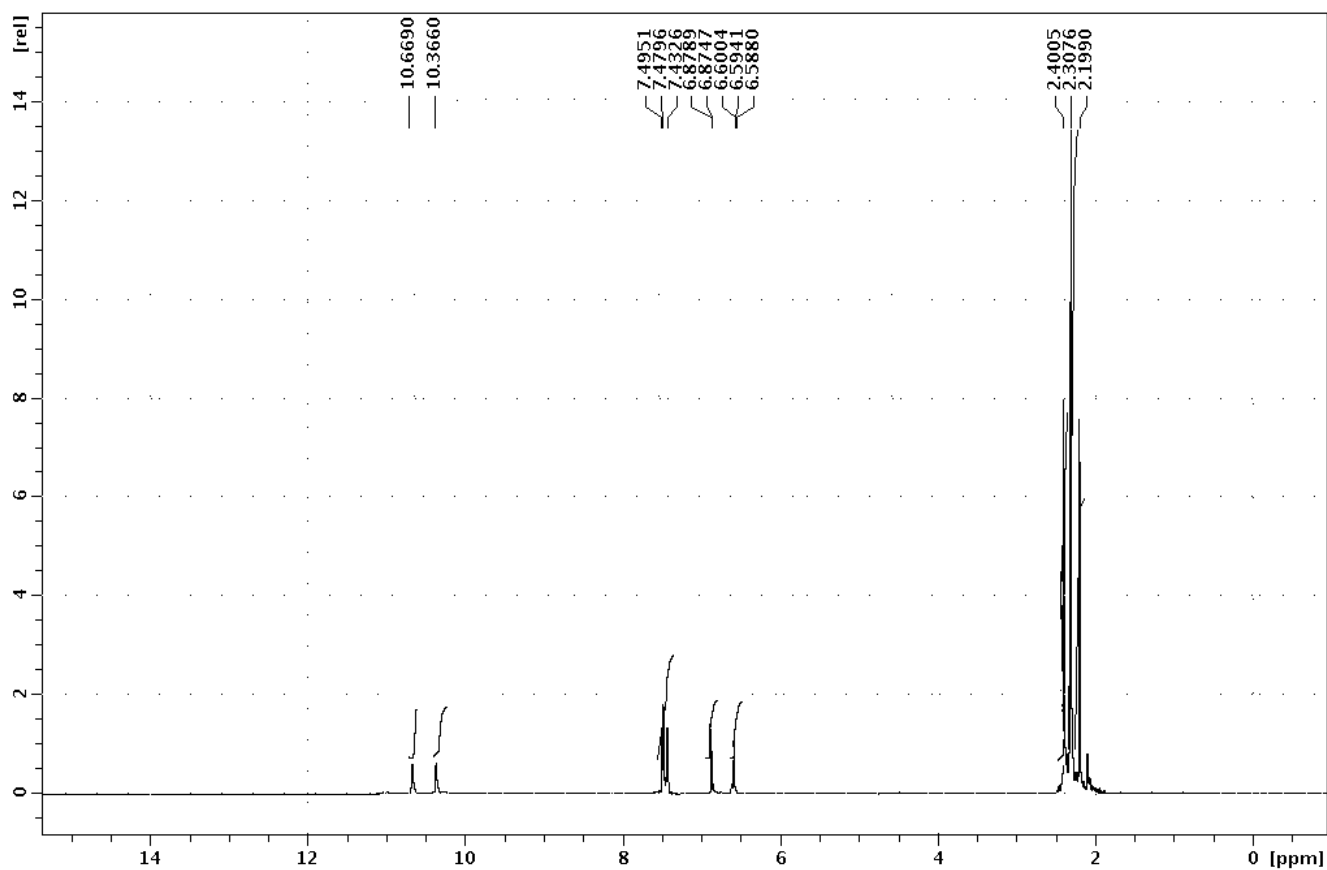
^1H , ^{13}C HMBC(400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

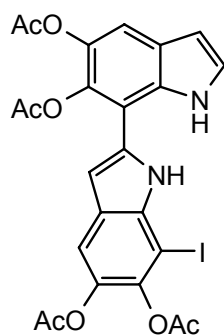




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

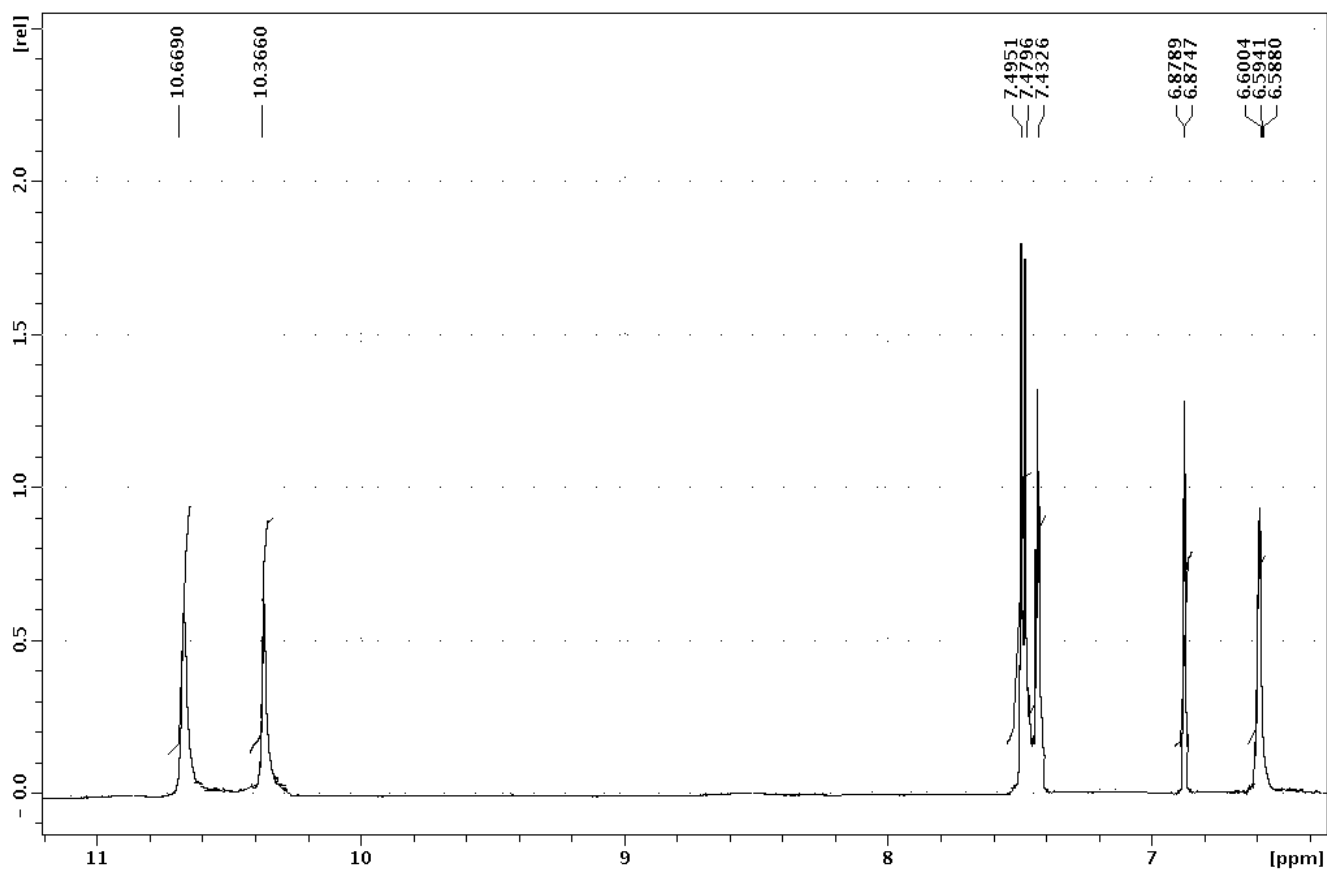
^1H NMR(400 MHz; $(\text{CD}_3)_2\text{CO}$)

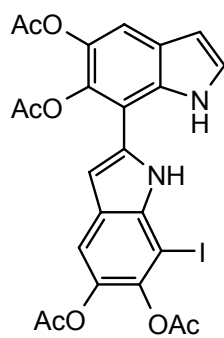




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

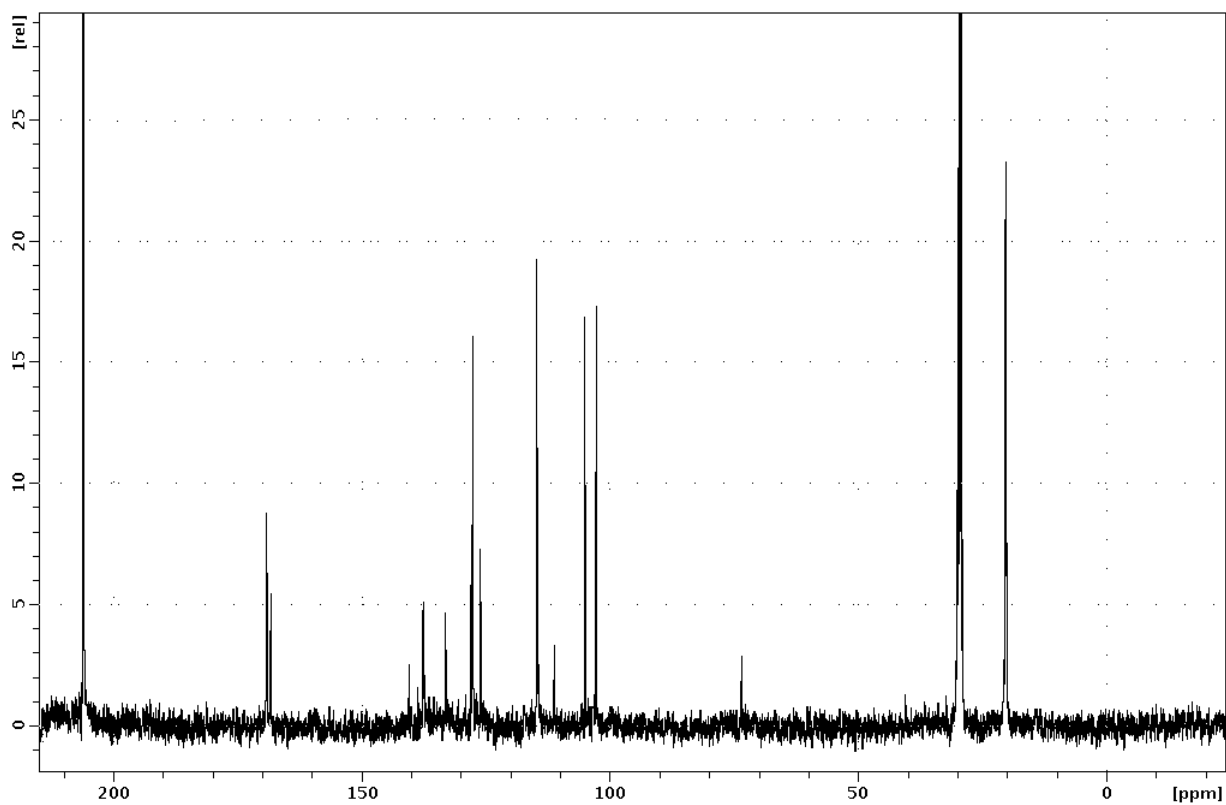
^1H NMR(400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

