Supplementary Materials

Ferrocene-catalyzed aromatization and competitive oxidative ring transformations of 1,2-dihydro-1-arylpyridazino[4,5-d]pyridazines

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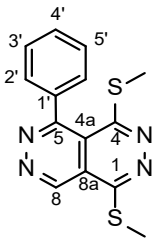
Content:

S.1. Copies of the 1D- and 2D NMR spectra of the products isolated after the reactions of 1a–e and 2a–e with DDQ (S.1.1. – S.1.52): pp. 2–39.

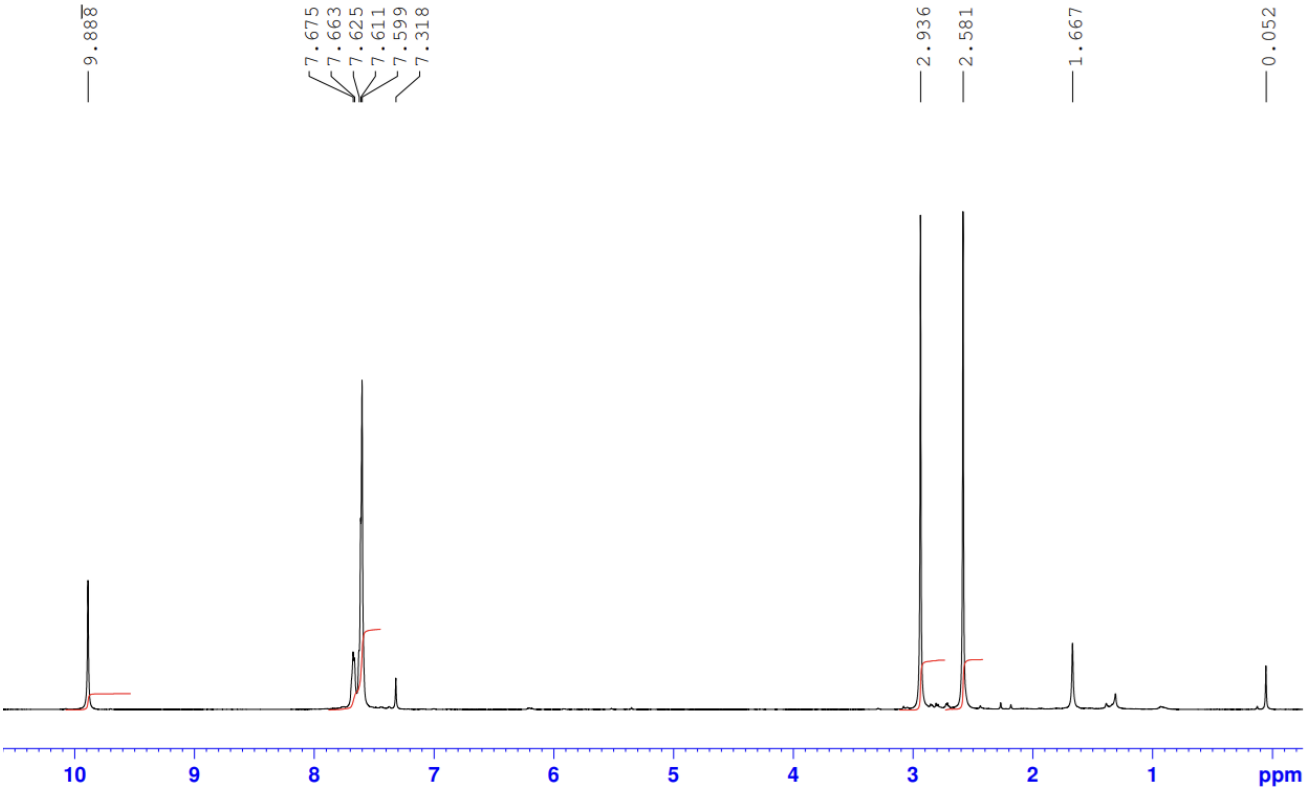
Detailed pictorial presentation of diagnostic ^{1}H-^{13}C HMBC correlations by cross-sections of perpendicular lines supplemented with their lists collected in tables: S.1.16 (compound 5bc); S.1.21 (compound 6a); S.1.26 (compond 6c); S.1.44 (compound 32c); S.1.51 (compound 34c).

S.1. Copies of the 1D- and 2D NMR spectra of the products isolated after the dehydroaromatization

S.1.1. ^{1}H-NMR of **3a**

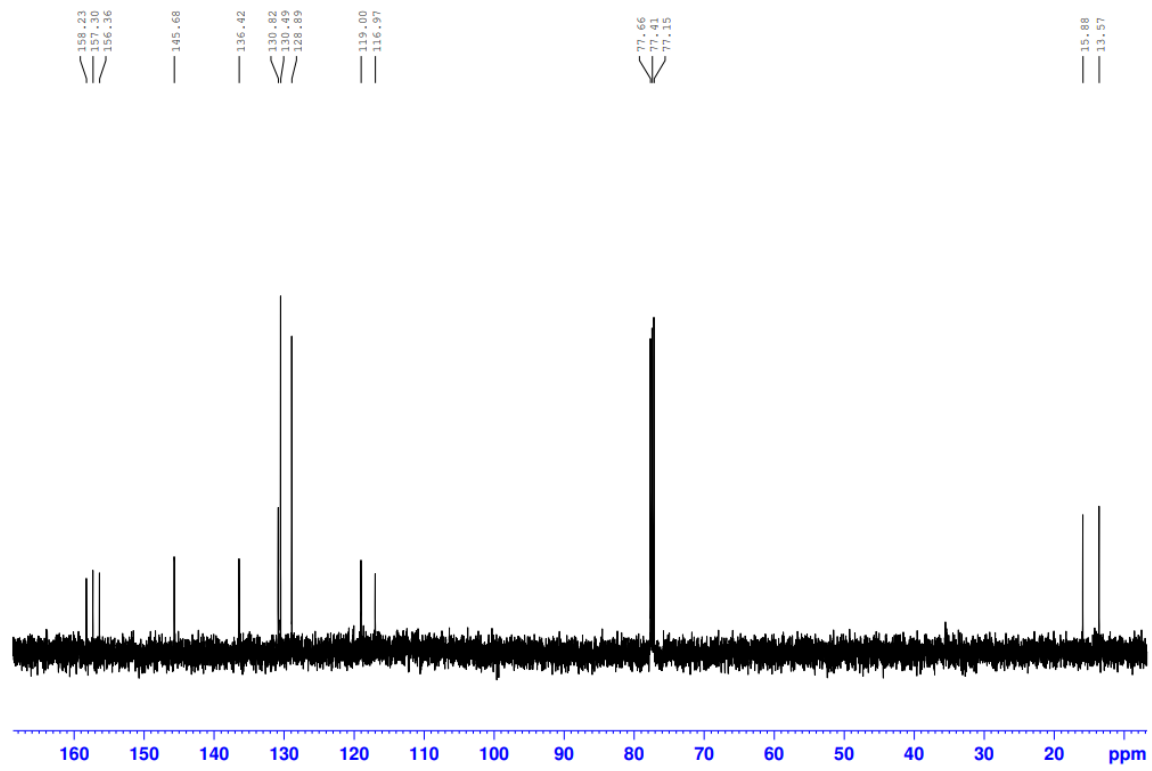


^{1}H-NMR ($CDCl_3$): 9.85 (s, 1H, H-8); 7.63 (m, 1H, H-4′); 7.60-7.52 (overlapping m's, 4H, H-2′,6′ and H-3′,5′); 2.90 (s, 3H, SCH_3 on C-1); 2.54 (s, 3H, SCH_3 on C-4).

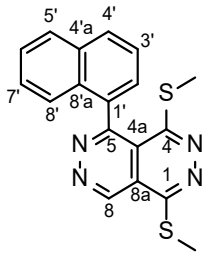


S.1.2. ^{13}C-NMR of **3a**

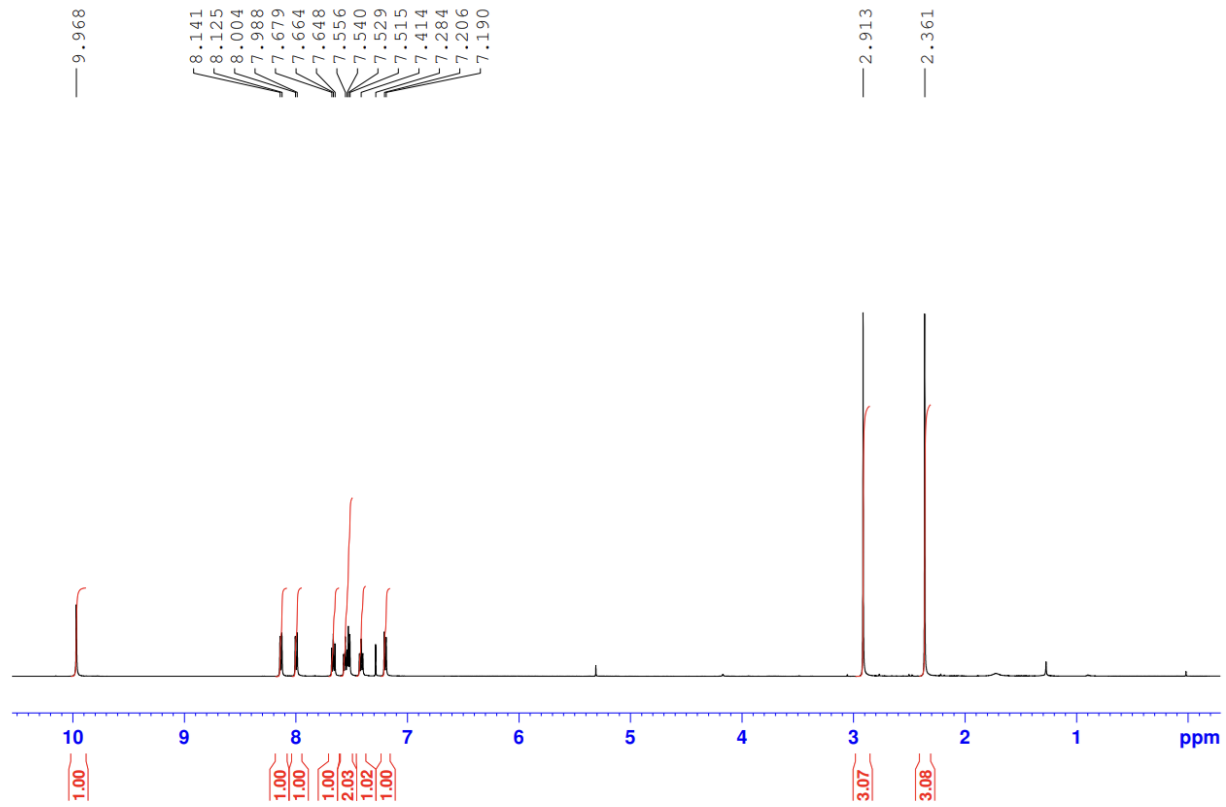
^{13}C-NMR ($CDCl_3$): 158.2 (C-5); 157.3 (C-4); 156.4 (C-1); 145.7 (C-8); 136.4 (C-1′); 130.8 (C-4′); 130.5 (C-3′,5′); 128.9 (C-2′,6′); 119.0 (C-4a); 117.0 (C-8a); 15.9 (SCH_3 on C-4); 13.6 (SCH_3 on C-1).



S.1.3. ^{1}H-NMR of **3b**

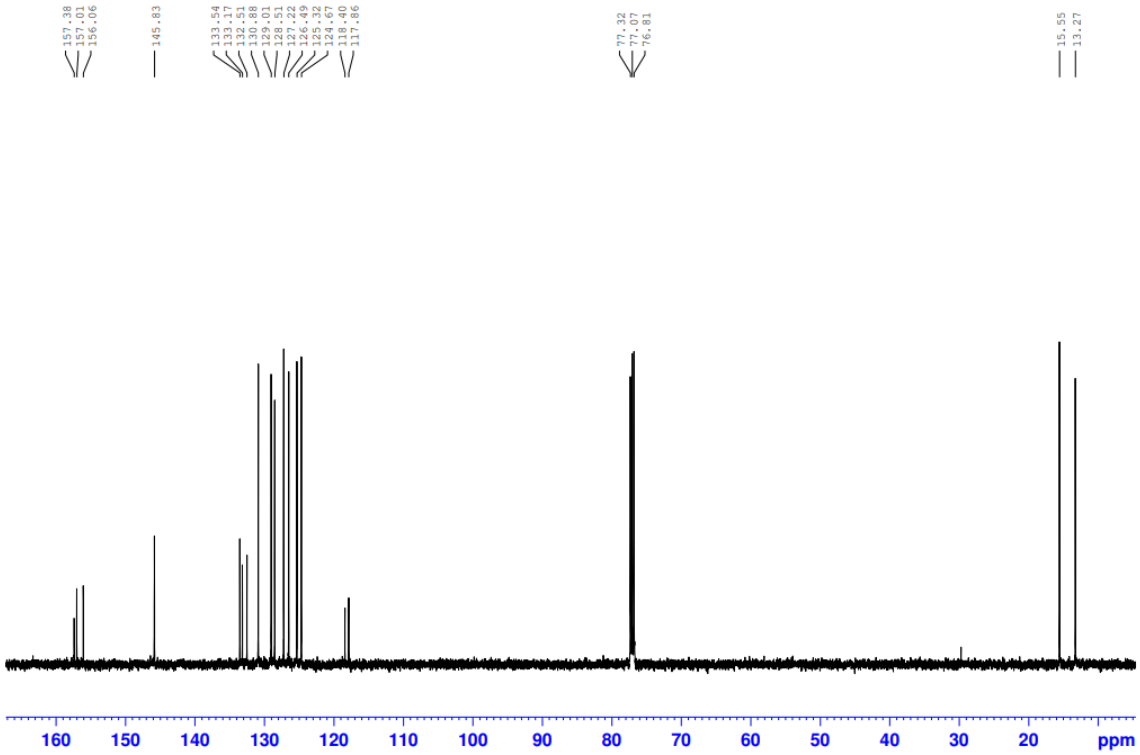


^{1}H-NMR ($CDCl_3$): 9.97 (s, 1H, H-8); 8.14 (d, *J* = 8.1 Hz, 1H, H-4′); 8.00 (d, *J* = 8.1 Hz, 1H, H-5′); 7.66 (dd, *J* = 8.1 Hz and 7.7 Hz, 1H, H-3′); 7.56 (dd, *J* = 8.4 Hz and 7.7 Hz, 1H, H-6′); 7.52 (d, *J* = 7.4 Hz, 1H, H-2′); 7.41 (dd, *J* = 8.4 Hz and 7.7 Hz, 1H, H-7′); 7.20 (d, *J* = 8.4 Hz, 1H, H-8′); 2.91 (s, 3H, SC$\underline{H}_3$ on C-1); 2.36 (s, 3H, SC$\underline{H}_3$ on C-4).

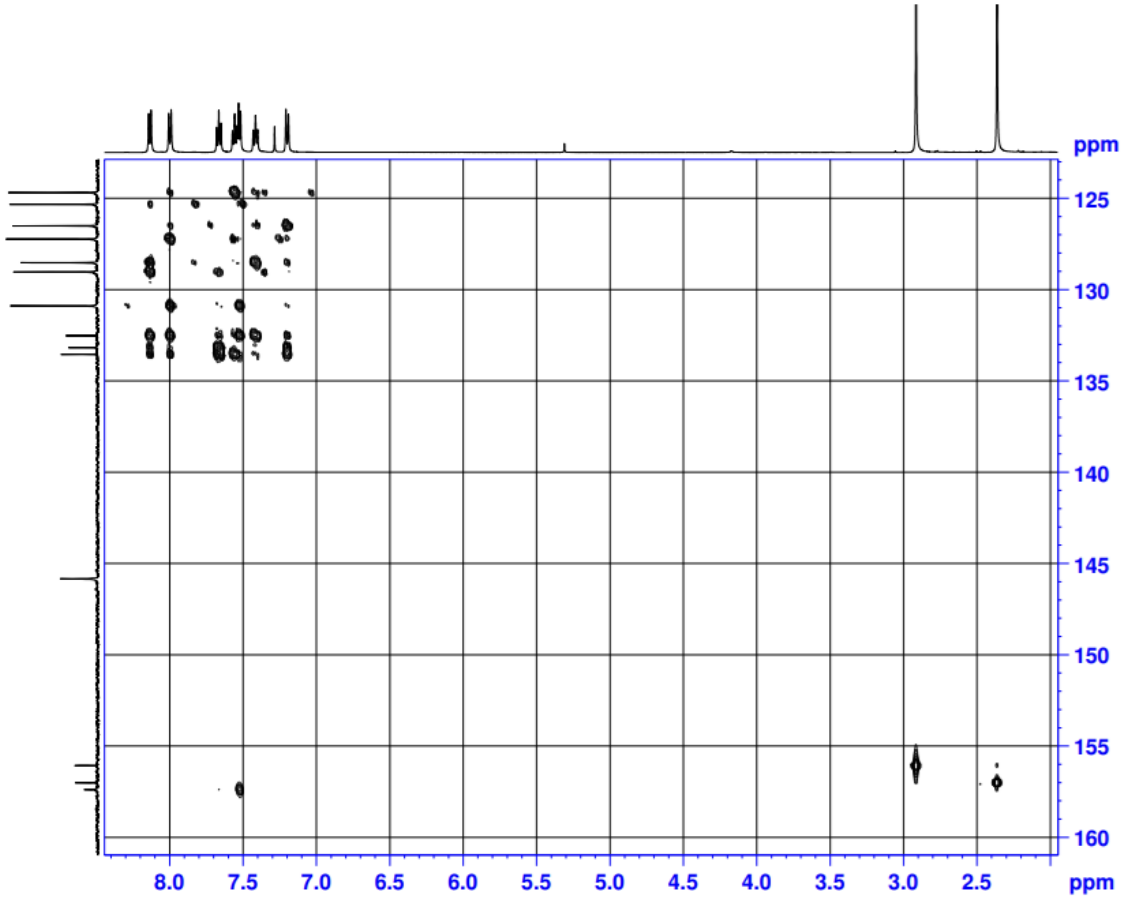


S.1.4. ^{13}C-NMR of **3b**

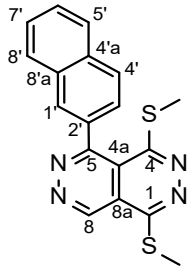
^{13}C-NMR ($CDCl_3$): 157.4 (C-5); 157.0 (C-4); 156.1 (C-1); 145.9 (C-8); 133.5 (C-4'a); 133.2 (C-1'); 132.5 (C-8'a); 130.9 (C-4'); 129.0 (C-2'); 128.5 (C-5'); 127.2 (C-7'); 126.5 (C-6'); 125.3 (C-3'); 124.7 (C-8'); 118.4 (C-4a); 117.9 (C-8a); 15.6 (S<u>C</u>H$_3$ on C-4); 13.3 (S<u>C</u>H$_3$ on C-1).