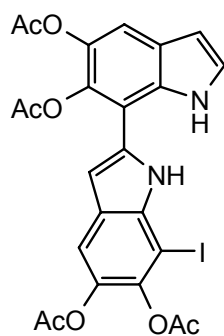




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

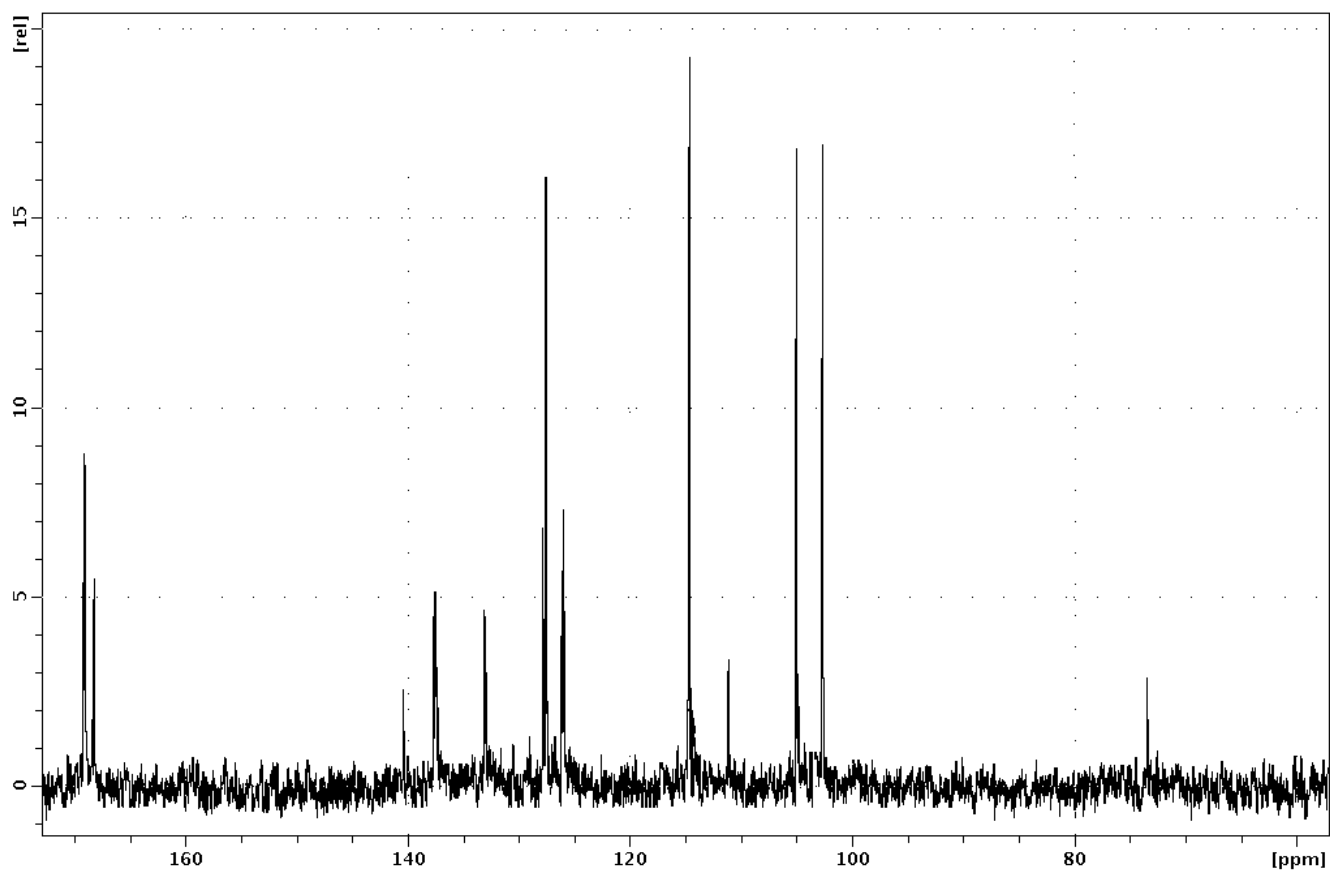
^{13}C NMR(400 MHz; $(\text{CD}_3)_2\text{CO}$)

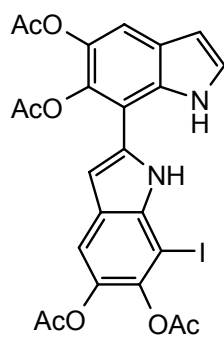




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

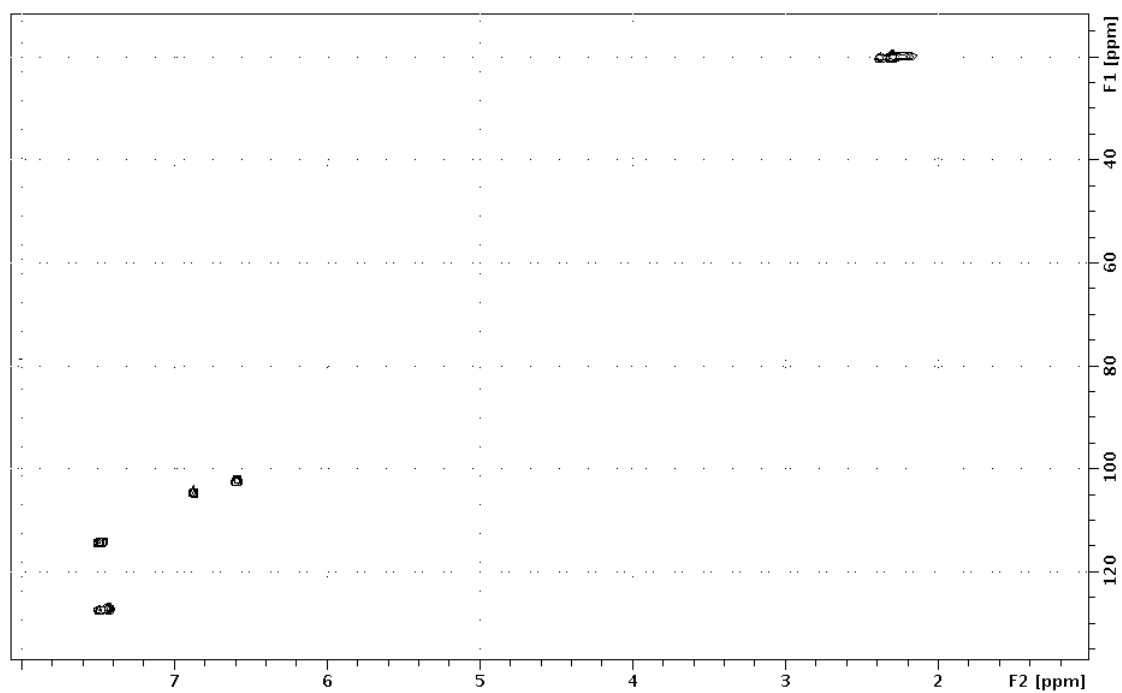
^{13}C NMR(400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

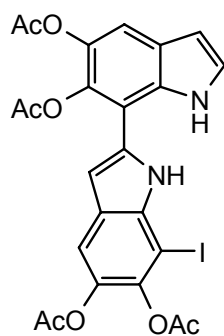




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

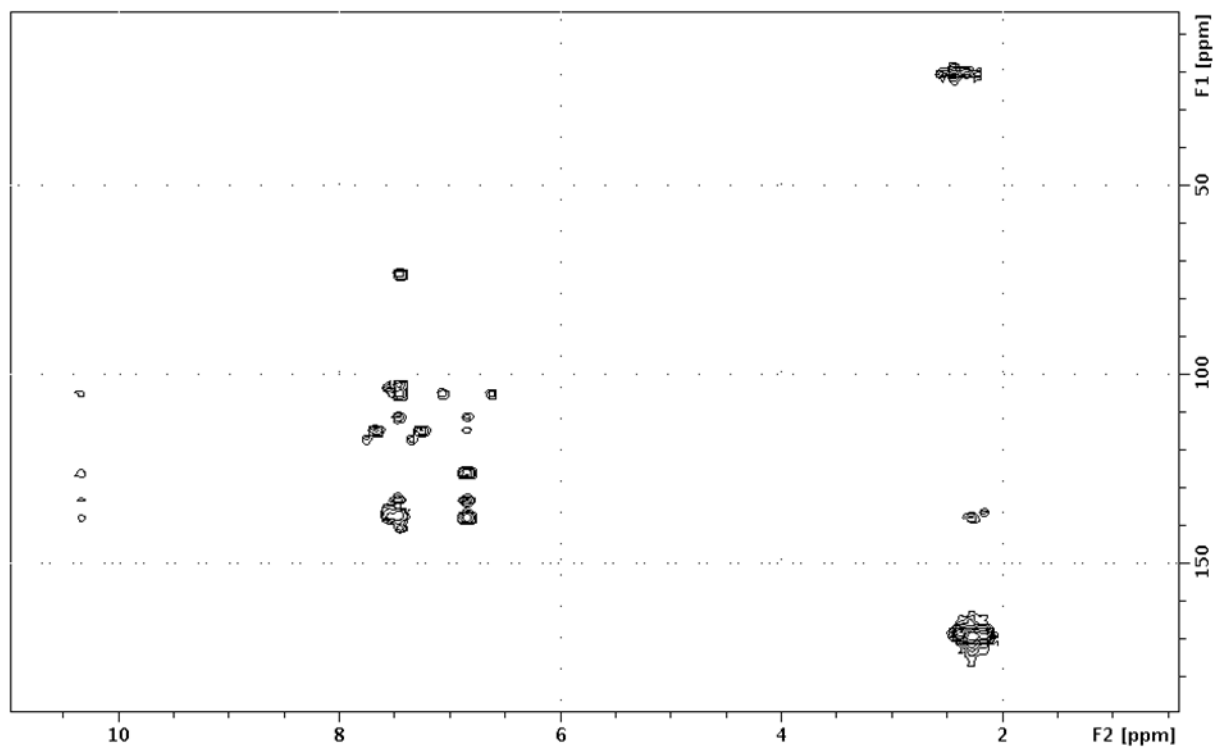
^1H , ^{13}C HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

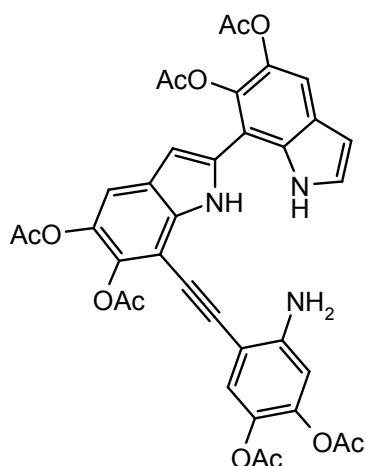




5,5',6,6'-tetraacetoxy-7-iodo-2,7'-biindole (14)

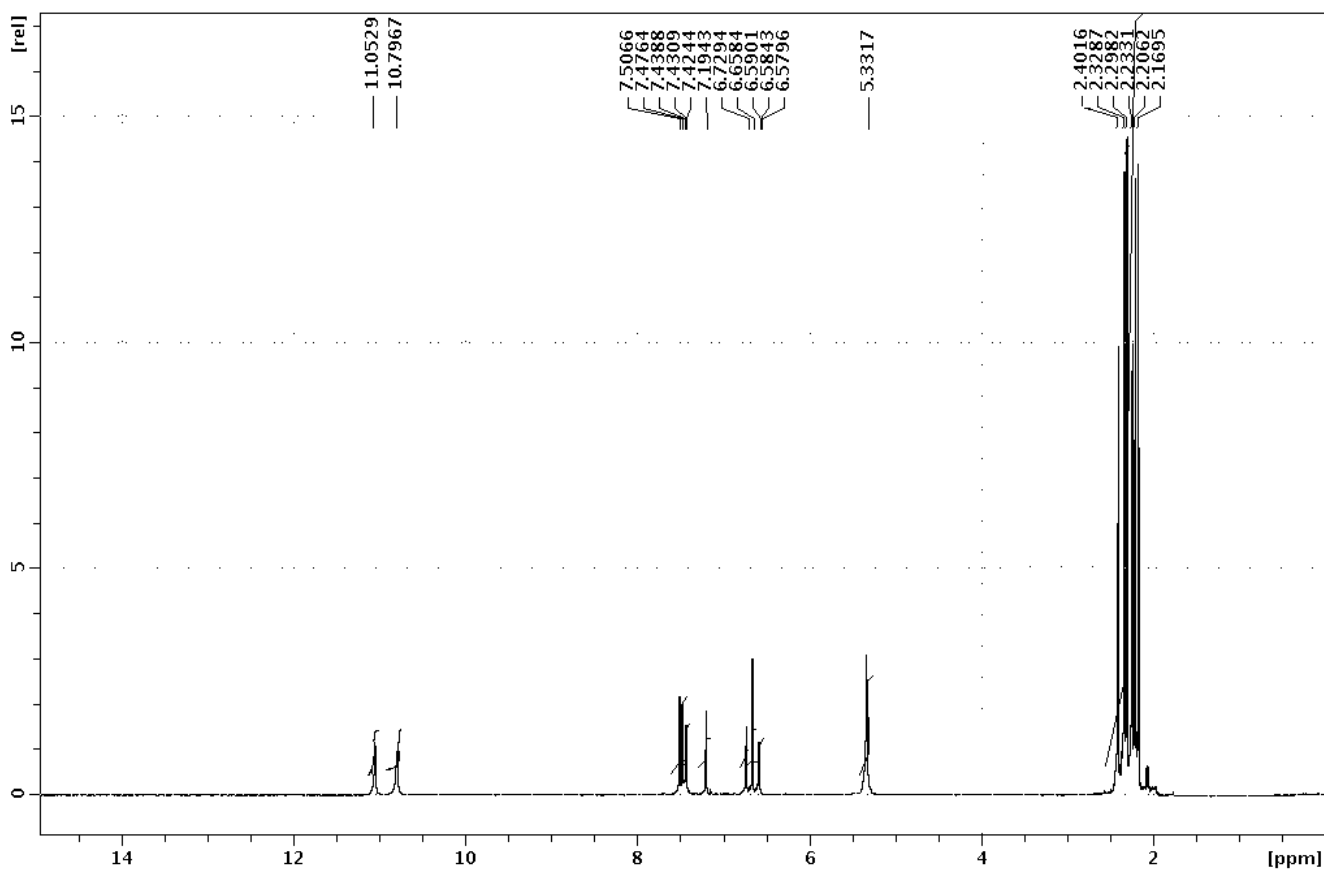
^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

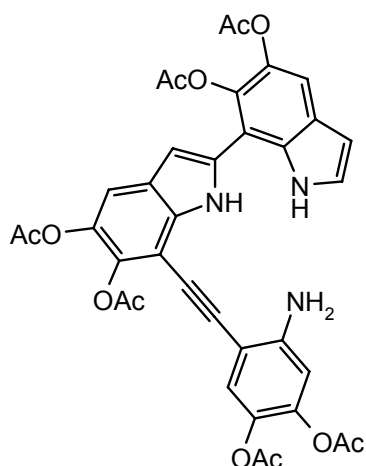




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

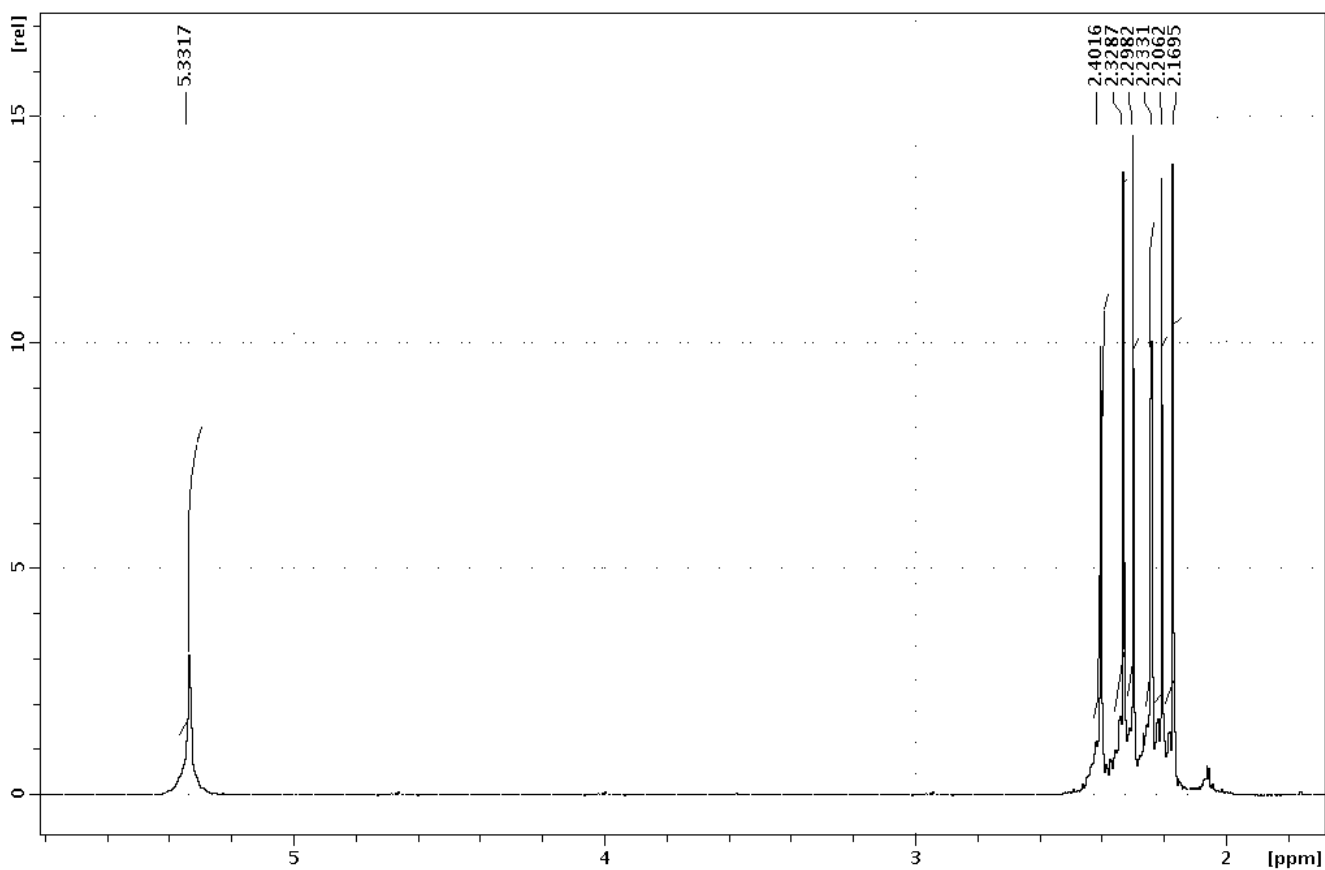
¹H NMR (400 MHz; (CD₃)₂CO)

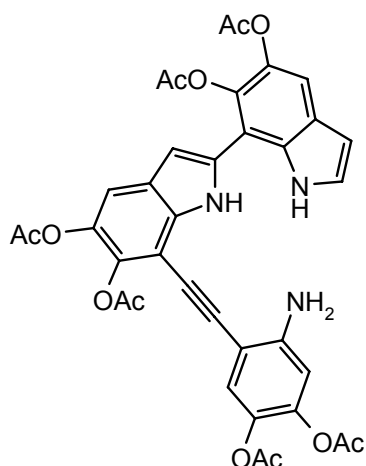




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

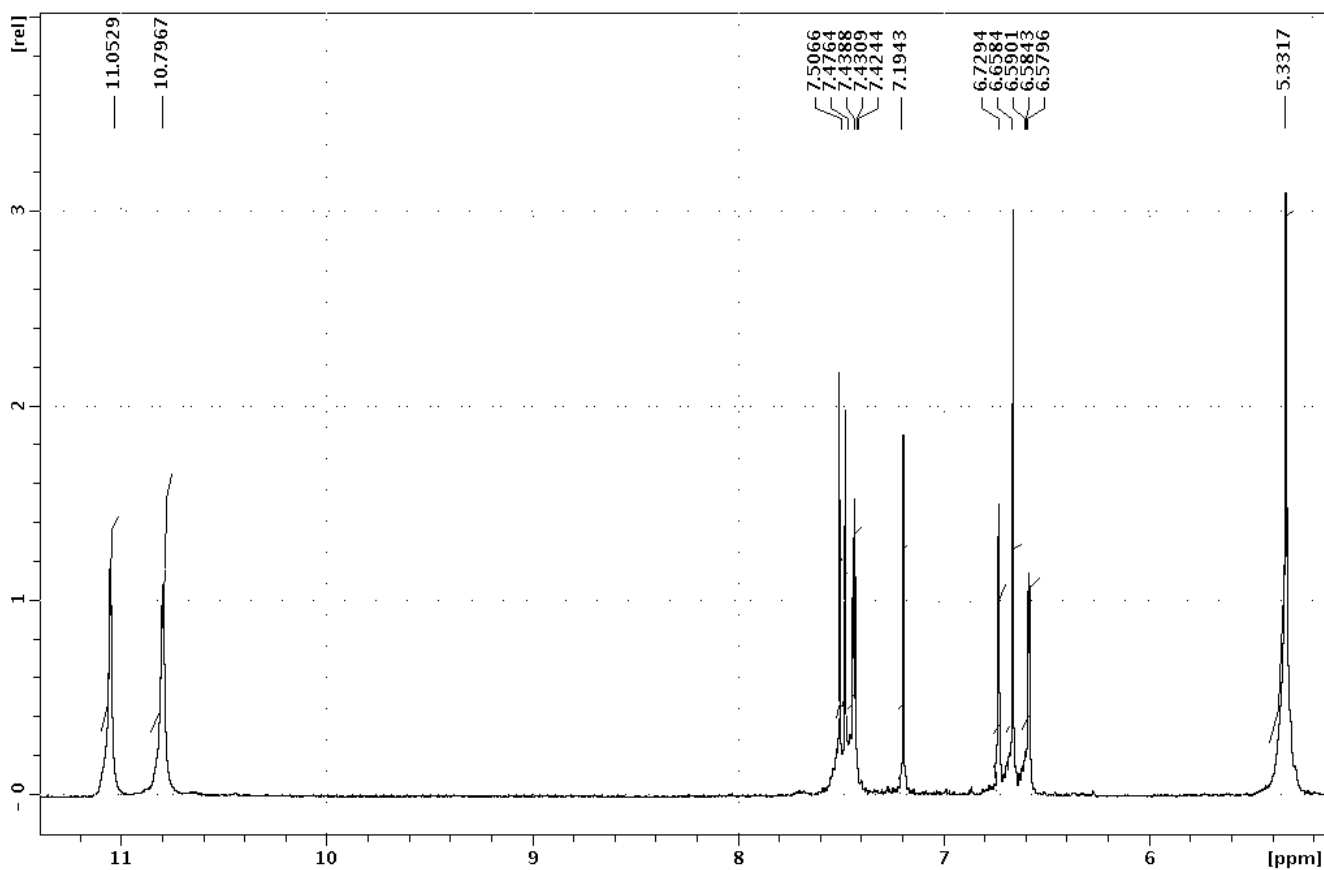
¹H NMR (400 MHz; (CD₃)₂CO) High field region

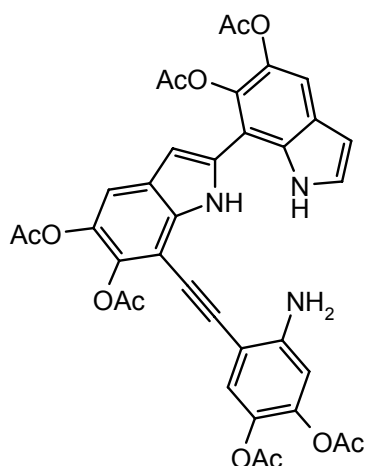




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

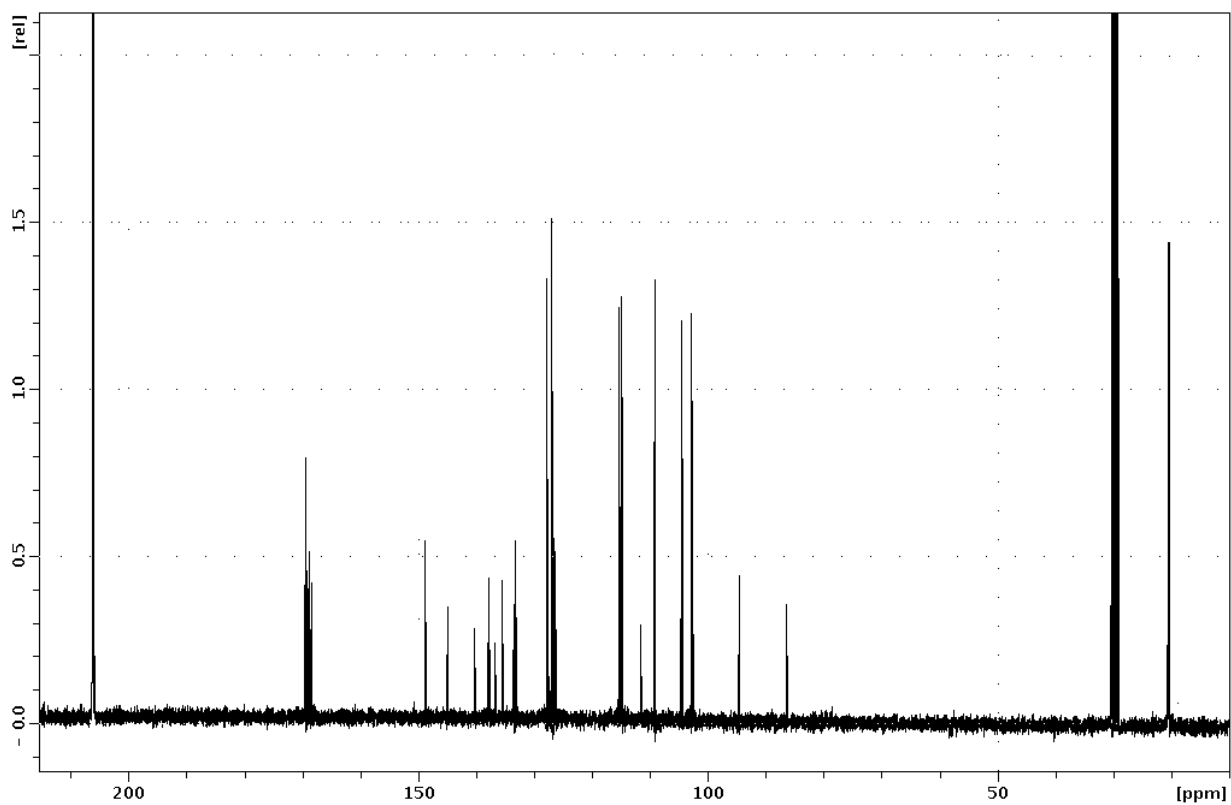
¹H NMR (400 MHz; (CD₃)₂CO) Low field region