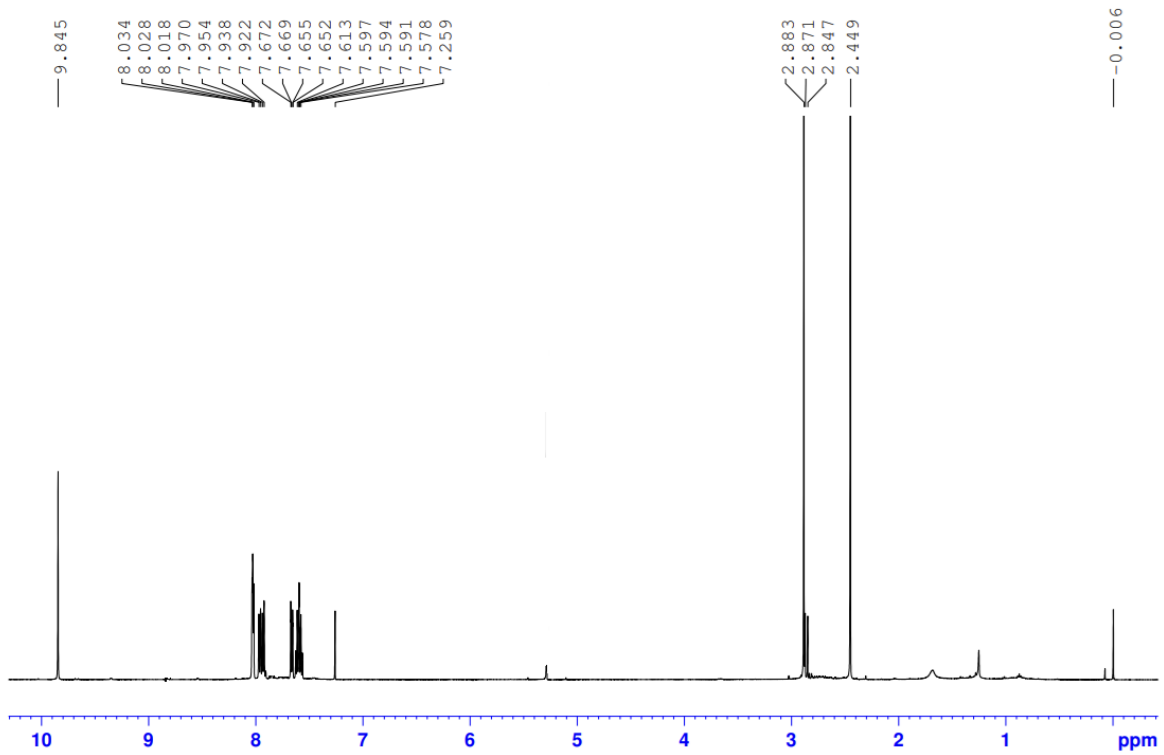
S.1.5. ^{1}H-^{13}C-HMBC spectrum of **3b**



S.1.6. ^{1}H-NMR of **3c**

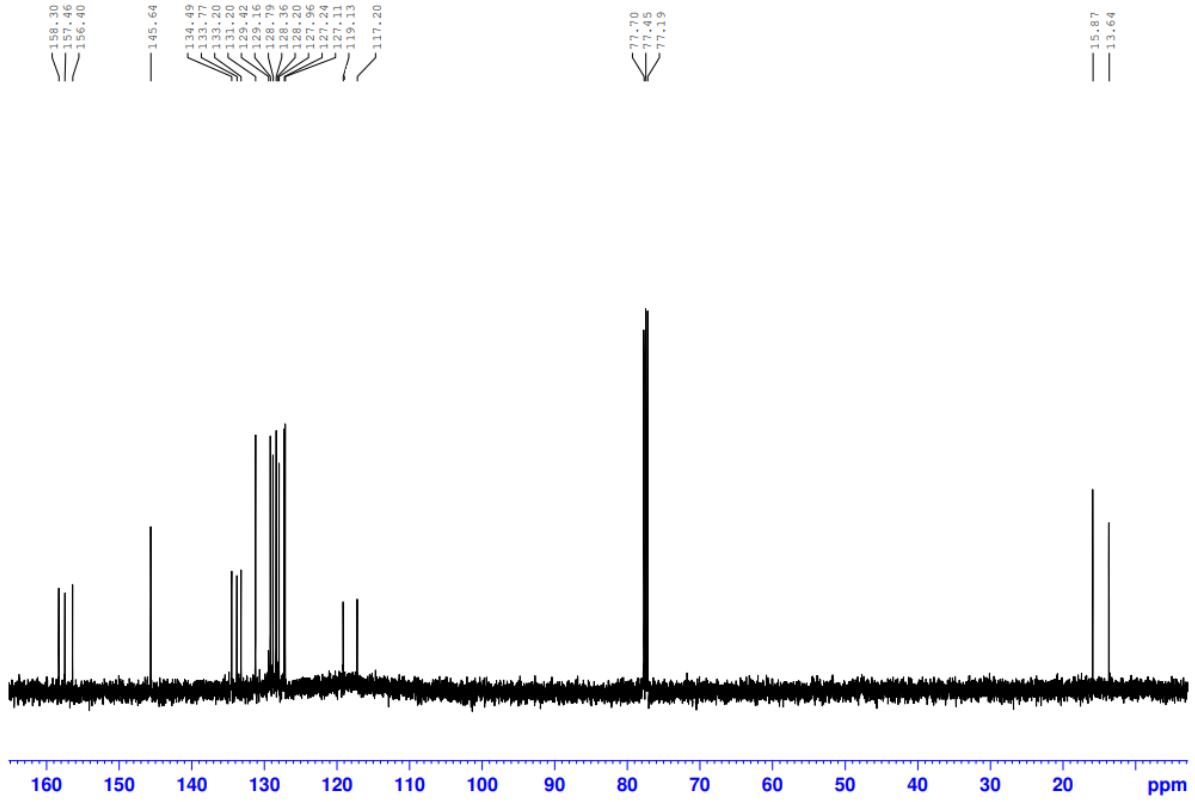


^{1}H-NMR ($CDCl_3$): 9.85 (s, 1H, H-8); 8.14 (d, *J* = 8.1 Hz, 1H, H-4′); 8.03 (overlapping br s and d, *J* = 8.1 Hz, 2H, H-1′ and H-4′, respectively); 7.96 (d, *J* = 8.2 Hz, 1H, H-5′); 7.93 (d, *J* = 8.4 Hz, 1H, H-8′); 7.66 (dd, *J* = 8.1 Hz and 1.5 Hz, 1H, H-3′); 7.61 (dd, *J* = 8.2 Hz and 7.7 Hz, 1H, H-6′); 7.58 (dd, *J* = 8.4 Hz and 7.7 Hz, 1H, H-7′); 2.88 (s, 3H, SCH_3 on C-1); 2.45 (s, 3H, SCH_3 on C-4).

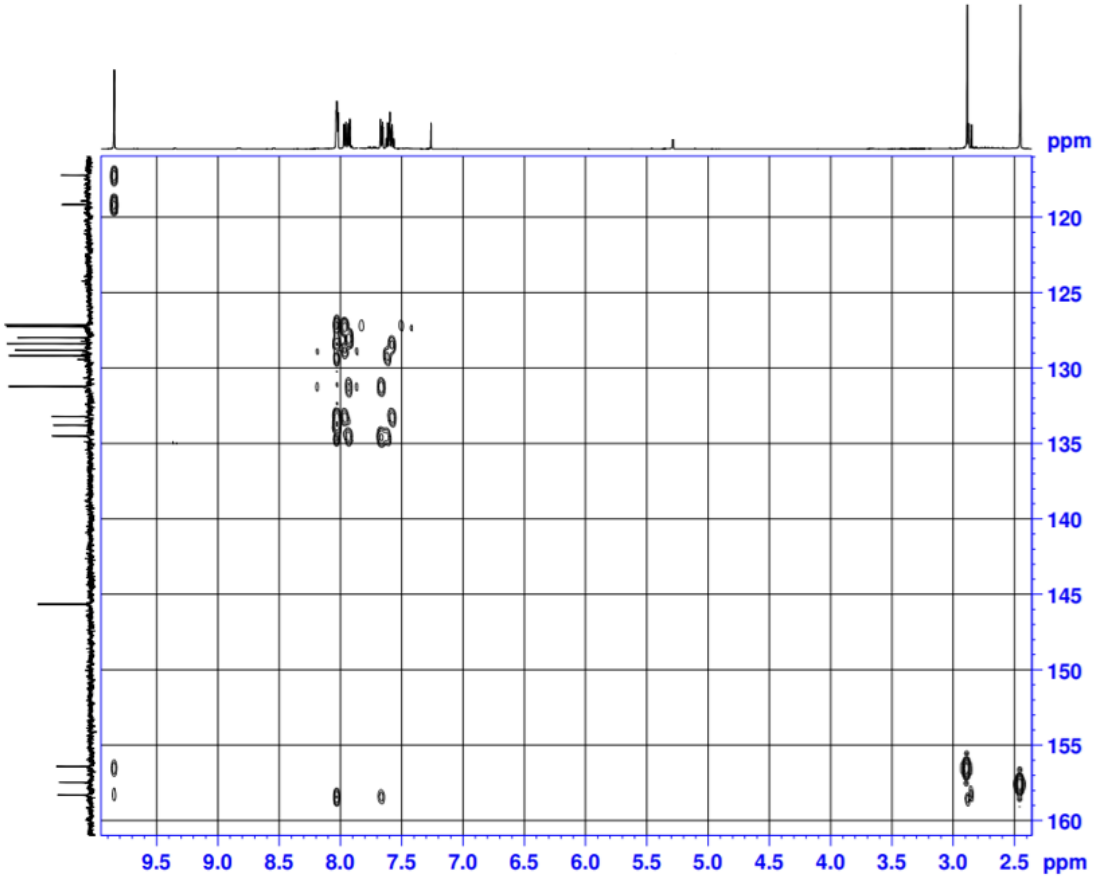


S.1.7. ^{13}C-NMR of **3c**

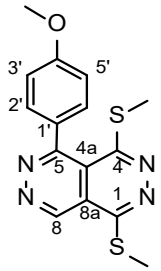
^{13}C-NMR ($CDCl_3$): 158.3 (C-5); 157.5 (C-4); 156.4 (C-1); 145.6 (C-8); 134.5 (C-4'a); 133.8 (C-2'); 133.2 (C-8'a); 131.2 (C-1'); 129.2 (C-8'); 128.8 (C-4'); 128.4 (C-5'); 128.0 (C-6'); 127.3 (C-7'); 127.1 (C-3'); 119.2 (C-4a); 117.2 (C-8a); 15.9 (S<u>C</u>H$_3$ on C-4); 13.6 (S<u>C</u>H$_3$ on C-1).



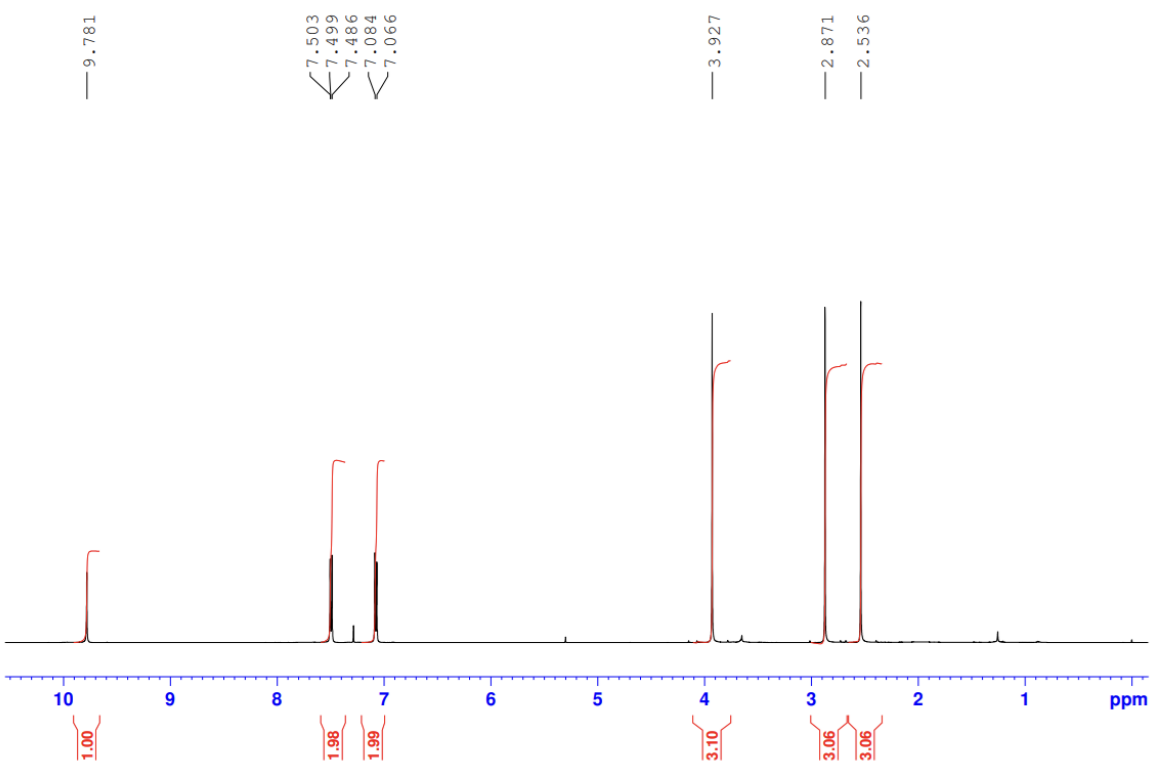
S.1.8. ^{1}H-^{13}C-HMBC spectrum of **3c**



S.1.9. ^{1}H-NMR of **3d**

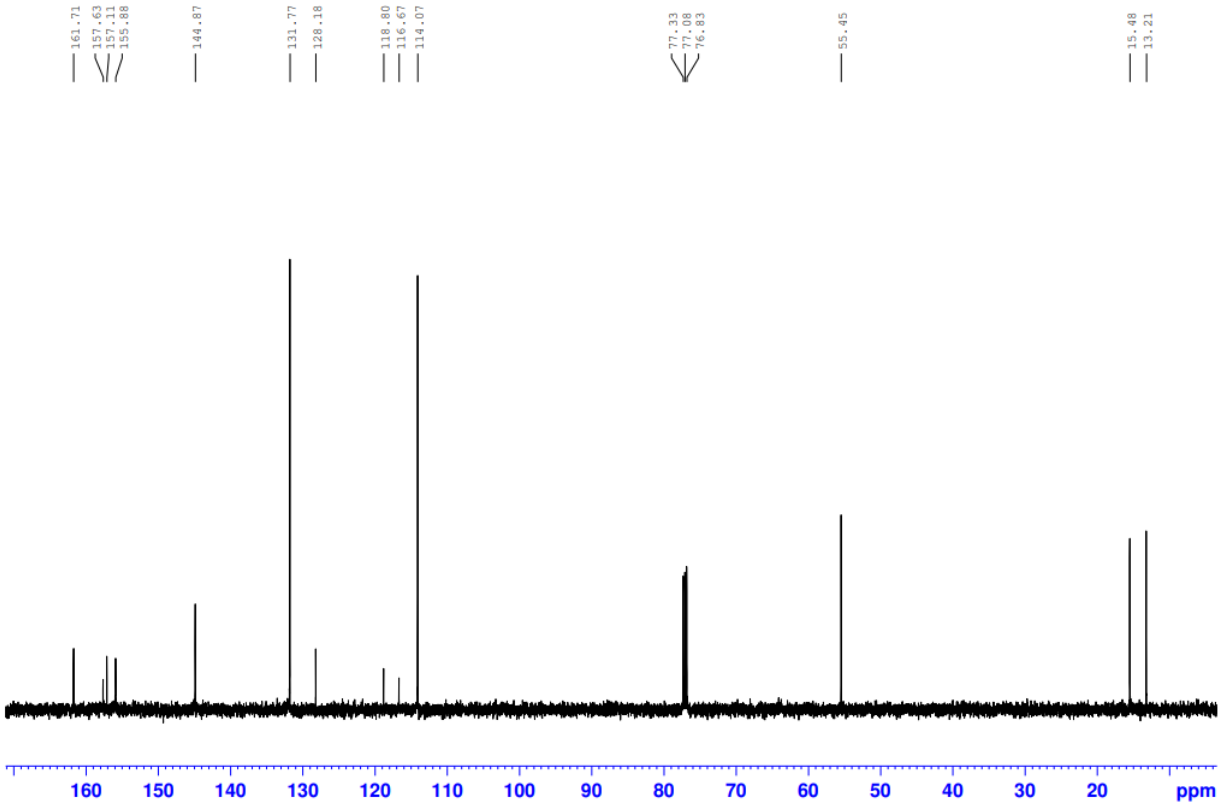


^{1}H-NMR ($CDCl_3$): 9.78 (s, 1H, H-8); 7.49 (d, J = 8.1 Hz, 2H, H-2′,4′); 7.08 (d, J = 8.1 Hz, 2H, H-3′,5′); 3.93 (s, 3H, $OC\underline{H}_3$ on C-4′); 2.87 (s, 3H, $SC\underline{H}_3$ on C-1); 2.54 (s, 3H, $SC\underline{H}_3$ on C-4).

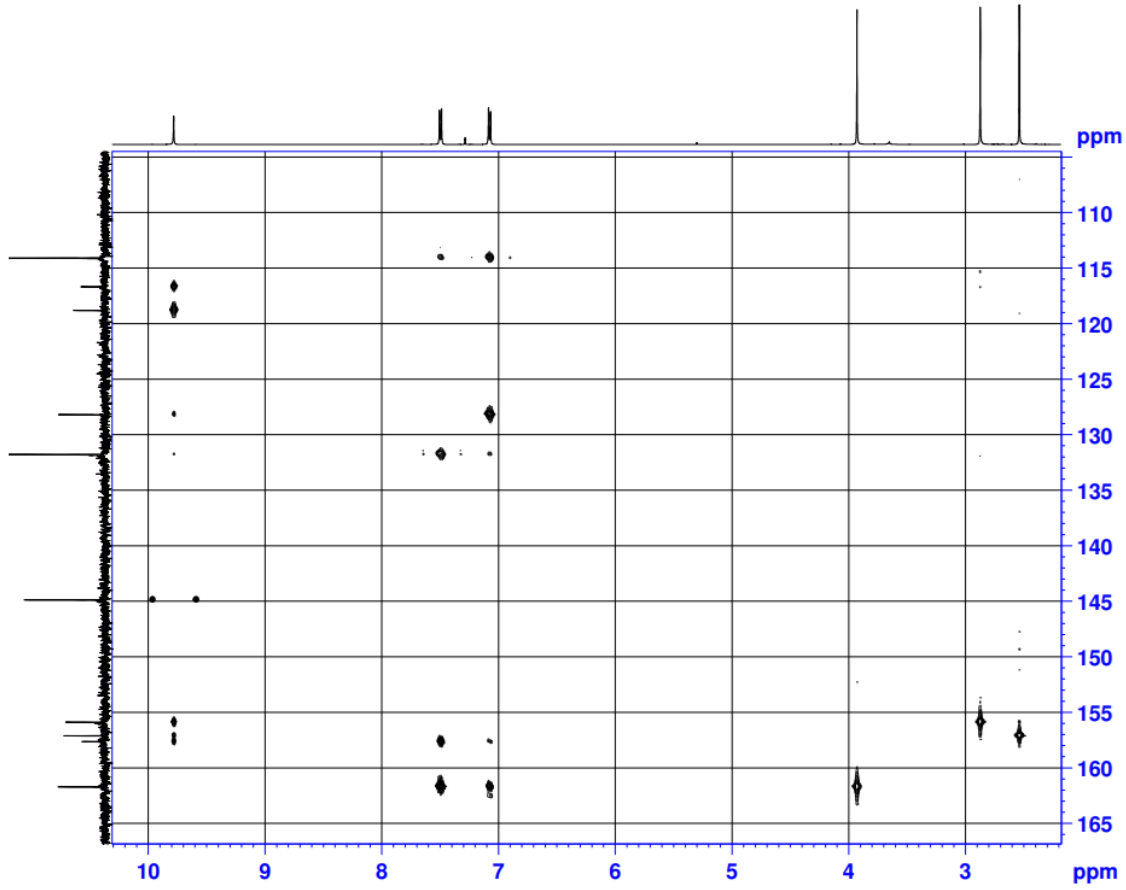


S.1.10 ^{13}C-NMR of **3d**

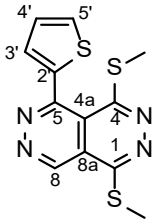
^{13}C-NMR ($CDCl_3$): 161.7 (C-4′); 157.7 (C-5); 157.1 (C-4); 155.9 (C-1); 144.9 (C-8); 131.8 (C-2′,6′); 128.2 (C-3′,5′); 118.8 (C-4a); 116.7 (C-8a); 114.1 (C-3′,5′); 55.5 ($O\underline{C}H_3$ on C-4′); 15.5 ($S\underline{C}H_3$ on C-4); 13.2 ($S\underline{C}H_3$ on C-1).



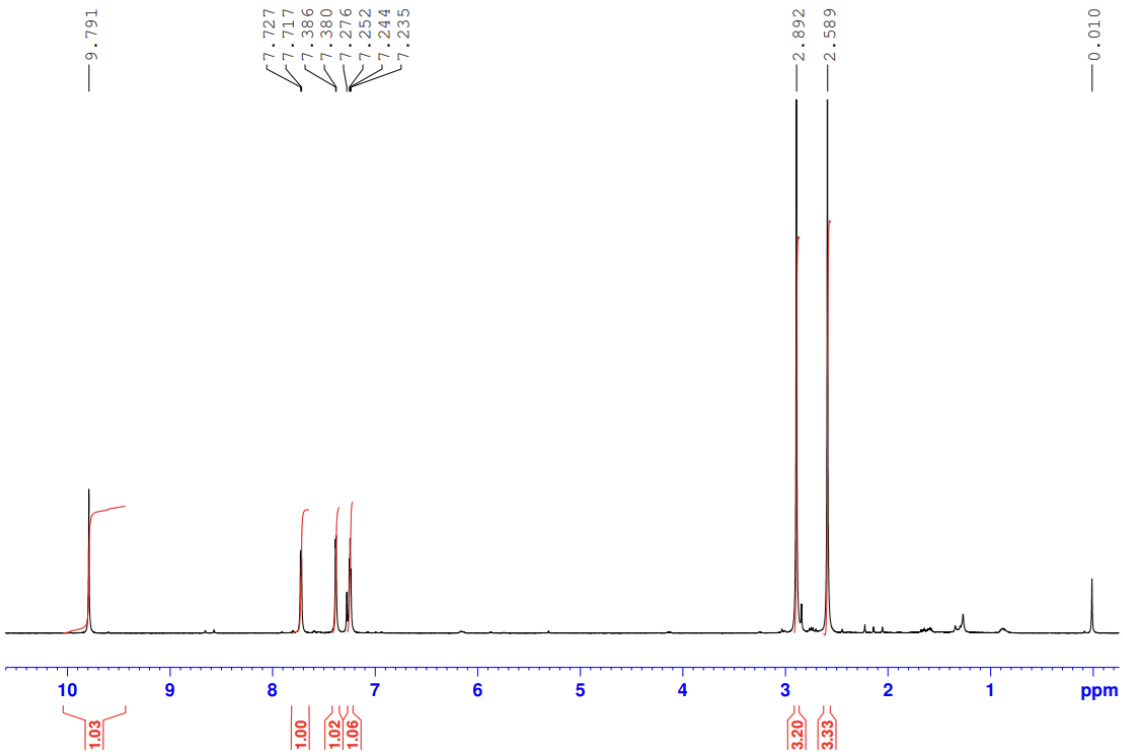
S.1.11. ^{1}H-^{13}C-HMBC spectrum of **3d**



S.1.12. ^{1}H-NMR of **3e**

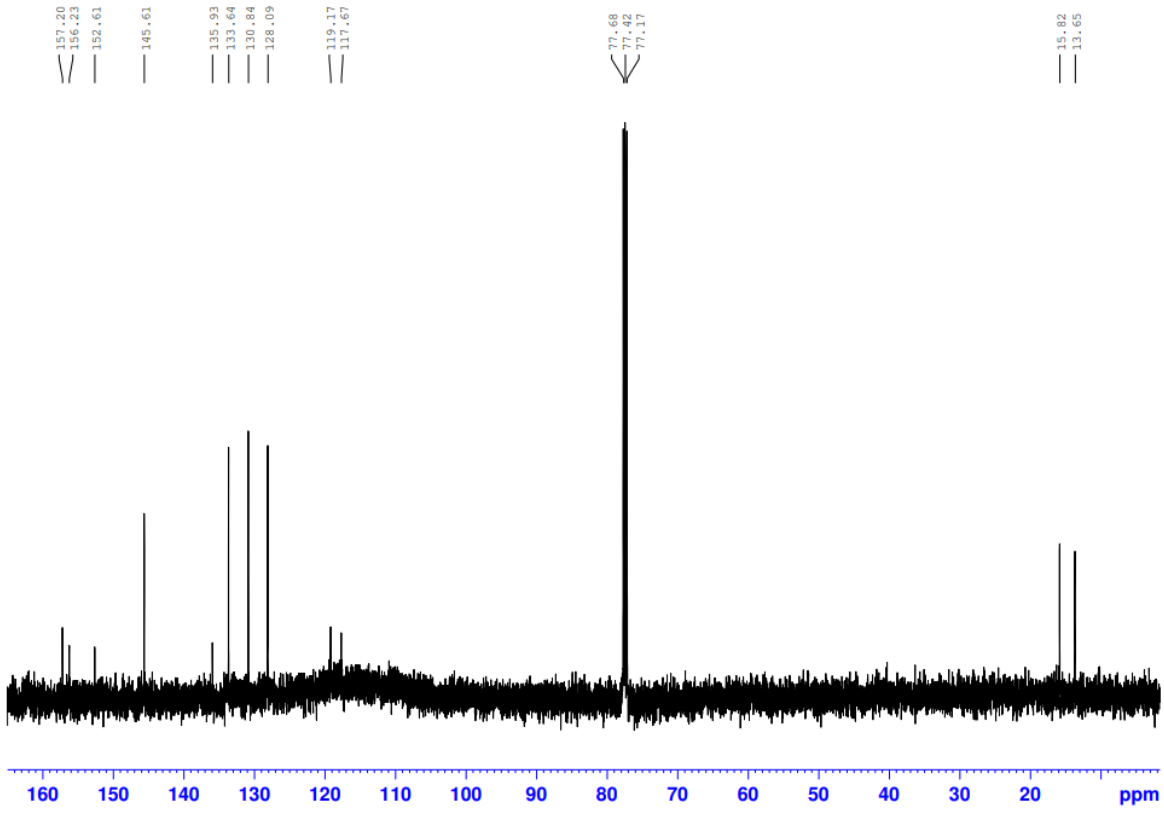


^{1}H-NMR ($CDCl_3$): 9.80 (s, 1H, H-8); 7.72 (d, J = 4.6 Hz, 1H, H-5'); 7.38 (d, J = 2.7 Hz, 1H, H-3'); 7.24 (dd, J = 4.6 Hz and 2.7 Hz, 1H, H-4'); 2.89 (s, 3H, SCH_3 on C-1); 2.59 (s, 3H, SCH_3 on C-4).