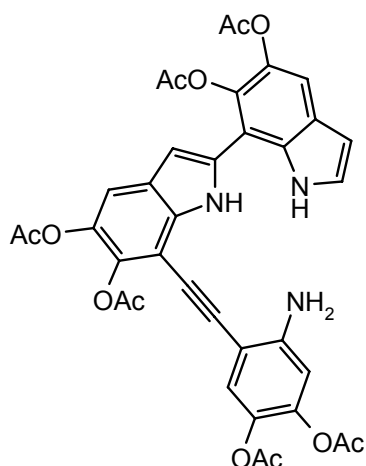




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

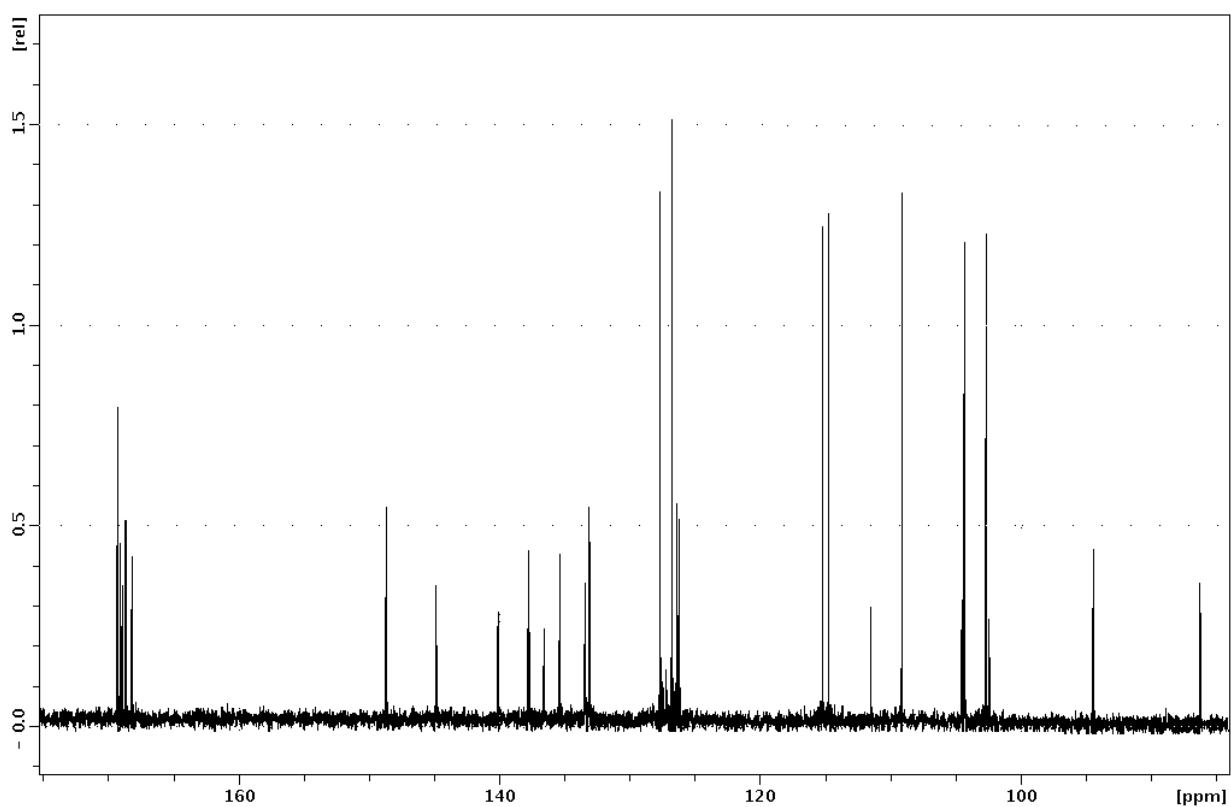
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

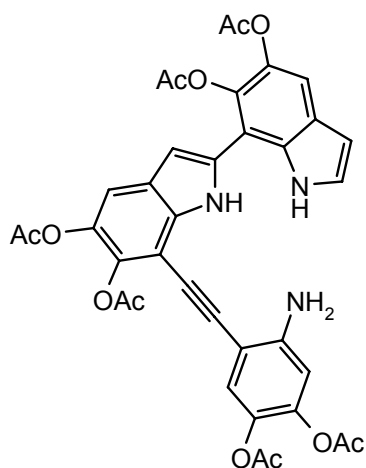




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

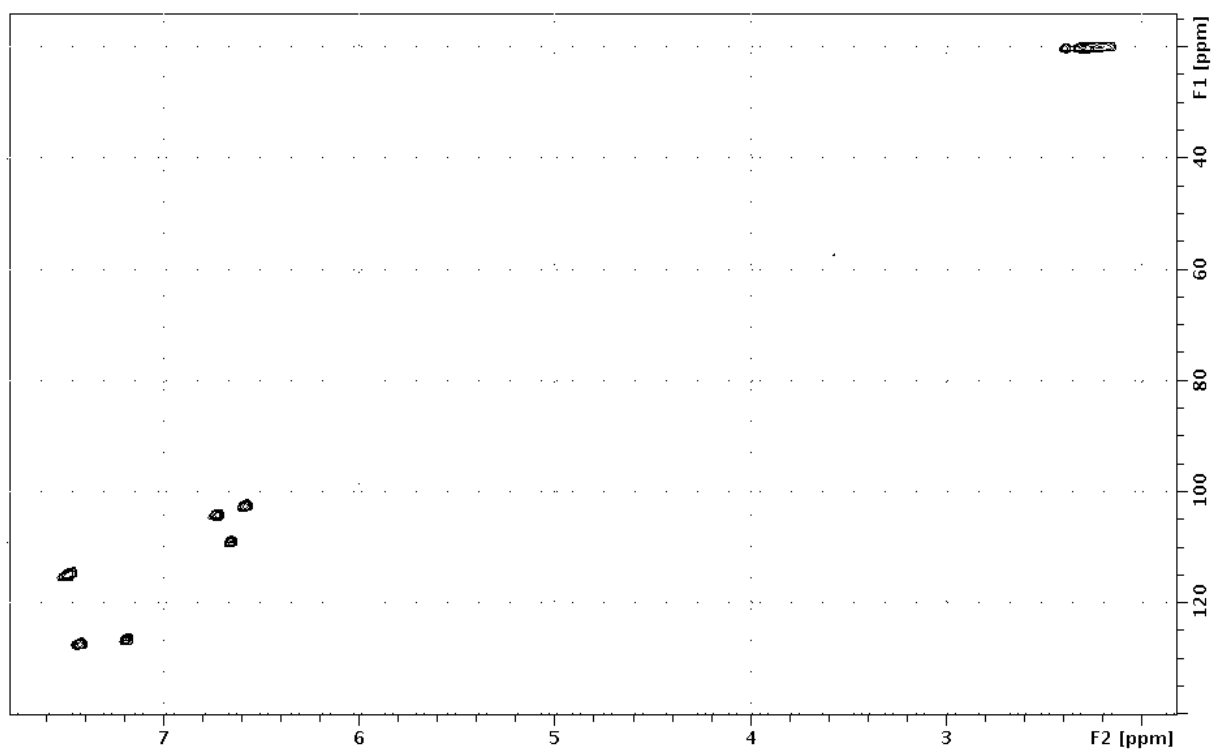
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

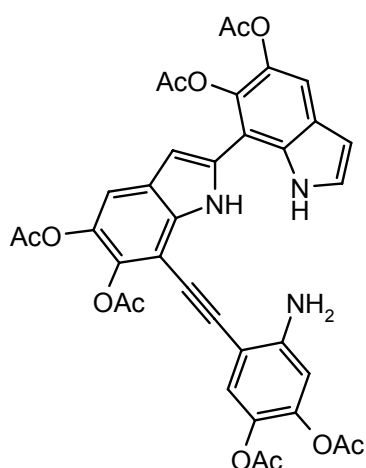




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7''''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

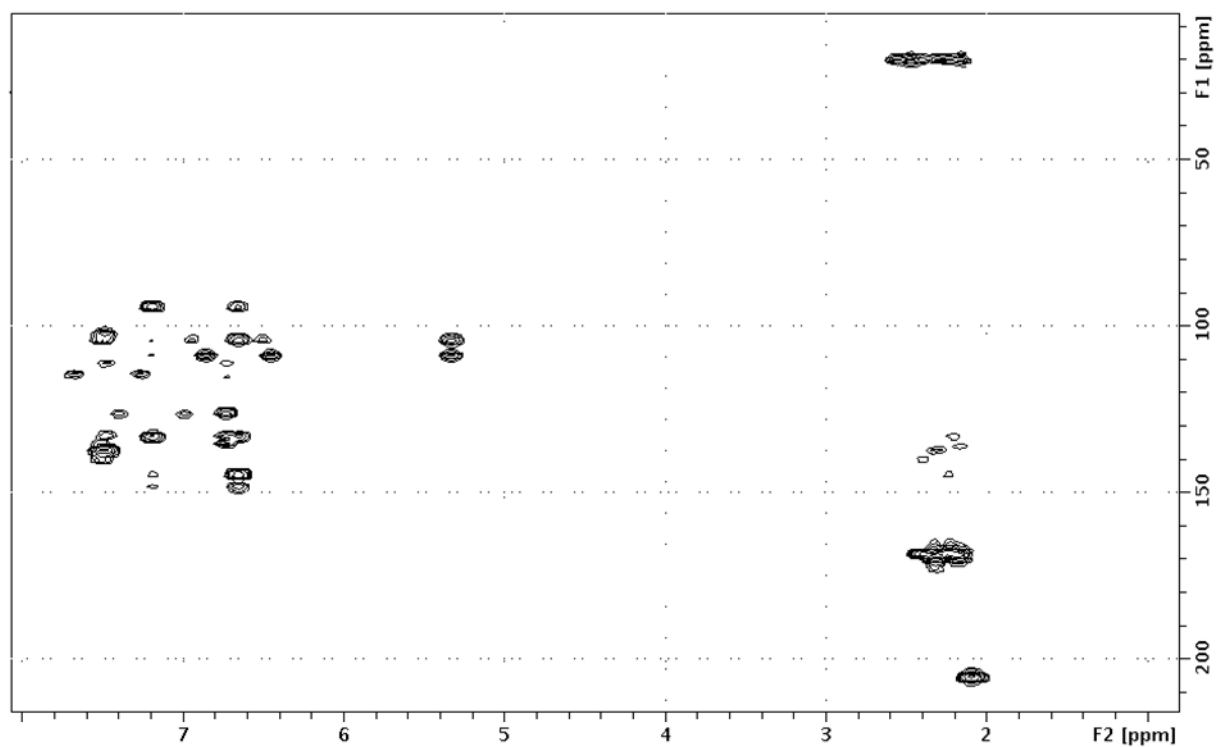
$^1\text{H}, ^{13}\text{C}$ HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

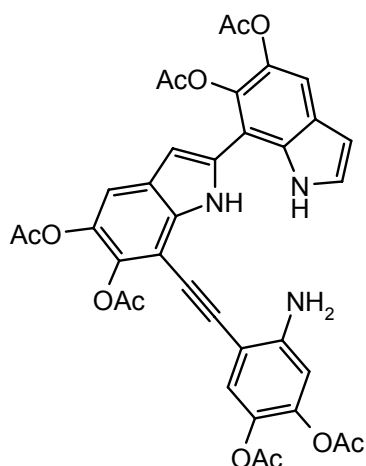




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

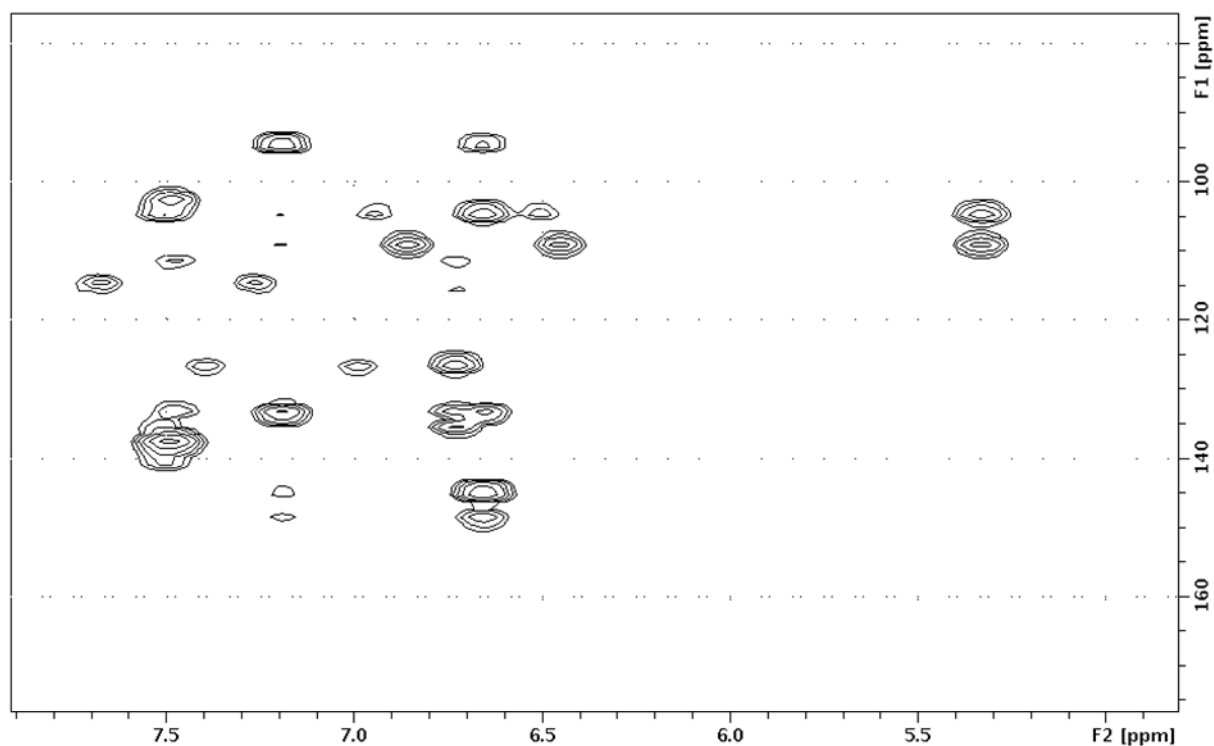
^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