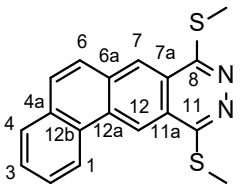


S.1.13. ^{13}C-NMR of **3e**

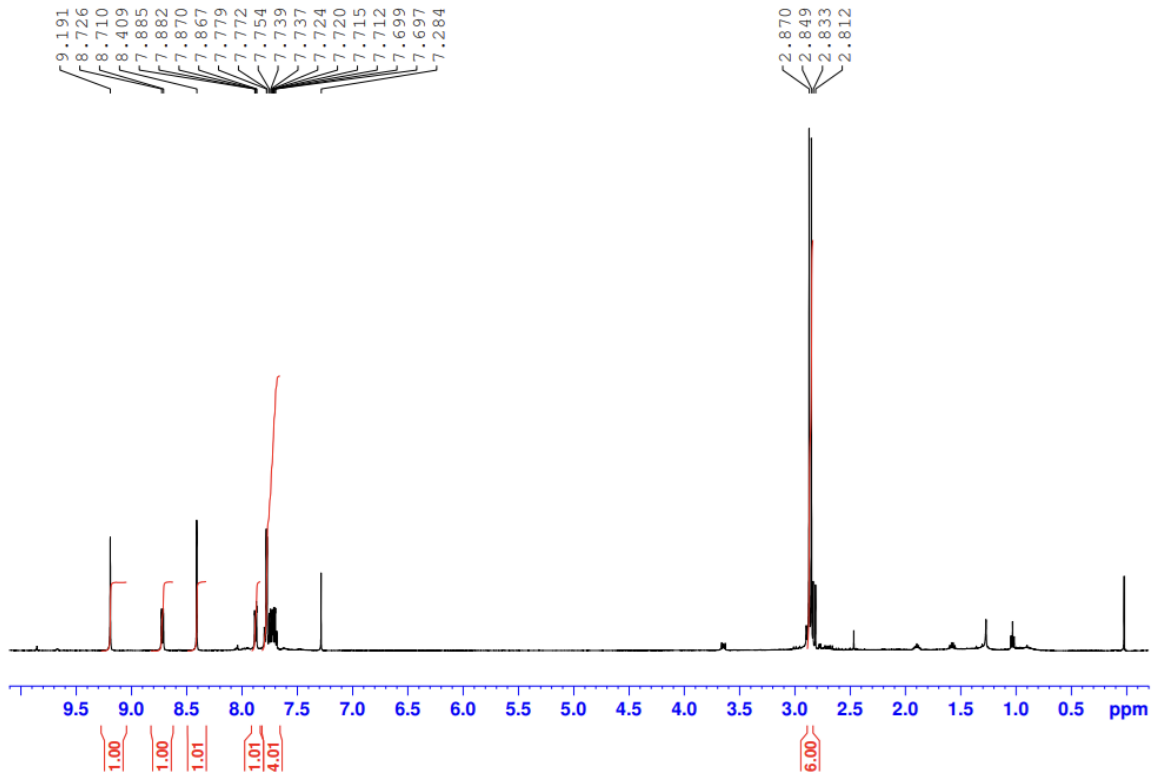
^{13}C-NMR ($CDCl_3$): 157.2 (C-4); 156.2 (C-1); 152.6 (C-5); 145.6 (C-8); 135.9 (C-2′); 133.7 (C-3′); 130.9 (C-5′); 128.1 (C-4′); 119.2 (C4a); 117.7 (C-8a); 15.8 (S<u>C</u>H$_3$ on C-4); 13,6 (S<u>C</u>H$_3$ on C-1).



S.1.14. ^{1}H-NMR of **5bc**

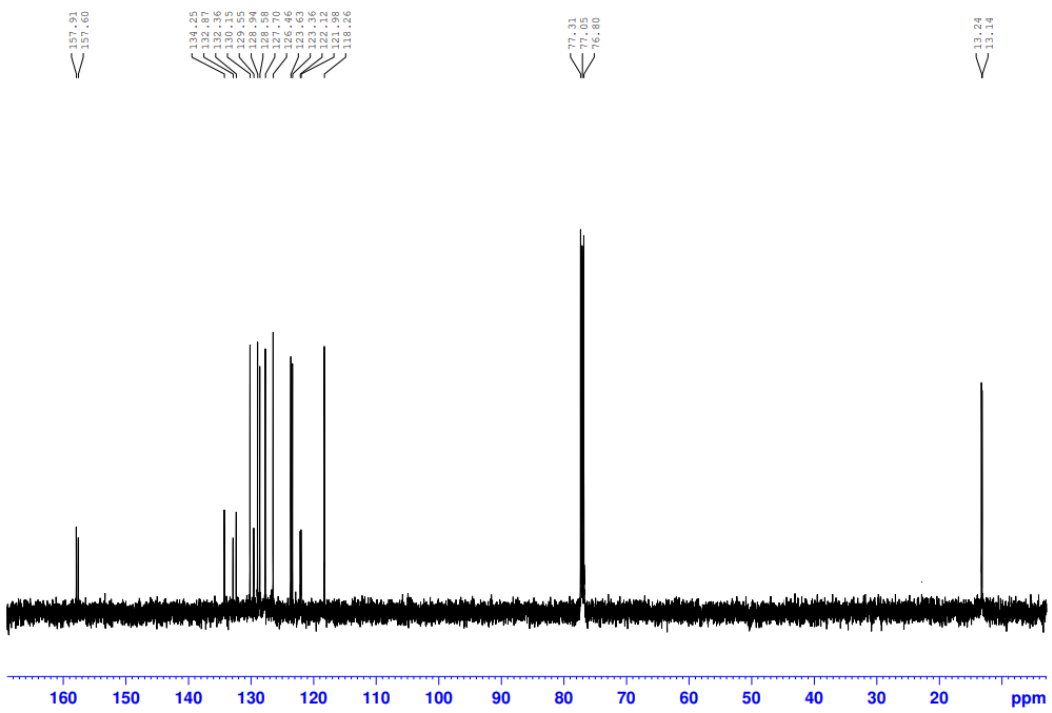


^{1}H-NMR ($CDCl_3$): 9.19 (s, 1H, H-12); 8.72 (br d, *J* = 7.7 Hz, 1H, H-1); 8.41 (s, 1H, H-7); 7.88 (br d, *J* = 7.7 Hz, 1H, H-4); 7.79 and 7.71 (A and B part of an *AB* spin system, J_{AB} = 9.1 Hz, 2x1H, H-6 and H-5, respectively); 7.74 (td, *J* = 7.7 Hz and 1.5 Hz, 1H, H-2); 7.70 (td, *J* = 7.7 Hz and 1.5 Hz, 1H, H-3); 2.85 (s, 3H, SC<u>H</u>$_3$ on C-8); 2.87 (s, 3H, SC<u>H</u>$_3$ on C-11).

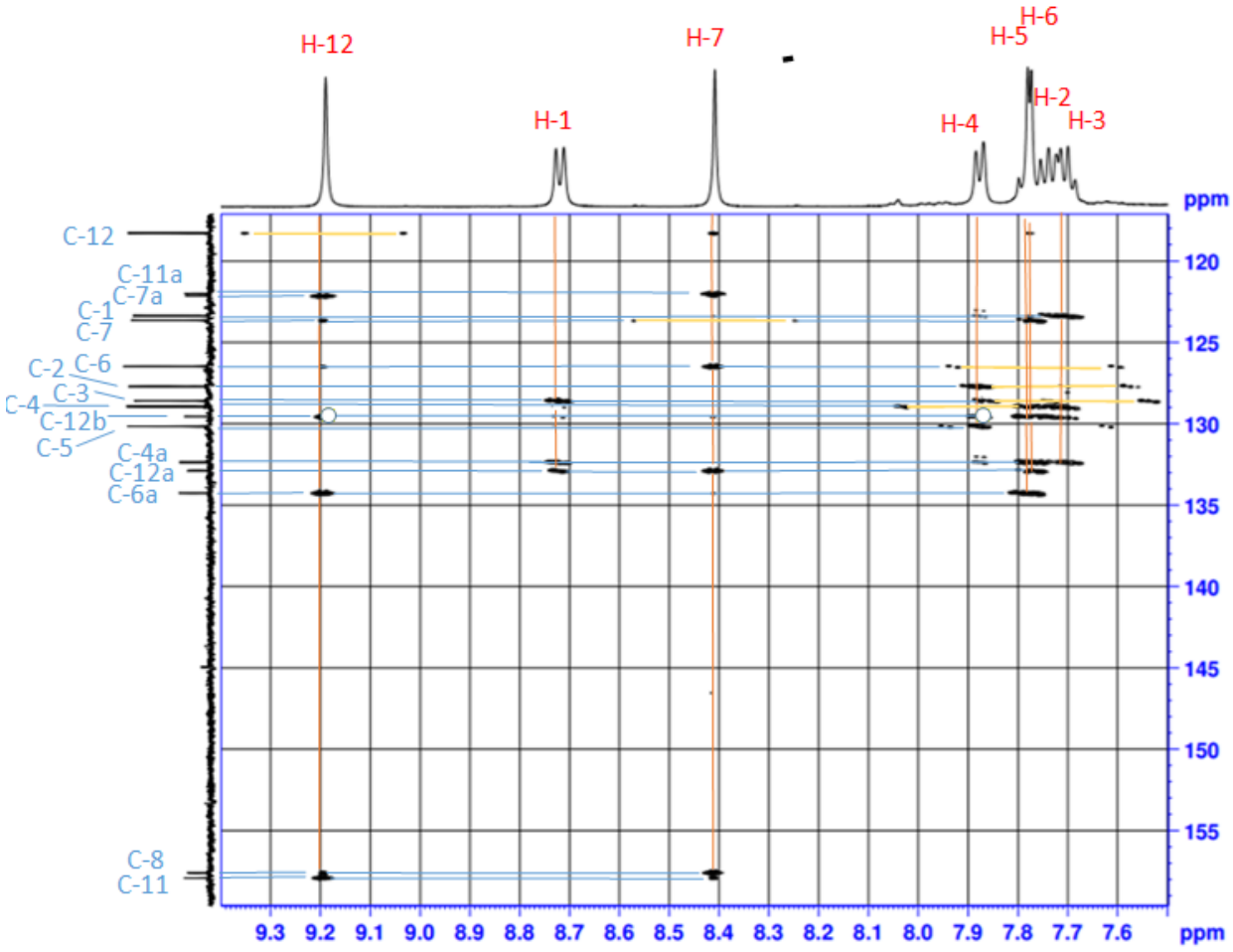


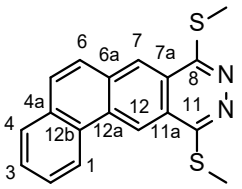
S.1.15. ^{13}C-NMR of **5bc**

^{13}C-NMR ($CDCl_3$): 157.9 (C-11); 157.6 (C-8); 134.3 (C-6a); 132.9 (C-12a); 132.4 (C-4a); 130.6 (C-5); 129.6 (C-12b); 129.0 (C-4); 128.6 (C-3); 127.7 (C-2); 126.5 (C-6); 125.6 (C-7); 123.4 (C-1); 122.1 (C-7a); 122.0 (C-11a); 118.3 (C-12); 13.2 (s, 3H, SC<u>H</u>$_3$ on C-8); 13.1 (s, 3H, SC<u>H</u>$_3$ on C-11).



S.1.16. ^{1}H-^{13}C-HMBC spectrum of **5bc** with presentation of the diagnostic cross-peak correlations providing the base of the structural elucidation. The horizontal yellow lines connect the „satellite" cross peaks generated by single bond ^{1}H-^{13}C correlations.

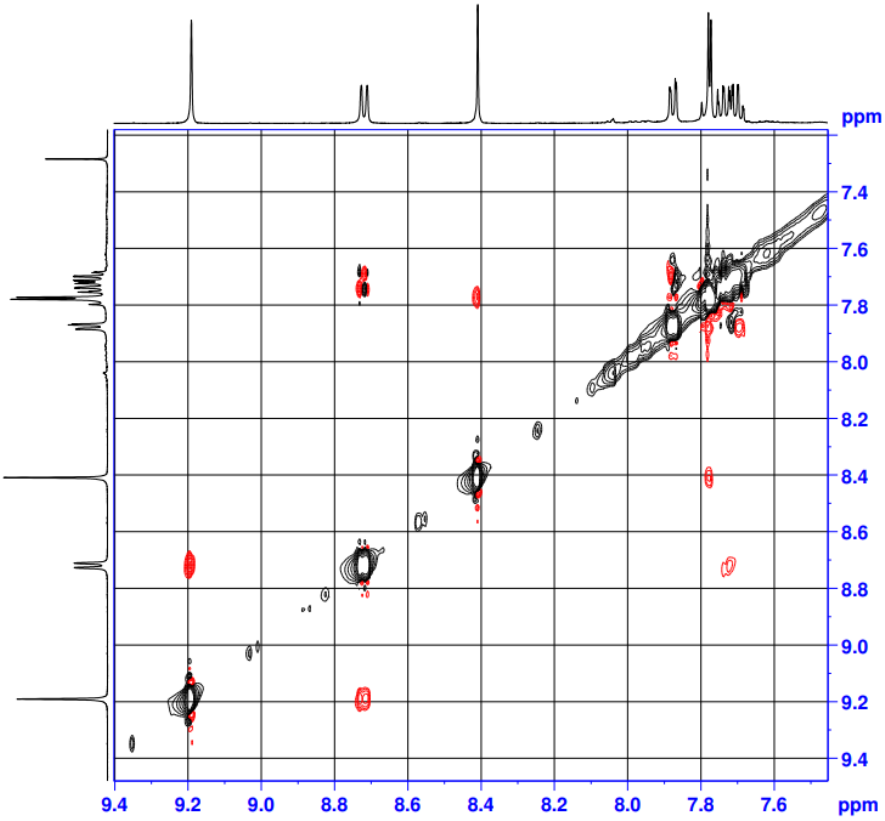




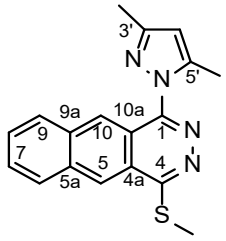
Diagnostic correlations discernible in the ^{1}H-^{13}C HMBC spectrum of **5bc.**

^{1}H-signal	Correlated ^{13}C-signals						
H-12	C-12 (satellites)	C-7a	C-7 (weak)	C-12b	C-6a	C-8	C-11
H-1	C-3	C-4a	C-12a				
H-7	C-12 (weak)	C-11a	C-7 (satellites)	C-5	C-12a	C-8	C-11
H-4	C-2	C-3	C-4 (satellites)	C-12b			
H-5	C-5 (satellites)	C-4a	C-12b	C-6a	C-4a		
H-6	C-6 (satellites)	C-7	C-12a	C-4a			
H-2	C-1	C-2 (satellites)	C-4	C-12b			
H-3	C-1	C-3 (satellites)	C-4a				

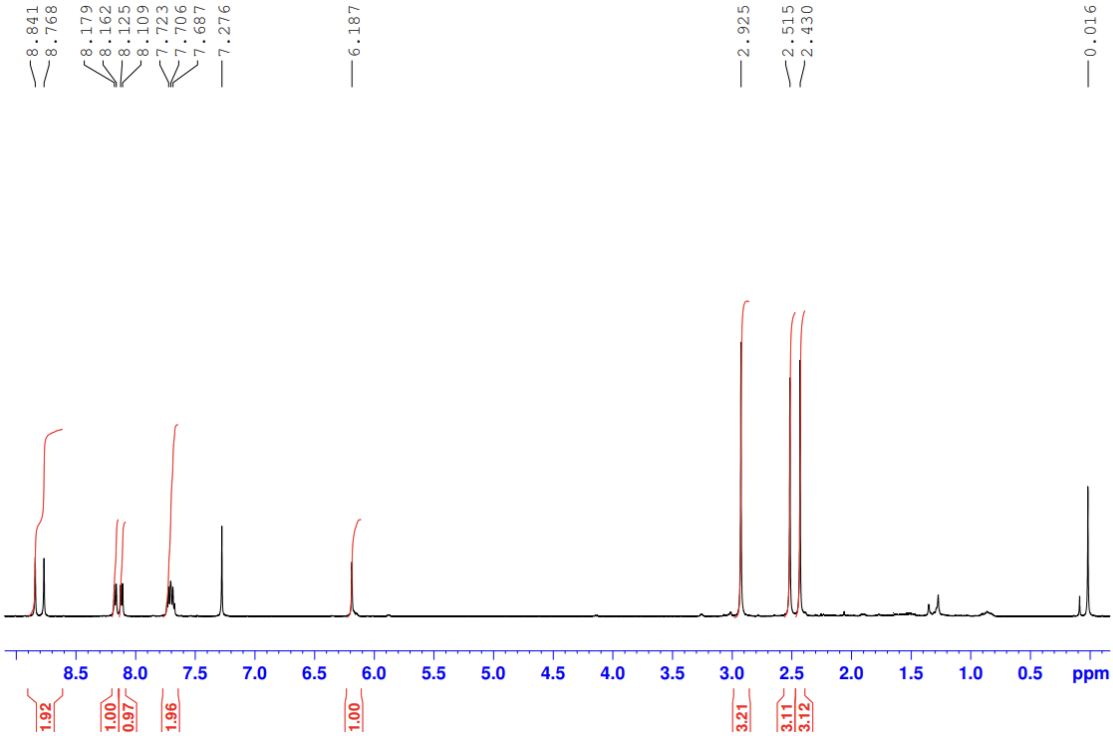
S.1.17. NOESY of **5bc**



S.1.18. . ^{1}H-NMR of **6a**

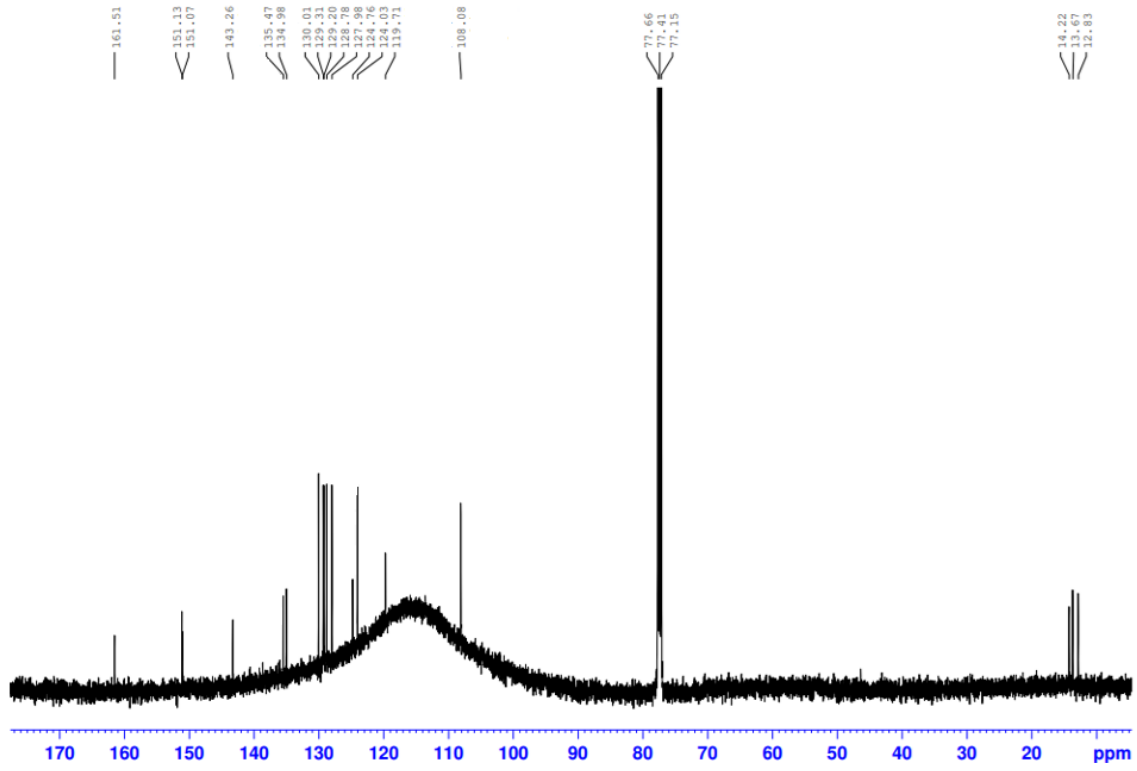


^{1}H-NMR ($CDCl_3$): 9.49 (s, 1H, H-12); 8.90 (br d, *J* = 8.1 Hz, 1H, H-1); 8.78 (s, 1H, H-7); 7.93 (br d, *J*=8.0 Hz, 1H, H-1); 7.86 and 7.84 (A and B part of an AB spin system, J_{AB} = 9.2 Hz, 2x1H, H-5 and H-6, respectively); 7.80 (t, *J* = 8.0 Hz, 1H, H-2); 7.75 (t, *J* = 8.0 Hz, 1H, H-3); 6.18 (s, 1H, H-4'); 2.96 (s, 3H, SCH_3); 2. 52 (s, 3H, CH_3 on C-5'); 2.43 (s, 3H, CH_3 on C-3').