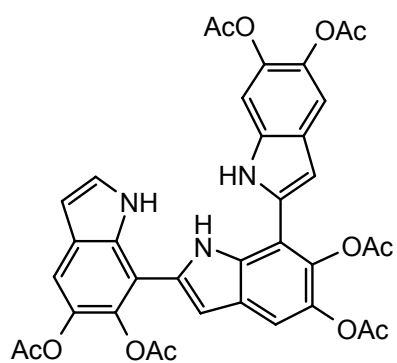




4,5-diacetoxy-2-[2'-(5'',5''',6'',6''')-tetraacetoxy-2'',7'''-biindol-7''-yl]-1'-ethynyl]-aniline (15)

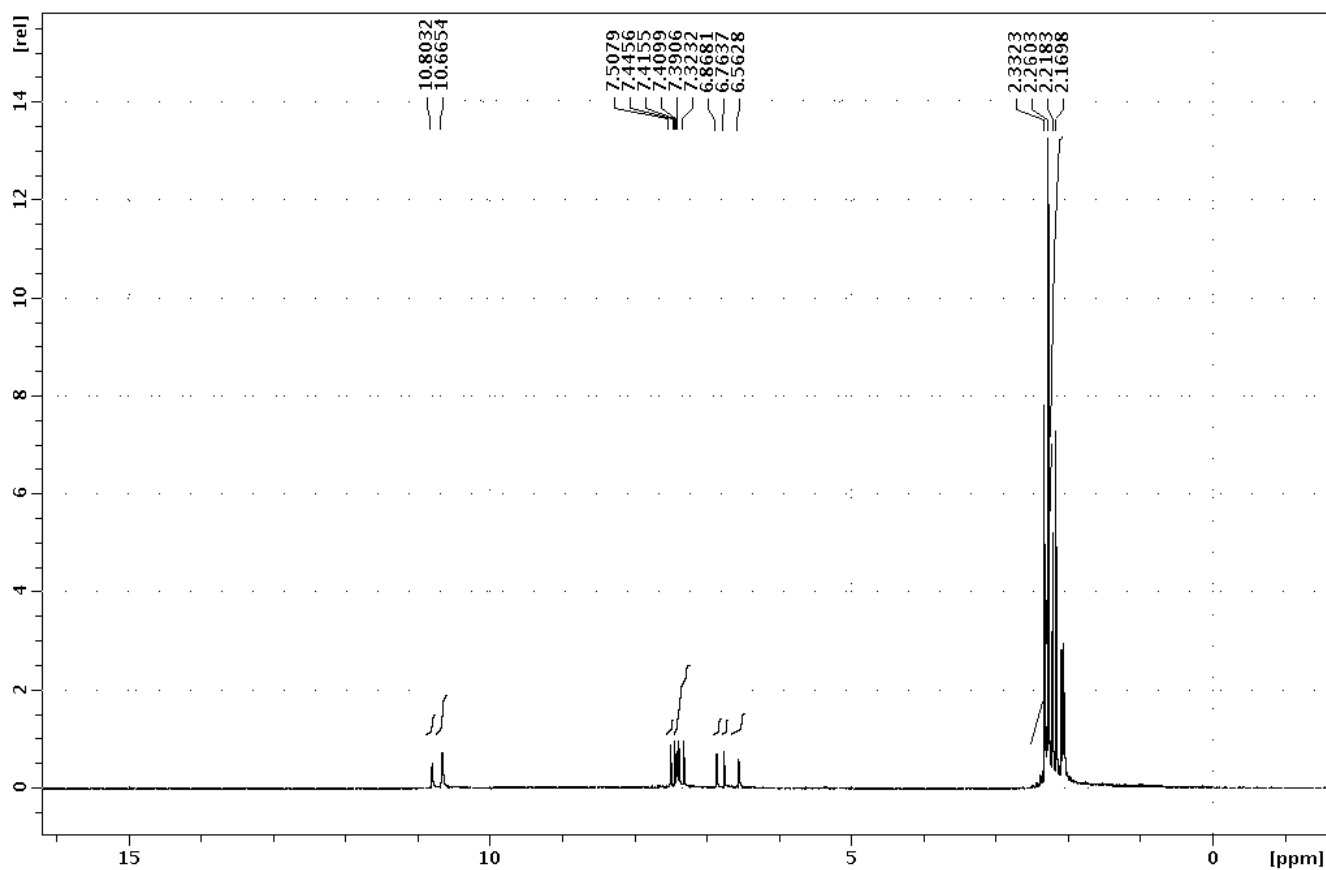
^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

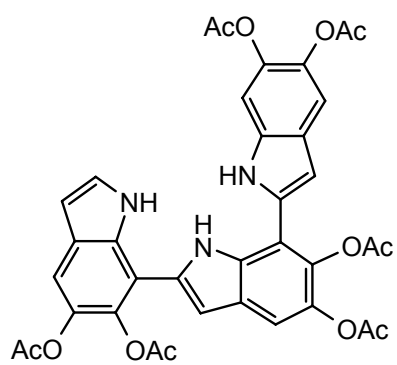




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-triindole (6-Ac)

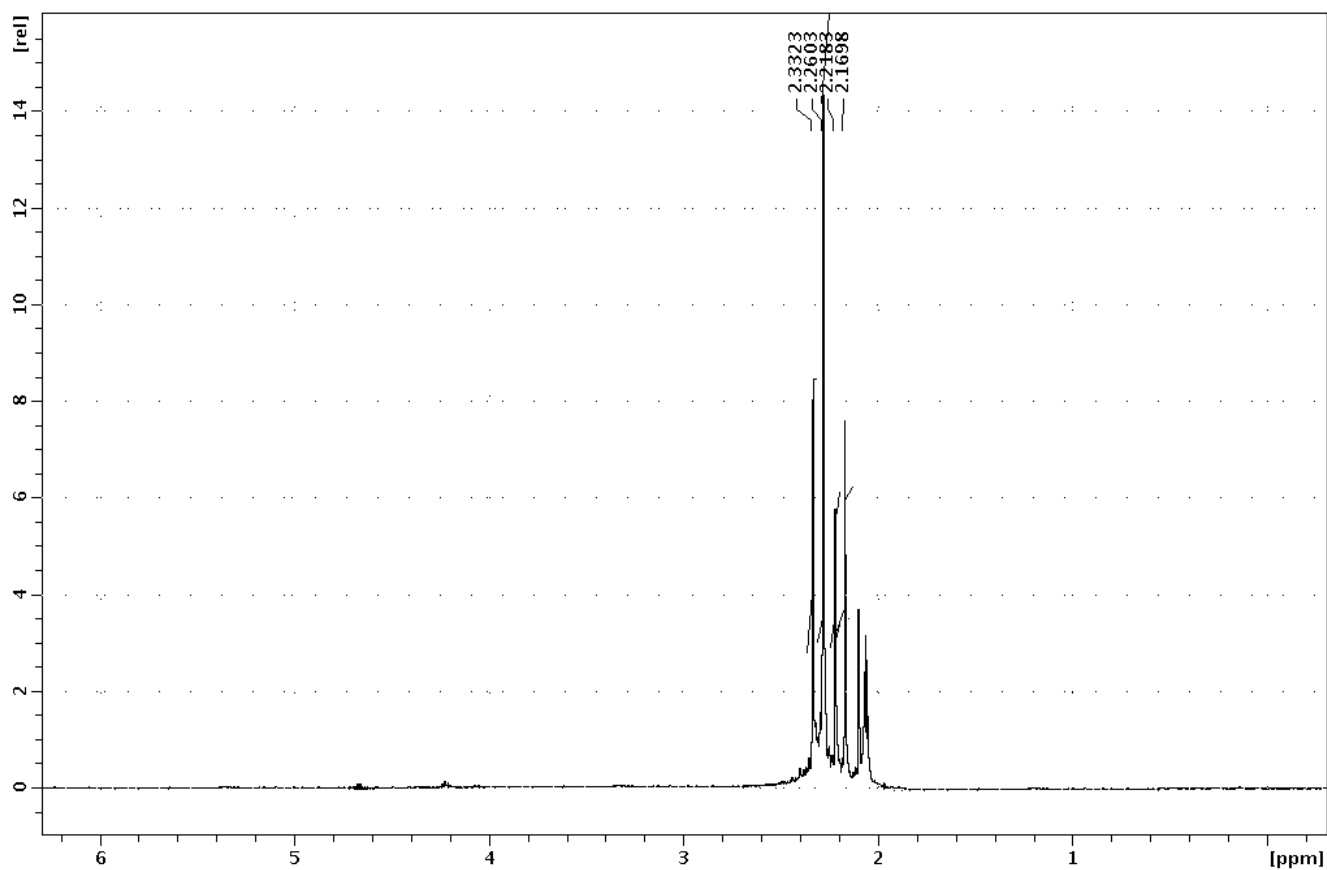
^1H NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

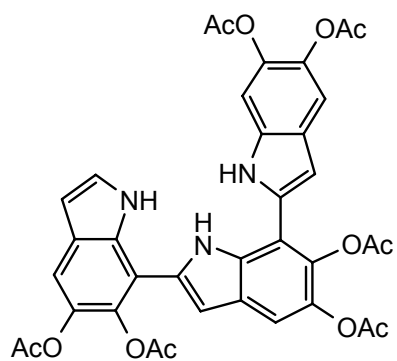




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

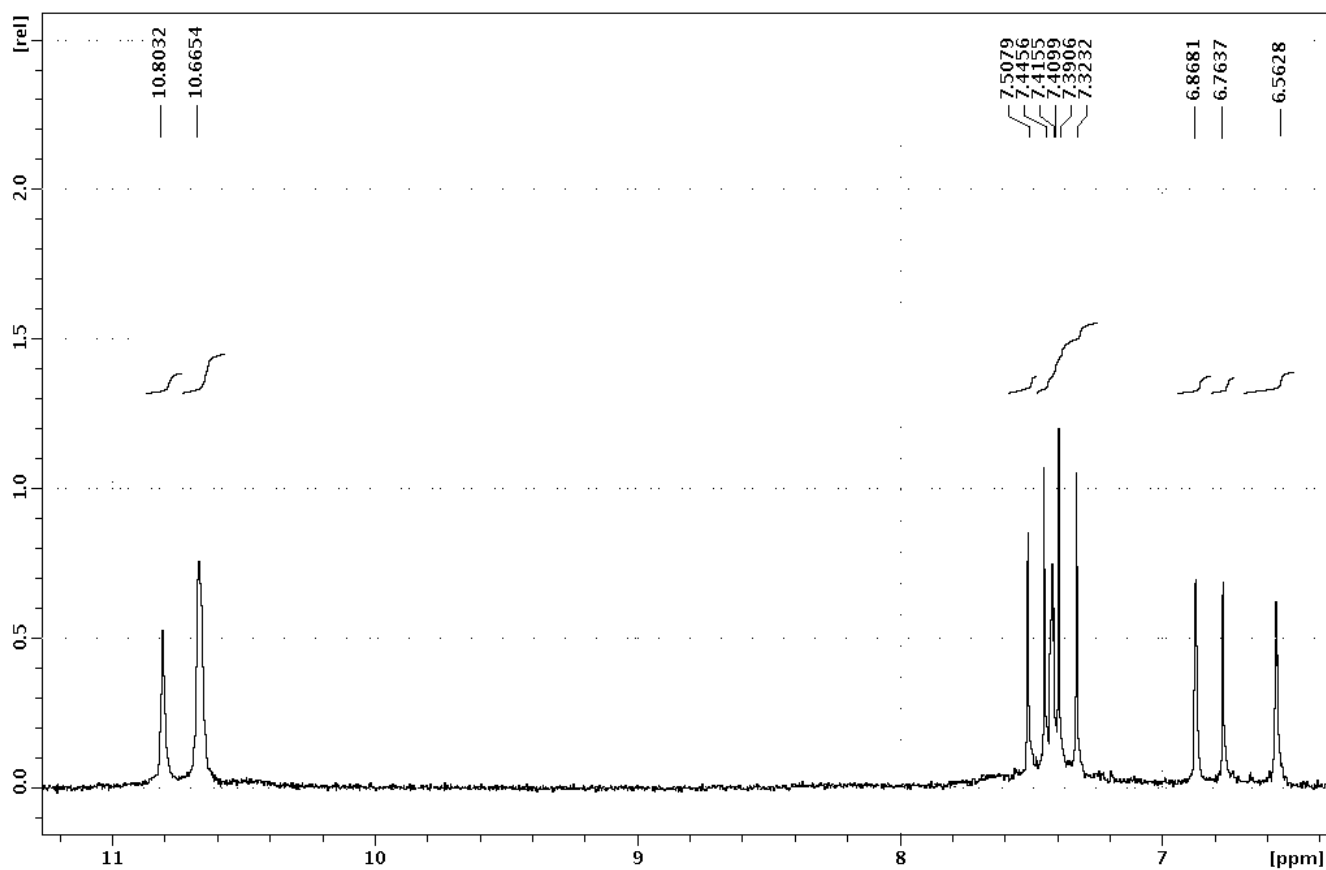
¹H NMR (400 MHz; (CD₃)₂CO) High field region

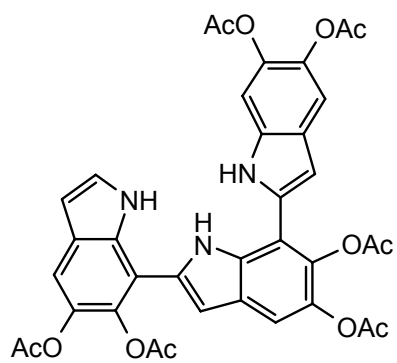




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

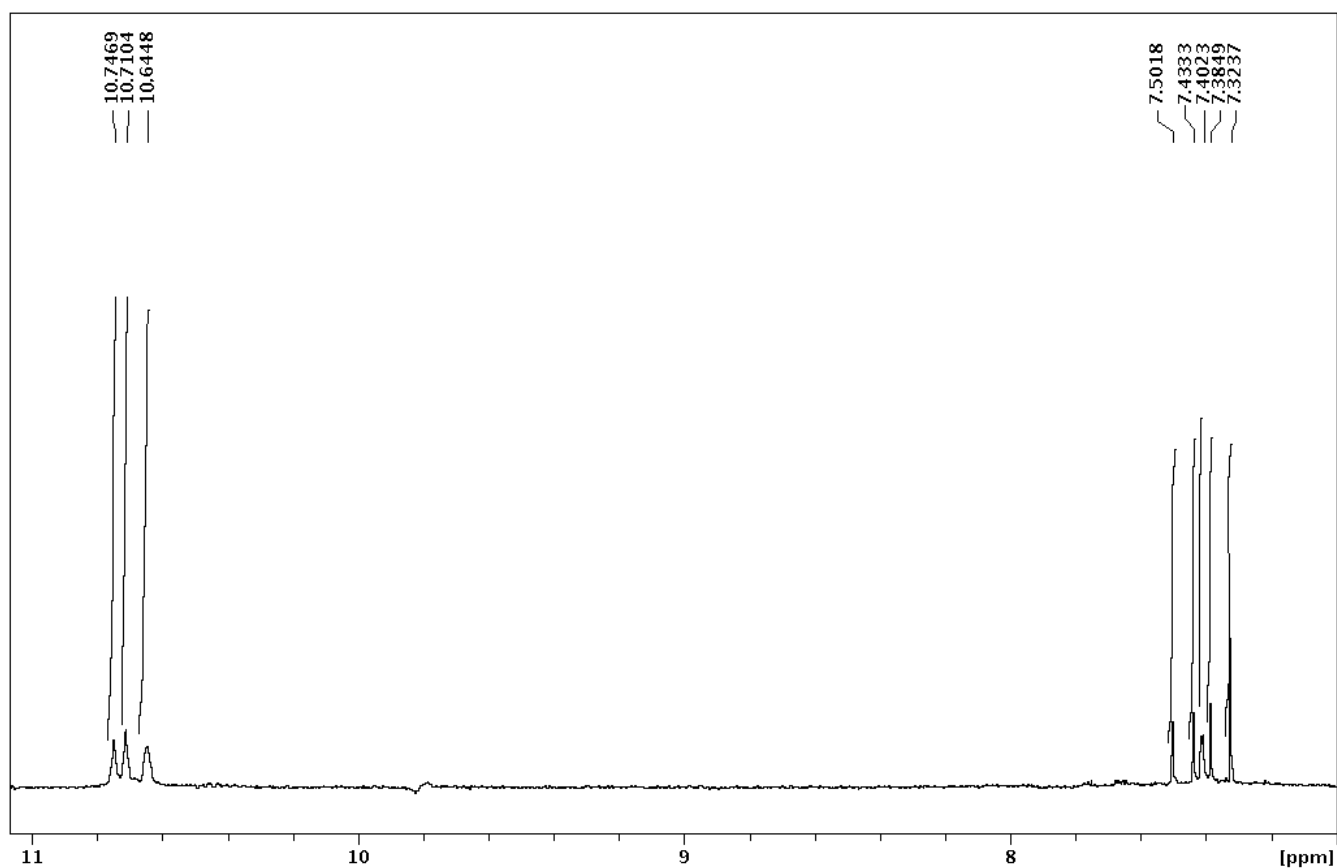
^1H NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$) Low field region

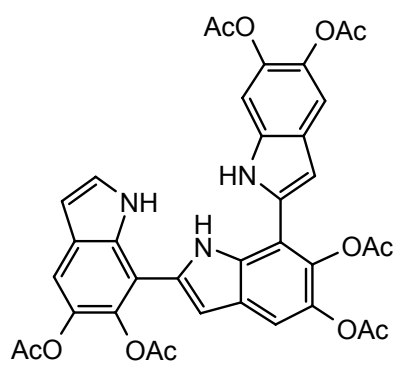




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

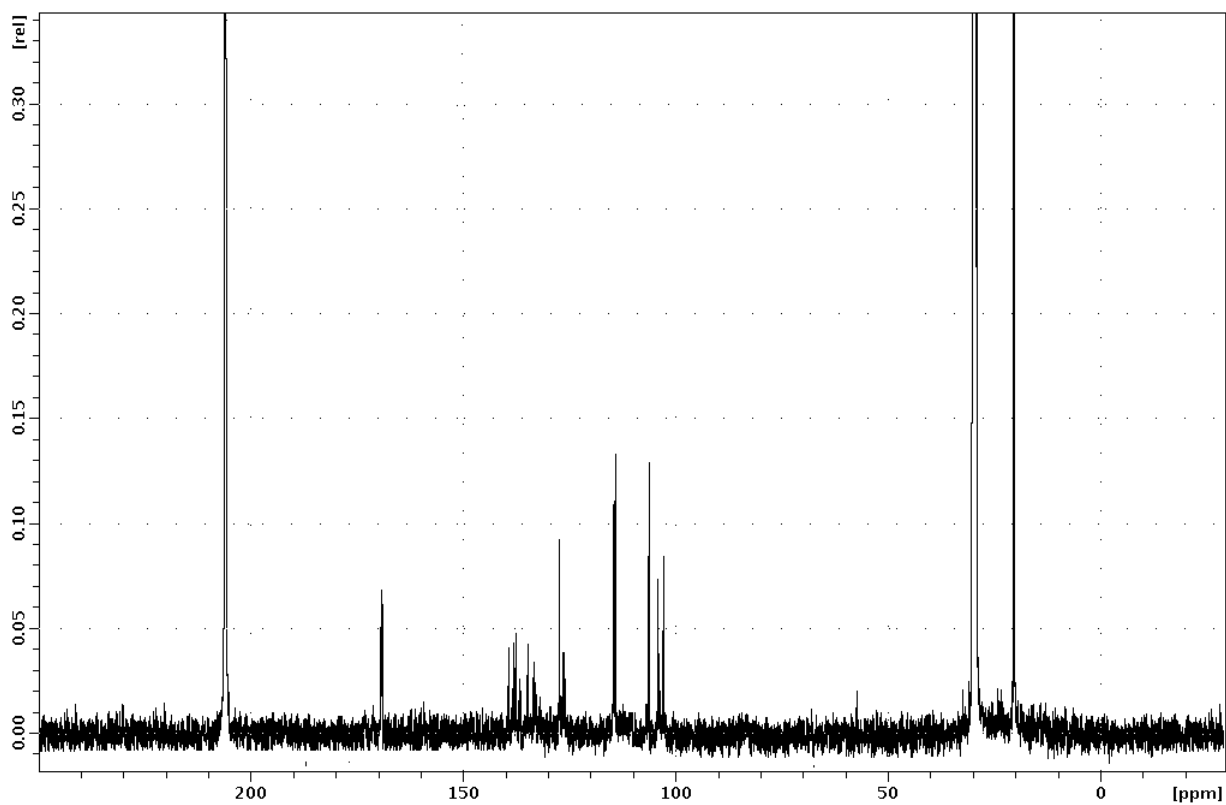
^1H NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$ plus 1% of NH_4Cl (10% in H_2O)) Low field region

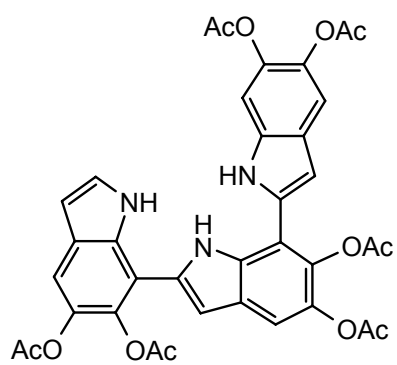




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

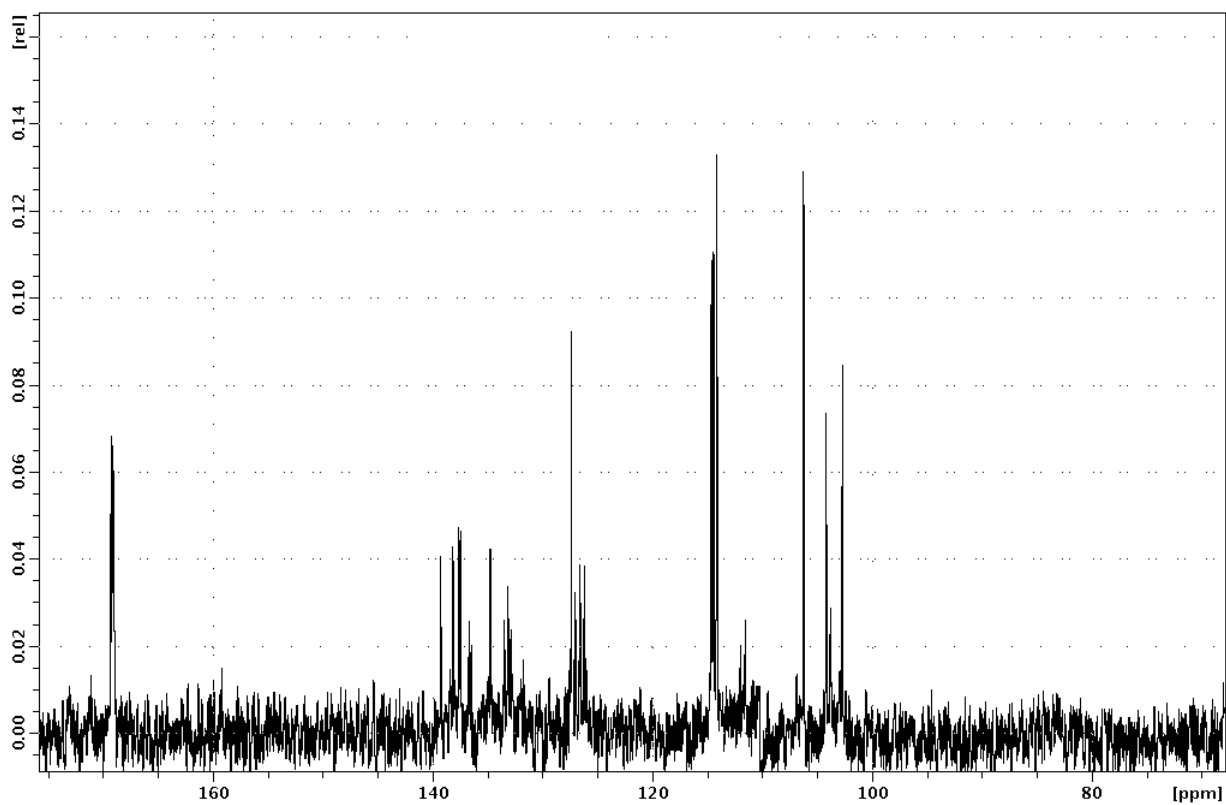
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$)

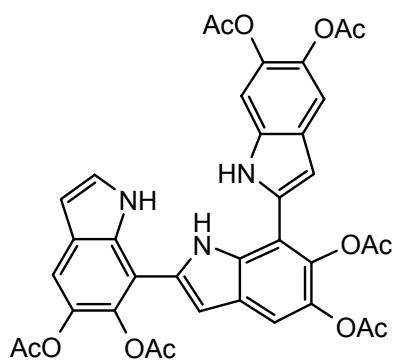




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

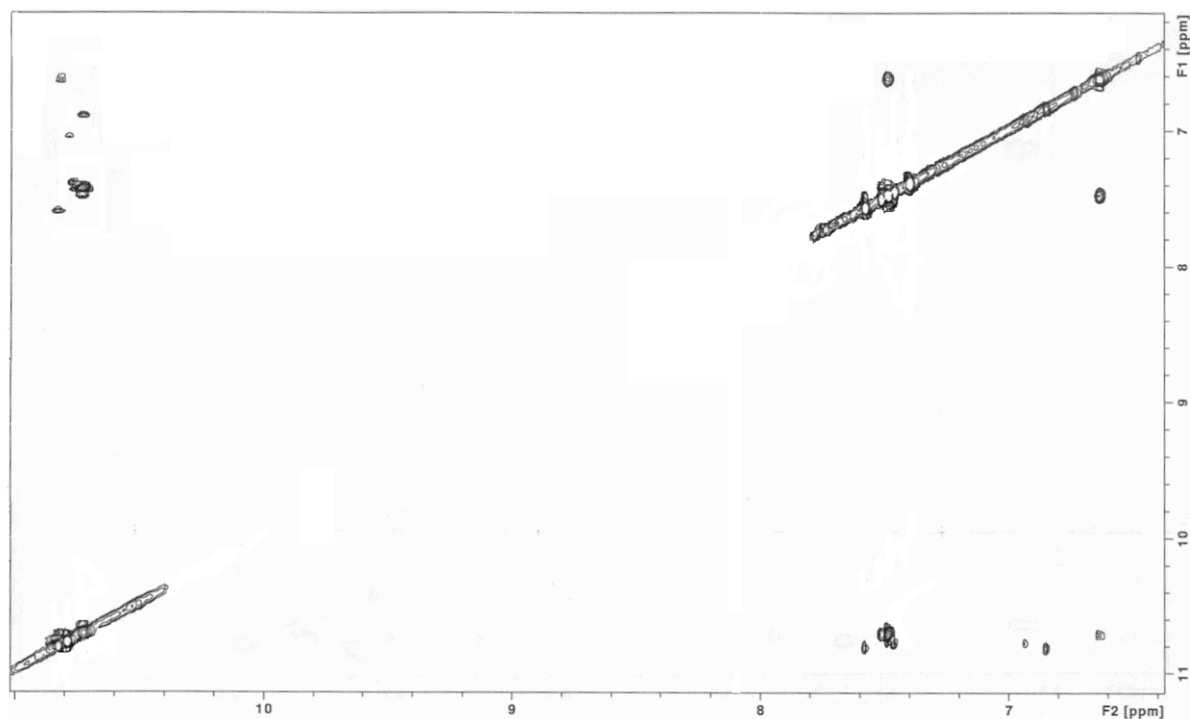
^{13}C NMR (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