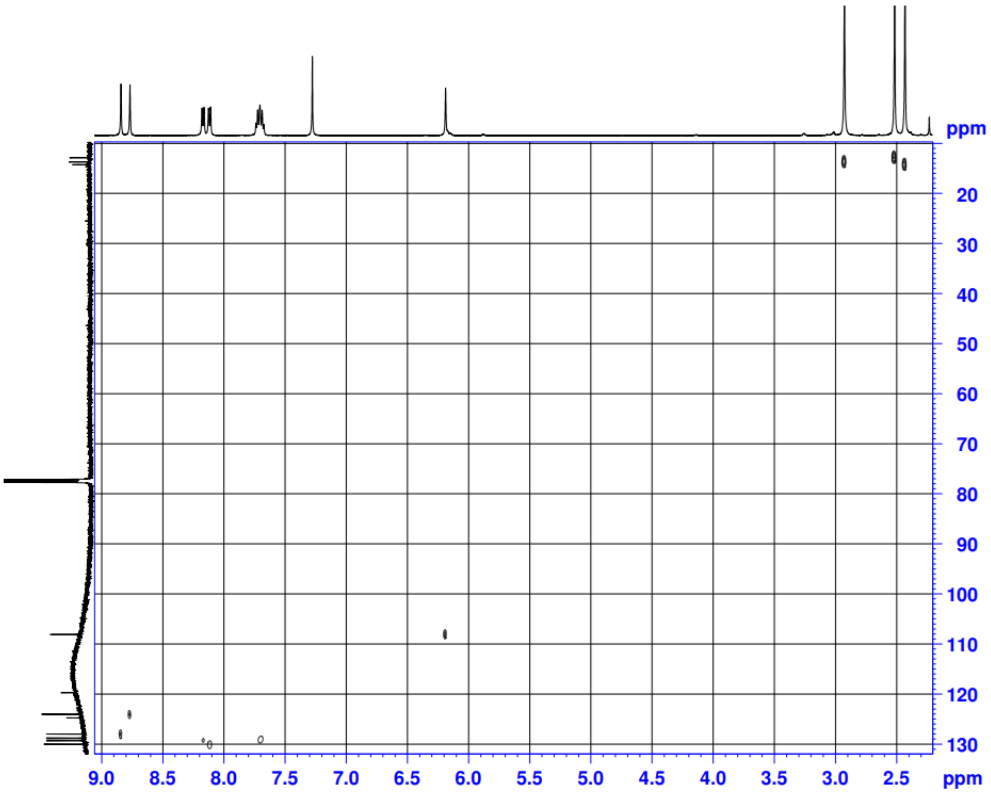


S.1.19. ^{13}C-NMR of **6a**

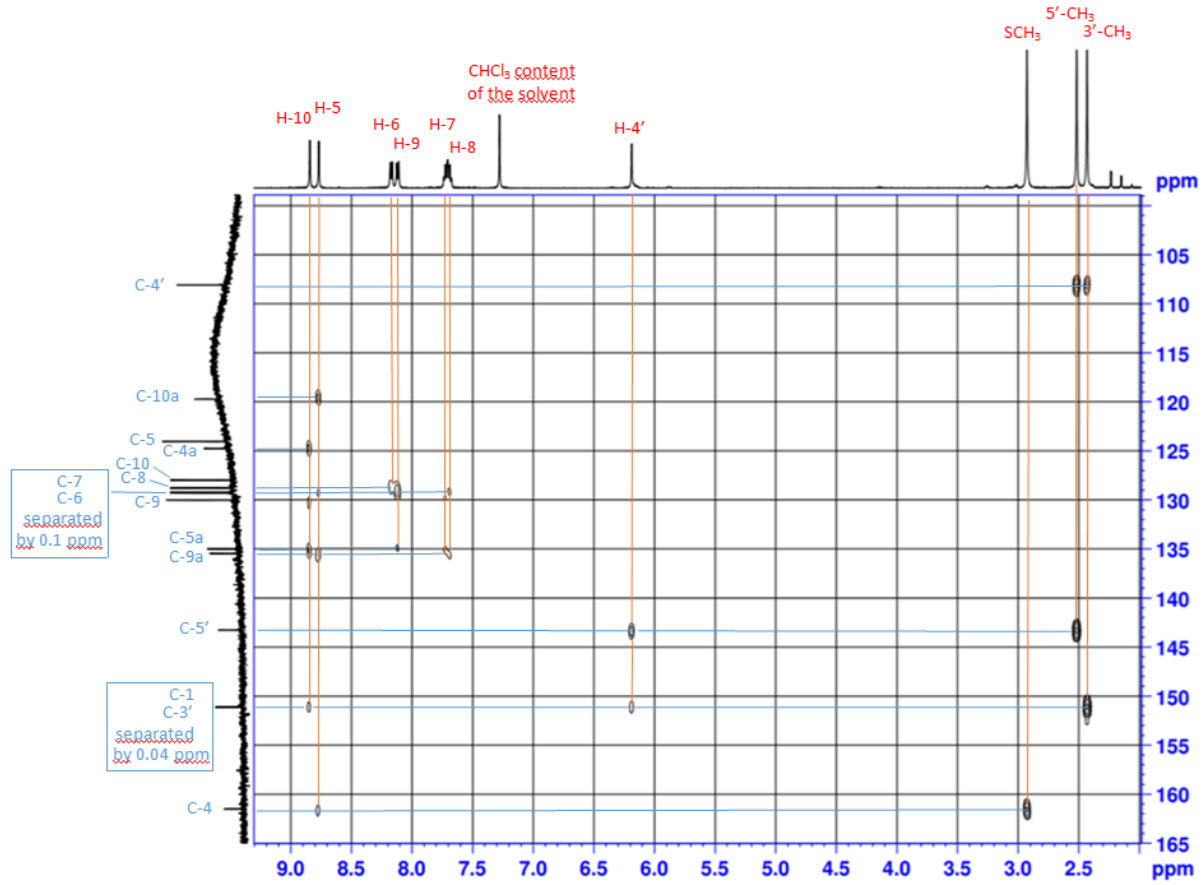
^{13}C-NMR ($CDCl_3$): 161.4 (C-11); 151.2 (C-3'); 150.9 (C-8); 143.3 (C-5'); 135.4 (C-6a), 133.7 (C-12a); 133.1 (C-4a); 130.6 (C-5); 130.1 (C-12b); 129.5 (C-4); 129.3 (C-3); 128.2 (C-2); 127.6 (C-6); 127.3 (C-7); 125.5 (C-11a); 124.1 (C-1); 120.4 (C-7a); 118.4 (C-12); 108.2 (C-4'); 14.2 (CH_3 on C-3'); 13.8 (SCH_3), 12.9 (CH_3 on C-5').

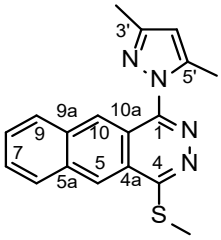


S.1.20. HSQC spectrum of **6a**



S.1.21. ^{1}H-^{13}C-HMBC spectrum of **6a**

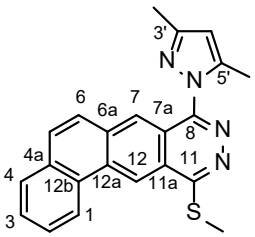




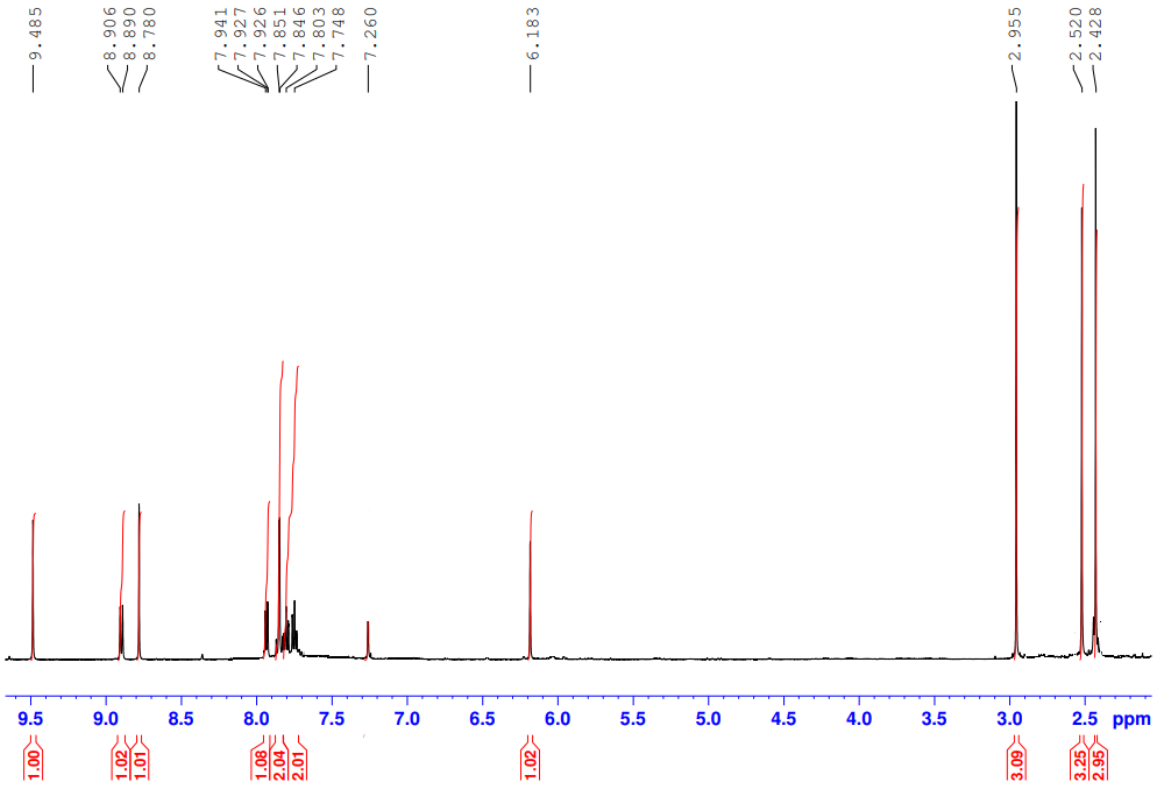
Diagnostic correlations discernible in the ^{1}H-^{13}C HMBC spectrum of **6a**.

^{1}H-signal	Correlated ^{13}C-signals			
H-10	C-4a	C-5a	C-9	C-1
H-5	C-10a	C-9a	C-4	
H-6	C-8			
H-9	C-7	C-5a		
H-8	C-6a	C-9a		
H-7	C-9	C-5a		
H-4′	C-5′	C-3′		
SCH_3	C-4			
5′-CH_3	C-4′	C-5′		
3′-CH_3	C-4′	C-3′		

S.1.22. ^{1}H-NMR of **6c**

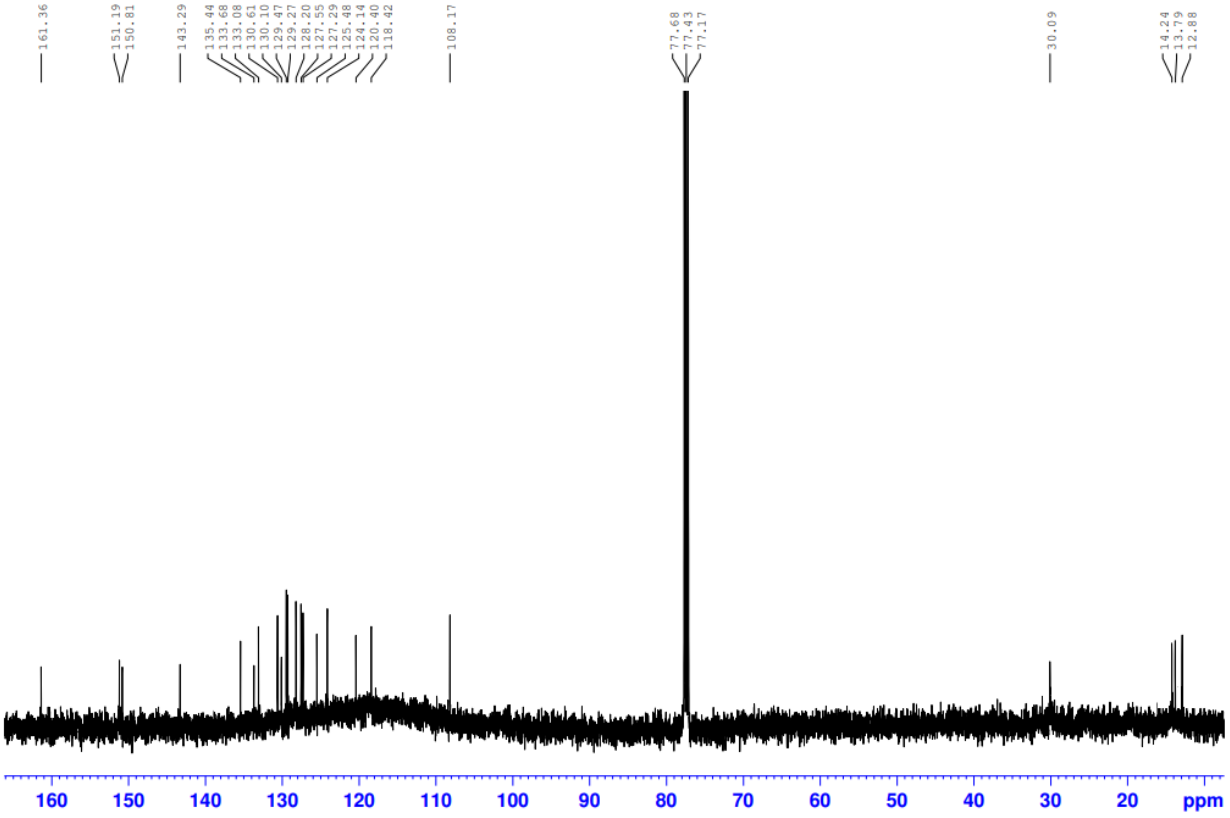


^{1}H-NMR ($CDCl_3$): 9.49 (s, 1H, H-12); 8.90 (br d, J = 8.1 Hz, 1H, H-1); 8.78 (s, 1H, H-7); 7.93 (br d, J=8.0 Hz, 1H, H-1); 7.86 and 7.84 (A and B part of an AB spin system, J_{AB} = 9.2 Hz, 2x1H, H-5 and H-6, respectively); 7.80 (t, J = 8.0 Hz, 1H, H-2); 7.75 (t, J = 8.0 Hz, 1H, H-3); 6.18 (s, 1H, H-4'); 2.96 (s, 3H, SCH_3); 2. 52 (s, 3H, CH_3 on C-5'); 2.43 (s, 3H, CH_3 on C-3').

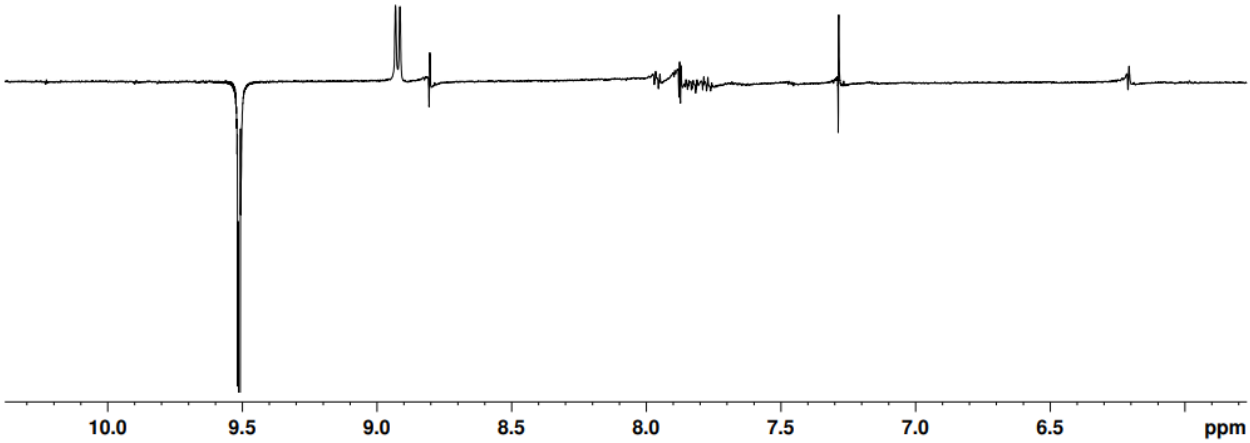


S.1.23. ^{13}C-NMR of **6c**

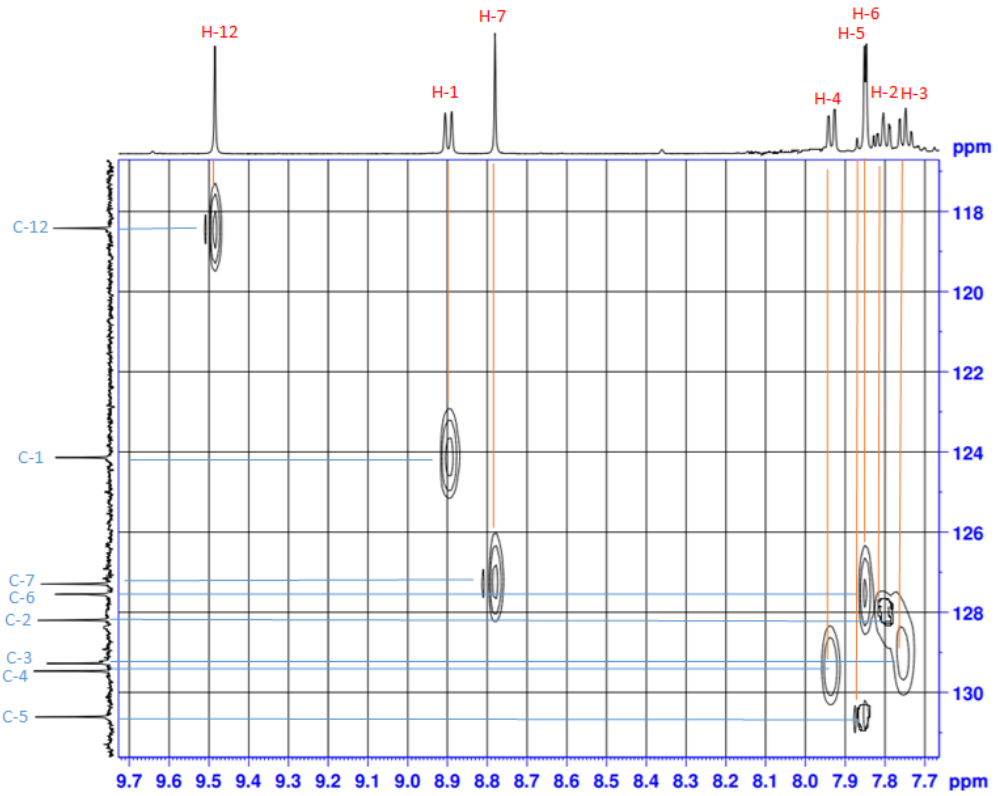
^{13}C-NMR ($CDCl_3$): 161.4 (C-11); 151.2 (C-3′); 150.9 (C-8); 143.3 (C-5′); 135.4 (C-6a), 133.7 (C-12a); 133.1 (C-4a); 130.6 (C-5); 130.1 (C-12b); 129.5 (C-4); 129.3 (C-3); 128.2 (C-2); 127.6 (C-6); 127.3 (C-7); 125.5 (C-11a); 124.1 (C-1); 120.4 (C-7a); 118.4 (C-12); 108.2 (C-4′); 14.2 ($\underline{C}H_3$ on C-3′); 13.8 (S$\underline{C}H_3$), 12.9 ($\underline{C}H_3$ on C-5′).



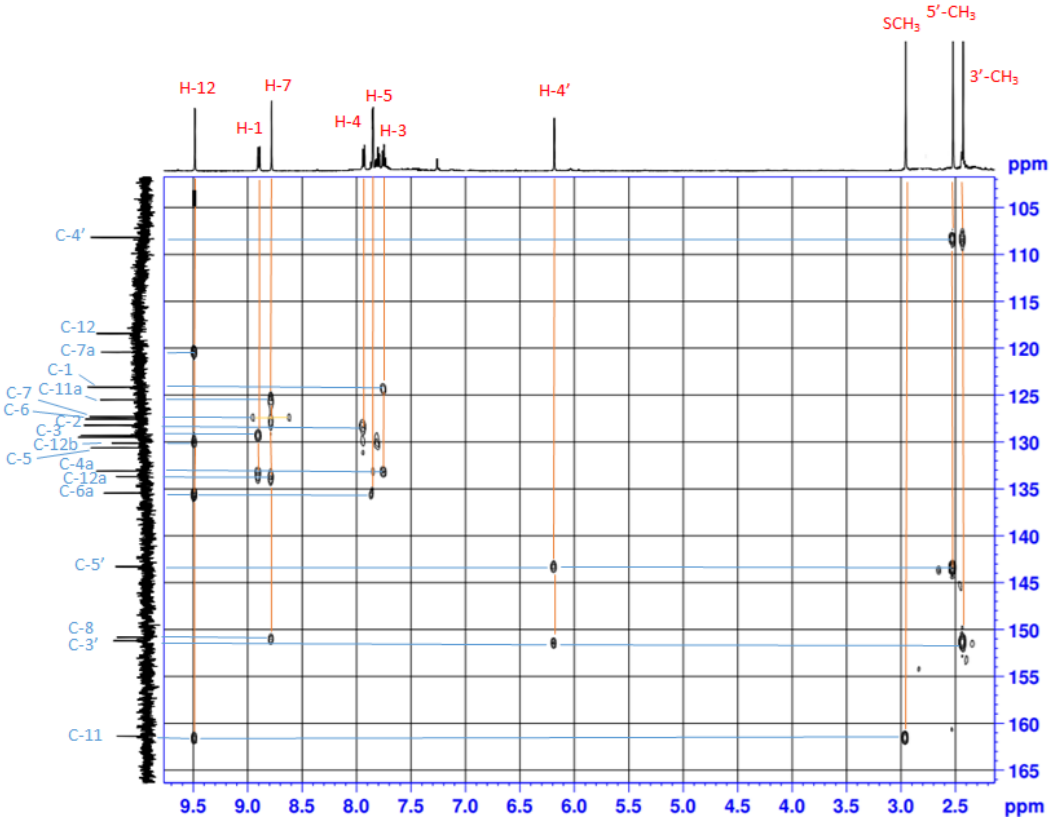
S.1.24. The most diagnostic region of the DNOE spectrum of **6c**

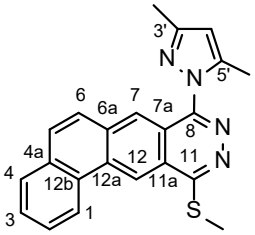


S.1.25. The diagnostic region of the HSQC spectrum of **6c** with indicated correlations explored in structural elucidation.



S.1.26. The diagnostic region of the HMBC spectrum of **6c** with indicated correlations explored in structural elucidation.

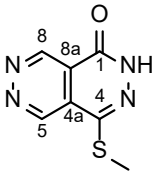




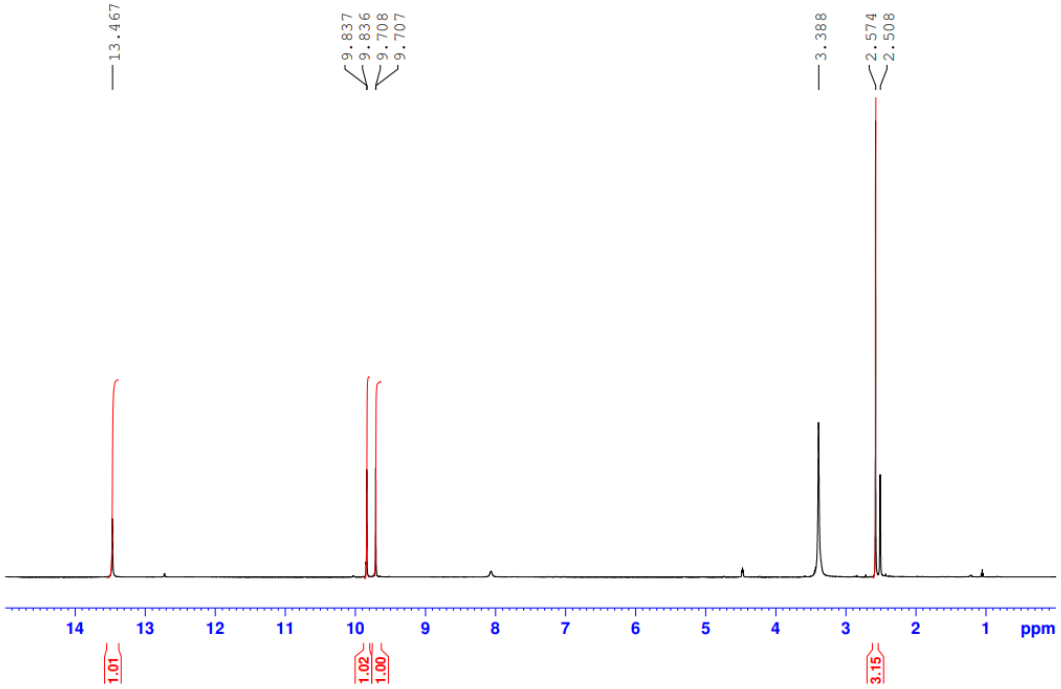
Diagnostic correlations discernible in the ^{1}H-^{13}C HMBC spectrum of **6c**.

^{1}H-signal	Correlated ^{13}C-signals			
H-12	C-7a	C-12b	C-6a	C-11
H-1	C-4a	C-3	C-12a	
H-7	C-11a	C-12a	C-8	C-7 (satellites)
H-4	C-2	C-12b		
H-5	C-6a	C-4a		
H-3	C-1	C-4a		
H-4′	C-3′	C-5′		
SCH_3	C-11			
5′-CH_3	C-5′			
3′-CH_3	C-3′			

S.1.27. ^{1}H-NMR of **7**

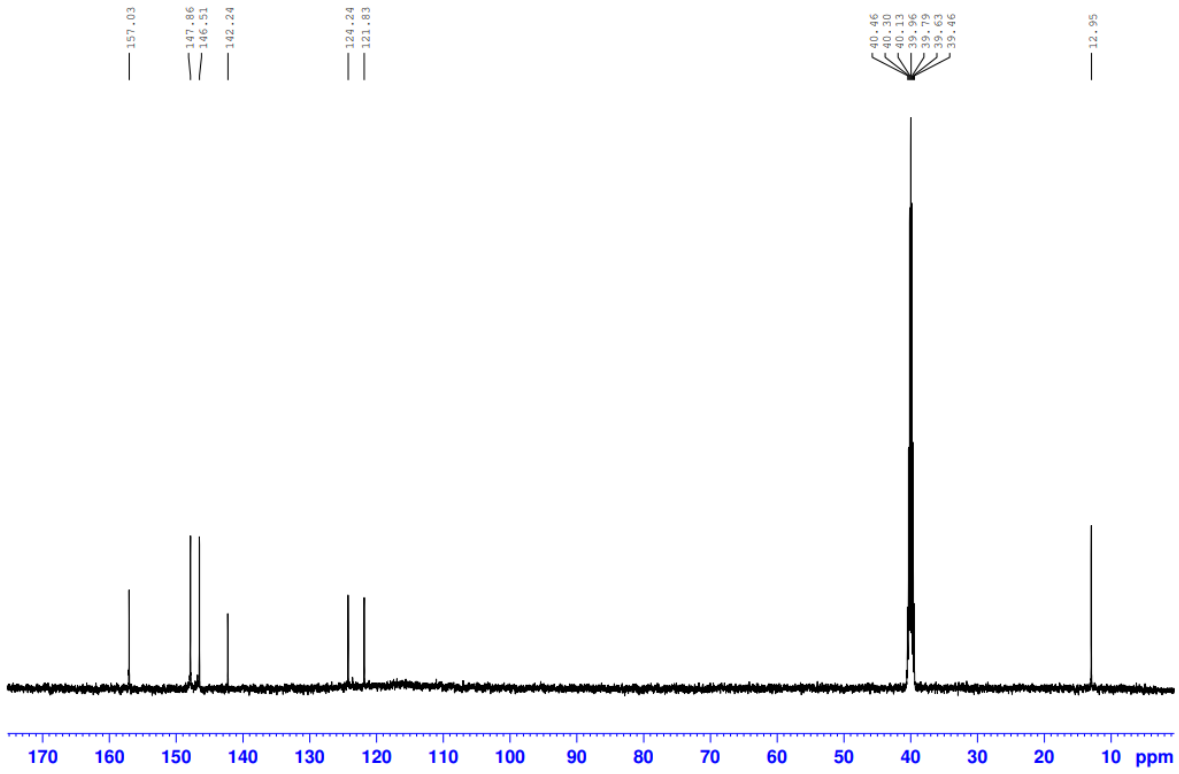


^{1}H-NMR (DMSO-d_6): 13.47 (s, 1H, NH); 9.84 (s, 1H, H-8); 9.71 (s, 1H, H-5); 2.57 (s, 3H, SC<u>H</u>$_3$).

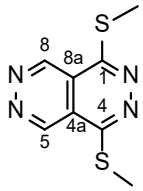


S.1.28. ^{13}C-NMR of **7**

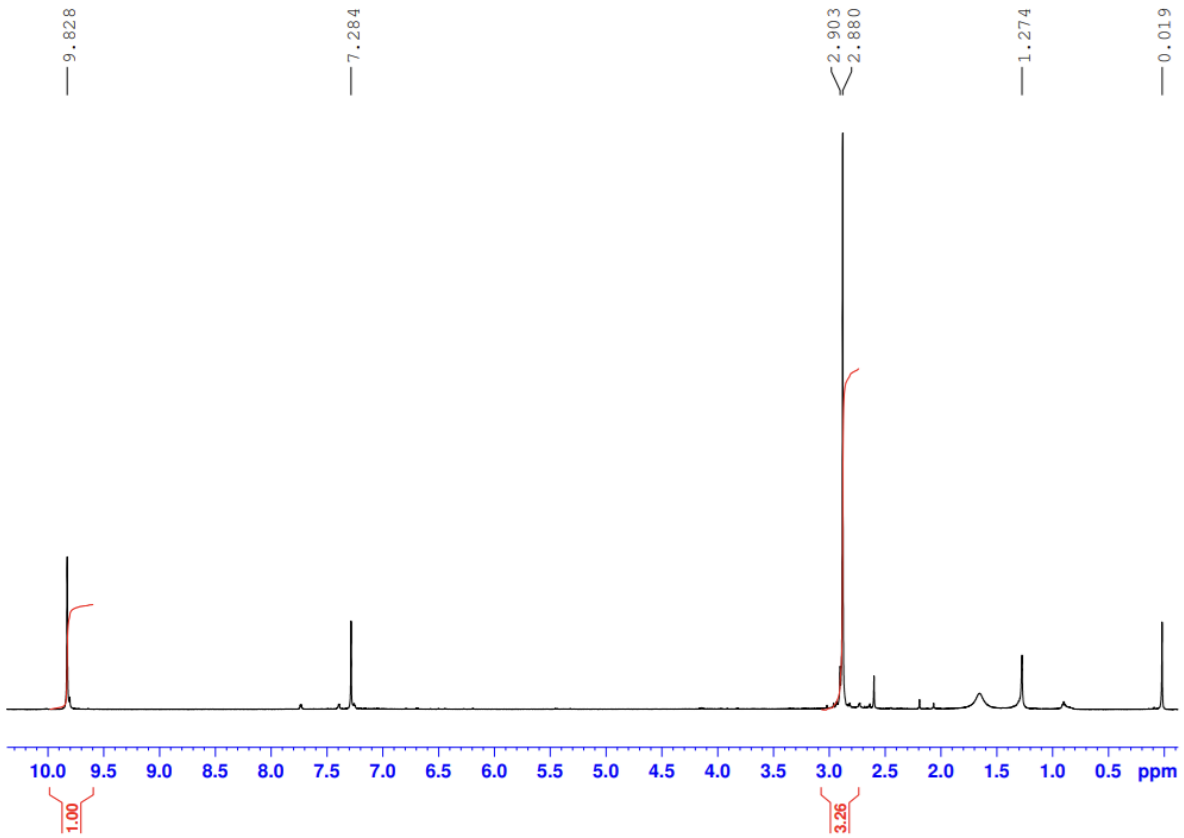
^{13}C-NMR (DMSO-d_6): 157.0 (C-1); 147.9 (C-8); 146.5 (C-5); 142.2 (C-4); 124.3 (C-4a); 121.8 (C-8a); 12.9 (S<u>C</u>H$_3$).



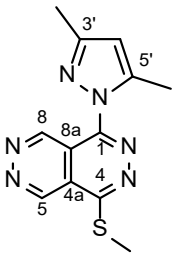
S.1.29. ^{1}H-NMR of **I**



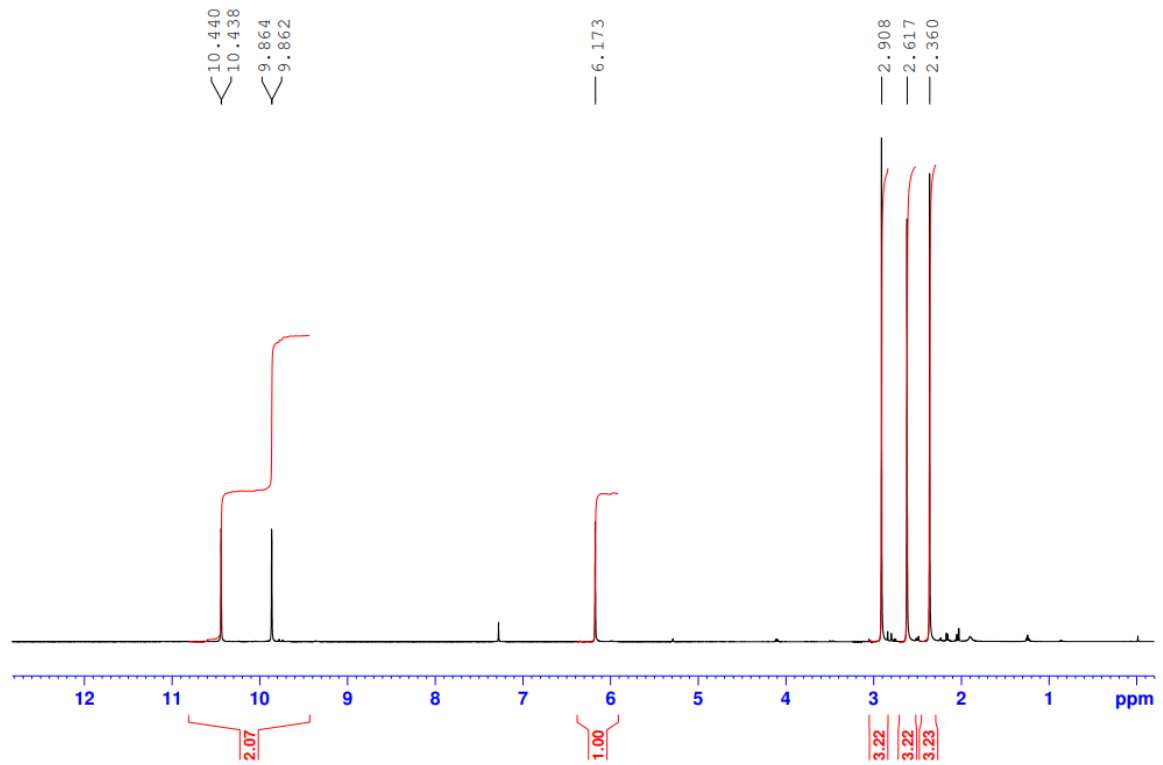
^{1}H-NMR ($CDCl_3$): 9.76 (s, 2H, H-5,8); 2.86 (s, 6H, S<u>C</u>H$_3$ on C-1 and C-4).



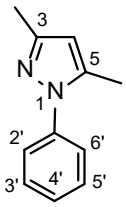
S.1.30. ^{1}H-NMR of **II**



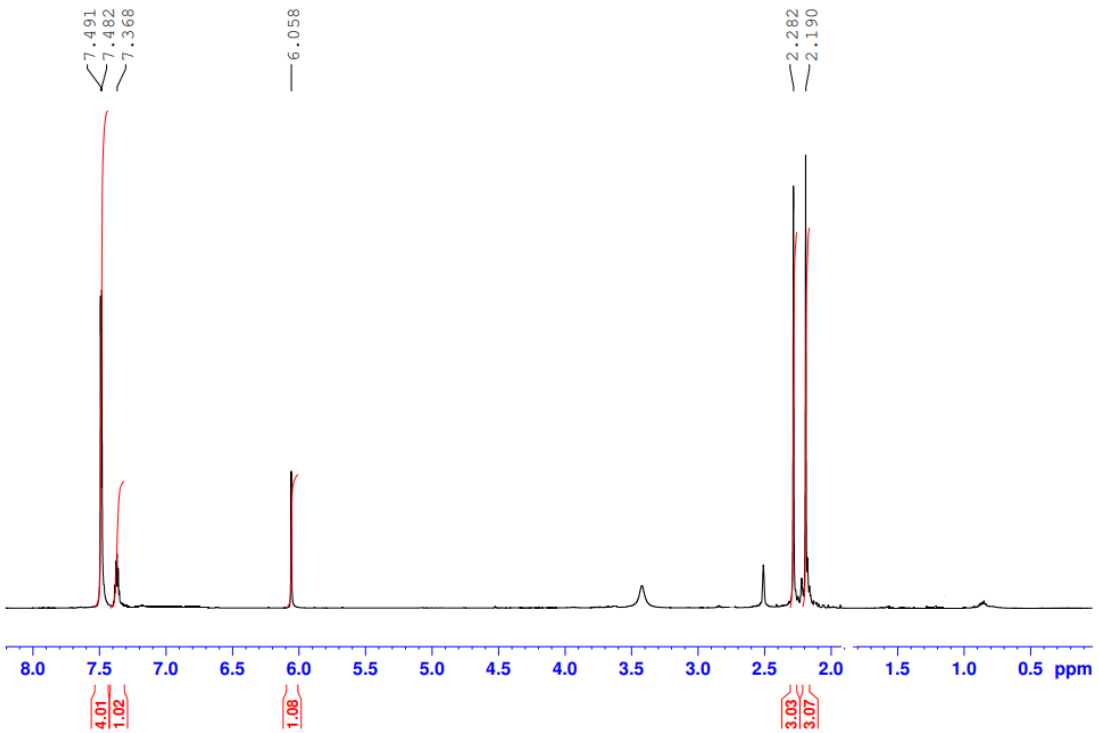
^{1}H-NMR ($CDCl_3$): 10.44 (d, *J* = 1.2 Hz, 1H, H-8); 9.86 (d, *J* = 1.2 Hz, 1H, H-5); 6.17 (s, 1H, H-4′); 2.91 (s, 3H, $SC\underline{H}_3$); 2.62 (s, 3H, $C\underline{H}_3$ on C-5′); 2.36 (s, 3H, $C\underline{H}_3$ on C-3′).



S.1.31. ^{1}H-NMR of **8a**

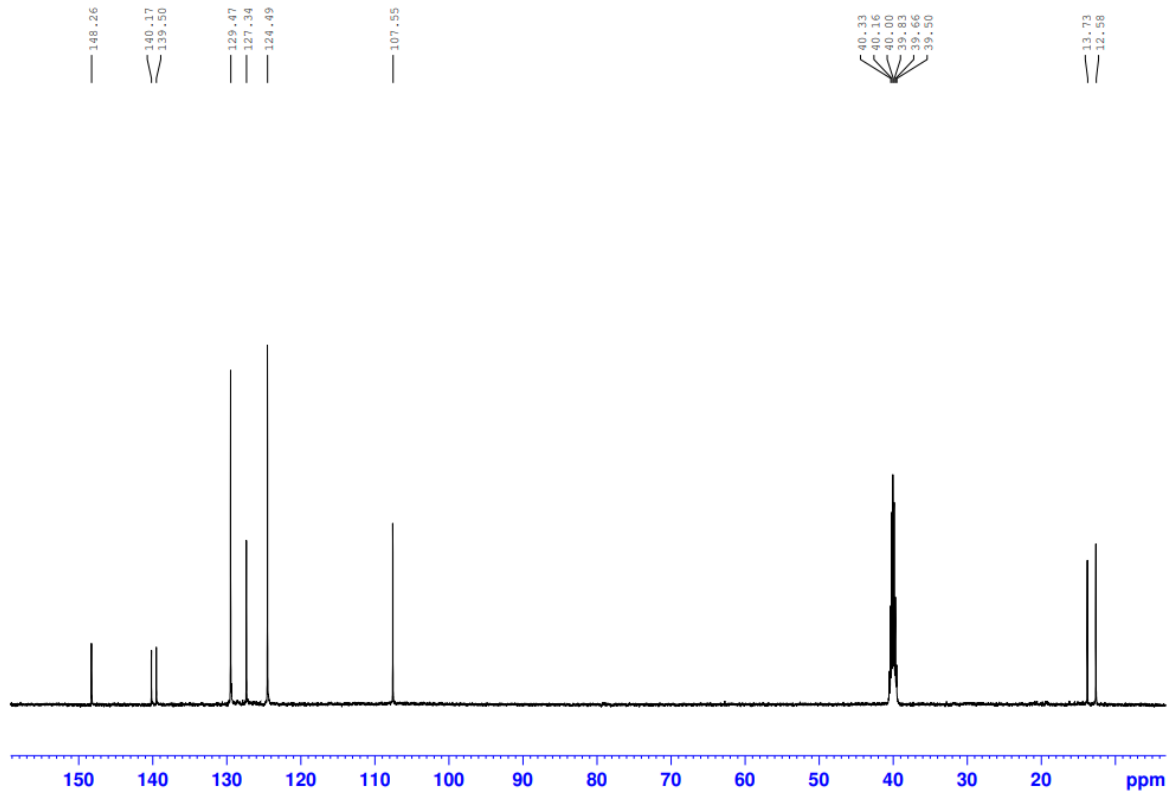


^{1}H-NMR (DMSO-d_6): 7.47 (d, J = 4.2 Hz, 4H, H-2',3',5',6'); 7.37 (m, 1H, H-4') 6.06 (s, 1H, H-4); 2.28 (s, 3H, C$\underline{H}_3$ on C-3); 2.19 (s, 3H, C$\underline{H}_3$ on C-5).