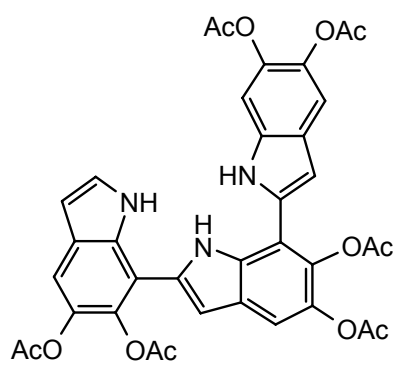




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

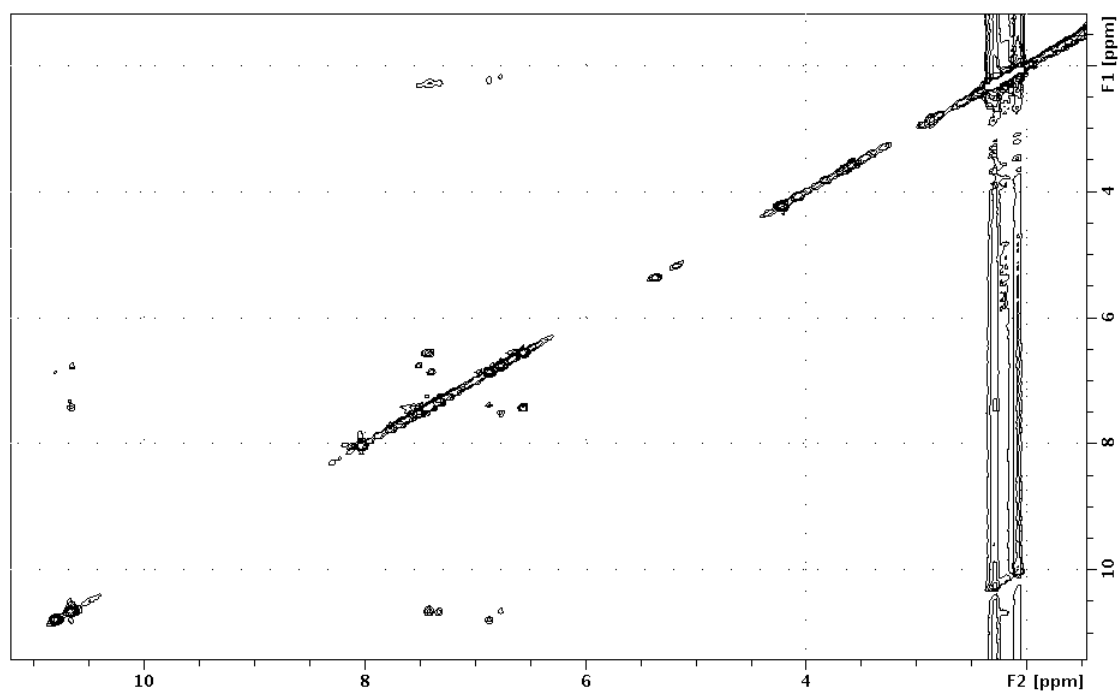
$^1\text{H}, ^1\text{H}$ COSY (400 MHz; $(\text{CD}_3)_2\text{CO}$ plus 1% of NH_4Cl (10% in H_2O)) Expanded region

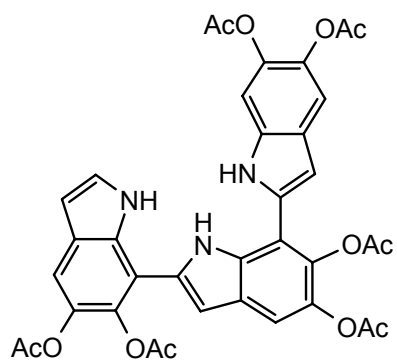




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

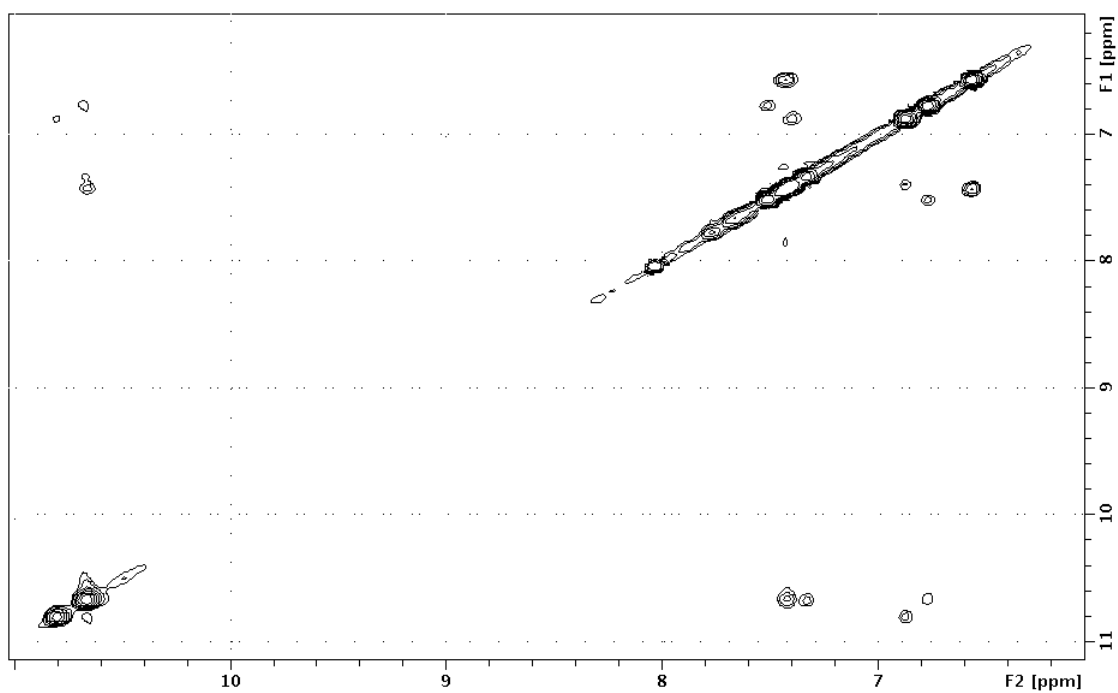
ROESY (400 MHz; (CD₃)₂CO)

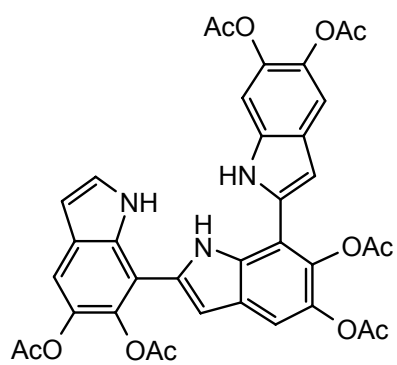




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

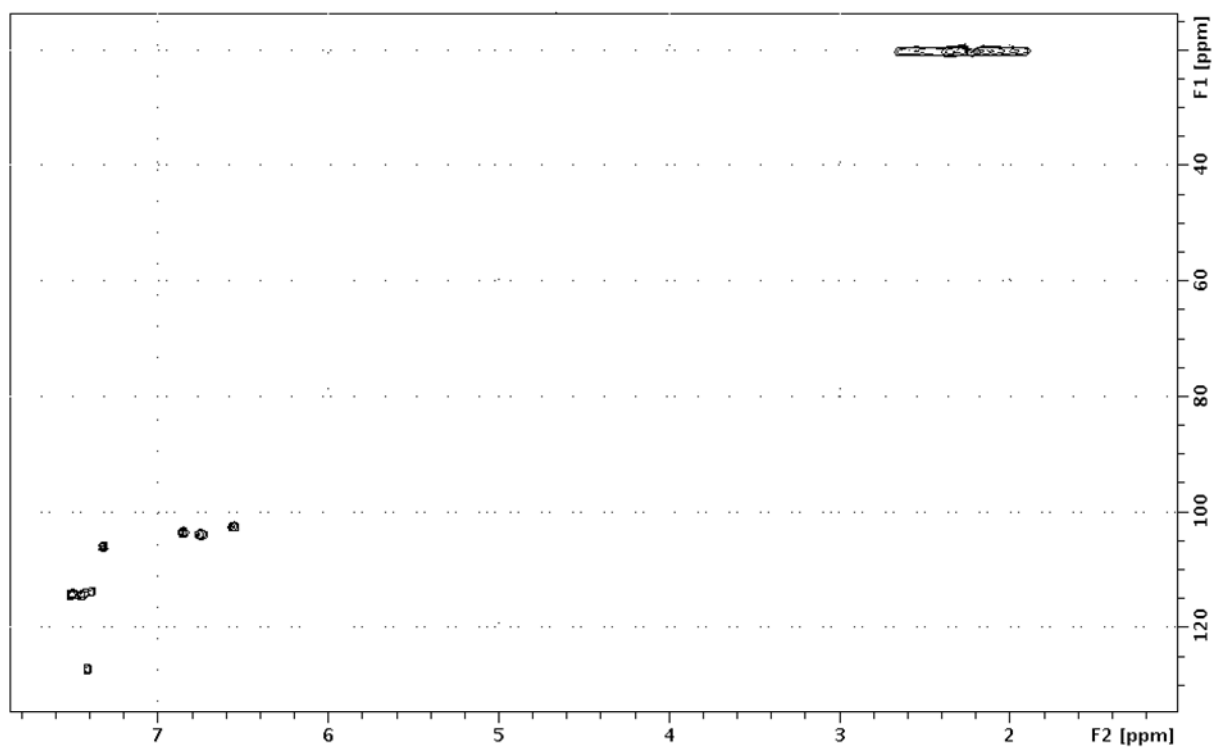
ROESY (400 MHz; (CD₃)₂CO) Expanded region

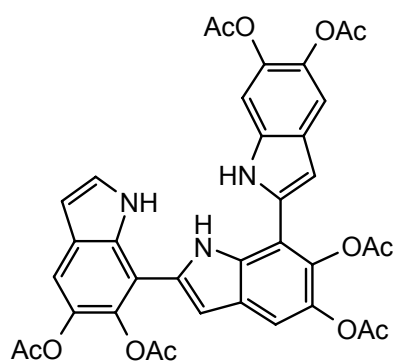




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

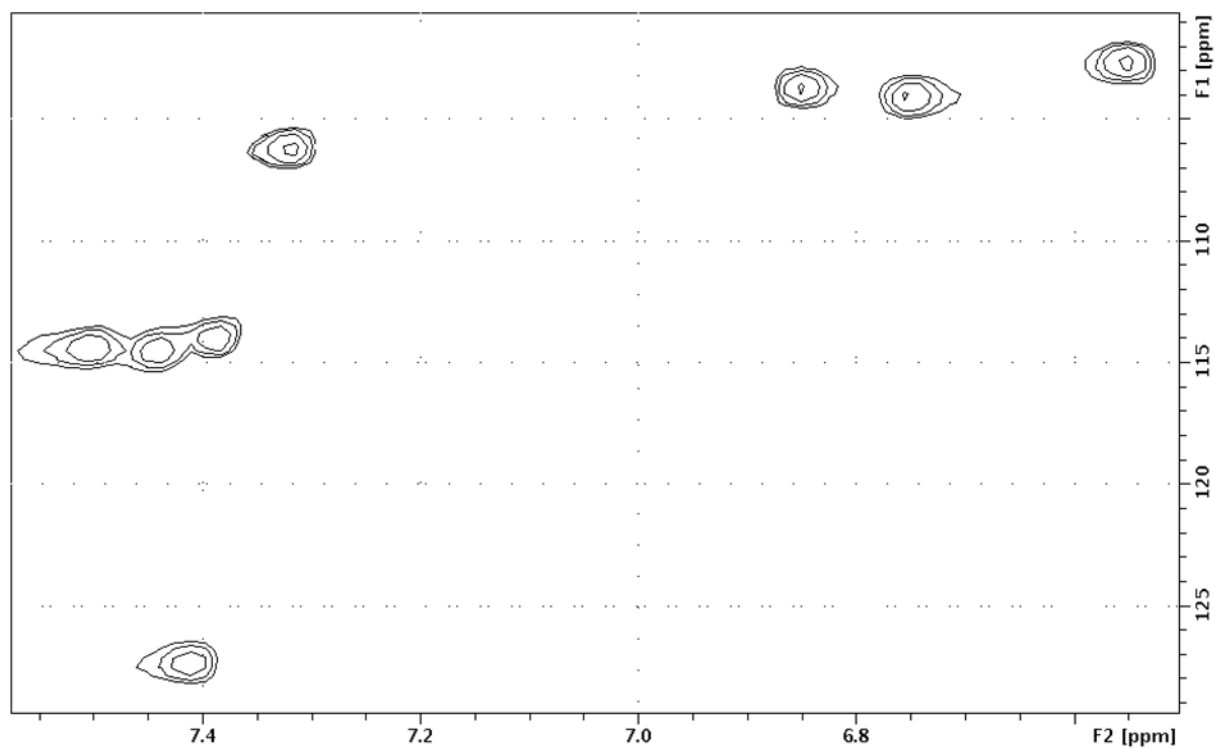
^1H , ^{13}C HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$)