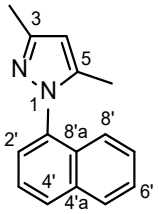


S.1.32. ^{13}C-NMR of **8a**

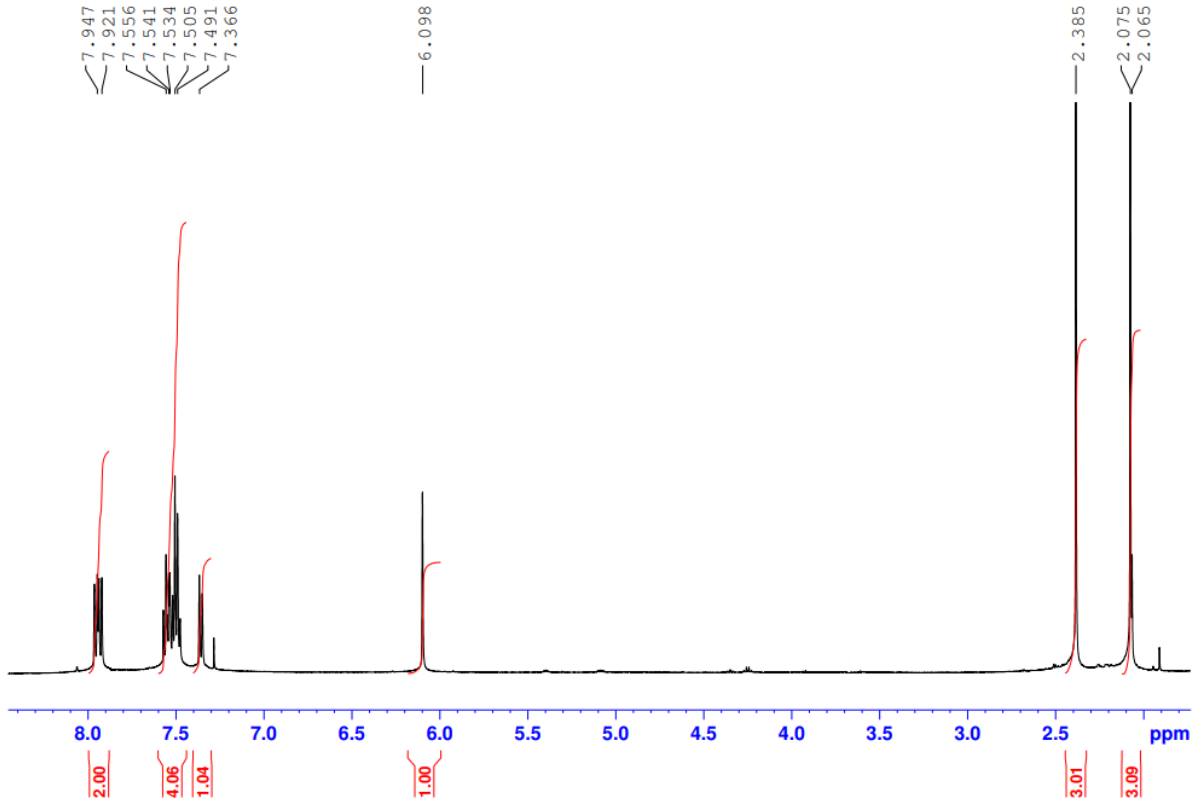
^{13}C-NMR ($CDCl_3$): 149.0 (C-3); 141.5 (C-5); 136.2 (C-1′); 134.2 (C-4′a); 130.9 (C-8′a); 125.4 (C-2′); 125.1 (C-8′); 123.2 (C-4′); 129.3 (C-5′); 127.3 (C-6′); 128.1 (C-3′); 126.6 (C-7′); 105.4 (C-4); 13.7 ($\underline{C}H_3$ on C-5); 11.4 ($\underline{C}H_3$ on C-3).



S.1.33. ^{1}H-NMR of **8b**

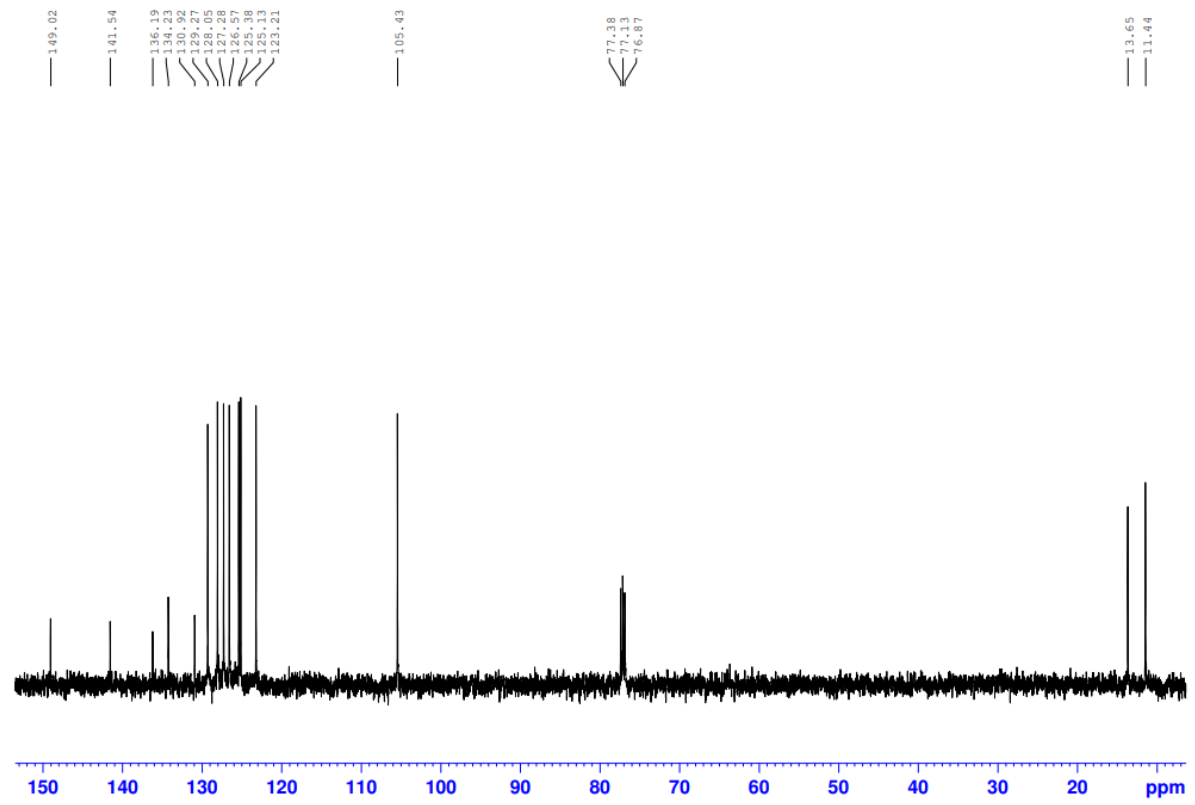


^{1}H-NMR ($CDCl_3$): 7.95 (d, *J* = 8.1 Hz, 1H, H-8′); 7.95 (d, *J* = 8.1 Hz, 1H, H-5′); 7.58–7.48 (overlapping m's, 4H, H-2′,3′,6′,7′); 7.36 (d, *J* = 7.9 Hz, 1H, H-4′); 6.10 (s, 1H, H-4); 2.39 (s, 3H, C<u>H</u>$_3$ on C-3); 2.08 (s, 3H, C<u>H</u>$_3$ on C-5).

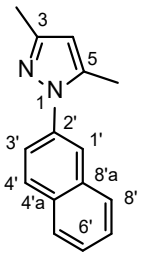


S.1.34. ^{13}C-NMR of **8b**

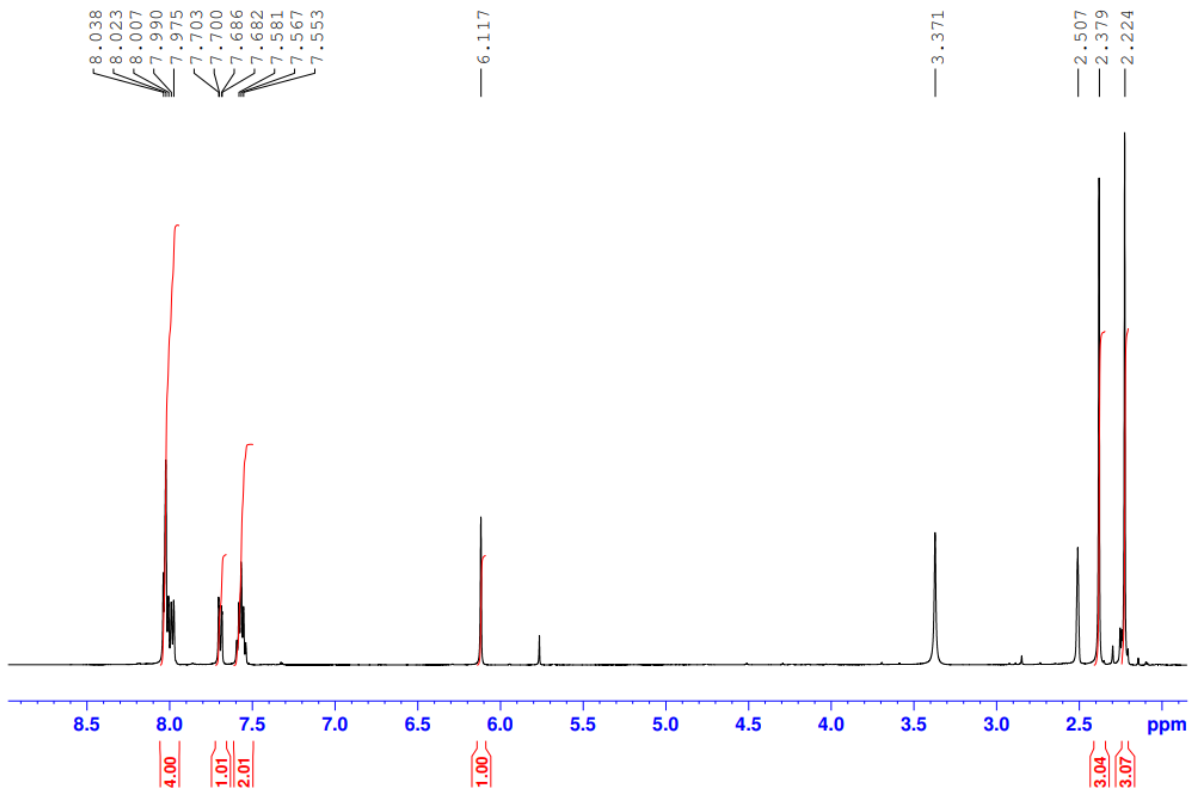
^{13}C-NMR ($CDCl_3$): 149.0 (C-3); 141.5 (C-5); 136.2 (C-1′); 134.2 (C-4′a); 130.9 (C-8′a); 125.4 (C-2′); 125.1 (C-8′); 123.2 (C-4′); 129.3 (C-5′); 127.3 (C-6′); 128.1 (C-3′); 126.6 (C-7′); 105.4 (C-4); 13.7 (<u>C</u>H$_3$ on C-5); 11.4 (<u>C</u>H$_3$ on C-3).



S.1.35. ^{1}H-NMR of **8c**

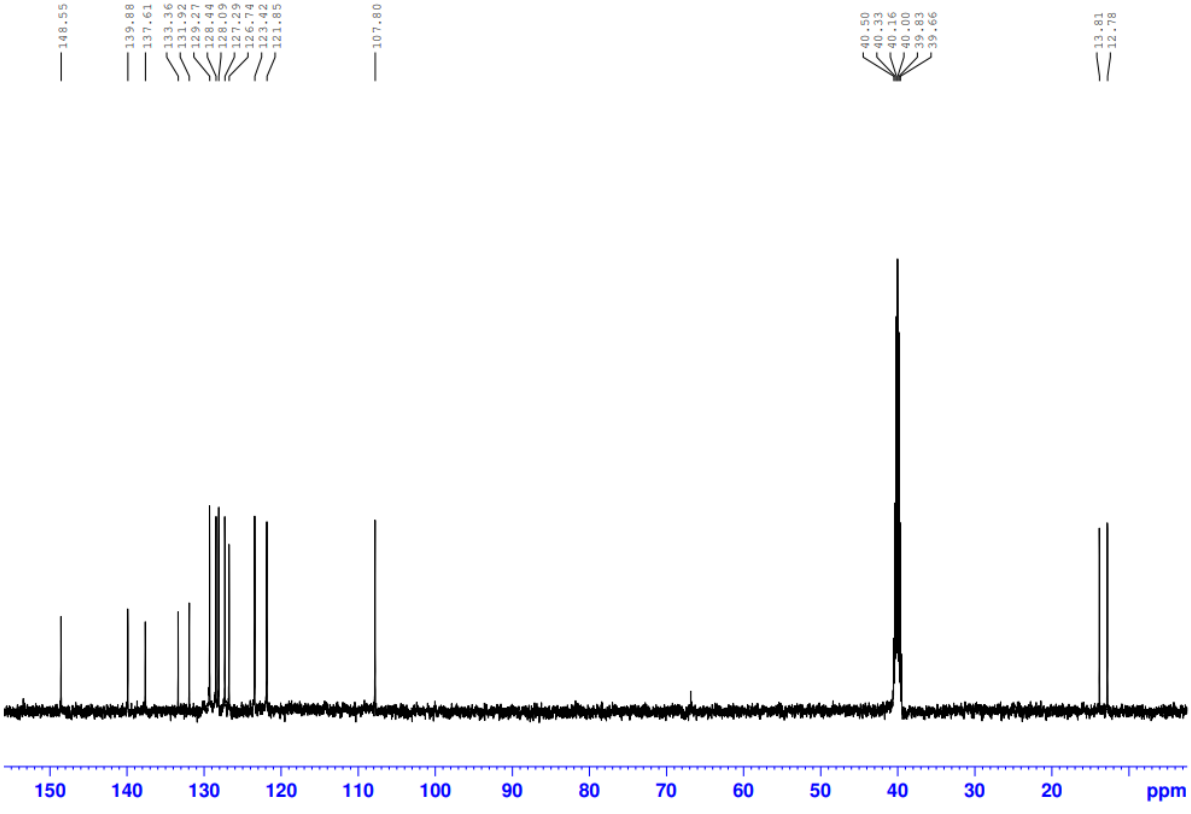


^{1}H-NMR (DMSO-d_6): 8.05–8.00 (three overlapping signals: two d's J = 8.9 Hz and 8.1 Hz, and a br s, 3H, H-4', H-5' and H-1'); 7.98 (d, J = 8.1 Hz, 1H, H-8'); 7.69 (dd, J = 8.9 Hz and 1.8 Hz,1H, H-3'); 7.58 (~t, J ~8 Hz, 1H, H-7'); 7.55 (~t, J ~8 Hz, 1H, H-6'); 6.11 (s, 1H, H-4); 2.38 (s, 3H, C$\underline{H}_3$ on C-3); 2.22 (s, 3H, C$\underline{H}_3$ on C-5).

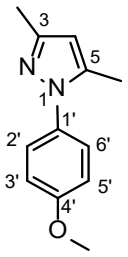


S.1.36. ^{13}C-NMR of **8c**

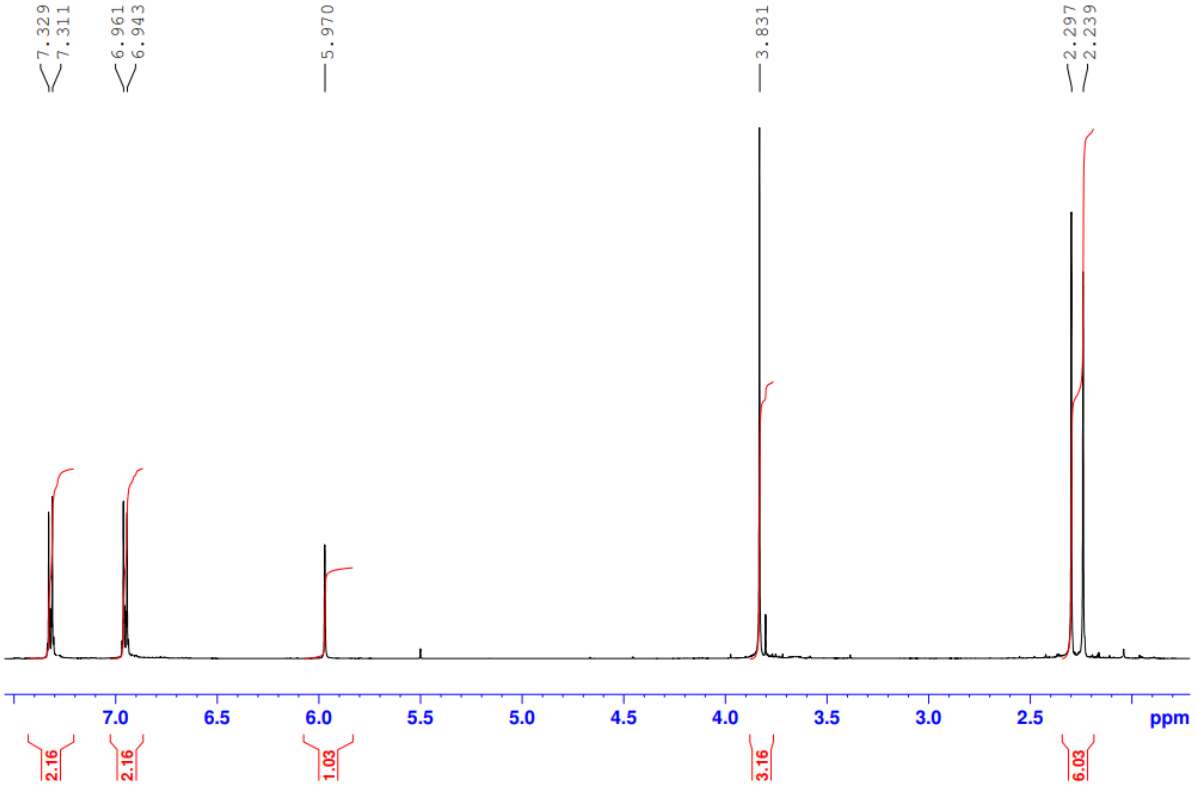
^{13}C-NMR (DMSO-*d*$_6$): 148.6 (C-3); 139.9 (C-5); 137.6 (C-2′); 133.4 (C-8′a); 131.9 (C-4′a); 129.3 (C-4′); 128.5 (C5′); 128.1 (C-8′); 127.3 (C-7′); 126.7 (C-6′); 123.4 (C-3′); 121.9 (C-1′); 107.8 (C-4); 13.8 (C$\underline{\text{H}}_3$ on C-5); 12.8 (C$\underline{\text{H}}_3$ on C-3).



S.1.37. ^{1}H-NMR of **8d**

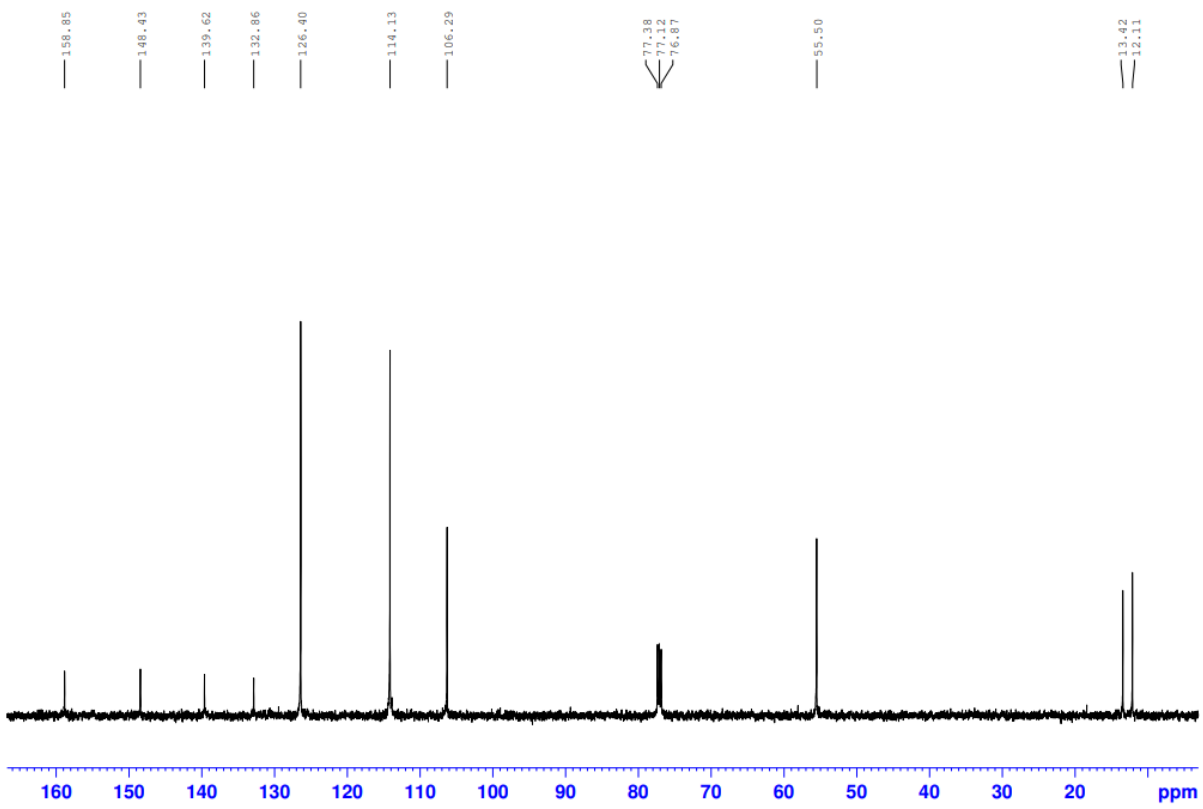


^{1}H-NMR ($CDCl_3$): 7.32 (d, *J* = 8.5 Hz, 2H, H-2′,6′); 6.95 (d, *J* = 8.5 Hz, 2H, H-3′,5′); 5.97 (s, 1H, H-4); 3.83 (s, 3H, O<u>C</u>H$_3$); 2.29 (s, 3H, <u>C</u>H$_3$ on C-3); 2.24 (s, 3H, <u>C</u>H$_3$ on C-5).

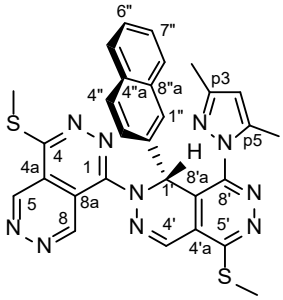


S.1.38. ^{13}C-NMR of **8d**

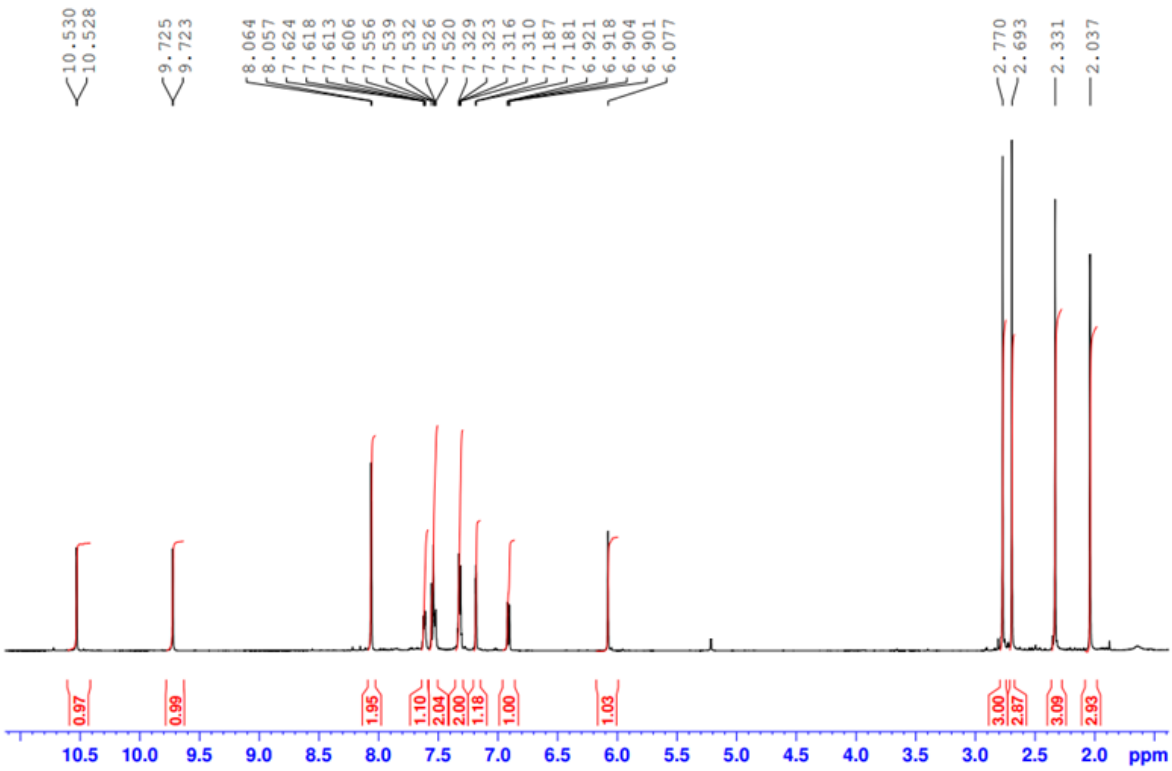
^{13}C-NMR ($CDCl_3$): 158.8 (C-4′); 148.4 (C-3); 139.6 (C-5); 132.9 (C-1′); 126.4 (C-2′,6′); 114.1 (C-3′,5′); 106.7 (C-4); 55.5 (O<u>C</u>H$_3$); 13.4 (<u>C</u>H$_3$ on C-5); 12.1 (<u>C</u>H$_3$ on C-3).



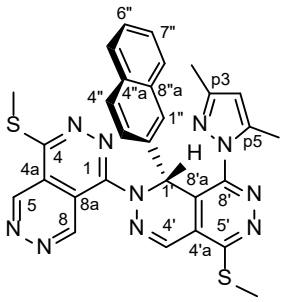
S.1.39. ^{1}H-NMR of **32c**



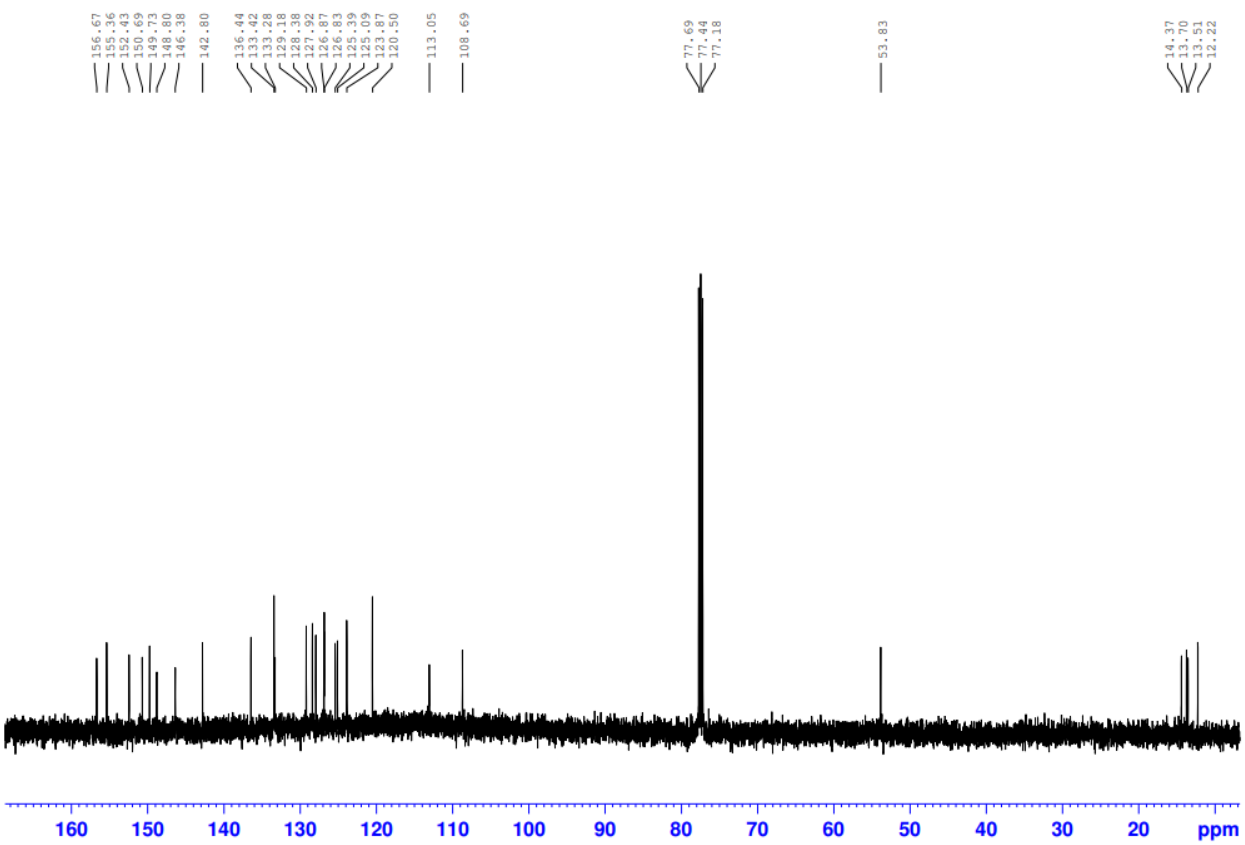
^{1}H-NMR ($CDCl_3$): 10.53 (d, *J* = 1.1 Hz, 1H, H-8); 9.72 (d, *J*=1.1 Hz, 1H, H-5); 8.064 and 8.059 (2xs, 2H, H-4′ and H-1′, resp.); 7.62 (m, 1H, H-5″); 7.55 (d, *J* = 8.6 Hz, 1H, H-4″); 7.53 (m, 1H, H-8″); 7.35-7.30 (m. 2H, H-6″ and H-7″); 7.18 (br s, 1H, H-1″); 6.91 (dd, *J* = 8.6 Hz and 1.6 Hz, 1H, H-3″); 6.07 (s, 1H, H-p4); 2.77 (s, 3H, SCH_3 on C-5′); 2.70 (s, 3H, SCH_3 on C-4); 2.35 (s, 3H, CH_3 on C-p5); 2.04 (s, 3H, CH_3 on C-p3).



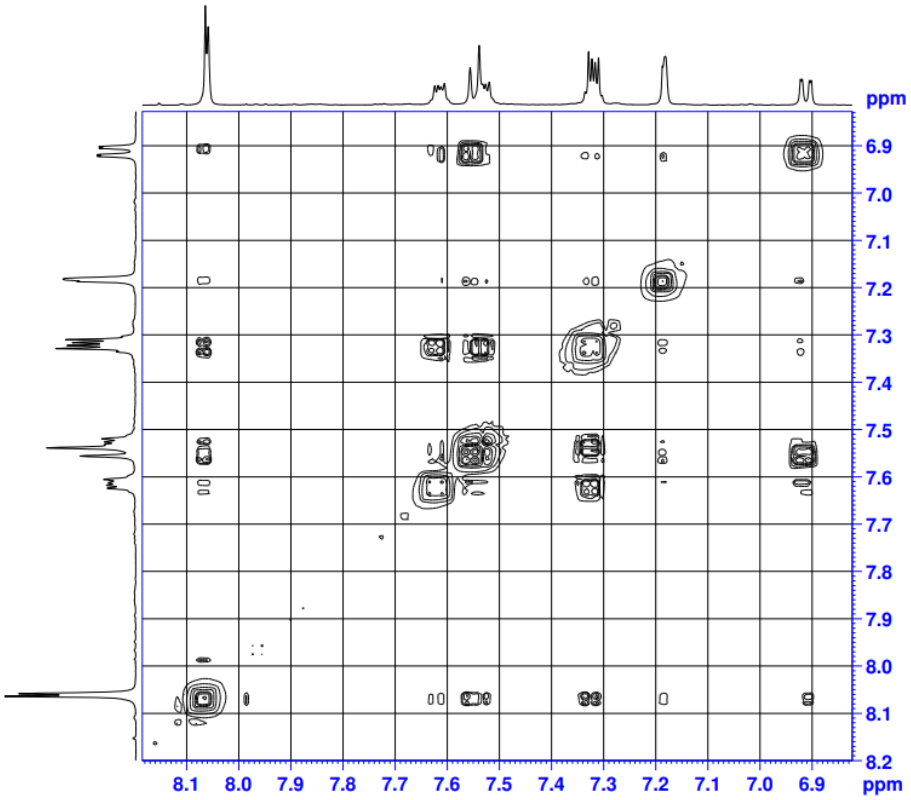
S.1.40. ^{13}C-NMR of **32c**



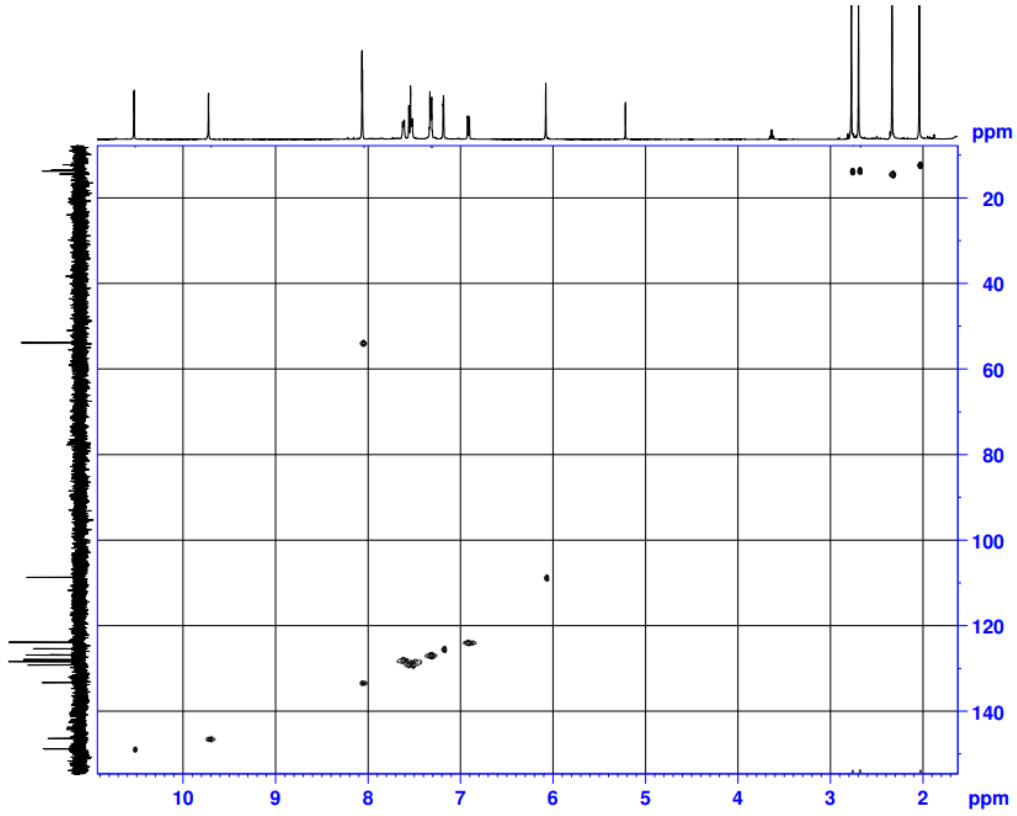
^{13}C-NMR ($CDCl_3$): 156.7 (C-5′); 155.4 (C-4); 152.5 (C-p3); 150.7 (C-8′), 149.7 (C-1); 148.8 (C-8); 146.4 (C-5); 142.8 (C-p5); 136.4 (C-2″); 133.42 and 133.28 (two hardly separated lines, C-4′ and C-4″a); 133.3 (C-8″a); 129.2 (C-4″); 128.4 (C-5″); 127.9 (C-8″); 126.87 and 126.83 (C-6″ and C-7″, interchangeable assignments); 125.4 (C-1″); 125.1 (C-8′a); 123.9 (C-3″); 120.5 (two coalesced lines C-4a and C-4′a); 113.1 (C-8a); 108.7 (C-p4); 53.8 (C-1′); 13.7 ($S\underline{C}H_3$ on C-5′); 13.5 ($S\underline{C}H_3$ on C-4); 14.4 ($\underline{C}H_3$ on C-p5); 12.3 ($\underline{C}H_3$ on C-p3).



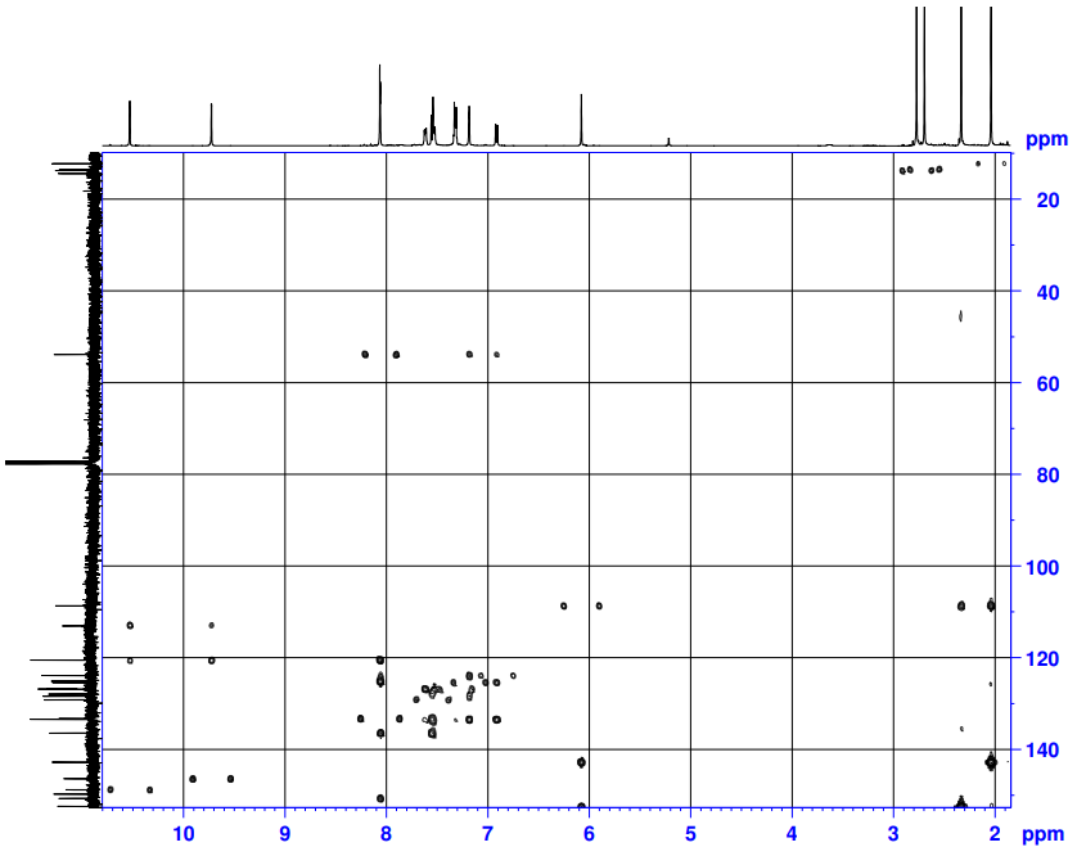
S.1.41. ^{1}H-^{1}H-COSY spectrum of **32c**



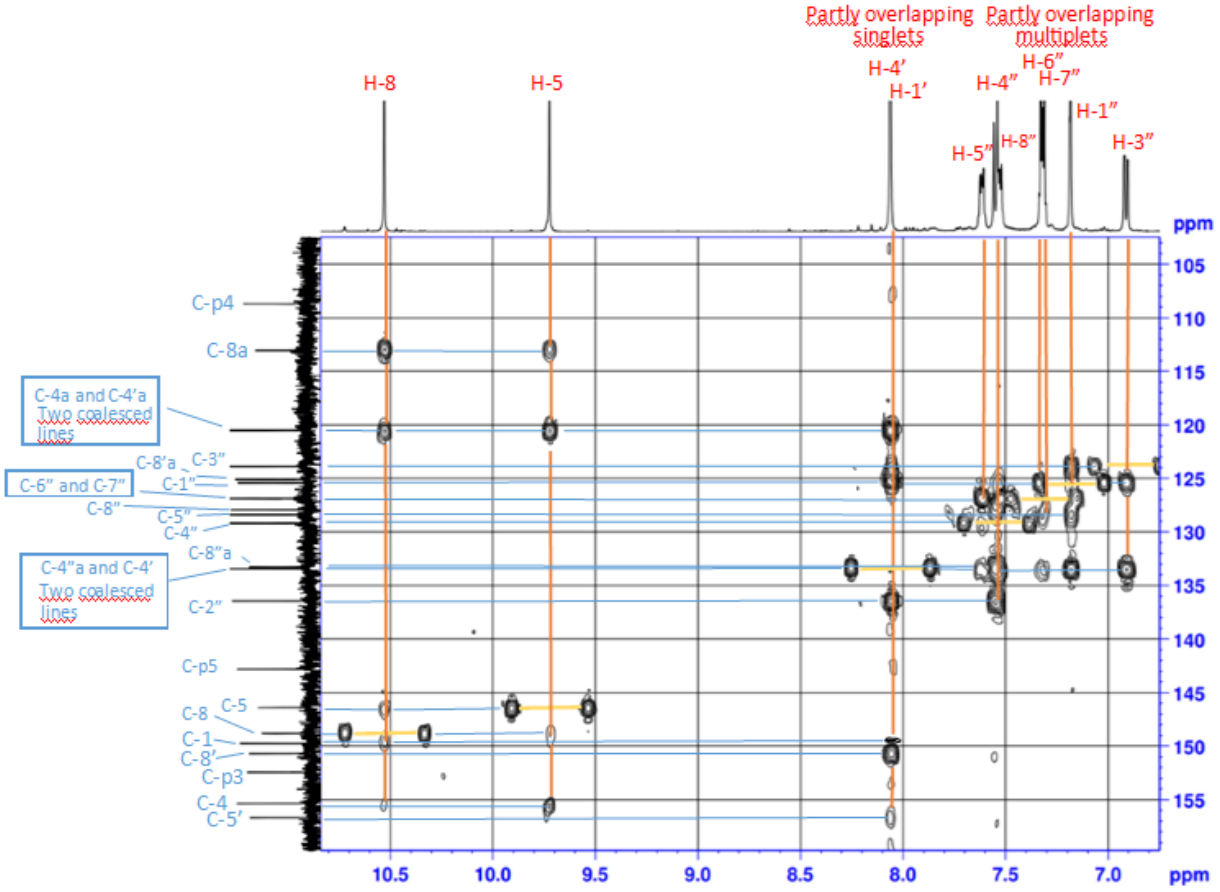
S.1.42. ^{1}H-^{13}C-HSQC spectrum of **32c**



S.1.43. ^{1}H-^{13}C-HMBC spectrum of **32c**



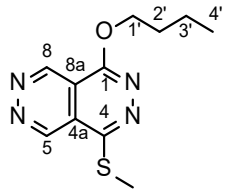
S.1.44. Downfield-shifted region of the ^{1}H-^{13}C-HMBC spectrum of **32c** with lowered level of the third dimension also showing weak but diagnostic cross peaks. Horizontal yellow lines connect the „satellite" peaks disclosing one-bond $^{1}H/^{13}C$ correlations.



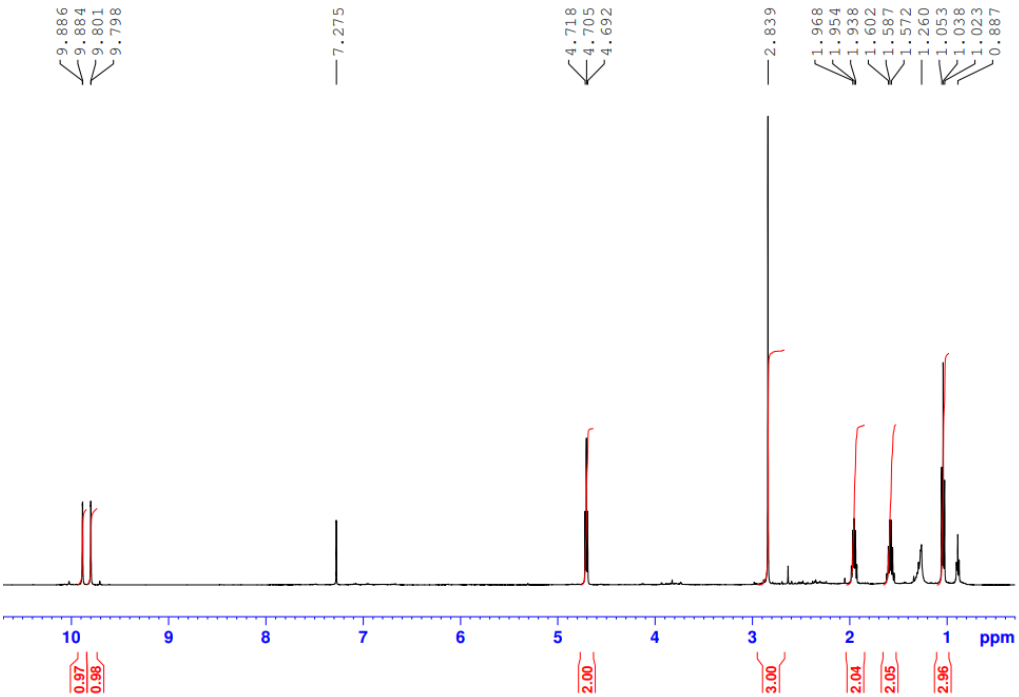
Diagnostic correlations discernible in the ^{1}H-^{13}C HMBC spectrum of **32c**.