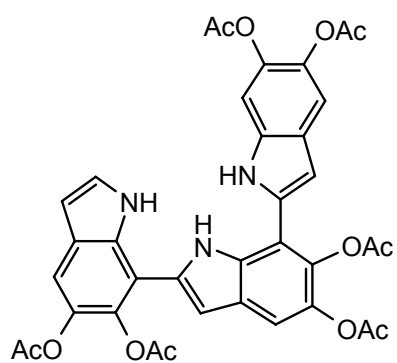




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

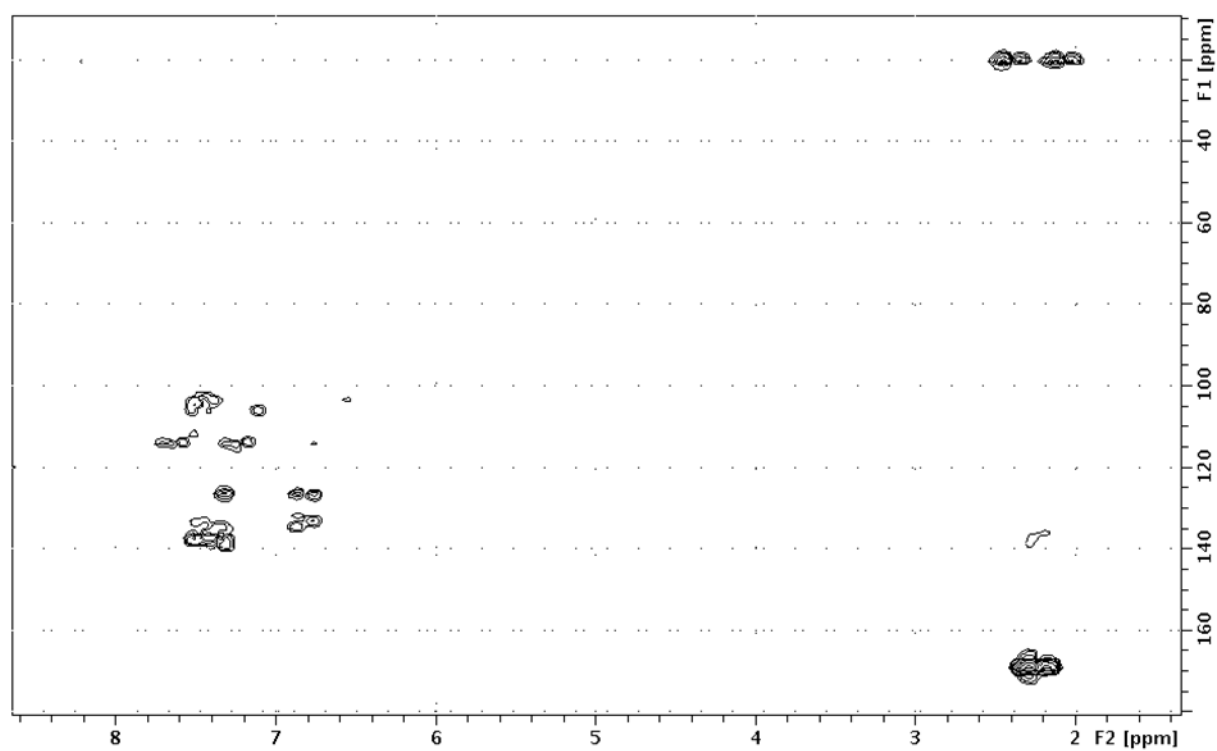
$^1\text{H}, ^{13}\text{C}$ HSQC (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region

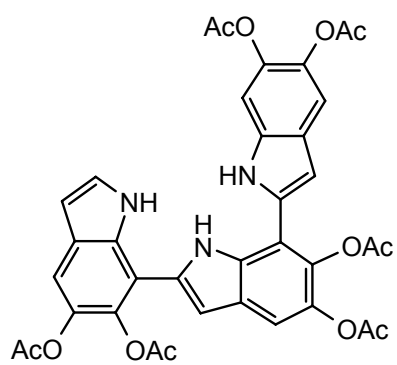




5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

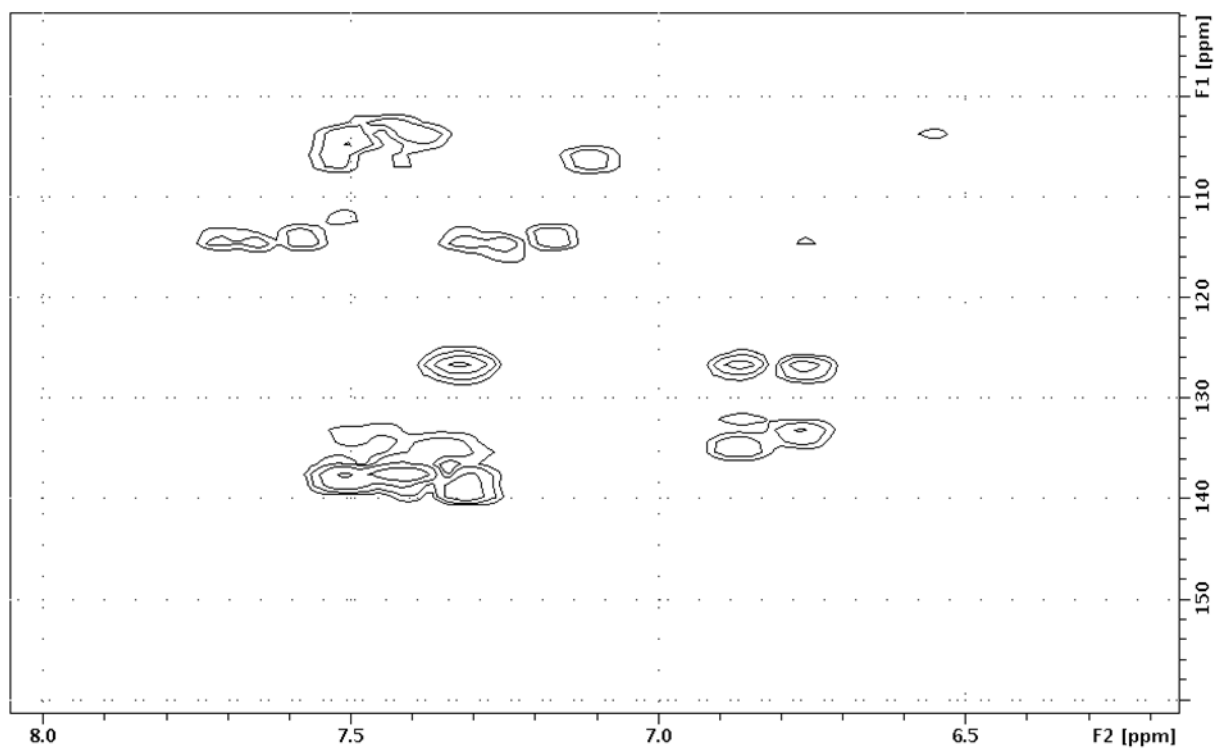
^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$)



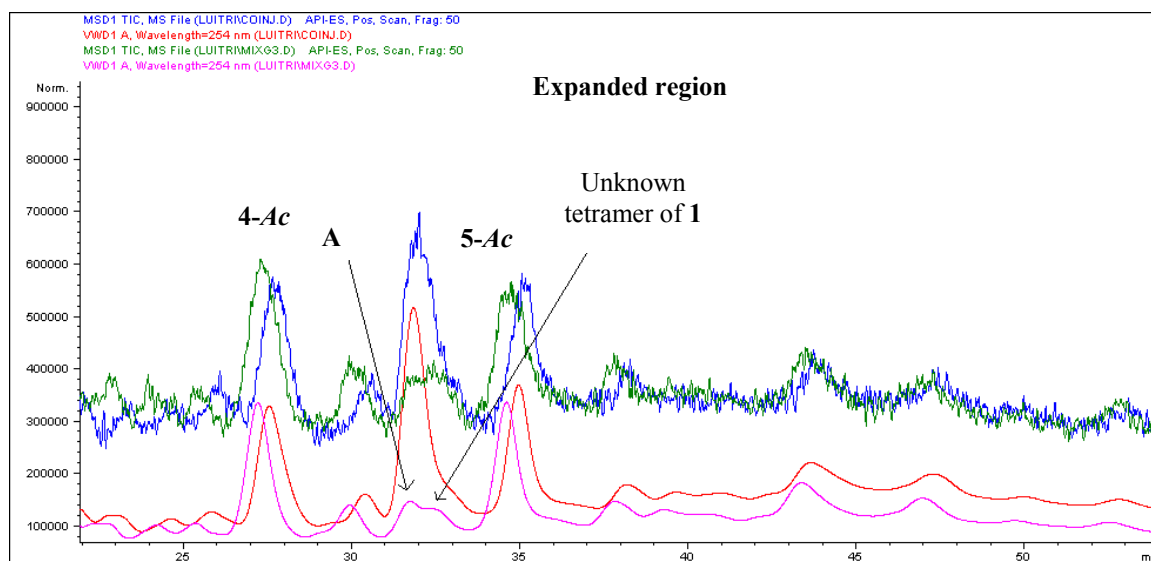
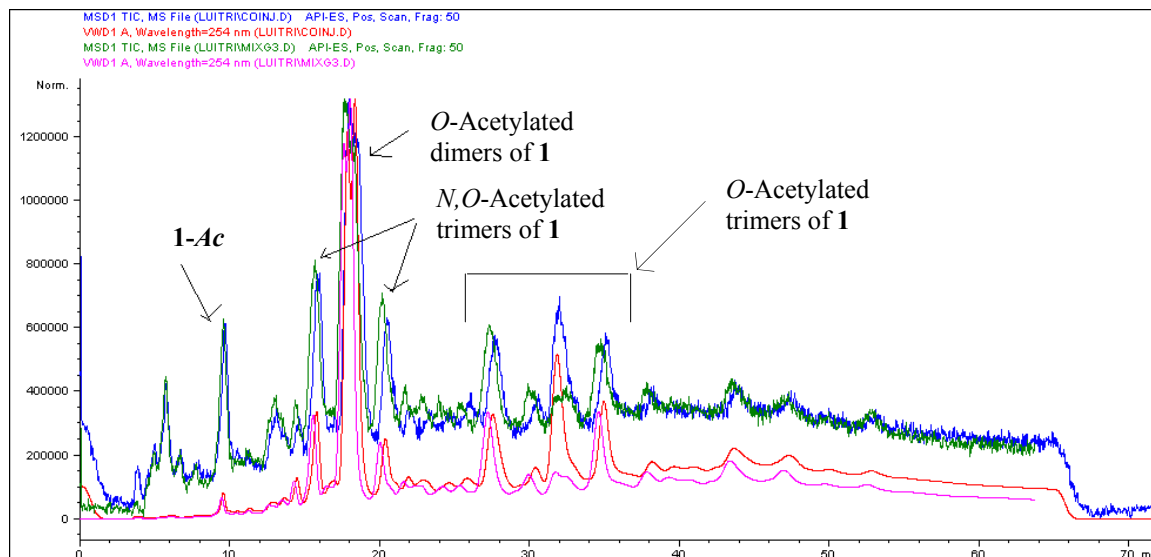


5,5',5'',6,6',6''-esaacetoxy-2,7':2',7''-terindolyl (6-Ac)

^1H , ^{13}C HMBC (400 MHz; $(\text{CD}_3)_2\text{CO}$) Expanded region



LC-MS elutograms of the oxidation mixture of **1**, after work up and acetylation, (**UV_{254nm} trace**; **ESI(+)-MS trace**) and of the coinjection of the same oxidation mixture with synthetic **6-Ac** (**UV_{254nm} trace**; **ESI(+)-MS trace**).



ESI(+)-MS spectra of the peak **A** (31.8 min) in the oxidation mixture of **1**, after work up and acetylation, and in the coinjection of the same oxidation mixture with synthetic **6-Ac**.