^{1}H signal	Correlated ^{13}C signals						
H-8	C-8a	C-4a	C-1	C-8 (satellites)	C-4 („W" pattern)		
H-5	C-8a	C-4a	C-5 (satellites)	C-8 (weak)	C-4		
H-1′	C-1	C-8′	C-8′a	C-4′a	C-1″	C-2″	C-3″
H-4′	C-4′a	C-8′a	C-4′ (satellites)				
H-5″	C-6″/C-7″ (separated by 0.04 ppm)	C-8″a	C-5′ (satellites)				
H-4″	C-8″a	C-4″ (satellites)	C-5″	C-2″			
H-7″	C-8″a	C-5″					
H-1″	C-4″a	C-1″ (satellites)	C-3″	C-1′ (cf. full HMBC)			
H-3″	C-4″a	C-3″ (satellites)	C-1″	C-1′ (cf. full HMBC)			

S.1.45. ^{1}H-NMR spectrum of **33**

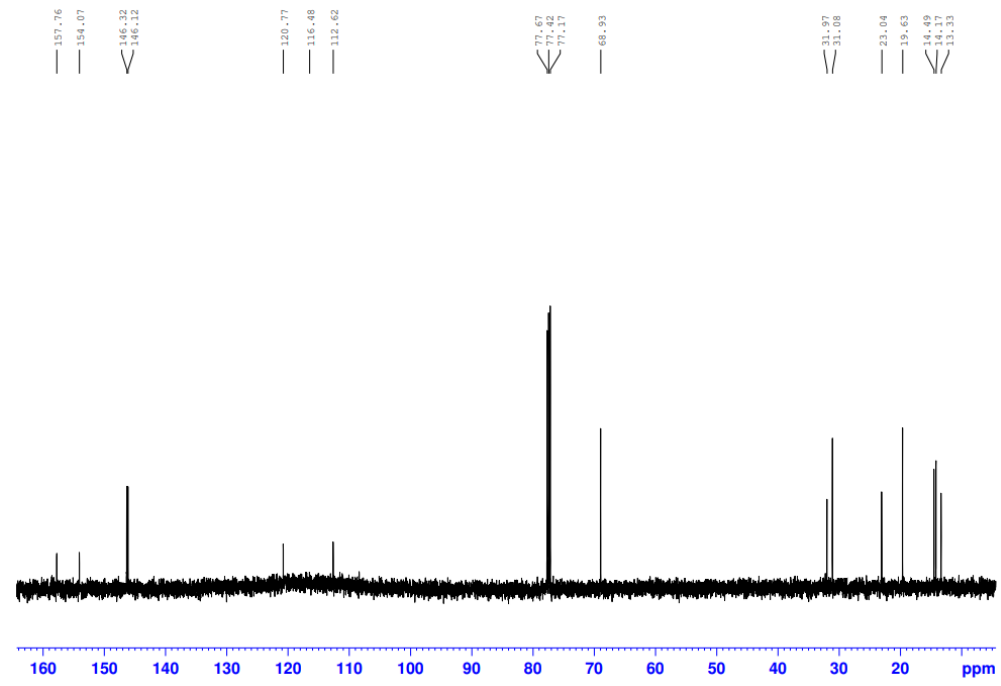


^{1}H-NMR ($CDCl_3$): 9.89 (d, *J* = 1.2 Hz, 1H, H-8); 9.88 (d, *J* = 1.2 Hz, 1H, H-5); 4.71 (t, *J* = 6.7 Hz, 2H, H-1′); 2.84 (s, 3H, SCH_3 on C-4); 1.95 (~qi, *J* ~ 7 Hz, 2H, H-2′); 1.58 (~sex, *J* ~ 7 Hz, 2H, H-3′); 1.03 (t, *J* = 7.4 Hz, 3H, H-4′). This sample contains *n*-hexane contamination (1.26 broad signal at 1.26 ppm and triplet at 0.89 ppm) left behind from the last purification process.

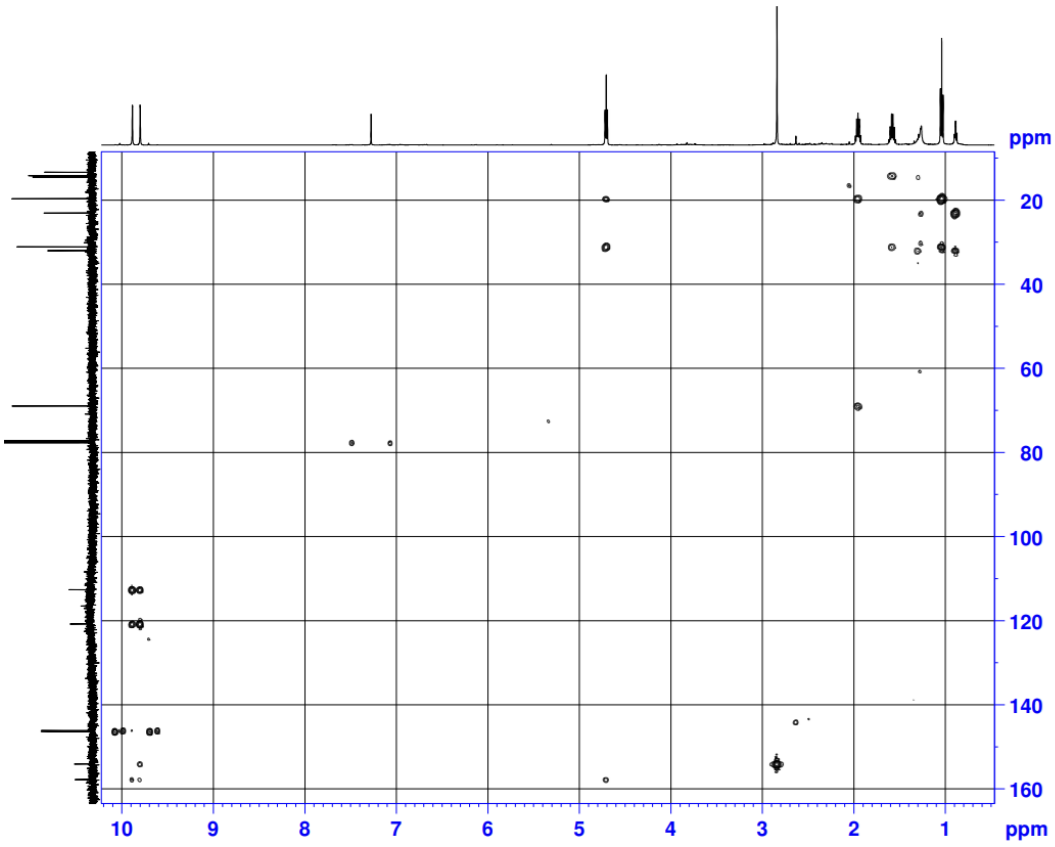


S.1.46. ^{13}C-NMR spectrum of **33**.

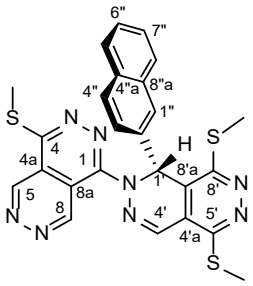
^{13}C-NMR ($CDCl_3$): 158.2 (C-1); 154.1 (C-4); 146.3 (C-8); 146.1 (C-5); 120.7 (C-4a); 112.6 (C-8a); 68.9 (C-1′); 31.1 (C-2′); 19.6 (C-3′); 14.2 (C-4′); 13.3 (SCH_3 on C-4). The signals at 31.2 ppm, 23.0 ppm and 14.5 ppm are originated from the *n*-hexane contamination.



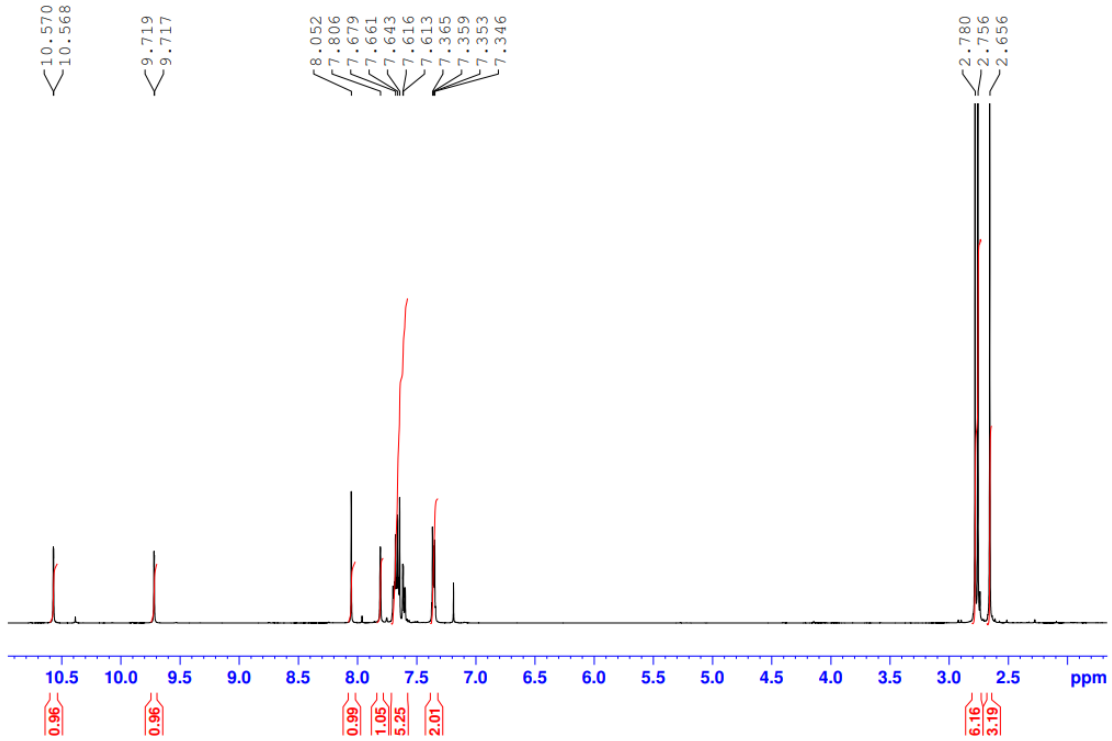
S.1.47. ^{1}H-^{13}C-HMBC spectrum of **33**



S.1.48. ^{1}H-NMR spectrum of **34c**

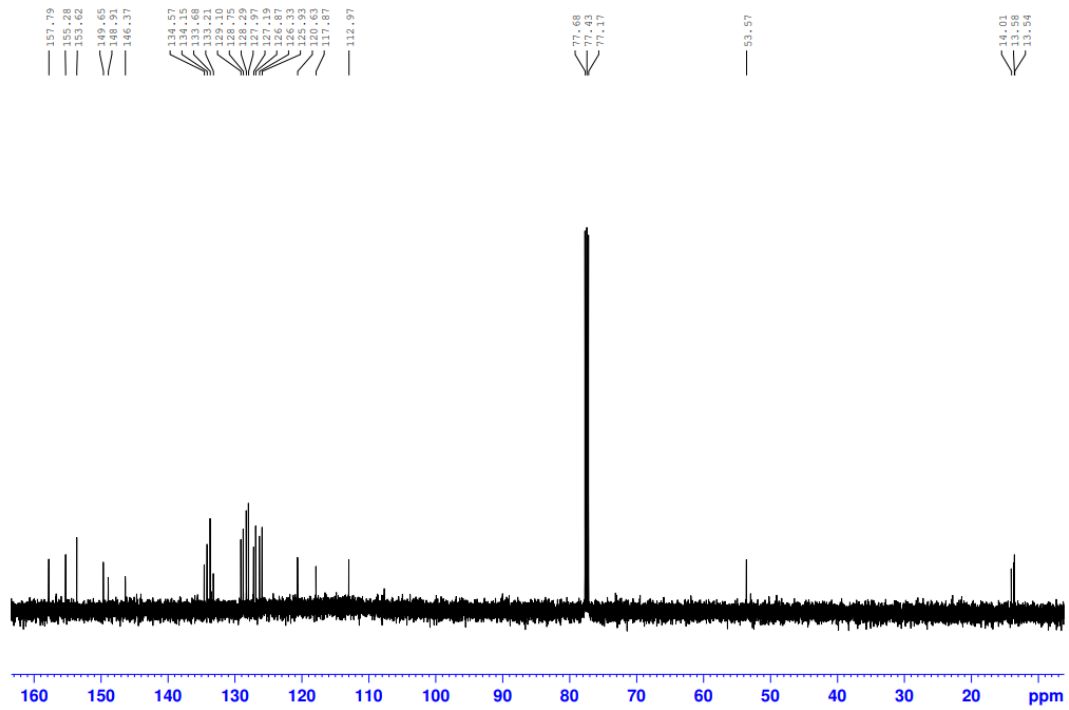


^{1}H-NMR ($CDCl_3$): 10.57 (d, *J* = 1.1 Hz, 1H, H-8); 9.72 (d, *J*=1.1 Hz, 1H, H-5); 8.05 (s, 1H, H-4′); 7.81 (br s, 1H. H-1″); 7.71-7.64 and 7.65 (overlapping m's and br s, 4H, H-4″, H-5″, H-8″ and H-1′, resp.); 7.61 (dd, *J* = 8.6 Hz and 1.8 Hz, 1H, H-3″); 7.37-7.34 (m, 2H, H-6″ and H-7″); 2.78 (s, 3H, SC<u>H</u>$_3$ on C-4); 2.76 (s, 3H, SC<u>H</u>$_3$ on C-5′); 2.66 (s, 3H, SC<u>H</u>$_3$ on C-8′).

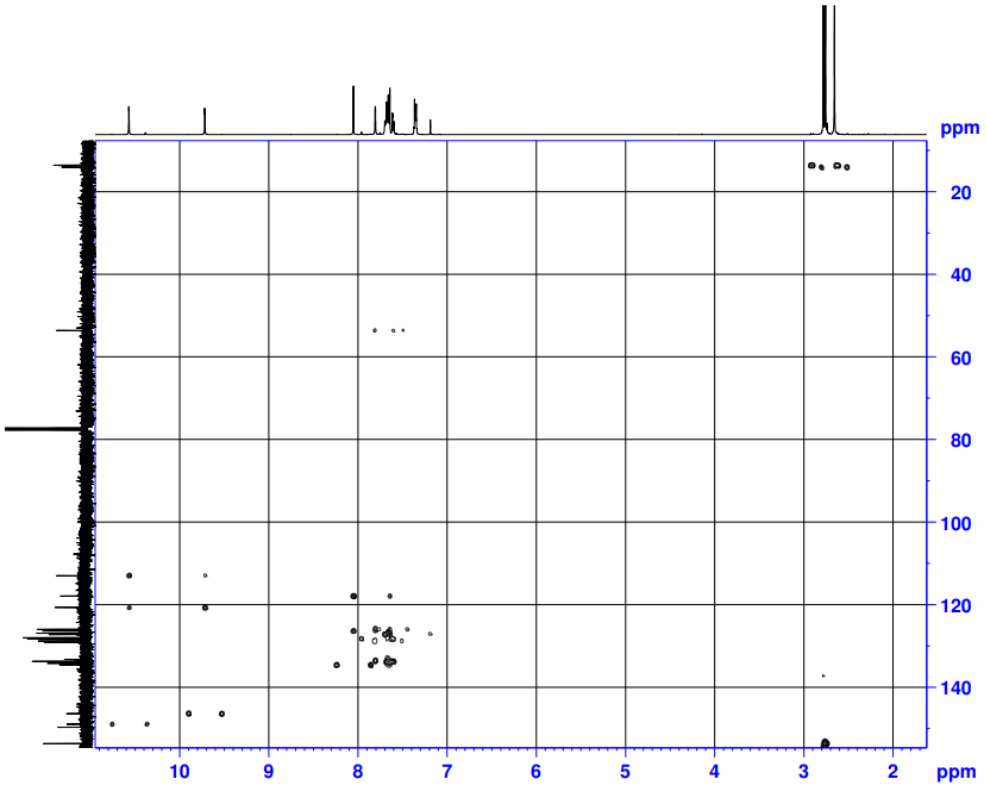


S.1.49. ^{13}C-NMR spectrum of **34c**

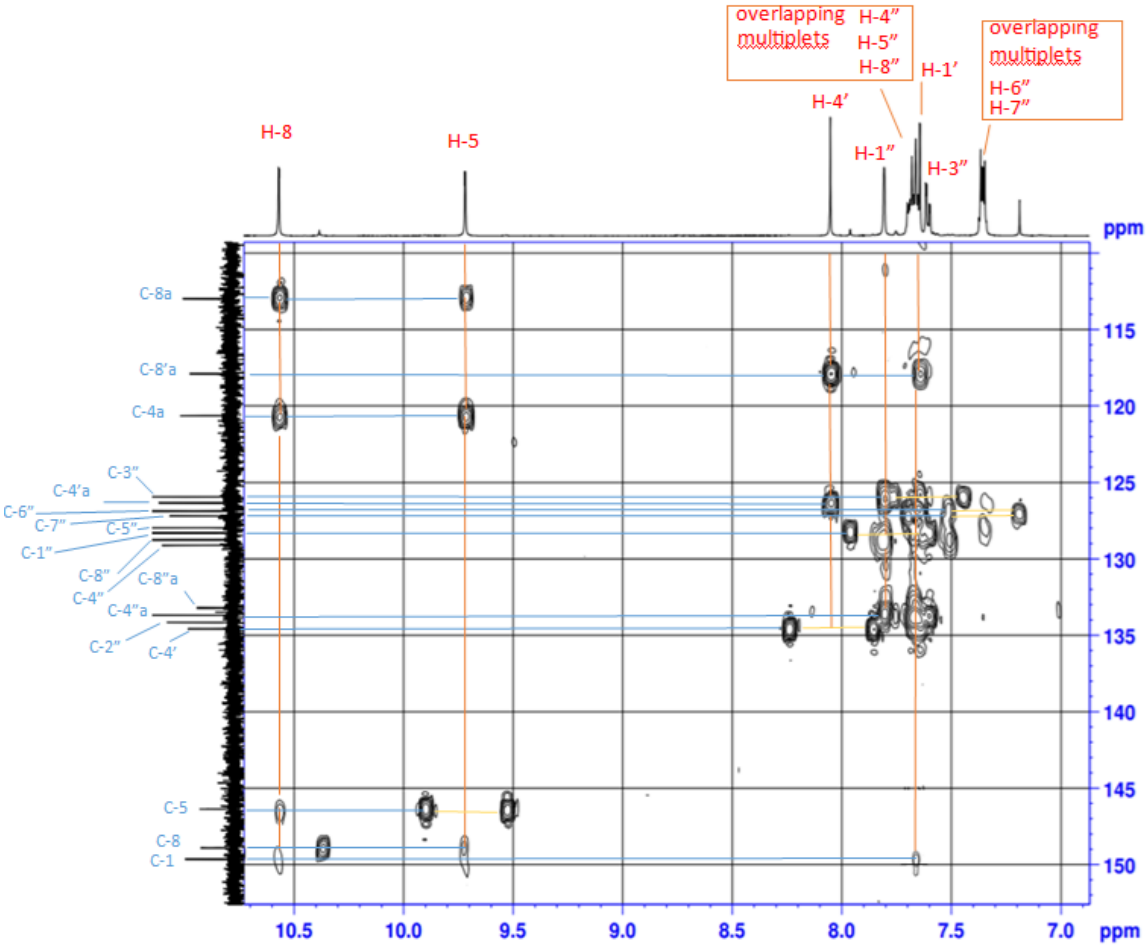
^{13}C-NMR ($CDCl_3$): 156.8 (C-8′); 155.3 (C-4); 153.6 (C-5′); 150.7 (C-8′), 149.6 (C-1); 148.9 (C-8); 146.4 (C-5); 134.7 (C-4′); 134.6 (C-2″); 133.7 (C-4″a); 133.2 (C-8″a); 129.2 (C-4″); 128.8 (C-8″); 128.3 (C-1″); 128.0 (C-5″); 127.2 (C-7″); 126.9 (C-6″); 126.4 (C-4′a); 125.9 (C-3″); 120.6 (C-4a); 117.8 (C-8′a); 113.0 (C-8a); 53.6 (C-1′); 14.1 (S<u>C</u>H$_3$ on C-8′); 13.58 (S<u>C</u>H$_3$ on C-4); 13.54 (S<u>C</u>H$_3$ on C-5′).



S.1.50. ^{1}H-^{13}C-HMBC spectrum of **34c**

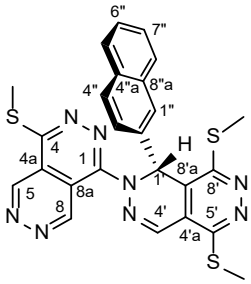


S.1.51. Downfield-shifted region of the ^{1}H-^{13}C-HMBC spectrum of **34c** with lowered level of the third dimension also showing weak but diagnostic cross peaks. Horizontal yellow lines connect the „satellite" peaks disclosing one-bond $^{1}H/^{13}C$ correlations.



Diagnostic correlations discernible in the ^{1}H-^{13}C HMBC spectrum of **34c**.

^{1}H signal	Correlated ^{13}C signals						
H-8	C-8a	C-4a	C-1	C-8 (satellites, cf full HMBC)			
H-5	C-8a	C-4a	C-5 (satellites)	C-8 (weak)	C-4		
H-4′	C-4′a	C-8′a	C-4′ (satellites)				
H-1″	C-4″a	C-1″ (satellites)	C-3″	C-1′ (cf. full HMBC)			
H-1′	C-1	C-8′a	C-4′a	C-1″	C-2″	C-3″	C-1′ (satellites, cf. full HMBC)
H-3″	C-4″a	C-3″ (satellites)	C-1″	C-1′ (cf. full HMBC)			



SS.1.52. ^{1}H-^{15}N-HMBC spectrum of **34c**

